Supporting Information

for

Efficient \([\text{NHC}\text{Au}(\text{NTf}_2)]\)-catalyzed hydrohydrazidation of terminal and internal alkynes

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Characterization data and copies of NMR spectra and mass spectrometric data
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1. Experimental section

1.1. Synthesis of gold complexes 2a and 2

To a solution of bis(4-tert-butyl-diphenylmethyl)phenyl)imidazolium chloride salt (100 mg, 0.072 mmol, 1 equiv) in acetone (2 mL) [AuCl(Me₂S)] (23 mg, 0.079 mmol, 1.1 equiv) and finely powdered potassium carbonate (69 mg, 0.50 mmol, 7.0 equiv) were added. The mixture was stirred at 50 °C for 5 h. The solvent was evaporated under reduced pressure and the residue suspended in 2 mL of DCM. The suspension was filtered through a pad of celite and then the celite washed with CH₂Cl₂. The filtrate was concentrated and pentane was added. The precipitate was collected by filtration and purified via column chromatography (cyclohexane/ethyl acetate 2:1, v/v) to obtain the corresponding gold complex 2a (77 mg, 0.048 mmol, 67% yield) as white solid. The ¹H NMR and ¹³C NMR data were in accord with the literature data.¹

¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.21 (m, 8H), 7.18 – 7.11 (m, 16H), 6.87 (s, 4H), 6.79 (d, J = 8.0 Hz, 8H), 5.79 (s, 2H), 5.32 (s, 4H), 2.24 (s, 6H), 1.25 (d, J = 2.2 Hz, 72H).

¹³C NMR (126 MHz, CDCl₃) δ 174.79, 149.11, 149.04, 141.19, 139.98, 139.76, 133.66, 130.09, 129.27, 128.98, 125.23, 124.97, 123.11, 50.21, 34.36, 34.34, 31.39, 31.36, 21.88.
To a solution of the (NHC)AuCl complex 2a (77 mg, 0.048 mmol, 1 equiv) in DCM (5 mL) silver bis(trifluoromethanesulfonyl)amide (20 mg, 0.048 mmol, 1 equiv) was added and the mixture was stirred at rt for 30 min. The formed suspension was filtered through a plug of celite and the celite washed with a small amount of DCM. The filtrate was evaporated under reduced pressure and the residue dried in vacuo to yield complex 2 (85 mg, 0.046 mmol, 96% yield) as white solid. The $^1$H NMR and $^{13}$C NMR data are in accord with the literature data.$^{[2]}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J = 8.4$ Hz, 8H), 7.11 (d, $J = 8.8$ Hz, 16H), 6.87 (s, 4H), 6.74 (d, $J = 8.3$ Hz, 8H), 5.38 (s, 2H), 5.21 (s, 4H), 2.26 (s, 6H), 1.28 (s, 36H), 1.22 (s, 36H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.61, 149.41, 141.54, 140.33, 140.11, 139.48, 133.33, 129.92, 129.54, 129.09, 125.42, 125.05, 123.44, 50.82, 34.52, 34.46, 31.50, 31.47, 21.95.
1.2. Terminal alkynes

\[ N' \text{-Octan-2-ylidene} \text{benzohydrazide} \ (6a): \] 1-Octyne (55 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure a) for the hydrohydrazidation of alkynes to afford 6a (115 mg, 0.47 mmol, 94% yield) as light yellow solid. The \(^1\)H NMR data are in accord with the literature data.\(^3\)

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta 10.37 \text{ (s, 1H)}, 7.89 – 7.67 \text{ (m, 2H)}, 7.64 – 7.37 \text{ (m, 3H)}, 2.43 – 2.16 \text{ (m, 2H)}, 2.03 – 1.85 \text{ (m, 3H)}, 1.62 – 1.38 \text{ (m, 2H)}, 1.38 – 1.17 \text{ (m, 6H)}, 0.97 – 0.76 \text{ (m, 3H)}.\)

\[ N' \text{-}(1\text{-Cyclohexylethylidene}) \text{benzohydrazide} \ (6b): \] Cyclohexylacetylene (54 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6b (90 mg, 0.37 mmol, 74% yield) as colorless solid. The \(^1\)H NMR, \(^{13}\)C NMR and MS data are in accord with the literature data.\(^4\)

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta 10.33 \text{ (s, 1H)}, 7.81 \text{ (d, } J = 7.6 \text{ Hz, 2H)}, 7.50 \text{ (m, 3H)}, 2.24 \text{ (s, 1H)}, 1.91 \text{ (s, 3H)}, 1.71 \text{ (s, 5H)}, 1.39 – 1.15 \text{ (m, 5H)}.\)

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)): \(\delta 165.85, 163.16, 134.27, 131.15, 128.22, 127.57, 46.59, 29.73, 25.64, 25.57, 14.92.\)

HRMS (APCI): \(m/z\) calcd. for C\(_{15}\)H\(_{21}\)N\(_2\)O: 245.16484 [M+H]\(^+\); found: 245.16509.

\[ N' \text{-}(3,3\text{-Dimethylbutan-2-ylidene}) \text{benzohydrazide} \ (6c): \] tert.-Butylacetylene (41 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6c (80 mg, 0.37 mmol, 73% yield) as a colorless solid. The \(^1\)H NMR, \(^{13}\)C NMR and MS data are in accord with the literature data.\(^5\)

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta 10.29 \text{ (s, 1H)}, 7.82 \text{ (d, } J = 7.1 \text{ Hz, 2H)}, 7.61 – 7.38 \text{ (m, 3H)}, 1.93 \text{ (s, 3H)}, 1.14 \text{ (s, 9H)}.\)

\(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta 168.26, 163.23, 134.35, 131.19, 128.27, 127.59, 38.70, 27.64, 12.88.\)

