

Electron supporting information.

Rare-earth dichloro and bis(alkyl) complexes supported by bulky amido-imino ligand. Synthesis, structure, reactivity and catalytic activity in isoprene polymerization.

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Fig. 1. ^1H NMR of **2Y**.

Fig. 2. ^1H NMR of **2Y** (next day).

Fig. 3. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2Y** (next day).

Fig. 4. Molecular structure of **2Lu**.

Fig. 5. $^1\text{2Lu}$.

Fig. 6. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2Lu** (next day).

Fig. 7. ^1H NMR of **3**.

Fig. 8. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3**.

Fig. 9. ^1H NMR of **4Y**. **Fig. 10.** $^{13}\text{C}\{^1\text{H}\}$ NMR of **4Y**. **Fig. 11.** ^1H NMR of **4Lu**. **Fig. 12.** $^{13}\text{C}\{^1\text{H}\}$ NMR of **4Lu**.

Fig. 13. ^1H NMR of **5**.

Fig. 14. $^{13}\text{C}\{^1\text{H}\}$ NMR of **5**.

Fig. 15. EPR spectrum of **6**.

Fig. 16. EPR spectrum of **8**.

Fig. 17. EPR spectrum of **10**.

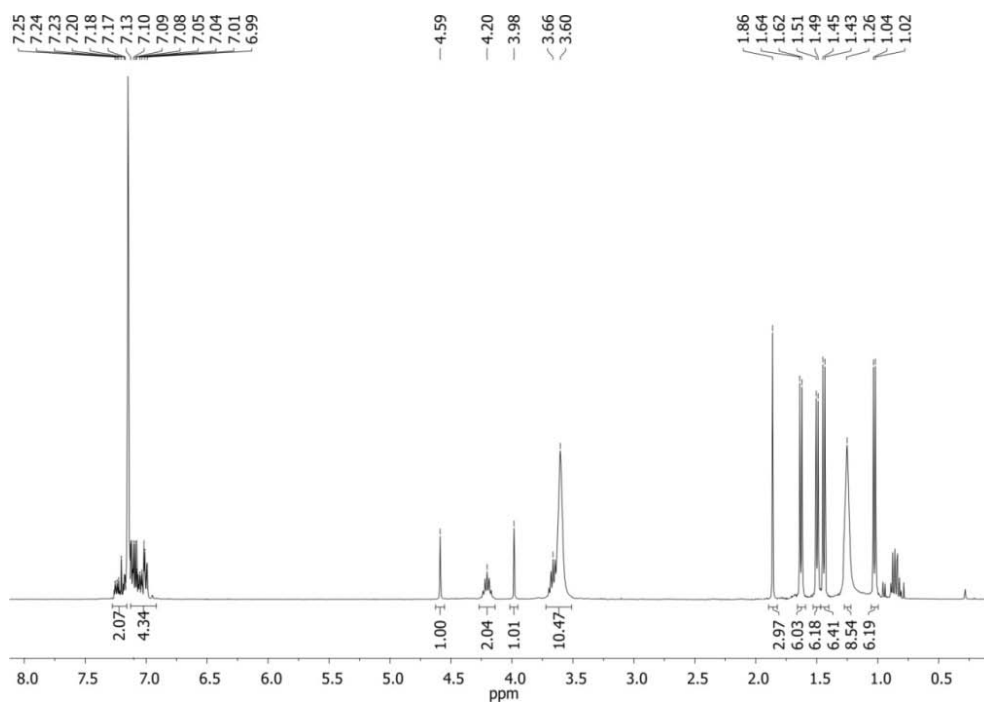


Fig. 1. ^1H NMR spectrum of **2Y**.

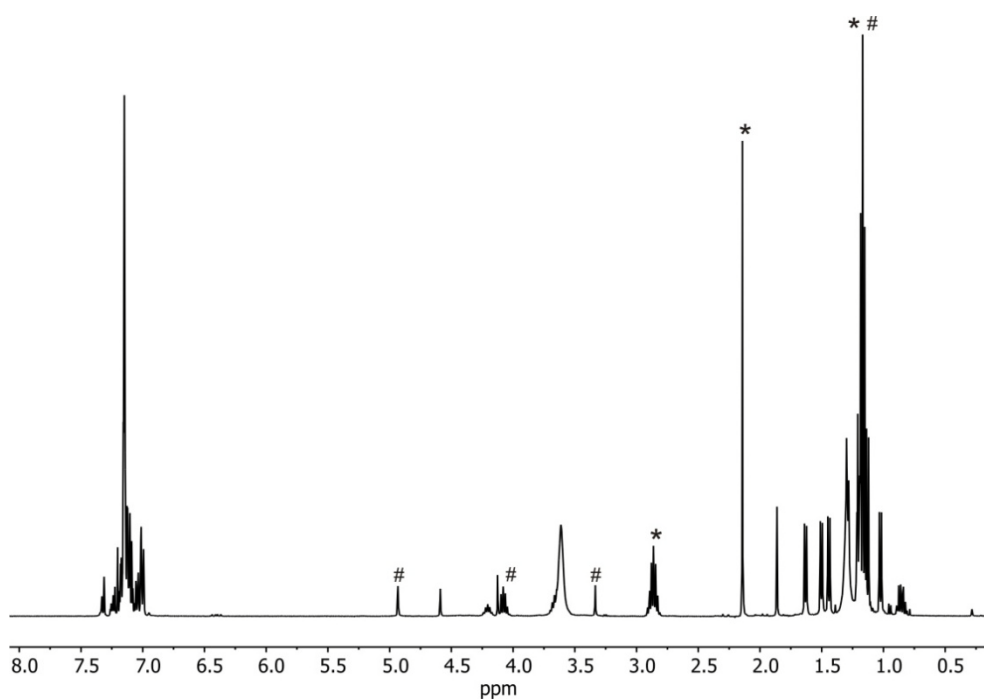


Fig. 2. ^1H NMR spectrum of **2Y** (next day). # – signals attributed to $[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(=\text{CH}_2)\text{C}(=\text{CH}_2)\text{N}(\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]\text{YCl}(\text{THF})_n$; * – signals attributed to $[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{N}(\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]$.

