Electronic Supplementary Information

Carbon nanotube-copper ferrite-catalyzed aqueous 1,3-dipolar cycloaddition of *in situ*-generated organic azides with alkynes

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A. General Information

Chemicals were purchased from Aldrich and used as received. Sonication was performed using a Branson Sonifier 450 ultrasonicating probe. XPS spectra were acquired on a VGESCALAB 210 spectrometer. Electron microscopy observations were carried out on a Philips CM12 microscope operated at 100 kV. NMR spectra were recorded on a Bruker Avance 400 at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts are given in ppm relative to the NMR solvent residual peak. Mass spectra were recorded using a Waters Micromass ZQ ESI-Quad spectrometer. IR-spectra were recorded using a Perkin-Elmer 2000 FT-IR. Wavenumbers are given in cm^{-1} at their maximum intensity. MWCNTs were prepared at the University of Xiamen (China) by catalytic decomposition of methane on a Ni-Mg-O catalyst.[1] The amphiphilic DANTA unit was synthesized by following the procedure from our previous report.[2] *n*-Octylazide was prepared by known literature procedure.[3]

B. Hybrid assembly

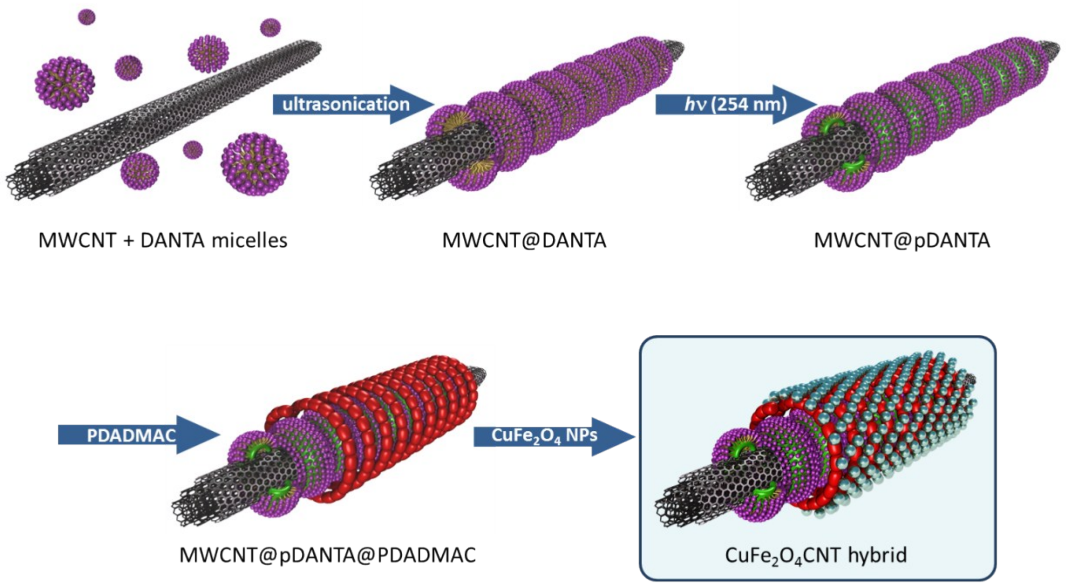


Figure S1. Overview of the $CuFe_2O_4$ assembly strategy.

1. Self-assembly and polymerization of the amphiphile on the CNT

DANTA (60 mg) was dissolved in 25 mM Tris aqueous buffer (6 mL, pH 8) before MWNTs (150 mg) were added. After 10 min of sonication with an ultra-sonic probe (5 min, 300 ms pulses per second, 25 W output power) a stable suspension was obtained and transferred into Eppendorf® tubes (6 × 1.5 mL) and centrifuged (5000 ×*g*, 3 min) to remove amorphous carbon. The supernatants were collected and centrifuged (15000 ×*g*, 45 min) to separate the DANTA-decorated nanotubes from amphiphile in excess. The supernatant was discarded while the pellets were resuspended in fresh Tris-buffer and centrifuged again (15000 ×*g*, 45 min). The final pellets were resuspended in buffer (4.5 mL) and submitted to UV irradiation (254 nm, 8 h) to polymerize the diacetylene groups and yield stabilized nanoring assemblies. Polymerization reinforces the cohesion of amphiphiles on the surface of the nanotube and leads to more robust assemblies.

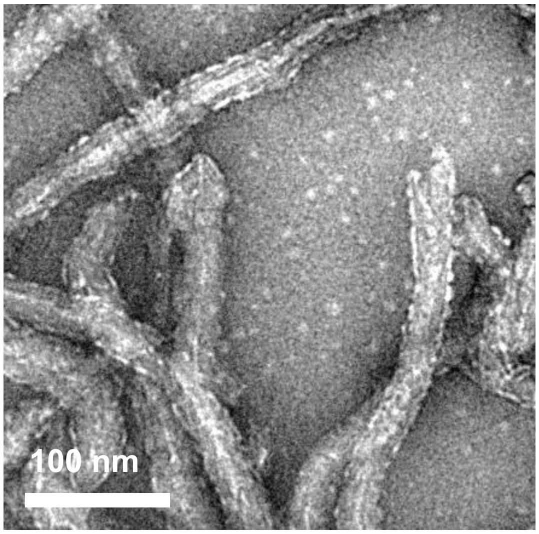


Figure S2. TEM image of pDANTA nanorings at the surface of MWCNTS.

2. Assembly of the second layer on the nanoring-coated nanotubes

After polymerization, the Tris-buffer volume was adjusted to 4.5 mL and the suspension was stirred in the presence of PDADMAC (2.1 mL of a 20% water solution) for 1 h to permit the formation of the two layer assembly. Polymer in excess was removed by centrifugation (15000 ×*g*, 30 min) and the pellets were re-suspended in Tris-buffer (1.5 mL). This operation was repeated twice with Tris-buffer and two more times with pure water. The final pellets were combined and re-suspended in water (4 mL).

3. Synthesis of $CuFe_2O_4$ NPs

$Cu(acac)_2$ (34 mg, 0.13 mmol) and $Fe(acac)_3$ (91.4 mg, 0.26 mmol) were mixed in oleylamine (5 mL) under nitrogen atmosphere. The reaction mixture was heated to 220 °C to afford a dark brown solution. After 1.5 h, the solution was cooled down to room temperature, ethanol (20 mL) was added and the precipitate was separated by centrifugation (8000 ×*g*, 10 min). The obtained nanoparticles were re-dispersed in hexane (15 mL) to obtain a stable yellow-brown dispersion.

4. Deposition of $CuFe_2O_4$ NPs

The hexane dispersion of nanoparticles (125 µL) was transferred to Eppendorf® tubes (16 × 125 µL) and precipitated with ethanol (1 mL in each tube). After centrifugation (11000 ×*g*, 10 min), the obtained precipitate was re-dispersed in THF (1 mL). To each Eppendorf® tube containing the MWCNT/DANTA/PDADMAC hybrid (100 µL) were added $CuFe_2O_4$ nanoparticles in

THF (1 mL). The mixture was vortex-stirred for 5 min and left to stand at room temperature for 30 min. The suspension was then centrifuged (3000 ×*g*, 5 min) and the colorless supernatant was discarded. The obtained pellets were washed 2 times by centrifugation/redispersion in THF. All pellets were combined and re-dispersed in water (7 mL) to yield the $CuFe_2O_4$CNT nanohybrid suspension that was used for catalysis experiments. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of $CuFe_2O_4$CNT nanohybrid suspension gave a copper concentration of 0.8 mM.