HRMS (APCI): \(m/z\) calcd. for C\(_{13}\)H\(_{19}\)N\(_2\)O: 219.14919 [M+H]\(^+\); found: 219.14897.

\[ N' \text{-}(1\text{-Phenylethylidene}) \text{benzohydrazide} \ (6d): \] Phenylacetylene (51 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6d (117 mg, 0.49 mmol, 98% yield) as colorless solid. The \(^1\)H NMR data are in accord with the literature data.\(^3\)

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta 10.78 \text{ (s, 1H)}, 8.00 – 7.70 \text{ (m, 4H)}, 7.60 \text{ (t, } J = 7.3 \text{ Hz, 1H)}, 7.53 \text{ (t, } J = 7.5 \text{ Hz, 2H)}, 7.50 – 7.39 \text{ (m, 3H)}, 2.39 \text{ (s, 3H)}.\)
4-(Dimethylamino)-N'-{(1-phenylethylidene)benzohydrazide} (6e): Phenylacetylene (51 mg, 0.50 mmol) and 4-dimethylaminobenzohydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6e (135 mg, 0.48 mmol, 96% yield) as light yellow solid.

\[ \text{\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}_6): } \delta 10.37 \ (s, 1H), 7.82 \ (d, J = 6.5 \text{ Hz}, 4H), 7.48 \ - \ 7.37 \ (m, 3H), 6.75 \ (d, J = 8.7 \text{ Hz}, 2H), 3.00 \ (s, 6H), 2.35 \ (s, 3H). \]

\[ \text{\textsuperscript{13}C NMR (126 MHz, DMSO-\textit{d}_6): } \delta 152.42, 138.40, 129.66, 129.15, 128.34, 126.28, 120.13, 110.75, 39.73, 14.21. \]

(Because of overlapping signals, some aromatic C signals could not be observed.)

HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{17}H\textsubscript{20}N\textsubscript{3}O: 282.16009 [M+H]\textsuperscript{+} found: 282.15997.

4-Nitro-N'-{(1-phenylethylidene)benzohydrazide} (6f): Phenylacetylene (51 mg, 0.50 mmol) and 4-nitrobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6f (102 mg, 0.55 mmol, 72% yield) as yellow solid. The \textsuperscript{1}H NMR data are in accord with the literature data.\[^{[3]}\]

\[ \text{\textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6): } \delta 11.09 \ (s, 1H), 8.34 \ (d, J = 8.3 \text{ Hz}, 2H), 8.21 \ - \ 7.26 \ (m, 7H), 2.39 \ (s, 3H). \]

\[ \text{\textsuperscript{13}C NMR (126 MHz, DMSO-\textit{d}_6): } \delta 152.42, 138.40, 129.66, 129.15, 128.34, 126.28, 120.13, 110.75, 39.73, 14.21. \]

HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{17}H\textsubscript{20}N\textsubscript{3}O: 282.16009 [M+H]\textsuperscript{+} found: 282.15997.

\[ N'-(1-Mesitylethylidene)benzohydrazide \ (6g): \]

Mesitylacetylene (72 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6g (156 mg, 0.55 mmol, 97% yield) as colorless solid. The \textsuperscript{1}H NMR data are in accord with the literature data.\[^{[3]}\]

\[ \text{\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}_6): } \delta 9.33 \ (s, 1H), 7.50 \ (t, J = 7.3 \text{ Hz}, 2H), 7.45 \ - \ 7.36 \ (m, 3H), 6.98 \ (s, 2H), 2.27 \ (s, 3H), 2.17 \ (s, 3H), 2.11 \ (s, 6H). \]

\[ \text{\textsuperscript{13}C NMR (126 MHz, DMSO-\textit{d}_6): } \delta 152.28, 137.43, 136.45, 134.37, 129.41, 127.88, 120.11, 110.69, 39.68, 20.60, 19.09, 18.75. \]

(Because of low sample concentration, the amide C signal and some aromatic C signals could not be observed.)

HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{20}H\textsubscript{26}N\textsubscript{3}O: 324.20704 [M+H]\textsuperscript{+} found: 324.20717.

4-(Dimethylamino)-N'-(1-mesitylethylidene)benzohydrazide \ (6h): Mesitylacetylene (72 mg, 0.50 mmol) and 4-dimethylaminobenzohydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6h (144 mg, 0.45 mmol, 89% yield) as light yellow solid.

\[ \text{\textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6): } \delta 10.32 \ (s, 1H), 7.78 \ (d, J = 8.8 \text{ Hz}, 2H), 6.87 \ (s, 2H), 6.73 \ (d, J = 8.7 \text{ Hz}, 2H), 2.99 \ (s, 6H), 2.24 \ (s, 3H), 2.17 \ (s, 3H), 2.16 \ (s, 6H). \]

\[ \text{\textsuperscript{13}C NMR (75 MHz, DMSO-\textit{d}_6): } \delta 152.28, 137.43, 136.45, 134.37, 129.41, 127.88, 120.11, 110.69, 39.68, 20.60, 19.09, 18.75. \]

(Because of low sample concentration, the amide C signal and some aromatic C signals could not be observed.)

HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{20}H\textsubscript{26}N\textsubscript{3}O: 324.20704 [M+H]\textsuperscript{+} found: 324.20717.
N’-(1-(2,4,6-Triisopropylphenyl)ethylidene)benzohydrazide (6i): 2,4,6-Triisopropylphenylacetylene (114 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydradization of alkynes to afford 6i (150 mg, 0.41 mmol, 82% yield) as colorless solid.

1H NMR (500 MHz, DMSO-d6): δ 10.74 (s, 1H), 7.93 (s, 2H), 7.64 – 7.43 (m, 3H), 7.04 (s, 2H), 2.95 – 2.77 (m, 3H), 2.24 (s, 3H), 1.12 (s, 3H), 1.20 (s, 6H), 1.19 (s, 3H), 1.18 – 1.12 (m, 6H).

