

Supporting information for:

Stable homogeneous silver(I) catalysts for the highly efficient cycloaddition of
azides onto terminal alkynes in water

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General catalytic reaction procedure

In a test tube with a screw cap, add one mmole of organic benzyl halides (benzyl chloride). Next, add 1.2 mmoles of sodium azide salt. Immediately afterward, introduce one mmole of alkyne (phenylacetylene) and one milligram of complex **3**. Add 2 ml of water and allow the mixture to stir for 4 hours at a temperature of 40 °C. The product was extracted by adding ethyl acetate to the reaction mixture in a separation funnel. Upon the addition of ethyl acetate, a solid product was formed, which was then separated through filtration. All products were crystallized using a mixture of dichloromethane and n-hexane. However, in the case of product **j**, a precipitate could not be obtained. Consequently, purification was achieved using column chromatography with n-hexane and ethyl acetate.

General considerations. Reagents and solvents were used as received from commercial suppliers. $\text{K}[\text{SP}(\text{S})(\text{O}^i\text{Pr})_2]$ and $\text{Na}[(\text{S})_2\text{H}_2\text{B}(\text{mt})_2]$ were synthesized using established procedures.^{1,2} All the complexes reported in this manuscript are easy to synthesize, and their synthesis does not require the use of air-sensitive techniques. Additionally, all the catalytic reactions did not require the absence of light. Infrared spectra were recorded on a Bruker Vector 22 FT-IR spectrometer (ATR in the range 400-4000 cm^{-1}). C, H, N, and S analyses were performed with a vario EL CHNS elemental analyzer. NMR spectra were recorded in solution on a Bruker AV-400 spectrometer with SiMe_4 (for ^1H and ^{13}C) and H_3PO_4 (^{31}P) as external references. The UV-Vis. spectra were recorded on an Ultrospec 3100 Pro, UV-vis spectrophotometer using samples dissolved in dichloromethane.

Synthesis of **1**

Diphenylphosphinoferrocene, (dppf), (30 mg, 0.054 mmol) was reacted with silver tetrafluoroborate (10 mg, 0.054 mmol) in 4 ml of acetonitrile and dichloromethane. After 15 minutes of stirring, $\text{K}[\text{SP}(\text{S})(\text{O}^i\text{Pr})_2]$ (13.6 mg, 0.054 mmol) was added to the flask and the mixture was stirred further for 4 hours at room temperature. After filtering off precipitates, the solvent was removed under reduced pressure, which allowed obtainment of an orange-colored powder. The pure product was obtained by crystallization in a mixture of acetonitrile and dichloromethane solvents, layered with diethyl ether. (Yield: 32 mg, 68%). ^1H NMR (CD_2Cl_2 , 250 MHz): δ 7.86–7.77 (m, 7H), 7.50–7.42 (m, 12H), 4.87 (sept, 2H, $J = 8.0$ Hz), 4.42–4.30 (m, 4H), 4.26–4.20 (m, 4H), 1.34 (d, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 63.0 MHz): δ 134.3, 134.0, 130.1, 128.6, 128.5, 72.1, 23.6. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 104.0, –6.2, –

8.5. IR (cm^{-1} , KBr pellet): 3069 (w), 3052 (w), 2971 (m), 2930 (m), 1570 (m), 1480 (s), 1434 (s). UV-vis. (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$: 231, 280. Anal. Calcd. for $\text{C}_{40}\text{H}_{42}\text{AgFeO}_2\text{P}_3\text{S}_2$: C, 54.87; H, 4.84. Found: C, 54.81; H, 4.70.

Synthesis of 2

Dppf (30 mg, 0.054 mmol) was reacted with silver tetrafluoroborate (21 mg, 0.108 mmol) in 4 ml of acetonitrile and dichloromethane. After 15 minutes, sodium dihydrobis(methimazolyl)borate (28 mg, 0.108 mmol) was added, thereafter, the mixture was stirred for 4 hours at room temperature. Finally, the precipitates were removed by filtration and the solution phase was dried under reduced pressure, which gave an orange-colored powder. The pure product was obtained in a mixture of dichloromethane and acetonitrile solvents, layered with a few drops of diethyl ether. (Yield: 50 mg, 74%). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.53–7.43 (m, 8H), 7.43–7.34 (m, 12H), 6.92 (d, $J = 4.0$ Hz, 4H), 6.78 (d, $J = 4.0$ Hz, 4H), 4.73–4.68 (m, 4H), 4.14–4.12 (m, 4H), 3.63 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz): δ 159.90, 134.73, 134.46, 133.38, 133.22, 129.84, 128.49, 128.39, 122.86, 118.32, 74.68, 74.61, 74.46, 74.31, 53.71, 35.09. ^{31}P NMR (CD_2Cl_2 , 162 MHz): δ 0.7 ppm. IR (cm^{-1} , KBr pellet): 3072 (w), 3051 (w), 2928 (w), 2384 (m), 2296 (m), 1560 (w), 1451 (m), 1433 (m), 1413 (s), 1377 (s). UV-vis. (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$: 229, 262. Anal. Calcd. for $\text{C}_{50}\text{H}_{52}\text{Ag}_2\text{B}_2\text{FeN}_8\text{P}_2\text{S}_4$: C, 48.11; H, 4.20; N, 8.98. Found: C, 48.10; H, 4.01; N, 8.60.

Synthesis of 3

Dppf (50 mg, 0.09 mmol) was reacted with silver tetrafluoroborate (17.55 mg, 0.09 mmol) in 4 ml of acetonitrile and dichloromethane. After 15 minutes, 1,4 dithiane (11 mg, 0.09 mmol) was added, thereafter, the mixture stirred for 4 hours at room temperature. Finally, the solution was evaporated under reduced pressure the orange-colored powder was collected. The product was purified by crystallization in dichloromethane layered with a few drops of diethyl ether. (Yield: 54 mg, 45%). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.61–7.40 (m, 14H), 7.40–7.33 (m, 38H), 7.33–7.30 (m, 11H), 4.58–4.48 (m, 8H), 4.37–4.26 (m, 8H), 4.19–4.08 (m, 4H), 3.71–3.54 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 133.3, 131.1, 129.3, 74.6, 72.6. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 6.31, 2.67, 2.01, 0.63, 0.01. IR (cm^{-1} , KBr pellet): 3055 (w), 2923 (w), 1631

(w), 1586 (m), 1480 (m), 1435 (s). UV-vis. (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$: 229, 269. Anal. Calcd for $\text{C}_{102}\text{H}_{84}\text{Ag}_2\text{B}_2\text{F}_8\text{Fe}_3\text{P}_6$: C, 59.69; H, 04.12. Found: C, 59.60; H, 04.02.

It is notable that compound **3** could be synthesized by following the above procedure and reacting dppf and AgBF_4 in a 2:3 molar ratio, in the absence of 1,4-dithiane, in a mixture of 4 ml of acetonitrile and dichloromethane.

Synthesis of 4

The procedure for the synthesis of compound **3** was used, except that 1,3-dithiane was used instead of 1,4-dithiane. ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.62–7.48 (m, 20H), 4.53–4.47 (m, 4H), 4.43–4.36 (m, 4H), 3.83 (s, 2H), 3.07–3.05 (m, 4H), 2.24–2.15 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 133.3, 133.2, 133.1, 132.0, 13.2, 131.0, 130, 129.3, 74.8, 73.3, 34.0, 30.7, 27.5. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 1.1. IR (cm^{-1} , KBr pellet): 3316 (w), 3045 (m), 1567 (w), 1477 (m), 1432 (s), 1058 (s). UV-vis. (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$: 220, 223, 253.

Synthesis of 5

Diphenylphosphinoethane (50 mg, 0.125 mmol) was reacted with silver tetrafluoroborate (24 mg, 0.125 mmol) in 4 ml of acetonitrile and dichloromethane. After 15 minutes, dihydrobis(methimazolyl)borate (33 mg, 0.125 mmol) was added, thereafter, the mixture stirred for 4 hours at room temperature. Finally, the precipitates were removed by filtration and the solution phase was dried under reduced pressure, which gave a colorless powder. The pure product was obtained in acetonitrile layered with a few drops of diethyl ether. (Yield: 64 mg, 69%). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.71–7.65 (m, 6H), 7.59–7.30 (m, 12H), 6.92 (s, 2H), 6.78 (s, 2H), 3.62 (s, 6H), 2.51 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): 159.9, 132.8, 128.7, 122.9, 118.3, 35.1. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 1.9. IR (cm^{-1} , KBr pellet): 3134 (w), 3070 (w), 3052 (w), 2922 (w), 2425 (m), 1548 (m), 1481 (m), 1450 (m), 1432 (s). UV-vis. (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$: 231, 263. Anal. Calcd. for $\text{C}_{34}\text{H}_{36}\text{AgBN}_4\text{P}_2\text{S}_2$: C, 54.78; H, 4.87; N, 7.52. Found: C, 54.70; H, 4.66; N, 7.40.

X-ray crystal structure determination and refinement

The yellow plate crystals of **2** and orange block crystals of **3** crystallized in the triclinic system in the P-1 space group. The X-ray experiments were carried out at 100(12) K using a Rigaku XtaLAB Synergy S Dualflex diffractometer with HyPix detector and a PhotonJet $\text{CuK}\alpha$ radiation source ($\lambda = 1.54184 \text{ \AA}$). The obtained data set was processed with CrysAlisPro

software.³ The structures were solved by direct methods and refined with the full-matrix least-squares method on F^2 with the use of SHELX2019 program packages.⁴ All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms attached to carbon and boron atoms were positioned with the idealized geometry. All hydrogen atoms were constrained during refinement with the appropriate riding model as implemented in SHELX during refinement. The data collection and refinement processes are presented in Table 1. The structural data have been deposited at the Cambridge Crystallographic Data Centre: (CCDC No 2358529 for **2** and 2358530 for **3**).

1. Alvarez, H. M.; Tran, T. B.; Richter, M. A.; Alyounes, D. M.; Rabinovich, D.; Tanski, J. M.; Krawiec, M. Homoleptic Group 12 Metal Bis(Mercaptoimidazolyl)Borate Complexes $M(\text{BmR})_2$ ($M = \text{Zn, Cd, Hg}$). *Inorg. Chem.* **2003**, *42* (6), 2149–2156. <https://doi.org/10.1021/ic025780m>.
2. Chen, W.-B.; Jin, G.-Y. Synthesis and Biological Activities of O, O-Dialkyl-Dithiophosphoryl-S-Acetoxy Triazolo Compounds. *Phosphorus. Sulfur. Silicon Relat. Elem.* **2003**, *178* (2), 311–317.
3. CrysAlisPRO (ver. 1.171.41.93a), Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* (2015) *C71*, 3-8.

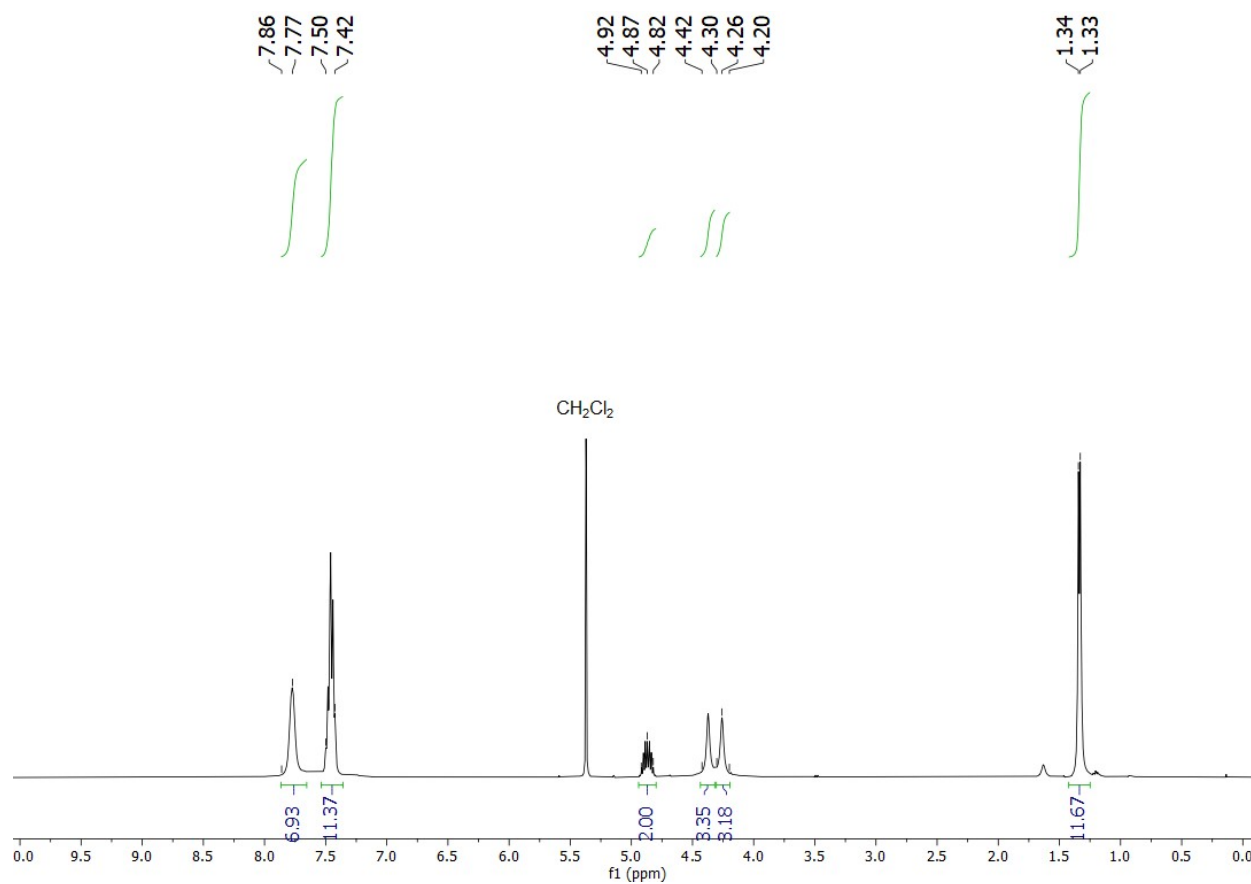


Figure S1. ^1H NMR spectrum of **1**.

