Supplementary Materials

Synthesis and characterization of new triazole-bispidinone scaffolds and their metal complexes for catalytic applications

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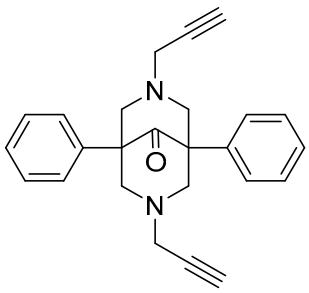
1. NMR DATA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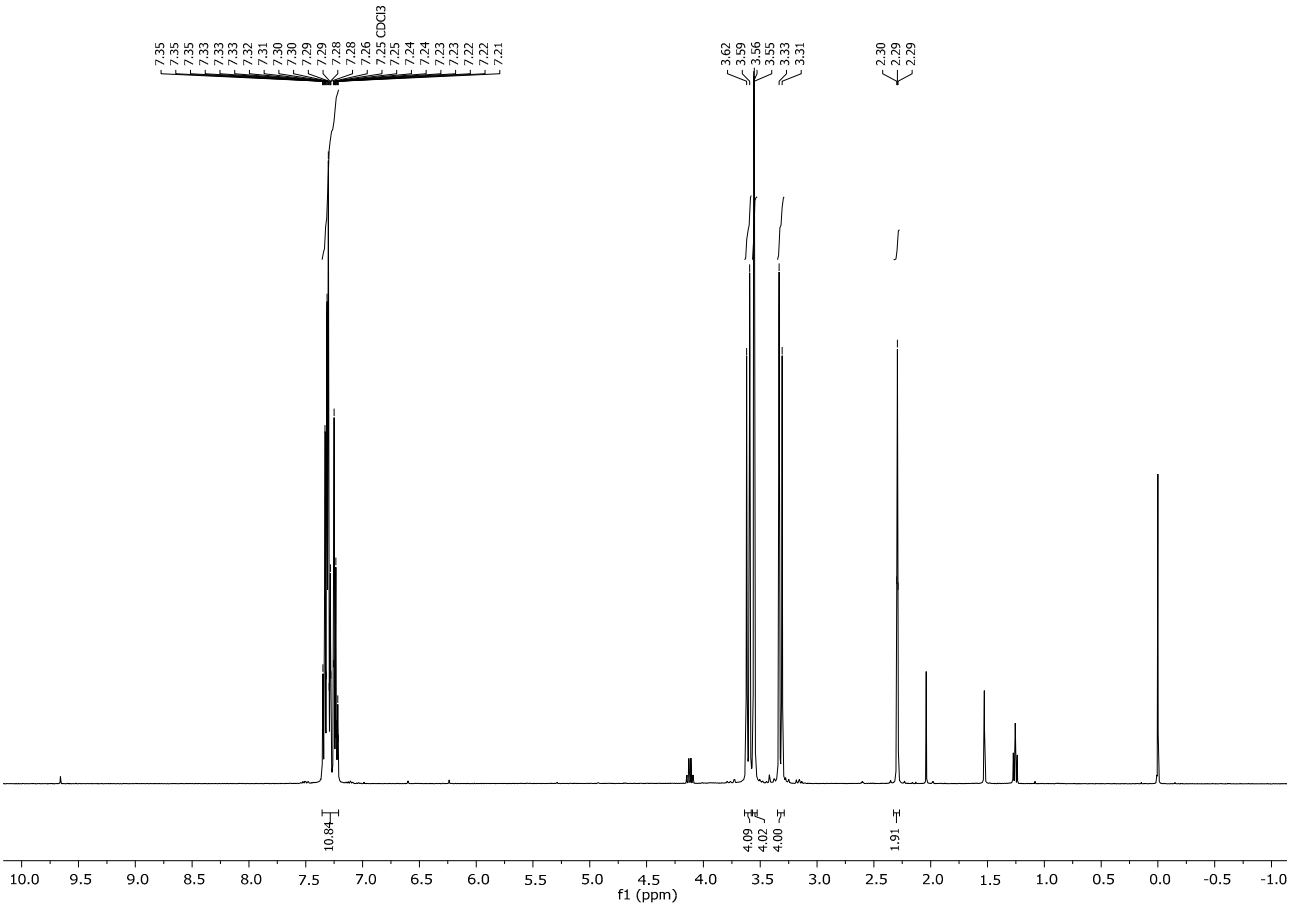
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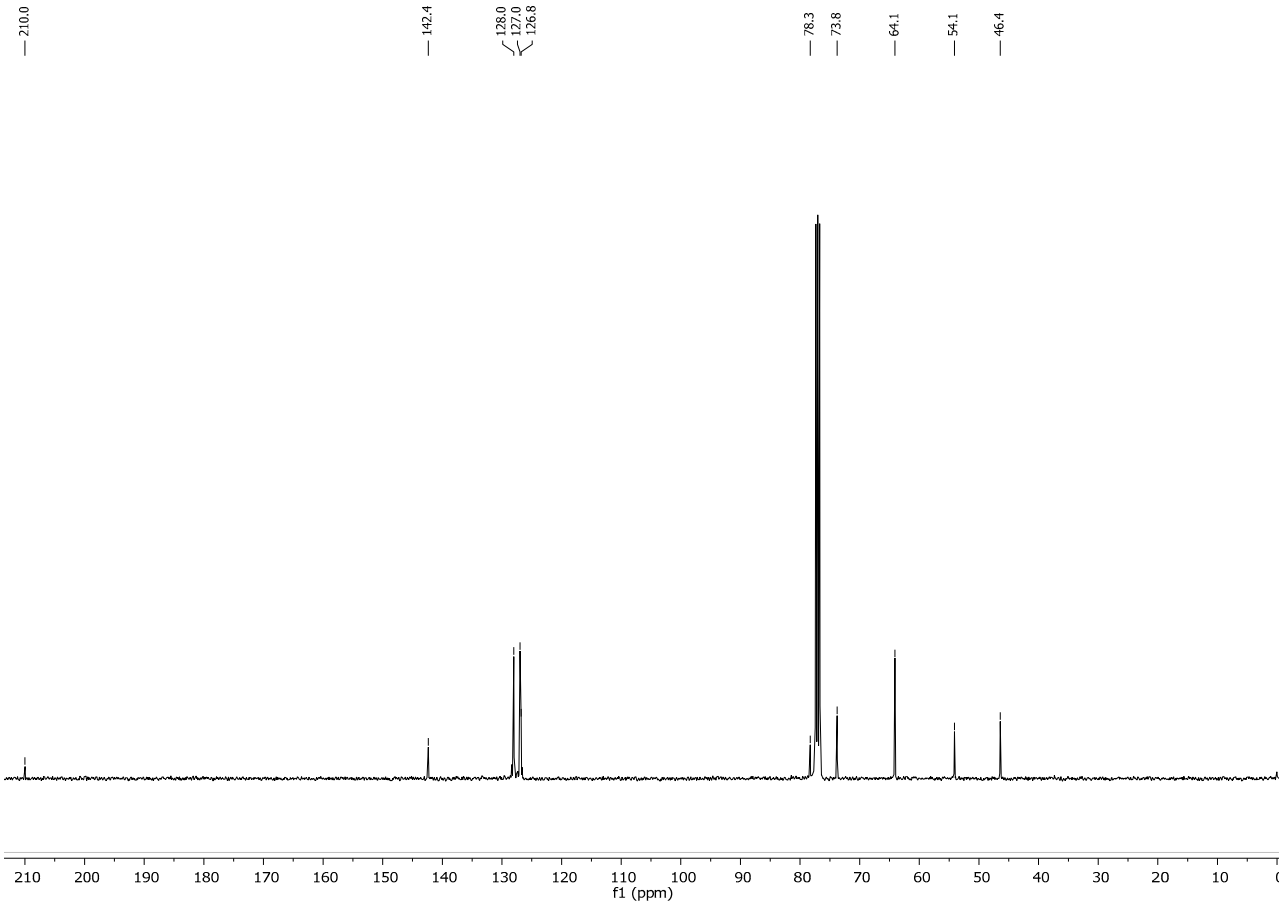
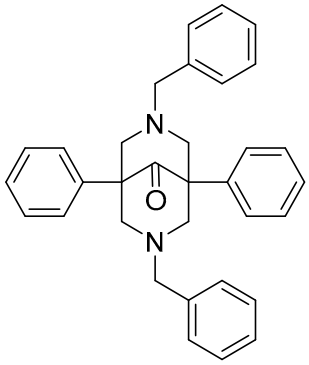


Figure S1. ^{1}H and ^{13}C-NMR spectra of compound **1**.



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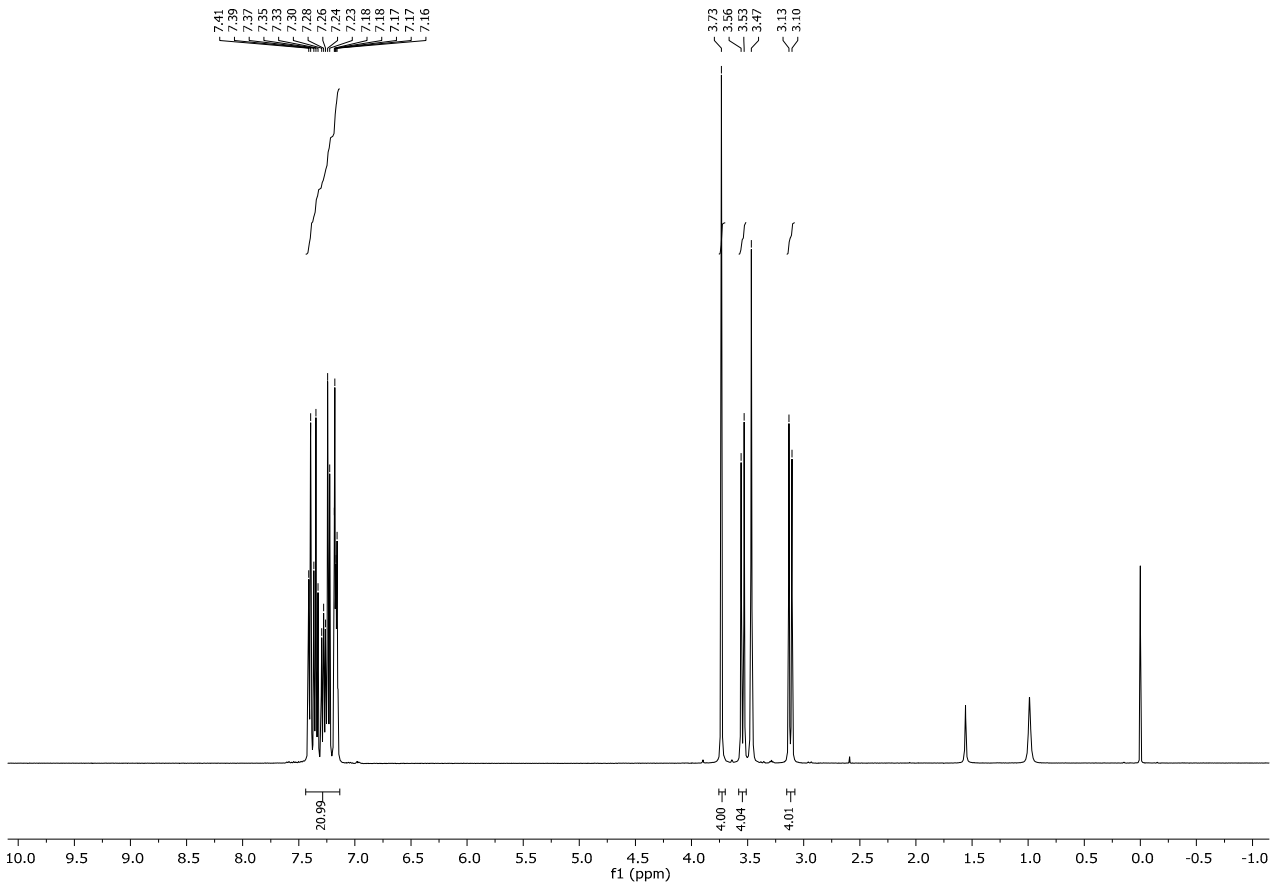
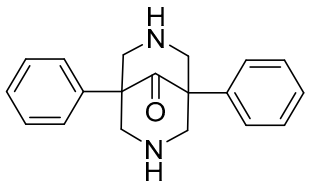


Figure S2. [1]H-NMR spectrum of compound **2** in accordance with literature. [Black, D.S.C.; Deacon, G.B.; Rose, M. Synthesis and metal complexes of symmetrically N-substituted bispidinones. *Tetrahedron* **1995**, *51*, 2055–2076, doi:10.1016/0040-4020(94)01069-C.]



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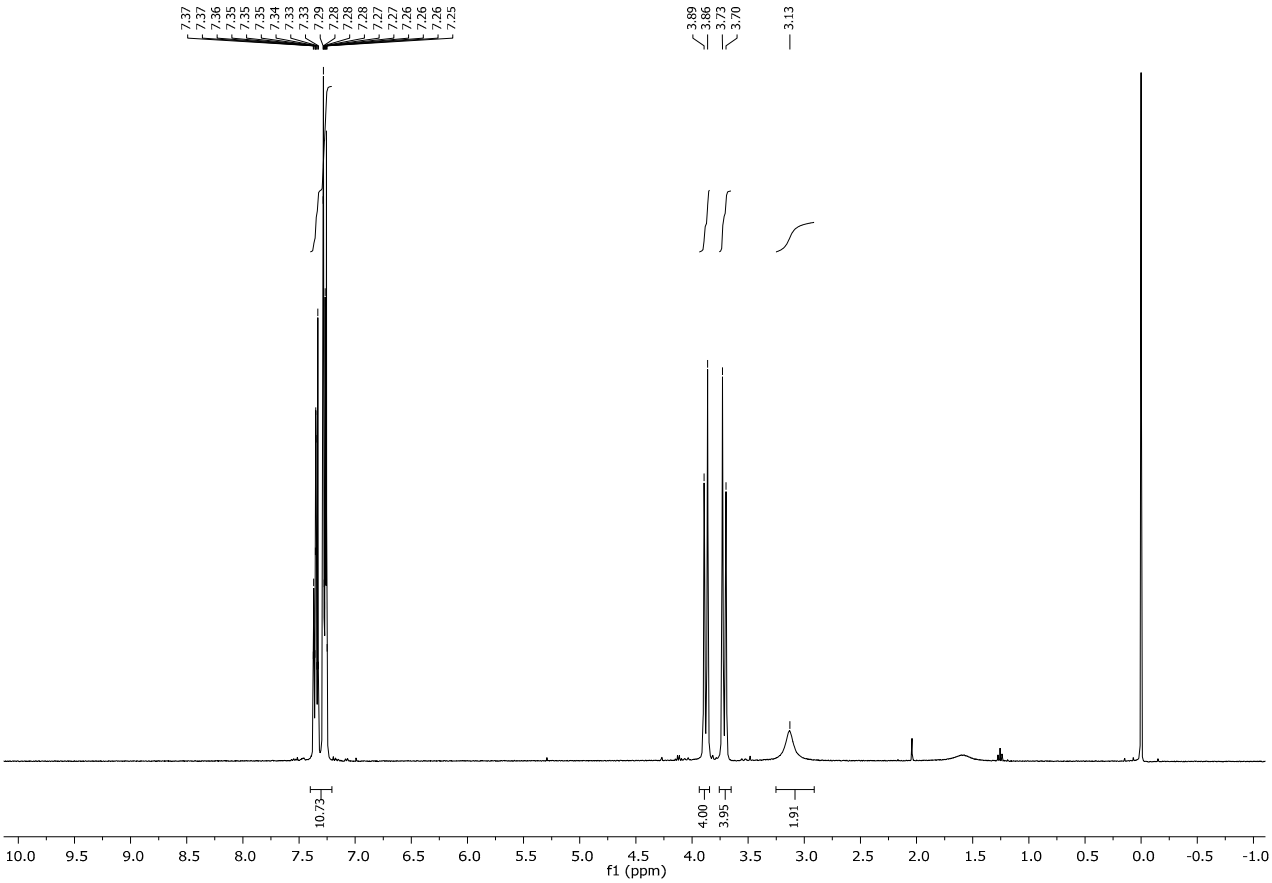
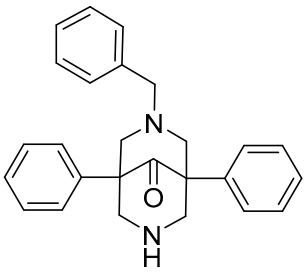


Figure S3. ^{1}H-NMR spectrum of compound **3** in accordance with literature. [Black, D.S.C.; Deacon, G.B.; Rose, M. Synthesis and metal complexes of symmetrically N-substituted bispidinones. *Tetrahedron* **1995**, *51*, 2055–2076, doi:10.1016/0040-4020(94)01069-C.]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N
H

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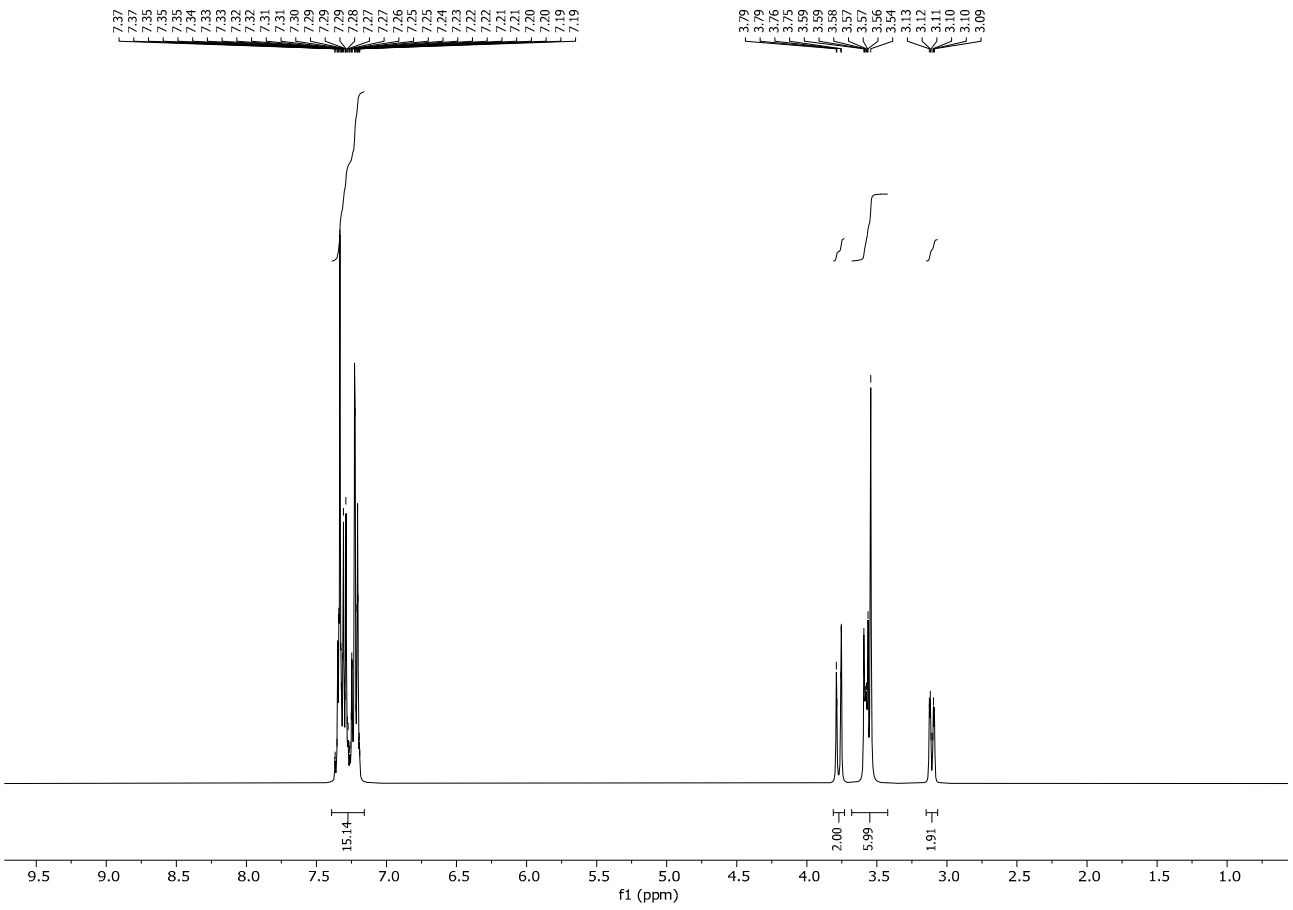
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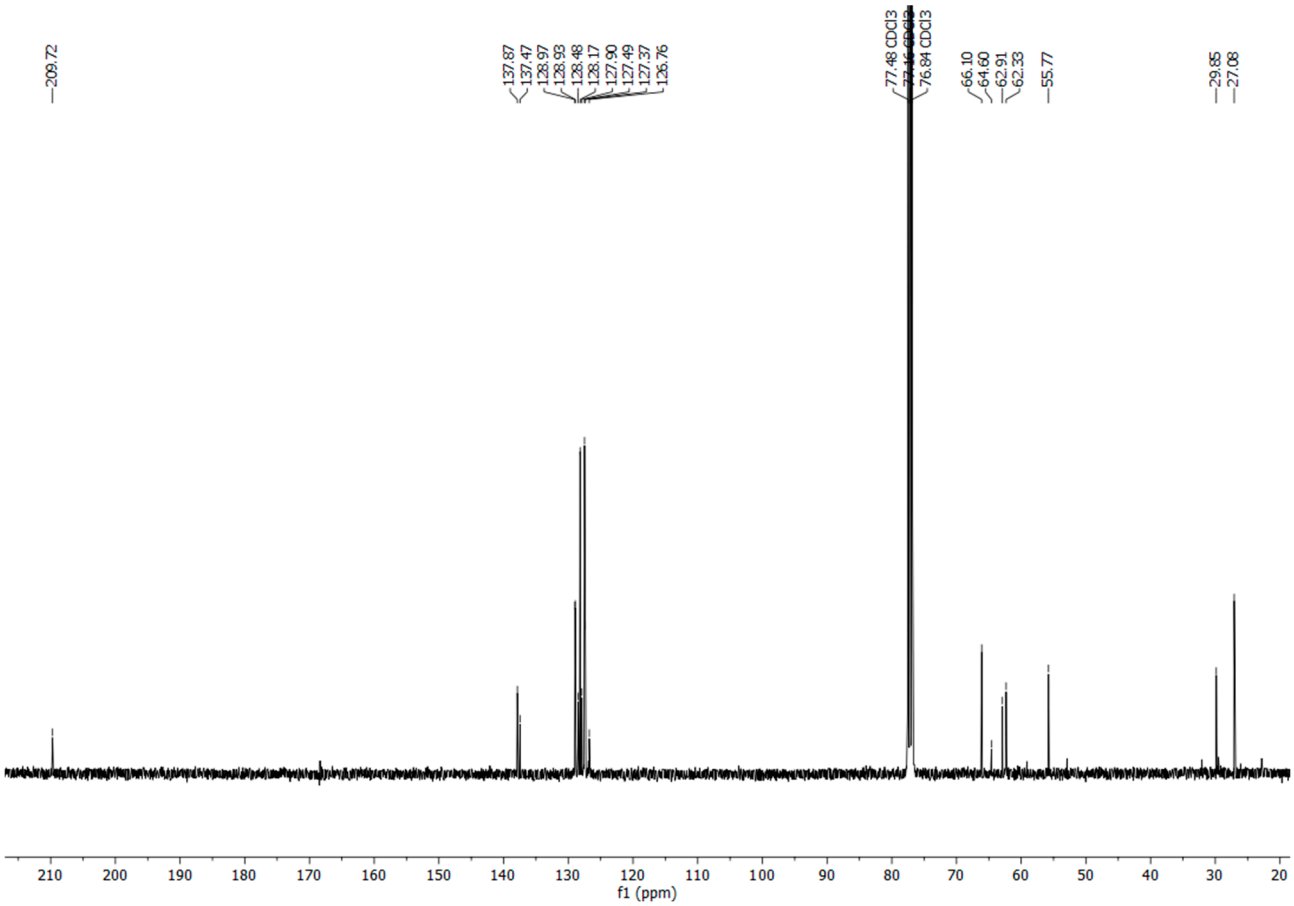

