Oxidative Nitrene Transfer from Azides to Alkynes via Ti(II)/Ti(IV) Redox Catalysis: Formal [2+2+1] Synthesis of Pyrroles

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General considerations

All air- and moisture-sensitive reactions were carried out in a nitrogen-filled glovebox. Solvents for air- and moisture-sensitive reactions were i) deoxygenated by sparging with N_2 and dried by passing through activated alumina columns of a Pure Process Technology solvent purification system (PhMe), degassed, filtered through basic alumina and stored over molecular sieves prior to use (PhBr) and iii) vacuum transferred from CaH_2 ($CDCl_3$). C_6D_5Br was synthesized following literature procedure,[1] degassed, dried over CaH_2, and filtered through basic alumina prior to use.

$Ti(N^tBu)Cl_2py_3$[2] and $Ti(NTol)I_2(THF)_3$[3] were synthesized according to literature procedure. Liquid alkynes, azides and other reagents were freeze-pump-thaw degassed three times and passed through activated basic alumina prior to use.

^1H and ^{13}C NMR spectra were recorded on Bruker Avance III HD 400 and 500 MHz spectrometers. Chemical shifts were referenced to the residual protio-solvent impurity for ^1H (s, 7.26 for $CHCl_3$; s 7.30 ppm, 7.02 ppm and 6.94 ppm for C_6D_4HBr[38]) and solvent carbons for ^{13}C (t, 77.2 ppm for $CDCl_3$). Qualitative GC MS spectra were recorded on a Agilent GC6890N-MSD5975 gas chromatograph-mass spectrometer fitted with a 7683 auto sampler. A HD-5 column (5% diphenyl siloxane in the polymer) was used in the gas chromatograph and electron ionization technique was used for mass spectrometry detection. GC chromatographs were collected on Agilent 7890B GC system equipped with the HP-5 column (30m, 0.32 mm, 0.25 µm, 7 inch cage), a oxidation-methanation reactor (Polyarc® System, Activated Research Company) and a FID detector for quantitative carbon detection.

General procedure for catalytic reactions

For all reactions, 0.5 ml of the respective stock solution and the required reagents were added to a Teflon tape lined screw-cap NMR tube in a N_2-filled glovebox. This was then sealed with a Teflon screw cap and heated at 80/115 °C for 2 – 16 h (internal alkyne scope, Table 1) and 6 h (terminal alkyne scope. Quantitative ^1H NMR spectra of the catalytic mixture were taken before and after heating on the Bruker Avance III HD 400 and 500 MHz spectrometers (Acquisition time = 5 s; delay time = 30 s; dummy scans = 0; number of scans = 8). Three different stock solutions were prepared with C_6D_5Br and triphenylmethane acting as an internal standard.

Internal alkyne screen

In each reaction, internal alkyne (1.0 mmol, 5 equiv.) and 0.5 ml of stock solution were added. Stock solution were prepared by adding $Ti(NTol)(THF)_3I_2$ (10 mol %, 0.02 mmol), triphenylmethane (10 mol %, 0.02 mmol) and 1-azidoadamantane (0.2 mmol, 1.0 equiv.) to C_6D_5Br.

Azide screen

In each reaction, $Ti(NTol)(THF)_3I_2$ (10 mol %, 0.01 mmol), azide (0.1 mmol, 1.0 equiv.) and 0.5 ml of stock solution were added. Reagents have to be added in this particular sequence to prevent trimerization from occurring prematurely. Stock solution was prepared by adding 3-hexyne (0.5 mmol, 5 equiv.) and triphenylmethane (20 mol %, 0.02 mmol) to C_6D_5Br.

Terminal alkyne screen

In each reaction, terminal alkyne (0.42 mmol, 2.1 equiv.), 1-azidoadamantane or (*p*-tolyl)azide (0.2 mmol, 1.0 equiv.) and 0.5 ml of stock solution were added. Stock solution was prepared by adding $Ti(N^tBu)py_3Cl_2$ (10 mol %, 0.02 mmol), triphenylmethane (10 mol %, 0.02 mmol) to C_6D_5Br.

Characterization of starting materials in C_6D_5Br

Characterization of 3-Hexyne (2a) and 1-Hexyne (2e) in C_6D_5Br were reported previously.[3]

Triphenylmethane

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.15 (t, $^4J_{HH}$ = 7.5 Hz, 6H, Ar-*H*), 7.10 – 7.06 (m, 9H, Ar-*H*), 5.45 (s, 1H, C-*H*)

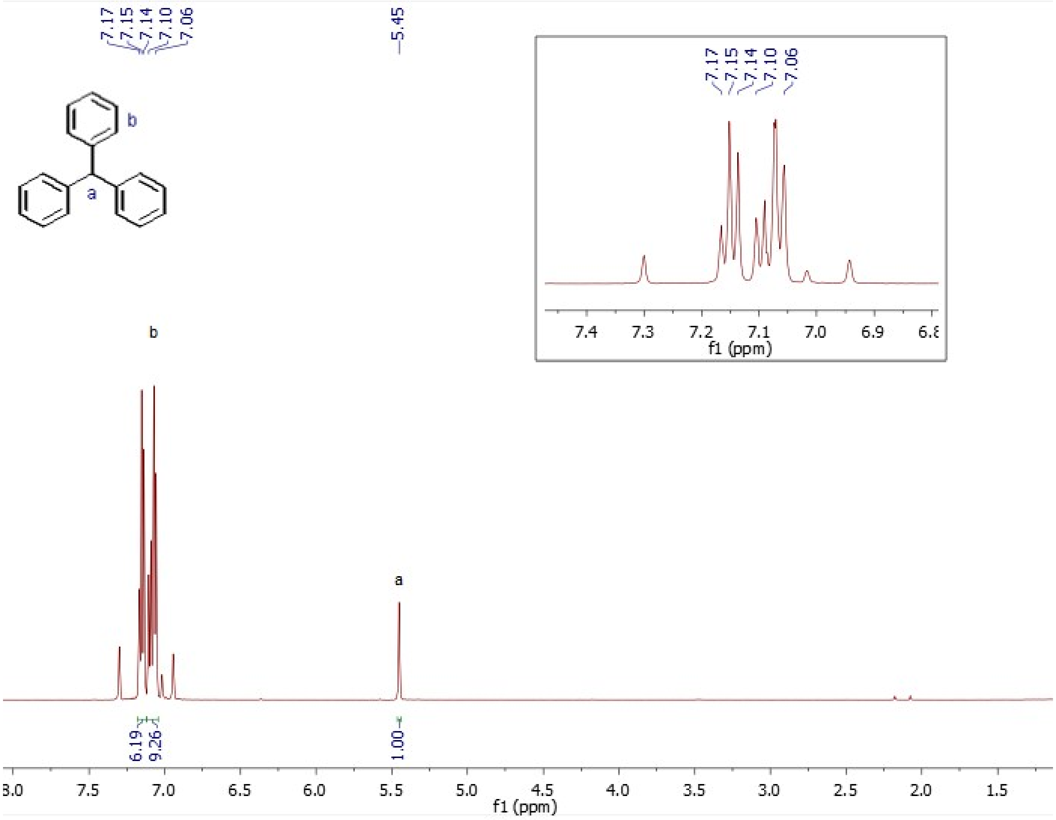


Figure S1: ^{1}H spectrum of triphenylmethane in C_6D_5Br.

(*p*-tolyl)azide (1a)

(*p*-tolyl)azide was synthesized according to literature procedures.[4]

^{1}H NMR (500 MHz, C_6D_5Br): δ 6.89 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *o*-Tol-*H*), 6.74 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *m*-Tol-*H*), 2.11 (s, 3H, C*H*$_3$)

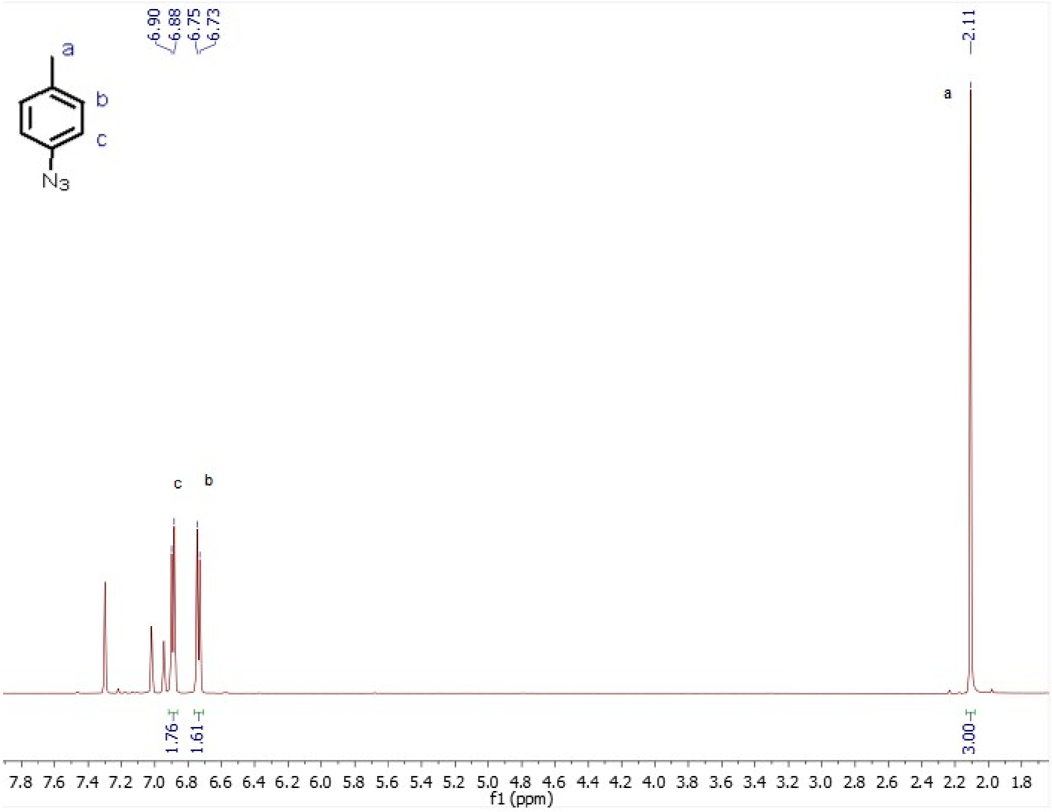


Figure S2: ^{1}H spectrum of (*p*-tolyl)azide in C_6D_5Br.

1-azidoadamantane (1b)

^{1}H NMR (500 MHz, C_6D_5Br): δ 1.90 (br s, 3H, C-H), 1.64 (m, 6H, CH_2), 1.45 (app q, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 15.8 Hz 6H, CH_2)

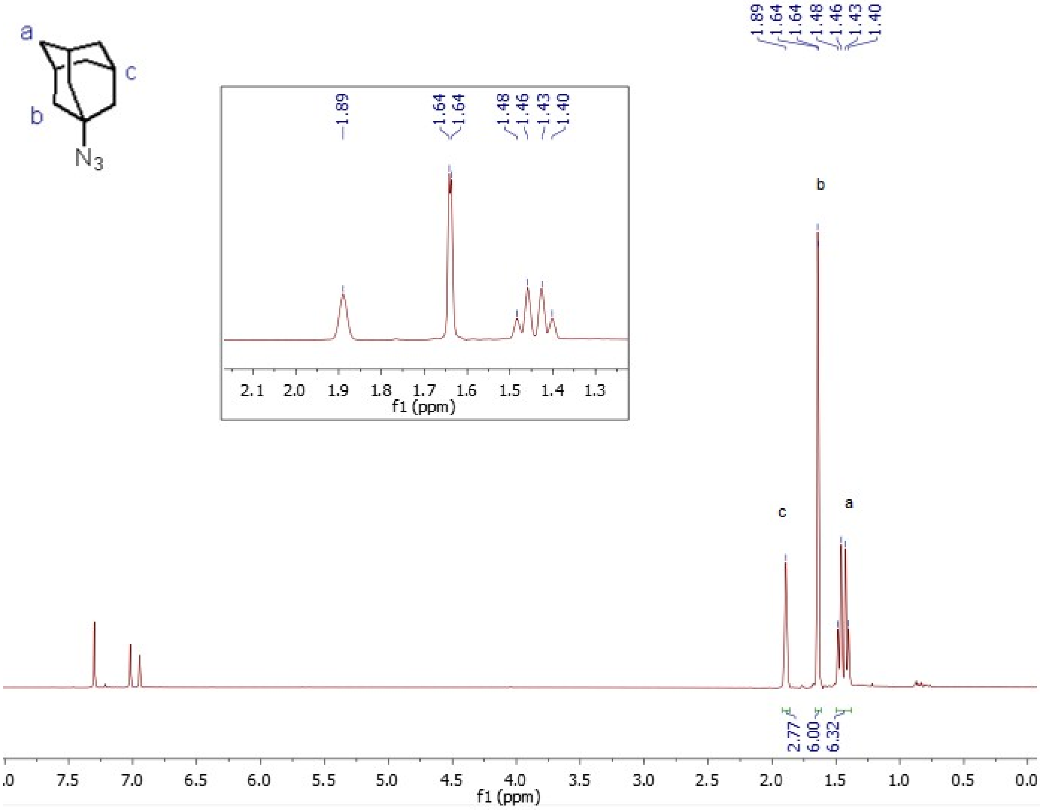


Figure S3: ^{1}H spectrum of 1-azidoadamantane in C_6D_5Br.

1-azidodecane (1c)

1-azidodecane was synthesized according to literature procedures.[5]

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.96 (t, 2H, $H_3C(CH_2)_8$-C*H₂*-N_3), 1.39 – 1.34 (m, 2H, $H_3C(CH_2)_7$-C*H₂*-CH_2N_3), 1.29 – 1.25 (m, 2H, $H_3C(CH_2)_6$-C*H₂*-$(CH_2)_2N_3$), 1.21 – 1.15 (m, 12H, H_3C-(C*H₂*)$_6$- $(CH_2)_3N_3$), 0.88 (t, 3H, *H₃*C-$(CH_2)_9N_3$)

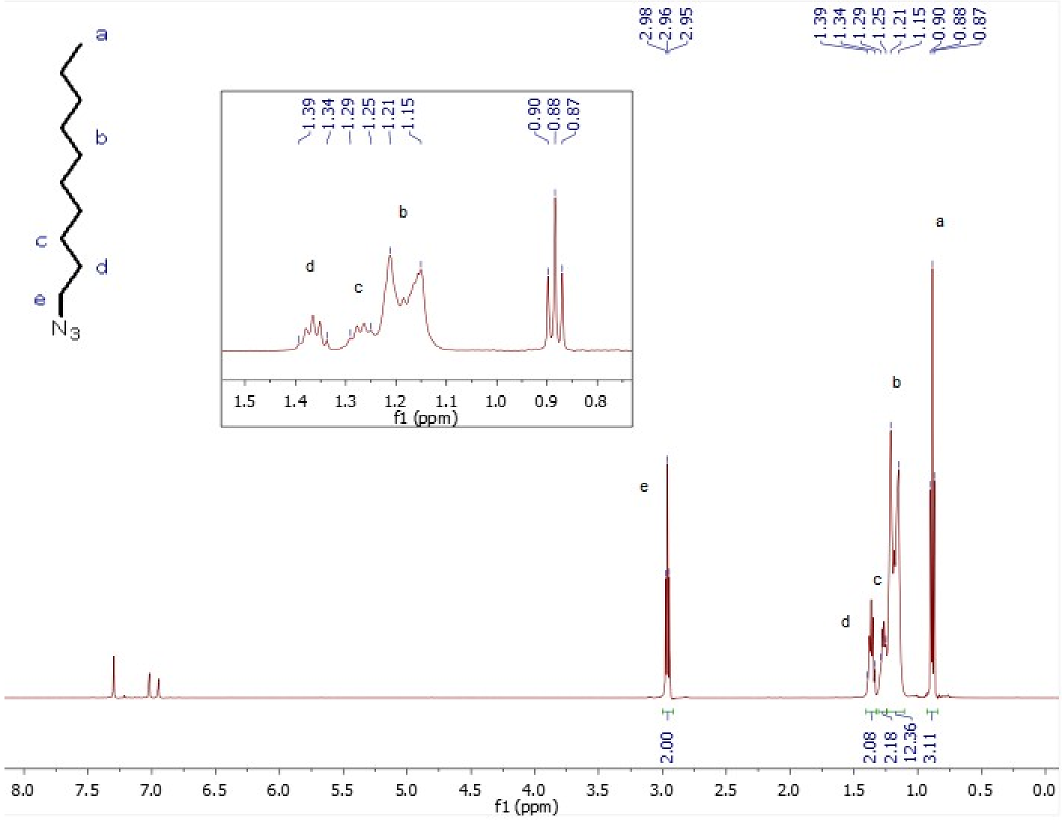


Figure S4: ^{1}H spectrum of 1-azidodecane in C_6D_5Br.

Benzylazide (1d)

Benzylazide was synthesized according to literature procedures.[6]

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.18 – 7.13 (m, 3H, Ph-*H*), 7.07 – 7.06 (m, 2H, Ph-*H*), 3.99 (s, 2H, C*H₂*)

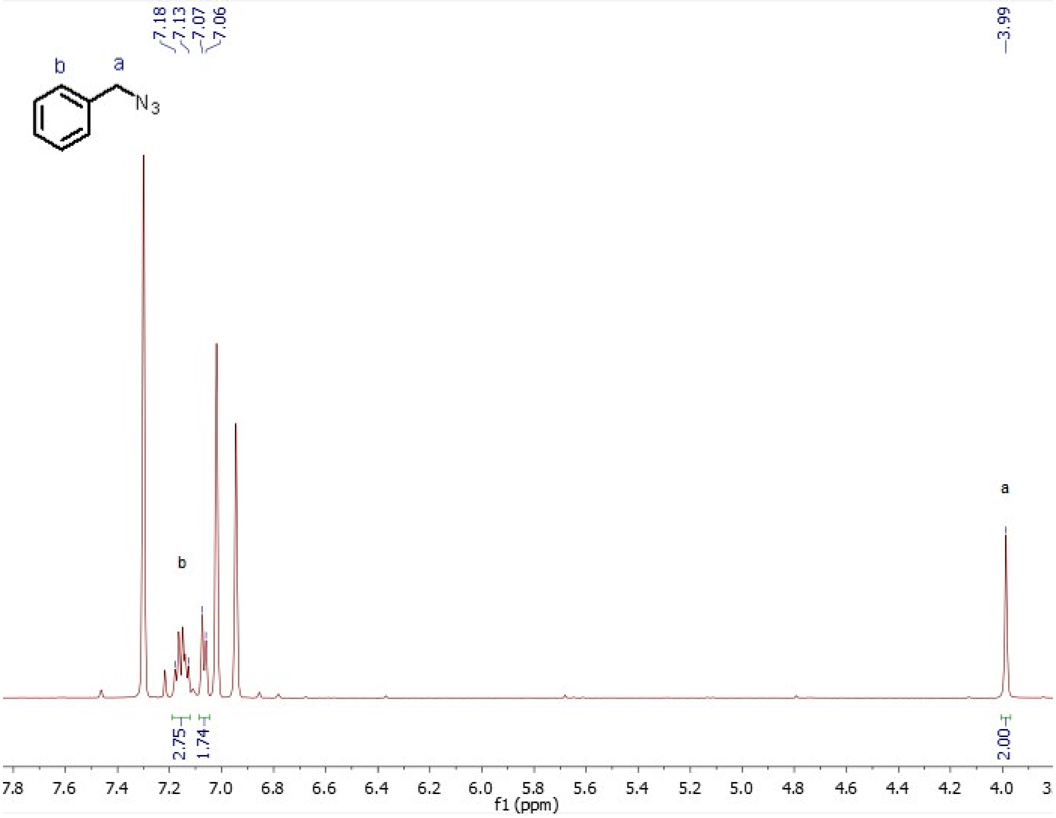


Figure S5: ^{1}H spectrum of benzylazide in C_6D_5Br.

Azidomethyl phenyl sulfide (1e)

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.33 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *o*-Ph-*H*), 7.11 – 7.05 (m, 3H, *m*-Ph-*H* and *p*-Ph-*H*), 4.17 (s, 2H, C*H*$_2$)

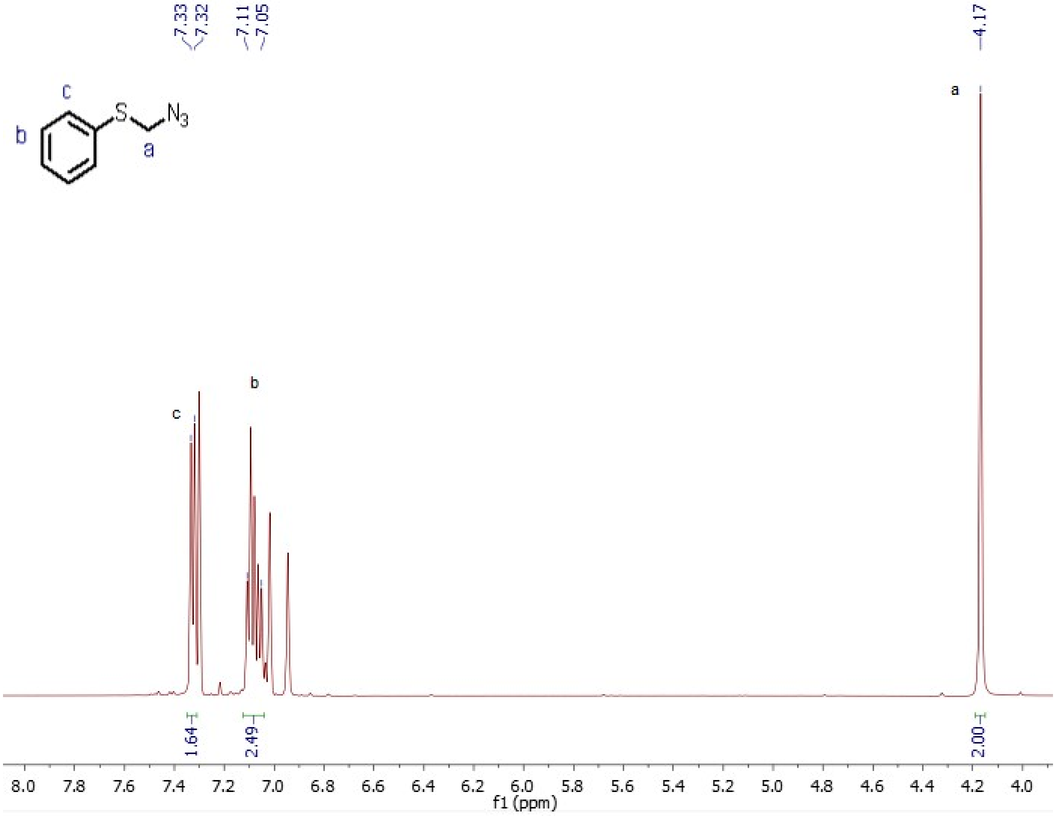


Figure S6: ^{1}H spectrum of azidomethyl phenyl sulfide in C_6D_5Br.

Trityl azide (1f)

Trityl azide was synthesized according to the literature procedure[7] and used directly without any further purification.

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.27 (d, $^3J_{HH}$ = 7.6 Hz, 6H, *o*-Ph-*H*), 7.18 – 7.10 (m, 9H, *m*-Ph-*H* and *p*-Ph-*H*)

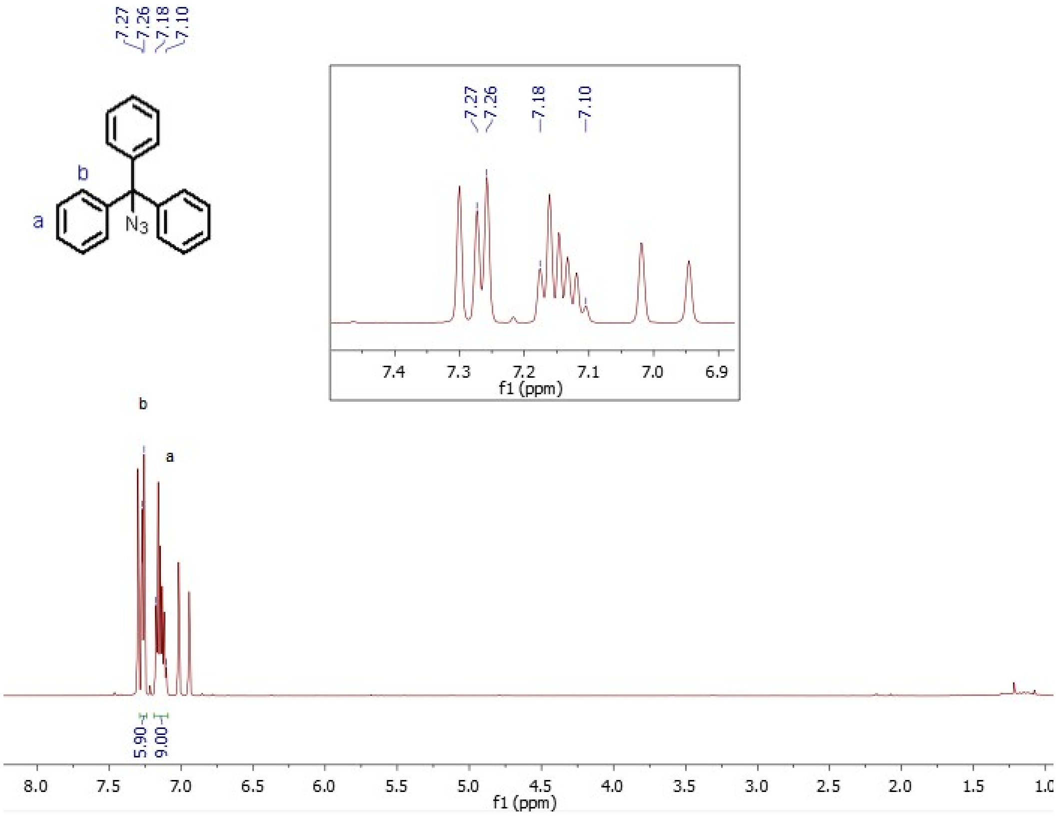


Figure S7: ^{1}H spectrum of trityl azide in C_6D_5Br.

2-butyne (2b)

^{1}H NMR (500 MHz, C_6D_5Br): δ 1.60 (s, 6H, CH_3)

The other peaks in the spectrum belong to 1-azidoadamantane.

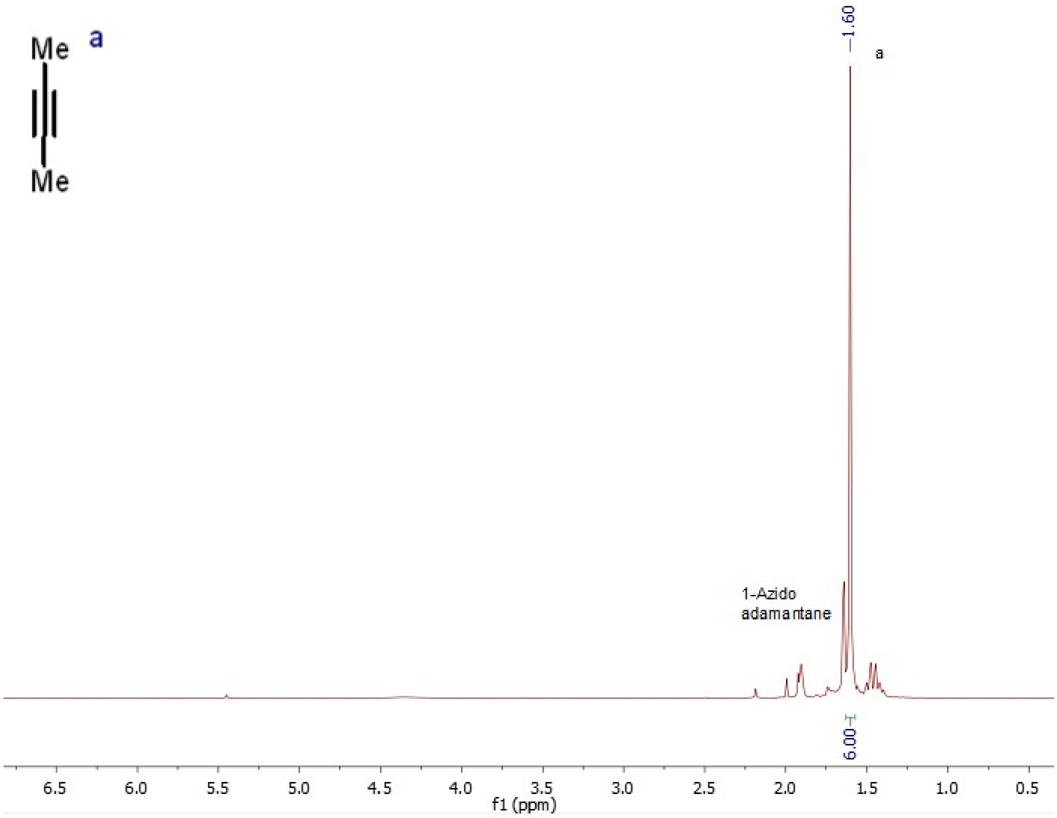


Figure S8: ^{1}H spectrum of 2-butyne in C_6D_5Br.

Diphenylacetylene (2c)

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.51 (d, $^{3}J_{HH}$ = 7.2 Hz, 4H, *o*-Ph-*H*), 7.18 – 7.12 (m, 6H, *m*-Ph-*H* and *p*-Ph-*H*)

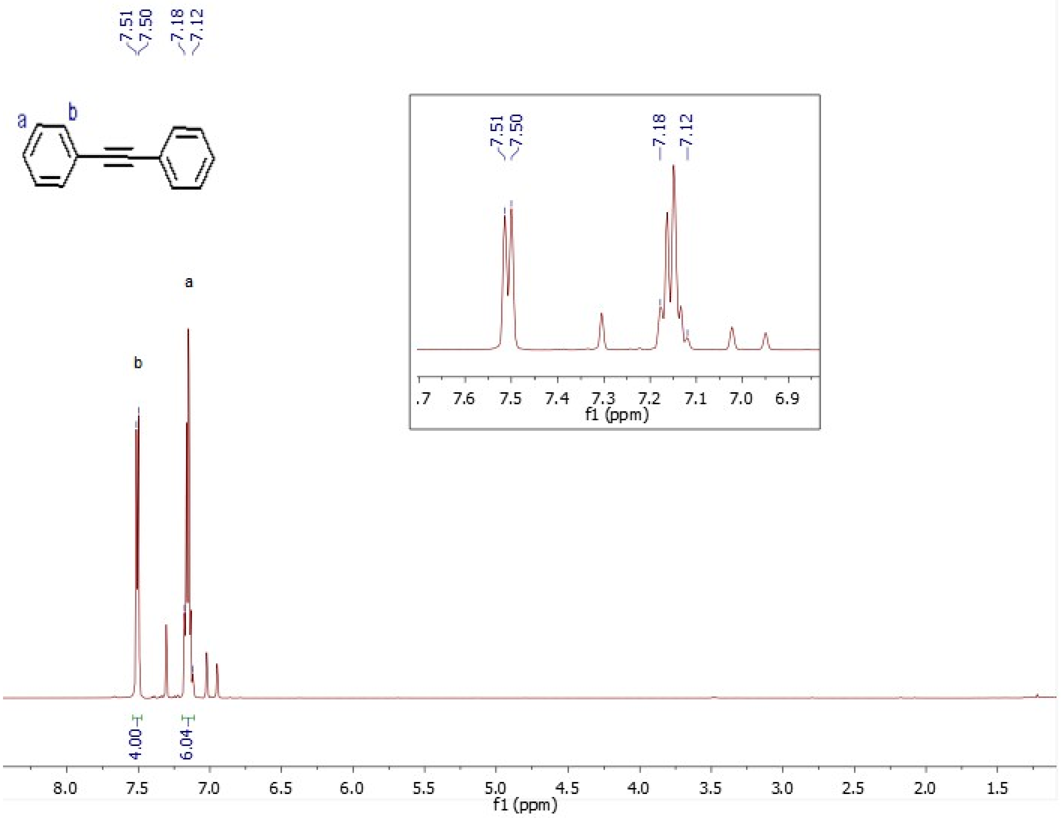


Figure S9: ^{1}H spectrum of diphenylacetylene in C_6D_5Br.

1-Phenyl-1-propyne (2d)

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.41 (d, $^3J_{HH}$ = 6.8 Hz, 2H, *o*-Ph-*H*), 7.13 – 7.09 (m, 3H, *m*-Ph-*H* and *p*-Ph-*H*), 1.84 (s, 3H, CH_3)

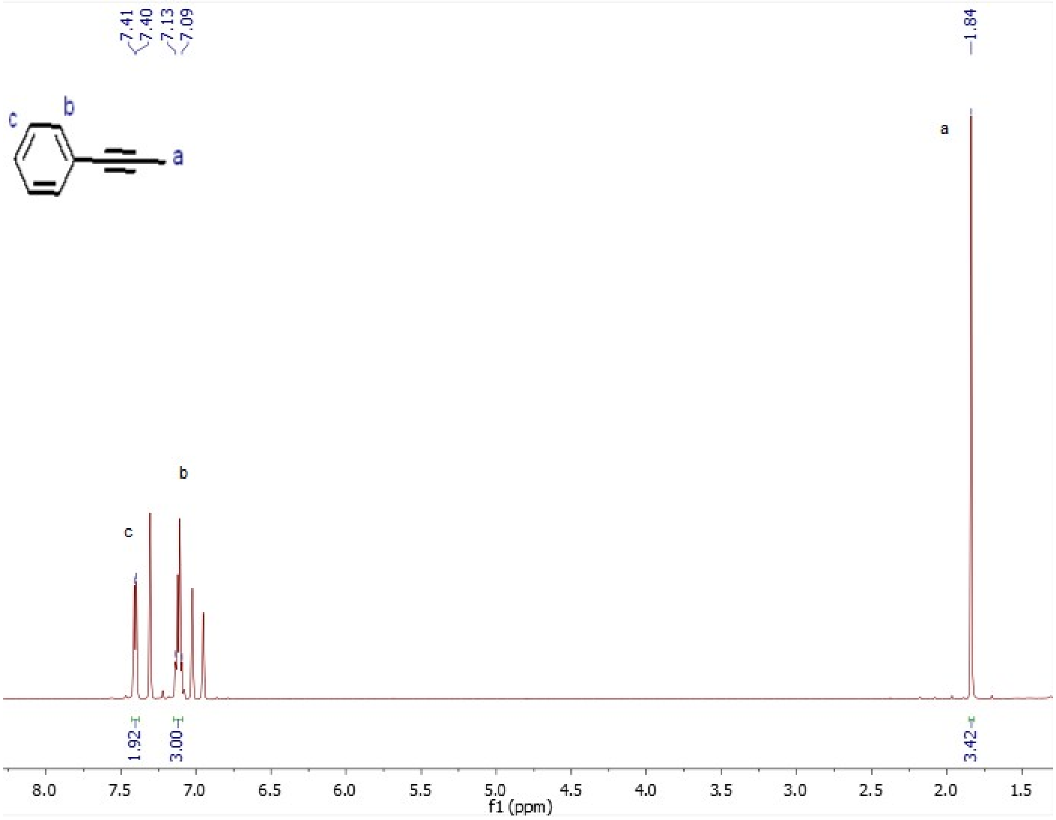


Figure S10: ^{1}H spectrum of 1-phenyl-1-propyne in C_6D_5Br.

(*p*-tolyl)acetylene (2f)

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.32 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *m*-Tol-*H*), 6.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *o*-Tol-*H*), 2.95 (s, 1H, Tol≡*H*), 2.10 (s, 2H, Ar-C*H₃*)

The other peaks in the spectrum belong to 1-azidoadamantane.

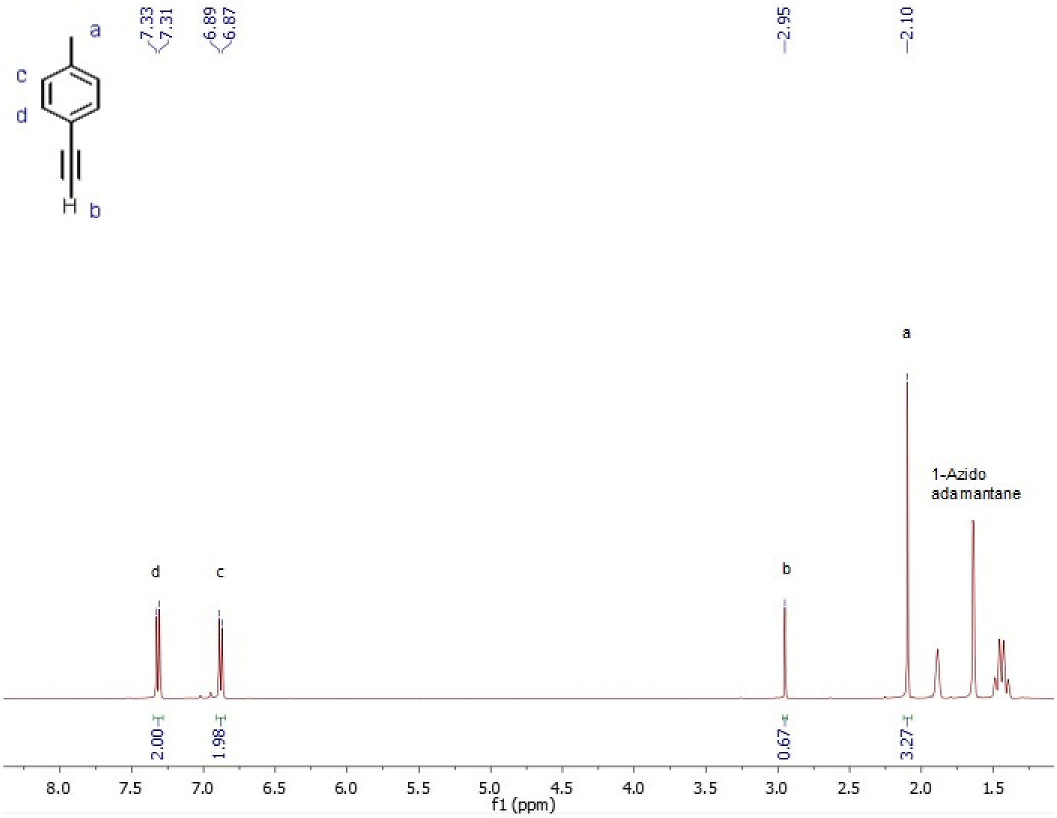


Figure S11: ^{1}H spectrum of *p*-tolylacetylene in C_6D_5Br.

(*t*-butyl)acetylene (2g)
^{1}H NMR (500 MHz, C_6D_5Br): δ 2.02 (s, 1H, ^{t}Bu≡*H*), 1.16 (s, 9H, ^{t}Bu)

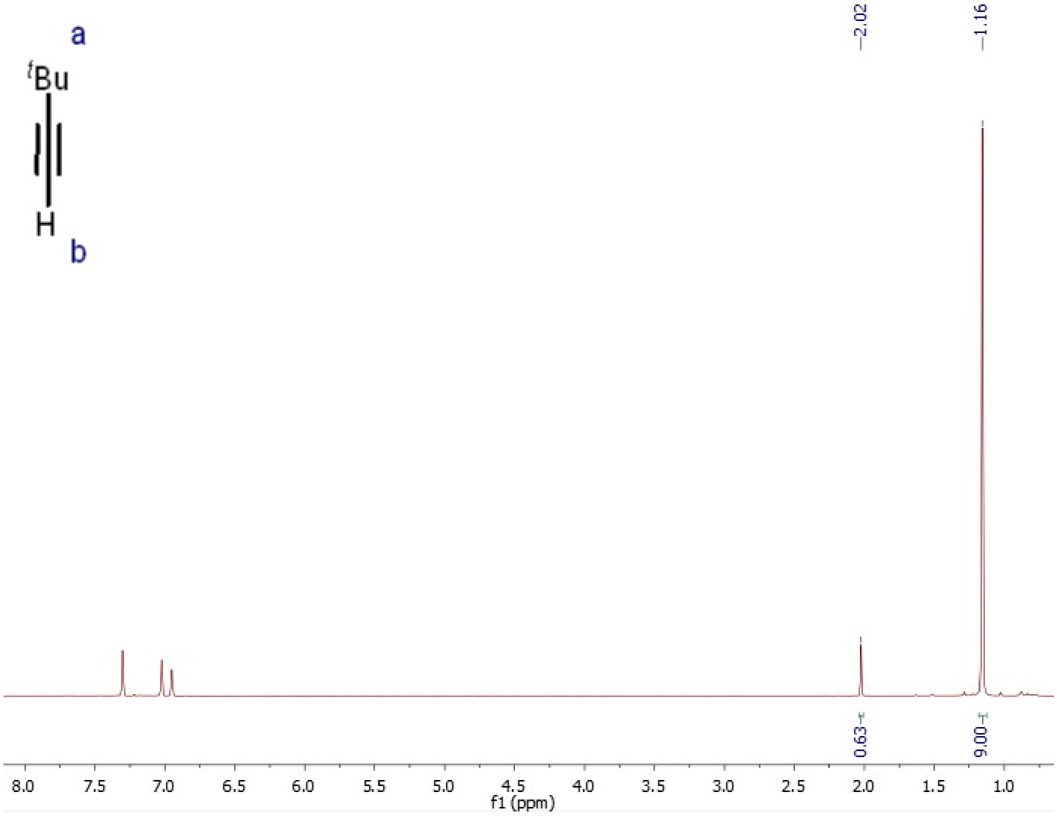


Figure S12: ^{1}H spectrum of *p*-tolylacetylene in C_6D_5Br.

(Trimethylsilyl)acetylene (2h)

^{1}H NMR (400 MHz, C_6D_5Br): δ 2.30 (s, 1H, C-*H*), 0.14 (s, 9H, Si(CH_3)$_3$)

The other peaks in the spectrum belong to 1-azidoadamantane.

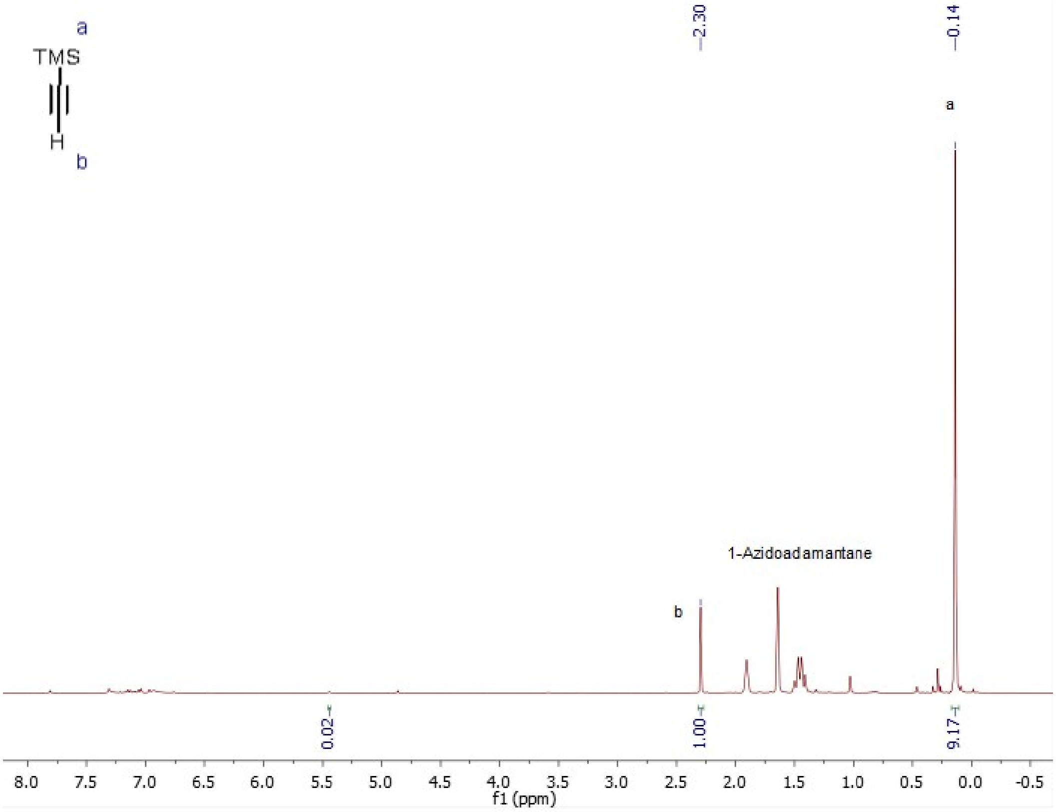


Figure S13: ^{1}H spectrum of (trimethylsilyl)acetylene in C_6D_5Br.

1,7-octadiyne (2i)

^{1}H NMR (500 MHz, C_6D_5Br): δ 1.99 (s, 4H, HC≡C(CH_2)(CH$_2$)$_2$(CH_2)C≡CH), 1.88 (s, 2H, *H*C≡C(CH$_2$)(CH$_2$)$_2$(CH$_2$)C≡C*H*), 1.45 (s, 4H, HC≡C(CH$_2$)(CH_2)$_2$(CH$_2$)C≡CH)

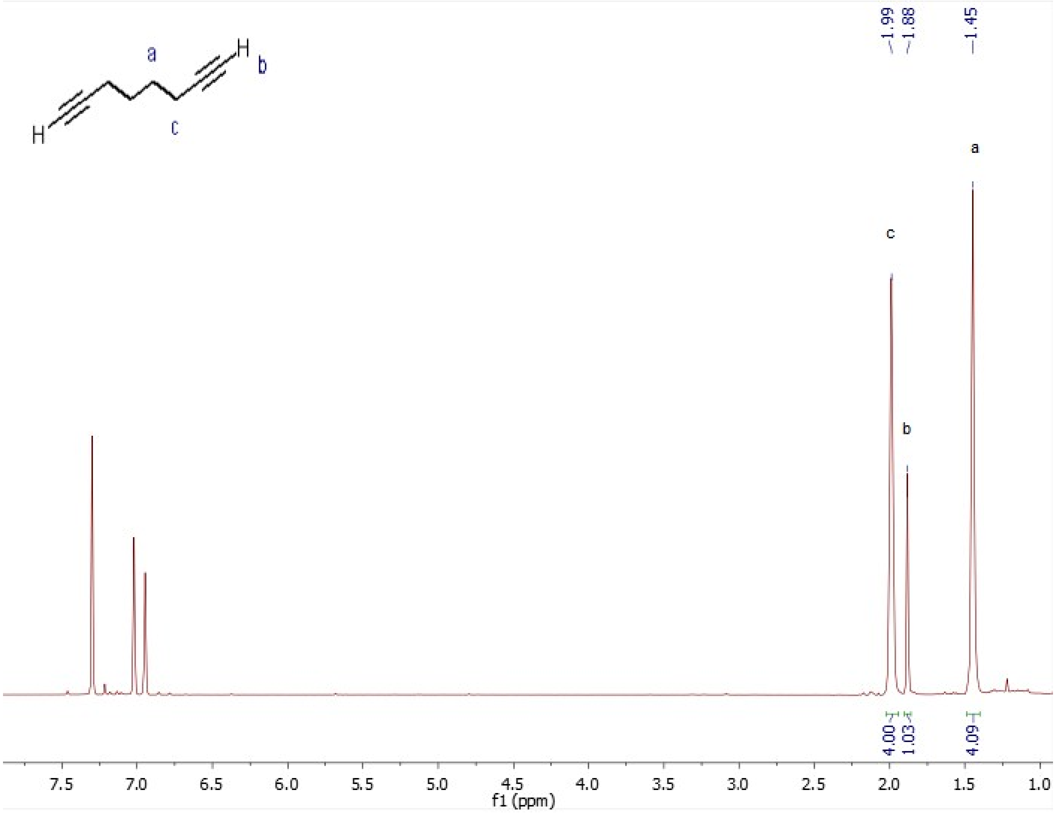
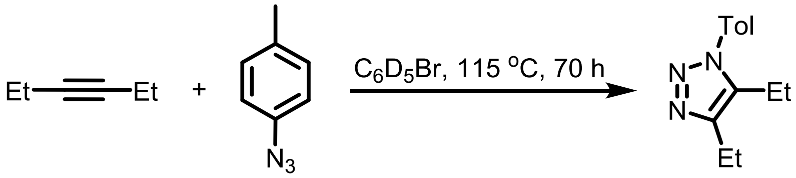


Figure S14: ^{1}H spectrum of 1,7-octadiyne in C_6D_5Br.

Characterization of uncatalyzed triazole products in C_6D_5Br

1-(*p*-tolyl)-4,5-(diethyl)-1,2,3-triazole (6aa)



3-hexyne (16 mg, 0.1 mmol, 1.0 equiv.), (*p*-tolyl)azide (13 mg, 0.1 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 70 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give a mixture of title compound, leftover starting reagents and side products originating from (*p*-tolyl)azide such as *p*-toluidine and 1,2-di-*p*-tolyldiazene

1-(*p*-tolyl)-4,5-(diethyl)-1,2,3-triazole

^1H NMR (500 MHz, C_6D_5Br): δ 7.14 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *o*-Tol-*H*), 7.01 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *m*-Tol-*H*), 2.65 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 4-CH_2CH$_3$), 2.44 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 5-CH_2CH$_3$), 2.16 (s, 3H, Tol-CH_3), 1.35 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 4-CH$_2$CH_3), 0.85 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 5-CH$_2$CH_3)

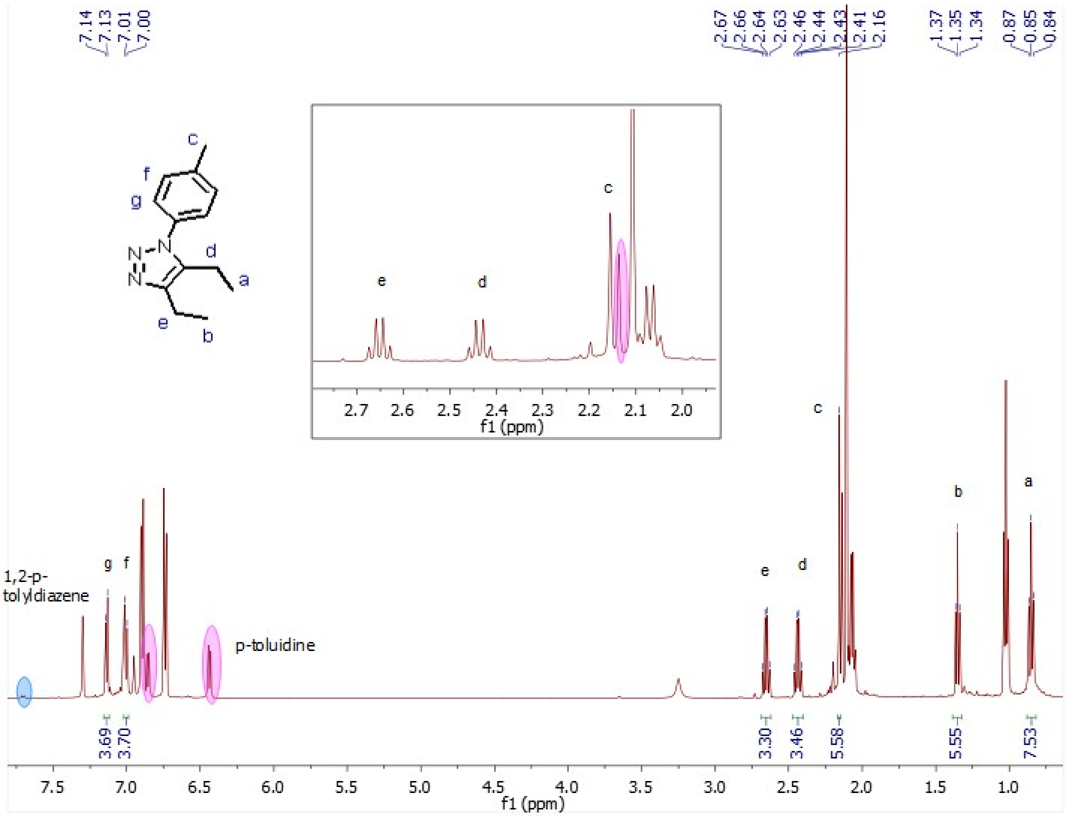


Figure S15: ^1H spectrum of 1-(*p*-tolyl)-4,5-(diethyl)-1,2,3-triazole in C_6D_5Br.

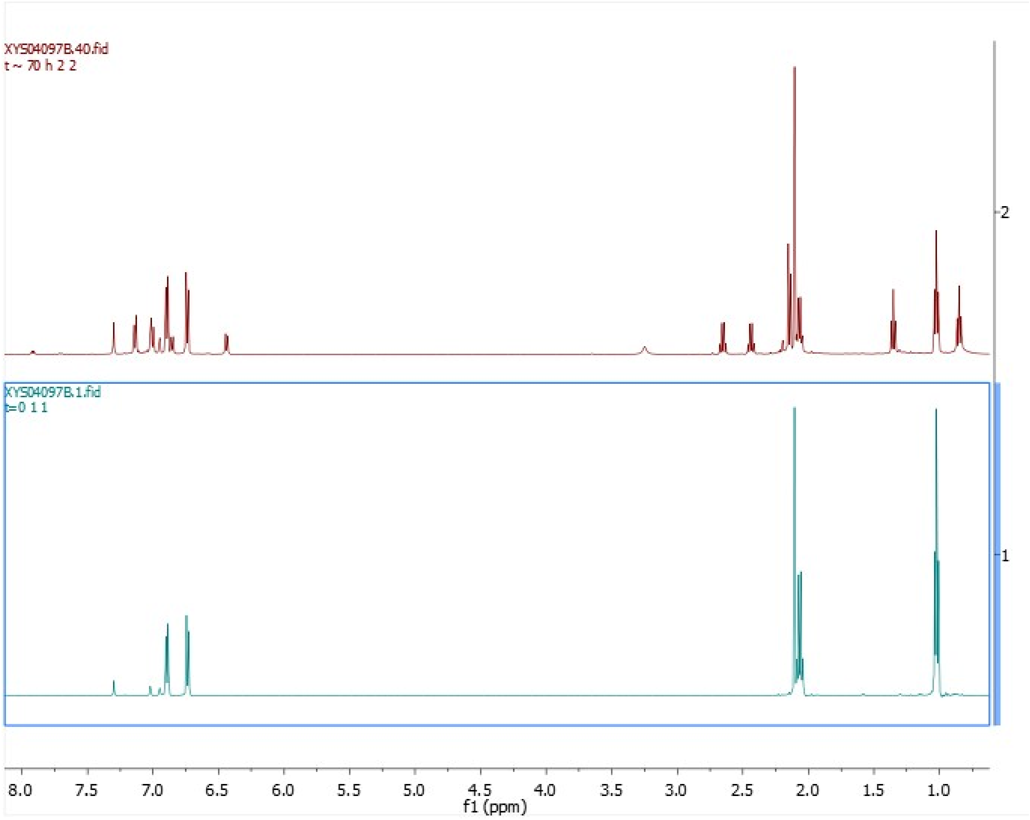
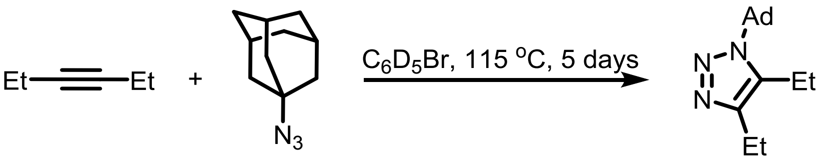


Figure S16: Before (bottom, t = 0 h) and after (top, t = 70 h) ^{1}H spectrum of 3-hexyne and (*p*-tolyl)azido reaction in C_6D_5Br.

1-adamantyl-4,5-di(ethyl)-1H-1,2,3-triazole (6ba) (partial)



3-hexyne (45 µL, 0.39 mmol, 2.1 equiv.), 1-Azidoadamantane (33 mg, 0.19 mmol, 1 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 5 days. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give the title compound and leftover starting reagents.