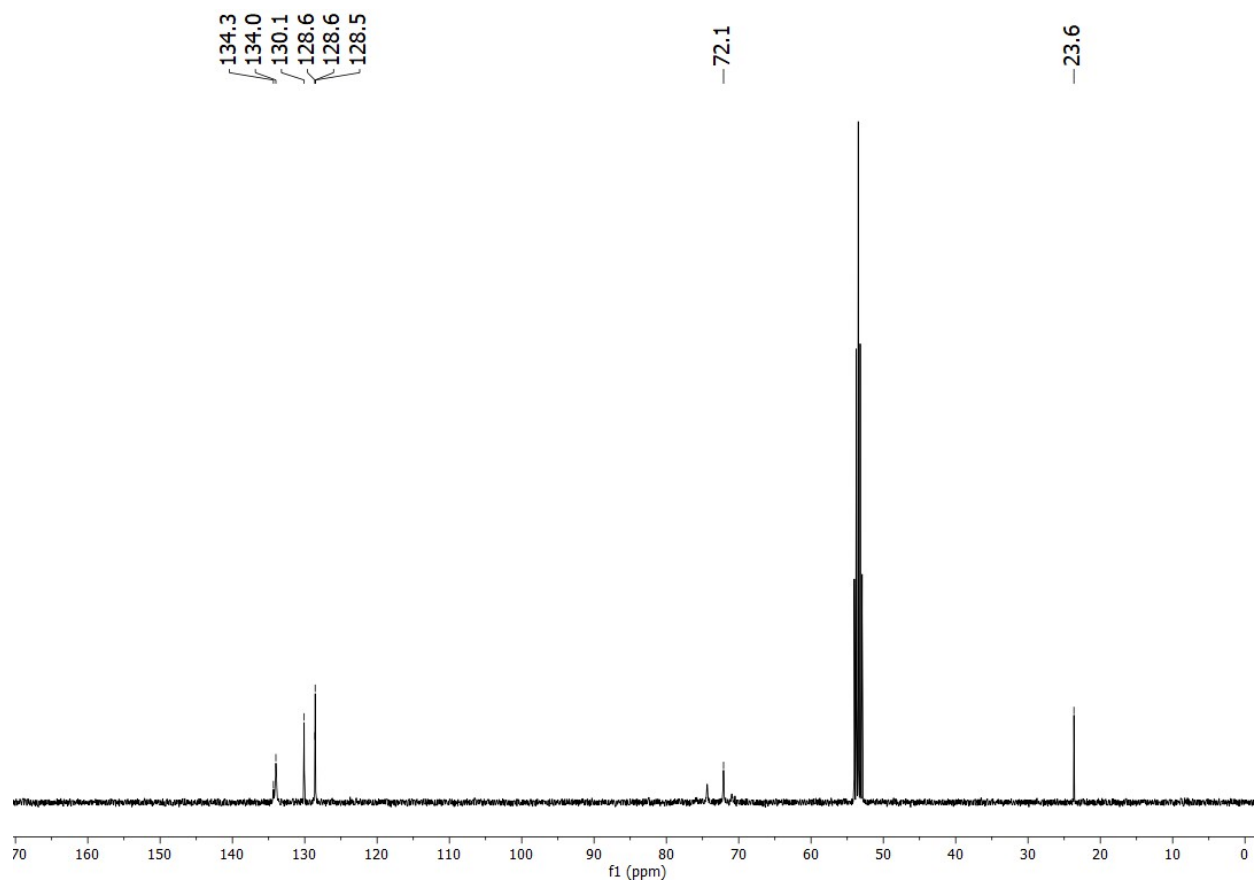


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1**

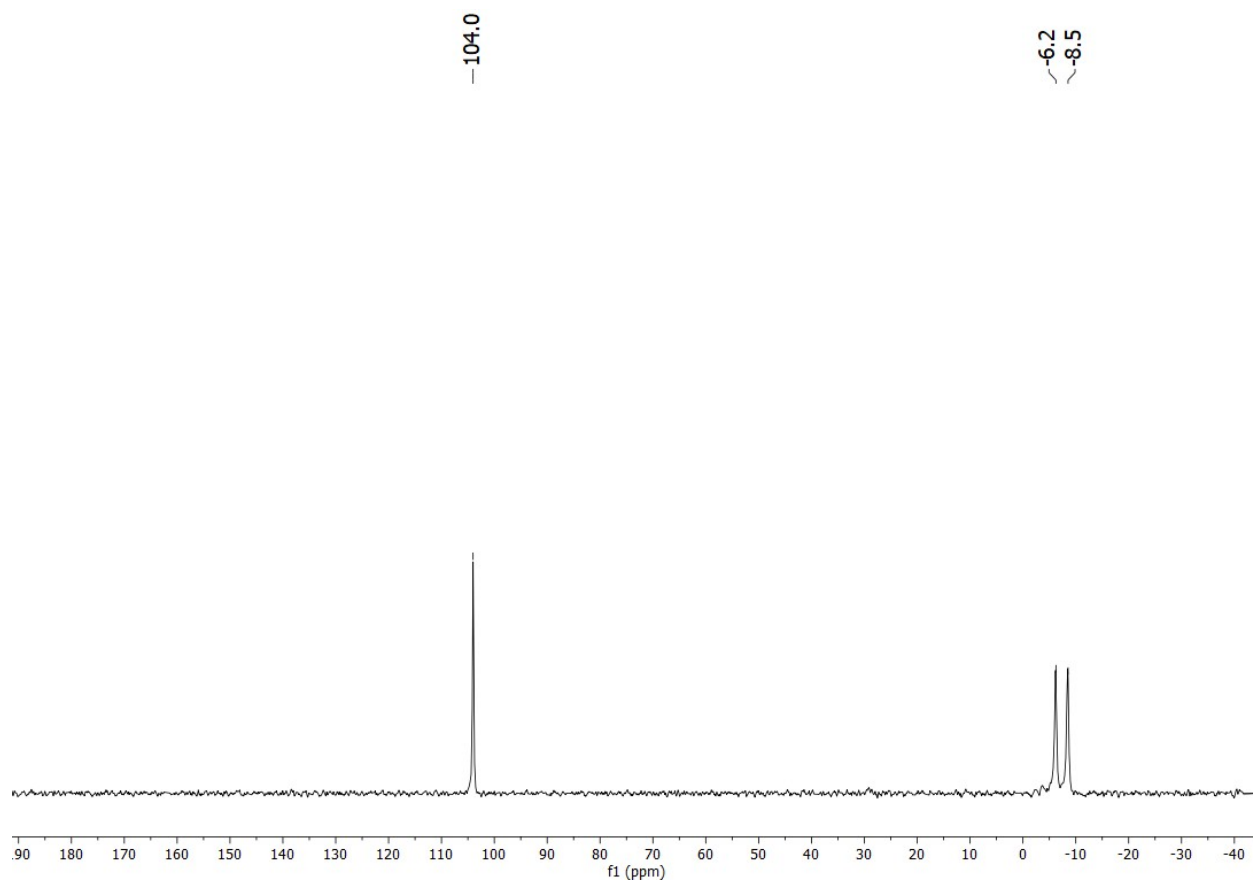


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1**

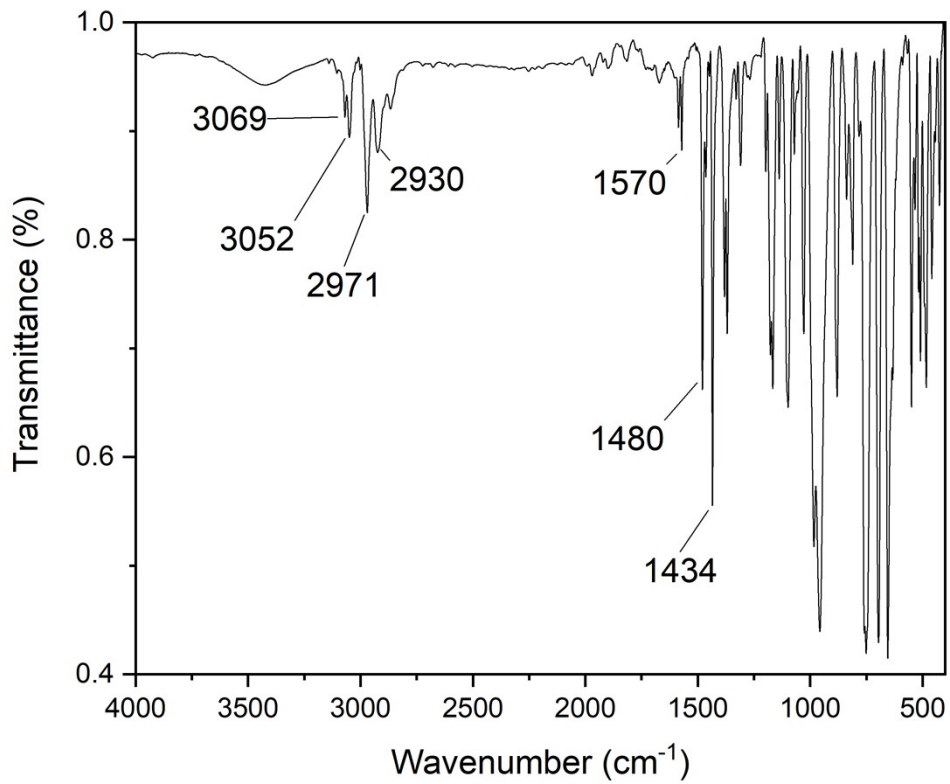


Figure S4. IR spectrum of **1**

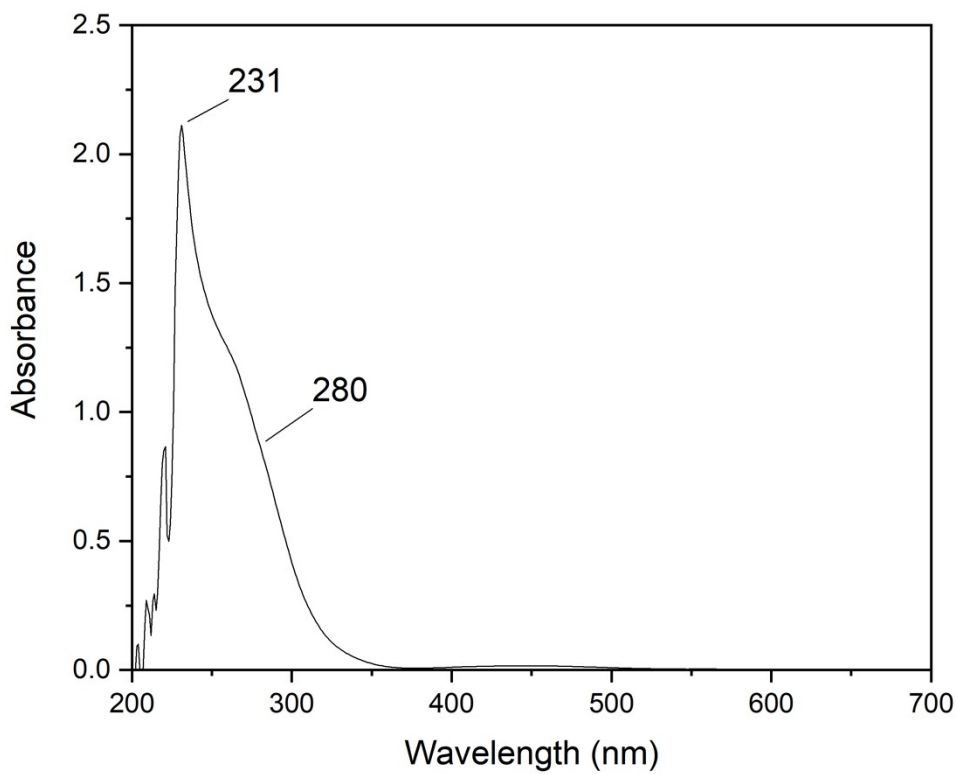


Figure S5. UV-Visible spectrum of **1**

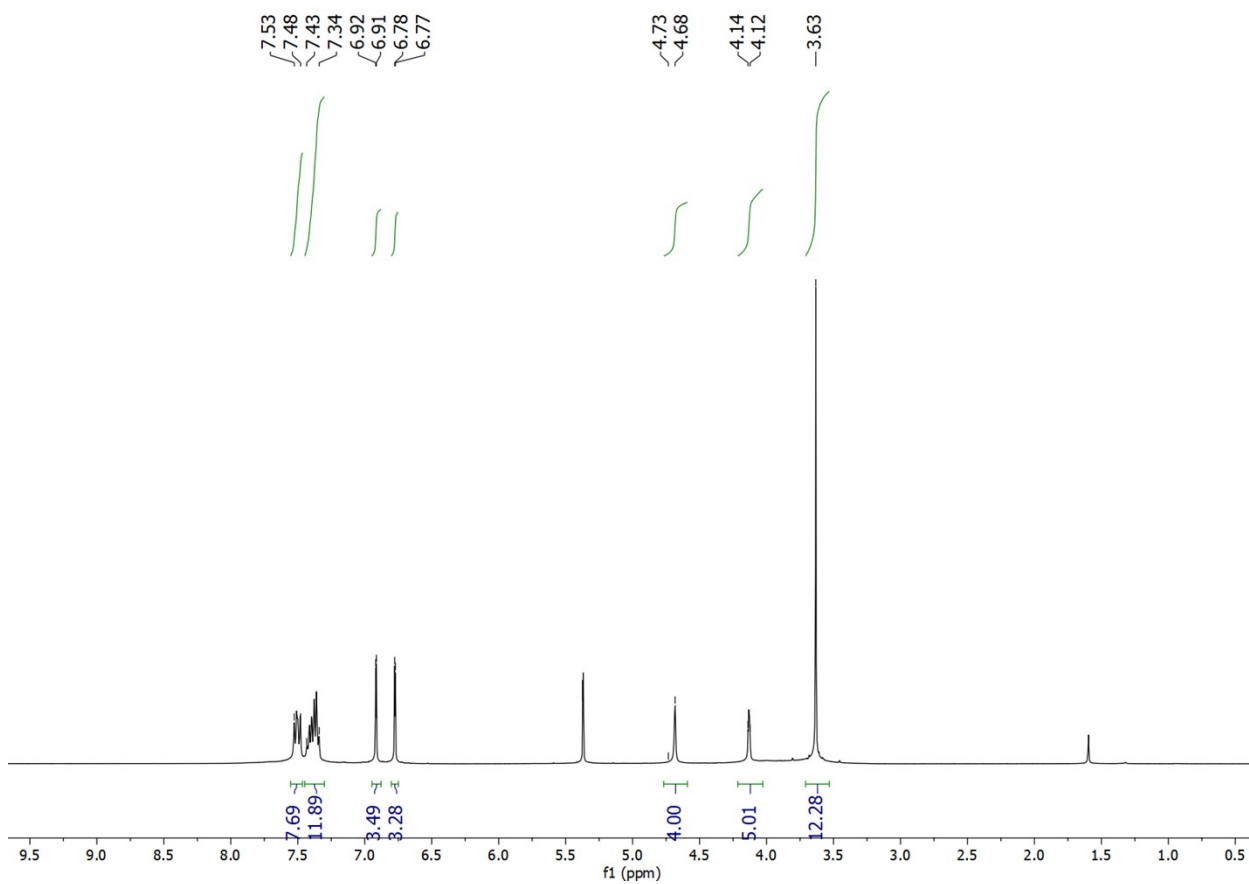


Figure S6. ^1H NMR of **2**. Peaks at 1.5 and 5.3 ppm belong to traces of water and dichloromethane.

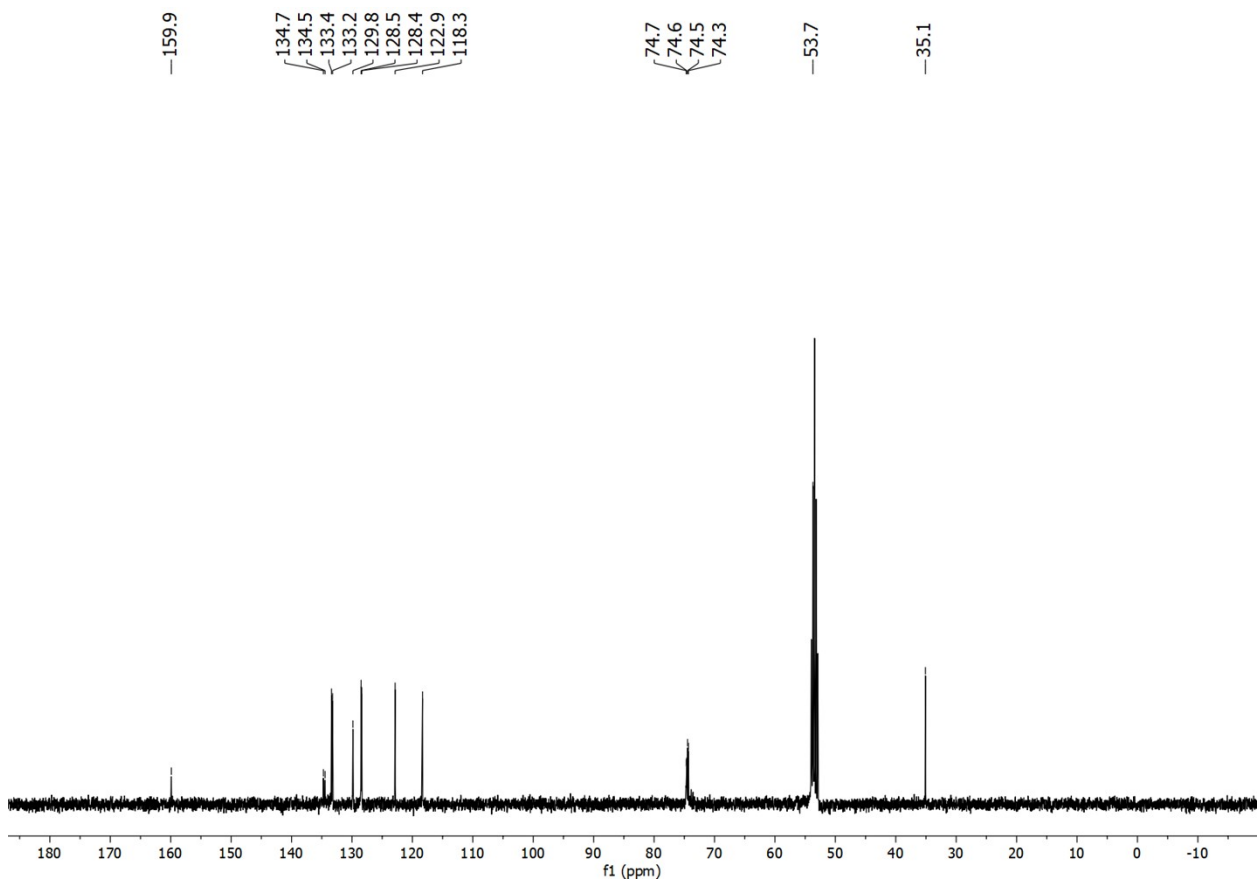


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2**

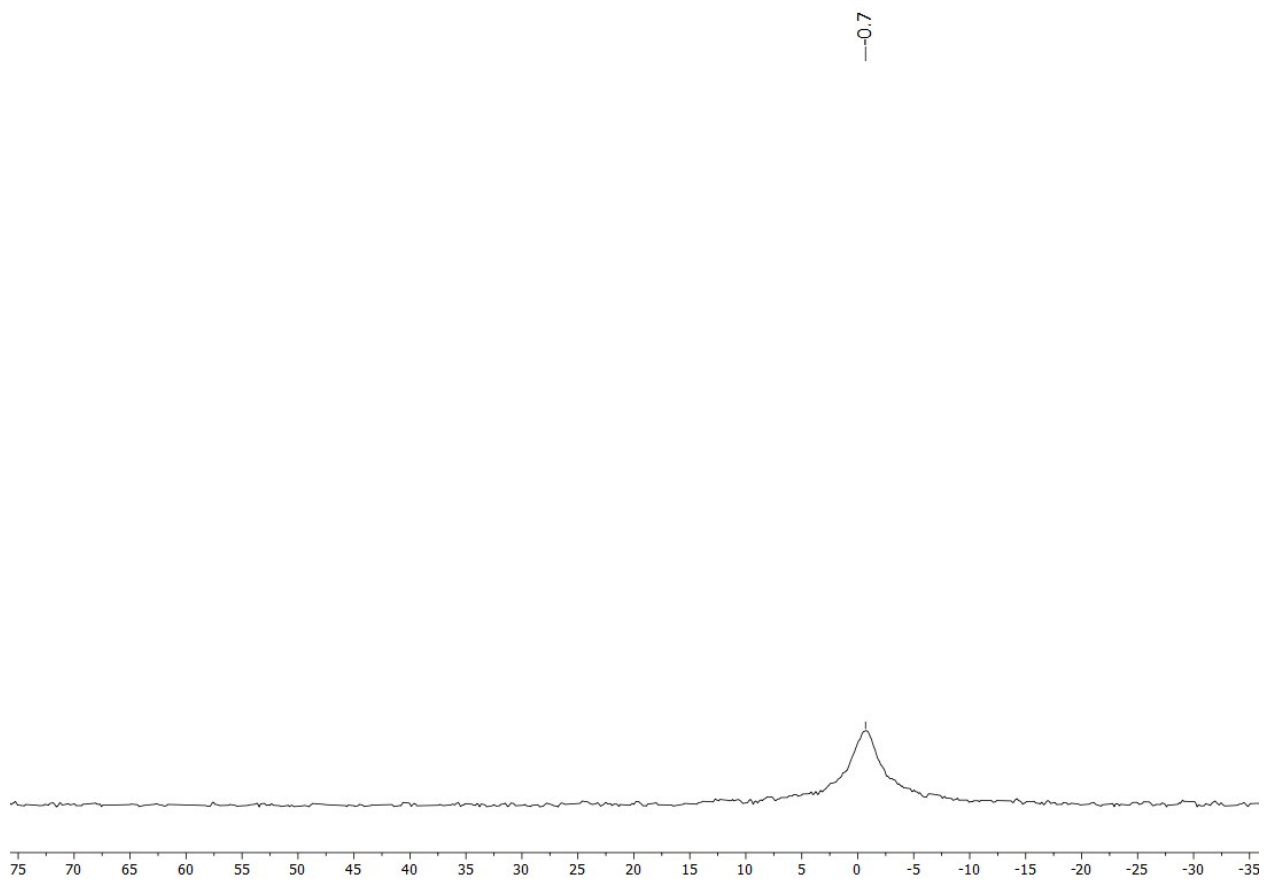


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR of **2**

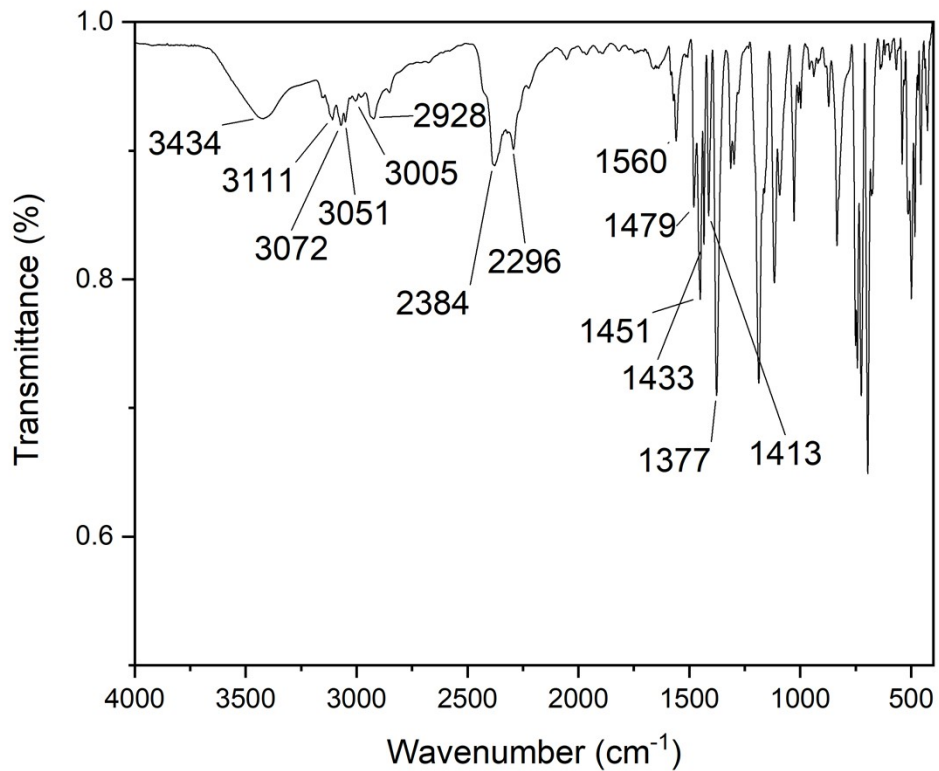


Figure S9. IR spectrum of **2**

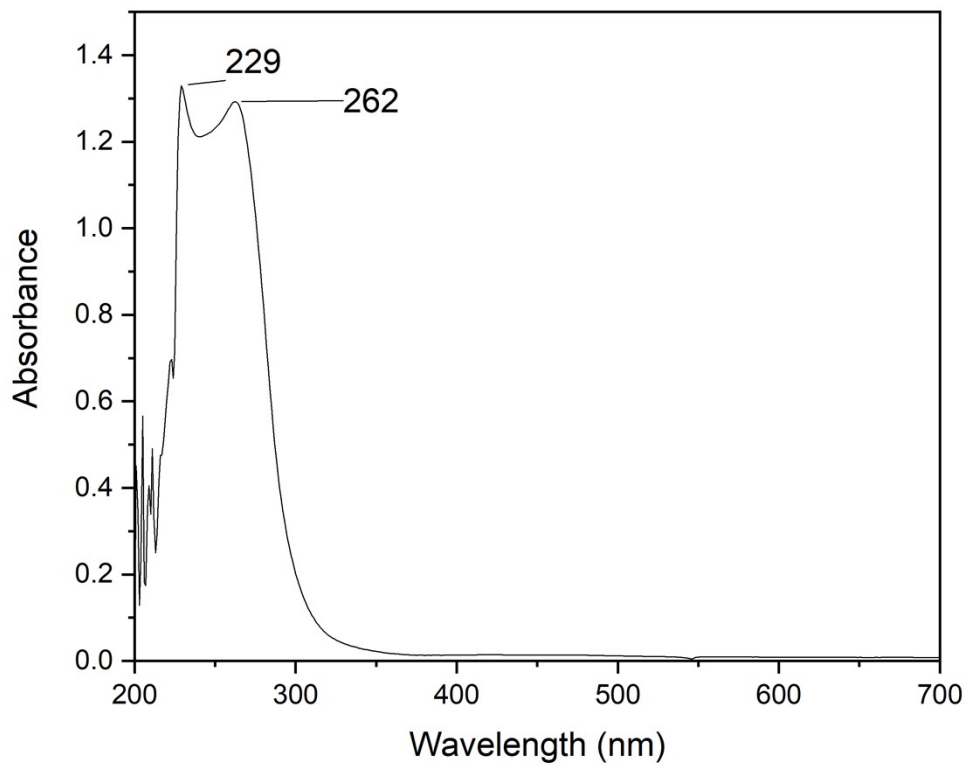


Figure S10. UV-Visible spectrum of **2**

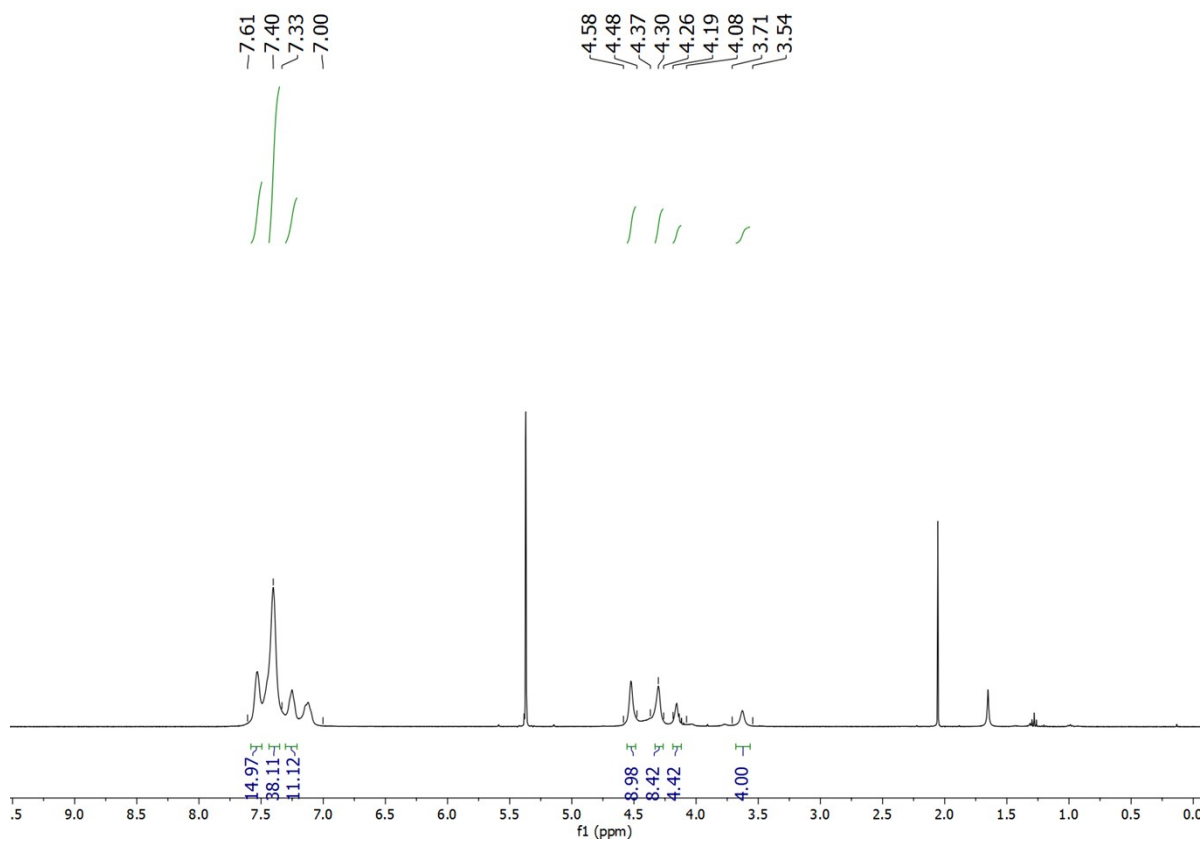


Figure S11. ^1H NMR spectrum of **3**. Signals at ~ 2.0 and ~ 5.4 ppm belong to trances of water and dichloromethane.