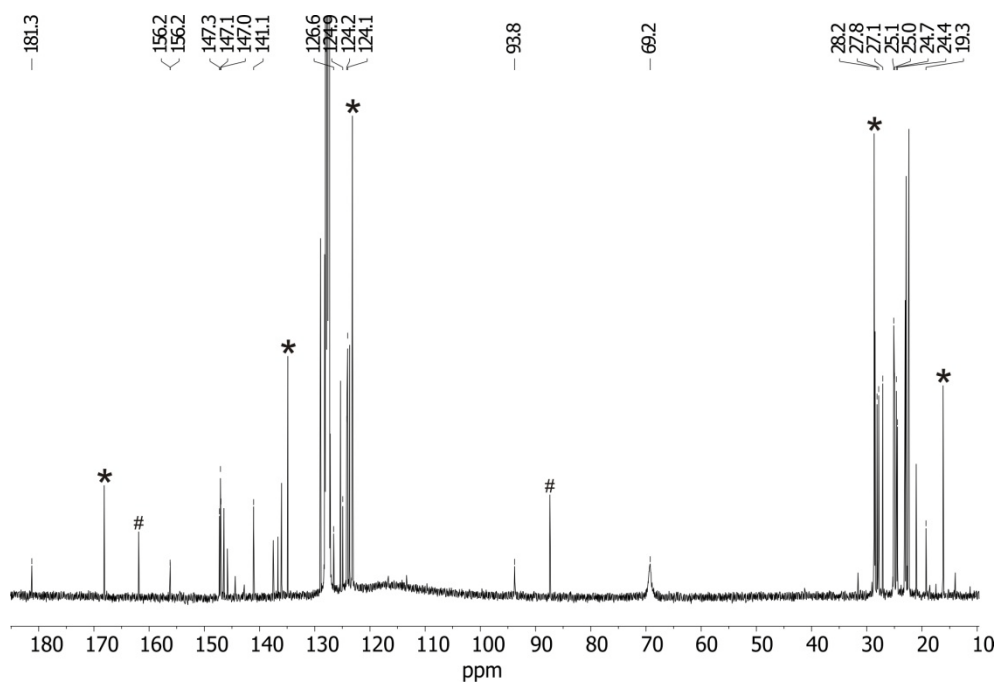


Fig. 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2Y** (next day). # – signals attributed to $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(=\text{CH}_2)\text{C}(=\text{CH}_2)\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{Pr}_2)]\text{YCl}(\text{THF})_n$; * – signals attributed to $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{Pr}_2)]$.