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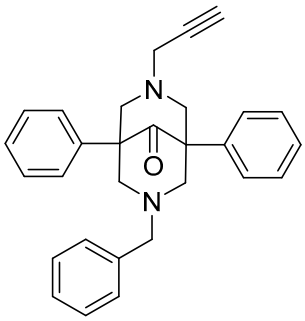
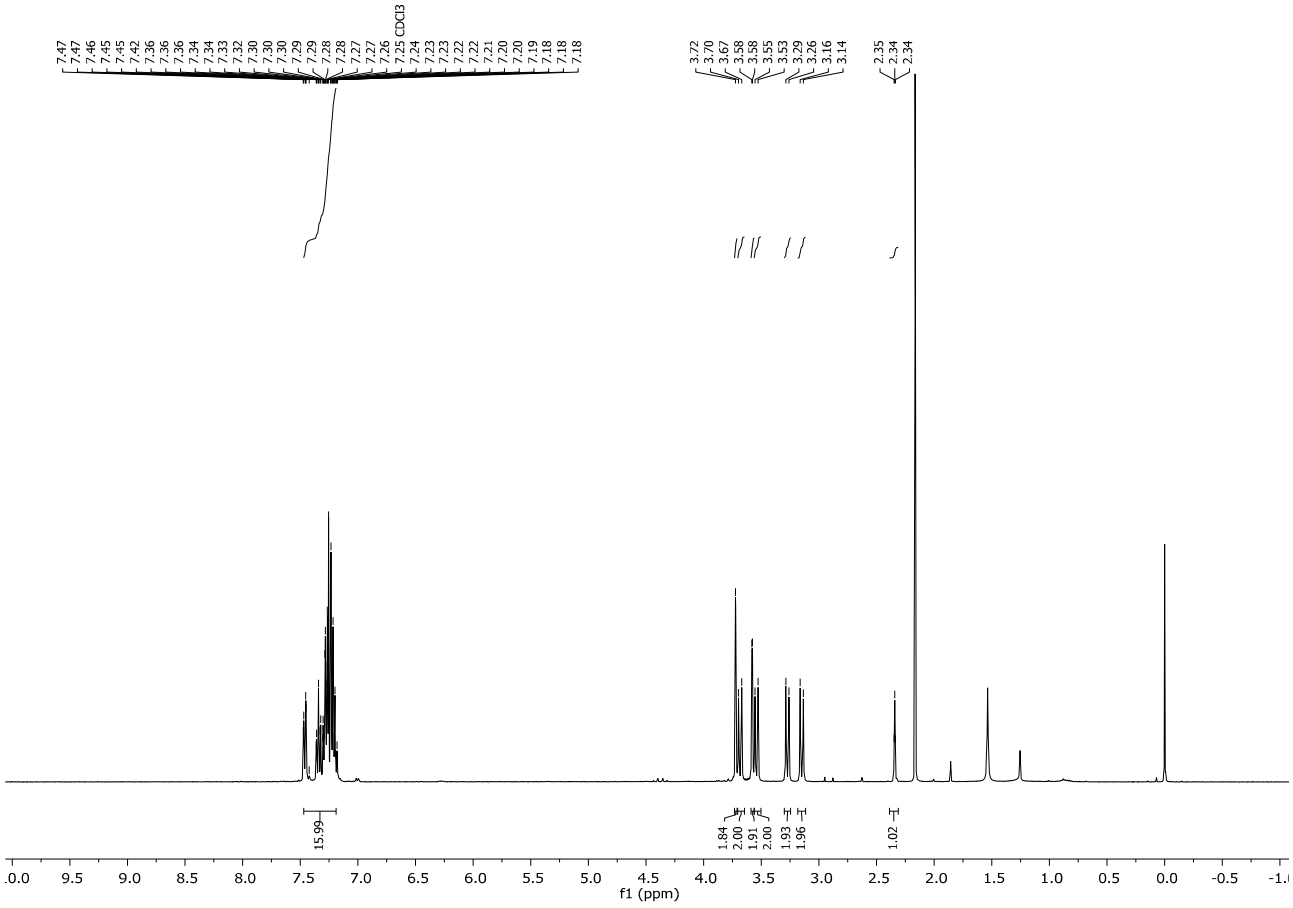

N
O
N

5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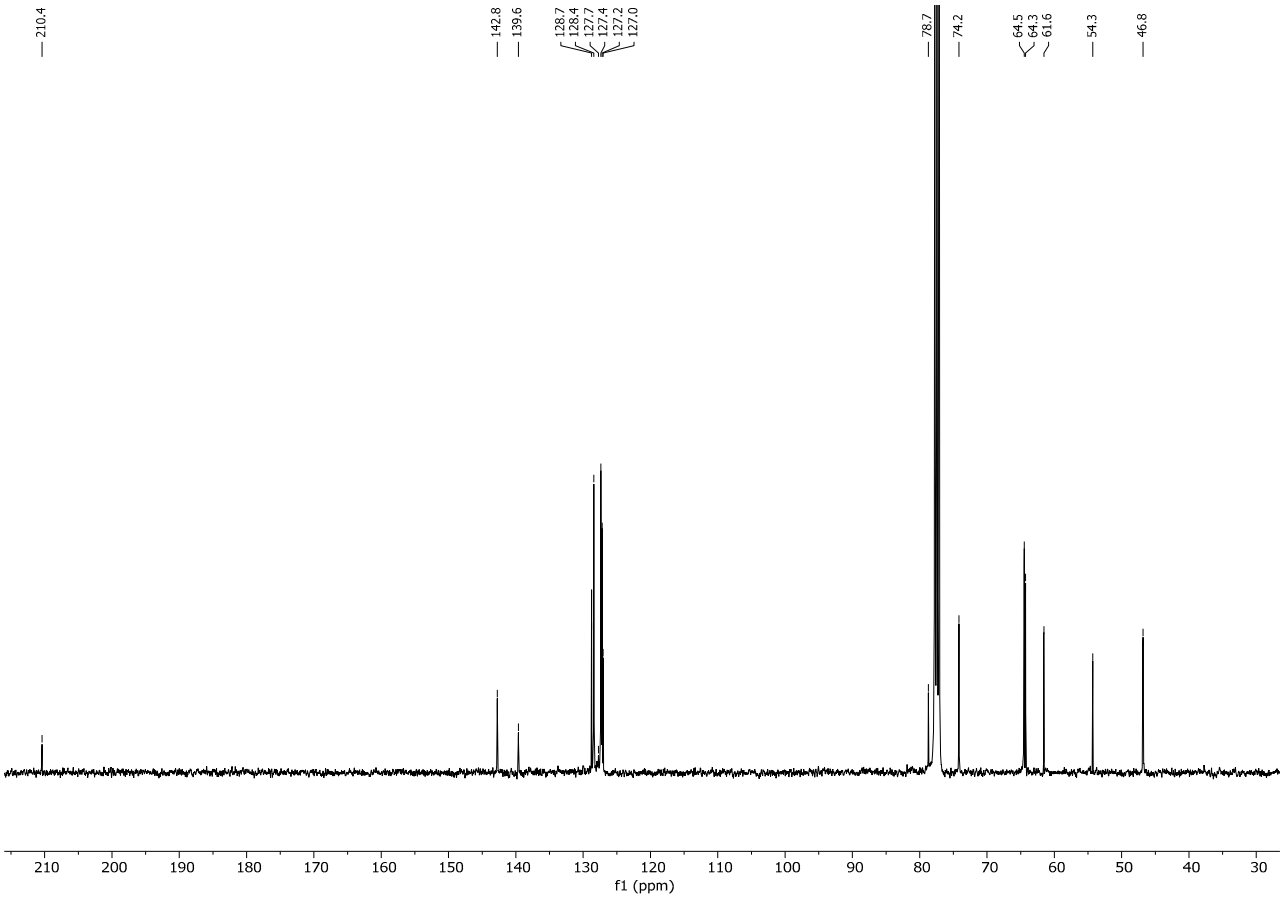


Figure S5. ^{1}H and ^{13}C-NMR spectra of compound **5**.

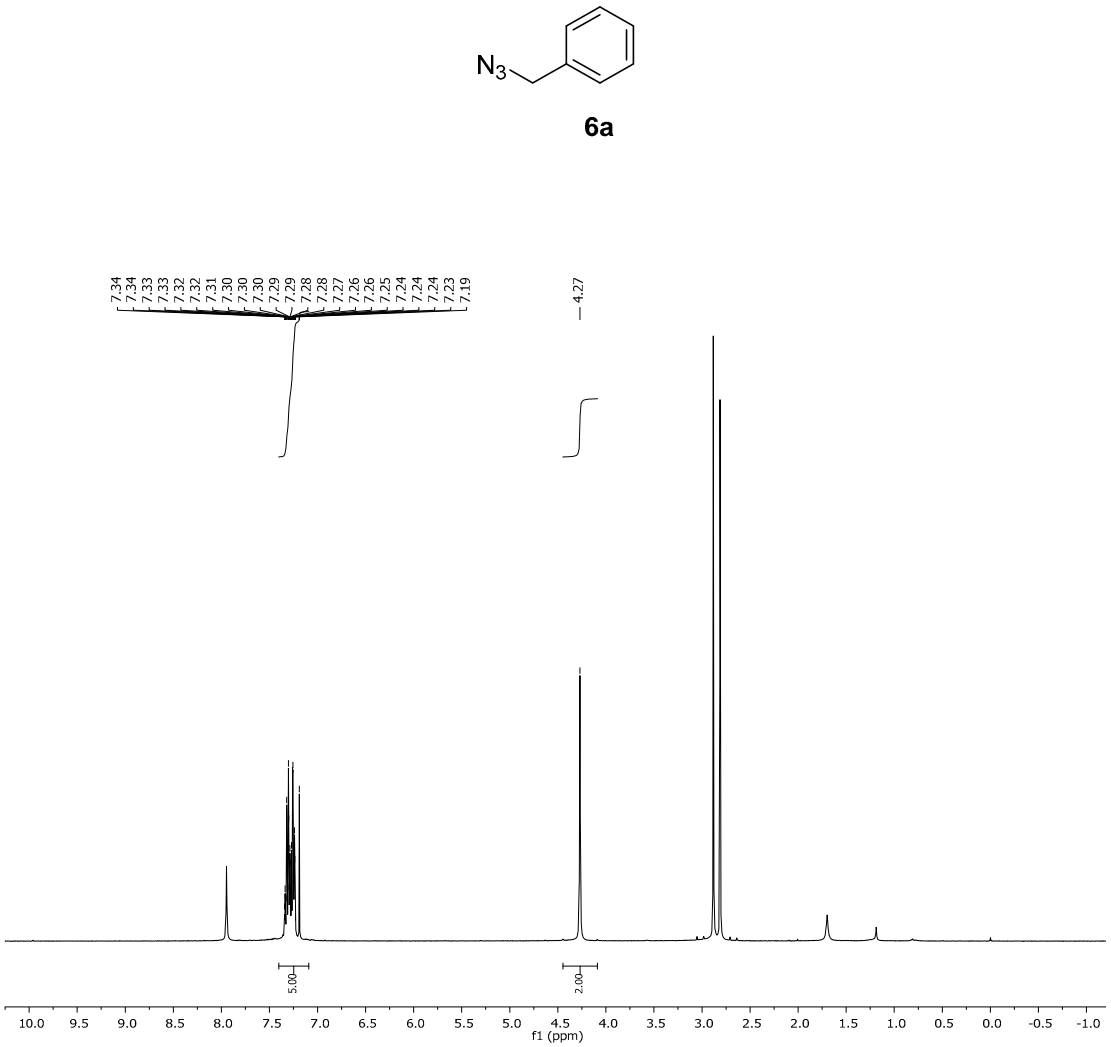


Figure S6. ^{1}H-NMR spectrum of compound **6a** in accordance with literature. [Zhong, Z.; Chesti, J.; Armstrong, A.; Bull, J.A. Synthesis of Sulfoximine Propargyl Carbamates under Improved Conditions for Rhodium Catalyzed Carbamate Transfer to Sulfoxides *J. Org. Chem.* **2022** *87*, 16115-16126; doi: 10.1021/acs.joc.2c02083B.]

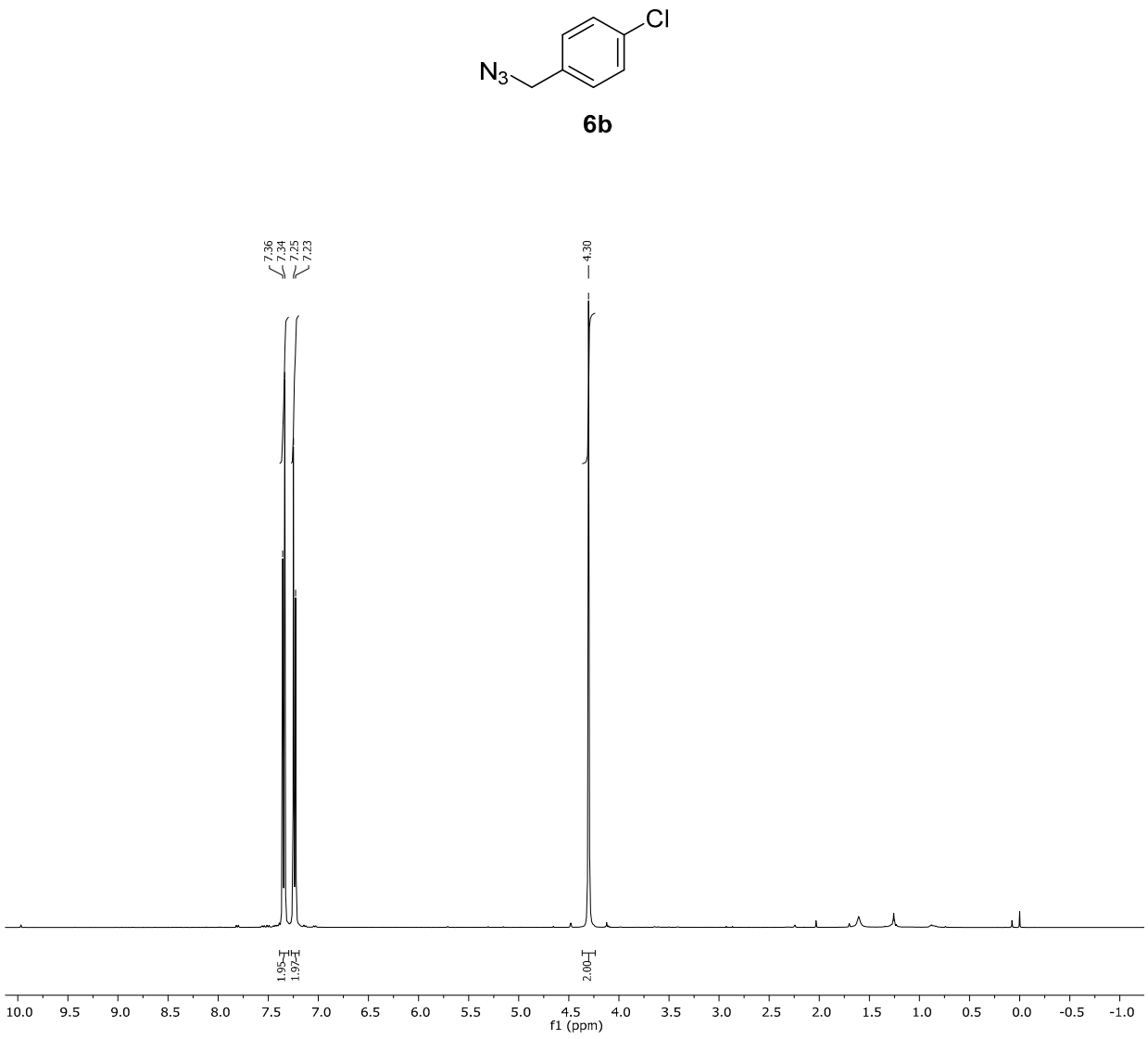
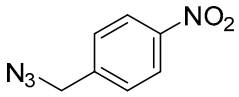


Figure S7. ^{1}H-NMR spectrum of compound **6b** in accordance with literature. [Vairoletti, F.; Paulino, M.; Mahler, G.; Salinas, G.; Saiz, C. Structure-Based Bioisosterism Design, Synthesis, Biological Evaluation and In Silico Studies of Benzamide Analogs as Potential Anthelmintics. *Molecules* **2022**, *27*, 2659; doi: 10.3390/molecules27092659.]



