Electronic Supplementary Material (ESI) for Chemical Communications

Nickel(0)/NaHMDS Adduct-Mediated Intramolecular Alkylation of Unactivated Arenes Via a Homolytic Aromatic Substitution Mechanism

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Supporting Information

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General Experimental Considerations

General: All non-aqueous reactions were run under argon atmosphere with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents obtained by filtration through drying columns or by distillation over sodium (1,4-dioxane). H_2O as solvent was degassed and saturated with argon prior to use. Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), and/or ceric ammonium molybdate.

Nuclear magnetic resonance spectra were recorded either on 300 or 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ = 7.26 ppm). The data was reported as follows: chemical shift, multiplicity (s = singlet, s (br) = broad singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublets of doublets, t = triplet, app. t = apparent triplet, q = quadruplet and m = multiplet), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.16 ppm) as the internal standard. Infrared spectra (FTIR) are reported in reciprocal centimeters (cm^{-1}). Melting points are uncorrected.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

Scheme 1. Intermolecular direct alkylation attempts (^{1}H NMR yields using trimethoxybenzene as internal standard)

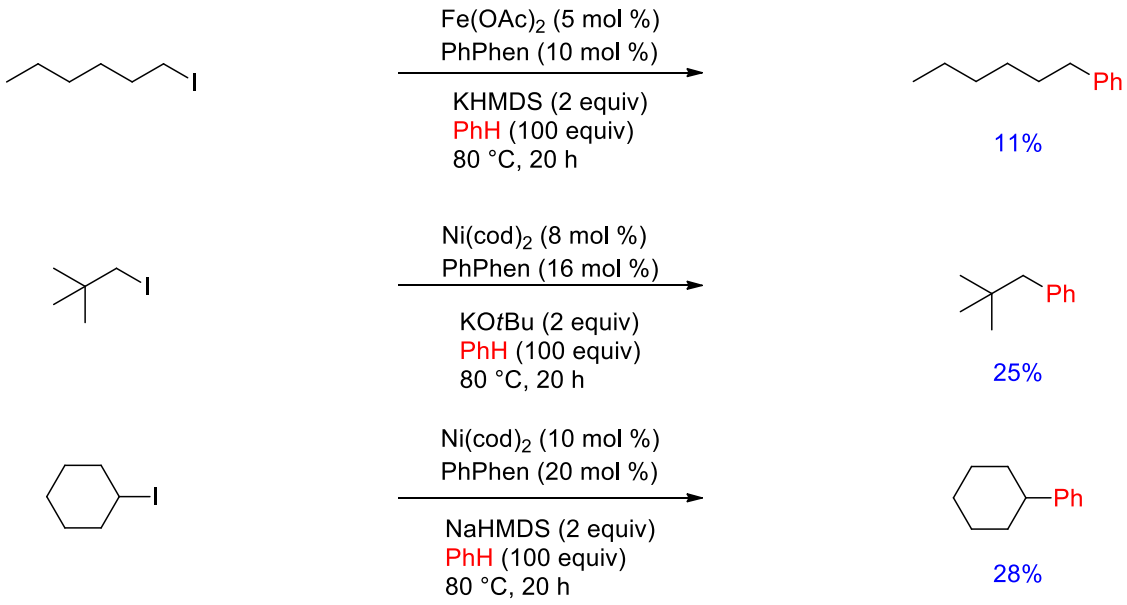
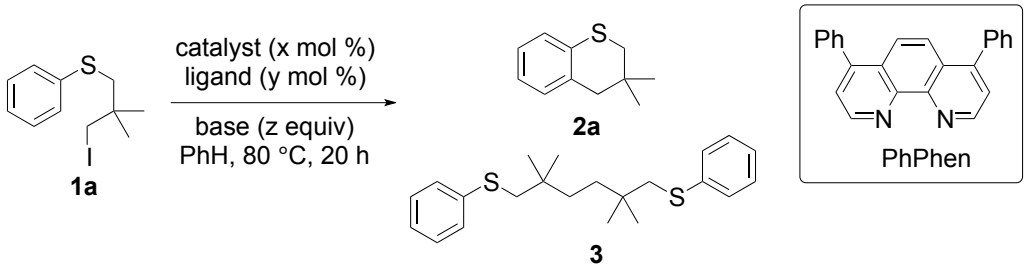


Table 1. Reaction Optimization

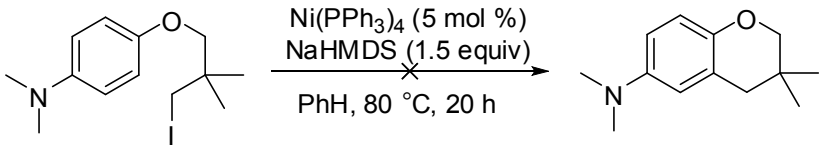


				yield (%)[a]		
entry	catalyst (x)	ligand (y)	base (z)	**1a**	**2a**	**3**
1	$Fe(OAc)_2$ (10)	PhPhen (20)	KO*t*Bu (2.0)	18	37	0
2	$Fe(OAc)_2$ (10)	PhPhen (20)	NaHMDS (2.0)	72	0	0
3	$NiCl_2$ (10)	PhPhen (20)	NaHMDS (2.0)	37	25	0
4	$Ni(cod)_2$ (10)	PhPhen (20)	NaHMDS (2.0)	0	47	10
5	$Ni(PPh_3)_4$ (10)	PhPhen (20)	NaHMDS (2.0)	0	55	13
6	$Ni(PPh_3)_4$ (10)	---	NaHMDS (2.0)	0	73	8
7	$Ni(PPh_3)_4$ (5)	---	NaHMDS (2.0)	0	68	4
8	$Ni(PPh_3)_4$ (5)	---	LiHMDS (2.0)	51	25	5
9	$Ni(PPh_3)_4$ (5)	---	KHMDS (2.0)	0	0	0

10	$Ni(PPh_3)_4$ (5)	---	KO*t*Bu (2.0)	59	27	0
11	**$Ni(PPh_3)_4$ (5)**	**---**	**NaHMDS (1.5)**	**5**	**75**	**4**
12	---	---	NaHMDS (1.5)	100	0	0
13[b]	---	---	NaHMDS (1.5)	82	0	0
14	$Ni(PPh_3)_4$ (5)	---	---	100	0	0

[a] H NMR yield using trimethoxybenzene as internal standard. [b] Reaction was run at 120 °C

Scheme 2. Cyclization of substrates containing an oxygen tether



Crude GC/MS (EI) shows starting material as well as several compounds having the fragmentation pattern of *N,N,*4-trimethylaniline, thus indicating that the aryl translocation from oxygen to carbon has taken place in the course of the reaction.[1]

Scheme 3. Radical scavenger studies

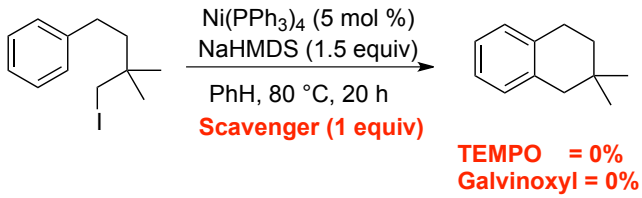
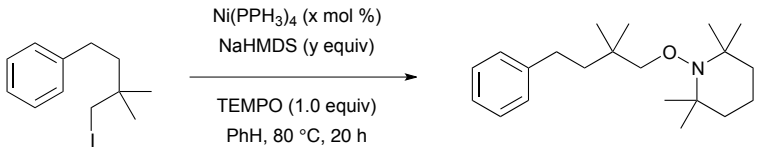


Table 2. TEMPO Scavenging Experiments



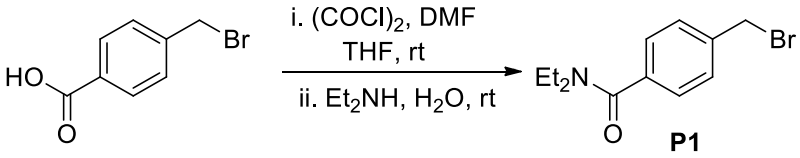
4a **6a**

			yield (%)[a]	
entry	$Ni(PPh_3)_4$ (x)	NaHMDS (y)	6a	4a
1	5	1.5	33	63
2	5	---	5	93
3	---	1.5	0	93
4	---	---	0	96

[a]Isolated yields.

Synthesis of starting materials

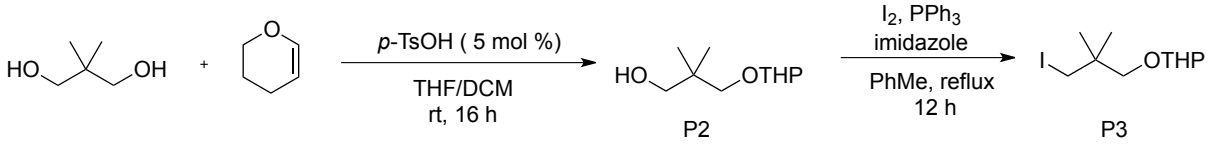
4-(bromomethyl)-*N,N*-diethylbenzamide (P1):

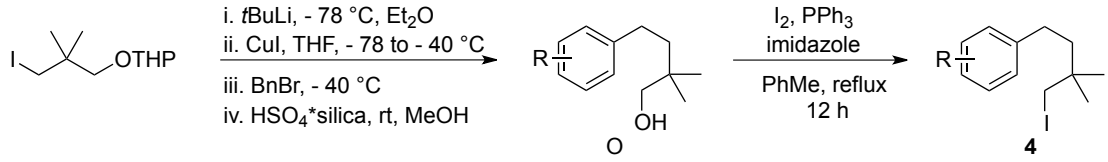


To a solution of the benzyl bromide (2.3 mmol, 1.0 equiv) in THF (10 mL) at rt was added oxalyl chloride (2.56 mmol, 1.1 equiv) dropwise over 40 min. The reaction was stirred for a further 30 min at rt. The residue was concentrated *in vacuo*, dissolved in THF, then added to a rapidly stirring solution of diethylamine (4.6 mmol, 2.0 equiv) in H_2O. The slightly exothermic reaction was allowed to cool down to rt, then extracted with EtOAc (3x25 mL). Combined organic layers were dried with Na_2SO_4, filtered and concentrated to give a white solid (506 mg, 81% yield), which was used as is.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.36 (m, 4H), 4.62 & 4.52 (s, 2H), 3.58-3.27 (m, 4H), 1.27-1.14 (m, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.7, 138.7, 138.4, 137.4, 129.2, 128.7, 126.9, 126.8, 45.8, 43.3, 39.4, 32.8, 14.3, 12.9 ppm. **IR** (film) cm^{-1} 2971, 1628, 1459. **HRMS** (ESI Pos): expe. for $C_{12}H_{16}BrNNaO$ $[M+Na]^+$: 292.03157 m/z, calc. 292.03075 m/z. **mp**: 56-58 °C.

