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Synthesis and functionalization of triply-fused porphyrin dimers

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Keywords: porphyrinoids / organolithium / C-C coupling / cycloaddition / fused ring-systems

Current applications of porphyrins in medicine and optics, such as photodynamic therapy or nonlinear absorption, increasingly require the use of far-red absorbing dyes. Modifications to the porphyrin structure to accommodate these conditions can be achieved by extending the conjugation of the porphyrin π-system, which will cause a bathochromic shift in the absorption spectrum. Thus, conjugated porphyrin oligomers have found widespread use. However, past synthetic strategies have mainly targeted symmetric porphyrin dimers, trimers, and oligomers which limit the practical use of such chromophores. To further extend the absorption profile, a series of symmetric and unsymmetric dimeric and oligomeric porphyrin β-β, meso-meso, β'-β' triply-fused systems were synthesised *via* oxidative coupling methods. This required an analysis and optimization of the various synthetic strategies. These arrays exhibit a dramatic bathochromic shift into the near-infrared region, many displaying absorption of greater than 1050 nm. Additionally, post-fusing chemical transformations, namely organolithium, cycloaddition and transition-metal catalysed reactions, at the meso- and β- positions enables the fine-tuning of such arrays with the aim of enhancing the bathochromic shift and their potential optical applications.

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Introduction

Long wavelength absorption of porphyrins is desired for a wide range of applications[1] and there are many means to achieve such a characteristic. These include: the synthesis of porphyrin arrays connected *via* conjugated linkers,[2] the construction of perturbed porphyrinoid macrocycles *via* various cycloaddition reactions[3] and the construction of fused or directly linked porphyrin arrays.[4] The latter is favorable as triply linked porphyrin arrays result in the extension of the absorption profile into the near-IR region. Pioneering methods developed by Sugiura *et al.*[5] and Osuka and co-workers[6] can be adopted for the generation of so-called triply fused porphyrin dimers and higher arrays.[4a,7] By doing so, a λ_{max} of 1050 nm and beyond may be achieved and these covalently linked multiporphyrin arrays can act as multichromophoric model systems for the study of electron transfer in light-harvesting systems. Although the Osuka group, amongst others,[4b,8] have extensively researched this area, their work primarily deals with symmetric arrays and photophysical studies of such porphyrins.[9] Only limited research has been carried out on so-called unsymmetrical fused dimers[10] and post-modifications of fused arrays.[11] We envisaged developing both novel symmetric fused dimers and unsymmetric arrays, for the purpose of applying them to fields of research such as NLO,[12] OLEDs[13] and two-photon absorption PDT (2PA-PDT).[14] By the introduction of various substituents to the porphyrin periphery[15] and subsequent post-fusing modifications, the arrays can be fine-tuned for PDT, *via* the introduction of water solubilizing groups,[14a, 16] and NLO *via* the introduction of donor/acceptor groups to generate push-pull systems.[17] Thus, synthetic strategies for the development of such arrays will be described. Following the synthesis of meso-meso directly linked porphyrins by Susumu *et al.* in 1996 *via* a condensation reaction,[18] there have been substantial developments in the synthesis of such arrays. These include total synthesis,[19] Ulmann coupling,[20] oxidative fusing of free meso porphyrins with oxidants such as silver salts ($AgPF_6$),[5,21] DDQ/$Sc(OTf)_3$,[22]and hypervalent iodine (PIFA),[23] along with electrochemical oxidation[24] and recently a method involving the use of a manganes(IV)-oxo porphyrin as a catalyst in the two-electron oxidation process.[25] A method developed by us[26] involving the oxidative dimerization of porphyrin anions can also be applied and, additionally, a stepwise synthetic strategy involving the activation of the porphyrin and subsequent Suzuki coupling.[27] These meso-meso directly linked porphyrin dimers are vital precursors for the synthesis of triply fused bisporphyrins and thus can be used or optimized to synthesize such arrays, depending on the substitution pattern on the periphery required, i.e. it being symmetric or unsymmetric. Similar to singly linked bisporphyrins,

there are various synthetic strategies[7] which have been developed for their generation since their first synthesis *via* electrochemical oxidation by Osuka and co-workers.[6] One electron chemical oxidation[28] of monomeric zinc(II) porphyrins bearing free meso positions is the most attractive route for the synthesis of symmetric triply-fused porphyrin dimers and a variety of oxidants can be utilized. The most efficient are $Sc(OTf)_3$/DDQ and hypervalent iodine (PIFA), although other oxidants such as gold derivatives can be used and give similar yields.[29] We primarily focused on the synthesis of novel symmetric triply-fused bisporphyrins and higher arrays *via* the above strategies and also the synthesis of unsymmetric fused dimers by similar principles. In order to fine tune oligomeric porphyrins, post-fusing functionalizations can be executed. These derivatizations enable fused dimers to be more attractive candidates for application purposes. Within our group, focus is on PDT, NLO and OLEDs and, with these in mind, synthetic modifications of the peripheries of fused porphyrin dimers were undertaken. These included activation reactions such as brominations and nitrations, which would enable, for example, the attachment of sugars for PDT *via* Click chemistry[16b] or push-pull substituents for NLO.[30] Also, functionalizations such as cycloaddition and organolithium reactions could be beneficial for the enhancement of the bathochromic shift of the array. Most previous post-modifications of fused arrays have dealt with the pre-installation of activating substituents, whereas we wanted to investigate direct functionalizations of these arrays and synthetic strategies to enable such.

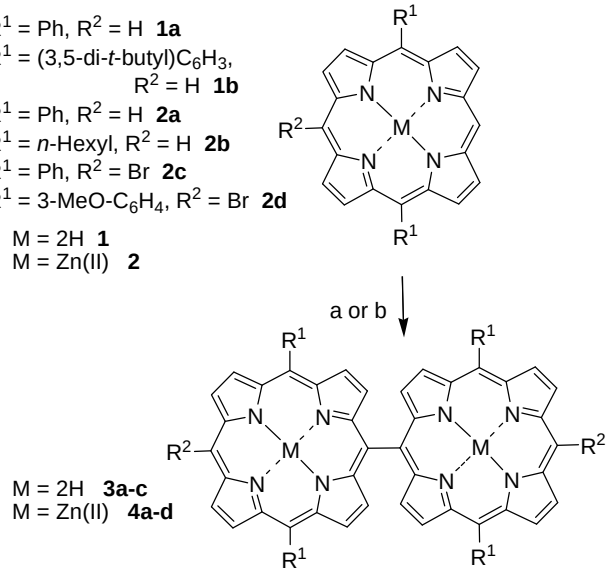
Results and Discussion

Previously we described that directly-linked symmetric dimers can be generated in excellent yields using organolithium reagents. The introduction of meso substituents *via* organolithium reactions is a versatile method of introducing aryl and alkyl substituents to the porphyrin periphery,[31] and for the synthesis of free-base meso-meso directly linked bisporphyrins in good yields *via* radical dimerization.[26b,32]

Taking 5,15-disubstituted porphyrins **1a**[33] and **1b**,[18] free base dimers **3a**,[26a] **3b** [26a] and **3c** were obtained in good yields of 59-74 % (Table 1). Syntheses of zinc(II) derivatives of **3a**[21c] and **3c**[8c] have been performed previously by DDQ and PIFA oxidation methods in similar yields but from trisubstituted precursors. Additionally, hypervalent iodine reagents, e.g. Bis(trifluoroacetoxy)iodobenzene (PIFA), can be applied for the synthesis of directly linked porphyrin arrays. It contains a highly electrophilic iodine center which can promote diverse coupling reactions,[34] including the synthesis of meso-meso directly-linked bisporphyrins in excellent yields.[23b] Interestingly, high yields were obtained for electronegative substituents such as trifluoroalkyl groups and thus bromosubstituted monomers were chosen as starting materials, enabling the generation of activated bisporphyrins. Likewise, 5,15-disubstituted porphyrins were employed for the synthesis of bisporphyrins incorporating two free meso positions, with the same objective in mind, as post-fusing modifications at these positions could be implemented. Using 0.8 equivalents of PIFA, to avoid formation of the triply-fused dimers, bromo-substituted symmetric dimers **4c**[5]and **4d** were synthesized in good to excellent yields of 58 and 86 %, from **2c**[2a] and **2d** respectively (Table 1). The reaction mechanism involves the oxidative generation of a porphyrin cation radical, which dimerizes to form the bisporphyrin product. Drawing attention the the 3-methoxy substituent in **4d**, we generated materials bearing this group due to our interest in Foscan® derivatives,[35] for which it is a useful precursor. Attempts to synthesize dimers **4a** and **4b**, bearing free meso positions, in acceptable yields from **2a**[2a] and **2b**[36] proved unsuccessful. The desired dimers were only synthesized in very low yields, identified by mass spectrometry and UV-vis analysis of the reaction mixtures.

Due to the inevitable formation of oligomerized products, dimers **4a** and **4b** were not isolated and this method of synthesizing bisporphyrins with unsubstituted meso positions was not feasible. Also, it must be noted that this PIFA oxidation method can also be used for the synthesis of triply fused β-β, meso-meso, β'-β' linked bis-porphyrins, using an excess of PIFA oxidant.[8c] Moreover, for most cases in the literature, bromosubstituted directly linked dimers were synthesized *via* stepwise strategies[37] or by using other oxidants such as $AgPF_6$ and I_2.[5]

Table 1: Synthesis of directly linked bisporphyrins *via* PIFA oxidation and organolithium reactions[a,b]



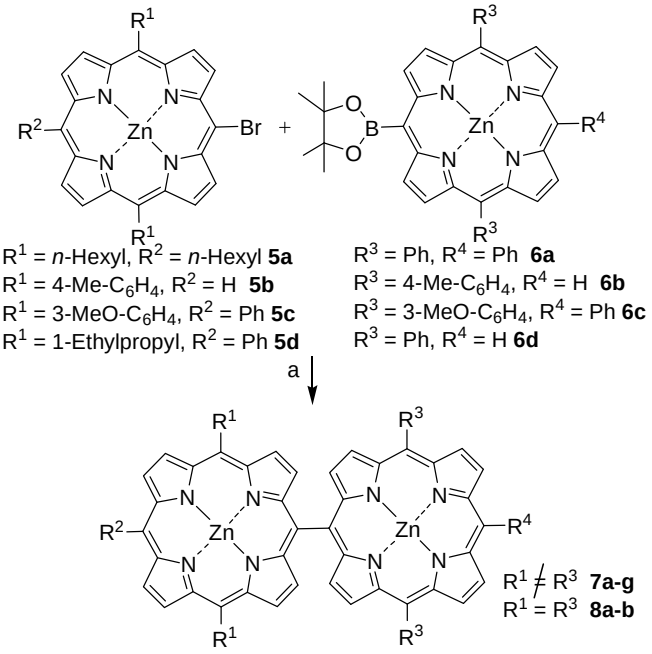
Entry	R^1	R^2	product	Yield [%]
1	Ph	Ph	**3a**[a]	68
2	Ph	*n*-Butyl	**3b**[a]	59
3	Ar	Ph	**3c**[a]	74
4	*n*-Hexyl	H	**4a**[b]	n/d*
5	Ph	H	**4b**[b]	n/d*
6	Ph	Br	**4c**[b]	58
7	3-MeO-C_6H_4	Br	**4d**[b]	86

Reagents and conditions: [a] i) RLi, -78 to 0 °C, THF, 1 h ii) DDQ, 1 h. [b] i) PIFA, CH_2Cl_2, -78 °C ii) rt, 0.75 h. iii) $NaBH_4$, MeOH. *n/d = not determined

To overcome the challenge of synthesizing directly-linked porphyrin dimers bearing free meso positions, a stepwise approach, culminating in a Suzuki-Miyuara coupling between a bromoporphyrin and borylated porphyrin to give singly linked bisporphyrins is necessary.[38] This strategy was adopted to synthesize unsymmetric hexasubstituted dimers and dimers with free meso positions which would enable 'post fusing' modifications. The Suzuki coupling of bromoporphyrins **5a-d** with borylated porphyrins **6a-d**,[39] produced the desired dimers **7a-f** in yields ranging from 43-66 % (Table 2). Although the yields for these Suzuki couplings were good, they were hindered by the competing homocouplings of the borylated porphyrins **6a** and **6b**, generating dimers **8a**[5] and **8b** as side products in yields of 18 and 22 %, respectively. Such directly linked dimers were used in

subsequent fusing reactions to form triply linked dimers and also, in the cases of meso free dimers **7c-d**, in functionalization reactions.

Table 2: Synthesis of directly linked porphyrin dimers *via* Suzuki coupling.

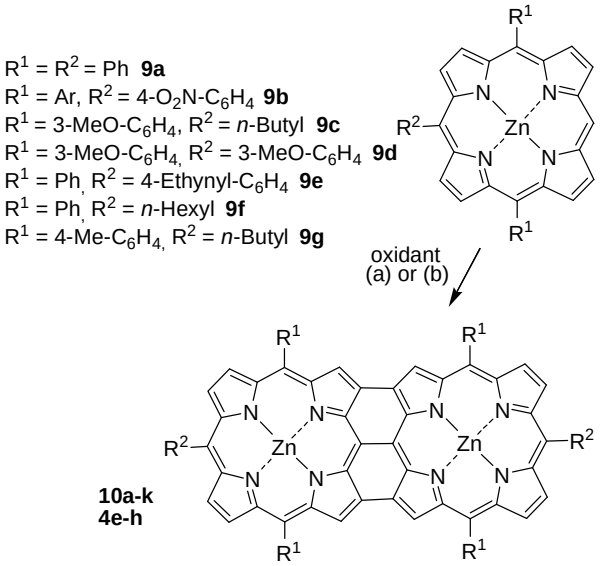


Entry	R^1	R^2	R^3	R^4	# [a]	Yield [%]
1	*n*-Hexyl	*n*-Hexyl	Ph	H	**7a**	52
2	Ph	Ph	4-Me-C_6H_4	H	**7b**	76
3	3-MeO-C_6H_4	Ph	3-MeO-C_6H_4	H	**7c**	56
4	1-Ethylpropyl	Ph	4-Me-C_6H_4	H	**7d**	63
5	3-MeO-C_6H_4	Ph	4-Me-C_6H_4	H	**7e**	61
6	Ph	Ph	3-MeO-C_6H_4	Ph	**7f**	69
7	Ph	Ph	Ph	Ph	**8a**	18
8	4-Me-C_6H_4	H	4-Me-C_6H_4	H	**8b**	20

Reagents and conditions: [a] $Pd(PPh_3)_4$ (0.1-0.2 eq.), Cs_2CO_3 (2.1 eq.), toluene : DMF (3:1 v/v), 80 °C, 18-24 h.

We aspired to synthesize a variety of A_3 and A_2B symmetric bisporphyrins with a range of substituents, some permitting follow-up chemistry be carried out. The central metal ion is of great importance to the oxidative process and thus zinc porphyrins were employed for the synthesis, as they have a lower first oxidation potential and therefore are more easily oxidized than Ni or Pd counterparts.[40] Similarly to singly-linked arrays, the reaction mechanism involves oxidative double ring closure *via* generation of a porphyrin cation radical,[7, 41] which undergoes radical cation coupling. It has been shown that electron withdrawing substituents on the porphyrin periphery can affect yields for oxidative fusing,[29] although it was shown recently that an electron deficient porphyrin tape can be synthesized in good yields.[42] In spite of this, a series of symmetric dimers were synthesized and yields compared in relation to substituents (Table 3). Comparable yields were obtained with both DDQ/$Sc(OTf)_3$ and PIFA oxidants. The novel triply fused bisporphyrins **10b-k** could thus be prepared from 5,10,15 trisubstituted zinc(II)porphyrin precursors **9a-g**[5, 15, 32, 43] in moderate to excellent yields of 42-73 %, following the Osuka oxidation method and this strategy can be applied for the synthesis of other fused arrays. For some oxidations with DDQ/$Sc(OTf)_3$, two products were observed: the desired triply fused dimer and also the directly linked bisporphyrins **4e-g** as a side product, thereby affecting yields for dimers **10c**, **10f**[32] and **10g**. Through optimization of conditions *via* raising reaction temperature and increasing reaction duration, formation of these side products were minimized. For the dimers bearing meso free positions, **10h** and **10i**, and bromo dimers **10j** and **10k** both the DDQ and PIFA method were employed. Unfortunately, due to the inherent polymerizations of monomers **2a** and **2b**, dimers **10h** and **10i** were not isolated, although their formation was indicated by near-IR absorption profiles.

Table 3: Synthesis of triply fused symmetric dimers.



Entry	R^1	R^2	Product	Yield [%]
1	Ph	Ph	**10a** [a]	67[8c]
2	Ar [c]	4-O_2N-C_6H_4	**10b** [a]	56
3	3-MeO-C_6H_4	*n*-Butyl	**10c, 4e** [a]	60, 23
4	3-MeO-C_6H_4	3-MeO-C_6H_4	**10d** [a]	73
5	Ph	4-Ethynyl-C_6H_4	**10e** [a]	67
6	Ph	*n*-Hexyl	**10f, 4f** [a]	42, 30[32]
7	4-Me-C_6H_4	*n*-Butyl	**10g, 4g** [a]	58, 29
8	Ph	H	**10h** [b]	n/d*
9	*n*-Hexyl	H	**10i** [b]	n/d*
10	Ph	Br	**10j** [a,b], **4h**	n/d*
11	3-MeO-C_6H_4	Br	**10k** [a,b]	15

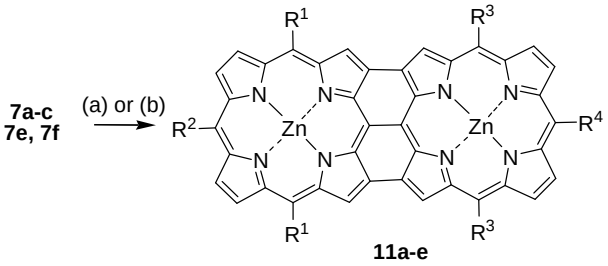
Reagents and conditions: [a] DDQ (5 eq.), $Sc(OTf)_3$ (5 eq.), toluene, 50 °C, 3 h. [b] i) PIFA (2.5 eq.), CH_2Cl_2, -78 °C – rt, 3 h. ii) $NaBH_4$ (10 eq.), MeOH, 0.5 h. [c]Ar = 3,5-di-*tert*-butyl-C_6H_3. *n/d = not determined

Similar to the singly linked bisporphyrin counterparts, this strategy for obtaining free meso dimers is not attractive. For **10k** best results were acquired using PIFA as oxidant, although yields were much lower than for alkyl and aryl substituted dimers **10a-g**. Previous syntheses of fused bromodimers using these oxidants also gave poor results, with Anderson and co-workers reporting only 9 % yield for the (3,5-di-*tert*-butyl)phenyl derivative of **10j** using DDQ.[44] This is due to the electron-withdrawing nature of the bromo-substituent which raises the oxidation potential of the porphyrin and thereby reducing the yields of such arrays. Using DDQ, the singly directly linked derivative of **10j** (**4h**)[21c] was isolated in a 10 % yield, but the desired triply-fused dimer was not obtained.

Adopting a synthetic strategy similar to that for the symmetric arrays, directly-linked unsymmetric bisporphyrins were fused oxidatively using DDQ/$Sc(OTf)_3$ or PIFA (Table 4). With dimers **7a-c**, **7e** and **7f**, attempts at triply fusing had mixed results. For the free meso arrays, dimers **11b-d** were not detected. Although all

crude samples exhibited typical triply-fused near-infrared absorption profiles, the desired dimers were not detected *via* mass spectrometry and purification was not possible. Again, there is preferential fusing at this 'free-meso' side of the directly linked bisporphyrin resulting in a mixture of dimeric and tetrameric products. Due to the poor solubility of these arrays, isolation of such was not achieved *via* chromatographic methods. Trace quantities of *n*-hexyl substituted dimer **11a** were detected but full characterization was not achievable due to the low yields obtained. Using the milder PIFA oxidant, oligomerization was not minimized, with similar results observed for dimers **11c-d**. For the hexasubstituted dimer **11e**, this problem was not encountered and it was obtained in a good yield of 56 % following oxidation of **7f**, using DDQ/$Sc(OTf)_3$, indicating that the method can be applied to unsymmetric directly linked dimers.

Table 4: Synthesis of triply fused unsymmetric dimers.



Entry	R^1	R^2	R^3	R^4	#	Yield [%]
1	*n*-Hexyl	*n*-Hexyl	Ph	H	**11a**	<5
2	Ph	Ph	4-Me-C_6H_4	H	**11b**	n/d*
3	3-MeO-C_6H_4	Ph	3-MeO-C_6H_4	H	**11c**	n/d*
4	3-MeO-C_6H_4	Ph	4-Me-C_6H_4	H	**11d**	n/d*
5	Ph	Ph	3-MeO-C_6H_4	Ph	**11e**[a]	52

Reagents and conditions: [a] DDQ (1-5 eq.), $Sc(OTf)_3$ (1-5 eq.), toluene, 50 °C, 3 h. [b] i) PIFA (1-2.5 eq.), CH_2Cl_2, -78 °C – rt, 3 h. ii) $NaBH_4$ (10 eq.), MeOH, 0.5 h. *n/d = not detected

All triply-fused bisporphyrins exhibited characteristic ^{1}H NMR spectra, with a drastic shift in signals to higher fields observed upon fusing, due to a decrease in aromaticity with respect to their starting materials. As these arrays have extensive delocalized π-electron systems through the entire molecule, a profound effect on the ring current of the array is observed.[45] With these bisporphyrins, the inner *β*-protons resonate around 7.0 ppm, occurring as a singlet. This characteristic singlet was observed for all symmetric fused dimers **10a-10k** and unsymmetric dimer **11e**. The resolution of peaks was dependent of the solubility of the array in $CDCl_3$. In some cases, using pyridine-D_5 in $CDCl_3$ minimized aggregation enabling the generation of sharper and more distinguished peaks in ^{1}H NMR spectra. However, in spite of this, broad signals were still observed for the majority of fused arrays, possibly indicative of conformational equilibria in solution.

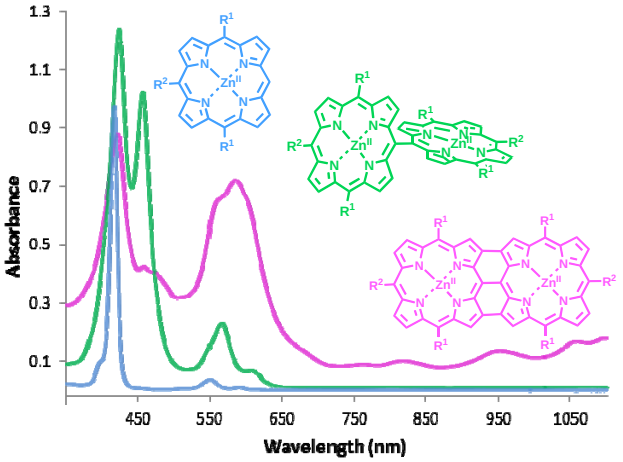


Figure 1: UV/vis/NIR absorption spectra of monomer **9g** (blue), direct dimer **4g** (green) and fused dimer **10g** (pink) in tetrahydrofuran. (where R^1 = 4-Me-C_6H_4, R^2 = *n*-Butyl)

The extension of conjugation in triply fused porphyrin arrays results in a significant bathochromic shift in the absorption profile due to lowering of HOMO-LUMO energy gaps, causing a sizeable shift into the near-infrared region.[46] Comparing fused dimer **10g** with its directly-linked dimeric counterpart **4g** and monomer **9g**, there was a significant difference in their profiles (Figure 1). Monomer **9g** exhibited a characteristic metallated porphyrin absorption profile with a λ_{max} of 590 nm. Directly-linked dimer **4g** exhibited a splitting of the Soret band due to excitonic coupling between the porphyrin units and had a λ_{max} of 566 nm. However, with triply-fused dimer **10g**, a substantial shift was observed. There was a broad splitting of the Soret band, at 414 and 576 nm, again due to excitonic coupling between porphyrin units and a λ_{max} well into the near-IR region of 1092 nm. Additionally, strong visible region absorbances were observed at 803 and 945 nm. A similar absorption profile was observed for dimers **10a-k** and such characteristic spectra provide a useful analytical tool as to the formation of the fused array. These absorption patterns were also observed for the crude mixtures of meso-free dimers **10h-i**, and their higher oligomers, demonstrating that fusing took place.

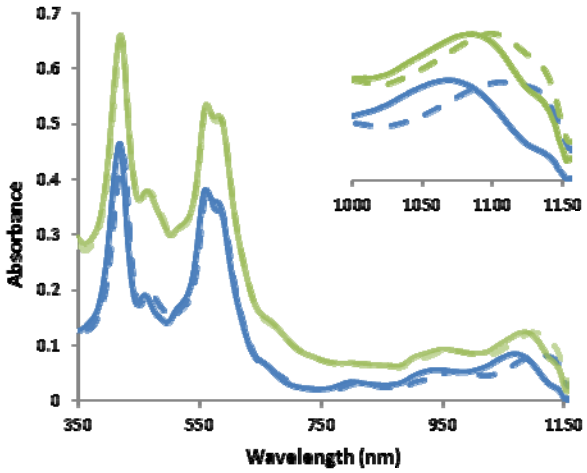
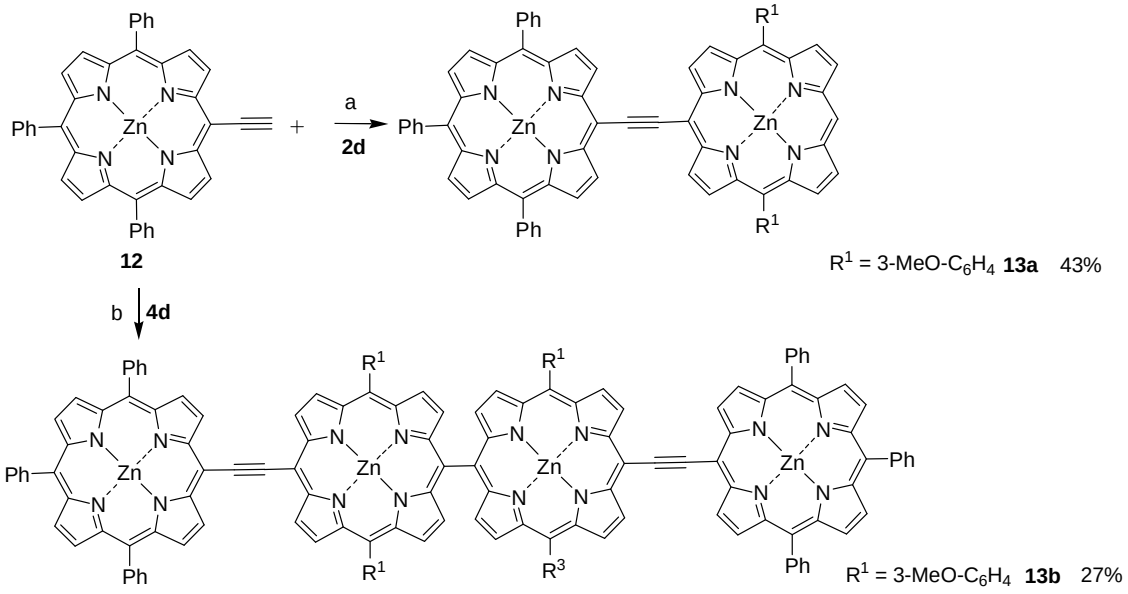


Figure 2: UV/vis/NIR spectrum of dimers **10a** (blue) and **10d** (green) in a) CH_2Cl_2 (solid line) and b) CH_2Cl_2 with 2% TEA (dashed line).

An interesting effect was seen when employing a coordinating solvent for the UV/vis/NIR analysis of fused dimers. Many studies have been carried out on solvent effects on the absorption profiles in monomeric porphyrins. The spectral shifts are generally attributed to displacement of the metal ion resulting in a distortion of the macrocycle, or from a charge transfer to the macrocycle

from the coordinating solvent resulting in an increase in the HOMO energy level, thereby reducing the energy gap.[47] As noted by Osuka and co-workers,[36] there is a red-shift in absorption on addition of a coordinating solvent. With dimers **10a** and **10d**, on comparing their profiles in CH_2Cl_2 against those in CH_2Cl_2 with 2 % triethylamine, a significant bathochromic shift was observed (Figure 2). With dimer **10a**, there was a red shift of 38 nm, from 1067 nm to 1105 nm, whilst with dimer **10d**, this effect is less pronounced with a shift of 13 nm observed.

For the development of a novel tetrameric porphyrin incorporating a fused moiety and a conjugated linker, two strategies were investigated. It was hoped that the alkynyl linker would enhance the optical properties of the array due to the increase in π-conjugation. The first strategy involved the synthesis of alkynyl linked dimer **13a** *via* copper-free Sonogashira coupling[48] of monobromo porphyrin **2d** with alkynyl porphyrin **12**[49] to produce dimer **13a** in a yield of 43% (Scheme 1). This yield was moderate due to separation difficulties as the desired dimer was shown to streak during column chromatography and some product was lost through contamination and co-elution with other fractions. Also detetected was the Glaser homocoupled dimer, in trace quantities (<5%), although copper-free Sonogashira conditions were used and was most likely formed *via* a palladium catalyzed homocoupling.[48b] This alkynyl dimer contains one free meso position whereby oxidative fusing can be carried out to generate the fused tetramer. The second strategy involved the copper-free Sonogashira coupling[48b] of directly linked bromo bisporphyrin **4d** with alkynyl porphyrin **12,** which gave the desired tetramer **13b** in 27% yield (Scheme 1). Yields for **13b** were low due to difficulties in separation and the formation of other oligomeric, namely trimeric and dimeric, derivatives of **13b** as side-products. Subsequent oxidation of dimer **13a** and tetramer **13b** to give the triply-fused tetramer **14** was executed using both the DDQ/$Sc(OTf)_3$ and the PIFA methods. After many attempts, the desired tetramer **14** was obtained from both strategies *via* either oxidation methods in moderate yields, the highest of which was obtained with PIFA oxidation of dimer **13a**. Here, there was less steric hindrance than **13b** for oxidative fusing to occur at the free meso side. Furthermore, the dimer exhibited better solubility in CH_2Cl_2 than tetramer **13b** and this affected the yield. The formation of **14** was confirmed by HRMS *m/z* calculated for $[C_{148}H_{88}N_{16}O_4Zn_4](M+2H)^+$ 2408.4340, found 2408.4282 and UV-vis analysis. ^{1}H NMR spectra were difficult to assign due to overshadowing solvent peaks, although oxidative fusing of the central porphyrin units was evident as there is significant shift of signals to higher fields in the ^{1}H NMR spectra. The characteristic singlet at 6.9 ppm signifies the inner *β*-protons of the central porphyrin units. These are substantial shifts from starting materials **13a** and **13b**, for which the *β*-protons are observed between 9 and 10.5 ppm. This is the first example of an alkynyl-linked array incorporating a triply fused bisporphyrin moiety and **14** exhibited unusual photophysical characteristics. There was a considerable change in absorption, the profile of which was identical from the synthetic strategies, *i.e.*, the oxidative fusing of tetramer **13b** and dimer **13a**. A significant difference in absorption can be seen for **14** compared to starting materials **13a** and **13b** (Figure 3).



Scheme 1: Synthesis of alkynyl dimer **13a** and tetramer **13b** *via* copper-free Sonogashira coupling. *Reagents and conditions:* [a] **12** (1 eq.), **2d** (1 eq.), $Pd_2(dba)_3$ (0.1 eq.), $AsPh_3$ (2.1 eq.), THF : TEA (3:1 v/v), 67 °C, 22 h. [b] **12** (2 eq.), **4d** (1 eq.), $Pd_2(dba)_3$ (0.15 eq.), $AsPh_3$ (2.1 eq.), THF : TEA (3:1 v/v), 67 °C, 48 h.

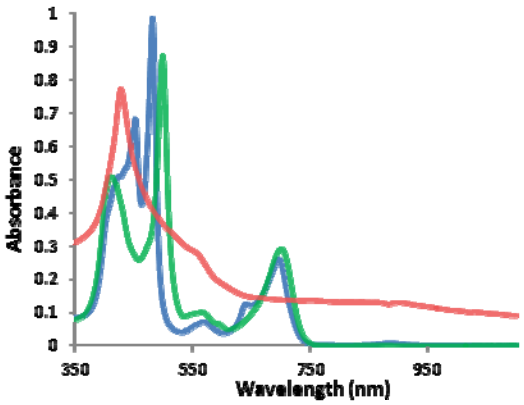
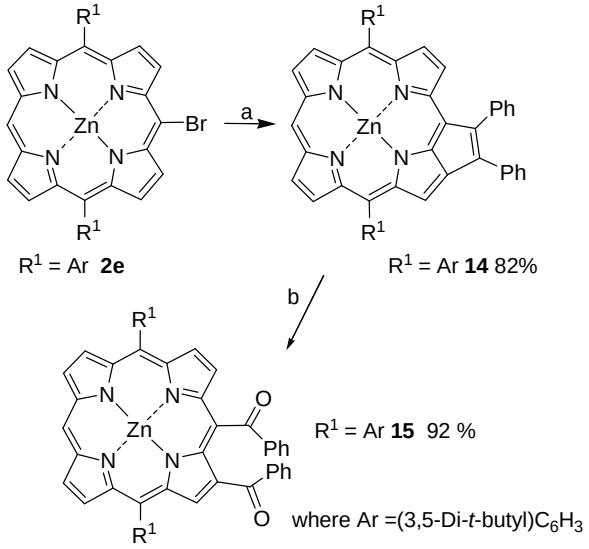


Figure 3: UV/vis/NIR spectra of dimer **13a** (blue), tetramer **13b** (green) and fused tetramer (red) in ethyl acetate.

With oligomers **13a-b**, there is a split in the Soret band, similar to the alkynyl-linked dimers and both oligomers have a maximum absorption wavelength of 696 and 700 nm, for dimer and tetramer respectively. Upon fusing, a completely different profile was observed, exhibiting a panchromatic spectrum with few distinguishable peaks. This could be attributed to aggregation effects of the fused tetramer, but it is clear there is absorbance in the near-IR region. Despite the inability to distinguish peaks, the presence of a triply-fused porphyrin moiety was confirmed *via* the shift in absorption.

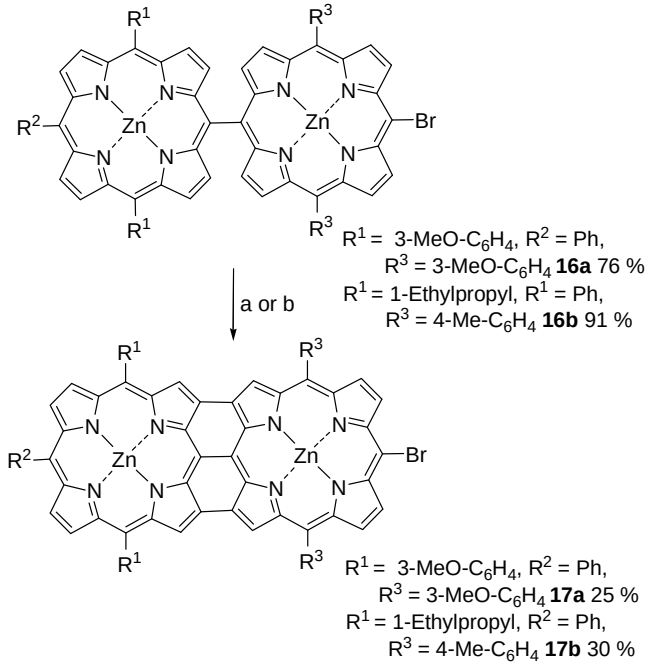
In further attempts to functionalize the *β* positions of dimers, a chlorin formation, using organolithium reagents was investigated. Although high yielding for the introduction of meso substituents, the introduction of *β* substituents *via* organolithium methods can be quite challenging and low yielding and can result in the formation of chlorins, bacteriochlorins and porphodimethenes, depending on reaction conditions and substrates.[50] Using 5,10,15,20-tetraphenylporphyrin (TPP) as the comparison, it was anticipated that introducing a *n*-butyl group at the *β*-position of fused symmetric dimer **10a** would generate a fused porphyrin-chlorin hybrid. Adopting a method developed by us, whereby TPP was monobutylated at the *β*-position in 17 % yield, the fused dimer **10a** was butylated under standard organolithium conditions.[23] Butylation was confirmed by HRMS *m/z* calculated for $[C_{80}H_{50}N_8Zn_2][M\text{-}2H]^+$ 1250.2741, found 1252.2770, with the main other component being unreacted starting material **10a**, separation from which was not possible. The classic reduction of the porphyrin periphery to generate a chlorin species was also attempted on **10a**. The diimide reduction of monomeric porphyrins, developed by Whitlock *et al.*,[51] to their respective chlorins and bacteriochlorins, is widely known. Preliminary studies indicated reduction of **10a** occured efficiently, although isolation of the porphyrin-chlorin hybrid was not possible due to its instability.

Cycloaddition reactions on monomeric porphyrins are widely known, generating perturbed macrocycles with enhanced photophysical properties.[3a,52] To investigate the reactivity of the fused dimers, we decided to adopt a [3+2] annulation strategy developed by Osuka and co-workers.[3b] This involves a palladium catalyzed C-C bond forming reaction *via* carbopalladation of a bromoporphyrin with internal alkynes.[53] The resulting product is a 7,8-dehydropurpurin incorporating a fused cyclopentadiene ring which causes a significant distortion of the porphyrin macrocycle.



Scheme 2: Synthesis of dehydropurpurin **14** and 1,5-diketone **15**. *Reagents and conditions:* [a)] Diphenylacetylene, $Pd_2(dba)_3$, $(o\text{-Tol})_3P$, toluene, *N,N*-dicyclohexylamine, 120 °C, 24 h. [b)] DDQ, $Sc(OTf)_3$, toluene, rt, 3 h.

Tetrapyrroles with exocyclic 5-membered rings have biological significance but in spite of this synthetic derivatives of such are not that common.[54] Resulting from the perturbation of the macrocycle, these species have interesting photophysical properties and exhibit a bathochromic shift in their absorption profile.[55] We sought to apply this chemistry to dimeric porphyrins and develop a novel 'fused on fused' system which we hoped would further enhance the properties of the triply-fused array.[56] The initial strategy involved the synthesis of a dehydropurpurin macrocycle with a free meso position and subsequent fusing using standard oxidative conditions which we anticipated would yield the desired triply-fused dimeric dehydropurpurin. To test reaction conditions, the [3+2] annulation was carried out on bromoporphyrin **2e**[57] with diphenylacetylene forming dehydropurpurin **14** in an excellent yield of 82 %. Attempts to triply-fuse **14**[3b] employing standard oxidative conditions using DDQ/$Sc(OTf)_3$ were ineffective, with the main product isolated being the ring-opened adduct **15**[3b](Scheme 2). Unfortunately, as discovered by Osuka and co-workers, the zinc-dehydropurpurins are unstable in solution and on exposure to air and light. The cyclopentadiene ring-opens to furnish 1,5-diketone **15**, assumed to occur from singlet oxygen generation. The outer C-C double bond in the cyclopentadiene ring presumably undergoes a [2+2] cycloaddition with singlet oxygen generated in situ, forming a dioxetane intermediate which decomposes to form the diketone product[58] and, hence, does not survive these strong oxidative conditions.



Scheme 3: Oxidative fusing of bromo-dimers **16a** and **16b** to give fused dimers **17a** and **17b**. *Reagents and conditions:* [a] i) PIFA (2.5 eq.), CH_2Cl_2, -78 °C – rt, 3 h. ii) $NaBH_4$ (10 eq.), MeOH, 0.5 h. [b] DDQ, $Sc(OTf)_3$, toluene, 50 °C, 3 h.

Related studies on [3+2] cycloadditons require triply fused bromo dimers. For this, using standard bromination conditions of NBS and chloroform, directly-linked dimers **7c** and **7d** could be brominated at their free meso position, yielding dimers **16a** and **16b** in excellent yields of 76 and 91 %, respectively (Scheme 3)**.** These bromoporphyrins were oxidised using both PIFA and DDQ/$Sc(OTf)_3$ respectively, to form the triply fused dimers **17a** and **17b**, in approximate yields of 25-30%, comparable for both methods. Preliminary results of the [3+2] cycloaddition reaction on these dimers indicate the formation of the desired cyclo-adducts in low yields, although further investigations are necessary.

