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

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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

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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

To my parents for their continual love and support

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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-X-C_6H_4-C≡C-C_6H_4-p-OC_nH_{2n+1} [X = 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 enatioselectivities 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 $[Pd(CH_3CN)_4](BF_4)_2$ 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, $PdCl_2(PPh_3)_2$.

Volume II

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Appendix A

Monodentate Thioureas and Their Palladium Complexes

Appendix A

Monodentate thiourea

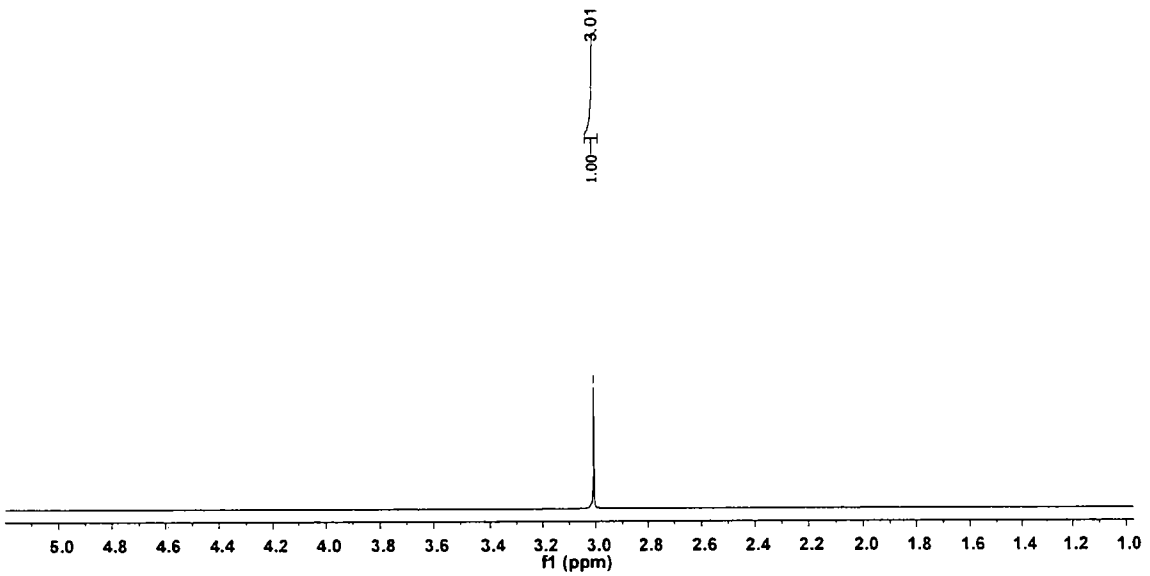


Figure A 1. The ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of tmtu.

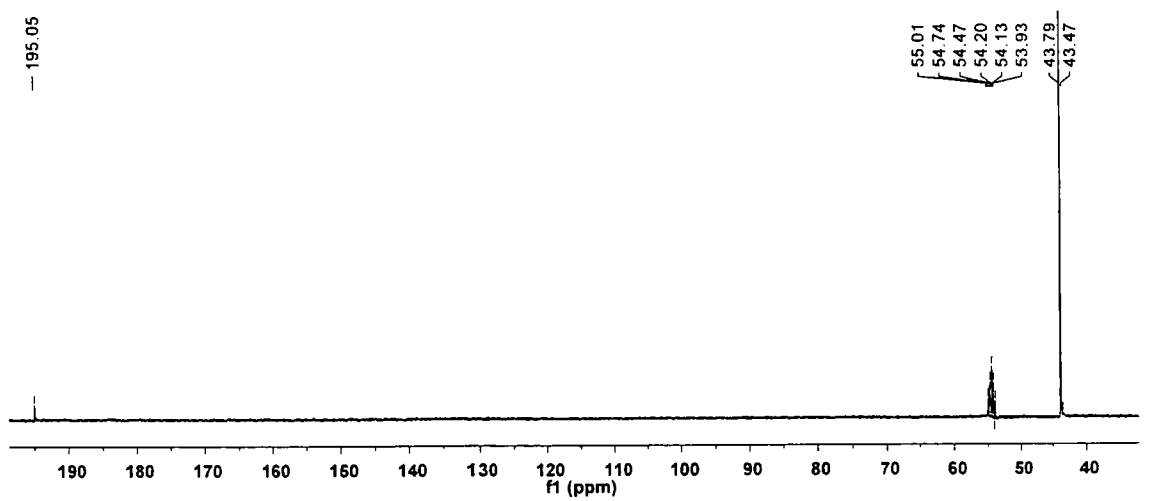


Figure A 2. The $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) spectrum of tmtu.

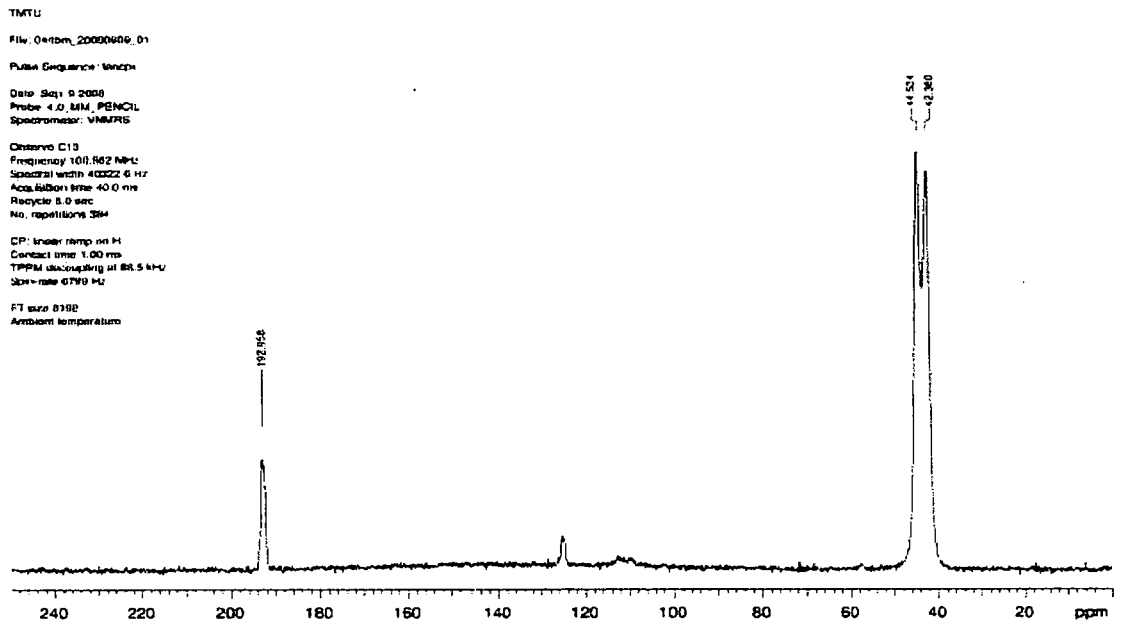


Figure A 3. Solid state $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of tmtu.

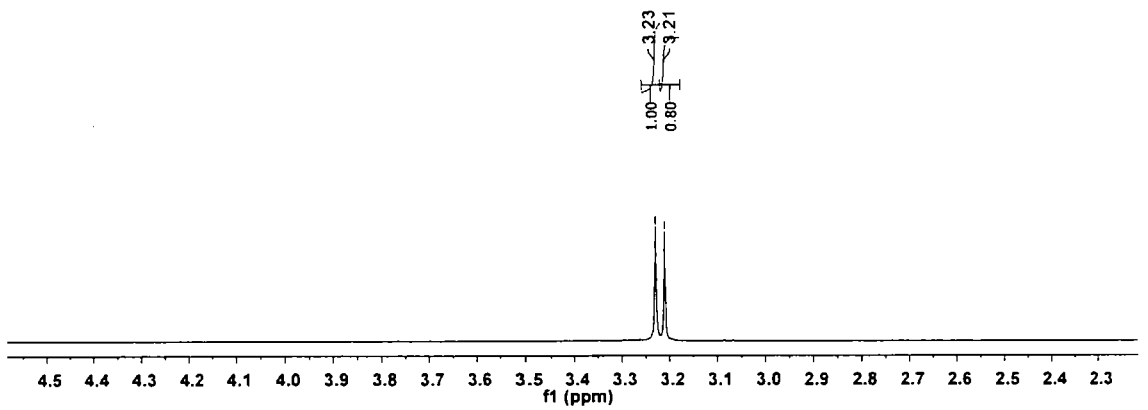


Figure A 4. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **Pd(tmtu)**.

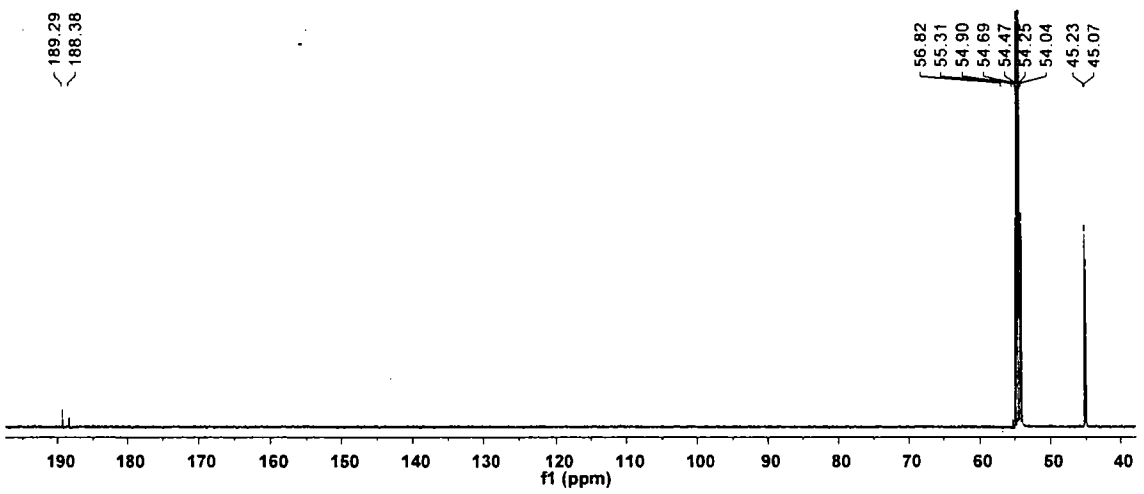


Figure A 5. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **Pd(tmtu)**.

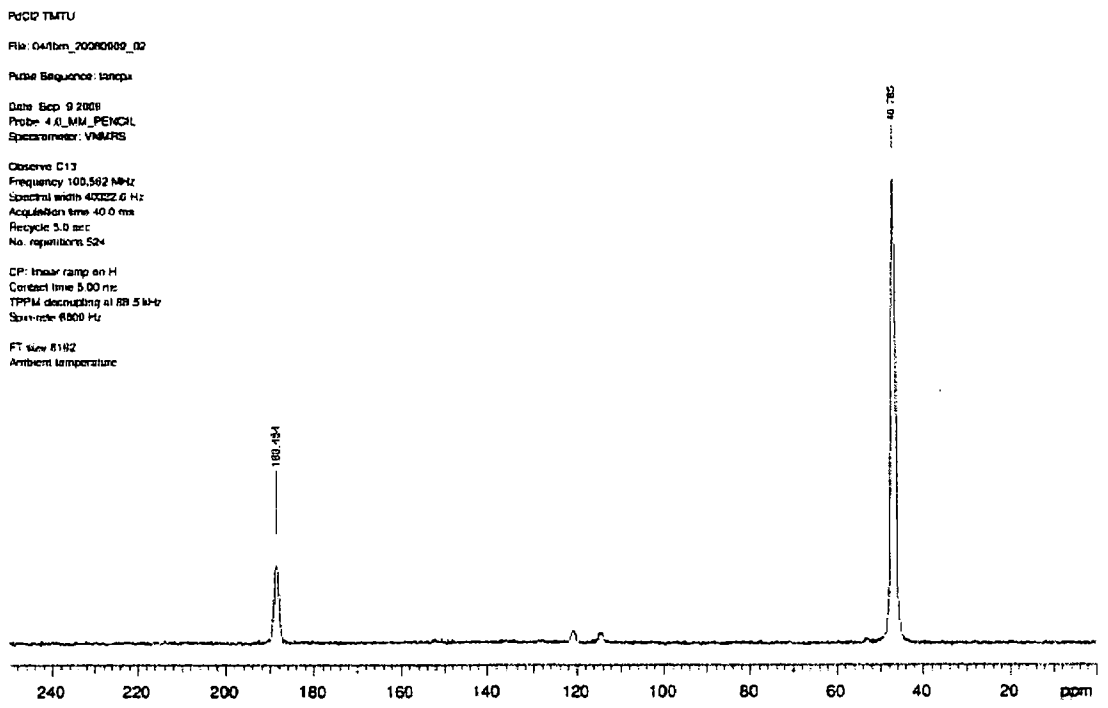


Figure A 6. The solid state $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **Pd(tmtu)**.

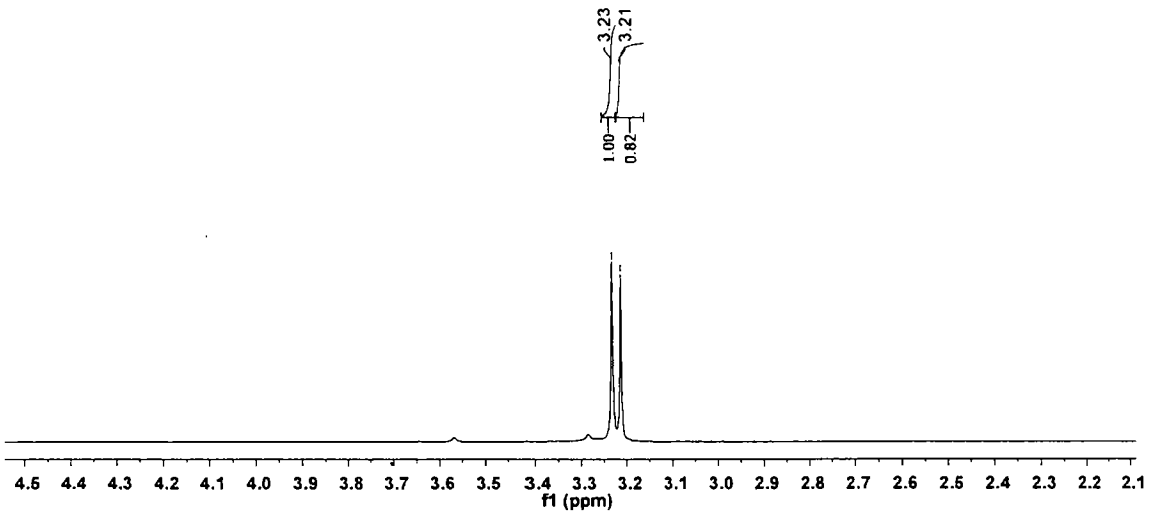


Figure A 7. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **Pd_2(tmtu)**.

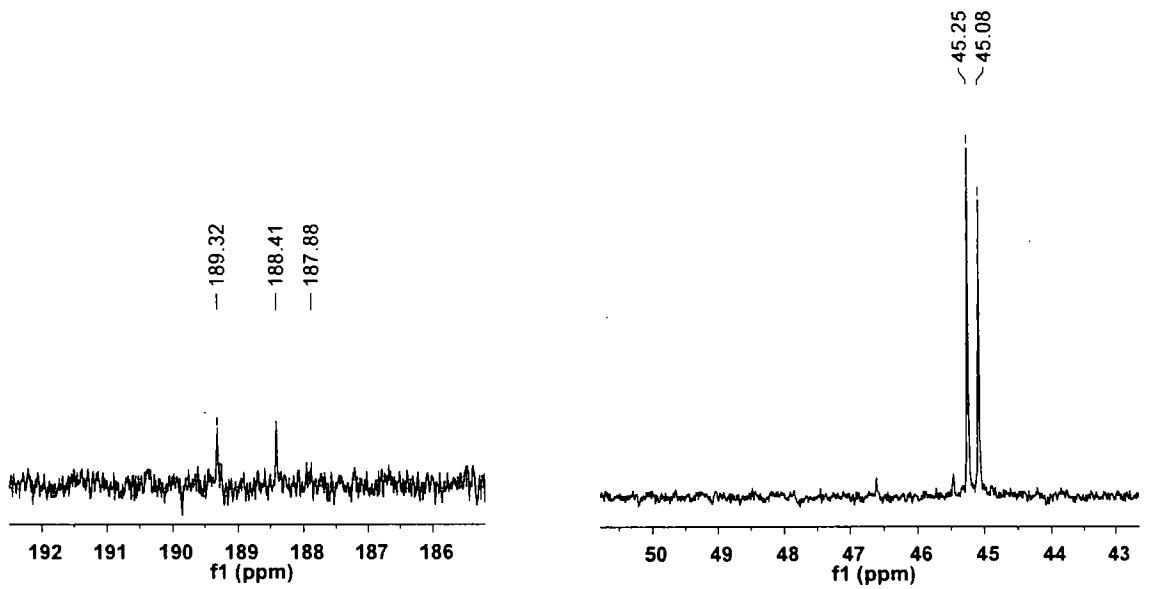


Figure A 8. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **Pd_2(tmtu)**.

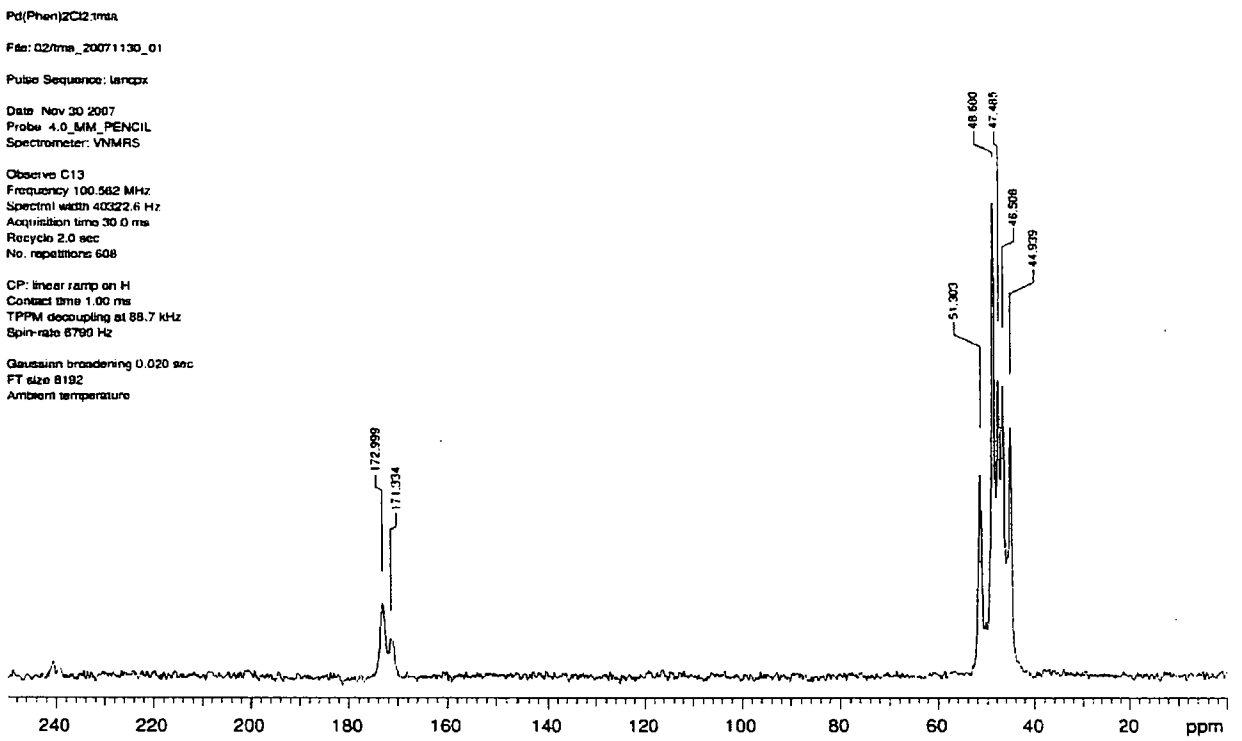


Figure A 9. The solid state $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **Pd_2(tmtu)**.

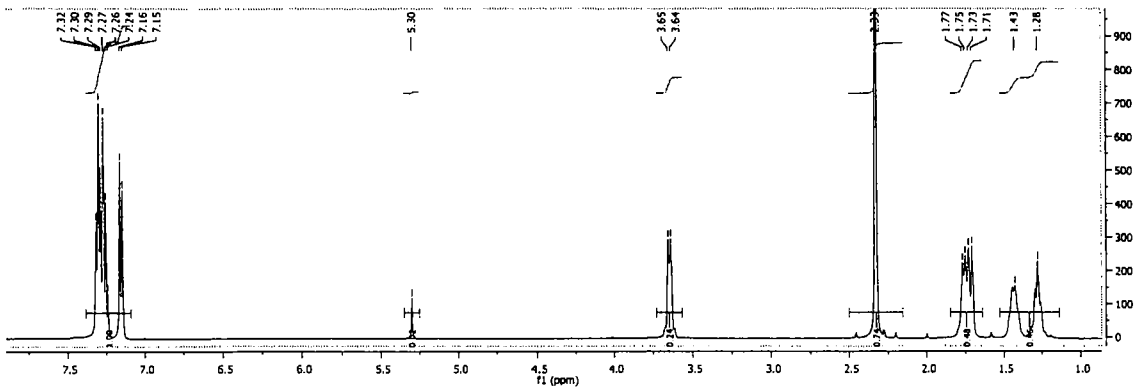


Figure A 10. The ^{1}H NMR (500 MHz, CD_2Cl_2, -60 °C) spectrum of **L(*rac*)**.

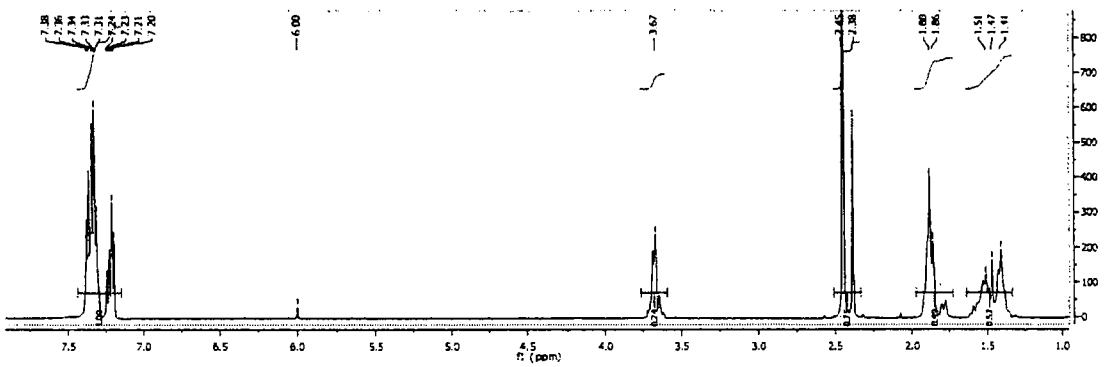


Figure A 11. The ^{1}H NMR (500 MHz, TCE-d_2, 100 °C) spectrum of **L(*rac*)**.

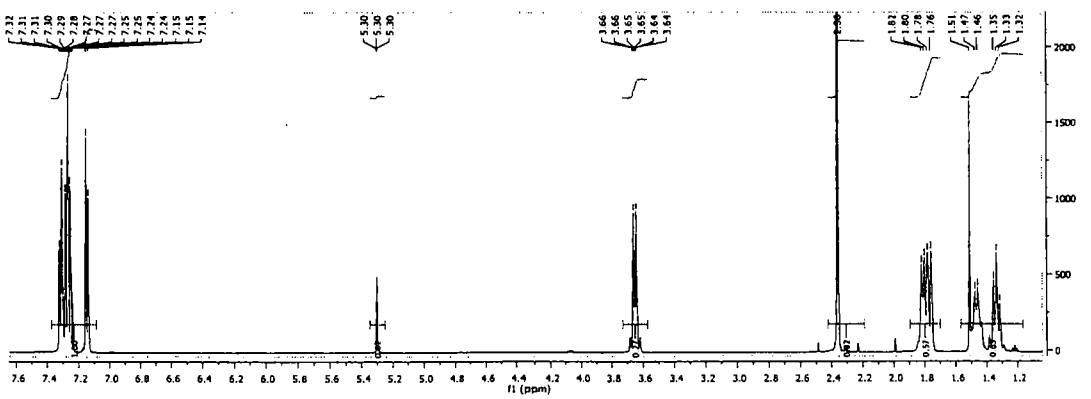


Figure A 12. The ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C) spectrum of **L(*rac*)**.

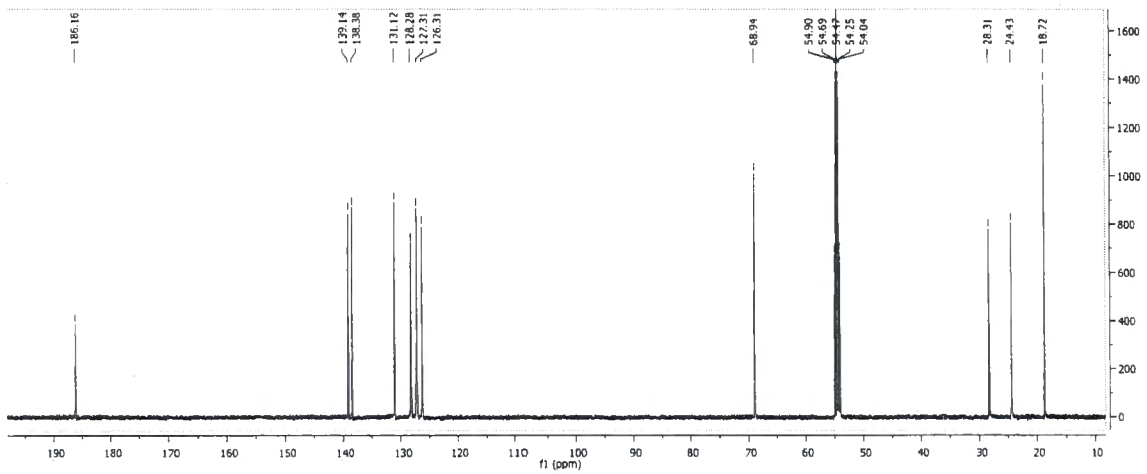


Figure A 13. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, -60 °C) spectrum of **L(*rac*)**.

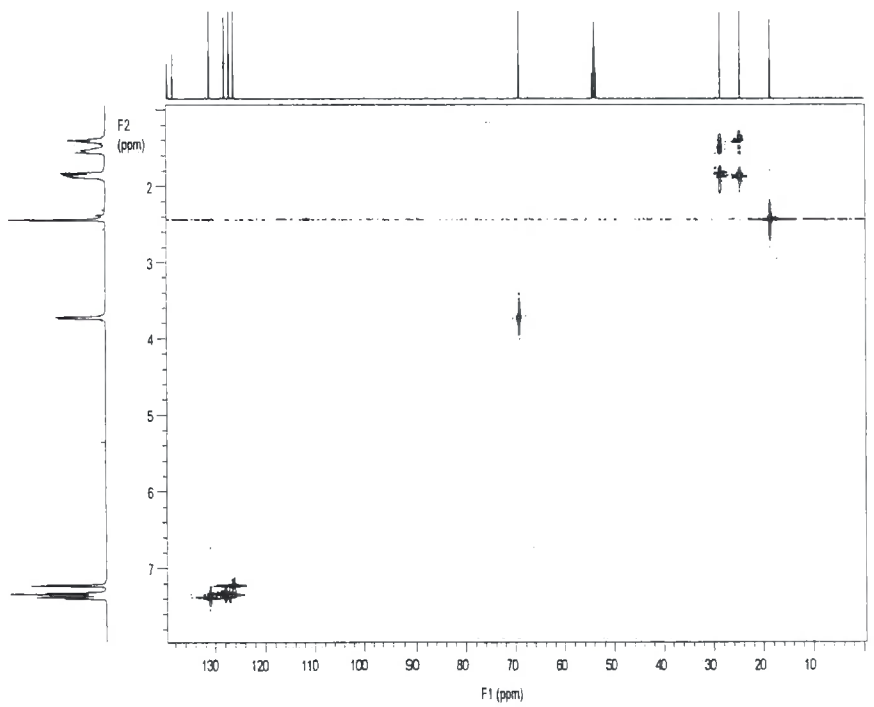


Figure A 14. The HSQC (20 °C) spectrum of **L(*rac*)**.

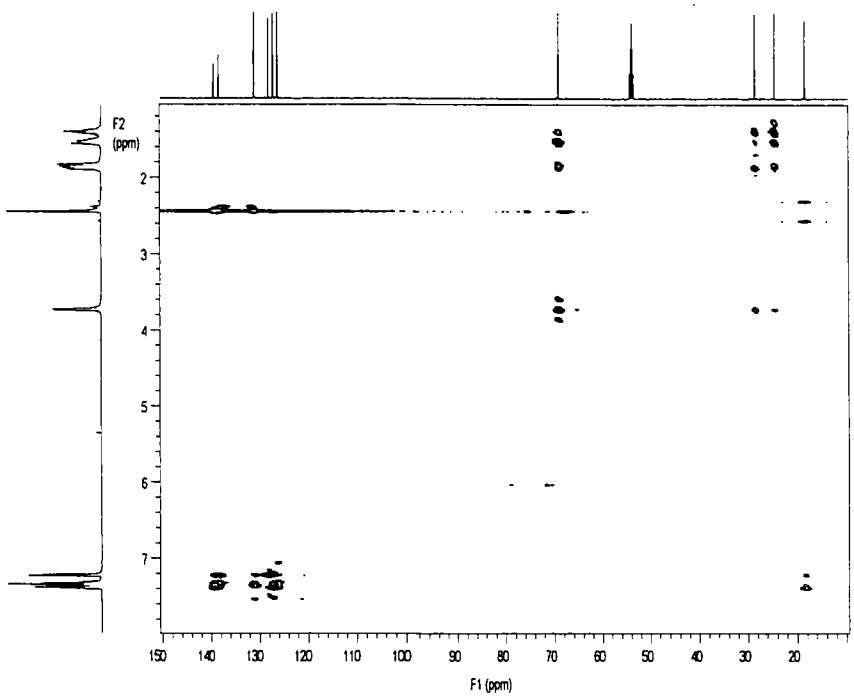


Figure A 15. The HMBC (20 °C) spectrum of **L(*rac*)**.

C_2 chiral thiourea palladium complexes

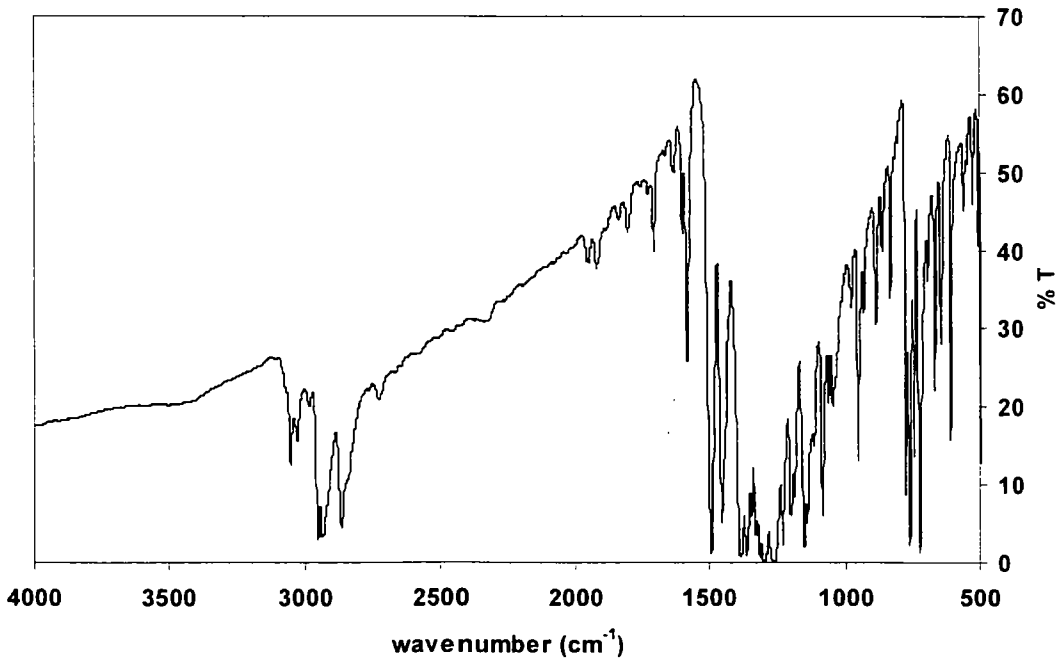


Figure A 16. IR spectrum of **L(*rac*)**.

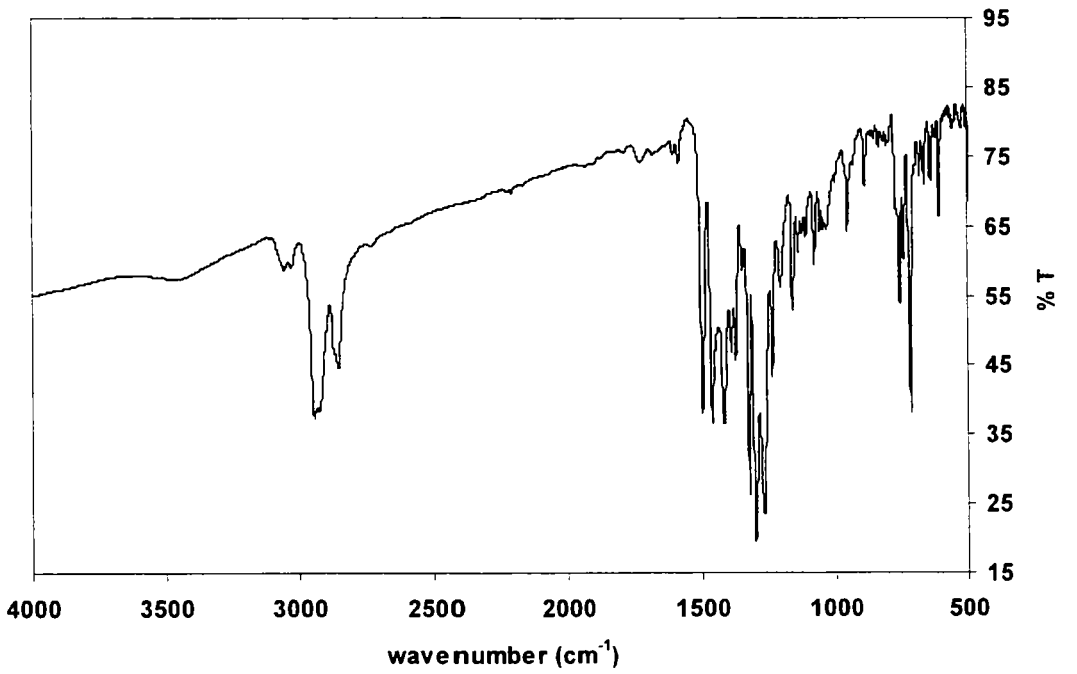


Figure A 17. IR spectrum of ***rac*-Pd / *meso*-Pd**.

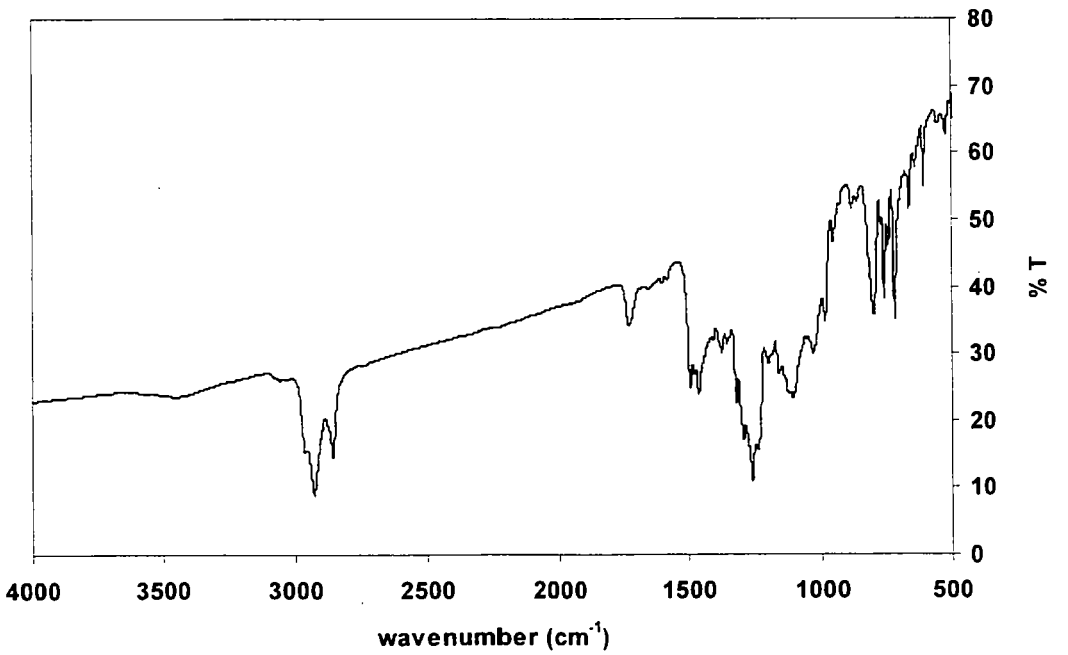


Figure A 18. IR spectrum of ***rac*-Pd_2 / *meso*-Pd_2**.

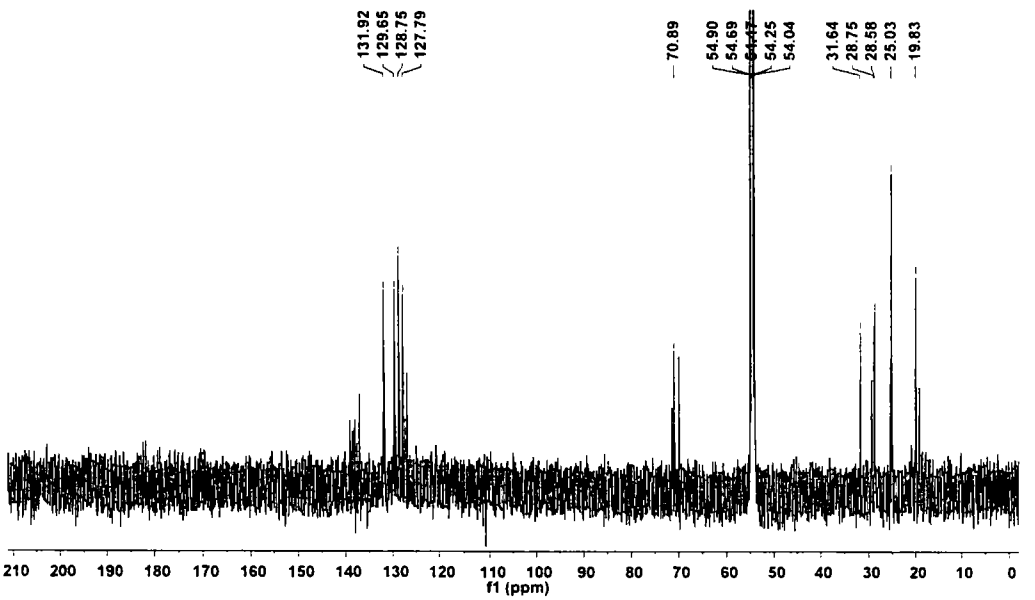


Figure A 19. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of ***rac*-Pd / *meso*-Pd** at room temperature.

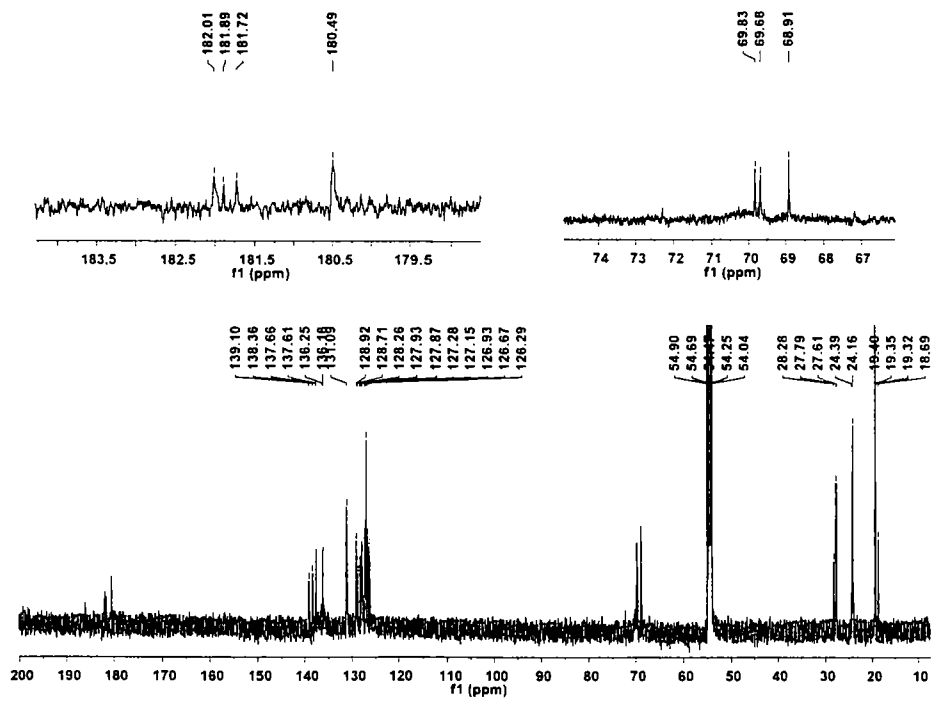


Figure A 20. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectra of ***rac*-Pd / *meso*-Pd** at -60 °C, the expanded C=S (top left) and C3 regions (top right).

