

Durham E-Theses

*Synthesis and applications of Palladium complexes
Part I. The synthesis, single crystal structures and
liquid crystalline phase behavior of Alkoxy substituted
Tolans. Part II. Palladium-Complexes of Thioureas
and phosphine sulfides*

Kittiya Wongkhan

How to cite:

Wongkhan, Kittiya (2008) Synthesis and applications of Palladium complexes Part I. The synthesis, single crystal structures and liquid crystalline phase behavior of Alkoxy substituted Tolans. Part II. Palladium-Complexes of Thioureas and phosphine sulfides. Doctoral thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/2139/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.



Synthesis and Applications of Palladium Complexes

**Part I. The Synthesis, Single Crystal Structures and Liquid
Crystalline Phase Behavior of Alkoxy Substituted Tolans**

**Part II. Palladium-Complexes of Thioureas and Phosphine
Sulfides**

Kittiya Wongkhan

The copyright of this thesis rests with the author or the university to which it was submitted. No quotation from it, or information derived from it may be published without the prior written consent of the author or university, and any information derived from it should be acknowledged.

**A thesis presented to Durham University in fulfillment of the thesis
requirement for the degree of Doctor of Philosophy in Chemistry**

Durham 2008



VOLUME 2

Declaration

The work described in this thesis was carried out in the Department of Chemistry at Durham University between October 2004 and December 2008, under the supervision of Prof. Todd B. Marder. All the work is my own, unless otherwise stated, and has not been submitted previously for a degree at this or any other university.

Kittiya Wongkhan

Statement of Copyright

The copyright of this thesis rests with the author. No quotation from it should be published without their prior consent and information derived from it should be acknowledged.

To my parents for their continual love and support

Acknowledgements

I would like to express my sincere gratitude and deep appreciation to my supervisor, Prof. Todd B. Marder, for his excellent supervision, inspiring guidance and encouragement throughout the course of this study. Thank you for supporting and backing me up no matter what decision I have made and provide plenty of advice and make me feel at home. I know you train me to be a good scientist and I am very grateful to have had you as my supervisor.

I would like to give a special thanks to Dr. Jonathan C. Collings who helped me to get started in the lab and prove read almost all documents I wrote including this thesis. Thanks for providing advice for the past four years. Thank to Andrew Crawford for encouragement, prove read some part of this thesis, and look after GC-MS.

I wish to thank Dr. Andrei Batsanov for running all of the single-crystal X-ray diffraction experiments I have submitted over four years and spending time on the structures reported in my thesis.

I thank Prof. Zhen Yang and his research group for supplying me all the thiourea ligands and for hosting me at Peking University, both in Beijing and Shenzhen. Thank to his students (Bo, Jing and Yingxiang) for synthesized the thiourea ligands.

I also thank to Prof. Aiwen Lei for supplying P-olefin ligand and very warm welcome to Wuhan University, Prof. Hiroto Nakano (Tohoku Pharmaceutical University) for supplying the POT and POZ ligands and Prof. Zhenfeng Xi (Peking University) for the supplying semibullvalene compounds, although none of the results on these systems are included in this thesis.

I wish to express my profound gratitude and sincere appreciation to the Royal Thai Government for the opportunity and financial support given in undertaking this study. My gratitude goes to Department of Chemistry, Ubon Rajathanee University, Thailand, for providing leave to allow me to come here.

Many thanks to all of the Chemistry department services at Durham University for all of the help I received. Dr. Alan Kenwrite, Catherine Hefferman and Ian Mckeag for all highfield solution NMR results, Jaroslava Dostal and Judith Magee for the elemental analysis sample, Dr. Micheal Jones and Lara Turner for mass spectrometry, Douglas Carswell for obtaining the DSC data, Professor Duncan W.

Bruce (York, UK) for assistance with polarised light microscopy (tplm) and discussions, Donocadh P. Lydon for preliminary training on how to use tplm, Dr. David Apperly for solid state NMR data, Dr. Jason Lynam (York, UK) for NMR simulation, Dr. Andrew Beeby for allowing me to use the Raman spectrometer and Lucas for training me on its case. I would like to thank Brian Hall for his work for the group and always having time to help me.

To my sweet parent, for all your support and allow me to choose what I want to do in my life and never complain while waiting for me to come home.

I would like to thank all Thai students: Pi Fai, Pi May, Nim, Bank, Nong Fai and Bath for making me so happy during my stay in Durham. Thank to the Cartner family: David, Pore and Christopher, for having me a place to stay, otherwise I would be a homeless by now.

Thank you to all of the Marder group and group visitors, past and present, for making the lab a nice place to work and me so welcome: Dr. Dave Coventry, Dr. Tolu Fasina, Nathan Bell, Dr. Ibraheem Mkhaliid, Maha Al-Haddad, Dr. Richard Ward, Michael Green, Mark Sinkinson, Tom Turner, Dr. Marco Gianni Grestani, Dr. Marie-Halen, Dr. Nicole, Dr. Andreas Steffen, Dr. Christain Kleeburg, Dr. Manolo Romero, Dr. Bianca Bitterlich, Jonathan Barnard, Meng Guan Tay, Peter Harrison, Laura M, Laura S, Zher Qiang Liu, Li Qiang, Lui Chao and Nim. I also thank the Bryce group for lending chemical and support: Chang Zhen, Kate, Jamie, Katy, Haying, Kiran and Kara.

To my best friend, PKN, thank you so much for your support, plenty of help, suggestions in chemistry, encouragement and proof reading the whole thesis. Thanks for coming here and being with me.

Finally, I give my heart and soul to thank Almighty Creator from up above for giving me so power, patient and inspired.

Kittiya Wongkhan

Publications

Synthesis of Thiourea-Oxazolines, a New Class of Chiral S,N-Heterobidentate Ligands: Application in Pd-catalyzed Asymmetric Bis-methoxycarbonylation of Terminal Olefins.

B. Liang, J. Liu, Y.-X. Gao, K. Wongkhan, D.-X. Shu, Y. Lan, A. Li, A. S. Batsanov, J. A. K. Howard, T. B. Marder, J.-H. Chen, and Z. Yang. *Organometallics* **2007**, *26*, 4756-4762

Acceleration of Reductive Elimination of Csp^3 -Pd-Ar *via* a Phosphine/Electron-Deficient Olefin Ligand: A Kinetic Investigation.

H. Zhang, X. Luo, K. Wongkhan, H. Duan, Q. Li, L. Zhu, J. Wang, A. S. Batsanov, J. A. K. Howard, T. B. Marder, and A. Lei, *Chem. Eur. J.*, accepted November 2008.

Synthesis, Single Crystal Structures and Liquid Crystal Phase Behavior of Three Homologous Series of para-Alkoxy Substituted Tolans.

K. Wongkhan, A. S. Batsanov, M. D. Green, J. C. Collings, J. A. K. Howard, D. W. Bruce and T. B. Marder. In preparation.

A Novel Self-Promoted Morita-Baylis-Hillman Dimerization Reaction and Preliminary Experimental and DFT Studies of its Mechanism.

Q. Li, K. Wongkhan, A. S. Batsanov, Y. Lan, Y. Wu, A. Lei, and T. B. Marder. In preparation.

The Dynamic Study of Palladium- C_2 -Symmetric Thiourea Complexes: VT-NMR Experimental and Simulations.

K. Wongkhan, J. Liu, T. P.W. Turner, A. S. Batsanov, J. A. K. Howard, J. M. Lynam, J.-H. Chen, Z. Yang and T. B. Marder. In preparation.

Abstract

Three series of alkoxy substituted tolans $p\text{-X-C}_6\text{H}_4\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-}p\text{-OC}_n\text{H}_{2n+1}$ [$X = \text{H}$ (series 1), CH_3 (series 2), OCH_3 (series 3)] with varying chain length were synthesized by Pd/Cu-catalysed Sonogashira cross-coupling reactions of terminal alkynes and iodoarenes, crystal structures and phase behavior of three series of tolans. Twenty-eight of the tolans were structurally characterised by single-crystal X-ray diffraction. Their phase behavior was characterised by tplm; only the tolans in series 3 show liquid crystalline phases. The melting points of the tolans decrease with increasing chain length due to a higher degree of flexibility of the terminal chain. An odd-even effect is clearly observed for the clearing point of the nematic phase upon both heating and cooling, with the higher temperature for even and low temperature for odd number carbon chains for series 3.

Monomeric and dimeric palladium dichloride complexes containing the monodentate thioureas, tetramethyl thiourea (tmtu) and a chiral C_2 symmetric thiourea were synthesized. Their structures were obtained from single-crystal X-ray diffraction. The structures of the mono-palladium complexes are the *trans*-isomers, whereas the dimer complexes present *cis*-configurations, and are also the first examples of palladium complexes with sulfur-bridging thiourea ligands. NMR studies of the monomeric and dimeric complexes with tmtu reveal that, in solution, the dimeric complexes are interconverting with mono-palladium complexes, which suggests that the systems are labile. A dynamic equilibrium in solution was also observed between the *rac*- and *meso*-dipalladium complexes with the C_2 -symmetric ligand. The energy barrier to exchange was obtained from a variable temperature NMR study. It is proposed that this equilibrium results from the monomer-dimer interconversion.

S,N-bidentate β -dimethyl and β -monomethyl oxazoline thiourea ligands and α -isoquinoline thiourea ligands and their palladium complexes have been obtained. Single-crystal X-ray diffraction analyses allow us to distinguish between some of their atropoisomers and diastereomers. Most of the Pd complexes were shown to be monomers in the solid state, although one ligand with a cyclohexyl group formed exclusively dimers, and one formed a trimer, as well as a monomer, depending on the solvent mixture that the crystals were grown from. The ligands were found to coordinate through their S and N atoms. All of the mono-palladium

complexes and most of the dimers have *cis*-configurations at the Pd centers; however, we also found a *trans*-configuration in the trimer and the dimer of one of the palladium complex of the β -monomethyl ligands. The structures show that the β -monomethyl oxazoline and α -isoquinoline thiourea complexes appear to be more weakly coordinated than the β -dimethyl oxazoline ones which may be responsible for their lower stabilities in solution. The structure of the ligands (in particular the 'up' or 'down' conformation of the atropoisomers) is intimately related to their enantioselectivities in bis(methoxycarbonylation) reactions of styrene using palladium complexes. The β -dimethyl ligands were, in general, found to be more selective in this reaction than the β -monomethyl oxazoline ones, with palladium complexes of the latter generally found to be less stable in NMR studies.

Several bis(phosphine) monosulfide and disulfide ligands and their palladium complexes have been synthesized and analyzed by single-crystal X-ray diffraction. The reaction with 1:1 molar ratios of Pd source to monosulfide ligands were found to produce monomeric palladium complexes with chelating ligands, apart from the reaction with bis(diphenylphosphino)butane monosulfide, which was found to result in a dimer being formed. The reactions with 1:2 molar ratios of Pd source to monosulfide ligand gave complexes which were coordinated only through the phosphine groups, except for that with bis(diphenylphosphino)methane monosulfides which formed cationic palladium complexes with two chelating ligands. Analogous reactions with the disulfide ligands and the Pd source $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ also resulted in cationic Pd complexes incorporating two chelating ligands. In some cases, in solution, the complexes showed dynamic equilibria between *cis*- and *trans*- isomers which suggests that the phosphine sulfide ligands are labile. The Pd-S-P angles in the complexes were found to be variable but, since there are none less than 90° , it is unlikely that there is any η^2 - π bonding involving the P=S bond. Preliminary results show that the activities of phosphine sulfide palladium complexes in the oxidative homo-coupling of phenylacetylene are comparable to that of the commonly used pre-catalyst, $\text{PdCl}_2(\text{PPh}_3)_2$.

Volume II

Table content

Declaration.....	ii
Statement of Copyright.....	ii
Acknowledgements.....	iv
Publications.....	vi
Abstract.....	vii

List of Figures

Appendix A

Figure A1. The ^1H NMR (400 MHz, CD_2Cl_2) spectrum of tmtu	2
Figure A2. The $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2) spectrum of tmtu	2
Figure A3. Solid state $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of tmtu	3
Figure A4. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of Pd(tmtu)	3
Figure A5. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of Pd(tmtu)	4
Figure A6. The solid state $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of Pd(tmtu)	4
Figure A7. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of Pd₂(tmtu)	5
Figure A8. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of Pd₂(tmtu)	5
Figure A9. The solid state $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of Pd₂(tmtu)	6
Figure A10. The ^1H NMR (500 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of L(rac)	7
Figure A11. The ^1H NMR (500 MHz, TCE- d_2 , $100\text{ }^\circ\text{C}$) spectrum of L(rac)	7
Figure A12. The ^1H NMR (500 MHz, CD_2Cl_2 , $20\text{ }^\circ\text{C}$) spectrum of L(rac)	7
Figure A13. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of L(rac)	8
Figure A14. The HSQC ($20\text{ }^\circ\text{C}$) spectrum of L(rac)	8
Figure A15. The HMBC ($20\text{ }^\circ\text{C}$) spectrum of L(rac)	9
Figure A16. IR spectrum of L(rac)	9
Figure A17. IR spectrum of rac-Pd / meso-Pd	10
Figure A18. IR spectrum of rac-Pd₂ / meso-Pd₂	10
Figure A19. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of rac-Pd / meso-Pd at room temperature.	11
Figure A20. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectra of rac-Pd / meso-Pd at $-60\text{ }^\circ\text{C}$, the expanded C=S (top left) and C3 regions (top right).	11
Figure A21. The ^1H NMR (400 MHz, CD_2Cl_2 , $20\text{ }^\circ\text{C}$) monitoring of the reaction of rac-Pd₂ / meso-Pd₂ converted to trans-rac-Pd / trans-meso-Pd with L(rac) at various times, * = rac-Pd₂ / meso-Pd₂	12
Figure A22. The ^1H NMR (500 MHz) spectra of rac-Pd₂ / meso-Pd₂ in CD_2Cl_2 (top) and TCE- d_2 (bottom) at room temperature.	12
Figure A23. The ^1H NMR (500 MHz) spectra of rac-Pd₂ / meso-Pd₂ in CD_2Cl_2 at room temperature (top) and $-60\text{ }^\circ\text{C}$ (bottom).	13
Figure A24. ^1H NMR (500 MHz) spectra of rac-Pd₂ / meso-Pd₂ in TCE- d_2 at room temperature (top) and $-30\text{ }^\circ\text{C}$ (bottom).	13
Figure A25. The ^1H NMR (500 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of R,R-Pd₂	13
Figure A26. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of R,R-Pd₂	14

Figure A27. The COSY spectrum (500 MHz, CD ₂ Cl ₂ , -60 °C) of R,R-Pd₂ in the aromatic (left) and aliphatic regions (right).....	14
Figure A28. The HSQC (CD ₂ Cl ₂ , -60 °C) spectrum of R,R-Pd₂	15
Figure A29. The HSQC NMR (CD ₂ Cl ₂ , -60 °C) spectrum in the aromatic region of R,R-Pd₂	15
Figure A30. The HMBC NMR (CD ₂ Cl ₂ , -60 °C) spectrum in the aromatic region of R,R-Pd₂	16
Figure A31. The ¹ H NMR (500 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of S,S-Pd₂	16
Figure A32. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of S,S-Pd₂	17
Figure A33. The ¹ H (500 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of rac-Pd₂ / meso-Pd₂	17
Figure A34. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of rac-Pd₂ / meso-Pd₂	18
Figure A35. The COSY (500 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of rac-Pd₂ / meso-Pd₂	18
Figure A36. The NOESY (500 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of rac-Pd₂ / meso-Pd₂	19
Figure A37. The NOESY (500 MHz) rac-Pd₂ / meso-Pd₂ in CD ₂ Cl ₂ at -60 °C.....	19
Figure A38. The HSQC NMR (CD ₂ Cl ₂ , -60 °C) spectrum of rac-Pd₂ / meso-Pd₂	20
Figure A39. The HSQC NMR (CD ₂ Cl ₂ , -60 °C) spectrum in aromatic region of rac-Pd₂ / meso-Pd₂	20
Figure A40. The ¹ H NMR (500 MHz, CD ₂ Cl ₂ , -60 °C) spectrum of rac-Pd₂ / meso-Pd₂ minus S,S-Pd₂	21
Figure A41. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectra of rac-Pd₂ / meso-Pd₂ at various temperatures.....	21
Figure A42. The ¹ H NMR (500 MHz, TCE-d ₂) spectra of rac-Pd₂ / meso-Pd₂ at various temperatures.....	22

Appendix B

Figure B1. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectrum of L2up	24
Figure B2. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂) spectrum of L2up	24
Figure B3. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectrum of L2down	25
Figure B4. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂) spectrum of L2down	25
Figure B5. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectrum of L3	26
Figure B6. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂) spectrum of L3	26
Figure B7. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectrum of L4	27
Figure B8. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂) spectrum of L4	27
Figure B9. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectrum of L5	28
Figure B10. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂) spectrum of L5	28
Figure B11. The ¹ H NMR (500 MHz, CD ₂ Cl ₂) spectrum of L6	29
Figure B12. The ¹³ C{ ¹ H} NMR (125 MHz, CD ₂ Cl ₂) spectrum of L6	29
Figure B13. The ¹ H NMR (700 MHz, CDCl ₃) spectrum of L7	30
Figure B14. The ¹³ C{ ¹ H} NMR (175 MHz, CDCl ₃) spectrum of L7	30
Figure B15. The ¹ H NMR (500 MHz, CDCl ₃) spectra of L8 at room temperature (top) and -30 °C (bottom).....	31
Figure B16. The ¹³ C{ ¹ H} NMR (125 MHz, CDCl ₃) spectra of L8 at room temperature (top) and -30 °C (bottom).....	31
Figure B17. The ¹ H NMR (700 MHz, CDCl ₃) spectrum of R-L9up (bottom) and the expanded spectrum in the aromatic region (top).....	32

Figure B18. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of R-L9up (bottom) and the expanded spectrum in the aromatic region (top).....	32
Figure B19. The ^1H NMR (700 MHz, CDCl_3) spectrum of S-L9down (bottom) and the expanded spectrum in the aromatic region.	33
Figure B20. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of S-L9down (bottom)	33
Figure B21. The ^1H NMR (700 MHz, CDCl_3) spectrum of R-L10	34
Figure B22. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of R-L10	34
Figure B23. The ^1H NMR (700 MHz, CDCl_3) spectrum of S-L10	35
Figure B24. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of S-L10	35
Figure B25. The ^1H NMR (700 MHz, CDCl_3) spectrum of L11up (bottom) and the expanded spectrum in the aromatic region (top).....	36
Figure B26. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of L11up (bottom) and the expanded spectrum in the aromatic region (top).....	36
Figure B27. The ^1H NMR (700 MHz, CDCl_3) spectrum of L11down (bottom) and the expanded spectrum in the aromatic region (top).....	37
Figure B28. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of L11down (bottom) and the expanded spectrum in the aromatic region (top).....	37
Figure B29. The ^1H NMR (700 MHz, CDCl_3) spectrum of L12	38
Figure B30. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of L12	38
Figure B31. The ^1H NMR (700 MHz, CDCl_3) spectrum of L13up (bottom) and the expanded spectrum in the aromatic region (top).....	39
Figure B32. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of L13up (bottom) and the expanded spectrum in the aromatic region (top).....	39
Figure B33. The ^1H NMR (700 MHz, CD_2Cl_2) spectrum of PdL2up	40
Figure B34. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CD_2Cl_2) spectrum of PdL2up	40
Figure B35. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL2down	41
Figure B36. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of PdL2down	41
Figure B37. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL3	42
Figure B38. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of PdL3	42
Figure B39. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL4	43
Figure B40. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of PdL4	43
Figure B41. The <i>in situ</i> ^1H NMR (400 MHz, CDCl_3) spectrum of PdL5	44
Figure B42. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of PdL5	44
Figure B43. The ^1H NMR (500 MHz, CDCl_3) spectrum of Pd₂L5	45
Figure B44. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of Pd₂L5	45
Figure B45. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL6	46
Figure B46. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of PdL6	46
Figure B47. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL7	47
Figure B48. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL7	47
Figure B49. The ^1H NMR (700 MHz, CDCl_3) spectrum of Pd₃L7 (bottom); expanded in the aromatic region (top left) and in the aliphatic region (top right).	48
Figure B50. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and mix spectra between PdL7 and Pd₃L7 (top).	48
Figure B51. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and Pd₃L7 (*) (in the region of C=S and C=N signals).	49
Figure B52. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and Pd₃L7 (*) (in the region of 125 – 144 ppm).	50
Figure B53. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and Pd₃L7 (*) (in the region of 60 – 75 ppm).....	50

Figure B54. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and Pd₃L7 (*) (in the region of 15 – 33 ppm).	51
Figure B55. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL8 (bottom) and the expanded spectrum in the aromatic region (top).....	52
Figure B56. The $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CD_2Cl_2) spectrum of PdL8 (bottom) and the expanded spectrum in the aromatic region (top).....	52
Figure B57. The ^1H NMR (700 MHz, CDCl_3) spectrum of Pd-R-L9up	53
Figure B58. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of Pd-R-L9up	53
Figure B59. The ^1H NMR (200 MHz, CDCl_3) spectrum of Pd₂-S-L9down	54
Figure B60. The ^1H NMR (700 MHz, CDCl_3) spectrum of the mixture of Pd-S-L9down and Pd₂-S-L9down (bottom) and the expanded spectrum in the aromatic region (top).....	54
Figure B61. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of Pd-S-L9down and Pd₂-S-L9down (bottom) and the expanded spectrum in the aromatic region (top). ...	55
Figure B62. The ^1H NMR (700 MHz, CDCl_3) spectrum of Pd-R-L10	56
Figure B63. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of Pd-R-L10	56
Figure B64. The ^1H NMR (700 MHz, CDCl_3) of the mixture of S-L10 palladium complexes (bottom) and the expanded spectrum in the aromatic region (top).....	57
Figure B65. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of the mixture of S-L10 palladium complexes (bottom) and the expanded spectrum in the aromatic region (top).....	57
Figure B66. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL11up (bottom) and the expanded spectrum in the aromatic region (top).....	58
Figure B67. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL11up (bottom) and the expanded spectrum in the aromatic region (top).....	58
Figure B68. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL11down	59
Figure B69. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL11down (bottom) and the expanded spectrum in the aromatic region (top).....	59
Figure B70. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL12	60
Figure B71. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL12	60
Figure B72. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL13up (bottom) and the expanded spectrum in the aromatic region (top).....	61
Figure B73. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL13up (bottom) and the expanded spectrum in the aromatic region (top).....	61
Figure B74. The ^1H NMR spectra (400 MHz, CDCl_3) of L4 (bottom), isolated PdL4 and the <i>in situ</i> 1:2 $\text{PdCl}_2(\text{PhCN})_2\text{:L4}$ (top).	62

Appendix C

Figure C1. The solid state $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex obtained from the reaction of $\text{PdCl}_2(\text{PhCN})_2$ to dppms at 1:1 molar ratio.	66
Figure C2. The solid state $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex obtained from the reaction of $\text{PdCl}_2(\text{PhCN})_2$ to dppbs at 1:1 molar ratio.	67
Figure C3. The <i>in situ</i> $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ to dppbs₂ in a 1:2 molar ratio in CD_2Cl_2	67

List of Tables

Appendix B

Table B1. Distances of Cl(1) and Cl(2) from the Pd-S-N(13) plane and the angle between planes Pd-S-N(13) to Cl(1)-Pd-Cl(2).	63
Table B2. Distances of Cl(1) and Cl(2) from the Pd-S-N(13) plane and the angle between planes Pd-S-N(13) to Cl(1)-Pd-Cl(2).	63

Appendix C

Table C1. Crystallographic data for dppbS:dppbSO	65
Table C2. Selected bond lengths and angles of the partial oxidized dppbSO	66
Table C3. Bond lengths, angles and $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts of phosphine sulfide complexes.*	68

Appendix A

**Monodentate Thioureas and Their
Palladium Complexes**



Appendix A

Monodentate thiourea

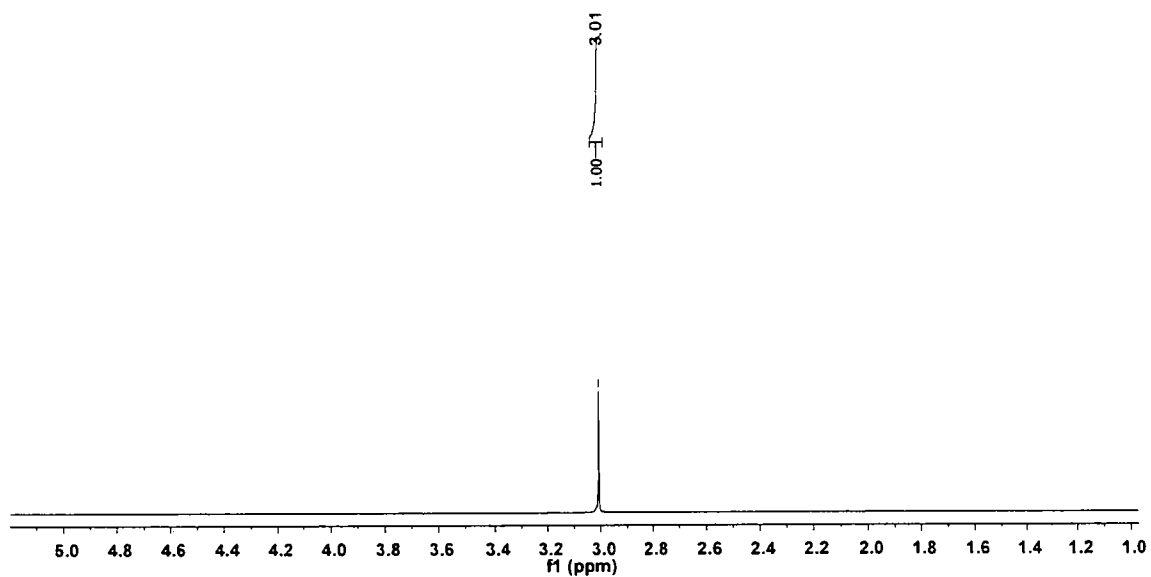


Figure A 1. The ^1H NMR (400 MHz, CD_2Cl_2) spectrum of tmtu.

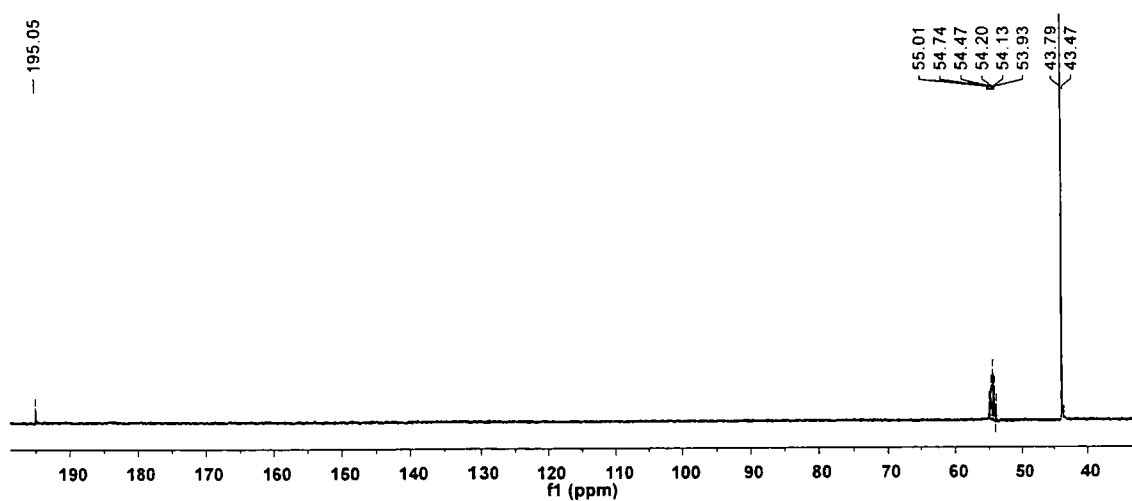


Figure A 2. The $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2) spectrum of tmtu.

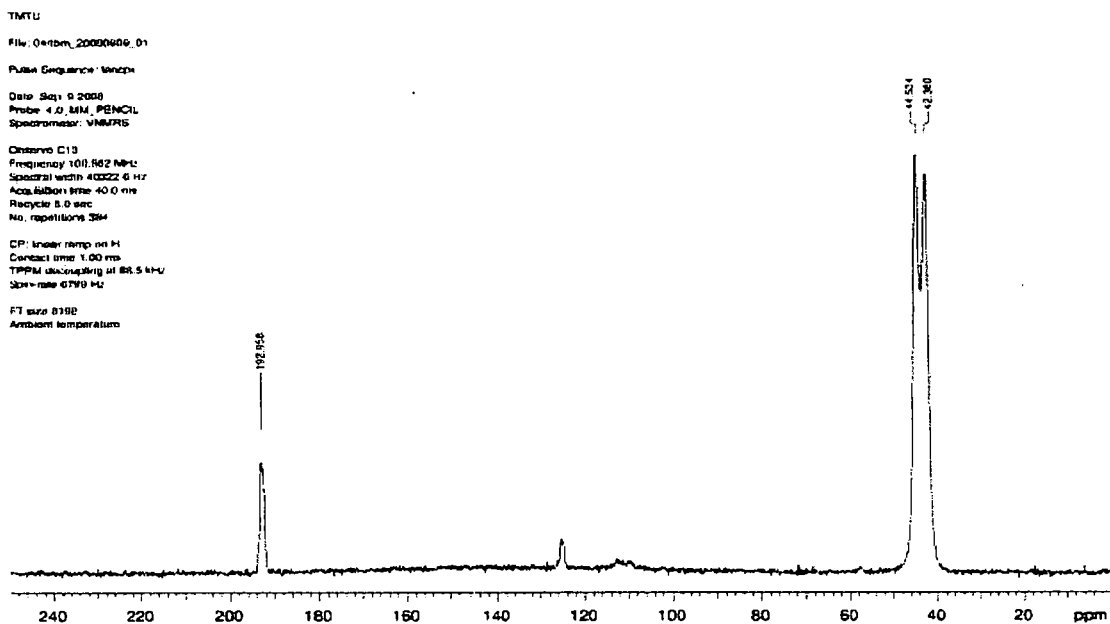


Figure A 3. Solid state $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of tmtu.

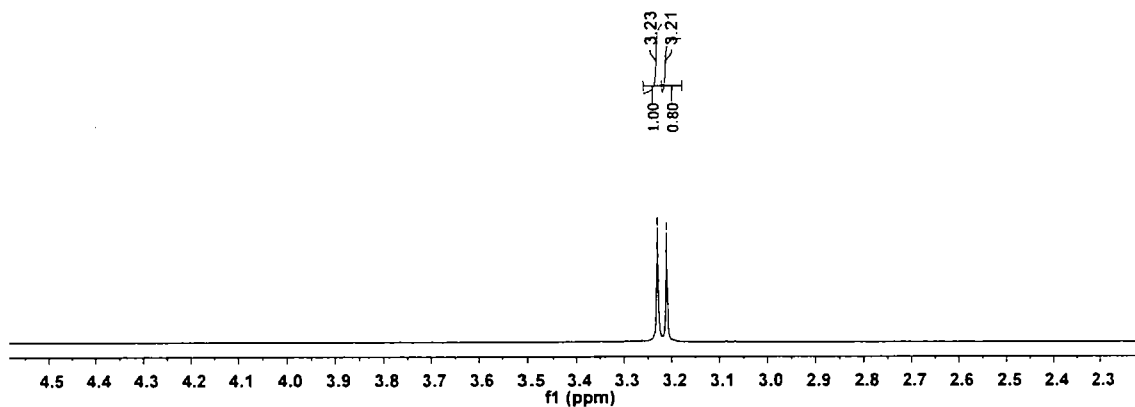


Figure A 4. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of $\text{Pd}(\text{tmtu})$.

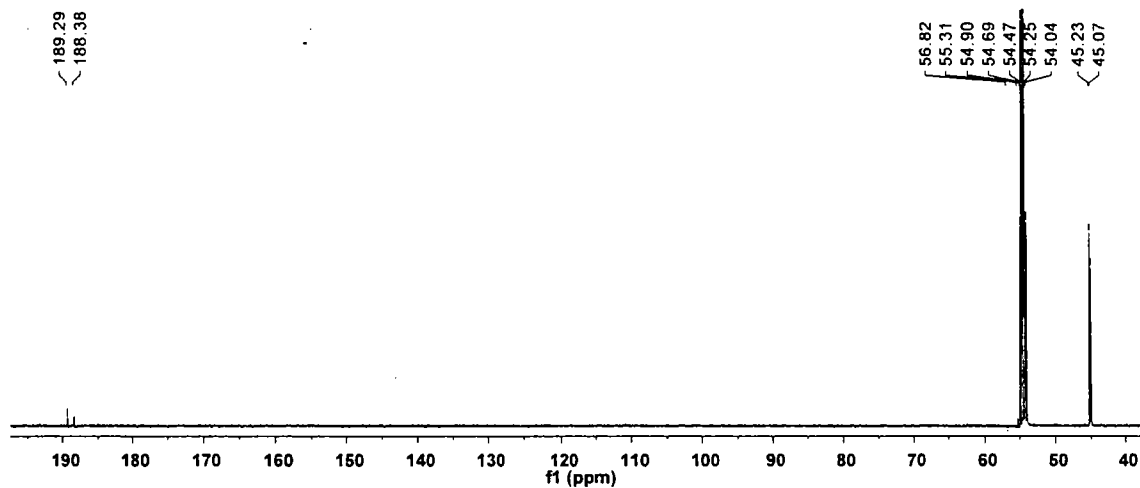


Figure A 5. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **Pd(tmtu)**.

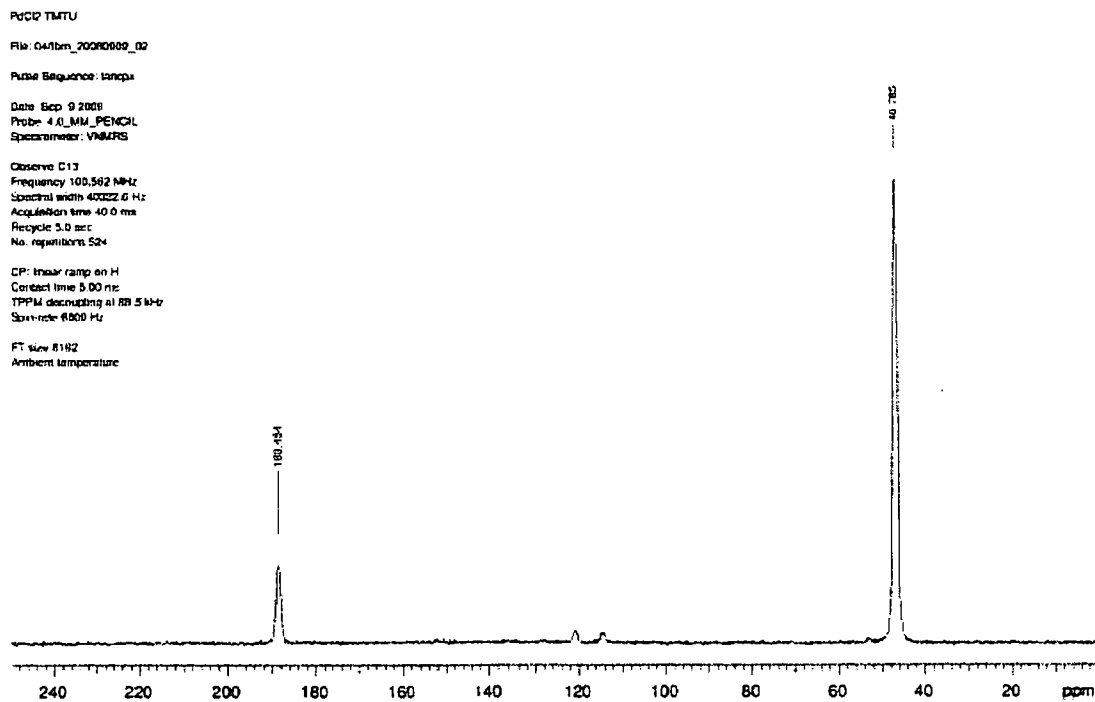


Figure A 6. The solid state $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **Pd(tmtu)**.

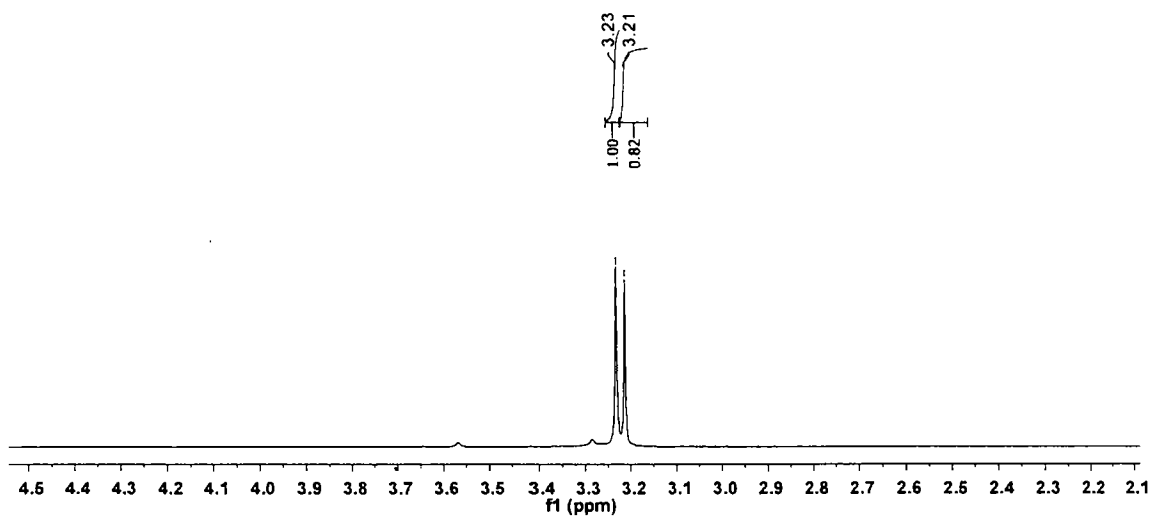


Figure A 7. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of $\text{Pd}_2(\text{tmtu})$.

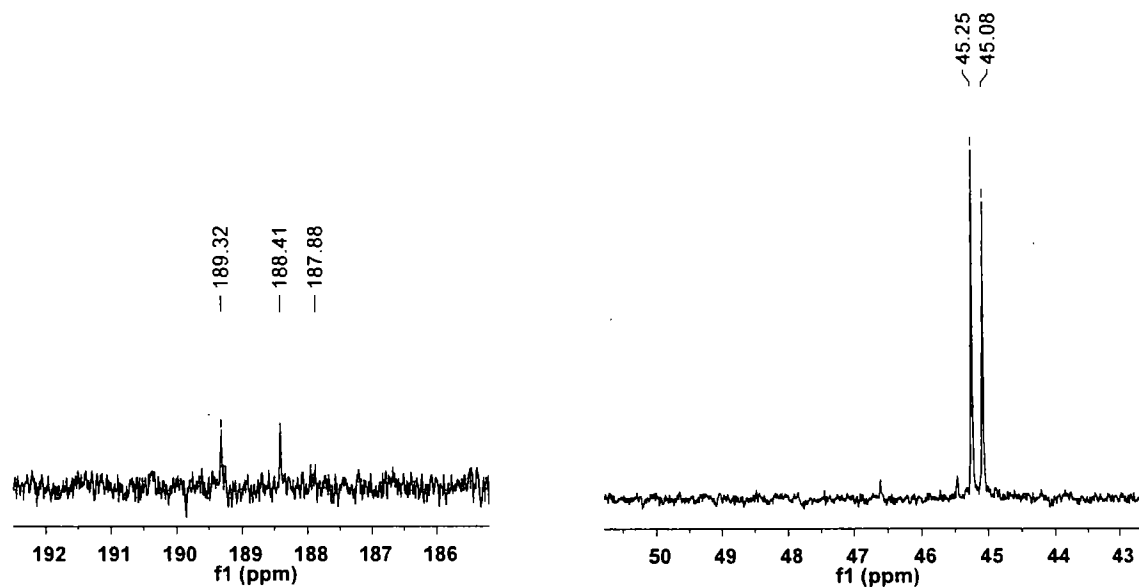


Figure A 8. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of $\text{Pd}_2(\text{tmtu})$.

Pd(Phen)2Cl2.tmsa

File: 02/tms_20071130_01

Pulse Sequence: lincpr

Date: Nov 30 2007

Probe: 4.0_MM_PENCIL

Spectrometer: VNMR5

Observe: C13

Frequency: 100.62 MHz

Spectral width: 40322.6 Hz

Acquisition time: 30.0 min

Recycle: 2.0 sec

No. repetitions: 608

CP: linear ramp on H

Contact time: 1.00 ms

TPPM decoupling at 88.7 kHz

Spin-rate: 8780 Hz

Gaussian broadening: 0.020 sec

FT size: 8192

Ambient temperature

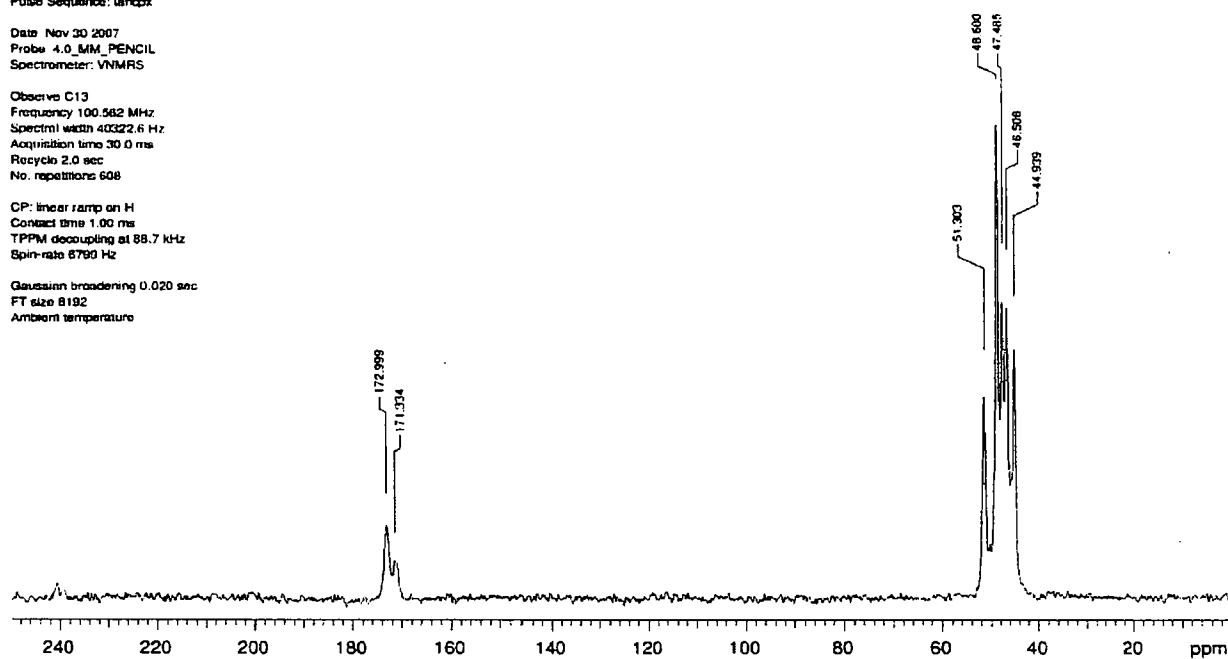


Figure A 9. The solid state $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of $\text{Pd}_2(\text{tmtu})$.

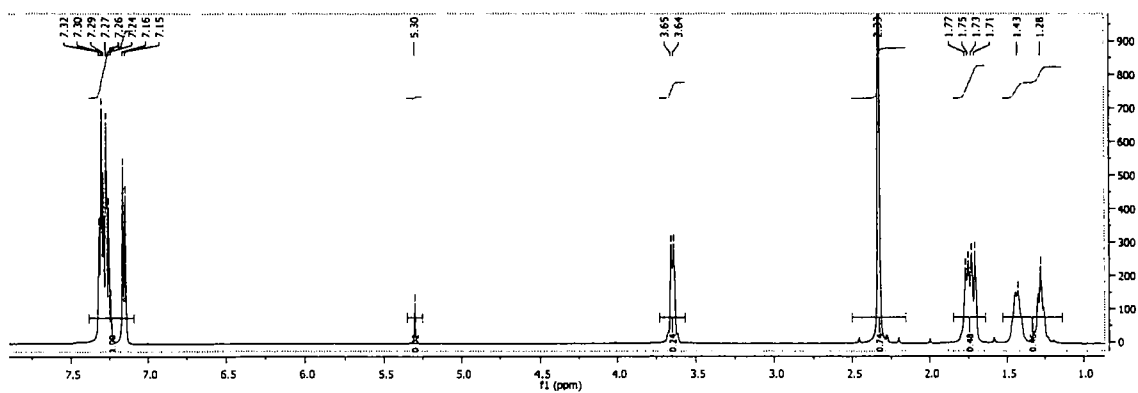


Figure A 10. The ^1H NMR (500 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of **L(rac)**.

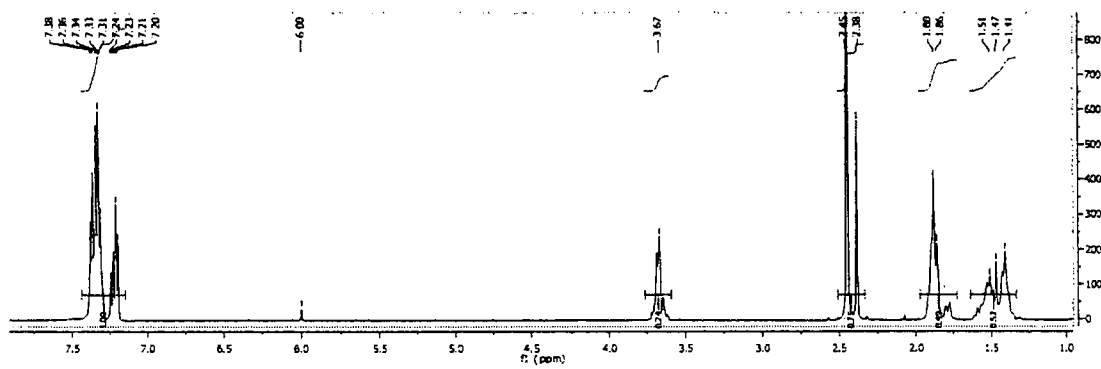


Figure A 11. The ^1H NMR (500 MHz, TCE-d_2 , $100\text{ }^\circ\text{C}$) spectrum of **L(rac)**.

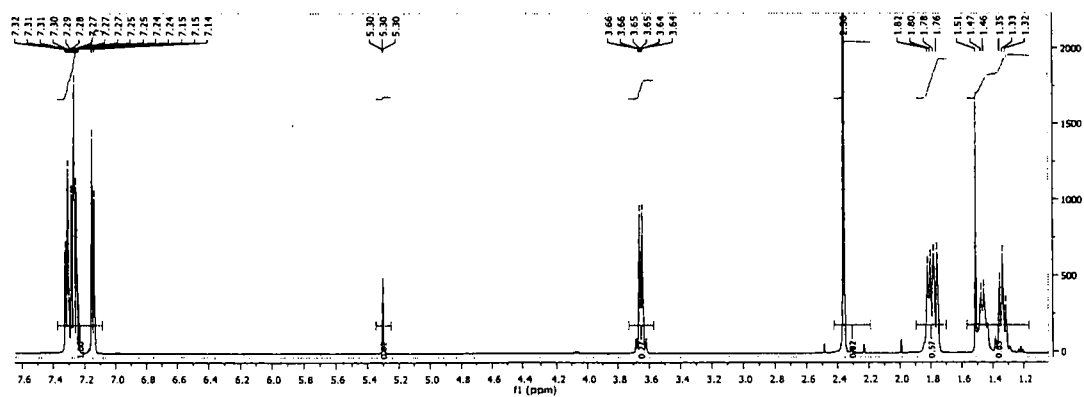


Figure A 12. The ^1H NMR (500 MHz, CD_2Cl_2 , $20\text{ }^\circ\text{C}$) spectrum of **L(rac)**.