Conclusions

A library of symmetric directly singly- and triply-linked dimers were synthesized in moderate to good yields *via* oxidative fusing, tolerating a wide range of functionalities on the porphyrin periphery. Attempts to triply fuse monomers and dimers bearing one or two free meso positions proved, in most cases, unsuccessful due to the inevitable formation of oligomerized products. Although having limited success with alkyl substituted dimers, this route is not *via*ble as yields were low. A series of unsymmetric directly-linked dimers were synthesized in good yields *via* a stepwise strategy. However, the oxidative double ring closing of free-meso dimers proved again unsuccessful. As a result, a change in strategy was needed for post-functionalization of triply-fused arrays. All triply linked dimers isolated exhibited a substantial bathochromic shift in their absorption profile into the near-infrared region, thus making these arrays potential candidates for optical applications such as PDT and NLO. There are considerable possibilities to develop a library of unsymmetrically fused dimers and fine-tune these for optical applications. The fused tetramer synthesized is the first example of a fused array incorporating alkynyl-linked porphyrins and other linkages could also be explored. Numerous strategies towards the functionalization of porphyrin arrays were investigated. For directly linked dimers, the reactivity reflects that of monomeric porphyrins with brominations and cycloadditions achievable in high yields. For fused arrays, the reactivity is somewhat diminished due to the poor solubility of the arrays. However, these investigations showed that fused dimers can be functionalized directly, *via* organolithium reactions, and indirectly *via* palladium catalyzed coupling reactions with pre-installed activators such as bromine. Such post-fusing modifications demonstrate the ability to fine-tune the arrays for optical applications, as there is an enhancement of bathochromic shift, and although further investigations are necessary, preliminary studies are promising. Further research into the diimide reduction reaction is necessary, and this would provide a straightforward route to chlorin fused dimers. By the introduction of more solubilizing substituents, an improved reactivity of the bromo-dimers should be observed. Also, *via* debromination methods, there is a possibility to generate fused dimers bearing free meso positions whereby the reactivity of such could be probed using organolithium methods.

Experimental Section

General Remarks: General information about methods used and synthetic procedures for additional compounds used as starting material are described in the Supporting Information.

General procedure for the oxidative coupling of 5,10,15 trisubstituted porphyrins using DDQ/Sc(OTf)$_3$: A 100 mL Schlenk tube was charged with metalloporphyrin (1 eq.), dissolved in dry toluene. The solution was degassed *via* three freeze-pump-thaw cycles. DDQ (5 eq.) and $Sc(OTf)_3$ (5 eq.) were added and the reaction was heated to 50 °C under argon for 3-18 h. THF was added and the reaction was stirred at room temperature for a further 1 h. The reaction mixture was then passed through a short plug of alox or silica gel, using CH_2Cl_2 then THF as eluent and the solvent was removed *in vacuo*. The residue was then purified using column chromatography on silica gel to yield the desired triply-fused dimer.

Bis[5,15-bis(3,5-di-*tert*-butylphenyl)-20-(4-nitrophenyl)porphyrin-13,15,17-triylato]zinc(II) (10b): 10 b was **s**ynthesized according to the general procedure above from {5,15-bis(3,5-di-*tert*-butylphenyl)-10-(4-nitrophenyl)porphyrinatozinc(II)} **9b** (20 mg, 0.023 mmol), DDQ (26 mg, 0.115 mmol), $Sc(OTf)_3$ (57 mg, 0.115 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h. THF (5 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 then CH_2Cl_2 : THF (1 : 1, v/v) as eluent to give an intense purple fraction. The solvents were removed and the residue was filtered through a second plug of alox using CH_2Cl_2 as eluent. The solvents were removed *in vacuo* and **10b** was isolated as a dark solid (13 mg, 0.007 mmol, 64%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 72H, *t*-butyl-*H*), 7.37 (s, 4H, H_β), 7.61 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 4H, H_β), 7.67 (m, 12H, Ar-*H*), 7.75 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 4H, H_β), 8.00 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, C_6H_4-*H*), 8.48 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, C_6H_4-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 30.8, 106.2, 107.5, 120.9, 122.2, 124.2, 127.7, 128.1, 130.1, 131.9, 133.4, 135.9, 139.5, 147.3, 147.8, 151.6, 153.5, 153.9, 154.1 ppm; UV/vis (THF): λ_{max} (log ε) = 423 (5.12), 566 (5.17), 886 (4.00), 967 (4.33), 1110 (4.63) nm; HRMS (MALDI) *m/z* calcd. for $[C_{108}H_{104}N_{10}O_4Zn_2](M^+)$: 1732.6825, found 1732.6816.

Bis[5-butyl-10,20-bis(3-methoxyphenyl)porphyrin-13,15,17-triylato]zinc(II) (10c):[59] Compound **10c** was synthesized from **9c** (20 mg, 0.031 mmol), DDQ (35 mg, 0.156 mmol), $Sc(OTf)_3$ (77 mg, 0.156 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h, according to the general procedure above. THF (6 mL) was added and reaction stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 as eluent to give side product **4e** and using CH_2Cl_2 : THF (1 : 1, v/v) as eluent to give fraction containing dimer **10c**. The solvents were removed *in vacuo* and the residue was subjected to column chromatography using CH_2Cl_2 as eluent to give two fractions, the

first being side product **4e**, the second being desired dimer **10c**. The solvents were removed and **10c** isolated as a dark solid (14 mg, 0.011 mmol, 70%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-D_5, 10:1): δ = 0.82 (m, 6H, CH_3), 1.46 (m, 4H, CH_2), 1.95 (m, 4H, CH_2), 3.78 (s, 12H, OCH_3), 5.17 (m, 4H, CH_2), 6.99 (m, 6H, H_β/C_6H_4-*H*), 7.14 (m, 8H, C_6H_4-*H*), 7.32 (m, 4H, C_6H_4-*H*), 7.53 (m, 8H, H_β), 8.15 (m, 2H, C_6H_4-*H*) ppm; UV/vis (THF): λ_{max} (log ε) = 422 (5.20), 459 (4.89), 559 (4.95), 949 (4.14), 1092 (4.41), 1094 (4.41) nm; HRMS (MALDI) *m/z* calcd. for $[C_{76}H_{58}N_8O_4Zn_2](M^+)$: 1274.3164, found 1274.3123.

Bis[5,10,20-bis(4-methoxyphenyl)porphyrin-13,15,17-triylato]zinc(II) (10d): Compound **10d** was synthesized according to the general procedure above, from **9d** (40 mg, 0.058 mmol), DDQ (66 mg, 0.289 mmol), $Sc(OTf)_3$ (142 mg, 0.289 mmol) in dry toluene (40 mL), heated at 50 °C for 4.5 h. THF (8 mL) was added and the reaction was stirred for a further 0.8 h at room temperature. The reaction mixture was filtered through a short plug of silica gel using CH_2Cl_2 as eluent giving one fraction which was discarded as no fusing product was detected *via* UV/vis/NIR analysis. Using CH_2Cl_2 : THF (1 : 1, v/v) as eluent a second (main) fraction containing **10d** was isolated. The solvents were removed *in vacuo* and **10d** was isolated as a dark purple solid (33 mg, 0.024 mmol, 83%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-D_5, 10 : 1): δ = 3.88 (s, 12H, OCH_3), 3.94 (s, 6H, OCH_3), 7.01 (s, 4H, H_β), 7.02 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 6H, C_6H_4-*H*), 7.09 (dd, $^3J_{H\text{-}H}$ = 8.3, 2.4 Hz, 4H, C_6H_4-*H*), 7.27 (m, 2H, C_6H_4-*H*), 7.29 (m, 2H, C_6H_4-*H*), 7.40 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 6H, C_6H_4-*H*), 7.51 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 4H, H_β), 7.56 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 4H, H_β), 7.63 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 4H, C_6H_4-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$/pyridine-D_5, 10 : 1): δ = 55.4, 112.3, 112.9, 118.8, 124.1, 124.8, 126.1, 126.5, 127.3, 130.3, 130.7, 133.8, 134.2, 135.9, 142.9, 152.8, 153.1, 154.4, 157.8, 158.9 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 420 (4.91), 471 (4.52), 562 (4.86), 584 (4.82), 820 (4.62), 952 (4.00), 1092 (4.23) nm; HRMS (MALDI) *m/z* calcd. for $[C_{82}H_{54}N_8O_6Zn_2](M^+)$: 1374.2749, found 1374.2723.

Bis[5-(4-ethynylphenyl)-10,20-diphenylporphyrin-13,15,17-triylato]zinc(II) (10e): Bisporphyrin **10e** was synthesized following the general procedure above from **9e** (60 mg, 0.109 mmol), DDQ (113 mg, 0.498 mmol), $Sc(OTf)_3$ (245 mg, 0.498 mmol) in dry toluene (60 mL), 50 °C for 3.5 h. THF (15 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 : THF (1 : 1, v/v) as eluent. The solvents were removed and **10e** was isolated as a dark solid (48 mg, 0.040 mmol, 79%). M.p. >300 ºC; ^{1}H NMR (600 MHz, $CDCl_3$/pyridine-D_5, 10 : 1): δ = 3.22 (s, 2H, C≡C-*H*), 6.98 (s, 4H, H_β), 7.50 (m, 20H, Ph-*H*), 7.66 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 8H, H_β), 7.71 (m, 8H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$/pyridine-D_5, 10:1): δ = 77.7, 83.7, 126.4, 126.5, 127.0, 130.6, 132.9, 135.9, 139.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.01), 563 (4.85), 586 (4.85), 671 (4.83), 968 (4.01), 1096 (4.27) nm; HRMS (MALDI) *m/z* calcd. for $[C_{80}H_{42}N_8Zn_2](M^+)$: 1242.2115, found 1242.2145.

Bis[5-butyl-10,20-bis(4-methylphenyl)porphyrin-13,15,17-triylato]zinc(II) (10g): Compound **10g** was synthesized according to the general procedure above from **9g** (30 mg, 0.049 mmol), DDQ (56 mg, 0.246 mmol), $Sc(OTf)_3$ (121 mg, 0.246 mmol) in dry toluene (30 mL), heated at 50 °C for 3.5 h. THF (7 mL) was added and the reaction was stirred for a further 0.5 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 as eluent to give side product **4g** and using THF as eluent to give a second fraction containing dimer **10g**. The solvents were removed *in vacuo* and the residue was subjected to column chromatography (silica gel, CH_2Cl_2 : *n*-hexane, 9 : 1 + 1% TEA) to give **10g** as the main fraction. The solvents were removed and **10g** was isolated as a dark purple solid (16 mg, 0.013 mmol, 54%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-D_5, 10 : 1): δ = 0.97 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 6H, CH_3), 1.47 (m, 4H, CH_2), 2.04 (m, 4H, CH_2), 2.57 (s, 12H, tolyl-CH_3), 3.89 (m, 4H, CH_2), 7.01 (s, 4H, H_β), 7.32 (d, $^3J_{H\text{-}H}$ = 7.2 Hz, 8H, C_6H_4-*H*), 7.59 (m, 4H, C_6H_4-*H*), 7.59 (m, 4H, H_β), 8.21 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$/ pyridine-D_5, 10 : 1): δ = 14.0, 20.9, 22.7, 35.0, 40.7, 117.5, 122.3, 126.8, 127.5, 135.7, 139.9, 148.4, 154.9 ppm; UV/vis (THF): λ_{max} (log ε) = 414 (4.99), 443 (4.70), 576 (4.89), 945 (4.16), 1092 (4.22) nm; HRMS (MALDI) *m/z* calcd. for $[C_{76}H_{58}N_8Zn_2](M^+)$: 1210.3367, found 1210.3375.

Bis[5-bromo-10,20-bis(3-methoxyphenyl)porphyrin-13,15,17-triylato]zinc(II) (10k):[59] Compound **10k** was synthesized from [5-bromo-10,20-(3- methoxyphenyl)porphyrinato]zinc(II) **2d** (60 mg, 0.091 mmol) dissolved in dry CH_2Cl_2 (60 mL) in a 100 mL Schlenk tube. The solution was degassed and was cooled to -78 °C. PIFA (32 mg, 0.075 mmol) was added at -78 °C, the reaction mixture was warmed to rt and stirred at this temperature for 2 h. $NaBH_4$ (12 mg, 0.305 mmol) in MeOH (5 mL) was added and the reaction was stirred for a further 45 min. The reaction mixture was added to H_2O (100 mL) and the organic layer was extracted using CH_2Cl_2 : THF (1 : 1, v/v). The organic layer was then washed with $NaHCO_3$ (2 × 50 mL), H_2O (30 mL) and dried over Na_2SO_4, which was then filtered and the solvents were removed *in vacuo*. The dark residue was re-dissolved and filtered through short plug of silica using $CHCl_3$: THF (1 : 1, v/v) as eluent to give a green fraction. The solvents were removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/*n*-hexane to give a dark purple solid (3 mg, 0.002 mmol, 14%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 12H, OCH_3), 7.04 (s, 4H, H_β), 7.16 (m, 4H, C_6H_4-*H*), 7.70 (m, 6H, C_6H_4-*H*), 7.73 (m, 10H, C_6H_4-*H*/H_β), 8.45 (m, 2H, H_β), 8.61 (m, 2H, H_β) ppm; UV/vis (CH_2Cl_2: THF , 1 : 1, v/v): λ_{max} (log ε) = 425 (5.01), 459 (4.66), 566 (4.68), 871 (3.98), 1110 (4.17) nm; HRMS (MALDI) *m/z* calcd. for $[C_{68}H_{40}Br_2N_8O_4Zn_2](M^+)$: 1318.0122, found 1318.0150.

Bis[(5-*n*-butyl)-10,20-bis(3-methoxyphenyl)porphyrin-15-ylato]zinc(II) (4e): 4e was isolated as a side product from the synthesis of **10c**. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 as eluent to give a fraction containing **4e**. The solvents were removed *in vacuo* yielding a red-purple solid (4 mg, 0.003 mmol, 19%). M.p. >300 ºC; R_f = 0.53 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89-0.93 (m, 6H, CH_3), 1.19 (m, 4H, CH_2), 1.93 (m, 4H, CH_2), 3.93 (s, 12H, OCH_3), 5.19 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, CH_2), 7.25 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4-*H*), 7.57 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, C_6H_4-*H*), 7.82 (m, 8H, C_6H_4-*H*), 8.08 (m, 4H, H_β), 8.67 (m, 4H, H_β), 9.12 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 4H, H_β) 9.71 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 22.5, 31.8, 41.0, 55.3, 109.9, 112.6, 119.6, 120.9, 127.9, 128.9, 131.7, 133.5, 142.5, 149.2, 154.9, 157.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.35), 457 (5.27), 568 (4.59) nm; HRMS (MALDI) *m/z* calcd. for $[C_{76}H_{62}N_8O_4Zn_2](M^+)$: 1278.3477, found 1278.3438.

Bis[(5-*n*-butyl)-10,20-bis(4-methylphenyl)porphyrin-15-ylato]zinc(II) (4g): 4g was synthesized as a side product of **10g**, and was isolated as the first fraction from filtration through a plug of alox using CH_2Cl_2 as eluent. The solvents were removed *in vacuo* to give a red-purple solid **4g** (8 mg, 0.007 mmol, 27%) M.p. >300 ºC; R_f = 0.45 (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 6H, CH_3), 1.19 (m, 4H, CH_2), 1.92 (m, 4H, CH_2), 2.64 (s, 12H, tolyl-CH_3), 5.17 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, CH_2), 7.50 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 8H, C_6H_4-*H*), 8.07 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 4H, H_β), 8.12 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 8H, C_6H_4-*H*), 8.65 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 4H, H_β), 9.10 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β), 9.68 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 21.3, 23.7, 35.6, 41.1, 118.7, 121.2, 122.1, 127.0, 128.8, 131.7, 131.9, 133.4, 134.1, 136.8, 139.7, 149.4, 149.9, 150.1, 154.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.54), 456 (5.45), 566 (4.80) nm; HRMS (MALDI) *m/z* calcd. for $[C_{76}H_{62}N_8Zn_2](M^+)$: 1214.3680, found 1214.3663.

[5,10,20-Trihexyl-15-(10',20'-diphenylporphyrin-5'-yl)-13,15,17-triylato]zinc(II) (11a): Bisporphyrin **11a** was synthesized from directly linked dimer **7a** (20 mg, 0.019 mmol), DDQ (22 mg, 0.096 mmol), $Sc(OTf)_3$ (47 mg, 0.096 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h. THF (6 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 : THF (1 : 1, v/v) as eluent. The solvents were removed

and the residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane, 5 : 1, v/v) to give three fractions, the first being unreacted starting material **7a** (3 mg, 14 %), the second of which contained **11a** and the third was oligomerized product. The solvents were removed and **11a** was isolated as a dark solid (3 mg, 0.002 mmol, 15 %). UV/vis (THF): λ_{max} (log ε) = 416 (4.97), 578 (4.70), 672 (4.56), 987 (3.87), 1106 (4.09) nm; HRMS (MALDI) *m/z* calcd. for $[C_{70}H_{62}N_8Zn_2](M^+)$: 1142.3680, found 1142.3625.

{5-[5'-Phenyl-10',20'-bis(3-methoxyphenyl)porphyrin-13',15',17'-triylato]-10,15,20-triphenylporphyrinato}zinc(II) (11e): Fused dimer **11e** was synthesized from dimer **7f** (40 mg, 0.032 mmol), DDQ (36 mg, 0.158 mmol), $Sc(OTf)_3$ (78 mg, 0.158 mmol) in toluene (50 mL). The reaction was heated to 50 °C and stirred at this temperature for 3 h. THF (8 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through plug of alox using CH_2Cl_2, then CH_2Cl_2 : THF (1 : 1, v/v) as eluent. The solvents were removed *in vacuo* to give a dark residue which was re-dissolved in CH_2Cl_2 and subjected to column chromatography (*n*-hexane : ethyl acetate, 6 : 1, v/v) to give two fractions, the first yielding unreacted starting material **7f** (6 mg, 15 %) and the second containing desired fused dimer **11e**. The solvents were removed *in vacuo* to yield a dark colored solid (21 mg, 0.017 mmol, 52%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-D_5, 20 : 1): δ = 3.93 (s, 6H, OCH_3), 7.03 (m, 4H, H_β), 7.13 (m, 4H, C_6H_4-*H*), 7.23 (m, 2H, C_6H_4-*H*), 7.43 (m, 2H, C_6H_4-*H*), 7.49-7.62 (m, 20H, Ph-*H*/ H_β), 7.70-7.83 (m, 8H, Ph-*H*/H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-D_5, 20 : 1): δ = 55.4, 112.9, 126.5, 126.9, 127.3, 128.8, 130.6, 130.9, 157.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.15), 455 (4.11), 556 (4.53), 579 (4.50), 917 (3.66), 1039 (3.90) nm; HRMS (MALDI) *m/z* calcd. for $[C_{78}H_{46}N_8O_2Zn_2](M^+)$: 1254.2327, found 1254.2286.

{5-[(10',20'-bis(3-methoxyphenyl)porphyrinato-5-yl)zinc(II)]ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (13a): This procedure was adapted from a method by Lindsey *et al*.[45] Alkynyl porphyrin **12** (56 mg, 0. 089 mmol), bromoporphyrin **2d** (60 mg, 0.089 mmol), $AsPh_3$ (57 mg, 0.185 mmol) and $Pd_2(dba)_3$ (8 mg, 0.008 mmol) were added to a 100 mL Schlenk tube and dried under high vacuum. The flask was purged with argon and dry THF (12 mL) and TEA (4 mL) were added. The solution was degassed *via* three freeze-pump-thaw cycles. The flask was sealed, and the reaction heated to 67 °C. After 22 h, the solvents were removed, the residue was re-dissolved in CH_2Cl_2 and was filtered through a plug of silica using CH_2Cl_2 as eluent. The solvents were removed and the residue was subjected to column chromatography (silica, *n*-hexane : ethyl acetate, 4 : 1, v/v) to give four fractions, fraction one being monomer **12** (8 mg, 14 %) with fractions two and three containing mixtures of undesired oligomers. The fourth fraction contained the desired dimer **13a**. The solvents were removed *in vacuo* to give a dark green solid **13a** (46 mg, 0.038 mmol, 43%). M.p. >300 ºC; R_f = 0.35 (*n*-hexane: EtOAc, 3 : 2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5, 20 : 1): δ = 4.07 (s, 6H, OCH_3), 7.38 (dd, $^3J_{H\text{-}H}$ = 7.3, 2.4 Hz, 2H, C_6H_4-*H*), 7.78 (m, 11H, Ph/C_6H_4-*H*), 7.89 (m, 2H, C_6H_4-*H*), 8.23 (m, 6H, Ph-*H*), 8.30 (m, 2H, C_6H_4-*H*), 9.01 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.04 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 9.11 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.21 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.30 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 9.96 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 10.11 (s, 1H, H_{meso}), 10.46 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 10.49 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-D_5 20:1): δ = 55.6, 100.7, 107.2, 113.1, 120.1, 120.8, 121.1, 122.0, 122.1, 122.4, 126.3, 126.4, 127.3, 127.4, 128.0, 130.6, 131.5, 131.6, 131.8, 132.0, 132.2, 132.7, 132.8, 133.1, 134.4, 134.5, 134.6, 143.0, 143.2, 143.3, 144.5, 149.6, 149.7, 149.8, 150.0, 150.4, 150.7, 152.6, 153.0 153.5, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 452 (5.06), 481 (5.22), 568 (4.08), 696 (4.64) nm; HRMS (MALDI) *m/z* calcd. for $[C_{74}H_{46}N_8O_2Zn_2](M^+)$: 1206.2327, found 1206.2341.

Bis{5-[(10',20'-bis(3-methoxyphenyl)porphyrinato-15'-yl)zinc(II)]ethynyl-10,15,20-triphenylporphyrin-15'-ylato}zinc(II) (13b): Alkynyl porphyrin **12** (65 mg, 0.104 mmol), bromoporphyrin dimer **4d** (66 mg, 0.049 mmol), $AsPh_3$ (32 mg, 0.104 mmol) and $Pd_2(dba)_3$ (7 mg, 0.007 mmol) were added to a Schlenk tube and dried under high vacuum. The flask was purged with argon and dry THF (10 mL) and TEA (1 mL) were added. The solution was degassed *via* three freeze-pump-thaw cycles. The flask was sealed, and the reaction heated to 67 °C. After 48 h reaction time, solvents were removed, the residue was re-dissolved in CH_2Cl_2 and filtered through a plug of silica using CH_2Cl_2 : ethyl acetate (9 : 1, v/v) as eluent. The solvents were removed and the residue was subjected to column chromatography (silica, *n*-hexane : ethyl acetate, 6 : 1, v/v) to give four fractions, the first three containing undesirable dimeric and trimeric products and the fourth of which contained the desired tetramer **13b**. The solvents were removed *in vacuo* to give dark green solid **13b** (34 mg, 0.011 mmol, 27%). M.p. >300 ºC; R_f = 0.27 (hexane : ethyl acetate = 3 : 2, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.93 (m, 12H, OCH_3), 7.26 (m, 4H, C_6H_4-*H*), 7.62 (m, 4H, C_6H_4-*H*), 7.84 (m, 22H, Ph/C_6H_4-*H*), 8.19 (m, 4H, H_α) 8.26 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 8H, C_6H_4-*H*), 8.32 (m, 8H, Ph-*H*), 8.73 (m, 4H, H_β), 8.95 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 8H, H_β), 9.24 (d, $^3J_{H\text{-}H}$ = 4.1 Hz, 4H, H_β), 9.28 (m, 4H, H_β), 10.55 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 8H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.4, 55.5, 101.0, 102.4, 113.6, 120.3, 122.5, 123.0, 126.7, 126.8, 127.4, 127.6, 127.7, 131.0, 132.1, 132.3, 133.2, 133.4, 134.2, 134.3, 134.5, 142.5, 142.6, 143.6, 150.1, 150.3, 150.4, 150.7, 152.9, 153.0, 155.0, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 411 (5.31), 498 (5.54), 564 (4.61), 700 (5.07) nm; HRMS (MALDI) *m/z* calcd. for $[C_{148}H_{90}N_{16}O_4Zn_4](M^+)$: 2410.4497, found 2410.4441.

{5-[5'-Bromo-10',20'-bis(3-methoxyphenyl)porphyrin-15'-ylato]-10,20-bis(3-methoxy)-15-phenylporphyrinato}zinc(II) (16a):[60] Bromo-bisporphyrin **16a** was produced from dimer **7c** (150 mg, 0.120 mmol), NBS (32 mg, 0.180 mmol) dissolved in $CHCl_3$ (50 mL) in a 100 mL RBF at 0 °C. Pyridine (0.1 mL) was added and the reaction was stirred at this temperature for 3 h. The solvents were removed *in vacuo* and the residue was re-dissolved in CH_2Cl_2 and filtered through a plug of silica using CH_2Cl_2 as eluent. The solvents were removed *in vacuo* to give a dark solid **16a** (120 mg, 0.091 mmol, 76%). M.p. >300 ºC; R_f = 0.54 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 6H, OCH_3), 3.94 (s, 6H, OCH_3), 7.23 (m, 4H, C_6H_4-*H*), 7.56 (m, 4H, C_6H_4-*H*), 7.80 (m, 11H, Ph/C_6H_4-*H*), 8.03 (m, 4H, H_α), 8.12 (d, $^3J_{H\text{-}H}$ = 5.3 Hz, 2H, Ph-*H*), 8.64 (m, 2H, H_α), 8.68 (m, 2H, H_α), 9.04 (q, $^3J_{H\text{-}H}$ = 12.1 Hz, 4H, H_α), 9.08 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_α), 9.85 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_α) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.3, 120.2, 120.3, 121.6, 122.6, 126.6, 127.2, 127.5, 131.8, 132.8, 133.7, 134.1, 134.5, 143.0, 143.4, 143.9, 144.1, 149.9, 150.2, 150.5, 150.9, 155.3, 157.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 418 (5.21), 450 (5.17), 558 (4.55) nm.

{5-[5'-Bromo-10',20'-bis(4-methylphenyl)porphyrin-15'-ylato]-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (16b): 16b was synthesized produced from dimer **7d** (30 mg, 0.026 mmol), NBS (5 mg, 0.026 mmol), dissolved in $CHCl_3$ (40 mL) at 0 °C. Pyridine (0.1 mL) was added and the reaction was stirred at this temperature for 3 h. Solvents were removed *in vacuo* and the residue was re-dissolved in CH_2Cl_2 and filtered through a plug of silica using CH_2Cl_2 as eluent. The solvents were removed *in vacuo* to give a purple solid **16b** (29 mg, 0.024 mmol, 91%). M.p. >300 ºC; R_f = 0.48 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 12H, CH_3), 2.66 (s, 6H, tolyl-*H*), 2.80 (m, 8H, CH_2), 5.05 (m, 1H, C*H*), 5.16 (m, 1H, C*H*), 7.51 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, C_6H_4-*H*), 7.83 (m, 3H, Ph-*H*), 8.08 (m, 4H, Ph-*H*/H_β), 8.13 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, C_6H_4-*H*), 8.32 (m, 2H, H_β), 8.66 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.04 (m, 2H, H_β), 9.10 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.41 (m, 2H, H_β), 9.77 (m, 2H, H_β), 9.87-9.88 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 21.5, 22.7, 29.7, 34.8, 50.5, 105.0, 113.5, 121.1, 122.5, 124.9, 126.4, 127.2, 127.4, 130.1, 132.1, 132.8, 133.1, 134.2, 134.3, 137.2, 139.6, 143.5, 143.6, 149.6, 150.3, 151.2, 155.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 414 (5.32), 450 (5.27), 554 (4.54) nm; HRMS (MALDI) *m/z* calcd. for $[C_{70}H_{57}N_8Zn_2Br](M^+)$: 1216.2472, found 1216.2509.

{5-[5'-Bromo-10',20'-bis(3-methoxyphenyl)porphyrin-13',15',17'-ylato]-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato}zinc(II)

(17a): [59,60] **17a** was synthesized from bromo-dimer **16a** (20 mg, 0.038 mmol) and PIFA (35 mg, 0.094 mmol) dissolved in CH_2Cl_2 (60 mL) in a 250 mL Schlenk tube. The reaction was stirred at room temperature for 3 h. $NaBH_4$ (7 mg, 0.190 mmol) in MeOH (5 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was poured on H_2O (50 mL) and was extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$ (2 × 50 mL) and H_2O (50 mL), dried over Na_2SO_4 and filtered. The solvents were removed to give a dark green residue which was re-dissolved in CH_2Cl_2 and filtered through a short plug of alox. The solvents were removed *in vacuo* to yield a dark green solid **17a** (22 mg, 0.011 mmol, 44%). M.p. >300 ºC; ^{1}H NMR (600 MHz, $CDCl_3$/pyridine-d_5, 10 : 1): δ = 3.86-3.93 (m, 12H, OCH_3), 6.55 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2H, H_β), 6.95 (m, 2H, aryl-*H*), 7.04 (m, 4H, C_6H_4-*H*), 7.12 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2H, H_β), 7.16 (m, 4H, C_6H_4-*H*), 7.35 (m, 2H, aryl-*H*), 7.45 (m, 4H, aryl-*H*), 7.64 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2H, H_β), 7.75 (m, 4H, C_6H_4-*H*), 8.44 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2H, H_β), 9.09-9.11 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β), 9.68-9.69 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β) ppm; UV/vis (THF): λ_{max} (log ε) = 423 (5.10), 562 (4.64), 1037 (3.94) nm.

{5-(5'-Bromo-10',20'-bis(4-methylphenyl)porphyrin-13',15',17'-ylato)-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (17b):[59] **17b** was synthesized from bromo dimer **16b** (20 mg, 0.016 mmol), DDQ (19 mg, 0.082 mmol), $Sc(OTf)_3$ (40 mg, 0.082 mmol) dissolved in toluene (25 mL) in a 100 mL Schlenk tube. The reaction was heated to 50 °C and stirred at this temperature for 3 h. THF (8 mL) was added and the reaction was stirred for a further 0.5 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 as eluent to give fraction one, which contained starting material **16b** and CH_2Cl_2 : THF (1 : 1, v/v) as eluent to give fused dimer **17b**. The solvents were removed *in vacuo* to give a dark green solid **17b** (12 mg, 0.010 mmol, 65%). M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 m, 12H, CH_3), 2.31 (m, 8H, CH_2), 2.53 (s, 6H, tolyl-CH_3), 5.44 (m, 2H, CH_2), 6.84 (m, 2H, H_β), 7.16 (m, 2H, H_β), 7.39-7.87 (m, 21H, Ph-*H*/H_β) ppm; UV/vis (THF): λ_{max} (log ε) = 422 (5.18), 565 (5.04), 965 (4.32) nm; HRMS (MALDI) *m/z* calcd. for $[C_{70}H_{53}N_8Zn_2Br](M^+)$: 1212.2159, found 1212.2200.

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Supporting Information Available. General methods including experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra, including 1D and 2D NMR spectra of compounds **10d**, **10e** and **11e** and **13a** are provided. This material is available free of charge *via* the Internet at xxxxxx.xxxx

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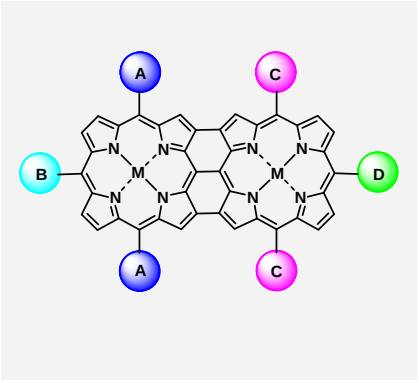
[59] The attainment of carbon spectra was not as straightforward and for dimers 10c, 10k, 17a and 17b the addition of pyridine-d^5 had a negative effect on the ^{13}C-NMR spectra as this solvent can overshadow the spectrum. Therefore for these dimers, carbon assignments were impossible to achieve.
[60] HRMS was attained but value had a *m/z* of approximately 0.9 higher than the exact mass. This could be attributed to a solubility issue of the dimer.

Entry for the Table of Contents

Layout 1:

((Key Topic))

A library of symmetric and unsymmetric singly-linked and triply-fused porphyrin dimers were synthesized in moderate to very good yields, tolerating a variety of functional groups. Numerous synthetic strategies, incorporating oxidative radical coupling, organolithium and palladium catalysed coupling methods were utilized.



(Aoife A. Ryan, Mathias O. Senge*)
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Synthesis and functionalization of triply-fused porphyrin dimers

Keywords: porphyrinoids / organolithium / C-C coupling / cycloaddition / fused ring-systems

Supporting Information

((Please insert the Supporting Information here))

SUPPORTING INFORMATION

DOI: xxxx/ejoc.xxxxxx
Title: Synthesis and functionalization of triply-fused porphyrin dimers
Author(s): Aoife A. Ryan and Mathias O. Senge*

CONTENTS

General methods

All commercial chemicals used were of analytical grade, were supplied by Sigma Aldrich and used without further purification unless otherwise stated. Anhydrous THF and diethylether distilled over sodium/benzophenone and dichloromethane dried over P_2O_5 were used. Anhydrous toluene was supplied by Acros chemicals. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ^{1}H NMR; 100.6 MHz for 13C NMR) and/or Bruker AV 600 (600 MHz for ^{1}H NMR; 150.9 MHz for ^{13}C NMR). Chemical shifts are reported in ppm referred locked on residual $CDCl_3$ solvent. The assignment of signals was confirmed by 2D spectra (COSY, HSQC) except for those porphyrins with low solubility. Photophysical measurements were performed in THF and CH_2Cl_2. UV-vis absorption measurements were performed with a Specord 250 spectrophotometer and a PerkinElmer ScanLambda 1050 for NIR measurements. HRMS spectra were measured on MaldiQ-Tof Premier Micromass and Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray ionisation source (ESI). Melting points were acquired on a Stuart SMP-10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 (fluorescence indicator F254; Merck) pre-coated aluminium sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230-400 mesh).

Experimental

General procedure A: Zinc(II) insertion: Adapting a method by Buchler *et. al*.[60] porphyrin (1 eq.) was dissolved in $CHCl_3$ (25 - 50 mL) and heated to reflux at 60 °C for 10 min. Zinc(II)acetate (5 eq.) in MeOH (1 mL) was added and the reaction heated under reflux for 30 min. Following reaction completion, solvents were removed *in vacuo* and the residue was re-dissolved in CH_2Cl_2. This solution was passed through a plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* to give a pink/purple solid.

General procedure B: Suzuki coupling for the synthesis of directly-linked dimers: A Schlenk tube was charged with bromoporphyrin (1 eq.), porphyrinyl boronate (1 eq.) and Cs_2CO_3 (2.1 eq.) and dried under high vacuum. Dry DMF (1 mL) and dry toluene (2 mL) were then added, and the mixture was degassed *via* three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (0.1 - 0.2 eq.) was then added, the flask sealed and stirred at 80 °C. The reaction was followed by TLC. Once the starting material was consumed, the reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over $MgSO_4$, evaporated to dryness, and subjected to column chromatography.

[5-Bromo-10,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) (2d): Compound **2d** was synthesized from 5-bromo-10,20-bis(3-methoxyphenyl)porphyrin (490 mg, 0.814 mmol) dissolved in $CHCl_3$ (60 mL) and zinc(II)acetate (300 mg, 0.137 mmol) dissolved in methanol (3 mL), according to standard procedure A to give a purple solid (350 mg, 0.526 mmol, 65%). M.p. = 272-275 ºC; R_f = 0.40 (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5, 20 : 1): δ = 3.99 (s, 6H, OCH_3), 7.34 (dd, $^3J_{H\text{-}H}$ = 8.3 Hz, 2.7 Hz, 2H, C_6H_4-*H*), 7.64 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, C_6H_4-*H*), 7.78 (m, 4H, C_6H_4-*H*), 9.02 (m, 4H, H_β), 9.27 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.74 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 10.09 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-d_5 20:1): δ = 55.5, 104.4, 106.2, 112.9, 113.0, 120.3, 120.8, 120.8, 127.2, 127.9, 131.8, 132.5, 132.6, 132.8, 144.4, 149.3, 150.2, 150.3, 157.8 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 417 (5.37), 550 (3.98), 592 (3.14) nm; HRMS (MALDI) *m/z* calcd. for $[C_{34}H_{23}N_4O_2ZnBr](M^+)$: 662.0296; found 662.0311.

Bis[5-phenyl-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin-15-yl] (3c): 5,15-di(3,5-di-*tert*-butyl)phenylporphyrin (60 mg, 0.087 mmol) was charged to a 250 mL Schlenk flask. THF (80 mL) was added

and the solution was degassed *via* vacuum. The flask was then cooled to 0 °C and PhLi (1.8 M in *n*-hexane, 0.29 mL, 0.524 mmol) was added dropwise. The reaction was allowed to stir at room temperature for 1 h. DDQ (113 mg, 0.348 mmol) in THF (15 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of silica using CH_2Cl_2 as eluent. The solvents were removed and the residue was recrystallized from CH_2Cl_2/MeOH to yield **3c** a dark solid (48 mg, 0.031 mmol, 74%). M.p. >300 ºC; R_f = 0.39 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.11 (s, 4H, N*H*), 1.46 (s, 72H, *t*-butyl-*H*), 7.72 (s, 4H, C_6H_3-*H*), 7.83 (m, 6H, Ph-*H*) 8.09 (m, 12 H, C_6H_3-*H*/H_β), 8.33 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 4H, Ph-*H*), 8.65 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 4H, H_β), 8.94 (s, 8H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.5, 102.6, 117.5, 120.6, 120.9, 122.2, 126.5, 127.6, 129.5, 129.8, 134.3, 140.8, 142.3, 148.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.24), 452 (5.17), 526 (4.54), 596 (4.14), 654 (3.94) nm; HRMS (MALDI) *m/z* calcd. for [$C_{108}H_{114}N_8$](M^+): 1522.9166, found 1522.9108.

{Bis[5-bromo-10,20-bis(3-methoxyphenyl)porphyrin-15-ylato]}zinc(II) (4d): 4d was synthesized from 5-bromo-10,20-(3-methoxyphenyl)porphyrinatozinc(II) **2d** (50 mg, 0.075 mmol) in CH_2Cl_2 (120 mL). PIFA (26 mg, 0.06 mmol) was added at -78 °C, the reaction mixture was warmed to rt and stirred at this temperature for 45 min. $NaBH_4$ (14 mg, 0.375 mmol) in MeOH (5 mL) was added and the reaction stirred for a further 45 min. The reaction mixture was added to H_2O (100 mL) and the organic layer was extracted using CH_2Cl_2. The organic layer was then washed with $NaHCO_3$ (2 × 50 mL), H_2O (30 mL) and dried over Na_2SO_4, which was then filtered and the solvents were removed *in vacuo*. The red residue was recrystallized from CH_2Cl_2/*n*-hexane to give a purple solid (43 mg, 0.032 mmol, 86%). M.p. >300 ºC; R_f = 0.40 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.93 (s, 12H, OC*H*$_3$), 7.23 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4-*H*), 7.57 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, C_6H_4-*H*), 7.73 (m, 4H, C_6H_4-*H*), 7.79 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, C_6H_4-*H*), 8.07 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β), 8.66 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β), 9.11 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β), 9.88 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 4H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 105.4, 113.5, 120.3, 122.3, 127.4, 127.5, 132.3, 133.2, 134.2, 143.5, 149.7, 150.0, 151.0, 155.2, 157.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.26), 455 (5.16), 562 (4.52) nm; HRMS (MALDI) *m/z* calcd. for [$C_{68}H_{44}Br_2N_8O_4Zn_2$]($M^+$): 1322.0435, found 1322.0432.

[5-Bromo-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (5b):

Produced from 5-bromo-10,20-bis(4-methylphenyl)porphyrin (275 mg, 0.482 mmol) dissolved in $CHCl_3$ (40 mL) and zinc(II)acetate (200 mg, 0.913 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (280 mg, 0.442 mmol, 92%). M.p. >300 ºC; R_f = 0.31 (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (s, 6H, tolyl-C*H*$_3$), 7.58 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, C_6H_4-*H*), 8.11 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, C_6H_4-*H*), 9.01 (t, $^3J_{H\text{-}H}$ = 4.3 Hz, 4H, H_β), 9.30 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.75 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 10.10 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 106.1, 120.7, 127.2, 131.7, 134.6, 136.9, 140.1, 149.2, 150.1, 150.5, 150.6 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 418 (5.47), 552 (4.03), 591 (3.16) nm; HRMS (MALDI) *m/z* calcd. for [$C_{34}H_{23}N_4ZnBr$](M^+): 630.0398; found 630.0387.

[5-Bromo-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato]zinc(II) (5c): Compound **5c** was synthesized from 5-bromo-10,20-bis(3-methoxyphenyl)-15-phenylporphyrin (300 mg, 0.442 mmol) dissolved in $CHCl_3$ (40 mL) and zinc(II)acetate (250 mg, 1.141 mmol) dissolved in methanol (2 mL), according to standard procedure A to give a purple solid (245 mg, 0.331 mmol, 75%). M.p. = 261-263 ºC; R_f = 0.42 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.01 (s, 6H, OC*H*$_3$), 7.34 (dd, $^3J_{H\text{-}H}$ = 8.7 Hz, 2.0 Hz, 2H, C_6H_4-*H*), 7.64 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, C_6H_4-*H*), 7.74 (m, 7H, Ph/C_6H_4-*H*), 8.17 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 2H, Ph-*H*), 8.83 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 8.88 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 8.98 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.71 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-d_5, 10:1): δ = 55.5, 103.9, 113.0, 120.6, 120.9, 121.4, 126.3,

127.1, 127.3, 127.8, 134.4, 135.2, 143.2, 144.5, 148.3, 148.8, 149.6, 157.7 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 423 (5.71), 558 (4.24), 598 (3.72) nm; HRMS (MALDI) *m/z* calcd. for $[C_{40}H_{27}N_4O_2ZnBr](M^+)$: 738.0609; found 738.0606.

