UNIVERSITY OF CRETE
DEPARTMENT OF CHEMISTRY

GENERAL POSTGRADUATE PROGRAMME

LABORATORY OF BIOINORGANIC CHEMISTRY

Master Thesis

NOVEL PORPHYRIN-BASED PHOTOSENSITIZERS WITH APPLICATION IN PHOTOVOLTAIC CELLS

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HERAKLION 2015

ΠΑΝΕΠΙΣΤΗΜΙΟ ΚΡΗΤΗΣ
ΤΜΗΜΑ ΧΗΜΕΙΑΣ

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Higher Education

2012-present *University of Crete*

MSc in Bioinorganic Chemistry

2012

Surveyor Diploma ISO 14001

International Register of Certificated Auditors (IRCA)

1998 - 2002 *University of Liverpool, UK.*

PhD in Organic and Physical Chemistry

- Title : “Podand-type Receptors for Sugar Recognition”
- Supervisor: Dr R. P. Bonar-Law.
- Design and synthesis of molecules capable of forming specific complexes with carbohydrates in solution. Involved both regular organic synthesis and use of spectroscopic techniques (UV-Vis, Fluorescence).Numerous presentations in different European Universities. Research at Universities of Cambridge and Dublin.

1994 – 1998 *University of Crete.*

B.Sc. Chemistry (7.69/10)

- Final year research project involved the synthesis of new amino acid tripyridylphenyl porphyrin derivatives.
- Demonstration of organic synthesis techniques to other students.
- Supervisors: M. Perre-Fauvet and A. G. Coutsolelos.

2006 – present *Teaching at different institutions.*

Relevant Experience

- **University of Crete**, Department of Chemistry, Courses: Chemistry Labs, General Chemistry Labs, Inorganic chemistry labs.
- **Technological Educational Institute of Crete (T.E.I.)**, Department of Human Nutrition and Dietetics, teaching courses: Organic Chemistry and Biochemistry, General and Inorganic Chemistry, Food Chemistry and Analysis, Food Quality Control.
- **Minoan International College**, International College of Hospitality and Tourism Management, teaching courses: Environmental Chemistry, Nutrition Science.
- **Institute of Professional Constitution**, teaching courses: General Chemistry I, II, Analytical Chemistry, Food Chemistry.
- **Tuition Center of Secondary EducstionΦροντιστήριο**, teaching courses: Chemistry in several High School classes.

2009 – present *University of Crete.*

Research Associate (P.D.407)

- Synthesis of novel porphyrin based materials for photovoltaic applications.

2004 – 2006 *University of Crete.*

Research Associate

- Design and synthesis of model compounds for cytochrome c oxidase.
- Involved with supervision of students and day-to-day running of the laboratory.

2002 - 2004 *University of Edinbourgh.*

Research Associate.

- Design and synthesis of novel chiral macrocycles with possible applications in catalysis.
- Involved with supervision of students.
- Frequent oral presentations, problem sessions and literature reviews.

10/1999 - 05/2000 *University of Liverpool.*

Organic Chemistry Laboratory Demonstrations.

- Supervision and instruction of undergraduate laboratories.
- Effective communication of instructions to groups improved.

06/1997 - 09/1997 *Université de Paris-Sud.*

Erasmus Fellowship.

- Synthesis of various porphyrins and collaborated successfully with the team.

10/1996 - 05/1997 *University of Crete.*

Assistant at the laboratory of Organic Chemistry.

- Demonstration of Organic Chemistry techniques.

Additional Information

- Technical knowledge: NMR, UV-Vis, IR, GC, HPLC, MALDI tof MS.
- Computing: Microsoft Windows, Word, Excel, Power Point, Chem&ISIS Draw,

web searching databases, Beilstein Crossfire, Scifinder Scholar, WinNMR, Windows 98 PC running Perkin-Elmer UV Winlab software, Apple Macintosh Power PC running ProFit data analysis software.

- Language literacy: Greek (native language), English (fluent in writing, speaking and reading), French (average).
- Member of the Royal Society of Chemistry (AMRSC) and Hellenic Society of Chemistry.
- Member of the Hellenic Societies of Liverpool and Edinburgh Universities.
- Elected member of the students union of the University of Crete for two successive years.

References

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Publications

1. Urea porphyrins as simple receptors for sugars”, K. Ladomenou and R. P. Bonar-Law, *Chemical Communications,* **2002**, 2108.

2. “A strategic design to approach novel synthetic models for cytochrome *c* oxidase” A. G. Coutsolelos, K. Ladomenou, G. Charalambidis, *Journal of Porphyrin and Phthalocyanines*, **2006**, 430.

3. “A strategic approach for the synthesis of new porphyrin rings, attractive for heme model purpose” K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, *Tetrahedron*, **2007**, 2882-2887.

4. “Synthesis and studies of a super-structured porphyrin derivative-a potential building block for C*c*O mimic models” G. Charalambidis, K. Ladomenou, B. Boitrel and A. G. Coutsolelos, *Eur. J. Org.Chem.*, **2009**, 1263-1268.

5. “Spectroscopic and electrochemical studies of novel model compounds for cytochrome *c* oxidase” K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, *Inorganica Chimica Acta,* 363, 10, 2201-2208 (**2010**).

6. “Porphyrins in Bio-inspired Transformations: Light-Harvesting to Solar Cell”, Manas Panda, Kalliopi Ladomenou, Athanassios G. Coutsolelos, *Coordination Chemistry Reviews*, 256 (**2012**) 2601– 2627.

7. “Meso substituted porphyrin derivatives *via* Palladium catalyzed amination showing wide range visible absorption: Synthesis and photophysical studies” Kalliopi Ladomenou, Theodore Lazarides, Georgios Charalambidis, Athanassios G. Coutsolelos, *Inorganic Chemistry*, **2012**, 51, 10548–10556.

8. "Synthesis, Characterization and Electronic Properties of *trans*-[4 (Alkoxycarbonyl)phenyl]porphyrin-[$Ru^{II}(bpy)_3]_2$ Complexes or Boron–Dipyrrin Conjugates as Panchromatic Sensitizers for DSSCs", Christina Stangel, Kalliopi Ladomenou, Georgios Charalambidis, Manas K. Panda, Theodore Lazarides, and Athanassios G. Coutsolelos, *Eur. J. Inorg. Chem.* **2013**, 1275–1286.

9. "CO and O_2 binding studies of new model complexes for CcO", Kalliopi Ladomenou, Georgios Charalambidis, Athanassios G. Coutsolelos, *Polyhedron,* 54 (**2013**) 47–53.

10."New hybrid materials with porphyrin-ferrocene and porphyrin-pyrene covalently linked to single-walled carbon nanotubes", Solon P. Economopoulos, Angeliki Skondra, Kalliopi Ladomenou, Nikolaos Karousis, Georgios Charalambidis, Athanassios G. Coutsolelos and Nikos Tagmatarchis, *RSC Adv.*, **2013**, 3, 5539-5546.

11."The importance of various anchoring groups attached on porphyrins as potential dyes for DSSC applications" , K. Ladomenou, T. N. Kitsopoulos, G. D. Sharma and A. G. Coutsolelos, *RSC Adv*., **2014**, 4, 21379.

12. Strategic Synthetic Approaches to Porphyrin-based Artificial Light-harvesting Systems for Solar Energy Utilization" A. Coutslelos, K. Ladomenou, G.Charalambidis, D. Daphnomili, *Handbook of Porphyrin Science, Spring*, **2014**, 180, 240.

13."Photochemical hydrogen generation with porphyrin-based systems" Kalliopi Ladomenou, Mirco Natali, Elisabetta Iengo, Georgios Charalampidis, Franco Scandola, Athanassios G. Coutsolelos, *Coordination Chemistry Reviews*, **2014**, *doi:10.1016/j.ccr.2014.10.001.*

14."Donor-π-acceptor, triazine-linked porphyrin dyads as sensitizers for dye-sensitized solar cells", Ganesh D. Sharma, Galateia E. Zervaki, Kalliopi Ladomenou, Emmanuel N. Koukaras, Panagiotis P. Angaridis, and Athanassios G. Coutsolelos*, Journal of Porphyrins and Phthalocyanines,* **2014**, 18, 1.

15. "A mono(carboxy) porphyrin-triazine-$(Bodipy)_2$ Triad as Donor for Bulk Heterojunction Organic Solar Cells", Ganesh D. Sharma, S. A. Siddiqui, Agapi Nikiforou, Galateia E. Zervaki, Irene Georgakaki, Kalliopi Ladomenou, Athanassios G. Coutsolelos, Materials Chemistry C, **2015**, *accepted*.

16. " "Click"-reaction: an alternative tool for new architectures of porphyrin based derivatives", Kalliopi Ladomenou, Vasilis Nikolaou, Georgios Charalambidis, Athanassios G. Coutsolelos, *Coordination Chemistry Reviews*, **2015**, *accepted*.

17.Patent No 20120100552**/26.10.2012** "A system for solar energy utilization based on hydrid materials porphyrin-laccase." Organization of Industrial Patents (OBI), Athens, A.G. Coutsolelos, T. Tron, M. Kafentzi, K. Ladomenou, T. Lazarides, A. Saitakis.

Textbooks

1. Kalliopi Ladomenou, «Laboratory Exercises in Organic and Structural Biochemistry», T.E.I Crete, Department of Human Nutrition and Dietetics, 2009.
2. Kalliopi Ladomenou, «*Food and Analytical Chemistry*», T.E.I Crete, Department of Human Nutrition and Dietetics, 2009.
3. Kalliopi Ladomenou, «Physical and chemical processes», I.E.K., **2013**.
4. Kalliopi Ladomenou, « Pharmacy Physics Laboratory Excersises», I.E.K., **2013**.
5. Kalliopi Ladomenou, « Chemical Technology », I.E.K., **2014**.
6. Kalliopi Ladomenou, « Monitoring and Evaluation of Cosmetics », I.E.K., **2014**.
7. Kalliopi Ladomenou, « Biochemistry », I.E.K., **2014**
8. Kalliopi Ladomenou, «Methods for Drug Control», I.E.K., **2014**
9. Kalliopi Ladomenou, « Analytical Chemistry», I.E.K., **2015**

Conferences

1. K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, 1st Symposium of Organic Synthesis, 4-6 November **2004**, Athens. “Synthesis of porphyrins as model compounds for cytochrome c oxidase”.
2. G. Coutsolelos, K. Ladomenou, G. Charalambidis, 1st European Conference on Chemistry for Life Sciences, 4-8 October, **2005**, Rimini, Italy. “Synthesis of new porphyrinsderivatives as model compounds for cytochrome c oxidase”.
3. K. Ladomenou, 11o Hellenic Chemistry Conference of Postgraduate students, July **2005**, Kolimpari, Chania.
4. K. Ladomenou, 12o Hellenic Chemistry Conference of Postgraduate students, July **2006**, Santorini.
5. G. Coutsolelos, G. Charalambidis, K. Ladomenou, 4th International Conference on Porphyrins and Phthalocyanines, 2-7 July, **2006**, Rome, Italy. “ A strategic design to approach novel synthetic models for Cytochrome *c* Oxidase”.

6. K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, 1o European Conference of Chemistry 27-31 August **2006**, Budapest, Hungary. “Novel synthetic models for cytochrome *c* oxidase”.
7. K. Ladomenou, “The Wine at the nutrition of the future” Scientific Conference, Traditional Cretan Diet and Health, Technological Educational Institute of Crete (T.E.I.), Heraklion, **2007**
8. G. Coutsolelos, G. Charalambidis, K. Ladomenou,10th International Meeting in Inorganic Chemistry, 1-4 July **2009**, Palermo, Italy, “Design and synthesis of super-structured porphyrin as building blogs for new materials, studies and applications”.
9. K. Ladomenou, , G. Charalambidis, A. G. Coutsolelos, 10th Chemistry Conference Greece-Cyprus 02-04 July **2009**, Heraklion, “Electrochemical and spectroscopic studies of novel compounds-models of cytochrome c oxidase”.
10. K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, 16th European Symposium on Organic Chemistry, 12-16 July **2009**, Prague, Czech Republic, “Electrochemical and spectroscopic studies of novel model compounds for cytochrome *c* oxidase”.
11. Athanassios G. Coutsolelos, Galateia E. Zervaki, Georgia Pagona, Georgios Charalambidis, Kalliopi Ladomenou, Nikos Tagmatarchis, 25th European Photovoltaic Solar Energy Conference and Exhibition**,** 6-17 September **2010**, Valencia, Spain, “Synthesis of novel porphyrin dimers for photovoltaic applications”.
12. Kalliopi Ladomenou, Georgios Charalambidis, Galateia E. Zervaki, Georgia Pagona, Nikos Tagmatarchis, Athanassios G. Coutsolelos, Sixth International Conference on Porphyrins and Phthalocyanines, July 4-9 2010, New Mexico, USA, “Novel hybrid materials based on porphyrin dimers for photovoltaic applications”.
13. Athanassios G. Coutsolelos, Kalliopi Ladomenou, Georgios Charalambidis, Galateia E. Zervaki, T. Lazarides, D. Daphnomili, 10th European Biological Inorganic Chemistry Conference, June 22-26, **2010**, Thessaloniki, Greece, “Bio inspired derivatives for solar energy utilization.”
14. G Coutsolelos, K. Ladomenou, G. Charalambidis, G. E. Zervaki, T. Lazarides, D. Daphnomili, WIRE: Week of Innovative Regions in Europe, 15-17 March **2010**, Granada, Spain.
15. Kalliopi Ladomenou, Georgios Charalambidis, Dimitra Daphnomili, Athanassios G. Coutsolelos, «Synthesis of novel porphyrin sensitizers for solar cell applications» **2011**, Manchester, UK.

16. Kalliopi Ladomenou, Georgios Charalambidis, Dimitra Daphnomili, Athanassios G. Coutsolelos, «Synthesis of porphyrin-based sensitizers for solar cell applications», First International Conference on Bioinspired Materials for Solar Energy Utilization, BIOSOL2011, 12-17 September, **2011**, Chania, Crete.

17. Kalliopi Ladomenou, Theodore Lazarides, Georgios Charalambidis and Athanassios G. Coutsolelos, «Peripherally substituted porphyrin derivatives showing wide range visible absorption: Synthesis and photophysical studies», Inorganic Phtophysics and Photochemistry:Fundamentals and Applications:Dalton Discussion 13, 10-12 September, **2012**, Sheffield, UK.

18. Kalliopi Ladomenou, Theodore Lazarides, Georgios Charalambidis and Athanassios G. Coutsolelos, «Peripherally substituted porphyrin derivatives showing wide range visible absorption: Synthesis and photophysical studies», Seventh International Conference on Porphyrins and Phthalocyanines, ICPP-7, July 1-6, **2012**, Jeju, KOREA.

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Γενικό Μεταπτυχιακό Πρόγραμμα (Master)–Κατεύθυνση Ανόργανη Χημεία

<u>2012</u>
Δίπλωμα Επιθεωρητή ISO 14001

International Register of Certificated Auditors (IRCA)
Δίπλωμα Επιθεωρητή/ Επικεφαλούς Επιθεωρητή για Συστήματα περιβαλλοντικής διαχείρισης (ISO 14001)

<u>1998 - 2002</u> *Πανεπιστήμιο του Λίβερπουλ, Αγγλία.*
Διδακτορικό δίπλωμα στην Οργανική Χημεία.

- Τίτλος : "Podand-type Receptors for Sugar Recognition"
- Εποπτ. Καθ.: Dr R. P. Bonar-Law.
- Σχεδιασμός και σύνθεση μορίων ικανών να σχηματίσουν συγκεκριμένα συμπλέγματα με τα σάκχαρα. Η έρευνα συμπεριλάμβανε τη χρησιμοποίηση αρκετών φασματοσκοπικών τεχνικών και προφορικές παρουσιάσεις σε διάφορα Ευρωπαϊκά πανεπιστήμια. Έρευνα στα πανεπιστήμια του Cambridge και του Dublin.

<u>1994 - 1998</u> *Πανεπιστήμιο Κρήτης.*
Πτυχίο Χημείας.

- Βαθμός πτυχίου: 7,69.
- Η διπλωματική εργασία συμπεριλάμβανε τη σύνθεση παραγώγων πορφυρινών και την παρουσίαση διαφόρων τεχνικών οργανικής χημείας σε άλλους φοιτητές.
- Εποπτ. Καθ.: M. Perre-Fauvet και Α. Κουτσολέλος.

Σχετική εμπειρία

2006 - Σήμερα *Διδακτική Εμπειρία.*

- **Π.Δ. 407/80 Πανεπιστήμιο Κρήτης**, Τμήμα Χημείας, ερευνητική εργασία και μαθήματα διδασκαλίας: Εργαστήρια Χημείας, Εργαστήρια Γενικής Χημείας, Εργαστήρια Ανόργανης Χημείας.

- **T.E.I. Κρήτης**

  - Σχολή Τεχνολογίας Γεωπονίας και Τεχνολογίας Τροφίμων, Τμήμα Τεχνολόγων Γεωπόνων, μάθημα διδασκαλίας Γεωργική Χημεία.

  - *Παράρτημα Σητείας, Τμήμα Διατροφής και Διαιτολογίας*, μαθήματα διδασκαλίας: Οργανική Χημεία και Δομική Βιοχημεία, Ποιοτικός Έλεγχος Τροφίμων, Γενική και Ανόργανη Χημεία, Χημεία και Ανάλυση Τροφίμων.

  - *Παράρτημα Ηρακλείου, Τμήμα Φυτικής Παραγωγής και Τμήμα Βιολογικών και Θερμοκηπιακών Καλλιεργειών και Ανθοκομίας*, μάθημα διδασκαλίας Γεωργική Χημεία.
- **Ιδιωτικό Ι.Ε.Κ. Morfi**, μαθήματα διδασκαλίας: Φυσικές και Χημικές Διεργασίες, Τεχνολογία Υλικών I & II, Χημική Τεχνολογία.
- **Ι.Ε.Κ. Ηρακλείου**, μαθήματα διδασκαλίας: Γενική Χημεία I & II, Αναλυτική Χημεία.
- **Minoan College**, Διεθνής Σχολή Τουριστικού Μάνατζμεντ, μαθήματα διδασκαλίας: Περιβαλλοντική Χημεία, Διατροφή.
- **Φροντιστήριο** ‘Ορίζοντες’, μάθημα διδασκαλίας: Χημεία.

2004 - 2006 *Πανεπιστήμιο Κρήτης.*

Ερευνητική θέση με τον καθηγητή Α. Κουτσολέλο.

- Σύνθεση μοντέλων κυτοχρωμικής οξειδάσης c, επιτήρηση μεταπτυχιακών φοιτητών.

2002 - 2004 *Πανεπιστήμιο Εδιμβούργου, Σκωτία.*

Ερευνητική θέση με τον καθηγητή Prof. David Leigh.

- Σχεδιασμός και σύνθεση καινούργιων χημικών κυκλικών ενώσεων με πιθανές εφαρμογές στην κατάλυση.
- Επιτήρηση φοιτητών και επίβλεψη της καθημερινής λειτουργίας του εργαστηρίου.
- Συχνές προφορικές παρουσιάσεις και λύσεις χημικών προβλημάτων.

10/1999 - 05/2000 *Πανεπιστήμιο Λίβερπουλ, Αγγλία.*

- Επιτήρηση και καθοδήγηση προπτυχιακών φοιτητών στα εργαστήρια.

06/1997 - 09/1997 *Université de Paris-Sud, Γαλλία.*

Υποτροφία Erasmus.

- Σύνθεση πορφυρινών, άριστη συνεργασία με όλη την ερευνητική ομάδα.

10/1996 - 05/1997 *Πανεπιστήμιο Κρήτης.*

Βοηθός στο εργαστήριο οργανικής χημείας.

- Παρουσίαση στους φοιτητές διάφορων τεχνικών της οργανικής χημείας.

Επιπλέον Πληροφορίες

- Τεχνικές γνώσεις: NMR, UV-Vis, IR, GC, HPLC.
- Γνώσεις Η/Υ: Microsoft Windows, Word, Excel, Power Point, Chem&ISIS Draw, web searching databases, Beilstein Crossfire, Scifinder Scholar, WinNMR, Windows 98 PC running Perkin-Elmer UV Winlab software, Apple Macintosh Power PC running ProFit data analysis software. **Κάτοχος ECDL**.
- Ξένες γλώσσες: Αγγλικά (άπταιστα), Γαλλικά (πολύ καλά).
- Μέλος της Royal Society of Chemistry (AMRSC) και της Ένωσης Ελλήνων Χημικών.
- Μέλος της Ελληνικής και Ευρωπαϊκής κοινότητας του πανεπιστημίων Λίβερπουλ και Εδιμβούργου.
- Εκλεγμένο μέλος στο φοιτητικό συμβούλιο του πανεπιστημίου της Κρήτης.

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Δημοσιεύσεις σε Διεθνή Περιοδικά

1. "Urea porphyrins as simple receptors for sugars", K. Ladomenou and R. P. Bonar-Law, *Chemical Communications,* **2002**, 2108.
2. "A strategic design to approach novel synthetic models for cytochrome *c* oxidase" A. G. Coutsolelos, K. Ladomenou, G. Charalambidis, *Journal of Porphyrin and Phthalocyanines*, **2006**, 430.
3. "A strategic approach for the synthesis of new porphyrin rings, attractive for heme model purpose" K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, *Tetrahedron*, **2007**, 2882-2887.

4. “Synthesis and studies of a super-structured porphyrin derivative-a potential building block for C*c*O mimic models” G. Charalambidis, K. Ladomenou, B. Boitrel and A. G. Coutsolelos, *Eur. J. Org.Chem.*, **2009**, 1263-1268.
5. “Spectroscopic and electrochemical studies of novel model compounds for cytochrome *c* oxidase” K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, *Inorganica Chimica Acta,* 363, 10, 2201-2208 (**2010**).
6. “Porphyrins in Bio-inspired Transformations: Light-Harvesting to Solar Cell”, Manas Panda, Kalliopi Ladomenou, Athanassios G. Coutsolelos, *Coordination Chemistry Reviews*, 256 (**2012**) 2601– 2627.
7. “Meso substituted porphyrin derivatives *via* Palladium catalyzed amination showing wide range visible absorption: Synthesis and photophysical studies” Kalliopi Ladomenou, Theodore Lazarides, Georgios Charalambidis, Athanassios G. Coutsolelos, *Inorganic Chemistry*, **2012**, 51, 10548−10556.
8. “Synthesis, Characterization and Electronic Properties of *trans*-[4 (Alkoxycarbonyl)phenyl]porphyrin-$[Ru^{II}(bpy)_3]_2$ Complexes or Boron–Dipyrrin Conjugates as Panchromatic Sensitizers for DSSCs”, Christina Stangel, Kalliopi Ladomenou, Georgios Charalambidis, Manas K. Panda, Theodore Lazarides, and Athanassios G. Coutsolelos, *Eur. J. Inorg. Chem.* **2013**, 1275–1286.
9. “CO and O_2 binding studies of new model complexes for CcO”, Kalliopi Ladomenou, Georgios Charalambidis, Athanassios G. Coutsolelos, *Polyhedron,* 54 (**2013**) 47–53.
10. “New hybrid materials with porphyrin-ferrocene and porphyrin-pyrene covalently linked to single-walled carbon nanotubes”, Solon P. Economopoulos, Angeliki Skondra, Kalliopi Ladomenou, Nikolaos Karousis, Georgios Charalambidis, Athanassios G. Coutsolelos and Nikos Tagmatarchis, *RSC Adv.*, **2013**, 3, 5539-5546.
11. “The importance of various anchoring groups attached on porphyrins as potential dyes for DSSC applications” , K. Ladomenou, T. N. Kitsopoulos, G. D. Sharma and A. G. Coutsolelos, *RSC Adv*., **2014**, 4, 21379.
12. Strategic Synthetic Approaches to Porphyrin-based Artificial Light-harvesting Systems for Solar Energy Utilization” A. Coutslelos, K. Ladomenou, G.Charalambidis, D. Daphnomili, *Handbook of Porphyrin Science, Spring*, **2014**, 180, 240.
13. “Photochemical hydrogen generation with porphyrin-based systems” Kalliopi Ladomenou, Mirco Natali, Elisabetta Iengo, Georgios Charalampidis, Franco Scandola, Athanassios G. Coutsolelos, *Coordination Chemistry Reviews*, **2014**, *doi:10.1016/j.ccr.2014.10.001.*

14. “Donor-π-acceptor, triazine-linked porphyrin dyads as sensitizers for dye-sensitized solar cells”, Ganesh D. Sharma, Galateia E. Zervaki, Kalliopi Ladomenou, Emmanuel N. Koukaras, Panagiotis P. Angaridis, and Athanassios G. Coutsolelos, *Journal of Porphyrins and Phthalocyanines,* **2014**, 18, 1.

15. “A mono(carboxy) porphyrin-triazine-(Bodipy)$_2$ Triad as Donor for Bulk Heterojunction Organic Solar Cells”, Ganesh D. Sharma, S. A. Siddiqui, Agapi Nikiforou, Galateia E. Zervaki, Irene Georgakaki, Kalliopi Ladomenou, Athanassios G. Coutsolelos, Materials Chemistry C, **2015**, *accepted*.

16. “ “Click”-reaction: an alternative tool for new architectures of porphyrin based derivatives”, Kalliopi Ladomenou, Vasilis Nikolaou, Georgios Charalambidis, Athanassios G. Coutsolelos, *Coordination Chemistry Reviews*, **2015**, *accepted*.

17. **Patent** No 20120100552**/26.10.2012** "A system for solar energy utilization based on hydrid materials porphyrin-laccase." Organization of Industrial Patents (OBI), Athens, A.G. Coutsolelos, T. Tron, M. Kafentzi, K. Ladomenou, T. Lazarides, A. Saitakis.

Συγγράμματα

1. Συγγραφή Εργαστηριακών Ασκήσεων Μαθήματος «Οργανική και Δομική Βιοχημεία», Καλλιόπη Λαδωμένου, *Τ.Ε.Ι. Κρήτης*, **2009**.
2. Συγγραφή Σημειώσεων Μαθήματος «Χημεία και Ανάλυση Τροφίμων», Καλλιόπη Λαδωμένου, *Τ.Ε.Ι. Κρήτης*, **2009**.
3. «Φυσικές και χημικές διεργασίες» Καλλιόπη Λαδωμένου, Βιβλίο, **2013**.
4. «Εργαστήρια Φαρμακευτικής Φυσικής» Καλλιόπη Λαδωμένου, Βιβλίο, **2013**.
5. «Χημική Τεχνολογία», Καλλιόπη Λαδωμένου, Βιβλίο, **2014**.
6. Καλλιόπη Λαδωμένου «Έλεγχος και Αξιολόγηση Καλλυντικών, Βιβλίο, **2014**.
7. «Βιοχημεία», Καλλιόπη Λαδωμένου, Βιβλίο, **2014**.
8. «Μέθοδοι Ελέγχου Φαρμάκων», Καλλιόπη Λαδωμένου, Βιβλίο, **2014**.
9. «Αναλυτική Χημεία», Καλλιόπη Λαδωμένου, Βιβλίο, **2015**.

Δημοσιεύσεις σε Διεθνή Συνέδρια

1. K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, 1st Symposium of Organic Synthesis, 4-6 November **2004**, Athens. “Synthesis of porphyrins as model compounds for cytochrome c oxidase”.

2. G. Coutsolelos, K. Ladomenou, G. Charalambidis, 1st European Conference on Chemistry for Life Sciences, 4-8 October, **2005**, Rimini, Italy. "Synthesis of new porphyrinsderivatives as model compounds for cytochrome c oxidase".

3. K. Ladomenou, 11o Hellenic Chemistry Conference of Postgraduate students, July **2005**, Kolimpari, Chania.

4. K. Ladomenou, 12o Hellenic Chemistry Conference of Postgraduate students, July **2006**, Santorini.

5. G. Coutsolelos, G. Charalambidis, K. Ladomenou, 4th International Conference on Porphyrins and Phthalocyanines, 2-7 July, **2006**, Rome, Italy. " A strategic design to approach novel synthetic models for Cytochrome *c* Oxidase".

6. K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, 1o European Conference of Chemistry 27-31 August **2006**, Budapest, Hungary. "Novel synthetic models for cytochrome *c* oxidase".

7. K. Ladomenou, "The Wine at the nutrition of the future" Scientific Conference, Traditional Cretan Diet and Health, Technological Educational Institute of Crete (T.E.I.), Heraklion, **2007**

8. G. Coutsolelos, G. Charalambidis, K. Ladomenou,10th International Meeting in Inorganic Chemistry, 1-4 July **2009**, Palermo, Italy, "Design and synthesis of super-structured porphyrin as building blogs for new materials, studies and applications".

9. K. Ladomenou, , G. Charalambidis, A. G. Coutsolelos, 10th Chemistry Conference Greece-Cyprus 02-04 July **2009**, Heraklion, "Electrochemical and spectroscopic studies of novel compounds-models of cytochrome c oxidase".

10. K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, 16th European Symposium on Organic Chemistry, 12-16 July **2009**, Prague, Czech Republic, "Electrochemical and spectroscopic studies of novel model compounds for cytochrome *c* oxidase".

11. Athanassios G. Coutsolelos, Galateia E. Zervaki, Georgia Pagona, Georgios Charalambidis, Kalliopi Ladomenou, Nikos Tagmatarchis, 25th European Photovoltaic Solar Energy Conference and Exhibition**,** 6-17 September **2010**, Valencia, Spain, "Synthesis of novel porphyrin dimers for photovoltaic applications".

12. Kalliopi Ladomenou, Georgios Charalambidis, Galateia E. Zervaki, Georgia Pagona, Nikos Tagmatarchis, Athanassios G. Coutsolelos, Sixth International Conference on Porphyrins and Phthalocyanines, July 4-9 2010, New Mexico, USA, "Novel hybrid materials based on porphyrin dimers for photovoltaic applications".

13. Athanassios G. Coutsolelos, Kalliopi Ladomenou, Georgios Charalambidis, Galateia E. Zervaki, T. Lazarides, D. Daphnomili, 10th European Biological Inorganic Chemistry Conference, June 22-26, **2010**, Thessaloniki, Greece, "Bio inspired derivatives for solar energy utilization."

14. G Coutsolelos, K. Ladomenou, G. Charalambidis, G. E. Zervaki, T. Lazarides, D. Daphnomili, WIRE: Week of Innovative Regions in Europe, 15-17 March **2010**, Granada, Spain.

15. Kalliopi Ladomenou, Georgios Charalambidis, Dimitra Daphnomili, Athanassios G. Coutsolelos, «Synthesis of novel porphyrin sensitizers for solar cell applications» **2011**, Manchester, UK.

16. Kalliopi Ladomenou, Georgios Charalambidis, Dimitra Daphnomili, Athanassios G. Coutsolelos, «Synthesis of porphyrin-based sensitizers for solar cell applications», First International Conference on Bioinspired Materials for Solar Energy Utilization, BIOSOL2011, 12-17 September, **2011**, Chania, Crete.

17. Kalliopi Ladomenou, Theodore Lazarides, Georgios Charalambidis and Athanassios G. Coutsolelos, «Peripherally substituted porphyrin derivatives showing wide range visible absorption: Synthesis and photophysical studies», Inorganic Phtophysics and Photochemistry:Fundamentals and Applications:Dalton Discussion 13, 10-12 September, **2012**, Sheffield, UK.

18. Kalliopi Ladomenou, Theodore Lazarides, Georgios Charalambidis and Athanassios G. Coutsolelos, «Peripherally substituted porphyrin derivatives showing wide range visible absorption: Synthesis and photophysical studies», Seventh International Conference on Porphyrins and Phthalocyanines, ICPP-7, July 1-6, **2012**, Jeju, KOREA.

ABSTRACT

The beauty and accuracy of light harvesting as well as the electron transfer process in natural photosynthesis are sources of inspiration for chemists, physicists and researchers of other disciplines to design artificial systems in order to convert solar energy into electricity or other forms of energy. More importantly, the understanding of the fundamentals of these processes is necessary in order to improve the design and the efficiency of artificial photoconversion systems, especially for photovoltaic applications. Porphyrins being ubiquitous in most of the natural pigments are an important building block for developing artificial molecular assemblies for solar photoconversion. The simplest mimicking unit of the natural photosynthetic center could be a porphyrin-derivative where an electron donor and an electron acceptor moiety are covalently linked or self-assembled *via* weak interactions. Intrinsic light-harvesting properties of porphyrins made them the best choice as sensitizers for organic photovoltaics, especially in photo-electrochemical dye-sensitized solar cells (DSSCs) or in hybrid solar cells. Twenty years after the discovery of DSSC by Grätzel, a porphyrin based sensitizer has exhibited one of the highest efficiency (~13%) reported so far.

In this master research project our aim was the synthesis of novel porphyrin based photosensitizers for DSSC applications. The research has been divided in four subsections, where different types of porphyins have been prepared in order to be used as dyes in DSSCs. In Section A different triads have been synthesized bearing a central metallated porphyrin linked with (i) two free-base porphyrin molecules and (ii) with two boron dipyrrin (BDP) molecules. Their photophysical properties were studied. In section B the synthesis and DSCC measurements of two porphyrin dyads are presented. The porphyrinic molecules consist of a zinc-metalated porphyrin and a free-base porphyrin unit covalently linked at their peripheries. Power conversion efficiency values were measured for these dimers in the range of 4-5%. In section C dyad porphyrins were synthesized using ruthenium metalated porphyrins and their DSSC performance was measured in the range of 1 %. Finally, in section D metallated porphyrins were prepapred bearing long alkyl chains and two carboxylic groups attached at the meso position of the porphyrin ring via triple bond.

Keywords: porphyrin, sensitizer, dye, chromophore, solar cell

ΠΕΡΙΛΗΨΗ

Η ομορφιά και η ακρίβεια της συλλογής του φωτός, καθώς και η διαδικασία μεταφοράς ηλεκτρονίων κατά την φωτοσύνθεση είναι πηγές έμπνευσης για τους χημικούς, φυσικούς και επιστήμονες άλλων κλάδων για να σχεδιάσουν τεχνητά συστήματα, ώστε να μετατρέπουν την ηλιακή ενέργεια σε ηλεκτρική ή άλλες μορφές ενέργειας. Επιπλέον, η κατανόηση των βασικών αρχών αυτών των διαδικασιών είναι αναγκαία για τη βελτίωση του σχεδιασμού και της αποτελεσματικότητας των τεχνητών συστημάτων φωτομετατροπής, ειδικά για φωτοβολταϊκές εφαρμογές. Οι πορφυρίνες οι οποίες είναι παρούσες στις περισσότερες από τις φυσικές χρωστικές ουσίες, αποτελούν σημαντικό δομικό στοιχείο για την ανάπτυξη τεχνητών μοριακών συσσωματωμάτων για την ηλιακή φωτομετατροπή. Η απλούστερη μονάδα του φυσικού φωτοσυνθετικού κέντρου θα μπορούσε να είναι ένα παράγωγο πορφυρίνης όπου ένας δότης ηλεκτρονίων και ένας δέκτης ηλεκτρονίων συνδέονται ομοιοπολικά ή αυτοσυναρμολογούνται μέσω ασθενών αλληλεπιδράσεων. Οι ιδιότητες των πορφυρινών βοηθούν στο να είναι η καλύτερη επιλογή ως ευαισθητοποιητές για τα οργανικά φωτοβολταϊκά, ιδίως για τους φωτο-ηλεκτροχημικούς φωτο-ευαισθητοποιημένων ηλιακών κελιών (DSSCs) ή σε υβριδικά ηλιακά κελιά. Είκοσι χρόνια μετά την ανακάλυψη των DSSC από τον Grätzel, μία πορφυρίνη ως ευαισθητοποιητής έχει μια από τις υψηλότερες αποδόσεις (~ 13%) που έχουν αναφερθεί μέχρι τώρα.

Σε αυτή τη μεταπτυχιακή εργασία στόχος μας ήταν η σύνθεση νέων πορφυρινών που δρουν ως φωτοευαισθητοποιητές για εφαρμογές στα φωτοβολταϊκά κελιά. Η έρευνα έχει χωριστεί σε τέσσερις υποενότητες, όπου διαφορετικές πορφυρίνες έχουν συντεθεί με σκοπό να χρησιμοποιηθούν ως χρωστικές ουσίες σε φωτοβολταϊκά κελιά (DSSC). Στο μέρος Α έχουν συντεθεί διαφορετικές τριάδες που φέρουν μια κεντρική μεταλλωμένη πορφυρίνη που συνδέονται (i) με δύο μόρια ελεύθερης πορφυρίνης (ii) με δυο μόρια bodipy (BDP). Μελετήθηκαν οι φωτοφυσικές τους ιδιότητες. Στο μέρος Β παρουσιάζεται η σύνθεση και οι μετρήσεις ηλεκτρικής απόδοσης (DSCC) δύο δυάδων πορφυρινών. Οι πορφυρίνες αποτελούνται από μια μεταλλωμένη πορφυρίνη με ψευδάργυρο και μια μη μεταλλωμένη πορφυρίνη ομοιοπολικά συνδεδεμένες. Οι τιμές της ηλεκτρικής τους απόδοσης που μετρήθηκαν για αυτά τα διμερή κυμαίνονται στο εύρος 4-5%. Στο μέρος Γ συντέθηκε ένα δυμερές πορφυρινών χρησιμοποιώντας μεταλλωμένη πορφυρίνη με ρουθήνιο και η απόδοσή τους (DSSC) μετρήθηκε στο εύρος του 1%. Τέλος, στο μέρος Δ συντέθηκαν μεταλλωμένες πορφυρίνες που φέρουν μακριές αλυσίδες αλκυλίου και δύο καρβοξυλικές ομάδες οι οποίες συνδέονται στη μεσο- θέση του πορφυρινικού δακτυλίου μέσω τριπλό δεσμό.

Λέξεις κλειδιά: πορφυρίνη, ευαισθητοποιητής, χρωστική, χρωμοφόρο, φωτοβολταϊκές κυψέλες

Contents

CHAPTER I

INTRODUCTION

1. INTRODUCTION

Efficient production of clean and sustainable energy will be the most significant scientific challenge in the next half-century.[1] The demand for energy is increasing with growing global population, which is projecting toward 10.6 billion by 2050. In addition, limited resources of fossil fuels and the harmful effects of combustive carbon emissions compelled researchers to find carbon-free and environmentally friendly energy sources.[2] Sunlight is the most abundant and one of the cleanest sources of energy. Therefore, the utilization of solar energy in terms of solar fuels or electricity has attracted much attention by the scientific community. Nature harnesses solar energy very efficiently *via* the photosynthetic process. The use and understanding of biological processes has been a growing area of research. By mimicking the light harvesting antennas of natural photosynthetic systems it is possible to enhance the light capture of photo-anodes in solar cells by using different absorbing units, which funnel the incident light to the sensitizer by energy transfer.

Various solar cells (silicon, organic, dye-sensitized) can mimic the fundamental principles of the natural photosynthetic units. For example solar cells capture sun radiation in terms of excited state electron–hole pairs followed by charge separation, which is in turn converted to electrical energy. The state of the art single crystal silicon solar cells is the most commonly used photovoltaic technology at present exhibiting 25% efficiency in the laboratory and 22% efficiency on an industrial scale.[3] Silicon based solar cells display high efficiencies and long stabilities, but have high energy costs due to silicon purification and solar cells manufacture. Therefore, the effort of the scientific community is focused on the preparation of solar cell systems with low cost and high efficiencies.

In this regard, dye-sensitized solar cells (DSSCs) became a viable and promising technology. This is due to the fact that they offer significant photo-conversion efficiency with a potentially lower cost than the classical silicon-based technology. The DSSC concept started in 1972 with chlorophyll-sensitized zinc oxide (ZnO) electrode.[4] By using two chlorophyll systems, photons were converted into electric current by charge injection of excited chlorophyll molecules into ZnO electrode. Almost twenty years later, a major breakthrough appeared, when O’Regan and

Grätzel reported a DSSC with 7.1% efficiency.[5] Since then many efforts have been made to improve the power conversion efficiency (PCE), using a plethora of chromophores. The basic structure of a DSSC comprised of an anode containing dye sensitizer grafted monolayer of mesoporous titanium dioxide (TiO_2) nanoparticle (anatase) on an Indium Tin Oxide (ITO) coated glass surface and a platinum cathode, sandwich together with a redox electrolyte (Figure 1).

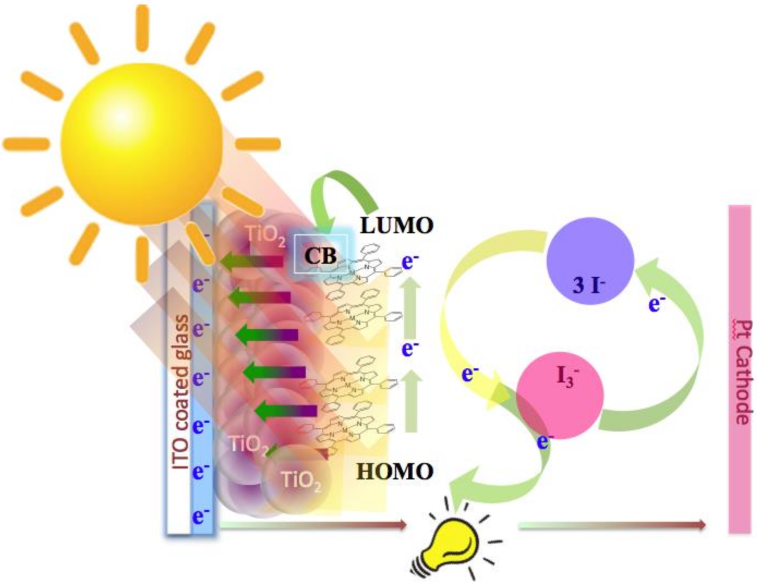


Figure 1. Schematic representation of a DSSC.

Solar irradiation excites the electrons of the dye from HOMO to LUMO level. Then the electrons from LUMO orbitals are injected into the conduction band (CB) of the TiO_2 semiconductor and subsequently carried out to counter Pt-electrode through the external circuit and thus produce electricity. Dye regeneration is performed by an electrolyte (iodine-based or cobalt complexes, redox mediator) through a reduction–oxidation process. Dyes with donor–acceptor (D–A) groups having their LUMO level above the TiO_2 conduction band and their HOMO level below the redox couple of the electrolyte are desirable for electrochemical cycle in DSSC. Strong electronic coupling and physical contact is needed between the light harvesting chromophore and the semiconductor surface for faster excited state electron transfer than excitation quenching by other physicochemical processes, which reduces the efficiency of the cell.

Among various components of the DSSC device, the sensitizer is one of the key components in achieving high efficiency and durability. Ruthenium polypyridyl complexes served as a leading player in DSSC technology and showed the best efficiencies (up to 11%) on ruthenium based systems under standard air-mass (AM) 1.5 illuminations.[6, 7] However, the high cost toxicity and low stability of the ruthenium complexes led researchers to search for alternate chromophores such as, porphyrins, phthalocyanines and other organic dyes.

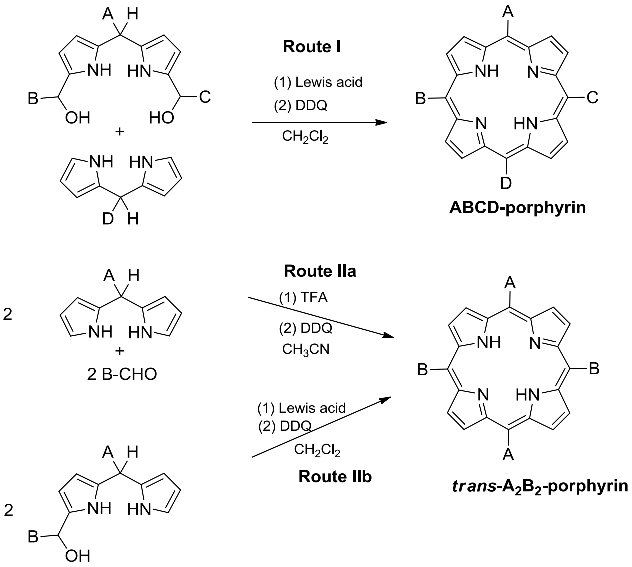
Inspired by nature and due to their remarkable role in photosynthesis, porphyrins have been extensively designed and synthesized for DSSC applications. Porphyrins as photosensitizers on DSSC are particularly interesting. Owing to appropriate LUMO and HOMO energy levels and very strong absorption of the Soret band in the 400–450 nm region, as well as the Q-bands in the 500–700 nm region, porphyrin derivatives can be suited as panchromatic photosensitizers for DSSCs and are potential candidates to replace ruthenium dyes. A number of reviews, articles on porphyrins, and their applications in photovoltaics have been reported covering most of the common features of the DSSC systems. In particular, reviews by Grätzel,[8] Officer,[9] Hagfelt,[7] Wamser[10] and Diau[11] nicely discuss all aspects of DSSC research. Apart from porphyrins some interesting studies containing phthalocyanines,[10] corroles,[12, 13] chlorins[14-16] and natural dyes[17] have also been studied in this area. Unlike all the aforementioned dyes, porphyrins have been mostly used achieving a record efficiency ~ 13 % in 2011 with without the need of cosensitization.[18, 19] Moreover, the photophysical and electrochemical properties of the porphyrins can be tuned by peripheral substituents and inner metal complexations, by taking advantage of their multiple reactive sites, including four *meso* and eight β-positions, [20-26] A drawback of porphyrins is the poor light-harvesting properties at wavelengths around 450 nm and above 600 nm. Elongation of strong electron-donating and electron-withdrawing groups can shift and broad the absorption of porphyrins making it possible to increase the light-harvesting property and the resulting DSSC efficiency. Therefore, the DSSC device performance can be further improved by careful structural optimization of the porphyrin chromophores in order to exhibit a panchromatic feature.

1.1 Porphyrin synthetic strategies

Porphyrin synthetic chemistry has been developed during the last decades. The target was not only the synthetic approach of the natural porphyrin rings but also the preparation of new ones for various purposes. As an extension, dyads, triads, push-pull porphyrins and more sophisticated structures and assemblies, as well as self-assembling systems have been prepared and well characterized. Among the aforementioned compounds the category of "push-pull" porphyrins are the ones that have been extensively studied and have been performed the best DSSC efficiencies. Therefore, it is necessary to overview their synthetic approaches and try to increase their low yields in order to be more competitive and applicable for future industrial use.

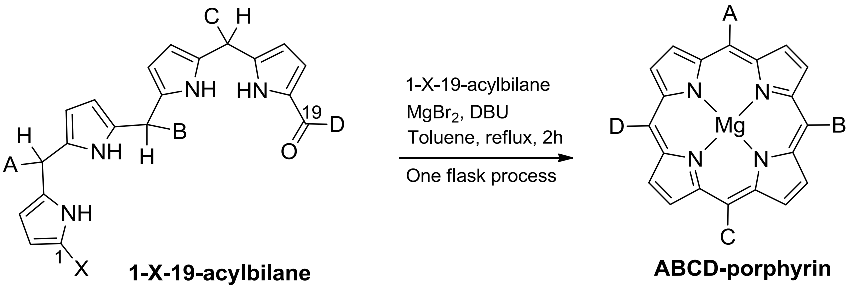
The porphyrinic family derivatives characterized as push-pull type chromophores, contain one donor moiety and one acceptor in *trans* position on the macrocycle. According to this requirement, there are several combinations concerning the nature of the substituents on the periphery of the porphyrin ring: four, three or two different substituted groups and the porphyrin ring are denoted as ABCD, A_2BC and A_2B_2 type, respectively. Better access to macrocyclic dyes with push–pull character will expand the range of accessible materials and advance various applications in optics,[27-30] nonlinear optical (NLO) studies for applications in photonics.[31] Tailoring the nature of the electron-donating and -withdrawing *meso* substituents is crucial for the efficient generation of electron transfer, which mimics natural processes and is related to solar energy conversion. Further progress in both research areas requires easy access to varied structures, which necessitates the development of appropriate synthetic strategies leading to unsymmetrically substituted porphyrins.

A number of rational synthetic routes to *meso*-substituted porphyrins have been developed that rely on dipyrromethane building blocks. The routes provide access to ABCD-porphyrins or *trans*-A_2B_2-porphyrins (Scheme 1).



Scheme 1. Synthetic Routes to *meso*-Substituted Porphyrins.

The ABCD type (Scheme 2) (four different *meso*- substituents) provides versatile building blocks for a whole range of use as biomimetic compounds, in material chemistry, and for DSSC dyes. Lindsey and coworkers for the synthesis of such a type of ABCD- porphyrins have reported the classical. “2 + 2” method, which allows synthesis of large quantities (~1 g) of various substituted ABCD-porphyrins with low or no detectable scrambling.[32, 33] The following criteria should be satisfied in order to achieve a suitable synthesis and access to new ABCD-porphyrins: (1) no scrambling at any stage of the synthesis, (2) limited reliance on chromatography, (3) scalable syntheses, (4) straightforward implementation in a reasonable period, (5) broad scope in terms of ABCD substituents, and (6) good yield. The procedures for forming the dipyrromethane and elaborating the dipyrromethane to give the dipyrromethane-1,9-dicarbinol are reasonably well developed and meet all six objectives.[34-39] However, the final porphyrin-forming step still presents a number of limitations despite extensive investigation.[33]



Scheme 2. Route to ABCD-Porphyrins *via* Bilanes.

The route to ABCD-porphyrins (depicted in Scheme 2) retains the desirable features of the existing “2 + 2” (dipyrromethane + dipyrromethane-1,9-dicarbinol) method, such as absence of scrambling, yet has significant advantages. The advantages include the absence of acid in the porphyrin-forming step, the use of a metal template for cyclization, the ability to carry out the reaction at high concentration, the lack of a quinone oxidant, avoidance of use of dichloromethane, and the increased yield of macrocycle formation to give the target ABCD metalloporphyrin.[32]

The introduction of *meso* substituents into porphyrins has given access to molecules with fine-tuned electron-donating or -withdrawing character of the incorporated groups. A *trans* porphyrin provides a linear substitution pattern that can be used for the construction of porphyrin-based architectures with a well-defined structure. Applications of *trans* porphyrins in model systems include charge separation devices that mimic photosynthesis,[40-44] enzyme models,[45] materials with nonlinear optical properties,[46, 47] chiral catalysts,[48] chiral sensors,[49] synthetic receptors for small molecules,[50] optoelectronic devices,[51, 52] potential sensitizers for photodynamic cancer therapy,[53] bilayer lipid membrane spanning arrays,[54] and liquid crystals.[55, 56]

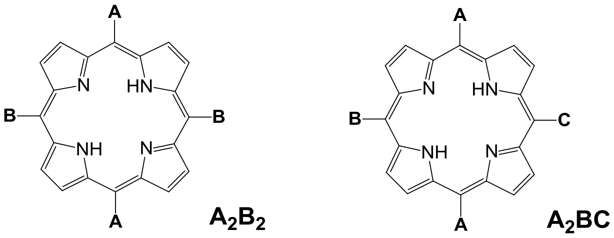


Figure 2. General structure of A_2B_2 and A_2BC porphyrins.

Different synthetic approaches leading to A_2BC- and A_2B_2-type porphyrins (Figure 2) have been reported. The simplest way to obtain 5,15-A_2B_2 systems involves the acid-catalyzed condensation of dipyrromethane with aldehyde.[57-59] Others involve self-condensation of dipyrromethane-1-carbinoles or the elegant 1-acyldipyrromethane route developed by Lindsey *et al.*[60-62] In practical terms, the acid-catalyzed condensation of dipyrromethane with two aldehyde units or two dipyrromethane units with aldehyde is still the simplest way to access 5,15-A_2BC compounds.[63] Condensation of dipyrromethane-dicarbinole with dipyrromethane has also been reported but turned out not to be an efficient way to access this substitution. Other pathways to both substitution patterns used a stepwise approach where preformed 5,15-A_2 compounds were subjected to further functionalization.[64] The functionalization of A_2-type porphyrins as starting materials by organolithium and palladium catalysed cross-coupling reactions is an efficient means to enable the introduction of almost any desired *meso* substituent.[65]

A convenient preparation of analytically pure multigram batches of 5-substituted dipyrromethanes has been achieved by the acid-catalyzed condensation of an aldehyde with excess pyrrole in solvent-free conditions.[66] Condensation of a dipyrromethane with an aldehyde in a MacDonald-type “2 + 2” condensation,[67] has been used to prepare a wide range of *meso*-substituted *trans*-porphyrins.[63] The product of a dipyrromethane-aldehyde condensation is frequently not just the desired *trans*-A_2B_2-porphyrin but also a mixture of porphyrins that can be extremely difficult to separate (especially the *trans*-A_2B_2 and *cis*-A_2B_2 isomers).[68] For condensations involving sterically hindered dipyrromethanes reaction conditions that cause no scrambling have been identified and a preparative procedure has been developed that gives pure *trans*-porphyrins in multigram batches.

The general synthetic pathways of new push-pull porphyrinic derivatives have been described above and could provide new chromophores for DSSCs. However what is needed in this particular area of research is a systematic study, which can help to improve the final efficiency of the device measured in cells.

In DSSCs the presence of an anchoring group is essential to graft the dye on a TiO_2 surface, in order to achieve fast electron injection into the TiO_2 semiconductor.[69] The efficiency of the electron-transfer step at the dye-semiconductor interface is highly dependent, among numerous other factors, on the way the chromophore is attached to the surface.[70-72] Therefore, different porphyrin anchoring groups have been used and researchers have studied their effect on the TiO_2 surface.[73-75]

1.2 Carboxylic acids as anchoring groups

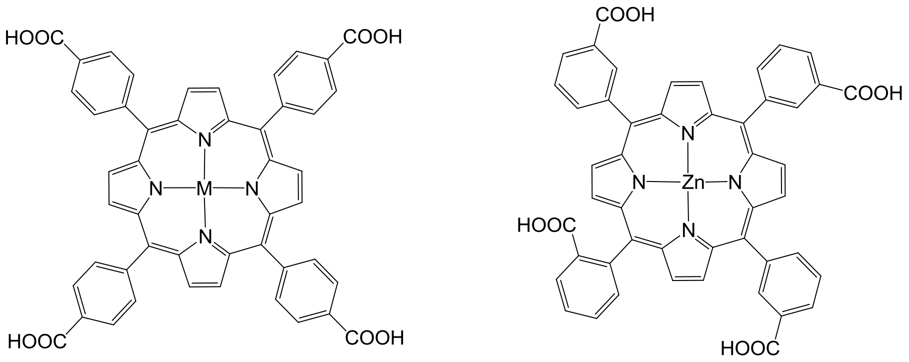
Carboxylic acid present in the *meso* and *β*–positions of a porphyrin ring is an anchoring group that has been extensively studied. At the *meso*-position, two main classes of linking moieties have been employed most often, the classic *meso*-substituted benzoic acid linking and the direct attachment of a *meso*-alkynylbenzoic acid moiety. For DSSCs employing a *β*–position linking group the conjugated ones have been mostly studied in the literature.

Carboxylic acid groups can form ester linkages with the surface of the metal oxide to provide a strongly bound dye and good electronic communication between the two parts. However, the link can be hydrolyzed through the presence of water, an important factor in terms of the stability of the cell. For carboxylate groups, bidentate connections have been shown to be the preferred binding mode on TiO_2.[76-78]

1.2.1 *Meso*-Substituted Benzoic Acids

The concept for the design of *meso* ethynyl linked porphyrins was first given by Anderson[79] and Therien.[80] Before the discovery of DSSC, the ability of porphyrin to sensitize TiO_2 semiconductor was first demonstrated by Grätzel in 1987.[81] However, Kay and Grätzel first introduced a porphyrin as a sensitizer in DSSC in 1993. A substituted porphyrin with propionic acid as anchoring group achieved an overall efficiency of 2.6% (J_{sc} = 9.4 mA/cm^2, V_{oc} = 0.52 V).[82]

Cherian and Wamser[83] in 2000 reported the first *meso*-substituted DSSC with 3.5% (J_{sc} = 0.133 mA/cm^2, V_{oc} = 0.36 V, and FF = 0.62) efficiency based on a free-base porphyrin **1** (Figure 3). That report also analyzed the adsorption properties of **1** on TiO_2 using XPS and resonance Raman spectroscopy to elucidate the binding characteristics of **1** and reported that low concentrations of dye in the adsorption solution (~0.1 mM) are important to avoid dye aggregation.



1: M=2H, TCPP
2: M=Zn, *p*-ZnTCPP

3: m-ZnTCPP

Figure 3. Molecular structures of porphyrins **1, 2** and **3**

One key issue to consider in designing porphyrin dyes relates to the position of the anchoring group in relation to the plane of macrocycle π-system. The presence of carboxyl anchoring groups attached to the *meso*-phenyl ring of the porphyrin has little influence on the ground-state electronic nature of the dye, because of the orthogonal orientation of the *meso*-phenyl ring.[84-86] However, a few studies have shown that the positioning of carboxyl group vary the performance of the solar cells.[74, 83, 87-89] For example, Campbell *et al.* have reported a 5-fold increase in the short circuit photocurrent (J_{sc}) and a significantly higher open circuit photovoltage (V_{oc}) on changing the position of the COOH groups from the *para* (in *p*-ZnTCPP **2**) to the *meta* position (in *m*-ZnTCPP **3**) (Figure 3).[9] This effect was attributed to a more efficient electron injection from the *meta* porphyrin, which binds flat on the TiO_2 surface, compared to that of the *para*, which binds vertically (Figure 4).[9]

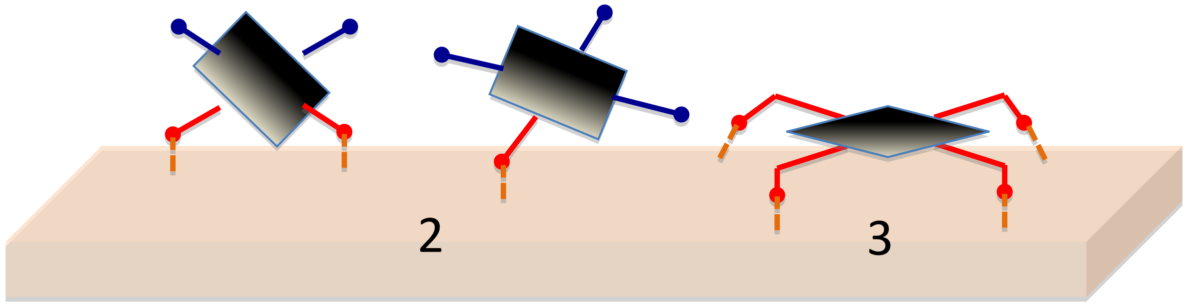


Figure 4. Different binding modes of porphyrins **2** and **3** onto TiO_2 surface.

