Supporting Information for

Brønsted Acid-Catalysed Intramolecular Hydroamination of Unactivated Alkenes: Metal Triflates as an *in situ* Source of Triflic Acid

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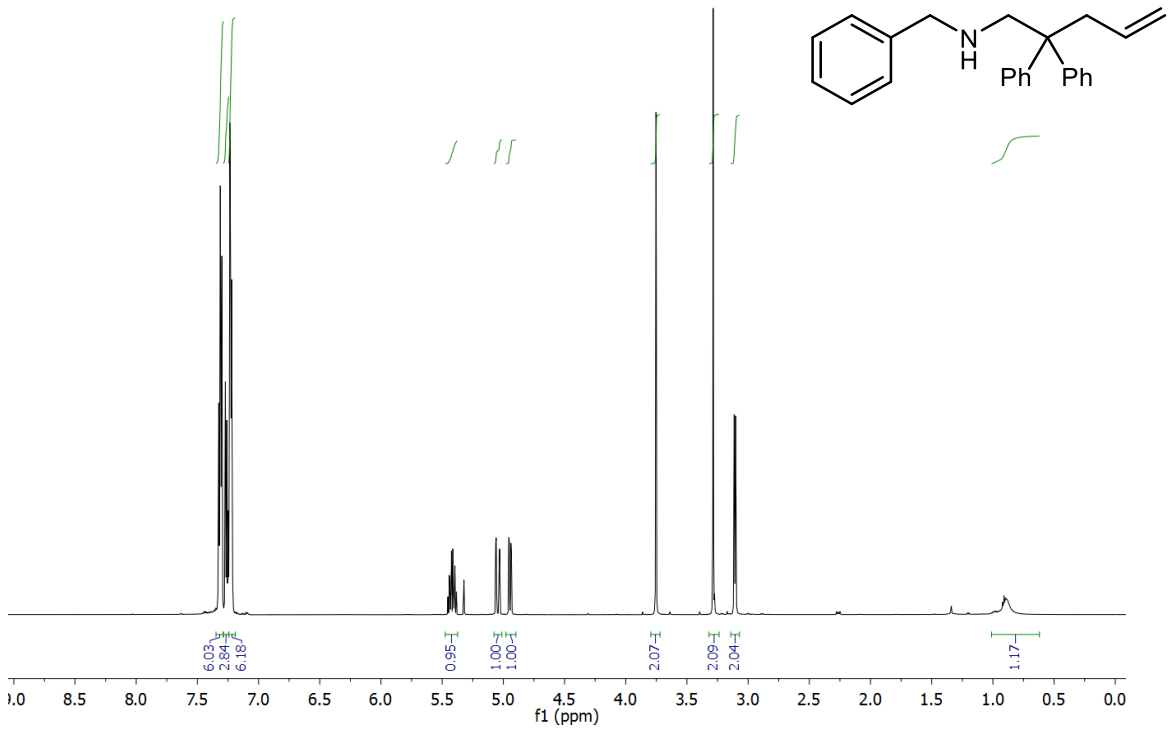


Figure S1. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of **1a**.

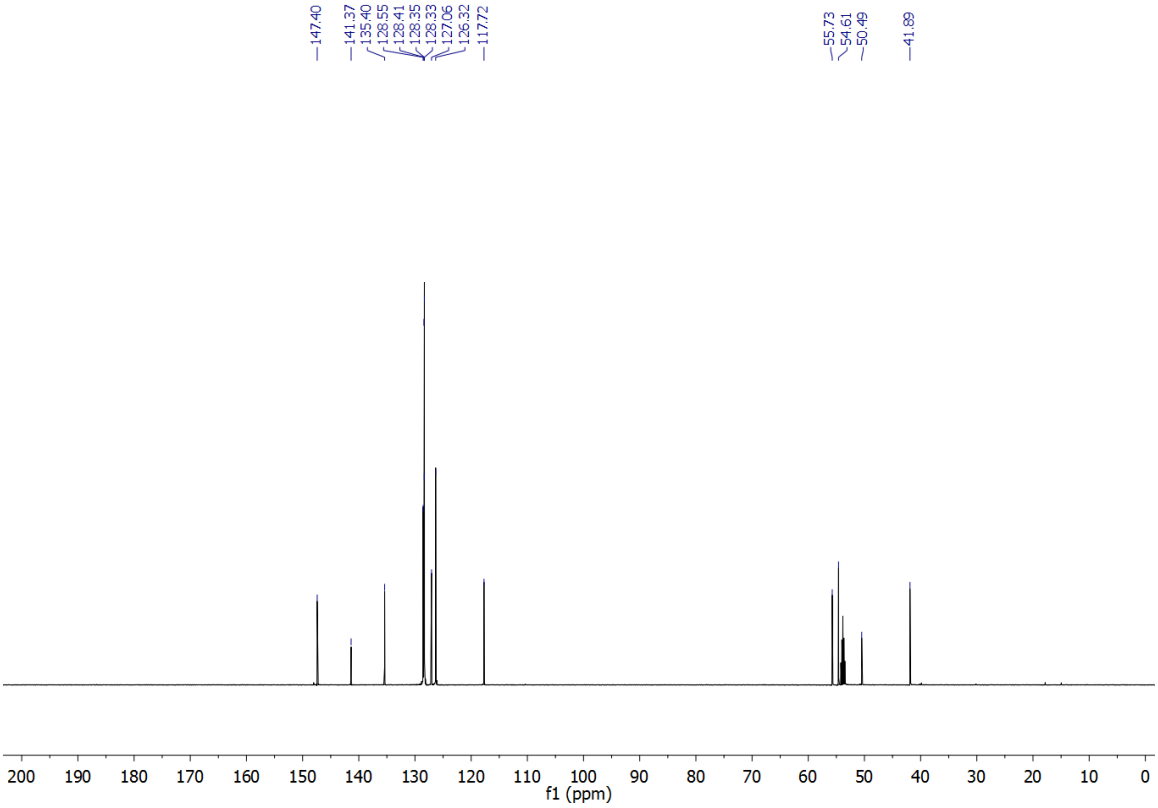


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, CD_2Cl_2) of 1**a**.

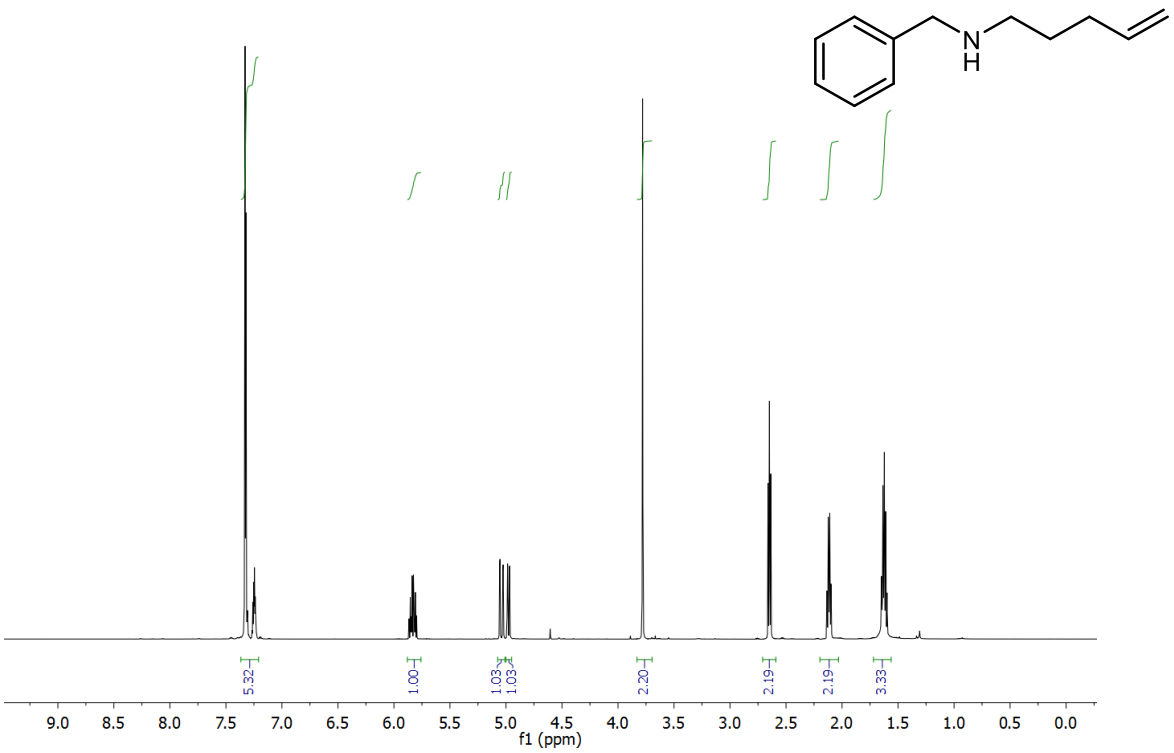


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1b**.