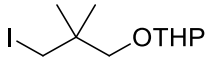
Route A





Synthesis of precursor **P1**

Mono-protected diol **P2** was synthesized according to the literature procedure and is in accordance to the given spectra.[2]



2-(3-iodo-2,2-dimethylpropoxy)tetrahydro-2H-pyran (P2):

To a solution of **P1** (28.5 mmol, 1.0 equiv) in toluene (100 mL) was added I_2 (31.3 mmol, 1.1 equiv), PPh_3 (31.3 mmol, 1.1 equiv) and imidazole (113.8 mmol, 4.0 equiv). The reaction was stirred under reflux for 12 h (or until complete by TLC). The reaction was allowed to cool down to rt, then quenched with a saturated aqueous solution of $NaHSO_3$. The layers were separated, and the organic layer was concentrated. The resulting solid suspension was triturated several times with hexanes. The filtrate was concentrated and then purified by flash chromatography in 0-5% EtOAc/Hex, giving 6.26 g (74%) of a clear, colourless oil.

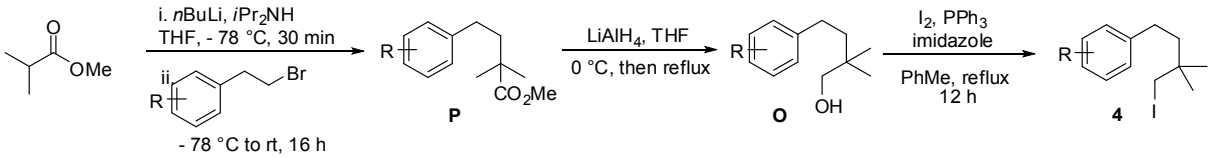
^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.56 (s, 1H), 3.86-3.78 (m, 1H), 3.54-3.45 (m, 2H), 3.21 (q, 2H, *J* = 9.7 Hz), 3.09 (d, 1H, *J* = 9.7 Hz), 1.82-1.46 (m, 6H), 1.04 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 98.9, 74.4, 61.9, 34.9, 30.5, 25.5, 24.5, 24.4, 20.7, 19.3. **IR** (film) cm^{-1} 2939, 2869, 1473, 1379, 1350, 1200, 1182, 1121, 1063, 1032, 995, 970, 903, 869, 815, 757, 609. **HRMS** (ESI, Pos) calcd for $C_{10}H_{19}Na_2O_2$ $[M+Na]^+$: 321.0322 m/z, found 321.0320 m/z.

Step 1: General procedure for the synthesis of alcohols **O**

To a solution of **P2** (6.9 mmol, 2.3 equiv) in Et_2O (7.0 mL) in a flame-dried flask under Argon was cannulated *t*BuLi (1.5 *M* in pentane, 14.4 mmol, 4.8 equiv) at – 78 °C. The reaction was stirred at – 78 °C for 1 h, then allowed to warm up to rt in 5 min. The resulting organolithium was then cannulated to a suspension of CuI (3.6 mmol, 1.2 equiv) in THF (6 mL) at – 78 °C. The reaction was transferred to a cryostat bath at – 40 °C. After 30 min, the corresponding benzyl bromide (3.0 mmol, 1.0 equiv) was added dropwise (neat, as a solution in THF if solid), and the reaction was stirred at – 40 °C for 16 h. The reaction was quenched with a saturated aqueous ammonium sulfate solution (20 mL), filtered, and extracted with ether (3x25 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, and

concentrated. The concentrate was dissolved in 6 mL MeOH, and 225 mg of HSO_4.silica was added. The reaction was stirred for 30 min at rt, then filtered and concentrated.

Route B



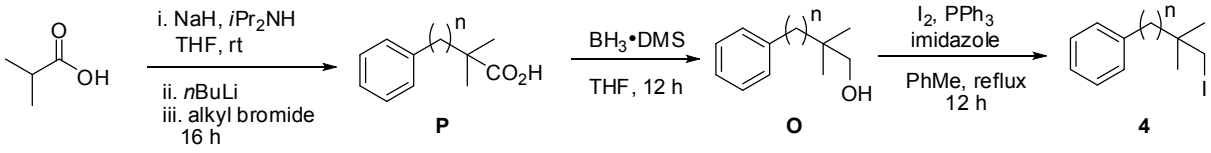
Step 1: General procedure for the synthesis of methyl esters **P**

To a solution of *i*Pr_2NH (1.2 equiv) in THF (0.33 mL/mmol *i*Pr_2NH) at 0 °C was added *n*BuLi (2.5 *M* in hexanes, 1.25 equiv). The reaction was stirred for 15 min at 0 °C, then cooled down to - 78 °C. Then, the LDA solution was slowly cannulated to a solution of methyl isobutyrate (1.0 equiv) in THF (15 mL), previously cooled down to - 78 °C. The resulting reaction was stirred for 30 min, then the corresponding phenethyl bromide (1.2 equiv) was added dropwise. The reaction was stirred for another 15 min at - 78 °C, then allowed to warm up to rt overnight. The reaction was acidified with 2*M* HCl, extracted with Et_2O (3x30 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated under vacuum.

Step 2: General procedure for the synthesis of alcohols **O**

To a suspension of $LiAlH_4$ (2.0 equiv) in THF (12 mL) at 0 °C, a solution of the methyl ester (1.0 equiv), in THF (5 mL) was added dropwise. The reaction was fitted with a reflux condenser and refluxed for 2 h. The reaction was then cooled down to 0 °C, where water and 15% NaOH were added (*n* mL H_2O, *n* mL 15% NaOH, and *3n* mL H_2O, where *n* = grams of $LiAlH_4$ used). The mixture was filtered on a pad of celite, eluted with Et_2O, dried with Na_2SO_4, filtered and concentrated *in vacuo*.

Route C



Step 1: General procedure for synthesis of carboxylic acids

To a solution of NaH (1.1 equiv) and *i*Pr_2NH (1.0 equiv) in THF (2.5 mL/mmol *i*Pr_2NH) was added dropwise isobutyric acid (1.0 equiv) at rt. The reaction was refluxed for 15 min, then cooled down to 0 °C. *n*BuLi (2.5 *M* in hexanes, 1.0 equiv) was added dropwise. The reaction was stirred at 0 °C for 20 min, then at 35 °C for 30 min. The reaction was cooled down to 0 °C, and the alkyl bromide (1.0 equiv) was added dropwise. The reaction was stirred at 0 °C for 30 min, then at 35 °C for 1 h. Then, the reaction was cooled to 0 °C and quenched slowly with water (20 mL). The layers were separated. The organic layer was washed with water (20 mL). The combined organic layers were extracted with 20 mL Et_2O. The combined aqueous layers were acidified with 2 *M* HCl, then back-extracted with 2x30 mL Et_2O. The combined organic layers from the back-extraction were washed with brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*.

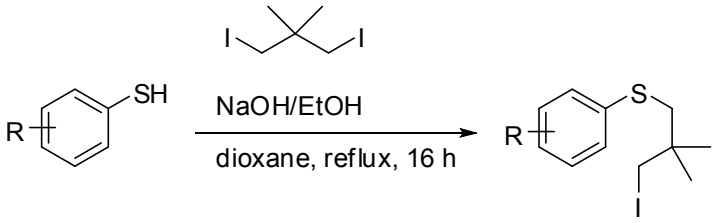
Step 2: General procedure for reduction of carboxylic acids

To a solution of the carboxylic acid (1.0 equiv) in THF (0.23 mL/mmol carboxylic acid) at 0 °C was added dropwise a solution of BH_3•DMS (1.5 equiv) in THF (0.48 mL/mmol BH_3•DMS). The reaction was stirred at 0 °C for 1 h, then allowed to warm up to rt overnight (or when complete by TLC). The reaction was cooled down to 0 °C, then quenched slowly with water (20 mL). The reaction was extracted with DCM 3x20 mL. The combined organic layers were dried with Na_2SO_4, filtered and concentrated *in vacuo*.

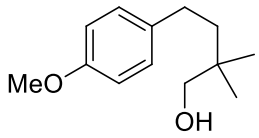
Route D

1,3-diiodo-2,2-dimethylpropane was synthesized according to the literature procedure and is in accordance to the given spectra.[3]

General procedure for the synthesis of phenylsulfanes

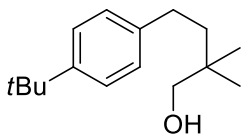


To a flask charged with NaOH (1.0 equiv) in EtOH (0.5 mL/mmol NaOH) was added thiophenol (1.0 equiv) in one portion at rt. The reaction mixture was refluxed until dissolution of the NaOH. A solution of 1,3-diiodo-2,2-dimethylpropane (4.0 equiv) in dioxane (0.17 mL/mmol 1,3-diiodo-2,2-dimethylpropane) was added in one portion and the yellow solution was refluxed for 16 h. The reaction was cooled to rt and then poured into ice water (20 mL). Et_2O (20 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (2x20 mL). The combined organic layers were dried over $MgSO_4$, filtered, then concentrated *in vacuo*.



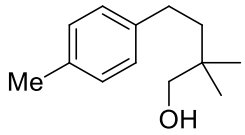
4-(4-methoxyphenyl)-2,2-dimethylbutan-1-ol (O1):

Synthesized according to route A, step 1. The residue was purified by flash chromatography (19:1 Hexanes/EtOAc), affording the title compound (251 mg, 40%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.14–7.08 (m, 2H), 6.85–6.80 (m, 2H), 3.78 (s, 3H), 3.37 (s, 2H), 2.56–2.49 (m, 2H), 1.56–1.50 (m, 2H), 1.40 (br s, 1H), 0.95 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.7, 135.3, 129.2, 113.8, 71.8, 55.3, 41.2, 35.3, 29.6, 23.9(2C). **IR** (film) cm^{-1} 3428, 2954, 1512, 1245, 1036, 822. **HRMS** (ESI, Pos) calcd for $C_{13}H_{20}AgO_2$ $[M+Ag]^+$: 315.0509 m/z, found 315.0509 m/z.



