

Supporting Information
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Supporting Information

Copper on iron: catalyst and scavenger for azide-alkyne cycloaddition

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General

Unless otherwise indicated, all starting materials were obtained from commercial suppliers, and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F₂₅₄. Visualization was performed with a 254 nm UV lamp. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-250 spectrometer in CDCl₃. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (δ 7.26 for ¹H, δ 77.0 for ¹³C). Coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet). Combination gas chromatography and low resolution mass spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 μ m HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230°C; interface: 300°C). IR spectra were obtained on a Bruker IFS55 spectrometer on a single-reflection diamond ATR unit. All melting points were measured on Büchi 501 apparatus and are uncorrected. High-resolution mass spectra were recorded on an Agilent Technologies 6210 Time of Flight mass spectrometer.

Microstructure of the powders was examined by powder X-ray diffraction (XRD) on a Philips Xpert diffractometer using Cu-K α radiation in the range of 30 to 130 deg with a step width of 0.02 deg in θ -2 θ geometry. The instrumental pattern was measured on a NIST SRM660a LaB₆ peak profile standard material. Morphology studies were performed on a FEI Quanta dual-beam scanning electron microscope (SEM) in backscattered electron (BSE) mode. Compositional changes were quantitatively determined by energy dispersive X-ray (EDX) analysis with a relative accuracy of 3 %.

The copper contents were measured with AAS. About 10 mg of the samples were dissolved in 0.5 ml cc HNO₃ and diluted to 10 ml by 1:1 MeOH/dist. water. These solutions were analyzed by FAAS (flame atomic absorption spectrometry) and GFAAS (graphite furnace atomic absorption spectrometry) by means of a Perkin Elmer AAnalyst 800 atomic absorption spectrometer. External calibration with matrix-matched standards were used. The recoveries were between 90-106%, the reproducibility of the sampling was below 5%.

Results of XRD measurements.

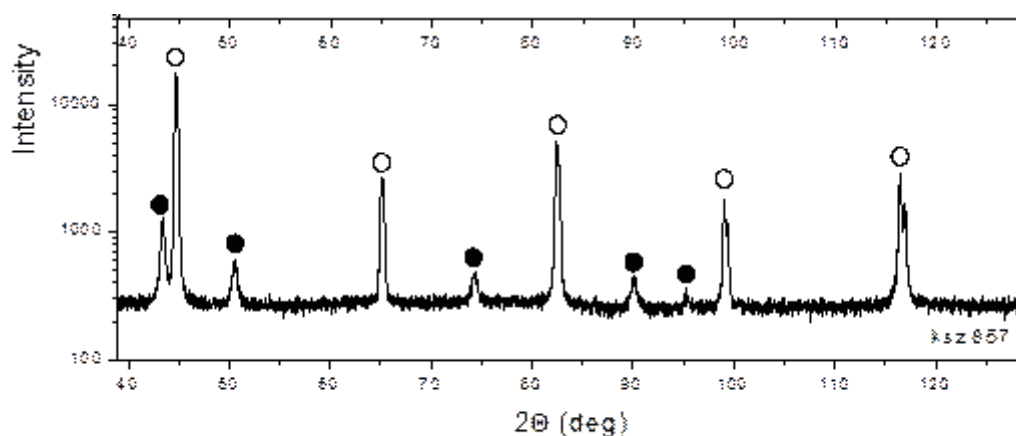
Original Cu/Fe catalyst

hkl	2 Θ [deg] (from fit)	2 Θ [deg] (literature)	$\Delta(2\Theta)$ [deg] (from fit)	d [nm]
111	43.37	43.33	0.41	23
200	50.54	50.48	0,54	18
220	74.31	74.20	0.56	20
311	90.10	90.02	0.71	18

~20 nm

from peak-intensities: $I_{111}(\text{Cu}) / I_{110}(\text{Fe}) = 0.055$

from peak-shift: $a_{\text{Cu}} = 0.3612$ nm (literature value: 0.3615 nm) deviation: -0.1%



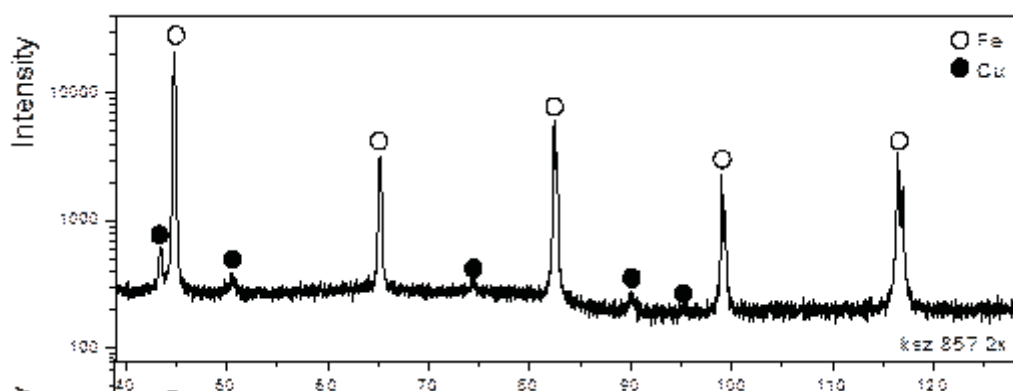
Cu/Fe catalyst after 2nd use

hkl	2 Θ [deg] (from fit)	2 Θ [deg] (literature)	$\Delta(2\Theta)$ [deg] (from fit)	d [nm]
111	43.43	43.33	0.31	30
200	50.56	50.48	0.43	23
220	74.33	74.20	0.41	27
311	---	90.02	----	---

~27 nm

from peak-intensities: $I_{111}(\text{Cu}) / I_{110}(\text{Fe}) = 0.016 \rightarrow$ the relative amount of Cu is decreased to 28 % of the initial state.

from peak-shift: $\lambda_{\text{Cu}} = 0.3608 \text{ nm}$ (literature value: 0.3615 nm) deviation: -0.2%



The Preparation of Copper on Iron Catalyst

To a round-bottom flask was charged with iron powder (5 g, 89.5 mmol) and water (deoxygenated with argon) (50 mL). The aqueous solution of CuSO_4 (125.6 mg, 0.79 mmol) (50ml) was dropped in the mixture under argon atmosphere over 1h and stirred with mechanic-stirrer vigorously for 3 h. The catalyst was separated with magnet and washed with deoxygenated water ($5 \times 20 \text{ mL}$) then acetone ($3 \times 20 \text{ mL}$) and dried under reduced pressure.

General procedure for the solvent screening

A mixture of terminal acetylene (0.5 mmol, 1 eq.), azide (0.5 mmol, 1 eq.) and 5 mol% Cu/Fe (5 w/w%) (32 mg, 0.025 mmol Cu) in DCM (300 μL) were heated at 30 °C. After 5 hour samples were taken and the conversions were determined by GC analysis.

Entry	Solvent	Conversion(%) ^a
1	DMF	5
2	EtOH	8
3	H ₂ O	80 ^b
4	MeCN	82
5	toluene	31
6	DCM	100

a: determined by GC, b: after 8 h.

General procedure for the catalyst screening

A mixture of terminal acetylene (1.5 mmol, 1 eq.), azide (1.5 mmol, 1 eq.) and 5 mol% Cu/Fe (5 w/w%) (96 mg, 0.075 mmol Cu) in DCM (900 μ L) were heated at 30 °C. After 4 hour samples were taken and the conversions were determined by GC analysis.

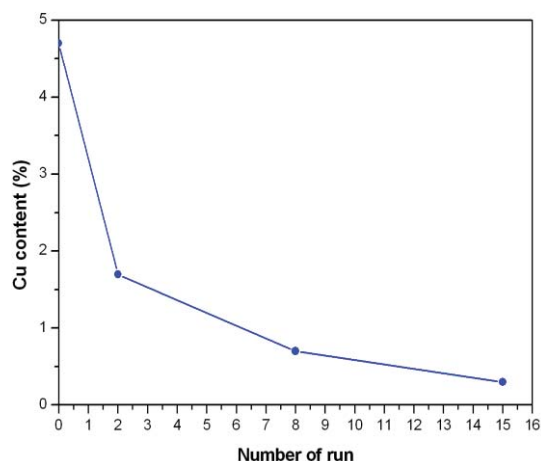
Entry	Catalyst	Conversion (%)
1	Fe powder	0
2	Cu turnings	10
3	Cu powder(\sim 500 μ m)	9
4	Cu powder(<100 μ m)	82
5	(1 wt%) Cu/Fe	97
6	(5 wt%) Cu/Fe	98

Recycling of the catalyst

A mixture of terminal acetylene (1.5 mmol, 1 eq.), azide (1.5 mmol, 1 eq.) and 5 mol% Cu/Fe (5 w/w%) (96 mg, 0.075 mmol Cu) in DCM (900 μ L) were heated for 7 h at 30 °C. The mixture was diluted with DCM (5 mL) and the catalyst was separated with magnet and washed with DCM (4 \times 5 mL) and acetone (2 \times 5 mL), dried under vacuum and was reused more than 10 times under the same conditions. In each run samples were taken after 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 7 hours and the conversions were determined by GC analysis

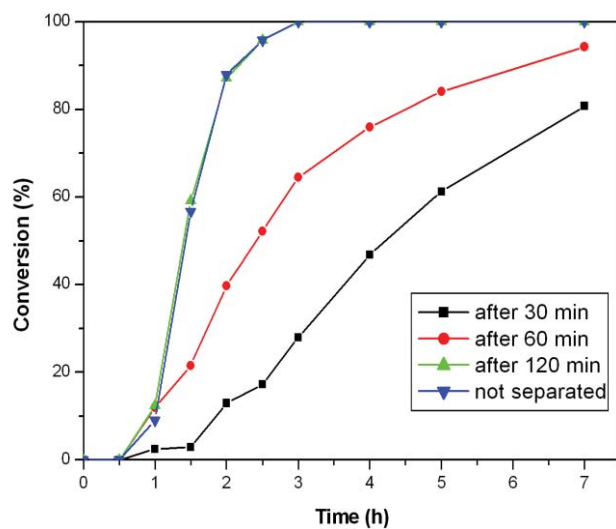
Determination of the copper content of catalysts

A mixture of terminal acetylene (1.5 mmol, 1 eq.), azide (1.5 mmol, 1 eq.) and 5 mol% Cu/Fe (5 w/w%) (96 mg, 0.075 mmol Cu) in DCM (900 μ L) were heated for 7 h at 30 °C. The mixture was diluted with DCM (5 mL) and the catalyst was separated with magnet and washed with DCM (4 \times 5 mL) and acetone (2 \times 5 mL), dried under vacuum and was reused more than 10 times under the same conditions. After the 2, 4, 8, 15 run the copper content of the catalyst was measured with AAS.



Examination of heterogeneity of the catalysis

A mixture of terminal acetylene (0.75 mmol, 1 eq.), azide (0.75 mmol, 1 eq.) and 5 mol% Cu/Fe (5 w/w%) (48 mg, 0.0375 mmol Cu) in DCM (450 μ L) were heated at 30 $^{\circ}$ C. After 30, 60 and 120 min. The catalyst was separated and samples were taken from the beginning after 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 7 hours and the conversions were determined by GC analysis



Copper contamination effect

To prove this assumption we studied the supposed ligand acceleration in the reaction. Into the reaction mixture of the Cu/Fe catalyzed click reaction of benzylazide and phenylacetylene we added 10 mol% of the appropriate triazole product at the beginning of the reaction. The induction period of the reaction was not observed, but the gradient of the curve showed the same reaction rate previously observed under the generally applied reaction conditions, indicating the relevance of strong ligand effect of the product in the catalytic transformation (Figure 1. Curve ■).