1-adamantyl-4,5-di(ethyl)-1H-1,2,3-triazole

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.65 (q, $^3J_{HH}$ = 7.5 Hz, 2H, C(4)-CH_2), 2.55 (q, $^3J_{HH}$ = 7.5 Hz, 2H, C(5)-CH_2), 2.21 (d, $^3J_{HH}$ = 3 Hz, 6H, N-C-(CH_2)$_2$), 2.01 (s (br), 3H, Ad-methine), 1.58 (s (br), 6H, Ad), 1.32 (t, $^3J_{HH}$ = 7.5 Hz, 2H, C(4)-CH_2-CH_3).
This is a partial line list; remaining methyl group hidden beneath 3-hexyne methyl group.

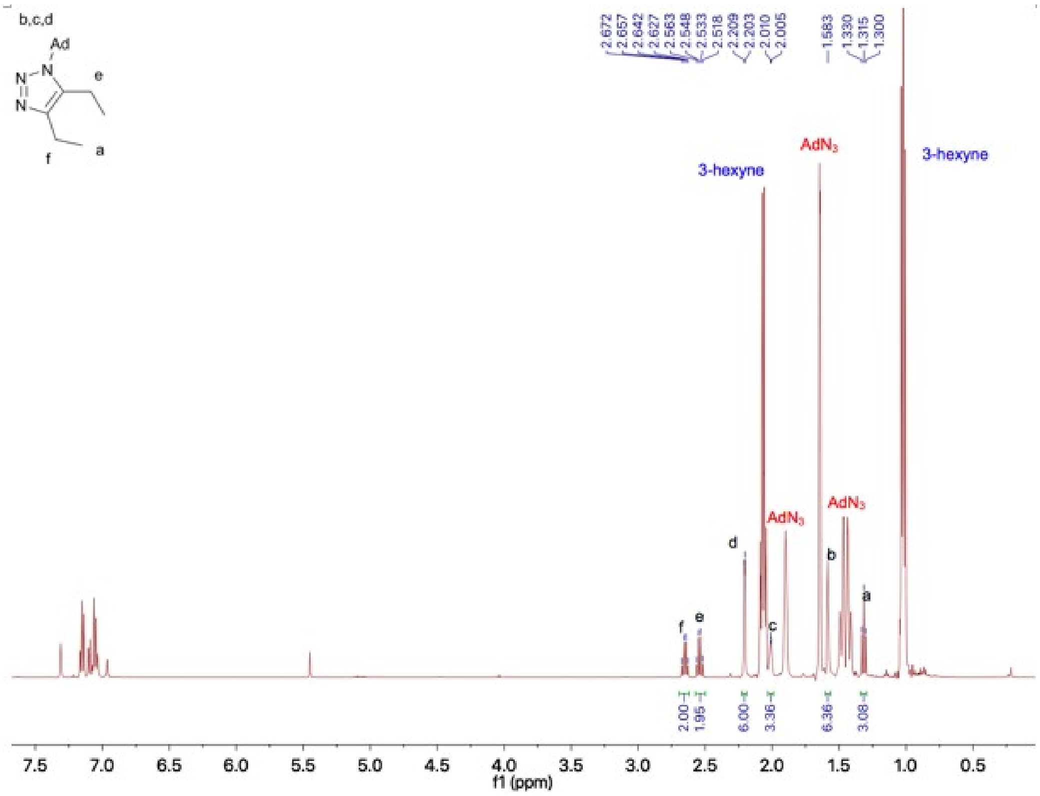


Figure S17: ^{1}H NMR spectrum of 1-adamantyl-4,5-diethyl-1H-1,2,3-triazole in C_6D_5Br.

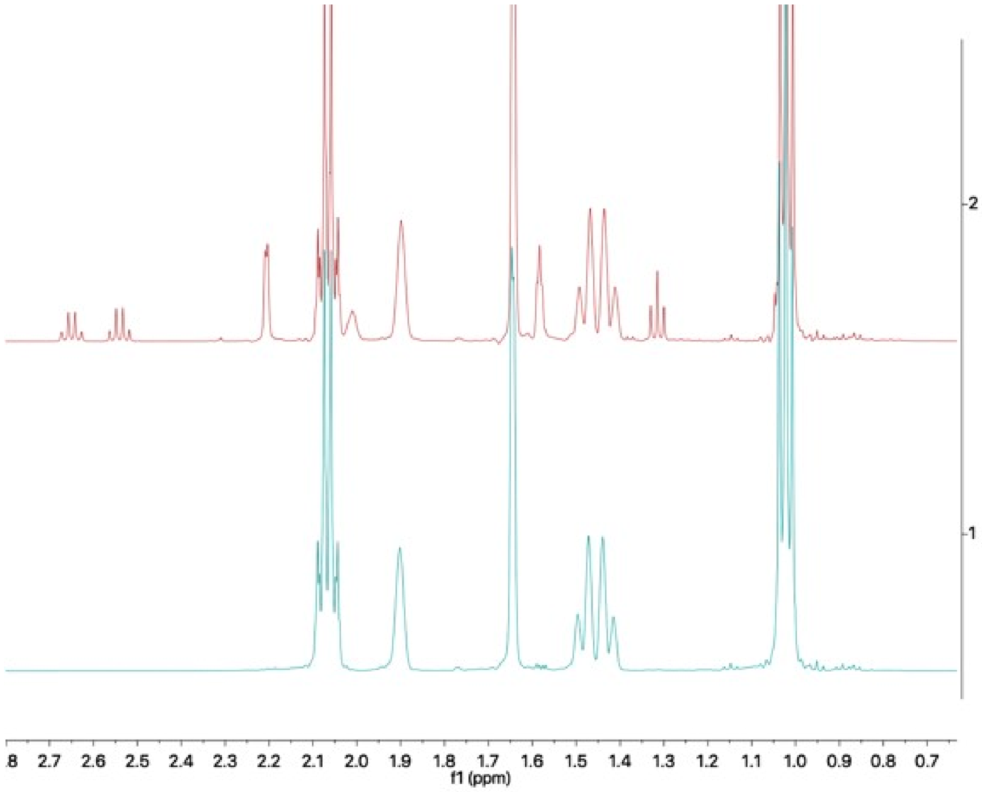
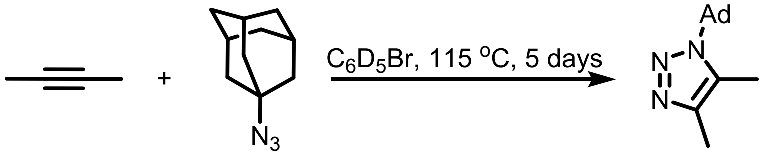


Figure S18: Before (bottom, t = 0 hr) and after (top, t = 5 days) ^{1}H spectrum of 3-hexyne and 1-azidoadamantane reaction in C_6D_5Br.

1-adamantyl-4,5-di(methyl)-1H-1,2,3-triazole (6bb) (partial)



2-butyne (14 mg, 0.26 mmol, 1.7 equiv.), 1-azidoadamantane (27 mg, 0.15 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 16 h. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give the title compound and leftover starting reagents.

1-adamantyl-4,5-di(methyl)-1H-1,2,3-triazole
^{1}H NMR (400 MHz, C_6D_5Br): δ 2.17 – 2.16 (m, 6H, Ad-C*H$_2$*), 2.15 (s, 3H, C4-C*H$_3$*), 2.09 (s, 3H, C5-C*H$_3$*)
This is a partial NMR line list, the remaining adamantyl peaks are buried under the peaks for the starting reagents.

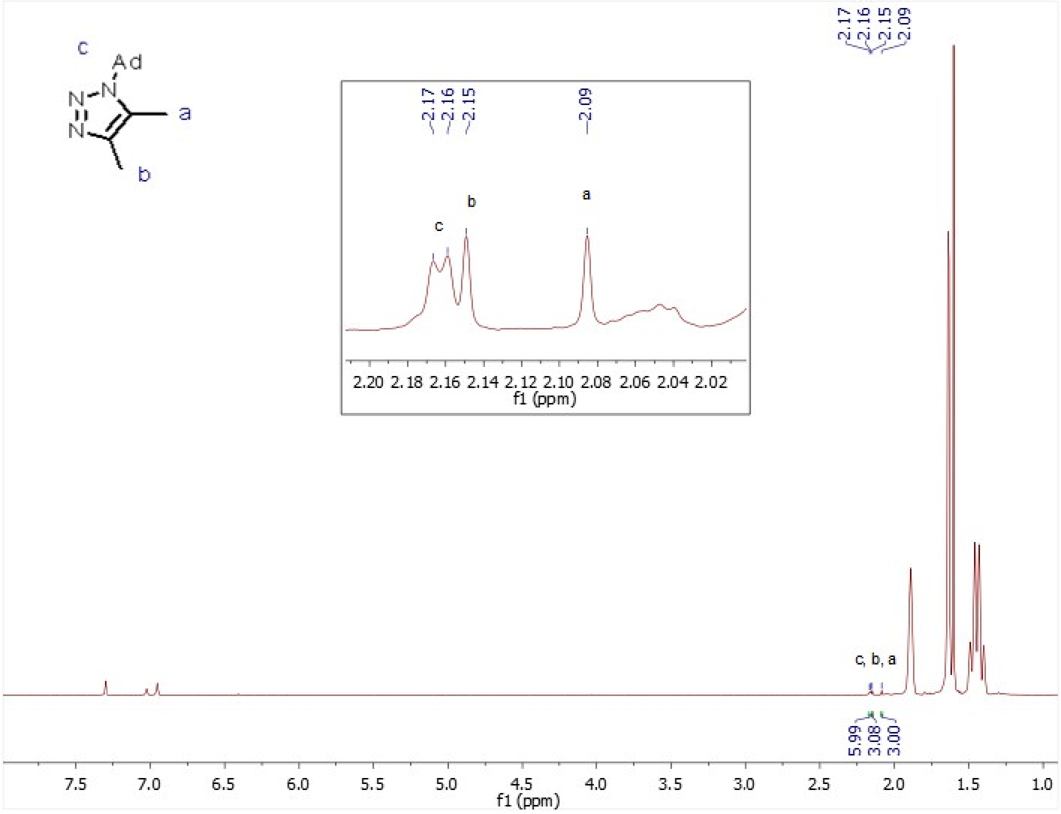


Figure S19: ^{1}H spectrum of 1-adamantyl-4,5-di(methyl)-1H-1,2,3-triazole in C_6D_5Br.

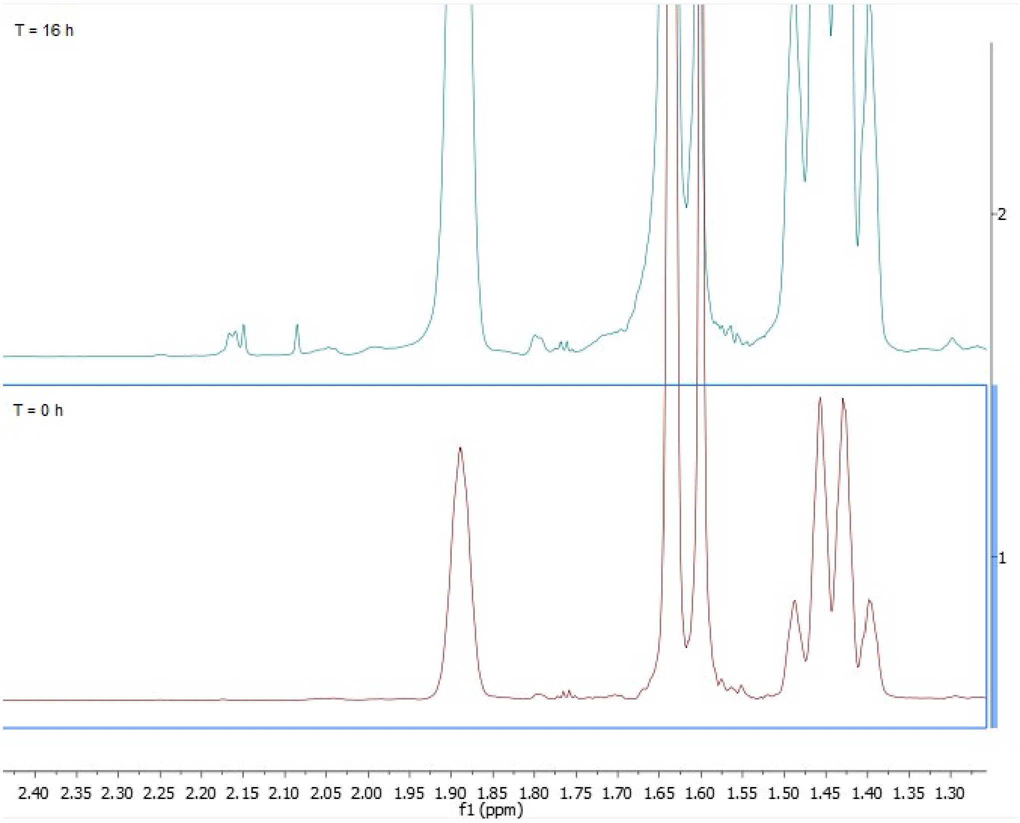
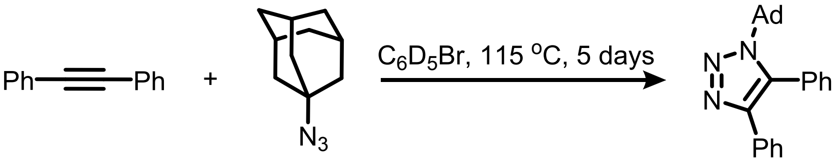


Figure S20: Before (bottom, t = 0 h) and after (top, t = 16 h) ^{1}H spectrum of 2-butyne and 1-azidoadamantane reaction in C_6D_5Br.

1-adamantyl-4,5-di(phenyl)-1H-1,2,3-triazole (6bc) (partial)



Diphenylacetylene (38 mg, 0.21 mmol, 1.1 equiv.), 1-azidoadamantane (33 mg, 0.19 mmol, 1 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 5 days. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give the title compound and leftover starting reagents.

1-adamantyl-4,5-di(phenyl)-1H-1,2,3-triazole

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.66 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ar-*H*) 7.23 (m, 3H, Ar-*H*), 2.18 (d, $^3J_{HH}$ = 3 Hz, 6H, N-C-(CH_2)$_3$)

This is a partial NMR line list, the remaining adamantyl and aryl peaks are buried under the peaks for the starting reagents.

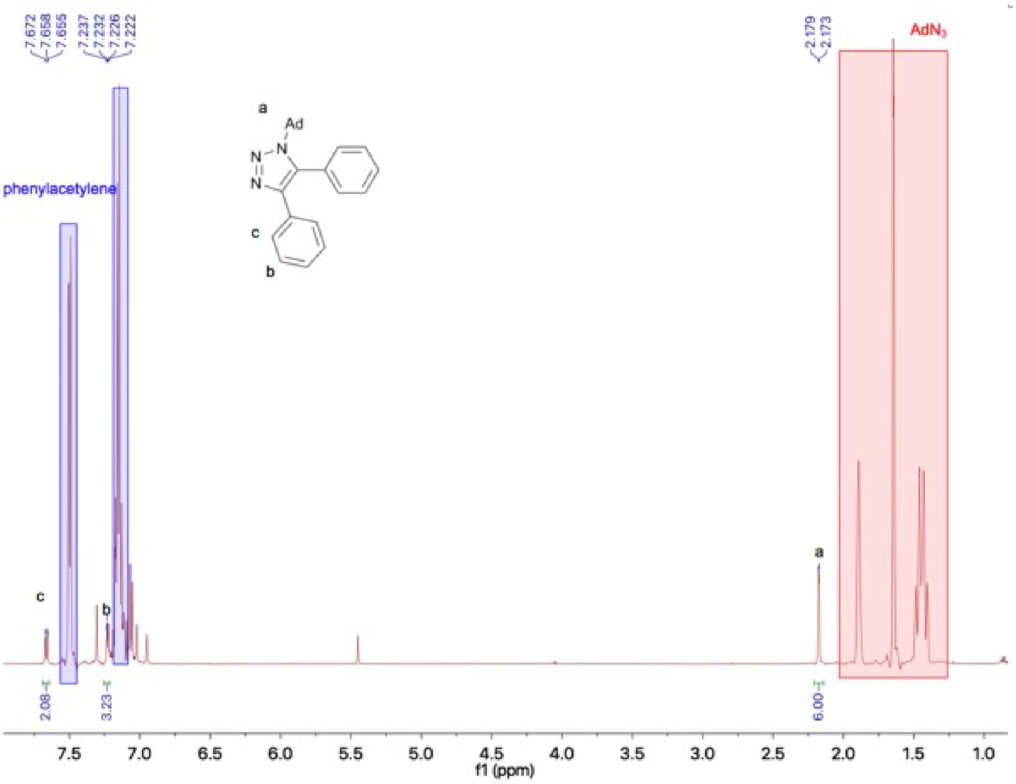


Figure S21: ^{1}H spectrum of 1-adamantyl-4,5-diphenyl-1H-1,2,3-triazole in C_6D_5Br.

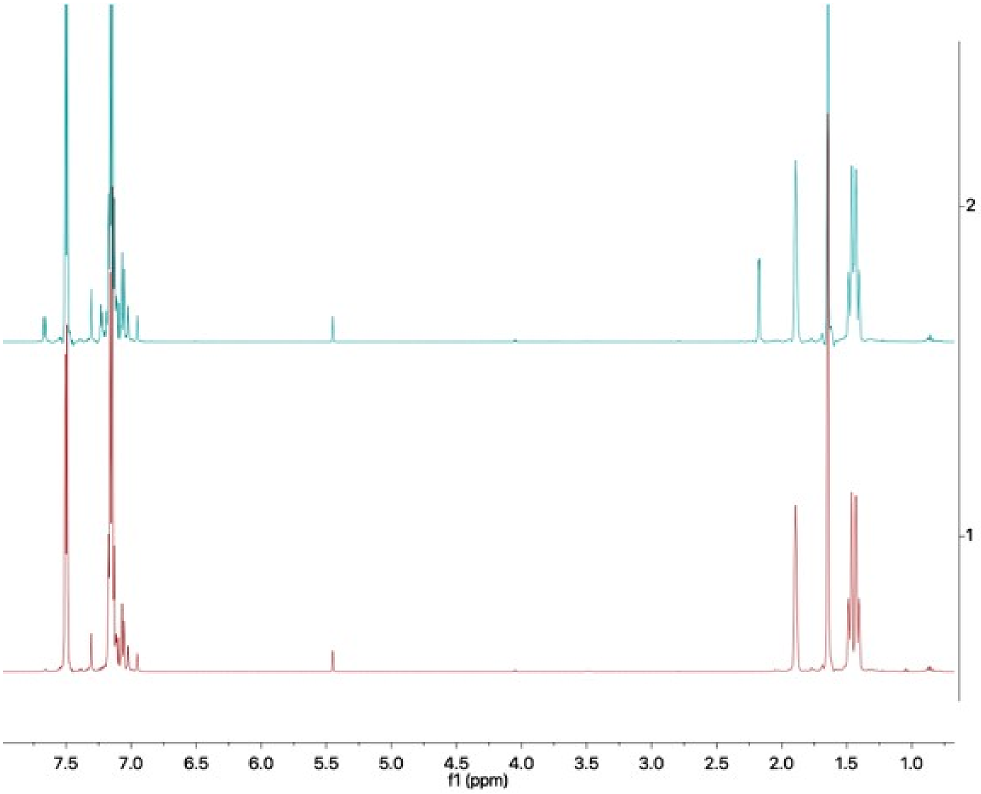
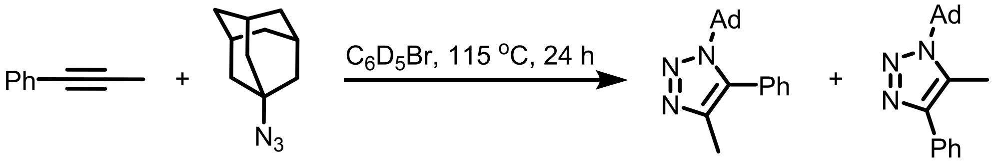


Figure S22: Before (bottom, t = 0 hr) and after (top, t = 5 days) ^{1}H spectrum of diphenylacetylene and 1-azidoadamantane reaction in C_6D_5Br.

1-adamantyl-4-methyl-5-phenyl-1H-1,2,3-triazole and 1-adamantyl-5-methyl-4-phenyl-1H-1,2,3-triazole (6bd)



1-Phenyl-1-propyne (75 µL, 0.59 mmol, 2.6 equiv.), 1-azidoadamantane (40 mg, 0.11 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 24 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give a mixture of both title compounds and leftover starting reagents.

1-adamantyl-4-methyl-5-phenyl-1*H*-1,2,3-triazole

^1H NMR (500 MHz, C_6D_5Br): δ 7.73 (d, $^3J_{HH}$ = 6.5, 2H, *o*-Ar-*H*), 7.35 (t, $^3J_{HH}$ = 7.5, 2H, *m*-Ar-*H*), 2.35 (s, 3H, C(4)-C*H$_3$*), 2.22 (d, $^3J_{HH}$ = 3.0 Hz, 6H, N-C-(C*H$_2$*)$_3$), 2.02 (s (br), 3H, Ad-methine), 1.59 (s (br), 6H, Ad)

This is a partial NMR line list; *p*-aryl C-H is hidden behind the peaks for starting materials

1-adamantyl-5-methyl-4-phenyl-1*H*-1,2,3-triazole

^1H NMR (500 MHz, C_6D_5Br): δ 7.23 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *m*-Ar-*H*), 2.15 (d, $^3J_{HH}$ = 3.0 Hz, 6H, N-C-(C*H$_2$*)$_3$), 2.07 (s, 3H, C(5)-C*H$_3$*)

This is a partial NMR line list; Remaining peaks are hidden behind starting materials**.**

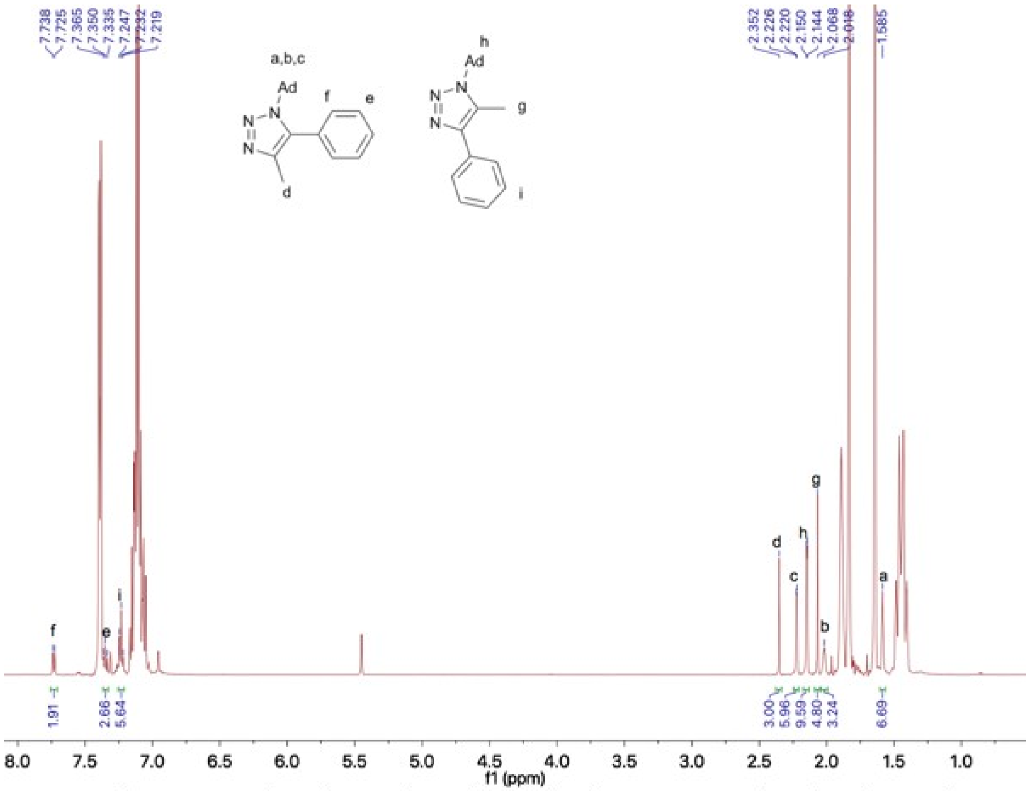


Figure S23: ^1H spectrum of 1-adamantyl-4-methyl-5-phenyl-1H-1,2,3-triazole and 1-adamantyl-5-methyl-4-phenyl-1H-1,2,3-triazole in C_6D_5Br.

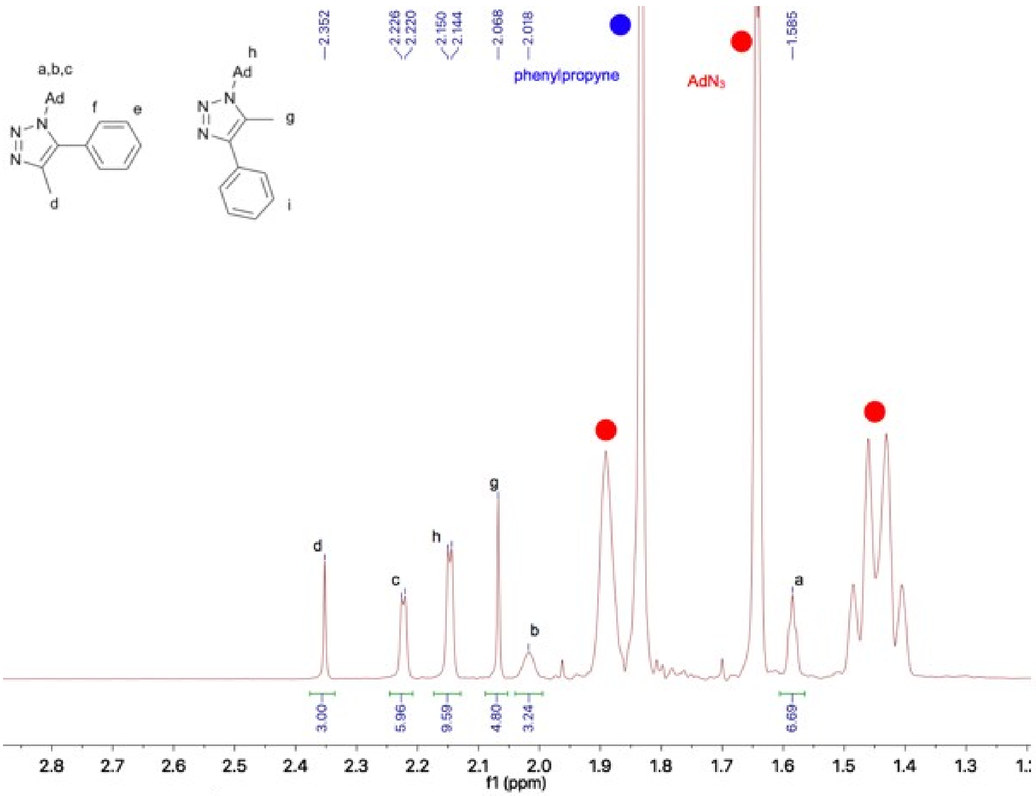


Figure S24: Zoom-in ^{1}H spectrum of the alkyl region of 1-adamantyl-4-methyl-5-phenyl-1H-1,2,3-triazole and 1-adamantyl-5-methyl-4-phenyl-1H-1,2,3-triazole in C_6D_5Br.

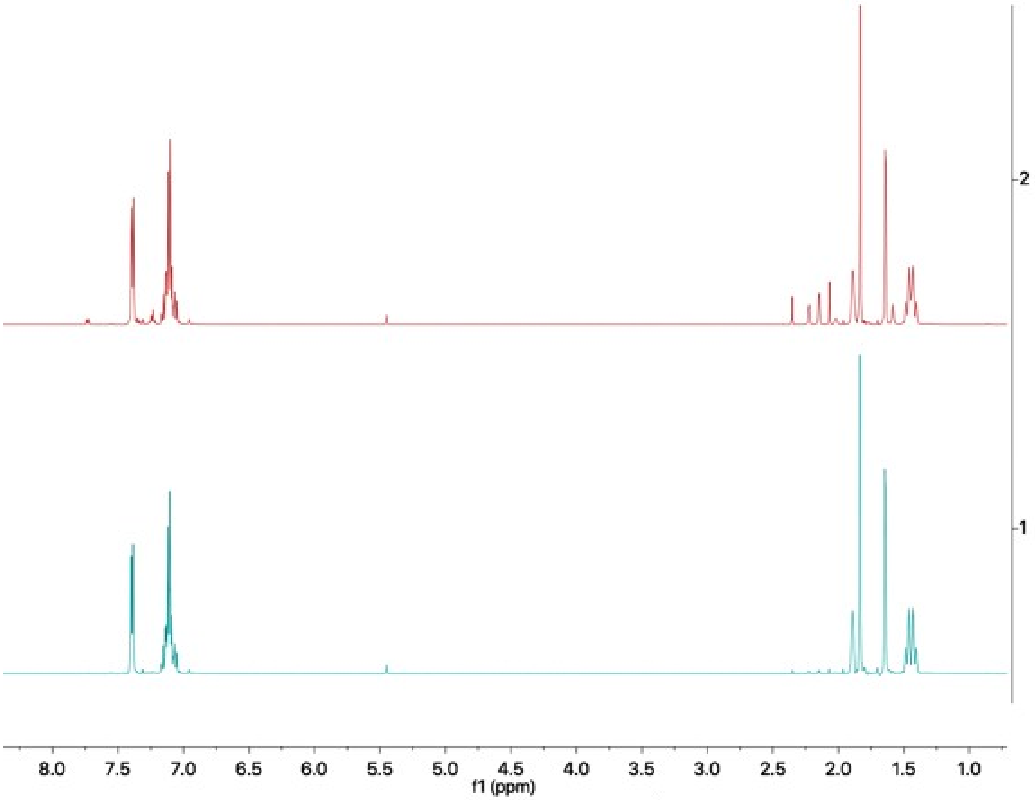
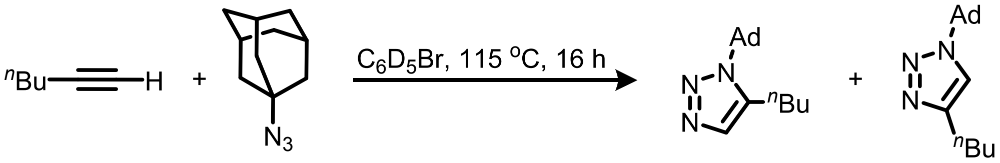


Figure S25: Before (bottom, t = 0 hr) and after (top, t = 24 h) ^{1}H spectrum of 1-phenyl-1-propyne and 1-azidoadamantane reaction in C_6D_5Br.

1-adamantyl-4-(*n*-butyl)-1H-1,2,3-triazole and 1-adamantyl-5-(*n*-butyl)-1H-1,2,3-triazole (6be) (partial)



1-hexyne (15 mg, 0.18 mmol, 1.6 equiv.), 1-azidoadamantane (20 mg, 0.11 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 16 h. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give a mixture of both title compounds and leftover starting reagents.

1-adamantyl-4-(*n*-butyl)-1H-1,2,3-triazole (partial)

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.12 (s, 1H, Ar-C*H*), 2.71 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2CH$_2$CH$_2$CH$_3$), 2.04 (m, 6H, Ad-CH_2), 1.98 (m, 3H, Ad-C*H*), 1.56 (m, 6H, Ad-CH_2), 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH$_2$CH$_2$CH$_2$CH_3)

Singlet at δ 2.04 is partially overlapped by the 1-hexyne substrate. This is a partial NMR line list, the remaining peaks for the *n*-butyl chain are overlapping with other peaks.

1-adamantyl-5-(*n*-butyl)-1H-1,2,3-triazole (partial)

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.44 (s, 1H, Ar-C*H*), 2.64 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2CH$_2$CH$_2$CH$_3$), 2.22 – 2.21 (m, 6H, Ad-CH_2)

Triplet peak for CH$_2$CH$_2$CH$_2$CH_3 is buried under the other regioisomer at δ 0.86. This is a partial NMR line list, the remaining peaks for the adamantyl group and *n*-butyl chain are overlapping with other peaks.

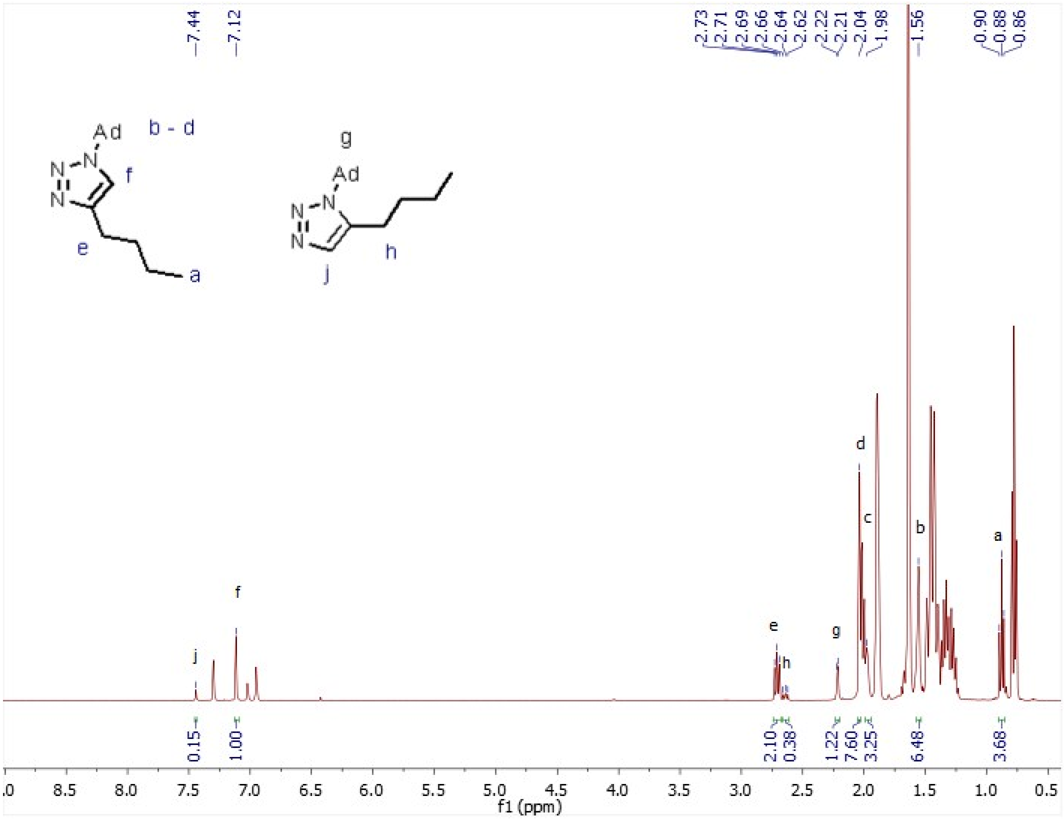


Figure S26: ^{1}H spectrum of 1-adamantyl-4-(*n*-butyl)-1H-1,2,3-triazole and 1-adamantyl-5-(*n*-butyl)-1H-1,2,3-triazole in C_6D_5Br.

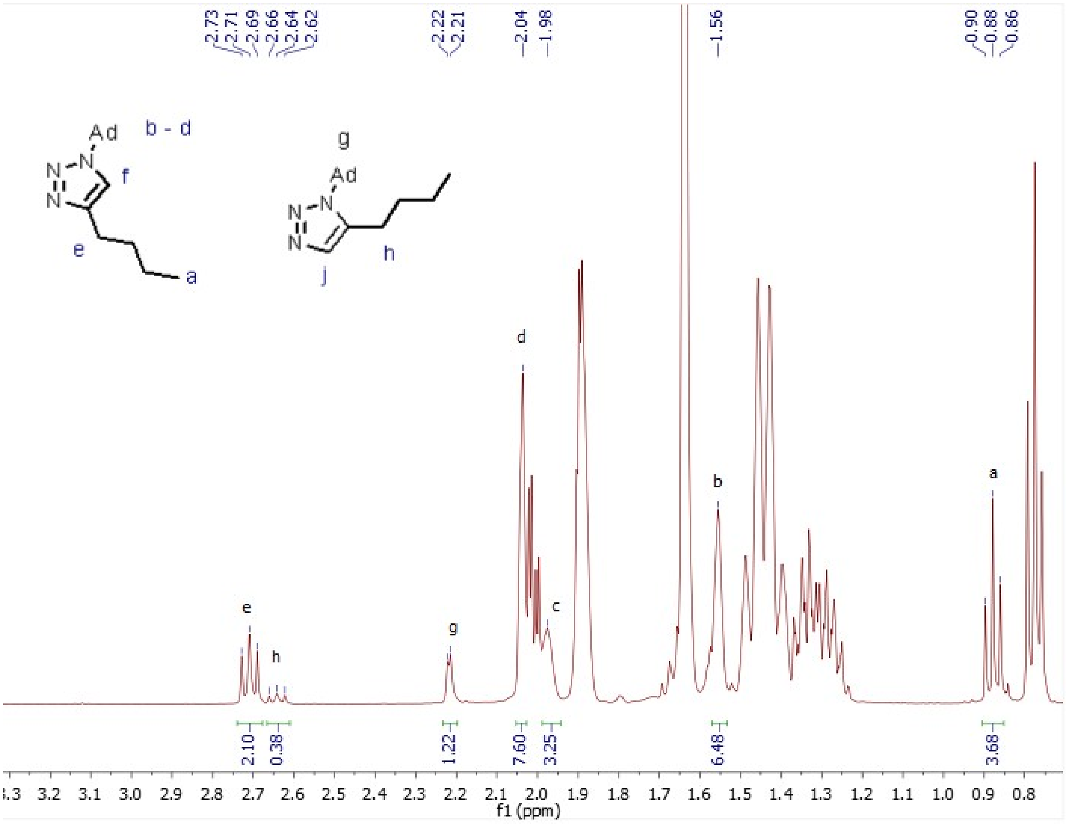


Figure S27: Zoom-in ^{1}H spectrum of 1-adamantyl-4-(*n*-butyl)-1H-1,2,3-triazole and 1-adamantyl-(5-*n*-butyl)-1H-1,2,3-triazole in C_6D_5Br.

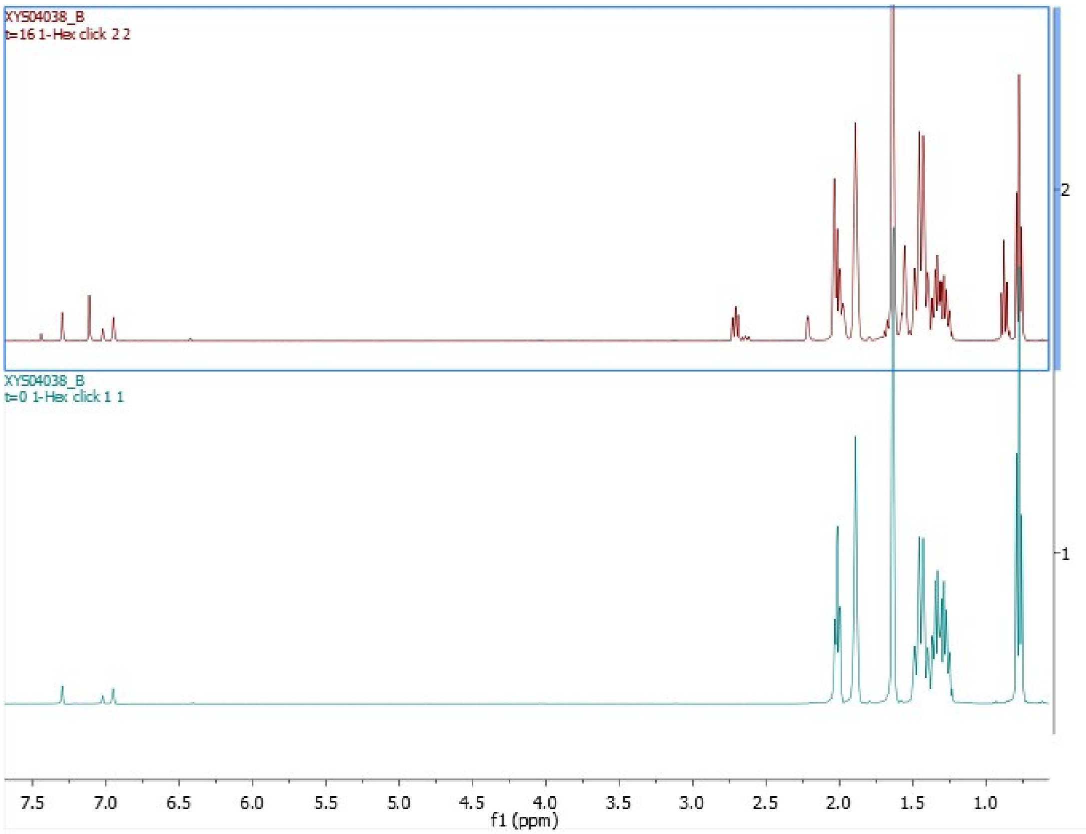
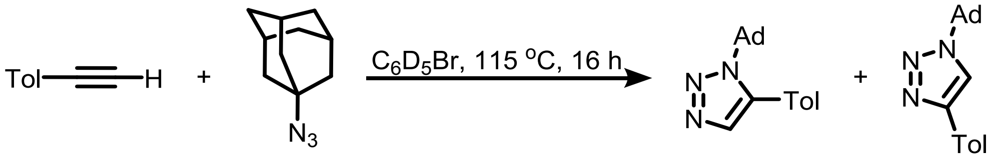


Figure S28: Before (bottom, t = 0 h) and after (top, t = 16 h) ^{1}H spectrum of 1-hexyne and 1-azidoadamantane reaction in C_6D_5Br.

1-adamantyl-4-(*p*-tolyl)-1H-1,2,3-triazole and 1-adamantyl-5-(*p*-tolyl)-1H-1,2,3-triazole (6bf) (partial)



(*p*-tolyl)acetylene (15 mg, 0.13 mmol, 1.4 equiv.), 1-azidoadamantane (16 mg, 0.09 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 16 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give a mixture of title compounds and leftover starting reagents.

1-adamantyl-4-(*p*-tolyl)-1H-1,2,3-triazole
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.88 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *o*-Tol-*H*), 7.87 (s, 1H, Ar-*H*), 7.13 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-Tol-*H*), 2.23 (s, 3H, Tol-CH_3), 2.07 – 2.06 (m, 6H, Ad-CH_2), 2.00 (br s, 3H, Ad-C*H*), 1.57 (m, 6H, Ad-CH_2)

1-adamantyl-5-(*p*-tolyl)-1H-1,2,3-triazole (partial)
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.53 (s, 1H, Ar-*H*), 7.10 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-Tol-*H*), 7.02 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-Tol-*H*), 2.17 (m, 9H, Tol-CH_3 and Ad-CH_2)
m-Tol-*H* peak at δ 7.02 ppm overlaps with C_6D_5Br solvent peak. This is a partial NMR line list, the remaining peaks for the adamantyl group are overlapping with other peaks.

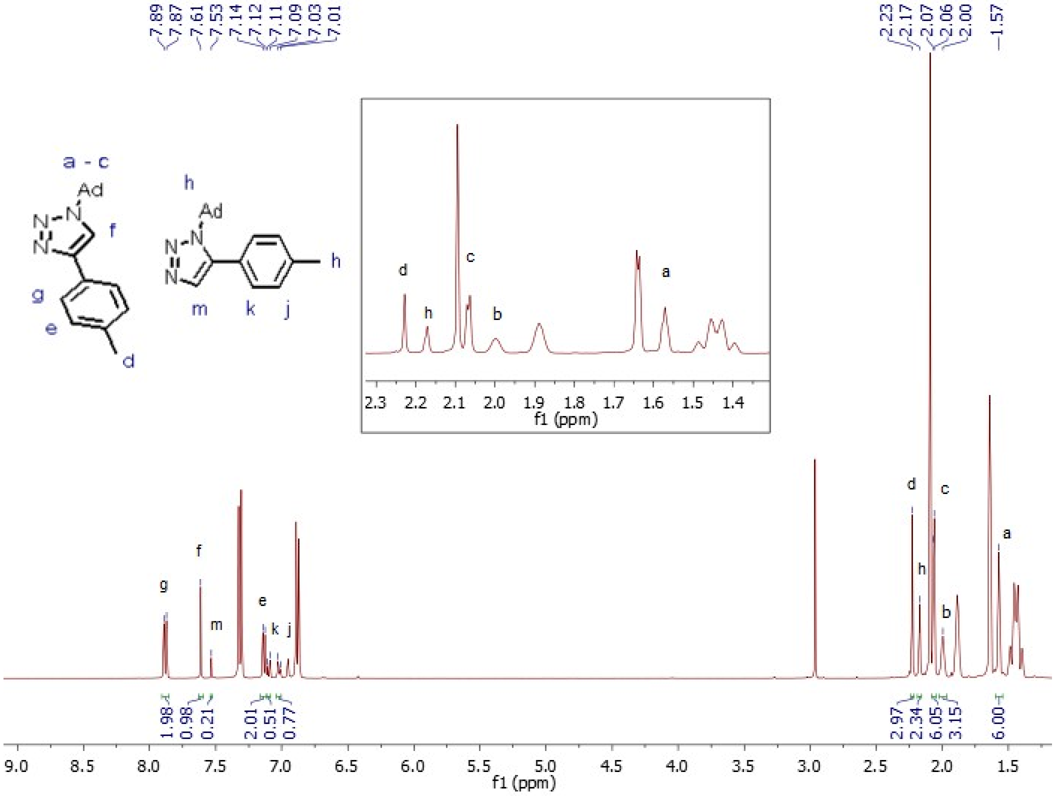


Figure S29: ^{1}H spectrum of 1-adamantyl-4-(*p*-tolyl)-1H-1,2,3-triazole and 1-adamantyl-5-(*p*-tolyl)-1H-1,2,3-triazole in C_6D_5Br.

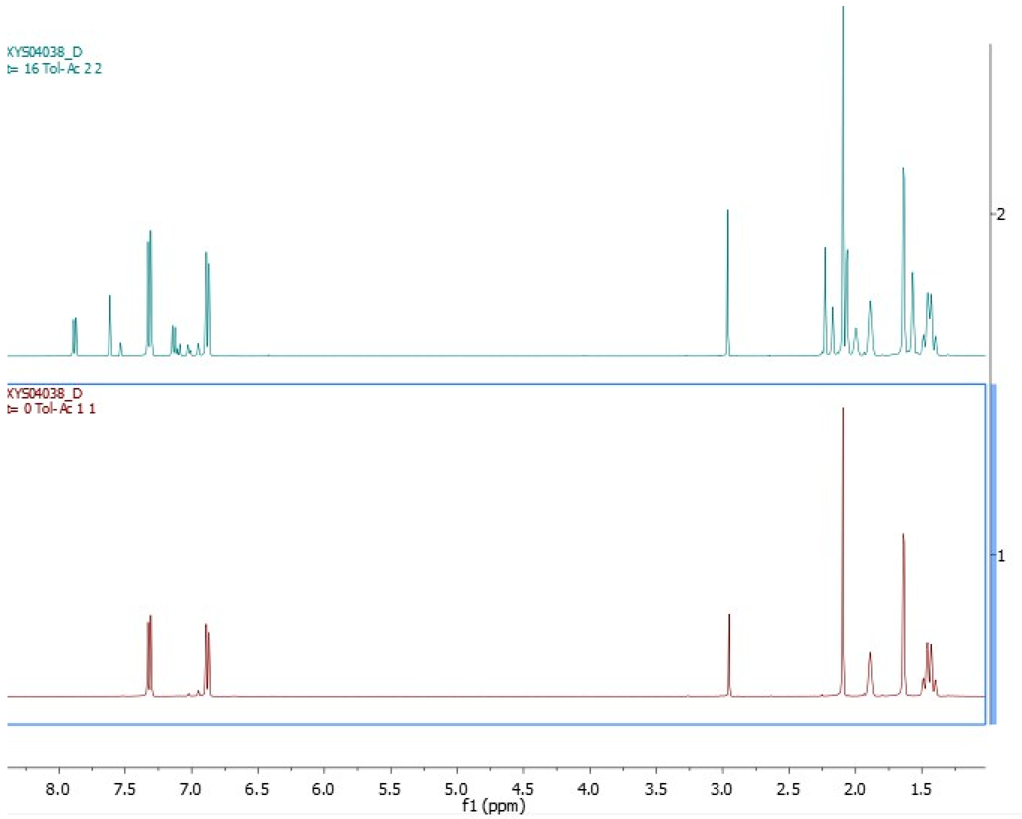
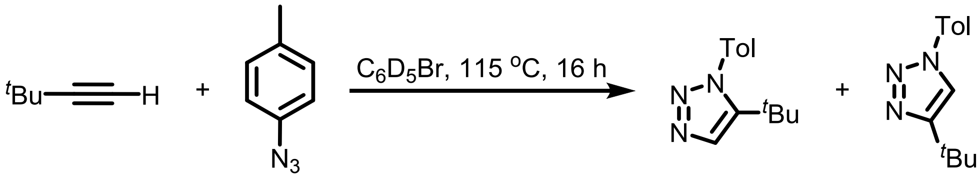


Figure S30: Before (bottom, t = 0 h) and after (top, t = 16 h) ^{1}H spectrum of (*p*-tolyl)acetylene and 1-azidoadamantane reaction in C_6D_5Br.

1-(*p*-tolyl)-4-(*t*-butyl)-1H-1,2,3-triazole and 1-(*p*-tolyl)-5-(*t*-butyl)-1H-1,2,3-triazole (6ag) (partial)



(*t*-butyl)acetylene (15 mg, 0.18 mmol, 1.1 equiv.), (*p*-tolyl)azide (21 mg, 0.16 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 16 h. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give a mixture of title compounds, leftover starting reagents and side products originating from (*p*-tolyl)azido such as *p*-toluidine and 1,2-di-*p*-tolyldiazene

1-(*p*-tolyl)-4-(*t*-butyl)-1H-1,2,3-triazole
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.46 (s, 1H, Ar-*H*), 7.44 (d, $^3J_{HH}$ = 8.4 Hz, 2H, *o*-Tol-*H*), 7.00 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *m*-Tol-*H*), 2.15 (s, 3H, Tol-CH_3), 1.40 (s, 9H, ^{t}Bu)

1-(*p*-tolyl)-5-(*t*-butyl)-1H-1,2,3-triazole (partial)
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.50 (s, 1H, Ar-*H*), 1.03 (s, 9H, ^{t}Bu)
This is a partial NMR line list, the remaining peaks cannot be positively identified from the other degradation impurities.

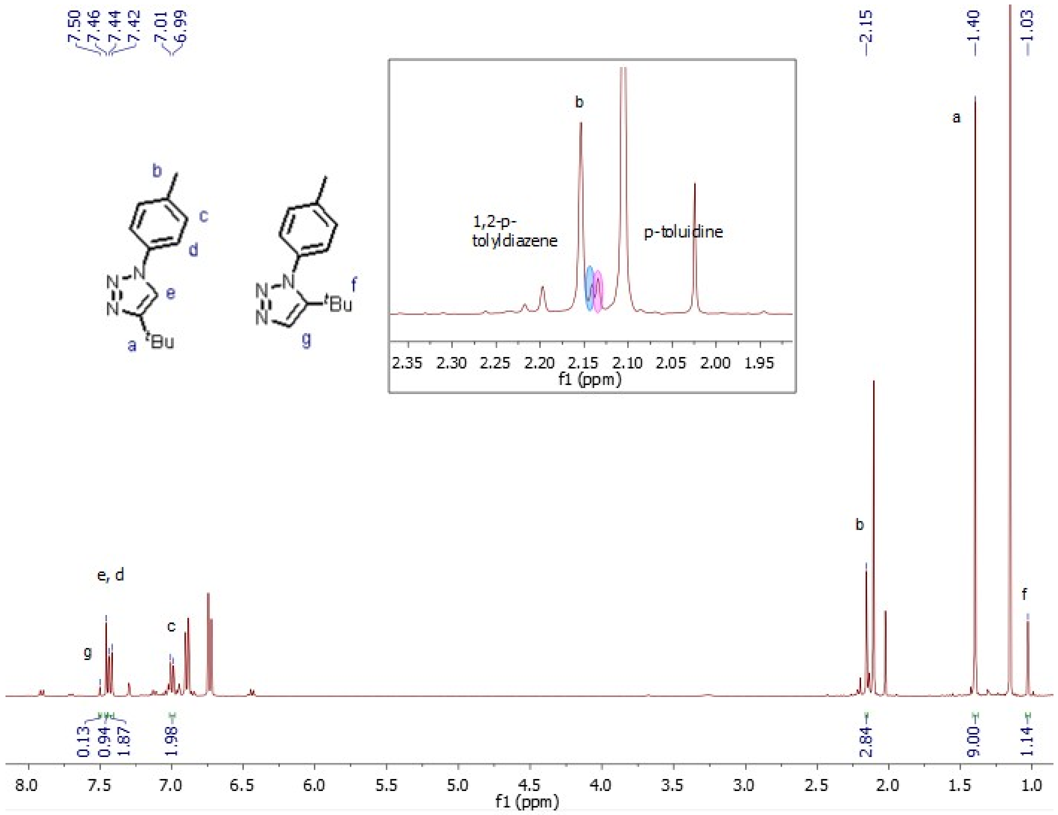


Figure S31: ^{1}H spectrum of 1-(*p*-tolyl)-4-(*t*-butyl)-1H-1,2,3-triazole and 1-(*p*-tolyl)-5-(*t*-butyl)-1H-1,2,3-triazole in C_6D_5Br.

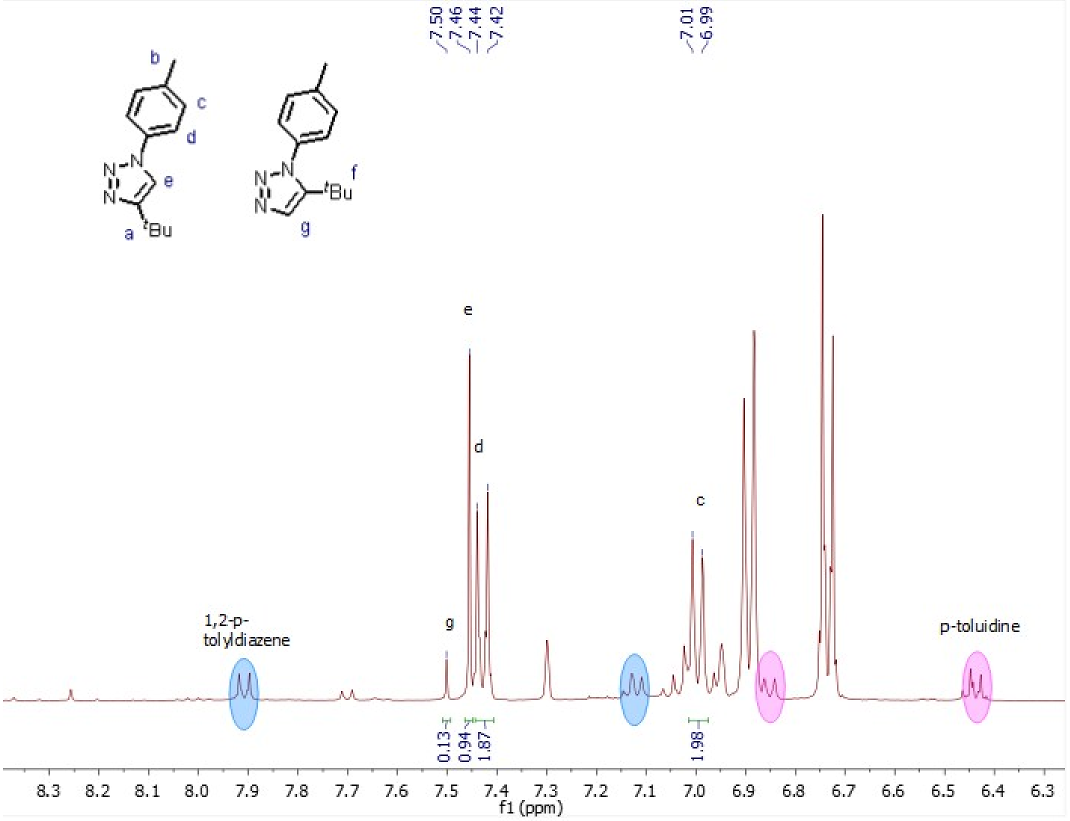


Figure S32: Zoom-in ^{1}H spectrum of 1-(*p*-tolyl)-4-(*t*-butyl)-1H-1,2,3-triazole and 1-(*p*-tolyl)-5-(*t*-butyl)-1H-1,2,3-triazole in C_6D_5Br.

