Supplementary Material

Highly flexible synthesis of indenylethylamines as ligand precursors for titanium complexes

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Dedicated to Professor Jürgen Martens in honor of his outstanding contribution to synthetic organic chemistry

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Figure S1. ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

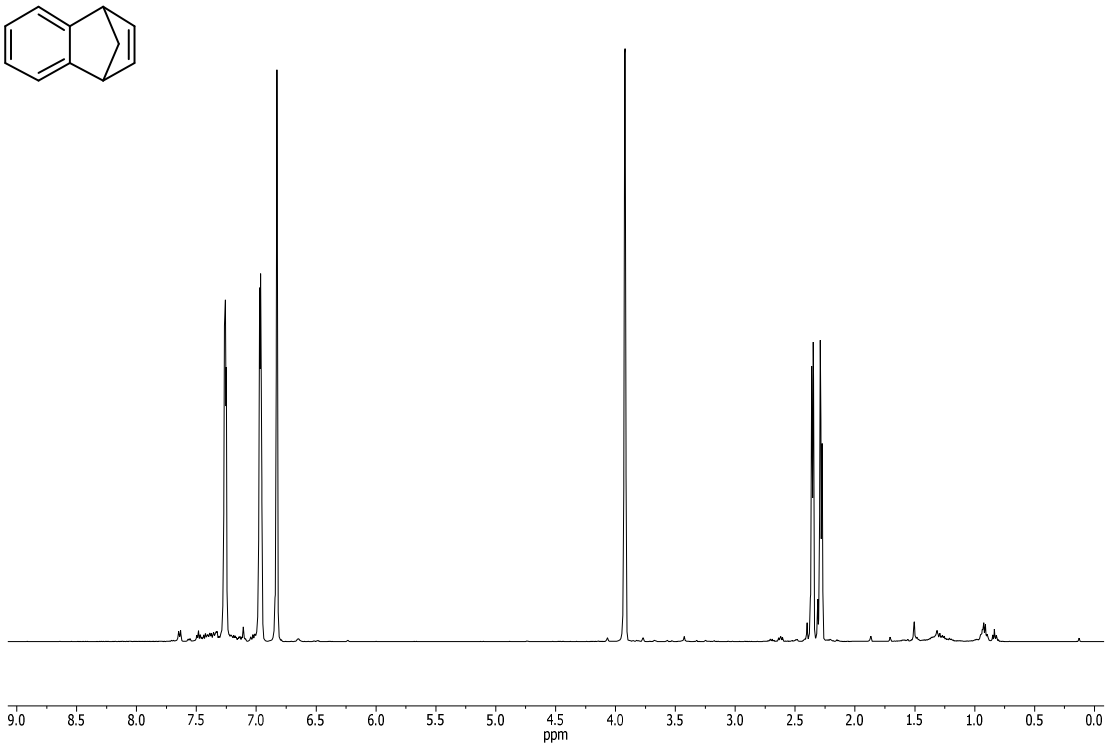


Figure S2. ^{13}C NMR spectrum of compound **9** in $CDCl_3$.

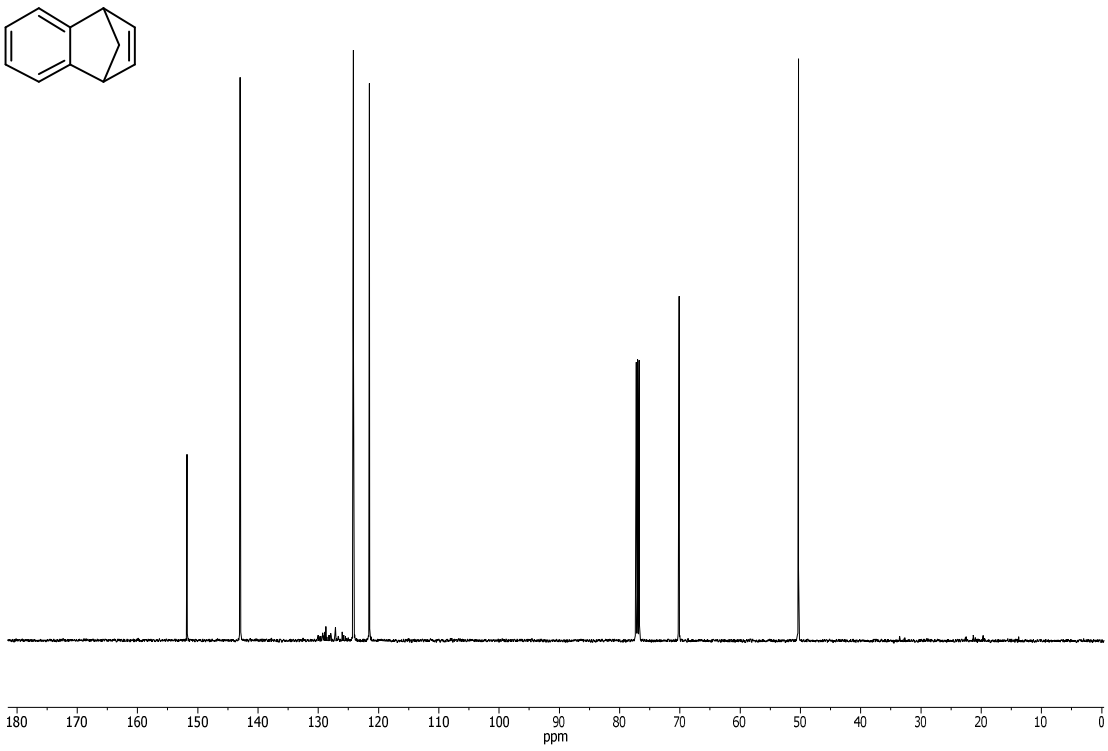


Figure S3. IR spectrum of compound **9**.

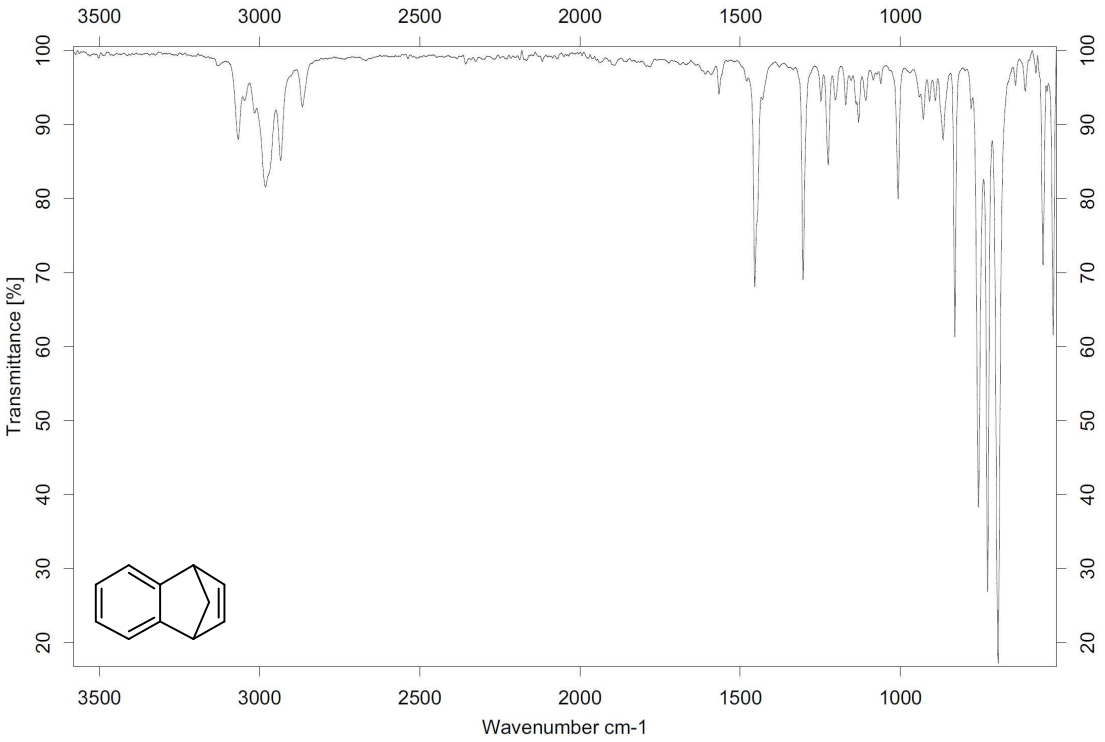


Figure S4. ^{1}H NMR spectrum of compound **10** in $CDCl_3$.

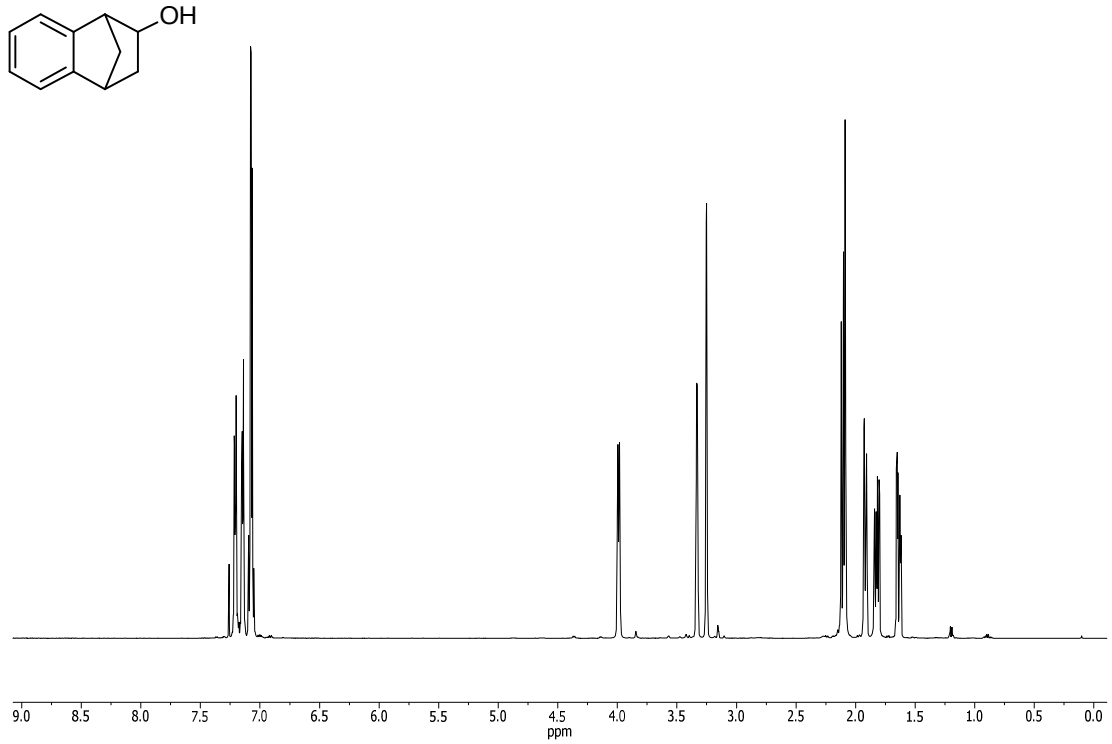


Figure S5. ^{13}C NMR spectrum of compound **10** in $CDCl_3$.

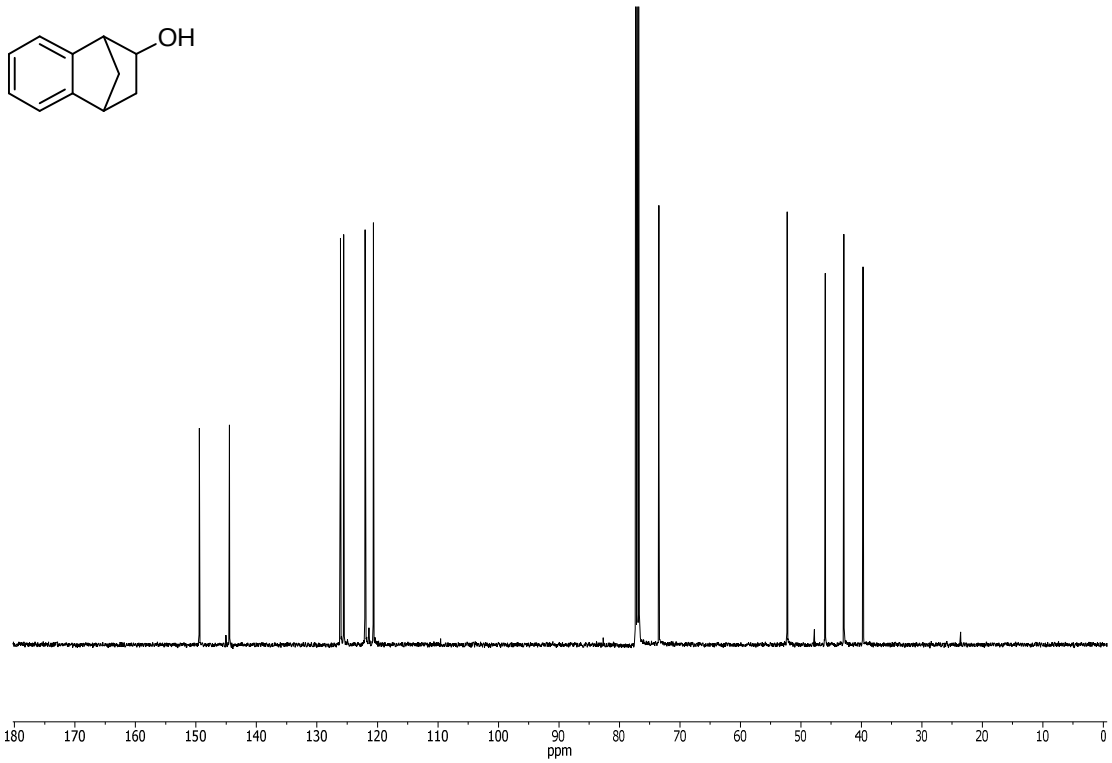


Figure S6. IR spectrum of compound **10**.

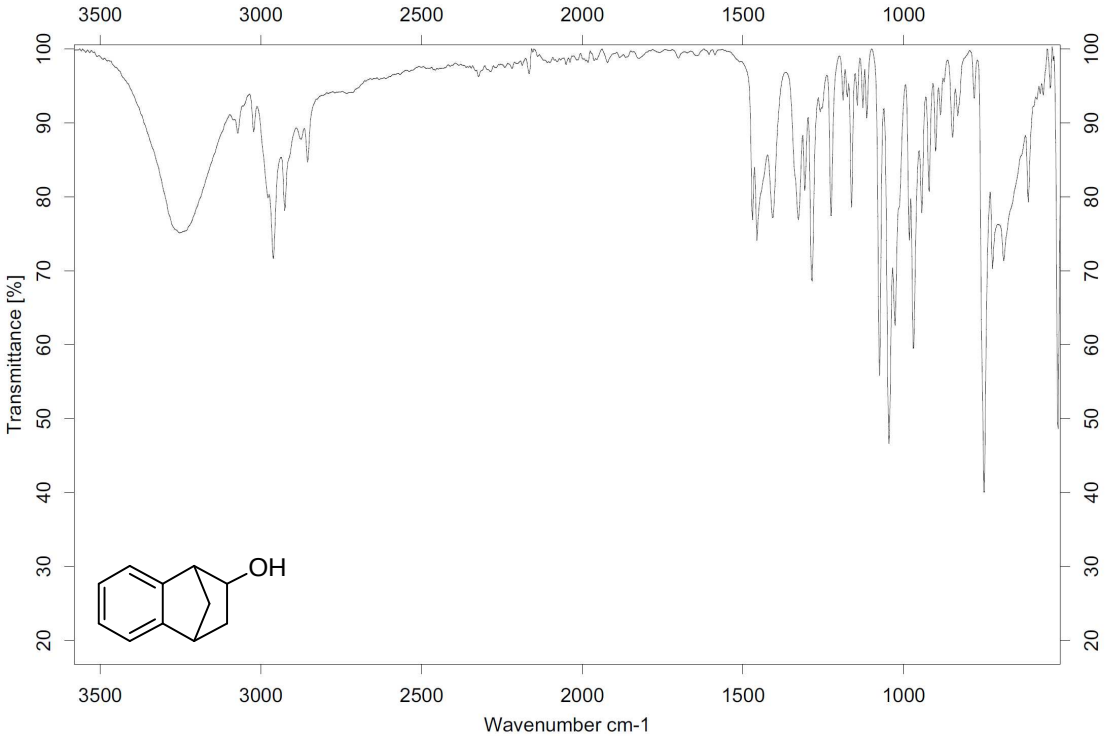


Figure S7. ^{1}H NMR spectrum of compound **11** in $CDCl_3$.

