*Supporting Information for:*

# Exploiting Natural Complexity for Substrate Controlled Regioselectivity and Stereoselectivity in Tantalum Catalysed Hydroaminoalkylation

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**Table of Contents:**

# S1. Materials and Instrumentation

## Materials

All reactions were performed under an inert $N_2$ atmosphere using either Schlenk or glovebox techniques using oven-dried glassware, unless otherwise stated. All glassware used was dried in a 160 °C oven overnight prior to use. Tantalum pentachloride (Strem), magnesium powder (Aldrich), zinc chloride (Strem), (chloromethyl)trimethylsilane (Aldrich), triphosgene (Oakwood), *N*-methyl-1-phenylethanamine (Enamine), and 2,6-dimethylaniline (Aldrich) were all used as received. Turpentine was provided by Holmen AB extracted by steam recovery. $Ta(CH_2SiMe_3)_3Cl_2$,[1] and sodium (2,6-dimethylphenyl)(methyl(1-phenylethyl)carbamoyl)amide (**L**$^-$**Na**$^+$),[2] were all synthesized according to literature protocol. All amines and terpenes/alkenes were purchased from Aldrich, Combi-Blocks, TCI, or Oakwood. Furthermore, all amines and alkenes used were all dried and degassed under over $CaH_2$, vacuum distilled, and transferred into glovebox prior to use. A detailed drying and degassing protocol for turpentine is described in section **S6**. Toluene, hexanes, and diethyl ether were dried over activated alumina columns and stored over activated molecular sieves (4 Å). $CDCl_3$ was dried over sieves and stored on the bench top. Toluene-$d_8$ was sparged with $N_2$ gas and dried on molecular sieves before use. Experiments conducted on an NMR tube scale for all HAA reactions were performed in J. Young NMR tubes (8" x 5 mm) sealed with screw-type Teflon caps or in a 2-dram vial sealed with a screw cap top with a Thermo Scientific™ PTFE/silicone disc septum with stir bar.

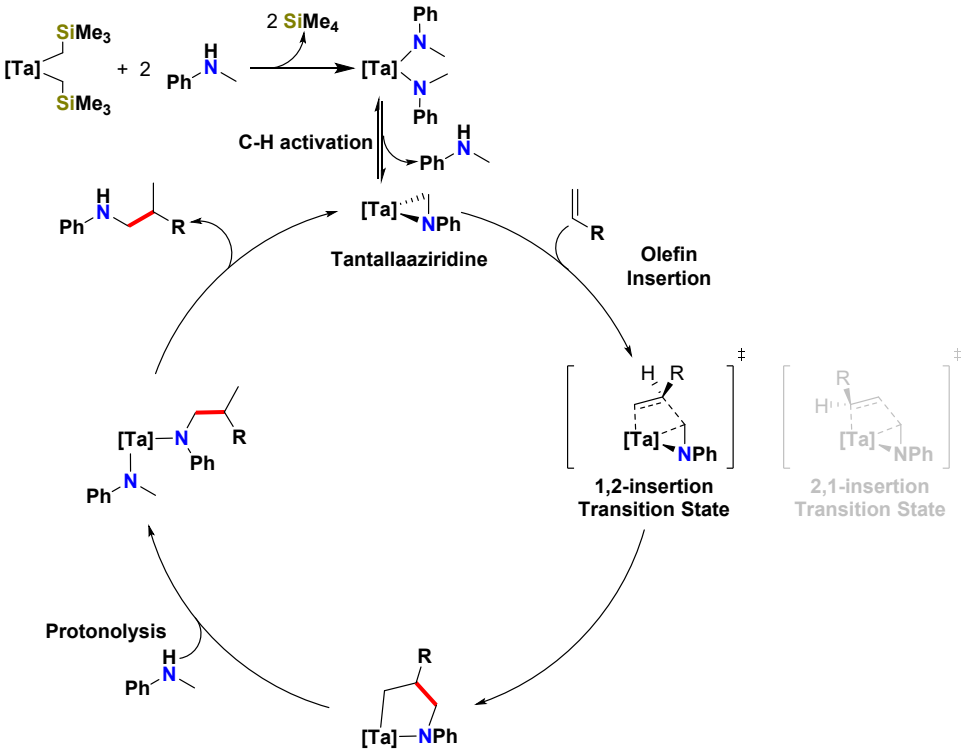
## Instrumentation

$^1$H experiments were taken on a Bruker Avance 300 MHZ and 400 MHz instruments. $^{13}$C and all 2D NMR experiments were recorded on the Bruker Avance 400 MHz. Chemical shifts (δ) are relative to the proteo solvent signal reported in parts per million (ppm). Coupling constants (*J*) are reported in Hz, and multiplicities are assigned by the following abbreviations: s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet, sx = sextet, tt = triplet of triplets and br =broad singlet. Assignment of all peaks are carried out through one-dimensional ($^1$H, $^{13}$C{$^1$H}) and two-dimensional ($^1$H-$^1$H COSY, HSQC ($^1$H, $^{13}$C{$^1$H}), HMBC ($^1$H, $^{13}$C{$^1$H})) spectra.

All Gas Chromatography-Mass Spectrometry (GC-MS) experiments were collected on an Agilent 7890B with an Agilent 5977 MS detector with a Chemical Ionization (CI) source using methane as reagent gas and helium as carrier gas. Agilent HP-5MS column ((5%-phenyl)-methylpolysiloxane phase), 30 m x 250 mm x 0.25 μm was employed. The inlet was heated to 250 °C at 6.86 psi and total flow 8.4 ml/min, 5:1 split ratio, and 4.5 mL/min split flow. The oven ramp started at 60 °C for 1-minute and a ramp of 25 °C/min until reaching 300 °C and held for 4-minutes at temperature.

High-Resolution Mass Spectrometry (HRMS) was carried out at the University of British Columbia Mass Spectrometry Centre on a Kratos MS-50 spectrometer. A positive electrospray ionization source is used with a Bruker MaXis Ultra-High Resolution tandem TOF mass spectrometer. Fragments are reported in mass to charge units (*m/z*).

## S2. Proposed Mechanism for Tantalum-Catalyzed Hydroaminoalkylation[3–5]



## S3. General Procedure for Hydroaminoalkylation

### General Procedure for Hydroaminoalkylation in J-Young:

Inside a nitrogen-filled glovebox, $Ta(CH_2SiMe_3)_3Cl_2$ (10.3 mg, 0.02 mmol) and ligand salt ($L^-Na^+$) (6.1 mg, 0.02 mmol) were weighed into a 1 dram vial. 0.3 mL of toluene-$d_8$ was then added by micropipette to the vial and the now yellow solution sat for 15 minutes. Amine (0.2 mmol) and alkene (0.2 mmol) were added sequentially by weight. After, 1,3,5-trimethoxybenzene (0.33 eq.) was then added as internal standard to the solution. The solution was then transferred to a J-Young NMR tube, and the vial was rinsed with 0.5 mL toluene-$d_8$ and transferred to J-Young NMR tube. The J-Young tube was then sealed with a screw-type Teflon cap and brought out to be heated in an oil bath. $^1$H NMR and GC-MS spectra were obtained after reaction completion. The products were then purified by silica gel column chromatography. The product was isolated by use of a rotary evaporator to remove solvent and dried under reduced pressure.

**NOTE**: Reactions set-up in J-Young are for the purpose of reaction monitoring.

### General procedure for hydroaminoalkylation reaction in a vial:

Inside a nitrogen-filled glovebox, $Ta(CH_2SiMe_3)_3Cl_2$ (10.3 mg, 0.02 mmol) and ligand salt ($L^-Na^+$) (6.1 mg, 0.02 mmol) were weighed into a 2 dram vial. 0.8 mL of toluene was directly added to the vial using a micropipette and the now yellow solution sat for 15 minutes. The amine (0.2 mmol) and alkene (0.2 mmol) were added sequentially to the vial. The vial was then sealed with a Thermo Scientific™ PTFE/silicone disc septum and screw thread cap, removed from the glovebox, and placed on a pre-heated aluminum block for heating. After, toluene was removed by rotary evaporator, and the product was then purified by silica gel column chromatography. The product was isolated by use of a rotary evaporator to remove solvent and dried under reduced pressure.

## S4. Non-catalytically reactive terpenes for hydroaminoalkylation

The following terpenes were screened in J-Young NMR tubes using the **General Procedure for Hydroaminoalkylation in J-Young**. Reactivity was evaluated by measuring $^1$H NMR before and after heating where 1,3,5,-trimethoxybenzene served as internal standard for yield measurement. Time points were taken after 24 hours of heating at each respective temperature to measure reaction progress by $^1$H NMR experiments. Conversion was determined by terpene consumption. No isolation attempts were made to elucidate any potential product structures from the reactions for camphene and squalene functionalization where some starting material conversion was observed.

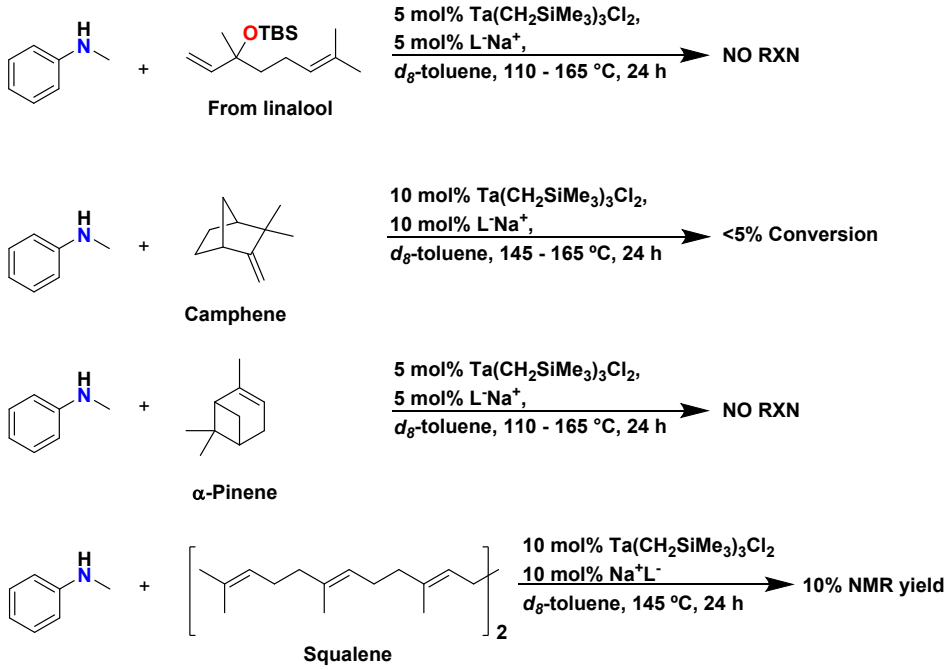
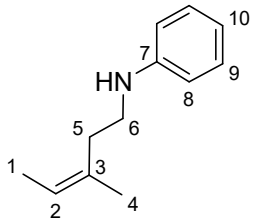



**Figure S1. Non-catalytically reactive terpenes in hydroaminoalkylation**

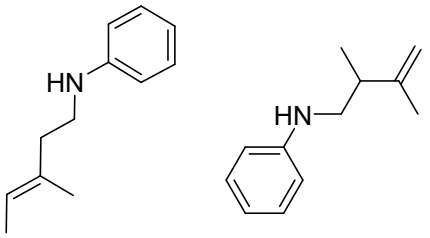
## S5. Synthesis and characterization of aminated terpenes

### Synthesis of aminated isoprene (1)




Synthesized following general procedure for hydroaminoalkylation: $Ta(CH_2SiMe_3)_3Cl_2$ (10.3 mg, 0.02 mmol), $L^-Na^+$ (6.1 mg, 0.02 mmol), *N*-methylaniline (21.4 mg, 0.2 mmol), isoprene (54.5 mg, 0.8 mmol), and toluene (0.8 mL). Reaction was heated for 24 hours at 130 °C. Silica gel column eluent: hexanes → 9:1 hexanes:ethyl acetate. Clear and colourless oil. 52% $^1$H NMR Yield. $T_R$ 6.63. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): 7.19 (t, 2H, $J_{H\text{-}H}$ = 8.1 Hz, CH of **9**), 6.71 (t, 1H, $J_{H\text{-}H}$ = 7.3 Hz, CH of **10**), 6.63 (d, 2H, $J_{H\text{-}H}$ = 8.8 Hz, CH of **8**), 5.40 (q, 1H, $J_{H\text{-}H}$ = 6.4 Hz, CH of **2**), 3.62 (br s, 1H, N*H*), 3.20 (t, 2H, $J_{H\text{-}H}$ = 7.1 Hz, $CH_2$ of **6**), 2.39 (t, 2H, $J_{H\text{-}H}$ = 7.2 Hz, $CH_2$ of **5**), 1.74 (t, 3H, $J_{H\text{-}H}$ = 1.4 Hz, $CH_3$ of **4**), 1.62 (d, 3H, $J_{H\text{-}H}$ = 7.2 Hz, $CH_3$ of **1**) ppm. $^{13}$C{$^1$H} NMR spectrum (100 MHz, $CDCl_3$, 298 K): 148.5 (C, **7**), 133.0 (C, **3**), 129.4 (CH, **9**), 121.8 (CH, **2**), 117.4 (CH, **10**), 113.0 (CH, **8**), 41.6 ($CH_2$, **6**), 31.2 ($CH_2$, **5**), 23.3 ($CH_3$, **4**), 13.6 ($CH_3$, **1**) ppm. HRMS (ESI): *m/z* calculated for $C_{12}H_{17}N$ [$M^+$]: 175.1362. Found: 175.1361.

