Supporting Information

A general metal-free route towards the synthesis of 1,2,3-triazoles from readily available primary amines and ketones

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1. General experimental methods

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker Avance II+ 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (tH), or the internal (NMR) solvent signal (13C). Mass spectra were acquired using a HP5989A apparatus (EI, 70 eV ionisation energy) with Apollo 300 data system, a Micromass Quattro II apparatus (ESI) with MASSLYNX data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the EI mode at a resolution of 10000) or a Bruker Daltonics Apex2 FT-ICR instrument (performed in the ESI mode at a resolution of 60000). Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography 70-230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. Reaction solvents (toluene) were used as received from commercial sources.

2. Optimization Studies

We started to investigate the optimization of reaction conditions by selecting acetophenone (1a) and 4-methoxybenzylamine (2a) as the model reagents with various diazo transfer reagents, catalysts and solvents to form 1,5-disubstituted triazole 4a as summarized in Table S1. We presumed that the addition of 4 Å molecular sieves favors imine formation by effectively removing water from the carbonyl + amine → imine + H2O equilibrium. Initial experiments were conducted via a MCR of these reagents in the presence of 4-nitrophenyl azide (3a) as the diazo-transfer reagent and 30 mol% of p-toluenesulfonic acid (TsOH) as the catalyst over 4 Å molecular sieves in toluene (0.4 mL, 1 molar) at 100°C in a sealed tube for 12 h (Table S1, entry 1). To our delight, this combination promoted the reaction with an excellent yield of 80%. The use of 3b as diazo transfer agent resulted in a significant reduction in the yield of the title compound 4a to 25% (Table S1, entry 2). Subsequently, performing the reaction with other azido compounds that are known as diazo transfer reagents, such as 3c and 3d resulted in much lower efficiencies (Table S1, entries 3 & 4). One possible reason for this is the formation of corresponding sulfonamide as a side product which derived from the nucleophilic substitution reaction of 2a with 3c and 3d. Interestingly, among the different Bronsted acid catalysts tried, CH3COOH gave the best result (Table S1, entries 5-7). We then examined various stoichiometries of the building blocks and different loading of CH3COOH catalyst on the reaction performance (Table S1, entries 8-10). The best result was obtained while using 1.4 equivalents of 2a and 30 mol% of CH3COOH catalyst, and the desired three-component-coupling product 4a was obtained in 93% yield (Table S1, entries 10). When performing the reactions with secondary amine catalysts such as L-proline and morpholine:p-toluene sulfonic acid salt, however, lower yields were obtained (Table S1, entry 12 and 13). Next, we performed the reaction with other azido compounds analogous to 3a such as 4-
azidobenzonitrile 3e (Table S1, entry 14) and ethyl 4-azidobenzoate (Table S1, entry 15) 3f. These reactions of less electron poor aryl azides were less efficient than the ones performed with 3a and also required longer reaction times for the complete consumption of the starting materials. Remarkably, this reaction also worked fine under acid free conditions without significantly affecting the yield of 4a (85%) although the required reaction time was longer (24 h) (Table S1, entry 17). This observation can be viewed as an additional advantage as this transformation could also be extended to acid sensitive substrates. The yields of the reactions are also influenced by the solvent (Table S1, entries 18-24): MeCN (85%), THF (70%), CICH₂CH₂Cl (56%), DMSO (78%), DMF (67%), EtOH (74%), 1,4-dioxane (57%). Therefore, a three-component reaction of 1a, 2a and 3a in a respective molar ratio of 1:1.4:1.1 using 30 mol% of acetic acid (8 mg, 0.13 mmol) as catalyst over 4 Å molecular sieves in 1 molar solution of toluene at 100°C in a sealed tube under argon atmosphere over a period of 12 h proved to be the conditions of choice.

Table S1: Optimization of reaction conditions for the organocatalyzed three-component reaction of acetophenone (1a), 4-methoxybenzylamine (2a) and organic azides (3a-d).[a]
<table>
<thead>
<tr>
<th>Entry</th>
<th>Ratio 1a:2a:3a</th>
<th>Catalyst (mol%)</th>
<th>Ar-N₃</th>
<th>Solvent</th>
<th>isolated Yield[^b]</th>
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<tr>
<td>1</td>
<td>1:1:1</td>
<td>TsOH (20)</td>
<td>3a</td>
<td>toluene</td>
<td>80</td>
</tr>
<tr>
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<td>1:1:1</td>
<td>TsOH (20)</td>
<td>3b</td>
<td>toluene</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>1:1:1</td>
<td>TsOH (20)</td>
<td>3c</td>
<td>toluene</td>
<td>trace</td>
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<tr>
<td>4</td>
<td>1:1:1</td>
<td>TsOH (20)</td>
<td>3d</td>
<td>toluene</td>
<td>trace</td>
</tr>
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<td>1:1:1</td>
<td>CF₃COOH (20)</td>
<td>3a</td>
<td>toluene</td>
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</tr>
<tr>
<td>6</td>
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<td>NEt₃,TsOH (20)</td>
<td>3a</td>
<td>toluene</td>
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<td>7</td>
<td>1:1:1</td>
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<td>toluene</td>
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</tr>
<tr>
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</tr>
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<td>13</td>
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<td>3a</td>
<td>1,4-dioxane</td>
<td>80</td>
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</tbody>
</table>

**Ar-N₃**

\[
\begin{align*}
3a & \quad \begin{array}{c}
\text{N}_3 \\
\text{NO}_2
\end{array} \\
3b & \quad \begin{array}{c}
\text{N}_3 \\
\text{COOH}
\end{array} \\
3c & \quad \begin{array}{c}
\text{SO}_2\text{N}_3 \\
\text{CN}
\end{array} \\
3d & \quad \begin{array}{c}
\text{N}_3 \\
\text{N}_3
\end{array} \\
3e & \quad \begin{array}{c}
\text{N}_3 \\
\text{COOEt}
\end{array} \\
3f & \quad \begin{array}{c}
\text{N}_3 \\
\text{NO}_2
\end{array}
\end{align*}
\]

[^a]: Reaction conditions: except where otherwise noted, 1a is always in 0.42 mmol amount and the molar ratio of 2a and 3a is calculated on the basis of this, reaction temperature is 100°C, solvent (0.4 mL, 1 molar), 4 Å molecular sieves (30 mg) and reaction time is 12 h.[^b]: isolated yield after column chromatography.[^c]: reaction...
performed without molecular sieves and reaction time is 20 h. [e] reaction time is 40 h. [f] reaction time is 56 h. 
[f] reaction time is 24 h. TsOH is \( \text{p-toluenesulfonic acid} \).

2. Mechanistic studies

We conducted several control experiments to gain a better understanding about the mechanism of the reaction. After some optimization we found that the reaction of 1a and 2a under acid free conditions for 2 hours at 100 °C followed by the addition of an equivalent of 3a at 50°C afforded the triazoline intermediate 6a in 75% yield in 6 hours (Fig. S1a). Subjecting the same reaction using 30 mol% of acid yields the triazole 4a (73%) as the sole product. This observation shows the high reactivity of the aminotriazoline intermediate 6a under acidic conditions. Then, two separate experiments were conducted and monitored by \(^1\text{H NMR spectroscopy}, with the isolated adduct 6a in the presence and absence of the catalyst in CDCl\textsubscript{3} at 65° C in a NMR tube (Fig. S1b). Interestingly, the reaction in the presence of acid was complete after 3 hours and exclusively yielded the expected products 4a and 5a in 1:1 ratio, presumably as a result of protonation of the N-3 of the aminotriazoline intermediate 6a followed by a ring opening/ring closure sequence (Fig. S1c). On the other hand, in the case of acid-free conditions, the reaction proceeded very slowly and complete conversion at 65°C was observed only after 40 hours. Furthermore, we monitored a one-pot reaction starting from 1a, 2a and 3a under acidic conditions (30% AcOH) at 65°C and the reaction was finished only after 48 hours. This observation demonstrated convincingly that the Schiff base formation is slow at this temperature. Taken together, the results of these experiments are in agreement with the hypothesis that imine/enamine formation is the rate determining step. We presume that the imine/enamine species is in equilibrium with the starting material 1a and 2a, and the formation of the key intermediate 6a from a 3+2 cycloaddition reaction between transiently generated enamine and 3a displaces this equilibrium. Thus this overall process could be considered as an application of thermodynamically controlled dynamic covalent chemistry.
**Figure S1.** Proposed mechanistic experiments and catalytic cycles. a) Scheme showing the synthesis of the triazoline intermediate 6a and its subsequent conversion to 4a and 5a. b) The $^1$H NMR spectra showing the clean formation of the triazole 4a and 5a upon heating the triazoline intermediate 6a in presence of 8 mol% of CH$_3$COOH in CDCl$_3$ at 65 °C. c) Postulated mechanism. R$_3$NH$_3^+$CH$_3$COO$^-$ indicates the in situ formation of the organic salt when CH$_3$COOH reacts with R$_3$NH$_2$. 
4. Experimental Procedures

4.1 Preparation of azides

4-Nitrophenyl azide, 3a. 4-Nitroaniline (28.0 g, 0.20 mol) was suspended in 2.4 N HCl solution (300 mL) and methanol (60 mL) was added to aid the solubility. After cooling the solution to 0 °C, NaNO₂ (6 M, 40 mL) in water was added dropwise. The mixture was stirred at 0 °C for 30 minutes, after which a solution of NaN₃ (4.1 M, 60 mL) in water was added dropwise over 20 minutes and the whole reaction mixture was stirred for an hour at room temperature. The reaction mixture was extracted with diethyl ether and the organic fraction was washed with a saturated NaHCO₃ solution and brine, dried over MgSO₄ and concentrated in under reduced pressure affording the pure compound 3a as a yellow solid in 95% yield (31.48 g). Spectroscopic data for 3a was consistent with previously reported data for this compound.²

2-Azido-5-nitrobenzoic acid, 3b. This compound has been prepared according to the procedure reported by Smith et al. Material identity was confirmed by MS, ¹H and ¹³C NMR.³

Imidazole-1-sulfonyle azide, 3d. This compound has been prepared according to the procedure reported by Goddard-Borger et al. Material identity was confirmed by MS, ¹H and ¹³C NMR.⁴

CAUTION: As organic azides are potentially explosive, all aryl azides have been stored in the freezer in the dark.