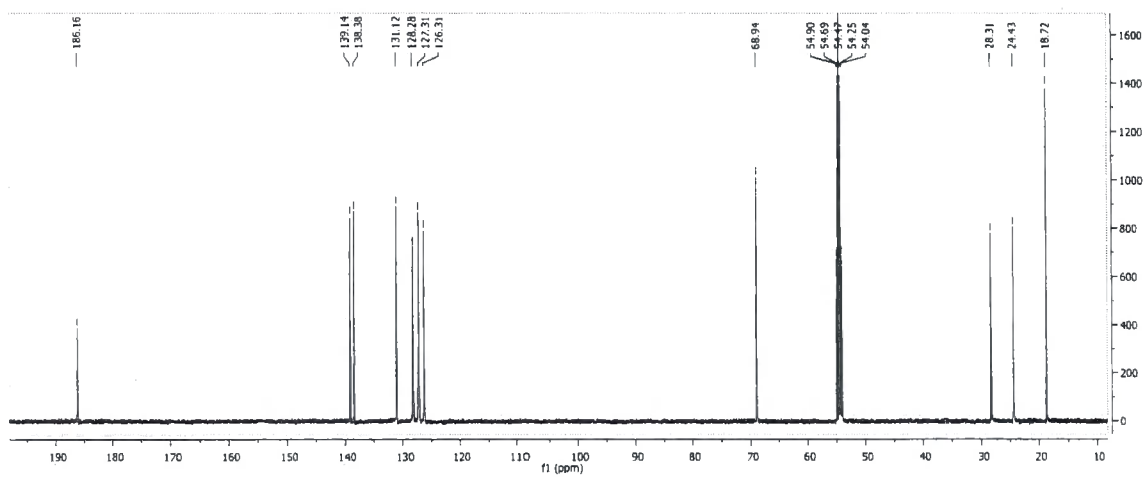


Figure A 13. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of **L(rac)**.

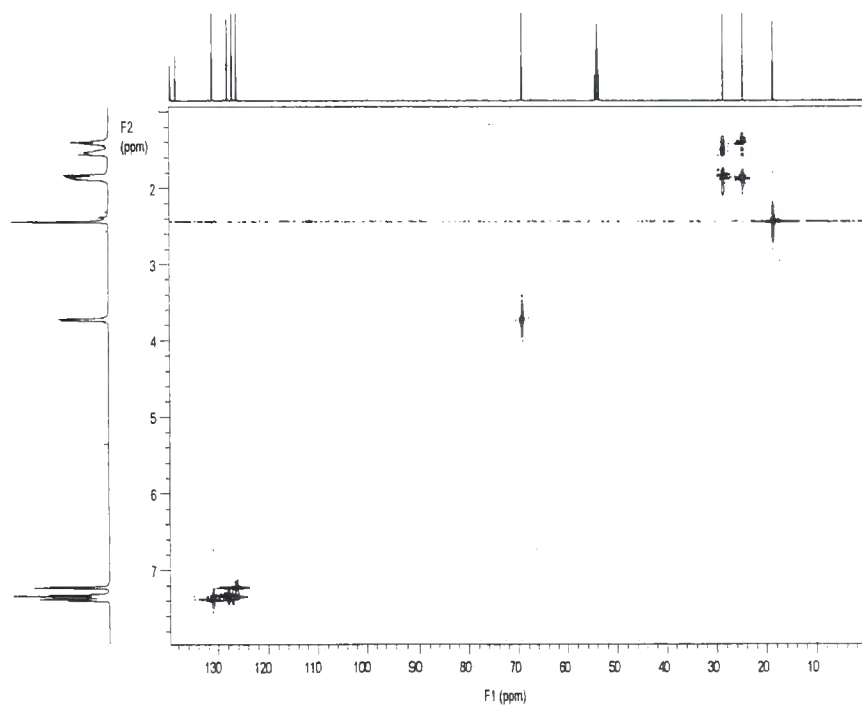


Figure A 14. The HSQC ($20\text{ }^\circ\text{C}$) spectrum of **L(rac)**.

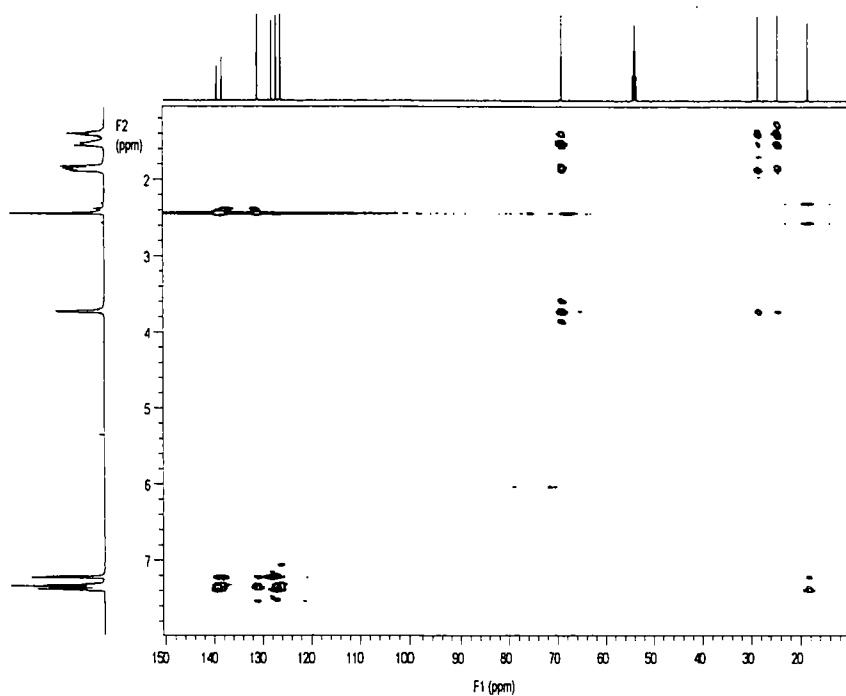


Figure A 15. The HMBC (20 °C) spectrum of **L(rac)**.

C₂ chiral thiourea palladium complexes

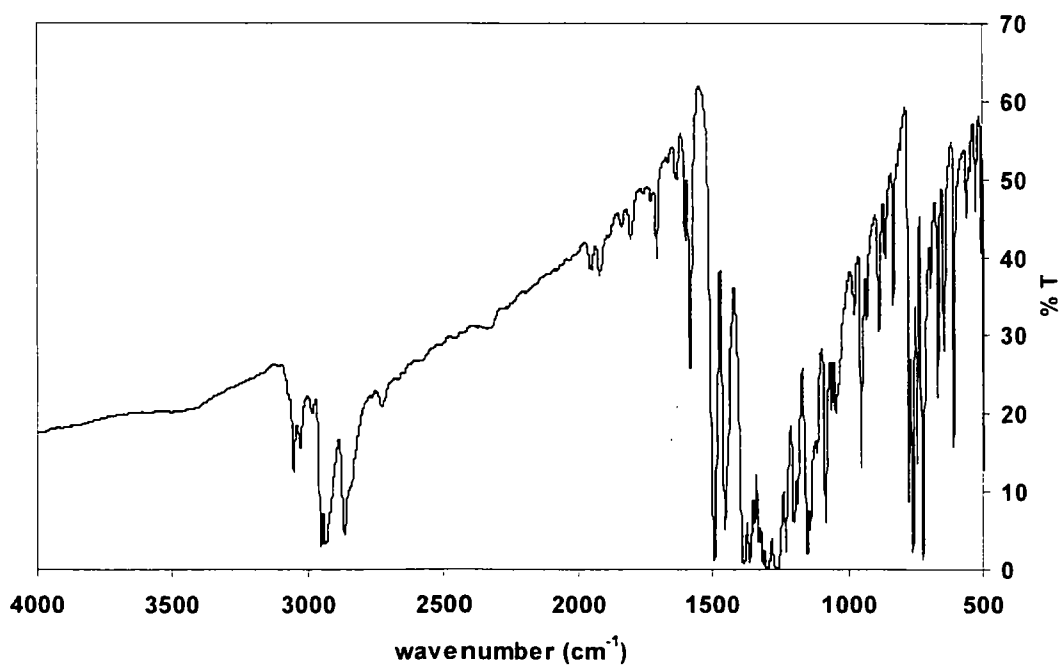
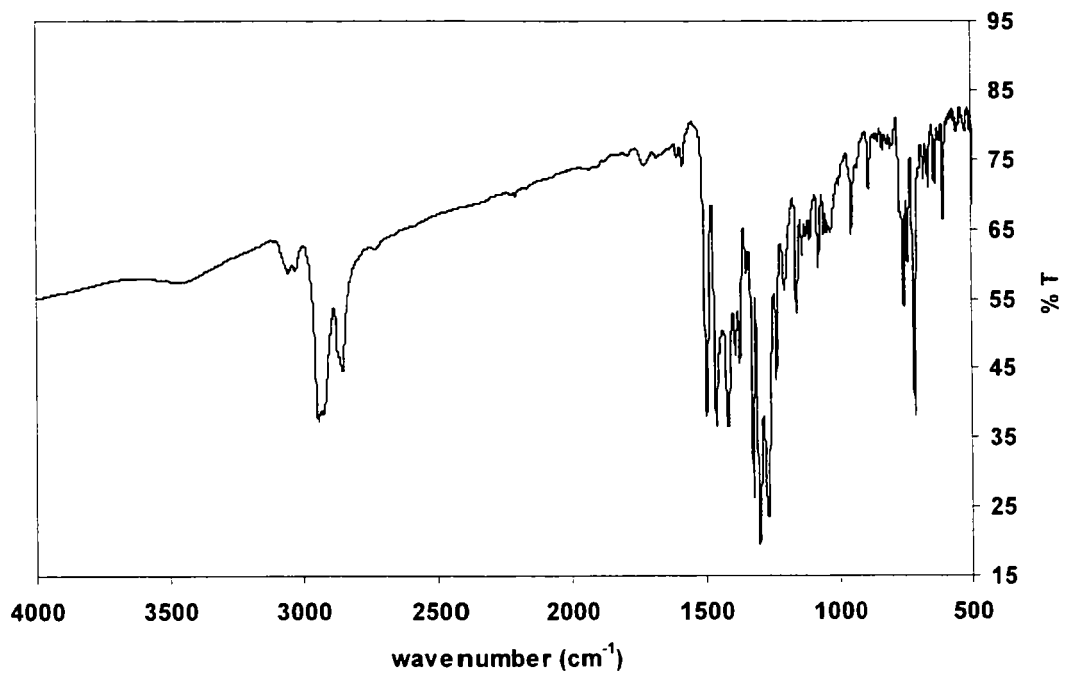
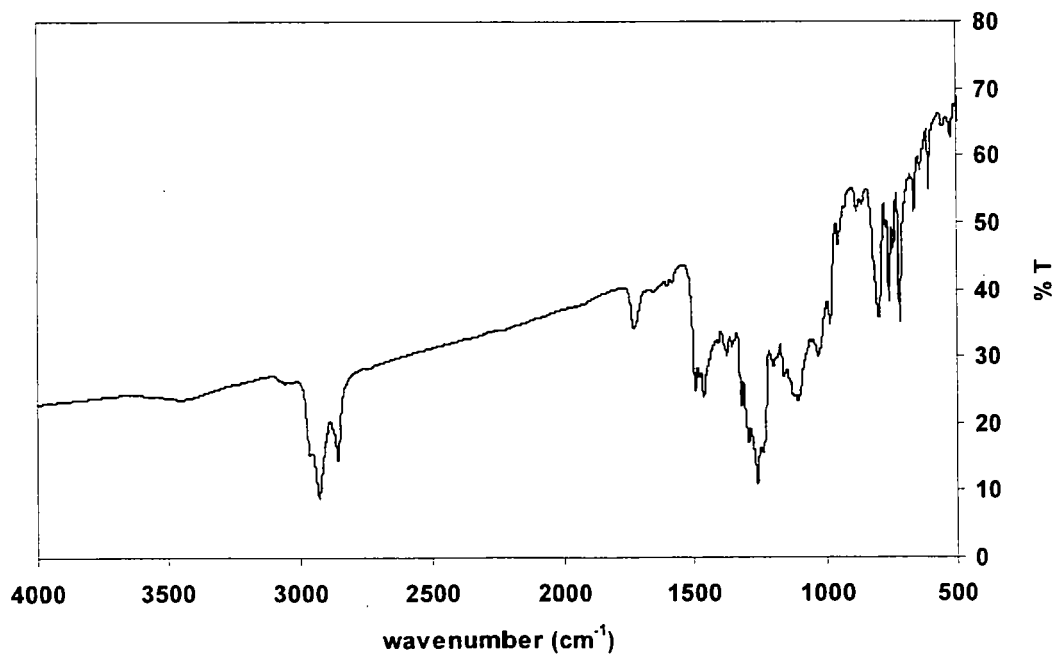


Figure A 16. IR spectrum of **L(rac)**.

Figure A 17. IR spectrum of *rac*-Pd / *meso*-Pd.Figure A 18. IR spectrum of *rac*-Pd₂ / *meso*-Pd₂.

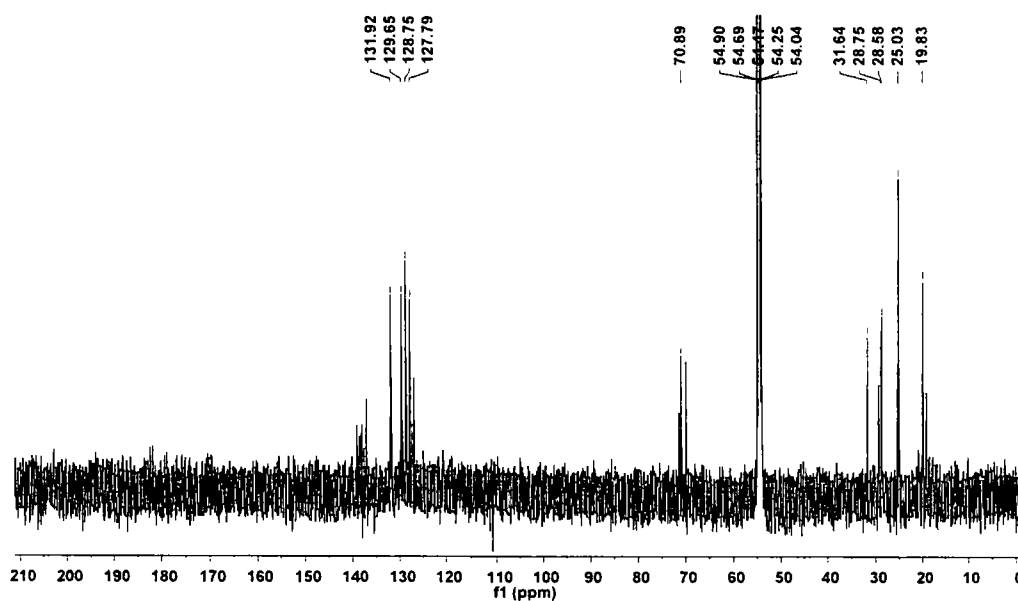


Figure A 19. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of *rac*-Pd / *meso*-Pd at room temperature.

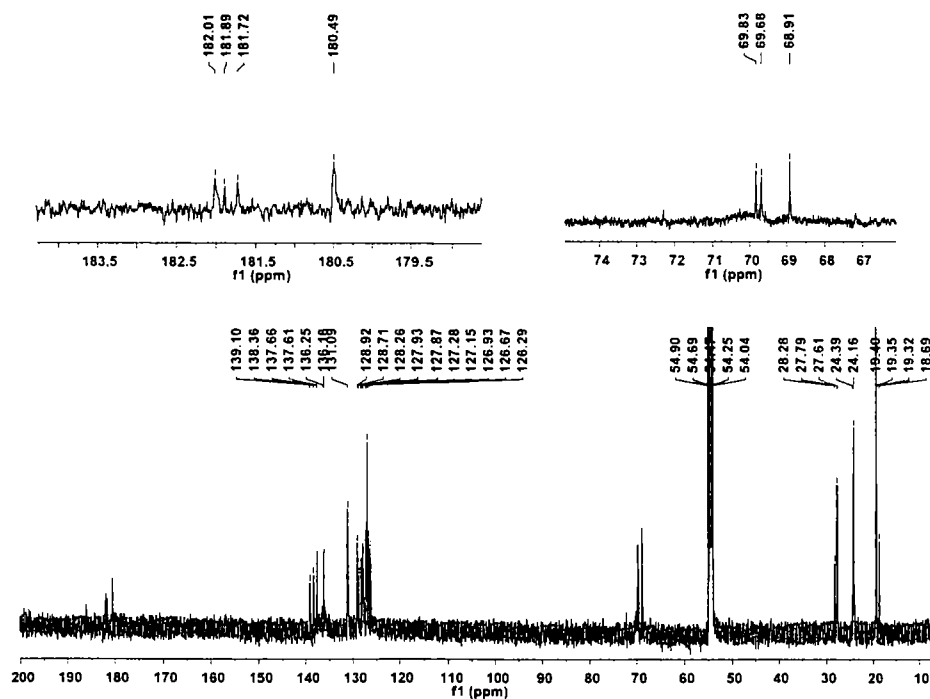


Figure A 20. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectra of *rac*-Pd / *meso*-Pd at 60 °C, the expanded C=S (top left) and C3 regions (top right).

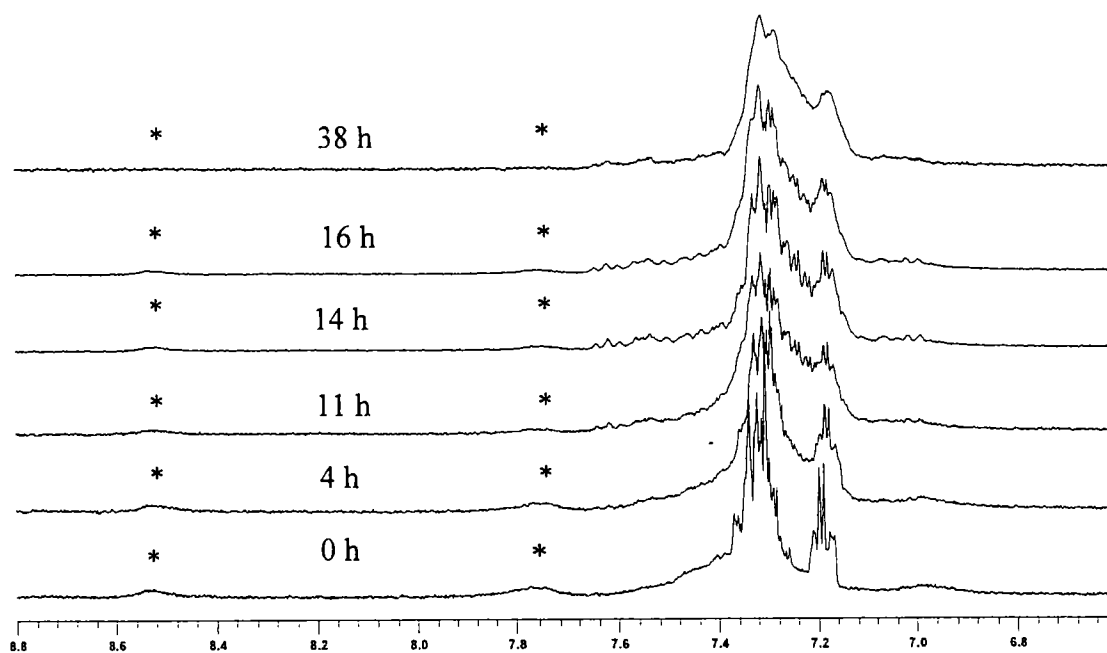


Figure A 21. The ^1H NMR (400 MHz, CD_2Cl_2 , 20 $^\circ\text{C}$) monitoring of the reaction of $\text{rac-Pd}_2 / \text{meso-Pd}_2$ converted to $\text{trans-rac-Pd} / \text{trans-meso-Pd}$ with $\text{L}(\text{rac})$ at various times, * = $\text{rac-Pd}_2 / \text{meso-Pd}_2$.

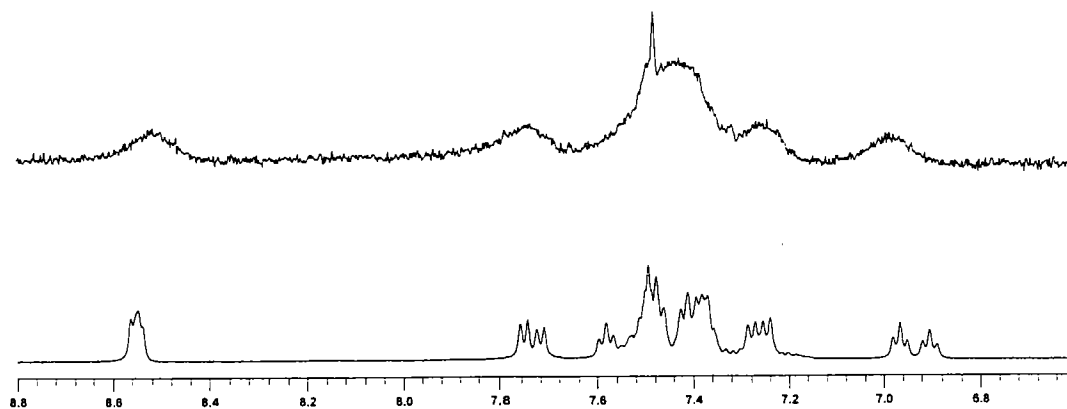


Figure A 22. The ^1H NMR (500 MHz) spectra of $\text{rac-Pd}_2 / \text{meso-Pd}_2$ in CD_2Cl_2 (top) and TCE-d_2 (bottom) at room temperature.

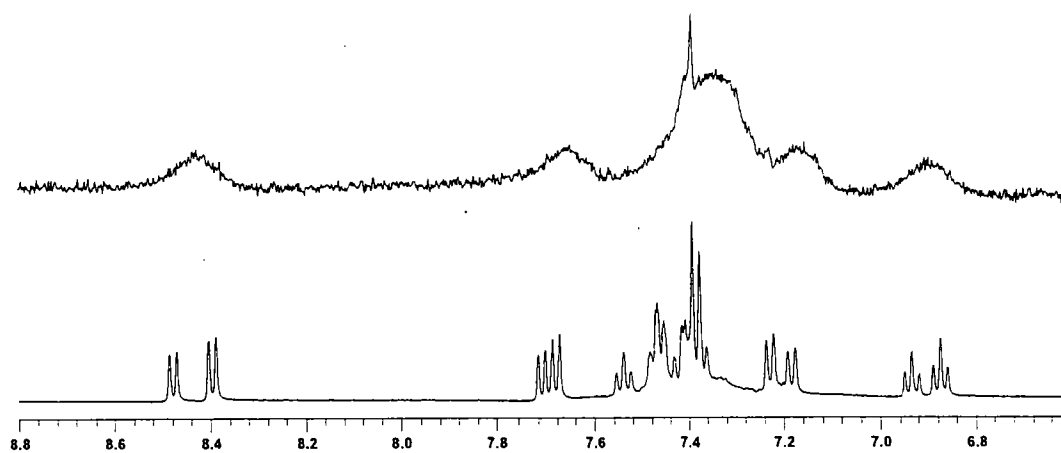


Figure A 23. The ^1H NMR (500 MHz) spectra of *rac*- Pd_2 / *meso*- Pd_2 in CD_2Cl_2 at room temperature (top) and $-60\text{ }^\circ\text{C}$ (bottom).

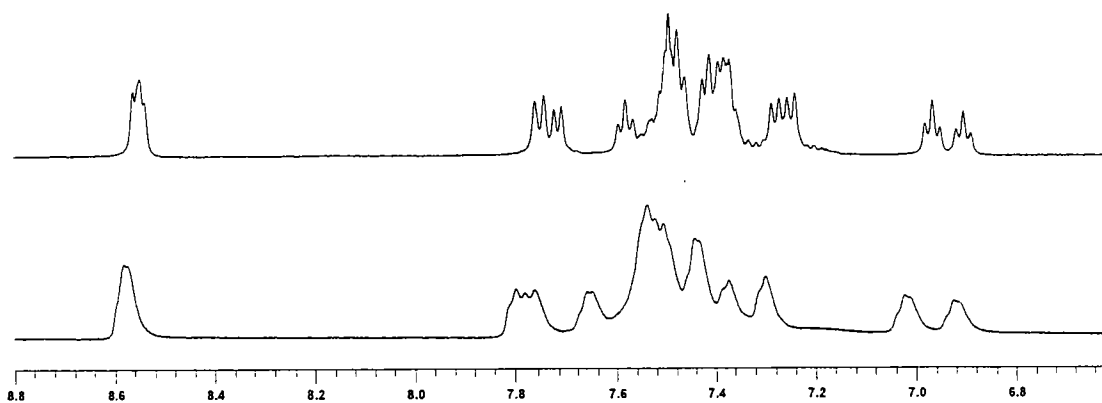


Figure A 24. ^1H NMR (500 MHz) spectra of *rac*- Pd_2 / *meso*- Pd_2 in TCE-d_2 at room temperature (top) and $-30\text{ }^\circ\text{C}$ (bottom).

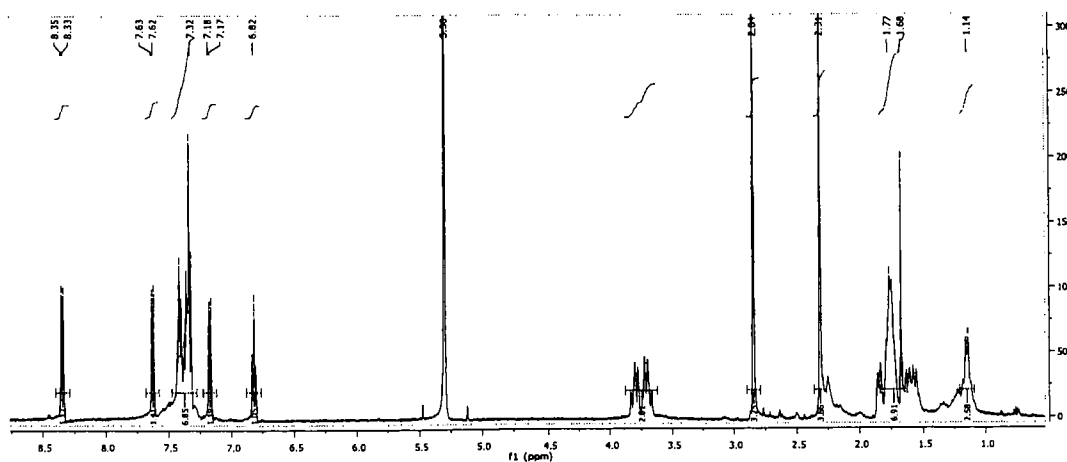


Figure A 25. The ^1H NMR (500 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of *R,R*- Pd_2 .

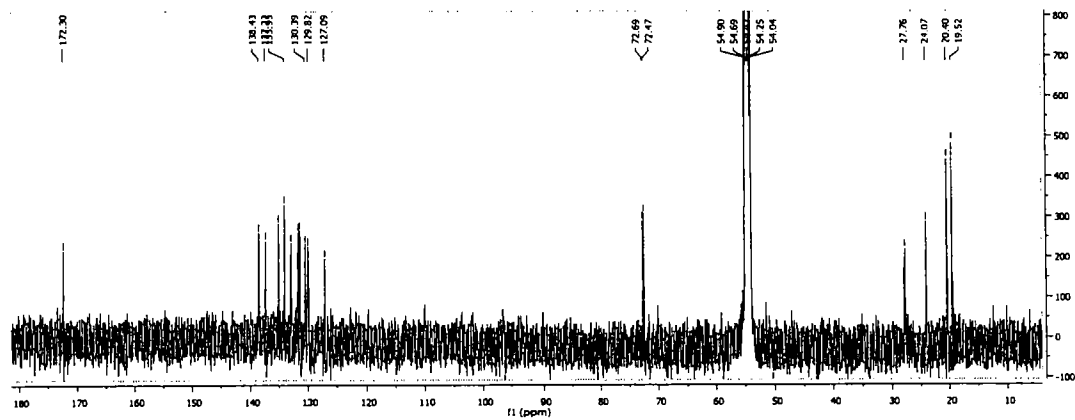


Figure A 26. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2 , -60°C) spectrum of R,R-Pd_2 .

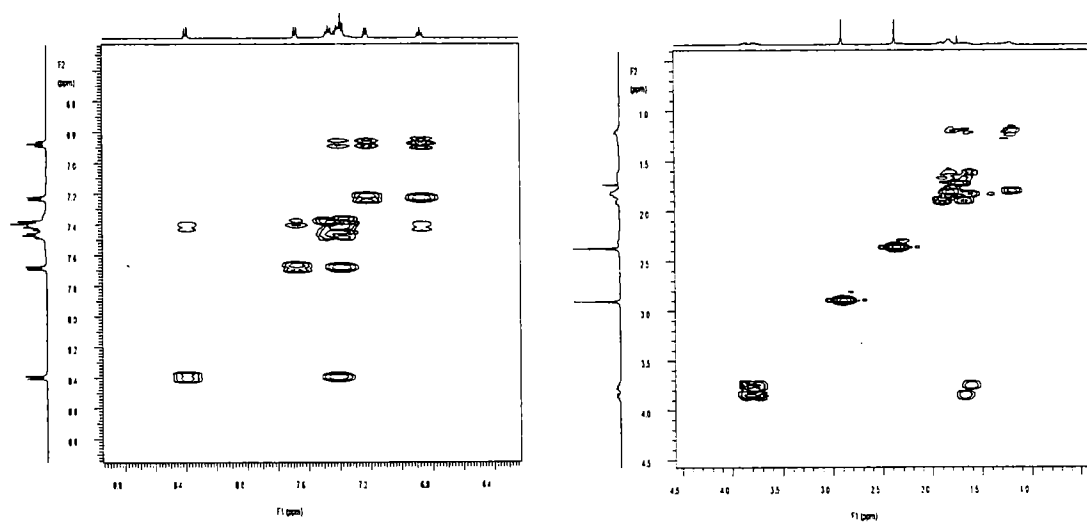


Figure A 27. The COSY spectrum (500 MHz, CD_2Cl_2 , -60°C) of $\text{Pd}_2(\text{R,R})$ in the aromatic (left) and aliphatic regions (right).

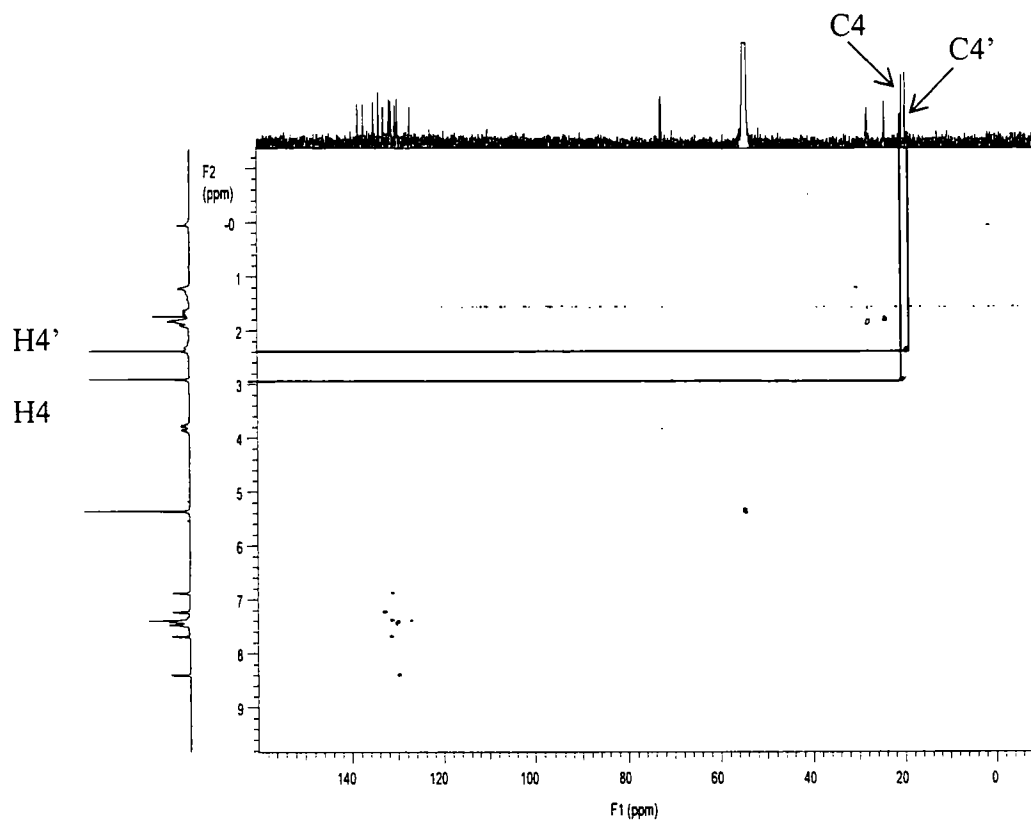


Figure A 28. The HSQC (CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum of **R,R-Pd₂**.

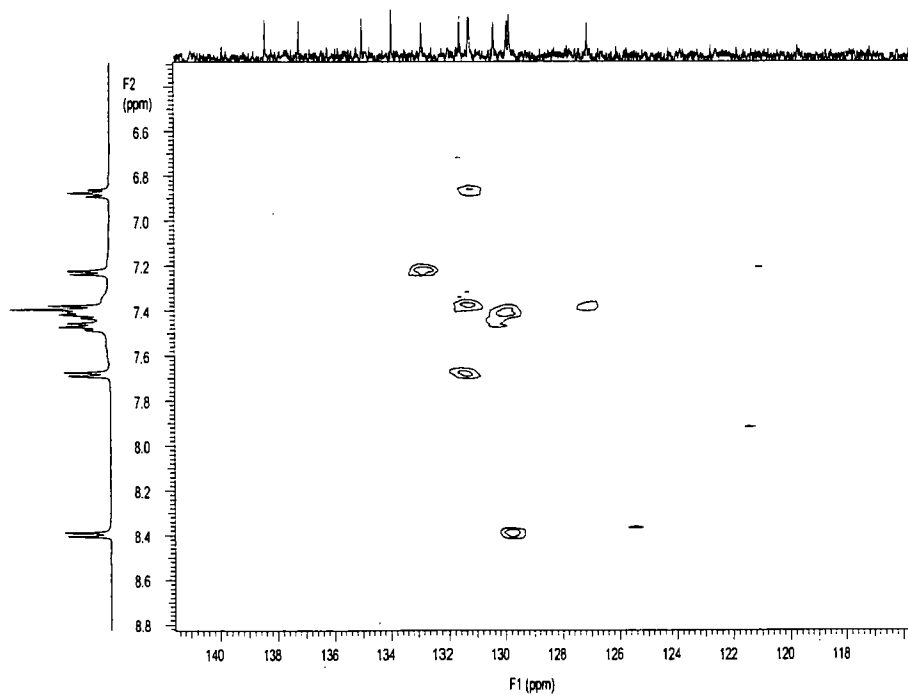


Figure A 29. The HSQC NMR (CD_2Cl_2 , $-60\text{ }^\circ\text{C}$) spectrum in the aromatic region of **R,R-Pd₂**.

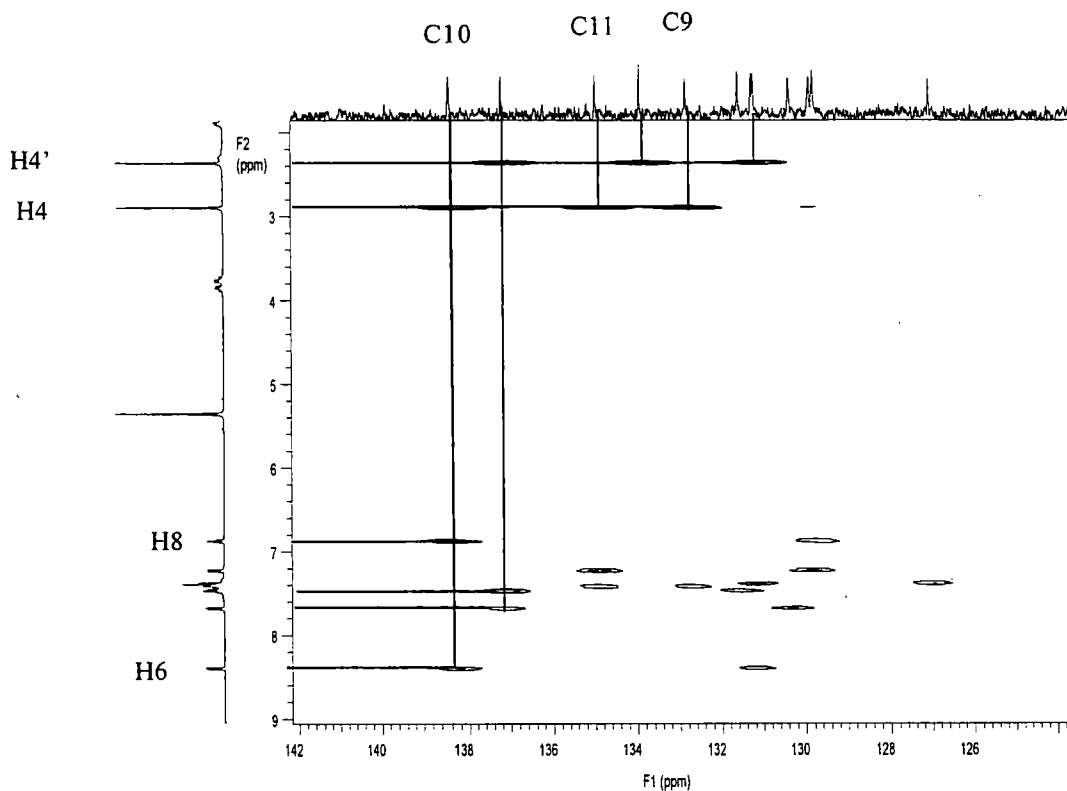


Figure A 30. The HMBC NMR (CD_2Cl_2 , -60°C) spectrum in the aromatic region of **R,R-Pd₂**.

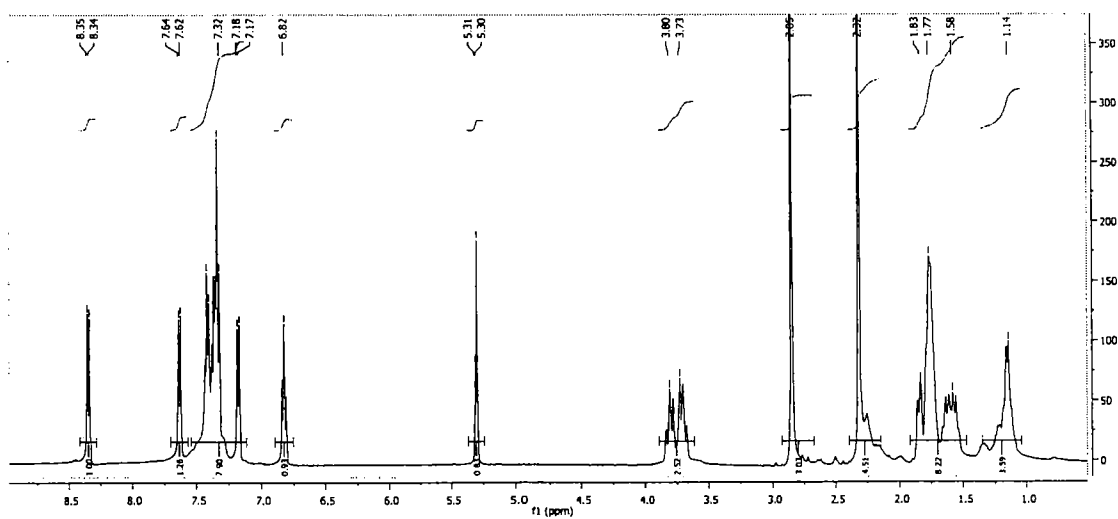


Figure A 31. The ^1H NMR (500 MHz, CD_2Cl_2 , -60°C) spectrum of **S,S-Pd₂**.

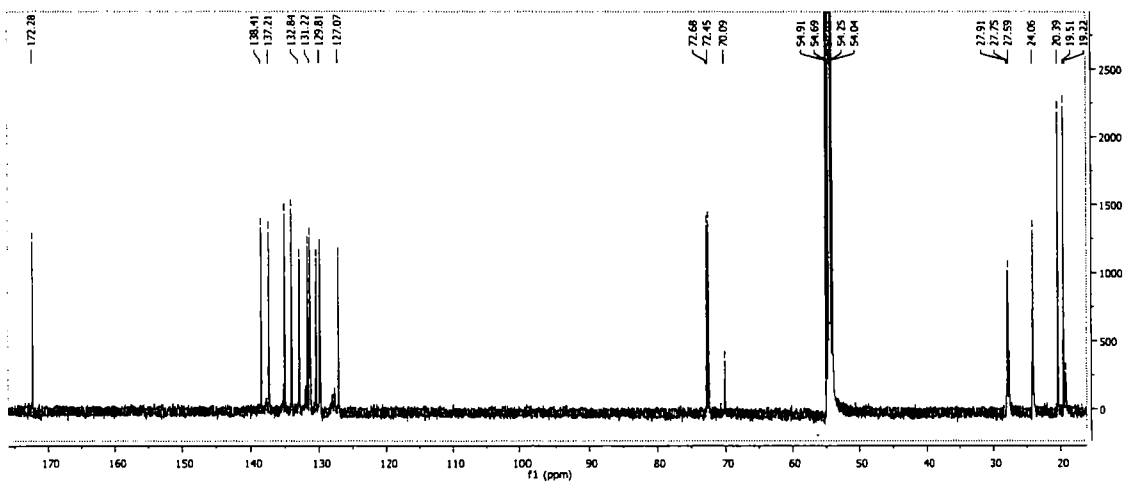


Figure A 32. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2 , -60°C) spectrum of *S,S*- Pd_2 .

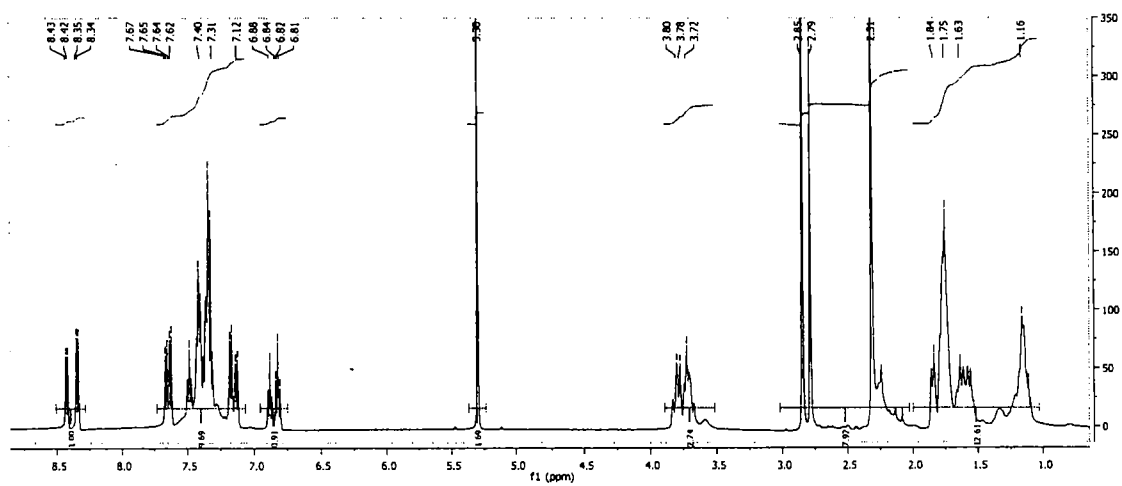


Figure A 33. The ^1H (500 MHz, CD_2Cl_2 , -60°C) spectrum of *rac*- Pd_2 / *meso*- Pd_2 .

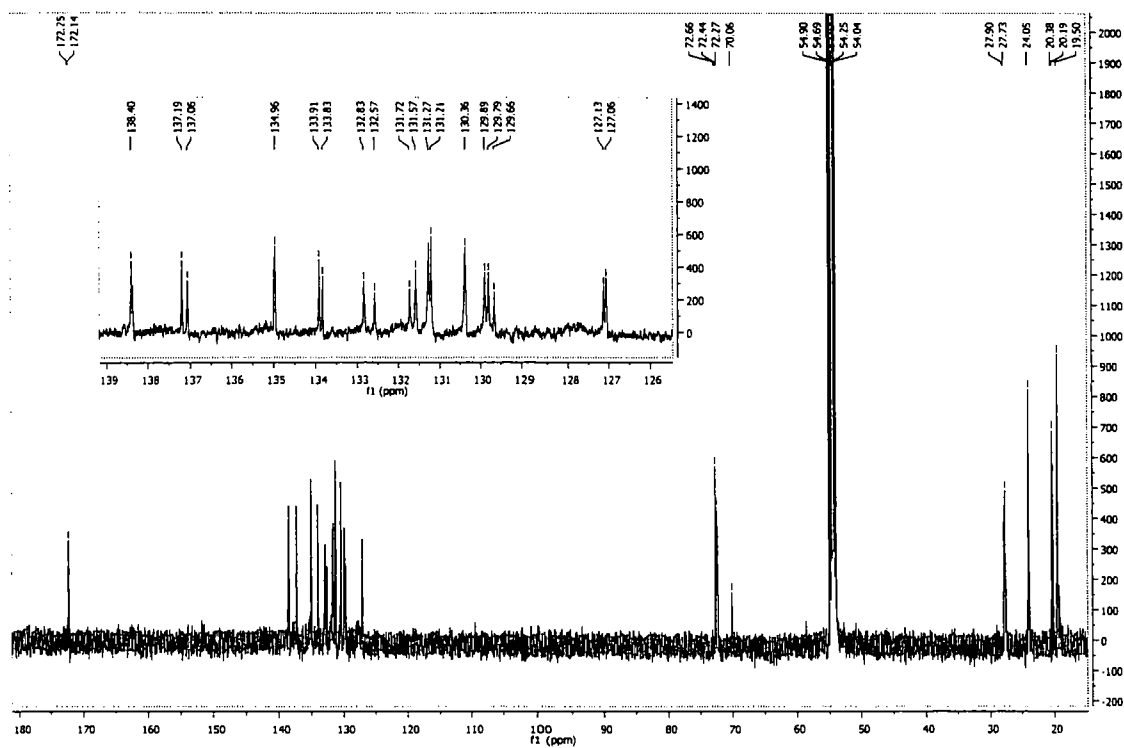


Figure A 34. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2 , -60°C) spectrum of *rac*- Pd_2 / *meso*- Pd_2 .

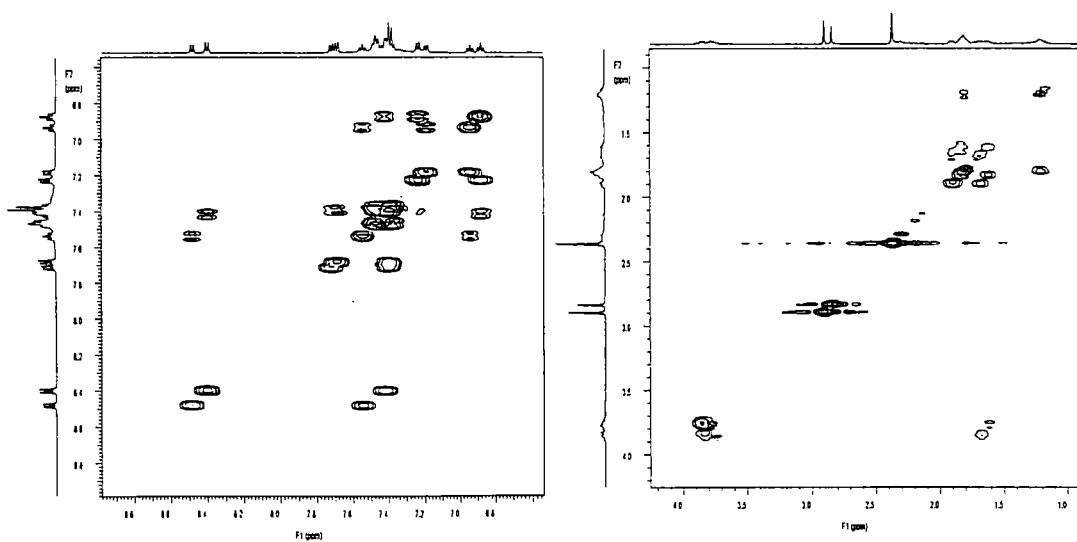


Figure A 35. The COSY (500 MHz, CD_2Cl_2 , -60°C) spectrum of *rac*- Pd_2 / *meso*- Pd_2 .