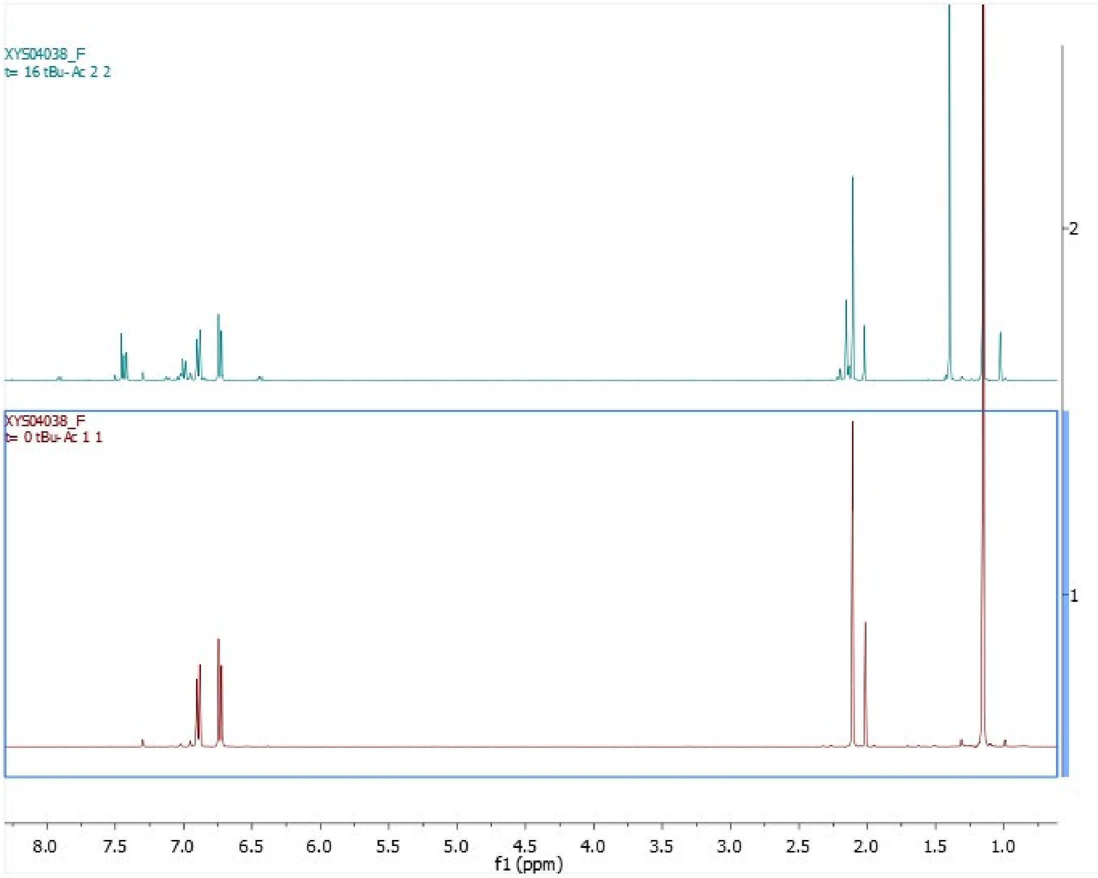
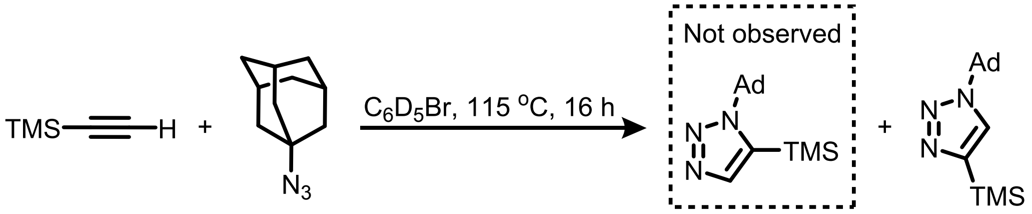


Figure S33: Before (bottom, t = 0 h) and after (top, t = 16 h) ^{1}H spectrum of (*t*-butyl)acetylene and (*p*-tolyl)azido reaction in C_6D_5Br.

1-adamantyl-4-(trimethylsilyl)-1H-1,2,3-triazole (6bh)



(Trimethylsilyl)acetylene (16 mg, 0.16 mmol, 1.7 equiv.), 1-azidoadamantane (16 mg, 0.09 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 16 h. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give a mixture of title compound and leftover starting reagents.

1-adamantyl-4-(trimethylsilyl)-1H-1,2,3-triazole
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.56 (s, 1H, Ar-*H*), 2.03 (m, 6H, Ad-C*H*$_2$), 1.96 (br s, 3H, Ad-C*H*), 1.54 (br s, 6H, Ad-C*H*$_2$), 0.38 (s, 9H, Si(C*H*$_3$)$_3$)

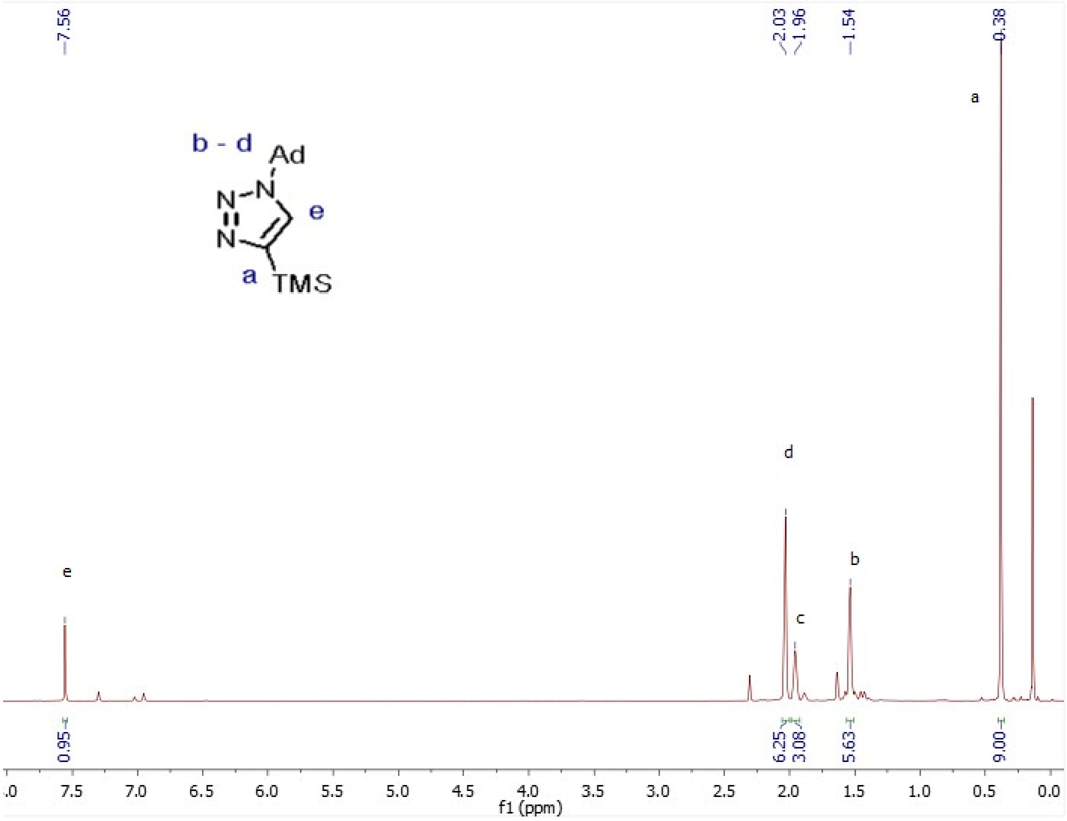


Figure S34: ^{1}H spectrum of 1-adamantyl-4-(trimethylsilyl)-1H-1,2,3-triazole in C_6D_5Br.

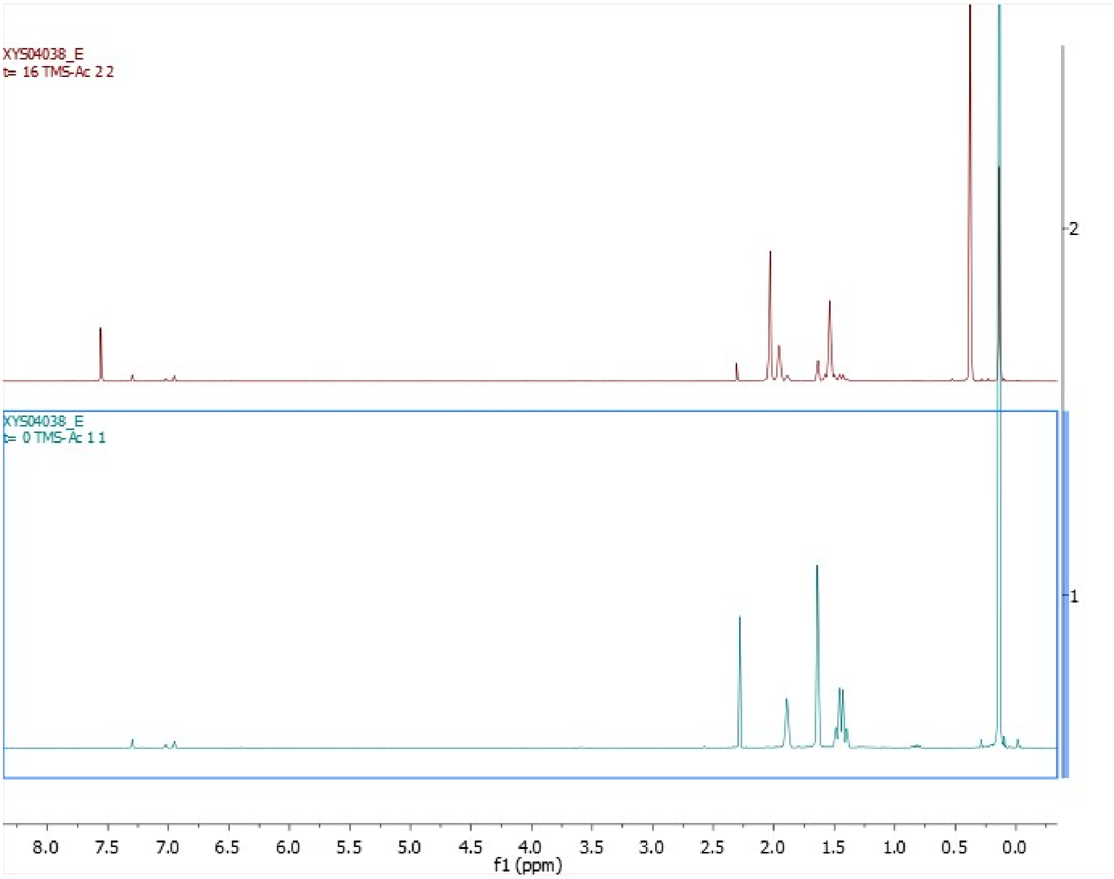
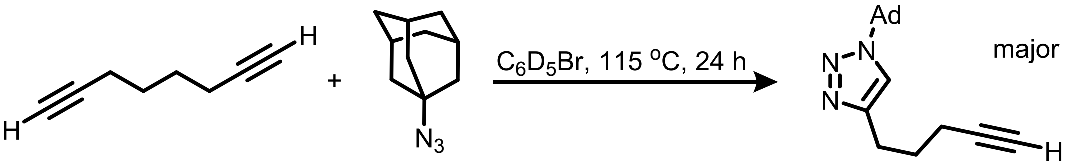


Figure S35: Before (bottom, t = 0 h) and after (top, t = 16 h) ^{1}H spectrum of (trimethylsilyl)acetylene and 1-azidoadamantane reaction in C_6D_5Br.

1-adamantyl-4-(5-hexyn-1-yl)-1H-1,2,3-triazole (6bi)



1,7-octadiyne (11 mg, 0.10 mmol, 0.43 equiv.), 1-Azidoadamantane (40. mg, 0.23 mmol, 1 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 24 h. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give a mixture of title compound and leftover starting reagents.

1-adamantyl-4-(5-hexyn-1-yl)-1H-1,2,3-triazole

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.10 (s, 1H, Ar-*H*), 2.67 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-C*H$_2$*), 2.07 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, HC≡C-C*H$_2$*) 2.02 (d, $^3J_{HH}$ = 7.5 Hz, 6H, N-C-(C*H$_2$*)$_2$ of adamantyl group), 1.56 (m, 6H, Ad).

This is a partial NMR line list, the remaining peaks for the hexynyl chain and adamantyl group are overlapping with other peaks.

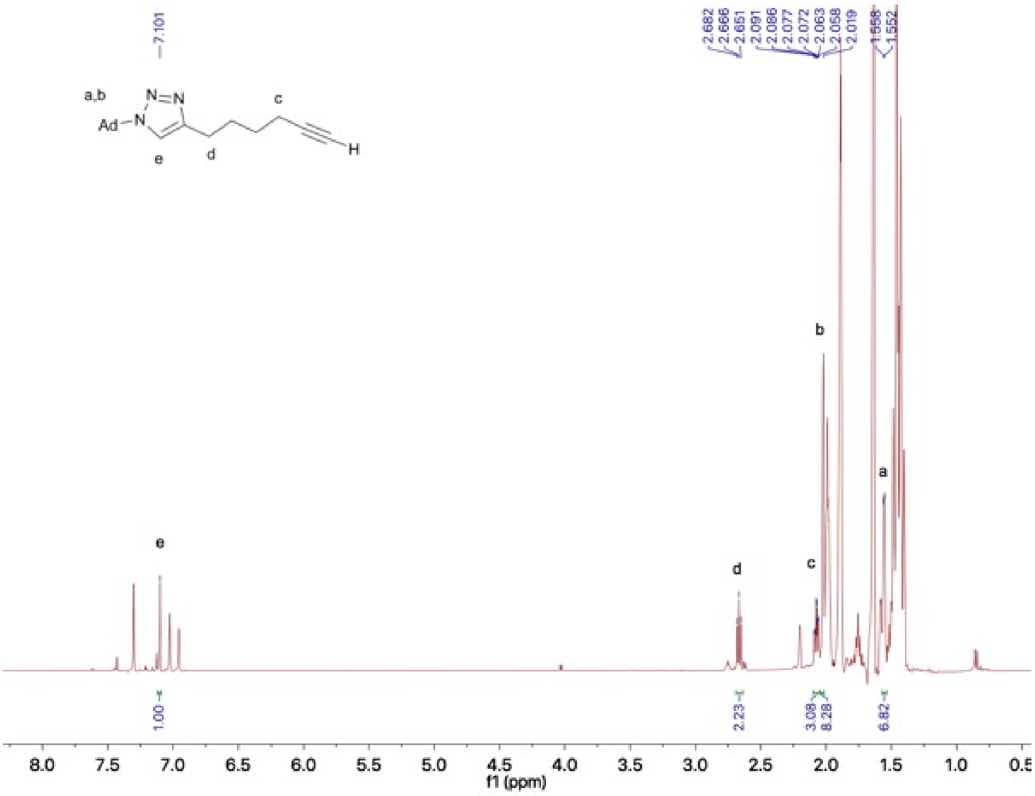


Figure S36: ^{1}H spectrum of 1-adamantyl-4-(5-hexyn-1-yl)-1H-1,2,3-triazole in C_6D_5Br.

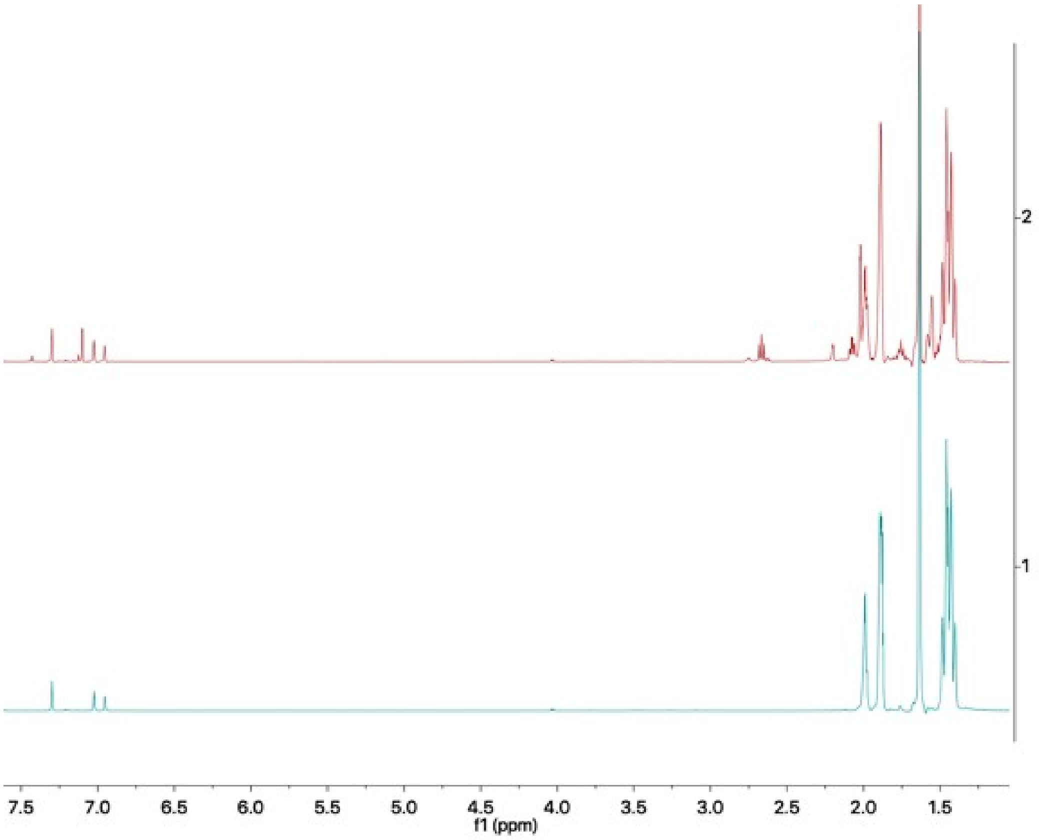
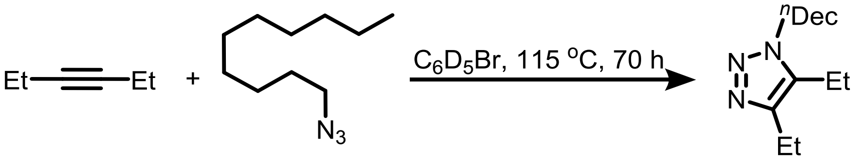


Figure S37: Before (bottom, t = 0 h) and after (top, t = 24 h) ^{1}H spectrum of 1,7-octadiyne and 1-azidoadamantane reaction in C_6D_5Br.

1-(*n*-decyl)-4,5-(diethyl)-1,2,3-triazole (6ca) (partial)



3-hexyne (16 mg, 0.1 mmol, 1.0 equiv.), 1-azidodecane (19 mg, 0.1 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 70 h. After which, the reaction mixture was analyzed by ^{1}H NMR without any further work-up to give a mixture of title compound and leftover starting reagents.

1-(*n*-decyl)-4,5-(diethyl)-1,2,3-triazole
^{1}H NMR (500 MHz, C_6D_5Br): δ 3.92 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $H_3C(CH_2)_8$-CH_2-N), 2.57 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 4-CH_2CH$_3$), 2.35 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 5-CH_2CH$_3$), 1.71 – 1.68 (m, 2H, $H_3C(CH_2)_7$-CH_2-CH$_2$N), 0.95 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 5-CH$_2$CH_3)
This is a partial NMR line list, the remaining peaks are buried under the starting reagents.

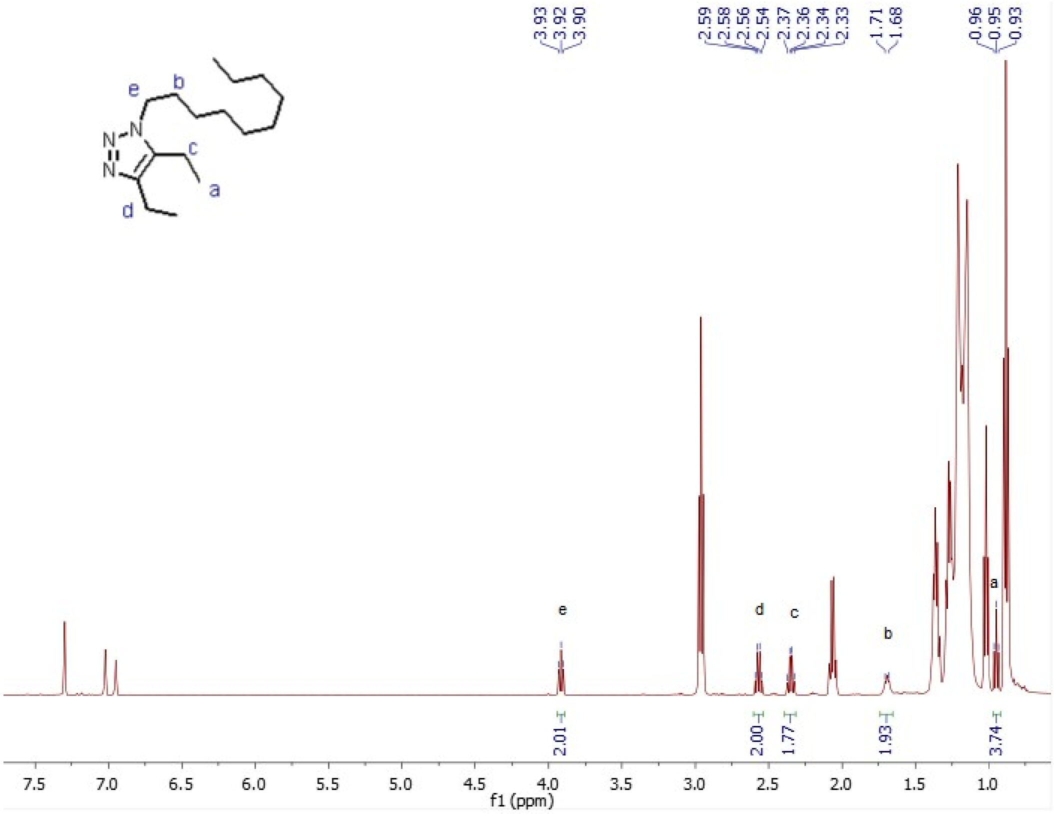


Figure S38: ^{1}H spectrum of 1-(*n*-decyl)-4,5-(diethyl)-1,2,3-triazole in C_6D_5Br.

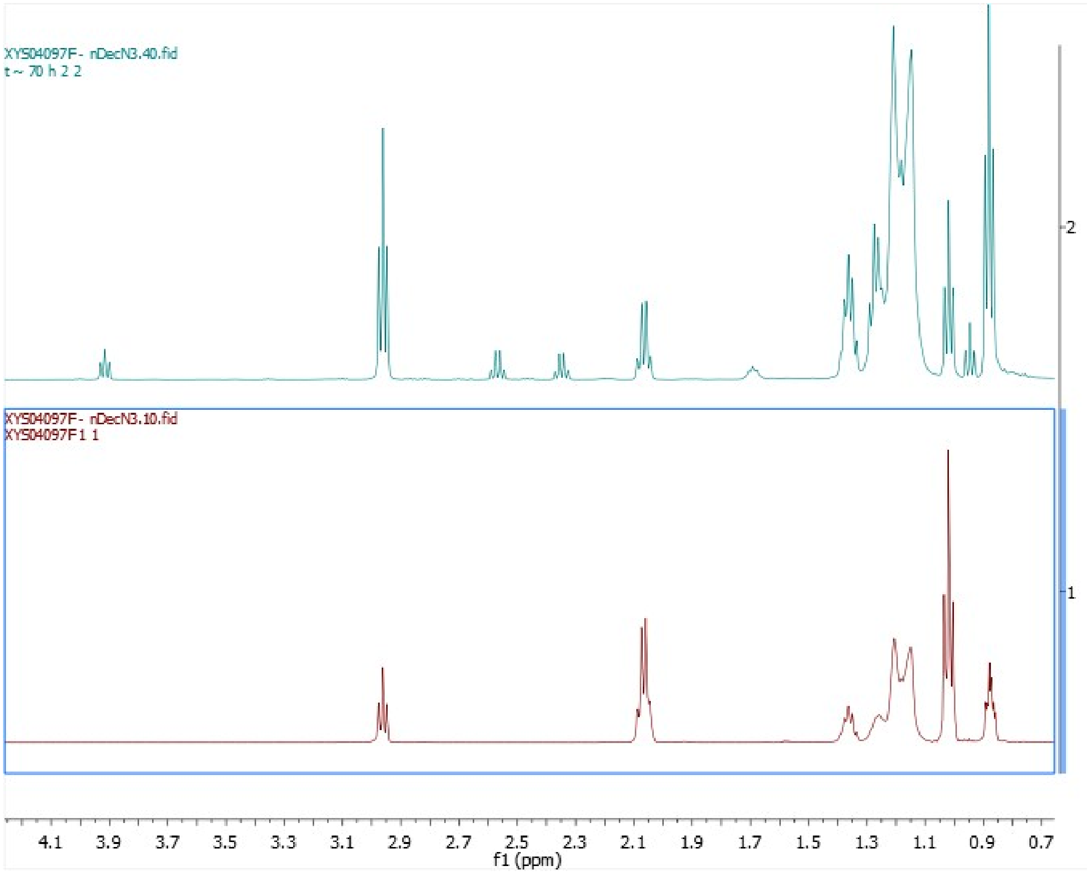
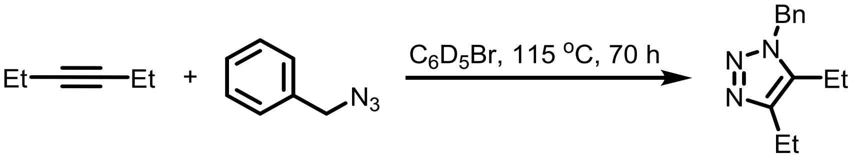


Figure S39: Before (bottom, t = 0 h) and after (top, t = 70 h) zoom-in ^{1}H spectrum of 3-hexyne and 1-azidodecane reaction in C_6D_5Br.

1-(benzyl)-4,5-(diethyl)-1,2,3-triazole (6da) (partial)



3-hexyne (16 mg, 0.1 mmol, 1.0 equiv.), benzylazide (14 mg, 0.1 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 70 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give a mixture of title compound and leftover starting reagents.

1-(benzyl)-4,5-(diethyl)-1,2,3-triazole

^1H NMR (500 MHz, C_6D_5Br): δ 6.98 – 6.97 (m, 2H, Ar-*H*), 5.17 (s, 2H, Ar-C*H₂*), 2.54 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 4-C*H₂*CH₃), 2.23 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 5-C*H₂*CH₃), 1.26 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 4-CH₂C*H₃*), 0.71 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 5-CH₂C*H₃*).

This is a partial NMR line list, the remaining aryl peaks are buried under the starting reagents.

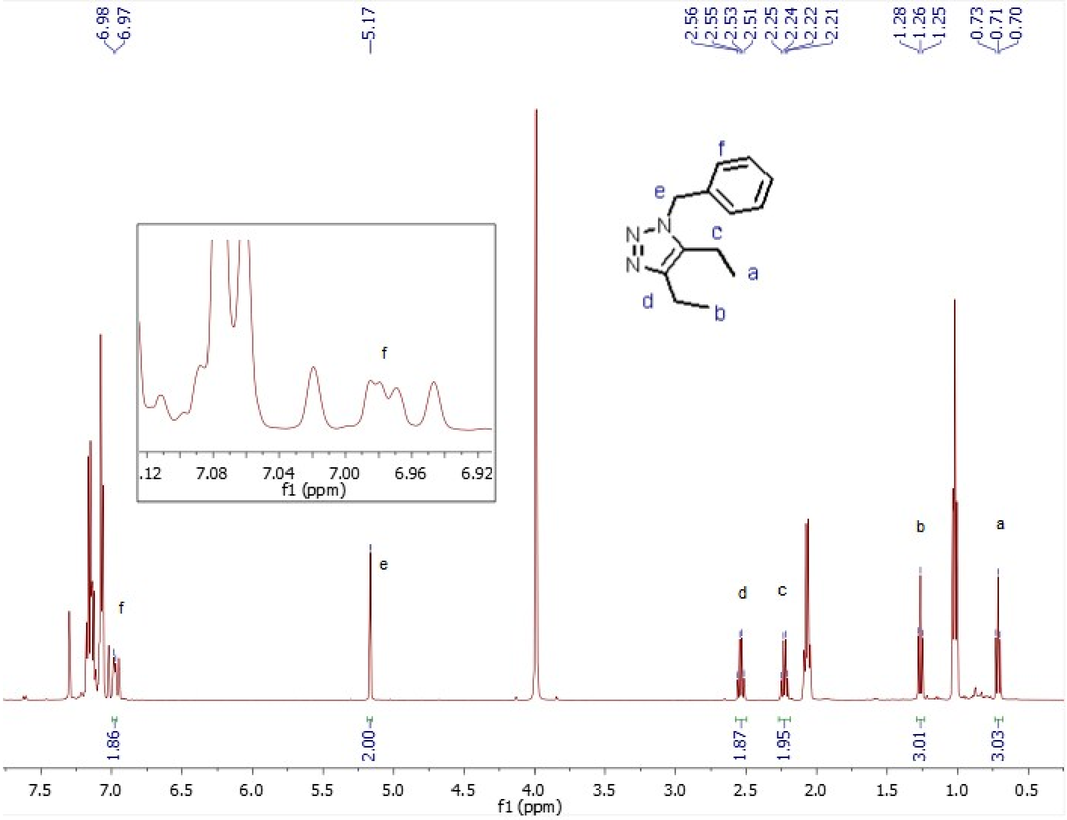


Figure S40: ^1H spectrum of 1-(benzyl)-4,5-(diethyl)-1,2,3-triazole in C_6D_5Br.

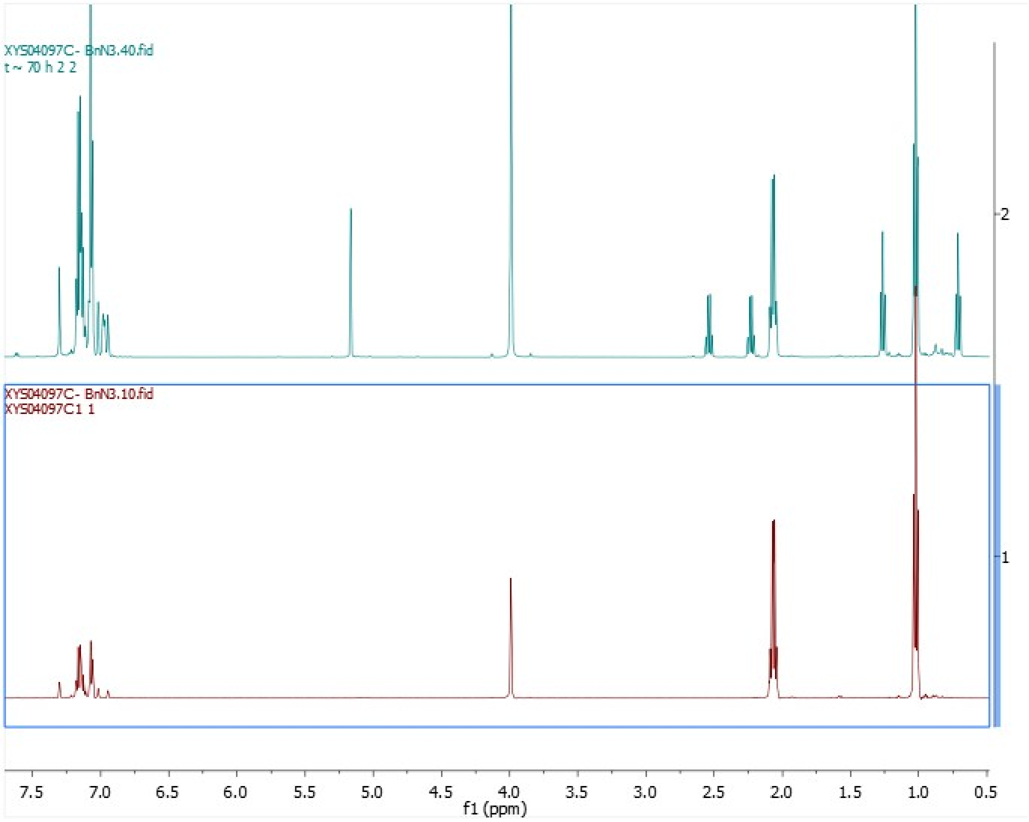
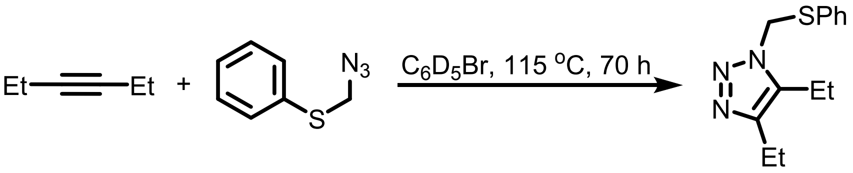


Figure S41: Before (bottom, t = 0 h) and after (top, t = 70 h) ^1H spectrum of 3-hexyne and benzylazide reaction in C_6D_5Br.

1-(methyl phenyl sulfide)-4,5-(diethyl)-1,2,3-triazole (6ea) (partial)



3-hexyne (16 mg, 0.1 mmol, 1.0 equiv.), azidomethyl phenyl sulfide (18 mg, 0.1 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 70 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give a mixture of title compound and leftover starting reagents.

1-(methyl phenyl sulfide)-4,5-(diethyl)-1,2,3-triazole
^{1}H NMR (500 MHz, C_6D_5Br): δ 5.28 (s, 2H, PhS-C*H₂*), 2.49 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 4-CH_2CH_3), 2.33 (q, $^3J_{HH}$ = 7.6 Hz, 2H, 5-CH_2CH_3), 1.21 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 4-CH_2CH_3), 0.93 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 5-CH_2CH_3)
This is a partial NMR line list, the decomposition peaks are overlapping with the aryl peaks.

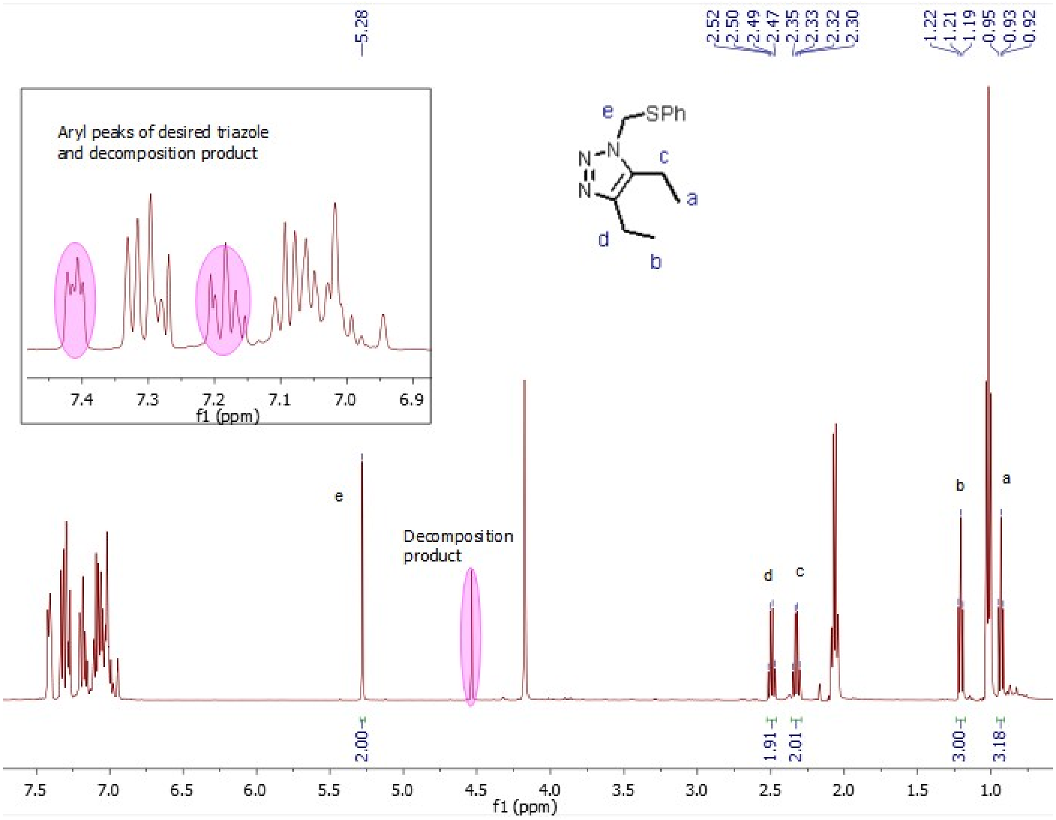


Figure S42: ^{1}H spectrum of 1-(methyl phenyl sulfide)-4,5-(diethyl)-1,2,3-triazole in C_6D_5Br.

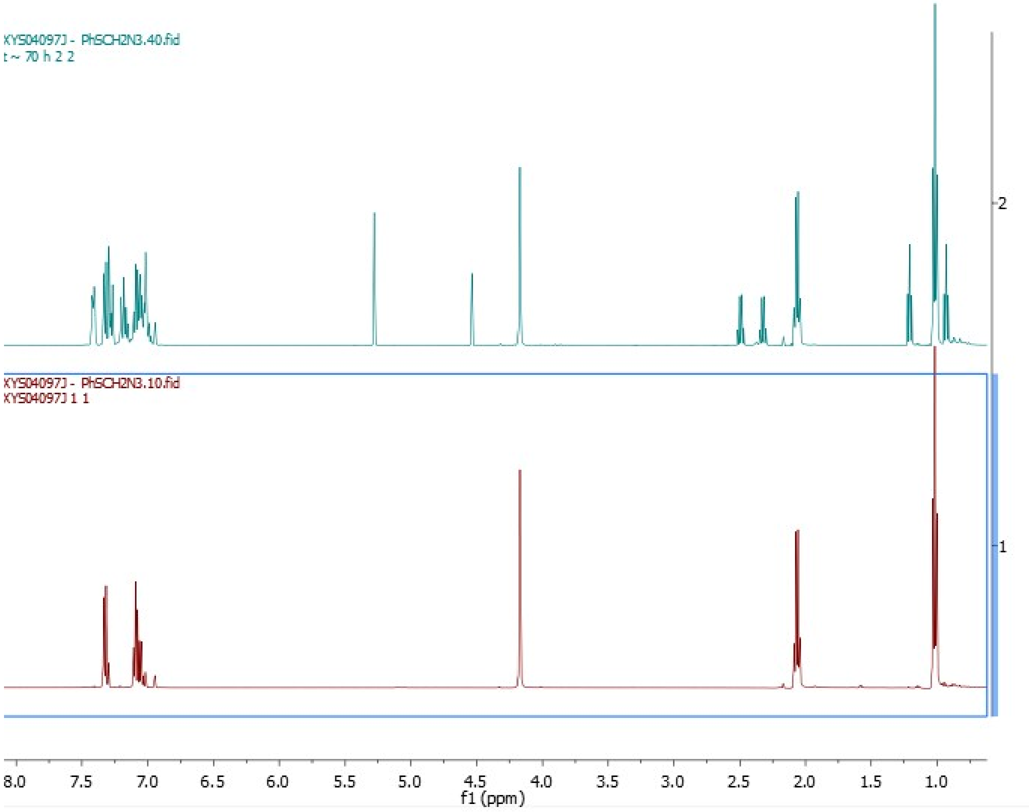
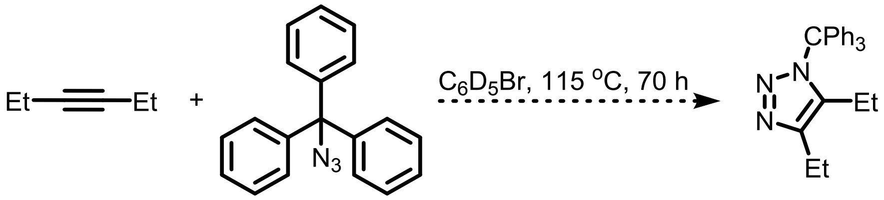


Figure S43: Before (bottom, t = 0 h) and after (top, t = 70 h) ^{1}H spectrum of 3-hexyne and azidomethyl phenyl sulfide reaction in C_6D_5Br.

Attempted reaction of trityl azide and 3-hexyne (6fa) in C_6D_5Br



3-hexyne (16 mg, 0.1 mmol, 1.0 equiv.), trityl azide (28 mg, 0.1 mmol, 1.0 equiv.) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 70 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give leftover starting reagents, degradation products and a small new quartet peak that we cannot positively attribute as the desired product.

In light of the slow/no reactivity, we do not think that this by-product formation will be significant in our catalytic reaction.

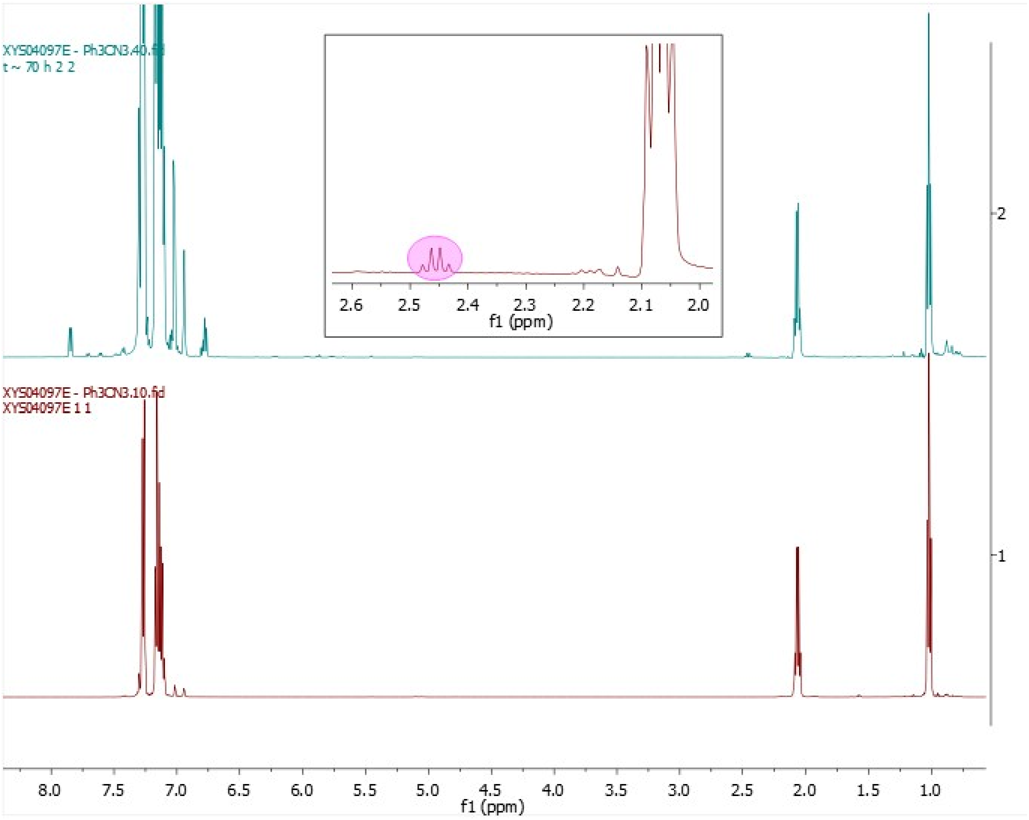
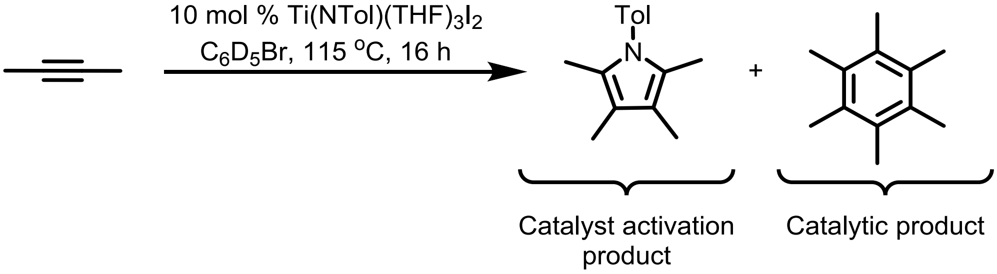


Figure S44: Before (bottom, t = 0 h) and after (top, t = 70 h) ^1H spectrum of 3-hexyne and trityl azide reaction in C_6D_5Br.

Characterization of cyclotrimerization byproducts in C_6D_5Br

Characterization of hexaethylbenzene (9a), 1,3,5-tri-*n*-butyl-benzene (9e) and 1,2,4-tri-*n*-butyl-benzene (9e) in C_6D_5Br were reported previously.[3]

Hexamethylbenzene (9b)



2-butyne (13 mg, 0.24 mmol, 1.0 equiv.), $Ti(NTol)(THF)_3I_2$ (11 mg, 0.02 mmol, 10 mol %) and 0.5 mL of C_6D_5Br were added to a NMR tube in a N_2-filled glovebox. The tube was sealed and heated at 115 °C for 16 h. After which, the reaction mixture was analyzed by ^1H NMR without any further work-up to give a mixture of the title compounds.

Hexamethylbenzene

^1H NMR (500 MHz, C_6D_5Br): δ 2.11 (s, 18H, CH_3)

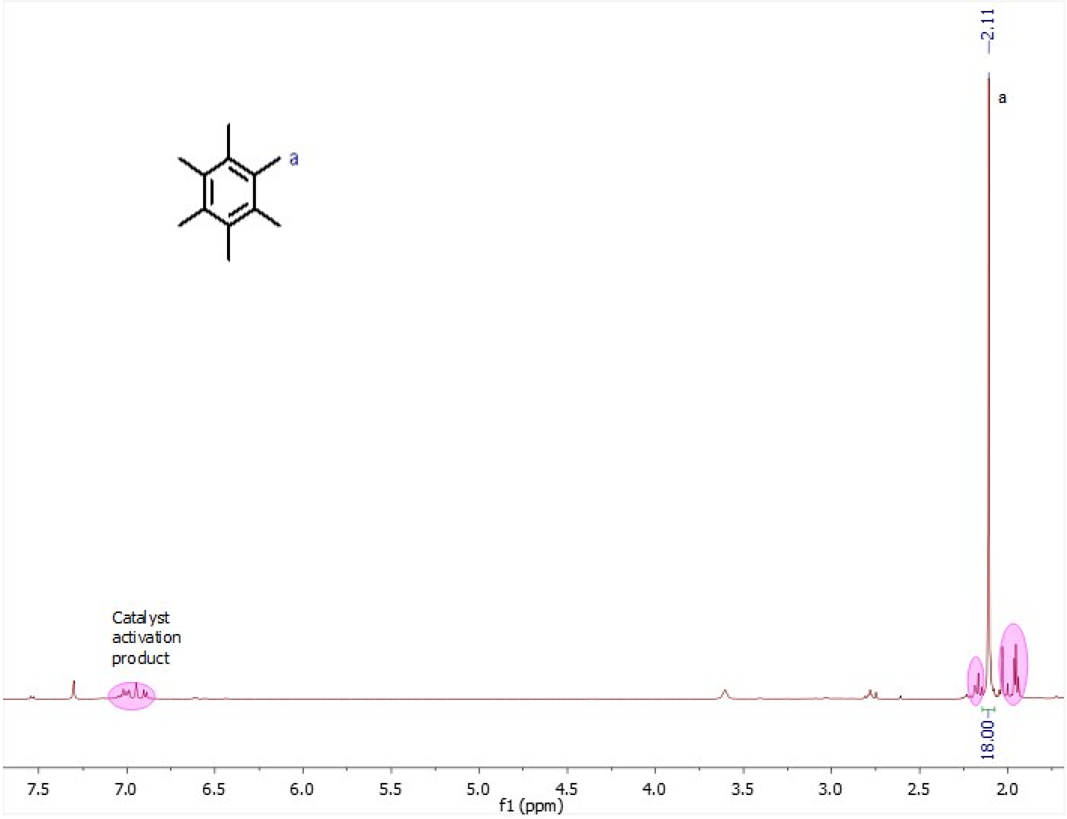


Figure S45: ^1H spectrum of hexamethylbenzene in C_6D_5Br.

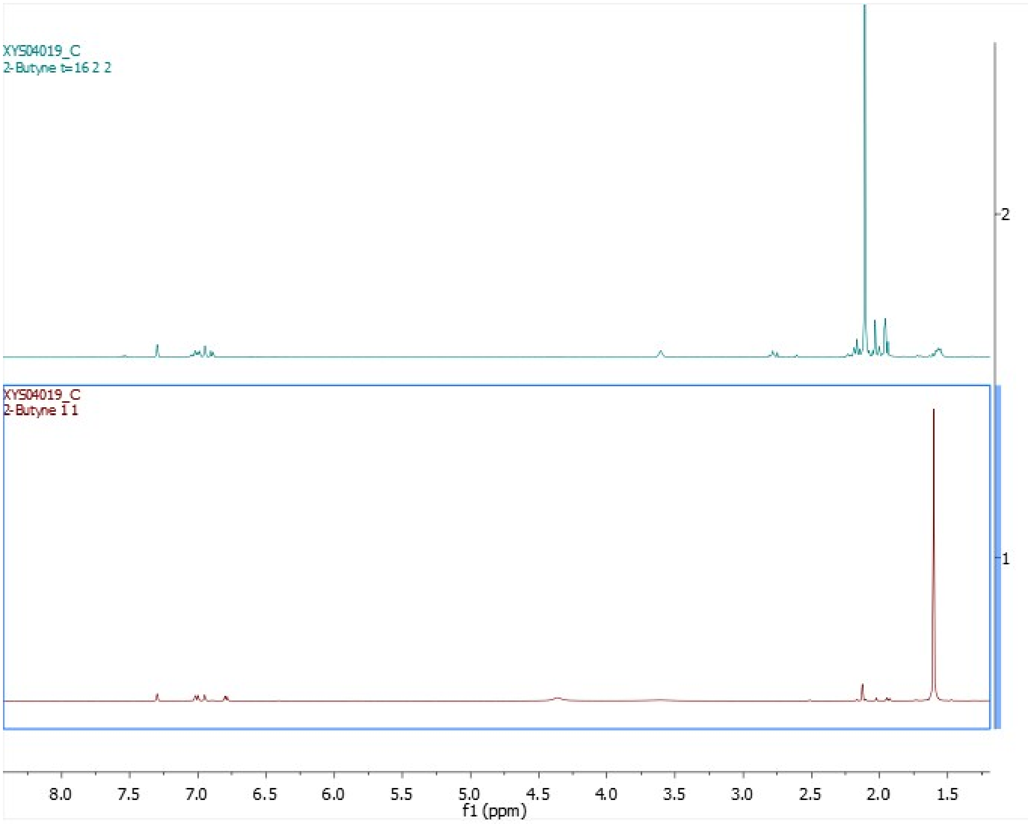
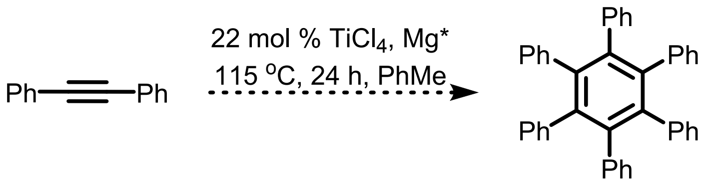


Figure S46: Before (bottom, t = 0 h) and after (top, t = 16 h) ^{1}H spectrum of hexaethylbenzene in C_6D_5Br.

Attempted cyclotrimerizaton of diphenylacetylene (9c)



Diphenylacetylene (128 mg, 0.72 mmol, 1 equiv.), $TiCl_4$ (30 mg, 0.16 mmol, 22 mol %), Mg* (41 mg, 0.098 mmol, 14 mol %) and 0.5 mL of toluene were added to a 20 mL scintillation vial equipped with a small stirbar in a N_2-filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 24 h. After which, the reaction mixture was concentrated *in vacuo* to dryness before dissolving in minimal C_6D_5Br. The mixture was filtered through celite before analysis to give a mixture of mostly starting materials and residual toluene.

In light of the slow/no reactivity, we do not think that this by-product formation will be significant in our catalytic reaction.

*Anthracene peaks

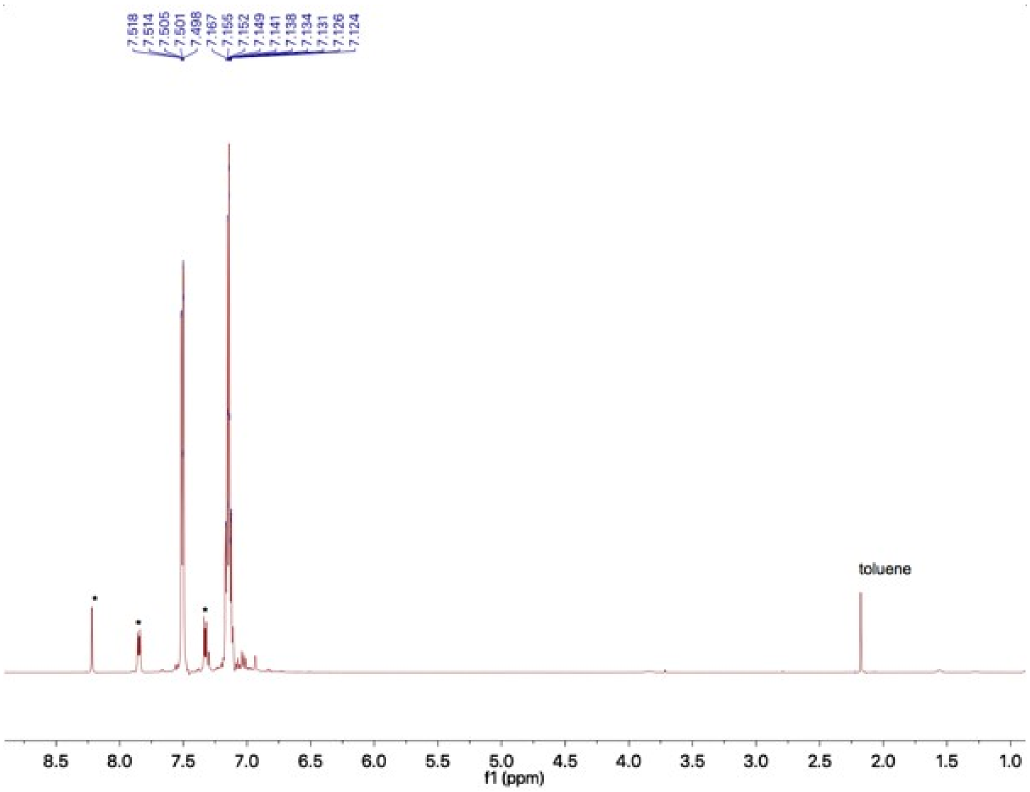
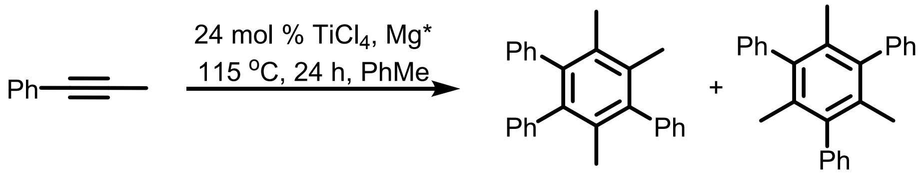


Figure S47: Post reaction ^1H spectrum of diphenylacetylene treated with $TiCl_4$ and Mg* in C_6D_5Br.
* Major peaks in the aromatic region are identical to diphenylacetylene.

1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene (9d) (partial)



1-phenyl-1-propyne (78 mg, 0.67 mmol, 1 equiv.), $TiCl_4$ (30 mg, 0.16 mmol, 24 mol %), Mg* (31 mg, 0.07 mmol, 10 mol %) and 0.5 ml PhMe were added to a 20 mL scintillation vial equipped with a small stirbar in a N_2-filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 24 h. After which, the reaction mixture was concentrated *in vacuo* to dryness before dissolving in minimal C_6D_5Br. The mixture was filtered through celite before analysis to give a mixture of the two products, starting material and residual anthracene peaks from Mg*.