In 2007 Galoppini and coworkers[87] studied tetrachelated zinc porphyrins with four *meta*-substituted linkers at four *meso* positions of the porphyrin to give inside on how the distance and attachment of the sensitizing chromophore on colloidal TiO_2 and ZnO films influence interfacial processes and solar cell efficiencies. The *meta* substitution favored a planar binding mode to the metal oxide surfaces, as determined by a combination of studies that included IR, UV, and solar cell efficiencies on TiO_2. All studies indicated that only *p*-ZnTCPP **2** aggregated, suggesting close packing of the dye molecules on the semiconductor surface. Aggregation effects were not observed for the *meta* porphyrins. The greater efficiency of the rigid planar *meta*-substituted systems was explained in terms of a greater charge injection into the TiO_2 semiconductor from rings that lie flat, and closer, to the surface.In the same study it was observed that the main binding modes for this class of molecules are a chelating and/or a bidentate bridging of the carboxylate on the TiO_2 surface (Figure 5).[77, 90-92]

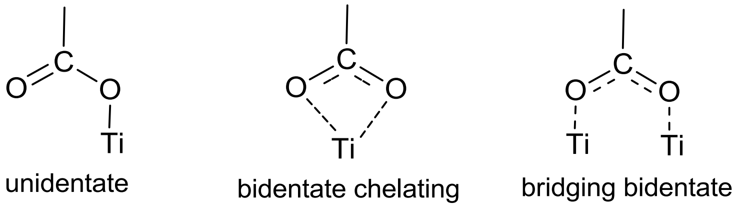
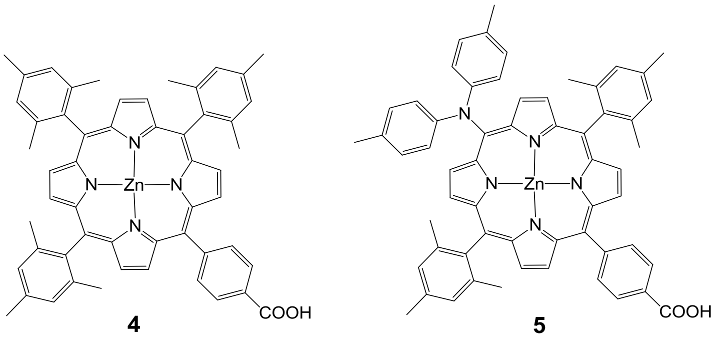


Figure 5. Main binding modes of the carboxylate group to TiO_2.

In 2009, Imahori *et al.* studied a series of monocarboxyphenyl triaryl porphyrins in DSSCs.[93] Zn porphyrin **4** (Figure 6) yielded the highest efficiency of 4.6% (J_{sc} = 9.4 mA/cm^2, V_{oc} = 0.76 V, and FF = 0.64) in a standard DSSC. As a part of their study, they optimized the adsorption time and adsorption solvent for dye loading on TiO_2 films and determined that lower adsorption times and protic solvents (methanol) led to the best efficiencies. In an another publication from the same group integration of a push-pull structure with a *trans* diphenylamino substituent **5** gave a very high efficiency of 6.5% (J_{sc} = 13.1 mA/cm^2, V_{oc} = 0.72 V, and *FF* = 0.69) (Figure 6).[94]



4 **5**

Figure 6. Molecular structures of porphyrins **4, 5**

Moreover, in order to synthesize a dye with a broad spectral coverage two porphyrin units can be linked at the *meso* position either directly[95] or by suitable π-conjugated linker.[96] Furthermore, unsymmetrical porphyrin dyads can lead to enhancement of the solar cell efficiency.[97] Combining the strategy of donor substation and the “built-in” energy gradient of the hetero-dimer taking advantage of the different energy levels of zinc coordinated and non-coordinated porphyrins,[97] Segawa *et al.* synthesized a N-fused carbazole zinc porphyrin-free base porphyrin triad and obtained highly efficient light to current conversion throughout the visible to NIR region.[98] The same research group synthesized ethynyl-linked porphyrin hetero-dimers substituted by a series of electron donors, namely, 3,6-di-tert-butylphenyl **6**, bis(4-methoxyphenyl)amino **7**, bis (4-tert-butylphenyl)amino **8** and 3,6-di-tert-butylcarbazol-9-yl **9** (Figure 7).[58] Despite the increased electron injection driving forces due to the bathochromic shift, the intensification of long-wavelength absorption bands and the elevated LUMO levels, the substitution of diphenylamino groups (**7** and **8**) with stronger electron-donating abilities gave rise to surprising mediocrity in the short-circuit photocurrent densities (J_{sc}). For that reason the overall energy conversion efficiencies followed the order **7** (3.94%) (J_{sc} = 10.55 mA/cm^2, V_{oc} = 0.543 V, and *FF* = 0.69) < **6** (4.57%) (J_{sc} = 12.51 mA/cm^2, V_{oc} = 0.541 V, *FF* = 0.68) < **8** (4.83%) (J_{sc} = 13.15 mA/cm^2, V_{oc} = 0.541 V, *FF* = 0.68) < **9** (5.21%) (J_{sc} = 14.26 mA/cm^2, V_{oc} = 0.547 V and *FF* = 0.67) (Table 1).

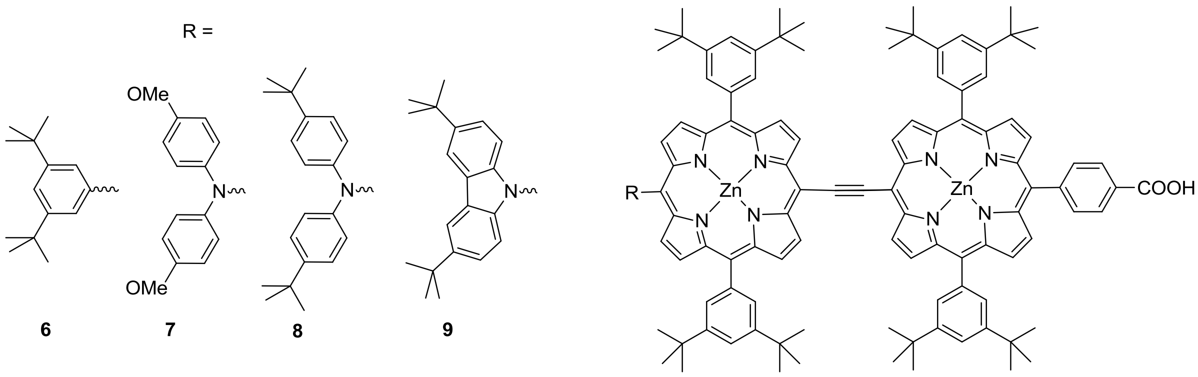
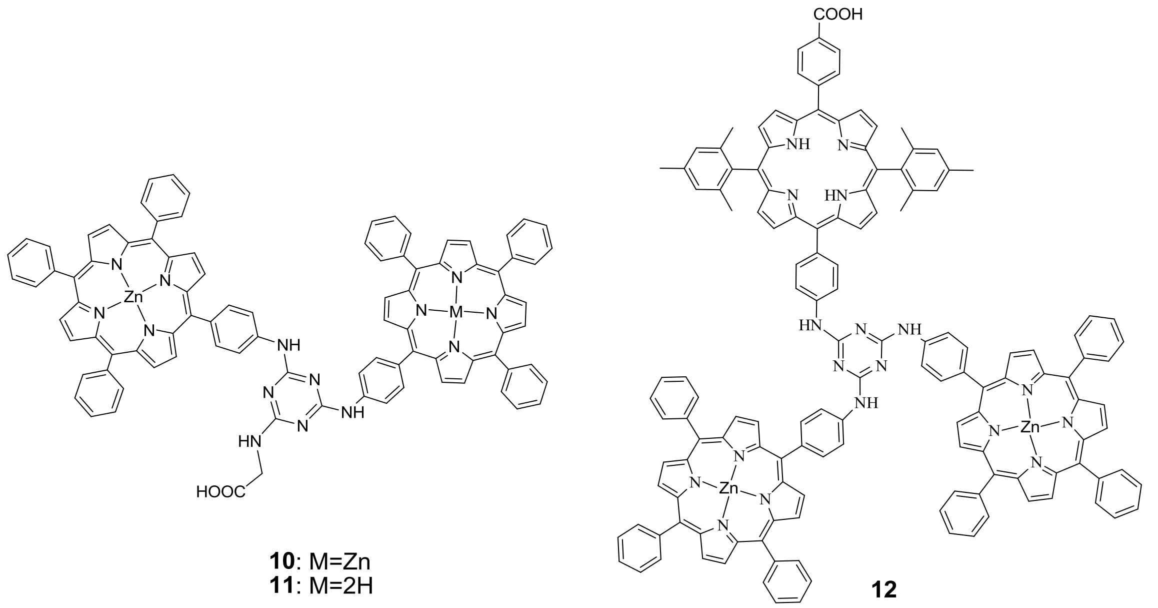


Figure 7. Molecular structures of the dyes studied **6**-**9**.

Table1: Photovoltaic performances of DSSCs using **6-9** as sensitizers.

Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
6	541	12.5	0.68	4.6
7	543	10.5	0.69	3.9
8	541	13.1	0.68	4.8
9	547	14.3	0.67	5.2

1,3,5-triazine, a known mediator of intramolecular photoinduced electron transfer between chromophores, tethered two porphyrin units.[99] The synthesis was performed by taking advantage of the stepwise and temperature-dependent reactivity of cyanuric chloride. The dyads were also functionalized by a terminal carboxylic acid group of a glycine moiety attached to the triazine group (Figure 8). The study of the photophysical and electronic properties of the two compounds revealed no significant electronic interaction in their ground states but broadened spectral absorptions and suitable frontier orbital energy levels for use in DSSCs. Porphyrins **10** and **11** were fabricated for DSSC, demonstrating efficient intramolecular electron-transfer and charge-separation phenomena mediated by the triazine group. The PCE values were of 3.61% (J_{sc} = 8.82 mA/cm^2, V_{oc} = 0.63 V, and *FF* = 0.65) and 4.46% (J_{sc} = 9.94 mA/cm^2, V_{oc} = 0.66 V, and *FF* = 0.68), respectively. The higher PCE value of the **11**-based DSSC is attributed to its larger dye loading and higher J_{sc}, V_{oc}, and *FF* values.



10: M=Zn
11: M=2H

12

Figure 8. Molecular structures of porphyrins **10-12**.

Coutsolelos and *coworkers*,[99] synthesized *via* stepwise amination reactions of cyanuric chloride a propeller shaped, triazine bridged, and unsymmetrical porphyrin triad **12**. Photophysical and electrochemical studies of the triad revealed no significant electronic interactions between the porphyrin units in the triad ground state, but the frontier orbital energy levels are suitable for use as sensitizer in DSSCs, as they favour the electron injection and dye regeneration processes. These results were corroborated by DFT calculations which suggested that the triad **12** could also be described as a “push-pull” 2D-π-A system, with the A residing on the anchoring (carboxylic acid) group, that has the potential to promote triazine-mediated electron transfer and injection into the TiO_2 electrode. Solar cells sensitized by triad **12** exhibited PCE of 4.91% (J_{sc} = 10.9 mA/cm^2, V_{oc} = 0.66 V, and FF = 0.68). The PCE of the latter solar cell was further improved up to 5.56% (J_{sc} = 12.4 mA/cm^2, V_{oc} = 0.64 V, and FF = 0.70) by co-sensitization by incorporation of chenodeoxychlolic acid (CDCA) in the dye solution (Table 2).

Table2: Photovoltaic performances of DSSCs using **10-12** as sensitizers.

Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
10	630	8.8	0.65	3.6
11	660	9.9	0.68	4.5
12	660	10.9	0.68	4.9
12[a]	640	12.4	0.70	5.6

[a] co-sensitization with CDCA

Moreover, Hung *et al.* synthesized a series of 1D-π-3A zinc porphyrin dyes **13-17** with three *p*-carboxyphenyl anchoring groups with various substituents at the *meso* position (Figure 9).[100] Porphyrin **15** is slightly red shifted compared to the other porphyrins. The Soret band of **15**, **16**, **17** is broadened because of the presence of an electron donating amino unit. Higher than 5 % PCE has been achieved for a DSSC sensitized with either **15-17**. The strong electron donating character, better electron injection, intrinsic anti-aggregation and suppressed charge recombination capacity contributed to the highest PCE of 6.10 % (J_{sc}=12.66 mA/cm^2, V_{oc} =0.70 V and *FF* = 0.69) for the DSSC sensitized with **16** (Table 3). Moreover, it was demonstrated that the DSSC based on multi-anchoring unit porphyrin dye is more stable than their mono-anchoring analogs.

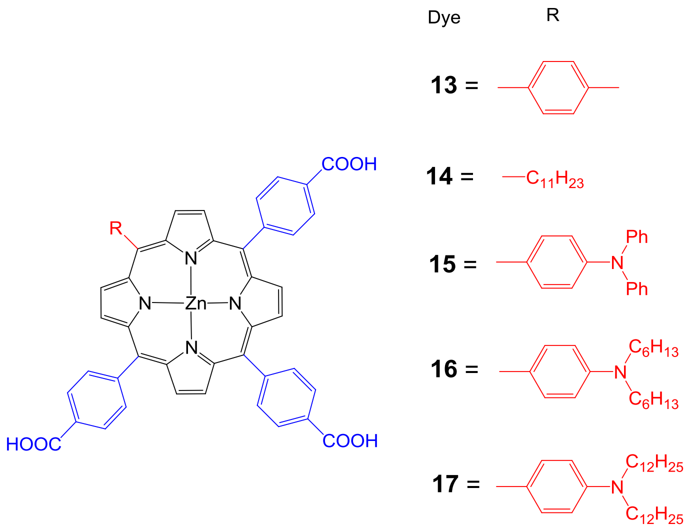
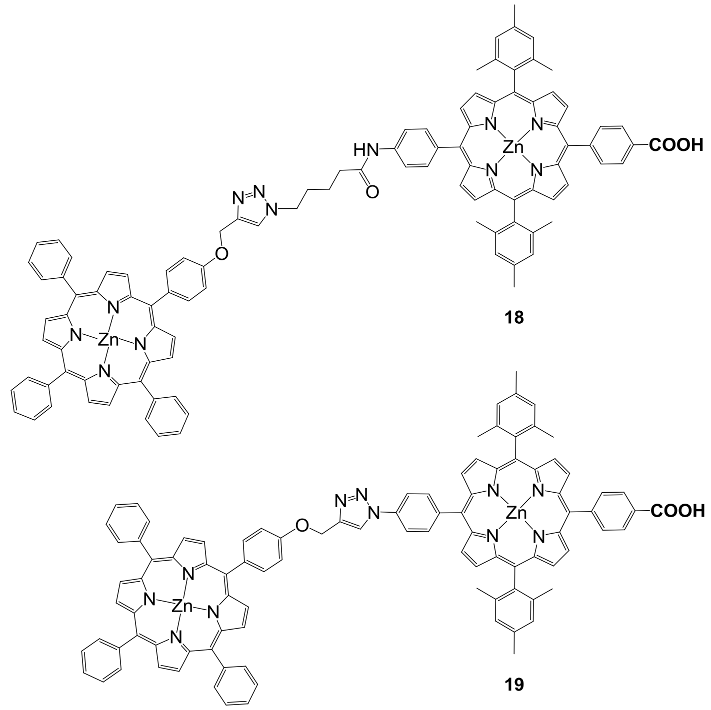


Figure 9. Molecular structures of dyes **13-17**.

Table 3: Photovoltaic performances of DSSCs using **13-17** as sensitizers.

Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
13	630	10.55	0.68	4.51
14	590	9.36	0.69	3.80
15	660	11.75	0.69	5.36
16	700	12.66	0.69	6.10
17	650	13.61	0.66	5.80

Coutsolelos and coworkers designed two novel porphyrin dyads **(18** and **19)** consisting of two zinc-metallated porphyrin units, covalently linked at their peripheries through 1,2,3-triazole containing bridges and functionalized by a terminal carboxylic acid group **(Figure 10)**.[101] The two porphyrin dyads were synthesized though click reactions and possess suitable frontier orbital energy levels for use as sensitizers in DSSCs. Dyad **18** was synthesized using $CuSO_4 \cdot 5H_2O$, SA and a mixture of $CHCl_3$–H_2O. The reaction mixture was stirred at 50 °C for 72 hours yielding 42% of the final dimer. On the contrary for the synthesis of dyad **19**, CuI, DIPEA and a mixture of THF–CH_3CN was used. The reaction mixture was stirred at room temperature for 12 hours obtaining the final dyad **19** in 41% yield. Fabrication of the corresponding solar cells revealed that the device based on the dyad with the shorter triazole containing bridge (**19**) results in a better photovoltaic performance (3.82 and 5.16% for **18** and **19**, respectively). As demonstrated by the J–V curves and the IPCE and EI spectra of the two solar cells, the higher PCE value of the latter can be attributed to its enhanced short circuit current (J_{sc}) under illumination, its longer electron lifetime (τ_e) and more effective charge recombination resistance between the injected electrons and the electrolyte, as well as its higher dye loading on the TiO_2 surface.



18

19

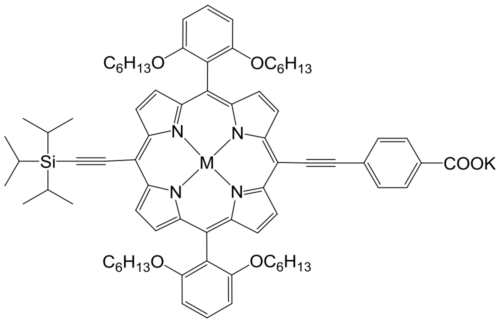
Figure 10. Porphyrin sensitizers **18** and **19** for dye-sensitized solar cells.

Although *meso*-carboxyphenyl tethered porphyrins have been widely studied in DSSCs, there remains a concern about the torsional angle decoupling of the phenyl rings from the conjugated system of the macrocycle, which potentially limits the electronic communication between the excited dye and the linkage to the semiconductor. Therefore more attention has been paid to other structural designs such as porphyrins with *meso*-alkynylbenzoic acid or *β*-linked conjugated tethers and devices using these designs have reached remarkably high efficiencies.

1.2.2 Conjugated bridge carboxylic acids at the *meso*-position

The type of linkage between the porphyrin and the binding group is very important. It has been shown that conjugated linkers make a significant difference in the overall cell performance.

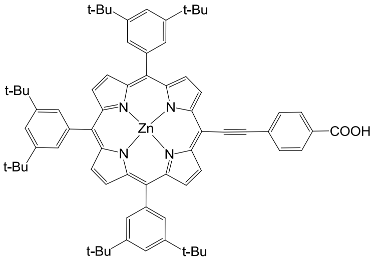
The use of *meso*-linked alkynylbenzoic acid tethers is a relatively new design strategy in porphyrin DSSC research. The first report of alkynylbenzoic acid tethered porphyrins was by Stromberg *et al.* in 2007[102] in which the reported photocurrent of the device was only 0.035 mA cm^{-2}. Since then two main groups of Joseph Hupp and Eric Diau have studied this novel tether style. The use of the *meso*-alkynylbenzoic acid tether has led to an increase in solar cell efficiency for porphyrin DSSCs.[103, 104] In a paper by Hupp and *coworkers*, dye **20** (Figure 11) was reported to give efficiencies of 2.5% (J_{sc}=5.9 mA/cm^2, V_{oc} =0.65 V and FF = 0.66) in standard TiO_2 DSSC.[105] In the report on **20**, ZnO was also tested as a semiconductor, and it was determined that the more acidic dyes that tend to slightly corrode the ZnO surface showed better electron injection dynamics.



20

Figure 11. Molecular structure of compound **20**.

To solve the problem of porphyrin aggregation, 3,5-di-tertbutylphenyl groups were introduced at the *meso*-positions of the porphyrin ring. Based on this molecular design, Yeh and *coworkers*[26] reported *meso*-substituted zinc porphyrin derivatives, for which **21** (Figure 12) served as a reference compound. With the diarylamino group attached at the *meso*-position of the porphyrin core, **22** attained 6.0% efficiency (J_{sc}=13.60 mA/cm^2, V_{oc} =0.701 V and FF = 0.629). The appearance of porphyrins with a push–pull framework such as **22** and **23** indicated the arrival of a new period of DSSC.[104] Porphyrin **23** had two long alkyl chains in order to improve the thermal and photochemical stability of a device with an efficiency of 6.8% (J_{sc}=13.68 mA/cm^2, V_{oc} =0.711 V and FF = 0.695), (Table 4).



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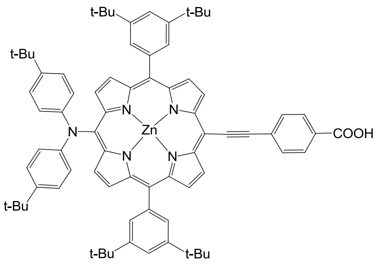

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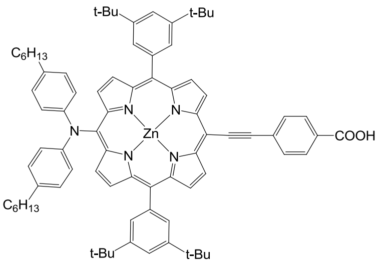


23

Figure 12. Molecular structures of dyes **21-23.**

Table 4: Photovoltaic performances of DSSCs using **21-23** as sensitizers.

Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
21	617	5.79	0.667	2.4
22	701	13.60	0.629	6.0
23	711	13.68	0.695	6.8

In 2010, the device performance of **23** was further improved by Grätzel and coworkers,[21] giving an efficiency of 10.9%, (J_{sc}=18.6 mA/cm^2, V_{oc} =0.77 V and *FF* = 0.76) In 2011, Grätzel and collaborators reported the meso-porphyrin dye **24** achieving a PCE of 11.9% in conjunction with the cobalt(III/II) tris(2,2-bipyridine)-based redox electrolyte and up to 12.3% when cosensitized with another organic dye which, until recently, had been the record of efficiency in DSSC over the past three years.[106] This record was recently broken (February 2014) with the dye **26** reported by Nazzeruddin and co-workers, achieving an unprecedented PCE of ~13%.[18] Almost the same PCE was performed with porphyrin **25** reported by Grätzel and Yeh in 2014 (Figure 13).[19, 106]

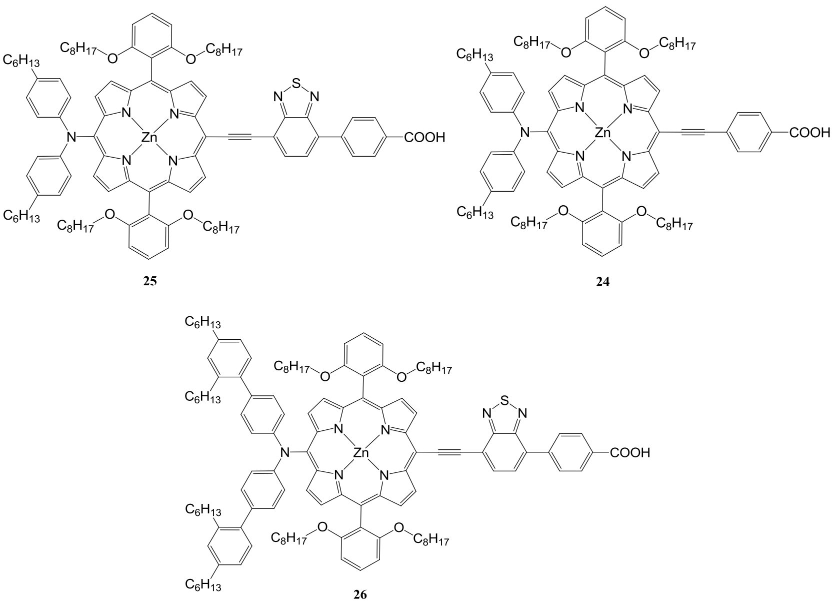


Figure 13. Chemical structures of dyes **24-26**.

Lin *et al.*[107] prepared a series of new porphyrins (**27-30**) with near-IR light harvesting properties, for DSSCs, by attaching a pyrene or a 4-dimethylaminophenyl group in combination with anthracene to modify the porphyrin core (Figure 14). It was shown that the incorporation of these moieties renders feasible tuning of spectral and redox properties of the porphyrins. The PCE values of the dyes was in the range of 6.7 – 9.73 % and **27** sensitized DSSC showed a maximum PCE of 9.73 % (J_{sc} = 17.77 mA/cm^2, V_{oc} = 0.73 V and FF = 0.75), (Table 5). These high performances are due to the following factors (a) expansion of the porphyrin spectral range, (b) reduction of the dye aggregation bye suitable dye soaking processes, (c) addition of polar electron releasing groups.

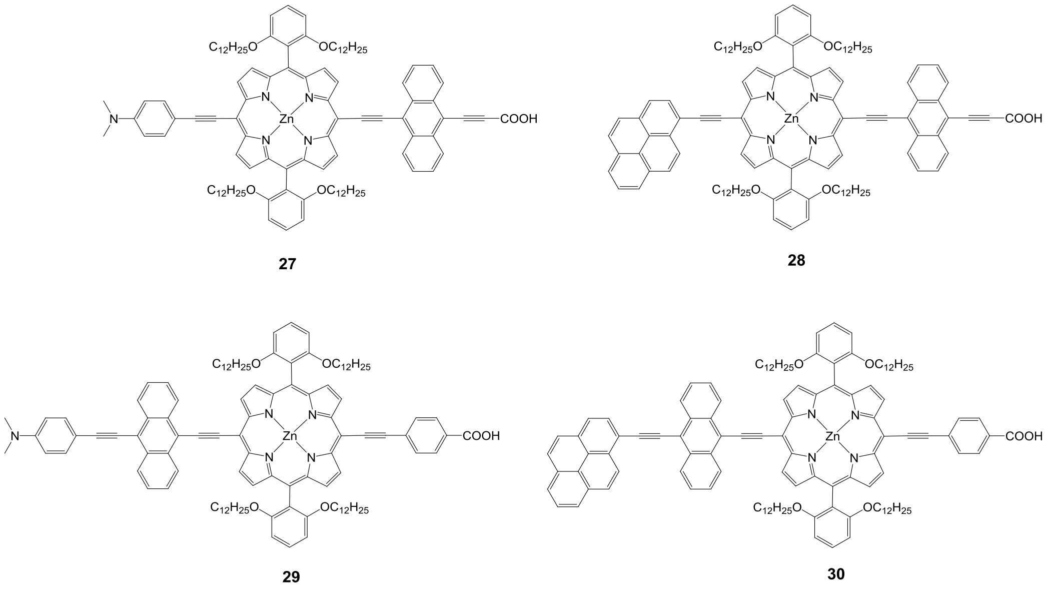


Figure 14. Molecular structures of dyes **27-30**.

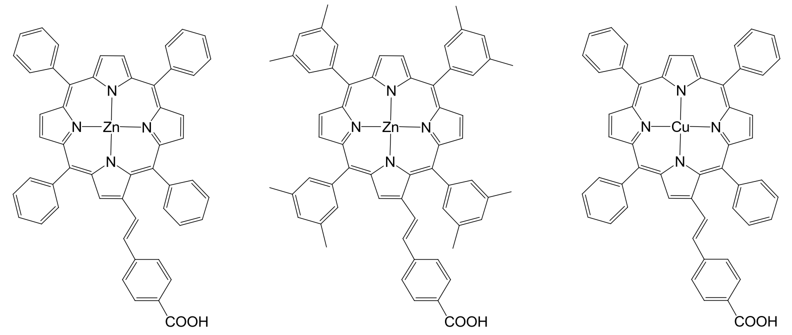
Table 5: Photovoltaic performances[a] of DSSCs using **27-30** as sensitizers.

Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
27	730	17.77	0.75	9.73
28	680	14.17	0.72	6.97
29	720	17.76	0.74	9.51
30	680	14.20	0.69	6.70

[a] Under AM1.5 illumination (power 100 mW cm^{-2}) with an active area of 0.096 cm^2.

1.2.3 Conjugated bridge carboxylic acids at the *β*-position

The use of conjugated *β*-substituted anchoring groups was first demonstrated in 2004 by Grätzel *et al.* when they introduced a dye **31** with an energy conversion efficiency of 4.1% (J_{sc} = 8.86 mA/cm^2, V_{oc} = 0.65 V and *FF* = 0.71).[78] Also, for porphyrins with carboxylic binding groups, the Zn containing diamagnetic metalloporphyrin **32** had very high incident monochromatic photon-to-current conversion efficiencies compared to those observed for the Cu containing paramagnetic metalloporphyrin **33** (Figure 15, Table 6).



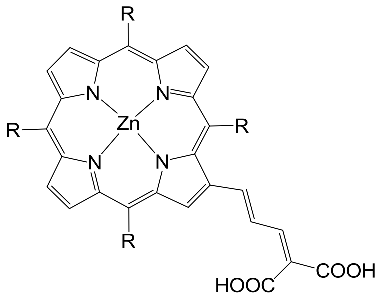
31 **32** **33**

Figure 15. Molecular structures of porphyrins **31-33**.

Table 6: Photovoltaic performances of DSSCs using **31-33** as sensitizers.

Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
31	654	8.86	0.71	4.11
32	660	9.70	0.75	4.80
33	490	1.35	0.69	0.45

In 2007, Officer and *co-workers* reported a series of porphyrins **34-39** with a conjugated bridge to a dicarboxylic acid acceptor moiety (Figure 16).[108] Porphyrin **35** gave the best efficiency 7.1% and the rest of the dyes featured efficiencies over 5% (Table 7).



34: R=Ph
35: R=4-methylPh
36: R=4-ethylPh
37: R=4-*n*-butylPh
38: R=4-*n*-octylPh
39: R=3,5-dimethylPh

Figure 16. Molecular structures of dyes **34-39**.

Table 7: Photovoltaic performances[a] of DSSCs using zinc tetraarylporphyrin malonic acids as sensitizers.

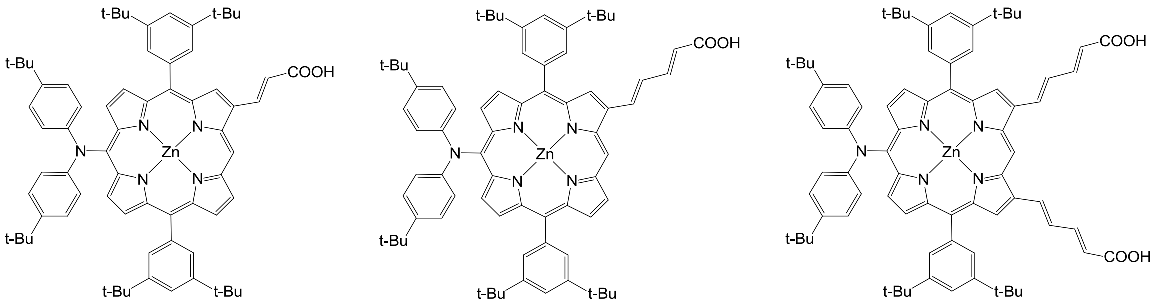
Dye	V_{oc}, mV	J_{sc}, mA cm^{-2}	FF	*n*, %
34	638	12.1	0.66	5.1
35	680	14.0	0.74	7.1
36	642	14.8	0.63	5.8
37	701	13.4	0.68	6.4
38	649	13.4	0.61	5.3
39	685	13.3	0.68	6.1

[a] Data obtained under cell illumination AM 1.5. 100mW/cm^2.

Since the 2007 report on β-linked porphyrins, Officer and *coworkers* used β-linked derivatives to study several aspects of solar cell design and performance. The aspects of design under study included the use of a post adsorbed phosphinic acid blocking moiety to improve efficiencies by minimizing recombination events at the electrode surface.[109] They also studied the use of ionic liquid electrolytes as a replacement for volatile organic solvents in typical liquid electrolytes.[110] The Officer group had also studied the open-circuit voltage and electron injection dynamics using β-substituted porphyrins and suggested that the reason for limitations to the V_{oc} and J_{sc} were related to reduced electron lifetime and less favorable electron injection dynamics.[111, 112]

In 2011 three porphyrins with structures based on a molecular design that relies on donor-π-acceptor interactions (Figure 17).[113] At the *meso* position of the porphyrin was present a *bis* (4-tert-butylphenyl) amino group and at the opposite side were 2-

propenoic or 2,4-pentadienoic acid anchoring groups at the *β*-pyrrolic positions. The efficiencies of all compounds are present in Table 8 and among the dyes prepared, the doubly functionalized carboxylic acid derivative **42** gave rise to the highest power conversion with an efficiency of 7.47%.



40 **41** **42**

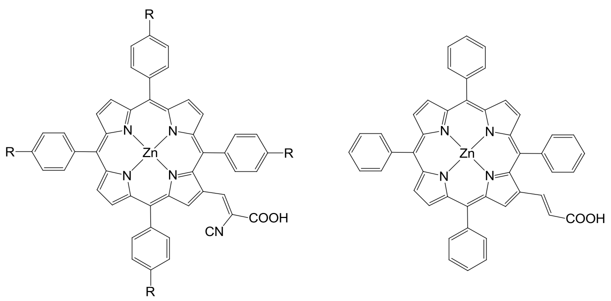
Figure 17. Molecular structures of porphyrins **40-42**.

Table 8. Photovoltaic performance of DSSCs using porphyrins **40-42** as sensitizers.

Dye	J_{sc}, mA cm^{-2}	V_{oc}, mV	FF	n, %
40	12.1	660	0.62	4.95
41	13.9	670	0.64	5.91
42	18.4	710	0.57	7.47

1.2.4 Cyanoacrylic Acids

Another anchoring group that has been extensively used is the cyanoacrylic acid. In 2005, tetraphenylporphyrin with a *β*-substituted cyanoacrylic acid (Figure 18), exhibited an efficiency of 5.2% (J_{sc} = 13.5 mA/cm^2, V_{oc} = 0.56 V).[76] Dye **43** had a better efficiency compared to the carboxylic acid porphyrin **45** 4.0% (J_{sc} = 10.9 mA/cm^2, V_{oc} = 0.55 V), synthesized from the same group.



43: R = -H
44: R = $-CH_3$

45

Figure 18. Molecular structures of dyes **43-45**.

In another study β-substituted zinc porphyrin analogues **43** and **44** (Figure 18) were synthesized, where **44** had an added methyl group at the phenyl ring attached to the meso-position of the porphyrin macrocycle.[114] These results showed that the different solvents used in the sensitization process affected how the dyes were aggregated and how much of the dyes were adsorbed on the semiconductor surface. The highest efficiency of 4.2% ((J_{sc} = 13.0 mA/cm^2, V_{oc} = 0.48 V and FF = 0.67), 30 min soaking time and 4.0% (J_{sc} = 12.8 mA/cm^2, V_{oc} = 0.46 V and FF = 0.67), 1 hour soaking time was achieved for **43** and **44** analogues, respectively. The difference in the photovoltaic properties between **43** and **44** was caused by the amount of tilting of the molecular dye plane toward the dye surface. The **44** molecular planes were closer to the TiO_2 surface due to the increased steric effect caused by the addition of a methyl group (Figure 19). This increased the surface area of the dye adsorbed in the TiO_2, resulting a much lower dye concentration. The soaking condition and the use of co-adsorbents giving much higher photovoltaic performances could control the amount of aggregation of the dye.

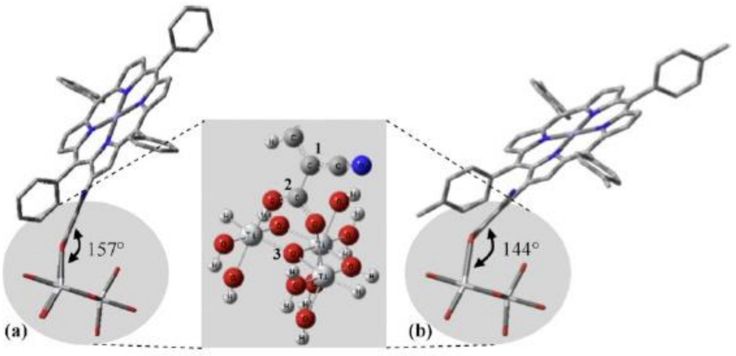


Figure 19. Possible adsorption configurations of (a) **43** and (b) **44**. The inset shows the bidentate adsorption of the dye. C1–C2–O3 determines the dye molecular angle against the TiO_2.

In other work, three push-pull structured new porphyrin dyes with various linkers (the **46** dye with 4-ethynylbenzene, the **47** dye with 2-ethynylthiophene, and the **48** dye with 5-ethynyl-2,3-dihydrothieno[3,4-b][1,4]dioxine) were synthesized in order to understand the influence of substitution of the *p*-linker with various hetero-aromatic groups (Figure 20) on the light-harvesting ability of the sensitizers.[115] These push–pull structured porphyrin sensitizers worked efficiently in DSSC devices, a detailed examination with impedance and transient photovoltage decay measurements revealed that a fast recombination process took place at the dye-sensitizer TiO_2–electrolyte interface due to the introduction of cyanoacrylic acid as an anchoring group. Based on these studies the **49** porphyrin with a rigid π-linker feature structure (5-ethynylthiophene-2-carboxylic acid) was further designed and synthesized, which attained an improved PCE of 9.53% (Table 9).

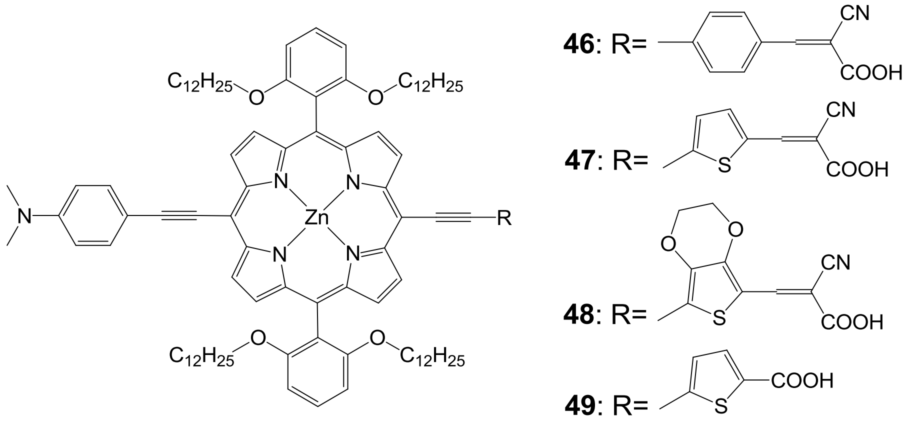


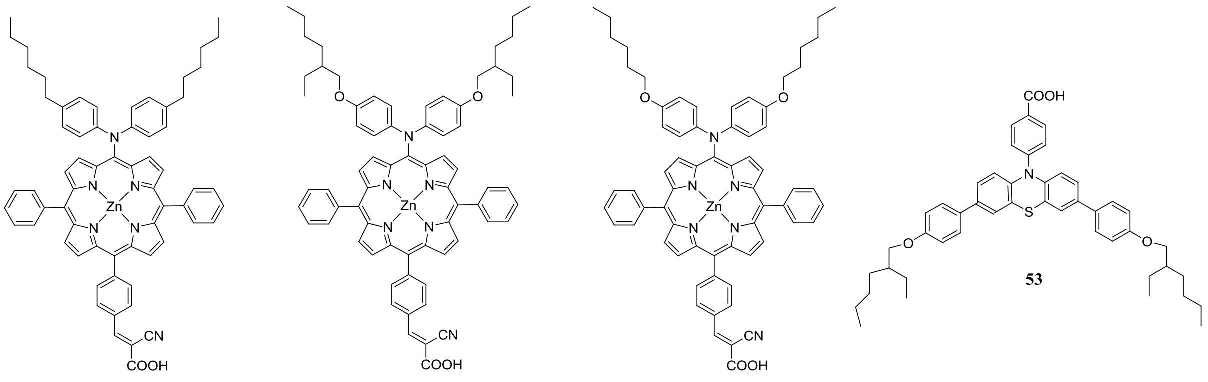
Figure 20. Molecular structures of compounds **46-49**.

Table 9. Photovolataic performances of DSSC using **46-49**.

Dye	J_{sc}, mA cm^{-2}	V_{oc}, V	FF	n%
46	15.70	0.648	0.70	7.12
47	15.36	0.685	0.70	7.37
48	16.35	0.657	0.71	7.63
49	17.65	0.75	0.72	9.53

A series of push-pull structured (D-π-A) porphyrin dyes with an electron donating group attached at the *meso* position (**50-52**) were designed by Kim *et al.*[116] for the use of sensitizers for DSSCs (Figure 21). The absorption bands of these porphyrin dyes were broadened and red shifted upon introduction of alkoxy chains to the electron donating groups at *meso* position opposite to the anchoring cyanoacrylic acid group. Among the sensitizers, the highest PCE of DSSC fabricated with **52** was 4.7 % (J_{sc} =

11.8 mA/cm^2, V_{oc} = 0.593 V and FF = 0.651) and further improved up to 7.6 % (J_{sc}= 15.9 mA/cm^2, V_{oc} = 0.68 V and FF = 0.703) when **53** used as coadsorbent (Table 10).



50 **51** **52**

Figure 21. Molecular structure of compounds **50-52** and coadsorbant **53**.

Table 10. Photovolataic performances of DSSC using **50-52**.

Dye	J_{sc}, mA cm^{-2}	V_{oc}, V	FF	n%
50	4.9 (10.9)^a	0.546 (0.593)	0.74 (0.77)^a	2.0 (5.0)^a
51	9.6 (13.4)^a	0.548 (0.632)^a	0.69 (0.72)^a	3.6 (6.1)^a
52	11.8 (15.9)^a	0.617 (0.678)^a	0.65 (0.70)	4.7 (7.6)^a

[a] Compound **53** was used as the co-adsorbent.

Diau and Yeh[117] synthesized *p*-extended porphyrin dye **54** and **55** with long alkoxyl chains at the *ortho* positions and cyanoacrylic acid as an anchoring group (Figure 22). The efficiencies of both compounds were quite poor 5.8% (J_{sc} = 11.30 mA/cm^2, V_{oc} = 0.69 V and FF = 0.74) for **54** and 3.6% (J_{sc} = 7.17 mA/cm^2, V_{oc} = 0.67 V and FF = 0.75) for **55**. This was due to the floppy structural nature and limited molecular rigidity of the cyanoacrylic acid anchor, which might lead the porphyrins to tilt down the TiO_2 surface for an efficient charge recombination to occur.[118, 119]

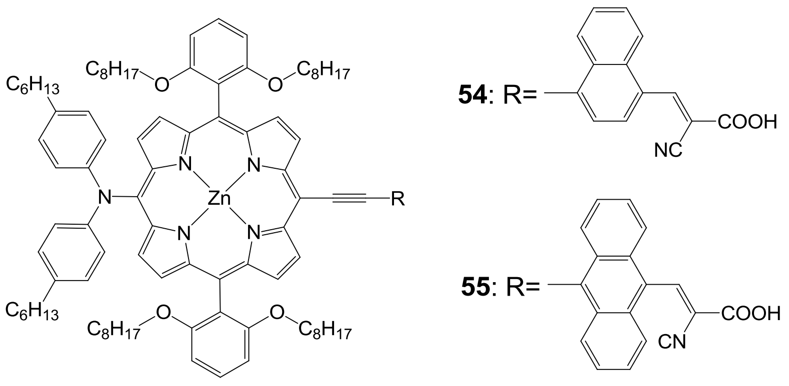
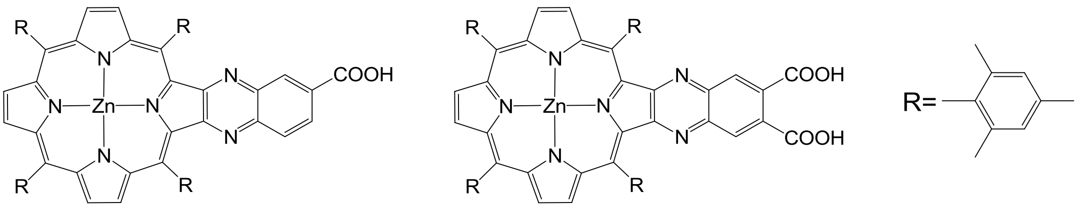


Figure 22. Molecular structure of dyes **54** and **55**.

1.2.5 Fused Porphyrins

One issue with porphyrins as sensitizers in DSSCs is their limited absorptivity in the red and near infrared regions of the solar spectrum. With *meso*-tetraphenylporphyrins the phenyl moieties are typically considered perpendicular to the plane of the macrocycle and therefore are not in conjugation with the porphyrin system. One design strategy for increasing the light absorption of porphyrin sensitizers is to lock the *meso*-phenyl ring into the plane of the macrocycle in order to improve the conjugation between the porphyrin and the phenyl rings. This strategy has the added benefit of increasing the molecular asymmetry of the molecule. The combination of added conjugation and increased molecular asymmetry manifests itself as a red shift in the absorption spectrum of the molecule. The following examples synthesized towards this strategy.

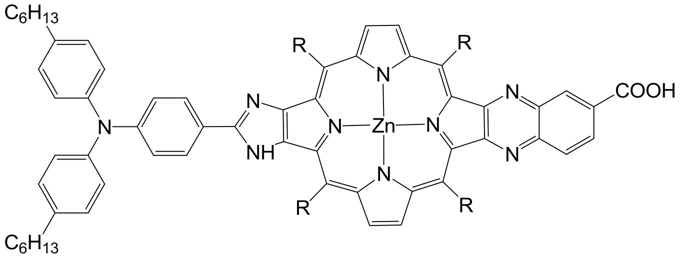
One way to improve the light harvesting property of porphyrin sensitizers is to introduce the unsymmetrical π-elongation in the porphyrins.[94, 120-126] Imahori and coworkers reported novel β-linked porphyrins **56** and **57** (Figure 23) with carboxyquinoxalino or dicarboxyquinoxalino moieties respectively.[122] Compound **56** gave a solar energy conversion efficiency of 5.2% (J_{sc} = 11.2 mA/cm^2, V_{oc} = 0.72 V and FF = 0.68)in a standard DSSC, while the dicarboxy derivative **57** gave 4% (J_{sc} = 9.3 mA/cm^2, V_{oc} = 0.67 V and FF = 0.64) efficiency. The superior performance of the **56**-sensitized solar cell to the **57**-sensitized one was originated from both the more favorable electron injection and charge collection efficiency.



56 **57**

Figure 23. Molecular structure of dyes **56** and **57**.

A push-pull porphyrin **58** was synthesized and studied with an electron donating triarylamino group at the *β,β’*-edge through a fused imidazole group and an electron withdrawing carboxyquinoxalino anchoring group at the opposite *β,β*`-edge (Figure 24) and employed as sensitizer for DSSC. [127] The **58-**sensitized solar cell exhibited a relatively high PCE of 6.8% (J_{sc} = 13.9 mA/cm^2, V_{oc} = 0.68 V and FF = 0.71), which was larger than that of the **56**-sensitized solar cell 6.3% (J_{sc} = 13.2 mA/cm^2, V_{oc} = 0.71 V and FF = 0.67) with chenodeoxycholic acid as co-absorbent, to reduce porphyrin aggregation on TiO_2. The short-circuit current and FF of the **58**-sensitized solar cell were larger than those of the **56**-sensitized solar cell, whereas the open circuit potential of the **58**-sensitized cell was smaller than that of the **56**-sensitized cell, leading to an overall improved cell performance of **58**.



58

Figure 24. Molecular structure of dye **58**.

Yeh and coworkers[117] synthesized *p*-extended porphyrin dyes **59** and **60** with long alkoxyl chains at the *ortho* positions of the *meso* phenyls, and *meta* di-*tert*-butylphenyl-substituted porphyrins for DSSCs; their optical, electrochemical and photovoltaic properties were investigated and compared with those of **61** and **62** (Figure 25).

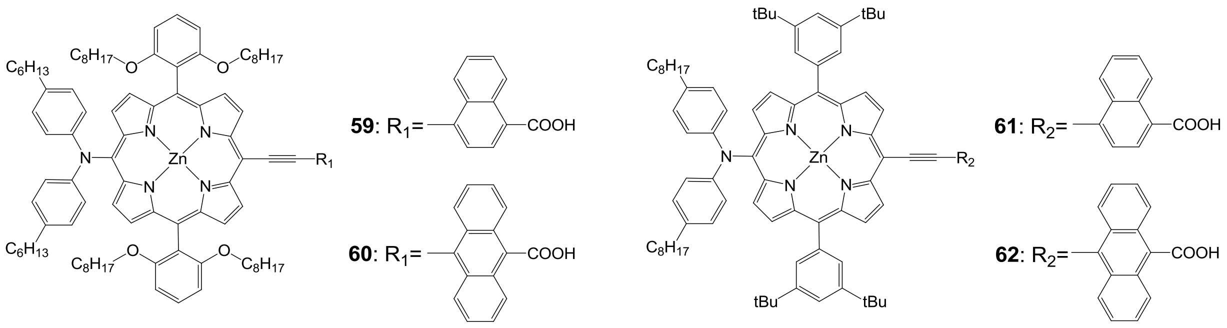


Figure 25. Molecular structure of dye **59-62**.

For the naphthalene-bridged porphyrins, the *ortho*-substituted long alkoxyl chains in the two *meso*-phenyls of **59** played a key role to prevent dye aggregation so that both J_{SC} and V_{OC} were significantly enhanced for **59** than for **61**. As a result, the PCE of **59** reached 8.04%, which was ~11% higher than that of **61** (7.23%). The devices made of **62** were found to perform extremely poorly due to a serious problem of dye aggregation on the TiO_2 surface that significantly reduced the efficiency of electron injection from the excited state of the dye molecule to the conduction band of TiO_2.[103] However, the *ortho*-substituted long alkoxyl chains in **60** exhibited dramatic effects to decrease the degree of dye aggregation so that the IPCE values of **60** were significantly improved by a factor of three over those of **62**. As a result, J_{SC} of the **60** device was improved by more than a factor of two over that of the **62** device. Therefore, the device performance of **60** reached efficiency of 6.03%, which was remarkably improved by 135% compared with that of **62** (Table 11).

Table 11. Photocatalytic parameters under global AM 1.5 irradiation for DSSCs absorbed on nanocrystalline TiO_2 anodes.

Dye	J_{sc}, mA cm^{-2}	V_{oc}, V	FF	*n*, %
59	15.37	0.745	0.702	8.04
60	11.59	0.720	0.723	6.03
61	14.6	0.713	0.721	7.23
62	5.09	0.679	0.743	2.57

1.3 Supramolecular Assemblies

In nature, self-assembly through noncovalent binding motifs, such as hydrogen bonding, metal-ligand coordination, electrostatic, π-π, and weak van der Waals interactions, play a dominant role. For example, photosynthetic antenna reaction center pigments use such intermolecular interactions to precisely arrange the donor-acceptor entities in a protein matrix, exhibiting a cascade of energy and electron transfer processes.[128] These principles of photosynthesis[129] have attracted significant scientific attention in order to prepare artificial supramolecular photosynthetic architectures that mimic the photoinduced energy and electron transfer processes.[130-134] Several examples have been reported with noncovalent methodologies and especially the highly versatile metal-ligand binding approach was employed for assembling the different entities in donor-acceptor type dyads or triads.[135-138]

Based on this biomimetic approach, several groups have constructed supramolecular solar cells that could serve as an alternative to semiconductor-based ones for renewable energy production. The metal-ligand binding method was used for self-assembling the different units on the electrode surface. The TiO_2 surface was modified with axially coordinating nitrogenous (pyridine or imidazole) ligands bearing a carboxylic acid. The carboxyl group binds to the TiO_2 leaving the nitrogenous entity to axially coordinate the metal center of the chromophore. In this way unfavorable phenomena such as molecular aggregation on the semiconductor surface and poor injection and recombination kinetics between the dye and the TiO_2 can be eliminated.

As well as zinc porphyrins, ruthenium metalloporphyrins were also tested as chromophores in supramolecular DSSCs (Figure 26). The binding of a pyridyl ligand is significantly stronger in Ru-porphyrins compared to the zinc analogs. Isonicotinic acid was used as a linker for the attachment of the metalloporphyrins (Ru(CO)OEP **63**, Ru(CO)TPP **64** and ZnTPP **65**) in the TiO_2 surface.[139]

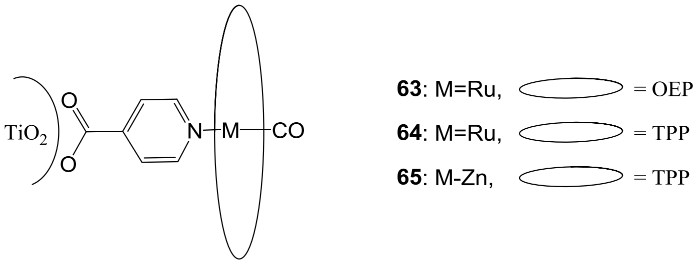


Figure 26 Functionalization of TiO_2 surface with Ru porphyrins through isonicotinic acid. Adapted from Ref. 203.

DSSCs were prepared in order to study the influence of the binding strength in the photovoltaic performance of the cells. The efficiency was highest for the ruthenium porphyrin DSSCs and was lowest for the zinc DSSC, verifying the relationship between the strength of the binding and the power conversion efficiency. However the DSSC with sensitization from a 1:1 solution of **63**:**64** gave the best overall performance of the porphyrin devices with an efficiency 1.8 times greater than that of the **65** device and 1.4 times greater than the **63** and **64** devices, which had nearly the same conversion efficiencies. This observation showed that a mixed assembly might lead to enhance photovoltaic behavior, likely due to increased light absorption.

This research work is divided in four subsections where different porphyrin based molecules have been synthesized in order to be used as chromophores in dye sensitized solar cells (DSSC).

Section A: Porphyrin based triads

The first part describes the synthesis and photophysical studies of a central metallated porphyrin derivatized with (i) two free-base porphyrin molecules (ii) two boron dipyrrin (BDP) molecules forming trimeric compounds.

Section B: Porphyrin based dyads

The second part presents the synthesis and DSSC measurements of two porphyrin dyads, which consist of a zinc-metalated porphyrin and a free-base porphyrin unit covalently linked at their peripheries.

Section C: Metal-ligand porphyrin based dyads

The third part presents the formation of a dyad porphyrin where a ruthenium porphyrin is attached to a mono-pyridine based porphyrin and its DSSC performance was measured.

Section D: Porphyrin based photosensitizers with long alkyl chains

Finally, in the fourth part of this manuscript is described the synthesis of a metallated porphyrin bearing long alkyl chains and two carboxylic groups attached at the meso position of the porphyrin ring via triple bond.

