Supporting Information for

A gold-triggered dearomative spirocarbocyclization/Diels–Alder reaction cascade towards diverse bridged N-heterocycles

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General Methods

NMR spectra were recorded on a 300, 400 or 600 MHz instrument using CDCl$_3$ or DMSO-$d_6$ as solvent. The mixture of CDCl$_3$ and DMSO-$d_6$ was applied as solvent wherever was necessary. The $^1$H and $^{13}$C chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. Spectra were acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer (Synapt G2 HDMS, Waters, Milford, MA). Samples were infused at 3μL/min and spectra were obtained in positive (or: negative) ionization mode with a resolution of 15000 (FWHM) using leucine enkephalin as lock mass. For chromatography, analytical TLC plates and 70-230 mesh silica gel were used. All the solvents and chemicals were purchased and used as available. Data for $^1$H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for $^{13}$C NMR are reported in terms of chemical shift (δ, ppm).

The microwave irradiation experiments were carried out in a dedicated CEM-Discover monomode microwave apparatus, operating at a frequency of 2.45GHz with continuous irradiation power from 0 to 300 W and utilization of the standard absorbance level of 100 W. The reactions were carried out in 10 mL glass tubes, sealed with Teflon septum and placed in the microwave cavity. The reactions were irradiated at the required set temperature for the stipulated time and then cooled to the ambient temperature with air jet cooling.
General procedure for the synthesis of Ugi products

**Table S1: Starting materials for Ugi reaction**

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<th>Aldehydes</th>
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S3
A screw-cap vial equipped with a magnetic stir bar was charged with aldehyde (0.8 mmol, 1.0 equiv.), amine (0.88 mmol, 1.1 equiv.), alkynoic acid (0.88 mmol, 1.1 equiv), isonitrile (0.88 mmol, 1.1 equiv.), and methanol (3 mL). The reaction mixture was stirred at 50 °C for 12-24 h. The reaction solution was then concentrated under reduced pressure. The obtained residue was purified by column chromatography on silica gel with EtOAc/Heptane (v/v, 1/2) to provide the desired Ugi products 1a-u as solid.

Ugi products were in many cases found to appear as mixture of two rotamers, so it should be noted that in this case, the \(^1\)H and \(^{13}\)C NMR spectra are not very characteristic.

\((E)-N-(\text{tert-butyl})-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (1a)\)

\[
\begin{align*}
(E)-N-(\text{tert-butyl})-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide & (1a) \\
\text{Pale yellow solid, Yield 78\% (Mixture of rotamers ≈ 1.2: 1), Melting point: 86-88 °C.} \\
\text{\(^1\)H NMR (400 MHz, CDCl} & _3) \delta = 10.92 \text{ (s, 0.52H), 10.81 (s, 0.47H), 7.47 (d, } J = 6.9 \text{ Hz, 0.98H),} \\
7.41 - 7.32 \text{ (m, 1.62H), 7.26 (d, } J = 3.5 \text{ Hz, 0.52H), 7.23 - 7.18 \text{ (m, 1.86H), 7.14 (dd, } J = 7.0, \\
2.7 \text{ Hz, 1.14H), 7.03 (m, 1.53H), 6.94 - 6.87 \text{ (m, 0.76H), 6.86 - 6.80 (m, 0.55H), 6.79 - 6.70} \\
\text{(m, 1.06H), 6.64 (d, } J = 15.7 \text{ Hz, 0.55H), 6.58 (d, } J = 16.1 \text{ Hz, 0.51H), 5.86 (s, 0.53H), 5.83} \\
\text{(s, 0.54H), 5.73 (dd, } J = 15.7, 9.5 \text{ Hz, 0.59H), 5.30 (d, } J = 9.5 \text{ Hz, 0.55H), 4.19 (d, } J = 9.0 \\
\text{Hz, 0.48H), 1.70 (s, 1.47H), 1.69 (s, 1.55H), 1.38 (s, 9H).} \\
\text{\(^{13}\)C NMR (101 MHz, CDCl} & _3) \delta = 171.6, 170.0, 156.0, 155.7, 154.8, 154.6, 138.6, 136.9, 135.5, 135.2, 132.1, 130.6, 130.6, \\
129.6, 129.1, 129.0, 128.8, 128.6, 128.6, 127.0, 126.8, 125.1, 121.4, 120.7, 119.1, 119.1, \\
118.0, 118.0, 90.4, 90.1, 69.6, 64.2, 52.7, 52.6, 28.5, 28.5, 3.9, 3.9.} \\
\text{HRMS (ESI) calculated for C}_{24}\text{H}_{27}\text{N}_{2}\text{O}_3^+: 391.2021, \text{ found 391.2020.}
\end{align*}
\]

\((E)-N-(\text{tert-butyl})-2-(N-(2-hydroxyphenyl)propiolamido)-4-phenylbut-3-enamide (1b)\)
Pale yellow solid, Yield 66% (Mixture of rotamers ≈ 3: 1), Melting point: 79-81 °C. **¹H NMR (400 MHz, DMSO-**d**₆)** δ = 11.39 (s, 1H), 8.58 (s, 1H), 7.48 – 7.18 (m, 6H), 7.17 – 7.04 (m, 2H), 6.88 (d, J = 8.2 Hz, 1H), 6.84 (t, J = 7.5 Hz, 0.32H), 6.77 (t, J = 7.5 Hz, 0.72H), 6.61 (d, J = 15.8 Hz, 0.75H), 6.55 (d, J = 16.0 Hz, 0.24H), 6.05 (dd, J = 15.8, 8.4 Hz, 0.22H), 5.72 (dd, J = 15.8, 8.5 Hz, 0.80H), 5.41 (d, J = 8.5 Hz, 0.76H), 5.08 (d, J = 8.3 Hz, 0.22H), 1.99 (s, 1H), 1.32 (s, 6.86H), 1.29 (s, 2.10H). **¹³C NMR (101 MHz, CDCl**₃) δ = 171.9, 168.7, 156.1, 153.9, 136.6, 136.0, 135.7, 134.5, 132.9, 131.2, 129.2, 129.1, 129.0, 129.0, 128.9, 128.8, 128.4, 126.8, 126.7, 125.6, 122.3, 119.4, 117.6, 82.7, 76.5, 63.2, 60.2, 51.8, 51.5, 51.0, 28.9, 28.7, 28.7, 21.2, 14.6. **HRMS (ESI)** calculated for C₂₃H₂₅N₂O₃⁺ ([M+H]⁺): 377.1865, found 377.1863.