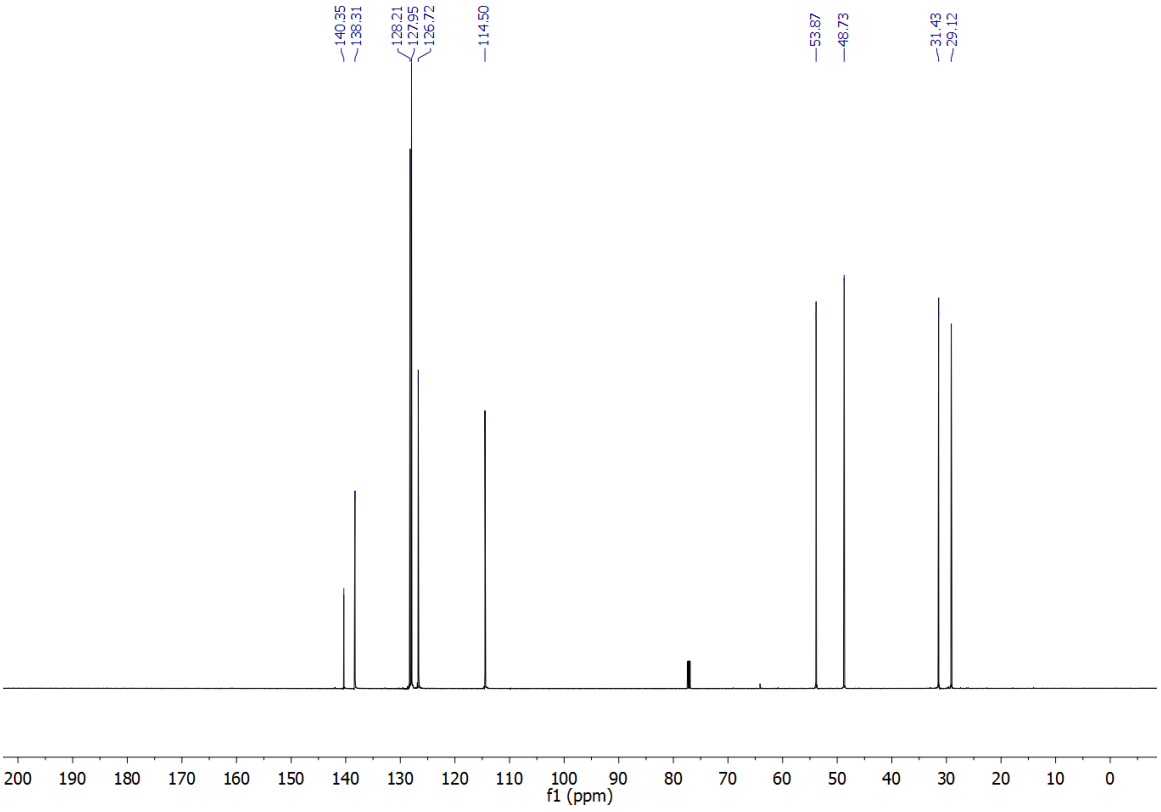


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, $CDCl_3$) of **1b**.

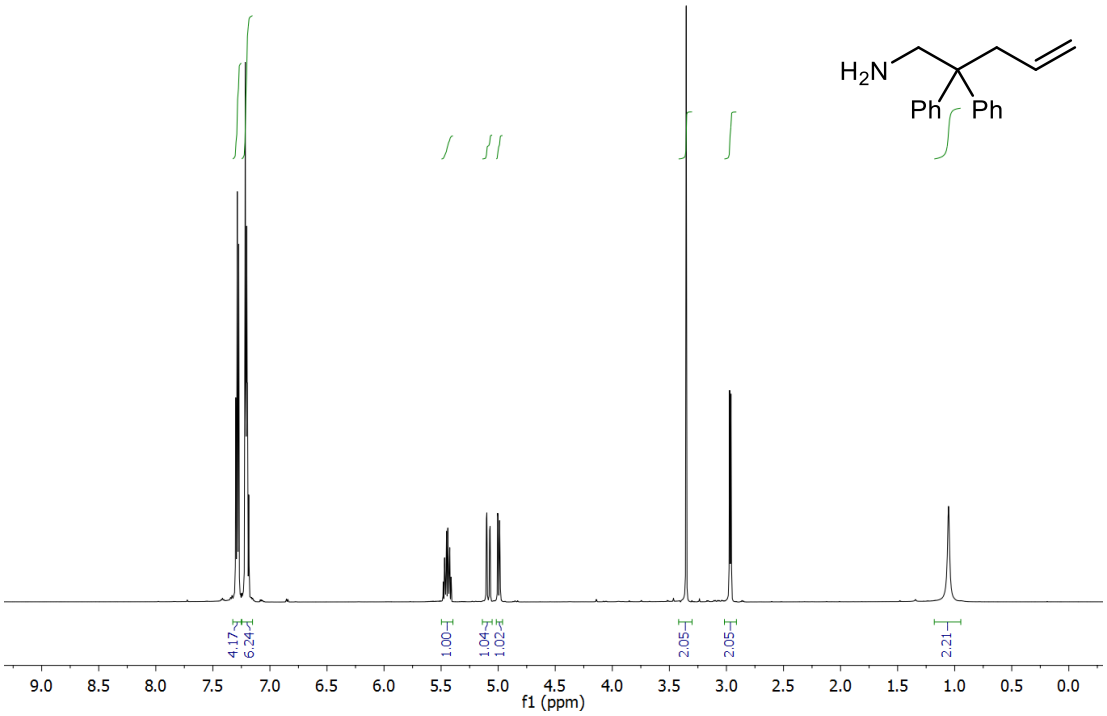


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1c**.