**Note:** The major product could not be completely separated from the minor isomers, thus presented NMR spectra are those of the enriched fractions from column. The following structures are proposed minor products:



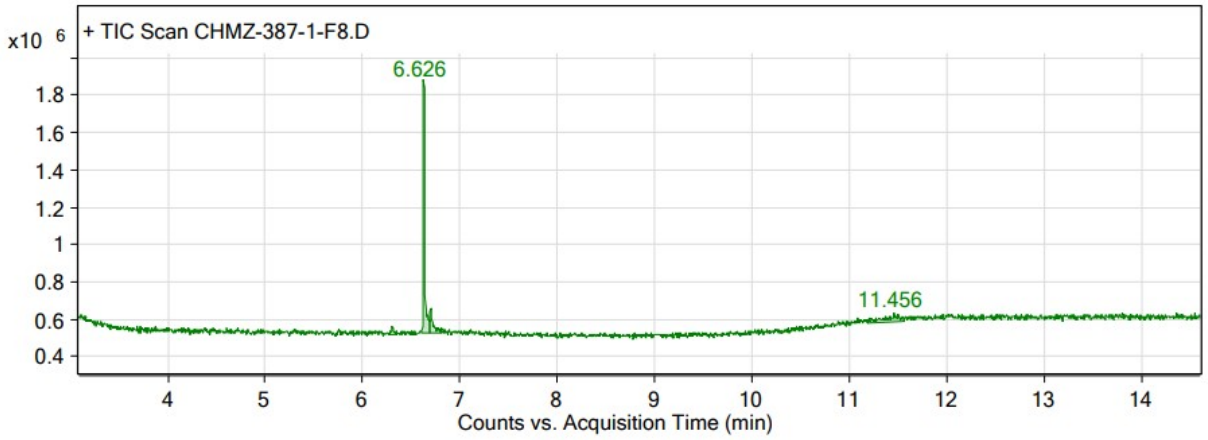




**Figure S2. GC-MS chromatogram of 1 after silica gel column chromatography. $T_R$ = 6.63**

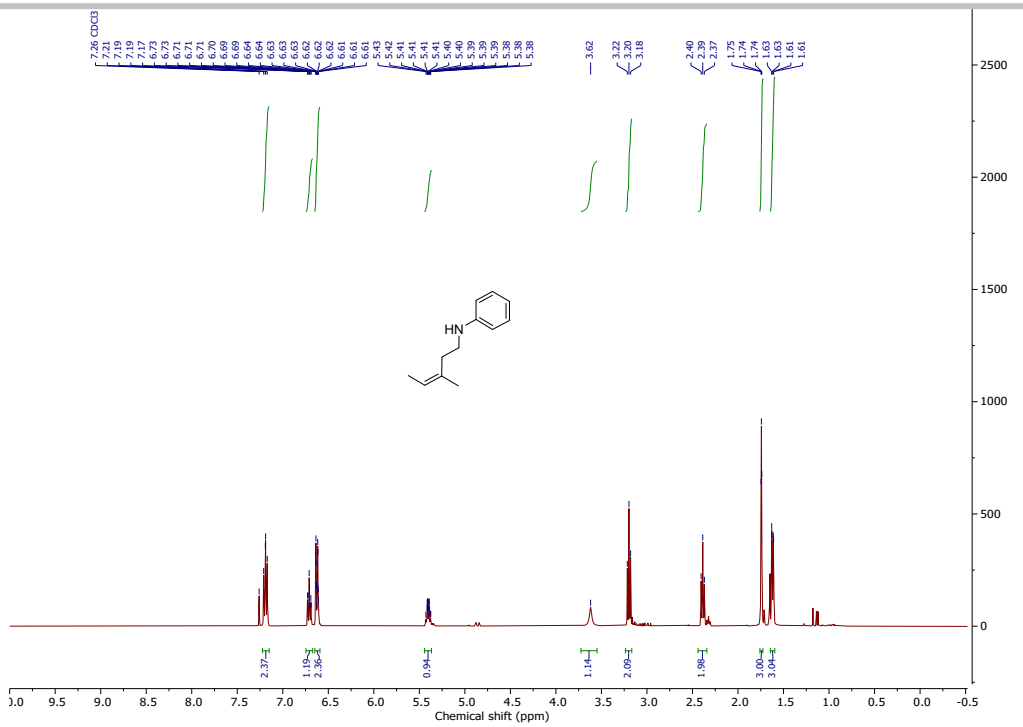



**Figure S3. $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1**

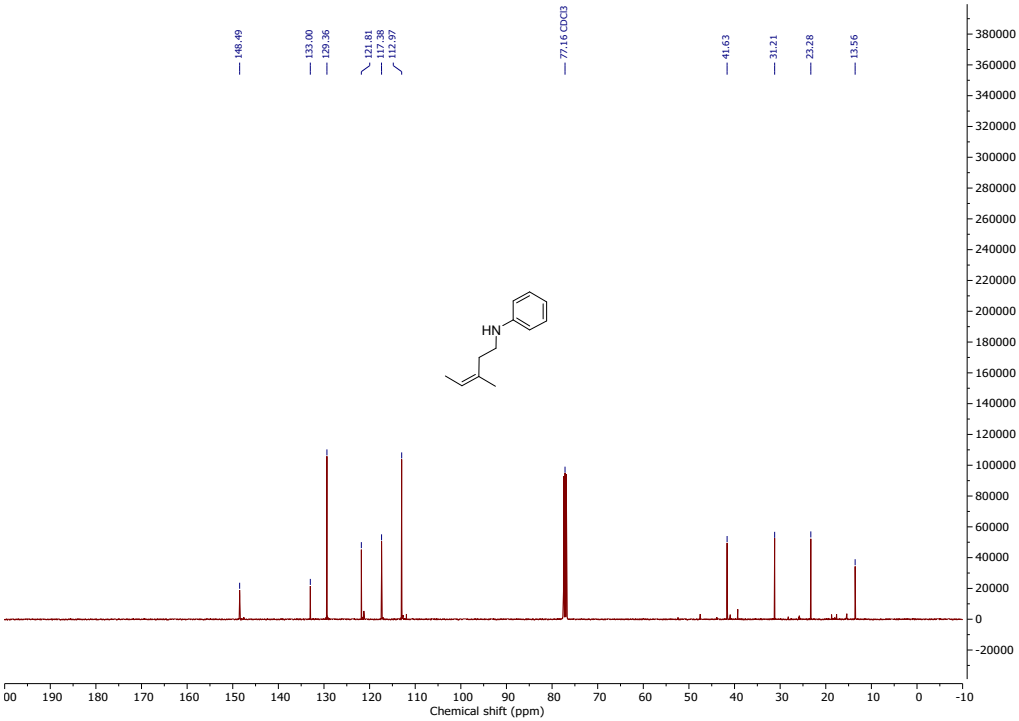



**Figure S4. $^{13}$C{$^{1}$H} NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 1**

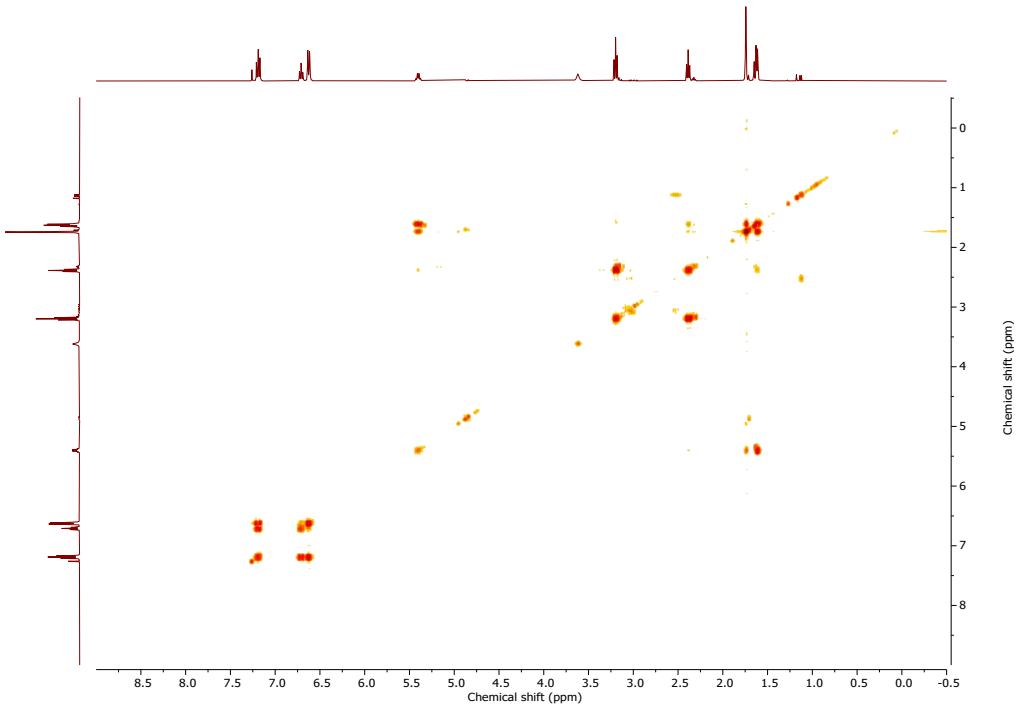



**Figure S5. $^{1}$H-$^{1}$H COSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1**

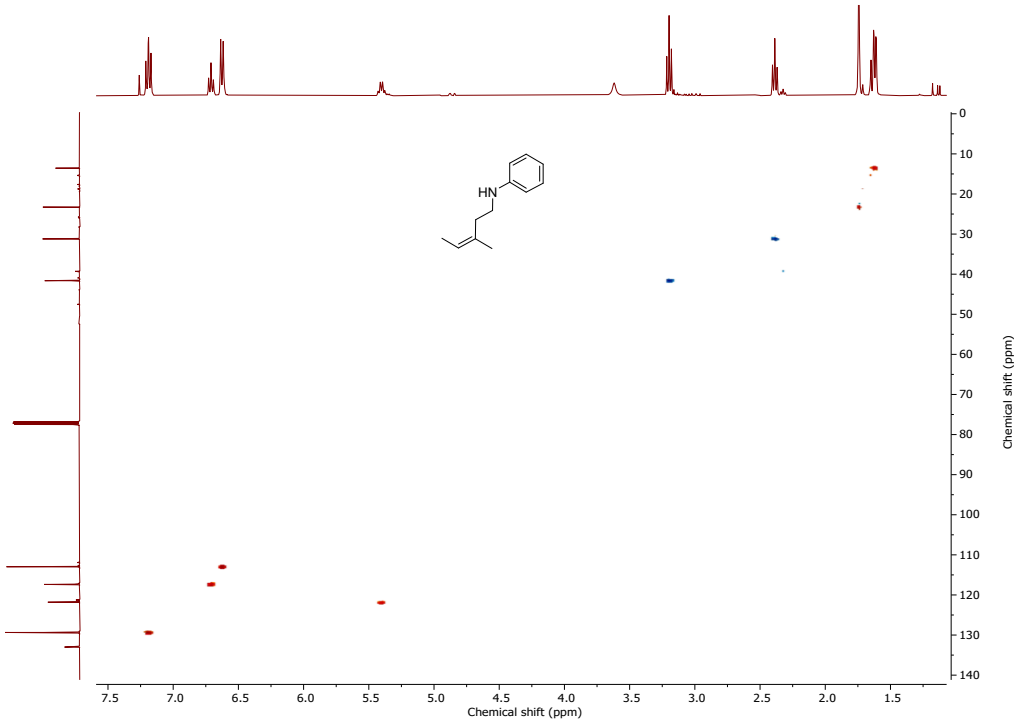



**Figure S6. $^{1}$H—$^{13}$C{$^{1}$H} HSQC NMR spectrum (400 MHz $^{1}$H, 100 MHz $^{13}$C{$^{1}$H}, $CDCl_3$, 298 K) of 1**

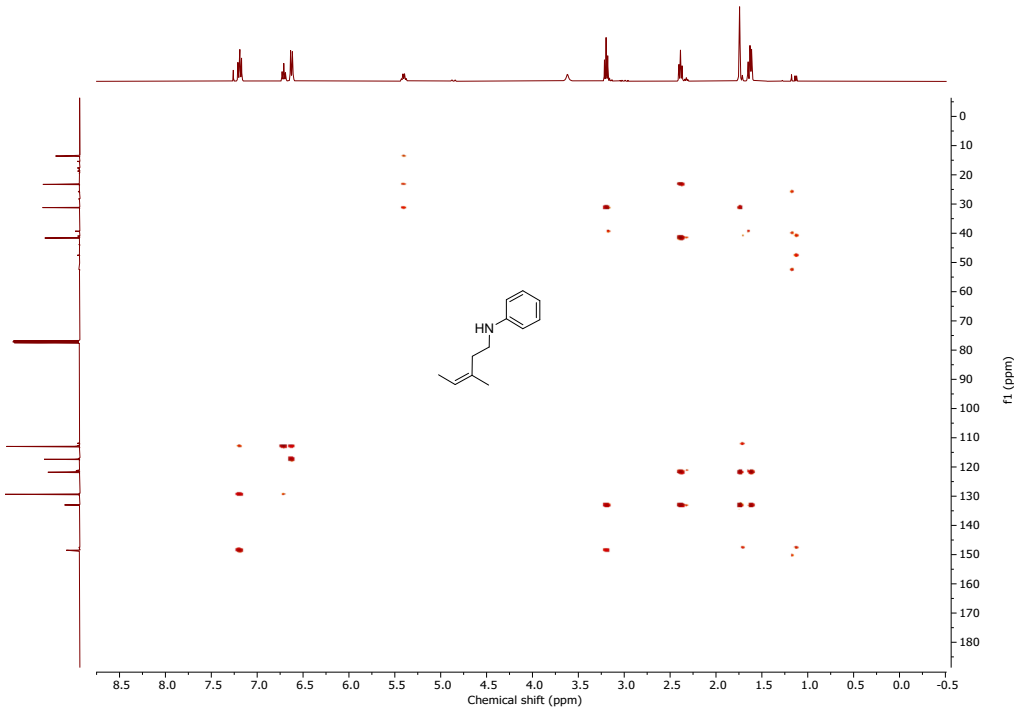



**Figure S7. $^{1}H$—$^{13}C\{^{1}H\}$ HMBC NMR spectrum (400 MHz $^{1}H$, 100 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of 1**

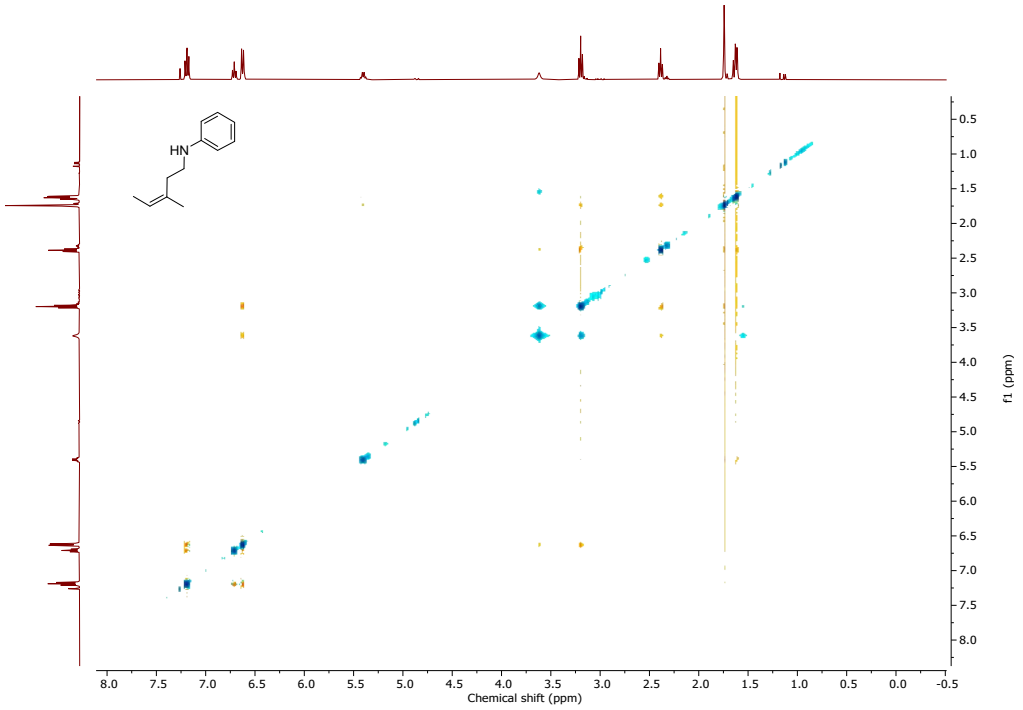
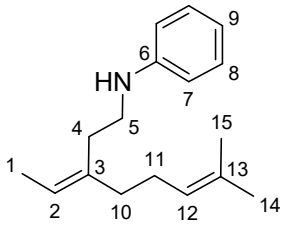