5. General procedure for the one pot Click reaction

The preparation of **3aa** is given as a representative example. To a solution of benzyl bromide **1a** (11.8 µL, 0.1 mmol), NaN_3 (7.2 mg, 0.11 mmol) and phenylacetylene **2a** (11 µL, 0.1 mmol) in H_2O/EtOH 4:1 (1 mL), was added $CuFe_2O_4$CNT (0.8 mM aqueous suspension, 0.4 mol%). The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (monitored by TLC), the catalyst was removed by filtration and the product was extracted with ethyl acetate (3 × 5 mL). The catalyst was further washed with ethanol (3 × 2 mL). The combined organic layers were concentrated under vacuum to afford pure triazole **3aa** in 90 % yield (for some products, column chromatography on silica gel was required).

6. Procedure for recycling experiments

To a solution of benzyl bromide **1a** (11.8 µL, 0.1 mmol), NaN_3 (7.2 mg, 0.11 mmol) and phenylacetylene **2a** (11 µL, 0.1 mmol) in H_2O/EtOH mixture (4:1, 1 mL), was added $CuFe_2O_4$CNT (0.8 mM aqueous suspension, 0.4 mol%). The reaction mixture was stirred at room temperature until complete conversion (monitored by TLC), after which the catalyst was separated from the reaction mixture by magnetic recovery (2 cm neodymium magnet). The product was extracted from the supernatant with ethyl acetate (3 × 5 mL). The catalyst pellet was further washed with ethanol (3 × 2 mL) and the combined organic layers were evaporated under vacuum to afford pure triazole **3aa**. The catalyst was resuspended in water and reused in subsequent experiments.

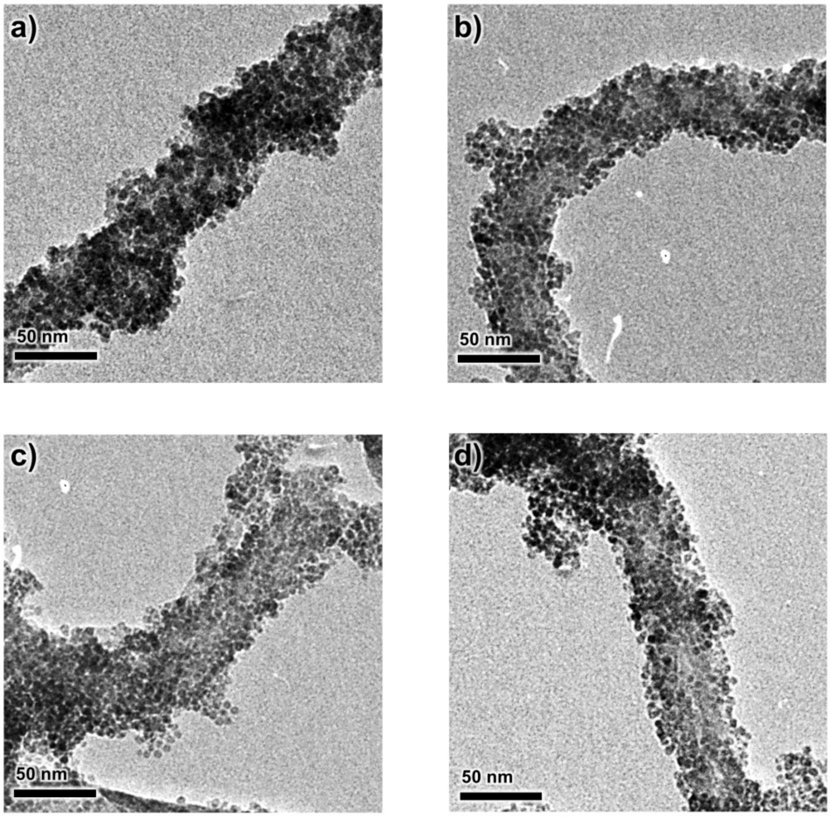
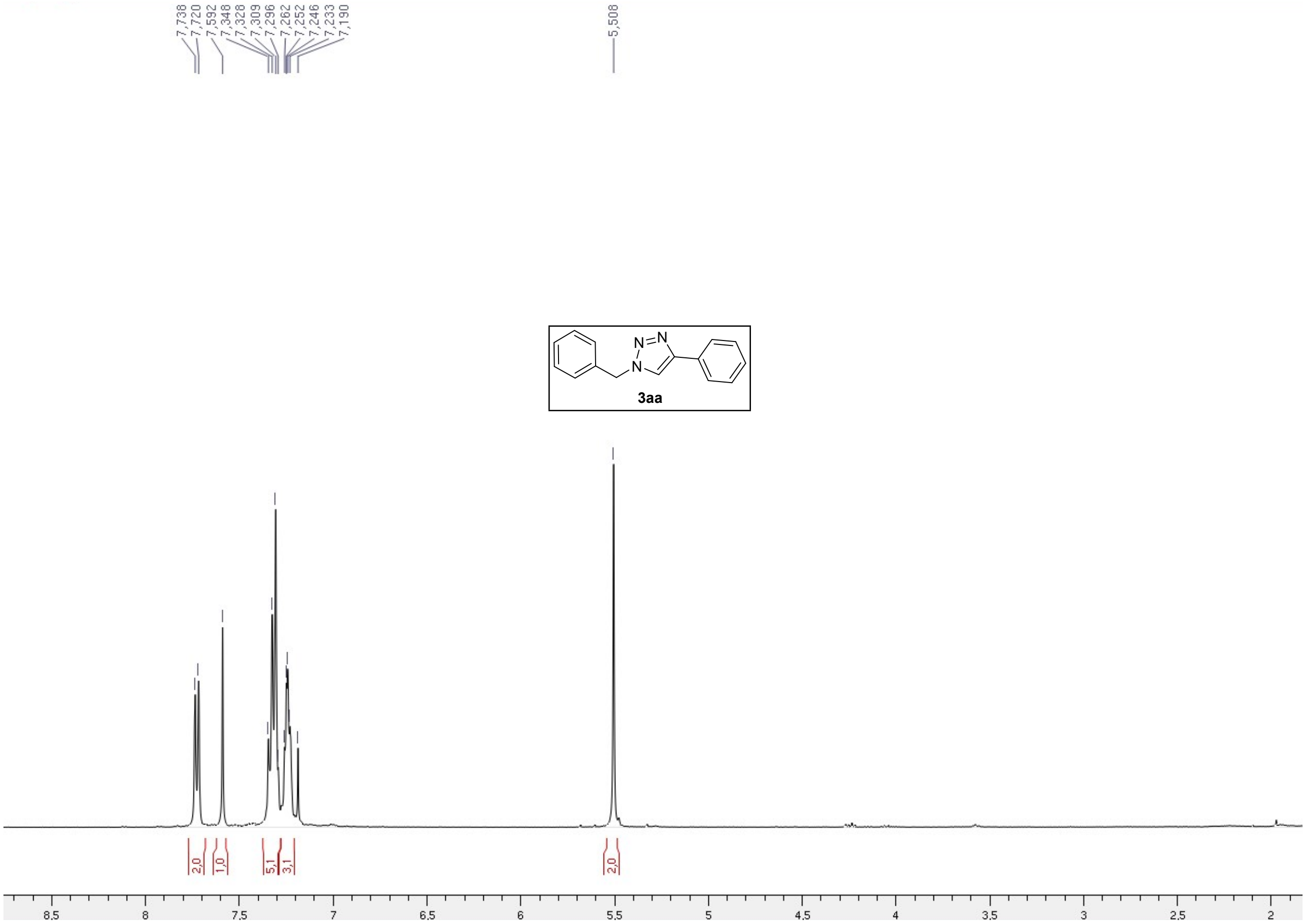


Figure S3. TEM images of the $CuFe_2O_4$CNT catalyst before reaction (a) and after the first (b), second (c), and third (d) reuse.