However, the triazole ligand utilized in this study was originated from a standard homogeneous $\text{Cu}(\text{PPh}_3)_2\text{NO}_3$ catalyzed click reaction. Despite the recrystallization of the triazole product after its synthesis, it might contain copper impurities, therefore we checked the possible copper contamination effect on the reaction. Running the reaction with 10 mol% triazole in the absence of Cu/Fe catalyst, surprisingly, we detected the heterocyclic product (Figure 1. Curve □). We observed the selective formation of the 1,4 regioisomer of the triazole compound signaling the presence of copper contaminants in the added ligand (612 $\mu\text{g/g}$ copper was measured by AAS). To exclude the copper impurities effect we synthesized the triazole regioisomers under classic thermal conditions without copper catalyst. We checked the activity of copper-free triazoles in azide alkyne click reaction in the absence of Cu/Fe catalyst, and we did not observe the formation of triazoles even after 48 hours (Figure 1. Curve Δ). With this ligand, in the presence of 5 mol% Cu/Fe catalyst the induction period was shorter (Figure 1. Curve \blacktriangle) than the ligand free version (Figure 1. Curve \bullet) and longer than it was found in the case of reaction performed with copper contaminated triazole (Figure 1. Curve ■). On the basis of the results of these experiments we conclude that the triazole product accelerates its formation in this transformation supposedly through coordination to copper.

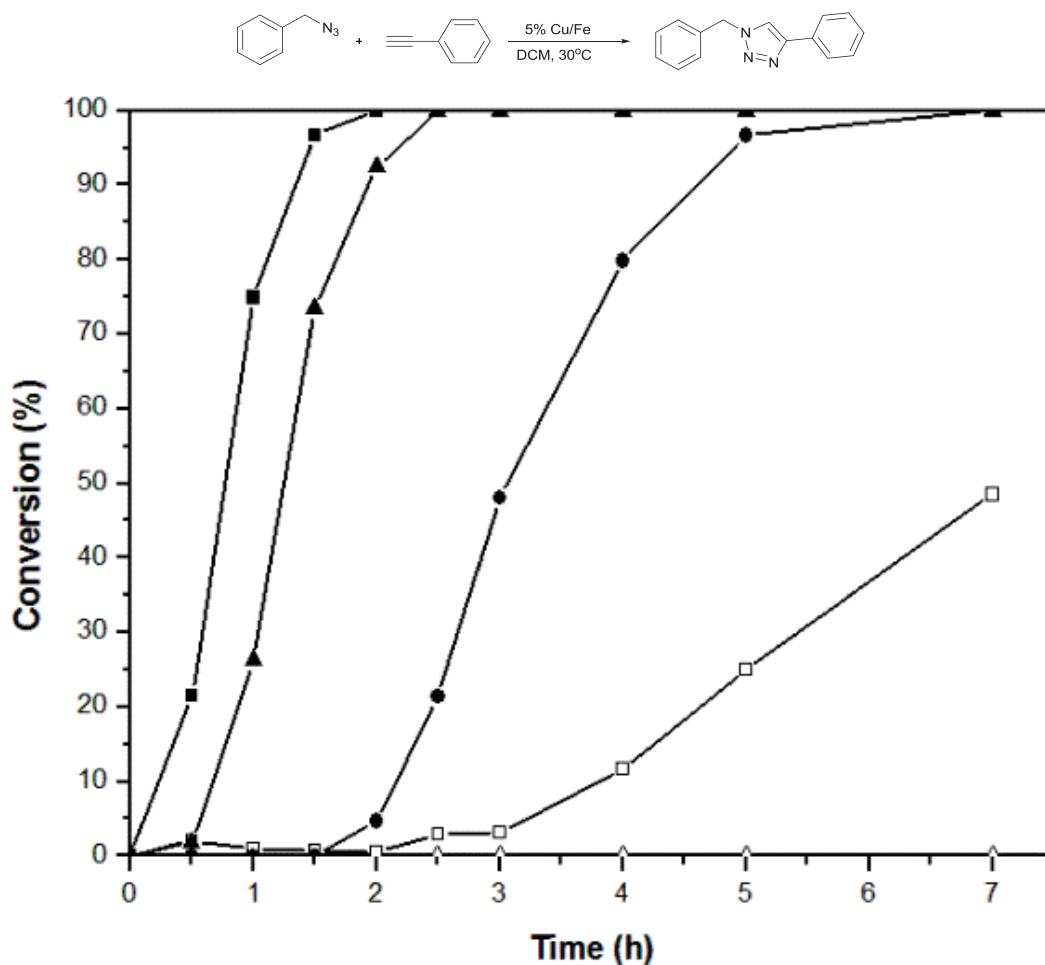
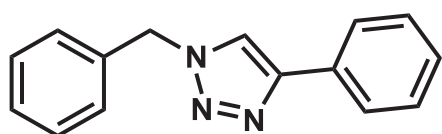


Figure 1. Study of ligand acceleration. A mixture of terminal acetylene (0.75 mmol, 1 eq.), azide (0.75 mmol, 1 eq.) and 5 mol% Cu/Fe (5w/w%) (48 mg, 0.0375 mmol Cu) in DCM (450 μ L) were stirred at 30 $^{\circ}$ C. ■: reaction with 10 mol% triazole prepared in copper catalyzed click reaction. ▲: reaction with 10 mol% triazole prepared in thermal click reaction (copper free). ●: reference reaction; □: reaction in the absence of Cu/Fe catalyst with 10 mol% triazole prepared in homogeneous copper catalyzed click reaction (measured copper content: 612 μ g/g). △: reaction in the absence of Cu/Fe catalyst with 10 mol% triazole prepared in thermal click reaction (copper free).

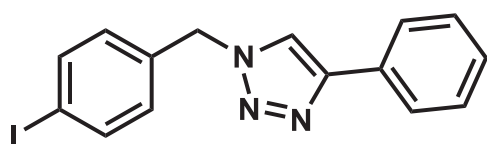
Synthesis of Triazoles

A mixture of terminal acetylene (0.5 mmol, 1 eq.), azide (0.5 mmol, 1 eq.), 5 mol% Cu/Fe (5 w/w%) (32 mg, 0.025 mmol Cu) and DCM (200 μ L) were heated for 8-24 h at 30 $^{\circ}$ C. After the appropriate time the mixture was diluted with DCM (5 mL). The catalyst was separated with magnet and washed with DCM (4 \times 5 mL). The organic phase was separated and dried with Na₂SO₄, filtered, and the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give desired triazole.

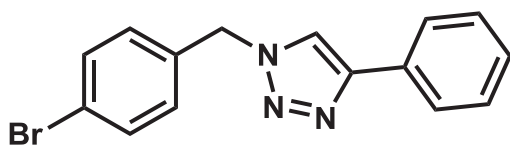
Characterization of the products



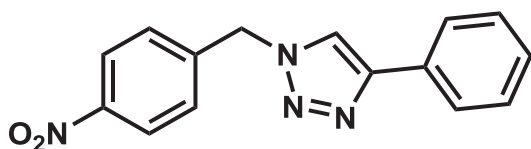
1-Benzyl-4-phenyl-1H-1,2,3-triazole (3aa)¹ General procedure was followed (8 h), white solid, 115 mg (0.49mmol, 98% yield), Mp.: 128-130 $^{\circ}$ C, R_f = 0.48 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.81 (d, 2H, J = 6.75 Hz), 7.69 (s, 1H), 7.42-7.27 (m, 8H), 5.53 (s, 2H), ¹³C NMR (62.5 MHz, CDCl₃): δ 148.0, 134.6, 130.4, 128.9, 128.6, 128.5, 128.0, 127.8, 125.5, 119.5, 54.0, MS (EI, 70 eV): m/z (%): 235(8, [M⁺]), 206(24), 180(8), 130(9), 116(100), 104(24), 91(97), 65(25).



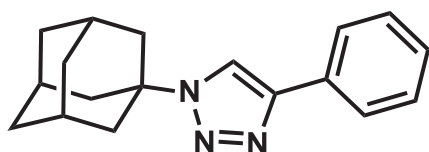
1-(4-Iodobenzyl)-4-phenyl-1H-1,2,3-triazole (3ba)¹ General procedure was followed (8 h), white crystals, 169 mg (0.47 mmol, 94%), Mp.: 153-156 $^{\circ}$ C, R_f = 0.40 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.81-7.78 (m, 2H), 7.72-7.67 (m, 3H), 7.44-7.29 (m, 3H), 7.04 (d, 2H, J = 8.21 Hz), 5.51 (s, 2H), ¹³C NMR (62.5 MHz, CDCl₃): δ 146.6, 138.2, 134.3, 130.3, 129.7, 128.8, 128.2, 125.6, 119.4, 94.5, 52.4, MS (EI, 70 eV): m/z (%): 361(5, [M⁺]), 332(5), 230(4), 217(9), 206(12), 116(100), 89 (43).



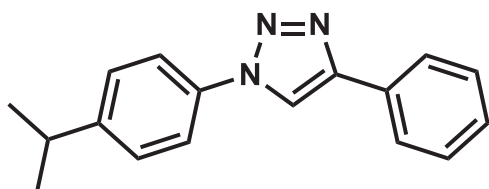
1-(4-Bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3ca)¹ General procedure was followed (12 h), white crystals, 140mg (0.45 mmol, 89%), Mp.: 150-152°C, R_f = 0.35 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.80 (d, 2 H, J = 7.1 Hz), 7.69 (s, 1H), 7.50 (d, 2H, J = 8.3 Hz), 7.43-7.32 (m, 3H), 7.16 (d, 2H, J = 8.2Hz) 5.51 (s, 2H), ¹³C NMR (62.5 MHz, CDCl₃): δ 133.6, 132.2, 129.6, 128.8, 128.2, 125.6, 122.8, 53.4, MS (EI, 70 eV): m/z (%): 315(4, [M⁺]), 286, 284(7), 206(10), 169, 171(16), 116(100), 89(35).



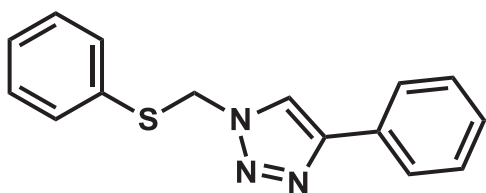
1-(4-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3da)¹ General procedure was followed (12 h), white solid. 138 mg (0.49 mmol, 98% yield), Mp.: 151-153 °C, R_f = 0.59 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 8.21 (d, 2H, J = 8.5 Hz), 7.81-7.77 (m, 2H), 7.45-7.30 (m, 6H), 5.68 (s, 2H), ¹³C NMR (62.5 MHz, CDCl₃): δ 141.7, 130.0, 128.9, 128.5, 128.4, 125.7, 124.3, 119.7, 53.1, MS (EI, 70 eV): m/z (%): 280(4, [M⁺]), 251(4), 205(4), 116(100), 106(10), 89(31).



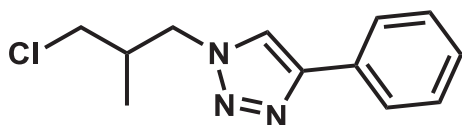
1-(1-Adamantyl)-4-phenyl-1H-1,2,3-triazole (3ea)¹ General procedure was followed (24 h), white solid, 112 mg (0.40 mmol, 80% yield), Mp.: 193-195 °C, R_f = 0.65 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.79-7.75 (m, 3H), 7.37-7.20 (m, 3H), 2.21 (br s, 9 H), 1.72 (br s, 6H), ¹³C NMR (62.5 MHz, CDCl₃): δ 146.7, 131.0, 128.7, 127.7, 125.5, 116.0, 59.5, 43.0, 35.8, 29.3, MS (EI, 70 eV): m/z (%): 279(4, [M⁺]), 223(4), 181(5), 135(100), 116(13), 107(15), 93(30), 79(37), 67(15).