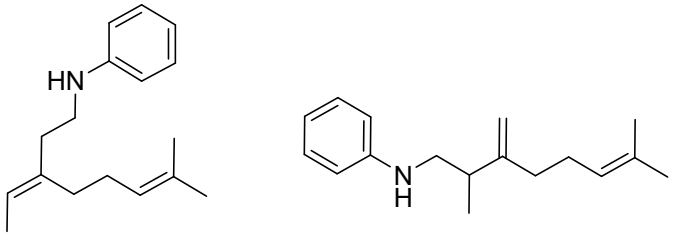

**Figure S8. $^{1}H$—$^{1}H$ NOSY NMR spectrum (400 MHz $^{1}H$, $CDCl_3$, 298 K) of 1**

## Synthesis of aminated β-myrcene (2)




Synthesized following general procedure for hydroaminoalkylation: $Ta(CH_2SiMe_3)_3Cl_2$ (10.3 mg, 0.02 mmol), $L^-Na^+$ (6.1 mg, 0.02 mmol), *N*-methylaniline (21.4 mg, 0.2 mmol), β-myrcene (27.2 mg, 0.2 mmol), and toluene (0.8 mL). Reaction was heated for 24 hours at 130 °C. Silica gel column eluent: hexanes → 85:10:5 hexanes:ethyl acetate:triethylamine. Yellow oil. 50% $^1$H NMR Yield. $T_R$ 8.78. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): 7.19 (t, 2H, $J_{H\text{-}H}$ = 7.9 Hz, CH of **8**), 6.71 (t, 1H, $J_{H\text{-}H}$ = 7.4 Hz, CH of **9**), 6.62 (d, 2H, $J_{H\text{-}H}$ = 7.7 Hz, CH of **7**), 5.41 (q, 1H, $J_{H\text{-}H}$ = 6.7 Hz, CH of **2**), 5.08-5.16 (m, 1H, CH of **12**), 3.63 (br s, 1H, N*H*), 3.18 (t, 2H, $J_{H\text{-}H}$ = 7.4 Hz, $CH_2$ of **5**), 2.39 (t, 2H, $J_{H\text{-}H}$ = 7.3 Hz, $CH_2$ of **4**), 2.00-2.00 (m, 4H, $CH_2$ of **10** & **11**), 1.70 (s, 3H, $CH_3$ of **14**), 1.64 (d, 3H, $J_{H\text{-}H}$ = 6.9 Hz, $CH_3$ of **1**), 1.62 (s, 3H, $CH_3$ of **15**) ppm. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K): 148.5 (C, **6**), 136.9 (C, **3**), 131.8 (C, **13**), 129.4 (CH, **8**), 124.2 (CH, **12**), 121.4 (CH, **2**), 117.4 (CH, **9**), 113.0 (CH, **7**), 42.0 ($CH_3$, **5**), 36.9 ($CH_2$, **10**), 29.7 ($CH_2$, **4**), 27.1 ($CH_2$, **11**), 25.8 ($CH_3$, **14**), 17.9 ($CH_3$, **15**), 13.6 ($CH_3$, **1**) ppm. HRMS (ESI): *m/z* calculated for $C_{18}H_{25}N$ [$M^+$]: 243.1991. Found: 243.1987.

**Note:** The major product could not be completely separated from the minor isomers, thus presented NMR spectra are those of the enriched fractions from column. The following structures are the proposed minor products:



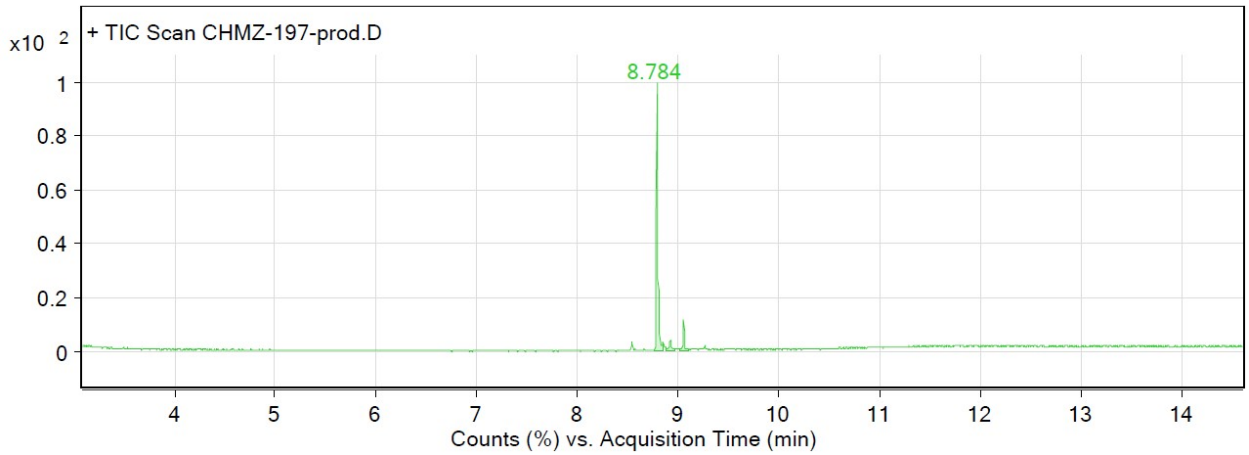




**Figure S9. GC-MS chromatogram of 2 after silica gel column chromatography. $T_R$ = 8.78.**

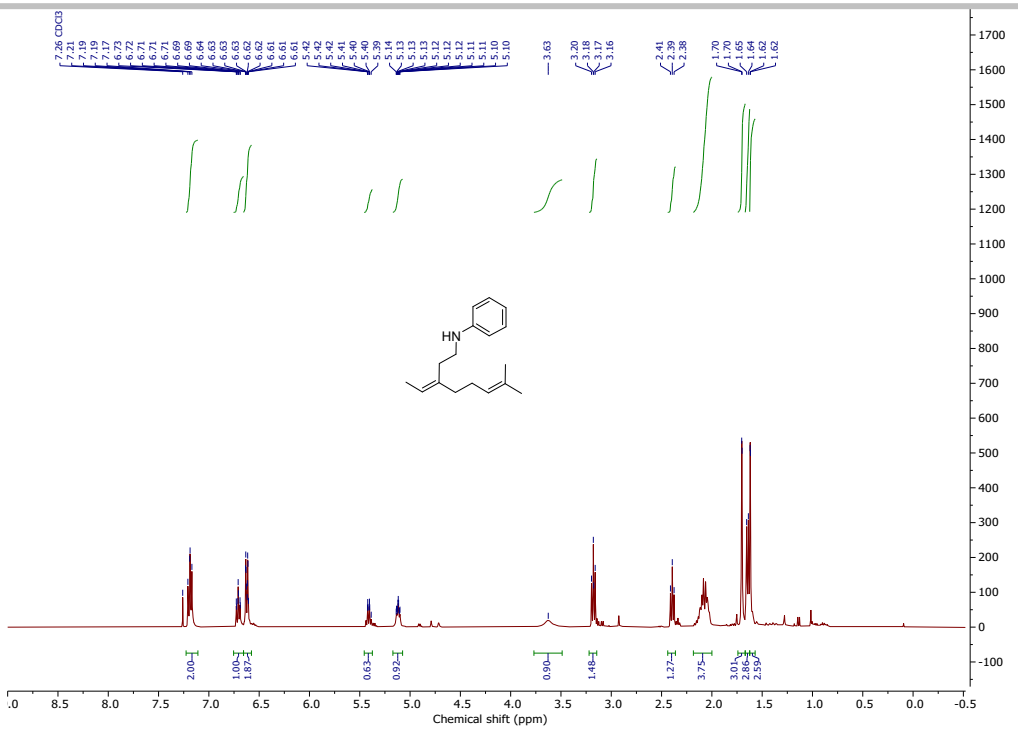



**Figure S10. $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2**

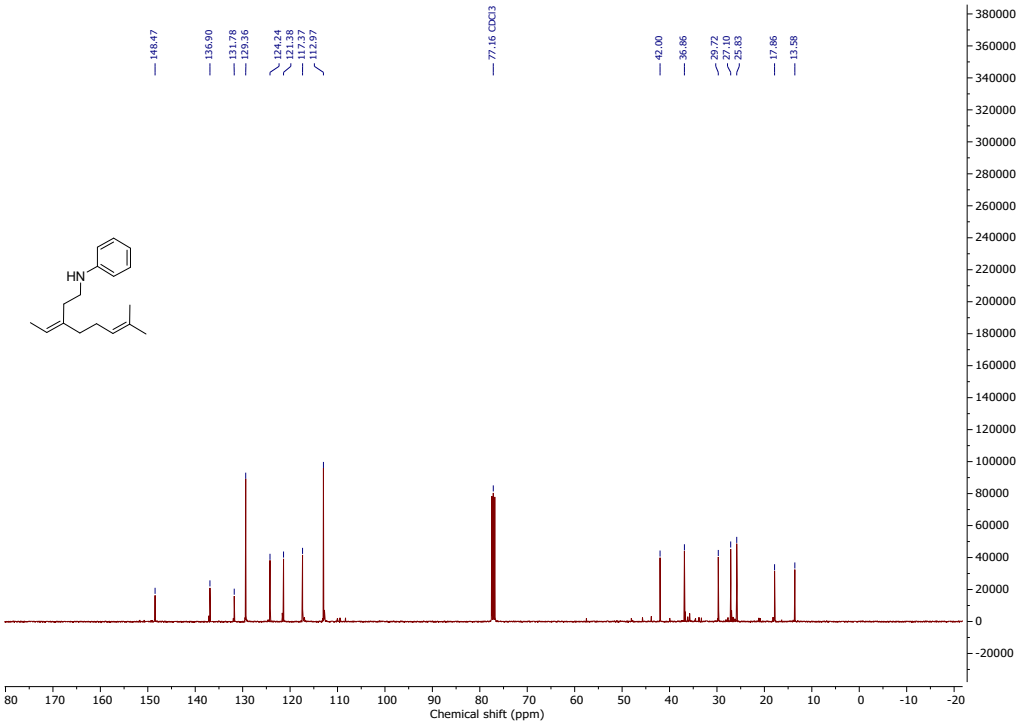



**Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 2**

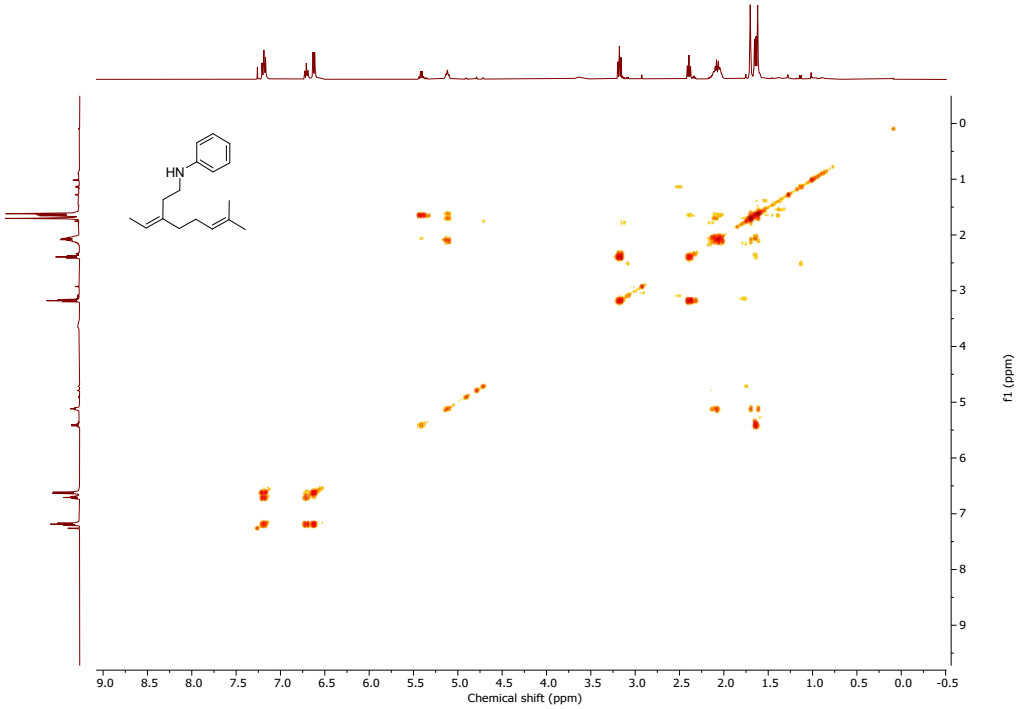



**Figure S12. $^{1}$H—$^{1}$H COSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2**

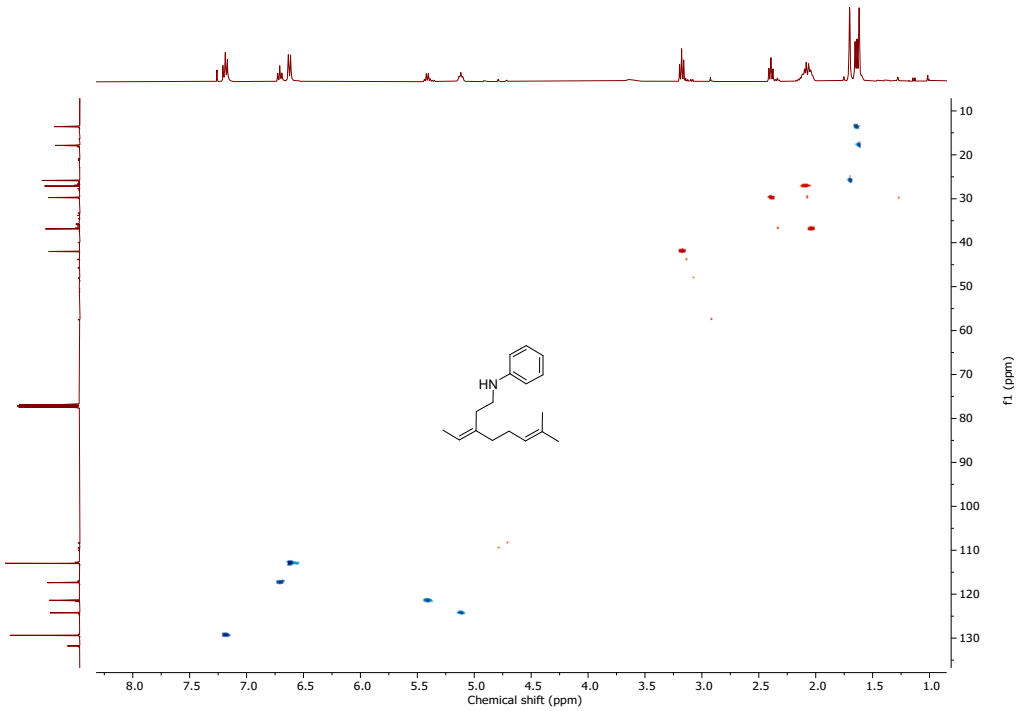



**Figure S13. $^{1}$H—$^{13}$C{$^{1}$H} HSQC NMR spectrum (400 MHz $^{1}$H, 100 MHz $^{13}$C{$^{1}$H}, $CDCl_3$, 298 K) of 2**

