Supplementary Material

Highly flexible synthesis of indenylethylamines as ligand precursors for titanium complexes

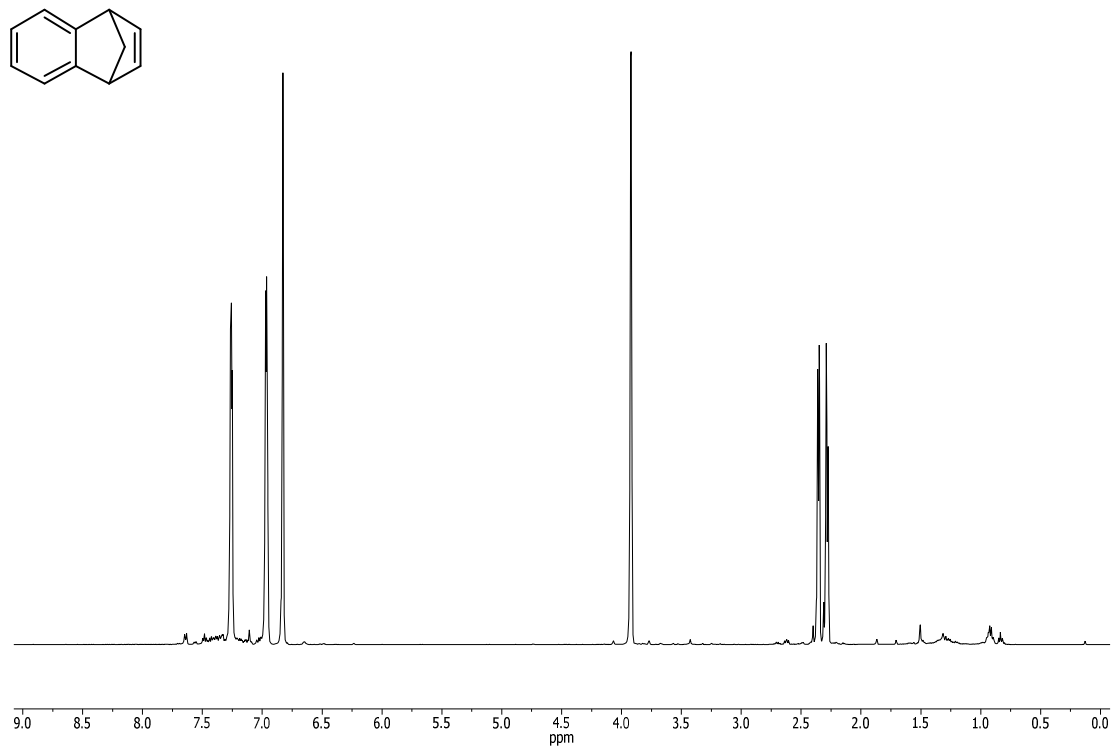**Jan H. Ross, Stefan H. Rohjans, Marc Schmidtmann, and Sven Doye***

Institut für Chemie, Universität Oldenburg, Carl-von-Ossietzky-Strasse 9-11,
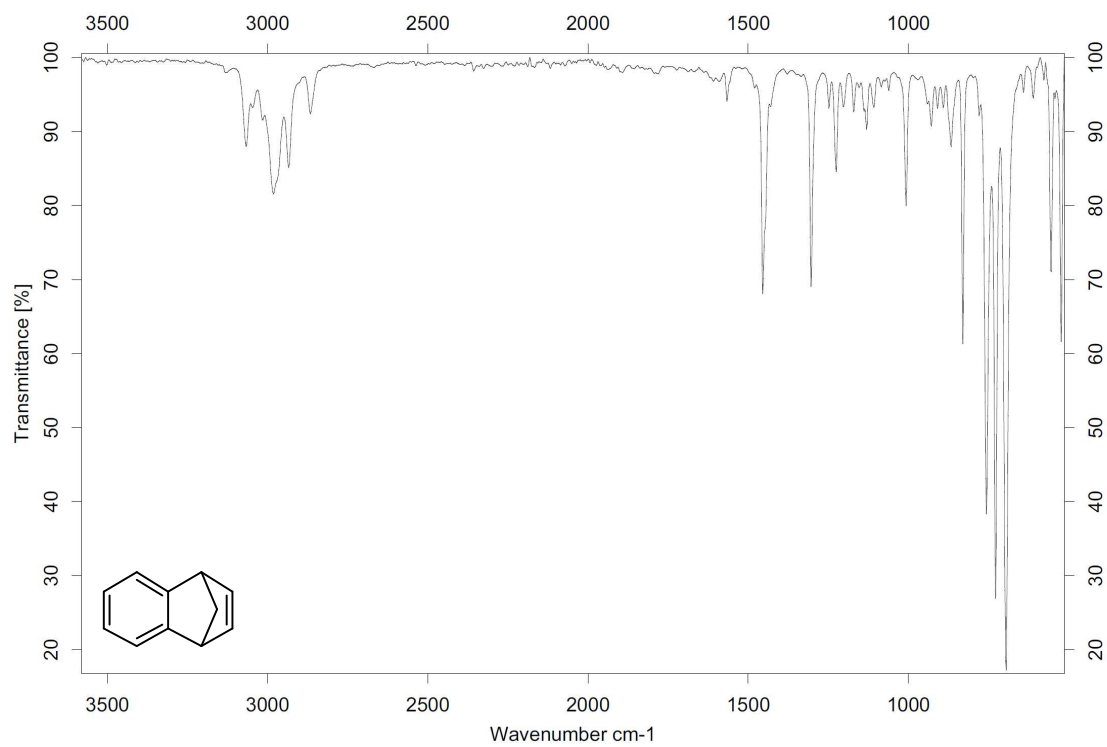*26111 Oldenburg, Germany*
E-mail: doye@uni-oldenburg.de

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

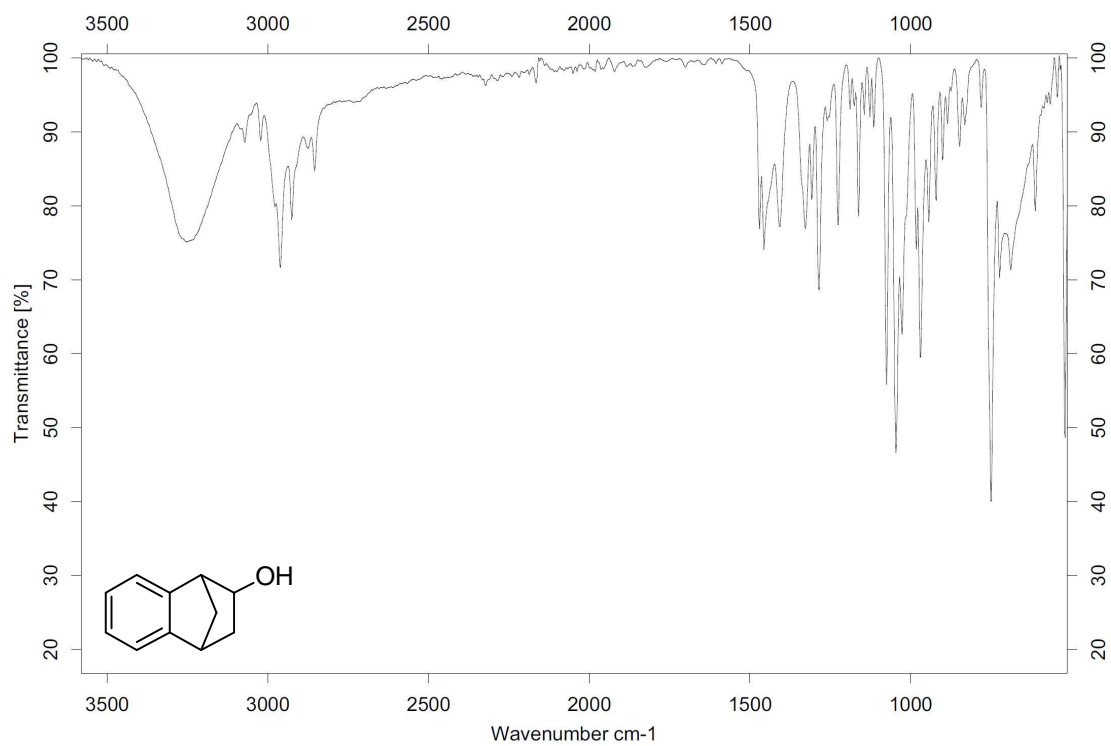## Table of contents

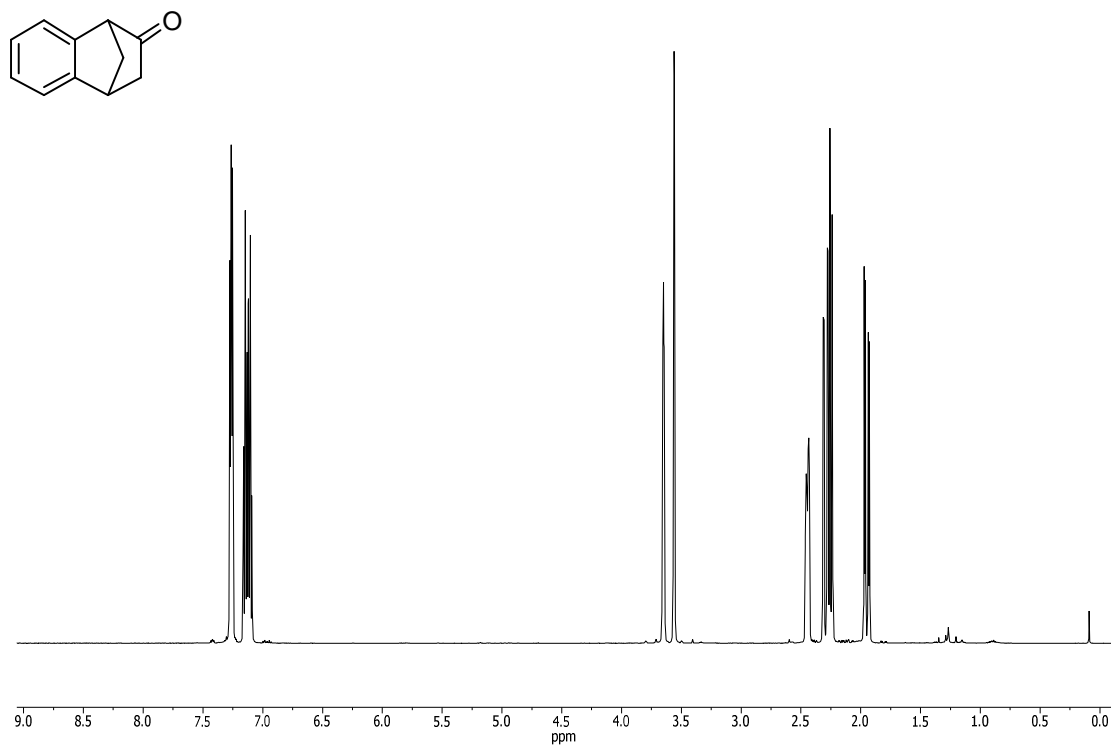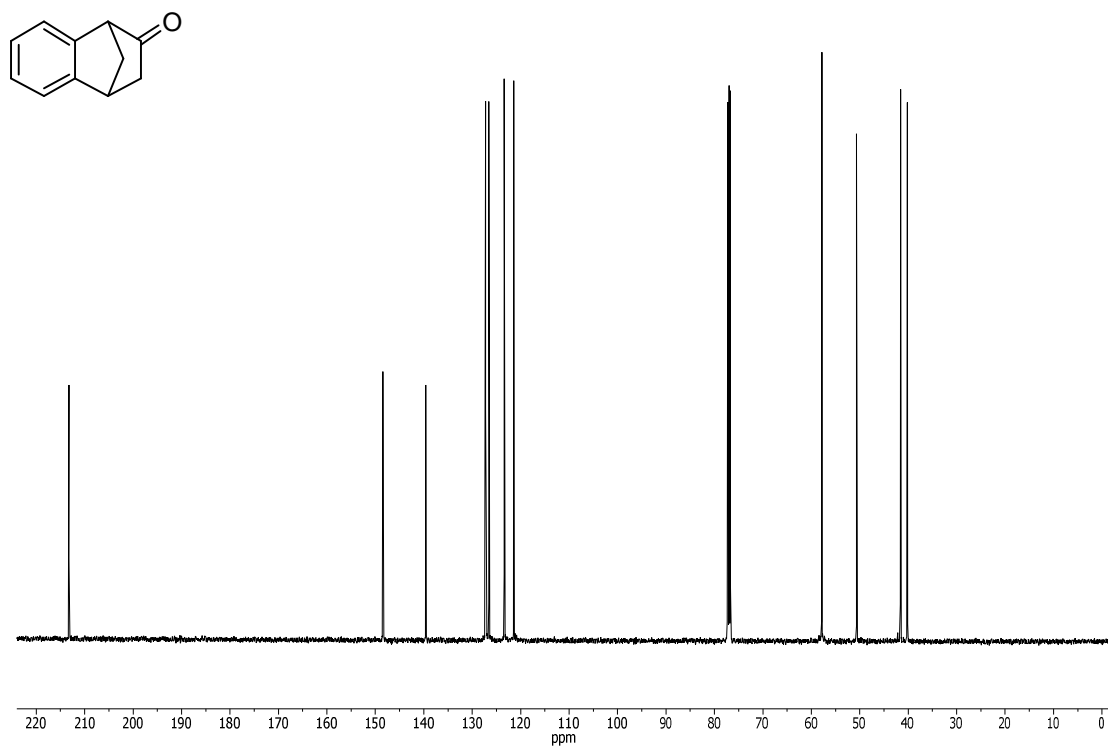**Figure S1.** ^{1}H NMR spectrum of compound **9** in CDCl$_3$.

Figure S2. ^{13}C NMR spectrum of compound **9** in CDCl$_3$.
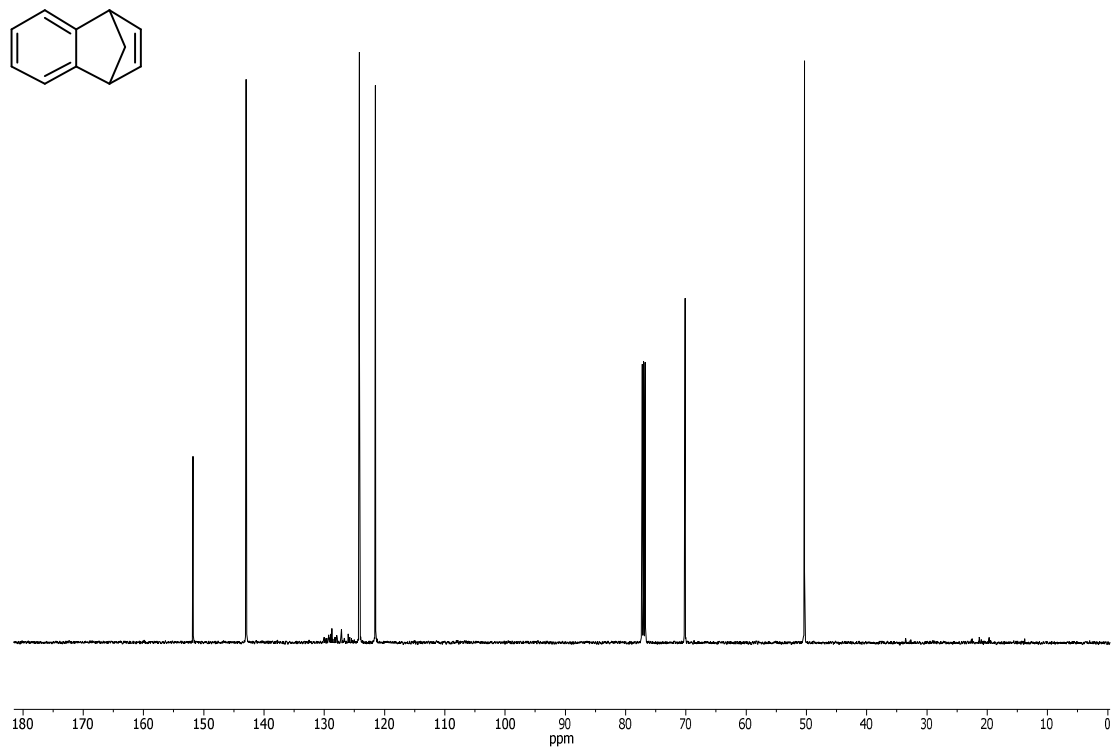
Figure S3. IR spectrum of compound **9**.

