Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Acid-Mediated Decarboxylative C–H Coupling between Arenes and *O*-Allyl Carbamates

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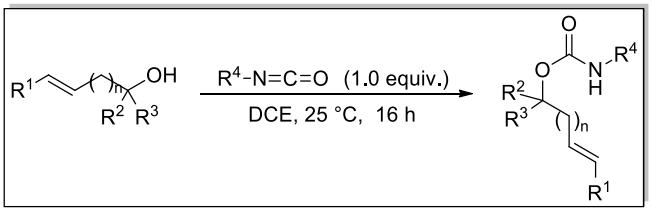
General Information

All available chemicals and solvents were purchased from commercial sources and were used without any further purification. Thin layer chromatography (TLC) was performed using 0.25 mm silica gel precoated plates Si 60-F254 (Merck, Darmstadt, Germany) visualized by UV-254 light and CAM staining. Purification by flash column chromatography (FCC) was conducted by using silica gel Si 60, 230-400 mesh, 0.040-0.063 mm (Merck). Melting points were determined on a Stuart Scientific SMP3 and are corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 and 101 MHz, respectively) or Bruker Avance 300 (300 and 75 MHz, respectively); chemical shifts are indicated in parts per million downfield from SiMe4, using the residual proton ($CHCl_3$ = 7.27 ppm) and carbon ($CDCl_3$ = 77.0 ppm) solvent resonances as internal reference. Coupling constants values J are given in Hz. FTIR spectra were recorded on a Tensor 27 (ATR Diamond) Bruker infrared spectrophotometer and are reported in frequency of absorption (cm^{-1}). Elemental analyses were executed on Perkin-Elmer CHN Analyzer Series II 2400. High-resolution mass spectra (HRMS) were recorded using a mass spectrometer MicroTOF from Bruker with an electron spray ion source (ESI) and a TOF detector or using a mass spectrometer from Thermo Fisher Scientific with an electron spray ion source (ESI) and a LTQ Orbitrap as detector at Institut Parisien de Chimie Moléculaire.

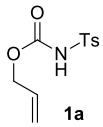
Preparation of Starting Materials

General procedure for the synthesis of *O*-allyl *N*-substituted carbamates 1a-b, 1d-g



In a round bottom flask was poured the appropriate allyl alcohol (10.00 mmol) dissolved in DCE (15 mL) followed by the addition of the suitable isocyanate (10.00 mmol). The resulting solution was allowed to reach at 25 °C under N_2, and the stirring was continued for 16 h. Then, after evaporation of the solvent and the volatiles under vacuum, the title compound was obtained. Starting from corresponding allyl alcohol and isocyanate, yield, spectroscopic and analytical data of *O*-allyl-carbamates *N*-substituted carbamates **1a-b**, **1d-g** are as follows.

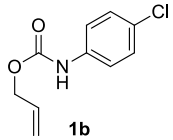
***O*-Allyl-*N*-tosylcarbamate (1a)**



1a

Allyl alcohol (660 µL); tosyl isocyanate (1.98 g). **1a** (2.54 g, 99%). The characterization of product **1a** is consistent with that reported in the literature.1

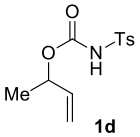
***O*-Allyl-*N*-(4-chlorophenyl)carbamate (1b)**



1b

Allyl alcohol (660 µL); 4-chlorophenylisocyanate (1.53 g). **1b** (1.88 g, 89%). The characterization of product **1b** is consistent with that reported in the literature.[2]

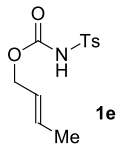
***O*-But-3-en-2-yl-*N*-tosylcarbamate (1d)**



1d

But-3-en-2-ol (721 mg); tosyl isocyanate (1.98 g). **1d** (2.53 g, 94%). The characterization of product **1d** is consistent with that reported in the literature.[1]

***O*-But-2-en-1-yl-*N*-tosylcarbamate (1e)**

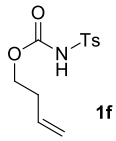


1e

Crotyl alcohol (721 mg); tosyl isocyanate (1.98 g). **1e** (2.56 g, 96%). The characterization of product **1e** is consistent with that reported in the literature.[3]

1 S. Nicolai, C. Piemontesi, and J. Waser, A palladium-catalyzed aminoalkynylation stratedy towards bicyclic heterocycles: synthesis of (±)-trachelanthamidine, *Angew. Chem. Int. Ed.,* 2011, **50**, 4680-4683.
2 Y. Sabesan, and M. Scott,*N*-Methylimidazole-catalyzed synthesis of carbamates from hydroxamic acids via the Lossen rearrangement, *Org. Lett.,* 2013, **15**, 602-605.
3 D. Xing, D., and Yang, Gold(I)-catalyzed highly regio- and stereoselective decarboxylative amination of allylic *N*-tosylcarbamates via base-induced aza-Claisen rearrangement in water, *Org. Lett.,* 2010, **12**, 1068-1071.

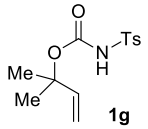
***O*-But-3-en-1-yl-*N*-tosylcarbamate (1f)**



1f

Crotyl alcohol (721 mg); tosyl isocyanate (1.98 g). **1f** (2.56 g, 96%). The characterization of product **1f** is consistent with that reported in the literature.[4]

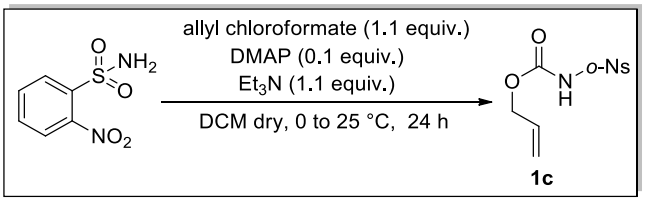
***O*-2-Methylbut-3-en-2-yl-*N*-tosylcarbamate (1g)**



1g

2-Methylbut-3-en-2-ol (861 mg); tosyl isocyanate (1.98 g). **1g** (2.69 g, 95%). The characterization of product **1g** is consistent with that reported in the literature. [3]

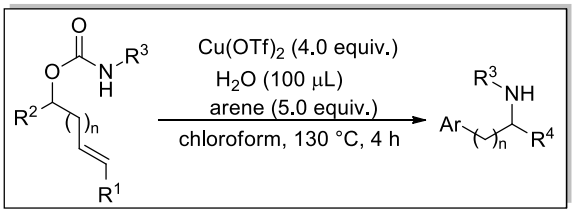
Procedure for the synthesis of *O*-allyl *N*-(*o*-nosyl) carbamate 1c



Triethylamine (111.3 mg, 1.1 mmol) was added to a solution of allylchloroformate (132.6 mg, 1.1 mmol), DMAP (12.2 mg, 0.1 mmol) and the 2-nitrobenzene sulfonamide (202.2 mg, 1.0 mmol) in dry DCM (20 mL) at 0 °C. Then the reaction was allowed to warm to room temperature. After 24 h, the reaction was diluted with DCM (10 mL), washed with HCl 10% solution (2×5 mL), saturated $NaHCO_3$ solution (2×10 mL) and brine (10 mL), dried over $MgSO_4$ and filtered. Compound **1c** was obtained in 70% yield (2.0 g). The characterization of product **1c** is consistent with that reported in the literature.[5]

Arylation/Hydroamination procedures

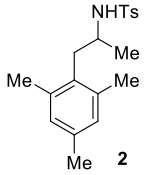
General procedure for the synthesis of arylated/hydroaminated products



In a sealed tube, $Cu(OTf)_2$ (4.0 mmol, 1.45 g) and H_2O (100 μL) were added to a solution of the appropriate *O*-allyl carbamate (1.0 mmol), arene (5.0 mmol) in chlorobenzene (0.4 M). The resulted solution was magnetically stirred and heated at 130 °C in oil bath for 3-4 hours. The reaction mixture was filtered and the solvent was evaporated under reduced pressure. The residue was purified by FCC. Starting from *O*-allyl carbamate **1a**,**1c-f**, aromatic source, yield and physical, spectroscopic and analytical data of compounds **2**, **5**-**15**, **17**-**18** are as follows.

4 J. Rajabi, M. M. Lorion, V. L. Ly, F. Liron, J. Oble, G. Prestat, and G. Poli, Dormant versus evolving aminopalladated intermediates: toward a unified mechanistic scenarion in Pd^{II}-catalyzed aminations, *Chem. Eur. J.,* 2014, **20**, 1539-1546.
5 F. Foschi, C. Loro, R. Sala, J. Oble, L. Lo Presti, E. M. Beccalli, G. Poli, and G. Broggini, Intramolecular aminoazidation of unactivated terminal alkenes by palladium-catalyzed reactions with hydrogen peroxide as oxidant, *Org. Lett.,* 2020, **22**, 1402-1406.

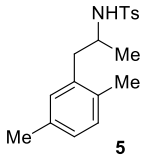
1-(2,4,6-Trimethylphenyl)-2-tosylamino-propane (2)



2

1a (255.3 mg); mesitylene (0.69 mL); FCC–AcOEt/hexane (1:1). **2** (254.9 mg, 77%); light brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, 2H, *J* = 8.2 Hz), 7.19 (d, 2H, *J* = 8.2 Hz), 6.74 (s, 2H), 4.33 (d, 1H, *J* = 6.6 Hz), 3.50-3.41 (m, 1H), 2.79 (dd, 1H, *J* = 14.1, 7.4 Hz,), 2.64 (dd, 1H, *J* = 14.1, 8.0 Hz), 2.41 (s, 3H), 2.23 (s, 3H), 2.14 (s, 6H), 1.14 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.1, 137.5, 136.6, 135.8, 131.5, 129.5, 129.2, 127.0, 49.9, 36.9, 21.5, 21.4, 20.8, 20.3; IR ν $_{max}$ 2926, 1321, 1154 cm^{-1}. Anal. Calcd. for $C_{19}H_{26}NO_2S$ $[M+H]^+$ HRMS(ESI): 332.1679; found: 332.1679.

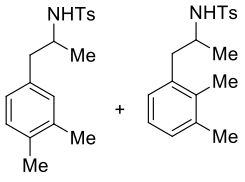
1-(2,5-Dimethylphenyl)-2-tosylamino-propane (5)



5

1a (255.3 mg); *p*-xylene (0.62 mL); FCC–AcOEt/hexane (2:3). **5** (250.5 mg, 79%); light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, 2H, *J* = 8.2 Hz), 7.20 (d, 2H, *J* = 8.1 Hz), 6.95-6.89 (m, 2H), 6.76 (s, 1H), 4.72 (d, 1H, *J* = 6.7 Hz), 3.48-3.41 (m, 1H), 2.73 (dd, 1H, *J* = 13.7, 6.9 Hz), 2.59 (dd, 1H, *J* = 13.7, 7.4 Hz), 2.41 (s, 3H), 2.24 (s, 3H), 2.09 (s, 3H), 1.15 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.0, 137.5, 135.5, 135.4, 133.2, 130.9, 130.5, 129.5, 127.5, 126.9, 50.1, 41.1, 21.7, 21.5, 20.9, 18.9; IR ν $_{max}$ 2934, 1324, 1151 cm^{-1}. Anal. Calcd. For $C_{18}H_{23}NO_2S$: C, 68.11; H, 7.30; N, 4.41. Found: C, 68.31; H, 7.171; N, 4.39.

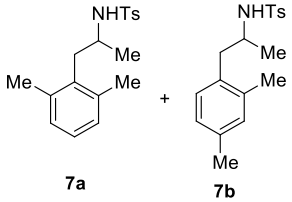
1-(3,4-Dimethylphenyl)-2-tosylamino-propane (6a) and 1-(2,3-dimethylphenyl)-2-tosylamino-propane (6b)



6a **6b**

1a (255.3 mg); *o*-xylene (0.60 mL); FCC–AcOEt/hexane (1:4). **6a** + **6b** (241.0 mg, 76%, **6a**:**6b**: 1/1.4 isomeric ratio after purification); light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) major isomer **6a**: δ 7.59 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 2H, *J* = 8.7 Hz), 7.00-6.96 (m, 1H), 6.74-6.73 (m, 2H), 4.26 (d, 1H, *J* = 6.9 Hz), 3.51-3.45 (m, 1H), 2.64-2.55 (m, 2H), 2.42 (s, 3H), 2.24 (s, 3H), 2.17 (s, 3H), 1.13 (d, 3H, *J* = 6.5 Hz); ^{1}H NMR ($CDCl_3$, 400 MHz) minor isomer: δ 7.48 (d, 2H, *J* = 8.4 Hz), 7.16 (d, 2H, *J* = 7.8 Hz), 7.00-6.96 (m, 2H), 6.84-6.83 (m, 1H), 4.34 (d, 1H, *J* = 6.2 Hz), 3.41-3.35 (m, 1H), 2.71 (d, 2H, *J* = 7.2 Hz), 2.41 (s, 3H), 2.17 (s, 3H), 1.19 (s, 3H), 1.19 (d, 3H, *J* = 6.4 Hz);^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.0,142.9, 137.6, 137.4, 136.7, 134.9, 134.3, 130.6, 129.8, 129.5, 129.4, 128.7, 128.3, 127.0, 126.9, 126.7, 125.5, 50.9, 49.9, 42.9, 41.9, 22.0, 21.5, 20.6, 19.7, 19.3, 15.1; IR ν $_{max}$ 2923, 1321, 1159 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}NO_2S$ $[M+H]^+$ HRMS(ESI): 318.1528; found: 318.1522.

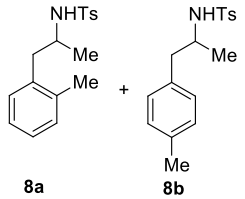
1-(2,6-Dimethylphenyl)-2-tosylamino-propane (7a) and 1-(2,4-dimethylphenyl)-2-tosylamino-propane (7b)



7a **7b**

1a (255.3 mg); *m*-xylene (0.62 mL); FCC–DCM. **7a** + **7b** (228.3 mg, 72%; **7a**:**7b**: 1/1 isomeric ratio after purification); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) mixture of two isomers **7a** + **7b**: δ 7.57 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 9.0 Hz), 7.19 (d, 4H, 8.1 Hz), 7.02-6.98 (m, 1H), 6.92 (d, 1H, *J* = 7.5 Hz), 6.88-6.82 (m, 4H), 4.37 (t, 2H, *J* = 7.5 Hz), 3.54-3.38 (m, 2H), 2.85 (dd, 1H, *J* = 13.9, 7.0 Hz), 2.73-2.58 (m, 3H), 2.42(s, 3H), 2.41 (s, 3H), 2.28 (s, 4H), 2.19 (s, 4H), 2.09 (s, 4H), 1.14 (d, 6H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.1, 143.0, 137.4, 137.3, 136.4, 136.1, 136.0, 134.4, 132.4, 131.4, 130.1, 129.5, 128.5, 127.0, 126.9, 50.1, 49.8, 40.8, 37.2, 21.7, 21.6, 21.5, 21.4, 20.9, 20.4, 19.2; IR ν $_{max}$ 2925, 1325, 1159 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}NO_2S$ $[M+H]^+$ HRMS(ESI): 318.1528; found: 318.1522.