CHAPTER II
RESULTS AND DISCUSSION

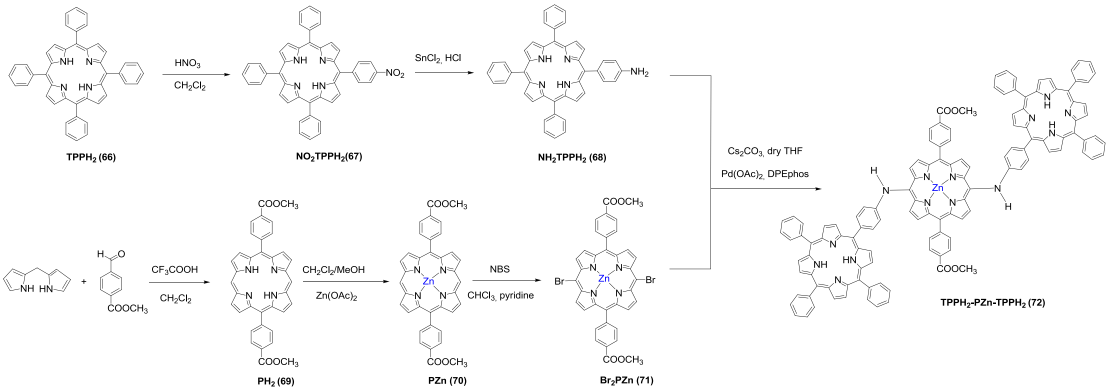
2. RESULTS AND DISCUSSION

2.1 SECTION A: Porphyrin based triads

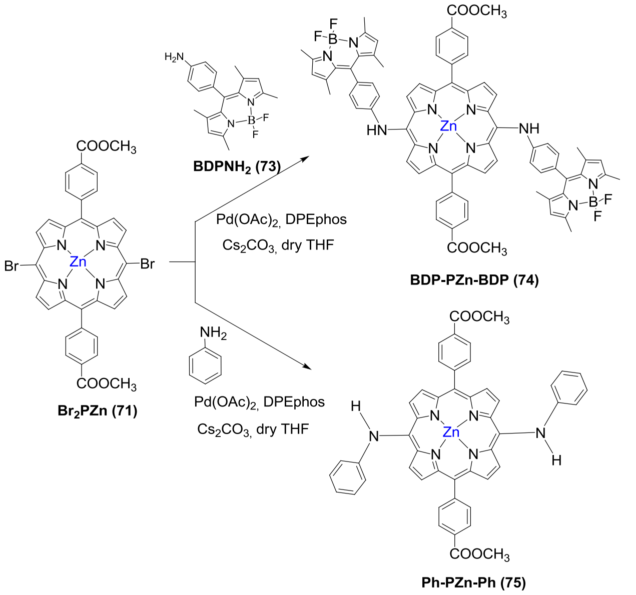
2.1.1 Synthesis and studies of trimeric compounds

The synthesis of the trimeric compounds is shown in Schemes 3 and 4. **NH_2TPPH_2** (**68**) porphyrin was synthesized in two steps followed a literature procedure incorporated with our own modification in a 63 % overall yield.[140] Porphyrin **PH_2** (**69**) was prepared in one step by acid-catalyzed condensation of dipyrromethane with 4-carboxymethylbenzaldehyde, followed in situ oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Metallation with zinc acetate obtained porphyrin **PZn** (**70**), bromination with two equivalents of N-Bromosuccinimide (NBS) in the presence of pyridine gave dibromo porphyrin **Br_2PZn** (**71**) in an excellent yield.[141, 142] Triad porphyrins were successfully synthesized under palladium-catalyzed double amination conditions with coupling of Zn-*meso*-dibromoporphyrin **Br_2PZn** (**71**) (1 eq) and three different amines. The synthesis can be carried out under mild conditions, typically giving high yields. All reactions were carried out in THF at 68 ^oC under argon atmosphere with excess amine (4.8 eq), and the use of 0.1 eq of palladium acetate, 0.15 eq of bis(2-diphenylphosphinophenyl)ether (DPEphos) in the presence of 2.8 eq of cesium carbonate as a weak base. The desired products were separated by flash column chromatography and the excess of amines were recovered. Firstly, Zn-*meso*-dibrominated porphyrin (**Br_2PZn**) (**71**) was coupled with **NH_2TPPH_2** (**68**) in 63 % yield. The progress of the reaction was monitored by TLC and after 4 days porphyrin **Br_2PZn** (**71**) had been consumed forming the desired compound (**$TPPH_2$-PZn-$TPPH_2$**) (**72**). In addition a trace amount of monoamination product was present. To the best of our knowledge this is the first time that a triad porphyrin has been synthesized linked with a NH group. Then **$BDPNH_2$** (**73**) (Scheme 4) was used as an amine and triad porphyrin **BDP-PZn-BDP** (**74**) was prepared in high yield, 93 %, the reaction was again monitored by TLC and after 20 h all starting material had been consumed. Compound **$BDPNH_2$** (**73**) was synthesized according to the literature.[143] Finally, under the same conditions aniline was coupled with porphyrin **Br_2PZn** (**71**) in order to obtain compound **Ph-PZn-Ph** (**75**) in 91 % yield. A trace amount of monoamination byproduct was also present after the flash column chromatography and was removed by washing the product with CH_2Cl_2, since triad **Ph-PZn-Ph** (**75**) is not soluble in this solvent. Single crystals of this compound were obtained suitable for diffraction analysis. All new compounds were characterized on the basis of their ^{1}H and ^{13}C NMR spectra, MALDI-TOF mass spectra.

As already has been mentioned all compounds were fully characterized by NMR experiments including ^{1}H, ^{13}C, COSY, HMQC and HMBC. In the ^{1}H-NMR (*d*$_8$-THF) spectra of all trimeric compounds the protons of the NH bridge are considerably shifted downfield at 9.04, 9.54 and 9.19 ppm, respectively compared to the free amino components. All synthesized products can exist in a mixture of two atropisomers (*αα*- and *αβ* –isomers), but in both ^{1}H and ^{13}C spectra only one set of resonances were observed indicating that there is a free rotation around the C-N bond at ambient temperature, as has been reported in the literature.[144, 145] In the case of trimer **TPPH$_2$-PZn-TPPH$_2$** (**72**) we observed a split of the peak corresponding to the NH bridge whereas for compounds **BDP-PZn-BDP** (**74**) and **Ph-PZn-Ph** (**75**) only a singlet peak was present. Possibly, in the case of **TPPH$_2$-PZn-TPPH$_2$** (**72**), where three porphyrins are linked, the rotation around the bond between the amino nitrogen atom and the porphyrin *meso*-carbon atom has a higher rotation barrier compared to the other two trimers.



Scheme 3. Synthesis of trimer **TPPH$_2$-PZn-TPPH$_2$** (**72**)



Scheme 4. Synthesis of trimers **BDP-PZn-BDP (74)** and **Ph-BDP-Ph (75)**

2.1.2. Single-Crystal X-ray Diffraction Structures

An ORTEP of **Ph-PZn-Ph** (**75**) is depicted in Figure 27. The porphyrin plane displays a slight ruffling from planarity (0.0336) and the distances and angles of **Ph-PZn-Ph** (**75**) are similar to Zn-tetraphenyl pophyrin.[146] Due to the coordination of Zn with two THF molecules, Zn is in the plane of the N4[147] contrary to four of five coordinated Zn-porphyrins. The average bond distance of Zn-N is 2.0645 Å. Two THF molecules are weakly bound axially to Zn (Zn-O distance 2.403 Å). The dihedral angle formed by the plane P_1 (of the phenyl ring of the aniline) to the P2 (plane of the porphyrin ring) is 81.51^o (0.14) and is slightly bigger than the other phenyl ring forms (73.99^o (0.12)). The torsion angle of aniline (C_{11}-N_3-C_{meso}-C_a) is 88.77^o.

Close intermolecular packing arrangement observed, mainly the short contact of 2.239 Å formed by the H of the secondary amine with the carbonyl group of the ester of a neighbouring porphyrin ring. The hydrogen of the THF(H_3) forms shorts contacts (2.366 Å) with the β-H_9 and with aniline group [H_{1s} with C_{14}(2.886 Å)] (Figure 28).

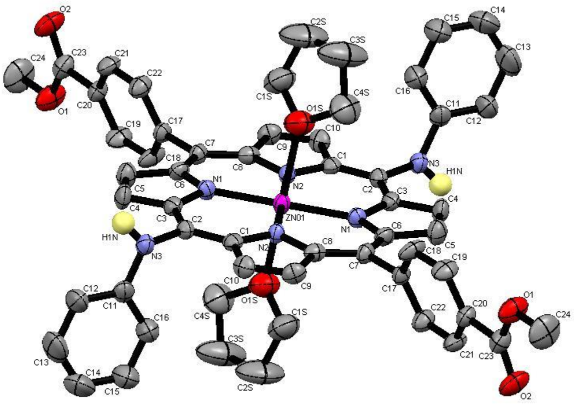


Figure 27. ORTEP view of molecular structure **Ph-PZn-Ph**·3THF. Thermal ellipsoids are drawn at 50 % occupancy. Hydrogen atoms have been omitted for clarity except amine hydrogen (labeled H1N) and one of the THF molecules found in the asymmetric unit. Atoms having the same label are generated from each other by symmetry.

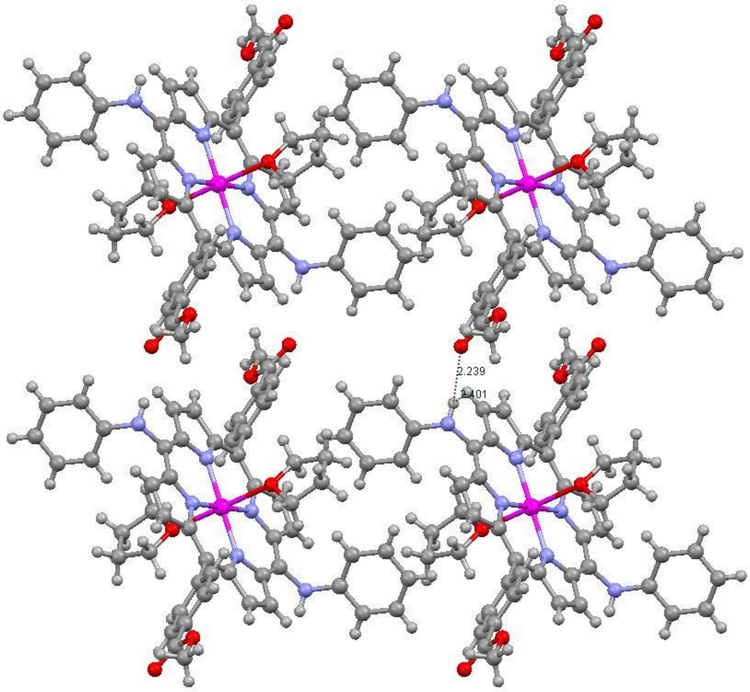


Figure 28. Packing arrangement of trimeric compound **Ph-PZn-Ph** (**75**). The packing was viewed along a axis.

2.1.3 Electrochemistry

Cyclic voltammetry was used in order to study the electrochemical properties of the trimers. For trimer **$TPPH_2$-PZn-$TPPH_2$** (**72**) it was not possible to obtain any voltammograms in either CH_2Cl_2, THF, or acetonitrile due to stability and/or solubility difficulties. Trimer **BDP-PZn-BDP** (**74**) was studied in CH_2Cl_2 and **Ph-PZn-Ph** (**75**) in THF, all data reported vs the ferrocene/ferrocenium couple (Fc/Fc^+). Cyclic voltammograms are shown in Figure 29. **$BDPNH_2$** (**73**) in CH_2Cl_2 showed a reversible oxidation at 0.76 V due to formation of the BDP cationic radical (Figure 29c).[51-52] Reference triad **Ph-PZn-Ph** (**75**) in THF showed one reversible oxidation at -0.01 V, attributed to the oxidation of the porphyrin ring[1] (Figure 29b). The cyclic voltammetry of **BDP-PZn-BDP** (**74**) shows one reversible process at 0.04 V and one irreversible at 0.76 V. The first one is attributed to the first porphyrin oxidation and the second to the oxidation of the BDP, respectively (Figure 29a). In addition triad **BDP-PZn-BDP** (**74**) shows one reversible process at -1.74 V, attributed to BDP reduction. Porphyrin reductions in the case of **BDP-PZn-BDP** (**74**) and **Ph-PZn-Ph** (**75**) could not be observed.

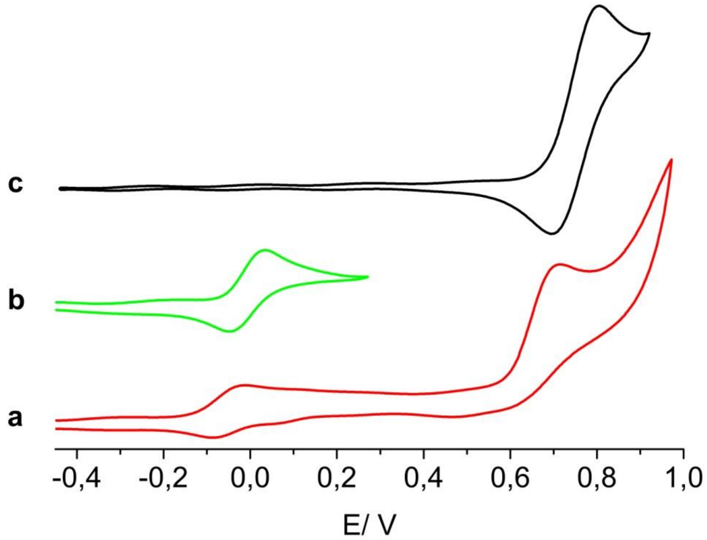


Figure 29. Cyclic voltammograms of (a) **BDP-PZn-BDP** (**74**) in CH_2Cl_2, (b) **Ph-PZn-Ph** (**75**) in THF and (c) **$BDPNH_2$** (**73**) in CH_2Cl_2 containing 0.1M $(TBA)PF_6$ as supporting electrolyte. The voltages are vs Fc/Fc^+.

2.1.4 Photophysical Properties - Electronic Absorption Spectra

The electronic absorption spectra of compounds **NH_2TPPH_2** (**68**), **$TPPH_2$-PZn-$TPPH_2$** (**72**) and **Ph-PZn-Ph** are presented in Figure 30, and those of compounds **$BDPNH_2$**, **BDP-PZn-BDP** and **Ph-PZn-Ph** (**75**) in Figure 31. All absorption spectra were measured in Toluene. The absorption maxima and molar absorption coefficients (ε) of the Soret and Q bands are listed in Table 12. Compound **NH_2TPPH_2** (**68**) exhibits typical free-base porphyrin absorption features[148] with an intense Soret band at 422 nm and moderate Q bands at 516, 552, 594 and 650 nm. **Ph-PZn-Ph** (**75**) shows the characteristic bands of Zn-meso-arylamino substituted porphyrins with a Soret at 444 nm and two Q bands at 561 and 614 nm.[145] The spectrum of triad **$TPPH_2$-PZn-$TPPH_2$** (**72**) shows the characteristic absorptions of the individual macrocyclic components, namely strong absorptions assigned to the Zn-meso-arylamino substituted porphyrin and the **NH_2TPPH_2** (**68**) chromophores (Figure 30). Triad **$TPPH_2$-PZn-$TPPH_2$** (**72**) displays a broad Soret band centered at ca. 420 nm with a shoulder on its high energy side (ca. 445 nm) attributable to the central porphyrin of the triad. Thus the absorption spectrum of **$TPPH_2$-PZn-$TPPH_2$** (**72**) is largely the sum of those of its components indicating that there is little electronic interaction between the central and the peripheral porphyrin chromophores in the ground state. Similarly, the absorption spectrum of triad **BDP-PZn-BDP** (**74**) (Figure 31) clearly shows features attributed to both of its components namely an intense absorption at 503 nm due to the BDP chromophores and the characteristic porphyrin based peaks (Soret at 445 nm and Q bands at 561, 614 nm).[149] Therefore, in triad **BDP-PZn-BDP** (**74**), as in **$TPPH_2$-PZn-$TPPH_2$** (**72**), there is weak electronic interaction between the two side BDP molecules and the central Zn-porphyrin in the ground state.

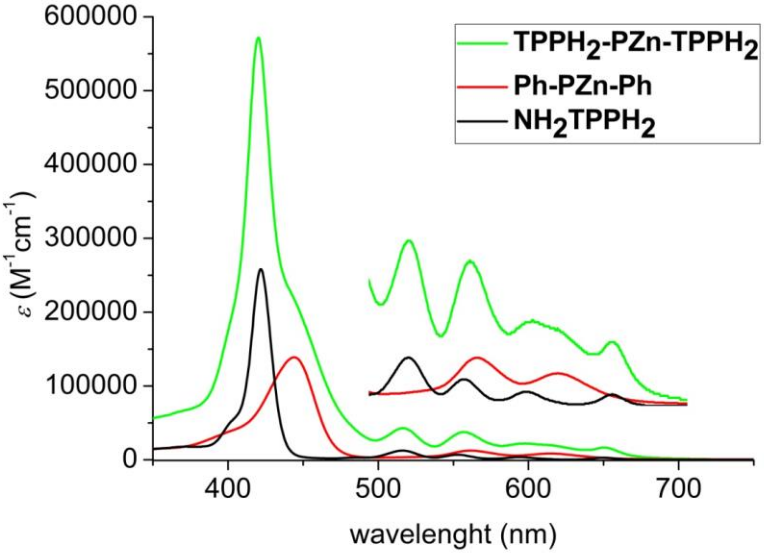


Figure 30. UV-Vis absorption spectra of **NH_2TPPH_2** (**68**), **$TPPH_2$-PZn-$TPPH_2$** (**72**) and **Ph-PZn-Ph** (**75**) in Toluene and expansion of the Q bands.

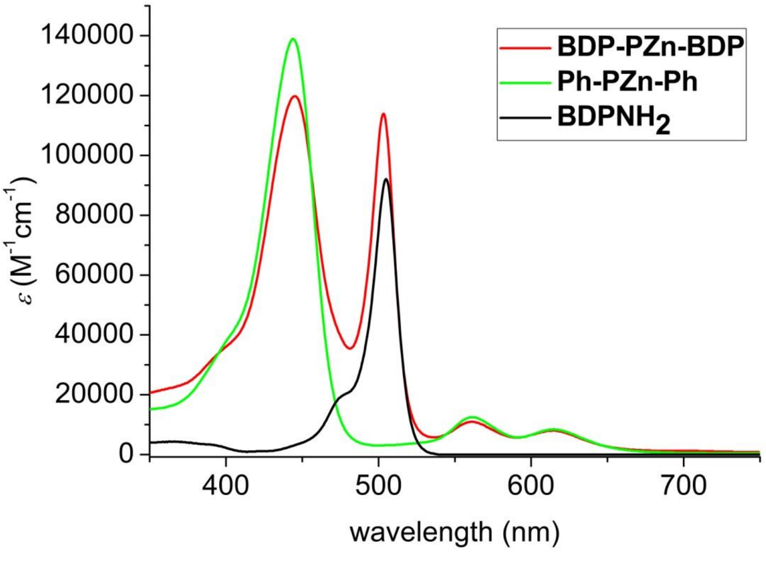


Figure 31. UV-Vis absorption spectra of **$BDPNH_2$** (**73**), **BDP-PZn-BDP** (**74**) and **Ph-PZn-Ph** (**75**) in Toluene.

Table 12. Spectroscopic Data of trimeric compounds and **$TPPNH_2$**, **$BDPNH_2$**

	Absorption	Emission		
Compound	λ_{max}/ nm (ε/ $mM^{-1}cm^{-1}$)	λ_{max}/ nm	Φ	τ/ ns
$TPPH_2$-PZn-$TPPH_2$ (**72**)	420 (571.6), 445 sh (213.6) 516 (17.2), 556 (15.0), 595 (8.7), 650 (6.6)	661, 719	0.12	2.9, 9.8
BDP-PZn-BDP (**74**)	445 (119.8), 503 (113.9), 561 (11.0), 614 (8.1)	518, 684	0.073	3.8
Ph-PZn-Ph (**75**)	444 (138.9), 561 (12.5), 614 (8.5)	698	0.11	3.5
NH_2TPPH_2 (**68**)	422 (258.2), 516 (12.5), 552 (6.8), 594 (3.6), 650 (2.8)	661, 722	0.11	8.8
$BDPNH_2$ (**73**)	505 (92.1)	519	0.38[a]	3.1[a]

a. Values were taken from reference.[149]

2.1.5 Photophysical Properties - Emission Spectra

Steady state and time resolved emission spectroscopy in toluene at ambient temperature was used in order to study all trimeric compounds**.** A summary of measured spectroscopic data is presented in Table 1. **$BDPNH_2$** (**73**) shows the intense fluorescence of a BDP dye at 502 nm in toluene. **NH_2TPPH_2** (**68**) displays two emission bands at 661 and 722 nm. The reference porphyrin **Ph-PZn-Ph** (**75**) exhibits a broad fluorescence band with maximum at 698 nm and with a lifetime of τ_1 = 3.5 ns. Triad **$TPPH_2$-PZn-$TPPH_2$** (**72**) when irradiated at 517 nm, corresponding to selective excitation of **NH_2TPPH_2** (**68**), shows emission which closely resembles that of the free base porphyrin chromophore at 661 and 719 nm (Figure 32a). Also, when excited at 467 nm corresponding mainly to the central Zn porphyrin, an almost identical spectrum was observed (Figure 32a). The excitation spectrum of **$TPPH_2$-PZn-$TPPH_2$** (**72**) monitoring at the emission of the free base side porphyrins at 661 nm shows absorption features from both chromophores constituting **$TPPH_2$-PZn-$TPPH_2$** (**72**) (Figure 32b). In addition, time resolved emission measurements with pulsed excitation of mainly the peripheral porphyrins at 400 nm, show that **$TPPH_2$-PZn-$TPPH_2$** (**72**) exhibits a dual exponential decay with lifetimes of 2.9 and 9.8 ns respectively. By comparison with the fluorescence lifetimes of reference compound **Ph-PZn-Ph** (**75**) and **NH_2TPPH_2** (**68**) we attribute the short lifetime of **$TPPH_2$-PZn-$TPPH_2$** (**72**) to the central Zn-porphyrin and the longer one to the peripheral freebase porphyrins. Combination of the results from the excitation spectrum and the time-resolved fluorescence measurements of **TPPH$_2$-PZn-TPPH$_2$** (**72**) show that excitation of either of the chromophores of **TPPH$_2$-PZn-TPPH$_2$** (**72**) into its first singlet excited state results in partial energy transfer to the first singlet excited state of the other chromophore. This is expected because, as shown by the emission spectra of **TPPH$_2$-PZn-TPPH$_2$** (**72**) and **Ph-PZn-Ph** (**75**) in toluene glass at 77 K, the first singlet excited states of the freebase (1.88 eV) and Zn-porphyrin chromophores (1.82 eV) of **TPPH$_2$-PZn-TPPH$_2$** (**72**), are almost isoenergetic (energy deference of ca. 500 cm^{-1}). In the case of triad **BDP-PZn-BDP** (**74**), irradiation at 491 nm, corresponding to selective excitation of the two BDP units, results in emission from the Zn-porphyrin chromophore at 684 nm, as well as residual fluorescence from the two BDP groups at 518 nm (Figure 33a). The BDP based emission in **BDP-PZn-BDP** (**74**) is strongly quenched when compared to the emission measured for **BDPNH$_2$** (**73**). Moreover, the excitation spectrum of **BDP-PZn-BDP** (**74**) monitoring at the fluorescence of the porphyrin moiety at 685 nm shows an intense BDP absorption feature at 499 nm (Figure 33b). This is a clear indication of BDP to porphyrin singlet energy transfer following excitation of the BDP unit.

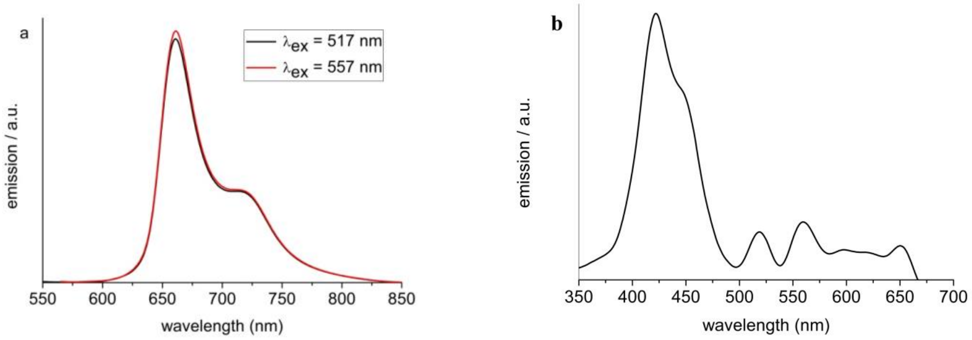


Figure 32. (a) Emission spectra of **TPPH$_2$-PZn-TPPH$_2$** (**72**) exciting at 517 nm (peripheral porphyrin) and 557 nm (central porphyrin) and (b) excitation spectrum of **TPPH$_2$-PZn-TPPH$_2$** (**72**) monitoring at 661 nm at room temperature in toluene.

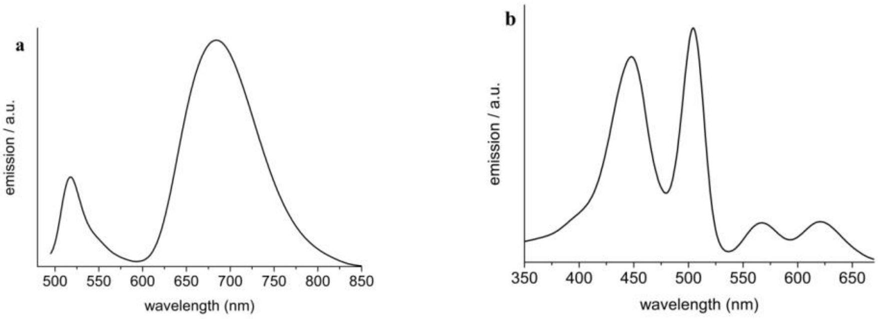
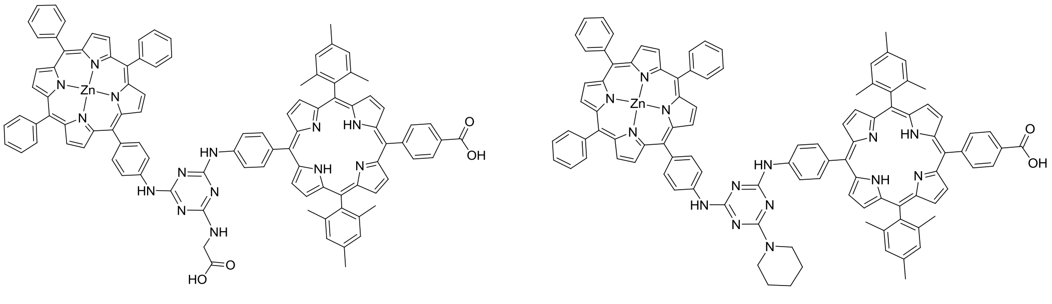


Figure 33. (a) Emission spectrum of **BDP-PZn-BDP** (**74**) exciting at 491 nm (BDP chromophore) and (b) excitation spectrum of **BDP-PZn-BDP** (**74**) monitoring at 685 nm at room temperature in toluene.

2.2 SECTION B: Porphyrin based dyads

2.2.1 Synthesis and characterization

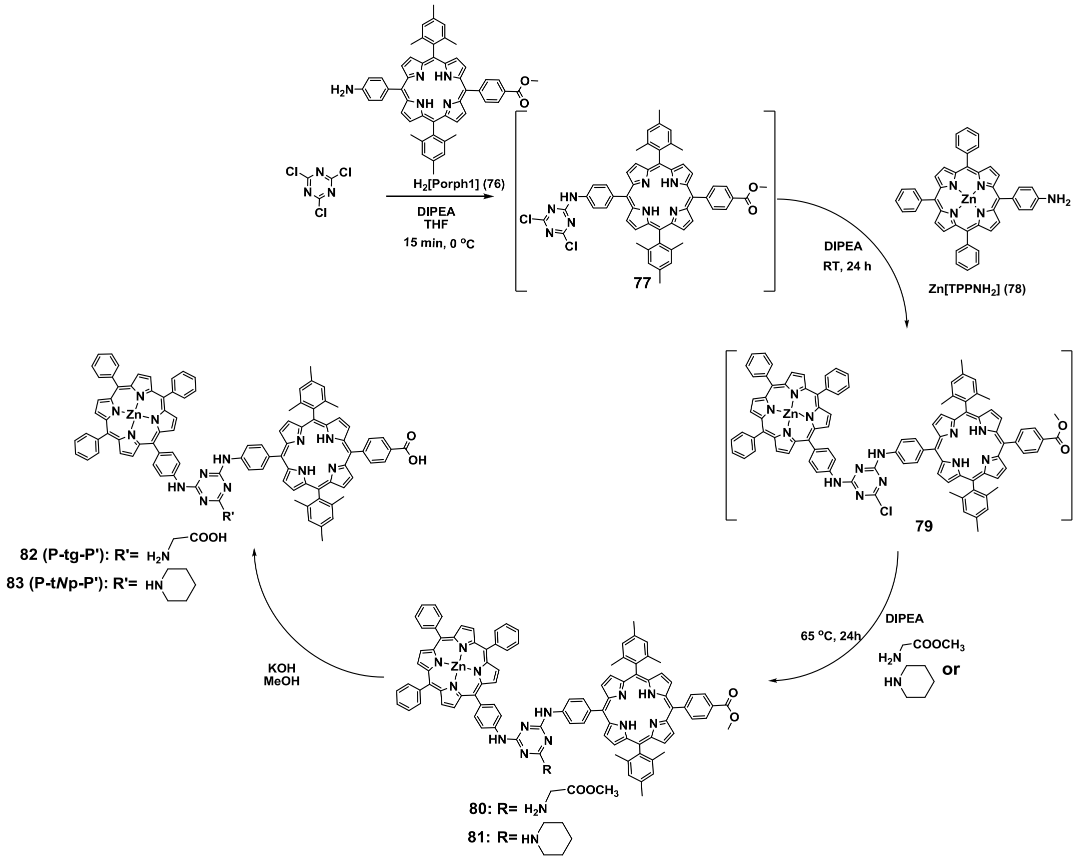
As shown in Scheme 5, porphyrin dyads (ZnP)-[triazine-gly]-(H_2PCOOH) (**82**) and (ZnP)-[triazine-*N*pip]-(H_2PCOOH) (**83**), abbreviated as **P-tg-P´** and **P-t*N*p-P´**, respectively, consist of a *meso* aryl-substituted zinc-metallated porphyrin unit P (namely 5-(4-aminophenyl)-10,15,20-triphenylporphyrin zinc) and a free-base porphyrin unit P´ (namely 5-(4-carboxyphenyl)-15-(4-aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin) which are connected, through aryl-amino groups at their peripheries, by a central 1,3,5-triazine moiety. In the former, the triazine ring is further functionalized by a glycine group, while in the latter by an *N*-piperidine group. Both porphyrin dyads contain potential anchoring groups for attachment onto the TiO_2 surface of DSSC electrodes: the former two carboxylic acid groups, while the latter one carboxylic acid and one *N*-substituted piperidine group.



Scheme 5. Porphyrin dyads **82** and **83**.

The syntheses of two dyads, shown in Scheme 6, was accomplished via stepwise amination reactions of cyanuric chloride, which is the precursor of the bridging 1,3,5-triazine group of both dyads. The potential of cyanuric chloride to provide access to a variety of triazine-bridged assemblies, such as macrocycles,[150] dendrimers,[151, 152] and multiporphyrin arrays,[153-156] has been demonstrated in the past. Furthermore, we recently reported symmetrical and unsymmetrical triazine-bridged porphyrin dyads and triads.[**Error! Bookmark not defined.**,**Error! Bookmark not defined.**]

The initial step for the synthesis of both dyads involves the reaction of cyanuric chloride with H_2[Porph] in the presence of the base DIPEA at 0 °C in THF (Scheme 2). The reaction was monitored by TLC indicating the disappearance of the reactants and the formation of the mono-porphyrin-triazine adduct **77**. The latter was not isolated but further reacted at room temperature with Zn[TPP-NH_2] (**78**) affording the di-porphyrin-triazine adduct **79**. The third chlorine atom of cyanuric chloride was substituted by a glycine-methyl ester moiety in a one-pot reaction at 65 °C resulting in the di-porphyrin-triazine-glycine methyl ester adduct **80**, as confirmed by ^{1}H NMR spectroscopy and MALDI-TOF spectrometry. In the ^{1}H NMR spectrum of **80**, the signals of the aromatic H’s *ortho* to the amino groups of Zn[TPP-NH_2] (**78**), after attachment to the triazine ring, are downfield displaced compared to those of free Zn[TPP-NH_2] (**78**). Basic hydrolysis of the methyl ester groups of **3a** resulted in the formation of porphyrin dyad **P-tg-P′** (**82**), in almost quantitative yield, as indicated by ^{1}H NMR spectroscopy, MALDI-TOF spectrometry, UV-vis absorption spectroscopy. In the ^{1}H NMR spectrum of **82**, with respect to that of **80**, it should be noted the absence of the signal attributed to the methyl-ester H’s after hydrolysis reaction.



Scheme 6. The experimental route for the syntheses of the dyads

Porphyrin dyad **P-t*N*p-P′** (**83**) was synthesized in a similar method, following the above mentioned sequence of reactions. Piperidine group was introduced in a substitution reaction of the third chlorine atom of cyanuric chloride yielding the di-porphyrin-triazine-piperidine adduct **81**. Hydrolysis reaction resulted in the formation of the desired porphyrin dyad **83.** ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF spectrometry, UV-vis absorption spectroscopy, confirmed the identity and purity of the product.

2.2.2 Photophysical studies

The UV-vis absorption spectra of dyads **P-tg-P′** (**82**) and **P-t*N*p-P′** (**83**) in THF solutions are shown in Figure 34a and 34b, respectively (black color). The absorption spectra of both dyads exhibit the typical porphyrin absorption bands, with intense Soret band in the 400-450 nm range and four moderate bands in the 500-700 nm with no additional features. This indicates that in ground states of the dyads there is no significant electronic interaction between the two porphyrin units attached to the triazine ring. The absorption spectra of **P-t*g*-P′**(**82**) and **P-t*N*p-P′**(**83**) adsorbed onto

TiO_2 film (Figure 34a and 34b, red color) shows the usual porphyrin Soret and Q bands. In general, when porphyrins are adsorbed onto the TiO_2 surface, they form either *H*- or *J*-aggregates. The broader and red shifted bands of both porphyrin dyads may be attributed to intermolecular interactions that result in the formation of *J*-type aggregates.[157-159] As can be seen from Figure 34b, the red shift and broadening are more pronounced for dyad **P-tg-P´**(**82**), suggesting a stronger electronic coupling, which may be due to the presence of two carboxylic acid anchoring units in its molecular structure.[159] Furthermore, it is an indication of an enhanced light harvesting ability of **P-t*g*-P´** (**82**) compared to **P-t*N*p-P´**(**83**).

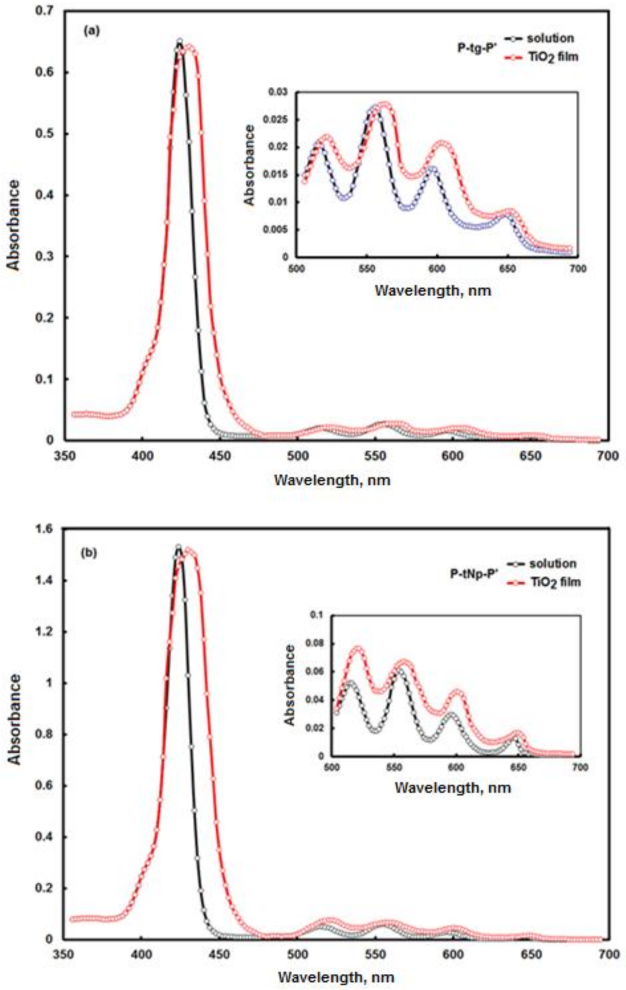


Figure 34. Normalized UV-vis absorption spectra of dyads (a) P-tg-P´ (**82**) and (b) P-t*N*p-P´ (**83**) in THF solutions (black color lines) and after adsorbed onto TiO_2 films (red color lines).

Table 13. Photophysical data, and calculated optical band gaps E_g^{opt} for dyads P-t*g*-P´(**82**) and P-t*N*p-P´(**83**).

Compound	Absorption λmax, nm (ε, × 10^{-5} $M^{-1}.cm^{-1}$) in solution[a]	Absorption λmax, nm on TiO_2 film	Emission λmax, nm in solution[a]
P-tg-P´ (**82**)	424 (5.277), 517 (0.141), 560 (0.195), 601 (0.118), 647 (0.046)	430, 522, 564, 604, 654	612, 656, 717
P-t*N*p-P´ (**83**)	424 (5.146), 515 (0.162), 555 (0.188), 596 (0.093), 649 (0.038)	430, 522, 560, 600, 648	608, 655, 718

[a] measured in THF at 298K

In Figure 35 the steady-state fluorescence spectra of the two dyads **P-t*g*-P´**(**82**) and **P-t*N*p-P´** (**83**) in THF solutions are shown. Exciting the porphyrin dyads at the Soret band (424 nm) results in photoluminescence with three peaks of unequal intensities: 612, 656 and 718 nm for the former (black color line), and 608, 655 and 717 nm for the latter (red color line), respectively. Since both dyads contain free-base and zinc-metallated porphyrin units, their fluorescence spectra result from the superposition of the fluorescence spectra of these two moieties.

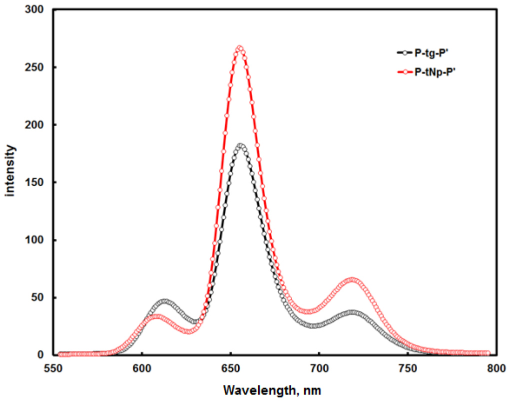


Figure 35. Isoabsorbing fluorescence spectra of dyads **P-tg-P´**(**82**) (black color line) and **P-t*N*p-P´** (**83**) (red color line) in THF solutions.

2.2.3 Electrochemical studies

The electrochemical behavior of **P-tg-P′** (**82**) and **P-t*N*p-P′** (**83**) porphyrin dyads was investigated with cyclic and square-wave voltammetry measurements.[7] The corresponding cyclic and voltammogram is presented in Figure 36, while the relevant electrochemical data are listed in Table 14. The first oxidation for both dyads is a reversible process occurring at E_{ox}^{1} = +1.07 V vs NHE, while the first reductions are reversible processes observed at E_{red}^{1} = -0.86 and E_{red}^{1} = -0.85 V vs NHE for P-tg-P′ (**82**) and P-t*N*p-P′ (**83**), respectively. In general, both dyads exhibit the typical electrochemical processes of assemblies consisted of aryl-substituted Zn-metallated and free-base porphyrin units.

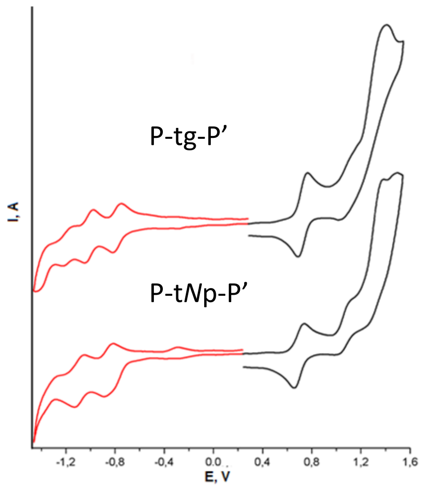
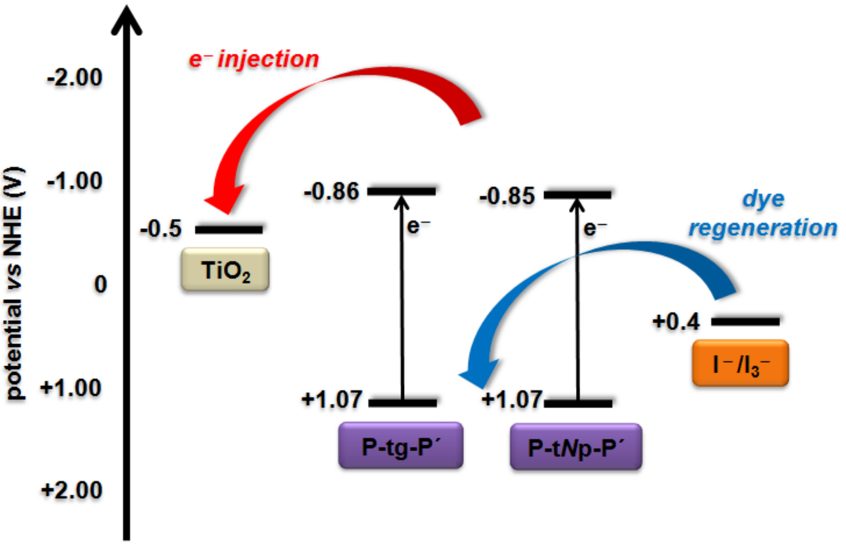


Figure 36. Cyclic voltamograms of dyads P-tg-P′(**82**) and P-t*N*p-P′ (**83**) in DMSO vs NHE. The ferrocene/ferrocenium (Fc/Fc^{+}) redox couple wave is observed at 0.69 V.

Table 14. Electrochemical data, and calculated band gaps E_g^{elec} for dyads P-t*g*-P′(**82**) and P-t*N*p-P′(**83**).

Compound	E^{1}_{ox}, V	E^{2}_{ox}, V	E^{1}_{red}, V	E^{2}_{red}, V	E^{3}_{red}, V	E^{4}_{red}, V
P-tg-P′(**82**)	1.07	1.36	-0.86	-1.10	-1.28	-1.50
P-t*N*p-P′(**83**)	1.07	1.32	-0.85	-1.08	-1.32	-1.49

An efficient sensitizer should have HOMO and LUMO energy levels which are compatible with the redox potential of electrolyte and conduction band (CB) edge of TiO_2, respectively, so that efficient electron injection and regeneration processes are enabled. For efficient electron injection from the photoexcited sensitizer into the TiO_2 CB, the LUMO energy level of the sensitizer should be higher than the TiO_2 CB edge (-0.5 V vs NHE). In addition, for efficient electron regeneration of the sensitizer radial cation (after photoinduced electron injection), the HOMO energy level of the sensitizer should be lower than the potential of the electrolyte redox I^-/I_3^- couple (+0.4 V vs NHE). As mentioned above, the first oxidation potential for both dyads is +1.07 V vs NHE, while the first reduction potentials are -0.86 and -0.85 V vs NHE for **P-t*g*-P´** (**82**) and **P-t*N*p-P´**(**83**), respectively, which means that there is sufficient driving force for efficient electron injection and dye regeneration processes for the **P-t*g*-P´** (**82**) and **P-t*N*p-P´**(**83**) sensitized solar cells. This is also depicted schematically in the energy diagram shown in Scheme 7.[160]



Scheme 7. Energy diagram depicting HOMO and LUMO potentials of the dyads.

2.2.4 Photovoltaic properties

Porphyrin dyads **P-tg-P´** (**82**) and **P-t*N*p-P´** (**83**) were used as sensitizers for the fabrication of DSSCs. The current-voltage (*J*-*V*) characteristics under illumination (AM 1.5, 100 mW/cm^2) of the two DSSCs are presented in Figure 37a while the corresponding photovoltaic parameters are summarized in Table 4. The device based on the **P-tg-P′** (**82**) dyad exhibits short circuit photocurrent (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) values of 11.44 mA/cm^2, 0.68 V and 0.70, respectively, resulting in an overall PCE value of 5.44%, while the values of the corresponding photovoltaic parameters of the **P-t*N*p-P′**(**83**) based solar cell are 9.84 mA/cm^2, 0.62 V, 0.68, giving a PCE value of 4.15%.

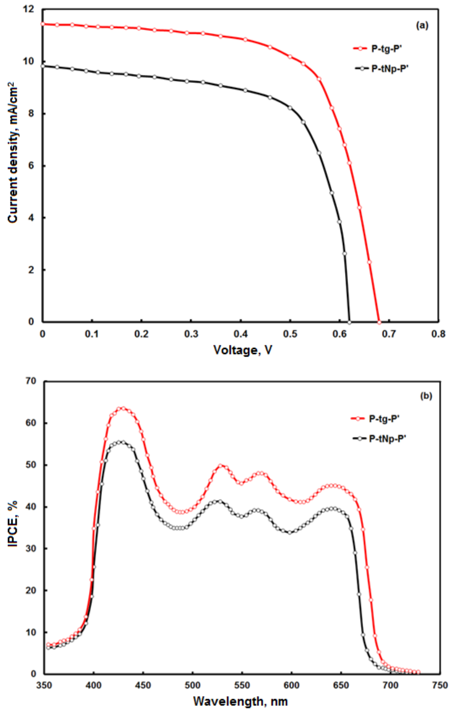


Figure 37. (a) Current-voltage (*J*-*V*) characteristics, and (b) IPCE spectra of DSSCs based on **P-tg-P′** (**82**) (red color lines) and **P-t*N*p-P′** (**83**) (black color lines).

Table 15. Photovoltaic parameters of DSSCs sensitized by dyads **P-tg-P′** (**82**) and **P-t*N*p-P′** (**83**).

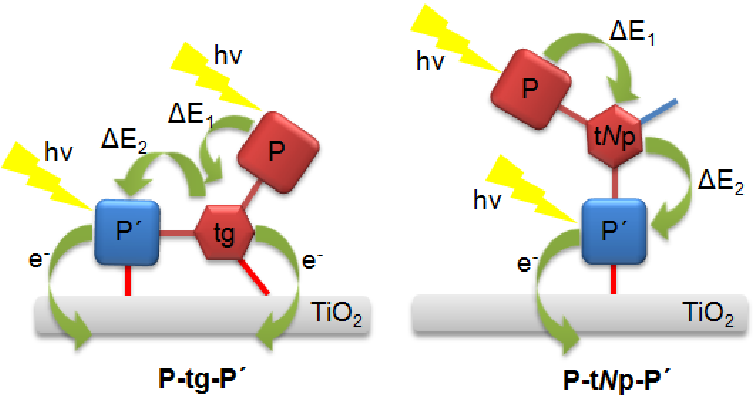
DSSC sensitized by	J_{sc}[a], mA/cm^2	V_{oc}[b], V	FF[c]	PCE[d] (%)
P-tg-P′ (**82**)	11.44	0.68	0.70	5.44
P-t*N*p-P′ (**83**)	9.84	0.62	0.68	4.15

[a] short circuit current
[b] open circuit voltage
[c] fill factor,
[d] photoconversion efficiency.

A major reason for the higher PCE value of the P-tg-P′ based solar cell is its enhanced J_{sc} value. This is reflected in the IPCE spectral responses of the **P-tg-P′** (**82**) and **P-t*N*p-P′** (**83**) sensitized DSSCs, which, as shown in Figure 37b, extend up to ~ 680 nm for both solar cells. The **P-tg-P′** (**82**) solar cell exhibits a stronger and more extended IPCE response than the latter solar cell, which accounts for its higher J_{sc} value.

Furthermore, analysis of the amounts of dye adsorbed onto the TiO_2 surface of the photoanodes of the two DSSCs by desorption method,[161] revealed that the dye loading for the **P-tg-P′** (**82**) based TiO_2 photoanode is higher than that of the **P-t*N*p-P′** (**83**) based photoanode. This might be related to the more effective binding of the former dyad onto the TiO_2 surface, due to the presence of two carboxylic acid anchoring groups on its structure, compared to one carboxylic acid group and a hindered *N*-piperidine binding site in the latter. Therefore, **P-tg-P′** (**82**) is supposed to exhibit a lower tendency to form π-π stacked dye aggregates onto the TiO_2 surface that of **P-t*N*p-P′**(**83**), resulting in an increased electron injection efficiency into the TiO_2 CB and an increased overall PCE.[162]

The different photovoltaic performances of the P-tg-P′ and P-t*N*p-P′ based solar cells can be related to the fact that dyad P-tg-P′ contains two carboxylic acid anchoring group, while dyad P-t*N*p-P′ contains only one carboxylic acid anchoring group and an *N*-piperidine binding site. Considering that *N*-piperidine binding site is hindered and not as effectively binding site as carboxylic acids, the attachment of P-tg-P′ and P-t*N*p-P′ onto the TiO_2 surface can be depicted by a branched system bound through two carboxylic acid groups and a linear system bound through one carboxylic acid group, respectively (Scheme 8). In the former case, this leads to the formation of a more compact layer of dye adsorbed onto the TiO_2 film (as evidenced by the higher dye loading), and results in a cooperative electron transfer to the TiO_2 surface and more efficient electron injection (as evidenced by the longer electron lifetime and higher charge recombination resistance).

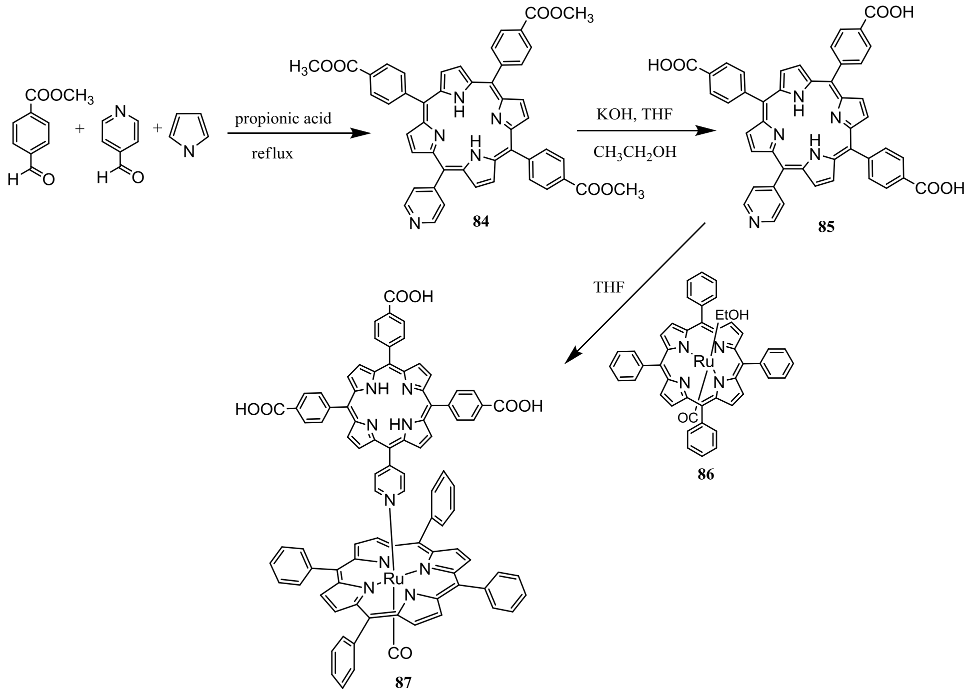


Scheme 8. Binding sites that are placed on the dyads.

2.3 SECTION C: Metal-ligand porphyrin based dyads

2.3.1 Synthesis of dimeric compounds

The preparation of Ruthenium tetraphenyl porphyrin TPP **86** was achieved by addition of $Ru_3(CO)_{12}$ to TPP in refluxing decalin under nitrogen atmosphere. The corresponding metal complex **86** was obtained in high yields and was characterized. UV–Vis absorption spectra of the formed metal-complexes are of normal type for five and four coordinated porphyrins.



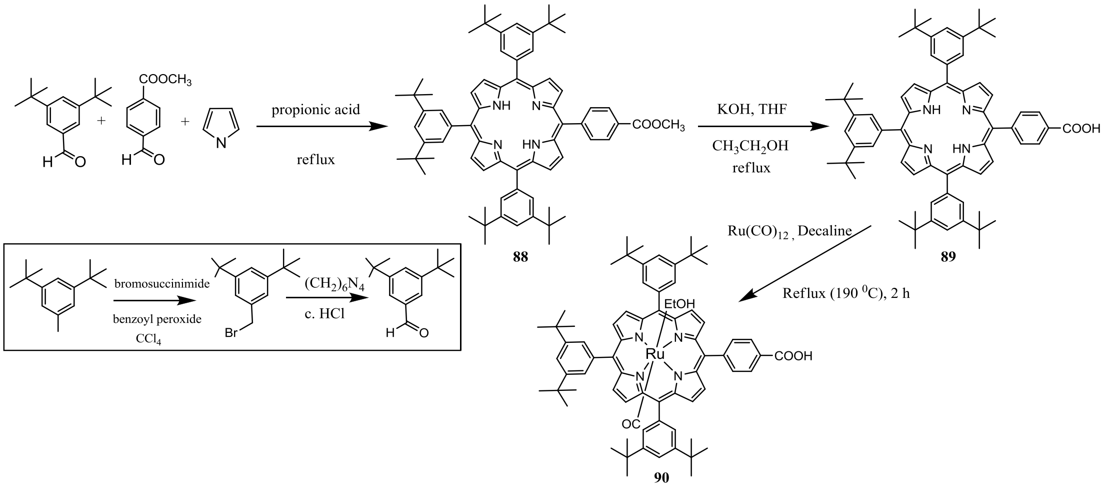
Scheme 9. Synthesis of porphyrins **84-87**.

Then, mono pyridyl tetraester porphyrin was obtained by reaction of methyl-4-formyl benzoate, pyridine-4-carbaldehyde and pyrrole (added dropwise) propionic acid at reflux for 2 h. The product **84** was isolated by column chromatography in 36% yield. Hydrolysis of the product produced porphyrin **85** in 85% yield. In the final step Ru TPP **86** and porphyrin **85** was left stirring at reflux under nitrogen overnight The product was isolated with precipitation using hexane and washing the solid with cold hexane and methanol until the washings were colorless, to obtain dimer **87** in quantitative yield (Scheme 9). The complex was characterized by ^{1}H-NMR in d_8-THF where, all the peaks corresponding to the product (**87**) were observed. Formation of the complex was indicated by the presence of two pyridine peaks that were appeared at 6.21 and 2.00 ppm due to the shielding of the RuTPP **86** porphyrin. Even though dissociation of the compound was noticed in a percentage about 70/30 (free porphyrins : **87**). Porphyrin dyad **87** was used as sensitizer for DSSCs. The PCE was measured 1.3 %. Then, porphyrin **87** was attached onto TiO_2 and gave a very similar PCE 1.31 %. In another effort the dyad was attempted to be formed onto TiO_2. Therefore, porphyrin **85** with three carboxylic acids as anchoring groups were attached onto TiO_2 then RuTPP **86** was added and then excess was washed with THF. This system gave a lower PCE 0.76 %, that indicates possibly the dissociation of the chromophores (Table 16).

Table 16. Photovoltaic parameters of DSSCs sensitized by dyads **85-87**

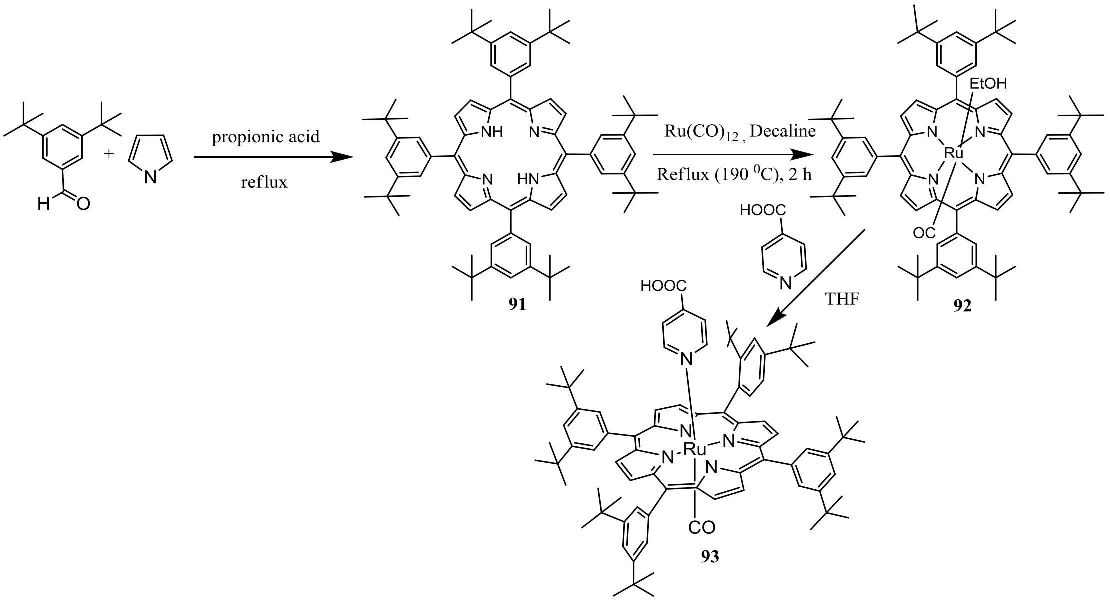
Dye	V_{oc}/mV	J_{sc}/mAcm^{-2}	FF	n/%
85	525	3.41	0.73	1.3
87	534	3.32	0.74	1.31
85 + 86	522	2.0	0.71	0.76

3,5-Di-tert-butylbenzaldehyde was synthesized by reaction of 3,5-di-tert-butyltoluene**,** bromosuccinimide, and benzoyl peroxide in $CC1_4$ at reflux for 4 h to obtain the desired product in 63% yield. Then 3 equivalents of 3,5-di-tert-butylbenzaldehyde**,** 1 eq of 4-formylbenzoate and 4 eq of pyrrole was refluxed in propionic acid for 1.5 h. After column chromatography the porphyrin **88** was obtained in 5 % yield as purple solid.[163] Then the carboxylic acid **89** derivative was obtained by saponification using excess of KOH in THF/MeOH mixture followed by dropwise addition of 2 N HCl until formation of the precipitate.[164] Insertion of ruthenium was achieved by addition of $Ru_3(CO)_{12}$ to porphyrin **89** in refluxing decalin under N_2 atmosphere. The corresponding metal complex **90** was obtained in high yield 95% (Scheme 10).



Scheme 10. Synthesis of compounds **88-90**.

Tetra(3,5-di-*tert*-butylphenyl)-porphyrin **91** was obtained by reaction of the aldehyde with pyrrole in propionic acid at reflux for 2.5 h. The product obtained as purple solid after participation in 15% yield. Insertion of ruthenium was achieved by addition of $Ru_3(CO)_{12}$ to porphyrin **91** in refluxing decalin under N_2 atmosphere. The corresponding metal complexe **92** was obtained in high yield (**Scheme 11**). UV–Vis absorption spectrum of the formed metal-complex is of normal type for five and four coordinated porphyrins. Indicative for the formation of the metal complex is the blue or red shift for the Soret band related to the free base. At the Ru(III) coordinated complex the Soret band is blue shifted related to the free base. Also the appearance of two Q bands for the metal porphyrin instead of four for the free base is characteristic for the metallation. In addition, the absence of negative chemical shift in the ^{1}H NMR spectra due to the hydrogen of pyrrole ring was indicative for the insertion of metal. The carboxylic acid derivative was obtained by saponification using excess of KOH in THF/MeOH mixture followed by dropwise addition of 2 N HCl until formation of the precipitate. In the final step Ru porphyrin **92** and isonicotinic acid was left stirring at reflux under nitrogen overnight. The product was isolated with precipitation using hexane and washing the solid with cold hexane and methanol until the washings were colorless, to obtain dimer **93** in quantitative yield. Studies of the ^{1}H-NMR spectrum showed that the protons of the bound pyridine are shielded by the porphyrin ring-current and resonate at 5.78 and 1.76 ppm.