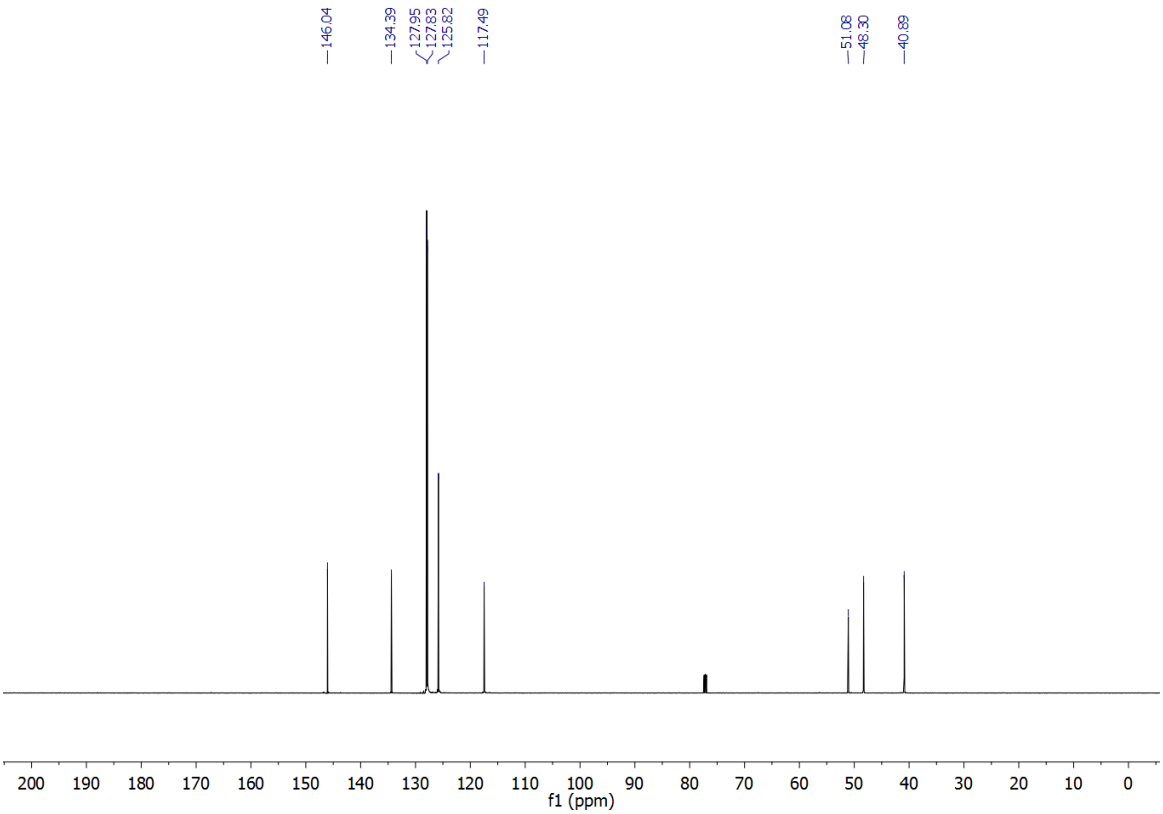


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, $CDCl_3$) of **1c**.

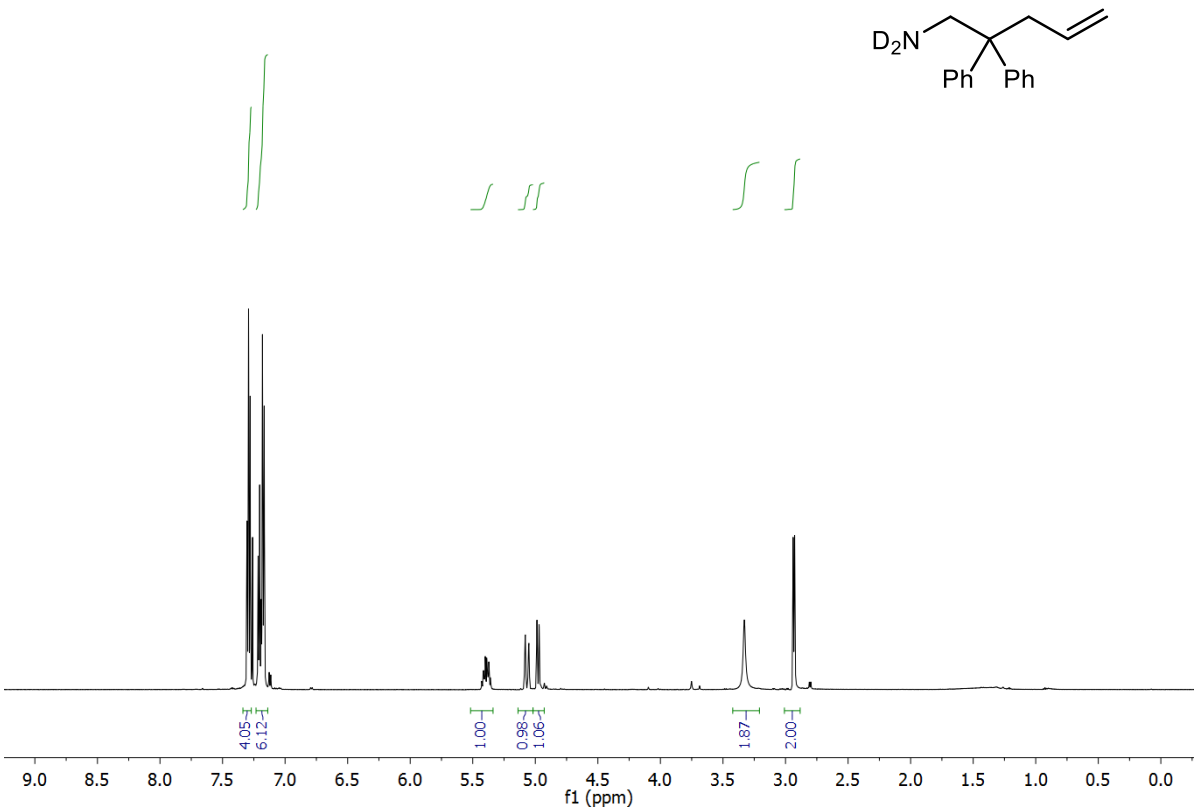


Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1c-*d*$_2$**.

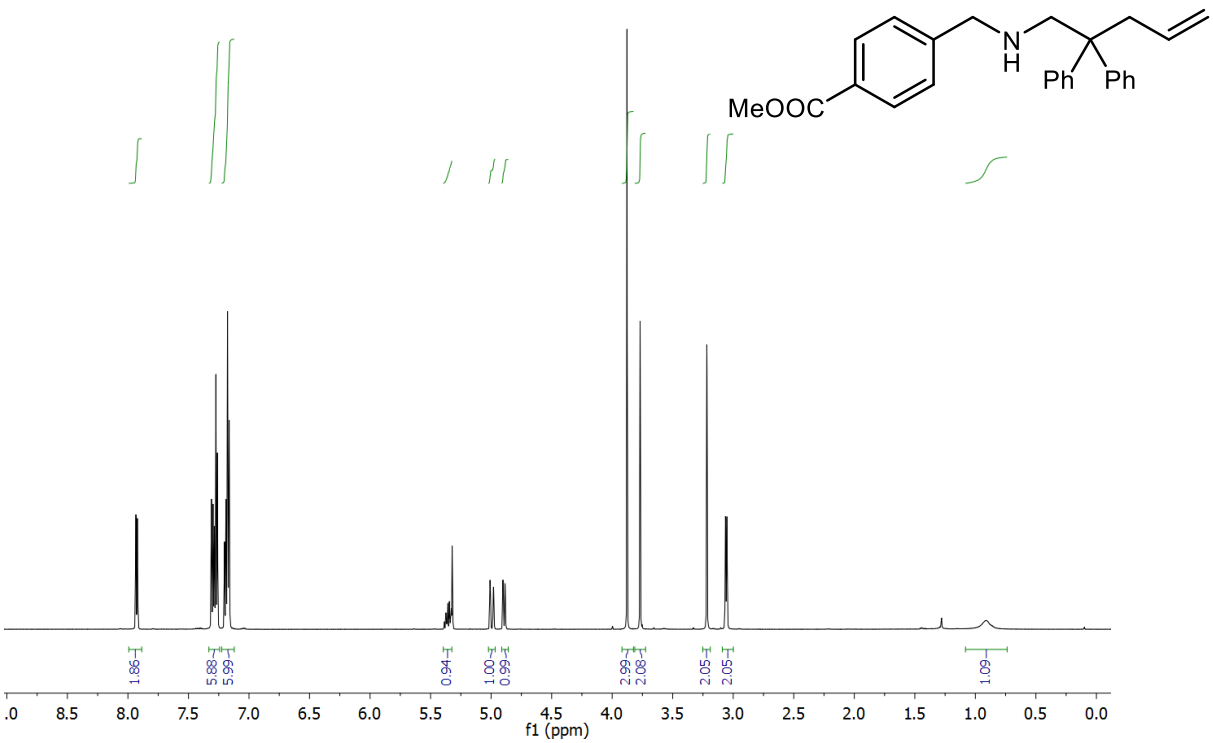


Figure S8. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of 4-[(2,2-diphenyl-4-pentenylamino)-methyl]benzoate.