4.2 General procedure for the preparation of substituted 1,2,3-triazoles.

To an oven-dried screw-capped reaction tube equipped with a magnetic stirring bar was added the ketone, amine, 4-nitrophenyl azide (3a), acetic acid (0-30 mol%) and 4 Å molecular sieves (50 mg). The mixture was dissolved in the proper solvent and stirred at 100 °C for 12-72 hours. The crude reaction mixture was then directly purified by column chromatography (silica gel) at first with CH₂Cl₂ as eluent to remove all 4-nitroaniline formed during the reaction followed by using a mixture of heptane and ethyl acetate as eluent to afford the corresponding 1,2,3-triazoles as off-white solids or semi-solids.

NMeO

4a: 93% yield

1-(4-Methoxybenzyl)-5-phenyl-1H-1,2,3-triazole (4a): Acetophenone (50 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (silica gel) at first with CH₂Cl₂ as eluent to afford the corresponding 1,2,3-triazoles as off-white solids or semi-solids.

¹H NMR (300 MHz, CDCl₃) δ 7.72 (s, 1H), 7.45 - 7.42 (m, 3H), 7.28 - 7.25 (m, 2H), 7.01 (d, 2H, J = 8.6 Hz), 6.79 (d, 2H, J = 8.7 Hz), 5.48 (s, 2H), 3.78 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 138.1, 133.4, 129.6, 129.1, 129.0, 128.8, 127.6, 127.1, 114.3, 55.4, 51.5; MS (EI): m/z: 265 (M⁺); HRMS (ESI⁺): m/z calcld for C₁₆H₁₆N₃O [M+H]⁺: 266.1287, found 266.1284. Spectroscopic data for 4a are consistent with previously reported data for this compound.⁵
4b: 89% yield

1-(4-Methoxybenzyl)-5-(4-methoxyphenyl)-1H-1,2,3-triazole (4b): 4-Methoxy acetophenone (63 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4b (110 mg, 89% yield) as an off white semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.66 (s, 1H), 7.18 (d, 2H, $J = 8.5$ Hz), 7.03 (d, 2H, $J = 8.5$ Hz), 6.94 (d, 2H, $J = 8.6$ Hz), 6.81 (d, 2H, $J = 8.6$ Hz), 5.45 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.6, 159.5, 137.8, 133.1, 130.4, 128.7, 127.8, 119.2, 114.5, 114.2, 55.5, 55.3, 51.3; MS (EI): m/z: 295 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{17}$H$_{18}$N$_3$O$_2$ [M+H]$^+$: 296.1393, found 296.1399. Spectroscopic data for 4b are consistent with previously reported data for this compound$^5$.

4c: 68% yield

4-(1- (4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)aniline (4c): 4-Aminoacetophenone (56 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 40 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 4:6) affording 4c (79 mg, 68% yield) as an off white semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.64 (s, 1H), 7.06 - 7.03 (m, 4H), 6.81 (d, 2H, $J = 8.2$ Hz), 6.69 (d, 2H, $J = 7.9$ Hz), 5.44 (s, 2H), 3.89 (s, 1H), 3.78 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.5, 147.7, 138.4, 132.9, 130.2, 128.8, 128.0, 116.5, 115.1, 114.2, 55.4, 51.2; MS (EI): m/z: 280 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{16}$H$_{18}$N$_3$O [M+H]$^+$: 281.1397, found 281.1396.

4d: 88% yield
1-(4-Methoxybenzyl)-5-(o-tolyl)-1H-1,2,3-triazole (4d): 2-Methylacetophenone (56 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4d (103 mg, 88% yield) as an off white semi-solid.

\[ \text{1H NMR} (300 \text{ MHz, CDCl}_3) \delta 7.62 (s, 1H), 7.40 - 7.35 (m, 1H), 7.23 (d, 2H, J = 7.0 Hz), 7.04 (d, 1H, J = 7.5 Hz), 6.87 (d, 2H, J = 8.95 Hz), 6.71 (d, 2H, J = 8.74 Hz), 5.27 (s, 2H), 3.75 (s, 3H), 1.86 (s, 3H); \]

\[ \text{13C NMR} (75 \text{ MHz, CDCl}_3) \delta 159.60, 138.1, 136.5, 133.9, 130.5, 130.0, 129.5, 127.1, 126.7, 126.0, 114.0, 55.4, 51.6, 19.7; \]

\[ \text{MS (EI): m/z: 279 (M}^+); \]

\[ \text{HRMS (ESI): m/z calcd for C}_{17}H_{18}N_3O [M+H]^+: 280.1444, \text{ found 280.1445.} \]

5-(4-Chlorophenyl)-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4e): 4-Chloroacetophenone (64 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4e (98 mg, 79% yield) as an off-white solid. m.p. 56 - 57 °C.

\[ \text{1H NMR} (300 \text{ MHz, CDCl}_3) \delta 7.71 (s, 1H), 7.40 (d, 2H, J = 8.1 Hz), 7.18 (d, 2H, J = 8.5 Hz), 6.91 (d, 2H, J = 8.6 Hz), 6.80 (d, 2H, J = 8.7 Hz), 5.46 (s, 2H), 3.78 (s, 3H); \]

\[ \text{13C NMR} (100 \text{ MHz, CDCl}_3) \delta 159.7, 136.9, 135.9, 133.6, 130.4, 129.3, 128.7, 127.4, 125.6, 114.4, 55.4, 51.6; \]

\[ \text{MS (EI): m/z: 299 (M}^+); \]

\[ \text{HRMS (ESI): m/z calcd for C}_{16}H_{16}ClN_4O [M+H]^+: 300.0899, \text{ found 300.0896.} \]

1-(4-Methoxybenzyl)-5-(4-nitrophenyl)-1H-1,2,3-triazole (4f): 4-Nitroacetophenone (69 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 40 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4f (80 mg, 62% yield) as an off-white solid m.p. 86 - 87 °C.

\[ \text{1H NMR} (300 \text{ MHz, CDCl}_3) \delta 8.28 (d, 2H, J = 8.7 Hz), 7.82 (s, 1H), 7.46 (d, 2H, J = 8.5 Hz), 7.00 (d, 2H, J = 8.5 Hz), 6.81 (d, 2H, J = 8.6 Hz), 5.54 (s, 2H), 3.78 (s, 3H); \]

\[ \text{13C NMR} (100 \text{ MHz, CDCl}_3) \delta 159.8, 148.4, 135.9, 134.2, 133.6, 129.9, 128.6, 126.9, 124.2, 114.5, 55.4, 52.1; \]

\[ \text{MS (EI): m/z: 310 (M}^+); \]

\[ \text{HRMS (ESI): m/z calcd for C}_{16}H_{15}N_4O_3 [M+H]^+: 311.1138, \text{ found 311.1130.} \]
**1-(4-Methoxybenzyl)-5-methyl-1H-1,2,3-triazole (4g):** Acetone (72 mg, 1.26 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4g (52 mg, 62% yield) as an off-white solid. m.p. 69 - 70 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.45 (s, 1H), 7.12 (d, 2H, $J = 8.5$ Hz), 6.87 (d, 2H, $J = 8.5$ Hz), 5.43 (s, 2H), 3.79 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.6, 133.6, 132.7, 128.8, 126.9, 114.4, 55.4, 51.3, 8.6; MS (EI): m/z: 203 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{11}$H$_{14}$N$_3$O [M+H]$^+$: 204.1131, found 204.1131.

**5-Tert-butyl-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4h):** Pinacolone (41 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4h (85 mg, 83% yield) as an off white semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.46 (s, 2H), 7.02 (d, 2H, $J = 8.8$ Hz), 6.84 (d, 2H, $J = 8.8$Hz), 5.63 (s, 2H), 3.78 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.4, 145.5, 131.7, 128.2, 128.0, 114.3, 55.4, 52.6, 30.4, 30.0; MS (EI): m/z: 245 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{14}$H$_{20}$N$_3$O [M+H]$^+$: 246.1601, found 246.1601.

**5-(3,5-Bis (trifluoromethyl)phenyl)-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4i):** 3',5'-Bis (trifluoromethyl)acetophenone (107 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-
nitrophenyl azide (68 mg, 0.42 mmol), (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4i (117 mg, 70% yield) as an off white solid. m.p. 70 - 71 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1H), 7.82 (s, 1H), 7.63 (s, 2H), 7.02 (d, 2H, $J = 8.5$ Hz), 6.81 (d, 2H, $J = 8.7$ Hz), 5.50 (s, 2H), 3.78 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.0, 135.2, 134.3, 132.8, 132.3, 129.5, 129.3, 128.8, 126.6, 124.7, 123.3, 121.0, 114.6, 55.4, 52.4; MS (EI): m/z: 401 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{18}$H$_{14}$F$_6$N$_3$O [M+H$^+$]: 402.1035, found 402.1039.