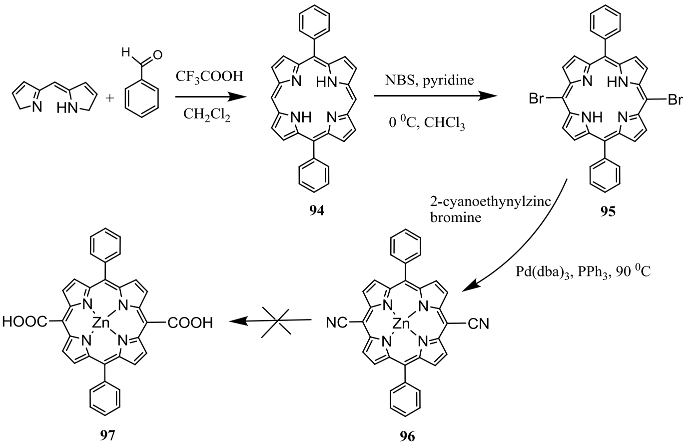


Scheme 11. Synthesis of compounds **91-93**.

2.4 SECTION D: Porphyrin based photosensitizers with long alkyl chains

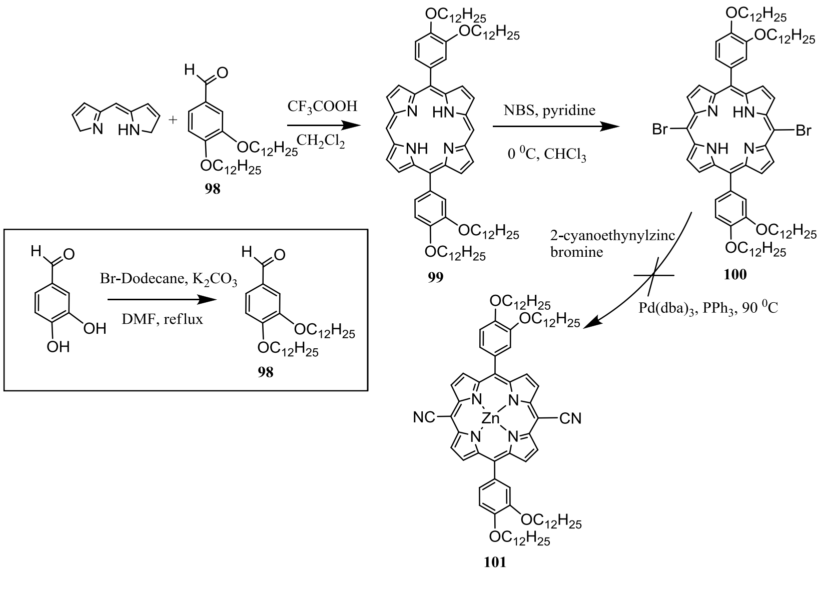
2.4.1 Synthesis of porphyrinic compounds

The aim of this section was the synthesis of porphyrin molecules bearing anchoring groups (carboxylic acids) directly attached on the porphyrin ring. Therefore, 5,15 diphenyl porphyrin **94** was synthesized by reacting dippyromethane with benzaldehyde in the presence of TFA under nitrogen at r.t. for 3 h. Then, DDQ was added after 1h Et_3N was added and the product obtained after filtration through silica gel, in 27% yield. In the next step di-Br porphyrin **95** was obtained by reacting porphyrin **94** with NBS in the presence of pyridine in $CHCl_3$ in 89% yield. This product was reacted with tris(dibenzylideneacetone)dipalladium(0), triphenylphosphine and 2-cyanoethylzinc bromide in dry dioxane under nitrogen. The di-CN porphyrin **96** was obtained as green solid after column chromatography in 94% yield. Attempts to hydrolyze the porphyrin in order to obtain the di acid final porphyrin **97** failed due to solubility problems. In order to overcome this problem we added long alkyl chains on the phenyl ring (Scheme 12).



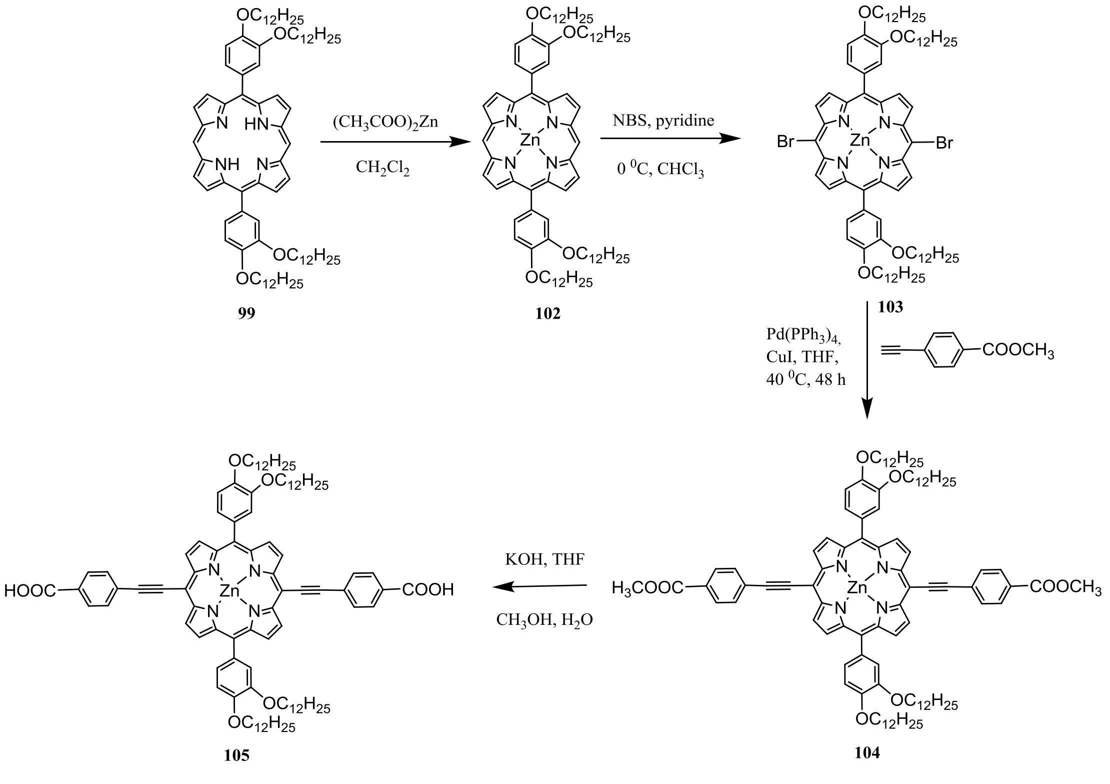
Scheme 12. Synthesis of the cyano-phenyl porphyrin **94-97**.

Aldehyde **98** with long alkyl chain was synthesized by reaction of 3,4 dihydroxy benzaldehyde with bromododecane and K_2CO_3 in the DMF at reflux, overnight. The product was obtained in 76% yield, as white crystals after recrystalization in ethanol. Porphyrin **99** was synthesized by reacting dippyromethane with aldehyde **98** in the presence of TFA under nitrogen at r.t. for 3 h. Then, DDQ was added after 40 min Et_3N was added and the product obtained after filtration through silica gel, in 26% yield. In the next step di-Br porphyrin **100** was obtained by reacting porphyrin **99** with NBS in the presence of pyridine in $CHCl_3$ in 85% yield. All attempts to obtain di-CN porphyrin **101** under standard experimental procedure failed (same as experimental procedure for porphyrin **96**) (Scheme 13).



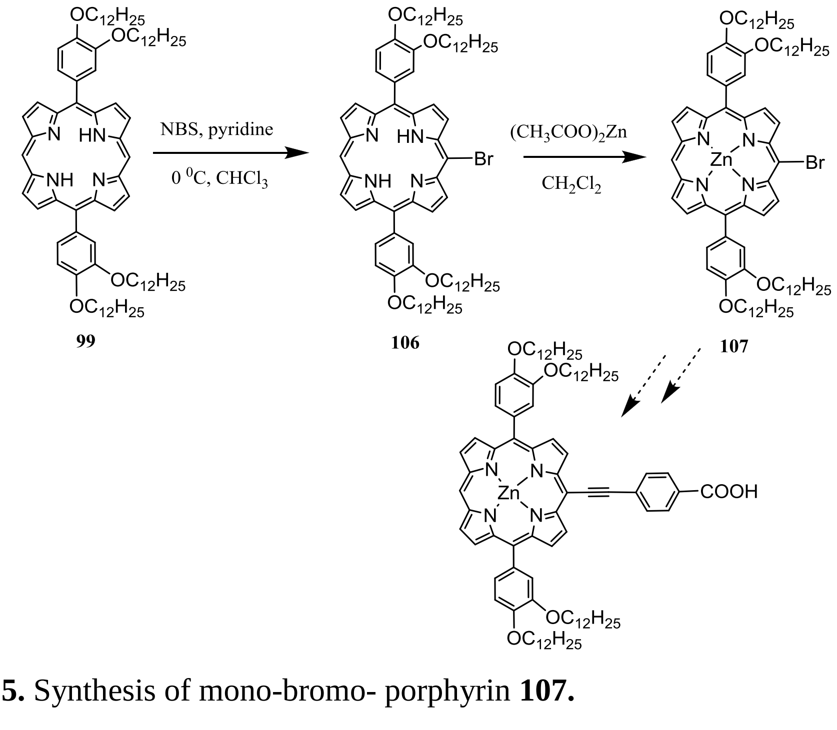
Scheme 13. Synthesis of porphyrins **99-100**.

Since the di-acid porphyrin could not be obtained we changed our synthetic plan and we prepared porphyrin 105, where two carboxylic acids were attached at the meso position of the porphyrin ring via a triple bond (Scheme X). Free base porphyrin 99 was metallated using zinc acetate in dichloromehane stirring at rt overnight. Pure product 102 was obtained after column chromatography in 79% yield. Then bis bromination of the porphyrin gave desired product 103 in 96% yield. Sonogashira coupling was used in order to introduce the ethyne link between the porphyrin and the carboxylic acid anchoring group. Therefore, bis-brominated porphyrin, tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ and copper(I) iodide were dried under vacuum. The system was flushed with nitrogen, then THF and dry triethylamine were added. The solution was degassed by three freeze-thaw cycles. Once it had returned to room temperature, methyl benzoate-ester was added and the mixture stirred at 40 ^{0}C for 24 h. The reaction mixture was cleaned with column chromatography to obtain product 104 in 81% yield. Finally, bis-carboxylic acid porphyrin was obtained by reaction of porphyrin and 2 N KOH, in a THF/MeOH mixture. The acid 105 was precipitated by the slow addition of 1 N HCl in 94% yield (Scheme 14).



Scheme 14. Synthesis of di-acid porphyrin porphyrin **105**.

Mono-brominated porphyrin was obtained by reacting free base porphyrin **99** with 1 equivalent of N-bromosuccinimide at 0 ^{0}C for 1h. The reaction was monitored with TLC and after reaction completion all three compounds were present: starting material, reaction product and bis-bromo porphyrin. Mono brominated compound **106** was separated by column chromatography in 57% yield. Then, metallated porphyrin was prepared by reacting **106** with zinc acetate in dichloromehane stirring at rt overnight. Pure product **107** obtained after column chromatography in 96% yield. In an effort to prepare first the zinc porphyrin and then add the bromide at the meso position gave a mixture of three products with very similar retention factors (Rfs) and it was not possible to separate them by column chromatography. In a future work mono brominated porphyrin will react with methyl benzoate-ester in a Sonogashira coupling reaction. Then, the ester group will be hydrolyzed in order to obtain mono carboxylic acid porphyrin.



Scheme 15. Synthesis of mono-bromo- porphyrin **107.**

CHAPTER III

EXPERIMENTAL PART

3. EXPERIMENTAL PART

3.1 SECTION A: Porphyrin based triads

3.1.1 Materials

$BDPNH_2$ (73) and porphyrins **PH_2 (69), PZn (70), Br_2PZn (71)** were prepared according to the literature.[142, 143] All dry solvents used were dried by the appropriate techniques.[165]

3.1.2 NMR spectra

^1H NMR spectra were recorded on Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers as solutions in deuterated solvents by using the solvent peak as the internal standard.

3.1.3 Mass spectra

High-resolution mass spectra were performed on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer.

3.1.4 X-ray Crystallography

Single crystals for **Ph-PZn-Ph (75)** were obtained by slow evaporation of a THF/pentane mixture (1:1 v/v). The crystals were protected with paratone-N and were mounted for data collection. Intensity data were collected at STOE IPDSII diffractometer using graphite monochromated Mo-Kα radiation (λ=0.71070 Å). The data were collected at 300 K using two ω scans with an increment of 1^o, an exposure time of 2 min for each oscillation and distance of 100 mm. Data reduction including absorption correction and cell dimension post refinement were performed using X-Area software package. The structure was solved using SIR 92[166] program and refined by full matrix least squares on F^2 values for all reflections using (*SHELX-S97).* All non hydrogen atoms were refined with anisotropic displacement parameters using *SHELXL-97.*[167] All the hydrogen atoms were introduced at calculated positions as riding on bonded atoms.

3.1.5 Electrochemistry

Cyclic and square wave voltammetry experiments were carried out at room temperature using an AutoLab PGSTAT20 potentiostat and appropriate routines available in the operating software (GPES version 4.9). All measurements were carried out in freshly distilled and deoxygenated dichloromethane and THF with a solute concentration of ca. 1.0 mM in the presence of tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. A three-electrode cell setup was used with a platinum working electrode, a saturated calomel (SCE) reference electrode, and a platinum wire as counter electrode. All potentials are reported versus the ferrocene/ferrocenium couple (0.44 V versus SCE under the above conditions).

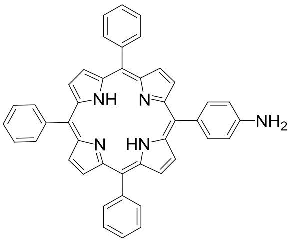
3.1.6 Photophysical Measurements

UV-Vis absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes. The emission spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range 200-850 nm). Quantum yields were determined from corrected emission spectra following the standard methods[168] using meso-tetraphenylporphyrin (TPP) (Φ = 0.11 in toluene[169]) or zinc meso-tetraphenylporphyrin (ZnTPP) (Φ = 0.03 in toluene[169]) as standards. Emission lifetimes were determined by the time-correlated single-photon counting technique using an Edinburgh Instruments mini-tau lifetime spectrophotometer equipped with an EPL 405 pulsed diode laser at 406.0 nm with a pulse width of 71.52 ps and pulse periods of 200 ns and 100 ns and a high-speed red sensitive photomultiplier tube (H5773-04) as detector.

3.1.7 Computational Methods

Theoretical calculations of the trimeric compounds were performed using density functional theory (DFT)[170] on GAUSSIAN 03[171] program. Gas phase geometry optimization of the compounds was carried out employing Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP).[172, 173] 6-31G(d) basis sets was used for lighter atoms and LANL2DZ basis set was used for Zn atom. The geometry optimization of reference compound **Ph-PZn-Ph (75)** was carried out adopting the coordinates from the X-ray structure, while input structure of the **TPPH$_2$-PZn-TPPH$_2$ (72)** and **BDP-PZn-BDP (74)** was modeled on the optimized structure of the **Ph-PZn-Ph (75)** using *ChemCraft* software (version 1.6). The global minimum of the optimized structure was confirmed by observation of no negative frequencies in frequency calculation. Single point calculations of all the compounds were carried out employing the geometry optimized coordinates. TDDFT calculations were performed in THF solvent using polarizable continuum model (PCM) implemented on Gaussian 03.[174] All the computed structures and the orbitals were visualized by *ChemCraft* software (version 1.6).

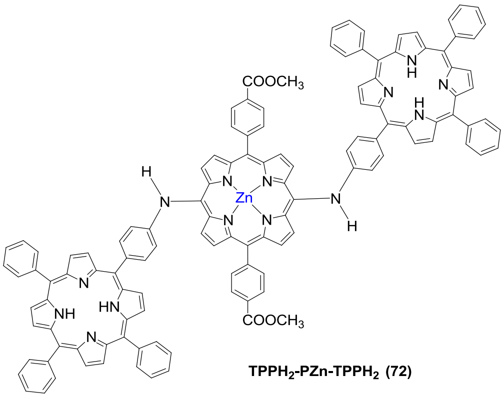
3.1.8 Synthesis of 5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (NH$_2$TPPH$_2$) (68)



NH$_2$TPPH$_2$ (68)

Tetraphenyl porphyrin (2 g, 3.25 mmol) was dissolved in dichloromethane (300 mL). Nitric acid 65 % (4.2 mL, 61.75 mmol) was added with a dropping funnel at 0 °C over a 2 h period. The reaction was monitored by TLC and when it was converted to the desired product the solution was washed 3 x 150 mL with saturated solution of $NaHCO_3$ and then 3 x 150 mL with H_2O and dried using sodium sulfate. The solvent was removed under reduced pressure and the crude product was dissolved in HCl (65 mL), tin chloride (2 g, 10.5 mmol) was added and the solution was refluxed overnight. The mixture was neutralized by addition of aqueous ammonia, and washed with ethyl acetate (5 x 150 mL) dried and solvent was removed. The desired product **68** was isolated by silica column chromatography CH_2Cl_2 to obtain the desired product as a purple solid (1.3 gr, 63 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (d, J = 4.5 Hz, 2 H), 8.86 (s, 6 H), 8.24 (m, 6 H), 8.00 (d, J = 8.5, 2 H), 7.77 (m, 9H), 7.05 (d, J = 8.5, 2 H), 3.99 (s, 2H), -2.71 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2, 142.4, 135.8, 134.7, 132.5,131.2, 127.8, 126.8, 121.0, 120.1, 119.9, 113.6; UV/vis (Toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 422 (258.2), 516 (12.5), 552 (6.8), 594 (3.6), 650 (2.8); HRMS (MALDI-TOF) calcd for $C_{44}H_{32}N_5$ $[M+H]^+$ 630.2658, found 630.2662.

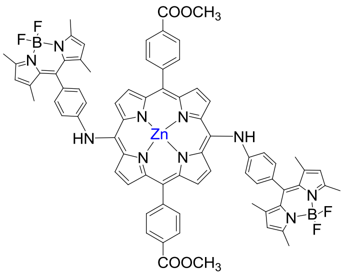
3.1.9 Synthesis of trimer porphyrin $TPPH_2$-PZn-$TPPH_2$ (72)



$TPPH_2$-PZn-$TPPH_2$ (72)

Zn-*meso*-dibromoporphyrin **Br_2PZn** (48 mg, 0.06 mmol), palladium acetate (1.3 mg, 0.006 mmol), bis(2-diphenylphosphinophenyl)ether (DPEphos) (4.8 mg, 0.009 mmol) and cesium carbonate (55 mg, 0.17 mmol) were added in a dry Schlenk tube. Then monoaminophenyl porphyrin **(NH_2TPPH_2)** (181 mg, 0.29 mmol) and dry THF (6 mL) were added. The mixture was refluxed at 68 ^oC under argon for 4 days. The reaction was monitored by TLC. The desired compound was isolated by silica column chromatography THF:Hex (3/7) to obtain **$TPPH_2$-PZn-$TPPH_2$** (**72**) as a purple solid (71 mg, 63 %). ^1H-NMR (300 MHz, d_8-THF): δ 9.77 (d, J = 4.5 Hz, 4H), 9.04 (d, 2H), 8.89 (d, J = 4.8 Hz, 4H), 8.79 (m, 16H), 8.48 (d, J = 8.1 Hz, 4H), 8.40 (d, J = 8.1 Hz, 4H), 8.19 (m, 12H), 7.97 (d, J = 8.4 Hz, 4H), 7.75 (m, 18H), 7.30 (d, J = 8.4 Hz, 4H), 4.10 (s, 6H), -2.67 (s, 4H); ^{13}C NMR (75 MHz, d_8-THF): δ 167.5, 155.0, 152.6, 150.5, 149.3, 146.5, 143.6, 143.5, 136.7, 136.4, 135.5, 133.1, 132.6, 131.8, 130.9, 130.5, 129.6, 128.7, 127.7, 126.1, 122.5, 121.2, 120.9, 120.3, 113.6, 52.5; UV/vis (Toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 420 (571.6), 445 sh (213.6) 516 (17.2), 556 (15.0), 595 (8.7), 650 (6.6); HRMS (MALDI-TOF) calcd for $C_{124}H_{83}N_{14}O_4Zn$ $[M+H]^+$ 1895.6013, found 1895.6009.

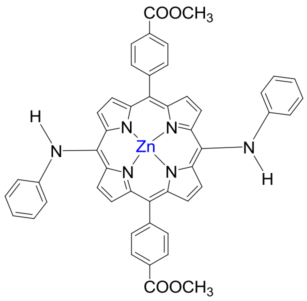
3.1.10 Synthesis of porphyrin BDP-PZn-BDP (74)



BDP-PZn-BDP

Zn-*meso*-dibromoporphyrin **Br$_2$PZn** (**71**) (32 mg, 0.04 mmol), palladium acetate (0.9 mg, 0.004 mmol), bis(2-diphenylphosphinophenyl)ether (DPEphos) (3.2 mg, 0.006 mmol) and cesium carbonate (36 mg, 0.11 mmol) were added in a dry Schlenk tube. Then **BDPNH$_2$ (73)** (65 mg, 0.19 mmol) and dry THF (5 mL) were added. The mixture was refluxed at 68 ^{o}C under argon for 20 h. The reaction was monitored by TLC. The desired compound was isolated by column chromatography THF:Hex (3/7) to obtain **BDP-PZn-BDP** (**74**) as a purple solid (49 mg, 93 %). ^{1}H NMR (500 MHz, d_8-THF): δ 9.54 (s, 2H), 9.40 (d, *J* = 4.5 Hz, 4H), 8.71 (d, *J* = 4.5 Hz, 4H), 8.41 (d, *J* = 8.0 Hz, 4H), 8.28 (d, *J* = 8.0 Hz, 4H), 7.01 (m, 8H), 6.00 (s, 4H), 4.06 (s, 6H), 2.45 (s, 12H), 1.69 (s, 12H); ^{13}C NMR (75 MHz, d_8-THF): δ 167.4, 155.9, 155.5, 152.1, 150.3, 148.9, 144.2, 143.6, 135.4, 133.0, 132.3, 130.5, 130.0, 129.8, 128.4, 124.7, 121.5, 120.3, 119.7, 115.6, 52.4, 15.0, 14.6; UV/vis (Toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 445 (119.8), 503 (113.9), 561 (11.0), 614 (8.1); HRMS (MALDI-TOF) calcd for $C_{74}H_{60}B_2F_4N_{10}O_4Zn$ [M]$^+$ 1314.4213, found 1314.4217.

3.1.11 Synthesis of porphyrin Ph-PZn-Ph (75)



Ph-PZn-Ph (75)

Zn-*meso*-dibromoporphyrin **Br$_2$PZn** (**71**) (32 mg, 0.04 mmol), palladium acetate (0.9 mg, 0.004 mmol), bis(2-diphenylphosphinophenyl)ether (DPEphos) (3.2 mg, 0.006 mmol) and cesium carbonate (36 mg, 0.11 mmol) were added in a dry Schlenk tube. Then aniline (18 μl, 0.19 mmol) and dry THF (5 ml) were added. The mixture was refluxed at 68 ^{o}C under argon for 15 h. The reaction was monitored by TLC. The desired compound was isolated by column chromatography THF:Hex (2/8) to obtain **Ph-PZn-Ph** (**75**) as a purple solid (30 mg, 91 %). ^{1}H NMR (500 MHz, d_8-THF): δ 9.39 (d, *J* = 4.5 Hz, 4 H), 9.19 (s, 2 H), 8.67 (d, *J* = 4.5 Hz, 4H), 8.39 (d, *J* = 7.5 Hz, 4H), 8.27 (d, *J* = 7.5 Hz, 4 H), 7.04 (m, 4 H), 6.84 (d, *J* = 7.5, 4 H), 6.65 (m, 2 H), 4.04 (s, 6 H); ^{13}C NMR (75 MHz, d_8-THF): δ 167.5, 155.2, 152.4, 150.2, 149.3, 135.6, 132.1, 130.5, 130.3, 129.8, 128.5, 120.5, 120.2, 118.6, 115.3, 52.5; UV/vis

(Toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 444 (138.9), 561 (12.5), 614 (8.5); HRMS (MALDI-TOF) calcd for $C_{48}H_{34}N_6O_4Zn$ $[M]^+$ 822.1933, found 822.1929.

3.2 SECTION B: Porphyrin based dyads

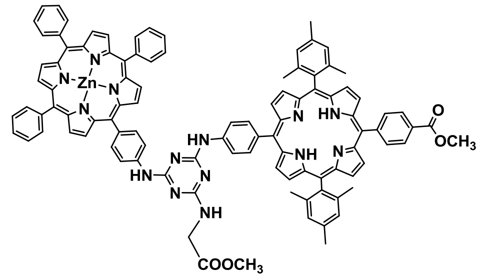
3.2.1 Photophysical measurements

UV-vis absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes. Emission spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red sensitive WRE-343 photomultiplier tube (wavelength range: 200-850 nm).

3.2.2 Electrochemistry measurements

Cyclic and square wave voltammetry experiments were carried out at room temperature using an AutoLab PGSTAT20 potentiostat and appropriate routines available in the operating software (GPES, version 4.9). Measurements were carried out in freshly distilled and deoxygenated THF, with scan rate 100 mV.s^{-1}, with a solute concentration of 1.0 mM in the presence of tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. A three-electrode cell setup was used with a platinum working electrode, a saturated calomel (SCE) reference electrode, and a platinum wire as counter electrode. The system was calibrated by ferrocene.

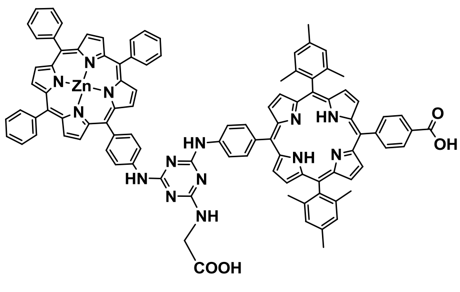
3.2.3 Synthesis of dyad (ZnP)-[triazine-gly]-($H_2PCOOCH_3$) (80)



80

To a THF solution (1 mL) of cyanuric chloride (0.0096 g, 0.052 mmol) and DIPEA (11 µL, 0.062 mmol) a THF solution (1 mL) of porphyrin H_2[Porph] (0.040 g, 0.052 mmol) was added, under Ar at 0 °C. The mixture was stirred at 0 °C for 15 min, and upon reaction completion (monitored by TLC), it was left to warm at room temperature. Next, a THF solution (2 mL) of Zn[TPPNH$_2$] (0.072 g, 0.104 mmol) and DIPEA (22 μL, 0.124 mmol) was added and the mixture was stirred at room temperature overnight. An excess of glycine methylester (0.065 g, 0.52 mmol) and DIPEA (180 μL, 1.04 mmol) were added and the mixture was stirred at 65 ^{o}C for 24h. The volatiles were removed under reduced pressure and after dilution in CH_2Cl_2; the residue was purified by column chromatography (silica gel, CH_2Cl_2/ethanol 5%). The product **80** was isolated as a purple solid. Yield: 0.052 g (61.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.04 (*s br*, 2H), 8.93 (*s br*, 8H), 8.71 (*m*, 6H), 8.39 (*m*, 2H), 8.30 (*m*, 2H), 8.19 (*s br*, 9H), 8.00 (*d*, *J* = 8.1 Hz, 4H), 7.93 (*d*, *J* = 7.5 Hz, 1H), 7.72 (*m*, 9H), 7.52 (*m*, 1H), 7.20 (*m*, 5H), 4.08 (*s*, 3H), 3.75 (*s*, 3H), 2.58 (*s*, 6H), 1.78 (*s*, 12H), -2.62 (*s*, 2H). UV-vis (CH_2Cl_2), λ, nm: 421, 515, 550, 591, 648. HRMS (MALDI-TOF): *m/z* calcd for $C_{102}H_{79}N_{14}O_4Zn$, 1627.5622 [M+H]$^+$: found 1627.5637.

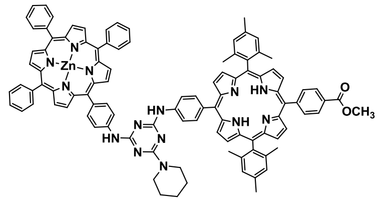
3.2.4 Ester hydrolysis, synthesis of compound P-tg-P′ (82)



82 (P-tg-P')

To a THF solution (22 mL) of **80** (0.030 g, 0.018 mmol), 6 mL MeOH, 7.5 mL H_2O and KOH (0.450 g, 0.008 mol) were added. After stirring the reaction mixture at room temperature overnight, the organic solvents were removed under reduced pressure and then a solution of HCl (0.5M) was added dropwise, until pH~6. The precipitate was filtered, washed with water, extracted with CH_2Cl_2 and purified by column chromatography (silica gel, CH_2Cl_2/EtOH 10%). The product **P-tg-P′** (**82**) was isolated as a purple solid. Yield: 0.025 g (89%). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 9.80 (*s br*, 2H), 8.97 (*s br*, 5H), 8.78 (*s br*, 7H), 8.65 (*s br*, 4H), 8.42 (*s br*, 4H), 8.32 (*s br*, 2H), 8.22 (*s br*, 8H), 7.83 (*s br*, 7H), 7.32 (*s br*, 6H), 6.91 (*m*, 1H), 6.62 (*s*, 1H), 4.00 (*s*, 2H), 3.40 (*s*, 6H), 1.25 (*s*, 12H), -2.68 (*s*, 2H); ^{13}C NMR (125 MHz, DMSO-d$_6$): δ (ppm) 171.8, 168.2, 165.7, 164.5, 149.7, 149.2, 145.7, 142.8, 138.4, 137.7, 134.5, 134.2, 131.5, 130.2, 129.0, 128.7, 127.8, 127.4, 126.6, 120.2, 120.1, 117.7, 62.6, 52.0, 34.0, 29.2, 22.1, 21.1; UV-vis (DMSO), λ, nm ($\varepsilon \times 10^{-3}$, $M^{-1}.cm^{-1}$): 429 (527.7), 517 (14.1), 560 (19.5), 601 (11.8), 647 (4.6). HRMS (MALDI-TOF): *m/z* calcd. for $C_{100}H_{75}N_{14}O_4Zn$: 1599.5309 $[M+H]^+$, found 1599.5291.

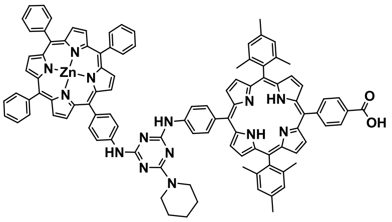
3.2.5 Synthesis of dyad (ZnP)-[triazine-*N*pip]-(H_2PCOOH) (81)



81

To a THF solution (1 mL) of cyanuric chloride (0.0096 g, 0.052 mmol) and DIPEA (11 μL, 0.062 mmol) a THF solution (1 mL) of porphyrin H_2[Porph] (0.040 g, 0.052 mmol) was added, under Ar at 0 ^oC. The mixture was stirred at 0 ^oC for 15 min, and upon reaction completion (monitored by TLC), it was left to warm at room temperature. Next, a THF solution (2 mL) of Zn[TPPNH_2] (0.072 g, 0.104 mmol) and DIPEA (22 μL, 0.124 mmol) was added and the mixture was stirred at room temperature overnight. An excess of piperidine (78 μl, 0.52 mmol) and DIPEA (180 μL, 1.04 mmol) were added and the mixture was stirred at 65 ^oC for 24h. The volatiles were removed under reduced pressure and after dilution in CH_2Cl_2, the residue was purified by column chromatography (silica gel, CH_2Cl_2/ethanol 2%). The product **81** was isolated as a purple solid. Yield: 0.055 g (65%). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.11 (*d*, *J* = 4.8 Hz, 2H), 8.97 (*t*, *J* = 4.8Hz, 7H), 8.74 (*m*, 7H), 8.41 (*m*, 3H), 8.34 (*m*, 3H), 8.24 (*m*, 9H), 8.04 (*d*, *J* = 8.1Hz, 4H), 7.76 (*m*, 8H), 7.30 (*s*, 4H), 4.08 (*s*, 3H), 3.94 (*s br*, 5H), 2.62 (*s*, 6H), 1.84 (*s*, 12H), -2.57 (*s*, 2H). HRMS (MALDI-TOF): *m/z* calcd for $C_{104}H_{83}N_{14}O_2Zn$: 1623.6037 $[M+H]^+$, found 1623.6055. UV-vis (CH_2Cl_2), λ, nm: 421, 515, 551, 590, 648.

3.2.6 Ester hydrolysis, synthesis of compound P-t*N*p-P′ (83)

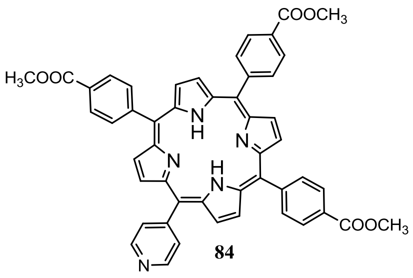


83 (P-t*N*p-P′)

To a THF solution (22 mL) of **81** (0.030 g, 0.018 mmol), 6 mL MeOH, 7.5 mL H_2O and KOH (0.450 g, 0.008 mol) were added. After stirring the reaction mixture at room temperature overnight, the organic solvents were removed under reduced pressure and then a solution of HCl (0.5M) was added dropwise, until pH~6. The precipitate was filtered, washed with water, extracted with CH_2Cl_2 and purified by column chromatography (silica gel, CH_2Cl_2/EtOH 5%). The product **P-t*N*p-P′ (83)** was isolated as a purple solid. Yield: 0.025 g (86%). ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) 8.98 (*d*, *J* = 4.5 Hz, 2H), 8.94 (*d*, *J* = 4.2 Hz, 2H), 8.83 (*s br*, 6H), 8.76 (*s br*, 2H), 8.66 (*s br*, 4H), 8.43 (*d*, *J* = 8.1 Hz, 2H), 8.29 (*m*, 6H), 8.16 (*m*, 7H), 7.72 (*m*, 6H), 7.30 (*m*, 6H), 6.92 (*s*, 5H), 6.59 (*s*, 1H), 5.88 (*s*, 2H), 2.59 (*s br*, 10H), 2.21 (*s*, 6H), 1.73 (*s*, 12H), -2.49 (*s*, 2H); ^{13}C NMR (75 MHz, THF-d_8): δ (ppm) 168.2, 166.4, 151.8, 151.2, 147.7, 146.7, 144.9, 140.3, 139.8, 139.0, 138.5, 136.0, 135.7, 132.8, 132.4, 129.2, 128.9, 128.3, 127.4, 126.2, 121.6, 119.2, 118.9, 118.8, 118.4, 31.1, 30.1, 22.0. UV-vis (THF), λ, nm ($\varepsilon \times 10^{-3}$, $M^{-1}.cm^{-1}$): 424 (514.6), 515 (16.2), 555 (18.8), 596 (9.3), 649 (3.8). HRMS (MALDI-TOF): *m/z* calcd for $C_{103}H_{81}N_{14}O_2Zn$ 1609.5880 $[M+H]^+$, found 1609.5910.

3.3 SECTION C: Metal-ligand porphyrin based dyads

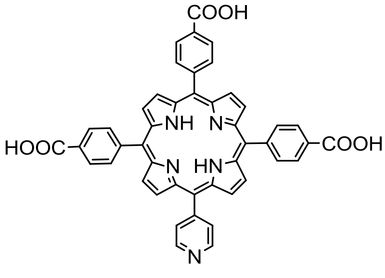
3.3.1 Synthesis of 5,10,15-tris(4’-carboxymethylphenyl)-20-(4’-pyridyl) porphyrin (84)



84

A mixture of methyl-4-formyl benzoate (13 mmol) and pyridine-4-carbaldehyde (7 mmol) was dissolved in hot propionic acid. Pyrrole (17 mmol) was added dropwise and the mixture was refluxed for 2 h. Removal of the propionic acid was followed by repeat washing of the crude mixture with water. The solid was chromatographed on dry SiO_2. Elution of the product **84** was achieved by a mixture of CH_2Cl_2/EtOH (100 : 0.5 v/v, yield 36%). ^{1}HNMR (500 MHz, $CDCl_3$): d 9.05 (d, *J* = 5.7 Hz, 2H), 8.84 (m, 8H), 8.46 (m, 6H), 8.3 (m, 6H), 8.17 (d, *J* = 5.7, 2H), 4.14 (s, 9H), -2.83 (s, 2H). UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 421 (256.4), 517 (12.8), 551 (6.4), 595 (3.8), 651 (2.3). HRMS (MALDI-TOF): m/z calcd for $C_{49}H_{35}N_5O_6+H^+$: 790.2666 $[M + H]^+$. Found: 790.2672.

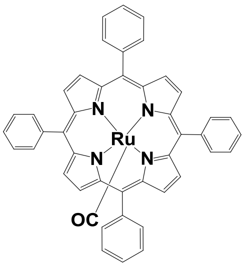
3.3.2 Synthesis of 5,10,15-tris(4’-carboxyphenyl)-20-(4’-pyridyl) porphyrin (85)



85

To a solution of methylester porphyrin **84** (0.0752 mmol) in THF/MeOH (10:6 v/v), aqueous 0.5 M KOH (80 mL) was added and stirred at room temperature for 24 h. The course of the reaction was monitored by TLC (CH_2Cl_2/MeOH 9:1 v/v). The solution was evaporated to dryness to afford the potassium salt as orange solid. The solid was dissolved in distilled water (100 mL), aqueous 2 N HCl was added dropwise until pH reached 3 and a precipitate was formed. It was filtered, washed several times with distilled water to afford a purple solid **85** (yield 93%). ^{1}HNMR (500 MHz, $CDCl_3$): d 9.08 (d, *J* = 5.6 Hz, 2H), 8.81 (m, 8H), 8.6 (m, 6H), 8.41 (m, 6H), 8.19 (d, *J* = 5.6, 2H), -2.81 (s, 2H). UV/vis (THF) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 420 (256.9), 516 (12.2), 552 (6.8), 596 (3.3), 653 (2.7). HRMS (MALDI-TOF):m/z calcd for $C_{46}H_{29N5}O_6+H^+$: 748.2196 $[M + H]^+$. Found: 748.2187.

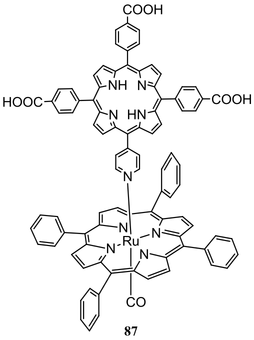
3.3.3 Synthesis of Ru-TPP porphyrin (86)



86

A mixture of TPP porphyrin (100 mg, 0.163 mmol), $Ru_3(CO)_{12}$ (150 mg, 0.235 mmol) and decalin (50 mL) was refluxed for 2 h under nitrogen atmosphere. The mixture was reduced to dryness under vacuum and the crude solid was dissolved in CH_2Cl_2 (40 mL). After washing with aqueous NaCl (2x 30 mL) the organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/ EtOH, 100:0.3 v/v) to obtain **86** as a dark red solid (115 mg, 95%).[175]

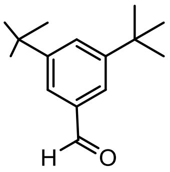
3.3.4 Dimer RuTPP and 5,10,15-tris(4’-carboxyphenyl)-20-(4’-pyridyl) porphyrin (87)



87

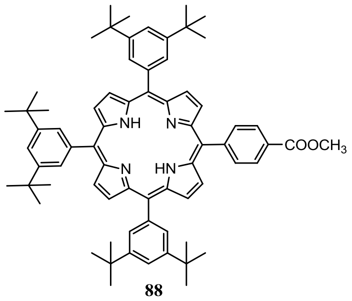
RuTPP **86** and porphyrin **85** was left stirring at reflux under nitrogen overnight The product was isolated with precipitation using hexane and washing the solid with cold hexane and methanol until the washings were colorless, to obtain dimer **87** in quantitative yield. When dissolved in d_8-THF the complex was present in 75% yield and the two monomers in 25% yield. ^{1}HNMR (500 MHz, d_8-THF): 9.00 (brs, 0,5 H), 8.87 (brs, 2 H), 8.71 (s, 12 H), 8.64 (s, 4 H), 8.45 (m, 3.5 H), 8.37 (m, 6 H), 8.32 (m, 5.5 H), 8.23 (m, 9 H), 8.12 (brd, 4 H), 8.07 (brd, 1 H), 7.74 (m, 16 H), 7.38 (brs, 2 H), 6.21 (d, 2 H), 2.08 (d, 2 H), -2.73 (s, 0.5 H), -3.18 (s, 2 H). UV/vis (THF) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 411, 520, 590, 645. HRMS (MALDI-TOF):m/z calcd for $C_{91}H_{58}N_9O_7Ru+H^+$: 1491.3581 $[M + H]^+$. Found: 1491.3586.

3.3.5 3,5-Di-tert-butylbenzaldehyde



A solution of 228 g of 3,5-di-tert-butyltoluene**,** 300 g of bromosuccinimide, and 1 g of benzoyl peroxide in 600 ml of $CC1_4$, was heated at reflux for 4 hr. After filtration the $CC1_4$, was removed on a rotary evaporator and the residue was added to a solution of 430 g of hexamethylenetetramine in 300 ml of water and 300 ml of ethanol. This solution was refluxed for 4 h, 200 ml of concentrated HC1 was added, and refluxing was continued for 30 min. The organic product was isolated to yield 153 g (63%). [176]

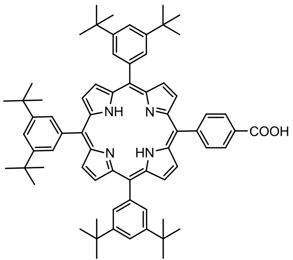
3.3.6 Synthesis of 5-(4-Methoxycarbonylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)- porphyrin (88)



88

Pyrrole (10.2 mL, 0.147 mol, 3.9 equiv.) was added dropwise at 130 °C to a solution of methyl 4-formylbenzoate (6.23 g, 0.038 mol, 1equiv.) and 3,5-di-*tert*-butylbenzaldehyde (24.11 g, 0.110 mol, 3.1 equiv.) in propionic acid (640 mL). The reaction mixture was refluxed for 1.5 h. The propionic acid was then evaporated off and the resulting precipitate was purified by chromatography on silica gel (CH_2Cl_2/Hex 6:4) affording the methoxyporphyrin **88** (1.57 g, 5%) as a purple solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 6H, H_β), 8.78 (d, *J* = 5Hz, 2H, H_β), 8.43 (d, *J* = 8 Hz, 2H, Ar), 8.32 (d, *J* = 8 Hz, 2H, Ar), 8.09 (d, *J* = 2Hz, 4H, Ar), 8.08 (d, *J* = 2 Hz, 2H, Ar), 7.80 (t, *J* = 2 Hz, 3H, Ar), 4.12 (s, 3H, -$COOCH_3$), 1.53 (s, 54H, t-Bu), -2.69 (s, 2H, NH). HRMS (MALDI-TOF):m/z calcd for $C_{70}H_{80}N_4O_2+H^+$: 1009.6360 $[M + H]^+$. Found: 1009.6367.[163]

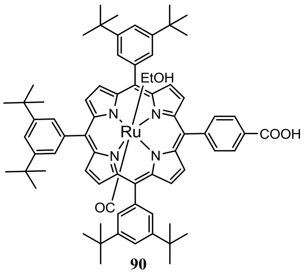
3.3.7 Synthesis of 5-(4-Carboxylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)-porphyrin (89)



89

To a solution of porphyrin **88** (0.0752 mmol) in THF/MeOH (10:6 v/v), aqueous 0.5 M KOH (73 mL) was added and stirred at room temperature for 24 h. The course of the reaction was monitored by TLC (CH_2Cl_2/MeOH 9:1 v/v). The solution was evaporated to dryness to afford the potassium salt as orange solid. The solid was dissolved in distilled water (100 mL), aqueous 2 N HCl was added dropwise until pH reached 3 and a precipitate was formed. It was filtered, washed several times with distilled water to afford a purple solid **89** (yield 95%). HRMS (MALDI-TOF): m/z calcd for $C_{69}H_{78}N_4O_2$+H^+: 995.6203 [M + H]$^+$. Found: 995.6210.[164]

3.3.8 Synthesis of Ruthenium-5-(4-Carboxylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)- porphyrin (90)

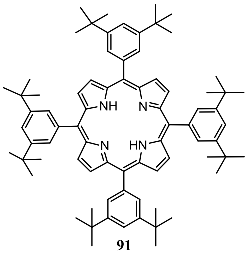


90

A mixture of porphyrin **89** (150 mg, 0.132 mmol), $Ru_3(CO)_{12}$ (150 mg, 0.235 mmol) and decalin (50 mL) was refluxed for 2 h under nitrogen atmosphere. The mixture was reduced to dryness under vacuum and the crude solid was dissolved in CH_2Cl_2 (40 mL). After washing with aqueous NaCl (2x 30 mL) the organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/ EtOH, 100:0.3 v/v) to obtain **90** as a dark red solid (158 mg, 95%). ^{1}HNMR (500 MHz, $CDCl_3$): 8.92 (s, 6 H), 8.81 (d, *J* = 4.8, 2 H), 8.53 (brd, 2 H), 8.38 (brd, 2 H), 8.08 (m, 6 H), 7.80 (brs, 3 H), 1.53 (s, 56 H, H_{tert-}

$_{butyl}$).UV/vis (CH2Cl2) λ_{max}, nm 415, 531, 565. HRMS (MALDI-TOF): m/z calcd for $C_{70}H_{77}N_4O_3Ru+H^+$: 1124.5117 $[M + H]^+$. Found: 1124.5122.

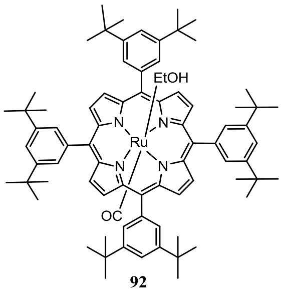
3.3.9 Synthesis of 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)-porphyrin (91)



91

In a two neck round-bottomed flask aldehyde and propionic acid were stirred for 10 min. Then pyrrole was added and the mixture was refluxed at 141 ^{0}C for 2.5 h. Then the solution left come to room temperature, methanol was added and the flask was put in an ice-bath. Purple solid was participated and filtered. The solid was washed with methanol and the product **91** obtained in 15% yield (190 mg). UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 421, 518, 554, 593, 648; HRMS (MALDI-TOF): m/z calcd for $C_{76}H_{94}N_4+H^+$: 1063.7557 $[M + H]^+$. Found: 1063.7562.[177]

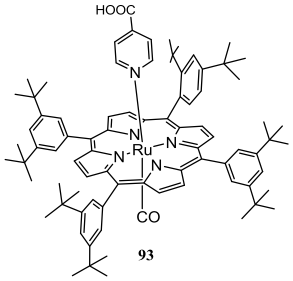
3.3.10 Synthesis of Ruthenium - 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)-porphyrin (92)



92

A mixture of porphyrin **91** (150 mg, 0.132 mmol), $Ru_3(CO)_{12}$ (150 mg, 0.235 mmol) and decalin (50 mL) was refluxed for 2 h under nitrogen atmosphere. The mixture was reduced to dryness under vacuum and the crude solid was dissolved in CH_2Cl_2 (40 mL). After washing with aqueous NaCl (2x 30 mL) the organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/ EtOH, 100:0.5 v/v) to obtain **92** as a dark red solid (160 mg, 95%). ^{1}HNMR (500 MHz, $CDCl_3$): 8.75 (s, 8 H, H_{pyr}), 8.04 (d, *J* = 14.0, 8 H, H_{ortho}), 7.75 (s, 4 H, H_{para}), 1.52 (s, 72 H, $H_{tert\text{-}butyl}$). UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 415, 531, 565. HRMS (MALDI-TOF): m/z calcd for $C_{77}H_{93}N_4ORu+H^+$: 1192.6471 $[M + H]^+$. Found: 1192.6476.

3.3.11 Synthesis of dimer of isonicotinic acid and Ru - 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)-porphyrin (93)

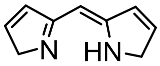


93

Ru porphyrin **92** and isonicotinic acid was left stirring at reflux under nitrogen overnight The product was isolated with precipitation using hexane and washing the solid with cold hexane and methanol until the washings were colorless, to obtain dimer **93** in quantitative yield. ^{1}HNMR (500 MHz, $CDCl_3$): 8.65 (s, 8 H, H_{pyr}), 8.02 (s, 4 H, H_{aryl}), 7.88 (s, 4 H, H_{aryl}), 7.72 (s, 4 H, H_{aryl}), 5.78 (brs, 2 H, H_{pyrid}), 1.76 (brs, 2 H, H_{pyrid}), 1.48 (m, 72 H, $H_{tert\text{-}butyl}$). HRMS (MALDI-TOF): m/z calcd for $C_{83}H_{98}N_5O_3Ru+H^+$: 1315.6791 $[M + H]^+$. Found: 1315.6796. λ_{max}, nm (*ε*, mM^{-1} cm^{-1}) 415 (525.0), 532 (425.2)

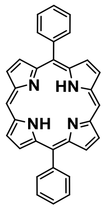
3.4 SECTION D: Porphyrin based photosensitizers with long alkyl chains

3.4.1 Synthesis of dippyromethane



A mixture of paraformaldehyde (0.75 gr, 25 mmol) and pyrrole (175 ml, 2,5 mol) was degassed with a steam of nitrogen for 10 min at room temperature. The mixture was heated at 55 °C for about 10 min under nitrogen to obtain a clear solution. MgBr2 (2.3 gr, 12.5 mmol) was then added and the misture was stirred at 55 °C for 2 h. The heat source was removed and NaOH (5 gr, 0.125 mmol) was added. The mixture was stirred for 1 h and then filtered. Then it was stored on the freezer overnight. The color of the filtrate was pale yellow. The filtrate was concentrated and the pyrrole was removed with distillation under vacuum at 60 °C. The product was purified with column chromatography using solvents Hex/CH_2Cl_2/EtOAc (7:2:1), to obtain white crystals (1.54 gr, 42 %).[35]

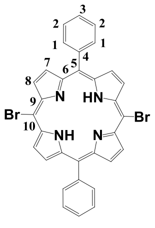
3.4.2 Synthesis of meso 5,15 di-phenyl porphyrin (94)



94

In a two-neck round-bottomed flask dichloromethane (300 ml), benzaldehyde (0.28 ml, 2.7 mmol) and dippyromethane (400 mg, 2.7 mmol) were bubbled with nitrogen for 10 min. Then trifluoroacetic acid (130 μl, 1.7 mmol) was added and left stirring for 3 h, after which time 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (850 mg, 3.7 mmol) was added and left stirring 1 h. Subsequently, triethylamine (1.0 ml) was added and the reaction mixture was filtrated directly through silica, the solvent was removed under reduced pressure to obtain a purple solid **94** (340 mg, 27 %). ^{1}H NMR and ^{13}C NMR (75 MHz, $CDCl_3$) not obtained due to solubility problems; UV/vis ($CHCl_3$) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 405 (412.0), 500 (18.1), 535 (5.1), 574 (5.72), 629 (1.4) ; HRMS M$^+$ calcd for $C_{32}H_{22}N_4$: 462.1844, found: 462.1847 . Anal. Calcd for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11. Found: C, 82.84; H, 4.53; N, 12.02.

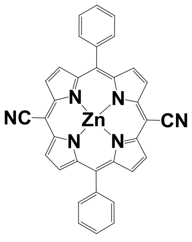
3.4.3 Synthesis of meso 5,15 di-bromo 10,20 di-phenyl porphyrin (95)



95

5,15 di-phenyl porphyrin **94** (100 mg, 0.22 mmol) is dissolved in chloroform (50 ml) and cooled to 0 ^{o}C. Pyridine (200 μl) as an acid scavenger and N-bromosuccionimide (80 mg, 0.44 mmol) were added and the reaction was followed by TLC CH_2Cl_2/Hex (1:1). After 1 h the reaction reached to completion and quenched with 4 ml acetone. The solvent was removed and the solid washed several times methanol, dried and a purple solid was obtained **95** (122 mg, 89 %), ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.62 (d, J = 4.8 Hz, 4 H, H_7,H_8), 8.84 (d, J = 4.8 Hz, 4 H, H_7,H_8), 8.16 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 4 H, H_1), 7.79 (m, 6 H, H_2, H_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 141.5, 134.6, 133.1, 132.4, 128.2, 126.9, 121.6, 103.9; UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 425 (95.1), 523 (7.2), 561 (5.6), 604 (2.7), 660 (2.8). HRMS (MALDI-TOF) calcd for $C_{32}H_{20}Br_2N_4$ $[M + H]^+$ 619.0133, found 619.0139.

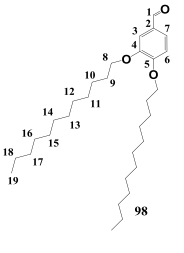
3.4.4 Synthesis of meso 5,15 di-cyanol 10,20 di-phenyl porphyrin (96)



96

In an oven-dried schlenk flask meso 5,15 di-bromo 10,20 di-phenyl porphyrin **95** (31 mg, 0.05 mmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 0.005 mmol) and triphenylphosphine (2.6 mg, 0.01 mmol) were added. The flask was evacuated and flashed with nitrogen. Then dry dioxane and 2-cyanoethylzinc bromide (1 ml, 0.5 mmol) were added. The mixture was heated at 90 ^oC for 1 h and cooled down to room temperature. After that time CH_2Cl_2 (10 ml) was added and the mixture washed two time with aqueous NH_4Cl and two times with brine, died with sodium sulfate, filtrated and solvent removed. After column chromatography Hex/THF (15:1) the product obtained as a green solid **96** (27 mg, 94 %)**.**^1H NMR and ^{13}C NMR (75 MHz, $CDCl_3$) not obtained due to solubility problems. HRMS (MALDI-TOF) calcd for $C_{34}H_{18}N_6Zn$ $[M + H]^+$ 575.0963, found 575.0958.

3.4.5 Synthesis of 3,4-bis(dodecyloxy)benzaldehyde (98)

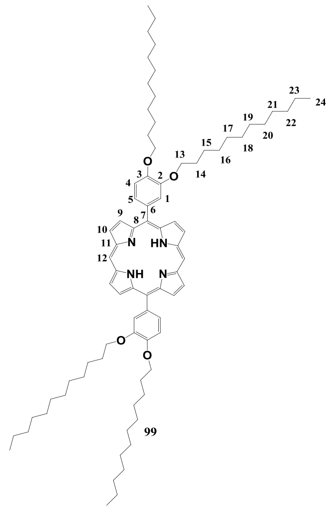


98

In a 100 ml two-neck round bottomed flask 3,4-dihydroxybenzaldehyde (250 mg, 1.8 mmol) was dissolved in 2 ml DMF. Then potassium carbonate (1 gr, 7.2 mmol) was added flashed with nitrogen and stirred for at room temperature. After 5 min 1-bromododecane (1 ml, 7.2 mmol) was added and the mixture left stirring overnight. The crude product was washed three times with NaOH (1 M) and 3 x H_2O, dried over sodium sulfate, filtrated. Solvent was removed and a white-brown was formed that was recrystalized with ethanol in order to obtain a white solid **98** (650 mg, 76 %). ^1H

NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1 H, $H_{1,}$), 7.41 (m, 2 H, H_7, H_3), 6.95 (d, J = 8.1 Hz, 1 H, H_6), 4.06 (m, 4 H, H_8), 1.85 (m, 4 H, H_9), 1.49-1.45 (m, 36 H, H_{10}-H_{18}), 0.87 (t, J_1 = 6.3 Hz, J_2 = 6.9 Hz, 6 H, H_{19}); ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.2, 154.8, 149.5, 129.9, 126.8, 111.8, 110.9, 69.2, 32.1, 29.8, 29.7, 29.5, 29.2, 29.1, 26.1, 22.8, 14.3. HRMS (MALDI-TOF) calcd for $C_{31}H_{54}O_3$ $[M + H]^+$ 475.4151, found 475.4156.

3.4.6 Synthesis of meso 5,15 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (99)

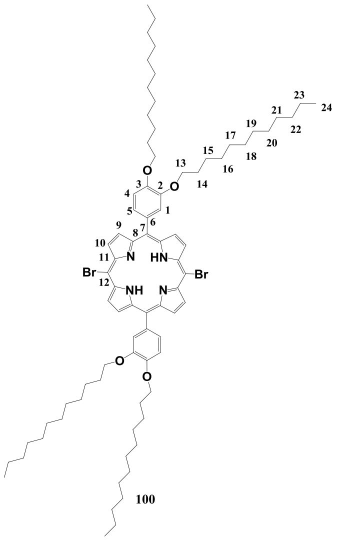


99

In a two-neck round-bottomed flask dichloromethane (130 ml), 3,4-bis(dodecyloxy)benzaldehyde (525 mg, 1.1 mmol) and dippyromethane (162 mg, 1.1 mmol) were bubbled with nitrogen for 10 min. Then trifluoroacetic acid (53 μl, 0.7 mmol) was added and left stirring for 3 h, after which time 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (340 mg, 1.5 mmol) was added and left stirring for 40 min. Subsequently, triethylamine (0.6 ml) was added and the reaction mixture was filtrated directly through silica, the solvent was removed under reduced pressure to obtain a purple solid **99** (350 mg, 26 %). ^1H NMR (300 MHz, $CDCl_3$): δ 10.29 (s, 2 H, $H_{12,}$), 9.38 (d, J = 4.5, 4 H, H_{10}), 9.15 (d, J = 4.8 Hz, 4 H, H_9), 7.85 (s, 2 H, H_1), 7.77 (d, J = 8.1 Hz, 2 H, H_5), 7.30 (d, J = 8.1, 2 H, H_4), 4.33 (t, J = 6.5, 4 H, $H_{13'}$), 4.18 (t, J = 6.5, 4 H, H_{13}), 2.06 (m, 4 H, $H_{14'}$), 1.98 (m, 4 H, H_{14}), 1.65 (m, 4 H, $H_{15'}$), 1.49 (m, 4 H, H_{15}), 1.32-1.27 (m, 64 H, $H_{16\&16'}$-$H_{23\&23'}$), 0.92-0.83 (m, 12 H, $H_{24\&24'}$), -3.07 (s, 2 H, NH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.2, 147.6, 145.2, 134.1, 131.6, 131.2, 128.0, 121.1, 119.2, 112.2, 105.3, 32.1, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.4, 26.2, 22.9, 22.8, 14.3, 14.2. UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 412 (369.8), 505

(21.2), 543 (9.9), 578 (7.0), 633 (2.9). HRMS (MALDI-TOF) calcd for $C_{80}H_{118}N_4O_4$ $[M + H]^+$ 1199.9231, found 1199.9238.