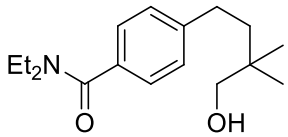
4-(4-tert-butylphenyl)-2,2-dimethylbutan-1-ol (O2):

Synthesized according to route A, step 1. The residue was purified by flash chromatography (19:1 Hexanes/EtOAc), affording the title compound (241 mg, 35%) as a clear oil.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 3.44 (s, 2H), 2.65-2.60 (m, 2H), 1.90 (br s, 1H), 1.66-1.62 (m, 2H), 1.39 (s, 9H), 1.03 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.5, 140.2, 128.0, 125.3, 71.9, 40.9, 35.4, 34.4, 31.6, 30.0, 23.9. **IR** (film) cm^{-1} 3355, 2955, 2867, 1109. **HRMS** (ESI Pos): calc. for $C_{16}H_{26}NaO$ $[M+Na]^+$: 257.1876 *m/z* , found 257.1872 *m/z*.



2,2-dimethyl-4-p-tolylbutan-1-ol (O3):

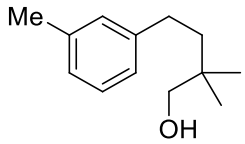
Synthesized according to route A, step 1. The residue was purified by flash chromatography (19:1 Hexanes/EtOAc), affording the title compound (208 mg, 36%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.17 (s, 4H), 3.41 (s, 2H), 2.64-2.58 (m, 2H), 2.39 (s, 3H), 1.65-1.59 (m, 2H), 1.02 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.2, 135.0, 129.1, 128.2, 71.9, 41.2, 35.3, 30.1, 23.9, 21.1. **IR** (film) cm^{-1} 2959, 1514, 1466, 807. **LRMS** (CI, Pos): calc. for $C_{13}H_{19}^{\bullet}$ [M-OH$^{\bullet}$]: 175.2 *m/z*, found 175.1 *m/z*.



N,N-diethyl-4-(4-hydroxy-3,3-dimethylbutyl)benzamide (O4):

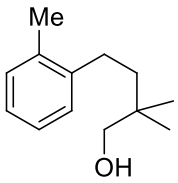
Synthesized according to route A, step 1. The residue was purified by flash chromatography (20-30% EtOAc/Hex), affording the title compound (371 mg, 45%) as a clear oil.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.27 (d, 2H, *J* = 8.1 Hz), 7.20 (d, 2H, *J* = 8.1 Hz), 3.53-3.27 (m, 4H), 3.34 (s, 2H), 2.60-2.56 (m, 2H), 2.16 (br s, 1H), 1.57-1.52 (m, 2H). 1.23-1.11 (m, 6H), 0.94 (s,

6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 171.7, 144.6, 134.6, 128.4, 126.5, 71.6, 40.8, 35.4, 30.5, 25.8, 24.0, 14.3, 13.1 ppm. **IR** (film) cm^{-1} 3407, 2937, 1608, 1460. **HRMS** (ESI Pos): expe. for $C_{17}H_{27}NNaO_2$ $[M+Na]^+$: 300.1938 m/z, calc. 300.1934 m/z.



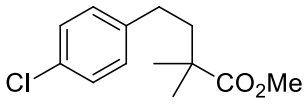
2,2-dimethyl-4-m-tolylbutan-1-ol (O5):

Synthesized according to route A, step 1. The residue was purified by flash chromatography (19:1 Hexanes/EtOAc), affording the title compound (189 mg, 32%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.19 (t, 1H, *J* = 7.0 Hz), 7.04-7.01 (m, 3H), 3.39 (s, 2H), 2.59-2.54 (m, 2H), 2.36 (s, 3H), 1.67 (br s, 1H), 1.60-1.56 (m, 2H), 0.98 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.2, 137.9, 129.2, 128.3, 126.4, 125.4, 71.9, 41.1, 35.4, 30.6, 23.9, 21.5. **IR** (film) cm^{-1} 3469, 2943, 2869, 1753, 1445, 1378, 1038, 1018, 905, 698. **HRMS** (ESI Pos): expe. for $C_{13}H_{19}$ $[M-H_2O]^+$: 175.1475 m/z, calc. 175.1481 m/z.



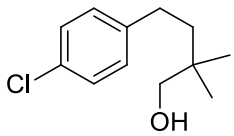
2,2-dimethyl-4-o-tolylbutan-1-ol (O6):

Synthesized according to route A, step 1. The residue was purified by flash chromatography (19:1 Hexanes/EtOAc), affording the title compound (90 mg, 16%) as a clear oil.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.15-7.08 (m, 4H), 3.43 (s, 2H), 2.60-2.56 (m, 2H), 2.37 (s, 3H), 1.55 (br s, 1H), 1.55-1.48 (m, 2H), 1.04 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 141.4, 135.8, 130.3, 128.9, 126.2, 126.0, 72.0, 39.7, 35.5, 28.0, 23.8, 19.4 ppm. **IR** (film) cm^{-1} 3457, 2942, 2868, , 1732, 1363, 1125, 1105, 1017, 904, 815. **HRMS** (ESI Pos): expe. for $C_{13}H_{20}AgO$ $[M+Ag]^+$: 299.0556 *m/z*, calc. 299.0560 *m/z*.



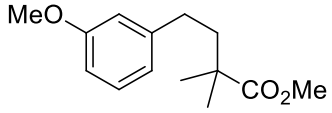
methyl 4-(4-chlorophenyl)-2,2-dimethylbutanoate (P3):

Synthesized according to route B, step 1 on a 10 mmol scale. The residue was purified by flash chromatography (39:1 hexanes/EtOAc), affording the title compound (84 mg, 88%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.23–7.16 (m, 2H), 7.11–7.02 (m, 2H), 3.65 (s, 3H), 2.54–2.43 (m, 2H), 1.83–1.73 (m, 2H), 1.23 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 177.8, 140.6, 131.4, 129.6, 128.3, 51.6, 42.4, 42.2, 30.8, 25.1(2C). **IR** (film) cm^{-1} 2951, 1721, 1492, 1453, 1259, 1192, 1170, 1130, 1088, 1041, 811, 520. **HRMS** (ESI, Pos) calcd for $C_{13}H_{17}Cl_1Na_1O_2$ $[M+Na]^+$: 263.0809 m/z, found 263.0806 m/z. **mp**: 40-41 °C



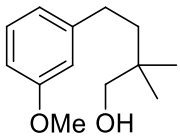
4-(4-chlorophenyl)-2,2-dimethylbutan-1-ol (O7):

Synthesized according to route B, step 2, on a 2.5 mmol scale. The title compound (539 mg, Quant.) was obtained as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.14–7.06 (m, 2H), 7.02–6.94 (m, 2H), 3.22 (s, 2H), 2.46–2.37 (m, 2H), 2.33 (br s, 1H), 1.45–1.35 (m, 2H), 0.82 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 141.6, 131.2, 129.7, 128.4, 71.6, 40.7, 35.2, 29.9, 23.8(2C). **IR** (film) cm^{-1} 3322, 2954, 2865, 1572, 1492, 1304, 1260, 1159, 1093, 1015, 807. **HRMS** (ESI, Pos) calcd for $C_{12}H_{17}Cl_1Li_1O_1$ $[M+Li]^+$: 218.1114 m/z, found 218.1113 m/z.



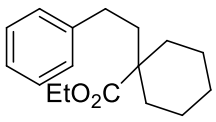
methyl 4-(3-methoxyphenyl)-2,2-dimethylbutanoate (P4):

Synthesized according to route B, step 1, on a 1.20 mmol scale. The residue was purified by flash chromatography (19:1 hexanes/EtOAc), affording the title compound (219 mg, 77%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.27-7.18 (m, 1H), 6.80-6.74 (m, 3H), 3.81 (s, 3H), 3.70 (s, 3H), 2.58-2.52 (m, 2H), 1.90-1.83 (m, 2H), 1.28 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 178.2, 159.8, 143.9, 129.4, 120.7, 114.2, 111.2, 55.1, 51.7, 42.7, 42.3, 31.6, 25.2. **IR** (film) cm^{-1} 2950, 1730, 1602, 1489, 1455, 1262, 1193, 1151, 1128, 1046, 775. **HRMS** (ESI, Pos) calcd for $C_{14}H_{20}Na_1O_3$ $[M+Na]^+$: 259.1305 m/z, found 259.1300 m/z.



4-(3-methoxyphenyl)-2,2-dimethylbutan-1-ol (O8):

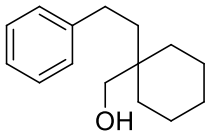
Synthesized according to route B, step 2, on a 0.75 mmol scale. The title compound (158 mg, Quant.) was obtained as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.23 (t, 1H, J = 7.9 Hz), 6.84-6.76 (m, 3H), 3.82 (s, 3H), 3.40 (s, 2H), 2.62-2.58 (m, 2H), 1.94 (br s, 1H), 1.62-1.58 (m, 2H), 1.00 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 159.8, 145.1, 129.5, 120.9, 114.1, 111.1, 71.8, 55.2, 40.8, 35.2, 30.7, 23.9. **IR** (film) cm^{-1} 3373, 2950, 2871, 1601, 1585, 1489, 1455, 1259, 1152, 1048, 784, 694. **HRMS** (ESI, Pos) calcd for $C_{13}H_{20}Na_2O_2$ $[M+Na]^+$: 231.1356 m/z, found 231.1347 m/z.



ethyl 1-phenethylcyclohexanecarboxylate (P5):

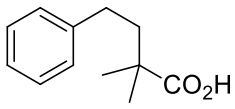
Synthesized according to route B, step 1, on a 7.6 mmol scale. The residue was purified by flash chromatography (39:1 hexanes/EtOAc), affording the title compound (1.34 g, 68%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.31-7.27 (m, 2H), 7.21-7.16 (m, 3H), 4.20 (q, 2H, J = 7.2 Hz), 2.55-2.51 (m, 2H), 2.17-2.14 (m, 2H), 1.84-1.79 (m, 2H), 1.59-1.56 (m, 3H), 1.46-1.27 (m, 5H), 1.32 (t, 3H, J = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 176.1, 142.2, 128.2,

128.1, 126.6, 59.5, 46.7, 42.4, 34.1, 30.5, 25.8, 23.1, 14.2. **IR** (film) cm^{-1} 2930, 2854, 1722, 1452, 1173, 1129, 1026, 745, 698. **HRMS** (ESI, Pos) calcd for $C_{17}H_{24}Na_1O_2$ $[M+Na]^+$: 283.1669 m/z, found 283.1659 m/z.