[5-Bromo-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato]zinc(II) (5d): Compound **5d** was produced from 5-bromo-10,20-bis(1-ethylpropyl)-15-phenylporphyrin (300 mg, 0.495 mmol) dissolved in $CHCl_3$ (40 mL) and zinc(II)acetate (250 mg, 1.142 mmol) dissolved in methanol (2 mL), according to standard procedure A to give a purple solid (260 mg, 0.389 mmol, 79%). M.p. >300 ºC; R_f = 0.57 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 12H, C*H*$_3$), 2.81 (m, 4H, C*H*$_2$), 2.98 (m, 4H, C*H*$_2$), 5.12 (m, 2H, C*H*), 7.75 (m, 3H, Ph-*H*), 8.17 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, Ph-*H*), 8.84 (s, 2H, H_β), 9.62 (s, 2H, H_β), 9.75 (m, 4H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 35.0, 50.5, 122.6, 122.8, 123.0, 123.8, 126.2, 127.2, 129.6, 130.0, 130.5, 131.7, 132.3, 134.3, 143.9, 147.4, 149.7, 152.6 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 423 (5.65), 561 (4.15), 605 (3.85) nm; HRMS (MALDI) *m/z* calcd. for $[C_{36}H_{35}N_4ZnBr](M^+)$: 666.1337; found 666.1312.

[5,15-Bis(3-methoxyphenyl)-10-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-20-phenylporphyrinato]zinc(II) (6c): Borylated porphyrin **6c** was synthesized adapting a procedure by Therien *et. al*.[38a] Bromoporphyrin **5c** (150 mg, 0.202 mmol) and $Pd(PPh_3)_4$ (7 mg, 0.010 mmol) were charged to a Schlenk flask and dried under high vacuum. 1,2-Dichloroethane (10 mL) and NEt_3 (0.6 mL) were then added and the solution was degassed *via* three freeze-pump-thaw cycles, before the flask was purged with argon. Pinacolborane (0.25 mL, 1.700 mmol) was then added and the flask was sealed and stirred at 90 °C. The reaction was followed by TLC using CH_2Cl_2:*n*-hexane (2:1, v/v). Once the starting material was consumed, the reaction was quenched with a saturated KCl solution (10 mL), washed with water, and dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was subjected to column chromatography using CH_2Cl_2: *n*-hexane (1:1, v/v) yielding **6c**. The solvents were removed *in vacuo* give a purple solid (89 mg, 0.113 mmol, 56%). M.p. >300 ºC; R_f = 0.31 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 12H, C*H*$_3$), 3.95 (s, 6H, OC*H*$_3$), 7.30 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, C_6H_4-*H*), 7.67 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, C_6H_4-*H*), 7.77 (m, 5H, Ph/C_6H_4-*H*) 7.86 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, C_6H_4-*H*) 8.25 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, Ph-*H*), 8.99 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.02 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.16 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.96 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 55.5, 85.3, 113.5, 120.3, 120.7, 126.5, 127.3, 127.5, 127.7, 131.5, 132.1, 132.8, 133.0, 134.4, 142.8, 144.2, 149.9, 150.3, 154.5, 157.8 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 419 (5.58), 551 (4.17), 591 (3.39) nm; HRMS (MALDI) *m/z* calcd. for $[C_{46}H_{39}N_4O_4ZnB](M^+)$: 786.2356; found 786.2351.

[5,10,15-Trihexyl-20-(10',20'-diphenylporphyrin-5'-yl)porphyrinato]zinc(II) (7a): Compound **7a** was synthesized from **5a** (43 mg, 0.061 mmol), **6d** (40 mg, 0.061 mmol), Cs_2CO_3 (45 mg, 0.139 mmol) and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), DMF (3 mL) and toluene (7 mL) following general procedure B to give a purple solid. Yield = 39 mg (0.034 mmol, 52%). M.p. >300 ºC; R_f = 0.53 (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 9H, C*H*$_3$), 1.38 (m, 6H, C*H*$_2$), 1.59 (m, 6H, C*H*$_2$), 1.85 (m, 6H, C*H*$_2$), 2.57 (m, 6H, C*H*$_2$), 4.83 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, C*H*$_2$), 4.90 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 4H, C*H*$_2$), 7.72 (m, 6H, Ph-*H*), 8.08 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 8.22 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 8.30 (m, 4H, Ph-*H*), 8.75 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.17 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.22 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.43 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.51 (m, 4H, H_β), 10.38 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.7, 22.8, 28.7, 30.4, 31.9, 32.0, 35.5, 35.8, 38.9, 39.1, 117.6, 119.4, 121.1, 121.4, 126.6, 127.4, 128.5, 128.6, 128.7, 128.8, 129.1, 129.2, 131.4, 131.8, 132.5, 134.0, 134.1, 134.5, 142.6, 148.5, 148.9, 149.4, 149.8, 150.1, 150.6, 154.4, 154.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.33), 450 (5.10), 559 (4.37) nm; HRMS (MALDI) *m/z* calcd. for $[C_{70}H_{66}N_8Zn_2](M^+)$: 1146.3993, found 1146.4038.

[5-(10',15',20'-Triphenylporphyrin-5'-ylato)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (7b): Compound **7b** was synthesized from bromo-porphyrin **5b** (70 mg, 0.110 mmol), borylated porphyrin **6a** (80 mg, 0.110 mmol), Cs_2CO_3 (90 mg, 0.275 mmol) and $Pd(PPh_3)_4$ (19 mg, 0.017 mmol), DMF (4 mL) and toluene (10 mL) following general procedure B. The residue was subjected to column chromatography (silica gel, CH_2Cl_2 : *n*-hexane, 2 : 3, v/v) to give two fractions. The first fraction contained a mixture of debrominated **5b** and deborylated **6a**, the second (red fraction) was dimer **7b**. Solvents were removed to give a purple solid. Yield = 97 mg (0.084 mmol, 76%). M.p. >300 ºC; R_f = 0.58 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5 10:1): δ = 2.64 (s, 6H, tolyl-C*H*$_3$), 7.48 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 4H, C_6H_4-*H*), 7.64 (m, 9H, Ph-*H*), 7.80 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 7.86 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 8.13 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 4H, C_6H_4-*H*), 8.21 (m, 6H, Ph-*H*), 8.50 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 8.60 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 8.92 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 8.95 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.10 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 9.41 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 10.24 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-d_5 10:1): δ = 22.7, 105.9, 119.9, 120.8, 121.1, 121.3, 126.2, 126.3, 127.0, 127.2, 131.2, 131.4, 131.6, 132.0, 133.5, 133.6, 134.5, 134.6, 136.6, 140.4, 143.5, 143.7, 149.5, 149.6, 149.7, 150.0, 150.4, 150.6, 154.5, 154.9, 155.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.16), 449 (5.18), 555 (4.53) nm; HRMS (MALDI) *m/z* calcd. for $[C_{72}H_{46}N_8Zn_2](M^+)$: 1150.2428, found 1150.2389.

{5-[10',20'-Bis(3-methoxyphenyl)porphyrin-15'-ylato]-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato}zinc(II) (7c): Compound **7c** was synthesized from bromoporphyrin **2d** (71 mg, 0.097 mmol), borylated porphyrin **6c** (80 mg, 0.102 mmol), Cs_2CO_3 (70 mg, 0.214 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), DMF (3 mL) and toluene (10 mL) following general procedure B**.** The residue was subjected to column chromatography (silica, CH_2Cl_2: *n*-hexane, 2:1, v/v) to give two fractions. Fraction one consisted of debrominated and deborylated starting materials. The red second fraction yielded dimer **7c**. The solvents were removed *in vacuo* to give a purple solid (71 mg, 0.057 mmol, 56%). M.p. >300 ºC; R_f = 0.39 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 8H, OC*H*$_3$), 3.95 (s, 4H, OC*H*$_3$) 7.23 (m, 2H, C_6H_4-*H*), 7.25 (m, 2H, C_6H_4-*H*), 7.58 (m, 4H, C_6H_4-*H*), 7.84 (m, 11H, Ph/C_6H_4-*H*), 8.12 (m, 4H, H_β), 8.33 (m, 2H, Ph-*H*), 8.72 (m, 2H, H_β), 8.78 (m, 2H, H_β), 9.06 (m, 4H, H_β), 9.22 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.52 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 10.42 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.5, 106.7, 113.4, 113.5, 119.6, 120.1, 120.3, 121.2, 121.7, 121.9, 126.6, 127.3, 127.4, 127.5, 127.6, 131.9, 132.0, 132.5, 133.9, 134.5, 142.9, 143.9, 144.0, 149.7, 149.9, 150.2, 150.6, 154.6, 155.0, 157.8, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.32), 455 (5.14), 558 (4.36) nm; HRMS (MALDI) *m/z* calcd. for $[C_{74}H_{50}N_8O_4Zn_2](M^+)$: 1242.2538, found 1242.2524.

{5-[10',20'-Bis(4-methylphenyl)porphyrin-15'-ylato]-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (7d): Compound **7d** was synthesized from bromoporphyrin **5d** (76 mg, 0.114 mmol), borylated porphyrin **6b** (78 mg, 0.114 mmol), Cs_2CO_3 (78 mg, 0.239 mmol) and $Pd(PPh_3)_4$ (13 mg, 0.011 mmol), DMF (3 mL) and toluene (10 mL) following general procedure B. After 20 h at 90 °C, the solvents were removed and the residue was filtered through short plug of silica using CH_2Cl_2 as eluent. The solvents were removed *in vacuo* and the residue was subjected to column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1:2, v/v) to give three fractions. Fraction three yielded the desired dimer **7d**. The solvents were removed *in vacuo* to give a purple solid **7d** (69 mg, 0.060 mmol, 53%). M.p. >300 ºC; R_f = 0.45 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 12H, C*H*$_3$), 2.66 (s, 6H, tolyl-C*H*$_3$), 2.80 (m, 8H, C*H*$_2$), 5.03 (m, 1H, C*H*), 5.14 (m, 1H, C*H*), 7.52 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 4H, C_6H_4-*H*), 7.84 (m, 3H, Ph-*H*), 8.10 (m, 2H, H_β), 8.17 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 6H, Ph/C_6H_4-*H*), 8.32 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, H_β), 8.77 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2H, H_β), 9.04 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2H, H_β), 9.22 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.43 (m, 2H, H_β), 9.53 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.77 (m, 2H, H_β), 10.60 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.4, 21.5, 22.7, 29.7, 31.6, 34.7, 50.6, 106.5, 121.5, 125.0, 126.5, 127.3, 127.5, 130.0, 131.8, 131.9,

132.5, 134.0, 134.4, 137.1, 139.7, 143.5, 149.8, 150.0, 150.8, 154.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.42), 454 (5.37), 560 (4.64) nm; HRMS (MALDI) *m/z* calcd. for $[C_{70}H_{58}N_8Zn_2](M^+)$: 1138.3367, found 1138.3351.

{5-[10',20'-Bis(4-methylphenyl)porphyrin-5'-ylato]-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato}zinc(II) (7e): Compound **7e** was produced from bromoporphyrin **5c** (98 mg, 0.132 mmol), borylated porphyrin **6b** (90 mg, 0.132 mmol), Cs_2CO_3 (107 mg, 0.330 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol), DMF (3 mL) and toluene (12 mL) following general procedure B. The residue was subjected to column chromatography (silica, CH_2Cl_2 : *n*-hexane, 2:3, v/v) to give three fractions. Fraction one was starting material **5c**, fraction two was dimer **8b** (20%) and fraction three yielded the desired dimer. The solvents were removed *in vacuo* to give a purple solid **7e** (97 mg, 0.080 mmol, 61%). M.p. >300 ºC; R_f = 0.54 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (s, 6H, tolyl-C*H*$_3$), 3.88 (s, 6H, OC*H*$_3$), 7.22 (dd, $^3J_{H\text{-}H}$ = 8.6, 2.1 Hz, 2H, C_6H_4-*H*), 7.52 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, C_6H_4(tolyl)-*H*), 7.56 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, C_6H_4-*H*), 7.78 (m, 7H, Ph/C_6H_4-*H*), 8.11 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 8.15 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 6H, C_6H_4(tolyl)/H_β), 8.33 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, Ph-*H*), 8.72 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 8.77 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 9.05 (m, 4H, H_β), 9.19 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 2H, H_β), 9.49 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2H, H_β), 10.37 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$/pyridine-d_5): δ = 21.5, 55.4, 106.6, 113.4, 120.2, 120.4, 126.5, 127.3, 127.5, 127.6, 131.8, 133.8, 134.0, 134.3, 134.5, 137.1, 139.6, 143.7, 144.0, 149.7, 149.8, 149.9, 150.3, 150.5, 150.7, 150.8, 154.5, 155.0, 157.8, 157.9, 127.6, 131.9, 132.0, 132.2, 132.9, 134.0, 134.4, 134.5, 142.7, 142.9, 143.9, 149.7, 149.8, 149.9, 150.2, 150.6, 150.7, 154.7, 155.0, 157.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.54), 454 (5.32), 550 (4.68) nm; HRMS (MALDI) *m/z* calcd. for $[C_{74}H_{50}N_8O_2Zn_2](M^+)$: 1210.2640, found 1210.2672.

{5-(10',20'-Bis(3-methoxyphenyl)porphyrin-15-phenyl-5'-ylato)-10,15,20-triphenyl)porphyrinato}zinc(II) (7f): Compound **7f** was synthesized from bromoporphyrin **5c** (102 mg, 0.137 mmol), borylated porphyrin **6a** (100 mg, 0.137 mmol), Cs_2CO_3 (98 mg, 0.301 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), DMF (3 mL) and toluene (12 mL) following general procedure B**.** The residue was subjected to column chromatography (silica, CH_2Cl_2 : *n*-hexane, 5 : 4, v/v) to give two fractions. Fraction one consisted of debrominated starting material **5c** and homocoupled dimer **8a** (18%). The red second fraction yielded dimer **7f**. The solvents were removed *in vacuo* to give a purple solid (120 mg, 0.095 mmol, 69%). M.p. >300 ºC; R_f = 0.36 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (d, $^3J_{H\text{-}H}$ = 1.8 Hz, 6H, OC*H*$_3$), 7.24 (dd, $^3J_{H\text{-}H}$ = 11.2 Hz, 2H, C_6H_4-*H*), 7.54 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, C_6H_4-*H*), 7.77 (m, 16H, Ph/C_6H_4-*H*), 8.22 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β) 8.28 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 8.25 (m, 6H, Ph-*H*), 8.35 (m, 2H, C_6H_4-*H*), 8.73 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.02 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.08 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.21 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.50 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.76 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.4, 113.5, 120.2, 120.4, 126.5, 126.6, 127.4, 128.3, 131.0, 131.9, 132.0, 133.9, 134.4, 142.7, 142.9, 143.8, 144.0, 149.7, 150.2, 150.3, 150.6, 150.7, 154.9, 155.0, 157.8, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.20), 455 (5.02), 559 (4.41) nm; HRMS (MALDI) *m/z* calcd. for $[C_{78}H_{50}N_8O_2Zn_2](M^+)$: 1258.2640, found 1258.2618.

[Bis-5,15-bis(4-methylphenyl)porphyrin-15-ylato]zinc(II) (8b): Compound **8b** was synthesized as side product in the synthesis of **7e**. Dimer **8b** was isolated following column chromatography (silica, CH_2Cl_2 : *n*-hexane, 2 : 3, v/v) as the second fraction. The solvents removed to give red solid **8b** (31 mg, 0.028 mmol, 20%). M.p. >300 ºC; R_f = 0.45 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-D_5, 20:1): δ = 2.58 (s, 12H, tolyl-C*H*$_3$), 7.43 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 8H, C_6H_4-*H*), 7.79 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 4H, H_β), 8.08 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 8H, C_6H_4-*H*), 8.54 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 4H, H_β), 9.06 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 4H, H_β), 9.36 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 4H, H_β), 10.2 (s, 2H, H_{meso}) ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.29), 446 (5.32), 552 (4.69) nm; HRMS (MALDI) *m/z* calcd. for $[C_{68}H_{46}N_8Zn_2](M^+)$: 1102.2428, found 1102.2433.

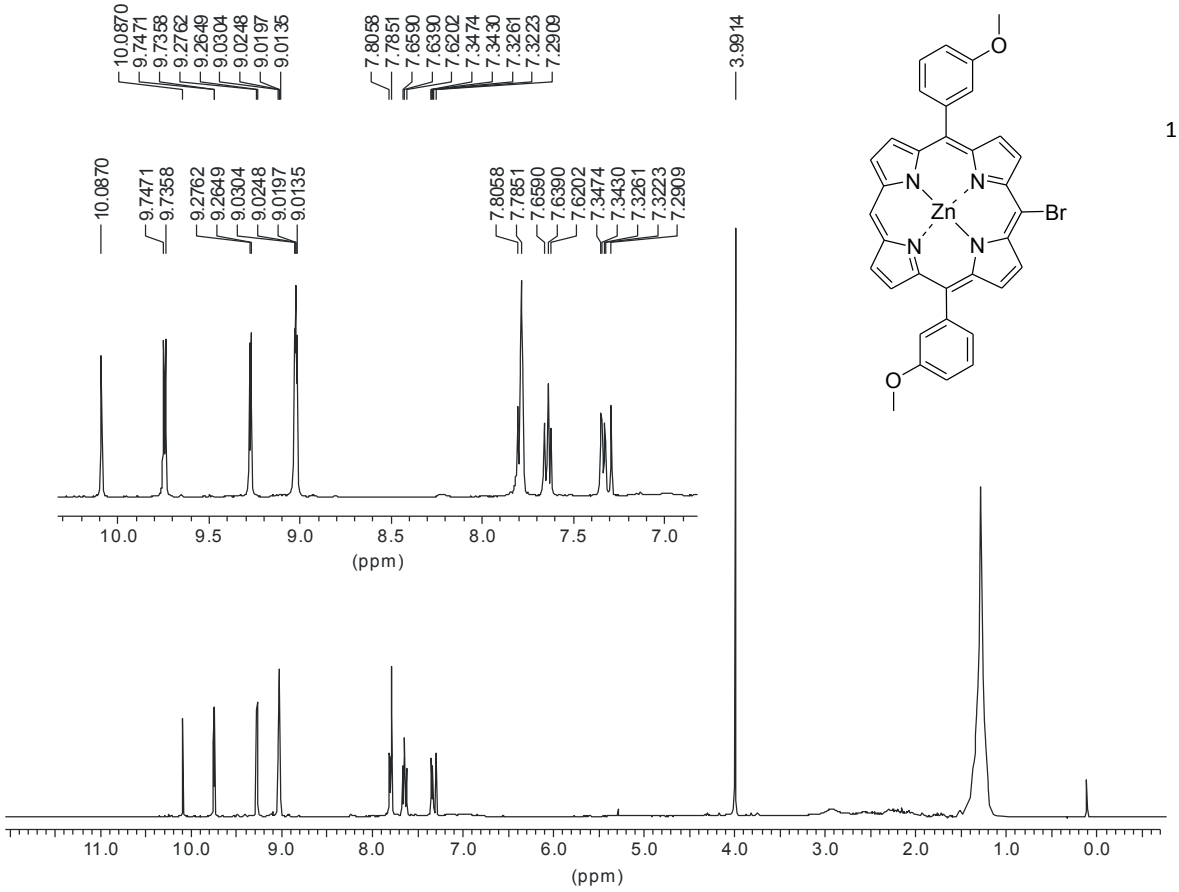
[5,15-Bis(3,5-di-*tert*-butyl-phenyl)-10-(4-nitrophenyl)porphyrinato]zinc(II) (9b): A Schlenk flask was charged with K_3PO_4 (165 mg, 0.780 mmol) and anhydrous THF (20 mL) under an argon atmosphere, then {5,15-bis(3,5-di-*tert*-butyl-phenyl)-10-bromoporphyrinato}zinc(II) (65 mg, 0.078 mmol), 4-nitrophenyl boronic pinacol ester (78 mg, 0.314 mmol) and $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) were added and the solution was degassed *via* three freeze-pump-thaw cycles. The reaction was heated to reflux for 7-10 hours (TLC control) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. This mixture was washed with saturated $NaHCO_3$, H_2O, and brine, and then dried over Na_2SO_4. The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallization from CH_2Cl_2/MeOH to give the desired compound **9b** in a yield of 52 mg (0.060 mmol, 77 %) of a purple solid following filtration through a plug of silica using CH_2Cl_2 as eluent. M.p. = 189-191 ºC; R_f = 0.54 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 36H, *t*-butyl-*H*), 7.86 (t, $^3J_{H\text{-}H}$ = 1.8 Hz, 2H, Ar-*H*), 8.14 (d, $^3J_{H\text{-}H}$ = 1.8 Hz, 4H, Ar-*H*), 8.43 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, C_6H_4-*H*), 8.66 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, C_6H_4-*H*), 8.90 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.12 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.20 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.47 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 10.36 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.8, 106.6, 121.0, 121.6, 124.4, 128.3, 129.9, 130.9, 132.0, 132.9, 133.2, 135.0, 146.7, 150.0 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 418 (5.39), 550 (4.08), 591 (3.28) nm; HRMS (MALDI) *m/z* calcd. for [$C_{54}H_{55}N_5O_2Zn_2$] (M^+): 869.3647, found 869.3654.

[5-(*n*-Butyl)-10,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) (9c): Compound **9c** was synthesized from 5-(*n*-butyl)-10,20-bis(3-methoxyphenyl)porphyrin (30 mg, 0.052 mmol) dissolved in $CHCl_3$ (25 mL) and zinc(II)acetate (30 mg, 0.137 mmol) dissolved in methanol (2 mL), according to standard procedure A to give a purple solid (29 mg, 0.046 mmol, 88%). M.p. = 191-194 ºC; R_f = 0.37 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 3H, C*H*$_3$), 1.90 (m, 2H, C*H*$_2$), 2.61 (m, 2H, C*H*$_2$), 4.02 (s, 6H, OC*H*$_3$), 2.64 (s, 12H, tolyl-C*H*$_3$), 5.12 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, C*H*$_2$), 7.36 (dd, $^3J_{H\text{-}H}$ = 3.2, 1.8 Hz, 1H, C_6H_4-*H*), 7.38 (dd, $^3J_{H\text{-}H}$ = 3.2, 1.8 Hz, 1H, C_6H_4-*H*), 7.68 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, C_6H_4-*H*), 7.81 (m, 2H, C_6H_4-*H*), 7.87 (m, 2H, C_6H_4-*H*), 9.09 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β) 9.12 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.34 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 9.64 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 10.14 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 23.8, 35.7, 41.3, 55.5, 105.2, 113.4, 119.7, 120.4, 122.1, 127.3, 127.6, 128.9, 131.5, 132.1, 132.6, 144.2, 149.5, 149.7, 150.1, 157.9 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 416 (5.56), 550 (4.14), 589 (3.30) nm; HRMS (MALDI) *m/z* calcd. for [$C_{38}H_{32}N_4O_2Zn$](M^+): 640.1817; found 640.1849.

[5,10,15-Tris(3-methoxyphenyl)porphyrinato]zinc(II) (9d): Compound **9d** was synthesized from 5,10,15-tris(3-methoxyphenyl)porphyrin (80 mg, 0.127 mmol) dissolved in $CHCl_3$ (25 mL) and zinc(II)acetate (80 mg, 0.365 mmol) dissolved in methanol (2 mL), according to standard procedure A to give a purple solid (82 mg, 0.119 mmol, 94%). M.p. = 162-165 ºC; R_f = 0.17 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 6H, OC*H*$_3$), 4.09 (s, 3H, OC*H*$_3$), 7.27 (s, 2H, C_6H_4-*H*), 7.34 (dd, $^3J_{H\text{-}H}$ = 2.2 Hz, 2H, C_6H_4-*H*), 7.68 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, C_6H_4-*H*), 7.81 (s, 2H, C_6H_4-*H*), 7.86 (d, $^3J_{H\text{-}H}$ = 7.4 Hz, 2H, C_6H_4-*H*), 8.14 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, C_6H_4-*H*), 9.02 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.05 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.14 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 9.39 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H_β), 10.23 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.5, 55.6, 105.8, 112.0, 113.4, 120.3, 120.4, 127.4, 127.7, 131.7, 131.8, 132.1, 132.6, 135.4, 144.1, 149.9, 150.0, 150.2, 157.9, 159.2 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.27), 543 (4.09), 579 (3.50) nm; HRMS (MALDI) *m/z* calcd. for [$C_{41}H_{30}N_4O_3Zn$](M^+): 690.1609; found 690.1629.

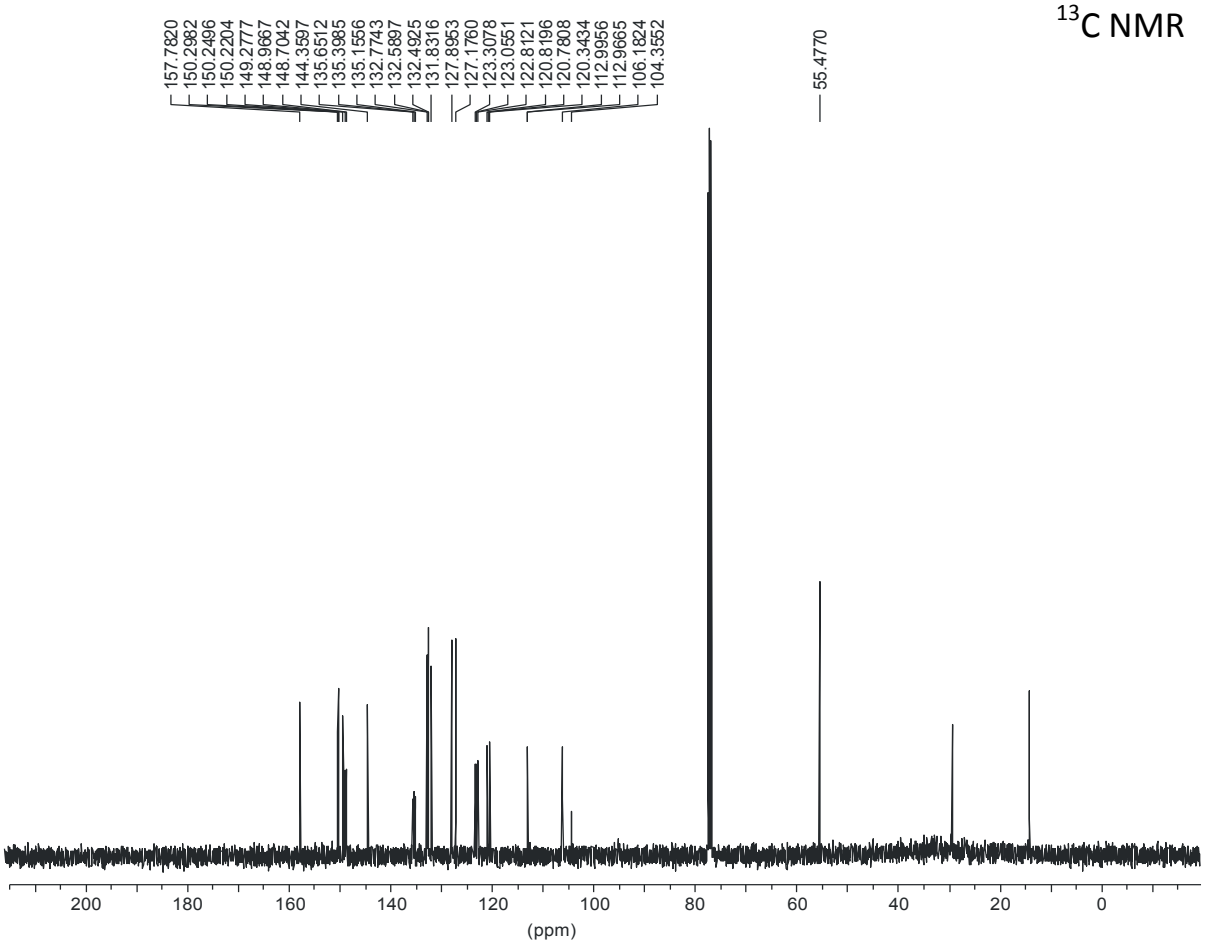
[5-(*n*-Butyl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (9g): Compound **9g** was synthesized from 5-(*n*-butyl-10,20-bis(4-methylphenyl)porphyrin (150 mg, 0.259 mmol) dissolved in $CHCl_3$ (25 mL) and

zinc(II)acetate (150 mg, 0.685 mmol) dissolved in methanol (2 mL), according to standard procedure A to give a purple solid (148 mg, 0.243 mmol, 94%). M.p. = 284 ºC; R_f = 0.33 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 3H, C*H*$_3$), 1.88 (m, 2H, C*H*$_2$), 2.77 (s, 6H, C_6H_4-C*H*$_3$), 5.08 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, C*H*$_2$), 7.61 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, C_6H_4-*H*), 8.13 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, C_6H_4-*H*), 9.07 (m, 4H, H_β), 9.30 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 2H, H_β), 9.61 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 2H, H_β), 10.09 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.3, 21.6, 23.8, 35.7, 41.3, 105.0, 119.9, 121.9, 127.3, 128.7, 131.3, 132.1, 132.5, 134.5, 137.0, 140.1, 149.7, 149.8, 149.9, 150.0 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 416 (5.61), 550 (4.18), 590 (3.54) nm; HRMS (MALDI) *m/z* calcd. for $[C_{38}H_{32}N_4Zn](M^+)$: 608.1918; found 608.1938



^{1}H NMR

2d



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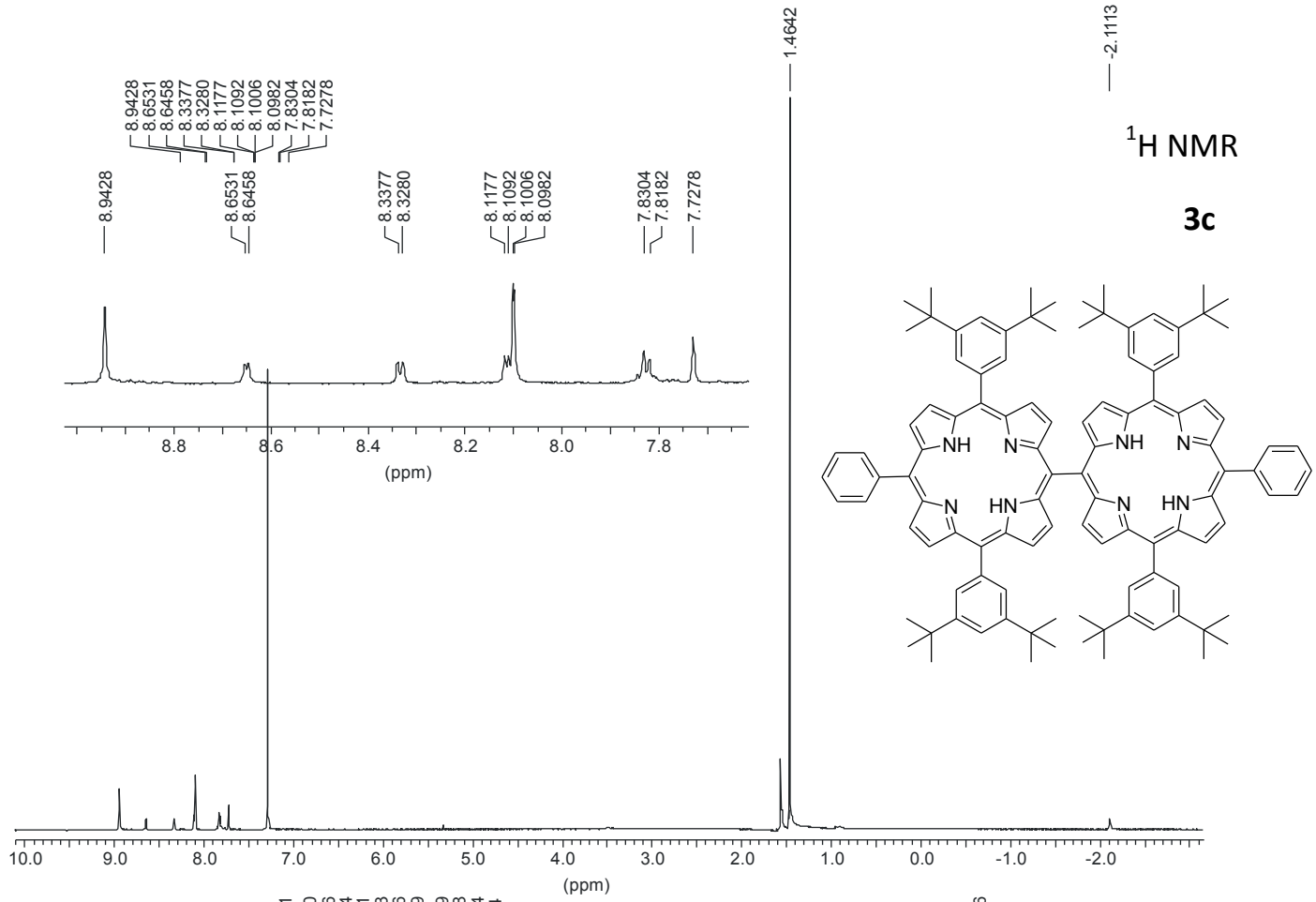
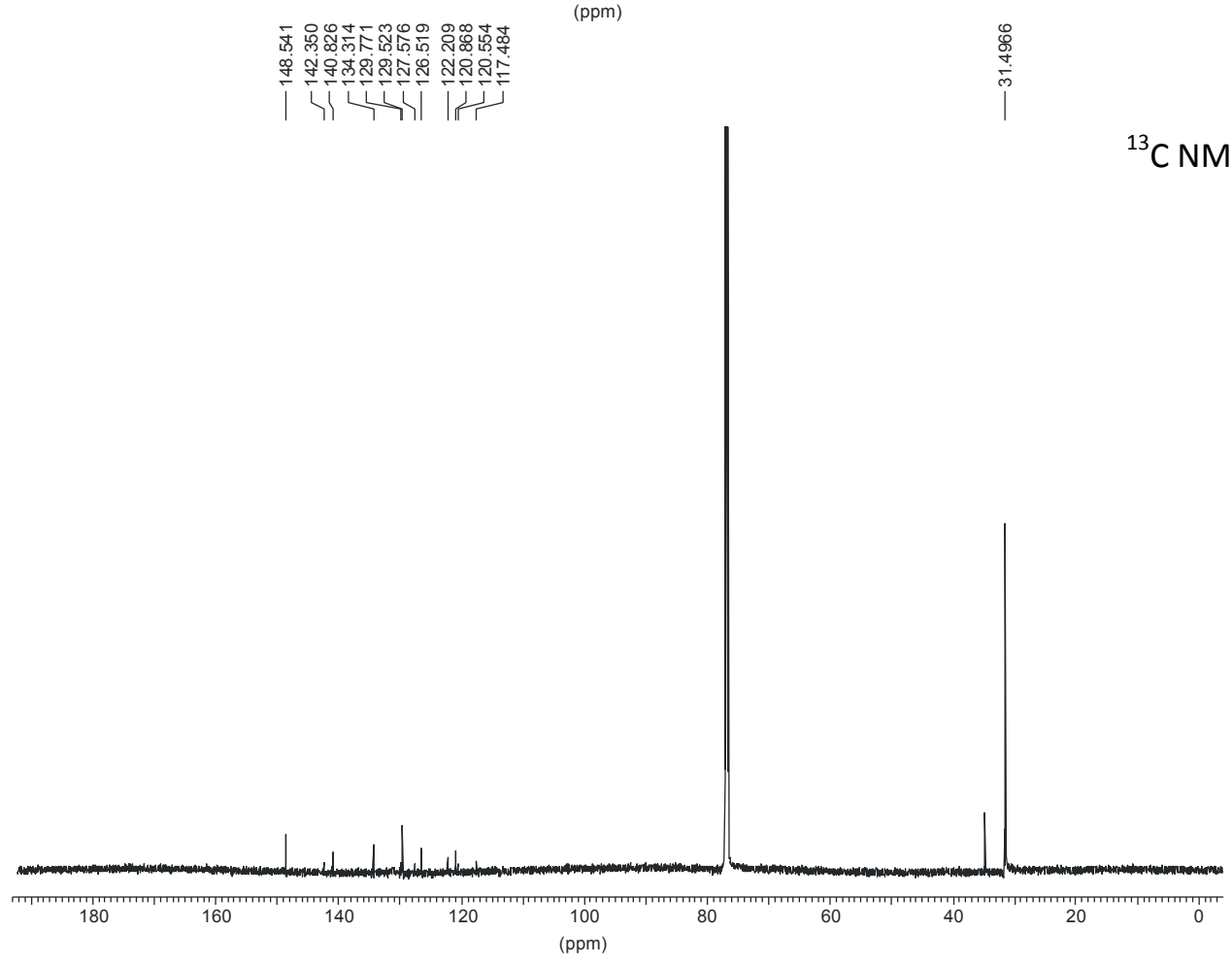


^{1}H NMR

3c



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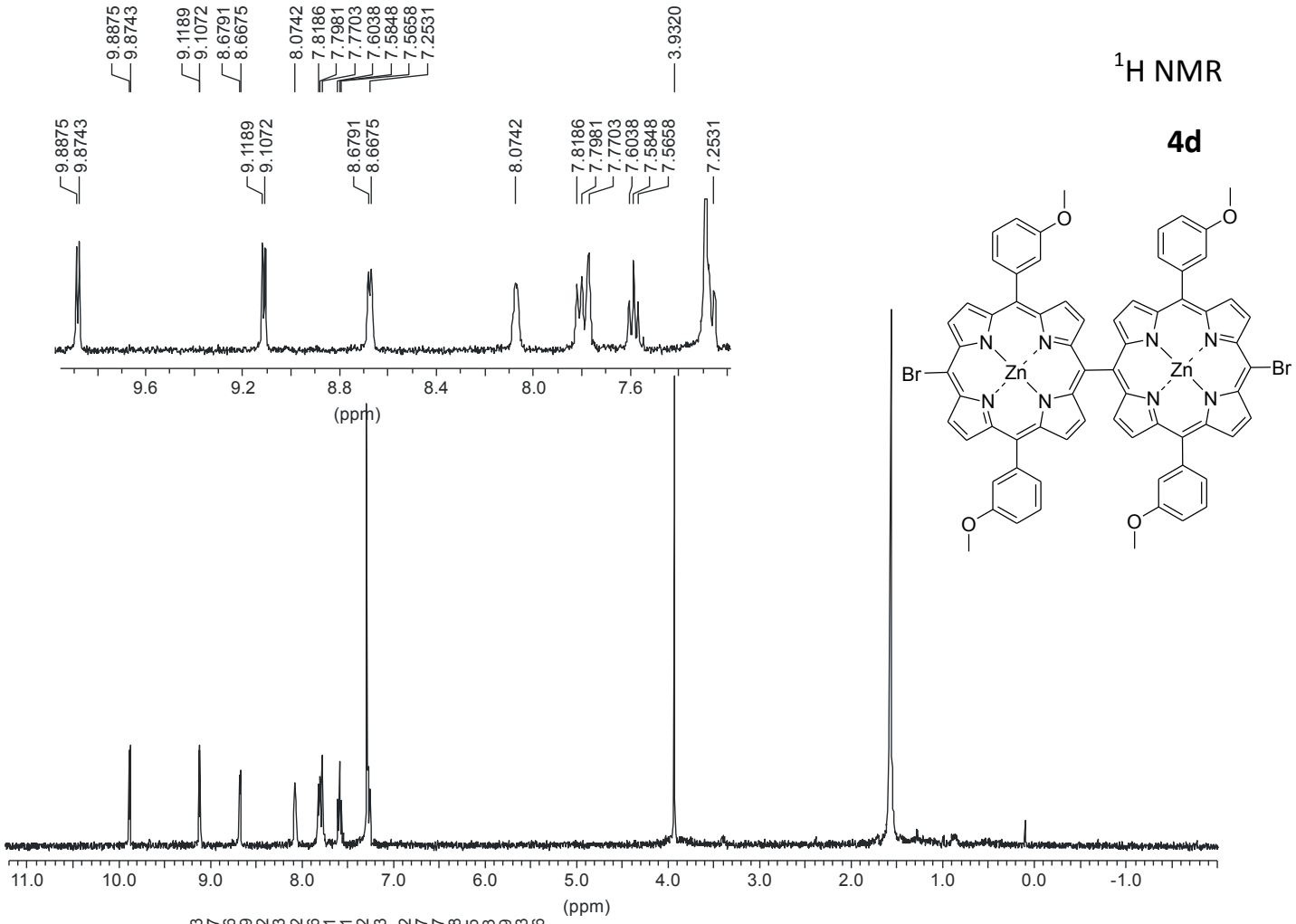