C. NMR spectra of triazole compounds

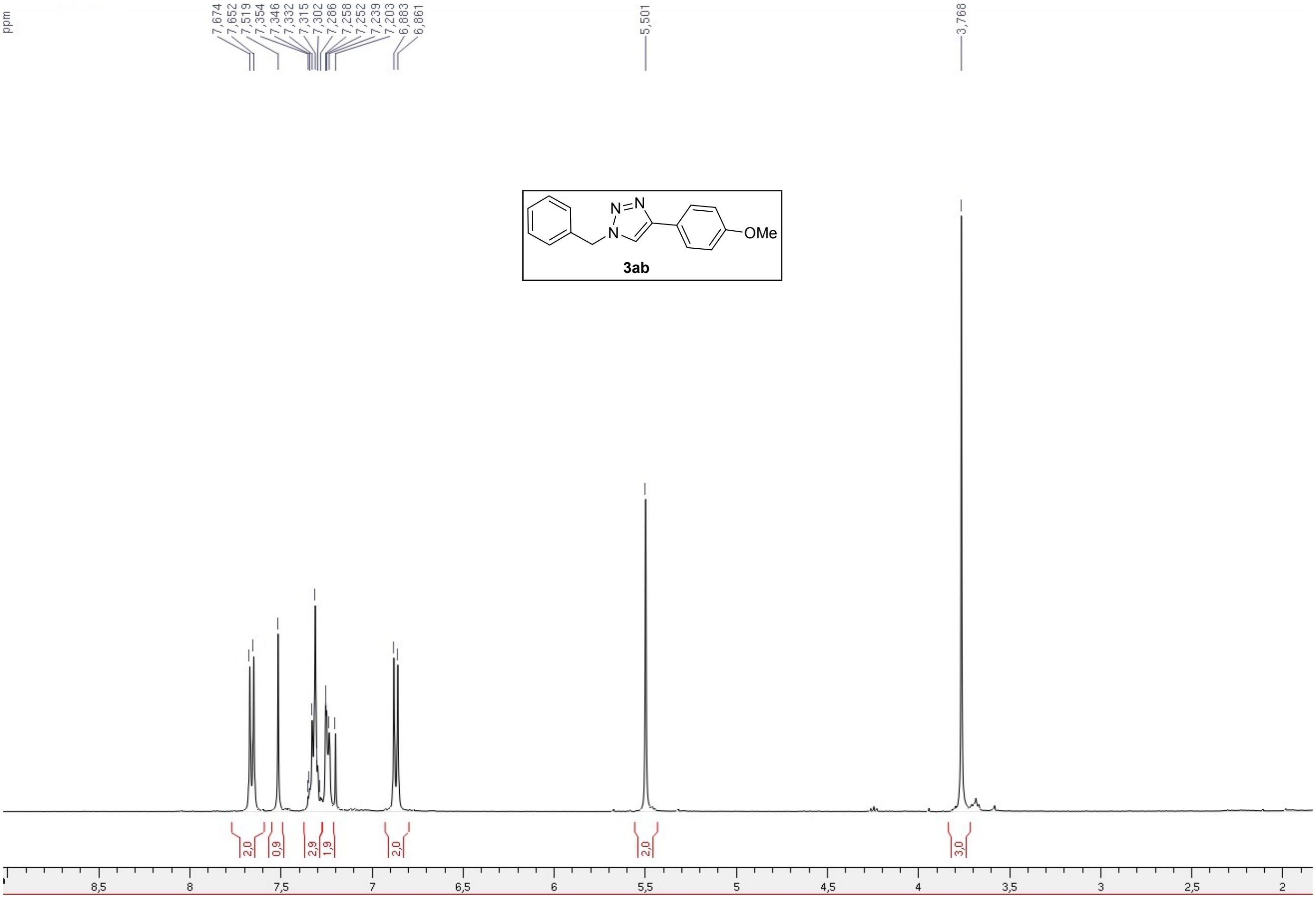
1. 3aa

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.73 (d, *J*= 7.2 Hz, 2H), 7.59 (s, 1H), 7.35–7.29 (m, 5H), 7.26–7.23 (m, 3H), 5.51 (s, 2H) ppm. NMR data are consistent with the literature.[4]