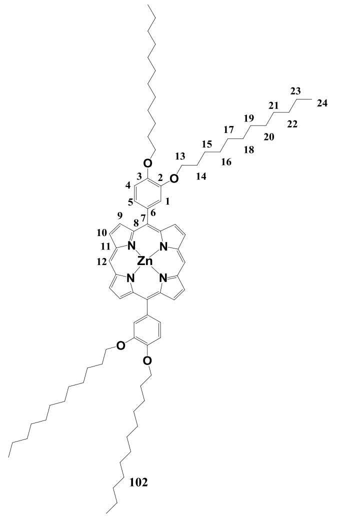
3.4.7 Synthesis of meso 5,15 di-bromo 10,20 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (100)



100

Meso 5,15 di-[3,4-bis(dodecyloxy)]phenyl porphyrin **99** (120 mg, 0.1 mmol) is dissolved in chloroform (25 ml) and cooled to 0 ^{o}C. Pyridine (100 µl) as an acid scavenger and N-bromosuccionimide (36 mg, 0.2 mmol) were added and the reaction was followed by TLC CH_2Cl_2/Hex (1:9). After 1 h the reaction reached to completion and quenched with 2 ml acetone. The solvent was removed and the solid washed several times methanol, dried and a purple solid was obtained **100** (115 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (d, *J* = 4.8, 4 H, H_{10}), 8.91 (d, *J* = 4.5, 4 H, H_9), 7.71 (s, 2 H, H_1), 7.65 (d, *J* = 8.1, 2 H, H_5), 7.23 (s, 2 H, H_4), 4.31 (t, *J* = 6.6, 4 H, $H_{13'}$), 4.14 (t, *J* = 6.6, 4 H, H_{13}), 2.05 (m, 4 H, $H_{14'}$), 1.91 (m, 4 H, H_{14}), 1.62 (m, 4 H, $H_{15'}$), 1.49 (m, 4 H, H_{15}), 1.31-1.25 (m, 64 H, $H_{16\&16'}$-$H_{23\&23'}$),0.93-0.82 (m, 12 H, $H_{24\&24'}$), -2.72 (s, 2 H, NH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.3, 147.3, 134.0, 132.3, 127.8, 121.5, 120.8, 111.8, 103.7, 69.6, 32.0, 31.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 26.2, 22.9, 22.8, 14.3, 14.2. UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 425 (98.0), 524 (7.3), 560 (5.5), 604 (2.6), 660 (2.7). HRMS (MALDI-TOF) calcd for $C_{80}H_{116}Br_2N_4O_4$ $[M + H]^+$ 1355.7442, found 1355.7449.

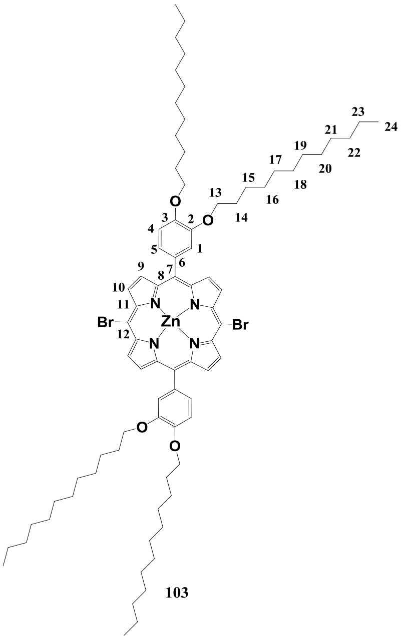
3.4.8 Synthesis of Zn-meso 5,15 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (102)



102

To a stirred solution of porphyrin **99** (120 mg, 0.1 mmol) in dichloromethane (35 mL) a solution of zinc acetate dehydrate (0.13 g, 0.6 mmol) in methanol (10 mL) was added. The reaction was stirred for 16 h at room temperature. Evaporation of the solvent and flash chromatography on silica, eluting with CH_2Cl_2:Hex (2/8), was carried out to remove excess zinc salts. Evaporation of the solvent gave the zinc porphyrin **102** as a purple solid (100 mg, 79%). UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 451 (69.6), 584 (8.1), 644 (1.7). HRMS (MALDI-TOF) calcd for $C_{80}H_{116}N_4O_4Zn$ $[M + H]^+$ 1261.8366, found 1261.8358.

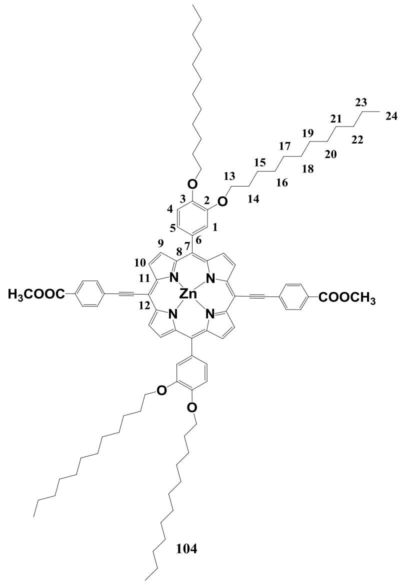
3.4.9 Synthesis of Zn-meso 5,15 di-bromo 10,20 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (103)



103

To a stirred solution of porphyrin **100** (175 mg, 0.13 mmol) in dichloromethane (35 mL) a solution of zinc acetate dehydrate (0.13 g, 0.6 mmol) in methanol (10 mL) was added. The reaction was stirred for 16 h at room temperature. Evaporation of the solvent and flash chromatography on silica, eluting with CH_2Cl_2/Hex (2:8), was carried out to remove excess zinc salts. Evaporation of the solvent gave the zinc porphyrin **103** as a purple solid (177 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.65 (brs, 4 H, H_{10}), 8.96 (brs, 4 H, H_9), 7.64 (brs, 4 H, H_1, H_5), 7.18 (brs, 2 H, H_4), 4.26 (brs, 4 H, $H_{13'}$), 4.07 (brs, 4 H, H_{13}), 2.00 (brt, 4 H, $H_{14'}$), 1.84 (brs, 4 H, H_{14}), 1.62 (brs, 4 H, $H_{15'}$), 1.46-1.22 (m, 68 H, H_{15}, $H_{16\&16'}$-$H_{23\&23'}$),0.91-0.82 (m, 12 H, $H_{24\&24'}$). UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 451, 585, 644. HRMS (MALDI-TOF) calcd for $C_{80}H_{114}Br_2N_4O_4Zn$ $[M + H]^+$ 1417.6577, found 1417.6570.

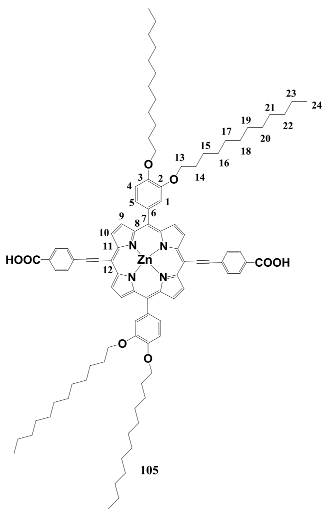
3.4.10 Synthesis of Zn-meso 5,15 di-methyl 4-ethynylbenzoate 10,20 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (104)



104

Porphyrin **103** (50 mg, 0.035 mmol), methyl benzoate-ester (21 mg, 0.21 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol) were added in a schlenk flask. The flask was evacuated and flashed with nitrogen. Then dry THF (20 ml) and Et_3N (1.5 ml) were added and the mixture was heated in 40 ^{0}C for 48 h. The color of the solution became dark green and the desired product was eluted with column chromatography using solvents CH_2Cl_2/Hex (4:6). A dark green solid **104** was obtained (45 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.37 (brs, 4 H, H_{10}), 8.92 (brs, 4 H, H_9), 7.85-7.63 (m, 12 H, H_1, H_5, H_4, H_{Phe_ester}), 4.34 (brs, 4 H, $H_{13'}$) 4.12 (m, 4 H, H_{13}), 3.75 (s, 6 H, H_{COOCH3}), 2.08 (brs, 4 H, $H_{14'}$), 1.89 (brs, 4 H, H_{14}), 1.69 (brs, 4 H, $H_{15'}$), 1.47-1.18 (m, 68 H, H_{15}, $H_{16\&16'}$-$H_{23\&23'}$), 0.92-0.78 (m, 12 H, $H_{24\&24'}$); ^{3}C NMR (300 MHz, $CDCl_3$): δ 166.6, 151.8, 150.5, 149.2, 147.2, 134.8, 132.9, 132.5, 131.0, 130.6, 129.6, 129.1, 128.3, 127.8, 123.1, 120.9, 111.9, 100.5, 95.6, 95.5, 69.6, 52.2, 32.1, 29.9, 29.8, 29.6, 29.5, 26.5, 26.2, 22.9, 22,8, 14.3, 14.2. UV/vis ($CHCl_3$) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 451 (69.7), 584 (8.1), 644 (1.8). HRMS (MALDI-TOF) calcd for $C_{100}H_{128}N_4O_8Zn$ $[M + H]^+$ 3154.8126, found 3154.8132.

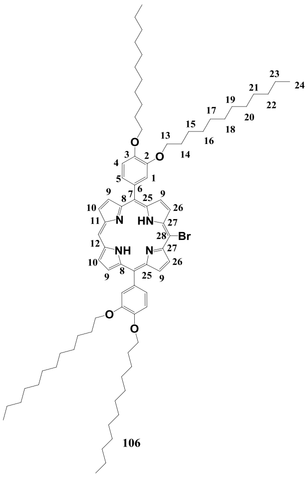
3.4.11 Synthesis of Zn-meso 5,15 di-methyl 4-ethynylbenzoic acid 10,20 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (105)



105

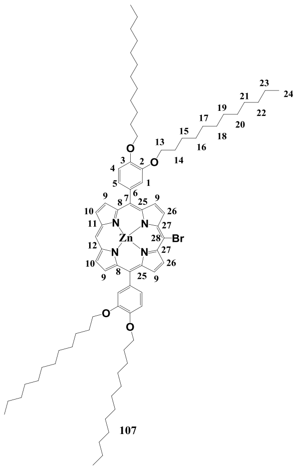
To a solution of porphyrin **104** (20 mg, 0.013 mmol) in THF (25 ml) , MeOH (5 ml), H_2O (8 ml) KOH (0.2 gr, 3.8 mmol)) was added and stirred at room temperature for 24 h. The course of the reaction was monitored by TLC (CH_2Cl_2/MeOH 95:5 v/v). The solution was evaporated to dryness to afford the potassium salt as solid. The solid was dissolved in distilled water (100 mL), aqueous 2 N HCl was added dropwise until pH reached 3 and a precipitate was formed. It was filtered, washed several times with distilled water to afford a green solid **105** (18 mg, 94%). UV-Vis (THF): λ nm (ε: M^{-1} cm^{-1}): 548 (1086), 589 (34171), 322 (2793), 608 (7292), 660 (334730); ^{1}H NMR and ^{13}C NMR (75 MHz, $CDCl_3$) not obtained due to solubility problems. UV/vis (THF) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 452 (74.2), 609 (8.1), 660 (1.9). HRMS (MALDI-TOF) calcd for $C_{98}H_{124}N_4O_8Zn$ $[M + H]^+$ 1549.8789, found 1549.8778.

3.4.12 Synthesis of meso 5 mono-bromo 10,20 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (106)



Meso 5,15 di-[3,4-bis(dodecyloxy)]phenyl porphyrin **99** (120 mg, 0.1 mmol) is dissolved in chloroform (25 ml) and cooled to 0 ^{o}C. Pyridine (100 μl) as an acid scavenger and N-bromosuccionimide (36 mg, 0.2 mmol) were added and the reaction was followed by TLC CH_2Cl_2/Hex (1:9). After 1 h the reaction reached to completion and quenched with 2 ml acetone. The solvent was removed and the desired product was isolated with column chromatography solvents used petroleum ether/CH_2Cl_2 (7:3). The porphyrin obtained as a purple solid **106** (52 mg, 57 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.11 (s, 1 H, H_{12}), 9.74 (d, *J* = 4.5, 2 H, H_{26}), 9.25 (d, *J* = 4.5, 2 H, H_{10}), 9.03, (d, *J* = 4.5, 4 H, H_9), 7.79 (d, *J* = 2.0, 2 H, H_1), 7.69 (d, *J* = 8.0, 2 H, H_5), 7.24 (s, 2 H, H_4), 4.31 (t, *J* = 6.5, 4 H, $H_{13'}$), 4.16 (t, *J* = 6.5, 4 H, H_{13}), 2.06 (m, 4 H, $H_{14'}$), 1.93 (m, 4 H, H_{14}), 1.68 (m, 4 H, $H_{15'}$), 1.52 (m, 4 H, H_{15}), 1.49-1.24 (m, 64 H, $H_{16\&16'}$-$H_{23\&23'}$),0.95-0.86 (m, 12 H, $H_{24\&24'}$), -2.95 (s, 2 H, NH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.3, 147.4, 134.0, 132.5, 132.2, 131.9, 131.6, 127.9, 120.9, 120.4, 112.0, 105.6, 103.6, 32.1, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.4, 26.2, 22.9, 22.8, 14.3, 14.2. UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 425, 524, 561, 603, 660. HRMS (MALDI-TOF) calcd for $C_{80}H_{117}BrN_4O_4$ $[M + H]^+$ 1277.8336, found 1277.8331.

3.4.13 Synthesis of Zn-meso 5 mono-bromo 10,20 di-[3,4-bis(dodecyloxy)]phenyl porphyrin (107)



107

To a stirred solution of porphyrin **106** (150 mg, 0.12 mmol) in dichloromethane (35 mL) a solution of zinc acetate dehydrate (0.13 g, 0.6 mmol) in methanol (10 mL) was added. The reaction was stirred for 16 h at room temperature. Evaporation of the solvent and flash chromatography on silica, eluting with CH_2Cl_2/Hex (2:8), was carried out to remove excess zinc salts. Evaporation of the solvent gave the zinc porphyrin **107** as a purple solid (155 mg, 96%). HRMS (MALDI-TOF) calcd for $C_{80}H_{115}BrN_4O_4Zn$ $[M + H]^+$ 1339.7471, found 1339.7479.

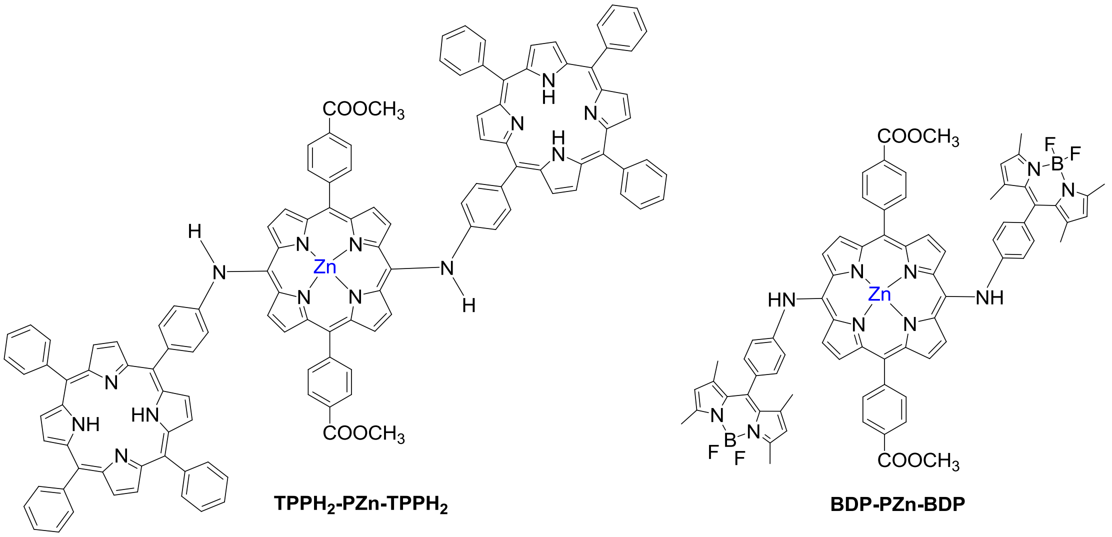
CHAPTER IV
CONCLUSIONS / PROSPECTS

4. CONCUSIONS AND PROSPECTS

In this Master thesis four types of porphyrin-based molecules are presented in order to be used as dyes for DSSC applications.

Our strategic approach was systematic and targeted on various aspects of the synthesized chromophore in order to improve or understand how to improve the efficiency of the material formed. For this reason the synthesis of triade chromophpres has been performed, also dyad functionalized porphyrins are prepared and finally a monomeric porphyrinic derivative with selected decoration. All materials were fully characterized and studied as dyes in DSSCs.

The first type of sensitizers are trimeric compounds consisting of **three dyes**, one with three porphyrin molecules (a central metalated and two free base) and another with two Bodipy and a metalated porphyrin molecule (Scheme 15). The use of different chromophores increased the absorption region of the compounds making it more possible to increase their light-harvesting properties and their resulting DSSC efficiency. Moreover, these dyes are bearing two carboxylic ester groups where upon hydrolysis, the acids that will be formed can act as anchoring groups and therefore their DSSC efficiency could be measured.

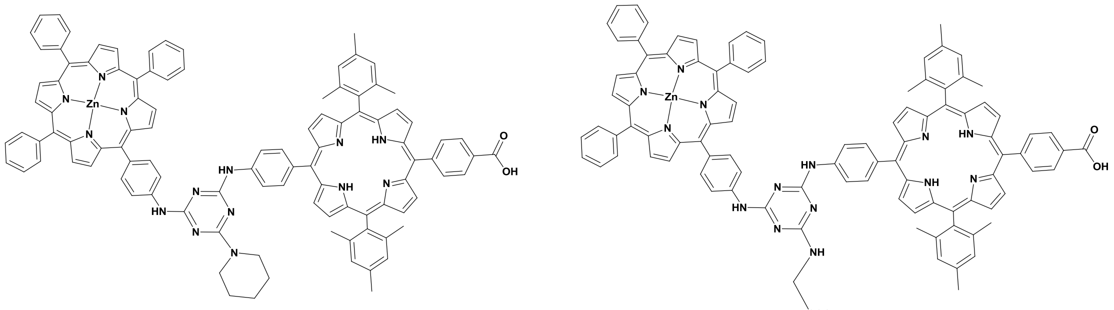


$TPPH_2$-PZn-$TPPH_2$

BDP-PZn-BDP

Scheme 15. Trimeric compounds synthesized for DSSC applications

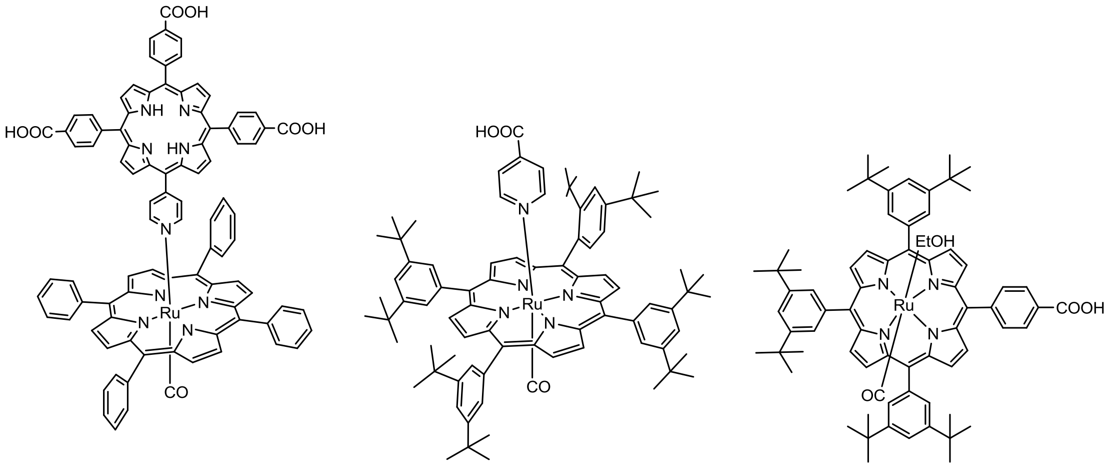
The second type of sensitizers consists of **dimeric** compounds (one free base and one metalated porphyrin) linked with a triazole ring (Scheme 16). Both porphyrin dyads contain potential anchoring groups for attachment onto the TiO_2 surface of DSSC electrodes. One has two carboxylic acid groups, while the other one carboxylic acid and one *N*-substituted piperidine group. These dyads were used as sensitizers for the fabrication of DSSCs. The overall energy conversion efficiencies for both compounds measured in the range of 4 to 5%.



P-t*N*p-P' **P-tg-P'**

Scheme16. Dimeric porphyrin based dyes.

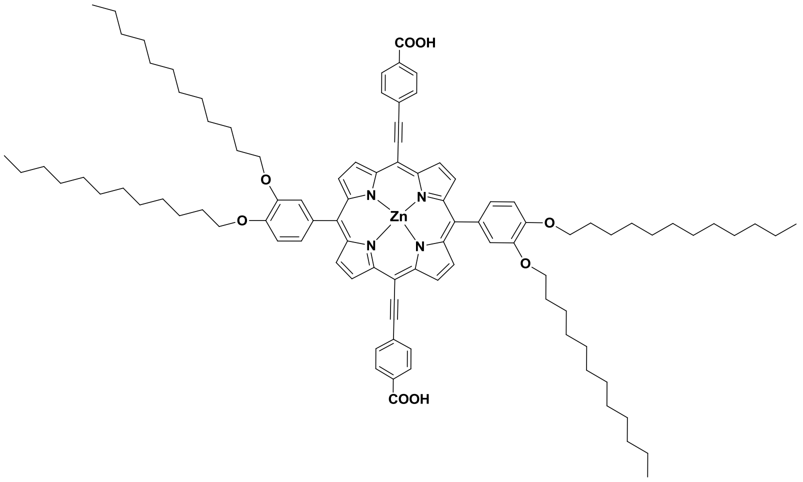
The third type of compounds consists of **ruthenium-pyridine** linked **dyad** bearing three carboxylic acids as anchoring groups. The energy conversion efficiency was measured ~1 %, almost the same as the porphyrin monomer with one pyridine and three carboxylic acids. This indicates that the second porphyrin does not improve the efficiency of the dye. Also, Ru-porphyrins were prepared having anchoring groups either on the porphyrin ring or on a pyridine linked to metallated porphyrin (Scheme 17).



Scheme 17. Ru-pyridine linked dyads and Ru-porphyrin

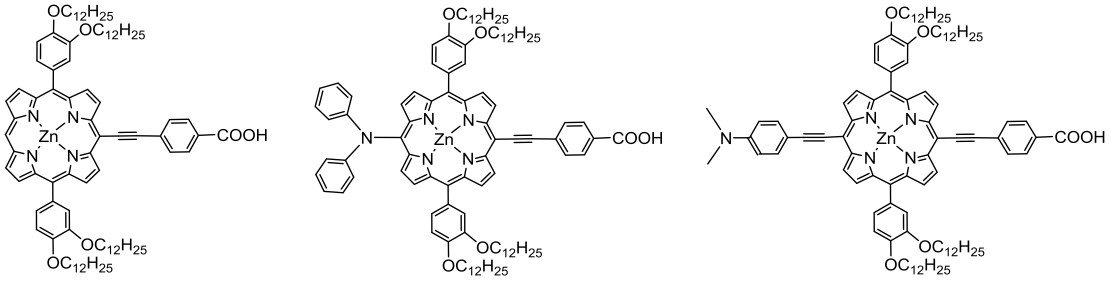
At the fourth part porphyrin compounds with **long alkyl chains** and **two carboxylic groups** linked via triple bond at the *meso* position of the porphyrin ring (Scheme 18).

These types of compounds are promising candidates for DSSC applications due to the decrease of aggregation of the dyes due to the presence of long alkyl chains.



Scheme 18. Porphyrin chromophore with long alkyl chains

In a future work the dye with one carboxylic acid can be prepared, along with a donor-acceptor system and their DSSC efficiencies could be measured (Scheme 19).



Scheme 19. Future porphyrin-based sensitizers

Overall, a number of novel porphyrin based chromophores have been synthesized and well characterized. Some of them gave very good energy conversion efficiencies and others have very good potentials for further development.

REFERENCES

[1] N.S. Lewis, D.G. Nocera, Proceedings of the National Academy of Sciences, 103 (2006) 15729-15735.

[2] M.I. Hoffert, K. Caldeira, G. Benford, D.R. Criswell, C. Green, H. Herzog, A.K. Jain, H.S. Kheshgi, K.S. Lackner, J.S. Lewis, H.D. Lightfoot, W. Manheimer, J.C. Mankins, M.E. Mauel, L.J. Perkins, M.E. Schlesinger, T. Volk, T.M.L. Wigley, Science, 298 (2002) 981-987.

[3] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Progress in Photovoltaics: Research and Applications, 21 (2013) 1-11.

[4] H. Tributsch, Photochemistry and Photobiology, 16 (1972) 261-269.

[5] B. O'Regan, M. Gratzel, Nature, 353 (1991) 737-740.

[6] M.K. Nazeeruddin, C. Klein, P. Liska, M. Grätzel, Coordination Chemistry Reviews, 249 (2005) 1460-1467.

[7] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chemical Reviews, 110 (2010) 6595-6663.

[8] M.K. Nazeeruddin, E. Baranoff, M. Grätzel, Solar Energy, 85 (2011) 1172-1178.

[9] W.M. Campbell, A.K. Burrell, D.L. Officer, K.W. Jolley, Coordination Chemistry Reviews, 248 (2004) 1363-1379.

[10] C.C. Wamser, M.G. Walter, A.B. Rudine, Journal of Porphyrins and Phthalocyanines, 14 (2010) 759-792.

[11] L.L. Li, E.W.G. Diau, Chem Soc Rev, 42 (2013) 291-304.

[12] I. Aviv, Z. Gross, Chemical Communications, (2007) 1987-1999.

[13] Z. Gross, H.B. Gray, A. Zaban, J.R. Winkler, B.S. Brunschwig, A. Mahammed, S. Chappel, D. Walker, Journal of Porphyrins and Phthalocyanines, 10 (2006) 1259-1262.

[14] X.-F. Wang, O. Kitao, H. Zhou, H. Tamiaki, S.-i. Sasaki, The Journal of Physical Chemistry C, 113 (2009) 7954-7961.

[15] X.-F. Wang, A. Matsuda, Y. Koyama, H. Nagae, S.-i. Sasaki, H. Tamiaki, Y. Wada, Chemical Physics Letters, 423 (2006) 470-475.

[16] X.-F. Wang, H. Tamiaki, L. Wang, N. Tamai, O. Kitao, H. Zhou, S.-i. Sasaki, Langmuir, 26 (2010) 6320-6327.

[17] H. Zhou, L. Wu, Y. Gao, T. Ma, Journal of Photochemistry and Photobiology A: Chemistry, 219 (2011) 188-194.

[18] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F.E. CurchodBasile, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, K. NazeeruddinMd, M. Grätzel, Nat Chem, 6 (2014) 242-247.

[19] A. Yella, C.-L. Mai, S.M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh, M. Grätzel, Angewandte Chemie International Edition, 53 (2014) 2973-2977.

[20] C.-P. Hsieh, H.-P. Lu, C.-L. Chiu, C.-W. Lee, S.-H. Chuang, C.-L. Mai, W.-N. Yen, S.-J. Hsu, E.W.-G. Diau, C.-Y. Yeh, Journal of Materials Chemistry, 20 (2010) 1127-1134.

[21] T. Bessho, S.M. Zakeeruddin, C.-Y. Yeh, E.W.-G. Diau, M. Grätzel, Angewandte Chemie International Edition, 49 (2010) 6646-6649.

[22] H. He, A. Gurung, L. Si, Chemical Communications, 48 (2012) 5910-5912.

[23] W. Zhou, Z. Cao, S. Jiang, H. Huang, L. Deng, Y. Liu, P. Shen, B. Zhao, S. Tan, X. Zhang, Organic Electronics, 13 (2012) 560-569.

[24] M.S. Kang, S.H. Kang, S.G. Kim, I.T. Choi, J.H. Ryu, M.J. Ju, D. Cho, J.Y. Lee, H.K. Kim, Chemical Communications, 48 (2012) 9349-9351.

[25] C. Jiao, N. Zu, K.-W. Huang, P. Wang, J. Wu, Organic Letters, 13 (2011) 3652-3655.

[26] C.-W. Lee, H.-P. Lu, C.-M. Lan, Y.-L. Huang, Y.-R. Liang, W.-N. Yen, Y.-C. Liu, Y.-S. Lin, E.W.-G. Diau, C.-Y. Yeh, Chemistry – A European Journal, 15 (2009) 1403-1412.
[27] K.S. Suslick, C.T. Chen, G.R. Meredith, L.T. Cheng, Journal of the American Chemical Society, 114 (1992) 6928-6930.
[28] T. Morotti, M. Pizzotti, R. Ugo, S. Quici, M. Bruschi, P. Mussini, S. Righetto, European Journal of Inorganic Chemistry, 2006 (2006) 1743-1757.
[29] E. Collini, S. Mazzucato, M. Zerbetto, C. Ferrante, R. Bozio, M. Pizzotti, F. Tessore, R. Ugo, Chemical Physics Letters, 454 (2008) 70-74.
[30] P.C. Ray, P. Bonifassi, J. Leszczynski, The Journal of Physical Chemistry A, 112 (2008) 2870-2879.
[31] M.C. Ruiz Delgado, J. Casado, V. Hernandez, J.T. Lopez Navarrete, J. Orduna, B. Villacampa, R. Alicante, J.-M. Raimundo, P. Blanchard, J. Roncali, The Journal of Physical Chemistry C, 112 (2008) 3109-3120.
[32] D.K. Dogutan, S.H.H. Zaidi, P. Thamyongkit, J.S. Lindsey, The Journal of Organic Chemistry, 72 (2007) 7701-7714.
[33] S.H.H. Zaidi, R.M. Fico, J.S. Lindsey, Organic Process Research & Development, 10 (2005) 118-134.
[34] P.D. Rao, B.J. Littler, G.R. Geier, J.S. Lindsey, The Journal of Organic Chemistry, 65 (2000) 1084-1092.
[35] J.K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, J.S. Lindsey, Organic Process Research & Development, 7 (2003) 799-812.
[36] K. Muthukumaran, M. Ptaszek, B. Noll, W.R. Scheidt, J.S. Lindsey, The Journal of Organic Chemistry, 69 (2004) 5354-5364.
[37] S.H.H. Zaidi, K. Muthukumaran, S.-i. Tamaru, J.S. Lindsey, The Journal of Organic Chemistry, 69 (2004) 8356-8365.
[38] S.-i. Tamaru, L. Yu, W.J. Youngblood, K. Muthukumaran, M. Taniguchi, J.S. Lindsey, The Journal of Organic Chemistry, 69 (2004) 765-777.
[39] S.H.H. Zaidi, R.S. Loewe, B.A. Clark, M.J. Jacob, J.S. Lindsey, Organic Process Research & Development, 10 (2006) 304-314.
[40] M.R. Wasielewski, Chemical Reviews, 92 (1992) 435-461.
[41] D. Gust, T.A. Moore, A.L. Moore, Accounts of Chemical Research, 26 (1993) 198-205.
[42] A. Osuka, S. Marumo, N. Mataga, S. Taniguchi, T. Okada, I. Yamazaki, Y. Nishimura, T. Ohno, K. Nozaki, Journal of the American Chemical Society, 118 (1996) 155-168.
[43] P.A. Liddell, D. Kuciauskas, J.P. Sumida, B. Nash, D. Nguyen, A.L. Moore, T.A. Moore, D. Gust, Journal of the American Chemical Society, 119 (1997) 1400-1405.
[44] J.-P. Collin, A. Harriman, V. Heitz, F. Odobel, J.-P. Sauvage, Coordination Chemistry Reviews, 148 (1996) 63-69.
[45] H. Volz, M. Holzbecher, Angewandte Chemie International Edition in English, 36 (1997) 1442-1445.
[46] M. Yeung, A.C.H. Ng, M.G.B. Drew, E. Vorpagel, E.M. Breitung, R.J. McMahon, D.K.P. Ng, The Journal of Organic Chemistry, 63 (1998) 7143-7150.
[47] I.M. Blake, H.L. Anderson, D. Beljonne, J.-L. Brédas, W. Clegg, Journal of the American Chemical Society, 120 (1998) 10764-10765.
[48] R.L. Halterman, X. Mei, Tetrahedron Letters, 37 (1996) 6291-6294.
[49] Y. Furusho, T. Kimura, Y. Mizuno, T. Aida, Journal of the American Chemical Society, 119 (1997) 5267-5268.
[50] R.R. French, J. Wirz, W.-D. Woggon, Helvetica Chimica Acta, 81 (1998) 1521-1527.
[51] R.W. Wagner, J.S. Lindsey, Journal of the American Chemical Society, 116 (1994) 9759-9760.
[52] R.W. Wagner, J.S. Lindsey, J. Seth, V. Palaniappan, D.F. Bocian, Journal of the American Chemical Society, 118 (1996) 3996-3997.

[53] J.A. Lacey, D. Phillips, L.R. Milgrom, G. Yahioglu, R.D. Rees, Photochemistry and Photobiology, 67 (1998) 97-100.
[54] N. Nishino, R.W. Wagner, J.S. Lindsey, The Journal of Organic Chemistry, 61 (1996) 7534-7544.
[55] Q.M. Wang, D.W. Bruce, Tetrahedron Letters, 37 (1996) 7641-7644.
[56] Q.M. Wang, D.W. Bruce, Angewandte Chemie International Edition in English, 36 (1997) 150-152.
[57] D.T. Gryko, M. Tasior, Tetrahedron Letters, 44 (2003) 3317-3321.
[58] C.O. Paul-Roth, J.A.G. Williams, J. Letessier, G. Simonneaux, Tetrahedron Letters, 48 (2007) 4317-4322.
[59] D. Daphnomili, M. Grammatikopoulou, C. Raptopoulou, G. Charalambidis, T. Lazarides, A.G. Coutsolelos, Bioinorganic Chemistry and Applications, 2010 (2010).
[60] D.S. Sharada, A.Z. Muresan, K. Muthukumaran, J.S. Lindsey, The Journal of Organic Chemistry, 70 (2005) 3500-3510.
[61] D.K. Dogutan, J.S. Lindsey, The Journal of Organic Chemistry, 73 (2008) 6728-6742.
[62] D.K. Dogutan, M. Ptaszek, J.S. Lindsey, The Journal of Organic Chemistry, 73 (2008) 6187-6201.
[63] J. S. Lindsey, in: The Porphyrin Handbook (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, 2000, vol. 1, pp. 45–118.
[64] B. Vaz, R. Alvarez, M. Nieto, A.I. Paniello, A.R. de Lera, Tetrahedron Letters, 42 (2001) 7409-7412.
[65] M.O. Senge, M. Fazekas, M. Pintea, M. Zawadzka, W.J. Blau, European Journal of Organic Chemistry, 2011 (2011) 5797-5816.
[66] B.J. Littler, M.A. Miller, C.-H. Hung, R.W. Wagner, D.F. O'Shea, P.D. Boyle, J.S. Lindsey, The Journal of Organic Chemistry, 64 (1999) 1391-1396.
[67] G.P. Arsenault, E. Bullock, S.F. MacDonald, Journal of the American Chemical Society, 82 (1960) 4384-4389.
[68] B.J. Littler, Y. Ciringh, J.S. Lindsey, The Journal of Organic Chemistry, 64 (1999) 2864-2872.
[69] K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, S. Murasawa, Journal of Electroanalytical Chemistry, 396 (1995) 27-34.
[70] J.N. Clifford, E. Palomares, M.K. Nazeeruddin, M. Grätzel, J. Nelson, X. Li, N.J. Long, J.R. Durrant, Journal of the American Chemical Society, 126 (2004) 5225-5233.
[71] E. Palomares, M.V. Martinez-Diaz, S.A. Haque, T. Torres, J.R. Durrant, Chemical Communications, (2004) 2112-2113.
[72] J.R. Durrant, S.A. Haque, E. Palomares, Coordination Chemistry Reviews, 248 (2004) 1247-1257.
[73] T. Ma, K. Inoue, K. Yao, H. Noma, T. Shuji, E. Abe, J. Yu, X. Wang, B. Zhang, Journal of Electroanalytical Chemistry, 537 (2002) 31-38.
[74] T. Ma, K. Inoue, H. Noma, K. Yao, E. Abe, Journal of Photochemistry and Photobiology A: Chemistry, 152 (2002) 207-212.
[75] F. Odobel, E. Blart, M. Lagree, M. Villieras, H. Boujtita, N. El Murr, S. Caramori, C. Alberto Bignozzi, Journal of Materials Chemistry, 13 (2003) 502-510.
[76] Q. Wang, W.M. Campbell, E.E. Bonfantani, K.W. Jolley, D.L. Officer, P.J. Walsh, K. Gordon, R. Humphry-Baker, M.K. Nazeeruddin, M. Grätzel, The Journal of Physical Chemistry B, 109 (2005) 15397-15409.
[77] M.K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Grätzel, The Journal of Physical Chemistry B, 107 (2003) 8981-8987.
[78] M.K. Nazeeruddin, R. Humphry-Baker, D.L. Officer, W.M. Campbell, A.K. Burrell, M. Grätzel, Langmuir, 20 (2004) 6514-6517.

[79] T.E.O. Screen, K.B. Lawton, G.S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson Iii, S.J. Martin, D.D.C. Bradley, H.L. Anderson, Journal of Materials Chemistry, 11 (2001) 312-320.
[80] V.S. Lin, S.G. DiMangno, M.J. Therien, Science, 264 (1994) 1105-1111.
[81] K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier, M. Graetzel, The Journal of Physical Chemistry, 91 (1987) 2342-2347.
[82] A. Kay, M. Graetzel, The Journal of Physical Chemistry, 97 (1993) 6272-6277.
[83] S. Cherian, C.C. Wamser, The Journal of Physical Chemistry B, 104 (2000) 3624-3629.
[84] E.S. Schmidt, T.S. Calderwood, T.C. Bruice, Inorg Chem, 25 (1986) 3718-3720.
[85] J. Seth, V. Palaniappan, T.E. Johnson, S. Prathapan, J.S. Lindsey, D.F. Bocian, Journal of the American Chemical Society, 116 (1994) 10578-10592.
[86] C. Bruckner, P.C.D. Foss, J.O. Sullivan, R. Pelto, M. Zeller, R.R. Birge, G. Crundwell, Physical Chemistry Chemical Physics, 8 (2006) 2402-2412.
[87] J. Rochford, D. Chu, A. Hagfeldt, E. Galoppini, Journal of the American Chemical Society, 129 (2007) 4655-4665.
[88] S. Rangan, S. Katalinic, R. Thorpe, R.A. Bartynski, J. Rochford, E. Galoppini, The Journal of Physical Chemistry C, 114 (2009) 1139-1147.
[89] J. Rochford, E. Galoppini, Langmuir, 24 (2008) 5366-5374.
[90] G.B. Deacon, R.J. Phillips, Coordination Chemistry Reviews, 33 (1980) 227-250.
[91] K.S. Finnie, J.R. Bartlett, J.L. Woolfrey, Langmuir, 14 (1998) 2744-2749.
[92] A. Vittadini, A. Selloni, F.P. Rotzinger, M. Grätzel, The Journal of Physical Chemistry B, 104 (2000) 1300-1306.
[93] H. Imahori, S. Hayashi, H. Hayashi, A. Oguro, S. Eu, T. Umeyama, Y. Matano, The Journal of Physical Chemistry C, 113 (2009) 18406-18413.
[94] H. Imahori, Y. Matsubara, H. Iijima, T. Umeyama, Y. Matano, S. Ito, M. Niemi, N.V. Tkachenko, H. Lemmetyinen, The Journal of Physical Chemistry C, 114 (2010) 10656-10665.
[95] J.K. Park, J. Chen, H.R. Lee, S.W. Park, H. Shinokubo, A. Osuka, D. Kim, The Journal of Physical Chemistry C, 113 (2009) 21956-21963.
[96] A.J. Mozer, M.J. Griffith, G. Tsekouras, P. Wagner, G.G. Wallace, S. Mori, K. Sunahara, M. Miyashita, J.C. Earles, K.C. Gordon, L. Du, R. Katoh, A. Furube, D.L. Officer, Journal of the American Chemical Society, 131 (2009) 15621-15623.
[97] J.T. Dy, K. Tamaki, Y. Sanehira, J. Nakazaki, S. Uchida, T. Kubo, H. Segawa, Electrochemistry, 77 (2009) 206-209.
[98] Y. Liu, H. Lin, J.T. Dy, K. Tamaki, J. Nakazaki, D. Nakayama, S. Uchida, T. Kubo, H. Segawa, Chemical Communications, 47 (2011) 4010-4012.
[99] G.E. Zervaki, M.S. Roy, M.K. Panda, P.A. Angaridis, E. Chrissos, G.D. Sharma, A.G. Coutsolelos, Inorg Chem, 52 (2013) 9813-9825.
[100] R.B. Ambre, G.-F. Chang, C.-H. Hung, Chemical Communications, 50 (2014) 725-727.
[101] V. Nikolaou, P.A. Angaridis, G. Charalambidis, G.D. Sharma, A.G. Coutsolelos, Dalton Transactions, (2015).
[102] J.R. Stromberg, A. Marton, H.L. Kee, C. Kirmaier, J.R. Diers, C. Muthiah, M. Taniguchi, J.S. Lindsey, D.F. Bocian, G.J. Meyer, D. Holten, The Journal of Physical Chemistry C, 111 (2007) 15464-15478.
[103] H.-P. Lu, C.-L. Mai, C.-Y. Tsia, S.-J. Hsu, C.-P. Hsieh, C.-L. Chiu, C.-Y. Yeh, E.W.-G. Diau, Physical Chemistry Chemical Physics, 11 (2009) 10270-10274.
[104] H.-P. Lu, C.-Y. Tsai, W.-N. Yen, C.-P. Hsieh, C.-W. Lee, C.-Y. Yeh, E.W.-G. Diau, The Journal of Physical Chemistry C, 113 (2009) 20990-20997.
[105] R.A. Jensen, H. Van Ryswyk, C. She, J.M. Szarko, L.X. Chen, J.T. Hupp, Langmuir, 26 (2009) 1401-1404.
[106] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, Science, 334 (2011) 629-634.

[107] C.-H. Wu, M.-C. Chen, P.-C. Su, H.-H. Kuo, C.-L. Wang, C.-Y. Lu, C.-H. Tsai, C.-C. Wu, C.-Y. Lin, Journal of Materials Chemistry A, 2 (2014) 991-999.

[108] W.M. Campbell, K.W. Jolley, P. Wagner, K. Wagner, P.J. Walsh, K.C. Gordon, L. Schmidt-Mende, M.K. Nazeeruddin, Q. Wang, M. Grätzel, D.L. Officer, The Journal of Physical Chemistry C, 111 (2007) 11760-11762.

[109] A. Allegrucci, N.A. Lewcenko, A.J. Mozer, L. Dennany, P. Wagner, D.L. Officer, K. Sunahara, S. Mori, L. Spiccia, Energy & Environmental Science, 2 (2009) 1069-1073.

[110] V. Armel, J.M. Pringle, M. Forsyth, D.R. MacFarlane, D.L. Officer, P. Wagner, Chemical Communications, 46 (2010) 3146-3148.

[111] A.J. Mozer, P. Wagner, D.L. Officer, G.G. Wallace, W.M. Campbell, M. Miyashita, K. Sunahara, S. Mori, Chemical Communications, (2008) 4741-4743.

[112] T.D. Santos, A. Morandeira, S. Koops, A.J. Mozer, G. Tsekouras, Y. Dong, P. Wagner, G. Wallace, J.C. Earles, K.C. Gordon, D. Officer, J.R. Durrant, The Journal of Physical Chemistry C, 114 (2010) 3276-3279.

[113] M. Ishida, S.W. Park, D. Hwang, Y.B. Koo, J.L. Sessler, D.Y. Kim, D. Kim, The Journal of Physical Chemistry C, 115 (2011) 19343-19354.

[114] M.P. Balanay, K.H. Kim, S.H. Lee, D.H. Kim, J Photoch Photobio A, 248 (2012) 63-72.

[115] J. Lu, X. Xu, K. Cao, J. Cui, Y. Zhang, Y. Shen, X. Shi, L. Liao, Y. Cheng, M. Wang, Journal of Materials Chemistry A, 1 (2013) 10008-10015.

[116] S.H. Kang, I.T. Choi, M.S. Kang, Y.K. Eom, M.J. Ju, J.Y. Hong, H.S. Kang, H.K. Kim, Journal of Materials Chemistry A, 1 (2013) 3977-3982.

[117] N.M. Reddy, T.Y. Pan, Y.C. Rajan, B.C. Guo, C.M. Lan, E.W. Diau, C.Y. Yeh, Phys Chem Chem Phys, 15 (2013) 8409-8415.

[118] T. Ripolles-Sanchis, B.C. Guo, H.P. Wu, T.Y. Pan, H.W. Lee, S.R. Raga, F. Fabregat-Santiago, J. Bisquert, C.Y. Yeh, E.W.G. Diau, Chemical Communications, 48 (2012) 4368-4370.

[119] H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S.E. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chabera, A.P. Yartsev, V. Sundstrom, The journal of physical chemistry. A, 115 (2011) 3679-3690.

[120] H. Imahori, T. Umeyama, S. Ito, Accounts of Chemical Research, 42 (2009) 1809-1818.

[121] S. Eu, S. Hayashi, T. Umeyama, A. Oguro, M. Kawasaki, N. Kadota, Y. Matano, H. Imahori, The Journal of Physical Chemistry C, 111 (2007) 3528-3537.

[122] S. Eu, S. Hayashi, T. Umeyama, Y. Matano, Y. Araki, H. Imahori, The Journal of Physical Chemistry C, 112 (2008) 4396-4405.

[123] M. Tanaka, S. Hayashi, S. Eu, T. Umeyama, Y. Matano, H. Imahori, Chemical Communications, (2007) 2069-2071.

[124] S. Hayashi, Y. Matsubara, S. Eu, H. Hayashi, T. Umeyama, Y. Matano, H. Imahori, Chem Lett, 37 (2008) 846-847.

[125] S. Hayashi, M. Tanaka, H. Hayashi, S. Eu, T. Umeyama, Y. Matano, Y. Araki, H. Imahori, The Journal of Physical Chemistry C, 112 (2008) 15576-15585.

[126] A. Kira, Y. Matsubara, H. Iijima, T. Umeyama, Y. Matano, S. Ito, M. Niemi, N.V. Tkachenko, H. Lemmetyinen, H. Imahori, The Journal of Physical Chemistry C, 114 (2010) 11293-11304.

[127] H. Hayashi, A.S. Touchy, Y. Kinjo, K. Kurotobi, Y. Toude, S. Ito, H. Saarenpaa, N.V. Tkachenko, H. Lemmetyinen, H. Imahori, Chemsuschem, 6 (2013) 508-517.

[128] J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, Nature, 318 (1985) 618-624.

[129] W.W.P. Beverley R. Green, Light-Harvesting Antennas in Photosynthesis, Kluwer, Dordrecht, Netherlands, 2003.

[130] P.V. Kamat, The Journal of Physical Chemistry C, 111 (2007) 2834-2860.

[131] S. Fukuzumi, Physical Chemistry Chemical Physics, 10 (2008) 2283-2297.

[132] V. Balzani, A. Credi, M. Venturi, Chemsuschem, 1 (2008) 26-58.

[133] H. Imahori, S. Fukuzumi, Adv. Funct. Mater., 14 (2004) 525-536.

[134] R. Chitta, F. D'Souza, Journal of Materials Chemistry, 18 (2008) 1440-1471.
[135] A. Kira, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, J.K. Park, D. Kim, H. Imahori, Journal of the American Chemical Society, 131 (2009) 3198-3200.
[136] M.K.R. Fischer, I. López-Duarte, M.M. Wienk, M.V. Martínez-Díaz, R.A.J. Janssen, P. Bäuerle, T.s. Torres, Journal of the American Chemical Society, 131 (2009) 8669-8676.
[137] N.K. Subbaiyan, I. Obraztsov, C.A. Wijesinghe, K. Tran, W. Kutner, F. D'Souza, The Journal of Physical Chemistry C, 113 (2009) 8982-8989.
[138] F. D'Souza, O. Ito, Coordination Chemistry Reviews, 249 (2005) 1410-1422.
[139] M.T. Brumbach, A.K. Boal, D.R. Wheeler, Langmuir, 25 (2009) 10685-10690.
[140] W.J. Kruper, T.A. Chamberlin, M. Kochanny, The Journal of Organic Chemistry, 54 (1989) 2753-2756.
[141] S.G. DiMagno, V.S.Y. Lin, M.J. Therien, The Journal of Organic Chemistry, 58 (1993) 5983-5993.
[142] J.A. Mikroyannidis, G. Charalambidis, A.G. Coutsolelos, P. Balraju, G.D. Sharma, Journal of Power Sources, 196 (2011) 6622-6628.
[143] H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, Journal of the American Chemical Society, 123 (2000) 100-110.
[144] G.-Y. Gao, Y. Chen, X.P. Zhang, Organic Letters, 6 (2004) 1837-1840.
[145] Y. Chen, X.P. Zhang, J Org Chem, 68 (2003) 4432-4438.
[146] A.J. Golder, D.C. Povey, J. Silver, Q.A.A. Jassim, Acta Crystallographica Section C, 46 (1990) 1210-1212.
[147] C.K. Schauer, O.P. Anderson, S.S. Eaton, G.R. Eaton, Inorganic Chemistry, 24 (1985) 4082-4086.
[148] K.M. Kadish, K.M. Smith, R. Guilard, in: Eds. (Ed.), Academic, San Diego, CA, 2000.
[149] S. Mula, K. Elliott, A. Harriman, R. Ziessel, The Journal of Physical Chemistry A, 114 (2010) 10515-10522.
[150] Dennis W.P.M. Löwik, Christopher R. Lowe, European Journal of Organic Chemistry, 2001 (2001) 2825-2839.
[151] M.B. Steffensen, E.E. Simanek, Organic Letters, 5 (2003) 2359-2361.
[152] W. Zhang, E.E. Simanek, Organic Letters, 2 (2000) 843-845.
[153] T. Carofiglio, A. Varotto, U. Tonellato, The Journal of Organic Chemistry, 69 (2004) 8121-8124.
[154] K. Ichihara, K. Ichihara, Chem. Lett., 24 (1995) 631.
[155] T. Carofiglio, E. Lubian, I. Menegazzo, G. Saielli, A. Varotto, The Journal of Organic Chemistry, 74 (2009) 9034-9043.
[156] T. Lazarides, G. Charalambidis, A. Vuillamy, M. Réglier, E. Klontzas, G. Froudakis, S. Kuhri, D.M. Guldi, A.G. Coutsolelos, Inorg Chem, 50 (2011) 8926-8936.
[157] C.-Y. Lin, Y.-C. Wang, S.-J. Hsu, C.-F. Lo, E.W.-G. Diau, The Journal of Physical Chemistry C, 114 (2010) 687-693.
[158] C.-Y. Lin, C.-F. Lo, L. Luo, H.-P. Lu, C.-S. Hung, E.W.-G. Diau, The Journal of Physical Chemistry C, 113 (2009) 755-764.
[159] C.-F. Lo, L. Luo, E.W.-G. Diau, I.J. Chang, C.-Y. Lin, Chemical Communications, (2006) 1430-1432.
[160] H.J. Snaith, Advanced Functional Materials, 20 (2010) 13-19.
[161] M.K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, Journal of the American Chemical Society, 127 (2005) 16835-16847.
[162] M. Pastore, F. De Angelis, The Journal of Physical Chemistry Letters, 4 (2013) 956-974.
[163] A. Nakano, Y. Yasuda, T. Yamazaki, S. Akimoto, I. Yamazaki, H. Miyasaka, A. Itaya, M. Murakami, A. Osuka, The Journal of Physical Chemistry A, 105 (2001) 4822-4833.
[164] M. Tanasova, C. Vasileiou, O.O. Olumolade, B. Borhan, Chirality, 21 (2009) 374-382.
[165] W.L.F. Armarego, C. Chai, in, Elsevier Inc., 2009.

[166] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, Journal of Applied Crystallography, 26 (1993) 343-350.
[167] G.M. Sheldrick, Acta Crystallographica Section A, Volume 64 (2008) 112-122
[168] G.A. Crosby, J.N. Demas, The Journal of Physical Chemistry, 75 (1971) 991-1024.
[169] P.G. Seybold, M. Gouterman, Journal of Molecular Spectroscopy, 31 (1969) 1-13.
[170] W. Kohn, L. Sham, J. Phys. Rev., 140 (1965) A1133.
[171] Gaussian 03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J. Montgomery, J. A., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, G. Inc., Ed.; Wallingford CT: **2004**.
[172] A.D. Becke, Phys. Rev. A, 38 (1988) 3098-3100.
[173] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B, 37 (1988) 785-789.
[174] M. Cossi, V. Barone, R. Cammi, J. Tomasi, Chemical Physics Letters, 255 (1996) 327-335.
[175] S. Ariel, D. Dolphin, G. Domazetis, B.R. James, T.W. Leung, S.J. Rettig, J. Trotter, G.M. Williams, Canadian Journal of Chemistry, 62 (1984) 755-762.
[176] M.J. Plater, S. Aiken, G. Bourhill, Tetrahedron, 58 (2002) 2405-2413.
[177] M.J. Webb, N. Bampos, Chemical Science, 3 (2012) 2351-2366.

ANNEX

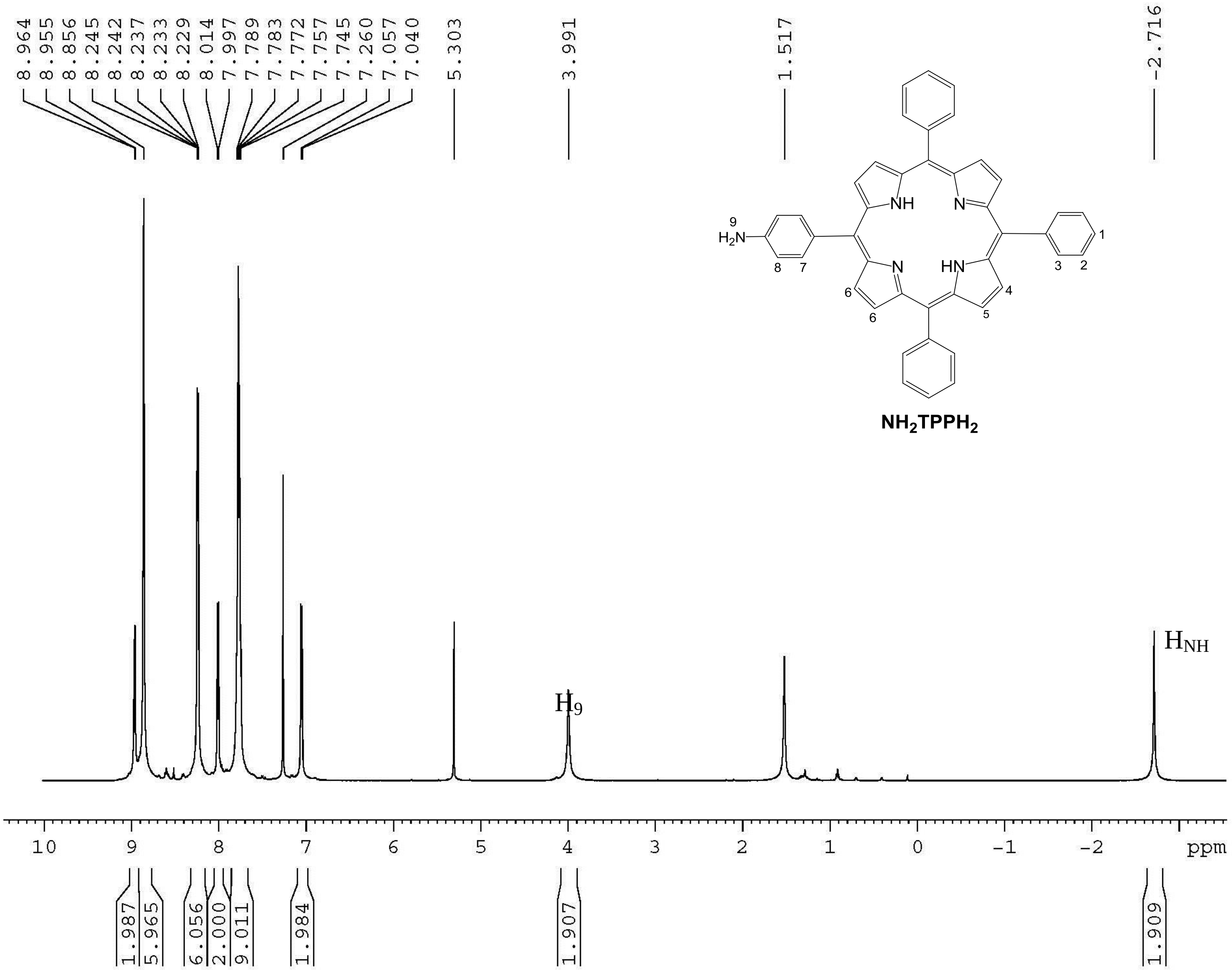


Figure S1. ^{1}H-NMR spectrum in $CDCl_3$ of compound **NH_2TPPH_2**, **68**.