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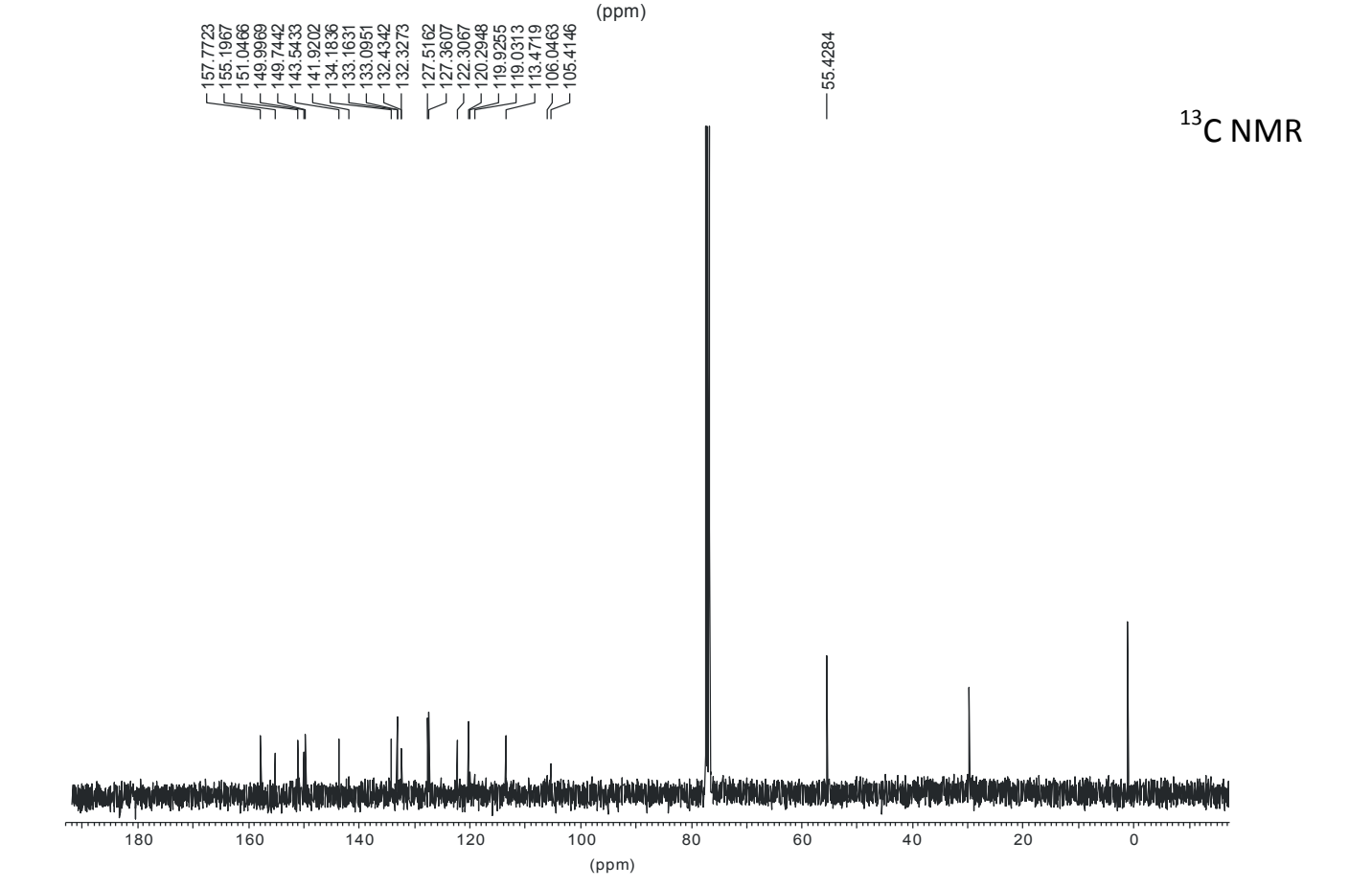
4d



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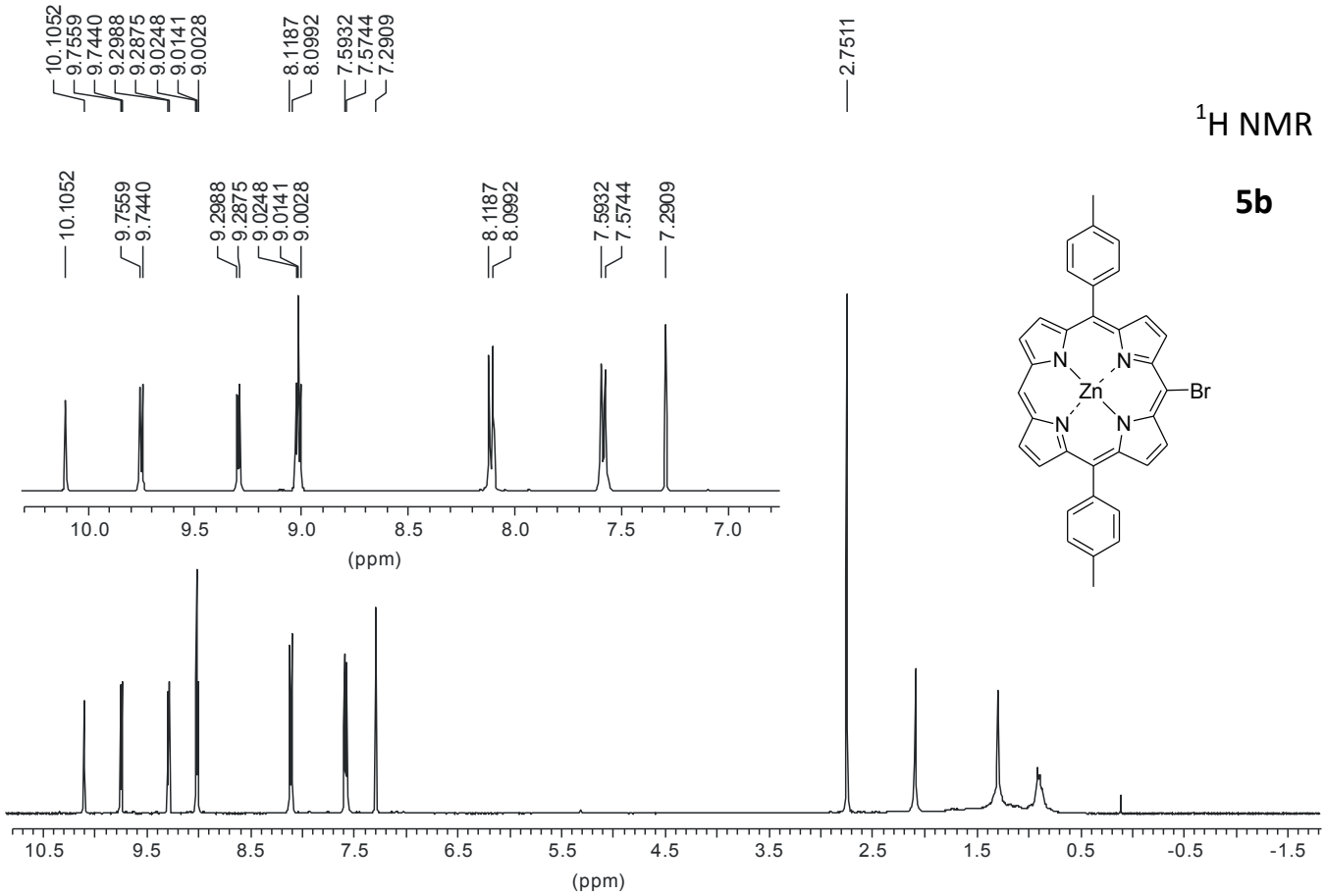
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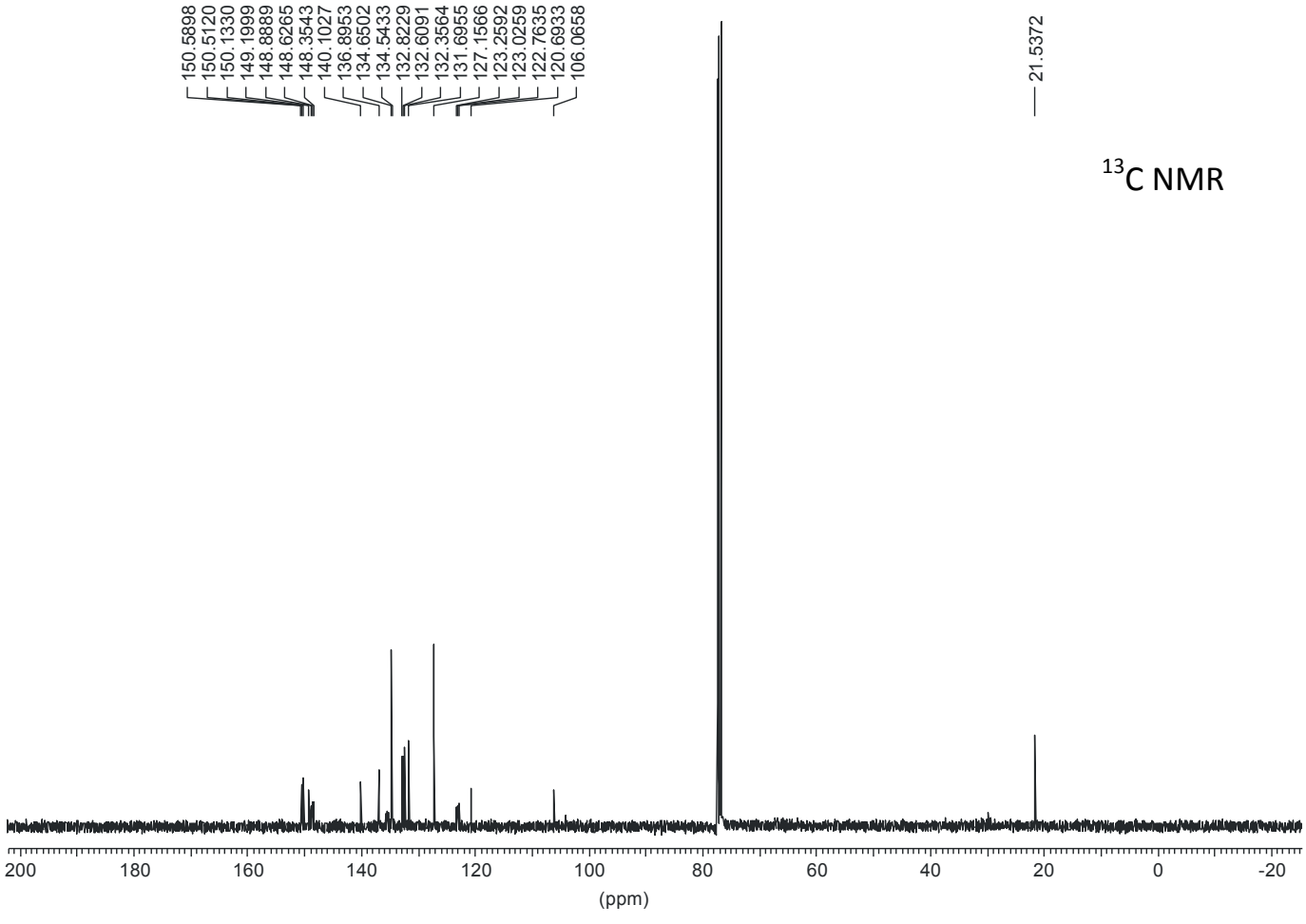
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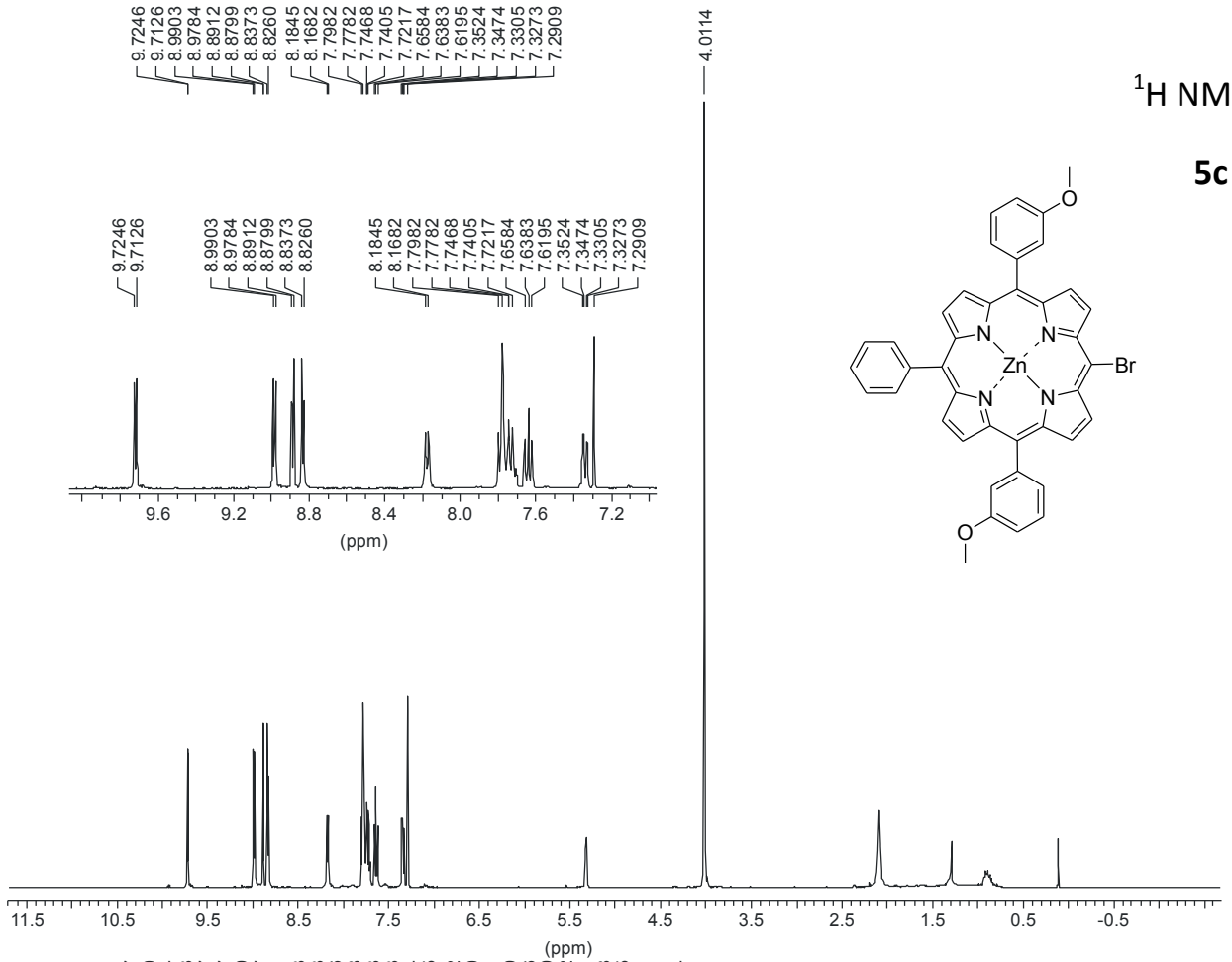
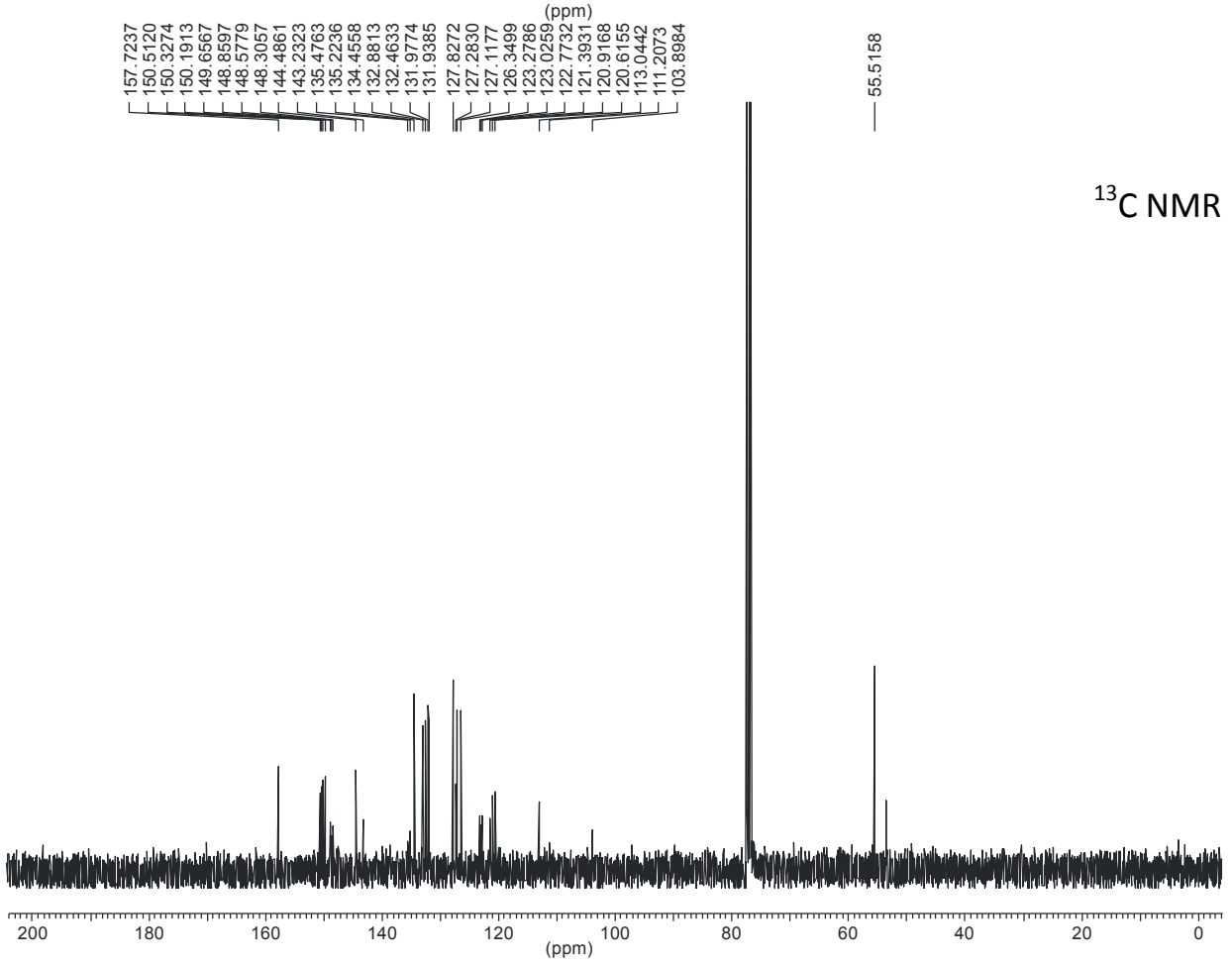


^{1}H NMR

5c



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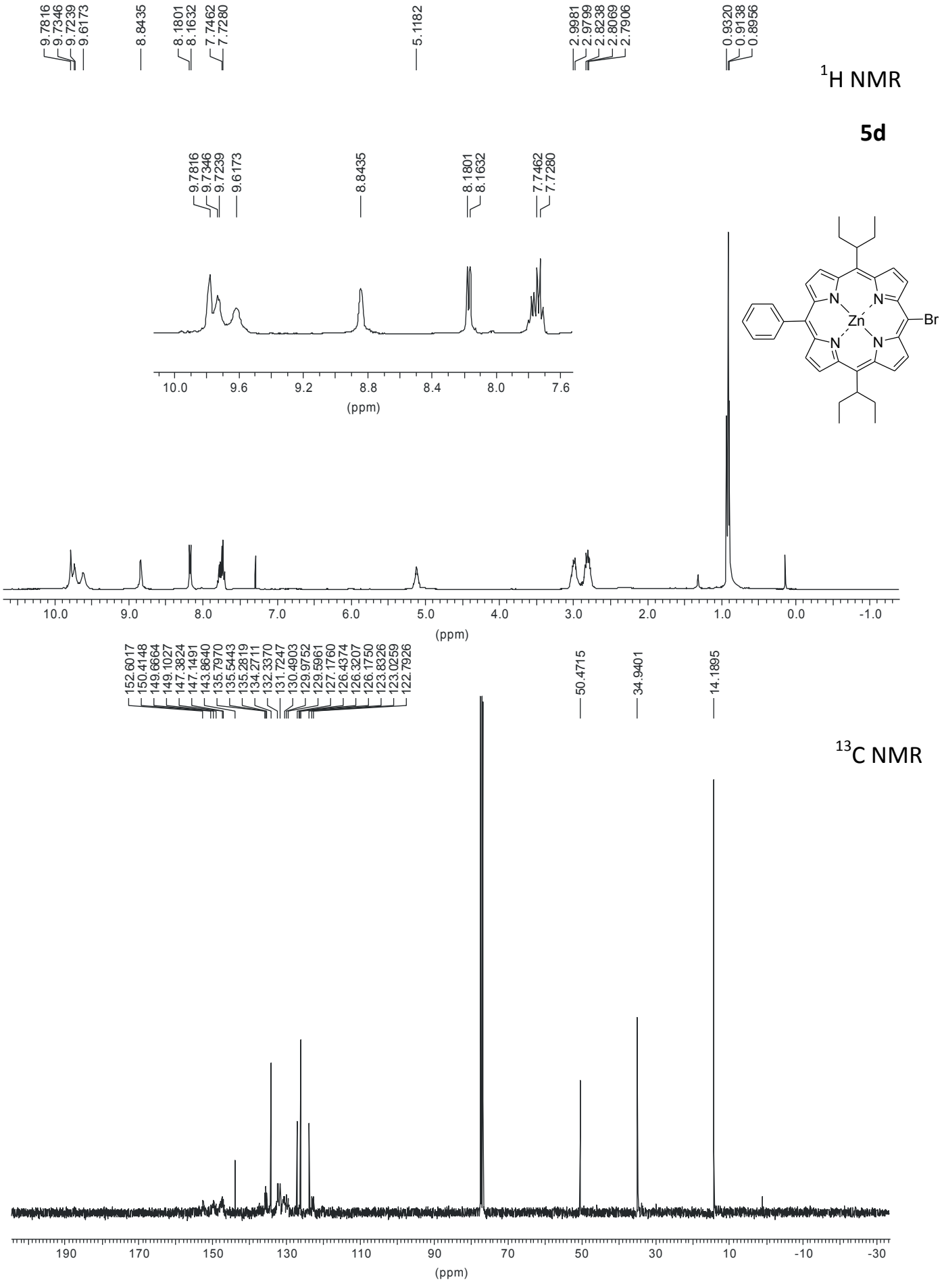
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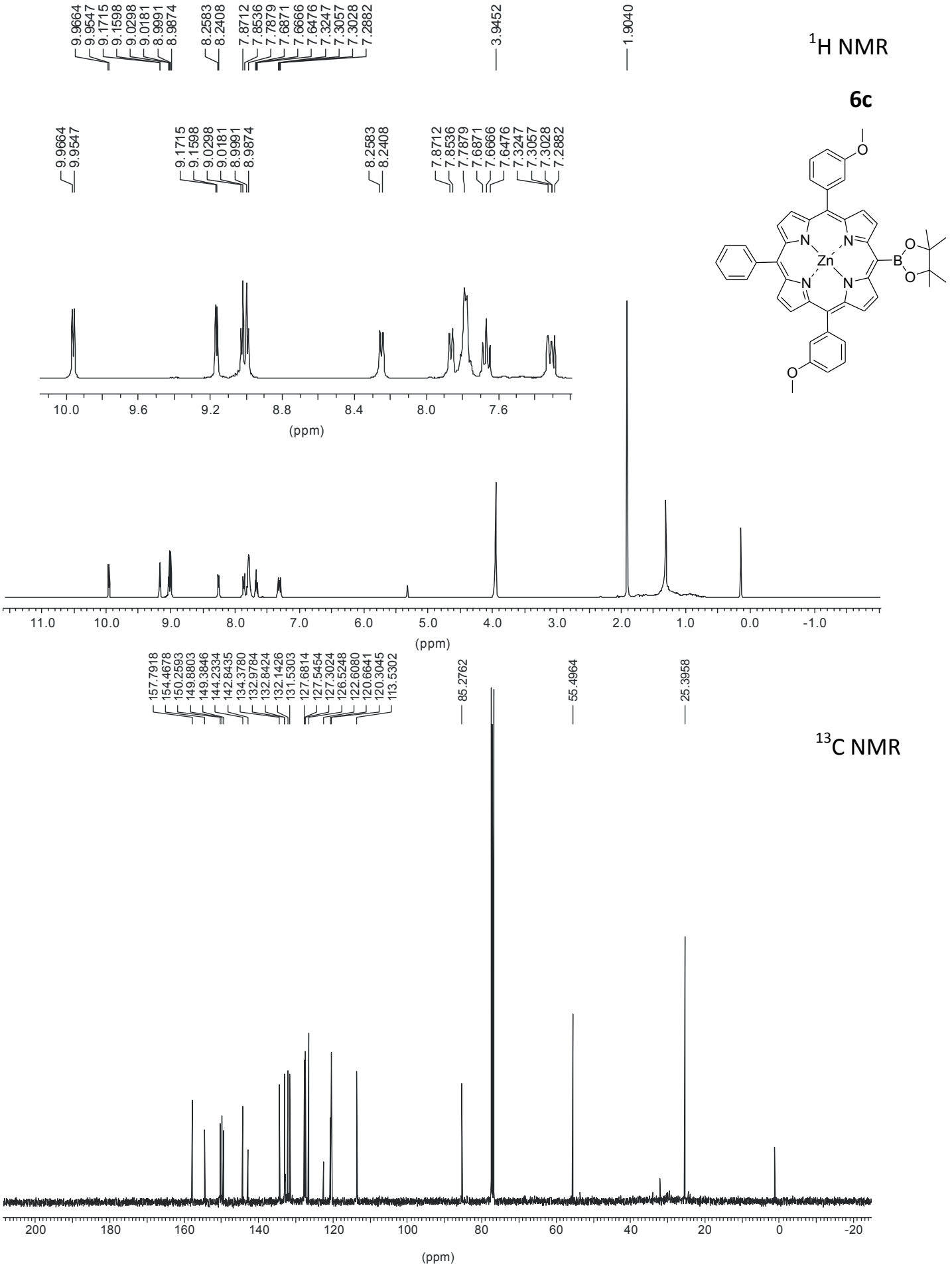
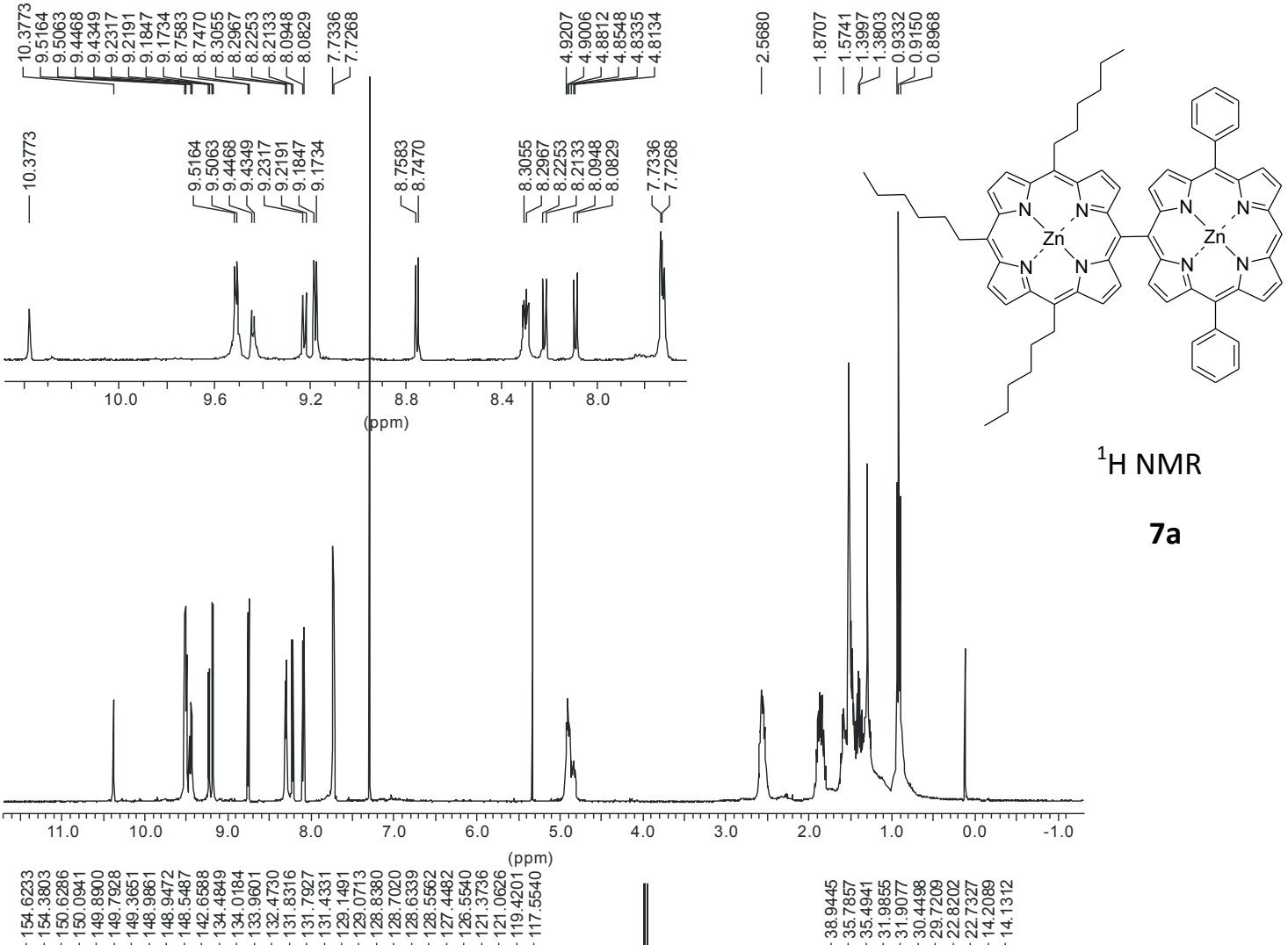


^{1}H NMR

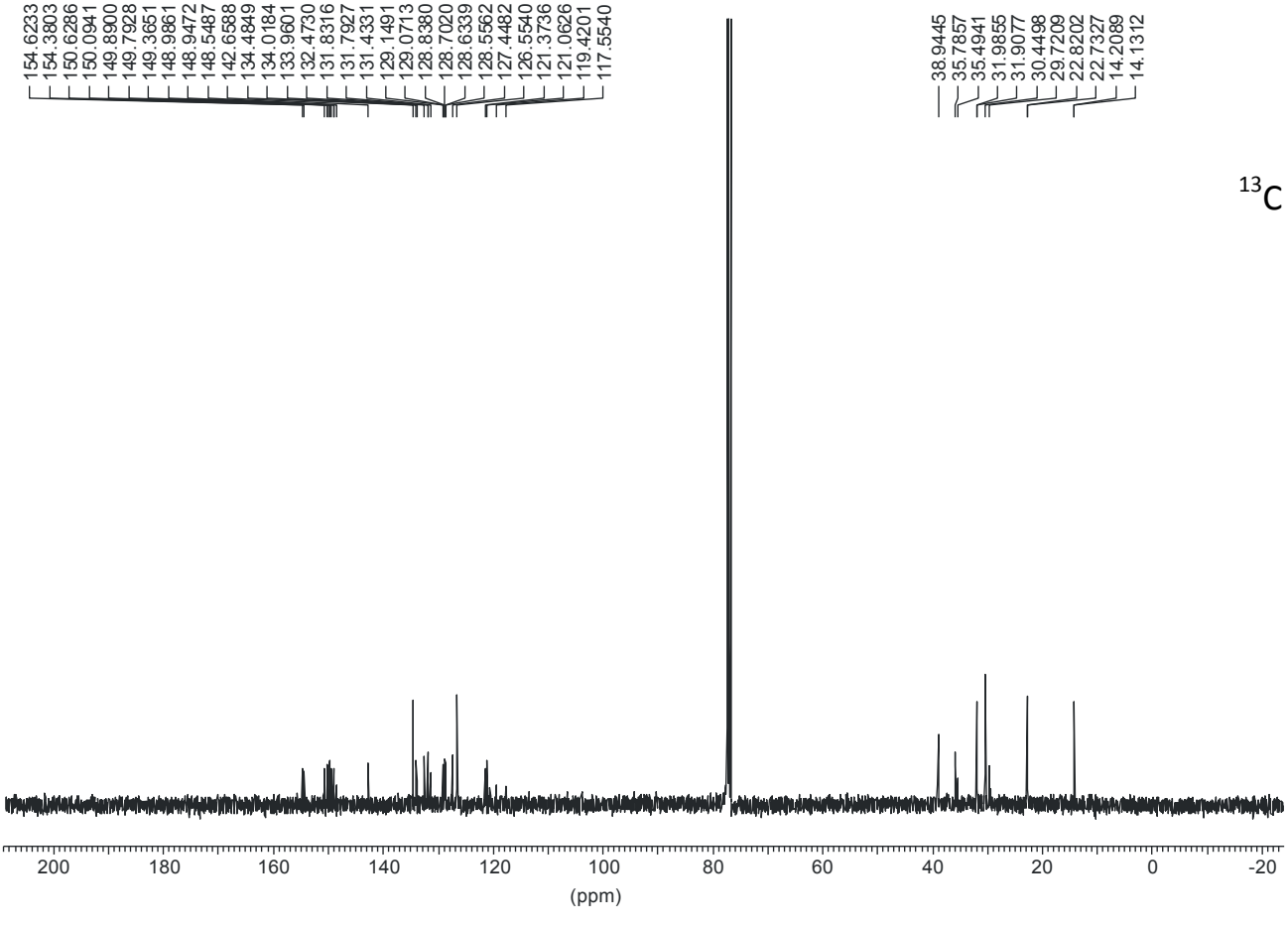
6c

^{13}C NMR



^{1}H NMR

7a



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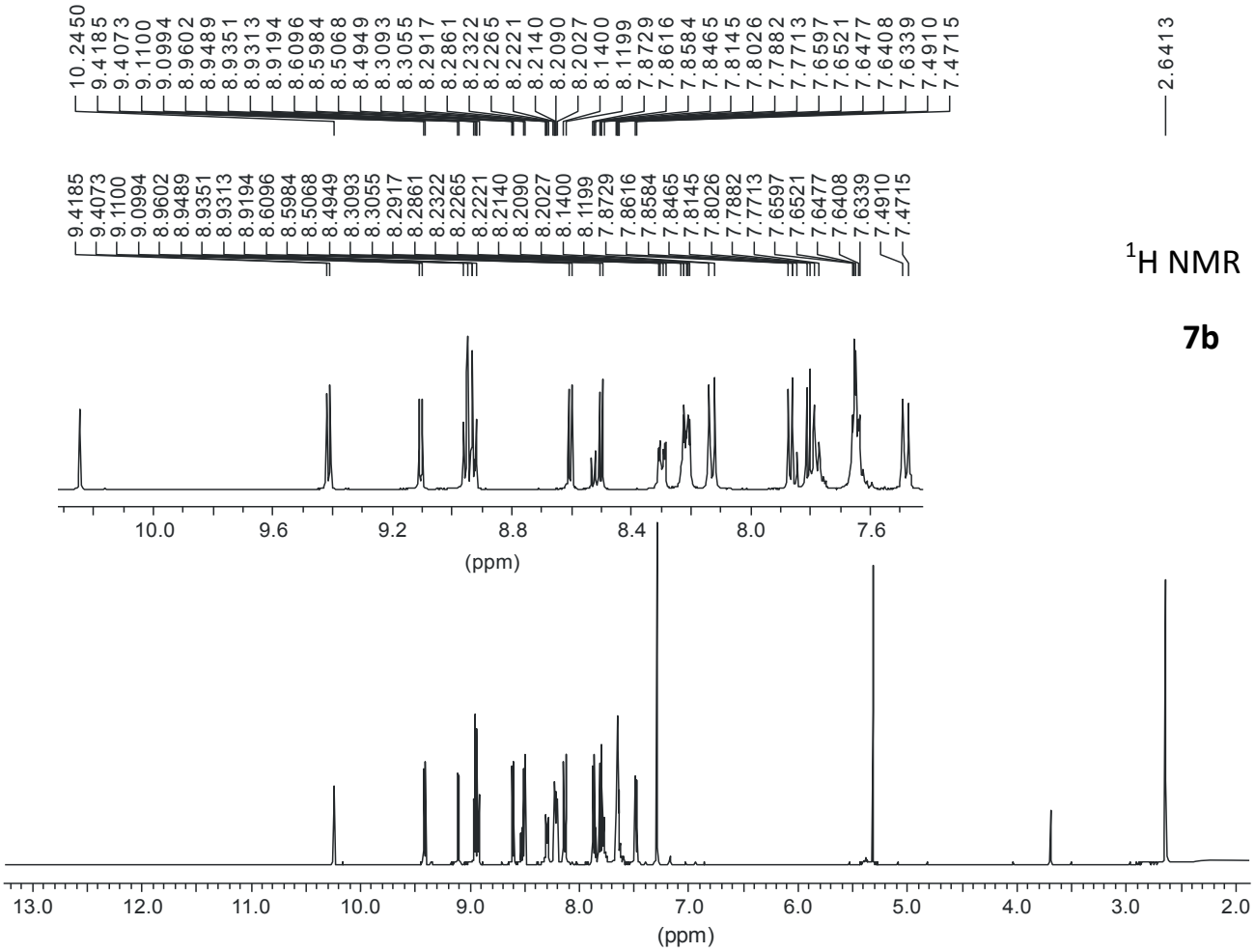
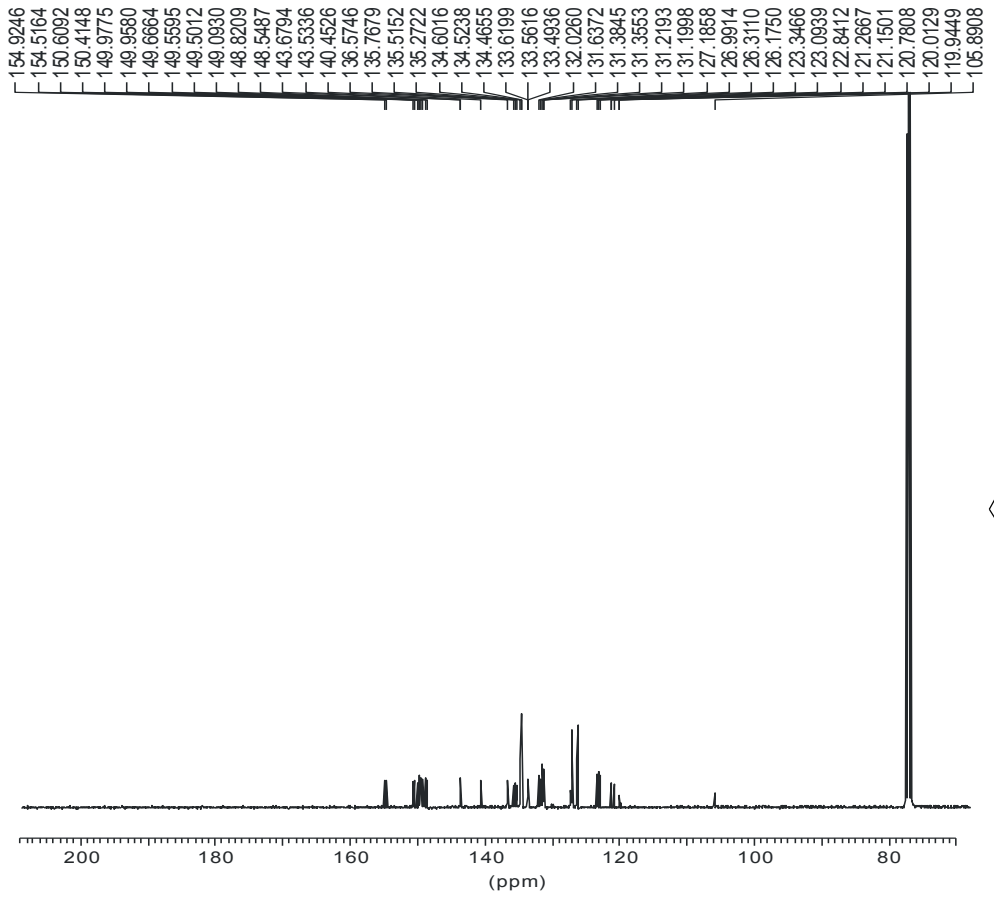