1,2,4-trimethyl-3,5,6-triphenylbenzene

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.08 (s, 3H, C1-CH_3), 2.05 (s, 3H, C2-CH_3 or C4-CH_3) , 1.90 (s, 3H, C2-CH_3 or C4-CH_3)
This is a partial NMR line list, the aromatic region is unable to be differentiated from the other isomer and starting material.

1,3,5-trimethyl-2,4,6-triphenylbenzene

^{1}H NMR (500 MHz, C_6D_5Br): δ 1.88 (s, 9H, Ar-CH_3)
This is a partial NMR line list, the aromatic region is unable to be differentiated from the other isomer and starting material.
* Anthracene peaks

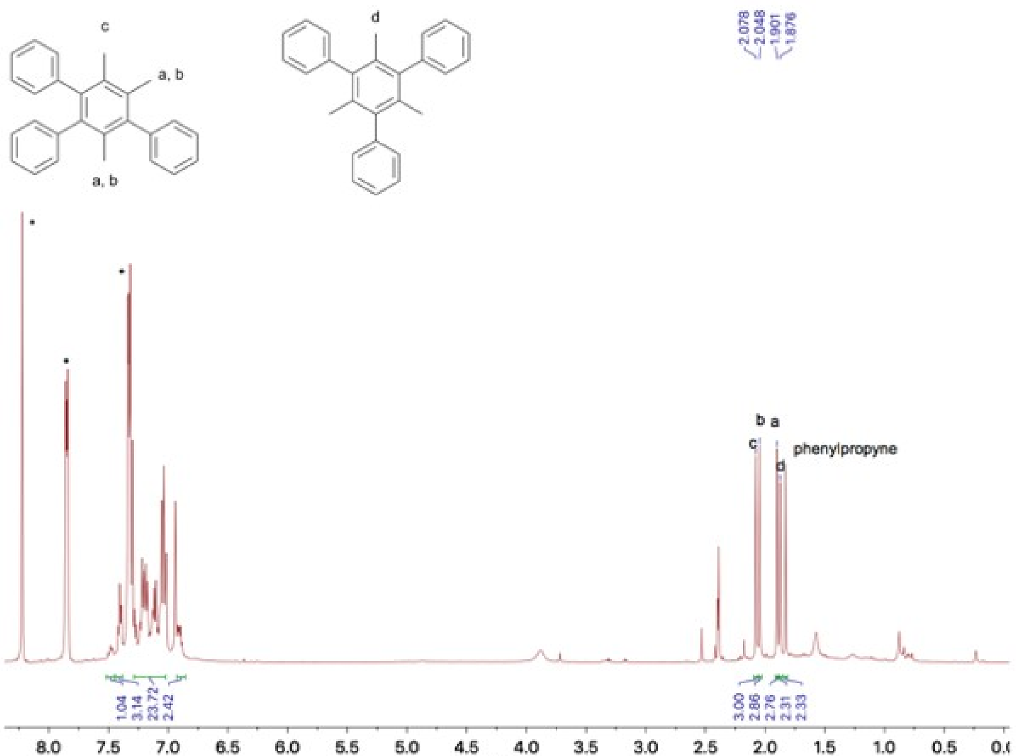


Figure S48: ^{1}H spectrum of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene in C_6D_5Br.

* Integration of the aryl region is consistent with the integration of two trimerization isomers and remaining 1-phenyl-1-propyne.

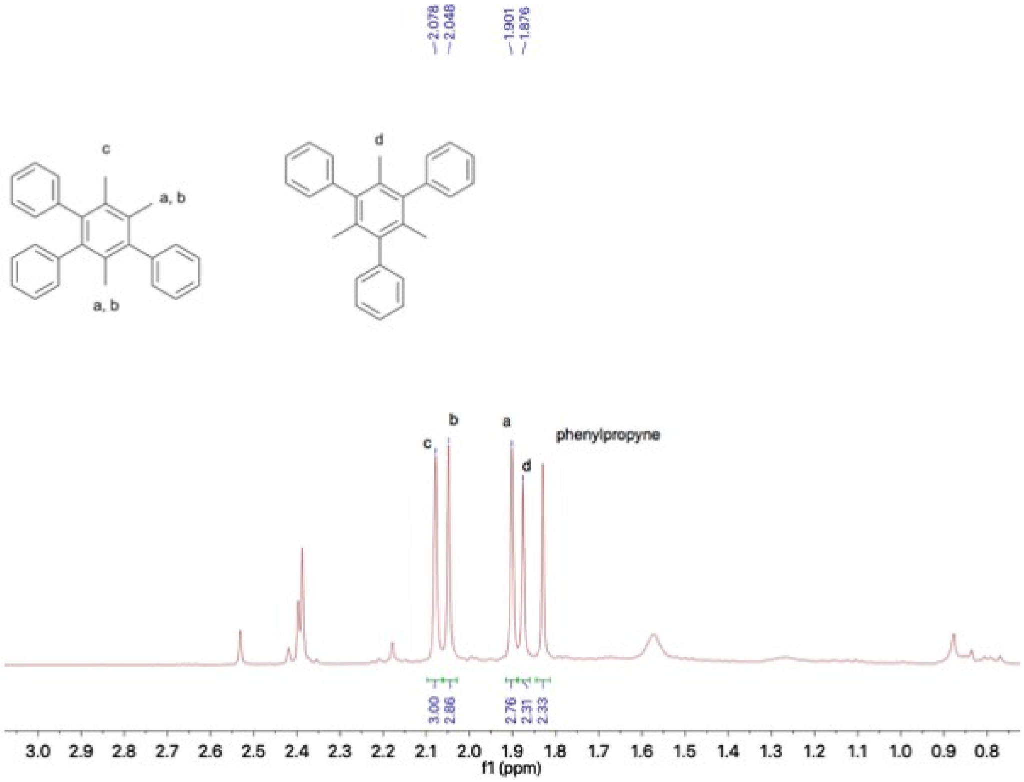


Figure S49: Zoom-in ^{1}H spectrum of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene in C_6D_5Br.

1,3,5-tri(*p*-tolyl)benzene (9f)[8]

Title compound was synthesized following literature procedure and purified with a silica column using pure hexanes as eluent.

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.80 (s, 3H, Ar-*H*), 7.57 (d, $^3J_{HH}$ = 7.9 Hz, 6H, *m*-Tol-*H*), 7.18 (d, $^3J_{HH}$ = 7.9 Hz, 6H, *o*-Tol-*H*), 2.28 (s, 9H, CH_3)

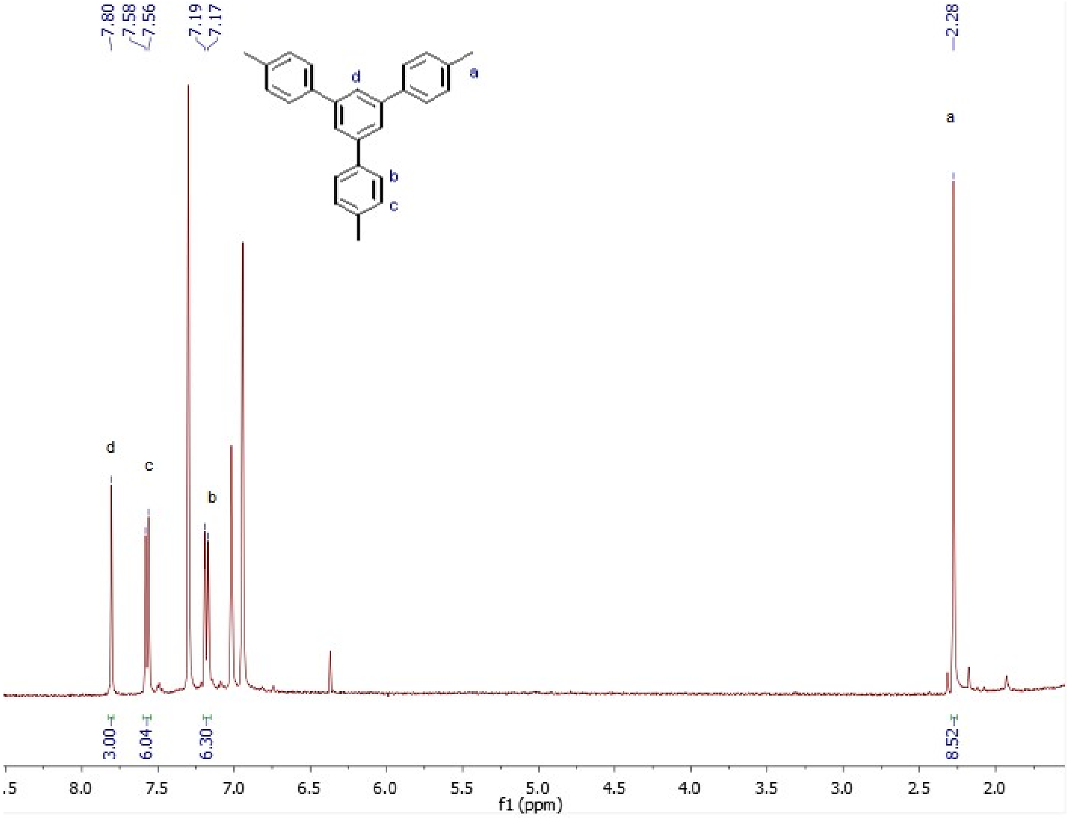


Figure S50: ^{1}H spectrum of 1,3,5-tri(*p*-tolyl)benzene in C_6D_5Br.

1,2,4-tri(*p*-tolyl)benzene (9f)[9]

Title compound was synthesized following literature procedure and purified further with an alumina plug (pure hexanes eluent).

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.70 – 7.69 (m, 1H, Ar-*H*), 7.60 – 7.46 (m, 4H, Ar-*H* and Tol-*H*), 7.16 – 7.14 (m, 6H, Tol-*H*), 6.93 – 6.91 (m, 4H, Tol-*H*), 2.27 (s, 3H, Tol-CH_3), 2.12 (s, 6H, Tol-CH_3)
Multiplet between 6.93 – 6.91 is partially overlapped by C_6D_5Br solvent peak.

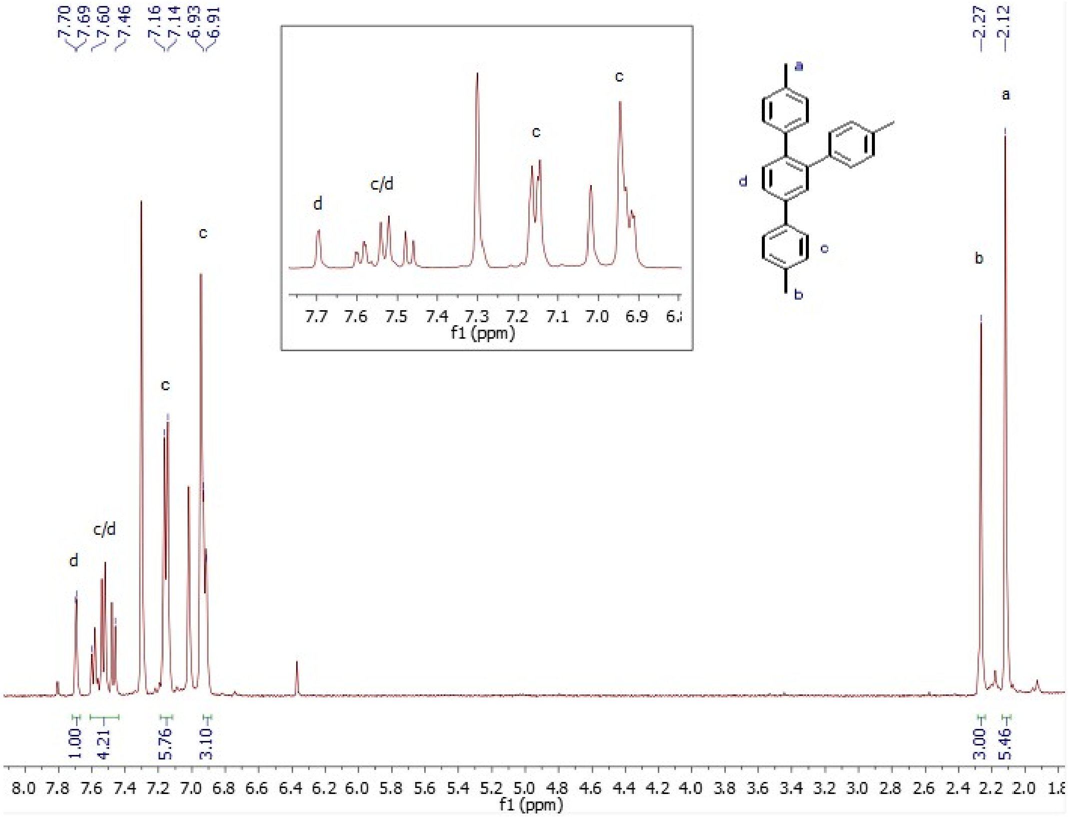
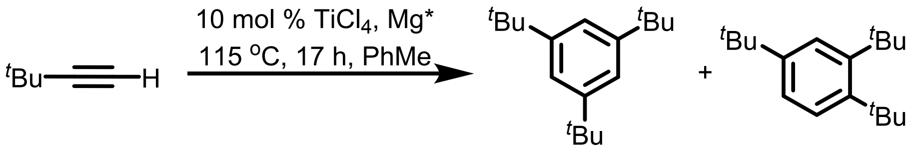


Figure S51: ^{1}H spectrum of 1,2,4-tri(*p*-tolyl)benzene in C_6D_5Br.

1,3,5-tri(*t*-butyl)benzene and 1,2,4-tri(*t*-butyl)benzene (9g)



(*t*-butyl)acetylene (56 mg, 0.69 mml, 1 equiv.), $TiCl_4$ (13 mg, 0.07 mmol, 10 mol %), Mg* (30 mg, 0.07 mmol, 12 mol %) and 0.5 ml PhMe were added to a 4 mL scintillation vial equipped with a small stirbar in a N_2-filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 17 h. After which, the reaction mixture was concentrated *in vacuo* to dryness before dissolving in minimal C_6D_5Br. The mixture was filtered through celite before analysis to give a mixture of the two products and the residual anthracene peaks from Mg*.

1,3,5-tri(*t*-butyl)benzene
^{1}H NMR (500 MHz, C_6D_5Br): δ 7.34 (s, 3H, Ar-*H*), 1.33 (s, 27H, ^{t}Bu)

1,2,4-tri(*t*-butyl)benzene
^{1}H NMR (500 MHz, C_6D_5Br): δ 7.66 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C3-Ar-*H*), 7.50 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C5 or C6-Ar-*H*), 7.10 (dd, $^3J_{HH}$ = 8.5 Hz and $^4J_{HH}$ = 2.1 Hz, 1H, C5 or C6-Ar-*H*), 1.52 (s, 9H, ^{t}Bu), 1.48 (s, 9H, ^{t}Bu), 1.27 (s, 9H, ^{t}Bu)

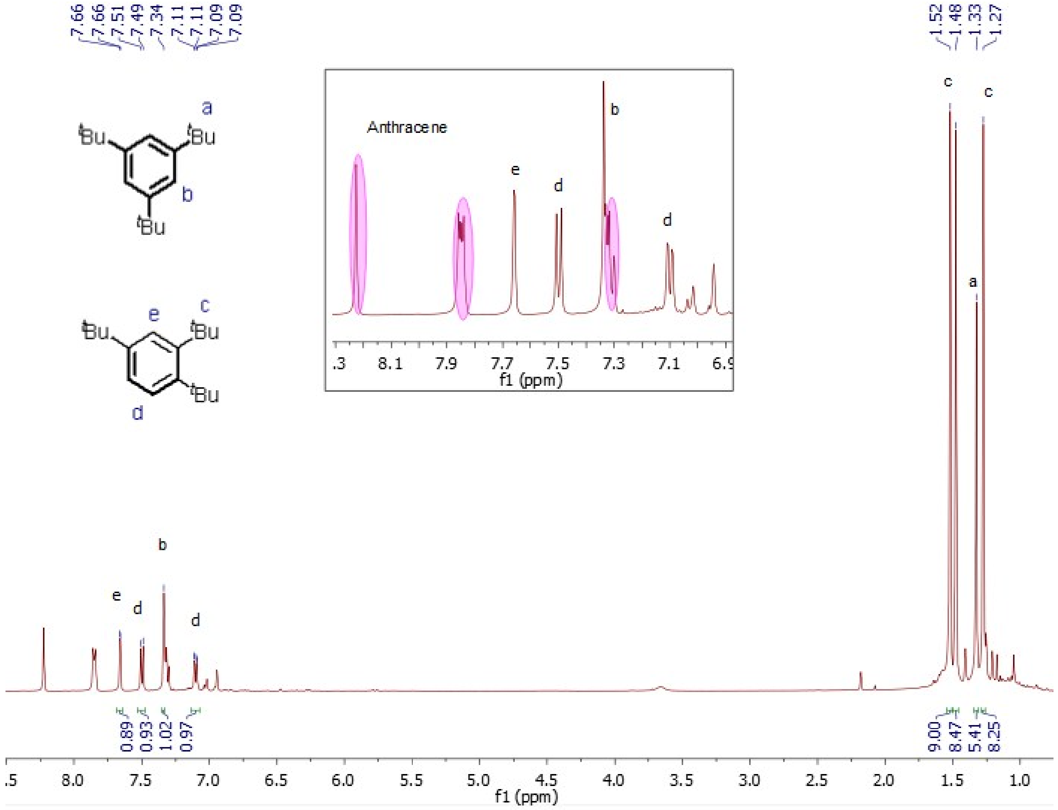
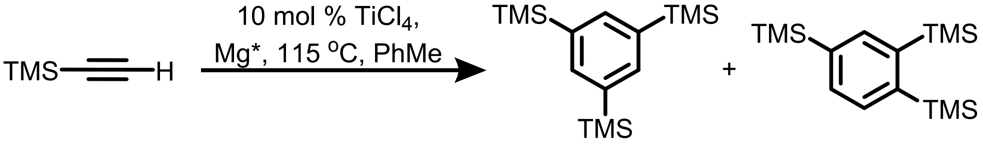


Figure S52: ^{1}H spectrum of 1,3,5-tri(t-butyl)benzene and 1,2,4-tri(t-butyl)benzene in C_6D_5Br.

1,3,5-tris(trimethylsilyl)benzene and 1,2,4-tris(trimethylsilyl)benzene (9h)



(Trimethylsilyl)acetylene (60 mg, 0.61 mml, 1 equiv.), $TiCl_4$ (12 mg, 0.06 mmol, 10 mol %), Mg* (30 mg, 0.07 mmol, 12 mol %) and 0.5 ml PhMe were added to a 4 mL scintillation vial equipped with a small stirbar in a N_2-filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 17 h. After which, the reaction mixture was concentrated *in vacuo* to dryness before dissolving in minimal C_6D_5Br. The mixture was filtered through celite before analysis to give a mixture of the two products and the residual anthracene peaks from Mg*.

1,3,5-tris(trimethylsilyl)benzene
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.85 (s, 3H, Ar-*H*), 0.30 (s, 27 H, Si(C*H*$_3$)$_3$)
Singlet at δ 7.85 is partially overlapped by residual anthracene peak.

1,2,4-tris(trimethylsilyl)benzene
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.95 (s, 1H, C3-Ar-*H*), 7.67 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C5 or C6-Ar-*H*), 7.47 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C5 or C6-Ar-*H*), 0.38 (s, 9H, Si(C*H*$_3$)$_3$), 0.37 (s, 9H, Si(C*H*$_3$)$_3$), 0.27 (s, 9H, Si(C*H*$_3$)$_3$)

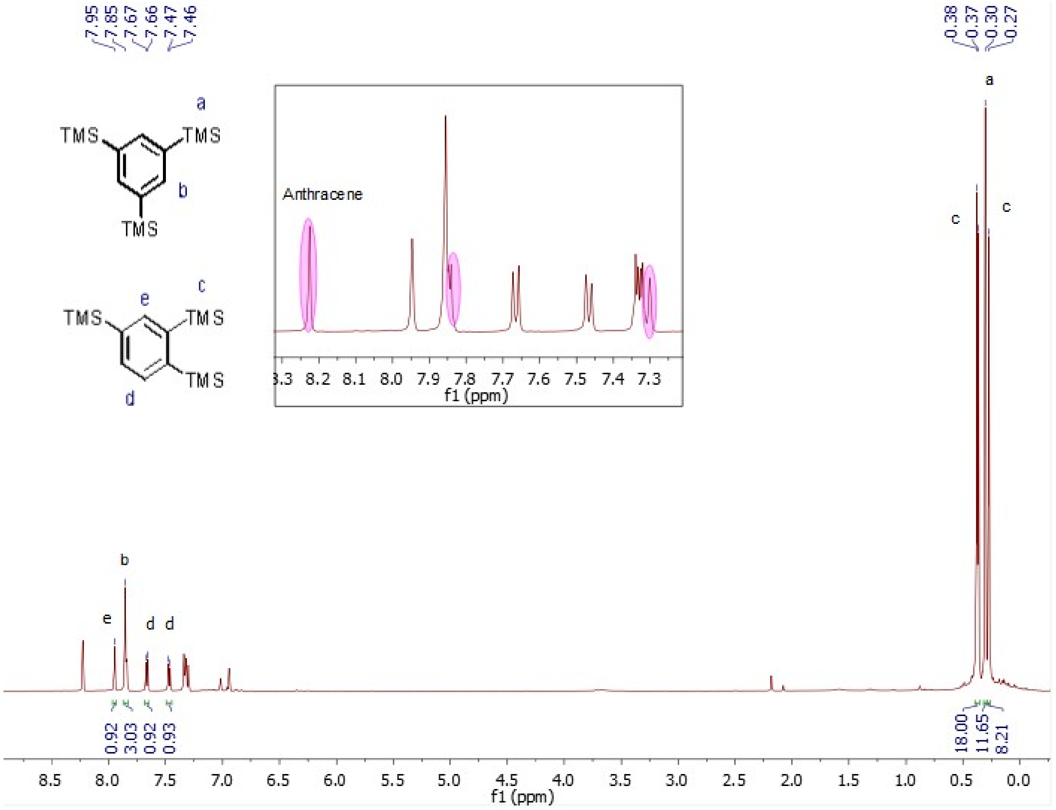
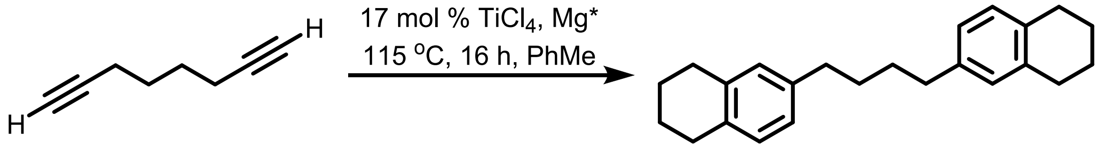


Figure S53: ^{1}H spectrum of 1,3,5-tris(trimethylsilyl)benzene and 1,2,4-tris(trimethylsilyl)benzene in C_6D_5Br.

1,4-bis(5,6,7,8-tetrahydronaphthalen-2-yl)butane (9i)



1,7-Octadiyne (81 mg, 0.76 mmol, 1 equiv.), $TiCl_4$ (24 mg, 0.13 mmol, 17 mol %), Mg* (29 mg, 0.069 mmol, 9 mol %) and 0.5 ml PhMe were added to a 20 mL scintillation vial equipped with a small stirbar in a N_2-filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 16 h. After which, the reaction mixture was concentrated *in vacuo* to dryness before dissolving in minimal C_6D_5Br. The mixture was filtered through celite before analysis to the product, starting material and residual anthracene peaks from Mg*.

1,4-bis(5,6,7,8-tetrahydronaphthalen-2-yl)butane

^{1}H NMR (500 MHz, C_6D_5Br): δ 7.02-6.78 (m (br), 6H, Ar-*H*), 2.62-2.60 (m (br), 8H, Ar-C*H*$_2$), 2.52 (m (br), 4H, Ar-C*H*$_2$), 1.62 (m (br), 12H, CH_2-C*H*$_2$C*H*$_2$-CH_2).

* Anthracene peaks

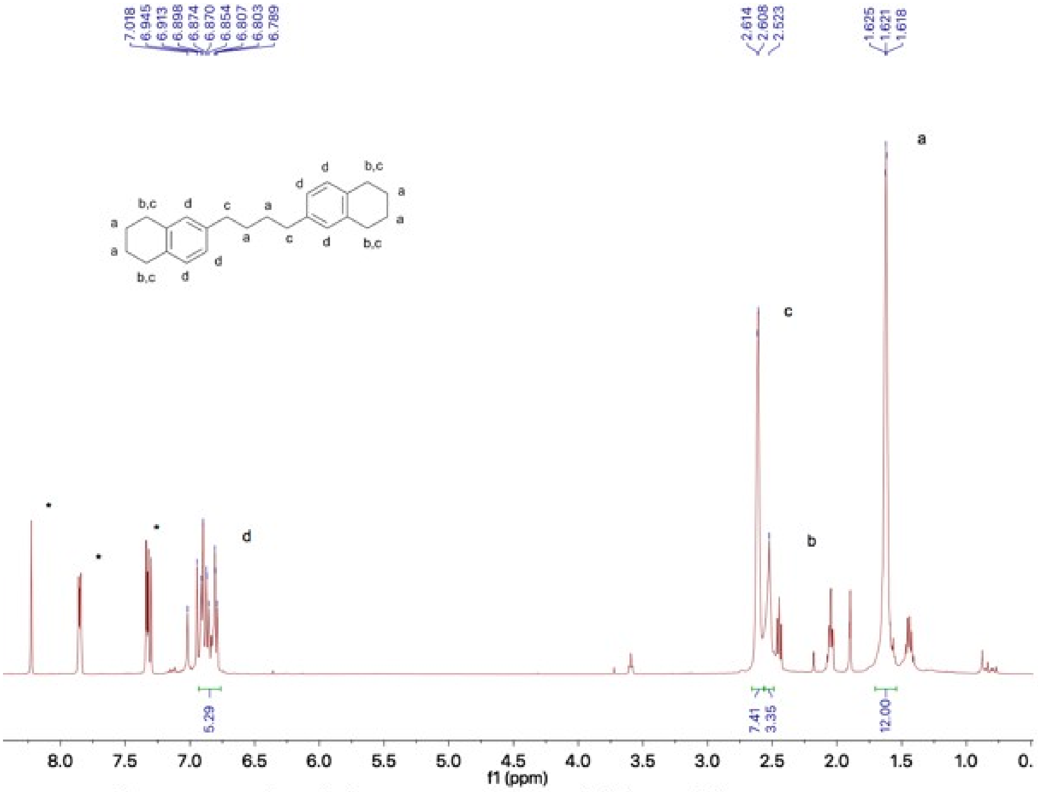
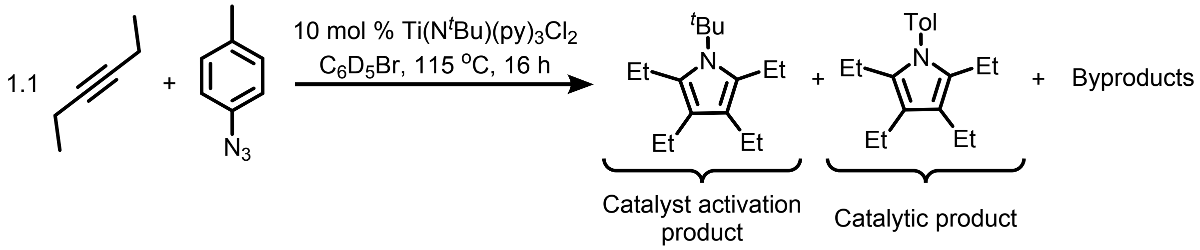


Figure S54: ^{1}H spectrum of 1,4-bis(5,6,7,8-tetrahydronaphthalen-2-yl)butane in C_6D_5Br.

NMR analysis of initial catalytic run with (*p*-tolyl)azide and 3-hexyne



(*p*-tolyl)azide (26 mg, 0.20 mmol, 1 equiv.) and Ti(N^{t}Bu)(py)$_3$Cl$_2$ (8 mg, 0.02 mmol, 10 mol %) were massed into a screw cap NMR tube. C_6D_5Br (0.5 mL) and 3-hexyne (25 µL, 0.22 mmol, 1.1 equiv.) were then added, and the tube was sealed and heated to 110˚C. The reaction mixture was monitored *in-situ* without workup to give the following products.

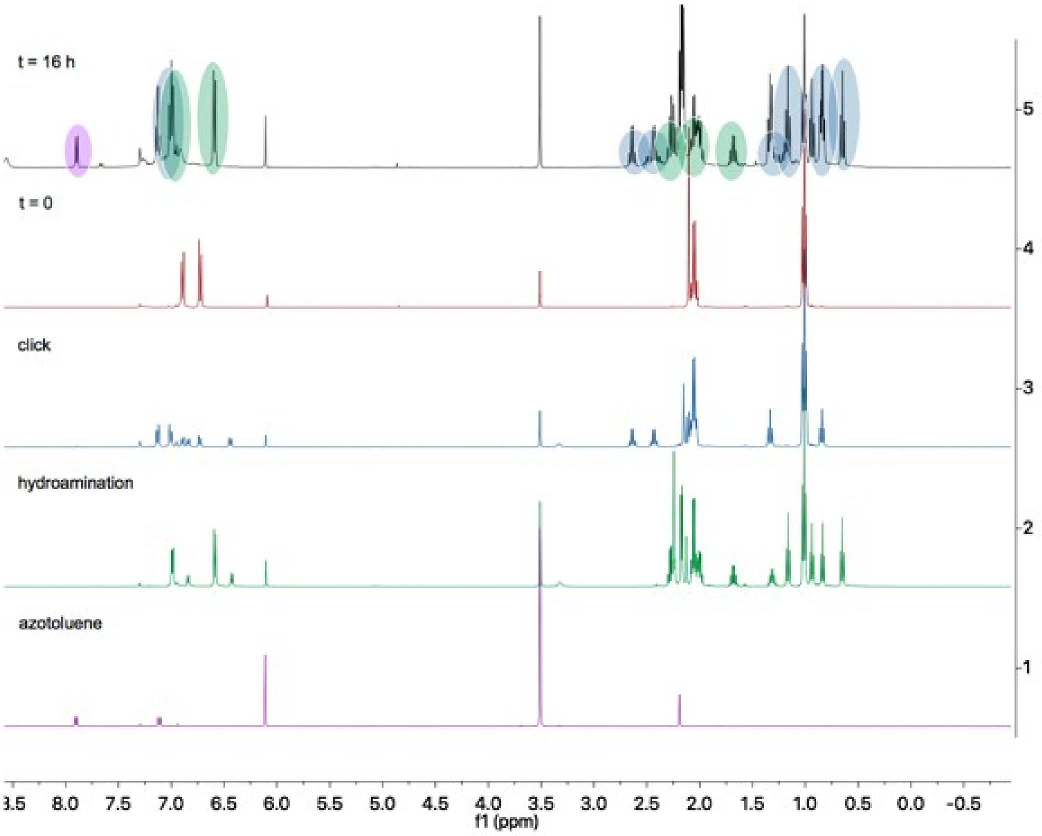


Figure S55: Stacked ^{1}H spectrum of (*p*-tolyl)azide reaction with 3-hexyne at t = 16 h (5), t = 0 h (4) click (3), hydroamination control (2) and authentic 4,4'-azotoluene (1) in C_6D_5Br.
* Byproducts in the catalytic mixture are highlighted by their respective colors.

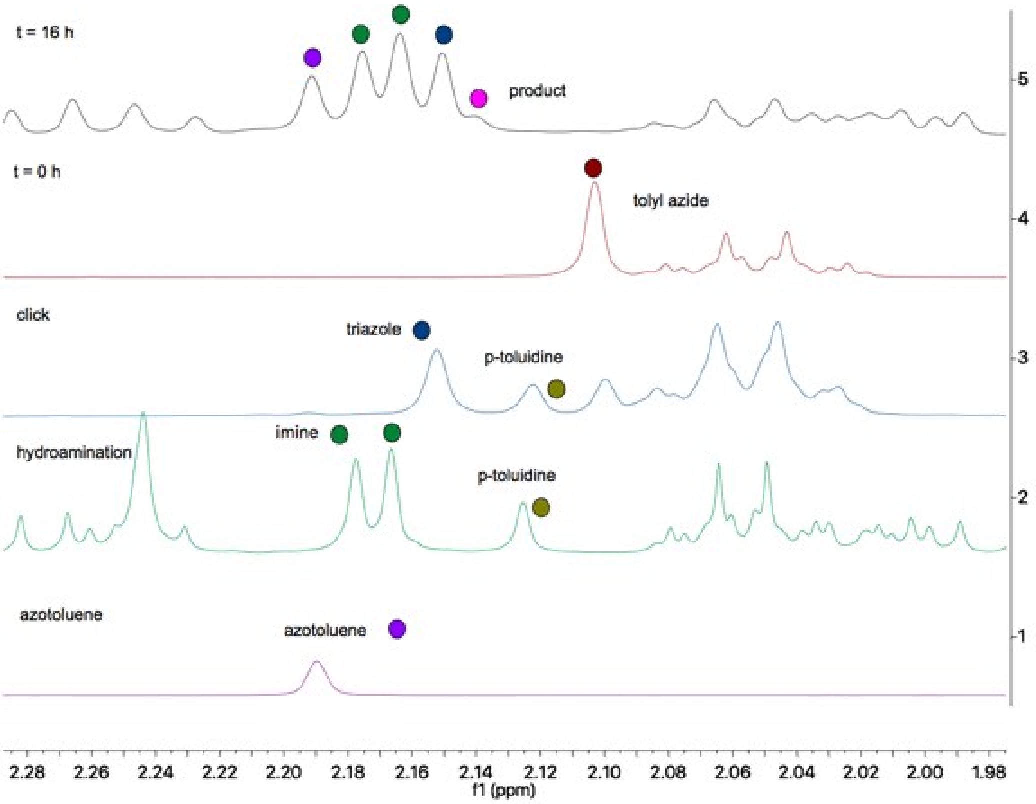


Figure S56: Zoom-in stacked ^{1}H spectrum of (*p*-tolyl)azide reaction with 3-hexyne at t = 16 h (5), t = 0 h (4) click (3), hydroamination control (2) and authentic 4,4'-azotoluene (1) in C_6D_5Br.
* Byproducts in the catalytic mixture are highlighted by their respective colors.

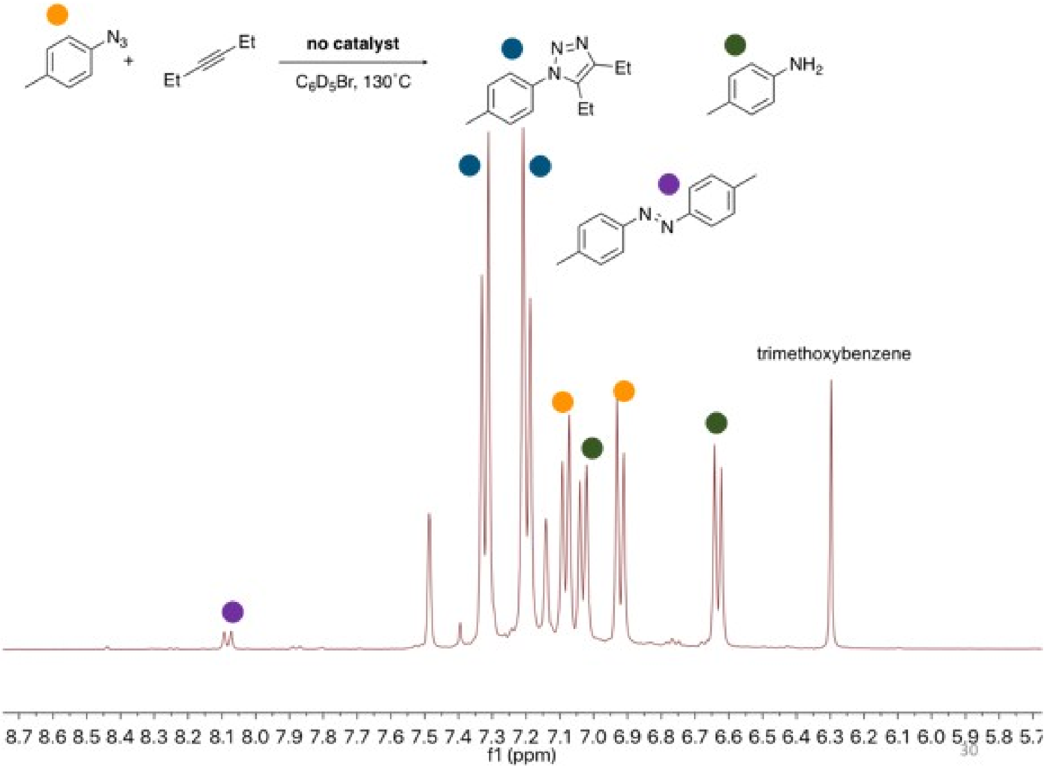


Figure S57: Zoom-in ^{1}H spectrum (aryl region) of (*p*-tolyl)azide reaction with 3-hexyne in the absence of catalyst. Byproducts are shown.

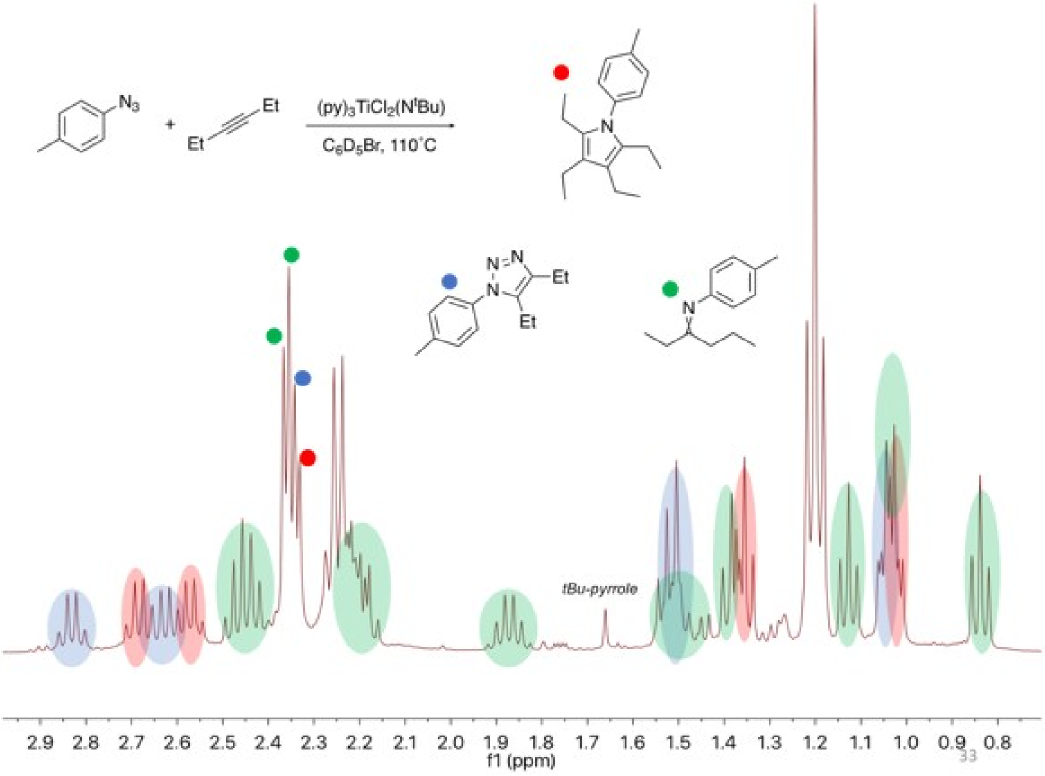
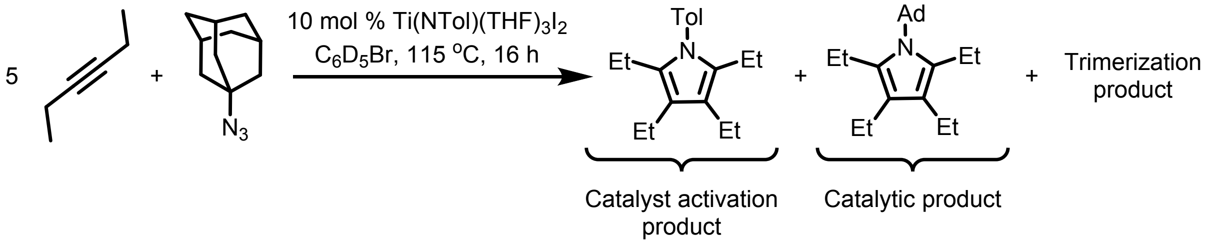


Figure S58: Zoom-in ^{1}H spectrum (alkyl region) of (*p*-tolyl)azide reaction with 3-hexyne in the absence of catalyst. Byproducts are shown.

NMR analysis of catalytic reactions with internal alkyne substrates (Table 1)

NMR analysis of 3-hexyne and 1-azidoadamantane reaction (Table 1, Entry 1)



A standard catalytic run with 2-butyne (79 µL, 1.0 mmol) and 0.5 mL of stock solution (internal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,3,4,5-tetraethyl-1-adamantyl-1*H*-pyrrole

^{1}H NMR (400 MHz, C_6D_5Br): δ 2.83 (q, $^3J_{HH}$ = 7.0 Hz, 4H, C3-CH_2), 2.39 (q, $^3J_{HH}$ = 7.0 Hz, 4H, C2-CH_2), 2.28 (d, $^3J_{HH}$ = 3 Hz, 6H, N-C-(CH_2)$_3$), 2.02 (s (br), 3H, Ad-methine), 1.59 (m, 6H, Ad), 1.15 (t, $^3J_{HH}$ = 7.0 Hz, 6H, C3-CH$_2$-CH_3)

Peaks at δ 2.39, 2.02, 1.59, and 1.15 overlap with activation product, 3-hexyne, 1-azidoadamantane, trimerization byproduct and 3-hexyne respectively.

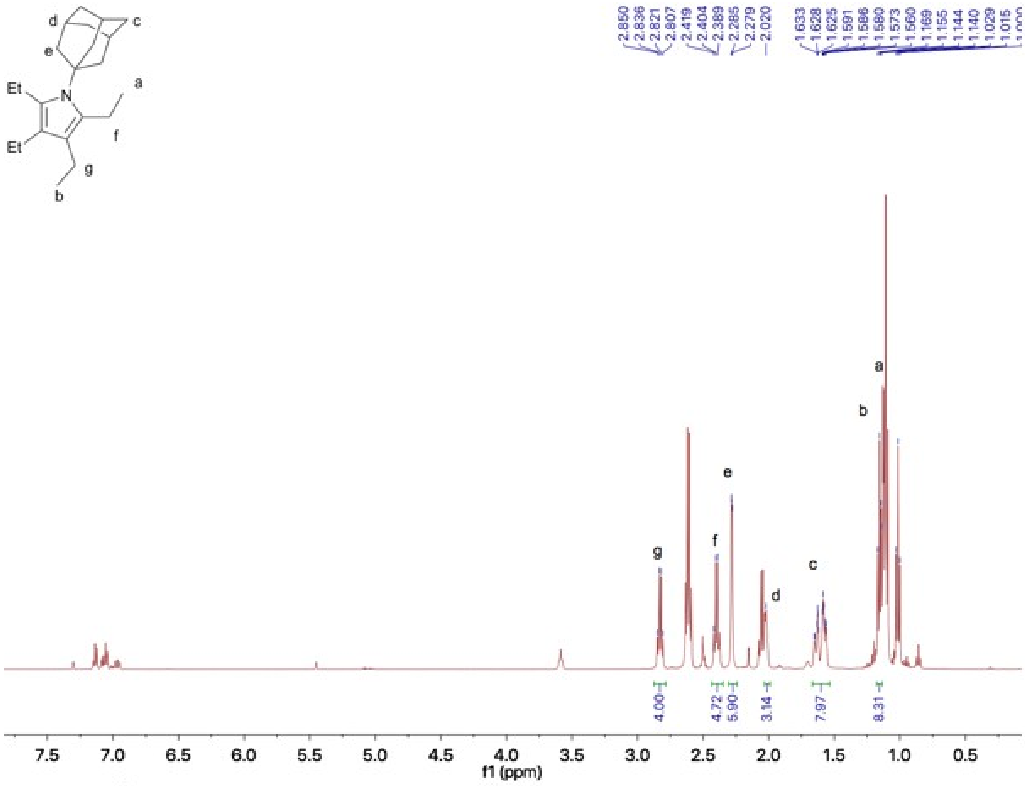


Figure S59: ^{1}H spectrum of 3-hexyne reaction with 1-azidoadamantane in C_6D_5Br.

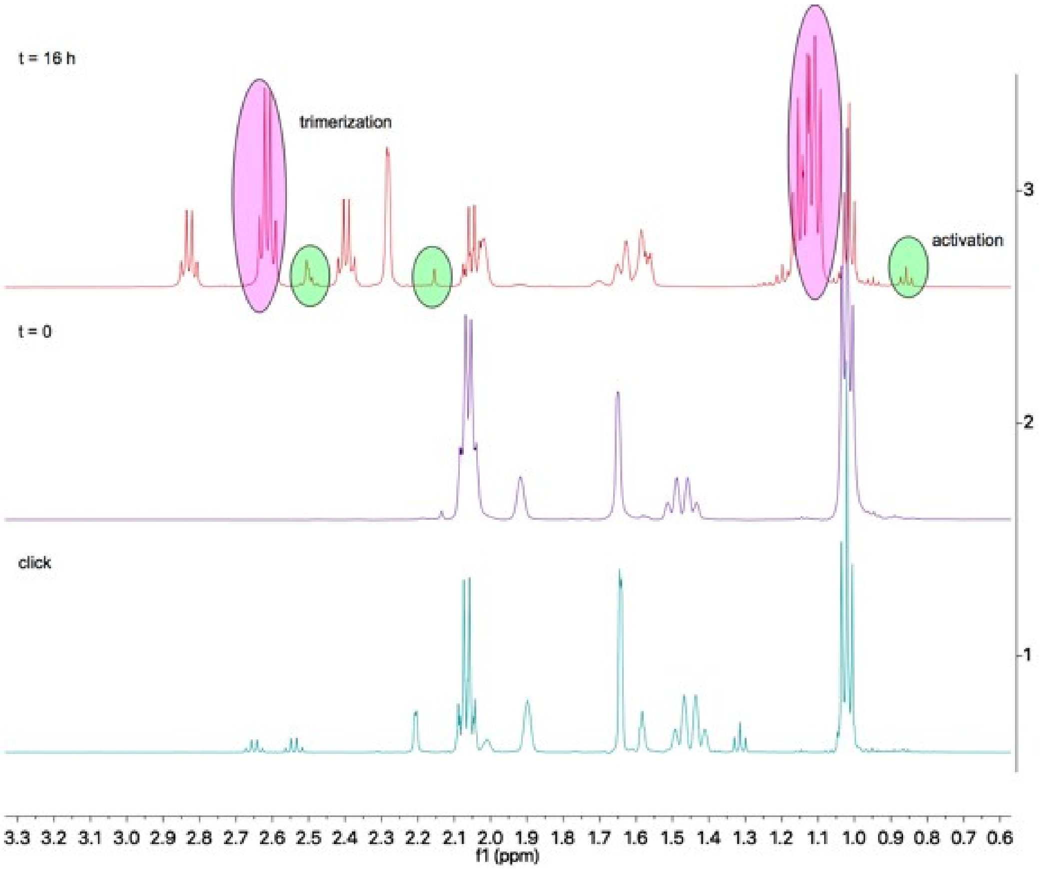
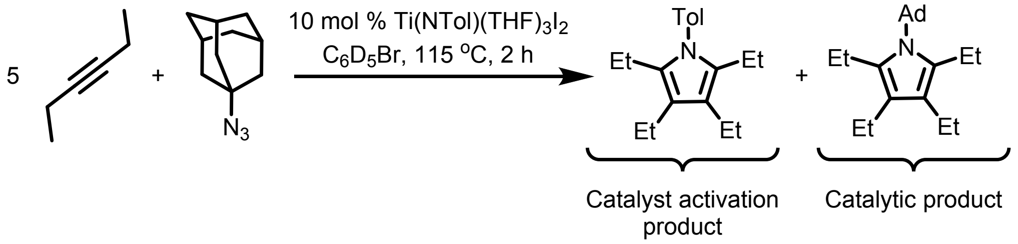


Figure S60: Zoom-in stacked ^{1}H spectrum of 3-hexyne reaction with 1-azidoadamantane t= 16 h (3), t = 0 h (2) and click reaction (1) in C_6D_5Br.

* Trimerization and activation pyrrole peaks are obtained from literature values[3] and highlighted in pink and green respectively.

NMR analysis of 1-azidoadamantane and 3-hexyne reaction (Table 1, Entry 2)



A standard catalytic run with [Ti] (6 mg, 0.01 mmol), 1-azidoadamantane (18 mg, 0.1 mmol, 1 equiv.) and 0.5 mL of stock solution (azide screen) was prepared and the reaction mixture was heated for 2 h. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

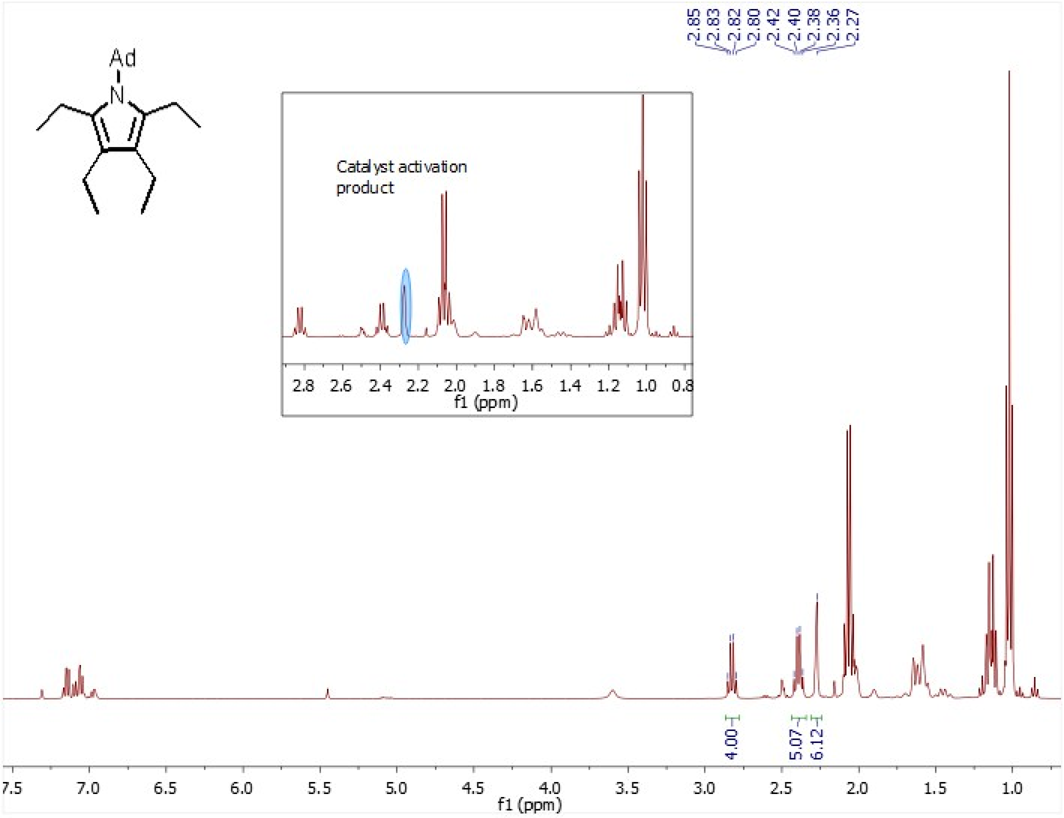


Figure S61: ^{1}H spectrum of 1-azidoadamantane reaction with 3-hexyne (t = 2 h) in C_6D_5Br.

Isolation of 2,3,4,5-tetraethyl-1-adamantyl-1*H*-pyrrole

To a 7 ml scintillation vial equipped with a stir-bar was added Ti(NTol)I_2(THF)$_3$ (35 mg, 0.056 mmol, 10 mol %), 1-azidoadamantane (101 mg, 0.56 mmol, 1 equiv.), 2.8 ml C_6H_5Br and 3-hexyne (0.32 ml, 231 mg, 2.82 mmol, 5 equiv.) in the following order in a N_2-filled glovebox. The vial was then sealed and heated at 115 °C for 2 h. After which, the reaction mixture was transferred into a 20 ml scintillation vial and dried under *vacuo* while heated to 50 °C for several hours to give a black oil. The oil was taken up in minimal petroleum ether and purified over a silica column using an eluent of 3 % ethyl acetate / petroleum ether. The desired product elutes after the activation product (2,3,4,5-tetraethyl-1-tolyl-1*H*-pyrrole).

Due to a contamination by silicon oil during the column purification, the desired product was taken up again in ~ 1 ml petroleum ether and loaded onto a small silica plug in a pipette. ~ 1 ml of petroleum ether was first used to remove the impurities before washing the rest of the plug with ~ 2ml ethyl acetate. A light orange eluent was collect and dried under *vacuo* to give the desired product as a pale orange solid with some grease impurities (40 mg, 23 % yield).

2,3,4,5-tetraethyl-1-adamantyl-1*H*-pyrrole

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84 (q, $^3J_{HH}$ = 7.3 Hz, 4H, *o*-N-pyr-CH_2CH$_3$), 2.40 – 2.34 (m, 10H, *m*-N-pyr-CH_2CH$_3$ and Ad-CH_2), 2.18 (br s, 3H, Ad-C*H*), 1.74 (q, $^3J_{HH}$ = 12.2 Hz, 6H, Ad-CH_2), 1.19 (t, $^3J_{HH}$ = 7.3 Hz, 6H, *o*-N-pyr-CH$_2$CH_3), 1.11 (t, $^3J_{HH}$ = 7.5 Hz, 6H, *o*-N-pyr-CH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ 130.5, 121.8, 60.5, 43.4, 36.5, 30.6, 21.7, 18.1, 17.5, 16.8

GC-HRMS (m/z): calcd. for $C_{22}H_{35}N$, 313.2770 ; found, 313.2756

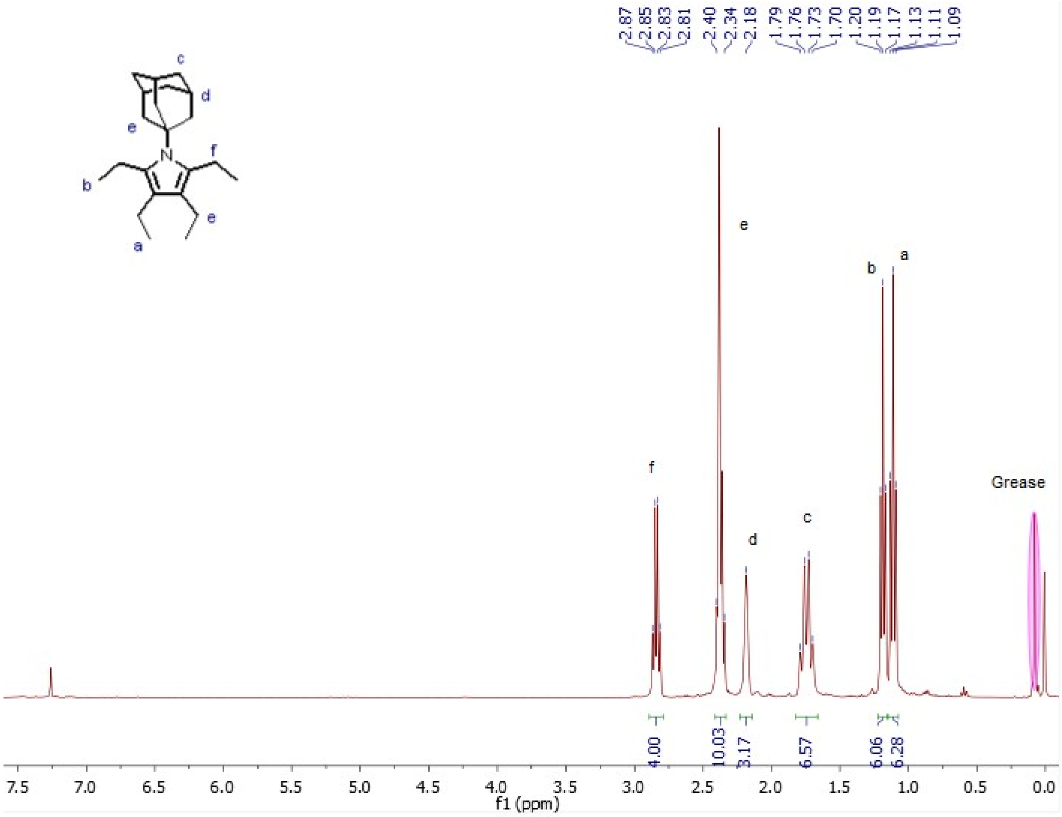


Figure S62: ^{1}H spectrum of 2,3,4,5-tetraethyl-1-adamantyl-1*H*-pyrrole in $CDCl_3$.