Figure S4. ^{1}H NMR spectrum of compound **10** in CDCl$_3$.
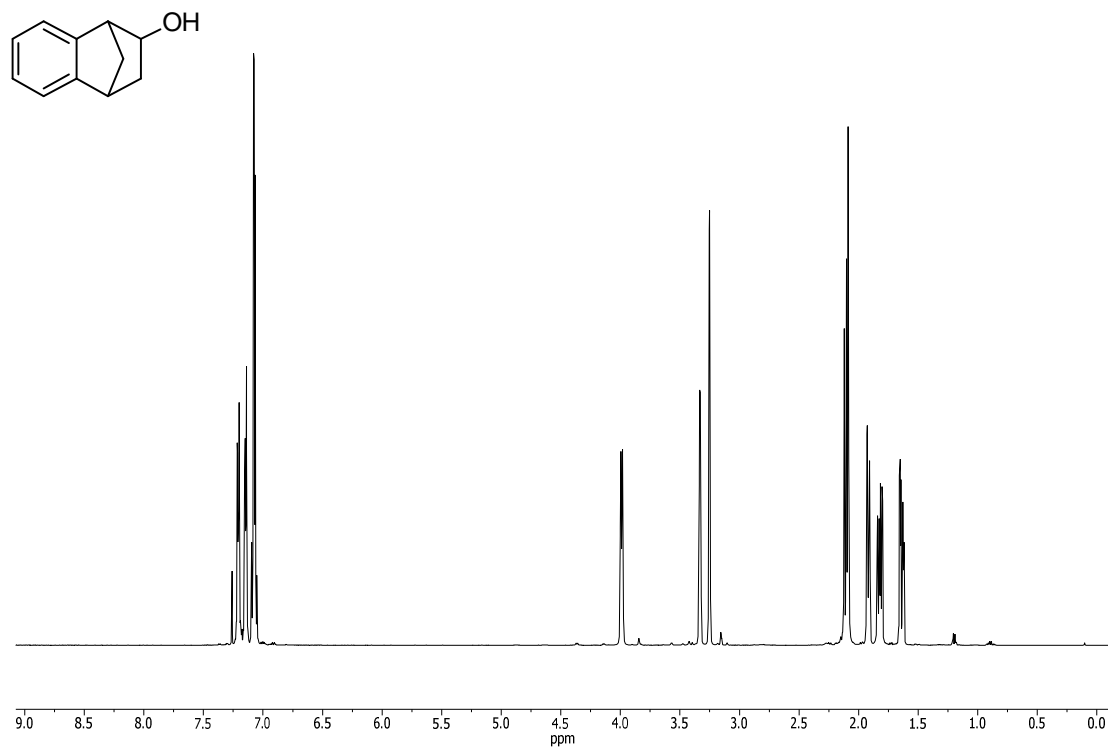
Figure S5. ^{13}C NMR spectrum of compound **10** in CDCl$_3$.
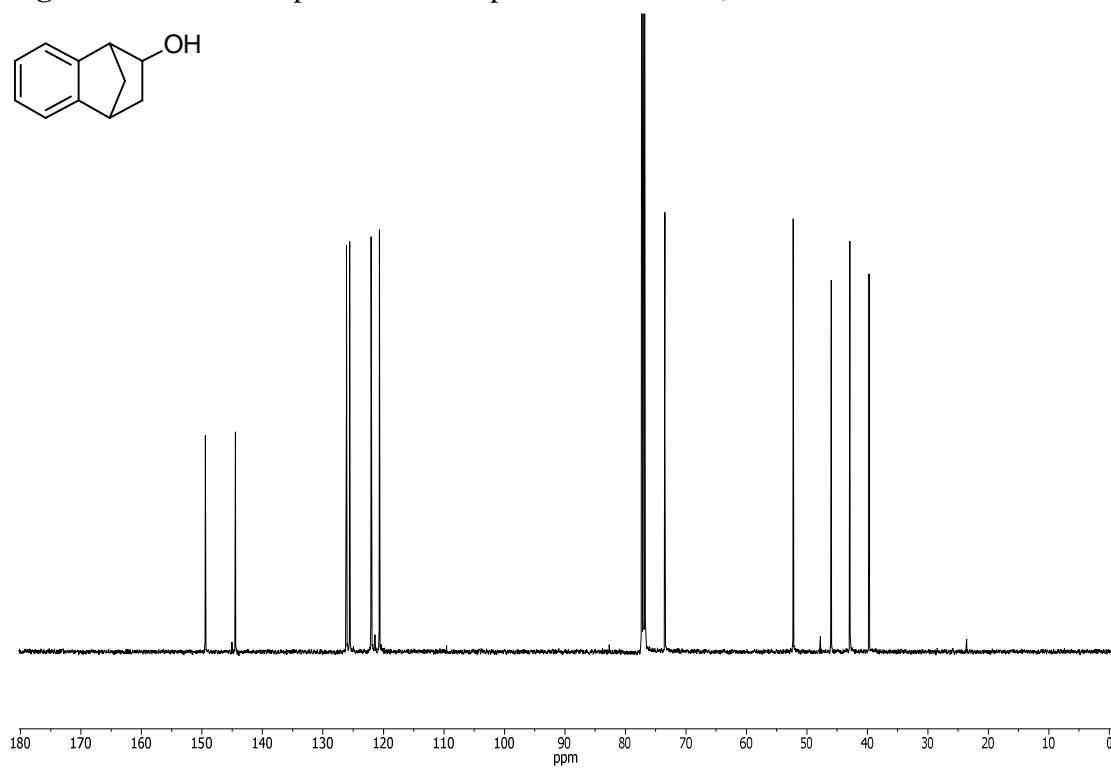
Figure S6. IR spectrum of compound **10**.

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**.
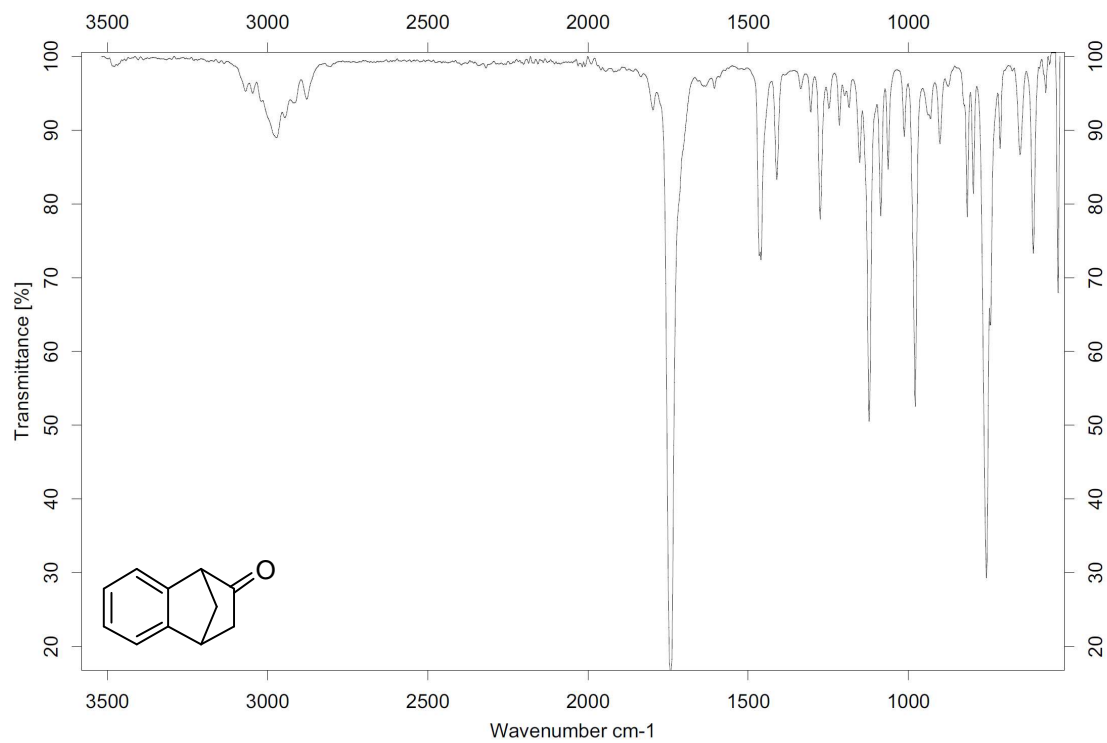
Figure S10. ^{1}H NMR spectrum of compound **14** in CDCl$_3$.

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 CDCl₃.
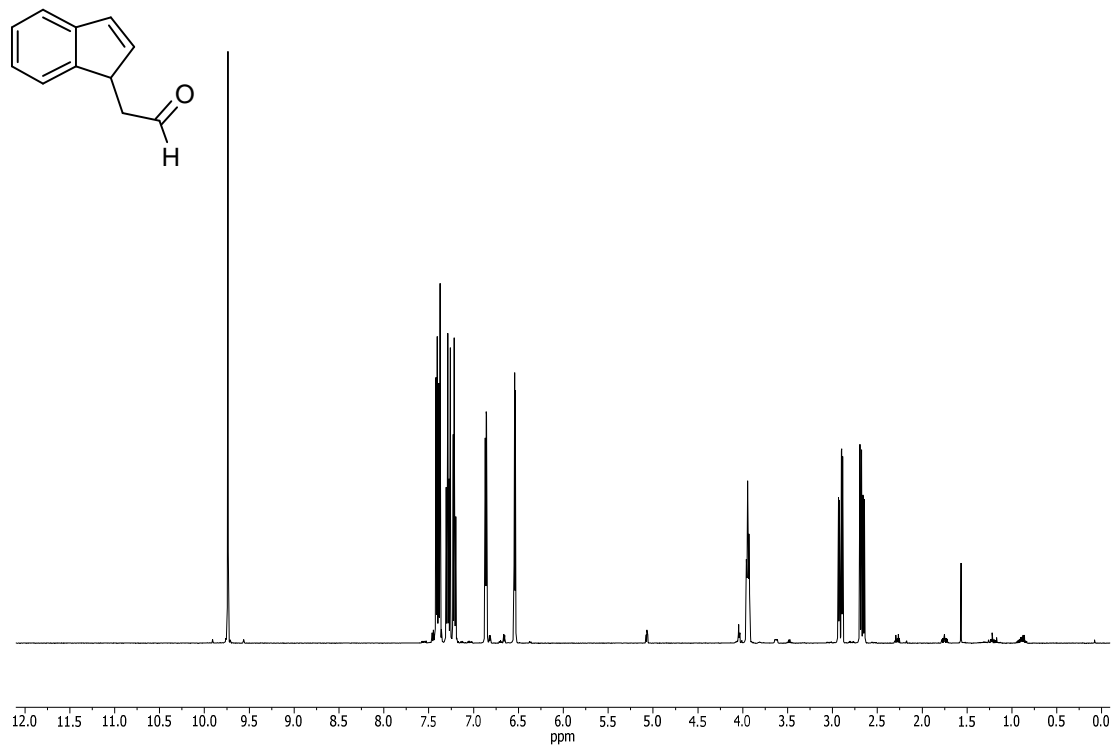
Figure S14. ^{13}C NMR spectrum of compound **5** in CDCl₃.
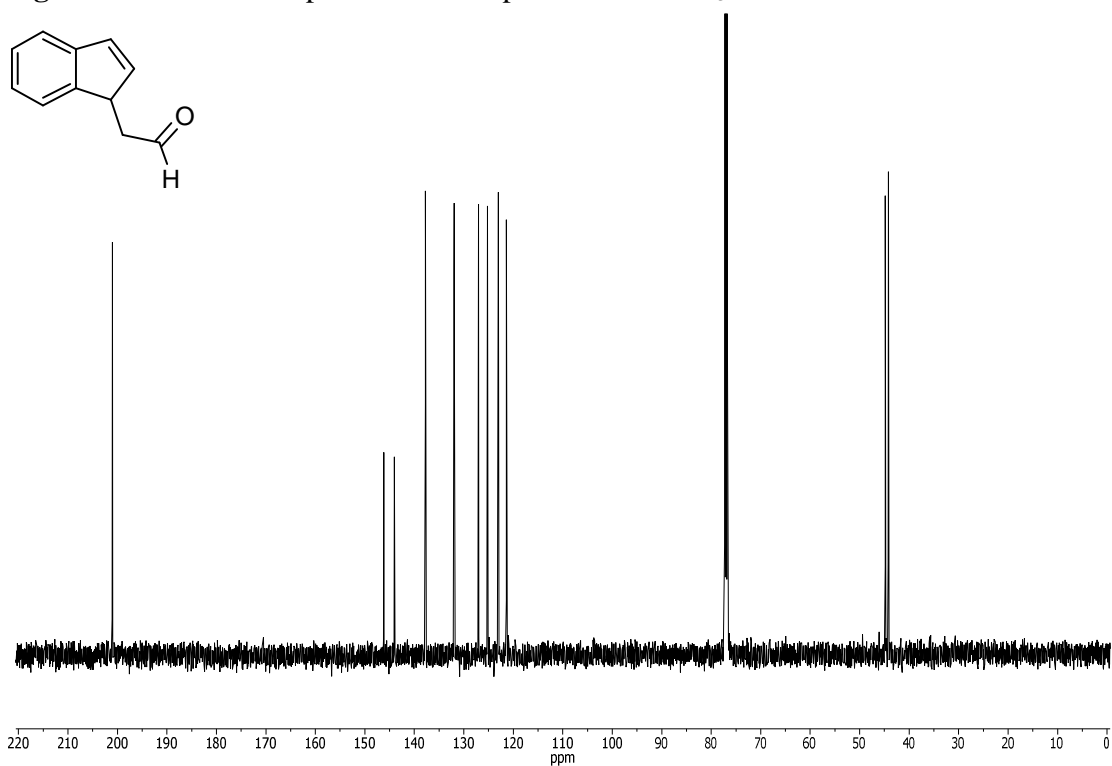
Figure S15. IR spectrum of compound **5**.