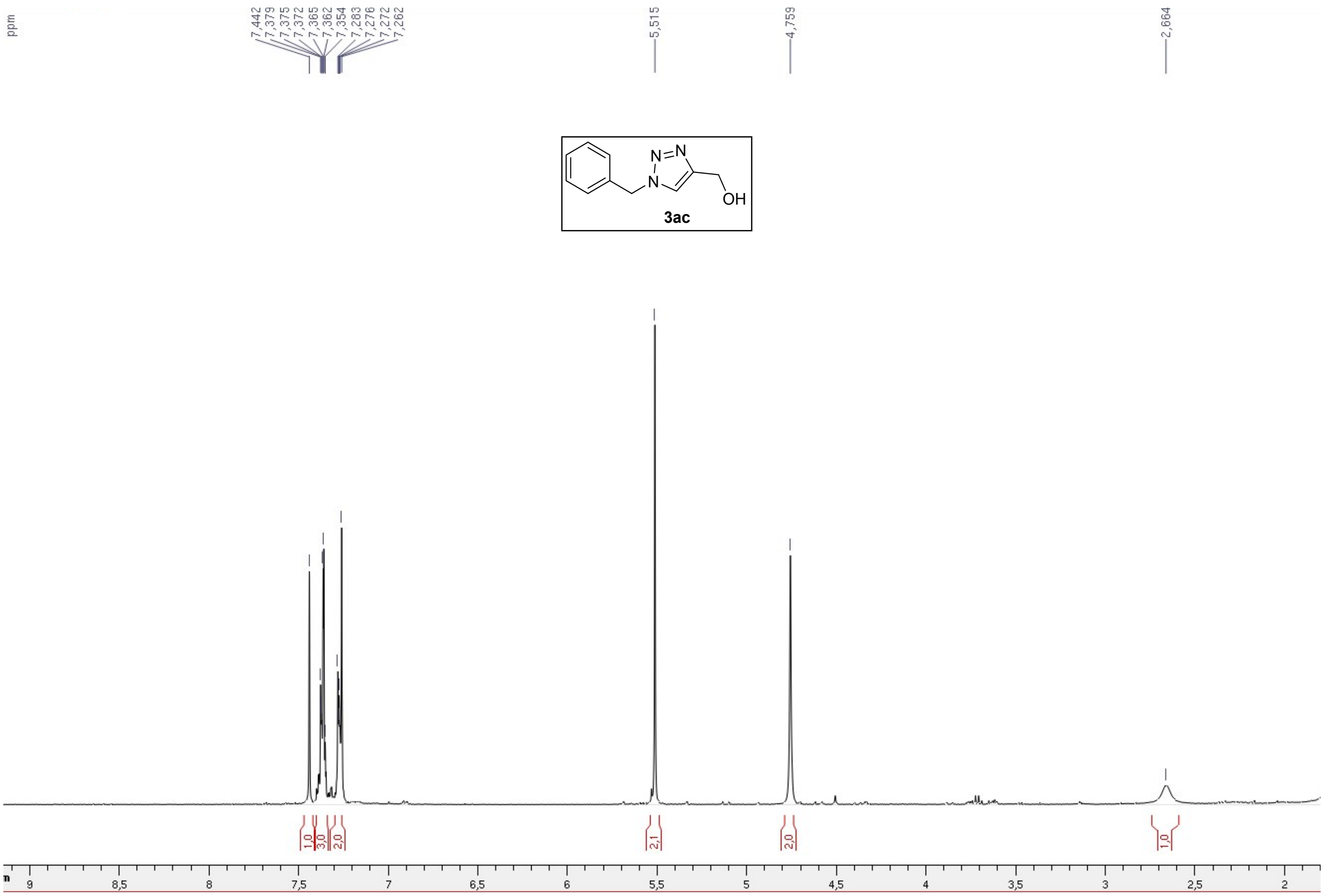
2. 3ab

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.66 (d, *J*= 8.8 Hz, 2H), 7.52 (s, 1H), 7.35–7.29 (m, 3H), 7.26–7.24 (m, 2H), 6.87 (d, *J*= 8.8 Hz, 2H), 5.50 (s, 2H), 3.77 (s, 3H) ppm. NMR data are consistent with the literature.[5]



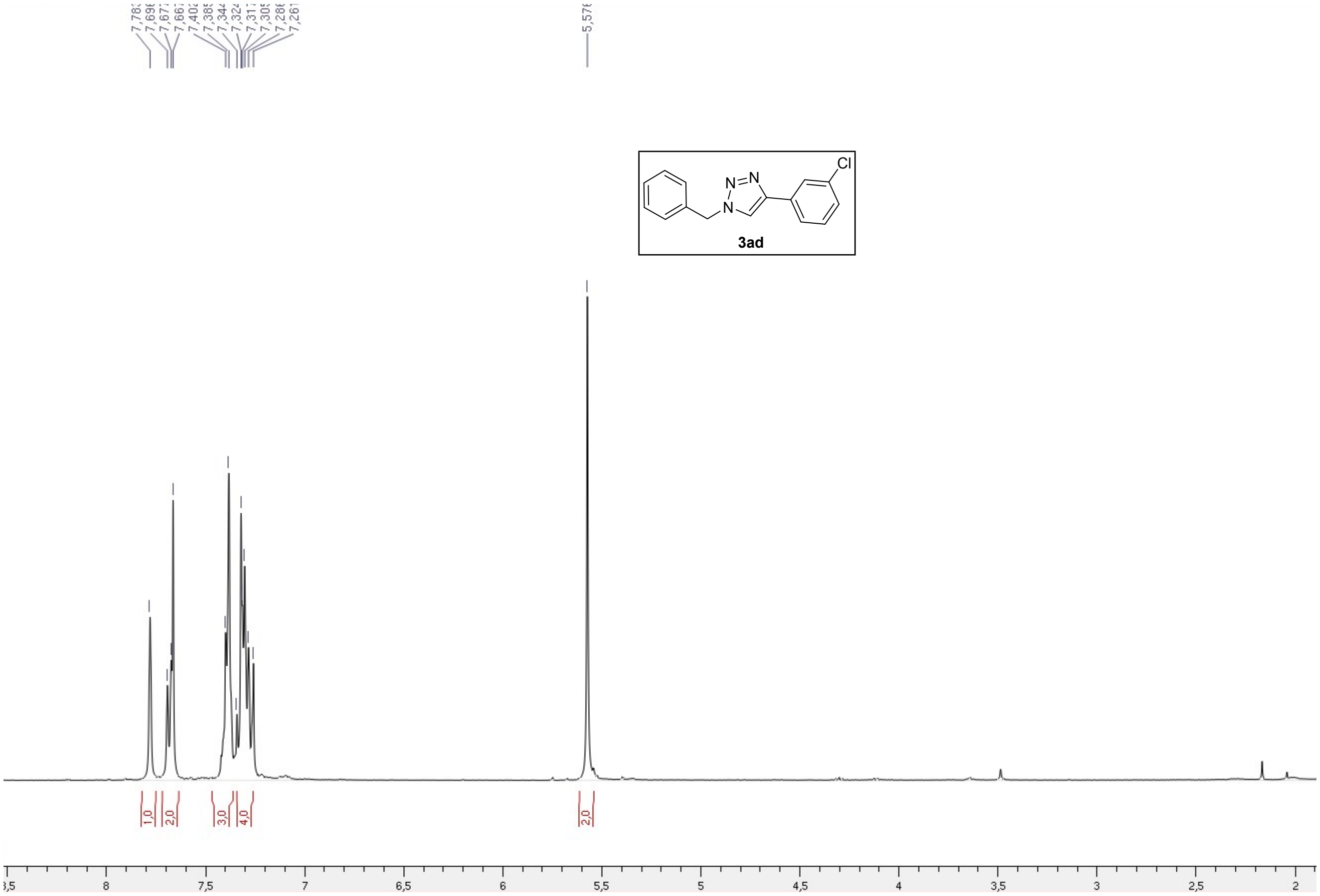
3. 3ac

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.38–7.35 (m, 3H), 7.28–7.26 (m, 2H), 5.51 (s, 2H), 4.76 (s, 2H), 2.66 (brs, 1H) ppm. NMR data are consistent with the literature.[6]