13C NMR (126 MHz, DMSO-d6): δ 163.12, 161.54, 148.20, 145.05, 135.53, 133.88, 131.37, 128.24, 127.78, 120.44, 33.62, 30.00, 24.51, 23.94, 23.84, 20.67.


4-(Dimethylamino)-N’-(1-(2,4,6-triisopropylphenyl)ethylidene)benzohydrazide: (6j): 2,4,6-Triisopropylphenylacetylene (114 mg, 0.50 mmol) and 4-dimethylaminobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydradization of alkynes to afford 6j (97 mg, 0.24 mmol, 48% yield) as colorless solid.

1H NMR (500 MHz, DMSO-d6): δ 10.33 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.03 (s, 2H), 6.72 (d, J = 8.4 Hz, 2H), 2.98 (s, 6H), 2.92 – 2.81 (m, 3H), 2.21 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.9 Hz, 6H), 1.15 (d, J = 6.8 Hz, 6H).

13C NMR (126 MHz, DMSO-d6): δ 152.24, 148.08, 145.14, 135.80, 129.43, 120.41, 120.09, 110.65, 33.62, 29.97, 24.50, 23.96, 23.88, 20.34. (Because of low sample concentration, the amide C signal and some aromatic C signals could not be observed.)

HRMS (ESI): m/z calcd. for C26H38N3O: 408.30094 [M+H]+; found: 408.30119.

4-Nitro-N’-(1-(2,4,6-triisopropylphenyl)ethylidene)benzohydrazide (6k): 2,4,6-Triisopropylphenylacetylene (114 mg, 0.50 mmol) and 4-nitrobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydradization of alkynes to afford 6k (150 mg, 0.37 mmol, 73% yield) as colorless solid.

1H NMR (500 MHz, DMSO-d6): δ 11.08 (s, 1H), 8.35 (d, J = 8.3 Hz, 2H), 8.18 (d, J = 8.3 Hz, 2H), 7.05 (s, 2H), 2.95 – 2.79 (m, 3H), 2.25 (s, 3H), 1.25 – 1.14 (m, 18H).

13C NMR (126 MHz, DMSO-d6): δ 163.26, 161.52, 149.08, 148.33, 144.97, 139.60, 135.30, 129.34, 123.40, 120.49, 33.62, 30.03, 24.52, 23.92, 23.80, 20.98.


N’-(1-(4-(Dimethylamino)phenyl)ethylidene)benzohydrazide (6l): 4-Dimethylaminophenylacetylene (73 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydradization of alkynes to afford 6l (139 mg, 0.49 mmol, 98% yield) as light yellow solid.

1H NMR (500 MHz, DMSO-d6): δ 10.60 (s, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 2.96 (s, 6H), 2.28 (s, 3H).

13C NMR (126 MHz, DMSO-d6): δ 163.28, 156.98, 151.16, 134.32, 131.22, 128.28, 127.63, 127.59, 125.13, 111.38, 39.78, 14.22.

4-(Dimethylamino)-N’-(1-(4-(dimethylamino)phenyl)ethylidene)-benzohydrazide (6m): 4-Dimethylaminophenylacetylene (73 mg, 0.50 mmol) and 4-dimethylaminobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6m (150 mg, 0.46 mmol, 92% yield) as yellow solid.

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 10.20 (s, 1H), 7.83 – 7.76 (m, 2H), 7.69 (d, $J = 8.3$ Hz, 2H), 6.77 – 6.71 (m, 4H), 2.99 (s, 7H), 2.95 (s, 6H), 2.26 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 163.98, 153.99, 152.39, 151.14, 129.42, 127.31, 125.97, 120.95, 111.58, 110.86, 39.78, 39.66, 13.64.

HRMS (ESI): m/z calcd. for C$_{19}$H$_{25}$N$_4$O: 325.20229 [M+H]$^+$; found: 325.20241.

N’-(1-(4-(Dimethylamino)phenyl)ethylidene)-4-nitrobenzohydrazide (6n): 4-Dimethylphenylacetylene (73 mg, 0.50 mmol) and 4-nitrobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6n (159 mg, 0.55 mmol, 97% yield) as orange solid.

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 11.05 – 10.88 (m, 1H), 8.36 – 8.28 (m, 3H), 8.11 (d, $J = 8.3$ Hz, 2H), 7.94 (d, $J = 8.1$ Hz, 1H), 7.74 (d, $J = 7.9$ Hz, 1H), 6.74 (d, $J = 8.5$ Hz, 2H), 6.64 (d, $J = 8.1$ Hz, 1H), 2.97 (s, 6H), 2.90 (s, 2H), 2.30 (s, 3H), 2.26 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 161.79, 158.28, 151.35, 148.95, 140.12, 130.48, 129.21, 127.72, 127.13, 124.78, 124.43, 122.72, 111.36, 39.76, 14.42.

HRMS (ESI): m/z calcd. for C$_{17}$H$_{19}$N$_4$O$_3$: 327.14517 [M+H]$^+$; found: 327.14546.

N’-(1-(4-Methoxyphenyl)ethylidene)benzohydrazide (6o): 4-Methoxyphenylacetylene (66 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6o (131 mg, 0.49 mmol, 98% yield) as colorless solid. The $^1$H NMR data are in accord with the literature data.\[3\]

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 10.69 (s, 1H), 7.87 (d, $J = 30.3$ Hz, 4H), 7.71 – 7.41 (m, 4H), 7.01 (d, $J = 7.9$ Hz, 2H), 3.82 (s, 3H), 2.35 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 164.18, 153.14, 142.00, 133.92, 131.53, 129.70 – 129.13 (m), 128.23, 127.41, 127.04, 125.24, 125.21, 123.09, 120.92, 14.40.

HRMS (APCI): m/z calcd. for C$_{16}$H$_{14}$F$_3$N$_2$O: 307.10527 [M+H]$^+$; found: 307.10522.