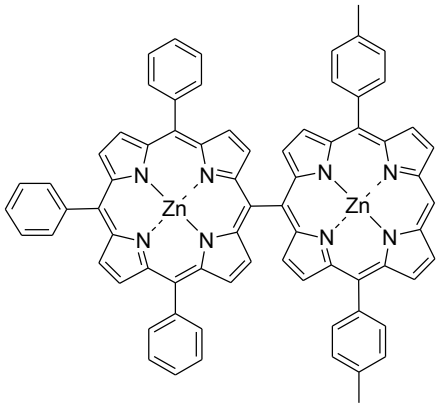
^{1}H NMR

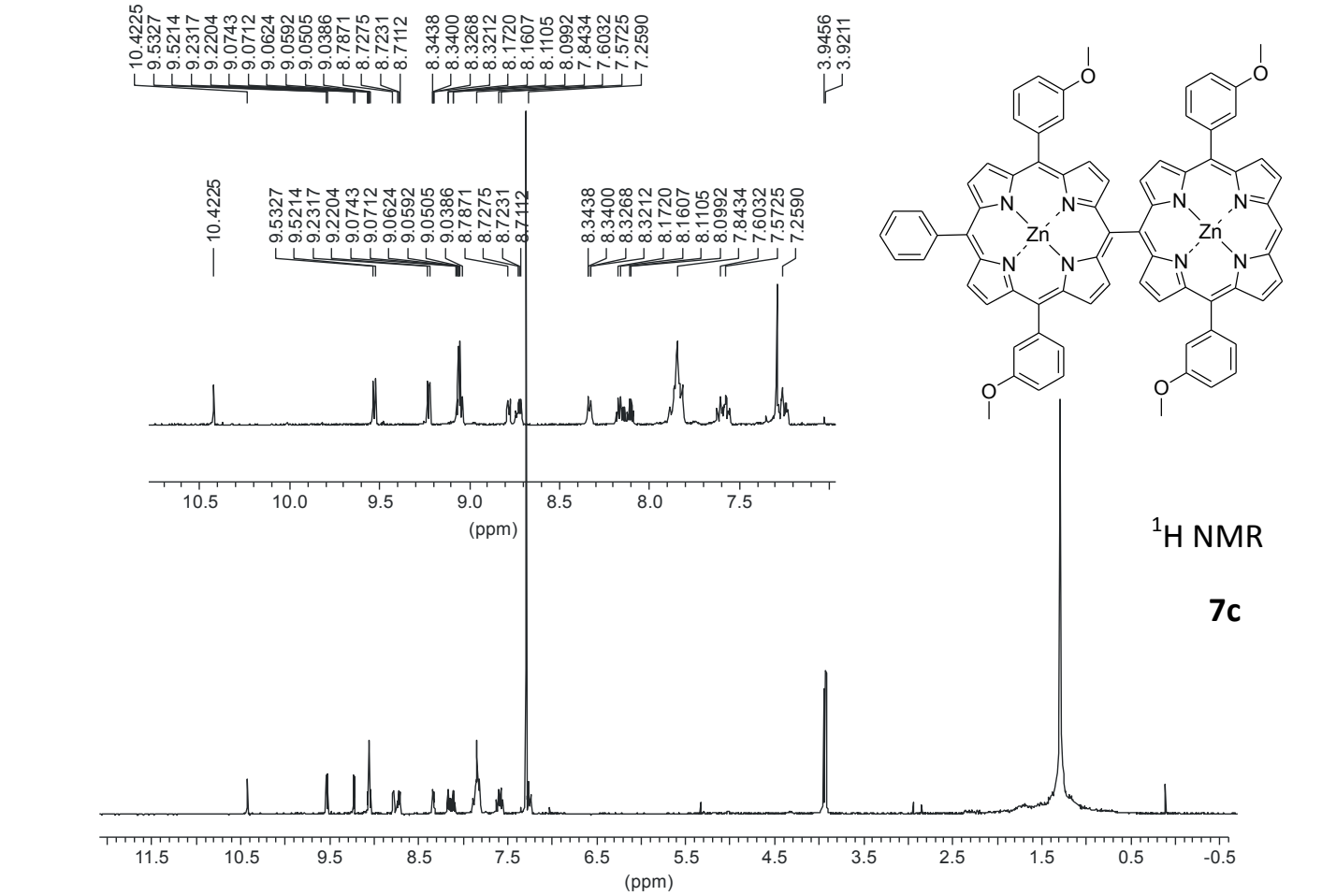
7b



^{13}C NMR

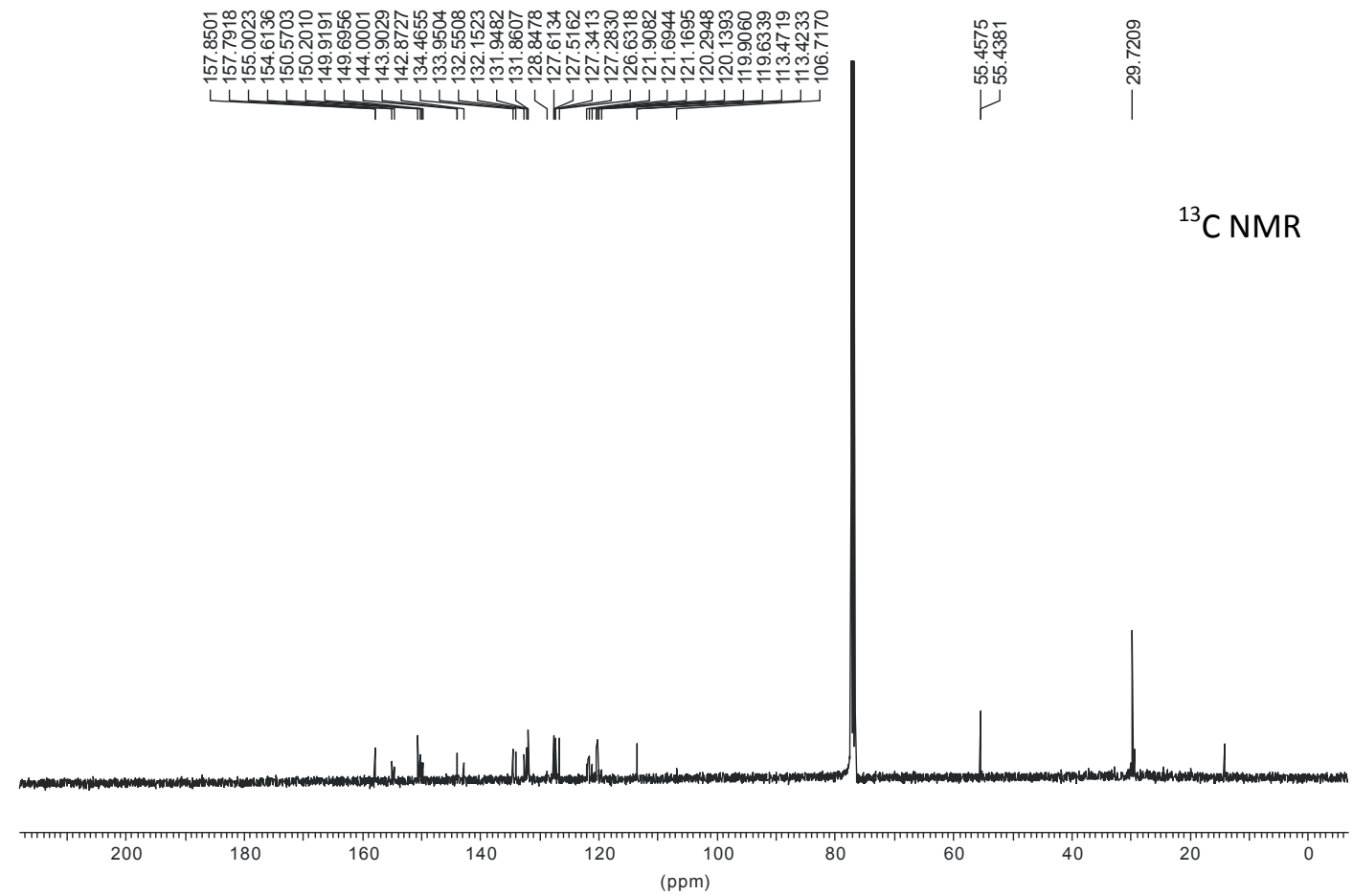
7b





^{1}H NMR

7c



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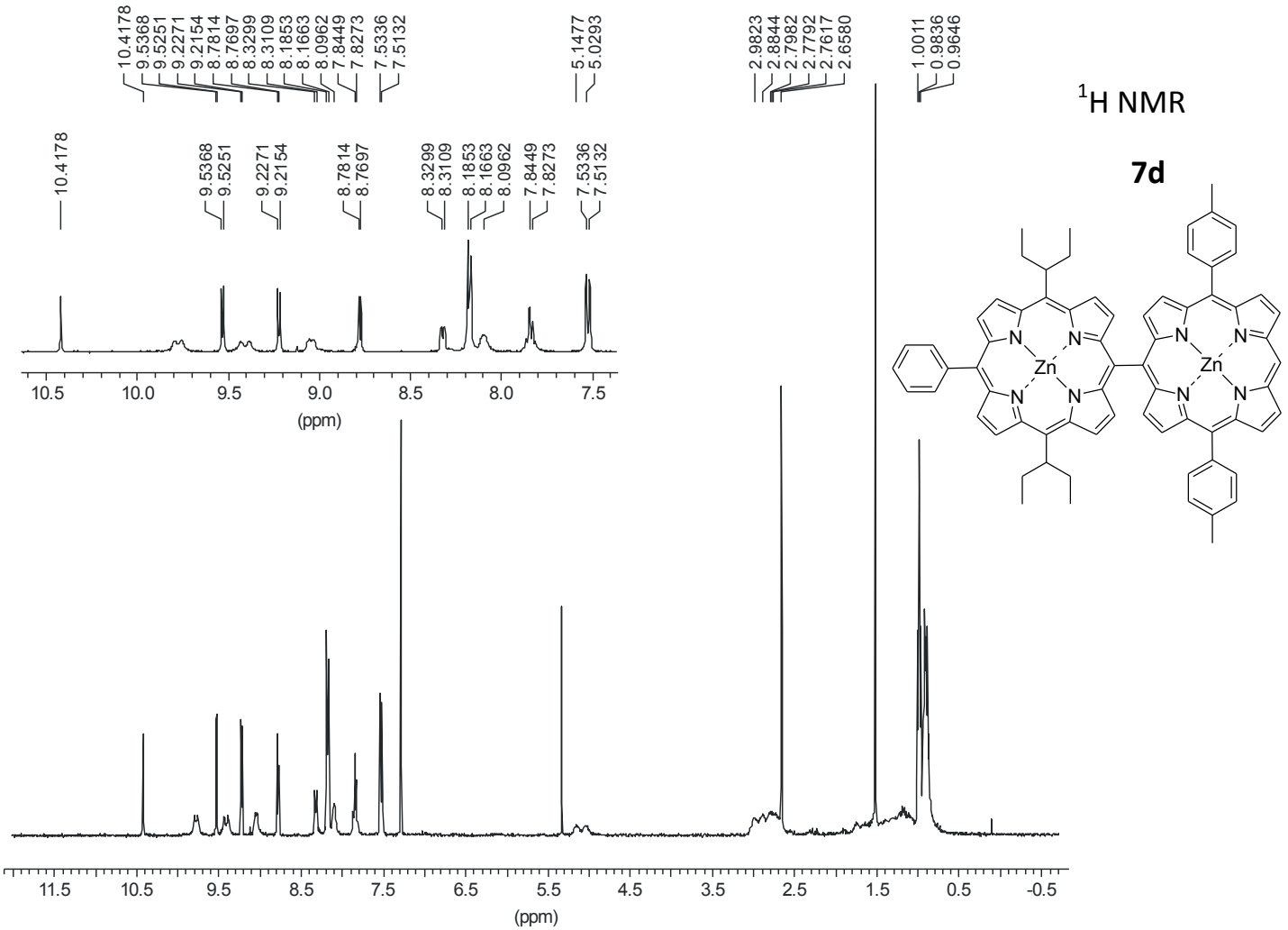
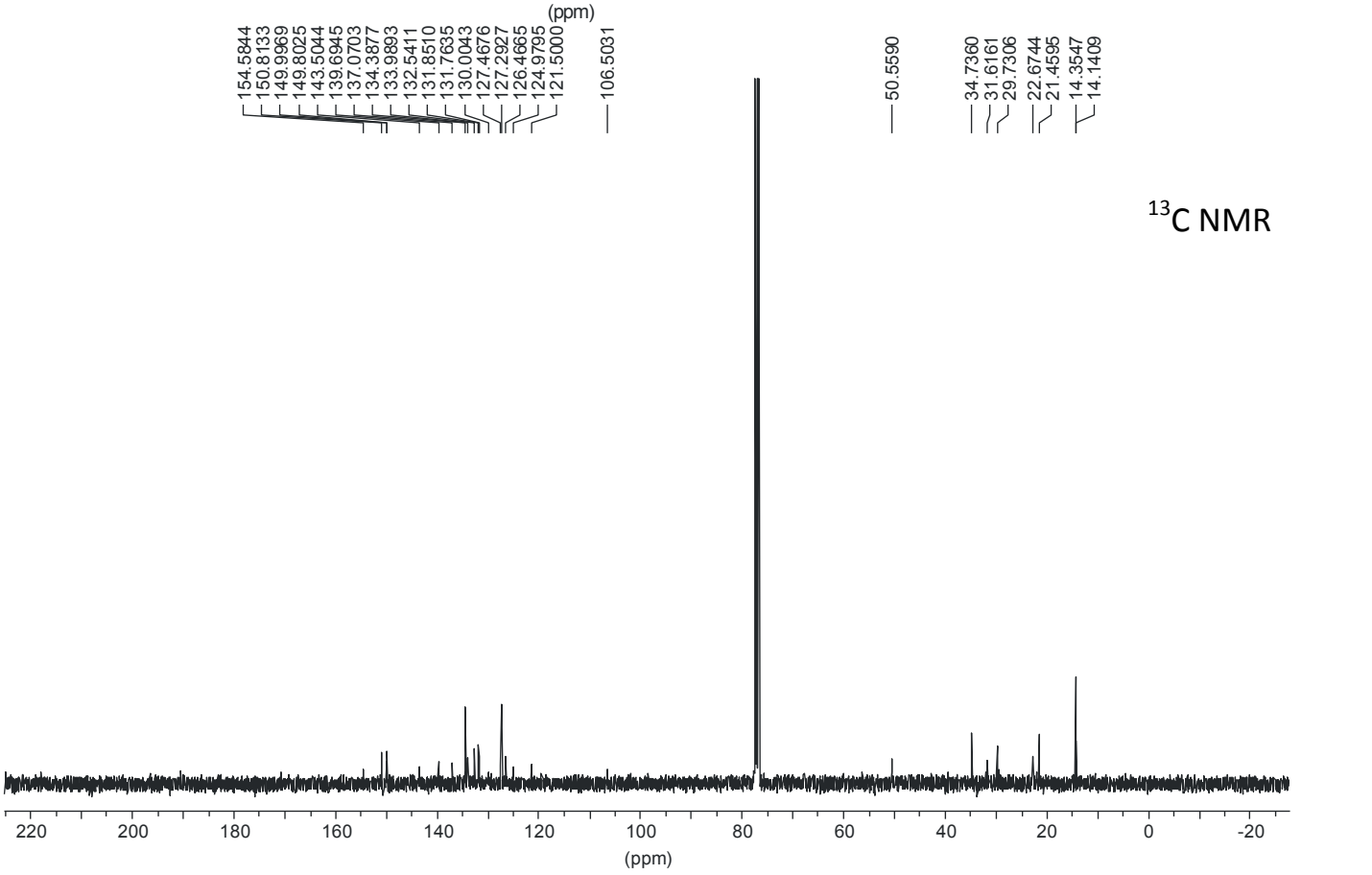


^{1}H NMR

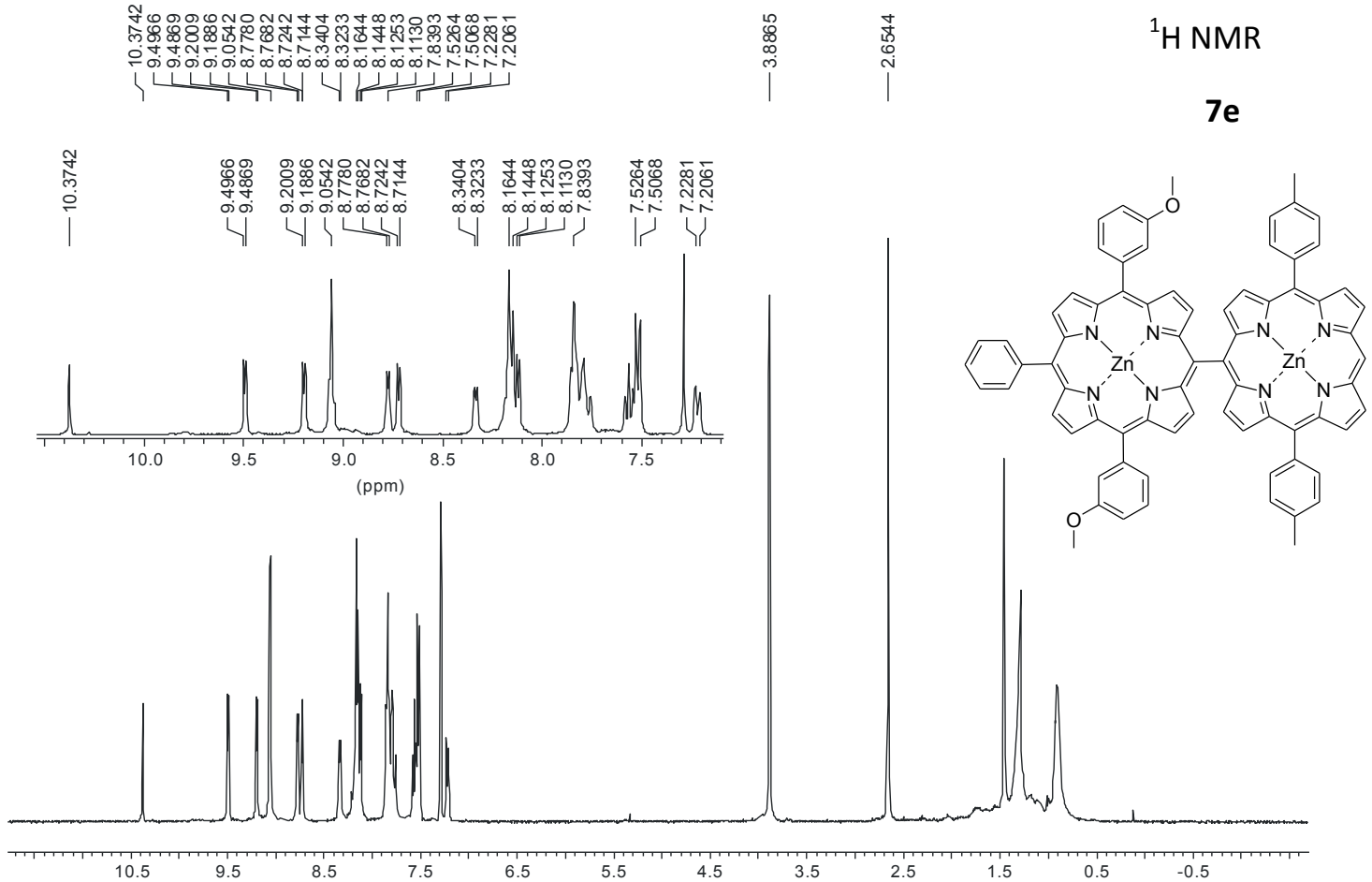
7d



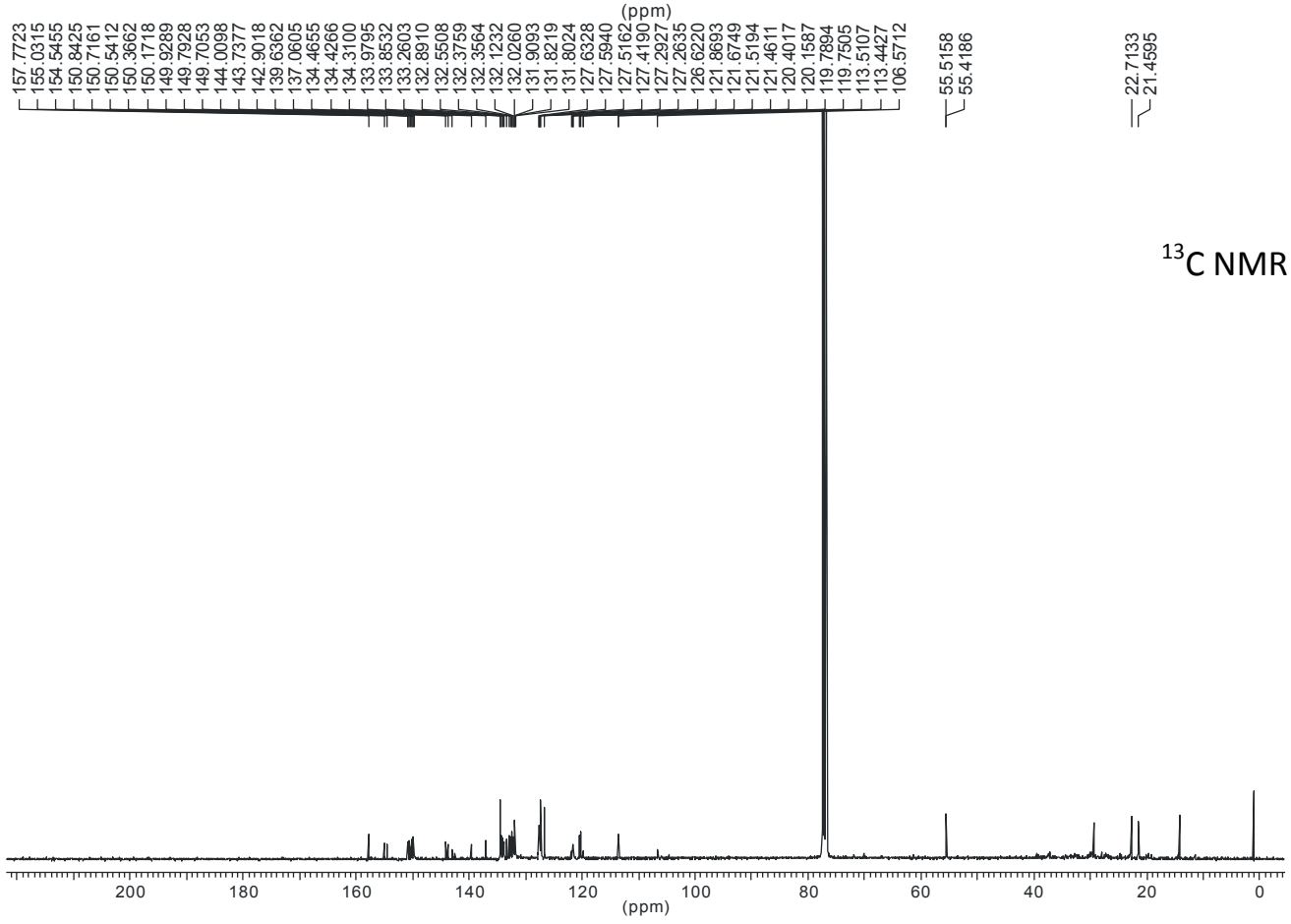
^{13}C NMR

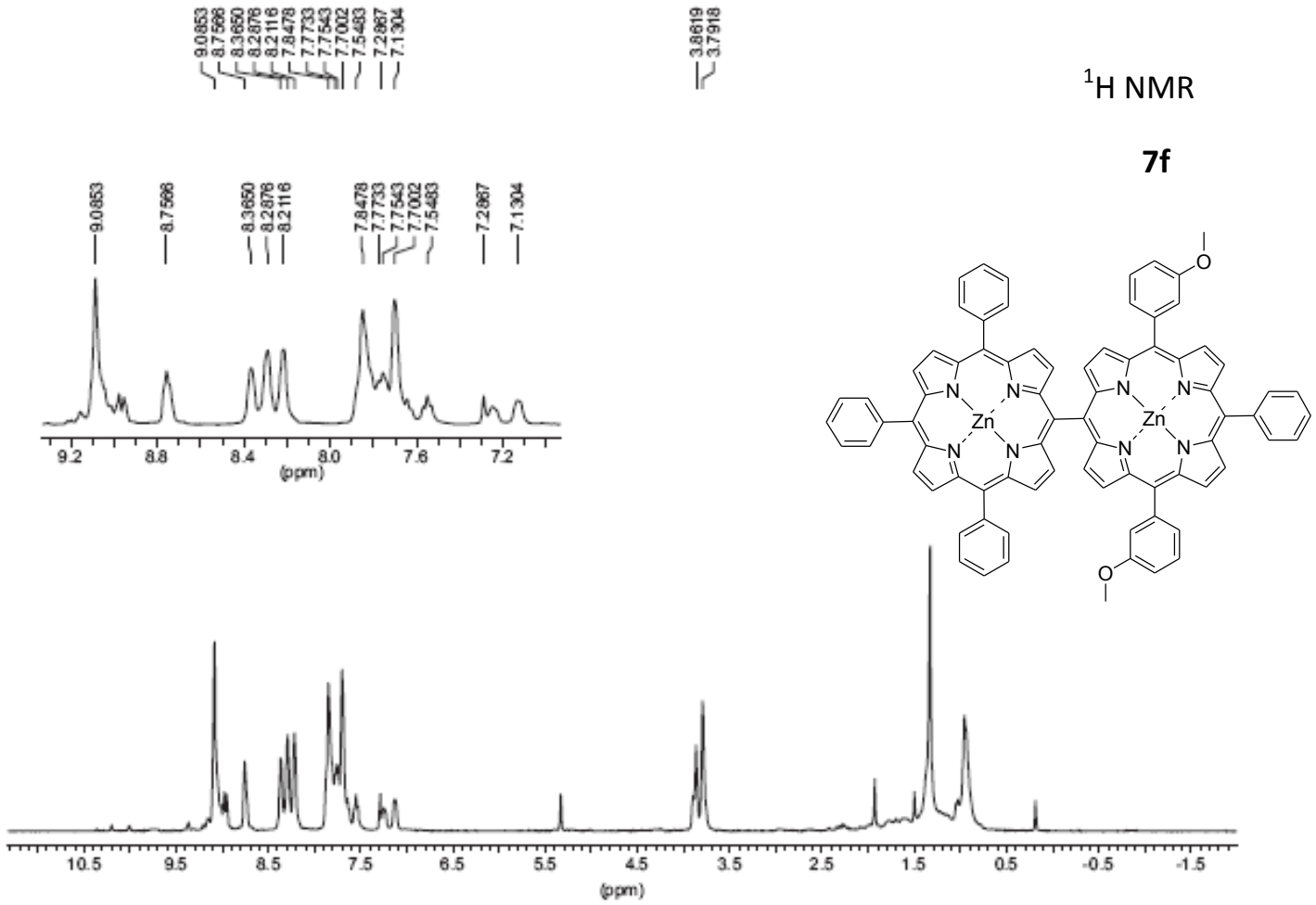
^{1}H NMR

7e



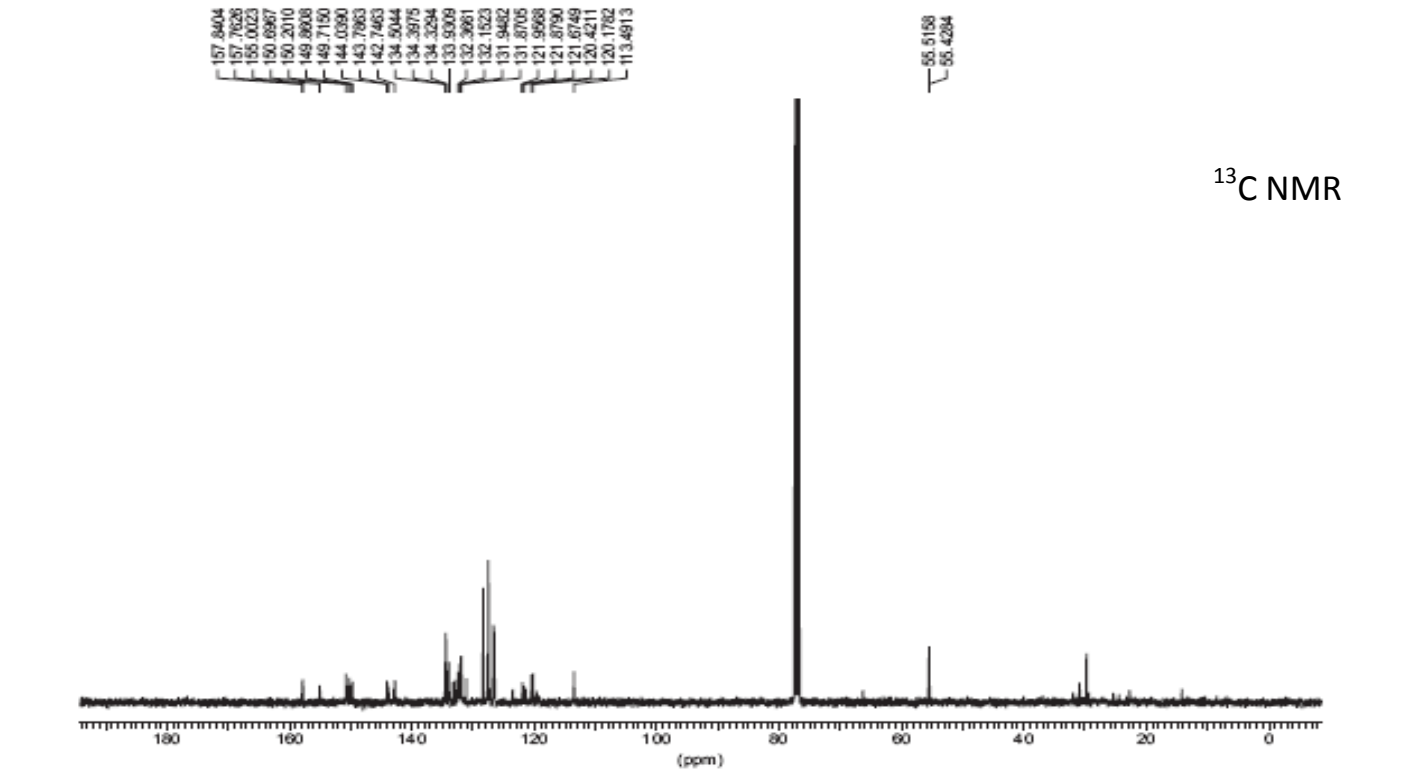
^{13}C NMR



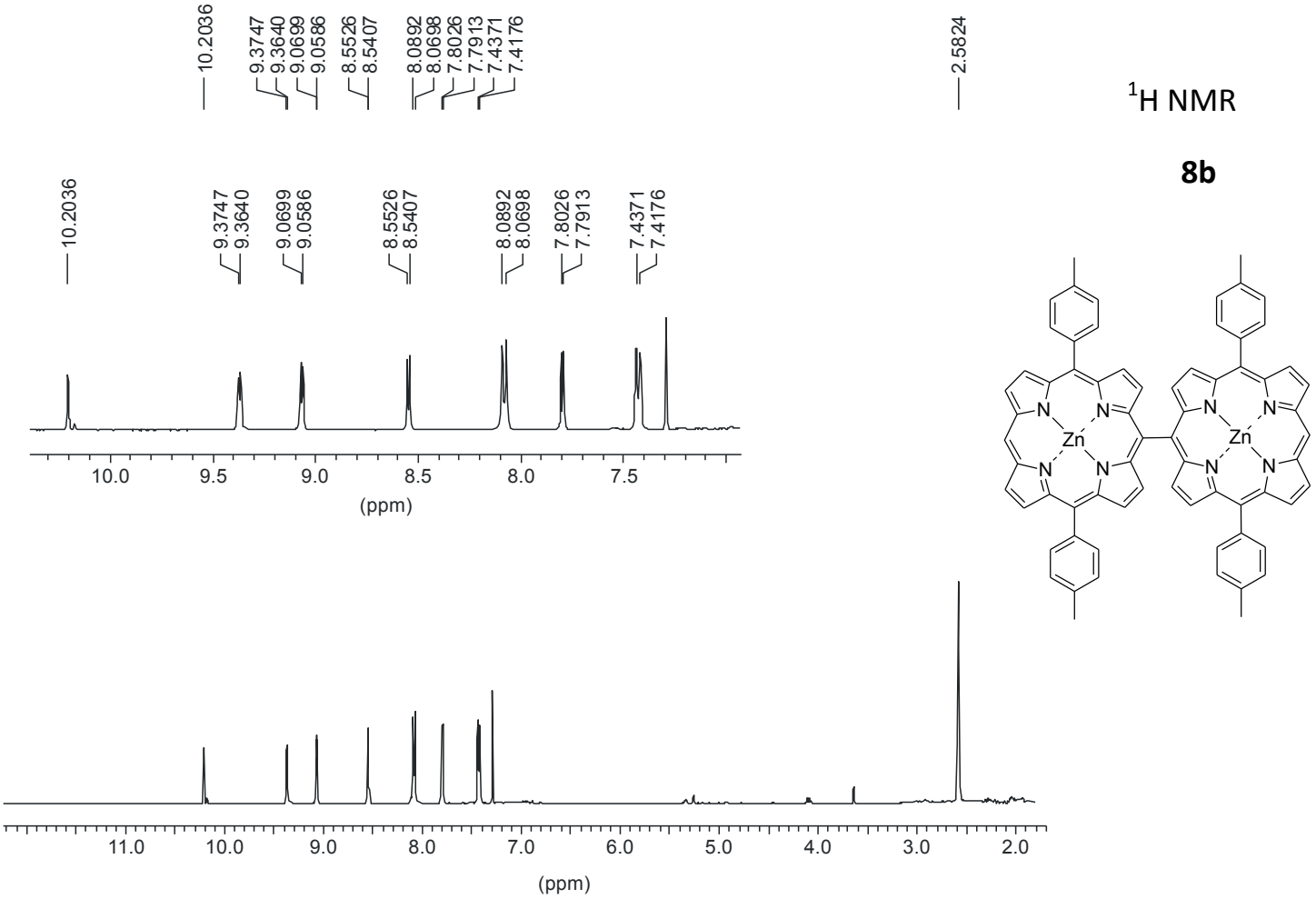


^{1}H NMR

7f

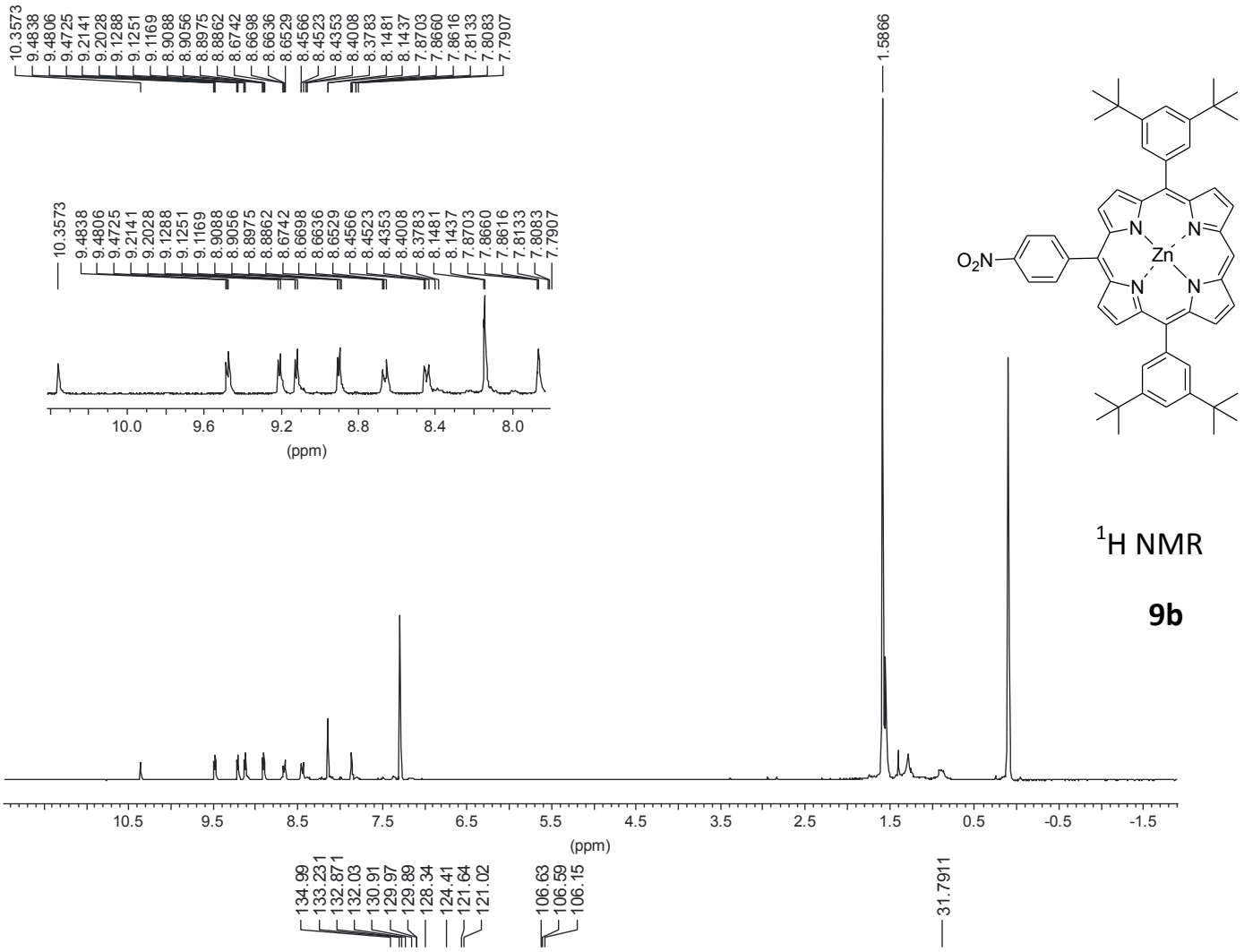


^{13}C NMR


10.2036
9.3747
9.3640
9.0699
9.0586
8.5526
8.5407
8.0892
8.0698
7.8026
7.7913
7.4371
7.4176
2.5824
(ppm)
(ppm)
Zn
Zn
N