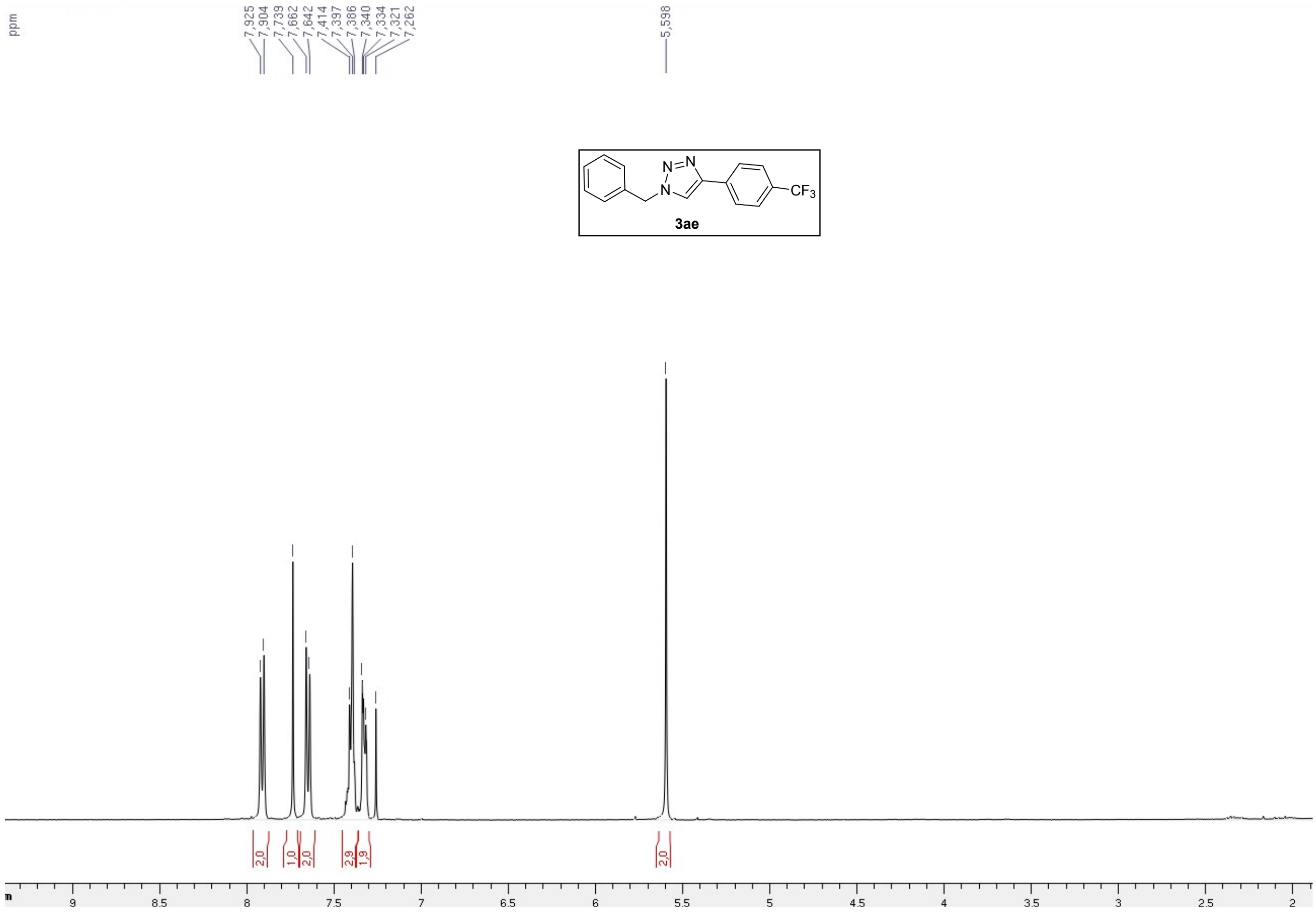
4. 3ad

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.78 (s, 1H), 7.69–7.66 (m, 2H), 7.40–7.28 (m, 4H), 7.34–7.28 (m, 3H), 5.57 (s, 2H) ppm. NMR data are consistent with the literature.[7]



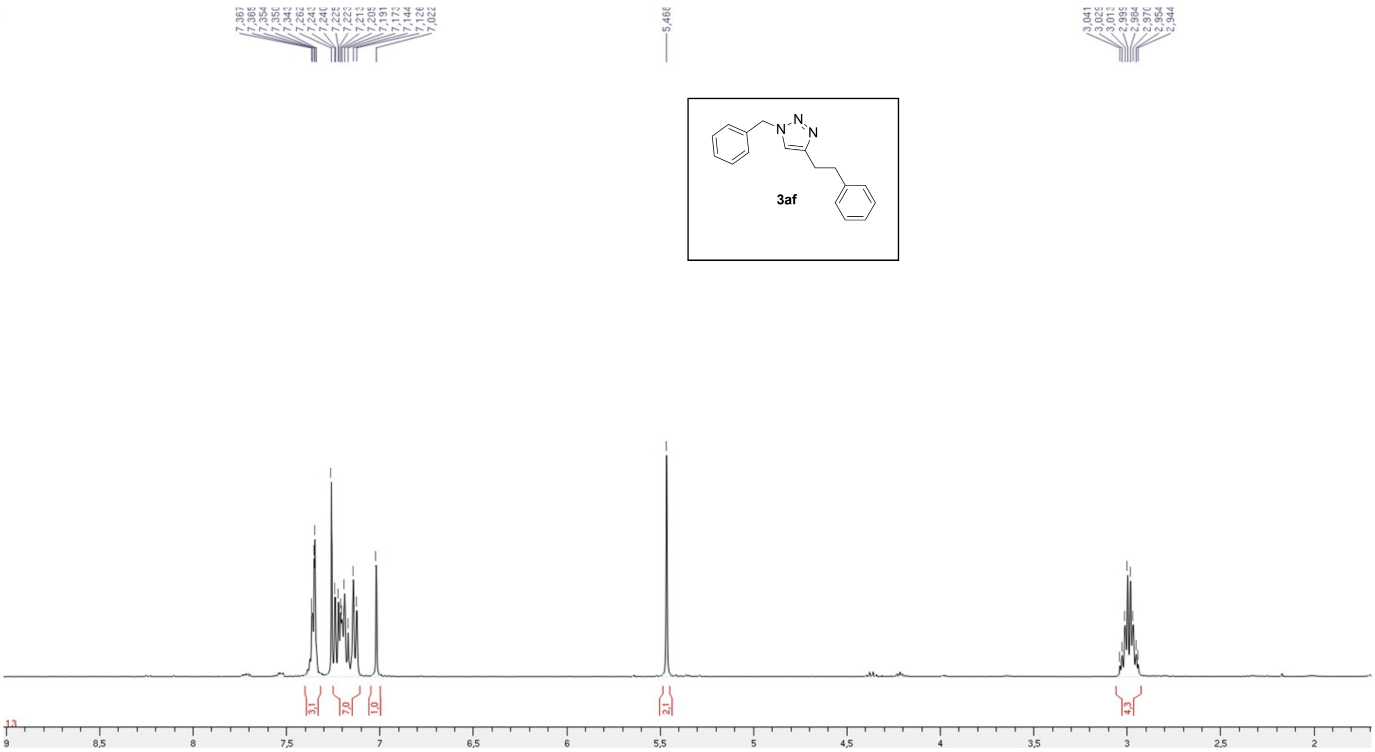
5. 3ae

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.91 (d, *J*= 8.4 Hz, 2H), 7.74 (s, 1H), 7.65 (d, *J*= 8.4 Hz, 2H), 7.41–7.39 (m, 3H), 7.34–7.32 (m, 2H), 5.59 (s, 2H) ppm. NMR data are consistent with the literature.[8]