N’-(1-(4-Trifluoromethyl)phenyl)ethylidene)benzohydrazide (6p): 4-Trifluoromethylphenylacetylene (85 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 6p (136 mg, 0.44 mmol, 89% yield) as colorless solid. The $^1$H NMR, $^{13}$C NMR and MS data are in accord with the literature data.\[5\]

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 10.89 (s, 1H), 8.13 – 7.96 (m, 2H), 7.93 – 7.85 (m, 2H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 2H), 2.41 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 164.18, 153.14, 142.00, 133.92, 131.53, 129.70 – 129.13 (m), 128.23, 127.41, 127.04, 125.24, 125.21, 123.09, 120.92, 14.40.

HRMS (APCI): m/z calcd. for C$_{16}$H$_{14}$F$_3$N$_2$O: 307.10527 [M+H]$^+$; found: 307.10522.
4-(Dimethylamino)-N’-(1-(4-(trifluoromethyl)phenyl)ethylidene)-benzohydrazide (6q): 4-Trifluoromethylphenylacetylene (85 mg, 0.50 mmol) and 4-dimethylaminobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrizidation of alkynes to afford 6q (99 mg, 0.28 mmol, 57% yield) as light yellow solid.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.52 (s, 1H), 8.04 (d, $J = 8.1$ Hz, 2H), 7.84 – 7.77 (m, 4H), 6.77 (d, $J = 9.0$ Hz, 2H), 3.01 (s, 6H), 2.41 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 152.46, 142.29, 129.82, 129.09, 128.82, 128.19, 126.88, 125.22, 123.15, 119.85, 110.80, 110.68, 39.69, 14.04. (Because of overlapping signals, some aromatic C signals and signals of the CF$_3$ multiplet could not be observed.)

HRMS (ESI): m/z calcd. for C$_{18}$H$_{19}$F$_3$N$_3$O: 350.14747 [M+H]$^+$; found: 350.14751.

4-Nitro-N’-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzohydrazide (6r): 4-Trifluoromethylphenylacetylene (85 mg, 0.50 mmol) and 4-nitrobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrizidation of alkynes to afford 6r (70 mg, 0.55 mmol, 76% yield) as colorless solid.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 11.23 (s, 1H), 8.35 (d, $J = 8.3$ Hz, 2H), 8.20 – 7.65 (m, 6H), 2.43 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 162.71, 154.55, 149.21, 141.76, 139.61, 130.73 – 129.92 (m), 129.56, 127.21, 126.98, 125.95, 125.31, 125.25, 123.38, 122.34, 14.73.

HRMS (ESI): m/z calcd. for C$_{16}$H$_{13}$F$_3$N$_3$O$_3$: 352.09035 [M+H]$^+$; found: 352.09046.
1.3. Internal alkynes

*N*-{(Hexan-3-yldene)benzohydrazide (7a): 3-Hexyne (41 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 7a (104 mg, 0.48 mmol, 95% yield) as colorless solid. The $^1$H NMR data are in accord with the literature data.$^3$

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 10.46 (s, 1H), 7.86 – 7.68 (m, 2H), 7.57 – 7.37 (m, 3H), 2.44 – 2.18 (m, 4H), 1.64 – 1.41 (m, 2H), 1.15 – 0.98 (m, 3H), 0.91 (t, $J$ = 7.1 Hz, 3H).

*N*-{(1-Phenylbutylidene)benzohydrazide and *N*-{(1-phenylbutan-2-yldene)benzohydrazide (7b): 1-Phenyl-1-butyne (65 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford a mixture of 7b (110 mg, 0.55 mmol, 83% yield, 48:52 ratio) as colorless solid.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.64 (s, 1H), 10.56 (s, 1H), 7.84 – 7.78 (m, 2H), 7.75 – 7.69 (m, 2H), 7.57 – 7.42 (m, 7H), 7.37 – 7.27 (m, 6H), 7.28 – 7.19 (m, 5H), 3.83 (s, 2H), 3.65 (s, 2H), 2.33 ($q$, $J$ = 7.6 Hz, 2H), 2.30 – 2.20 (m, 2H), 1.11 – 1.00 (m, 3H), 0.94 (t, $J$ = 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 165.41, 163.76, 163.39, 137.31, 136.32, 134.13, 131.23, 128.92, 128.73, 128.60, 128.44, 128.22, 126.51, 126.46, 42.19, 35.69, 29.79, 22.21, 10.78, 9.75.

HRMS (APCI): m/z calcd. for $C_{17}H_{19}N_2O$: 267.14919 [M+H]$^+$; found: 267.14934.

*N*-{(1-(3-Methoxyphenyl)hexylidene)benzohydrazide and *N*-{(1-(3-methoxyphenyl)hexane-2-yldene)benzohydrazide (7c): 1-(Hex-1-yn-1-yl)-3-methoxybenzene (94 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford a mixture of 7c (126 mg, 0.39 mmol, 78% yield, 50:50 ratio) as pale yellow, viscous oil.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.66 (s, 1H), 10.61 (s, 1H), 7.83 – 7.72 (m, 4H), 7.58 – 7.39 (m, 8H), 7.26 – 7.21 (m, 2H), 6.88 – 6.78 (m, 5H), 3.79 (s, 3H), 3.74 (s, 3H), 3.72 (s, 4H), 2.36 – 2.28 (m, 2H), 2.24 (s, 2H), 1.49 – 1.25 (m, 8H), 0.84 – 0.79 (m, 6H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 164.84, 163.33, 159.43, 159.34, 138.87, 137.75, 134.09, 131.26, 129.64, 129.43, 128.23, 127.56, 121.16, 120.91, 119.05, 114.86, 114.66, 114.52, 111.84, 54.92, 42.59, 36.14, 35.75, 31.06, 28.58, 28.09, 27.01, 25.75, 22.11, 21.87, 21.76, 13.79, 13.70, 13.59.