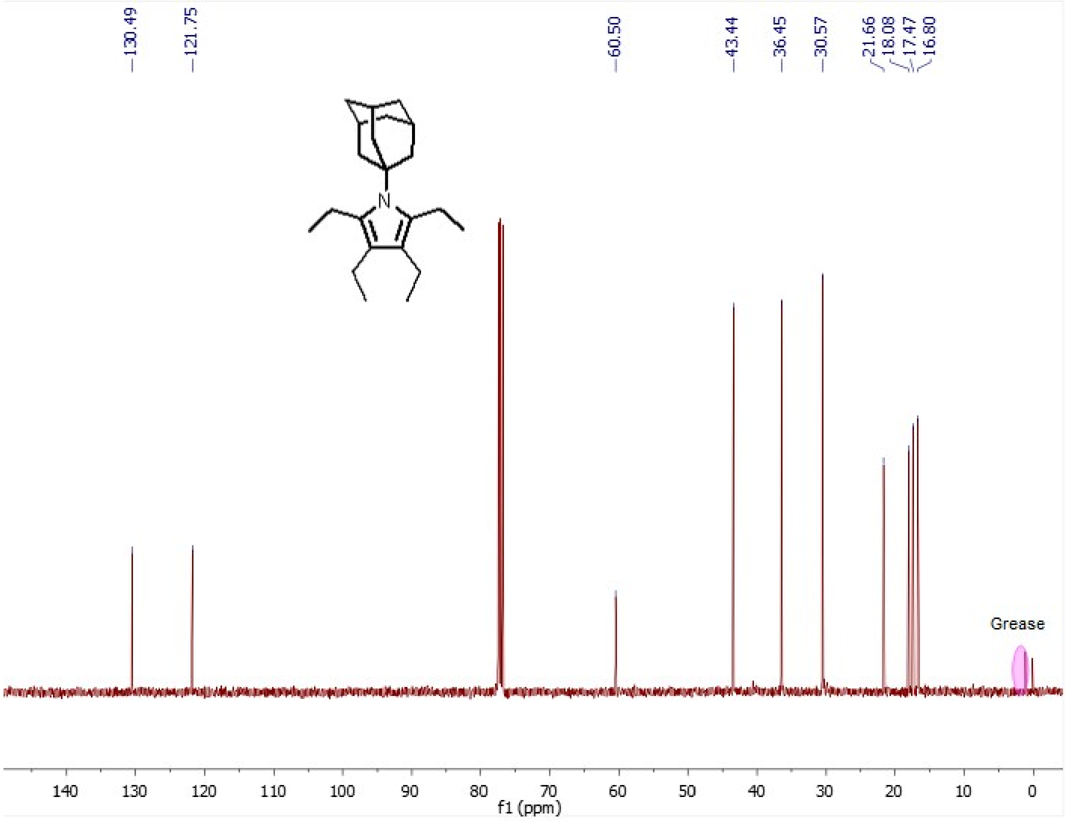
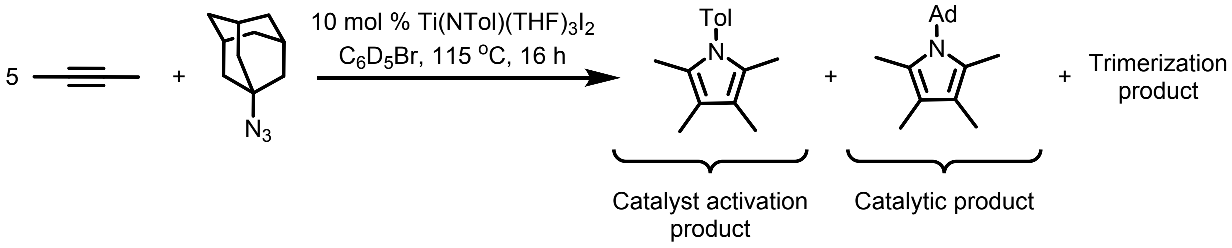


Figure S63: ^{13}C spectrum of 2,3,4,5-tetraethyl-1-adamantyl-1*H*-pyrrole in $CDCl_3$.

NMR analysis of 2-butyne and 1-azidoadamantane reaction (Table 1, Entry 3)



A standard catalytic run with 2-butyne (79 µL, 1.0 mmol) and 0.5 mL of stock solution (internal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,3,4,5-tetramethyl-1-(adamantyl)-1*H*-pyrrole (partial)

^{1}H NMR (400 MHz, C_6D_5Br): δ 2.35 (s, 6H, *o*-N-pyr-C*H$_3$*), 2.25 – 2.24 (m, 6H, Ad-C*H$_2$*), 1.92 (s, 6H, *m*-N-pyr-C*H$_3$*), 1.63 – 1.55 (m, 6H, Ad-C*H$_2$*)

Peaks at δ 1.63 – 1.55 overlap with the 2-butyne starting reagent and the Ad-C*H* peak cannot be positively identified from the reaction mixture.

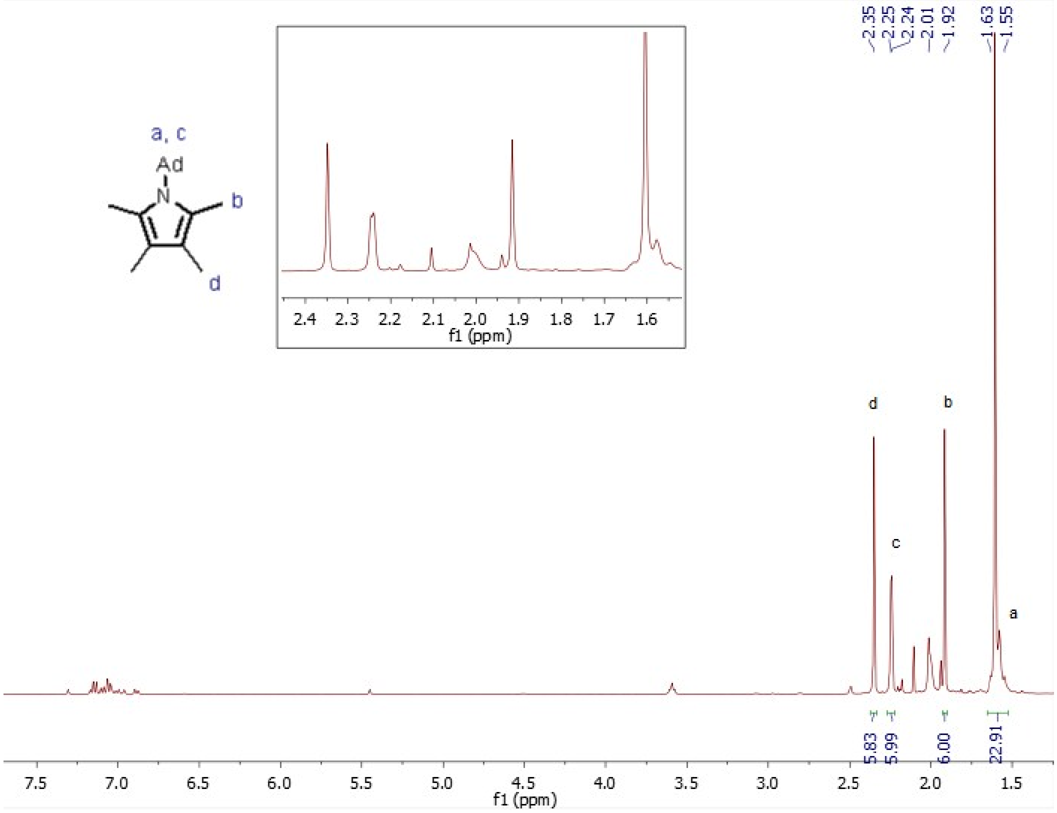


Figure S64: ^{1}H spectrum of 2-butyne reaction with 1-azidoadamantane in C_6D_5Br.

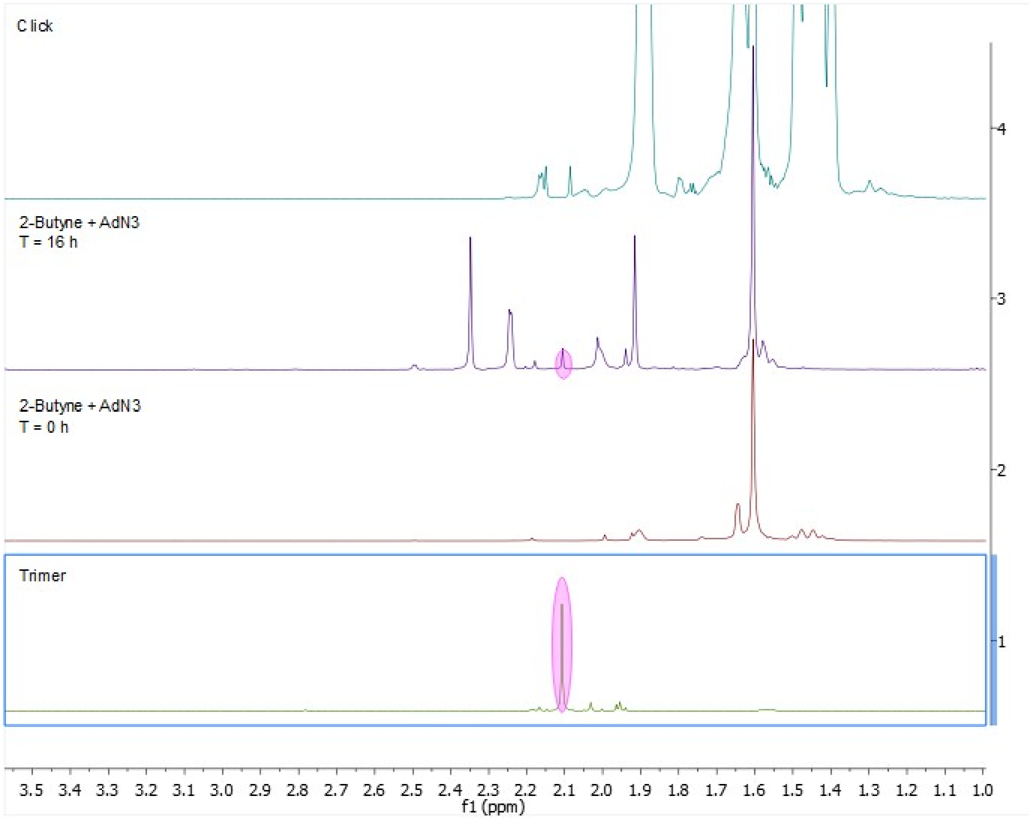
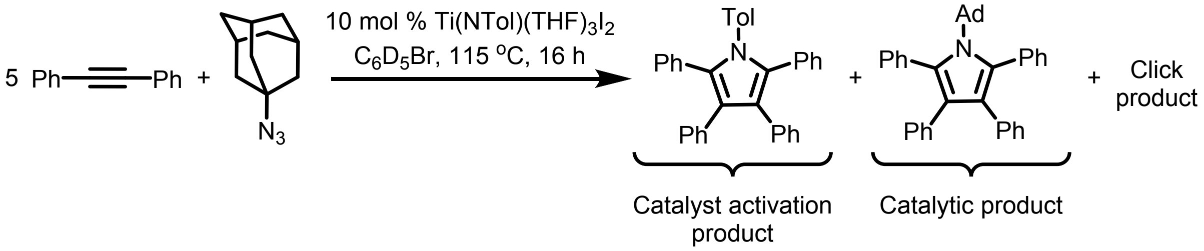


Figure S65: Zoom-in stacked ^{1}H spectrum of click reaction (4), 2-butyne reaction with 1-azidoadamantane t= 16 h (3), t = 0 h (2) and trimer reaction (1) in C_6D_5Br.

NMR analysis of diphenylacetylene and 1-azidoadamantane reaction (Table 1, Entry 4)



A standard catalytic run with diphenylacetylene (174 mg, 1.0 mmol) and 0.5 mL of stock solution (internal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,3,4,5-tetraphenyl-1-adamantyl-1*H*-pyrrole

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.50 *or* 2.20 (d, $^3J_{HH}$ = 3.0 Hz, 6H, N-C-(CH_2)$_3$)

The rest of the peaks are buried beneath starting materials. A definitive assignment of peaks from product could not be made. Maximum product yield based on generated peaks after reaction is <5%.

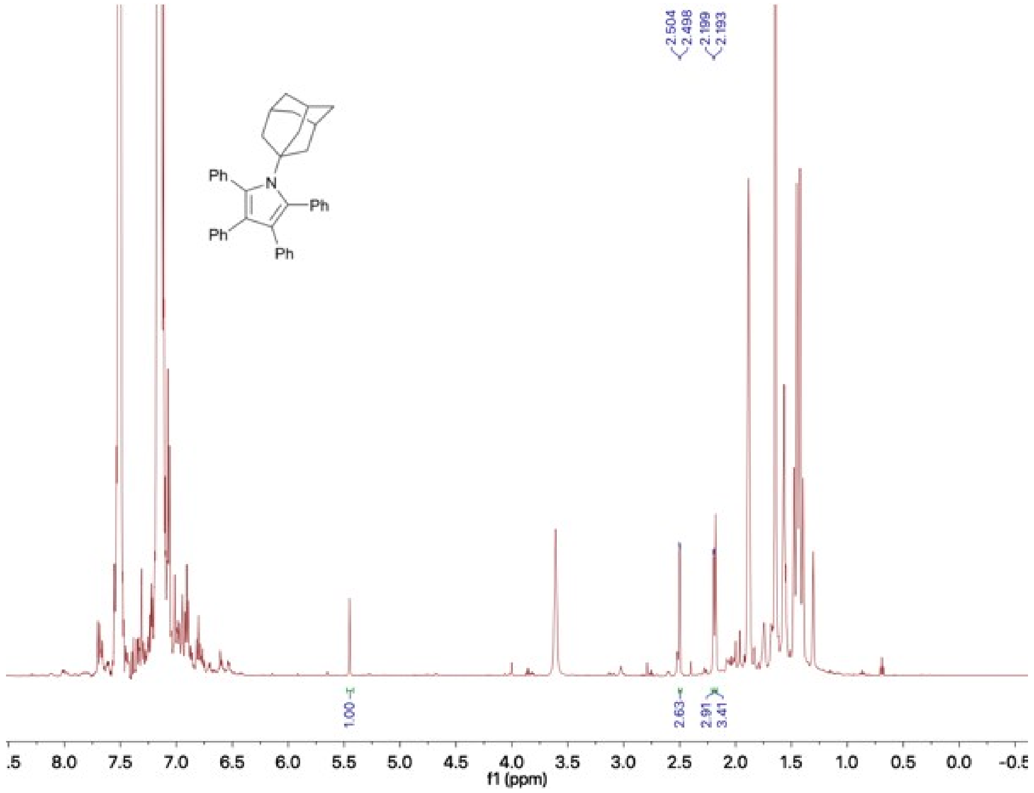


Figure S66: ^{1}H spectrum of diphenylacetylene reaction with 1-azidoadamantane in C_6D_5Br.

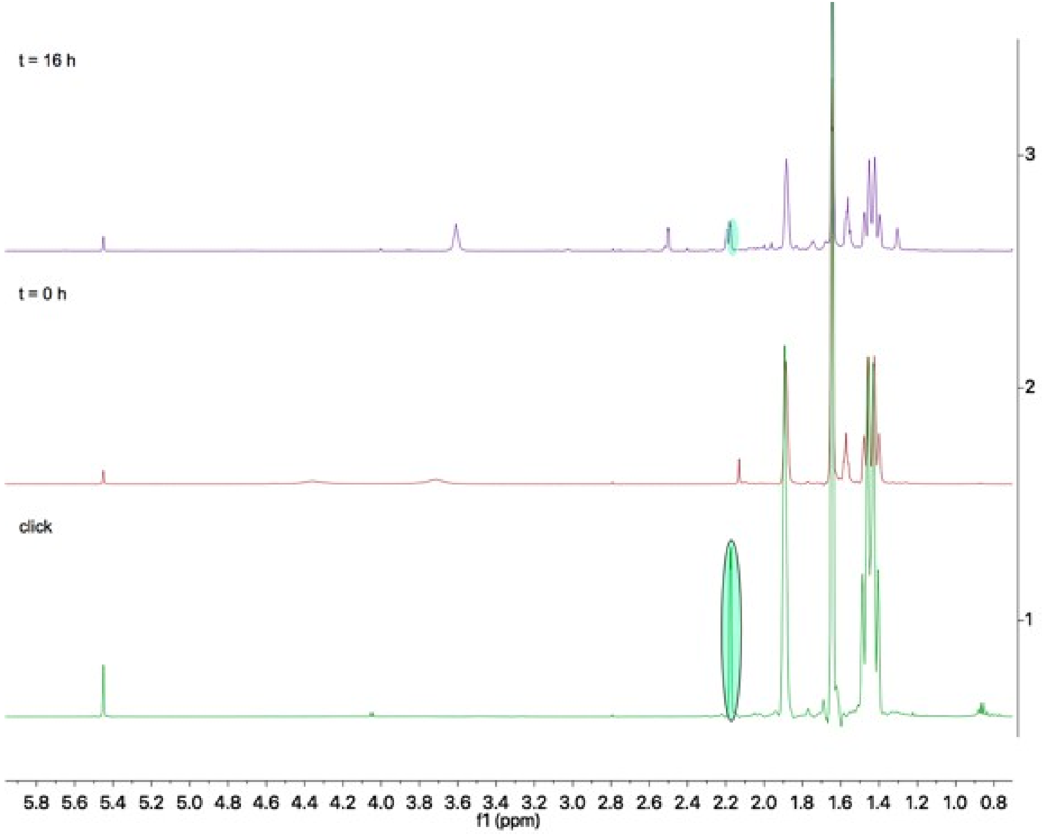
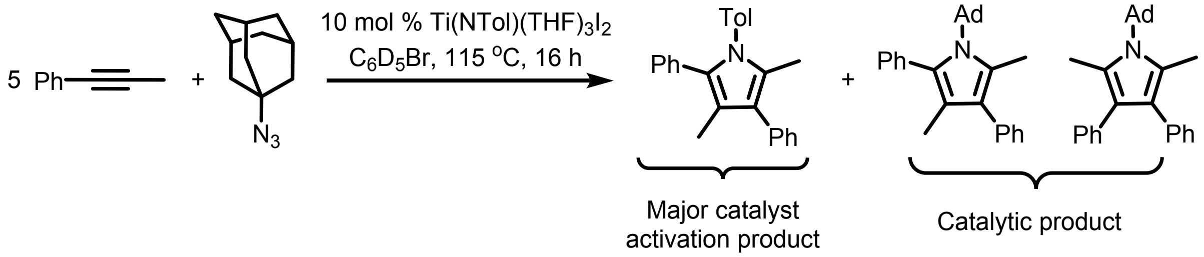


Figure S67: Stacked ^{1}H spectrum of diphenylacetylene reaction with 1-azidoadamantane t= 16 h (3), t = 0 h (2) and click reaction (1) in C_6D_5Br.

NMR analysis of 1-phenyl-1-propyne and 1-azidoadamantane reaction (Table 1, Entry 5)



A standard catalytic run with 1-phenyl-1-propyne (125 µL, 1.0 mmol, 5.0 equiv.) and 0.5 mL of stock solution (internal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,4-dimethyl-3,5-diphenyl-1-adamantyl-1*H*-pyrrole

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.55 (s, 3H, C(2)-CH_3), 2.17 (d, $^3J_{HH}$ = 3.0 Hz, 6H, N-C-(CH_2)$_3$), 1.77 (s, 3H, C(4)-CH_3)

This is a partial line list, aromatic peaks and remaining adamantyl peaks are buried beneath starting materials or could not be determined

2,5-dimethyl-3,4-diphenyl-1-adamantyl-1*H*-pyrrole

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.50 (s, 3H, C(2)-CH_3), 2.15 (d, $^3J_{HH}$ = 3.0 Hz, 6H, N-C-(CH_2)$_3$), 1.99 (s, 3H, C(5)-CH_3)

This is a partial line list; aromatic peaks and remaining adamantyl peaks are buried beneath starting materials or could not be determined. NMR evidence suggests a breach in symmetry for this molecule. This could occur through arene interactions with solvent or hindered rotation of the adamantyl group.

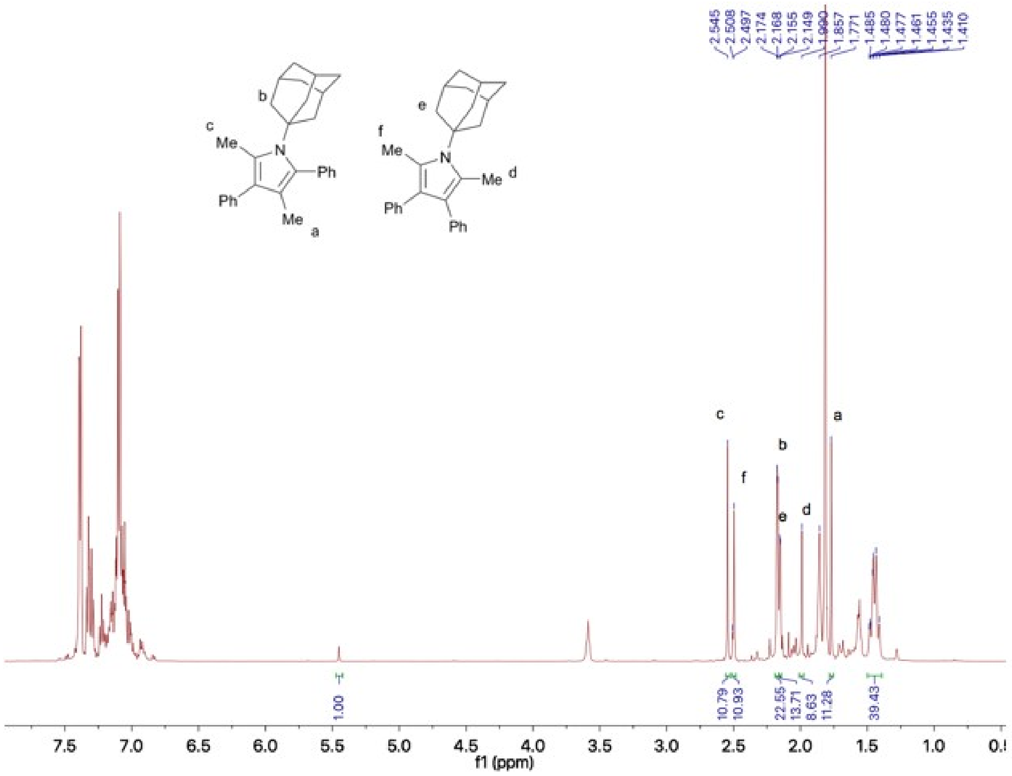


Figure S68: ^{1}H spectrum of 1-phenyl-1-propyne reaction with 1-azidoadamantane in C_6D_5Br.

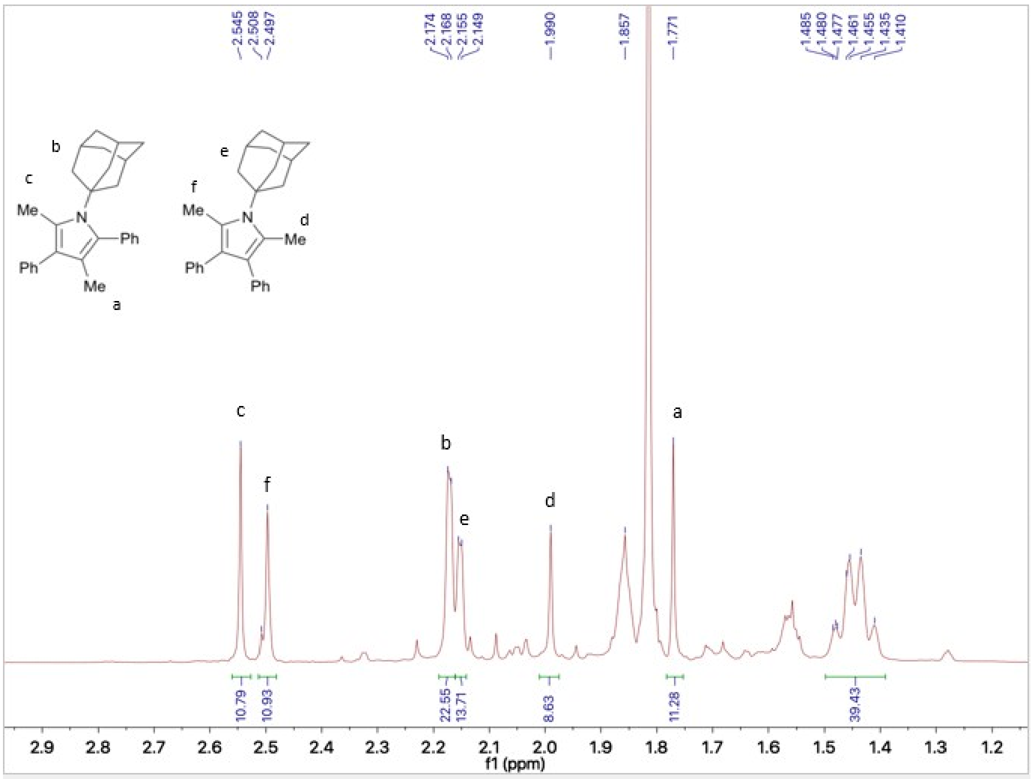


Figure S69: Zoom-in ^{1}H spectrum of 1-phenyl-1-propyne reaction with 1-azidoadamantane in C_6D_5Br.

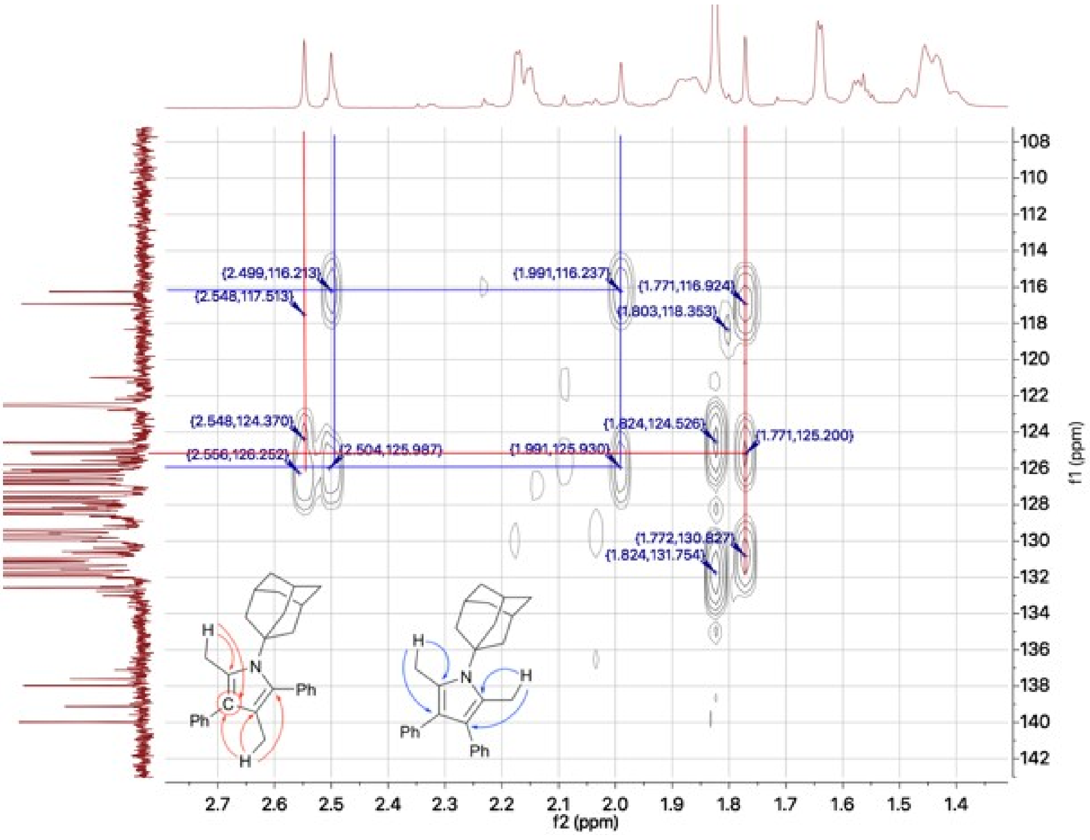


Figure S70: ^{1}H-^{13}C spectrum of 1-phenyl-1-propyne reaction with 1-azidoadamantane in C_6D_5Br.

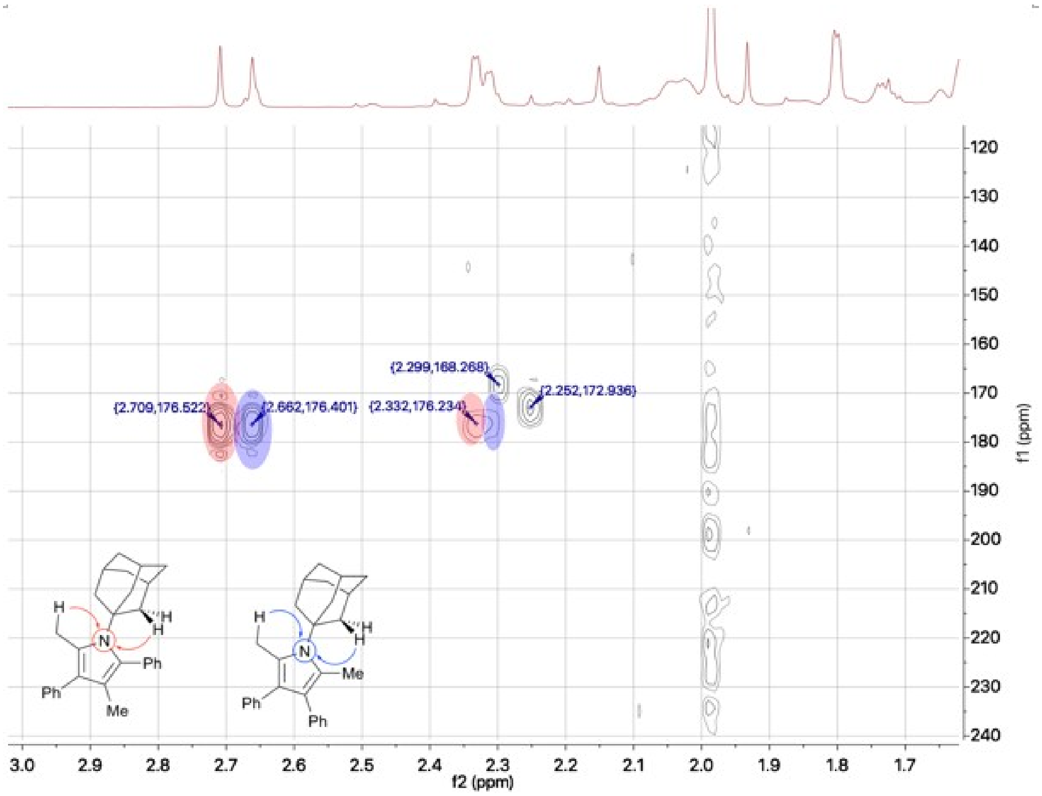


Figure S71: ^{1}H-^{15}N spectrum of 1-phenyl-1-propyne reaction with 1-azidoadamantane in C_6D_5Br.

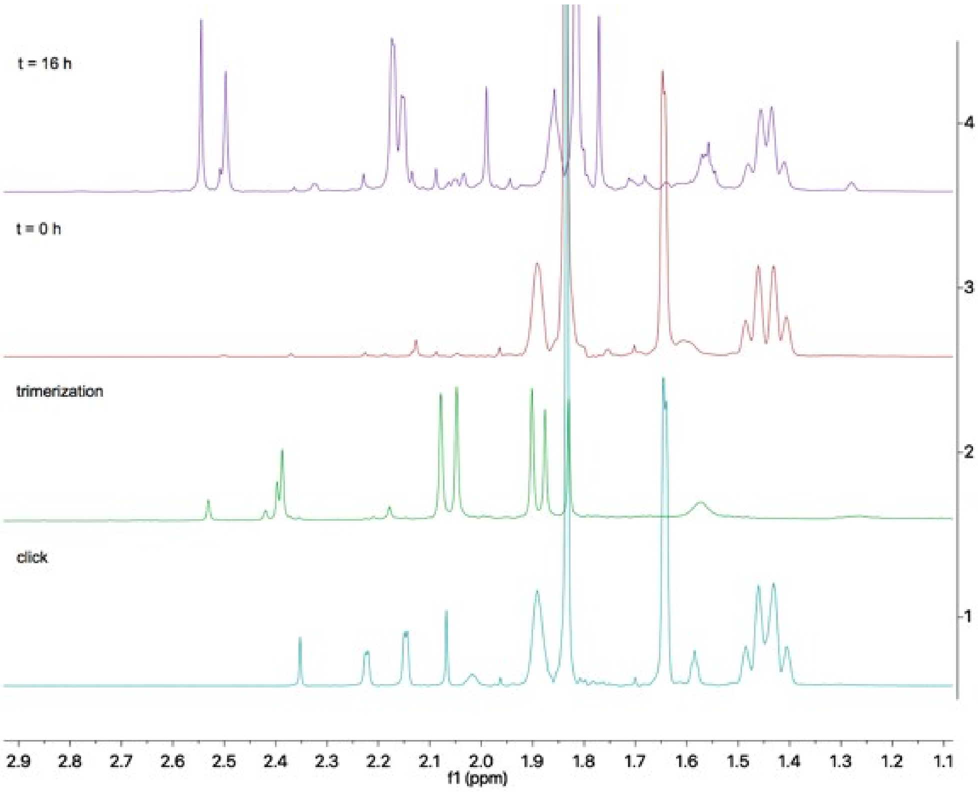


Figure S72: Zoom-in stacked ^{1}H spectrum of 1-phenyl-1-propyne reaction with 1-azidoadamantane t= 16 h (4), t = 0 h (3), trimerization (2) and click reaction (1) in C_6D_5Br.

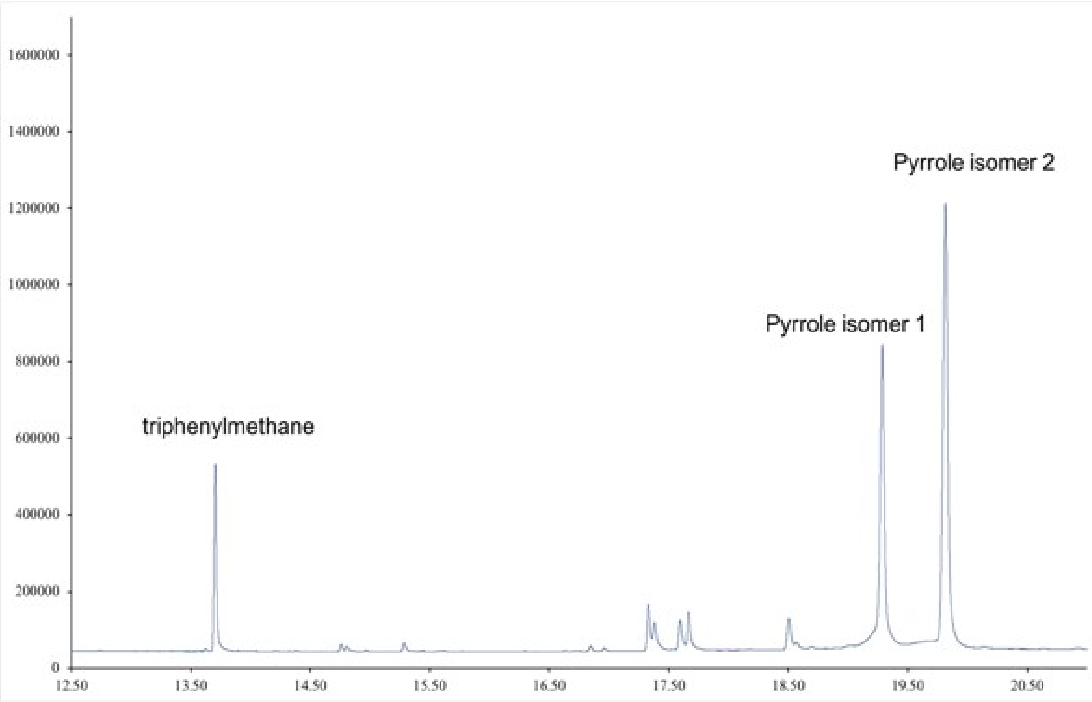
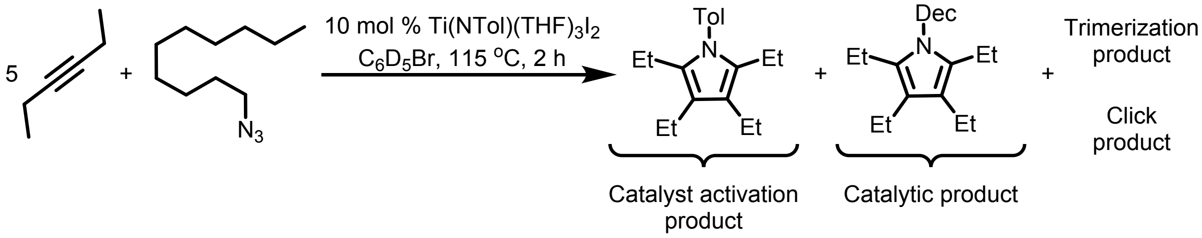


Figure S73: GC/FID trace of 1-phenyl-1-propyne reaction with 1-azidoadamantane in C_6D_5Br.

NMR analysis of 1-azidodecane and 3-hexyne reaction (Table 1, Entry 9)



A standard catalytic run with [Ti] (6 mg, 0.01 mmol), 1-azidodecane (19 mg, 0.1 mmol, 1 equiv.) and 0.5 mL of stock solution (azide screen) was prepared and the reaction mixture was heated for 2 h. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,3,4,5-tetraethyl-1-decyl-1*H*-pyrrole (partial)
^{1}H NMR (400 MHz, C_6D_5Br): δ 3.62 – 3.58 (m, 2H, $H_3C(CH_2)_8$-CH_2-N), 2.51 (q, $^3J_{HH}$ = 7.5 Hz, 4H, *o*-CH_2-CH_3), 2.43 (q, $^3J_{HH}$ = 7.5 Hz, 4H, *m*-CH_2-CH_3), 0.88 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H_3C-$(CH_2)_9$N)

The peak at δ 3.62 – 3.58 and 0.88 overlaps with THF from the catalyst and other alkyl impurities respectively. This is a partial NMR line list, the remaining peaks cannot be positively identified.

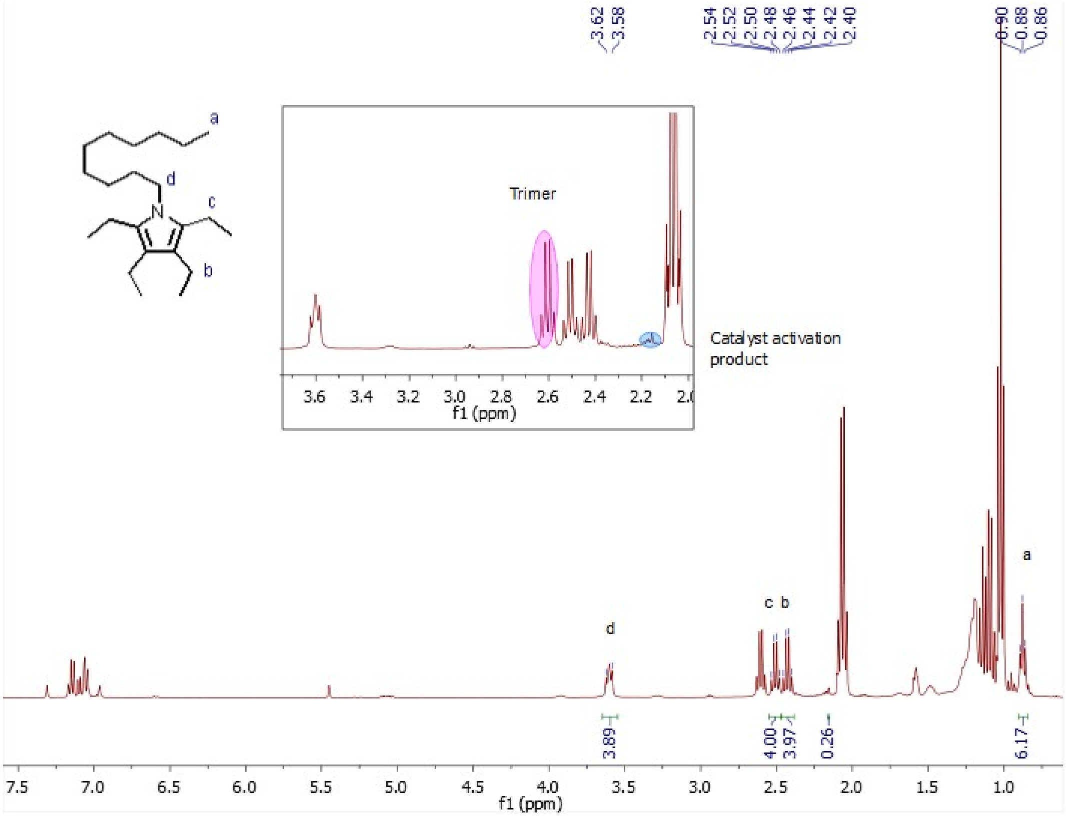


Figure S74: ^{1}H spectrum of 1-azidodecane reaction with 3-hexyne in C_6D_5Br.

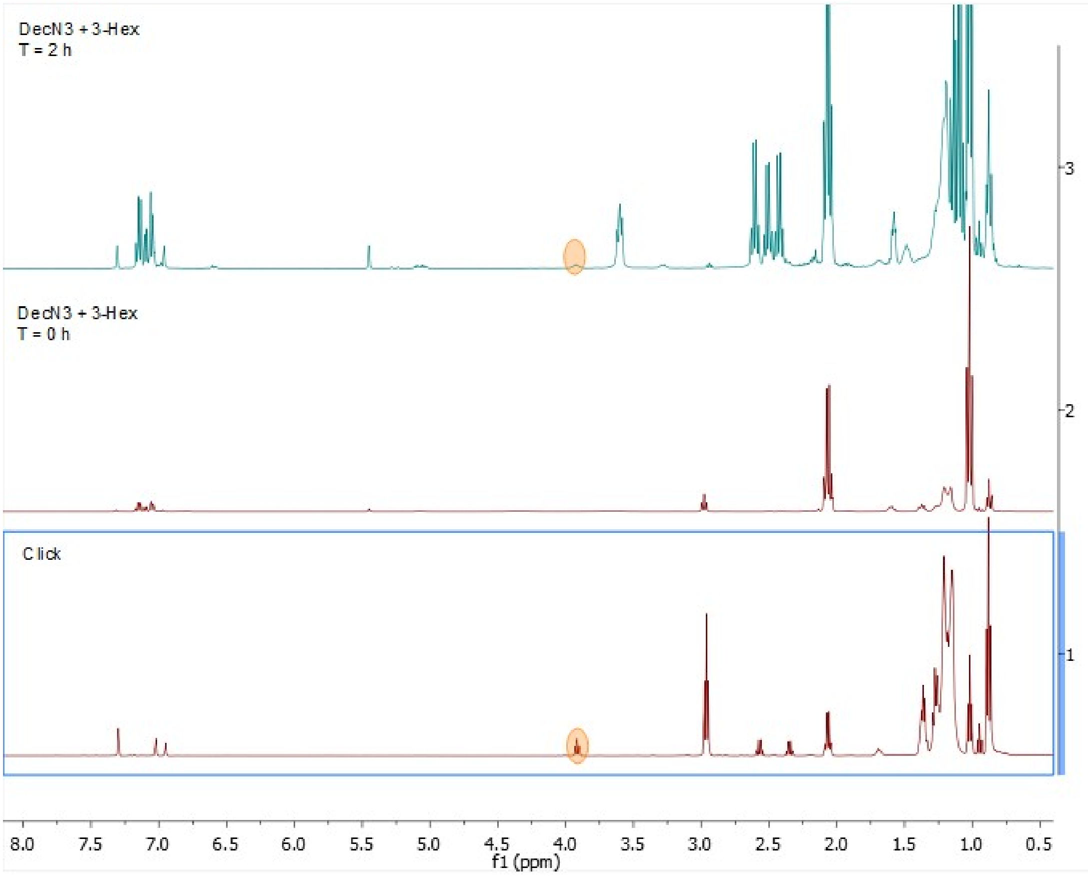


Figure S75: Stacked ^{1}H spectrum of 1-azidodecane reaction with 3-hexyne t = 2 h (3), t = 0 h (2) and click reaction (1) in C_6D_5Br.

Isolation of 2,3,4,5-tetraethyl-1-decyl-1*H*-pyrrole

To a 7 ml scintillation vial equipped with a stir-bar was added Ti(NTol)I$_2$(THF)$_3$ (35 mg, 0.056 mmol, 10 mol %), 1-azidodecane (103 mg, 0.57 mmol, 1 equiv.), 2.5 ml C_6H_5Br and 3-Hexyne (0.32 ml, 231 mg, 2.82 mmol, 5 equiv.) in the following order in a N_2-filled glovebox. The vial was then sealed and heated at 115 °C for 2 h. After which, the reaction mixture was transferred into a 20 ml scintillation vial and dried under *vacuo* while heated to 50 °C for several hours to give a black oil. The oil was taken up in minimal dichlormethane and purified over a silica column using an eluent of 3 % ethyl acetate / petroleum ether. The desired product elutes before the activation product (2,3,4,5-tetraethyl-1-tolyl-1*H*-pyrrole).

Two fractions were collected that contained the desired product with small amount of trimerisation and activation product present. (83 mg, 46 % corrected yield).

2,3,4,5-tetraethyl-1-decyl-1*H*-pyrrole

^{1}H NMR (400 MHz, CDCl$_3$): δ 3.69 (m, 2H, N-C*H$_2$*-(CH$_2$)$_8$CH$_3$), 2.54 (q, $^3J_{HH}$ = 7.5 Hz, 4H, *o*-N-pyr-C*H$_2$*CH$_3$), 2.40 (q, $^3J_{HH}$ = 7.5 Hz, 4H, *m*-N-pyr-C*H$_2$*CH$_3$), 1.65 – 1.60 (m, 2H, NCH$_2$-C*H$_2$*-(CH$_2$)$_7$CH$_3$), 1.33 – 1.27 (m, 14H, N(CH$_2$)$_2$-(C*H$_2$*)$_7$-CH$_3$), 1.15 (t, $^3J_{HH}$ = 7.5 Hz, 6H, *o*-N-pyr-CH$_2$C*H$_3$*), 1.11 (t, $^3J_{HH}$ = 7.5 Hz, 6H, *o*-N-pyr-CH$_2$C*H$_3$*), 0.89 (t, $^3J_{HH}$ = 7.5 Hz, 3H, N(C*H$_2$*)$_9$-C*H$_3$*)

^{13}C NMR (101 MHz, CDCl$_3$): δ 128.1, 119.0, 43.7, 32.5, 32.0, 29.7, 29.5, 27.4, 22.8, 18.0, 17.9, 17.3, 16.1, 14.3.

GC-HRMS (m/z): calcd. for $C_{22}H_{35}N$, 319.3239 ; found, 319.3247

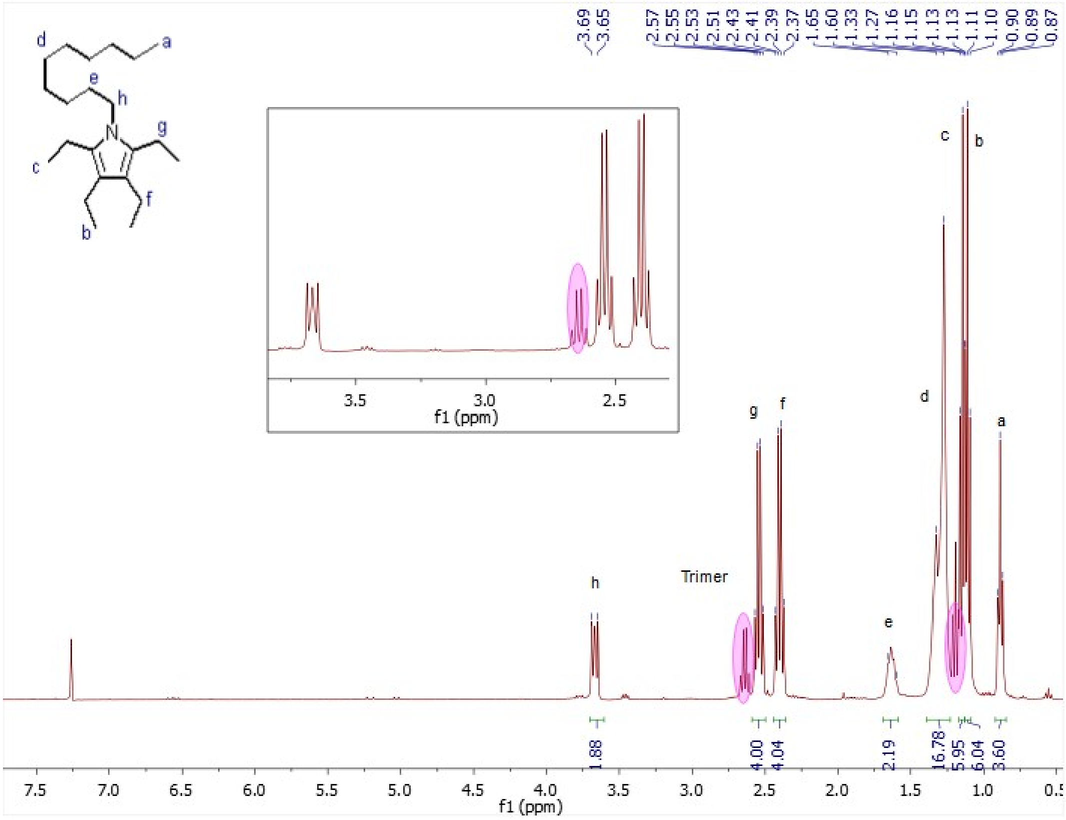


Figure S76: ^{1}H spectrum of 2,3,4,5-tetraethyl-1-decyl-1*H*-pyrrole in CDCl$_3$.

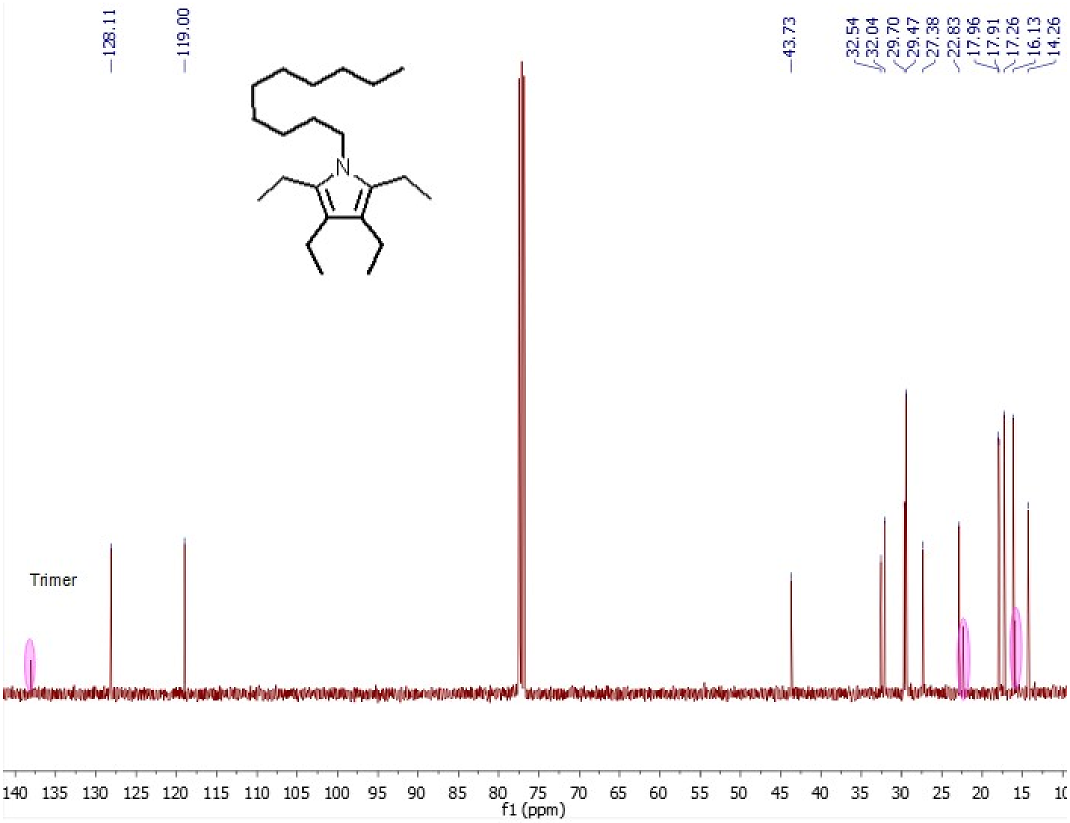
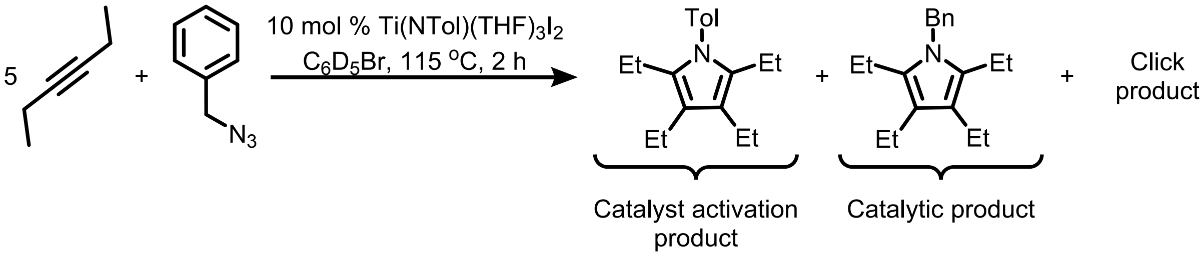


Figure S77: ^{13}C spectrum of 2,3,4,5-tetraethyl-1-decyl-1*H*-pyrrole in CDCl$_3$.

NMR analysis of benzylazide and 3-hexyne reaction (Table 1, Entry 10)



A standard catalytic run with [Ti] (7 mg, 0.01 mmol), benzylazide (13 mg, 0.1 mmol, 1 equiv.) and 0.5 mL of stock solution (azide screen) was prepared and the reaction mixture was heated for 2 h. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,3,4,5-tetraethyl-1-benzyl-1*H*-pyrrole

^{1}H NMR (500 MHz, C$_6$D$_5$Br): δ 6.76 (d, $^3J_{HH}$ = 7.0 Hz, 2H, *o*-Ar-*H*), 4.88 (s, 2H, Ar-C*H$_2$*), 2.44 (q, $^3J_{HH}$ = 7.5 Hz, 4H, pyr-C*H$_2$*), 2.36 (q, $^3J_{HH}$ = 7.5 Hz, 4H, pyr-C*H$_2$*) 1.15 (t, $^3J_{HH}$ = 7.5 Hz, 6H, pyr-CH$_2$-C*H$_3$*), 0.91 (t, $^3J_{HH}$ = 7.5 Hz, 6H, pyr-CH$_2$-C*H$_3$*).
Remaining aromatic peaks are hidden behind the internal standard or starting material.