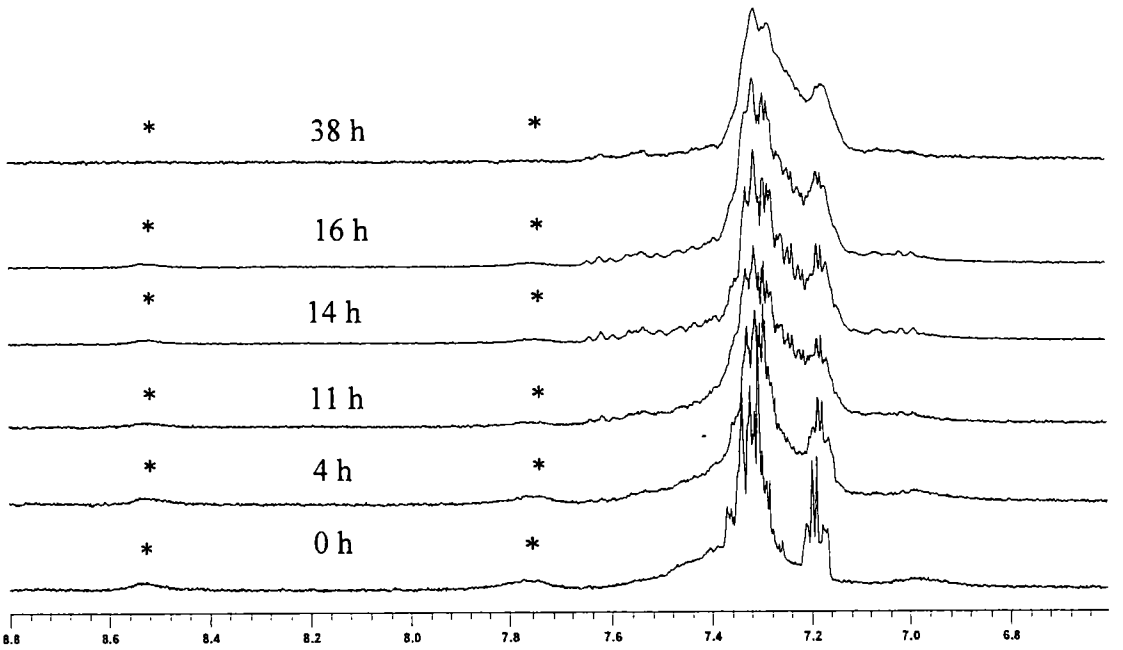


Figure A 21. The ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) monitoring of the reaction of ***rac*-Pd_2 / *meso*-Pd_2** converted to ***trans-rac*-Pd / *trans-meso*-Pd** with **L(*rac*)** at various times, * = ***rac*-Pd_2 / *meso*-Pd_2**.

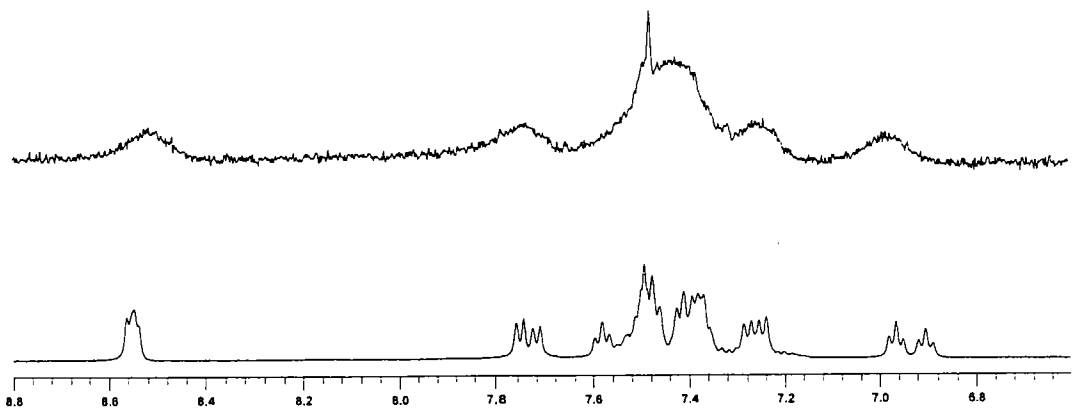


Figure A 22. The ^{1}H NMR (500 MHz) spectra of ***rac*-Pd_2 / *meso*-Pd_2** in CD_2Cl_2 (top) and TCE-d_2 (bottom) at room temperature.

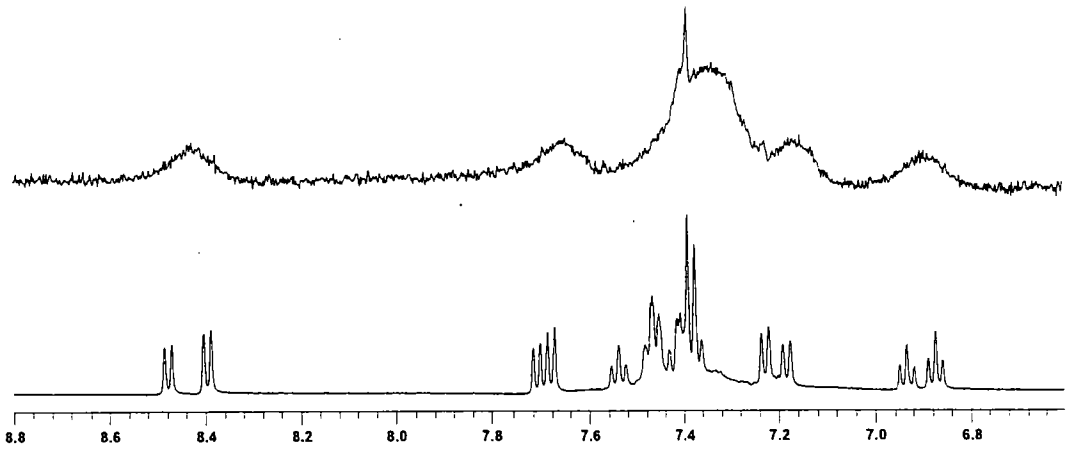


Figure A 23. The ^{1}H NMR (500 MHz) spectra of ***rac*-Pd_2 / *meso*-Pd_2** in CD_2Cl_2 at room temperature (top) and -60 °C (bottom).

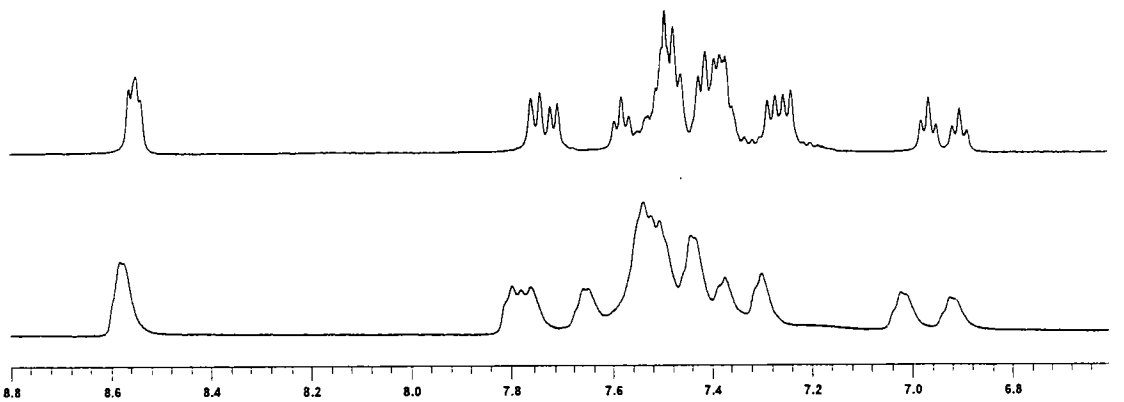


Figure A 24. ^{1}H NMR (500 MHz) spectra of ***rac*-Pd_2 / *meso*-Pd_2** in TCE-d_2 at room temperature (top) and –30 °C (bottom).

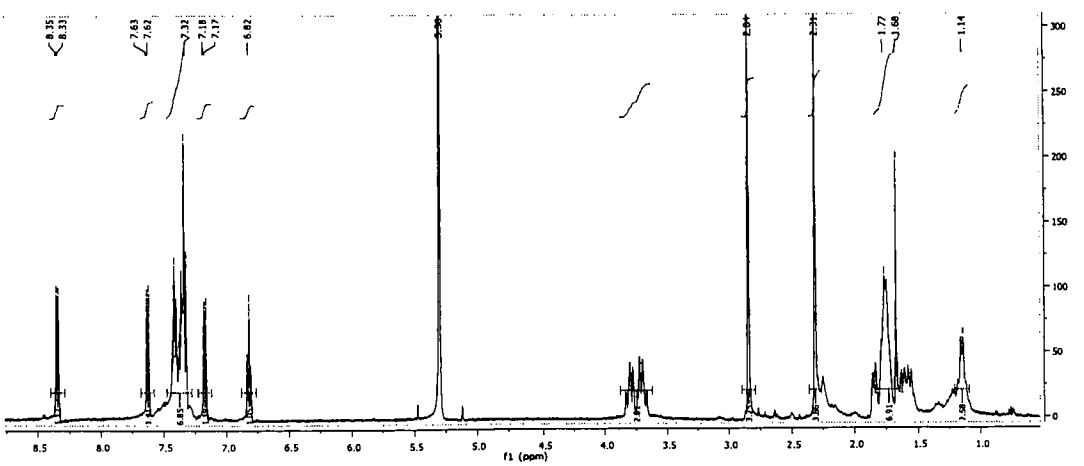


Figure A 25. The ^{1}H NMR (500 MHz, CD_2Cl_2, -60 °C) spectrum of **R,R-Pd_2**.

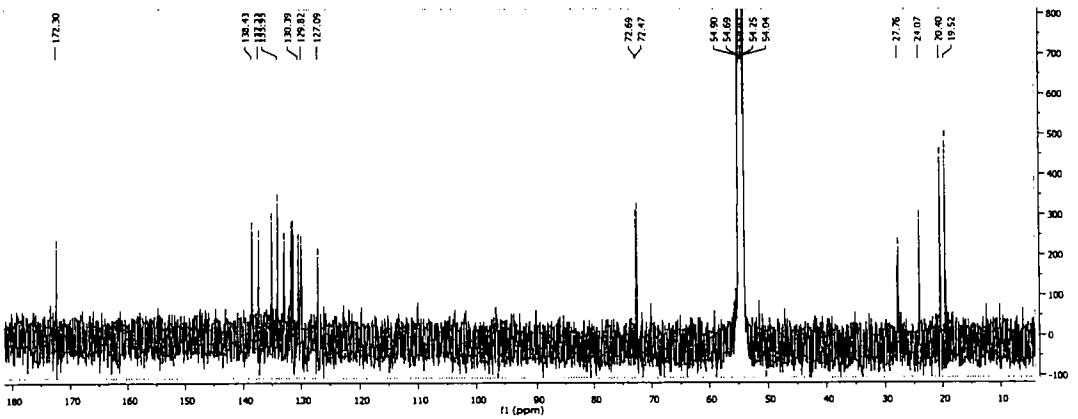


Figure A 26. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, -60 °C) spectrum of **R,R-Pd$_2$**.

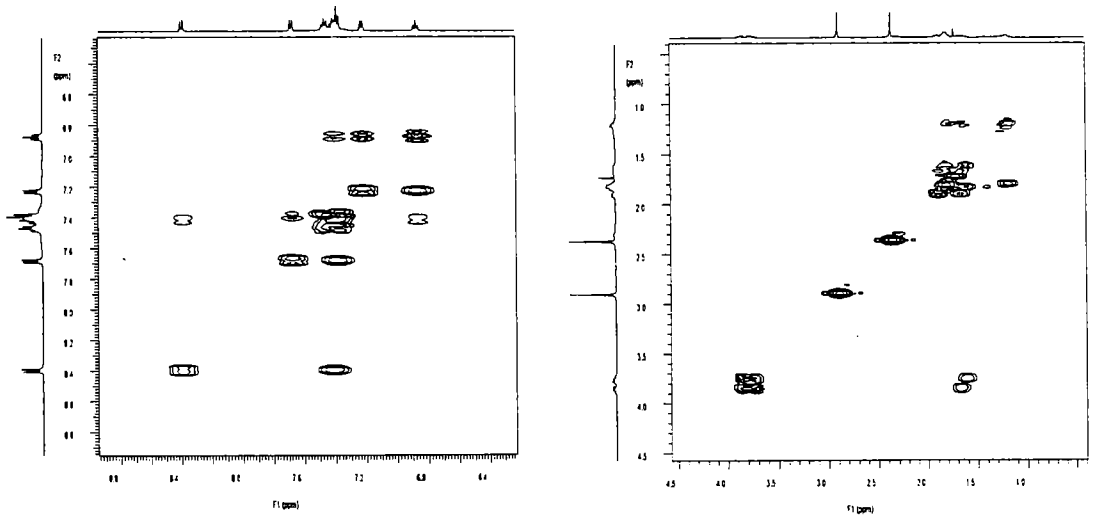


Figure A 27. The COSY spectrum (500 MHz, CD_2Cl_2, -60 °C) of **Pd$_2$(R,R)** in the aromatic (left) and aliphatic regions (right).

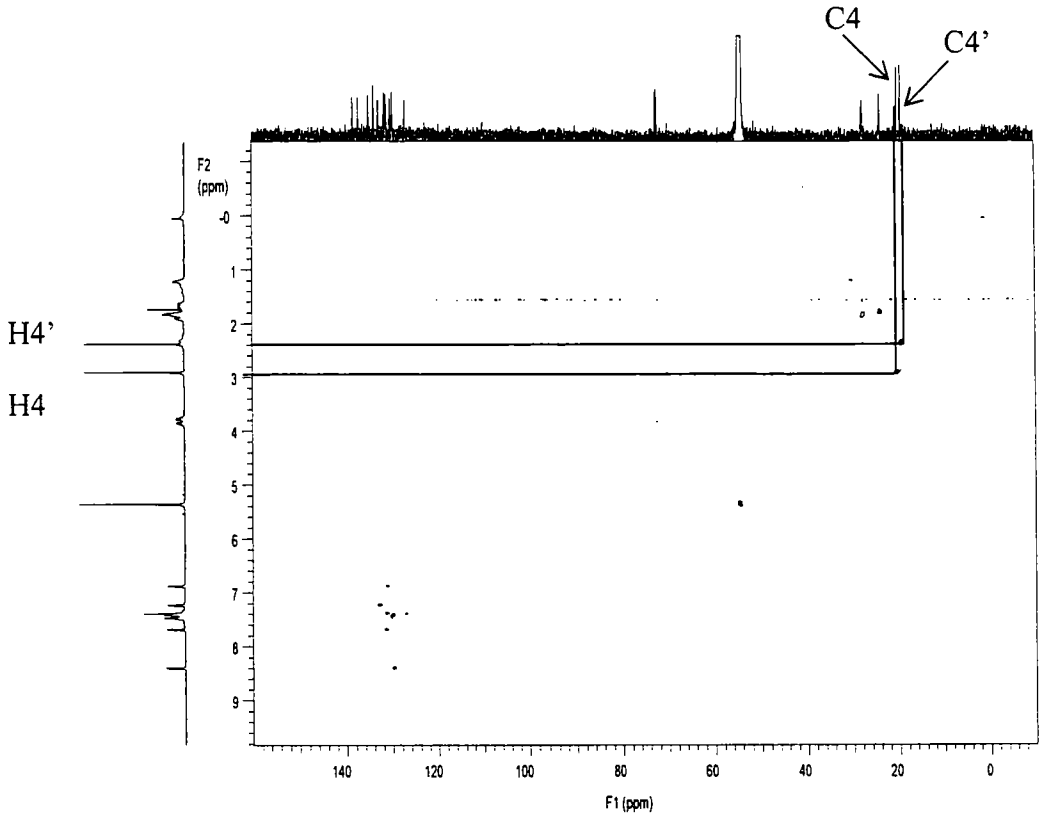


Figure A 28. The HSQC (CD_2Cl_2, -60 °C) spectrum of **R,R-Pd$_2$**.

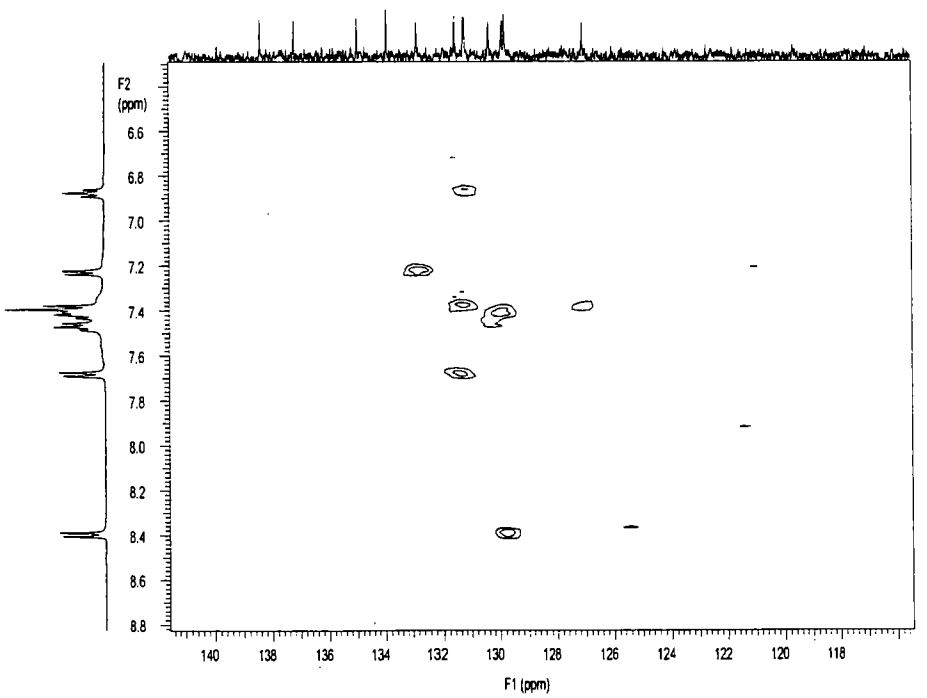


Figure A 29. The HSQC NMR (CD_2Cl_2, -60 °C) spectrum in the aromatic region **o**f **R,R-Pd$_2$**.

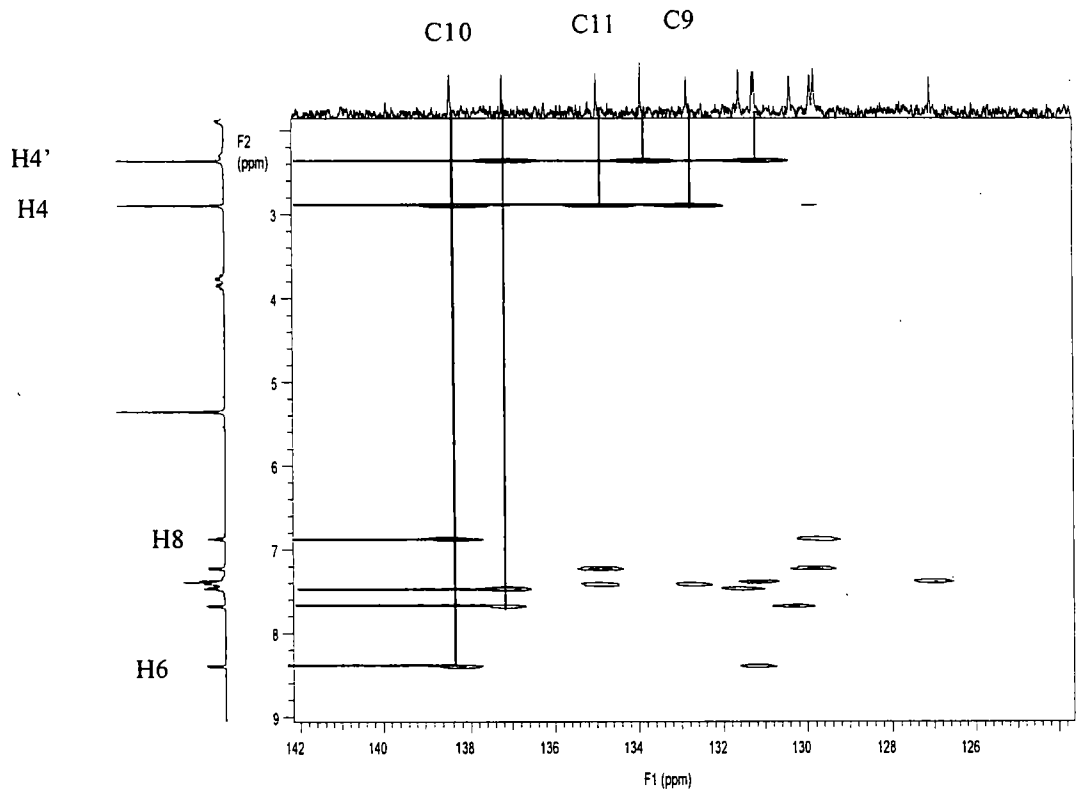


Figure A 30. The HMBC NMR (CD_2Cl_2, -60 °C) spectrum in the aromatic region of **R,R-Pd$_2$**.

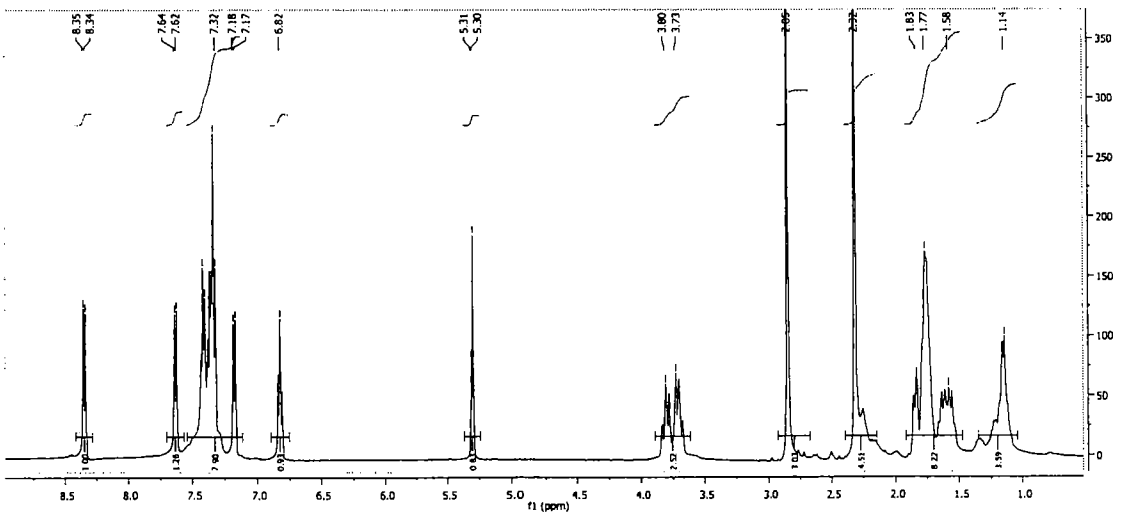


Figure A 31. The ^{1}H NMR (500 MHz, CD_2Cl_2, -60 °C) spectrum of **S,S-Pd$_2$**.

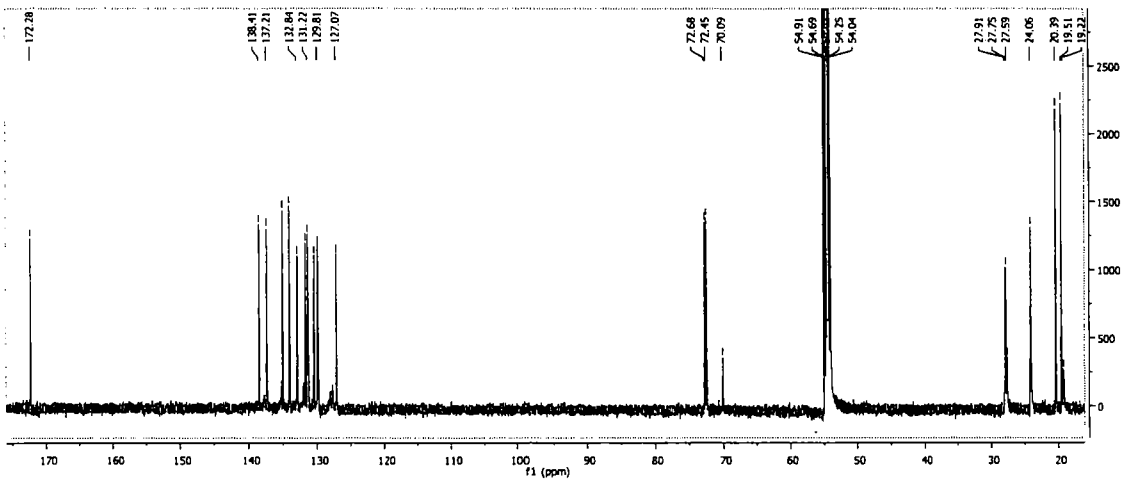


Figure A 32. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, -60 °C) spectrum of **S,S-Pd$_2$**.

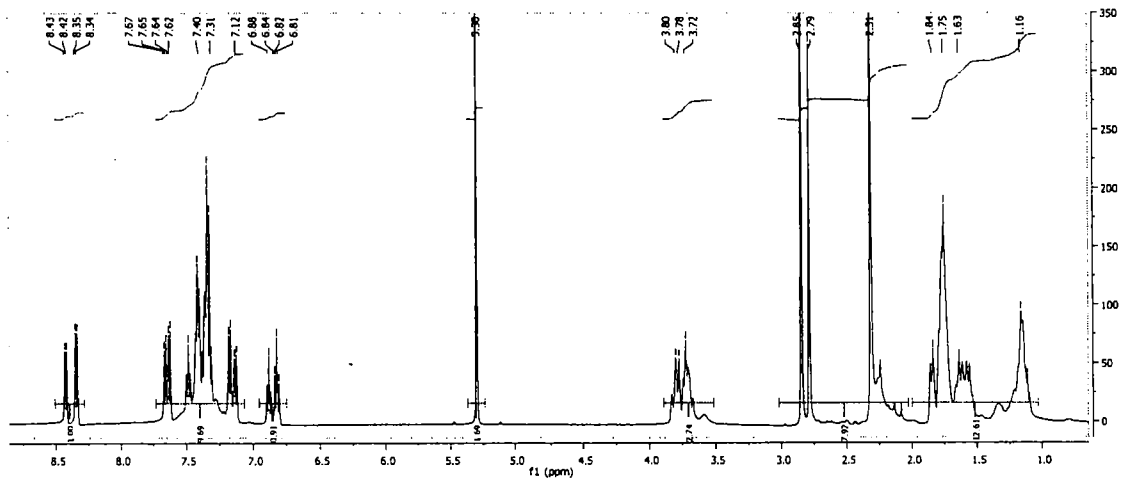


Figure A 33. The ^{1}H (500 MHz, CD_2Cl_2, -60 °C) spectrum of ***rac*-Pd$_2$ / *meso*-Pd$_2$**.

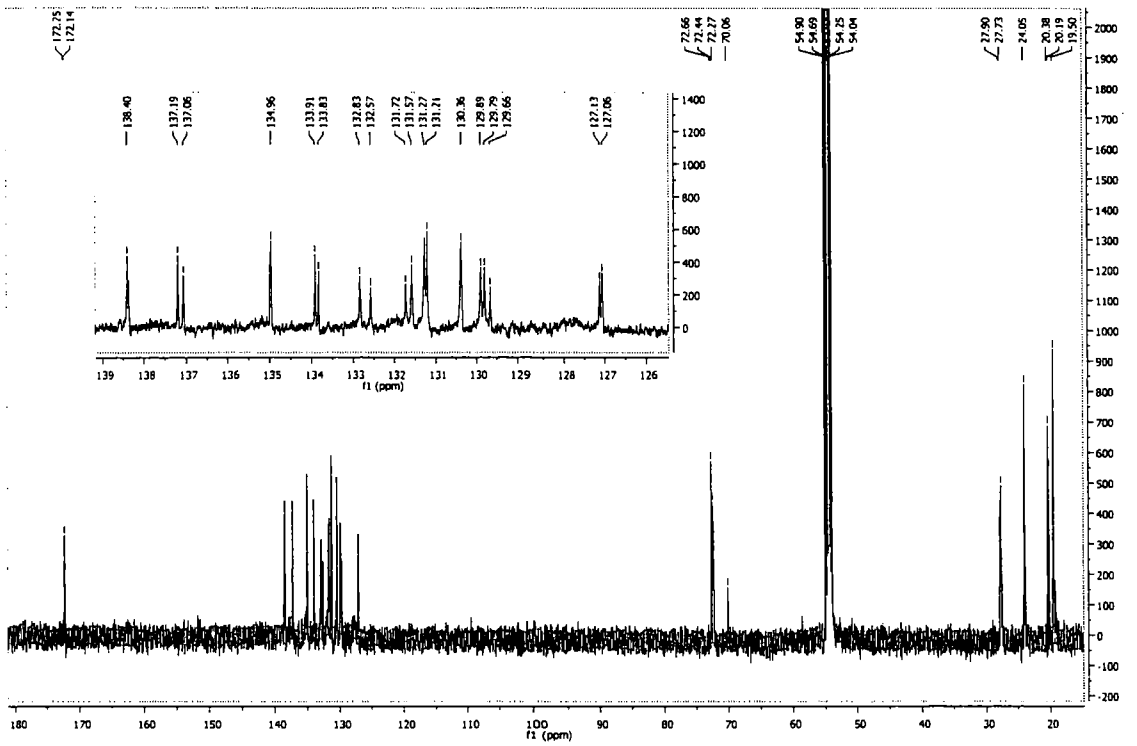


Figure A 34. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, -60 °C) spectrum of ***rac*-Pd$_2$ / *meso*-Pd$_2$**.

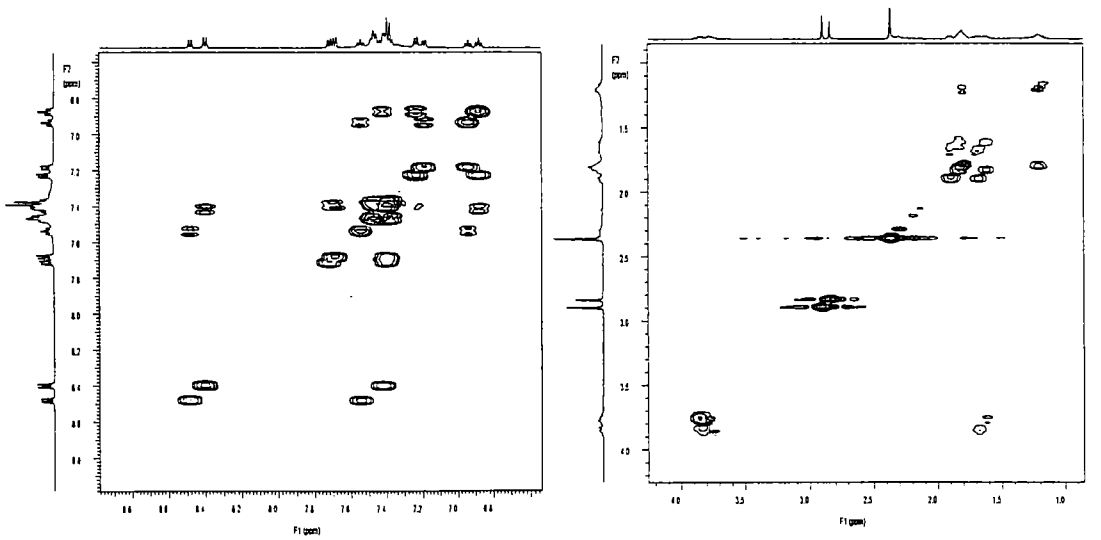


Figure A 35. The COSY (500 MHz, CD_2Cl_2, -60 °C) spectrum of ***rac*-Pd$_2$ / *meso*-Pd$_2$**.

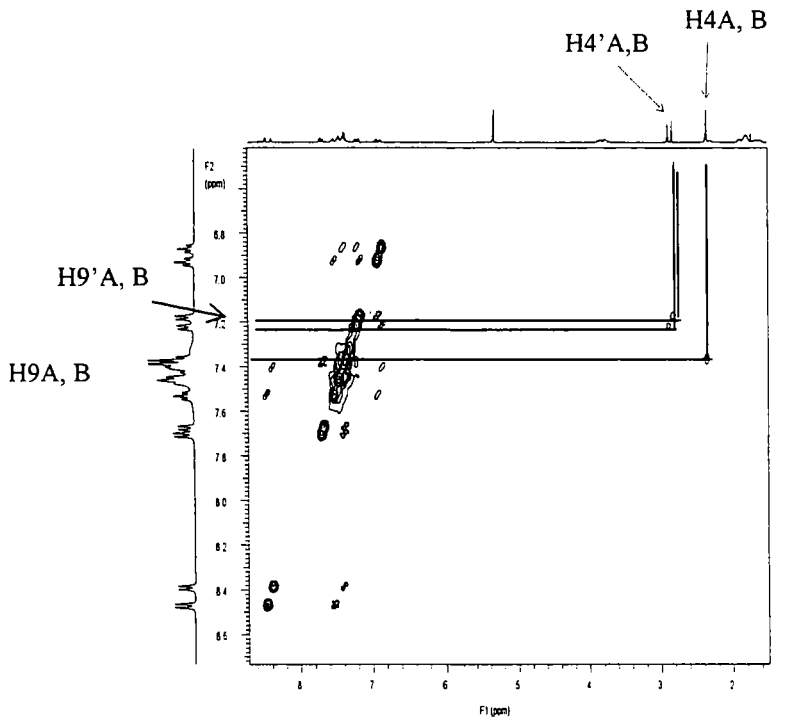


Figure A 36. The NOESY (500 MHz, CD_2Cl_2, -60 °C) spectrum of ***rac*-Pd_2 / *meso*-Pd_2**.

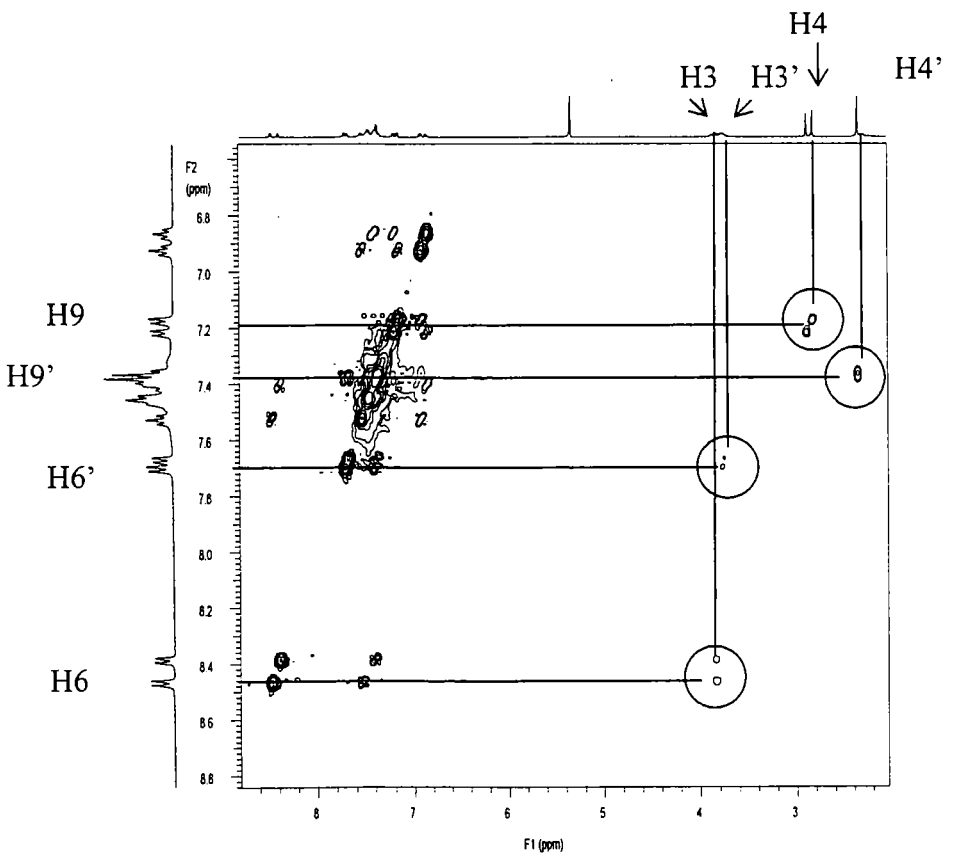


Figure A 37. The NOESY (500 MHz) ***rac*-Pd_2 / *meso*-Pd_2** in CD_2Cl_2 at -60 °C.

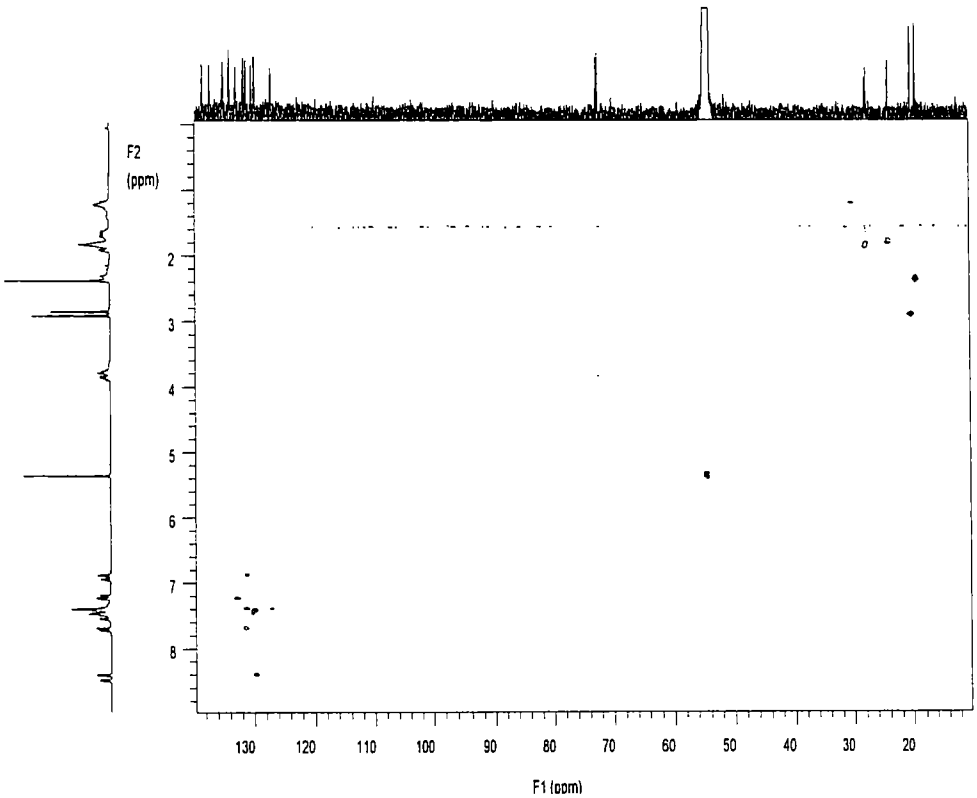


Figure A 38. The HSQC NMR (CD_2Cl_2, -60 °C) spectrum of ***rac*-Pd_2 / *meso*-Pd_2**.

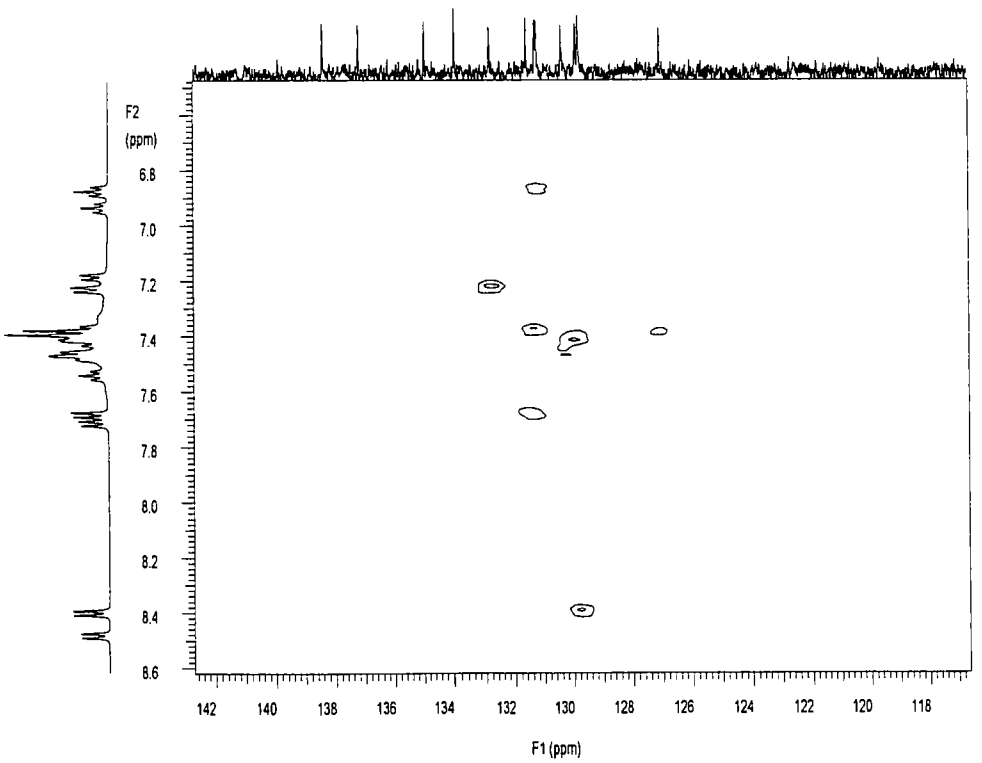


Figure A 39. The HSQC NMR (CD_2Cl_2, -60 °C) spectrum in aromatic region of ***rac*-Pd_2 / *meso*-Pd_2**.