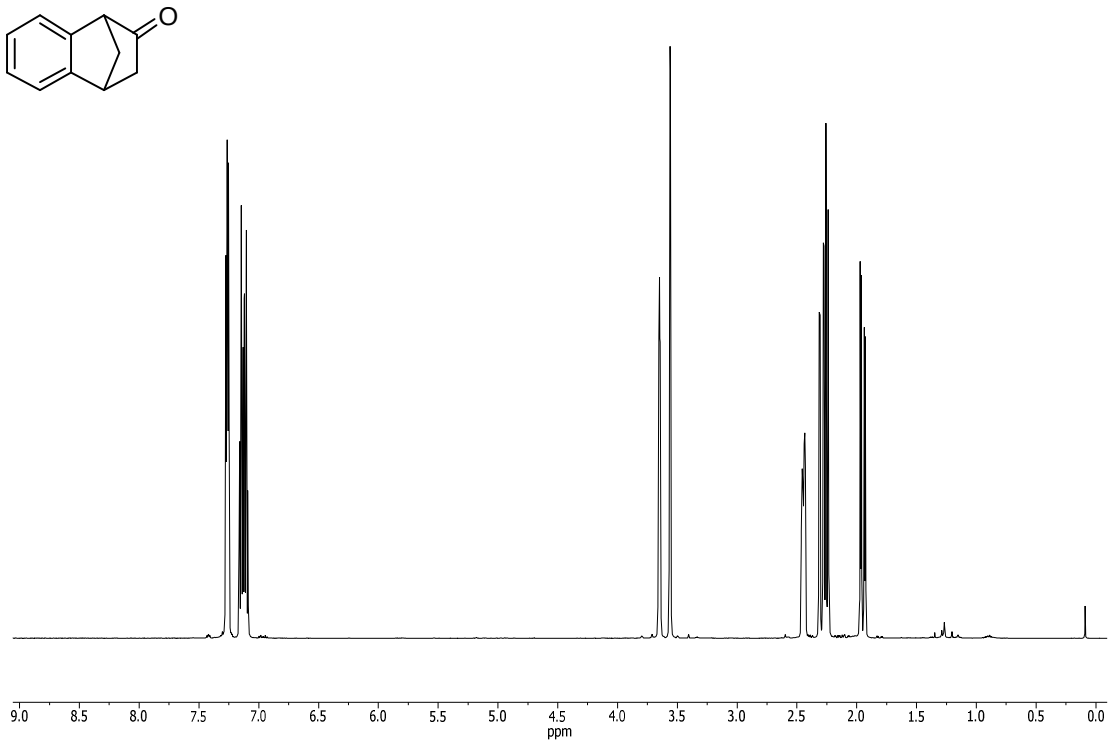


Figure S8. ^{13}C NMR spectrum of compound **11** in $CDCl_3$.

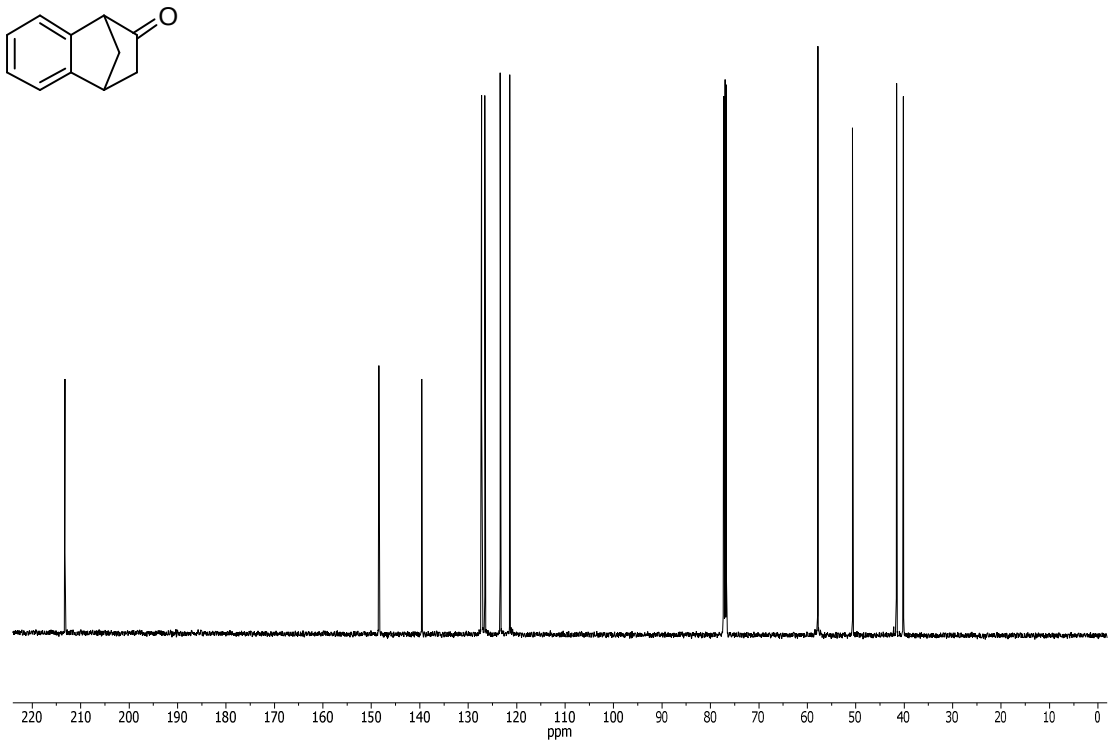


Figure S9. IR spectrum of compound **11**.

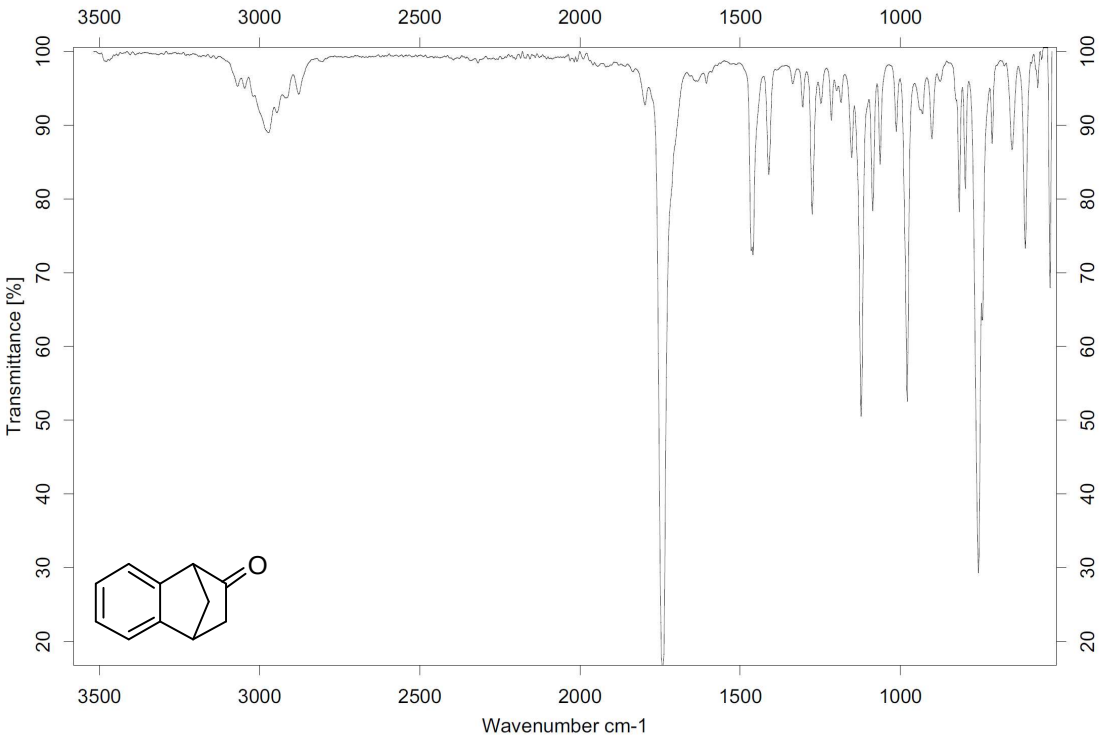


Figure S10. ^{1}H NMR spectrum of compound **14** in $CDCl_3$.

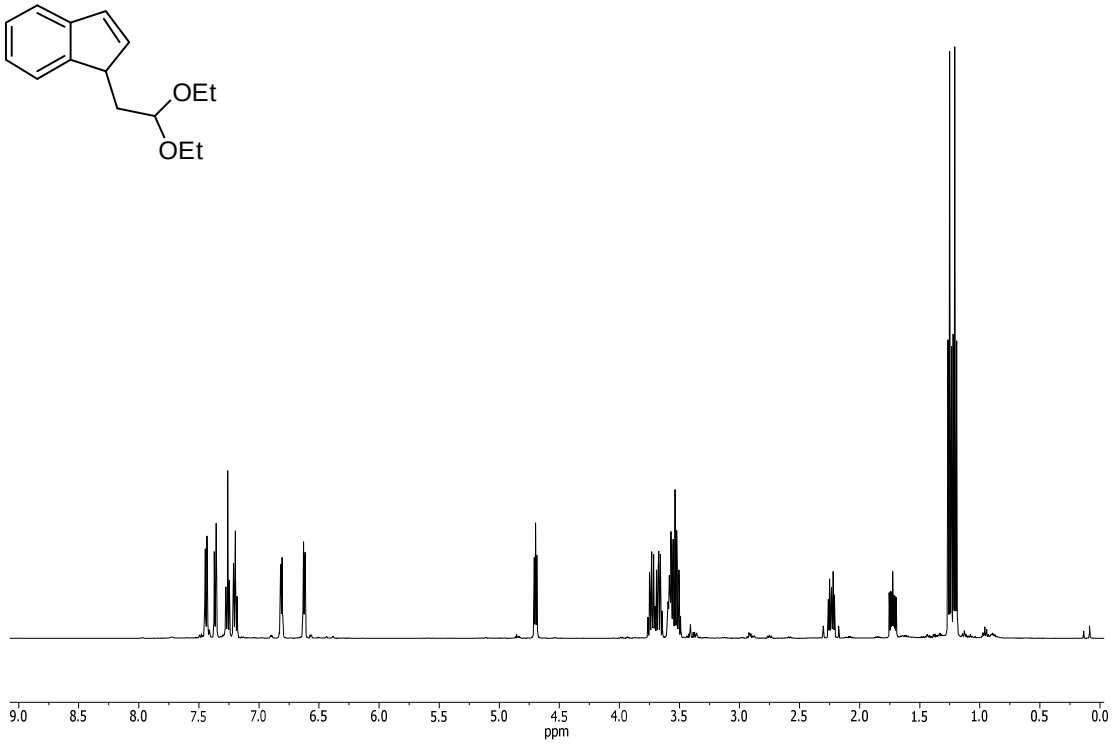


Figure S11. ^{13}C NMR spectrum of compound **14** in $CDCl_3$.

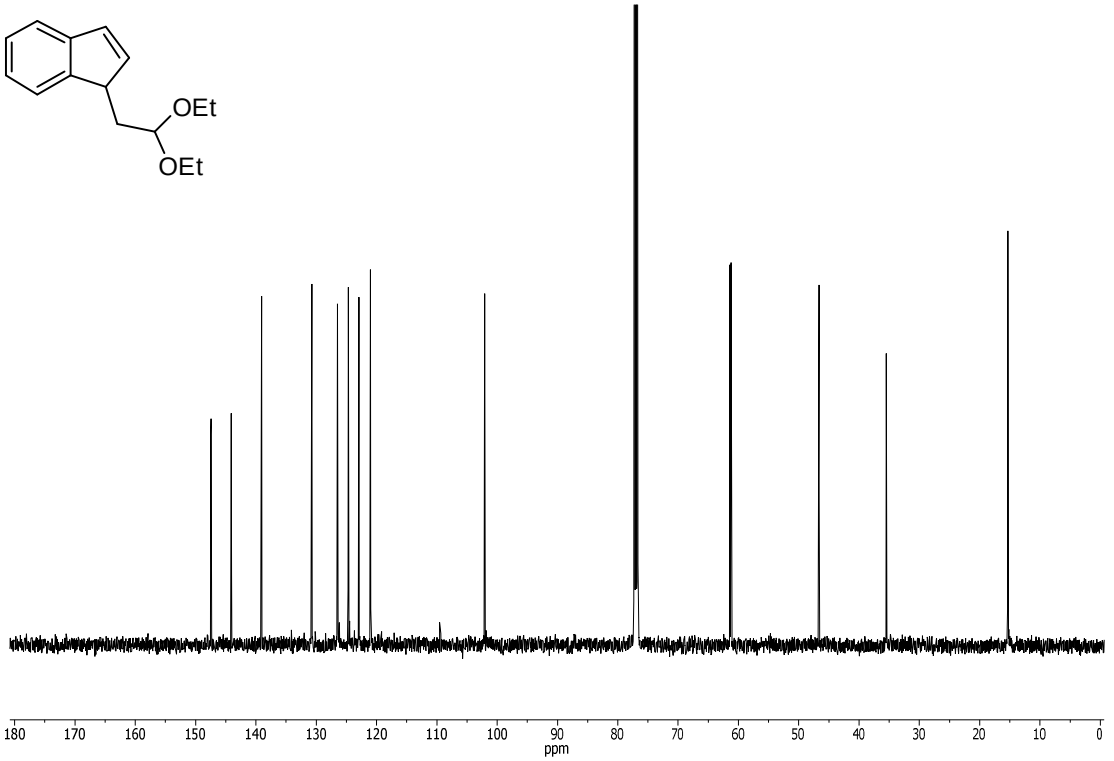


Figure S12. IR spectrum of compound **14**.