HRMS (EI): m/z calcd. for $C_{20}H_{24}N_2O_2$: 324.1832 [M]; found: 324.1823
N’-(1-(3-(Trifluoromethyl)phenyl)hexylidene)-benzohydrazide and N’-(1-(3-(trifluoromethyl)phenyl)hexane-2-ylidene)benzohydrazide (7d):
1-(Hex-1-yn-1-yl)-3-(trifluoromethyl)benzene (113 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydratization of alkynes to afford a mixture of 7d (107 mg, 0.32 mmol, 65% yield, 48:52 ratio) as colorless viscous oil.

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 10.73 (s, 1H), 10.64 (s, 1H), 7.83 – 7.38 (m, 19H), 3.94 (s, 2H), 3.81 – 3.70 (m, 2H), 2.35 (t, $J$ = 7.9 Hz, 2H), 2.28 – 2.19 (m, 2H), 1.55 – 1.43 (m, 2H), 1.42 – 1.35 (m, 2H), 1.29 – 1.18 (m, 4H), 0.86 – 0.75 (m, 6H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): $\delta$ 164.36, 163.53, 162.52, 138.89, 137.80, 134.02, 133.24, 132.81, 131.27, 129.61, 129.37, 128.20, 127.57, 125.45, 125.35, 125.31, 123.24, 123.20, 42.03, 36.24, 35.42, 28.93, 27.99, 26.96, 22.05, 21.68, 13.61, 13.53.

HRMS (ESI): $m/z$ calcd. for C$_{20}$H$_{21}$N$_2$O$_2$: 362.1600 [M]; found: 267.1592.

N’-(1,2-Diphenylethylidene)benzohydrazide (7e):
Diphenylacetylene (89 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydratization of alkynes to afford 7e (142 mg, 0.45 mmol, 90% yield) as colorless solid. The $^1$H NMR data are in accord with the literature data.[3]

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 10.99 (s, 1H), 7.86 (s, 2H), 7.74 (d, $J$ = 7.6 Hz, 2H), 7.56 (t, $J$ = 7.4 Hz, 1H), 7.48 (t, $J$ = 7.6 Hz, 2H), 7.38 (s, 3H), 7.30 (t, $J$ = 7.5 Hz, 2H), 7.26 – 7.15 (m, 3H), 4.41 (s, 2H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): $\delta$ 164.36, 163.53, 162.52, 138.89, 137.80, 134.02, 133.24, 132.81, 131.27, 129.61, 129.37, 128.20, 127.57, 125.45, 125.87, 125.31, 123.24, 123.20, 42.03, 36.24, 35.42, 28.93, 27.99, 26.96, 22.05, 21.68, 13.61, 13.53.

HRMS (ESI): $m/z$ calcd. for C$_{20}$H$_{21}$N$_2$O$_2$: 362.1600 [M]; found: 267.1592.

4-(Dimethylamino)-N’-(1,2-diphenylethylidene)benzohydrazide (7f):
Diphenylacetylene (89 mg, 0.50 mmol) and 4-dimethylamino-benzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydratization of alkynes to afford (165 mg, 0.46 mmol, 92% yield) as colorless solid.

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 10.54 (s, 1H), 7.83 (d, $J$ = 6.7 Hz, 2H), 7.67 (d, $J$ = 8.4 Hz, 2H), 7.39 – 7.17 (m, 8H), 6.72 (d, $J$ = 7.8 Hz, 2H), 4.41 (s, 2H), 2.98 (d, $J$ = 2.0 Hz, 6H).

$^{13}$C NMR (75 MHz, DMSO-d$_6$): $\delta$ 152.39, 137.78, 136.46, 129.68, 128.97, 128.68, 128.32, 128.11, 126.61, 126.33, 119.87, 110.62, 39.65, 32.03.

HRMS (ESI): $m/z$ calcd. for C$_{23}$H$_{24}$N$_3$O: 358.19139 [M+H]$^+$$; found: 358.19155.
**N’-(1,2-Diphenylethylidene)-4-nitrobenzohydrazide (7g)**: Diphenylacetylene (89 mg, 0.50 mmol) and 4-nitrobenzhydrazide (90 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 7g (143 mg, 0.55 mmol, 79% yield) as colorless solid.

\[ ^1H \text{NMR (300 MHz, DMSO-d}_6\text{)}: \delta 11.36 \text{ (s, 1H), 8.33 \text{ (d, } J = 8.3 \text{ Hz, 2H), 7.99 \text{ (d, } J = 8.4 \text{ Hz, 2H), 7.91} \text{ – 7.83 \text{ (m, 1H), 7.72} \text{ – 7.46 \text{ (m, 1H), 7.46} \text{ – 7.12 \text{ (m, 8H), 4.41 (s, 2H).}}] \]

\[ ^13C \text{NMR (75 MHz, DMSO-d}_6\text{)}: \delta 156.41, 149.03, 139.69, 137.07, 136.27, 129.44, 128.66, 128.35, 128.19, 126.98, 123.32, 32.68. \]

HRMS (ESI): m/z calcd. for C\(_{21}\)H\(_{18}\)N\(_3\)O\(_3\): 360.13427 [M+H]+; found: 360.13446.