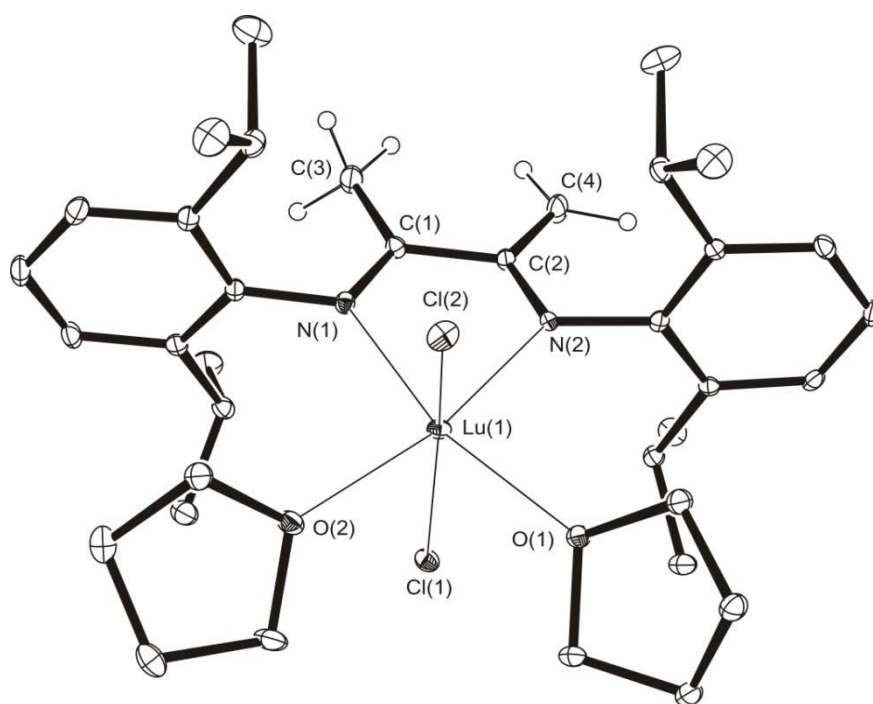


Fig. 4. Molecular structure of complex $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{Me})\text{C}(\text{=CH}_2)\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{Pr}_2)]\text{LuCl}_2(\text{THF})_2$ (**2Lu**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms of 2,6-diisopropylphenyl substitutes and THF molecules are omitted for clarity. Selected distances [Å] and angles [°]: Lu(1)-N(1) 2.3353(16), Lu(1)-N(2) 2.3048(17), Lu(1)-Cl(1) 2.5383(5), Lu(1)-Cl(2) 2.5316(6), Lu(1)-O(1) 2.3312(13), Lu(1)-O(2) 2.3280(14), N(1)-C(1) 1.327(3), N(2)-C(2) 1.342(3), C(1)-C(3) 1.438(3), C(1)-C(2) 1.485(3), C(2)-C(4) 1.417(3); N(2)-Lu(1)-N(1) 70.62(6), Cl(1)-Lu(1)-Cl(2) 162.306(17), O(1)-Lu(1)-O(2) 100.09(5), N(1)-C(1)-C(3) 124.46(19), N(1)-C(1)-C(2) 116.45(17), C(3)-C(1)-C(2) 119.07(19), N(2)-C(2)-C(4) 124.81(18), N(2)-C(2)-C(1) 116.77(18), C(4)-C(2)-C(1) 118.42(18).

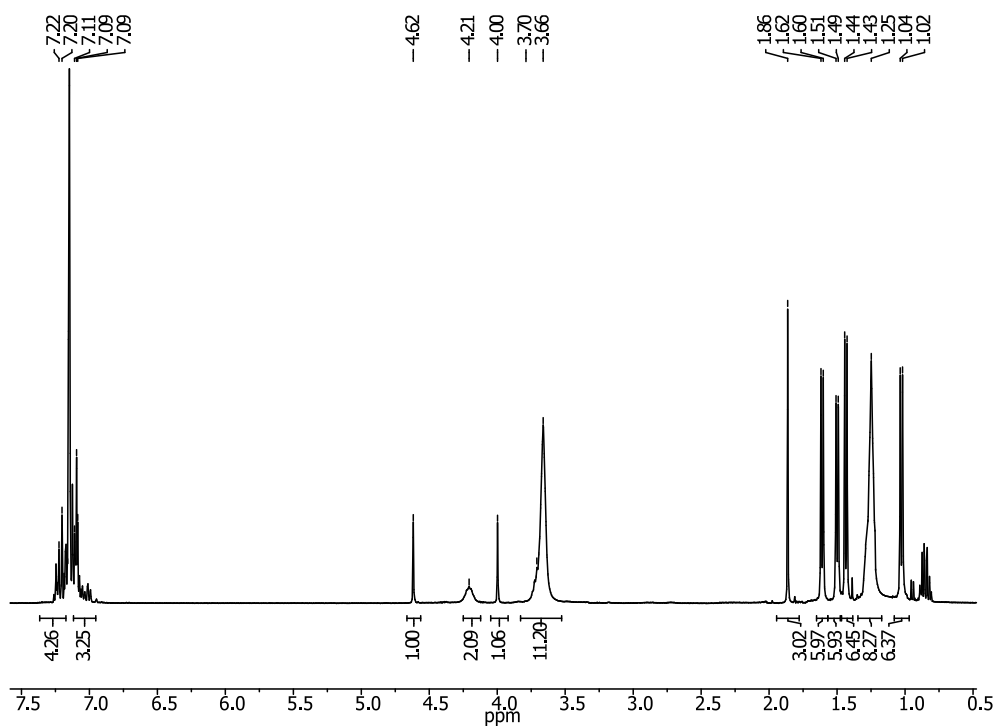


Fig. 5. ^1H NMR spectrum of **2Lu**.

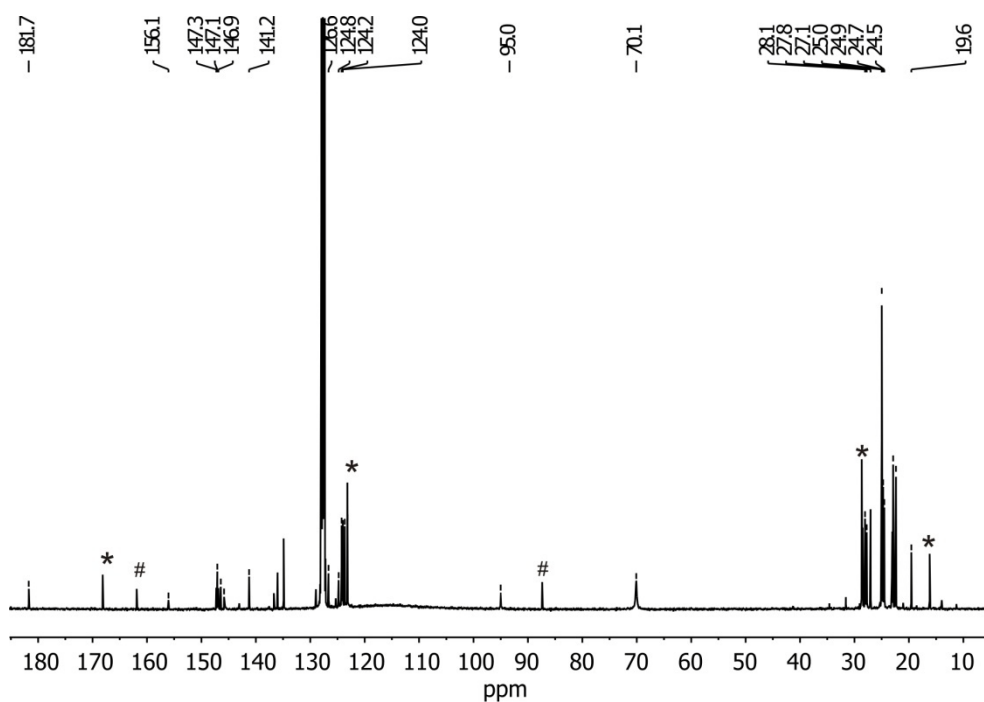


Fig. 6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2Lu**. # – signals attributed to $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(=\text{CH}_2)\text{C}(=\text{CH}_2)\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{Pr}_2)]\text{LuCl}(\text{THF})_n$; * – signals attributed to $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{Pr}_2)]$.