1-(4-Isopropylphenyl)-4-phenyl-1H-1,2,3-triazole (3fa) General procedure was followed (8 h), slightly yellow solid, 130 mg (0.49 mmol, 98%), Mp.: 53-55 °C, R_f = 0.75 (hexane-ethyl acetate, 3:1), ^1H NMR (250 MHz, CDCl_3): δ 8.18 (s, 1H), 7.91 (d, 2H, J = 7.0 Hz), 7.70 (d, 2H, J = 8.5 Hz), 7.48-36 (m, 5H), 2.99 (q, 2H), 1.29 (d, 6H, J = 7.0 Hz), ^{13}C NMR (62.5 MHz, CDCl_3): δ 149.7, 148.1, 134.9, 130.3, 128.8, 128.3, 127.6, 125.7, 120.5, 117.6, 33.8, 23.8, IR (ATR) 3121, 3052, 2973, 2860, 1519, 1455, 1229, 1039 cm^{-1} , MS (EI, 70 eV): m/z (%): 263(2, $[\text{M}^+]$), 235(43), 220(100), 204(13), 193(91), 165(22), 110(75), 103(32), 89(38), 77(34), HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$ 264.1495 found 264.1501.

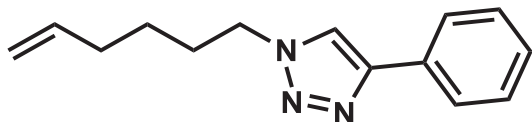


4-Phenyl-1-((phenylthio)methyl)-1H-1,2,3-triazole (3ga)¹ General procedure was followed (8 h), white crystals, 131 mg (0.49 mmol, 98% yield), Mp.: 92-94 °C, R_f = 0.50 (hexane-ethyl acetate, 3:1), ^1H NMR (250 MHz, CDCl_3): δ 7.81-7.78 (m, 3H), 7.45-7.30 (m, 8H), 5.65 (s, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 148.1, 132.2, 131.7, 130.2, 129.4, 128.8, 128.6, 128.2, 125.6, 119.0, 53.8, MS (EI, 70 eV): m/z (%): 267(4, $[\text{M}^+]$), 238(13), 130(100), 123(18), 116(17), 103(61), 77(43), 51(18).

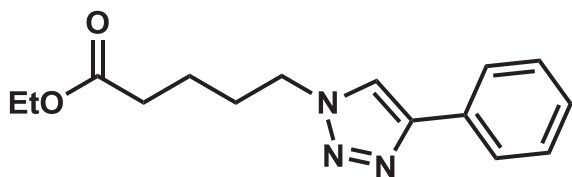


1-(3-Chloro-2-methylpropyl)-4-phenyl-1H-1,2,3-triazole (3ha)¹ General procedure was followed (12 h), White crystals. 94 mg (0.40 mmol, 80% yield), Mp.: 50-51 °C, R_f = 0.40 (hexane-ethyl acetate, 3:1), ^1H NMR (250 MHz, CDCl_3): δ 7.85-7.80 (m, 3H), 7.45-7.29 (m, 3H), 4.49-4.32 (m, 2H), 3.45 (d, 2H, J = 5.1), 2.63-2.51 (m, 1H), 1.09 (2, 3H, J = 6.8), ^{13}C

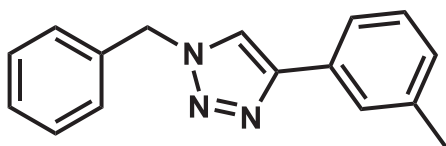
NMR (62.5 MHz, CDCl₃): δ 130.3, 128.8, 128.1, 125.6, 120.4, 52.4, 47.3, 36.1, 15.4, MS (EI, 70 eV): m/z (%): 235(9, [M⁺]), 172(14), 158 (11), 145(6), 130(45), 117(100), 103(35), 89(21), 77(16), 63(16), 55(31).



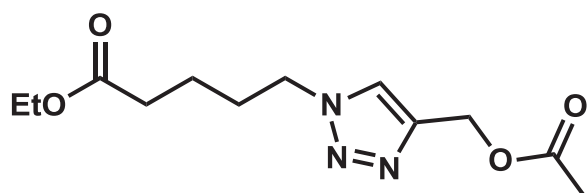
1-(Hex-5-enyl)-4-phenyl-1H-1,2,3-triazole (3ia)¹ General procedure was followed (12 h), White crystals. 104 mg (0.46 mmol, 92% yield), Mp.: 52-53 °C, R_f = 0.48 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.83 (d, 2H, J = 8.0 Hz), 7.74 (s, 1H), 7.44-7.31 (m, 3H), 5.83-5.67 (m, 1H), 5.04-4.95 (m, 2H), 4.37 (t, 2H, J = 7.1 Hz), 2.13-2.05 (m, 2H), 2.00-1.88 (m, 2H), 1.50-1.38 (m, 2H), ¹³C NMR (62.5 MHz, CDCl₃): δ 137.6, 130.6, 128.7, 128.0, 125.4, 119.4, 115.2, 50.1, 32.9, 29.6, 25.5, MS (EI, 70 eV): m/z (%): 227(18, [M⁺]), 198(26), 156(32), 117(100), 102(35), 89(42), 55(69).



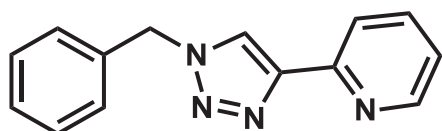
Ethyl-5-(4-phenyl-1H-1,2,3-triazol-1-yl)-pentanoate (3ja)¹ General procedure was followed (12 h), white crystals. 127 mg (0.46 mmol, 93% yield), Mp.: 50-53 °C, R_f = 0.57 (hexane-ethyl acetate, 1:1), ¹H NMR (MHz, CDCl₃): δ 7.78 (t, 3H, J = 8.2 Hz), 7.41-7.29 (m, 3H), 4.37 (t, 2H, J = 7.0 Hz), 4.13-4.05 (m, 2H), 2.32 (t, 2H, J = 7.1 Hz) 2.02-1.91 (m, 2H), 1.71-1.59 (m, 2H), 1.21 (t, 3H, J = 7.1 Hz), ¹³C NMR (62.5 MHz, CDCl₃): δ = 172.8, 130.5, 128.7, 128.0, 125.6, 119.5, 60.4, 49.9, 33.3, 29.5, 21.7, 14.1, MS (EI, 70 eV): m/z (%): 273(9, [M⁺]), 228(4), 200(43), 144(30), 129(57), 116(60), 101(73), 83(50), 55(100).



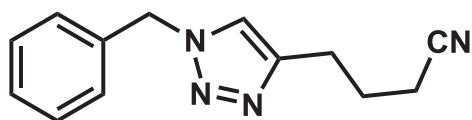
1-Benzyl-4-m-tolyl-1H-1,2,3-triazole (3ab)¹ General procedure was followed (8 h), white crystals. 122 mg (0.49 mmol, 98% yield), Mp.: 147-149 °C, R_f = 0.45 (hexane–ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.66 (s, 2H), 7.58 (d, 1H, J = 7.5 Hz), 7.38-7.25 (m, 6H), 7.13 (d, 1H, J = 7.5 Hz), 5.55 (s, 2H), 2.38 (s, 3H), ¹³C NMR (62.5 MHz, CDCl₃): δ 148.2, 138.4, 134.6, 130.3, 129.0, 128.8, 128.63, 128.60, 127.9, 126.2, 122.7, 119.4, 54.1, 21.3, MS (EI, 70 eV): m/z (%): 249(8, [M⁺]), 220(25), 179(10), 130(100), 103(17), 91(83), 77(18).



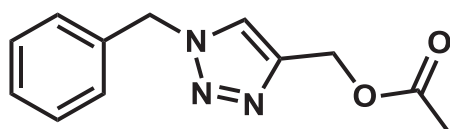
Ethyl 5-(4-(acetoxymethyl)-1H-1,2,3-triazol-1-yl)pentanoate (3jc)¹ General procedure was followed (12 h), colourless oil, 130 mg (0.48 mmol, 97%). R_f = 0.61 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 7.57 (s, 1H), 5.12 (s, 2H), 4.31 (t, 2H, J = 7.1 Hz), 4.05 (q, 2H, J = 7.1 Hz), 2.27 (t, 2H, J = 7.1 Hz), 2.00 (s, 3H), 1.96-1.84 (m, 2H), 1.64-1.52 (m, 2H), 1.17 (t, 3H, J = 7.1 Hz), ¹³C NMR (62.5 MHz, CDCl₃): δ 172.7, 170.7, 60.3, 57.4, 49.8, 33.2, 29.3, 21.5, 20.7, 14.0, MS (EI, 70 eV): m/z (%): 269(2, [M⁺]), 226(10), 199(12), 154(20), 136(20), 108(30), 101 (48), 84(69), 55(100).



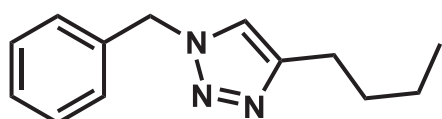
1-Benzyl-4-pyridyl-1H-1,2,3-triazole (3ad)¹ General procedure was followed (8 h), light brown crystals, 100 mg (0.42 mmol, 85% yield), Mp.: 113-115 °C, R_f = 0.32 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 8.51 (d, 1H, J = 4.6 Hz), 8.15 (d, 1H, J = 7.9 Hz), 8.03 (s, 1H), 7.73 (td, 1H, J_1 = 7.8 Hz, J_2 = 1.8 Hz), 7.36-7.29 (m, 5H), 7.20-7.15 (m, 1H), 5.55 (s, 2H), ¹³C NMR (62.5 MHz, CDCl₃): δ 150.2, 149.3, 148.6, 136.8, 134.3, 129.1, 128.7, 128.2, 122.7, 121.8, 120.1, 54.3, MS (EI, 70 eV): m/z (%): 236 (5, [M⁺]), 207(47), 180(10), 117(51), 91(100), 65(23).



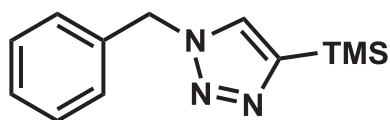
4-(1-Benzyl-1H-1,2,3-triazol-4-yl)butanenitrile (3ae)¹ General procedure was followed (12 h), white solid, 108 mg (0.48 mmol, 95% yield), Mp.: 64-66 °C, R_f = 0.20 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 7.31-7.29 (m, 3 H), 7.22-7.18(m, 3 H), 5.43 (s, 2H), 2.77 (t, 2H, J = 7.0 Hz), 2.34 (t, 2 H, J = 7.25 Hz), 1.98 (p, 2H, J = 7.0 Hz). ¹³C NMR (62.5 MHz, CDCl₃): δ 145.9, 134.5, 129.0, 128.6, 127.9, 121.1, 119.3, 54.0, 24.7, 24.1, 16.4, MS (EI, 70 eV): m/z (%): 226(3, [M⁺]), 197(4), 144(4), 130(4), 104(4), 91(100), 65(12).