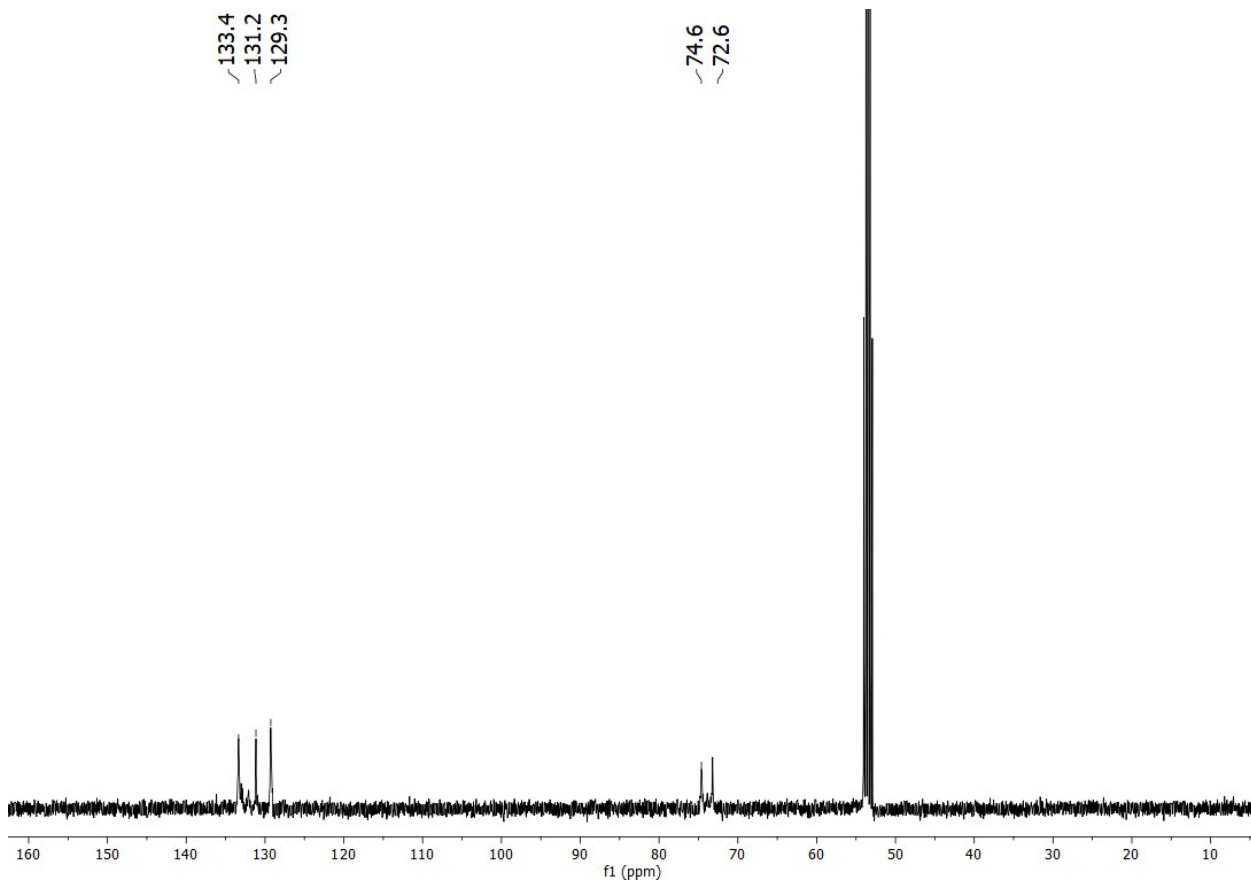


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3**

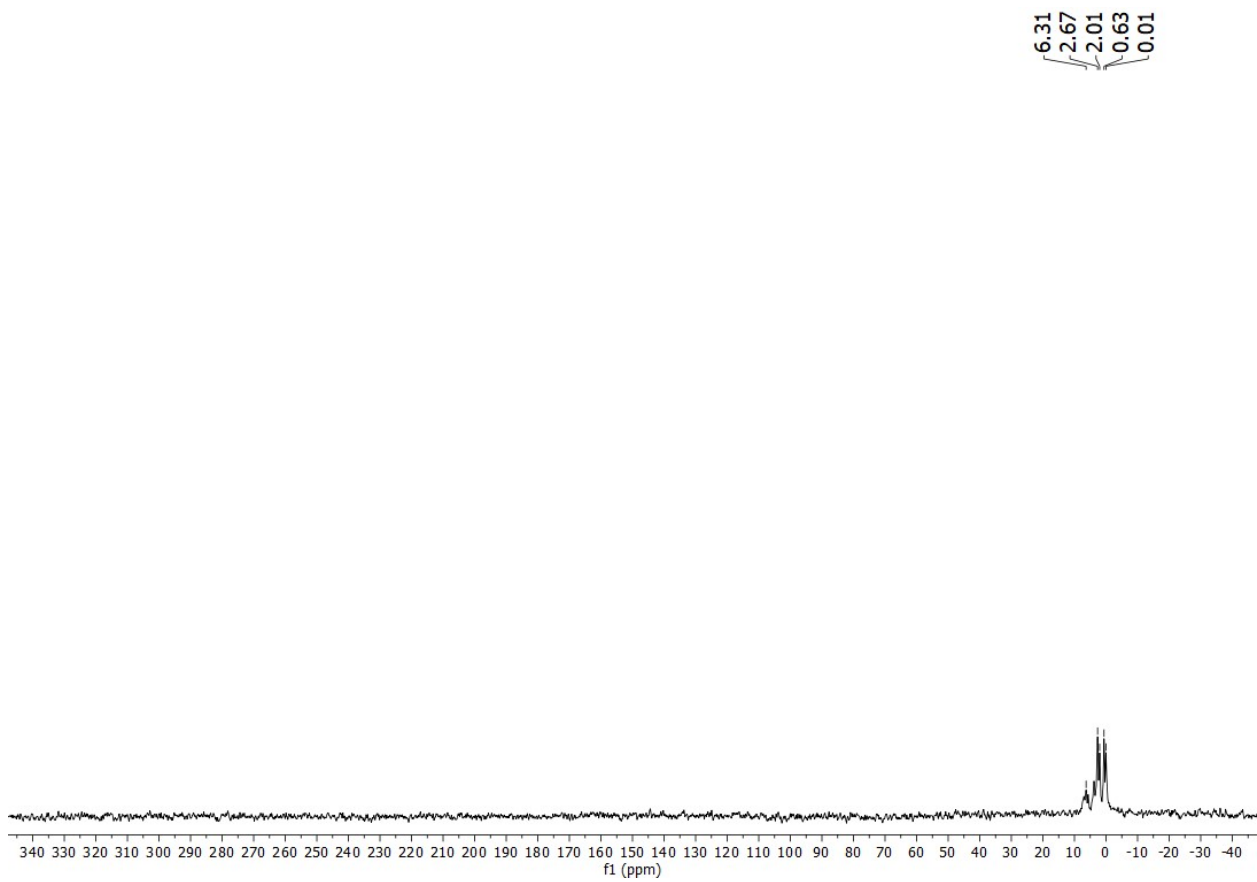


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR of **3**

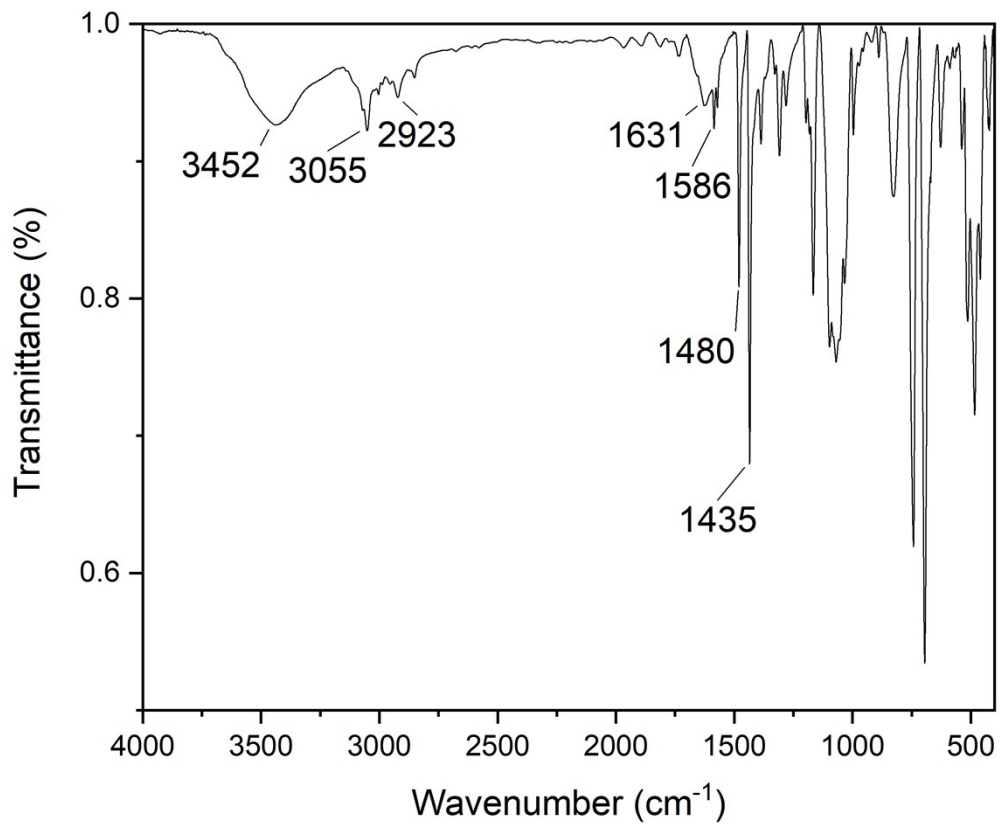


Figure S14. IR spectrum of **3**

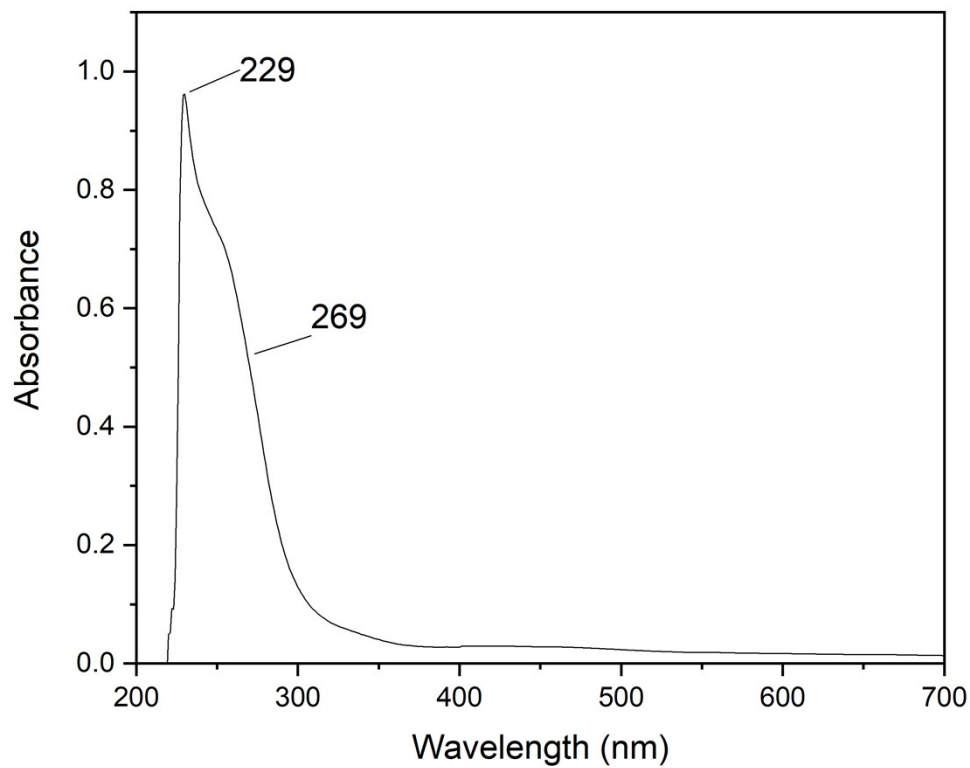


Figure S15. UV-Visible spectrum of **3**

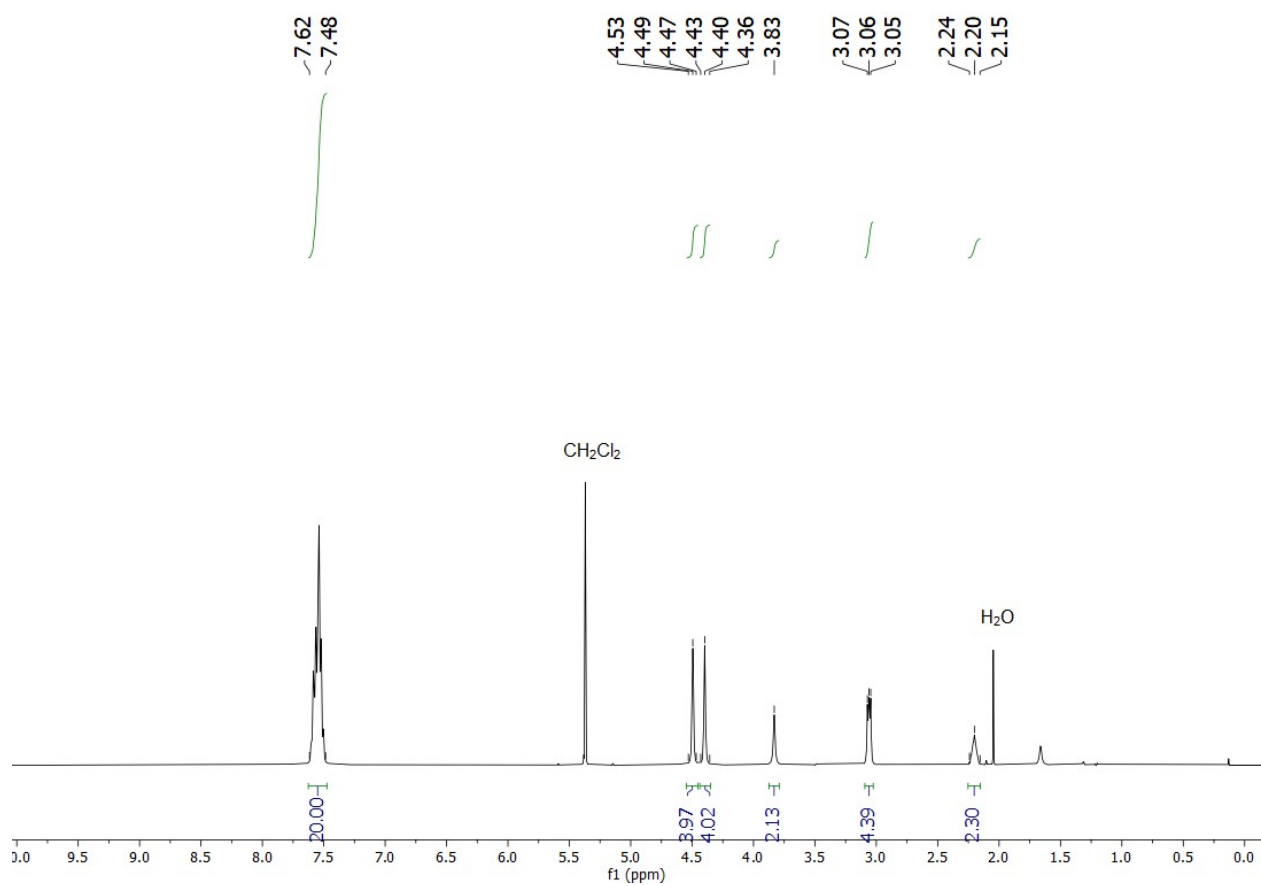


Figure S16. ^1H NMR of **4**

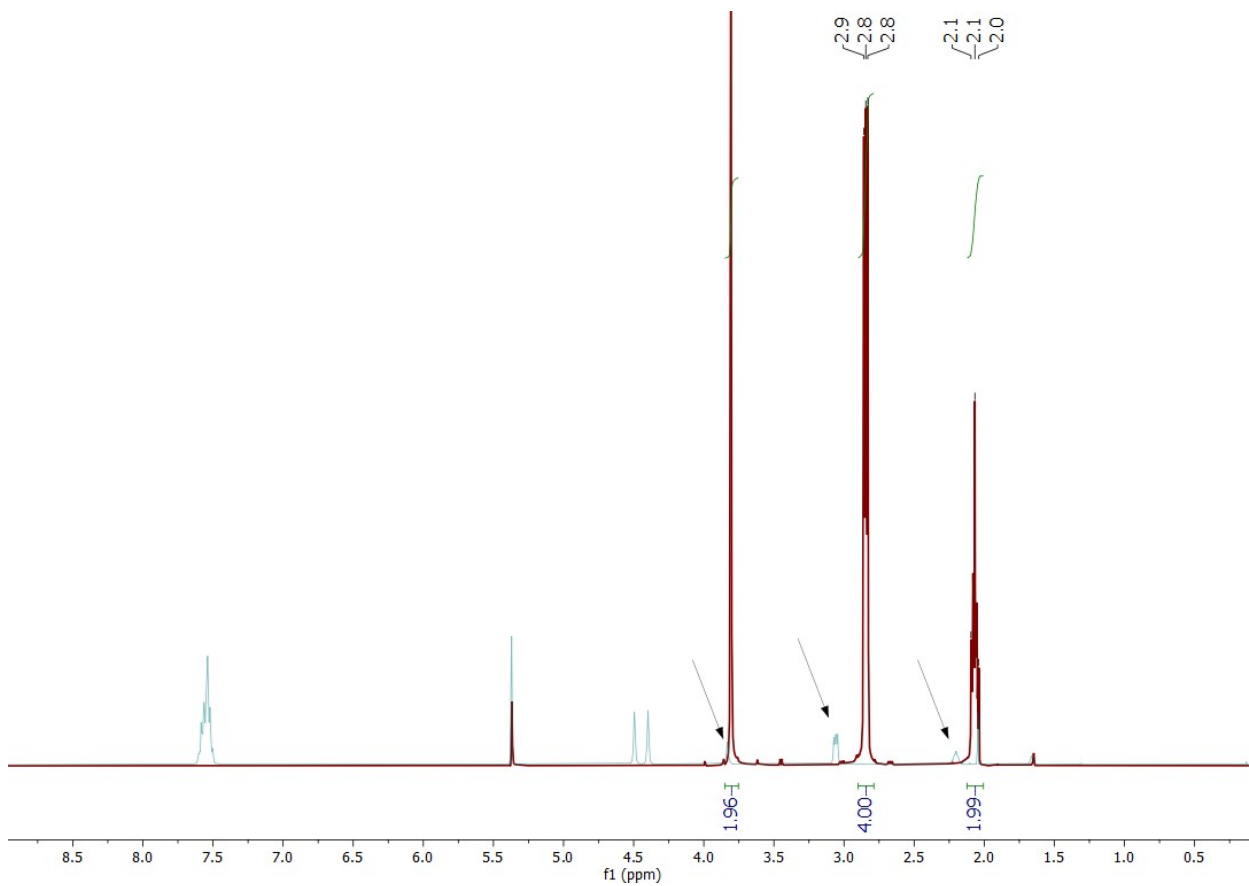


Figure S17. Superimposed spectra of the free (red) and coordinated 1,3 dithiane (blue). Arrows point to the coordinated dithiane signals.