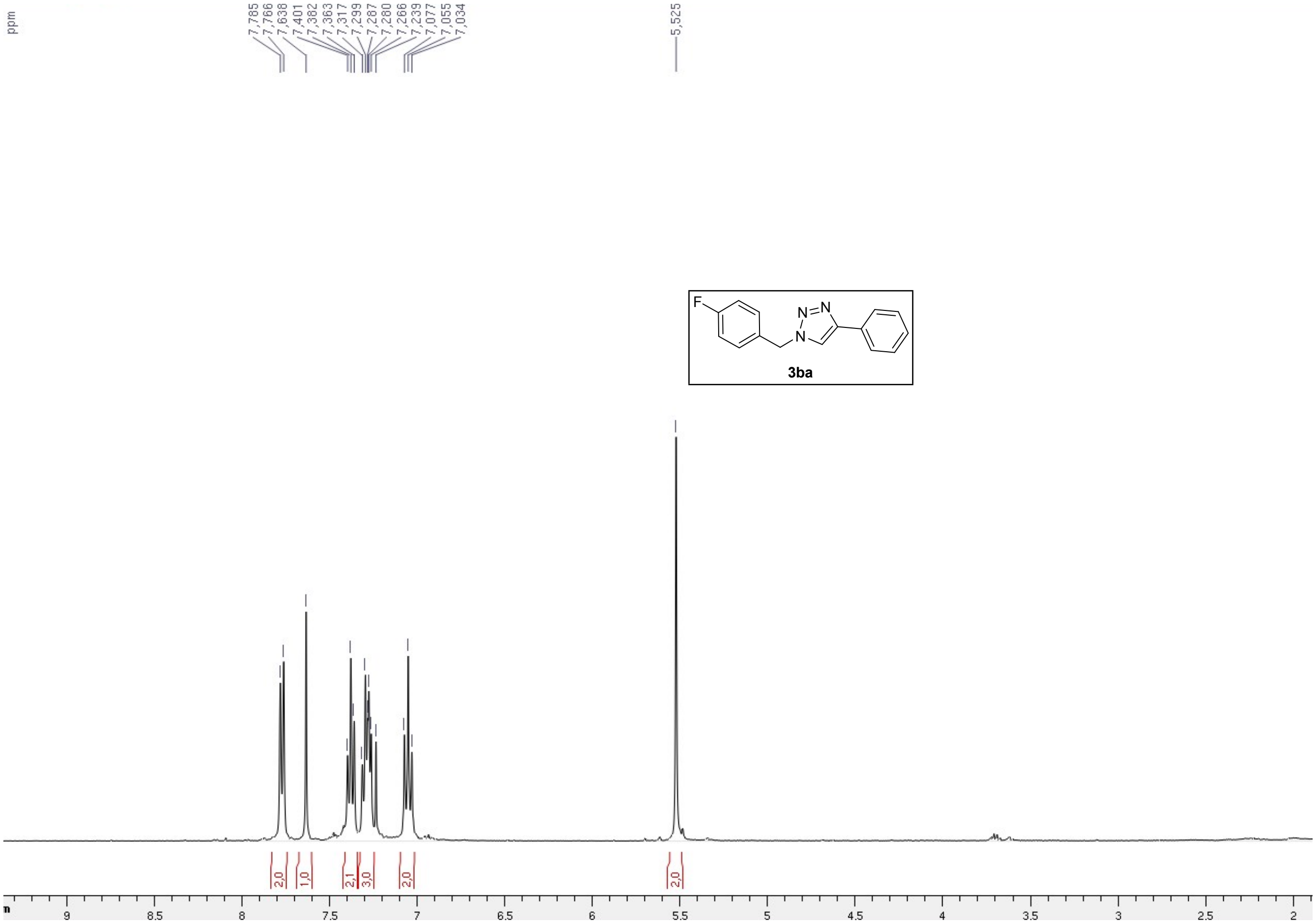
6. 3af

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37–7.33 (m, 3H), 7.25–7.12 (m, 7H), 7.02 (s, 1H), 5.46 (s, 2H), 3.03–2.94 (m, 4H) ppm. NMR data are consistent with the literature.[9]



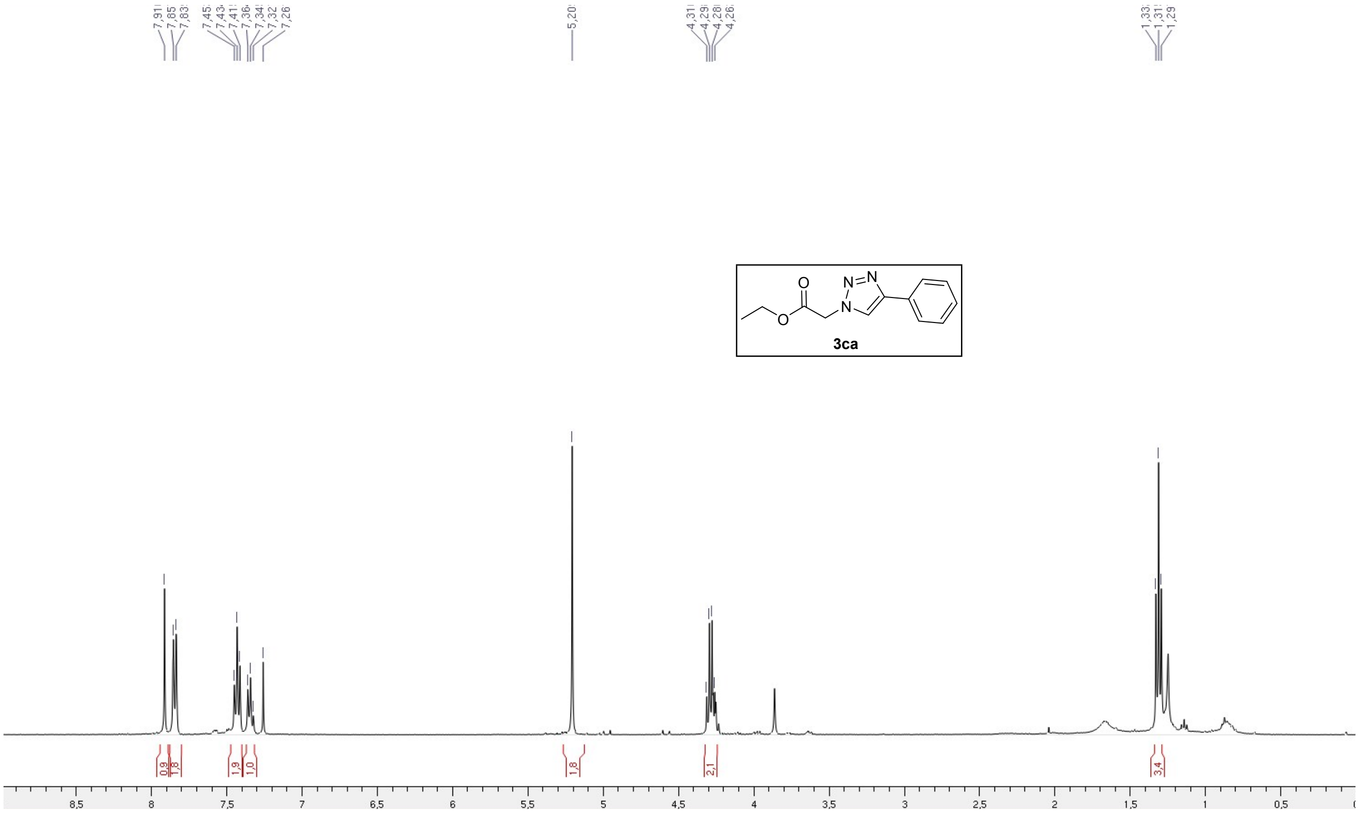
7. 3ba

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.78 (d, *J*= 8.1 Hz, 2H), 7.64 (s, 1H), 7.40–7.36 (m, 2H), 7.32–7.24 (m, 3H), 7.06 (t, *J*= 8.1 Hz, 2H), 5.23 (s, 2H) ppm. NMR data are consistent with the literature.[10]