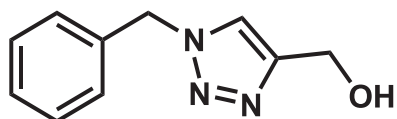
(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl acetate (3ac)¹ General procedure was followed (12 h), slightly yellow crystals, 108 mg (0.47 mmol, 93%), Mp.: 55-56 °C, R_f = 0.50 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 7.51 (s, 1H), 7.32-7.21 (m, 5H), 5.46 (s, 2H), 5.11 (s, 2H), 1.98 (s, 3H), ¹³C NMR (62.5 MHz, CDCl₃): δ 170.6, 142.9, 134.2, 128.9, 128.6, 127.9, 123.5, 57.3, 53.9, 20.6, MS (EI, 70 eV): m/z (%):231(1, [M⁺]), 188(6), 161(5), 91(100), 65(14).



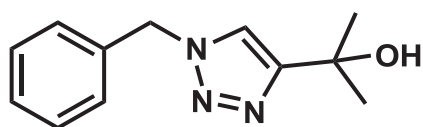
1-Benzyl-4-butyl-1H-1,2,3-triazole (3af)¹ General procedure was followed (16 h), white crystals, 99 mg (0.46 mmol, 92% yield), Mp.: 57-59 °C, R_f = 0.35 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.34-7.32 (m, 3H), 7.24-7.18 (m, 3H), 5.46 (s, 2H), 2.66 (t, 2H, J = 7.5 Hz), 1.65-1.54 (m, 2H), 1.40-1.25 (m, 2H), 0.88 (t, 3H, J = 7.25 Hz), ¹³C NMR (62.5 MHz, CDCl₃): δ 134.9, 128.9, 128.4, 127.8, 53.8, 31.4, 25.3, 22.2, 13.7, MS (EI, 70 eV): m/z (%): 215(1, [M⁺]), 173(5), 144(3), 104(5), 91(100), 65(10).



1-Benzyl-4-trimethylsilyl-1H-1,2,3-triazole (3ag)² General procedure was followed (12 h), white solid, 71 mg (0.31 mmol, 61%), Mp.: 53-55 °C, R_f = 0.43 (hexane-ethyl acetate, 3:1), ¹H NMR (250 MHz, CDCl₃): δ 7.43 (s, 1H), 7.37-7.24 (m, 5H), 5.54 (s, 2H), 0.29 (s, 9H), ¹³C NMR (62.5 MHz, CDCl₃): δ = 148.2, 136.1, 130.20, 130.15, 129.7, 129.2, 129.1, 54.5, 0.0, MS (EI, 70 eV): m/z (%): 216(2, [M⁺]), 173(48), 144(8), 104(4), 91(100), 65(10), 58(13).



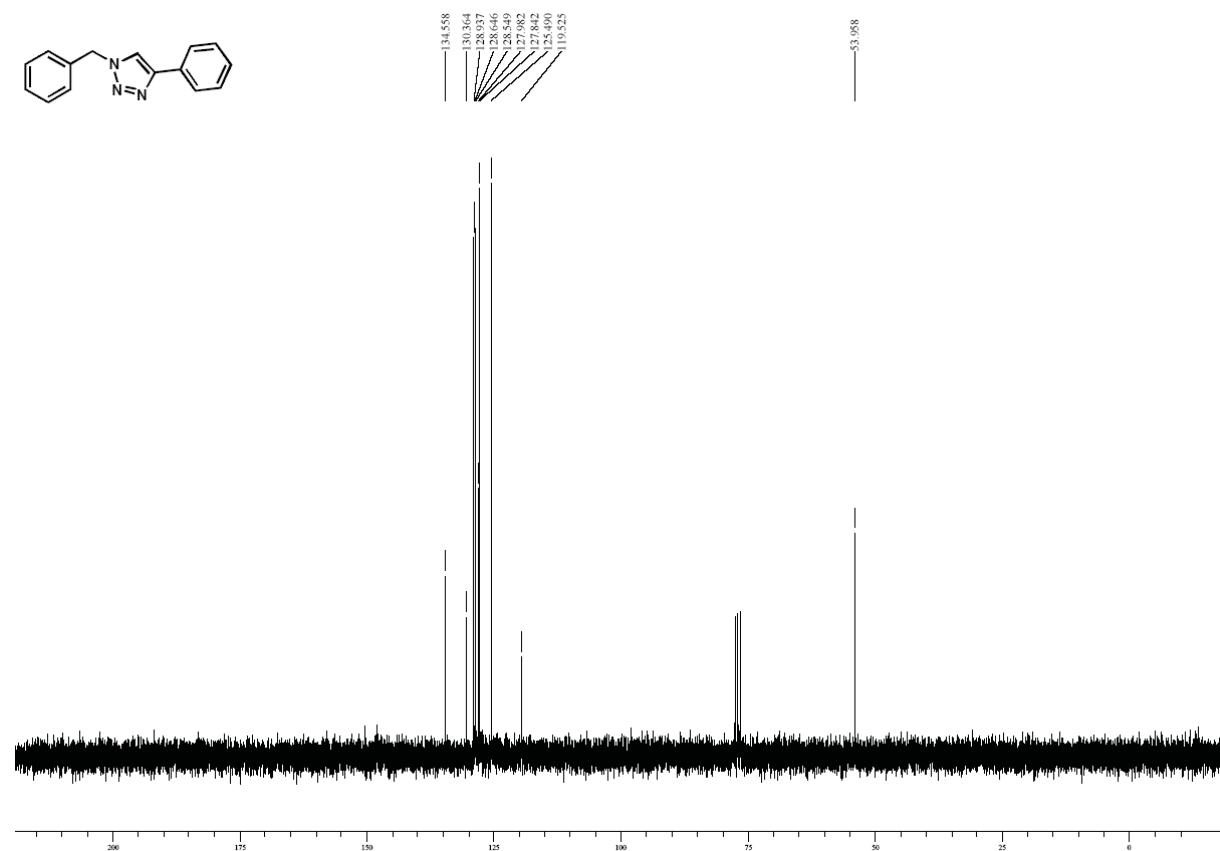
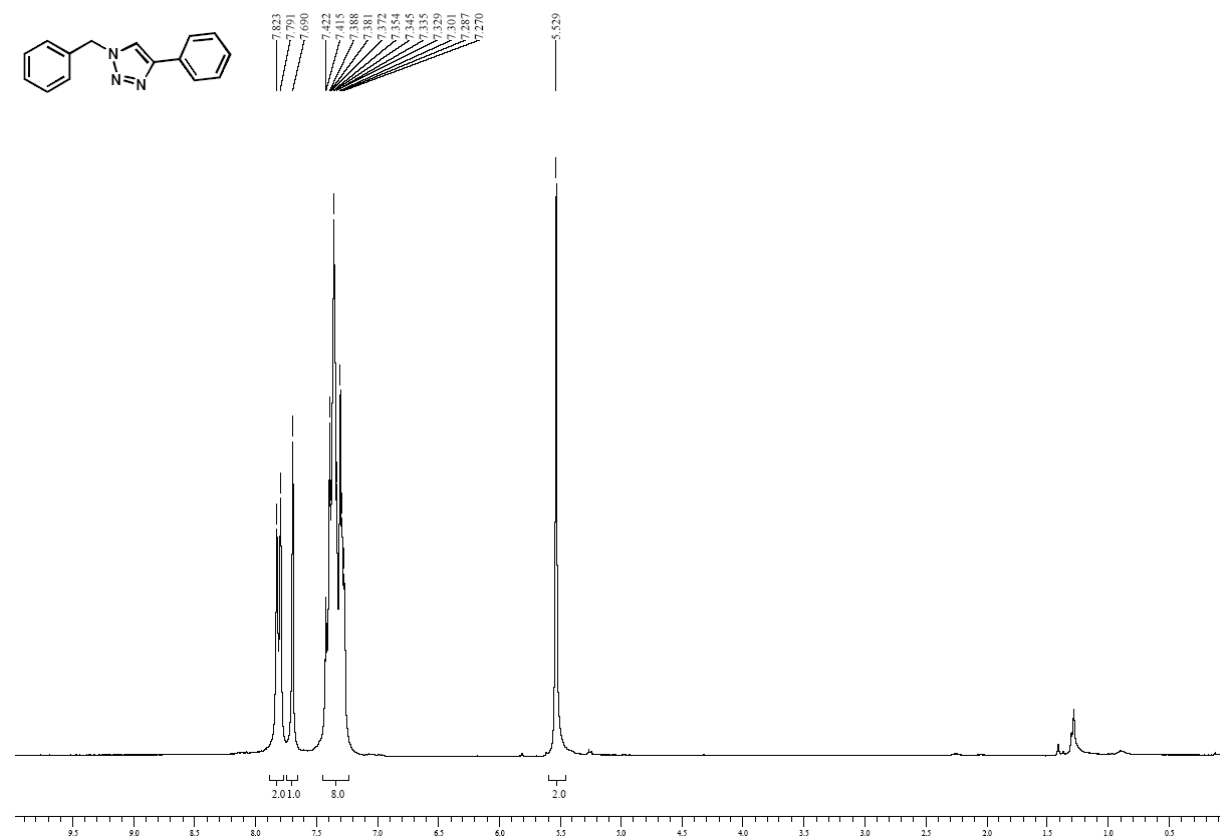
1-Benzyl-4-methanol-1H-1,2,3-triazole (3ah)² General procedure was followed (12 h), white solid, 89 mg (0.47 mmol, 95%), Mp.: 52-53 °C, R_f = 0.09 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 7.38 (s, 1H), 7.28-7.14 (m, 5H), 5.38 (s, 2H), 4.63 (s, 2H), 4.10 (bs, 1H), ¹³C NMR (62.5 MHz, CDCl₃): δ 148.2, 134.4, 129.0, 128.6, 128.0, 121.8, 55.9, 54.0, MS (EI, 70 eV): m/z (%): 187 (2, [M⁺]), 158(30), 130(23), 104(8), 91(100), 77(8), 65(21).

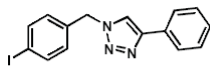


2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol (3ai)³ General procedure was followed (12 h), white solid, 104 mg (0.48 mmol, 96%), Mp.: 78-80 °C, R_f = 0.18 (hexane-ethyl acetate, 1:1), ¹H NMR (250 MHz, CDCl₃): δ 7.36-7.23 (m, 6H), 5.46 (s, 1H), 3.13 (bs, 1H), 1.58 (s, 6H), ¹³C NMR (62.5 MHz, CDCl₃): δ 156.0, 134.5, 129.0, 128.6, 128.0, 119.0, 68.4, 54.0, 30.3, MS (EI, 70 eV): m/z (%): 217(1, [M⁺]), 202(18), 170(4), 104(4), 91(100), 65(13).