**E-N-(1-(tert-buty lamino)-1-oxo-4-phenylbut-3-en-2-yl)-N-(2-hydroxyphenyl)pent-2-ynamide (1c)**

Pale yellow solid, Yield 63%, Melting point: 72-74 °C. **¹H NMR (300 MHz, DMSO-**d**₆)** δ = 11.38 (s, 1H), 8.53 (s, 1H), 7.32 – 7.15 (m, 5H), 7.14 – 7.04 (m, 2H), 6.86 (d, J = 8.1 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 5.73 (dd, J = 15.9, 8.5 Hz, 1H), 5.39 (d, J = 8.5 Hz, 1H), 2.04 (q, J = 7.4 Hz, 2H), 1.31 (s, 9H), 0.73 (t, J = 7.4 Hz, 3H). **¹³C NMR (75 MHz, DMSO-**d**₆)** δ = 171.7, 155.7, 154.2, 135.8, 135.0, 132.4, 130.1, 128.6, 128.4, 128.1, 126.2, 125.8, 122.4, 118.6, 116.9, 94.3, 74.1, 62.6, 59.6, 51.3, 28.4, 28.3, 14.0, 12.4, 11.4. **HRMS (ESI)** calculated for C₂₅H₂₉N₂O₃⁺ ([M+H]⁺): 405.2178, found 405.2181.

**E-N-(1-(tert-buty lamino)-1-oxo-4-phenylbut-3-en-2-yl)-N-(2-hydroxyphenyl)hex-2-ynamide (1d)**
Pale yellow solid, Yield 49%, Melting point: 79-81 °C.  

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ = 11.39 (s, 1H), 8.56 (s, 1H), 7.30 – 7.16 (m, 5H), 7.14 – 7.05 (m, 2H), 6.86 (d, $J = 8.2$ Hz, 1H), 6.74 (t, $J = 7.5$ Hz, 1H), 6.59 (d, $J = 15.9$ Hz, 1H), 5.72 (dd, $J = 15.9$, 8.5 Hz, 1H), 5.39 (d, $J$ = 8.5 Hz, 1H), 2.06 (t, $J = 6.6$ Hz, 2H), 1.31 (s, 9H), 1.17 – 1.04 (m, 2H), 0.62 (t, $J = 7.1$ Hz, 3H). 

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ = 171.7, 155.7, 154.2, 135.8, 135.0, 132.4, 130.1, 128.6, 128.4, 128.1, 126.2, 125.8, 122.4, 118.6, 116.9, 92.9, 62.7, 51.3, 28.3, 20.5, 19.7, 12.7. 

HRMS (ESI) calculated for C$_{26}$H$_{31}$N$_2$O$_3^+$ ([M+H]$^+$): 419.2334, found 419.2338.

(E)-N-(1-(tert-butylamino)-1-oxo-4-phenylbut-3-enyl)-N-(2-hydroxyphenyl)hept-2-ynamide (1e)

Pale yellow solid, Yield 39%, Melting point: 94-95 °C.  

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ = 11.38 (s, 1H), 8.55 (s, 1H), 7.30 – 7.15 (m, 5H), 7.13 – 7.05 (m, 2H), 6.86 (d, $J = 8.2$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.59 (d, $J = 15.9$ Hz, 1H), 5.72 (dd, $J = 15.9$, 8.5 Hz, 1H), 5.39 (d, $J$ = 8.5 Hz, 1H), 2.08 (t, $J = 6.4$ Hz, 2H), 1.31 (s, 9H), 1.14 – 0.86 (m, 4H), 0.70 (t, $J = 7.0$ Hz, 3H). 

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ = 171.7, 155.7, 154.2, 135.8, 135.0, 132.3, 130.1, 128.6, 128.4, 128.1, 126.2, 125.7, 122.4, 118.6, 116.9, 93.0, 74.7, 62.6, 51.3, 29.0, 28.3, 20.7, 17.4, 13.1. HRMS (ESI) calculated for C$_{27}$H$_{33}$N$_2$O$_3^+$ ([M+H]$^+$): 433.2491, found 433.2483.

(E)-N-(tert-butyl)-2-(N-(2-hydroxyphenyl)-3-phenylpropiolamido)-4-phenylbut-3-enamide (1f)
Pale yellow solid, Yield 59% (Mixture of rotamers ≈ 1.2: 1), Melting point: 118-120 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta = 11.51$ (s, 0.57H), 9.56 (s, 0.52H), 8.63 (s, 0.49H), 7.68 (s, 0.56H), 7.48 – 7.14 (m, 10H), 7.12 – 7.03 (m, 2H), 6.97 – 6.85 (m, 1H), 6.81 – 6.73 (m, 1H), 6.65 (d, $J = 15.9$ Hz, 1H), 6.15 (dd, $J = 15.9$, 8.3 Hz, 0.22H), 5.81 (dd, $J = 15.9$, 8.3 Hz, 0.73H), 5.48 (d, $J = 8.3$ Hz, 0.68H), 5.15 (d, $J = 8.3$ Hz, 0.23H), 1.33 (s, 5H), 1.12 (s, 4H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta =$ 171.5, 169.1, 165.6, 155.9, 152.8, 147.9, 140.3, 135.8, 135.4, 135.2, 132.6, 132.1, 130.4, 129.8, 128.7, 128.6, 128.3, 128.1, 127.5, 127.4, 127.3, 126.9, 126.3, 125.5, 122.2, 118.9, 118.7, 117.0, 116.7, 66.8, 51.4, 50.5, 32.5, 28.3, 28.2. HRMS (ESI) calculated for C$_{29}$H$_{29}$N$_2$O$_3$+ ([M+H]$^+$): 453.2178, found 453.2176.