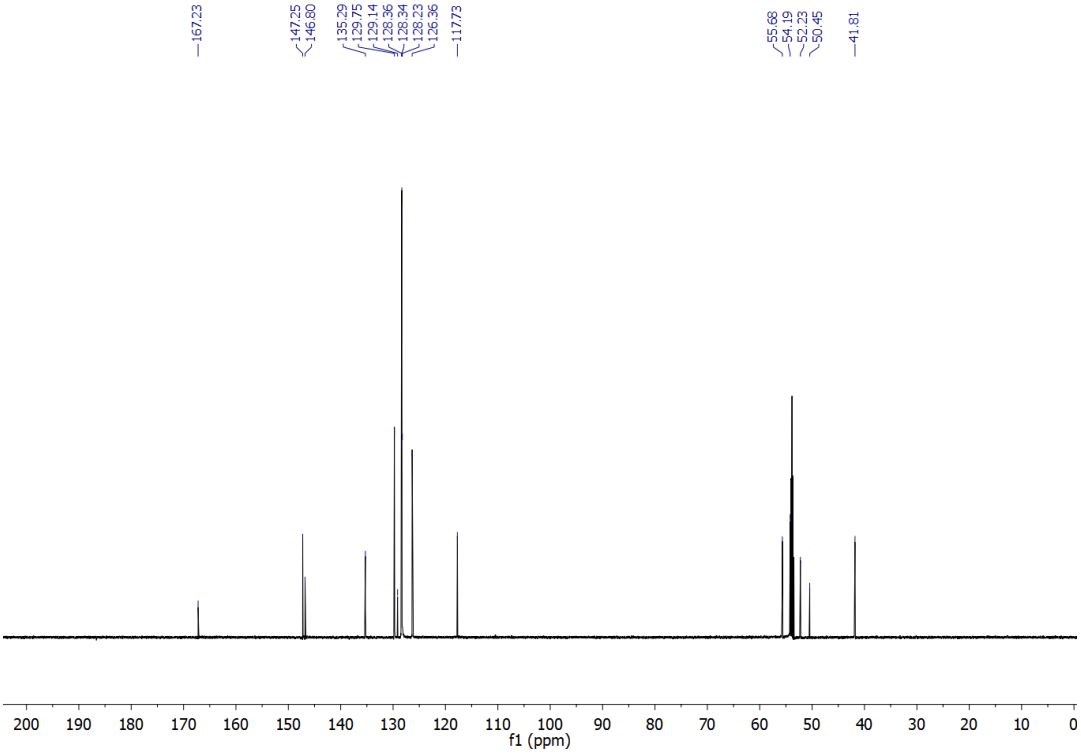


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, CD_2Cl_2) of 4-[(2,2-diphenyl-4-pentenylamino)-methyl]benzoate.

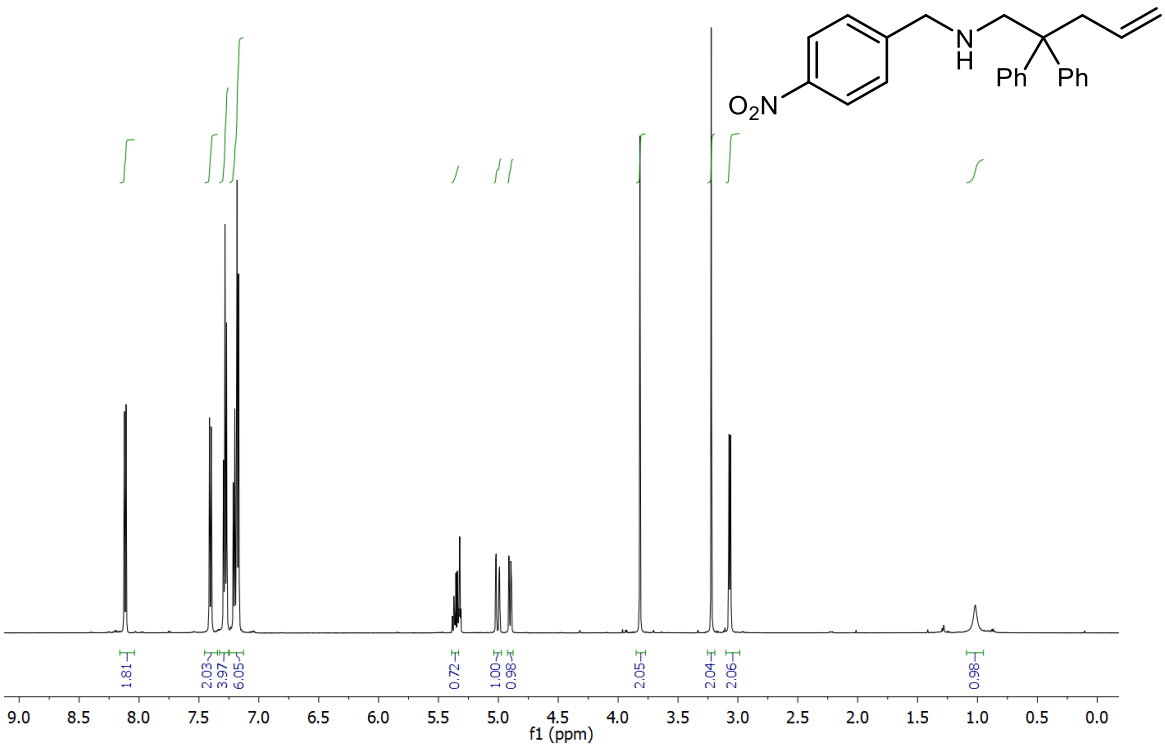


Figure S10. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of 4-nitrobenzyl(2,2-diphenyl-4-pentenyl) amine.

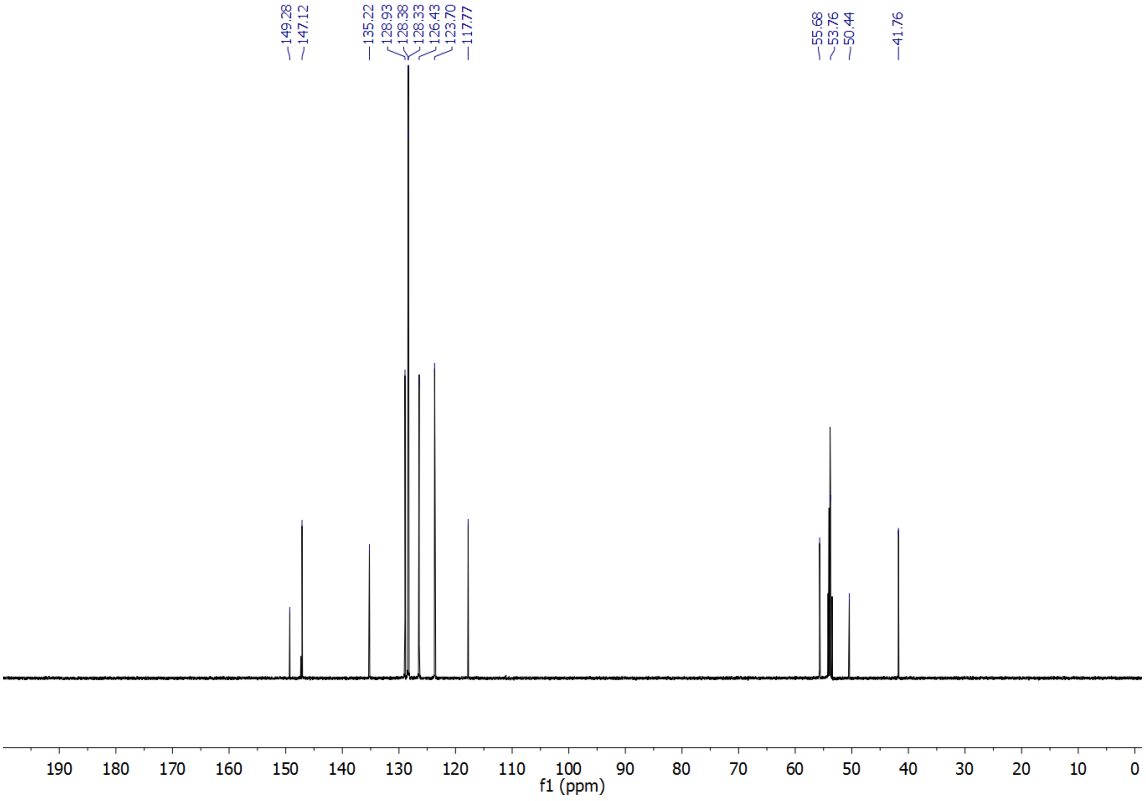


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, CD_2Cl_2) of 4-nitrobenzyl(2,2-diphenyl-4-pentenyl) amine.