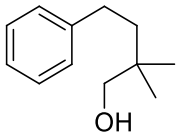
(1-phenethylcyclohexyl)methanol (O9):

Synthesized according to route B, step 2, on a 5.0 mmol scale. The residue was purified by flash chromatography (4:1 hexanes/EtOAc), affording the title compound (966 mg, 88%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.36-7.21 (m, 5H), 3.55 (s, 2H), 2.64-2.59 (m, 2H), 1.94 (br s, 1H), 1.75-1.63 (m, 2H), 1.55-1.45 (m, 10H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.5, 128.4 (2 C's), 125.6, 68.4, 37.3, 37.0, 32.4, 29.7, 26.5, 21.6. **IR** (film) cm^{-1} 3344, 2922, 2850, 1452, 1031, 754, 696. **HRMS** (ESI, Pos) calcd for $C_{15}H_{22}Na_1O_1$ $[M+Na]^+$: 241.1563 m/z, found 241.1565 m/z.



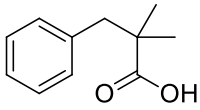
2,2-dimethyl-4-phenylbutanoic acid (P6)[4]:

Synthesized according to route C, step 1, on a 55 mmol scale. The residue was purified by flash chromatography (5% EtOAc/Hex), affording the title compound (7.43 g, 71%) as a white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.05 (br s, 1H), 7.35-7.31 (m, 2H), 7.25-7.21 (m, 3H), 2.69-2.65 (m 2H), 1.95-1.91 (m, 2H), 1.34 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 185.1, 142.4, 128.5 (2 C's), 125.0, 42.6, 42.4, 31.6, 25.1. **IR** (film) cm^{-1} 2973, 2933, 1698, 1473, 1236, 1203, 935, 744, 698, 546, 501. **HRMS** (ESI, Pos) calcd for $C_{13}H_{18}Na_1O_2$ $[M+Na]^+$: 215.1043 m/z, found 215.1041 m/z. **mp**: 80-83 °C



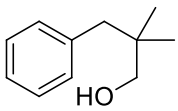
2,2-dimethyl-4-phenylbutan-1-ol (O10)[5]:

Synthesized according to route C, step 2, on a 35 mmol scale. The residue was purified by flash chromatography (5% EtOAc/Hex), affording the title compound (4.62 g, 74%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.34-7.29 (m, 2H), 7.25-7.20 (m, 3H), 3.42 (s, 2H), 2.65-2.60 (m, 2H), 1.64 (br s, 1H), 1.63-1.59 (m, 2H), 1.01 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.3, 128.5, 128.4, 125.8, 71.9, 41.0, 35.4, 30.6, 24.5, 23.9. **IR** (film) cm^{-1} 3353, 2952, 2868, 1496, 1454, 1415, 1382, 1337, 1047, 736, 697. **HRMS** (ESI, Pos) calcd for $C_{12}H_{18}Li_1O_1$ $[M+Li]^+$: 184.1503 m/z, found 184.1503 m/z.



2,2-dimethyl-3-phenylpropanoic acid (P7)[6]:

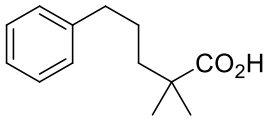
Synthesized according to route C, step 1, on a 55 mmol scale. The residue was purified by flash chromatography (5% EtOAc/Hex), affording the title compound (8.14 g, 84%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.29-7.13 (m, 5H), 2.88 (s, 2H), 1.20 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 184.8, 137.8, 130.4, 128.2, 126.7, 46.0, 43.6, 24.8. **IR** (film) cm^{-1} 2972, 1685, 1470, 1456, 1289, 1223, 1134, 939, 739, 701, 595, 546. **HRMS** (ESI, Pos) calcd for $C_{11}H_{14}Na_1O_2$ $[M+Na]^+$: 201.0886 m/z, found 201.0889 m/z. **mp**: 50-51 °C



2,2-dimethyl-3-phenylpropan-1-ol (O11)[7]:

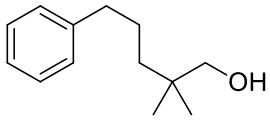
Synthesized according to route C, step 2, on a 30 mmol scale. The residue was purified by flash chromatography (5% EtOAc/Hex), affording the title compound (4.90 g, 99%) as a clear

oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.28-7.12 (m, 5H), 3.30 (d, 2H, *J* = 6.0 Hz), 2.56 (s, 2H), 0.87 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 138.9, 130.6, 128.0, 126.1, 71.3, 44.9, 36.6, 24.1. **IR** (film) cm^{-1} 3239, 2866, 1467, 1385, 1361, 1040, 775, 718, 699, 517. **HRMS** (ESI, Pos) calcd for $C_{11}H_{16}Na_1O_1$ $[M+Na]^+$: 187.1093 m/z, found 187.1092 m/z. **mp**: 32-33 °C



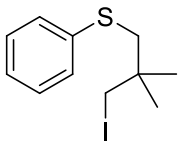
2,2-dimethyl-5-phenylpentanoic acid (P7)[8]:

Synthesized according to route C, step 1, on a 9.0 mmol scale. The residue was purified by flash chromatography (5% EtOAc/Hex), affording the title compound (310 mg, 17%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.18 (br s, 1H), 7.37-7.33 (m, 2H), 7.28-7.24 (m, 3H), 2.70-2.66 (m, 2H), 1.71-1.67 (m, 4H), 1.27 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 185.3, 142.3, 128.5, 125.6, 42.2, 40.3, 36.4, 26.9, 25.41. **IR** (film) cm^{-1} 2942, 1697, 1475, 1453, 1278, 1199, 941, 748, 698. **HRMS** (ESI, Pos) calcd for $C_{13}H_{18}Na_1O_2$ $[M+Na]^+$: 229.1202 m/z, found 229.1199 m/z. **mp**: 29-30 °C



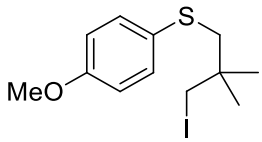
2,2-dimethyl-5-phenylpentan-1-ol (O12):

Synthesized according to route C, step 2, on a 1.5 mmol scale. The residue was purified by flash chromatography (5-10% EtOAc/Hex), affording the title compound (212 mg, 76%) as a clear oil.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35-7.32 (m, 2H), 7.25-7.23 (m, 3H), 3.35 (s, 2H), 2.65 (t, 2H, *J* = 8.2 Hz), 1.69-1.61 (m, 3H), 1.37-1.33 (m, 2H), 0.92 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.8, 128.5 (2 C's), 125.8, 72.0, 38.4, 37.0, 35.2, 26.1, 24.0. **IR** (film) cm^{-1} 3354, 2936, 2864, 1495, 1471, 1453, 1389, 1363, 1028, 747, 697. **HRMS** (ESI Pos): expe. for $C_{13}H_{20}NaO$ $[M+Na]^+$: 215.1410 m/z, calc. 215.1406 m/z.



(3-iodo-2,2-dimethylpropyl)(phenyl)sulfane (1a):

Synthesized according to route D on a 3 mmol scale. The crude product was purified by flash chromatography (39:1 Hexanes:EtOAc) affording the title compound (817 mg, 89%) as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41-7.16 (m, 5H), 3.33 (s, 2H), 3.03 (s, 2H), 1.15 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 137.3, 129.8, 129.0, 126.3, 46.1, 35.5, 26.7, 22.2. **IR** (film) cm^{-1} 2960, 1582, 1479, 1438, 1381, 1365, 1205, 1088, 1024, 734, 689, 605. **HRMS** (ESI, Pos) calcd for $C_{11}H_{15}Ag_1I_1S_1$ $[M+Ag]^+$: 412.8985 m/z, found 412.8990 m/z.



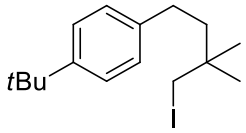
(3-iodo-2,2-dimethylpropyl)(4-methoxyphenyl)sulfane (1b)

Synthesized according to route D on a 4 mmol scale. The residue was purified by flash chromatography (39:1 Hexanes/EtOAc), affording the title compound (945 mg, 70%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.38 (d, 2H, *J* = 8.8 Hz), 6.83 (d, 2H, *J* = 8.8 Hz), 3.79 (s, 3H), 3.30 (s, 2H), 2.94 (s, 2H), 1.13 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 158.7, 133.6, 127.7, 114.5, 55.6, 48.5, 36.2, 26.7, 22.5. **IR** (film) cm^{-1} 2958, 1592, 1492, 1461, 1283, 1240, 1172, 1030, 822, 639, 604, 522. **HRMS** (ESI, Pos) calcd for $C_{12}H_{17}I_1O_1S_1$ $[M]^+$: 336.0039 m/z, found 336.0038 m/z.

General procedure **E**

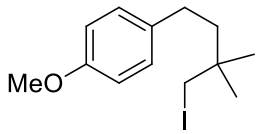
To a solution of alcohol **O** (1.0 equiv) in toluene was added I_2 (1.1 equiv), PPh_3 (1.1 equiv) and imidazole (4.0 equiv). The reaction was stirred under reflux for 12 h (or until complete by TLC). The reaction was allowed to cool down to rt, then quenched with a saturated *aqueous*

solution of $NaHSO_3$. The layers were separated, and the organic layer was concentrated. The residue was purified by flash chromatography in 100% Hexanes.