1-(2 -Methylphenyl)-2-tosylamino-propane (8a) and 1-(4-methylphenyl)-2-tosylamino-propane (8b)

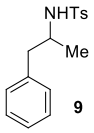


8a **8b**

1a (255.3 mg); toluene (0.53 mL); FCC–DCM. **8a** + **8b** (87.9 mg, 29%); yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) major isomer: δ 7.62-7.56 (m, 2H,), 7.23-7.19 (m, 2H), 7.13-7.01 (m, 3H), 6.99 (d, 1H, *J* = 13.4 Hz), 4.32 (d, 1H, *J* = 4.7 Hz), 3.52-3.43 (m, 1H), 2.77 (dd, 1H, *J* =10.3, 5.2 Hz), 2.67-2.62 (m, 1H), 2.41 (s, 3H), 2.15 (s, 3H), 1.14 (d, 3H, *J* = 4.9 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) minor isomer: δ 7.62-7.56 (m, 2H), 7.23-7.19 (m, 2H), 7.13-7.01 (m, 2H), 6.89 (d, 2H, *J* = 5.9 Hz), 4.24 (d, 1H, *J* = 5.5 Hz), 3.52-3.43 (m, 1H), 2.67-2.62 (m, 2H), 2.43 (s, 3H), 2.31 (s, 3H), 1.11 (d, 3H, *J* = 4.9 Hz);^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.1, 143.0,

137.4, 136.4, 136.3, 135.5, 130.6, 130.2, 129.6, 129.2, 127.1, 126.9, 126.8, 126.0, 50.9, 49.9, 42.9, 41.2, 21.7, 21.5, 21.4, 19.3; IR ν_{max} 2917, 1378, 1157 cm^{-1}. Anal. Calcd. For $C_{17}H_{21}NO_2S$: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.44; H, 7.21; N, 7.27.

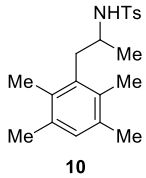
1-Phenyl-2-tosylamino-propane (9)



9

1a (255.3 mg); benzene (0.45 mL); FCC–AcOEt/hexane (1:4). **9** (211.1 mg, 73%); light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (d, 2H, *J* = 8.3 Hz), 7.24-7,21 (m, 5H), 7.04-7.01 (m, 2H), 4.47 (d, 1H, *J* = 7.4 Hz), 3.57-3.49 (m, 1H), 2.74-2.64 (m, 2H), 2.42 (s, 3H), 2.24 (s, 3H), 1.10 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.1, 137.7, 137.1, 129.6, 129.4, 128.5, 126.9, 126.6, 50.9, 43.5, 21.5, 21.3. The characterization of product **9** is consistent with that reported in the literature.[6]

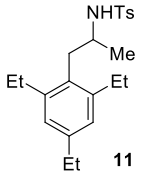
1-(2,3,5,6-Tetramethylphenyl)-2-tosylamino-propane (10)



10

1a (255.3 mg); 1,2,4,5-tetramethyl benzene (671.1 mg); FCC–AcOEt/hexane (4:1). **10** (269.2 mg, 78%); light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, 2H, *J* = 8.3 Hz), 7.15 (d, 2H, *J* = 8.2 Hz), 6.82 (s, 1H), 4.51 (d, 1H, *J* = 6.7 Hz), 3.45-3.38 (m, 1H), 2.90 (dd, 1H, *J* =14.3, 7.8 Hz), 2.77 (dd, 1H, *J* = 14.3, 7.5 Hz), 2.41 (s, 3H), 2.16 (s, 6H), 2.04 (s, 6H), 1.19 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.9, 137.2, 134.1, 133.9, 132.5, 130.2, 129.3, 126.9, 50.3, 37.2, 21.9, 21.5, 20.7, 16.1; IR ν_{max} 2925, 1378, 1155 cm^{-1}. Anal. Calcd. for $C_{20}H_{28}NO_2S$ $[M+H]^+$ HRMS(ESI): 346.1835; found: 346.1835.

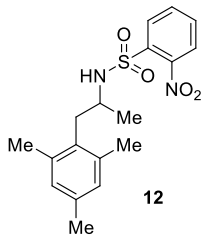
1-(2,4,6-Triethylphenyl)-2-tosylamino-propane (11)



11

1a (255.3 mg); 1,3,5-triethyl benzene (0.94 mL); FCC–AcOEt/hexane (4:1). **11** (276.2 mg, 74%); light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, 2H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.3 Hz), 6.81 (s, 2H), 4.48 (s, 1H), 3.43-3.36 (m, 1H), 2.82 (dd, 1H, *J* = 14.1, 7.2 Hz), 2.69 (dd, 1H, *J* = 14.1, 8.4 Hz), 2.61-2.55 (m, 2H), 2.54-2.43 (m, 4H), 2.41 (s, 3H), 1.27-1.25 (m, 3H), 1.15-1.09 (m, 9H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.0, 142.7, 142.6, 137.3, 129.8, 129.5, 127.1, 126.0, 50.6, 35.4, 28.5, 26.1, 21.5, 21.4, 15.5, 15.4; IR ν_{max} 2931, 1321, 1161 cm^{-1}. Anal. Calcd. for $C_{22}H_{32}NO_2S$ $[M+H]^+$ HRMS(ESI): 374.2148; found: 374.2149.

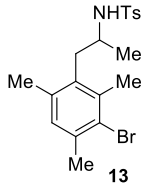
1-Mesityl-2-(*o*-nosylamino)-propane (12)



12

1c (286.3 mg); mesitylene (0.69 mL); FCC–AcOEt/hexane (1:4). **12** (162.9 mg, 45%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, 1H, *J* = 7.4 Hz), 7.79 (d, 1H, *J* = 7.6 Hz), 7.68-7.61 (m, 2H), 6.62 (s, 2H), 5.31 (t, 1H, *J* = 3.4 Hz), 3.85-3.78 (m, 1H), 2.85 (dd, 1H, *J* = 14.2, 8.0 Hz), 2.72 (dd, 1H, *J* = 14.2, 7.5 Hz) 2.19 (s, 6H), 2.16 (s, 3H), 1.26 (d, 3H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 136.5, 136.4,135.7, 134.8, 132.8, 131.1, 130.4, 129.2, 125.4, 125.4, 51.2, 36.6, 22.4, 20.3; IR ν_{max} 2919, 1537, 1347, 1162 cm^{-1}. Anal. Calcd. for $C_{18}H_{22}N_2O_4S$: C, 59.65; H, 6.12; N, 7.73. Found: C, 58.52; H, 5.91; N, 7.56.

1-(3-Bromo-2,4,6-trimethylphenyl)-2-tosylamino-propane (13)

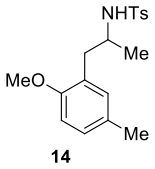


13

1a (255.3 mg); mesitylbromide (0.77 mL); FCC–AcOEt/hexane (1:4). **13** (335.4 mg, 82%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, 2H, *J* = 8.2 Hz), 7.15 (d, 2H, *J* = 8.1 Hz), 6.83 (s, 1H), 4.35 (d, 1H, *J* = 7.5 Hz), 3.46-3.39 (m, 1H), 2.87 (dd, 1H, *J* = 14.3, 7.9 Hz), 2.71 (dd, 1H, *J* = 14.3, 7.3 Hz), 2.42 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H), 2.18(s, 3H), 1.19 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.2, 139.9, 136.9, 136.3, 135.2, 133.5, 130.3, 129.4, 126.8, 126.6, 50.1, 37.9, 23.9, 22.1, 21.6, 20.7, 20.5; IR ν_{max} 2925, 1328, 1157 cm^{-1}. Anal. Calcd. for $C_{19}H_{25}BrNO_2S$ $[M+H]^+$ HRMS(ESI): 410.0784; found: 410.0783.

6 C. Michon, F. Medina, F. Capet, and P. Roussel, Inter- and intramolecular hydroamination of unactivated alkenes catalysed by a combination of copper and silver salts: the unveiling of a Brønsted acid catalysis, *Adv. Synth. Catal.*, 2010, **352**, 3293-3305.

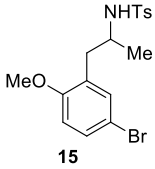
1-(2-Methoxy-5-methylphenyl)-2-tosylamino-propane (14)



14

1a (255.3 mg); 4-methyl anisole (0.63 mL); FCC–DCM. **14** (256.5 mg, 77%); light brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (d, 2H, *J* = 8.2 Hz), 7.08 (d, 2H, *J* = 8.1 Hz), 6.94 (d, 1H, *J* = 8.3 Hz), 6.66-6.63 (m, 2H), 4.99 (d, 1H, *J* = 5.3 Hz), 3.74 (s, 3H), 3.45-3.38 (m, 1H), 2.69 (dd, 1H, *J* = 13.6, 8.9 Hz), 2.51 (dd, 1H, *J* = 13.6, 4.9 Hz), 2.38 (s, 3H), 2.18 (s, 3H), 1.25 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 169.4, 142.4, 137.2, 131.8, 130.0, 129.2, 128.2, 126.8, 125.7, 110.4, 55.4, 51.2, 37.3, 27.1, 22.8, 21.4; IR ν $_{max}$ 2925, 2851, 1319, 1157 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}NO_3S$ [M+H]$^+$ HRMS(ESI): 334.1471; found: 334.1471.

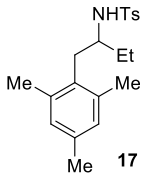
1-(5-Bromo-2-methoxyphenyl)-2-tosylamino-propane (15)



15

1a (255.3 mg); 4-bromo anisole (0.63 mL); FCC–AcOEt/hexane (1:4). **15** (266.0 mg, 67%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, 2H, *J* = 8.2 Hz), 7.23-7.20 (m, 1H), 7.11 (d, 2H, *J* = 8.1 Hz), 6.95 (d, 2H, *J* = 2.3 Hz), 4.79 (d, 1H, *J* = 6.2 Hz), 3.77 (s, 3H), 3.47-3.39 (m, 1H), 2.71 (dd, 1H, *J* = 13.6, 10.7 Hz), 2.49 (dd, 1H, *J* = 13.6, 4.9 Hz), 2.40 (s, 3H), 1.26 (d, 3H, *J* = 3.6 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 156.2, 142.8, 136.9, 133.5, 130.5, 129.4, 128.4, 126.7, 113.1, 112.1, 55.6, 51.2, 37.1, 23.0, 21.5; IR ν $_{max}$ 2927, 2853 1323, 1157 cm^{-1}. Anal. Calcd. for $C_{17}H_{21}BrNO_3S$ [M+H]$^+$ HRMS(ESI): 398.0420; found: 398.0418.

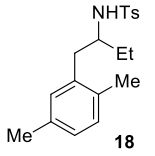
1-(2,4,6-Trimethylphenyl)-2-tosylamino-butane (17)



17

1e (269.3 mg); mesitylene (0.69 mL); FCC–AcOEt/hexane (1:4). **17** (265.8 mg, 77%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, 2H, *J* = 8.4 Hz), 7.15 (d, 2H, *J* = 8.3 Hz), 6.71 (s, 2H), 4.26 (d, 1H, *J* = 7.5 Hz), 3.36-3.29 (m, 1H), 2.78 (dd, 1H, *J* = 14.1, 7.8 Hz), 2.66 (dd, 1H, *J* = 14.1, 7.6 Hz), 2.40 (s, 3H), 2.23 (s, 3H), 2.15 (s, 6H), 1.55-1.45 (m, 2H), 0.84 (t, 3H, *J* = 7.4 Hz);^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.8, 137.6, 136.5, 135.7, 129.3, 129.2,126.9, 55.5, 34.9, 21.5, 20.8, 20.3, 10.1; IR ν $_{max}$ 2916, 1318, 1153 cm^{-1}. Anal. Calcd. for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05. Found: C, 69.72; H, 8.09; N, 4.28.

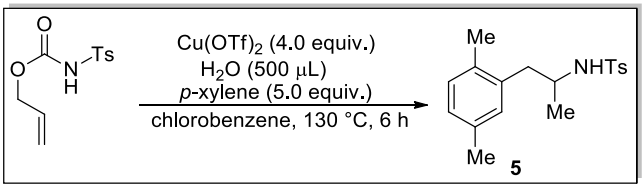
1-(2,5-Dimethylphenyl)-2-tosylamino-butane (18)



18

1d (269.3 mg); *p*-xylene (0.62 mL); FCC–AcOEt/hexane (1:4). **18** (135.8 mg, 41%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 2H, *J* = 8.2 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 6.93-6.88 (m, 2H), 6.73 (s, 1H), 4.36 (d, 1H, *J* = 6.9 Hz), 3.36-3.27 (m, 1H), 2.68-2.63 (m, 2H), 2.40 (s, 3H), 2.23 (s, 3H), 2.11 (s, 3H), 1.63-1.43 (m, 2H), 0.85 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.9, 137.5, 135.6, 135.3, 133.1, 130.9, 130.5, 129.4, 127.4, 126.9, 55.6, 38.7, 27.7, 21.5, 20.9, 18.9, 9.7; IR ν $_{max}$ 2921, 1323, 1155 cm^{-1}. Anal. Calcd. for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.66; H, 7.68; N, 4.42.

Gram-scale synthesis of 1-(2,5-Dimethylphenyl)-2-tosylamino-propane 5

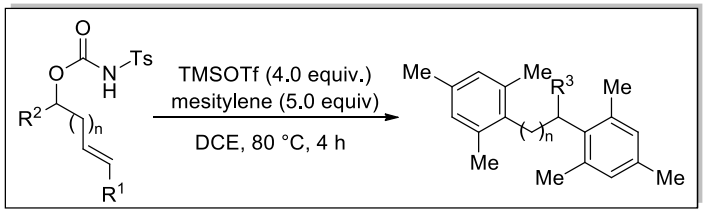


5

In a sealed tube, $Cu(OTf)_2$ (8.0 mmol, 2.89 g) and H_2O (500 μL) were added to a solution of the *O*-allyl *N*-tosyl carbamate **1a** (5.0 mmol, 1.28 g), *p*-xylene (10.0 mmol, 1.23 mL) in chlorobenzene (0.4 M). The resulted solution was magnetical stirred and heated at 130 °C in oil bath for 6 hours. The reaction was filtered, and the solvent was evaporated under reduced pressure. Compound **5** was afforded (1.09 g, 69%) as a light brown oil after FCC– AcOET/hexane (2:3).

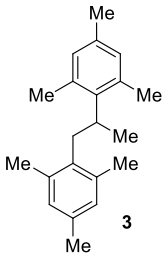
Diarylation procedures

General procedure for the synthesis of diarylated products with mesitylene



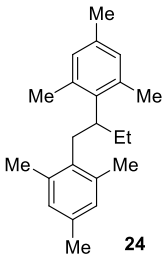
In a sealed tube, TMSOTf (4.0 mmol, 0.726 mL) was added dropwise to a solution of the appropriate *O*-allyl carbamate (1.0 mmol), mesitylene (5.0 mmol, 0.69 mL) in DCE (0.25 M). The resulted solution was magnetical stirred and heated at 80 °C in oil bath for 4 hours. Then the reaction was allowed to warm to room temperature. The reaction was diluted with DCM (10 mL), washed with saturated $NaHCO_3$ solution (2×10 mL), dried over $MgSO_4$ and filtered. The residue was purified by FCC. Starting from *O*-allyl carbamate **1a**,**1d-e**, yield and physical, spectroscopic and analytical data of compound **3**, **24**-**25** are as follows.

1,2-Bis(2,4,6-trimethylphenyl)-propane (3)



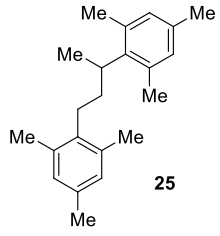
1a (255.3 mg); FCC–AcOEt/hexane (1:4). **3** (221.4 mg, 79%); brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.96 (s, 4H), 3.58-3.49 (m, 1H), 3.26 (dd, 1H, *J* = 13.6, 7.7 Hz), 3.12 (dd, 1H, *J* = 13.6, 6.3 Hz), 2.72 (s, 2H), 2.39 (s, 5H), 2.35 (s, 7H), 2.18 (s, 2H), 1.48 (d, 3H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.2, 137.7, 136.5, 135.8, 135.0, 134.9, 128.9, 126.9, 77.3, 77.0, 76.7, 36.0, 34.2, 21.2, 20.8, 20.6, 20.2, 18.9. Anal. Calcd. for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 90.13; H, 9.96.