1-(4-Methoxybenzyl)-5-(1-naphthyl)-1H-1,2,3-triazole (4j): 1-Acetonaphthone (71 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4j (105 mg, 80% yield) as an off white semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.00 - 7.90 (m, 2H), 7.78 (s, 1H), 7.53 - 7.21 (m, 5H), 6.75 (d, 2H, $J = 8.6$ Hz), 6.61 (d, 2H, $J = 8.6$ Hz), 5.26 (s, 2H), 3.70 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.5, 135.8, 134.9, 133.6, 132.1, 130.4, 129.4, 129.0, 128.6, 127.3, 127.1, 126.6, 125.1, 124.9, 124.6, 113.9, 55.3, 51.9; MS (EI): m/z: 315 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{20}$H$_{18}$N$_3$O [M+H$^+$]: 316.1444, found 316.1444.

1-(4-Methoxybenzyl)-5-(3-phenanthryl)-1H-1,2,3-triazole (4k): 3-Acetyl phenantherene (92 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4k (138 mg, 91% yield) as an off white solid. m.p. 164 - 165 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.45 (s, 1H), 8.24 (d, 1H, $J = 7.2$ Hz), 7.94 (t, 2H, $J = 8.3$ Hz), 7.88 (s, 1H), 7.84 - 7.75 (m, 2H), 7.66 - 7.58 (m, 2H), 7.50 (d, 1H, $J = 8.3$ Hz), 7.11 (d, 2H, $J = 8.7$ Hz), 6.85 (d, 2H, $J = 8.7$ Hz), 5.57 (s, 2H), 3.79 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.7, 138.5, 133.7, 132.4, 132.3, 130.9, 129.9, 129.4, 128.9, 128.8, 128.6, 128.1, 127.4, 127.1, 126.9, 126.4, 124.9, 123.8, 122.8, 114.5, 55.5, 51.8; MS (EI): m/z: 365 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{24}$H$_{20}$N$_3$O [M+H$^+$]: 366.1601, found 366.1606.
2-(1-(4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)pyridine (4l): 2- Acetyl pyridine (51 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH\textsubscript{2}Cl\textsubscript{2} followed by heptane/EtOAc = 3:7) affording 4l (91 mg, 82% yield) as an off white solid. m.p. 73 - 74 °C.

\[ ^1H \text{NMR (300 MHz, CDCl}_3\text{)} \delta 8.72 (d, 1H, J = 4.7 Hz), 7.98 (s, 1H), 7.77 - 7.71 (m, 1H), 7.55 - 7.52 (m, 1H), 7.31 - 7.27 (m, 1H), 7.20 (d, 2H, J = 8.3), 6.77 - 6.74 (m, 2H), 6.09 (s, 2H), 3.73 (s, 3H); ^{13}C \text{NMR (75 MHz, CDCl}_3\text{)} \delta 159.3, 149.6, 147.2, 137.1, 135.5, 133.8, 129.5, 128.3, 123.4, 122.9, 113.9, 55.3, 52.6; MS (EI): m/z: 266 (M\textsuperscript{+}); HRMS (ESI\textsuperscript{+}): m/z calcd for C\textsubscript{15}H\textsubscript{15}N\textsubscript{4}O [M+H]\textsuperscript{+}: 267.1240, found 267.1241.

3-(1-(4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)-1H-indole (4m): 3-Acetyl indole (67 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH\textsubscript{2}Cl\textsubscript{2} followed by heptane/EtOAc = 5:5) affording 4m (106 mg, 83% yield) as an off white solid. m.p. 192 - 193 °C.

\[ ^1H \text{NMR (300 MHz, CDCl}_3\text{)} \delta 8.57 (s br, 1H), 7.89 (s, 1H), 7.54 (d, 1H, J = 7.9 Hz), 7.46 (d, 1H, J = 8.1 Hz), 7.33 - 7.19 (m, 3H), 7.05 - 7.00 (m, 3H), 6.80 (d, 2H, J = 8.7 Hz), 5.53 (s, 2H), 3.77 (s, 3H); ^{13}C \text{NMR (75 MHz, CDCl}_3\text{)} \delta 159.4, 136.0, 133.7, 132.6, 131.8, 128.5, 128.2, 126.3, 124.2, 123.4, 121.3, 119.3, 114.3, 111.7, 55.4, 51.4; MS (EI): m/z: 304 (M\textsuperscript{+}); HRMS (ESI\textsuperscript{+}): m/z calcd for C\textsubscript{18}H\textsubscript{17}N\textsubscript{4}O [M+H]\textsuperscript{+}: 305.1397, found 305.1395.
5-(Furan-2-yl)-1H-1,2,3-triazole (4n): 2- Acetyl furan (46 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4n (96 mg, 68% yield) as an off-white semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.86 (s, 1H), 7.55 - 7.54 (m, 1H), 7.13 (d, 2H, $J = 8.8$ Hz), 6.82 (d, 2H, $J = 8.8$ Hz), 6.53 - 6.48 (m, 2H), 5.71 (s, 2H), 3.77 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.6, 143.7, 141.5, 132.5, 128.9, 128.8, 127.3, 114.3, 111.9, 110.5, 55.4, 52.5; MS (EI): m/z: 255 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{14}$H$_{14}$N$_3$O$_2$ [M+H$^+$]: 256.1080, found 256.1082.

5-(1-(4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)pyrimidine-2,4 (1H,3H)-dione (4o): 5-Acetyluracil (64 mg, 0.42 mmol), 4-methoxybenzylamine (77 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and DMF (0.6 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by DCM/MeOH = 95:5) affording 4o (83 mg, 67% yield) as an off-white solid. m.p. 253 - 254 °C.

$^1$H NMR (300 MHz, d$_6$-DMSO) δ 8.28 (s, 1H), 7.67 (s, 1H), 7.56 (s, 1H), 7.05 (d, 2H, $J = 8.6$ Hz), 6.85 (d, 2H, $J = 8.6$ Hz), 5.45 (s, 2H), 3.71 (s, 3H); $^{13}$C NMR (75 MHz d$_6$-DMSO) δ 162.3, 158.8, 151.7, 144.8, 137.5, 134.1, 129.7, 129.1, 127.8, 113.9, 55.1, 51.3; MS (EI): m/z: 299 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{14}$H$_{14}$N$_5$O$_3$ [M+H$^+$]: 300.1091, found 300.1096.
1-(4-Methoxybenzyl)-5-ferrocenyl-1H-1,2,3-triazole (4p): 1-Acetylferrocene (100 mg, 0.42 mmol), 4-methoxybenzylamine (168 mg, 1.2 mmol), 4-nitrophenyl azide (143 mg, 0.88 mmol), 4 Å molecular sieves (50 mg) and toluene (1 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 2:8) affording 4p (130 mg, 79% yield) as a red semi solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.74 (s, 1H), 7.03 (d, 2H, $J = 8.5$ Hz), 6.86 (d, 2H, $J = 8.5$ Hz), 5.58 (s, 2H), 4.37 (s, 2H), 4.32 (s, 2H), 4.08 (s, 4H), 3.79 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.5, 136.3, 133.1, 128.1, 127.9, 114.4, 70.9, 69.8, 69.6, 68.6, 55.4, 51.3; MS (EI): m/z: 373 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{20}$H$_{20}$FeN$_3$O [M+H$^+$]: 374.0950, found 374.0958.

1-(4-Methoxybenzyl)-5-methyl-1H-1,2,3-triazole-4-carbaldehyde (4q): Propiophenone (56 mg,0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4q (96 mg, 83% yield) as an off-white solid. m.p. 74 - 75 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.43 - 7.42 (m, 3H), 7.17 - 7.13 (m, 2H), 6.99 - 6.94 (m, 2H), 6.79 - 6.74 (m, 2H), 5.35 (s, 2H), 3.76 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.4, 141.7, 134.5, 129.7, 129.3, 129.0, 128.9, 127.8, 127.7, 114.1, 55.4, 51.7, 10.7; MS (EI): m/z: 279 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{17}$H$_{18}$N$_3$O [M+H$^+$]: 280.1444, found 280.1443.
5-Butyl-1-(4-methoxybenzyl)-4-propyl-1H-1,2,3-triazole (4r): 5-nonanone (59 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4r (94 mg, 78% yield) as an off white semi-solid.

¹H NMR (300 MHz, CDCl₃) δ 7.10 (d, 2H, J = 8.67 Hz), 6.85 (d, 2H, J = 8.67 Hz), 5.40 (s, 2H), 3.79 (s, 3H), 2.56 (t, 2H, J = 7.53 Hz), 2.46 (t, 2H, J = 7.71 Hz), 1.74 - 1.64 (m, 4H), 1.28 - 1.25 (m, 2H), 0.95 (t, 3H, J = 7.35 Hz), 0.87 - 0.82 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.6, 145.5, 133.2, 128.6, 127.7, 114.4, 55.4, 51.62, 31.0, 27.3, 23.0, 22.6, 14.1, 13.8; MS (EI): m/z: 287 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₇H₂₆N₃O [M+H]⁺: 288.2070, found 288.2072.

1-(4-Methoxybenzyl)-4-methyl-5-thiophen-2-yl)-1H-1,2,3-triazole (4s): 2-Propanoyl thiophene (59 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4s (106 mg, 89% yield) as an off white semi-solid.

¹H NMR (300 MHz, CDCl₃) δ 7.49 - 7.47 (m, 1H), 7.13 - 7.10 (m, 1H), 7.01 (d, 2H, J = 8.5 Hz), 6.95 - 6.94 (m, 1H), 6.80 (d, 2H, J = 8.7 Hz), 5.46 (s, 2H), 3.76 (s, 3H), 2.35 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 142.9, 129.3, 128.7, 128.3, 128.1, 127.7, 127.6, 127.0, 114.1, 55.3, 51.8, 11.0; MS (EI): m/z: 285 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₅H₁₆N₃OS [M+H]⁺: 286.1008, found 286.1009.