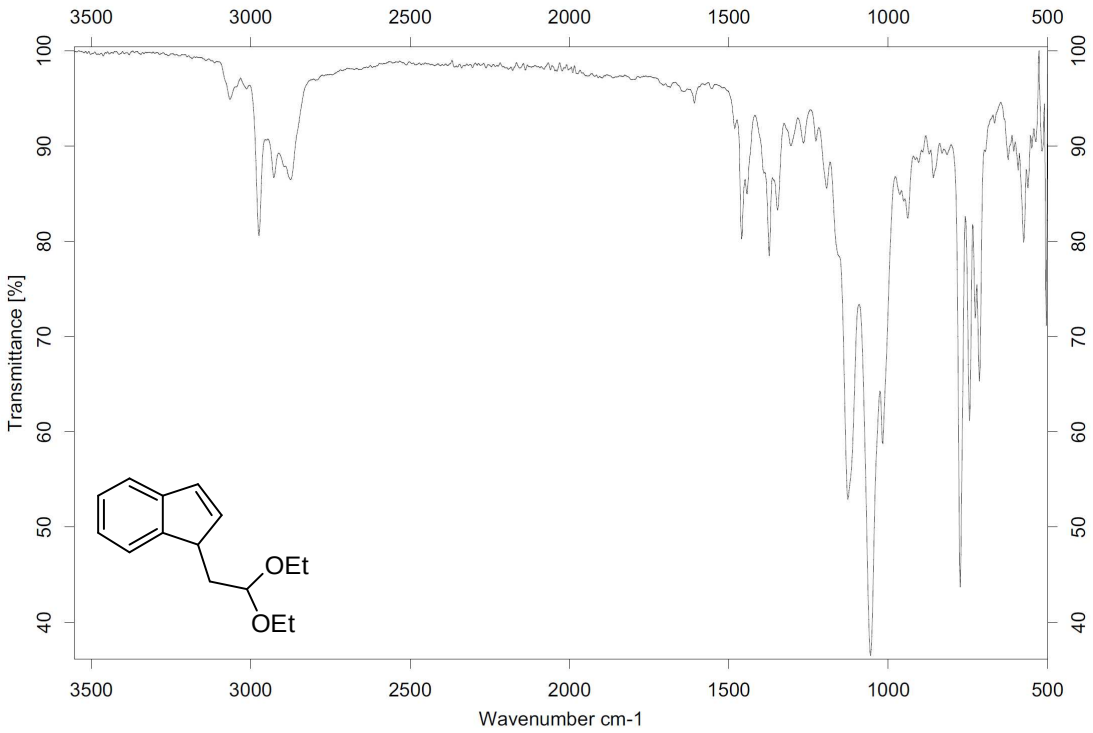


Figure S13. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

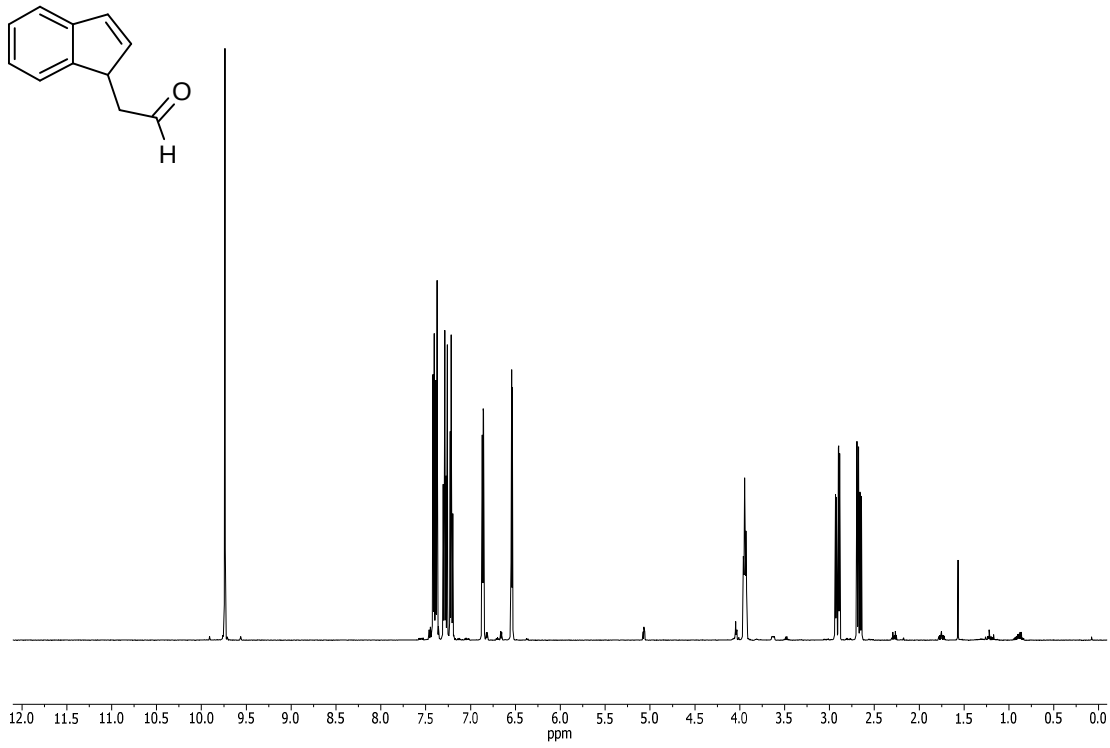


Figure S14. ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

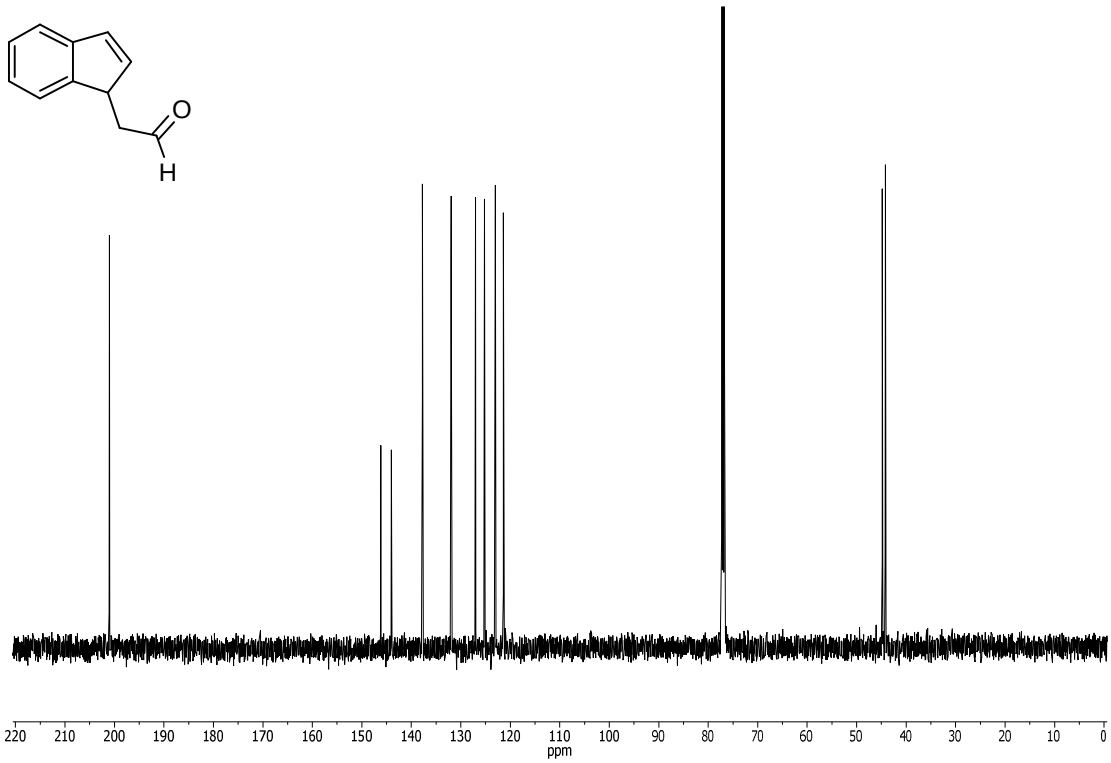


Figure S15. IR spectrum of compound **5**.

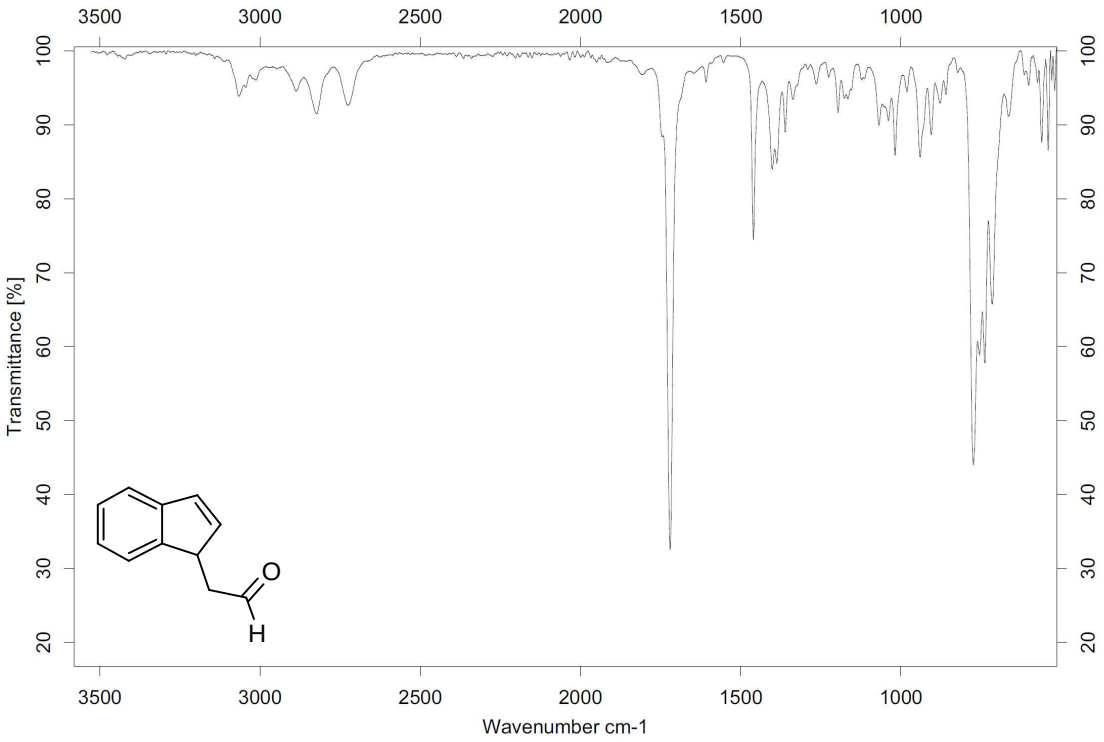


Figure S16. ^{1}H NMR spectrum of compound **3a** in $CDCl_3$.

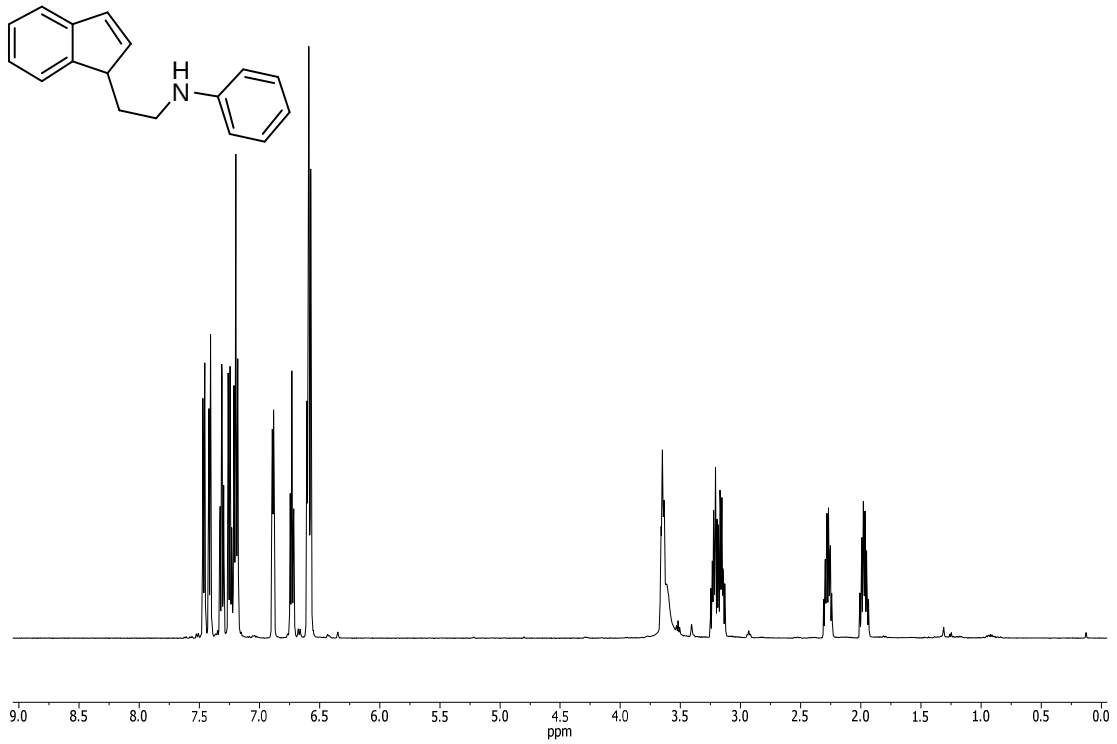


Figure S17. ^{13}C NMR spectrum of compound **3a** in $CDCl_3$.

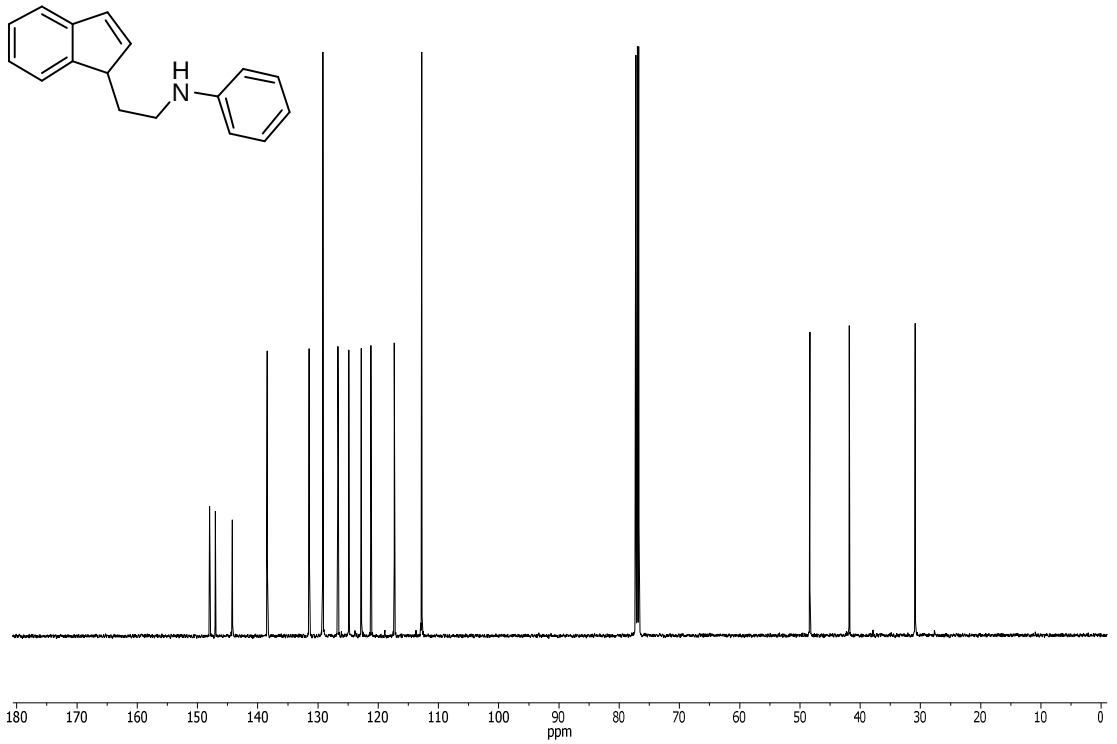


Figure S18. IR spectrum of compound **3a**.

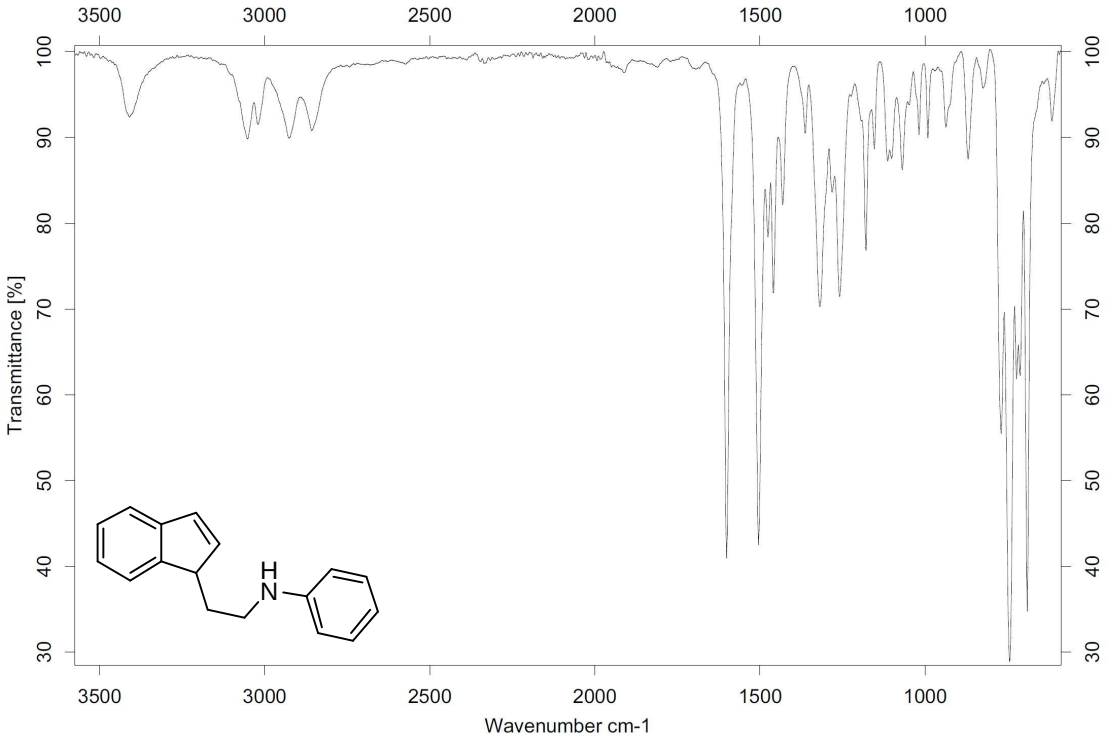


Figure S19. ^{1}H NMR spectrum of compound **3b** in $CDCl_3$.

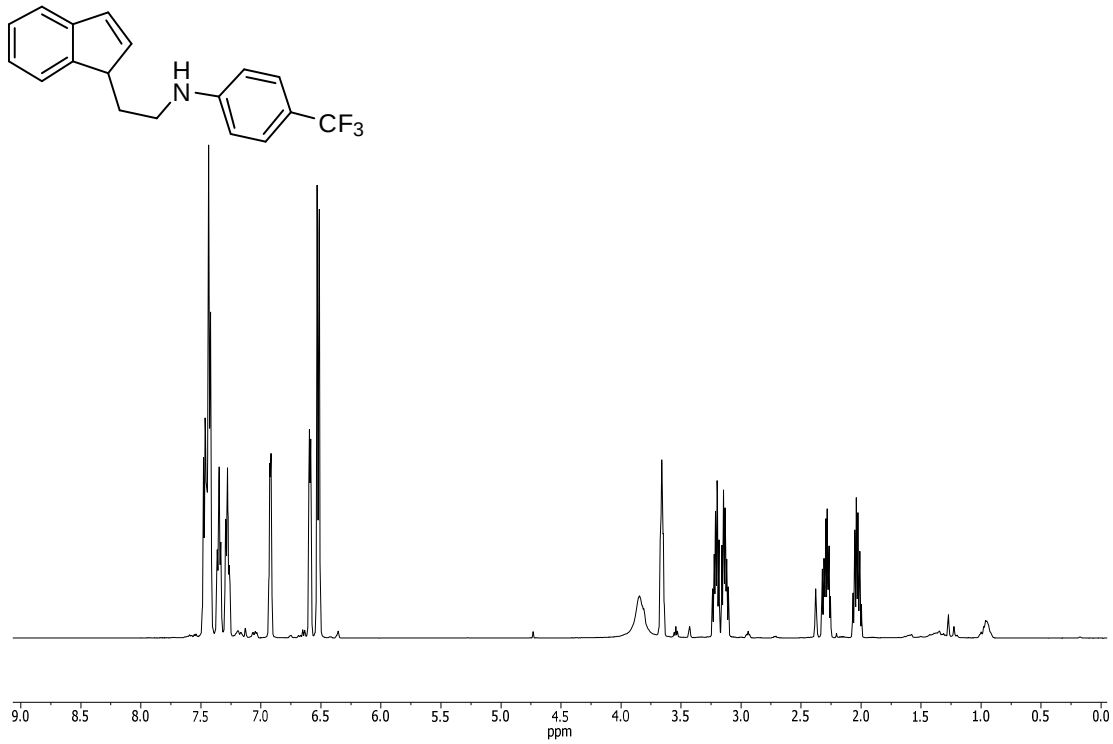


Figure S20. ^{13}C NMR spectrum of compound **3b** in $CDCl_3$.