1,2-Bis(2,4,6-trimethylphenyl)-butane (24)



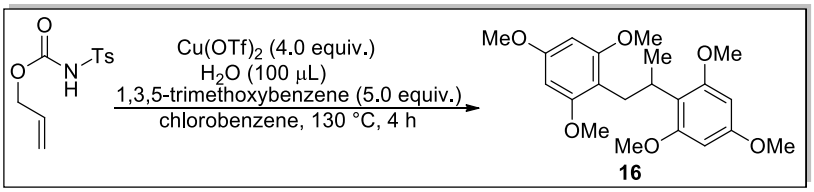
1e (269.3 mg); FCC–AcOEt/hexane (1:4). **24** (94.2 mg, 32%); brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.82 (s, 1H), 6.79 (s, 2H), 6.72 (s, 1H), 3.26-3.18 (m, 1H), 3.02 (d, 2H, *J* = 7.8 Hz), 2.54 (s, 3H), 2.25 (s, 6H), 2.15 (s, 6H), 2.04-1.96 (m, 1H), 1.92 (s, 3H), 1.83-1.72 (m, 1H), 0.78 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.8, 137.5, 136.6, 136.4, 135.6, 134.9, 134.8, 131.1, 129.0, 128.9, 42.9, 33.6, 26.8, 21.6, 21.5, 20.8, 20.7, 20.2, 13.0. Anal. Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.99; H, 10.18.

1,3-Bis(2,4,6-trimethylphenyl)-butane (25)



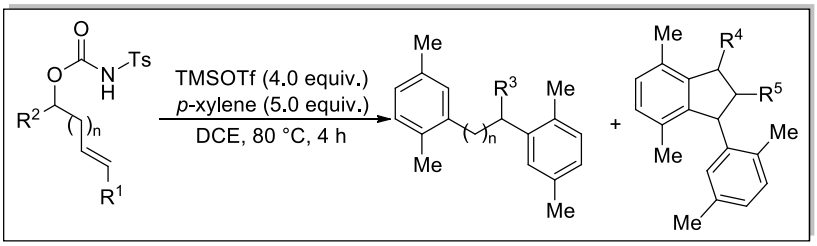
1d (269.3 mg); FCC–AcOEt/hexane (1:4). **25** (203.0 mg, 69%); brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86-6.79 (m, 4H), 3.38-3.29 (m, 1H), 2.68-2.61 (m, 1H), 2.46 (dd, 1H, *J* = 12.1, 5.4 Hz), 2.41 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H), 2.26 (s, 9H), 1.91-1.78 (m, 2H), 1.41 (d, 3H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 139.9, 136.4, 136.1, 135.8, 134.9, 134.8, 35.5, 35.2, 28.8, 20.8, 20.7, 19.6, 19.1. Anal. Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.76; H, 10.48.

Procedure for the synthesis of diarylated product 1,2-bis(2,4,6-trimethoxyphenyl)-propane 16



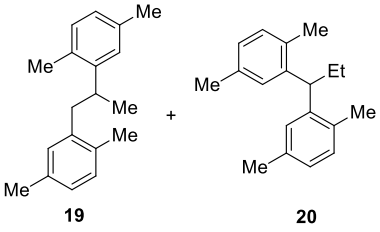
In a sealed tube, $Cu(OTf)_2$ (4.0 mmol, 1.45 g) and H_2O (100 μL) were added to a solution of the *O*-allyl *N*-tosyl carbamate **1a** (1.0 mmol, 255.3 mg), 1,3,5-trimethoxybenzene (5.0 mmol, 840.9 mg) in chlorobenzene (0.4 M). The resulted solution was magnetical stirred and heated at 130 °C in oil bath for 4 hours. The reaction was filtered, and the solvent was evaporated under reduced pressure. Compound **16** was afforded (229.5 mg, 61%) as a white wax after FCC–hexane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.09 (d, 4H, *J* = 6.7 Hz), 3.79 (s, 6H), 3.71 (s, 12H), 3.65-3.56 (m, 1H), 3.00 (dd, 1H, *J* = 9.5, 5.7 Hz), 2.88 (dd, 1H, *J* = 9.5, 5.4 Hz), 1.25 (d, 3H, *J* = 5.4 Hz); ^{13}C NMR ($CDCl_3$, 95 MHz) δ 158.3, 158.8, 158.7, 116.9, 112.1, 91.5, 90.4, 55.6, 55.3, 55.2, 29.5, 27.8, 18.4; IR ν_{max} 2854 cm^{-1}. Anal. Calcd. for $C_{21}H_{29}O_6$ [M+H]+ HRMS(ESI): 377.1959; found: 377.1959.

General procedure for the synthesis of diarylated products with *p*-xylene



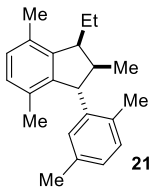
In a sealed tube, TMSOTf (4.0 mmol, 0.726 mL) was added dropwise to a solution of the appropriate *O*-allyl carbamate (1.0 mmol), *p*-xylene (5.0 mmol, 0.62 mL) in DCE (0.25 M). The resulted solution was magnetical stirred and heated at 80 °C in oil bath for 4 hours. Then the reaction was allowed to warm to room temperature. The reaction was diluted with DCM (10 mL), washed with saturated $NaHCO_3$ solution (2×10 mL), dried over $MgSO_4$ and filtered. The residue was purified by FCC. Starting from *O*-allyl carbamate **1a**,**1d-e**, yield and physical, spectroscopic and analytical data of compound **19-23** are as follows.

1,2-Bis(2,5-dimethylphenyl)-propane (19) and 1,1-bis(2,5-trimethylphenyl)-propane (20)


19 + 20

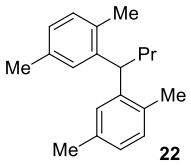
1a (255.3 mg); FCC–AcOEt/hexane (0.05:9.95). **19** + **20** (153.8 mg, 61%); white wax. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.14 (s, 1H), 7.03-7.01 (m, 4H), 6.95-6.87 (m, 7H), 4.08 (t, 1H, *J* = 7.4 Hz), 3.24-3.17 (m, 1H), 2.86 (dd, 1H, *J* = 13.4, 5.3 Hz), 2.74 (dd, 1H, *J* = 13.4, 9.2 Hz), 2.35-2.19 (m, 24H), 1.99-1.92 (m, 2H), 1.19 (d, 3H, *J* = 6.8 Hz), 0.97 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 145.5, 142.5, 139.1, 135.5, 135.1, 134.9, 133.2, 133.0, 132.0, 130.8, 130.2, 130.1, 130.0, 127.8, 126.6, 126.4, 126.2, 44.4, 41.4, 35.4, 28.9, 21.3, 21.2, 21.0, 20.6, 19.2, 19.1, 19.0, 13.0. Anal. Calcd. for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 91.18; H, 9.39.

1-(2,5-Dimethylphenyl)-3-ethyl-2,4,7-trimethyl-indane (21)


21

1a (255.3 mg); FCC–hexane. **21** (102.3 mg, 35%); white wax. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, 1H, *J* = 7.1 Hz), 6.95-6.89 (m, 2H), 6.82 (d, 1H, *J* = 7.5 Hz), 6.67 (s, 1H), 4.25 (d, 1H, *J* = 9.4 Hz), 3.22-3.17 (m, 1H), 2.54-2.48 (m, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.18 (s, 3H), 1.83-1.72 (m, 1H), 1.60 (s, 3H),1.57-1.53 (m, 1H),1.11 (d, 3H, *J* = 6.9 Hz), 0.91 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.2, 144.8, 143.4, 135.6, 132.8, 131.6, 130.6, 129.6, 128.5, 128.1, 127.9, 126.4, 51.6, 50.3, 47.2, 22.6, 21.0, 19.8, 19.0, 18.9, 13.5, 12.9. Anal. Calcd. for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.08; H, 9.81.

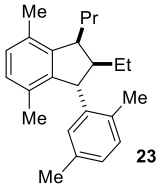
1,2-Bis(2,5-Dimethylphenyl)-butane (22)



22

1e (269.3 mg); FCC–AcOEt/hexane (0.05:9.95). **22** (194.3 mg, 73%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, 2H, *J* = 7.6 Hz), 6.97 (s, 2H), 6.92 (d, 2H, *J* = 7.2 Hz), 4.21 (t, 1H, *J* = 7.4 Hz), 2.30 (s, 6H), 2.25 (s, 6H), 1.93-1.88 (m, 2H), 1.44-1.34 (m, 2H), 0.95 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.7, 135.1, 133.1, 130.1, 127.9, 126.4, 42.2, 38.2, 21.3, 21.2, 19.2, 14.2. Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.94; H, 10.09.

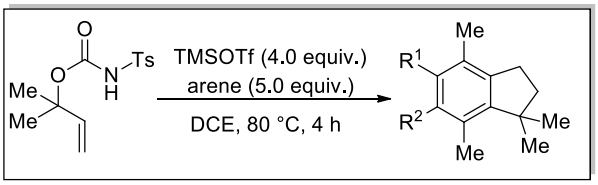
1-(2,5-Dimethylphenyl)-2-ethyl-4,7-dimethyl-3-propyl-indane (23)



23

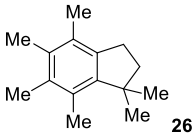
1d (269.3 mg); FCC–hexane. **23** (76.9 mg, 24%); white wax. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04 (d, 1H, *J* = 7.7 Hz), 6.91 (d, 2H, *J* = 7.8 Hz), 6.79 (d, 1H, *J* = 7.5 Hz), 6.67 (s, 1H), 4.28 (d, 1H, *J* = 10.5 Hz), 3.38-3.33 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.29-2.23 (m, 1H), 2.18 (s, 3H), 1.73-1.58 (m, 2H), 1.55 (s, 3H), 1.47-1.36 (m, 2H), 1.33-1.18 (m, 2H), 0.92-0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.4, 145.0, 143.6, 135.6, 132.9, 131.7, 130.4, 129.5, 128.6, 128.1, 127.8, 126.4, 58.5, 49.9, 43.0, 32.2, 21.0, 21.0, 20.4, 19.9, 19.2, 19.1, 14.9, 13.2. Anal. Calcd. for $C_{24}H_{32}$: C, 89.94; H, 10.06. Found: C, 89.70; H, 10.25.

General procedure for the synthesis of indane structures



In a sealed tube, TMSOTf (4.0 mmol, 0.726 mL) was added dropwise to a solution of the appropriate α,α-dimethyl substituted *O*-allyl-tosyl carbamate **1g** (1.0 mmol, 283.3 mg), arene (5.0 mmol) in DCE (0.25 M). The resulted solution was magnetical stirred and heated at 80 °C in oil bath for 4 hours. Then the reaction was allowed to warm to room temperature. The reaction was diluted with DCM (10 mL), washed with saturated $NaHCO_3$ solution (2×10 mL), dried over $MgSO_4$ and filtered. The residue was purified by FCC. Starting from arenes, yield and physical, spectroscopic and analytical data of compound **26-28** are as follows.

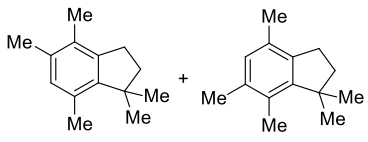
1,1,4,5,6,7-Hexamethyl-2,3-dihydro-indane (26)



26

1,2,4,5-Tetramethyl benzene (671.1 mg); FCC–AcOEt/hexane (3:7). **26** (175.9 mg, 87%): light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.80 (t, 2H, *J* = 7.3 Hz), 2.32 (s, 3H), 2.22 (s, 6H), 2.21 (s, 3H), 1.91 (t, 2H, *J* = 7.3 Hz), 1.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 146.0, 139.7, 133.9, 133.2, 129.6, 129.5, 43.0, 28.9, 28.0, 16.5, 16.3, 16.1, 15.9. The characterization of product **26** is consistent with that reported in the literature.[7]

1,1,4,5,7-Pentamethyl-2,3-dihydro-indane (27a) and 1,1,4,6,7-pentamethyl-2,3-dihydro-indane (27b)



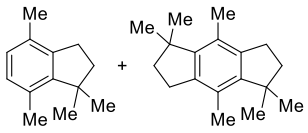
27a **27b**

Mesitylene (0.69 mL); FCC–AcOEt/hexane (3:7). **27a** + **27b** (167.5 mg, 89%, **27a/27b**: 2/1 isomeric ratio after purification); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) major isomer: δ 6.87 (s, 1H), 2.86 (t, 2H, *J* = 7.1 Hz), 2.33-2.21 (m, 9H), 1.94 (t, 2H, *J* = 7.1 Hz), 1.29 (s, 6H); ^{1}H NMR ($CDCl_3$, 400 MHz) minor isomer δ 6.87 (s, 1H), 2.76 (t, 2H, *J* = 7.3 Hz), 2.33-2.21 (m, 9H), 1.94 (t, 2H, *J* = 7.1 Hz), 1.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.4, 148.8,

7 Y. Zhang, L. Chen, and T. Lu, A copper(II) triflate-catalyzed tandem Friedel-Crafts alkylation/cyclization process towards dihydroindenes, *Adv. Synth. Catal.*, 2011, **353**, 1055-1060.

139.9, 139.4, 135.3, 134.7, 132.8, 132.2, 130.7, 129.5, 129.4, 128.9, 120.9, 43.1, 41.2, 29.2, 28.9, 27.9, 27.8, 21.1, 20.0, 18.7, 16.4, 15.3, 14.9. Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.03; H, 10.82.

1,1,4,5,6,7-Hexamethyl-2,3-dihydro-indane (28) and 1,1,4,5,5,8-hexamethyl-hydrindacene (29)