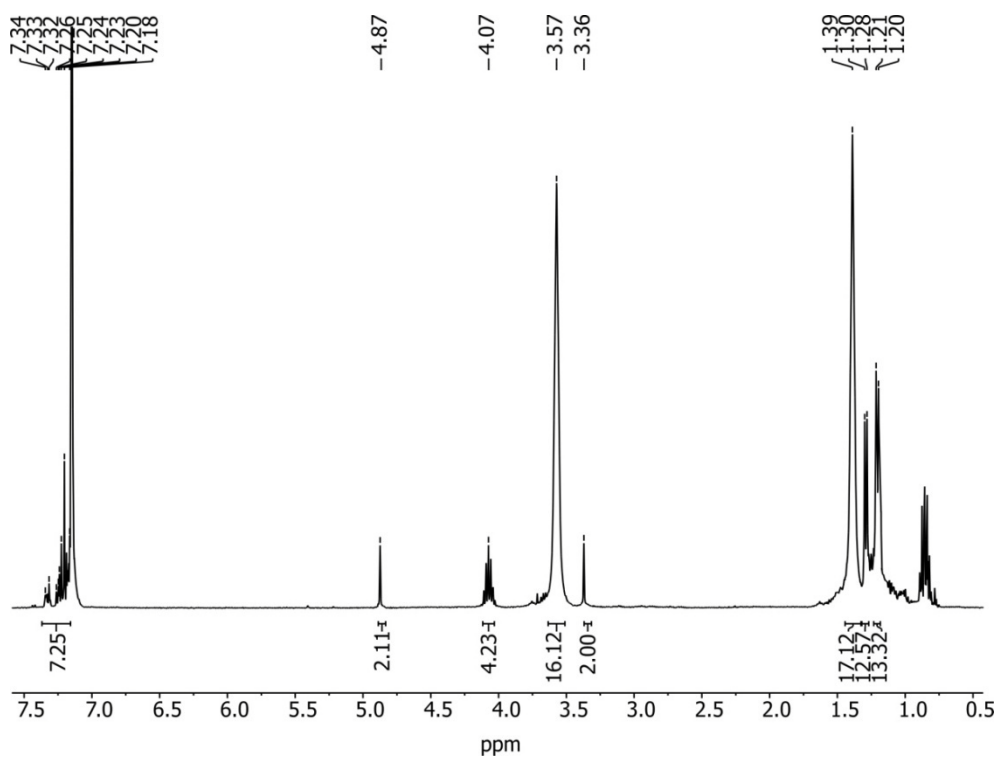


Fig. 7. ^1H NMR spectrum of 3.

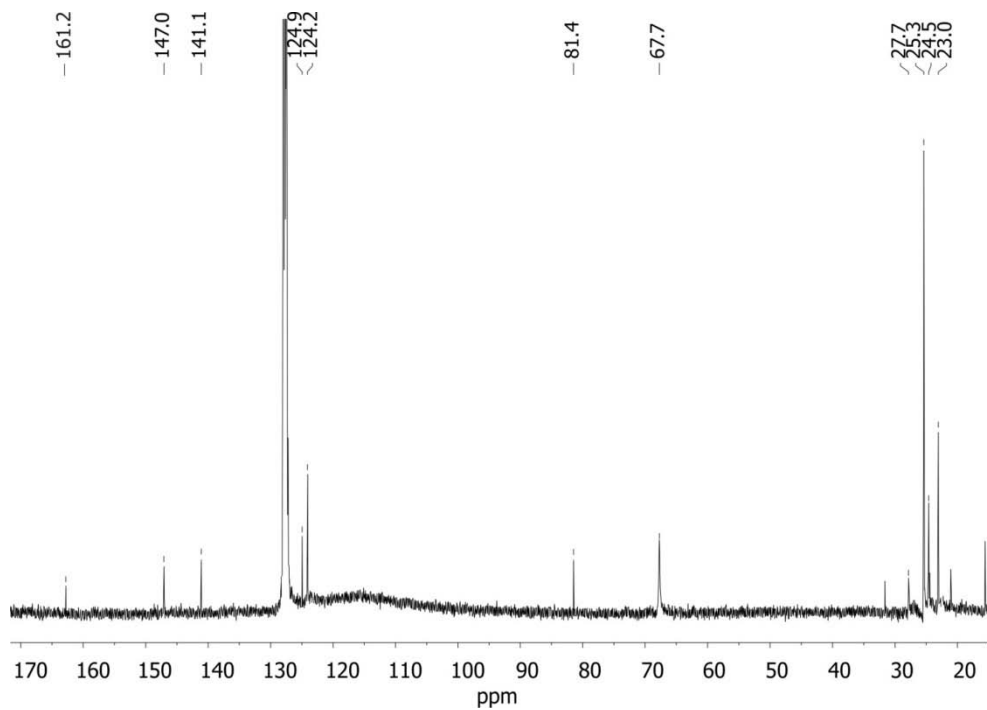


Fig. 8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3.