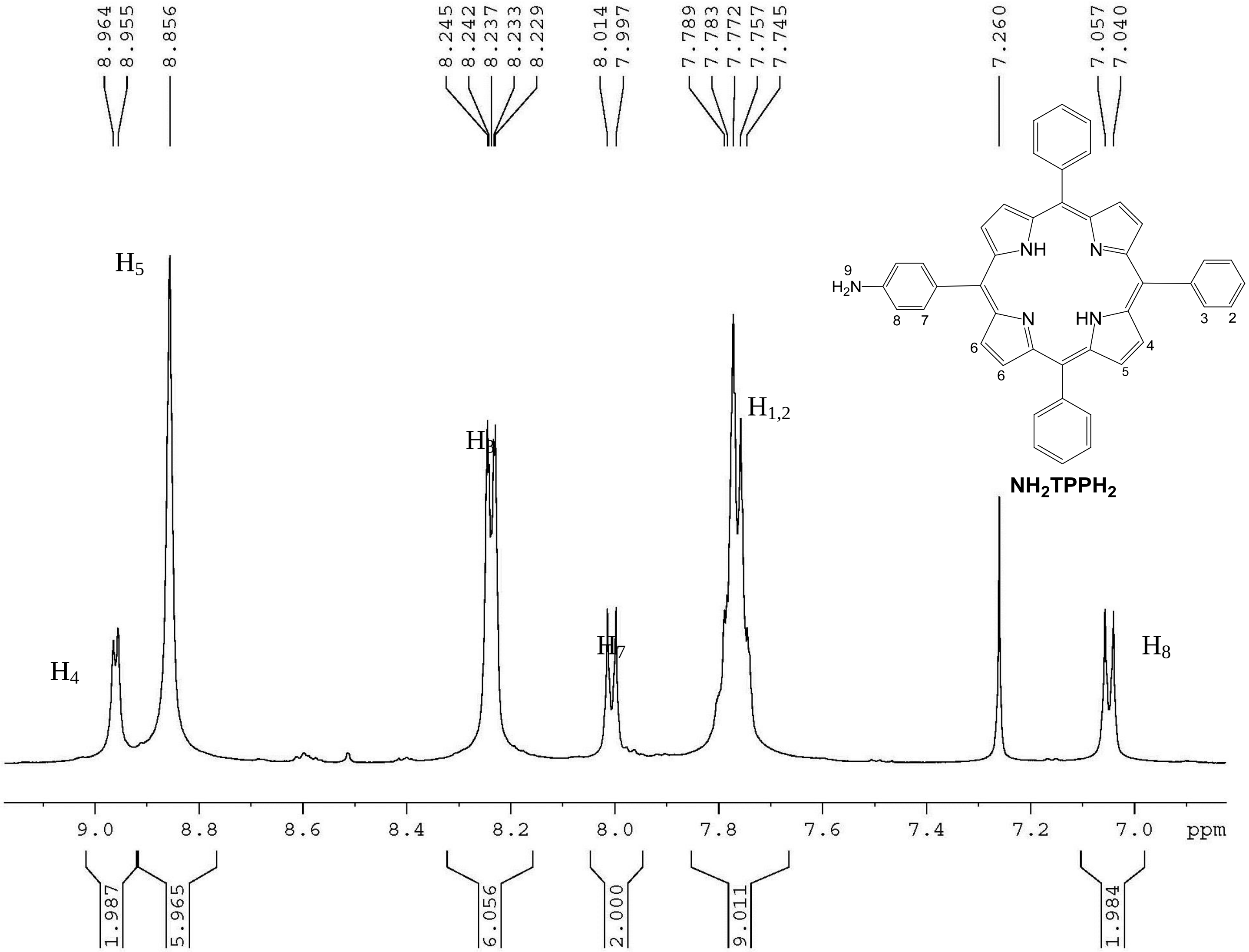


Figure S1a. Aromatic region of ^{1}H-NMR spectrum in $CDCl_3$ of compound **NH_2TPPH_2, 68**.

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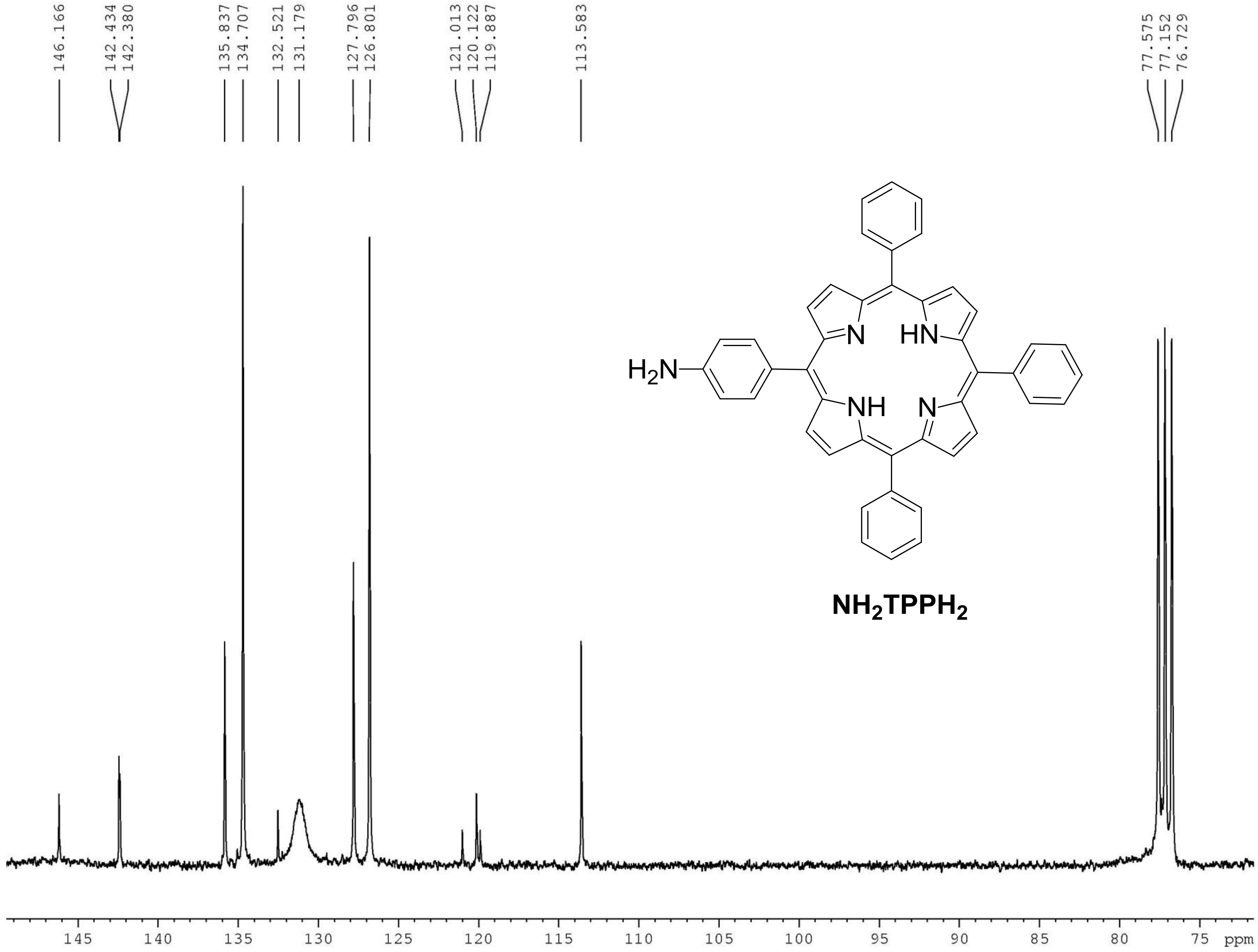


Figure S2. ^{13}C-NMR spectrum in $CDCl_3$ of compound **NH_2TPPH_2, 68**.

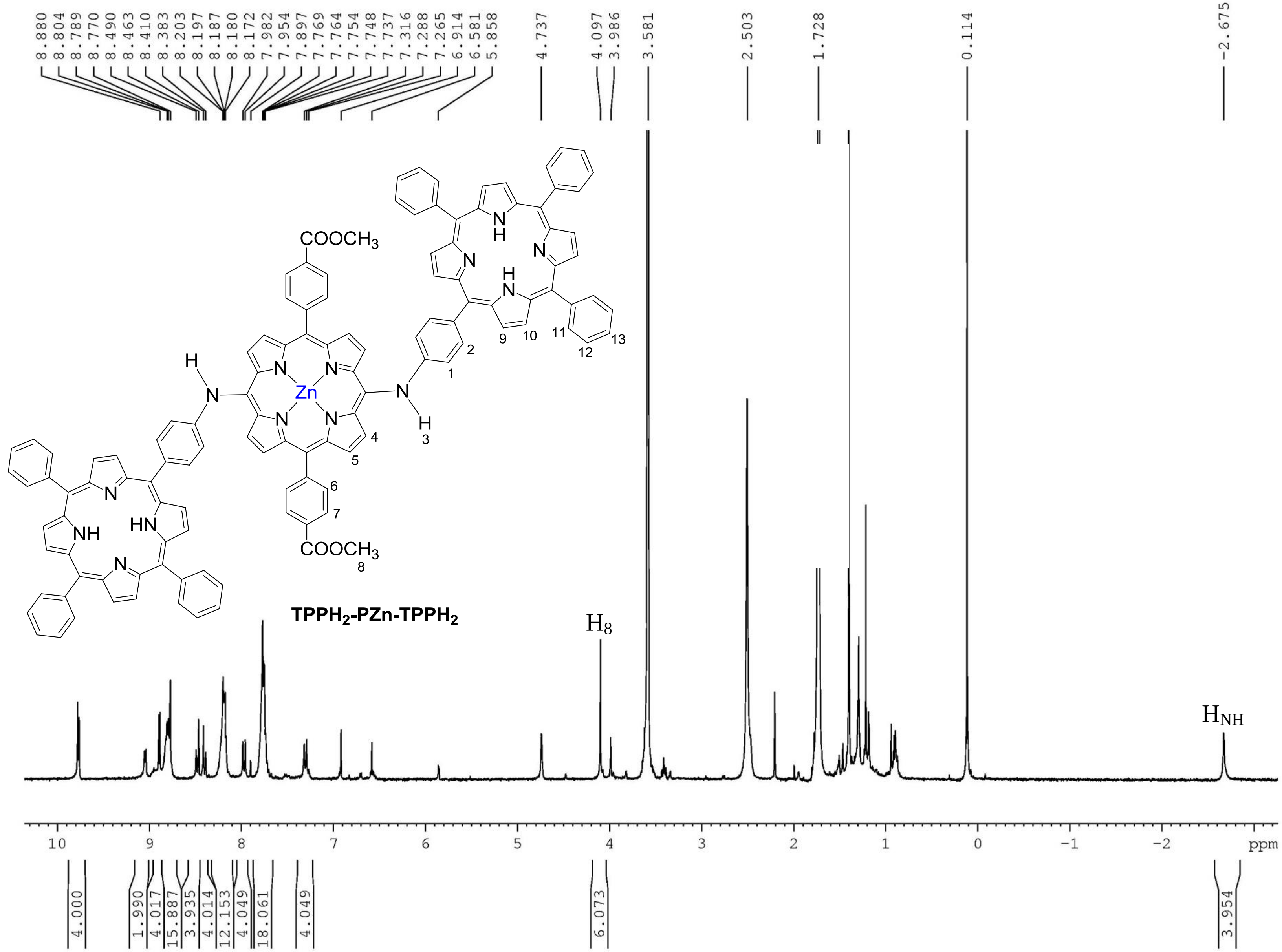
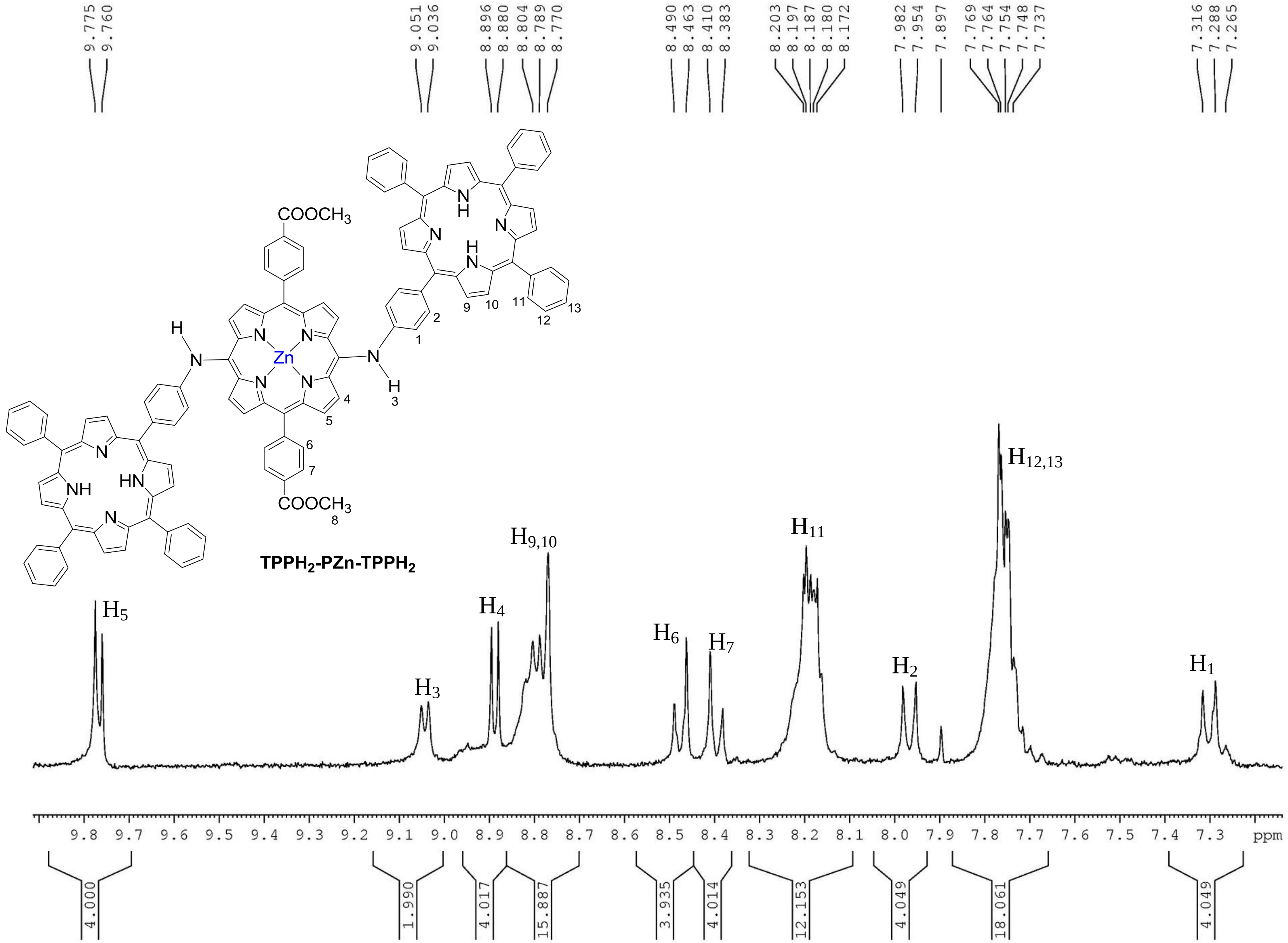


Figure S3. ^{1}H-NMR spectrum in d_8-THF of compound **TPPH$_2$-PZn-TPPH$_2$**, **72**.



TPPH$_2$-PZn-TPPH$_2$

Figure S3a. Aromatic region of ^{1}H-NMR spectrum in *d$_8$*-THF of compound **TPPH$_2$-PZn-TPPH$_2$, 72**.

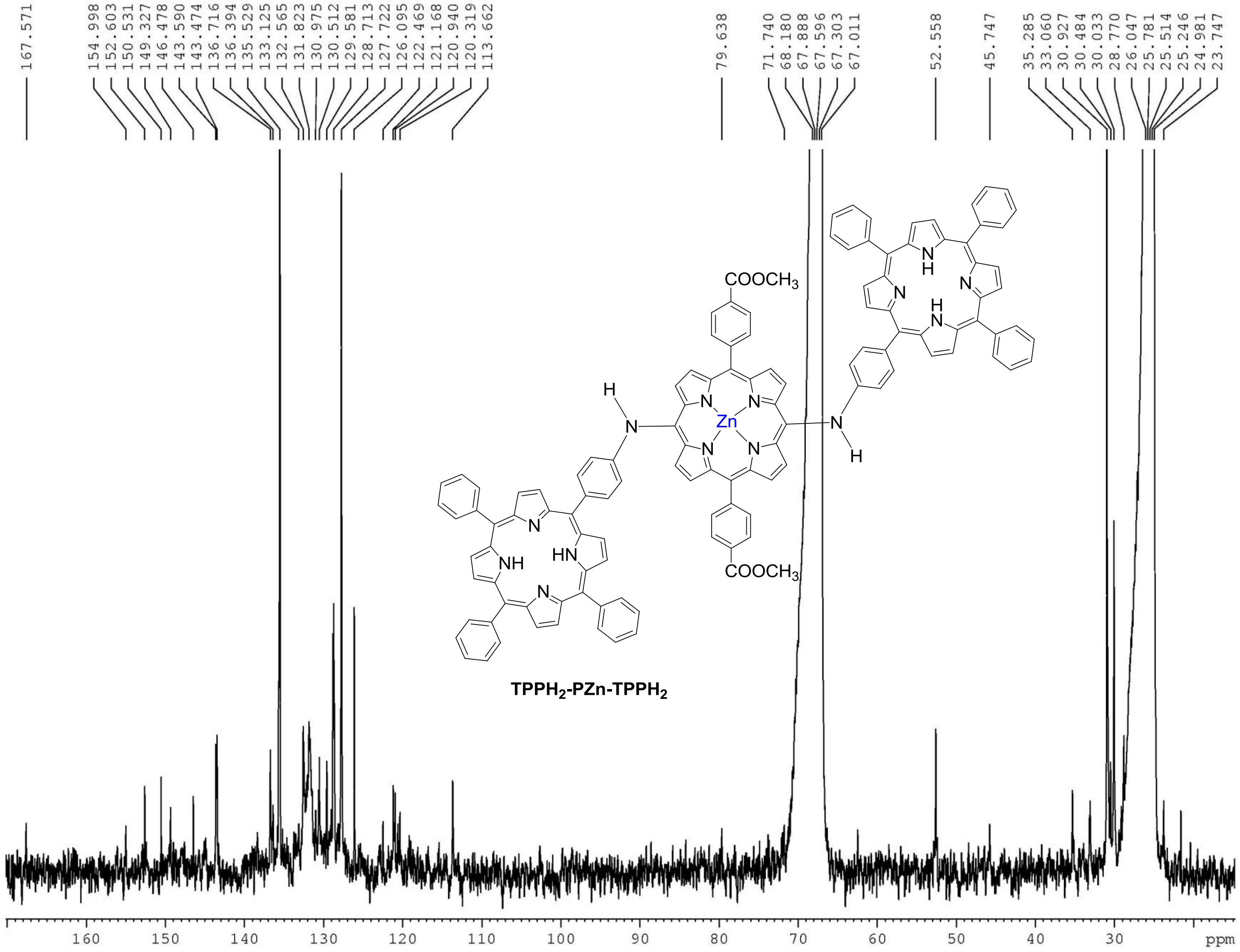


Figure S4. ^{13}C-NMR spectrum in *d$_8$*-THF of compound **TPPH$_2$-PZn-TPPH$_2$, 72**.

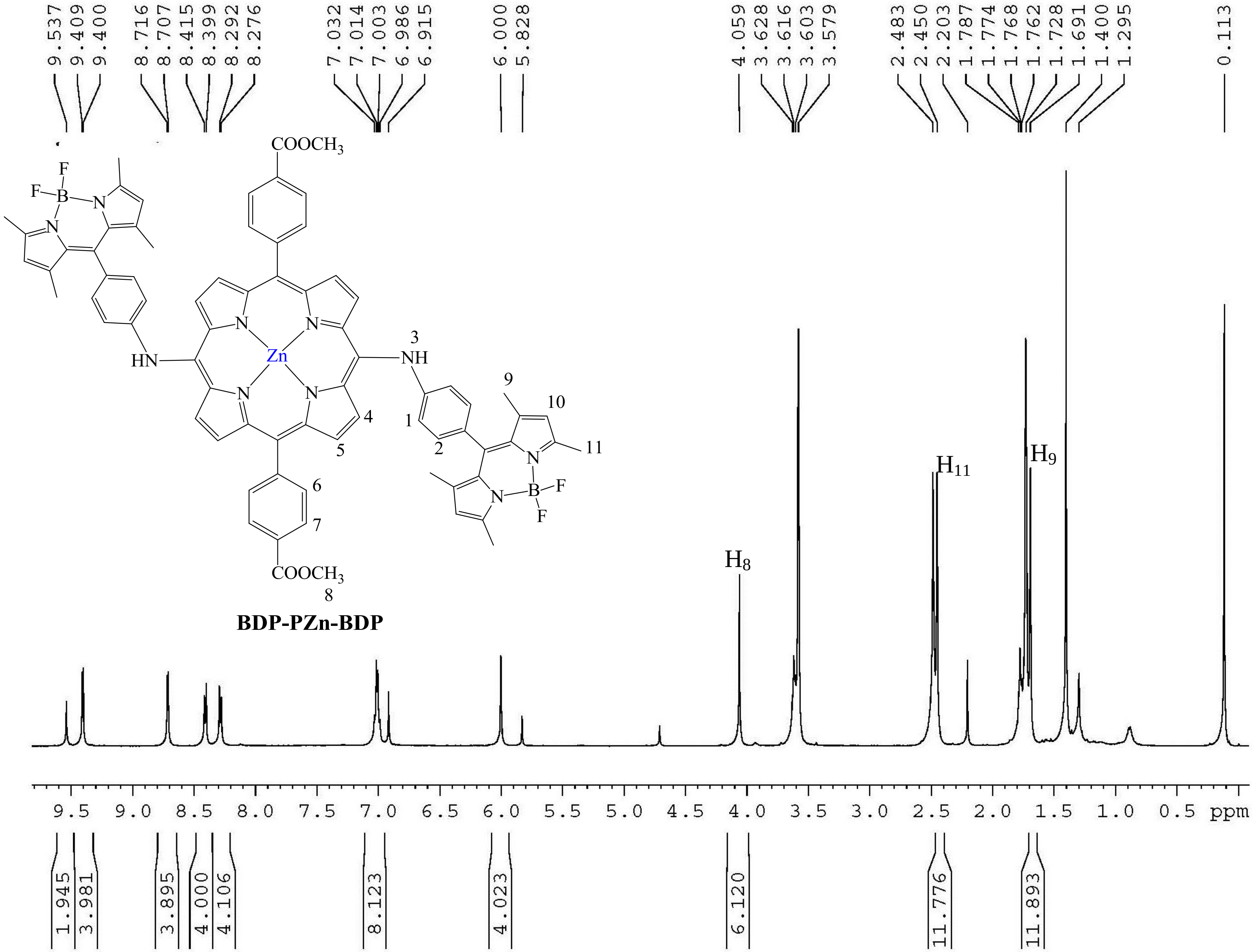


Figure S5. ^{1}H-NMR spectrum in d_8-THF of compound **BDP-PZn-BDP**, **74**.

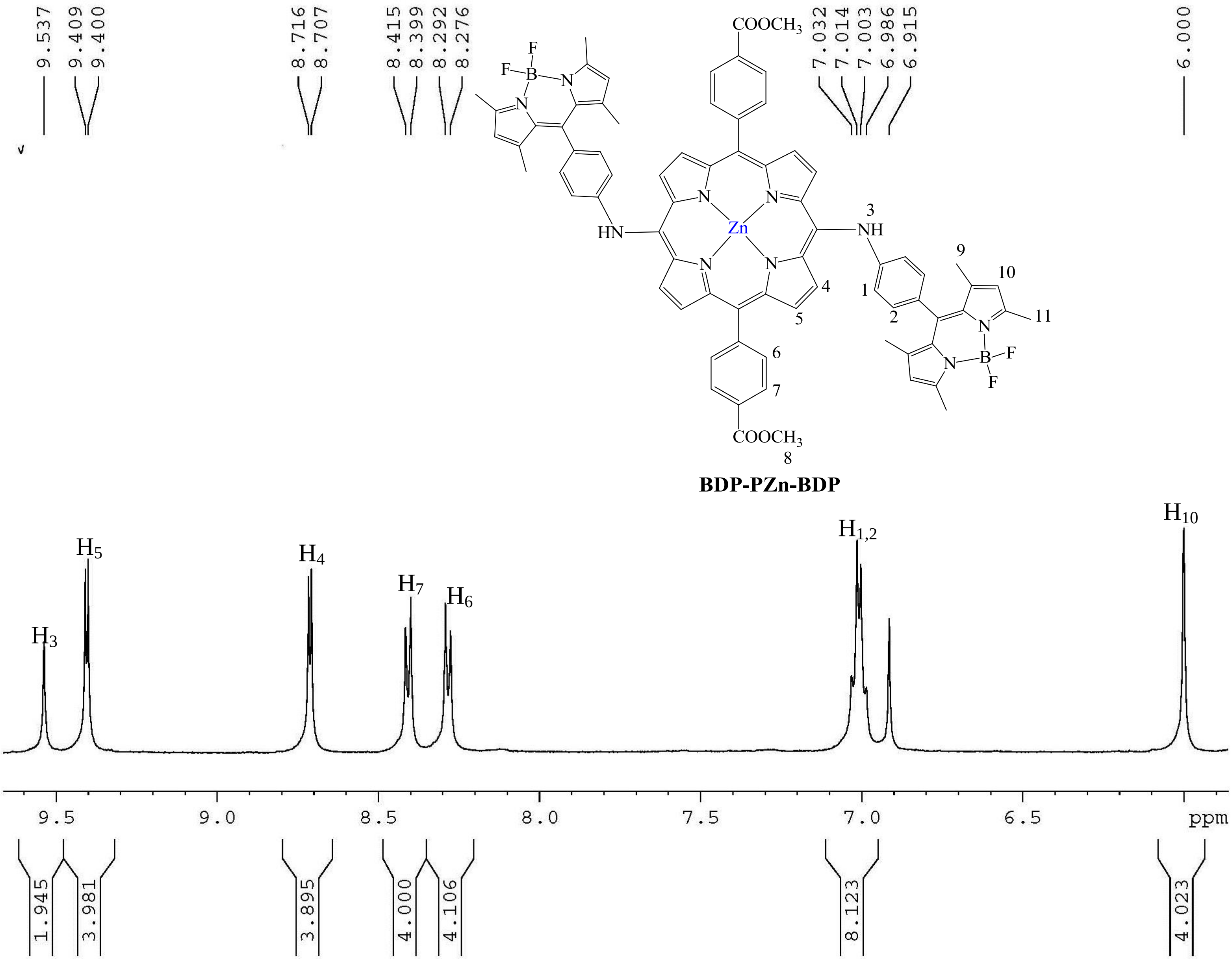


Figure S5a. Aromatic region of ^{1}H-NMR spectrum in d_8-THF of compound **BDP-PZn-BDP**, **74**..

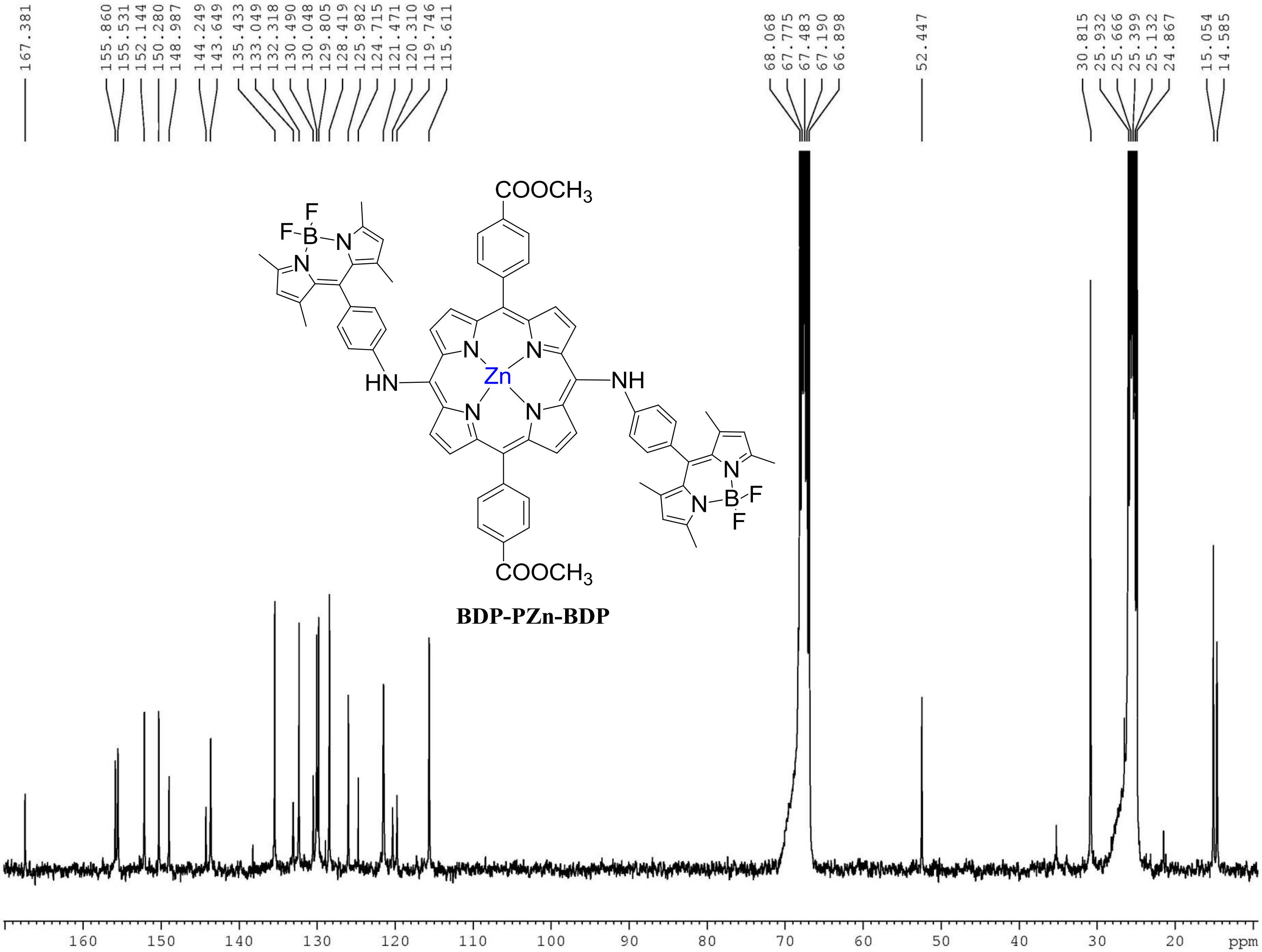


Figure S6. ^{13}C-NMR spectrum in d_8-THF of compound **BDP-PZn-BDP**, **74**.

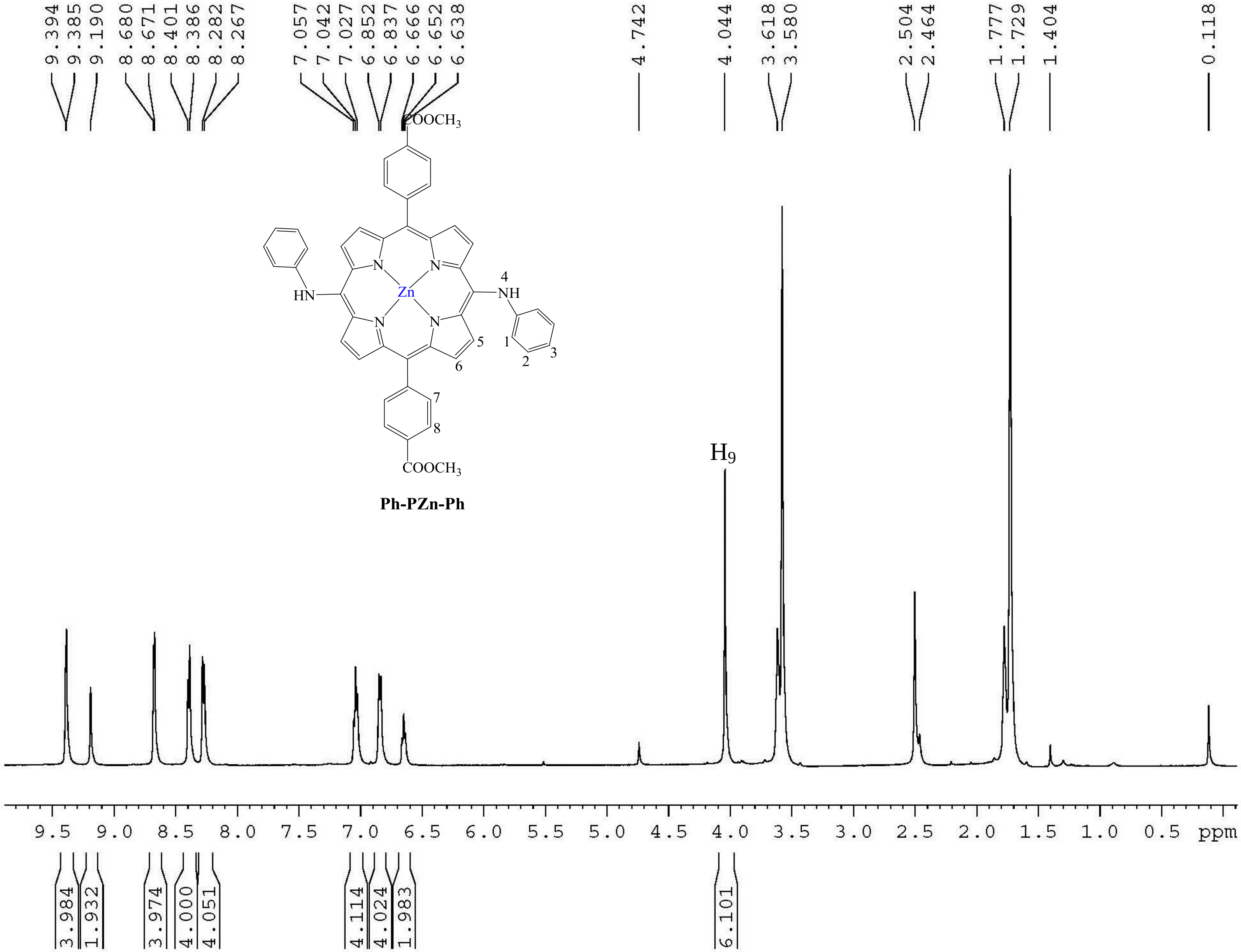


Figure S7. ^{1}H-NMR spectrum in d_8-THF of compound **Ph-PZn-Ph**, **75**.

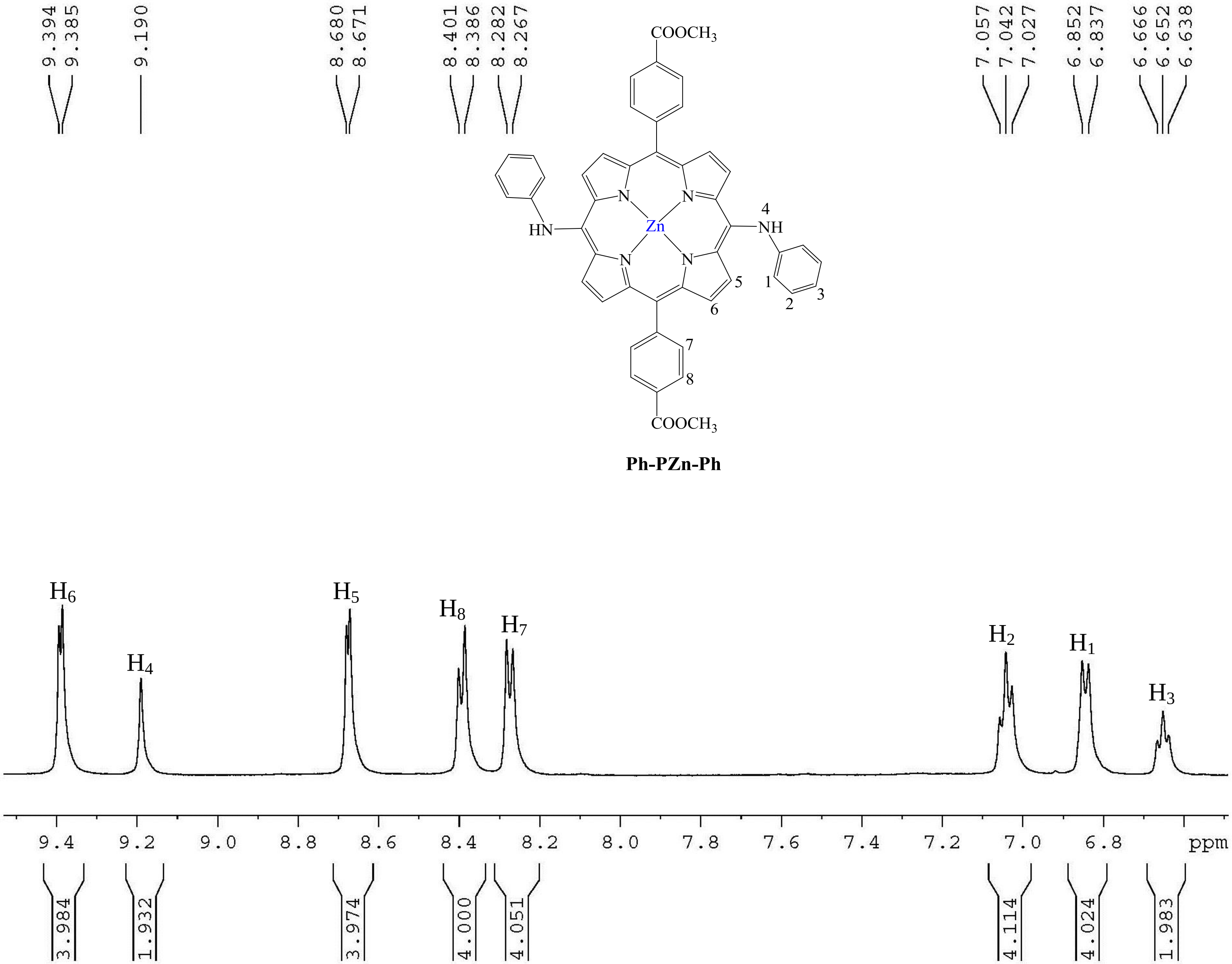


Figure S7a. Aromatic region of ^{1}H-NMR spectrum in d_8-THF of compound **Ph-PZn-Ph**, **75**.

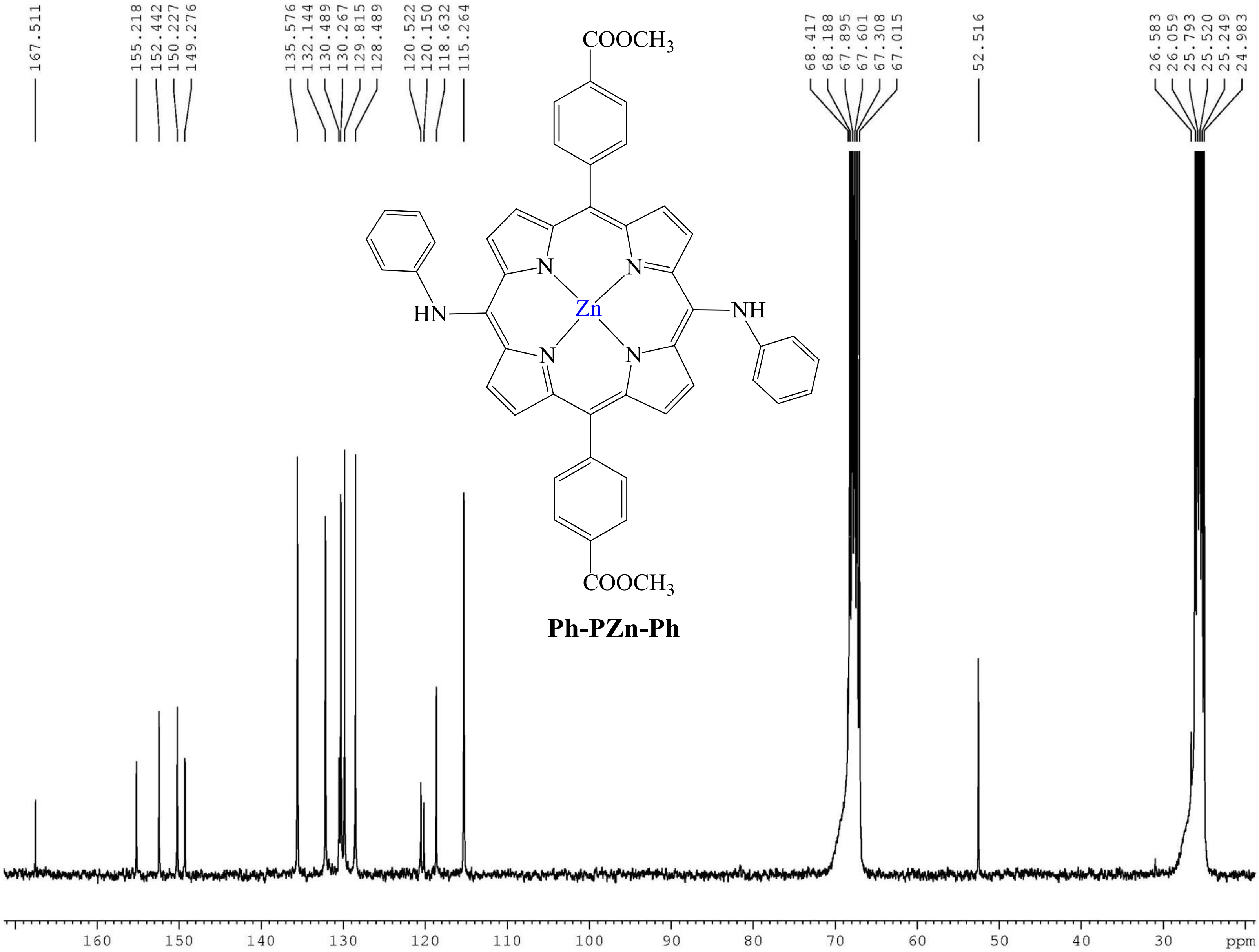


Figure S8. ^{13}C-NMR spectrum in *d*$_8$-THF of compound **Ph-PZn-Ph**, **75**.

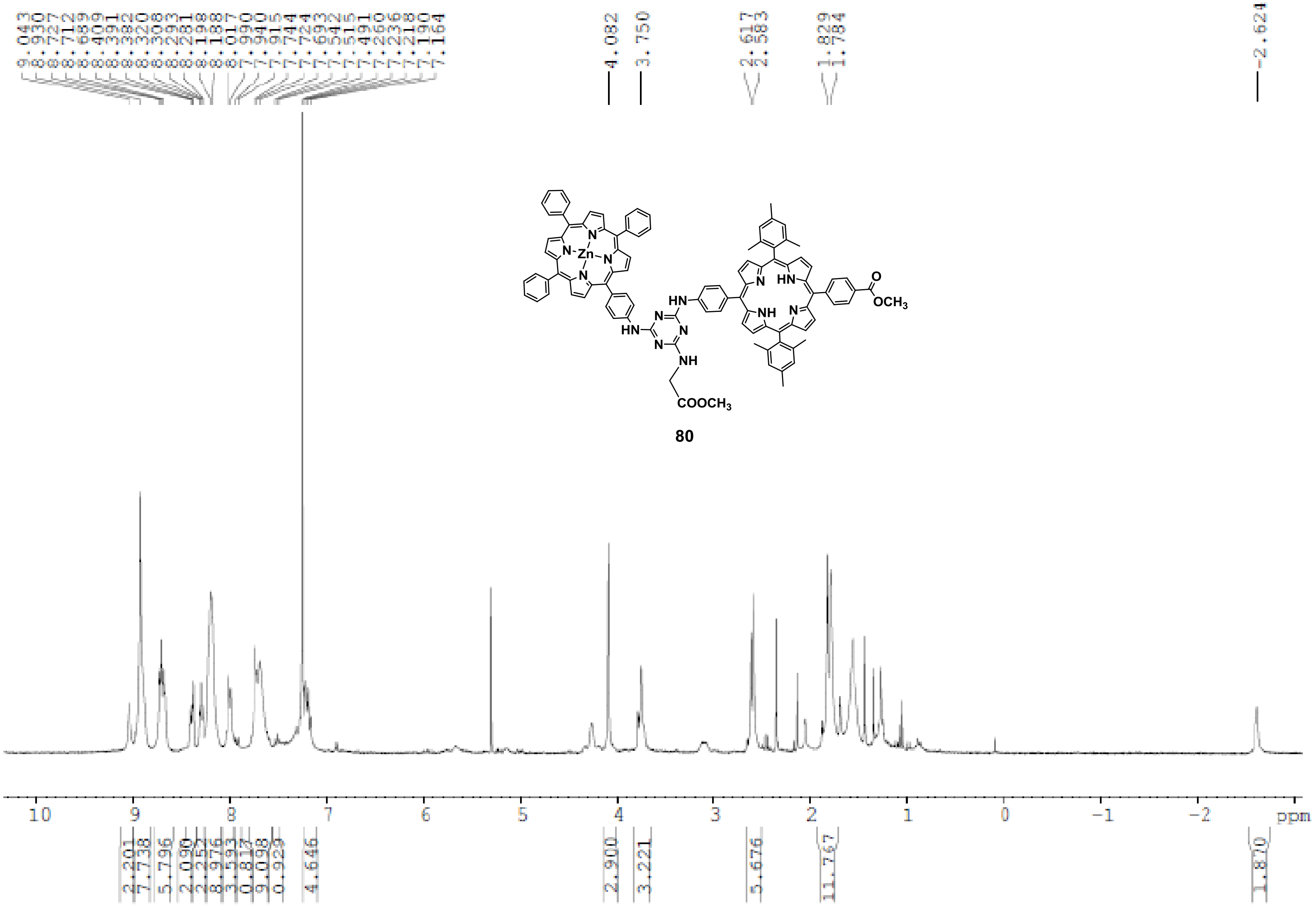


Figure S9. ^{1}H-NMR spectrum in $CDCl_3$ of compound **80.**

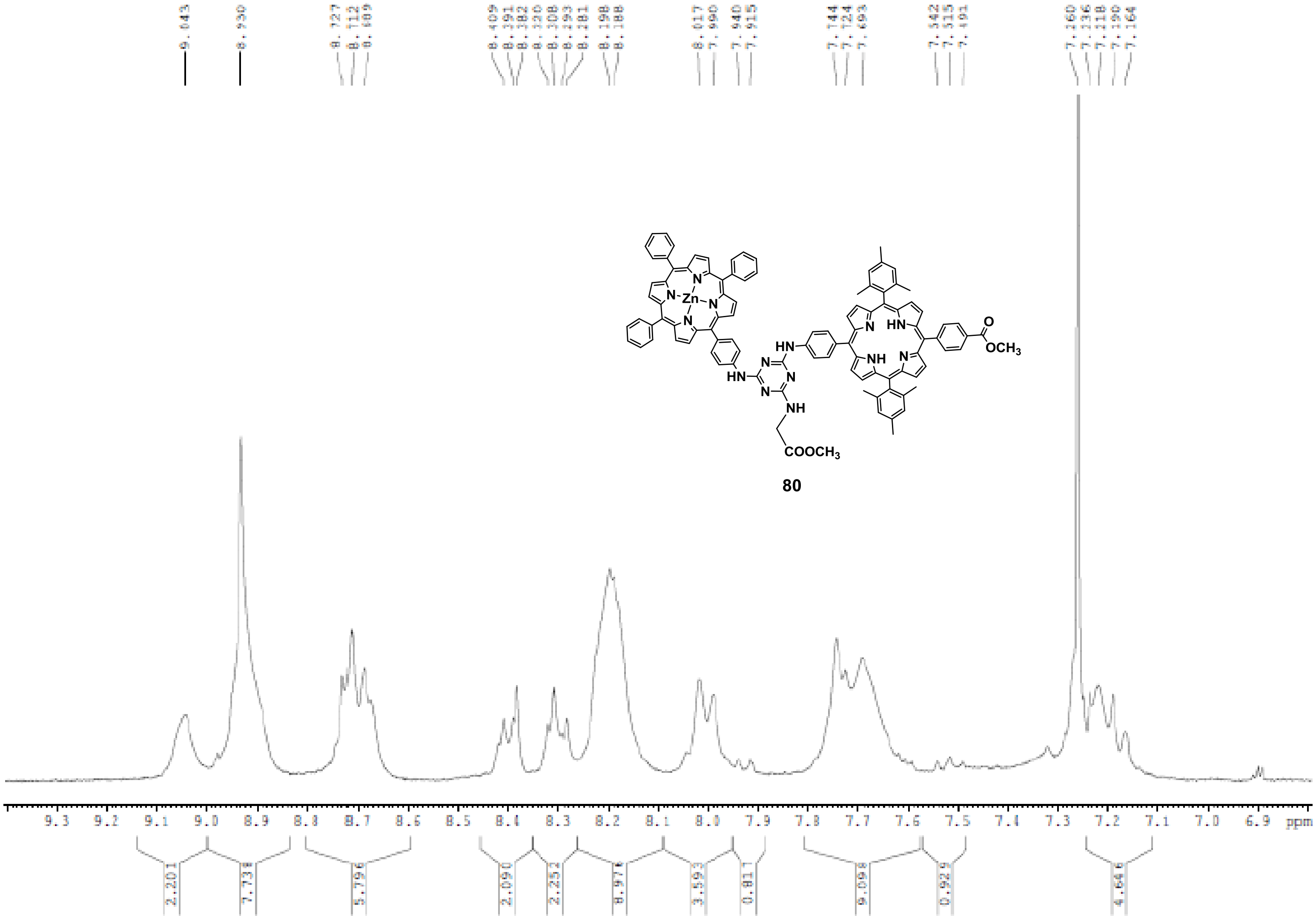


Figure S9a. Aromatic region of ^{1}H-NMR spectrum in $CDCl_3$ of compound **80.**

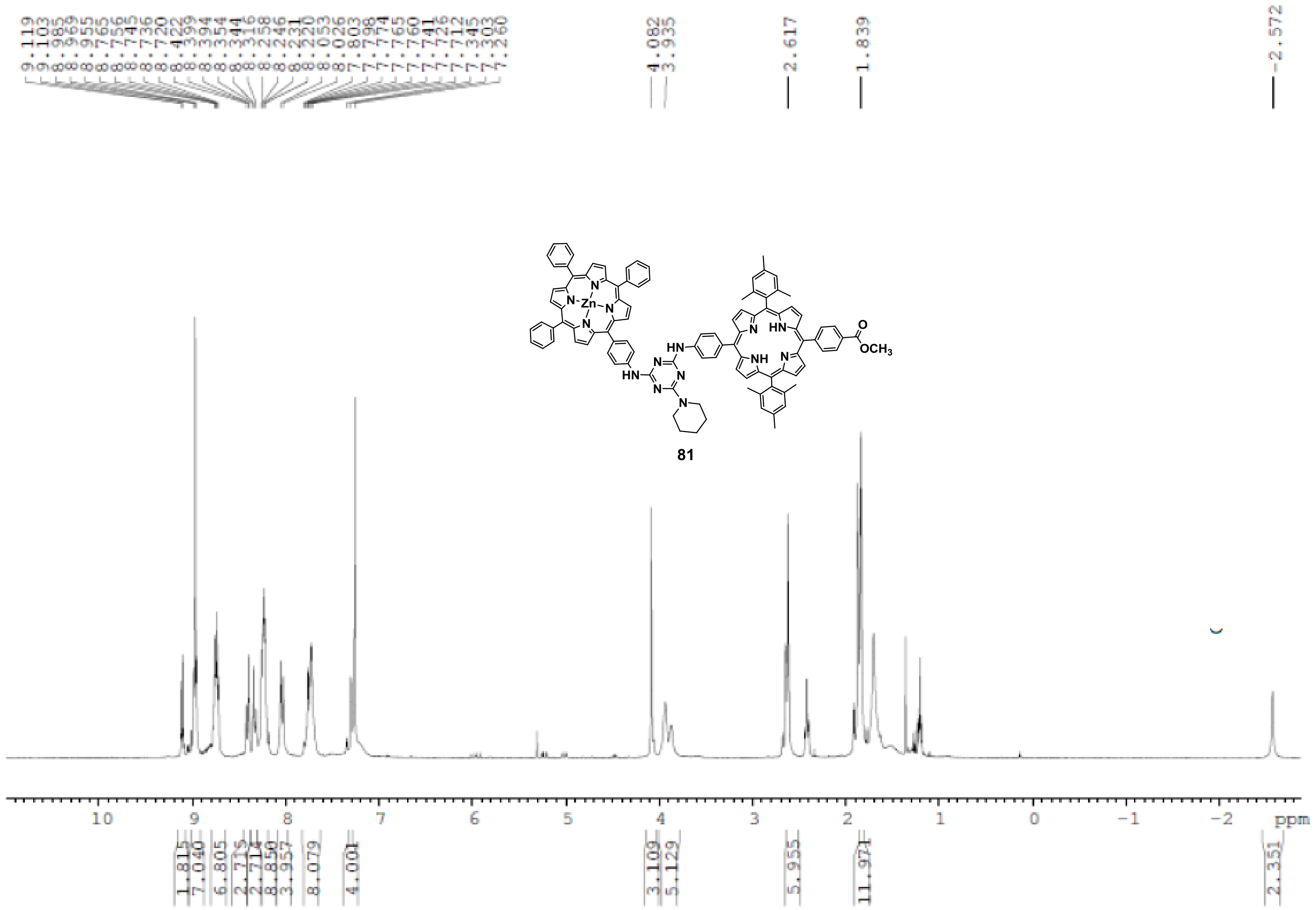


Figure S10. ^{1}H-NMR spectrum in $CDCl_3$ of compound **81.**

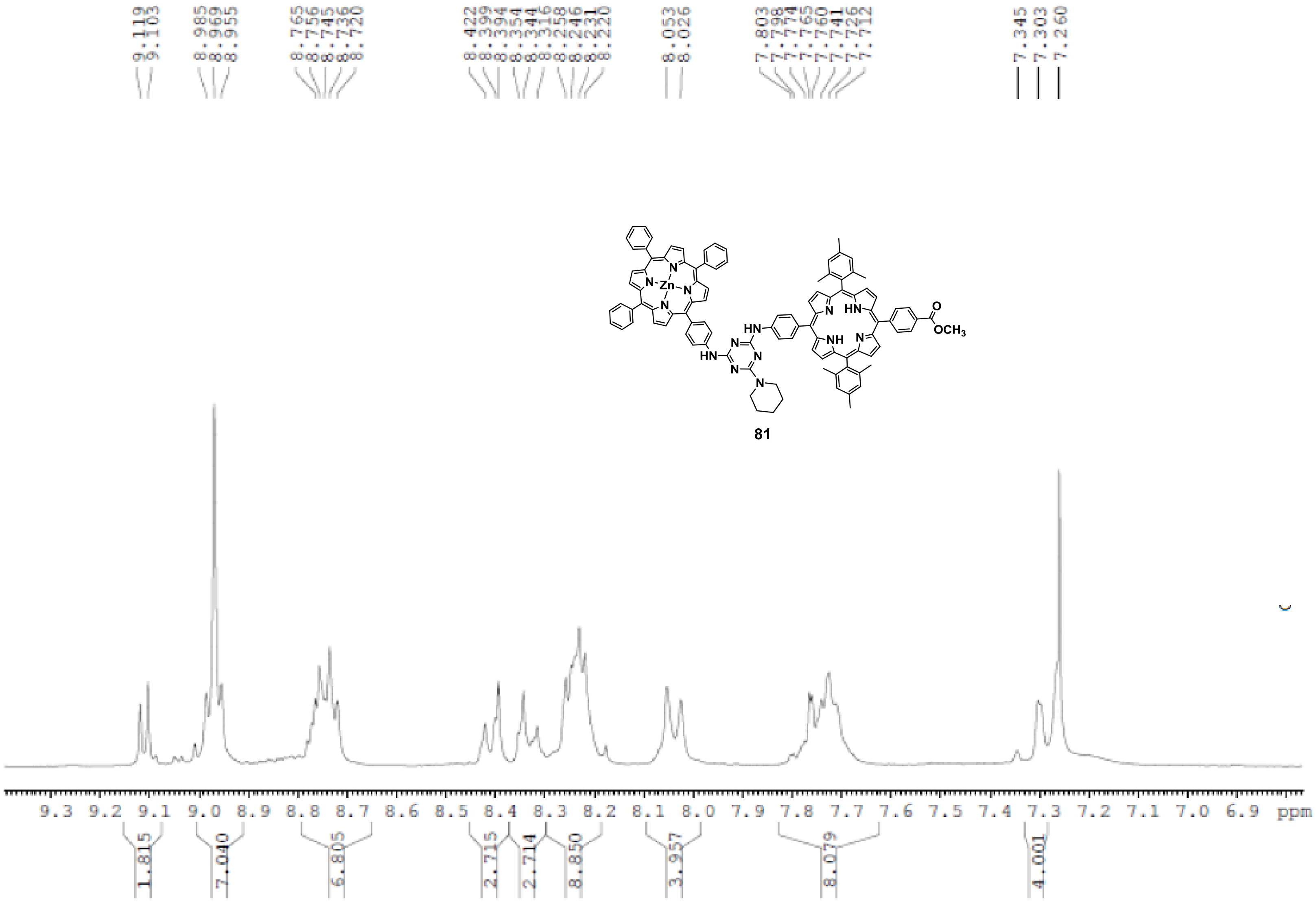


Figure S10a. Aromatic region of ^{1}H-NMR spectrum in $CDCl_3$ of compound **81.**