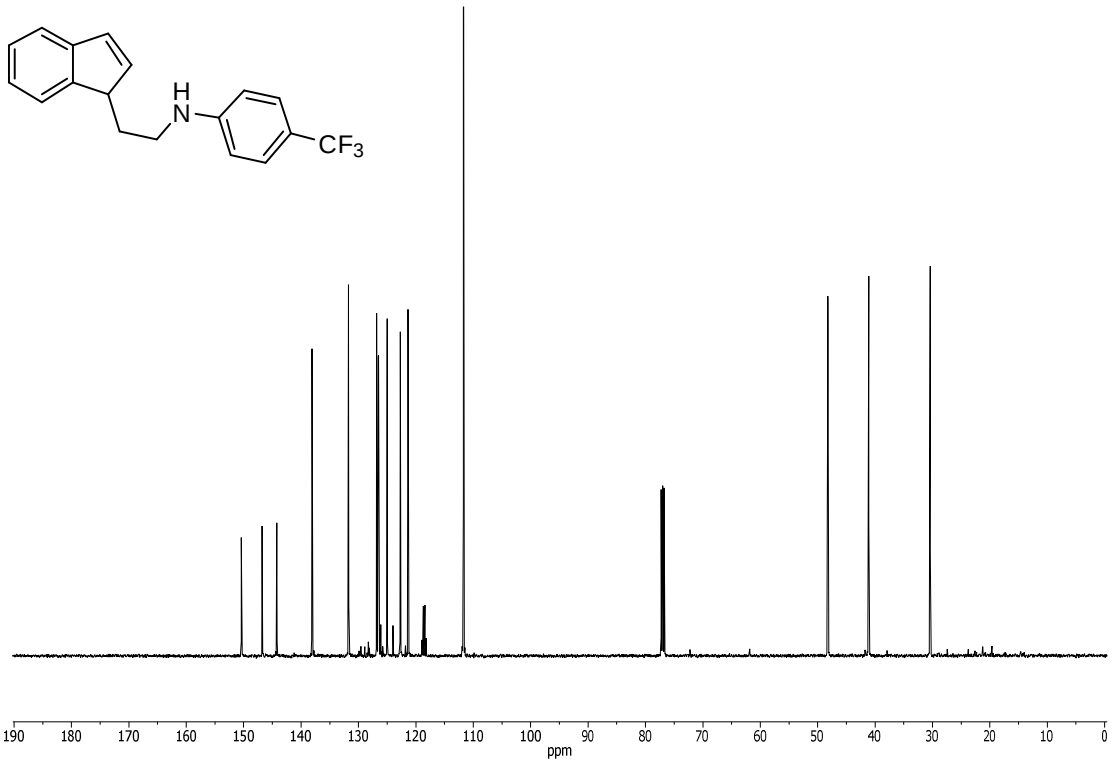


Figure S21. ^{19}F NMR spectrum of compound **3b** in $CDCl_3$.

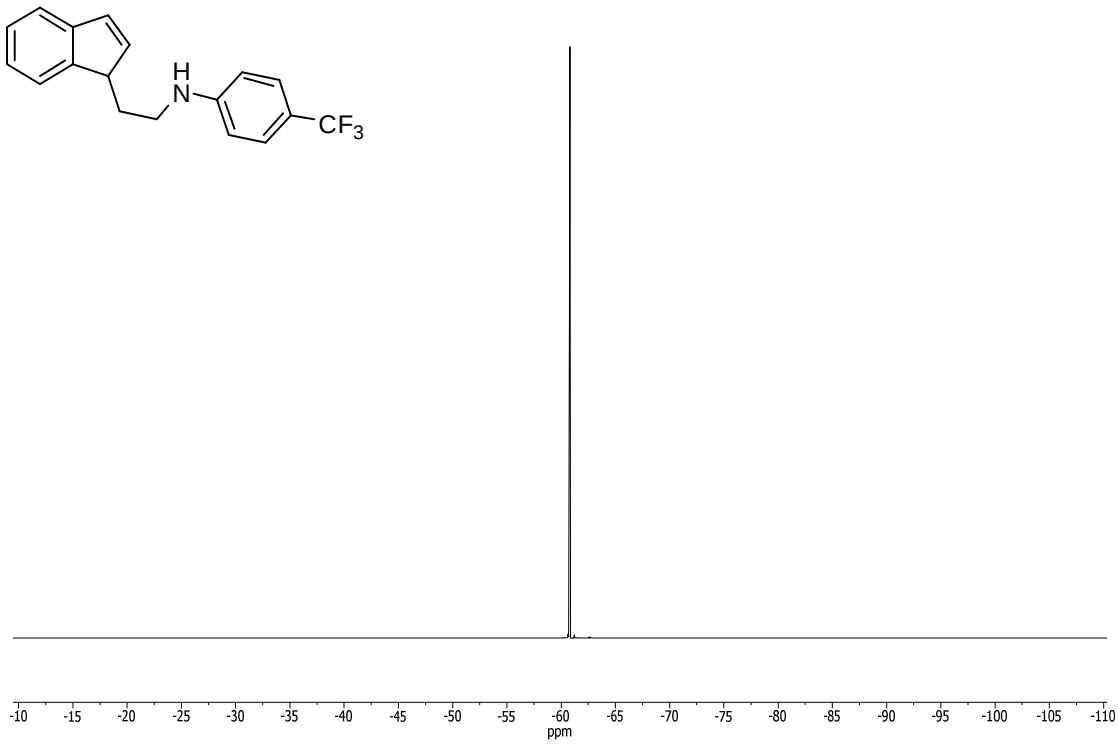


Figure S22. IR spectrum of compound **3b**.

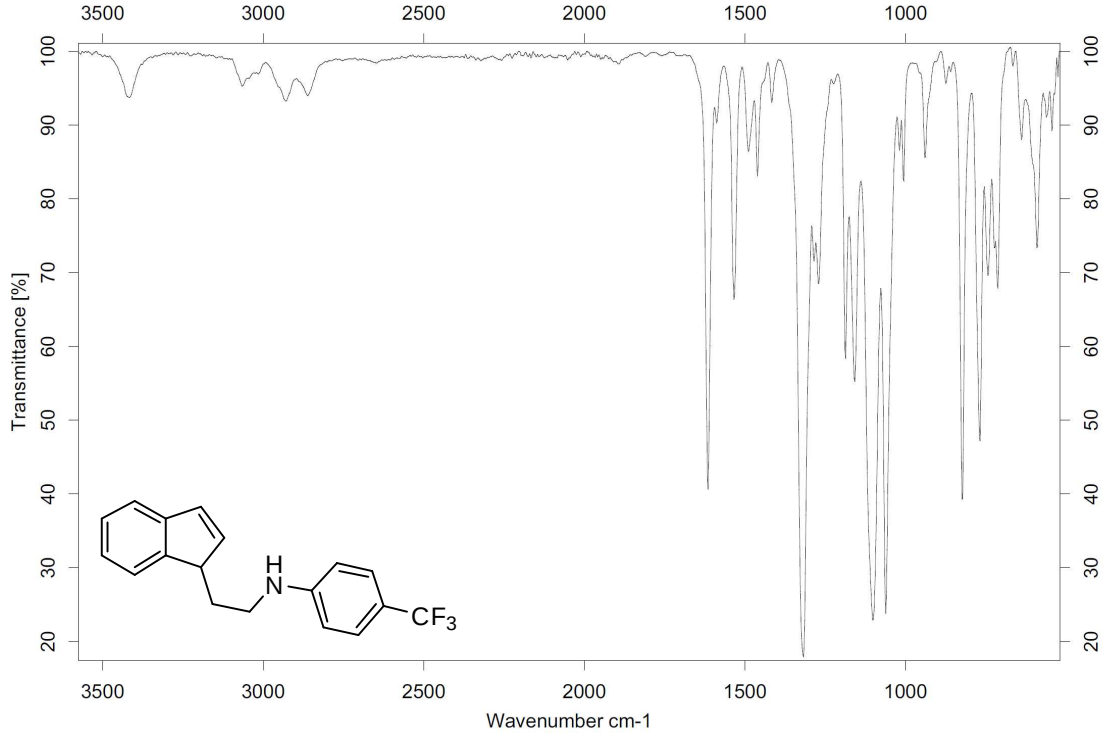


Figure S23. ^{1}H NMR spectrum of compound **3c** in $CDCl_3$.

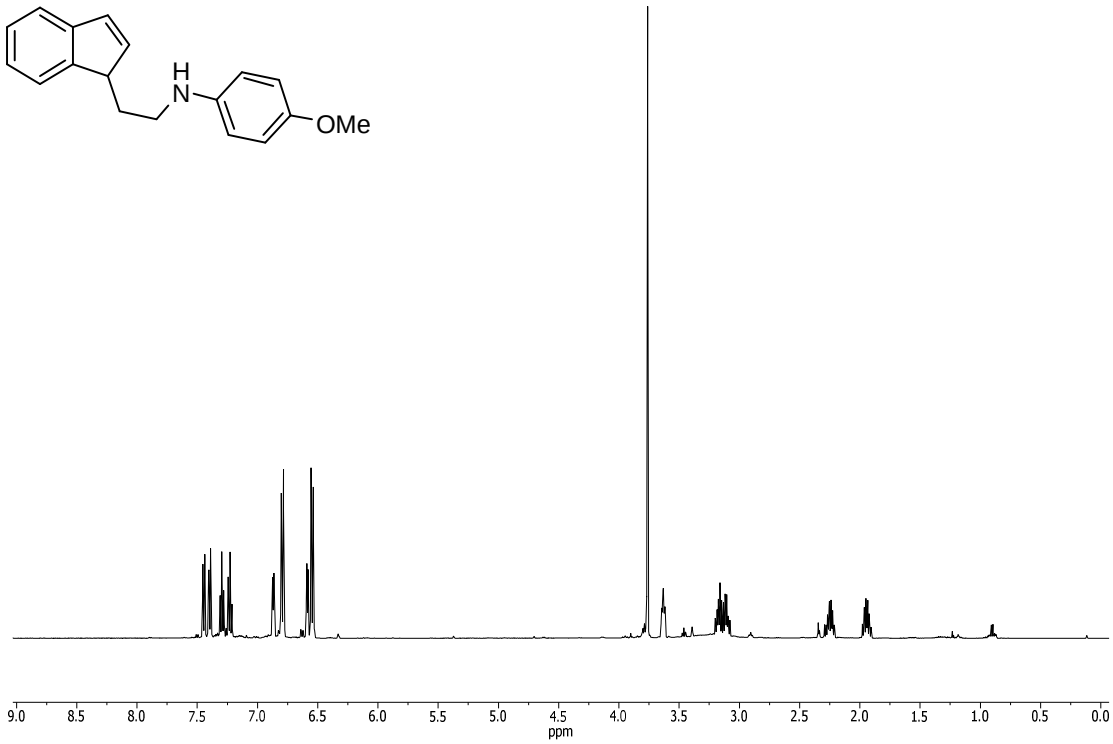


Figure S24. ^{13}C NMR spectrum of compound **3c** in $CDCl_3$.

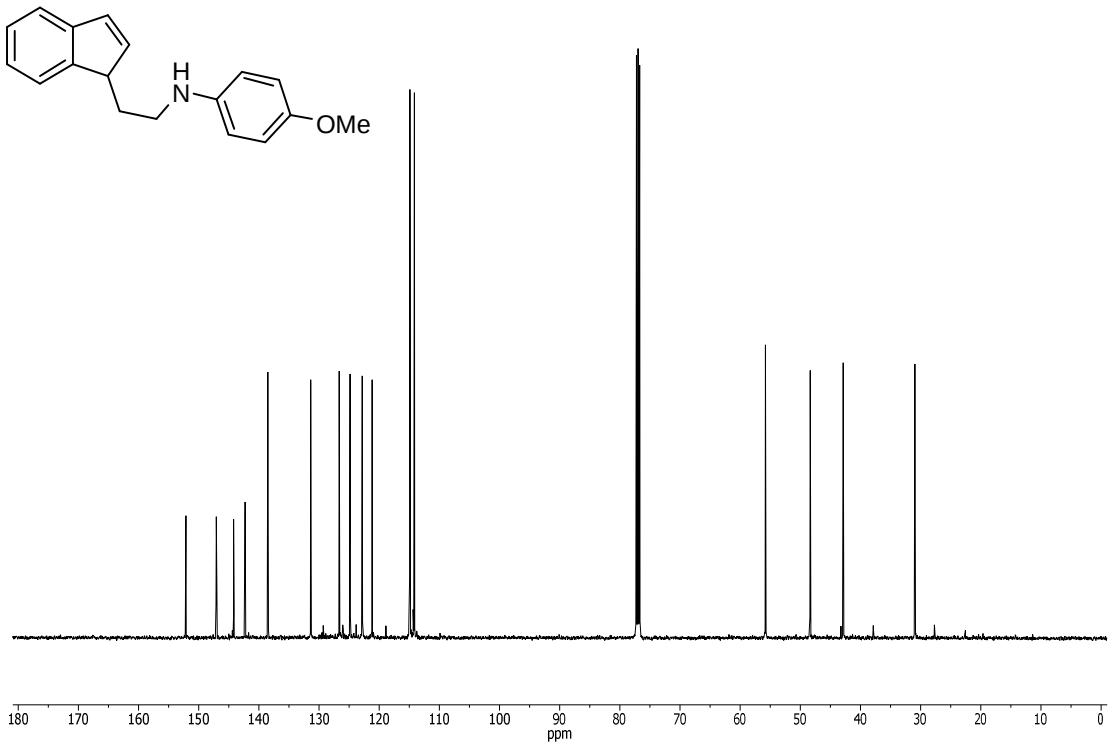


Figure S25. IR spectrum of compound **3c**.

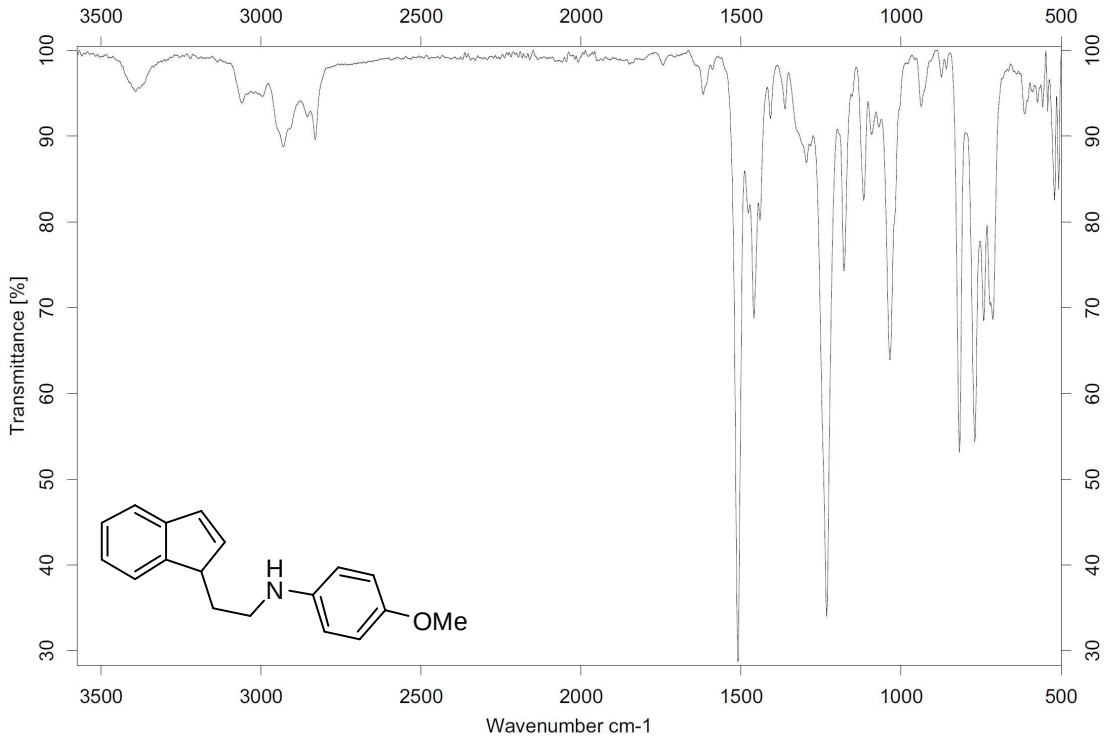


Figure S26. ^{1}H NMR spectrum of compound **4d** in $CDCl_3$.