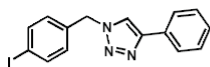
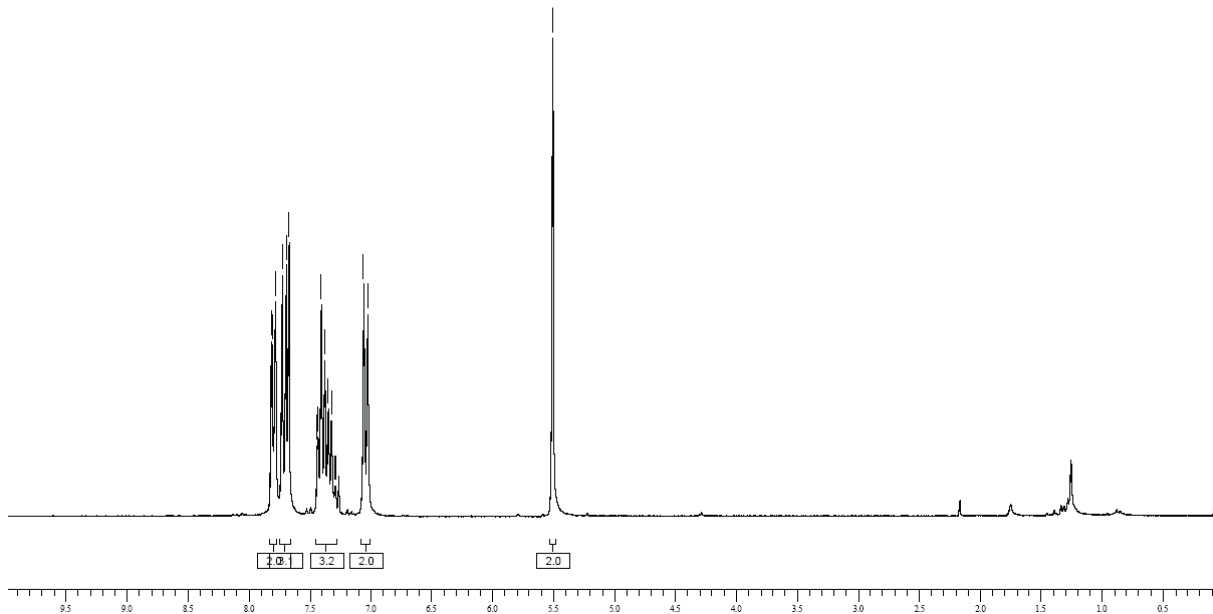
1. Gonda, Zs.; Novák, Z. *Dalton. Lett.* **2002**, *4*, 2803-2806.
2. Kim, Y. J.; Park, C. J.; Kang, H.; Song, H. *Chem. Commun.* **2010**, *46*, 439-441.
3. Appukkuttan, P.; Dehaen, W.; Fokin, V. V.; Eycken, V. d. E. *Org. Lett.* **2004**, *6*, 4223-4225.

NMR spectras





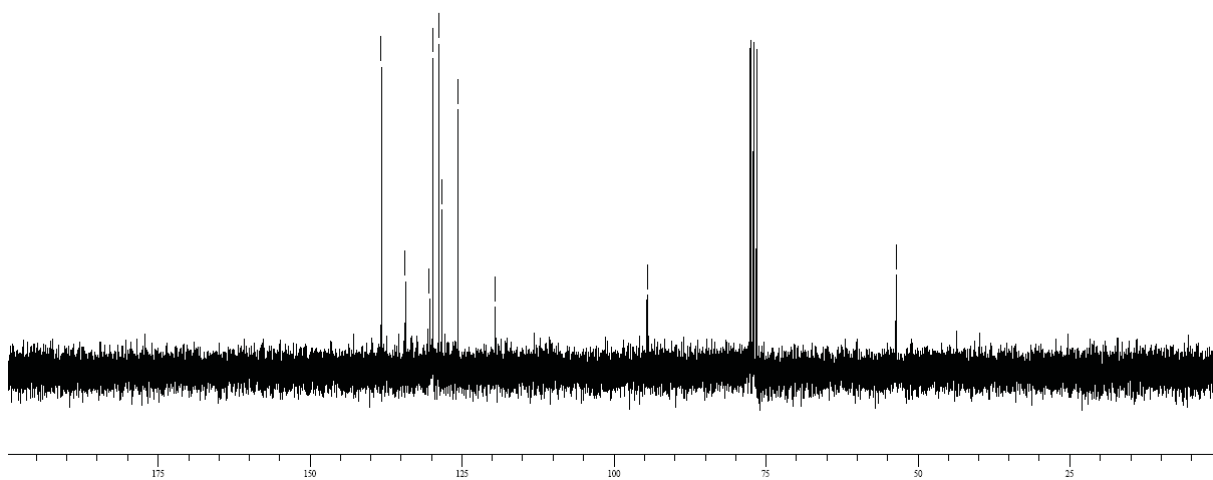
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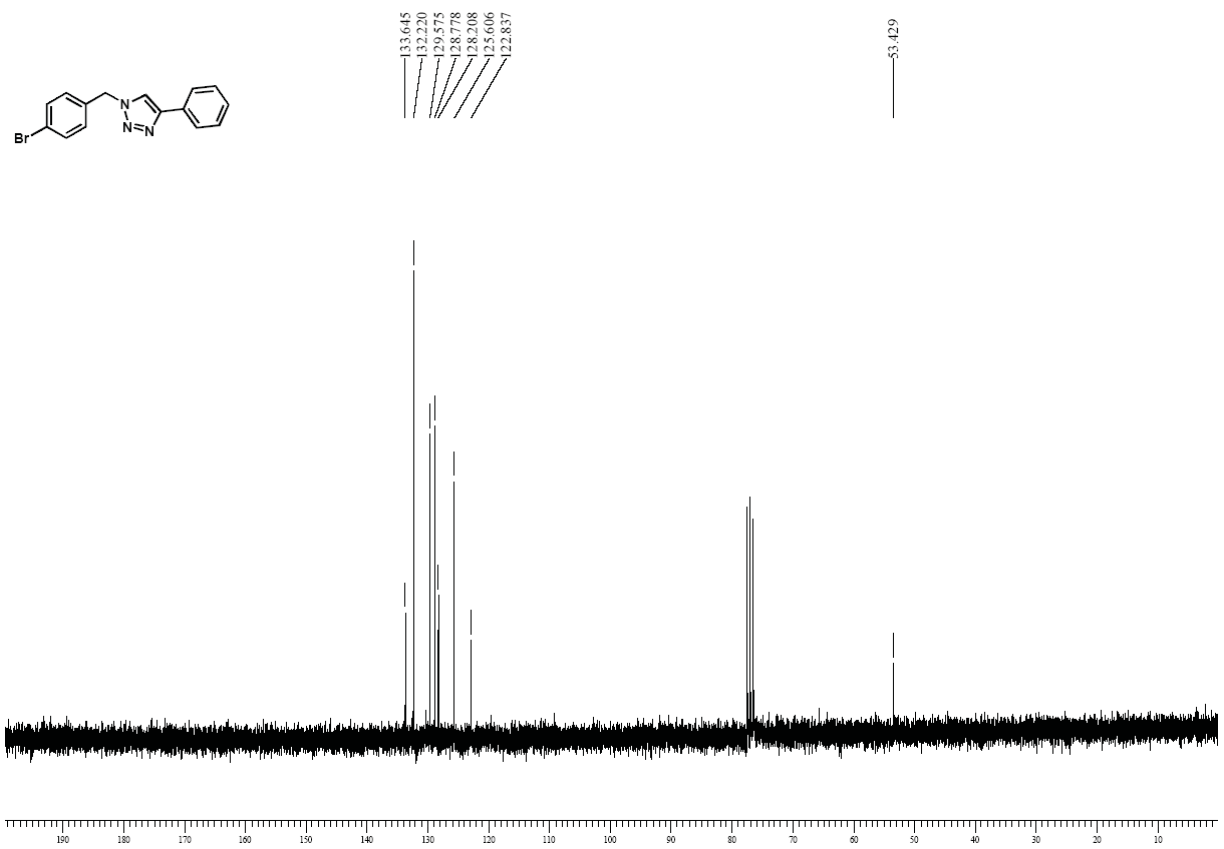
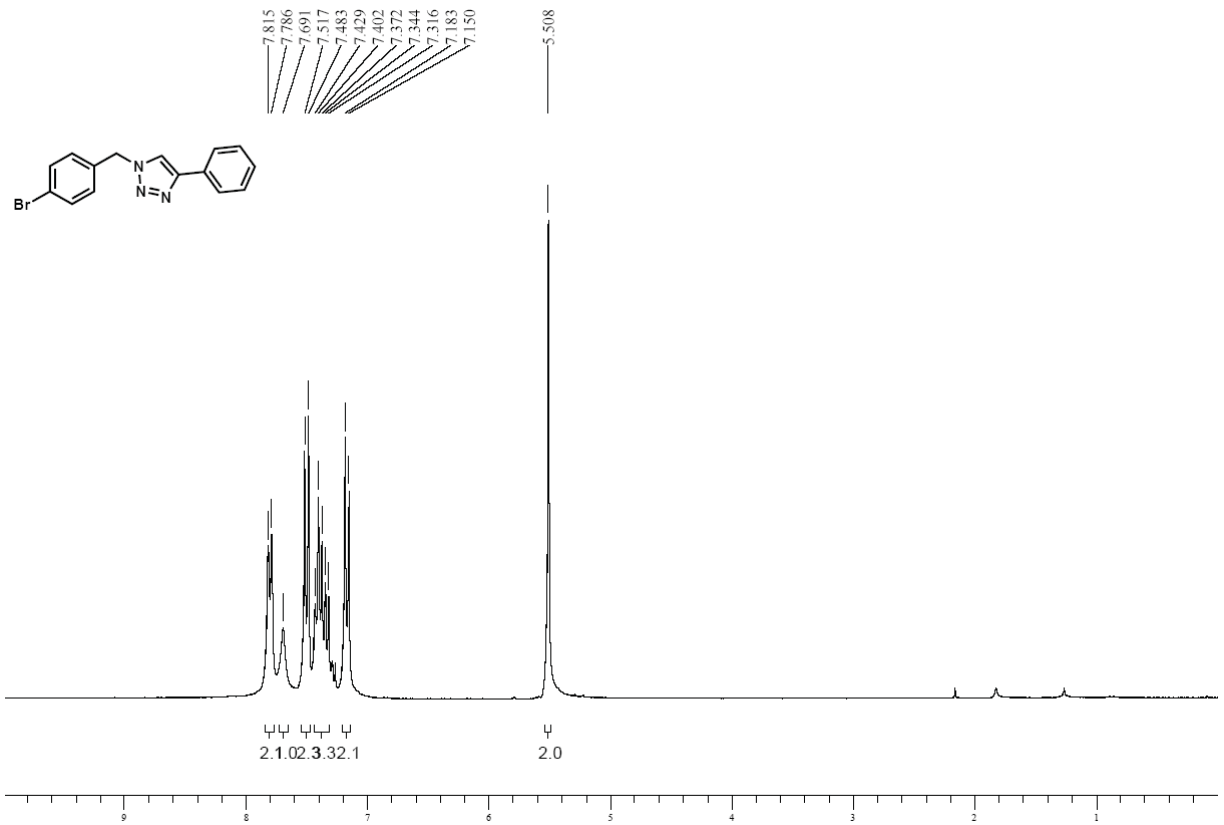