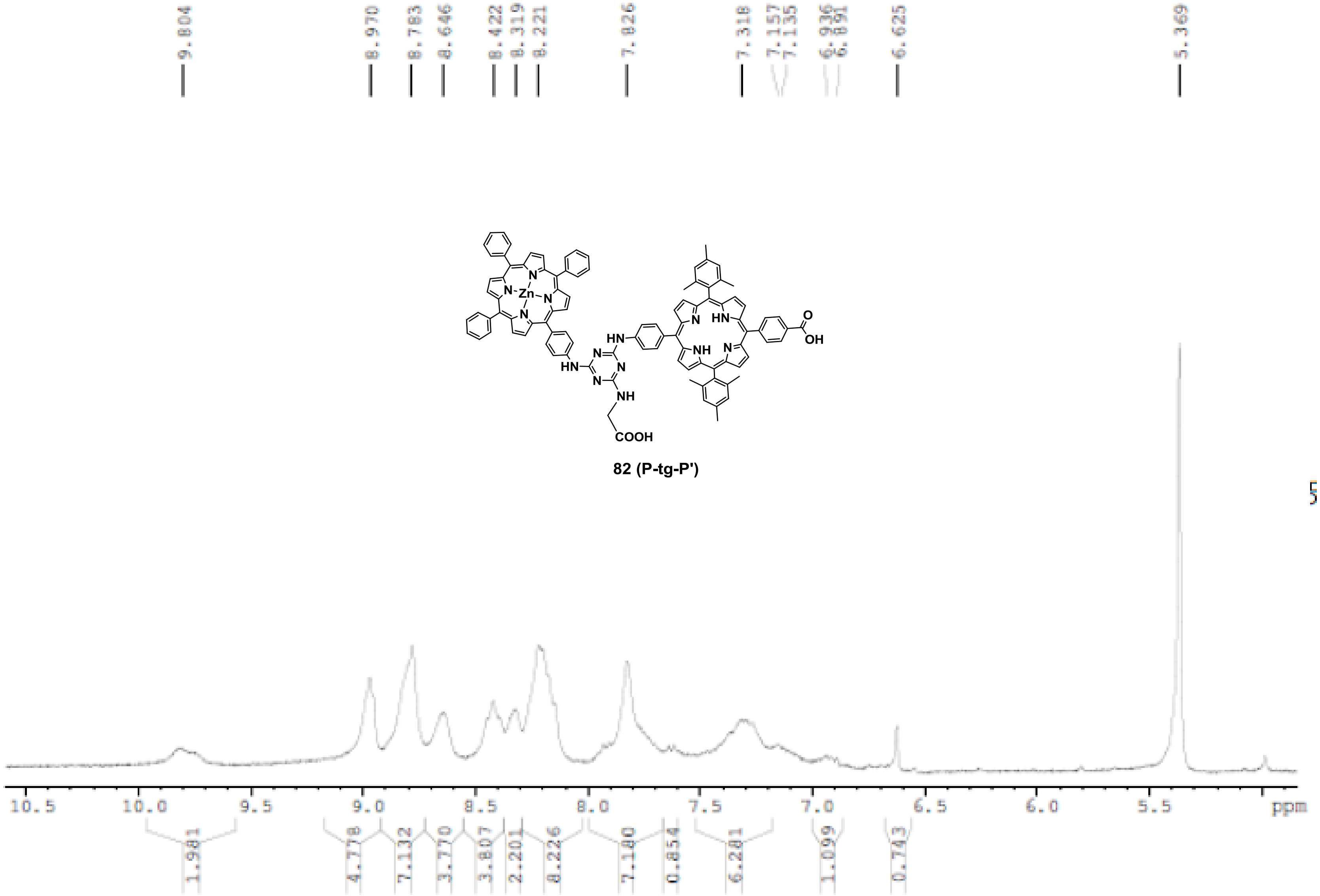


Figure S11. ^{1}H-NMR spectrum in d_6-DMSO of compound **82.**

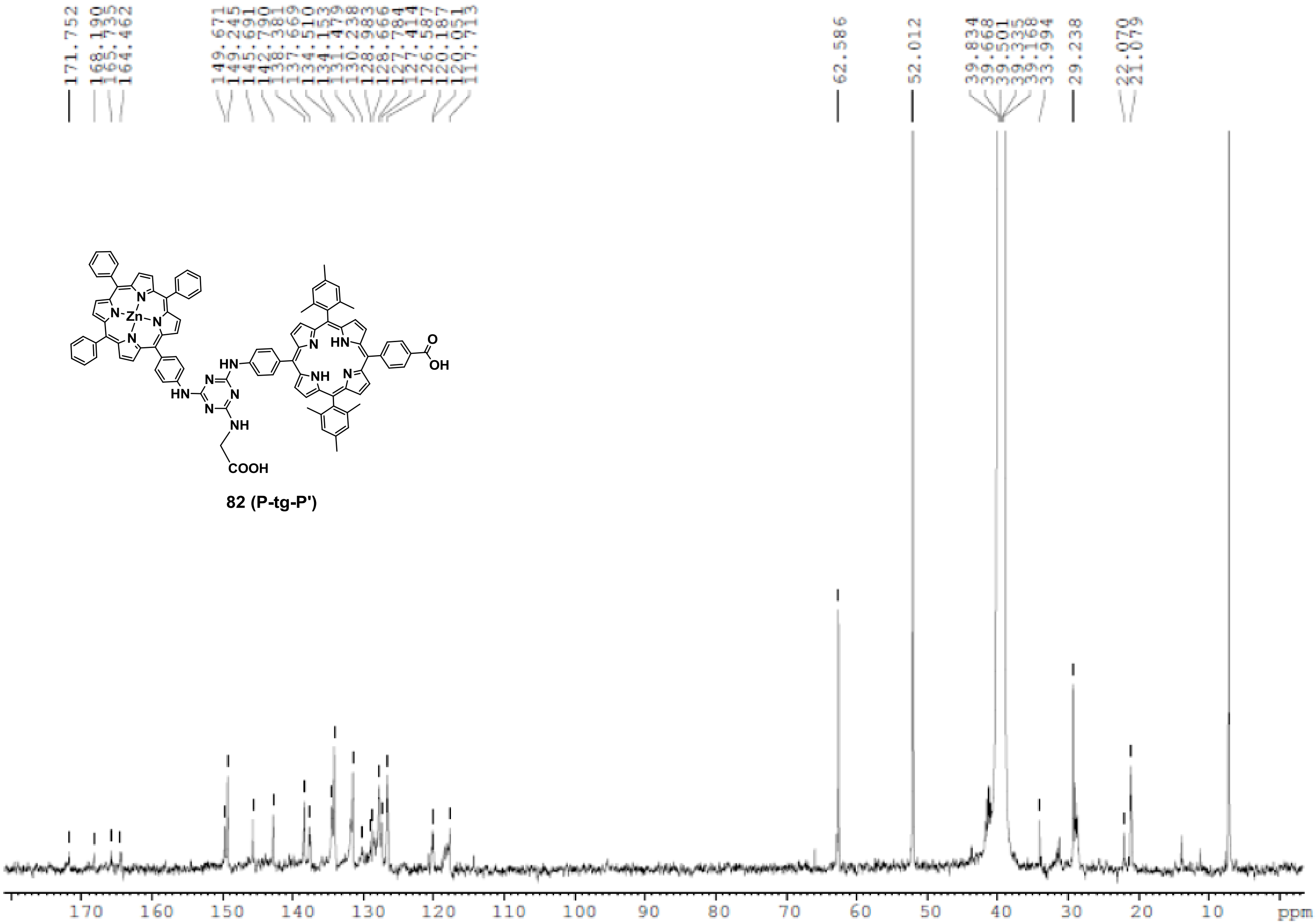


Figure S12. ^{13}C-NMR spectrum in d_6-DMSO of compound **82.**

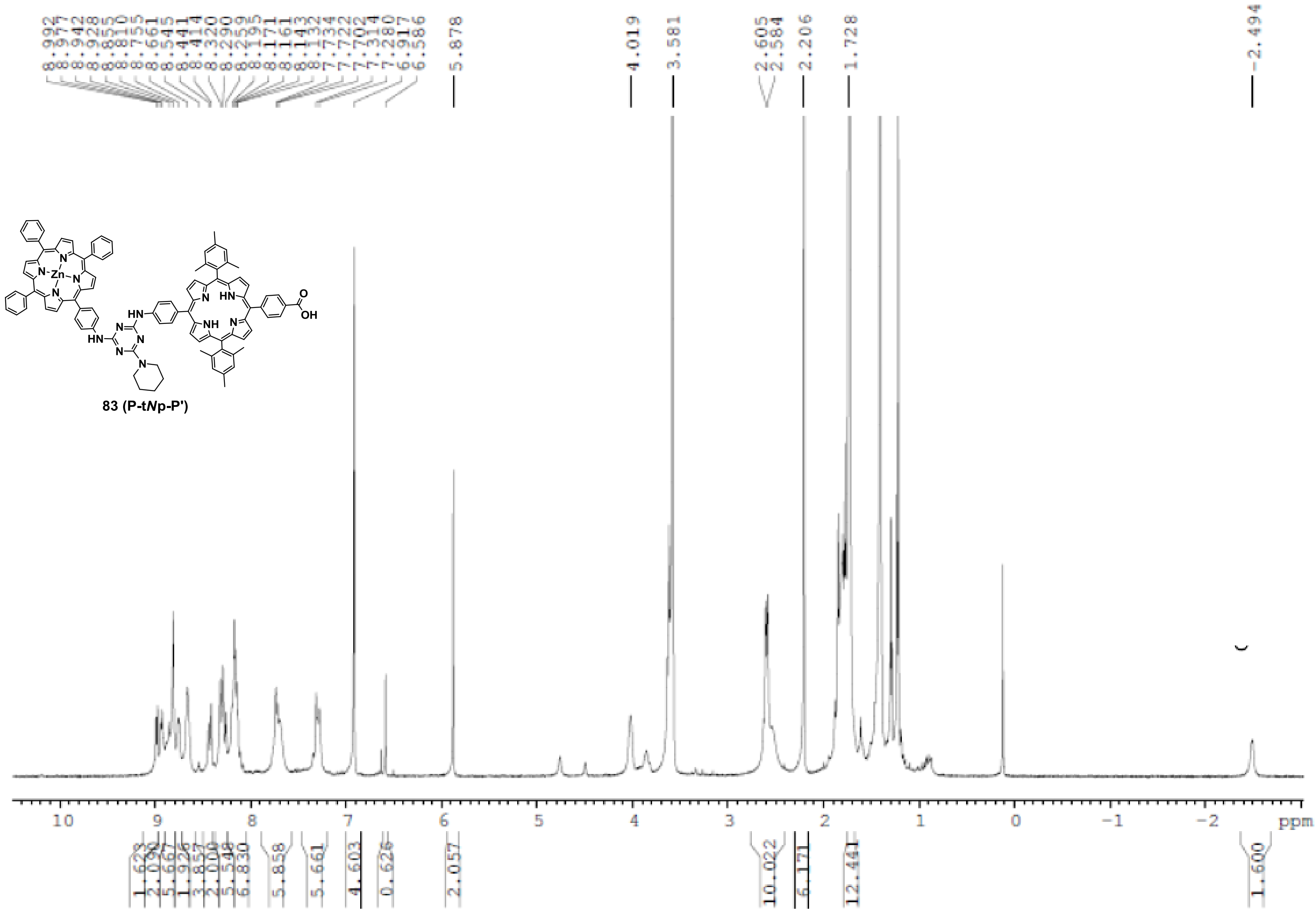


Figure S13. ^{1}H-NMR spectrum in $CDCl_3$ of compound **83.**

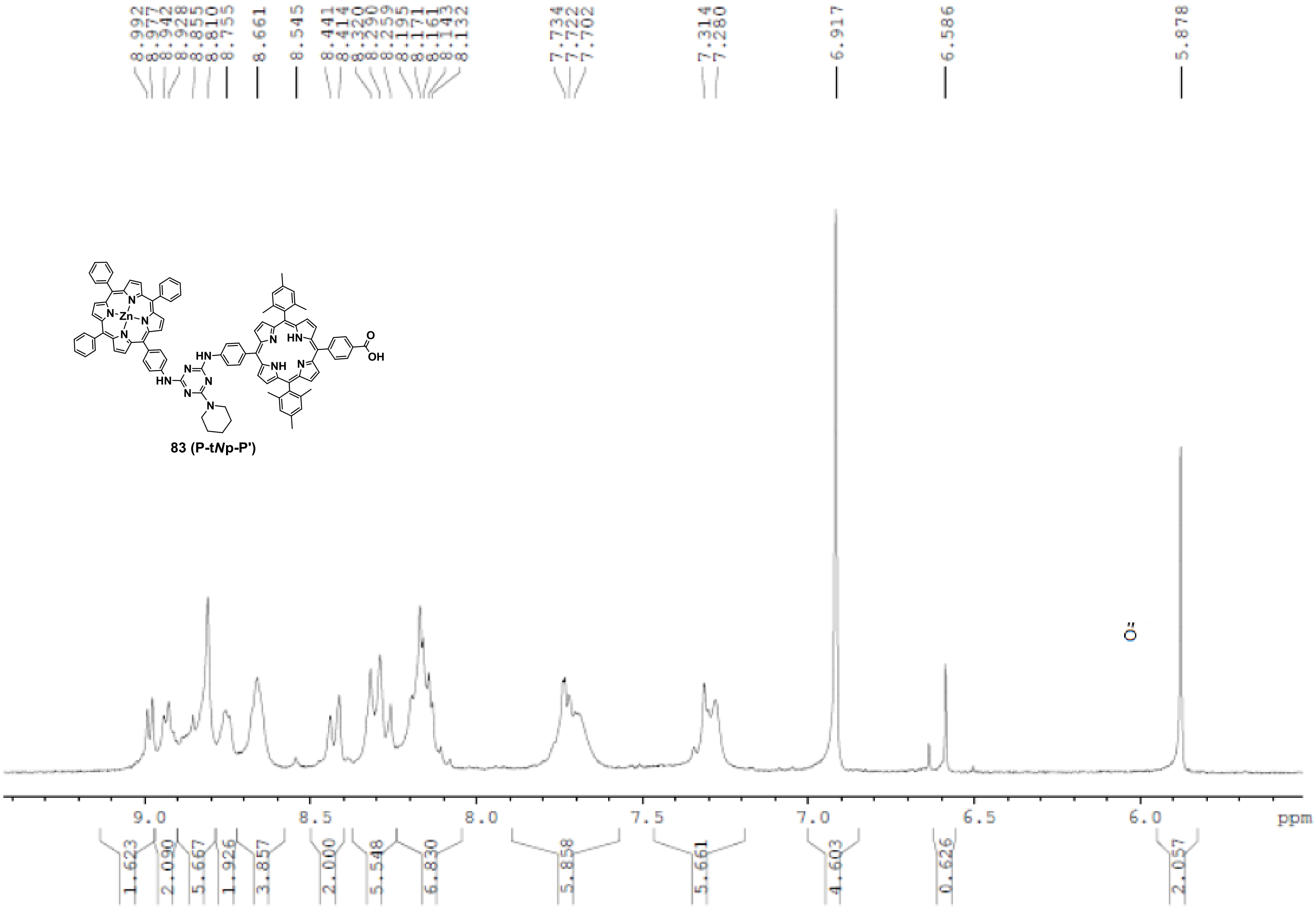


Figure S13a. Aromatic region ^{1}H-NMR spectrum in d_6-DMSO of compound **83.**

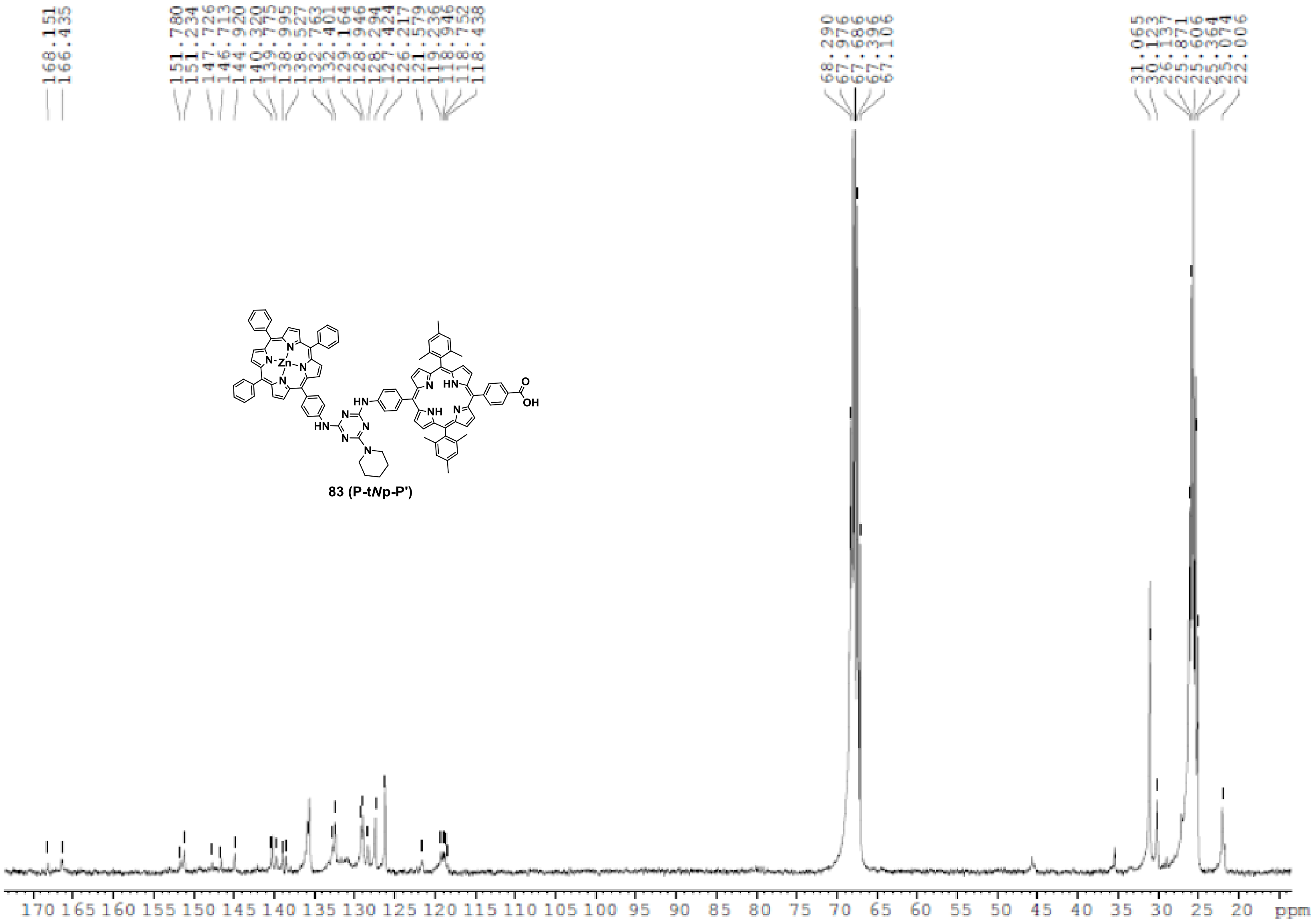


Figure S14. ^{13}C-NMR spectrum in d_6-DMSO of compound **83.**

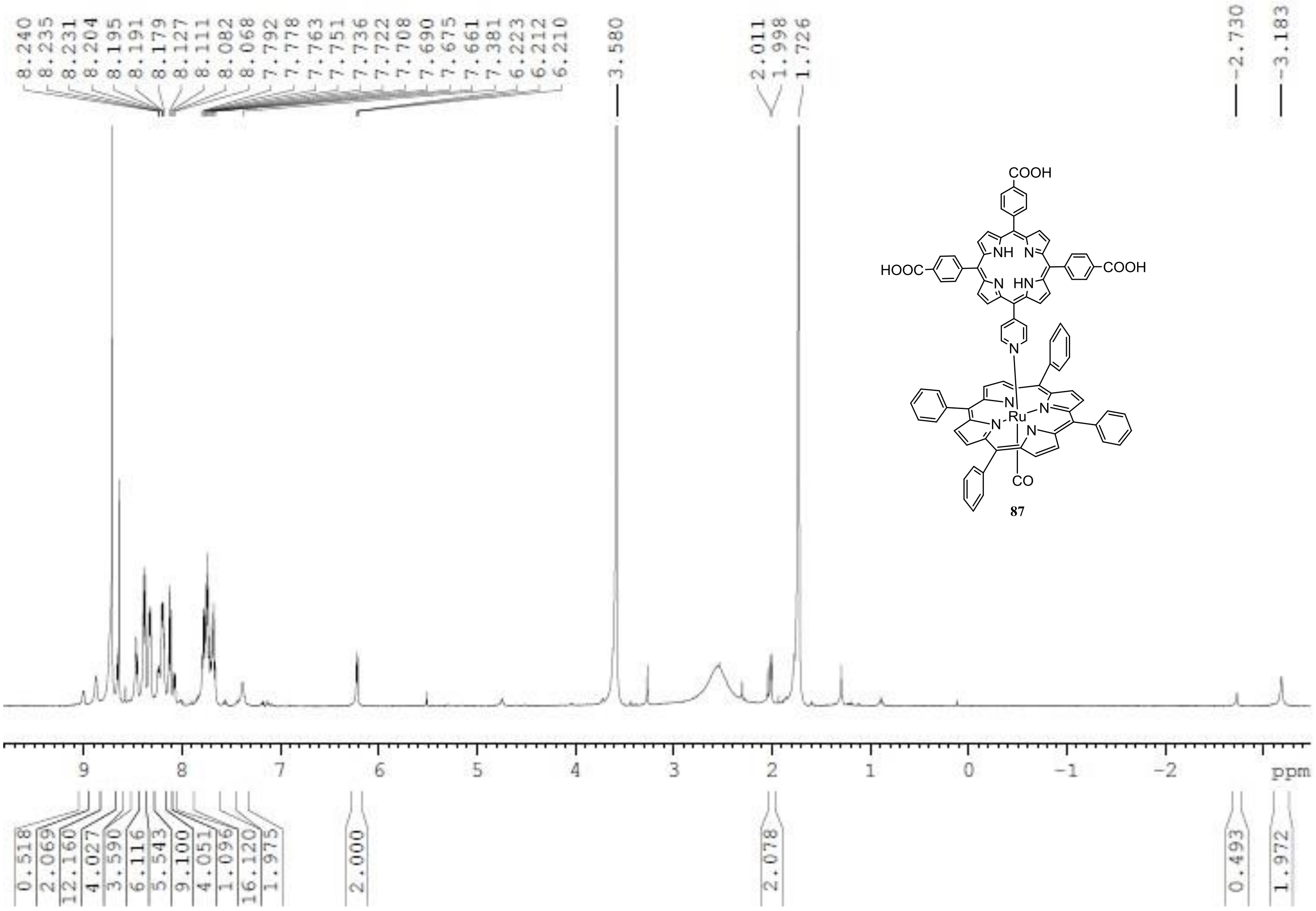


Figure S15. ^{1}H-NMR spectrum in d_8-THF of compound **87.**

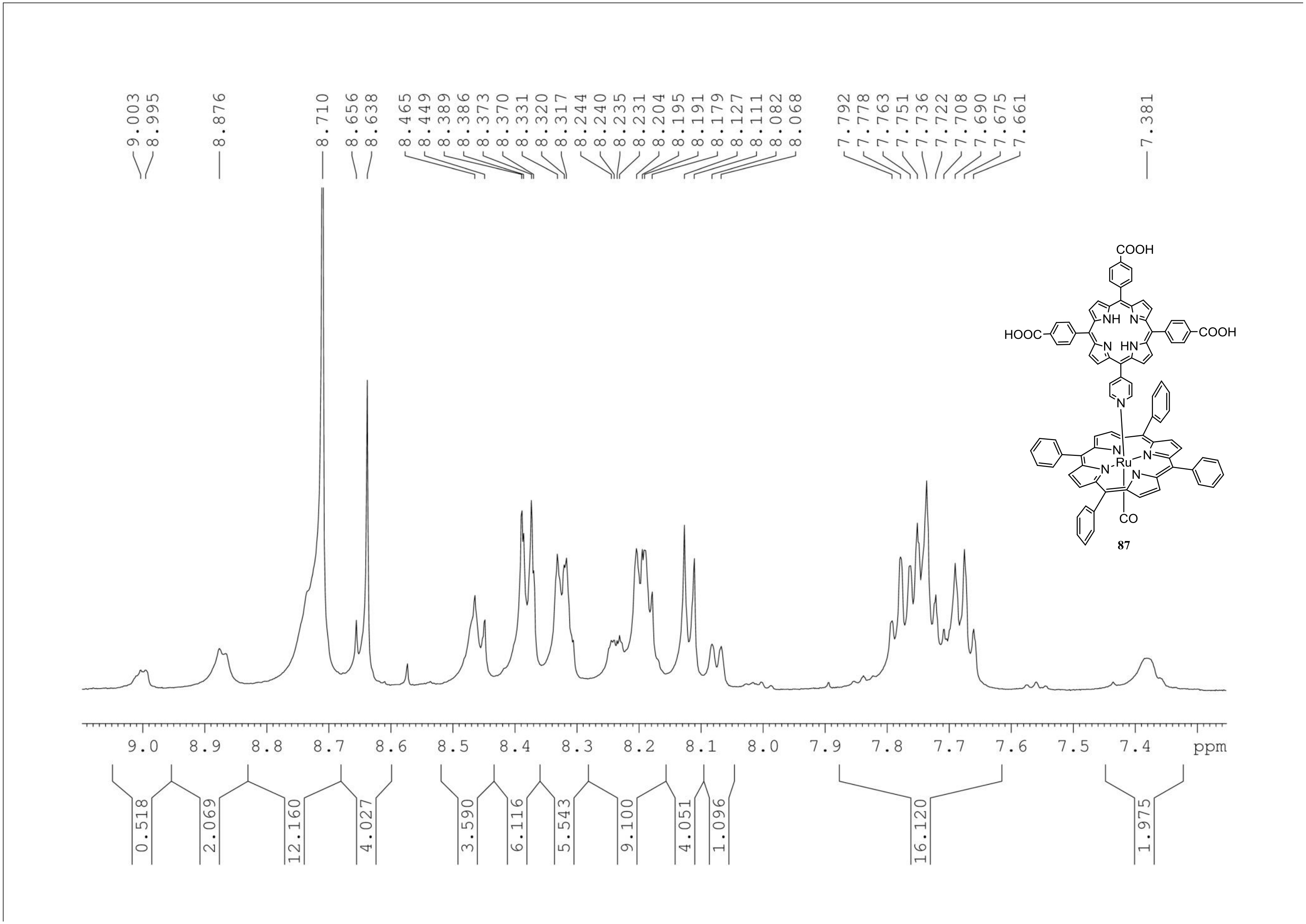


Figure S15a. Aromatic region of ^{1}H-NMR in d_8-THF of compound **87**.

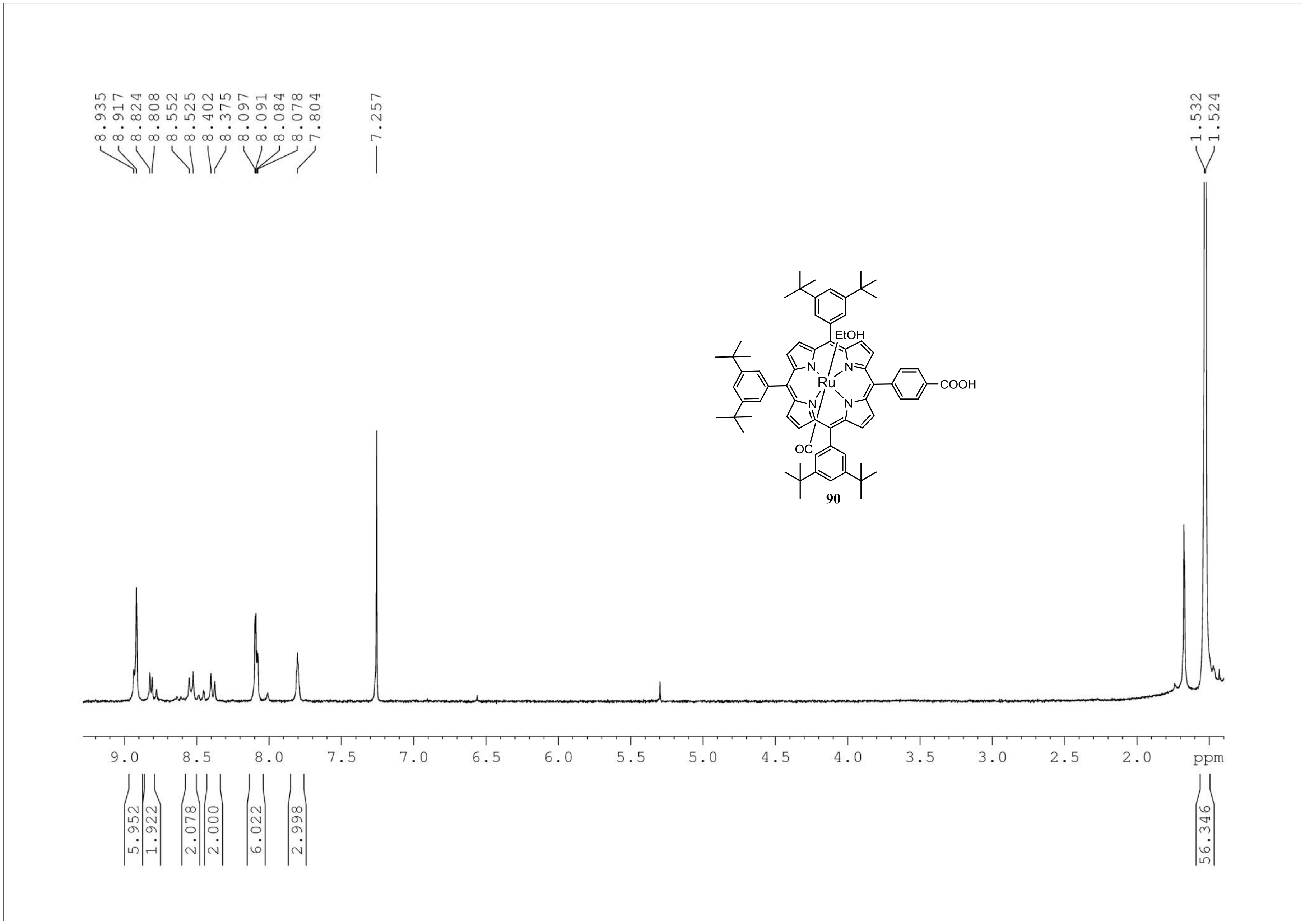


Figure S16. ^{1}H-NMR in $CDCl_3$ of compound **90**.

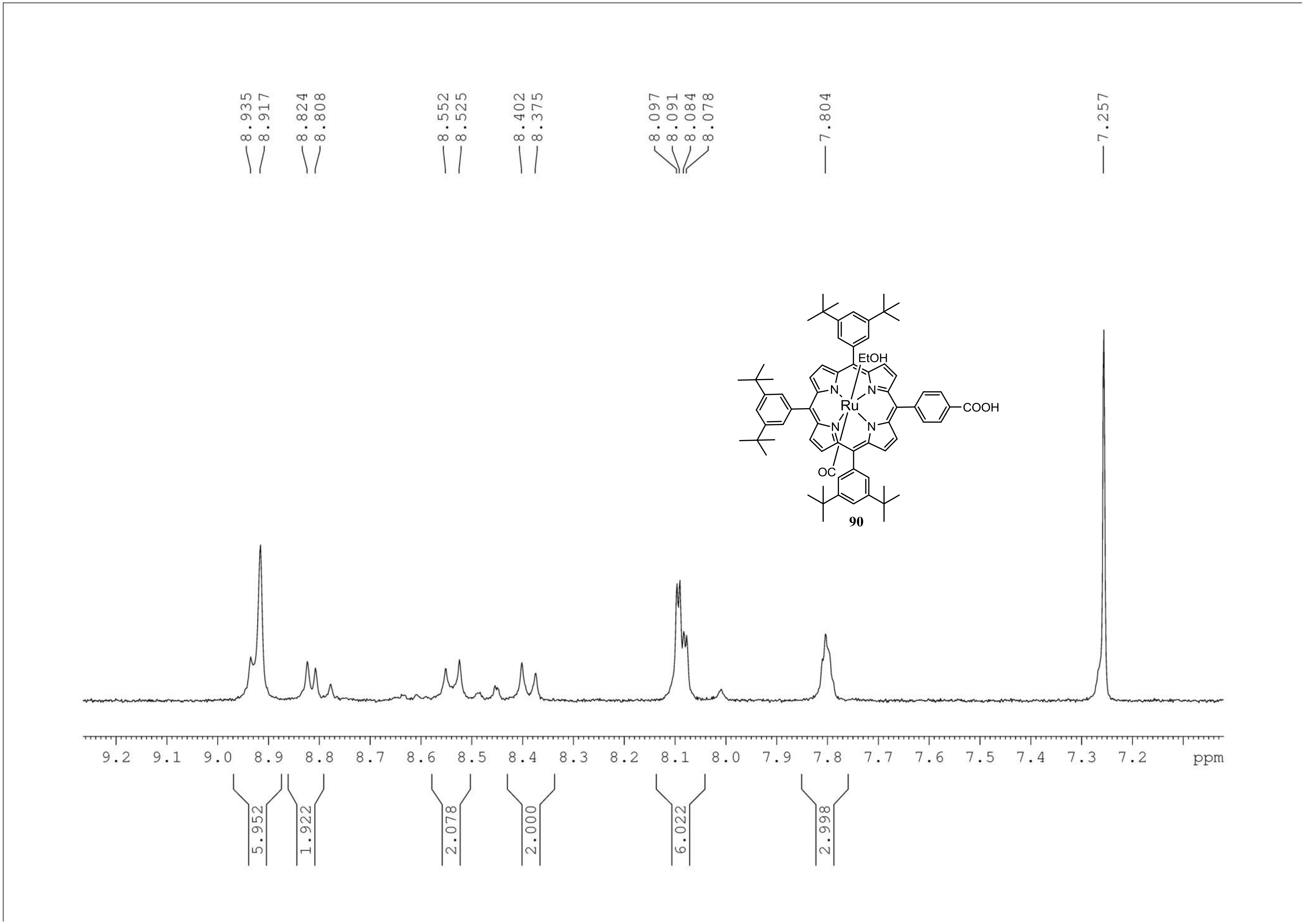


Figure S16a. Aromatic region ^{1}H-NMR in $CDCl_3$ of compound **90**.

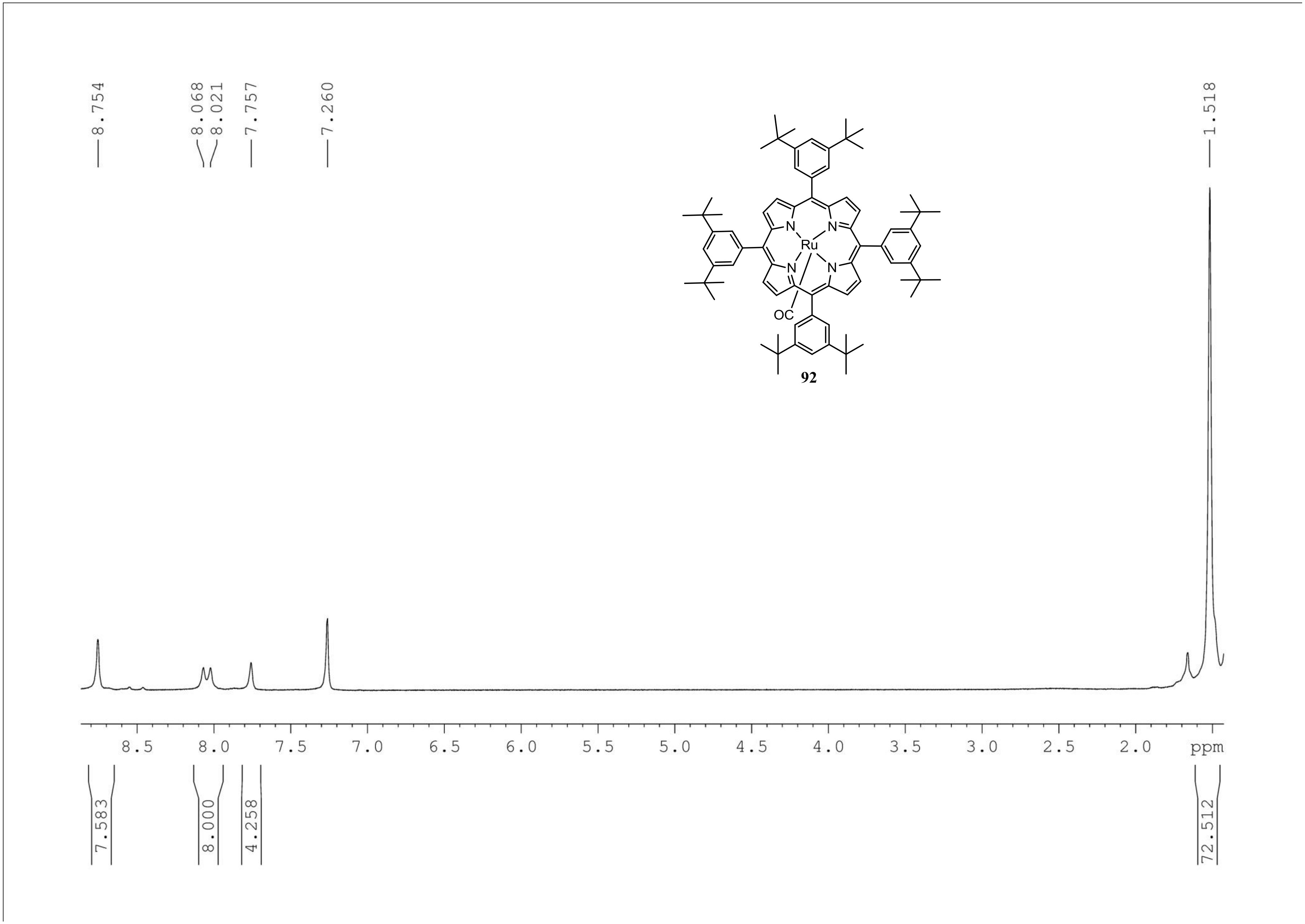


Figure S17. ^{1}H-NMR in $CDCl_3$ of compound **92**.

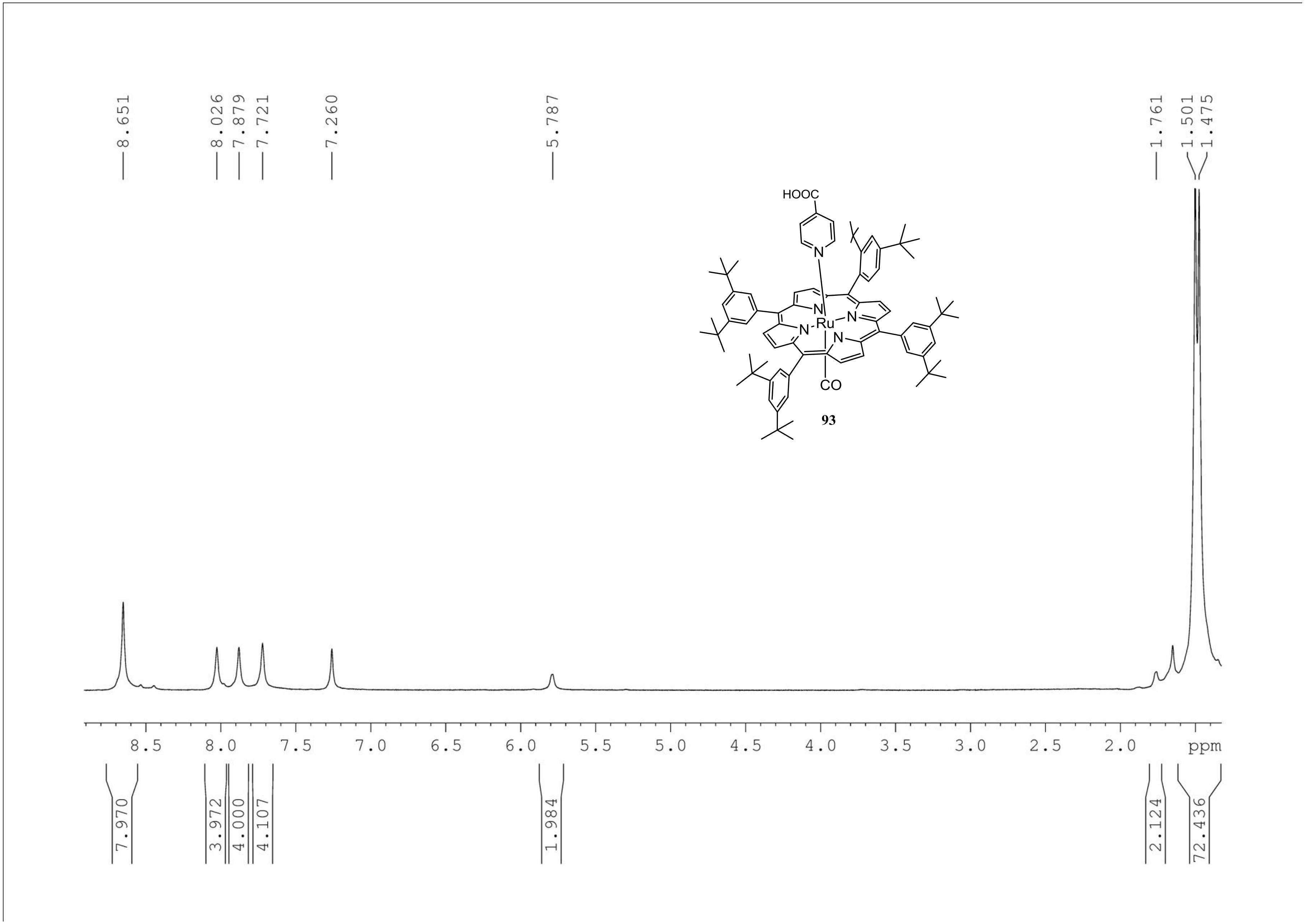


Figure S18. ^{1}H-NMR in $CDCl_3$ of compound **93**.

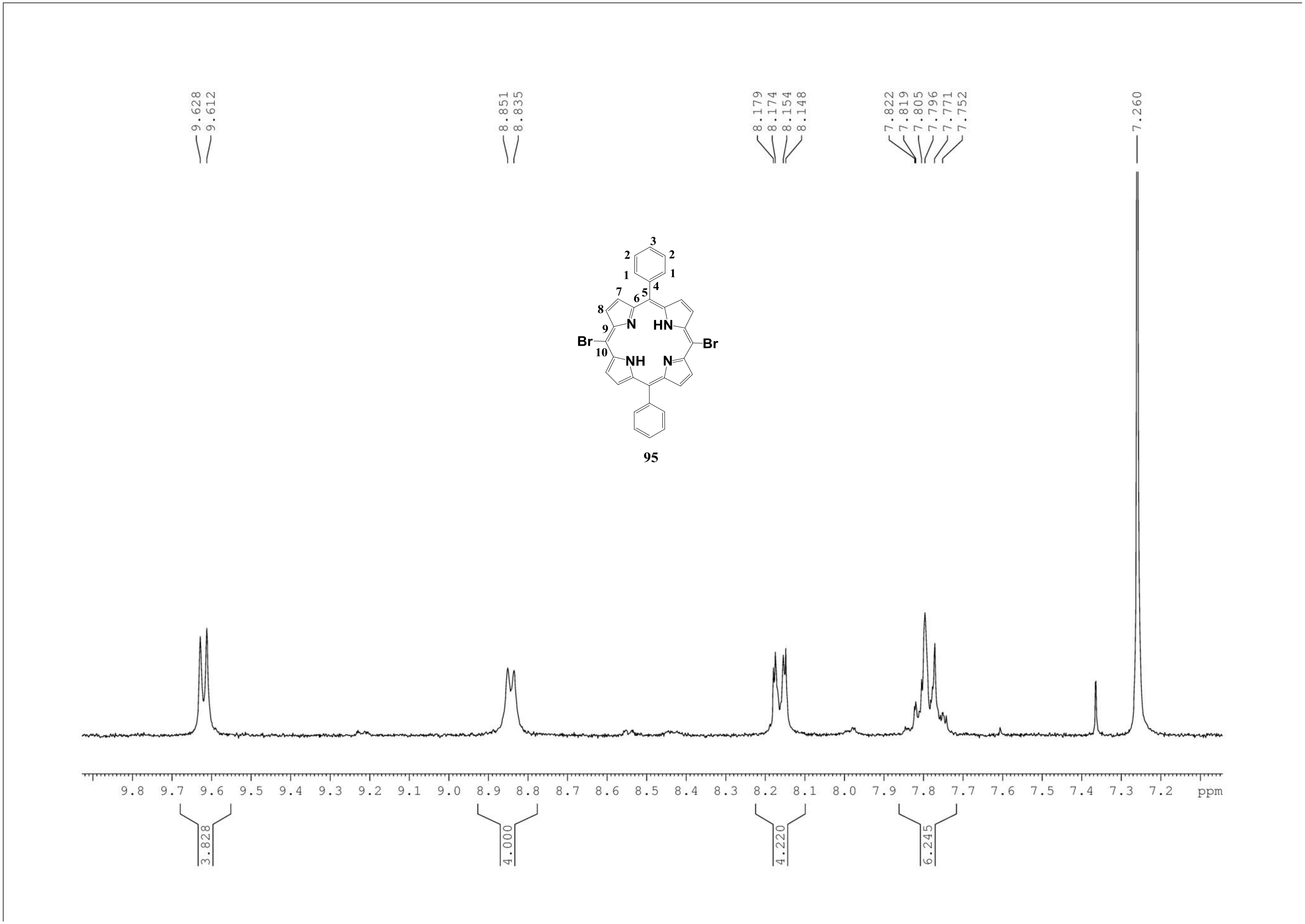


Figure S19. ^{1}H-NMR in $CDCl_3$ of compound **95**.

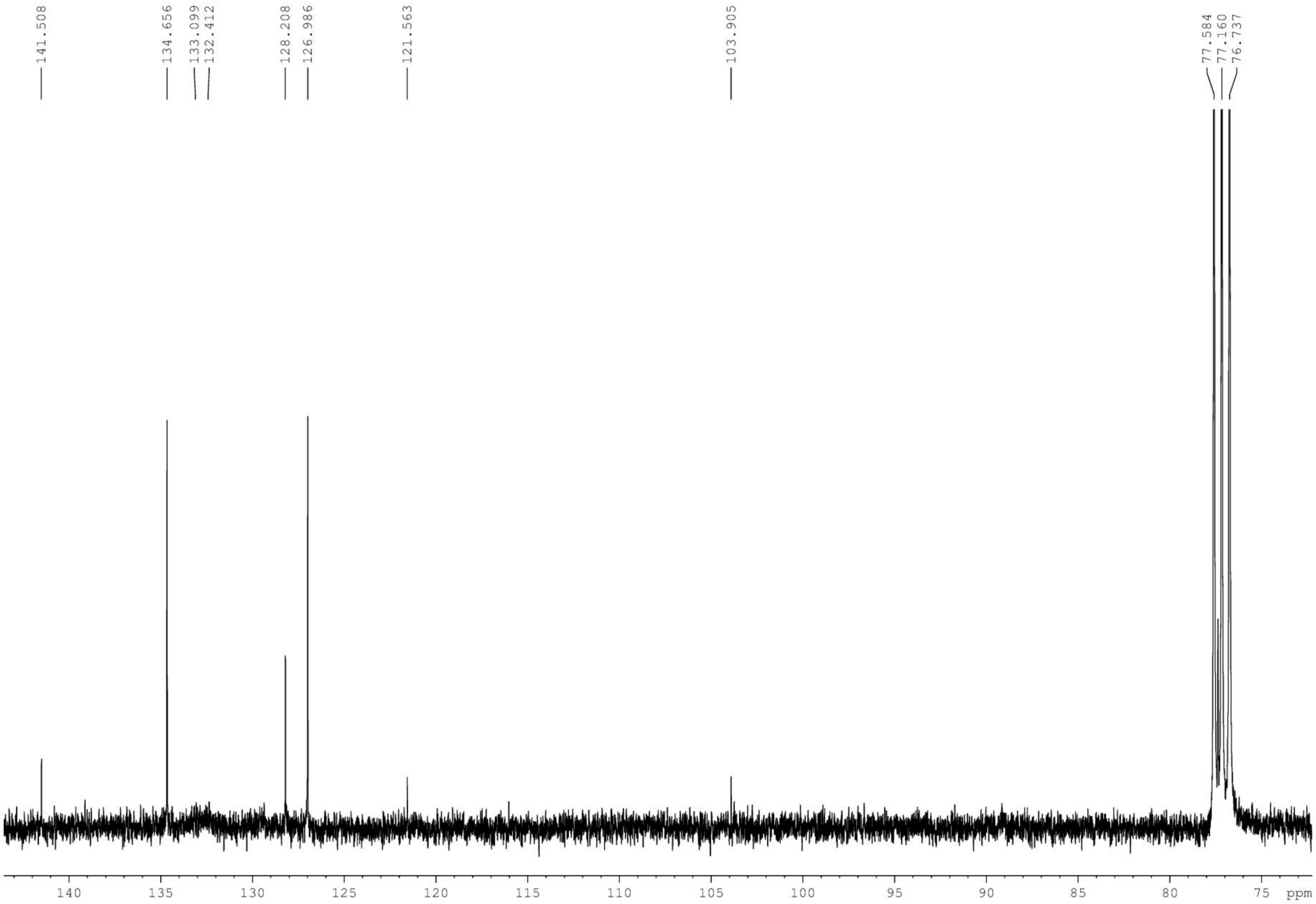


Figure S20. ^{13}C-NMR in CDCl$_3$ of compound **95**.

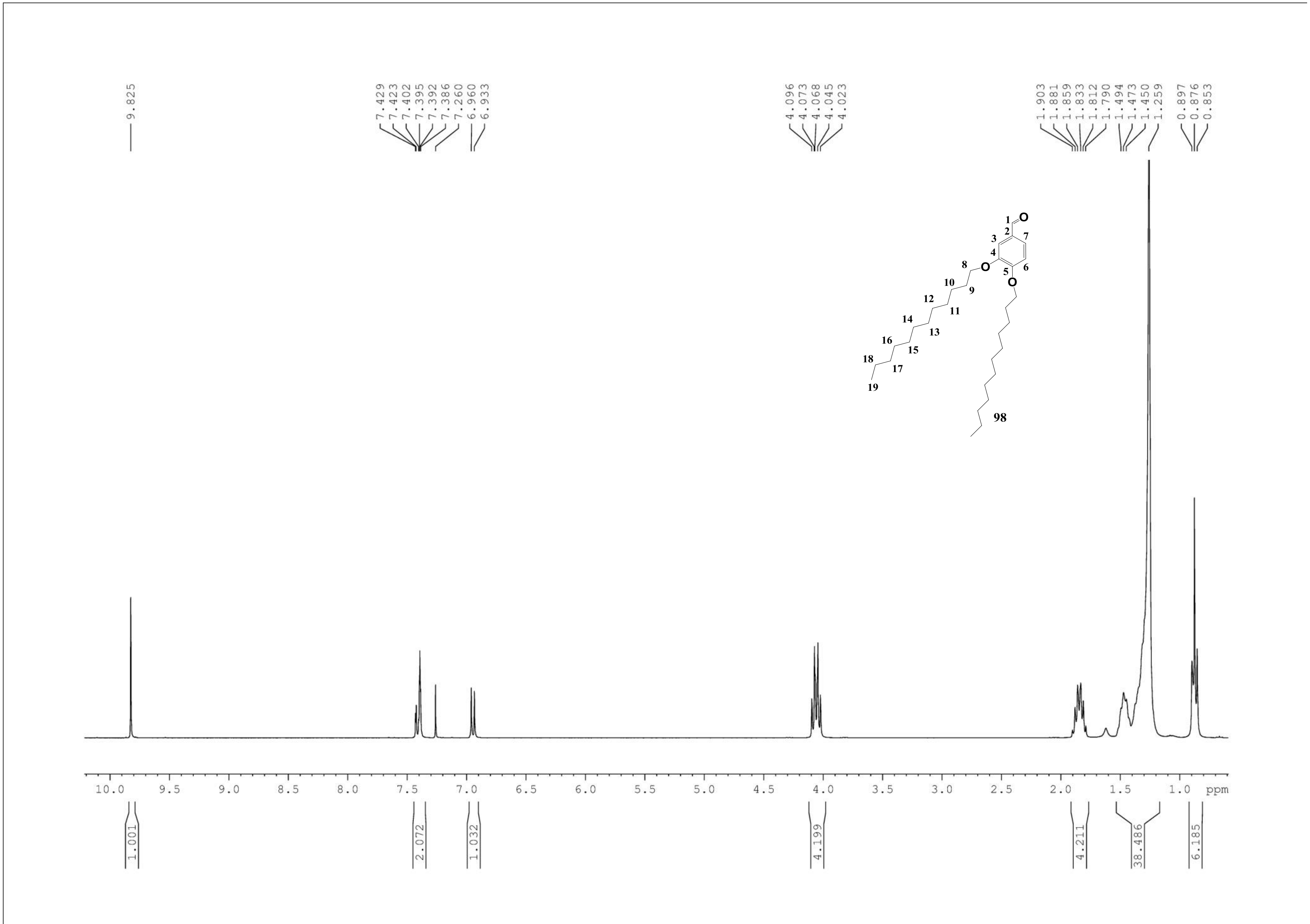


Figure S21. ^{1}H-NMR in $CDCl_3$ for compound **98**.