^{1}H NMR

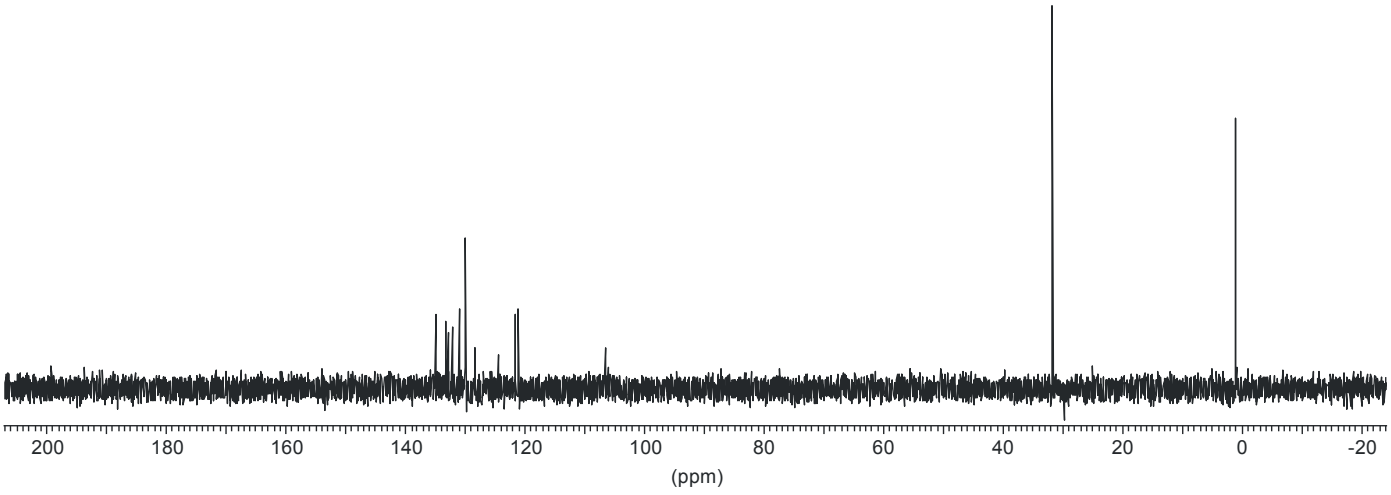
8b



^{1}H NMR

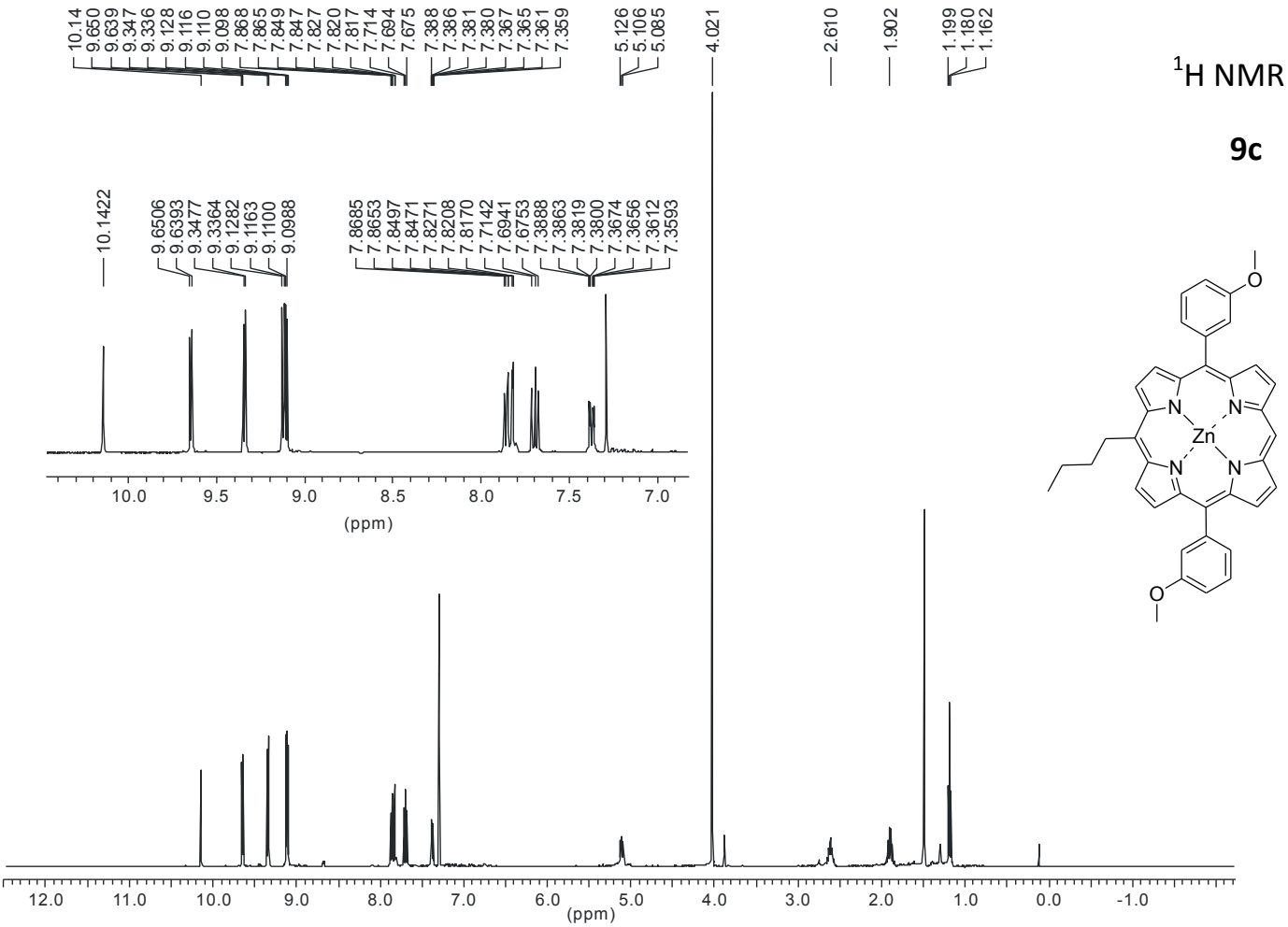
9b

^{13}C NMR

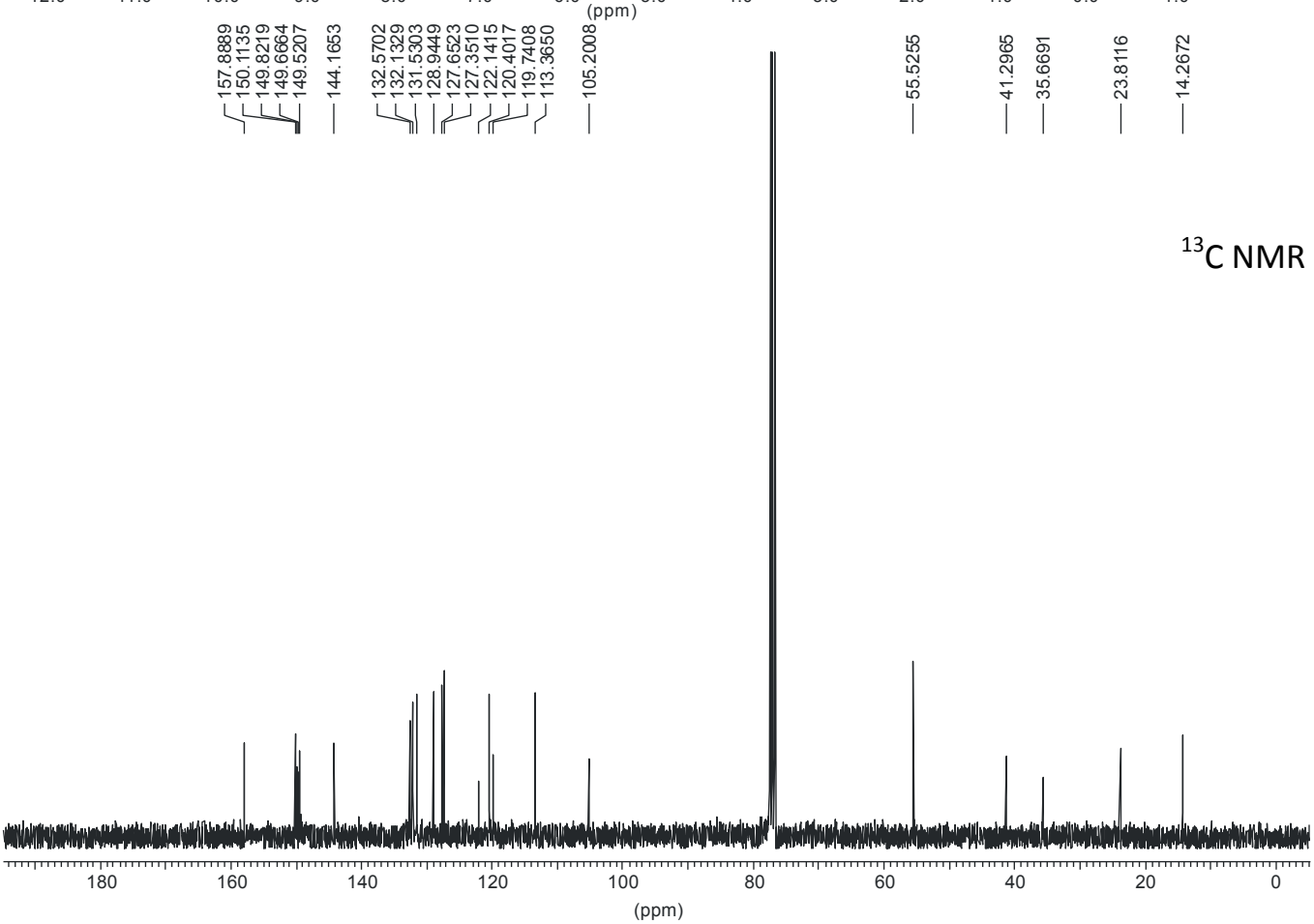


^{1}H NMR

9c

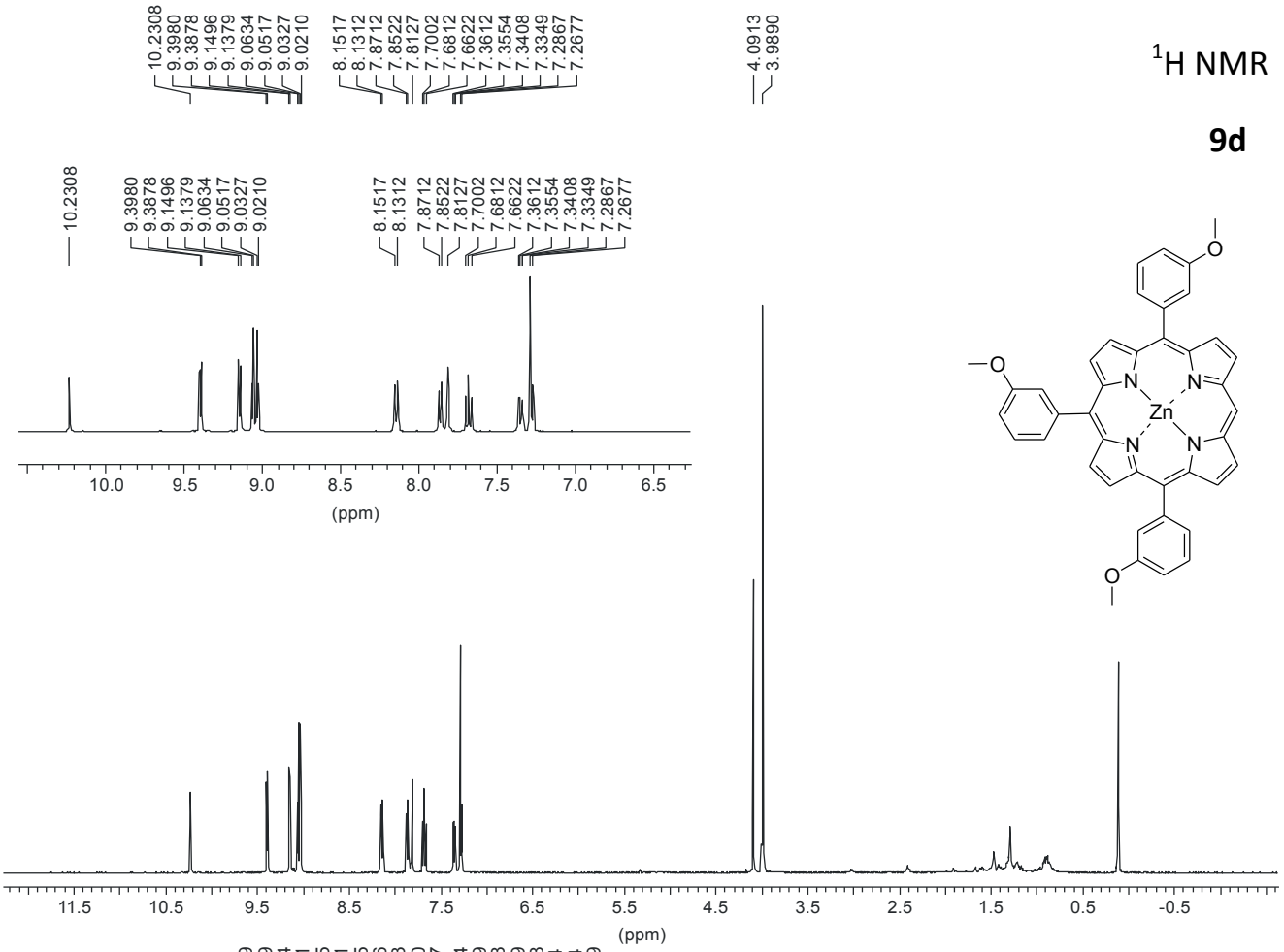


^{13}C NMR

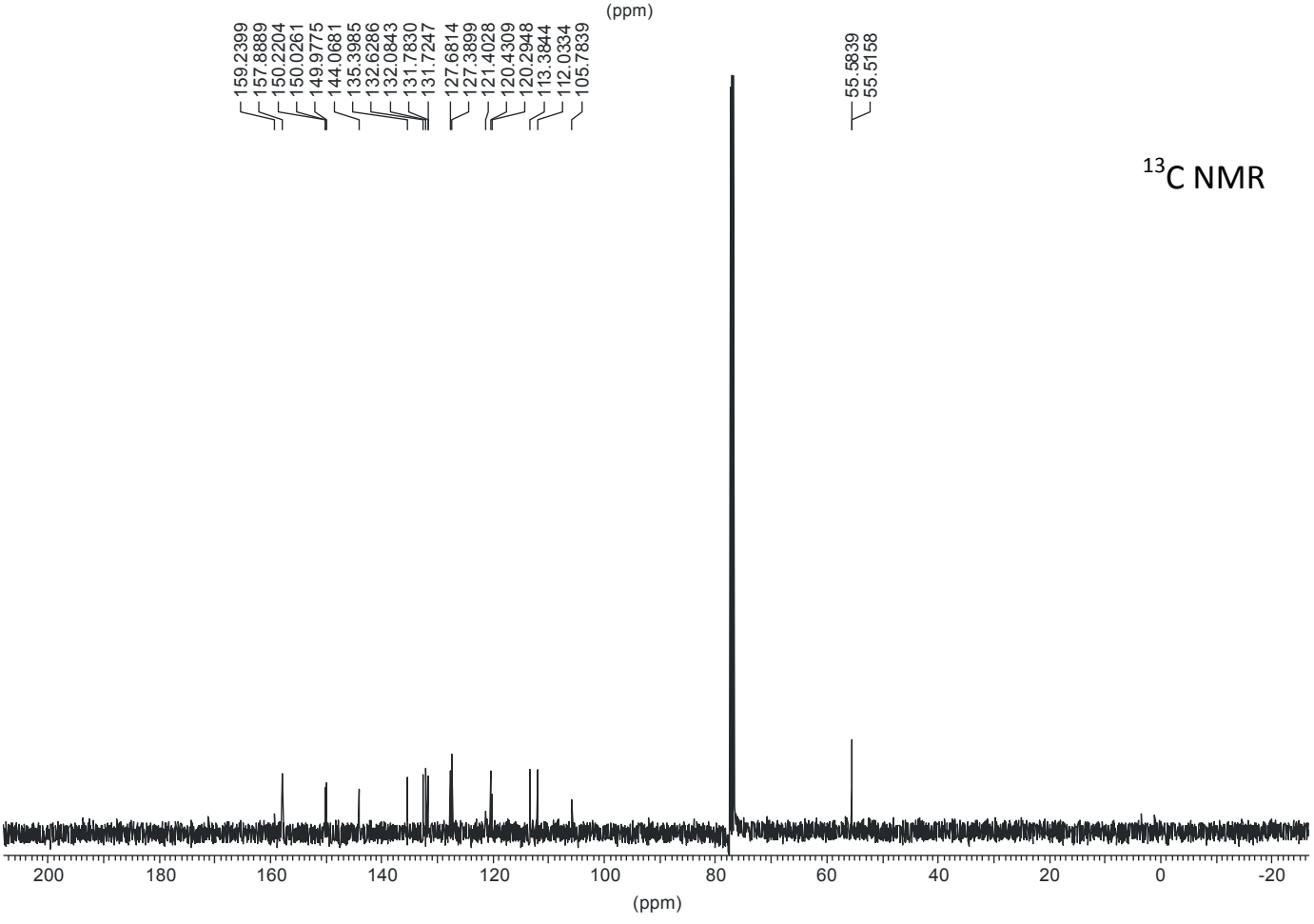


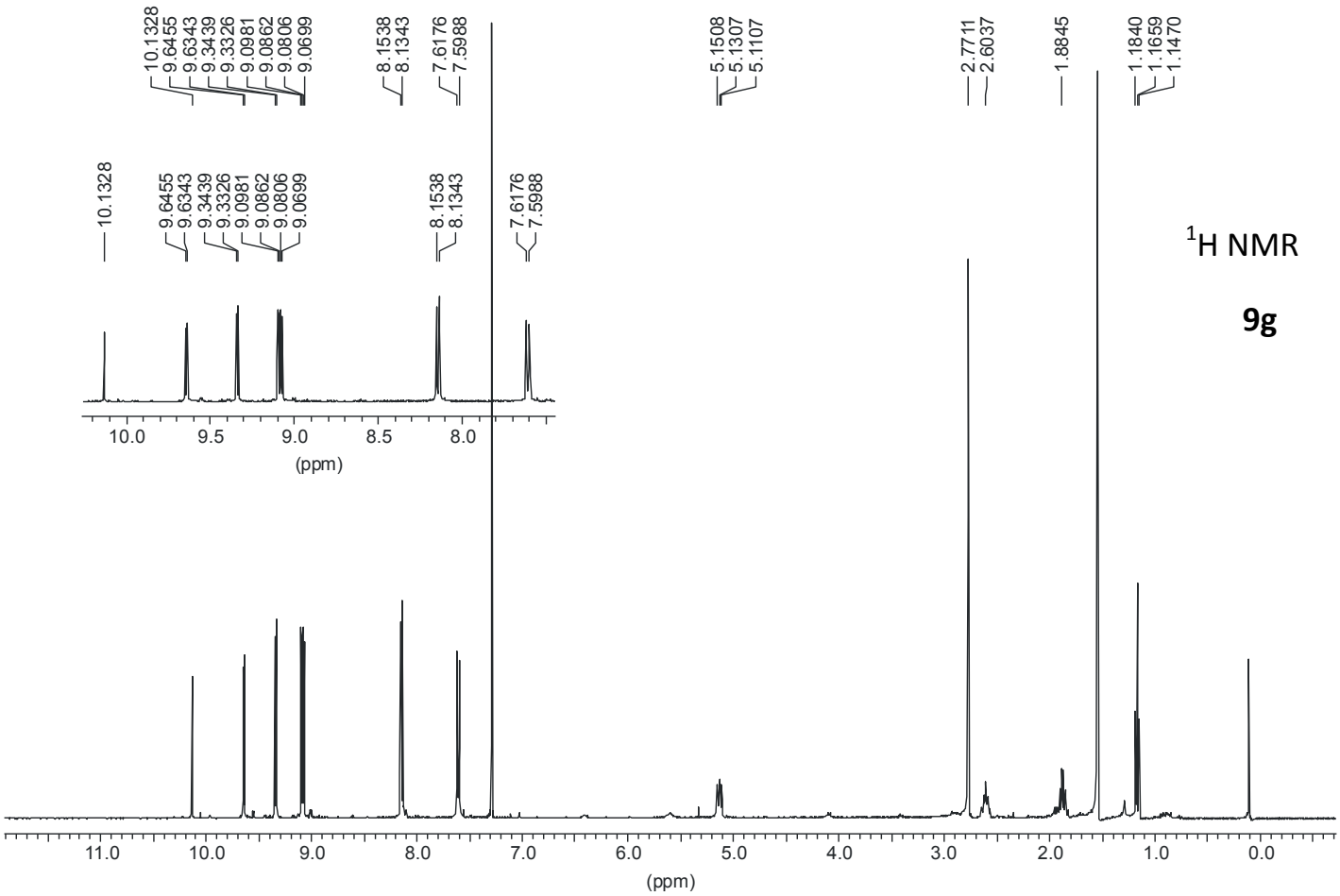
^{1}H NMR

9d



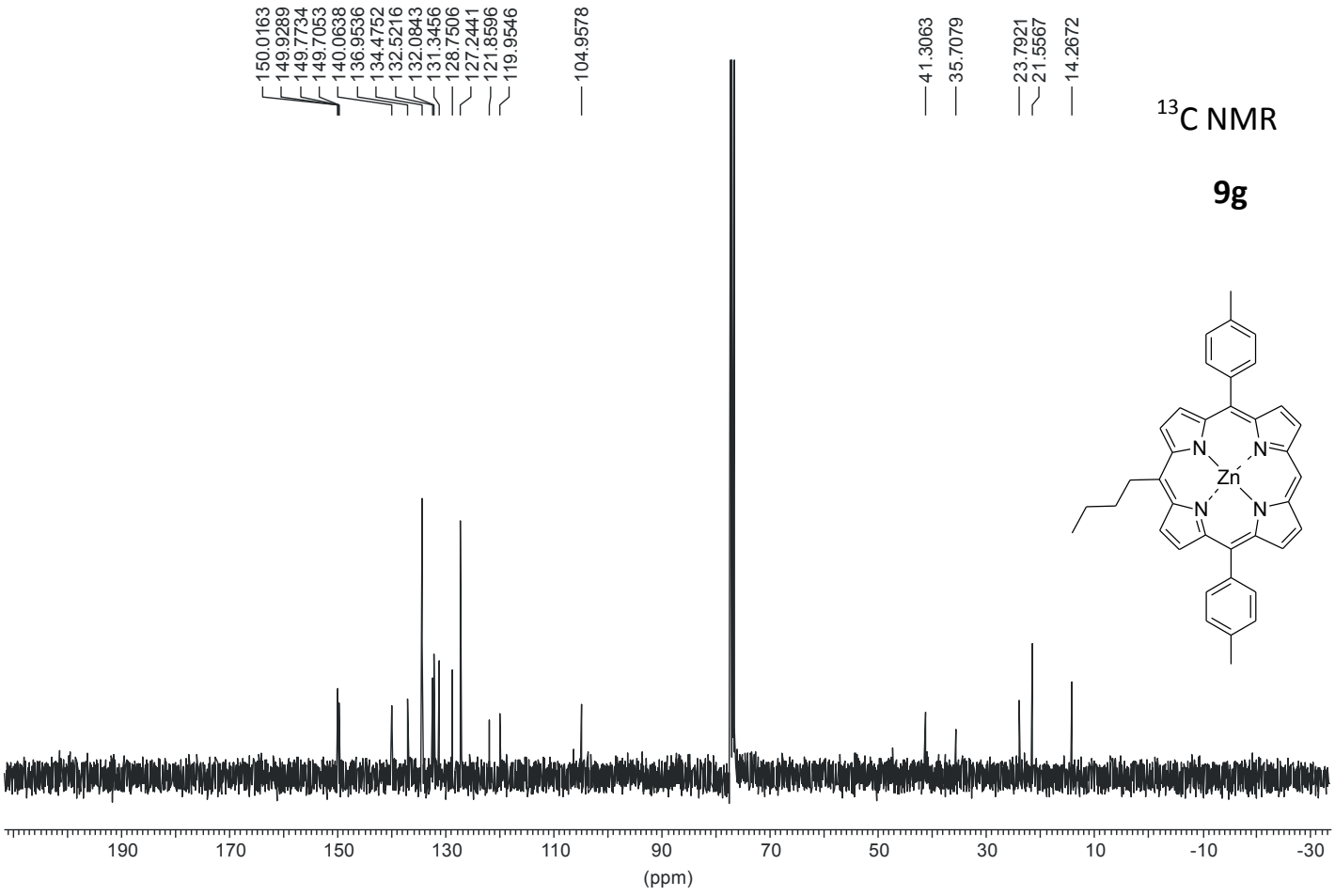
^{13}C NMR





^{1}H NMR

9g

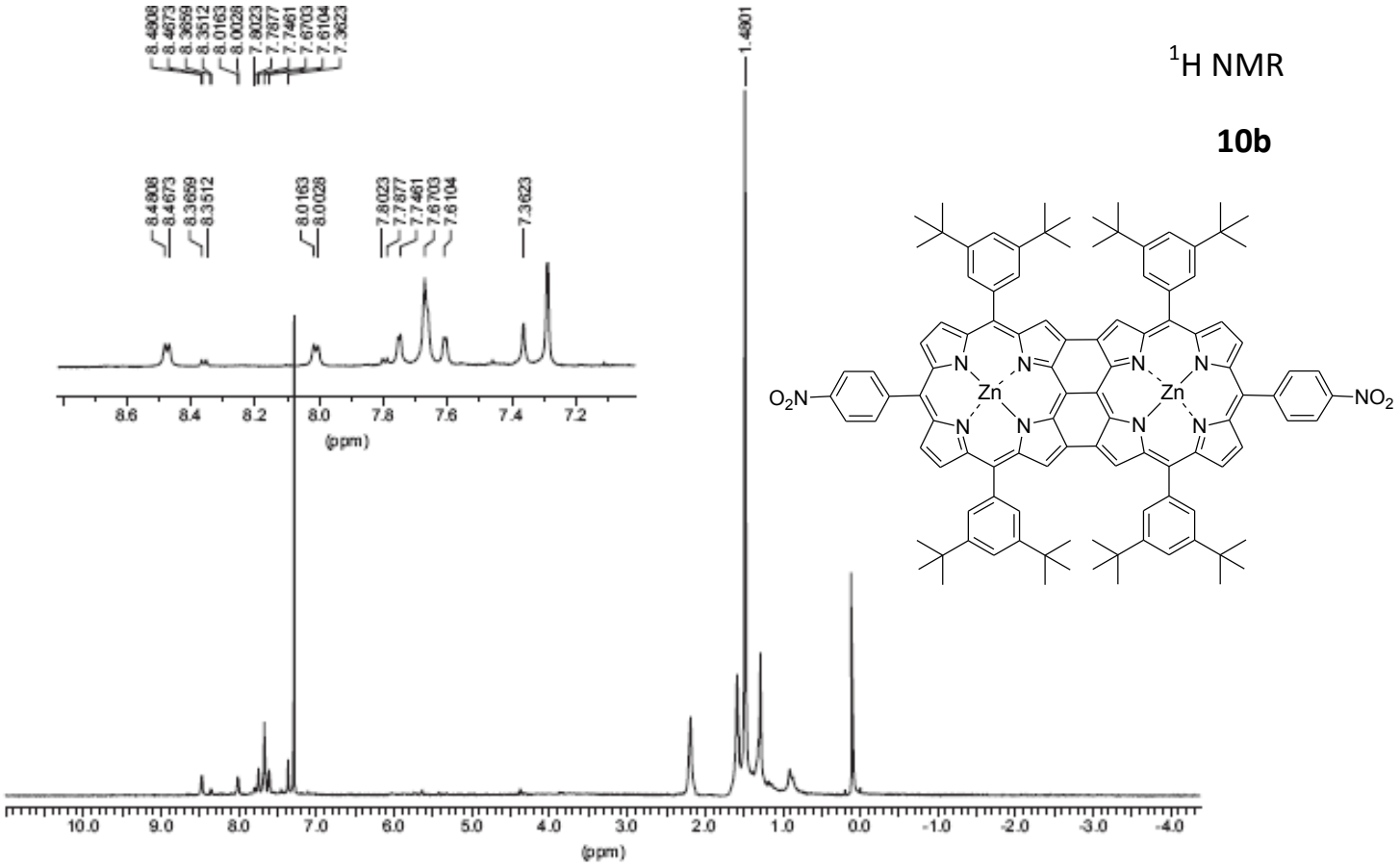


^{13}C NMR

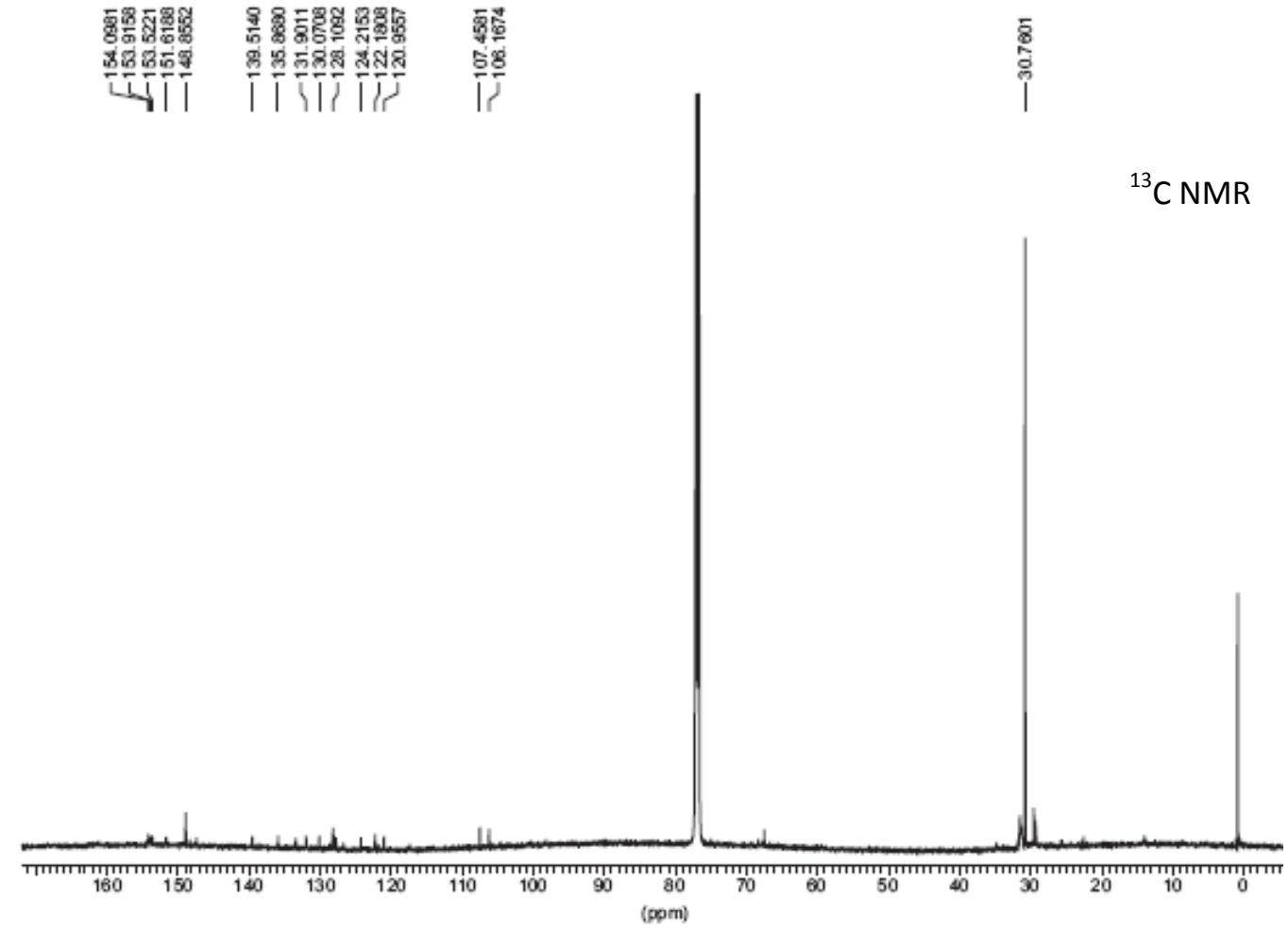
9g

^{1}H NMR

10b

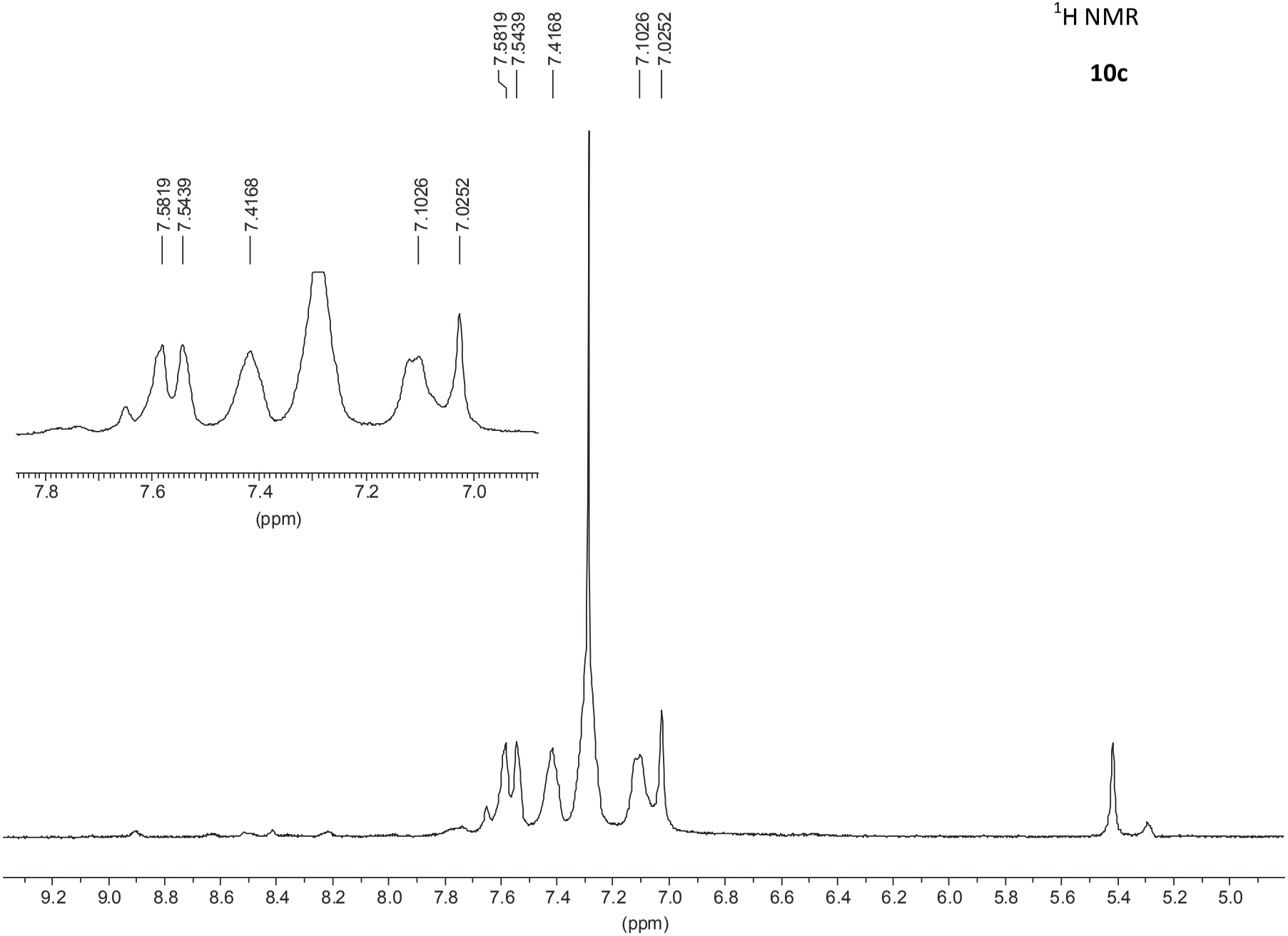


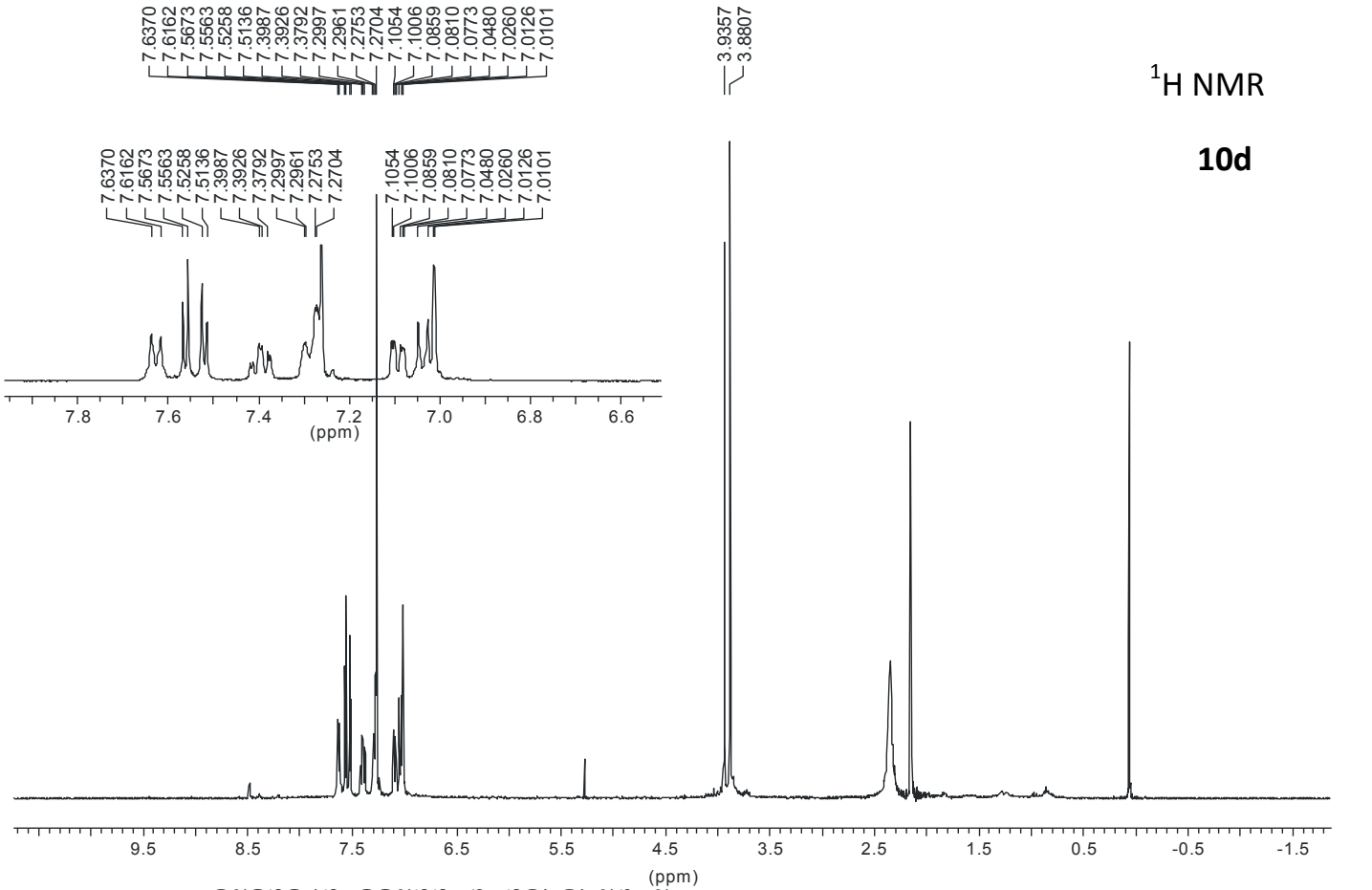
^{13}C NMR



^{1}H NMR

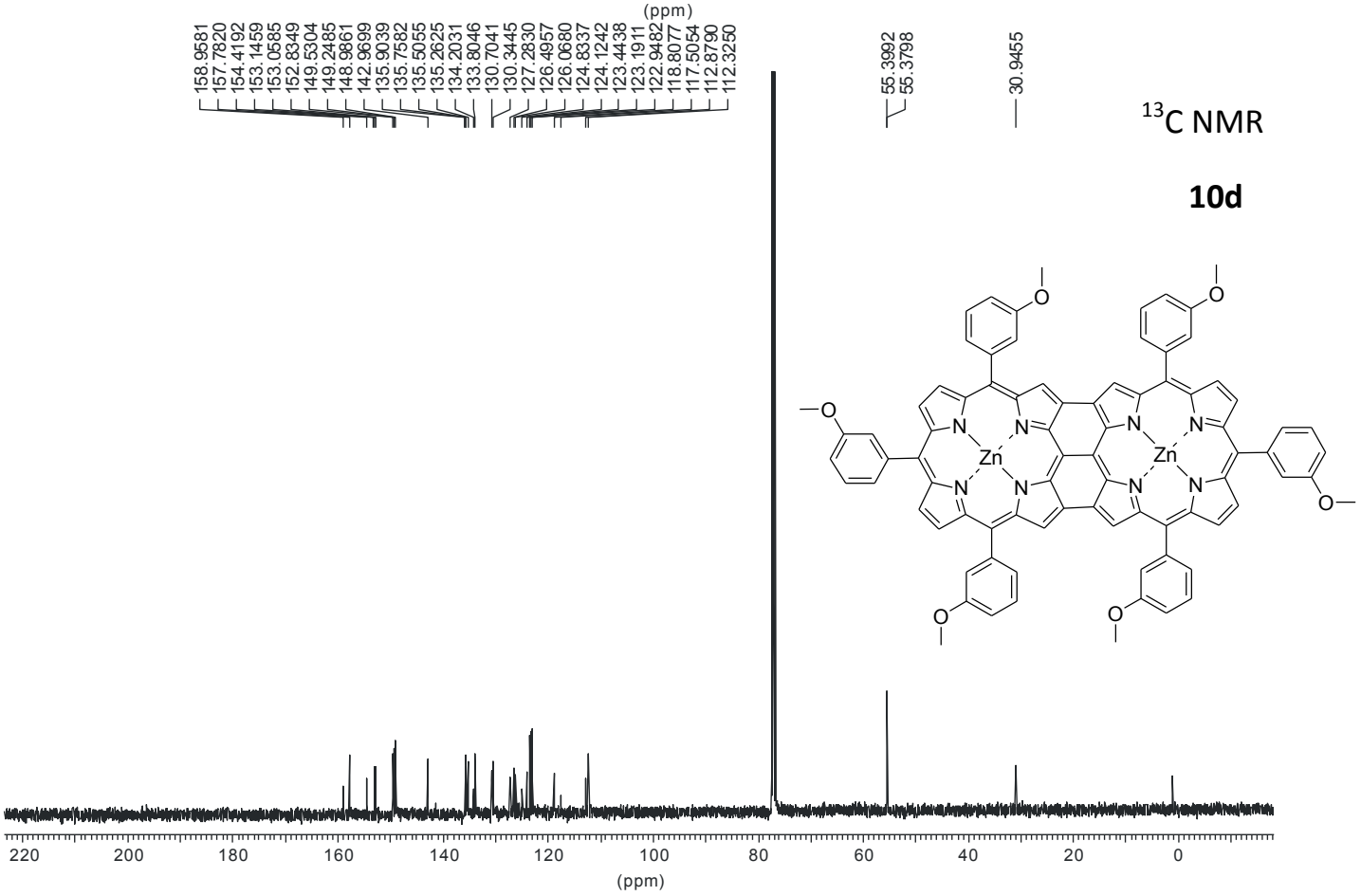
10c


7.5819
7.5439
7.4168
7.1026
7.0252
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0
(ppm)
7.8 7.6 7.4 7.2 7.0
(ppm)