Figure S16. ^{1}H NMR spectrum of compound **3a** in CDCl$_3$.
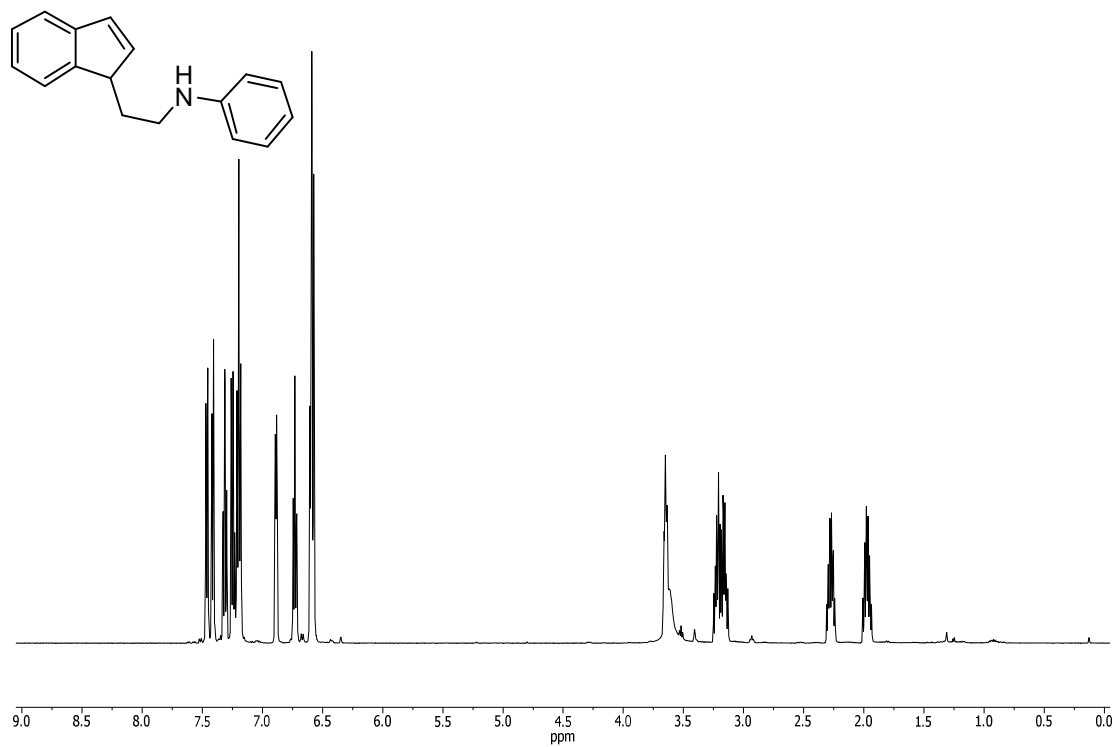
Figure S17. ^{13}C NMR spectrum of compound **3a** in CDCl$_3$.
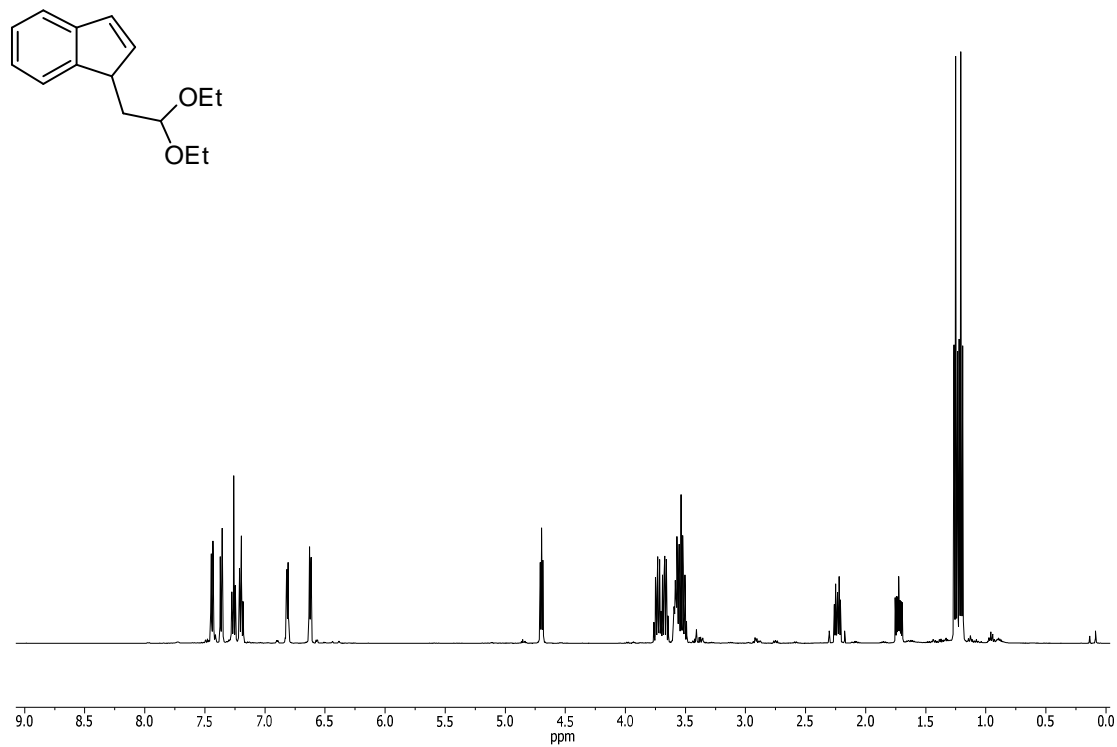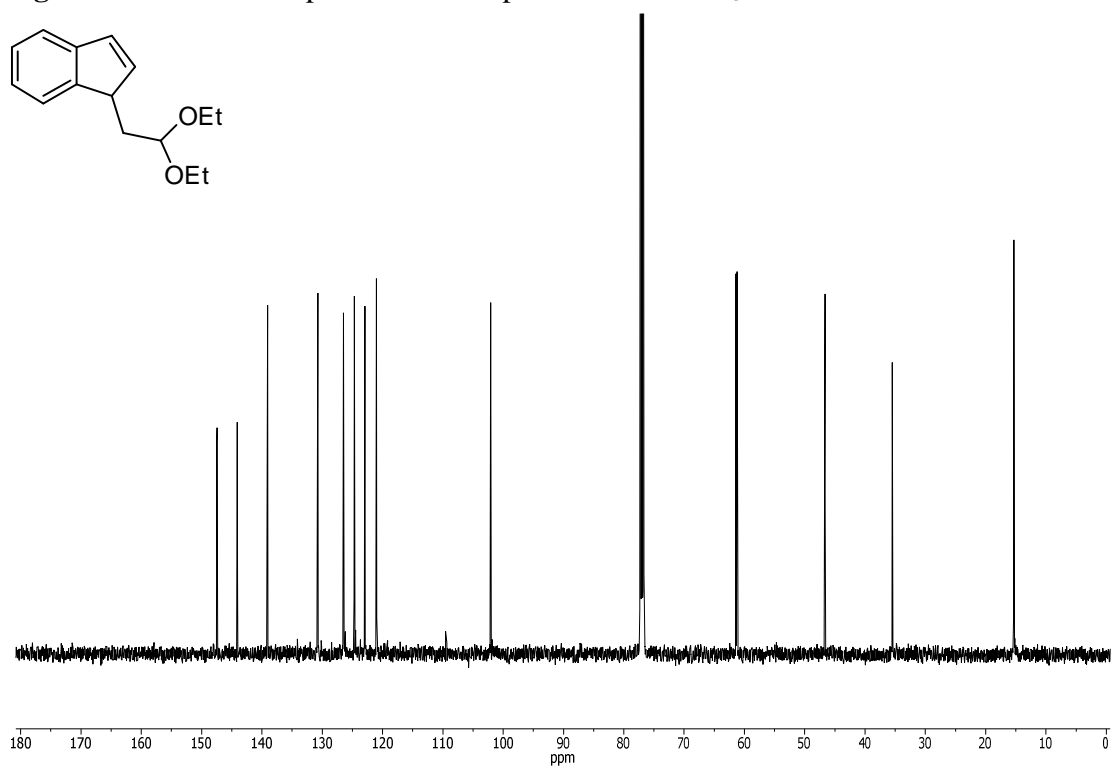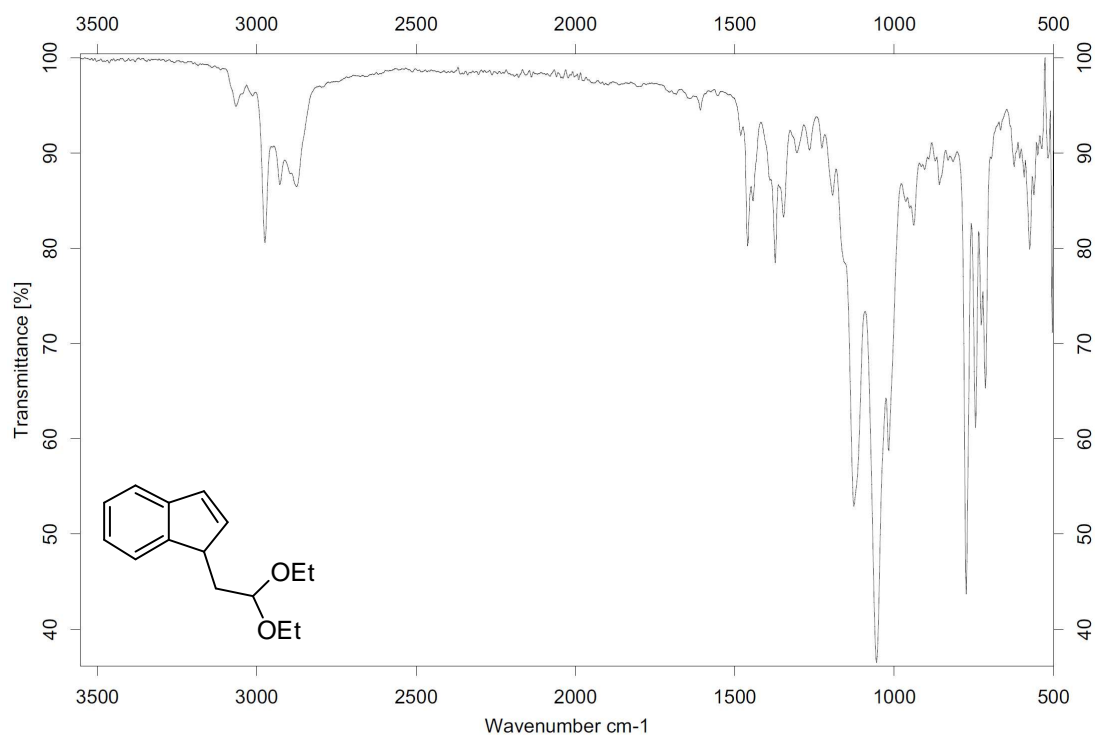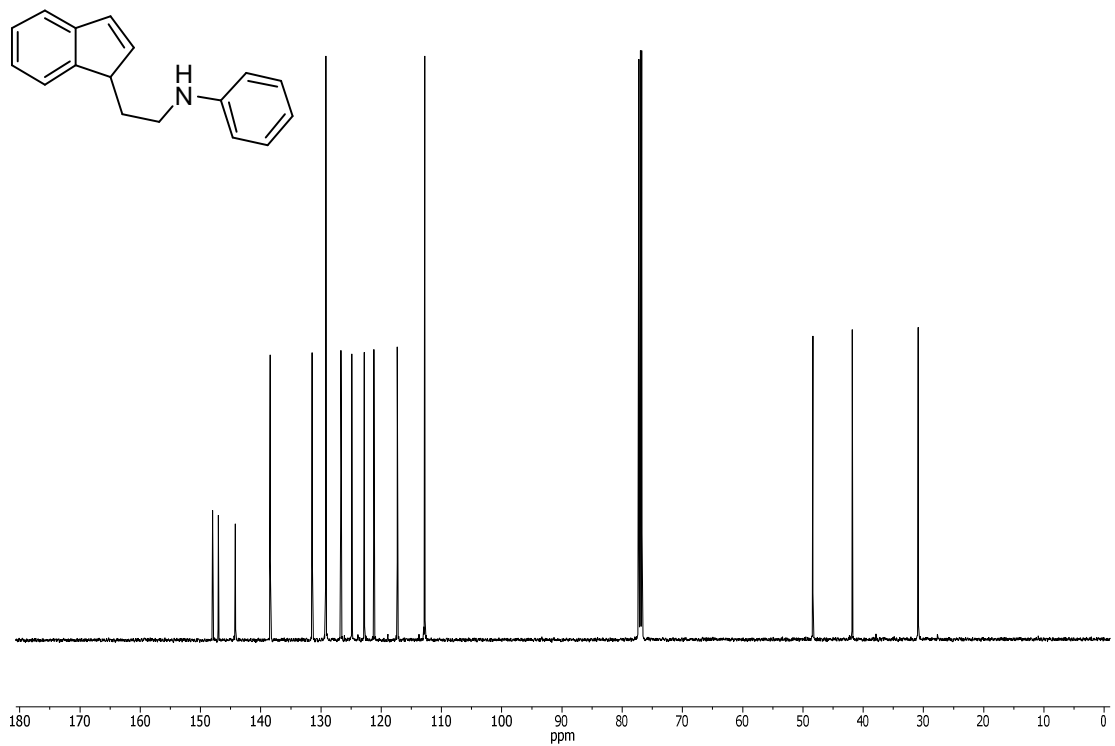
Figure S18. IR spectrum of compound **3a**.

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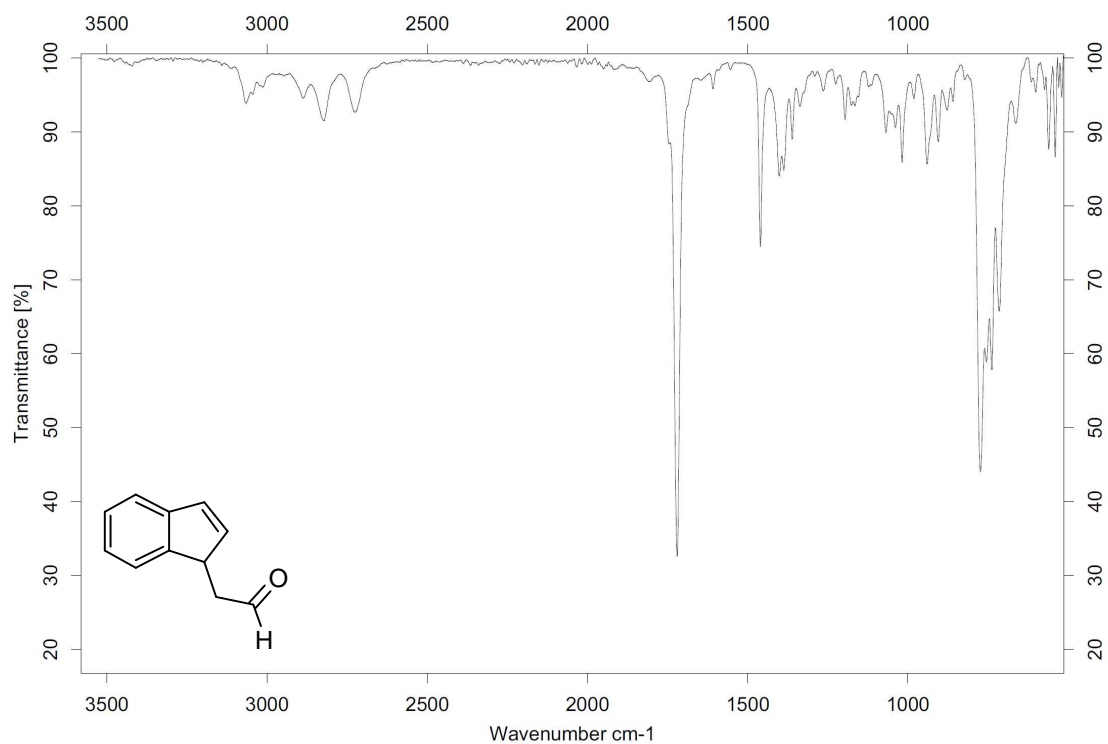
Figure S25. IR spectrum of compound **3c**.

Figure S26. ^{1}H NMR spectrum of compound **4d** in CDCl$_3$.
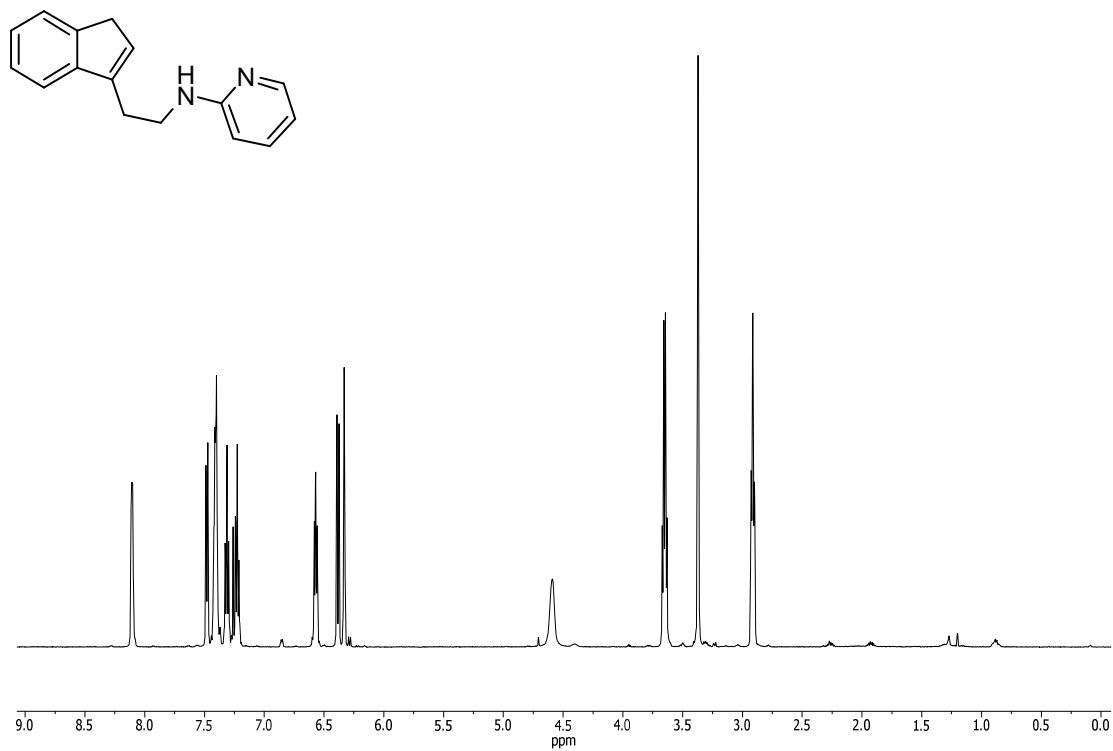
Figure S27. ^{13}C NMR spectrum of compound **4d** in CDCl$_3$.
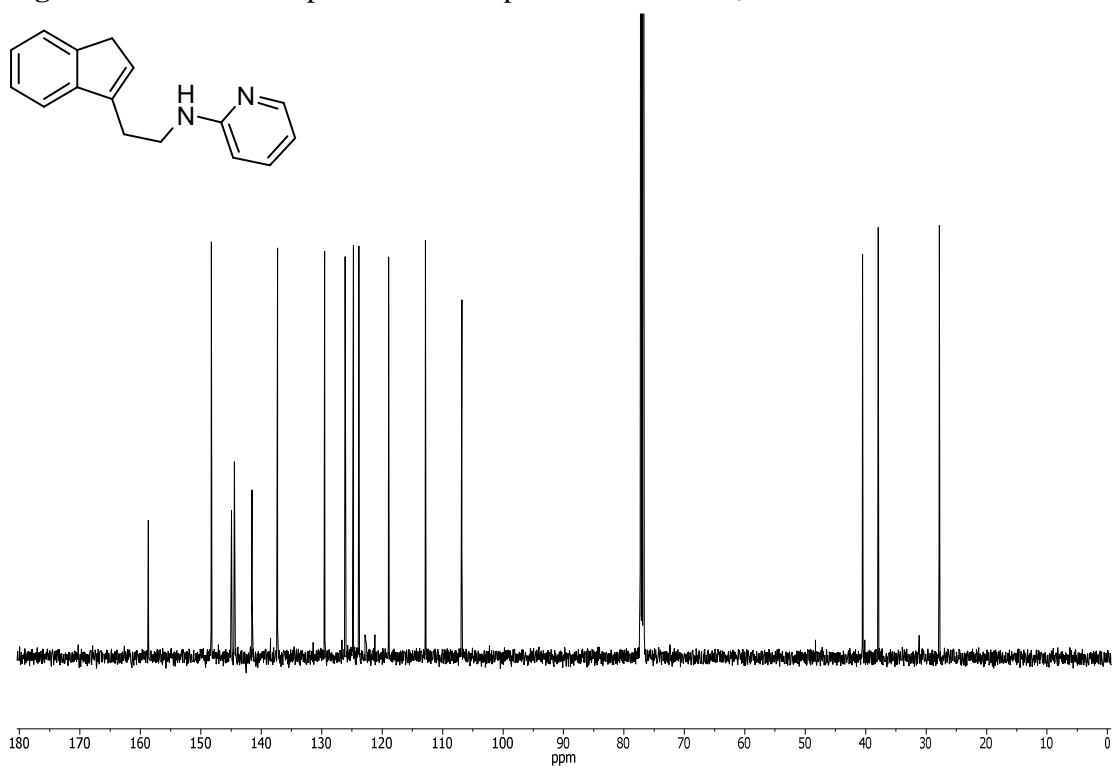
Figure S28. IR spectrum of compound **4d**.