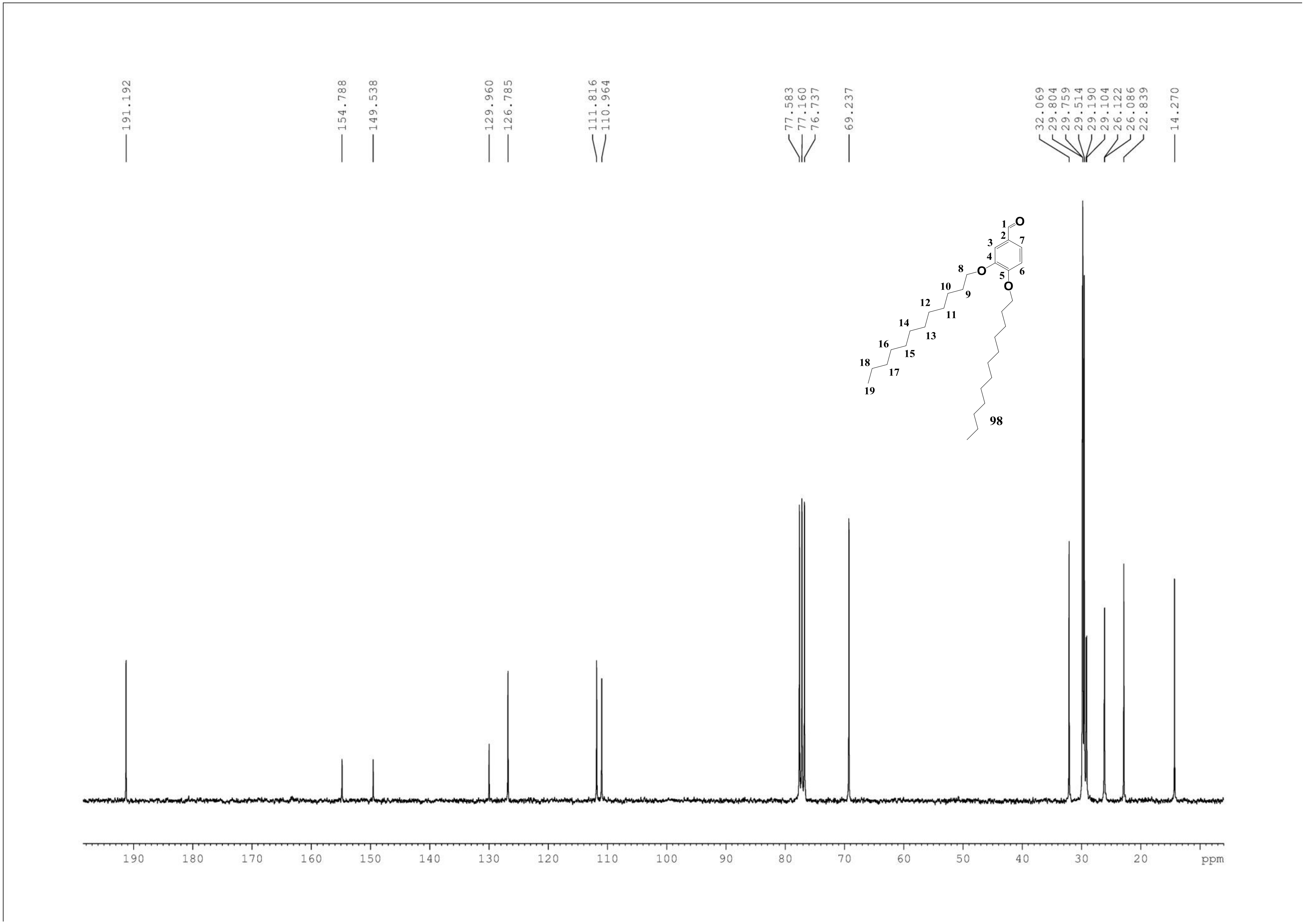


Figure S22. ^{13}C-NMR in $CDCl_3$ for compound **98.**

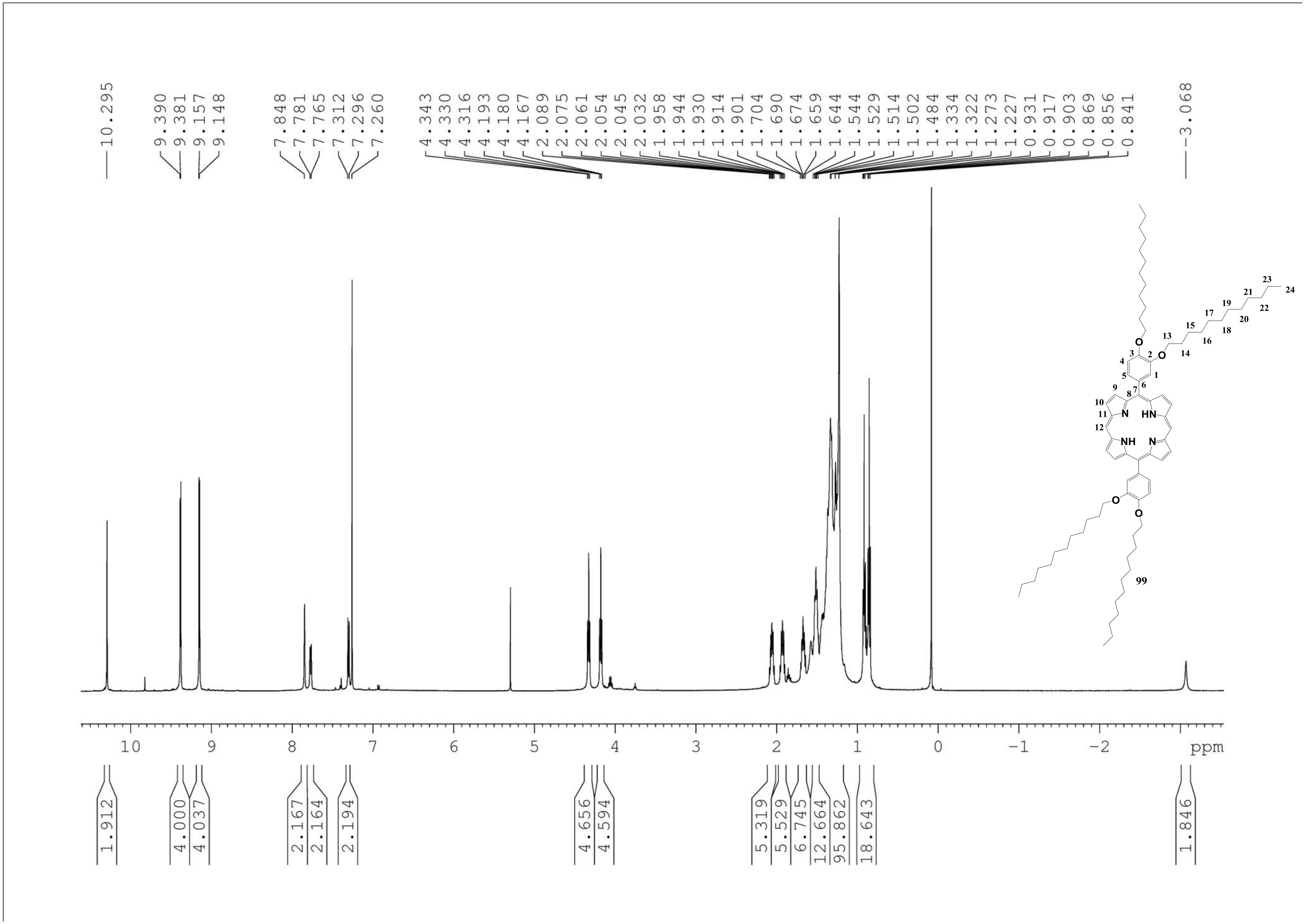


Figure S23.^{1}H-NMR in $CDCl_3$ for compound **99**.

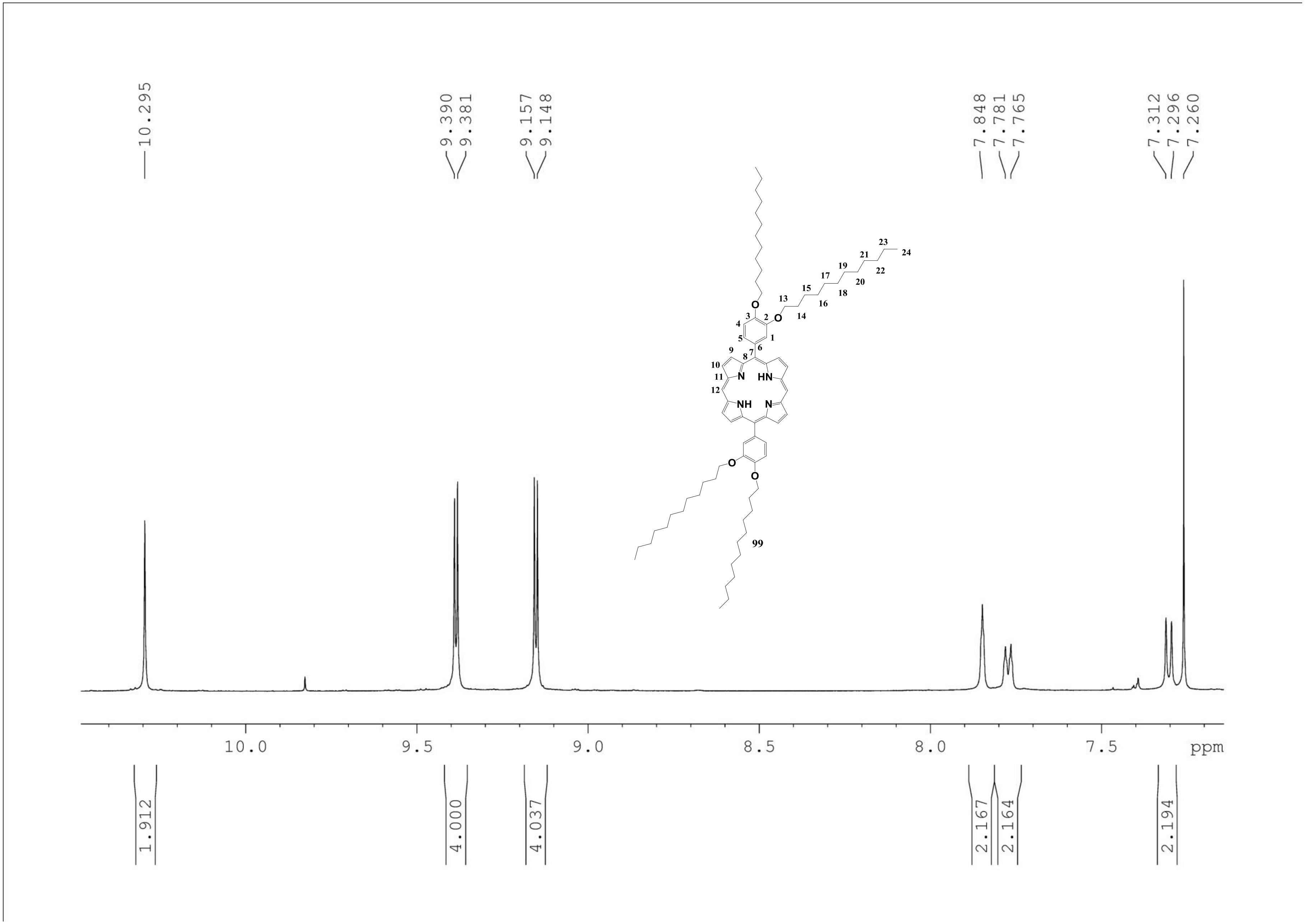


Figure S23a. Aromatic region of ^{1}H-NMR of compound in $CDCl_3$ **99**.

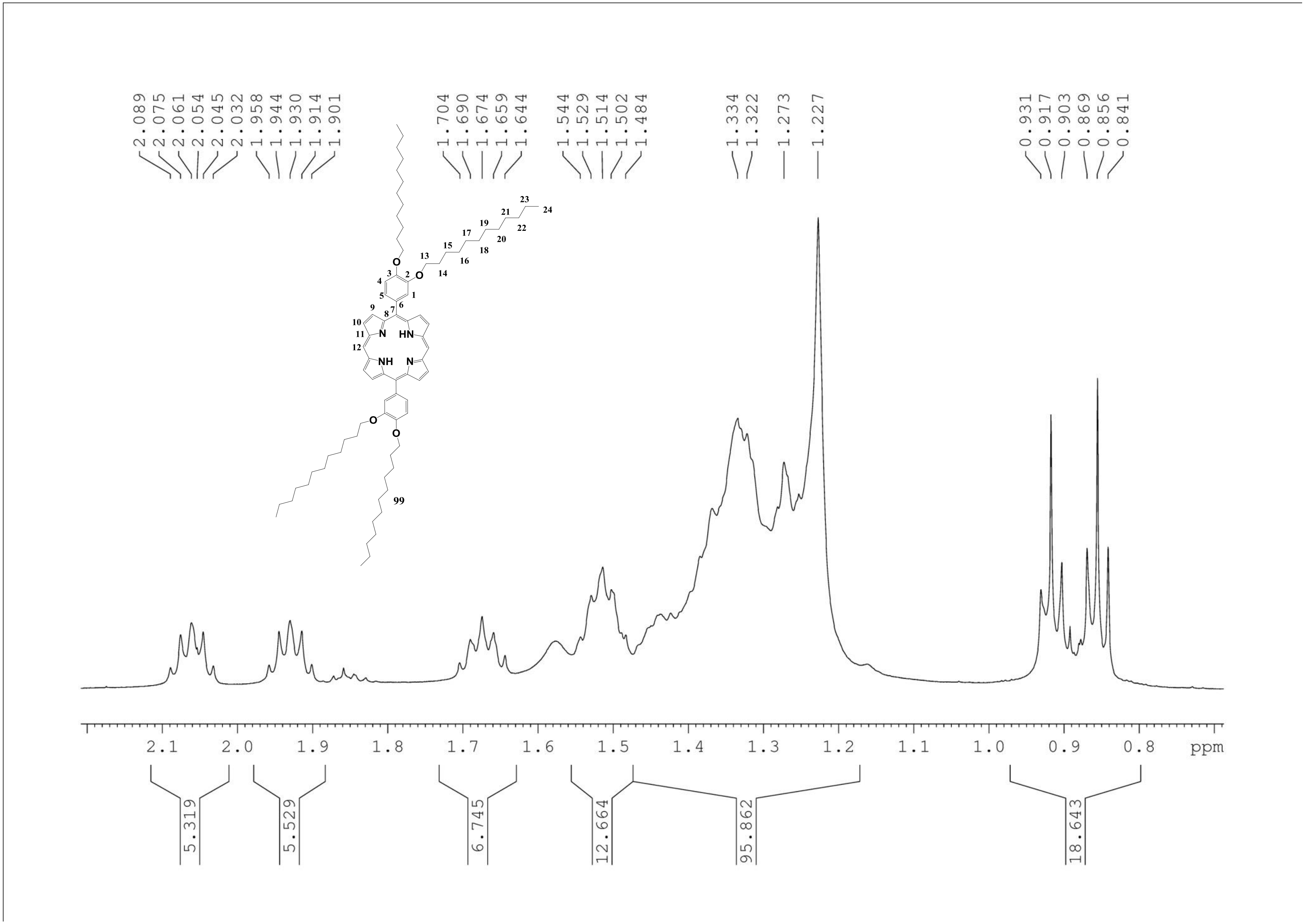


Figure 23b. Aliphatic region of ^{1}H-NMR of compound in $CDCl_3$ **99**.

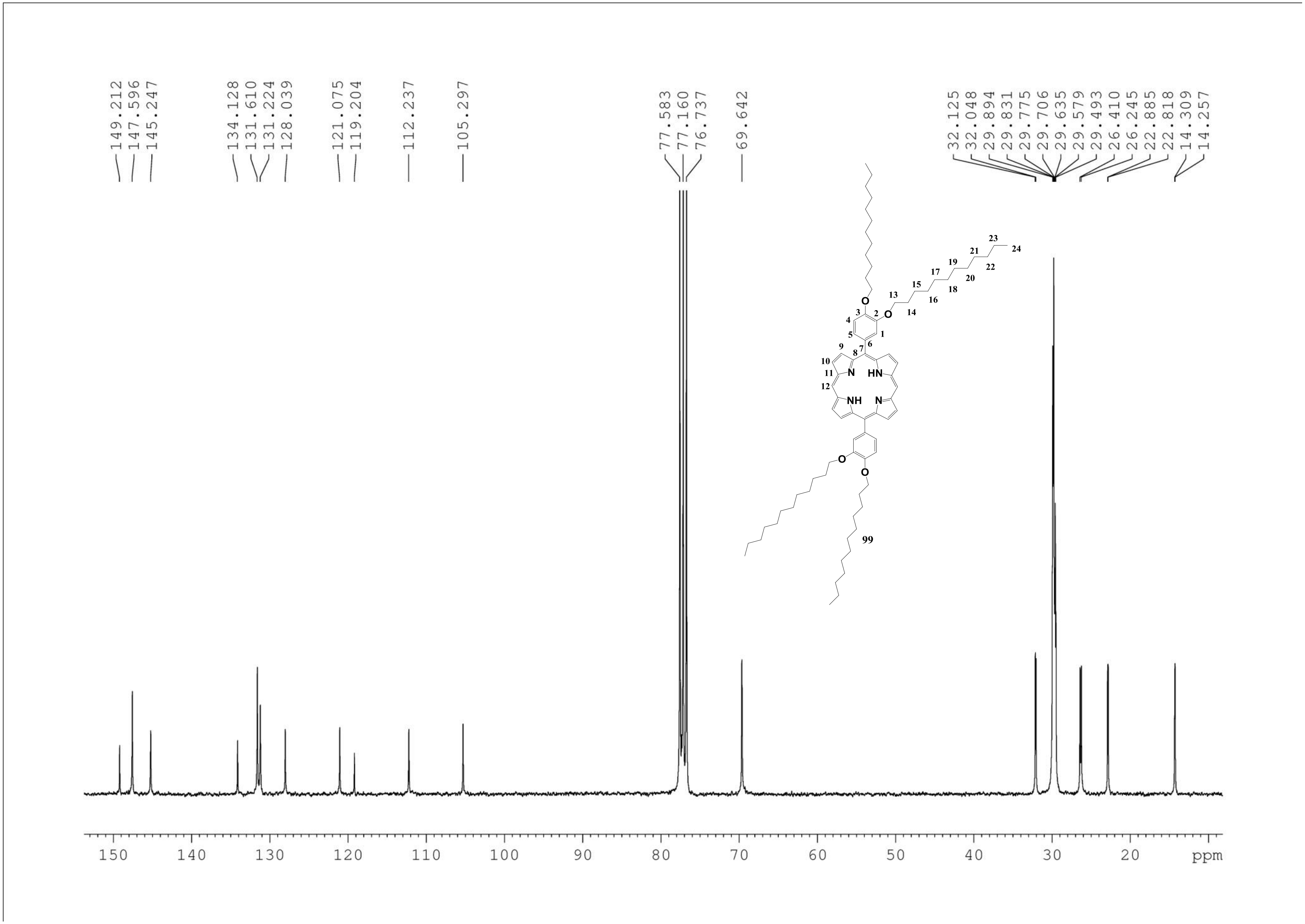


Figure S24. ^{13}C-NMR in CDCl$_3$ of compound **99**.

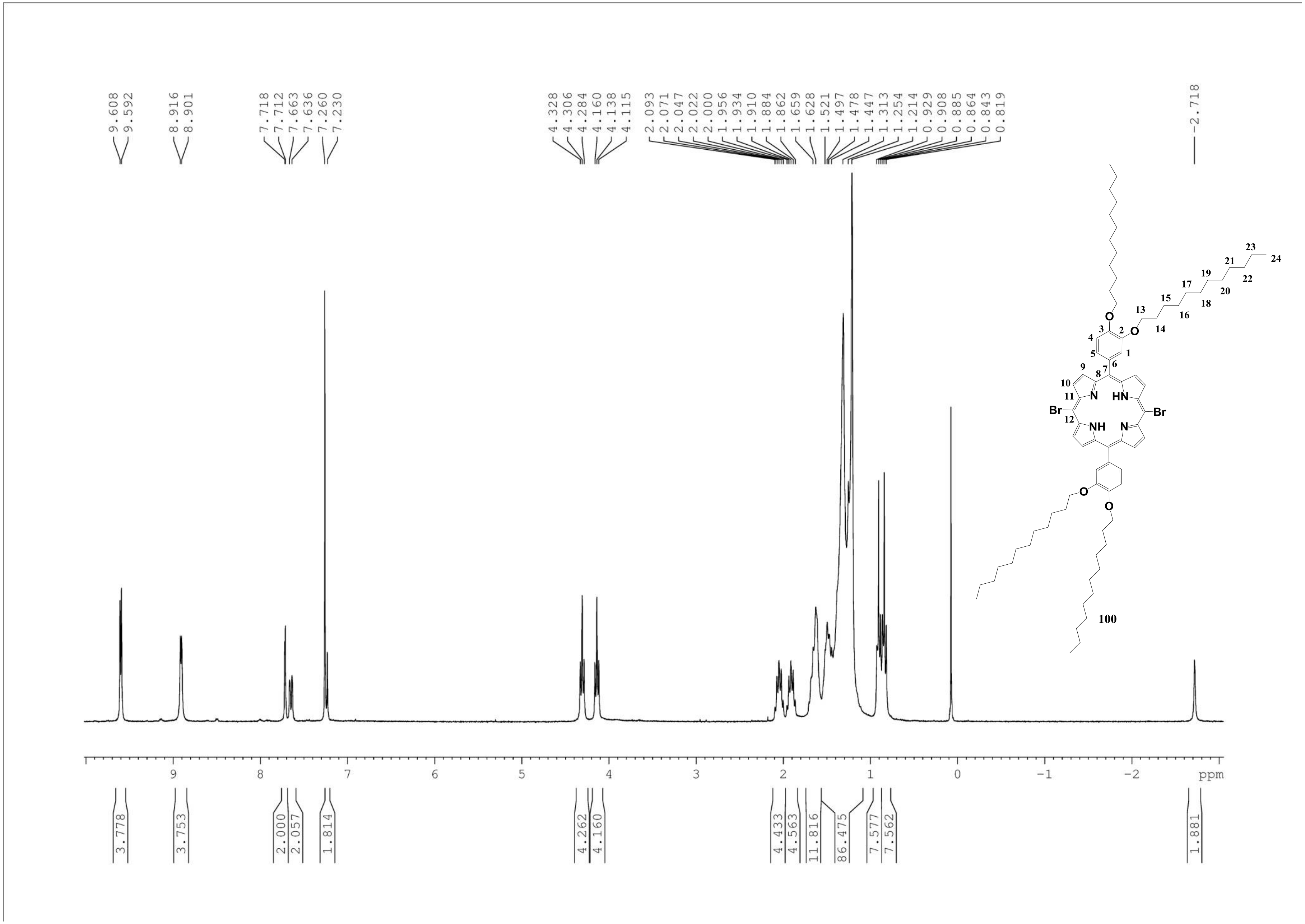


Figure S25. ^{1}H-NMR in CDCl$_3$ of compound **100**.

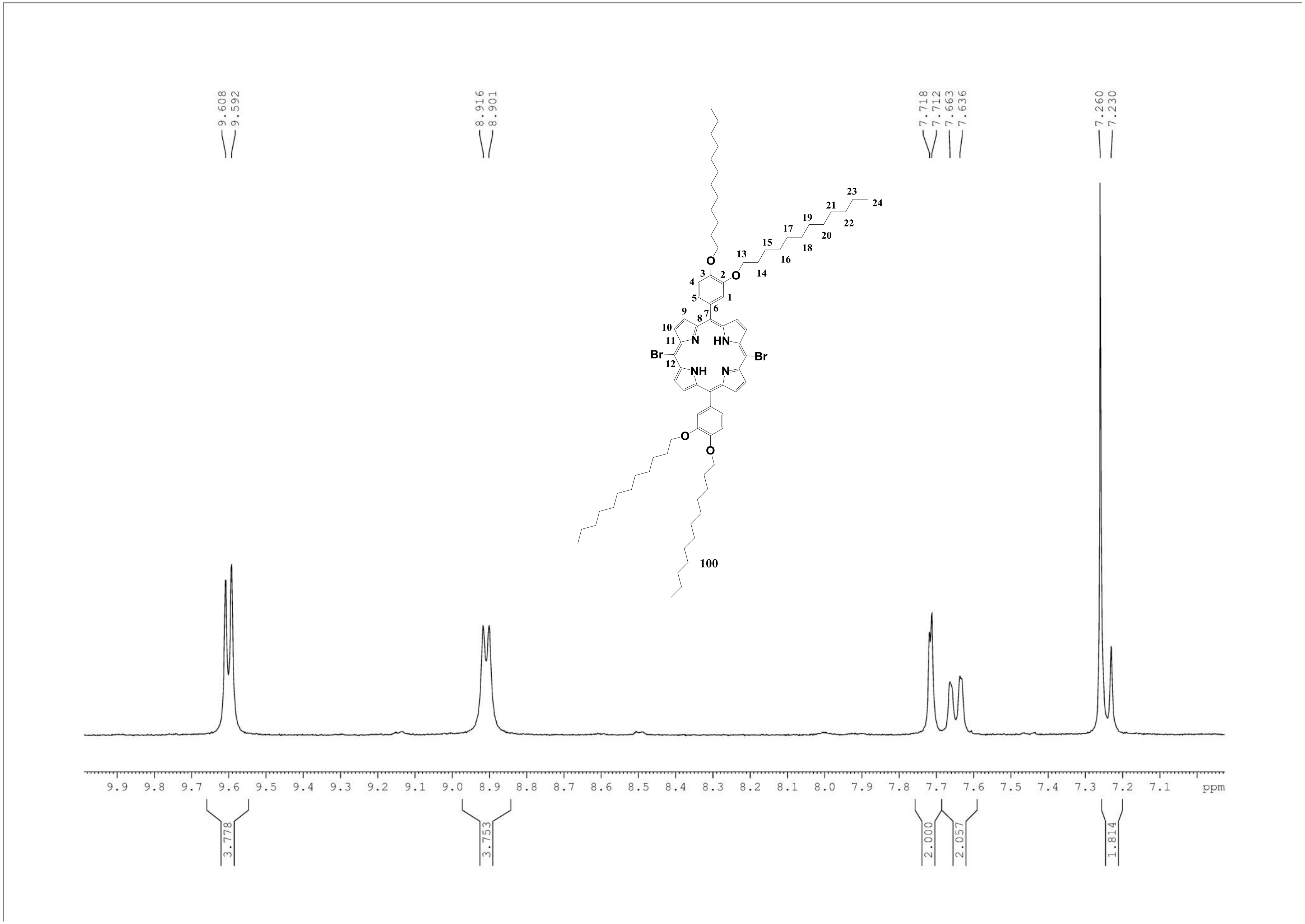


Figure S25a. Aromatic region ^{1}H-NMR of compound **100** in $CDCl_3$.

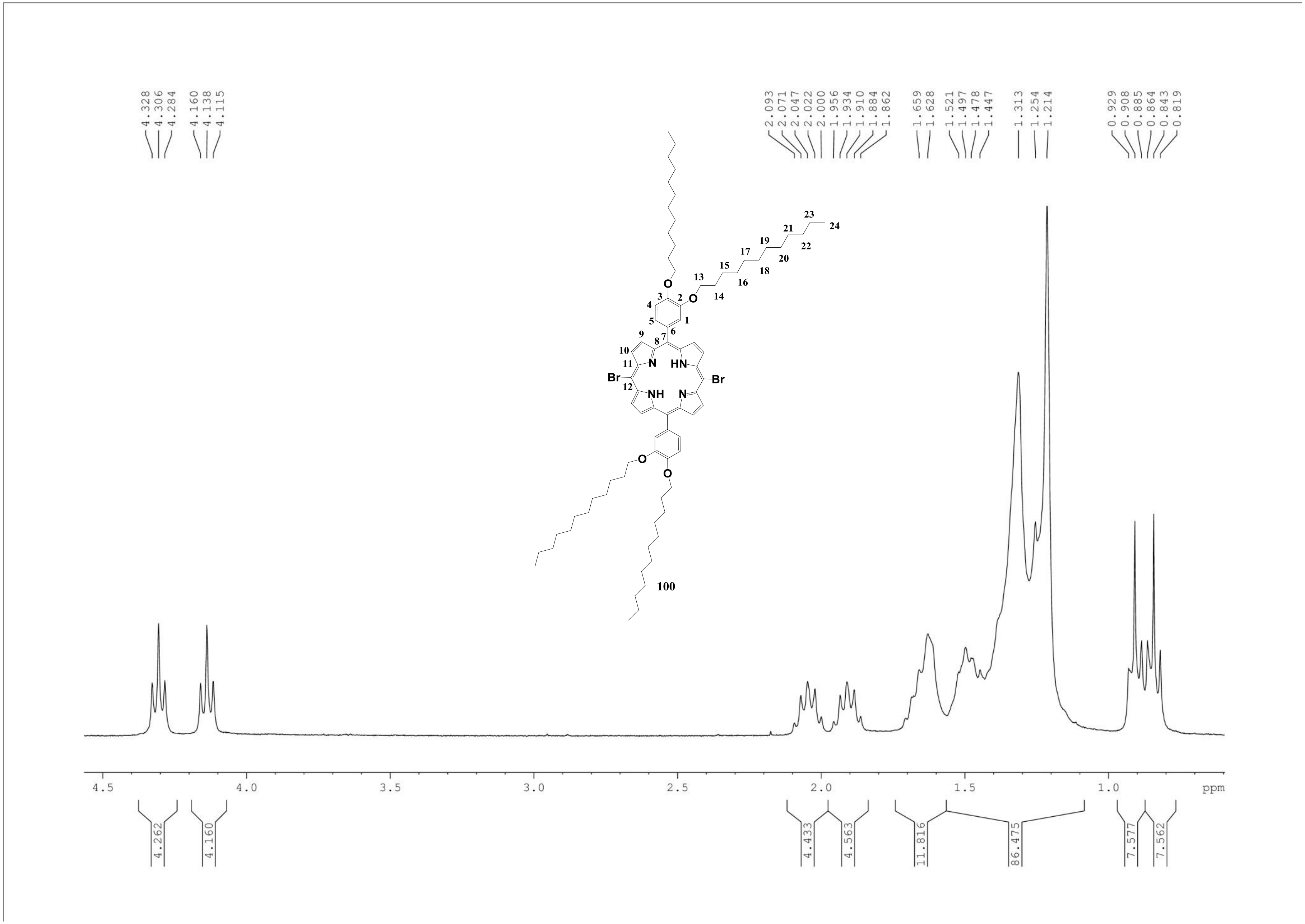


Figure S25b. Aliphatic region ^{1}H-NMR of compound **100** in $CDCl_3$.

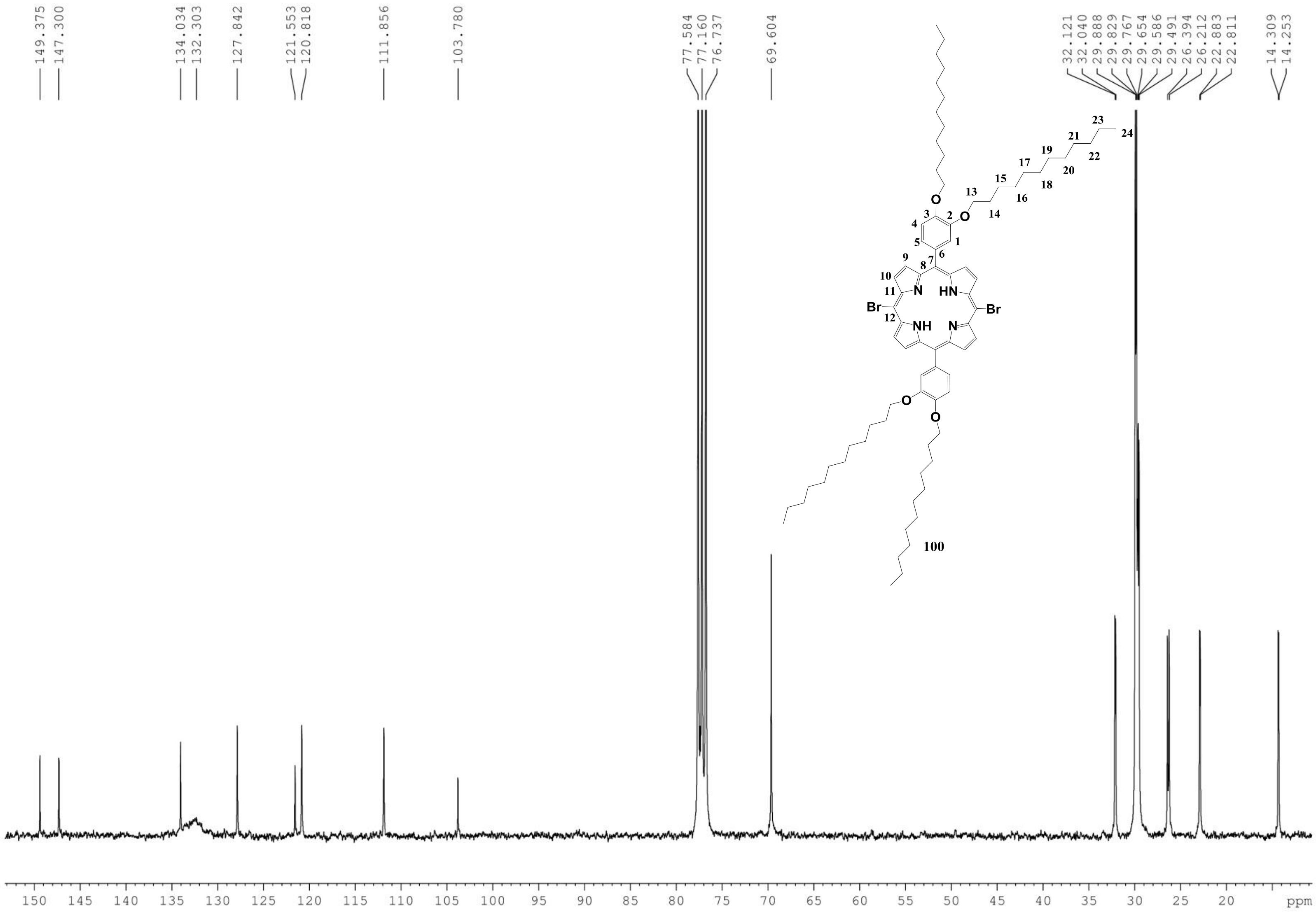


Figure S26. ^{13}C-NMR in CDCl$_3$ of compound **100**.

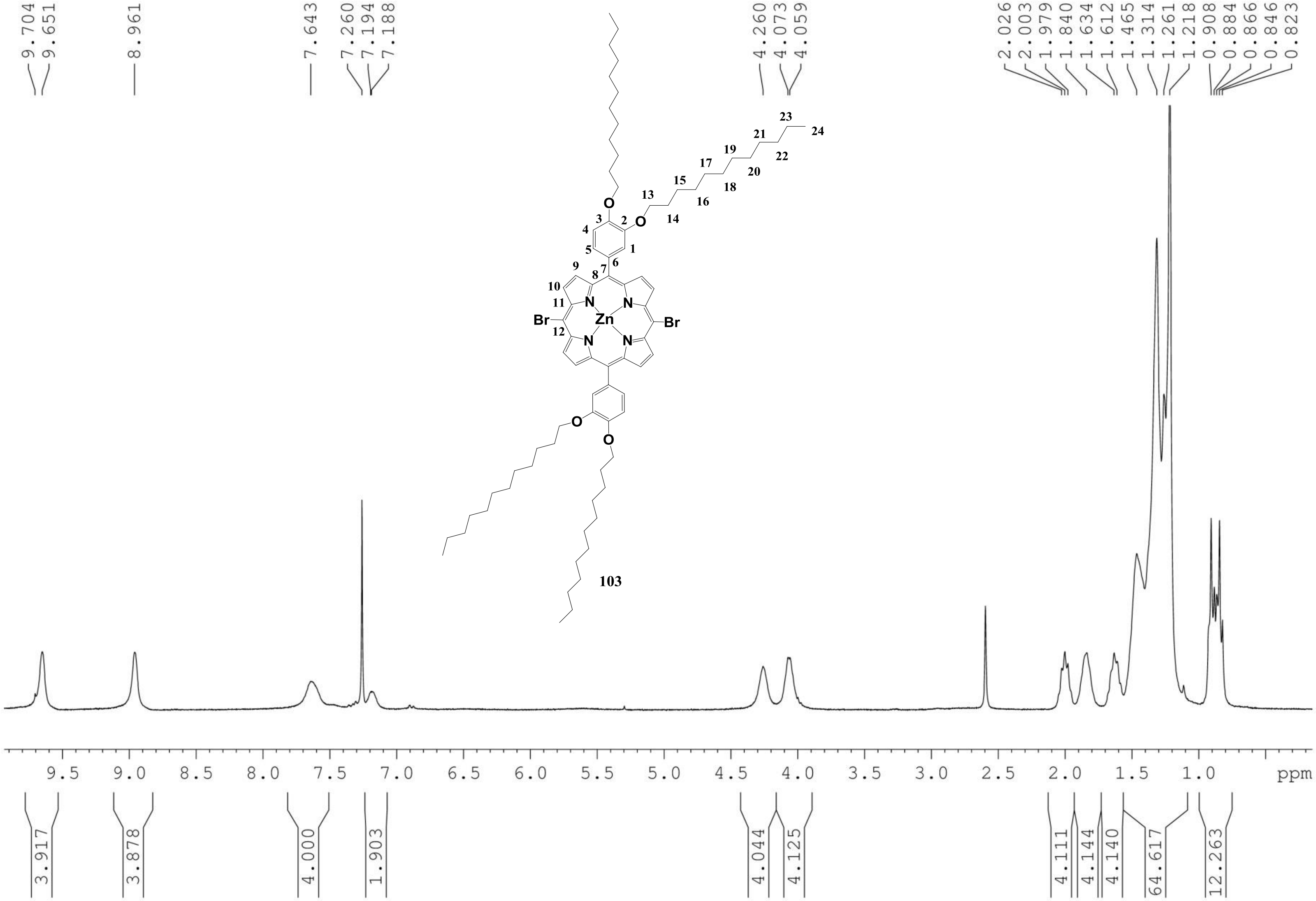


Figure S27. ^{1}H-NMR in $CDCl_3$ of compound **103**.

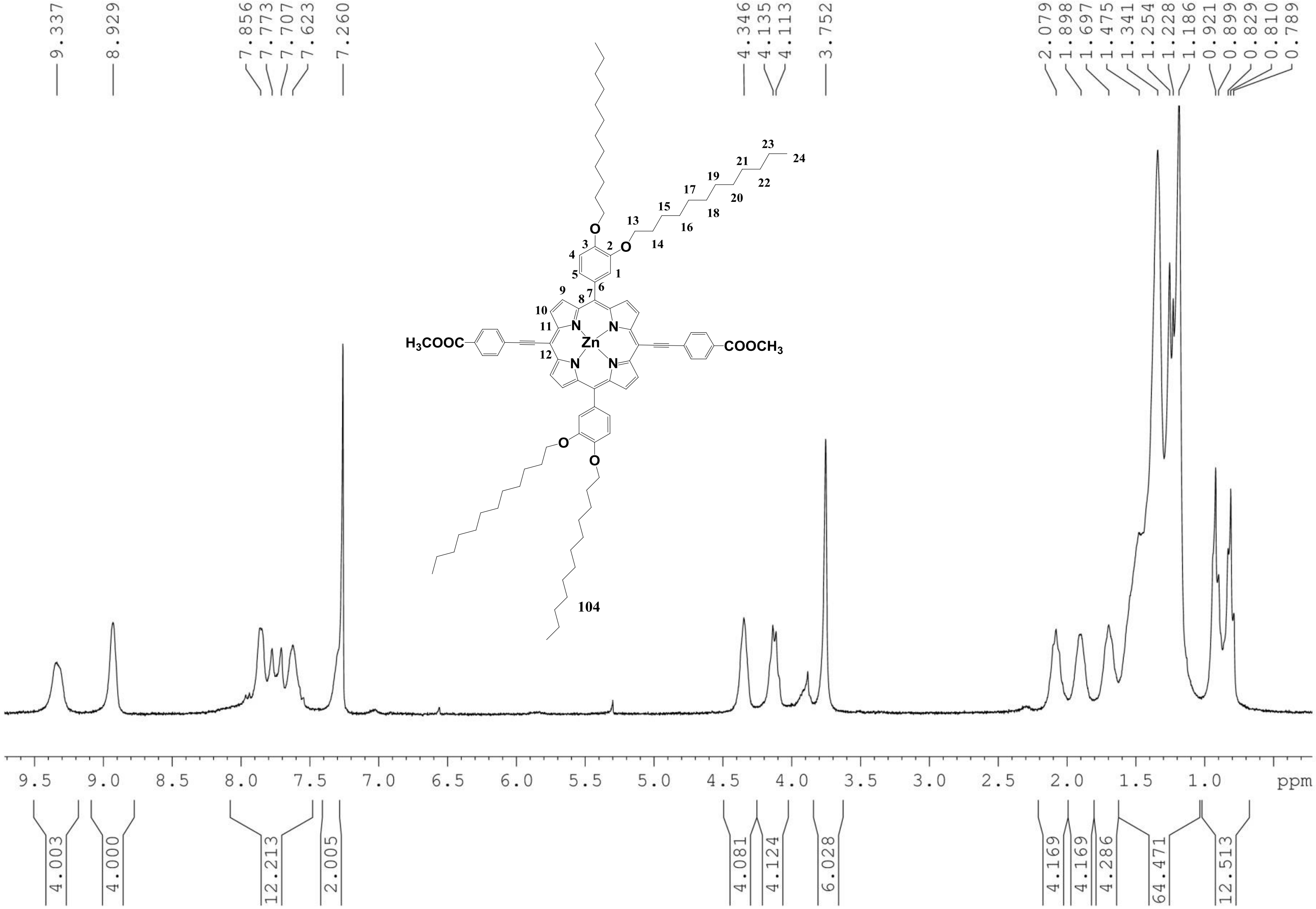


Figure S28. ^{1}H-NMR in CDCl$_3$of compound **104**.

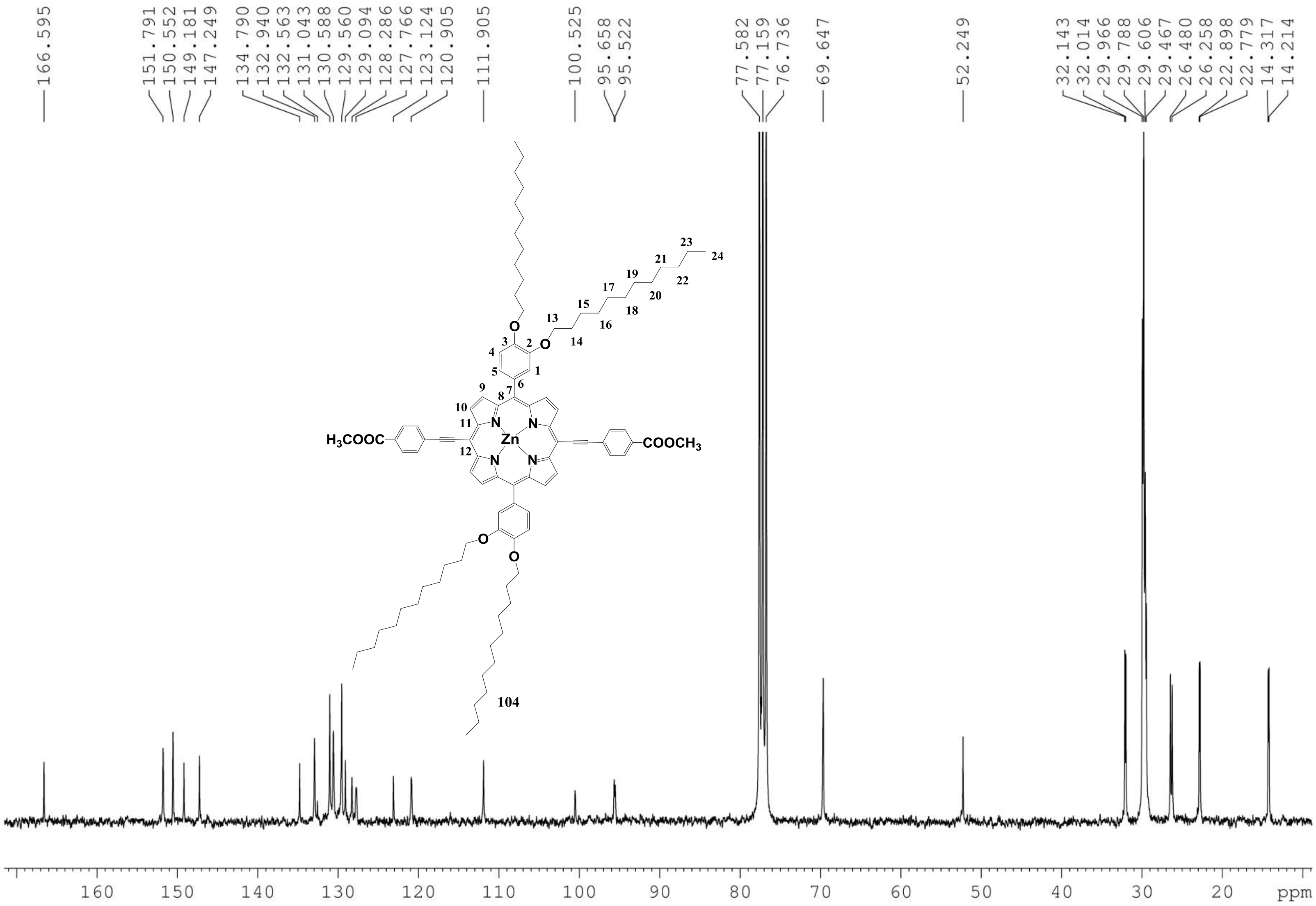


Figure S29. ^{13}C-NMR in $CDCl_3$of compound **104**.

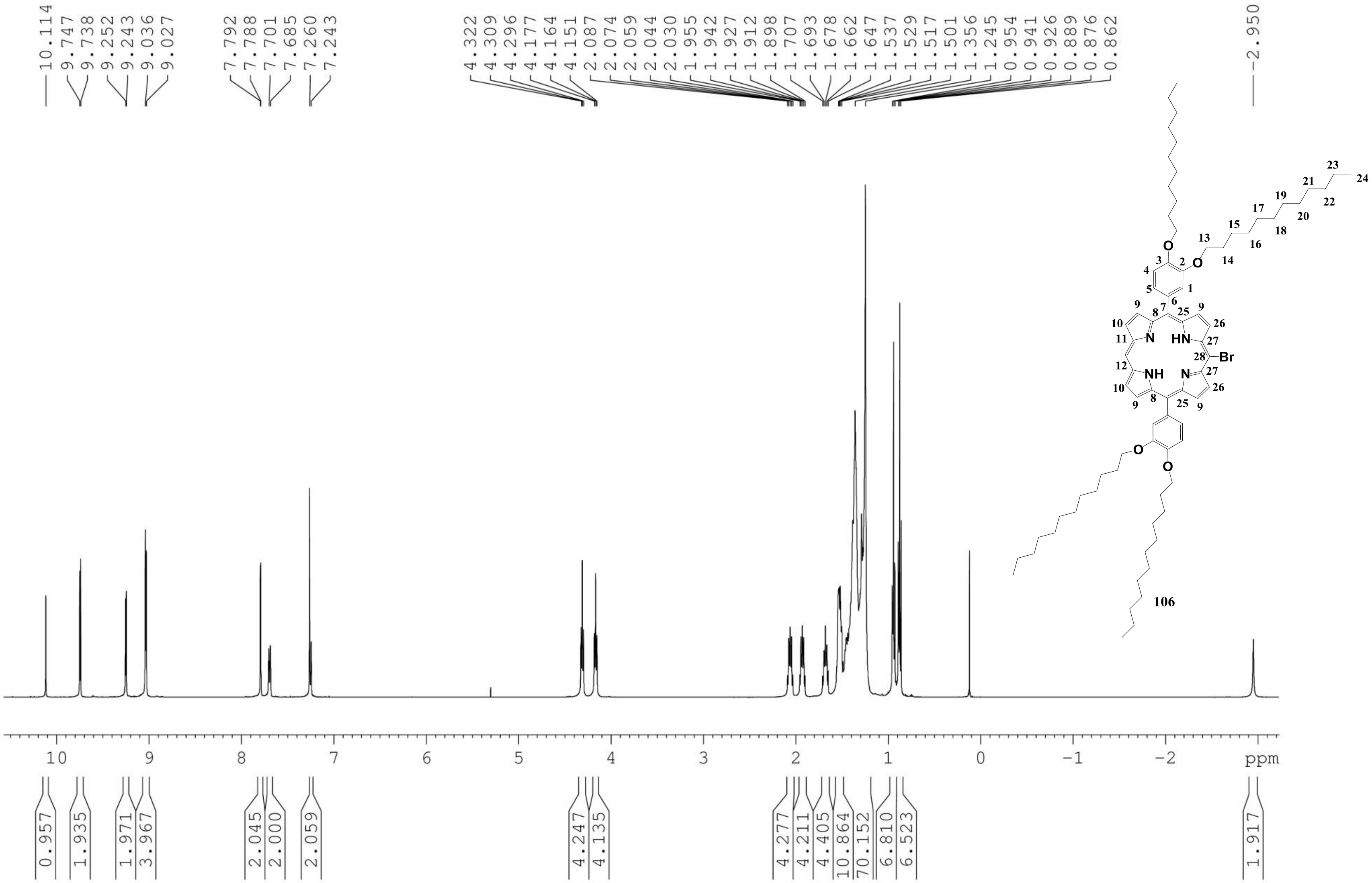


Figure S30. ^{1}H-NMR in $CDCl_3$ of compound **106**.

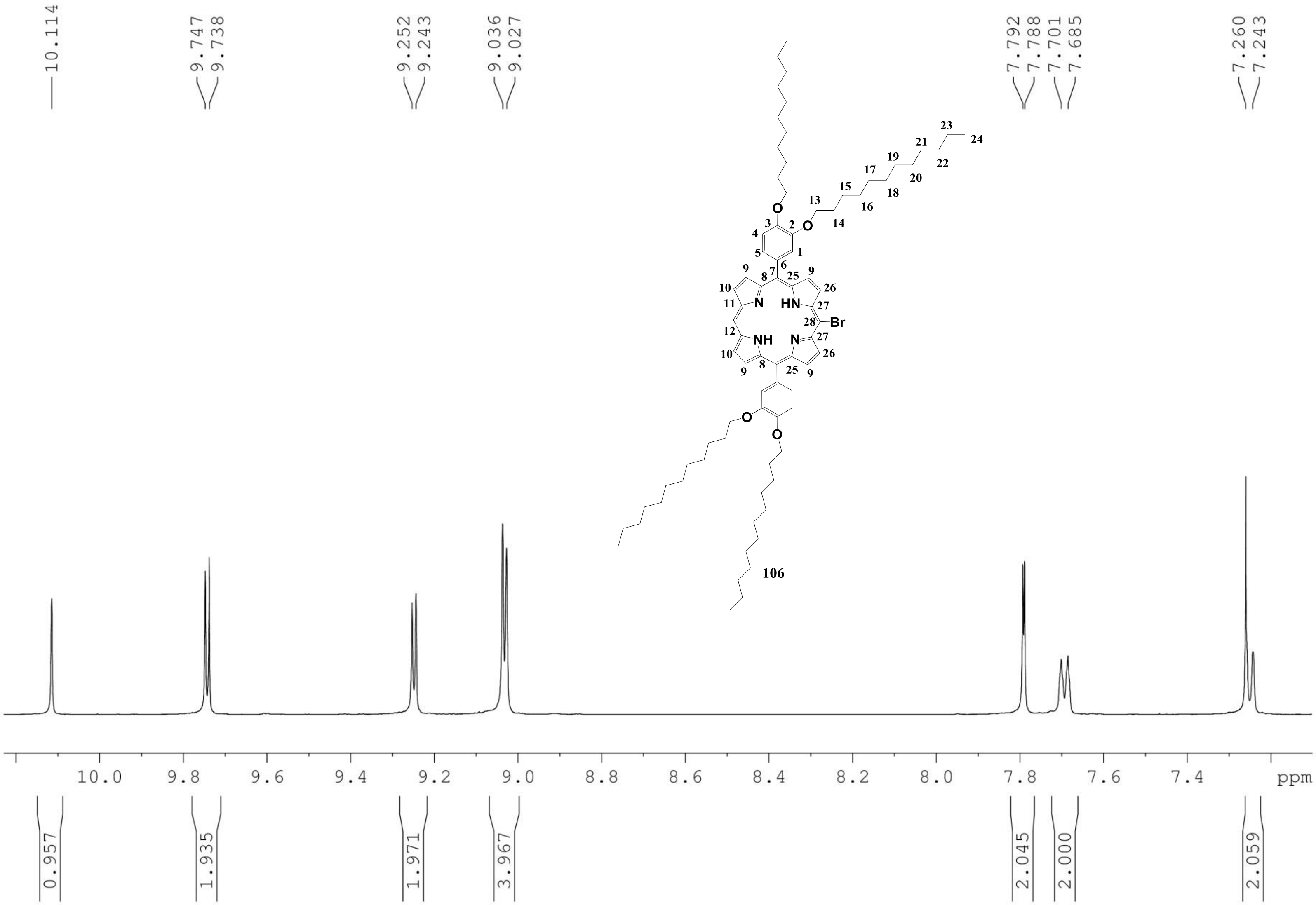


Figure S30a. Aromatic region ^{1}H-NMR in $CDCl_3$of compound **106**.

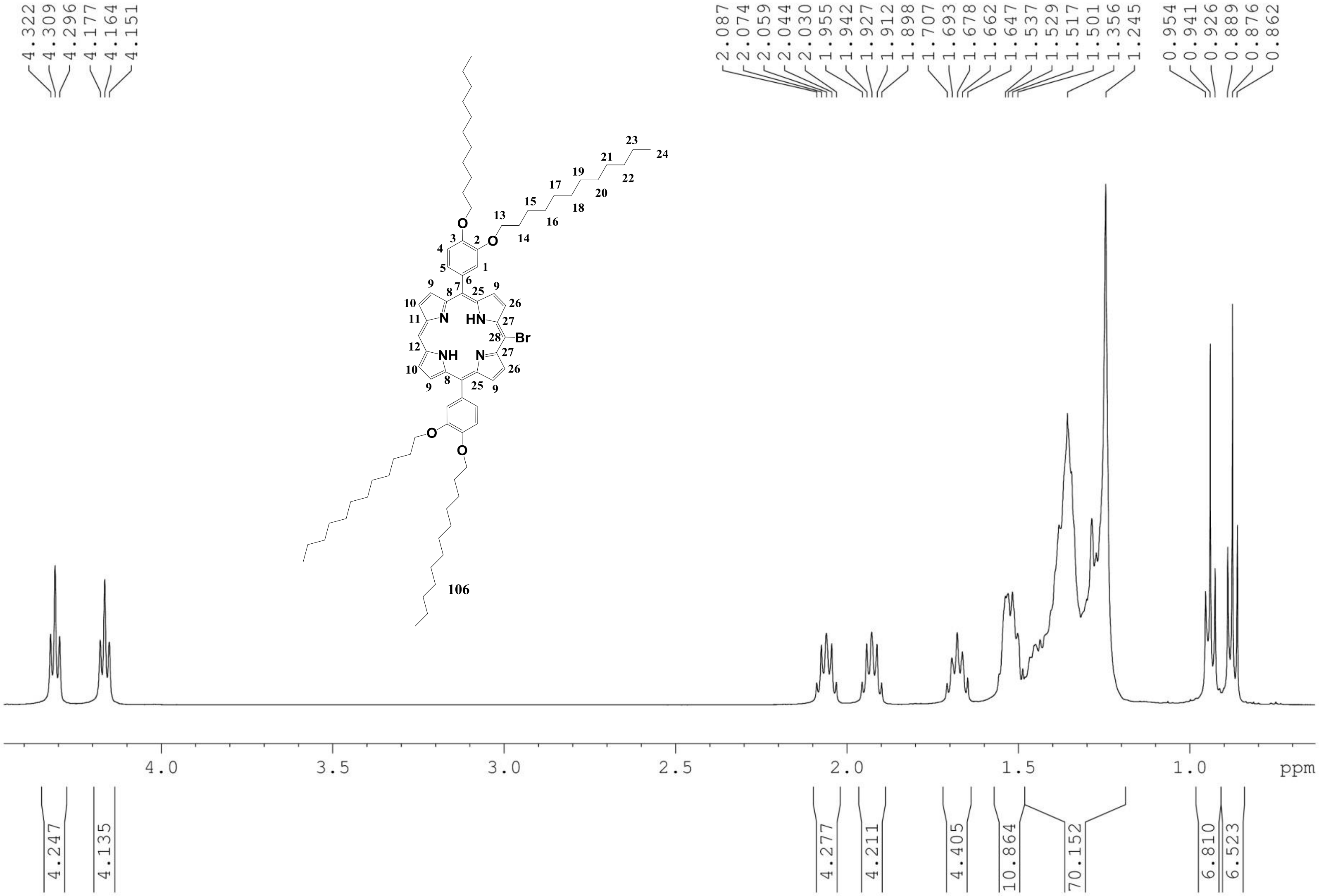


Figure S30b. Aliphatin region ^{1}H-NMR in $CDCl_3$ of compound **106**.

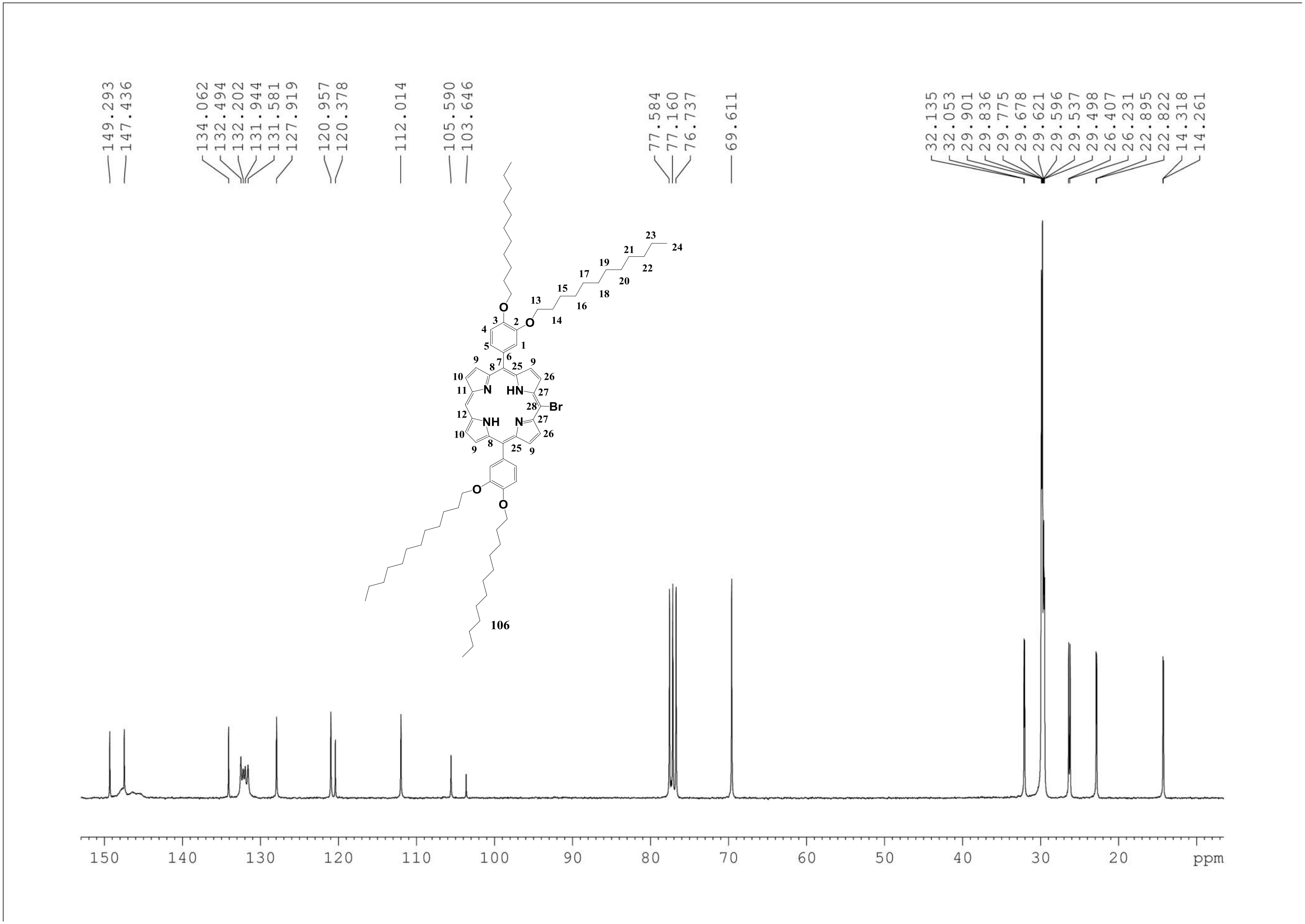


Figure S31. ^{13}C-NMR in CDCl$_3$of compound **106**.