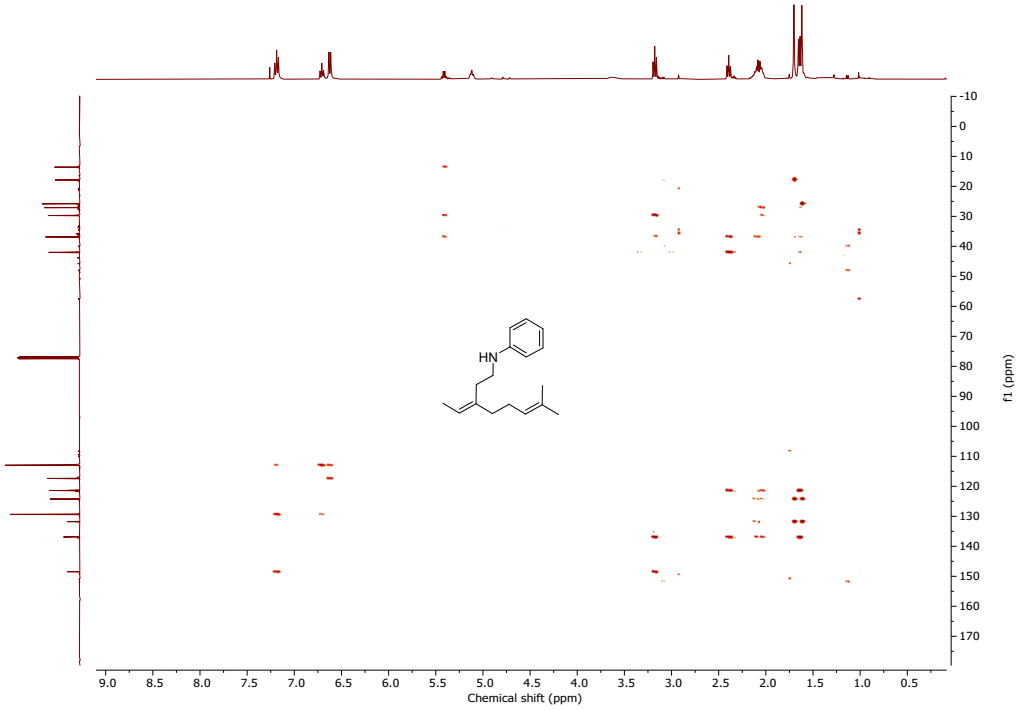



**Figure S14. $^{1}H$—$^{13}C\{^{1}H\}$ HMBC NMR spectrum (400 MHz $^{1}H$, 100 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of 2**

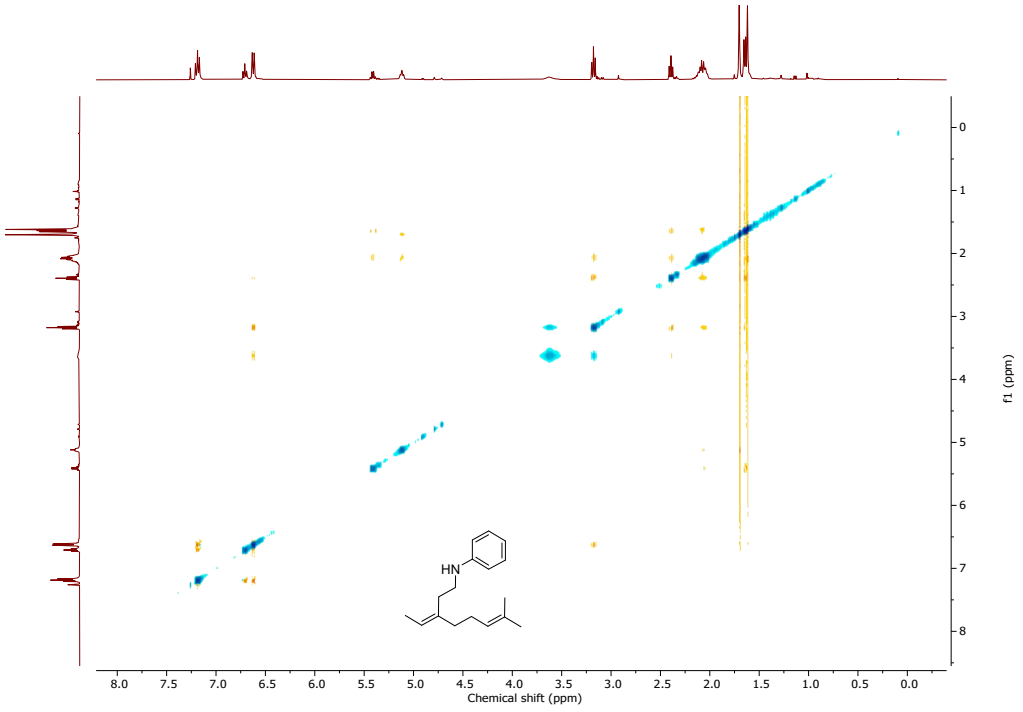
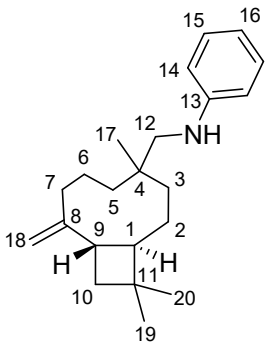



**Figure S15. $^{1}H$—$^{1}H$ NOSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2**

## Synthesis of 3 & 4

## For a detailed discussion on characterization and quantification from turpentine refer to section S7

## Synthesis of 5




Synthesized following general procedure for hydroaminoalkylation: $Ta(CH_2SiMe_3)_3Cl_2$ (10.3 mg, 0.02 mmol), $L^-Na^+$ (6.1 mg, 0.02 mmol), *N*-methylaniline (21.4 mg, 0.2 mmol), β-caryophyllene (40.9 mg, 0.2 mmol), and toluene (0.8 mL). The reaction was heated for 24 hours at 130 °C. Silica gel column chromatography: hexanes → 85:10:5 hexanes:ethyl acetate:triethylamine. clear pale-yellow oil. 76% $^1$H NMR Yield. $T_R$ 10.61. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): 7.18 (t, 2H, $J_{H-H}$ = 7.8 Hz, CH of **15**), 6.69 (t, 1H, $J_{H-H}$ = 7.1 Hz, CH of **16**), 6.63 (d, 2H, $J_{H-H}$ = 8.0 Hz, CH of **14**), 4.75-4.85 (m, 2H, =$CH_2$ of **18**), 3.64 (br s, 1H, N*H*), 2.87-2.90 (m, 2H, $CH_2$ of **12**), 2.61 (q, 3H, $J_{H-H}$ = 8.7 Hz, CH, **9**), 2.29-2.38 (m, 1H, ½ $CH_2$ of **7**), 2.07-2.16 (m, 1H, ½ $CH_2$ of **7**), 1.38-1.76 (m, 11H, CH of **1**, $CH_2$ of **2**, **3**, **5**, **6**, & **10**), 1.09 (s, 6H, $CH_3$ of **19** or **20**), 0.95 (s, 3H, $CH_3$ of **17**) ppm. $^{13}$C{$^1$H} NMR spectrum (100 MHz, $CDCl_3$, 298 K): 154.6 (C, **8**), 149.1 (C, **13**), 129.3 (CH, **15**), 117.1 (CH, **16**), 112.9 (CH, **14**), 109.6 ($CH_2$, **18**), 55.8 (CH, **1**) 54.0 ($CH_2$, **12**) 43.1 (CH, **9**), 37.9 ($CH_2$, **10**), 37.3 (C, **4** or **11**), 37.2 ($CH_2$, **3**), 36.9 ($CH_2$, **7**), 33.7 (C, **4** or **11**), 33.1 ($CH_2$, **5**), 30.1 ($CH_3$, **19** or **20**), 25.0 ($CH_3$, **17**), 24.5 ($CH_2$, **2** or **6**), 23.8 ($CH_2$, **2** or **6**), 22.5 ($CH_3$, **19** or **20**) ppm. HRMS (ESI): *m/z* calculated for $C_{22}H_{33}N$ [$M^+$]: 311.2613. Found: 311.2616.

**NOTE**: NMR spectra for **5** contain ~5% of an unknown impurity. The assignment is tentative as some of the correlations overlap in HMBC due to lack of resolution between $^{13}$C{$^1$H} signals with <0.5 ppm difference in the $^{13}$C{$^1$H} NMR spectrum.

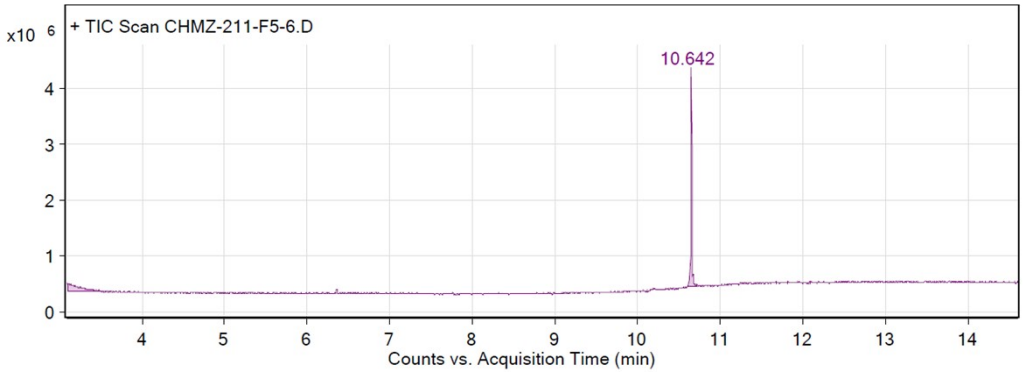



**Figure S16. GC-MS chromatogram of 5 after silica gel column chromatography. $T_R$ = 10.64.**

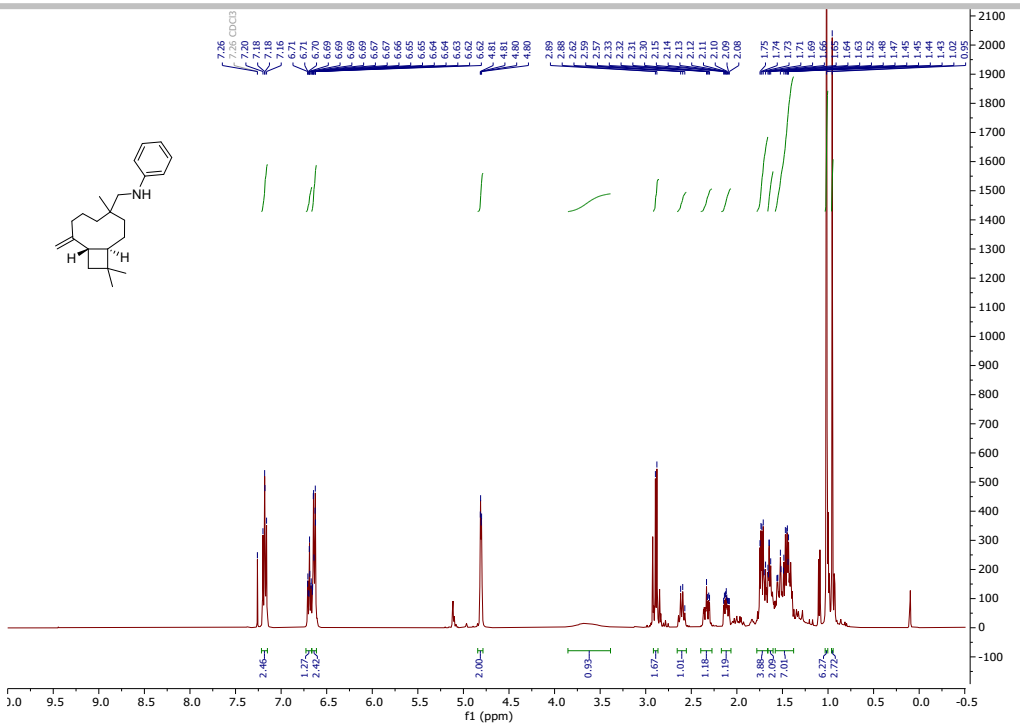



**Figure S17. $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 6**

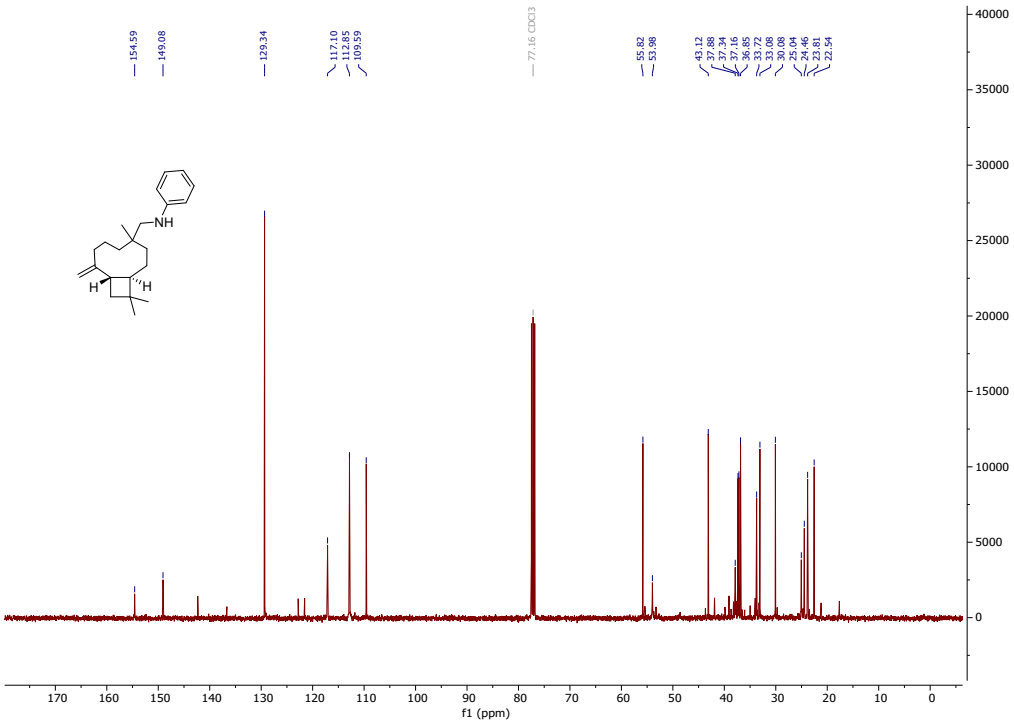



**Figure S18. $^{13}$C{$^{1}$H} NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 5**

**Key 2D NMR diagnostic correlations which allowed for structural assignment:**

Multiplicity-edited Heteronuclear Single Quantum Coherence (**HSQC**) spectrum supported the presence of a newly formed quaternary carbon centre. Further, $^{1}H—^{13}C\{^{1}H\}$ Heteronuclear Multi-Bond Coherence (**HMBC**) from this new quaternary carbon centre did not have any $^{3}J$ correlations to a $^{1}H$ resonance at 2.61 ppm corresponding to **9**. We did however find a diagnostic $^{3}J$ correlation between the 1H resonance of **9** with **18,** the alkenyl $=CH_2$ $^{13}C\{^{1}H\}$ resonance at 109.6 ppm. These key correlations along with other HSQC and HMBC correlations, allowed for structural elucidation alongside the X-ray structure.