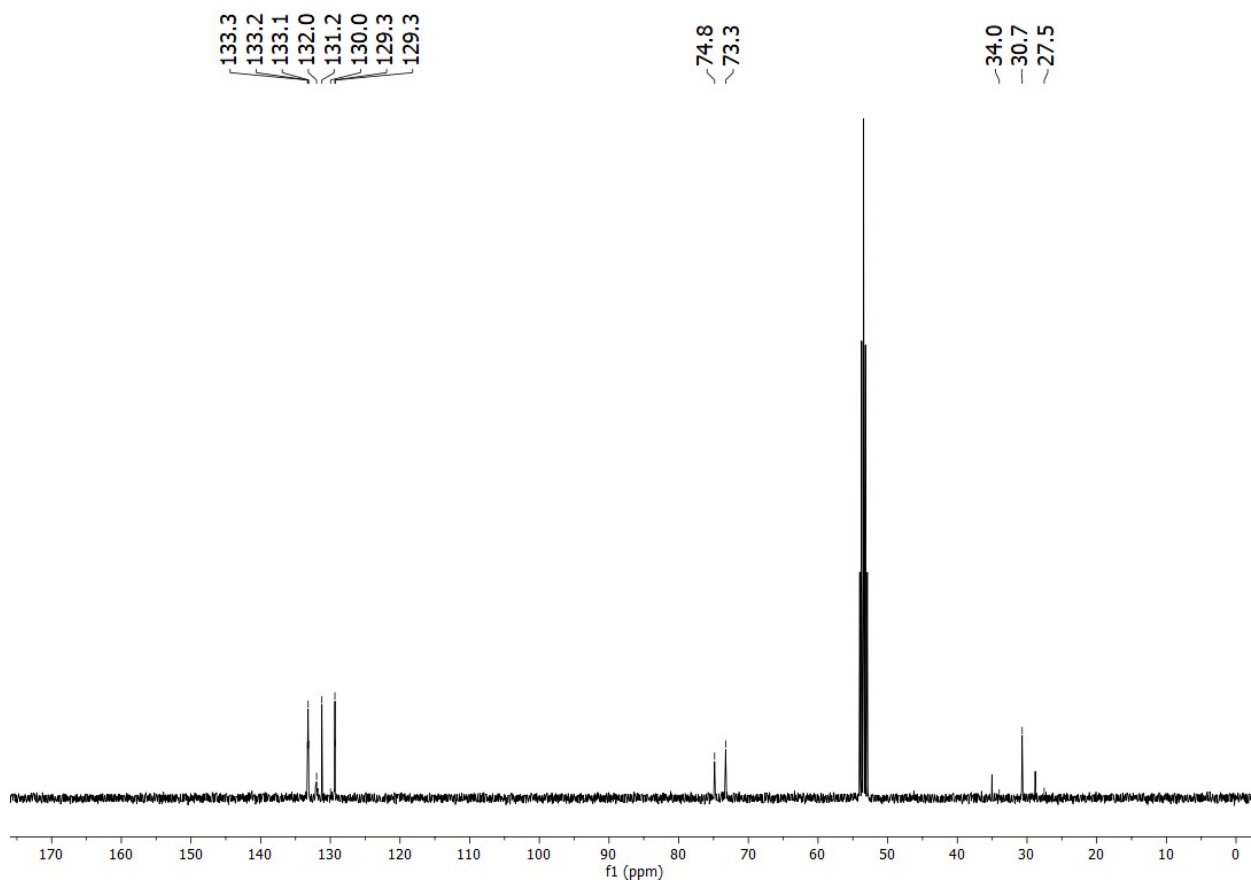


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR of 4

-1.1

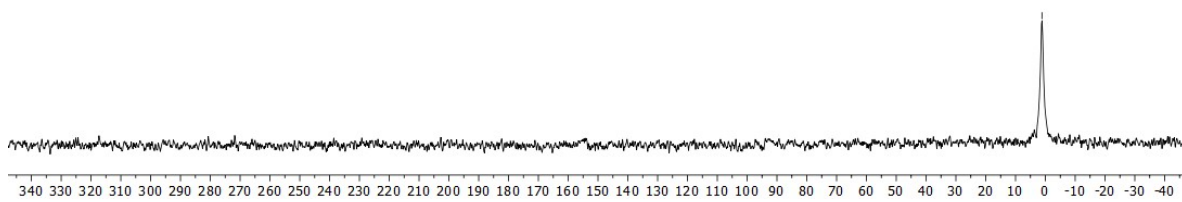


Figure S19. $^{31}\text{P}\{^1\text{H}\}$ NMR of **4**

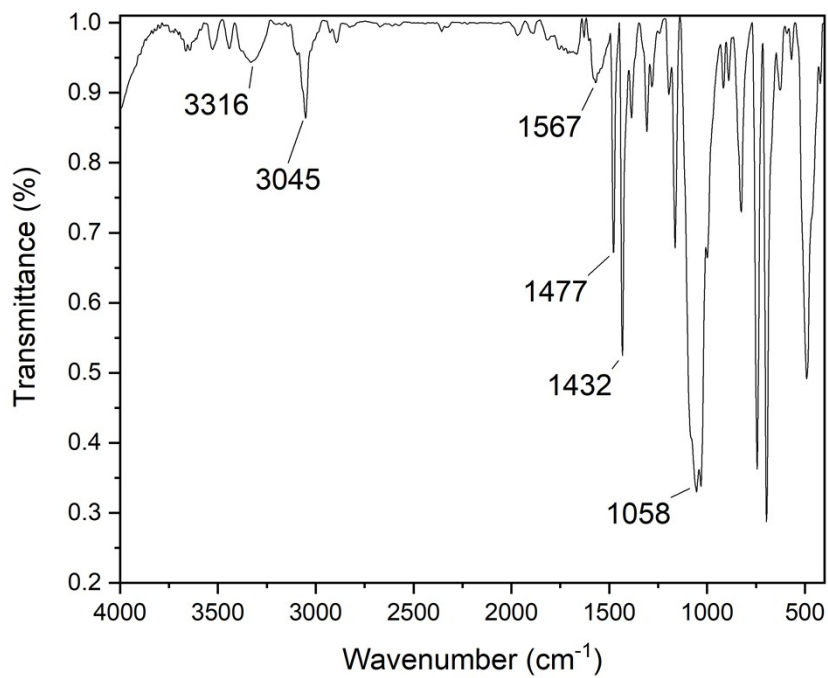


Figure S20. IR spectrum of **4**

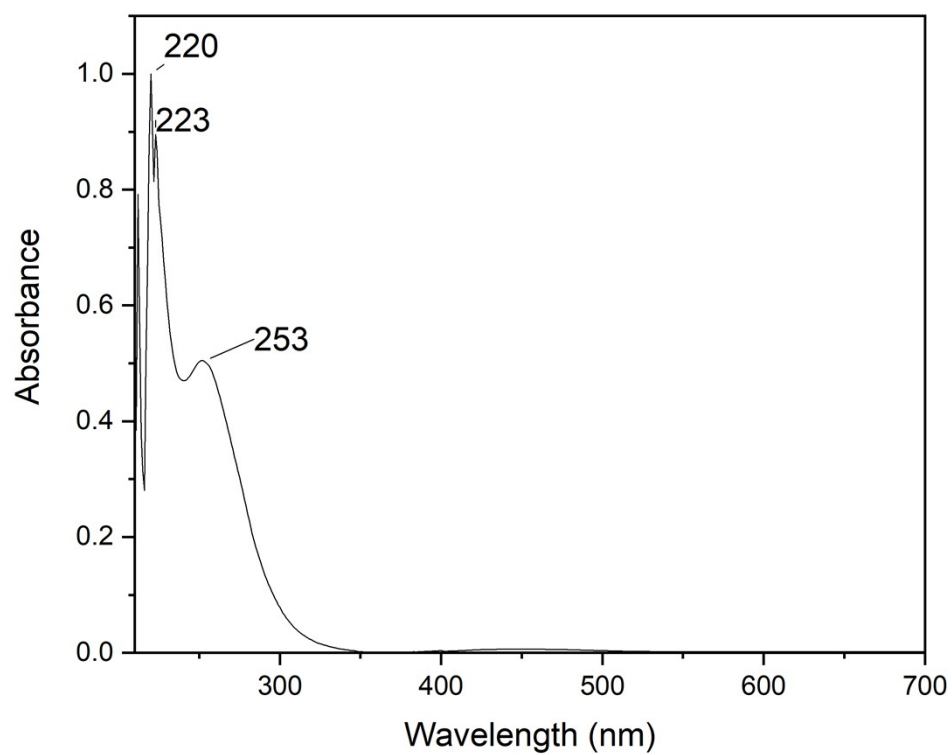


Figure S21. UV-Visible spectrum of **4**

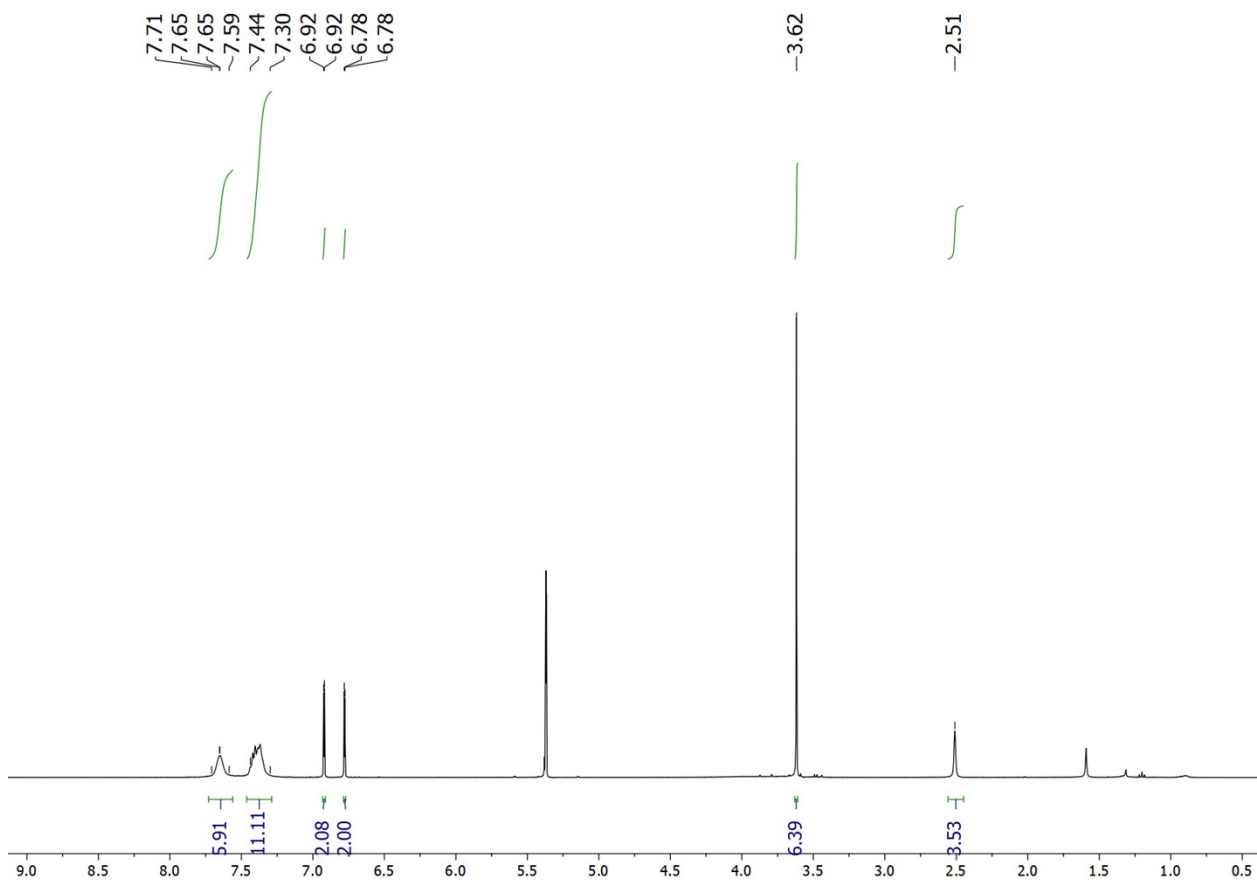


Figure S22. ^1H NMR of **5**

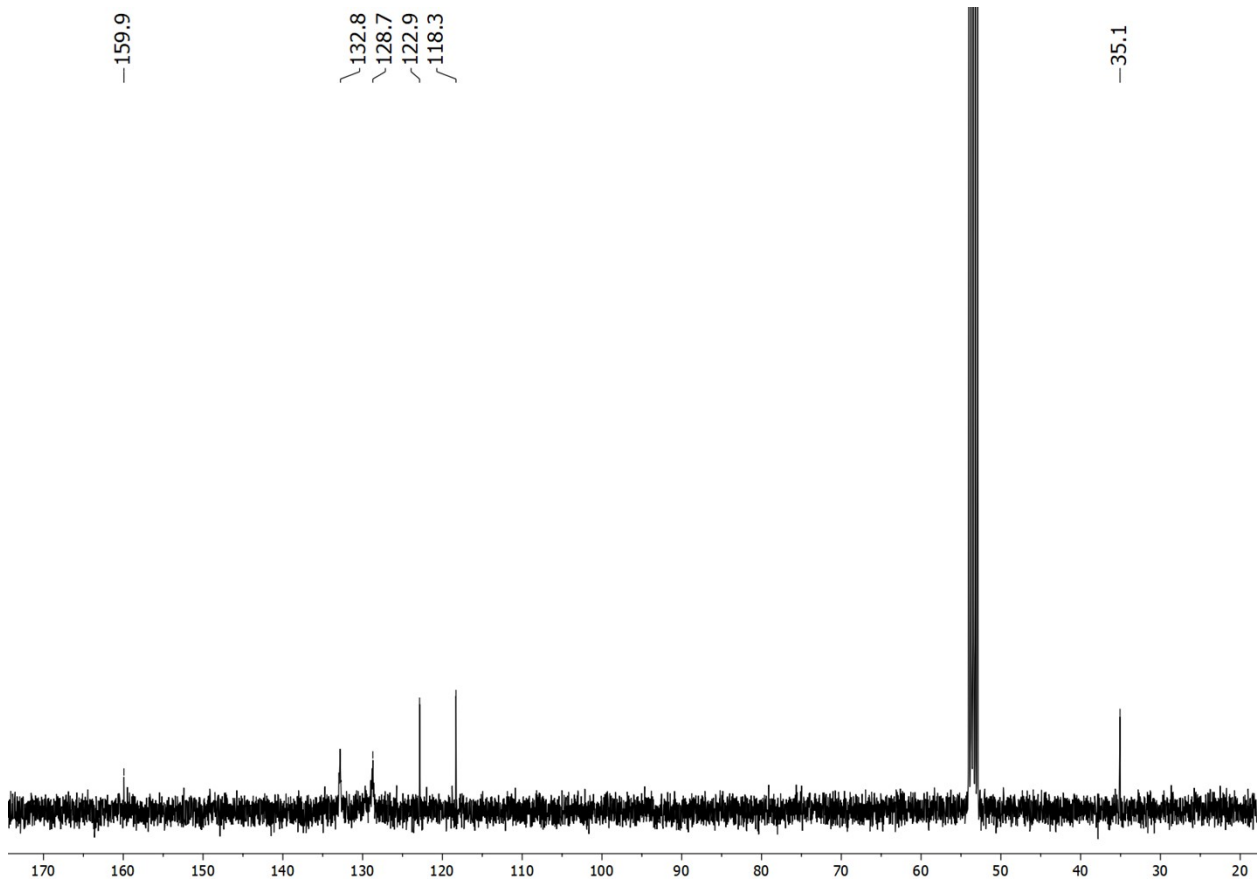


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR of **5**

-1.9

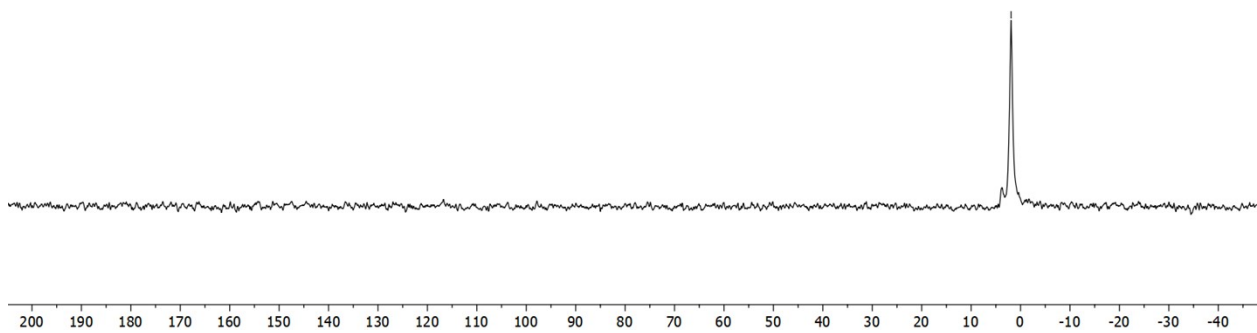


Figure S24. $^{31}\text{P}\{^1\text{H}\}$ NMR of **5**

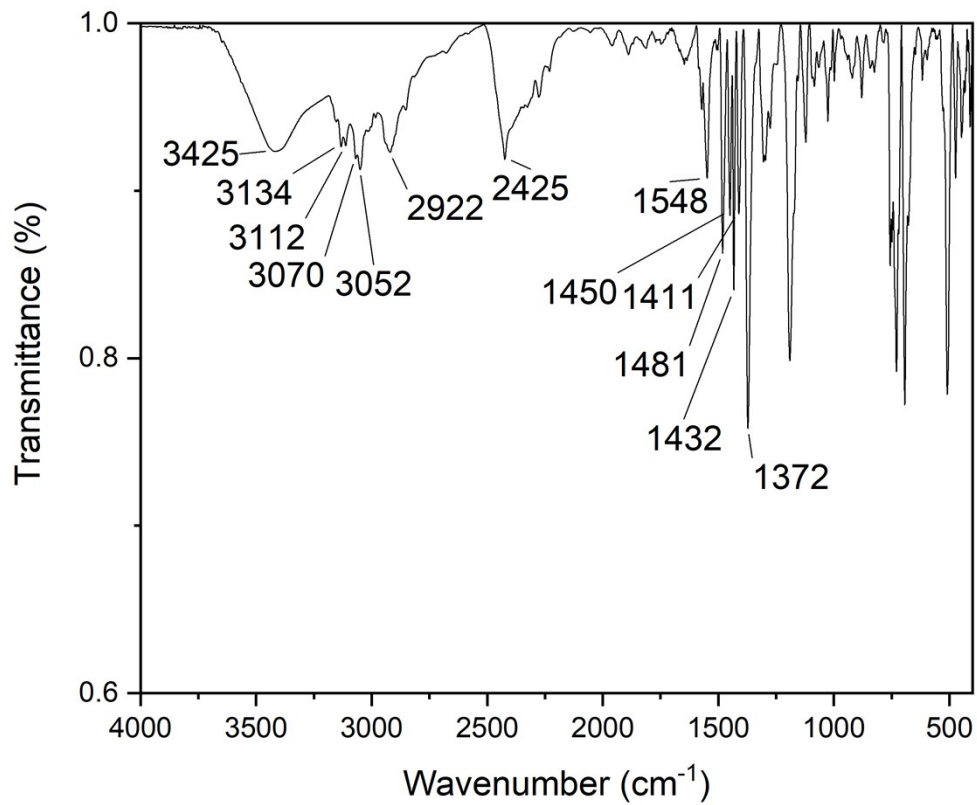


Figure S25. IR spectrum of **5**

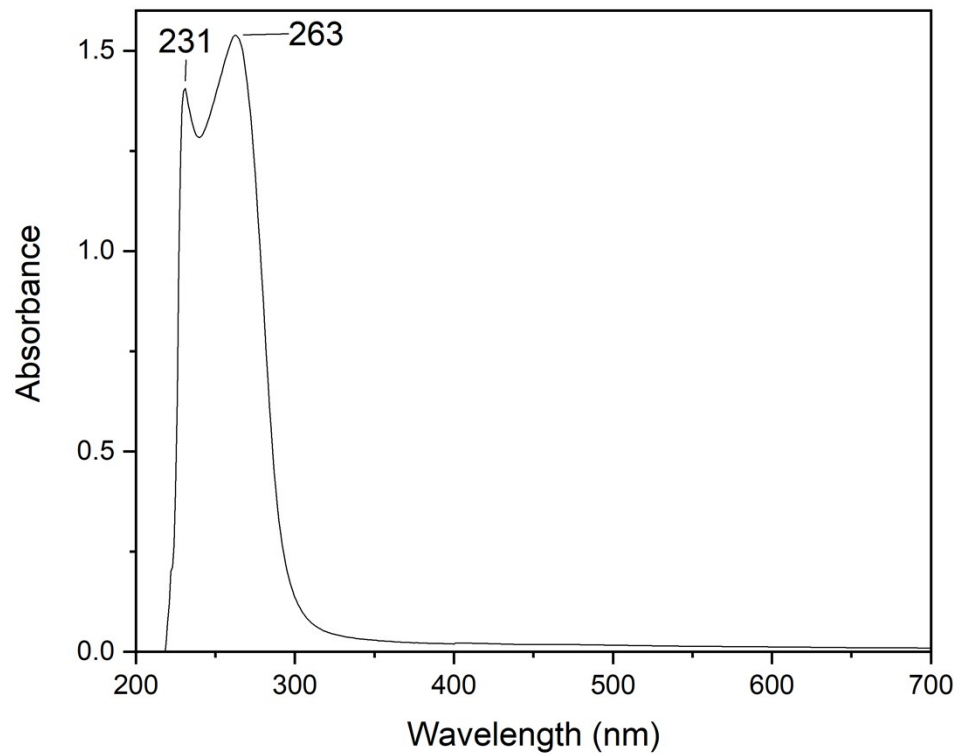


Figure S26. UV-Visible spectrum of **5**

Table S1. Table 1. Parameters of hydrogen bonds and C-H... π interactions (\AA , $^\circ$) for complexes **2** and **3**.

D-H...A	D-H	H...A	D...A	<DHA
2				
C11-H11A...S15B ⁱ	0.95	2.88	3.745(5)	153
C24A-H24A...S15B ⁱⁱ	0.95	2.91	3.682(4)	139
C10B-H10B...S15A ⁱⁱⁱ	0.95	2.97	3.435(5)	111
C11B-H11B...S15A ⁱⁱⁱ	0.95	2.87	3.381(5)	115
C13B-H13D...S15B	0.98	2.62	3.142(5)	113
C24B-H24B...N36	0.95	2.58	3.364(6)	140
C4A-H4AA... $\pi_{[N9A...C14A]}$ ^{iv}	0.98	2.81	3.540(6)	132
C4B-H4BB... $\pi_{[N3A...C5A]}$ ^v	0.98	2.99	3.627(6)	124
C13A-H13A... $\pi_{[N9B...C14B]}$ ^{vi}	0.98	2.77	3.517(5)	133
C25B-H25B... $\pi_{[N3A...C5A]}$ ^{vii}	0.95	2.83	3.593(6)	138
C33B-H33B... $\pi_{[N23A...C28A]}$ ^{viii}	1.00	2.96	3.692(4)	131
C34-H34C... $\pi_{[N17B...C22B]}$ ^{ix}	0.98	3.00	3.522(7)	115
3				
C5-H5A...F1	0.95	2.46	3.322(13)	151
C49-H49A...F2 ^x	0.95	2.50	3.282(9)	140

Symmetry codes: (i) $x-1, y+1, z$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z$; (iv) $1+x, y, z$; (v) $x, -1+y, z$; (vi) $-1+x, 1+y, z$; (vii) $1-x, 1-y, 1-z$; (viii) x, y, z ; (ix) $1-x, -y, 1-z$, (x) $-x+1, -y+1, -z+2$.

Table S2. Crystal data and structure refinement parameters for complexes **2** and **3**.

Identification code	2	3
CCDC	2358529	2358530
Empirical formula	C ₅₂ H ₅₅ Ag ₂ B ₂ FeN ₉ P ₂ S ₄	C ₁₀₂ H ₈₄ Ag ₂ B ₂ F ₈ Fe ₃ P ₆
Formula weight [g•mol ⁻¹]	1289.44	2052.42
Crystal size [mm]	0.183 x 0.146 x 0.056	0.054 x 0.037 x 0.026
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> [Å]	9.5392(2)	12.8144(3)
<i>b</i> [Å]	16.1160(3)	13.4377(3)
<i>c</i> [Å]	18.3419(3)	14.5283(2)
α [°]	81.786(2)	75.994(2)
β [°]	79.192(2)	82.191(2)
γ [°]	89.248(2)	72.494(2)
Volume [Å ³]	2741.06(9)	2309.54(9)
<i>Z</i>	2	1
Density (calc.) [g•cm ⁻³]	1.562	1.476
Absorption coefficient [mm ⁻¹]	10.098	8.529
<i>F</i> (000)	1308	1040
θ range [°]	2.478 to 77.436	3.142 to 78.114
Reflections collected / unique	39725 / 11029 [R(int) = 0.0394]	31137 / 9269 [R(int) = 0.0354]
	-8<= <i>h</i> <=11	-15<= <i>h</i> <=16
Index ranges <i>hkl</i>	-20<= <i>k</i> <=20	-17<= <i>k</i> <=16
	-22<= <i>l</i> <=21	-15<= <i>l</i> <=18
restraints/parameters	0/650	6/557
Goodness of fit on <i>F</i> ²	1.088	1.033
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0446 wR2 = 0.1137	R1 = 0.0502 wR2 = 0.1324
R indices (all data)	R1 = 0.0478 wR2 = 0.1155	R1 = 0.0556 wR2 = 0.1361
Max electron density/e•Å ⁻³	2.356	1.187
Min electron density/e•Å ⁻³	-1.286	-1.165

Table S3. Optimization table for catalyst **3**.

Cat. mol%	Temp. (°C)	Product yield (%)
1	40	99
0.5	40	99
0.05	40	99
0.025	40	70
0.05	25	90
Recovered 3	40	50

Reaction conditions: phenylacetylene (1 mmol, 1.0 equiv), sodium azide (1.2 equiv), benzyl chloride (1 equiv), catalyst **3** (1 mol%), H₂O (2 mL), 4 h, 40 °C.

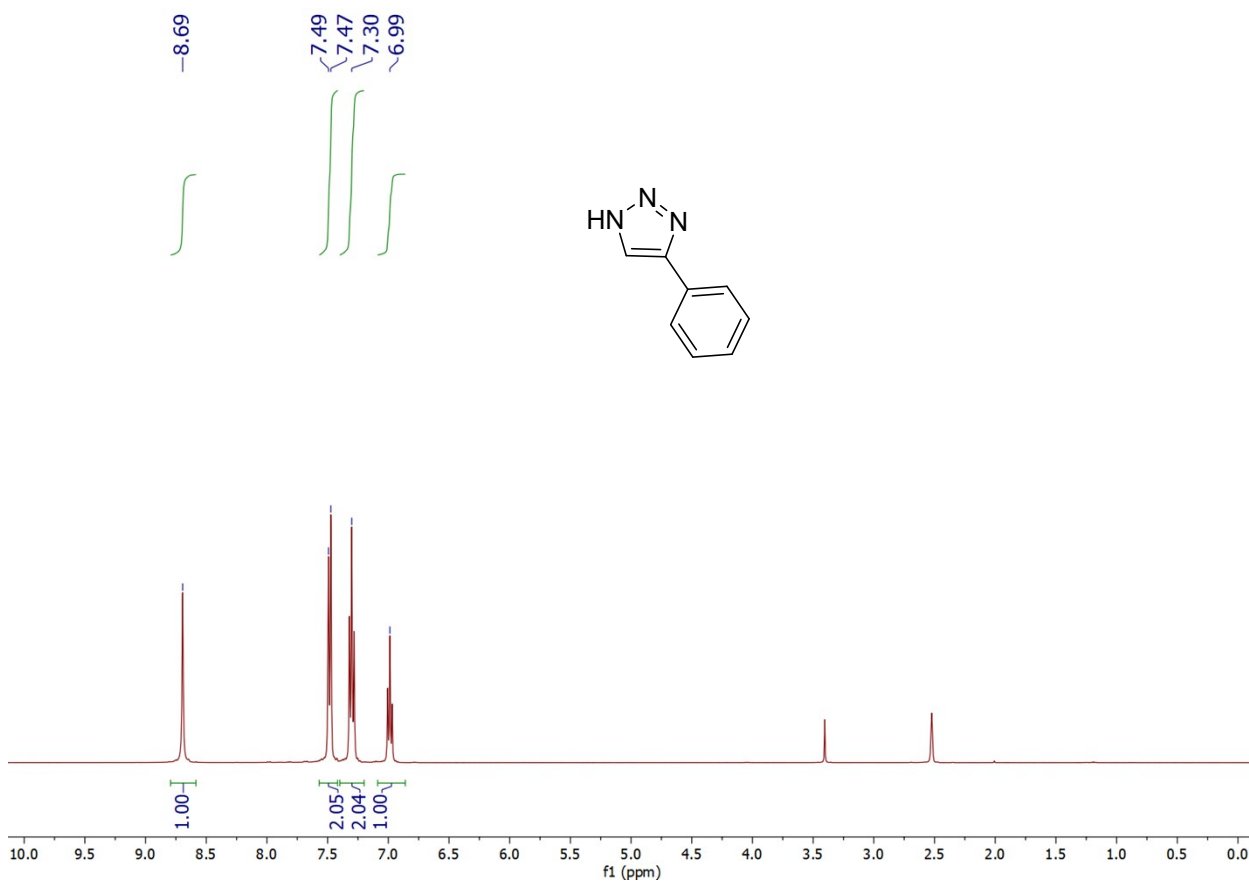


Figure S27. ¹H NMR spectrum of click product **a**. Signals at ~2.5 and ~3.4 ppm belong to traces of solvent and water.

¹H NMR (400 MHz, DMSO) δ 8.69 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 2H).

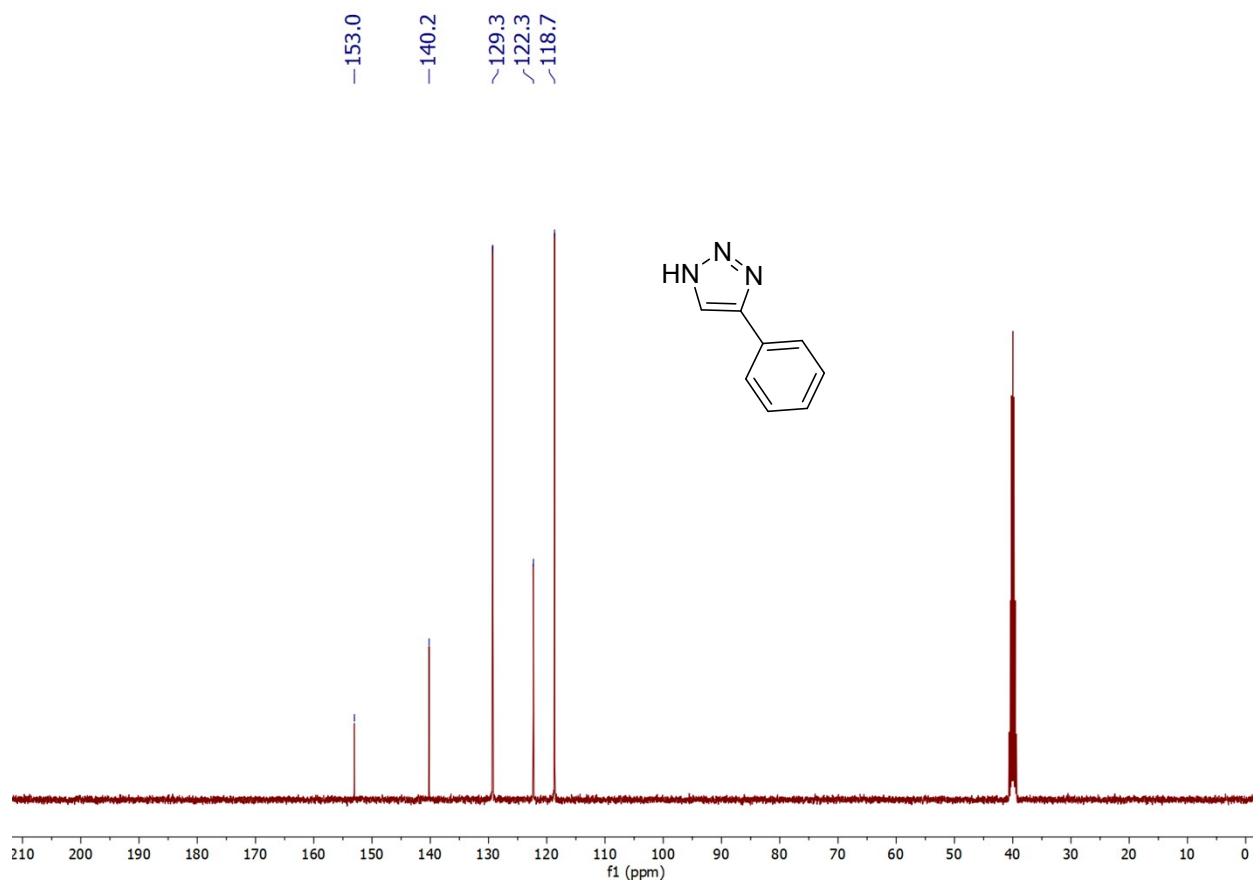


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **a**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 153.0, 140.2, 129.3, 122.3, 118.7.