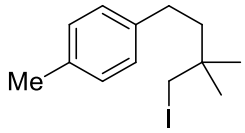
1-tert-butyl-4-(4-iodo-3,3-dimethylbutyl)benzene (4c):

The reaction was performed according to general procedure **E** on a 1 mmol scale. The residue was purified by flash chromatography (19:1 Hexanes/EtOAc), affording the title compound (279 mg, 81%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38 (d, 2H, *J* = 8.2 Hz), 7.20 (d, 2H, *J* = 8.2 Hz), 3.23 (s, 2H), 2.60-2.55 (m, 2H), 1.73-1.69 (m, 2H), 1.38 (s, 9H), 1.17 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.7, 139.5, 128.1, 125.4, 43.4, 34.4, 33.7, 31.6, 30.4, 26.8, 24.0 ppm. **LRMS** (CI, Pos) calcd for $C_{16}H_{26}I_1$ $[M+H]^+$: 345.3 m/z, found 345.2 m/z. **IR** (film) cm^{-1} 2958, 1364, 1268.



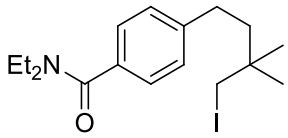
1-(4-iodo-3,3-dimethylbutyl)-4-methoxybenzene (4b):

The reaction was performed according to general procedure **E** on a 1.2 mmol scale. The residue was purified by flash chromatography (49:1 Hexanes/EtOAc), affording the title compound (282 mg, 74%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.18–7.10 (m, 2H), 6.90–6.82 (m, 2H), 3.81 (s, 3H), 3.24 (s, *2*H), 2.55–2.47 (m, 2H), 1.67–1.60 (m, 2H), 1.12 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.8, 134.6, 129.3, 113.9, 55.4, 43.7, 33.6, 30.0, 26.8, 24.0. **IR** (film) cm^{-1} 2956, 1612, 1510, 1463, 1243, 1176, 1035, 820, 608, 525. **HRMS** (ESI, Pos) calcd for $C_{13}H_{19}NAgIO$ $[M+Ag]^+$: 424.9526 m/z, found 424.9515 m/z.



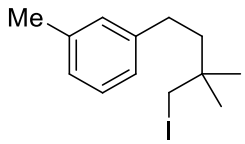
1-(4-iodo-3,3-dimethylbutyl)-4-methylbenzene (4d):

The reaction was performed according to general procedure **E** on a 1.1 mmol scale. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (243 mg, 75%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.15 (s, 4H), 3.26 (s, 2H), 2.57-2.53 (m, 2H), 2.38 (s, 3H), 1.70-1.65 (m, 2H), 1.15 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.5, 135.3, 129.2, 128.3, 43.6, 33.7, 30.5, 26.9, 24.0, 21.1. **IR** (film) cm^{-1} 2959, 2861, 1514, 1466, 1383, 1365, 1207, 1162, 807, 770, 609, 537, 500. **LRMS** (CI, Pos) calcd for $C_{13}H_{20}I_1$ $[M+H]^+$: 303.1 m/z, found 303.0 m/z.



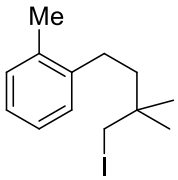
N,N-diethyl-4-(4-iodo-3,3-dimethylbutyl)benzamide (4f):

The reaction was performed according to general procedure **E** on a 1.3 mmol scale. The residue was purified by flash chromatography (10-20% EtOAc/Hex), affording the title compound (318 mg, 63%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.27 (d, 2H, *J* = 7.9 Hz), 7.20 (d, 2H, *J* = 7.9 Hz), 3.53-3.27 (m, 4H), 3.21 (s, 2H), 2.56-2.52 (m, 2H), 1.64-1.60 (m, 2H), 1.22-1.11 (m, 6H), 1.11 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 171.1, 143.9, 134.6, 128.2, 126.6, 43.4, 33.7, 31.1, 27.8, 23.5, 14.3, 12.9 ppm. **IR** (film) cm^{-1} 2961, 1608, 1462, 1282, 1094, 852, 605, 477. **HRMS** (ESI Pos): expe. for $C_{17}H_{26}INNaO$ $[M+Na]^+$: 410.0963 m/z, calc. 410.0951 m/z.



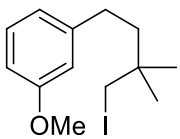
1-(4-iodo-3,3-dimethylbutyl)-3-methylbenzene (4h):

The reaction was performed according to general procedure **E** on a 0.96 mmol scale. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (190 mg, 62%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.25 (t, 1H, *J* = 7.5 Hz), 7.09-7.06 (m, 3H), 3.26 (s, 2H), 2.59-2.55 (m, 2H), 2.41 (s, 3H), 1.72-1.68 (m, 2H), 1.17 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.5, 138.1, 129.3, 128.4, 126.6, 125.5, 43.5, 33.7, 30.9, 26.8, 23.9, 21.5. **IR** (film) cm^{-1} 2959, 1608, 1466, 1383, 1365, 1225, 1206, 1163, 788, 761, 697, 614. **LRMS** (CI, Pos) calcd for $C_{13}H_{20}I_1$ $[M+H]^+$: 303.1 m/z, found 303.0 m/z.



1-(4-iodo-3,3-dimethylbutyl)-2-methylbenzene (4i):

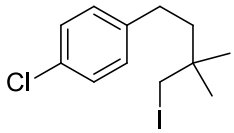
The reaction was performed according to general procedure **E** on a 0.83 mmol scale. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (150 mg, 60%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.18-7.11 (m, 4H), 3.27 (s, 3H), 2.58-2.52 (m, 2H), 2.37 (s, 3H), 1.62-1.55 (m, 2H), 1.18 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.6, 135.8, 130.4, 129.0, 126.3, 126.1, 42.2, 33.8, 28.3, 26.8, 23.8, 19.4 ppm. **IR** (film) cm^{-1} 2958, 2860, 1608, 1466, 1383, 1366, 1255, 1130, 878, 762. **LRMS** (CI, Pos) calcd for $C_{13}H_{20}I_1$ $[M+H]^+$: 303.1 m/z, found 303.0 m/z.



1-(4-iodo-3,3-dimethylbutyl)-3-methoxybenzene (4g):

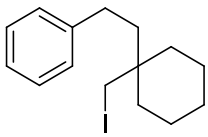
The reaction was performed according to general procedure **E** on a 0.73 mmol scale. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (203 mg, 87%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.22 (t, 1H, *J* = 7.8 Hz), 6.83-6.73 (m, 3H), 3.81 (s, 3H), 3.22 (s, 2H), 2.57-2.51 (m, 2H), 1.69-1.63 (m, 2H), 1.12 (s, 6H). **^{13}C**

NMR ($CDCl_3$, 75 MHz): δ 159.8, 144.2, 129.6, 120.8, 114.2, 111.1, 55.2, 43.3, 39.7, 31.0, 26.8, 23.6. **IR** (film) cm^{-1} 2957, 1601, 1489, 1465, 1260, 1152, 1048, 784, 694. **HRMS** (ESI, Pos) calcd for $C_{13}H_{19}INaO$ $[M+Na]^+$: 341.03728 m/z, found 341.03642 m/z.



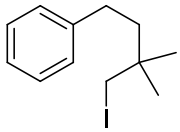
1-chloro-4-(4-iodo-3,3-dimethylbutyl)benzene (4e):

The reaction was performed according to general procedure **E** on a 2.5 mmol scale. The residue was purified by flash chromatography (100% hexanes), affording the title compound (699 mg, 87%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.16–7.08 (m, 2H), 7.04–6.97 (m, 2H), 3.08 (s, *2*H), 2.42–2.33 (m, 2H), 1.53–1.43 (m, 2H), 0.98 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 140.9, 131.5, 129.7, 128.5, 43.3, 33.5, 30.2, 26.7(2C), 23.6. **IR** (film) cm^{-1} 2959, 2865, 1491, 1467, 1384, 1365, 1204, 1162, 1092, 1014, 805, 660, 607, 519. **LRMS** (EI) calcd for $C_{14}H_{19}Cl_1I_1$ [M]: 322.00 m/z, found 322.0 m/z.



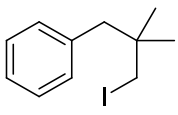
(2-(1-(iodomethyl)cyclohexyl)ethyl)benzene (4j):

The reaction was performed according to general procedure **E** on a 3.0 mmol scale. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (777 mg, 79%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.30-7.14 (m, 5H), 3.31 (s, 2H), 2.48-2.42 (m, 2H), 1.66-1.60 (m, 2H), 1.53-1.37 (m, 10 H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.5, 128.4 (2 C's), 125.8, 40.5, 35.1, 35.0, 29.3, 2621, 21.9, 21.8. **IR** (film) cm^{-1} 2923, 2848, 1496, 1452, 1220, 1168, 753, 718, 696, 600, 509. **HRMS** (ESI Pos): expe. for $C_{15}H_{21}Ag$ $[M+Ag]^+$: 434.9741 *m/z*, calc. 434.9733 *m/z*.



(4-iodo-3,3-dimethylbutyl)benzene (4a):

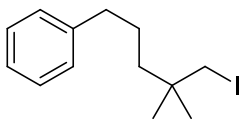
Pyridine (10 mL) was cooled in an ice/salt bath and *p*-TsCl (4.82 g, 23.0 mmol) was added as a solid portionwise. A solution of **O10** in pyridine (10 mL) was added and the reaction was allowed to warm to rt. The reaction mixture was stirred at rt for 16 h, then partitioned between DCM (100 mL) and 1 *M* aqueous HCl solution (50 mL). The layers were separated and the organic layer was sequentially washed with 1 *M* aqueous HCl solution (25 mL), H_2O (25 mL), 1 *M* aqueous NaOH solution (25 mL) and H_2O (25 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo* affording the crude tosylate (8.00 g, 93%) as a red oil, which was used as such in the iodination reaction. The crude tosylate (7.85 g, 23.6 mmol) was dissolved in 2-ethoxyethanol (25 mL) and NaI (7.08 g, 47.2 mmol) was added as a solid in one portion. The reaction mixture was heated to reflux for 16 h. The reaction was allowed to cool to room temperature and diluted with H_2O (50 mL) and Et_2O (100 mL). The layers were separated and the organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (4.30 g, 66%) as a pale red oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.29-7.19 (m, 5H), 3.22 (s, 2H), 2.57-2.51 (m, 2H), 1.67-1.61 (m, 2H), 1.11 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.5, 128.5, 128.4, 125.9, 43.5, 33.7, 31.0, 26.8, 23.9. **IR** (film) cm^{-1} 3025, 2959, 1497, 1454, 1384, 1365, 1204, 1163, 763, 735, 697, 611, 509. **LRMS** (CI, Pos) calcd for $C_{12}H_{18}I_1$ $[M+H]^+$: 289.0 m/z, found 289.0 m/z.