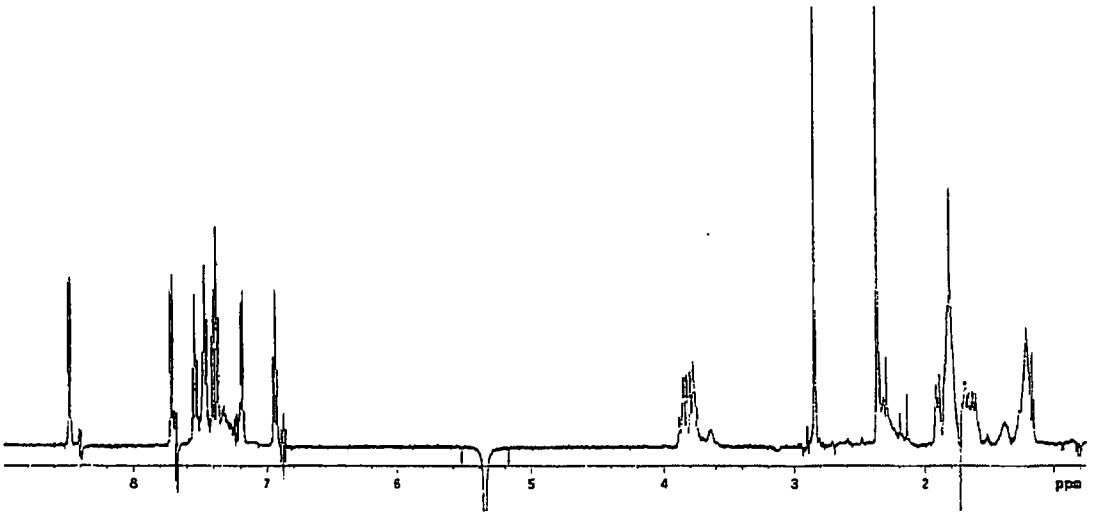


Figure A 40. The ^{1}H NMR (500 MHz, CD_2Cl_2, -60 °C) spectrum of ***rac*-Pd$_2$ / *meso*-Pd$_2$** minus **S,S-Pd$_2$**.

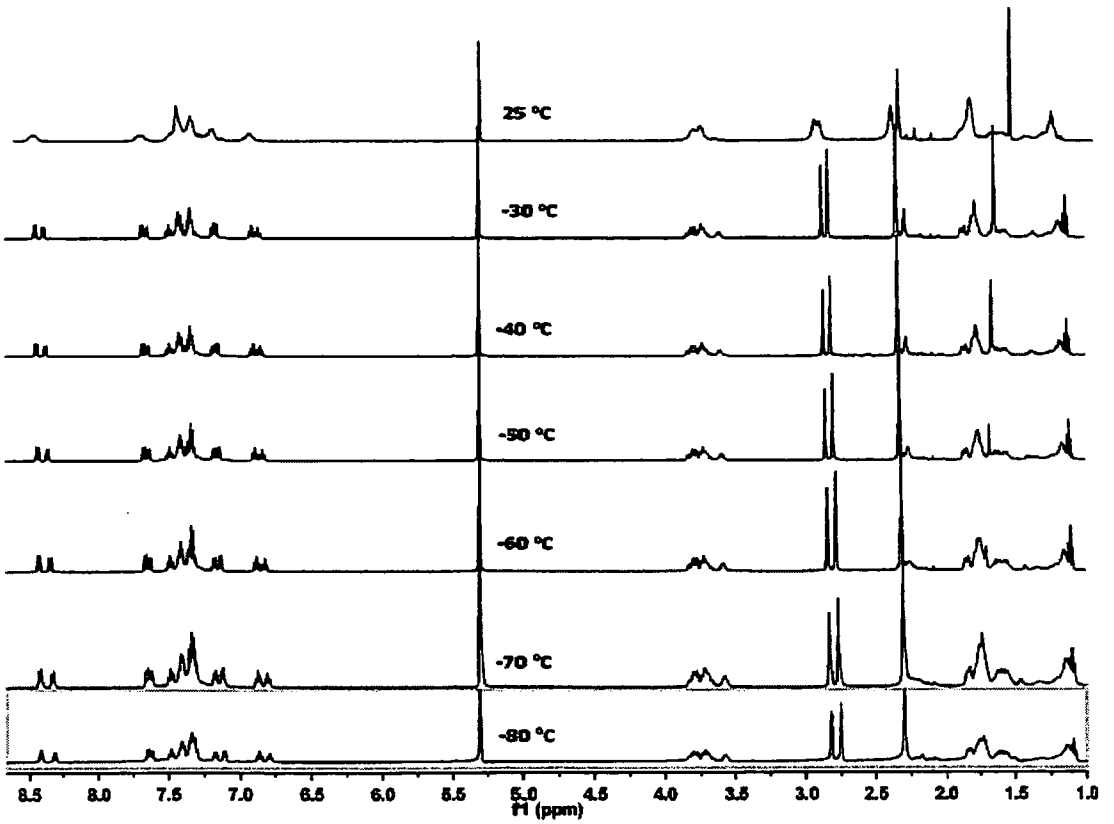


Figure A 41. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectra of ***rac*-Pd$_2$ / *meso*-Pd$_2$** at various temperatures.

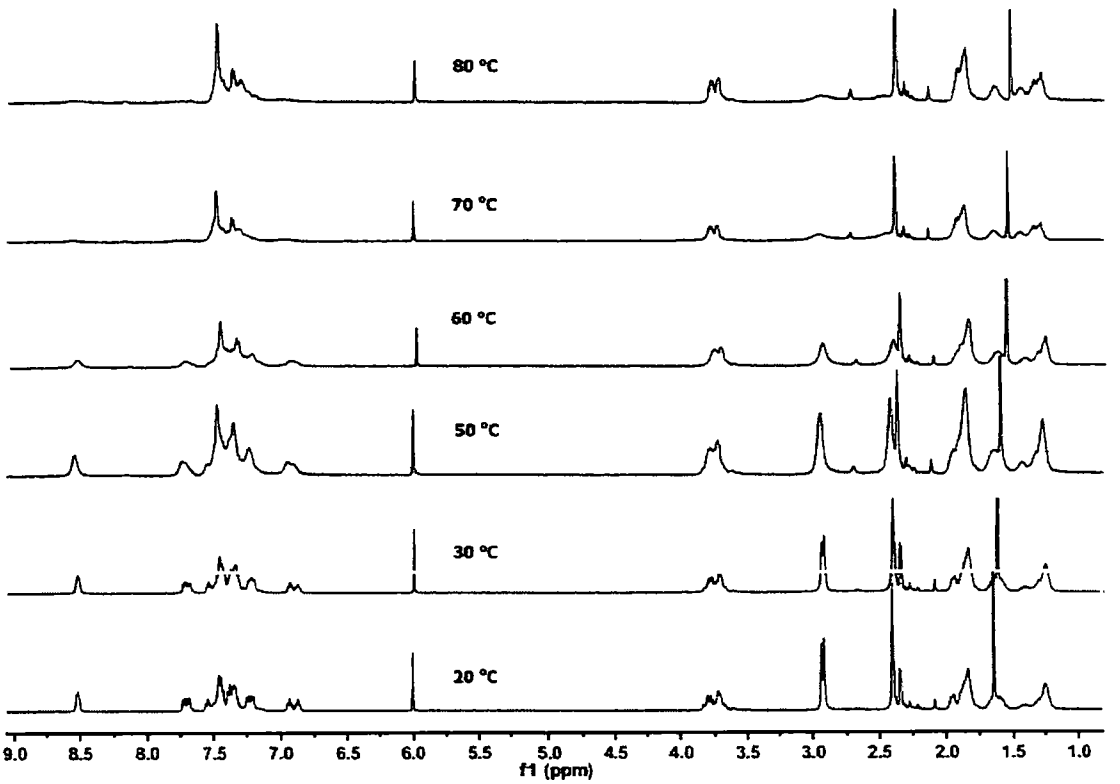


Figure A 42. The ^{1}H NMR (500 MHz, TCE-d_2) spectra of ***rac*-Pd$_2$ / *meso*-Pd$_2$** at various temperatures.

Appendix B

S,N-Bidentate Thioureas and Their Palladium Complexes

Appendix B

S,N-Bidentate thioureas

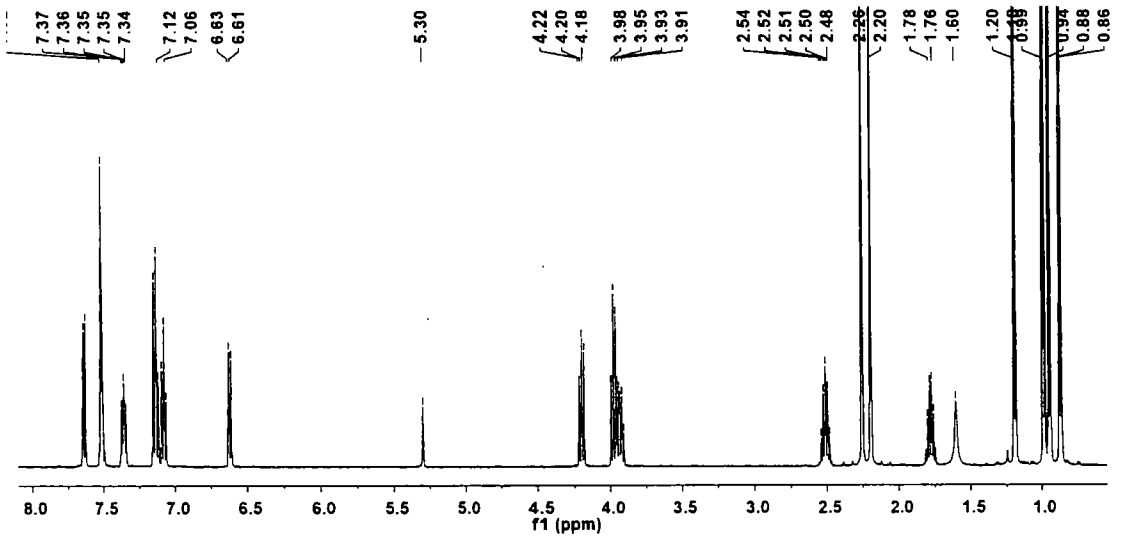


Figure B 1. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **L2up**.

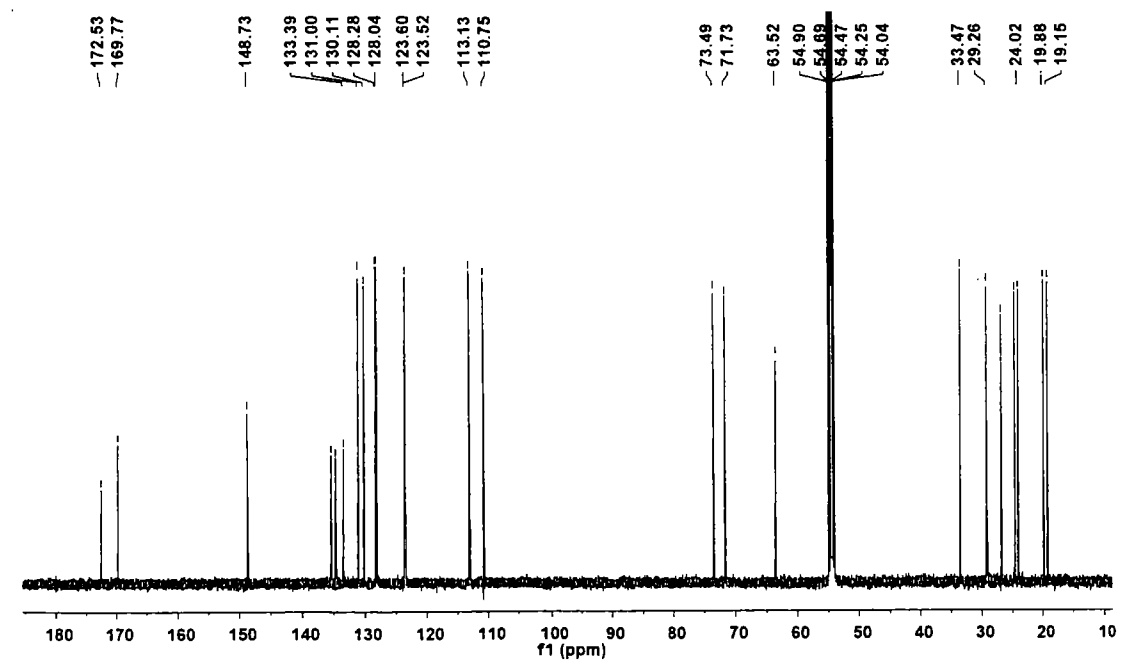


Figure B 2. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L2up**.

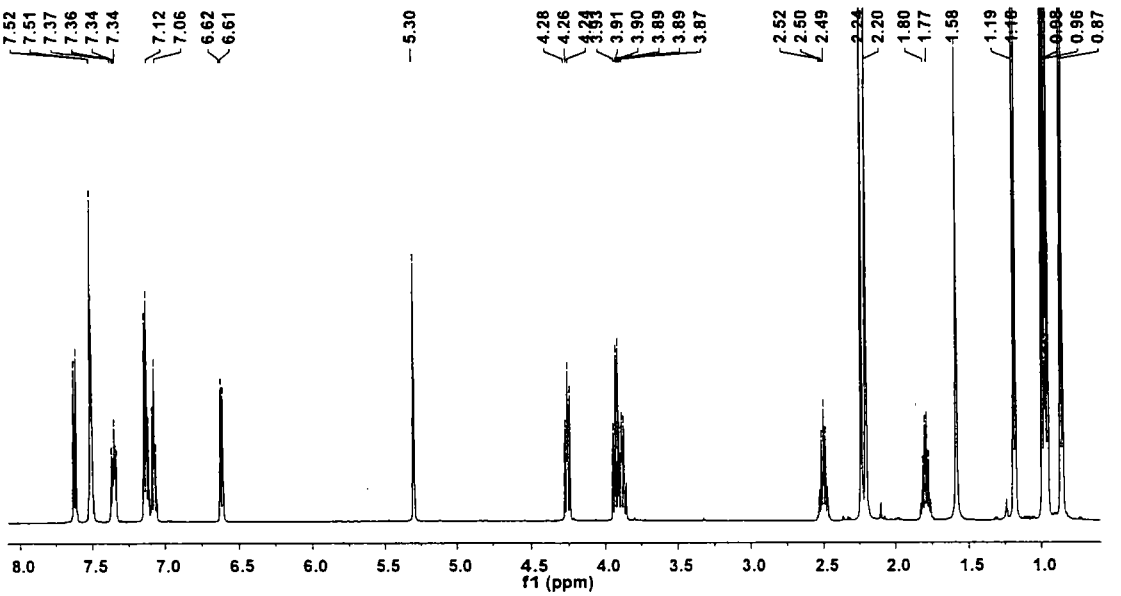


Figure B 3. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **L2down**.

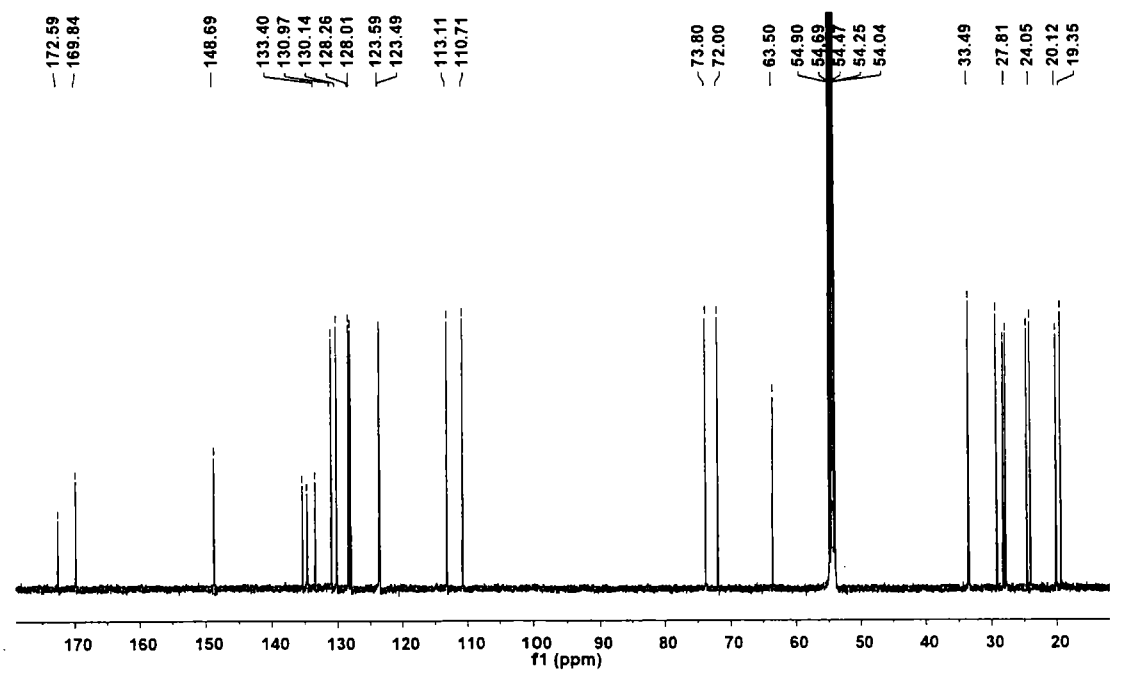


Figure B 4. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L2down**.

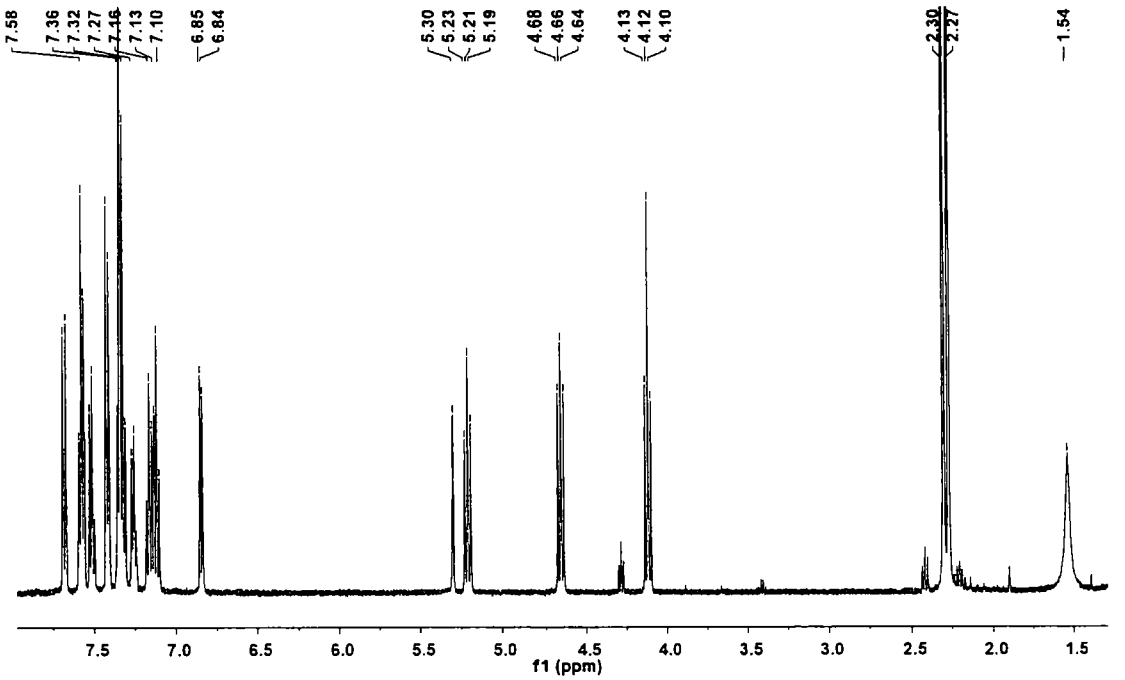


Figure B 5. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **L3**.

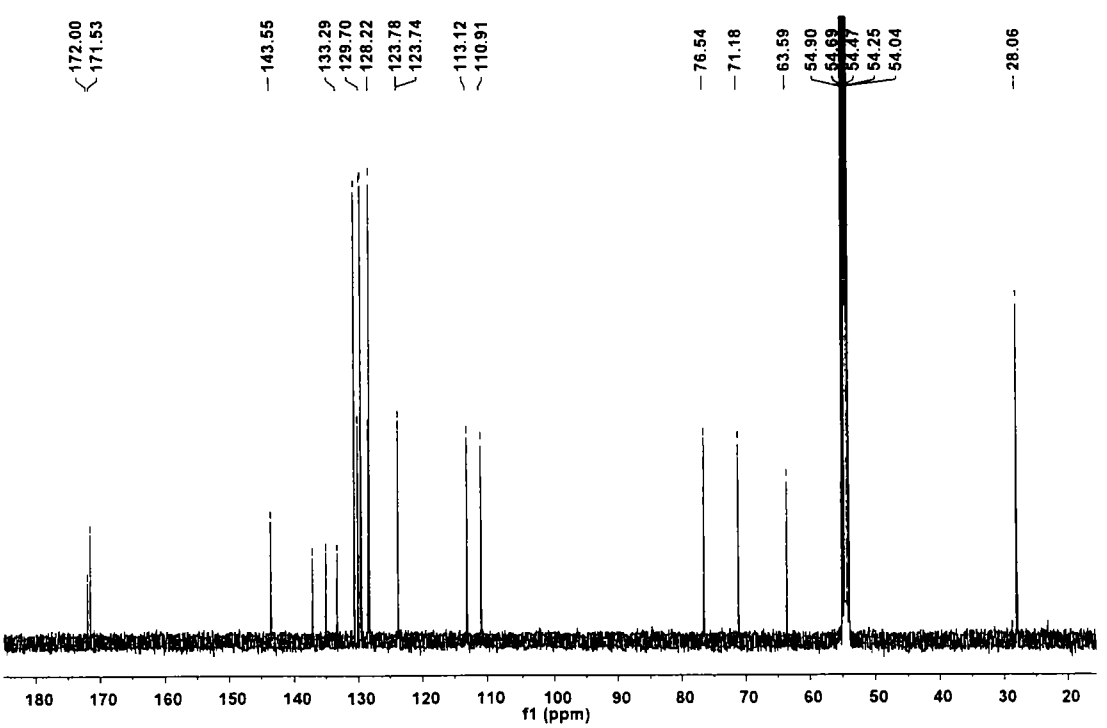


Figure B 6. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L3**.

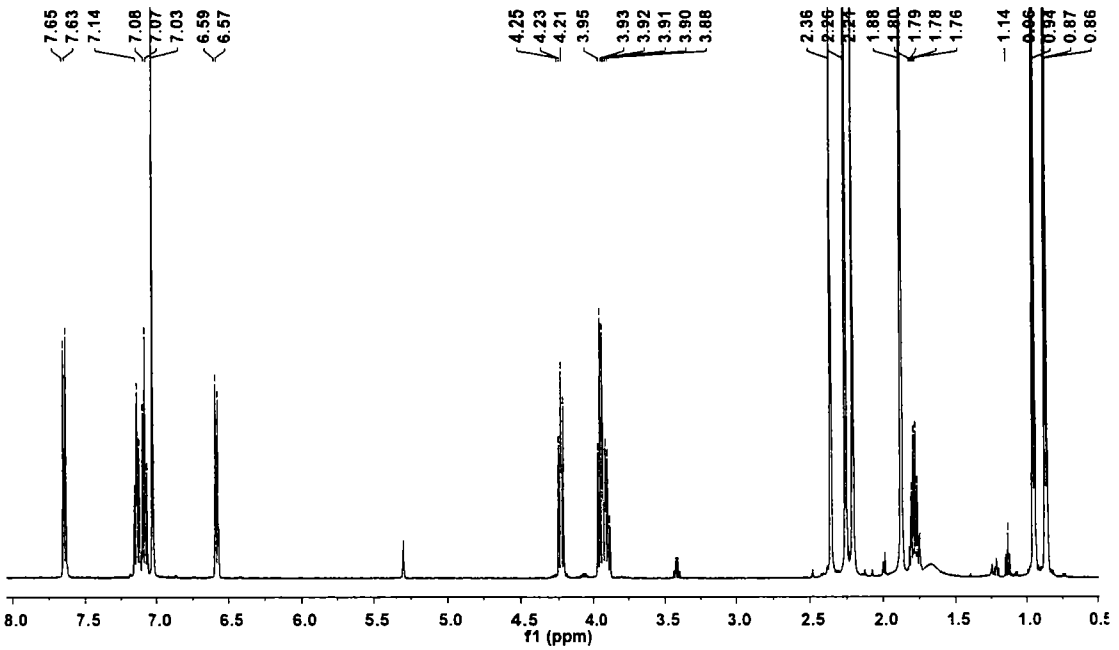


Figure B 7. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **L4**.

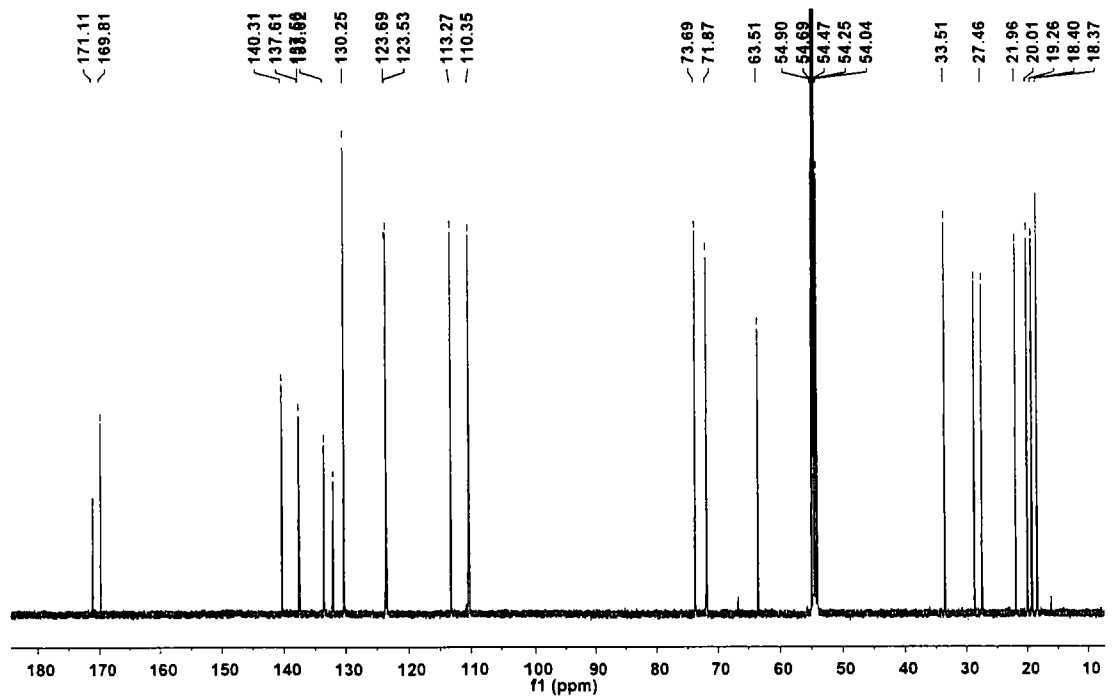


Figure B 8. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L4**.

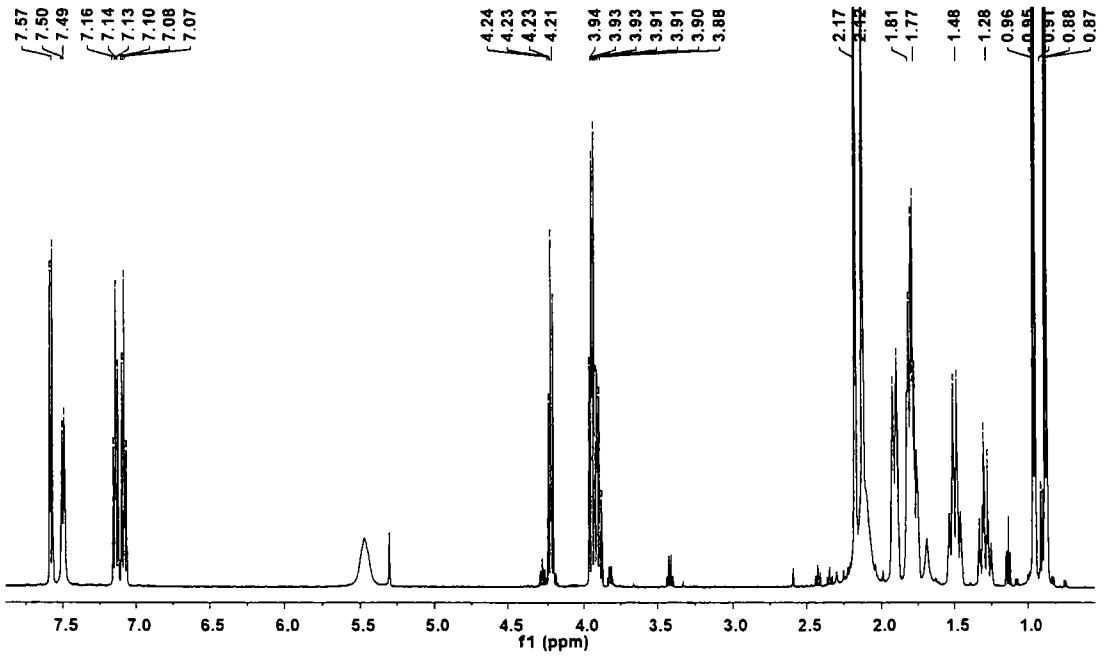


Figure B 9. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **L5**.

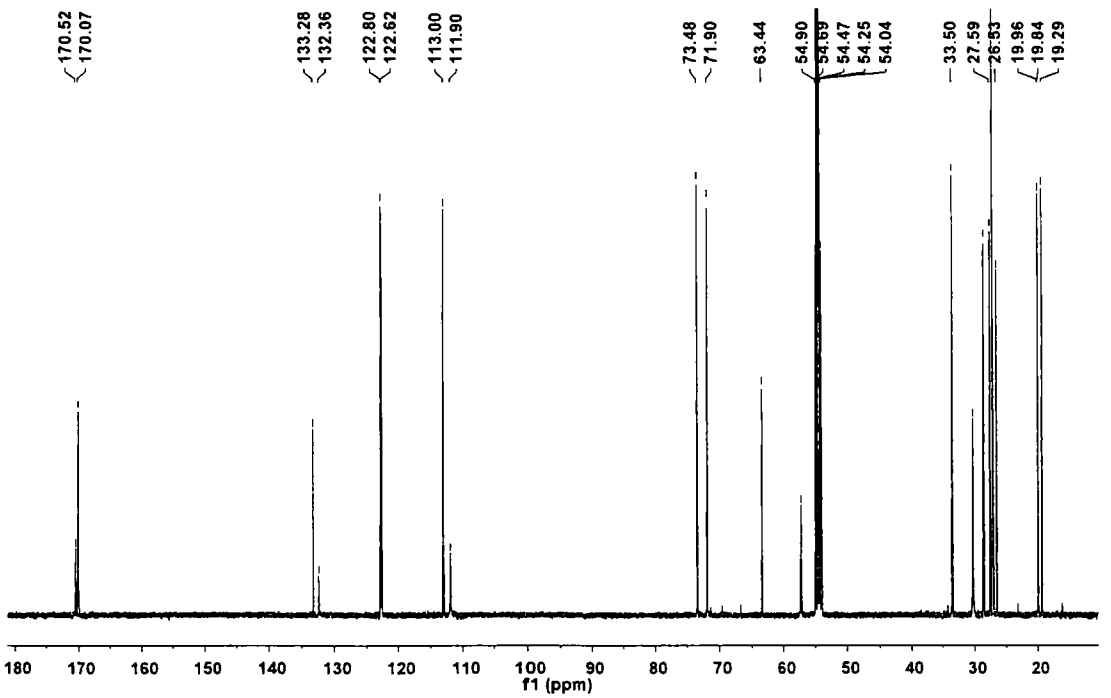


Figure B 10. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L5**.

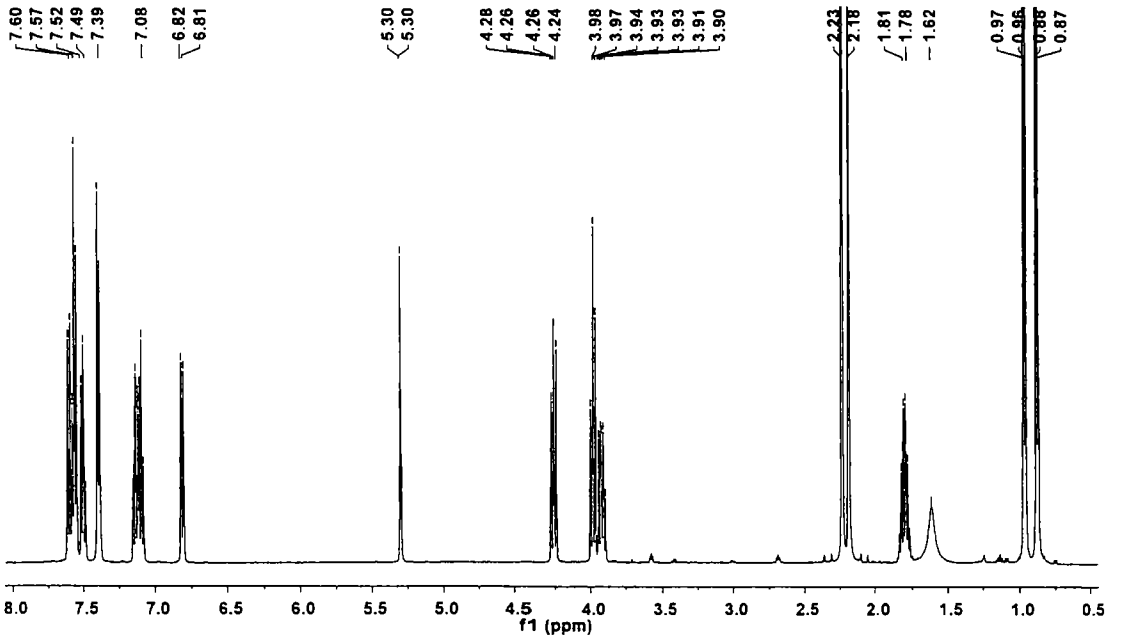


Figure B 11. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **L6**.

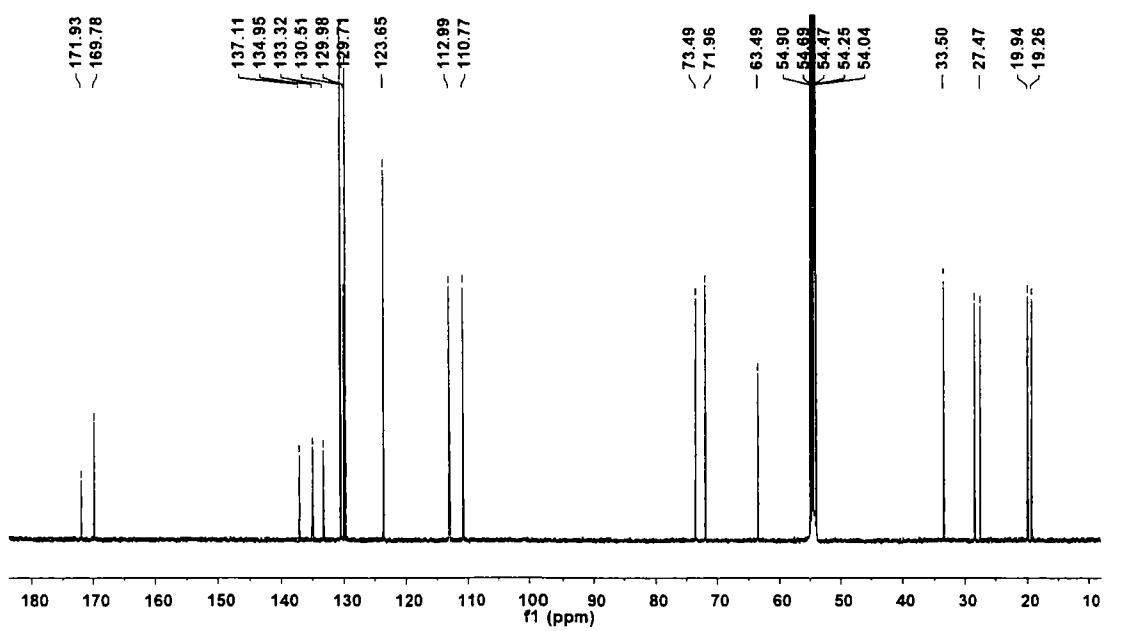


Figure B 12. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **L6**.

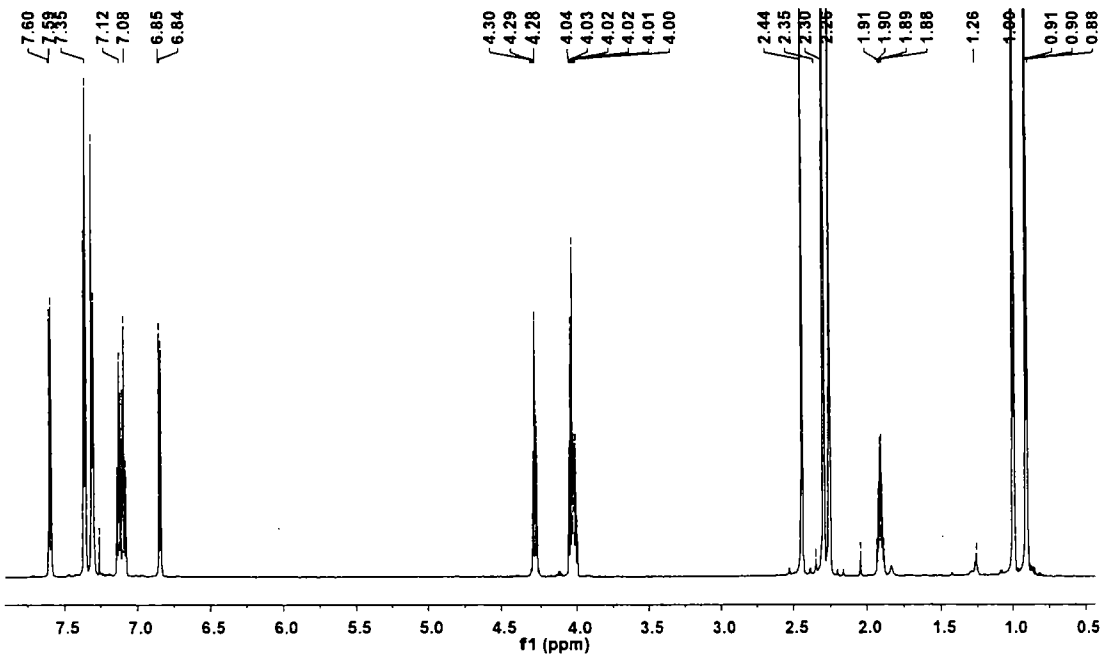


Figure B 13. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **L7**.

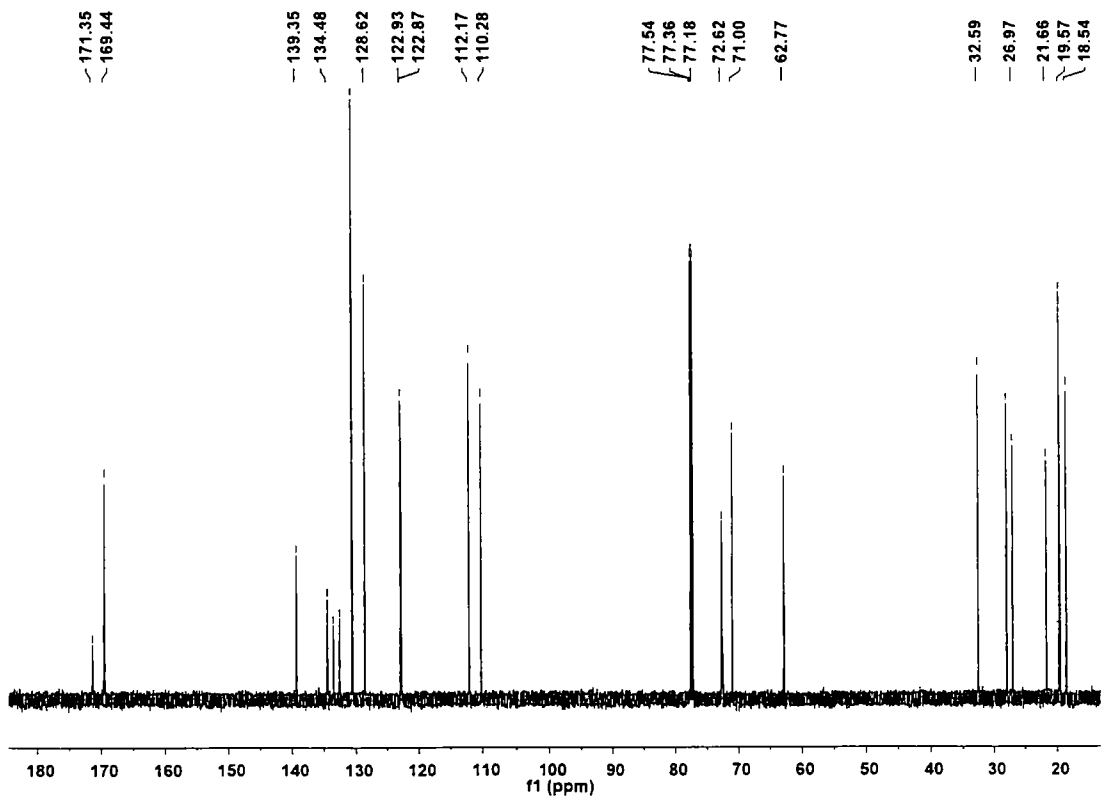


Figure B 14. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **L7**.