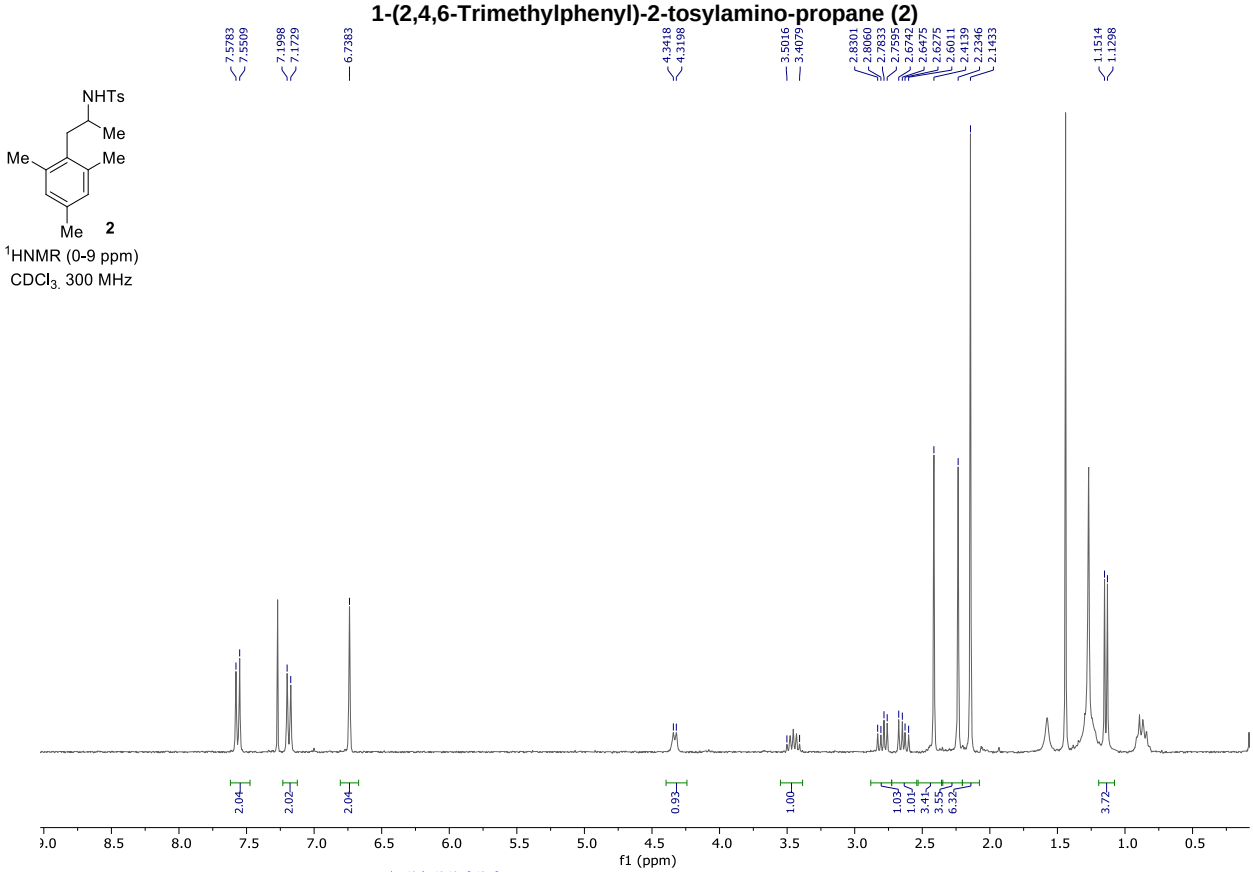


28 **29**

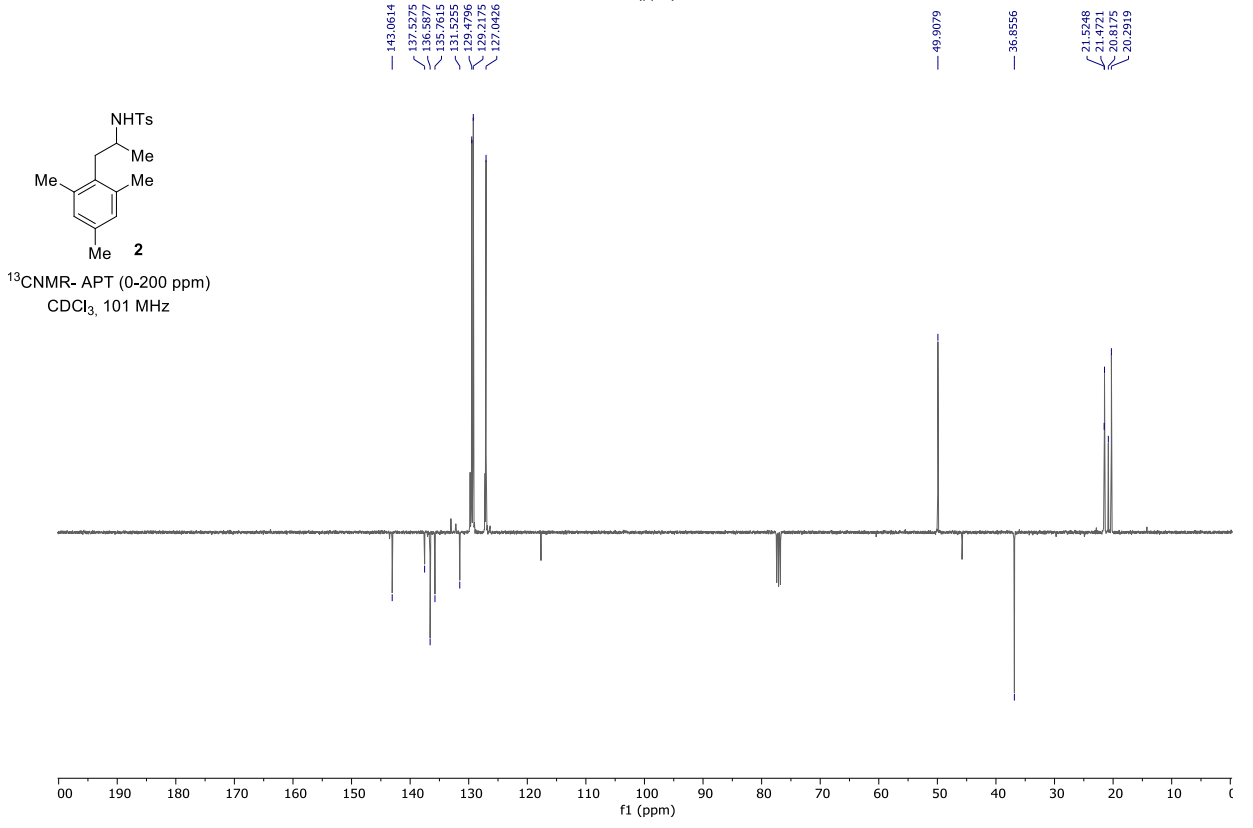
p-Xylene (0.62 mL); FCC–hexane. **28 + 29** (187.4 mg, 93%; **28**:**29**: 3/2 isomeric ratio after purification); colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.88-6.83 (m, 2H), 2.78-2.72 (m, 4H), 2.37 (s, 3H), 2.24 (s, 6H), 2.21 (s, 3H), 1.93-1.91 (m, 4H), 1.36 (s, 18 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.7, 145.8, 144.4, 141.8, 131.5, 130.3, 129.8, 128.2, 126.3, 45.4, 42.5, 41.9, 41.4, 27.5, 27.4, 26.8, 26.3, 18.0, 17.7, 14.2.

^{1}HNMR and ^{13}CNMR of Arylated/Hydroaminated products

1-(2,4,6-Trimethylphenyl)-2-tosylamino-propane (2)

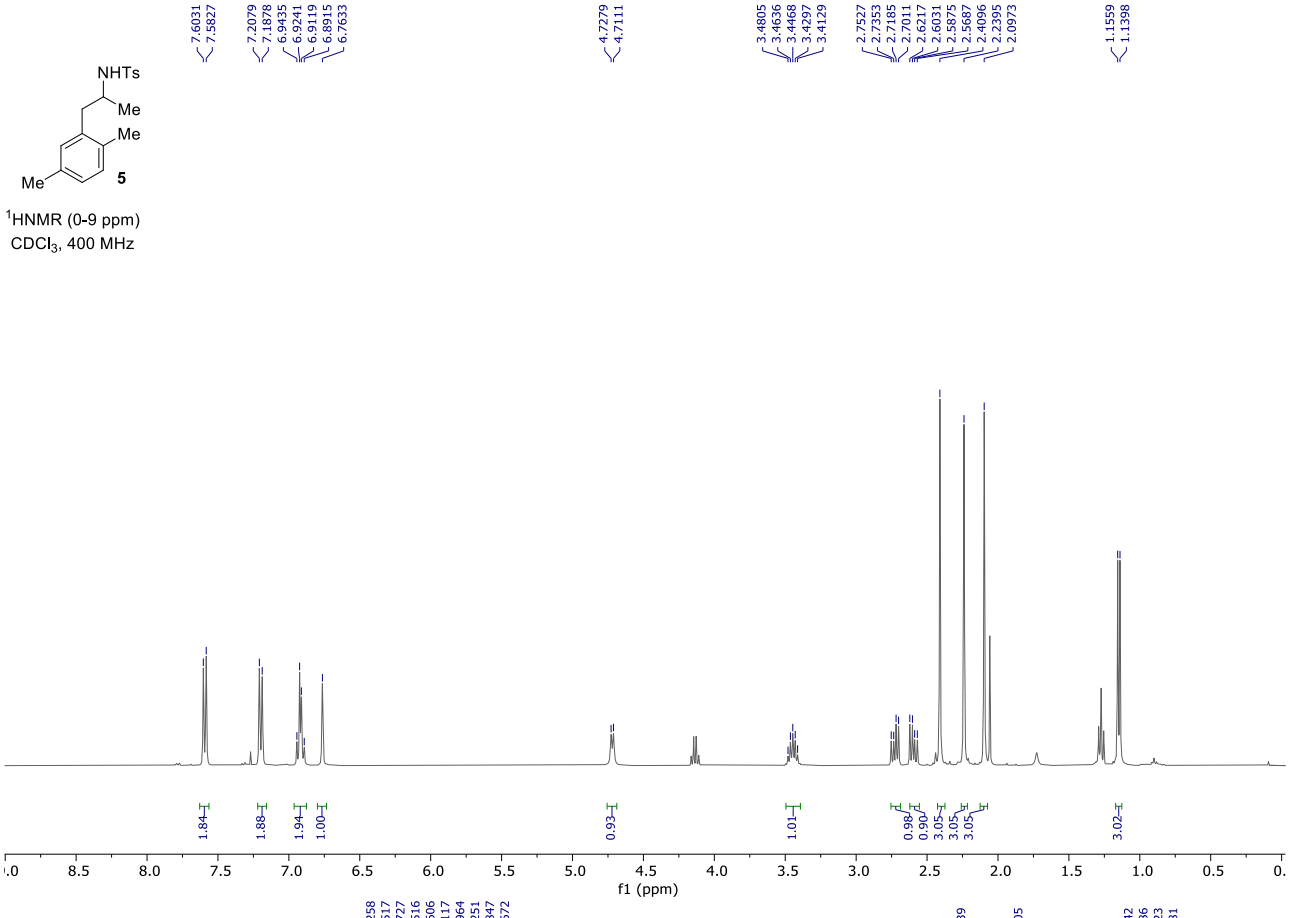


^{1}HNMR (0-9 ppm)
$CDCl_3$, 300 MHz

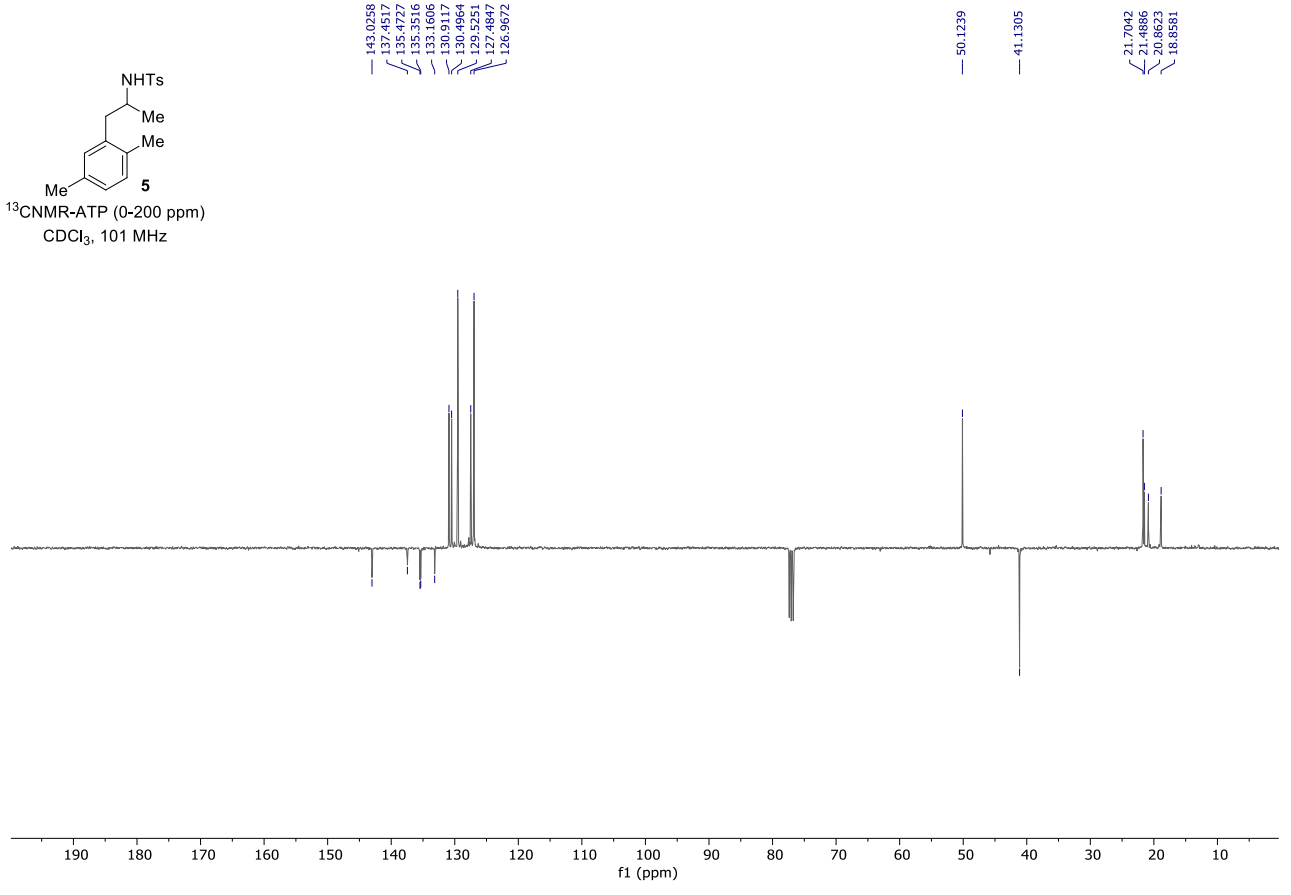


^{13}CNMR- APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2,5-Dimethylphenyl)-2-tosylamino-propane (5)