Figure S29. ^{1}H NMR spectrum of compound **4e** in CDCl$_3$.
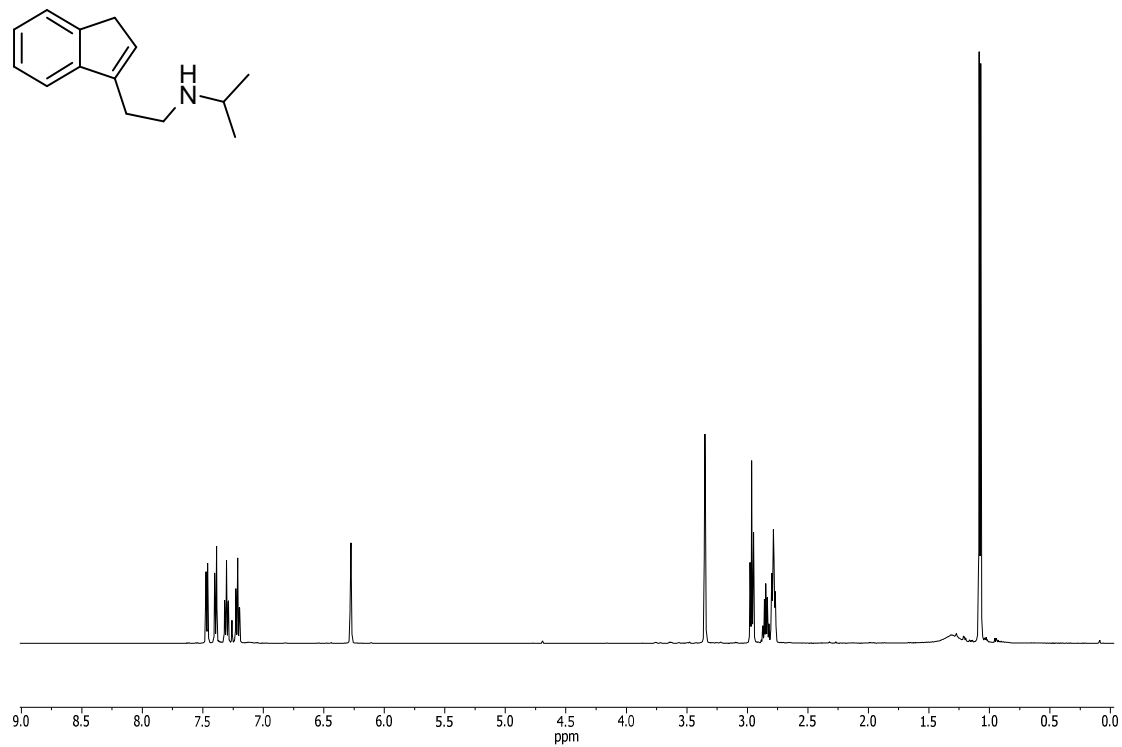
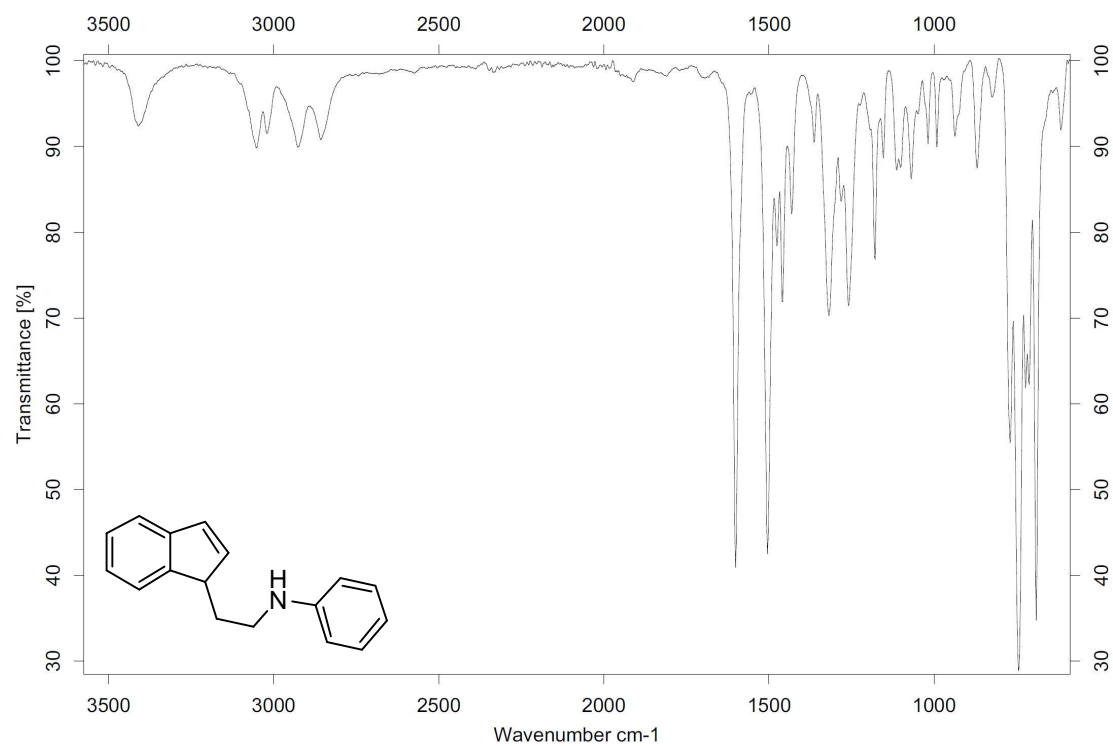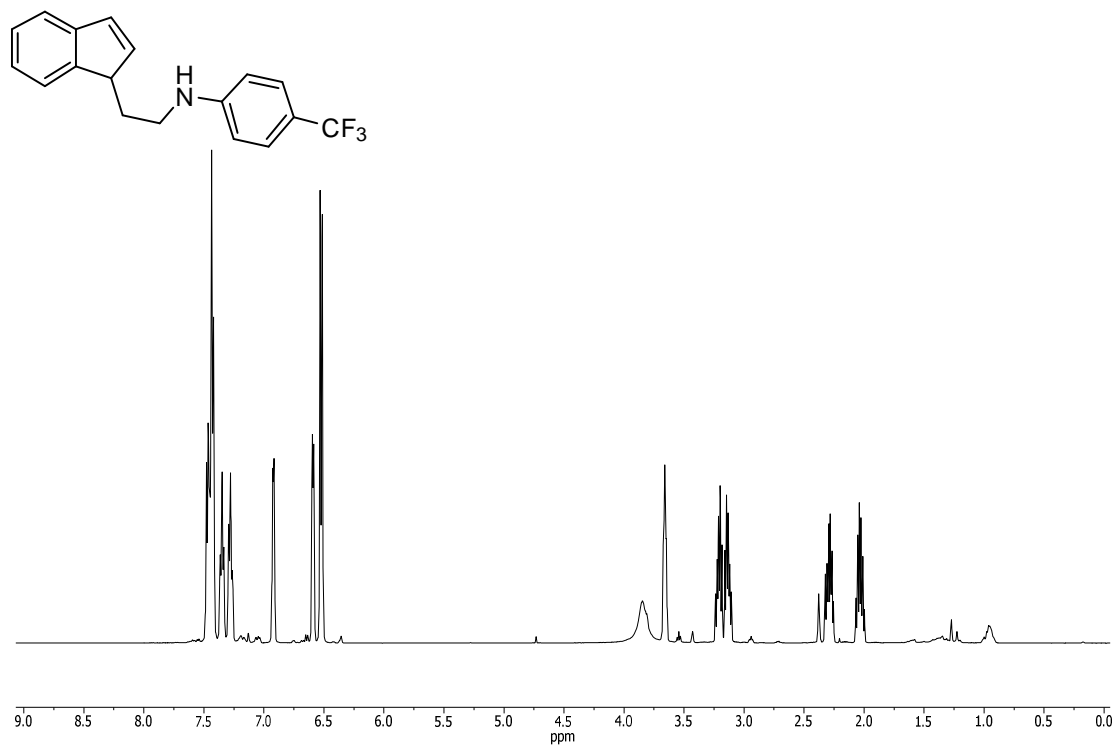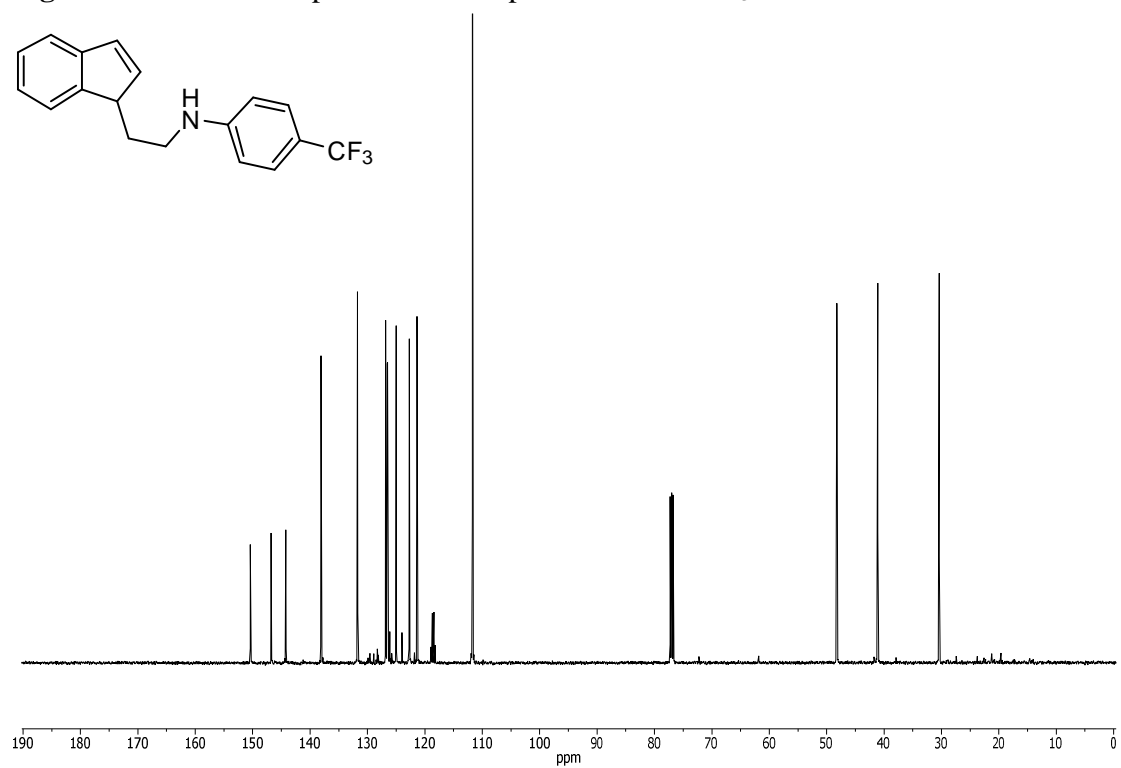**Figure S30.** ^{13}C NMR spectrum of compound **4e** in CDCl$_3$.
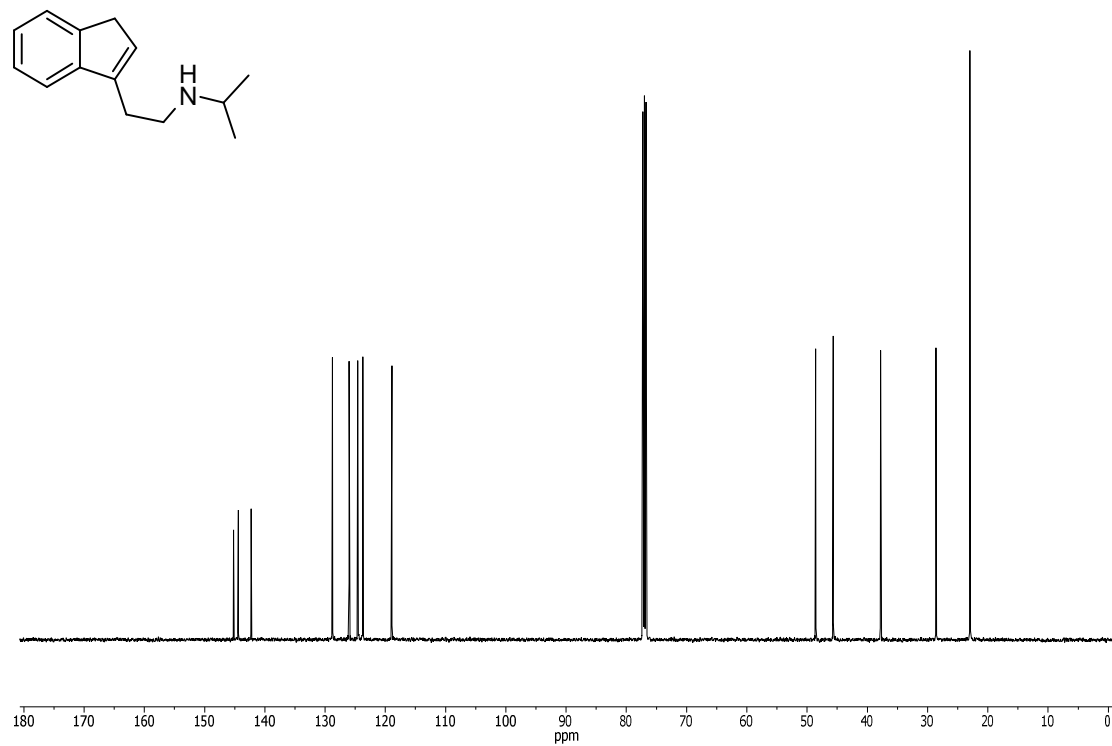
Figure S31. IR spectrum of compound **4e**.