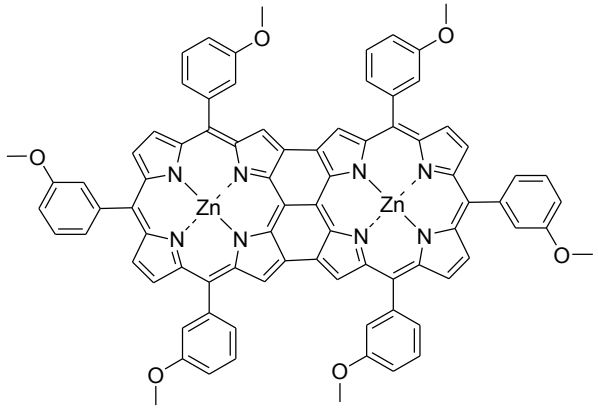
^{1}H NMR

10d



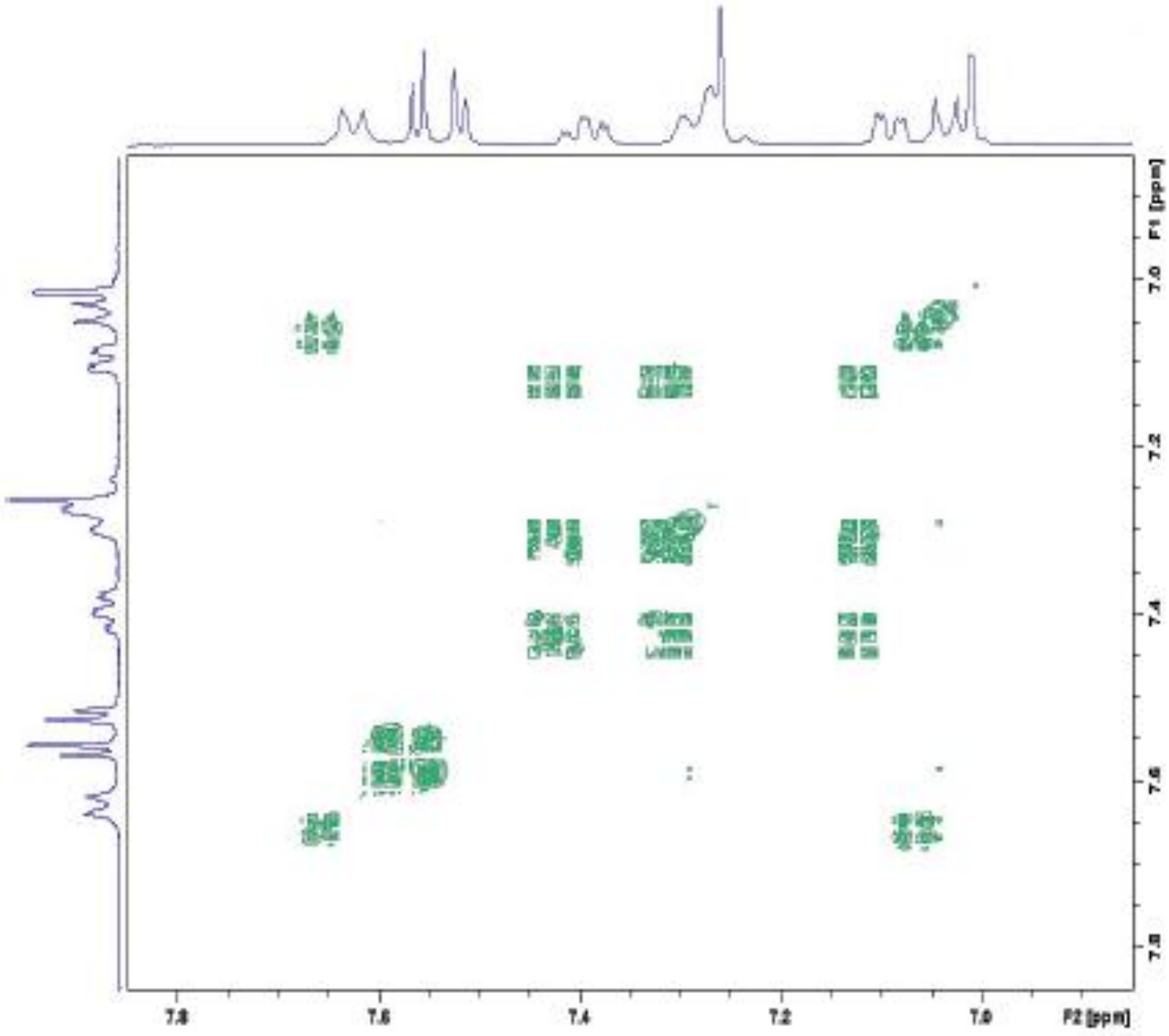
^{13}C NMR

10d



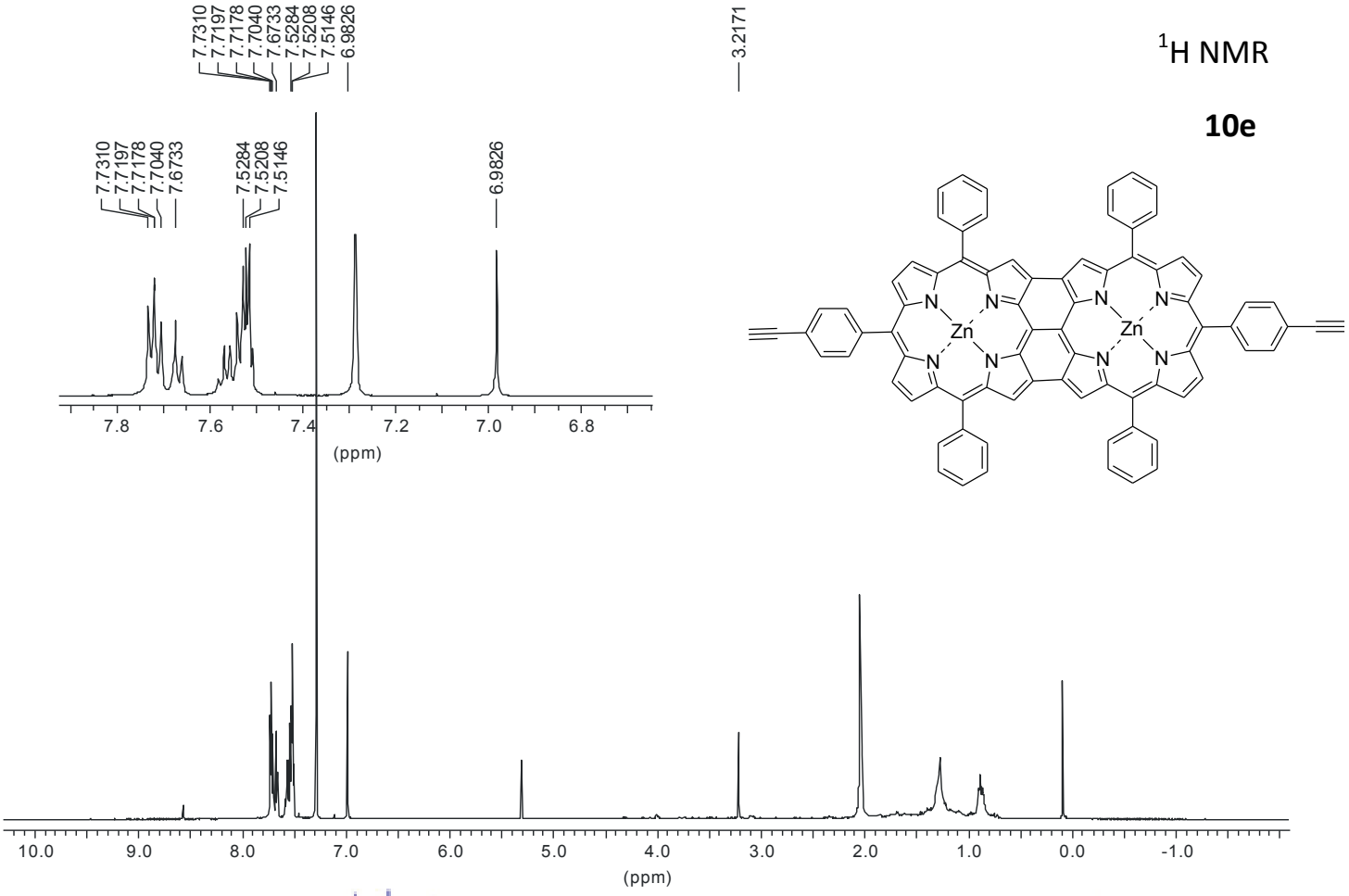
10d

TOCSY



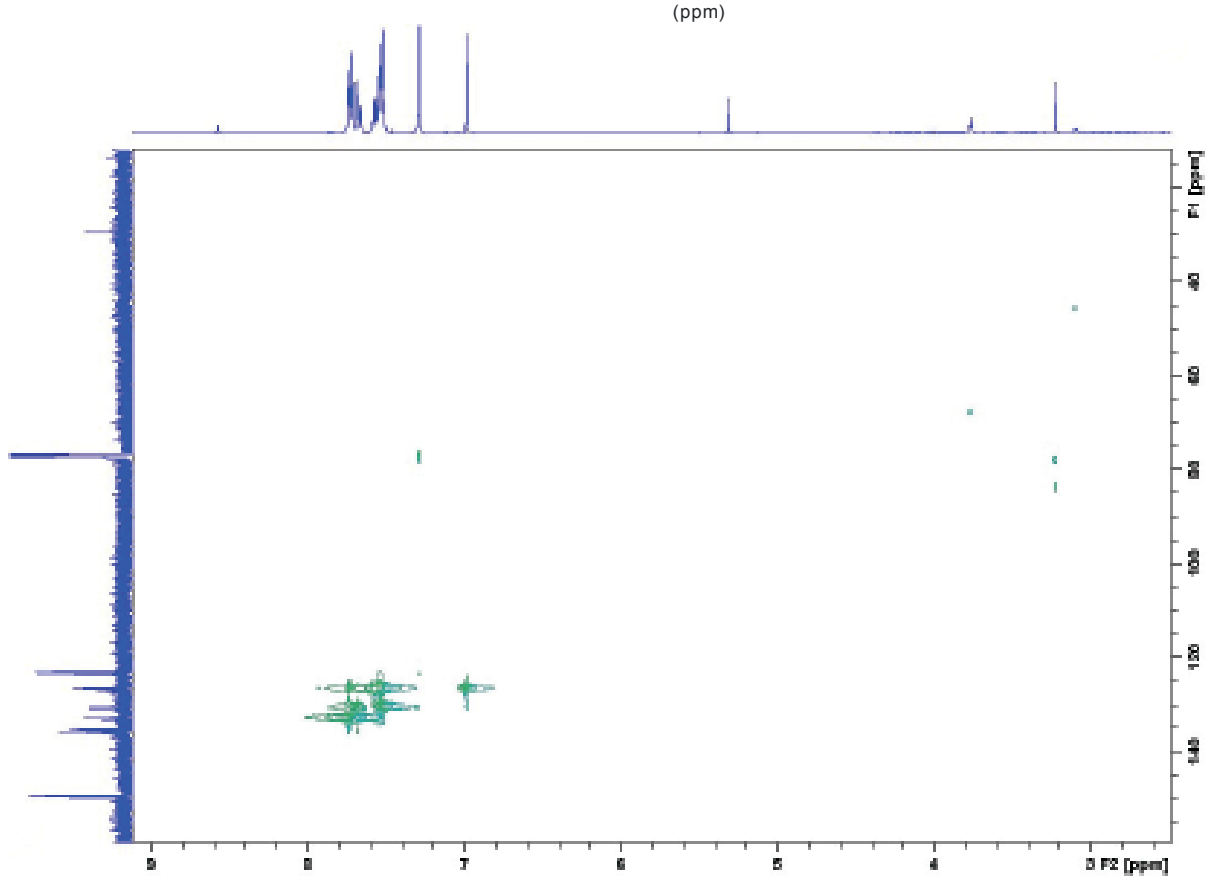
^{1}H NMR

10e



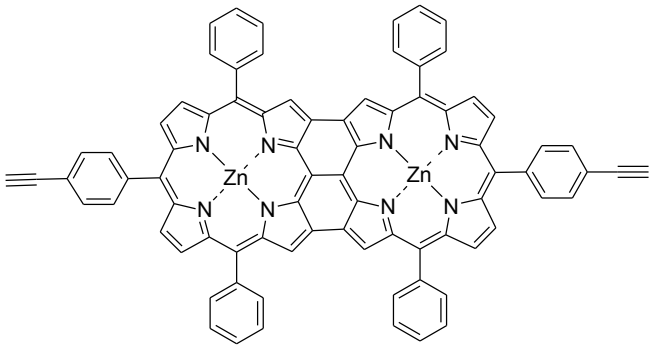
HSQC

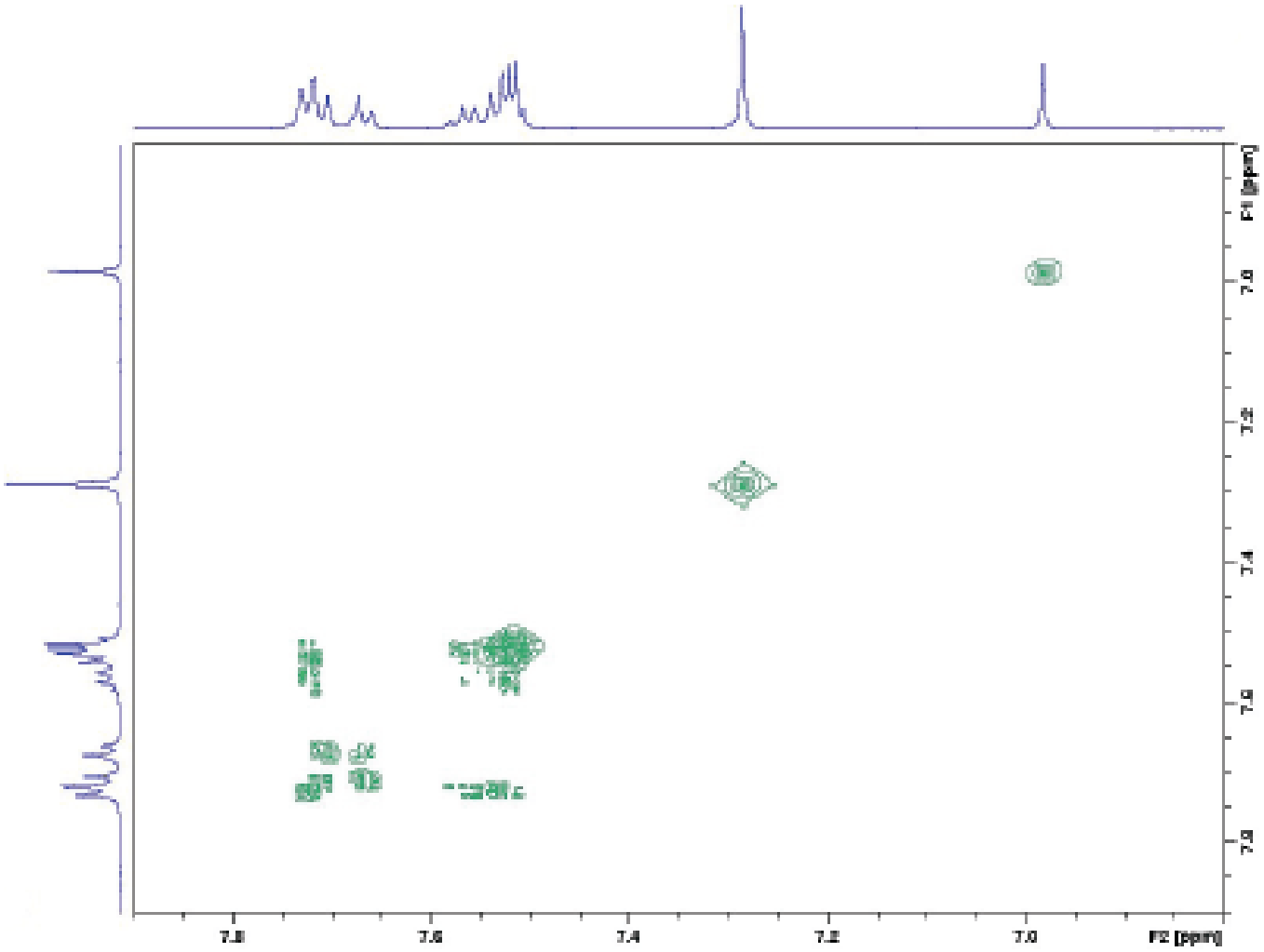
10e



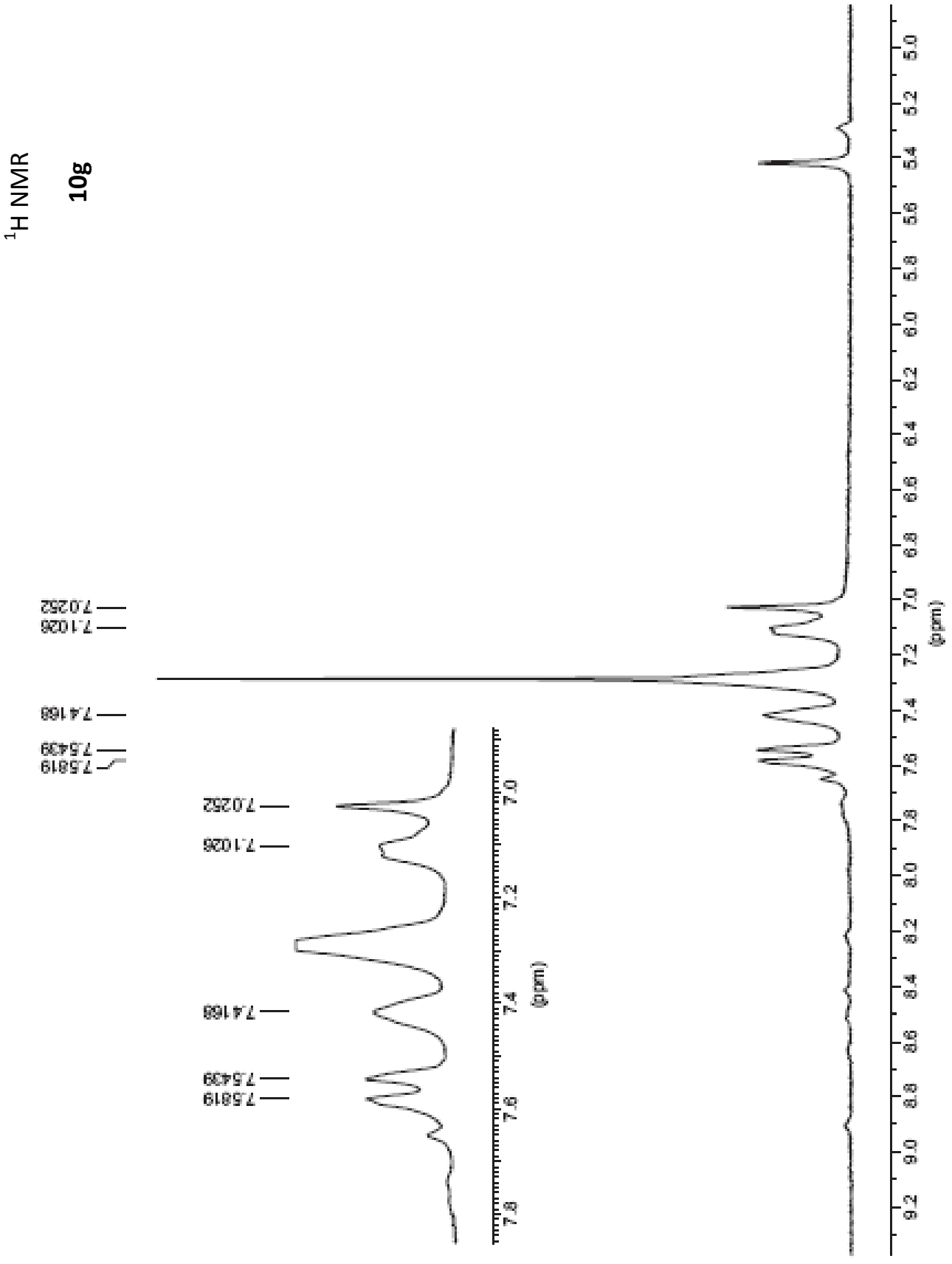
TOCSY

10e



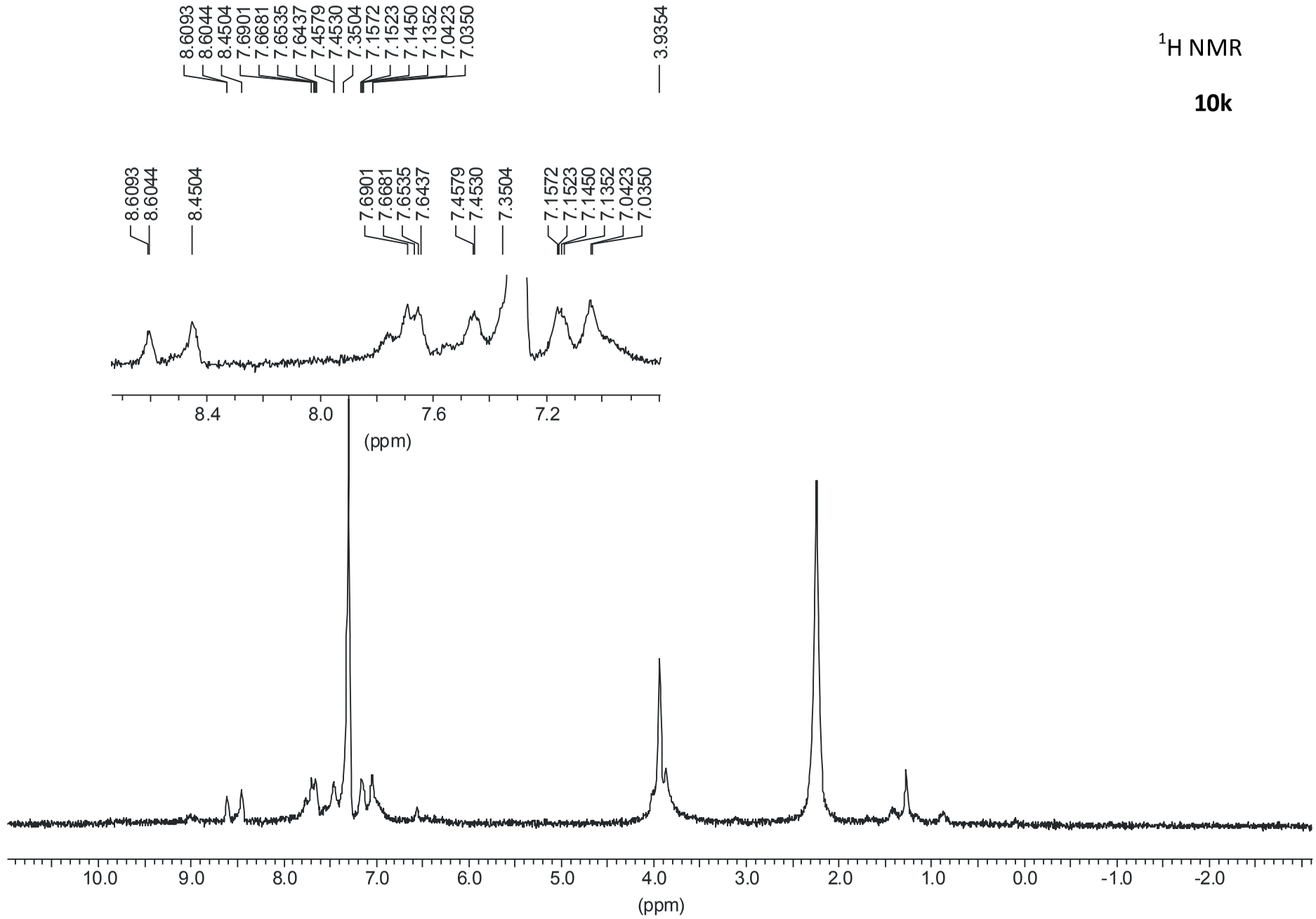


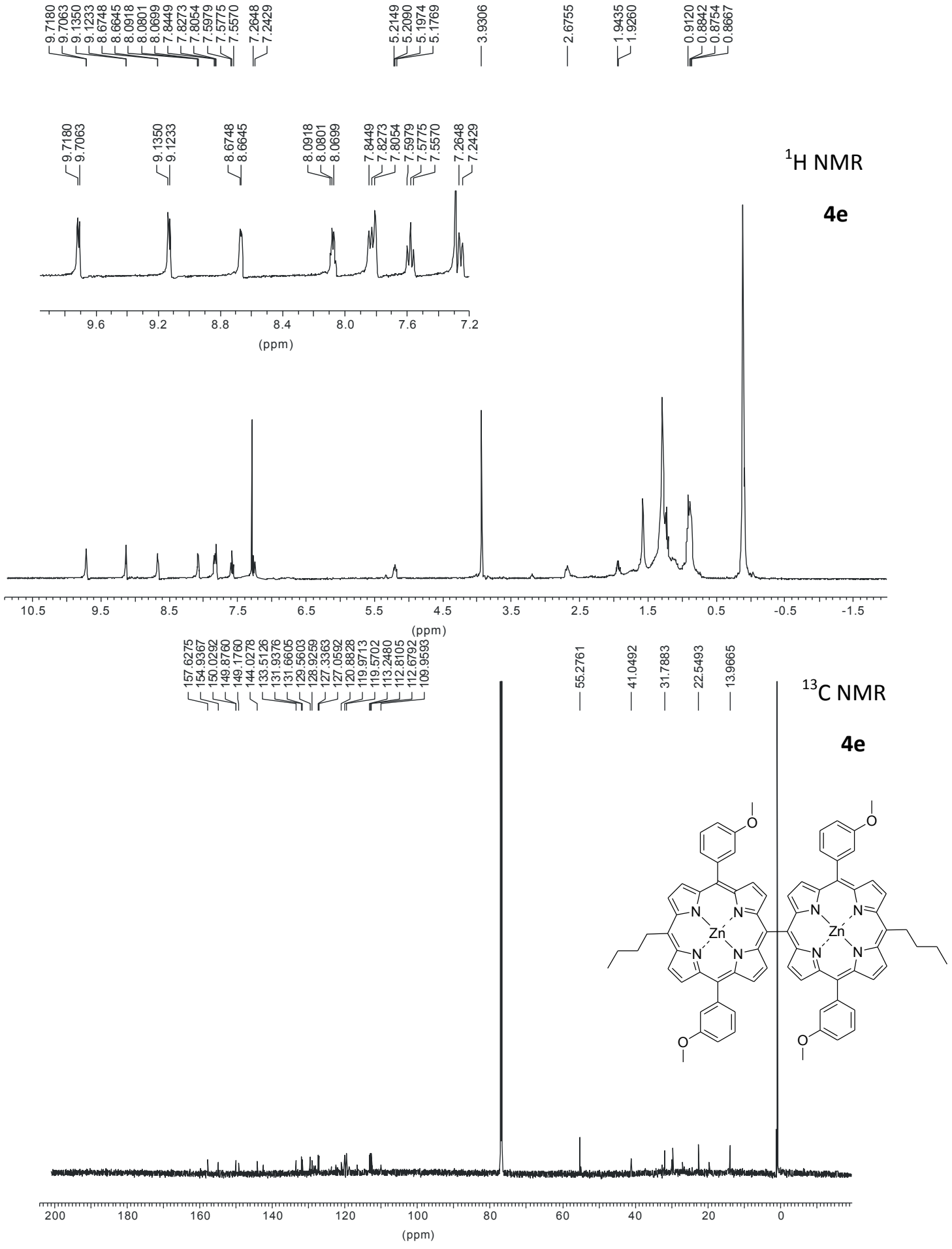
^{1}H NMR **10g**

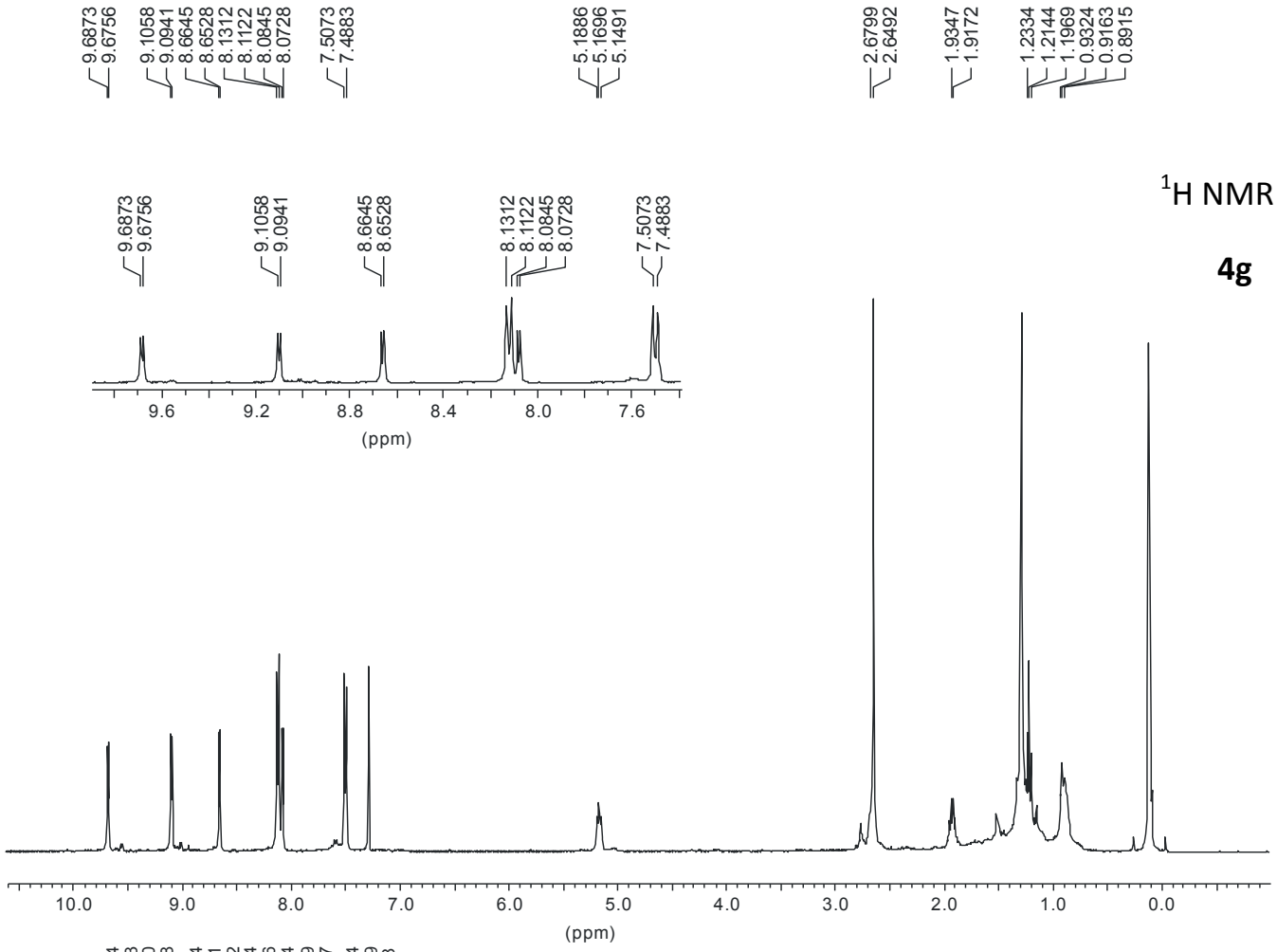


^{1}H NMR

10k

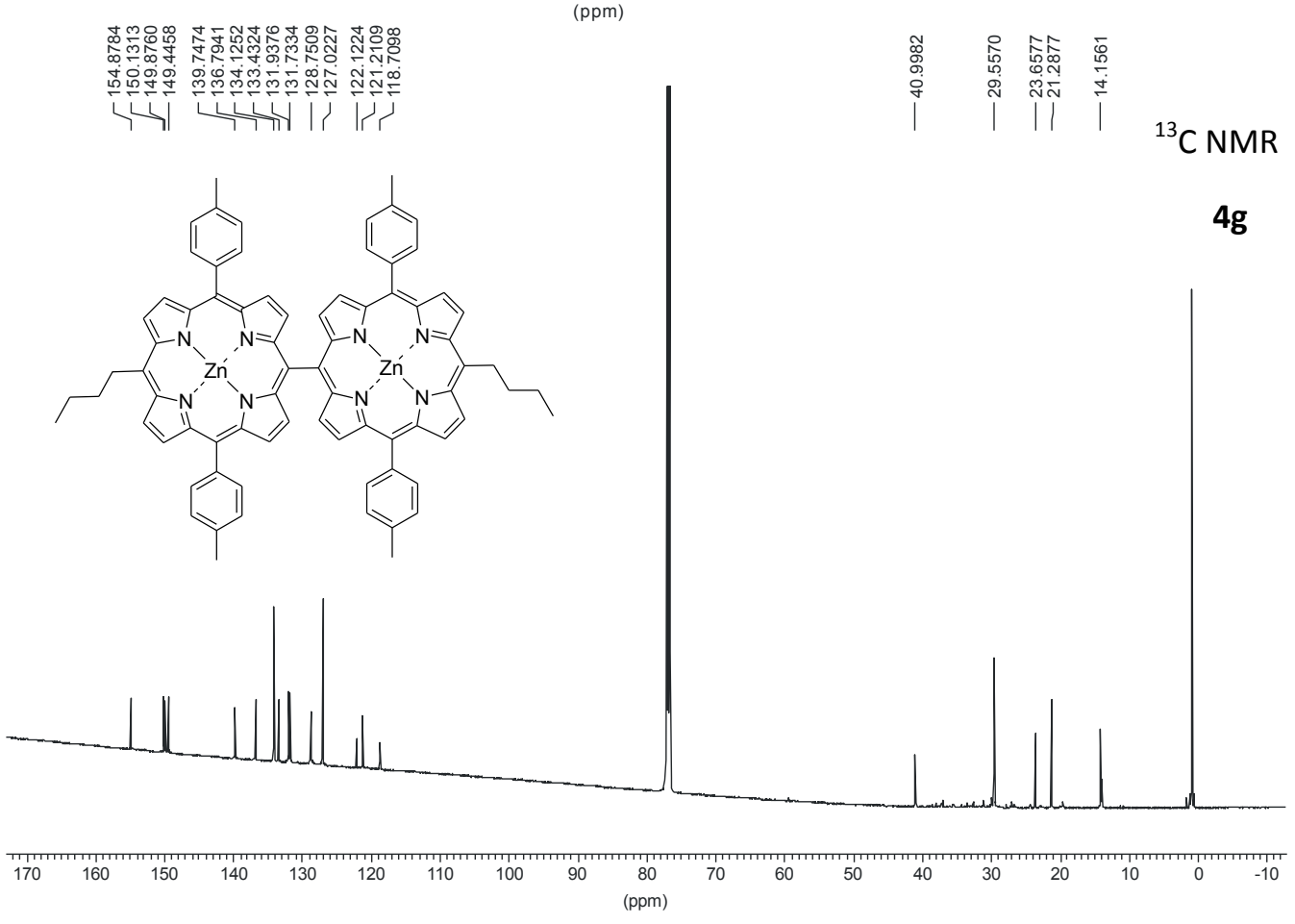

8.6093
8.6044
8.4504
7.6901
7.6681
7.6535
7.6437
7.4579
7.4530
7.3504
7.1572
7.1523
7.1450
7.1352
7.0423
7.0350
3.9354
8.4
8.0
7.6
7.2
(ppm)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
(ppm)


9.7180
9.7063
9.1350
9.1233
8.6748
8.6645
8.0918
8.0801
8.0699
7.8449
7.8273
7.8054
7.5979
7.5775
7.5570
7.2648
7.2429
5.2149
5.2090
5.1974
5.1769
3.9306
2.6755
1.9435
1.9260
0.9120
0.8842
0.8754
0.8667
(ppm)
^{1}H NMR
4e
157.6275
154.9367
150.0292
149.8760
149.1760
144.0278
133.5126
131.9376
131.6605
129.5603
128.9259
127.3363
127.0592
120.8828
119.9713
119.5702
113.2480
112.8105
112.6792
109.9593
55.2761
41.0492
31.7883
22.5493
13.9665
(ppm)
^{13}C NMR
4e
Zn
Zn