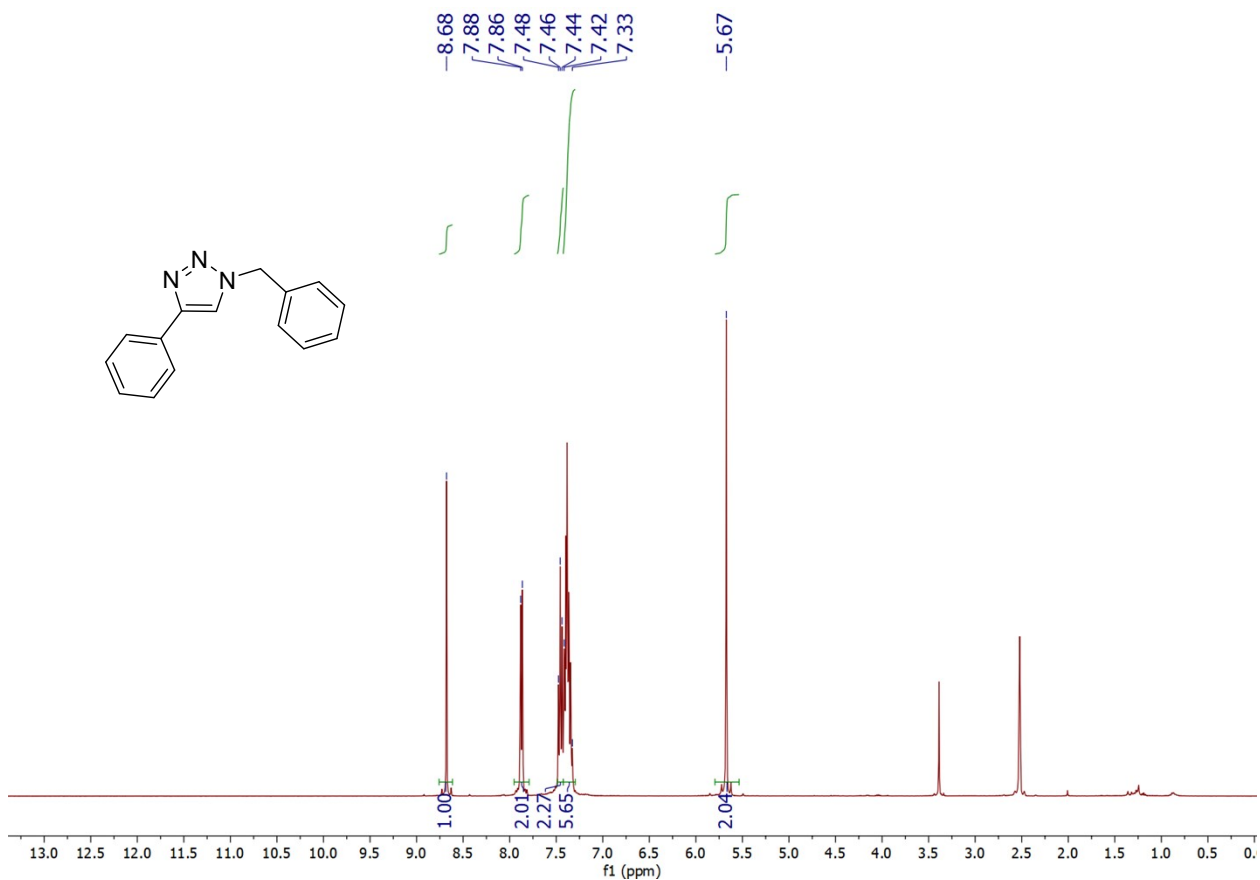


Figure S29. ¹H NMR spectrum of click product **b**. Signals at ~2.5 and ~3.4 ppm belong to traces of solvent and water.

¹H NMR (400 MHz, DMSO) δ 8.68 (s, 1H), 7.87 (d, $^3J = 8.0$ Hz, 2H), 7.48–7.33 (m, 7H), 5.67 (s, 2H).

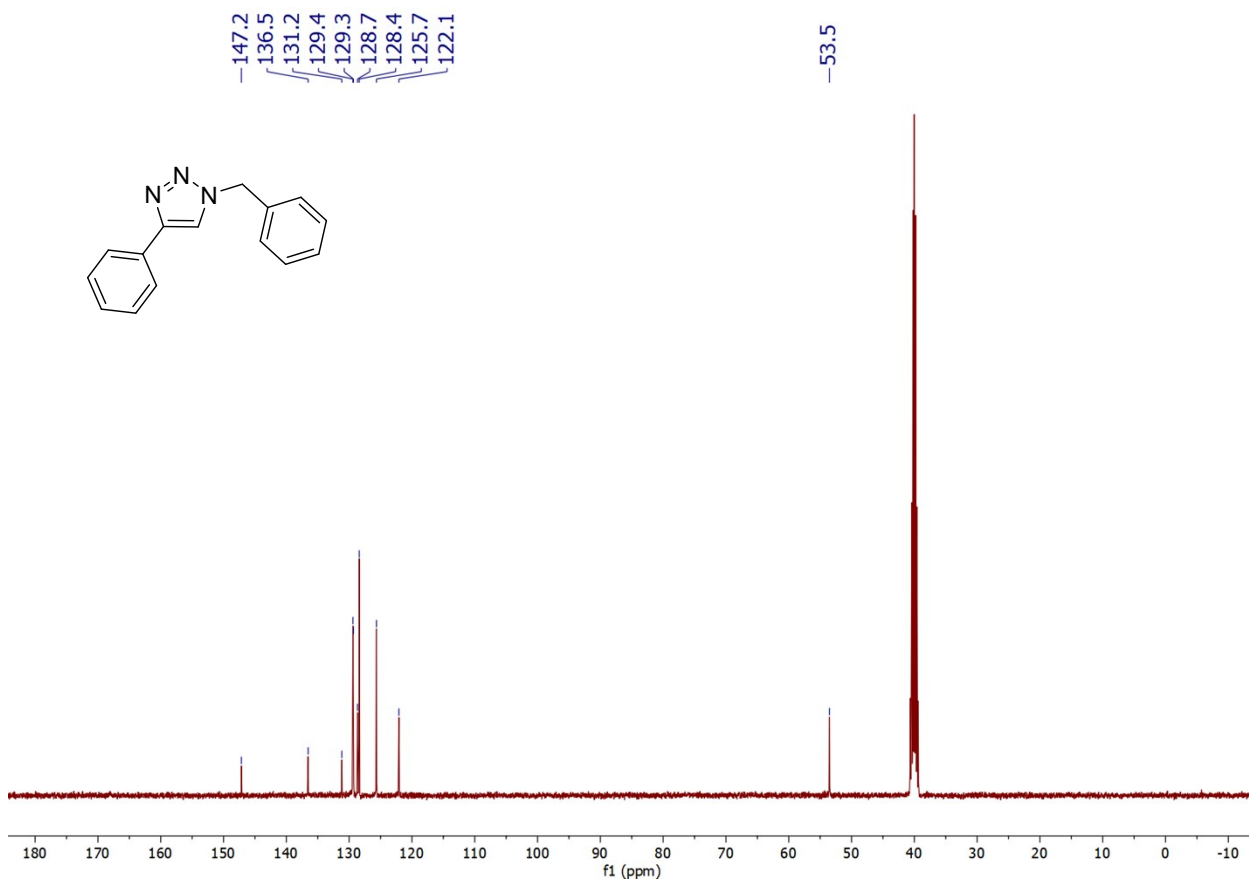


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **b**. Multiplet signal at ~40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 147.2, 136.5, 131.2, 129.4, 129.3, 128.7, 128.4, 125.6, 122.0, 53.5.

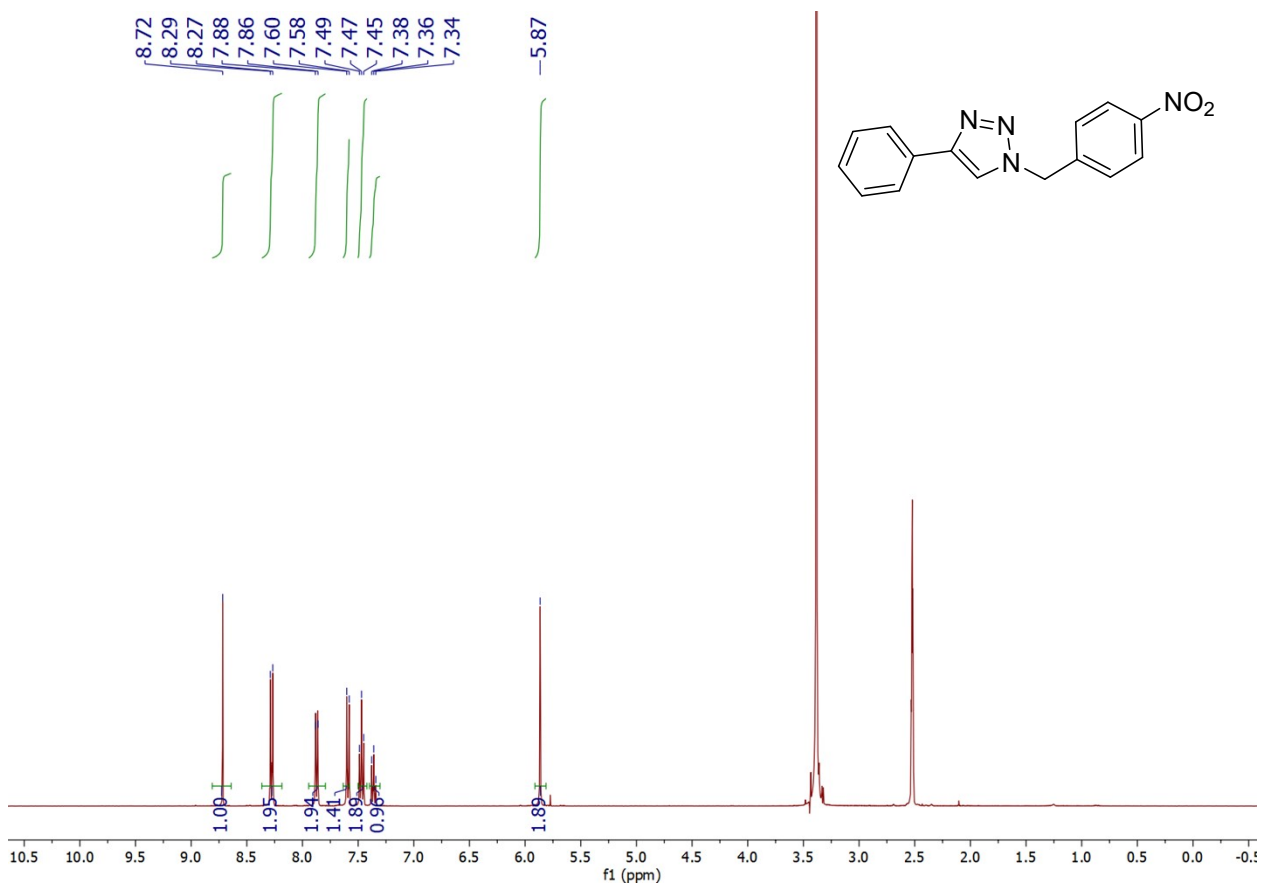


Figure S31. ¹H NMR spectrum of click product **c**. Signals at ~2.5 and ~3.4 ppm belong to traces of solvent and water.

¹H NMR (400 MHz, DMSO) δ 8.72 (s, 1H), 8.28 (d, $^3J = 8.0$ Hz, 2H), 7.87 (d, $^3J = 8.0$ Hz, 2H), 7.59 (d, $^3J = 8.0$ Hz, 2H), 7.47 (t, $^3J = 8.0$ Hz, 2H), 7.36 (t, $^3J = 8.0$ Hz, 1H), 5.87 (s, 2H).

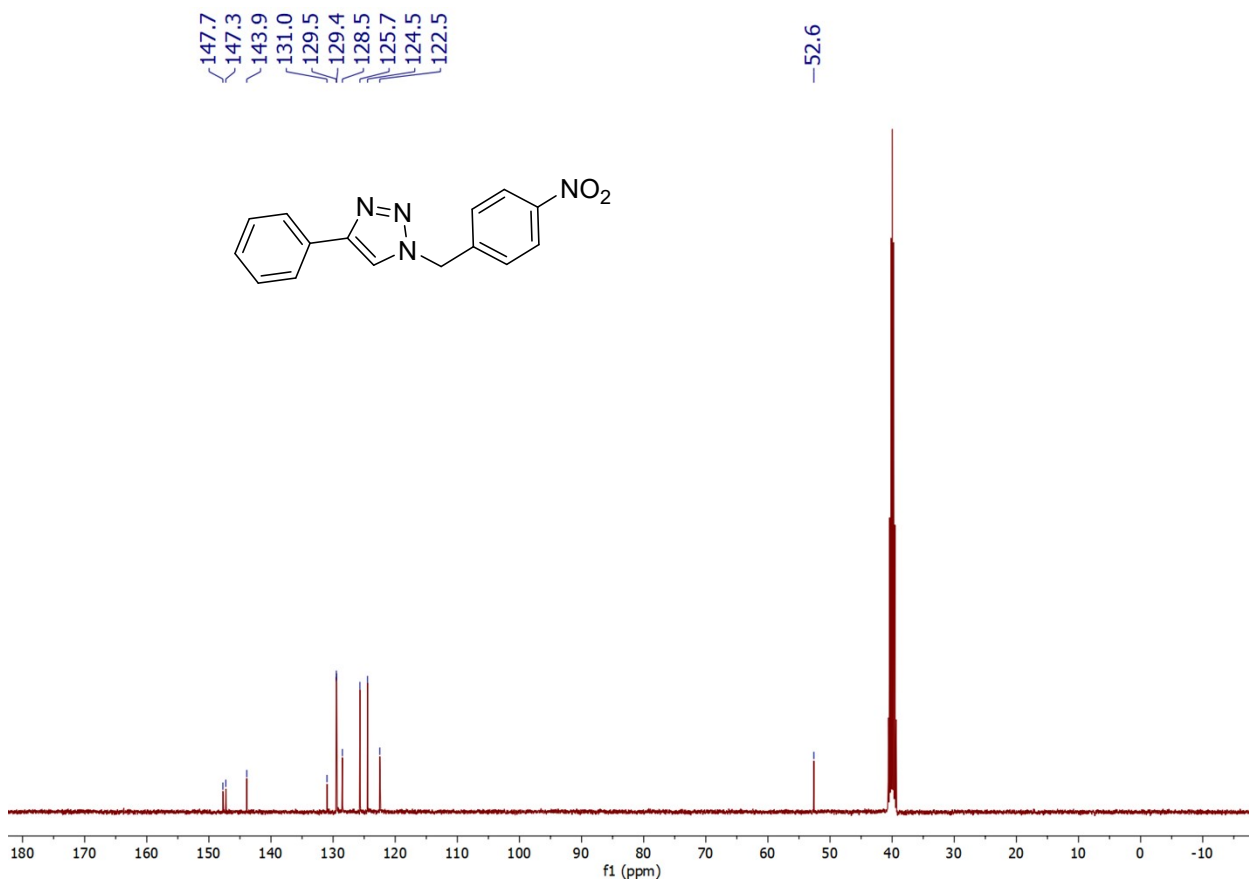


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **c**. Multiplet signal at ~40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 147.7, 147.3, 143.9, 131.0, 129.5, 129.4, 128.5, 125.7, 124.5, 122.5, 52.6.

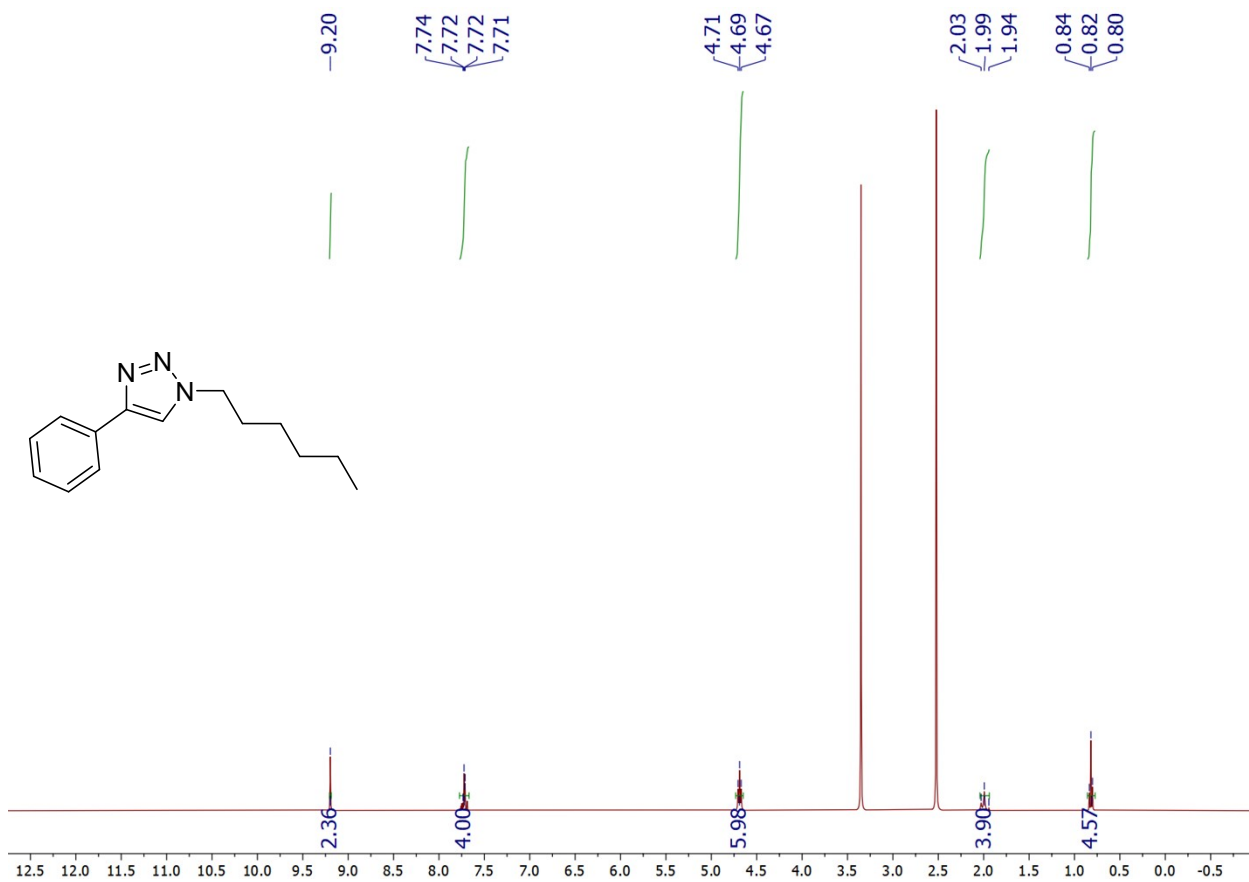


Figure S33. ^1H NMR spectrum of click product **d**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 9.20 (s, 2H), 7.74–7.71 (m, 4H), 4.69 (t, $^3J = 8.0$ Hz, 6H), 2.03–1.94 (m, 4H), 0.84–0.80 (m, 4H).

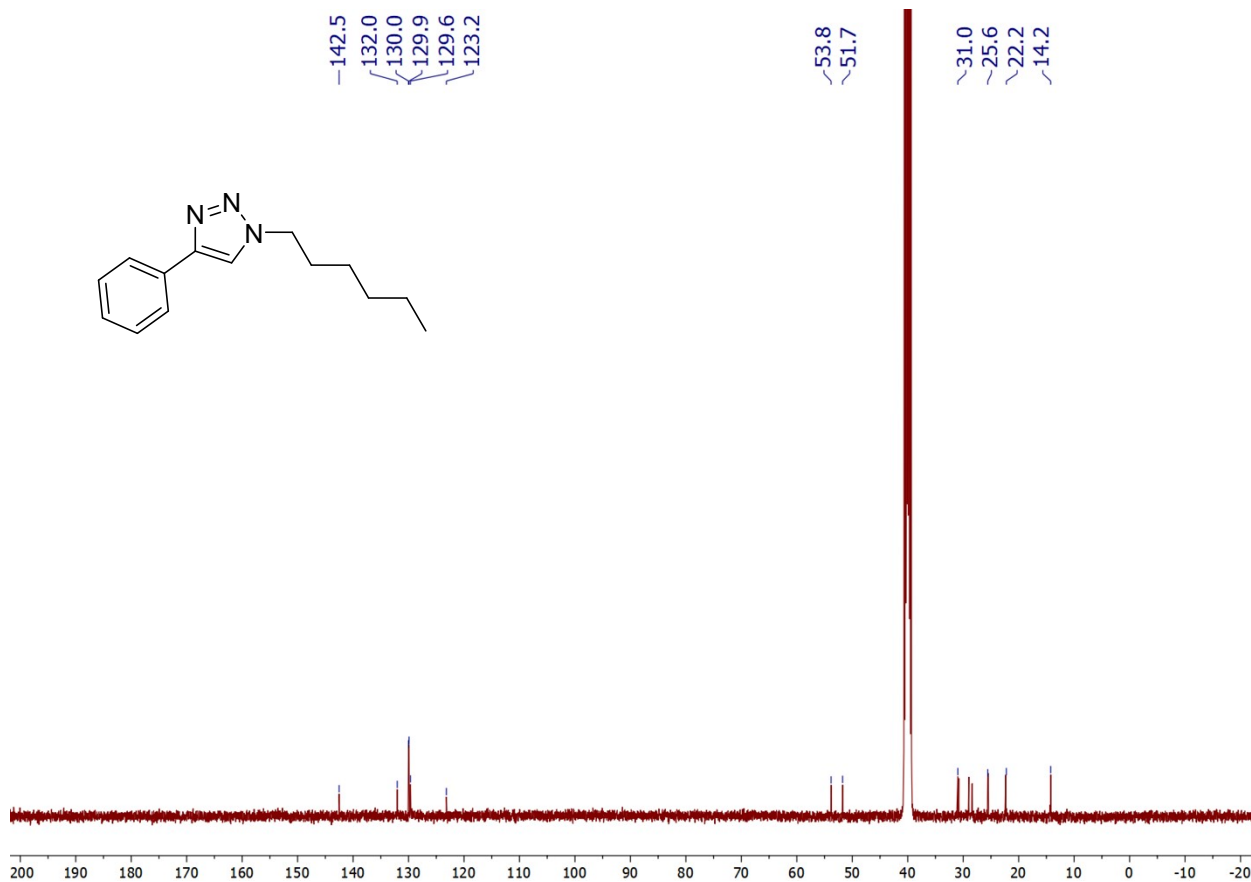


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **d**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 142.5, 132.0, 130.0, 129.6, 123.2, 53.8, 51.7, 31.0, 25.6, 22.4, 14.2.

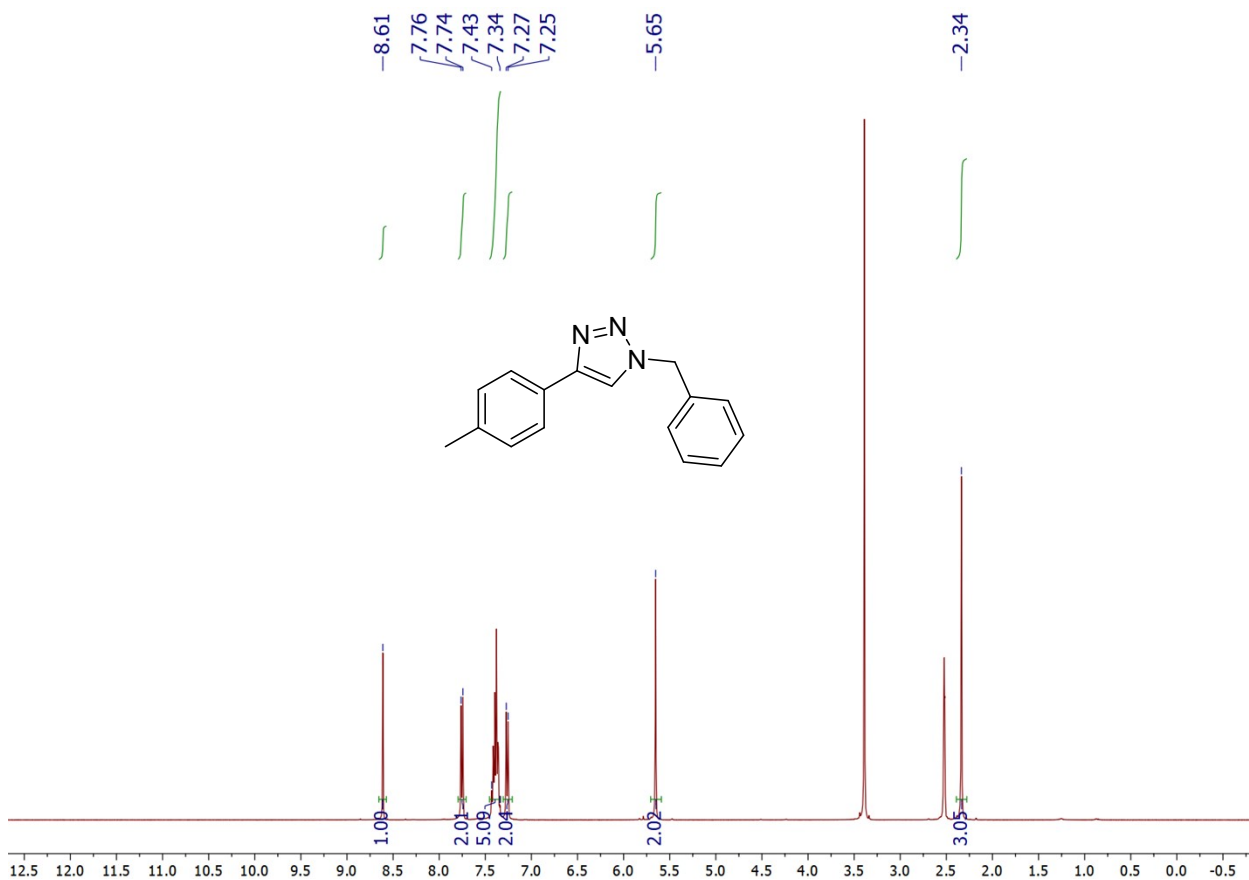


Figure S35. ¹H NMR spectrum of click product **e**. Signals at ~2.5 and ~3.4 ppm belong to traces of solvent and water.