(E)-N-cyclohexyl-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (1g)

Pale yellow solid, Yield 60% (Mixture of rotamers ≈ 3.5: 1), Melting point: 78-80 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 11.41$ (s, 1H), 8.79 (d, $J = 7.9$ Hz, 1H), 7.30 – 7.16 (m, 4H), 7.15 – 7.10 (m, 2H), 6.96 – 6.82 (m, 2H), 6.76 (t, $J = 7.5$ Hz, 1H), 6.60 (d, $J = 15.6$ Hz, 1H), 6.18 (dd, $J = 15.9$, 8.4 Hz, 0.22H), 5.73 (dd, $J = 15.9$, 8.5 Hz, 0.73H), 5.40 (d, $J = 8.4$ Hz, 0.67H), 4.98 (d, $J = 8.3$ Hz, 0.28H), 3.71 – 3.53 (m, 1H), 1.88 – 1.72 (m, 3H), 1.70 (s, 3H), 1.61 – 1.50 (m, 1H), 1.33 – 1.16 (m, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta =$ 171.7, 170.8, 156.0, 154.7, 136.7, 136.0, 135.7, 135.5, 132.9, 130.9, 129.2, 129.1, 129.0, 129.0, 129.0, 128.9, 128.8, 128.4, 126.9, 126.8, 125.9, 123.2, 122.4, 119.2, 117.5, 90.1, 74.0, 62.7, 60.2, 49.1, 48.9, 48.7, 32.6, 32.4, 32.4, 25.6, 25.5, 25.0, 24.8, 21.2, 14.6, 3.9, 3.7, 3.6. HRMS (ESI) calculated for C$_{29}$H$_{29}$N$_2$O$_3$+ ([M+H]$^+$): 417.2178, found 417.2179.

(E)-N-butyl-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (1h)
Pale yellow solid, Yield 38% (Mixture of rotamers ≈ 2.5: 1), Melting point: 61-63 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 11.37 (s, 0.69H), 10.42 (s, 0.29H), 8.88 (t, $J = 5.8$ Hz, 0.75H), 8.08 (t, $J = 5.8$ Hz, 0.32H), 7.38 – 7.15 (m, 4H), 7.15 – 7.02 (m, 2H), 6.96 – 6.46 (m, 4H), 6.21 (dd, $J = 15.8$, 8.5 Hz, 0.29H), 5.70 (dd, $J = 15.8$, 8.7 Hz, 0.67H), 5.39 (d, $J = 8.7$ Hz, 0.61H), 4.94 (d, $J = 8.5$ Hz, 0.32H), 3.22 – 3.03 (m, 2H), 1.97 (s, 0.60H), 1.69 (s, 2.45H), 1.50 – 1.36 (m, 2H), 1.33 – 1.24 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ = 172.7, 170.2, 156.0, 154.9, 154.7, 154.1, 144.4, 136.9, 136.6, 136.0, 135.8, 135.5, 132.9, 131.3, 130.9, 130.5, 129.2, 129.1, 128.8, 128.5, 128.4, 127.0, 126.8, 125.8, 122.6, 122.2, 119.9, 119.4, 119.3, 117.6, 117.0, 116.9, 114.9, 114.8, 90.1, 89.0, 74.6, 74.0, 65.2, 62.9, 31.5, 31.2, 19.9, 19.8, 14.2, 14.0, 3.6. HRMS (ESI) calculated for C$_{24}$H$_{27}$N$_2$O$_3$ + ([M+H]$^+$): 391.2021, found 391.2015.

(E)-N-benzyl-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (II)

Pale yellow solid, Yield 53% (Mixture of rotamers ≈ 2: 1), Melting point: 117-119 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 11.19 (s, 0.65H), 10.28 (s, 0.40H), 9.44 (t, $J = 6.1$ Hz, 0.67H), 8.67 (t, $J = 6.1$ Hz, 0.33H), 7.43 – 7.18 (m, 10H), 7.11 (t, $J = 7.7$ Hz, 2H), 6.92 – 6.74 (m, 2H), 6.66 – 6.59 (m, 1H), 6.20 (dd, $J = 15.8$, 8.6 Hz, 0.28H), 5.74 (dd, $J = 15.8$, 8.6 Hz, 0.65H), 5.48 (d, $J = 8.6$ Hz, 0.60H), 5.11 (d, $J = 8.6$ Hz, 0.31H), 4.53 – 4.29 (m, 2H), 1.99 (s, 0.72H), 1.70 (s, 2.24H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ = 173.1, 170.7, 155.9, 155.0, 154.8, 139.6, 138.8, 136.5, 136.0, 135.9, 135.6, 132.9, 131.5, 131.0, 130.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.2, 127.7, 127.6, 127.5, 127.2, 127.0, 126.8, 126.1, 125.8, 122.5, 122.0, 119.4, 117.5, 90.3, 74.6, 74.0, 64.9, 63.0, 60.2, 43.2, 14.6, 3.8, 3.6. HRMS (ESI) calculated for C$_{27}$H$_{25}$N$_2$O$_3$ + ([M+H]$^+$): 425.1865, found 425.1866.
(E)-N-(tert-butyl)-2-(N-(2-hydroxy-6-methylphenyl)but-2-ynamido)-4-phenylbut-3-enamide (Ij)