6c

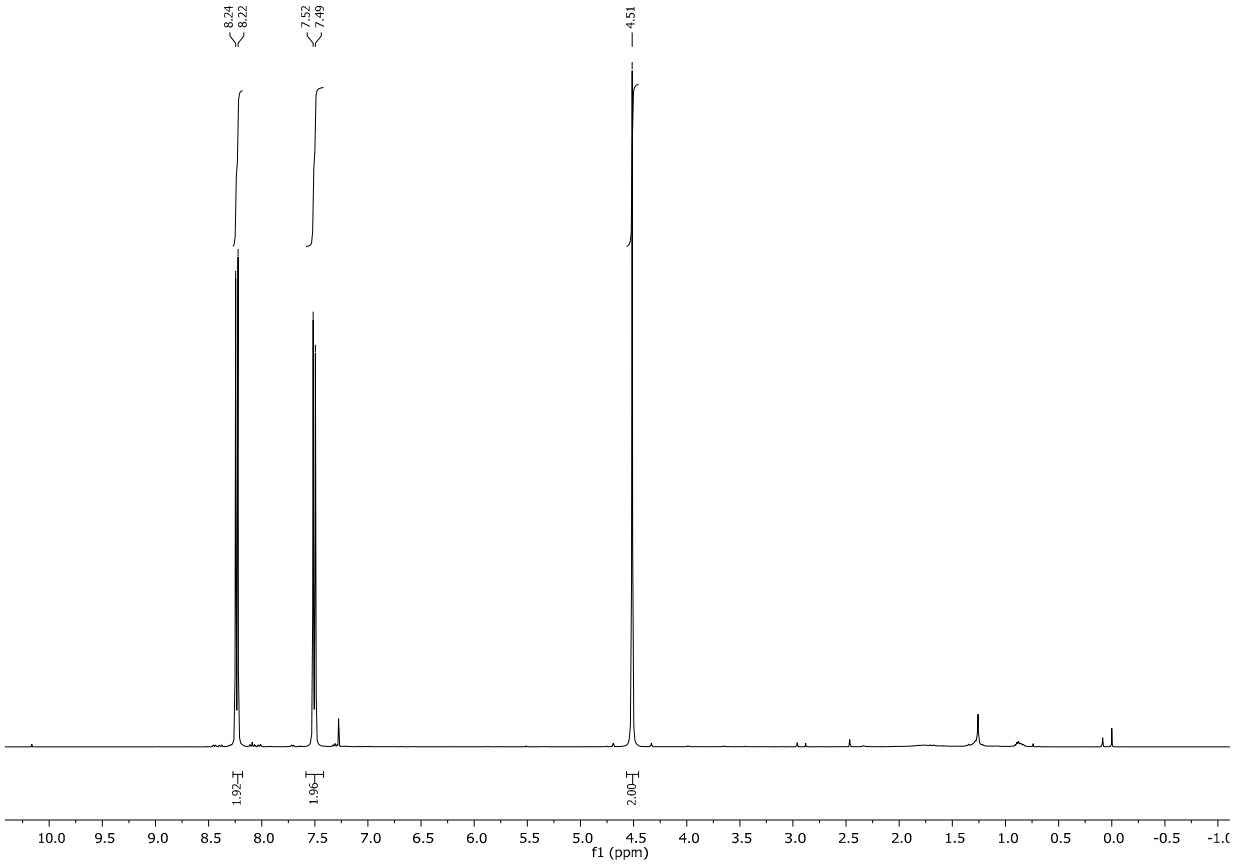


Figure S8. [1]H-NMR spectrum of compound **6c** in accordance with literature. [Rabet, P.T.G.; Fumagalli, G.; Boyd, S.; Greaney, M.F. Benzylic C–H Azidation Using the Zhdankin Reagent and a Copper Photoredox Catalyst, *Org. Lett*. **2016** *18*, 1646-1649; doi: 10.1021/acs.orglett.6b00512.]

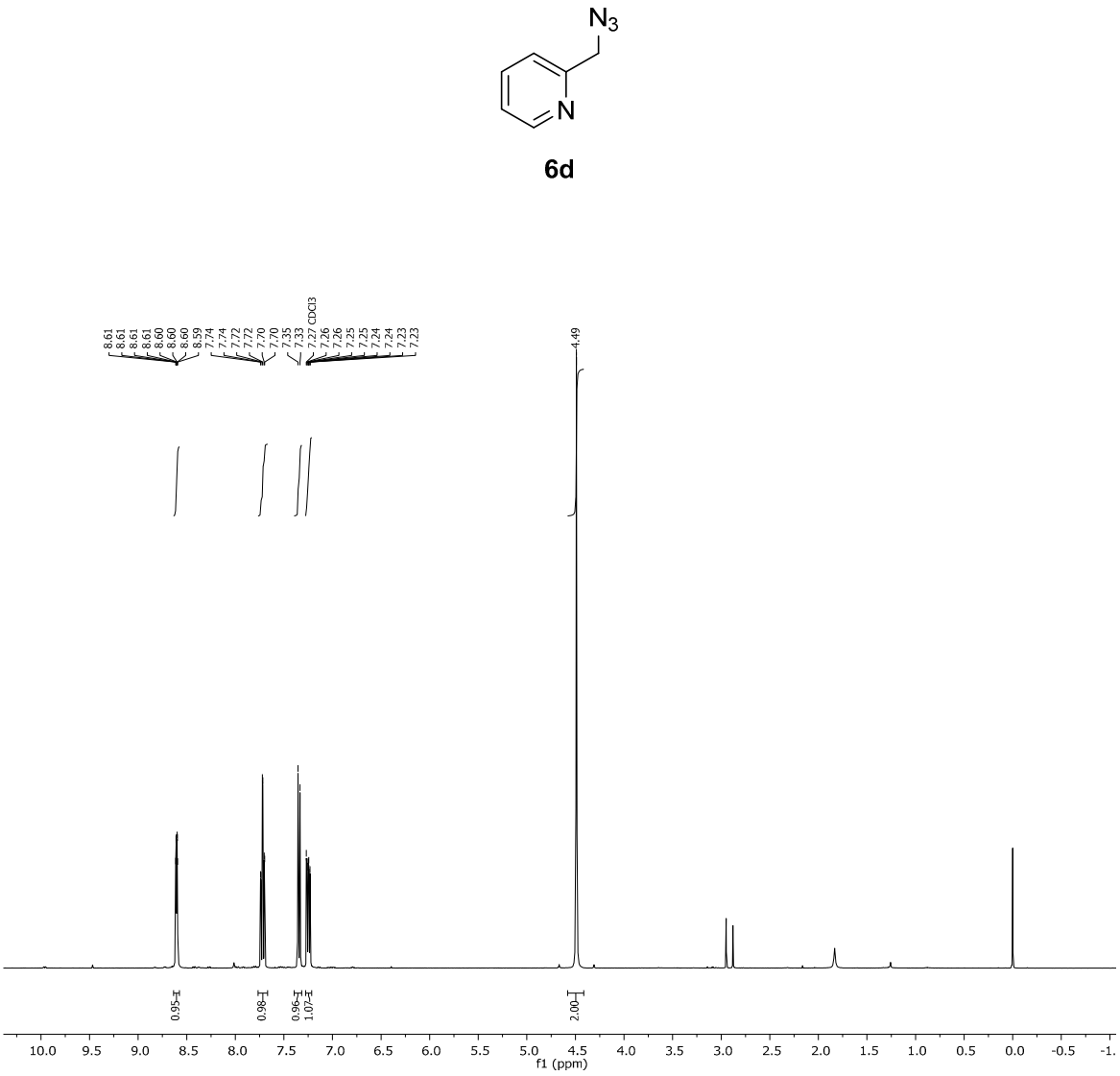
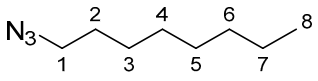


Figure S9. ^{1}H-NMR spectrum of compound **6d** in accordance with literature. [Sacchetti, A.; Urra-Mancilla, C.; Colombo Dugoni, G. Synthesis of DPA-triazole structures and their application as ligand for metal catalyzed organic reactions, *Tetrahedron*, **2022**, 132581; doi: 10.1016/j.tet.2021.132581.]

Figure S10. ^{1}H-NMR spectrum of compound **6e** in accordance with literature. [Sacchetti, A.; Urra-Mancilla, C.; Colombo Dugoni, G. Synthesis of DPA-triazole structures and their application as ligand for metal catalyzed organic reactions, *Tetrahedron*, **2022**, 132581; doi: 10.1016/j.tet.2021.132581.]



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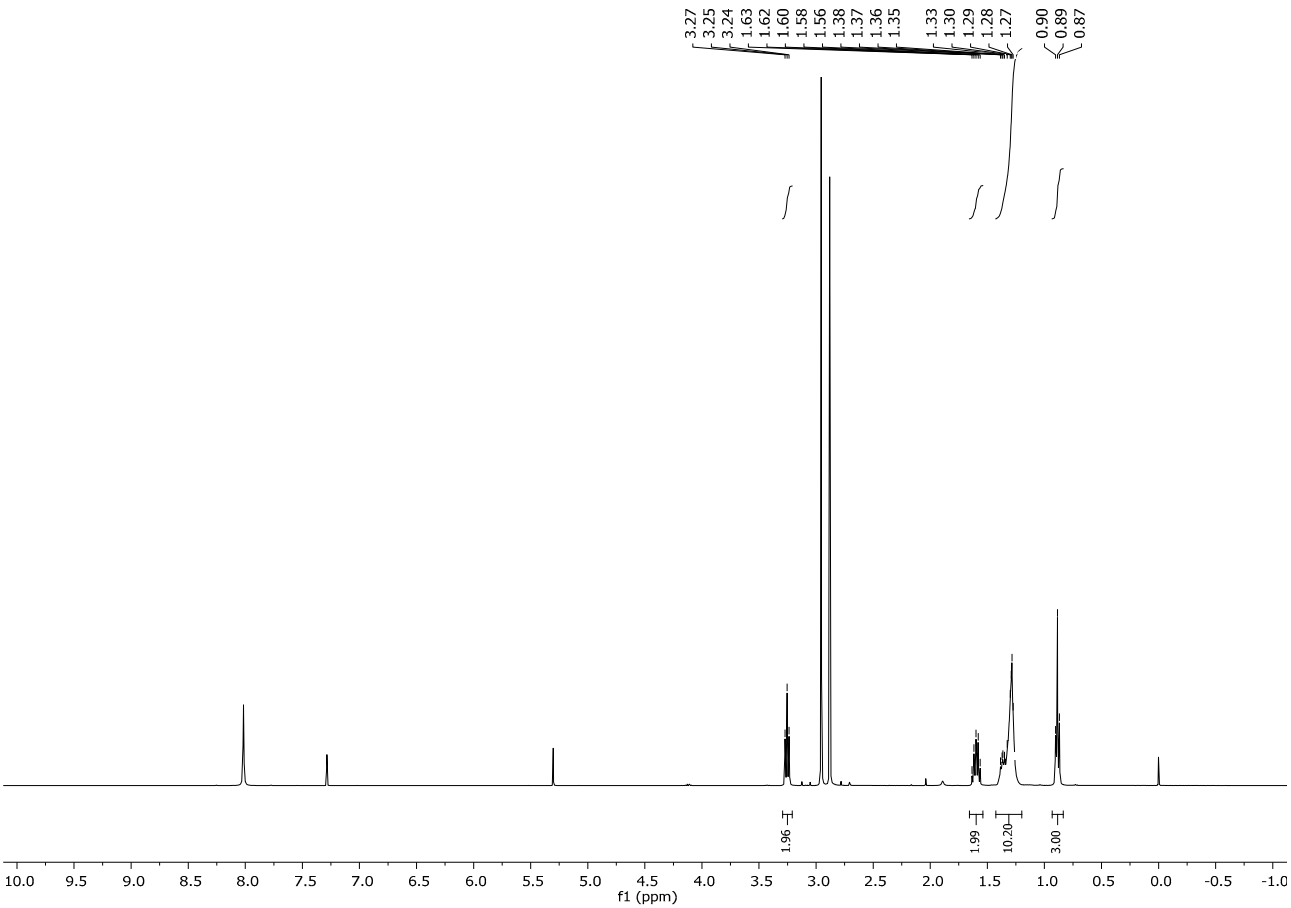
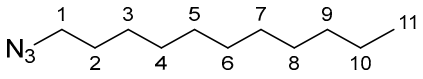


Figure S11. [1]H-NMR spectrum of compound **6f** in accordance with literature. [Proietti, G.; Prathap, K.J.; Ye, X.; Olsson, R.T.; Dinér, P. Nickel Boride Catalyzed Reductions of Nitro Compounds and Azides: Nanocellulose-Supported Catalysts in Tandem Reactions. *Synthesis* **2022***; 54,* 133-146; doi: 10.1055/a-1579-2190.]



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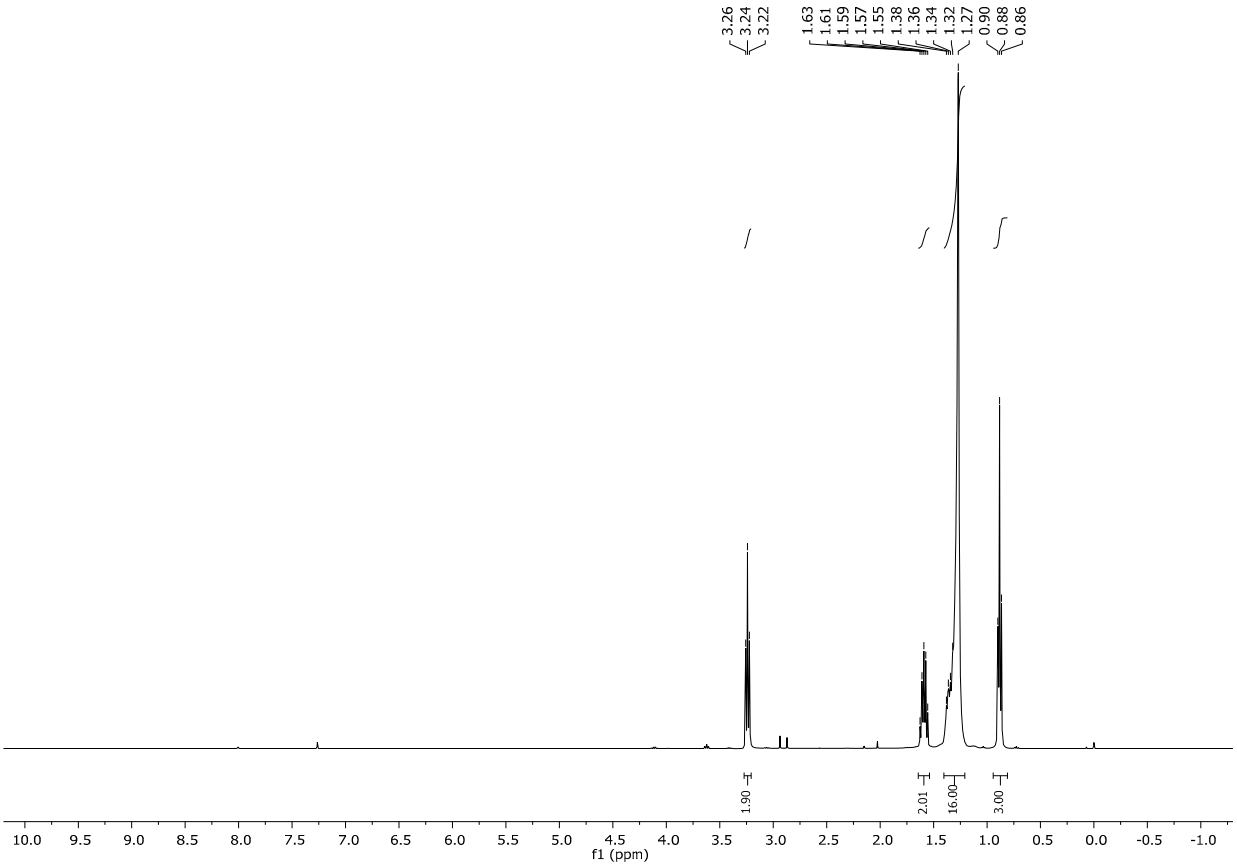


Figure S12. [1]H-NMR spectrum of compound **6g** in accordance with literature. [Natarajan, B.; Jayaraman, N. Synthesis and studies of Rh(I) catalysts within and across poly(alkyl aryl ether) dendrimers, *J. Organometallic Chem.*, 696, **2011**, 722-730; doi: 10.1016/j.jorganchem.2010.09.054.]

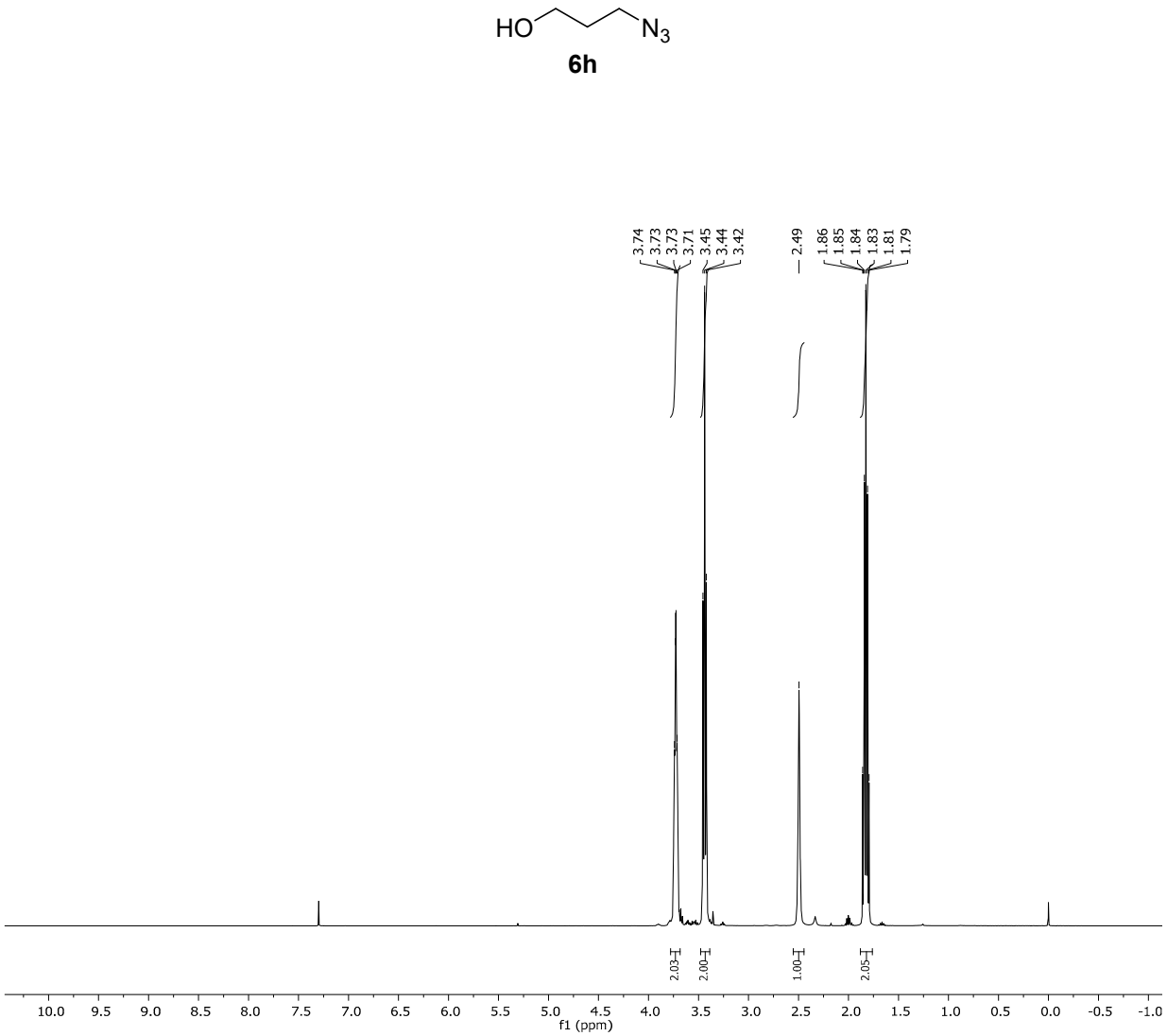


Figure S13. ^{1}H-NMR spectrum of compound **6h** in accordance with literature. [Macerata, E.; Mossini, E.; Scaravaggi, S.; Mariani, M.; Mele, A.; Panzeri, W.; Boubals, N.; Berthon, L.; Charbonnel, M-C.; Sansone, F.; Arduini, A.; Casnati, A. Hydrophilic Clicked 2,6-Bis-triazolyl-pyridines Endowed with High Actinide Selectivity and Radiochemical Stability: Toward a Closed Nuclear Fuel Cycle *J. Am. Chem. Soc.* **2016** *138* (23), 7232-7235; doi: 10.1021/jacs.6b03106.]