¹H NMR (400 MHz, DMSO) δ 8.61 (s, 1H), 7.75 (d, $^3J = 8.0$ Hz, 2H), 7.43–7.34 (m, 5H), 7.26 (d, $^3J = 8.0$ Hz, 2H), 5.65 (s, 2H), 2.34 (s, 3H).

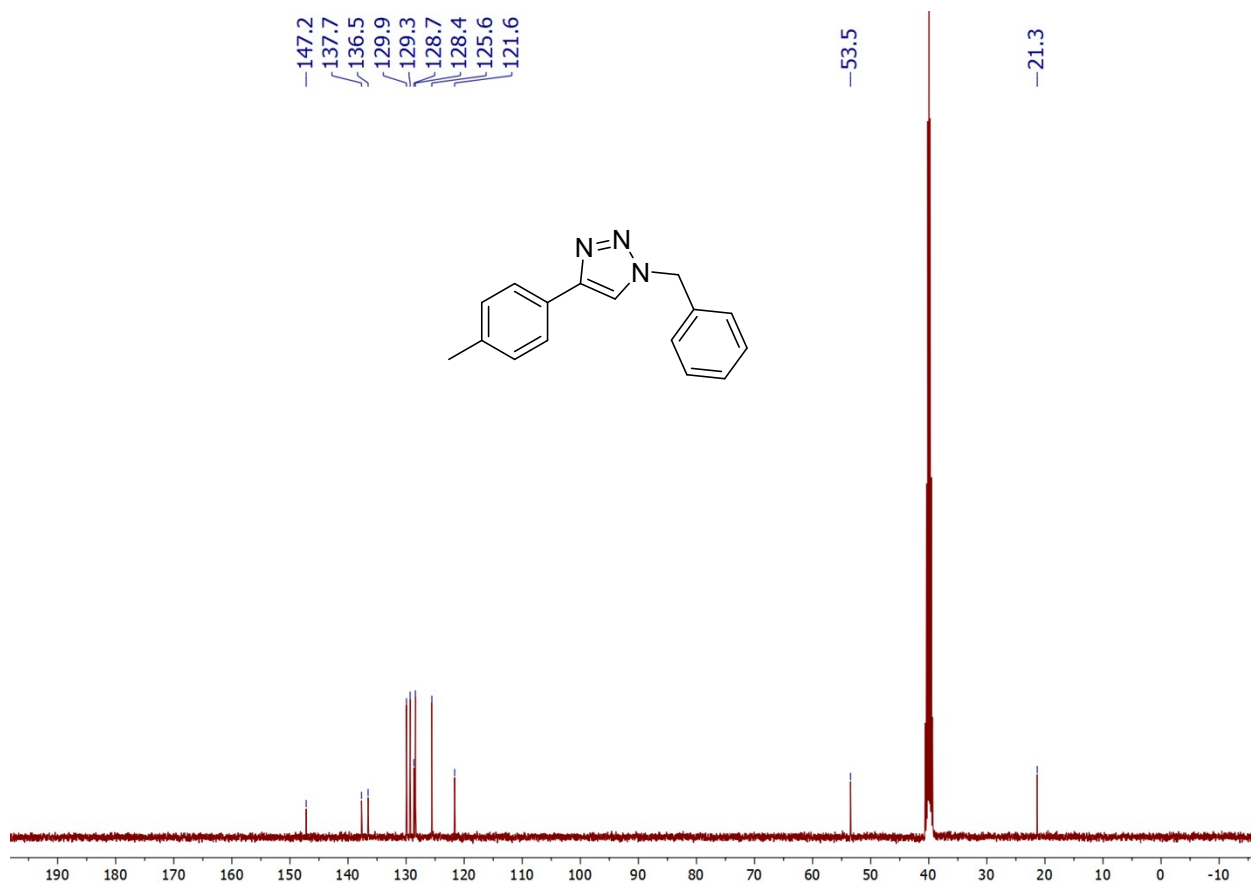


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **e**. Multiplet signal at ~40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 147.21, 137.68, 136.54, 129.93, 129.30, 128.65, 128.40, 125.57, 121.63, 53.47, 21.33.

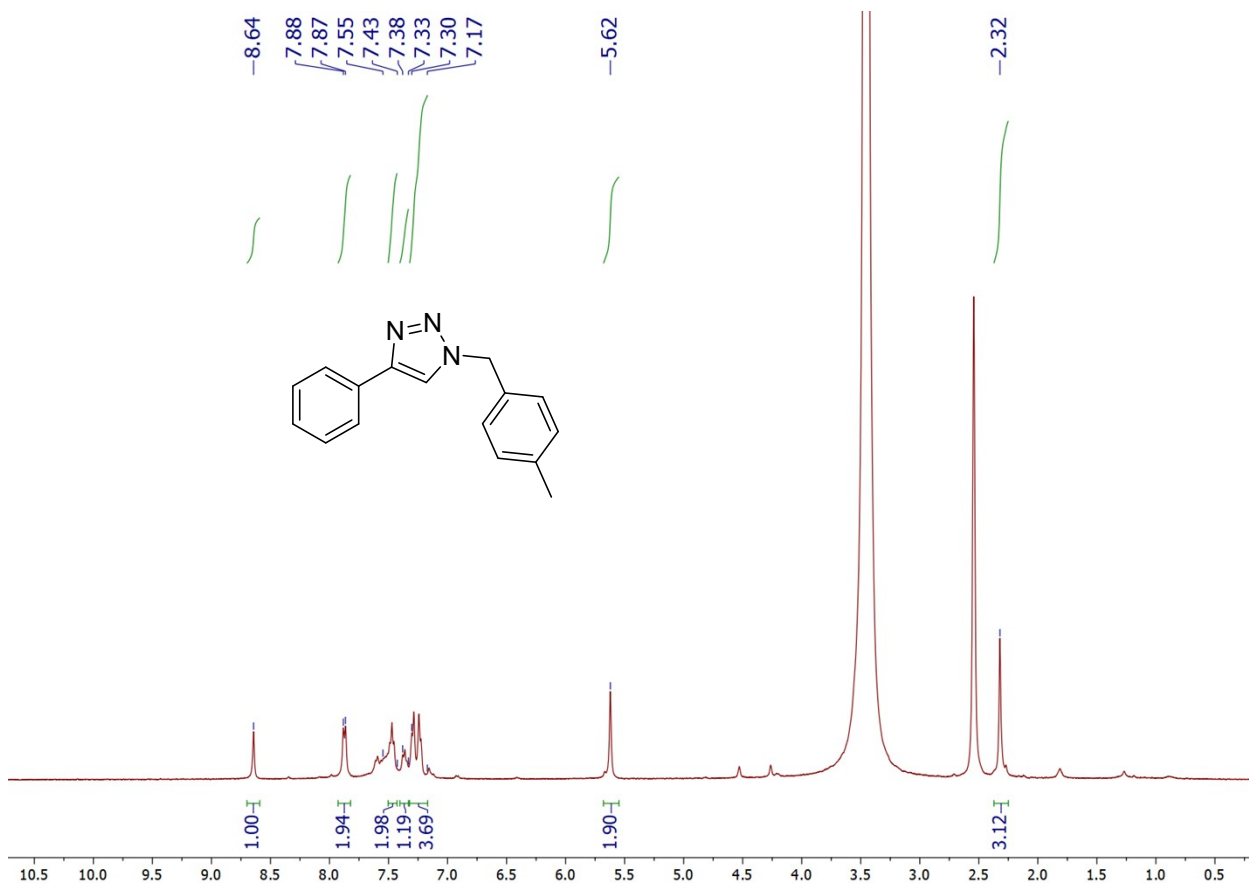


Figure S37. ¹H NMR spectrum of click product **f**. Signals at ~2.5 and ~3.4 ppm belong to traces of solvent and water.

¹H NMR (400 MHz, DMSO) δ 8.64 (s, 1H), 7.88 (s, 2H), 7.55–7.38 (m, 2H), 7.38–7.33 (m, 1H), 7.30–7.17 (m, 4H), 5.62 (s, 2H), 2.32 (s, 3H).

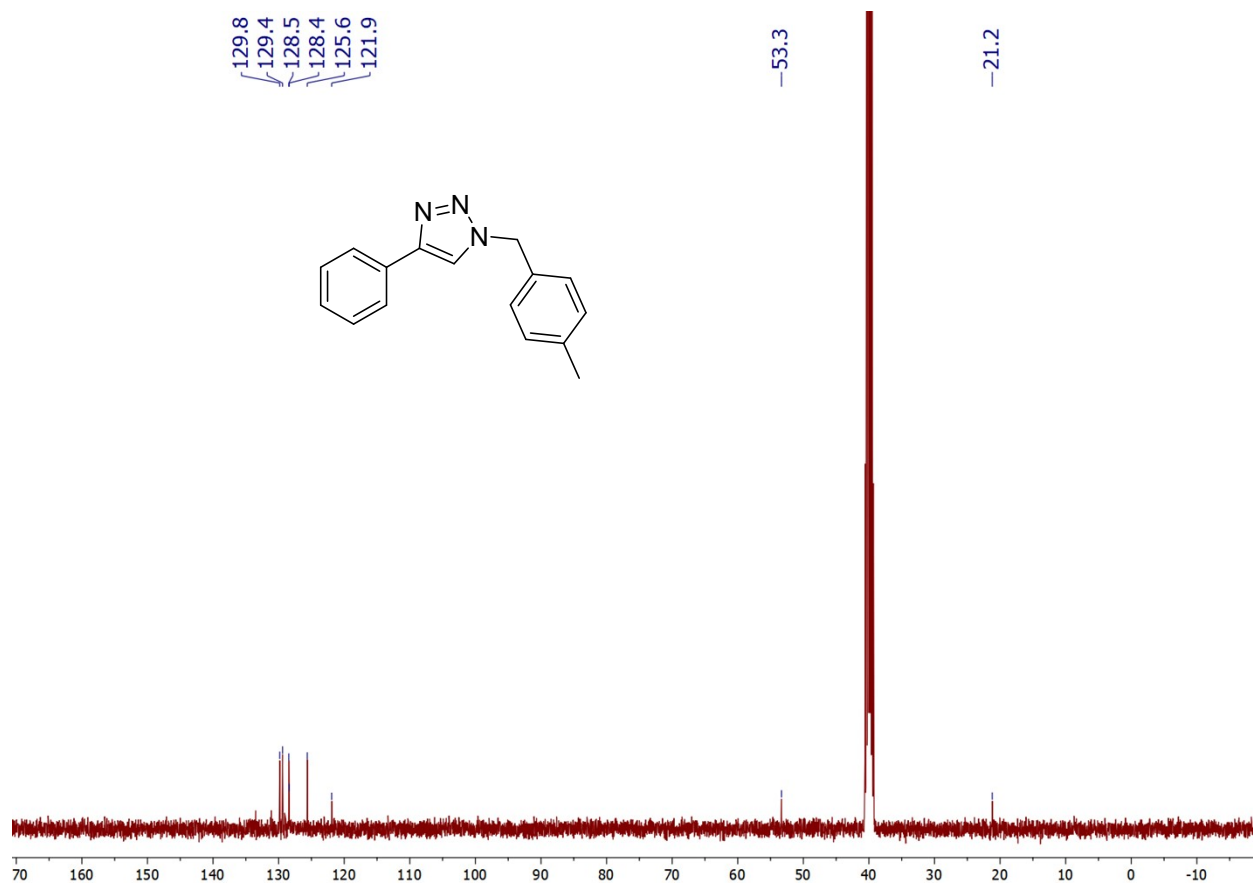


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **f**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 129.83, 129.40, 128.45, 128.40, 125.63, 121.91, 53.33, 21.19.

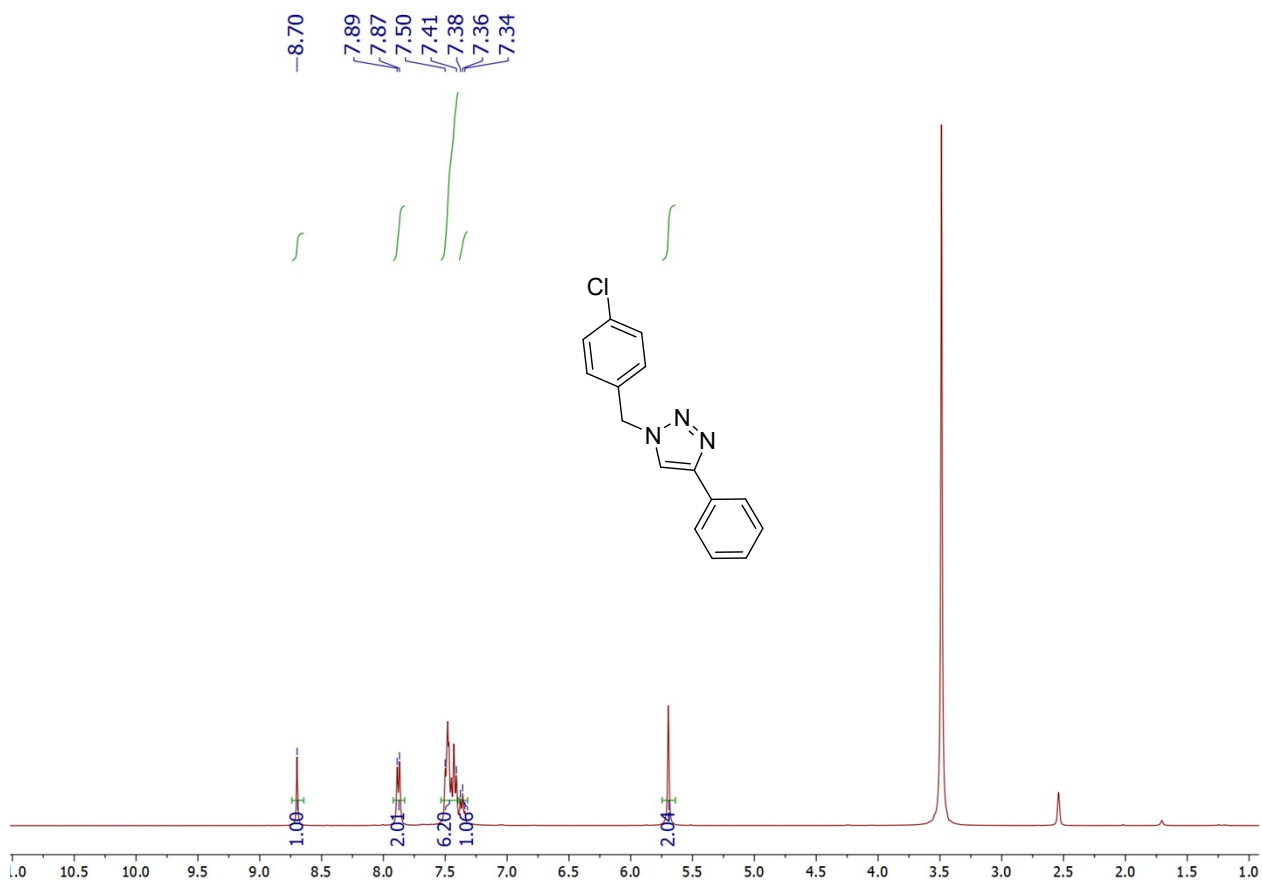


Figure S39. ^1H NMR spectrum of click product **g**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 8.70 (s, 1H), 7.88 (d, $^3J = 8.0$ Hz, 2H), 7.50–7.34 (m, 7H), 5.68 (s, 2H).

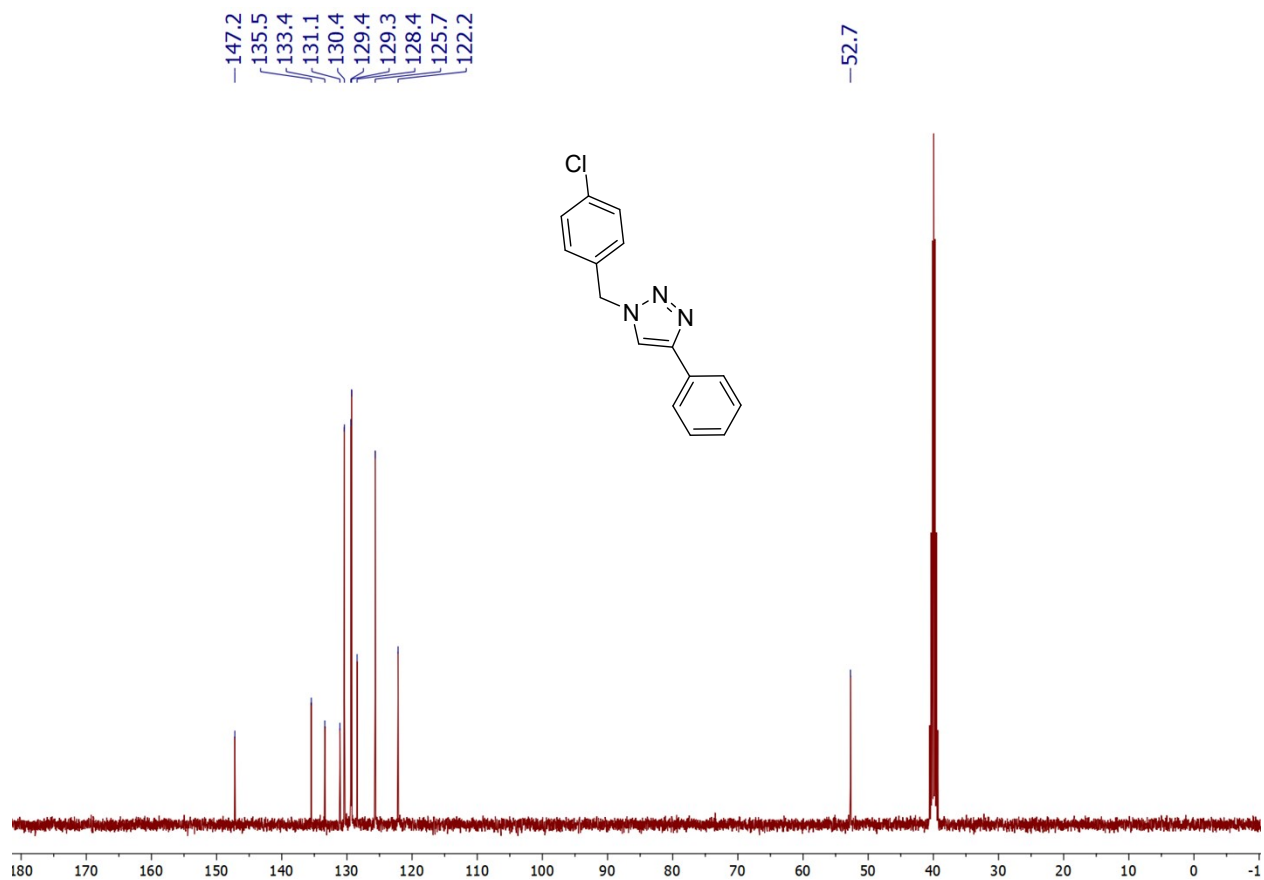


Figure S40. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **g**. Multiplet signal at ~40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 147.20, 135.47, 133.39, 131.07, 130.38, 129.40, 129.29, 128.44, 125.66, 122.15, 52.72.

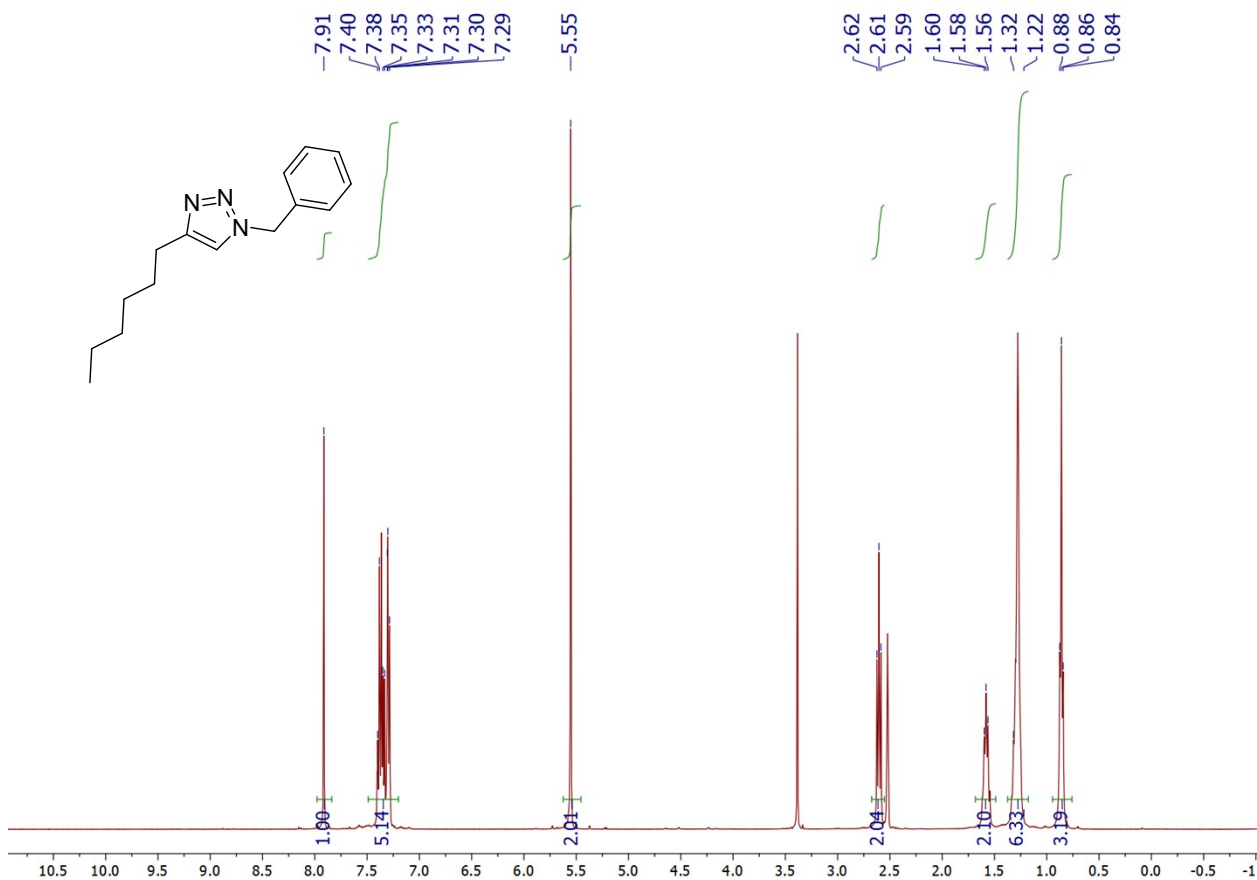


Figure S41. ^1H NMR spectrum of click product **h**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 7.91 (s, 1H), 7.40–7.29 (m, 5H), 5.55 (s, 2H), 2.62–2.59 (m, 2H), 1.60–1.56 (m, 2H), 1.32–1.22 (m, 6H), 0.88–0.84 (m, 3H).