Pale yellow solid, Yield 31%, Melting point: 71-73 °C. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta =$ 10.49 (s, 1H), 7.44 (s, 1H), 7.36 – 7.22 (m, 5H), 7.08 (t, $J =$ 7.8 Hz, 1H), 6.75 – 6.68 (m, 2H), 6.60 (d, $J =$ 15.8 Hz, 1H), 6.30 (dd, $J =$ 15.8, 9.2 Hz, 1H), 4.65 (d, $J =$ 9.2 Hz, 1H), 2.25 (s, 3H), 1.70 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta =$ 169.5, 154.9, 154.4, 138.8, 136.6, 135.5, 129.8, 129.1, 129.0, 128.5, 128.2, 126.9, 126.8, 123.7, 121.1, 114.2, 87.5, 74.4, 66.8, 60.2, 51.2, 28.8, 28.7, 21.2, 18.7, 14.6, 3.6. HRMS (ESI) calculated for C$_{25}$H$_{29}$N$_2$O$_3$+ ([M+H]$^+$): 405.2178, found 405.2170.

(E)-N-(tert-butyl)-2-(N-(2-hydroxy-4-methylphenyl)but-2-ynamido)-4-phenylbut-3-enamide (Ik)

Pale yellow solid, Yield 89%, Melting point: 165-167 °C. $^1$H NMR (600 MHz, DMSO-d$_6$) $\delta =$ 11.27 (s, 1H), 8.51 (s, 1H), 7.31 – 7.18 (m, 4H), 7.14 (d, $J =$ 7.1 Hz, 1H), 6.95 (d, $J =$ 7.9 Hz, 1H), 6.69 (s, 1H), 6.62 – 6.51 (m, 2H), 5.72 (dd, $J =$ 15.8, 8.5 Hz, 1H), 5.36 (d, $J =$ 8.5 Hz, 1H), 2.21 (s, 3H), 1.71 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (151 MHz, DMSO-d$_6$) $\delta =$ 172.3, 155.6, 154.8, 140.3, 136.1, 135.3, 132.4, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 128.7, 126.8, 123.3, 122.6, 120.1, 117.9, 90.0, 74.2, 63.2, 51.7, 28.9, 28.7, 21.4, 3.7. HRMS (ESI) calculated for C$_{25}$H$_{29}$N$_2$O$_3$+ ([M+H]$^+$): 405.2178, found 405.2182.

(E)-N-(tert-butyl)-2-(N-(2-hydroxy-5-methylphenyl)but-2-ynamido)-4-phenylbut-3-enamide (II)
Pale yellow solid, Yield 67\% (Mixture of rotamers ≈ 4: 1), Melting point: 95-97 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ = 11.10 (s, 1H), 8.50 (s, 1H), 7.34 – 7.21 (m, 3H), 7.15 – 7.08 (m, 2H), 7.01 (dd, $J$ = 8.3, 2.1 Hz, 1H), 6.90 (s, 1H), 6.76 (d, $J$ = 8.3 Hz, 1H), 6.60 (d, $J$ = 15.8 Hz, 1H), 6.17 (dd, $J$ = 16.0, 8.3 Hz, 0.19H), 5.72 (dd, $J$ = 15.8, 8.5 Hz, 0.82H), 5.36 (d, $J$ = 8.5 Hz, 0.75H), 4.93 (d, $J$ = 8.3 Hz, 0.18H), 2.13 (s, 3H), 1.71 (s, 3H), 1.30 (s, 9H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ = 172.2, 154.6, 153.6, 136.1, 135.3, 132.8, 131.4, 129.2, 129.1, 129.0, 128.9, 128.9, 128.7, 127.7, 126.8, 126.7, 125.5, 122.8, 117.1, 89.9, 74.2, 63.1, 51.7, 28.9, 28.7, 28.7, 20.3, 3.7. HRMS (ESI) calculated for C$_{25}$H$_{29}$N$_2$O$_3$+: 405.2178, found 405.2179.

(E)-N-(tert-butyl)-2-(N-(5-fluoro-2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (1m)

Pale yellow solid, Yield 49\% (Mixture of rotamers ≈ 4: 1), Melting point: 93-95 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 11.38 (s, 1H), 8.58 (s, 1H), 7.37 – 7.21 (m, 4H), 7.18 – 6.95 (m, 3H), 6.95 – 6.80 (m, 1H), 6.58 (d, $J$ = 16.1 Hz, 1H), 6.01 (dd, $J$ = 15.9, 8.1 Hz, 0.20H), 5.78 (dd, $J$ = 15.9, 8.3 Hz, 0.76H), 5.38 (d, $J$ = 8.3 Hz, 0.72H), 5.16 (d, $J$ = 8.1 Hz, 0.19H), 1.74 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ = 172.1, 169.0, 155.8, 154.4, 153.5, 152.9, 136.6, 136.0, 135.7, 134.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.4, 126.7, 126.7, 126.2, 126.1, 123.5, 122.3, 119.2, 119.0, 118.0, 117.9, 117.8, 117.6, 90.3, 73.9, 63.0, 51.8, 51.5, 51.0, 28.9, 28.7, 28.6, 3.6. HRMS (ESI) calculated for C$_{24}$H$_{26}$FN$_2$O$_3$+ ([M+H]$^+$): 409.1927, found 409.1926.