Figure S32. ^{1}H NMR spectrum of compound **4f** in CDCl$_3$.
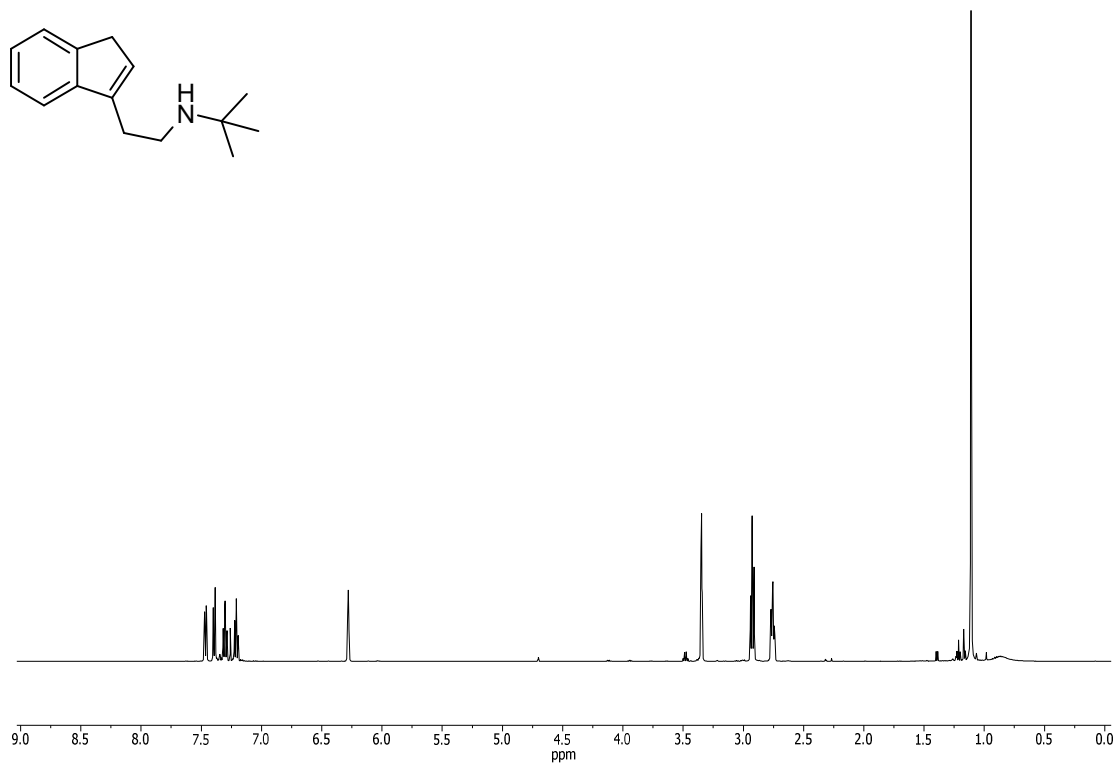
Figure S33. ^{13}C NMR spectrum of compound **4f** in CDCl$_3$.
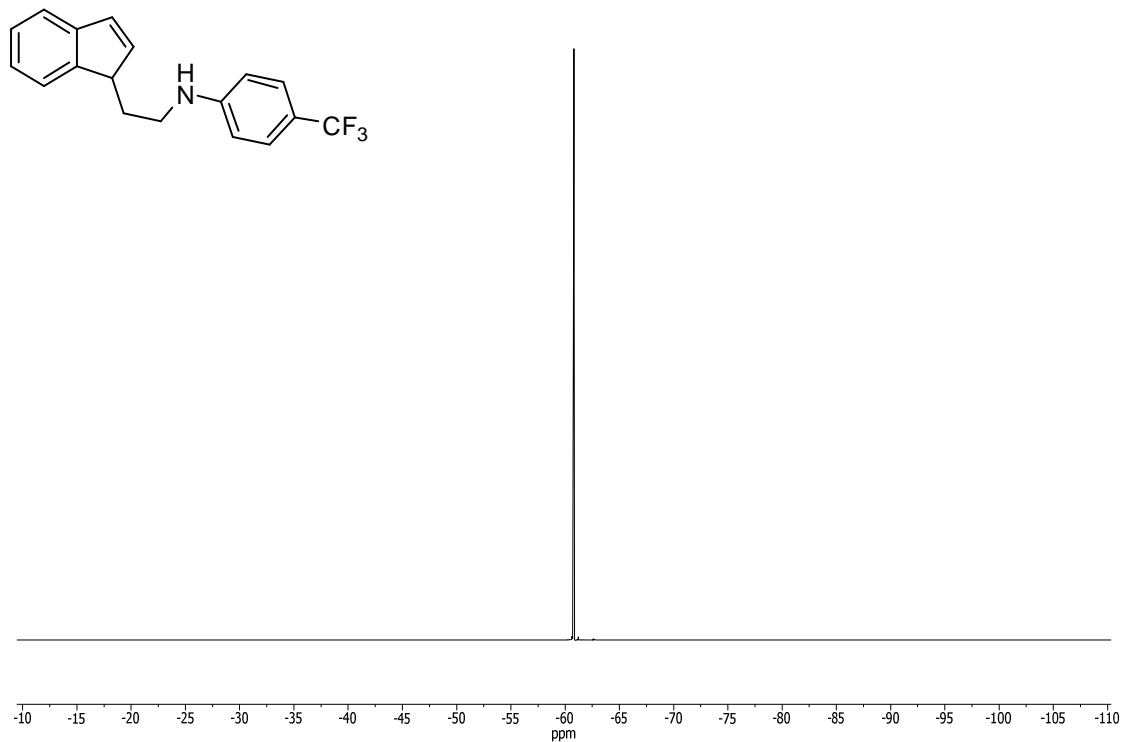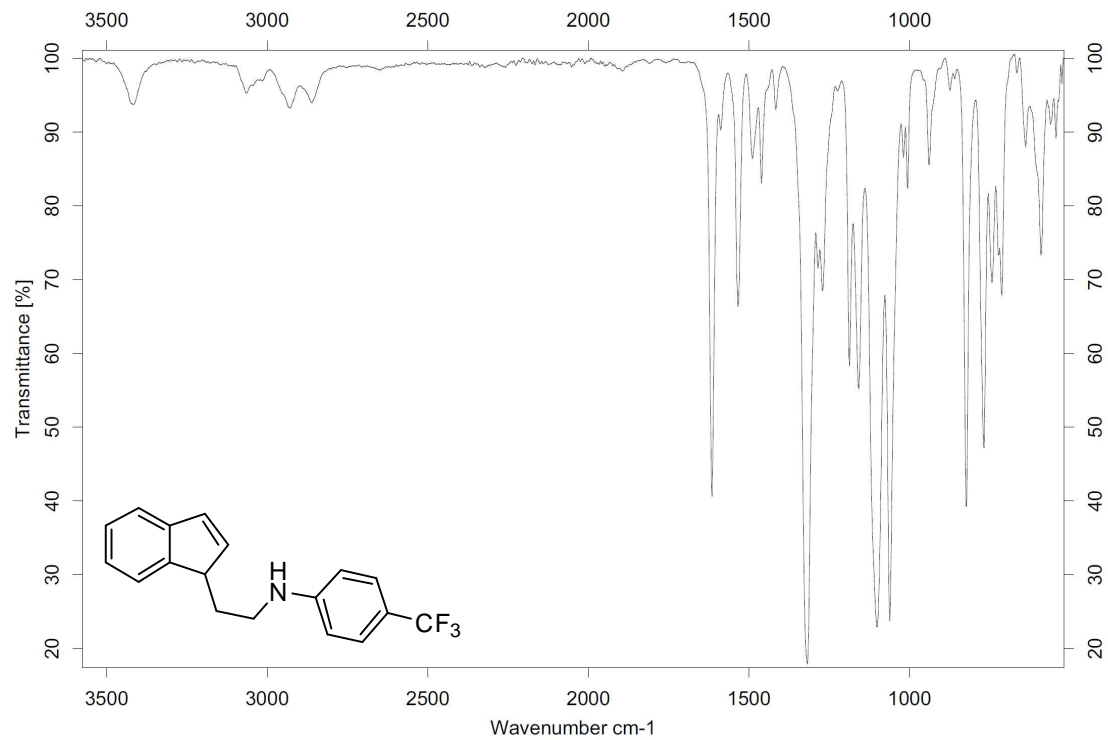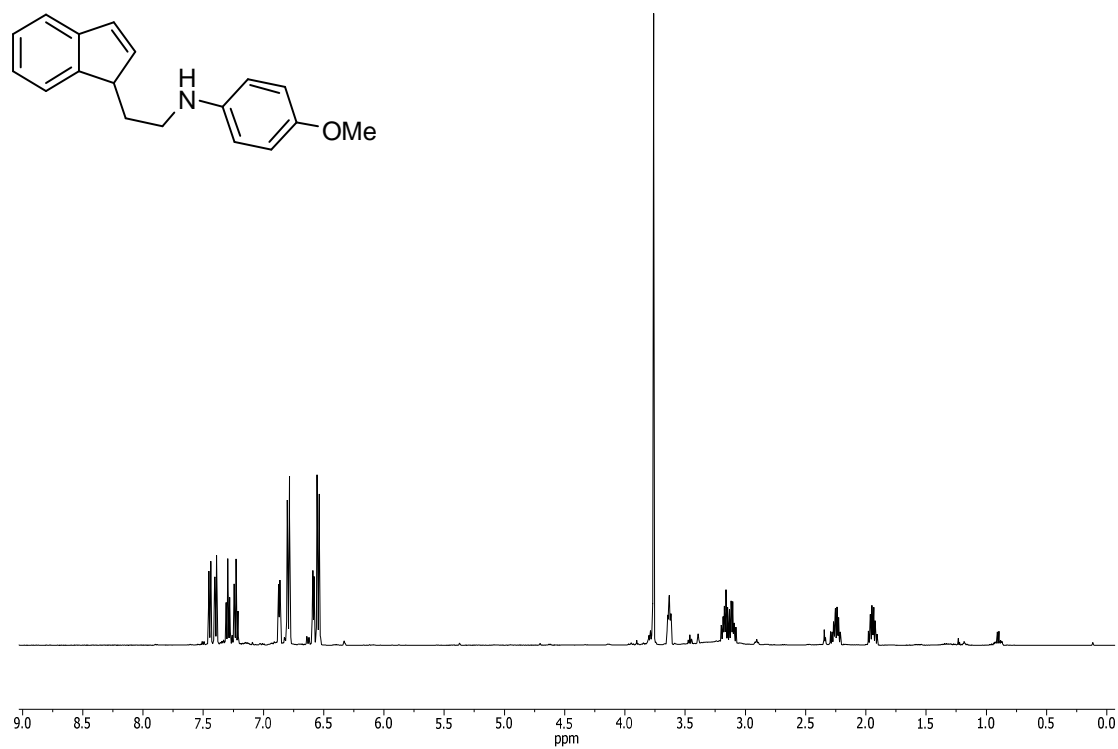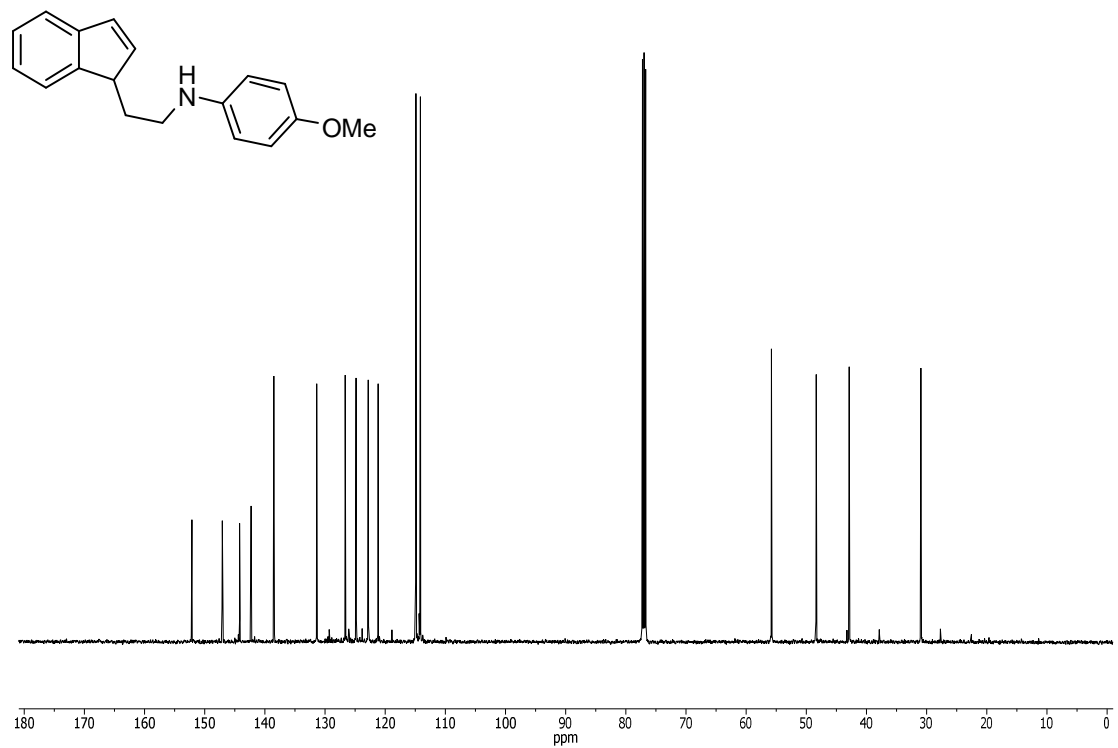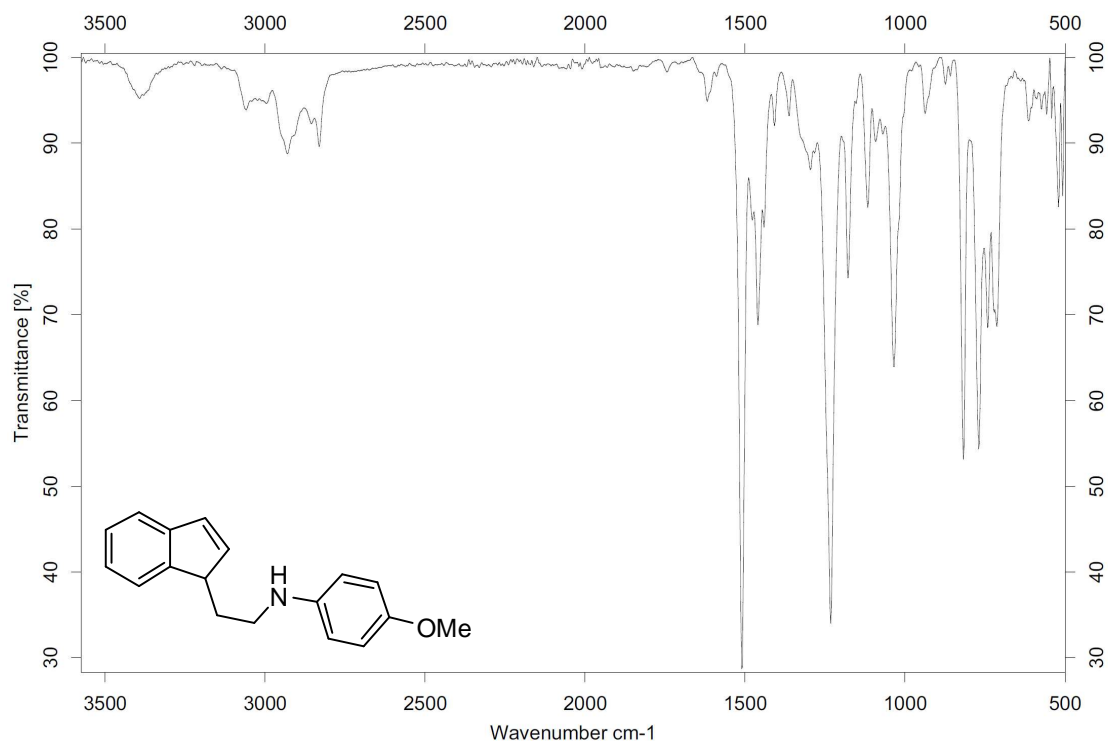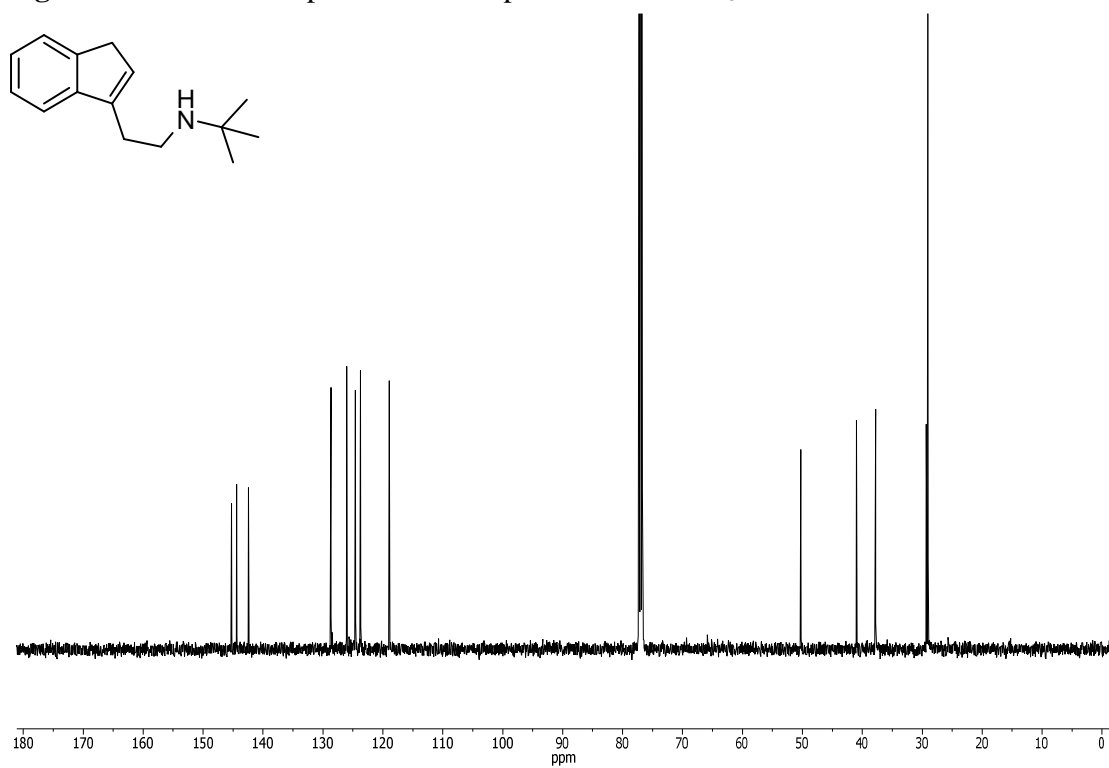
Figure S34. IR spectrum of compound **4f**.
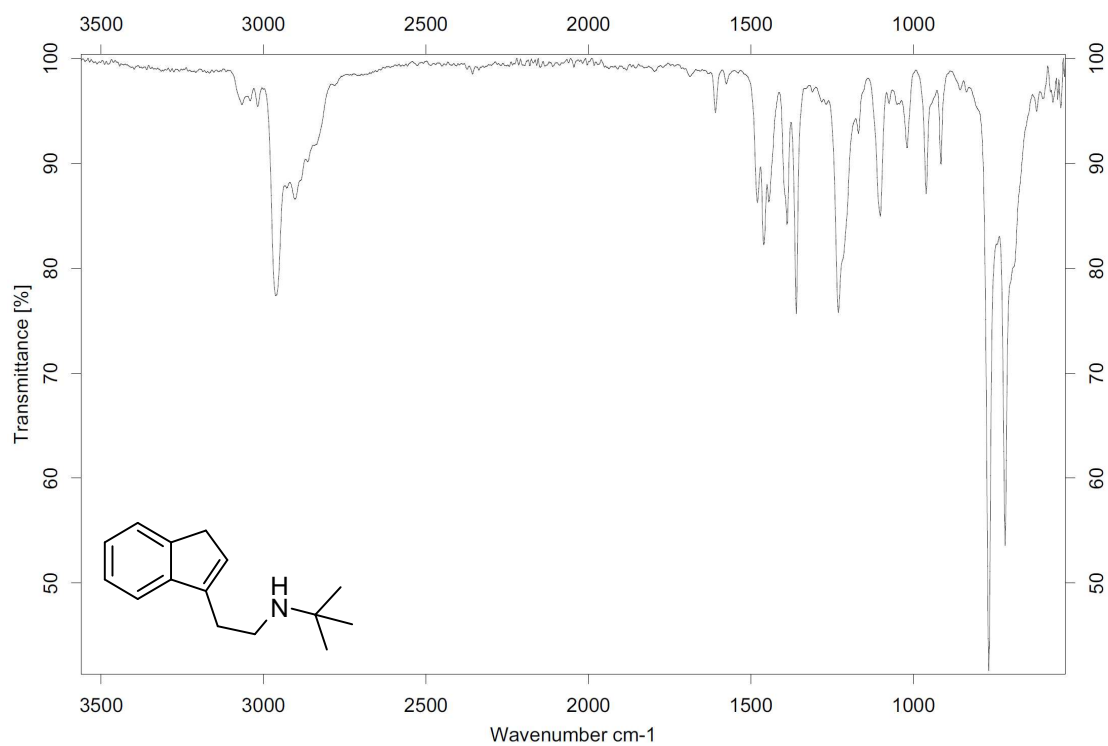
Figure S35. ^{1}H NMR spectrum of compound **4g** in CDCl$_3$.