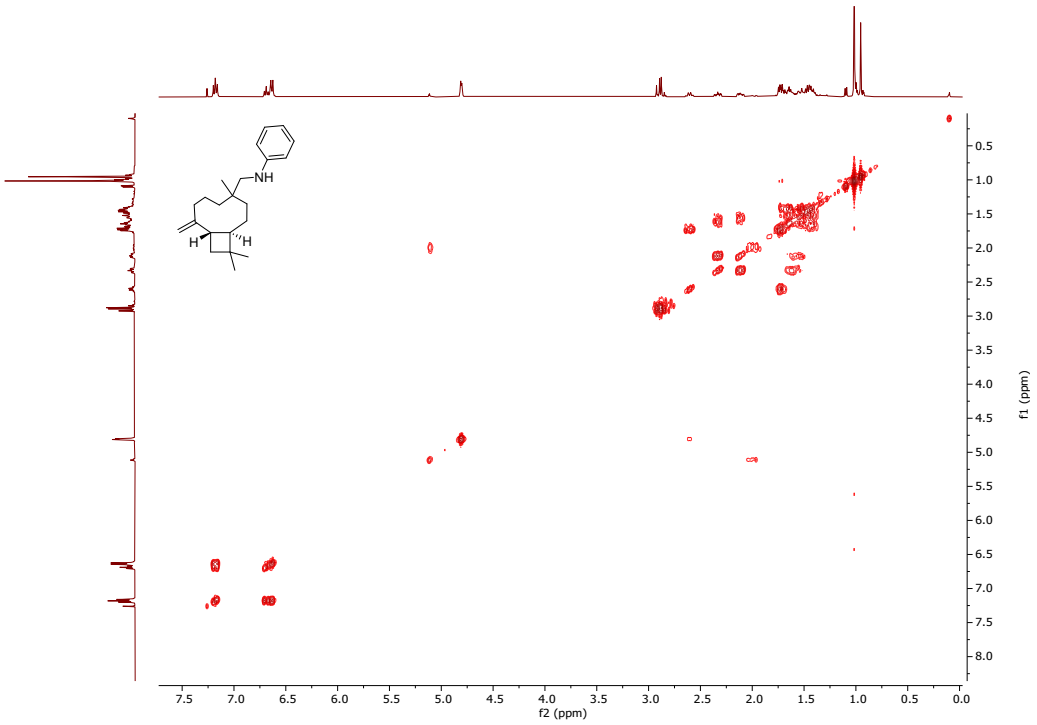



**Figure S19. $^{1}H—^{1}H$ COSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 5**

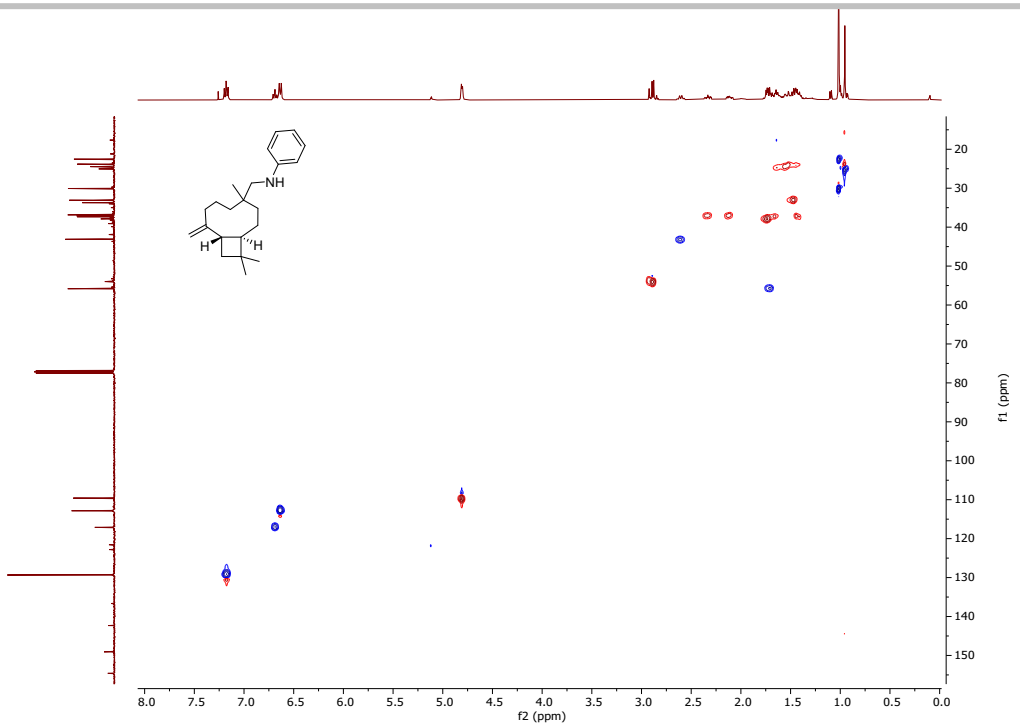



**Figure S20. $^{1}H$—$^{13}C\{^{1}H\}$ HSQC NMR spectrum (400 MHz $^{1}H$, 100 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of 5**

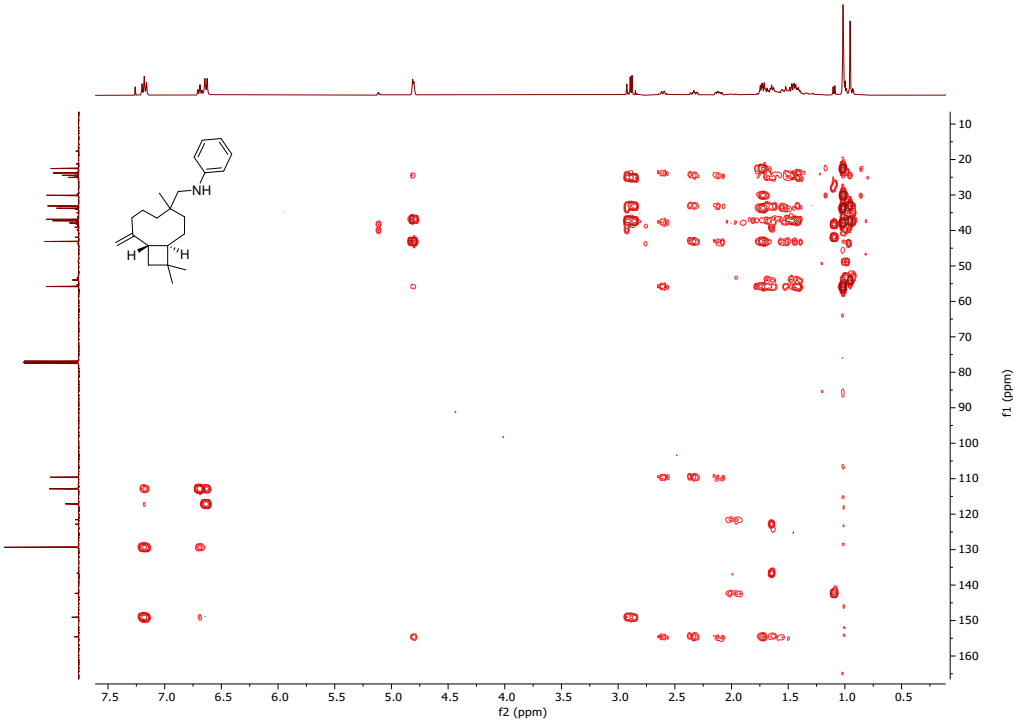
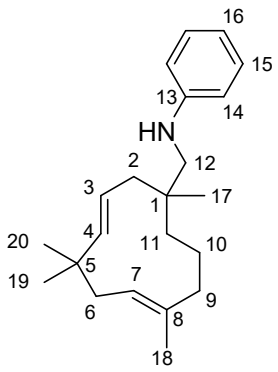



**Figure S21. $^{1}H$—$^{13}C\{^{1}H\}$ HMBC NMR spectrum (400 MHz $^{1}H$, 100 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of 5**

## Synthesis of 6




Synthesized following general procedure for hydroaminoalkylation: $Ta(CH_2SiMe_3)_3Cl_2$ (10.3 mg, 0.02 mmol), $L^-Na^+$ (6.1 mg, 0.02 mmol), *N*-methylaniline (21.4 mg, 0.2 mmol), humulene (40.9 mg, 0.2 mmol), and toluene (0.8 mL). Reaction was heated for 24 hours at 130 °C. Silica gel column chromatography: hexanes → 85:10:5 hexanes:ethyl acetate:triethylamine. Pale yellow oil. 77% $^1$H NMR Yield. $T_R$ 10.61. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): 7.18 (t, 2H, $J_{H\text{-}H}$ = 7.9 Hz, CH of **15**), 6.69 (t, 1H, $J_{H\text{-}H}$ = 7.3 Hz, CH of **16**), 6.64 (d, 2H, $J_{H\text{-}H}$ = 8.2 Hz, CH of **14**), 5.05-5.13 (m, 3H, CH of **3**, **4**, & **7**), 3.61 (br s, 1H, N*H*), 2.92 (s, 2H, $CH_2$ of **12**), 1.90-2.09 (m, 4H, $CH_2$ of **2** & **6**), 1.76-1.88 (m, 2H, $CH_2$ of **9**), 1.64 (d, 3H, $J_{H\text{-}H}$ = 1.1 Hz, $CH_3$ **18**), 1.31-1.38 (m, 2H, $CH_2$ of **11**), 1.14-1.30 (m, 2H, $CH_2$ of **10**), 1.10 (s, 3H, $CH_3$ of **19** or **20**), 1.09 (s, 3H, $CH_3$ of **19** or **20**), 0.99 (s, 3H, $CH_3$ of **17**) ppm. $^{13}$C{$^1$H} NMR spectrum (100 MHz, $CDCl_3$, 298 K): 149.2 (C, **6**), 142.3 (CH, **4**), 136.7 (C, **8**), 129.4 (CH, **15**), 122.8 (CH, **7**), 121.6 (CH, **3**), 117.1 (CH, **16**), 112.8 (CH, **14**), 53.2 ($CH_2$, **12**), 41.9 (CH, **6**), 39.9 ($CH_2$, **2**), 39.1 ($CH_2$, **9**), 38.2 (C, **5**), 37.7 (C, **1**), 34.0 ($CH_2$, **11**), 28.1 ($CH_3$, **19** or **20**), 26.9 ($CH_3$, **19** or **20**), 24.5 ($CH_3$, **17**), 21.2 ($CH_2$, **10**), 17.7 ($CH_3$, **8**) ppm. HRMS (ESI): *m/z* calculated for $C_{22}H_{33}N$ [$M^+$]: 311.2613. Found: 311.2614.

**Note:** if there are impurities present after column chromatography, heating product under reduced pressure with heat 135 °C for 4 hours achieves **6** in high purity.