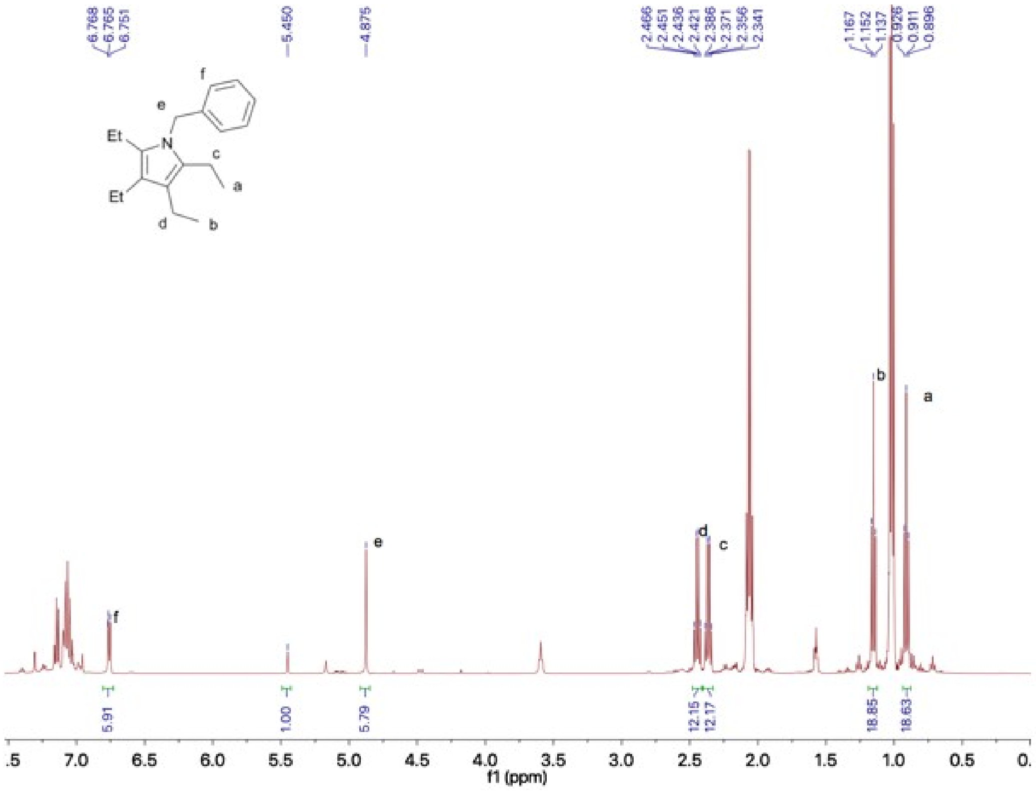


Figure S78: ^{1}H spectrum of benzylazide reaction with 3-hexyne in C_6D_5Br.

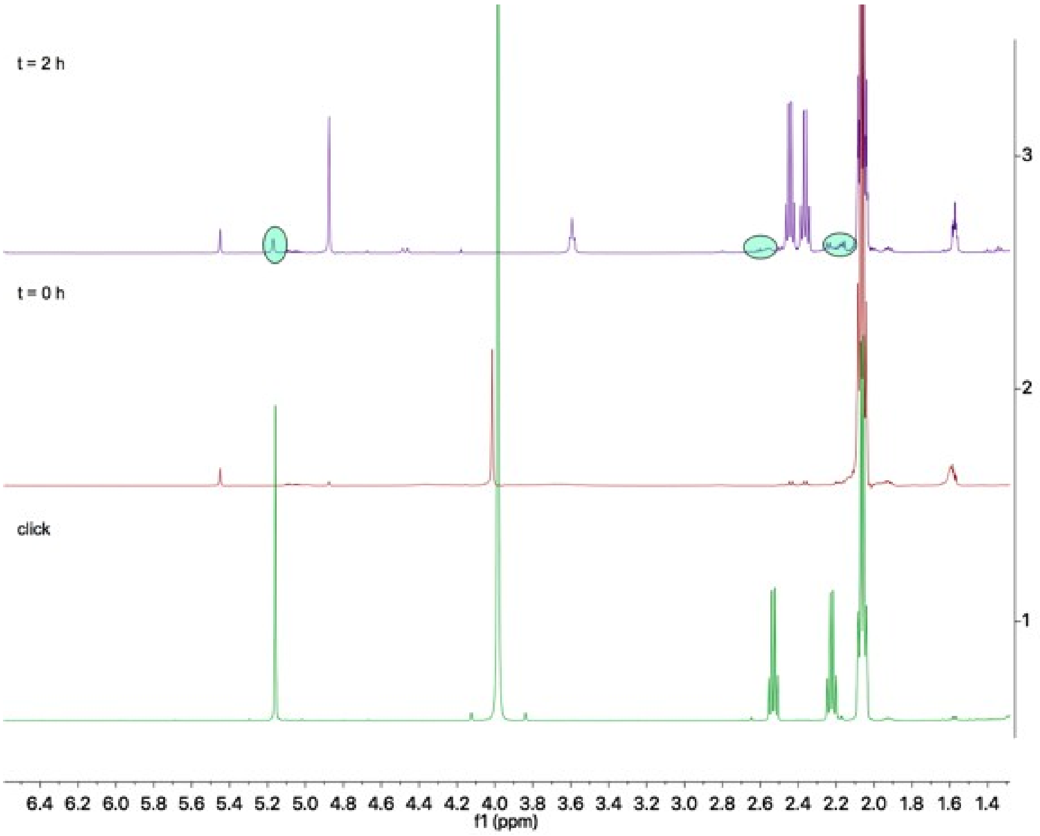


Figure S79: Zoom-in stacked ^{1}H spectrum of benzylazide reaction with 3-hexyne t = 2 h (3), t = 0 h (2), and click reaction (1) in C_6D_5Br.

* Click products highlighted in green

Isolation of 2,3,4,5-tetraethyl-1-benzyl-1*H*-pyrrole

To a 20 mL vial equipped with a magnetic stir bar, Ti(NTol)(THF)$_3$I$_2$ (37 mg, 0.059 mmol, 10 mol %) and benzyl azide (79 mg, 0.59 mmol, 1 equiv.) were dissolved in 2 mL of bromobenzene. To this solution was added 3-hexyne (350 µL, 3.1 mmol, 5.2 equiv.) and the vial was sealed with a teflon cap, removed from the glovebox, and heated at 115˚C for 2 hours. The vial was allowed to cool to 40˚C, at which point the cap was removed under air and the volatiles were removed *in vacuo*. This residue was purified by column chromatography (SiO$_2$, Hexanes:EtOAc 19:1 R$_f$ = 0.5) to give the title compound (76 mg, 59% yield).

2,3,4,5-tetraethyl-1-benzyl-1*H*-pyrrole

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *m*-Ar-*H*), 7.19 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-Ar-*H*), 6.84 (d, $^3J_{HH}$ = 6.8 Hz, 2H, *o*-Ar-*H*), 5.01 (s, 2H, Ar-C*H$_2$*), 2.44 (q, $^3J_{HH}$ = 7.6 Hz, 4H, pyr-C*H$_2$*-CH$_3$), 2.43 (q, $^3J_{HH}$ = 7.6 Hz, 4H, pyr-C*H$_2$*-CH$_3$), 1.13 (t, $^3J_{HH}$ = 7.4 Hz, 3H, pyr-CH$_2$-C*H$_3$*), 0.97 (t, $^3J_{HH}$ = 7.6 Hz, 3H, pyr-CH$_2$-C*H$_3$*).

^{13}C NMR (101 MHz, CDCl$_3$): δ 140.2, 128.8, 128.6, 126.8, 125.8, 119.6, 46.6, 18.0, 17.9, 17.4, 16.0.

GC-HRMS (m/z): calcd. for C$_{19}$H$_{27}$N, 269.2143 ; found, 269.2148

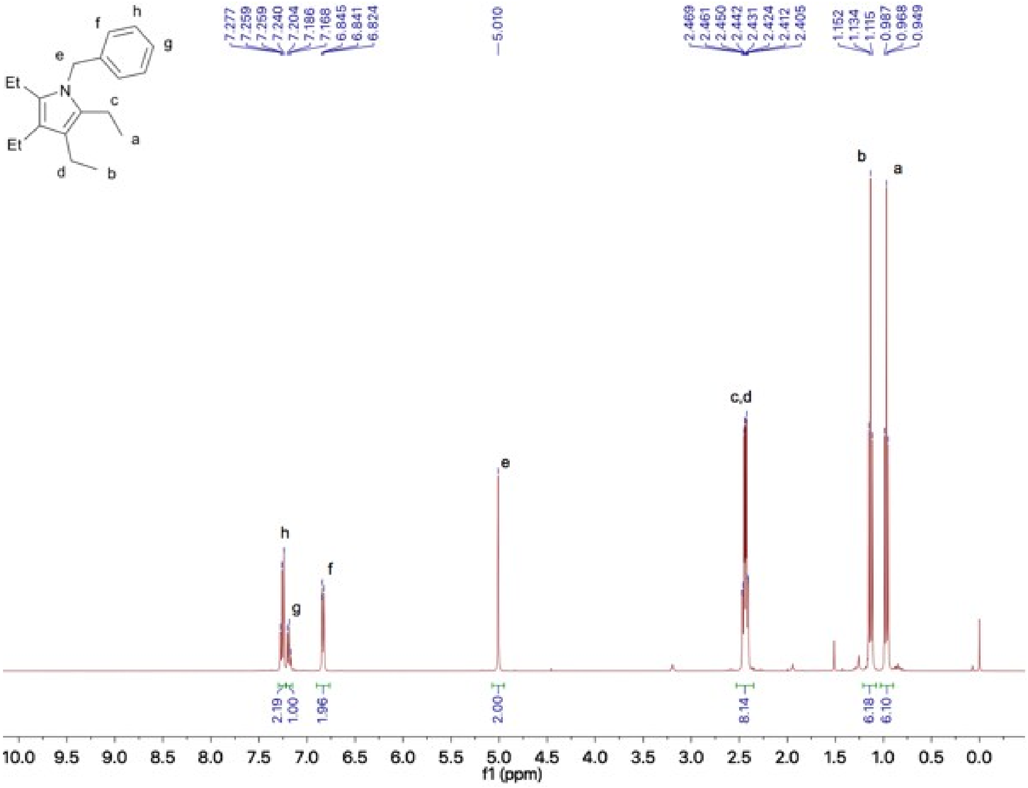


Figure S80: ^{1}H spectrum of 2,3,4,5-tetraethyl-1-benzyl-1*H*-pyrrole in CDCl$_3$.

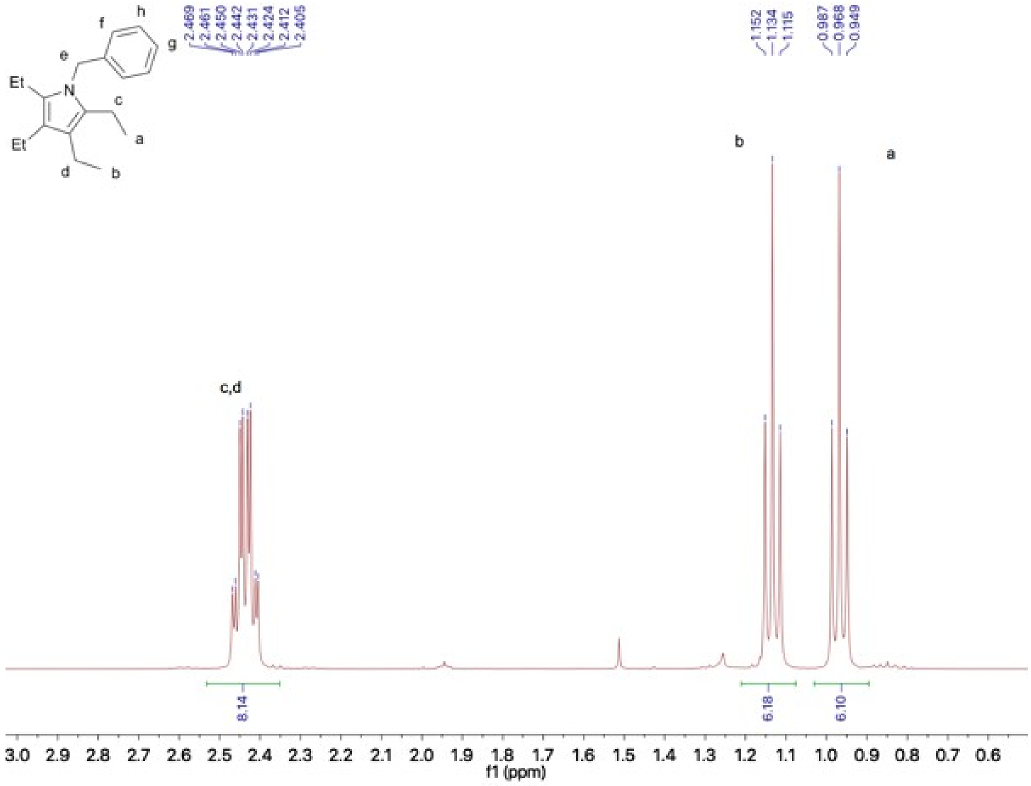


Figure S81: Zoom-in ^{1}H spectrum of 2,3,4,5-tetraethyl-1-benzyl-1*H*-pyrrole in $CDCl_3$.

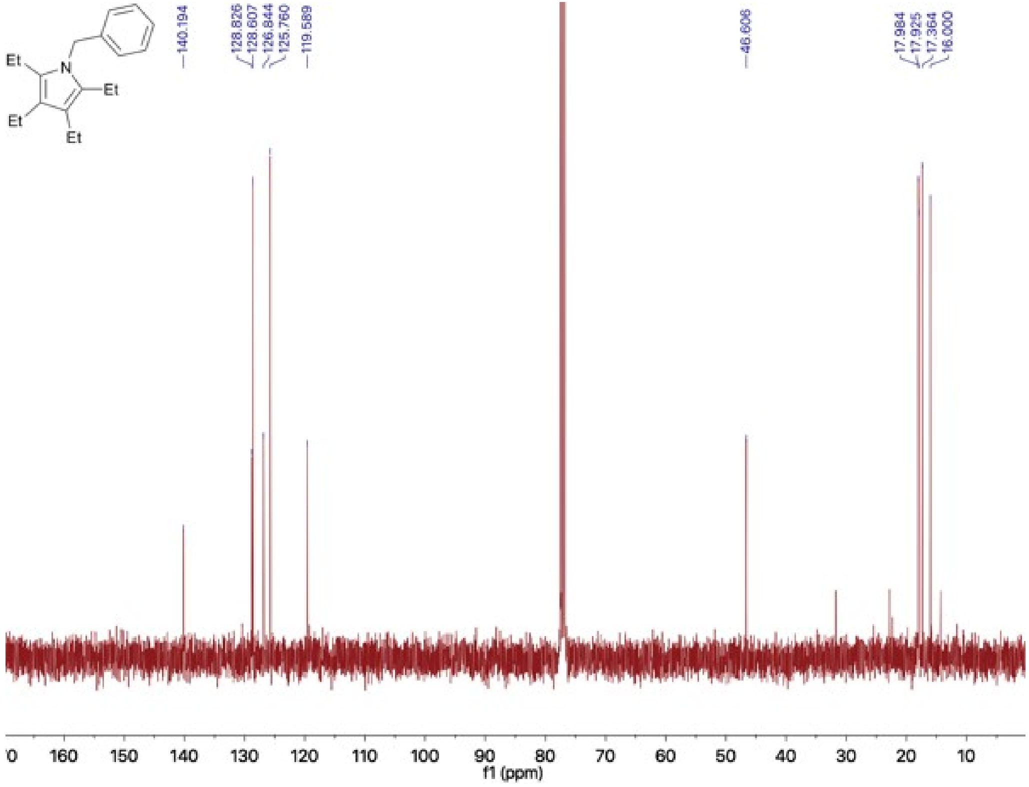
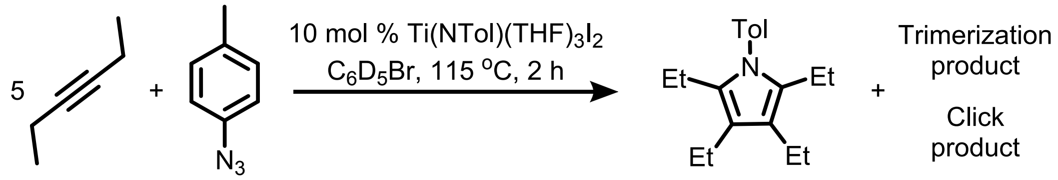


Figure S82: ^{13}C spectrum of 2,3,4,5-tetraethyl-1-benzyl-1*H*-pyrrole in $CDCl_3$.

NMR analysis of (*p*-tolyl)azide and 3-hexyne reaction (Table 1, Entry 11)



A standard catalytic run with [Ti] (7 mg, 0.01 mmol), (*p*-tolyl)azide (14 mg, 0.1 mmol, 1 equiv.) and 0.5 mL of stock solution (azide screen) was prepared and the reaction mixture was heated for 2 h. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.
Characterization of this pyrrole product was done previously.[3]

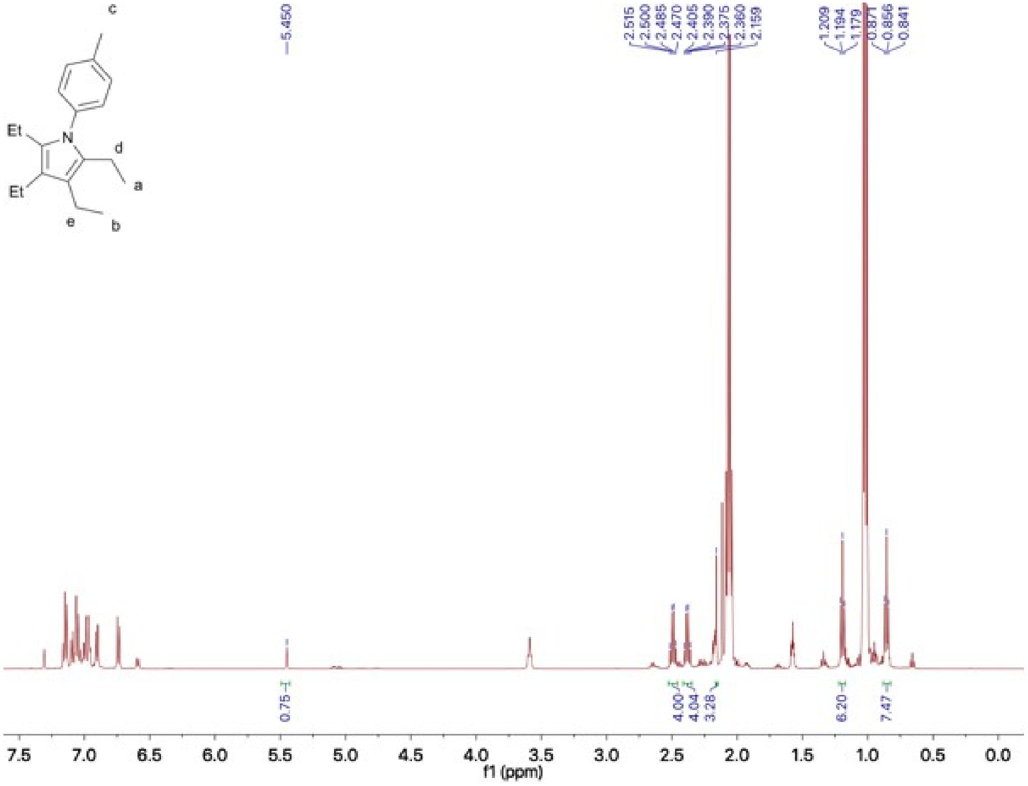


Figure S83: ^{1}H spectrum of (*p*-tolyl)azide reaction with 3-hexyne in C_6D_5Br.

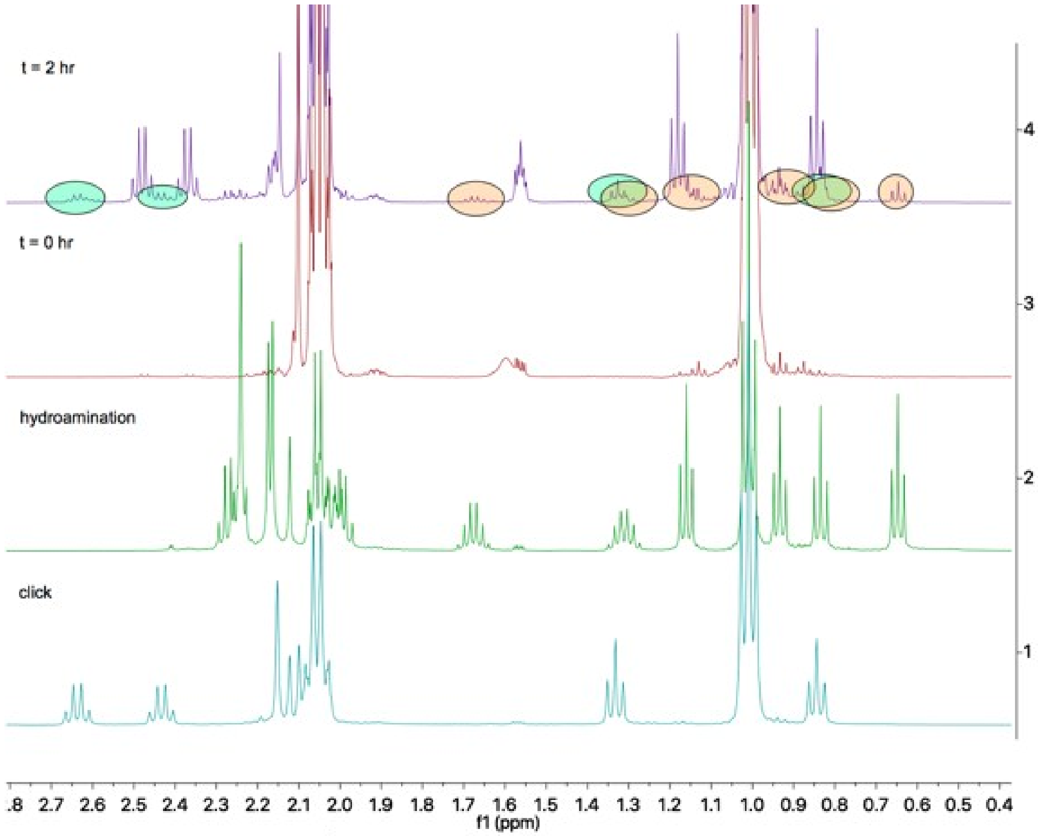


Figure S84: Zoom-in stacked ^{1}H spectrum of (*p*-tolyl)azide reaction with 3-hexyne t = 2 h (4), t = 0 h (3), hydroamination of 3-hexyne with *p*-toluidine (2) and click reaction (1).

* Triazole and hydroamination products are highlighted in green and orange, respectively.

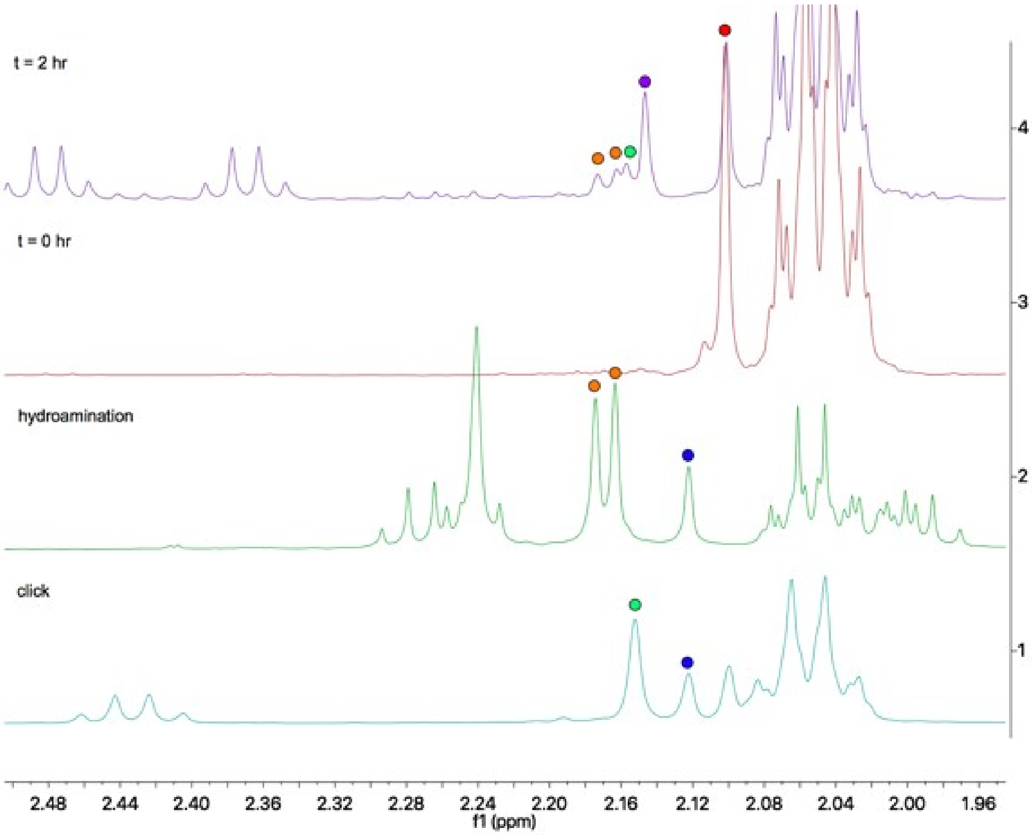
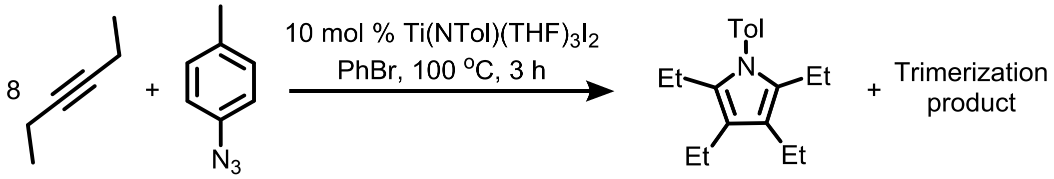


Figure S85: Zoom-in stacked ^1H spectrum of (*p*-tolyl)azido reaction with 3-hexyne t = 2 h (4), t = 0 (3), hydroamination of 3-hexyne with *p*-toluidine (2) and click reaction (1).

* The *p*-tolyl peaks from various groups are marked with colored dots (red = (*p*-tolyl)azido; blue = *p*-toluidine; purple = 2,3,4,5-tetraethyl-1-(*p*-tolyl)-1H-pyrrole; green = 4,5-diethyl-1-(*p*-tolyl)-1H-1,2,3-triazole; orange = N-(*p*-tolyl)hexan-3-imine (mixture of E and Z isomers)).

NMR analysis of (*p*-tolyl)azide and 3-hexyne reaction (Table 1, Entry 12)



21.6 mg of Ph_3CH was dissolved in 2 mL of bromobenzene (0.044 M Ph_3CH). 0.5 mL of this solution was then used to dissolve $Ti(NTol)(THF)_3I_2$ (6 mg, 0.01 mmol, 10 mol %) and (*p*-tolyl)azide (13.6 mg, 0.102 mmol, 1 equiv.) that had been massed out in a screw-cap NMR tube. 3-hexyne (94 µL, 0.83 mmol, 8.3 equiv) was subsequently added and the NMR tube was sealed and inverted to mix. The tube was heated at 100˚C in an oil bath for 3 hours. The catalytic mixture was analyzed directly without any further purification and the products were identified *in situ* to give a mixture of products shown above and leftover starting materials.

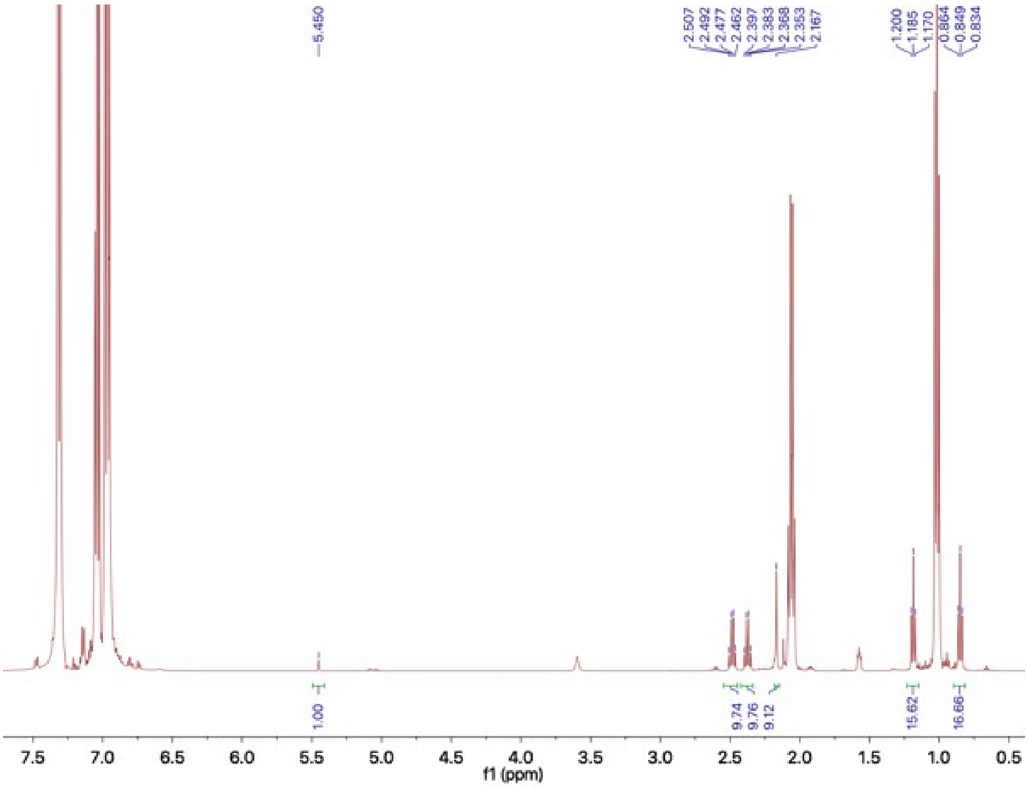
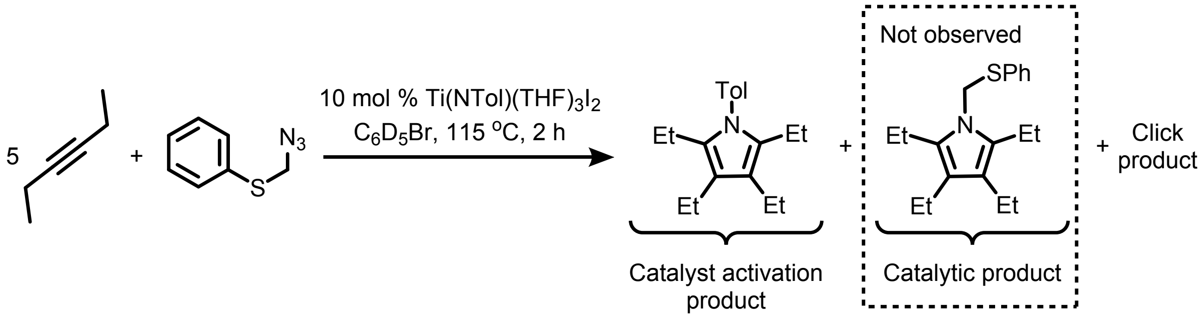


Figure S86: No-D NMR of (*p*-tolyl)azide reaction with 3-hexyne in PhBr.

NMR analysis of azidomethyl phenyl sulfide and 3-hexyne reaction (Table 1, Entry 13)



A standard catalytic run with [Ti] (6 mg, 0.01 mmol), azidomethyl phenyl sulfide (19 mg, 0.1 mmol, 1 equiv.) and 0.5 mL of stock solution (azide screen) was prepared and the reaction mixture was heated for 2 h. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials. The catalytic product was not observed although we do observe some unexplainable quartets in the spectrum.

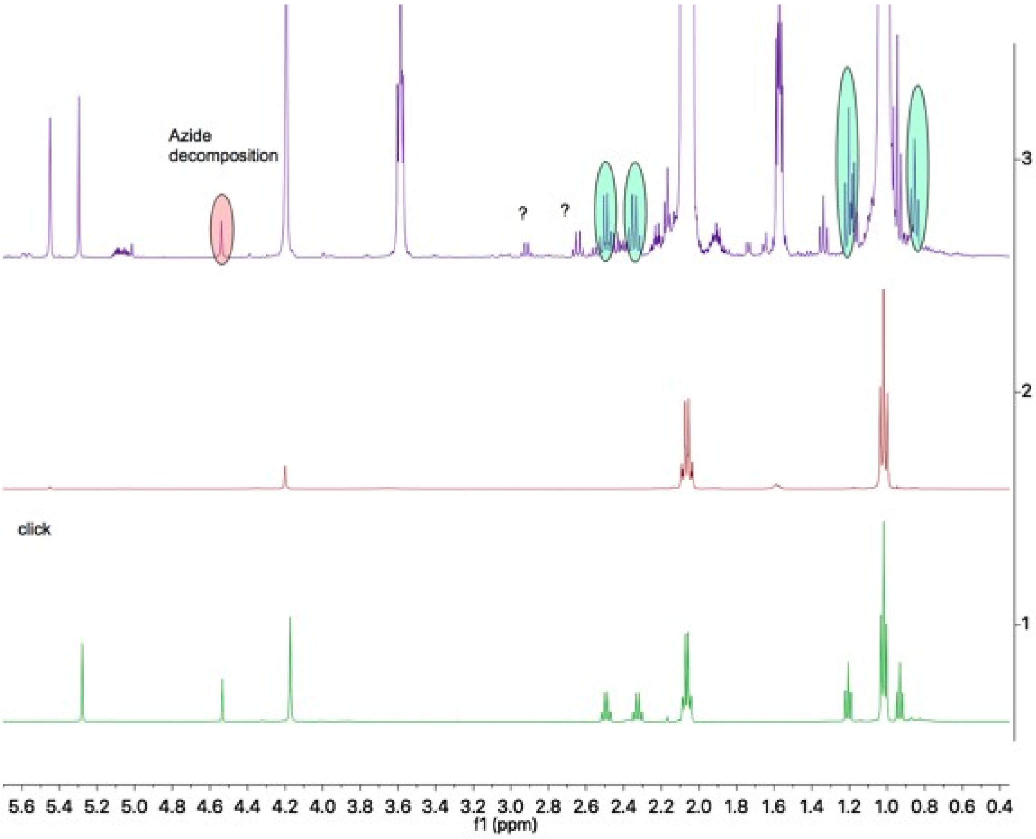
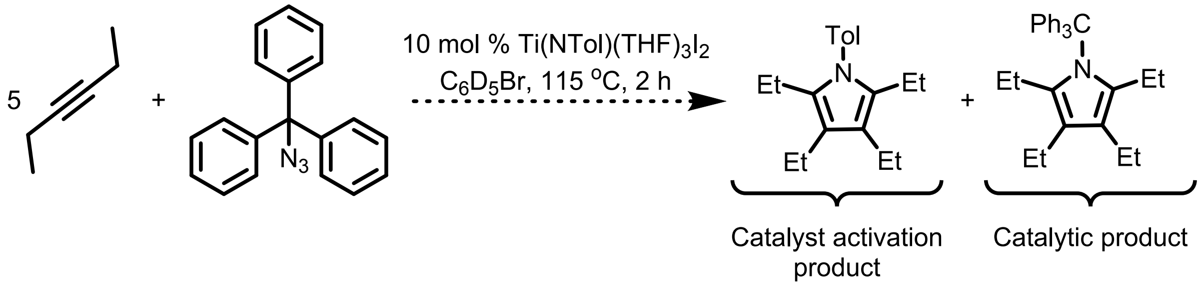


Figure S87: Stacked ^{1}H spectrum of azidomethyl phenyl sulfide reaction with 3-hexyne t= 2 h (3), t = 0 h (2) and click reaction (1) in C_6D_5Br.

NMR analysis of trityl azide and 3-hexyne reaction (Table 1, Entry 14)



A standard catalytic run with [Ti] (6 mg, 0.01 mmol), trityl azide (30 mg, 0.1 mmol, 1 equiv.) and 0.5 mL of stock solution (azide screen) was prepared and the reaction mixture was heated for 2 h. The catalytic mixture was analyzed directly without any further purification and were identified *in-situ* to not contain the desired products. Poor mass balances were also observed for both starting reagents.

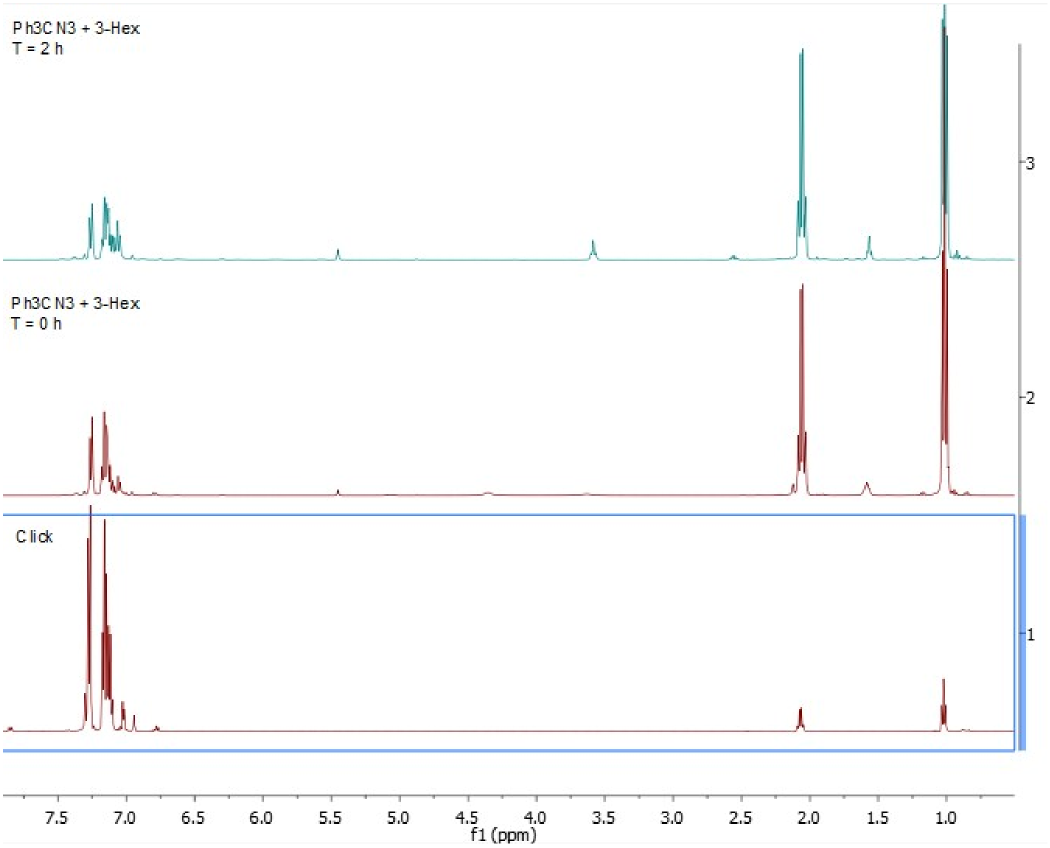


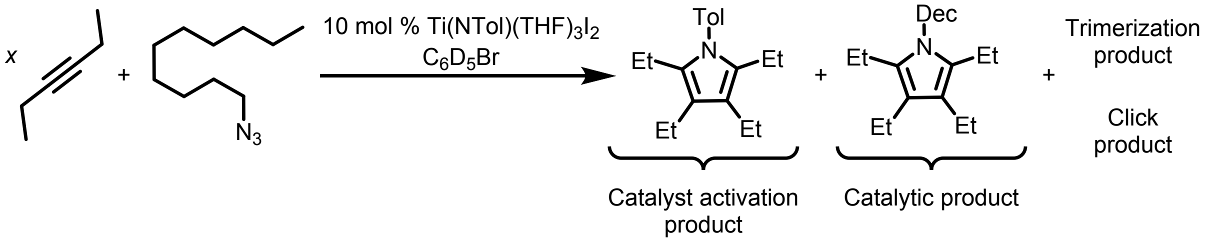
Figure S88: Stacked ^{1}H spectrum of tritylazide reaction with 3-hexyne t= 2 h (3), t = 0 h (2) and click reaction (1) in C_6D_5Br.

Table S1: Internal alkyne scope triazole yield, trimer yield and mass balance data

Table 1, Entry #	Azide	Alkyne	Triazole yield (%) 6	Trimer yield (%)[g] 9	Azide mass balance (%)	Alkyne mass balance (%)
1[a]	Ad **1b**	3-Hexyne **2a**	0	45	80	84
2[b]	Ad **1b**	3-Hexyne **2a**	0	1	85	89
3[a]	Ad **1b**	2-butyne **2b**	0	2	71	90
4[a]	Ad **1b**	Diphenyl-acetylene **2c**	0	0	*	*
5[a]	Ad **1b**	Phenyl propyne **2d**	0	0	*	92
6[d]	*n*-Dec **1c**	3-Hexyne **2a**			-	
7[e]	*n*-Dec **1c**	3-Hexyne **2a**			-	
8[b]	*n*-Dec **1c**	3-Hexyne **2a**			-	
9[b]	*n*-Dec **1c**	3-Hexyne **2a**	7	6	74	95
10[b]	Bn **1d**	3-Hexyne **2a**	11	0	70	89
11[b]	Tol **1a**	3-Hexyne **2a**	10	0	82	92
12[f]	Tol **1a**	3-Hexyne **2a**			-	
13[b]	$PhSCH_2$ **1e**	3-Hexyne **2a**	0	0	65	96
14[b]	Ph_3C **1f**	3-Hexyne **2a**	0	0	44	53

[a]Conditions: 0.2 mmol 1b (1 equiv.), 2 (5 equiv.), 10 mol % $(THF)_3TiI_2(Ntol)$ 115˚C, 0.5 mL C_6D_5Br, average of 2 runs. [b]Conditions: 0.1 mmol 1 (1 equiv.), 2a (x equiv.), 10 mol % $(THF)_3TiI_2(Ntol)$ 115˚C, 0.5 mL C_6D_5Br, average of 2-3 runs. [d]Conducted at 80˚C. [e]Conducted at 100˚C. [f]Conditions: 0.1 mmol 1a (1 equiv.), 0.8 mmol 2 (8 equiv.), 10 mol % $(THF)_3I_2Ti(Ntol)$, 115˚C, 0.5 mL C_6D_5Br, single run. [g]Trimer yields are calculated with respect to alkyne. * Overlap of peaks in NMR spectra makes positive identification difficult. - Data unavailable in non-quantitative NMR

Table S2: 1-azidodecane optimisation conditions with 3-hexyne

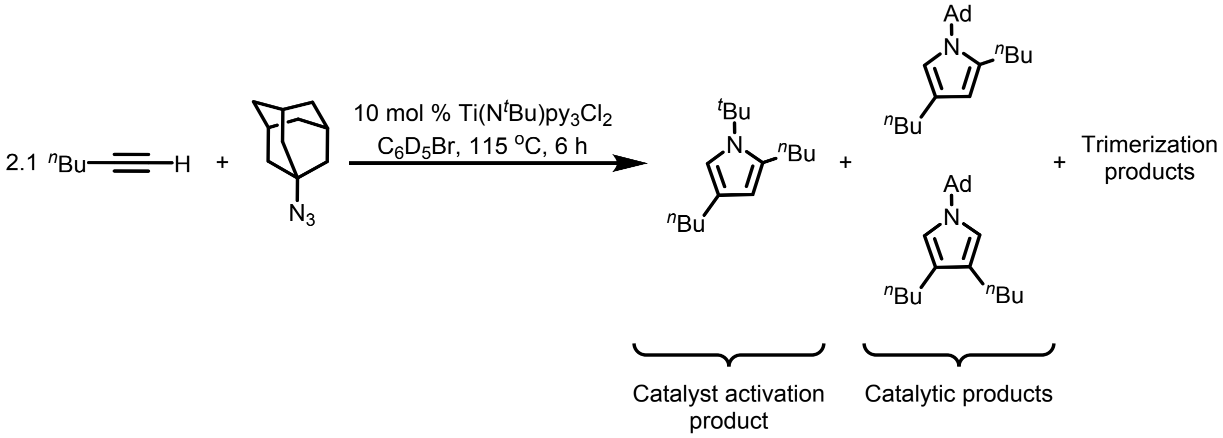


Entry #	3-hexyne equiv. (*x*)	time (h)	Temp (˚C)	Catalytic pyrrole yield (%) 3
1	3	6	80	37
2	3	6	100	35
3	3	6	115	34
4	0.5	3	115	5
5	4.5	3	115	45
6	8	3	115	74

Conditions: 0.1 mmol 1c (1 equiv.), 2a (x equiv.), 10 mol % $(THF)_3TiI_2(Ntol)$, 0.5 mL C_6D_5Br, single run

NMR analysis of catalytic reactions with terminal alkyne substrates (Table 2)

NMR analysis of 1-hexyne and 1-azidoadamantane reaction (Table 2, Entry 1)



A standard catalytic run with 1-hexyne (48.5 µL, 0.42 mmol, 2.1 equiv.), 1-azidoadamantane (35 mg, 0.2 mmol, 1.0 equiv.) and 0.5 mL of stock solution (terminal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover 1-azidoadamantane.

2,4-di-*n*-butyl-1-(adamantyl)-1*H*-pyrrole (partial)
^{1}H NMR (400 MHz, C_6D_5Br): δ 6.58 (app m, 1H, *o*-N-pyr-*H*), 5.96 (s, 1H, *m*-N-pyr-*H*), 2.82 – 2.78 (m, 2H, *o*-C*H₂*CH₂CH₂CH₃), 2.54 – 2.50 (m, 2H, *m*-C*H₂*CH₂CH₂CH₃), 2.07 (s, 6H, Ad-C*H₂*), 1.99 (s, 3H, Ad-C*H*), 1.57 (s, 6H, Ad-C*H₂*)
This is a partial NMR line list, the remaining *n*-butyl peaks are hidden under other peaks.

3,4-di-*n*-butyl-1-(adamantyl)-1*H*-pyrrole (partial)
^{1}H NMR (400 MHz, C_6D_5Br): δ 6.58 (app m, 2H, *o*-N-pyr-*H*), 2.70 – 2.66 (m, 2H, *m*-C*H₂*CH₂CH₂CH₃)
This is a partial NMR line list, the remaining adamantyl and *n*-butyl peaks are hidden under other peaks.

The pyr-*H* peak for both regioisomers overlap at δ 6.58 ppm in C_6D_5Br. In $CDCl_3$, the peaks appear as two overlapping peaks that correlate to two N peaks in ^{15}N-^1H HMBC. To obtain the spectra in $CDCl_3$, the catalytic reaction was ran as described above in the absence of internal standard (Ph_3CH). Following which, the reaction was dried under *vacuo* and retaken up in $CDCl_3$ without any further purification.

2,4-di-*n*-butyl-1-(adamantyl)-1*H*-pyrrole (partial)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60 (app m, 1H, *o*-N-pyr-*H*), 5.89 (s, 1H, *m*-N-pyr-*H*), 2.85 – 2.81 (m, 2H, *o*-C*H₂*CH₂CH₂CH₃), 2.24 (m, 9H, Ad-C*H₂* and Ad-C*H*), 1.77 (s, 6H, Ad-C*H₂*)
One of the activation peak is buried under the δ 5.89 peak. This is a partial NMR line list, the remaining *n*-butyl peaks are hidden under other peaks.

3,4-di-*n*-butyl-1-(adamantyl)-1*H*-pyrrole (partial)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.61 (app m, 2H, *o*-N-pyr-*H*), 2.79 – 2.75 (m, 2H, *m*-C*H₂*CH₂CH₂CH₃)
This is a partial NMR line list, the remaining adamantyl and *n*-butyl peaks are hidden under other peaks.

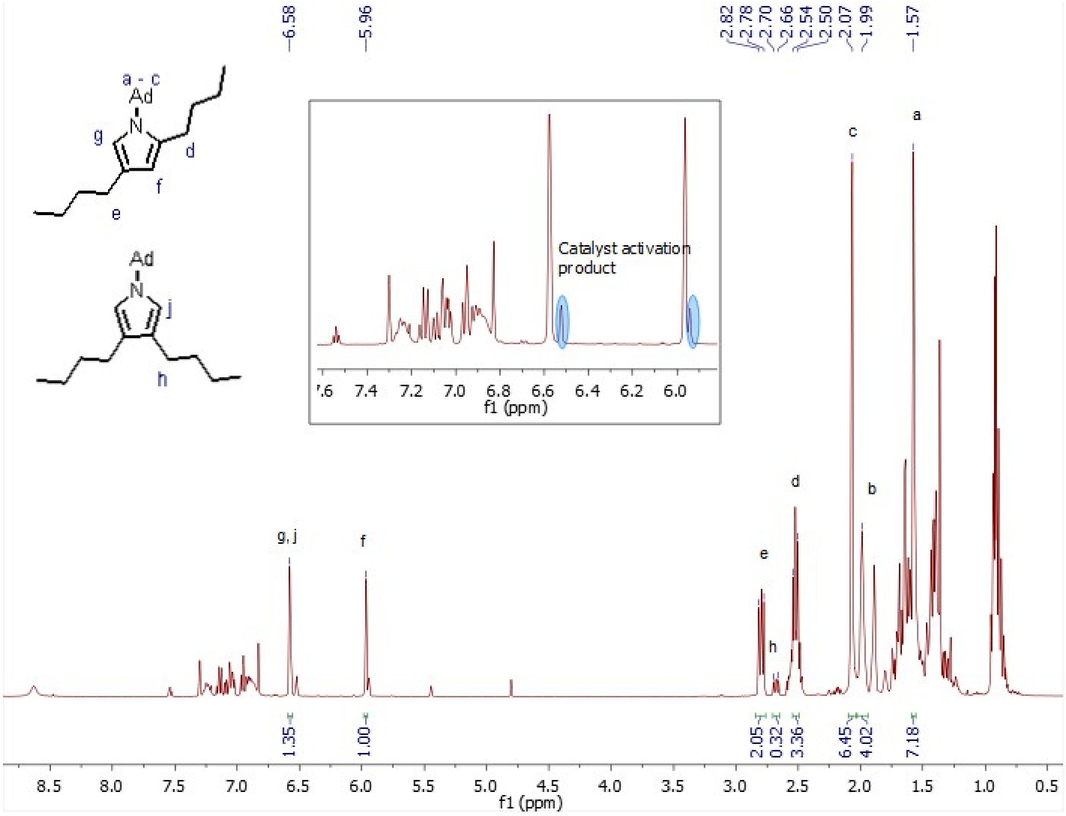


Figure S89: ^{1}H spectrum of 1-hexyne reaction with 1-azidoadamantane in C_6D_5Br.

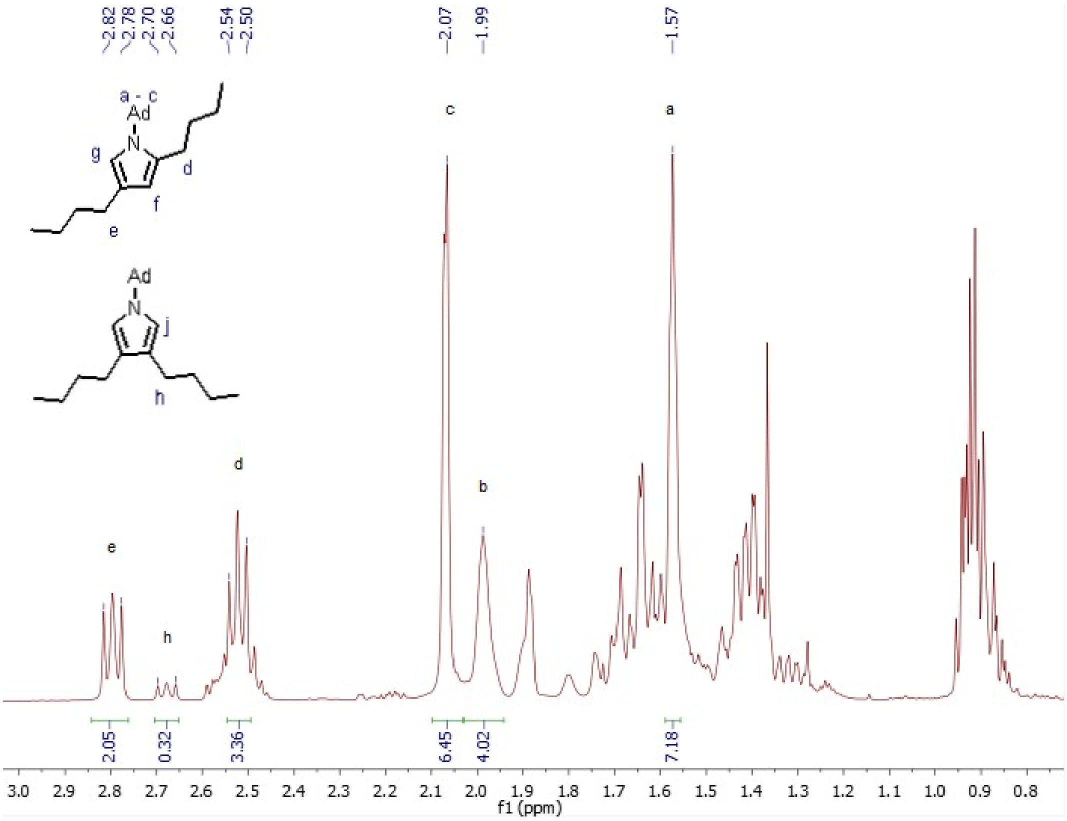


Figure S90: Zoom-in ^{1}H spectrum of 1-hexyne reaction with 1-azidoadamantane in C_6D_5Br.

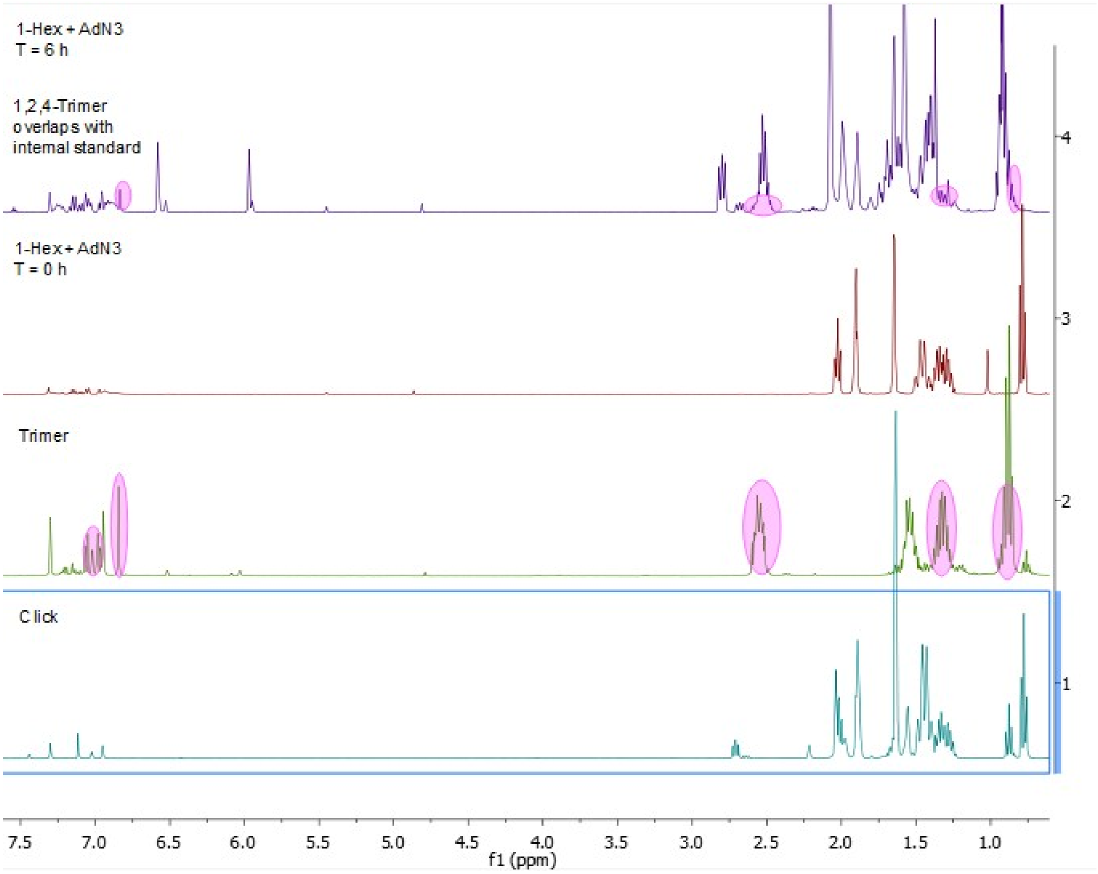


Figure S91: Stacked ^{1}H spectrum of 1-hexyne reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimerization reaction (2) and click reaction (1) in C_6D_5Br.