^{1}H NMR

4g

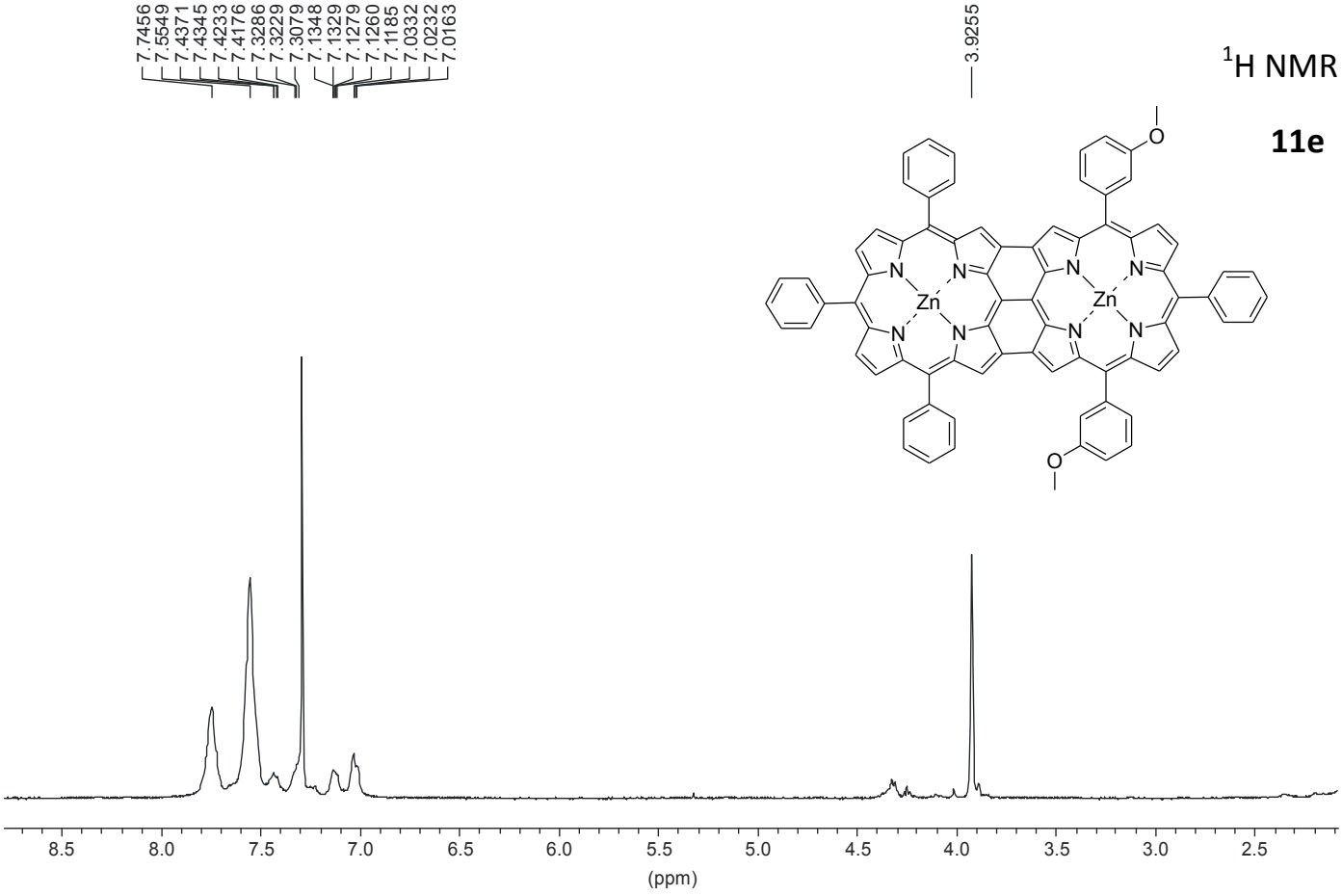


^{13}C NMR

4g

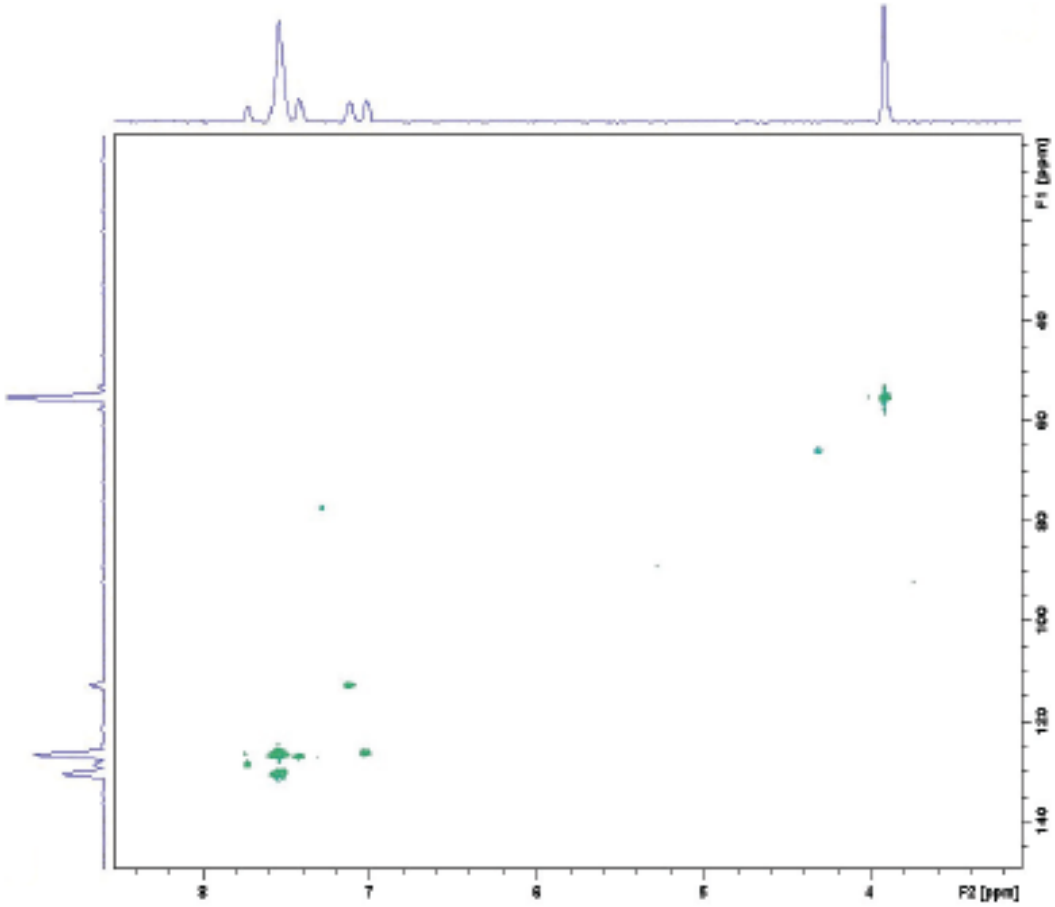
^{1}H NMR

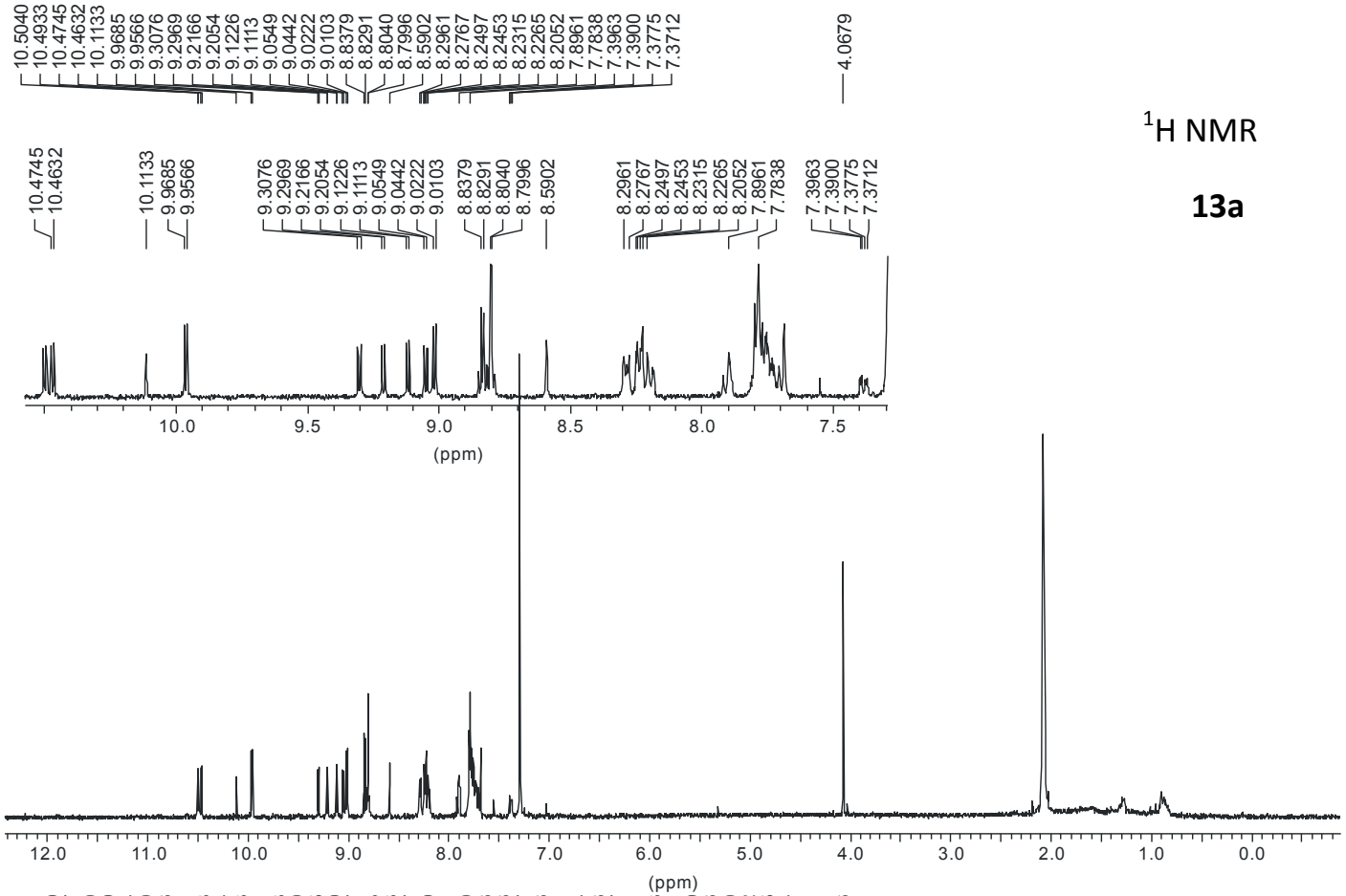
11e



HSQC

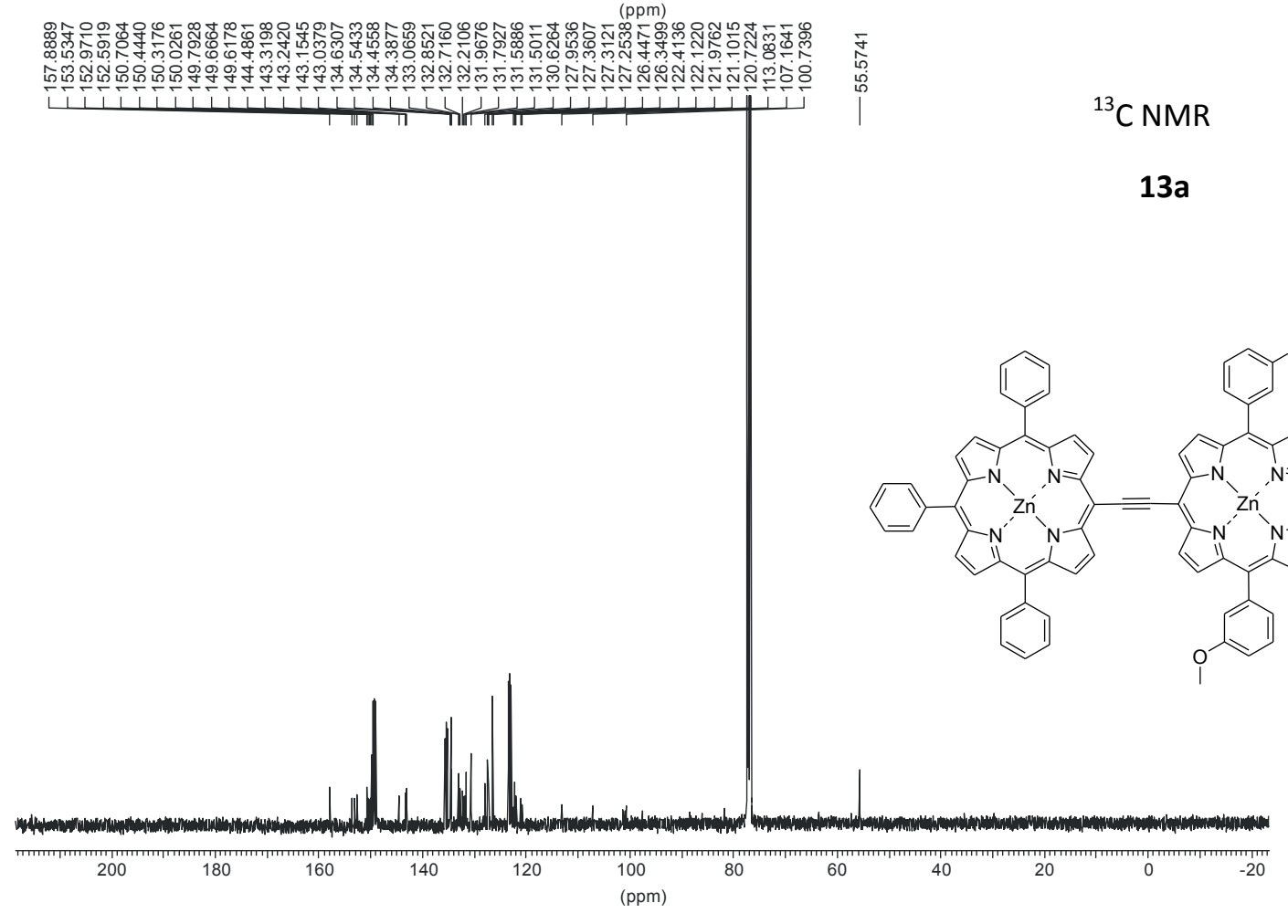
11e





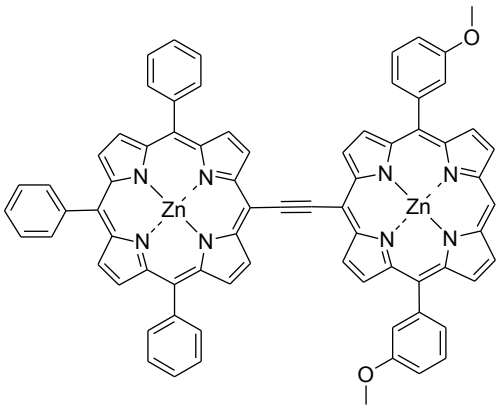
^{1}H NMR

13a



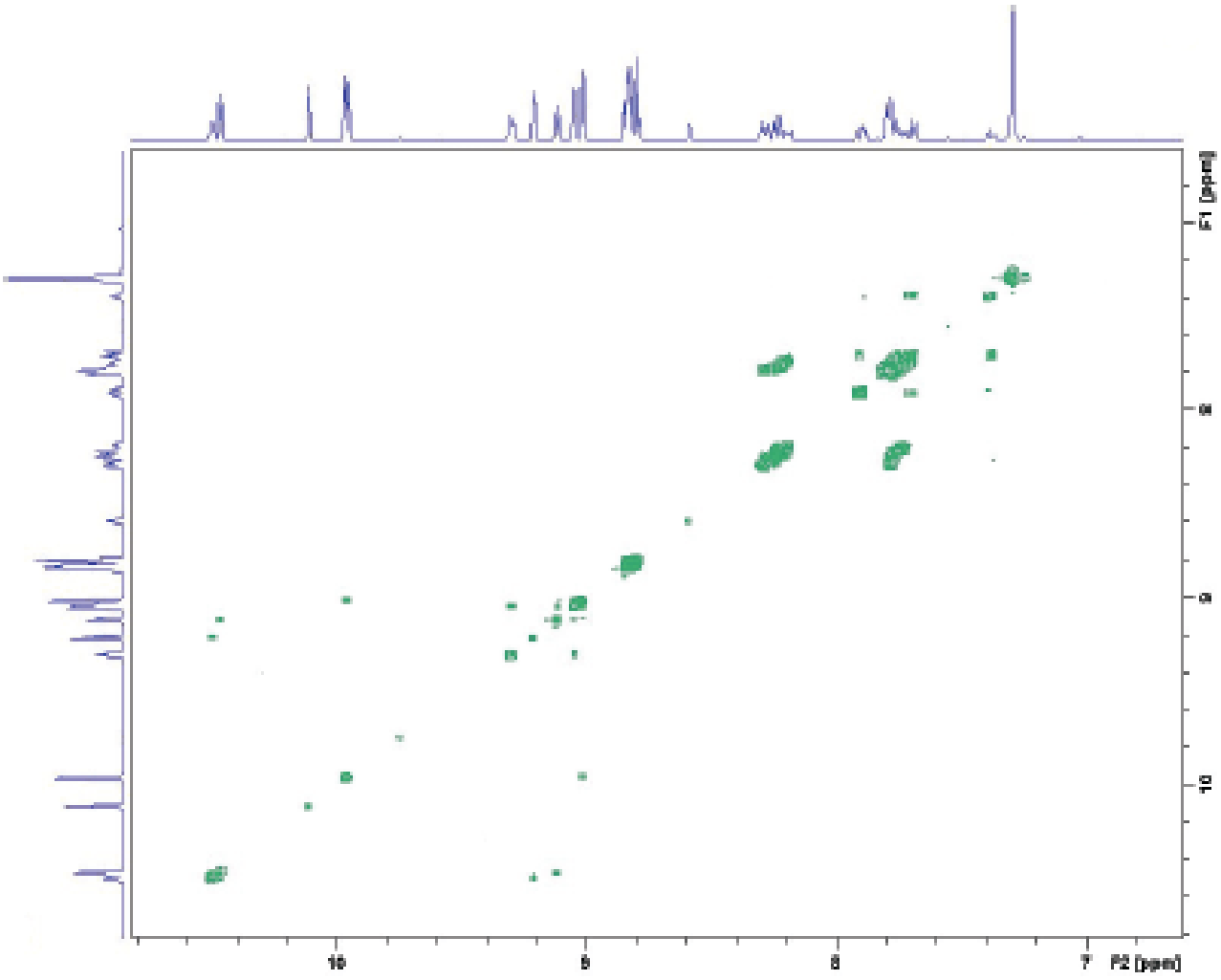
^{13}C NMR

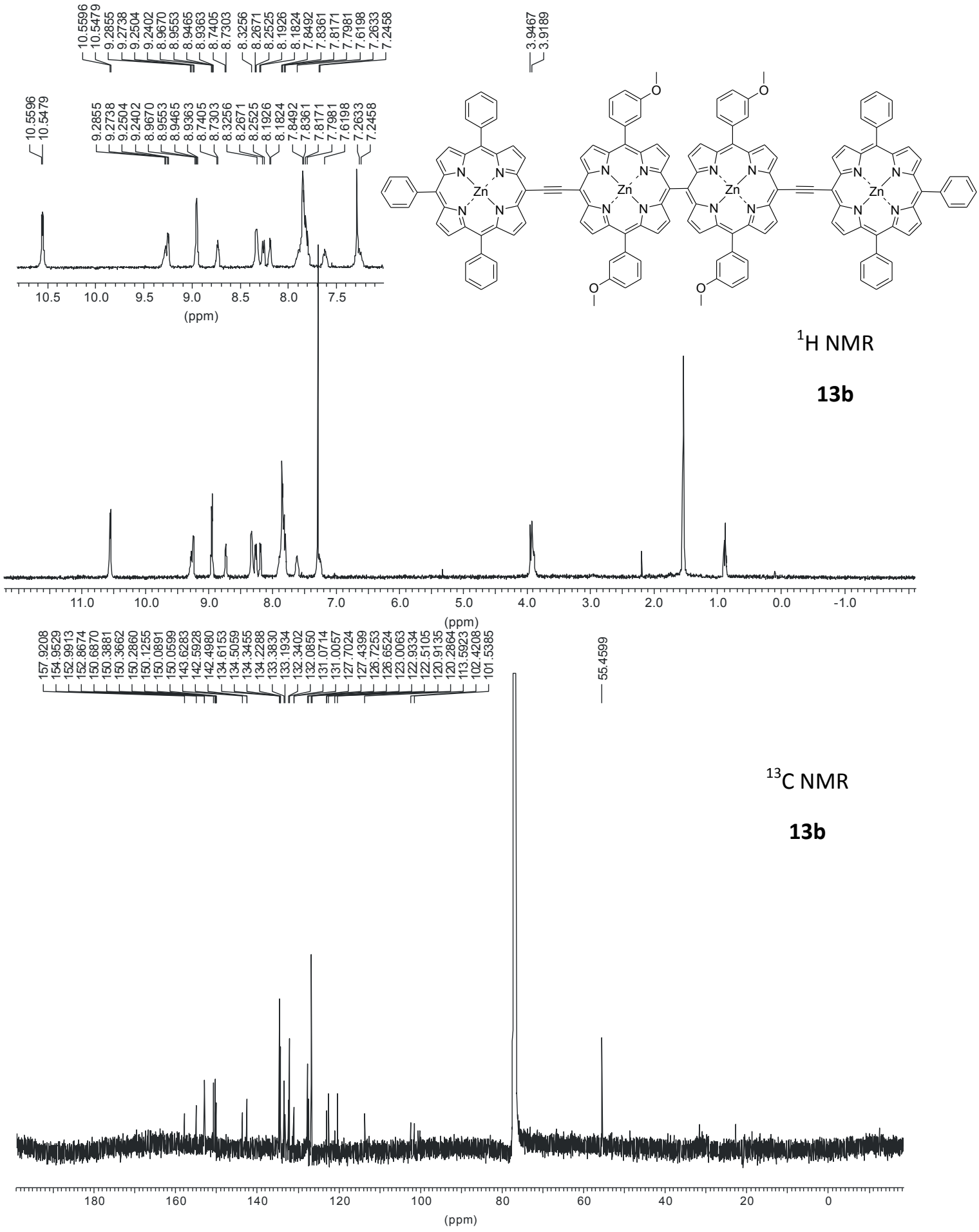
13a



TOCSY

13a

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10.5479
9.2855
9.2738
9.2504
9.2402
8.9670
8.9553
8.9465
8.9363
8.7405
8.7303
8.3256
8.2671
8.2525
8.1926
8.1824
7.8492
7.8361
7.8171
7.7981
7.6198
7.2633
7.2458
3.9467
3.9189
Zn
O
(ppm)
^{1}H NMR
13b
157.9208
154.9529
152.9913
152.8674
150.6870
150.3881
150.3662
150.2860
150.1255
150.0891
150.0599
143.6283
142.5928
142.4980
134.6153
134.5059
134.3455
134.2288
133.3830
133.1934
132.3402
132.0850
131.0714
131.0057
127.7024
127.4399
126.7253
126.6524
123.0063
122.9334
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120.9135
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113.5923
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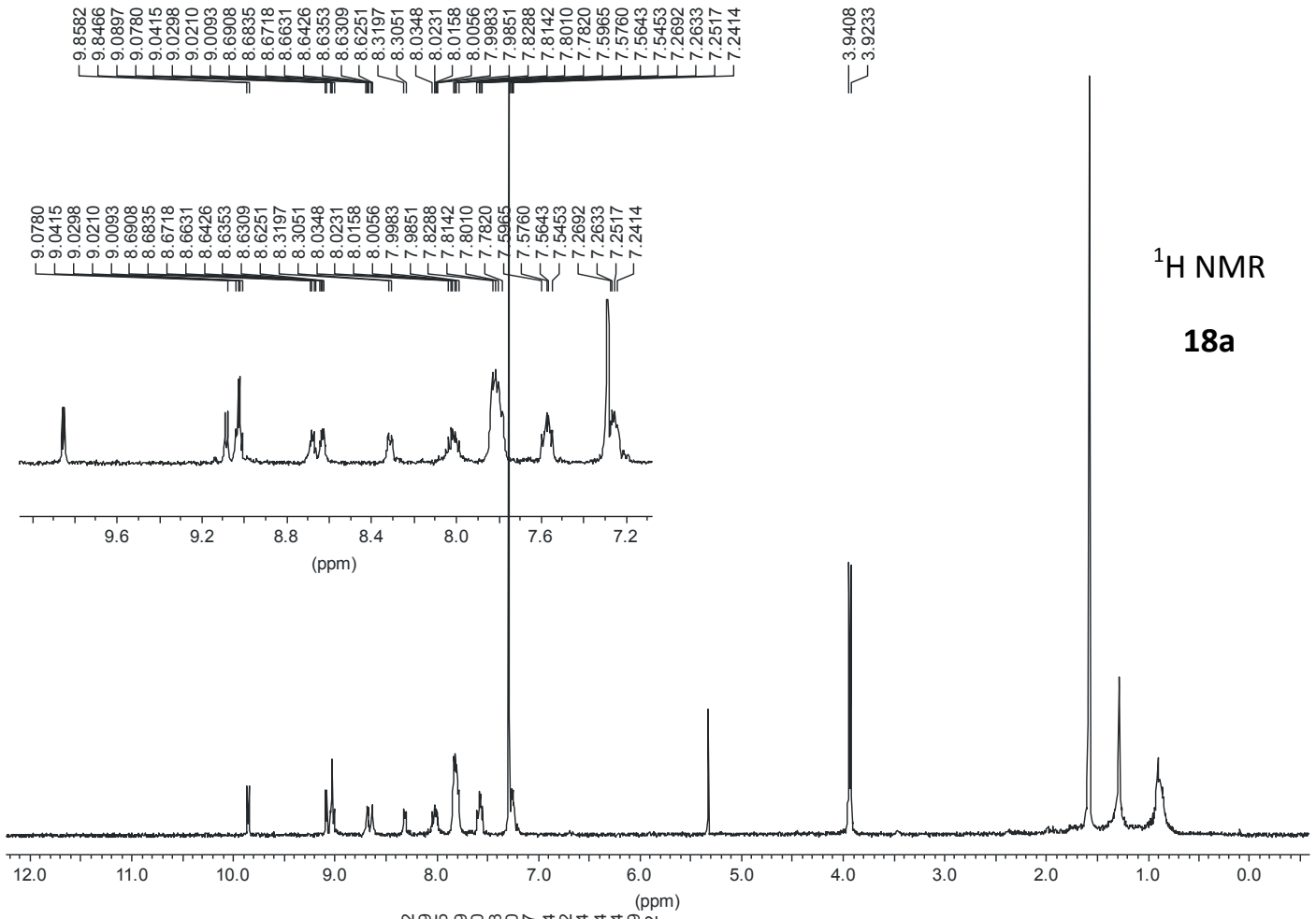
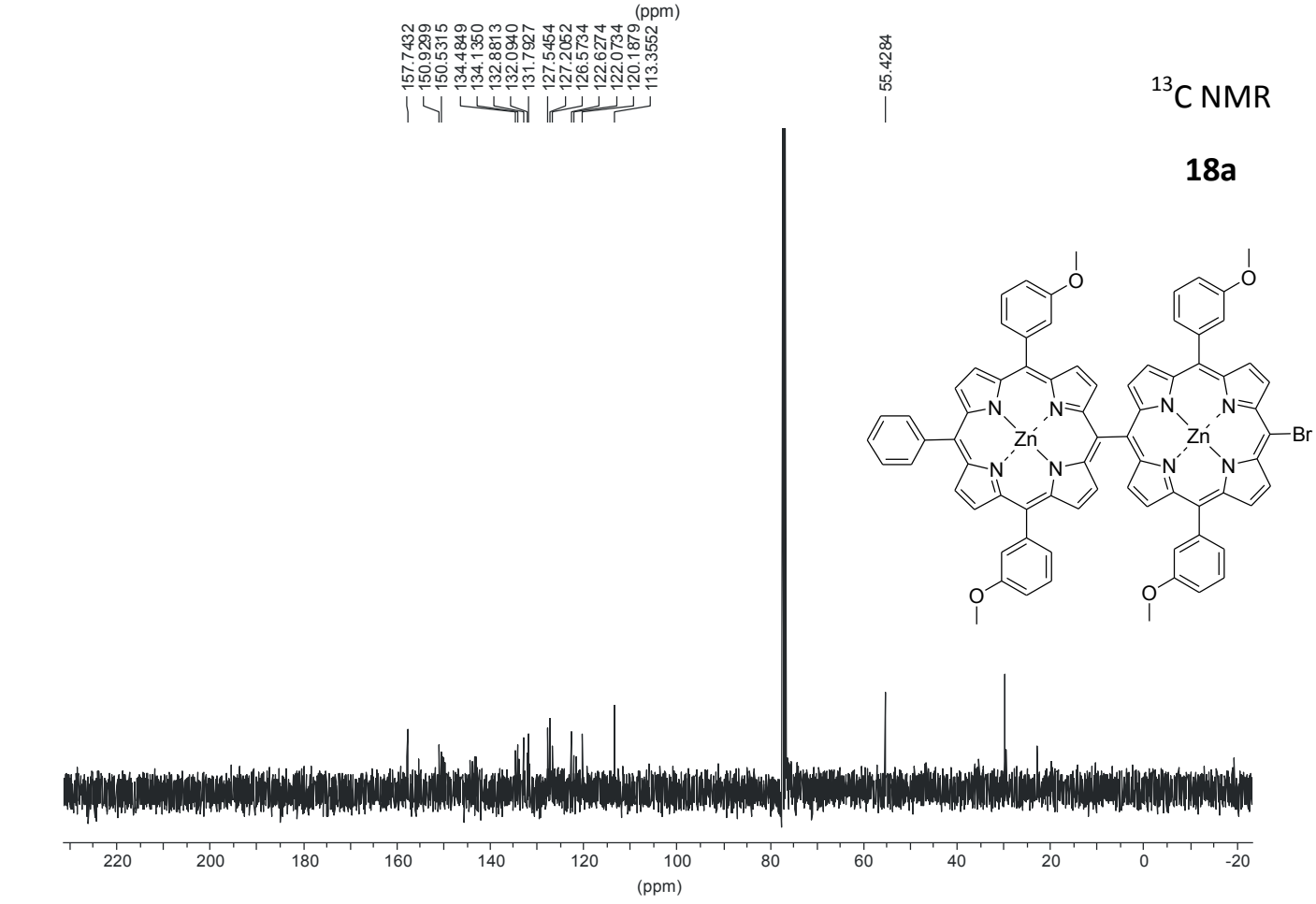
101.5385
55.4599
^{13}C NMR
13b



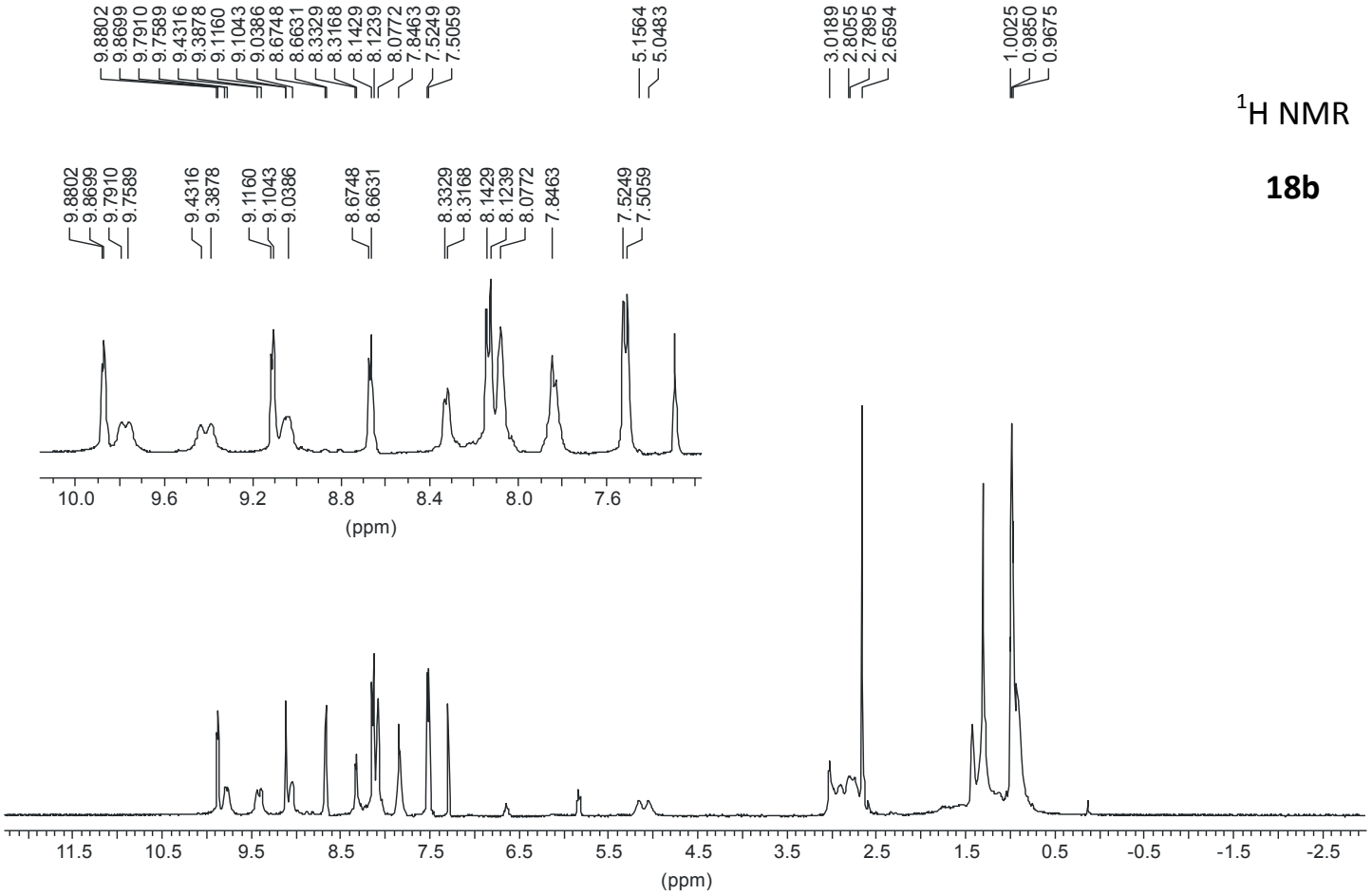
^{1}H NMR

18a



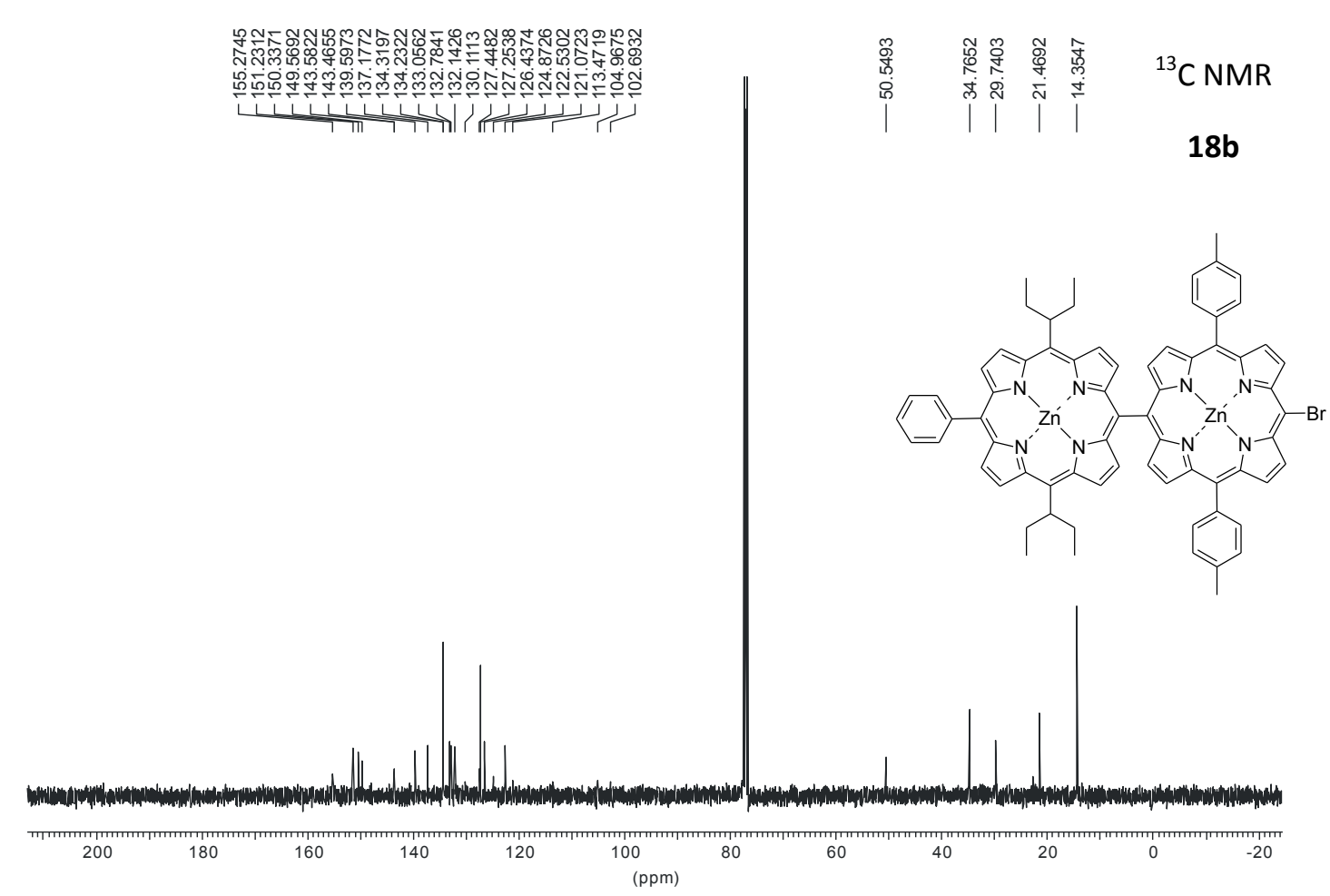
^{13}C NMR

18a



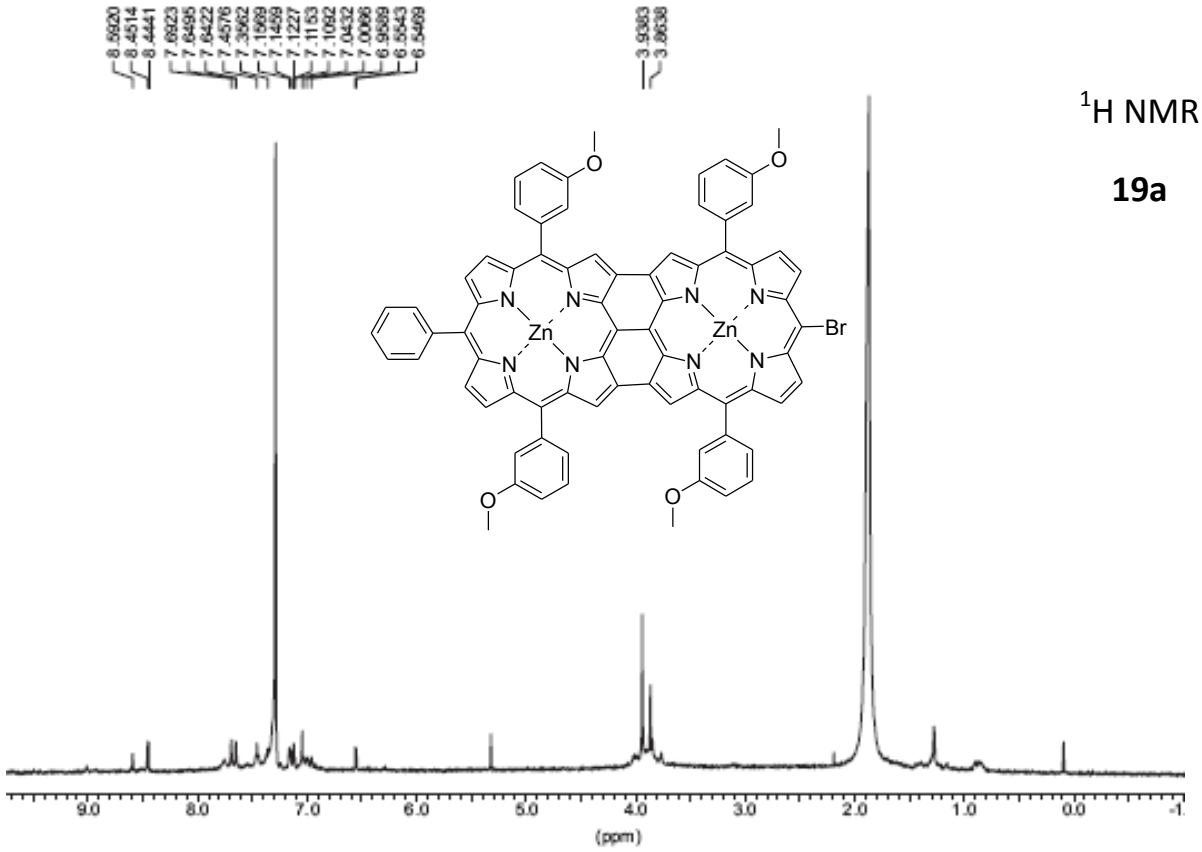
^{1}H NMR

18b



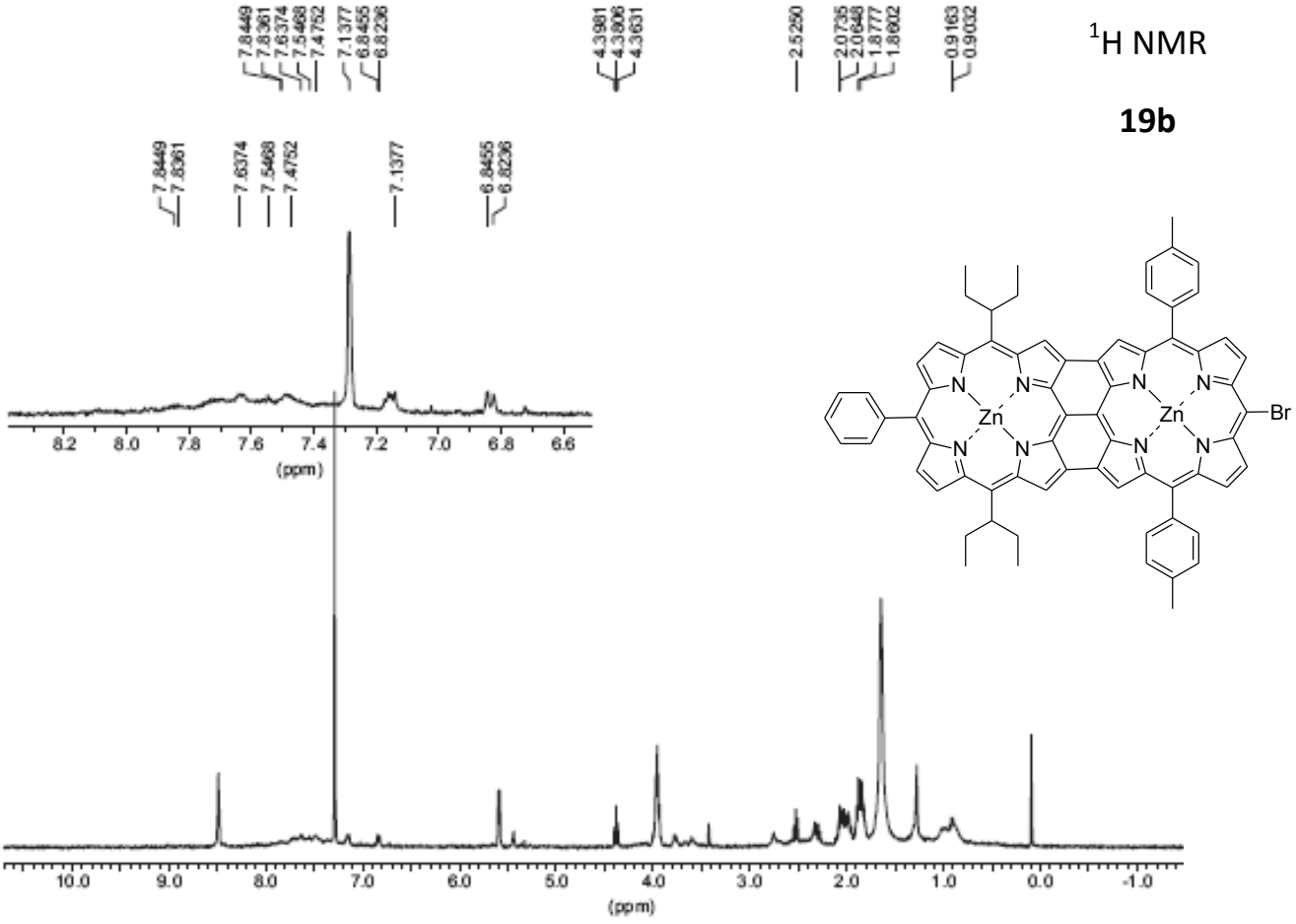
^{13}C NMR

18b



^{1}H NMR

19a



^{1}H NMR

19b