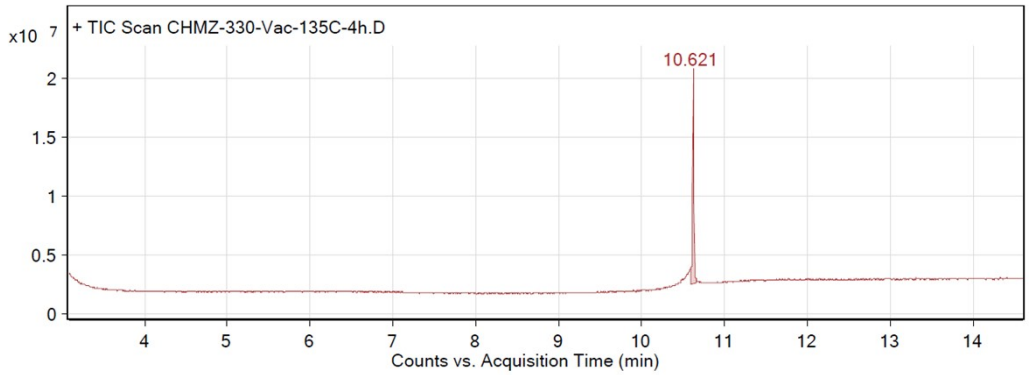



**Figure S22. GC-MS chromatogram of 5 after silica gel column chromatography. $T_R$ = 10.62.**

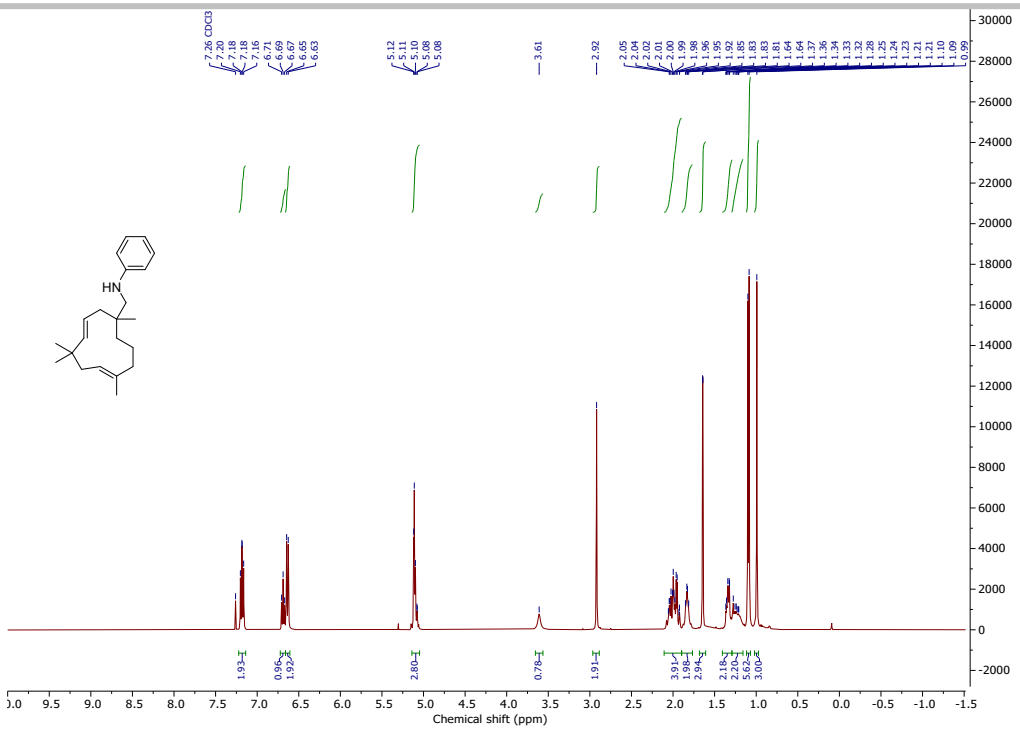



**Figure S23. $^{1}H$ NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 6**

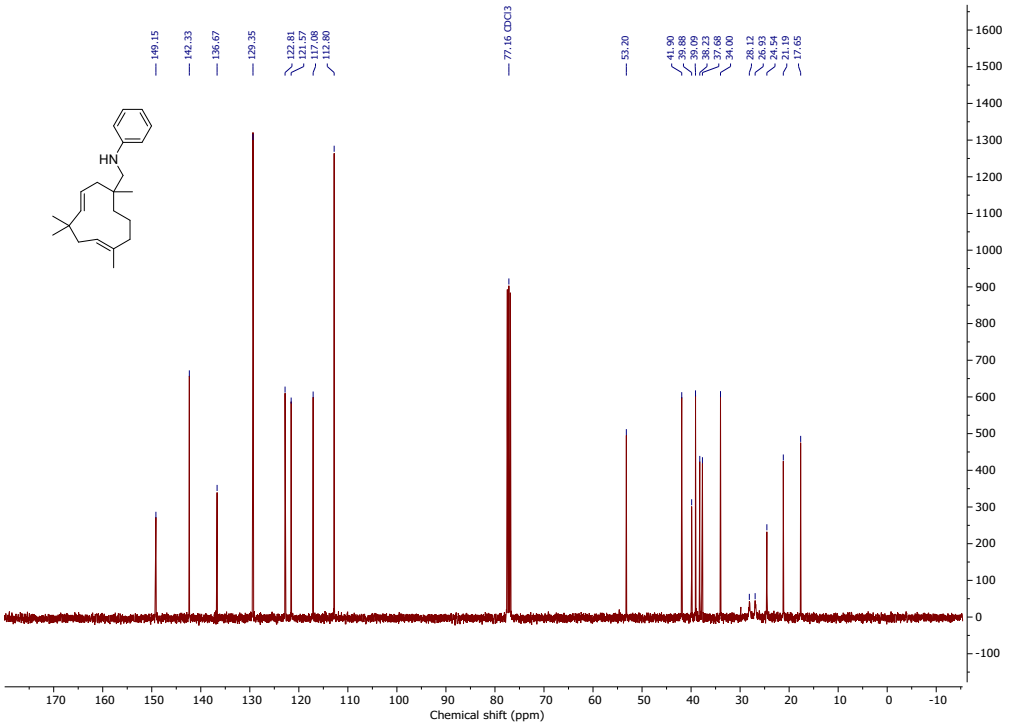



**Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 6**

**Key 2D NMR diagnostic correlations which allowed for structural assignment:**

A $^{3}J$ correlation, in the HMBC spectrum, between a $^{13}C\{^{1}H\}$ resonance at 39.9 ppm, corresponding to **2** with a $^{1}H$ resonance at 2.92 ppm which corresponds to **12**, the α $CH_2$ adjacent to nitrogen. This correlation is only possible by **C1—C2** reactivity from humulene. Further **C3—C4** and **C7—C8** remains untransformed as suggested by multiplicity edited HSQC as their chemical shifts are quite similar to the $^{13}C\{^{1}H\}$ chemical shifts in humulene for the same alkene carbons.[6]

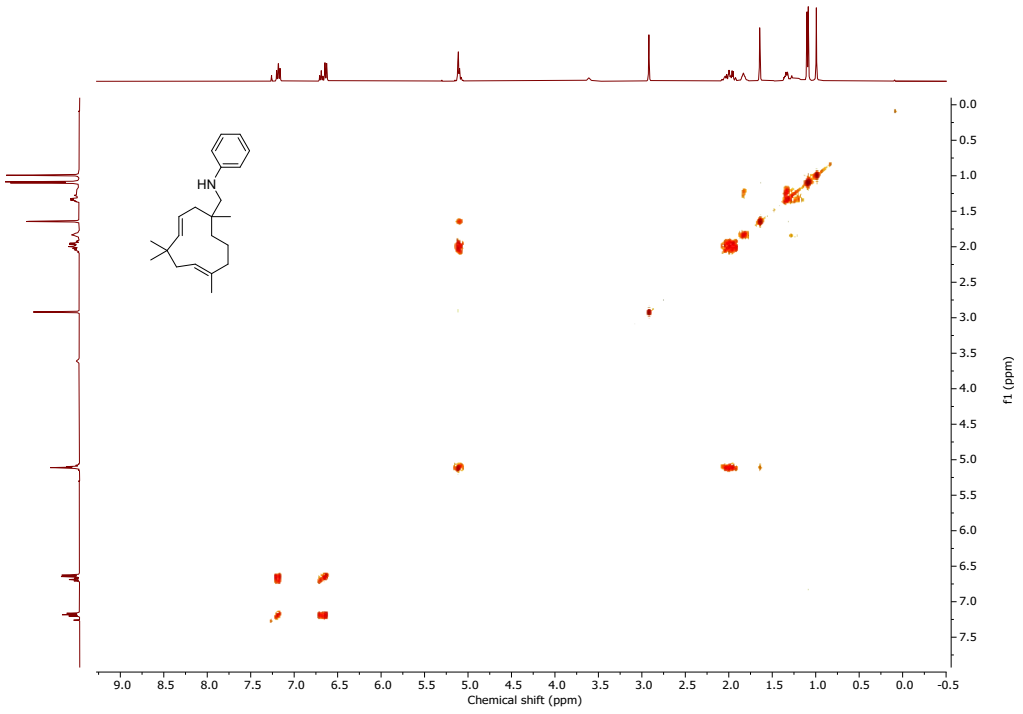



**Figure S25. $^{1}H—^{1}H$ COSY NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 6**

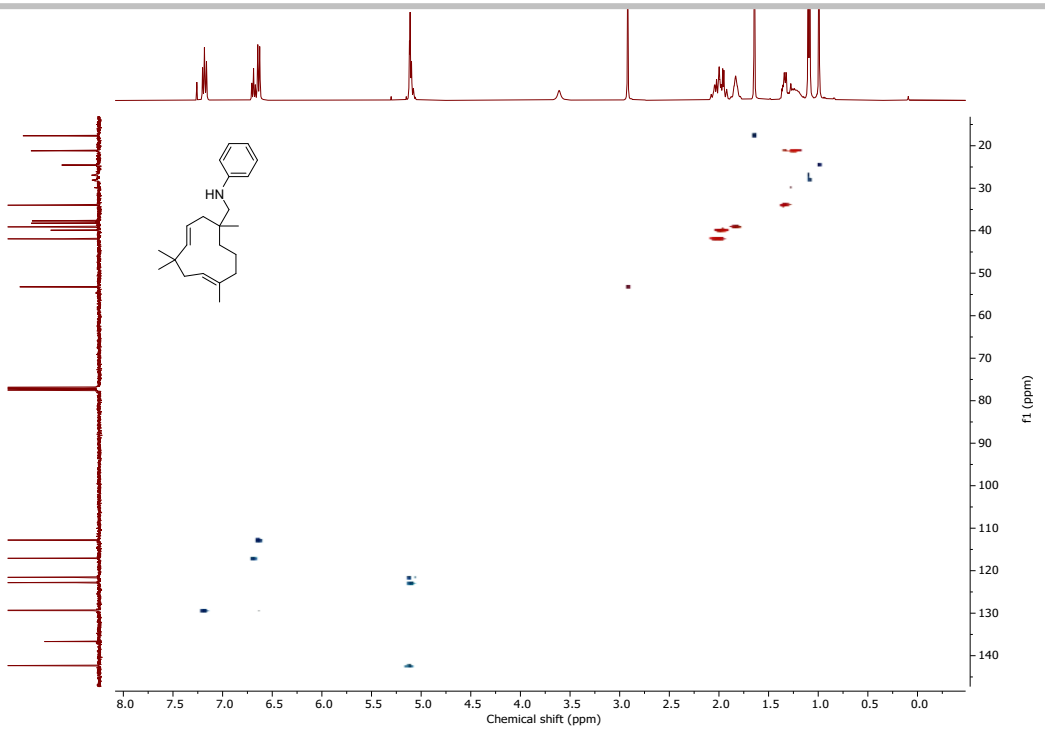



**Figure S26. $^{1}H$—$^{13}C\{^{1}H\}$ HSQC NMR spectrum (400 MHz $^{1}H$, 100 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of 6**

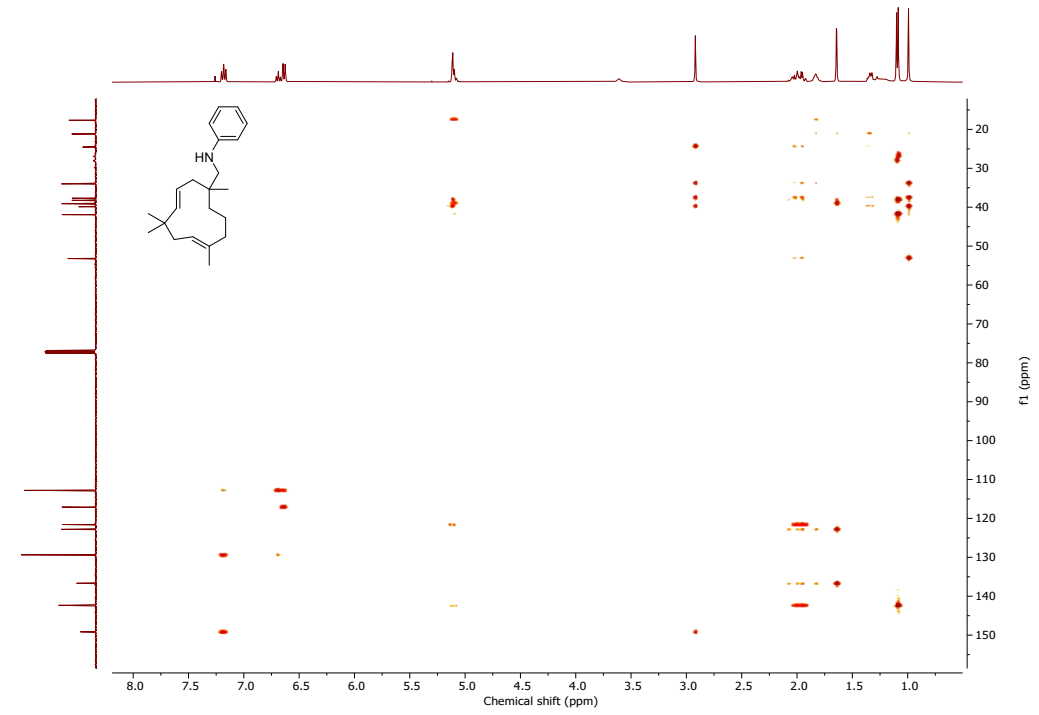



**Figure S27. $^{1}H$—$^{13}C\{^{1}H\}$ HMBC NMR spectrum (400 MHz $^{1}H$, 100 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of 6**

## S6. Turpentine drying and distillation protocol for hydroaminoalkylation

**Note:** Our sample of turpentine was provided by Holmen AB. Turpentine recovery proceeded by steam recovery.

**Equipment required:**

- 2 x 50 mL b14 Schlenk tube
- 1 x 50 mL Schlenk tube with Kontes® valve
- 1 x b14 vacuum distillation bridge
- 1 x b14 Ground glass stopper
- 1 x b14 Cap style glass stopper for outer joints
- 1 x PTFE Kontes® valve screw thread stopper
- 2 x Glass keys for Schlenk tubes
- 2 x Rubber septum
- 1 x metal cannula
- 1 x PTFE-coated magnetic stir bar
- Silicon grease

Please also refer to Borys' *An Illustrated Guide to Schlenk Line Techniques* which covers Schlenk line glassware, Schlenk line usage, and dynamic vacuum distillation.[7]

All glassware, metal cannula, and stir bar used were dried overnight in an oven set to 160 °C prior to use on $N_2$ gas Schlenk line. A Schlenk line with at least $1.0 \times 10^{-2}$ Torr ($1.0 \times 10^{-3}$ Torr is best) pressure reading is required to properly set up and use a Schlenk line and Schlenk glassware for air free techniques so as to not condense oxygen. The use of rubber bands and copper wire helped to secure the greased joints of the assembled apparatus.

### 1) Drying of turpentine with $CaH_2$:

A 50 mL Schlenk tube with stir bar was sealed with a glass stopper and glass key, the entire vessel was then evacuated on a Schlenk line. Afterwards, the vessel was cycled with 3x with $N_2$ and vacuum. The glass stopper was then opened under a stream of $N_2$ gas, and 10 mL of turpentine was transferred by a Pasteur pipette. $CaH_2$ (granular grade) was then carefully added to the Schlenk tube by a metal spatula, a ~3:1 turpentine:$CaH_2$ ratio was used for drying. **Caution:** this process can produce an exotherm and hydrogen gas if substrate is sufficiently wet. The vessel was then resealed with the glass stopper and allowed to stir overnight under $N_2$.

### 2) Dynamic vacuum distillation:

A vacuum distillation bridge, 50 mL Schlenk tube (with glass key), and glass cap were assembled then connected to the Schlenk line. The apparatus was then evacuated and refilled with $N_2$ gas 3x, and after, the glass cap was removed under a positive pressure of $N_2$. After, the glass stopper of the Schlenk tube containing $CaH_2$ and turpentine was also removed under a positive pressure of $N_2$ and now attached to the apparatus containing the vacuum distillation bridge. After assembly,

the glass key was then closed at the Schlenk tube containing turpentine/$CaH_2$. All gas and vacuum control now proceed by the receiving Schlenk tube. The Schlenk tube containing turpentine/$CaH_2$ was lowered into an oil bath and the entire apparatus was carefully introduced to vacuum. **Caution:** introducing vacuum may cause rapid distillation, thus gentle vacuum introduction is required. After, the receiving Schlenk tube is submerged in $LN_2$ and the entire system is now open to vacuum. Gentle heating (**See note below**) is required to transfer dried turpentine in which we heated up to 80 °C oil bath temperature under vacuum.

**Note:** For every 10 °C increase, we would allow the distillation to proceed for 20 minutes before increasing temperature once again.

### 3) Cannula transfer of dried turpentine

Once turpentine has fully transferred, the entire apparatus was returned to $N_2$ gas flow, and the receiving Schlenk tube was removed from the apparatus and closed with a rubber septum. Next, the Schlenk tube with Kontes® valve and Kontes® valve screw thread stopper was assembled and evacuated on the Schlenk line. Once the Schlenk tube with Kontes® valve was evacuated refilled with $N_2$ 3x, the screw thread cap was removed under a positive pressure of $N_2$ and replaced with a rubber septum. After, a metal cannula was used to transfer dried turpentine into the Schlenk tube with Kontes® valve under a positive pressure of $N_2$ to facilitate liquid transfer. After, the Schlenk tube with Kontes® valve was resealed with screw thread stopped and brought into the glovebox.

The receiving Schlenk tube containing residual $CaH_2$ was carefully quenched by the addition of methanol then water prior to disposal.

## S7. Yield quantification of aminated β-pinene (3) and aminated limonene (4) from turpentine

## Composition of turpentine determination

Qualitative analysis of turpentine was analyzed by GC-MS with EI source and referenced to the National Institute of Standards and Technology (**NIST**) **05 GC library** to identify species by mass spectrometry for chromatographic peak.