2-(5-(9-Ethyl-9H-carbazol-3-yl)-1-(4-methoxybenzyl)-1H-1,2,3-triazol-4-yl)acetic acid (4t): 4-(9-Ethyl-9H-carbazol-3-yl)-4-oxobutanoic acid (50 mg, 0.17 mmol), 4-methoxybenzylamine (49 mg, 0.35 mmol), 4-nitrophenyl azide (30 mg, 0.17 mmol), acetic acid (3 mg, 0.05 mmol), 4 Å molecular sieves (10 mg) and toluene (0.4 mL). Reaction time is 40 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 1:9) affording 4t (53 mg, 74%) as an off white solid. m.p. 90 - 91 °C.

¹H NMR (300 MHz, CDCl₃) δ 7.95 (d, 1H, J = 7.9Hz), 7.80 (s, 1H), 7.52 - 7.44 (m, 3H), 7.28 - 7.23 (m, 2H), 7.03 (d, 2H, J = 8.6 Hz), 6.79 (d, 2H, J = 8.5 Hz), 5.40 (s, 2H), 4.41 (q, 2H, J = 7.2 Hz), 3.78 – 3.76 (m, 5H), 3.70 – 3.70 (m, 5H),
1.47 (t, 3H, J = 7.1 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.1, 159.6, 140.5, 138.6, 137.2, 129.3, 127.7, 127.1, 126.7, 123.3, 122.5, 122.3, 120.8, 119.7, 115.9, 114.3, 109.1, 109.0, 55.4, 52.0, 37.2, 29.8, 14.0; MS (EI): m/z: 440 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{26}$H$_{35}$N$_4$O$_3$ [M+H]$^+$: 441.1921, found 441.1924.

2-Butanone (30 mg, 0.44 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The products was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 7:3) affording 4u (53 mg, 59% yield) and 4v (16 mg, 18% yield) as colorless semi-solids.

1-(4-Methoxybenzyl)-4,5-dimethyl-1H-1,2,3-triazole (4u): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.11 (d, 2H, J = 8.5 Hz), 6.85 (d, 2H, J = 8.5 Hz), 5.38 (s, 2H), 3.78 (s, 3H), 2.24 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.6, 141.2, 129.1, 128.7, 127.1, 114.3, 55.4, 51.6, 10.3, 8.0; MS (EI): m/z: 217 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{12}$H$_{16}$N$_3$O [M+H]$^+$: 218.1289, found 218.1284.

5-Isopropyl-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4v): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.49 (s, 1H), 7.11 (d, 2H, J = 8.6 Hz), 6.85 (d, 2H, J = 8.6 Hz), 5.43 (s, 2H), 3.79 (s, 3H), 2.51 (q, 2H, J = 7.7 Hz), 1.19 (t, 3H, J = 7.5 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.6, 138.7, 132.2, 128.7, 127.0, 114.4, 55.4, 51.3, 16.9, 12.2; MS (EI): m/z: 217 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{12}$H$_{16}$N$_3$O [M+H]$^+$: 218.1289, found 218.1282. Spectroscopic data for 4v are consistent with previously reported data for this compound.

Methyl isopropyl ketone (36 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The products was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 5:5) affording 4w (54 mg, 56% yield) and 6w (15 mg, 10% yield) as a colorless semi-solid.

5-Isopropyl-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4w): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.49 (s, 1H), 7.11 (d, 2H, J = 8.8 Hz), 6.85 (d, 2H, J = 8.6 Hz), 5.46 (s, 2H), 3.79 (s, 3H), 2.92 - 2.83 (m, 1H), 1.15 (d, 6H, J = 7.0 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.6, 143.5, 130.9, 128.6, 127.3, 114.4, 55.4, 51.3, 23.9, 22.5; MS (EI): m/z: 231 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{16}$H$_{20}$N$_3$O [M+H]$^+$: 232.1444, found 232.1449.

N-(4-Methoxybenzyl)-4,4,5-trimethyl-1-(4-nitrophenyl)-4,5-dihydro-1H-1,2,3-triazol-5-amine (6w): $^1$H NMR (300 MHz, CDCl$_3$) δ 8.05 (d, 2H, J = 8.8 Hz), 7.07 (d, 2H, J = 8.2 Hz), 6.84 (d, 2H, J = 8.5 Hz), 6.75 (d, 2H, J = 8.7 Hz), 4.86 (s, 1H), 3.94 (s, 2H), 3.80 (s, 3H), 1.24 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.8,
1-(4-Methoxybenzyl)-4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazole (4x): Cyclohexanone (41 mg, 0.84 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4x (91 mg, 91% yield) as a solid. m.p. 91 - 92 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.15 (d, 2H, $J = 8.8$ Hz), 6.85 (d, 2H, $J = 8.8$Hz), 5.36 (s, 2H), 3.79 (s, 3H), 2.74 - 2.72 (m, 2H), 2.43 - 2.39 (m, 2H), 1.78 - 1.73 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.6, 144.0, 131.9, 129.1, 127.1, 114.3, 55.4, 51.5, 22.6, 22.5, 22.0, 20.2; MS (EI): m/z: 243 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{14}$H$_{18}$N$_3$O [M+H]$^+$: 244.1444, found 244.1440.

1-(4-Methoxybenzyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (4y): Cyclooctanone (52 mg, 0.42 mmol), 4-methoxybenzylamine (77 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4y (101 mg, 89% yield) as a semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.10 (d, 2H, $J = 8.8$ Hz), 6.84 (d, 2H, $J = 8.7$Hz), 5.39 (s, 2H), 3.78 (s, 3H), 2.89 (t, 2H, $J = 6.4$ Hz), 2.62 (t, 2H, $J = 6.2$Hz), 1.74 - 1.72 (m, 2H), 1.54 - 1.50 (m, 2H), 1.39 - 1.37 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.5, 145.3, 133.2, 128.6, 127.6, 114.3, 55.4, 51.4, 28.4, 26.0, 26.0, 24.9, 24.7, 21.9; MS (EI): m/z: 271 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{16}$H$_{22}$N$_3$O [M+H]$^+$: 272.1757, found 272.1755.

1-(4-Methoxybenzyl)-4,5,6,7,8,9,10,11,12,13-decahydro-1H-cyclododeca[d][1,2,3]triazole (4z): Cyclododecanone (76 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl
azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4z (132 mg, 95% yield as a semisolid.

¹H NMR (300 MHz, CDCl₃) δ 7.09 (d, 2H, J = 8.7 Hz), 6.84 (d, 2H, J = 8.7 Hz), 5.42 (s, 2H), 3.78 (s, 3H), 2.59 (t, 2H, J = 7.0 Hz), 2.49 (t, 2H, J = 7.2 Hz), 1.88 - 1.80 (m, 2H), 1.61 - 1.52 (m, 2H), 1.42 - 1.19 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 146.1, 133.3, 128.5, 127.5, 114.3, 55.4, 51.7, 27.7, 26.2, 25.3, 24.8, 24.8, 24.5, 22.6, 22.6, 19.6; MS (EI): m/z: 327 (M⁺); HRMS (ESI⁺): m/z calcd for C₂₀H₂₈N₃O [M+H⁺]: 328.2383, found 328.2382.

O
N
N
N
MeO
4aa: 76 % yield

1-(4-Methoxybenzyl)-1,4,6,7-tetrahydropyrano[3,4-d][1,2,3]triazole (4aa): Tetrahydro-4H-pyran-4-one (42 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4aa (78 mg, 76% yield) as an off white solid. m.p. 75 - 76 °C.

¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, 2H, J = 8.8 Hz), 6.87 (d, 2H, J = 8.8 Hz), 5.42 (s, 2H), 4.80 (s, 2H), 3.85 (t, 2H, J = 5.5), 3.80 (s, 3H), 2.55 (t, 2H, J = 5.5); ¹³C NMR (75 MHz, CDCl₃) δ 159.9, 142.3, 129.5, 129.3, 126.5, 114.5, 64.2, 64.0, 55.4, 51.9, 22.0; MS (EI): m/z: 245 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₃H₁₆N₃O₂ [M+H⁺]: 246.1237, found 246.1239.

O
N
N
N
OMe
4ab: 73% yield

5-Benzyl-1-(4-methoxybenzyl)-4,5,6,7-tetrahydro-1H-[1,2,3]triazolo[4,5-c]pyridine (4ab): 1-Benzylpiperidin-4-one (79 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 5:2) affording 4ab (107 mg, 78% yield) as an off white solid. m.p. 75 - 76 °C.

¹H NMR (300 MHz, CDCl₃) δ 7.32 - 7.26 (m, 5H), 7.16 (d, 2H, J = 8.7 Hz), 6.85 (d, 2H, J = 8.6 Hz), 5.36 (s, 2H), 3.78 (s, 3H), 3.70 (s, 2H), 2.67 (s, 2H), 2.71 (t, 2H, J = 5.8 Hz), 2.49 (t, 2H, J = 5.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 159.7, 142.9, 138.0, 130.5, 129.3, 129.1, 128.5, 127.4, 114.4, 61.9, 55.4, 51.8, 49.9, 49.3, 21.0; MS (EI): m/z: 334 (M⁺); HRMS (ESI⁺): m/z calcd for C₂₀H₂₅N₄O [M+H⁺]: 335.1866, found 335.1869.
3-(4-Methoxybenzyl)-3,8-dihydroinden[1,2-d][1,2,3]triazole (4ac): 1-indanone (55 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4ac (99 mg, 95% yield) as an off white solid. m.p. 110 - 111 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.52 - 7.49 (m, 1H), 7.29 - 7.25 (m, 4H), 7.13 (t, 1H, $J = 8.6$ Hz), 6.88 (d, 2H, $J = 8.6$ Hz), 5.70 (s, 2H), 3.78 (s, 3H), 3.79 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.8, 155.9, 147.6, 141.3, 129.8, 129.0, 127.3, 127.2, 127.0, 126.7, 120.1, 114.6, 55.4, 53.1, 29.1; MS (EI): m/z: 277 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{17}$H$_{16}$N$_3$O [M+H]$^+$: 278.1288, found 278.1281.