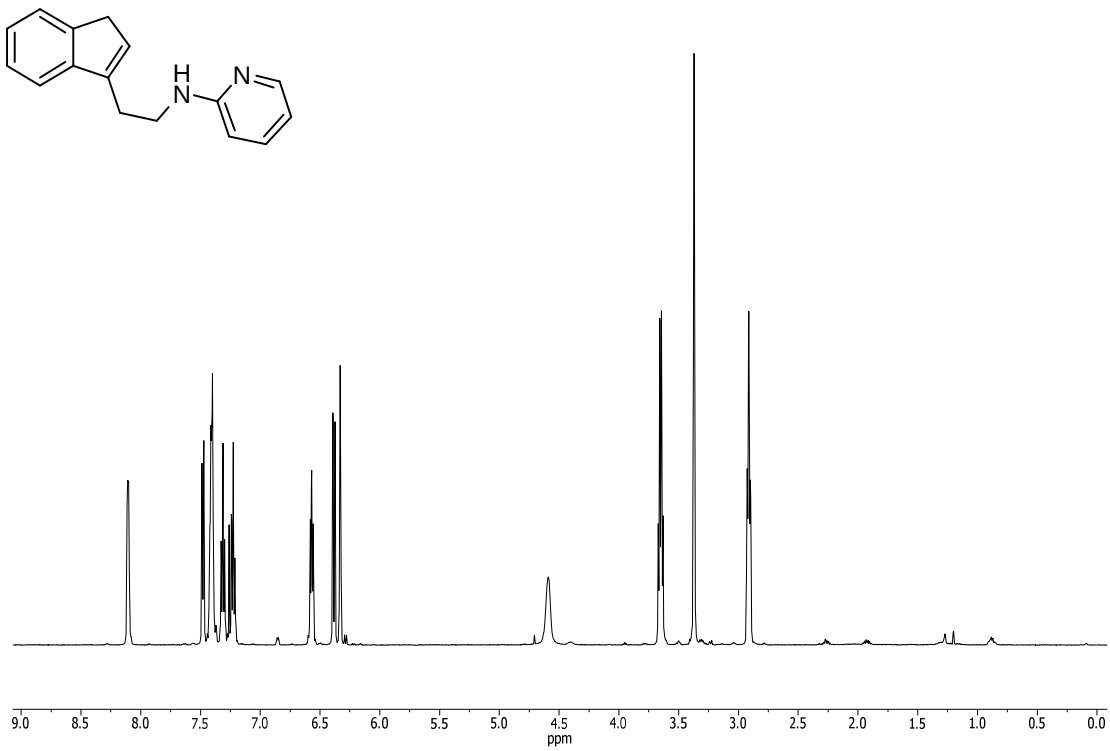


Figure S27. ^{13}C NMR spectrum of compound **4d** in $CDCl_3$.

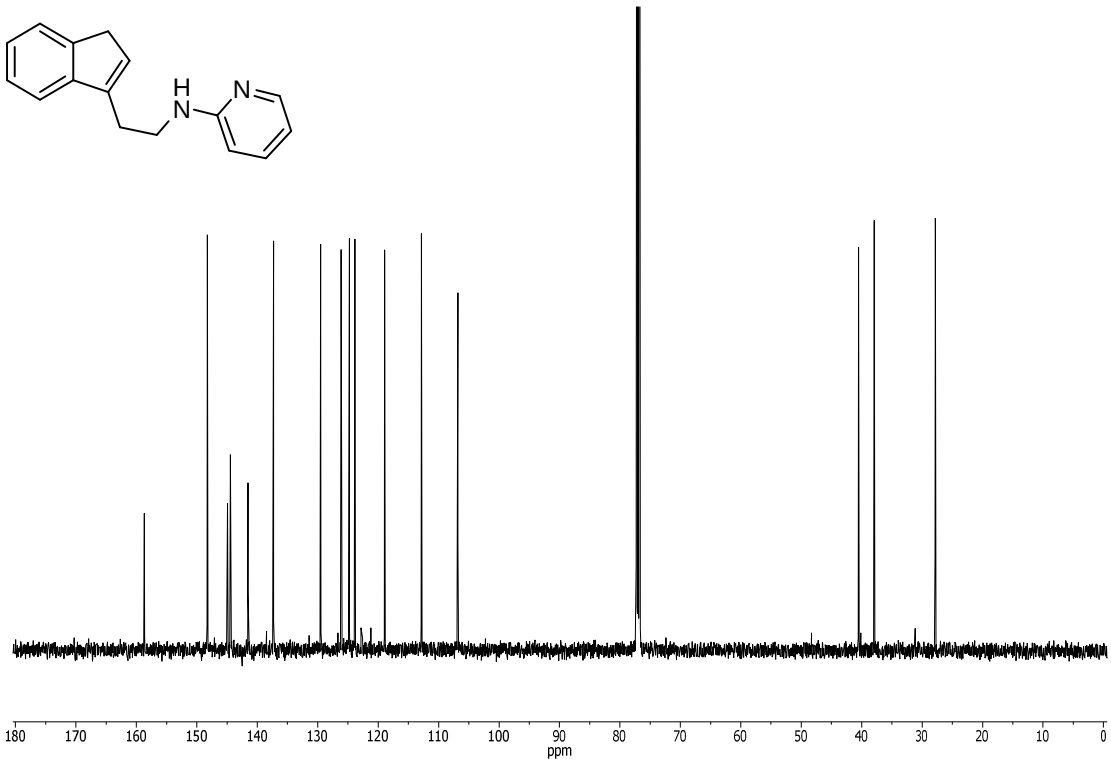


Figure S28. IR spectrum of compound **4d**.

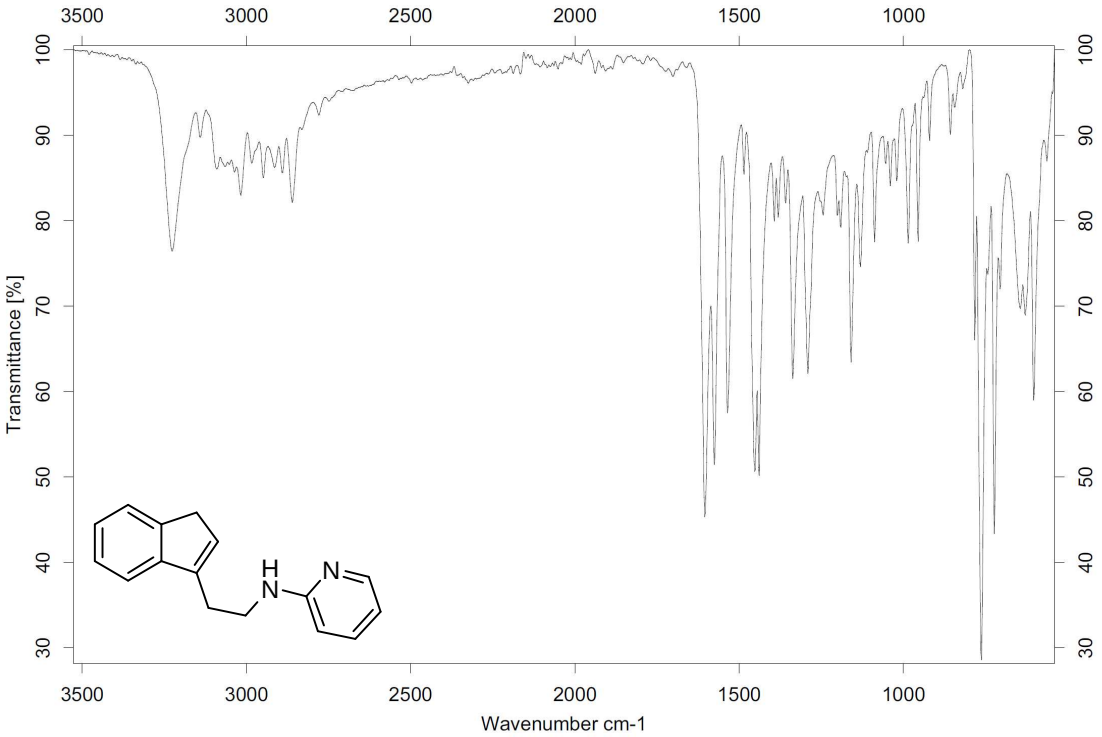


Figure S29. ^{1}H NMR spectrum of compound **4e** in $CDCl_3$.

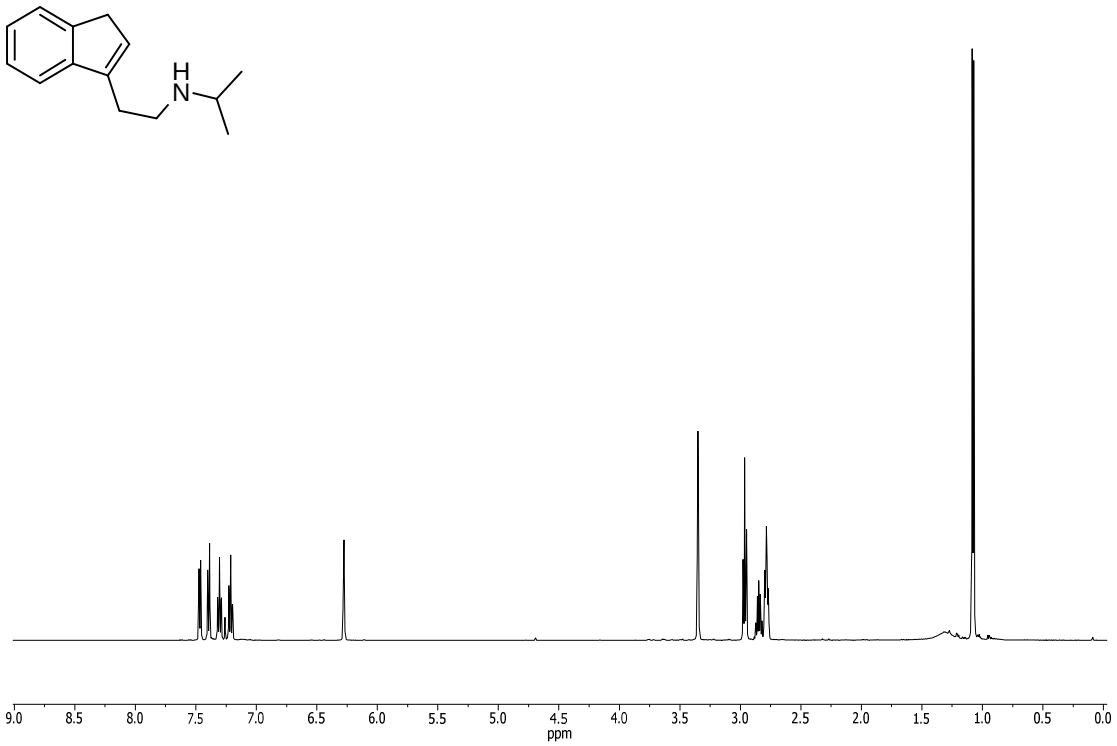


Figure S30. ^{13}C NMR spectrum of compound **4e** in $CDCl_3$.

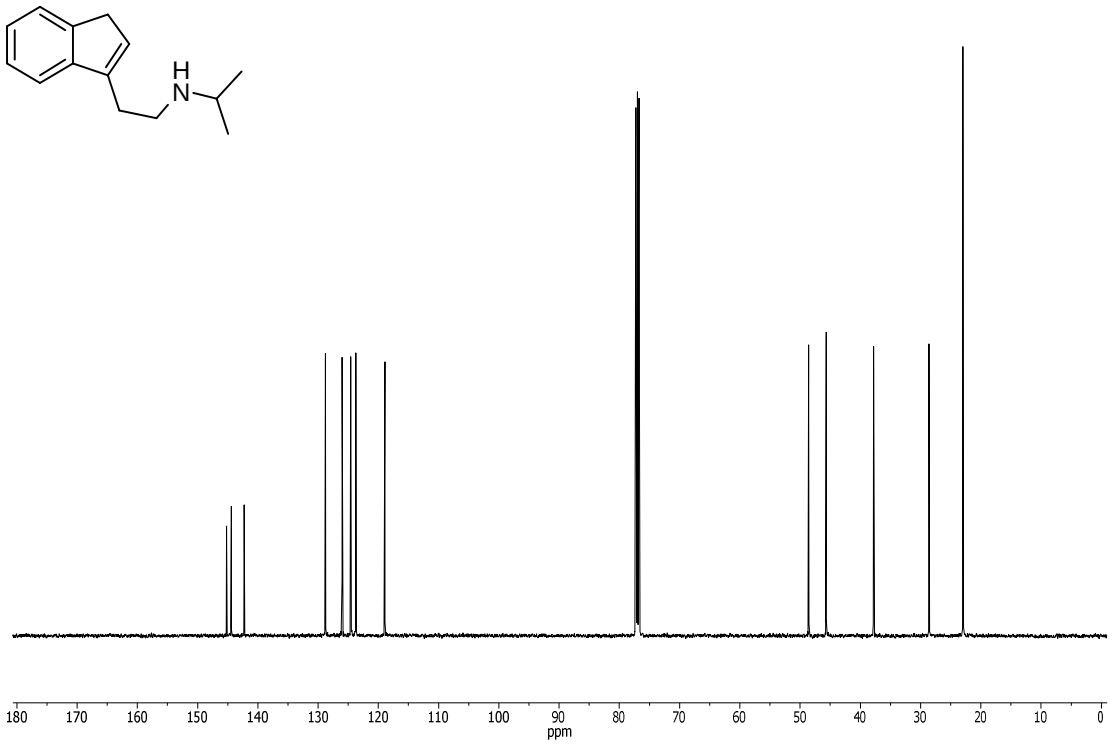


Figure S31. IR spectrum of compound **4e**.

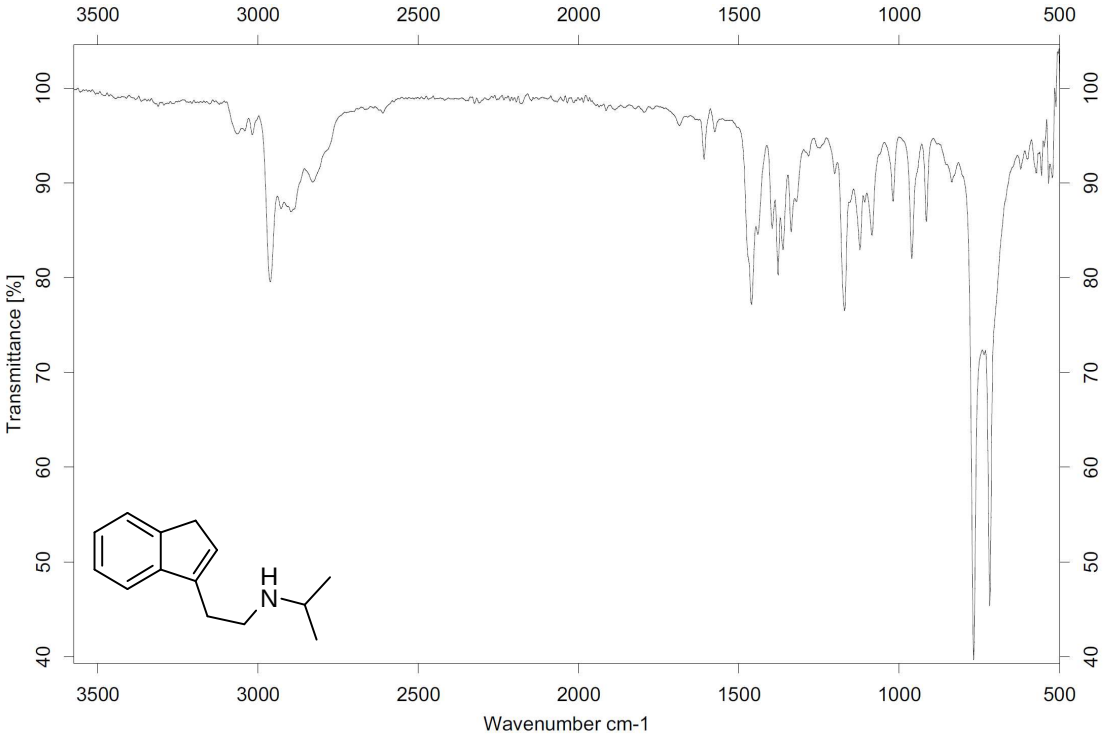


Figure S32. ^{1}H NMR spectrum of compound **4f** in $CDCl_3$.