(E)-N-(tert-butyl)-2-(N-(4-chloro-2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (1n)
Pale yellow solid, Yield 52%, Melting point: 84-86 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta =$ 11.96 (s, 1H), 8.62 (s, 1H), 7.26 (m, 3H), 7.18 – 7.15 (m, 2H), 6.96 – 6.87 (m, 2H), 6.82 (dd, $J = 8.5$, 2.4 Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 5.76 (dd, $J = 16.0$, 8.3 Hz, 1H), 5.40 (d, $J = 8.3$ Hz, 1H), 1.75 (s, 3H), 1.31 (s, 9H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta =$ 171.7, 156.7, 154.0, 135.6, 135.4, 134.1, 133.7, 128.6, 128.3, 128.2, 126.3, 124.9, 121.9, 118.6, 116.8, 89.9, 78.5, 73.6, 62.5, 51.4, 28.5, 28.3, 28.2, 3.0. HRMS (ESI) calculated for C$_{24}$H$_{26}$ClN$_2$O$_3$$^+$ ([M+H]$^+$): 425.1631, found 425.1633.

$(E)$-N-(tert-butyl)-2-(N-(4-hydroxy-[1,1'-biphenyl]-3-yl)but-2-ynamido)-4-phenylbut-3-enamide (1o)

Pale yellow solid, Yield 54%, Melting point: 193-195 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta =$ 11.55 (s, 1H), 8.60 (s, 1H), 7.57 – 7.46 (m, 4H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.19 (m, 4H), 7.17 – 7.10 (m, 2H), 6.95 (d, $J = 8.5$ Hz, 1H), 6.62 (d, $J = 15.8$ Hz, 1H), 5.85 (dd, $J = 15.8$, 8.2 Hz, 1H), 5.45 (d, $J = 8.2$ Hz, 1H), 1.70 (s, 3H), 1.33 (s, 9H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta =$ 171.7, 155.2, 154.2, 139.4, 135.8, 135.2, 131.0, 130.6, 128.8, 128.7, 128.5, 128.3, 128.1, 126.5, 126.2, 126.1, 125.9, 125.8, 122.6, 117.4, 89.5, 62.6, 51.3, 28.3, 3.0. HRMS (ESI) calculated for C$_{30}$H$_{31}$N$_2$O$_5$$^+$ ([M+H]$^+$): 467.2334, found 467.2332.

$(E)$-N-(tert-butyl)-4-(4-(dimethylamino)phenyl)-2-(N-(2-hydroxyphenyl)but-2-ynamido)but-3-enamide (1p)
Pale yellow solid, Yield 50%, Melting point: 82-84 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta =$ 11.43 (s, 1H), 8.47 (s, 1H), 7.18 (t, $J = 7.7$ Hz, 1H), 7.04 (d, $J = 7.9$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 2H), 6.85 (d, $J = 8.1$ Hz, 1H), 6.73 (t, $J = 7.6$ Hz, 1H), 6.56 (d, $J = 8.4$ Hz, 2H), 6.45 (d, $J = 15.3$ Hz, 1H), 5.49 – 5.20 (m, 1H), 5.31 (s, 1H), 2.85 (s, 6H), 1.68 (s, 3H), 1.30 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta =$ 172.8, 156.0, 154.6, 150.8, 135.7, 132.9, 130.7, 127.7, 126.1, 123.9, 119.1, 117.4, 117.2, 112.5, 89.8, 74.2, 63.5, 51.7, 28.7, 3.6. HRMS (ESI) calculated for C$_{26}$H$_{32}$N$_3$O$_3^+$ ([M+H]$^+$): 434.2443, found 434.2426.

(E)-N-(tert-butyl)-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-(4-methoxyphenyl)but-3-enamide (1q)

Pale yellow solid, Yield 28% (Mixture of rotamers ≈ 1.3: 1), Melting point: 138-139 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 8.09 – 7.81 (m, 2.55H), 7.40 – 7.17 (m, 3H), 7.16 – 6.93 (m, 2H), 6.92 – 6.81 (m, 1.32H), 6.81 – 6.49 (m, 2H), 4.41 (s, 0.54H), 3.47 (s, 0.43H), 2.43 (s, 1.75H), 2.05 (s, 1.22H), 2.02 (s, 1.74H), 1.73 (s, 1.25H), 1.40 (s, 4.46H), 1.31 (s, 3.50H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 167.4, 165.2, 155.3, 148.0, 144.5, 144.1, 134.4, 130.9, 130.1, 129.1, 129.0, 128.2, 126.9, 125.5, 121.9, 121.4, 120.6, 119.8, 119.3, 118.9, 118.7, 117.4, 115.5, 91.6, 67.1, 52.2, 52.2, 28.6, 28.5, 28.4, 28.3, 21.5, 3.6, 3.5. HRMS (ESI) calculated for C$_{25}$H$_{29}$N$_2$O$_4^+$ ([M+H]$^+$): 421.2127, found 421.2129.

(E)-4-(4-bromophenyl)-N-(tert-butyl)-2-(N-(2-hydroxyphenyl)but-2-ynamido)but-3-enamide (1r)

s12
Pale yellow solid, Yield 62% (Mixture of rotamers ≈ 3.5: 1), Melting point: 159-161 °C. $^1$H NMR (300 MHz, DMSO-<sub>d6</sub>) $\delta = 11.37$ (s, 1H), 8.55 (s, 1H), 7.53 – 7.35 (m, 2.4H), 7.25 – 7.16 (m, 1.25H), 7.09 (d, $J = 7.7$ Hz, 2.26H), 6.94 – 6.69 (m, 2.06H), 6.63 – 6.47 (m, 1.07H), 6.18 (dd, $J = 15.8$, 8.2 Hz, 0.21H), 5.76 (dd, $J = 15.8$, 8.2 Hz, 0.74H), 5.37 (d, $J = 8.4$ Hz, 0.76H), 4.94 (d, $J = 8.4$ Hz, 0.20H), 1.70 (s, 3H), 1.30 (s, 9H). $^{13}$C NMR (75 MHz, DMSO-<sub>d6</sub>) $\delta = 171.4$, 155.6, 154.2, 135.0, 133.8, 132.3, 131.6, 130.6, 130.2, 128.2, 125.6, 123.4, 121.2, 118.7, 117.0, 114.6, 89.4, 73.7, 62.6, 51.3, 28.3. HRMS (ESI) calculated for C<sub>24</sub>H<sub>26</sub>BrN<sub>2</sub>O<sub>3</sub> $^+([M+H]^+)$: 469.1126, found 469.1123.