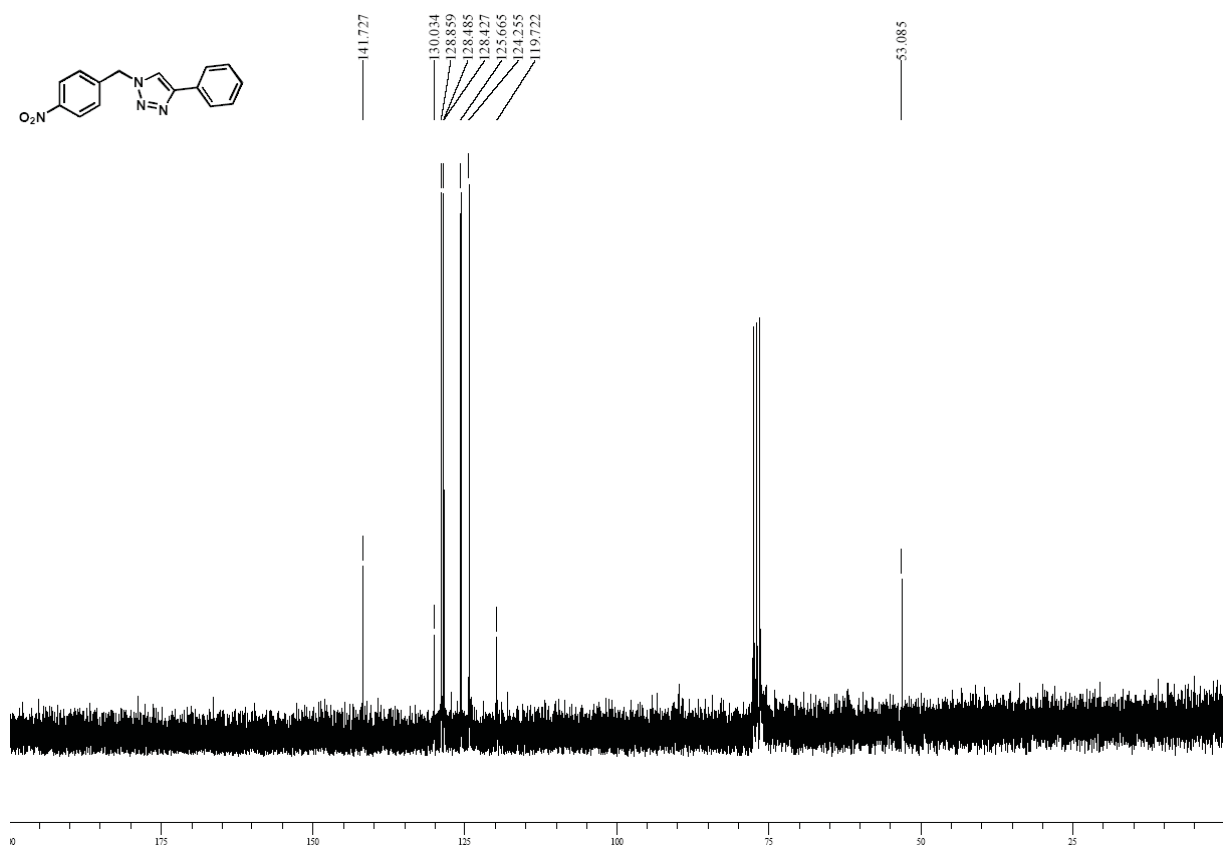
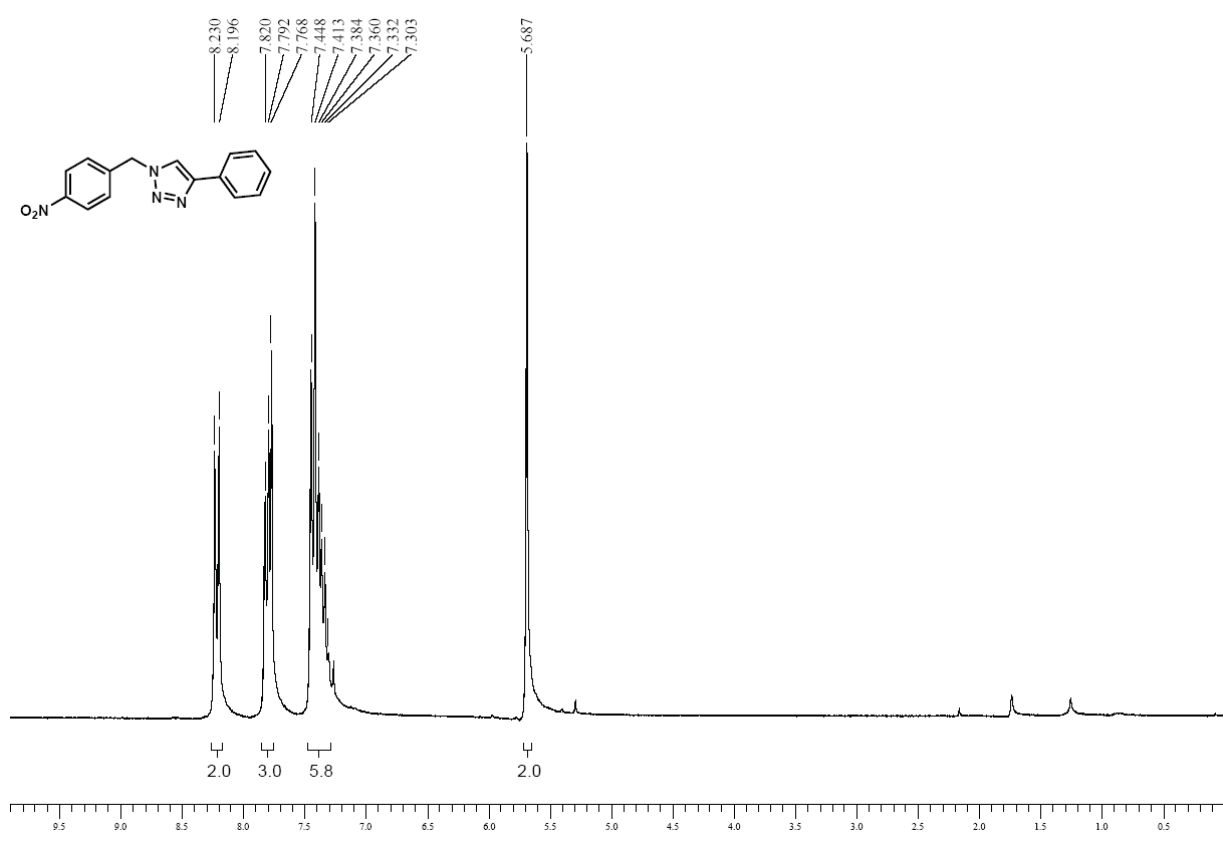
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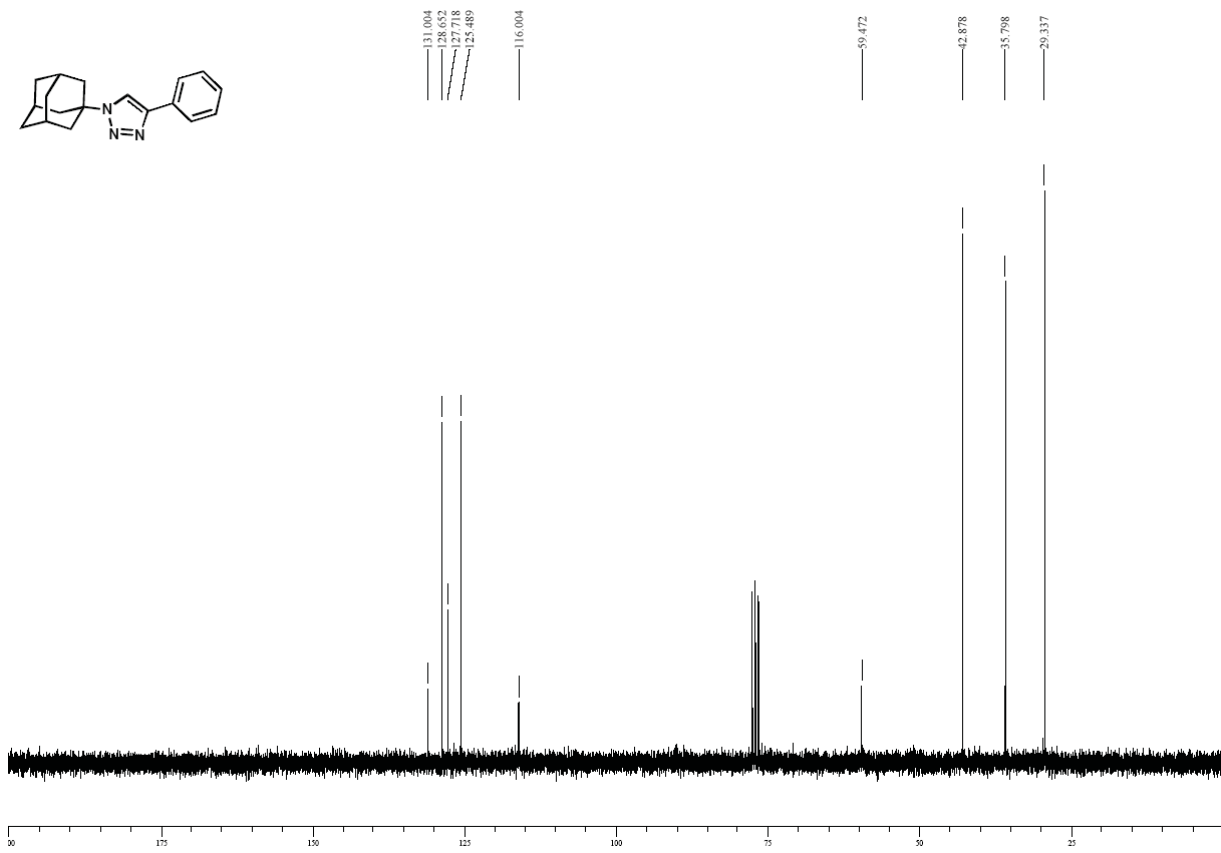
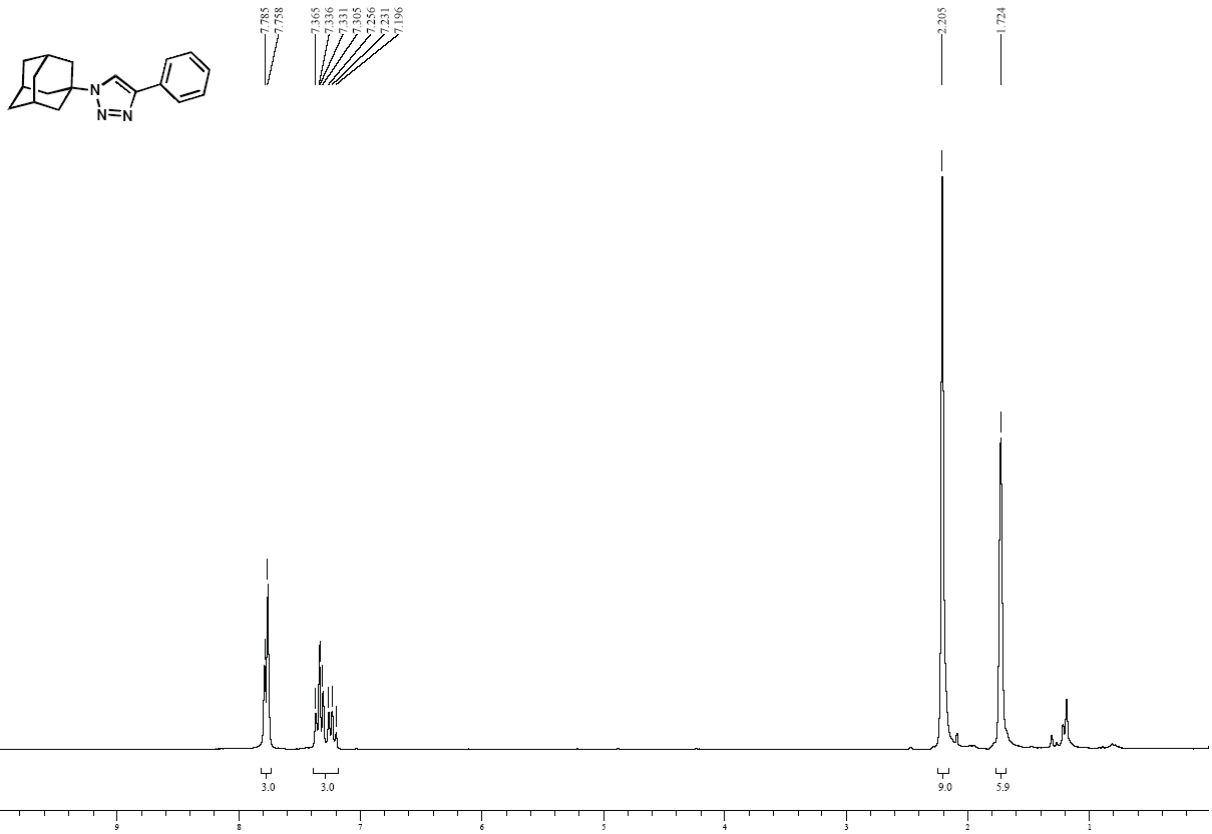
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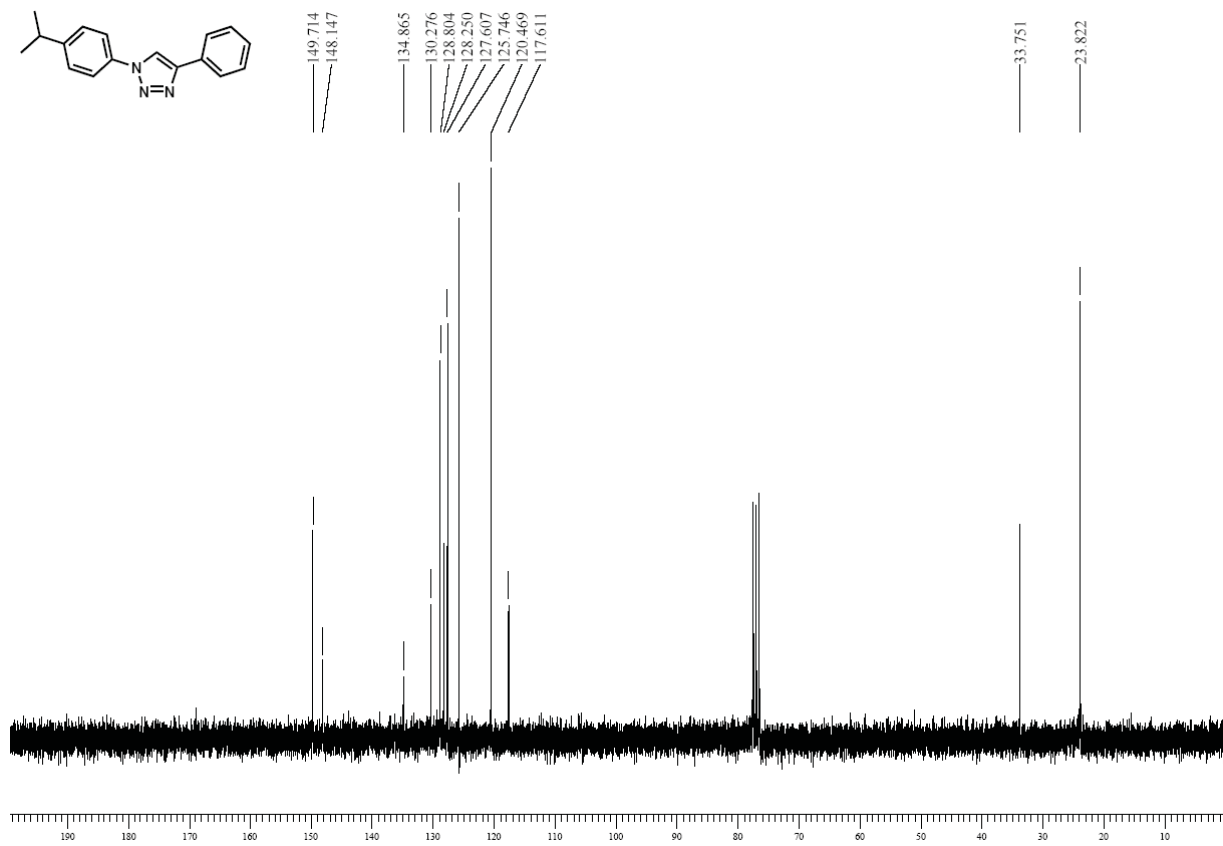
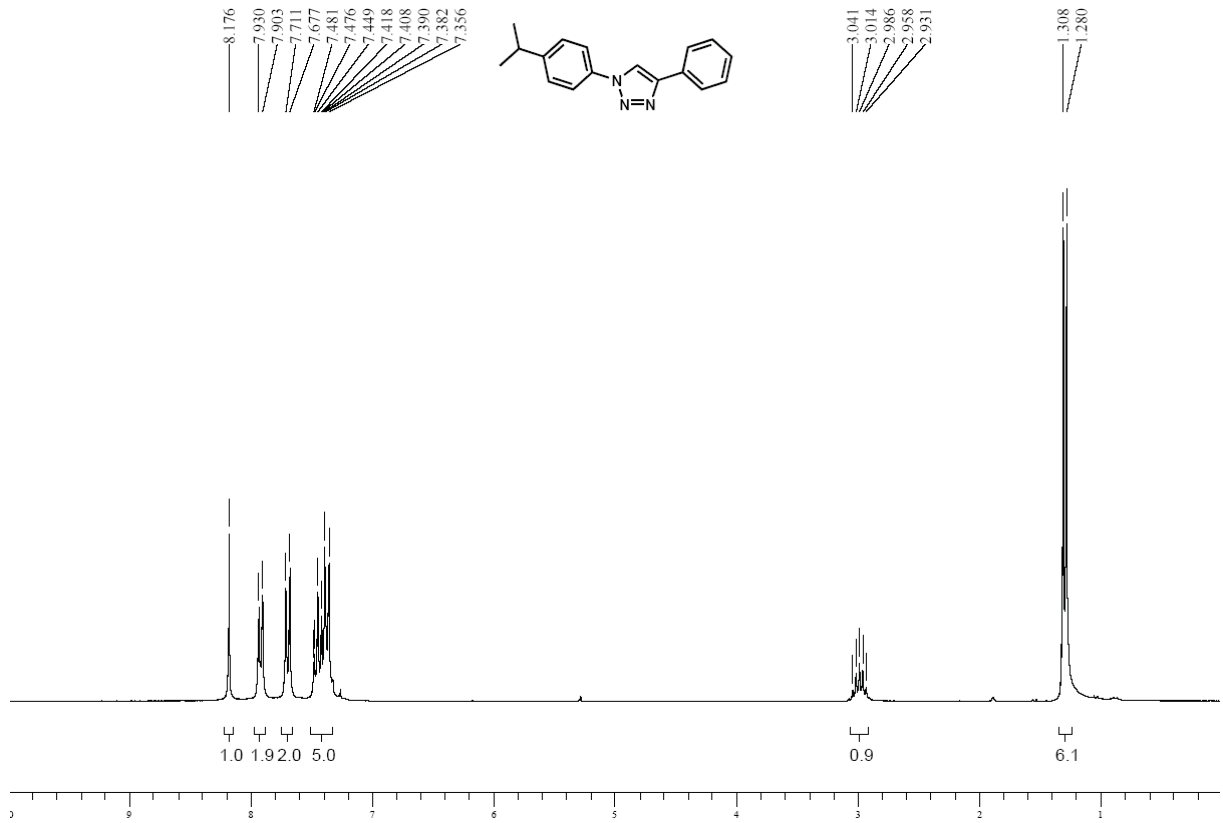
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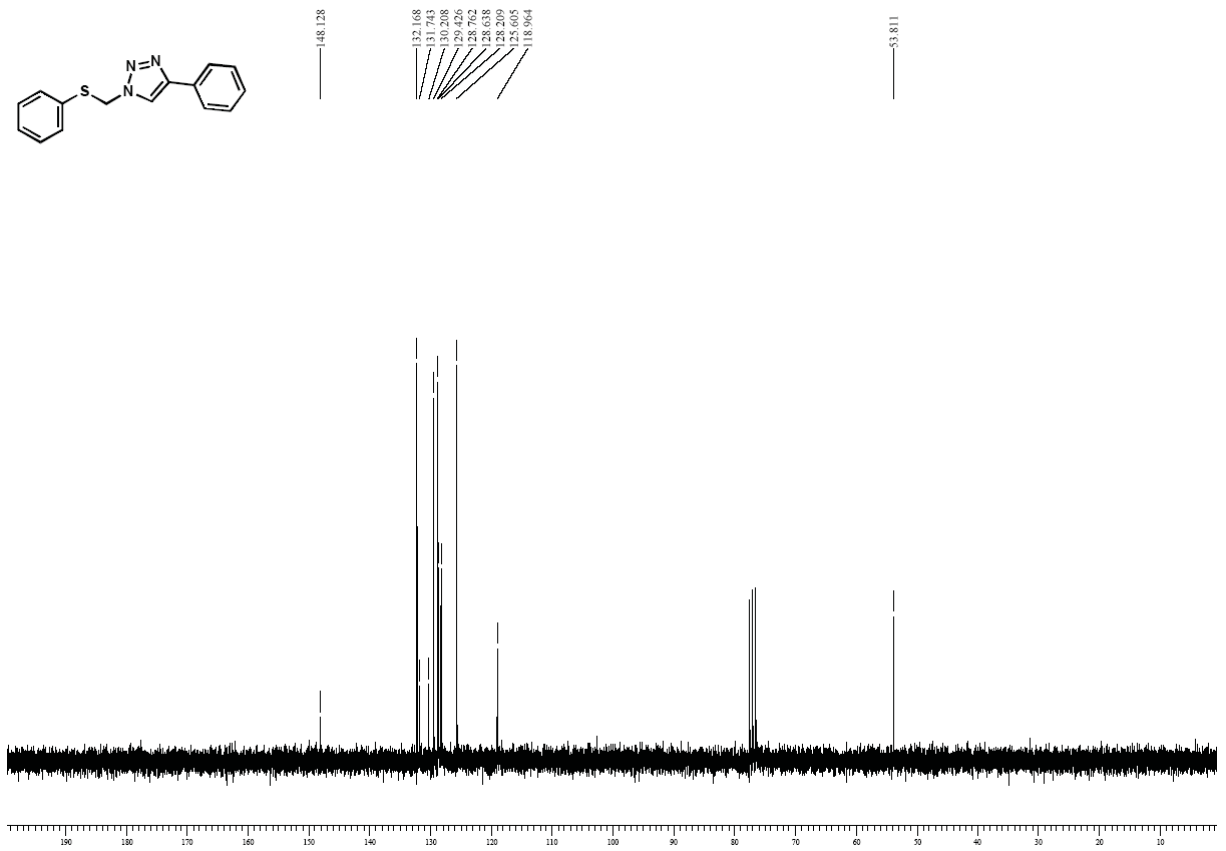
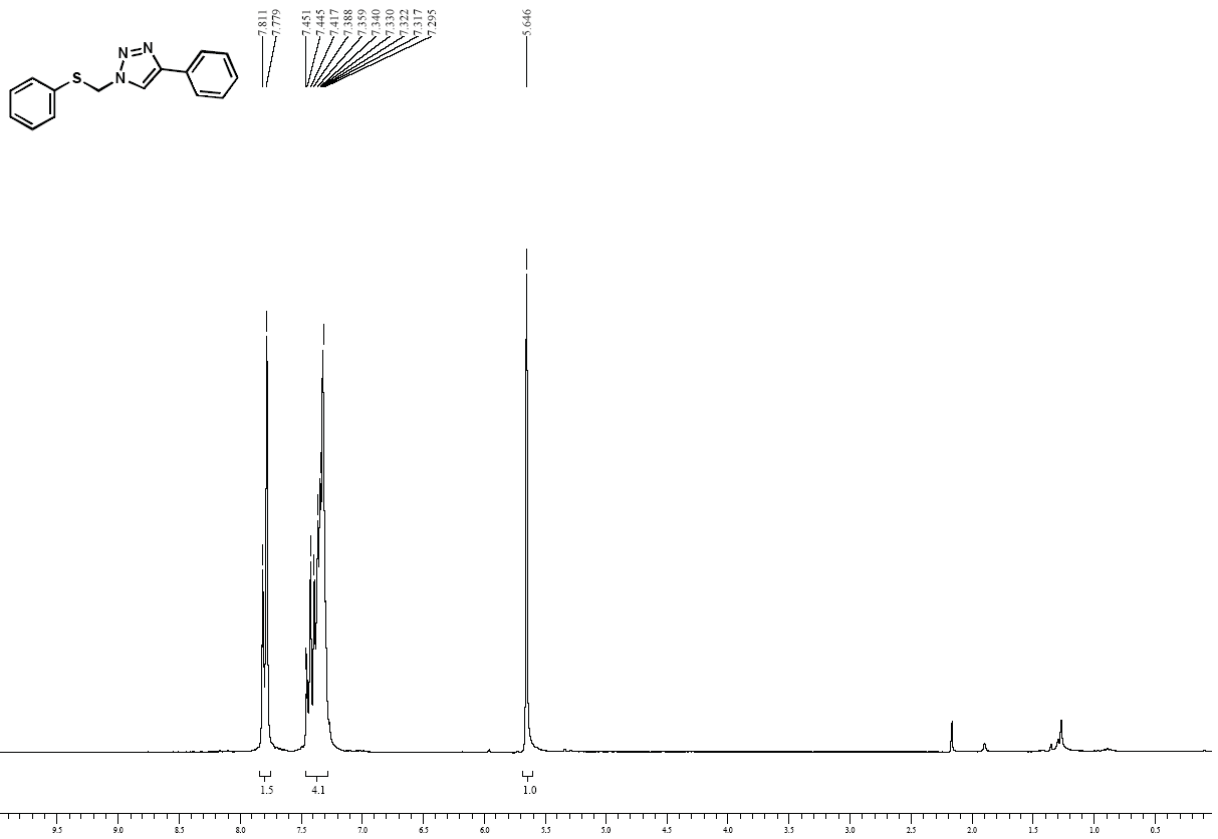