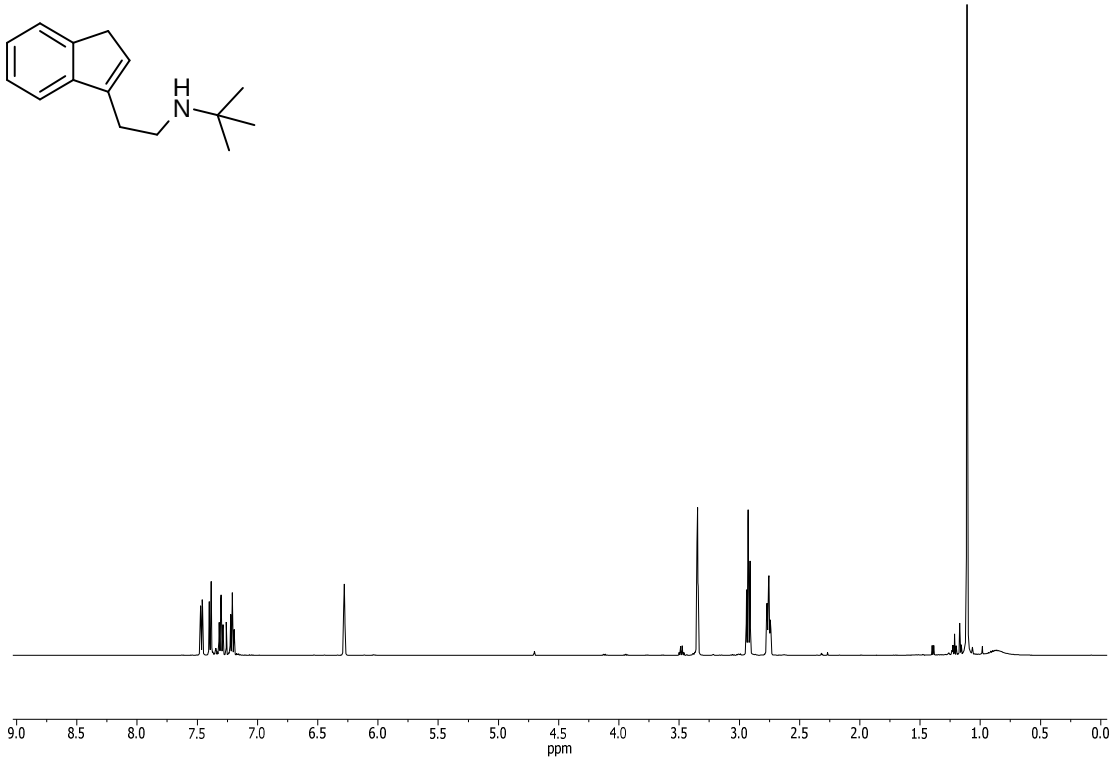


Figure S33. ^{13}C NMR spectrum of compound **4f** in $CDCl_3$.

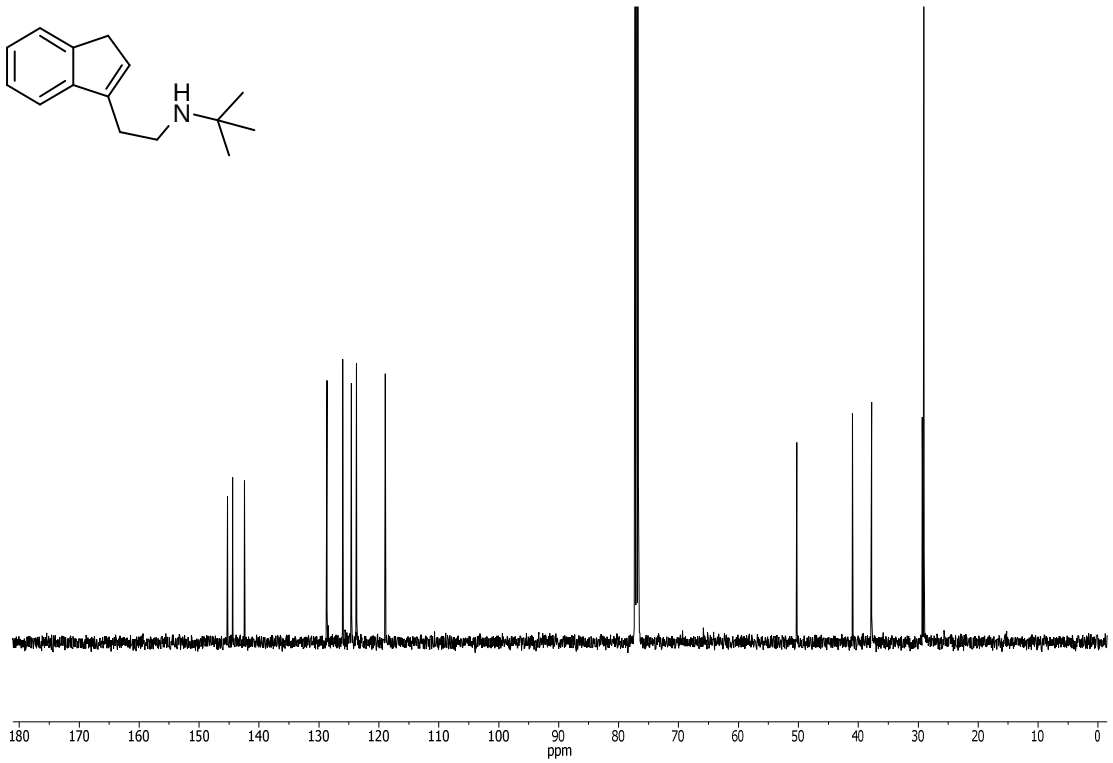


Figure S34. IR spectrum of compound **4f**.

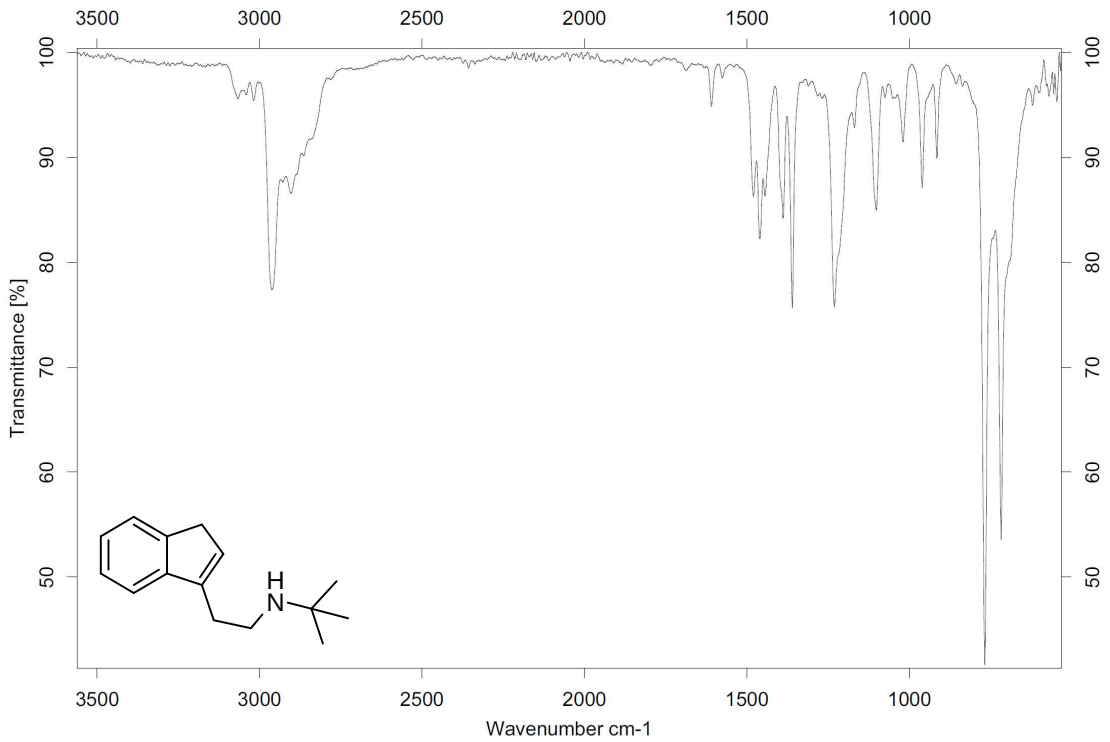


Figure S35. ^{1}H NMR spectrum of compound **4g** in $CDCl_3$.

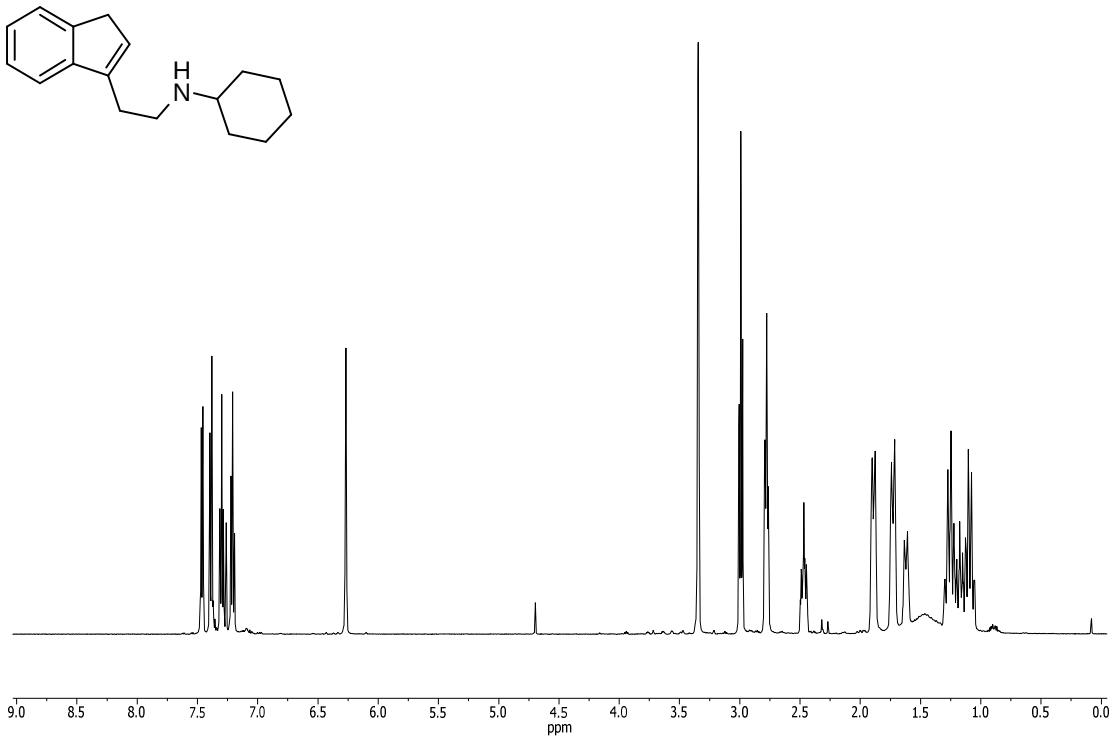


Figure S36. ^{13}C NMR spectrum of compound **4g** in $CDCl_3$.

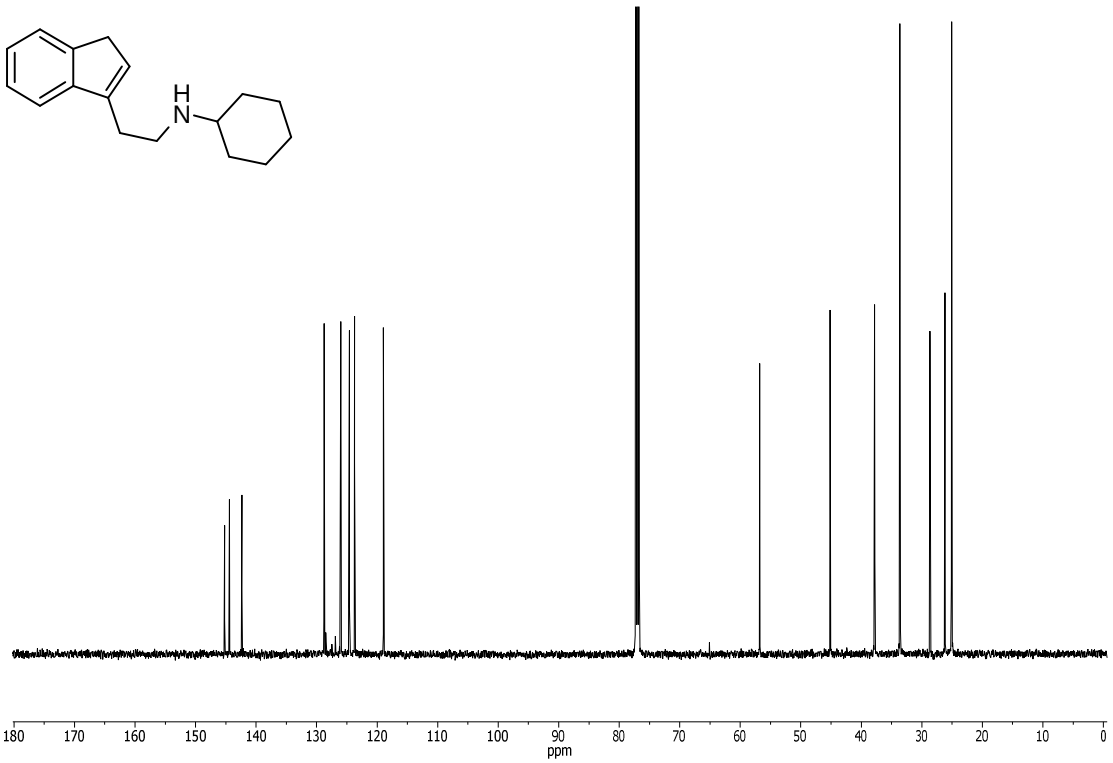


Figure S37. IR spectrum of compound **4g**.

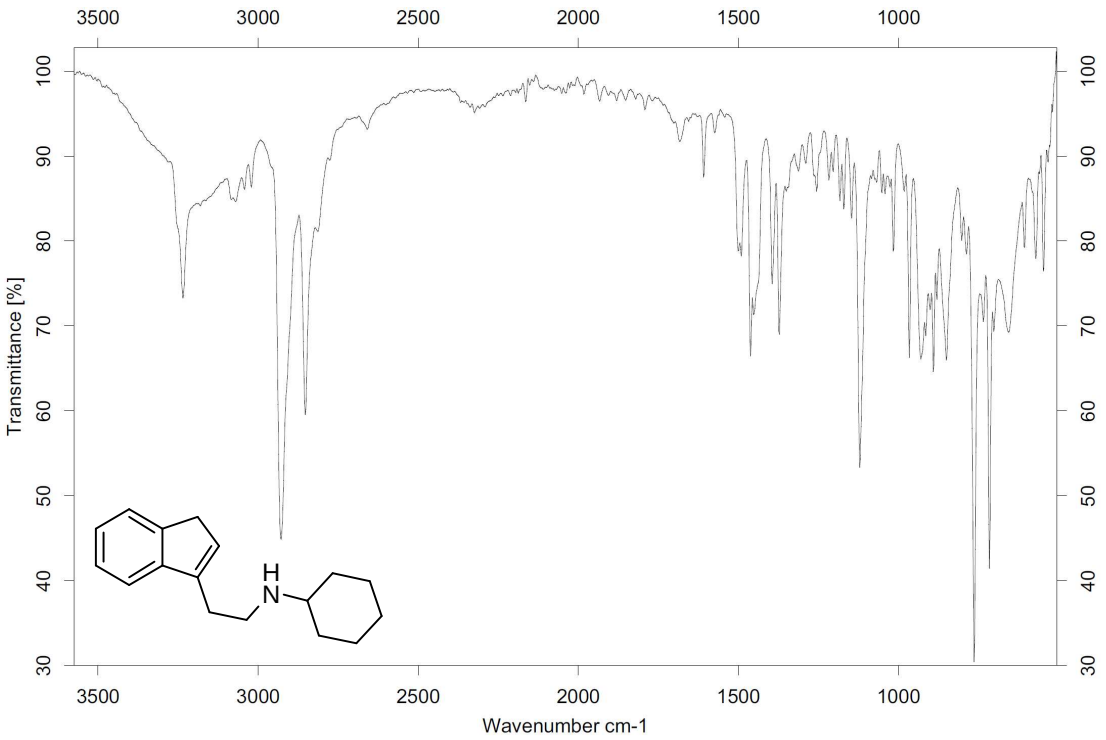


Figure S38. ^{1}H NMR spectrum of compounds **3h** and **4h** in $CDCl_3$.

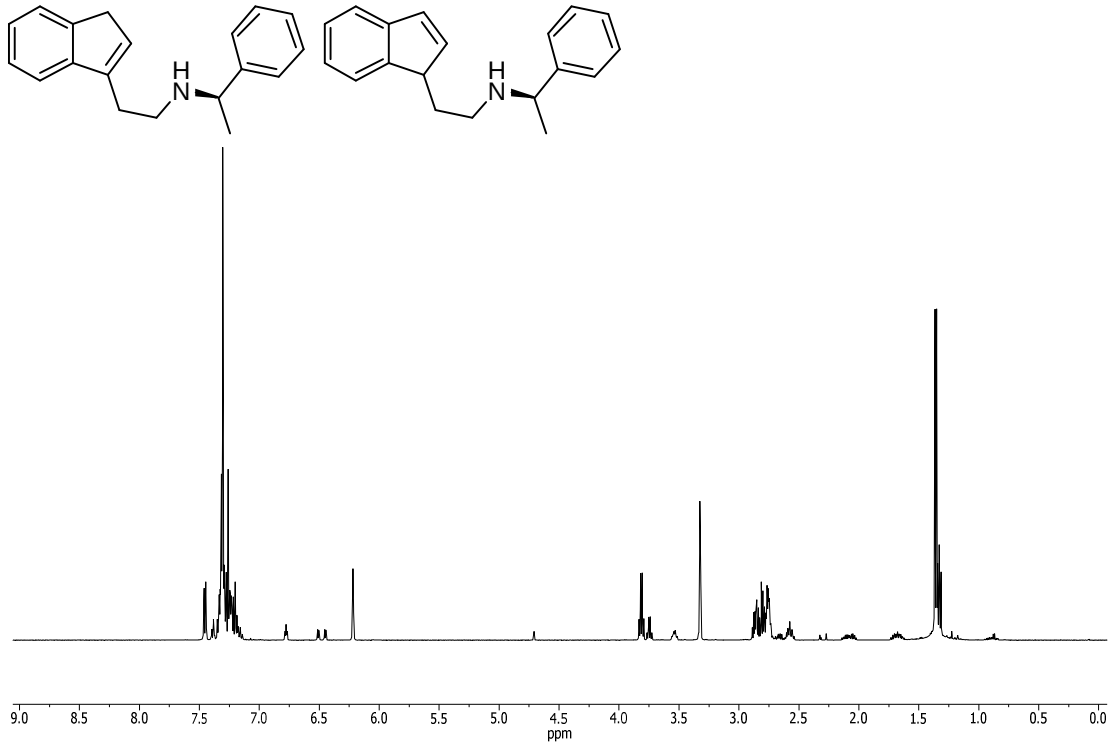


Figure S39. ^{13}C NMR spectrum of compounds **3h** and **4h** in $CDCl_3$.