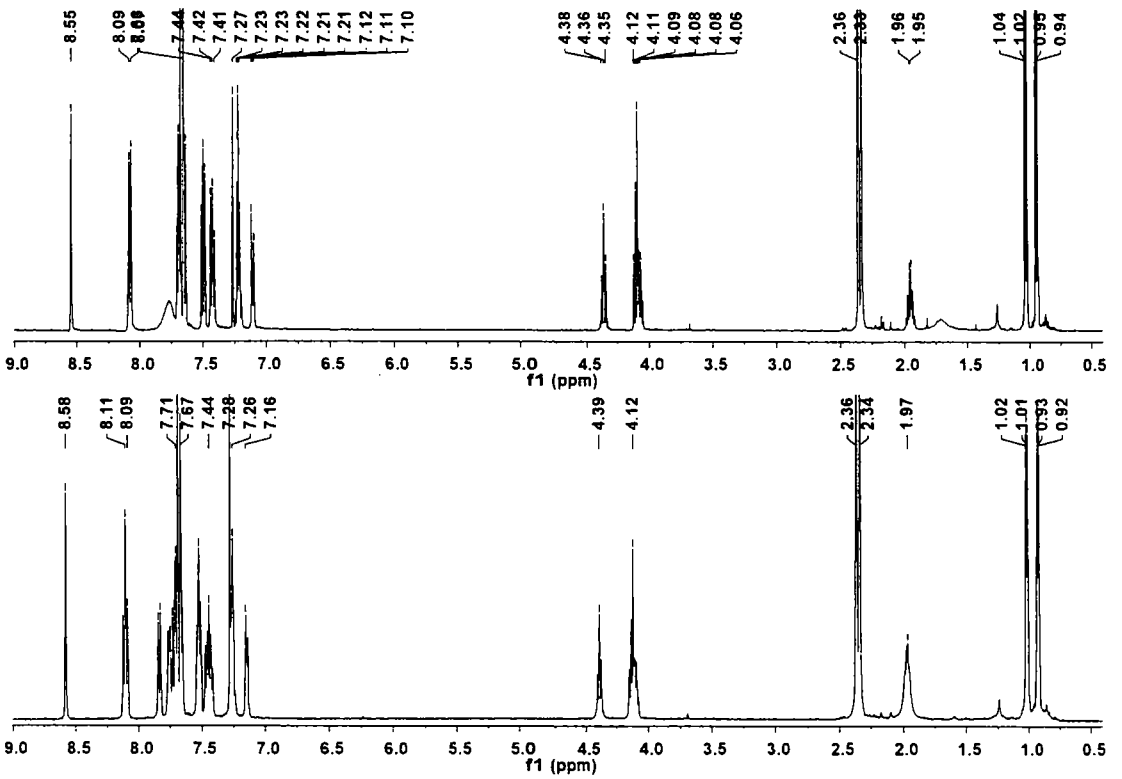


Figure B 15. The ^{1}H NMR (500 MHz, $CDCl_3$) spectra of **L8** at room temperature (top) and -30 °C (bottom).

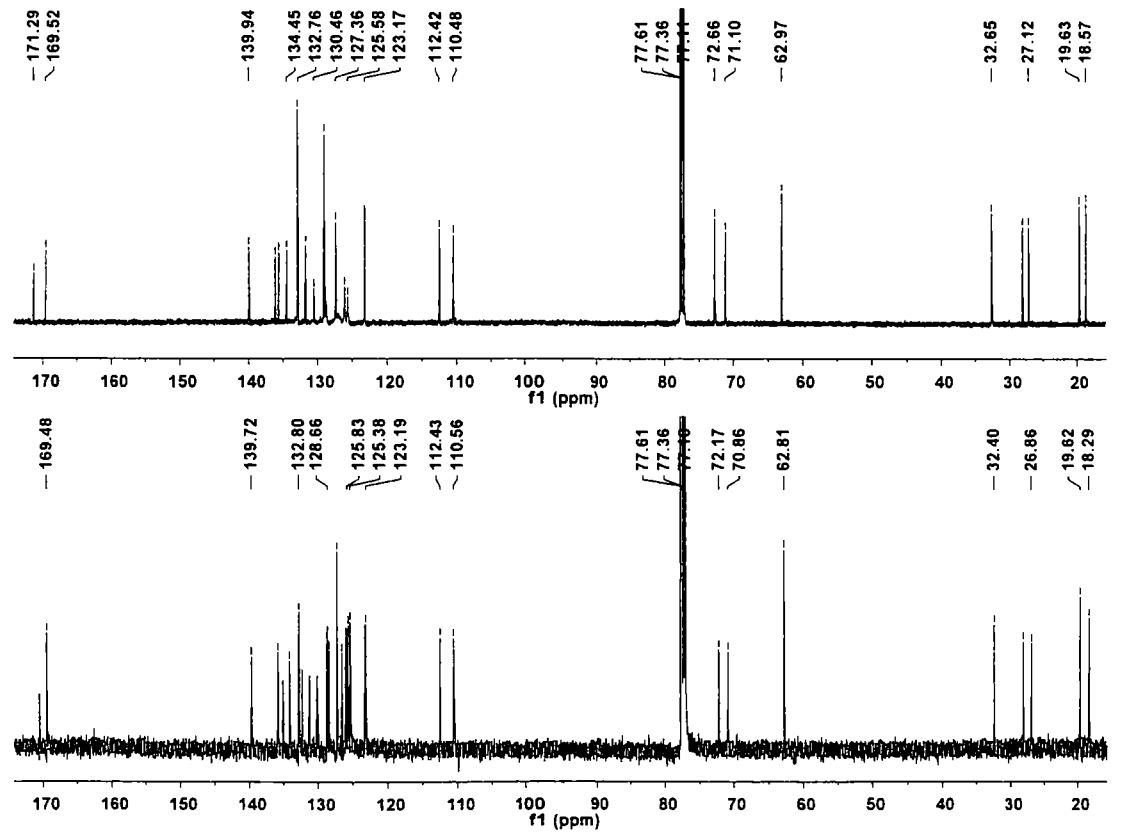


Figure B 16. The $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectra of **L8** at room temperature (top) and -30 °C (bottom).

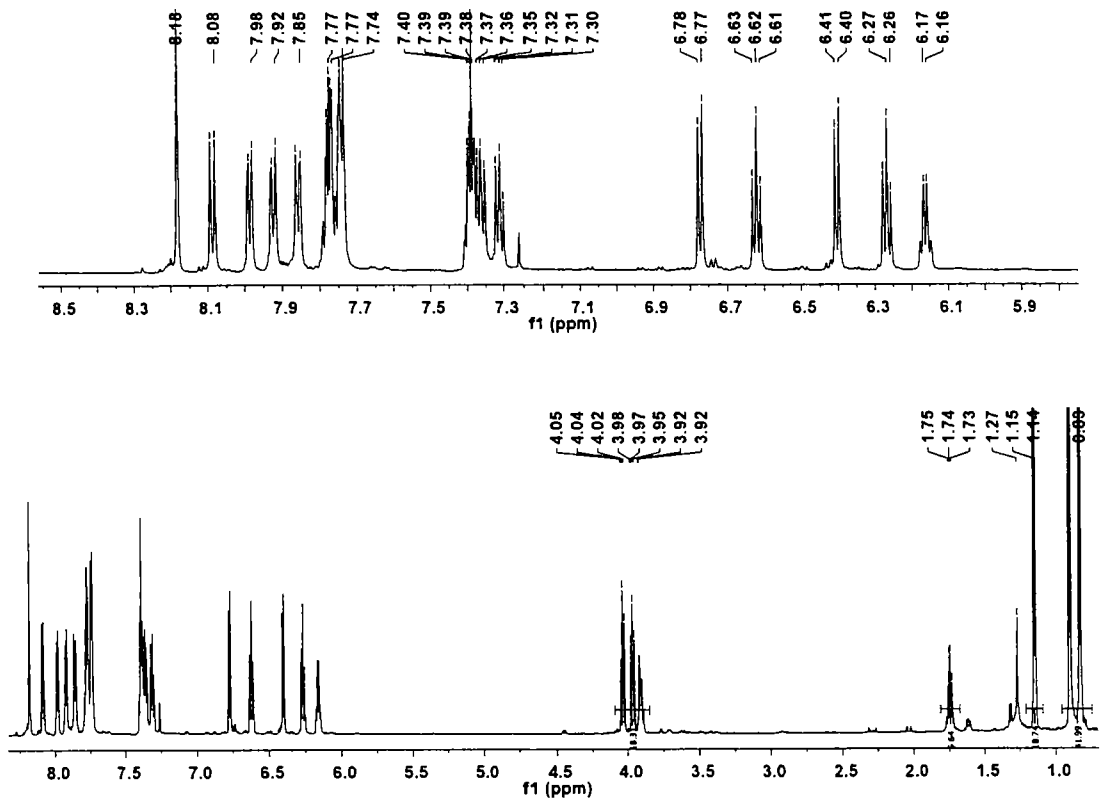


Figure B 17. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **R-L9up** (bottom) and the expanded spectrum in the aromatic region (top).

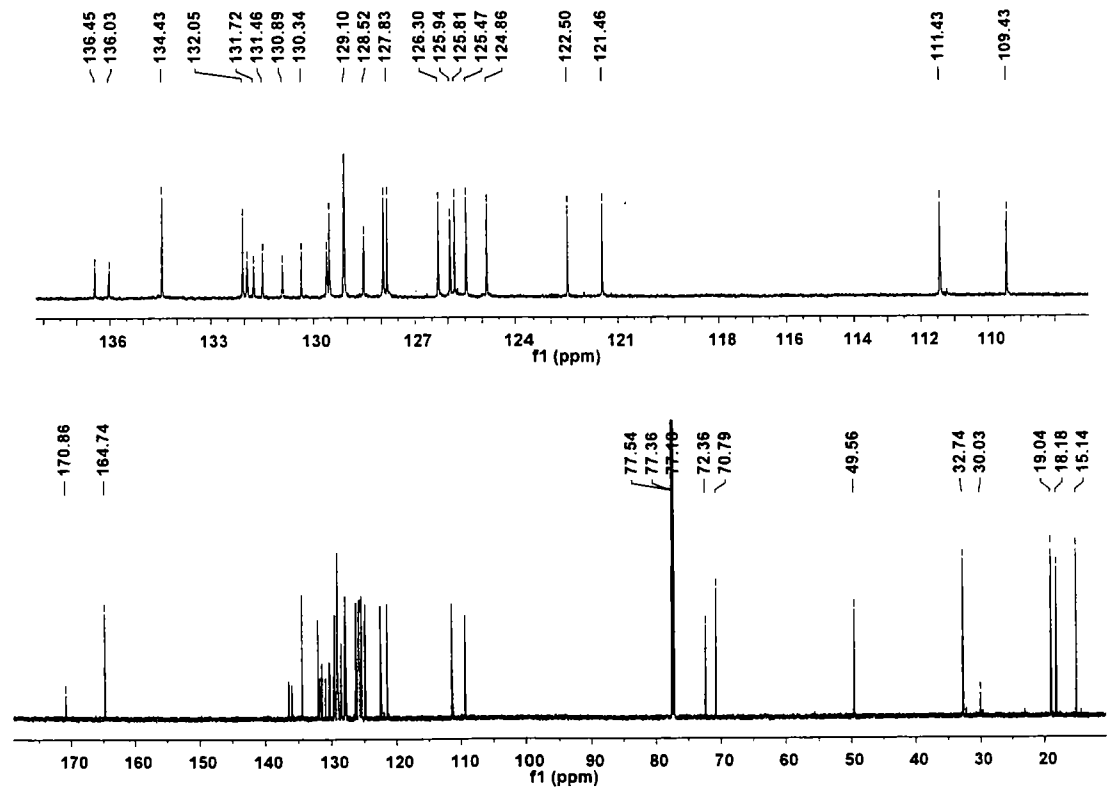


Figure B 18. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **R-L9up** (bottom) and the expanded spectrum in the aromatic region (top).

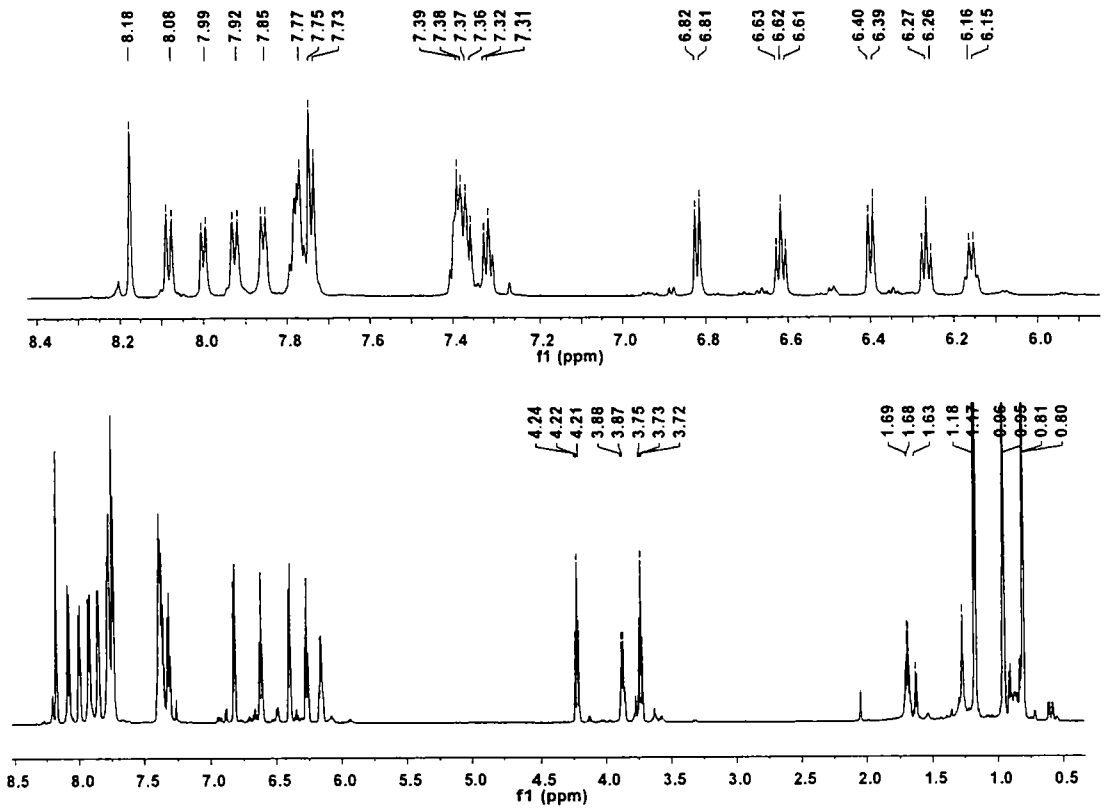


Figure B 19. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **S-L9down** (bottom) and the expanded spectrum in the aromatic region.

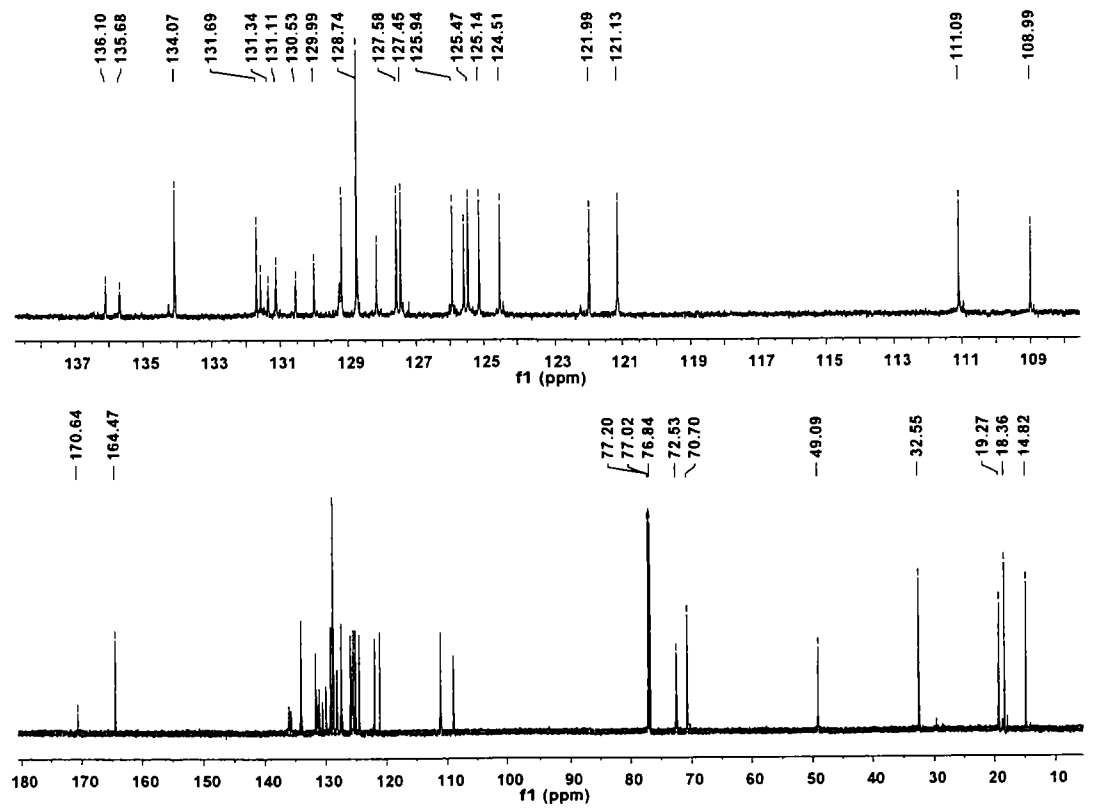


Figure B 20. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **S-L9down** (bottom) and the expanded spectrum in the aromatic region (top).

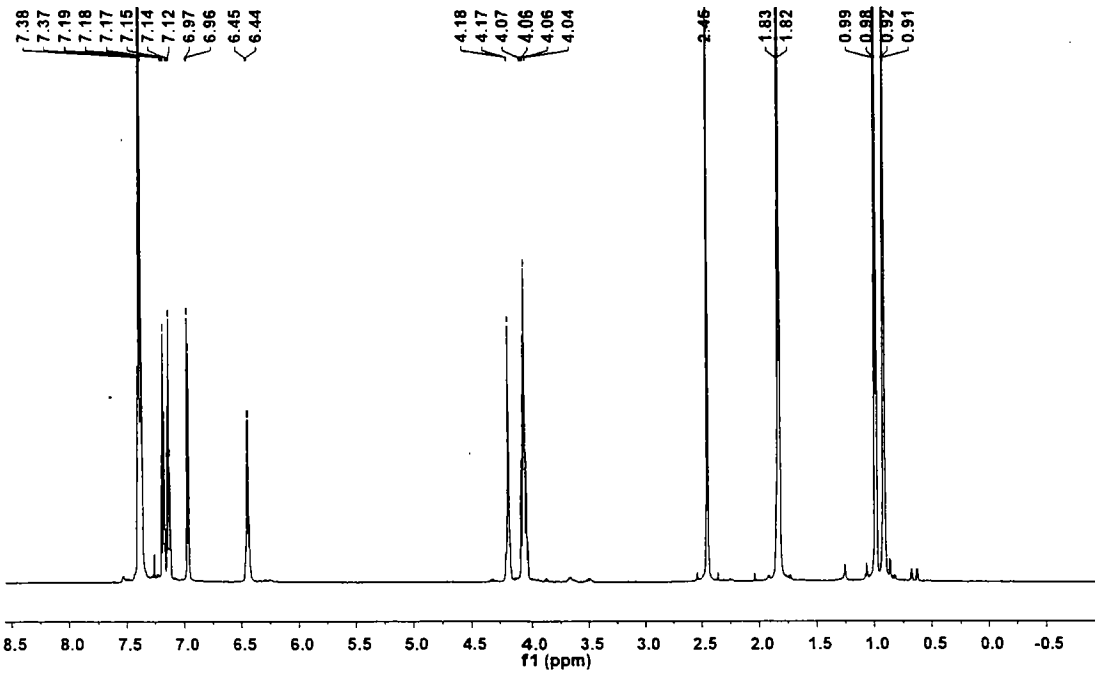


Figure B 21. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **R-L10**.

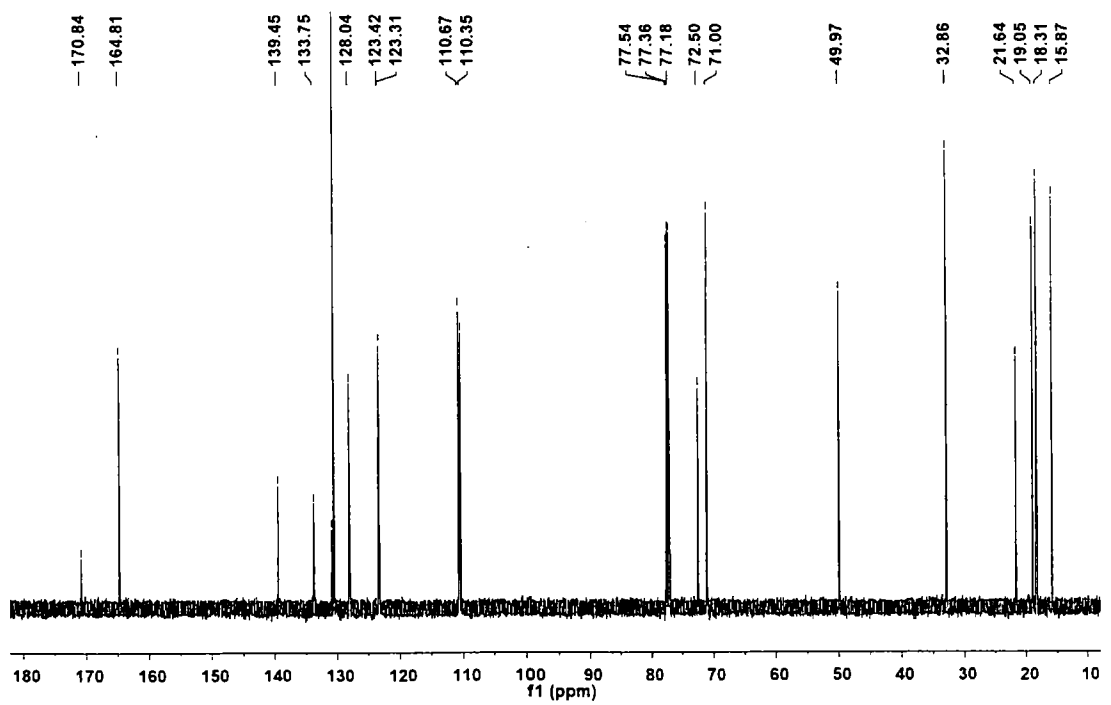


Figure B 22. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **R-L10**.

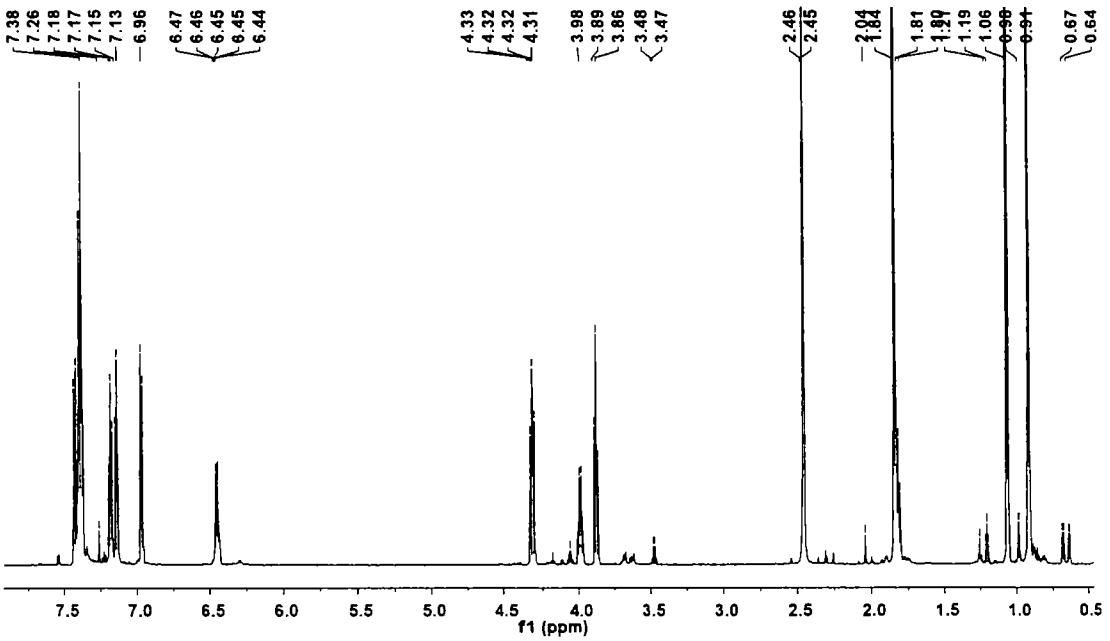


Figure B 23. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **S-L10**.

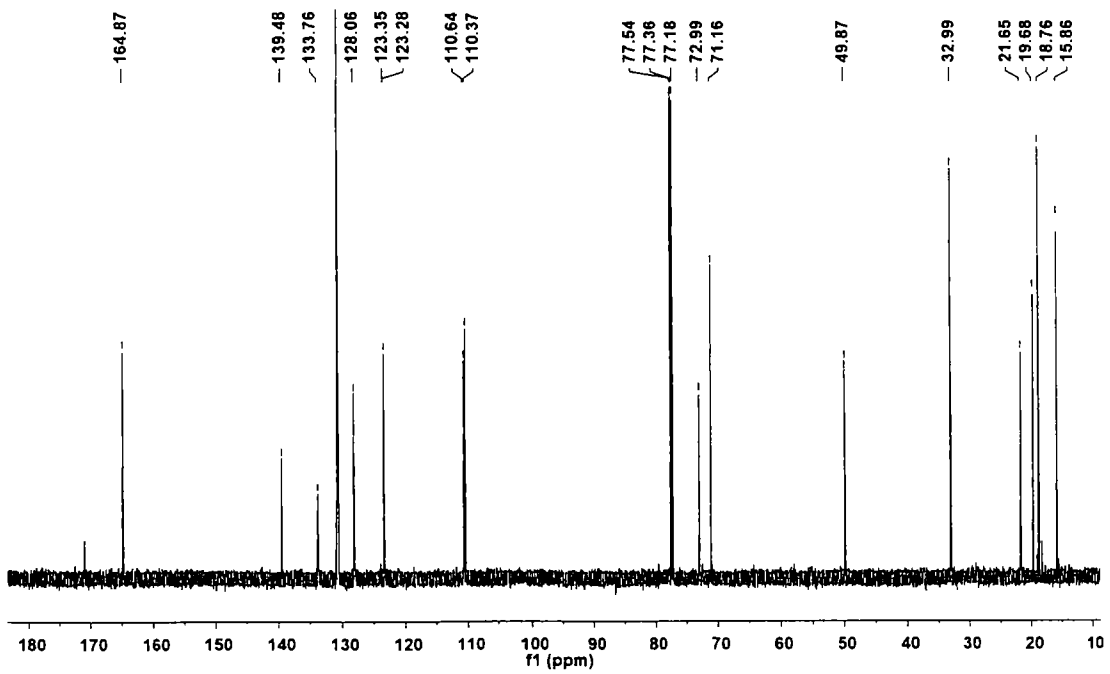


Figure B 24. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **S-L10**.

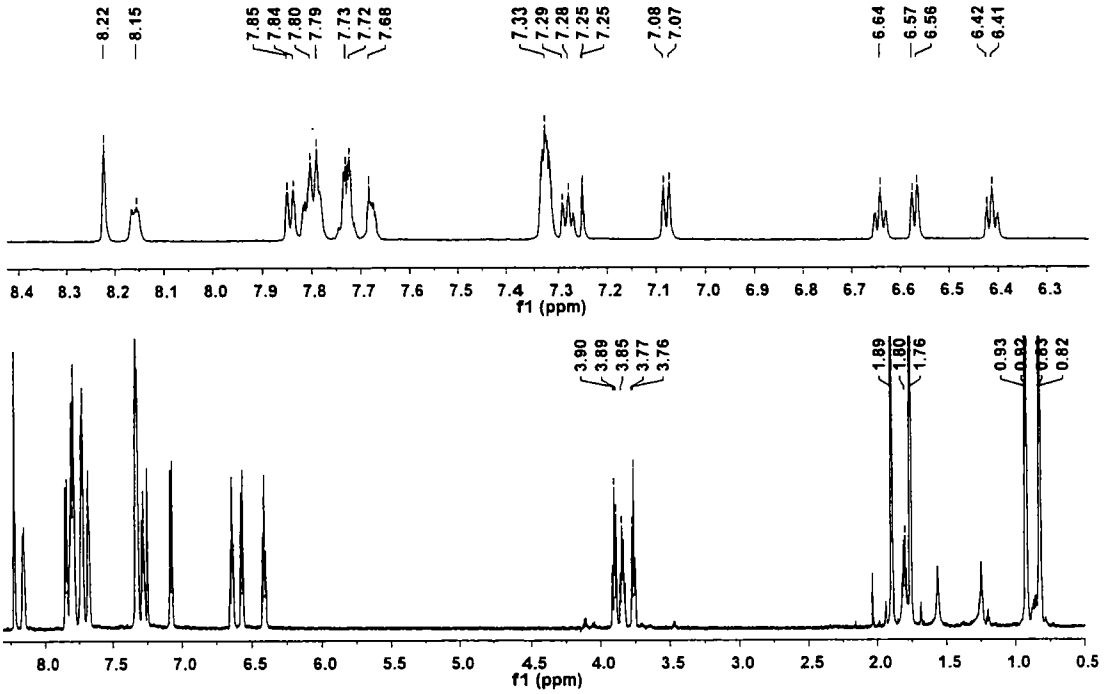


Figure B 25. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **L11up** (bottom) and the expanded spectrum in the aromatic region (top).

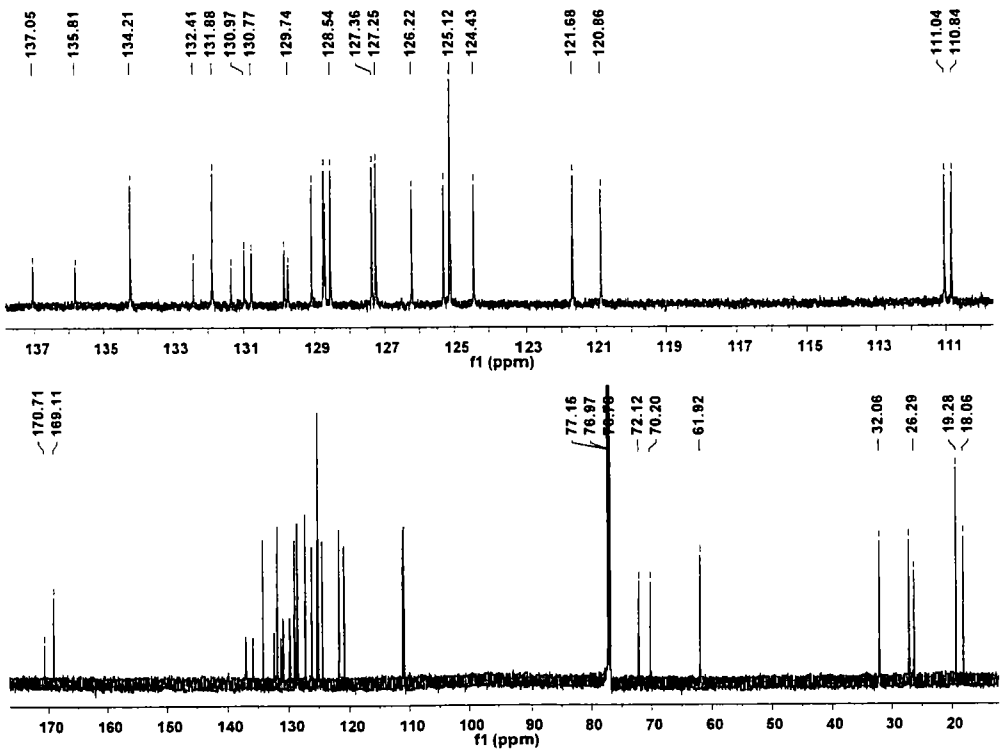


Figure B 26. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **L11up** (bottom) and the expanded spectrum in the aromatic region (top).

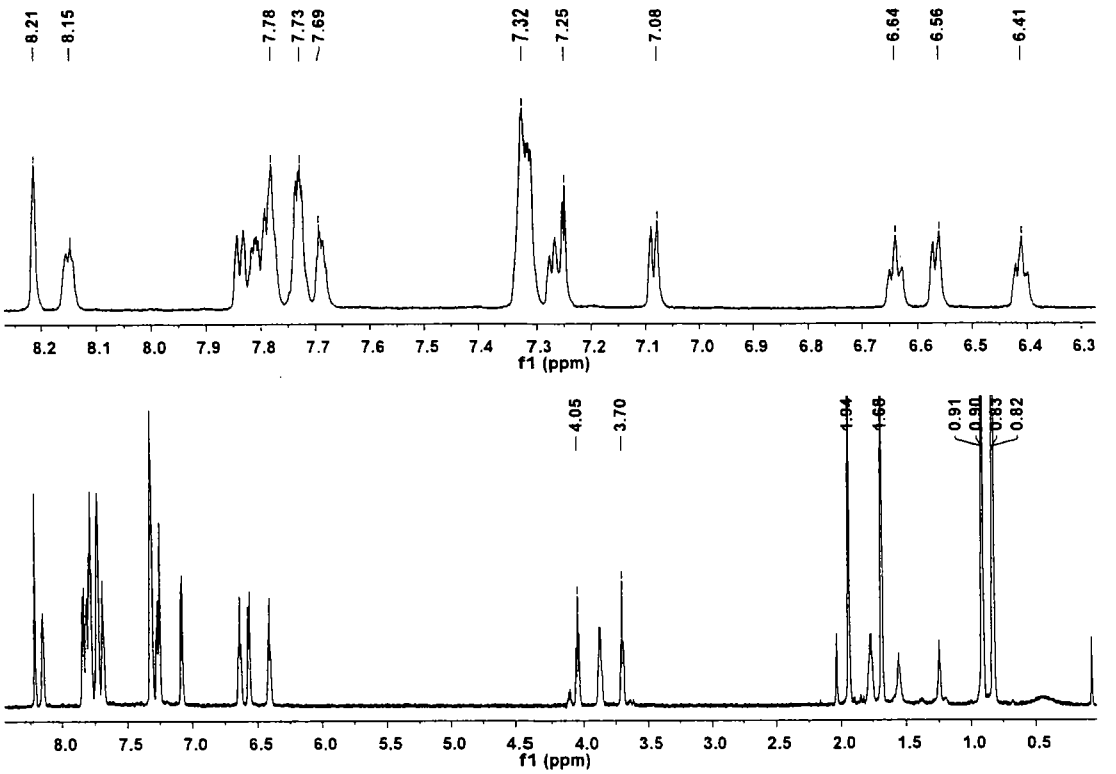


Figure B 27. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **L11down** (bottom) and the expanded spectrum in the aromatic region (top).

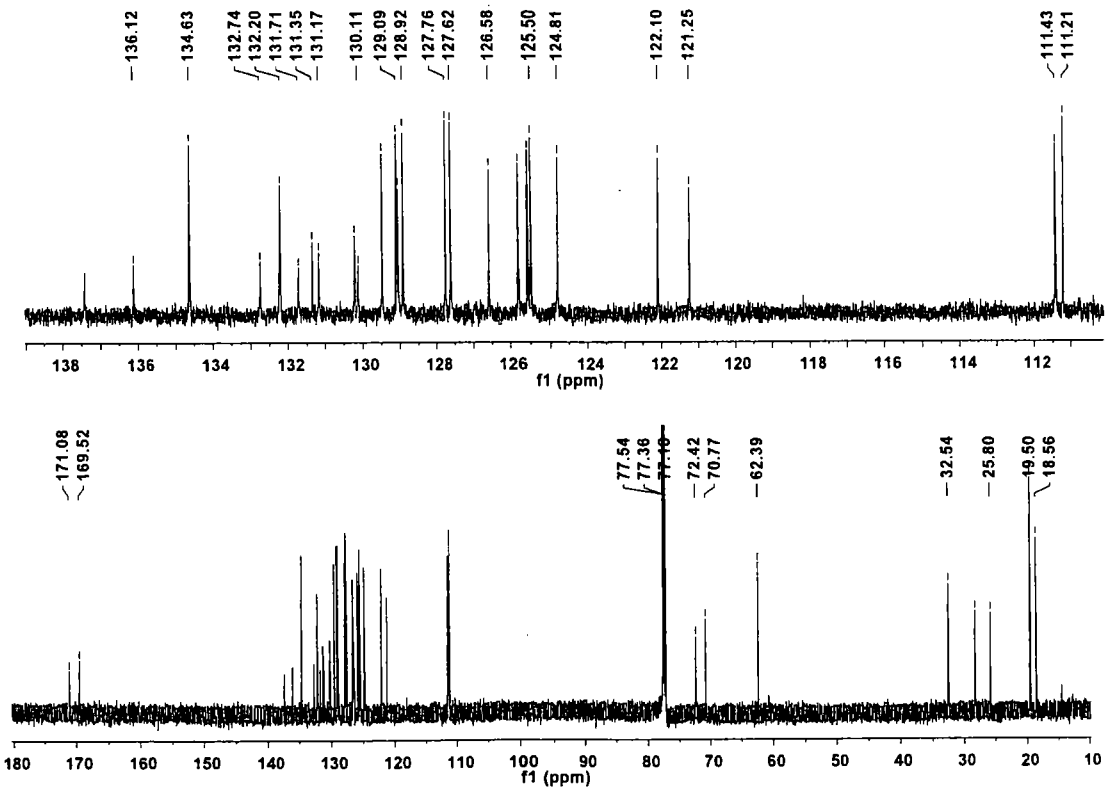


Figure B 28. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **L11down** (bottom) and the expanded spectrum in the aromatic region (top).

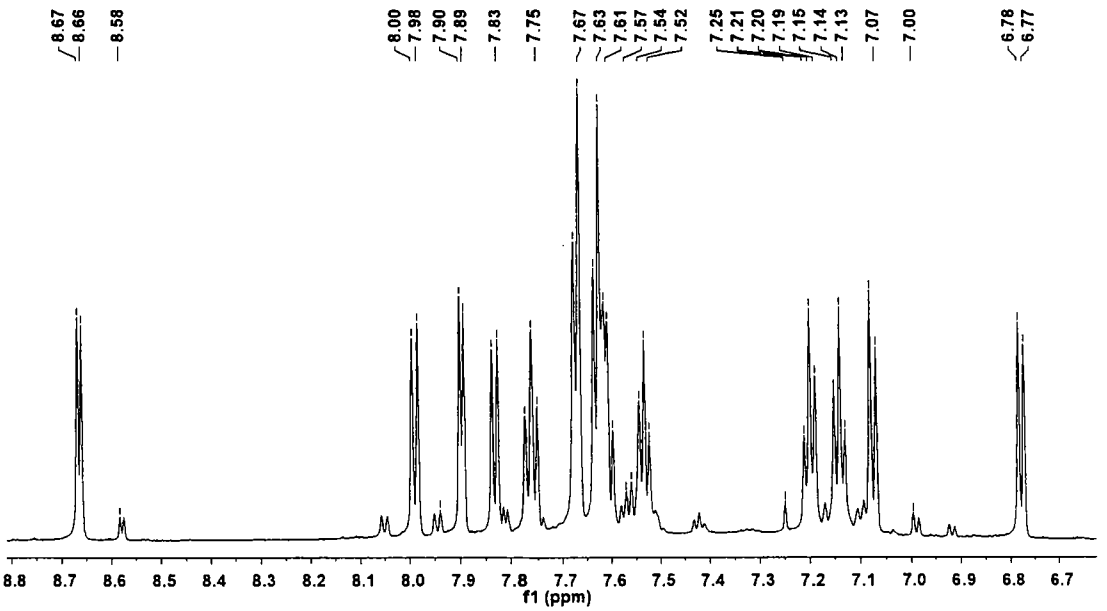


Figure B 29. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **L12**.

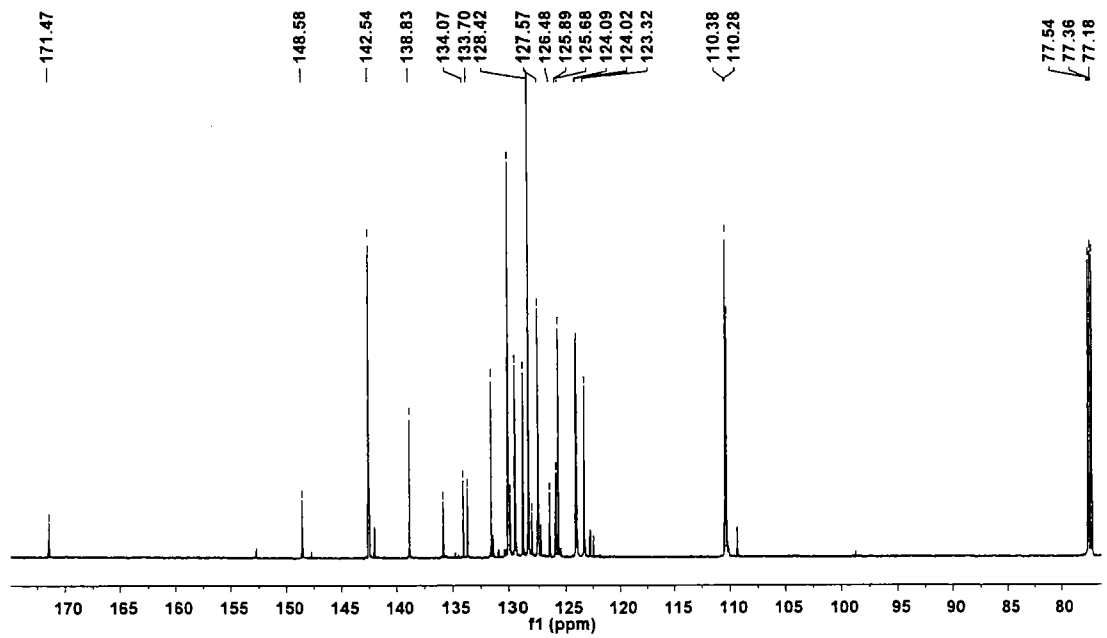


Figure B 30. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **L12**.