(3-iodo-2,2-dimethylpropyl)benzene (S1):

Pyridine (20 mL) was cooled in an ice/salt bath and *p*-TsCl (5.80 g, 30.4 mmol) was added as a solid portionwise. A solution of **O11** in pyridine (10 mL) was added and the reaction was

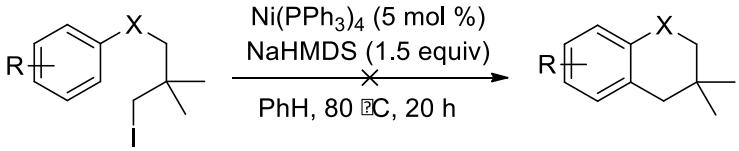
allowed to warm to rt. The reaction mixture was stirred at rt for 16 h, then partitioned between DCM (100 mL) and 1 *M* aqueous HCl solution (50 mL). The layers were separated and the organic layer was sequentially washed with 1 *M* aqueous HCl solution (25 mL), H_2O (25 mL), 1 *M* aqueous NaOH solution (25 mL) and H_2O (25 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo* affording the crude tosylate (7.99 g, 91%) as a pale yellow solid, which was used as such in the iodination reaction. The crude tosylate (7.99 g, 25.1 mmol) was dissolved in 2-ethoxyethanol (75 mL) and NaI (7.52 g, 50.2 mmol) was added as a solid in one portion. The reaction mixture was heated to reflux for 16 h. The reaction was allowed to cool to room temperature and diluted with H_2O (50 mL) and Et_2O (100 mL). The layers were separated and the organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (3.97 g, 58%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.32-7.19 (m, 5H), 3.14 (s, 2H), 2.66 (s, 2H), 1.06 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 138.3, 130.4, 128.0, 126.4, 46.4, 34.8, 27.2, 24.3. **IR** (film) cm^{-1} 2959, 1453, 1364, 1212, 773, 721, 700, 605, 494. **LRMS** (CI, Pos) calcd for $C_{11}H_{16}I_1$ $[M+H]^+$: 275.0 m/z, found 275.0 m/z.



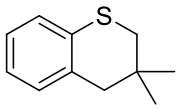
(5-iodo-4,4-dimethylpentyl)benzene (S2):

The reaction was performed according to general procedure **E**, on a 1.1 mmol scale. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (232 mg, 72%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.34 (m, 2H), 7.27-7.25 (m, 3H), 3.21 (s, 2H), 2.68 (t, 2H, *J* = 7.6 Hz), 1.68-1.60 (m, 2H), 1.48-1.44 (m, 2H), 1.08 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.5, 128.4 (2 C's), 125.9, 40.8, 36.7, 33.6, 26.9, 26.6, 24.4. **IR** (film) cm^{-1} 2958, 2934, 2858, 1495, 1466, 1453, 1384, 1365, 1222, 1205, 1161, 1030 746, 697, 609. **LRMS** (CI, Pos) calcd for $C_{13}H_{20}I_1$ $[M+H]^+$: 303.1 m/z, found 303.0 m/z.

General procedure **F**

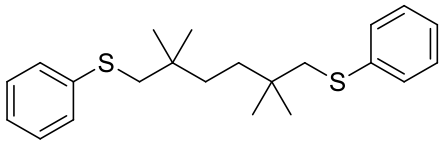


In a glovebox, $Ni(PPh_3)_4$ (27.7 mg, 0.025 mmol, 0.05 equiv) and NaHMDS (137.5 mg, 0.75 mmol, 1.5 equiv) were added to a microwave vial containing a stir bar. The vial was crimped and taken out of the glovebox. A solution of the corresponding iodide (0.5 mmol, 1.0 equiv) in 1.5 mL dry benzene was cannulated into the microwave vial. The flask was rinsed with 2x1.5 mL benzene for a total volume of 4.5 mL. The reaction was stirred at 80 °C for 20 h. The reaction was allowed to cool down to rt, then filtered through a pad of silica and celite, concentrated and purified by flash chromatography.



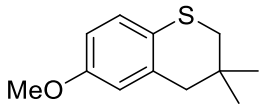
3,3-dimethylthiochroman (2a):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (62 mg, 70%) and dimer **3** (7 mg, 8%) as clear oils. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.13-6.94 (m, 4H), 2.76 (s, 2H), 2.58 (s, 2H), 1.13 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 132.9, 132.4, 130.8, 127.1, 126.0, 124.0, 43.5, 39.6, 28.5, 28.1. **IR** (film) cm^{-1} 2953, 2913, 1467, 1437, 1249, 1070, 1039, 740, 679. **LRMS** (CI, Pos) calcd for $C_{11}H_{15}S_1$ $[M+H]^+$: 179.1 m/z, found 179.1 m/z.



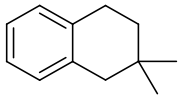
(2,2,5,5-tetramethylhexane-1,6-diyl)bis(phenylsulfane) (3):

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.34 (m, 4H), 7.28-7.24 (m, 3H), 7.16-7.13 (m, 3H), 2.88 (s, 4H), 1.30 (s, 4H), 1.00 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 138.5, 129.2, 128.9, 125.7, 49.9o, 35.2, 34.8, 27.0. **IR** (film) cm^{-1} 2956, 2056, 1583, 1479, 1438, 1384, 1365, 1089, 1025, 735, 689. **HRMS** (ESI, Pos) calcd for $C_{22}H_{31}S_2$ $[M+H]^+$: 359.18617 m/z, found 359.18744 m/z.



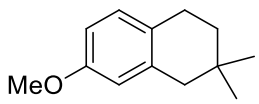
6-methoxy-3,3-dimethylthiochroman (2b):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (92 mg, 88%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.03-7.01 (m, 1H), 6.69-6.66 (m, 1H), 6.58-6.59 (m, 1H), 3.75 (s, 3H), 2.72 (s, 2H), 2.54 (s, 2H), 1.10 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 156.8, 134.4, 127.0, 123.3, 116.1, 112.8, 55.7, 43.9, 39.3, 29.1, 28.2. **IR** (film) cm^{-1} 2953, 2933, 1599, 1482, 1312, 1230, 1151, 1034, 807, 625. **HRMS** (ESI, Pos) calcd for $C_{12}H_{17}O_1S_1$ $[M+H]^+$: 209.0995 m/z, found 209.0990 m/z. **mp**: 39-40 °C.



2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (5a)[9]:

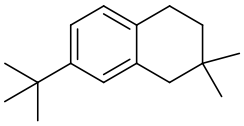
The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (59 mg,74%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.15-7.04 (m, 4H), 2.84 (t, 2H, *J* = 6.9 Hz), 2.58 (s, 2H), 1.60 (t, 2H, *J* = 6.9 Hz), 1.04 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 136.7, 135.9, 129.6, 128.9, 125.6 (2 C's), 43.7, 36.1, 29.6, 28.3, 26.8. **IR** (film) cm^{-1} 2949, 2911, 1494, 1452, 1364, 754, 738, 722. **LRMS** (CI, Pos) calcd for $C_{12}H_{17}$ $[M+H]^+$: 161.1 m/z, found 161.1 m/z.



7-methoxy-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (5b)[10]:

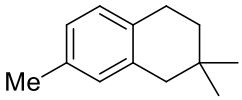
The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (84 mg, 88%) as a clear

oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.04–6.99 (m, 1H), 6.73–6.67 (m, 1H), 6.61–6.57 (m, 1H), 3.78 (s, *3*H), 2.74 (t, *J* = 6.8 Hz, *2*H), 2.52 (s, 2H), 1.56 (t, J = 6.8 Hz, 2H), 1.00 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 157.6, 137.7, 129.7, 128.0, 114.1, 111.8, 55.3, 43.9, 36.3, 29.5, 28.2(2C), 25.8. **IR** (film) cm^{-1} 2948, 2908, 1610, 1502, 1463, 1364, 1269, 1242, 1219, 1156, 1042, 837, 800, 697. **LRMS** (CI, Pos) calcd for $C_{14}H_{19}O_1$ $[M+H]^+$: 191.1 m/z, found 191.1 m/z.



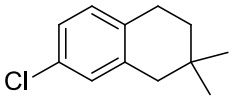
7-tert-butyl-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (5c):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (92 mg, 85%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.22-7.07 (m, 3H), 2.82 (t, 2H, *J* = 6.8 Hz), 2.60 (s, 2H), 1.61 (t, 2H, *J* = 6.8 Hz), 1.37 (s, 9H), 1.05 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.4, 136.1, 132.9, 128.5, 126.3, 122.6, 43.9, 36.2, 31.6, 28.5, 26.2 ppm. **IR** (film) cm^{-1} 2950, 2906, 2868, 1460, 1433, 1363, 1339, 1256, 1089, 821, 713. **LRMS** (EI) calcd for $C_{16}H_{24}$ [M]: 216.19 m/z, found 216.2 m/z.



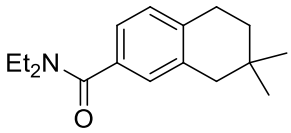
2,2,7-trimethyl-1,2,3,4-tetrahydronaphthalene (5d):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording the title compound (75 mg, 86%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.05-6.90 (m, 3H), 2.81 (t, 2H, *J* = 6.8 Hz), 2.54 (s, 2H), 2.33 (s, 3H0, 1.60 (t, 2H , *J* = 6.8 Hz), 1.03 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 136.4, 134.9, 132.7, 130.2, 128.8, 126.4, 43.6, 36.2, 29.6, 28.3, 26.2, 21.1. **IR** (film) cm^{-1} 2949, 2913, 2868, 1504, 1450, 1433, 1383, 1364, 1167, 807. **LRMS** (CI, Pos) calcd for $C_{13}H_{19}$ $[M+H]^+$: 175.2 m/z, found 175.2 m/z.