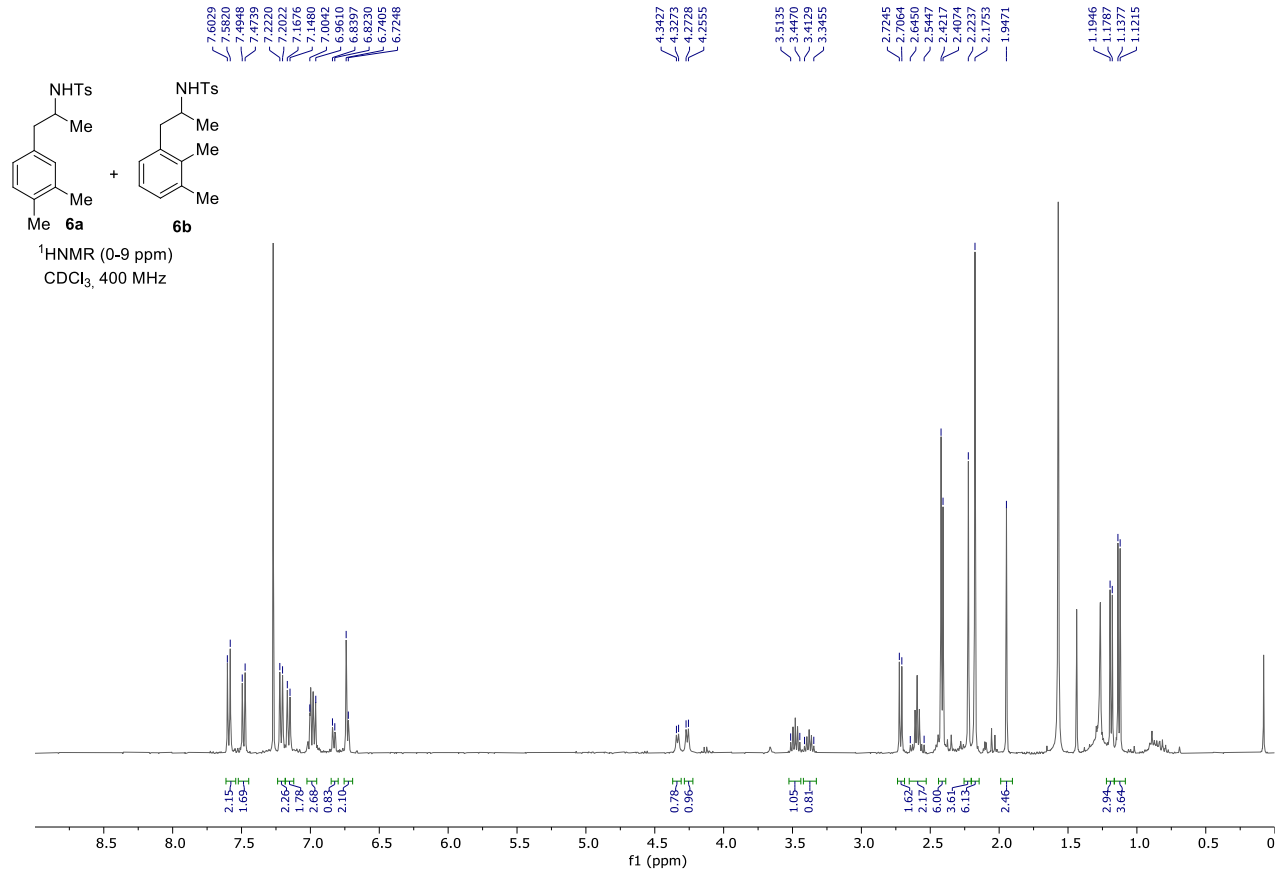


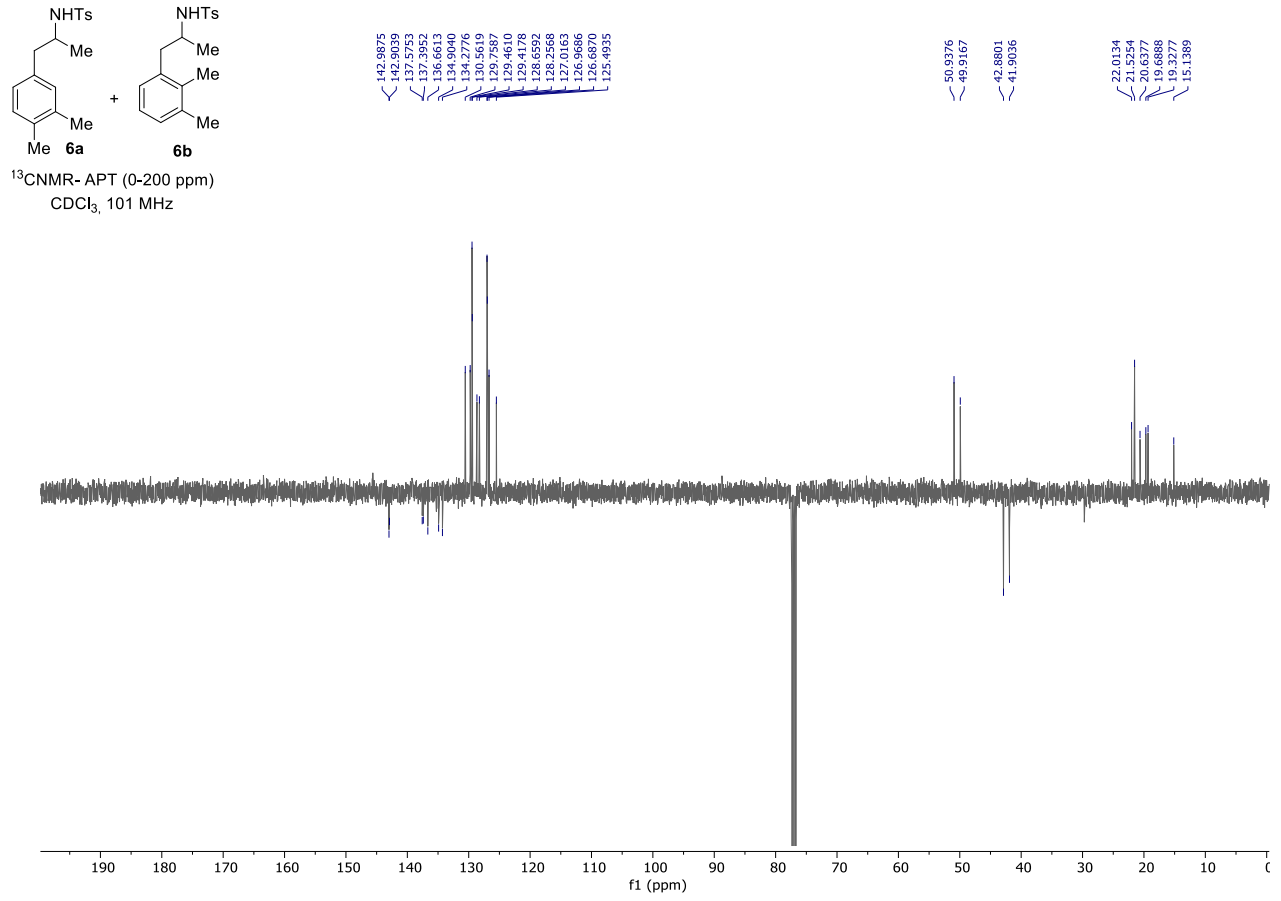
^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



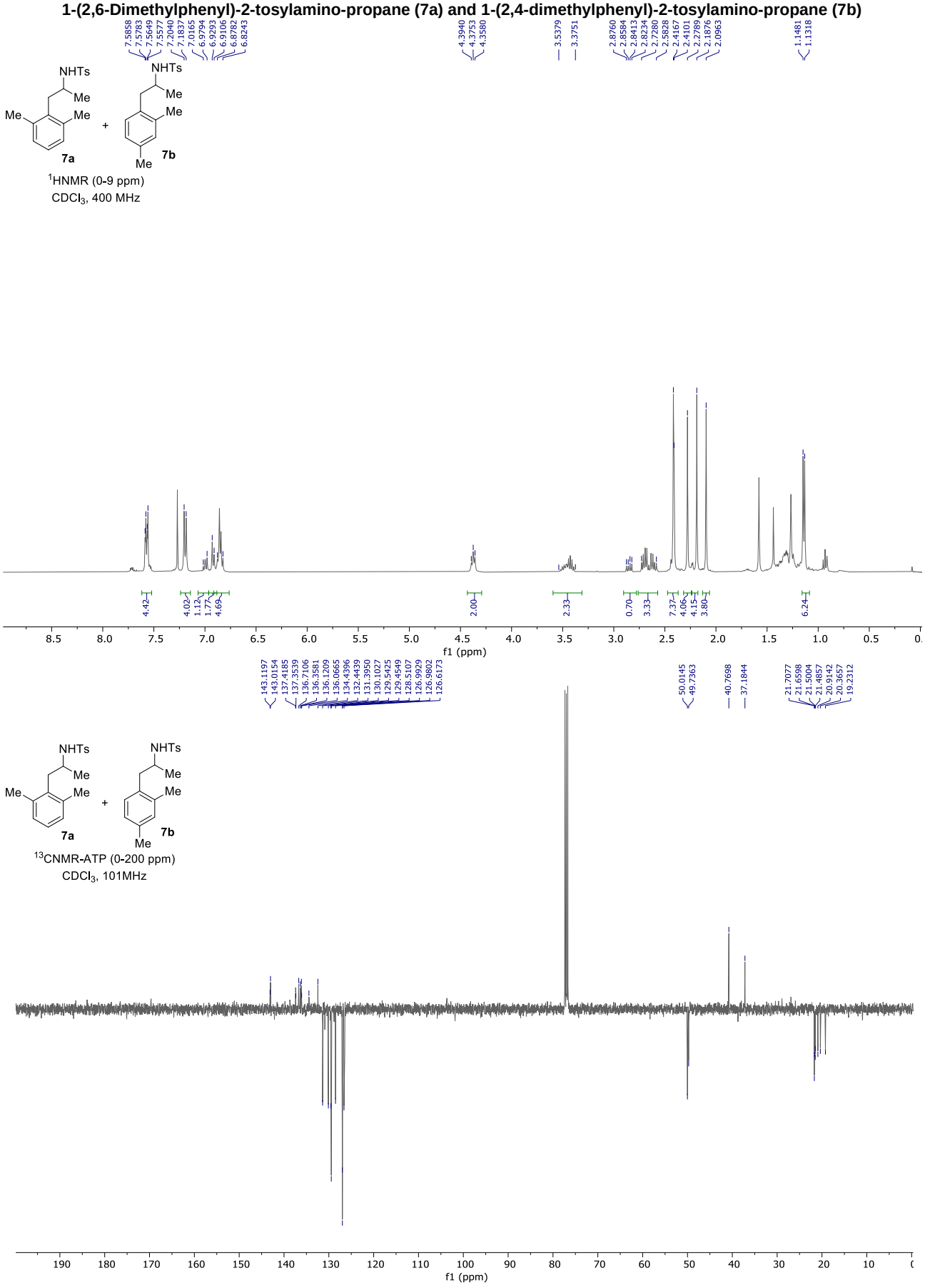
^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101 MHz

1-(3,4-Dimethylphenyl)-2-tosylamino-propane (6a) and 1-(2,3-dimethylphenyl)-2-tosylamino-propane (6b)

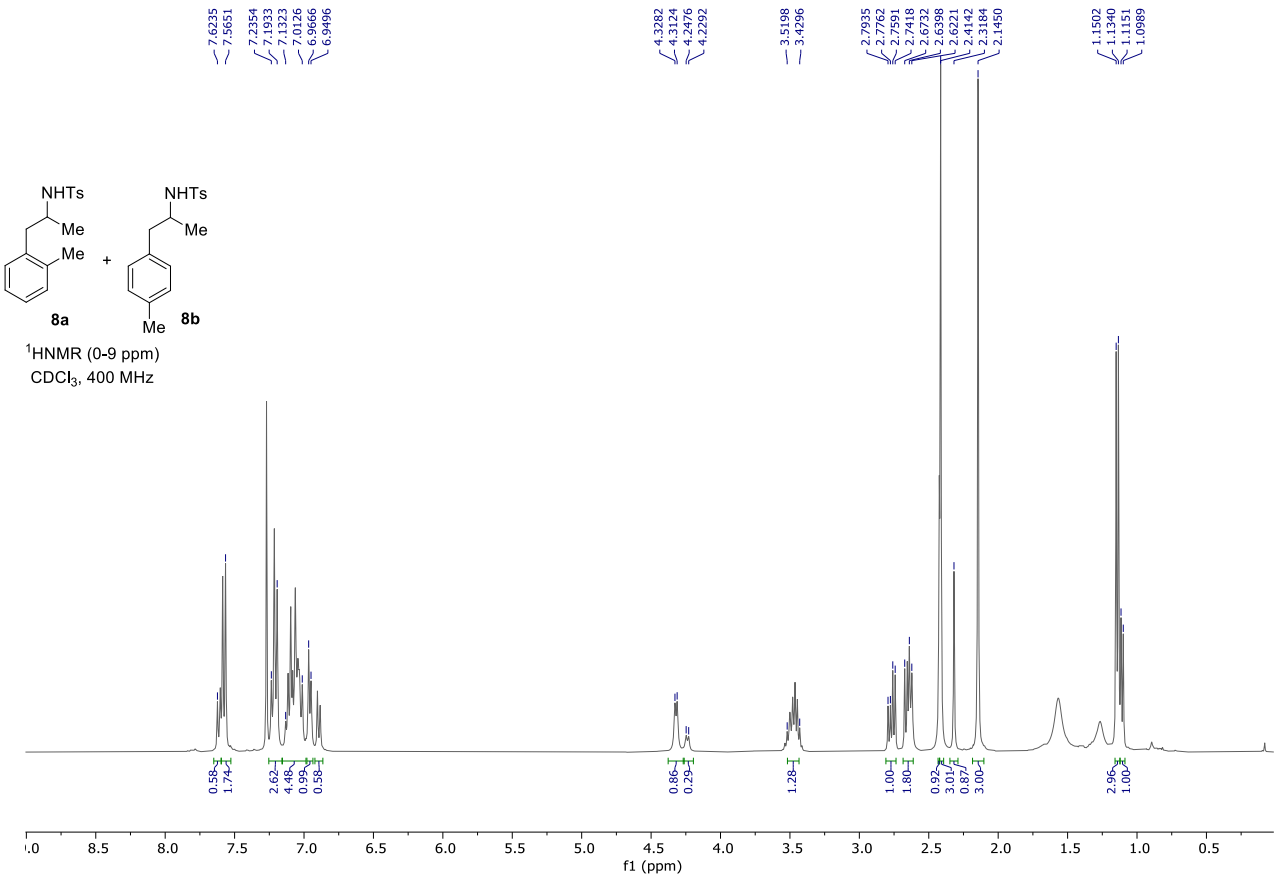


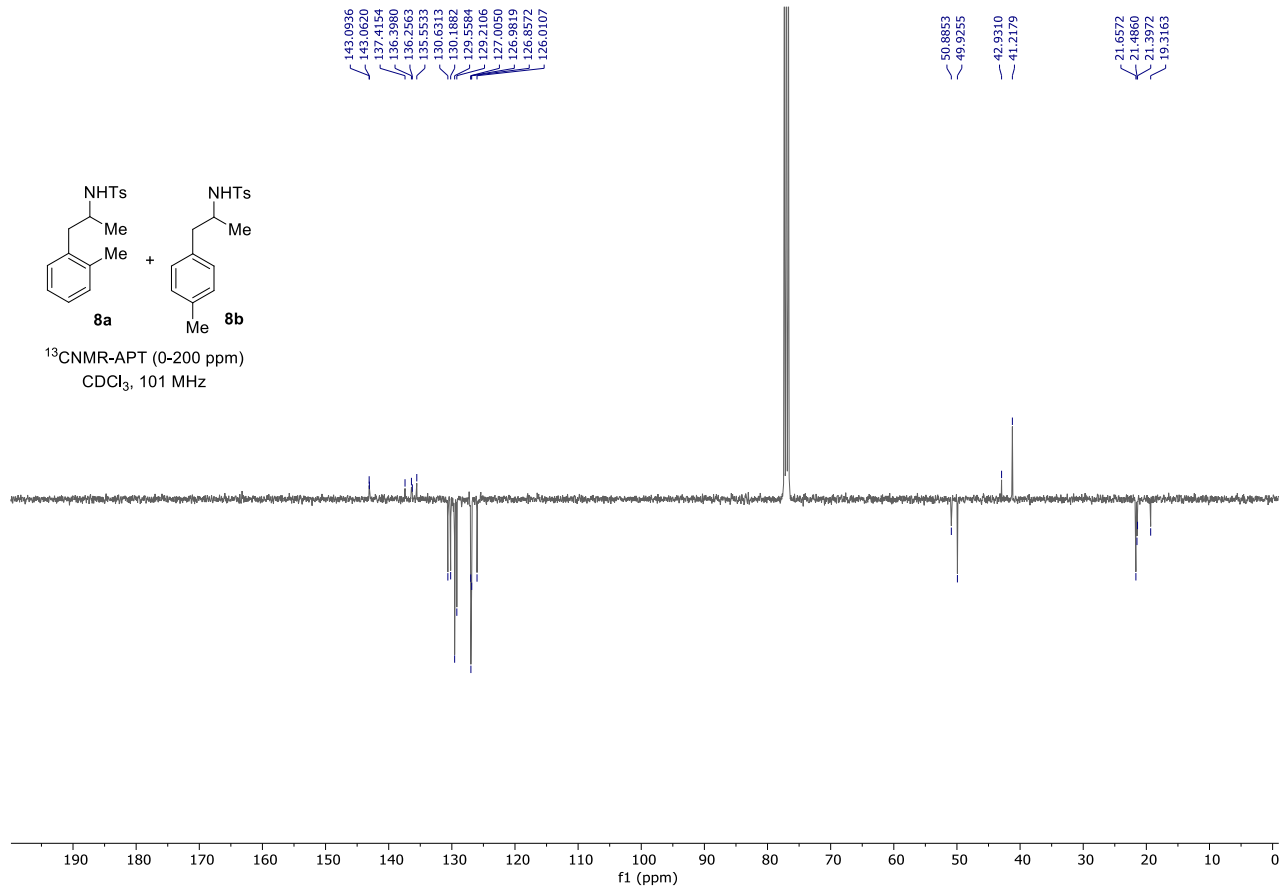


1-(2,6-Dimethylphenyl)-2-tosylamino-propane (7a) and 1-(2,4-dimethylphenyl)-2-tosylamino-propane (7b)

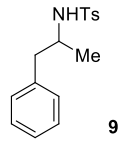


1-(2 -Methylphenyl)-2-tosylamino-propane (8a) and 1-(4-methylphenyl)-2-tosylamino-propane (8b)



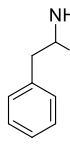


1-Phenyl-2-tosylamino-propane (9)



9

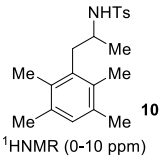
^{1}HNMR (0-10 ppm)
$CDCl_3$, 400 MHz



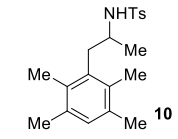
9

^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2,3,5,6-Tetramethylphenyl)-2-tosylamino-propane (10)

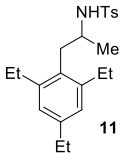


^{1}HNMR (0-10 ppm)
$CDCl_3$, 400 MHz

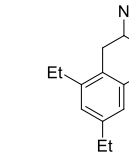


^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2,4,6-Triethylphenyl)-2-tosylamino-propane (11)