**N’-(1-Phenyl-2-(o-tolyl)ethylidene)benzohydrazide (7h)**: 1-Methyl-2-(phenylethynyl)benzene (96 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford 7h (80 mg, 0.24 mmol, 49% yield) as colorless solid.

\[ ^1H \text{NMR (500 MHz, DMSO-d}_6\text{)}: \delta 10.90 \text{ (s, 1H), 7.83} \text{ – 6.83 \text{ (m, 20H), 4.29 (s, 2H), 2.38 (s, 3H).}}] \]

\[ ^13C \text{NMR (126 MHz, DMSO-d}_6\text{)}: \delta 163.10, 147.77, 135.94, 134.30, 133.61, 133.40, 131.72, 130.50, 130.24, 130.06, 129.48, 129.33, 129.20, 128.94, 128.82, 128.45, 128.22, 127.57, 127.53, 127.06, 126.59, 126.25, 44.40, 19.19, 18.74. \]


**N’-(2-Phenyl-1-(m-tolyl)ethylidene)benzohydrazide and N’-(1-phenyl-2-(m-tolyl)ethylidene)benzohydrazide (7i)**: 1-Methyl-3-(phenylethynyl)benzene (96 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford a mixture of 7i (107 mg, 0.33 mmol, 68% yield, 70:30 ratio) as off-white solid.

\[ ^1H \text{NMR (500 MHz, DMSO-d}_6\text{)}: \delta 10.95 \text{ (s, 2H), 7.96} \text{ – 6.94 \text{ (m, 26H), 4.41 (s, 1H), 4.38 (s, 2H), 2.31 (s, 2H), 2.24 (s, 3H).}}] \]

\[ ^13C \text{NMR (126 MHz, DMSO-d}_6\text{)}: \delta 164.12, 154.92, 153.76, 153.76, 153.43, 136.41, 136.29, 134.01, 131.46, 129.99, 129.27, 128.81, 128.67, 128.61, 128.36, 128.24, 128.16, 127.86, 127.26, 127.04, 126.81, 126.33, 125.18, 124.16, 32.44, 21.06, 20.99. \]

$N'-(1\{3\text{-}\text{Methoxyphenyl}\}\text{-}\text{2-phenyl-}\text{ethylidene)}\text{benzohydrazide and } N'\{2\{3\text{-}\text{methoxyphenyl}\}\text{-}\text{1-phenylethylidene)}\text{benzo-}$

hydrazide (7j): 1-Methoxy-3-(phenylethynyl)benzene (104 mg, 0.50 mmol) and benzhydrazide (68 mg, 0.50 mmol) were reacted and purified according to the general procedure for the hydrohydrazidation of alkynes to afford a mixture of 7j (125 mg, 0.36 mmol, 73% yield, 60:40 ratio) as pale yellow, viscous oil.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 11.01 (s, 1H), 7.93 – 6.73 (m, 14H), 4.41 (s, 2H), 3.85 – 3.54 (m, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 164.26, 159.52, 159.22, 155.07, 138.93, 137.89, 137.51, 136.50, 134.00, 131.56, 129.82, 129.46, 129.39, 128.74, 128.42, 128.27, 128.21, 127.92, 126.88, 126.40, 120.35, 119.42, 114.95, 114.31, 112.41, 111.58, 55.07, 54.95, 32.57.

HRMS (EI): $m/z$ calcd. for $C_{22}H_{20}N_2O_2$: 344.1519 [M]; found: 344.1519.
2. NMR spectra

2.1. NMR spectra of complexes

Figure S1: $^1$H NMR of complex 2a in CDCl$_3$. 
Figure S2: $^{13}$C NMR of complex 2a in CDCl$_3$.

Figure S3: $^1$H NMR of complex 2 in CDCl$_3$. 
Figure S4: $^{13}$C NMR of complex 2 in CDCl$_3$.

Figure S5: $^1$H NMR of complex 1a in CDCl$_3$. 
Figure S6: $^{13}$C NMR of complex 1a in CDCl$_3$.

Figure S7: $^1$H NMR of complex 1 in CD$_2$Cl$_2$. 
Figure S8: $^{13}$C NMR of complex 1 in CD$_2$Cl$_2$. 
2.2. NMR spectra of hydrohazidation products

2.2.1. Terminal alkynes as substrates

Figure S9: $^1$H NMR of N'-octan-2-ylidene]benzohydrazide (6a) in DMSO-$d_6$. 
Figure S10: $^1$H NMR of $N'$-(1-cyclohexylethylidene)benzohydrazide (6b) in DMSO-$d_6$.

Figure S11: $^{13}$C NMR of $N'$-(1-cyclohexylethylidene)benzohydrazide (6b) in DMSO-$d_6$. 
Figure S12: $^1$H NMR of $N'$-(3,3-dimethylbutan-2-ylidene)benzohydrazide (6c) in DMSO-$_d_6$.

Figure S13: $^{13}$C NMR of $N'$-(3,3-dimethylbutan-2-ylidene)benzohydrazide (6c) in DMSO-$_d_6$. 
Figure S14: $^1$H NMR of $N'$-(1-phenylethylidene)benzohydrazide (6d) in DMSO-$d_6$.

Figure S15: $^1$H NMR of 4-(dimethylamino)-$N'$-(1-phenylethylidene)benzohydrazide (6e) in DMSO-$d_6$. 

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Figure S16: $^{13}$C NMR of 4-(dimethylamino)-N'-{(1-phenylethylidene)benzohydrazide (6e) in DMSO-$d_6$.}

Figure S17: $^1$H NMR of 4-nitro-N'-{(1-phenylethylidene)benzohydrazide (6f) in DMSO-$d_6$.
Figure S18: $^1$H NMR of $N'$-(1-mesitylethylidene)benzohydrazide (6g) in DMSO-$d_6$.

Figure S19: $^1$H NMR of 4-(dimethylamino)-$N'$-(1-mesitylethylidene)benzohydrazide (6h) in DMSO-$d_6$. 
Figure S20: $^{13}$C NMR of 4-(dimethylamino)-$N'$-(1-mesitylidyene)benzohydrazide (6h) in DMSO-$d_6$.

Figure S21: $^1$H NMR of $N'$-(1-(2,4,6-triisopropylpheny)ethylidyne)benzohydrazide (6i) in DMSO-$d_6$. 
Figure S22: $^{13}$C NMR of $N'$-\((1\{-2,4,6\text{-triisopropylphenyl}\)ethylidene)benzohydrazide (6i) in DMSO-$d_6$.