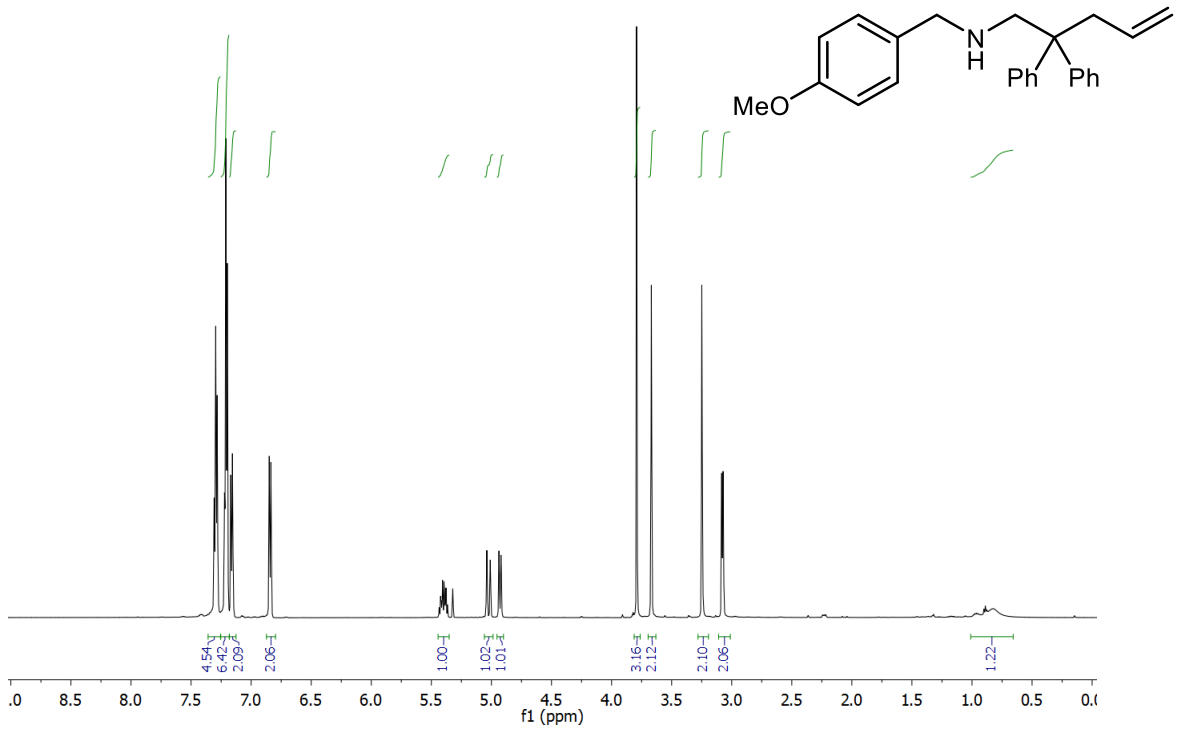


Figure S12. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of 4-methoxybenzyl(2,2-diphenyl-4-pentenyl)amine.

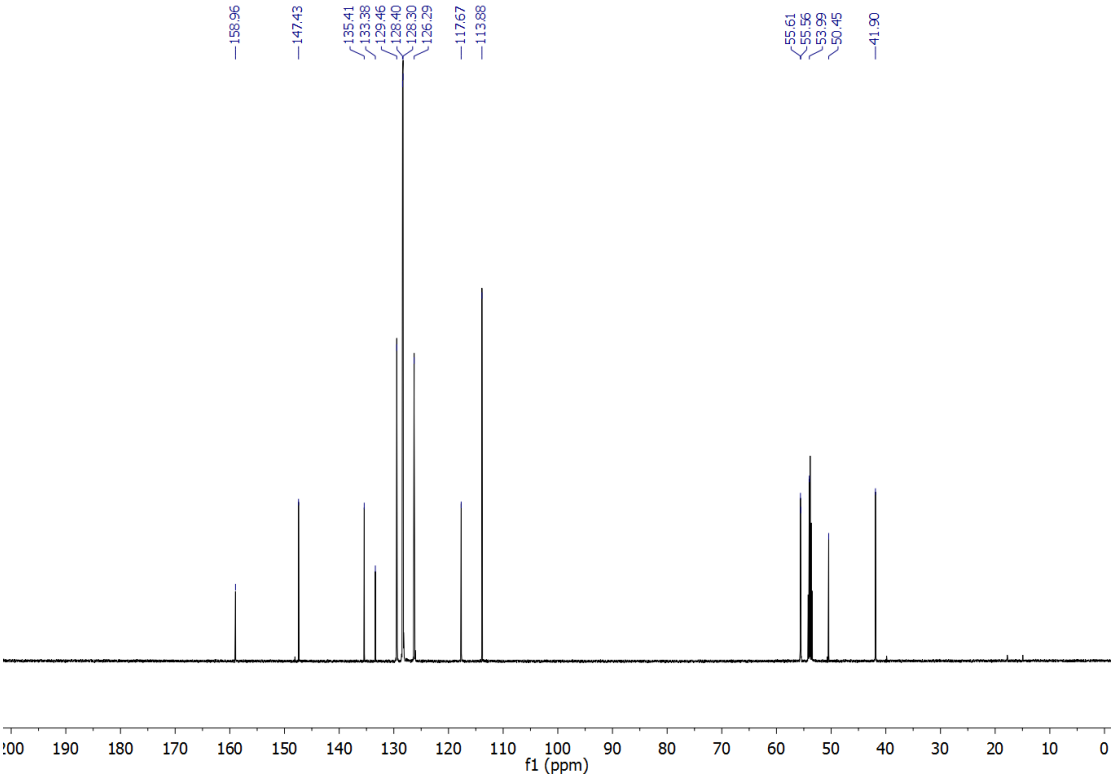


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, CD_2Cl_2) of 4-methoxybenzyl(2,2-diphenyl-4-pentenyl)amine.

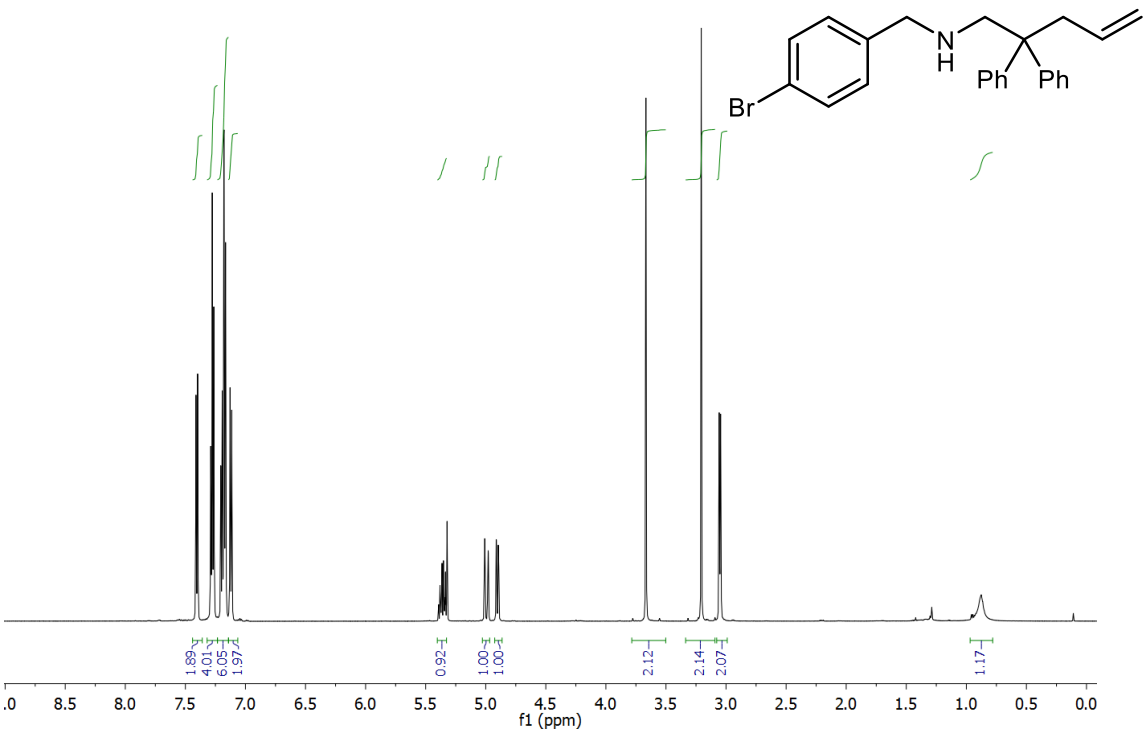


Figure S14. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of 4-bromobenzyl(2,2-diphenyl-4-pentenyl)amine.