1-(4-Methoxybenzyl)-4,5-dihydro-1H-naphth[1,2-d][1,2,3]triazole (4ad): 1-Tetralone (61 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4ad (103 mg, 85% yield) as a solid. m.p. 84 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.35 - 7.30 (m, 2H), 7.28 - 7.17 (m, 2H), 7.12 (d, 2H, $J = 8.8$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 5.77 (s, 2H), 3.76 (s, 3H), 3.02 (s, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.5, 145.7, 137.3, 131.4, 129.2, 128.5, 127.9, 127.3, 127.2, 125.0, 122.7, 114.5, 55.3, 52.7, 30.3, 20.8; MS (EI): m/z: 291 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{18}$H$_{18}$N$_3$O [M+H]$^+$: 292.1444, found 292.1447.
1-(4-Methoxybenzyl)-1,4,5,6-tetrahydrobenzo[3,4]cyclohepta[1,2-d][1,2,3]triazole (4ae): 1-Benzosuberone (67 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub> followed by heptane/EtOAc = 6:4) affording 4ae (119 mg, 94% yield) as an off white semi-solid.

1H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.29 - 7.24 (m, 4H), 7.16 (d, 2H, J = 8.7 Hz), 6.83 (d, 2H, J = 8.7 Hz), 5.59 (s, 2H), 3.77 (s, 3H), 2.93 (t, 2H, J = 7.3 Hz), 2.57 (t, 2H, J = 6.0 Hz), 2.23 - 2.14 (m, 2H); 13C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.4, 146.1, 142.4, 133.1, 130.1, 128.9, 128.3, 127.5, 126.8, 126.6, 114.3, 55.3, 51.7, 32.8, 29.9, 23.3; MS (EI): m/z: 305 (M<sup>+</sup>); HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>19</sub>H<sub>20</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 306.1601, found 306.1605.

1-(4-Methoxybenzyl)-1,8-dihydroindeno[1,2-d][1,2,3]triazole (4af): 2-Indanone (55 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub> followed by heptane/EtOAc = 6:4) affording 4af (86 mg, 75% yield) as an off white semi-solid.

1H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 - 7.76 (m, 1H), 7.34 - 7.27 (m, 4H), 7.21 - 7.16 (m, 1H), 6.91 (d, 2H, J = 8.7 Hz), 5.54 (s, 2H), 3.81 (s, 3H), 3.24 (s, 2H); 13C NMR (75 MHz, CDCl<sub>3</sub>) δ 160.1, 156.4, 144.8, 141.9, 133.7, 130.2, 127.6, 126.1, 125.9, 125.8, 119.9, 114.6, 55.5, 53.3, 28.0; MS (EI): m/z: 277 (M<sup>+</sup>); HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>17</sub>H<sub>16</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 278.1288, found 278.1288.

3-(4-Methoxybenzyl)-4,5-dihydro-3H-naphtho[1,2-d][1,2,3]triazole (4ag): 2-Tetralone (61 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub> followed by heptane/EtOAc = 6:4) affording 4ag (100 mg, 82% yield) as a semi solid.

1H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.93 (d, 1H, J = 7.3 Hz), 7.30 - 7.26 (m, 1H), 7.18 - 7.15 (m, 4H), 6.85 (d, 2H, J = 8.6 Hz), 5.47 (s, 2H), 3.78 (s, 3H), 3.0 (t, 2H, J = 7.7 Hz), 2.72 (t, 2H, J = 7.8 Hz); 13C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.7, 144.1, 133.4, 132.6, 129.0, 128.7, 128.2, 127.5, 127.4, 126.9, 122.1, 114.5, 55.4, 51.8, 28.5, 19.1; MS (EI): m/z: 291 (M<sup>+</sup>); HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 292.1443, found 292.1445.
2-((5-Phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridine (4ah): Acetophenone (52 mg, 0.42 mmol), pyridin-2-ylmethanamine (64 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 2:8) affording 4ah (70 mg, 67% yield) as an off-white semi solid.

1H NMR (300 MHz, CDCl₃) δ 8.56 (d, 1H, J = 5), 7.80 (s, 1H), 7.67 – 7.62 (m, 1H), 7.42 -7.40 (m, 5H), 7.27 -7.20 (m, 1H), 7.03 (d, 1H, J = 8), 5.70 (s, 2H); 13C NMR (75 MHz, CDCl₃) δ 155.5, 149.7, 138.8, 137.2, 133.2, 129.6, 129.1, 128.9, 126.7, 123.1, 121.7, 53.4; MS (EI): m/z: 236 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₄H₁₂N₄ [M+H]⁺: 265.1448, found 265.1442.

3-(1-(3,4,5-Trimethoxybenzyl)-1H-1,2,3-triazol-5-yl)-1H-indole (4ai): 3-Acetylindole (66 mg, 0.42 mmol), 3,4,5-trimethoxybenzylamine (115 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 6:4) affording 4ai (119 mg, 78% yield) as an off-white solid. m.p. 180 - 181 °C.

1H NMR (300 MHz, CDCl₃) δ 9.31 (s, 1H), 7.89 (s, 1H), 7.50 - 7.46 (m, 2H), 7.31 - 7.26 (m, 1H), 7.22 - 7.16 (m, 1H), 7.13 (d, 1H, J = 2.6 Hz), 6.23 (s, 2H), 5.52 (s, 2H), 3.79 (s, 3H), 3.63 (s, 6H); 13C NMR (75 MHz, CDCl₃) δ 153.5, 137.6, 136.1, 133.7, 132.2, 131.6, 126.3, 124.5, 123.3, 121.2, 119.2, 111.9, 104.3, 102.1, 60.9, 56.0, 52.1; MS (EI): m/z: 364 (M⁺); HRMS (ESI⁺): m/z calcd for C₂₀H₂₁N₄O₃ [M+H]⁺: 365.1608, found 365.1610.

1-(4-Fluorobenzyl)-4,5-dihydro-1H-naphtho[1,2-d][1,2,3]triazole (4aj): 1-Tetralone (61 mg, 0.42 mmol), 4-fluorobenzyamine (73 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8...
mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 5:2) affording 4aj (92 mg, 79% yield) as an off white semi-solid.

$$^1$$H NMR (300 MHz, CDCl₃) δ 7.32 - 7.14 (m, 6H), 7.06 - 7.0 (m, 2H), 5.81 (s, 2H), 3.04 (s, 4H); $$^{13}$$C NMR (75 MHz, CDCl₃) δ 164.2, 161.0, 145.9, 137.4, 131.5, 131.1, 129.4, 128.7, 128.5, 128.4, 127.2, 124.9, 122.5, 116.4, 116.1, 52.5, 30.4, 20.8; MS (EI): m/z: 279 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₇H₁₅FN₃ [M+H]⁺: 280.1244, found 280.1242.

N-(2-(5-Phenyl-1H-1,2,3-triazol-1-yl)ethyl)aniline (4ak): Acetophenone (52 mg, 0.42 mmol), N-phenylmethanediamine (71 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by CH₂Cl₂/MeOH = 95:5) affording 4ak (69 mg, 62% yield) as an off white semi solid.

$$^1$$H NMR (300 MHz, CDCl₃) δ 7.69 (s, 1H), 7.48 - 7.45 (m, 3H), 7.41 - 7.35 (m, 2H), 7.30 - 7.21 (m, 5H), 4.45 (t, 2H, J = 6 Hz), 3.10 (t, 2H, J = 6 Hz); $$^{13}$$C NMR (75 MHz, CDCl₃) δ 139.7, 138.3, 133.1, 129.6, 129.2, 129.0, 128.5, 128.1, 127.2, 127.1, 53.3, 48.2; MS (EI): m/z: 264 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₆H₁₇N₄ [M+H]⁺: 265.1448, found 265.1442.

N-(5-Phenyl-1H-1,2,3-triazol-1-yl)piperidine (4al): Acetophenone (50 mg, 0.42 mmol), 4-piperidinamine (58 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by CH₂Cl₂/MeOH = 95:5) affording 4al (53 mg, 56% yield) as an off white semi-solid.

$$^1$$H NMR (300 MHz, CDCl₃) δ 7.68 (s, 1H), 7.53 - 7.50 (m, 3H), 7.36 - 7.33 (m, 2H), 4.39 - 4.32 (m, 1H), 3.29 - 3.24 (m, 2H), 2.72 - 2.64 (m, 2H), 2.36 - 2.30 (m, 2H), 2.28 - 1.98 (m, 2H); $$^{13}$$C NMR (100 MHz, CDCl₃) δ 137.2, 133.0, 129.6, 129.3, 129.1, 127.5, 56.5, 45.8, 34.1; MS (EI): m/z: 228 (M⁺); HRMS (ESI⁺): m/z calcd for C₁₃H₁₇N₄ [M+H]⁺: 229.1448, found 229.1445.
1-Allyl-5-phenyl-1H-1,2,3-triazole (4am): Acetophenone (52 mg, 0.42 mmol), allylamine (34 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4am (49 mg, 61% yield) as an off white semi-solid. 