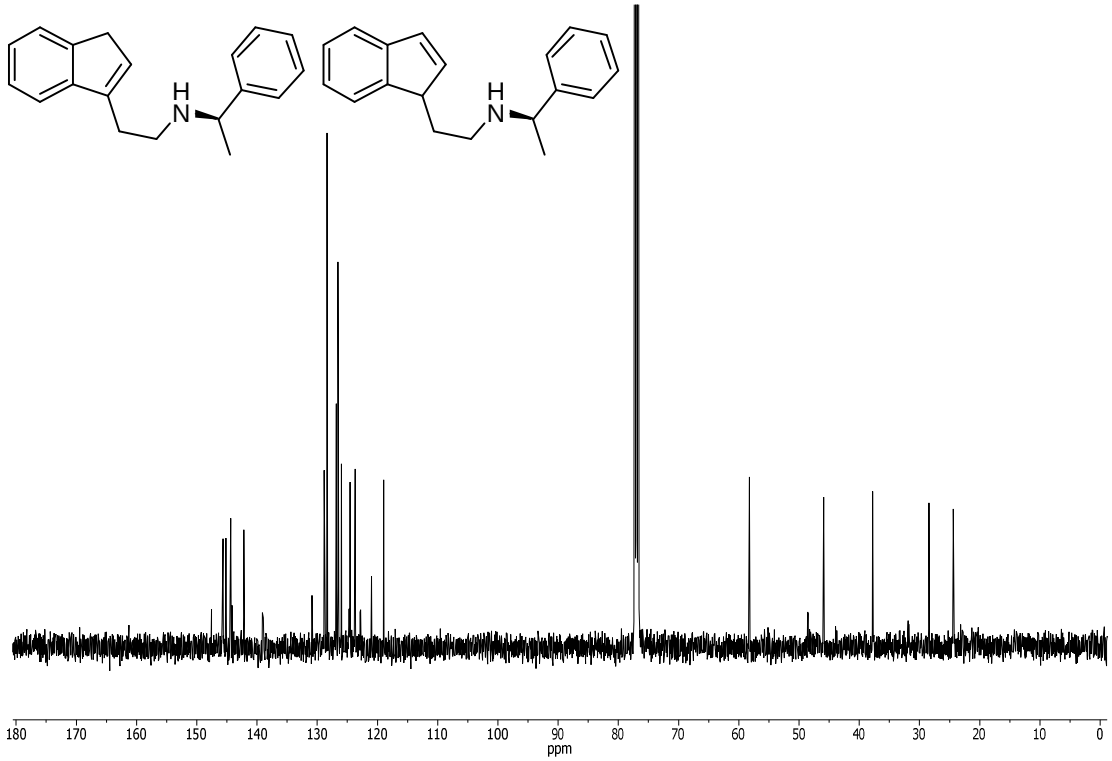


Figure S40. IR spectrum of compounds **3h** and **4h**.

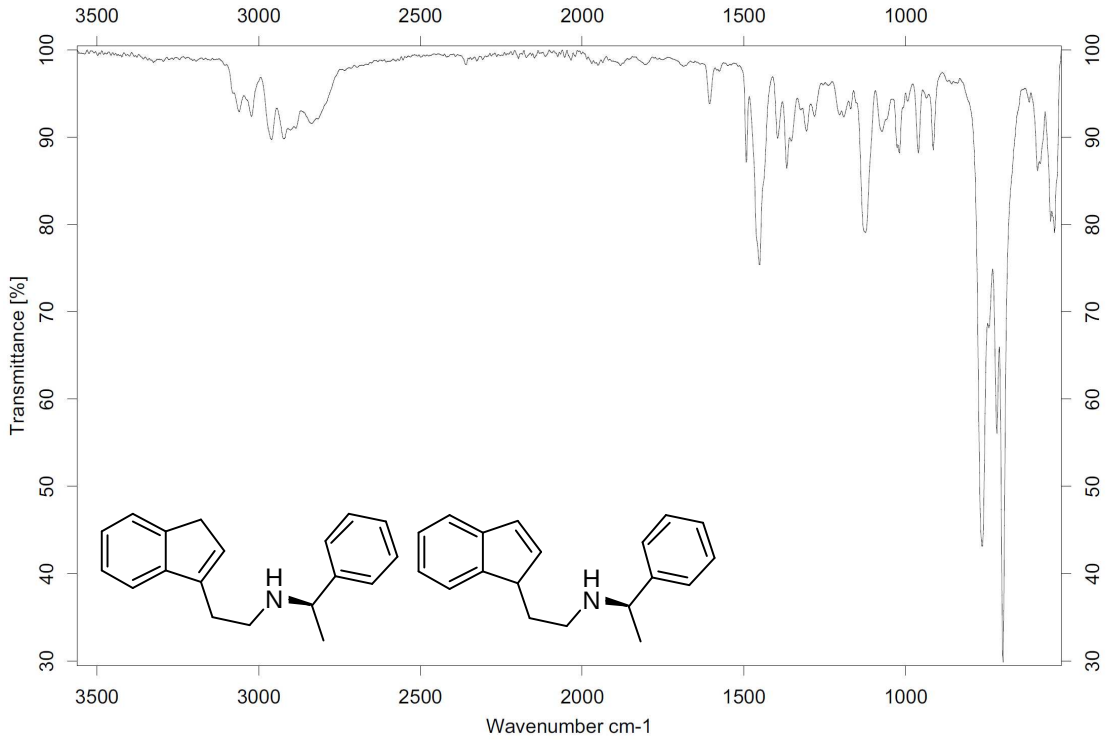
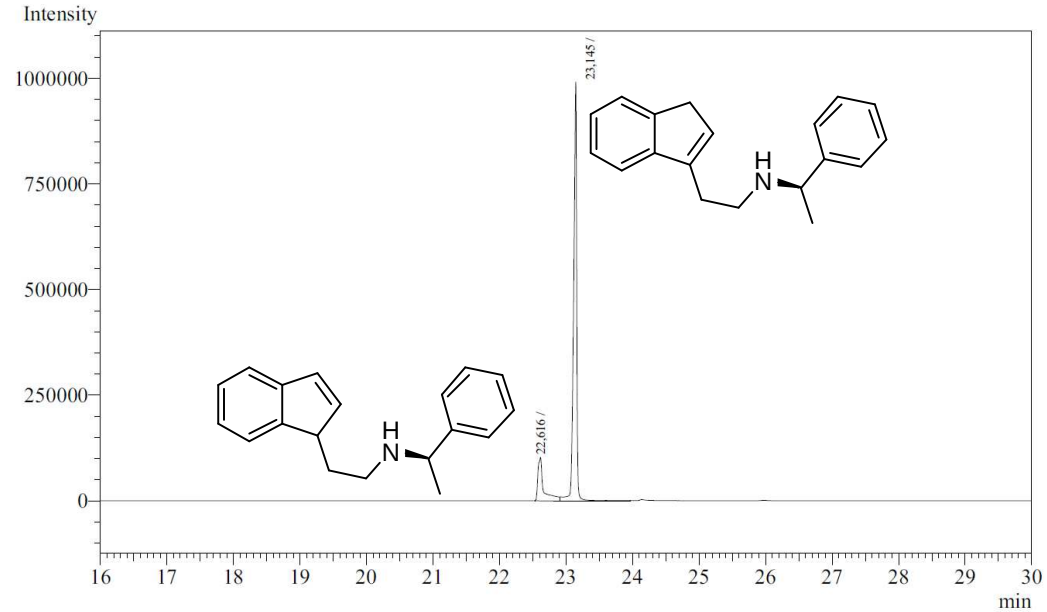


Figure S41. Gas chromatogram of compounds **3h** and **4h**.



Peak#	Ret.Time	Area	Height	Height%	Area%
1	22,616	616725	102398	9,4212	16,3430
2	23,145	3156917	984491	90,5788	83,6570
Total		3773642	1086889	100,0000	100,0000

Figure S42. ^{1}H NMR spectrum of compound **4h·HCl** in $CDCl_3$.

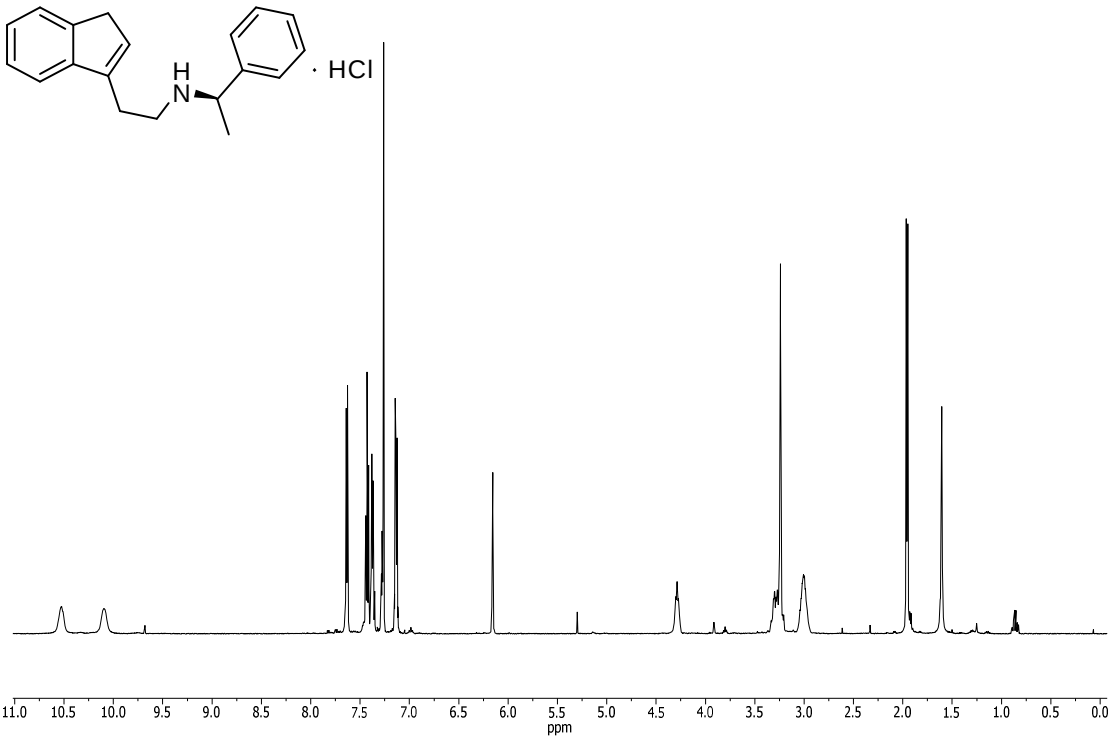


Figure S43. ^{13}C NMR spectrum of compound **4h·HCl** in $CDCl_3$.

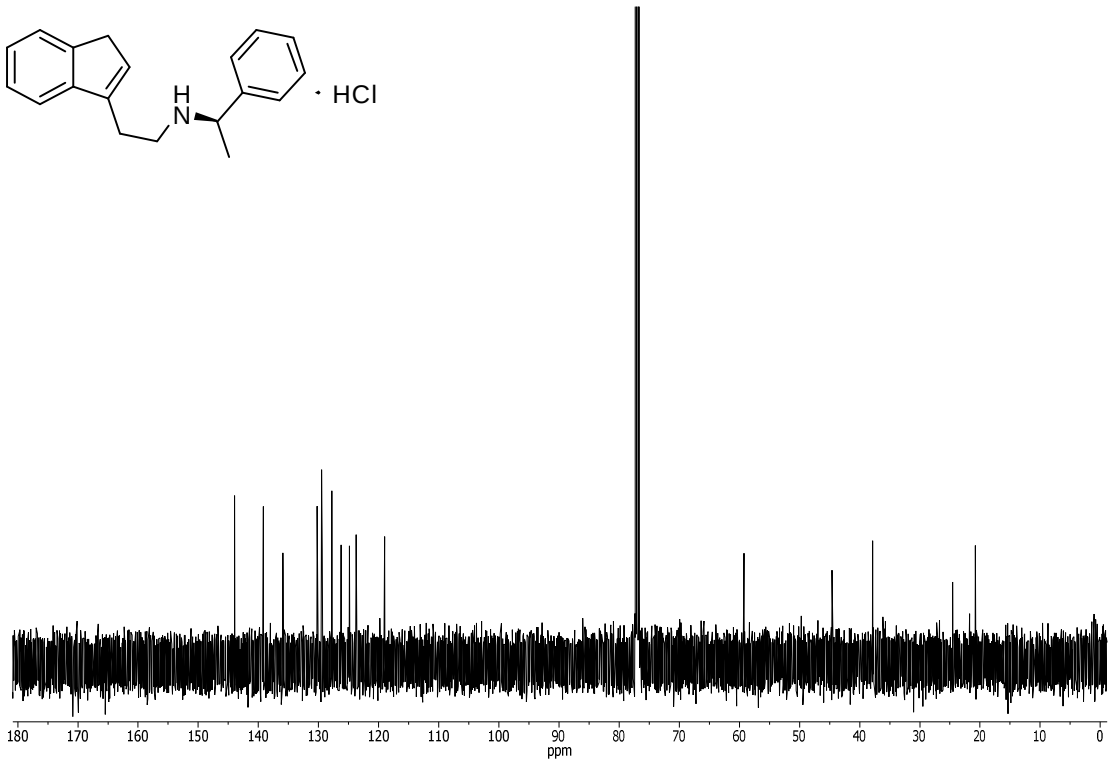


Figure S44. IR spectrum of compounds **4h·HCl**.

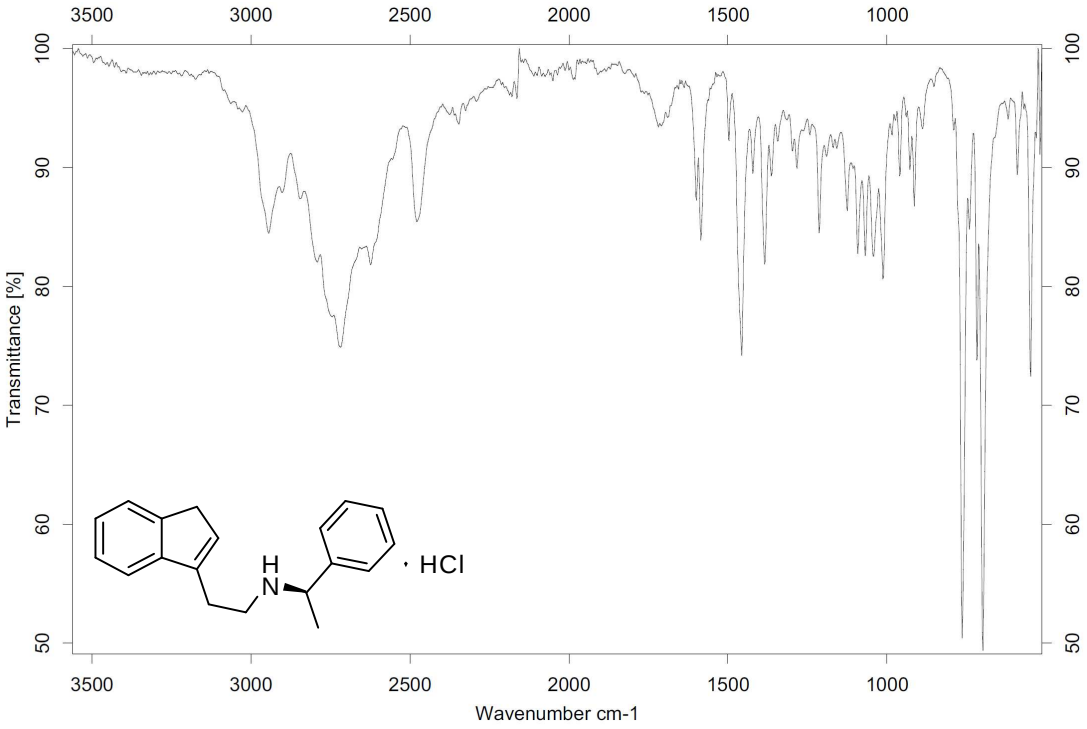


Figure S45. ^{1}H NMR spectrum of compound **16** in C_6D_6.