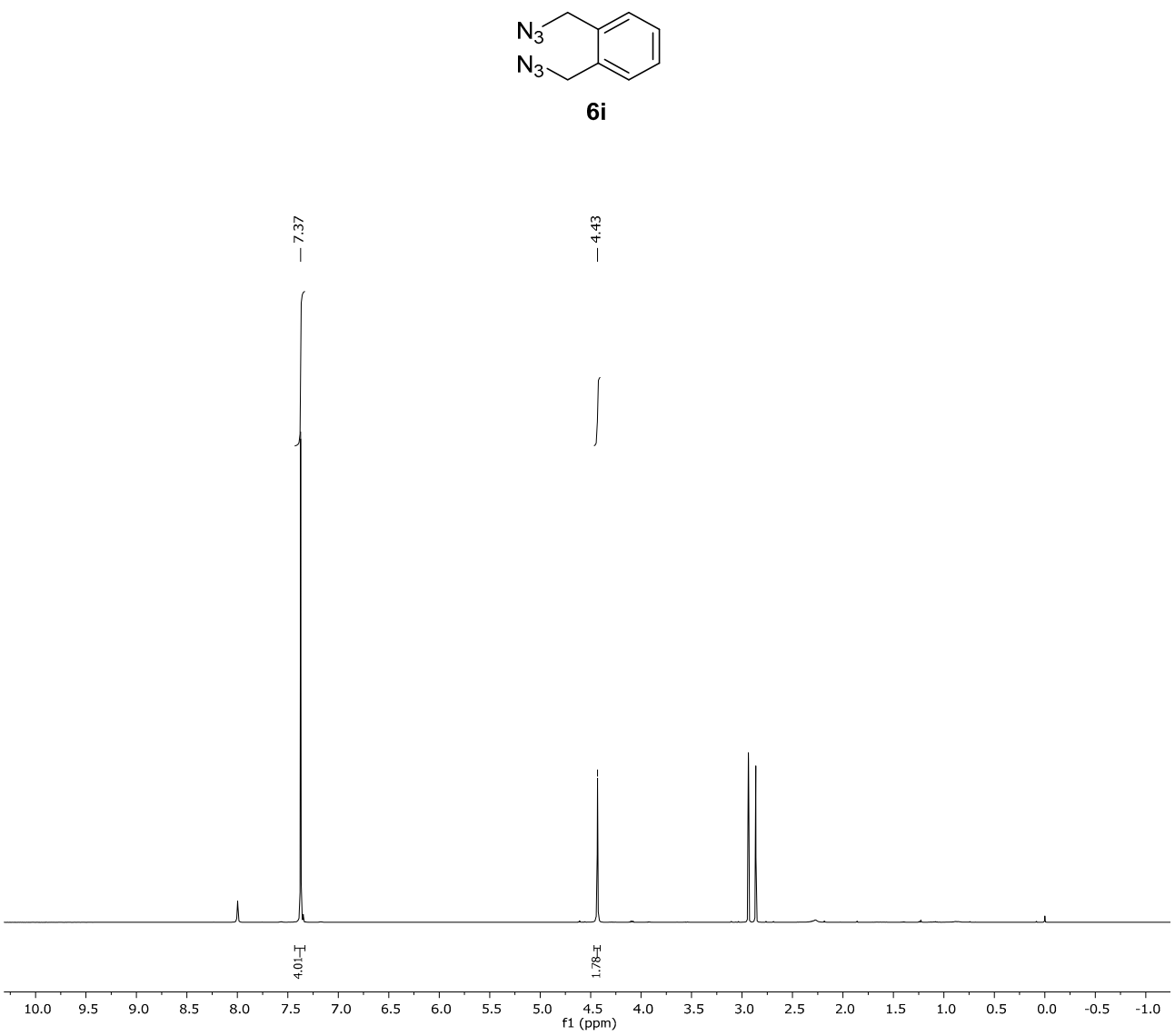
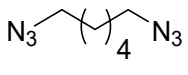


Figure S14. ^{1}H-NMR spectrum of compound **6i** in accordance with literature. [Guo, Z.-F.; Yan, H.; Li, Z.-F.; Lu, Z.-L. Synthesis of mono- and di-[12]aneN3 ligands and study on the catalytic cleavage of RNA model 2-hydroxypropyl-p-nitrophenyl phosphate with their metal complexes, *Org. Biomol. Chem*., **2011**, *9*, 6788-6796; doi: 10.1039/C1OB05942D.]



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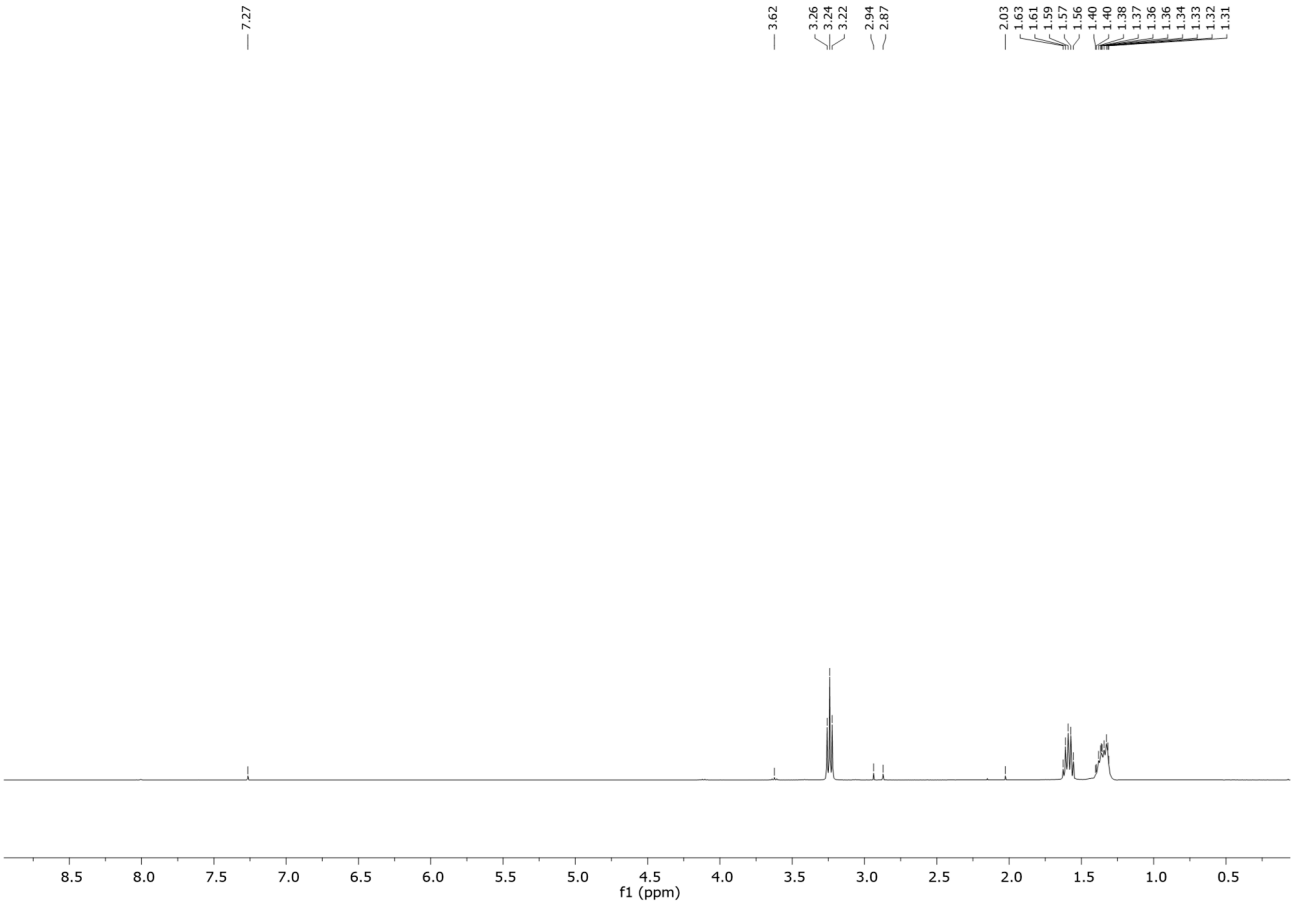
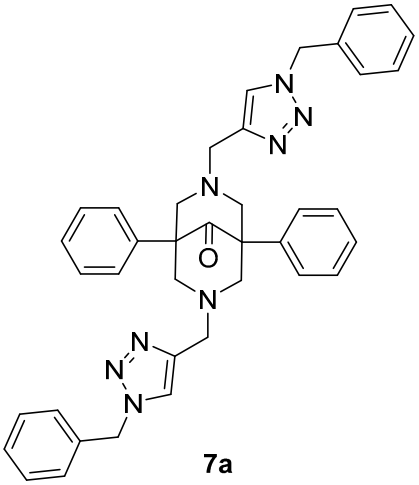
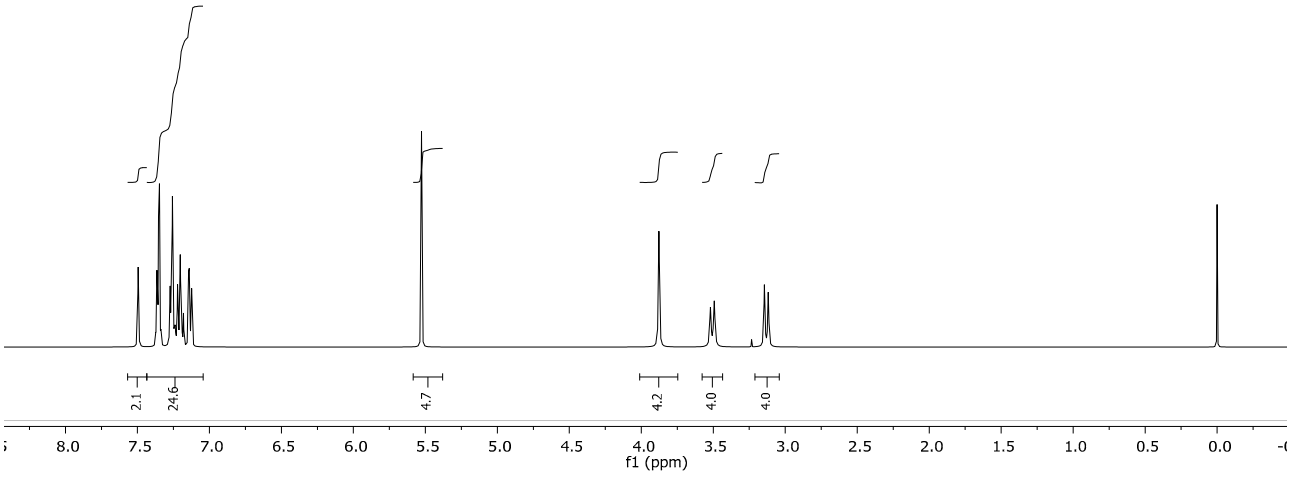


Figure S15. ^{1}H-NMR spectrum of compound **6j** in accordance with literature. [Peng, L.; Zhao, Y.; Okuda, Y.; Le, L.; Tang, Z.; Yin, S.-F.; Qiu, R.; Orita, A. Process-Divergent Syntheses of 4- and 5-Sulfur-Functionalized 1,2,3-Triazoles via Copper-Catalyzed Azide–Alkyne Cycloadditions of 1-Phosphinyl-2-sulfanylethynes *The Journal of Organic Chemistry* **2023** *88* (5), 3089-3108; doi: 10.1021/acs.joc.2c02876.]



7a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f1 (ppm)

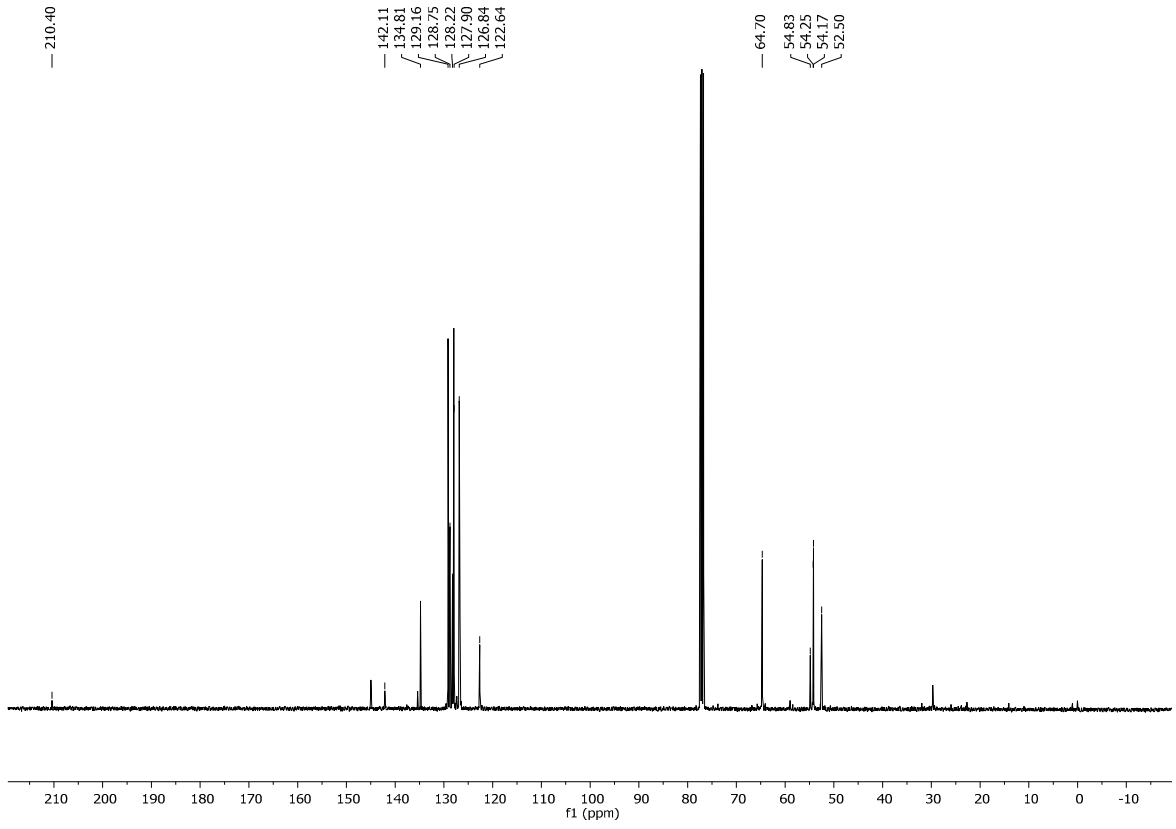
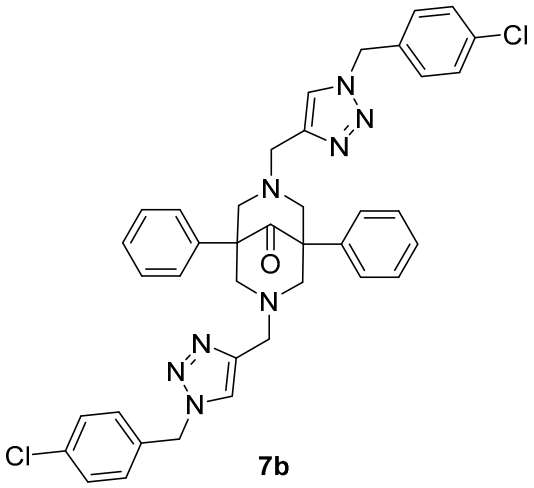


Figure S16. ^{1}H and ^{13}C-NMR spectra of compound **7a**.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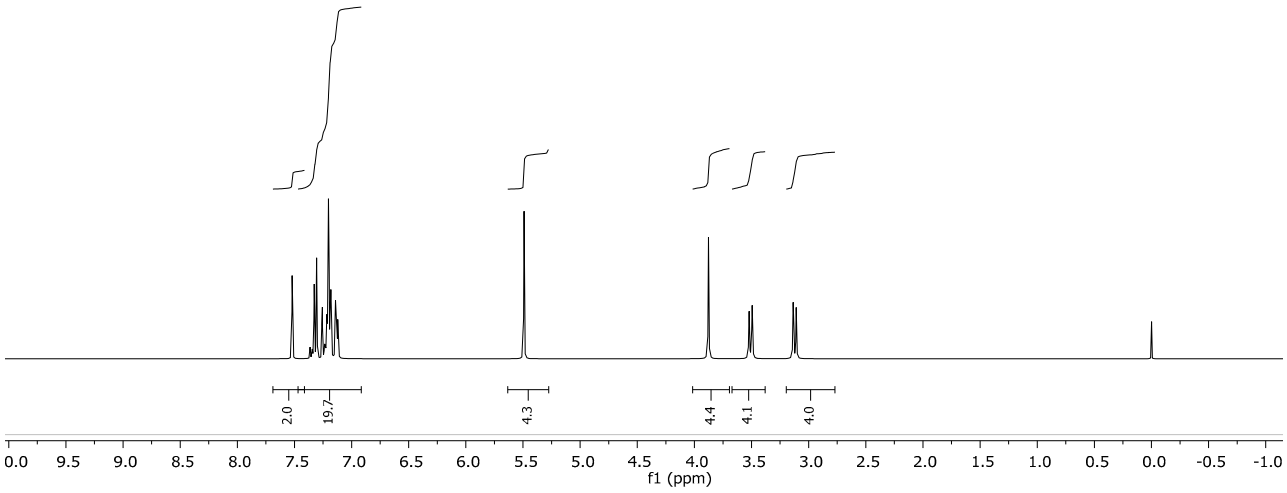
N
N
N
N
O
N
N
N
N
Cl

7b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19.7
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4.4
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4.0
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f1 (ppm)

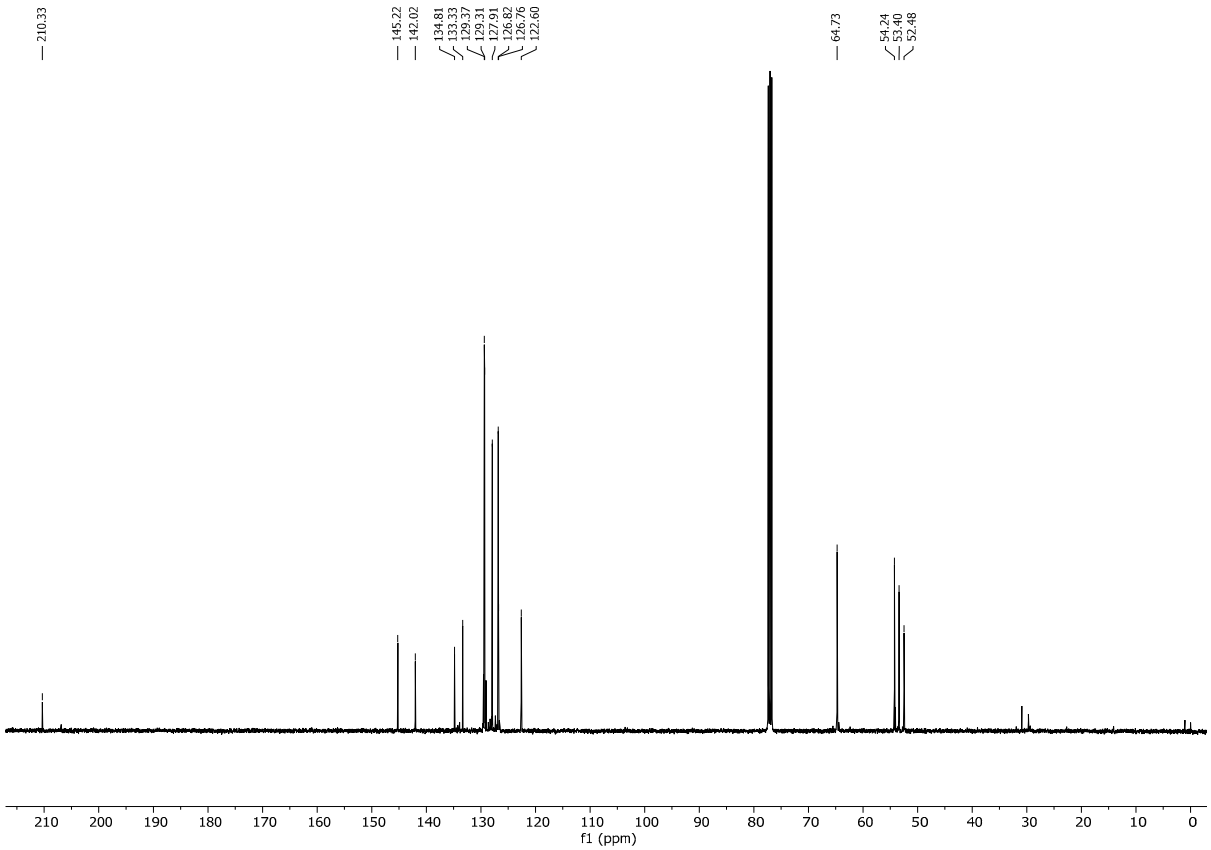
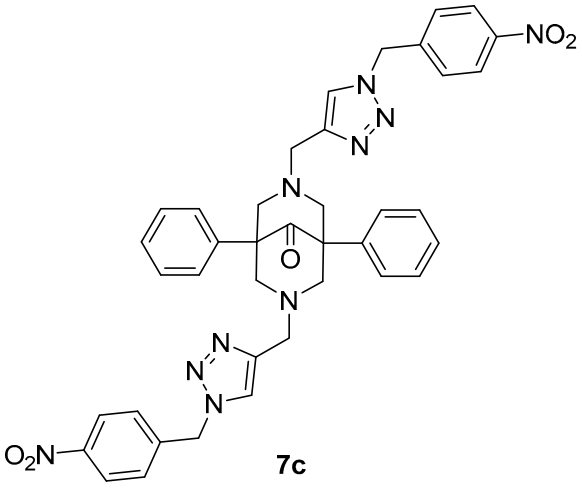
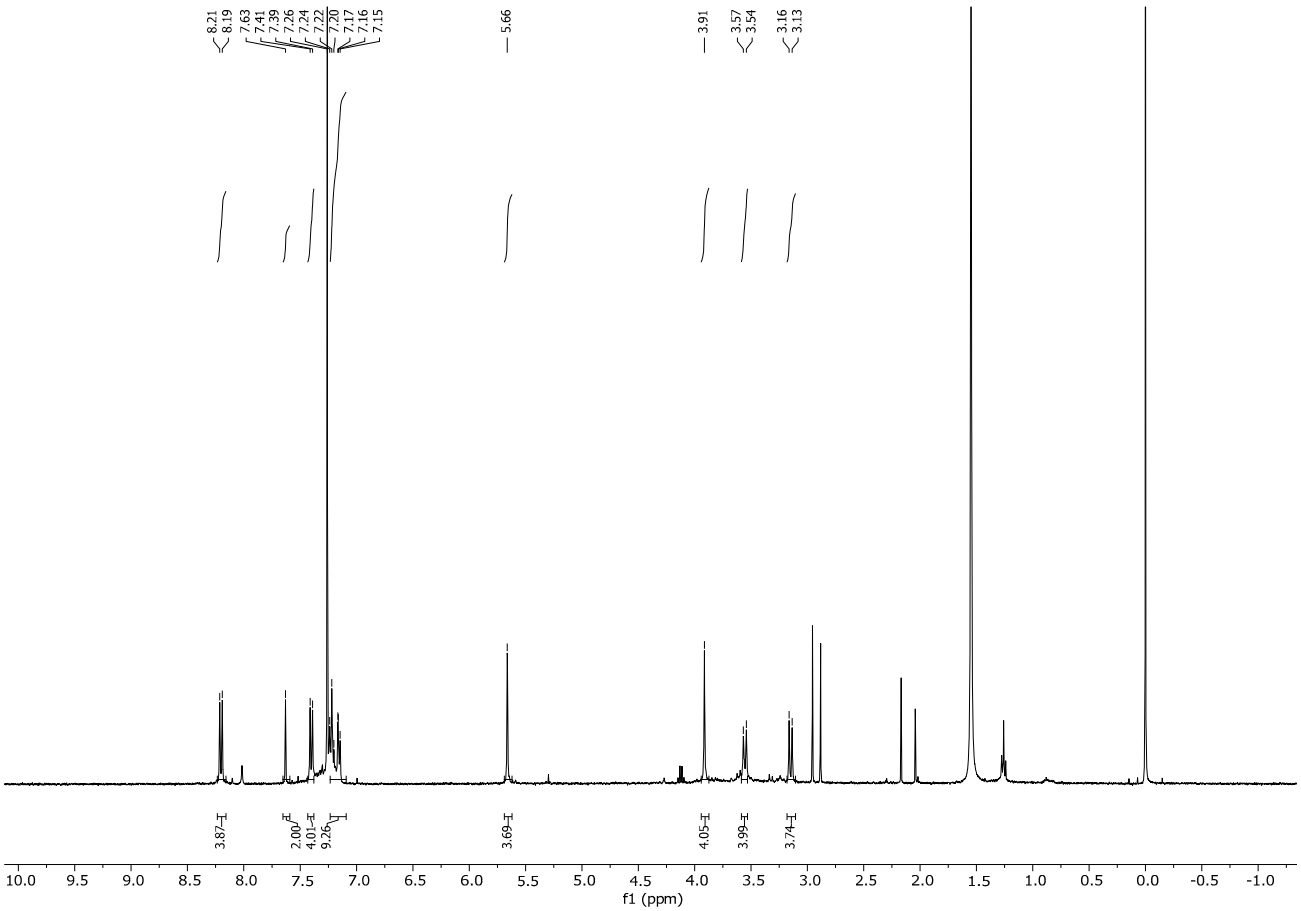