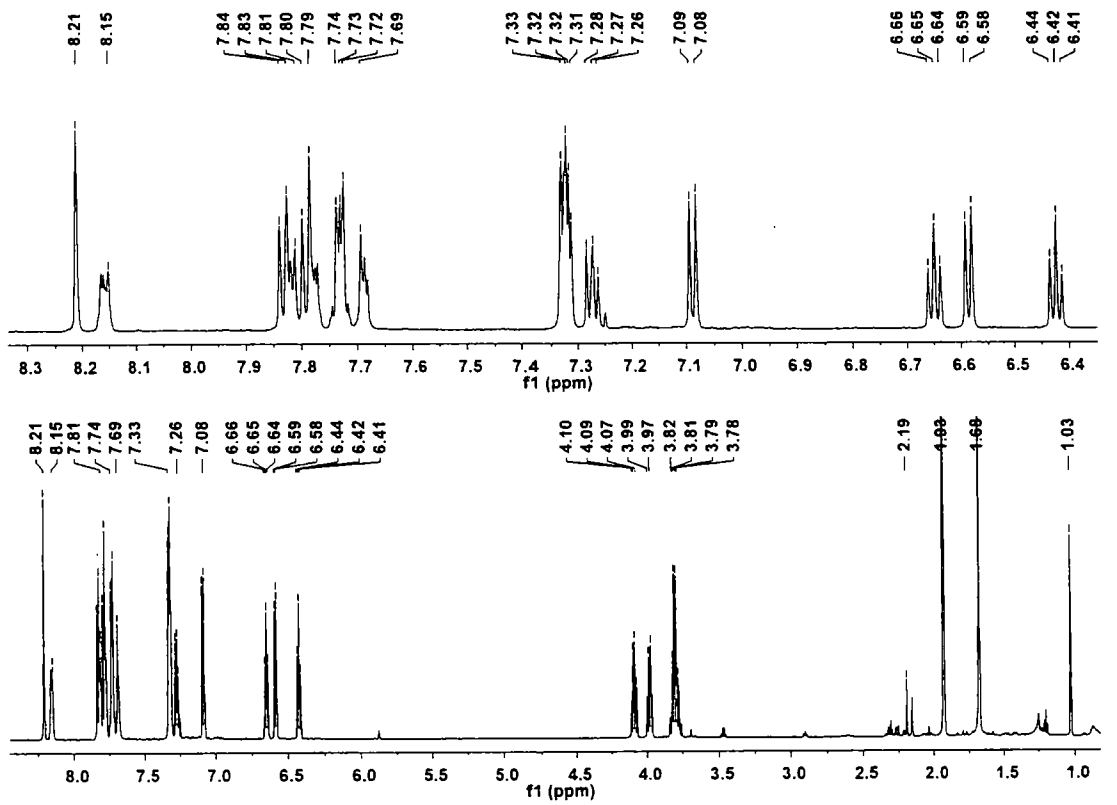


Figure B 31. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **L13up** (bottom) and the expanded spectrum in the aromatic region (top).

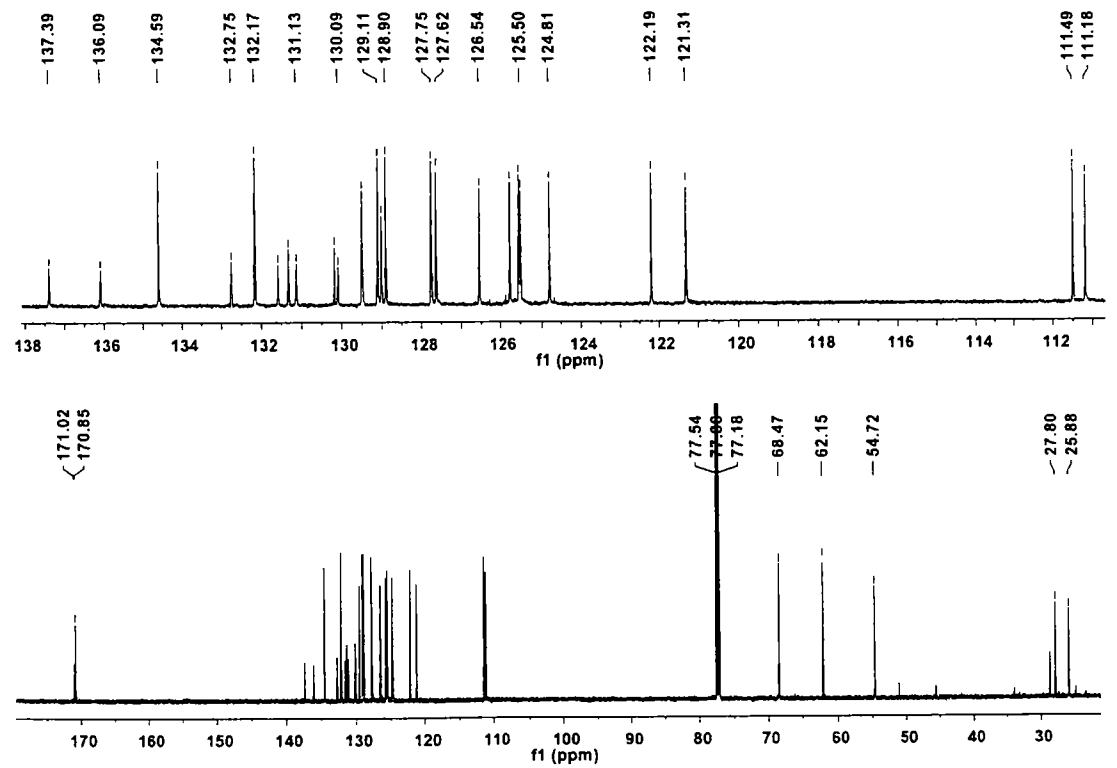


Figure B 32. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **L13up** (bottom) and the expanded spectrum in the aromatic region (top).

Palladium complexes

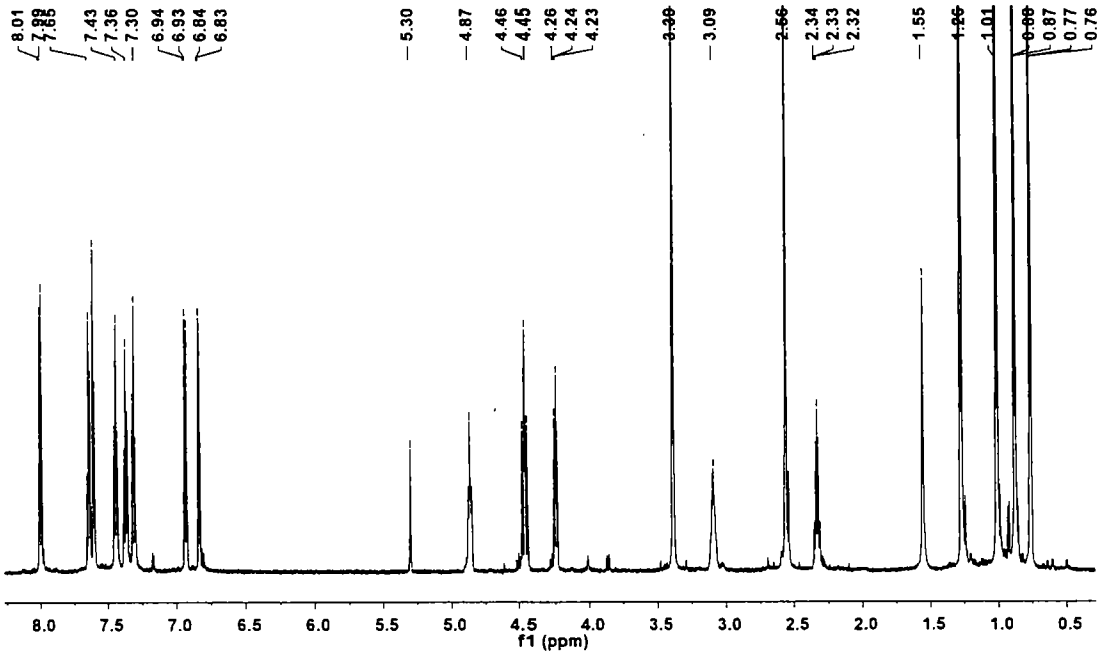


Figure B 33. The ^{1}H NMR (700 MHz, CD_2Cl_2) spectrum of **PdL2up**.

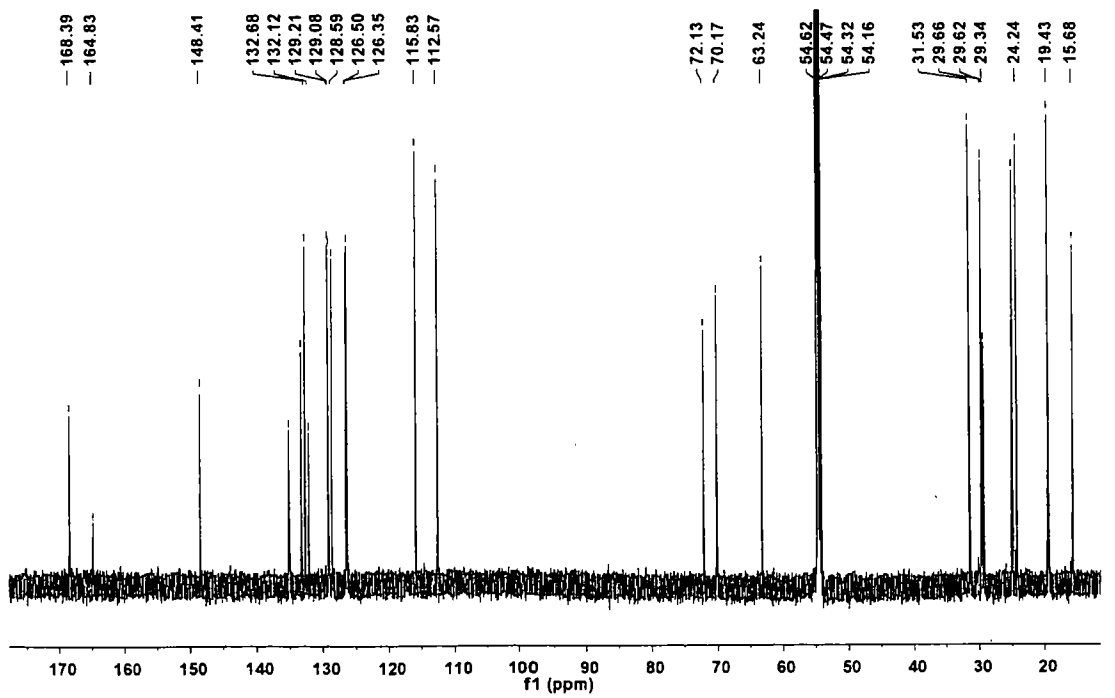


Figure B 34. The $^{13}C\{^{1}H\}$ NMR (175 MHz, CD_2Cl_2) spectrum of **PdL2up**.

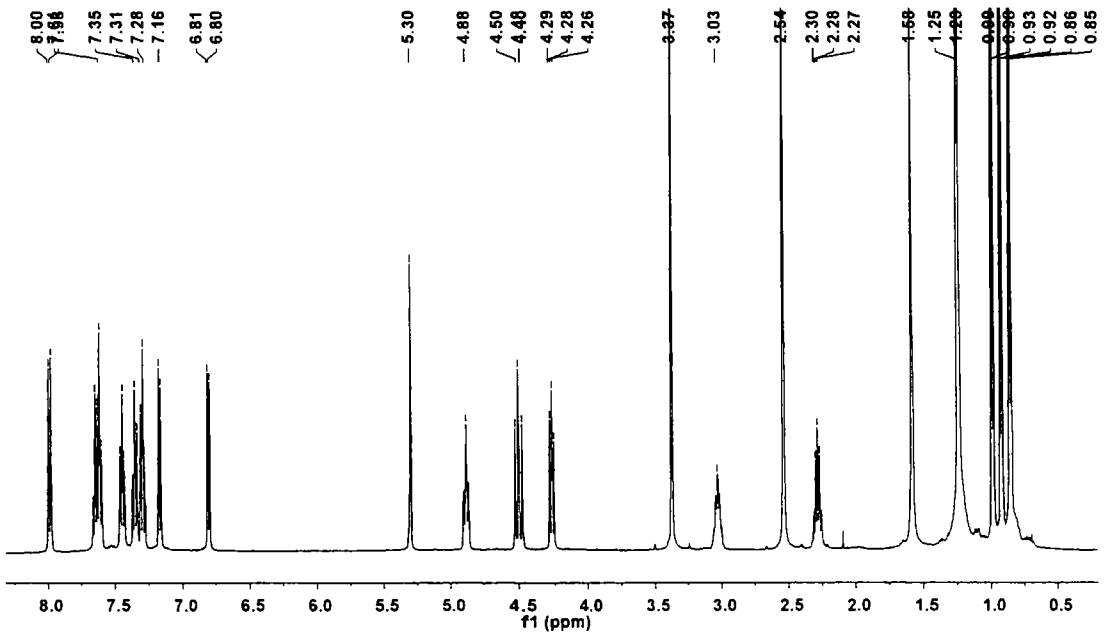


Figure B 35. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **PdL2down**.

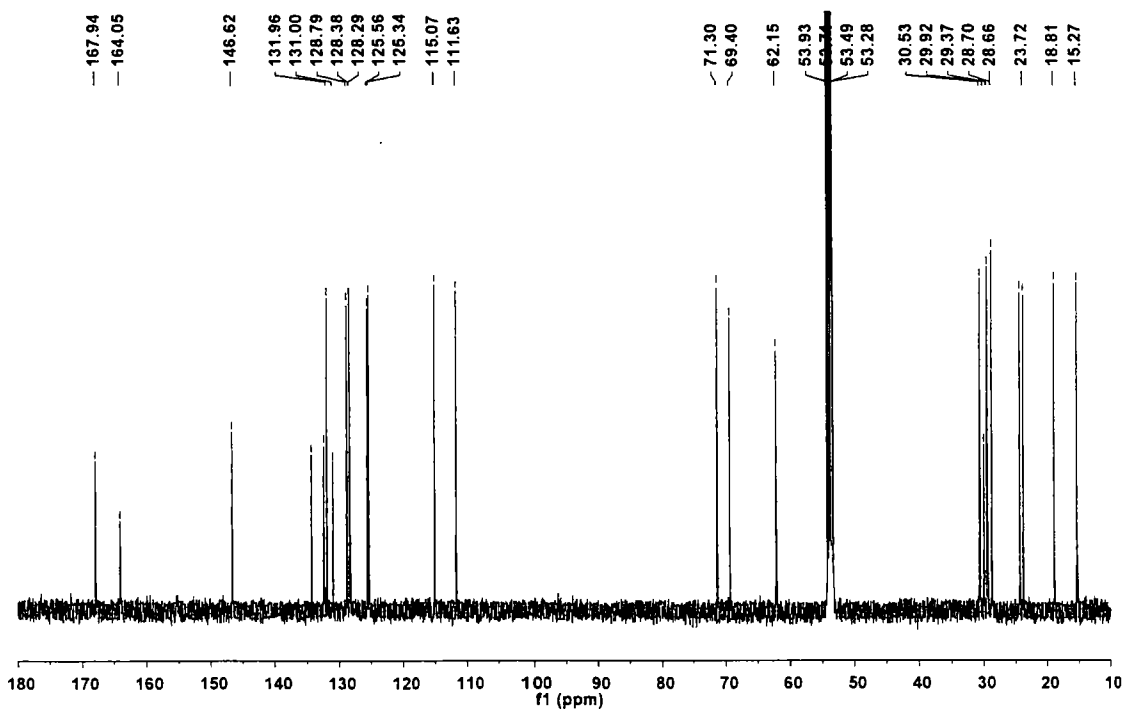


Figure B 36. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **PdL2down**.

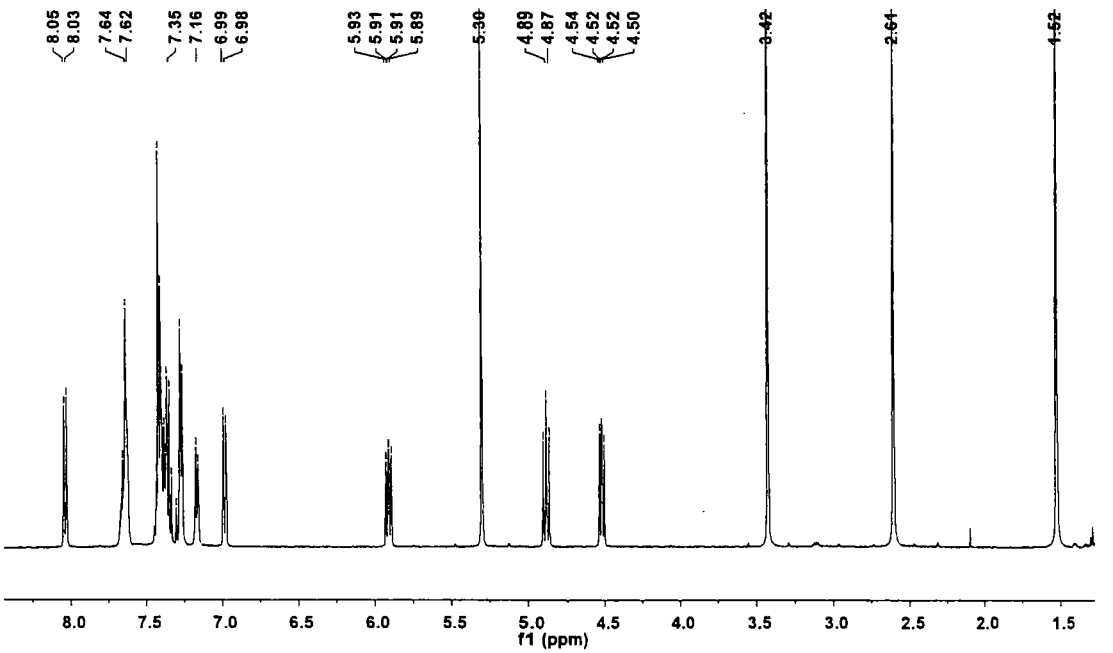


Figure B 37. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **PdL3**.

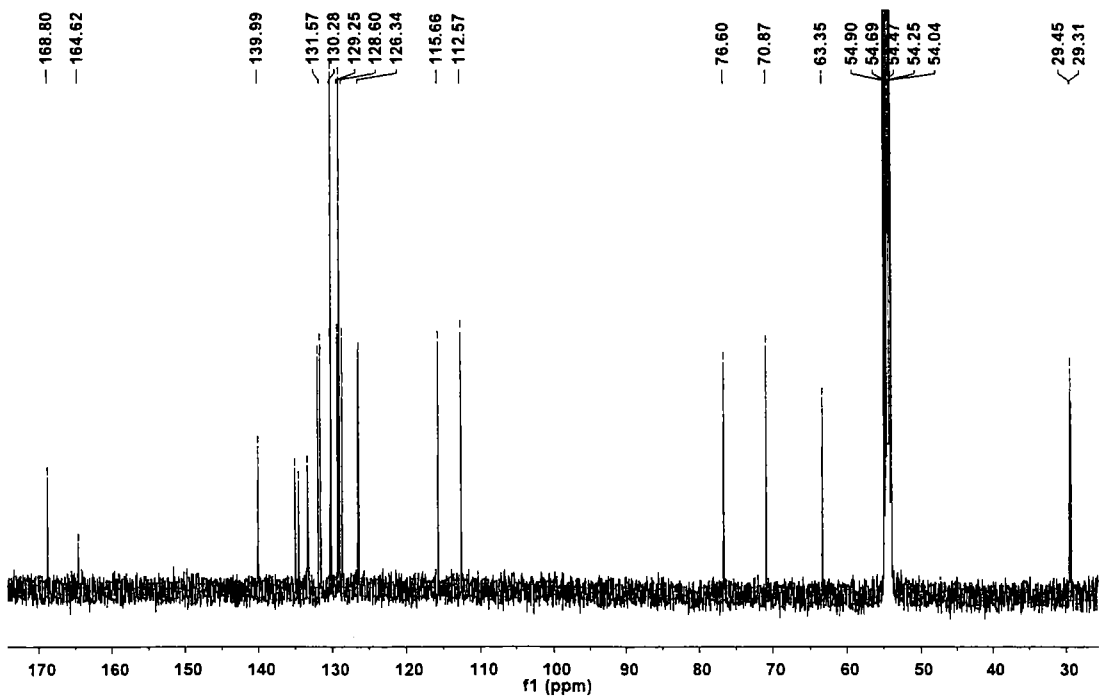


Figure B 38. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **PdL3**.

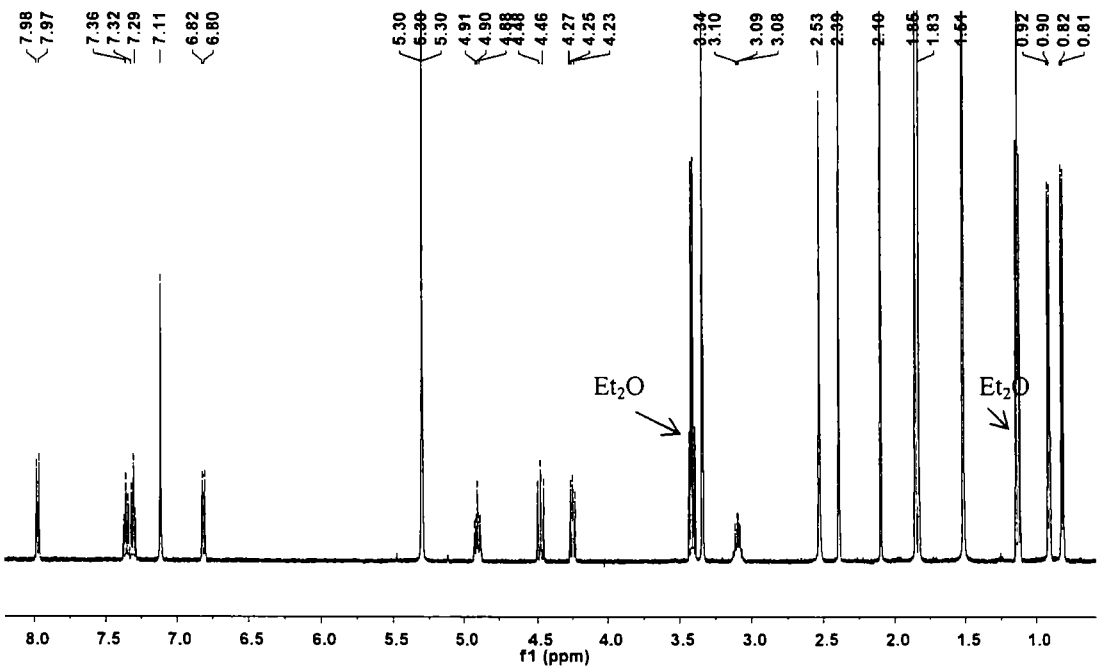


Figure B 39. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **PdL4**.

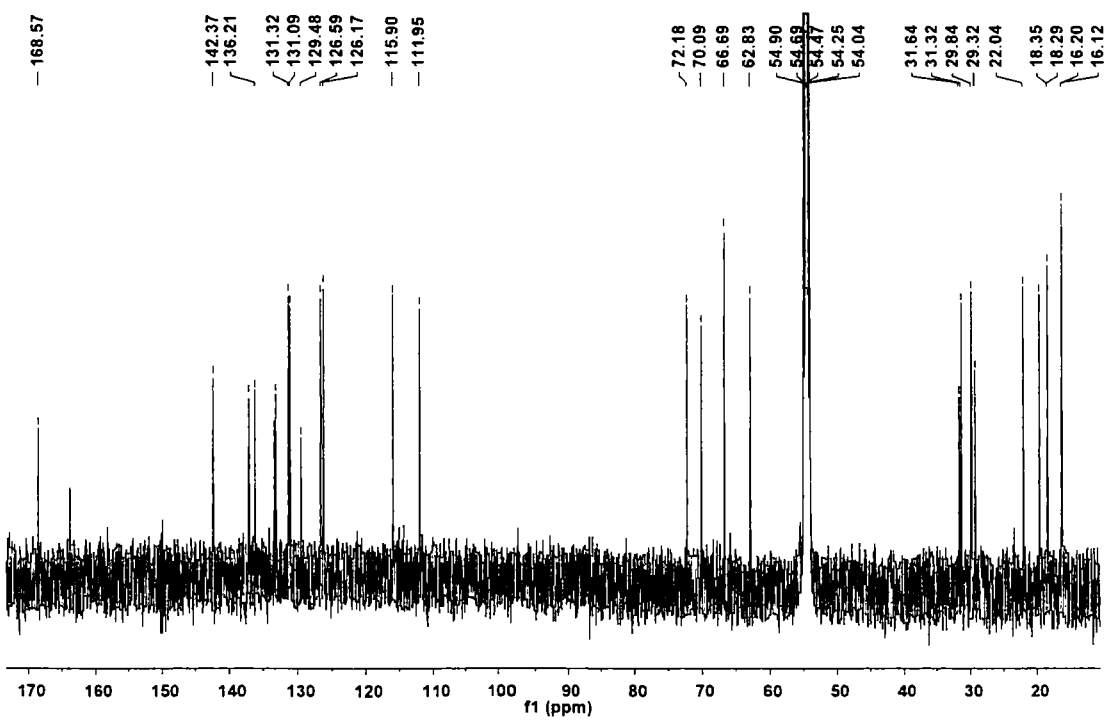


Figure B 40. The $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2) spectrum of **PdL4**.

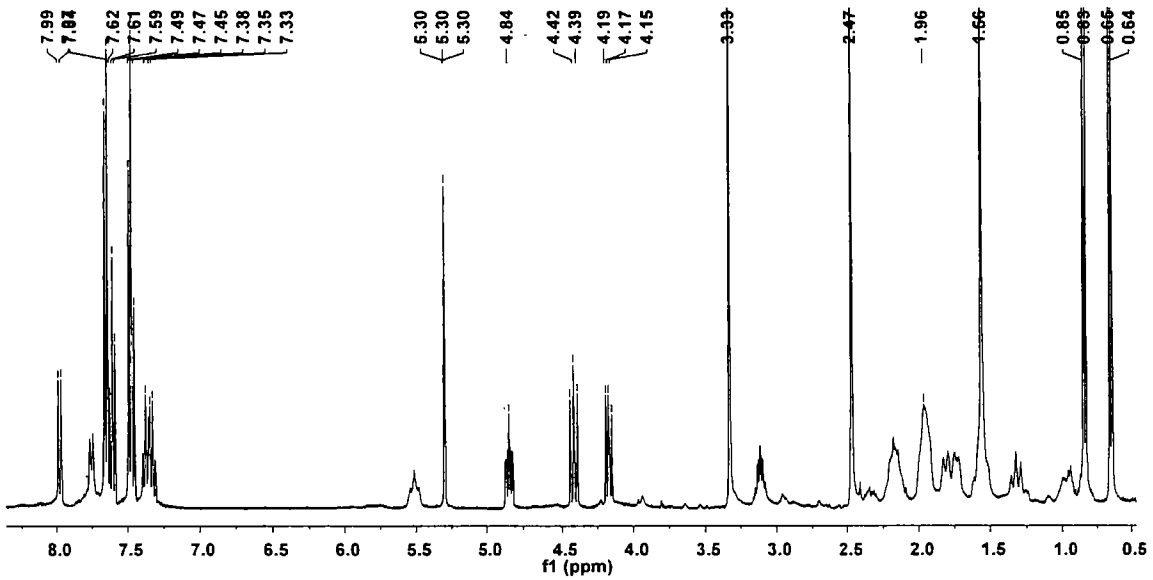


Figure B 41. The *in situ* ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **PdL5**.

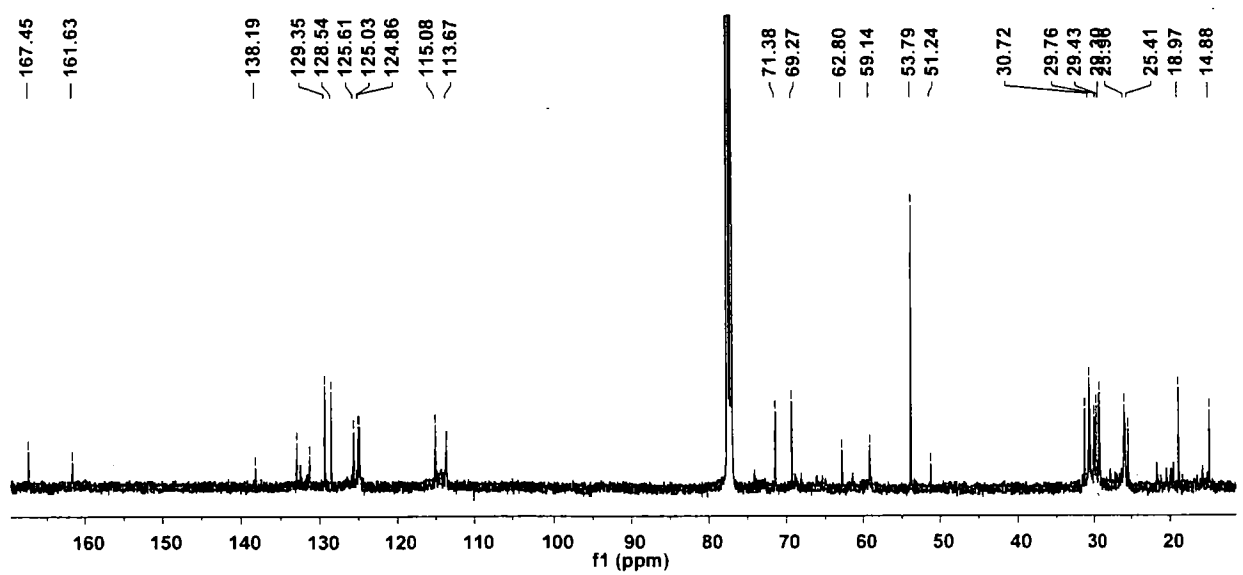


Figure B 42. The $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **PdL5**.

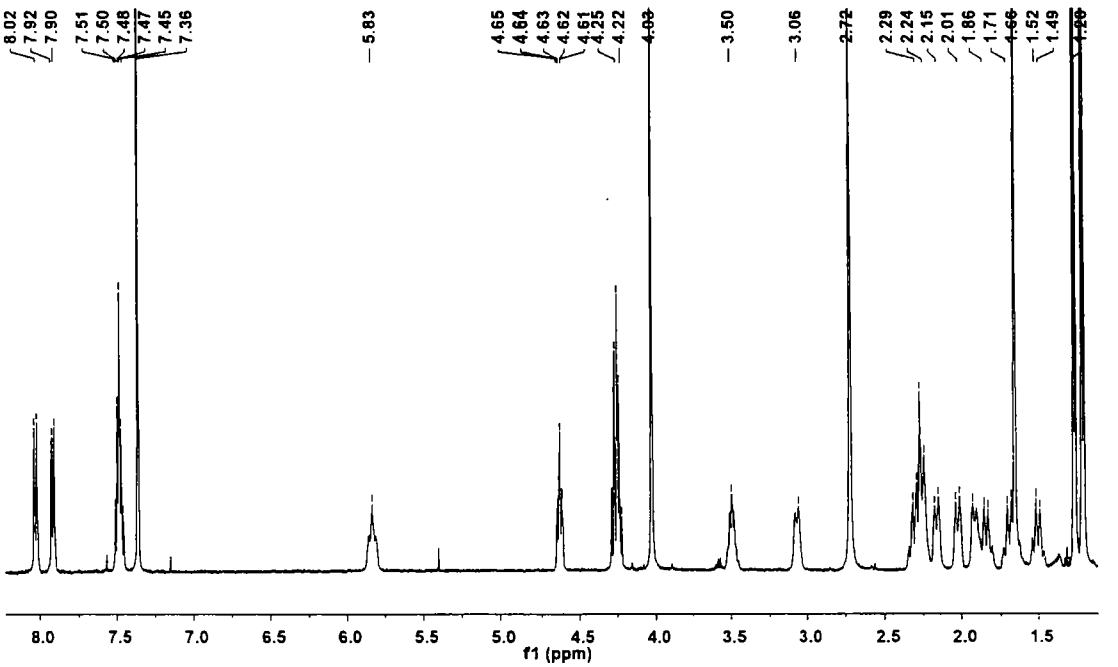


Figure B 43. The ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **Pd_2L5**.

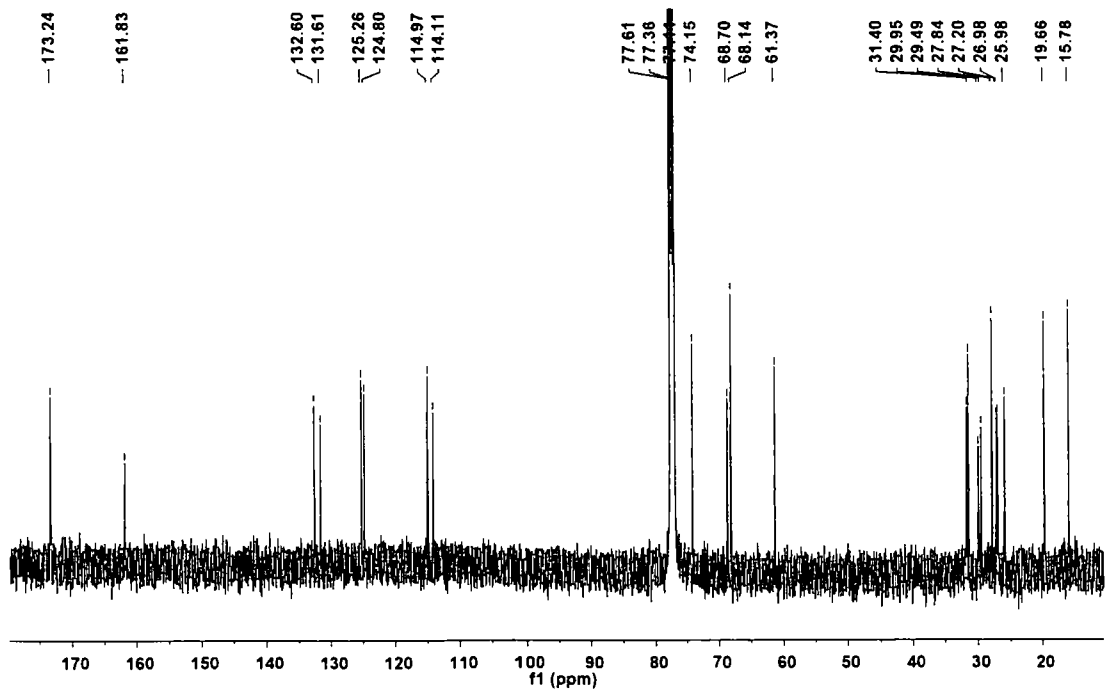


Figure B 44. The $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **Pd_2L5**.

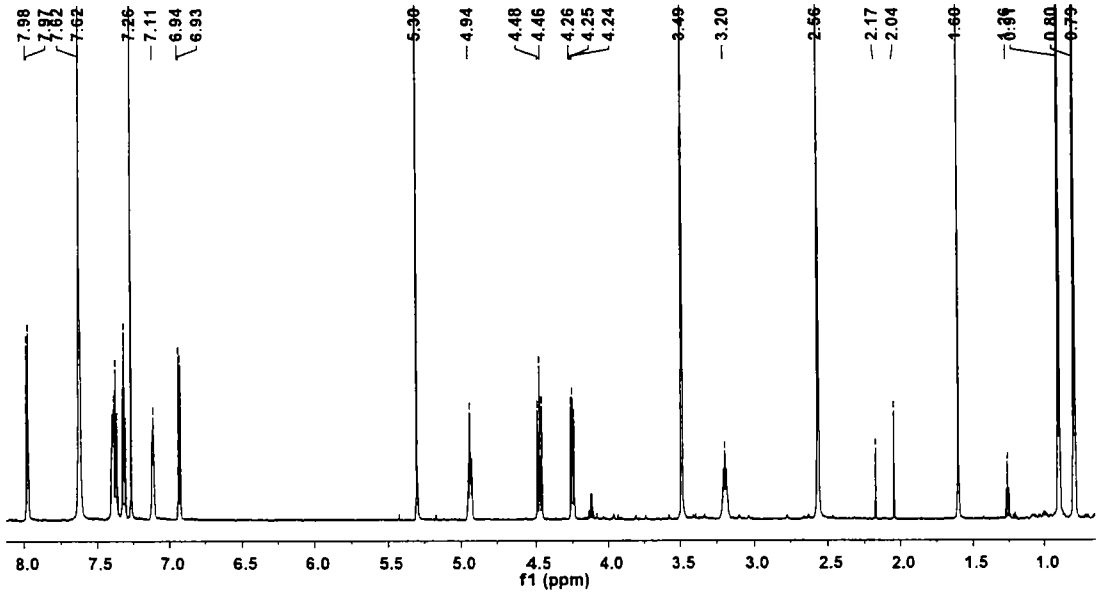


Figure B 45. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **PdL6**.

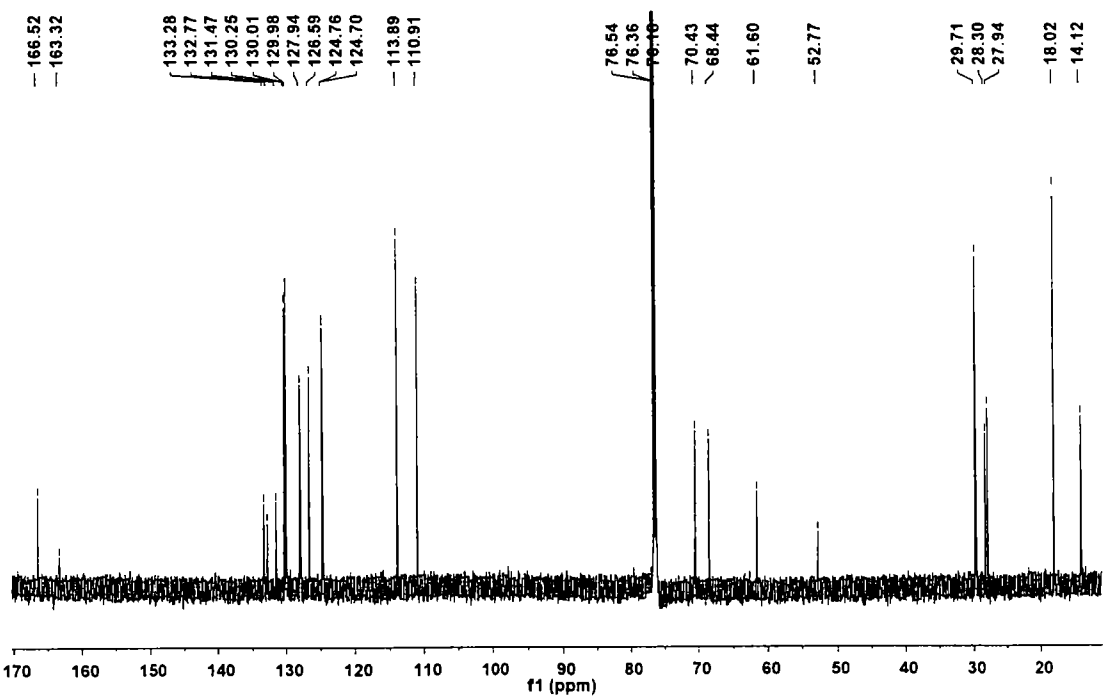


Figure B 46. The $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **PdL6**.

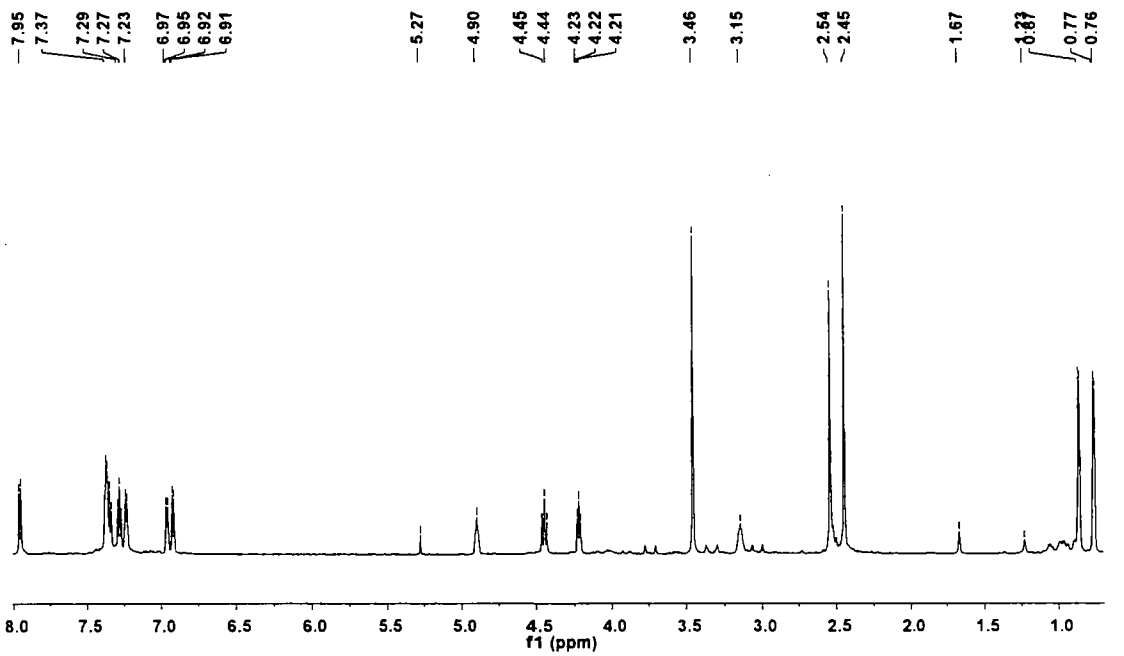


Figure B 47. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PdL7**.