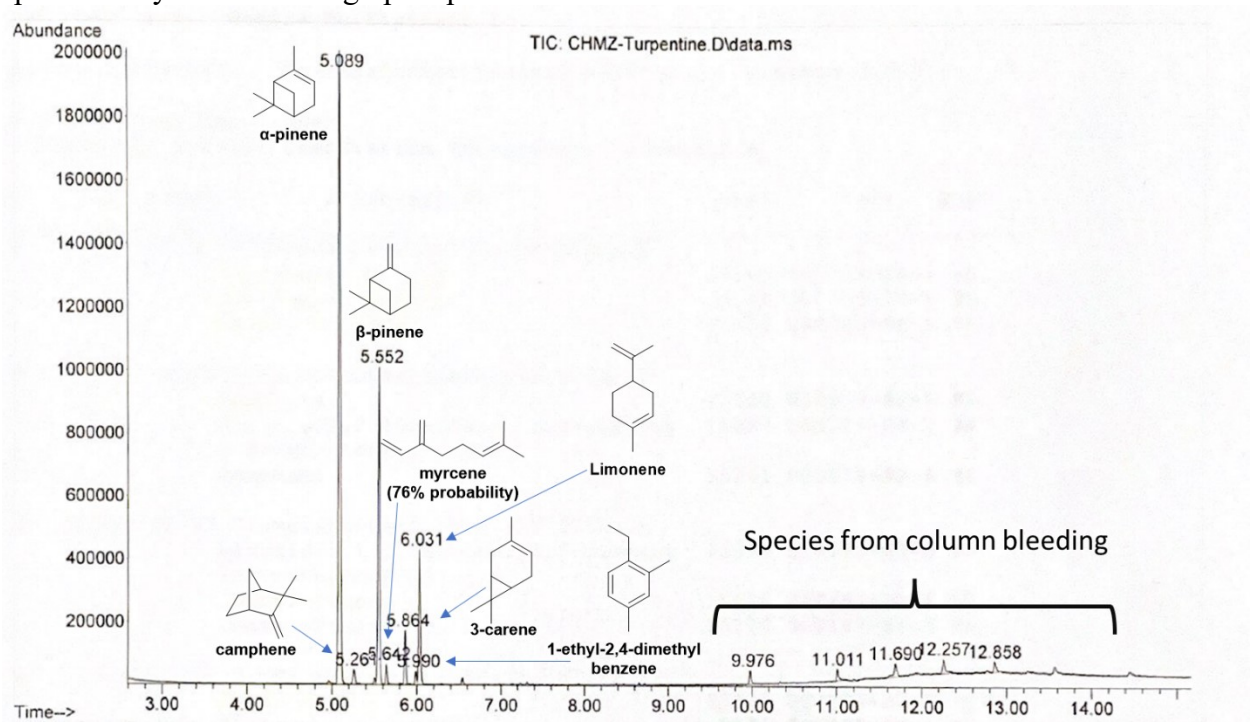
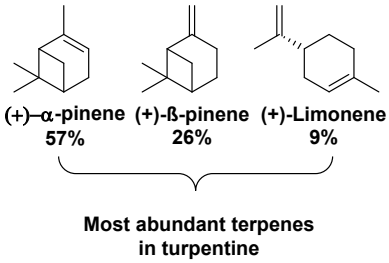



**Figure S28. GC-MS chromatogram of turpentine sample. Speciation was determined by NIST 05 GC Library**

## $^1$H NMR Quantification of α-pinene, β-pinene, and limonene in turpentine




Turpentine (136.2 mg, 1 mmol) was dissolved in 0.3 mL of toluene-$d_8$. After, 1,3,5-trimethoxybenzene (46.0 mg, 0.27 mmol) was added to the solution and mixed thoroughly by pipette prior to transfer to an NMR tube to serve as internal standard. 0.5 mL toluene-$d_8$ was used to rinse the vial and remaining solution was transferred to the NMR tube. Quantitative $^1$H{$^{13}$C} NMR experiments with 100 second $d_1$ allowed for monoterpene content concentration determination. Amounts of monoterpenes in turpentine were determined using integrals for multiplet resonances at 5.14 - 5.19, 4.72 - 4.74, and 4.66 - 4.69 ppm which representing olefinic $^1$H resonances representing the =C-H in α-pinene, =$CH_2$ in limonene, and =C-H in β-pinene, respectively. The integral at 3.37 ppm representing $OCH_3$ $^1$H resonance in 1,3,5-trimethoxybenzene (**internal standard**) was used to calculate amounts of each major monoterpene.

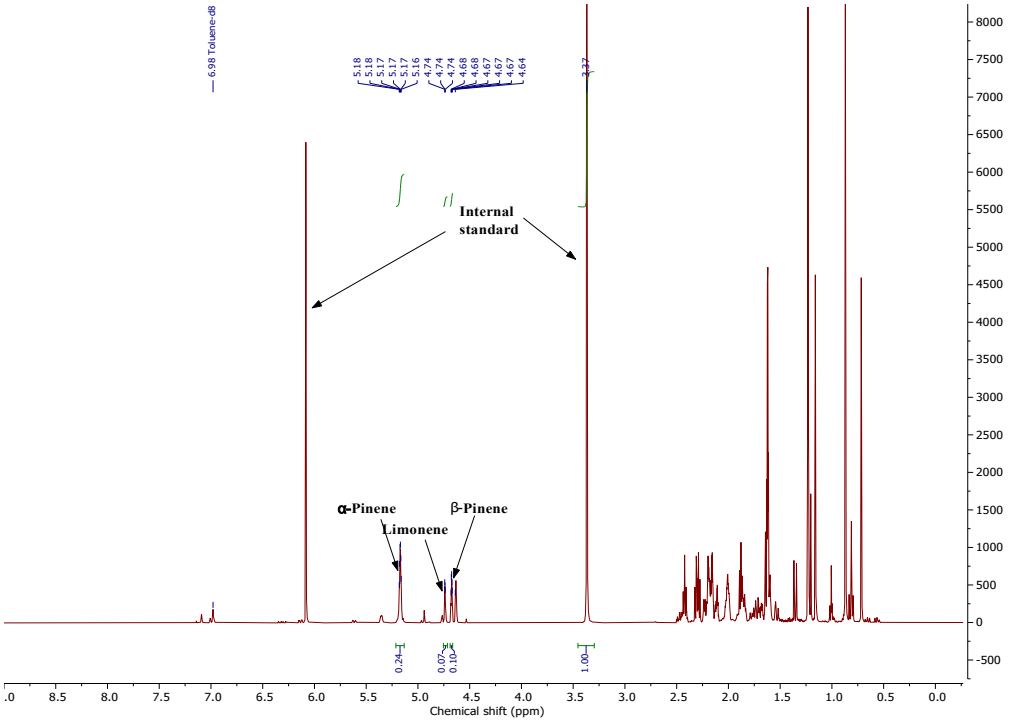
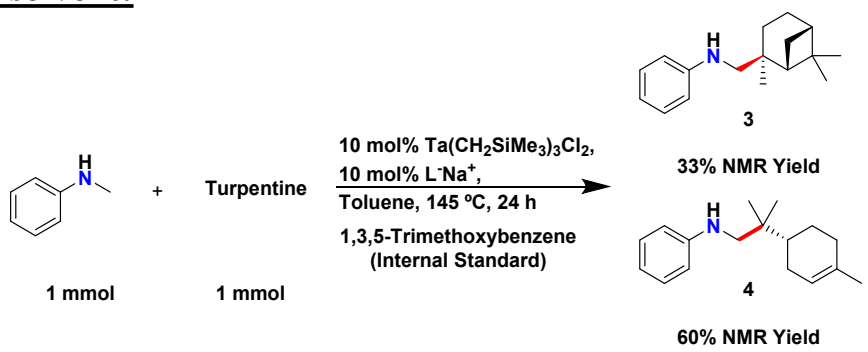



**Figure S29. $^1$H{$^{13}$C} NMR spectrum (400 MHz, $C_7D_8$, 298 K) of turpentine where 1,3,5-trimethoxybenzene served as internal standard.**

## Yield Quantification of 3 & 4

## With added solvent:




Inside a nitrogen-filled glovebox, $Ta(CH_2SiMe_3)_3Cl_2$ (51.3 mg, 0.1 mmol) and ligand salt ($L^-Na^+$) (30.4 mg, 0.1 mmol) were weighed into a 2 dram vial. After, 1 mL of toluene was then added to the vial and the now yellow solution sat for 15 minutes. Afterwards, *N*-methylaniline (107.2 mg, 1 mmol) and Turpentine (136.2 mg, 1 mmol) was added to the vial sequentially by a micropipette. The vial was then sealed with a Thermo Scientific™ PTFE/silicone disc septum and screw thread cap, removed from the glovebox, and placed on a pre-heated aluminum block for heating at 145 °C for 24 hours. After heating, unfunctionalized turpentine and excess *N*-methylaniline were removed under reduced pressure. 1,3,5-Trimethoxybenzene (10 mg, 0.06 mmol) was added to the crude reaction mixture and diluted with toluene-$d_8$ (0.8 mL), filtered through a Celite™-packed Pasteur pipette, and transferred to an NMR tube for quantitative $^1H\{^{13}C\}$ NMR experiments. Yield determination proceeded by integrating 6.13 ppm signal (ArH in 1,3,5-trimethoxybenzene) against 0.99 & 0.76 ppm singlet resonances representing $CH_3$ in **3** & **4**, respectively.

If desired for isolation, the dried crude mixture can be directly subjected to silica gel chromatography to isolate **3** and **4** as an inseparable 1.7:1 mixture, 9:1 hexanes:ethyl acetate as eluent.

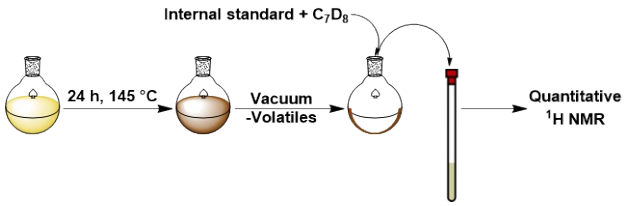



**Figure S30. Illustrative diagram for yield quantification of 3 & 4**

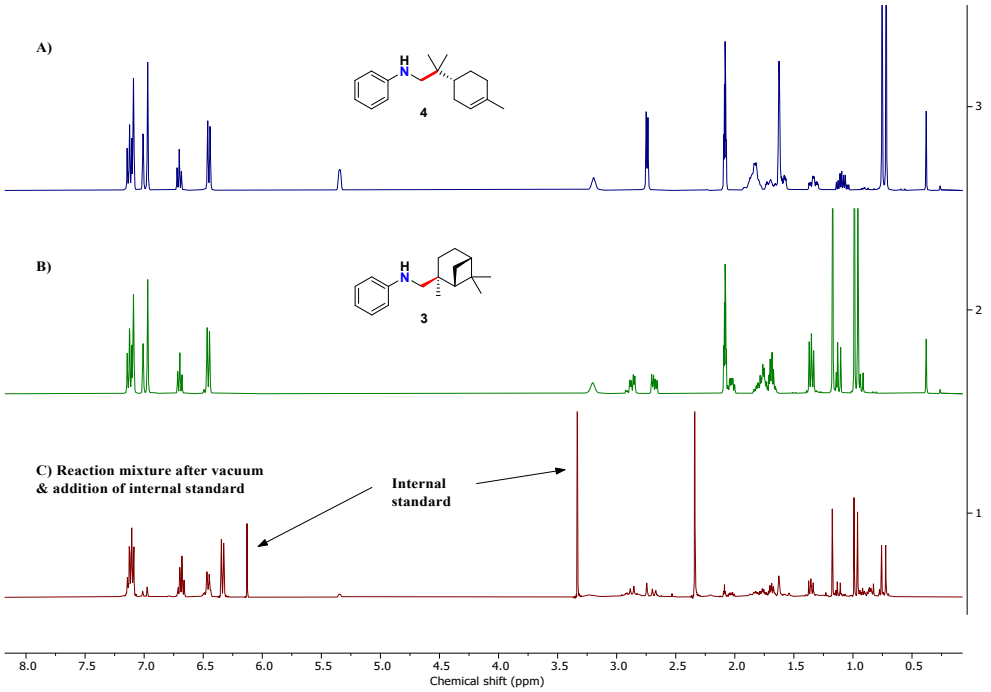



**Figure S31. Stacked $^1$H NMR spectra (400 MHz, $C_7D_8$, 298 K). A) Pure sample of 4 B) Pure sample of 3 C) Crude reaction mixture after applying vacuum & addition of TMB (internal standard) to measure yields by $^1$H NMR**

**Note:** Pure samples of **3** & **4** were prepared and isolated following literature procedure using commercially pure sources of β-pinene & limonene, respectively.[2] For characterization data of **3** and **4** refer to the literature.[2]

## GC-MS comparison of 3 & 4 generated from turpentine

Following literature procedure,[2] **3** and **4** were prepared from commercially pure sources of β-pinene and limonene, respectively. After purification by silica gel chromatography using a hexanes → 9:1 hexanes:ethyl acetate eluent allowed for isolation of **3** and **4**. Further, analysis by GC-MS of the purified revealed their retention times. A comparison of these retention times can be made with the reaction mixtures using turpentine to confirm the synthesis of **3** and **4** (**Figure S32**).

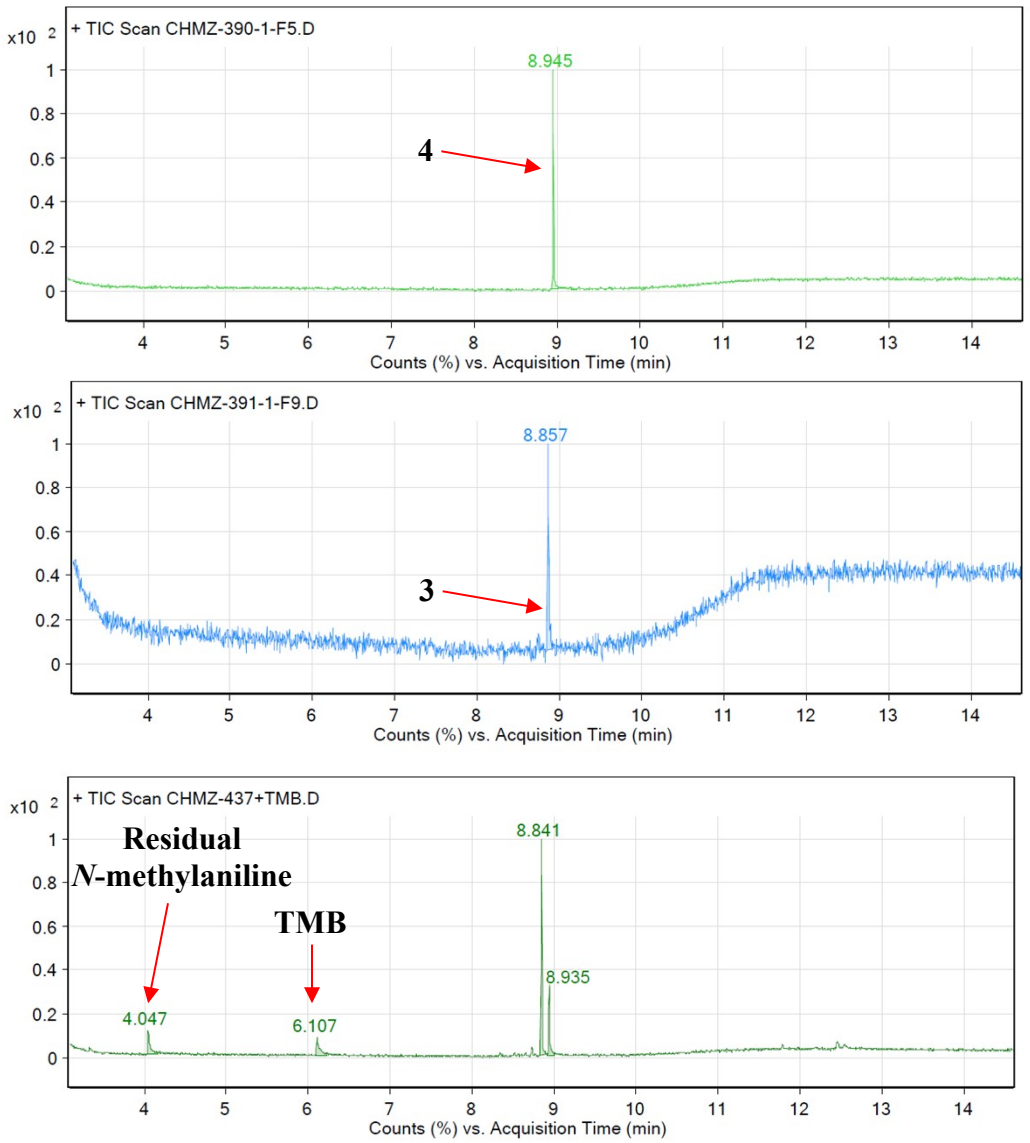
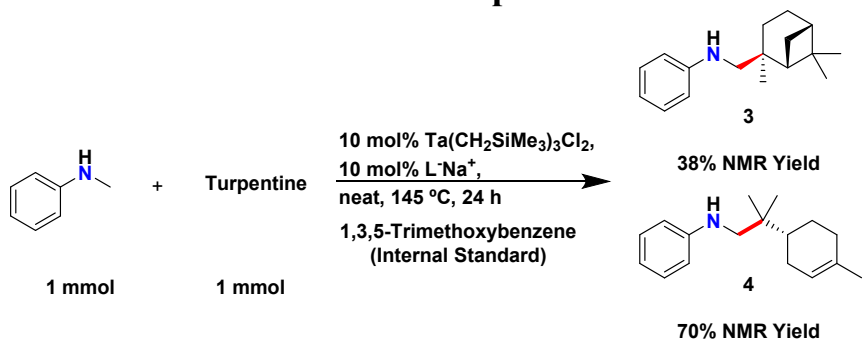