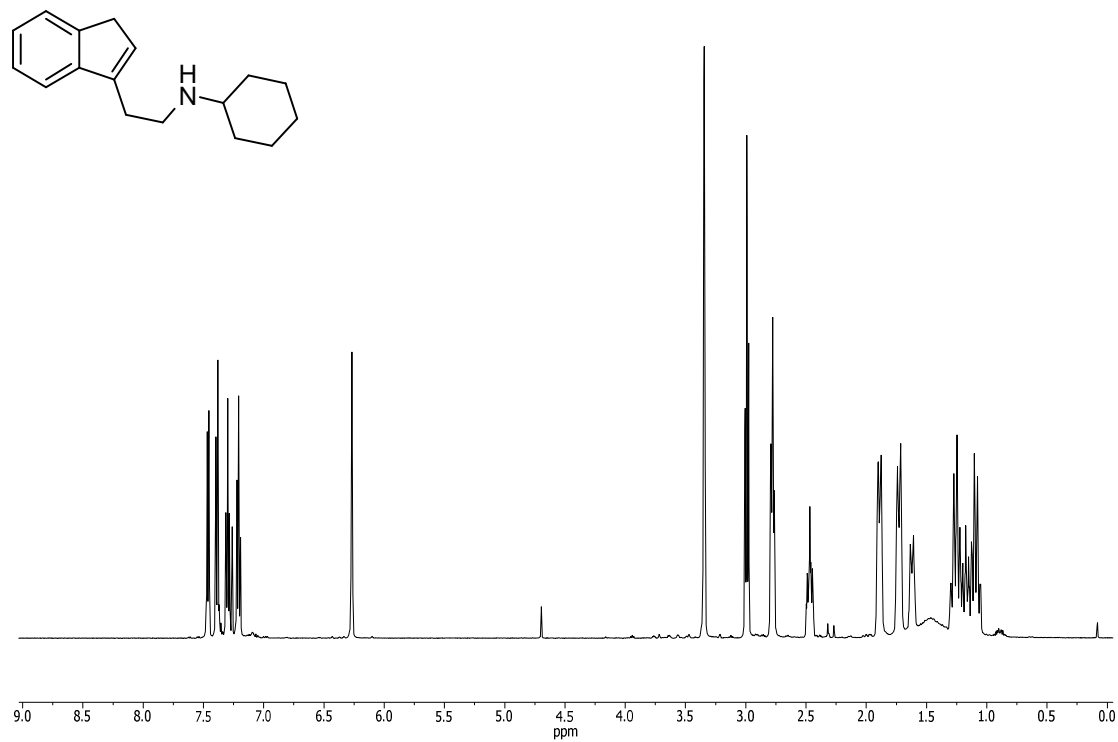
Figure S36. ^{13}C NMR spectrum of compound **4g** in CDCl$_3$.
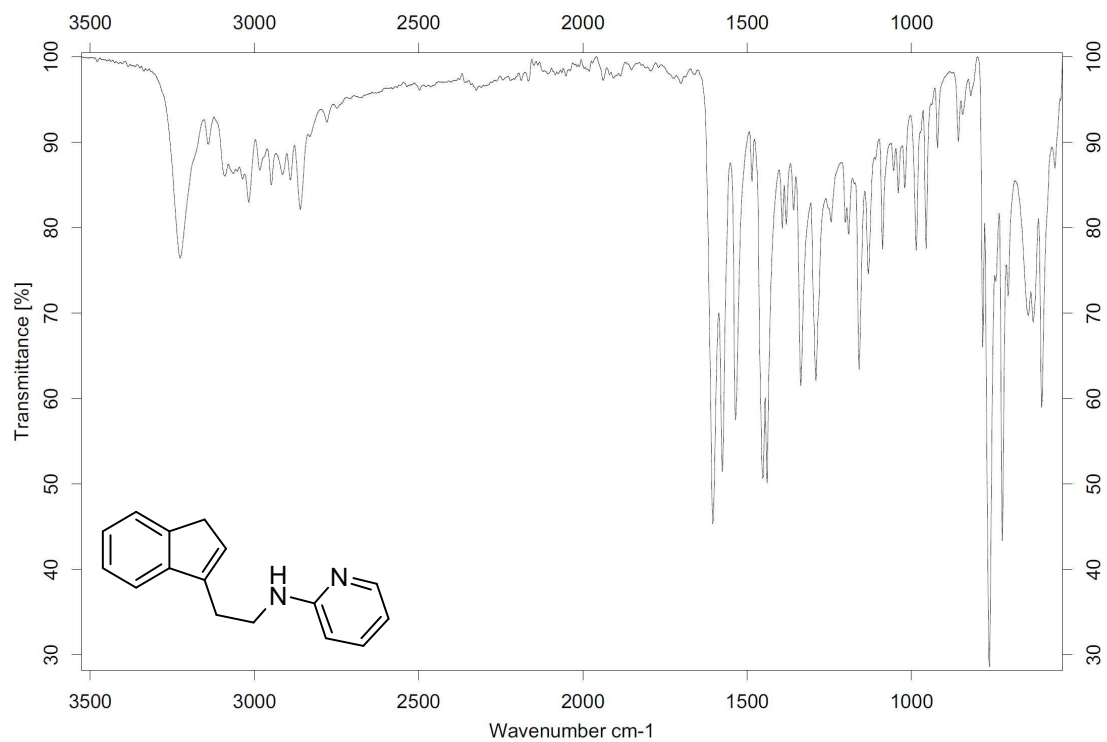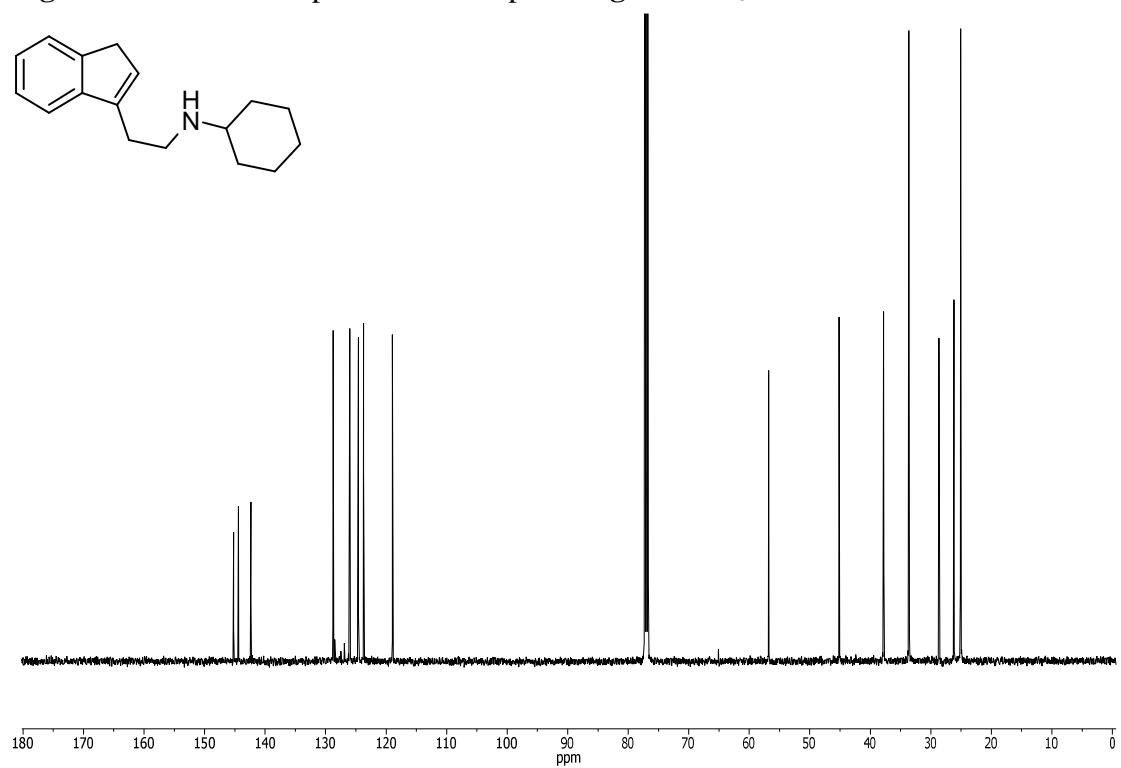
Figure S37. IR spectrum of compound **4g**.
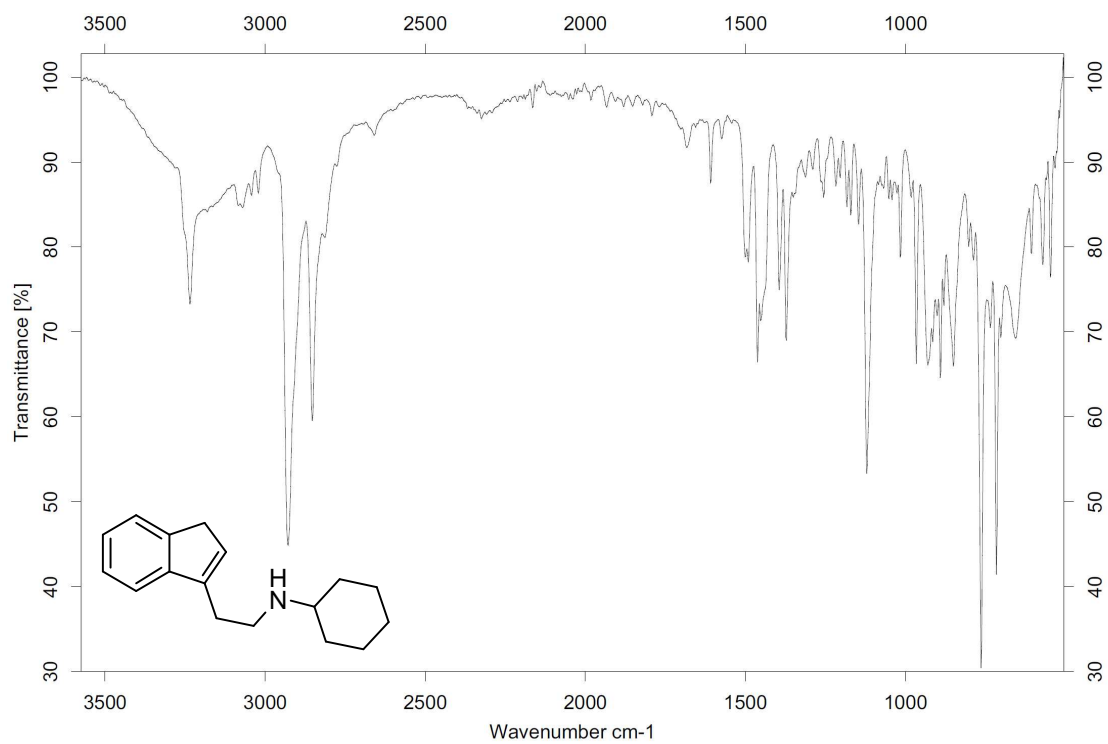
Figure S38. ^{1}H NMR spectrum of compounds **3h** and **4h** in CDCl$_3$.
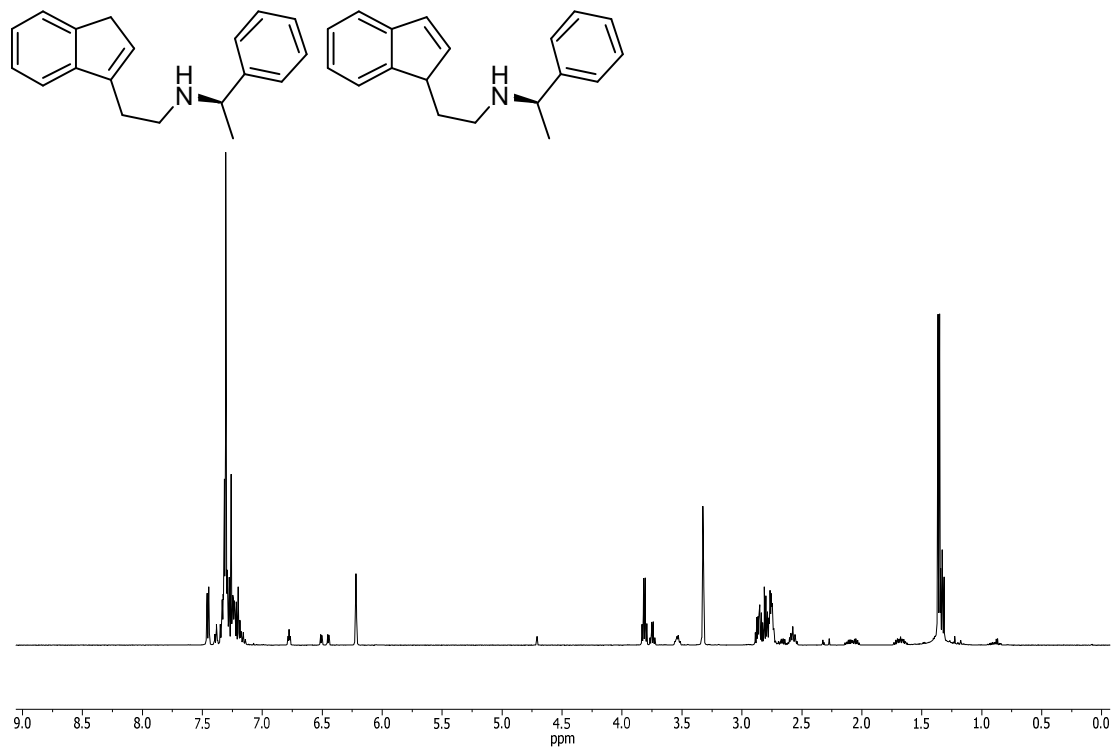
Figure S39. ^{13}C NMR spectrum of compounds **3h** and **4h** in CDCl$_3$.
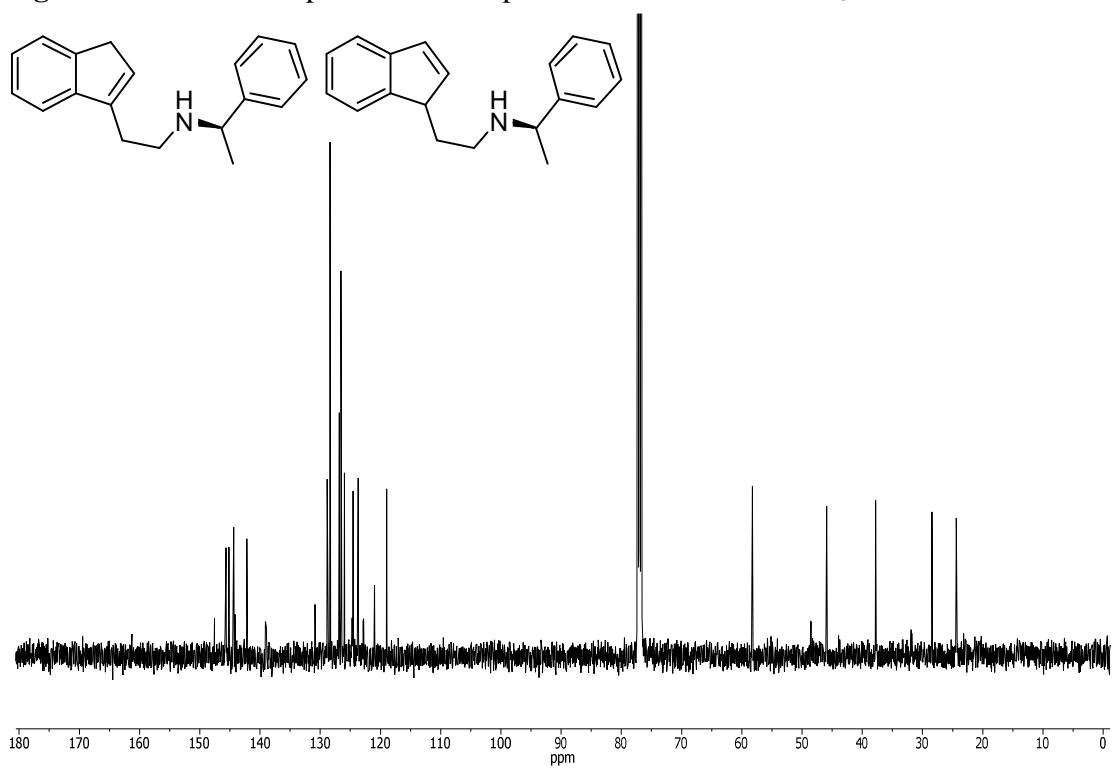
Figure S40. IR spectrum of compounds **3h** and **4h**.