Figure S23: $^1$H NMR of $4'$-(dimethylamino)-$N'$-\((1\{-2,4,6\text{-triisopropylphenyl}\)ethylidene)benzohydrazide (6j) in DMSO-$d_6$. 
Figure S24: $^{13}$C NMR of 4-(dimethylamino)-$N'$-(1-(2,4,6-triisopropylphenyl)ethylidene)benzohydrazide (6j) in DMSO-$d_6$.

Figure S25: $^1$H NMR of 4-nitro-$N'$-(1-(2,4,6-triisopropylphenyl)ethylidene)benzohydrazide (6k) in DMSO-$d_6$. 

S26
Figure S26: $^{13}$C NMR of 4-nitro-$N'$-(1-(2,4,6-triisopropylphenyl)ethylidene)benzohydrazone in (6k) DMSO-$d_6$.

Figure S27: $^1$H NMR of $N'$-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazone (6l) in DMSO-$d_6$. 

S27
Figure S28: $^{13}$C NMR of $N'$-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazide (6i) in DMSO-$d_6$.

Figure S29: $^1$H NMR of 4-(dimethylamino)-$N'$-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazide (6m) in DMSO-$d_6$. 
Figure S30: $^{13}$C NMR of 4-(dimethylamino)-$N'$-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazide (6m) in DMSO-$d_6$. 

Figure S31: $^1$H NMR of 4-nitro-$N'$-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazide (6n) in DMSO-$d_6$. 
Figure S32: $^{13}$C NMR of 4-nitro-$N'$-(1-(4-dimethylamino)phenyl)ethylidene)benzohydrazide (6n) in DMSO-$d_6$.

Figure S33: $^1$H NMR of $N'$-(1-(4-methoxyphenyl)ethylidene)benzohydrazide (6o) in DMSO-$d_6$. 
Figure S34: $^1$H NMR of $N'$-([1-(4-(trifluoromethyl)phenyl)ethylidene]benzohydrazide (6p) in DMSO-$d_6$.

Figure S35: $^{13}$C NMR of $N'$-([1-(4-(trifluoromethyl)phenyl)ethylidene]benzohydrazide (6p) in DMSO-$d_6$. 

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Figure S36: $^1$H NMR of 4-(dimethylamino)-N'-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzohydrazide (6q) in DMSO-$d_6$.

Figure S37: $^{13}$C NMR of 4-(dimethylamino)-N'-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzohydrazide (6q) in DMSO-$d_6$. 
Figure S38: $^1$H NMR of 4-nitro-$N'$-(1-(4-(trifluoromethyl)phenyl)ethyldene)benzohydrazide (6r) in DMSO-$d_6$.

Figure S39: $^{13}$C NMR of 4-nitro-$N'$-(1-(4-(trifluoromethyl)phenyl)ethyldene)benzohydrazide (6r) in DMSO-$d_6$. 
2.2.2. Internal alkynes as substrates

Figure S40: $^1$H NMR of $N'$-(hexan-3-ylidene)benzohydrazide (7a) in DMSO-$d_6$. 
Figure S41: $^1$H NMR of $N'(1$-phenylbutenylidene)benzohydrazide and $N'(1$-phenylbutan-2-yldene)benzohydrazide (7b) in DMSO-$d_6$.

Figure S42: $^{13}$C NMR of $N'(1$-phenylbutenylidene)benzohydrazide and $N'(1$-phenylbutan-2-yldene)benzohydrazide (7b) in DMSO-$d_6$. 
Figure S43: $^1$H NMR of $N'$-(1-(3-methoxyphenyl)hexylidene)benzohydrazide and $N'$-(1-(3-methoxyphenyl)hexan-2-ylidene)benzohydrazide (7c) in DMSO-$d_6$.

Figure S44: $^{13}$C NMR of $N'$-(1-(3-methoxyphenyl)hexylidene)benzohydrazide and $N'$-(1-(3-methoxyphenyl)hexan-2-ylidene)benzohydrazide (7c) in DMSO-$d_6$.
Figure S45: $^1$H NMR of $N'-(1-\text{(3-(trifluoromethyl)phenyl)}\text{hexidyldene})$benzohydrazide and $N'-(1-\text{(3-(trifluoromethyl)phenyl)}\text{hexan-2-yldene})$benzohydrazide (7d) in DMSO-$d_6$.

Figure S46: $^{13}$C NMR of $N'-(1-\text{(3-(trifluoromethyl)phenyl)}\text{hexidyldene})$benzohydrazide and $N'-(1-\text{(3-(trifluoromethyl)phenyl)}\text{hexan-2-yldene})$benzohydrazide (7d) in DMSO-$d_6$. 
Figure S47: $^1$H NMR of $N'-(1,2$-diphenylethylidene)benzohydrazide (7e) in DMSO-d$_6$.

Figure S48: $^1$H NMR of 4-(dimethylamino)-$N'-(1,2$-diphenylethylidene)benzohydrazide (7f) in DMSO-d$_6$. 

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Figure S49: $^{13}$C NMR of 4-(dimethylamino)-$N'$(1,2-diphenylethylidene)benzohydrazide (7f) in DMSO-$d_6$.

Figure S50: $^1$H NMR of 4-nitro-$N'$(1,2-diphenylethylidene)benzohydrazide (7g) in DMSO-$d_6$. 
Figure S51: $^{13}$C NMR of 4-nitro-$N'$-(1,2-diphenylethylidene)benzohydrazide (7g) in DMSO-$d_6$.

Figure S52: $^1$H NMR of $N'$-(2-phenyl-1-(o-tolyl)ethylidene)benzohydrazide and $N'$-(1-phenyl-2-(o-tolyl)ethylidene)-benzohydrazide (7h) in DMSO-$d_6$. 
Figure S53: $^{13}$C NMR of $N'$-(2-phenyl-1-(o-toly)ethylidene)benzohydrazide and $N'$-(1-phenyl-2-(o-toly)ethylidene)benzohydrazide (7h) in DMSO-$d_6$.