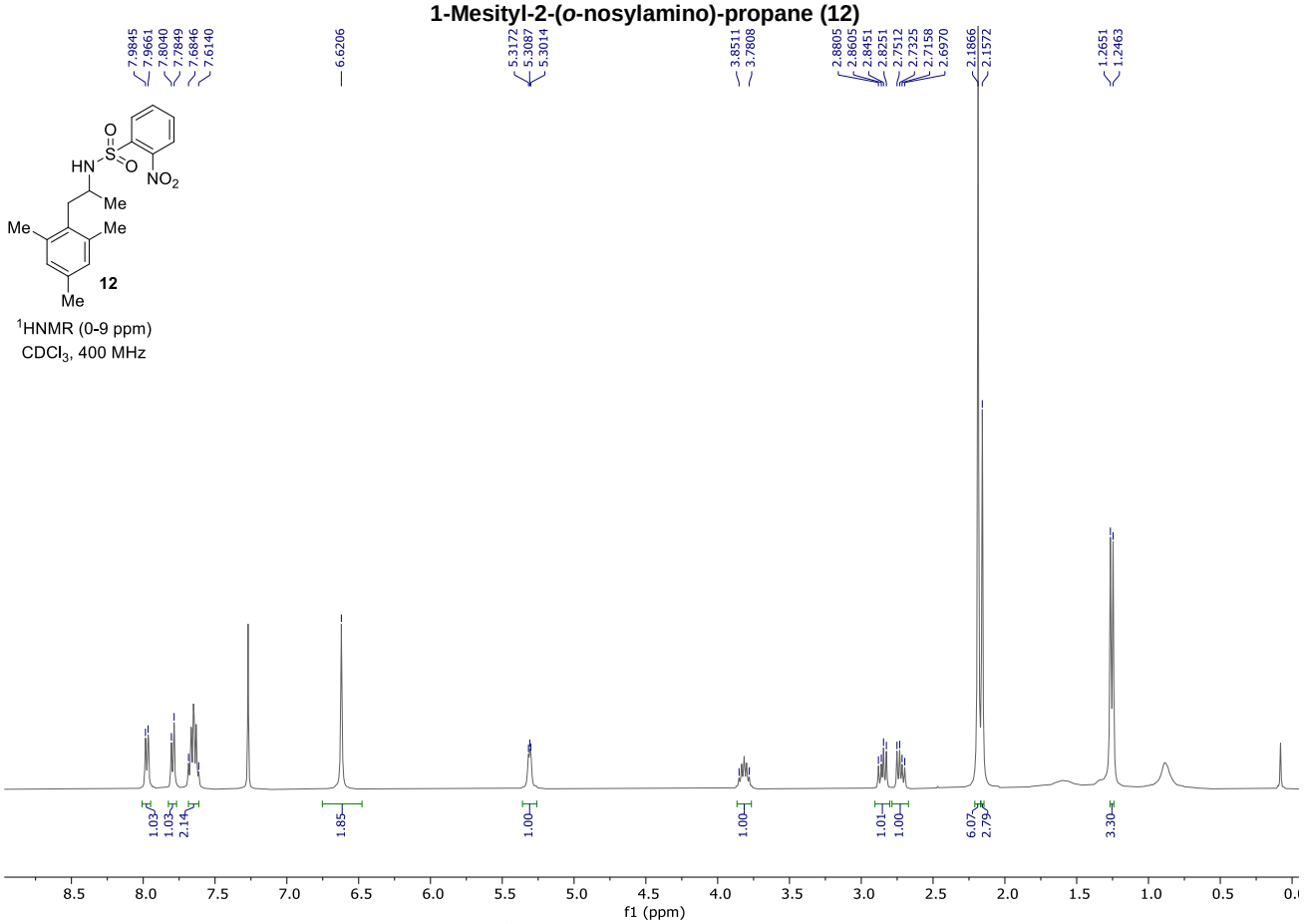


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz

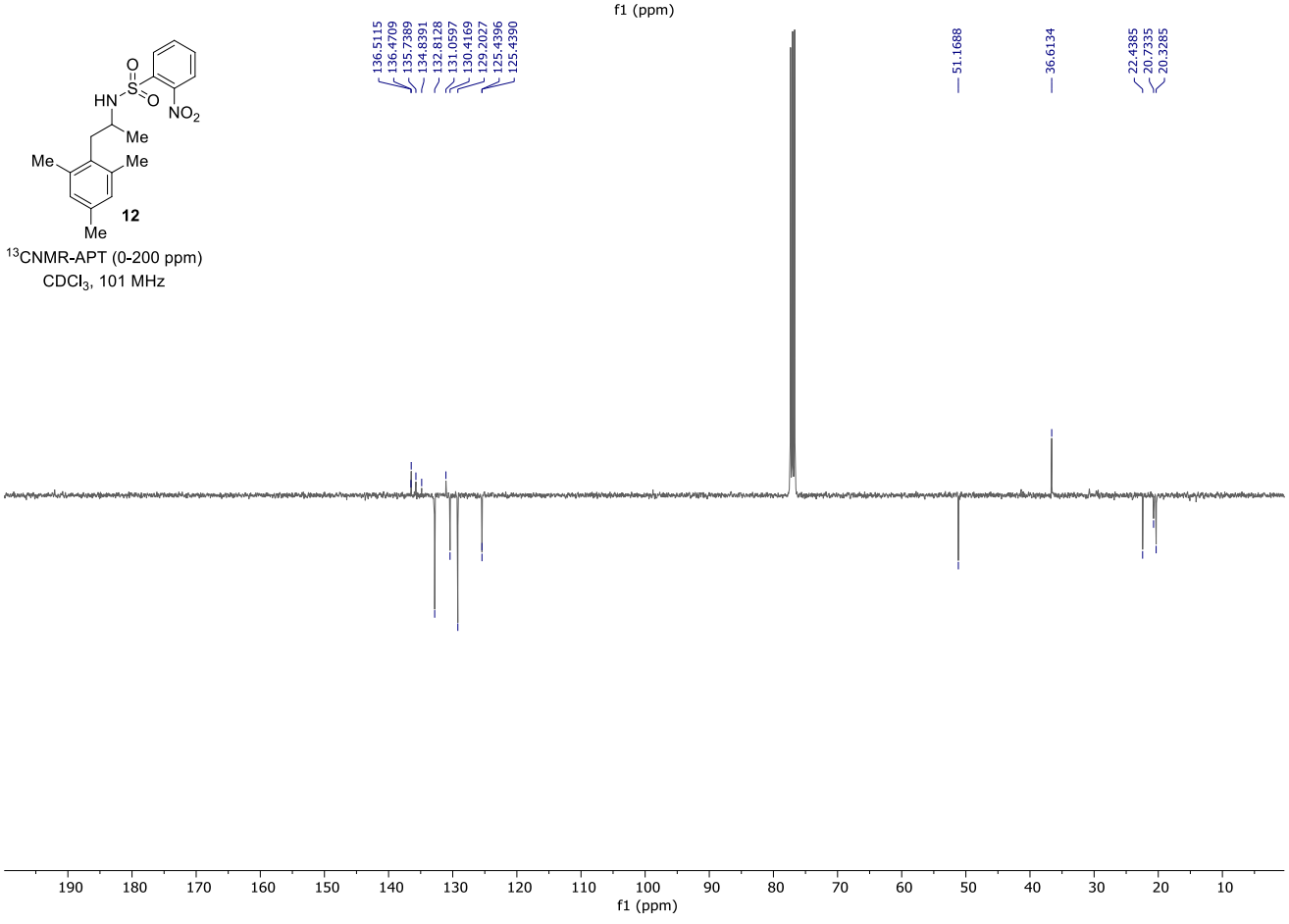


^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-Mesityl-2-(*o*-nosylamino)-propane (12)

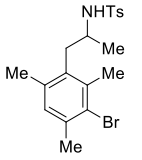


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz

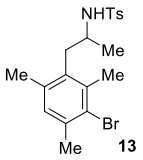


^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(3-Bromo-2,4,6-trimethylphenyl)-2-tosylamino-propane (13)

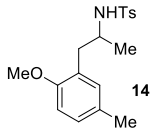


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



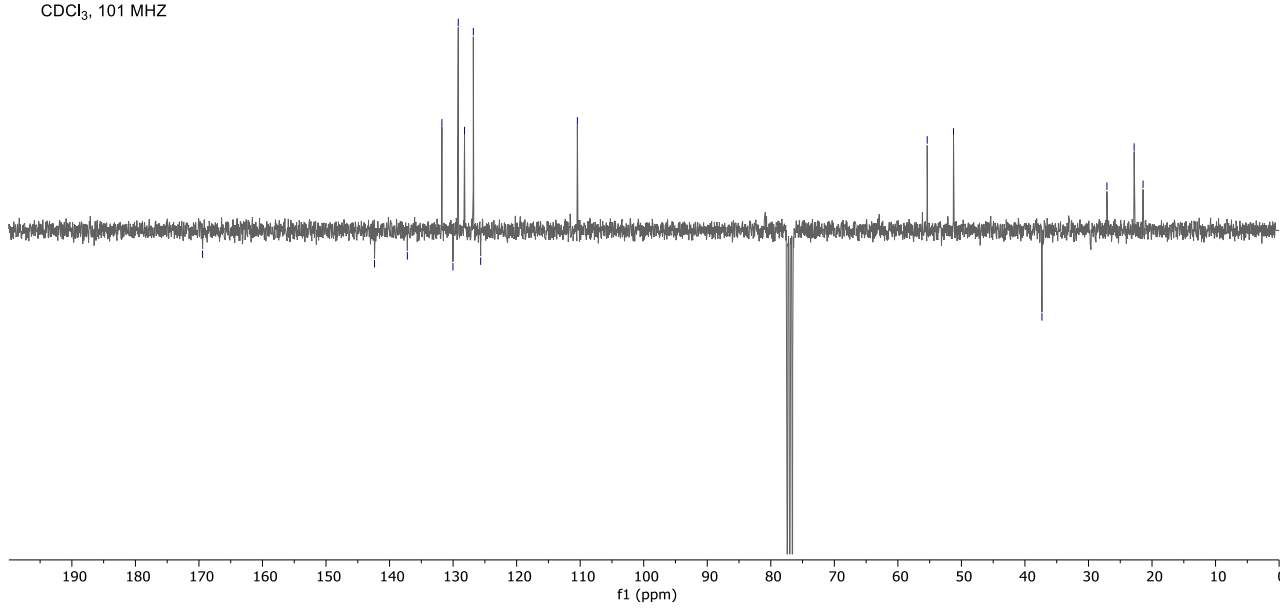
^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2-Methoxy-5-methylphenyl)-2-tosylamino-propane (14)

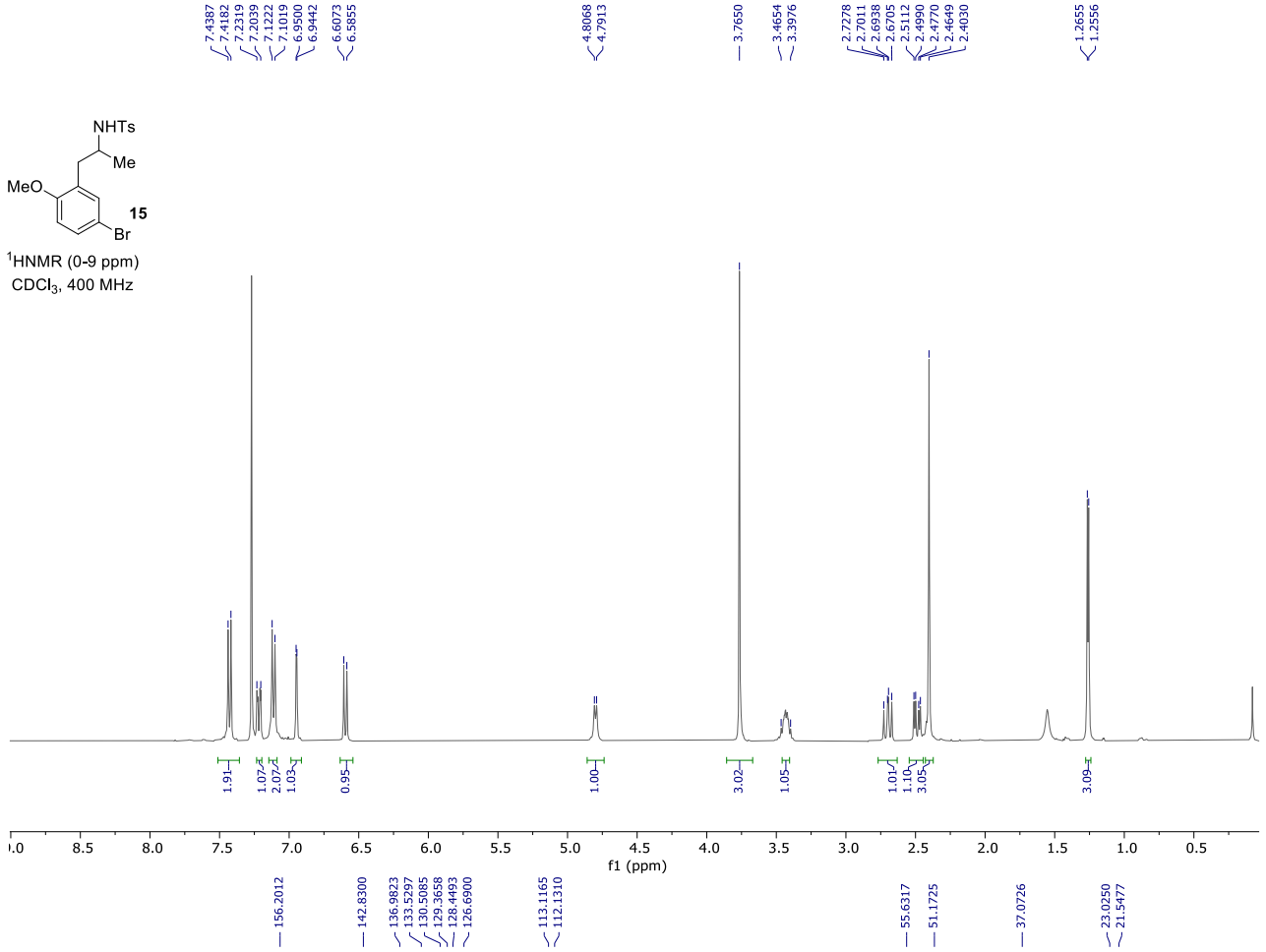


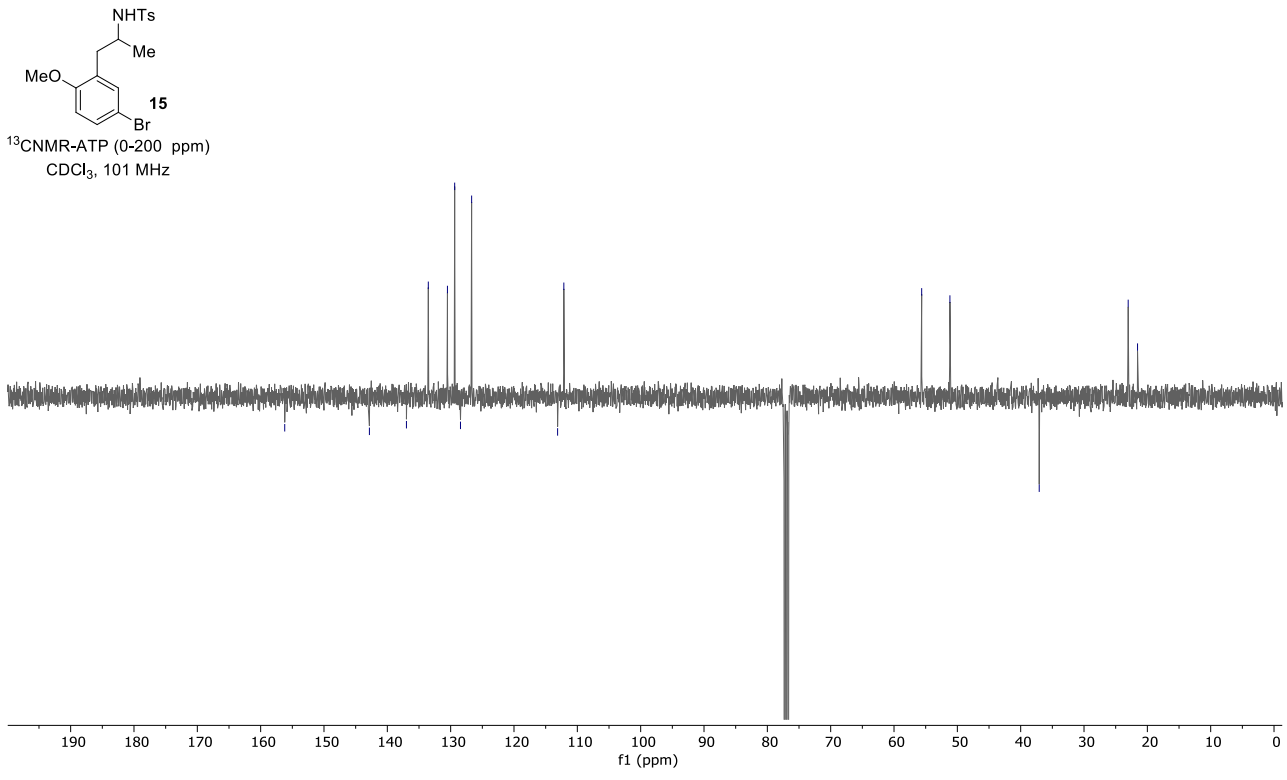
^{1}HNMR (0-9 ppm)
$CDCl_3$, 300 MHZ

^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHZ

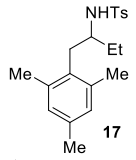


1-(5-Bromo-2-methoxyphenyl)-2-tosylamino-propane (15)