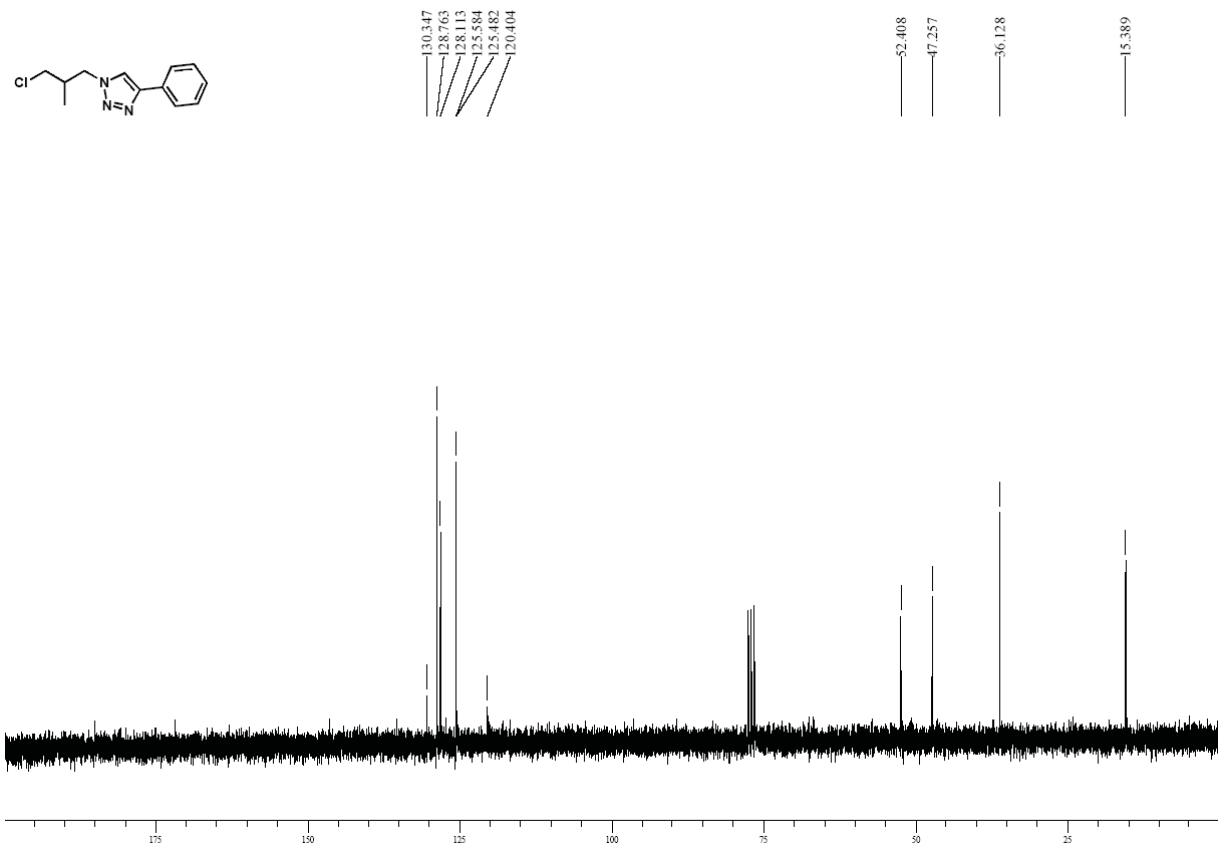
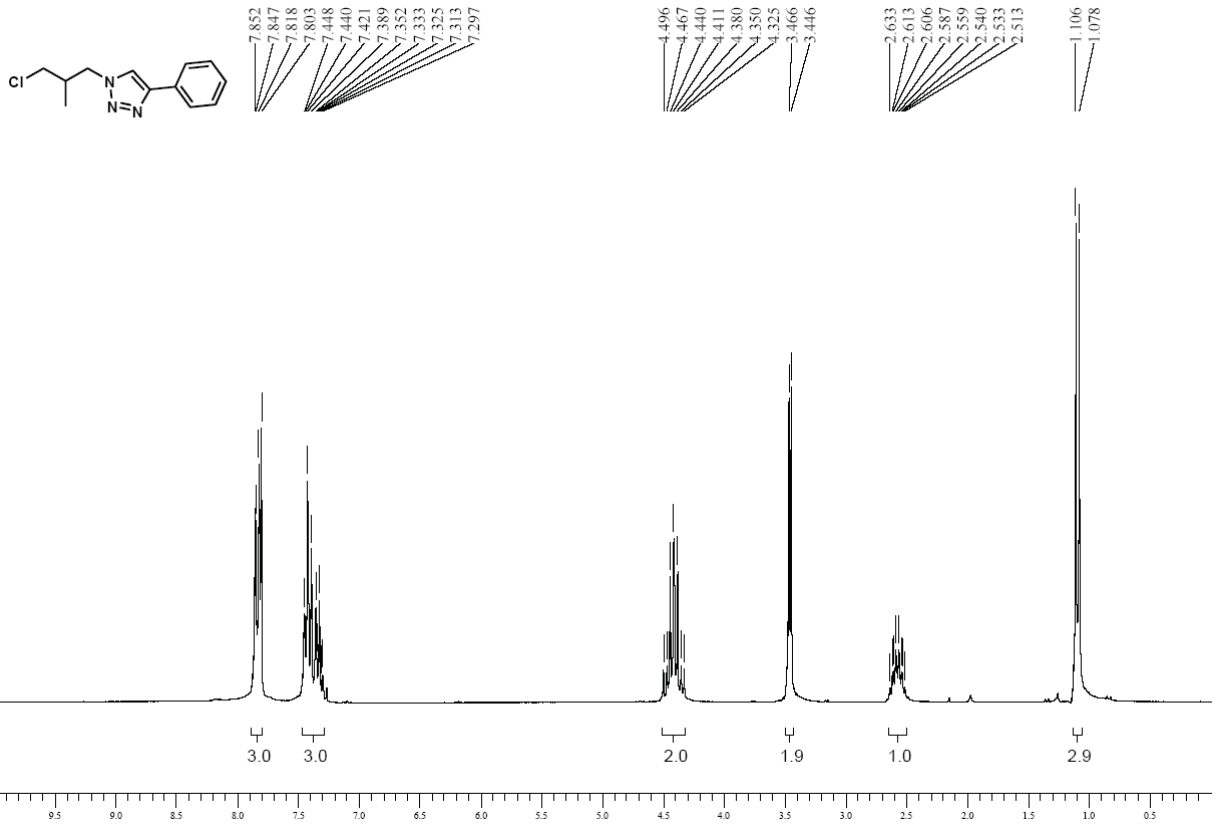