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.50 - 7.40 (m, 5H), 6.09 - 5.96 (m, 1H), 5.27 (d, 1H, $J$ = 9.3 Hz), 5.07 - 4.97 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.1, 133.1, 132.2, 129.6, 129.1, 128.8, 127.0, 118.8, 50.6; MS (EI): m/z: 185 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{11}$H$_{12}$N$_3$ [M+H]$^+$: 186.1026, found 186.1028. Spectroscopic data for 4am is consistent with previously reported data for this compound.$^7$

1-(2,2-Dimethoxyethyl)-5-phenyl-1H-1,2,3-triazole (4an): Acetophenone (50 mg, 0.42 mmol), 2,2-dimethoxyethanamine (61 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 4an (79 mg, 82% yield) as an off-white solid. m.p. 120 - 121 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (s, 1H), 7.49 - 7.48 (m, 5H), 4.89 (t, 1H, $J$ = 7.6 Hz), 4.41 (d, 2H, $J$ = 7.5 Hz), 3.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.9, 132.8, 129.5, 129.2, 129.0, 126.9, 103.4, 55.2, 49.6; MS (EI): m/z: 233 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{12}$H$_{16}$N$_3$O$_2$ [M+H]$^+$: 234.1237, found 234.1238.

(S)-5-Phenyl-1- (1-phenylethyl)-1H-1,2,3-triazole (4ao): Acetophenone (50 mg, 0.42 mmol), (S)-(−)-α-methylbenzylamine (71 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 5:2) affording 4ao (91 mg, 87% yield) as an off-white solid. m.p. 53 - 54 °C.
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.70 (s, 1H), 7.42 - 7.40 (m, 3H), 7.31 - 7.26 (m, 3H), 7.20 - 7.17 (m, 4H), 5.57 (q, 1H, \(J = 7.1 \) Hz), 2.02 (d, 3H, \(J = 7.0 \) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 141.4, 138.0, 133.3, 129.5, 129.4, 129.0, 128.9, 128.1, 127.3, 126.3, 58.5, 22.9\); MS (EI): m/z: 249 (M\(^+\)); HRMS (ESI\(^+\)): m/z calcd for C\(_{16}\)H\(_{16}\)N\(_3\) [M+H\(^+\)]: 250.1339, found 250.1339.

\[ \text{4ap: 83% yield} \]

\((S)-2-(5\text{-Phenyl-1H-1,2,3-triazol-1-yl})\text{butan-1-ol (4ap)}: \text{Acetophenone (50 mg, 0.42 mmol), (S)-2-aminobutan-1-ol (51 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH\(_2\)Cl\(_2\) followed by heptane/EtOAc = 4:6) affording 4ap (75 mg, 83% yield) as an off white semi-solid.} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.54 (s, 1H), 7.50 - 7.44 (m, 5H), 4.46 - 4.31 (m, 2H), 4.0 - 3.97 (m, 1H), 3.73 (s, br, 1H), 2.06 - 1.79 (m, 2H), 0.69 (t, 3H, \(J = 7.3 \)Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 139.6, 132.4, 129.6, 129.6, 129.1, 127.1, 65.0, 62.1, 25.1, 10.4\); MS (EI): m/z: 217 (M\(^+\)); HRMS (ESI\(^+\)): m/z calcd for C\(_{12}\)H\(_{16}\)N\(_3\)O [M+H\(^+\)]: 218.1288, found 218.1287.

\[ \text{4aq: 25% yield} \]

\(1-(4\text{-Methoxyphenyl})\text{-5-phenyl-1H-1,2,3-triazole (4aq): Acetophenone (50 mg, 0.42 mmol), 4-methoxyaniline (72 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH\(_2\)Cl\(_2\) followed by heptane/EtOAc = 6:4) affording 4aq (26 mg, 25% yield) as an off-white solid. m.p. 160 - 161 °C.} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.85 (s, 1H), 7.36 - 7.24 (m, 7H), 6.93 (d, 2H, \(J = 8.8 \) Hz), 3.84 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 160.2, 137.4, 133.3, 129.7, 129.3, 129.0, 128.7, 127.0, 126.7, 114.6, 55.7\); MS (EI): m/z: 251 (M\(^+\)); HRMS (ESI\(^+\)): m/z calcd for C\(_{15}\)H\(_{14}\)N\(_3\)O [M+H\(^+\)]: 252.1131, found 252.1132. Spectroscopic data for 4ar are consistent with previously reported data for this compound\(^7\).
1,1′-Bis(1-(4-methoxybenzyl)-1H-1,2,3-triazol-5-yl)ferrocene (7): 1, 1′-Diacetylferrocene (100 mg, 0.37 mmol), 4-methoxybenzylamine (282 mg, 2.07 mmol), 4-nitrophenyl azide (121 mg, 0.74 mmol), 4 Å molecular sieves (50 mg) and toluene (1 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 2:8) affording 7 (140 mg, 68% yield) as a red solid. m.p. 100 - 101 °C.

1H NMR (300 MHz, CDCl₃) δ 7.65 (s, 2H), 6.96 (d, 4H, J = 8.4 Hz), 6.84 (d, 4H, J = 8.5 Hz), 5.42 (s, 4H), 4.26 (s, 4H), 4.18 (s, 4H), 3.79 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 159.6, 135.1, 133.3, 128.1, 127.5, 114.5, 72.2, 71.7, 70.0, 55.5, 51.5; MS (EI): m/z: 560 (M⁺); HRMS (ESI⁺): m/z calcd for C₃₀H₂₉FeN₆O₂ [M+H⁺]: 561.1695, found 561.1691.

1,3,5-Tris (1- (4-methoxybenzyl)-1H-1,2,3-triazol-5-yl)benzene (8): 1,3,5-Triacetylbenzene (50 mg, 0.24 mmol), 4-methoxybenzylamine (140 mg, 1.03 mmol), 4-nitrophenyl azide (144 mg, 0.88 mmol), acetic acid (4 mg, 0.06 mmol), 4 Å molecular sieves (50 mg) and toluene (0.8 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 2:8) affording 8 (118 mg, 77% yield) an off-white solid. m.p. 167 - 168 °C.

1H NMR (300 MHz, CDCl₃) δ 7.65 (s, 3H), 7.28 (s, 3H), 6.84 (d, 6H, J = 8.6 Hz), 6.73 (d, 6H, J = 8.8 Hz), 5.35 (s, 6H), 3.72 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 159.8, 135.7, 133.9, 129.7, 128.8, 128.5, 126.9, 114.4, 55.4, 52.0; MS (EI): m/z: 639 (M⁺); HRMS (ESI⁺): m/z calcd for C₃₆H₃₄N₉O₃ [M+H⁺]: 640.2779, found 640.2781.
Tris (2-{5-phenyl-1H,1,2,3-triazol-1-yl}ethyl)amine (9): Acetophenone (295 mg, 2.4 mmol), tris(2-aminoethyl)amine (100 mg, 0.68 mmol), 4-nitrophenyl azide (370 mg, 2.2 mmol), acetic acid (4 mg, 0.06 mmol) 4 Å molecular sieves (30 mg) and toluene (0.6 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by CH$_2$Cl$_2$/MeOH= 95:5) affording 9 (230 mg, 65% yield) an off-white solid. m.p. 167 - 168 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 (s, 3H), 7.48 - 7.46 (m, 9H), 7.29 - 7.27 (m, 6H), 4.08 - 4.03 (t, 6H, $J$ = 6.6), 2.74 - 2.70 (t, 6H, $J$ = 6.96); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 138.1, 133.2, 129.8, 129.4, 128.9, 128.7, 127.0, 53.5, 46.2; MS (EI): m/z: 530 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{30}$H$_{31}$N$_{10}$ [M+H$^+$]: 531.2727, found 531.2728.

N1,N1'-(Butane-1,4-diyl)bis(N1-(3-(bis(3-(4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazol-1-yl)propyl)amino)propyl)-N3,N3-bis(3-(4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazol-1-yl)propyl)propane-1,3-diamine) (11): Poly(propylene imine)-dendrimer of generation 2 (70 mg, 0.09 mmol), cyclohexanone (106 mg, 1.08 mmol), 4-nitrophenyl azide (178 mg, 1.08 mmol), 4 Å molecular sieves (30 mg) and dioxane (1.5 mL). Reaction time is 24 h. The product was precipitated out in diethyl ether and affording 10 (106 mg, 73% yield) as an off white solid. m.p. 101 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 4.21 (s br, 16H), 3.35 (s br, 4H), 2.71 (s br, 16H), 2.60 (s br, 16H), 2.45 (s br, 32H), 1.96 - 1.56 (m, 62H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.4, 131.9, 52.2, 50.9, 45.8, 29.8, 27.5, 25.8, 22.8, 22.6, 22.0, 20.2; MS (ESI$^+$): m/z: 1622 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{88}$H$_{145}$N$_{30}$ [M+H$^+$]: 1622.2262, found 1622.2211.
1-(2-(1H-imidazol-4-yl)ethyl)-5-phenyl-1H-1,2,3-triazole (11a): Acetophenone (52 mg, 0.42 mmol), histamine (65 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by CH$_2$Cl$_2$/MeOH = 95:5) affording 11a (61 mg, 61% yield) as an off white semi solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.52 (s, 1H), 7.45 - 7.43 (m, 3H), 7.26 - 7.22 (m, 2H), 6.95 (s, 1H), 6.64 (s, 1H), 4.61 (t, 2H, $J = 7.0$ Hz), 3.22 (t, 2H, $J = 7.0$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.5, 135.1, 134.0, 132.9, 129.2, 128.8, 126.8, 116.5, 48.2, 28.1; MS (EI): m/z: 239 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{13}$H$_{14}$N$_5$ [M+H]$^+$: 240.1243, found 240.1248.