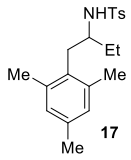




1-(2,4,6-Trimethylphenyl)-2-tosylamino-butane (17)

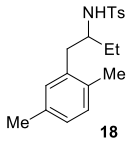


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



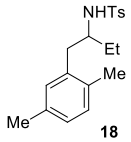
^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2,5-Dimethylphenyl)-2-tosylamino-butane (18)



18

^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz

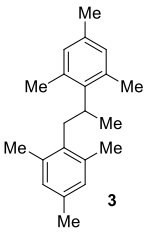


18

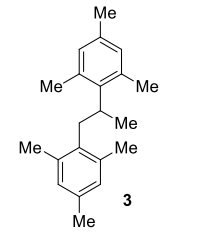
^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

^{1}HNMR and ^{13}CNMR of Diarylated products

1,2-Bis(2,4,6-trimethylphenyl)-propane (3)

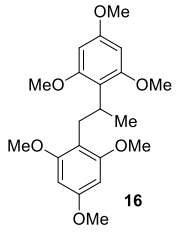


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



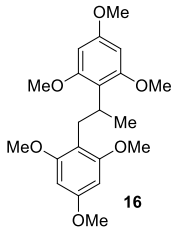
^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1,2-bis(2,4,6-trimethoxyphenyl)-propane (16)



16

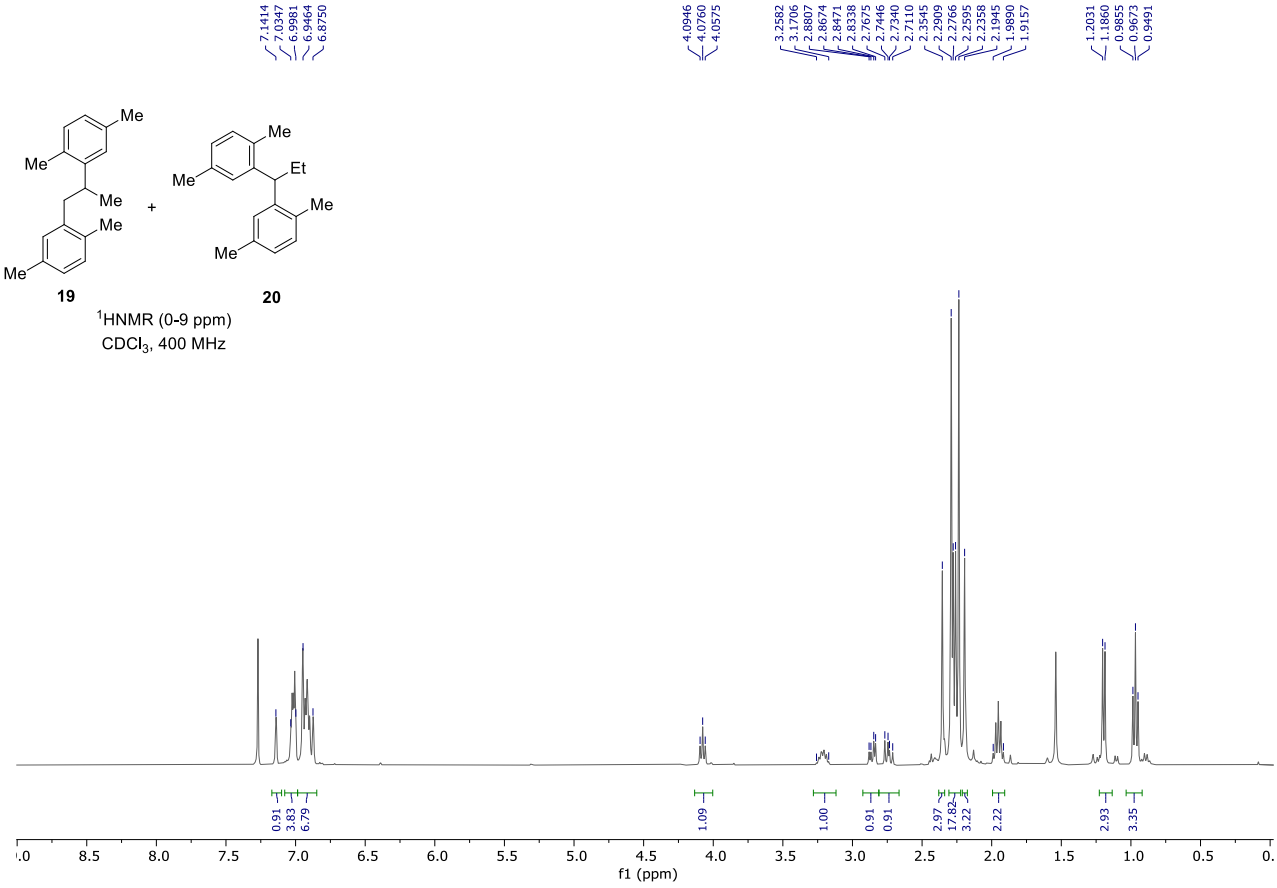
^{1}HNMR (0-9 ppm)
$CDCl_3$, 300 MHz



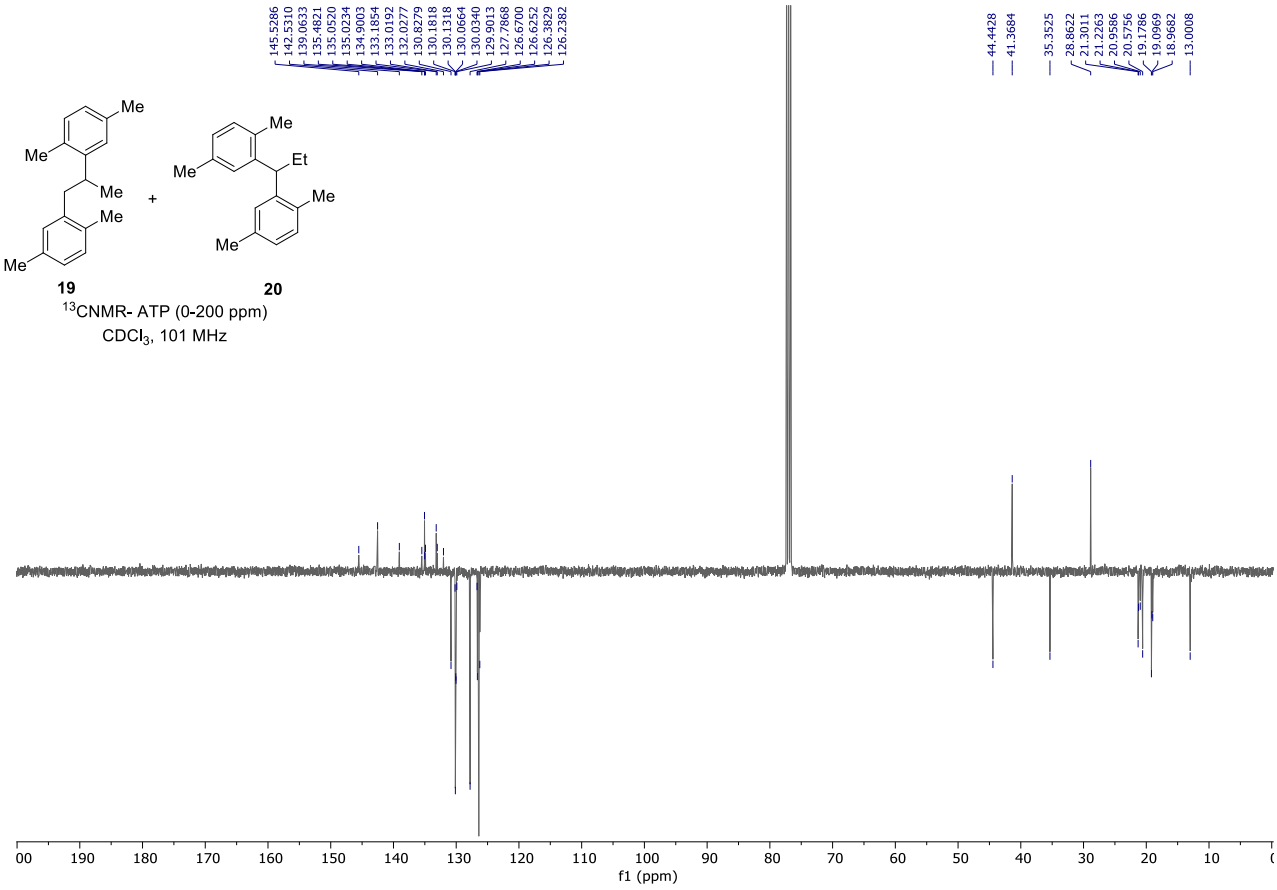
16

^{13}CNMR (0-200 ppm)
$CDCl_3$, 95 MHz

1,2-Bis(2,5-dimethylphenyl)-propane (19) and 1,1-bis(2,5-trimethylphenyl)-propane (20)

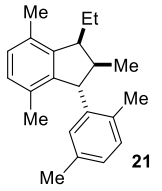


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz

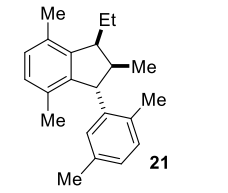


^{13}CNMR- ATP (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2,5-Dimethylphenyl)-3-ethyl-2,4,7-trimethyl-indane (21)

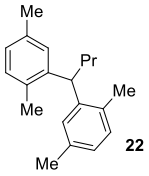


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



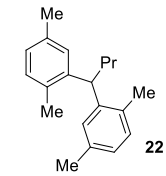
^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101 MHz

1,2-Bis(2,5-Dimethylphenyl)-butane (22)



22

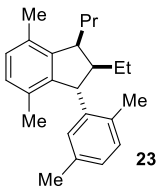
^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



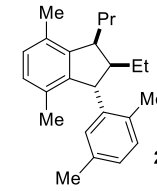
22

^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

1-(2,5-Dimethylphenyl)-2-ethyl-4,7-dimethyl-3-propyl-indane (23)

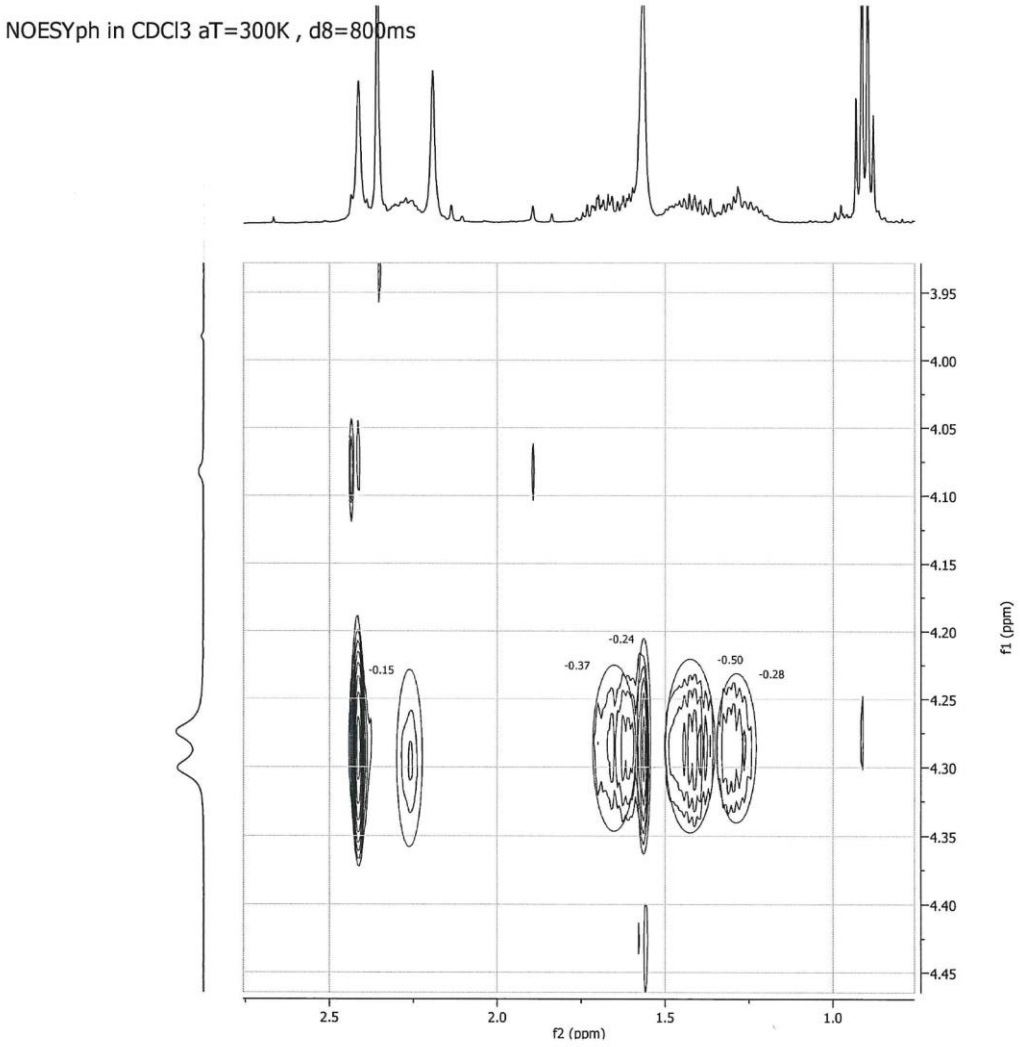


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz

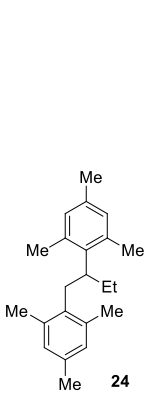


^{13}CNMR-APT (0-200 ppm)
$CDCl_3$, 101 MHz

NOESY experiment of compound 23

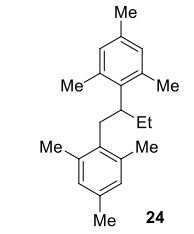


1,2-Bis(2,4,6-trimethylphenyl)-butane (24)