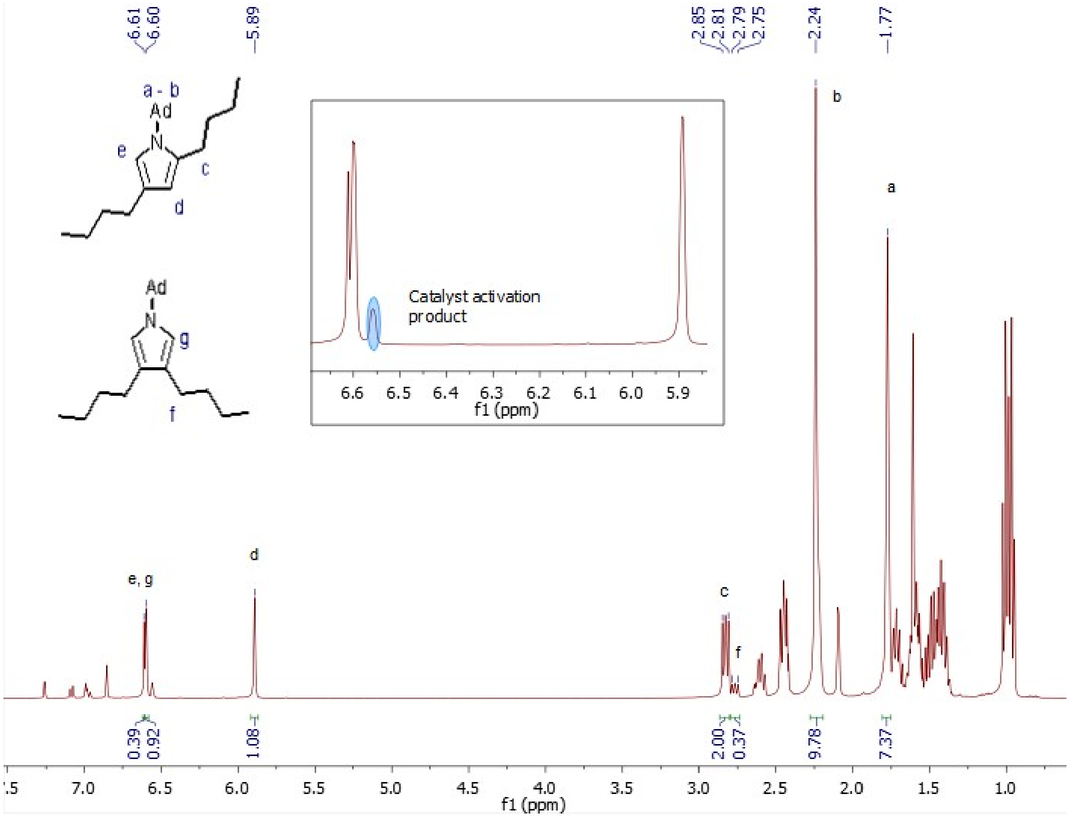


Figure S92: ^{1}H spectrum of 1-hexyne reaction with 1-azidoadamantane in $CDCl_3$.

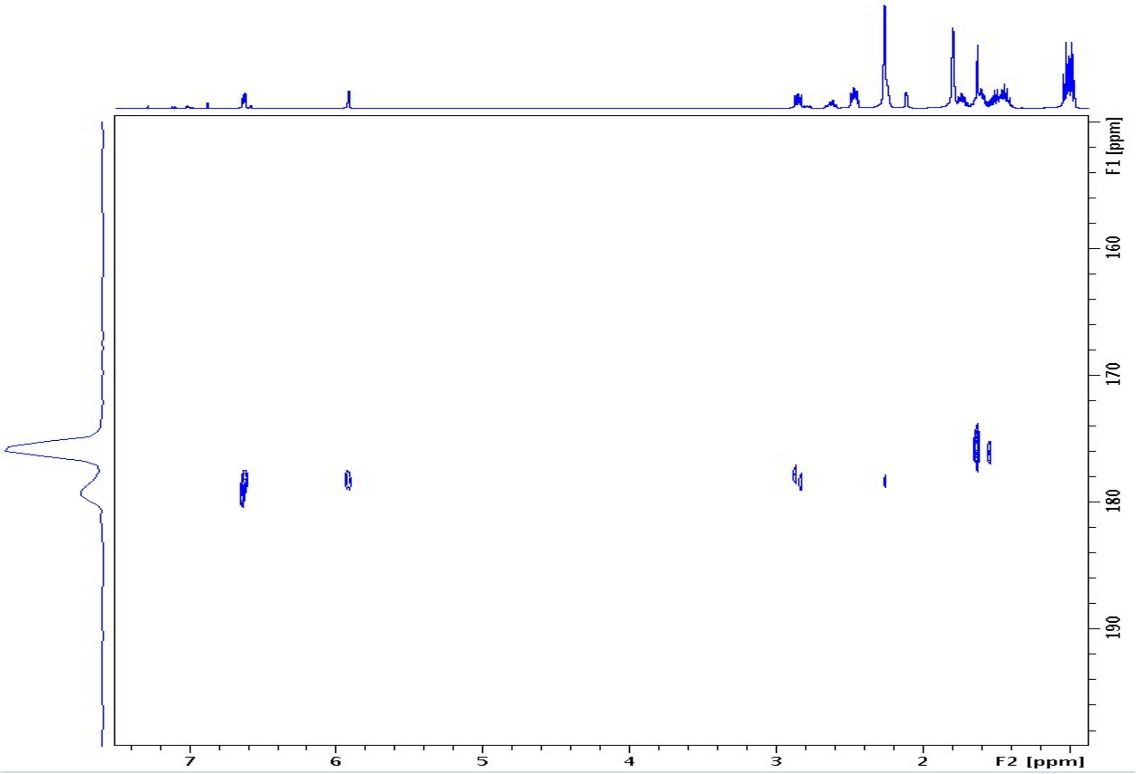
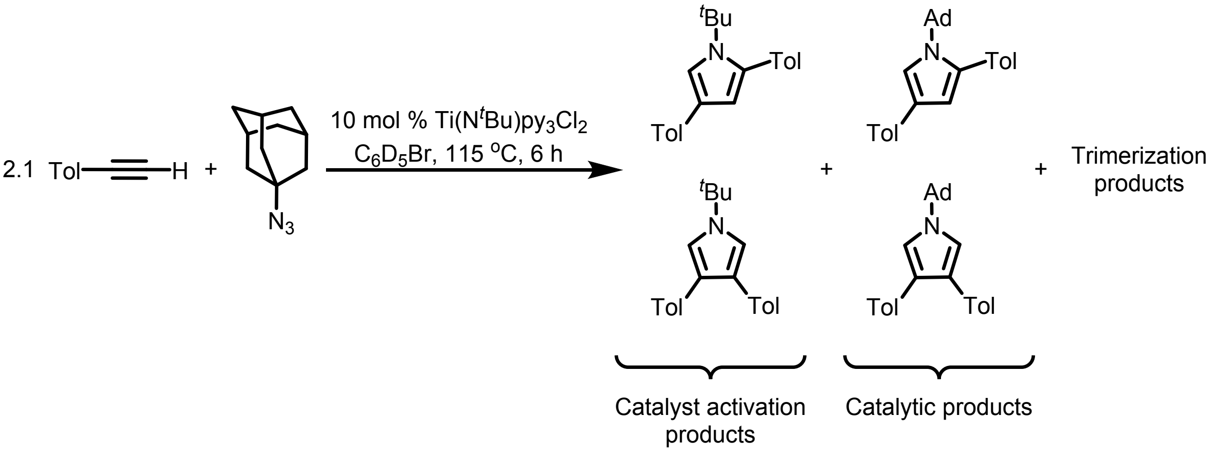


Figure S93: ^{15}N-^{1}H HMBC spectrum of 1-hexyne reaction with 1-azidoadamantane in $CDCl_3$.

NMR analysis of tolylacetylene and 1-azidoadamantane reaction (Table 2, Entry 2)



A standard catalytic run with tolylacetylene (53.5 µL, 0.42 mmol, 2.1 equiv.), 1-azidoadamantane (36 mg, 0.2 mmol, 1.0 equiv.) and 0.5 mL of stock solution (terminal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,4-di-*p*-tolyl-1-(adamantyl)-1*H*-pyrrole (partial)

^{1}H NMR (500 MHz, C_6D_5Br): δ 2.24 (s, 3H, *o*-C_6H_4-CH_3), 2.21 (s, 6H, *m*-N-pyr-C_6H_4-CH_3), 1.92 (m, 6H, Ad-CH_2), 1.65 – 1.64 (m, 6H, Ad-CH_2)

The peak at δ 2.21 overlaps with that of the other pyrrole regioisomer. This is a partial NMR line list, the remaining peaks are either buried under other products or cannot be positively identified in the reaction mixture.

3,4-di-*p*-tolyl-1-(adamantyl)-1*H*-pyrrole (partial)

^{1}H NMR (500 MHz, C_6D_5Br): δ 6.93 (s, 2H, *o*-N-pyr-*H*), 2.21 (s, 6H, *o*-N-pyr-C_6H_4-CH_3), 2.05 – 2.04 (m, 6H, Ad-CH_2), 2.00 (br s, 3H, Ad-C*H*), 1.44 (s, 6H, Ad-CH_2)

The peak at δ 2.21 overlaps with that of the other pyrrole regioisomer. This is a partial NMR line list, the remaining peaks are either buried under other products or cannot be positively identified in the reaction mixture.

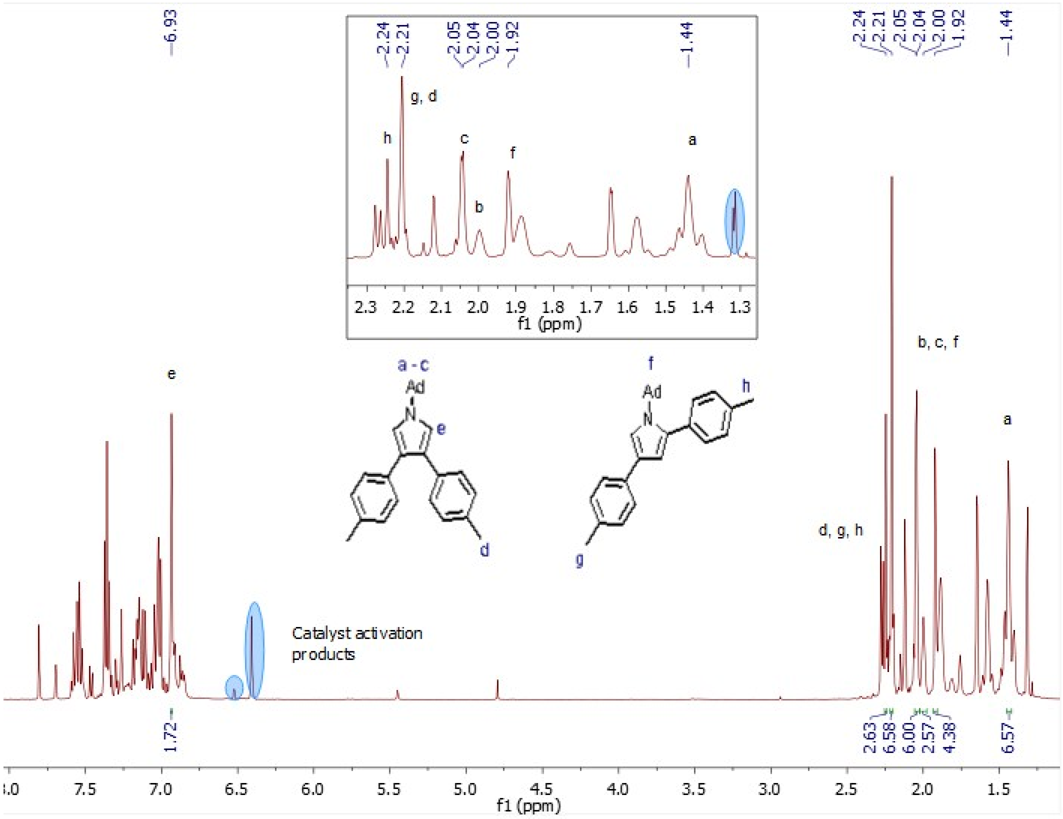


Figure S94: ^{1}H spectrum of tolylacetylene reaction with 1-azidoadamantane in C_6D_5Br.

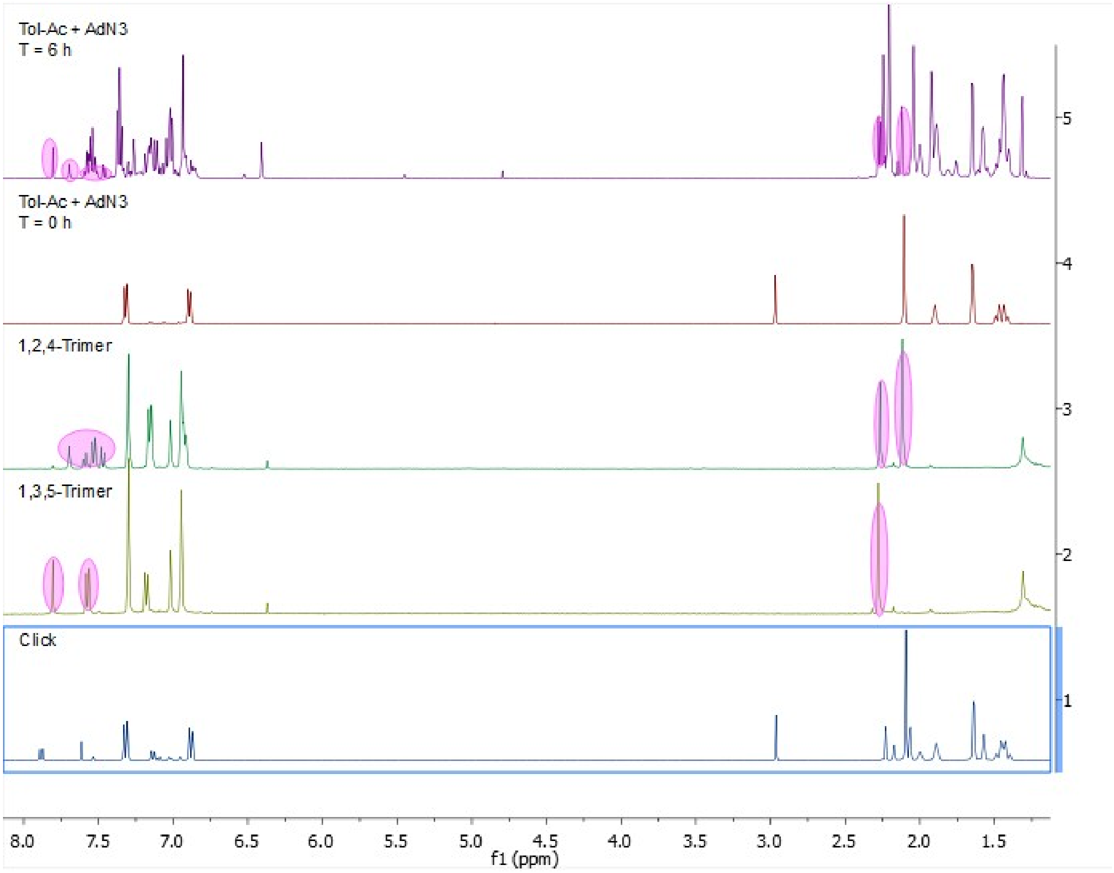
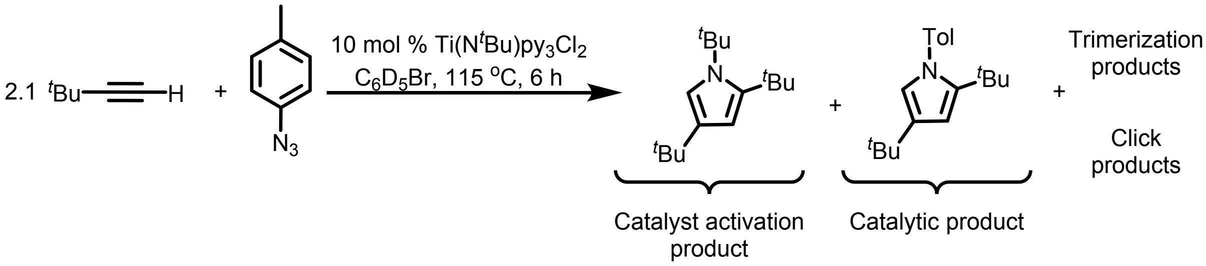


Figure S95: Stacked ^{1}H spectrum of tolylacetylene reaction with 1-azidoadamantane t= 6 h (5), t = 0 h (4), 1,2,4-trimer (3), 1,3,5-trimer (2) and click reaction (1) in C_6D_5Br.

NMR analysis of (*t*-butyl)acetylene and (*p*-tolyl)azide reaction (Table 2, Entry 3)



A standard catalytic run with (*t*-butyl)acetylene (54 µL, 0.44 mmol, 2.1 equiv.), (*p*-tolyl)azide (28 mg, 0.21 mmol, 1.0 equiv.) and 0.5 mL of stock solution (terminal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above, leftover starting materials and azide decomposition products.

2,4- di-(*t*-butyl)-1-(*p*-tolyl)-1*H*-pyrrole (partial)
^{1}H NMR (400 MHz, C_6D_5Br): δ 6.14 (d, $^4J_{HH}$ = 2.1 Hz, 1H, *m*-N-pyr-*H*), 2.17 (s, 3H, NC_6H_4-CH_3), 1.30 (s, 9H, *o*-N-pyr-^{t}Bu), 1.16 (s, 9H, *m*-N-pyr-^{t}Bu)
The peak at δ 1.16 overlaps with the remaining starting material, (*t*-butyl)acetylene. This is a partial NMR line list, the remaining aromatic peaks cannot be positively identified in the reaction mixture.

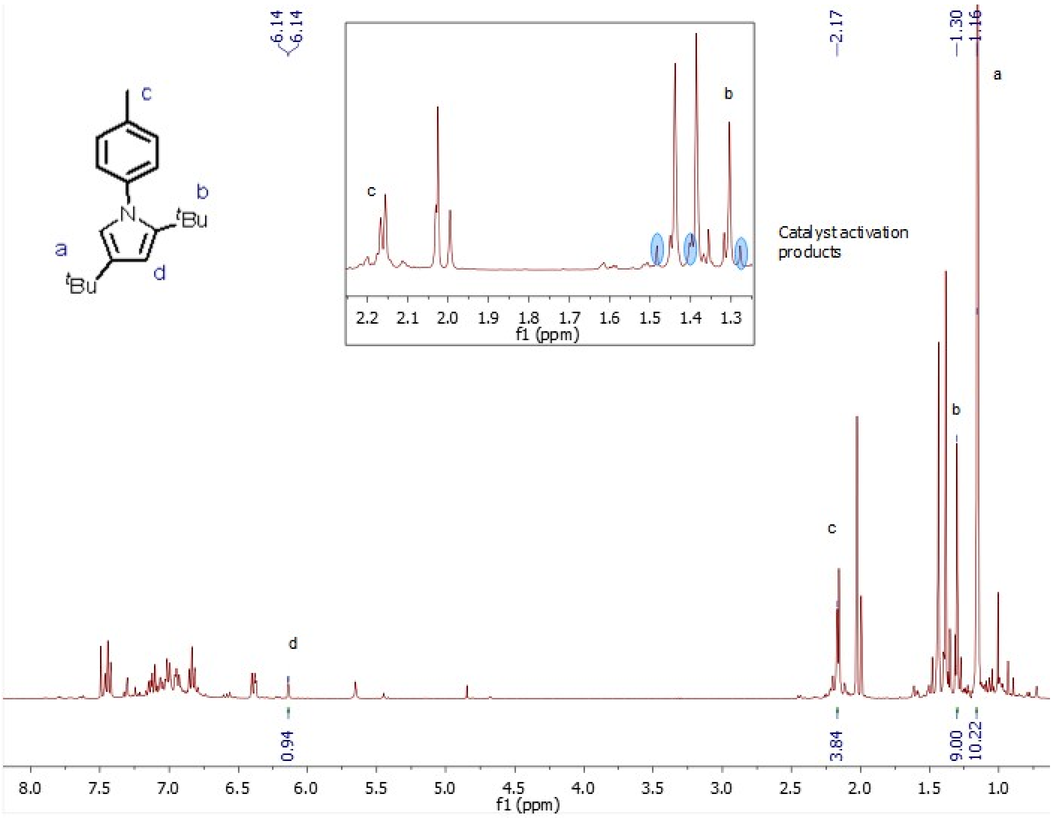


Figure S96: ^{1}H spectrum of (*t*-butyl)acetylene reaction with 1-azidoadamantane in C_6D_5Br.

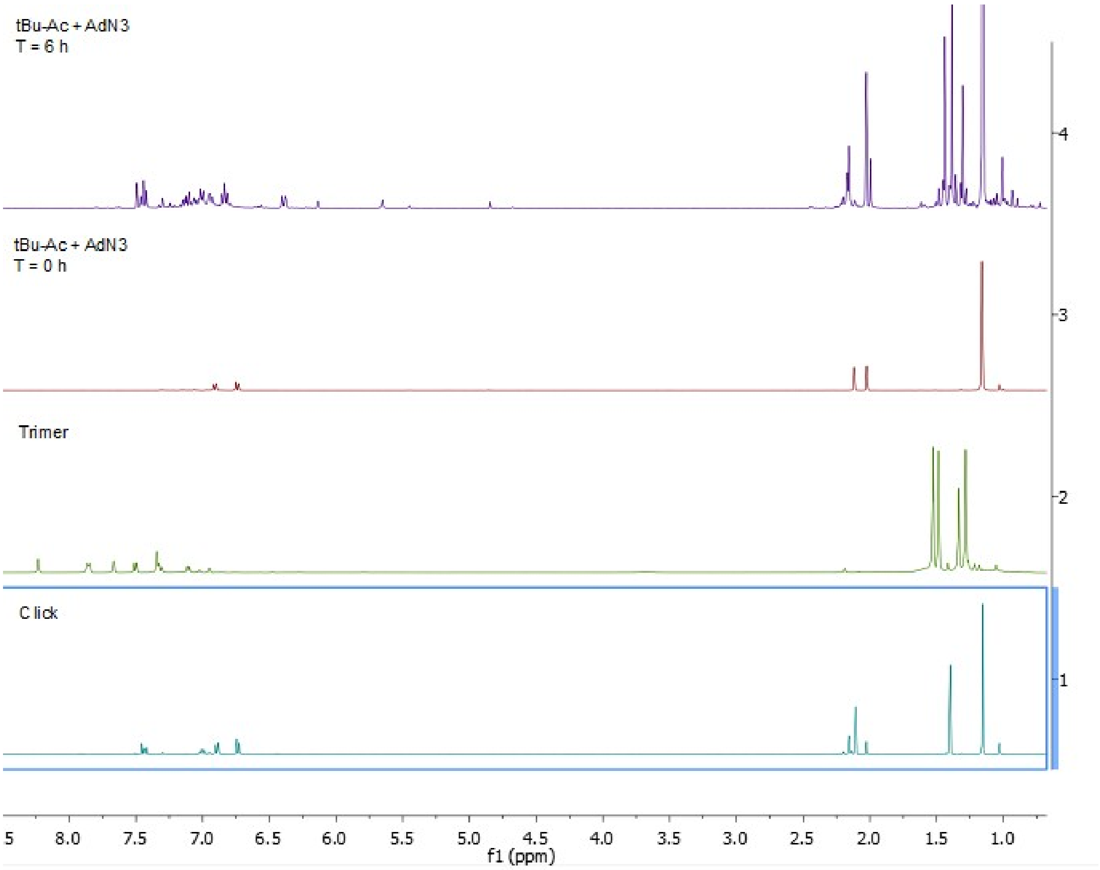


Figure S97: Stacked ^{1}H spectrum of (*t*-butyl)acetylene reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer reaction (2) and click reaction (1) in C_6D_5Br.

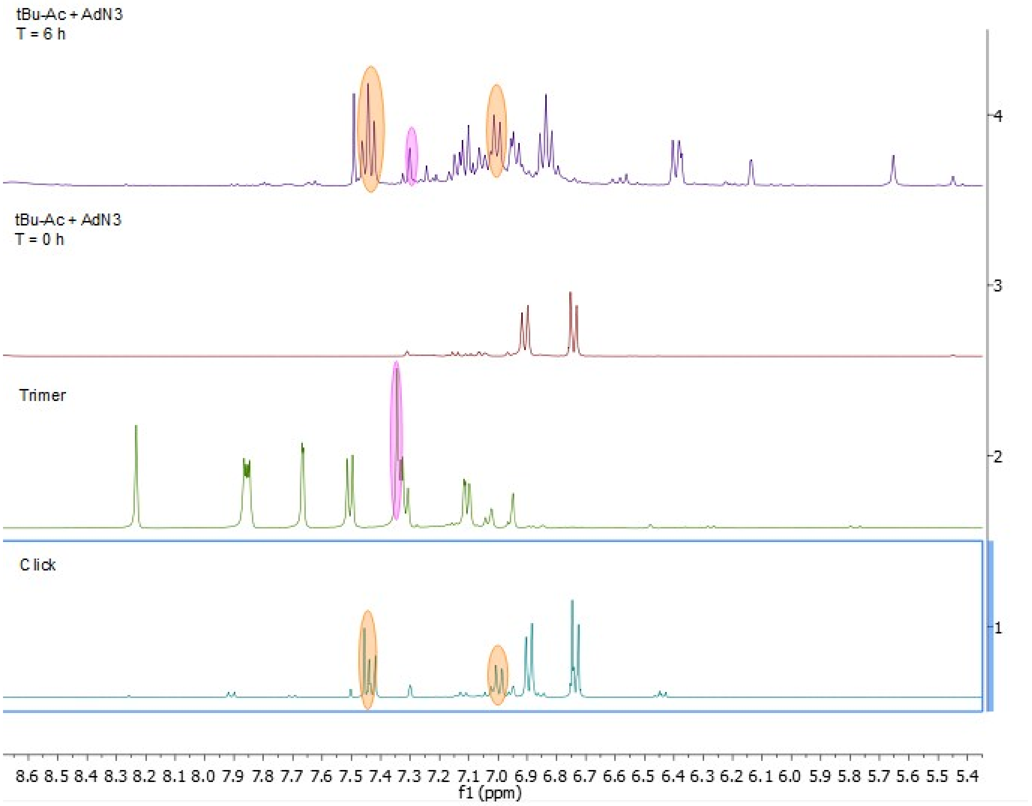


Figure S98: Zoom-in stacked ^{1}H spectrum of (*t*-butyl)acetylene reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer reaction (2) and click reaction (1) in C_6D_5Br.

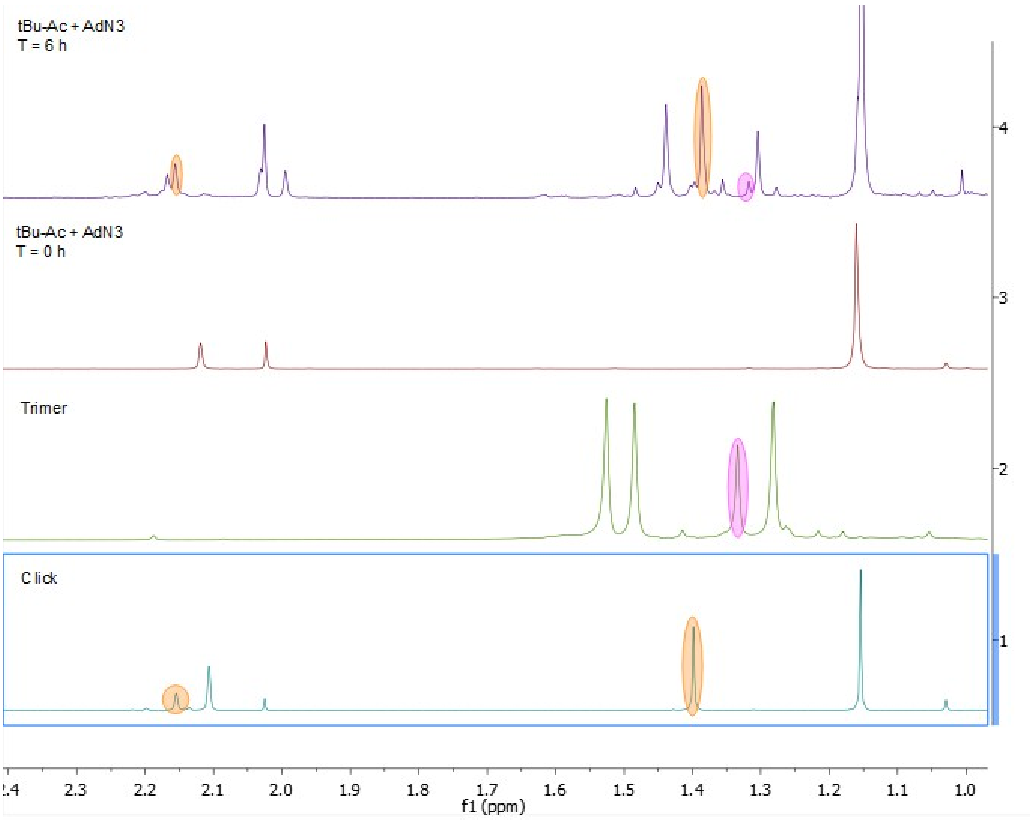
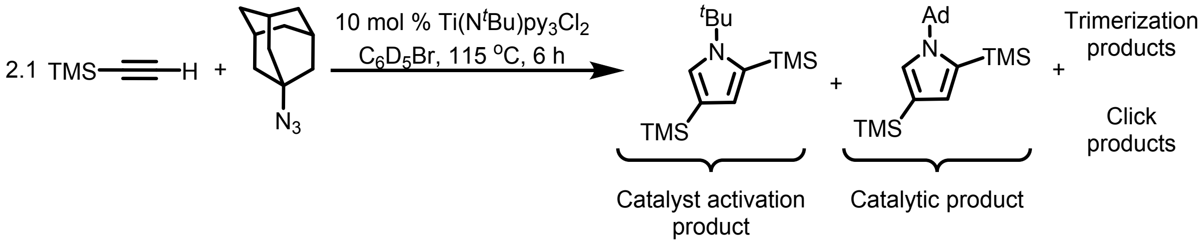


Figure S99: Zoom-in stacked ^{1}H spectrum of (*t*-butyl)acetylene reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer reaction (2) and click reaction (1) in C_6D_5Br.

NMR analysis of trimethylsilylacetylene and 1-azidoadamantane reaction (Table 2, Entry 4)



A standard catalytic run with (trimethylsilyl)acetylene (58 µL, 0.42 mmol, 2.1 equiv.), 1-azidoadamantane (35 mg, 0.2 mmol, 1.0 equiv.) and 0.5 mL of stock solution (terminal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2,4-bis-(trimethylsilyl)-1-(adamantyl)-1*H*-pyrrole (partial)

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.30 (d, $^4J_{HH}$ = 1.6 Hz, 1H, *o*-N-pyr-*H*), 6.82 (d, $^4J_{HH}$ = 1.6 Hz, 1H, *m*-N-pyr-*H*), 2.04 (m, 6H, Ad-C*H$_2$*), 1.58 (br s, 6H, Ad-C*H$_2$*), 0.38 (s, 9H, N-pyr-C2-Si(C*H$_3$*)$_3$), 0.29 (s, 9H, N-pyr-C4-Si(C*H$_3$*)$_3$)

The peak at δ 2.04 overlaps with that of the click product. This is a partial NMR line list, the remaining adamantyl peak is buried under other products.

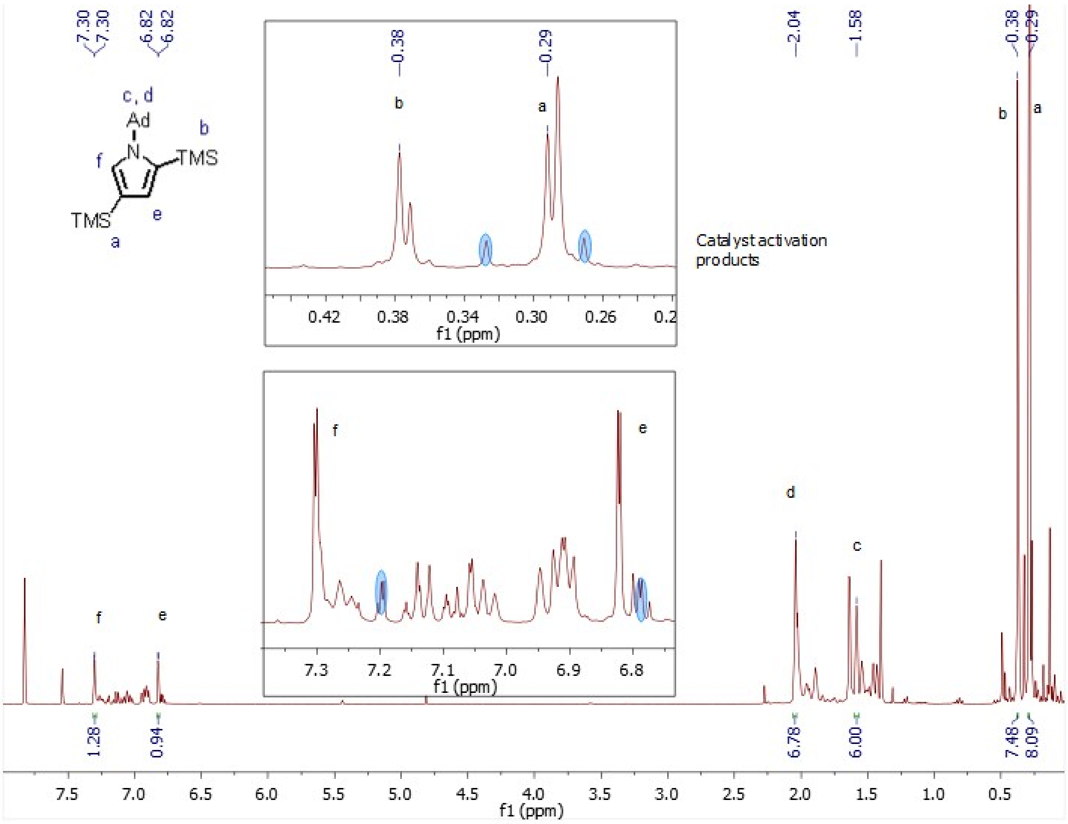


Figure S100: ^{1}H spectrum of (trimethylsilyl)acetylene reaction with 1-azidoadamantane in C_6D_5Br.

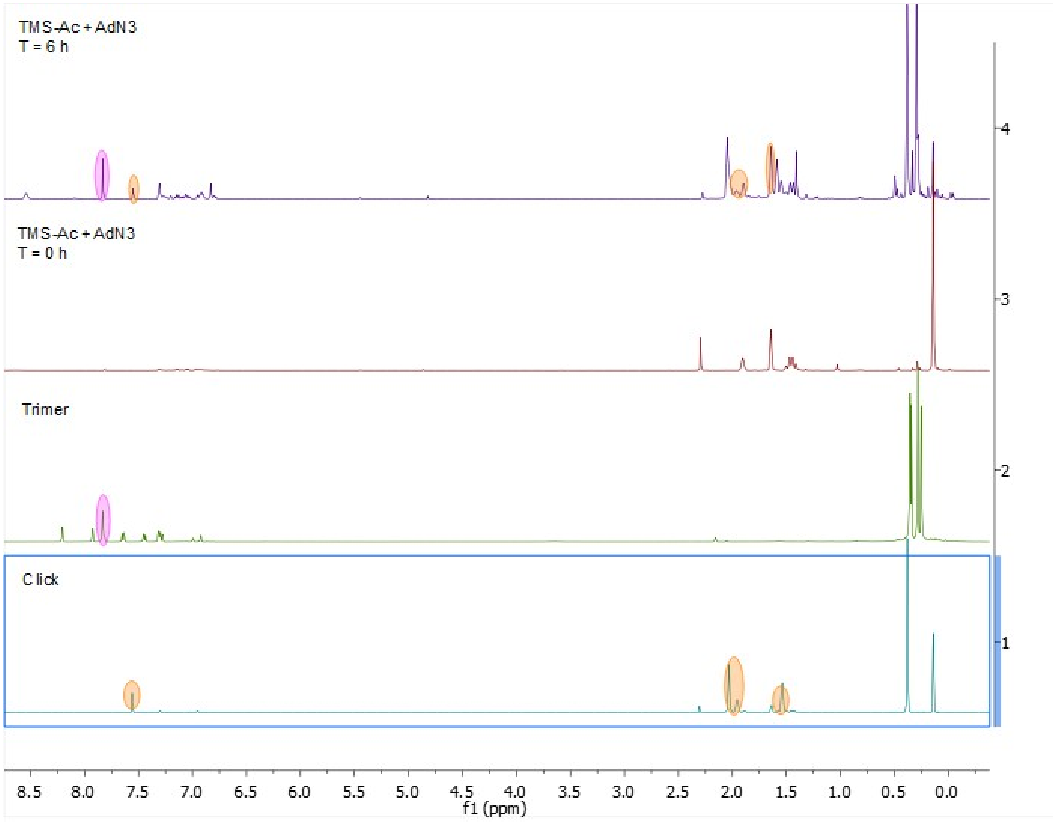


Figure S101: Stacked ^{1}H spectrum of (trimethylsilyl)acetylene reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer reaction (2) and click reaction (1) in C_6D_5Br.

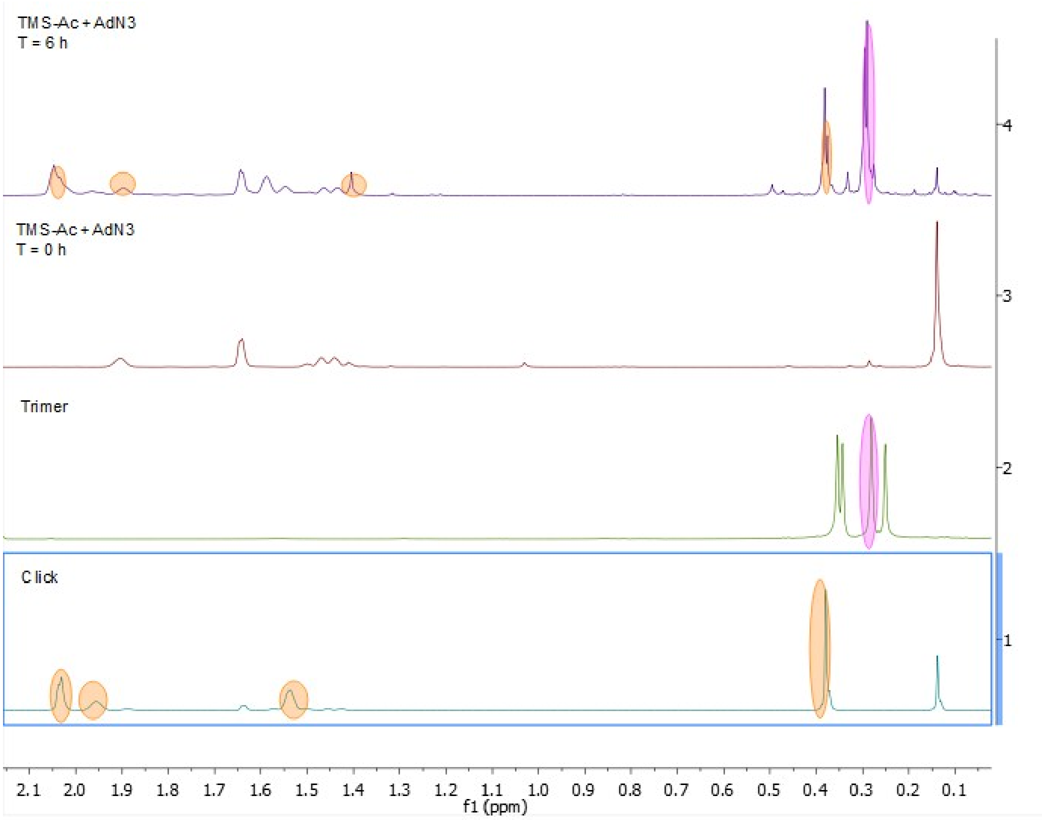
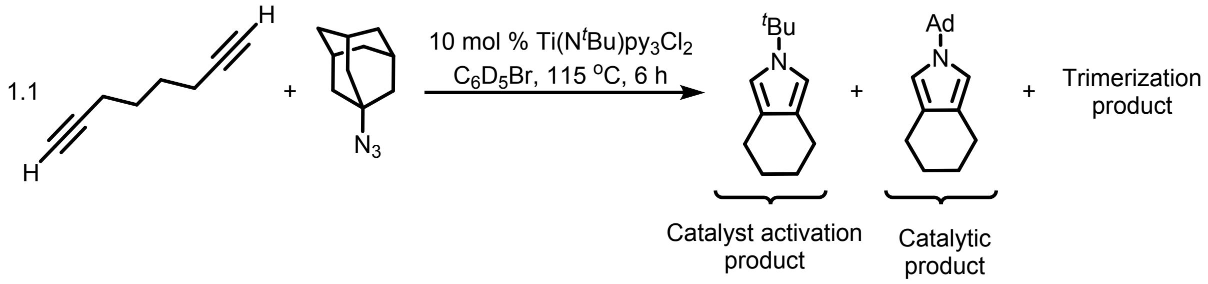


Figure S102: Zoom-in stacked ^{1}H spectrum of (trimethylsilyl)acetylene reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer reaction (2) and click reaction (1) in C_6D_5Br.

NMR analysis of 1,7-octadiyne and 1-azidoadamantane reaction (Table 2, Entry 5)



A standard catalytic run with 1,7-octadiyne (28 µL, 0.21 mmol, 1.1 equiv.),1-azidoadamantane (35 mg, 0.20 mmol, 1.0 equiv.) and 0.5 mL of stock solution (terminal alkyne screen) was conducted. The catalytic mixture was analyzed directly without any further purification and the products were identified *in-situ* to give a mixture of products shown above and leftover starting materials.

2-adamantyl-4,5,6,7-tetrahydro-2*H*-isoindole (partial)
^{1}H NMR (500 MHz, C_6D_5Br): δ 6.47 (s, 2H, pyr-*H*), 2.64 (m, 4H, pyr-CH_2), 1.97 (s (br), 3H, Ad), 1.87 (d, $^3J_{HH}$ = 3.0 Hz, 6H, N-C-(CH_2)$_3$) 1.70 (m, 4H, pyr-CH$_2$-CH_2)
All peaks other than the aromatic peak at δ 6.47 have some degree of overlap with starting material or trimerization.

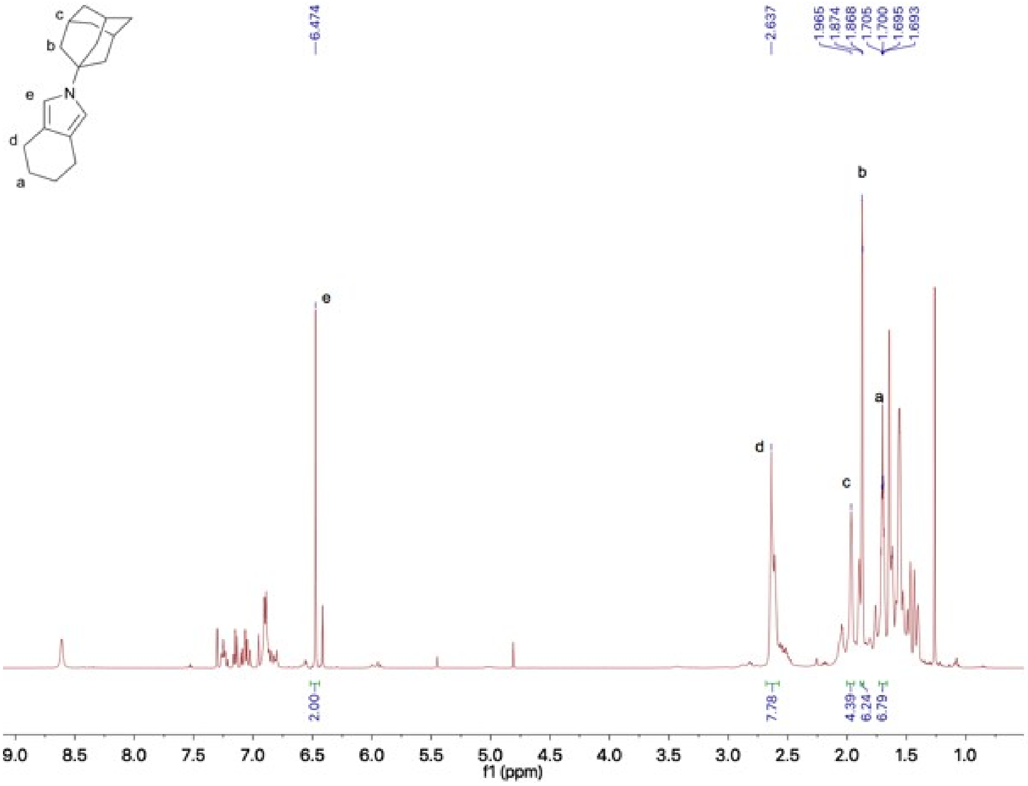


Figure S103: ^{1}H spectrum of 1,7-octadiyne reaction with 1-azidoadamantane in C_6D_5Br.

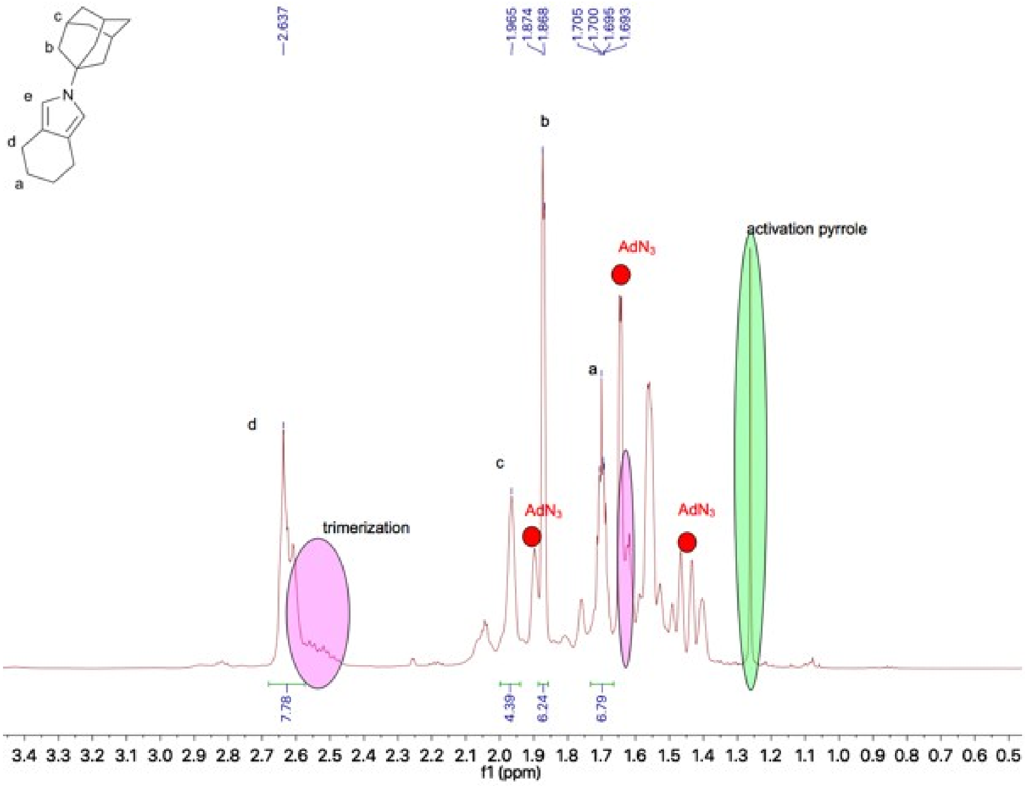


Figure S104: Zoom-in ^{1}H spectrum of 1,7-octadiyne reaction with 1-azidoadamantane in C_6D_5Br.

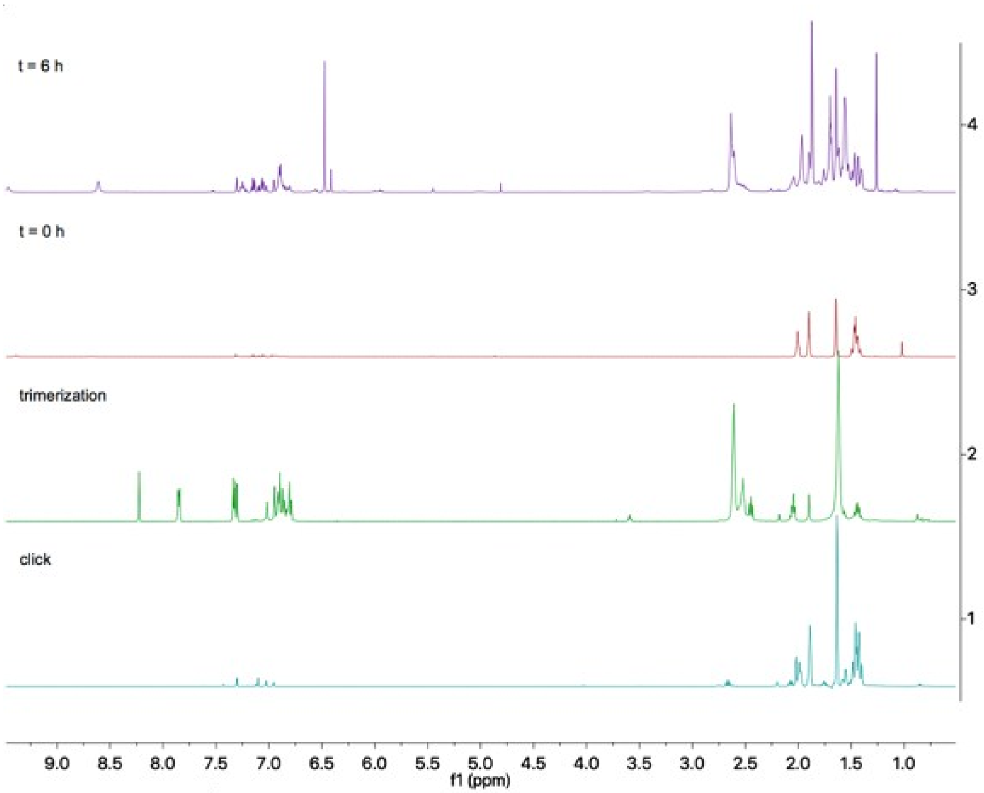


Figure S105: Stacked ^{1}H spectra of 1,7-octadiyne reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer (2) and click reaction (1) in C_6D_5Br.

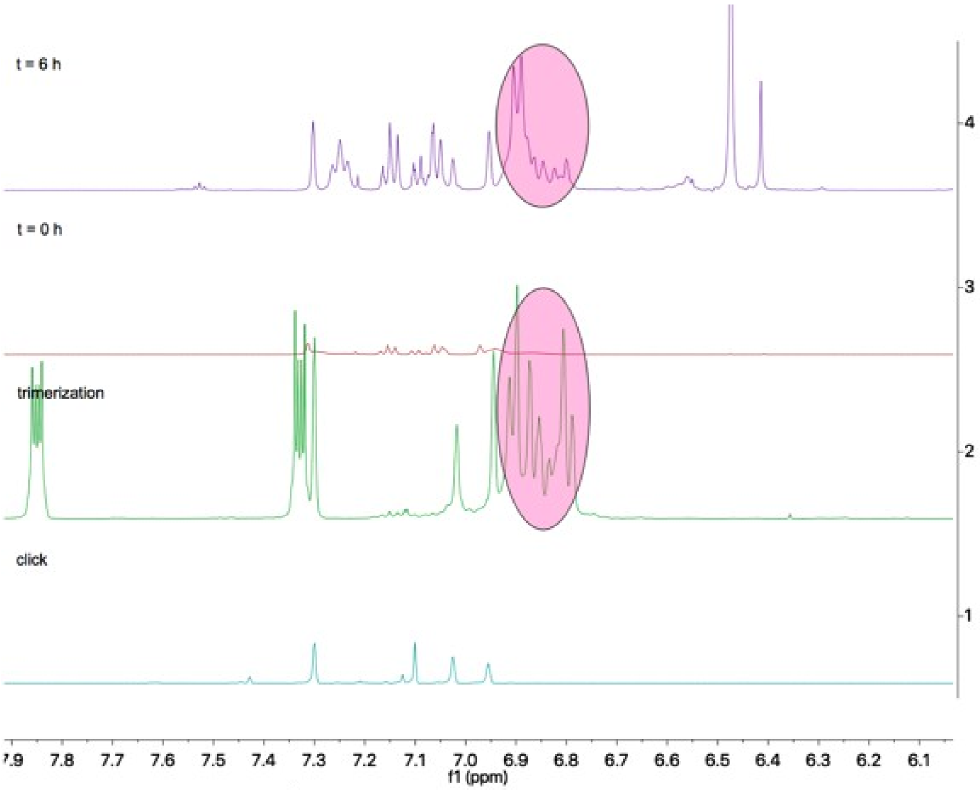


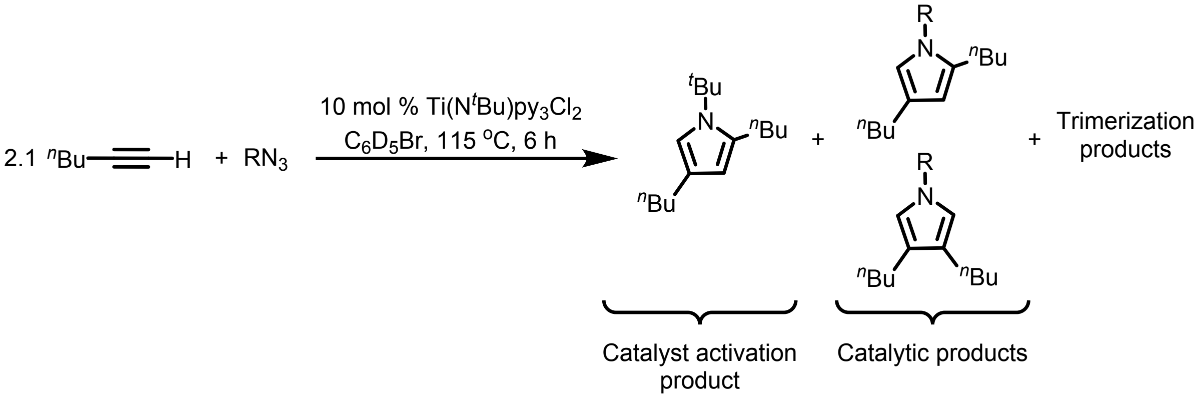
Figure S106: Zoom-in stacked ^{1}H spectra of 1,7-octadiyne reaction with 1-azidoadamantane t= 6 h (4), t = 0 h (3), trimer (2) and click reaction (1) in C_6D_5Br.