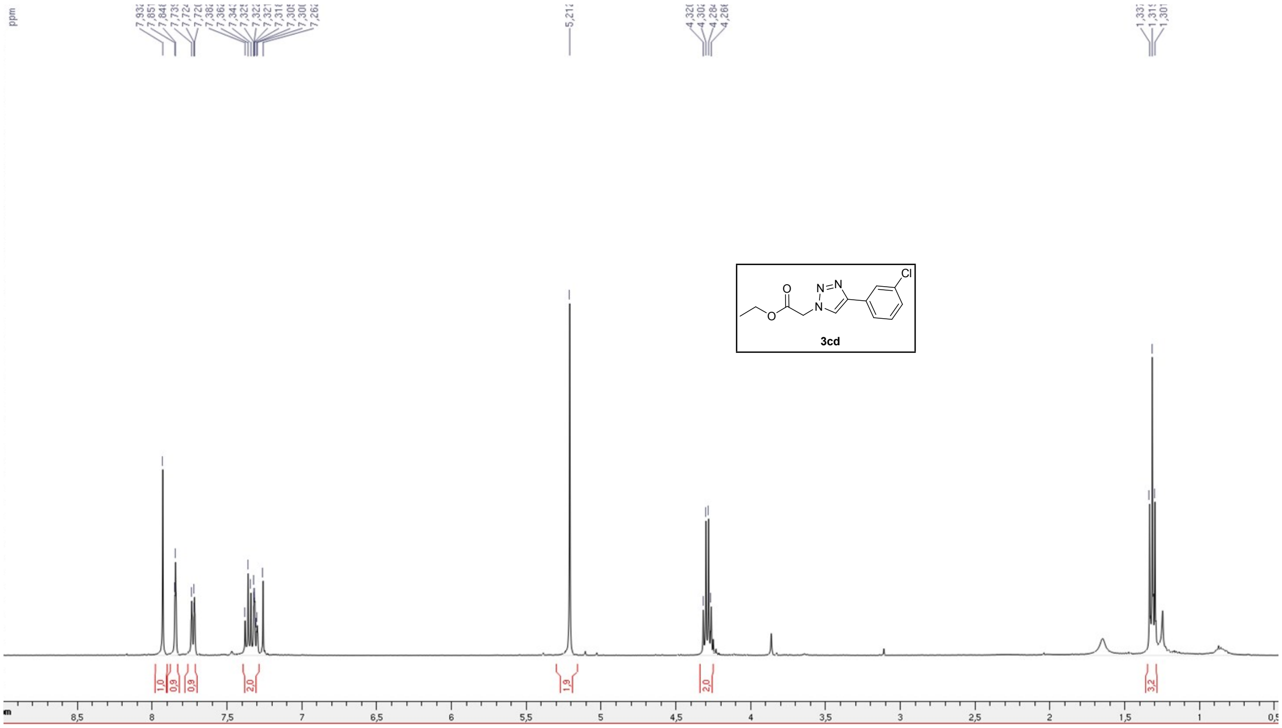
8. 3ca

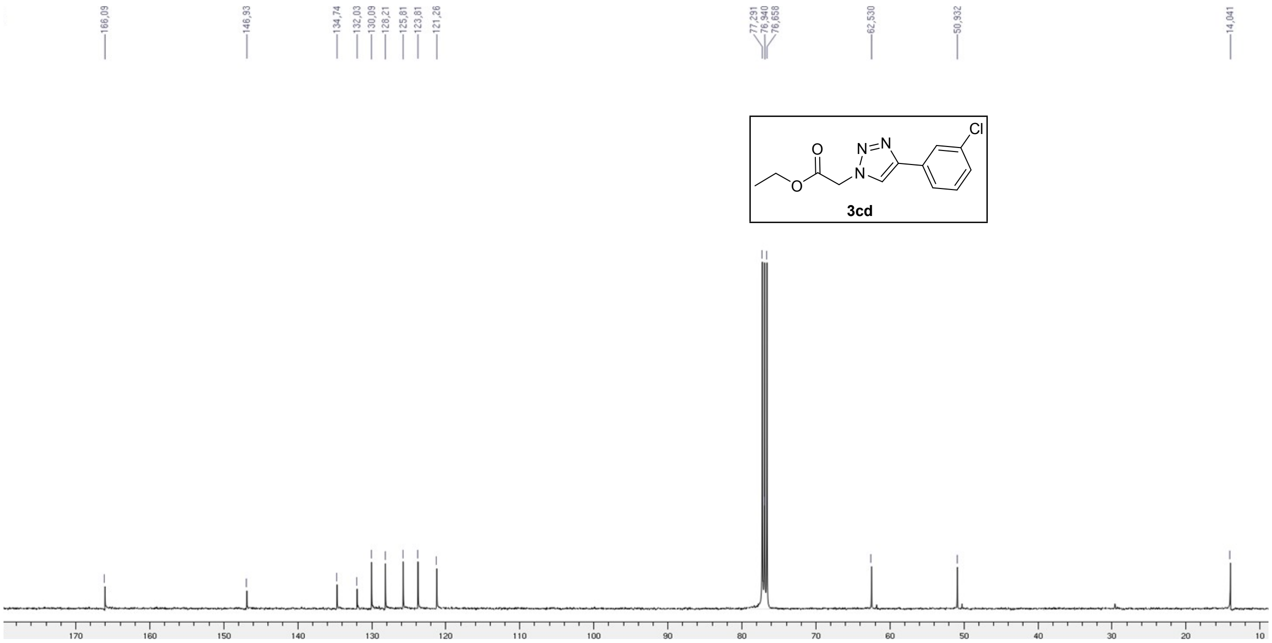
^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.92 (s, 1H), 7.85 (d, *J*= 7.8 Hz, 2H), 7.43 (t, *J*= 7.8 Hz, 2H), 7.36–7.33 (m, 1H), 5.21 (s, 2H), 4.29 (q, *J*= 6.8 Hz, 2H), 1.32 (t, *J*= 6.8 Hz, 3H) ppm. NMR data are consistent with the literature.[4]