Figure S17. ^{1}H and ^{13}C-NMR spectra of compound **7b**.


NO2
N
N
N
N
O
N
N
N
N
O2N

7c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f1 (ppm)

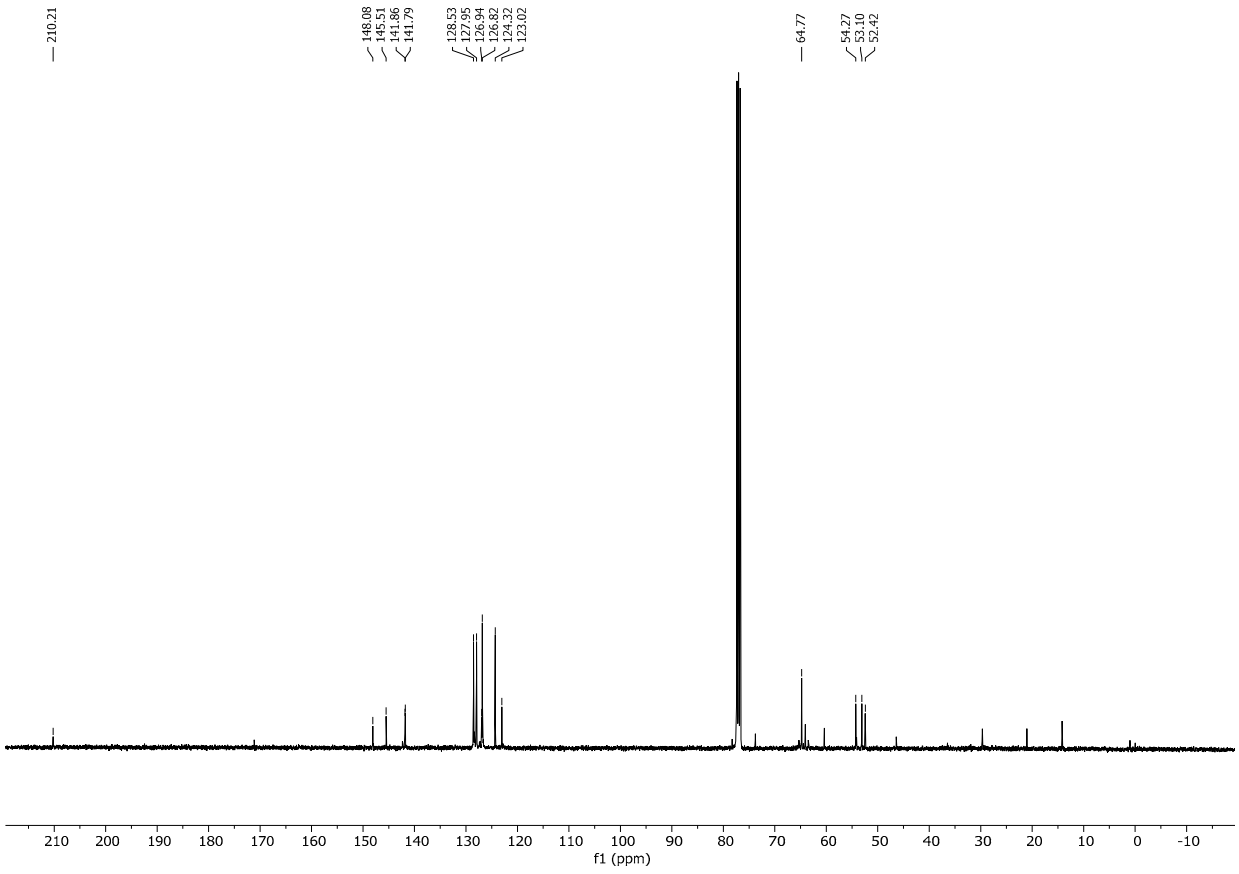
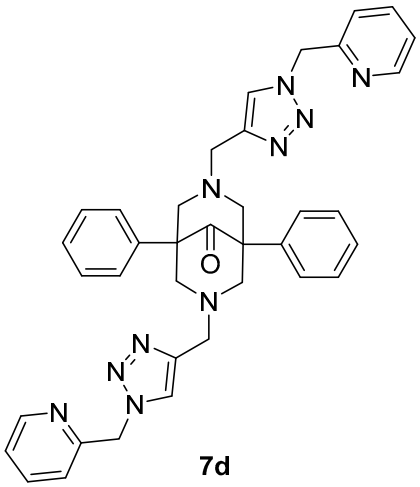
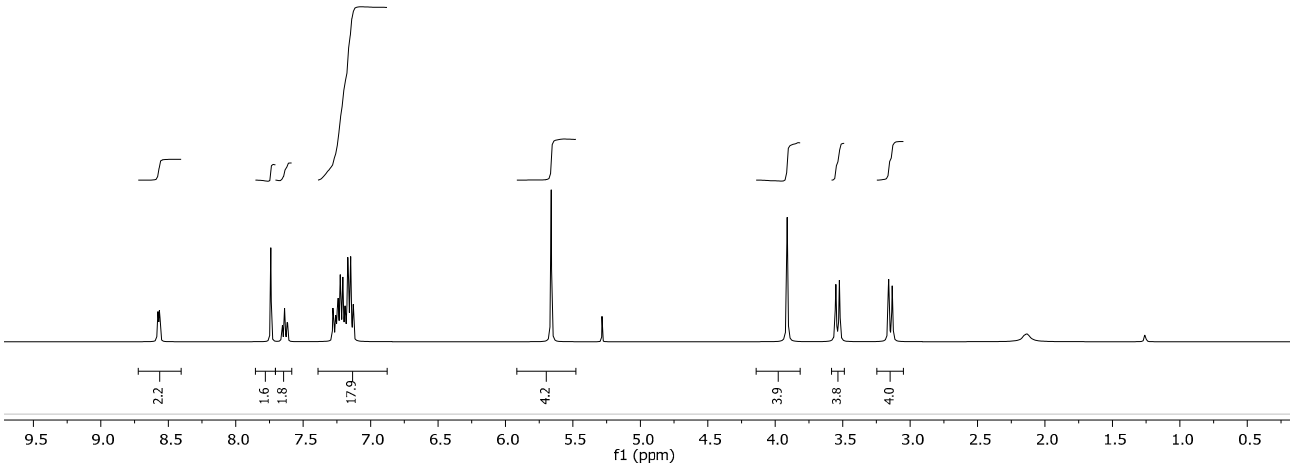


Figure S18. ^{1}H and ^{13}C-NMR spectra of compound **7c**.



7d


2.2
1.6
1.8
17.9
4.2
3.9
3.8
4.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

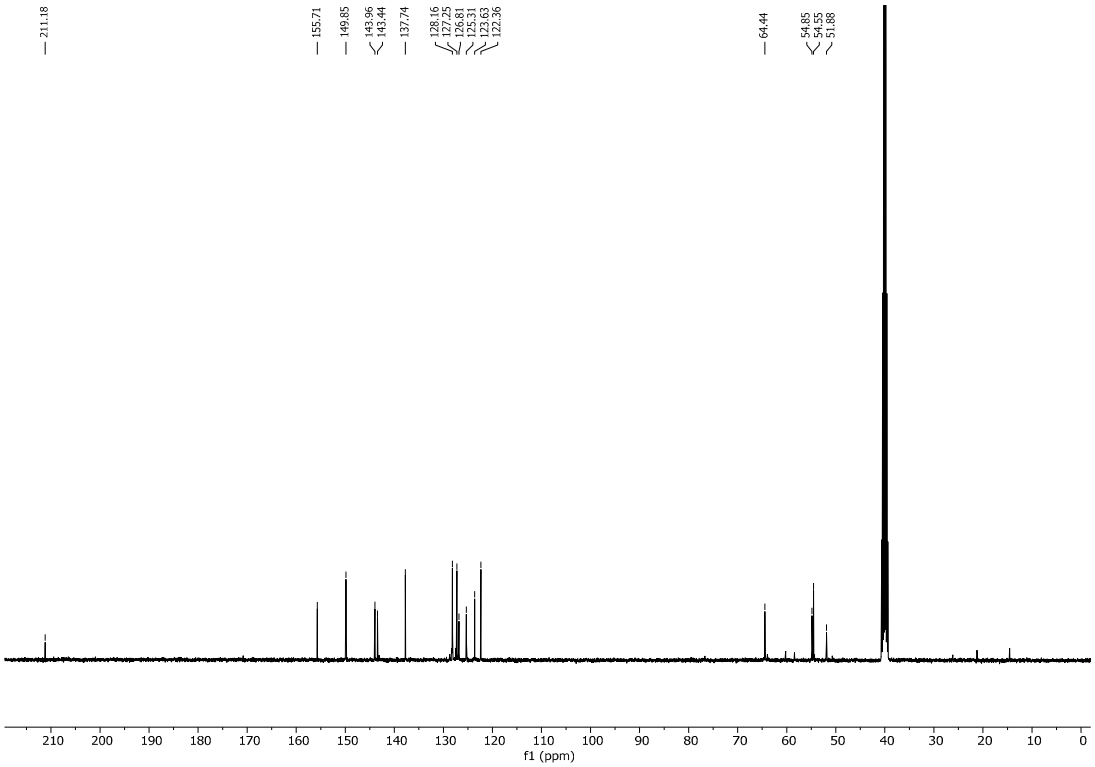
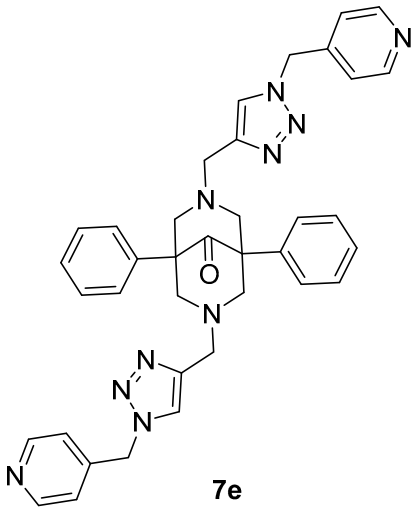
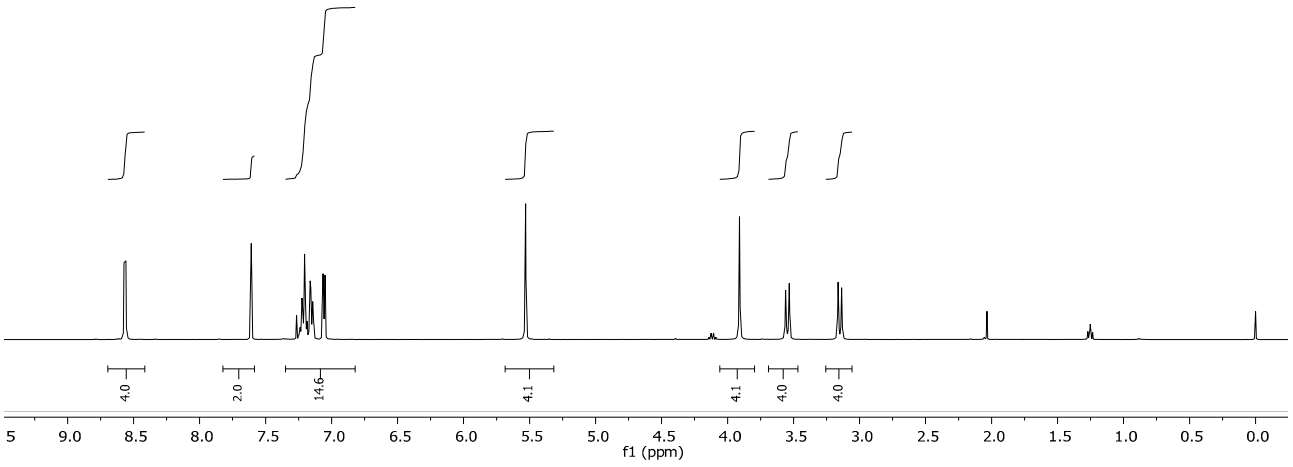


Figure S19. ^{1}H and ^{13}C-NMR spectra of compound **7d**.



7e


4.0
2.0
14.6
4.1
4.1
4.0
4.0
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

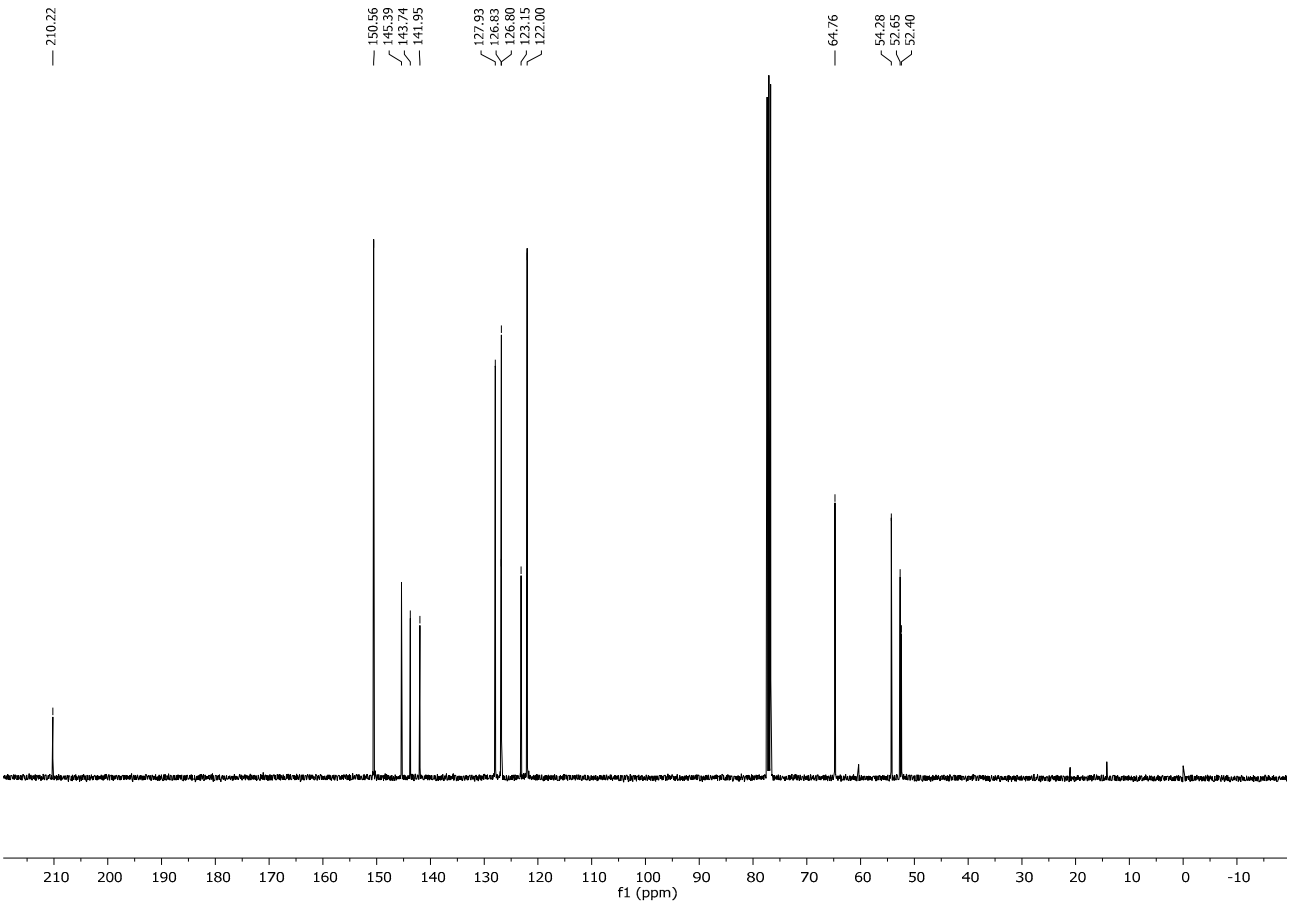
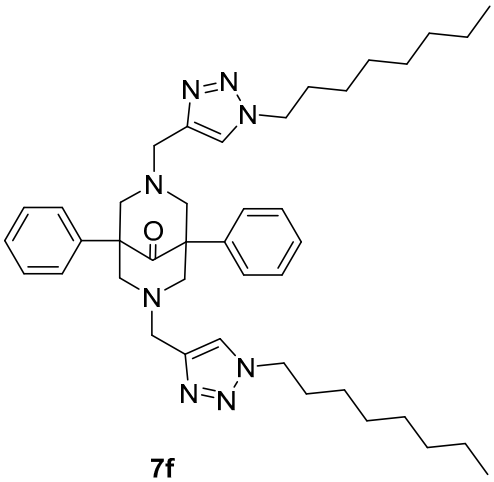
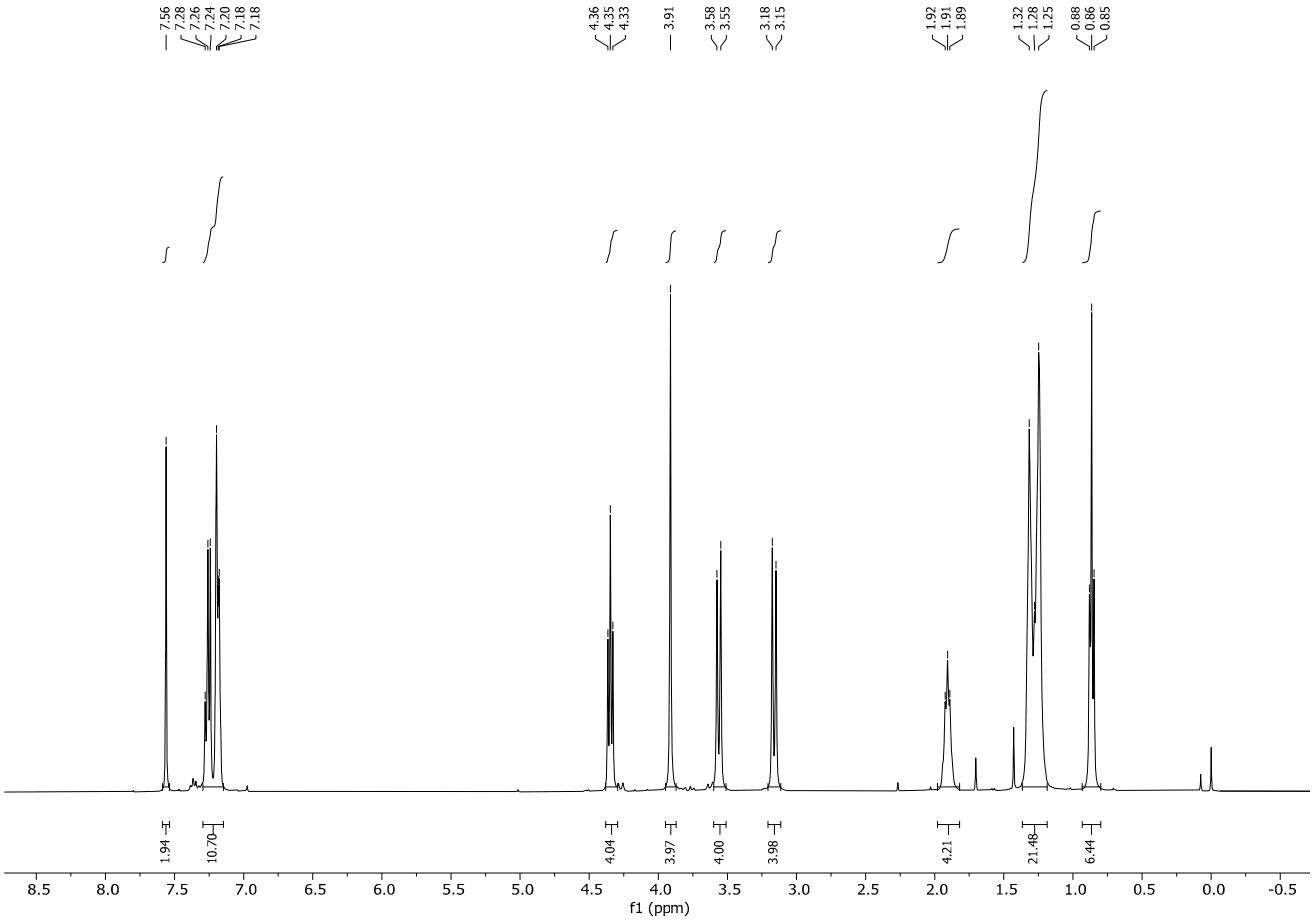


Figure S20. ^{1}H and ^{13}C-NMR spectra of compound **7e**.