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$_3$.
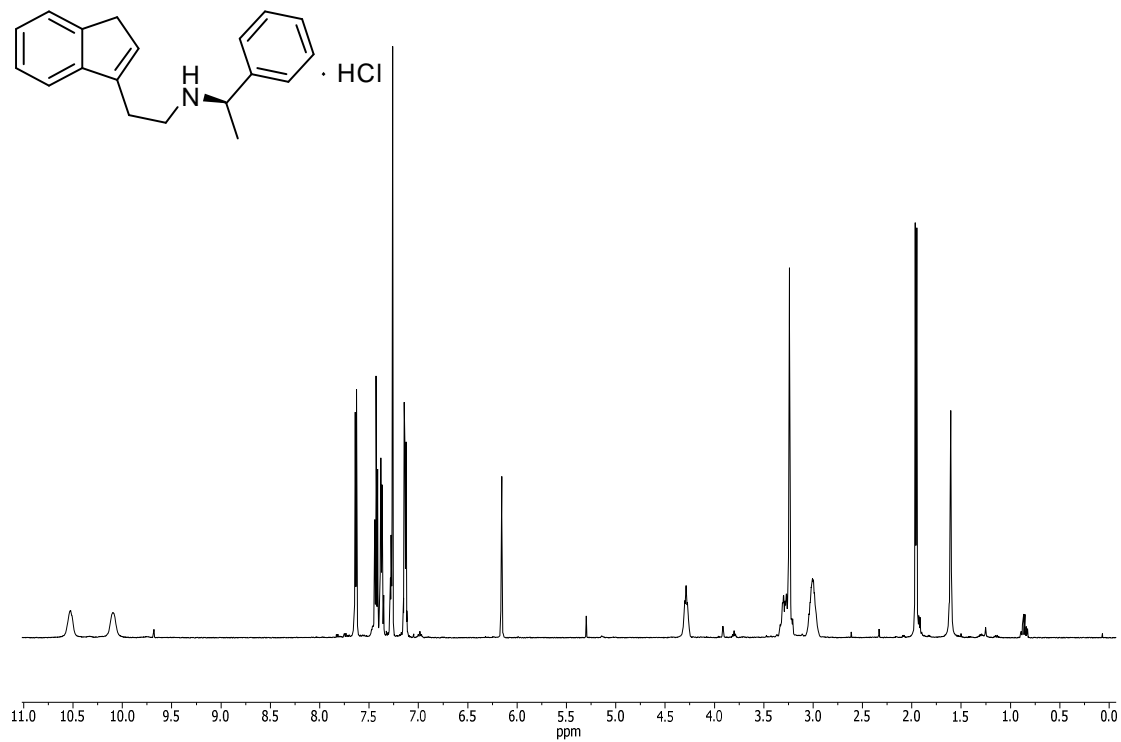
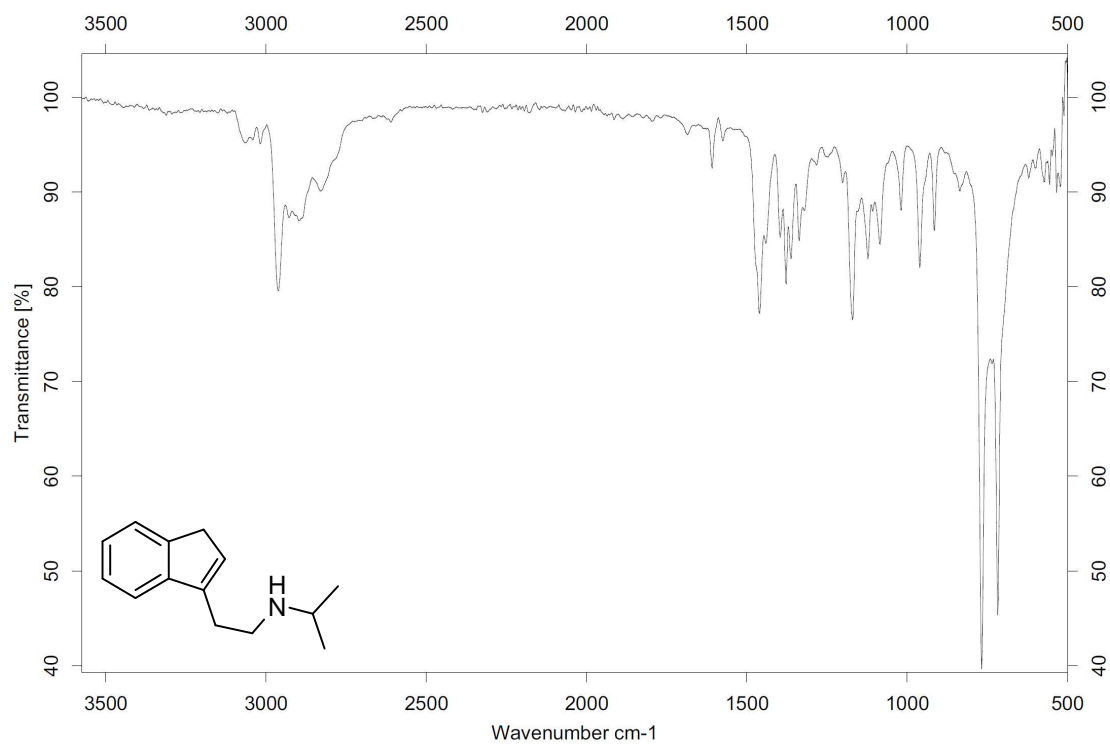**Figure S43.** ^{13}C NMR spectrum of compound **4h·HCl** in CDCl$_3$.