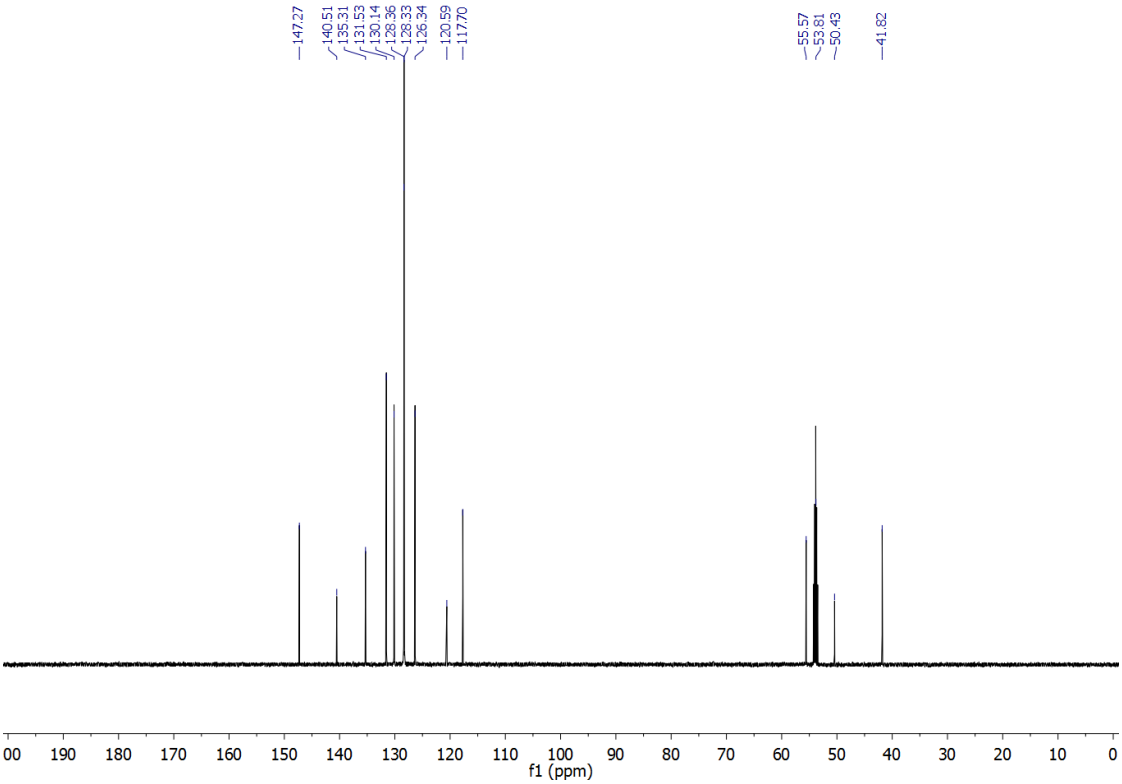


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, CD_2Cl_2) of 4-bromobenzyl(2,2-diphenyl-4-pentenyl)amine.

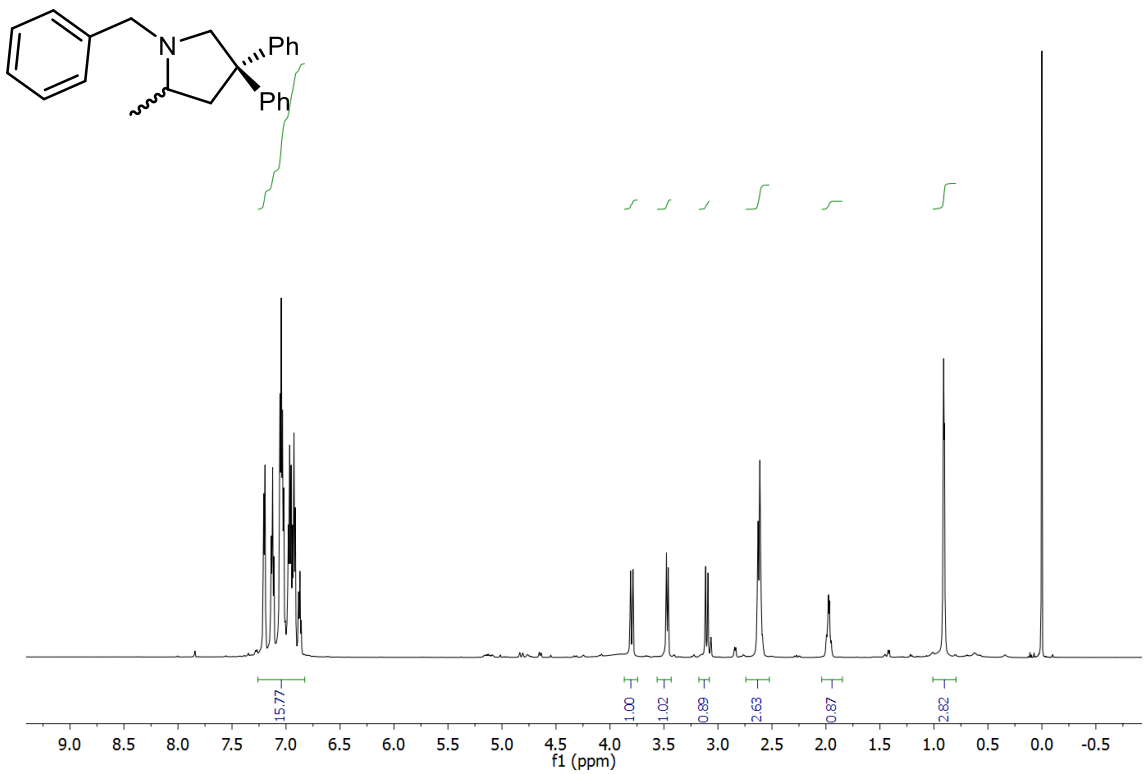


Figure S16. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of **1a**.[a,b]

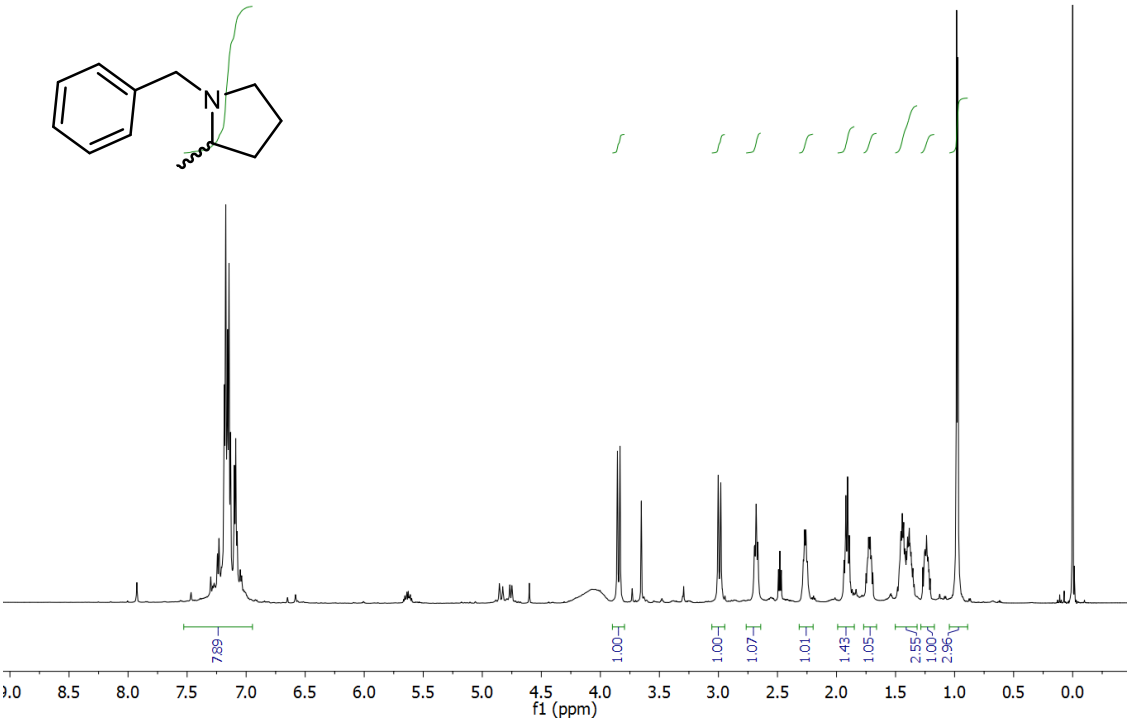


Figure S17. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of **1b**.[a,b]