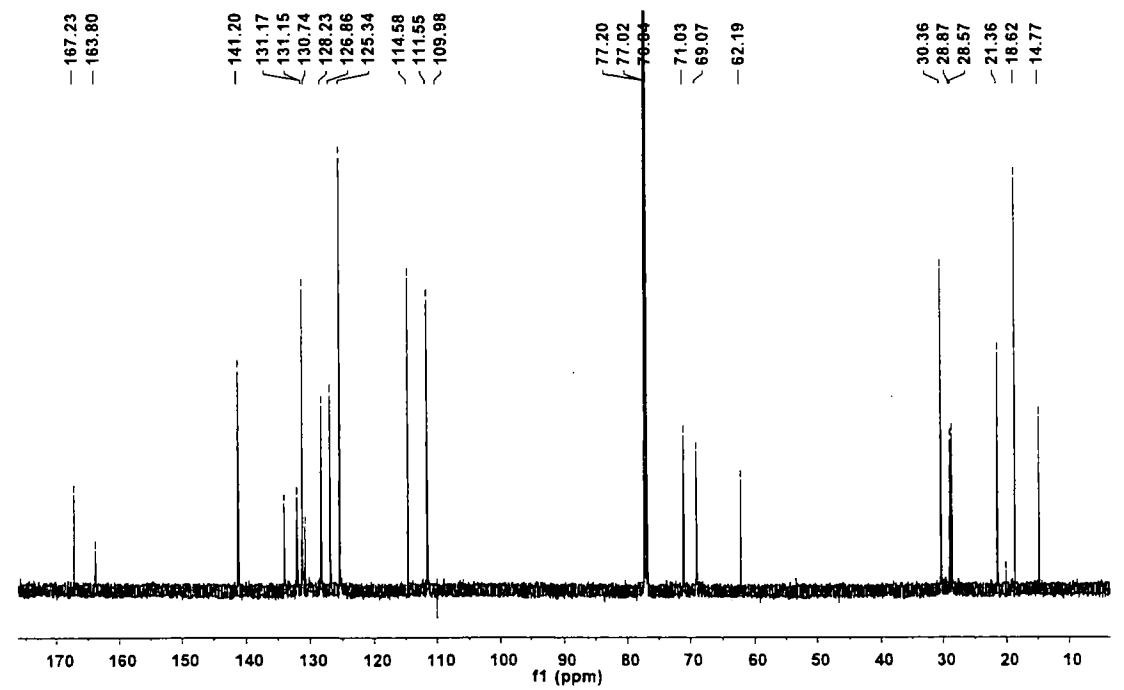


Figure B 48. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **PdL7**.

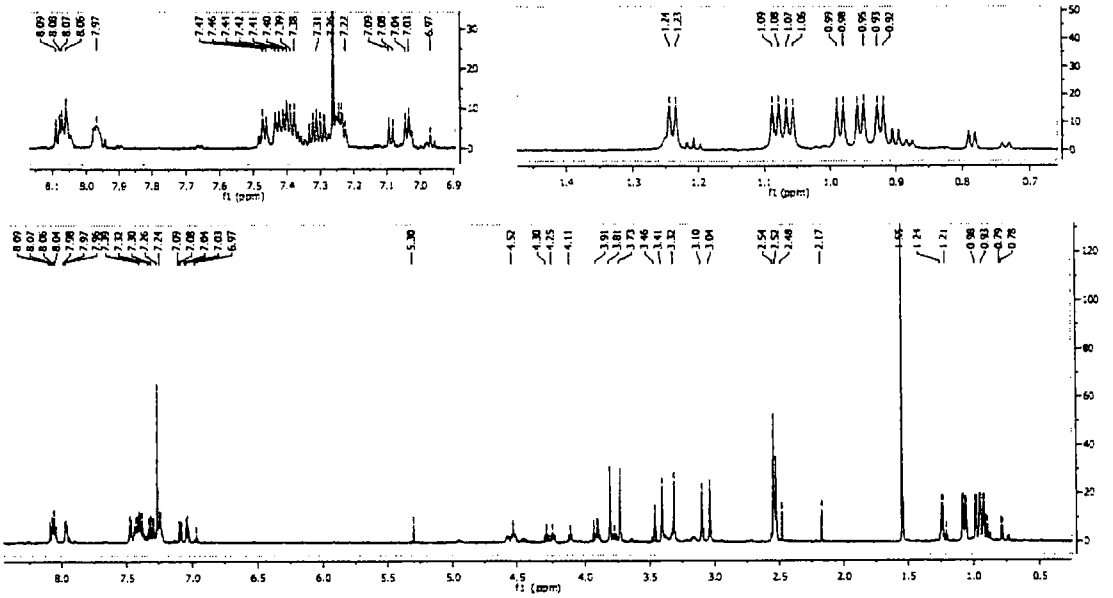


Figure B 49. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **Pd_3L7** (bottom); expanded in the aromatic region (top left) and in the aliphatic region (top right).

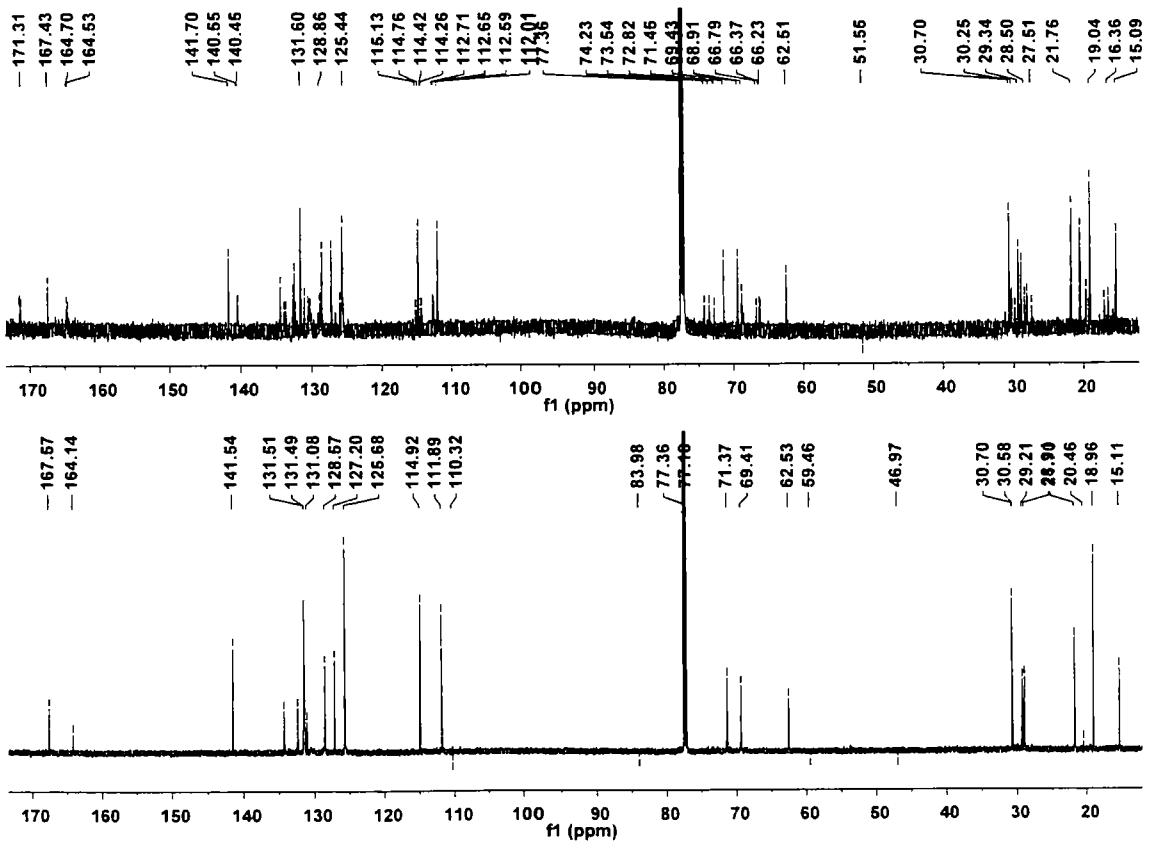


Figure B 50. The comparison of $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectra of PdL7 (bottom) and spectra of a mixture of PdL7 and Pd_3L7 (top).

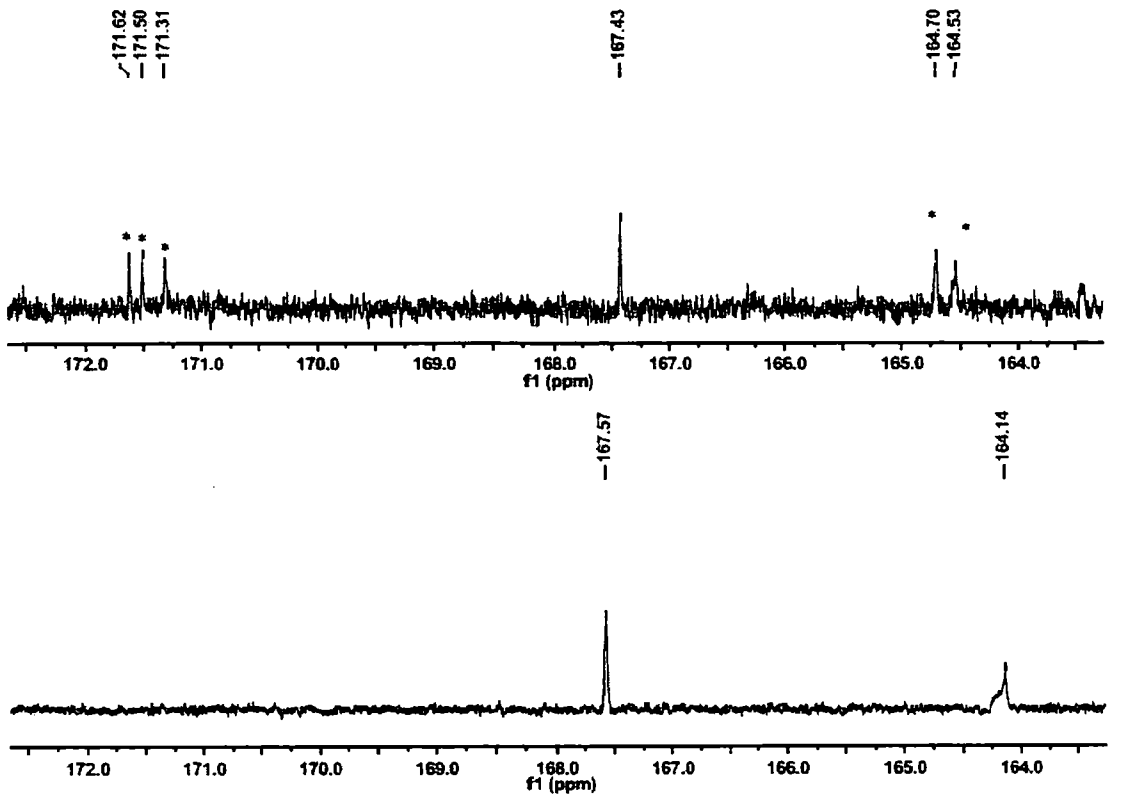


Figure B 51. The comparison of $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectra of **PdL7** (bottom) and **Pd_3L7** (*) (in the region of C=S and C=N signals).

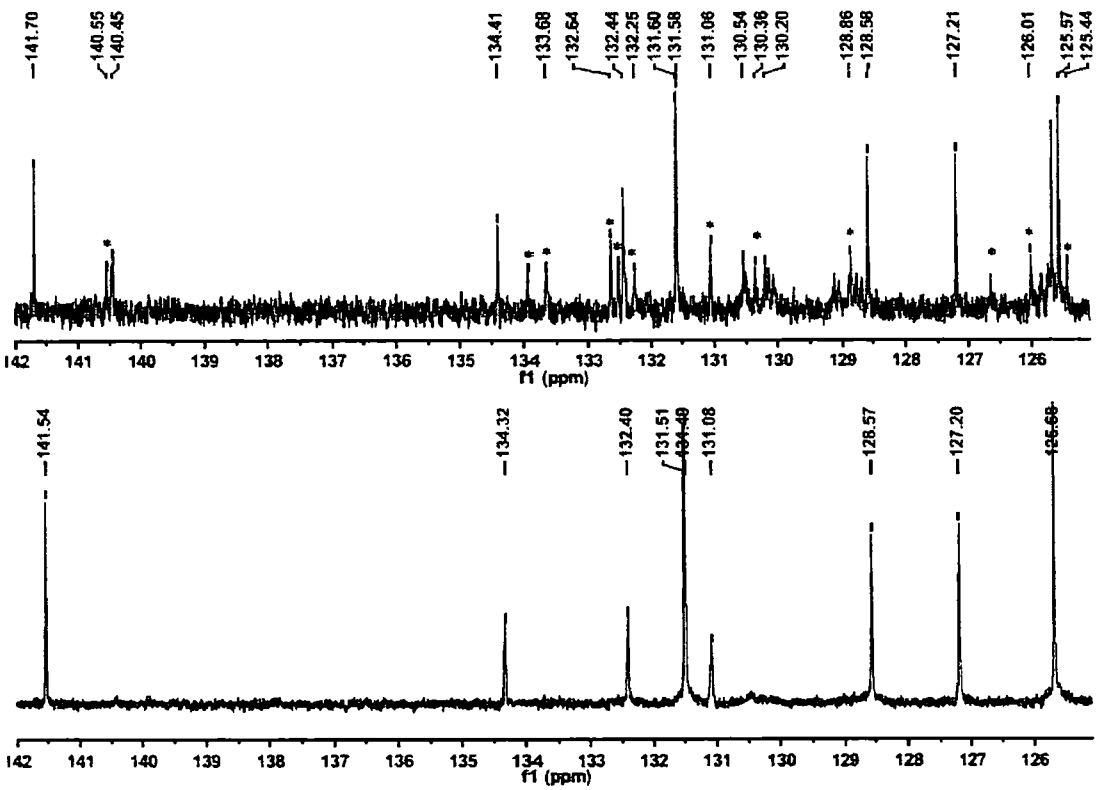


Figure B 52. The comparison of $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) spectra of **PdL7** (bottom) and **Pd_3L7** (*) (in the region of 125 – 144 ppm).

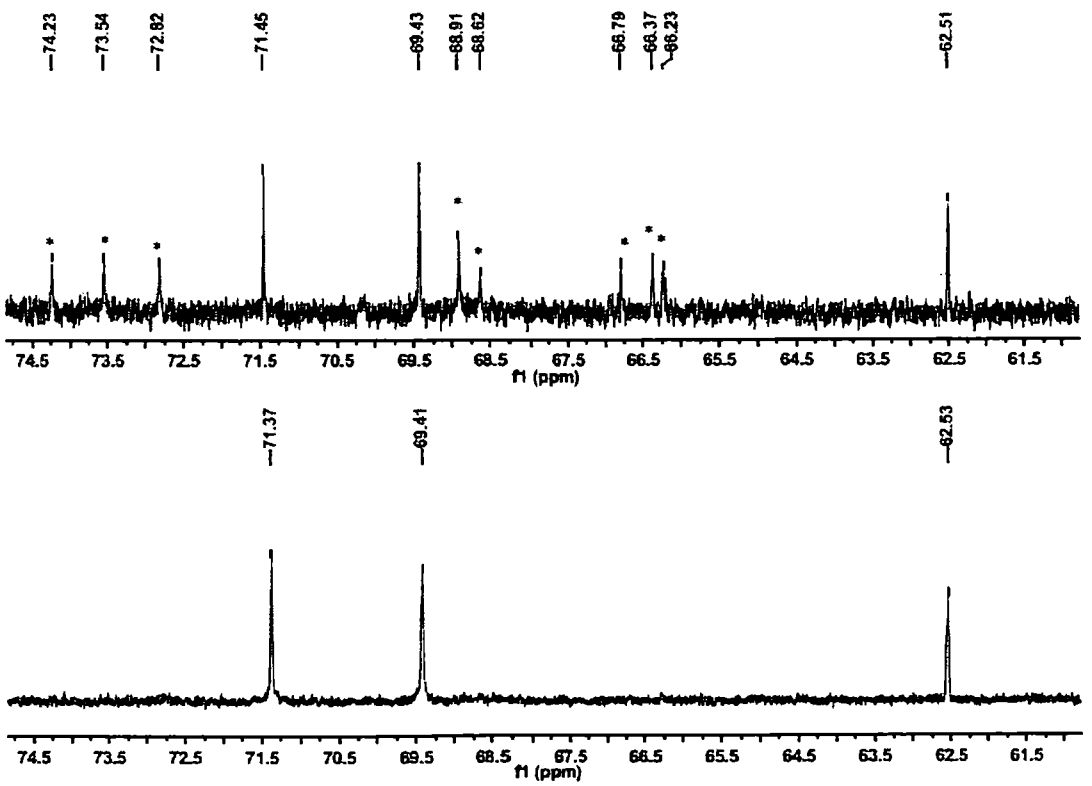


Figure B 53. The comparison of $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) spectra of **PdL7** (bottom) and **Pd_3L7** (*) (in the region of 60 – 75 ppm).

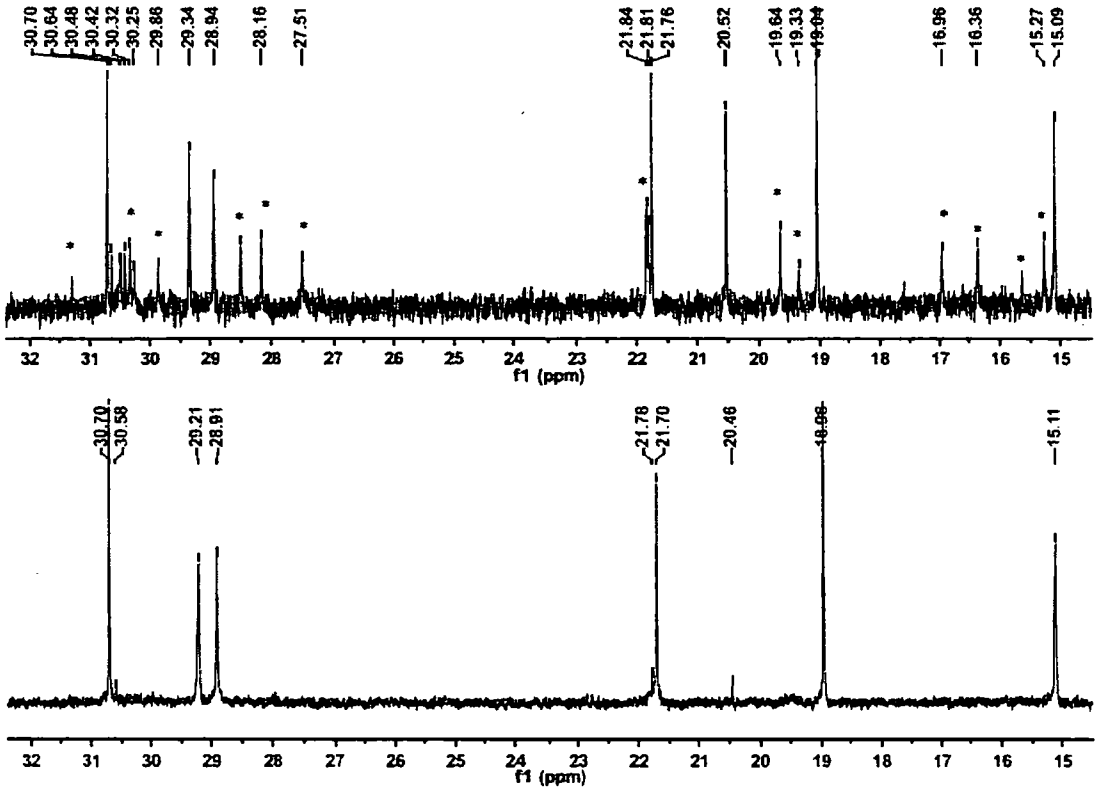


Figure B 54. The comparison of $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectra of **PdL7** (bottom) and **Pd_3L7** (*) (in the region of 15 – 33 ppm).

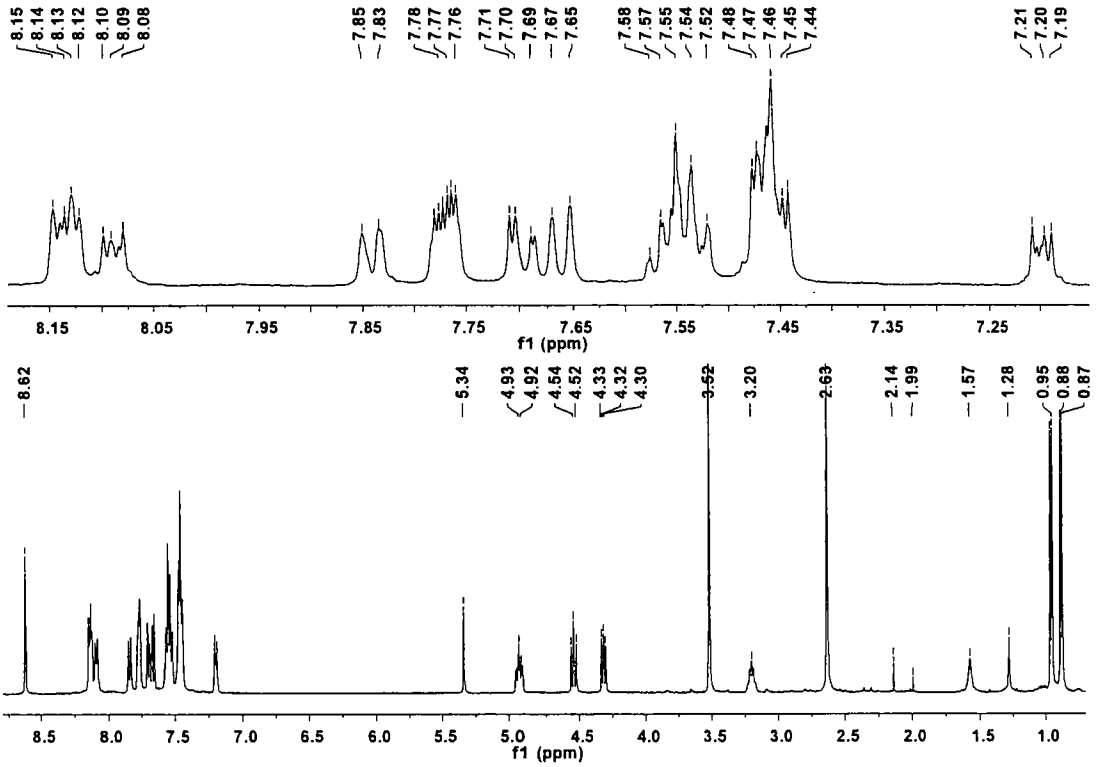


Figure B 55. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **PdL8** (bottom) and the expanded spectrum in the aromatic region (top).

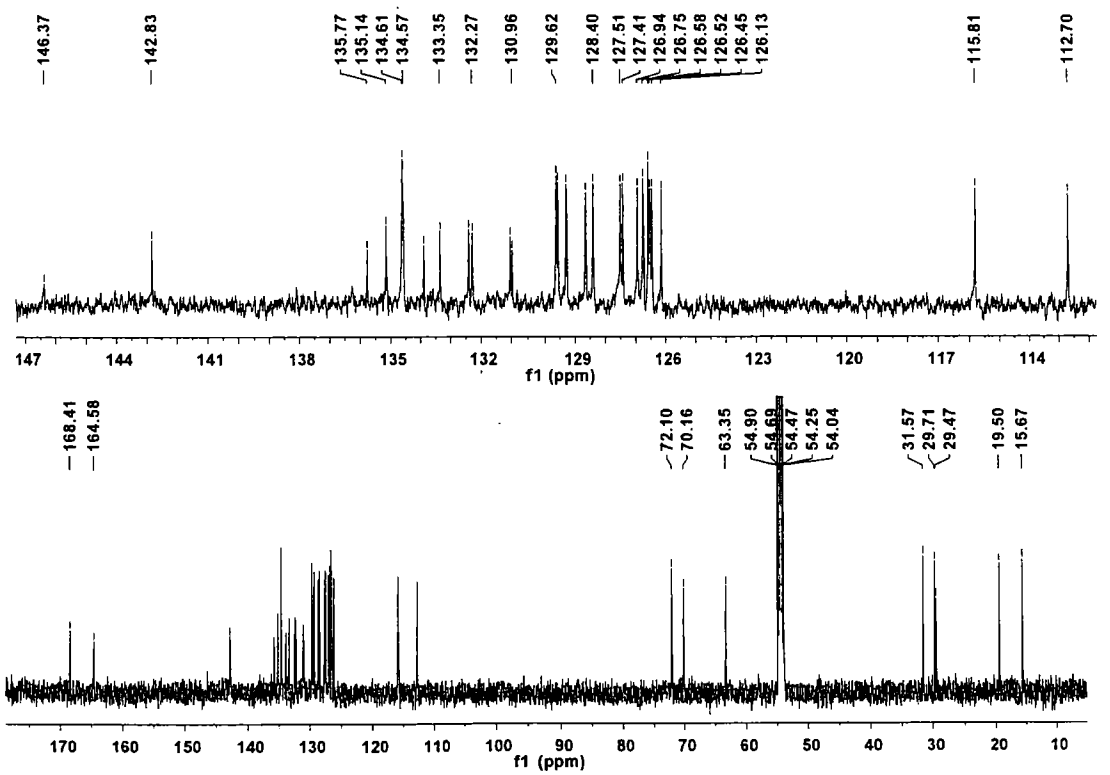


Figure B 56. The $^{13}C\{^{1}H\}$ NMR (500 MHz, CD_2Cl_2) spectrum of **PdL8** (bottom) and the expanded spectrum in the aromatic region (top).

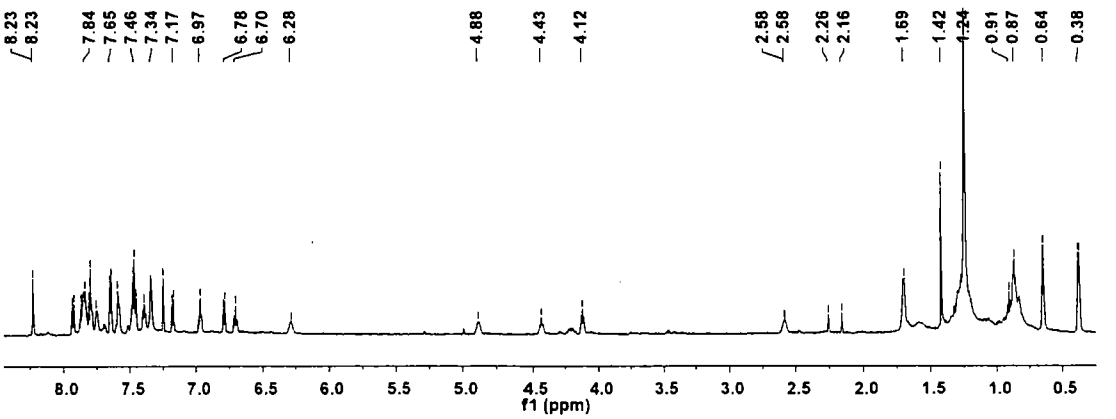


Figure B 57. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **Pd-R-L9up**.

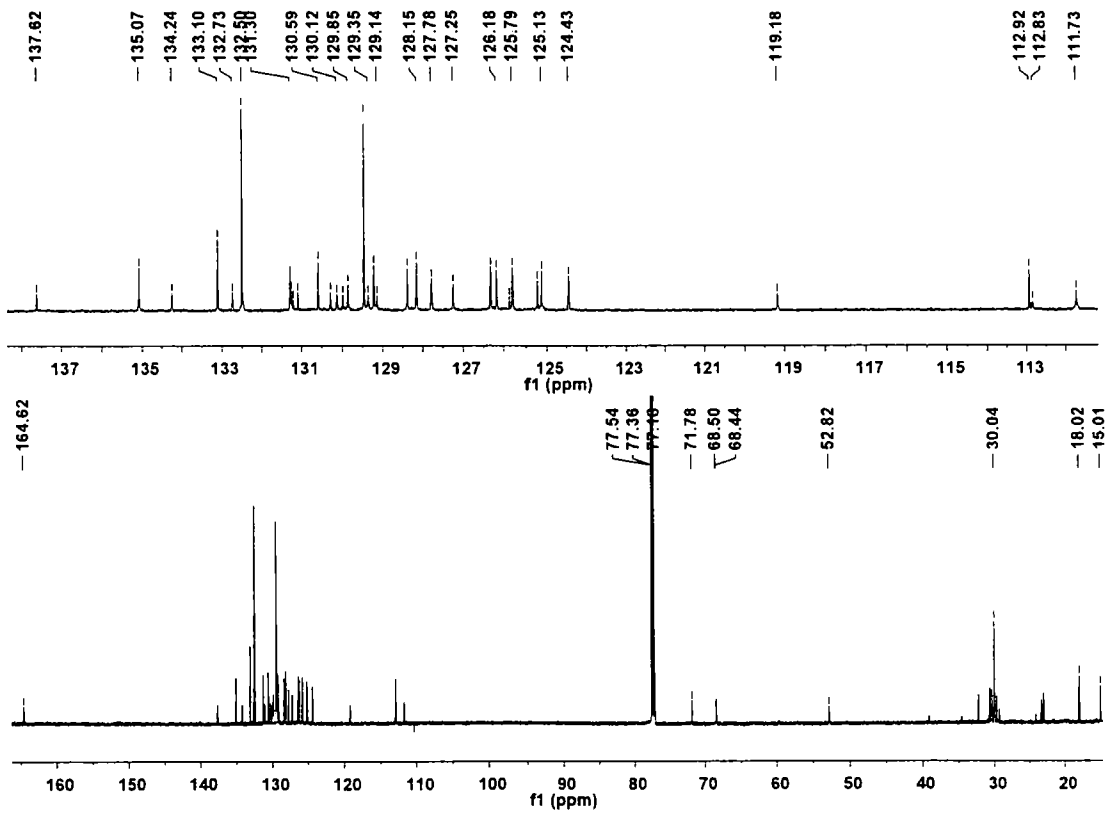


Figure B 58. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **Pd-R-L9up**.

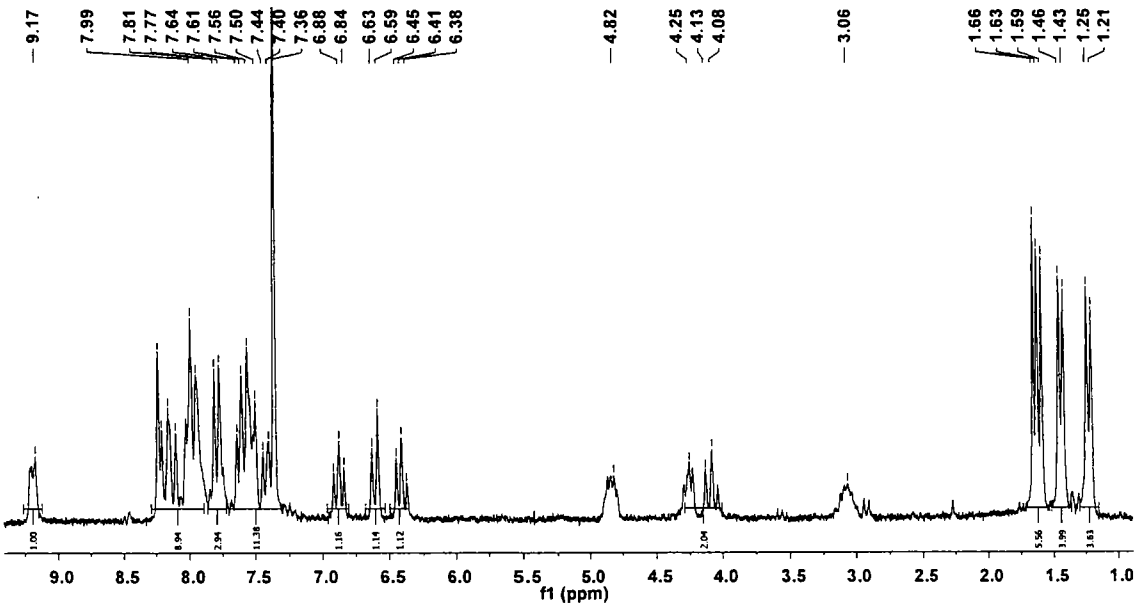


Figure B 59. The ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **Pd_2-S-L9down**.

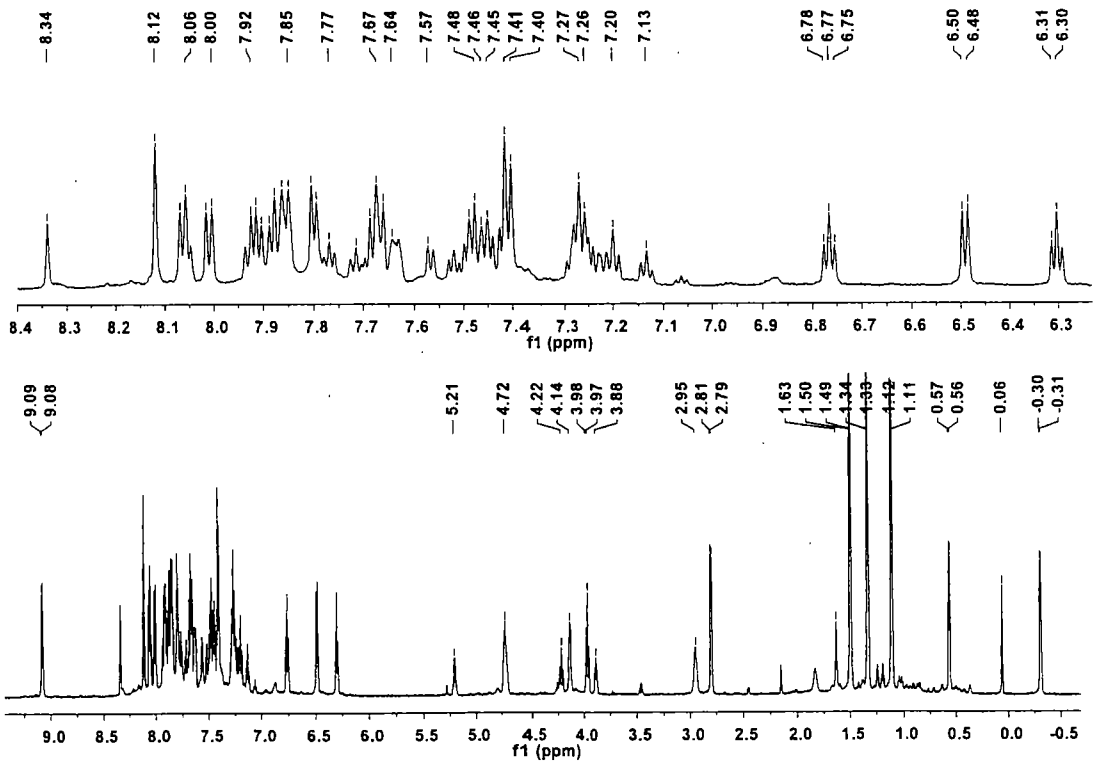


Figure B 60. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of the mixture of **Pd-S-L9down** and **Pd_2-S-L9down** (bottom) and the expanded spectrum in the aromatic region (top).

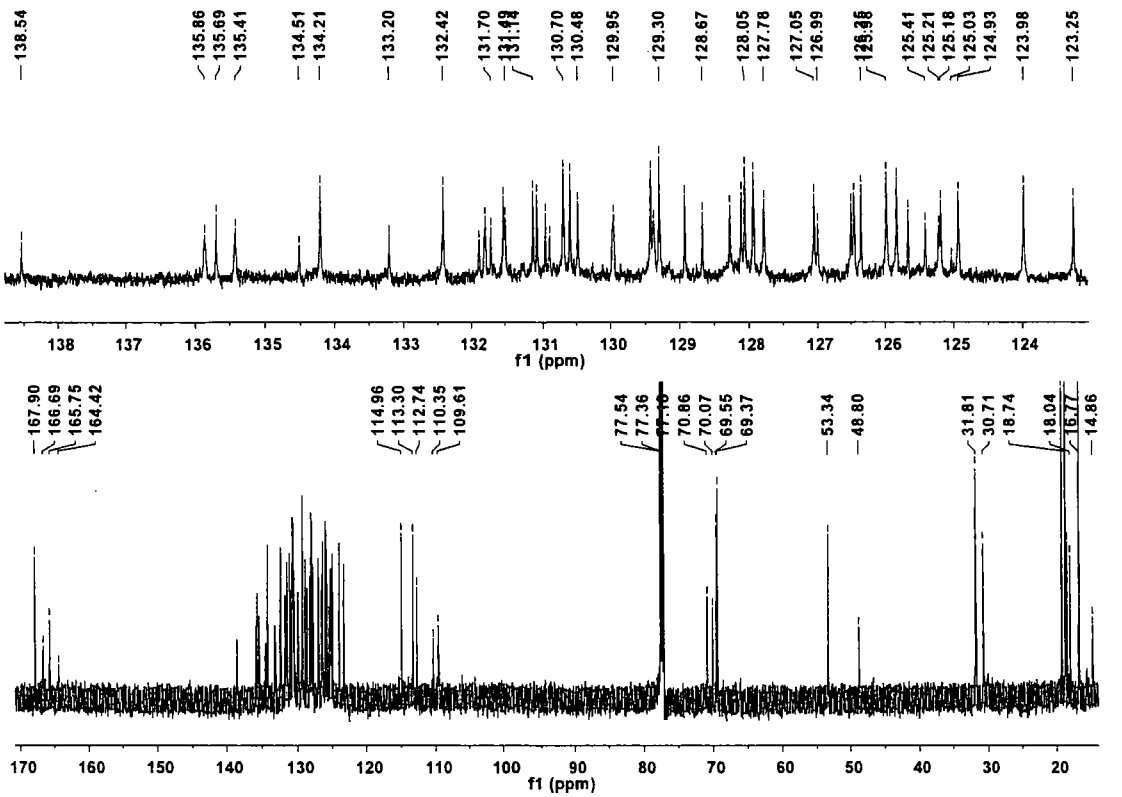


Figure B 61. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **Pd-S-L9down** and **Pd_2-S-L9down** (bottom) and the expanded spectrum in the aromatic region (top).

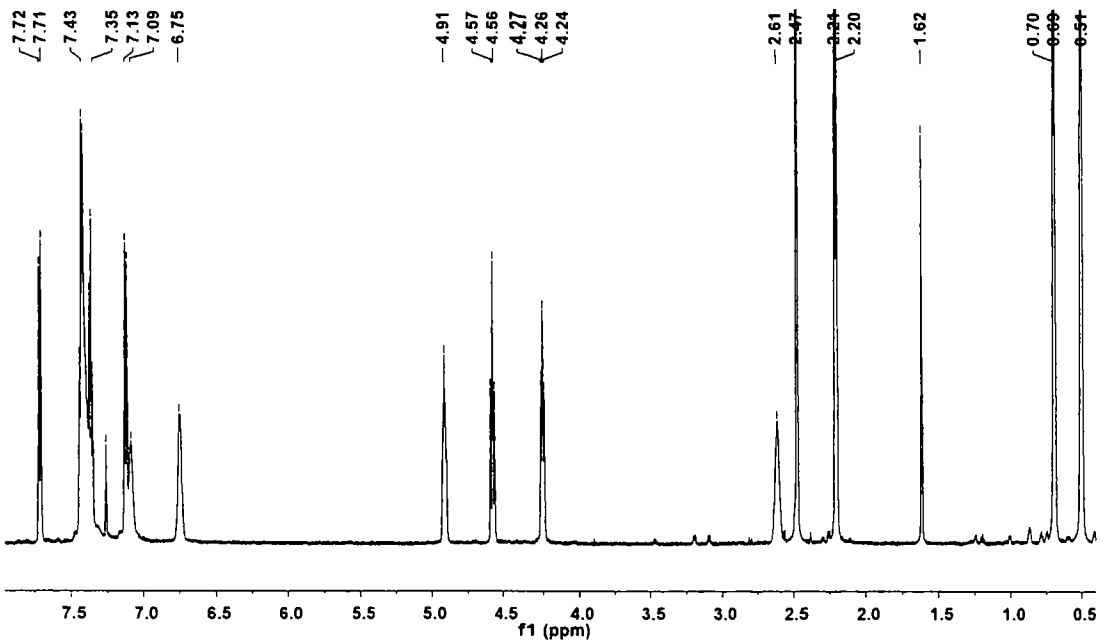


Figure B 62. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **Pd-R-L10**.

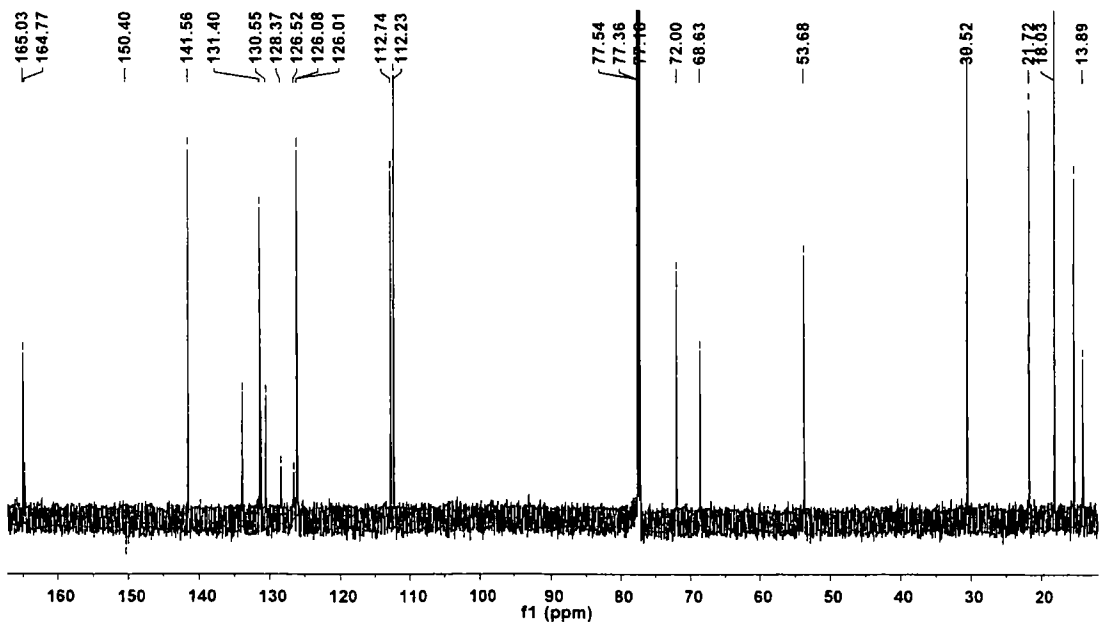


Figure B 63. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **Pd-R-L10**.