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

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

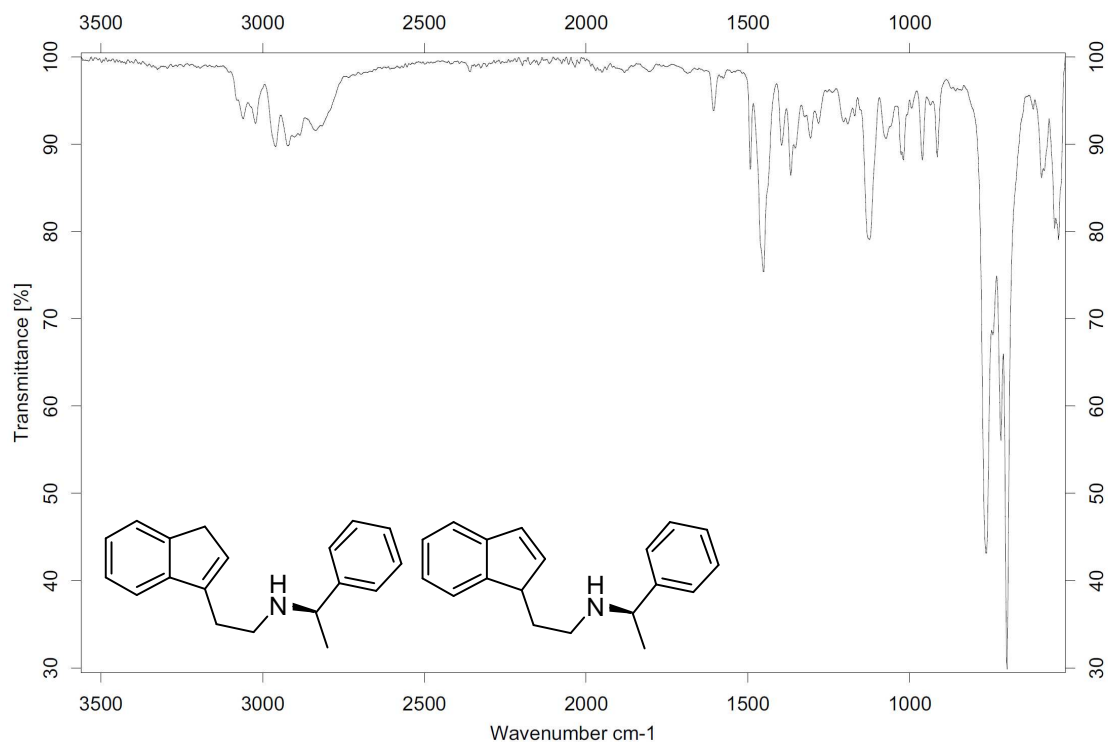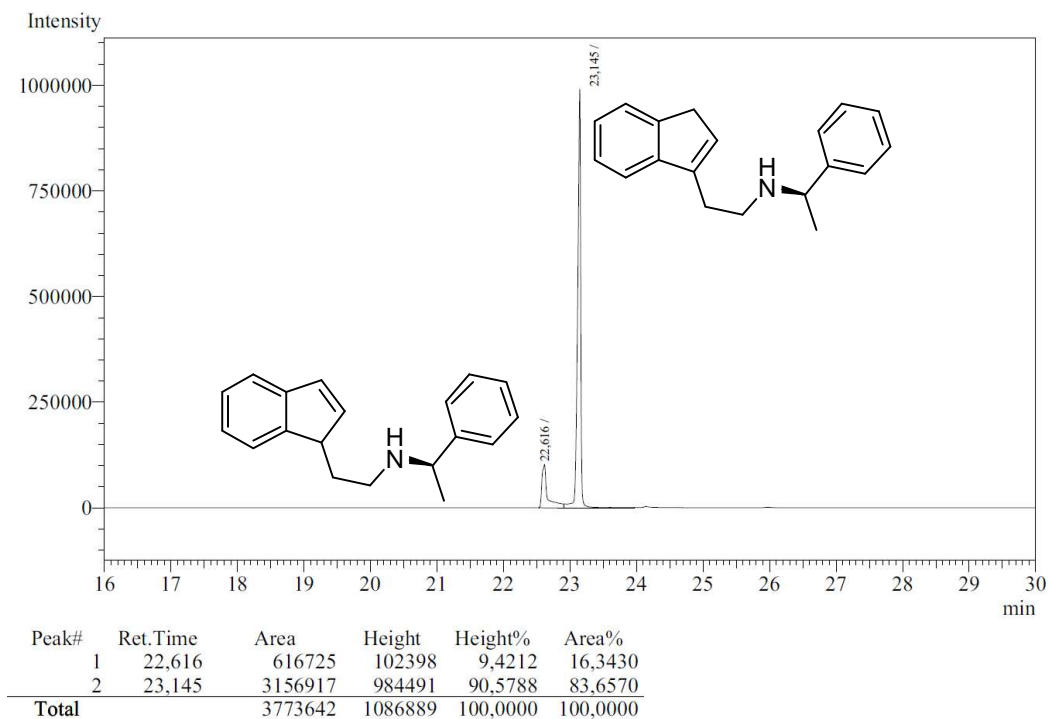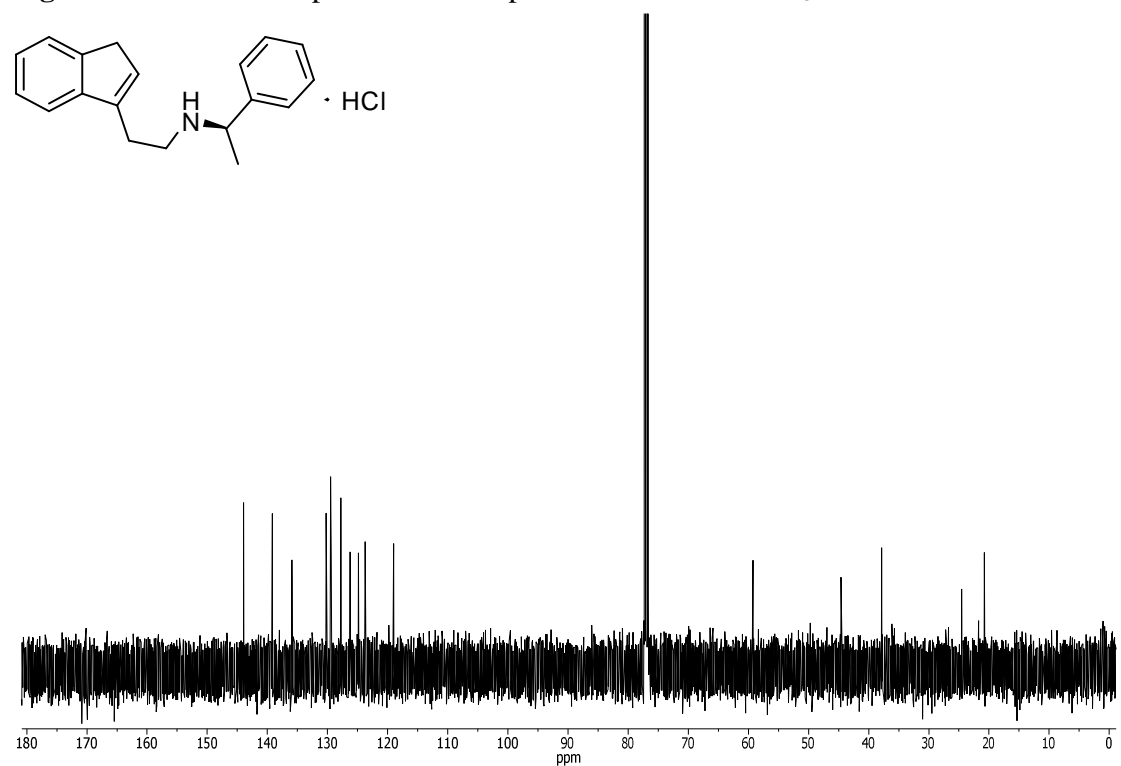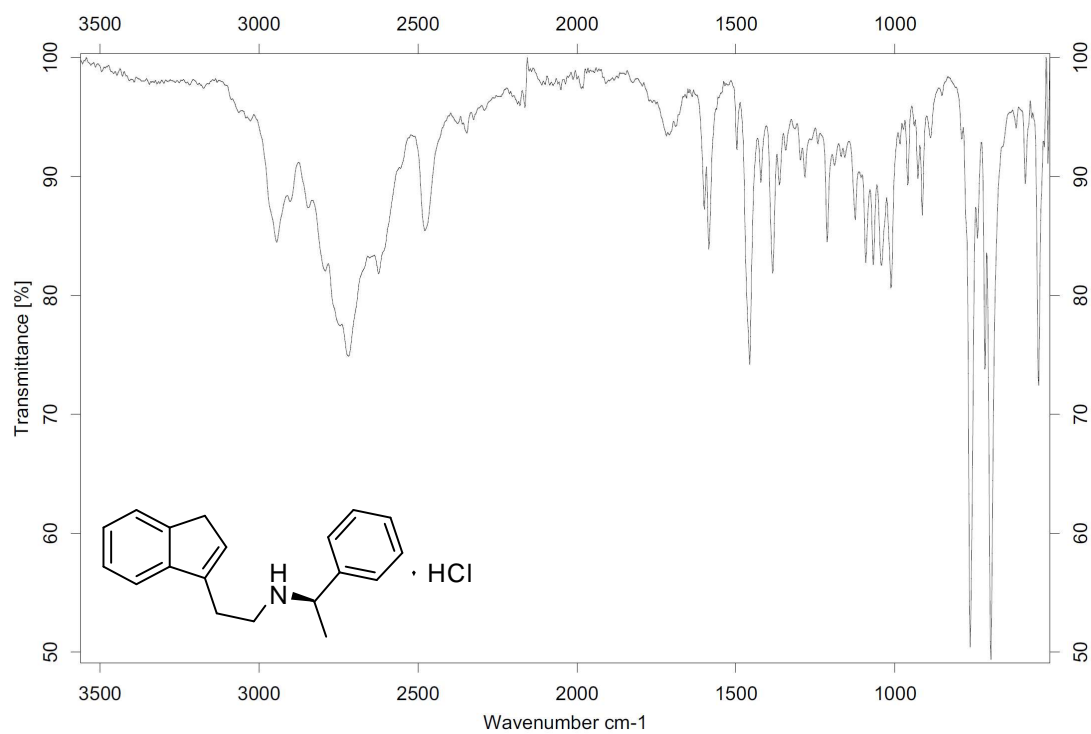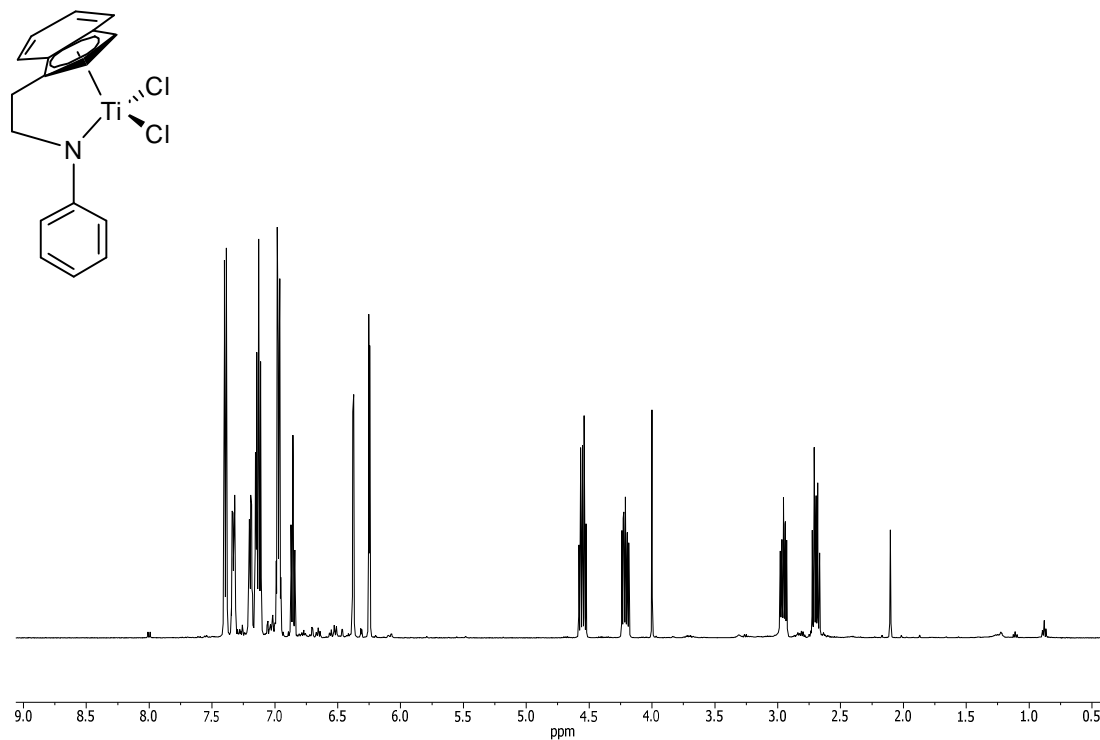**Figure S46.** ^{13}C NMR spectrum of compound **16** in C_6D_6.
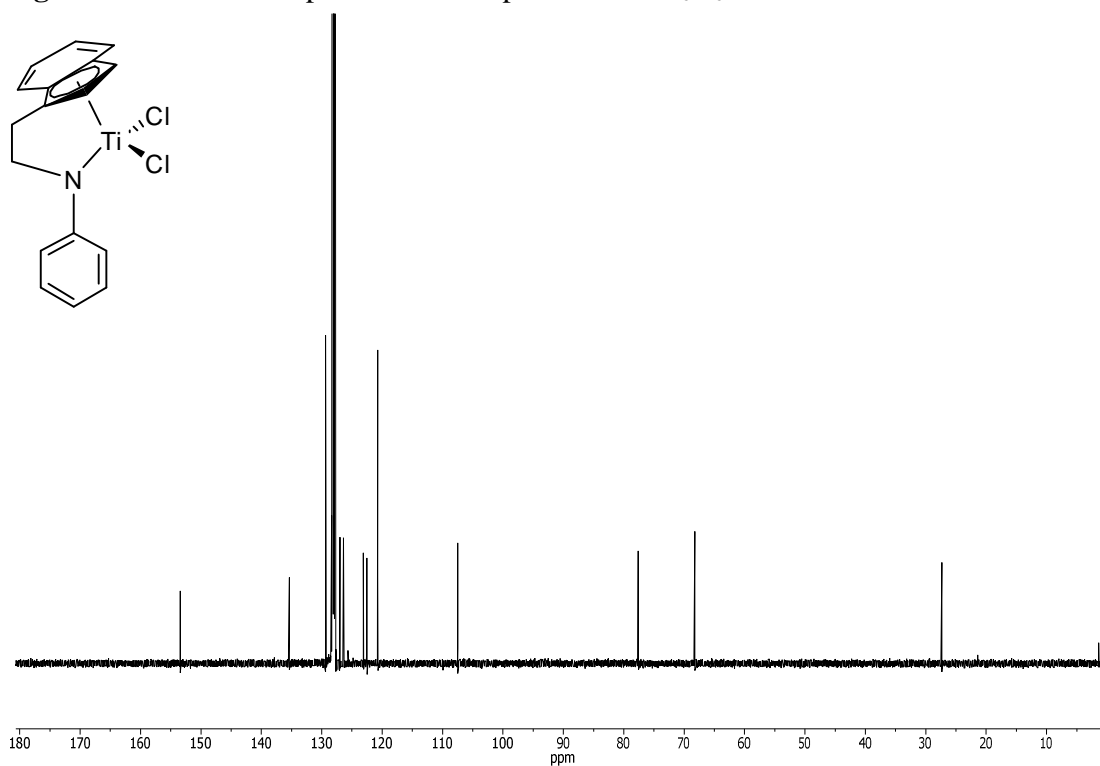
Figure S47. IR spectrum of compound **16**.
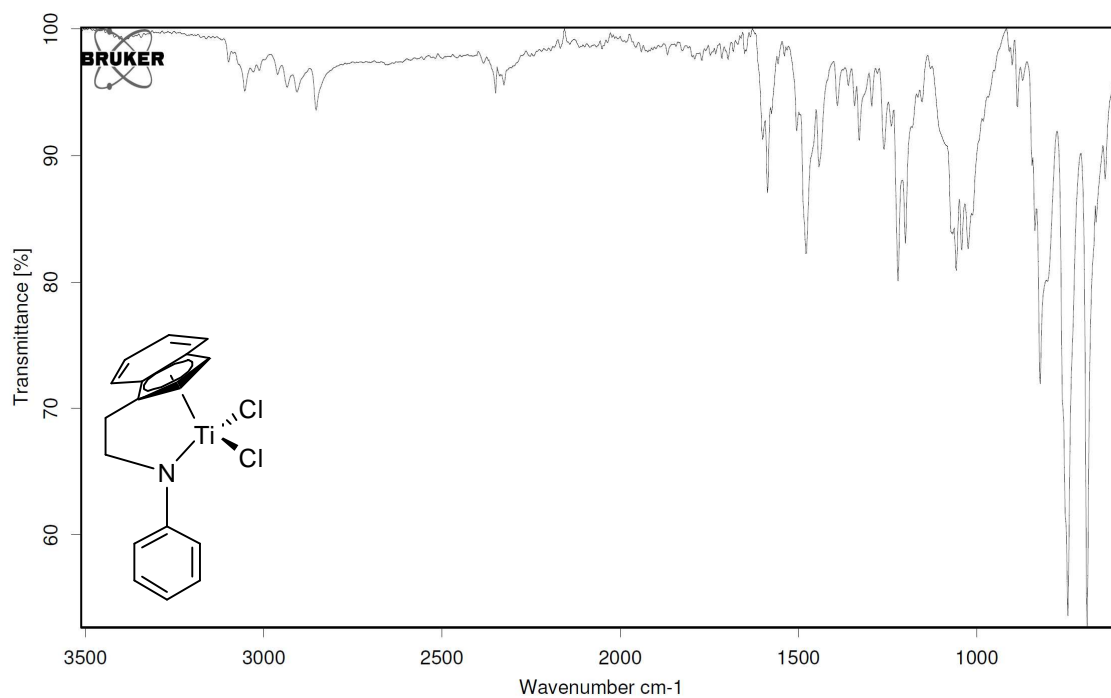
Figure S48. ORTEP-plot of compound **4h·HCl** (grey, C – white, H – green, Cl – blue, N).
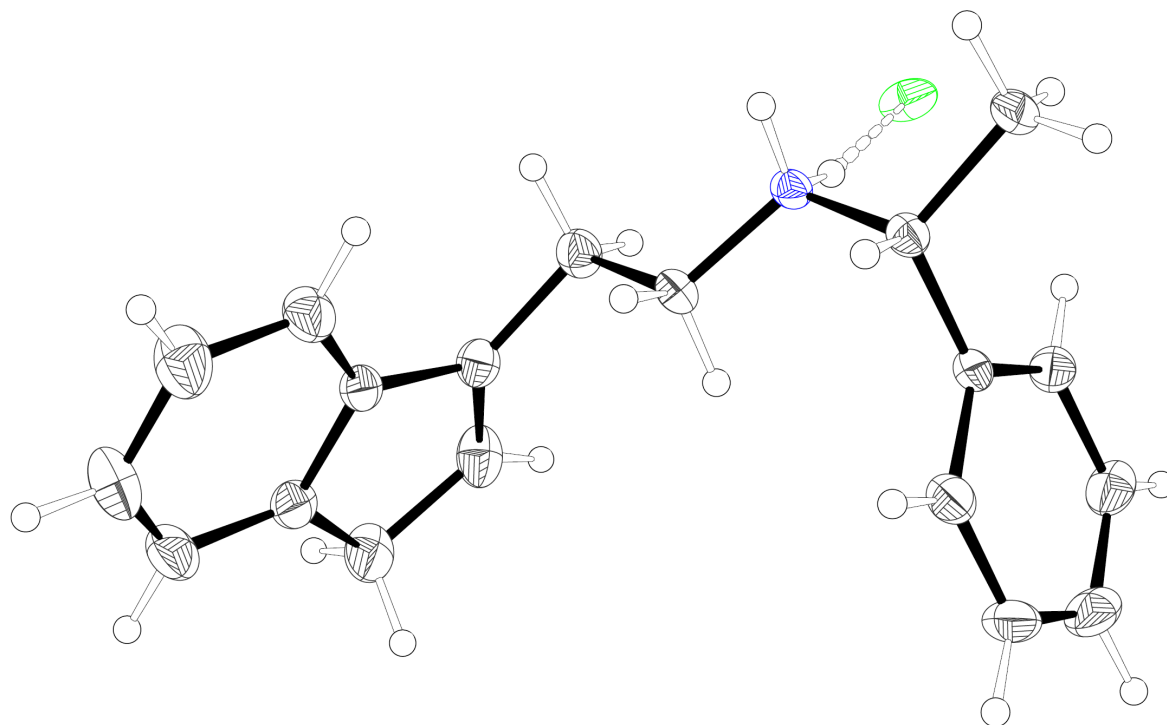
Compound **4h·HCl**: Colorless crystals, dimensions $0.320 \times 0.120 \times 0.040$ mm³, monoclinic, space group $P2_1$, unit cell dimensions: $a = 10.4522(4)$ Å, $b = 7.1194(2)$ Å, $c = 11.0487(4)$ Å, $\beta = 92.2592(16)°$, $V = 821.53(5)$ Å³, $Z = 2$, $\rho = 1.212$ Mg/M³, $\Theta_{max} = 30.030°$, radiation Mo K_α, $\lambda = 0.71073$ 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 [$I>2\sigma(I)$], intensities were corrected for Lorentz and polarization effects, an numerical absorption correction was applied using Bruker SADABS, $\mu = 0.226$ 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 [$I>2\sigma(I)$], 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).
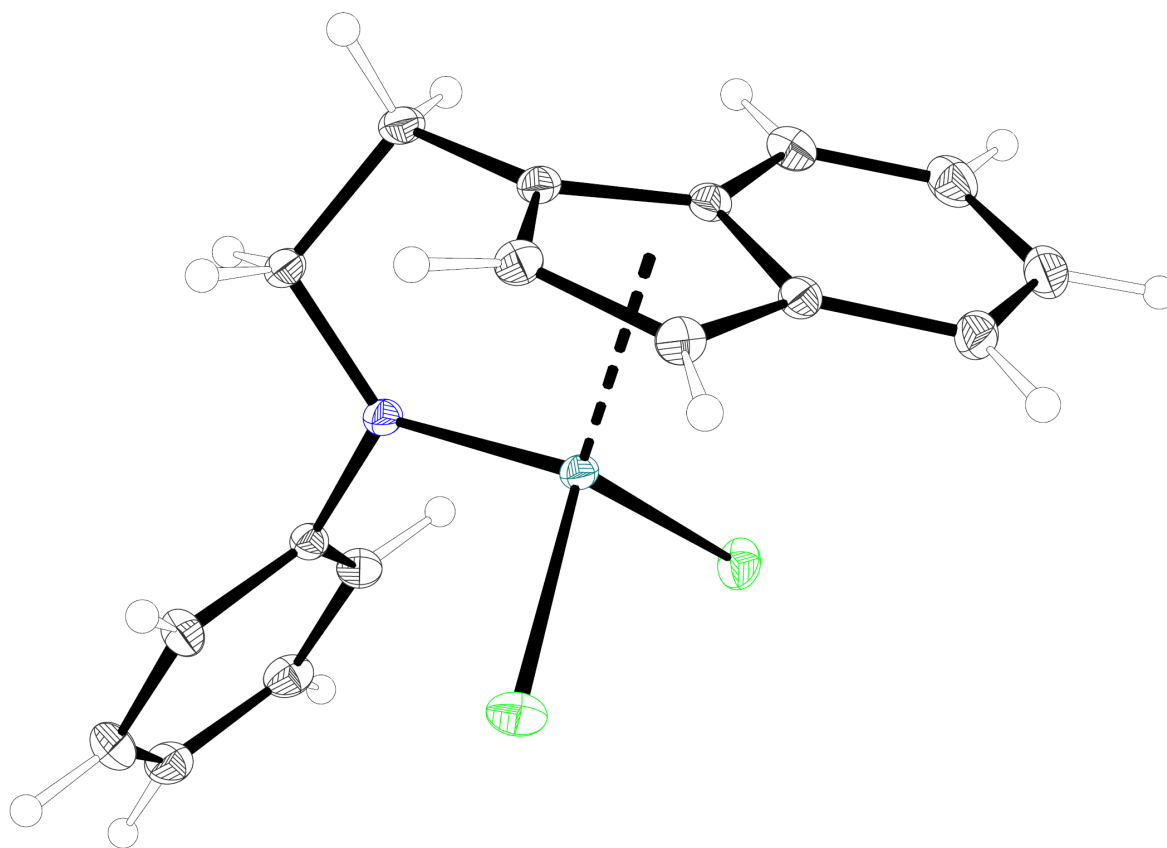
Complex **16**: Red crystals, dimensions $0.450 \times 0.200 \times 0.150$ mm³, triclinic, space group *P*-1, unit cell dimensions: $a = 7.0830(2)$ Å, $b = 9.5153(3)$ Å, $c = 12.3275(4)$ Å, $\alpha = 108.9989(12)°$, $\beta = 100.0458(13)°$, $\gamma = 99.3410(13)°$, $V = 751.81(4)$ Å³, $Z = 2$, $\rho = 1.555$ Mg/M³, $\Theta_{max} = 40.247°$, radiation Mo K_α, $\lambda = 0.71073$ 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 [$I>2\sigma(I)$], intensities were corrected for Lorentz and polarization effects, an numerical absorption correction was applied using Bruker SADABS, $\mu = 0.915$ 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 [$I>2\sigma(I)$], 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.