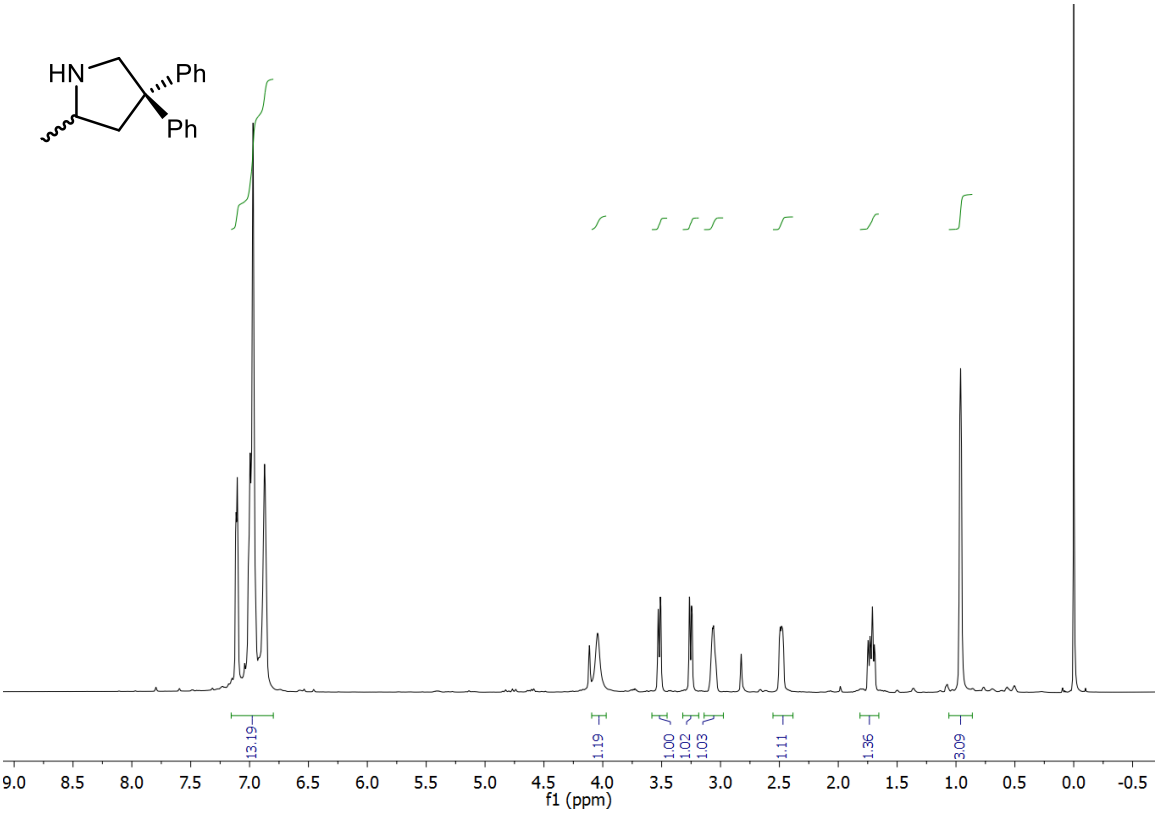


Figure S18. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of **1c**.[a,b]

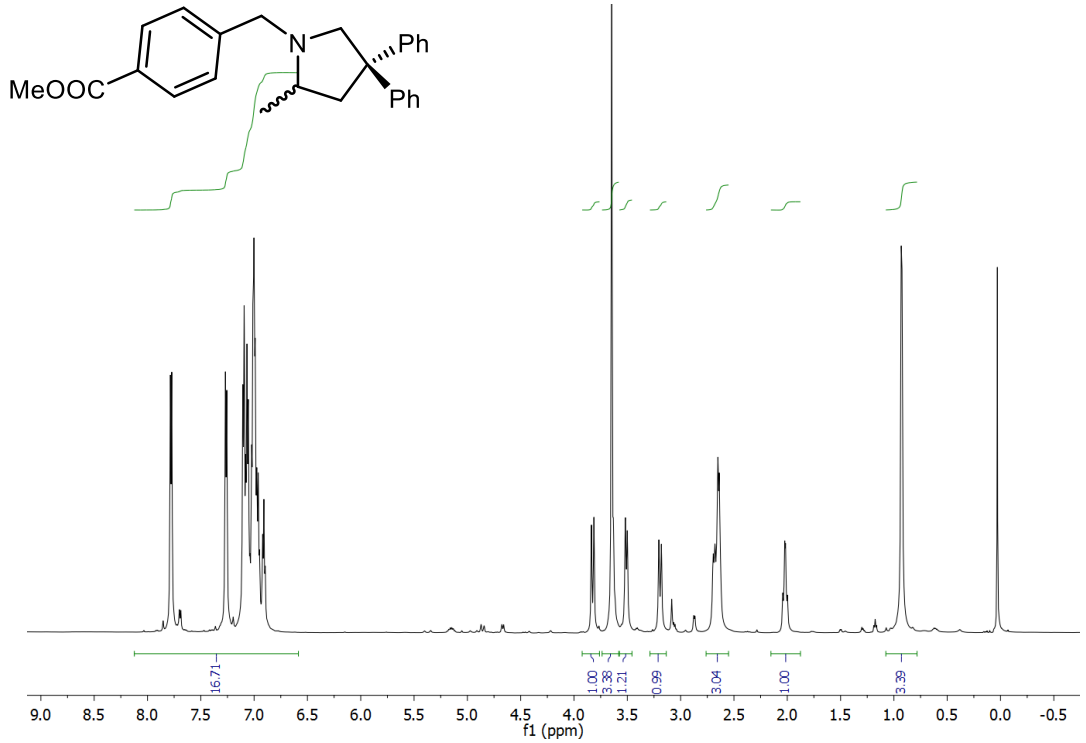


Figure S19. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of methyl 4-[(2,2-diphenyl-4-pentenylamino)-methyl]benzoate.[a,b]