3-(2-(5-Phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-indole (11b): Acetophenone (50 mg, 0.42 mmol), tryptamine (94 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 6:4) affording 11b (90 mg, 75% yield) as an off white solid. m.p. 123 - 124 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.09 (s, 1H), 7.63 (s, 1H), 7.41 - 7.14 (m, 6H), 7.06 - 7.00 (m, 3H), 6.83 (s, 1H), 4.60 (t, 2H, $J = 7.3$ Hz), 3.33 (t, 2H, $J = 7.3$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.4, 136.3, 133.0, 129.3, 128.9, 128.8, 127.1, 127.0, 122.6, 122.2, 119.6, 118.2, 111.4, 111.2, 48.8, 26.6; MS (EI): m/z: 288 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{18}$H$_{17}$N$_4$ [M+H]$^+$: 289.1445, found 289.1446. Spectroscopic data for 11b is consistent with previously reported data for this compound.$^7$
1-(((1S,4aS)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-5-phenyl-1H-1,2,3-triazole (11c): Acetophenone (50 mg, 0.42 mmol), dehydroabietylamine (166 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.8 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 5:5) affording 11c (132 mg, 76% yield) as an off-white solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.63 (s, 1H), 7.48 - 7.46 (m, 3H), 7.35 - 7.32 (m, 2H), 7.08 (d, 1H, $J$ = 8.1 Hz), 6.94 (d, 1H, $J$ = 8.1 Hz), 6.87 (s, 1H), 4.32 (s, 2H), 2.86 - 2.76 (m, 3H), 2.19 - 2.15 (m, 1H), 1.80 - 1.31 (m, 6H), 1.22 (s, 3H), 1.20 (s, 3H), 1.15 (s, 3H), 1.05 - 1.04 (m, 2H), 0.93 (s, 3H);

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.0, 145.8, 139.1, 134.7, 133.1, 129.4, 129.3, 128.3, 127.0, 124.1, 123.9, 58.4, 45.9, 39.4, 38.1, 37.7, 36.6, 33.6, 29.9, 25.6, 24.1, 24.0, 19.4, 18.7, 18.5; MS (EI): m/z: 413 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{28}$H$_{36}$N$_3$ [M+H]$^+$: 414.2903, found 414.2909.

13d: 81% yield

2-(5-Phenyl-1H-1,2,3-triazol-1-yl)octadecane-1,3,4-triol (13d): Acetophenone (50 mg, 0.42 mmol), phytosphingosine (185 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (1 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by CH$_2$Cl$_2$/MeOH = 95:5) affording 11d (150 mg, 81% yield) as an off-white semi-solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 (s, 1H), 7.50 - 7.49 (m, 3H), 7.45 - 7.43 (m, 2H), 4.81 - 4.78 (m, 1H), 4.37 - 4.33 (m, 1H), 4.11 - 4.07 (m, 2H), 3.59 - 3.54 (m, 1H), 2.93 (s, 1H), 1.38 - 1.08 (m, 26H), 0.88 (t, 3H, $J$ = 7.0 Hz);

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.0, 132.8, 130.0, 129.4, 129.3, 126.5, 75.5, 72.3, 62.0, 60.3, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 25.9, 22.8, 14.2; MS (EI): m/z: 445 (M$^+$); HRMS (ESI$^+$): m/z calcd for C$_{26}$H$_{44}$N$_3$O$_3$ [M+H]$^+$: 446.3376, found 446.3372.

13e1: 71% yield

(6bS,8aS,12aS,12bR)-9-{4-Mthoxybenzyl}-8a-methyl-1,2,6b,7,8,8a,9,12,12a,12b-decahydronaphtho[2',1':4,5]indeno[1,2-d][1,2,3]triazol-4-ol (13f1): Estrone (113 mg, 0.42 mmol), 4-methoxybenzylamine (160 mg, 1.18 mmol), 4-nitrophenyl azide (137 mg, 0.84 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (1.5 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH$_2$Cl$_2$ followed by heptane/EtOAc = 3:7) affording 13f1 (123 mg, 71% yield) as an off-white solid. m.p. 210 – 211 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.18 (d, 2H, $J$ = 8.7 Hz), 7.09 (d, 1H, $J$ = 8.7 Hz), 6.86 (d, 2H, $J$ = 8.7 Hz), 6.65 - 6.58 (m, 2H), 5.49 - 5.31 (m, 2H), 5.08 (s, 1H), 3.80 (s, 3H), 2.89 - 2.75 (m, 3H), 2.48 - 2.33 (m, 4H), 2.07 - 2.03 (m, 2H), 1.95 - 1.42 (m, 4H), 0.73 (s, 3H);

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.8, 154.0, 149.3, 138.0, 131.7, 129.2, 127.6, 126.2, 115.6, 114.3, 113.0, 61.7, 55.4, 52.7, 44.1, 41.5, 37.3, 34.0, 29.4,
(6bS,8aS, 12aS, 12bR)-9-Butyl-8a-methyl-1,2,6b,7,8a,9, 12, 12a, 12b-decahydronaphtho[2',1':4,5]indenol-[1,2,3]triazol-4-ol (13e2): Estrone (113 mg, 0.42 mmol), n-butyl amine (120 mg, 1.66 mmol), 4-nitrophenyl azide (137 mg, 0.84 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (1.5 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 3:7) affording 13e2 (130 mg, 88% yield) as an off white solid. m.p. 264 - 265 °C.

1H NMR (300 MHz, CDCl₃) δ 7.13 (d, 1H, J = 8.6 Hz), 6.70 - 6.66 (m, 1H), 6.62 (s, 1H), 5.61 (br, 1H), 4.30 - 4.19 (m, 2H), 2.93 - 2.77 (m, 3H), 2.50 - 2.25 (m, 5H), 1.98 - 1.92 (m, 4H), 1.89 - 1.35 (m, 5H), 1.05 (s, 3H), 0.97 (t, 3H, J = 7.3 Hz); 13C NMR (75 MHz, CDCl₃) δ 154.0, 154.3, 149.2, 138.1, 131.8, 126.2, 115.6, 113.0, 61.7, 49.1, 44.2, 41.4, 37.3, 34.3, 32.8, 29.5, 27.4, 26.0, 24.5, 20.0, 17.9, 13.7; MS (EI): m/z: 351 (M⁺); HRMS (ESI⁺): m/z calcd for C₂₂H₂₆N₃O [M+H]⁺: 352.2382, found 352.2381.

(1S,3aS,3bR,5aS,10aS,10bS,12aS)-7-(4-Methoxybenzyl)-10a,12a-dimethyl-1,2,3,3a,3b,4,5,5a,6,7,10a,10b,11,12,12a-hexadecahydrocyclopenta[7,8]phenanthro[2,3-d][1,2,3]triazol-1-ol (13f): 5α-Dihydrotestosterone (120 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.8 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH₂Cl₂ followed by heptane/EtOAc = 4:6) affording 13f (160 mg, 88% yield) as an off white solid. m.p. 96 - 97 °C.

1H NMR (300 MHz, CDCl₃) δ 7.13 (d, 2H, J = 8.5 Hz), 6.86 (d, 2H, J = 8.7 Hz), 5.35 (s, 2H), 3.79 (s, 3H), 3.65 (t, 1H, J = 8.5 Hz), 2.85 (d, 1H, J = 15.6 Hz), 2.40 - 2.24 (m, 2H), 2.09 - 1.83 (m, 3H), 1.72 - 1.22 (m, 11H), 1.15 - 0.85 (m, 4H), 0.75 (s, 3H), 0.66 (s, 3H); 13C NMR (75 MHz, CDCl₃) δ 159.6, 143.8, 130.6, 128.9, 127.1, 114.3, 81.8, 55.4, 53.8, 51.5, 50.9, 42.9, 42.2, 36.8, 36.7, 36.2, 35.6, 31.2, 30.5, 28.9, 24.6,
23.5, 20.8, 11.7, 11.2; MS (EI): m/z: 435 (M⁺); HRMS (ESI⁺): m/z calcd for C₂₇H₃₈N₃O₂ [M+H⁺]: 436.2958, found 436.2956.

4.3 Preparation of N- (4-Methoxybenzyl)-1- (4-nitrophenyl)-5-phenyl-4,5-dihydro-1H-1,2,3-triazol-5-amine (6a). To an oven-dried screw-capped reaction tube equipped with a magnetic stir bar was added acetophenone (500 mg, 4.2 mmol), 4-methoxybenzylamine (800 mg, 5.8 mmol) and 4 Å molecular sieves (500 mg). The mixture was dissolved in anhydrous toluene (4 mL) and stirred at 100 °C for 2 h. After cooling it down to room temperature, an equivalent of 4-nitrophenyl azide (680 mg, 4.2 mmol) was added and the reaction mixture was stirred for another 6 h at 50°C. The resulting reaction mixture was precipitated in diethyl ether, filtered and dried to afford 1.2 g of the triazoline intermediate 6a in 75% yield. m.p. 153 – 154 °C.

1H NMR (300 MHz, CDCl₃) δ 8.09 (d, 2H, J = 8.7 Hz), 7.54 – 7.26 (m, 7H), 7.01 (d, 2H, J = 8.2 Hz), 6.79 (d, 2H, J = 8.5 Hz), 4.82 (d, 1H, J = 18 Hz), 4.35 (d, 1H, J = 18.7 Hz), 3.77 (s, 3H), 3.37 (t, 1H, J = 10.9 Hz), 2.96 (d, 1H, J = 12.0 Hz), 2.60 (d, 1H, J = 10.1 Hz); 13C NMR (75 MHz, CDCl₃) δ 159.2, 144.7, 142.6, 141.5, 130.1, 129.7, 129.6, 129.0, 125.7, 125.6, 114.7, 114.1, 81.6, 80.2, 55.4, 45.9; MS (EI): m/z: 403 (M⁺); HRMS (ESI⁺): m/z calcd for C₂₂H₂₂N₅O₃ [M+H⁺]: 404.1717; found 404.1717.