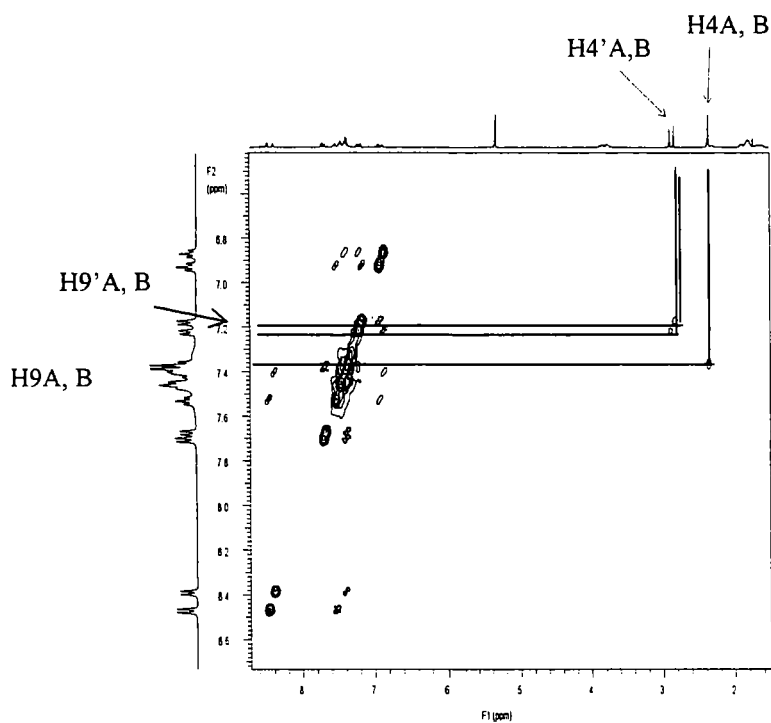


Figure A 36. The NOESY (500 MHz, CD_2Cl_2 , -60°C) spectrum of *rac*- Pd_2 / *meso*- Pd_2 .

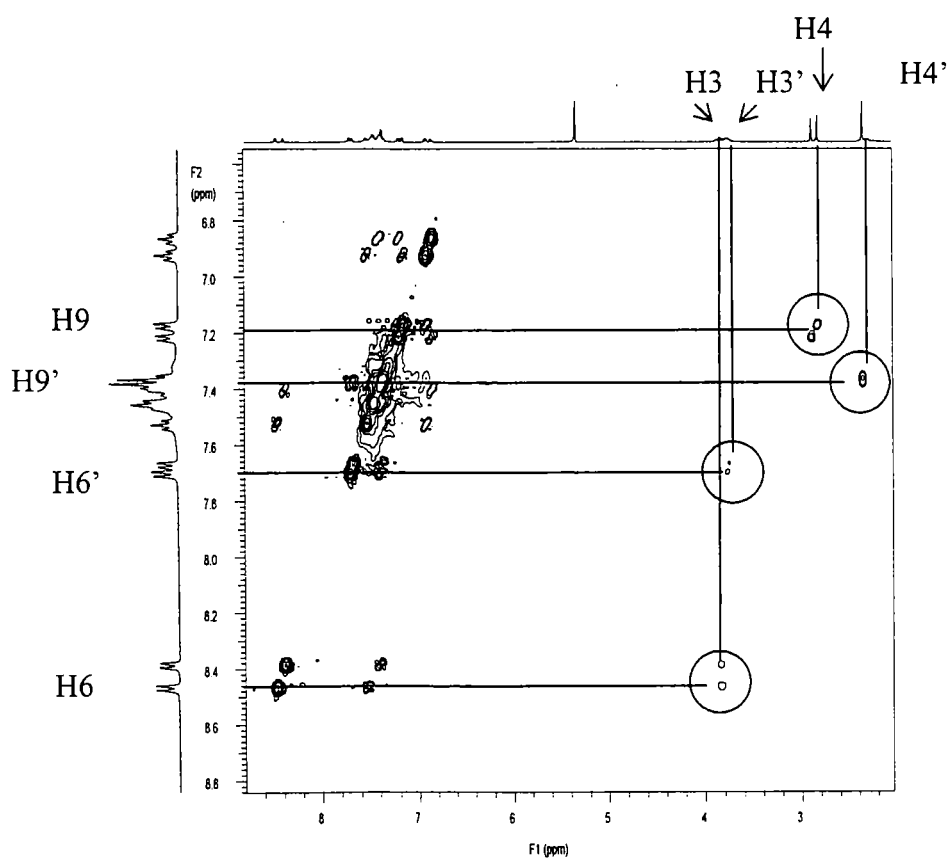


Figure A 37. The NOESY (500 MHz) *rac*- Pd_2 / *meso*- Pd_2 in CD_2Cl_2 at -60°C .

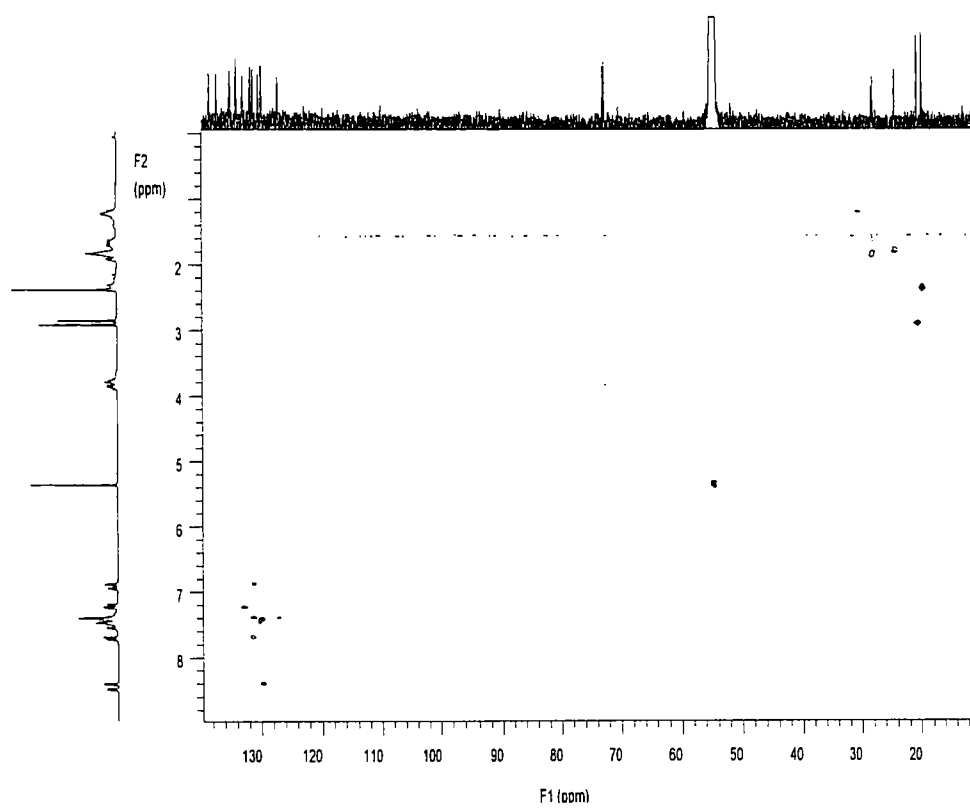


Figure A 38. The HSQC NMR (CD_2Cl_2 , -60°C) spectrum of *rac*- Pd_2 / *meso*- Pd_2 .

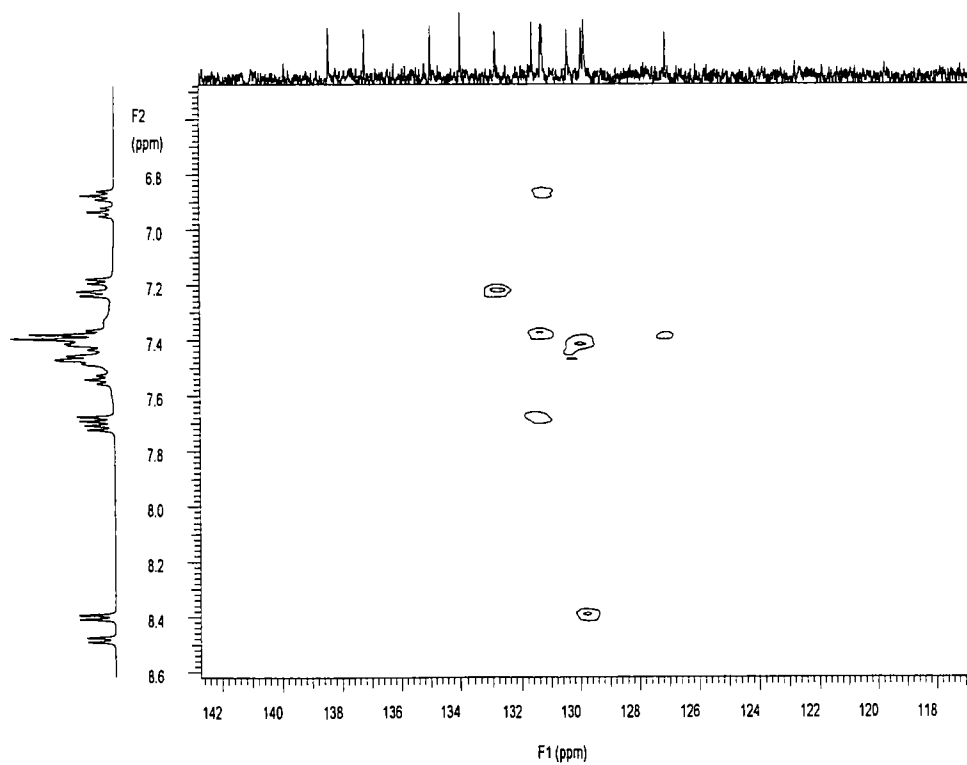


Figure A 39. The HSQC NMR (CD_2Cl_2 , -60°C) spectrum in aromatic region of *rac*- Pd_2 / *meso*- Pd_2 .

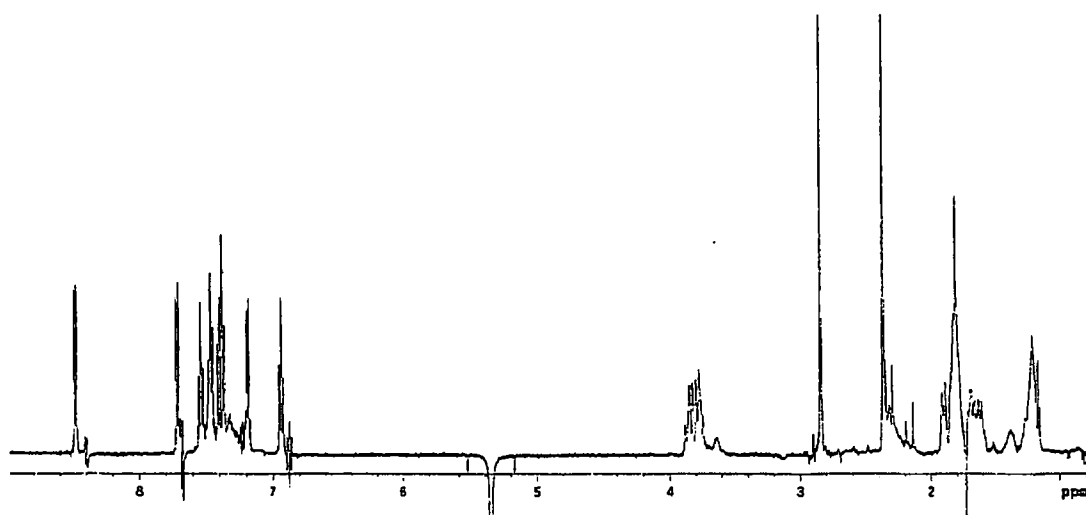


Figure A 40. The ¹H NMR (500 MHz, CD₂Cl₂, -60 °C) spectrum of *rac*-Pd₂ / *meso*-Pd₂ minus *S,S*-Pd₂.

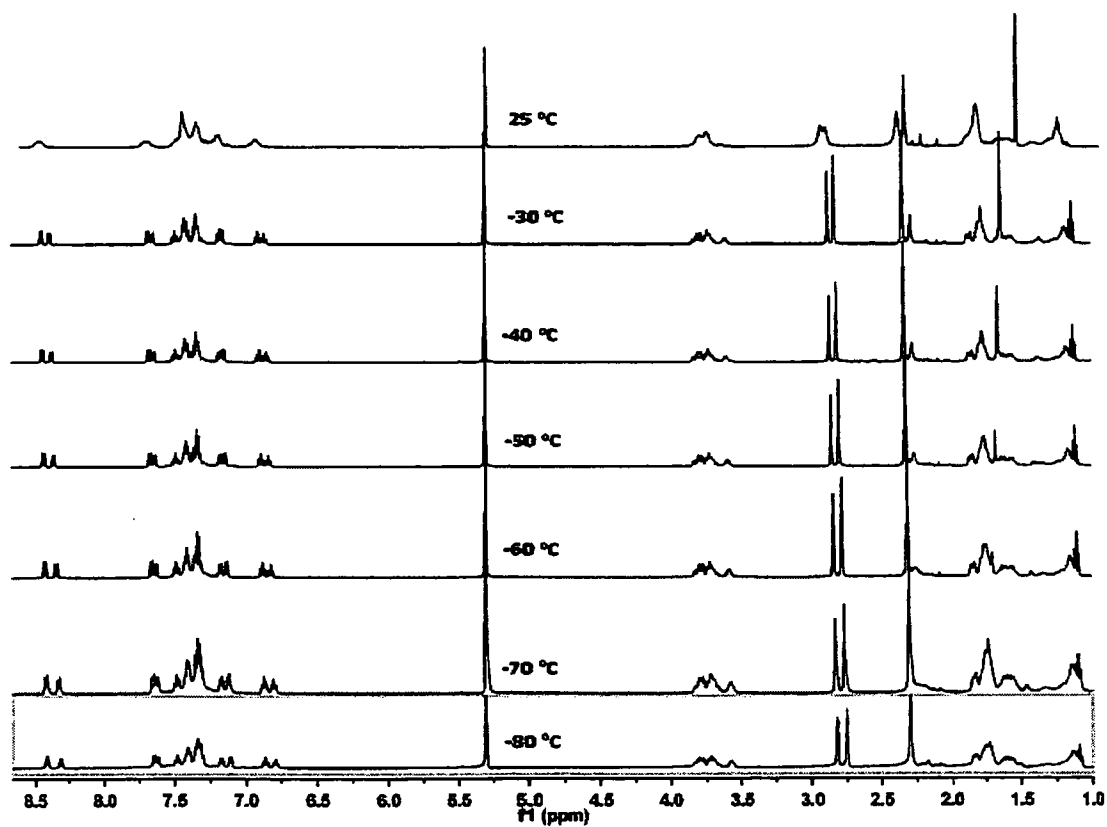


Figure A 41. The ¹H NMR (500 MHz, CD₂Cl₂) spectra of *rac*-Pd₂ / *meso*-Pd₂ at various temperatures.

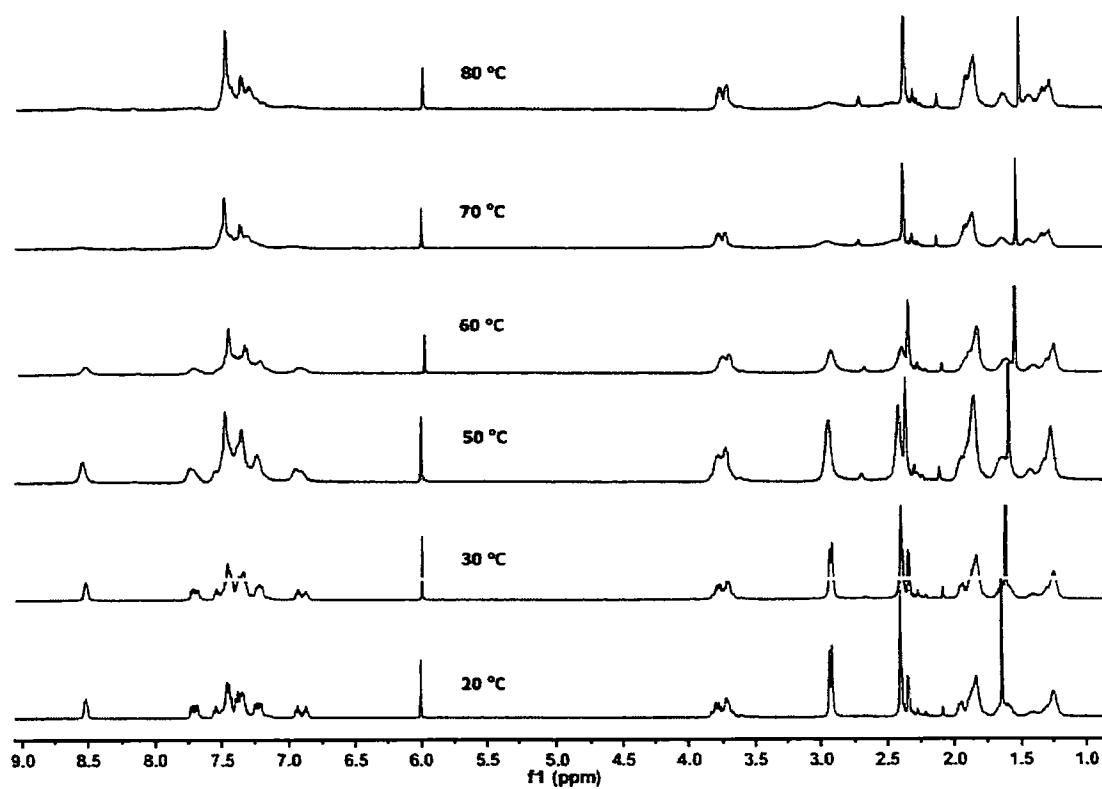


Figure A 42. The ^1H NMR (500 MHz, TCE- d_2) spectra of *rac*- Pd_2 / *meso*- Pd_2 at various temperatures.

Appendix B

S,N-Bidentate Thioureas and Their Palladium Complexes

Appendix B

S_2N -Bidentate thioureas

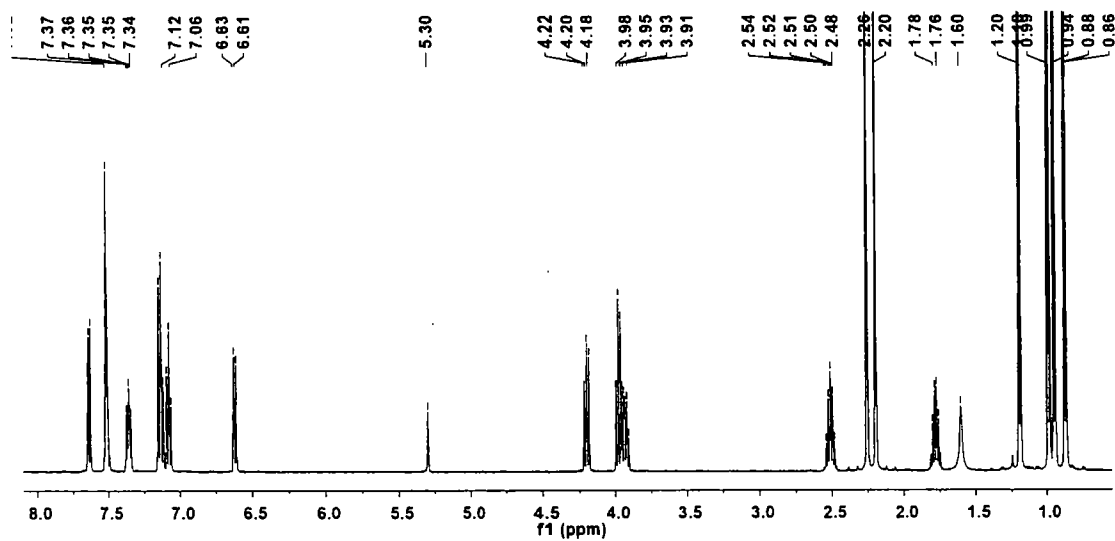


Figure B 1. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of **L2up**.

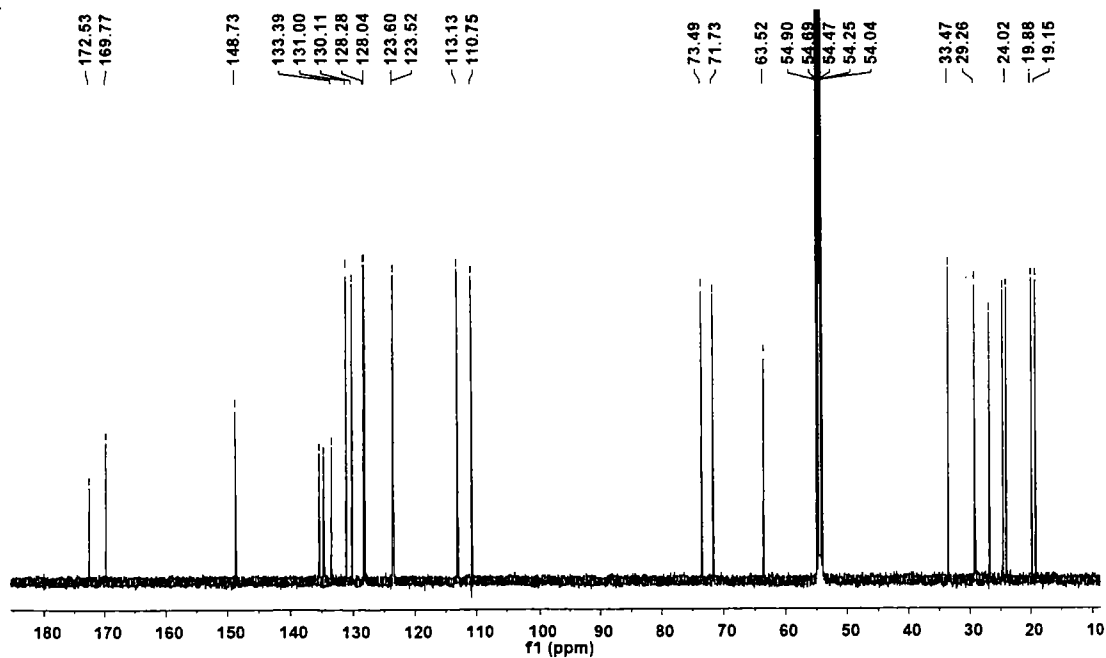


Figure B 2. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L2up**.

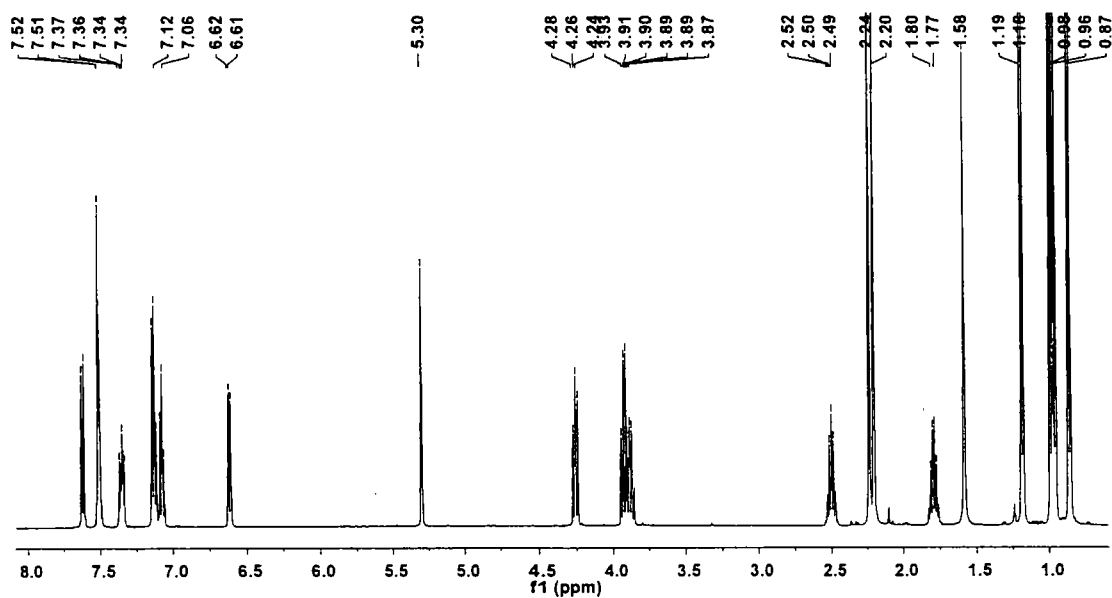


Figure B 3. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of **L2down**.

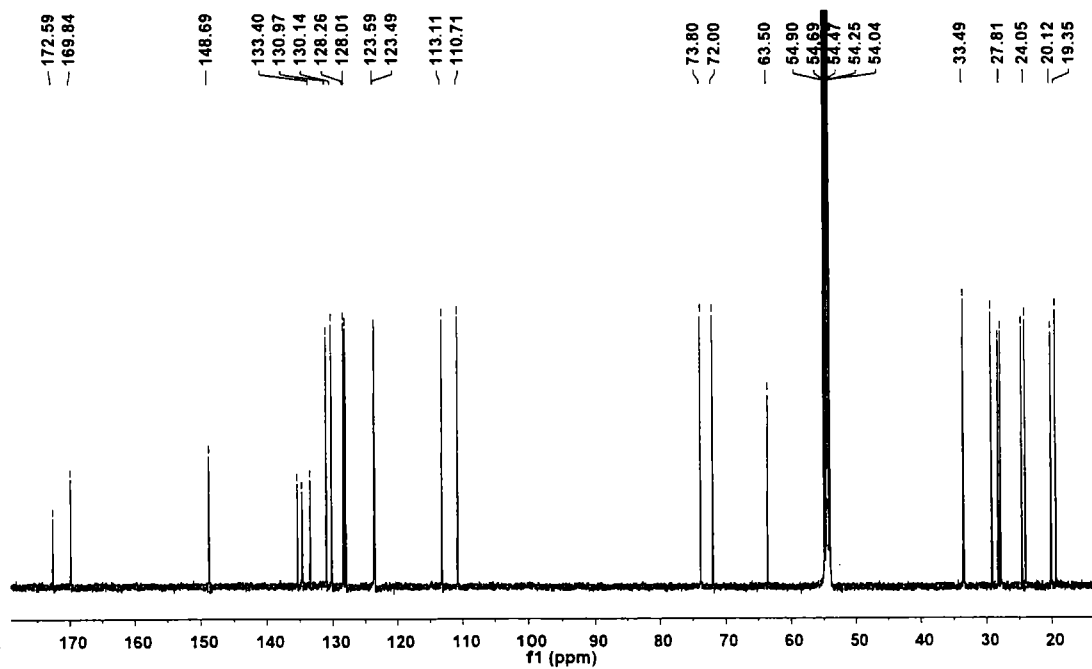


Figure B 4. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L2down**.

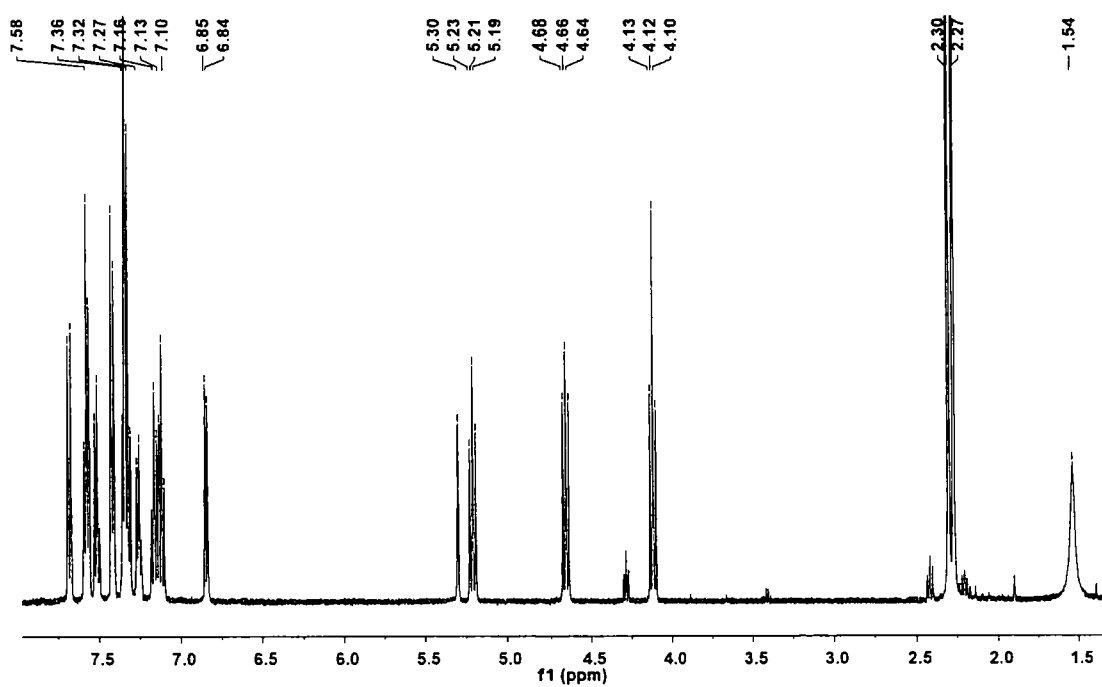


Figure B 5. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of L3.

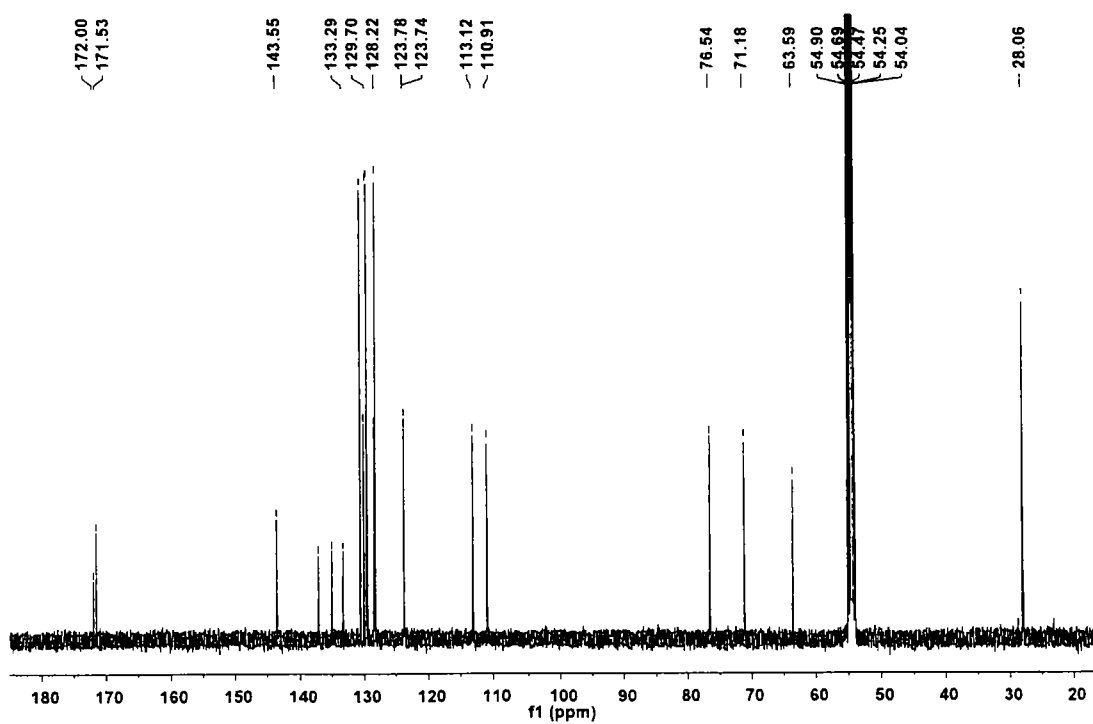


Figure B 6. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of L3.

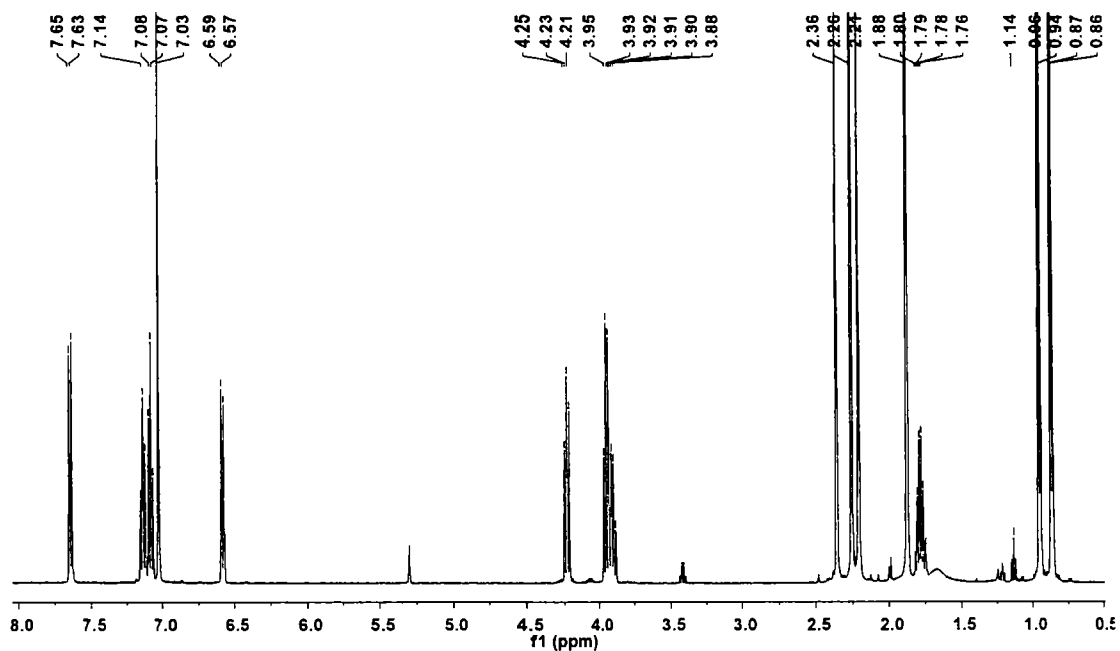


Figure B 7. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of L4.

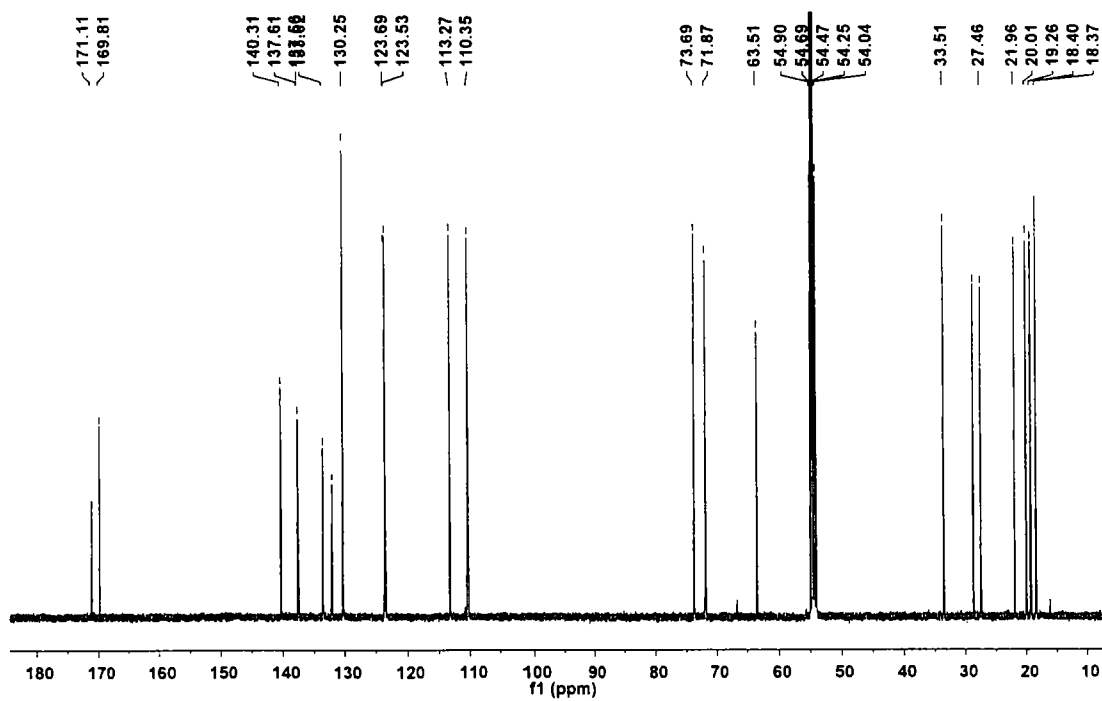


Figure B 8. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of L4.

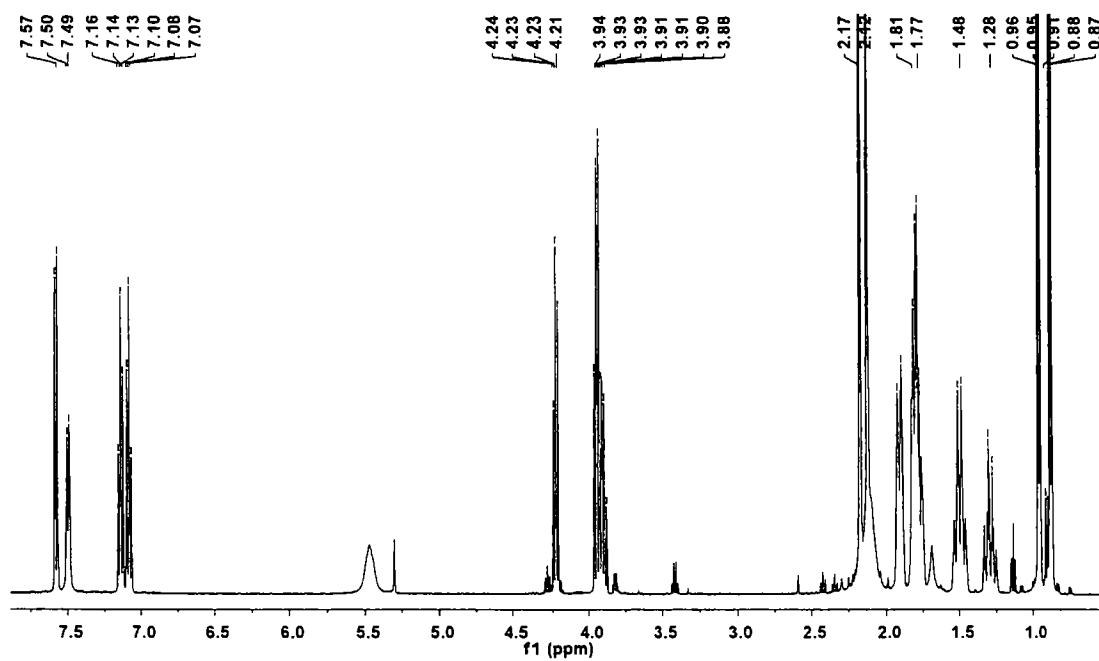


Figure B 9. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of L5.

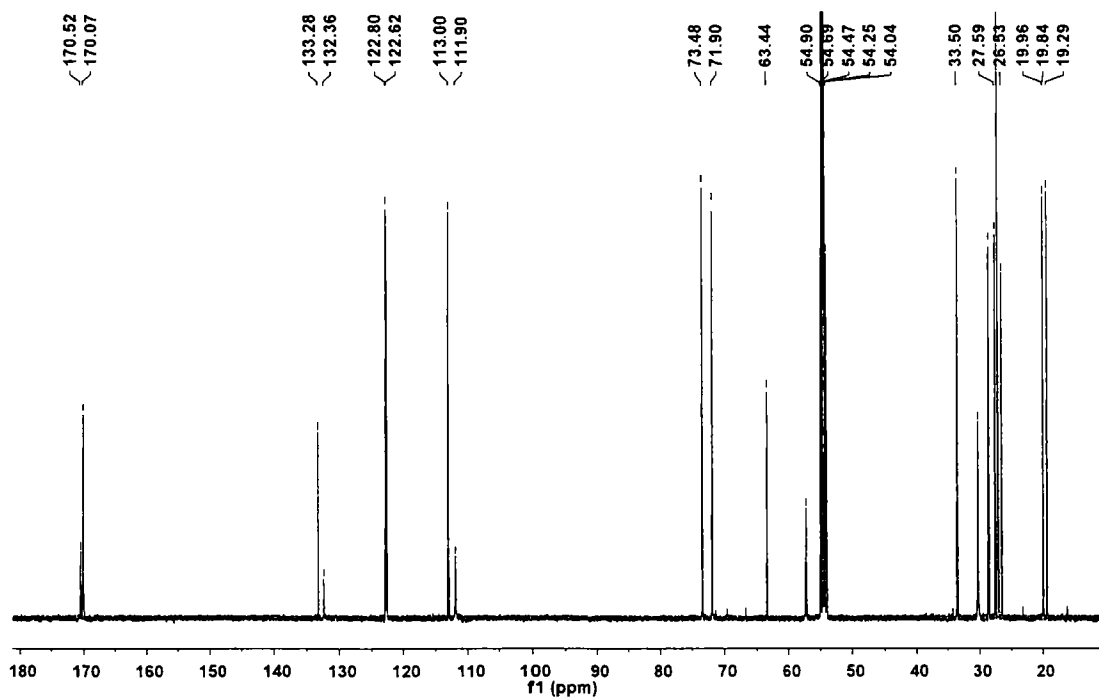


Figure B 10. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of L5.

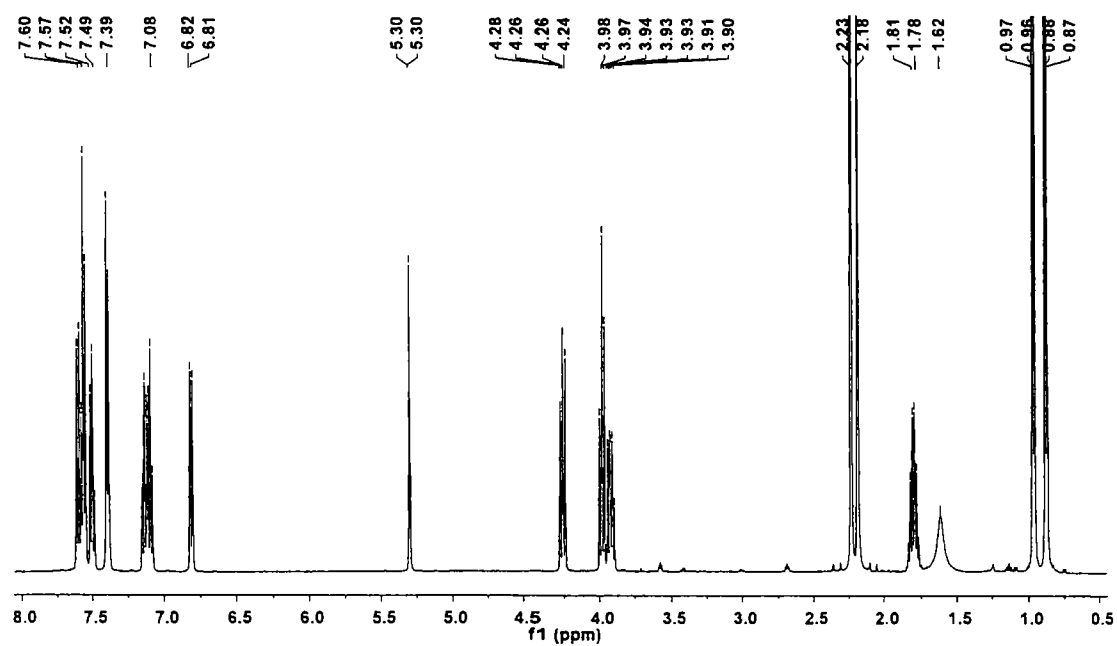


Figure B 11. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of L6.

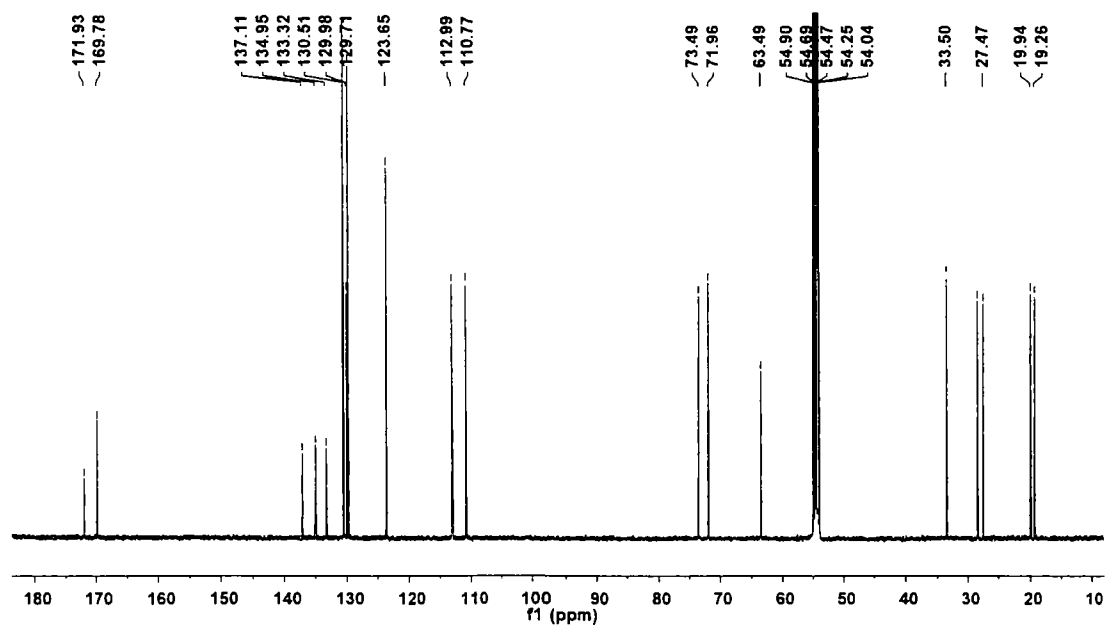
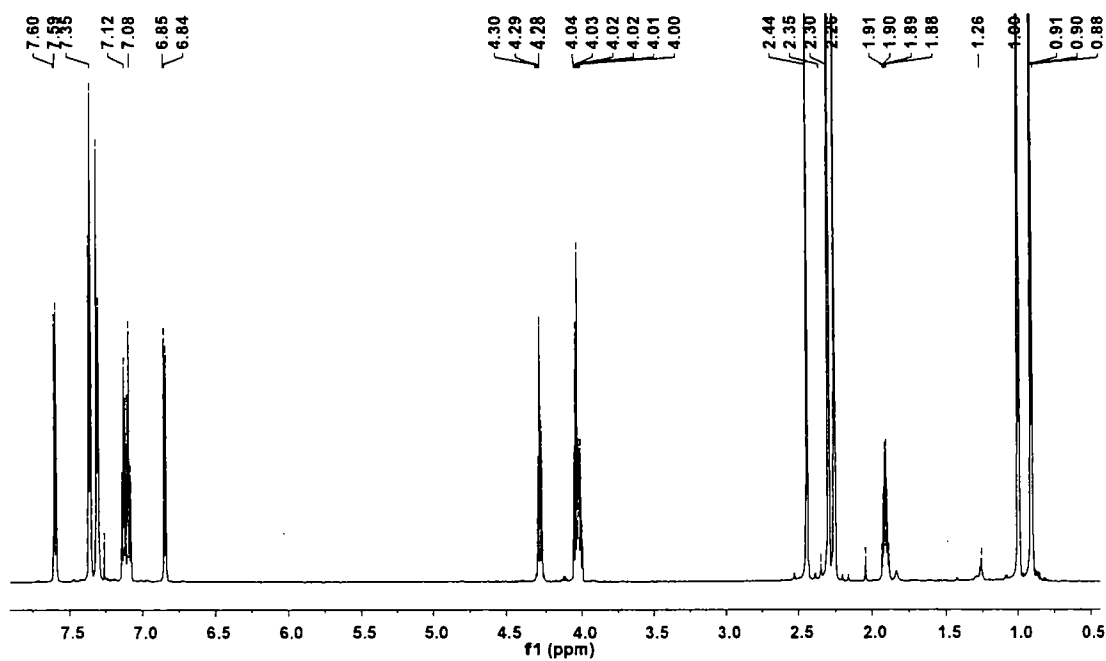
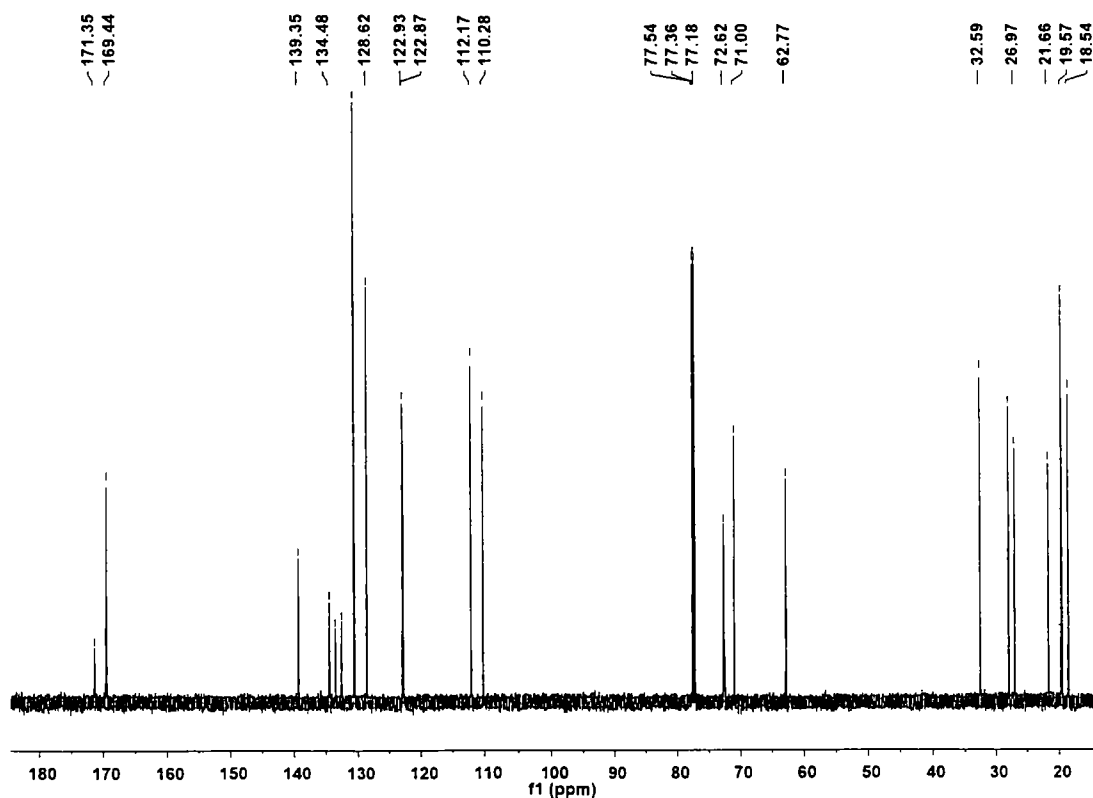


Figure B 12. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of L6.