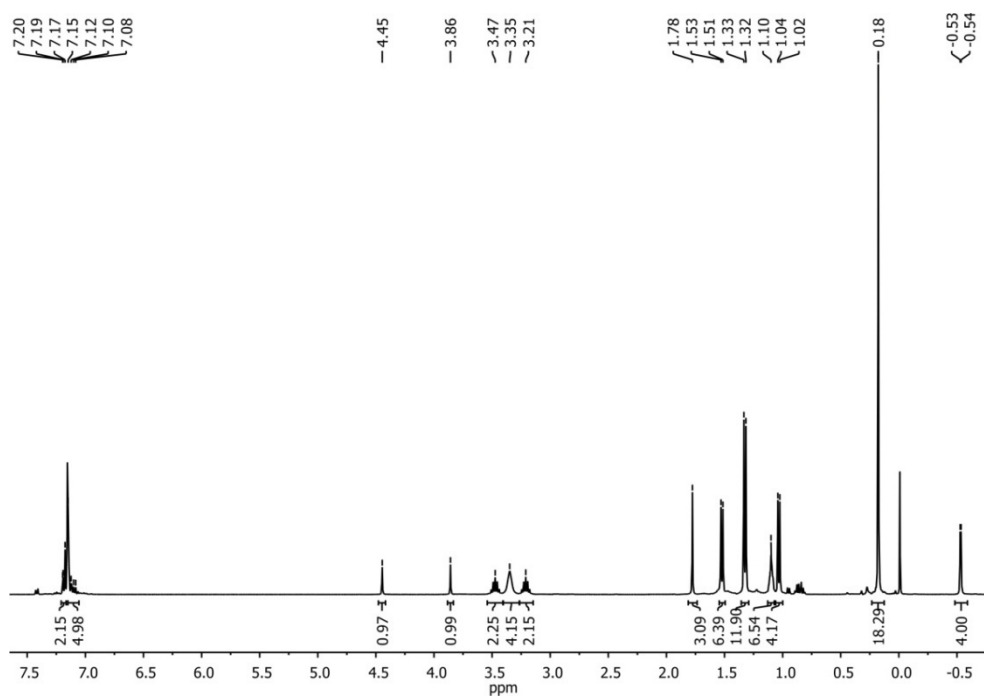


Fig. 9. ¹H NMR spectrum of 4Y.

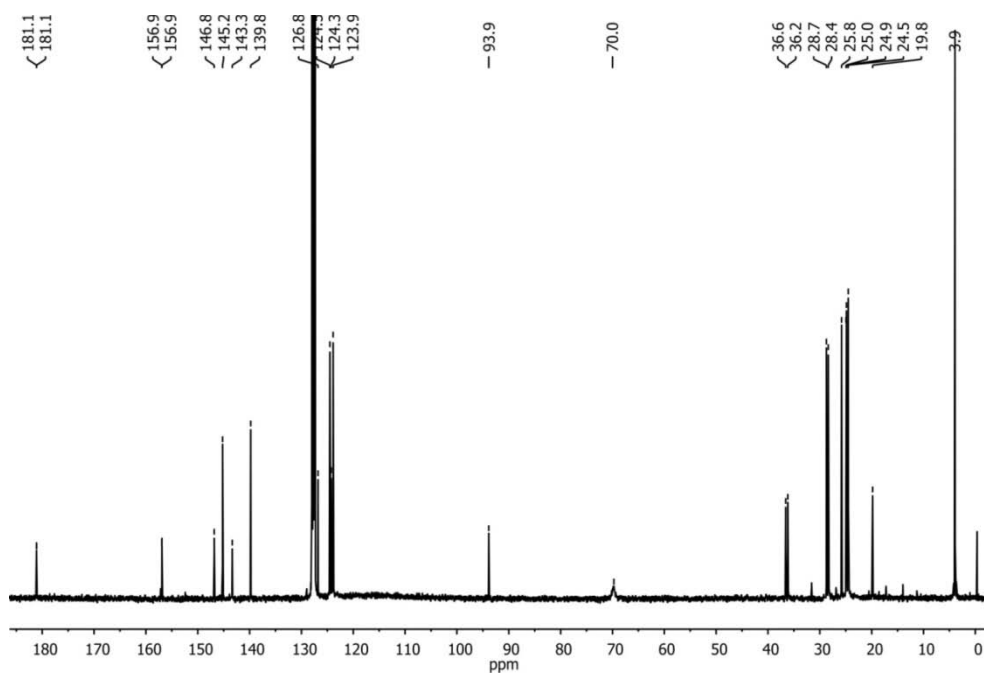


Fig. 10. ¹³C{¹H} NMR spectrum of 4Y.