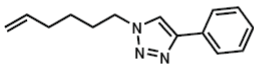




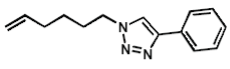
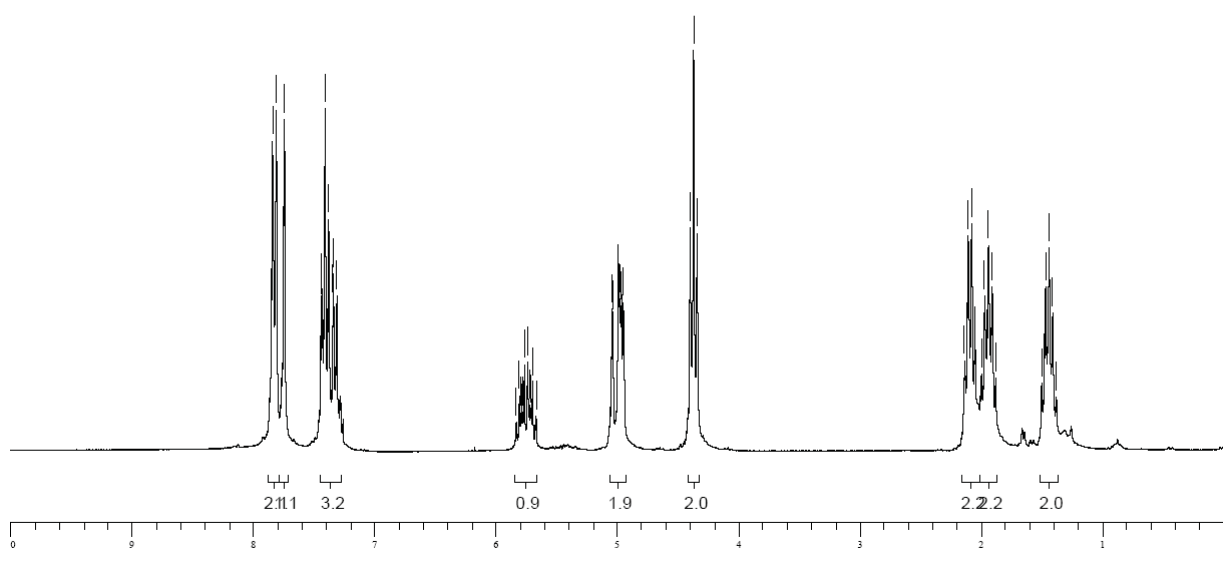








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