7f


7.56
7.28
7.26
7.24
7.20
7.18
7.18
4.36
4.35
4.33
3.91
3.58
3.55
3.18
3.15
1.92
1.91
1.89
1.32
1.28
1.25
0.88
0.86
0.85
1.94
10.70
4.04
3.97
4.00
3.98
4.21
21.48
6.44
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

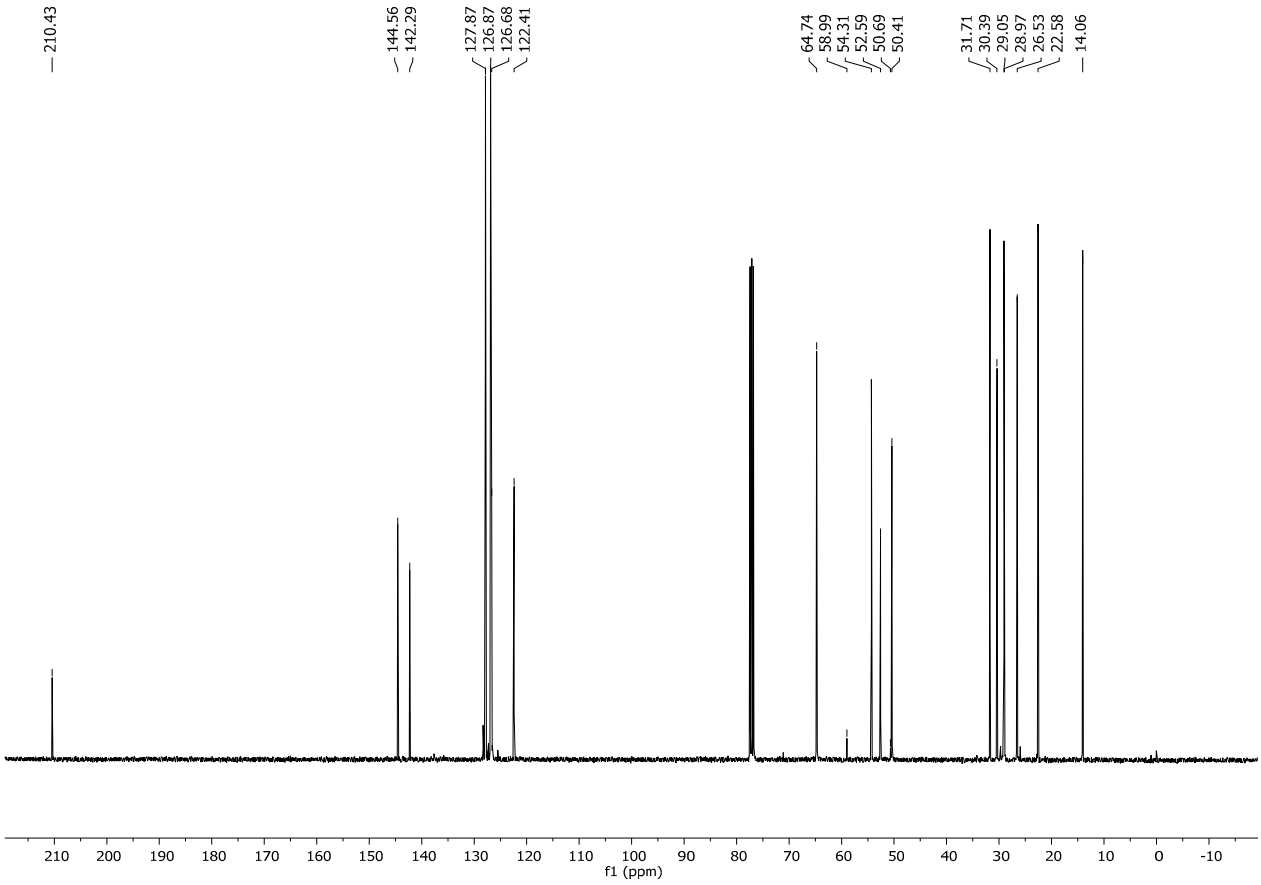
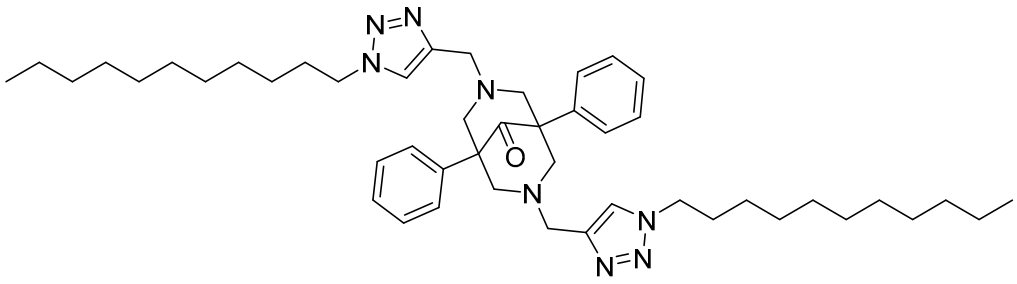
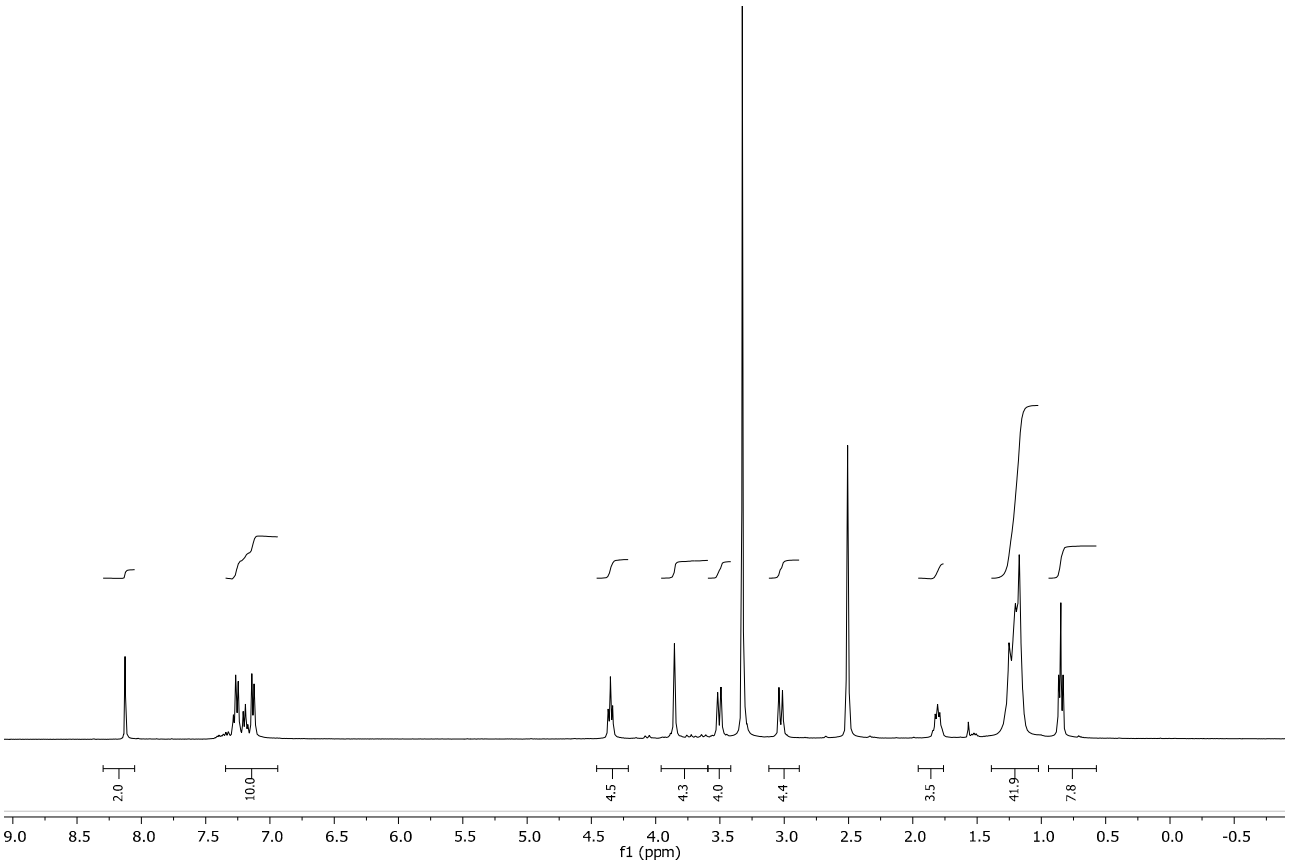


Figure S21. ^{1}H and ^{13}C-NMR spectra of compound **7f**.



7g


2.0
10.0
4.5
4.3
4.0
4.4
3.5
41.9
7.8
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

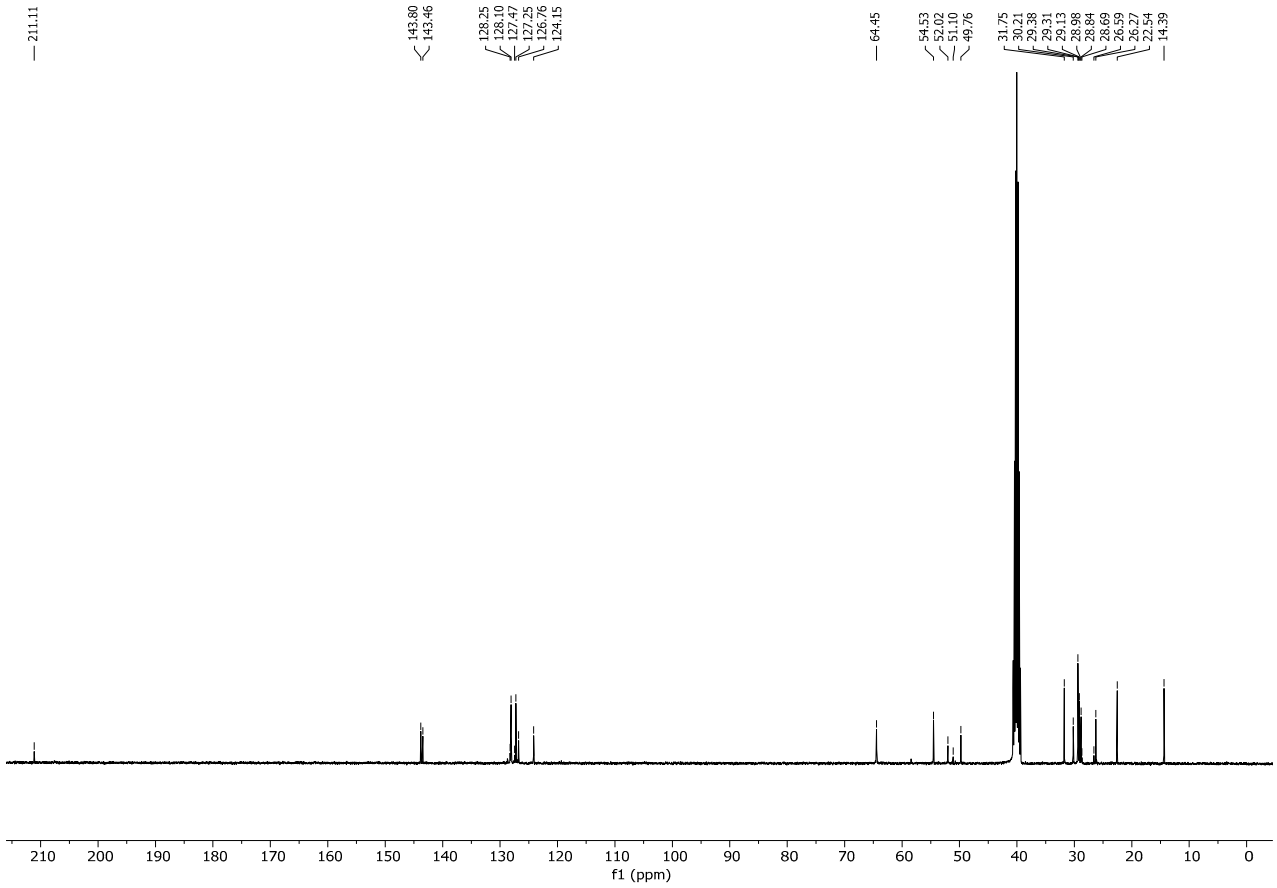
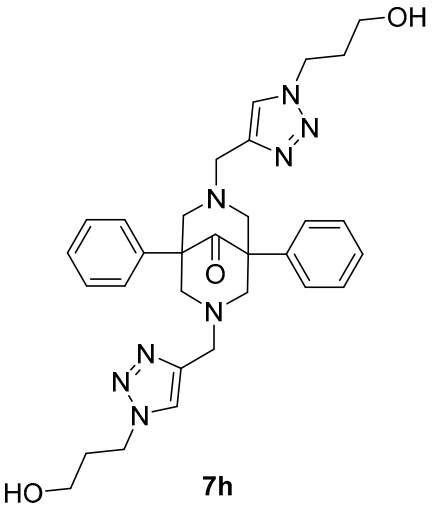
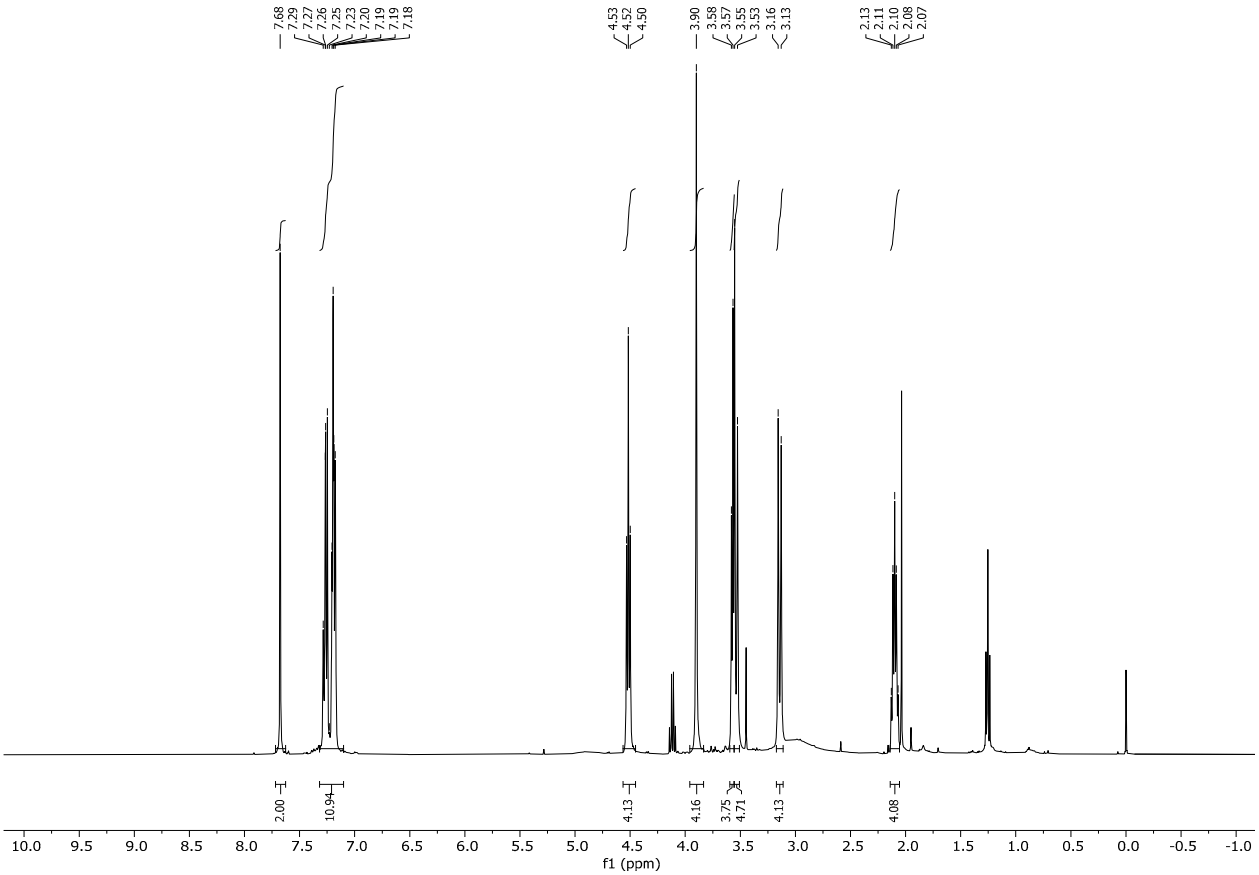


Figure S22. ^{1}H and ^{13}C-NMR spectra of compound **7g**.