Figure B 13. The ^1H NMR (700 MHz, CDCl_3) spectrum of L7.Figure B 14. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of L7.

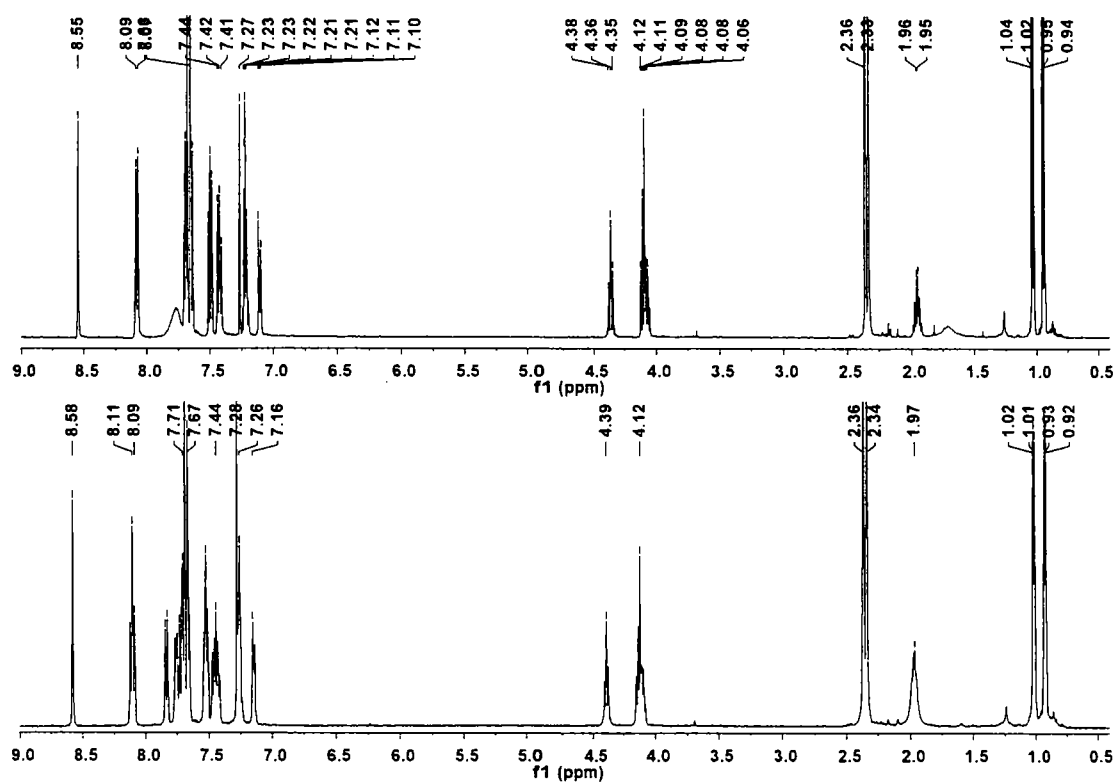


Figure B 15. The ^1H NMR (500 MHz, CDCl_3) spectra of **L8** at room temperature (top) and -30°C (bottom).

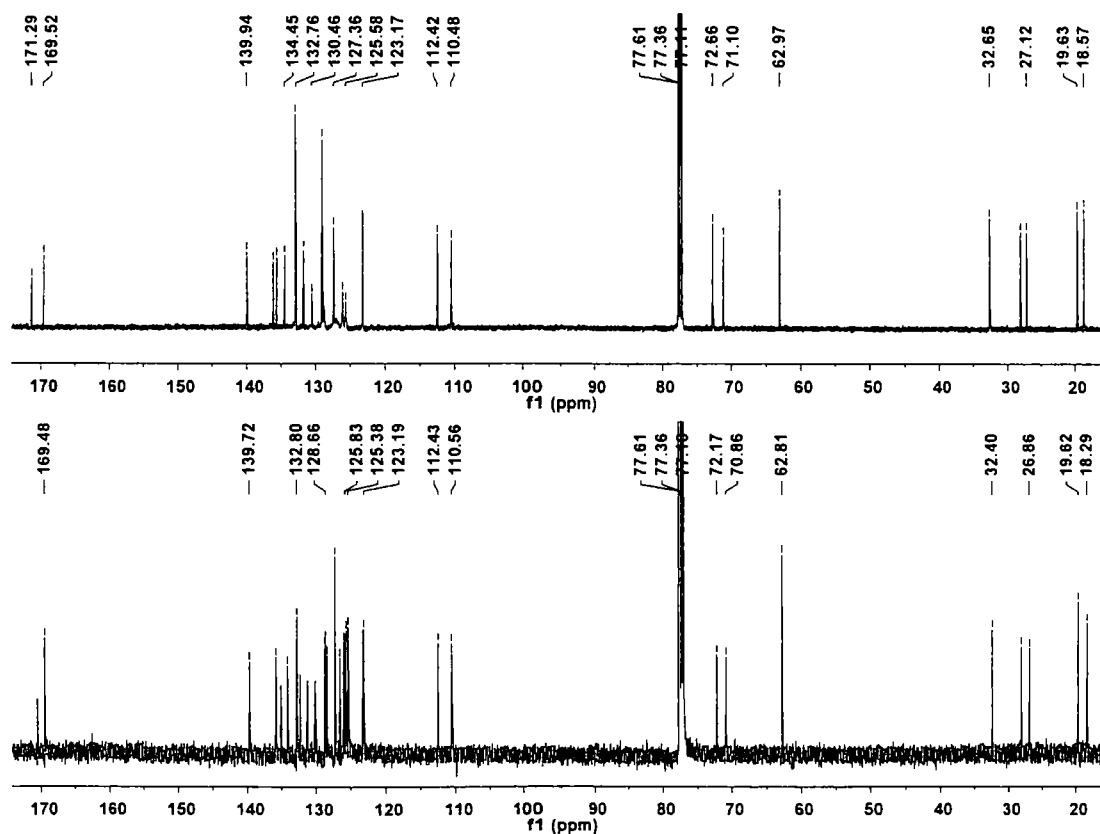


Figure B 16. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectra of **L8** at room temperature (top) and -30°C (bottom).

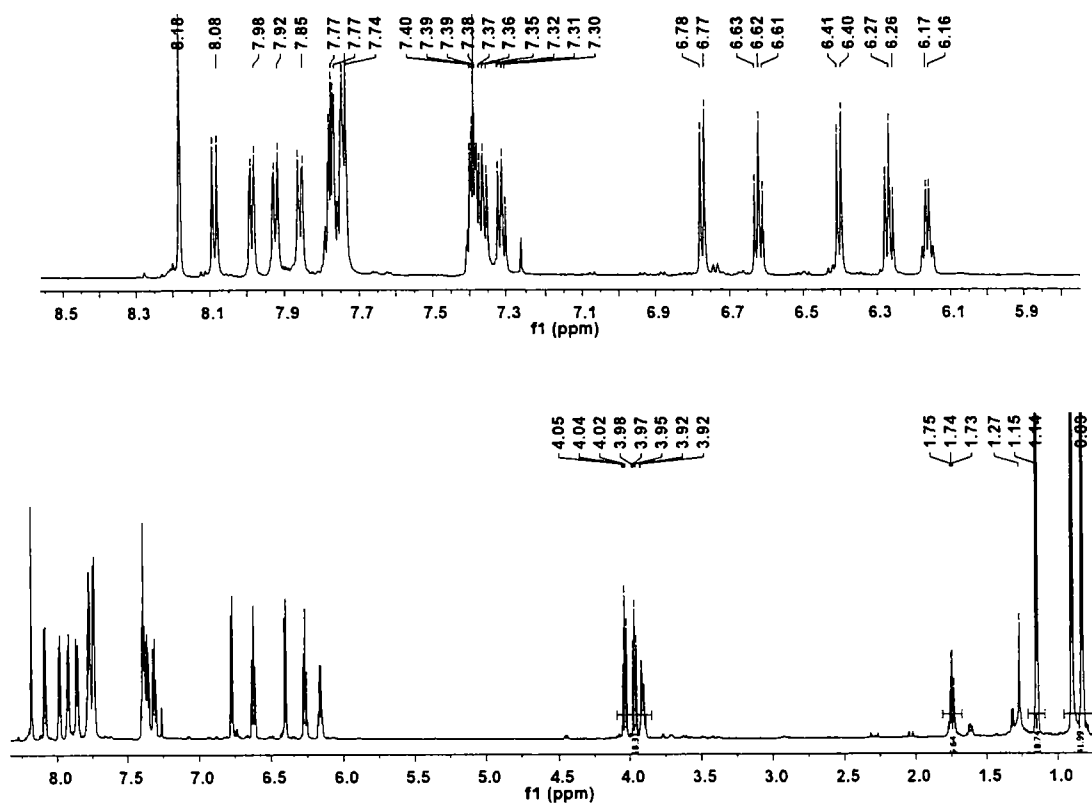


Figure B 17. The ^1H NMR (700 MHz, CDCl_3) spectrum of **R-L9up** (bottom) and the expanded spectrum in the aromatic region (top).

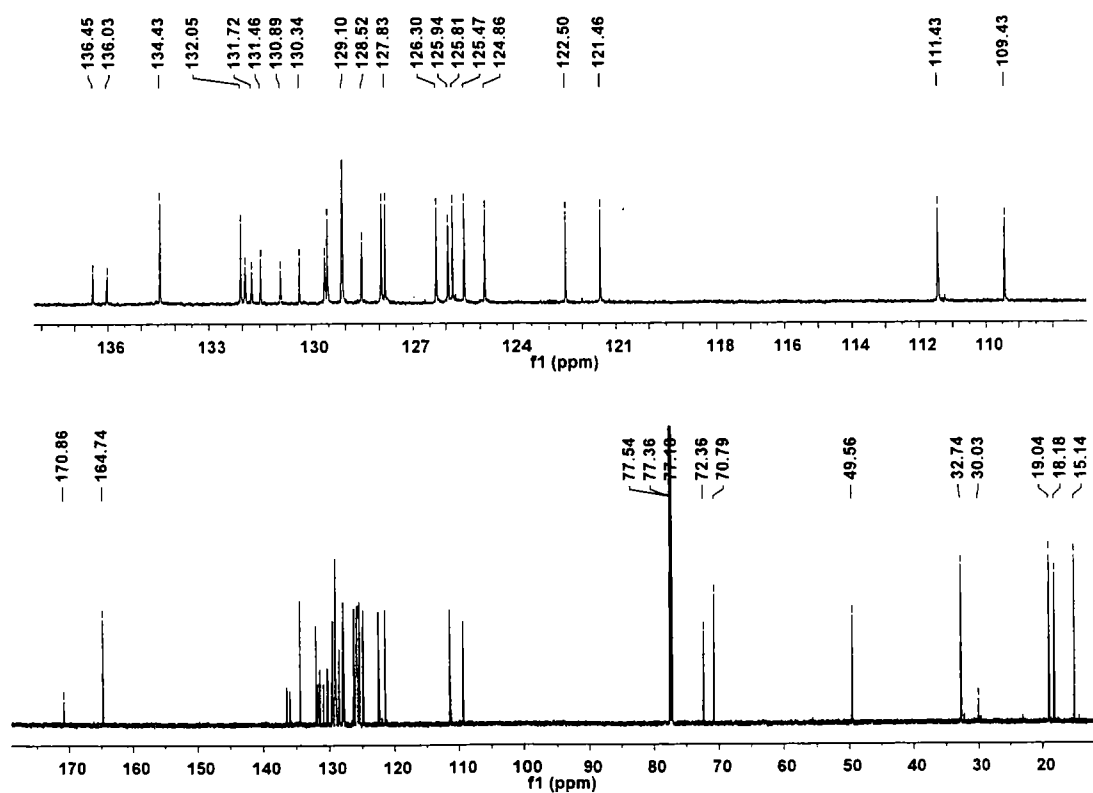


Figure B 18. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **R-L9up** (bottom) and the expanded spectrum in the aromatic region (top).

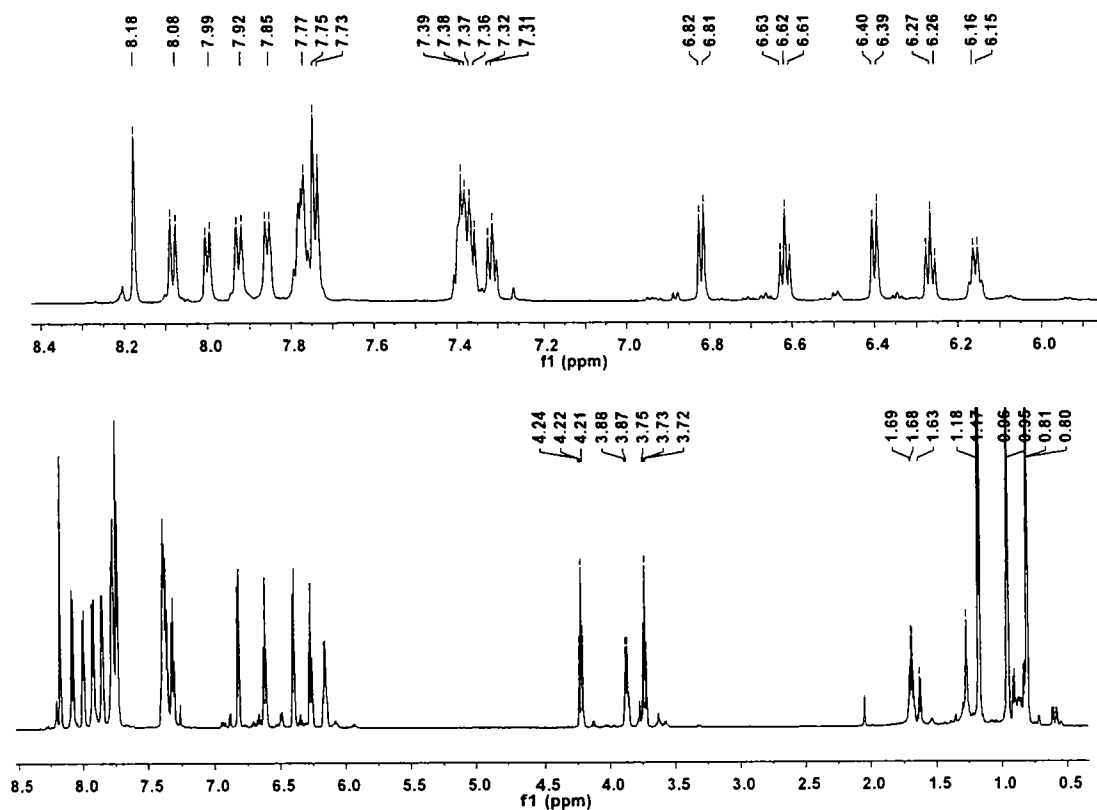


Figure B 19. The ^1H NMR (700 MHz, CDCl_3) spectrum of **S-L9down** (bottom) and the expanded spectrum in the aromatic region.

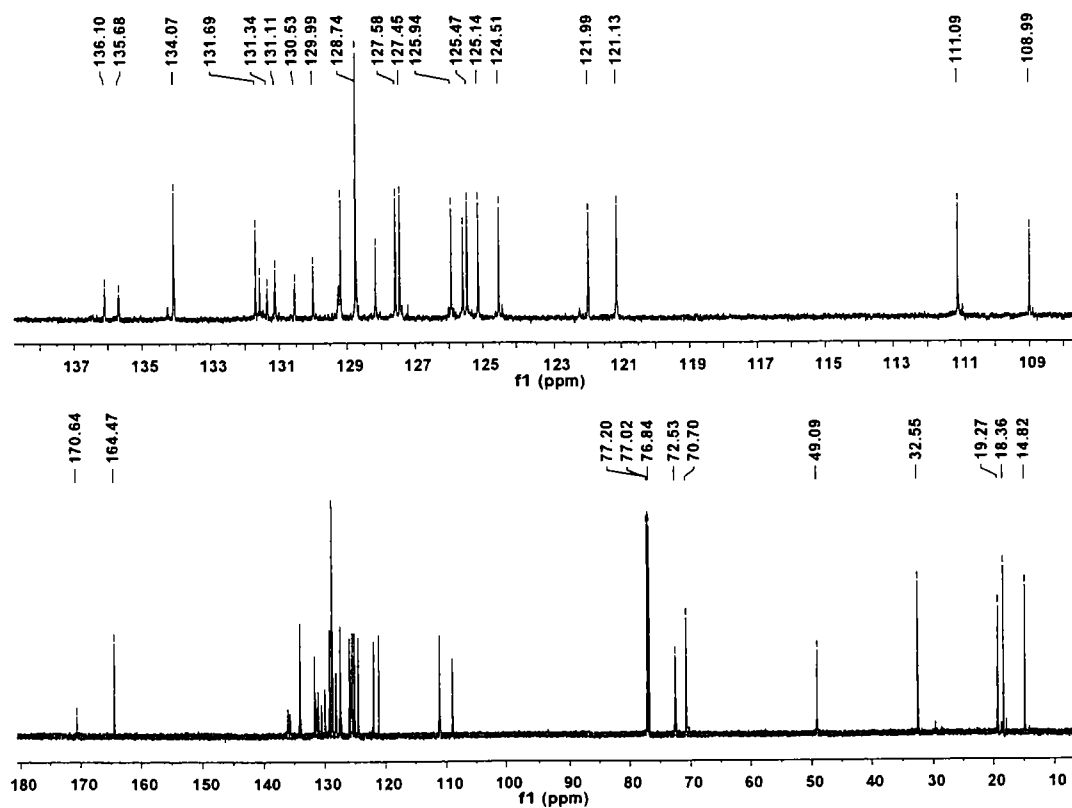


Figure B 20. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **S-L9down** (bottom) and the expanded spectrum in the aromatic region (top).

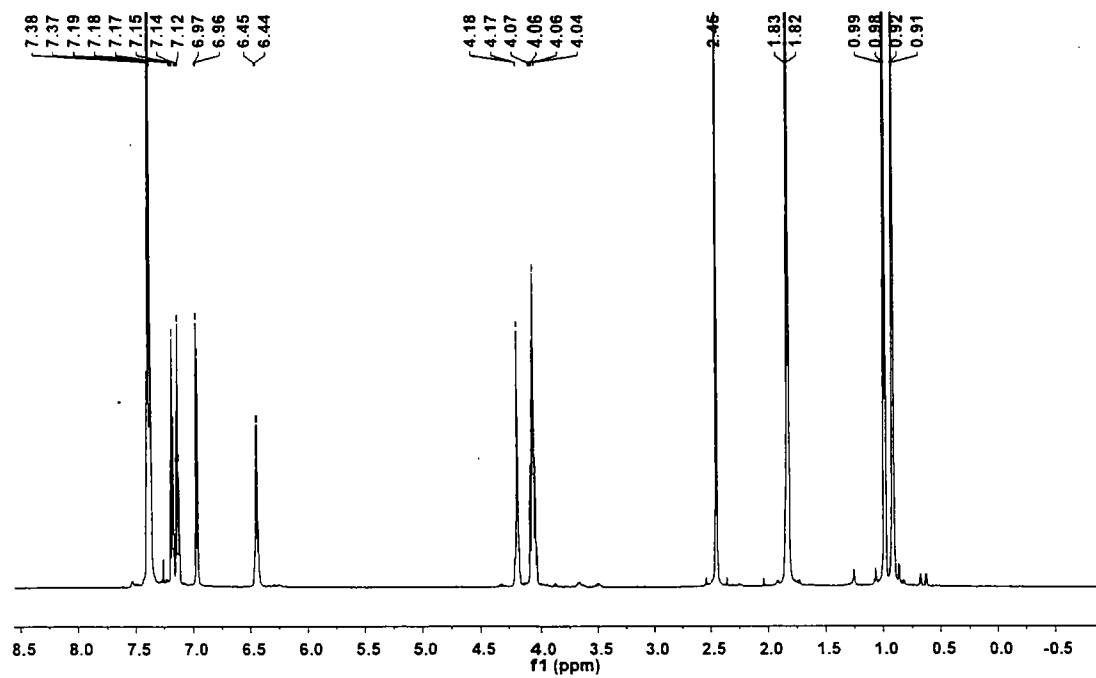


Figure B 21. The ^1H NMR (700 MHz, CDCl_3) spectrum of **R-L10**.

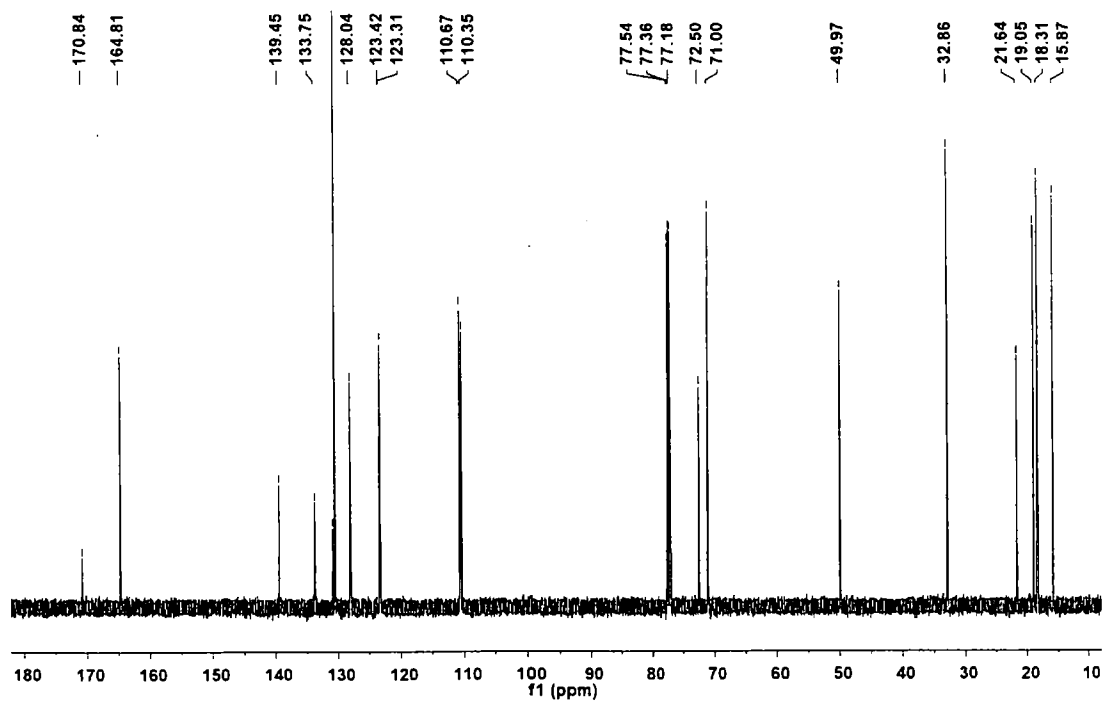


Figure B 22. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **R-L10**.

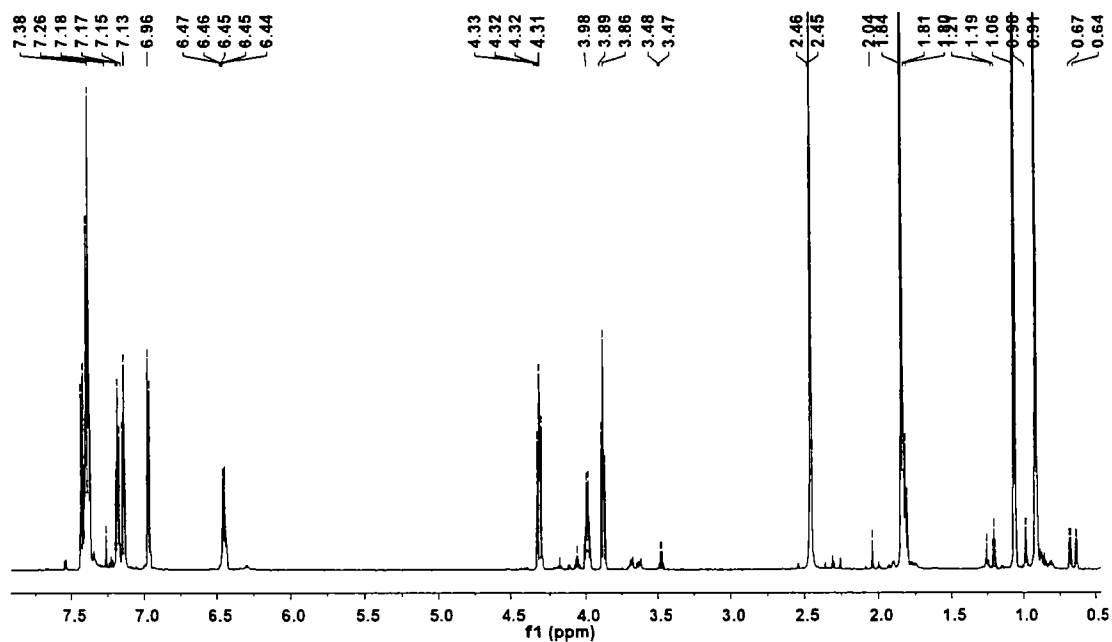


Figure B 23. The ^1H NMR (700 MHz, CDCl_3) spectrum of S-L10.

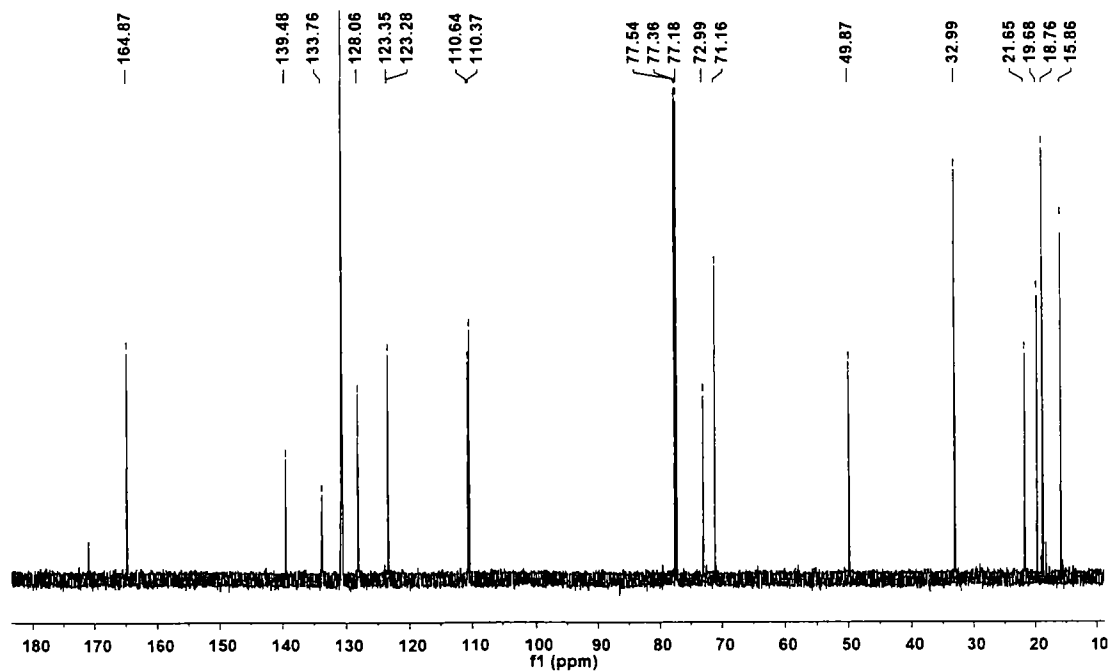


Figure B 24. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of S-L10.

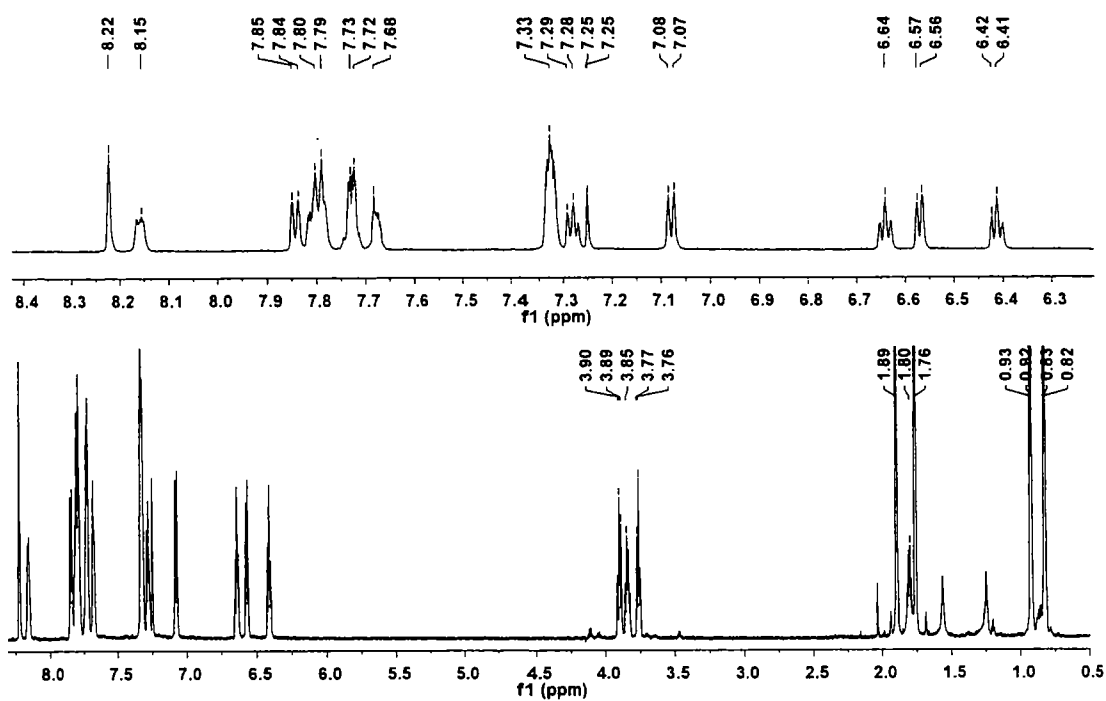


Figure B 25. The ^1H NMR (700 MHz, CDCl_3) spectrum of **L11up** (bottom) and the expanded spectrum in the aromatic region (top).

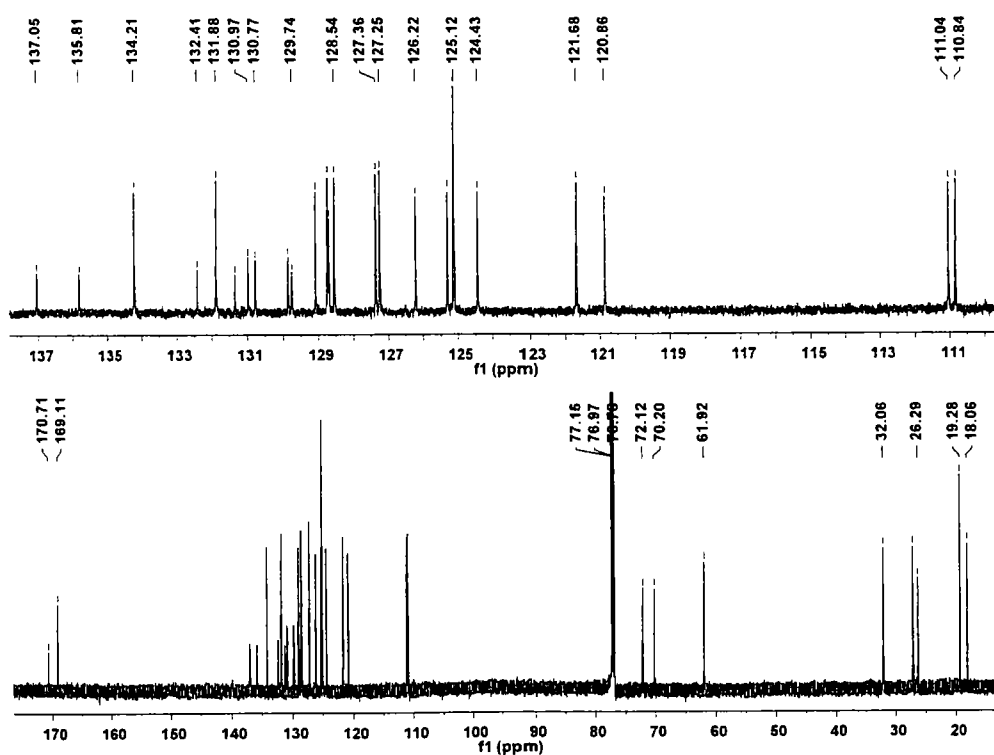


Figure B 26. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **L11up** (bottom) and the expanded spectrum in the aromatic region (top).

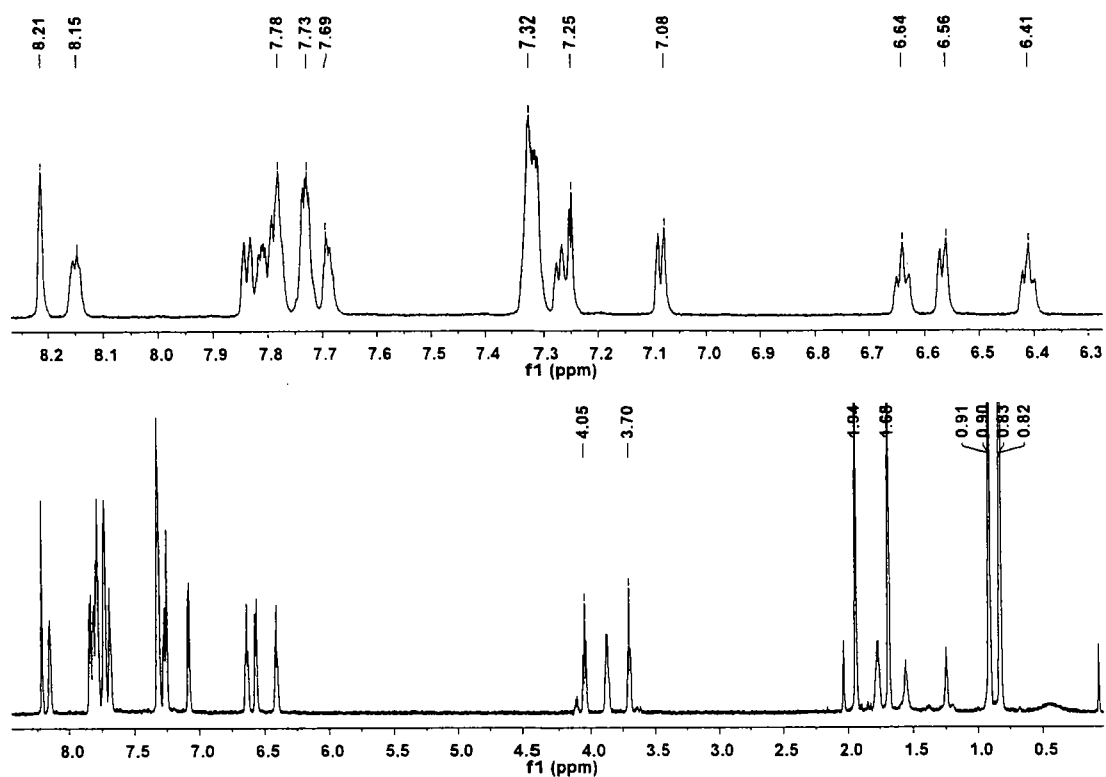


Figure B 27. The ^1H NMR (700 MHz, CDCl_3) spectrum of **L11down** (bottom) and the expanded spectrum in the aromatic region (top).

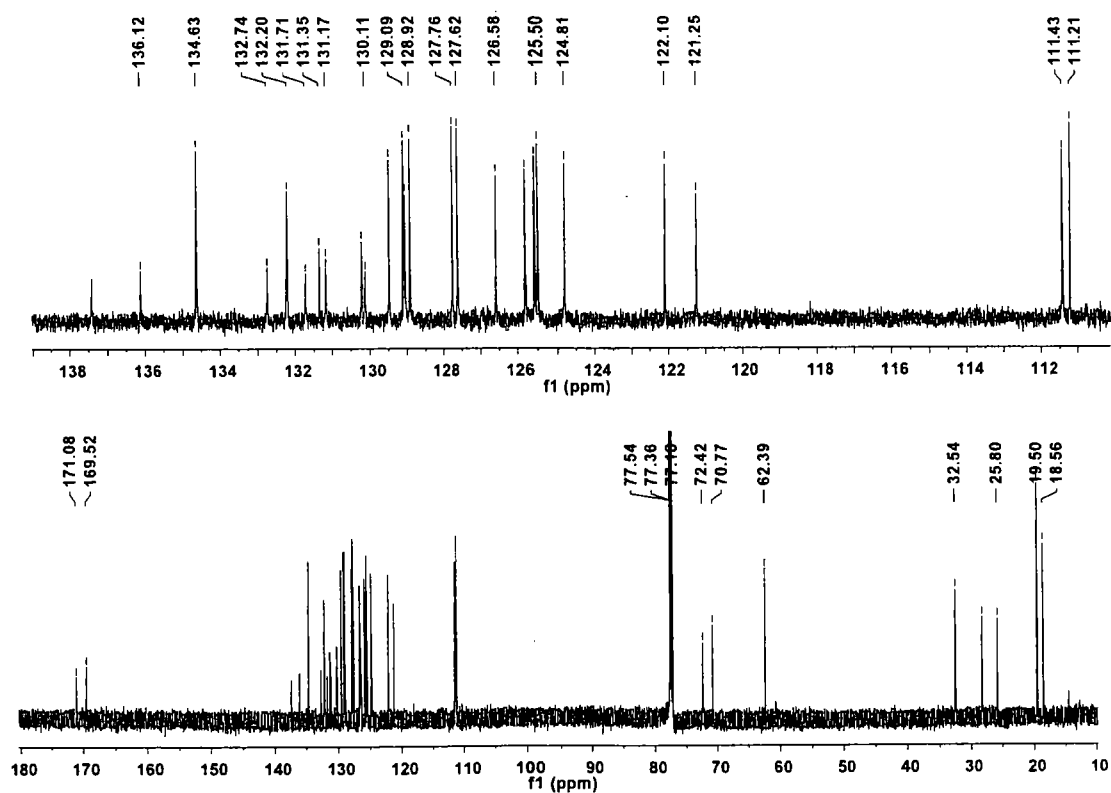


Figure B 28. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **L11down** (bottom) and the expanded spectrum in the aromatic region (top).

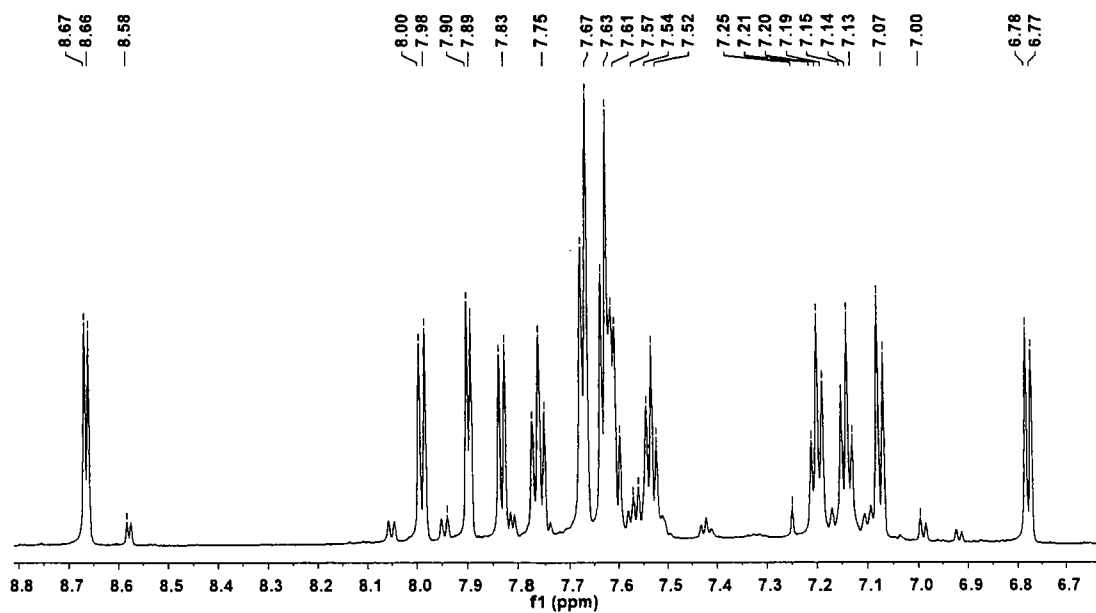


Figure B 29. The ^1H NMR (700 MHz, CDCl_3) spectrum of L12.

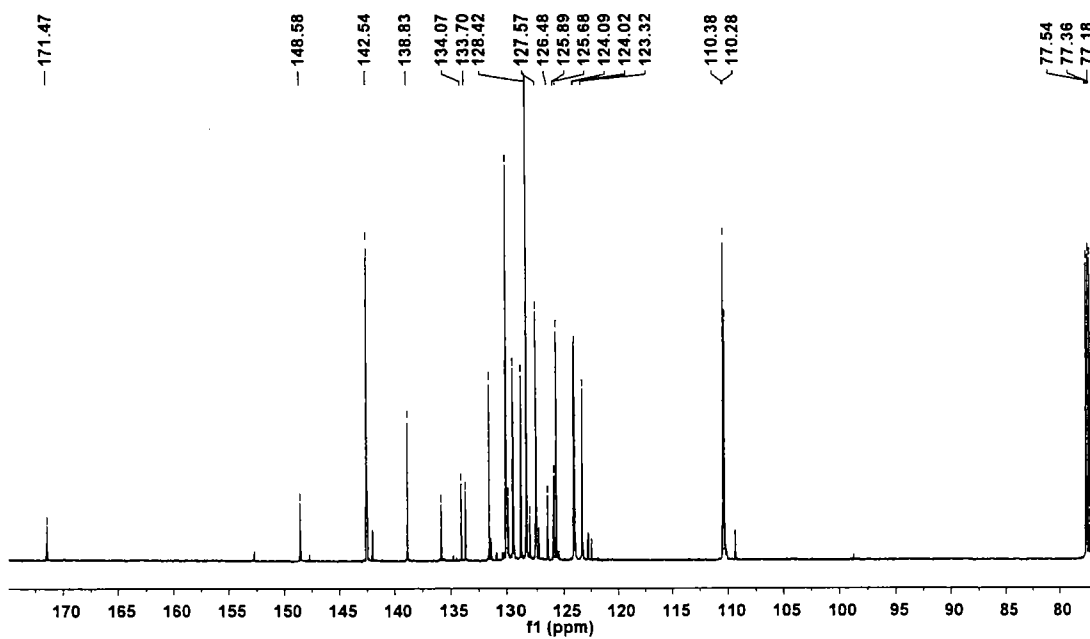


Figure B 30. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of L12.

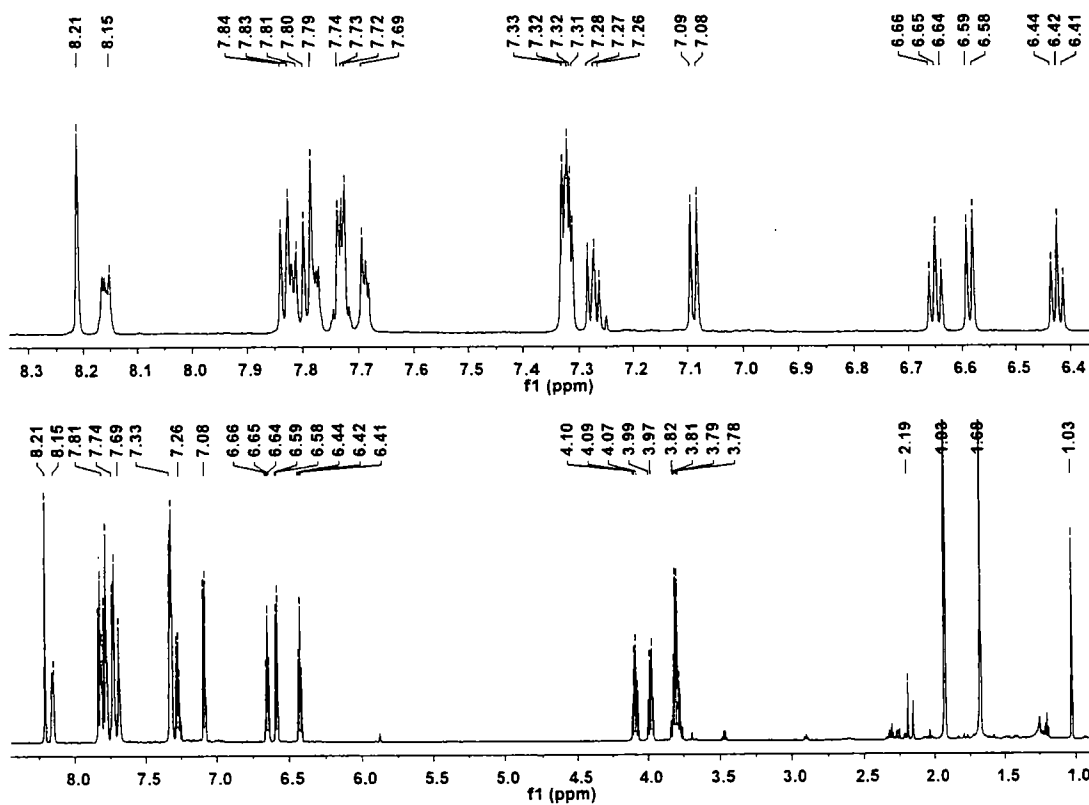


Figure B 31. The ^1H NMR (700 MHz, CDCl_3) spectrum of **L13up** (bottom) and the expanded spectrum in the aromatic region (top).