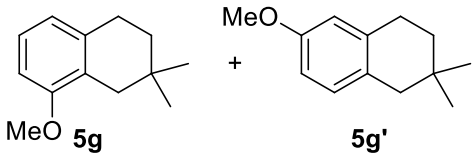
7-chloro-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (5e):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% hexanes), affording the title compound (72 mg, 74%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.13–6.90 (m, 3H), 2.75 (t, *J* = 6.6 Hz, 2H), 2.49 (s, 2H), 1.55 (t, *J* = 6.8 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 138.5, 134.3, 131.0, 130.2, 129.3, 125.6, 43.4, 35.8, 29.4, 28.1(2C), 26.1. **IR** (film) cm^{-1} 2950, 2918, 2869, 1486, 1449, 1431, 1365, 1089, 864, 852, 808, 664. **LRMS** (CI, Pos) calcd for $C_{12}H_{16}Cl_1$ $[M+H]^+$: 195.1 m/z, found 195.0 m/z.



N,N-diethyl-7,7-dimethyl-5,6,7,8-tetrahydronaphthalene-2-carboxamide (5f):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (10-15% EtOAc/Hexanes), affording the title compound (90 mg, 70%) as a clear oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.10-7.00 (m, 3H), 3.52-3.28 (m, 4H), 2.79 (t, 2H, *J* = 6.7 Hz), 2.52 (s, 2H), 1.56 (t, 2H, *J* = 6.7 Hz), 1.21-1.12 (m, 6H), 0.97 (s, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 171.7, 137.9, 137.1, 136.1, 134.7, 129.3, 128.6, 127.6, 126.9, 123.5, 43.5, 35.9, 29.5, 28.2, 26.5, 14.3, 13.0 ppm. **IR** (film) cm^{-1} 2915, 1627, 1425, 1381, 1364, 1315, 1290, 1255, 1221, 1162, 1118, 1091, 820, 752. **HRMS** (ESI Pos): expe. for $C_{17}H_{25}NNaO$ $[M+Na]^+$: 282.1836 m/z, calc. 282.1828 m/z.



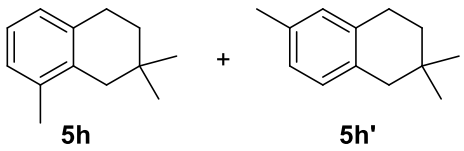
(3:1)

8-methoxy-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (5g):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording **5g** (59 mg, 62%) and **5g'** (22 mg, 23%) as clear oils. Major: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.14 (t, 1H, *J* = 8.1 Hz), 6.80 (d, 1H, *J* = 7.8 Hz), 6.71 (d, 2H, *J* = 8.1 Hz), 3.87 (s, 3H), 2.85 (t, 2H, *J* = 6.8 Hz), 2.51 (s, 2H), 1.59 (t, 2H, *J* = 6.8 Hz), 1.06 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.7, 137.3, 125.8, 125.4, 121.2, 106.8, 55.3, 37.0, 35.6, 29.0, 28.7, 26.8. **IR** (film) cm^{-1} 2948, 2914, 2869, 2843, 1585, 1467, 1252, 769. **LRMS** (CI, Pos) calcd for $C_{13}H_{19}O_1$ $[M+H]^+$: 191.1 m/z, found 191.1 m/z.

6-methoxy-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (5g')[11]:

Minor: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.97 (d, 1H, *J* = 8.5 Hz), 6.71-6.67 (m, 2H), 3.77 (s, 3H), 2.77 (t, 2H, *J* = 6.7 Hz), 2.47 (s, 2H), 1.54 (t, 2H, *J* = 6.7 Hz), 0.99 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.5, 136.9, 130.4, 128.7, 113.4, 111.9, 55.5, 42.9, 36.0, 29.7, 28.2, 27.0. **IR** (film) cm^{-1} 2949, 2917, 1610, 1503, 1466, 1261, 1243,1043. **LRMS** (CI, Pos) calcd for $C_{13}H_{19}O_1$ $[M+H]^+$: 191.1 m/z, found 191.1 m/z.

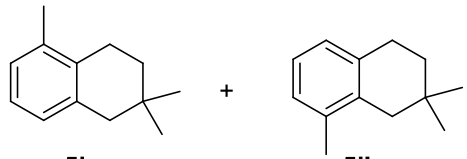


(3:1)

2,2,8-trimethyl-1,2,3,4-tetrahydronaphthalene (5h) + 2,2,6-trimethyl-1,2,3,4-tetrahydronaphthalene (5h'):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording an inseparable 3:1 mixture of **5h** and **5h'** (71 mg, 81%) as a clear oil. Major (**5h**): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.10-6.98 (m, 3H), 2.87 (t, 2H, *J* = 6.7 Hz), 2.45 (s, 2H), 2.30 (s, 3H), 1.61 (t, 2H, *J* = 6.7 Hz), 1.07 (s, 6H). Minor

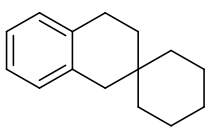
(**5h'**): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.10-6.98 (m, 3H), 2.82 (t, 2H, *J* = 6.7 Hz), 2.58 (s, 2H), 2.35 (s, 3H), 1.62-1.59 (m, 2H), 1.04 (s, 6H). Major + minor **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 136.8, 135.7, 135.6, 135.0, 134.8, 133.4, 129.4 (2 C's), 127.1, 126.7, 125.0, 43.2, 40.8, 36.1, 35.5, 29.6, 28.7, 27.0, 26.6, 21.0, 19.7. **IR** (film) cm^{-1} 2948, 2911, 2864, 1458, 1384, 1363, 804, 770, 736, 707. **LRMS** (CI, Pos) calcd for $C_{13}H_{19}$ $[M+H]^+$: 175.2 m/z, found 175.1 m/z.



5i (9:1) **5i'**

2,2,5-trimethyl-1,2,3,4-tetrahydronaphthalene (5i) + 2,2,8-trimethyl-1,2,3,4-tetrahydronaphthalene (5i'):

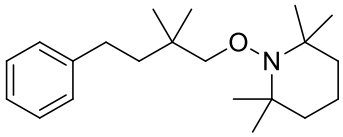
The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% Hexanes), affording an inseparable 10:1 mixture of **5i** and **5i'** (59 mg, 71%) as a clear oil. Major (**5i**): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.07-6.89 (m, 3H), 2.65 (t, *J* = 6.7 Hz, 2H), 2.57 (s, 2H), 2.24 (s, 3H), 1.62 (t, *J* = 6.7 Hz, 2H), 0.99 (s, 6H). Minor (**5i'**): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.07-6.89 (m, 3H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 2H), 2.23 (s, 3H), 1.56 (t, *J* = 6.7 Hz, 2H), 1.02 (s, 6H). Major (**5i**): **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 136.4(2C), 134.3, 127.4, 127.1, 125.4, 44.1, 36.2, 29.2, 28.1, 24.5, 19.7. **IR** (film) cm^{-1} 2948, 2909, 2866, 1460, 1430, 1384, 1364, 765, 704. **LRMS** (CI, Pos) calcd for $C_{13}H_{19}$ $[M+H]^+$: 175.2 m/z, found 175.1 m/z.



3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalene] (5j):

The reaction was performed according to general procedure **F**. The residue was purified by flash chromatography (100% hexanes), affording the title compound (94 mg, 94%) as a clear

oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.15-7.08 (m, 4H), 2.82 (t, 2H, *J* = 6.7 Hz), 2.63 (s, 2H), 1.68 (t, 2H, *J* = 6.7 Hz), 1.57-1.47 (m, 6H), 1.40-1.37 (m, 4H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 136.4 (2 C's), 129.7, 128.8, 125.6, 125.5, 41.4, 36.5, 33.4, 32.0, 26.9, 25.7, 21.9. **IR** (film) cm^{-1} 2918, 2845, 1494, 1449, 745, 712. **LRMS** (CI, Pos) calcd for $C_{15}H_{21}$ $[M+H]^+$: 201.2 m/z, found 201.1 m/z.



1-(2,2-dimethyl-4-phenylbutoxy)-2,2,6,6-tetramethylpiperidine (6):

The reaction was performed according to general procedure **F** in presence of TEMPO (78.1 mg, 1 mmol). The residue was purified by flash chromatography (100% hexanes), affording the TEMPO-adduct **6** (52 mg, 33%) as a clear oil and recovery of **4a** (90 mg, 63%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.29 (m, 2H), 7.24-7.19 (m, 3H), 3.60 (s, 2H), 2.67-62 (m, 2H), 1.66-1.62 (m, 2H), 1.56-1.30 (m, 6H), 1.23 (s, 6H), 1.18 (s, 6H), 1.06 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.9, 128.7, 125.9, 84.9, 60.7, 42.7, 40.3, 35.8, 33.9, 31.3, 25.6, 20.6, 17.3. **IR** (film) cm^{-1} 2928, 2870, 1470, 1373, 1133, 1059, 697. **HRMS** (ESI, Pos) calcd for $C_{21}H_{36}N_1O_1$ $[M+H]^+$: 318.2791 m/z, found 318.2793 m/z.