Table S3: Terminal alkyne scope triazole yield, trimer yield and mass balance data

Table 2, Entry #	**Alkyne**	**Triazole yield (%) 6**	**Trimer yield (%)^b 9**	**Azide mass balance (%)**	**Alkyne mass balance (%)**
1	1-Hexyne **2e**	10	24^c	quant.	quant.
2	(*p*-tolyl)acetylene **2f**	0	26	87	96
3	(*t*-butyl)acetylene **2g**	12	1	20	53
4	(trimethylsilyl)-acetylene **2h**	20	30	93	95
5^a	1,7-octadiyne **2i**	0	56	68	97

Conditions: AdN_3 (0.2 mmol, 1 equiv.), alkyne (0.42 mmol, 2.1 equiv.), 10 mol % $Ti(N^tBu)py_3Cl_2$, 115 °C, 6 h, 0.5 ml C_6D_5Br, average of 2 runs. ^{a}For **2i** (0.21mmol, 1.05 equiv.) was used. bTrimer yields are calculated with respect to alkyne. ^{c}1,2,4-trimer peak overlaps with the internal standard on NMR, results were supplemented by GC-FID.

Table S4: Azide scope with terminal alkynes



Entry #	Azide	Catalytic pyrrole yield (%)[a] 3	Trimer yield (%)[b] 9
1	Ad **1b**	65	8
2	Ph	38	8
3	Tol **1a**	40	8
4	*n*-Dec **1c**	7	32
5	Bn **1d**	0	20

Conditions : Azide (0.2 mmol, 1 equiv.), 1-hexyne (0.42 mmol, 2.1 equiv.), 10 mol % Ti(NtBu)py3Cl2, 115 °C, 6 h, 0.5 ml C6D5Br. [a]Pyrrole yields are calculated with respect to azide [b]Trimer yields are calculated with respect to alkyne.

Variable Time Normalization Data[10]

Reaction Order in Azide

A 5 mL stock solution of C_6D_5Br containing Ph_3CH (48.7 mg, 0.199 mmol, 0.0399 M), $Ti(NTol)(THF)_3I_2$ (62.9 mg, 0.101 mmol, 0.0202 M), and 1-azidoadamantane (178.8 mg, 1.009 mmol, 0.2017 M) was prepared using a 5 mL volumetric flask.

Three screw cap NMR tubes were then loaded with sample:
Sample A: The NMR tube was loaded with 0.50 mL of the stock solution, followed by 3-hexyne (57 µL, 0.50 mmol, 1.0 M) added *via* syringe.
Sample B: The NMR tube was charged with additional 1-azidoadamantane (11.1 mg, 0.063 mmol), followed by 0.50 mL of the stock solution and 3-hexyne (57 µL, 0.50 mmol, 1.0 M) *via* syringe.
Sample C: The NMR tube was charged with additional 1-azidoadamantane (6.3 mg, 0.036 mmol), followed by 0.50 mL of the stock solution and 3-hexyne (57 µL, 0.50 mmol, 1.0 M) *via* syringe.

Precise concentrations in solution were determined by ^1H NMR prior to heating the reactions. Time points were taken throughout the course of the reaction to obtain *in-situ* concentrations of reactants and products.

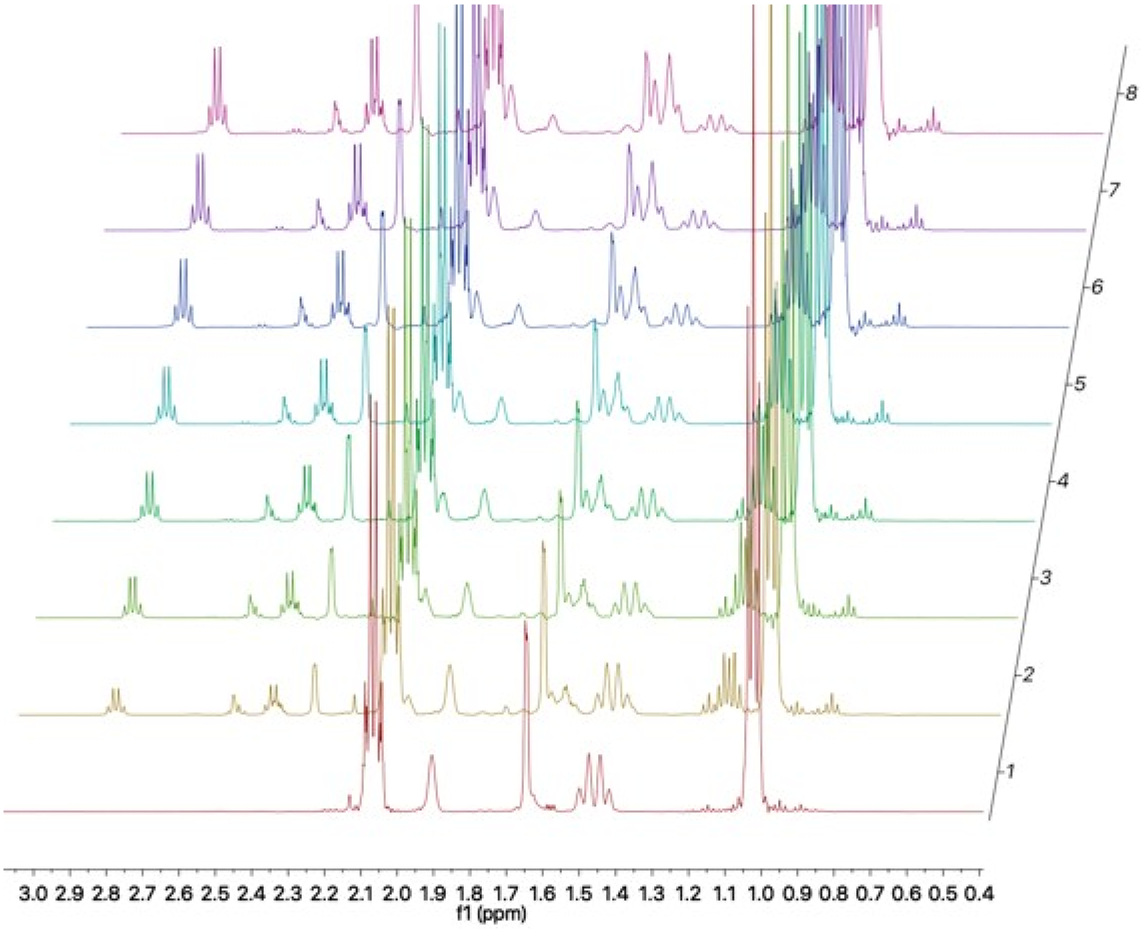


Figure S107: Zoom-in stacked ^1H spectra of time points in the reaction of Sample A.

Table S5: Concentrations and 0 order trapezoidal sum of time points of Sample A.

Sample A									**Azide**	
t (s)	AdN3 (Raw Int)	[AdN3]	3Hex (Raw Int)	[3Hex]	Cat	Pyrrole (Raw Int)	**[Pyrrole]**	[Trimer]	**0 Order** Trapezoidal	**Sum (Trapezoid)**
0	32.31	**0.21**	147.9	**0.98**	**0.017**	0	0	0	0	0
600	21.98	0.15	121.31	0.81	0.017	4.47	**0.045**	0	600	**600**
1265	17.63	0.12	112.07	0.74	0.017	7.12	**0.071**	0	665	**1265**
1797	15.23	0.10	111.54	0.74	0.017	8.45	**0.084**	0	532	**1797**
2516	13.1	0.09	107.35	0.71	0.017	9.79	**0.098**	0	719	**2516**
3809	10.76	0.07	102.13	0.68	0.017	11.06	**0.110**	0	1293	**3809**
4884	8.78	0.06	98.56	0.65	0.017	11.98	**0.119**	0	1075	**4884**
6214	7.88	0.05	97.61	0.65	0.017	13.11	**0.131**	0	1330	**6214**

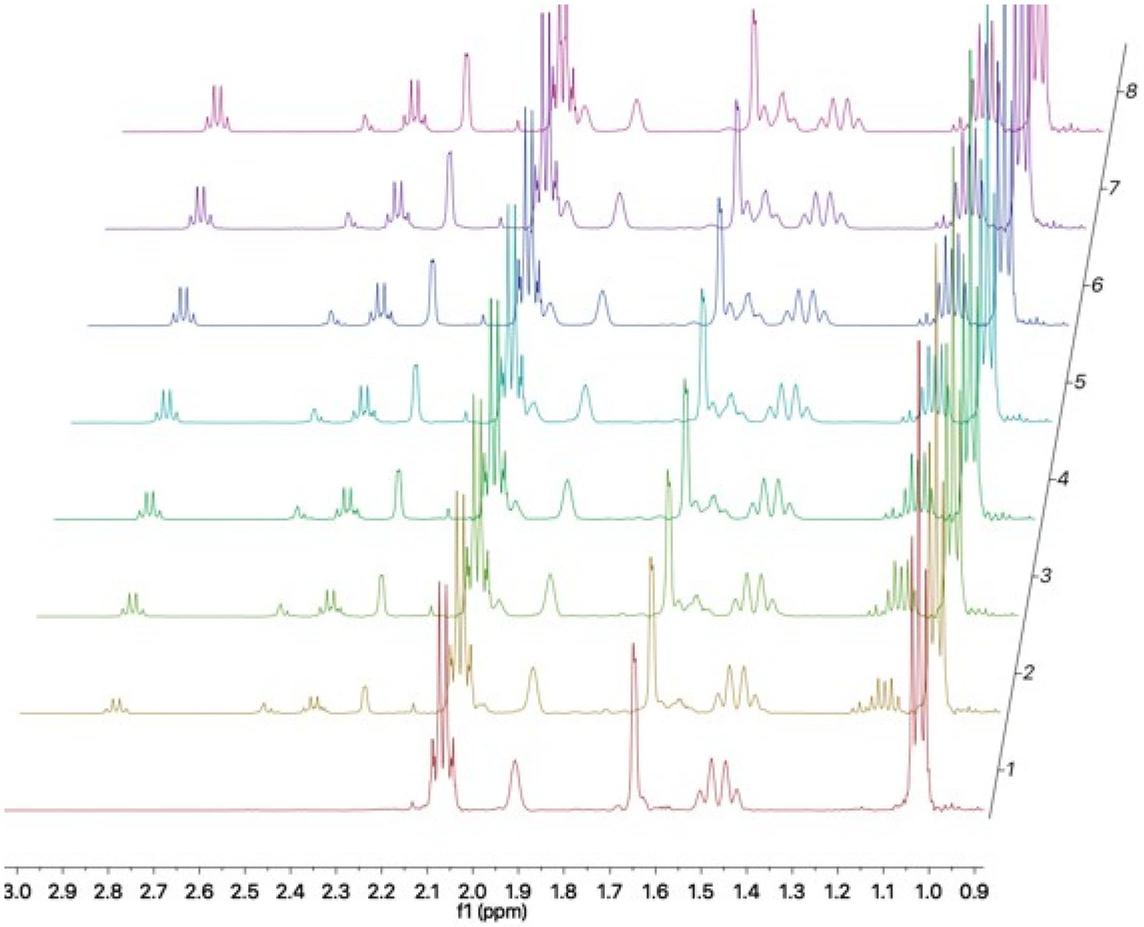


Figure S108: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample B.

Table S6: Concentrations and 0 order trapezoidal sum (with respect to azide concentration) of time points of Sample B.

Sample B									**Azide**	
t (s)	AdN3 (Raw Int)	[AdN3]	3Hex (Raw Int)	[3Hex]	Cat	Pyrrole (Raw Int)	**[Pyrrole]**	[Trimer]	**0 Order** Trapezoidal	**Sum (Trapezoid)**
0	50.42	**0.33**	151.28	**1.01**	**0.016**	0	**0**	0	0	0
637	41.29	0.27	126.95	0.84	0.016	4.95	**0.049**	0	637	**637**
1268	36.43	0.24	117.04	0.78	0.016	7.5	**0.075**	0	631	**1268**
1816	33.87	0.23	114.55	0.76	0.016	8.92	**0.089**	0	548	**1816**
2578	31.65	0.21	109.3	0.73	0.016	10.31	**0.103**	0	762	**2578**
3650	29.2	0.19	104.86	0.70	0.016	11.68	**0.116**	0	1072	**3650**
4709	27.57	0.18	102.31	0.68	0.016	12.71	**0.127**	0	1059	**4709**
6172	26.04	0.17	96.91	0.64	0.016	13.41	**0.134**	0	1463	**6172**

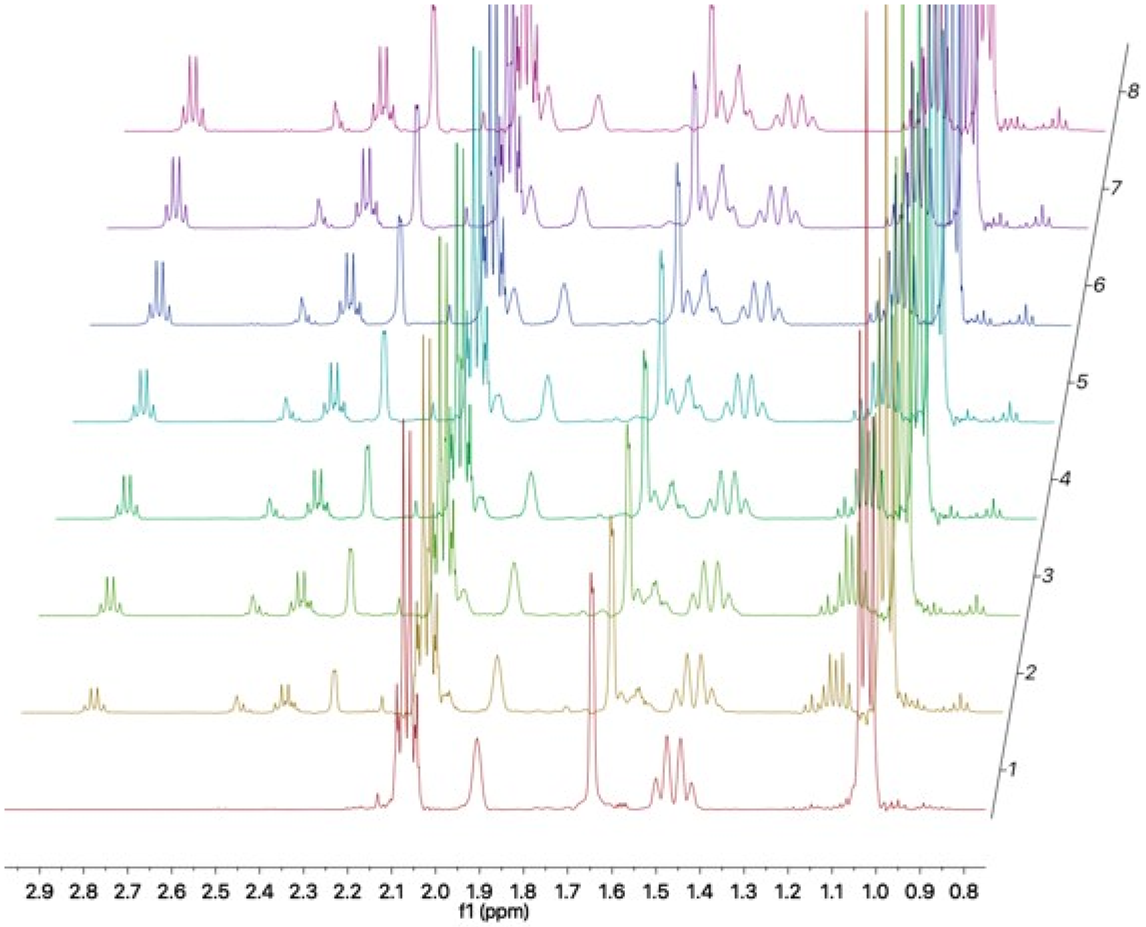


Figure S109: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample C.

Table S7: Concentrations and 0 order trapezoidal sum (with respect to azide concentration) of time points of Sample C.

Sample C									**Azide**	
	AdN3		3Hex			Pyrrole			**0 Order**	**Sum**
t (s)	(Raw Int)	[AdN3]	(Raw Int)	[3Hex]	Cat	(Raw Int)	**[Pyrrole]**	[Trimer]	Trapezoidal	**(Trapezoid)**
0	41.33	**0.27**	149.05	**0.99**	**0.017**	0	0	0	0	0
609	32.35	0.21	124.81	0.83	0.017	4.96	**0.049**	0	609	**609**
1245	27.83	0.18	115.97	0.77	0.017	7.37	**0.073**	0	636	**1245**
1802	25.49	0.17	114.78	0.76	0.017	8.41	**0.084**	0	557	**1802**
2405	23.33	0.15	110.21	0.73	0.017	9.68	**0.096**	0	603	**2405**
3596	20.42	0.14	103.16	0.69	0.017	11.27	**0.112**	0	1191	**3596**
4681	18.83	0.13	100.28	0.67	0.017	12.17	**0.121**	0	1085	**4681**
6226	17.52	0.12	99.01	0.66	0.017	12.95	**0.129**	0	1545	**6226**

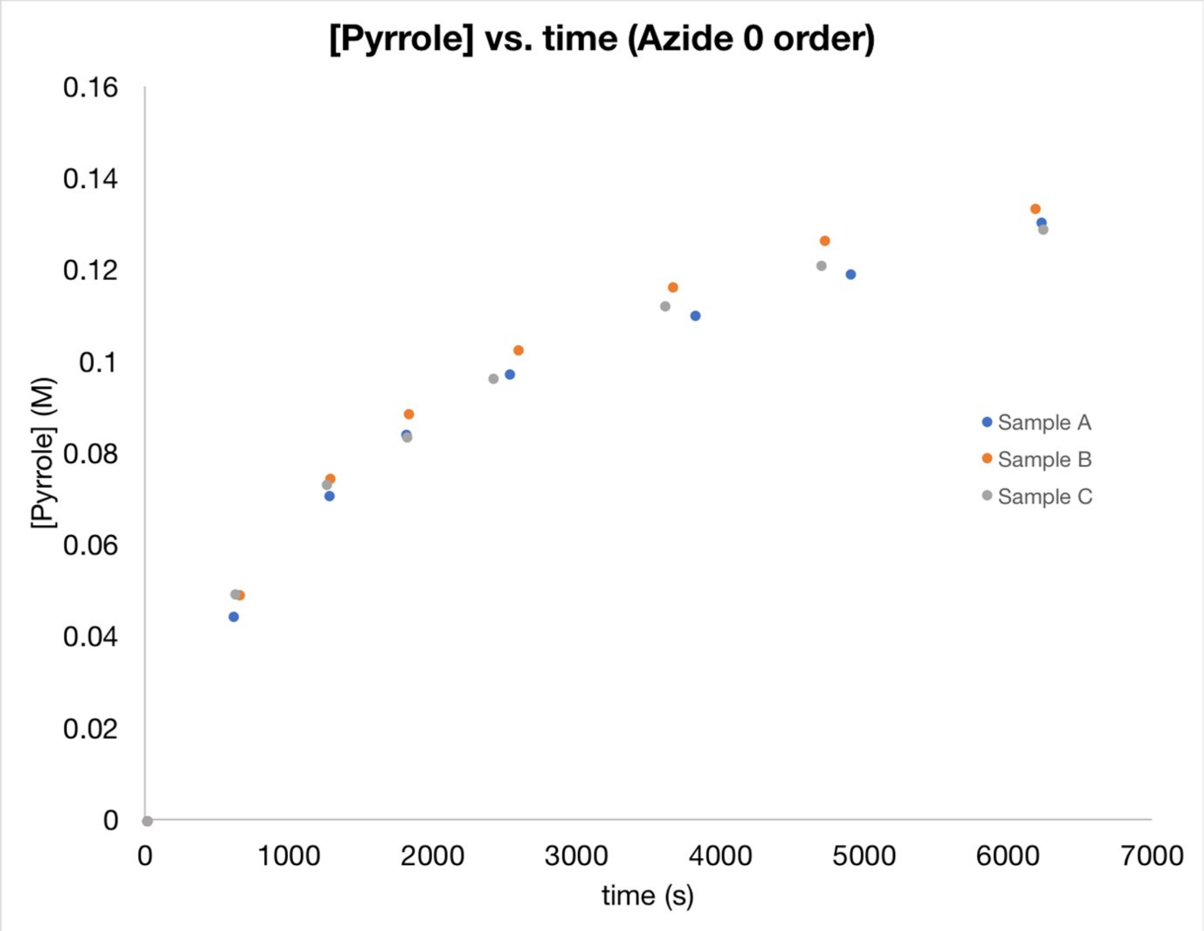


Figure S110: Concentration of pyrrole vs. time for Sample A ([AdN$_3$]$_0$ = 0.21 M), B ([AdN$_3$]$_0$ = 0.33 M) and C ([AdN$_3$]$_0$ = 0.27 M), showing 0th order with respect to AdN$_3$.

Reaction Order in Alkyne and Catalyst

A 5 mL stock solution of C_6D_5Br containing Ph_3CH (49 mg, 0.20 mmol, 0.040 M), Ti(Ntol)(THF)$_3$I$_2$ (125 mg, 0.20 mmol, 0.040 M), and 1-azidoadamantane (230 mg, 1.3 mmol, 0.26 M) was prepared using a 5 mL volumetric flask.

Five screw cap NMR tubes were then loaded with sample:
Sample A': The NMR tube was loaded with 0.50 mL of the stock solution, followed by 3-hexyne (45 µL, 0.40 mmol, 0.80 M) added *via* syringe.
Sample B': The NMR tube was loaded with 0.50 mL of the stock solution and 3-hexyne (52 µL, 0.46 mmol, 0.92 M) *via* syringe.
Sample C': The NMR tube was loaded with 0.50 mL of the stock solution and 3-hexyne (60 µL, 0.55 mmol, 1.1 M) *via* syringe.
Sample D': The NMR tube was charged with additional Ti(Ntol)(THF)$_3$I$_2$ (3.9 mg, 0.0063 mmol), followed by 0.50 mL of stock and 3-hexyne (45 µL, 0.40 mmol, 0.80 M).
Sample E': The NMR tube was charged with additional Ti(Ntol)(THF)$_3$I$_2$ (6.6 mg, 0.011 mmol) followed by 0.50 mL of stock and 3-hexyne (45 µL, 0.40 mmol, 0.80 M).

Precise concentrations in solution were determined by ^{1}H NMR prior to heating the reactions. Time points were taken throughout the course of the reaction to obtain *in situ* concentrations of reactants and products.

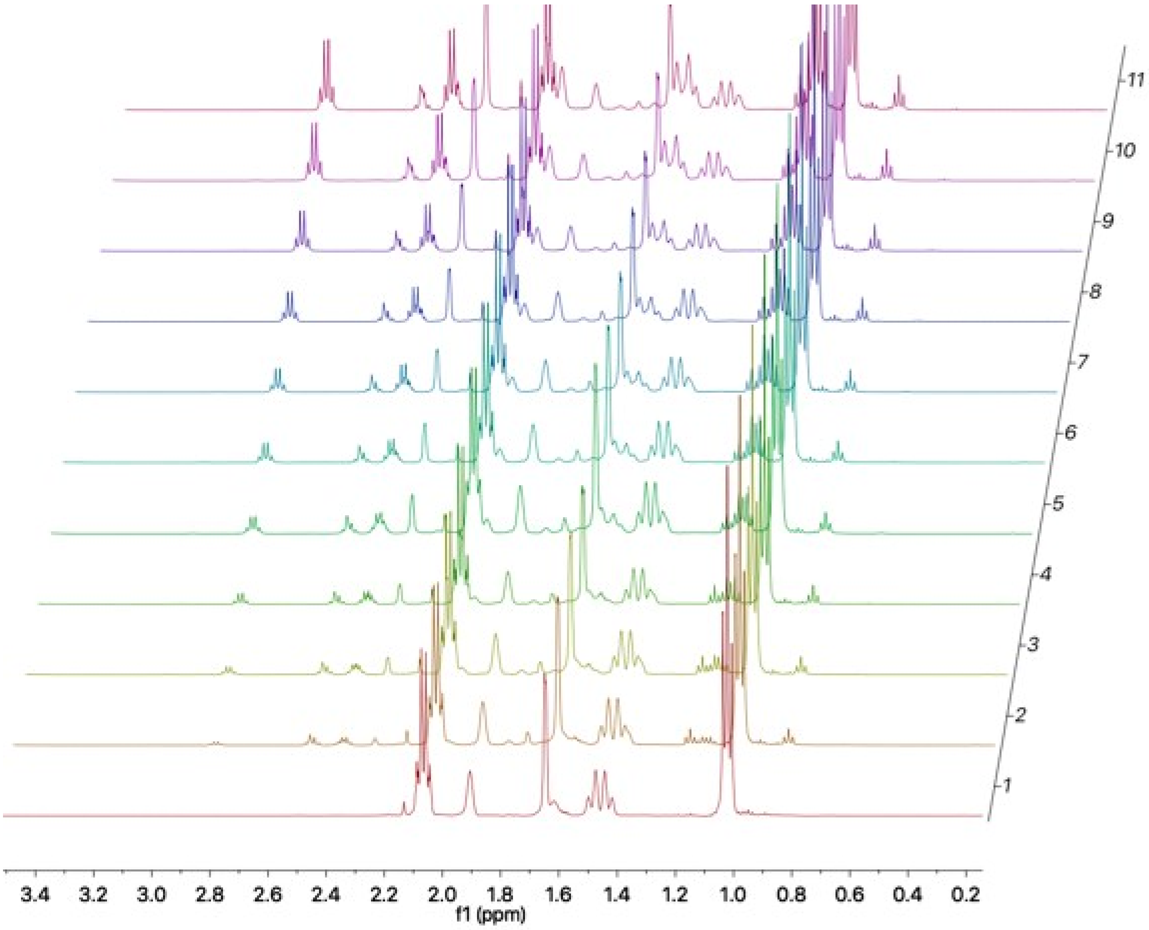


Figure S111: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample A'.

Table S8: Concentrations, second order trapezoidal sum (with respect to alkyne), and first order trapezoidal sum (with respect to catalyst) of time points of Sample A'.

t	AdN$_3$ (Raw Int)	**[AdN$_3$]**	3-Hex (Raw Int)	**[3-hex]**	[Cat]	Pyrrole (Raw Int)	**[Pyrrole]**	**Alkyne**		**Catalyst**
								2nd Order Trapezoidal	**Sum (Trapezoid)**	**First Order** Trapezoidal
0	20.870	0.278	104.590	0.697	0.030	0.000	**0.000**	0.000	**0.000**	0.000
210	16.450	0.219	86.350	0.576	0.030	0.990	**0.010**	85.069	**85.069**	6.258
660	15.380	0.205	81.250	0.542	0.030	2.660	**0.027**	140.449	**225.518**	19.668
1050	14.680	0.196	78.520	0.523	0.030	3.620	**0.036**	110.615	**336.132**	31.290
1590	13.420	0.179	72.500	0.483	0.030	4.810	**0.048**	136.842	**472.975**	47.382
2059	12.730	0.170	70.930	0.473	0.030	5.620	**0.056**	107.204	**580.178**	61.358
2782	12.180	0.162	68.220	0.455	0.030	6.980	**0.070**	155.547	**735.726**	82.904
3619	10.970	0.146	62.710	0.418	0.030	8.390	**0.084**	159.427	**895.152**	107.846
5246	9.200	0.123	54.780	0.365	0.030	10.810	**0.108**	249.544	**1144.696**	156.331
7560	7.740	0.103	48.500	0.323	0.030	12.980	**0.130**	274.254	**1418.950**	225.288
9394	6.960	0.093	44.940	0.300	0.030	13.980	**0.140**	177.919	**1596.869**	279.941

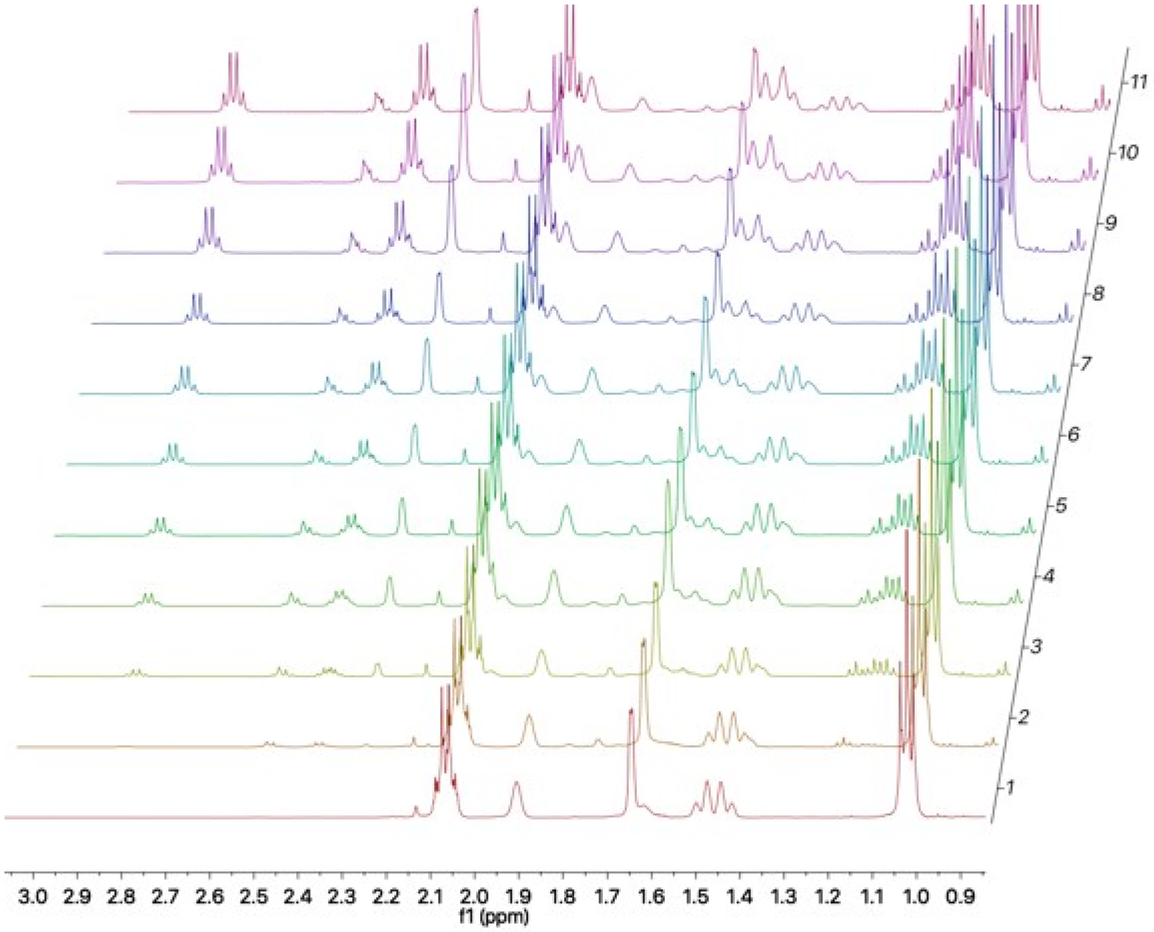


Figure S112: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample B′.

Table S9: Concentrations and second order trapezoidal sum (with respect to alkyne) of time points of Sample B′.

	AdN$_3$					Pyrrole		**2nd Order**	**Sum**
t	(Raw Int)	**[AdN$_3$]**	3-Hex (Raw Int)	**[3-hex]**	[Cat]	(Raw Int)	**[Pyrrole]**	Trapezoidal	**(Trapezoid)**
0	41.49	0.277	108.43	0.723	0.030	0	0	0	0
217	39.51	0.263	92.69	0.618	0.030	0.52	0.0052	97.528	97.528
724	34.95	0.233	88.14	0.588	0.030	3.05	0.0305	184.207	281.735
1121	32.26	0.215	82.52	0.550	0.030	4.69	0.0469	128.473	410.208
1697	29.06	0.194	76.79	0.512	0.030	6.55	0.0655	162.430	572.638
2163	27.28	0.182	73.85	0.492	0.030	7.65	0.0765	117.496	690.134
3019	24.56	0.164	68.94	0.460	0.030	9.5	0.095	193.922	884.056
3928	22.25	0.148	65.99	0.440	0.030	10.96	0.1096	183.882	1067.937
5549	18.39	0.123	57.81	0.385	0.030	13.1	0.131	276.046	1343.984
7785	15.06	0.100	52.43	0.350	0.030	14.82	0.1482	301.931	1645.915
9662	13.35	0.089	48.49	0.323	0.030	16.32	0.1632	212.411	1858.325

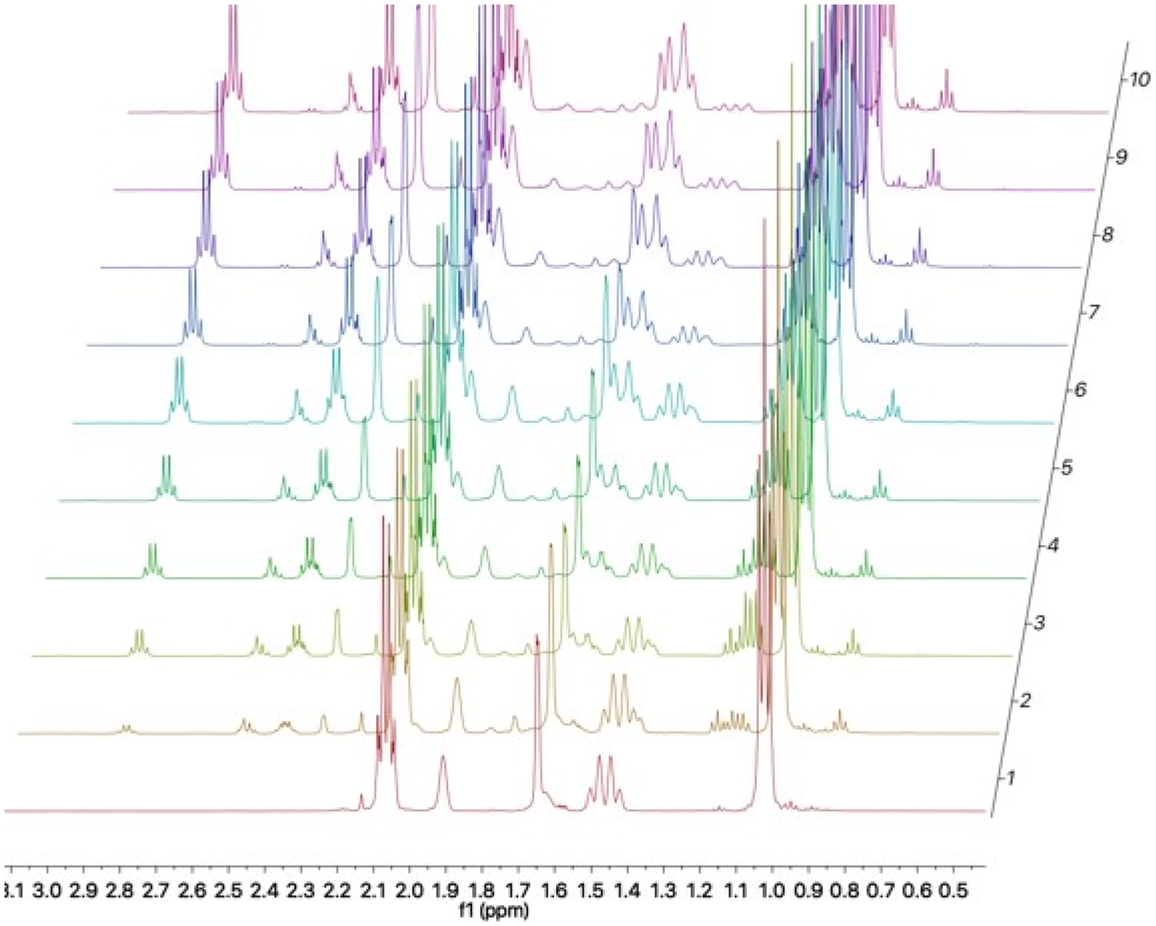


Figure S113: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample C'.

Table S10: Concentrations and second order trapezoidal sum (with respect to alkyne) of time points of Sample C'.

t	AdN_3 (Raw Int)	**[AdN_3]**	3-Hex (Raw Int)	**[3-Hex]**	[Cat]	Pyrrole (Raw Int)	**[Pyrrole]**	**2nd Order** Trapezoidal	**Sum (Trapezoid)**
0	42.67	0.284	145.75	0.972	0.030	0.00	0.000	0.00	0.00
271	35.69	0.238	120.99	0.807	0.030	2.09	0.021	214.24	214.24
937	29.80	0.199	107.94	0.720	0.030	6.76	0.068	387.83	602.07
1349	26.96	0.180	101.78	0.679	0.030	8.77	0.088	201.34	803.41
1727	25.31	0.169	98.21	0.655	0.030	10.11	0.101	167.98	971.39
3153	21.06	0.140	87.49	0.583	0.030	12.86	0.129	546.39	1517.78
4779	16.84	0.112	78.75	0.525	0.030	16.37	0.164	499.29	2017.07
6055	14.36	0.096	72.61	0.484	0.030	18.19	0.182	324.81	2341.88
7393	12.58	0.084	69.48	0.463	0.030	19.66	0.197	300.15	2642.03
9001	11.50	0.077	65.36	0.436	0.030	20.87	0.209	324.85	2966.88

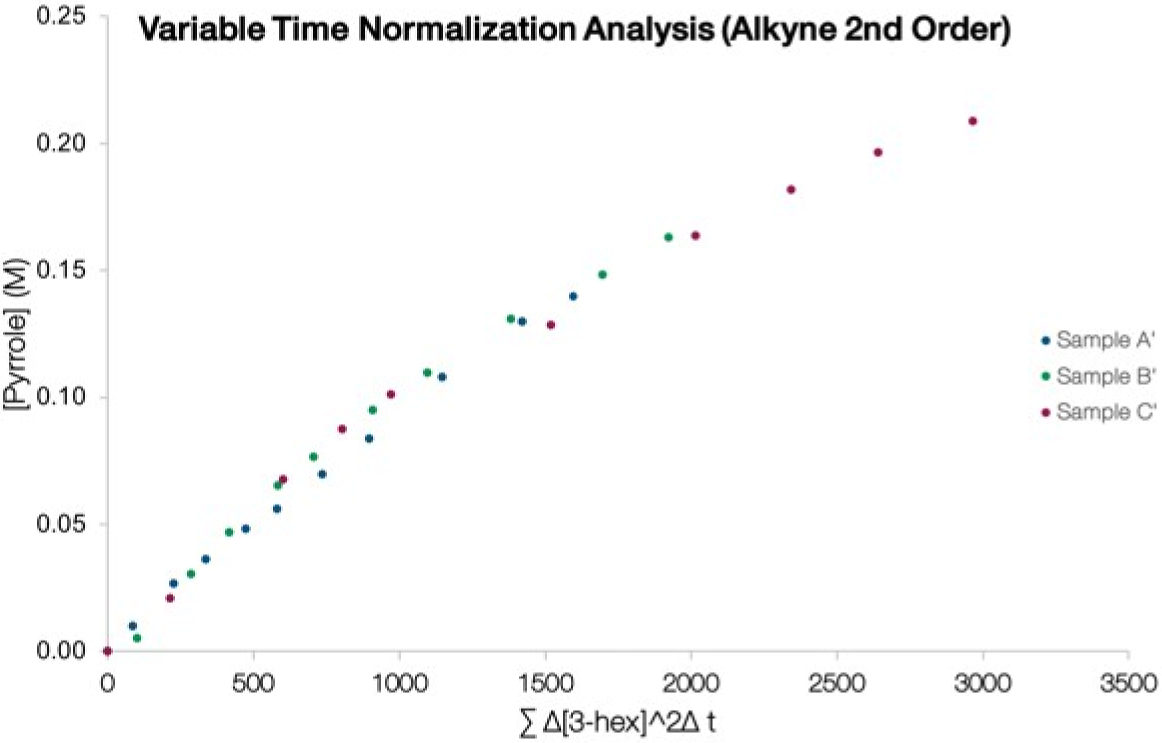


Figure S114: Concentration of pyrrole vs. time normalized for the concentration of 3-hexyne for Sample A' ($[3\text{-hex}]_0$ = 0.697 M), B' ($[3\text{-hex}]_0$ = 0.723 M), and C' ($[3\text{-hex}]_0$ = 0.972 M), showing 2nd order with respect to azide.

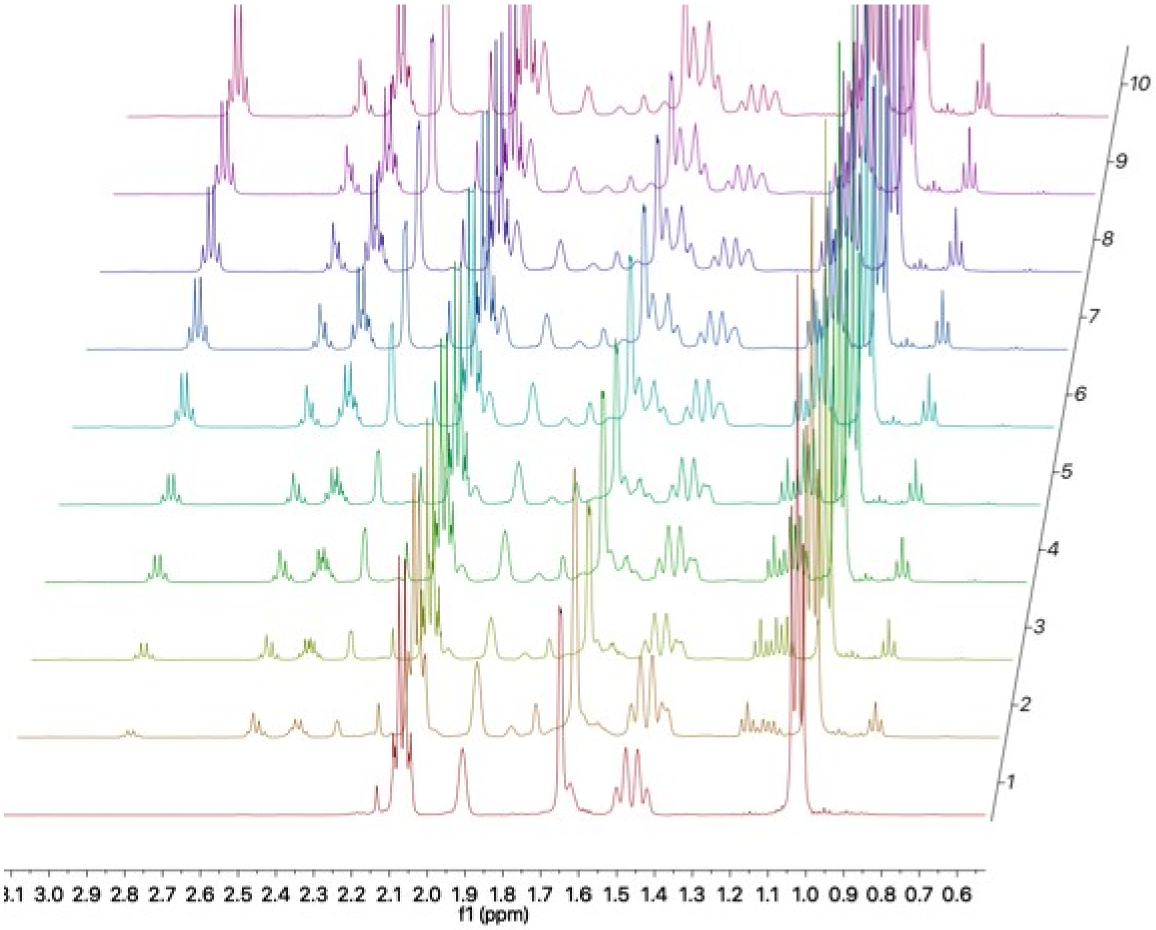


Figure S115: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample D'.

Table S11: Concentrations and first order trapezoidal sum (with respect to catalyst) of time points of Sample D'.

t	Cat	Pyrrole (Raw Int)	**[Pyrrole]**	**First Order** Trapezoidal
0	0.0416	0	0	0
270	0.0416	1.37	0.0137	11.232
690	0.0416	3.74	0.0374	28.704
1121	0.0416	5.36	0.0536	46.634
1534	0.0416	6.34	0.0634	63.814
3091	0.0416	9.42	0.0942	128.586
4600	0.0416	11.77	0.1177	191.360
6040	0.0416	13.27	0.1327	251.264
7338	0.0416	14.30	0.143	305.261
9001	0.0416	15.22	0.1522	374.442

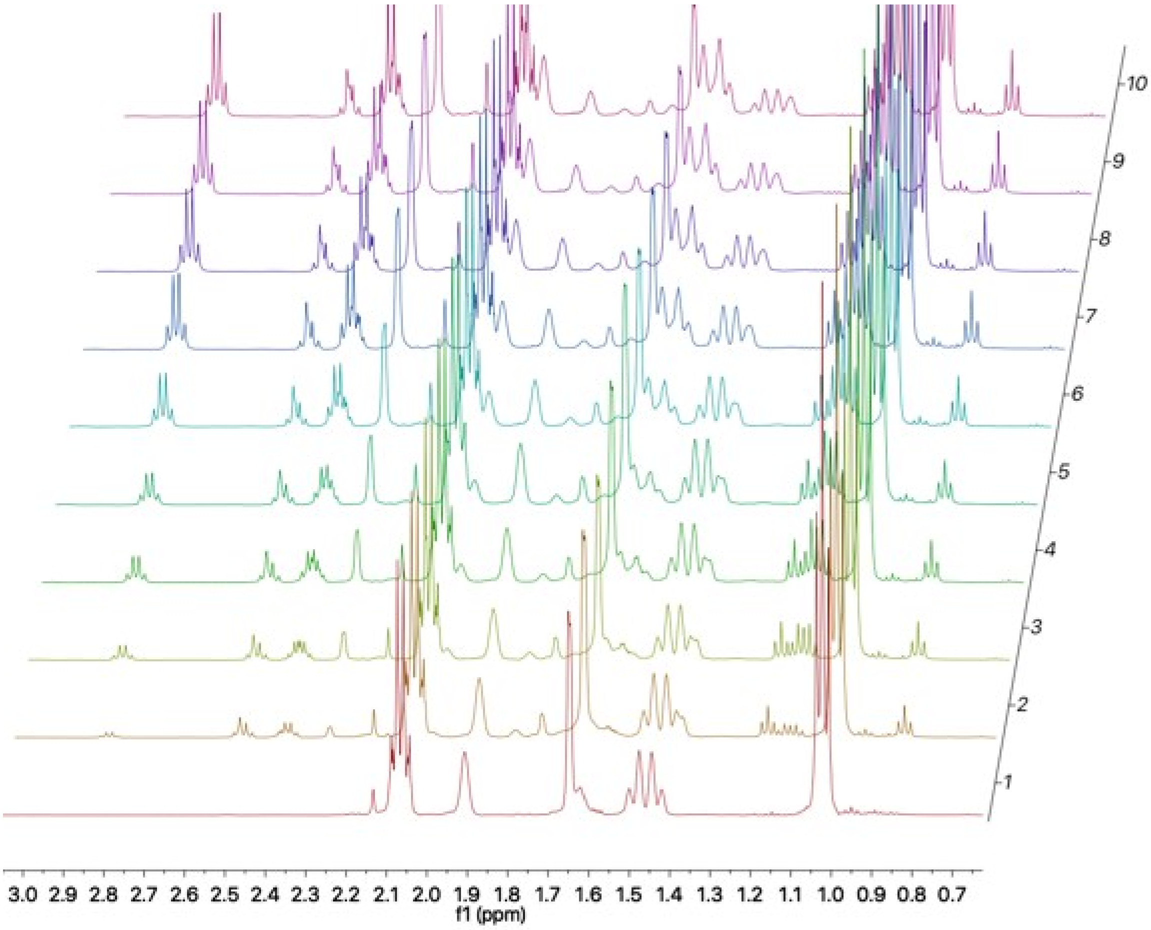


Figure S116: Zoom-in stacked ^{1}H spectra of time points in the reaction of Sample E'.

Table S12: Concentrations and first order trapezoidal sum (with respect to catalyst) of time points of Sample E'.

t	Cat	Pyrrole (Raw Int)	**[Pyrrole]**	**First Order** Trapezoidal
0	0.0408	0	0	0
276	0.0408	1.15	0.0115	11.261
799	0.0408	3.16	0.0316	32.599
1181	0.0408	5.17	0.0517	48.185
1591	0.0408	5.79	0.0579	64.913
3126	0.0408	9.24	0.0924	127.541
4560	0.0408	11.64	0.1164	186.048
6005	0.0408	13.03	0.1303	245.004
7262	0.0408	14.26	0.1426	296.290
9005	0.0408	15.10	0.151	367.404

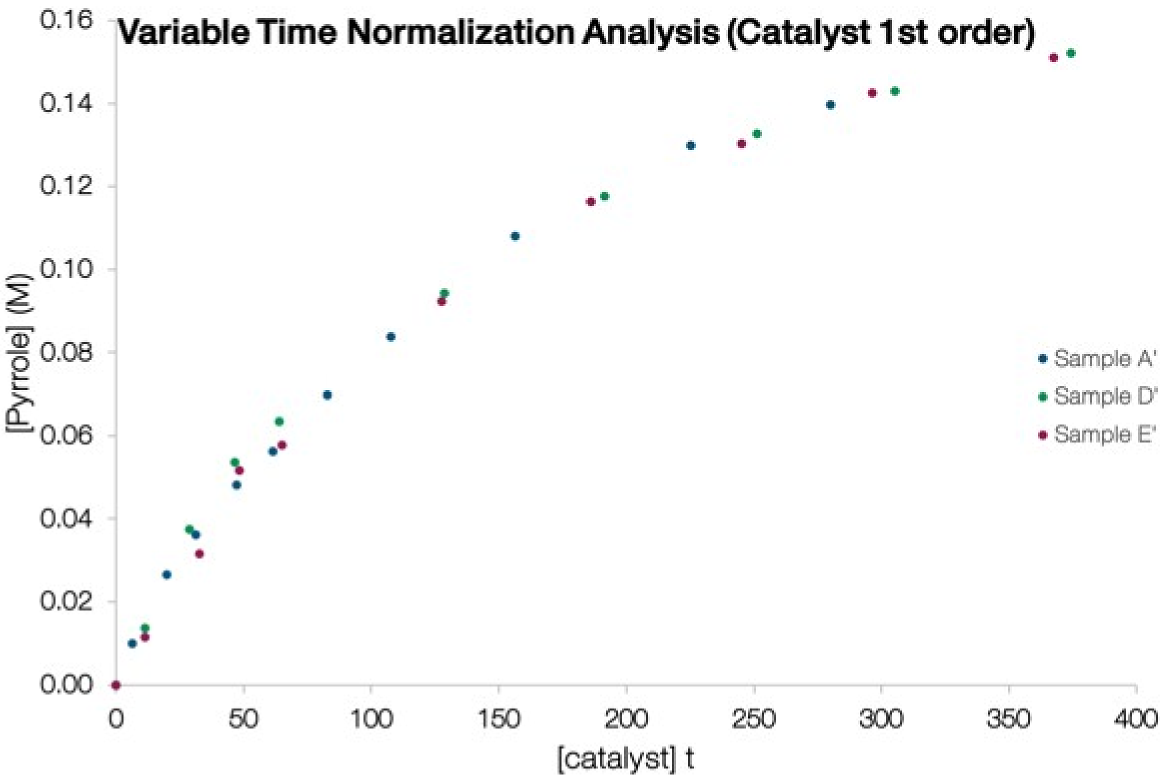


Figure S117: Concentration of pyrrole vs. time normalized for the concentration of 3-hexyne for Sample A' ($[Ti]_0$ = 0.030 M), D' ($[Ti]_0$ = 0.041 M), and E' ($[Ti]_0$ = 0.042 M), showing 1st order with respect to $(THF)_3TiI_2(Ntol)$.

Initial Rates for *n*-decN$_3$ reaction with 3-hexyne

Procedure

To a screw cap NMR tube, a volume of each stock plus C_6D_5Br for dilution was added *via* syringe to a total of 0.5 mL. The mixtures were heated at 115˚C for 120 seconds, and the reaction mixtures were analysed *in situ* by NMR.

Stock solutions

Azide (*n*-decN$_3$) - Stock: 0.496 M decN$_3$
Alkyne (3-hexyne) - Stock: 2.51 M 3-hexyne
Catalyst ($(THF)_3TiI_2(Ntol)$) - Stock: 0.0493 M $(THF)_3TiI_2(Ntol)$
Ph_3CH Standard - Stock: 0.101 M Ph_3CH

Table S13: Dilution table for the preparation of reaction mixtures A-G.

Reaction	**Standard** (µL)	**Azide** (µL)	**Alkyne** (µL)	**Catalyst** (µL)	**Dilution** (µL)	**Total** (µL)
A	100	100	100	100	100	500
B	100	50	100	100	150	500
C	100	150	100	100	50	500
D	100	100	50	100	150	500
E	100	100	150	100	50	500
F	100	100	100	50	150	500
G	100	100	100	150	50	500

Table S14: Initial concentrations of reagents and catalysts, and concentration of pyrrole product after 120 seconds for reaction mixtures A-G.

Variable	**Reaction**	**[Azide]**	**[Alkyne]**	**[Catalyst]**	**[Standard]**	**pyrrole (int)**	**[pyrrole]**
Basic Run	A	0.0992	0.502	0.00986	0.0202	5.32	**0.027**
Azide	B	0.0496	0.502	0.00986	0.0202	6.99	**0.035**
	C	0.149	0.502	0.00986	0.0202	4.68	**0.024**
Alkyne	D	0.0992	0.251	0.00986	0.0202	2.82	**0.014**
	E	0.0992	0.753	0.00986	0.0202	7.91	**0.040**
Catalyst	F	0.0992	0.502	0.00493	0.0202	3.43	**0.017**
	G	0.0992	0.502	0.0148	0.0202	6.63	**0.033**

Table S15: Ratio of initial concentrations of reagents and catalyst, and concentrations of pyrrole product after 120 seconds, compared to the ratio of the initial concentrations of reagents and catalyst raised to the power of best fit.

Rxn/Rxn	**[Azide]/[Azide]**	[Pyrrole]/[Pyrrole]	**inverse half [azide]/[azide]**
A/B	2	0.761	**0.707**
C/A	1.5	0.880	**0.816**
C/B	3	0.670	**0.577**
	[Cat]/[Cat]		**half order [catalyst]/[catalyst]**
A/F	2	1.55	**1.41**
G/A	1.5	1.25	**1.22**
G/F	3	1.93	**1.73**
	[Alkyne]/[Alkyne]		
A/D	2	1.89	
E/A	1.5	1.49	
E/D	3	2.80	

References

1. Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1970,** *92,* 5625-5640.
2. J. Blake, A.; E. Collier, P.; C. Dunn, S.; Li, W.-S.; Mountford, P.; V. Shishkin, O. *J. Chem. Soc., Dalton Trans.* **1997,** 1549-1558.
3. See, X. Y.; Beaumier, E. P.; Davis-Gilbert, Z. W.; Dunn, P. L.; Larsen, J. A.; Pearce, A. J.; Wheeler, T. A.; Tonks, I. A. *Organometallics* **2017,** *36,* 1383-1390.
4. Zhou, S.; Liao, H.; Liu, M.; Feng, G.; Fu, B.; Li, R.; Cheng, M.; Zhao, Y.; Gong, P. *Bioorg. Med. Chem.* **2014,** *22,* 6438-6452.
5. Gannarapu, M. R.; Vasamsetti, S. B.; Punna, N.; Kotamraju, S.; Banda, N. *MedChemComm* **2015,** *6,* 1494-1500.
6. Byeang Hyean, K.; Sun Min, P. S. L., Yoon 2'-deoxyuridine derivatives and hydrogels formed therewith US 6884882 B1, Apr 26, 2005, 2005.
7. Goswami, P. P.; Suding, V. P.; Carlson, A. S.; Topczewski, J. J. *Eur. J. Org. Chem.* **2016,** *2016,* 4805-4809.
8. Zhang, S.-L.; Xue, Z.-F.; Gao, Y.-R.; Mao, S.; Wang, Y.-Q. *Tetrahedron Lett.* **2012,** *53,* 2436-2439.
9. Rassadin, V. A.; Nicolas, E.; Six, Y. *Chem. Commun.* **2014,** *50,* 7666-7669.
10. (a) Burés, J. *Angew. Chem. Int. Ed. Engl.* **2016,** *55,* 2028-2031; (b) Burés, J. *Angew. Chem. Int. Ed. Engl.* **2016,** *55,* 16084-16087.