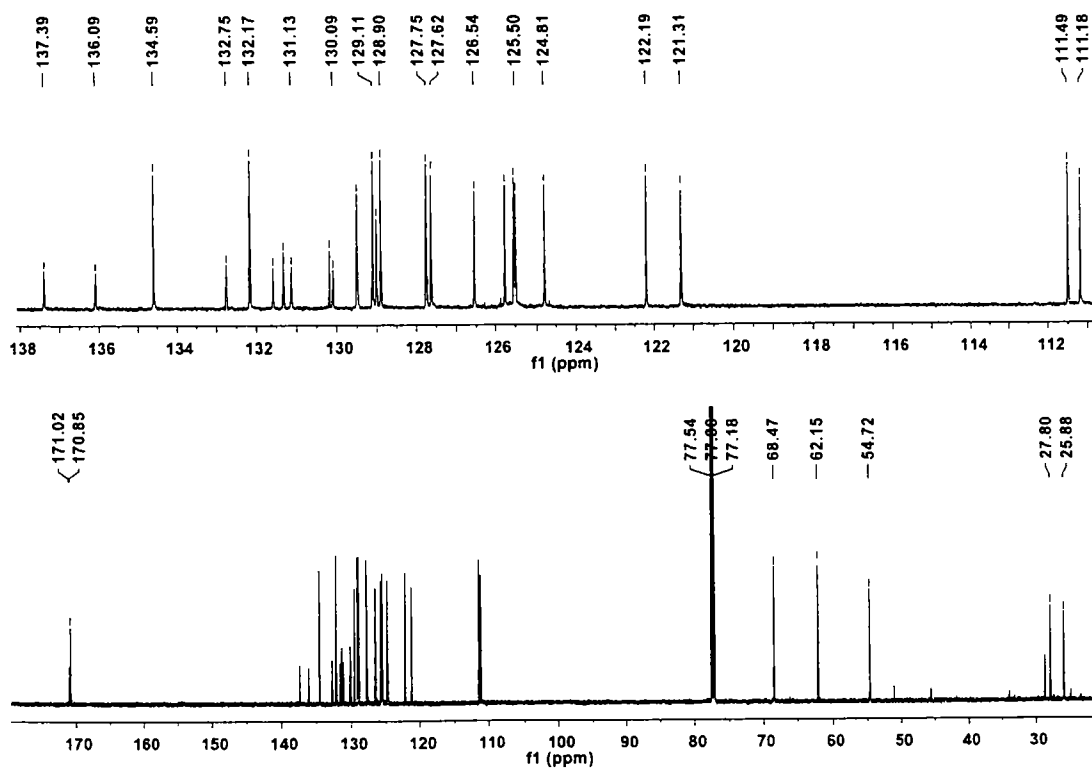


Figure B 32. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **L13up** (bottom) and the expanded spectrum in the aromatic region (top).

Palladium complexes

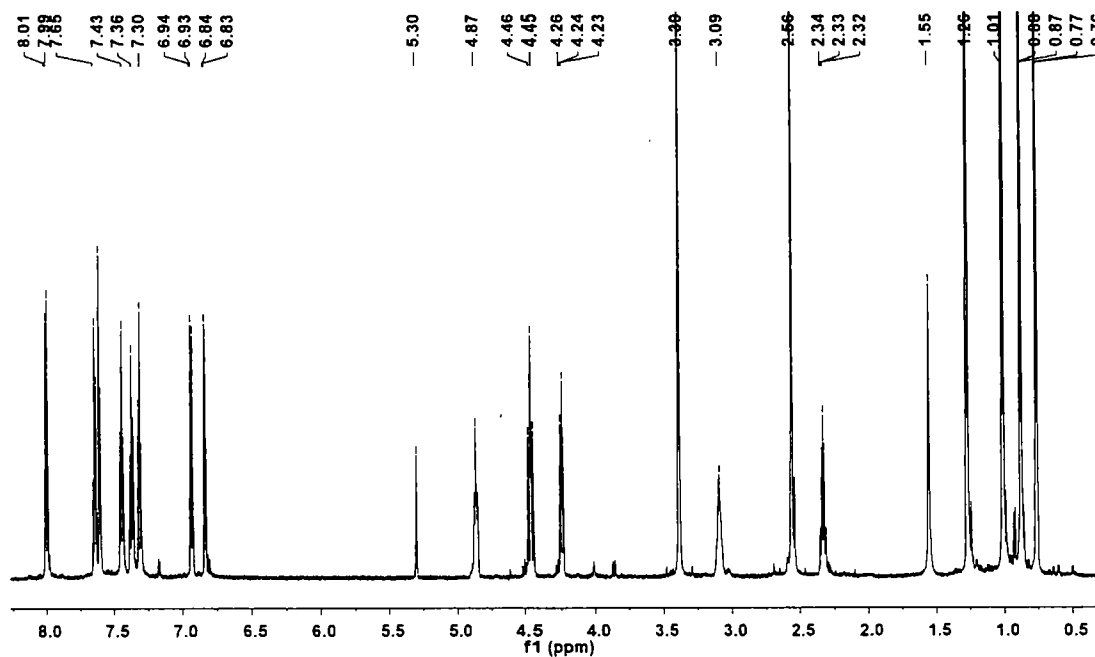


Figure B 33. The ^1H NMR (700 MHz, CD_2Cl_2) spectrum of **PdL2up**.

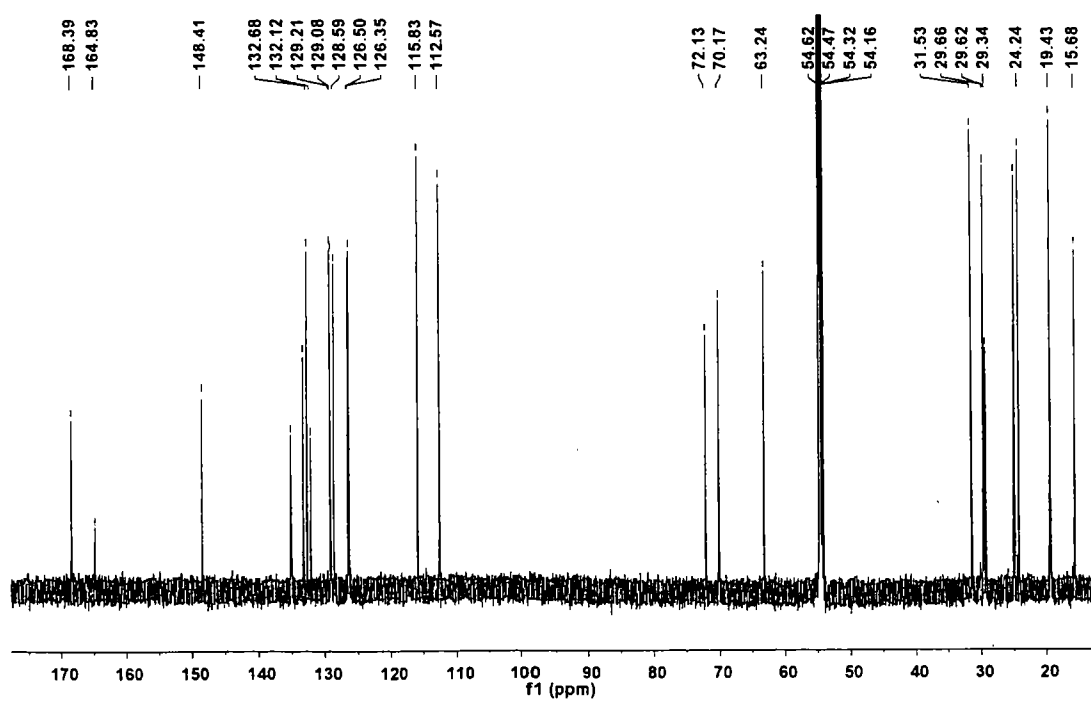


Figure B 34. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CD_2Cl_2) spectrum of **PdL2up**.

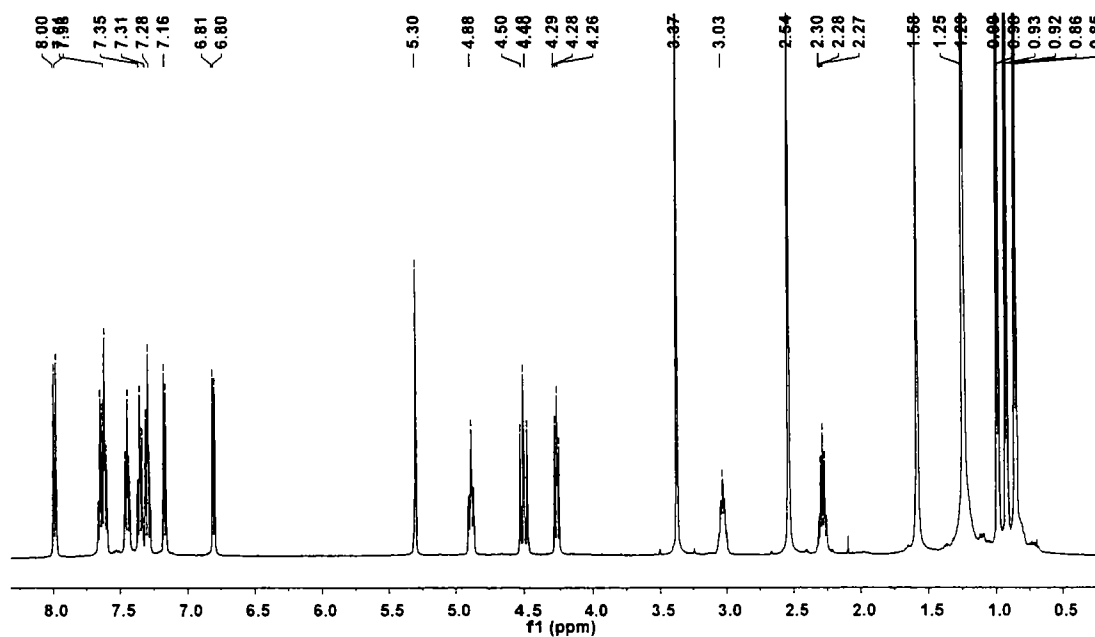


Figure B 35. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of **PdL2down**.

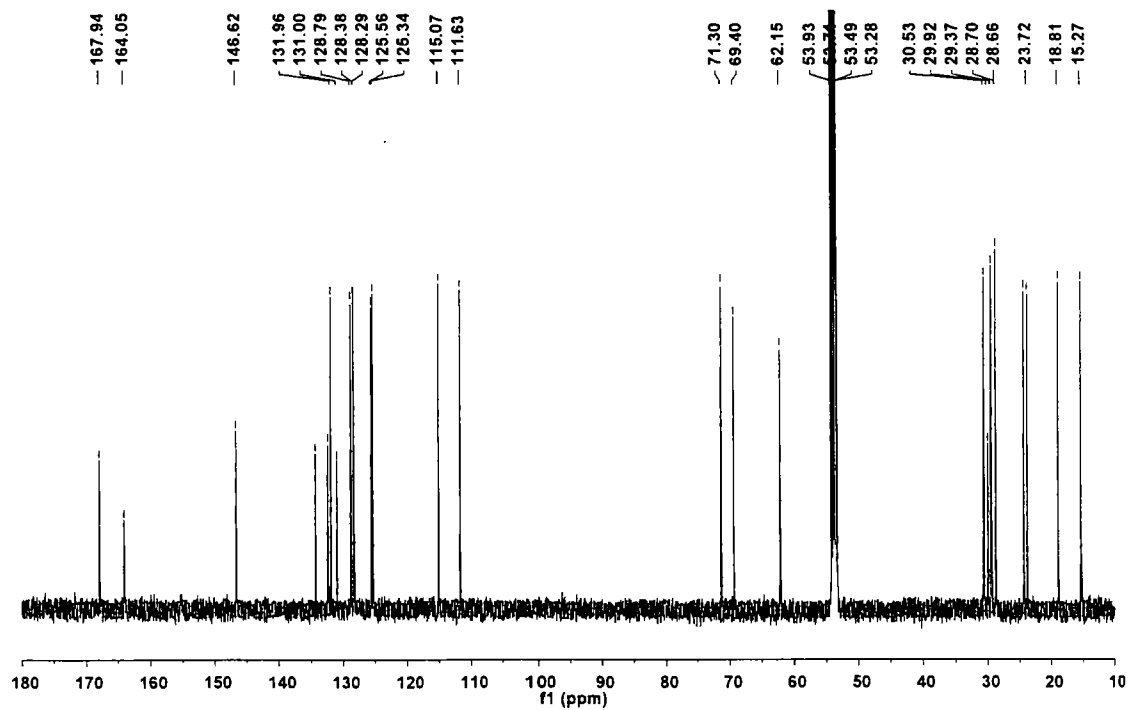


Figure B 36. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **PdL2down**.

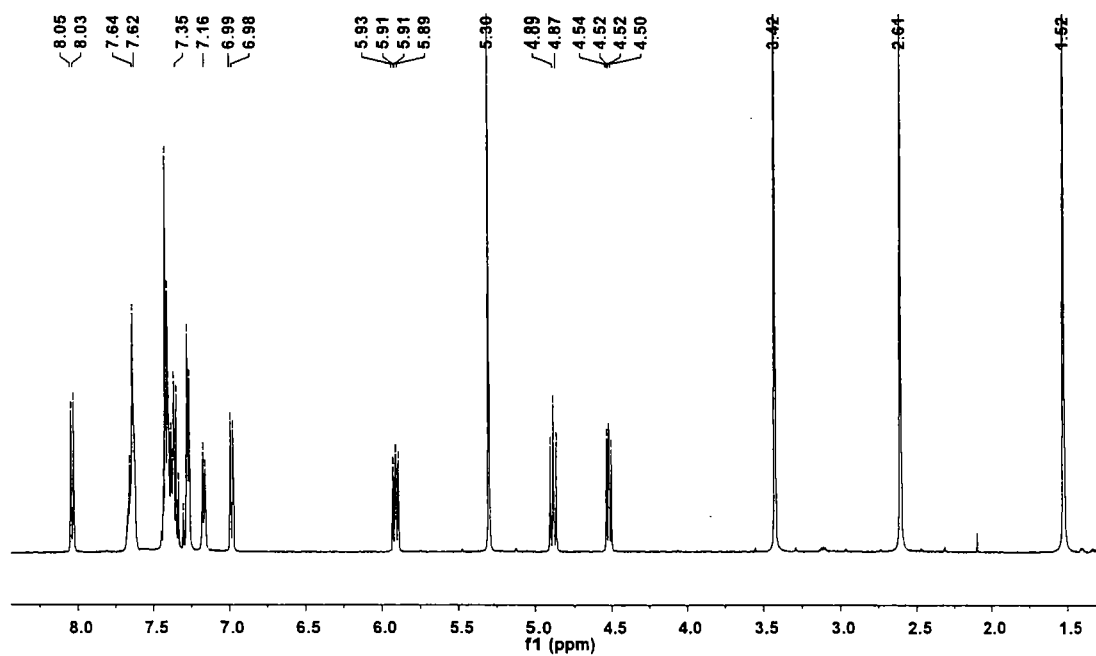


Figure B 37. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL3.

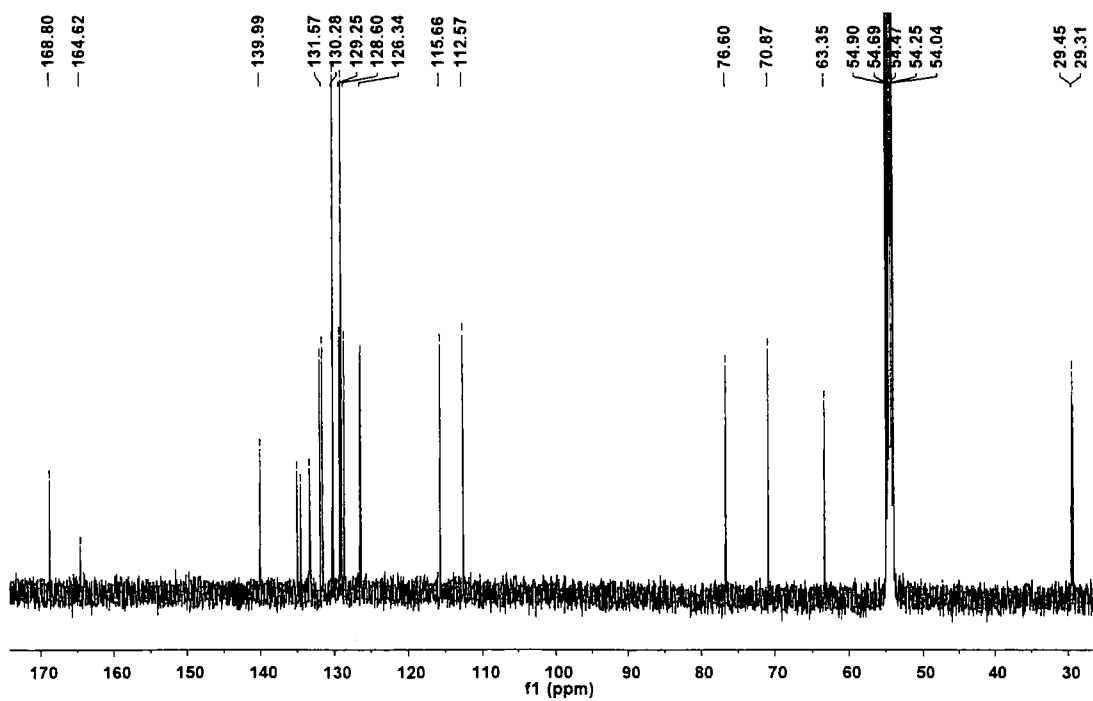


Figure B 38. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of PdL3.

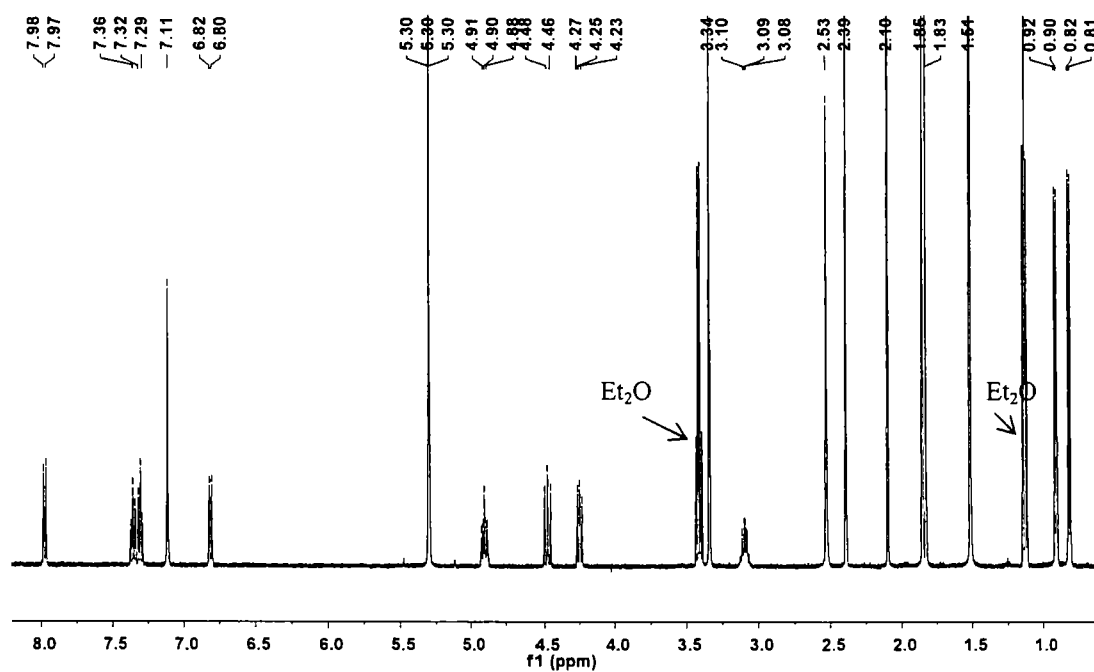


Figure B 39. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL4.

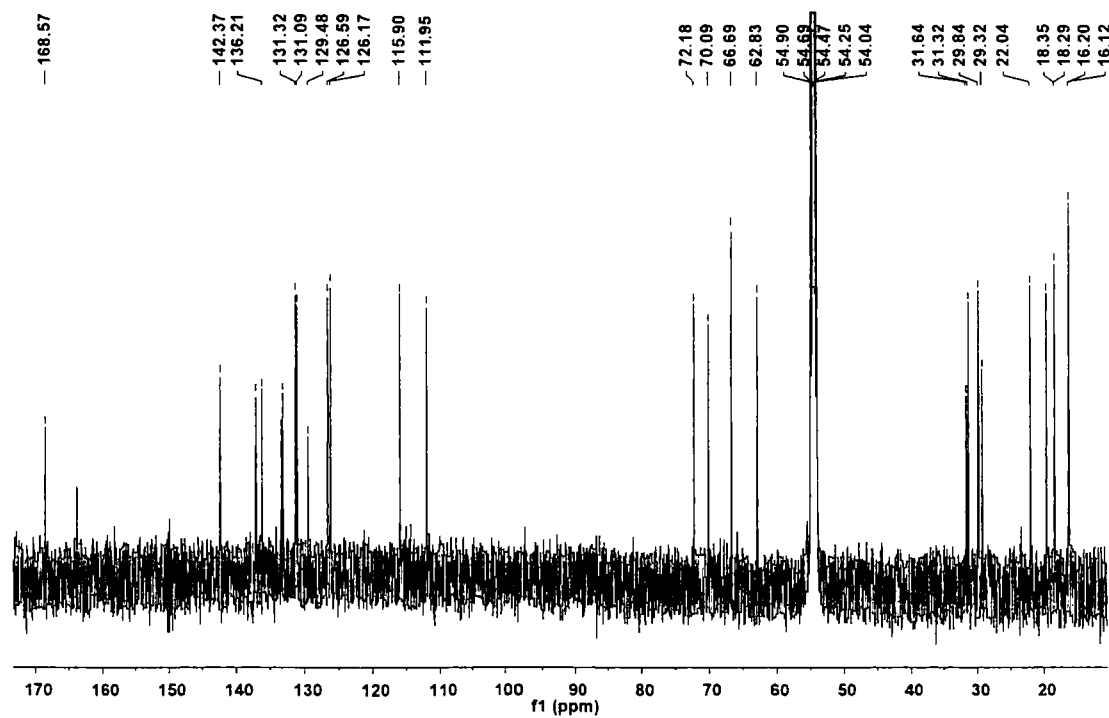


Figure B 40. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) spectrum of PdL4.

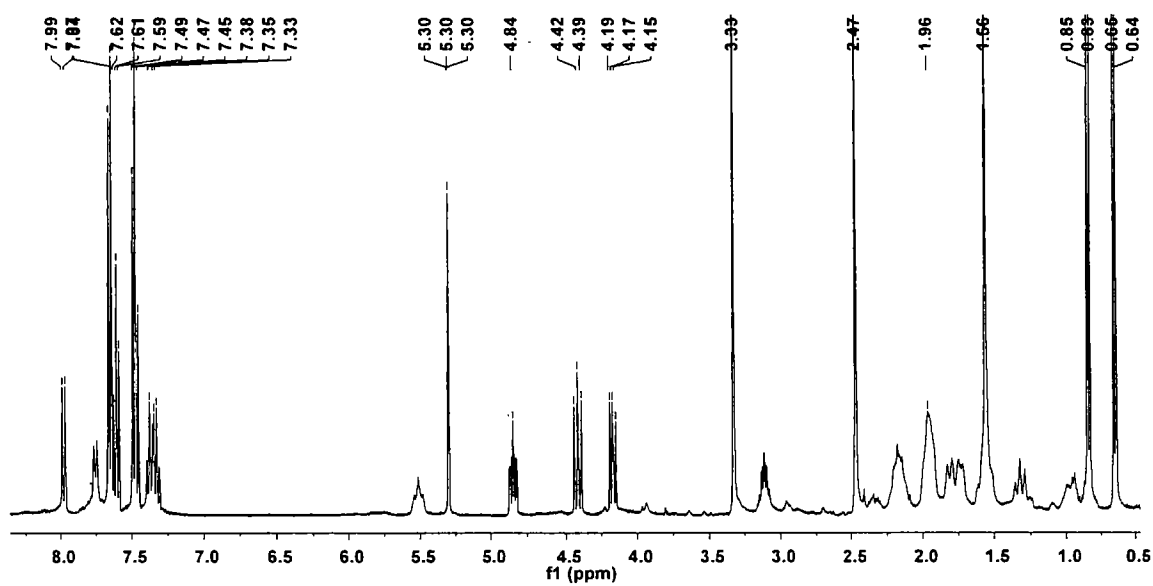


Figure B 41. The *in situ* ^1H NMR (400 MHz, CDCl_3) spectrum of **PdL5**.

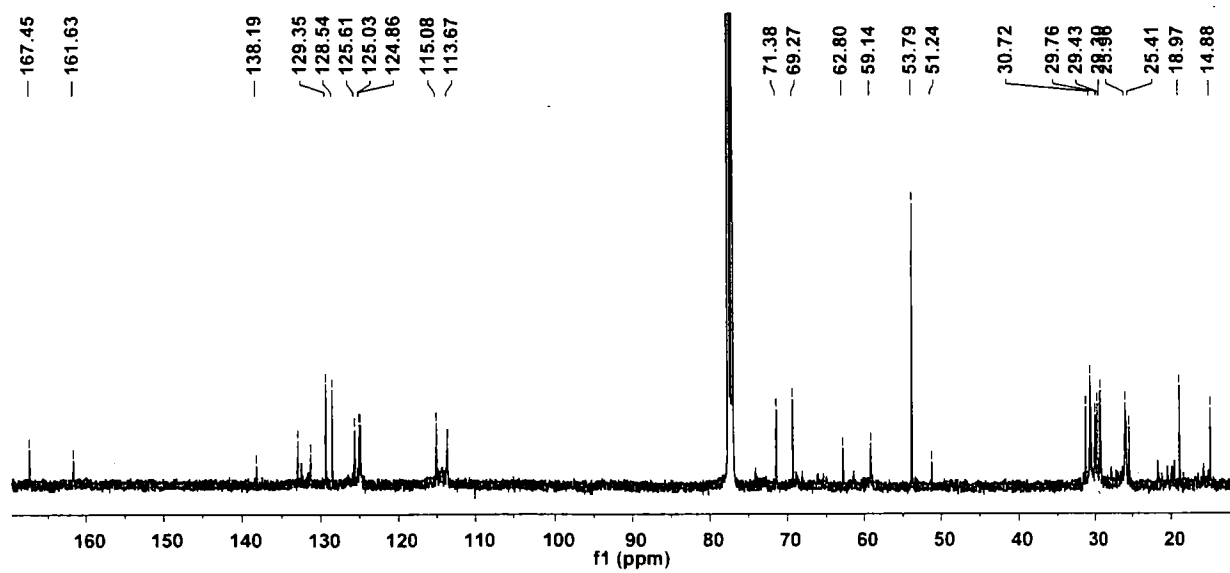


Figure B 42. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of **PdL5**.

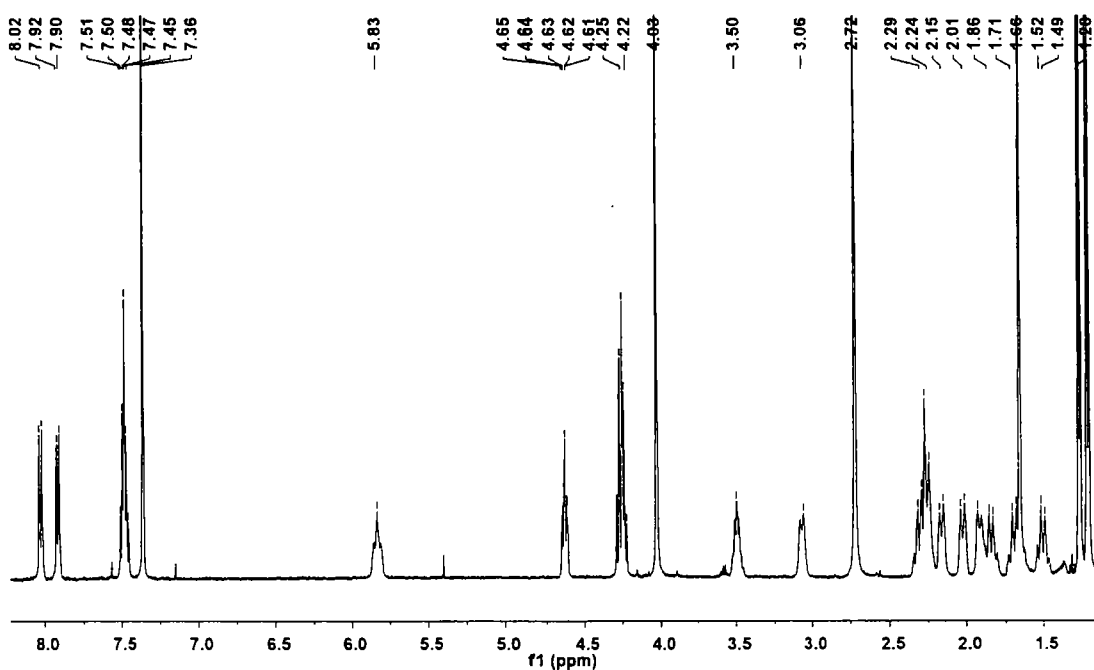


Figure B 43. The ^1H NMR (500 MHz, CDCl_3) spectrum of $\text{Pd}_2\text{L5}$.

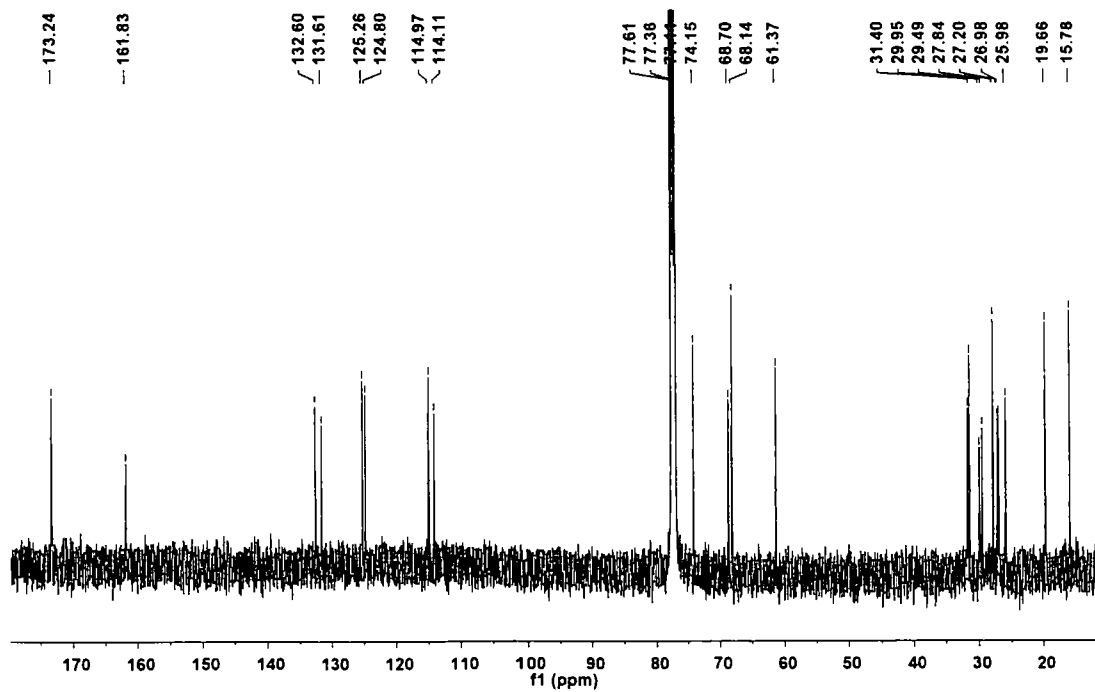


Figure B 44. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of $\text{Pd}_2\text{L5}$.

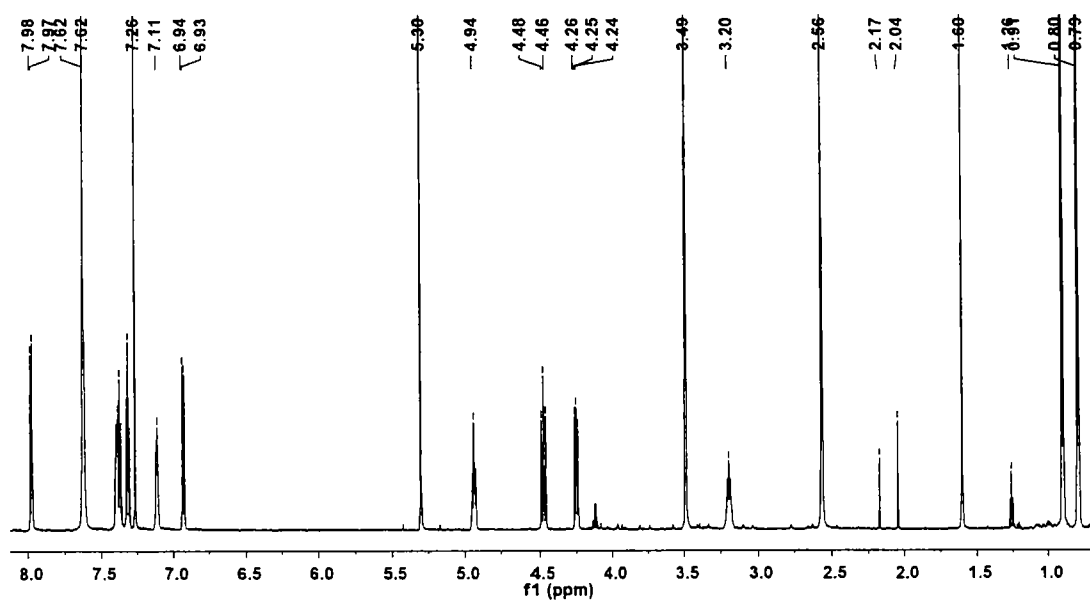


Figure B 45. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL6.

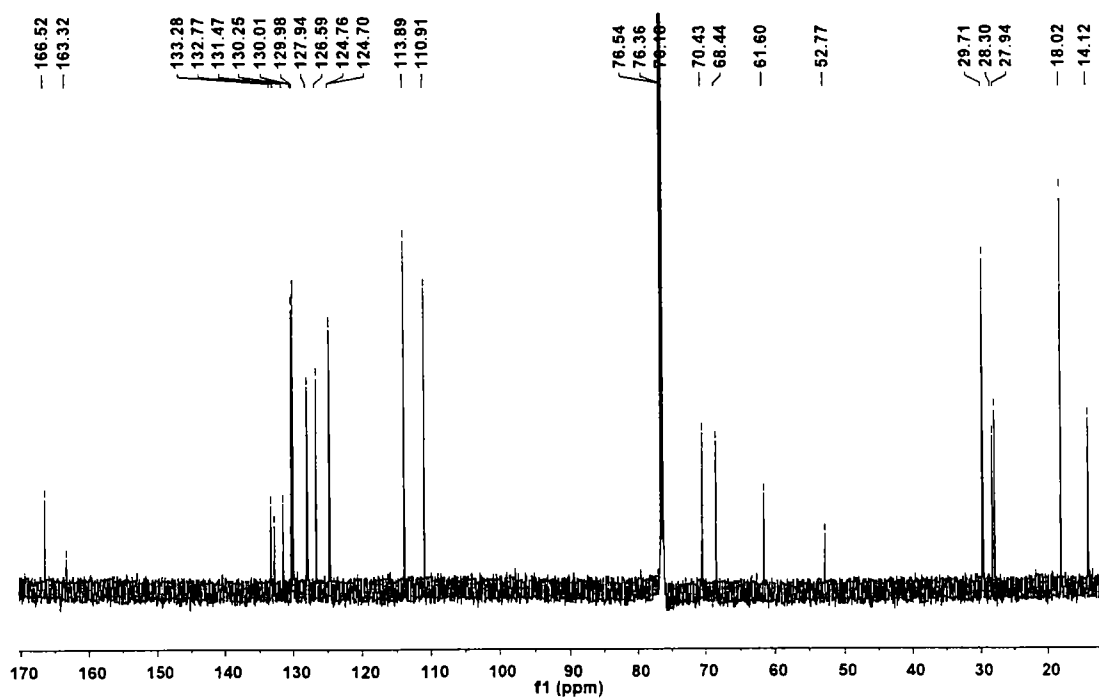


Figure B 46. The $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of PdL6.

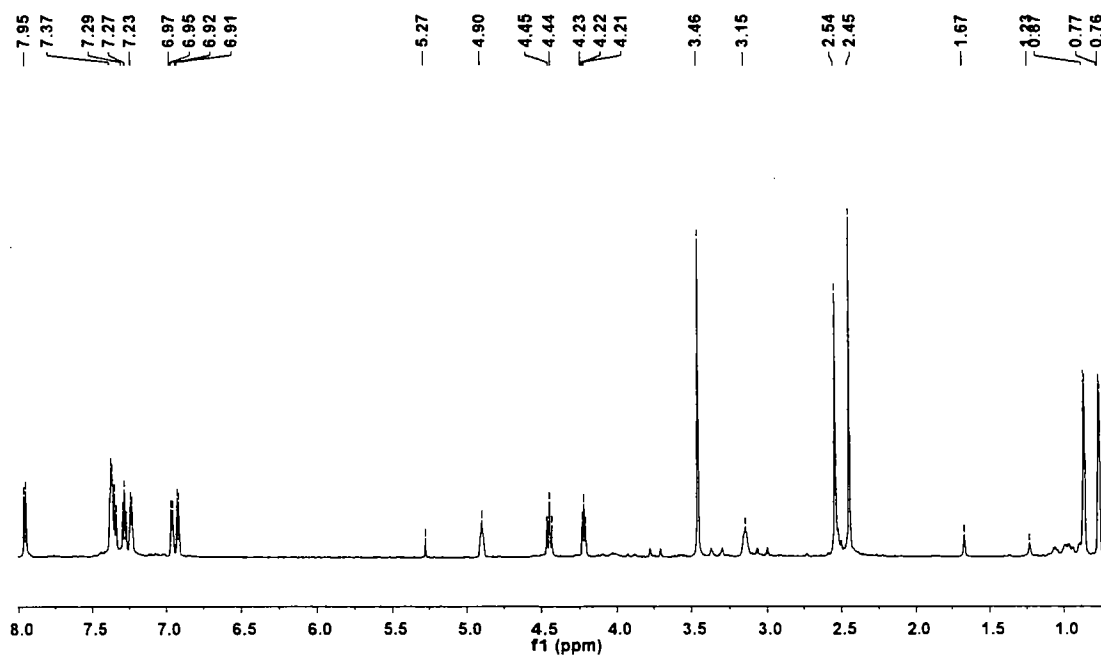


Figure B 47. The ^1H NMR (700 MHz, CDCl_3) spectrum of **PdL7**.

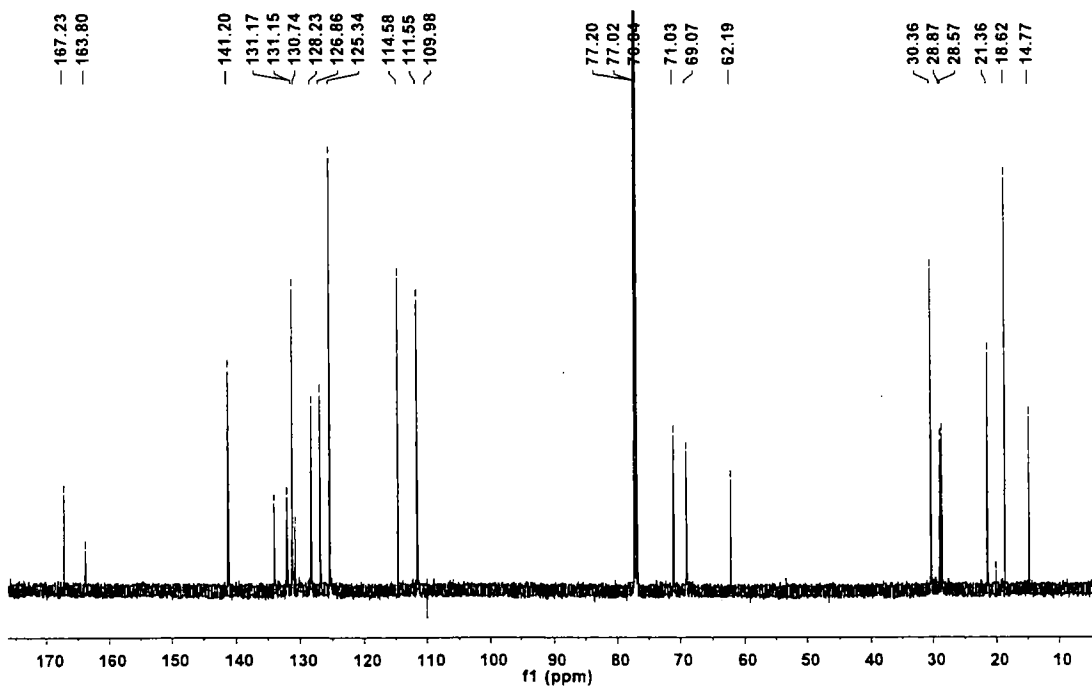


Figure B 48. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **PdL7**.

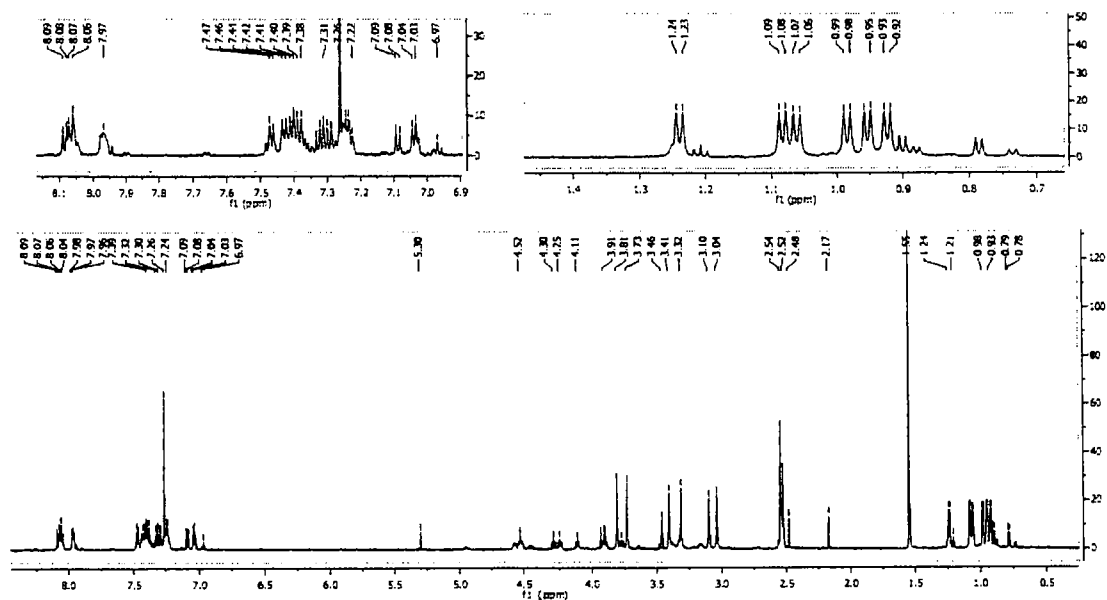


Figure B 49. The ^1H NMR (700 MHz, CDCl_3) spectrum of $\text{Pd}_3\text{L7}$ (bottom); expanded in the aromatic region (top left) and in the aliphatic region (top right).

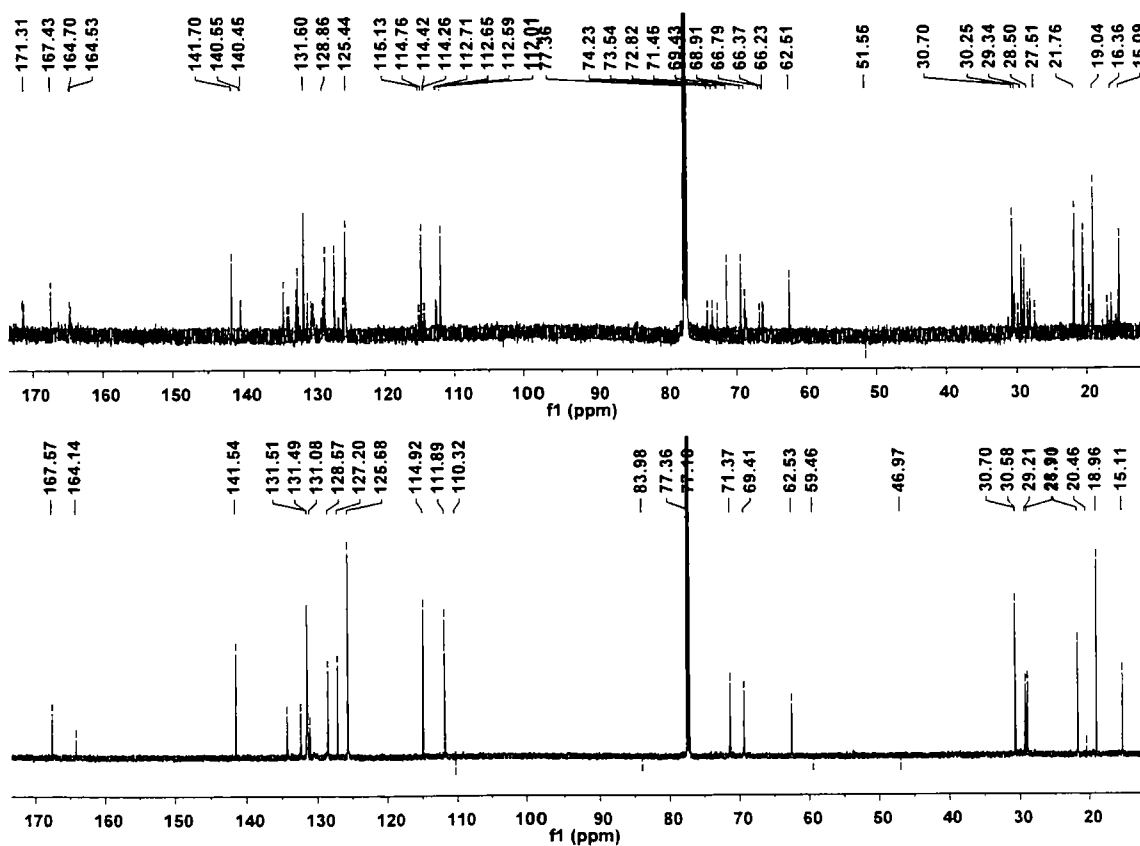


Figure B 50. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and spectra of a mixture of PdL7 and $\text{Pd}_3\text{L7}$ (top).