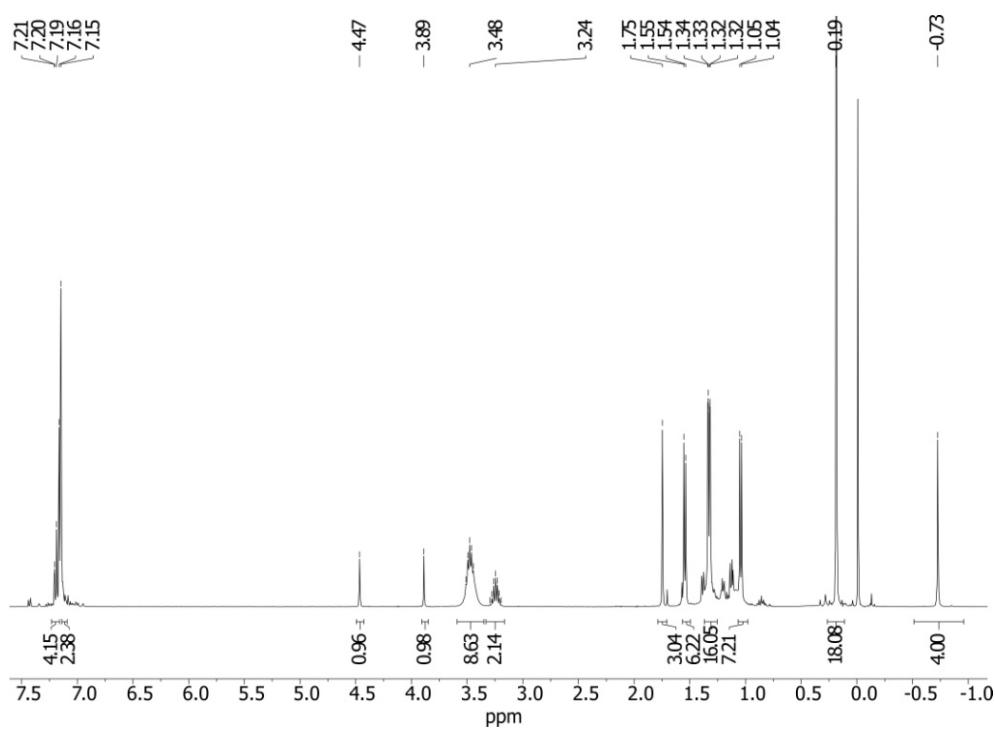


Fig. 11. ^1H NMR spectrum of 4Lu.

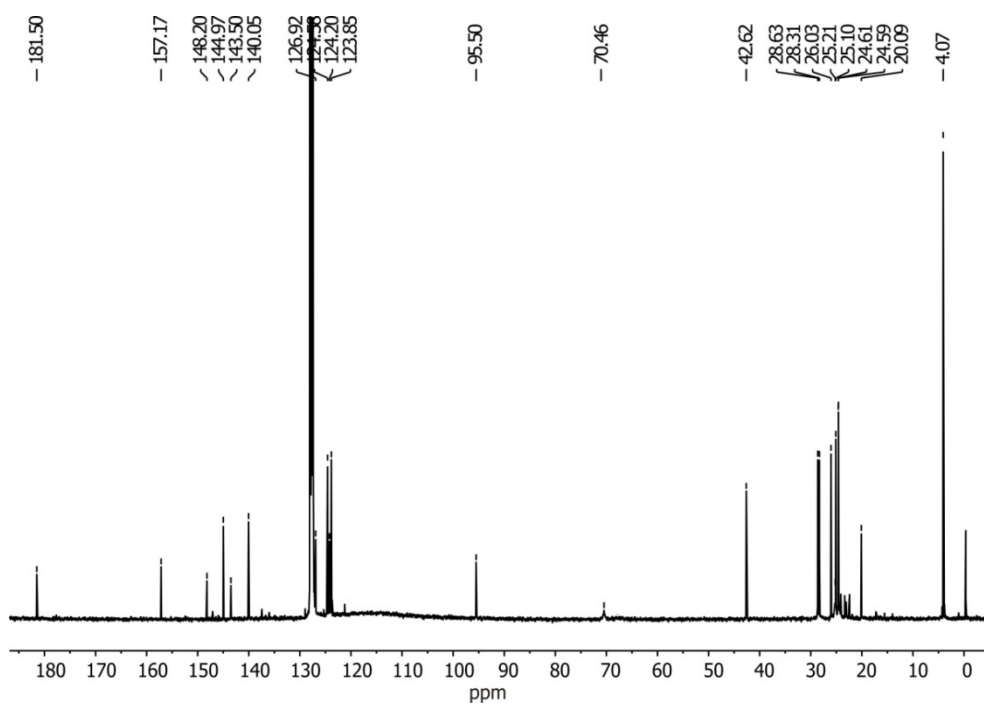


Fig. 12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4Lu.