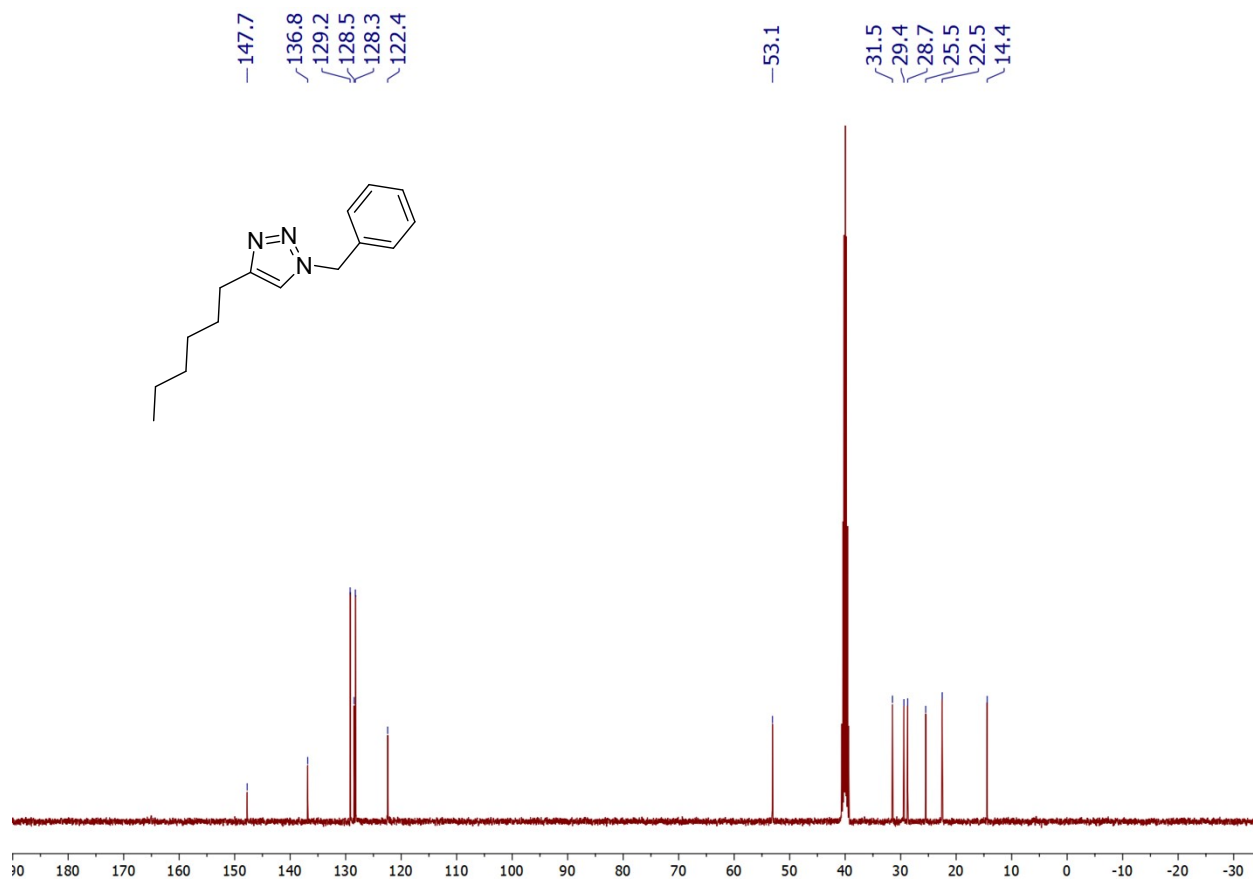


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **h**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 147.75, 136.84, 129.19, 128.49, 128.26, 122.43, 53.10, 31.48, 29.41, 28.74, 25.49, 22.52, 14.41.

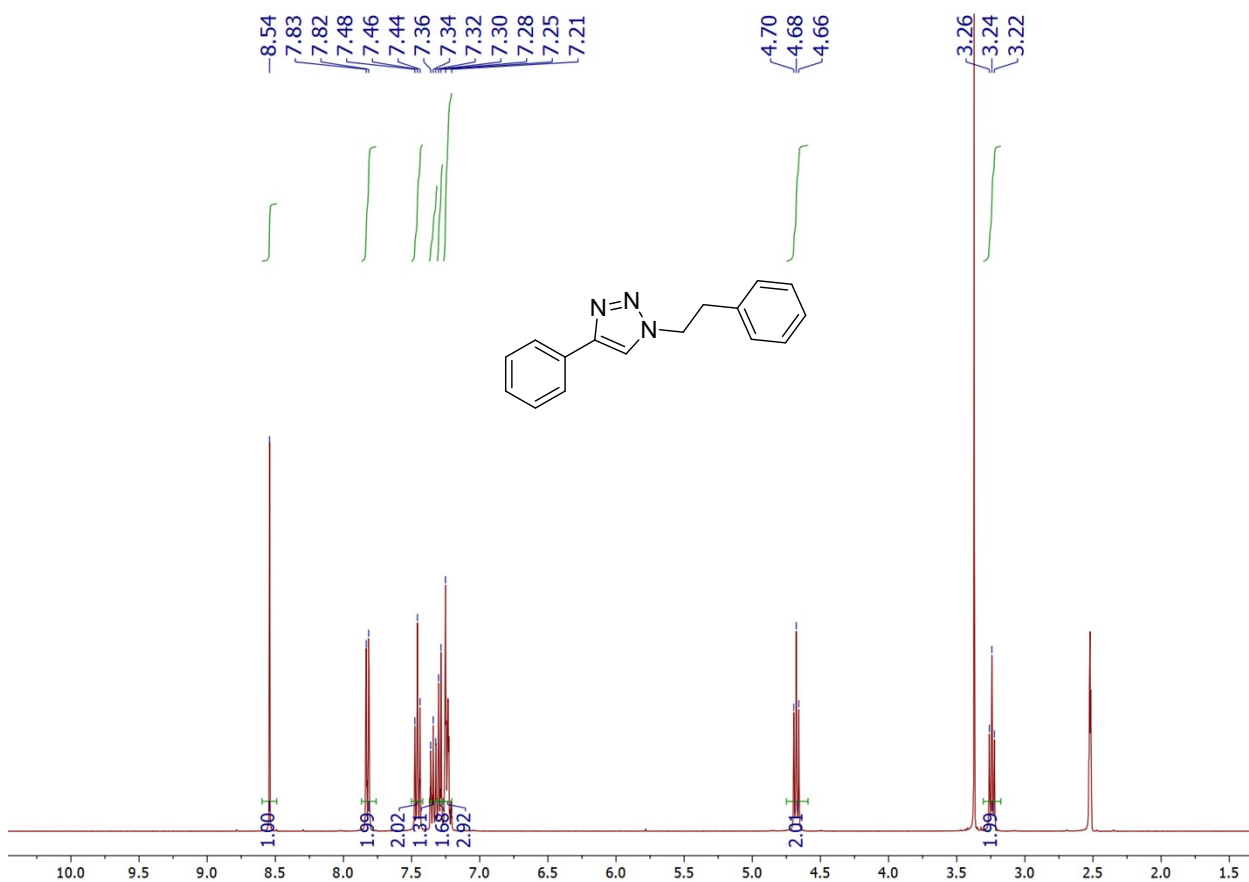


Figure S43. ^1H NMR spectrum of click product **i**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 8.54 (s, 1H), 7.83 (d, $^3J = 8.0$ Hz, 2H), 7.46 (t, $^3J = 8.0$ Hz, 2H), 7.34 (t, $^3J = 8.0$ Hz, 1H), 7.29 (d, $^3J = 8.0$ Hz, 2H), 7.25–7.21 (m, 3H), 4.66 (t, $^3J = 8.0$ Hz, 2H), 3.24 (t, $^3J = 8.0$ Hz, 2H).

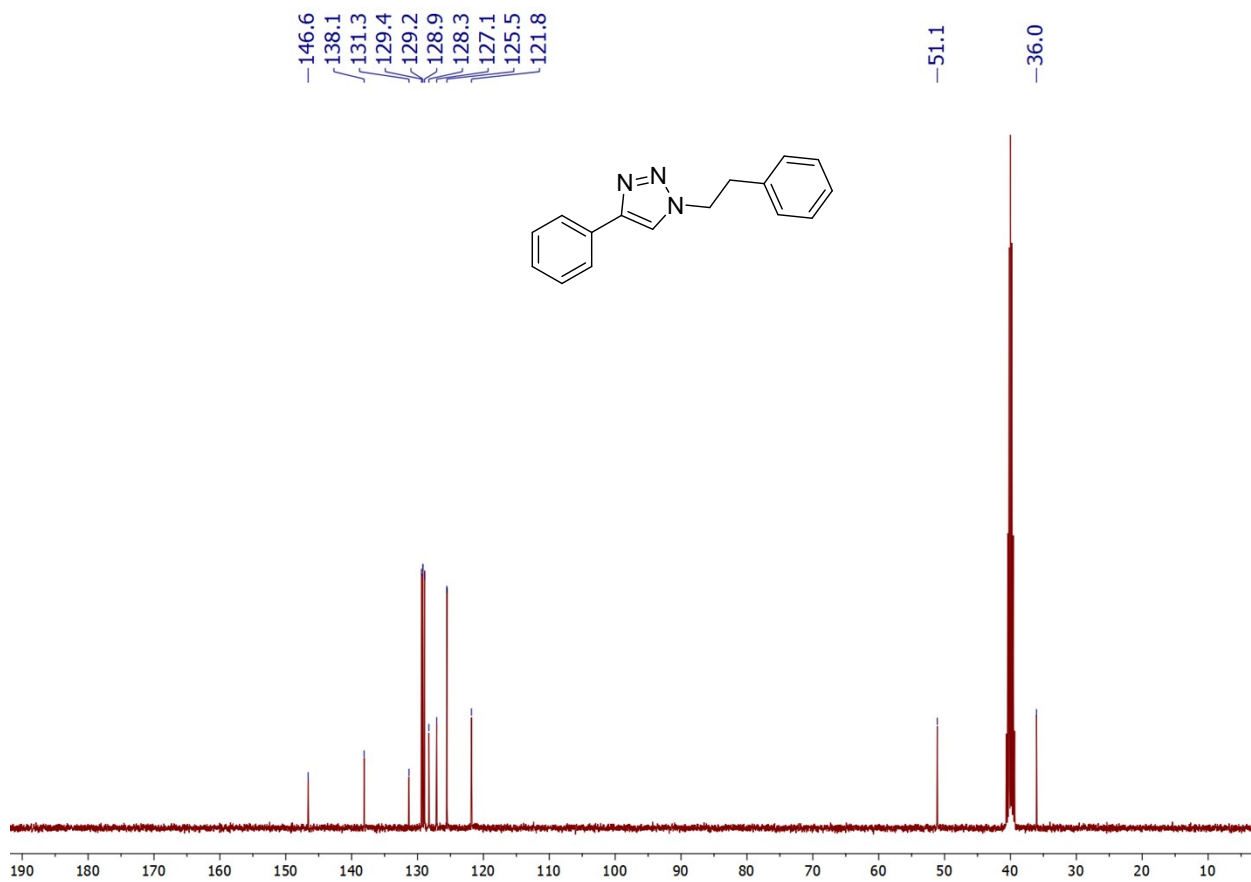


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **i**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 146.60, 138.10, 131.30, 129.40, 129.19, 128.93, 128.28, 127.09, 125.54, 121.81, 51.11, 36.04.

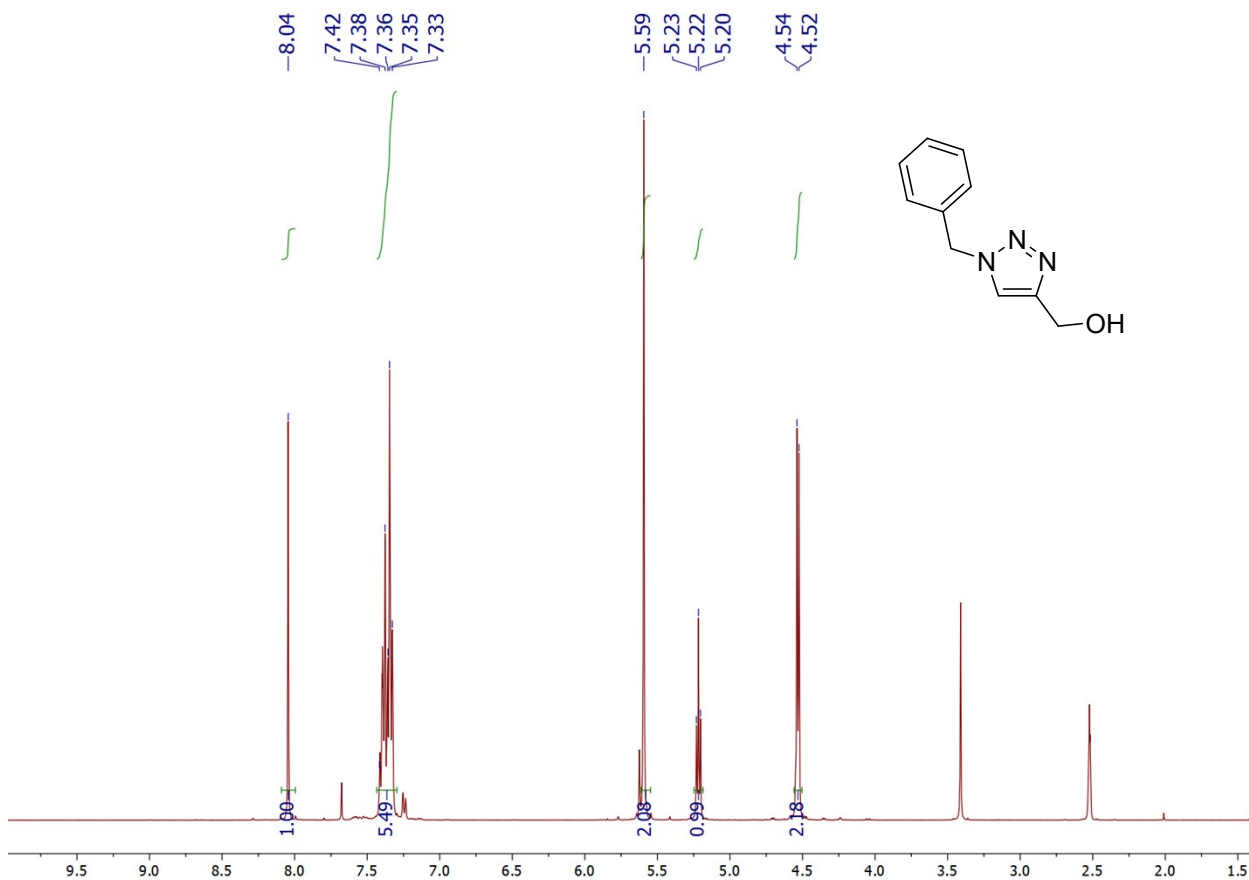


Figure S45. ^1H NMR spectrum of click product **j**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 8.04 (s, 2H), 7.42–7.33 (m, 5H), 5.59 (s, 2H), 5.22 (t, $^3J = 8.0$ Hz), 4.53 (d, $^3J = 8.0$ Hz, 2H).

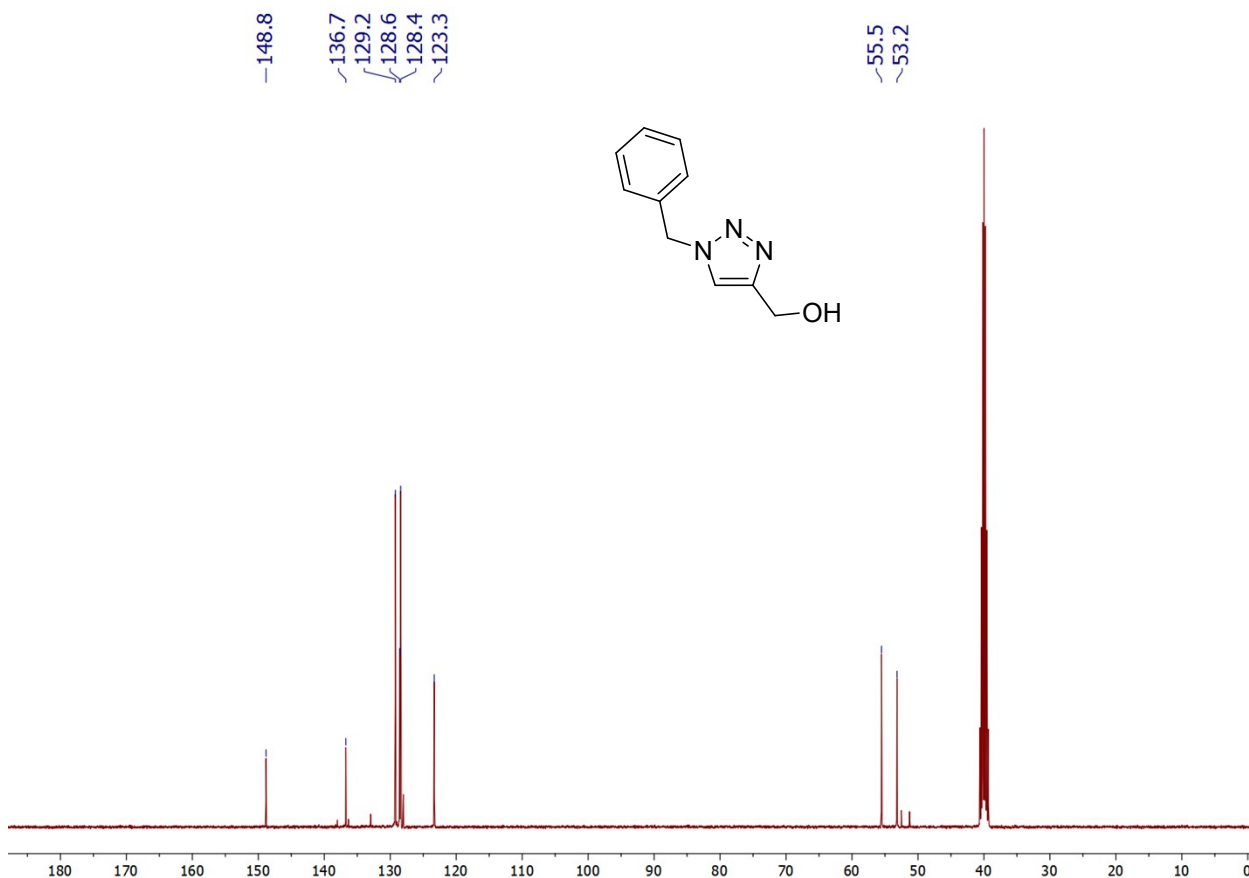


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **j**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 148.83, 136.73, 129.22, 128.57, 128.42, 123.33, 55.53, 53.18.

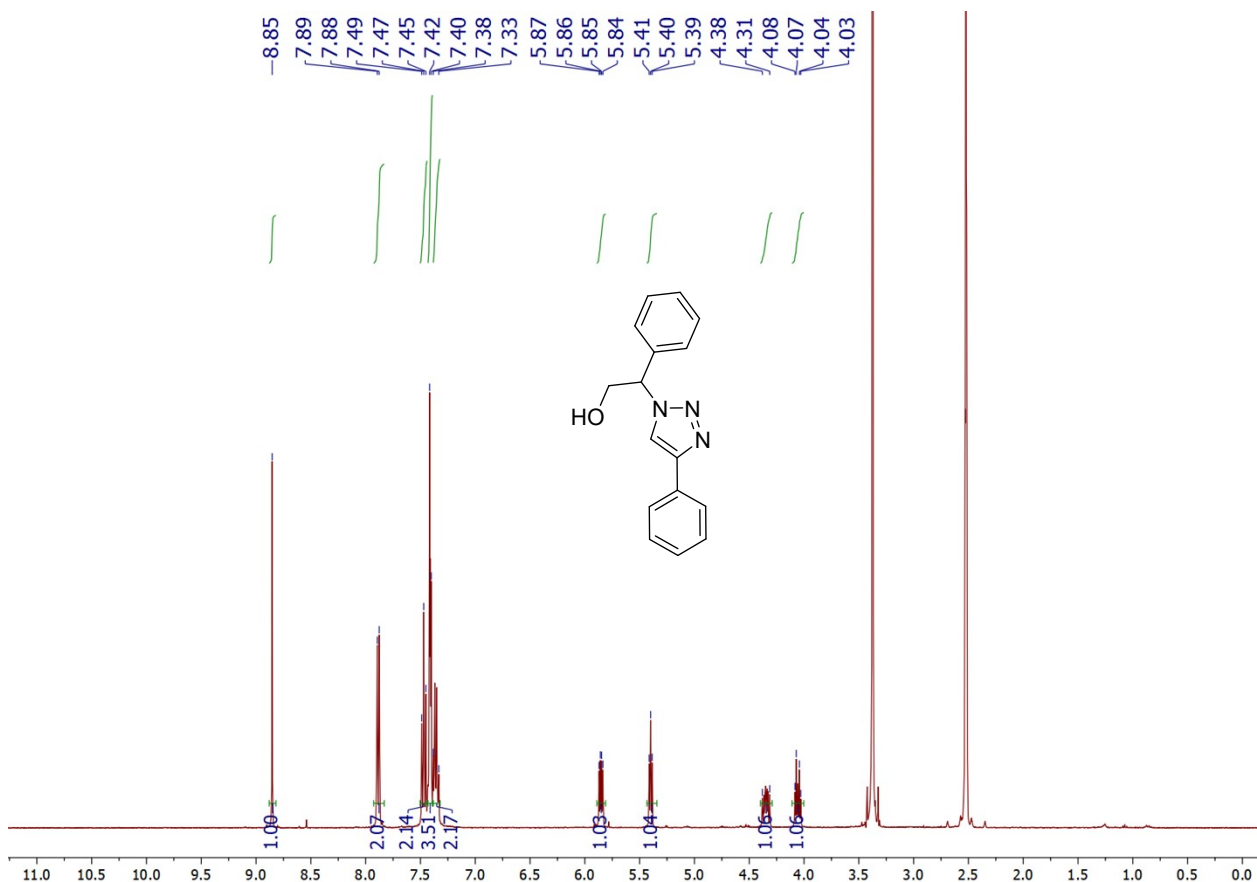


Figure S47. ^1H NMR spectrum of click product **k**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 8.85 (m, 1H), 7.88 (d, $^3J = 8.0$ Hz, 2H), 7.47 (t, $^3J = 8.0$ Hz, 2H), 7.43 (d, $^3J = 8.0$ Hz, 3H), 7.38–7.33 (m, 2H), 5.87–5.84 (m, 1H), 5.41–5.39 (m, 1H), 4.38–4.31 (m, 1H), 4.08–4.03 (m, 1H).

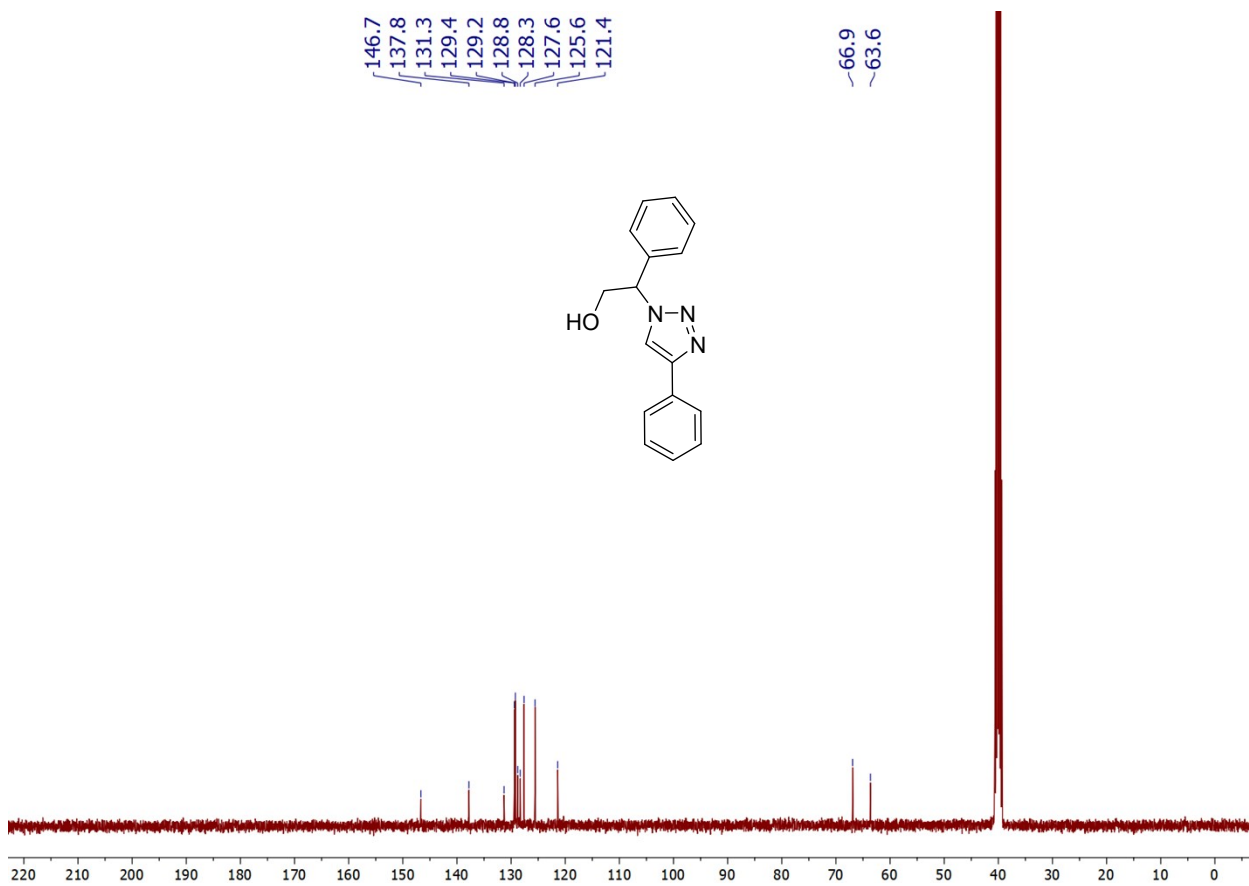


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **k**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 146.67, 137.80, 131.31, 129.39, 129.21, 128.78, 128.32, 127.61, 125.58, 121.39, 66.91, 63.62.