24

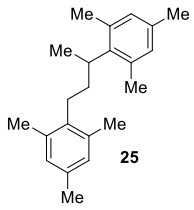
^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



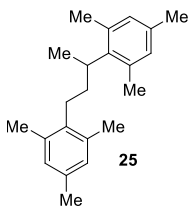
24

^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101 MHz

1,3-Bis(2,4,6-trimethylphenyl)-butane (25)

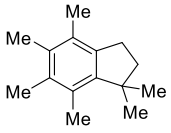


^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



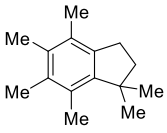
^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101 MHz

1,1,4,5,6,7-Hexamethyl-2,3-dihydro-indane (26)



26

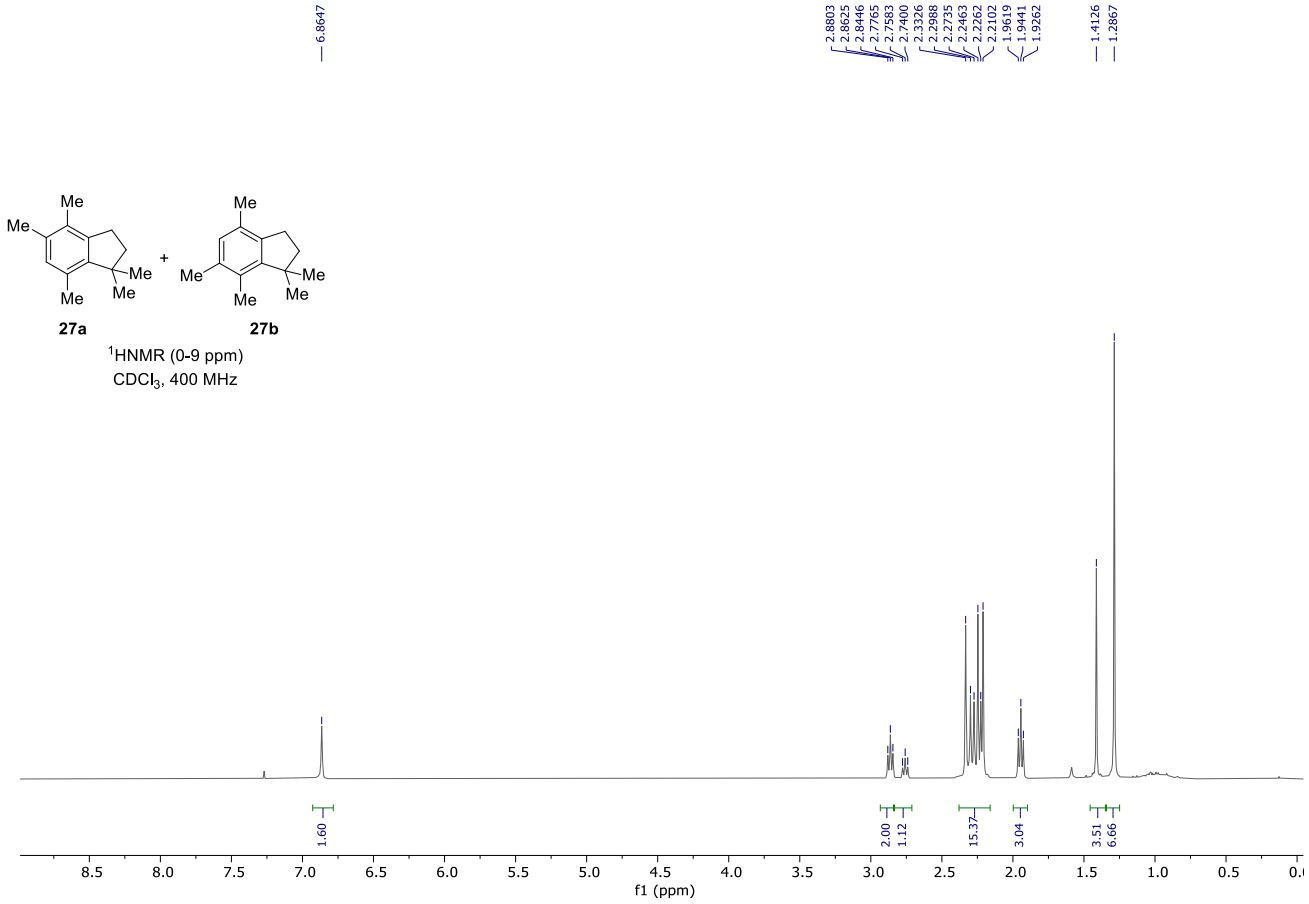
^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



26

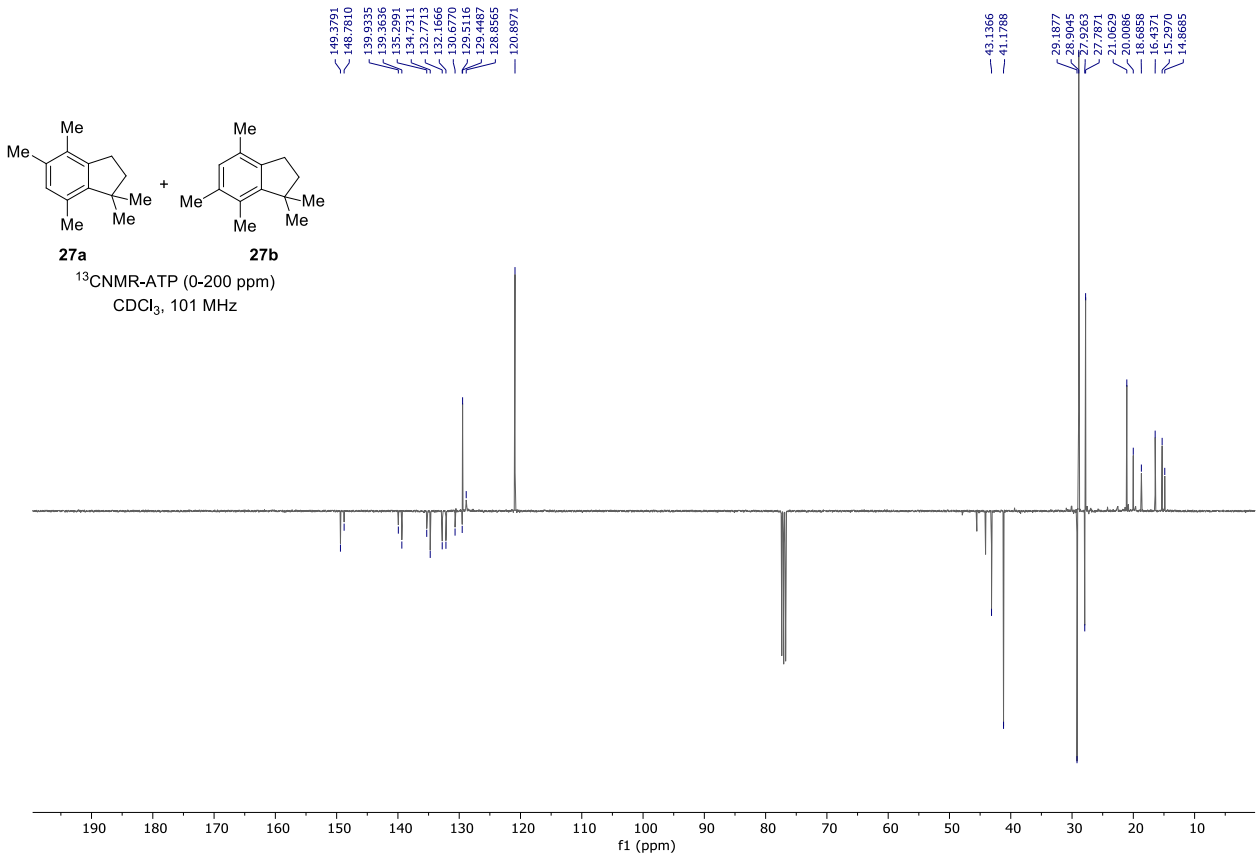
^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101MHz

1,1,4,5,7-Pentamethyl-2,3-dihydro-indane (27a) and 1,1,4,6,7-Pentamethyl-2,3-dihydro-indane (27b)



27a **27b**

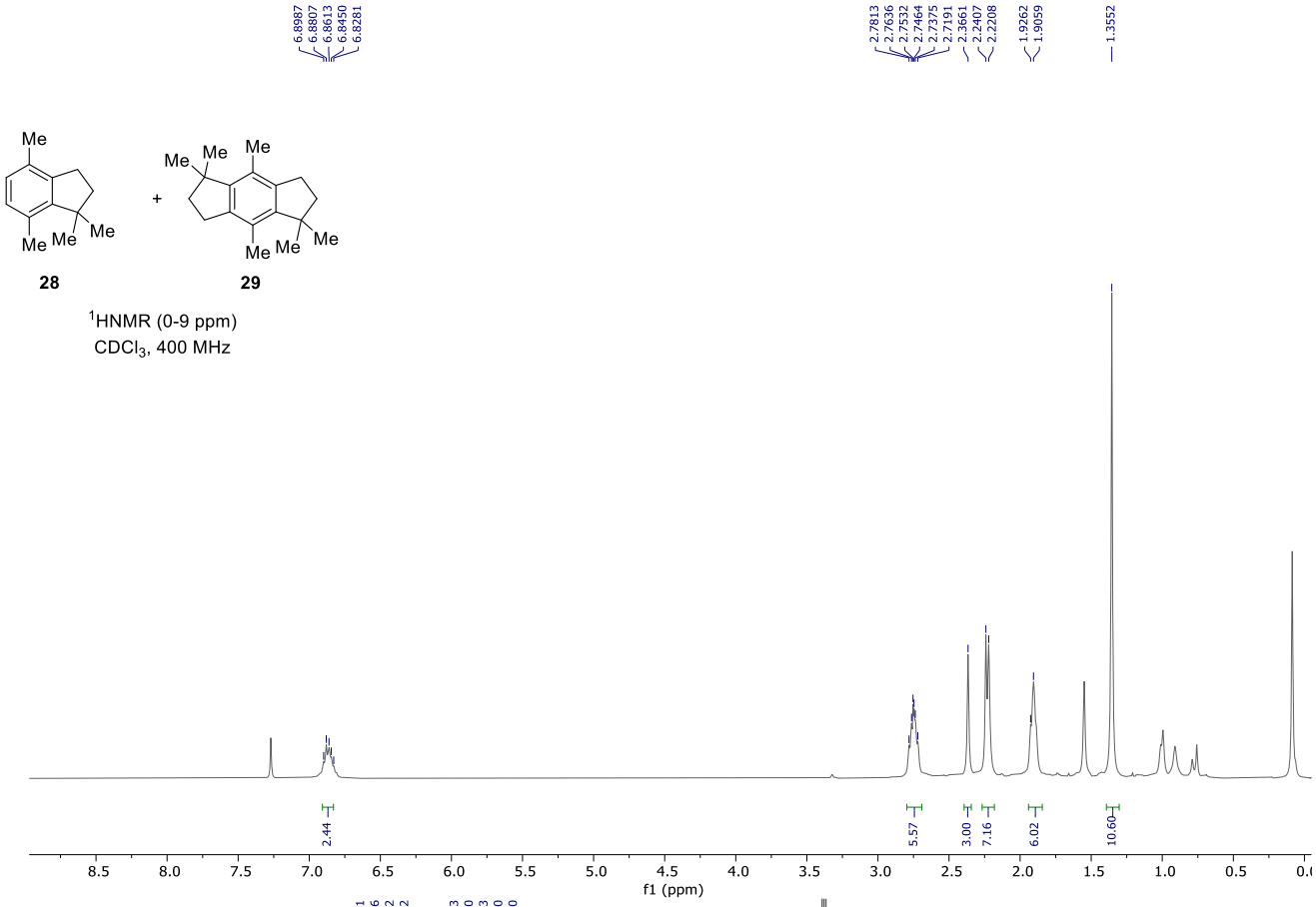
^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



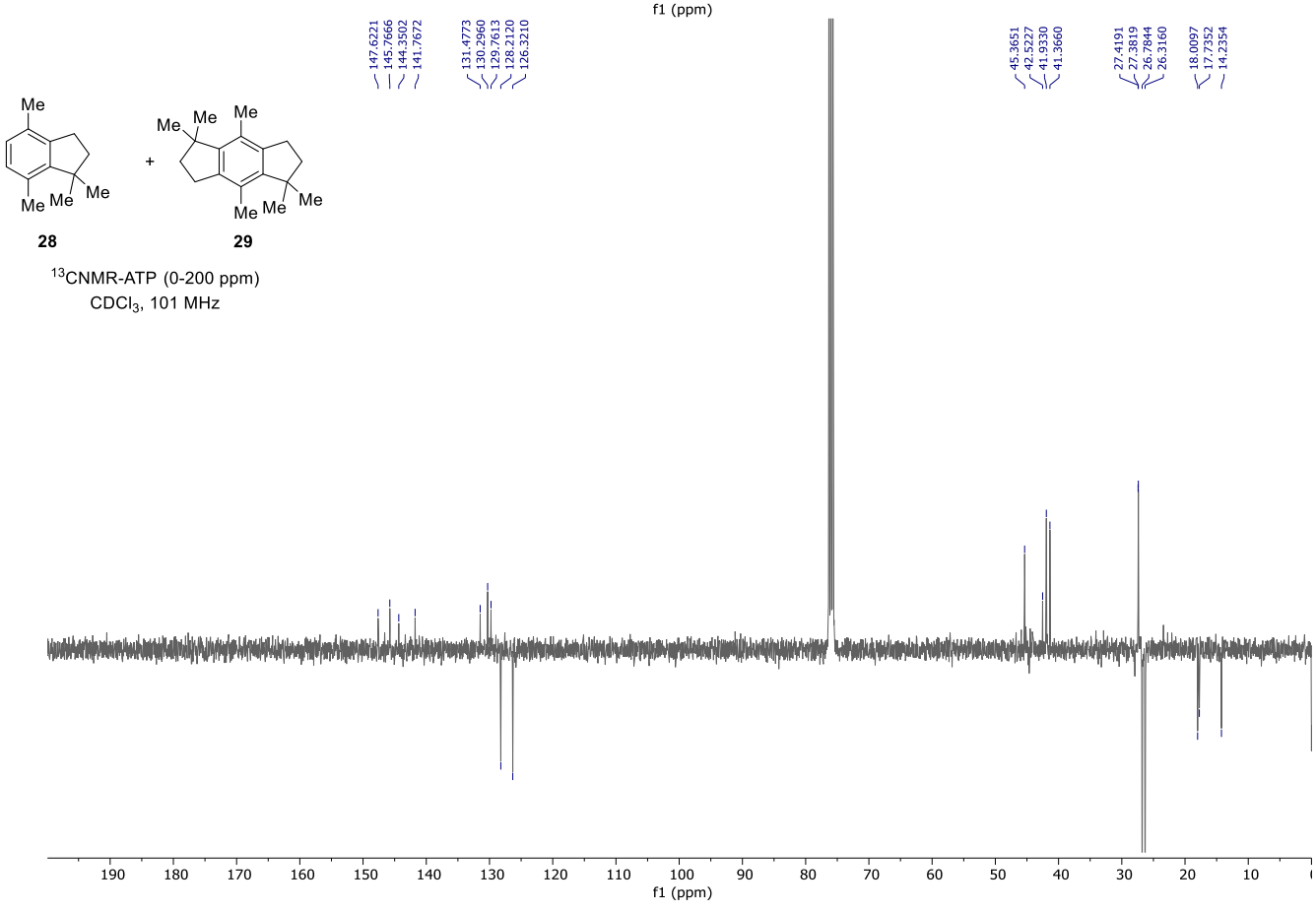
27a **27b**

^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101 MHz

1,1,4,5,6,7-Hexamethyl-2,3-dihydro-indane (28) and 1,1,4,5,5,8-hexamethyl-hydrindacene (29)



^{1}HNMR (0-9 ppm)
$CDCl_3$, 400 MHz



^{13}CNMR-ATP (0-200 ppm)
$CDCl_3$, 101 MHz