OH
N
N
N
N
O
N
N
N
N
HO

7h


7.68
7.29
7.27
7.26
7.25
7.23
7.20
7.19
7.19
7.18
4.53
4.52
4.50
3.90
3.58
3.57
3.55
3.53
3.16
3.13
2.13
2.11
2.10
2.08
2.07
2.00
10.94
4.13
4.16
3.75
4.71
4.13
4.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

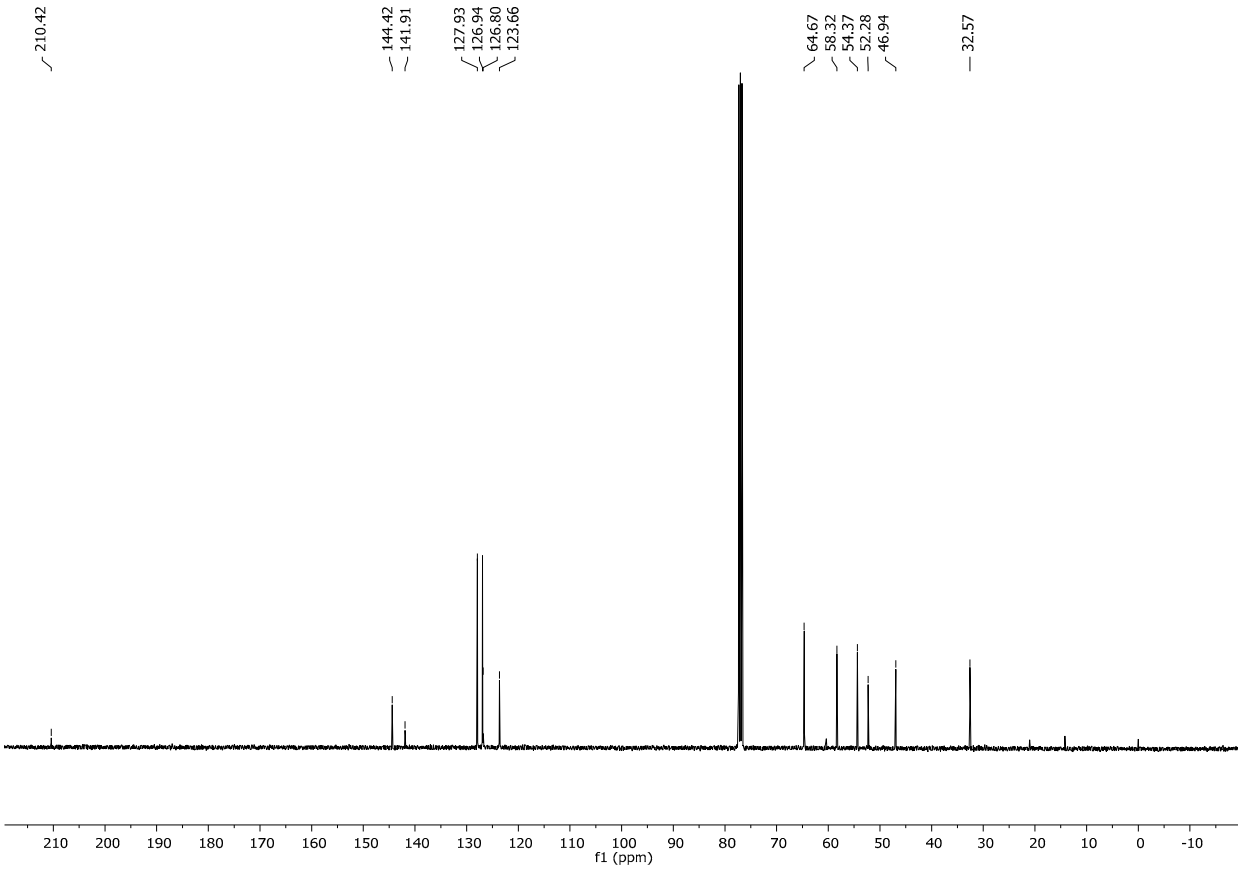
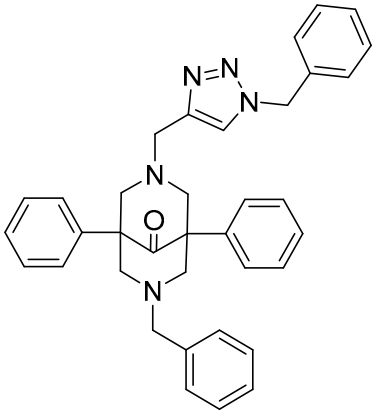
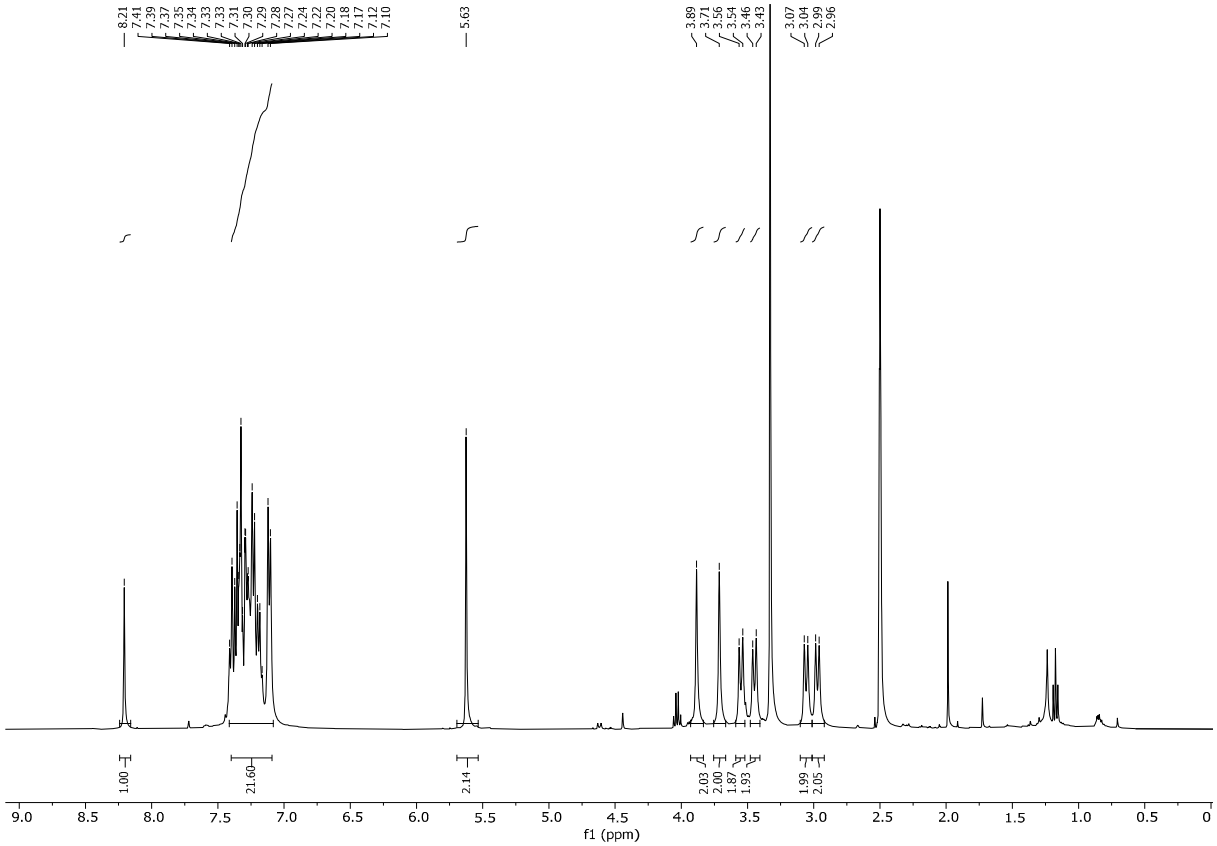


Figure S23. ^{1}H and ^{13}C-NMR spectra of compound **7h**.



8a


8.21
7.44
7.39
7.37
7.35
7.34
7.33
7.31
7.30
7.29
7.28
7.27
7.24
7.22
7.20
7.18
7.17
7.12
7.10
5.63
3.89
3.71
3.56
3.54
3.46
3.43
3.07
3.04
2.99
2.96
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21.60
2.14
2.03
2.00
1.87
1.93
1.99
2.05
f1 (ppm)

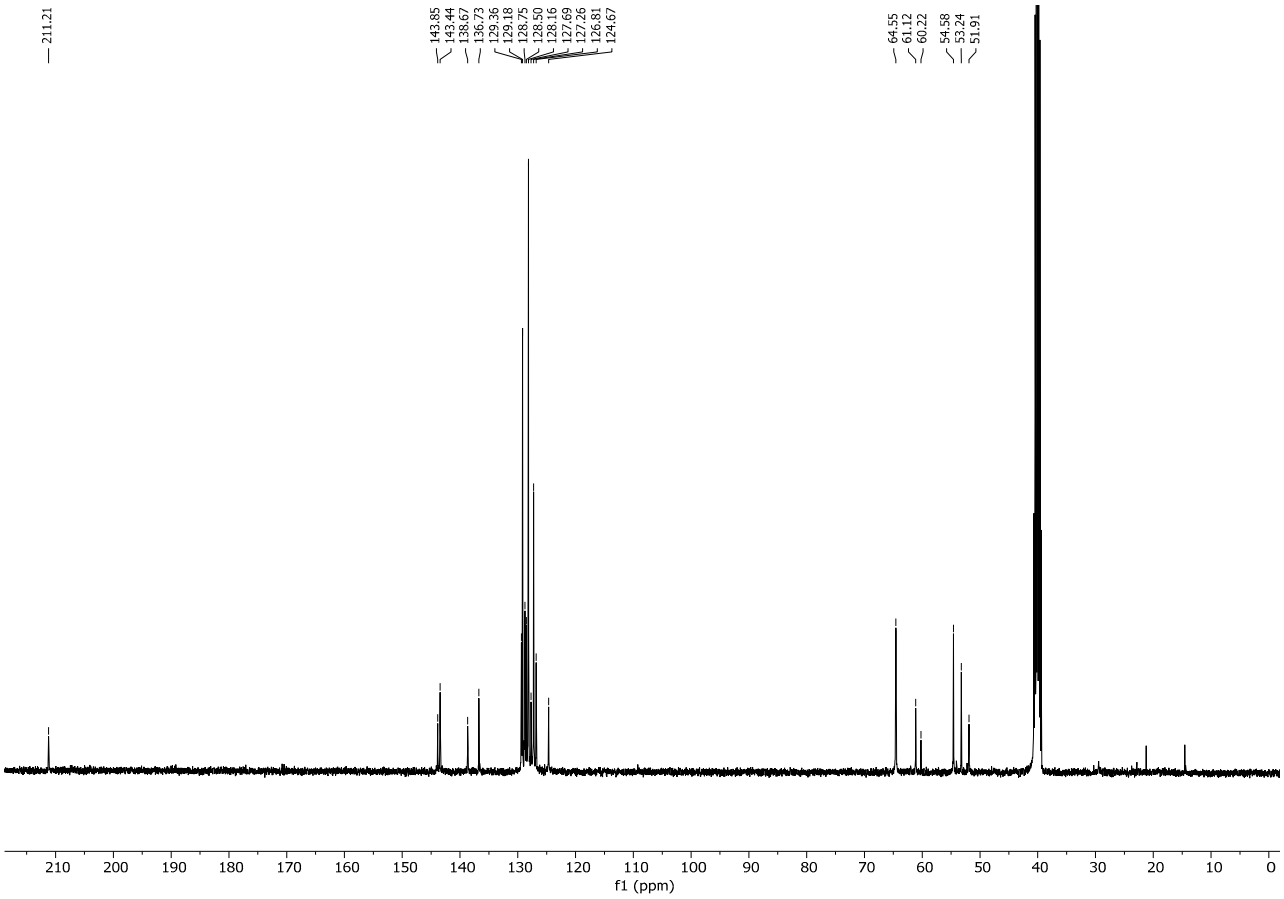
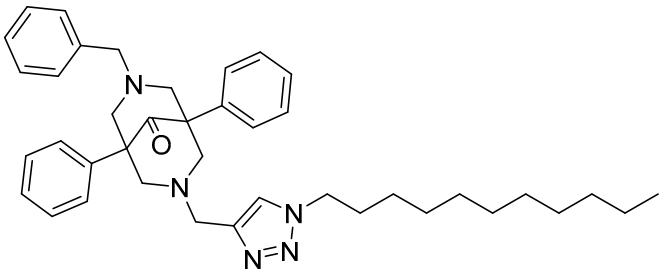
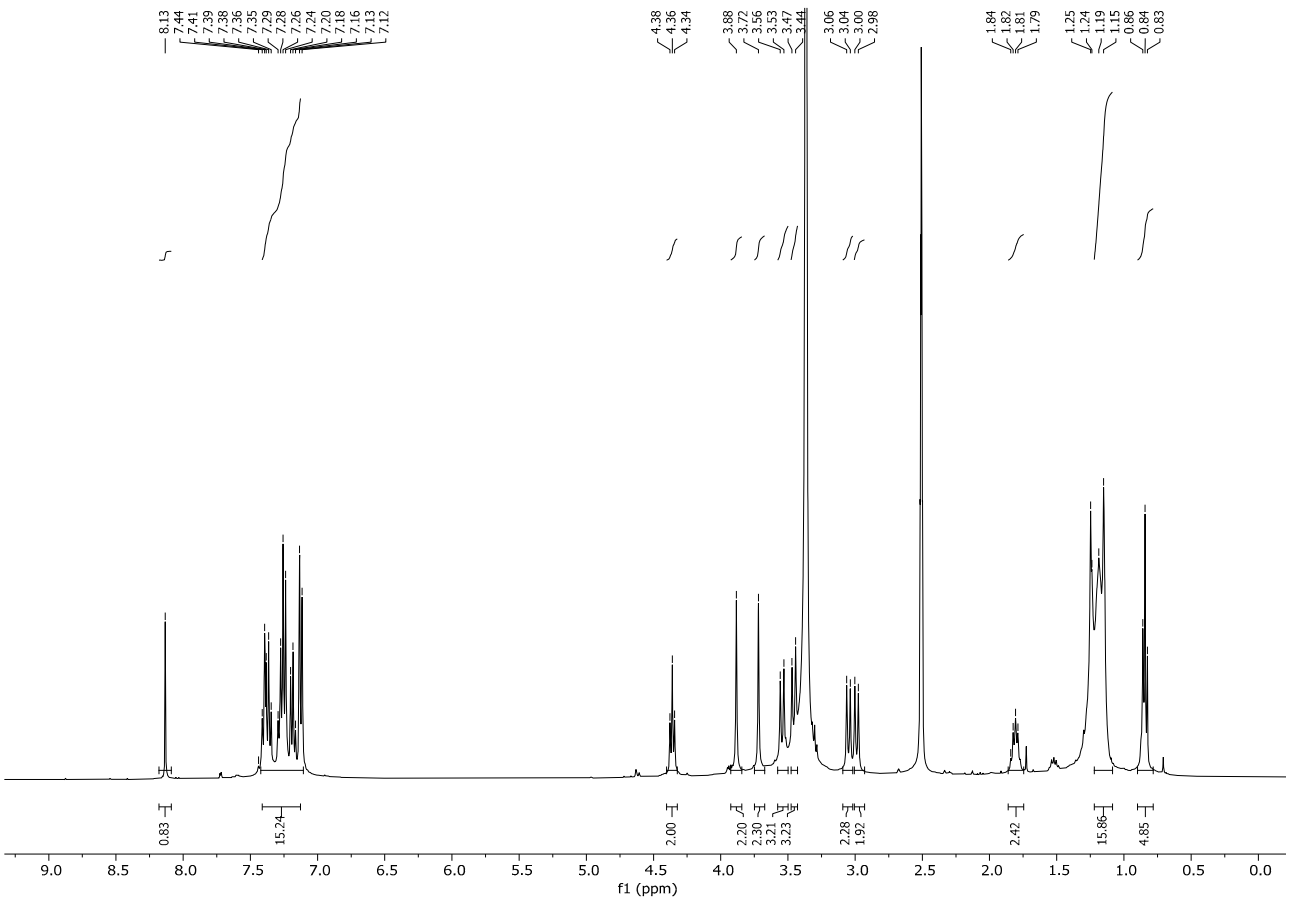


Figure S24. ^{1}H and ^{13}C-NMR spectra of compound **8a**.


N
O
N
N
N=N

8b


8.13
7.44
7.41
7.39
7.38
7.36
7.35
7.29
7.28
7.26
7.24
7.20
7.18
7.16
7.13
7.12
4.38
4.36
4.34
3.88
3.72
3.56
3.53
3.47
3.44
3.06
3.04
3.00
2.98
1.84
1.82
1.81
1.79
1.25
1.24
1.19
1.15
0.86
0.84
0.83
0.83
15.24
2.00
2.20
2.30
3.21
3.23
2.28
1.92
2.42
15.86
4.85
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

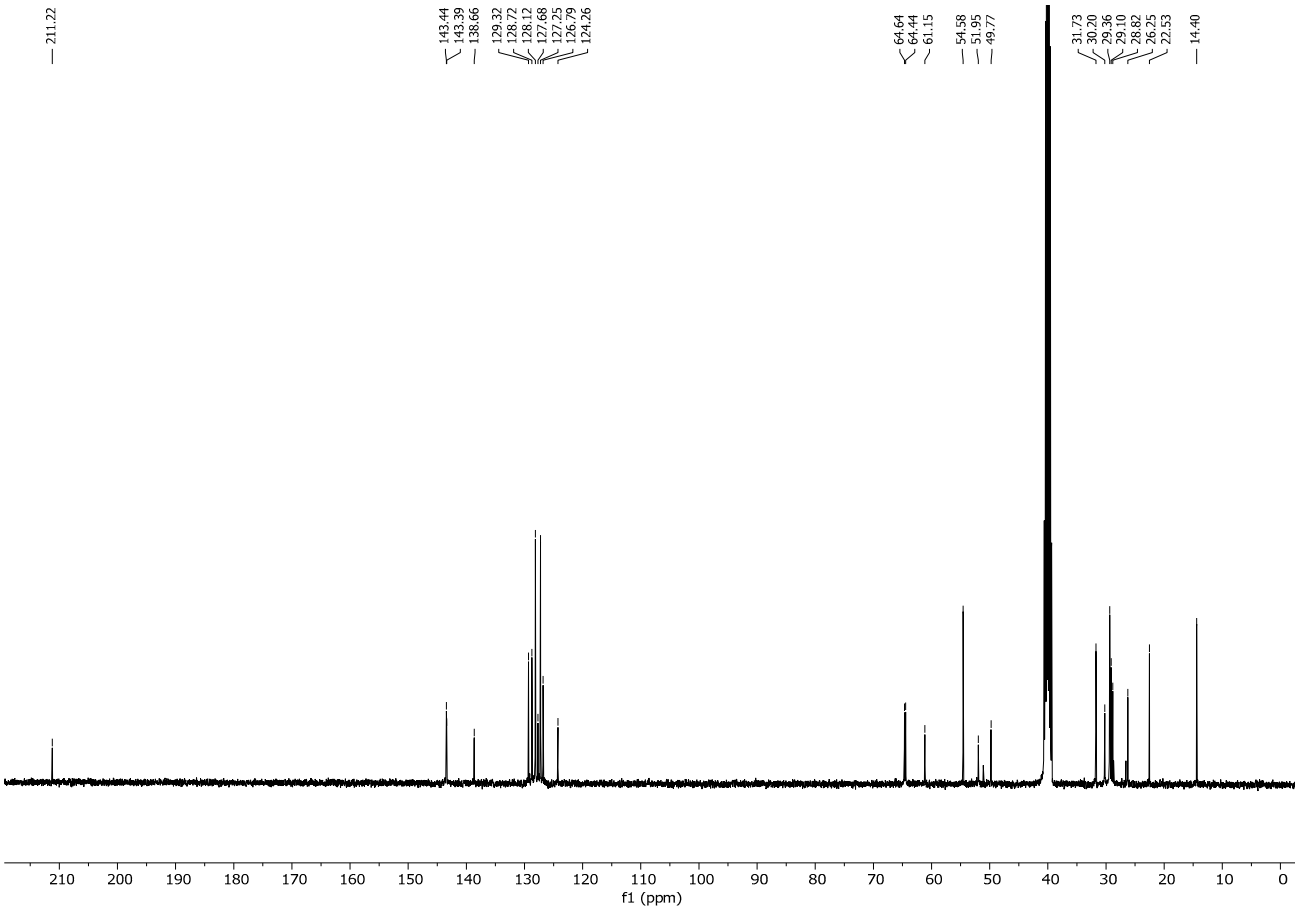
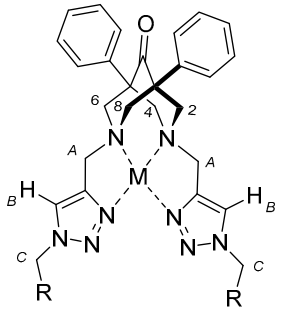


Figure S25. ^{1}H and ^{13}C-NMR spectra of compound **8b**.

2. NMR TITRATION OF BISPIDINE-METAL COMPLEXES

Table S1. Comparison of the free ligands **7a,b,d,h** and their metal complexes: list of the Δδ in the ^{1}H-NMR spectra.