(E)-N-(tert-butyl)-2-(N-(2-hydroxyphenyl)but-2-ynamido)-4-(4-nitrophenyl)but-3-enamide (1s)

Pale yellow solid, Yield 41% (Mixture of rotamers ≈ 2: 1), Melting point: 108-110 °C. $^1$H NMR (400 MHz, DMSO-<sub>d6</sub>) $\delta = 11.32$ (s, 1H), 8.57 (s, 1H), 8.26 – 8.06 (m, 2H), 7.61 – 7.09 (m, 4H), 6.99 – 6.60 (m, 3H), 6.50 – 6.35 (m, 0.43H), 6.01 (dd, $J = 15.9$, 8.4 Hz, 0.60H), 5.44 (dd, $J = 8.4$ Hz, 0.63H), 4.98 (d, $J = 8.4$ Hz, 0.30H), 1.70 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-<sub>d6</sub>) $\delta = 171.6$, 155.9, 154.7, 147.3, 142.5, 133.6, 132.8, 131.0, 130.2, 130.1, 129.0, 128.3, 128.2, 127.8, 127.8, 127.5, 125.8, 124.5, 124.4, 124.0, 123.9, 119.3, 117.6, 90.2, 74.0, 62.9, 51.8, 51.6, 51.6, 51.1, 28.9, 28.7, 28.7, 28.5, 28.5, 28.5, 14.6, 13.9, 4.0, 3.7, 3.6. HRMS (ESI) calculated for C<sub>24</sub>H<sub>26</sub>N<sub>3</sub>O<sub>5</sub> $^+([M+H]^+)$: 436.1872, found 436.1873.

(E)-N-(tert-butyl)-2-(N-(2-hydroxyphenyl)but-2-ynamido)-3-methyl-4-phenylbut-3-enamide (1t)
Pale yellow solid, Yield 44%, Melting point: 144-147 °C.\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta = 11.50\) (s, 1H), 8.50 (s, 1H), 7.27 (t, \(J = 7.4\) Hz, 2H), 7.19 (dd, \(J = 7.5, 4.4\) Hz, 2H), 7.12 (dd, \(J = 7.8, 1.6\) Hz, 1H), 6.88 (d, \(J = 7.5\) Hz, 2H), 6.81 (d, \(J = 8.1\) Hz, 1H), 6.74 (s, 1H), 6.46 (s, 1H), 5.35 (s, 1H), 1.69 (s, 3H), 1.50 (s, 3H), 1.32 (s, 9H).\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta = 172.2, 156.3, 155.1, 136.8, 133.0, 133.0, 131.4, 130.8, 128.8, 128.8, 128.8, 128.7, 128.6, 127.5, 125.9, 118.7, 117.2, 90.0, 74.3, 68.0, 51.7, 28.6, 28.5, 17.9, 3.6. HRMS (ESI) calculated for C\(25\)H\(29\)N\(2\)O\(3\)+: 405.2178, found 405.2175.

\((Z)-3\)-bromo-\(N\)\((tert\)-butyl\)-2\-(\(N\)\-(2-hydroxyphenyl)but-2-ynamido)-4-phenylbut-3-enamide (Iu)

Pale yellow solid, Yield 37%, Melting point: 96-98 °C.\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta = 11.25\) (s, 1H), 8.74 (s, 1H), 7.34 – 7.28 (m, 3H), 7.26 – 7.21 (m, 3H), 7.17 – 7.10 (m, 2H), 6.82 (d, \(J = 7.8\) Hz, 1H), 6.76 (td, \(J = 7.6, 1.4\) Hz, 1H), 5.80 (s, 1H), 1.70 (s, 3H), 1.33 (s, 9H).\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta = 169.7, 156.5, 155.1, 136.2, 135.1, 133.6, 131.1, 129.1, 128.9, 128.7, 128.6, 125.1, 118.8, 117.8, 117.2, 90.6, 74.0, 69.5, 52.0, 28.5, 17.9, 3.7. HRMS (ESI) calculated for C\(24\)H\(26\)BrN\(2\)O\(3\)+: 469.1126, found 469.1114.

**General procedure for the Microwave-assisted Intramolecular Diels-Alder Reaction**

\((\pm)-1a-u\) \(\rightarrow\) \((\pm)-2a-u\)
The cationic gold catalyst IPrAuOTf was first generated \textit{in situ} by mixing of (IPr)AuCl (10 mol\%) and AgOTf (10 mol\%) along with dichloroethane (2 mL) in a 10 mL microwave vial loaded with a stirring bar and kept stirring for 5 min and used without filtration. To this vial Ugi products 1a-u (0.20 mmol) was subsequently loaded and the reaction vessel was sealed and irradiated in the cavity of a CEM-Discover microwave reactor for 10 min at the set temperature of 115 °C. After completion, the reaction mixture was diluted with dichloromethane and evaporated under reduced pressure. The obtained residue was purified by silica gel column chromatography (EtOAc/Heptane = 1: 1) to afford the bridged compounds 2a-u.