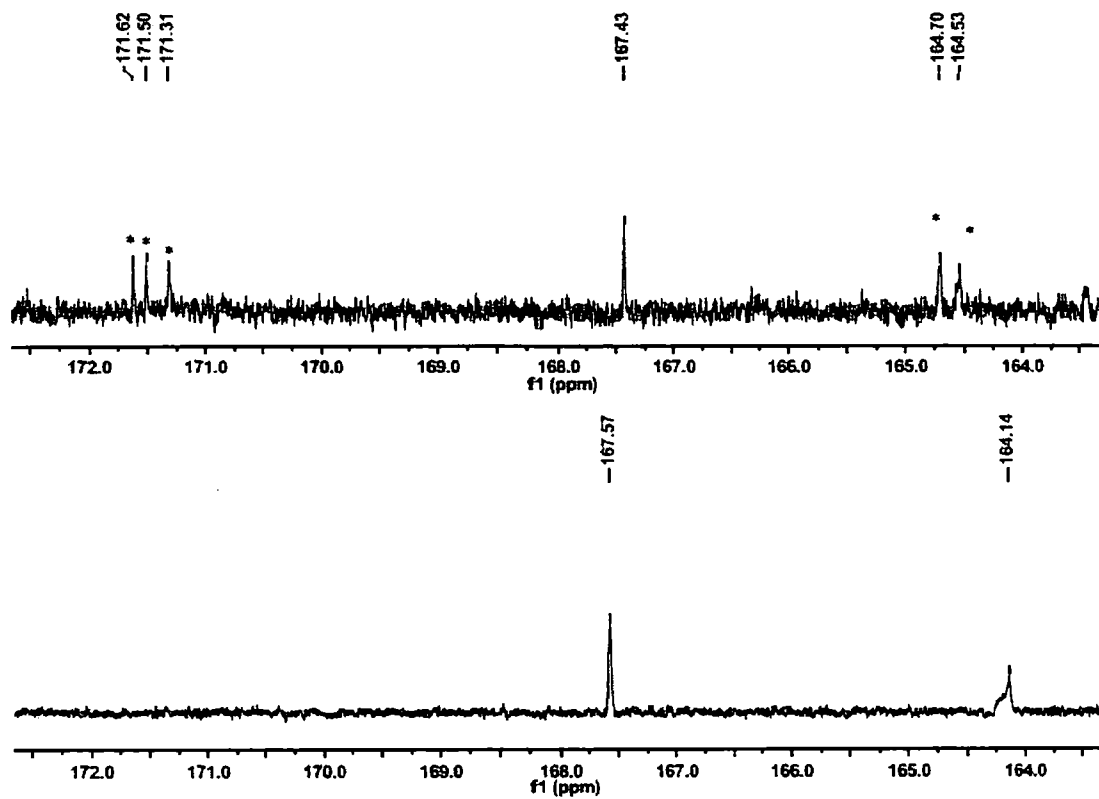


Figure B 51. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and $\text{Pd}_3\text{L7}$ (*) (in the region of C=S and C=N signals).

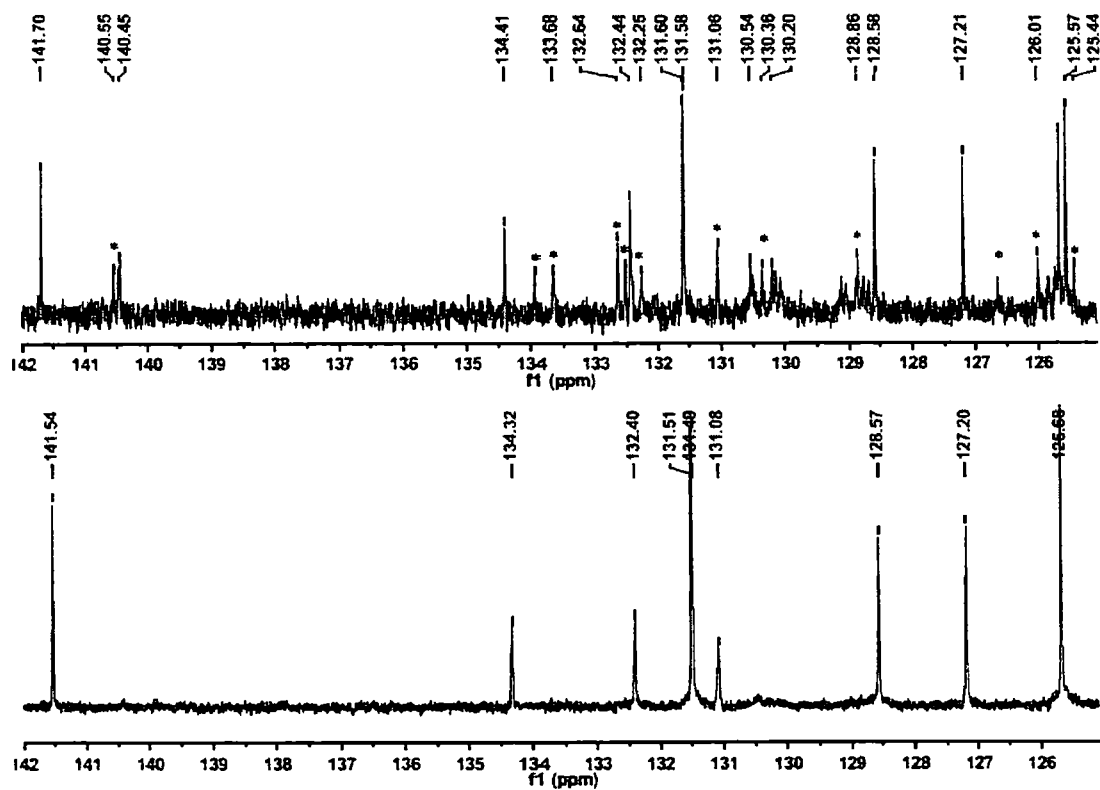


Figure B 52. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and $\text{Pd}_3\text{L7}^*$ (in the region of 125 – 144 ppm).

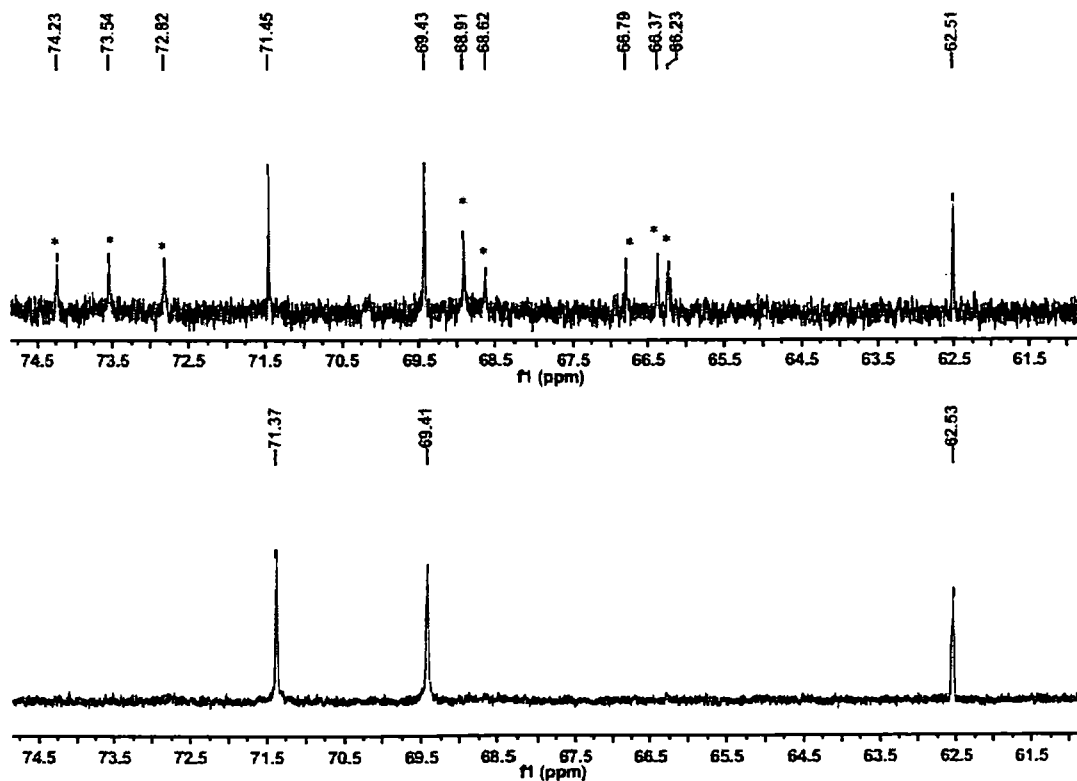


Figure B 53. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and $\text{Pd}_3\text{L7}^*$ (in the region of 60 – 75 ppm).

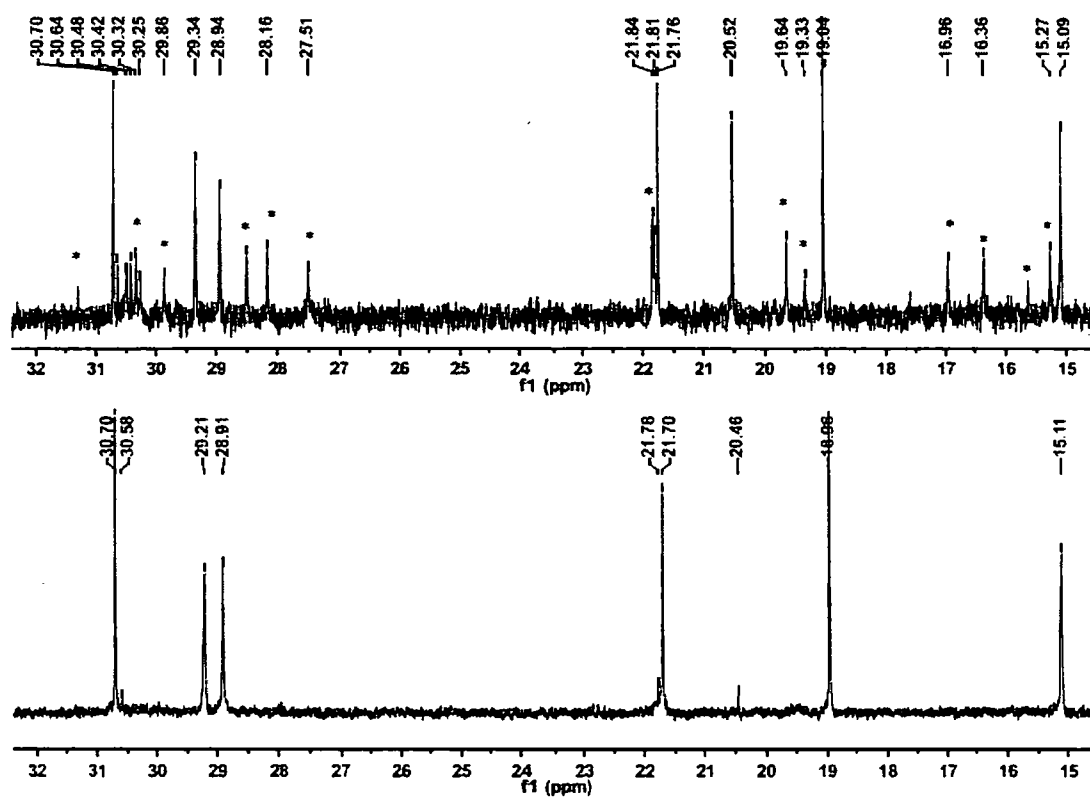


Figure B 54. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectra of PdL7 (bottom) and $\text{Pd}_3\text{L7}$ (*) (in the region of 15 – 33 ppm).

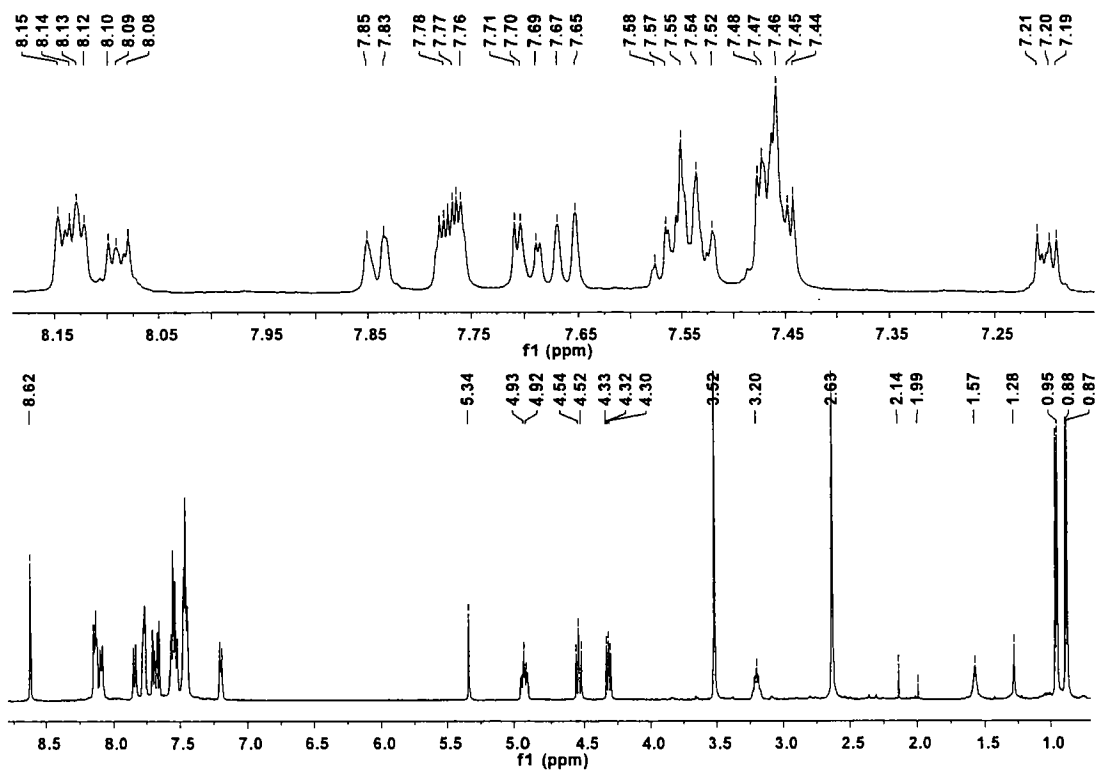


Figure B 55. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of PdL8 (bottom) and the expanded spectrum in the aromatic region (top).

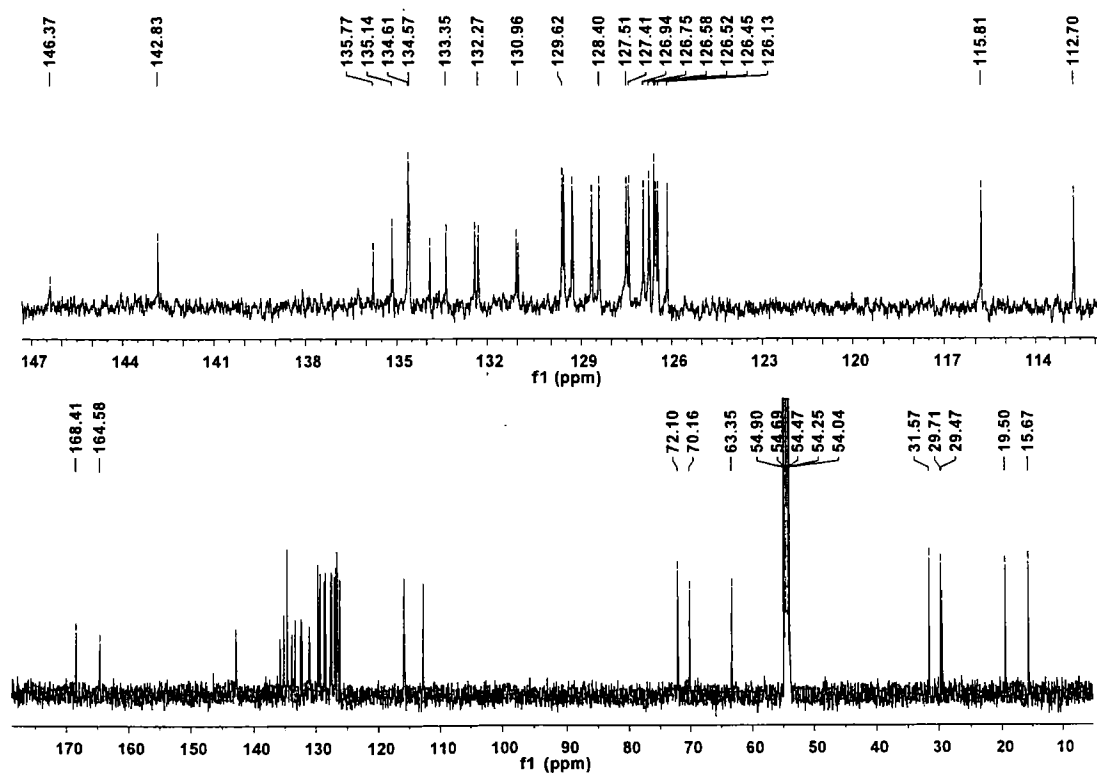


Figure B 56. The $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CD_2Cl_2) spectrum of PdL8 (bottom) and the expanded spectrum in the aromatic region (top).

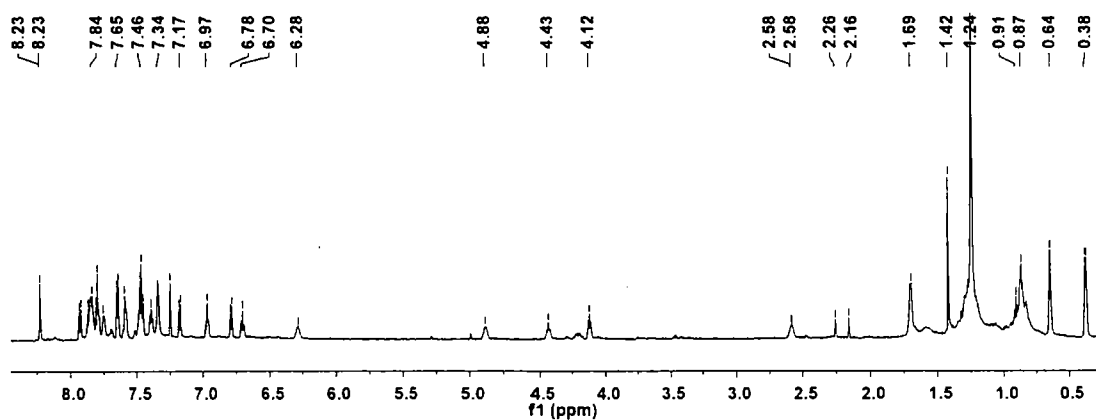


Figure B 57. The ^1H NMR (700 MHz, CDCl_3) spectrum of **Pd-R-L9up**.

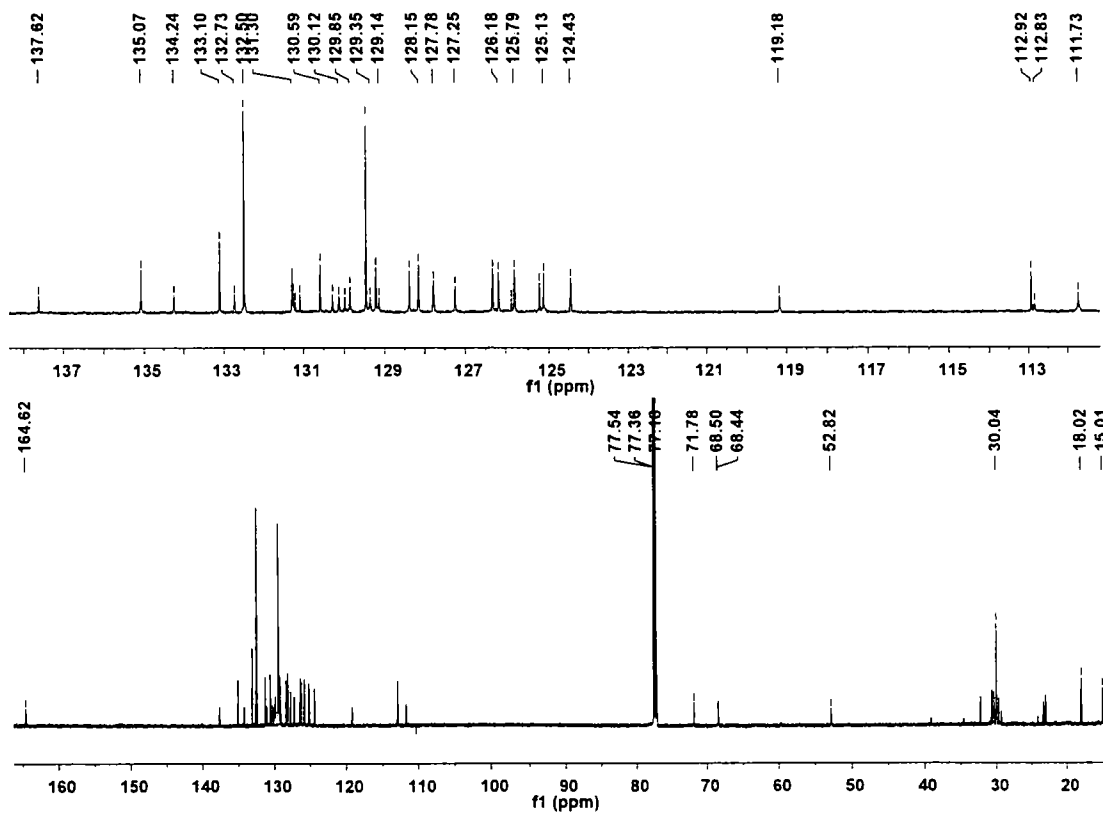


Figure B 58. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **Pd-R-L9up**.

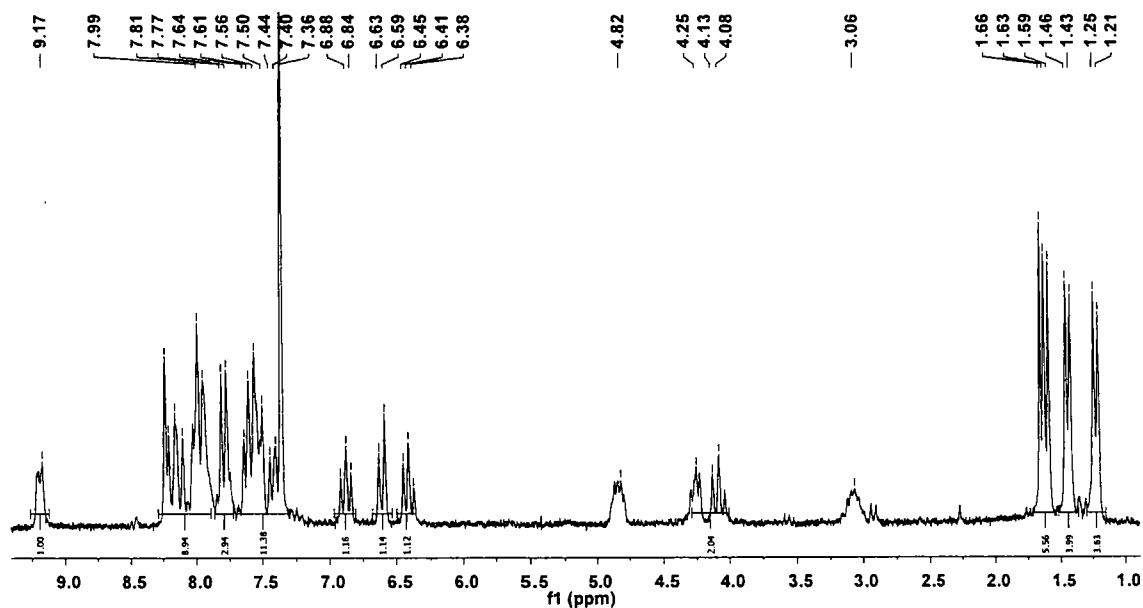


Figure B 59. The ^1H NMR (200 MHz, CDCl_3) spectrum of $\text{Pd}_2\text{-S-L9down}$.

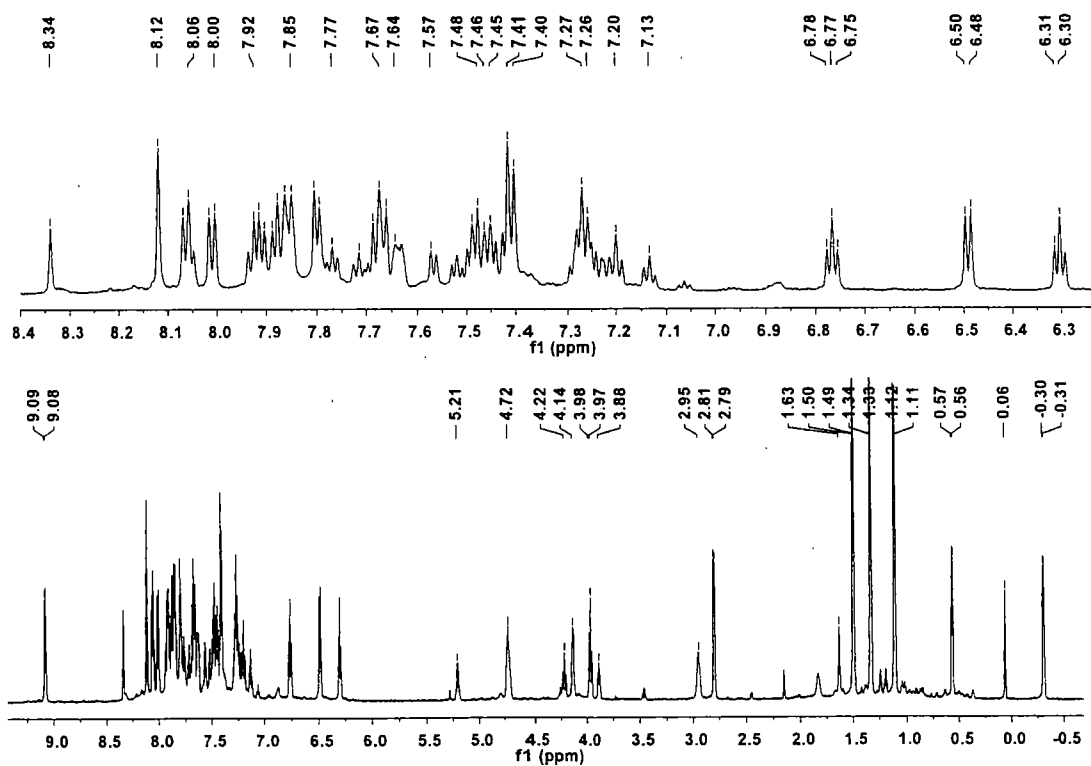


Figure B 60. The ^1H NMR (700 MHz, CDCl_3) spectrum of the mixture of Pd-S-L9down and $\text{Pd}_2\text{-S-L9down}$ (bottom) and the expanded spectrum in the aromatic region (top).

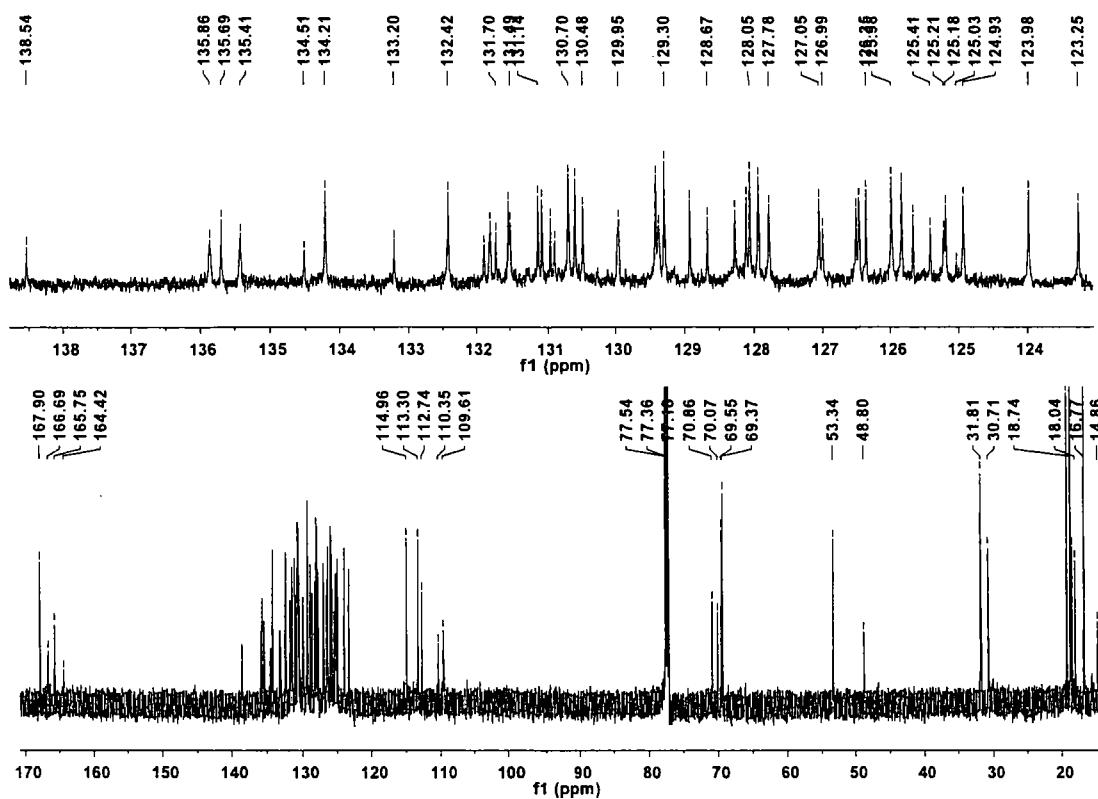


Figure B 61. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **Pd-S-L9down** and **Pd₂-S-L9down** (bottom) and the expanded spectrum in the aromatic region (top).

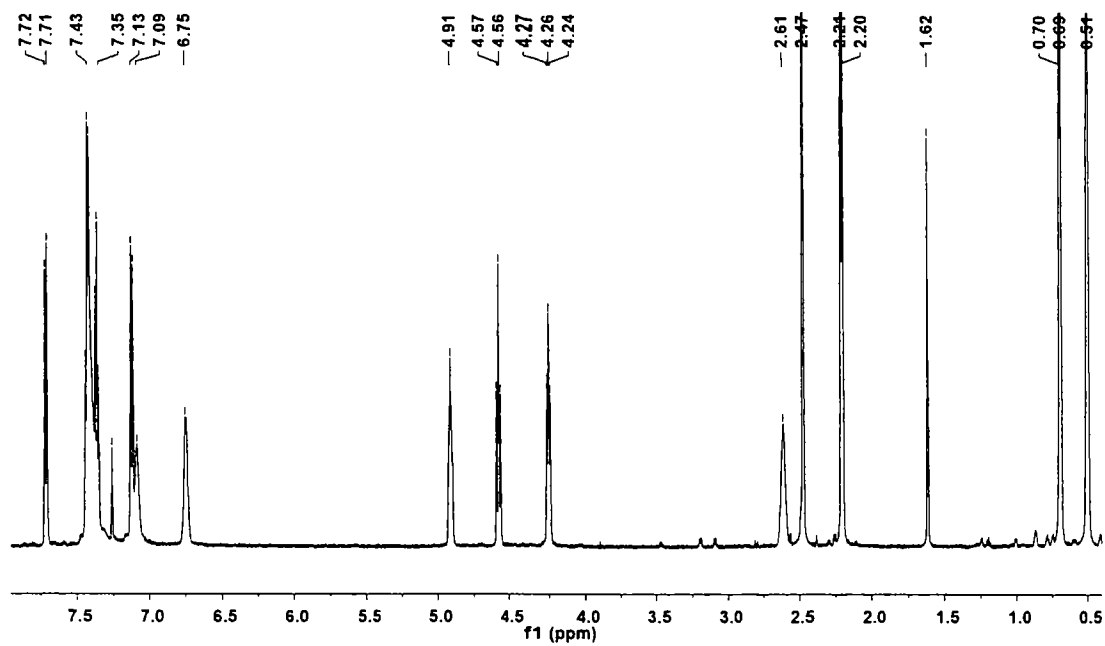


Figure B 62. The ^1H NMR (700 MHz, CDCl_3) spectrum of Pd-R-L10.

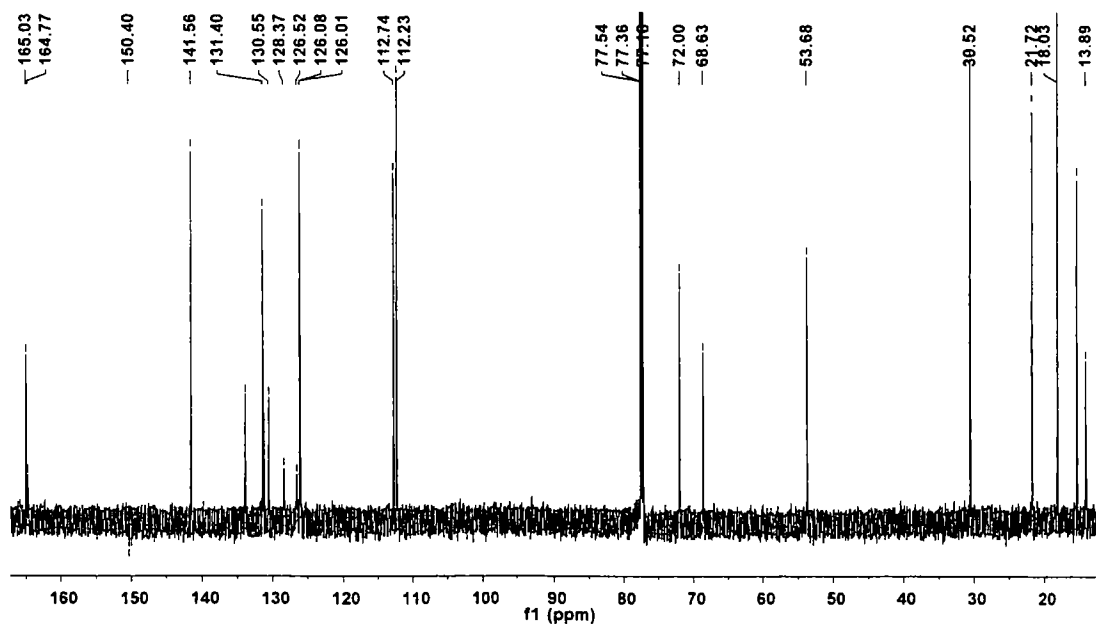


Figure B 63. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of Pd-R-L10.

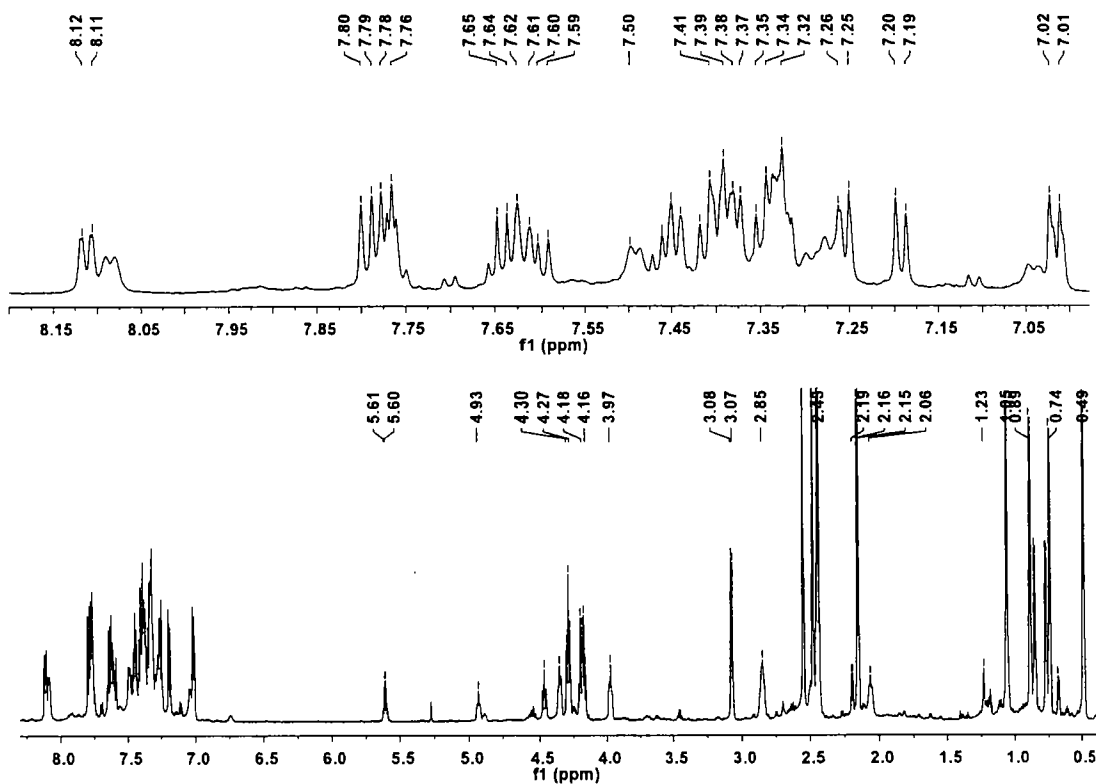


Figure B 64. The ^1H NMR (700 MHz, CDCl_3) of the mixture of S-L10 palladium complexes (bottom) and the expanded spectrum in the aromatic region (top).

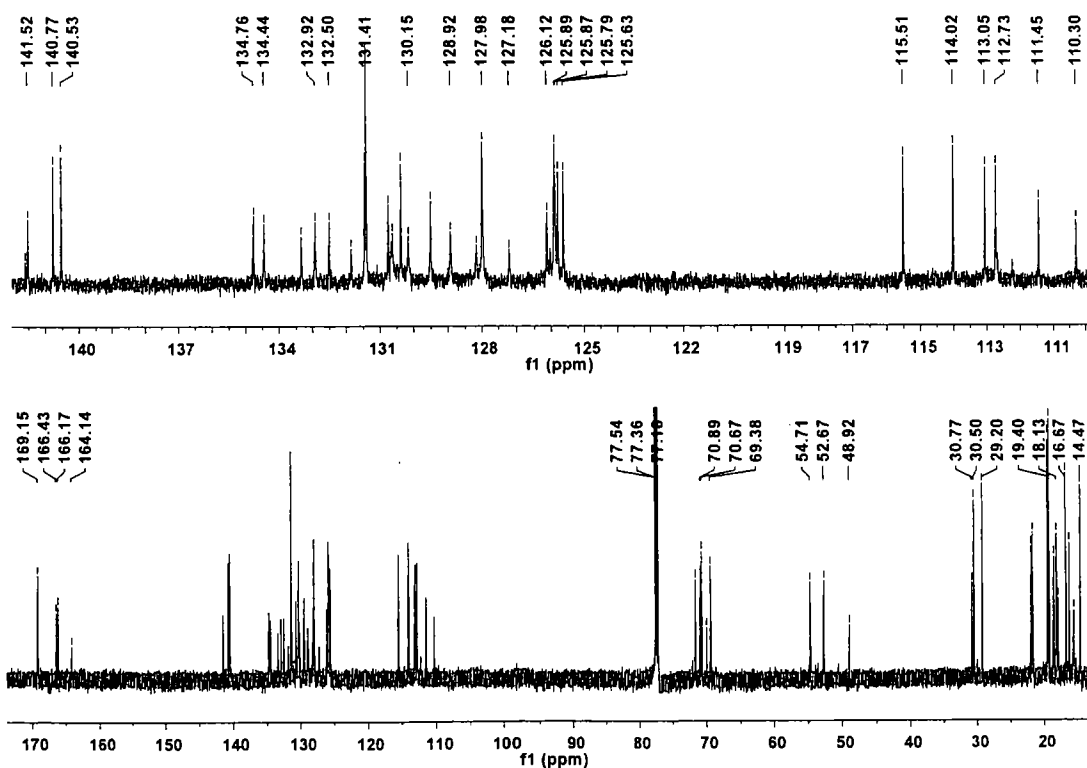


Figure B 65. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of the mixture of S-L10 palladium complexes (bottom) and the expanded spectrum in the aromatic region (top).

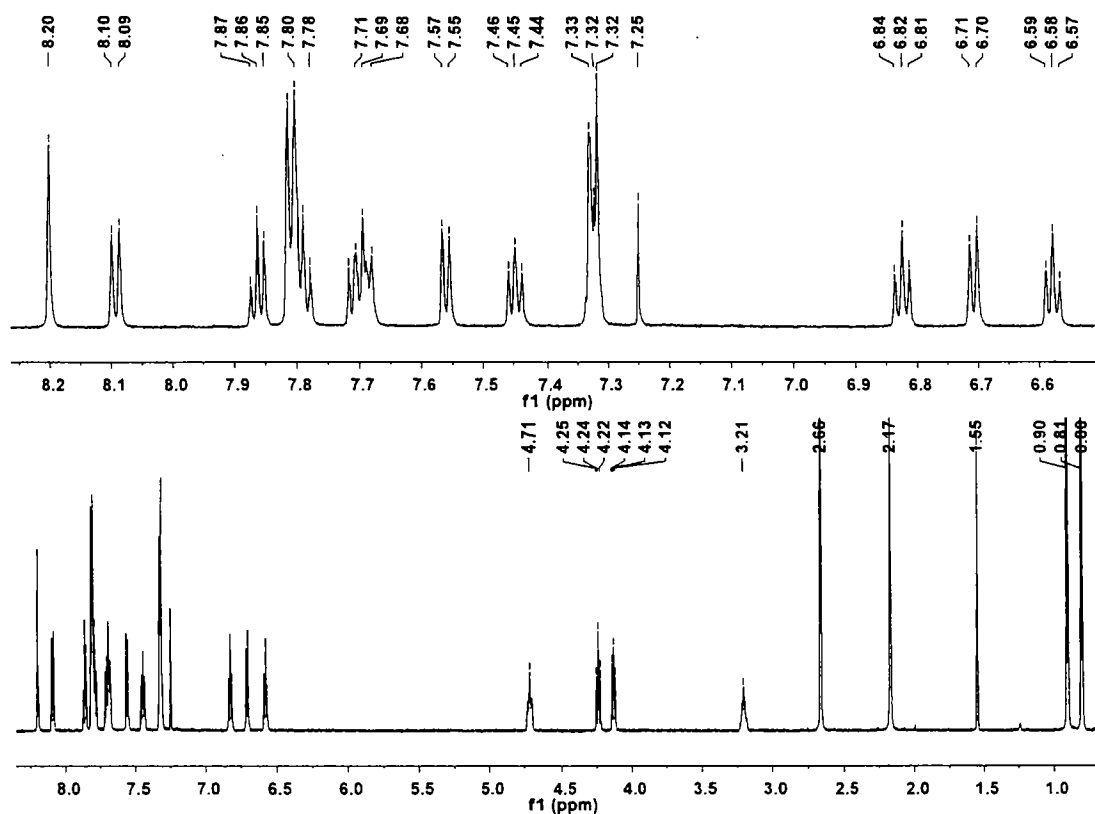


Figure B 66. The ^1H NMR (700 MHz, CDCl_3) spectrum of **PdL11up** (bottom) and the expanded spectrum in the aromatic region (top).

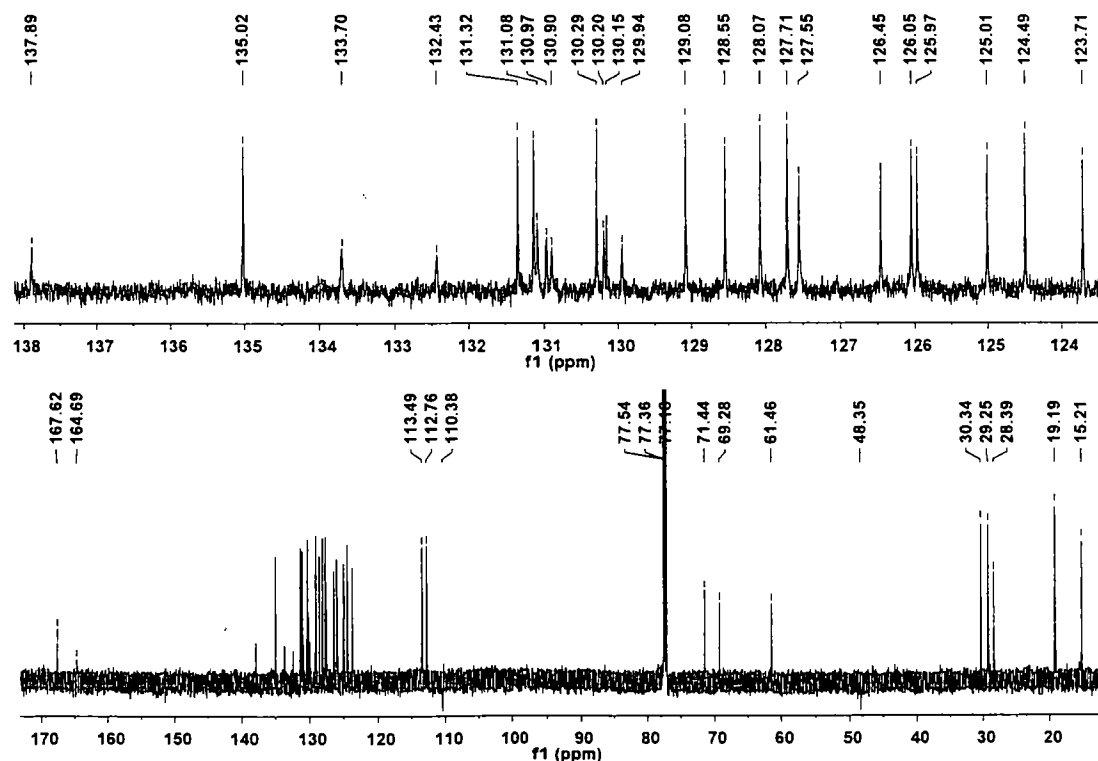


Figure B 67. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **PdL11up** (bottom) and the expanded spectrum in the aromatic region (top).

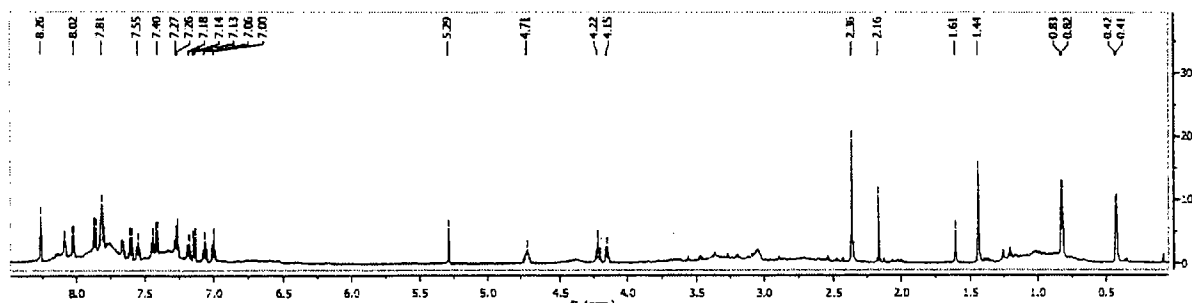


Figure B 68. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL11down.