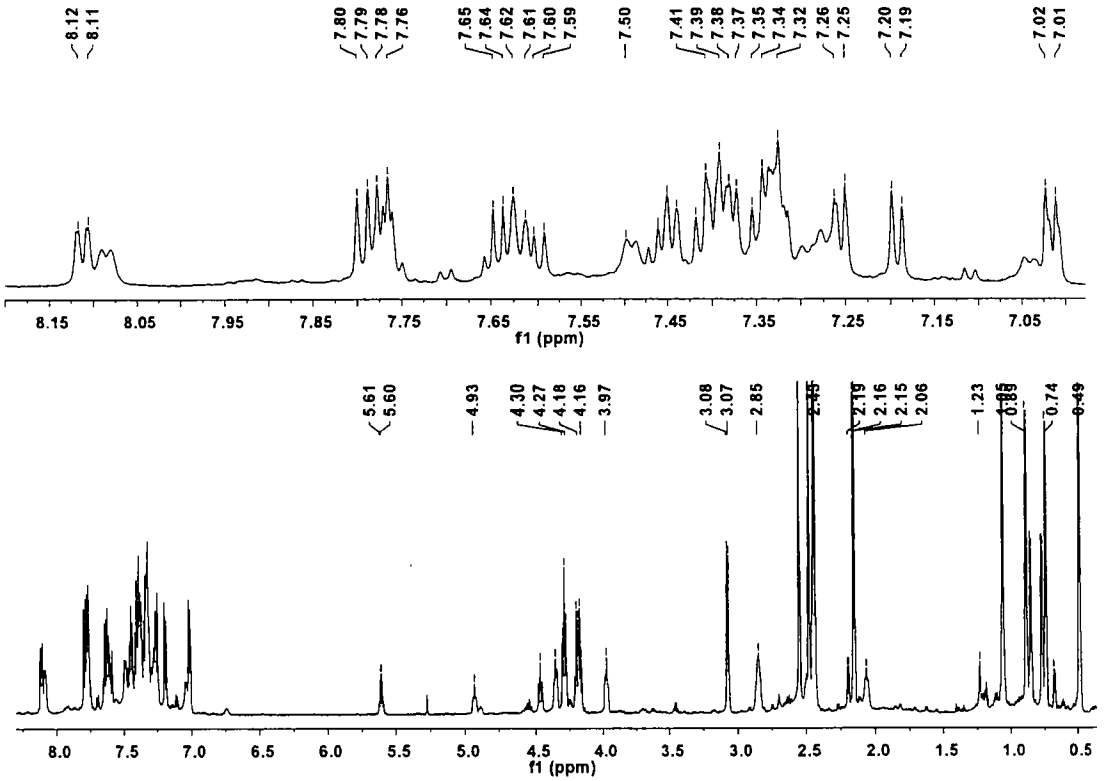


Figure B 64. The ^{1}H NMR (700 MHz, $CDCl_3$) of the mixture of **S-L10** palladium complexes (bottom) and the expanded spectrum in the aromatic region (top).

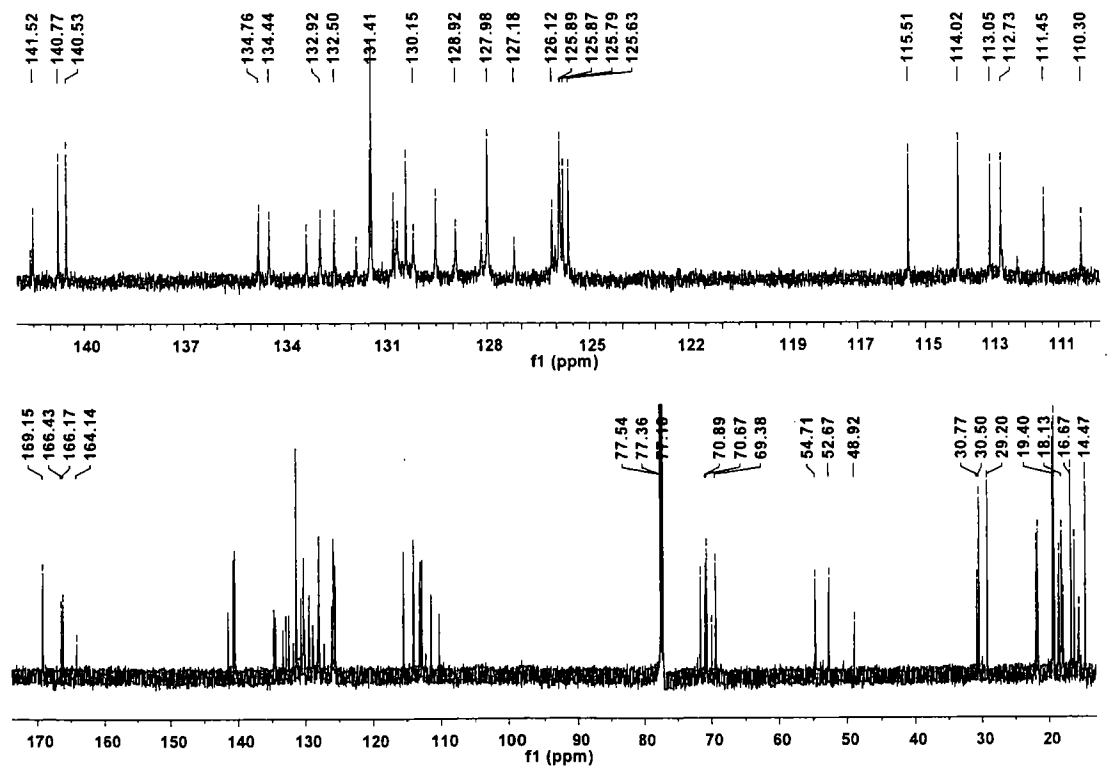


Figure B 65. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of the mixture of **S-L10** palladium complexes (bottom) and the expanded spectrum in the aromatic region (top).

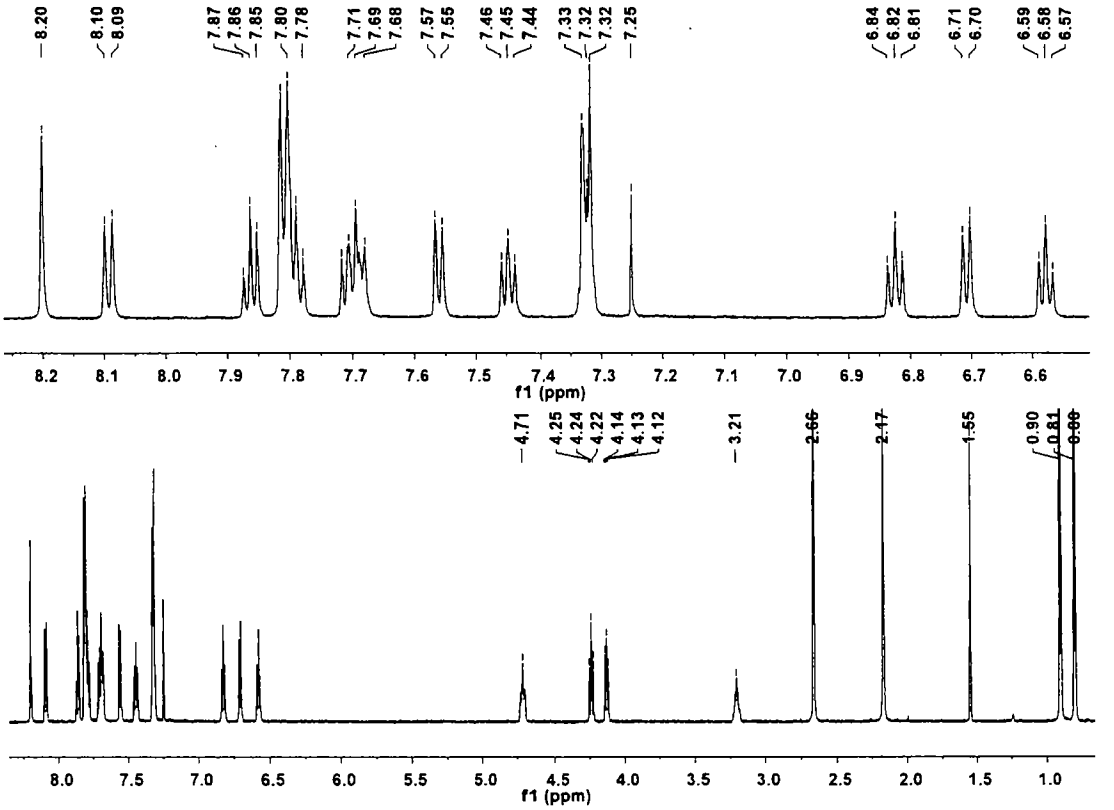


Figure B 66. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PdL11up** (bottom) and the expanded spectrum in the aromatic region (top).

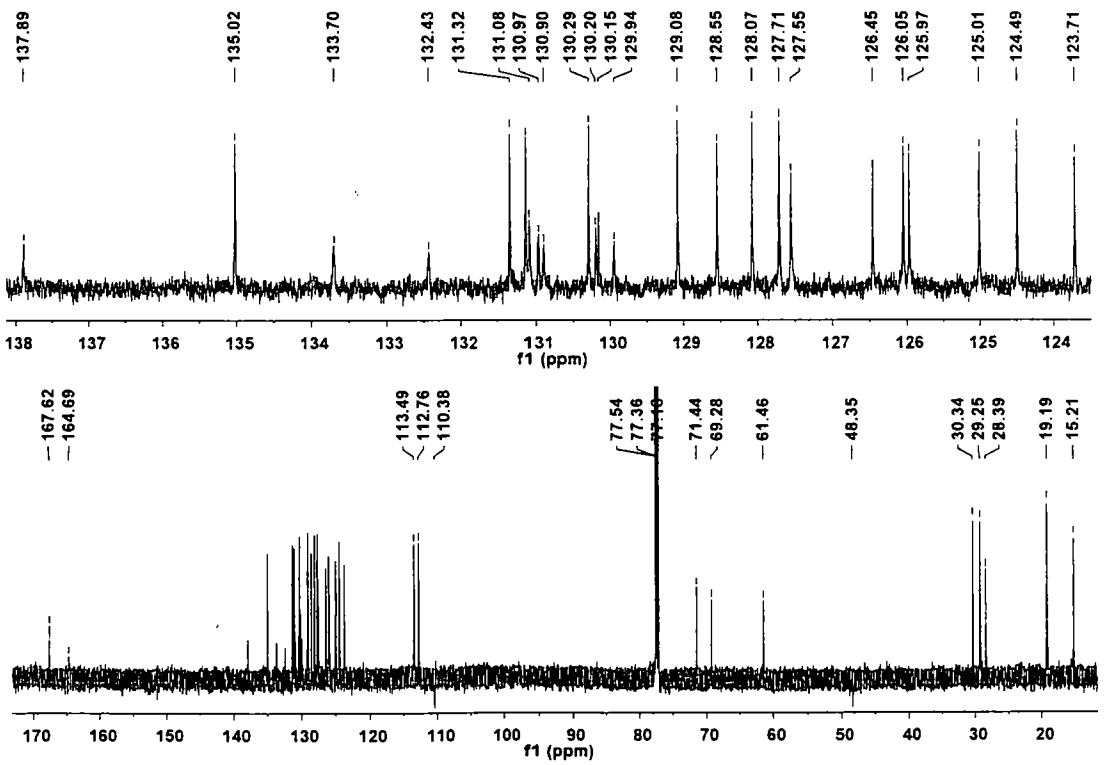


Figure B 67. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **PdL11up** (bottom) and the expanded spectrum in the aromatic region (top).

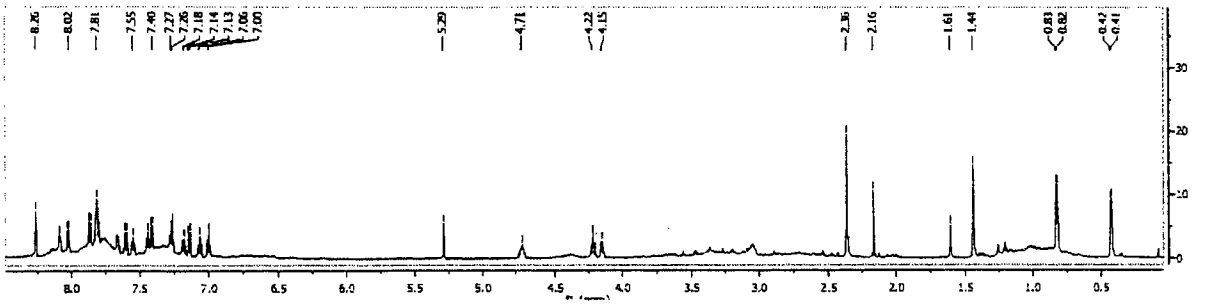


Figure B 68. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PdL11down**.

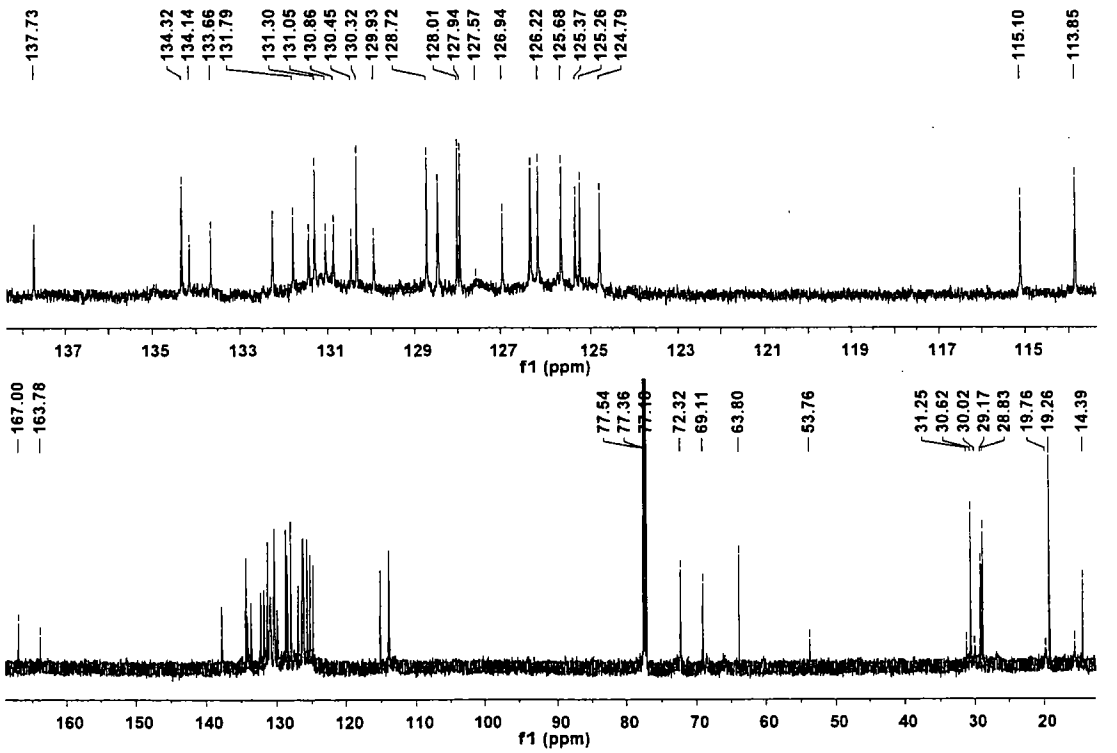


Figure B 69. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **PdL11down** (bottom) and the expanded spectrum in the aromatic region (top).

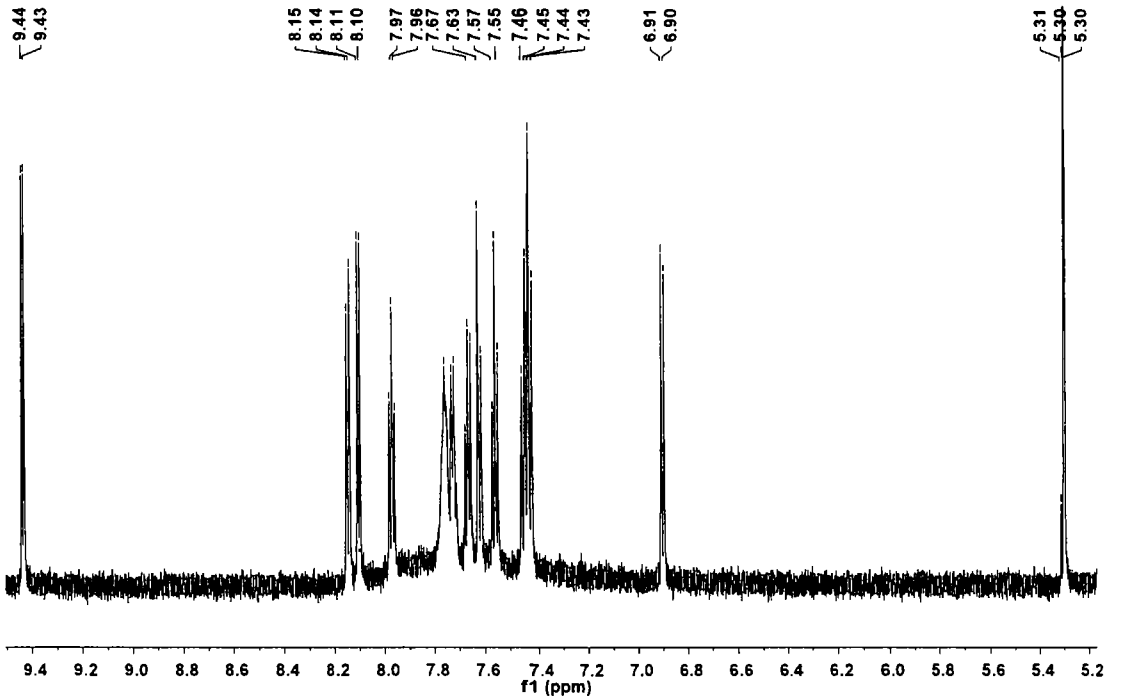


Figure B 70. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PdL12**.

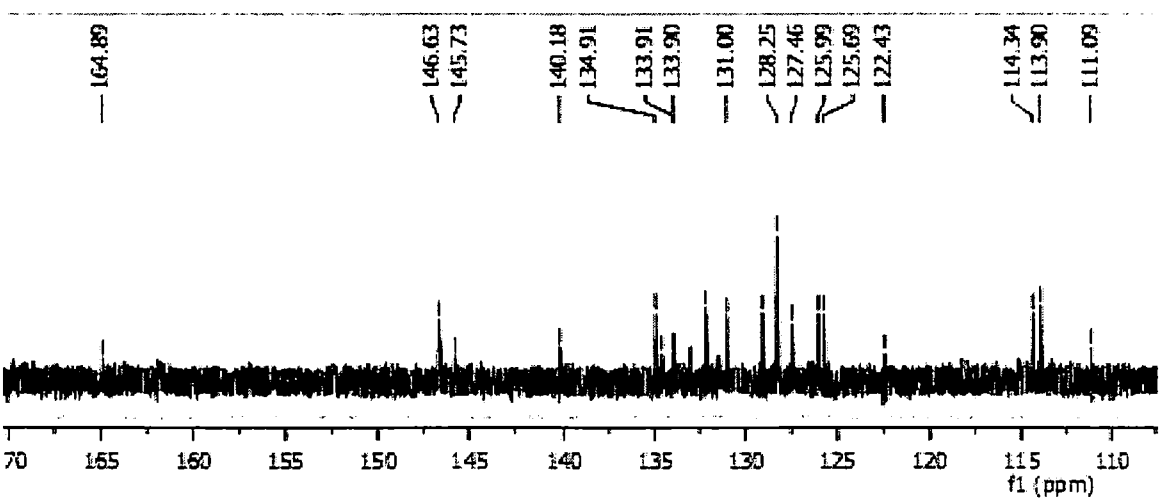


Figure B 71. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **PdL12**.

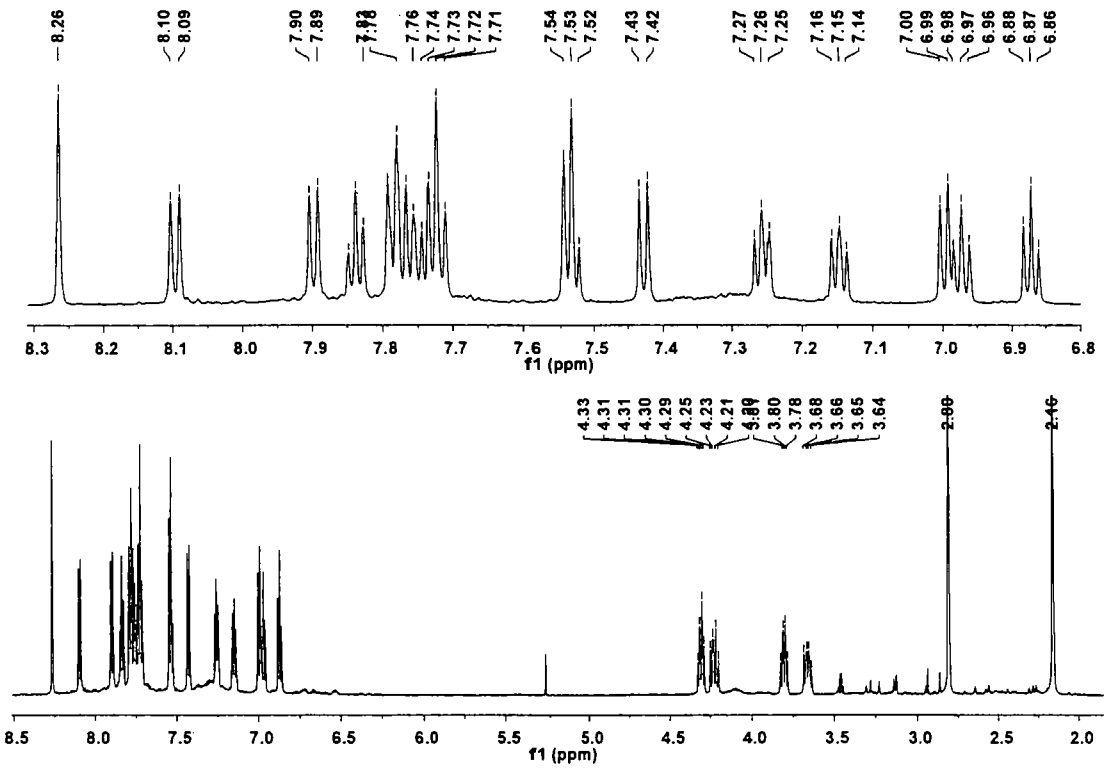


Figure B 72. The ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PdL13up** (bottom) and the expanded spectrum in the aromatic region (top).

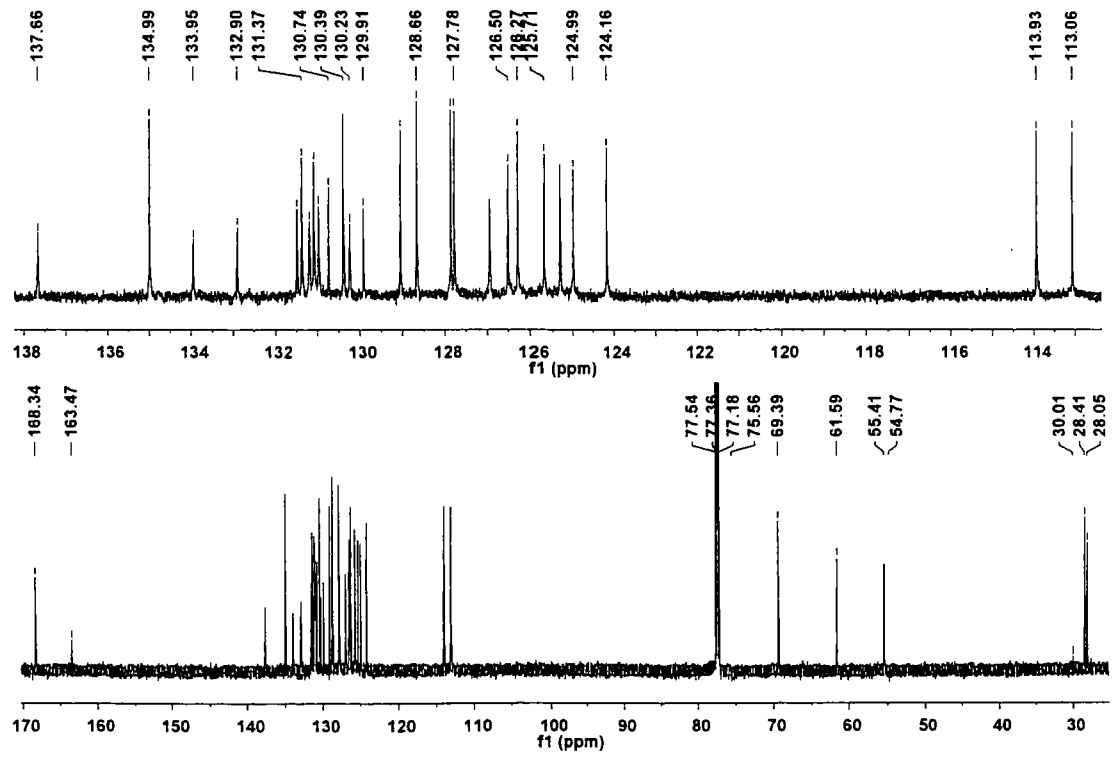


Figure B 73. The $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of **PdL13up** (bottom) and the expanded spectrum in the aromatic region (top).

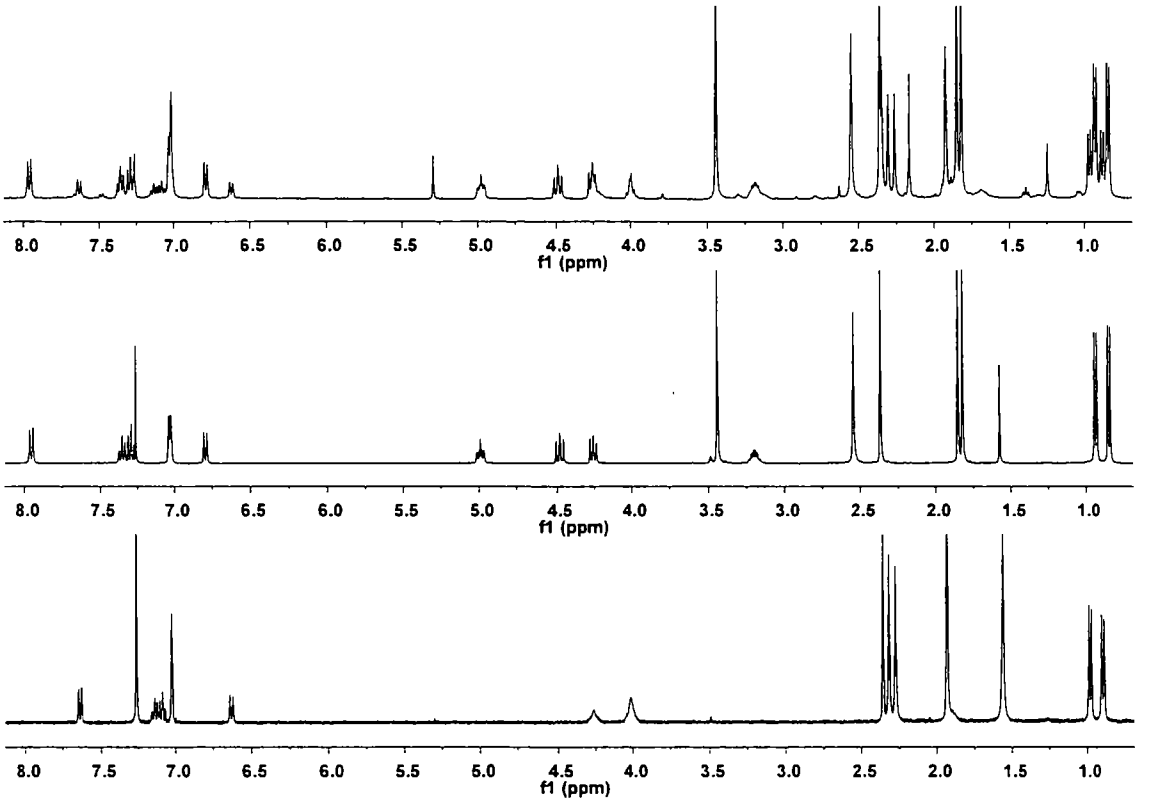


Figure B 74. The ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **L4** (bottom), isolated **PdL4** and the *in situ* 1:2 $PdCl_2(PhCN)_2$:**L4** reaction (top).

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
PdL4·0.5CH_2Cl_2	0.16	0.25	6.5
	0.02	0.24	5.9
PdL4·CH_3OH	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)	
Pd_2L5·CH_2Cl_2	0.07	0.11	3.2
Pd_2L5·2CH_2Cl_2	0.08	0.06	2.4
	0.13	0.14	4.7
Pd_2L5·4CH_2Cl_2	0.14	0.07	3.8
	0.09	0.08	3.0
Pd_2L5·$CHCl_3$·CH_3COCH_3	0.12	0.10	3.9
	0.10	0.09	3.3
Pd_2L5·H_2O	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	$0.75(C_{28}H_{28}P_2S)$, $0.25(C_{28}H_{28}OP_2S)$	$0.33(C_{28}H_{28}P_2S)$, $0.67(C_{28}H_{28}OP_2S)$
FW	462.50	469.22
T, K	120(2)	120(2)
Crystal system	Triclinic	Triclinic
Space group (no.)	*P*-1	*P*-1
a (Å)	9.3335(8)	6.1960(7)
b (Å)	11.5753(10)	8.6855(8)
c (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)
U (Å^3)	1191.44(18)	607.56(11)
Z	2	1
D_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 > 2σ	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) 1.820(2)	1.8155(14) 1.8228(13)
P(O)-CH_2 [a]	1.839(2)	1.8117(17)
P(O)-C_{Ar} [b]	1.826(2) 1.833(2)	1.8155(14) 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) 112.47(8)	113.72(6) 116.18(6)
O-P-C_{Ar} [b]	115.0(3) 119.7(3)	106.51(18) 112.0(2)
CH_2-P(S)-C_{Ar} [b]	105.74(11) 105.21(10)	115.05(7) 105.99(8)

[a] CH_2 next to P atom, [b] ipso aromatic carbons next to P atom.

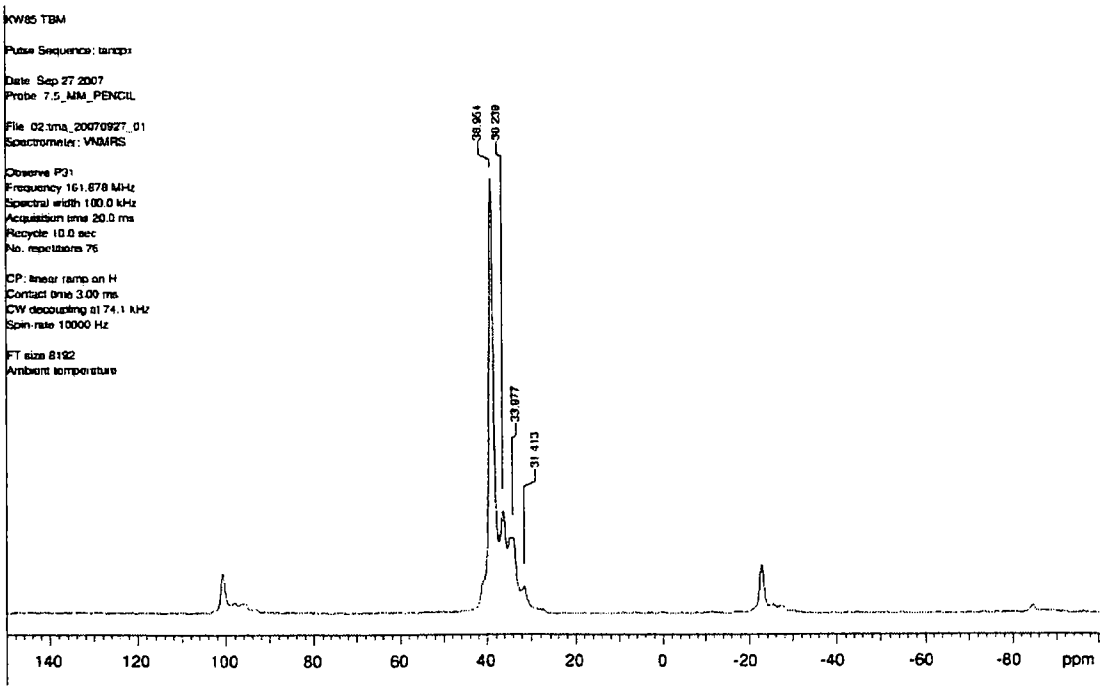


Figure C 1. The solid state $^{31}P\{^1H\}$ NMR spectrum of the complex obtained from the reaction of $PdCl_2(PhCN)_2$ with **dppmS** in a 1:1 molar ratio.

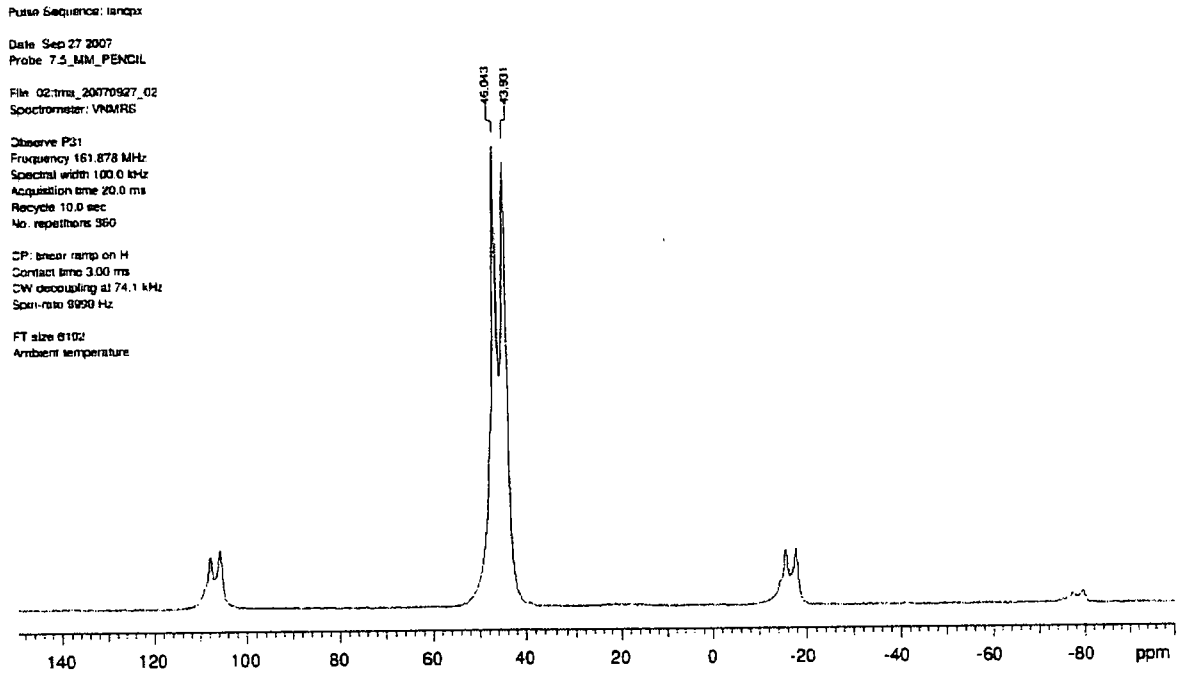


Figure C 2. The solid state $^{31}P\{^{1}H\}$ NMR spectrum of the complex obtained from the reaction of $PdCl_2(PhCN)_2$ with **dppbS** in a 1:1 molar ratio.

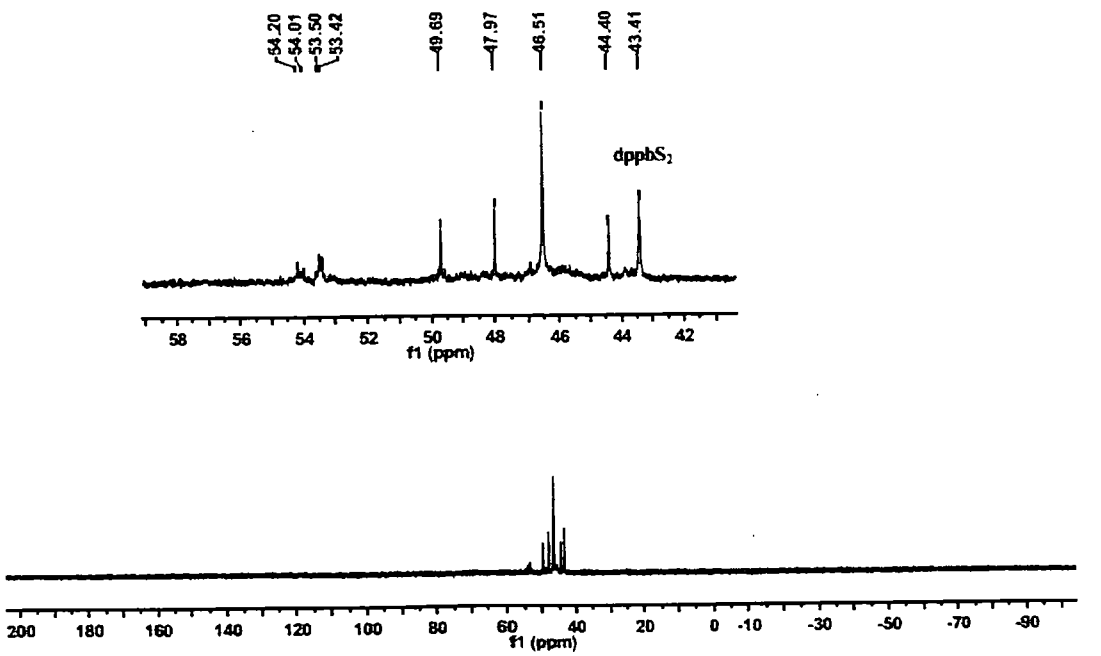


Figure C 3. The *in situ* $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of $[Pd(CH_3CN)_4](BF_4)_2$ with **dppbS$_2$** in a 1:2 molar ratio in CD_2Cl_2.