\textbf{Table S2}: Extended optimizations for the cascade dearomative spirocarbocyclization/ Diels–Alder reaction process$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts (10%)</th>
<th>Solvent</th>
<th>T/°C</th>
<th>Time</th>
<th>Conversion</th>
<th>Yield$^b$ of 2a%</th>
<th>d.r</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>(IMes)AuCl/AgOTf</td>
<td>CDCl$_3$</td>
<td>r.t.</td>
<td>16 h</td>
<td>75</td>
<td>52/43$^c$</td>
<td>3.3:1</td>
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<tr>
<td>2</td>
<td>(IMes)AuCl/AgOTf</td>
<td>MeNO$_2$</td>
<td>r.t.</td>
<td>16 h</td>
<td>43</td>
<td>Trace</td>
<td>0</td>
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<tr>
<td>3</td>
<td>(IMes)AuCl/AgOTf</td>
<td>Toluene</td>
<td>r.t.</td>
<td>16 h</td>
<td>54</td>
<td>30</td>
<td>15:1</td>
</tr>
<tr>
<td>4</td>
<td>(IMes)AuCl/AgOTf</td>
<td>DCM</td>
<td>r.t.</td>
<td>16 h</td>
<td>65</td>
<td>38</td>
<td>7.6:1</td>
</tr>
<tr>
<td>5</td>
<td>(IMes)AuCl/AgOTf</td>
<td>DCE</td>
<td>r.t.</td>
<td>16 h</td>
<td>70</td>
<td>45</td>
<td>16:1</td>
</tr>
<tr>
<td>6</td>
<td>HOTf (3 equiv.)</td>
<td>DCE</td>
<td>60 h</td>
<td>3 h</td>
<td>100$^d$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$SO$_4$ (3 equiv.)</td>
<td>DCE</td>
<td>60</td>
<td>3 h</td>
<td>100$^d$</td>
<td>0</td>
<td>0</td>
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</table>

$^a$ The reactions were run with 1a (0.05 mmol) and a catalyst loading of 10 mol\% in a screw-cap vial with solvent (1 mL). The catalyst was prepared by mixing the corresponding gold catalyst (10 mol\%) and silver catalyst (10 mol\%) \textit{in situ}. $^b$ Conversion and yields based on $^1$H NMR analysis using 2,4,6-trimethoxybenzaldehyde as internal standard. $^c$ Isolated yields. IMes = 1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene. $^d$ The decomposed of the starting material was observed.
Scale-up synthesis of bridged compound 2a

The cationic gold catalyst IPrAuOTf was first generated in situ by mixing of IPrAuCl (6 mol%) and AgOTf (6 mol%) along with dichloroethane (3 mL) in a 10 mL microwave vial loaded with a stirring bar and kept stirring for 5 min and used without filtration. To this vial the Ugi product 1a (1.10 g, 2.82 mmol) was subsequently loaded and the reaction vessel was sealed and irradiated in the cavity of a CEM-Discover microwave reactor for 10 min at the set temperature of 115 °C. After completion, the reaction mixture was diluted with dichloromethane and evaporated under reduced pressure. The obtained residue was purified by silica gel column chromatography (EtOAc/Heptane = 1: 1) to afford the bridged N-heterocycle 2a in 72% yield (0.78 g, 2.0 mmol).

Preliminary investigation on the cascade dearomative spirocarbocyclization/iodination process

To a screw capped vial equipped with a magnetic stir bar contained Ugi adducts 1k (0.1 mmol) in DCE (2 mL) solvent, added iodine monochloride (2.5 equiv) dissolved in DCE (1 mL) slowly dropwise at 0 °C. The resulting reaction mixture allows reaching at rt. The reaction was stirred for 16 h. After completion, dilute the reaction mixture with DCM (25 mL) and washed with aqueous Na2S2O3 solution (30 mL), and the aqueous solution was extracted with DCM. The combined organic layers dried over sodium sulfate and evaporated under reduced pressure. The subsequent residue obtained was purified by silica gel chromatography (15–30% EtOAc in hexane) to afford pure compounds 4 in yield of 20%.
N-(tert-butyl)-2-iodo-1,8-dimethyl-3,10-dioxo-6-phenyl-5a,6,7,9a-tetrahydro-3H,5H-7,9b-methanopyrrolo[2,1-a]isoindole-5-carboxamide (4)

Brown solid, Yield 20% (d.r.≈ 10: 1), Melting point: 162-163 °C. NMR data of the major diastereoisomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.26 – 7.18 (m, 3H), 7.10 – 7.03 (m, 2H), 6.66 (s, 1H), 6.12 (dt, $J$ = 6.6, 1.7 Hz, 1H), 4.29 (d, $J$ = 5.2 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.37 (t, $J$ = 2.7 Hz, 1H), 3.27 (dd, $J$ = 3.2, 1.7 Hz, 1H), 3.01 (dd, $J$ = 6.6, 4.1 Hz, 1H), 1.89 (s, 3H), 1.55 (s, 3H), 1.38 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 201.7, 174.6, 167.5, 164.4, 140.9, 139.1, 129.4, 128.3, 126.8, 126.7, 126.4, 120.6, 94.4, 66.7, 66.7, 61.4, 59.9, 51.7, 49.7, 45.2, 31.9, 30.6, 29.3, 28.0, 22.3 15.9. HRMS (ESI) calculated for C$_{25}$H$_{28}$IN$_2$O$_3$ $^+$ ([M+H]$^+$): 531.1141, found 531.1146.

Crystallographic data for compound 2a and 2k

Single crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature from a d1-chloroform-heptane mixture (1:2 v/v) for 2a and 2k. X-ray intensity data were collected at room temperature for 2a and 2k on a Rigaku Ultra 18S generator (Xenocs mirrors, Mo Kα radiation, $\lambda$ = 0.71073 Å) using a MAR345 image plate. The images were interpreted and integrated with CrysAlisPRO$^9$ and the implemented absorption correction was applied. The structures were solved using Olex2$^{10}$ with the ShelXS$^{11}$ structure solution program by Direct Methods and refined with the ShelXL$^{12}$ refinement package using full-matrix least-squares minimization on $F^2$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times $U_{eq}$ of the parent atoms (1.5 for methyl groups). CCDC 1900532 (compound 2a), CCDC 1900531 (compound 2k) contain the supplementary crystallographic data for this paper and can be obtained free of charge via http://www.ccdc.cam.ac.uk/getstructures or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; deposit@ccdc.cam.ac.uk).
Table S3: Crystal data and structure refinement details for compound 2a

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<td>Final R indexes [I&gt;=2σ (I)]</td>
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<td>Final R indexes [all data]</td>
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Figure S1. Crystal structure of compound 2a. Thermal ellipsoids are drawn at the 50% probability level.