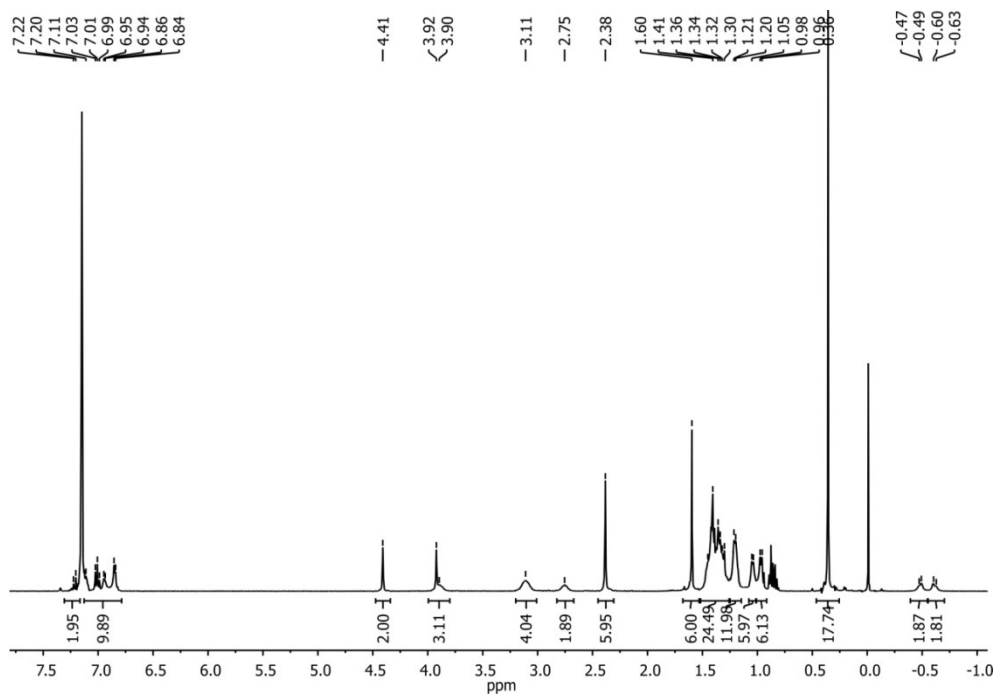


Fig. 13. ¹H NMR spectrum of 5.

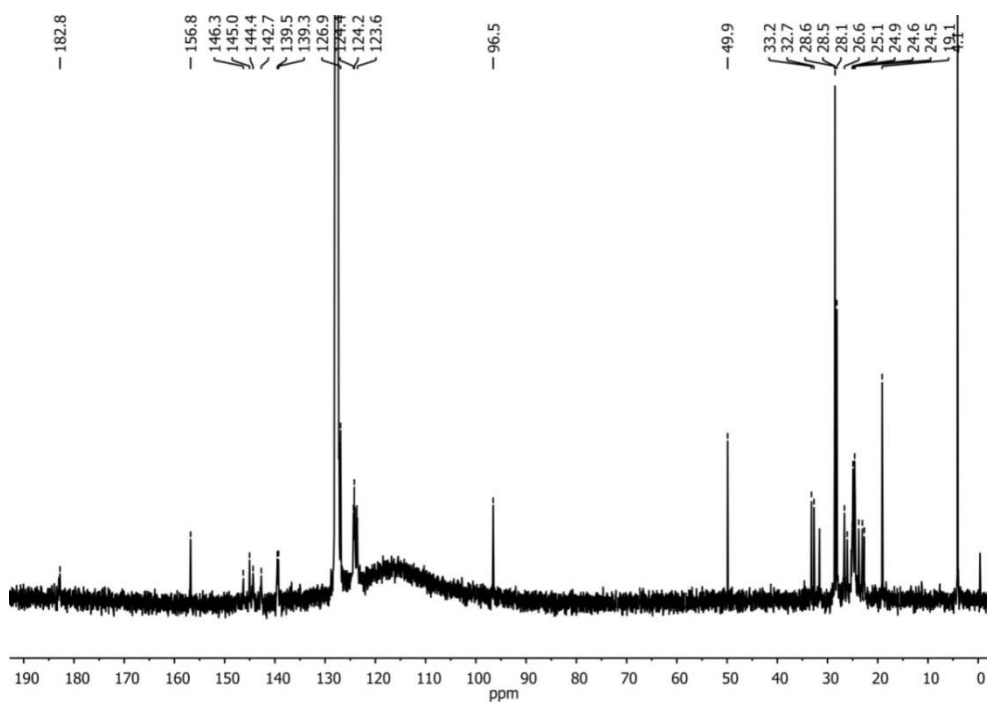


Fig. 14. ¹³C{¹H} NMR spectrum of 5.

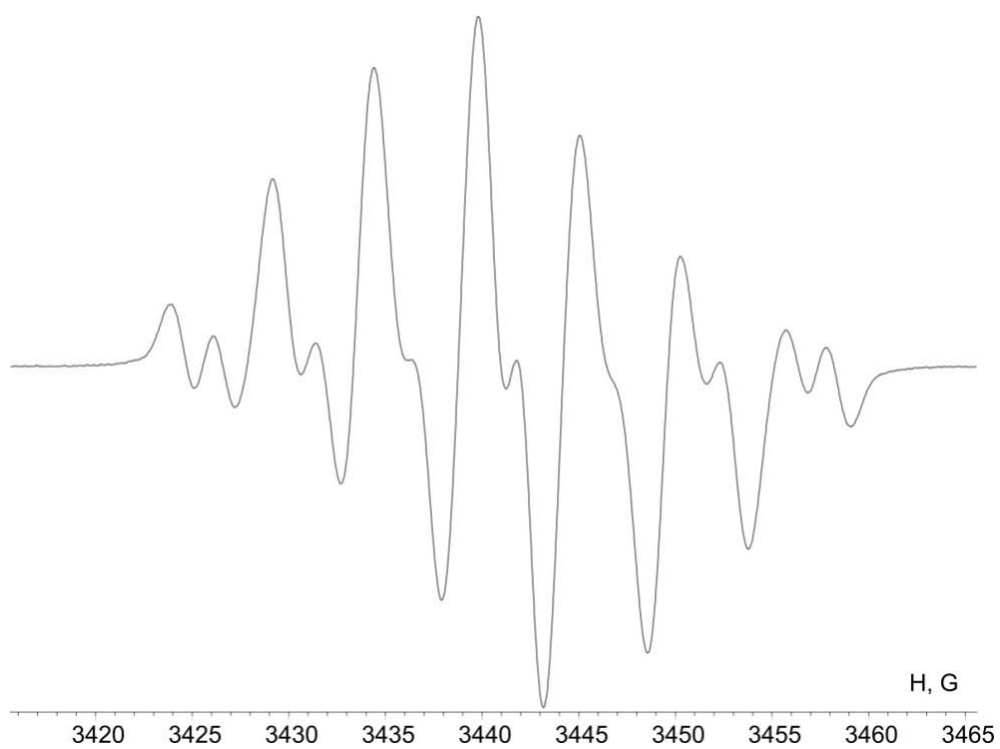


Fig. 15. EPR spectrum of **6**.