Figure S54: $^1$H NMR of $N'$-(2-phenyl-1-(m-toly)ethylidene)benzohydrazide and $N'$-(1-phenyl-2-(m-toly)ethylidene)benzohydrazide (7i) in DMSO-$d_6$. 
Figure S55: $^{13}$C NMR of $N'$-(2-phenyl-1-(m-tolyl)ethylidene)benzohydrazide and $N'$-(1-phenyl-2-(m-tolyl)ethylidene)benzohydrazide (7i) in DMSO-$d_6$.

Figure S56: $^1$H NMR of $N'$-(1-(3-methoxyphenyl)-2-phenylethylidene)benzohydrazide and $N'$-(2-(3-methoxyphenyl)-1-phenylethylidene)benzohydrazide (7j) in DMSO-$d_6$. 
Figure S57: $^{13}$C NMR of $N'$-(1-(3-methoxyphenyl)-2-phenylethylidene)benzohydrazide and $N'$-(2-(3-methoxyphenyl)-1-phenylethylidene)benzohydrazide (7j) in DMSO-d$_6$. 
3. Mass spectra

Figure S58: HRMS of complex 1.
Figure S59: HRMS of complex 2.

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Figure S60: HRMS of \( N'-(1\text{-cyclohexylethylidene}) \text{benzohydrazide (6b).} \)
Figure S61: HRMS of $N'$-(3,3-dimethylbutan-2-ylidene)benzohydrazide (6c).
Figure S62: HRMS of 4-(dimethylamino)-(1-phenylethylidene)benzohydrazide (6e).
Figure S63: HRMS of 4-(dimethylamino)-N'-{(1-mesitylethylidene)benzohydrazide (6h).
Figure S64: HRMS of \( N'\)-\((2,4,6\text{-triisopropylphenyl})\text{ethylidene}\)benzohydrazide (6i).
Figure S65: HRMS of 4-(dimethylamino)-N'-(1-(2,4,6-triisopropylphenyl)ethylidene)benzohydrazide (6j).
Figure S66: HRMS of 4-nitro-N'-(1-(2,4,6-trisopropylphenyl)ethylidene)benzohydrazide (6k).
Figure S67: HRMS of N’-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazide (6l).
Figure S68: HRMS of 4-(dimethylamino)-N’-(1-(4-(dimethylamino)phenyl)ethylidene)benzohydrazide (6m).
Figure S69: HRMS of 4-nitro-\(N\)'-\(1\)-(4-(dimethylamino)phenyl)ethyldiene)benzohydrazide (6n).
Figure S70: HRMS of N’-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzohydrazide (6p).
Figure S71: HRMS of 4-(dimethylamino)-N'-[1-(4-(trifluoromethyl)phenyl)ethylidene]benzohydrazide (6q).
Figure S72: HRMS of 4-nitro-N’-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzohydrazide (6r).
Figure S73: HRMS of $N'$-{1-phenylbutyldiene}benzohydrazide and $N'$-{1-phenylbutan-2-ylidene}benzohydrazide (7b).
Figure S74: HRMS of $N'$-(1-(3-methoxyphenyl)hexylidene)benzohydrazide and $N'$-(1-(3-methoxyphenyl)hexan-2-ylidene)benzohydrazide (7c).
Figure S75: HRMS of $N'$-(1-(3-(trifluoromethyl)phenyl)hexylidene)benzohydrazide and $N'$-(1-(3-(trifluoromethyl)phenyl)hex-2-ylidene)benzohydrazide (7d).
Figure S76: HRMS of 4-(dimethylamino)-N’-(1,2-diphenylethylidene)benzohydrazide (7f).
Figure S77: HRMS of 4-nitro-N’-(1,2-diphenylethylidene)benzohydrazide (7g).
Figure S78: HRMS of $N$'-(1-phenyl-2-(o-tolyl)ethylidene)benzohydrazide (7h).
Figure S79: HRMS of N’-(2-phenyl-1-(m-tolyl)ethyldiene)benzohydrazide and N’-(1-phenyl-2-(m-tolyl)ethyldene)benzohydrazide (7i).
Figure S80: HRMS of $N'$(1-(3-methoxyphenyl)-2-phenylethylidene)benzohydrazide and $N'$(2-(3-methoxyphenyl)-1-phenylethylidene)benzohydrazide (7j).
4. Gas chromatographic measurements

A chromatograph with a split/splitless injector system and a flame ionization detector was used. Chromatographic separation was performed by using a 15 m × 250 µm Varian CP-Sil 8 CB column (df = 1.0 µm) and nitrogen was used as carrier gas at a flow rate of 1.11 mL/min. All injections were carried out in the split flow mode with a split ratio of 7.6:1. The injector was maintained at a temperature of 200 °C and the detector at 270 °C. Quantification was accomplished by using mesitylene as internal standard. The concentration of the standard was equal to each of the substrates in the screening reactions.

The following ramping method was used for all substrate measurements: 3 min hold at 60 °C, 25°C/min heating to 300 °C, then hold at 300 °C for 6 min. (18.6 min total runtime).

**Table S1:** Retention times of all substrates and the internal standard

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<th>Compound name</th>
<th>Retention time / min</th>
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<td>Alkynes</td>
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<td>Cyclohexylacetylene</td>
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<td>t-Butylacetylene</td>
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<td>Phenylacetylene</td>
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<tr>
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<td>Mesitylacetylene</td>
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<td>2,4,6-Triisopropylphenylacetylene</td>
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<td></td>
<td>4-Dimethylaminophenylacetylene</td>
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<td>4-Trifluormethylphenylacetylene</td>
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Benzhydrazides and benzhydrazones could not be observed via GC due to low volatility.
5. References