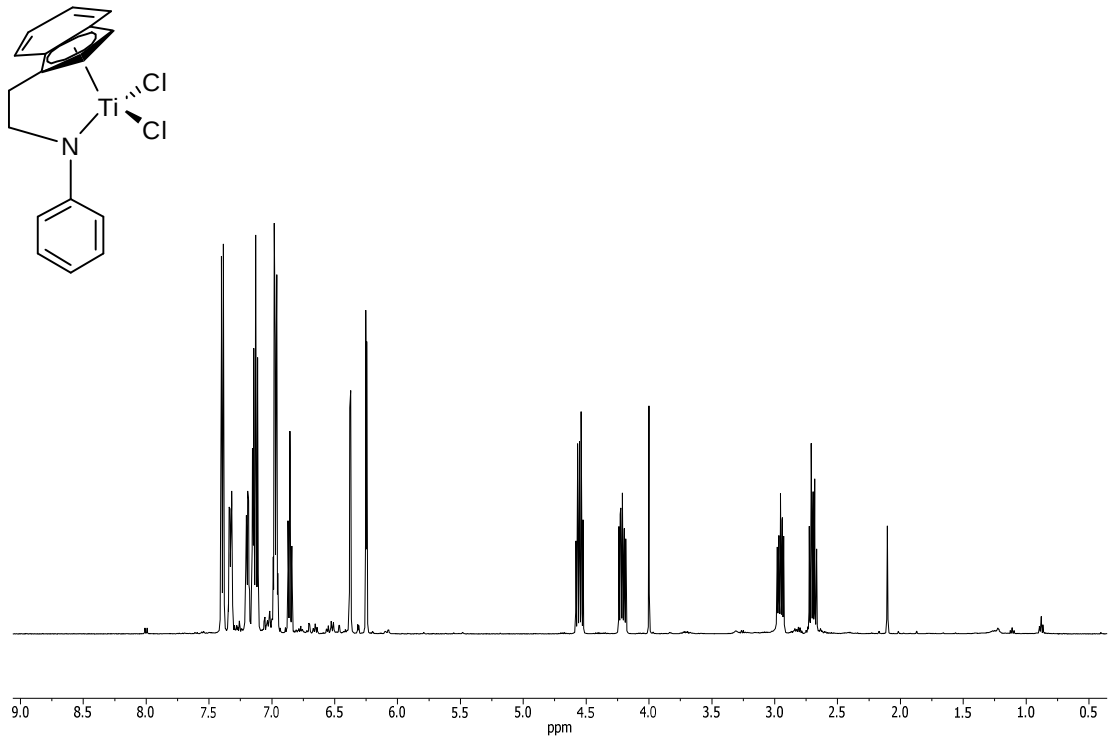


Figure S46. ^{13}C NMR spectrum of compound **16** in C_6D_6.

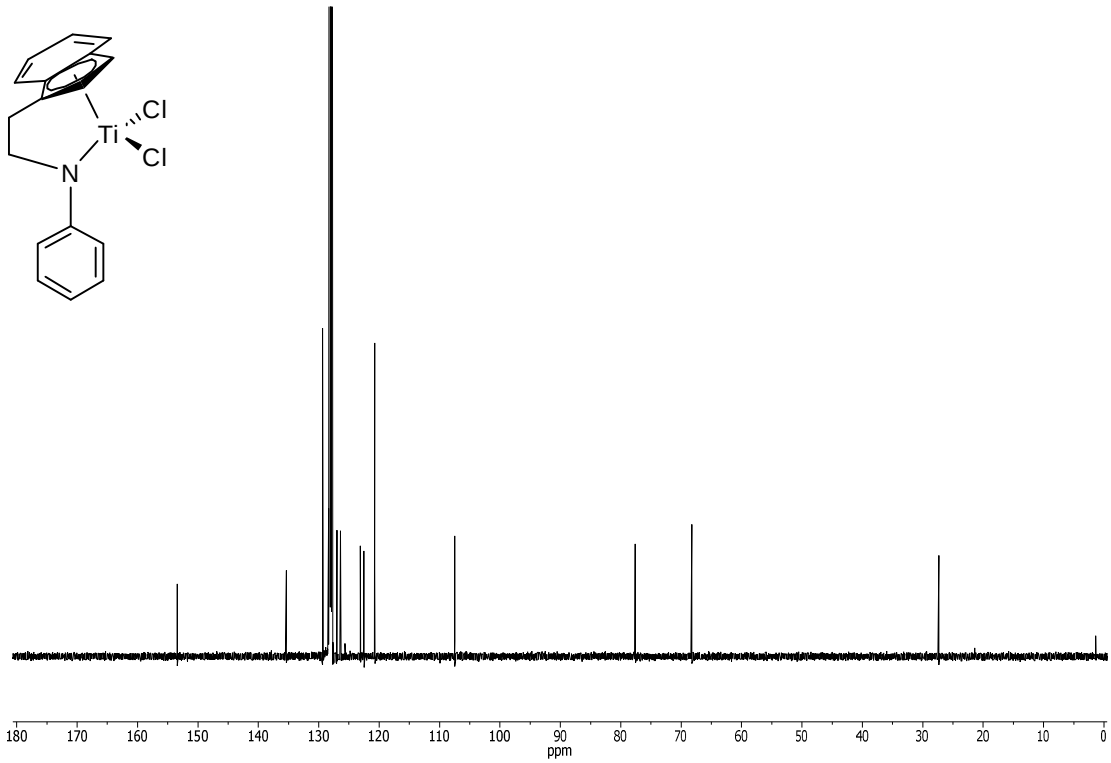


Figure S47. IR spectrum of compound **16**.

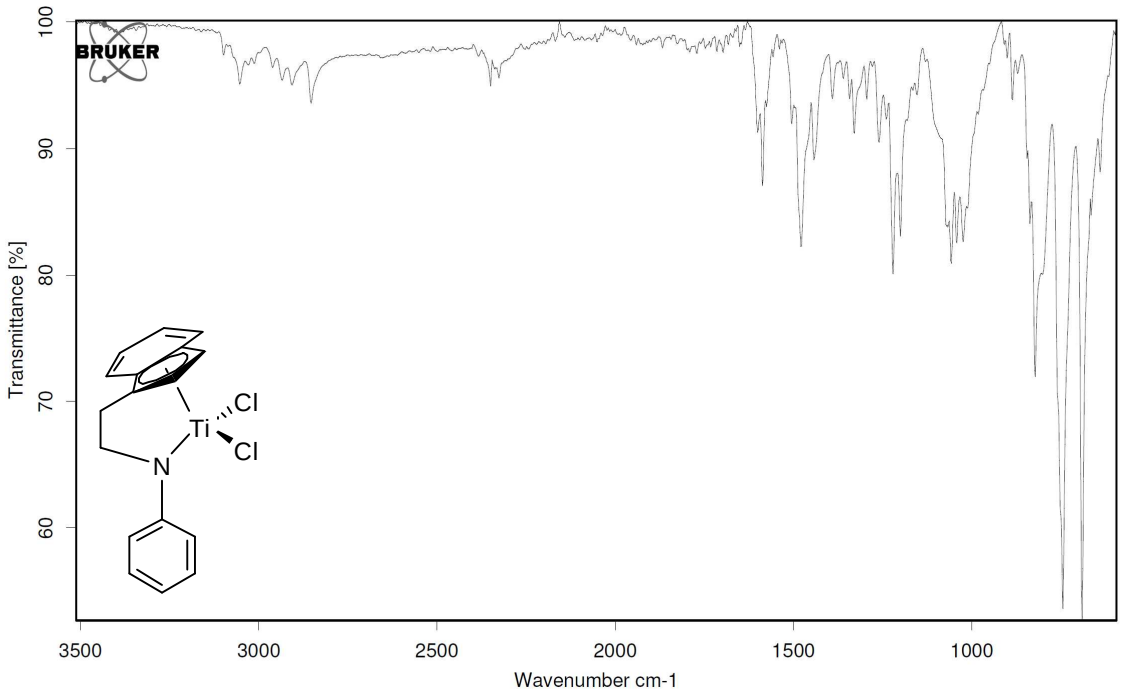
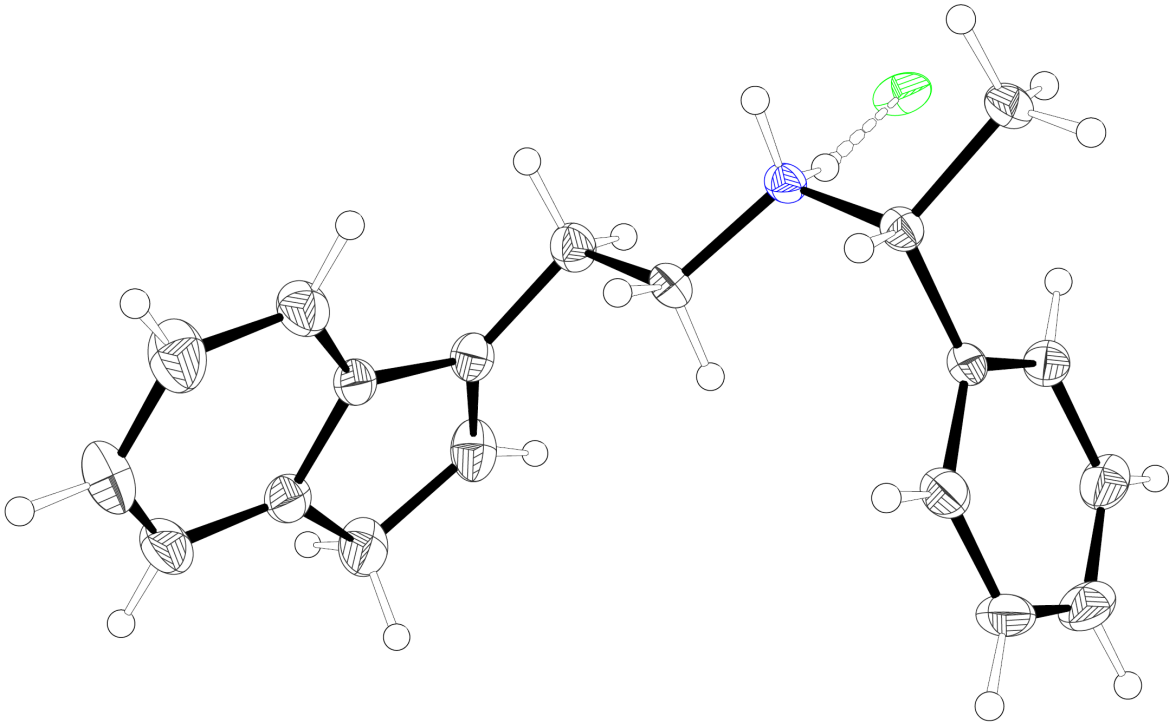
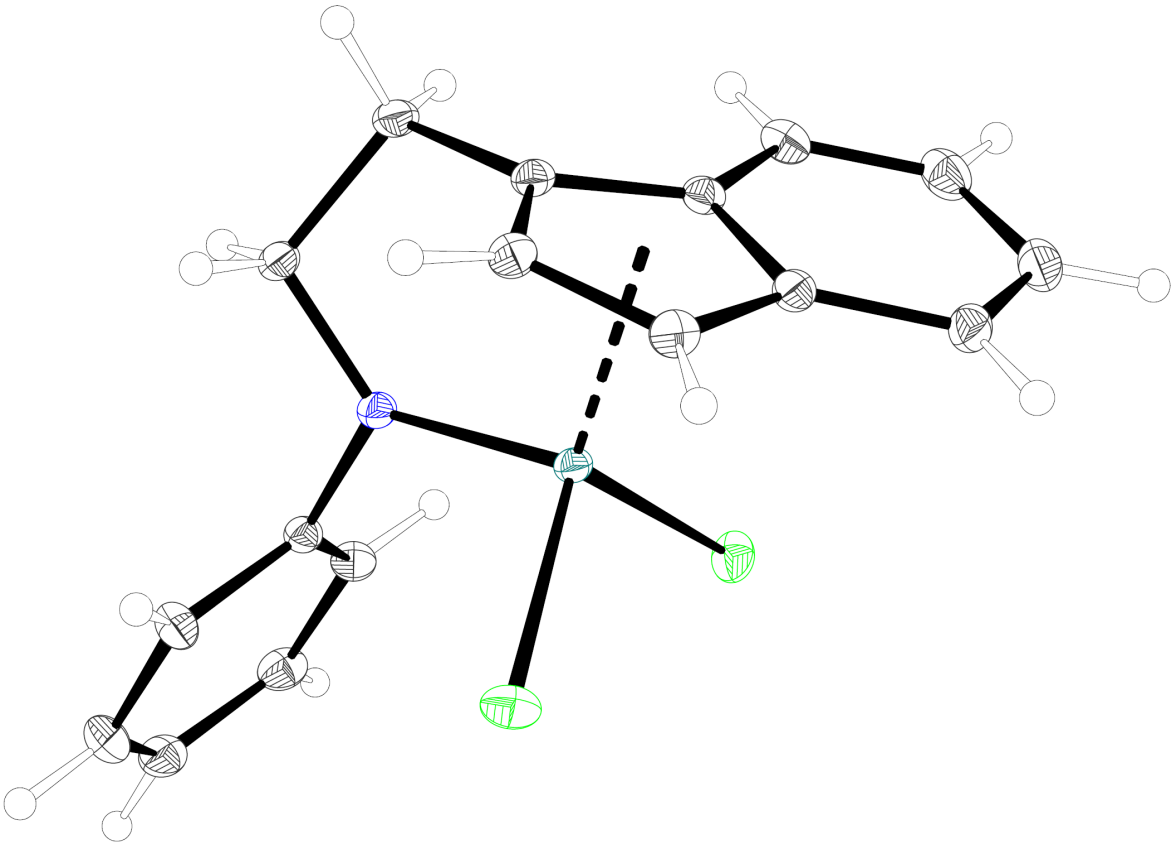


Figure S48. ORTEP-plot of compound **4h·HCl** (grey, C – white, H – green, Cl – blue, N).



Compound **4h·HCl**: Colorless crystals, dimensions 0.320 × 0.120 × 0.040 mm³, monoclinic, space group $P2_1$, unit cell dimensions: a = 10.4522(4) Å, b = 7.1194(2) Å, c = 11.0487(4) Å, β = 92.2592(16)°, V = 821.53(5) Å³, Z = 2, ρ = 1.212 Mg/M³, Θ_{max} = 30.030°, radiation Mo K_α, λ = 0.71073 Å, ϕ and ω-scans with Bruker KAPPA, APEX-II CCD at T = 120(2) K, 31908 reflections measured, 4812 unique [R_{int} = 0.0290], 4549 observed [I>2σ(I)], intensities were corrected for Lorentz and polarization effects, an numerical absorption correction was applied using Bruker SADABS, μ = 0.226 mm^{-1}, T_{min} = 0.9774, T_{max} = 1.0000, structure solved by direct methods and refined against F² with a full-matrix least-squares algorithm using the SHELXS-2014 software package, 199 parameters refined, hydrogen atoms bound to carbon atoms were treated using appropriate riding models, the nitrogen-bound hydrogen atoms were refined free, goodness of fit 1.039 for observed reflections, final residual values R_1 = 0.0323, wR_2 = 0.0800 for observed reflections [I>2σ(I)], largest diff. peak, hole 0.455 and –0.141 e Å^{-3}. CCDC-1013030 contains the supplementary crystallographic data for **4h·HCl**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S49. ORTEP-plot of compound **16** (grey, C – white, H – green, Cl – blue, N – teal, Ti).



Complex **16**: Red crystals, dimensions 0.450 × 0.200 × 0.150 mm³, triclinic, space group *P*-1, unit cell dimensions: a = 7.0830(2) Å, b = 9.5153(3) Å, c = 12.3275(4) Å, α = 108.9989(12)°, β = 100.0458(13)°, γ = 99.3410(13)°, V = 751.81(4) Å³, Z = 2, ρ = 1.555 Mg/M³, Θ_{max} = 40.247°, radiation Mo K_α, λ = 0.71073 Å, ϕ and ω-scans with Bruker KAPPA, APEX-II CCD at T = 120(2) K, 66743 reflections measured, 9465 unique [R_{int} = 0.0244], 8999 observed [I>2σ(I)], intensities were corrected for Lorentz and polarization effects, an numerical absorption correction was applied using Bruker SADABS, μ = 0.915 mm^{-1}, T_{min} = 0.7527, T_{max} = 0.8997, structure solved by direct methods and refined against F² with a full-matrix least-squares algorithm using the SHELXS-2014 software package, 190 parameters refined, hydrogen atoms bound to carbon atoms were treated using appropriate riding models, goodness of fit 1.030 for observed reflections, final residual values R_1 = 0.0184, wR_2 = 0.0560 for observed reflections [I>2σ(I)], largest diff. peak, hole 0.624 and –0.283 e Å^{-3}. CCDC-1013015 contains the supplementary crystallographic data for **16**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.