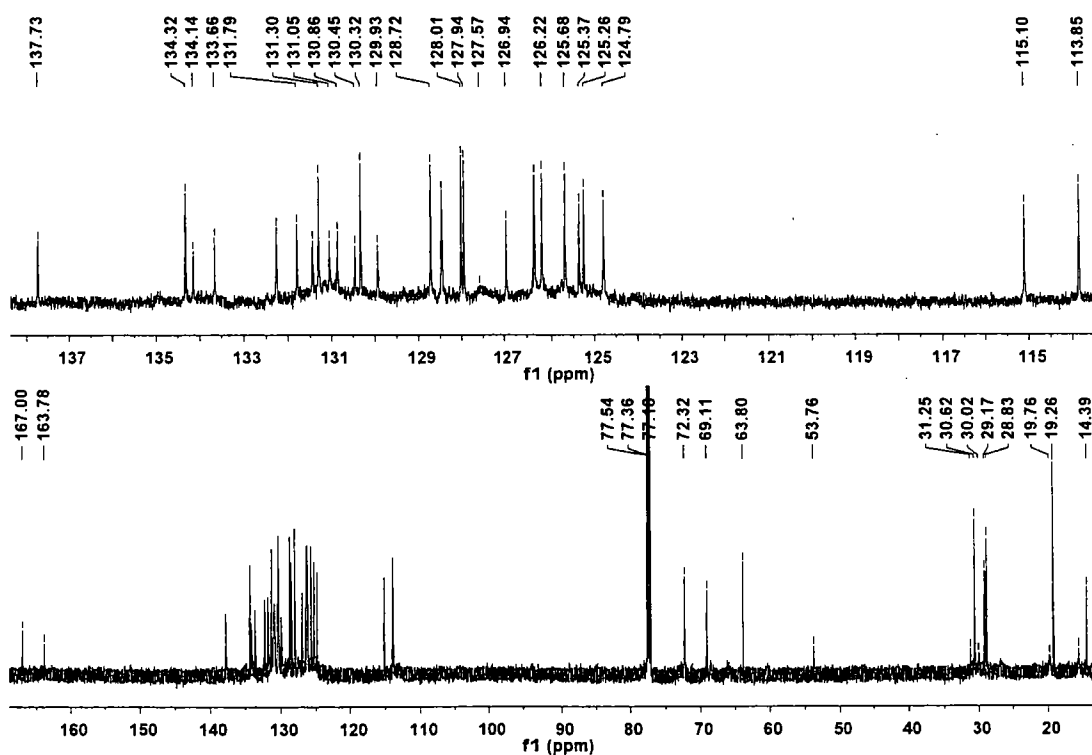


Figure B 69. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL11down (bottom) and the expanded spectrum in the aromatic region (top).

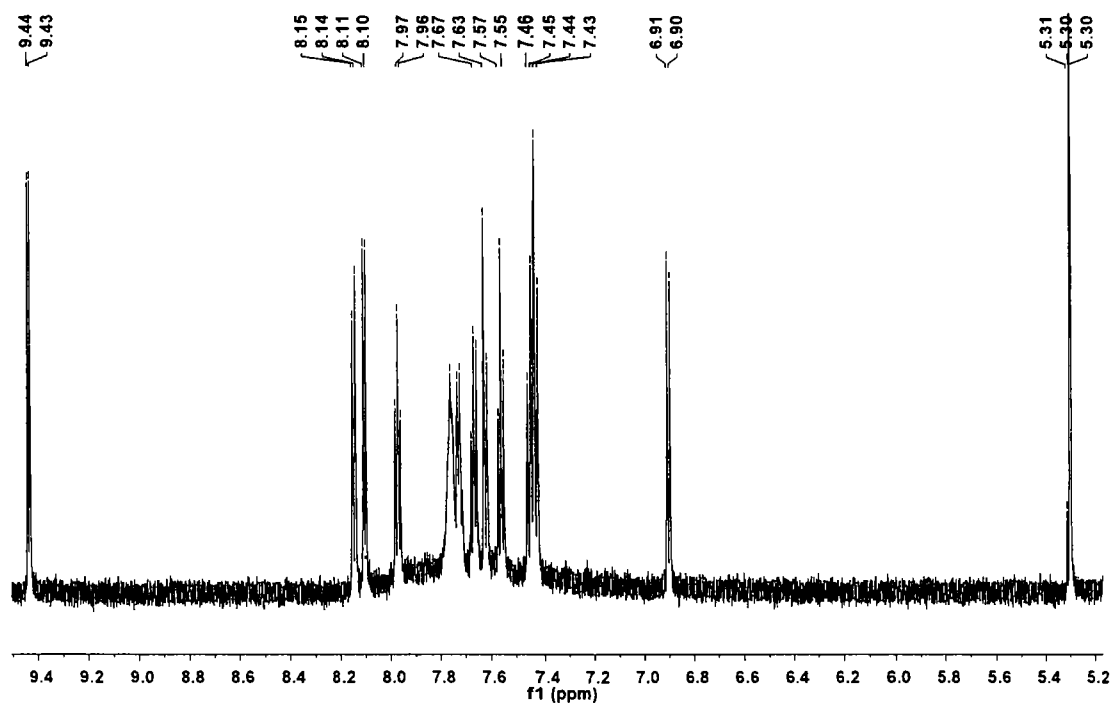


Figure B 70. The ^1H NMR (700 MHz, CDCl_3) spectrum of PdL12.

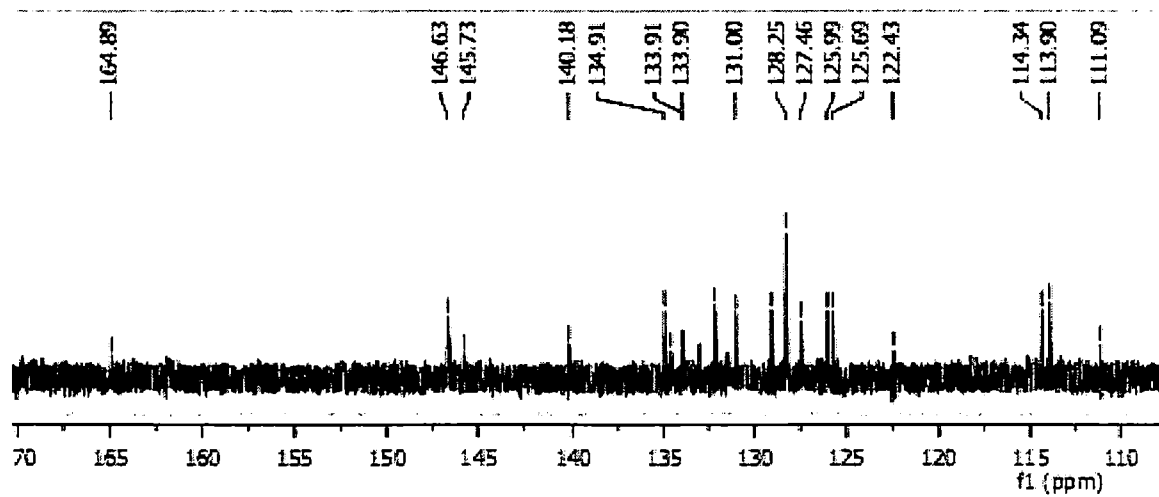


Figure B 71. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of PdL12.

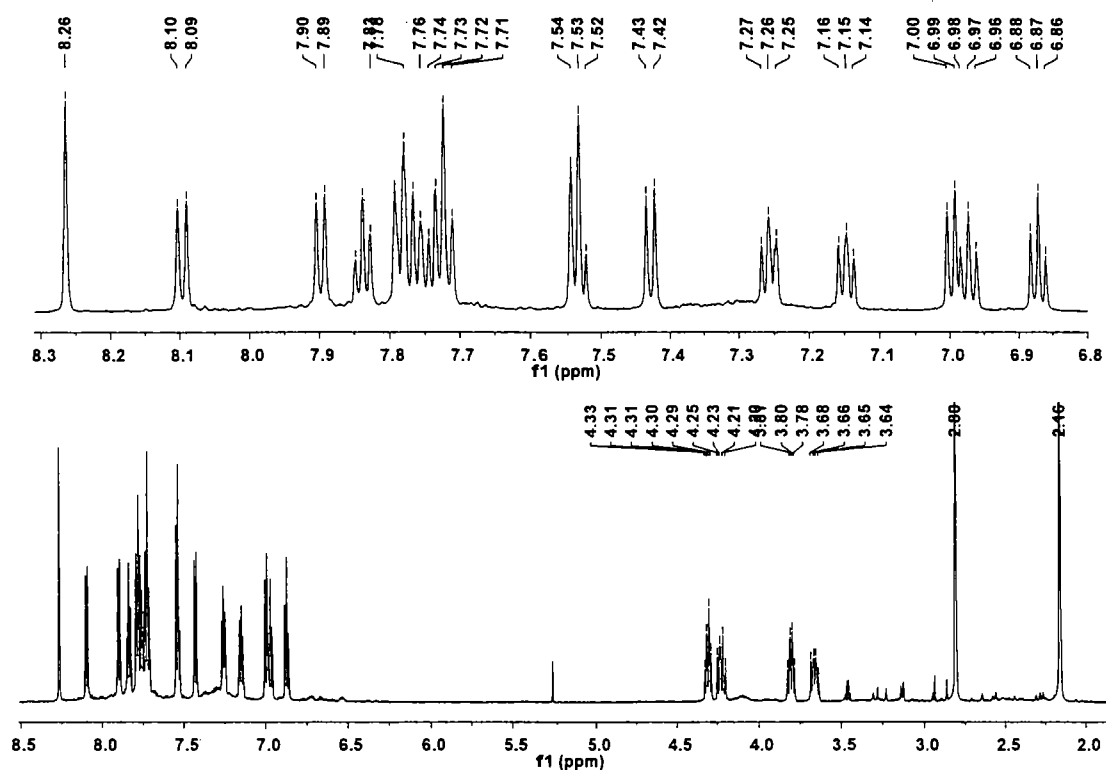


Figure B 72. The ^1H NMR (700 MHz, CDCl_3) spectrum of **PdL13up** (bottom) and the expanded spectrum in the aromatic region (top).

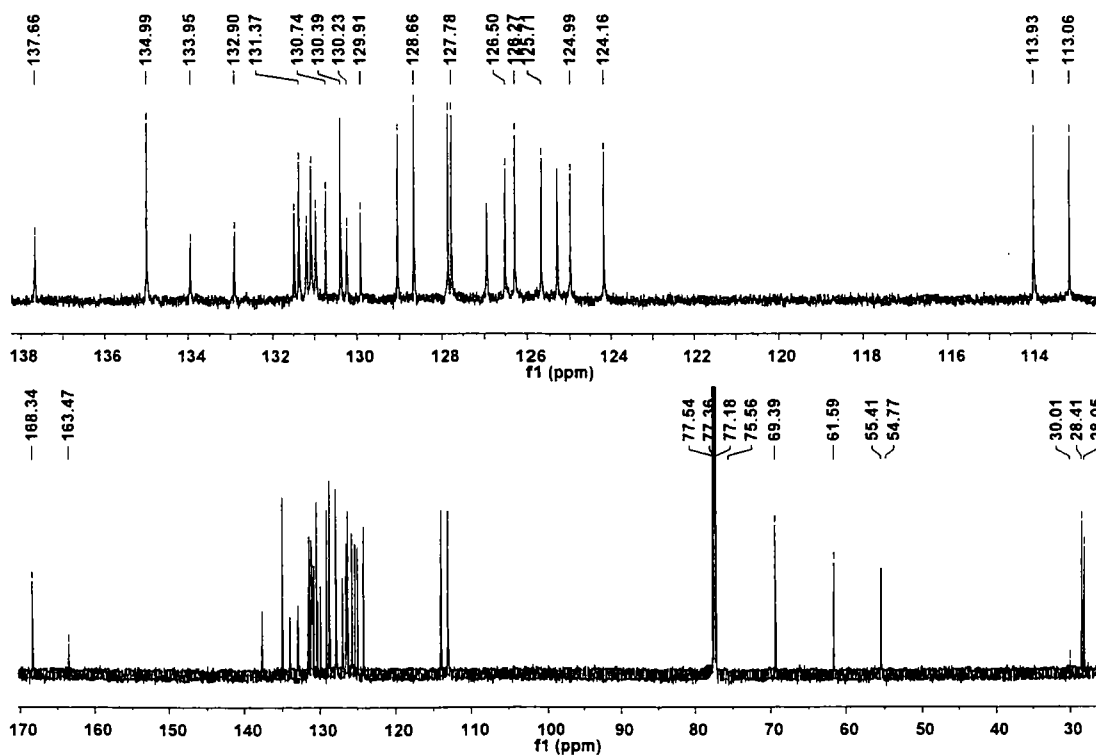


Figure B 73. The $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3) spectrum of **PdL13up** (bottom) and the expanded spectrum in the aromatic region (top).

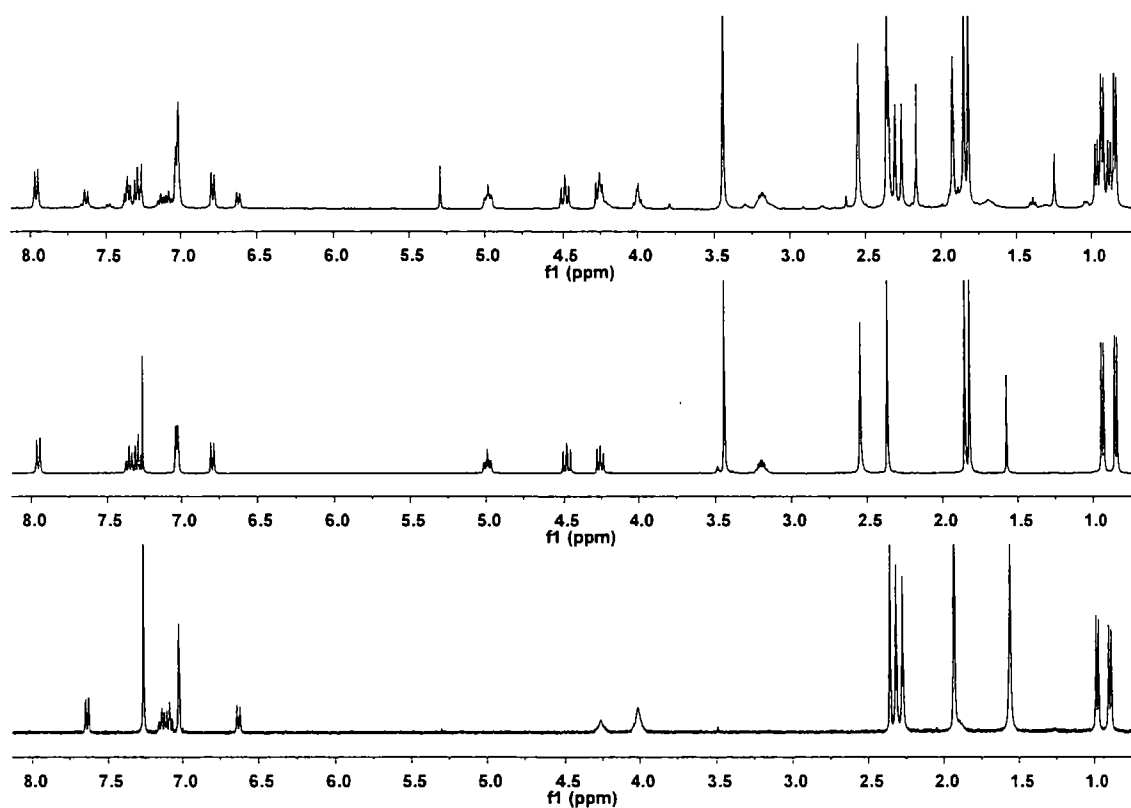


Figure B 74. The ^1H NMR spectra (400 MHz, CDCl_3) of **L4** (bottom), isolated **PdL4** and the *in situ* 1:2 $\text{PdCl}_2(\text{PhCN})_2:\text{L4}$ reaction (top).

Table B 1. Distances of Cl(1) and Cl(2) from the Pd-S-N(13) plane and the angle between planes Pd-S-N(13) to Cl(1)-Pd-Cl(2).

Compound	Cl.....Pd-S-N(13) (Å)		Pd-S-N(13) / Cl(1)-Pd-Cl(2) (deg)
	Cl(1)	Cl(2)	
PdL2up	0.02	0.18	4.4
PdL2down	0.26	0.07	6.7
PdL3	0.05	0.09	2.6
PdL4	0.22	0	5.5
PdL4·0.5CH₂Cl₂	0.16	0.25	6.5
	0.02	0.24	5.9
PdL4·CH₃OH	0.05	0.03	1.4
PdL6	0.18	0.04	4.8
PdL7	0.16	0.12	4.9
	0.01	0.22	5.4
PdL11up	0.16	0.03	4.1

Table B 2. Distances of Cl(1) and Cl(2) from the Pd-S-N(13) plane and the angle between planes Pd-S-N(13) to Cl(1)-Pd-Cl(2).

Compound	Cl.....Pd-S-N(13) (Å)		Pd-S-N(13) / Cl(1)-Pd-Cl(2) (deg)
	Cl(1)	Cl(2)	
Pd₂L5·CH₂Cl₂	0.07	0.11	3.2
Pd₂L5·2CH₂Cl₂	0.08	0.06	2.4
	0.13	0.14	4.7
Pd₂L5·4CH₂Cl₂	0.14	0.07	3.8
	0.09	0.08	3.0
Pd₂L5·CHCl₃·CH₃COCH₃	0.12	0.10	3.9
	0.10	0.09	3.3
Pd₂L5·H₂O	0.08	0.03	2.1
	0.09	0.09	3.1

Appendix C

Phosphine Sulfides and Their Palladium Complexes

Appendix C

Table C 1. Crystallographic data for **dppbS:dppbSO**.

Compound	dppbS:dppbSO (0.75:0.25)	dppbS:dppbSO (0.33:0.67)
Formula	0.75(C ₂₈ H ₂₈ P ₂ S), 0.25(C ₂₈ H ₂₈ OP ₂ S)	0.33(C ₂₈ H ₂₈ P ₂ S), 0.67(C ₂₈ H ₂₈ OP ₂ S)
FW	462.50	469.22
<i>T</i> , K	120(2)	120(2)
Crystal system	Triclinic	Triclinic
Space group (no.)	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.3335(8)	6.1960(7)
<i>b</i> (Å)	11.5753(10)	8.6855(8)
<i>c</i> (Å)	12.0754(2)	12.4660(12)
α (°)	88.72(1)	72.49(1)
β (°)	73.74(1)	76.18(1)
γ (°)	72.46(1)	74.62(1)
<i>U</i> (Å ³)	1191.44(18)	607.56(11)
<i>Z</i>	2	1
<i>D</i> _x (Mg cm ⁻³)	1.289	1.289
μ (mm ⁻¹)	0.285	0.282
Refls measured	12768	8282
Independent reflections	5447	3520
Data/restraints/parameters	5447/0/290	3520/0/149
Final R indices <i>I</i> > 2 σ	R1=0.0509, WR2=0.0944	R1=0.0413, WR2=0.0977
R indices (all data)	R1=0.0814, WR2=0.1039	R1=0.0542, WR2=0.1038

Table C 2. Selected bond lengths and angles of the partially oxidized **dppbSO**.

Bond (Å)	dppbS:dppbSO (0.75:0.25)	dppbS:dppbSO (0.33:0.67)
P-S	1.9486(9)	1.7839(12)
P-O	1.370(6)	1.632(5)
P(S)-CH ₂ ^a	1.811(2)	1.8117(17)
P(S)-C _{Ar} ^b	1.815(2)	1.8155(14)
	1.820(2)	1.8228(13)
P(O)-CH ₂ ^a	1.839(2)	1.8117(17)
P(O)-C _{Ar} ^b	1.826(2)	1.8155(14)
	1.833(2)	1.8228(13)
Angle (deg)		
S-P-CH ₂ ^a	114.09(8)	110.25(7)
O-P-CH ₂ ^a	113.8(3)	121.16(18)
S-P-C _{Ar} ^b	112.35(8)	113.72(6)
	112.47(8)	116.18(6)
O-P-C _{Ar} ^b	115.0(3)	106.51(18)
	119.7(3)	112.0(2)
CH ₂ -P(S)-C _{Ar} ^b	105.74(11)	115.05(7)
	105.21(10)	105.99(8)

^a CH₂ next to P atom, ^b ipso aromatic carbons next to P atom.

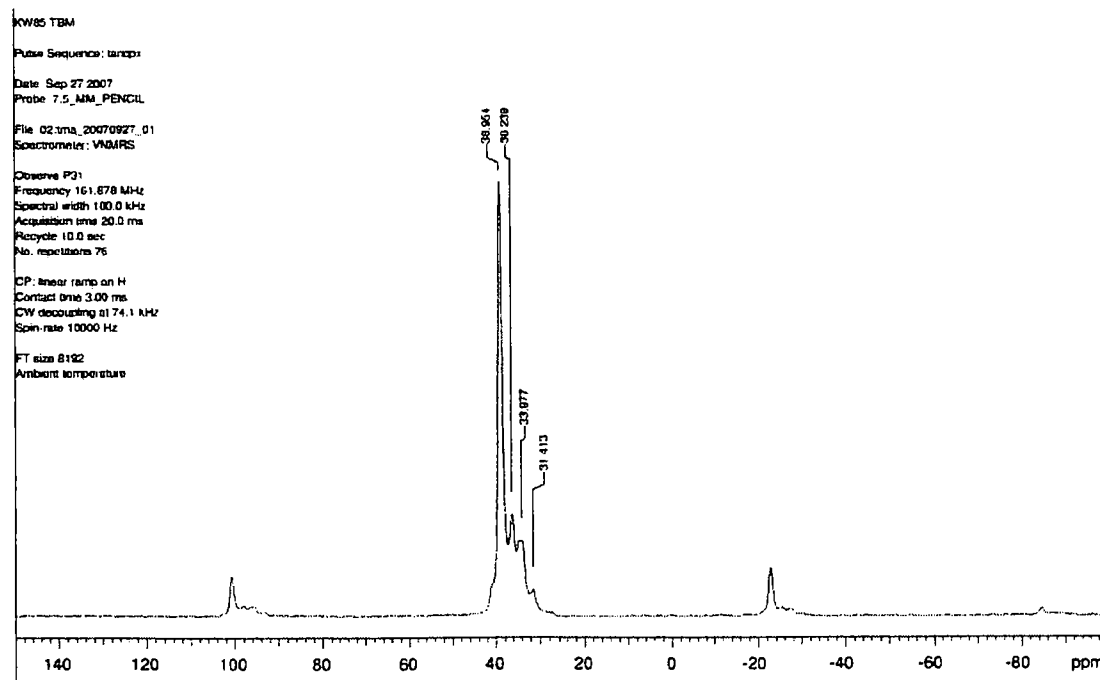


Figure C 1. The solid state ³¹P{¹H} NMR spectrum of the complex obtained from the reaction of PdCl₂(PhCN)₂ with **dppmS** in a 1:1 molar ratio.

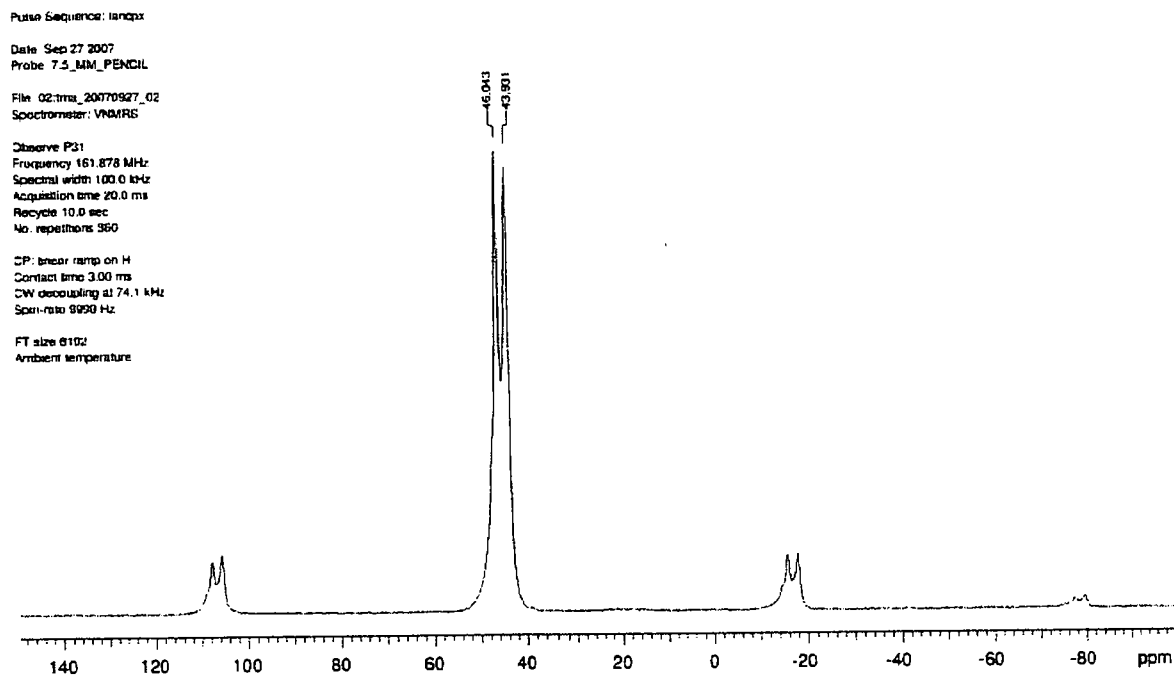


Figure C 2. The solid state $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex obtained from the reaction of $\text{PdCl}_2(\text{PhCN})_2$ with **dppbS** in a 1:1 molar ratio.

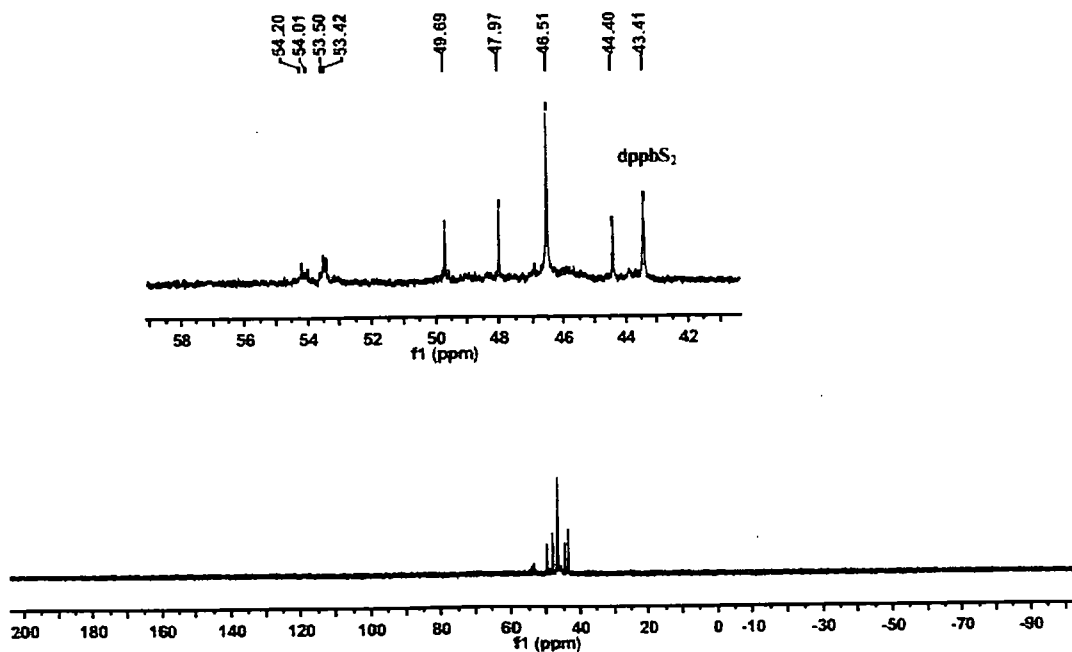


Figure C 3. The *in situ* $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ with **dppbS₂** in a 1:2 molar ratio in CD_2Cl_2 .

Table C 3. Bond lengths, angles and $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts of phosphine sulfide complexes.*

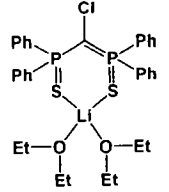
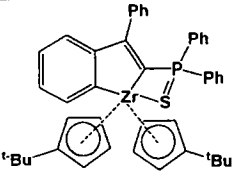
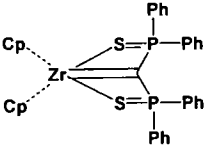
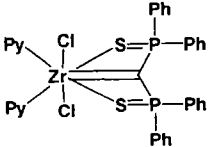
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
Li					
	2.440 2.461	1.995(1) 1.987(1)	106.23 106.97	45.5	1
Zr					
	2.797(1)	2.005(1)	85.4(4)		2
	2.7499(6) 2.7499(6)	2.019(1) 2.010(8)	81	21.2	3
	2.6813(8) 2.6912(8)	2.025(1) 2.020(1)	82	20.3	3

Table C 3 (continued)

Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.6813(8) 2.6912(8)	2.025(1) 2.020(1)	81	22.9	3
Nb					
NbCl ₅ (SPPH ₃)	2.577(3)	2.028(5)	116.6(2)		4
	2.573(4)	2.026(6)	111.5(2)		5
Cr					
Cr(CO) ₅ (SPMe ₃)	2.510(2)	1.990(3)	112.5(1)		6
	2.5056(10)	2.0184(12)	108.45(4)		7
Mo					
Mo(O)Cl ₃ (SPPH ₃)	2.460(1)	2.041(1)	111.31 (4)		8

Table C 3 (continued)

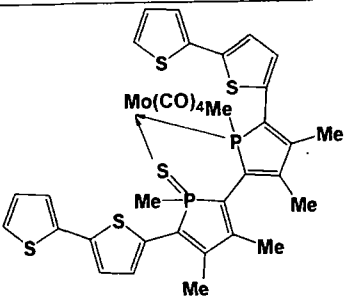
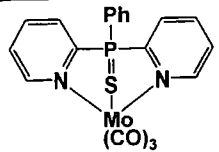
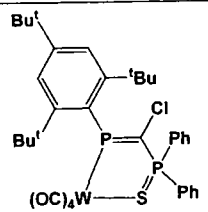
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
 <p>Chemical structure of a molybdenum complex. The central Mo atom is coordinated to four CO groups and two phosphorus atoms. Each phosphorus atom is part of a five-membered ring containing a sulfur atom and three methyl groups. The two phosphorus atoms are bridged by a sulfur atom.</p>	2.632(2)	1.980(3)	106.2(1)		9
 <p>Chemical structure of a molybdenum complex. The central Mo atom is coordinated to three CO groups and a bis-imidazole ligand. The phosphorus atom of the bis-imidazole ligand is also coordinated to a phenyl group.</p>	2.6242(14)	1.973(2)	85.43(5)	16.4	10
W					
W(CO) ₅ (SPPPh ₃)	2.6009(7)	2.004(1)	113.24(4)		11
 <p>Chemical structure of a tungsten complex. The central W atom is coordinated to four CO groups and a phosphorus atom. The phosphorus atom is part of a five-membered ring containing a sulfur atom and a phenyl group. The phosphorus atom is also coordinated to a phenyl group and a chlorine atom.</p>	2.566(3)	1.990(4)	102.9(2)	48.4	12

Table C 3 (continued)

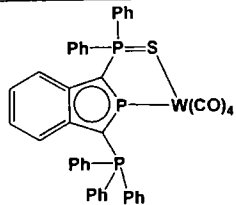
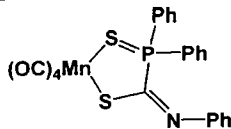
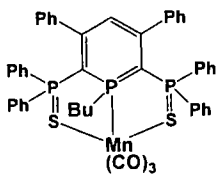
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.602(3)	2.015(2)	104.97(10)	27.4	7
[WCl(Me ₂ PCH ₂ P(S)Me ₂) ₂](PF ₆)	2.483(2) 2.451(2)	2.019(3) 2.027(3)	106.9(1) 108.3(1)		13
<u>Mn</u>					
	2.410	1.734	99.2		14
	2.4002(6) 2.4080(6) 2.401(1) 2.409(1)	2.0212(7) 2.0145(7) 2.034(2) 2.030(2)	103.1 103.9 105.3 106.4		15

Table C 3 (continued)

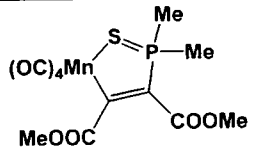
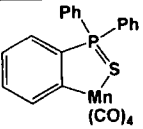
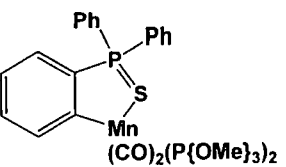
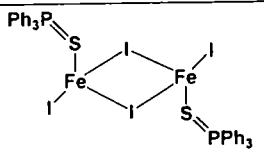
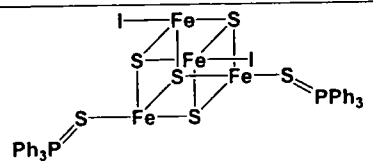
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.404	1.993	100.0		16
	2.410(1)	1.996(1)	99.64(3)	66.6	17
	2.412(1)	1.993(2)	99.59(6)	69.6	17
Fe					
	2.361	2.005	109.5		18
	2.316 2.321	2.014 2.017	108.0		19

Table C 3 (continued)

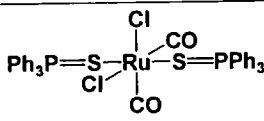
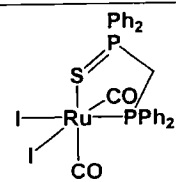
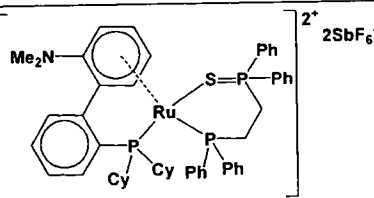
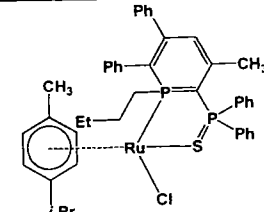
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
Ru					
	2.414(3) 2.426(3)	1.998 2.012	115.7 116.1		20
	2.4615(13)	2.0103(17)	105.0		21
[Ru(CO)Cl(dppmS) ₂] ₂ Cl	2.387 2.451	1.973 1.977	103.9 104.9		22
	2.421	2.016	105.4		23
	2.4239(5)	2.0283(7)	101.4		24

Table C 3 (continued)

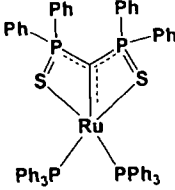
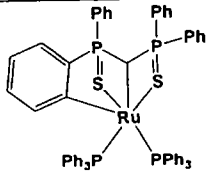
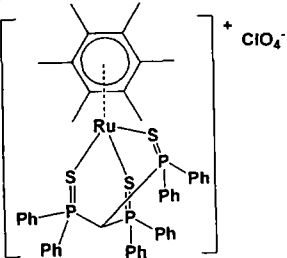
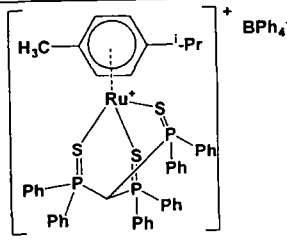
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.4739(5) 2.4843(5)	2.0269(7) 2.0206(6)	79.0	48.8 57.6	25
	2.620 – 2.504	1.986 – 1.996	72.3 – 90.0	62.5	25
	2.443(1)	2.003(1)	81.4(1)		26
	2.438(2) 2.443(2) 2.451(2)	2.030(3) 2.031(3) 2.031(3)	109.5(1) 109.5(1) 110.1(1)		27

Table C 3 (continued)

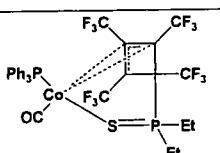
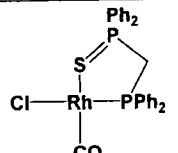
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
Co					
	2.350	1.980	93.0		28
Rh					
	2.403(2)	2.005(3)	98.6(1)	52.2	29
[Rh(CO) ₂ (dppmS ₂)]ClO ₄	2.397(2) 2.402(3)	1.996(2) 1.999(2)	101.06(9) 105.10(8)	37.2	30
[RhCl(Cp*)(<i>o</i> -Ph ₂ PNHC ₆ H ₄ P(S)Ph ₂ -P,S)]ClO ₄	2.402(3)	2.008(3)	117.1	47.4	31
RhCl(CO){Fe(η^5 -C ₅ Me ₄ P(S)Ph ₂)(η^5 -C ₅ Me ₄ PPh ₂)}	2.420(3) 2.435(3)	1.994(4) 2.001(4)	110.9(2) 112.4(1)	43.16	32
[RhCl(CO){Fe(η^5 -C ₅ Me ₄ P(S)Ph ₂)(η^5 -C ₅ Me ₄ PPh ₂)}] ₂ [RhCl ₂ (CO) ₂]	2.422(2)	2.010(3)	108.12(9)	43.23	32

Table C 3 (continued)

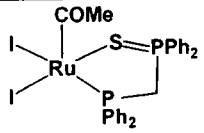
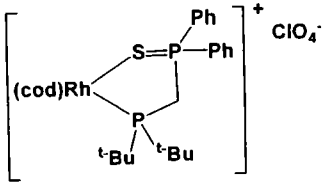
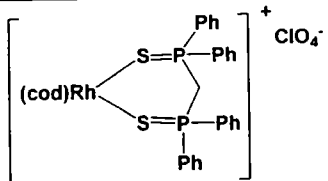
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.357(2)	2.027(2)	106.5		33
	2.349(2)	2.026(3)	105.2(4)		34
	2.403(5) 2.417(5)	2.001(6) 1.994(6)	102.4(2) 106.6(2)	35.3	30
Rh(cod){[(O)PPh ₂] ₂ [(S)PPh ₂]C}	2.307(5) 2.036(9)	2.036(9)	104.19(5)	40.0	35

Table C 3 (continued)

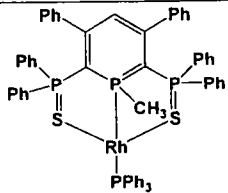
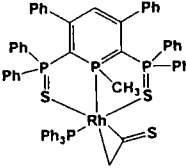
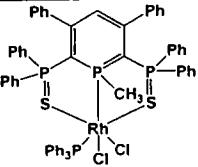
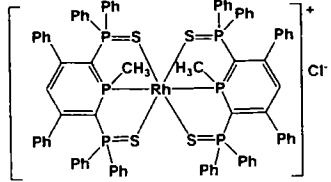
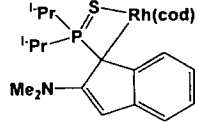
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.3197(6) 2.3213(6)	2.0219(7) 2.0235(8)	101.34(3) 107.73(3)	41.86	36
	2.5040(8) 2.4193(7)	2.0135(8) 2.025(1)	101.33(3) 106.94(3)	47.52 50.58	36
	2.374(2) 2.442(2)	2.041(3) 2.016(3)	103.1(1) 107.9(1)	52.27	37
	2.3641(8) – 2.4462(8)	2.017(1) 2.041(1)	108.26(4)	45.80 51.75	37
	2.3811(7)	2.01127(8)	81.41(3)		38

Table C 3 (continued)

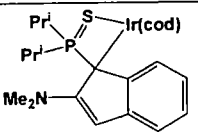
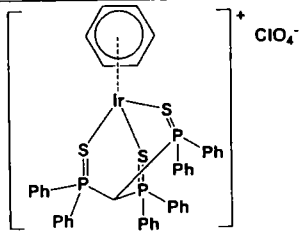
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
Ir					
$\text{IrI}_2(\text{CO})\text{Me}(\text{dppmS})$	2.4194(9)	2.0126(13)	105.4	65.0	33
$\text{IrI}_2(\text{CO})\text{Et}(\text{dppmS})$	2.416(2)	2.009(3)	105.68	65.2	39
$[\text{IrI}(\text{CO})\text{Me}(\text{dppmS})]_2\text{SO}_3\text{CF}_3$	2.4182(13)	2.0138(18)	102.25	62.2 63.4 64.3 65.2	33
$[\text{Ir}(\text{cod})\{(\text{PPh}_2)\text{CH}_2(\text{P}(\text{S})^t\text{Bu}_2)-\text{P},\text{S}\}]\text{BF}_4$	2.324(3)	2.034(5)	107.2(2)	59.4	34
$[\text{Ir}(\text{Cp}^*)(\text{dppmS}_2)(\text{PO}[\text{OMe}]_2)]\text{BF}_4$	2.389(2) 2.408(2)	1.998(2) 2.003(2)	112.3(1) 117.3(1)	30.7	40
	2.3653(8)	2.019(1)	82.63(4)	98.5	41
	2.409(3) – 2.440(3)	2.024(3) – 2.034(3)	107.9(1) – 108.4(1)	42.4	27

Table C 3 (continued)

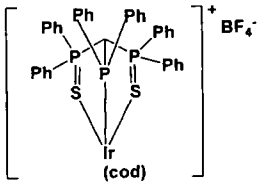
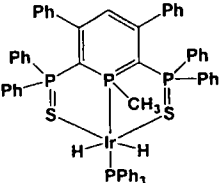
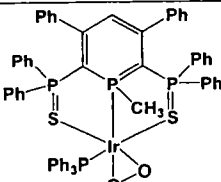
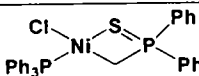
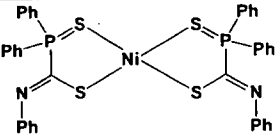
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.438(3) 2.574(3)	2.001(4) 1.977(4)	100.2(1) 105.0(1)	52.8	34
	2.4717(6) 2.4514(5)	2.0127(8) 2.0140(8)	112.3 117.3	50.3	42
	2.397(4) 2.405(5)	2.030(6) 2.033(6)	97.6 103.9	50.2	43
Ni					
	2.284(2)	1.999(3)	80.0		44
	2.197(2)	2.001(3)	105.4(1)	50.0	45

Table C 3 (continued)

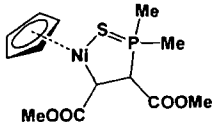
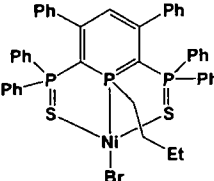
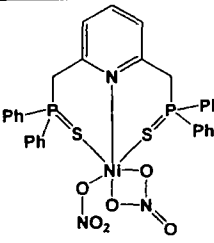
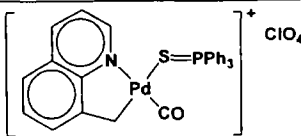
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.194	2.004	99.0		46
	2.185(1) 2.194(1)	2.039(2) 2.045(2)	104.3 106.7	58.26	47
	2.402(1) 2.481(1)	1.980(2) 1.981(2)	103.3 101.6		48
Pd					
	2.453(1)	2.009	105.39	45.65	49
<i>trans</i> -PdCl ₂ [(^t Bu) ₃ P(S)] ₂	2.334	2.014	112.04		50
PdI ₂ (dppmS)	2.331(2)	2.007(3)	101.3(1)	61.1	51

Table C 3 (continued)

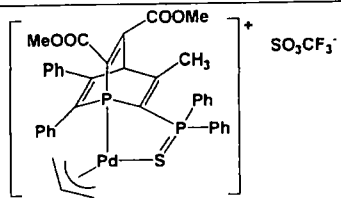
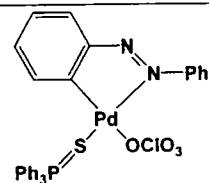
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
$\text{PdCl}_2(\text{dppmS})$	2.2874(4)	2.0150(5)	104.099(19)	56.37	51
<i>trans</i> - $[\text{Pd}(\text{dppmS})_2]\text{Cl}_2$	2.3256(8)	2.017(8)	99.84(4)		51
$\text{PdCl}_2(\text{dppmS}_2)$	2.3005(14) 2.3018(13)	2.0089(18) 2.0181(18)	105.11(7) 113.54(7)	37.87	52
$[(\eta^3\text{-allyl})\text{Pd}(\text{dppmS}_2)] [(\eta^3\text{-allyl})\text{PdCl}_2]$	2.391	1.985	104.4		53
<i>trans</i> - $\text{PdCl}_2[\text{Et}_2\text{PhP(S)}]_2$	2.350	2.013	107.6		54
	2.364(1)	2.005(1)	99.6	62.4	55
$[\text{Pd}(\text{dppmS}_2)(\text{dppm})](\text{ClO}_4)_2$	2.3858(14) 2.4069(13)	2.0026(18) 2.0064(17)	100.2 105.8	40.50	56
$[\text{Pd}(\text{dppmS}_2)(\text{dppp})](\text{ClO}_4)_2$	2.3878(10) 2.3960(10)	1.9994(14) 1.9966(14)	108.3 109.5	38.00	56
$[\text{Pd}(\text{dppmS}_2)_2](\text{BF}_4)_2$	2.314(2) – 2.34(1)	1.984(3) – 2.001(3)	107.3(2) – 112.4(1)	46.2	57
	2.326(1)	2.013(13)	103.7(1)	46.59	58

Table C 3 (continued)

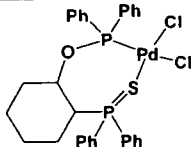
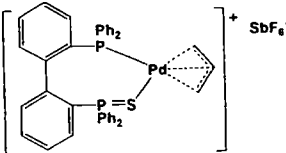
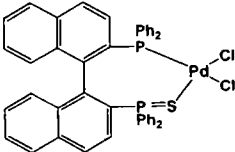
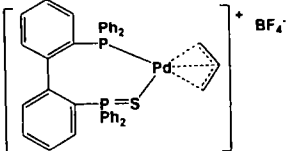
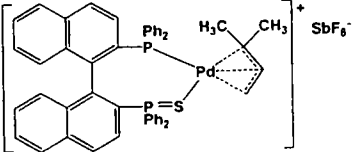
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.3112(9)	2.0220(12)	116.26(4)	35.9	59
	2.412(2)	2.001(3)	101.49(9)	41.2 41.3	60
	2.314(2)	1.991(3)	105.49(11)	39.77	61
	2.388(2)	1.994(3)	104.64(9)	42.1 44.1	61
	2.388(2)	2.003(2)	106.17(8)	47.3	60

Table C 3 (continued)

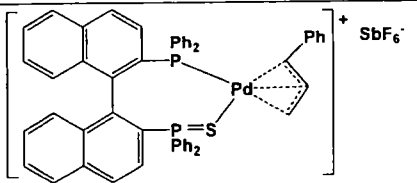
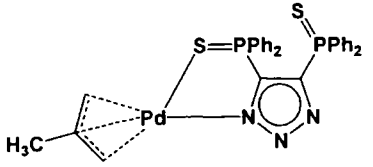
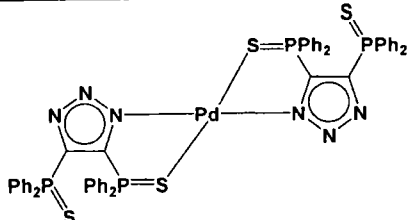
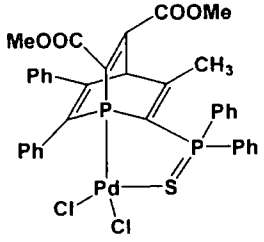
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.3904(12)	1.995(2)	104.74(6)	43.7 45.7	60
	2.3796(14)	2.0084(18) (pendant P=S) 1.9633(7)	94.04	46.8	62
	2.3159(13) 2.3228(13)	2.0306(17) 2.0187(18) (pendant P=S) 1.9633(7)	100.26 101.06		62
	2.3070(8)	2.026(1)	104.43	48.0	55

Table C 3 (continued)

Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.3877(5)	2.0090(6)	98.99	49.8 49.6	55
	2.312(4) 2.321(4)	1.995(5) 2.007(5)	97.9(2) 98.8(2)	56.5	63
	2.310(1) 2.353(1)	2.1018(2) 2.039(2)	94.24 108.19	54.36	47
	2.317(1) 2.3277(8)	2.036(1) 2.036(1)	104.64 106.51	52.6	64

Table C 3 (continued)

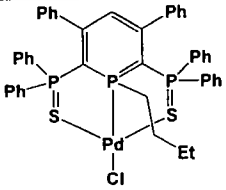
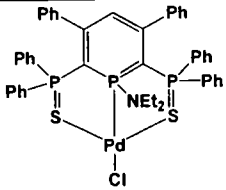
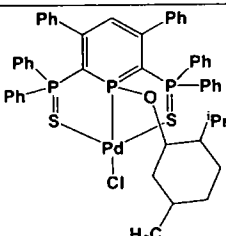
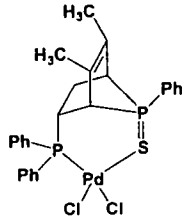
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.317(2) 2.321(2)	2.031(4) 2.037(3)	101.82 104.84	49.17	65
	2.3250(8) 2.3275(8)	2.029(1) 2.033(1)	101.81 104.62	51.77	47
	2.313(1) 2.328(1)	2.033(2) 2.033(2)	101.89 102.93	47.67 49.89	47
	2.299(1)	2.002(1)	116.8(1)	48.9	66

Table C 3 (continued)