M = Zn(II), Ln(III)
R = Ph, 2'Py, *p*-Cl-Ph, -CH_2CH_2OH

Entry	Compound	Δδ for $H_{2,4,6,8}$ eq (ppm)	Δδ for $H_{2,4,6,8}$ ax (ppm)	Δδ for H_A (ppm)	Δδ for H_B (ppm)	Δδ for H_C (ppm)
1	**7b·Zn(II)**	0.46	0.44	0.18	0.50	0.15
2	**7d·Zn(II)**	0.50	0.61	0.27	0.24	0.15
3	**7d·La(III)**	0.45	0.70	0.43	0.23	0.03
4	**7a·La(III)**	0.46	0.71	0.42	0.24	0.04
5	**7h·La(III)**	0.45	0.70	0.40	0.40	0.05

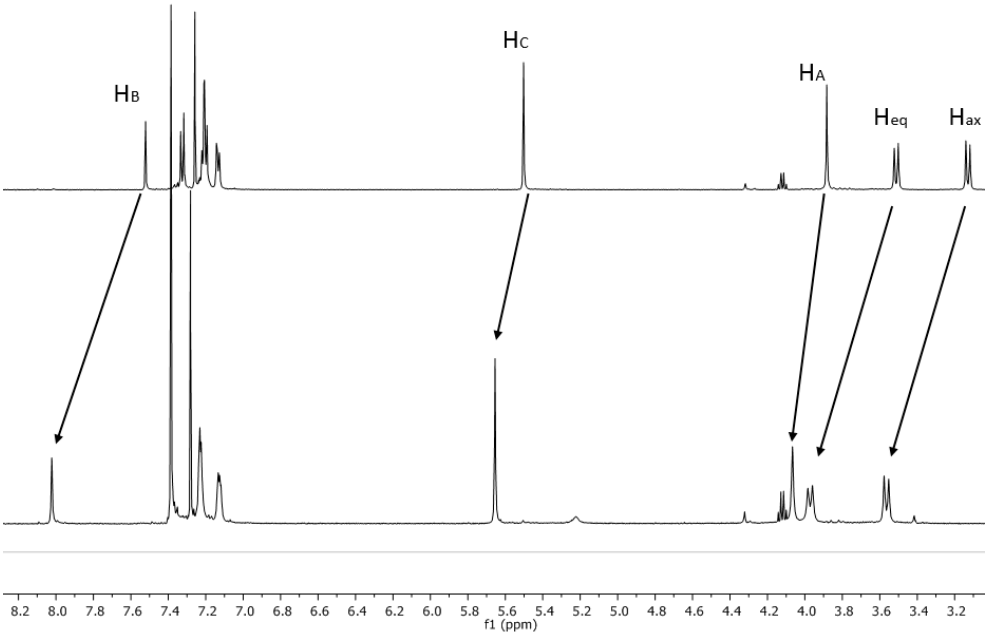


Figure S26. ^{1}H-NMR spectrum of compound **7b** and its Zn(II)-complex, **7b-Zn(II)**.

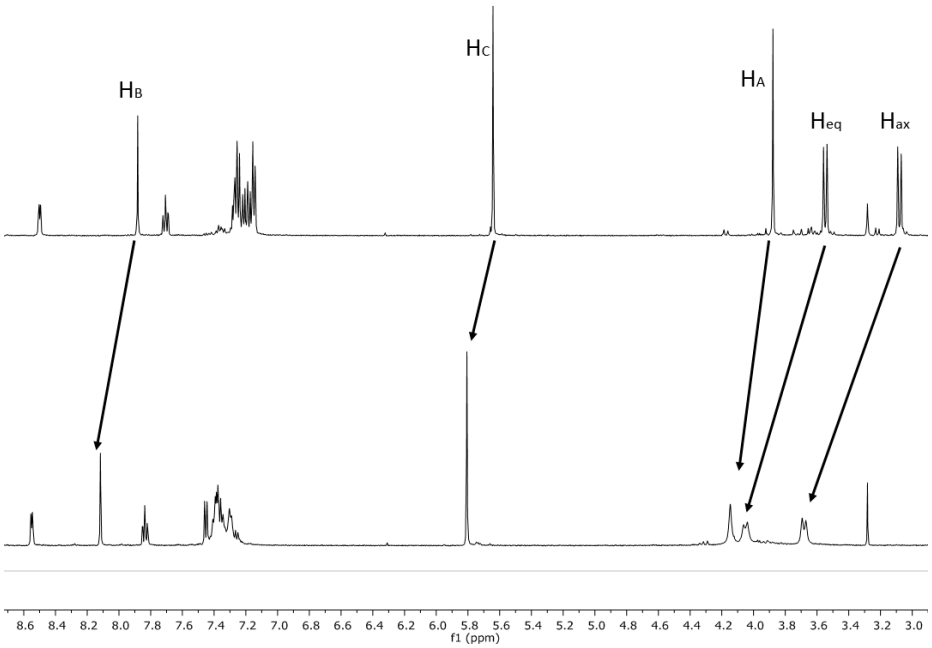


Figure S27. [1]H-NMR spectrum of compound **7d** and its Zn(II)-complex **7d-Zn(II)**.

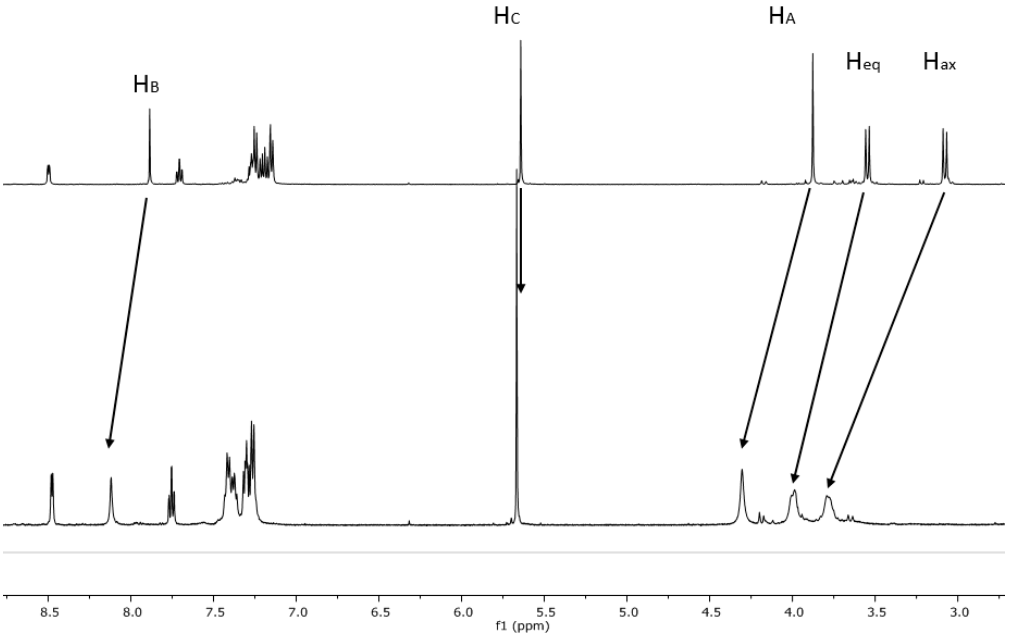


Figure S28. [1]H-NMR spectrum of compound **7d** and its La(III)-complex **7d-La(III)**.

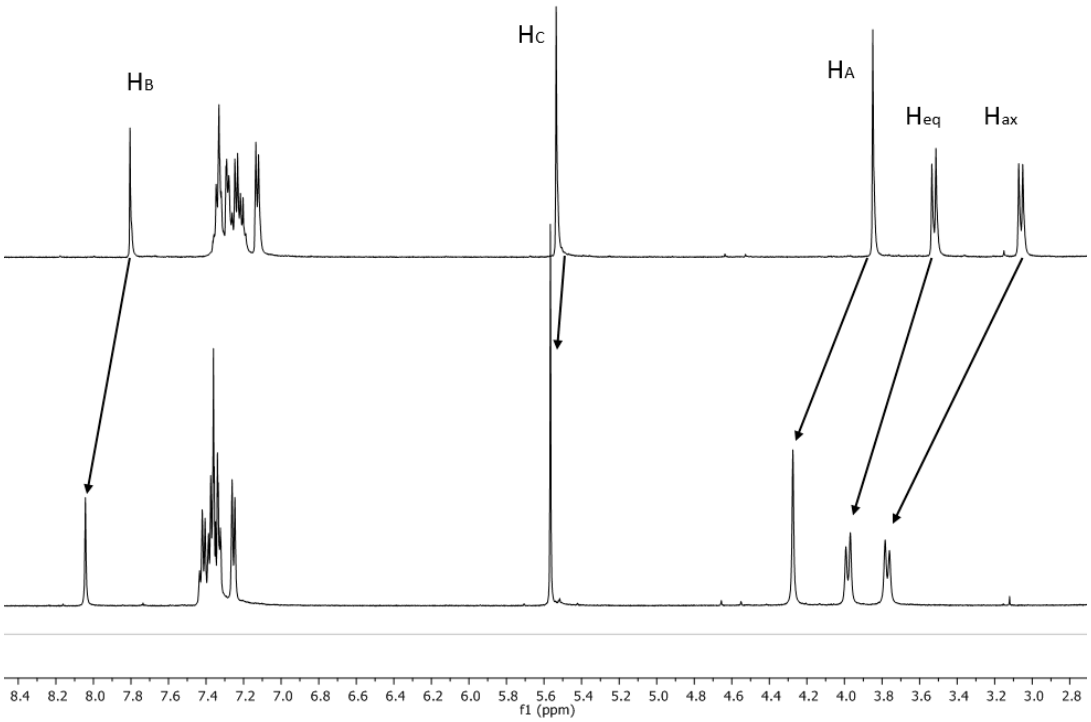
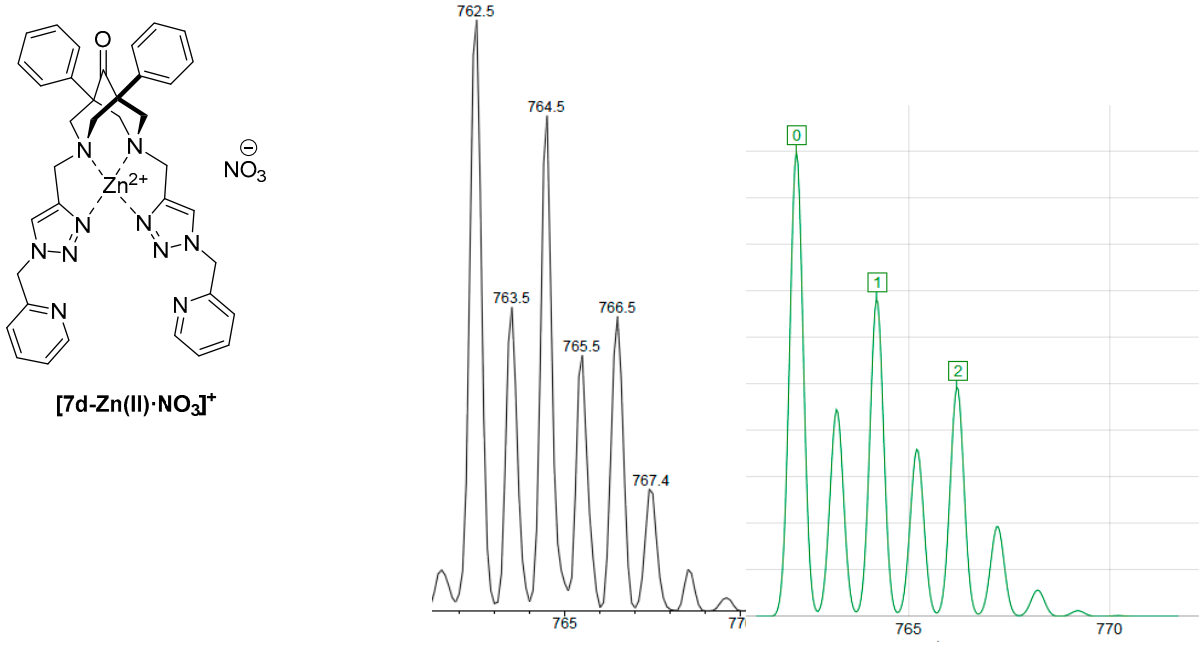


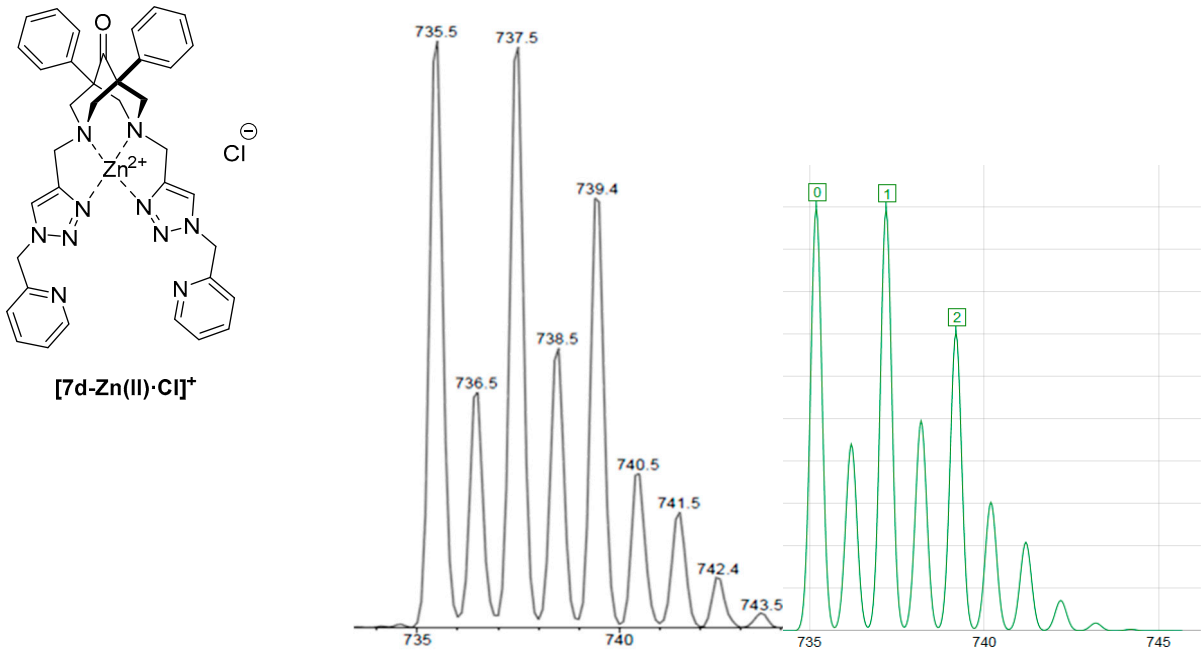
Figure S29. [1]H-NMR spectrum of compound **7a** and its La(III) complex **7a·La(III)**.

3. ESI-MS ANALYSIS



[7d-Zn(II)·NO3]+

Figure S30. Comparison of the experimental ESI-MS spectrum of compound **[7d-Zn(II)·NO3]+** (left) and the simulation of the isotopic pattern for the elemental composition $[C_{37}H_{36}N_{11}O_4Zn]^+$ (right).



[7d-Zn(II)·Cl]+

Figure S31. Comparison of the experimental ESI-MS spectrum of compound **[7d-Zn(II)·Cl]+** (left) and the simulation of the isotopic pattern for the elemental composition $[C_{37}H_{36}ClN_{10}OZn]^+$ (right).

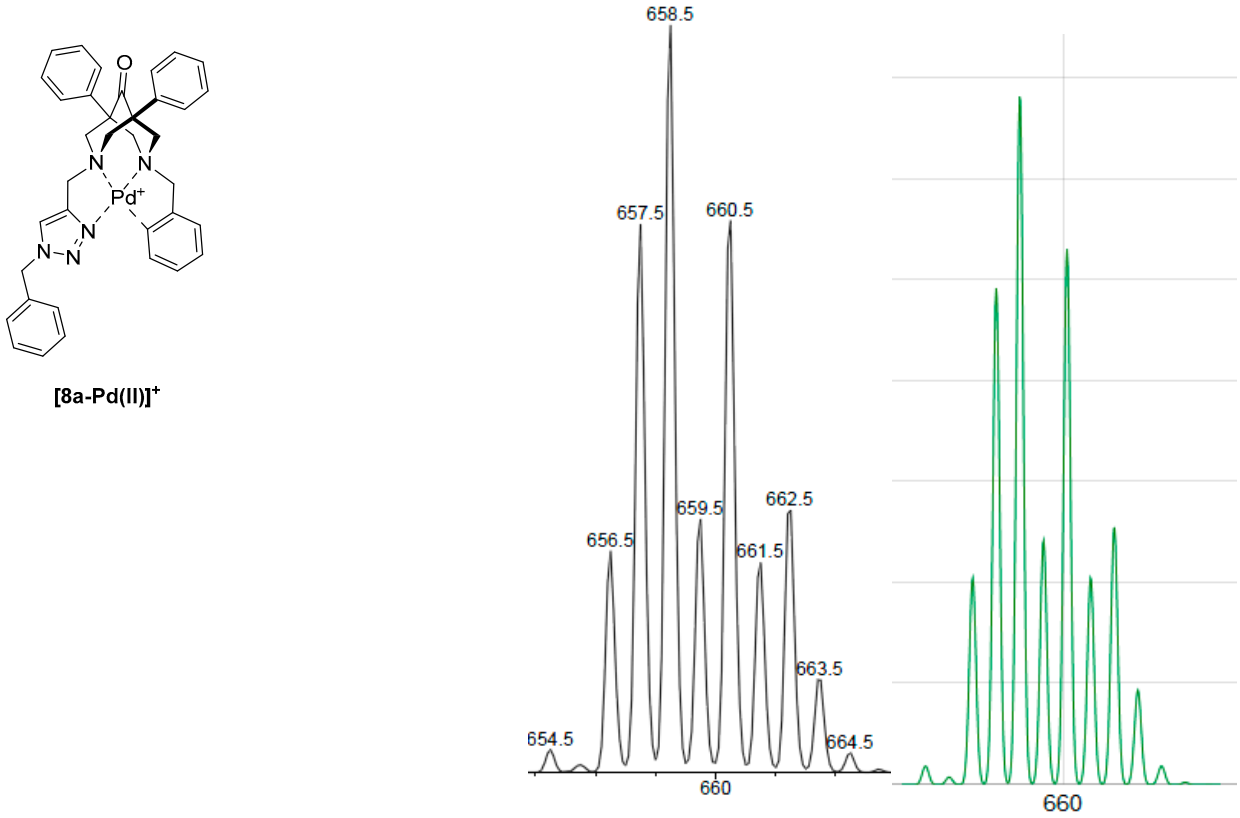


Figure S32. Comparison of the experimental ESI-MS spectrum of compound **[8a·Pd(II)]**$^{+}$ (left) and the simulation of the isotopic pattern for the elemental composition $[C_{36}H_{34}N_5OPd]^{+}$ (right).

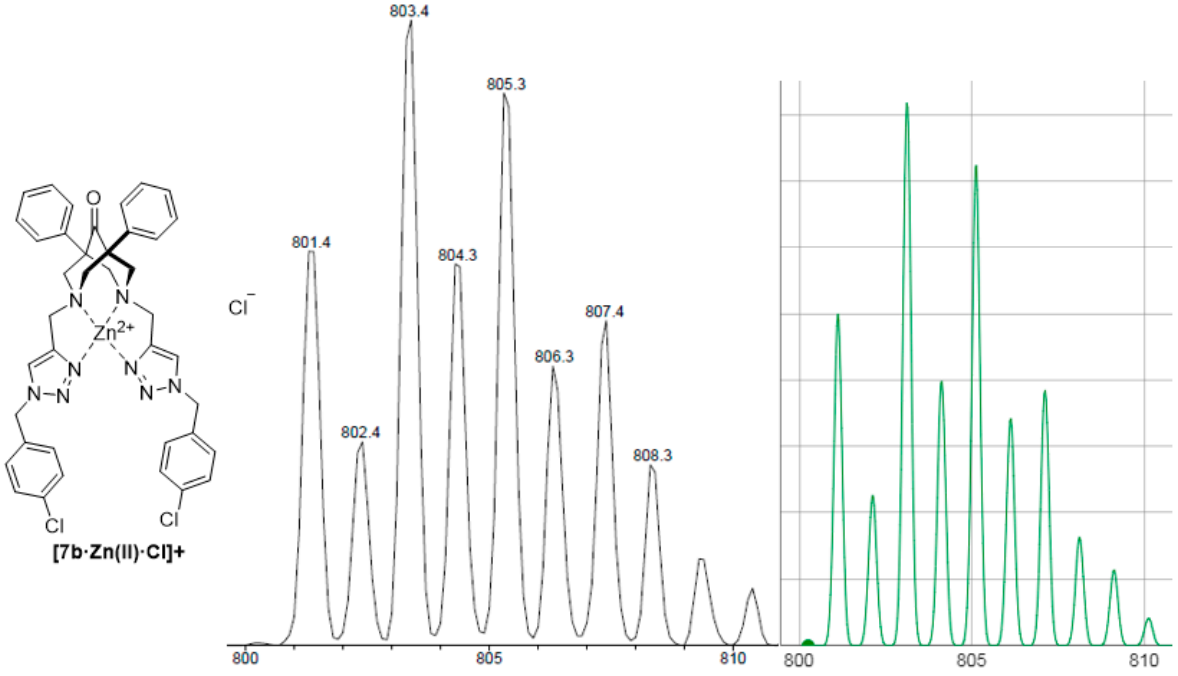


Figure S33. Comparison of the experimental ESI-MS spectrum of compound **[7b·Zn(II)·Cl]**$^{+}$ (left) and the simulation of the isotopic pattern for the elemental composition $[C_{39}H_{36}Cl_3N_8OZn]^{+}$ (right).