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

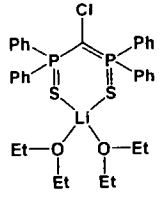
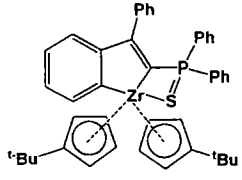
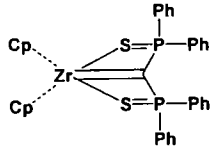
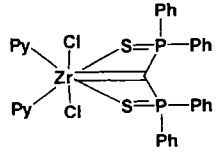
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Li					
	2.440 2.461	1.995(1) 1.987(1)	106.23 106.97	45.5	1
Zr					
	2.797(1)	2.005(1)	85.4(4)		2
	2.7499(6) 2.7499(6)	2.019(1) 2.010(8)	81	21.2	3
	2.6813(8) 2.6912(8)	2.025(1) 2.020(1)	82	20.3	3

Table C 3 (continued)

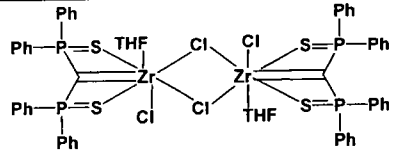
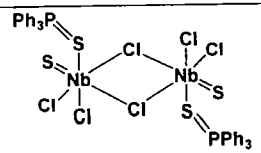
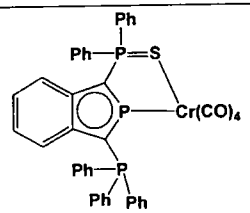
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.6813(8) 2.6912(8)	2.025(1) 2.020(1)	81	22.9	3
Nb					
$NbCl_5(SPPh_3)$	2.577(3)	2.028(5)	116.6(2)		4
	2.573(4)	2.026(6)	111.5(2)		5
Cr					
$Cr(CO)_5(SPMe_3)$	2.510(2)	1.990(3)	112.5(1)		6
	2.5056(10)	2.0184(12)	108.45(4)		7
Mo					
$Mo(O)Cl_3(SPPh_3)$	2.460(1)	2.041(1)	111.31 (4)		8

Table C 3 (continued)

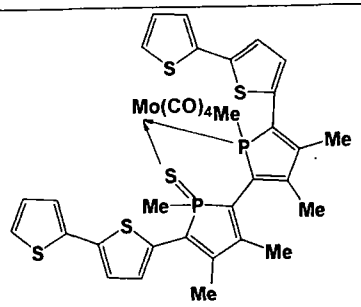
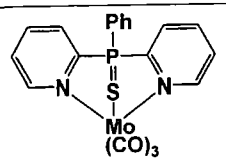
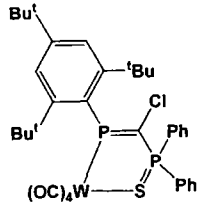
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.632(2)	1.980(3)	106.2(1)		9
	2.6242(14)	1.973(2)	85.43(5)	16.4	10
W					
$W(CO)_5(SPPh_3)$	2.6009(7)	2.004(1)	113.24(4)		11
	2.566(3)	1.990(4)	102.9(2)	48.4	12

Table C 3 (continued)

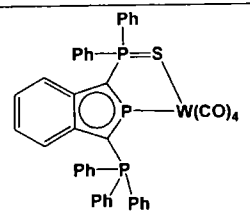
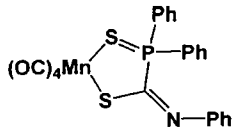
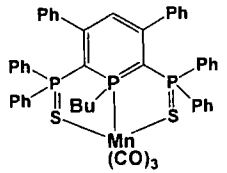
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.602(3)	2.015(2)	104.97(10)	27.4	7
$[WOCl(Me_2PCH_2P(S)Me_2)_2](PF_6)$	2.483(2) 2.451(2)	2.019(3) 2.027(3)	106.9(1) 108.3(1)		13
Mn					
	2.410	1.734	99.2		14
	2.4002(6) 2.4080(6) 2.401(1) 2.409(1)	2.0212(7) 2.0145(7) 2.034(2) 2.030(2)	103.1 103.9 105.3 106.4		15

Table C 3 (continued)

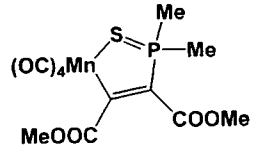
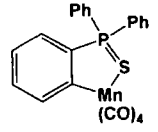
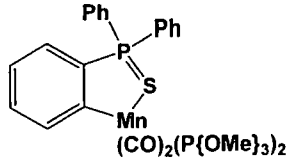
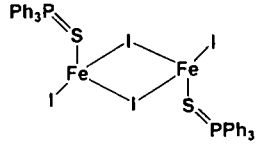
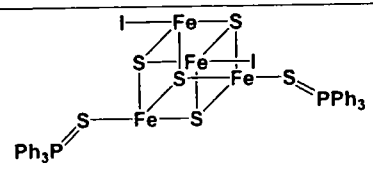
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.404	1.993	100.0		16
	2.410(1)	1.996(1)	99.64(3)	66.6	17
	2.412(1)	1.993(2)	99.59(6)	69.6	17
Fe					
	2.361	2.005	109.5		18
	2.316 2.321	2.014 2.017	108.0		19

Table C 3 (continued)

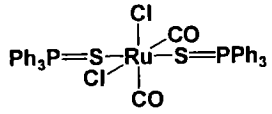
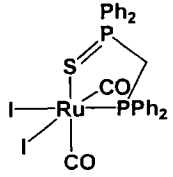
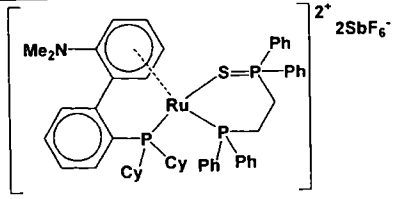
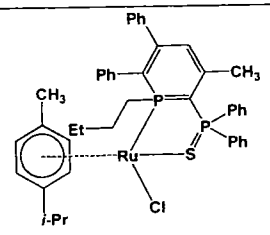
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Ru					
	2.414(3) 2.426(3)	1.998 2.012	115.7 116.1		20
	2.4615(13)	2.0103(17)	105.0		21
[Ru(CO)Cl(dppmS)$_2$]Cl	2.387 2.451	1.973 1.977	103.9 104.9		22
	2.421	2.016	105.4		23
	2.4239(5)	2.0283(7)	101.4		24

Table C 3 (continued)

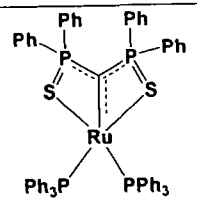
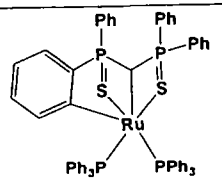
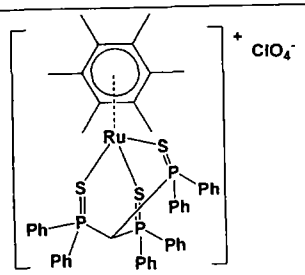
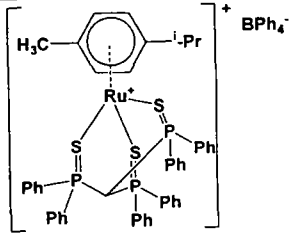
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.4739(5) 2.4843(5)	2.0269(7) 2.0206(6)	79.0	48.8 57.6	25
	2.620 – 2.504	1.986 – 1.996	72.3 – 90.0	62.5	25
	2.443(1)	2.003(1)	81.4(1)		26
	2.438(2) 2.443(2) 2.451(2)	2.030(3) 2.031(3) 2.031(3)	109.5(1) 109.5(1) 110.1(1)		27

Table C 3 (continued)

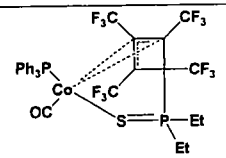
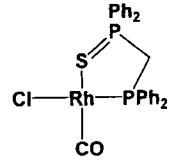
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Co					
	2.350	1.980	93.0		28
Rh					
	2.403(2)	2.005(3)	98.6(1)	52.2	29
$[Rh(CO)_2(dppmS_2)]ClO_4$	2.397(2) 2.402(3)	1.996(2) 1.999(2)	101.06(9) 105.10(8)	37.2	30
$[RhCl(Cp^*)(o\text{-}Ph_2PNHC_6H_4P(S)Ph_2\text{–}P,S]ClO_4$	2.402(3)	2.008(3)	117.1	47.4	31
$RhCl(CO)\{Fe(\eta^5\text{-}C_5Me_4P(S)Ph_2)(\eta^5\text{-}C_5Me_4PPh_2)\}$	2.420(3) 2.435(3)	1.994(4) 2.001(4)	110.9(2) 112.4(1)	43.16	32
$[RhCl(CO)\{Fe(\eta^5\text{-}C_5Me_4P(S)Ph_2)(\eta^5\text{-}C_5Me_4PPh_2)\}]_2[RhCl_2(CO)_2]$	2.422(2)	2.010(3)	108.12(9)	43.23	32

Table C 3 (continued)

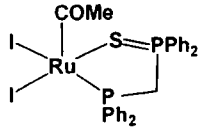
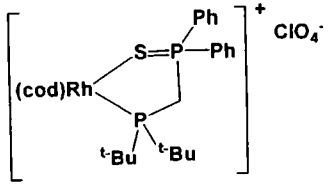
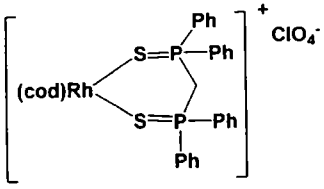
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.357(2)	2.027(2)	106.5		33
	2.349(2)	2.026(3)	105.2(4)		34
	2.403(5) 2.417(5)	2.001(6) 1.994(6)	102.4(2) 106.6(2)	35.3	30
Rh(cod){[(O)PPh_2]$_2$[(S)PPh_2]C}	2.307(5) 2.036(9)	2.036(9)	104.19(5)	40.0	35

Table C 3 (continued)

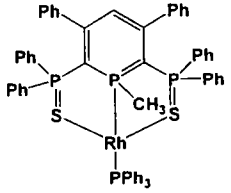
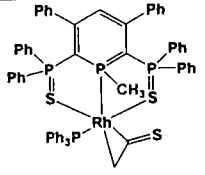
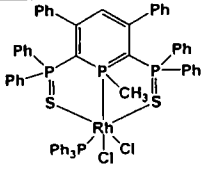
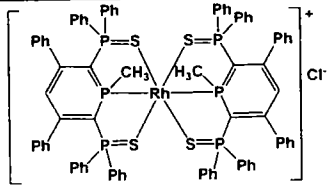
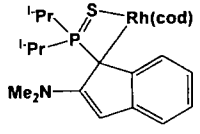
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.3197(6) 2.3213(6)	2.0219(7) 2.0235(8)	101.34(3) 107.73(3)	41.86	36
	2.5040(8) 2.4193(7)	2.0135(8) 2.025(1)	101.33(3) 106.94(3)	47.52 50.58	36
	2.374(2) 2.442(2)	2.041(3) 2.016(3)	103.1(1) 107.9(1)	52.27	37
	2.3641(8) – 2.4462(8)	2.017(1) 2.041(1)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

Table C 3 (continued)

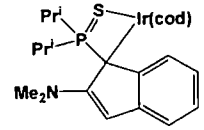
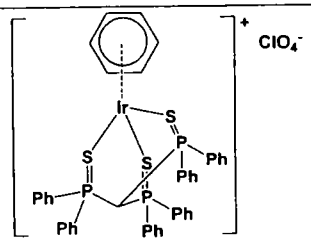
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Ir					
$IrI_2(CO)Me(dppmS)$	2.4194(9)	2.0126(13)	105.4	65.0	33
$IrI_2(CO)Et(dppmS)$	2.416(2)	2.009(3)	105.68	65.2	39
$[IrI(CO)Me(dppmS)]_2SO_3CF_3$	2.4182(13)	2.0138(18)	102.25	62.2 63.4 64.3 65.2	33
$[Ir(cod)\{(PPh_2)CH_2(P(S)^tBu_2)–P,S]BF_4$	2.324(3)	2.034(5)	107.2(2)	59.4	34
$[Ir(Cp^*)(dppmS_2)(PO[OMe]_2)]BF_4$	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)

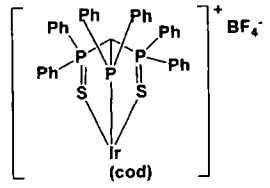
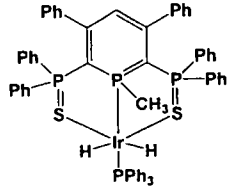
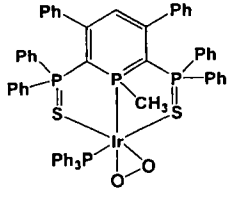
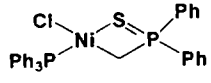
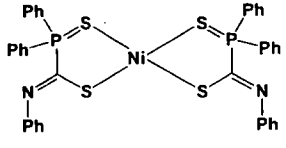
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.438(3) 2.574(3)	2.001(4) 1.977(4)	100.2(1) 105.0(1)	52.8	34
	2.4717(6) 2.4514(5)	2.0127(8) 2.0140(8)	112.3 117.3	50.3	42
	2.397(4) 2.405(5)	2.030(6) 2.033(6)	97.6 103.9	50.2	43
Ni					
	2.284(2)	1.999(3)	80.0		44
	2.197(2)	2.001(3)	105.4(1)	50.0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

Table C 3 (continued)

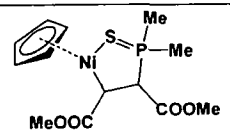
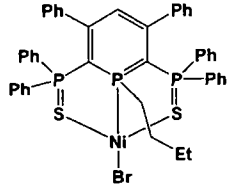
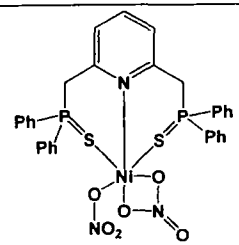
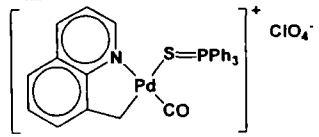
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.194	2.004	99.0		46
	2.185(1) 2.194(1)	2.039(2) 2.045(2)	104.3 106.7	58.26	47
	2.402(1) 2.481(1)	1.980(2) 1.981(2)	103.3 101.6		48
Pd					
	2.453(1)	2.009	105.39	45.65	49
trans-$PdCl_2[(^tBu)_3P(S)]_2$	2.334	2.014	112.04		50
PdI_2(dppmS)	2.331(2)	2.007(3)	101.3(1)	61.1	51

Table C 3 (continued)

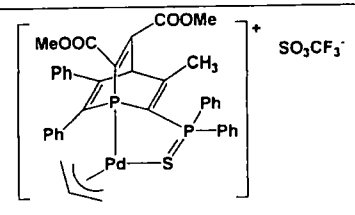
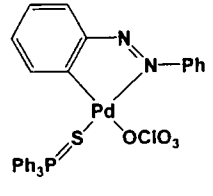
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
$PdCl_2(dppmS)$	2.2874(4)	2.0150(5)	104.099(19)	56.37	51
trans-$[Pd(dppmS)_2]Cl_2$	2.3256(8)	2.017(8)	99.84(4)		51
$PdCl_2(dppmS_2)$	2.3005(14) 2.3018(13)	2.0089(18) 2.0181(18)	105.11(7) 113.54(7)	37.87	52
$[(\eta^3\text{-allyl})Pd(dppmS_2)]$ $[(\eta^3\text{-allyl})PdCl_2]$	2.391	1.985	104.4		53
trans-$PdCl_2[Et_2PhP(S)]_2$	2.350	2.013	107.6		54
	2.364(1)	2.005(1)	99.6	62.4	55
$[Pd(dppmS_2)(dppm)](ClO_4)_2$	2.3858(14) 2.4069(13)	2.0026(18) 2.0064(17)	100.2 105.8	40.50	56
$[Pd(dppmS_2)(dppp)](ClO_4)_2$	2.3878(10) 2.3960(10)	1.9994(14) 1.9966(14)	108.3 109.5	38.00	56
$[Pd(dppmS_2)_2](BF_4)_2$	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)

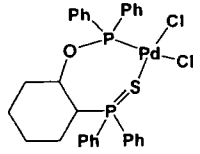
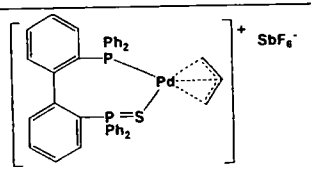
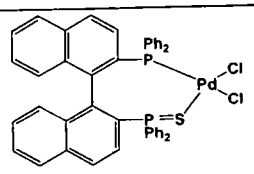
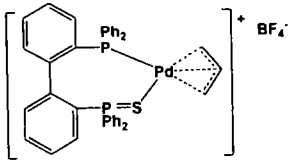
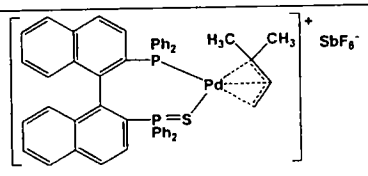
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.3112(9)	2.0220(12)	116.26(4)	35.9	59
	2.412(2)	2.001(3)	101.49(9)	41.2 41.3	60
	2.314(2)	1.991(3)	105.49(11)	39.77	61
	2.388(2)	1.994(3)	104.64(9)	42.1 44.1	61
	2.388(2)	2.003(2)	106.17(8)	47.3	60

Table C 3 (continued)

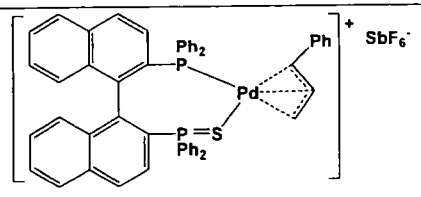
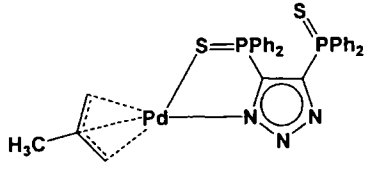
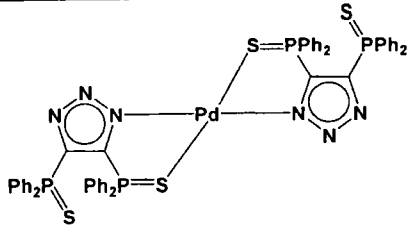
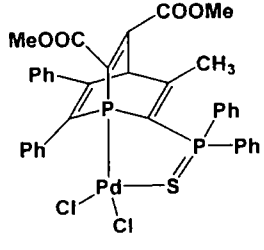
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.3904(12)	1.995(2)	104.74(6)	43.7 45.7	60
	2.3796(14)	2.0084(18) (pendant P=S 1.9633(7))	94.04	46.8	62
	2.3159(13) 2.3228(13)	2.0306(17) 2.0187(18) (pendant P=S 1.9633(7))	100.26 101.06		62
	2.3070(8)	2.026(1)	104.43	48.0	55

Table C 3 (continued)

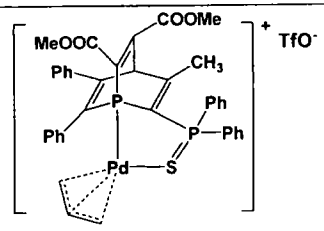
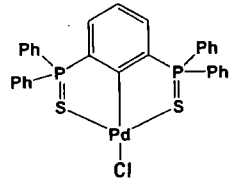
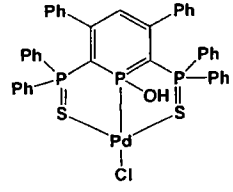
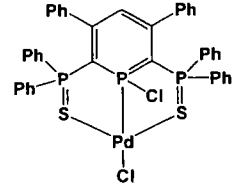
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.3877(5)	2.0090(6)	98.99	49.8 49.6	55
	2.312(4) 2.321(4)	1.995(5) 2.007(5)	97.9(2) 98.8(2)	56.5	63
	2.310(1) 2.353(1)	2.1018(2) 2.039(2)	94.24 108.19	54.36	47
	2.317(1) 2.3277(8)	2.036(1) 2.036(1)	104.64 106.51	52.6	64

Table C 3 (continued)

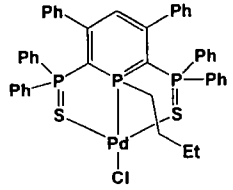
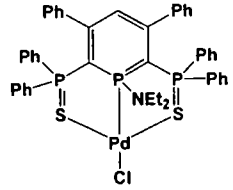
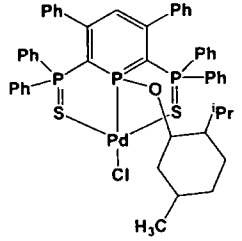
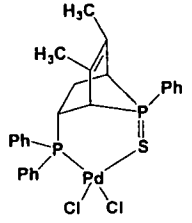
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.317(2) 2.321(2)	2.031(4) 2.037(3)	101.82 104.84	49.17	65
	2.3250(8) 2.3275(8)	2.029(1) 2.033(1)	101.81 104.62	51.77	47
	2.313(1) 2.328(1)	2.033(2) 2.033(2)	101.89 102.93	47.67 49.89	47
	2.299(1)	2.002(1)	116.8(1)	48.9	66

Table C 3 (continued)

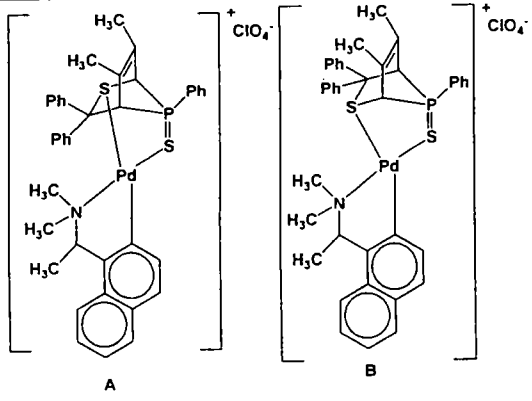
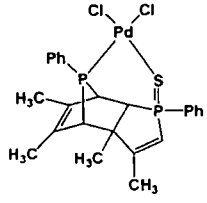
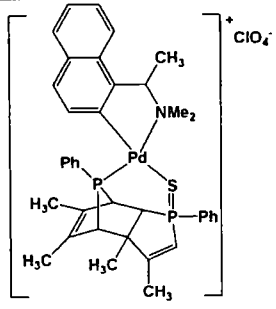
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
 A B	A 2.266(3) 2.468(3) B 2.308(3) 2.445(3)	A 1.984(5) B 1.999(5)	A 97.4(1) B 96.9(1)	A 99.7 B 100.0	66
	2.324(1)	2.017(1)	93.1(5)	60.54	67
	2.481(1)	1.987(2)	92.4(1)	62.0	67

Table C 3 (continued)

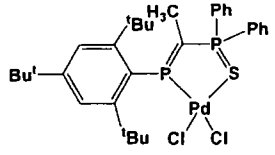
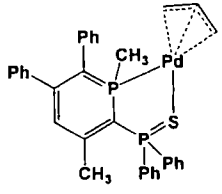
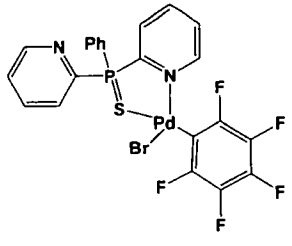
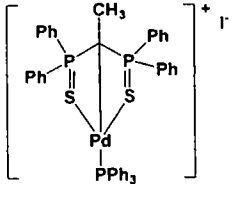
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.284(3)	2.012(4)	106.7(1)	55.5	68
	2.3371(6)	2.0288(8)	105.04	52.4	24
	2.307(2)	1.991(2)	94.23(8)	45.9	69
	2.3741(6) 2.3677(6)	2.0424(8) 2.0451(7)	78.58 79.10	39.8	70
$PdCl_2Fe[C_5Me_4P(S)Ph_2][C_5Me_4PPh_2]$	2.3278(7)	2.0237(9)	107.13(3)	40.9	71

Table C 3 (continued)

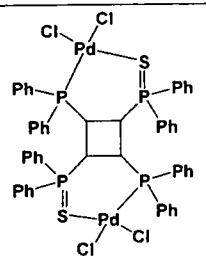
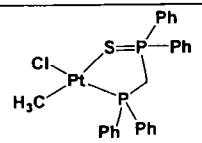
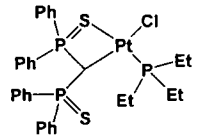
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.3187(10) 2.3530(10)	2.0092(12) 2.0077(13)	101.85(5) 104.43(4)	36.00	72
Pt					
trans-$PtCl_2(SPPh_3)(S(O)Me_2)$	2.300(4)	2.026(6)	105.7(2)	40.2	73
trans-$PtCl_2(SPPh_3)(S(O)Me(p\text{-tolyl})$	2.305(3)	2.018(4)	104.05(13)		73
	2.4243(18)	1.993(2)	96.41	36.6	74
$[PtMe\{(dppeS)\}\text{-}P,S]_2(BF_4)_2$	2.403(3) 2.427(3)	2.043(4)	103.27(13) 117.57(14)	38.0	74
$[PtCl(PEt_3)\{(PPh_2)(P(S)^tBu_2)\text{–}P,S\}]ClO_4$	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)

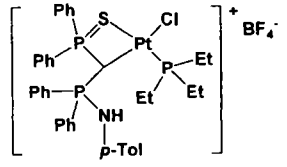
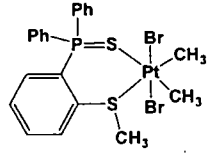
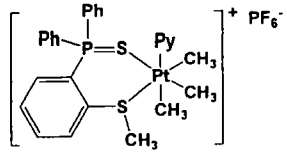
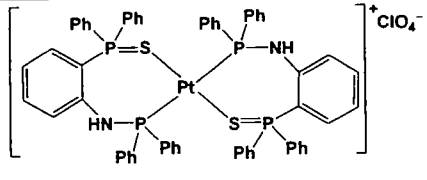
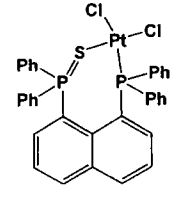
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.3090(10)	2.0091(3)	79.53(4)	50.7	78
	2.501(2)	1.986(2)	107.28(7)	36.2	79
	2.490(2)	1.996(2)	108.6(1)	36.2	80
	2.3432(4)	2.027(2)	108.19(7)	45.3	81
	2.286	2.018	103.65		82

Table C 3 (continued)

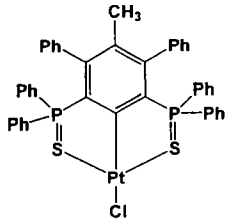
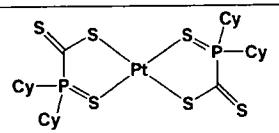
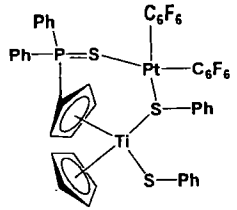
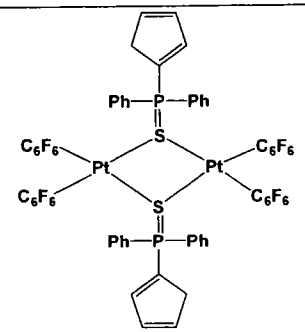
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.299(5) 2.307(5)	1.996(7) 2.002(7)	97.5(3) 99.3(3)	58.0	63
	2.314	2.017	102.50		83
	2.2401(3)	1.966(5)	99.05	26.68	84
	2.4094(17) 2.4227(17)	2.072(3)	81.30(5) – 101.99(8)	26.02	85

Table C 3 (continued)

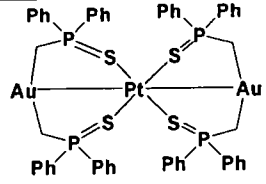
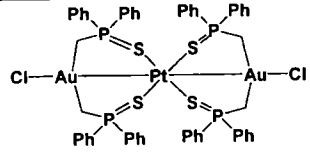
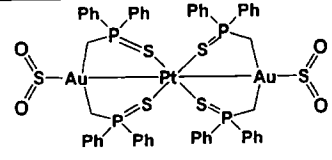
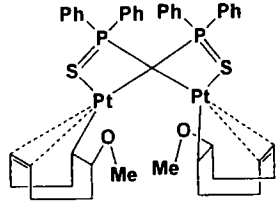
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.346(5)	2.033	104.16		86
	2.356(6) 2.372(6)	2.003 – 2.033	102.29 – 102.77		86
	2.360(3)	2.015	103.39		87
	2.484 2.479	2.001 2.010	79.50 79.84		88

Table C 3 (continued)

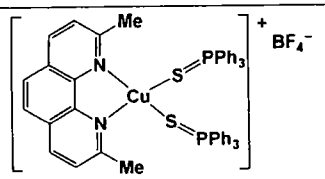
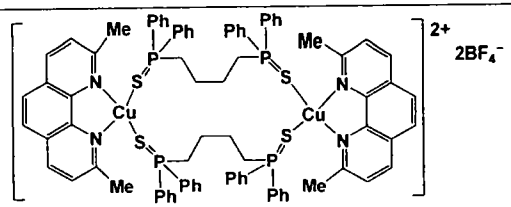
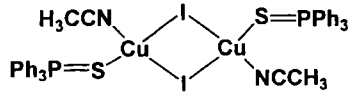
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Cu					
$[Cu(SPMe_3)_3]ClO_4$	2.253(5) – 2.264(5)	1.96667(7) – 2.009(7)	104.3(3) – 110.3(3)		89
	2.290	1.975 1.992	109.93 115.55		90
	2.294	1.946 1.957	108.04 106.77		90
$[Cu(dppeS)_2](ClO_4)_2$	2.392(3) 2.398(3)	1.975(3) 1.981(3)	98.96 99.62	50.9	91
	2.3444(13)	1.9880(1)	111.28(6)		92

Table C 3 (continued)

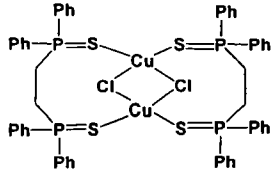
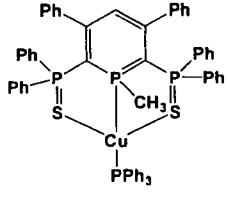
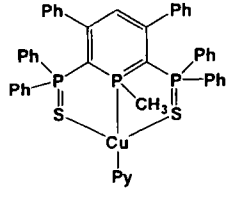
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
$[(CuCN)_2(dppeS_2)]_n$	2.5263(13)	1.9630(13)	103.52		93
$Cu_3Cl_3(SPMe_3)_3$	2.264(1) – 2.267(2)	2.024(2) 2.026(1)	103.88(6) – 104.72(5)		94
$CuCl(dppmS_2)$	2.259(2) 2.321(2)	1.970(2) 1.974(3)	91.52(8) 95.68(8)		95
$CuI(dppmS_2)$	2.247 2.259	1.980 1.985	102.15 106.37		96
$[Cu(dppmS_2)_2]PF_6$	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)

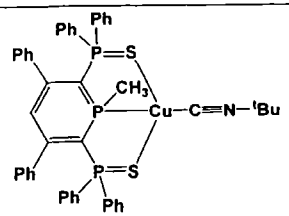
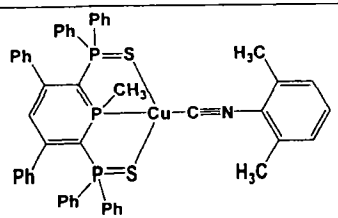
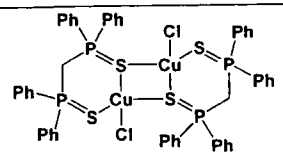
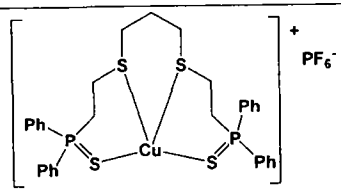
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.4119(9) 2.4280(13)	1.9987(9) 2.0052(11)	99.77(4) 102.09(3)	48.4	99
	2.3694(5) 2.4321(6)	2.0021(6) 2.0021(6)	102.03 103.87	47.3	99
$[Cu(dppfS_2)_2]BF_4$	2.140(5) 2.144(5)	1.985(5) 2.001(4)	100.8(2) 105.5(2)	45.63	100
$[\{Cu(dppf)\}_2(\mu\text{–}dppfS_2)](BF_4)_2$	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)

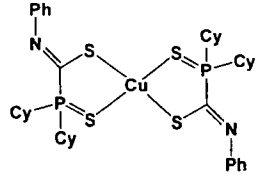
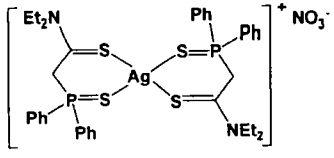
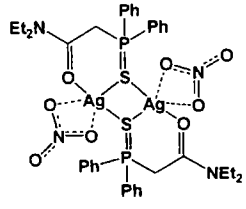
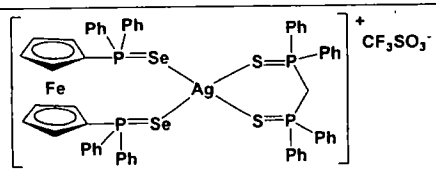
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.307(1)	1.999(1)	102.47(5)		104
Ag					
$[Ag(dppeS)]_2(NO_3)_2$	2.4574(9)	1.9920(10)	99.03(4)		105
$[Ag(dppmS_2)]NO_3$	2.583 – 2.635	1.960 – 1.977	96.06 – 101.16		106
	2.501 – 2.770	1.677 – 1.975	90.13 100.77 105.57		107
	2.572 2.722	2.010	104.32		108
	2.5919(12) 2.6012(11)	1.967 1.971	99.94 106.36	33.5	109

Table C 3 (continued)

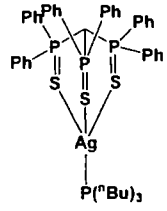
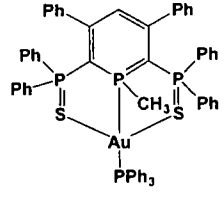
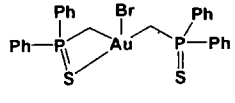
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.585(2) 2.639(3) 2.670(2)	1.990(3) – 1.999(3)	96.2(1) 97.3(1) 97.7(1)		110
$[Ag_2(\mu\text{-dppfS}_2)(\text{dppmS}_2)]_n[ClO_4^-]_{2n}$	2.530(2) – 2.801(2)	1.972(2) – 1.997(2)	103.95(9) 106.01(9) 107.74 Ag–S–Ag (83.43(6))		111
Au					
$AuBr(SPPh_3)$	2.286	2.016	105.62		112
$[Au(SPPh_3)_2](PO_2F_2)$	2.277(2)	2.023(3)	103.27(12)		113
$[Au(dppfS_2)][AuCl_4]$	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)

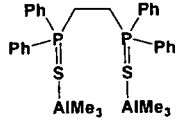
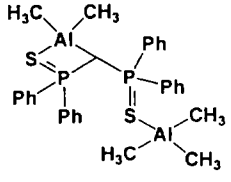
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
$\{AgCl(C_6F_5\}_2(\mu\text{-dppfS}_2)$	2.386(2)	2.020(3)	108.08(10)	45.7	114
Hg					
HgI_2(dppmS)	2.760(4)	1.968(6)	99.3(2)		116
$HgCl_2$(dppeS$_2$)	2.546(3) 2.559(3)	1.990(4) 1.998(3)	109.4(1) 110.4(1)		116
$HgBr_2$(dppeS$_2$)	2.552(2) 2.678(2)	1.990(4) 1.999(3)	104.79(11) 108.96(11)		52
Al					
$AlCl_3(SPPh_3)$	2.797(2)	2.028(2)	109.62(8)		117
	2.506(3)	1.989(2)	108.4(1)		118
	2.388(2) 2.460(2)	2.004(2) 2.009(2)	78.8(1) 108.7(1)		118

Table C 3 (continued)

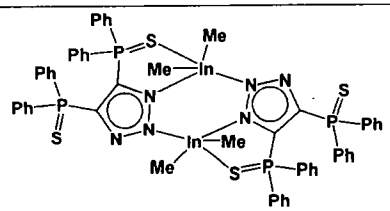
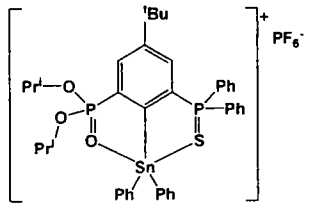
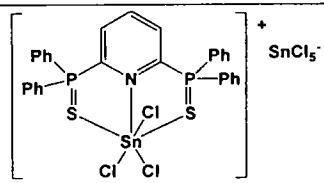
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
In					
trans-$InCl_3(SPMe_3)_2$	2.630(3) 2.663(3)	2.003(2) 2.014(3)	109.2(1) 117.7(1)		119
trans -$InBr_3(SPMe_3)_2$	2.643(3) 2.653(3)	1.998(2) 2.010(3)	110.6(1) 113.2(1)		119
$[InI_3(dppeS_2)]_2$	2.532	2.011	111.11		120
	2.780(1)	1.986(1) (P–S–In) 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)

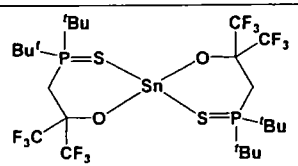
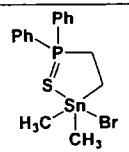
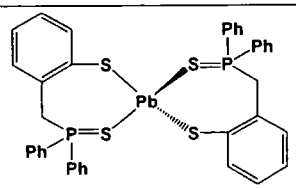
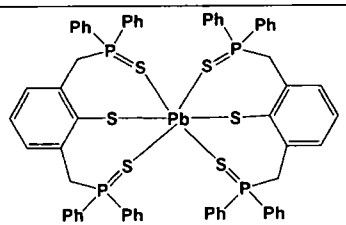
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.8381(7) 2.9137(7)	1.9798(9) 1.9922(9)	107.69 108.32	67.11	125
	2.872	1.976	91.89		137
Pb					
	2.885(12) 3.151(9)	1.973(13) 1.003(10) (disorderd)	117.44 – 118.05 (disorderd)	40.5	126
	2.953(8) 3.386(7)	1.909(11) 1.979(9)	113.8(3) 114.6(4)	36.6 40.2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

Table C 3 (continued)

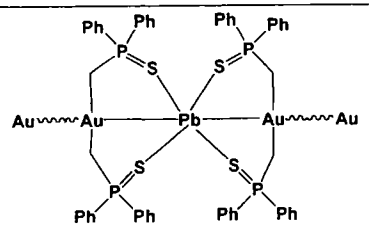
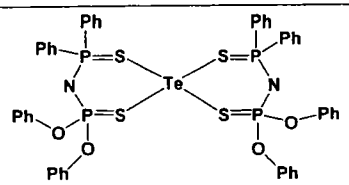
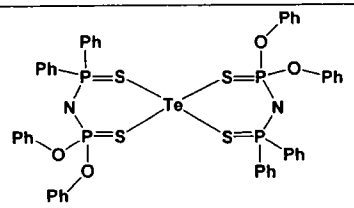
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.959(5) 2.976(6)	1.991 2.008	100.83 100.91		127
Te					
$TeCl_4(dppeS_2)$	2.633(4) 2.891(3)	1.950(4) 1.984(4)	109.3(2) 111.7(2)		128
	2.5311(8) – 2.9372(12)	1.9719(10) – 2.0604(10)	94.19(4) – 98.52(4)	35.43 43.39	129
	2.6759(16) 2.6851(12)	2.0134(16) 2.0061(16)	97.85(6) 97.03(6)	27.18 51.14	129
$\{TeCl_3(4\text{-}OMeC_6H_4)\}_2(\mu\text{-}dppfS_2)$	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)

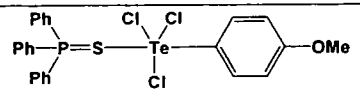
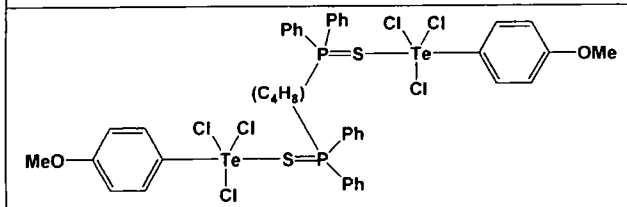
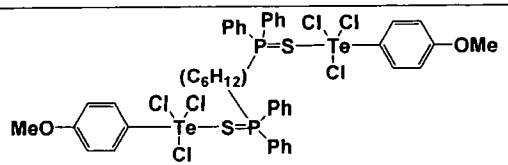
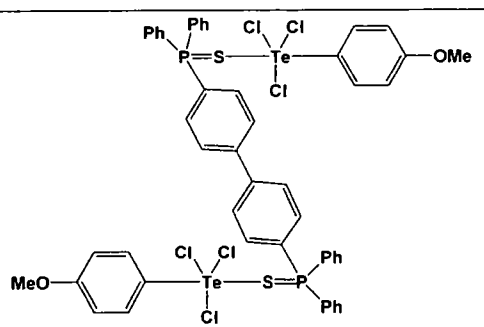
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.752(1)	2.008(1)	102.78(4)	43	130
	2.772(2)	2.012(2)	110.27(9)	51	130
	2.787	2.058	101.1	53	130
	2.785(2)	1.999(2)	103.16(7)	43	130

Table C 3 (continued)

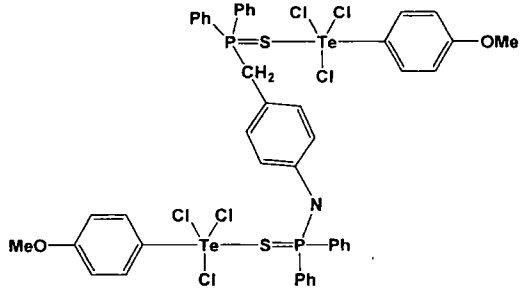
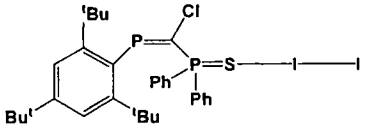
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
	2.753(1)	2.008(1)	105.29	55	130
I					
$Ph_3PS{\cdot}I_2$	2.753(2)	1.998(2)	108.78(7)	41.70	131
$Ph_3PS{\cdot}IBr$	2.656(1)	2.007(1)	107.63(5)		132
$(Me_2N)_3PS{\cdot}I_2$	2.705(3)	2.014(4)	103.63		132
	2.809(2)	1.990(3)	98.44(10)		12
$(p\text{-}FC_6H_4)_3PS{\cdot}I_2$	2.787(5) 2.792(6)	1.984(5) 1.997(6)	100.4(3) 102.9(2)	47.5	133
$Fc_2(Ph)PS{\cdot}I_2$	2.7670(12)	2.0015(14)	109.71(5)		134

Table C 3 (continued)

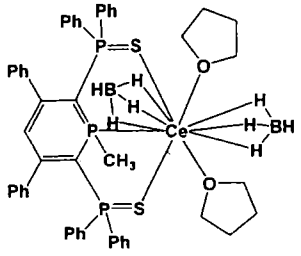
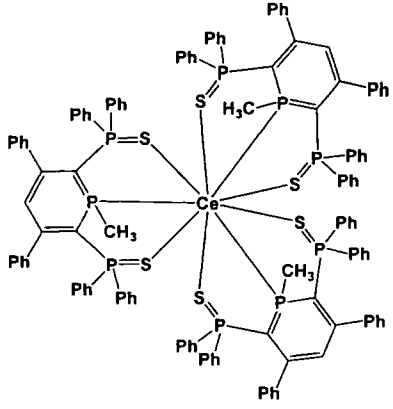
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Ce					
	2.947(2) 2.992(2)	2.007(3) 2.009(3)	99.11 110.53		135
	2.917(3) 2.995(5)	1.983(4) 1.998(4)	115.43 120.52		135

Table C 3 (continued)

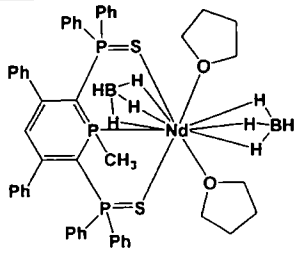
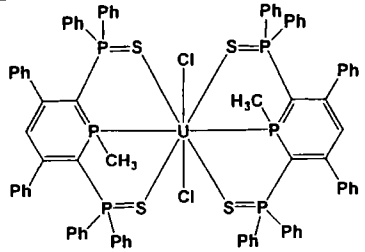
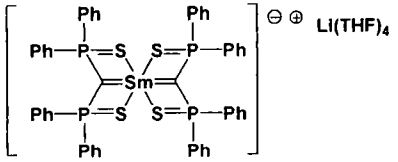
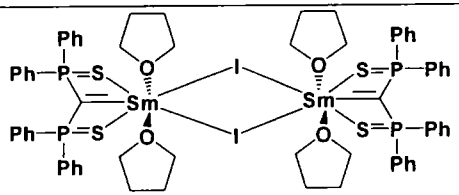
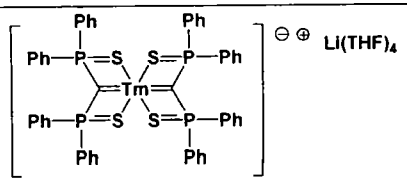
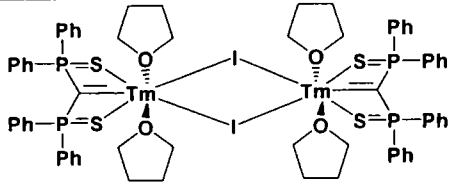
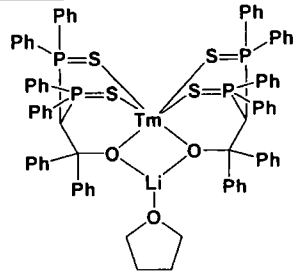
Compounds	M–S (Å)	P–S (Å)	M–S–P (deg)	δ (ppm)	ref(s)
Nd					
	2.9162(15) 2.9623(14)	2.007(2) 2.0086(19)	107.53 110.27		135
U					
	2.7799(10) 2.9892(12)	1.9995(15) 2.0184(16)	108.76 116.31		135
Sm					
	2.2816(2) – 2.851(2)	2.034 – 2.042	79.34 – 81.66		136

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
Tm					
	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.

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