4.4 Bulk synthesis of 1,2,3-triazole (4a) and the regeneration of the 4-nitrophenyl azide (5a)

1) CH₃COOH (30 mol%) 4Å MS, Toluene 100 °C, 12 h, -5a
2) NaNO₂, 1N HCl

To a 250 mL round-bottom flask equipped with a magnetic stir bar was added an equivalent of acetophenone (5 g, 42 mmol), 1.4 equivalents of 4-methoxybenzylamine (8 g, 58 mmol), one equivalent of 4-nitrophenyl azide (6.8 g, 42 mmol), 30 mol% of acetic acid (8 mg, 0.13 mmol) (0.8 mL, 12.6 mmol) and 4 Å molecular sieves (5 g). The mixture was dissolved in anhydrous toluene (30 mL) and stirred at 100 °C for 12 h. The solvent was evaporated off and the resulting reaction mixture was suspended in hydrochloric acid (3N, 100 mL) and methanol (30 mL) was added to aid the solubility. After cooling the solution to 0 °C, NaNO₂ (6 g) in water (20 mL) was added dropwise. The resulting solution was stirred at 0 °C for 30 minutes, after which reaction mixture was extracted with ethyl acetate at 0-5 °C. The aqueous layer was collected separately and the organic fraction was washed with a saturated NaHCO₃.
solution and brine, dried over MgSO₄ and concentrated in vacuo to afford 1,5-disubstituted 1,2,3-triazole 4a (9.7 g) in sufficient purity with an overall yield of 88%. To the aqueous layer, a solution of NaN₃ (4 g) in 20 mL of water was added dropwise at 0 °C and the whole was stirred for at least an hour at room temperature. The reaction mixture was extracted with diethyl ether and the organic fraction was washed with a saturated NaHCO₃ solution and brine, dried over MgSO₄ and concentrated in vacuo to get the desired azide compound 5a (5.6 g) in sufficient purity (82% yield).

5. References


6. $^1$H and $^{13}$C NMR spectra of products

$^1$H NMR Spectra of 4a (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4a (75 MHz, CDCl3):
\textsuperscript{1}H NMR Spectra of \textbf{4b} (300 MHz, CDCl\textsubscript{3}): 

\textsuperscript{13}C NMR Spectra of \textbf{4b} (75 MHz, CDCl\textsubscript{3}):
\(^1\)H NMR Spectra of 4c (300 MHz, CDCl3):

\[\text{Chemical Shifts (ppm)}\]

\[^1\]C NMR Spectra of 4c (125 MHz, CDCl3):

\[\text{Chemical Shifts (ppm)}\]
$^1$H NMR Spectra of 4d (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4d (75 MHz, CDCl3):
$^1$H NMR Spectra of 4e (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4e (100 MHz, CDCl3):
$^1$H NMR Spectra of 4f (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4f (75 MHz, CDCl3):
$^1$H NMR Spectra of 4g (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4g (75 MHz, CDCl3):
$^1$H NMR Spectra of 4h (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4h (75 MHz, CDCl3):
$^1$H NMR Spectra of 4i (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4i (75 MHz, CDCl3):
$^1$H NMR Spectra of 4j (300 MHz, CDCl3):

[Image of H NMR spectrum]

$^{13}$C NMR Spectra of 4j (75 MHz, CDCl3):

[Image of C NMR spectrum]
$^1$H NMR Spectra of 4k (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4k (75 MHz, CDCl3):
$^1$H NMR Spectra of 4l (300 MHz, CDCl3):

\[
\begin{array}{c}
\text{0.65} \\
\text{0.97} \\
\text{1.01} \\
\text{1.07} \\
\text{1.10} \\
\text{1.29} \\
\text{1.31} \\
\text{1.34} \\
\text{1.35} \\
\text{1.37} \\
\end{array}
\]

$^{13}$C NMR Spectra of 4l (75 MHz, CDCl3):

\[
\begin{array}{c}
\text{110.99} \\
\text{116.05} \\
\text{116.17} \\
\text{116.98} \\
\text{121.53} \\
\text{123.01} \\
\text{123.02} \\
\text{123.03} \\
\text{123.04} \\
\text{123.05} \\
\text{123.06} \\
\text{123.07} \\
\text{123.08} \\
\text{123.09} \\
\text{123.10} \\
\text{123.11} \\
\end{array}
\]
$^1$H NMR Spectra of 4m (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4m (75 MHz, CDCl3):
$^1$H NMR Spectra of 4n (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4n (75 MHz, CDCl3):
$^1$H NMR Spectra of $4o$ (300 MHz, DMSO):

$^{13}$C NMR Spectra of $4o$ (75 MHz, DMSO):
$^1$H NMR Spectra of 4p (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4p (75 MHz, CDCl3):
$^1$H NMR Spectra of 4q (300 MHz, CDCl3):

$^1$C NMR Spectra of 4q (75 MHz, CDCl3):
$^1$H NMR Spectra of 4r (300 MHz, CDCl3):

13C NMR Spectra of 4r (75 MHz, CDCl3):
$^1$H NMR Spectra of 4s (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4s (75 MHz, CDCl3):
$^{1}$H NMR Spectra of 4t (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4t (75 MHz, CDCl3):
$^1$H NMR Spectra of 4u (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4u (75 MHz, CDCl3):
$^1$H NMR Spectra of 4v (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4v (75 MHz, CDCl3):
**H NMR Spectra of 4w (300 MHz, CDCl3):**

**13C NMR Spectra of 4w (75 MHz, CDCl3):**
$^1$H NMR Spectra of 6w (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 6w (75 MHz, CDCl3):
$^1$H NMR Spectra of 4x (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4x (75 MHz, CDCl3):
$^1$H NMR Spectra of 4y (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4y (75 MHz, CDCl3):
$^1$H NMR Spectra of 4z (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4z (75 MHz, CDCl3):
$^1$H NMR Spectra of 4aa (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4aa (75 MHz, CDCl3):
$^1$H NMR Spectra of 4ab (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4ab (75 MHz, CDCl3):
$^1$H NMR Spectra of 4ac (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4ac (75 MHz, CDCl3):
$^1$H NMR Spectra of 4ad (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4ad (75 MHz, CDCl3):
$^1$H NMR Spectra of $4ae$ (300 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of $4ae$ (75 MHz, CDCl$_3$):
H NMR Spectra of 4af (300 MHz, CDCl3):

$^1$H NMR Spectra of 4af (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4af (75 MHz, CDCl3):
\textsuperscript{1}H NMR Spectra of 4ag (300 MHz, CDCl3):

\begin{center}
\includegraphics[width=\textwidth]{hnmr_spectrum.png}
\end{center}

\textsuperscript{13}C NMR Spectra of 4ag (75 MHz, CDCl3):

\begin{center}
\includegraphics[width=\textwidth]{cmr_spectrum.png}
\end{center}
$^1$H NMR Spectra of 4ah (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4ah (75 MHz, CDCl3):
$^1$H NMR Spectra of 4ai (300 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 4ai (75 MHz, CDCl$_3$):
$^1$H NMR Spectra of 4aj (300 MHz, CDCl$_3$):

![H NMR Spectra of 4aj](image)

$^{13}$C NMR Spectra of 4aj (75 MHz, CDCl$_3$):

![C NMR Spectra of 4aj](image)
$^1$H NMR Spectra of 4ak (300 MHz, CDCl₃):

$^{13}$C NMR Spectra of 4ak (75 MHz, CDCl₃):
$^1$H NMR Spectra of 4al (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4al (75 MHz, CDCl3):
$^1$H NMR Spectra of 4am (300 MHz, CDCl₃):

$^{13}$C NMR Spectra of 4am (75 MHz, CDCl₃):
$^1$H NMR Spectra of 4an (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4an (75 MHz, CDCl3):
$^1$H NMR Spectra of 4ao (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4ao (75 MHz, CDCl3):
$^1$H NMR Spectra of 4ap (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4ap (75 MHz, CDCl3):
$^1$H NMR Spectra of 4aq (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 4aq (75 MHz, CDCl3):
$^1$H NMR Spectra of 7 (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 7 (75 MHz, CDCl3):
$^1$H NMR Spectra of 8 (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 8 (75 MHz, CDCl3):
$^1$H NMR Spectra of 9 (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 9 (75 MHz, CDCl3):
$^1$H NMR Spectra of 11 (300 MHz, CDCl$_3$):
\( ^1H \) NMR Spectra of 13a (300 MHz, CDCl3):

\( ^{13}C \) NMR Spectra of 13a (75 MHz, CDCl3):
$^1$H NMR Spectra of 13b (300 MHz, CDCl3):

![NMR Spectra](image)

$^{13}$C NMR Spectra of 13b (75 MHz, CDCl3):

![NMR Spectra](image)
$^1$H NMR Spectra of 13c (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 13c (75 MHz, CDCl3):
$^1$H NMR Spectra of 13d (300 MHz, CDCl3):

![H NMR Spectra of 13d](image1)

$^{13}$C NMR Spectra of 13d (75 MHz, CDCl3):

![C NMR Spectra of 13d](image2)
$^1$H NMR Spectra of 13e1 (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 13e1 (75 MHz, CDCl3):
$^1$H NMR Spectra of 13e2 (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 13e2 (75 MHz, CDCl3):
$^1$H NMR Spectra of 13f (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 13f (75 MHz, CDCl3):
$^1$H NMR Spectra of 6a (300 MHz, CDCl3):

$^{13}$C NMR Spectra of 6a (75 MHz, CDCl3):