Table S4: Crystal data and structure refinement details for compound 2k
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<td>b/Å</td>
<td>10.0908(3)</td>
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<td>c/Å</td>
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<td>α/°</td>
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<tr>
<td>β/°</td>
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<tr>
<td>γ/°</td>
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<td>Crystal size/mm³</td>
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<tr>
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<tr>
<td>Absorption coefficient/mm⁻¹</td>
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<tr>
<td>(F(000))</td>
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<td>Independent reflections</td>
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<td>Final R indexes [(I\geq2\sigma(I))]</td>
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<tr>
<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole</td>
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**Figure S2.** Crystal structure of compound 2k. Thermal ellipsoids are drawn at the 50% probability level.

**References**


Copies of NMR spectra (Post-Ugi products)

$^1$H and $^{13}$C NMR spectra of compound 2a
$^1$H and $^{13}$C NMR spectra of compound 2b
$^1$H and $^{13}$C NMR spectra of compound 2c
$^1$H and $^{13}$C NMR spectra of compound 2d
$^1$H and $^{13}$C NMR spectra of compound 2e
$^1$H and $^{13}$C NMR spectra of compound 2f
$^1$H and $^{13}$C NMR spectra of compound 2g
$^1$H and $^{13}$C NMR spectra of compound 2h
$^1$H and $^{13}$C NMR spectra of compound 2i
$^1$H and $^{13}$C NMR spectra of compound 2j
$^1$H and $^{13}$C NMR spectra of compound 2k
$^1$H and $^{13}$C NMR spectra of compound 21
$^1$H and $^{13}$C NMR spectra of compound 2m
$^1$H and $^{13}$C NMR spectra of compound 2n
$^1$H and $^{13}$C NMR spectra of compound 2o
$^1$H and $^{13}$C NMR spectra of compound 2p
$^1$H and $^{13}$C NMR spectra of compound 2q
$^1$H and $^{13}$C NMR spectra of compound 2r
$^1H$ and $^{13}C$ NMR spectra of compound 2s
$^1$H and $^{13}$C NMR spectra of compound 2t
$^1$H and $^{13}$C NMR spectra of compound 2u.
Copies of NMR spectra (Ugi products)

$^1$H and $^{13}$C NMR spectra of compound 1a

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2. Title | 11Fm
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5. Owner | nmr
6. Site | spect
7. Instrument | spect
8. Author | 1
9. Solvent | CDCl3
10. Temperature | 298.0
11. Pulse Sequence | zg30
12. Experiment | 1D
13. Probe | 5 mm PABO 001
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16. Relaxation Delay | 2.0000
17. Pulse Width | 7.6500
18. PreSaturate Frequency | 19.
20. Acquisition Time | 1.3631
21. Acquisition Date | 2018-09-27782:22:00
22. Class | 2D
23. Spectrometer Frequency | 100.63
24. Spatial Width | 24038.5
25. Lowest Frequency | -1958.7
26. Nucleus | 13C
27. Acquired Size | 32768
28. Spectral Size | 65536
$^1$H and $^{13}$C NMR spectra of compound 1b
\(^1\)H and \(^13\)C NMR spectra of compound 1c
$^1$H and $^{13}$C NMR spectra of compound 1d
$^1$H and $^{13}$C NMR spectra of compound 1e

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\[ \text{Comment: spect} \]

\[ \text{Site: Bruker BioSpin GmbH} \]

\[ \text{Instrument: spect} \]

\[ \text{Author: mmr} \]

\[ \text{Solvent: DMSO} \]

\[ \text{Temperature: 300.0} \]

\[ \text{Pulse Sequence: zg70} \]

\[ \text{Experiment: 1H} \]

\[ \text{Probe: 5 mm BBDO BB-1H} \]

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\[ \text{Modulation Date: 2018-11-07T11:59:59} \]

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\[ \text{Acquisition Size: 16384} \]

\[ \text{Spectral Size: 65536} \]
\(^1\)H and \(^{13}\)C NMR spectra of compound If
$^1$H and $^{13}$C NMR spectra of compound 1g

![NMR spectra of compound 1g](image)

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S48
$^1$H and $^{13}$C NMR spectra of compound 1h
$^1$H and $^{13}$C NMR spectra of compound 1i
$^1$H and $^{13}$C NMR spectra of compound 1j

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Author | 
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Date | 2018-10-17
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Author | 
Solvent | DMSO
Temperature | 298.0
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Experiment | 1D
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Data | 
Spectrometer | FMRI
Spectral Width | 55269.5
Lowest Frequency | 55269.5
Nucleus | 13C
Acquired Size | 32768
Spectral Size | 65536
$^1$H and $^{13}$C NMR spectra of compound 1k
$^1$H and $^{13}$C NMR spectra of compound 11
$^1$H and $^{13}$C NMR spectra of compound **1m**
$^1$H and $^{13}$C NMR spectra of compound 1n
$^1$H and $^{13}$C NMR spectra of compound 10
$^1$H and $^{13}$C NMR spectra of compound 1p
$^1$H and $^{13}$C NMR spectra of compound 1q
$^1$H and $^{13}$C NMR spectra of compound 1r
$^1$H and $^{13}$C NMR spectra of compound 1s
$^1$H and $^{13}$C NMR spectra of compound 1t
$^1$H and $^{13}$C NMR spectra of compound 1u
$^1$H and $^{13}$C NMR spectra of compound 4