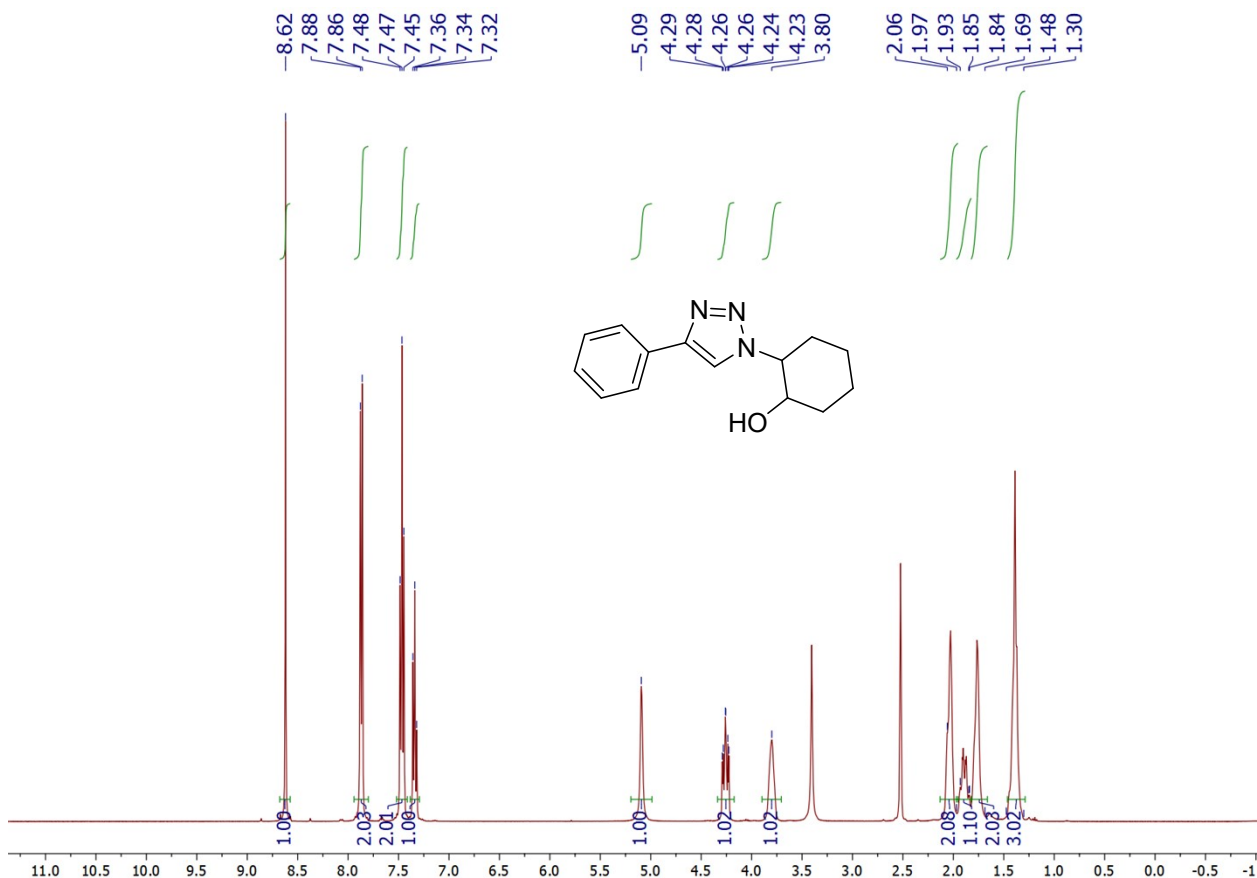


Figure S49. ^1H NMR spectrum of click product **1**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 8.62 (s, 1H), 7.87 (d, $^3J = 8.0$ Hz, 2H), 7.47 (t, $^3J = 8.0$ Hz, 2H), 7.34 (t, $^3J = 8.0$ Hz, 1H), 5.09 (s, 1H), 4.29–4.23 (m, 1H), 3.80 (s, 1H), 2.06–1.97 (m, 2H), 1.93–1.85 (m, 1H), 1.84–1.69 (m, 2H), 1.48–1.30 (m, 3H).

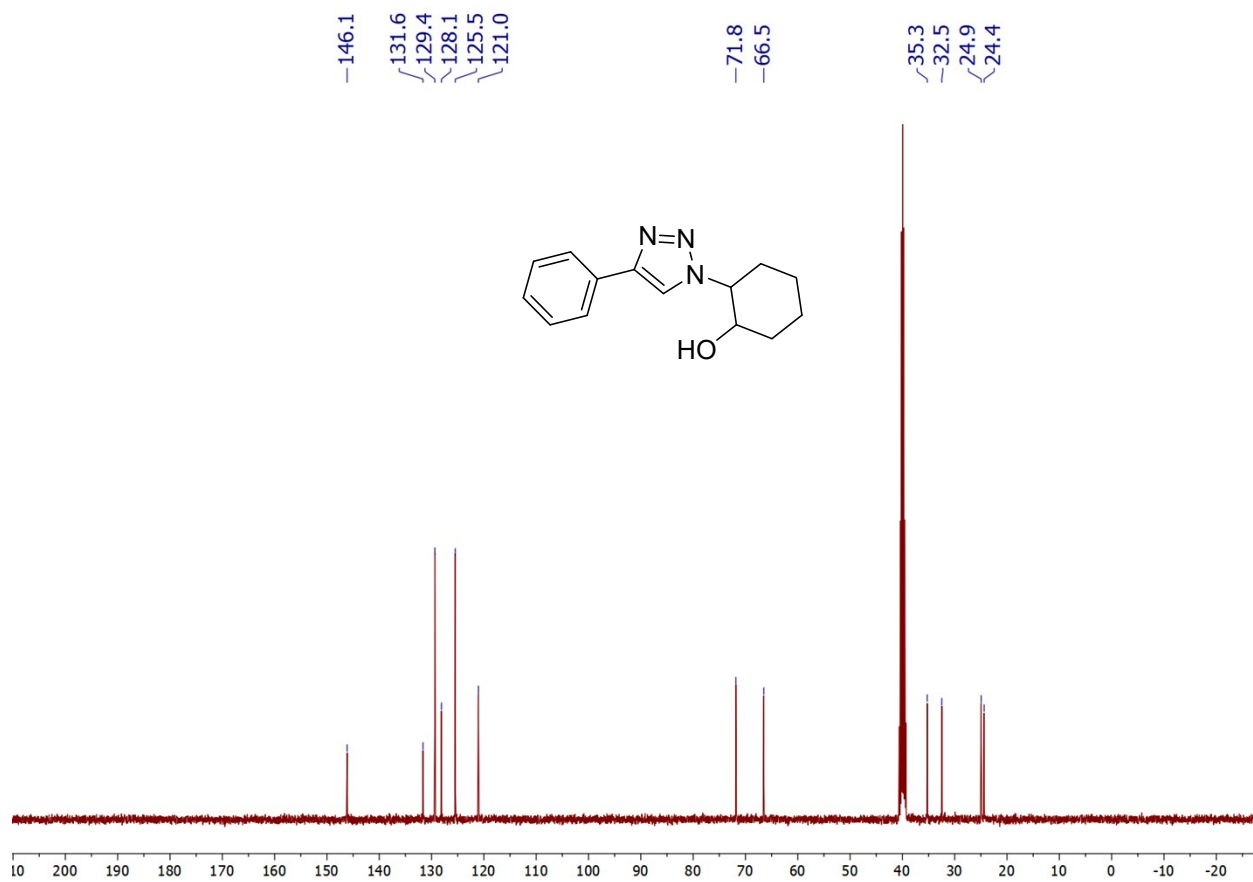


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **1**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 146.14, 131.64, 129.37, 128.11, 125.47, 121.05, 71.84, 66.50, 35.25, 32.47, 24.94, 24.39.

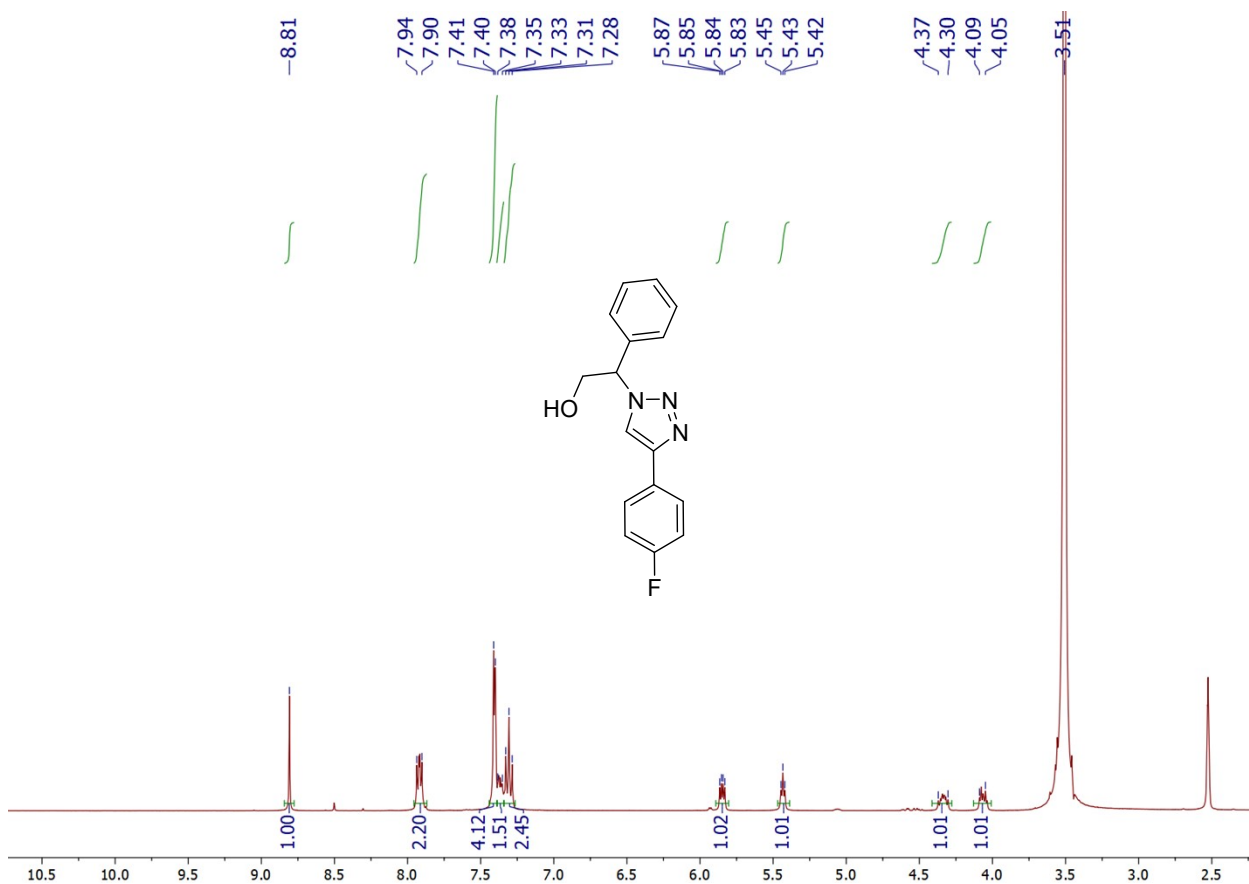


Figure S51. ^1H NMR spectrum of click product **m**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 8.81 (s, 1H), 7.94–7.90 (m, 2H), 7.41–7.40 (m, 4H), 7.38–7.35 (m, 1H), 7.33–7.28 (m, 2H), 5.87–5.83 (m, 1H), 5.45–5.42 (m, 1H), 4.37–4.30 (m, 1H), 4.09–4.05 (m, 1H).

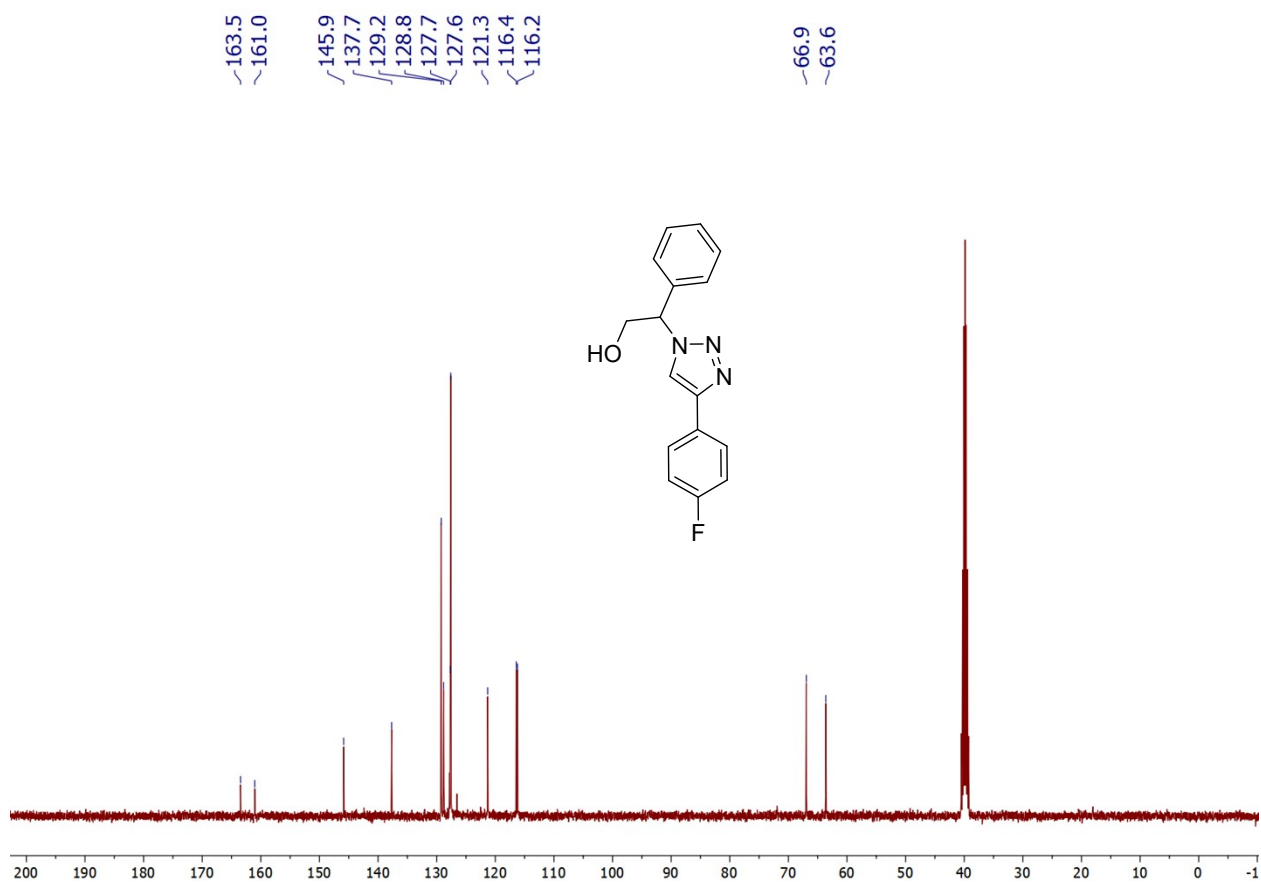


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **m**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 163.47, 161.04, 145.87, 137.68, 129.23, 128.82, 127.68, 127.60, 121.30, 116.42, 116.21, 66.94, 63.62.

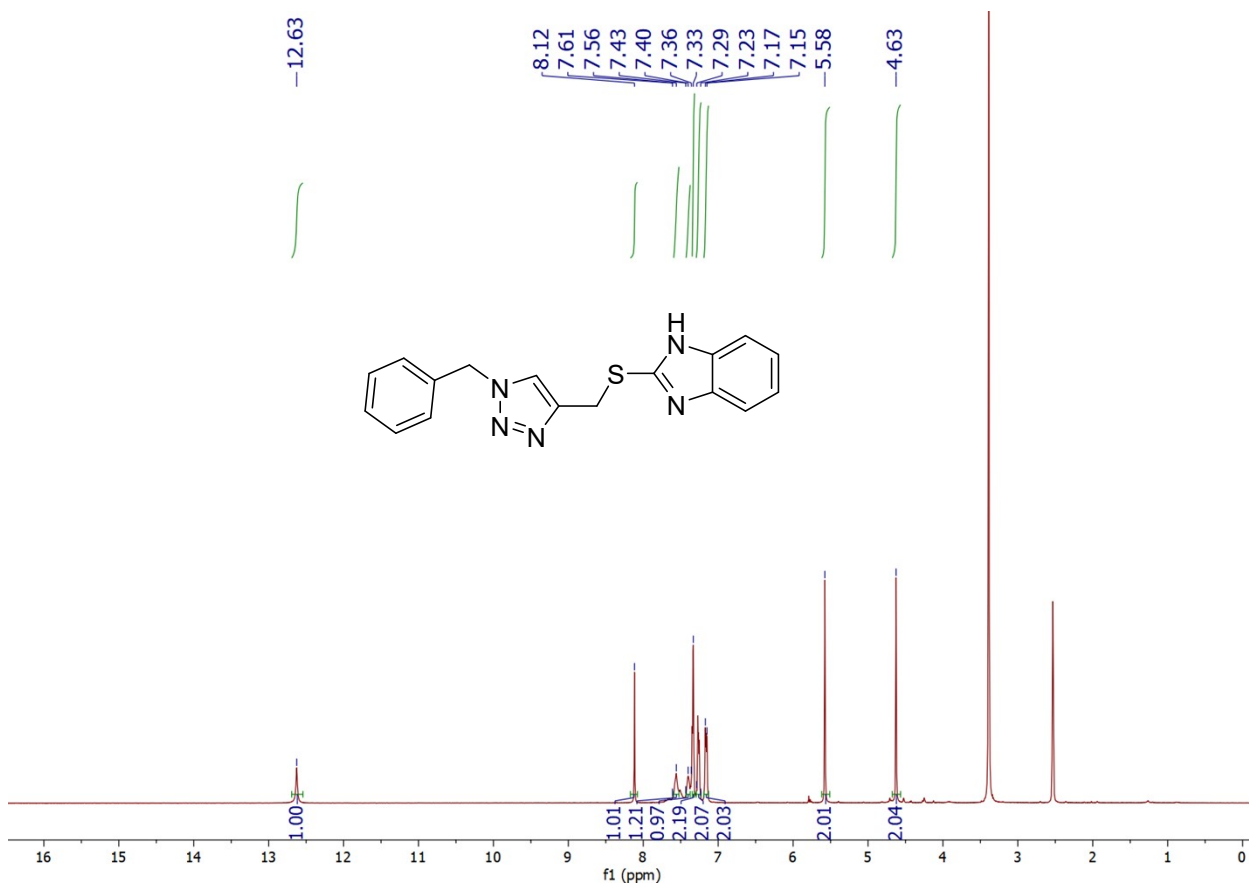


Figure S53. ^1H NMR spectrum of click product **n**. Signals at ~ 2.5 and ~ 3.4 ppm belong to traces of solvent and water.

^1H NMR (400 MHz, DMSO) δ 12.63 (s, 1H), 8.12 (s, 1H), 7.61–7.56 (m, 2H), 7.43–7.33 (m, 2H), 7.29–7.23 (m, 2H), 7.16 (d, $^3J = 8.0$ Hz, 2H), 5.58 (s, 2H), 4.63 (s, 2H).

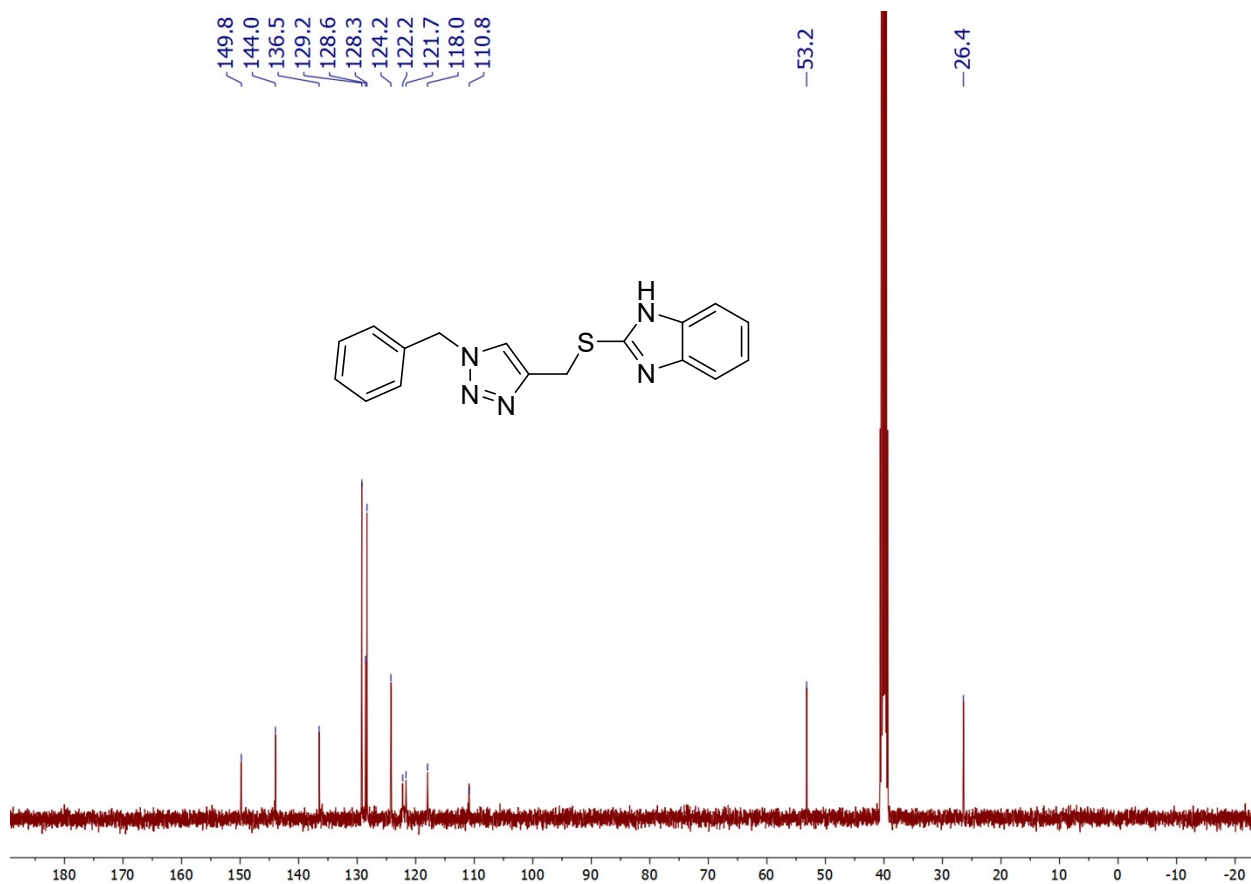


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of click product **n**. Multiplet signal at ~ 40 ppm belongs to traces of solvent.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 149.79, 143.96, 136.50, 129.20, 128.57, 128.32, 124.23, 122.22, 121.65, 117.98, 110.85, 53.21, 26.42.



Figure S55. A thin-layer chromatogram of the reaction mixture containing sodium azide, benzyl chloride, and phenyl acetylene is presented. On the left, the spot corresponds to the reaction catalyzed by fresh catalyst 3, while the right spot represents the reaction catalyzed by aged catalyst 3.