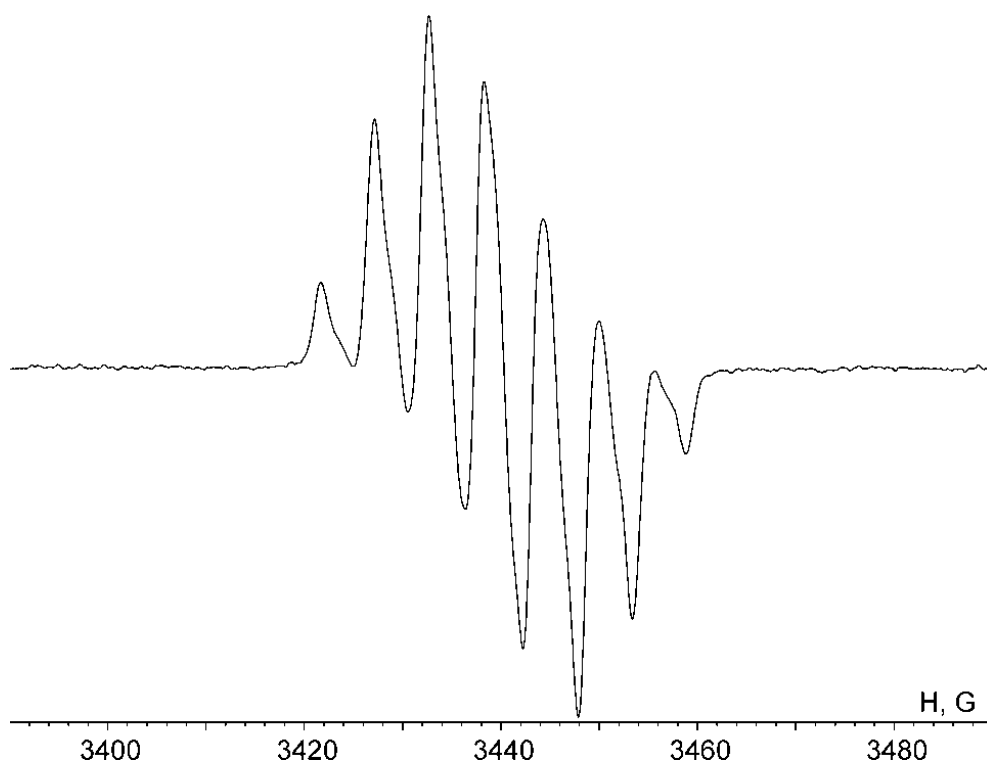


Fig. 16. EPR spectrum of **8**.

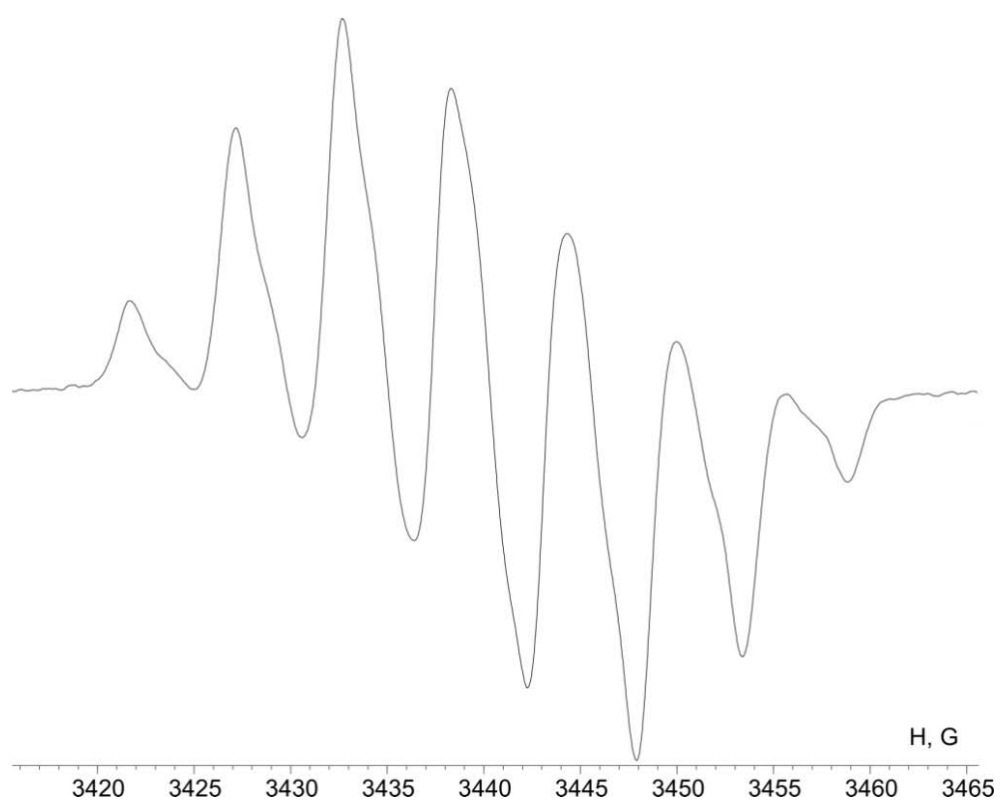


Fig. 17. EPR spectrum of **10**.