9. 3cd

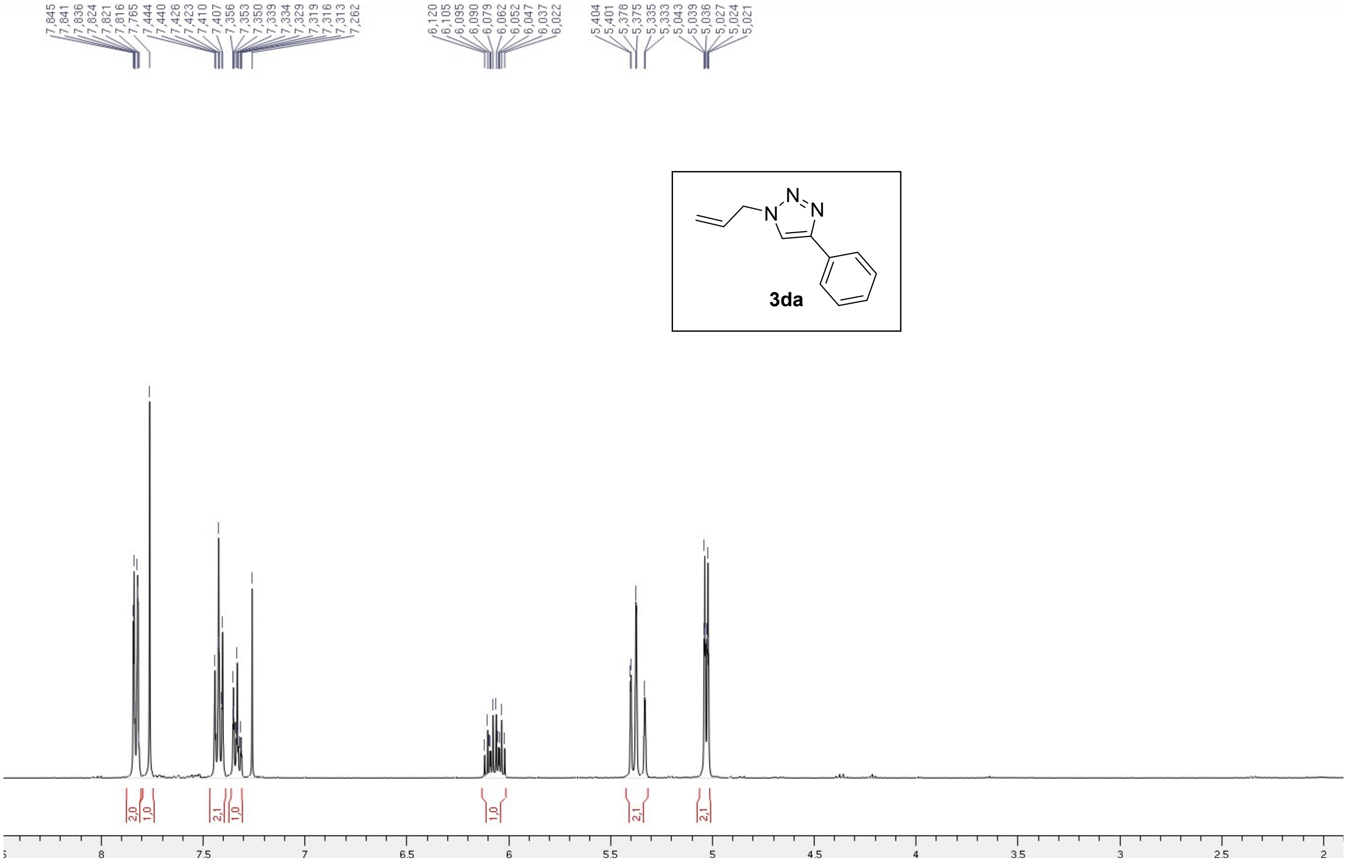
^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.93 (s, 1H), 7.86–7.85 (m, 1H), 7.74–7.72 (m, 1H), 7.38–7.30 (m, 2H), 5.21 (s, 2H), 4.30 (q, *J*= 6.9 Hz, 2H), 1.32 (t, *J*= 6.9Hz, 3H) ppm. ^{13}C-NMR (100 MHz, CDCl$_3$): 166.09, 146.93, 134.74, 132.03, 130.09, 128.2, 125.8, 123.8, 121.2, 62.53, 50.93, 14.04. ESI-MS (M+H$^+$) 266. IR (cm^{-1}): 2925, 1747 (C=O), 1209, 1021.





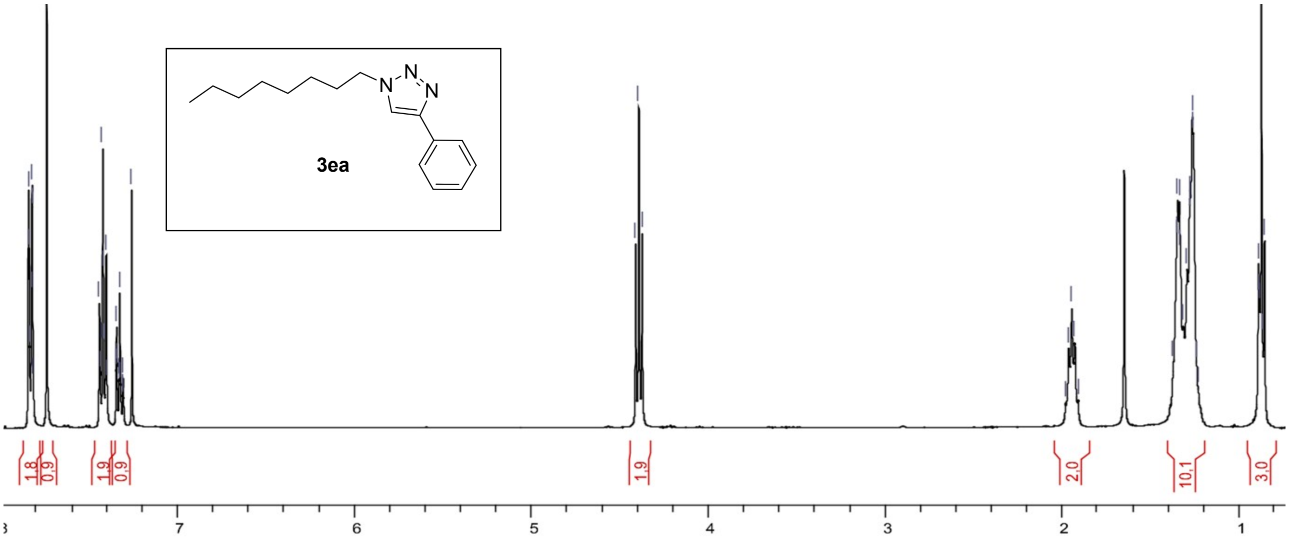
10. 3da

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.84–7.82 (m, 2H), 7.76 (s, 1H), 7.44–7.40 (m, 2H), 7.35–7.31 (m, 1H), 6.12–6.02 (m, 1H), 5.40–5.32 (m, 2H), 5.04–5.02 (m, 2H) ppm. NMR data are consistent with the literature.[11]



11. 3ea

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.84–7.81 (m, 2H), 7.74 (s, 1H), 7.44–7.40 (m, 2H), 7.35–7.30 (m, 1H), 4.39 (t, J = 7.39 Hz, 2H), 1.98–1.90 (m, 2H), 1.37–1.23 (m, 10H), 0.89–0.85 (t, J = 7.39 Hz, 3H) ppm. NMR data are consistent with the literature.[12]



D. References

1. P. Chen, H. B. Zhang, G. D. Lin, Q. Hong, K. R. Tsai, *Carbon* 1997, *35*, 1495-1501.
2. J. John, E. Gravel, A. Hagege, H. Li, T. Gacoin, E. Doris, *Angew. Chem. Int. Ed.,* **2011**, 50, 7533.
3. R. Chisholm, J. D. Parkin, A. D. Smith, G. Hahner, *Langmuir*, **2016**, 32, 3130.
4. D. Clarisse, P. Prakash, V. Geertsen, F. Miserque, E. Gravel, E. Doris, *Green Chem*., **2017**, 19, 3112.
5. V. H. Reddy, Y. V. R. Reddy, B. Sridhar, B. V. S. Reddy, *Adv. Synth. Catal.,* **2016**, 358, 1088.
6. M. Chetia, P. S. Gehlot, A. Kumar, D. Sarma, *Tetrahedron Lett.,* **2018**, 59, 397.
7. M. Madasu, C.-F. Hsia, M. H. Huang, *Nanoscale*, **2017**, 9, 6970.
8. H. Hiroki, K. Ogata, S.-I. Fukuzawa, *Synlett,* **2013**, 24, 843.
9. E. Tasca, G. L. Sorella, L. Sperni, G. Strukul, A. Scarso, *Green Chem*., **2015**, 17, 1414.
10. R. Gonzalez-Olvera, C. I. Urquiza-Castro, G. E. Negron-Silva, D. Angeles-Beltran, L. Lomas-Romero, A. Gutierrez-Carrillo, V. H. Lara, R. Santillan, J. A. Morales-Serna *RSC Adv*., **2016**, 6, 63660.
11. E. Tasca, G. L. Sorella, L. Sperni, G. Strukul, A. Scarso, *Green Chem*., **2015**, 17, 1414.
12. S. Wang, K. Jia, J. Cheng, Y. Chen, Y. Yuan, *Tetrahedron Lett.,* **2017**, 58, 3717.