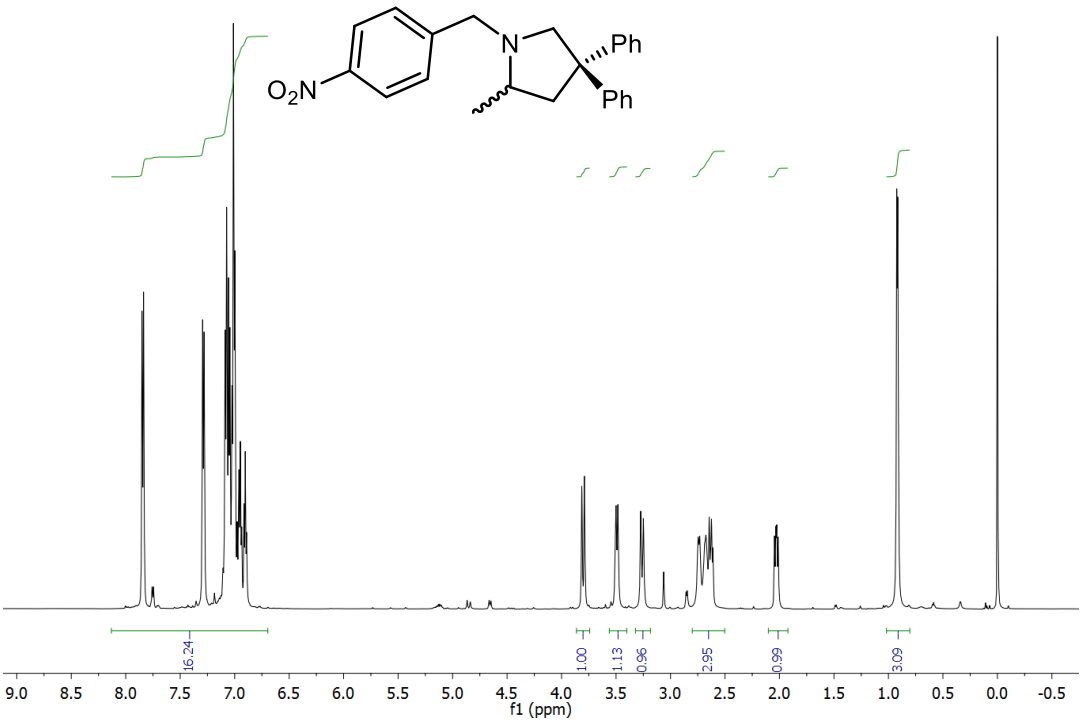


Figure S20. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of 4-nitrobenzyl(2,2-diphenyl-4-pentenyl) amine.[a,b]

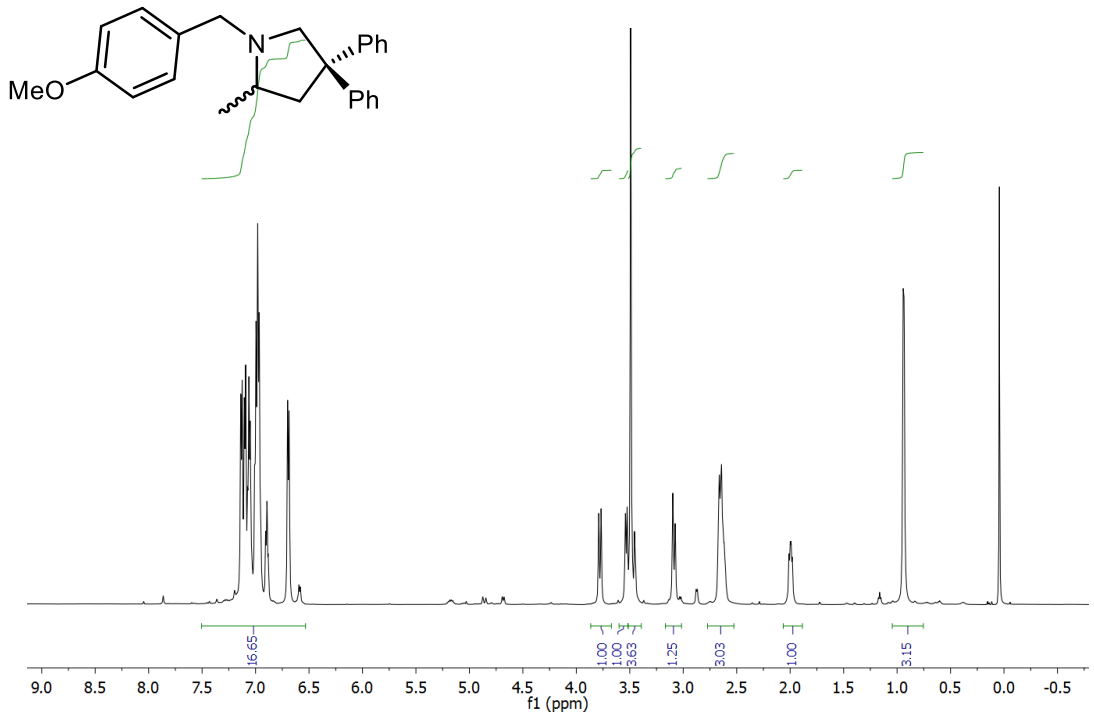


Figure S21. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of 4-methoxybenzyl(2,2-diphenyl-4-pentenyl)amine.[a,b]

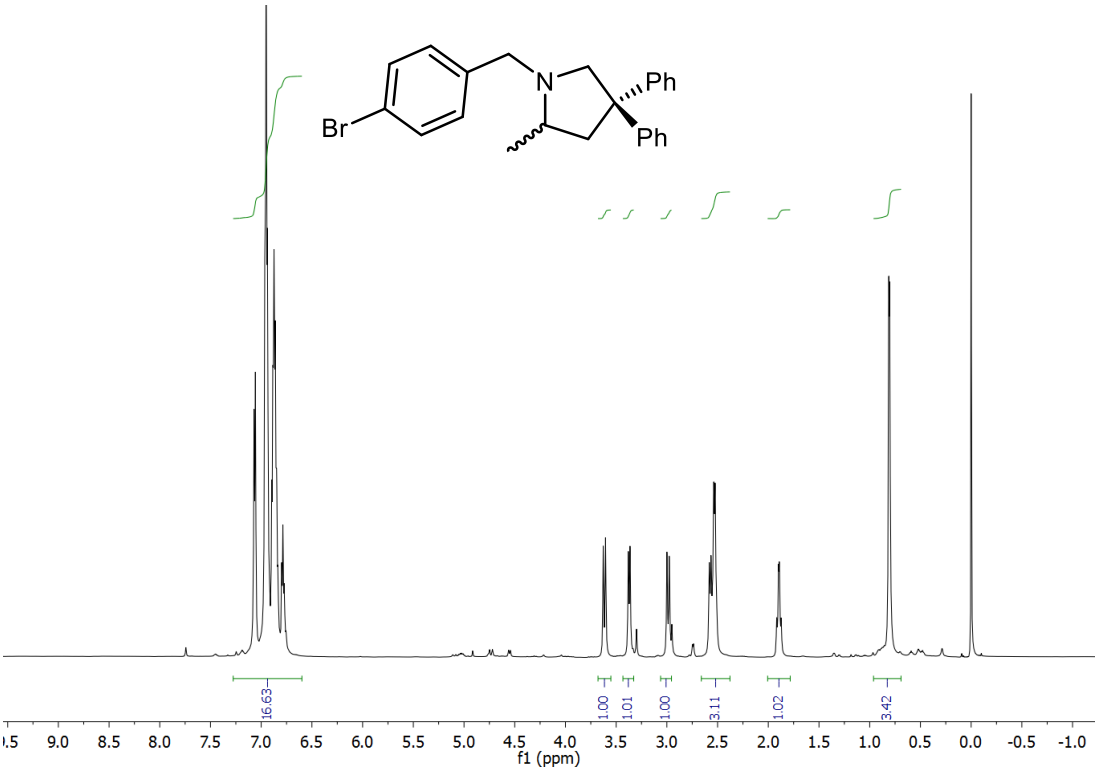
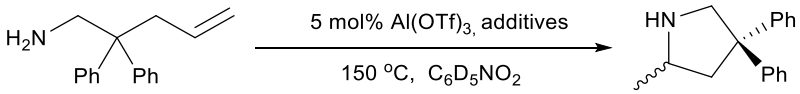


Figure S22. ^{1}H NMR spectrum (600 MHz, $C_6D_5NO_2$) of hydroamination product of 4-bromobenzyl(2,2-diphenyl-4-pentenyl)amine.[a,b]

a: The resonance at 0.0 ppm is the internal standard, hexamethylsiloxane (HMDSO).

b: Integrations of the aromatic region are inflated due to overlap with solvent resonances.

Table S1. Water's influence on $Al(OTf)_3$ catalyzed hydroamination.[a,b,c]



1c **2c**

Entry	*Additives*	Yield (%)	Conv. (%)
1	none	76	82
2	0.25 eq. H_2O	80	81
3	0.5 eq. H_2O	85	86
4	1 eq. H_2O	76	81
5	2 eq. H_2O	83	86

[a] All reactions were performed in sealed NMR tubes containing $C_6D_5NO_2$ with 0.8 M substrate, 5 mol% $Al(OTf)_3$. [b] Yields/conversions were recorded at 16h and determined by ^{1}H NMR using

hexamethyldisiloxane as internal standard (the standard deviations for % yields are < 5%). [c] Equivalents of H_2O relative to $Al(OTf)_3$.