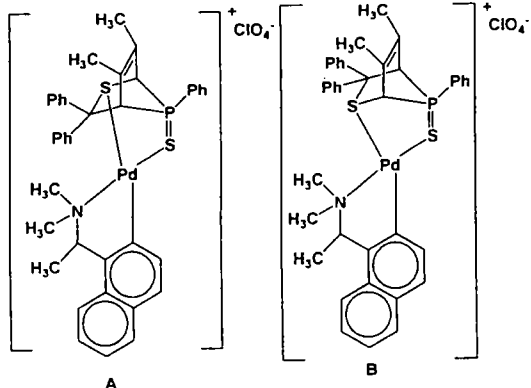
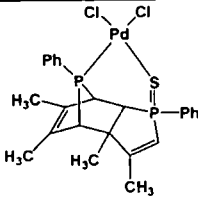
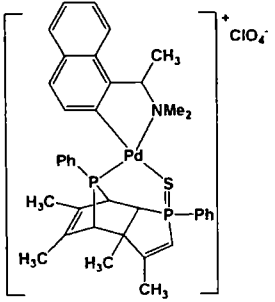
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
 <p>A</p> <p>B</p>	A 2.266(3) 2.468(3) B 2.308(3) 2.445(3)	A 1.984(5) B 1.999(5)	A 97.4(1) B 96.9(1)	A 99.7 B 100.0	66
	2.324(1)	2.017(1)	93.1(5)	60.54	67
	2.481(1)	1.987(2)	92.4(1)	62.0	67

Table C 3 (continued)

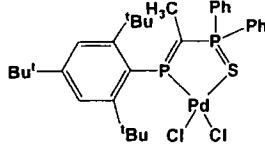
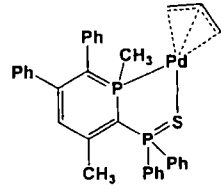
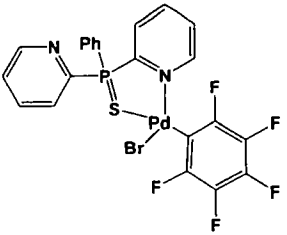
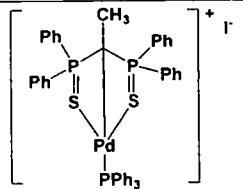
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.284(3)	2.012(4)	106.7(1)	55.5	68
	2.3371(6)	2.0288(8)	105.04	52.4	24
	2.307(2)	1.991(2)	94.23(8)	45.9	69
	2.3741(6) 2.3677(6)	2.0424(8) 2.0451(7)	78.58 79.10	39.8	70
$\text{PdCl}_2\text{Fe}[\text{C}_5\text{Me}_4\text{P}(\text{S})\text{Ph}_2][\text{C}_5\text{Me}_4\text{PPh}_2]$	2.3278(7)	2.0237(9)	107.13(3)	40.9	71

Table C 3 (continued)

Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.3187(10) 2.3530(10)	2.0092(12) 2.0077(13)	101.85(5) 104.43(4)	36.00	72
Pt					
<i>trans</i> -PtCl ₂ (SPPPh ₃)(S(O)Me ₂)	2.300(4)	2.026(6)	105.7(2)	40.2	73
<i>trans</i> -PtCl ₂ (SPPPh ₃)(S(O)Me(<i>p</i> -tolyl))	2.305(3)	2.018(4)	104.05(13)		73
	2.4243(18)	1.993(2)	96.41	36.6	74
[PtMe{(dppes)}-P,S] ₂ (BF ₄) ₂	2.403(3) 2.427(3)	2.043(4)	103.27(13) 117.57(14)	38.0	74
[PtCl(PEt ₃){(PPh ₂)(P(S) ^t Bu ₂)-P,S}]ClO ₄	2.283	2.045	107.21		75
[Pt(dppm)(dppmS ₂)](ClO ₄) ₂	2.394(2) 2.407(2)	2.021(3) 2.023(3)	101.16 106.70		76
	2.390(4)	2.014(5)	79.96		77

Table C 3 (continued)

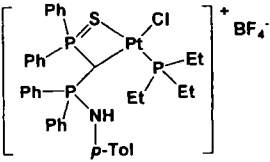
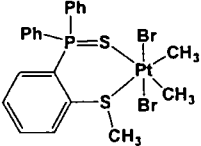
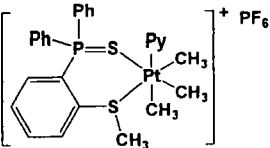
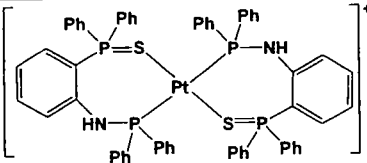
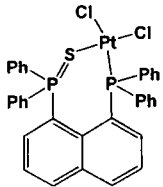
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.3090(10)	2.0091(3)	79.53(4)	50.7	78
	2.501(2)	1.986(2)	107.28(7)	36.2	79
	2.490(2)	1.996(2)	108.6(1)	36.2	80
	2.3432(4)	2.027(2)	108.19(7)	45.3	81
	2.286	2.018	103.65		82

Table C 3 (continued)

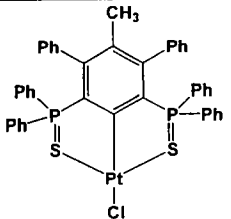
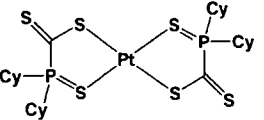
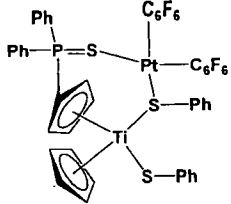
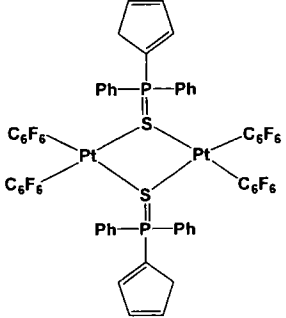
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.299(5) 2.307(5)	1.996(7) 2.002(7)	97.5(3) 99.3(3)	58.0	63
	2.314	2.017	102.50		83
	2.2401(3)	1.966(5)	99.05	26.68	84
	2.4094(17) 2.4227(17)	2.072(3)	81.30(5) – 101.99(8)	26.02	85

Table C 3 (continued)

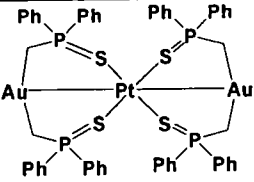
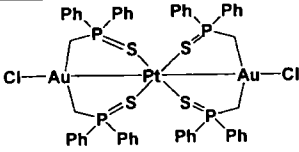
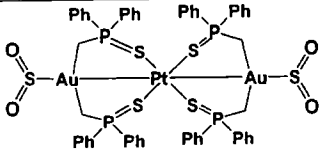
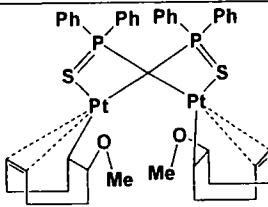
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.346(5)	2.033	104.16		86
	2.356(6) 2.372(6)	2.003 – 2.033	102.29 – 102.77		86
	2.360(3)	2.015	103.39		87
	2.484 2.479	2.001 2.010	79.50 79.84		88

Table C 3 (continued)

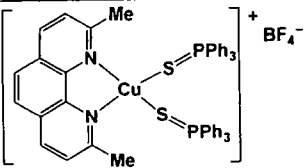
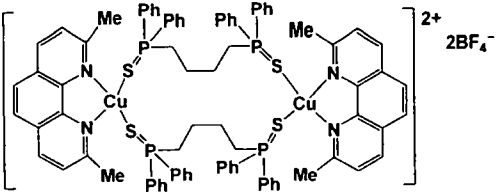
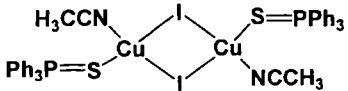
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
Cu					
[Cu(SPM ₃) ₃] ⁺ ClO ₄ ⁻	2.253(5) – 2.264(5)	1.96667(7) – 2.009(7)	104.3(3) – 110.3(3)		89
	2.290	1.975 1.992	109.93 115.55		90
	2.294	1.946 1.957	108.04 106.77		90
[Cu(dppeS) ₂](ClO ₄) ₂	2.392(3) 2.398(3)	1.975(3) 1.981(3)	98.96 99.62	50.9	91
	2.3444(13)	1.9880(1)	111.28(6)		92

Table C 3 (continued)

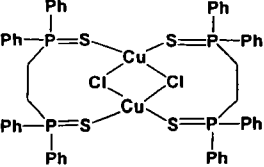
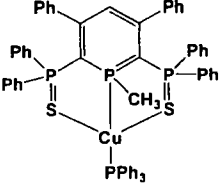
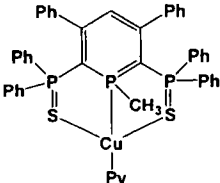
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
$[(\text{CuCN})_2(\text{dppeS}_2)]_n$	2.5263(13)	1.9630(13)	103.52		93
$\text{Cu}_3\text{Cl}_3(\text{SPMe}_3)_3$	2.264(1) – 2.267(2)	2.024(2) 2.026(1)	103.88(6) – 104.72(5)		94
$\text{CuCl}(\text{dppmS}_2)$	2.259(2) 2.321(2)	1.970(2) 1.974(3)	91.52(8) 95.68(8)		95
$\text{CuI}(\text{dppmS}_2)$	2.247 2.259	1.980 1.985	102.15 106.37		96
$[\text{Cu}(\text{dppmS}_2)_2]\text{PF}_6$	2.304 – 2.426	1.969 – 1.968	98.75 – 104.27		97
	2.303(3) 2.305(3)	1.985(3)	106.57(11) 109.88(10)		98
	2.355 – 2.388	2.003	100.56 – 102.43	49.8	99
	2.3621(6)	2.0072(8)	94.31	46.6	99

Table C 3 (continued)

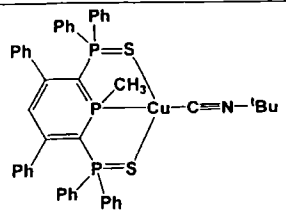
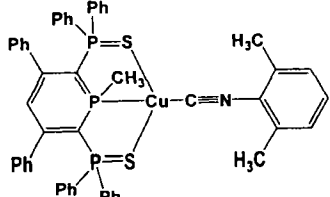
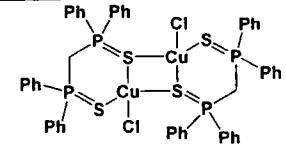
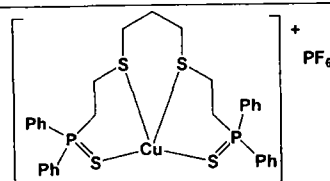
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.4119(9) 2.4280(13)	1.9987(9) 2.0052(11)	99.77(4) 102.09(3)	48.4	99
	2.3694(5) 2.4321(6)	2.0021(6) 2.0021(6)	102.03 103.87	47.3	99
[Cu(dppfS ₂) ₂](BF ₄)	2.140(5) 2.144(5)	1.985(5) 2.001(4)	100.8(2) 105.5(2)	45.63	100
[{Cu(dppf)} ₂ (μ -dppfS ₂)](BF ₄) ₂	2.231(4) 2.235(2)	1.990(3) 1.995(4)	117.5(2) 117.8(1)	40.72	101
	2.287(4) 2.376(4) 2.459(4)	1.976(5) 1.991(5)	73.7(1) 106.8(2) 110.1(2)		102
	2.296(2) 2.296(2)	1.971(2) 1.972(3)	99.56(10) 100.1(1)		103

Table C 3 (continued)

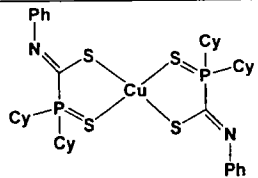
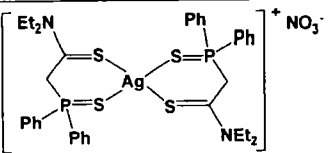
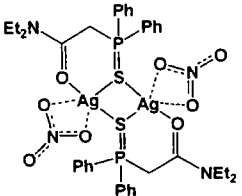
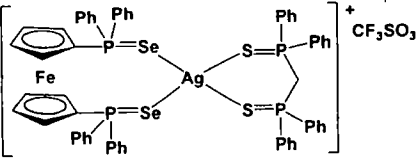
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.307(1)	1.999(1)	102.47(5)		104
Ag					
[Ag(dppeS)] ₂ (NO ₃) ₂	2.4574(9)	1.9920(10)	99.03(4)		105
[Ag(dppmS ₂)]NO ₃	2.583 – 2.635	1.960 – 1.977	96.06 – 101.16		106
	2.501 – 2.770	1.677 – 1.975	90.13 100.77 105.57		107
	2.572 2.722	2.010	104.32		108
	2.5919(12) 2.6012(11)	1.967 1.971	99.94 106.36	33.5	109

Table C 3 (continued)

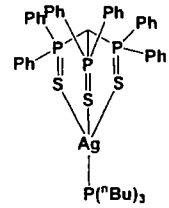
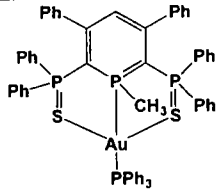
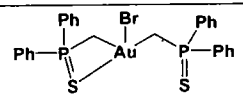
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.585(2) 2.639(3) 2.670(2)	1.990(3) – 1.999(3)	96.2(1) 97.3(1) 97.7(1)		110
$[\text{Ag}_2(\mu\text{-dppfS}_2)(\text{dppmS}_2)]_n[\text{ClO}_4^-]_{2n}$	2.530(2) – 2.801(2)	1.972(2) – 1.997(2)	103.95(9) 106.01(9) 107.74 Ag-S-Ag (83.43(6))		111
Au					
AuBr(SPPH ₃)	2.286	2.016	105.62		112
$[\text{Au}(\text{SPPH}_3)_2](\text{PO}_2\text{F}_2)$	2.277(2)	2.023(3)	103.27(12)		113
$[\text{Au}(\text{dppfS}_2)][\text{AuCl}_4]$	2.281(5) 2.299(5)	1.986(7) 2.023(7)	97.5(2) 103.6(3)	45.7	114
	2.288(11)	1.9838(15)	90.82(5)	41.16 42.55	99
	2.361(13)	1.972(13) 2.031(11)	81.67(5)		115

Table C 3 (continued)

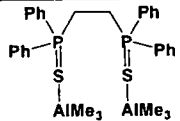
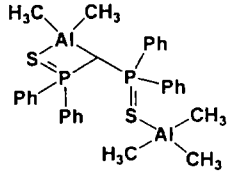
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
$\{\text{AgCl}(\text{C}_6\text{F}_5)_2(\mu\text{-dppfS}_2)\}$	2.386(2)	2.020(3)	108.08(10)	45.7	114
Hg					
$\text{HgI}_2(\text{dppmS})$	2.760(4)	1.968(6)	99.3(2)		116
$\text{HgCl}_2(\text{dppeS}_2)$	2.546(3)	1.990(4)	109.4(1)		116
	2.559(3)	1.998(3)	110.4(1)		
$\text{HgBr}_2(\text{dppeS}_2)$	2.552(2)	1.990(4)	104.79(11)		52
	2.678(2)	1.999(3)	108.96(11)		
Al					
$\text{AlCl}_3(\text{SPPH}_3)$	2.797(2)	2.028(2)	109.62(8)		117
	2.506(3)	1.989(2)	108.4(1)		118
	2.388(2)	2.004(2)	78.8(1)		118
	2.460(2)	2.009(2)	108.7(1)		

Table C 3 (continued)

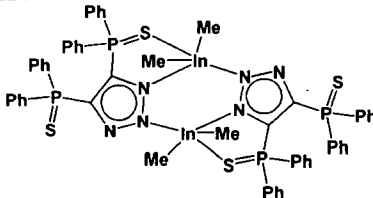
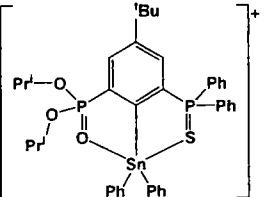
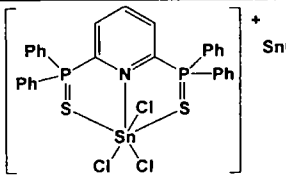
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
In					
<i>trans</i> -InCl ₃ (SPMe ₃) ₂	2.630(3) 2.663(3)	2.003(2) 2.014(3)	109.2(1) 117.7(1)		119
<i>trans</i> -InBr ₃ (SPMe ₃) ₂	2.643(3) 2.653(3)	1.998(2) 2.010(3)	110.6(1) 113.2(1)		119
[InI ₃ (dppeS ₂) ₂]	2.532	2.011	111.11		120
	2.780(1)	1.986(1) (P-S-In) 1.948(1)	96.7(4)	30.2 (P-S-In) 36.5	121
Sn					
	2.6295(9)	2.006(1)	96.38	54.8	122, 123
	2.514(1) 2.503(1)	1.989(2) 1.992(2)	98.72 99.20	47.0	124

Table C 3 (continued)

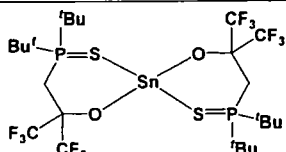
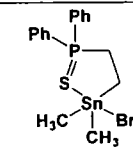
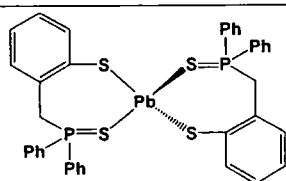
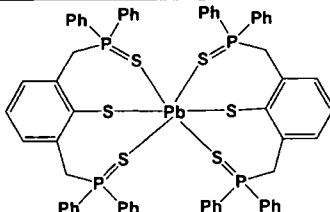
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.8381(7) 2.9137(7)	1.9798(9) 1.9922(9)	107.69 108.32	67.11	125
	2.872	1.976	91.89		137
Pb					
	2.885(12) 3.151(9)	1.973(13) 1.003(10) (disorderd)	117.44 – 118.05 (disorderd)	40.5	126
	2.953(8) 3.386(7)	1.909(11) 1.979(9)	113.8(3) 114.6(4)	36.6 40.2	126

Table C 3 (continued)

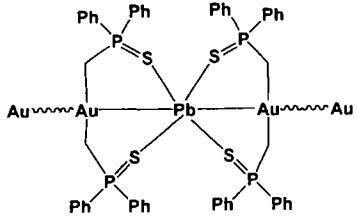
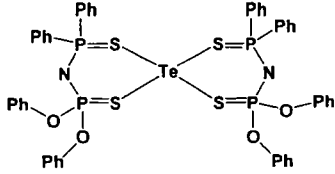
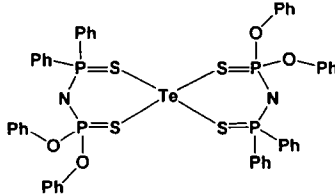
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.959(5) 2.976(6)	1.991 2.008	100.83 100.91		127
<u>Te</u>					
TeCl ₄ (dppeS ₂)	2.633(4) 2.891(3)	1.950(4) 1.984(4)	109.3(2) 111.7(2)		128
	2.5311(8) – 2.9372(12)	1.9719(10) – 2.0604(10)	94.19(4) – 98.52(4)	35.43 43.39	129
	2.6759(16) 2.6851(12)	2.0134(16) 2.0061(16)	97.85(6) 97.03(6)	27.18 51.14	129
{TeCl ₃ (4-OMeC ₆ H ₄)} ₂ (μ -dppfS ₂)	2.6910(12) 2.7560(6)	1.9994(16) 2.0062(17)	105.69(6) 111.69(6)	66.56	129

Table C 3 (continued)

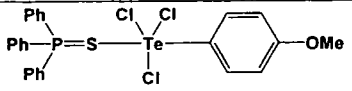
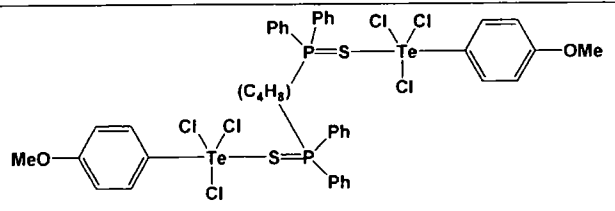
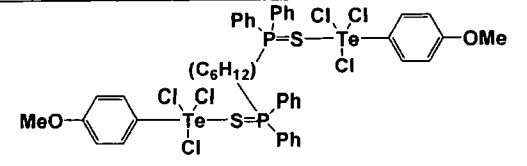
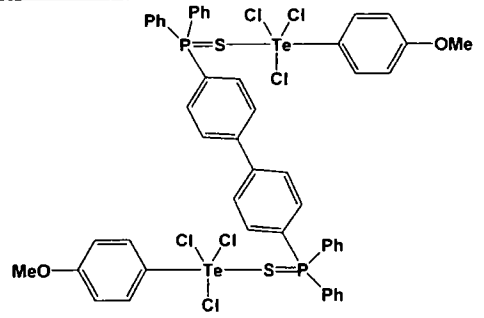
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.752(1)	2.008(1)	102.78(4)	43	130
	2.772(2)	2.012(2)	110.27(9)	51	130
	2.787	2.058	101.1	53	130
	2.785(2)	1.999(2)	103.16(7)	43	130



Table C 3 (continued)

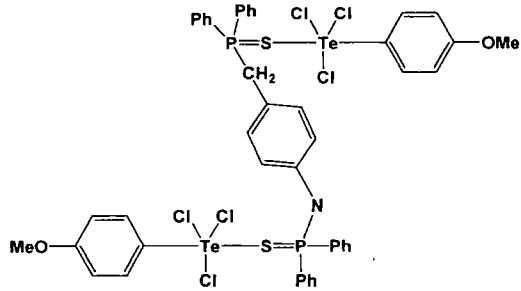
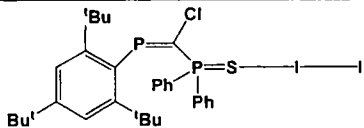
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
 <p style="text-align: center;">I</p>	2.753(1)	2.008(1)	105.29	55	130
$\text{Ph}_3\text{PS}\cdot\text{I}_2$	2.753(2)	1.998(2)	108.78(7)	41.70	131
$\text{Ph}_3\text{PS}\cdot\text{IBr}$	2.656(1)	2.007(1)	107.63(5)		132
$(\text{Me}_2\text{N})_3\text{PS}\cdot\text{I}_2$	2.705(3)	2.014(4)	103.63		132
	2.809(2)	1.990(3)	98.44(10)		12
$(p\text{-FC}_6\text{H}_4)_3\text{PS}\cdot\text{I}_2$	2.787(5)	1.984(5)	100.4(3)	47.5	133
	2.792(6)	1.997(6)	102.9(2)		
$\text{Fc}_2(\text{Ph})\text{PS}\cdot\text{I}_2$	2.7670(12)	2.0015(14)	109.71(5)		134

Table C 3 (continued)

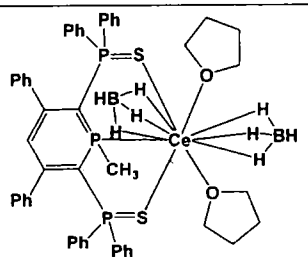
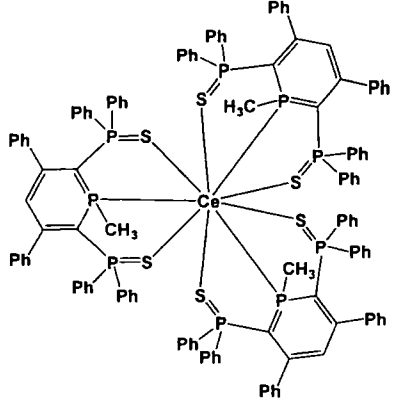
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
Ce					
 <p>The structure shows a central cerium atom coordinated to two thioether phosphine ligands (Ph₂P(S)Ph) and two thioether borane ligands (Ph₂B(S)H). The phosphorus atoms are coordinated to the cerium atom, and the boron atoms are also coordinated to the cerium atom. The ligands are arranged in a distorted octahedral geometry around the cerium center.</p>	2.947(2) 2.992(2)	2.007(3) 2.009(3)	99.11 110.53		135
 <p>The structure shows a central cerium atom coordinated to four thioether phosphine ligands (Ph₂P(S)Ph). The phosphorus atoms are coordinated to the cerium atom, and the sulfur atoms are also coordinated to the cerium atom. The ligands are arranged in a distorted octahedral geometry around the cerium center.</p>	2.917(3) 2.995(5)	1.983(4) 1.998(4)	115.43 120.52		135

Table C 3 (continued)

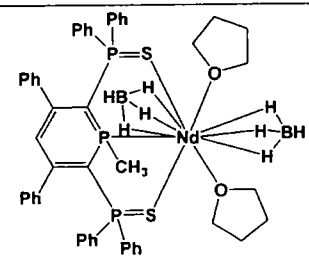
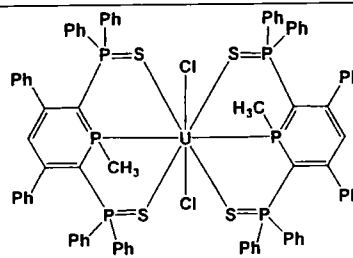
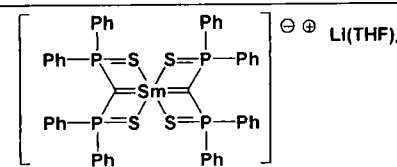
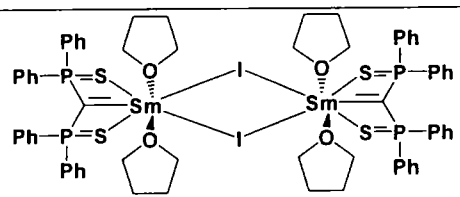
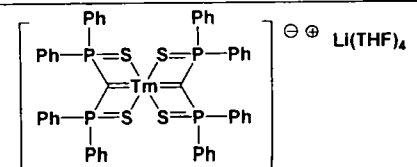
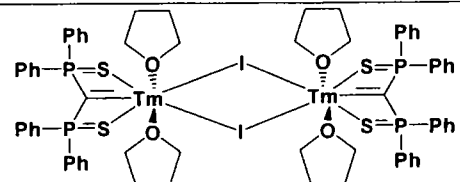
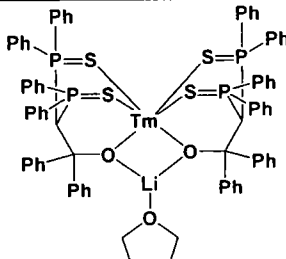
Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
<u>Nd</u>					
	2.9162(15) 2.9623(14)	2.007(2) 2.0086(19)	107.53 110.27		135
<u>U</u>					
	2.7799(10) 2.9892(12)	1.9995(15) 2.0184(16)	108.76 116.31		135
<u>Sm</u>					
	2.2816(2) – 2.851(2)	2.034 – 2.042	79.34 – 81.66		136

Table C 3 (continued)

Compounds	M-S (Å)	P-S (Å)	M-S-P (deg)	δ (ppm)	ref(s)
	2.891(1) – 2.922(11)	2.019 – 2.020	80.38 – 81.60		136
<u>Tm</u>					
	2.788(2) 2.747(2)	2.028 2.037	79.12 80.30		137
	2.777(1) 2.822(1)	2.024(2) 2.030(2)	80.16 80.62		137
	2.757 2.772	2.2022 2.033	95.91 99.57		137

* esd values are given in parentheses, where available. The values which do not show esd values were taken from the CSD.

References

1. Cantat, T.; Jacques, X.; Xavier, L. R.; Le Goff, F.; Mezailles, N.; Le Floch, P., *Angew. Chem. Int. Ed.* **2007**, *46*, 5947.
2. Miquel, Y.; Igau, A.; Donnadiou, B.; Majoral, J.-P.; Dupuis, L.; Pirio, N.; Meunier, P., *Chem. Commun.* **1997**, 279.
3. Cantat, T.; Ricard, L.; Mezailles, N.; Le Floch, P., *Organometallics* **2006**, *25*, 6030.
4. Stumpf, K.; Blachnik, R.; Roth, G.; Kastner, G., *Z. Kristallogr.* **2000**, *215*, 589.
5. Drew, M. G. B.; Hobson, R. J., *Inorg. Chim. Acta* **1983**, *72*, 233.
6. Baker, E. N.; Reay, B. R., *J. Chem. Soc., Dalton Trans.* **1973**, 2205.
7. Bajko, Z.; Daniels, J.; Gudat, D.; Hap, S.; Nieger, M., *Organometallics* **2002**, *21*, 5182.
8. Garner, C. D.; Howlander, N. C.; Mabbs, F. E.; Boorman, P. M.; King, T. J., *J. Chem. Soc., Dalton Trans.* **1978**, 1350.
9. Bevierre, M.-O.; Mercier, F.; Ricard, L.; Mathey, F., *Angew. Chem., Int. Ed.* **1990**, *29*, 655.
10. Casares, J. A.; Espinet, P.; Hernando, R.; Iturbe, G.; Villafane, F.; Ellis, D. D.; Orpen, A. G., *Inorg. Chem.* **1997**, *36*, 44.
11. Cook, J. B.; Nicholson, B. K.; Smith, D. W., *J. Organomet. Chem.* **2004**, *689*, 860.
12. Ito, S.; Liang, H.; Yoshifuji, M., *Chem. Commun.* **2003**, 398.
13. Cotton, F. A.; Llusar, R., *Acta Crystallogr.*, **1988**, *C44*, 952.
14. Antoniadis, A.; Hiller, W.; Kunze, U.; Schall, H.; Strahle, J., *Z. Naturforsch., B:* **1982**, *37*, 1289.
15. Doux, M.; Mezailles, N.; Ricard, L.; Le Floch, P.; Vaz, P. D.; Calhorda, M. J.; Mahabiersing, T.; Hartl, F., *Inorg. Chem.* **2005**, *44*, 9213.
16. Lindner, E.; Rau, A.; Hoehne, S., *Chem. Ber.* **1981**, *114*, 3281.
17. Depree, G. J.; Childerhouse, N. D.; Nicholson, B. K., *J. Organomet. Chem.* **1997**, *533*, 143.
18. Saak, W.; Haase, D.; Pohl, S., *Z. Naturforsch., B:* **1988**, *43*, 289.
19. Saak, W.; Pohl, S., *Z. Naturforsch., B:* **1988**, *43*, 813.
20. Chutia, P.; Kumari, N.; Sharma, M.; Woollins, J. D.; Slawin, A. M. Z.; Dutta, D. K., *Polyhedron* **2004**, *23*, 1657.
21. Dutta, D. K.; Chutia, P.; Woollins, J. D.; Slawin, A. M. Z., *Inorg. Chim. Acta* **2006**, *359*, 877.
22. Chutia, P.; Sharma, M.; Das, P.; Kumari, N.; J. D. Woollins; Slawin, A. M. Z.; Dutta, D. K., *Polyhedron* **2003**, *22*, 2725.
23. Faller, J. W.; Fontaine, P. P., *J. Organomet. Chem.* **2007**, *692*, 976.
24. Dochnahl, M.; Doux, M.; Faillard, E.; Ricard, L.; Le Floch, P., *Eur. J. Inorg. Chem.* **2005**, 125.
25. Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Floch, P. L., *Chem. Commun.* **2005**, 5178.
26. Valderrama, M.; Contreras, R.; Bascunan, M.; Alegria, S.; Boys, D., *Polyhedron* **1995**, *14*, 2239.
27. Valderrama, M.; Contreras, R.; Arancibia, V.; Munoz, P.; Boys, D.; Lamata, M. P.; Viguri, F.; Carmona, D.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A., *J. Organomet. Chem.* **1997**, *545-546*, 507.

28. Lindner, E.; Schlenker, T.; Fawzi, R.; Steimann, M., *Chem. Ber.* **1993**, *126*, 2433.
29. Baker, M. J.; Giles, M. F.; Guy, A.; Taylor, M. J.; Watt, R. J., *J. Chem. Soc., Chem. Commun.* **1995**, 197.
30. Abbassioun, M. S.; Chaloner, P. A.; Claver, C.; Hitchcock, P. B.; Masdeu, A. M.; Ruiz, A.; Saballs, T., *J. Organomet. Chem.* **1991**, *403*, 229.
31. Aucott, S. M.; Slawin, A. M. Z.; Woollins, J. D., *Polyhedron* **2003**, *22*, 361.
32. Broussier, R.; Laly, M.; Perron, P.; Gautheron, B.; Nifant'ev, I. E.; Howard, J. A. K.; Kuz'mina, L. G.; Kalck, P., *J. Organomet. Chem.* **1999**, *587*, 104.
33. Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A., *J. Am. Chem. Soc.* **1999**, *121*, 11233.
34. Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W., *J. Organomet. Chem.* **1993**, *452*, 205.
35. Grim, S. O.; Kettler, P. B.; Thoden, J. B., *Organometallics* **1991**, *10*, 2399.
36. Doux, M.; Mezailles, N.; Ricard, L.; Le Floch, P., *Organometallics* **2003**, *22*, 4624.
37. Doux, M.; Mezailles, N.; Ricard, L.; Le Floch, P.; Adkine, P.; Berclaz, T.; Geoffroy, M., *Inorg. Chem.* **2005**, *44*, 1147.
38. Wechsler, D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M., *Chem. Commun.* **2004**, 2446
39. Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A., *J. Am. Chem. Soc.* **2002**, *124*, 13597.
40. Valderrama, M.; Contreras, R., *J. Organomet. Chem.* **1996**, *513*, 7.
41. Wechsler, D.; Myers, A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M., *Inorg. Chem.* **2006**, *45*, 4562.
42. Doux, M.; Ricard, L.; Le Floch, P.; Jean, Y., *Organometallics* **2006**, *25*, 1101.
43. Doux, M.; Ricard, L.; Le Floch, P.; Jean, Y., *Organometallics* **2005**, *24*, 1608.
44. Mazany, A. M.; Jr. Fackler, J. P., *Organometallics* **1982**, *1*, 752.
45. Siasios, G.; Tiekink, E. R. T., *J. Chem. Soc., Dalton Trans.* **1996**, 2269.
46. Lindner, E.; Bouachir, F.; Hoehne, S., *Chem. Ber.* **1983**, *116*, 46.
47. Doux, M.; Mézailles, N.; Ricard, L.; Le Floch, P., *Eur. J. Inorg. Chem.* **2003**, *2003*, 3878.
48. Gan, X.; Duesler, E. N.; Parveen, S.; Paine, R. T., *J. Chem. Soc., Dalton Trans.* **2003**, 4704.
49. Ara, I.; Fornis, J.; Navarro, R.; Sicilia, V.; Urriolabeitia, E. P., *Polyhedron* **1997**, *16*, 1963.
50. Richadson, M. F., *Acta Crystallogr.* **1985**, *C41*, 27.
51. Wong, T. Y. H.; Rettig, S. J.; James, B. R., *Inorg. Chem.* **1999**, *38*, 2143.
52. Lobana, T. S.; Verma, R.; Singh, A.; Shikha, M.; Castineiras, A., *Polyhedron* **2002**, *21*, 205.
53. Turner, T. P. W. *Fourth year report: The coordination chemistry of phosphine sulfides and thioureas and their applications*; Durham University: Durham, M. Sc. (Chemistry) 2008.
54. Satek, L. C.; Ammon, H. L.; Stewart, J. M., *Acta Crystallogr.* **1975**, *B31*, 2691.
55. Piechaczyk, O.; Doux, M.; Ricard, L.; Le Floch, P., *Organometallics* **2005**, *24*, 1204.
56. Irisli, S.; Yanar, S., *Polyhedron* **2006**, *25*, 1333.
57. Aizawa, S.-I.; Kondo, M.; Miyatake, R.; Tamai, M., *Inorg. Chim. Acta* **2007**, *360*, 2809.

58. Fornies, J.; Navarro, R.; Sicilia, V.; Tomas, M., *Inorg. Chim. Acta* **1990**, *168*, 201.
59. Thurner, C. L.; Barz, M.; Spiegler, M.; Thiel, W. R., *J. Organomet. Chem.* **1997**, *541*, 39.
60. Faller, J. W.; Wilt, J. C., *Organometallics* **2005**, *24*, 5076.
61. Faller, J. W.; Wilt, J. C., *Org. Lett.* **2005**, *7*, 633.
62. Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S., *Inorg. Chim. Acta* **2002**, *330*, 38.
63. Kanbara, T.; Yamamoto, T., *J. Organomet. Chem.* **2003**, *688*, 15.
64. Doux, M.; Bouet, C.; Mezailles, N.; Ricard, L.; Le Floch, P., *Organometallics* **2002**, *21*, 2785.
65. Doux, M.; Mezailles, N.; Melaimi, M.; Ricard, L.; Le Floch, P., *Chem. Commun.* **2002**, 1566.
66. Qin, Y.; Selvaratnam, S.; Vittal, J. J.; Leung, P.-H., *Organometallics* **2002**, *21*, 5301.
67. Pullarkat, S. A.; Tan, K.-W.; Ma, M.; Tan, G.-K.; Koh, L. L.; Vittal, J. J.; Leung, P.-H., *J. Organomet. Chem.* **2006**, *691*, 3083.
68. Liang, H.; Ito, S.; Yoshifuji, M., *Org. Lett.* **2004**, *6*, 425.
69. Casares, J. A.; Coco, S.; Espinet, P.; Lin, Y.-S., *Organometallics* **1995**, *14*, 3058.
70. Cantat, T.; Mezailles, N.; Ricard, L.; Jean, Y.; Le Floch, P., *Angew. Chem. Int. Ed.* **2004**, *43*, 6382.
71. Broussier, R.; Bentabet, E.; Laly, M.; Richard, P.; Kuz'mina, L. G.; Serp, P.; Wheatley, N.; Kalck, P.; Gautheron, B., *J. Organomet. Chem.* **2000**, *613*, 77.
72. Stampfl, T.; Haid, R.; Langes, C.; Oberhauser, W.; Bachmann, C.; Kopacka, H.; Ongania, K.-H.; Brüggeller, P., *Inorg. Chem. Commun.* **2000**, *3*, 387.
73. Skvortsov, A. N.; Reznikov, A. N.; de Vekki, D. A.; Stash, A. I.; Belsky, V. K.; Spevak, V. N.; Skvortsov, N. K., *Inorg. Chim. Acta* **2006**, *359*, 1031.
74. Mastroilli, P.; Nobile, C. F.; Suranna, G. P.; Fanizzi, F. P.; Ciccarella, G.; Englert, U.; Li, Q., *Eur. J. Inorg. Chem.* **2004**, *6*, 1234.
75. Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W., *Can. J. Chem.* **1988**, *66*, 1272.
76. Alkan, L.; Irisli, S., *Acta Crystallogr.* **2005**, *E61*, m2706.
77. Browning, J.; Bushnell, G. W.; Dixon, K. W.; Pidcock, A., *Inorg. Chem.* **1983**, *22*, 2226.
78. Avis, M. W.; Goosen, M.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L., *Inorg. Chim. Acta* **1997**, *264*, 43.
79. Contreras, R.; Valderrama, M.; Beroggi, C.; Boys, D., *Polyhedron* **2001**, *20*, 3127.
80. Romero, P.; Valderrama, M.; Contreras, R.; Boys, D., *J. Organomet. Chem.* **2003**, *673*, 102.
81. Aucott, S. M.; Slawin, A. M. Z.; Woollins, J. D., *Eur. J. Inorg. Chem.* **2002**, *2002*, 2408.
82. Karacar, A.; Freytag, M.; Thonnessen, H.; Omelanczuk, J.; Jones, P. G.; Bartsch, R.; Schmutzler, R., *Z. Anorg. Allg. Chem.* **2000**, *626*, 2361.
83. Carr, S. W.; Colton, R.; Hoskins, B. F.; P. M. Piko; Dakternieks, D.; Tiekink, E. R. T., *Z. Kristallogr.* **1996**, *211*, 759.
84. Delgado, E.; Donnadiou, B.; Hernandez, E.; Lalinde, E.; Mansilla, N.; Moreno, M. T., *J. Organomet. Chem.* **1999**, *592*, 283.

85. Delgado, E.; Hernandez, E.; Lalinde, E.; Lang, H.; Mansilla, N.; Moreno, M. T.; Rheinwald, G.; Zamora, F., *Inorg. Chim. Acta* **2001**, *315*, 1.
86. Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Jr. Fackler, J. P., *Organometallics* **1987**, *6*, 1992.
87. King, C.; Heinrich, D. D.; Garzon, G.; Wang, J.-C.; Fackler, J. P. J., *J. Am. Chem. Soc.* **1989**, *111*, 2300.
88. Browning, J.; Dixon, K. R.; Hilts, R. W., *Organometallics* **1989**, *8*, 552.
89. Eller, P. G.; Corfield, P. W. R., *J. Chem. Soc., Dalton Trans.* **1971**, 105.
90. Reigle, R. K.; Casadonte, D. J. J.; Bott, S. G., *J. Chem. Cryst.* **1994**, *24*, 769.
91. Sivasankar, C.; Bera, J. K.; Nethaji, M.; Samuelson, A. G., *J. Organomet. Chem.* **2004**, *689*, 2726.
92. Lobana, T. S.; Mahajan, R.; Castineiras, A., *Transition Met. Chem.* **2001**, *26*, 440.
93. Zhou, X.-P.; Li, D.; Wu, T.; Zhang, X., *J. Chem. Soc., Dalton Trans.* **2006**, 2435.
94. Tiethof, J. A.; Stalick, J. K.; Meek, D. W., *Inorg. Chem.* **1973**, *12*, 1170.
95. Ainscough, E. W.; Bergen, H. A.; Brodie, A. M.; Brown, K. A., *J. Chem. Soc., Dalton Trans.* **1976**, 1649.
96. Lobana, T. S.; Singh, G.; Nishioka, T., *J. Coord. Chem.* **2004**, *57*, 955.
97. Jones, P. G., *Private Communication* **2004**, to the CSD, XADYAD.
98. Brown, K. L., *Acta Crystallogr.* **1979**, *B35*, 462.
99. Doux, M.; Ricard, L.; Le Floch, P.; Mezailles, N., *J. Chem. Soc., Dalton Trans.* **2004**, 2593.
100. Pilloni, G.; Longato, B.; Bandoli, G.; Corain, B., *J. Chem. Soc., Dalton Trans.* **1997**, 819.
101. Pilloni, G.; Longato, B.; Bandoli, G., *Inorg. Chim. Acta* **1998**, *277*, 163.
102. Ainscough, E. W.; Brodie, A. M.; Brown, K. L., *J. Chem. Soc., Dalton Trans.* **1980**, 1042.
103. Genge, A. R. J.; Gibson, A. M.; Guymmer, N. K.; Reid, G., *J. Chem. Soc., Dalton Trans.* **1996**, 4099.
104. Horn, E.; Kurosawa, K.; Tiekink, E. R. T., *Acta Crystallogr.* **2000**, *C56*, 1319.
105. Matrosov, E. I.; Starikova, Z. A.; Yanovsky, A. I.; Lobanov, D. I.; Aladzheva, I. M.; Bykhovskaya, O. V.; Struchkov, Y. T.; Mastryukova, T. A.; Kabachnik, M. I., *J. Organomet. Chem.* **1997**, *535*, 121.
106. Yatsimirskii, K. B.; Talanova, G. G.; E. A. Nazarova; Kabachnik, M. I.; Mastryukova, T. A.; Aladzheva, I. M.; I. V. Leont'eva; Antipin, M. Y.; Struchkov, Y. T., *Koord. Khim. (Russ.)* **1993**, *19*, 469.
107. Pasechnik, M. P.; Starikova, Z. A.; Yanovsky, A. I.; Aladzheva, I. M.; Bykhovskaya, O. V.; Matrosov, E. I.; Mastryukova, T. A.; Kabachnik, M. I., *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.)* **1997**, 846.
108. Pasechnik, M. P.; Aladzheva, I. M.; Matrosov, E. I.; Pisarevskii, A. P.; Struchkov, Y. T.; Mastryukova, T. A.; Kabachnik, M. I., *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.)* **1994**, 708.
109. Canales, S.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A., *J. Organomet. Chem.* **2000**, *613*, 50.
110. Grim, S. O.; Sangokoya, S. A.; Rheingold, A. L.; McFarlane, W.; Colquhoun, I. J.; Gilardi, R. D., *Inorg. Chem.* **1991**, *30*, 2519.
111. Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C., *J. Chem. Soc., Dalton Trans.* **1998**, 1277.

112. Hussain, M. S.; Isab, A. A.; Saeed, A.; Al-Arfaj, A. R., *Z. Kristallogr.* **2001**, *216*, 629.
113. LeBlanc, D. J.; Britten, J. F.; Lock, C. J. L., *Acta Crystallogr.* **1997**, *C53*, 1204.
114. Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C., *J. Organomet. Chem.* **2000**, *596*, 10.
115. Murray, H. H.; Garzon, G.; Raptis, R. G.; Mazany, A. M.; Porter, L. C.; Jr. Fackler, J. P., *Inorg. Chem.* **1988**, *27*, 836
116. Lobana, T. S.; Sandhu, M. K., *J. Chem. Soc., Dalton Trans.* **1990**, 691.
117. Burford, N.; Royan, B. W.; Spence, R. E. H.; Rogers, R. D., *J. Chem. Soc., Dalton Trans.* **1990**, 2111.
118. Self, M. F.; Lee, B.; Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H., *Polyhedron* **1990**, *9*, 313.
119. Robinson, W. T.; Wilkins, C. J.; Zeying, Z., *J. Chem. Soc., Dalton Trans.* **1988**, 2187.
120. Sigl, M.; Schier, A.; Schmidbaur, H., *Z. Naturforsch., B:* **1999**, *54*, 21.
121. Moya-Cabrera, M.; Jancik, V.; Castro, R. A.; Herbst-Irmer, R.; Roesky, H. W., *Inorg. Chem.* **2006**, *45*, 5167.
122. Fischer, J.; Schurmann, M.; Mehring, M.; Zachwieja, U.; Jurkschat, K., *Organometallics* **2006**, *25*, 2886.
123. Preut, H.; Godry, B.; Mitchell, T. N., *Acta Crystallogr.* **1992**, *C48*, 1491.
124. Sevcik, R.; Necas, M.; Novosad, J., *Polyhedron* **2003**, 1585.
125. Ionkin, A. S.; Marshall, W. J.; Fish, B. M., *Organometallics* **2006**, *25*, 4170.
126. Pérez-Lourido, P.; Romero, J.; García-Vázquez, J. A.; Sousa, A.; Zheng, Y.; Dilworth, J. R.; Zubietta, J., *J. Chem. Soc., Dalton Trans.* **2000**, 769.
127. Wang, S.; Garzon, G.; King, C.; Wang, J. C.; Jr. Fackler, J. P., *Inorg. Chem.* **1989**, *28*, 4623.
128. Carmalt, C. J.; Norman, N. C.; Farrugia, L. J., *Polyhedron* **1995**, *14*, 1405.
129. Necas, M.; Novosad, J.; Husebye, S., *J. Organomet. Chem.* **2001**, *623*, 124.
130. Matulova, V.; Man, S.; Necas, M., *Polyhedron* **2007**, *26*, 2569.
131. Apperley, D. C.; Bricklebank, N.; Burns, S. L.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A., *J. Chem. Soc., Dalton Trans.* **1998**, 1289.
132. Cross, W. I.; Godfrey, S. M.; Jackson, S. L.; McAuliffe, C. A.; Pritchard, R. G., *J. Chem. Soc., Dalton Trans.* **1999**, 2225.
133. Barnes, N. A.; Godfrey, S. M.; Halton, R. T. A.; Khan, R. Z.; Jackson, S. L.; Pritchard, R. G., *Polyhedron* **2007**, *26*, 4294.
134. Bricklebank, N.; Coles, S. J.; Forder, S. D.; Hursthouse, M. B.; Poulton, A.; Skabara, P. J., *J. Organomet. Chem.* **2005**, *690*, 328.
135. Arliguie, T.; Doux, M.; Mezailles, N.; Thuery, P.; Le Floch, P.; Ephritikhine, M., *Inorg. Chem.* **2006**, *45*, 9907.
136. Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P., *Chem. Commun.* **2005**, 5178.
137. Cantat, T.; Jaroschik, F.; Ricard, L.; Le Floch, P.; Nief, F.; Mezailles, N., *Organometallics* **2006**, *25*, 1329.