**Figure S32. Comparison of GC retention times Top) Aminated limonene (4) $T_R$ = 8.95 Middle) Aminated β-pinene (3) $T_R$ = 8.86 Bottom) Reaction mixture from turpentine functionalization after applying vacuum and adding internal standard TMB. Aminated β-pinene (3) $T_R$ = 8.84, Aminated limonene (4) $T_R$ = 8.94**

## Yield determination of 3 and 4 via neat turpentine reaction conditions

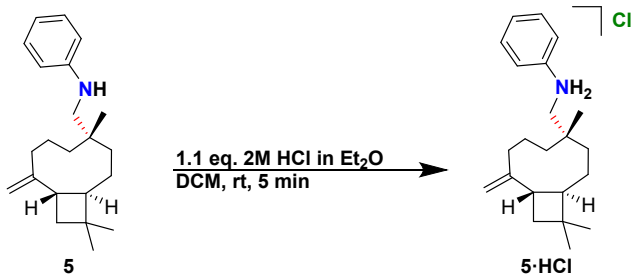



Inside a nitrogen-filled glovebox, $Ta(CH_2SiMe_3)_3Cl_2$ (51.3 mg, 0.1 mmol) and ligand salt ($L^-Na^+$) (30.4 mg, 0.1 mmol) were weighed into a 2 dram vial. Turpentine (136.2 mg, 1 mmol) was then directly added to the vial using a micropipette and the now yellow solution sat for 15 minutes. Afterwards, *N*-methylaniline (107.2 mg, 1 mmol) was added to the vial. The vial was then sealed with a Thermo Scientific™ PTFE/silicone disc septum and screw thread cap, removed from the glovebox, and placed on a pre-heated aluminum block for heating at 145 °C for 24 hours. After heating, unfunctionalized turpentine and *N*-methylaniline were removed under reduced pressure. 1,3,5-Trimethoxybenzene (10 mg, 0.06 mmol) was added to the crude reaction mixture and diluted with toluene-$d_8$ (0.8 mL), filtered through a Celite™-packed Pasteur pipette, and transferred to an NMR tube for quantitative $^1H\{^{13}C\}$ NMR experiments. Yield determination proceeded by integrating 6.13 ppm signal (ArH in 1,3,5-trimethoxybenzene) against 0.99 & 0.76 ppm singlet resonances representing $CH_3$ in **3** & **4**, respectively.

If desired for isolation, the dried crude mixture can be directly subjected to silica gel chromatography to isolate **3** and **4** as an inseparable 2:1 mixture, 9:1 hexanes:ethyl acetate as eluent.

## S8. Crystallographic data for 5·HCl

### Synthesis and crystallization of 5·HCl




5 5·HCl

**5** (80 mg, 0.26 mmol) was dissolved in 1-dram vial by 1 mL DCM and stirring. HCl in diethyl ether (0.15 mL, 0.29 mmol) was added slowly by syringe to the stirring solution, which turned the colourless solution to yellow. After 5 minutes of stirring at room temperature, solvent was removed under reduced pressure, revealing a white solid. Crystals suitable for X-ray diffraction were obtained from layering a saturated DCM solution and allowing for slow vapour diffusion.

### X-ray diffraction data

Appropriate single crystals were mounted on MiTeGen loops. Measurements were made using Cu Kα radiation (λ=1.54178 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXL-2013)[8] using the OLEX2 interface[9]. All hydrogen atoms were placed in calculated positions. The compound crystalized from DCM with 2 molecules in the asymmetric unit; however, only one is shown below for simplicity. The crystals were poorly diffracting and crystalized as a racemic twin complicating data collection/solving. For this structure, nonhydrogen atoms were refined anisotropically. In the case where anisotropic ellipsoids appeared as NPD's, an isotropic refinement was selected. For clarity and simplicity, a ball and stick represented was selected to illustrate the bond connectivity.

CCDC 2344466 contains the up-to-date supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

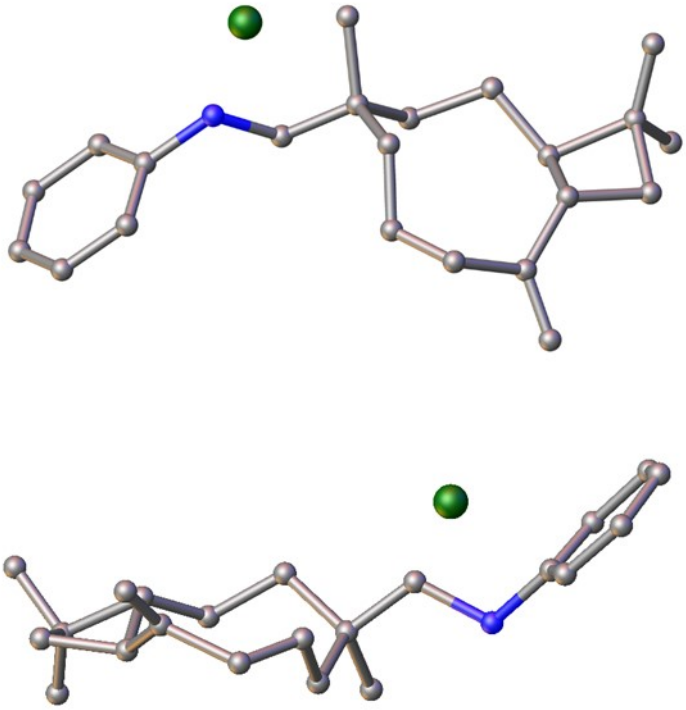


**Figure S33. Ball and Stick representation of the solved solid state structure of the compound 5·HCl. obtained from slow evaporation from DCM. Atoms were refined both isotropically and anisotropically to confirm structural atom connectivity. Hydrogen atoms have been removed for clarity.**

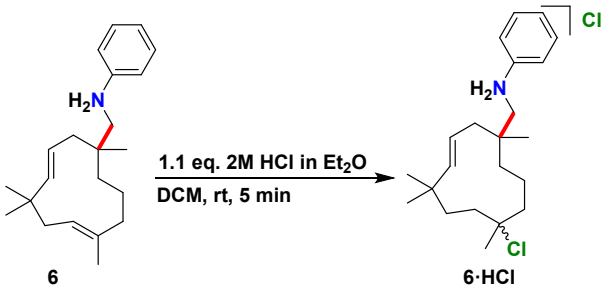
**Note: 5·HCl** allowed for assignment of relative stereochemistry in which the α-carbon *syn* to the closest cyclobutane methine C—H in this crystal structure.

**Table 1. Crystallographic data for CCDC 2344466**

| **Compound** | **5·HCl** |
|---|---|
| Empirical formula | $C_{22}H_{34}Cl_2N_2$ |
| Formula weight | 695.94 |
| Temperature/K | 100(2) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 7.0051(6) |
| b/Å | 18.9291(14) |
| c/Å | 36.914(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| V/Å$^3$ | 4894.8(7) |
| Z | 4 |
| ρ/ g/cm$^{-3}$ | 0.944 |
| μ/ mm$^{-1}$ | 1.375 |
| *F*(000) | 1520.0 |
| Crystal size/ mm$^3$ | 0.06 × 0.04 × 0.04 |
| Radiation | CuKα (λ = 1.54178) |
| 2θ range for data collection/° | 4.788 to 80.036 |
| Index ranges | $-5 \leq h \leq 5$, $-15 \leq k \leq 15$, $-30 \leq l \leq 30$ |
| Independent reflections | 2936 [$R_{int}$ = 0.1460, $R_{sigma}$ = 0.1045] |
| Data/restraints/parameters | 2936/222/271 |
| Goodness-of-fit on $F^2$ | 1.305 |
| R [I>=2θ (I)] (R1, wR2) | $R_1$ = 0.1423, $wR_2$ = 0.3421 |
| R (all data) (R1, wR2) | $R_1$ = 0.1935, $wR_2$ = 0.3828 |

## S9. Crystallographic data for 6·HCl

### Synthesis and crystallization of 6·HCl




**6** (80 mg, 0.26 mmol) was dissolved in 1-dram vial by 1 mL DCM and stirring. HCl in diethyl ether (0.15 mL, 0.29 mmol) was added slowly by syringe to the stirring solution, which turned the colourless solution to pale yellow. After 5 minutes of stirring at room temperature, solvent was removed under reduced pressure, revealing a cream coloured solid. Crystals suitable for X-ray diffraction were obtained from layering a saturated DCM solution with 1.5 mL $Et_2O$.

### X-ray diffraction data

Appropriate single crystals were mounted on MiTeGen loops. Measurements were made using Mo Kα radiation (λ=0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXL-2013)[8] using the OLEX2 interface[9]. All hydrogen atoms were placed in calculated positions. For all complexes, nonhydrogen atoms were refined anisotropically. The initial compound underwent reaction with HCl to produce the major product represented in the solid state structure. The crystal selected contained an unequal mixture of the HCl addition products and resulted in partial occupancies that do not match the exact calculated and predicted chemical representation.

CCDC 2238920 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

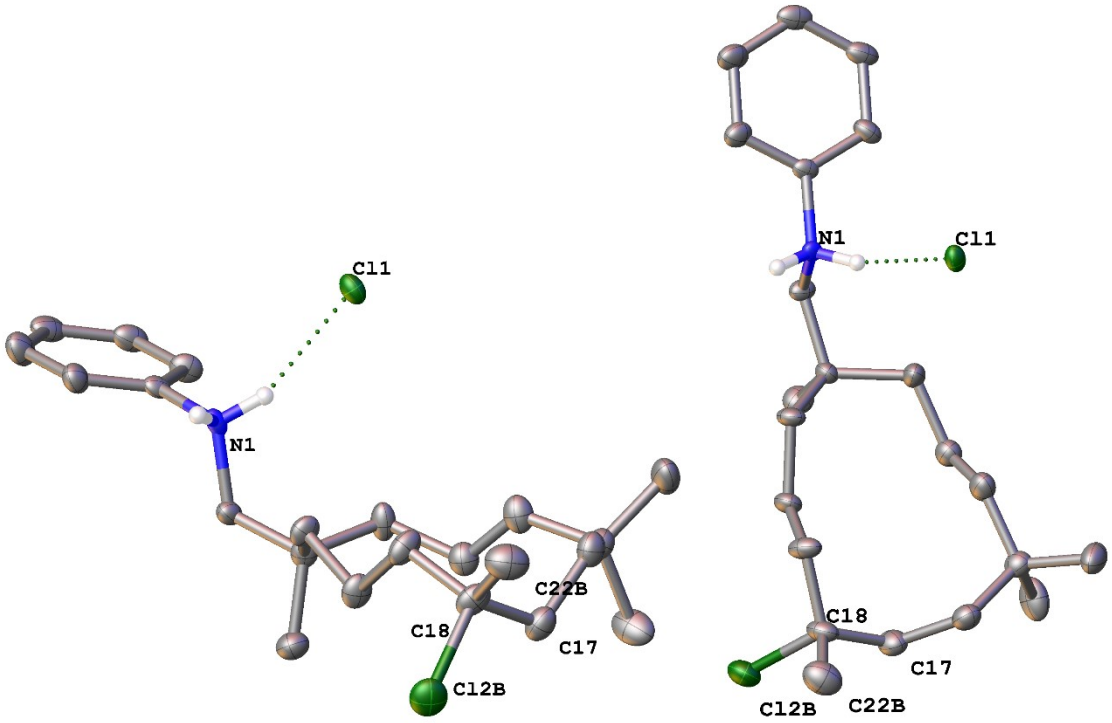



**Figure S34. ORTEP diagram (50% probability ellipsoids) of major disordered fragment of HCl addition product 6·HCl. N-H bonds shown, while all other hydrogens have been removed for clarity.**

**Table 2. Crystallographic data for CCDC 2238920**

| **Compound** | **6·HCl** |
|---|---|
| Empirical formula | $C_{22}H_{35}Cl_2N$ |
| Formula weight | 384.41 |
| Temperature/K | 100(2) |
| Crystal system | triclinic |
| Space group | *P-1* |
| a/Å | 7.6390(5) |
| b/Å | 9.6446(5) |
| c/Å | 15.2699(9) |
| α/° | 90.880(2) |
| β/° | 100.392(2) |
| γ/° | 102.199(2) |
| V/Å$^3$ | 1079.90(11) |
| Z | 2 |
| ρ/ g/cm$^{-3}$ | 1.182 |
| μ/ mm$^{-1}$ | 0.306 |
| *F*(000) | 416.0 |
| Crystal size/ mm$^3$ | 0.18 × 0.16 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 2.716 to 48.87 |
| Index ranges | -8 ≤ h ≤ 8, -11 ≤ k ≤ 11, 0 ≤ l ≤ 17 |
| Independent reflections | 3561 [$R_{int}$ = 0.1045, $R_{sigma}$ = 0.0364] |
| Data/restraints/parameters | 3561/206/246 |
| Goodness-of-fit on $F^2$ | 0.715 |
| R [I>=2θ (I)] (R1, wR2) | $R_1$ = 0.0581, $wR_2$ = 0.1700 |
| R (all data) (R1, wR2) | $R_1$ = 0.0773, $wR_2$ = 0.1864 |

## S10. References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