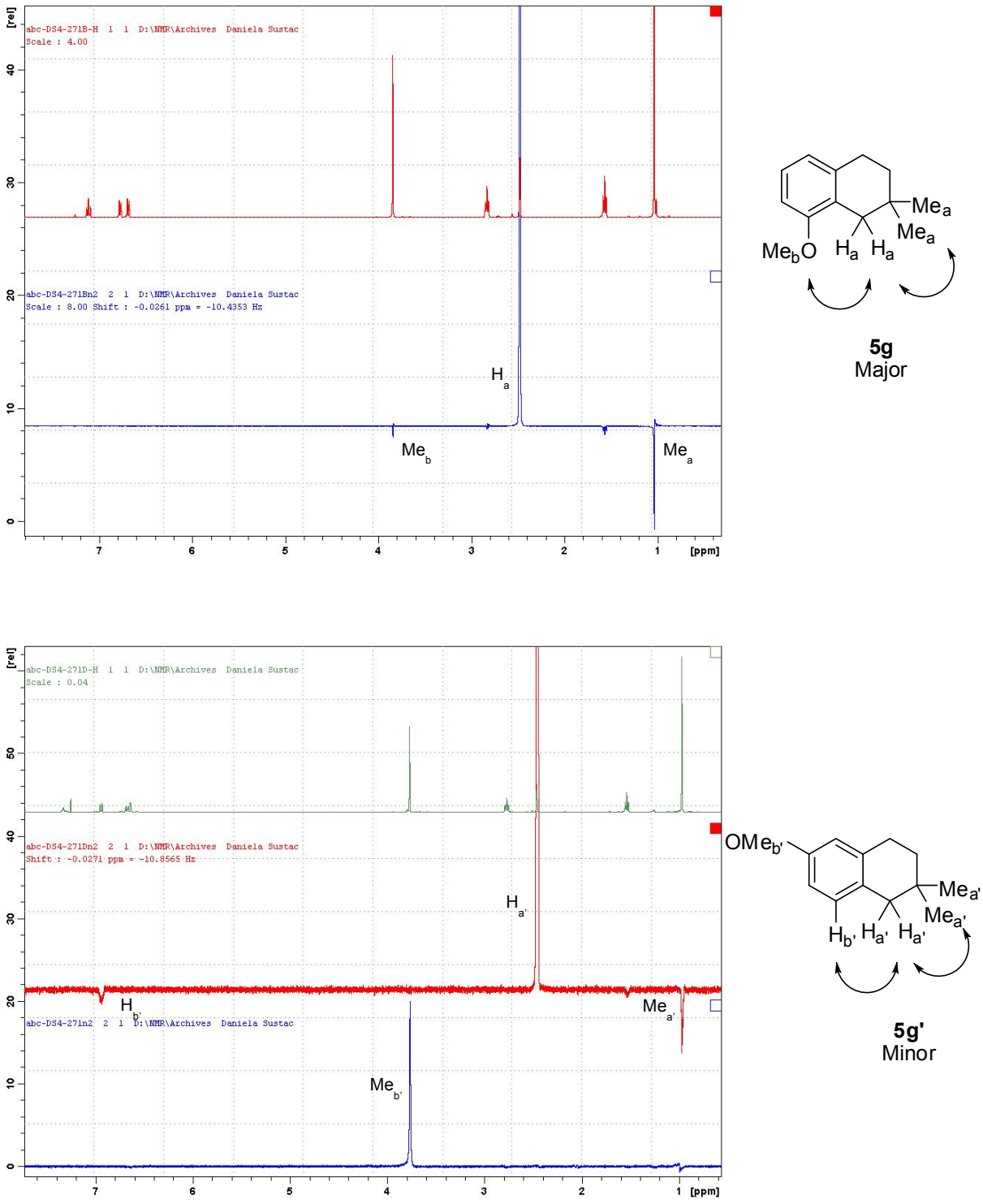


Figure 1. NOE experiment for **5g** and **5g'**

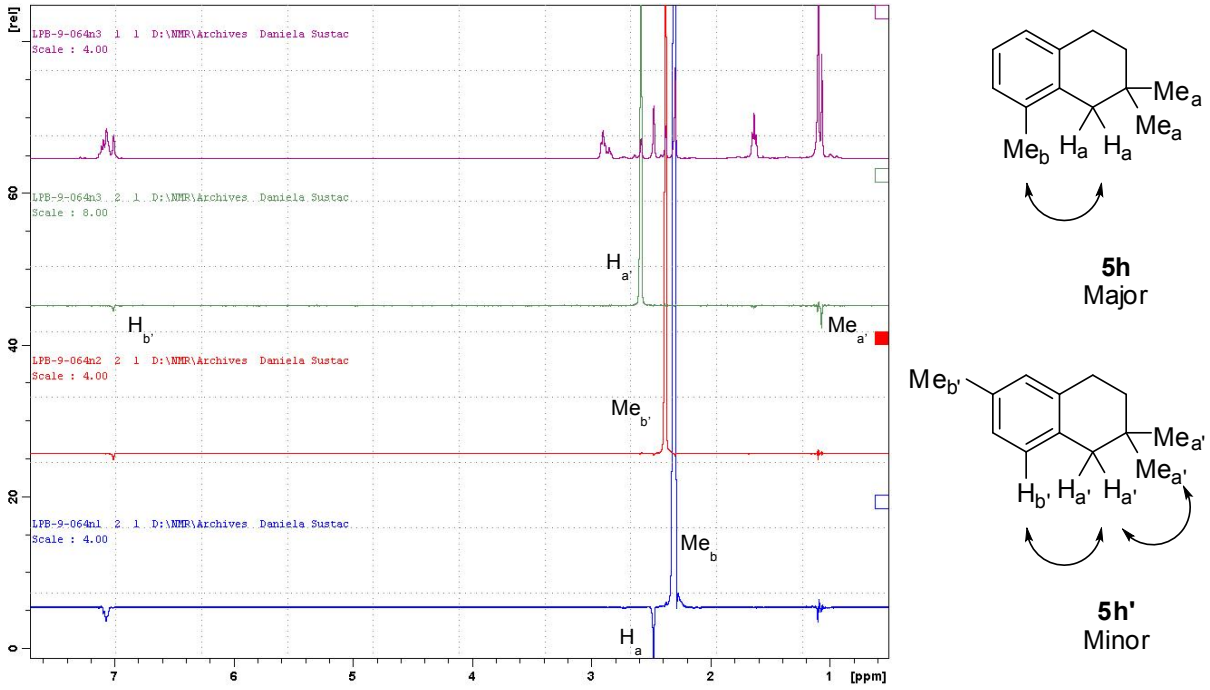
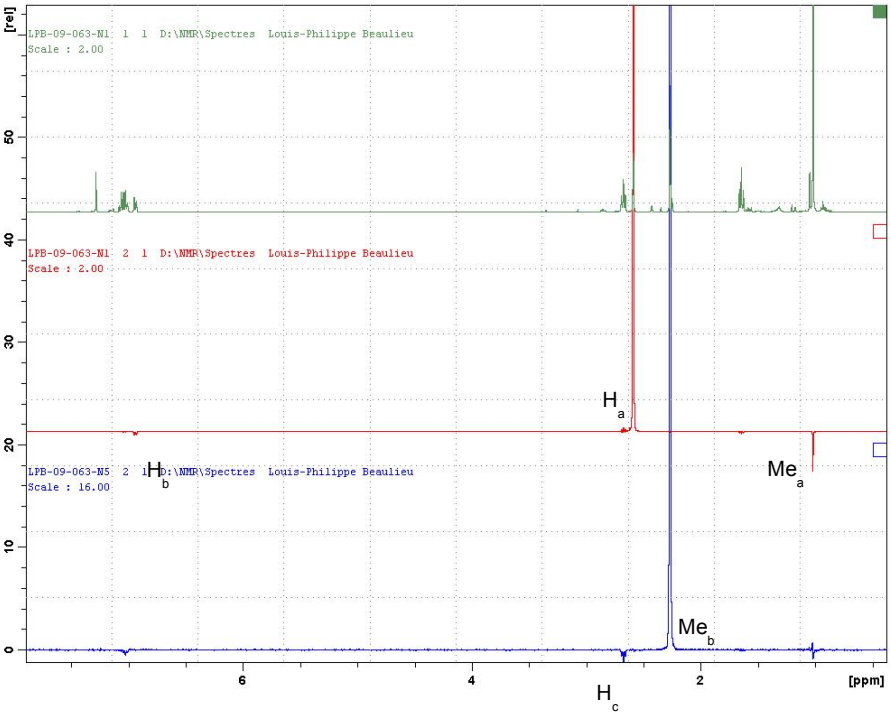
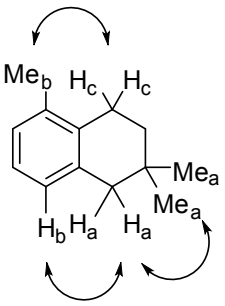
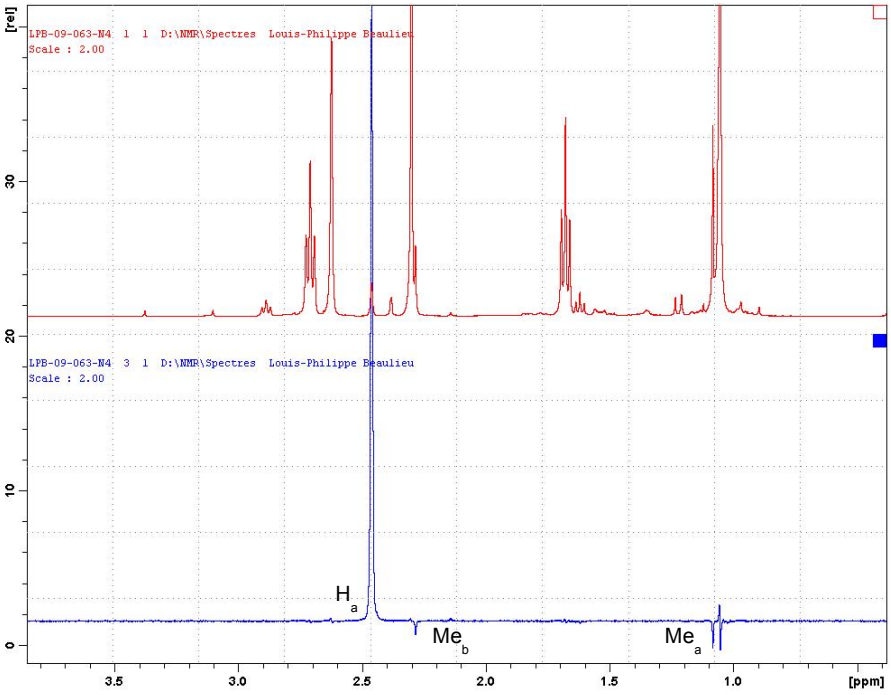


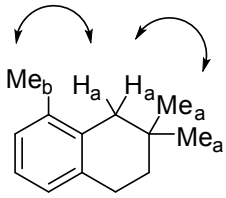
Figure 2. NOE experiment for **5h** and **5h'**





5i
Major





5i'
Minor

Figure 3. NOE experiment for **5i** and **5i'**

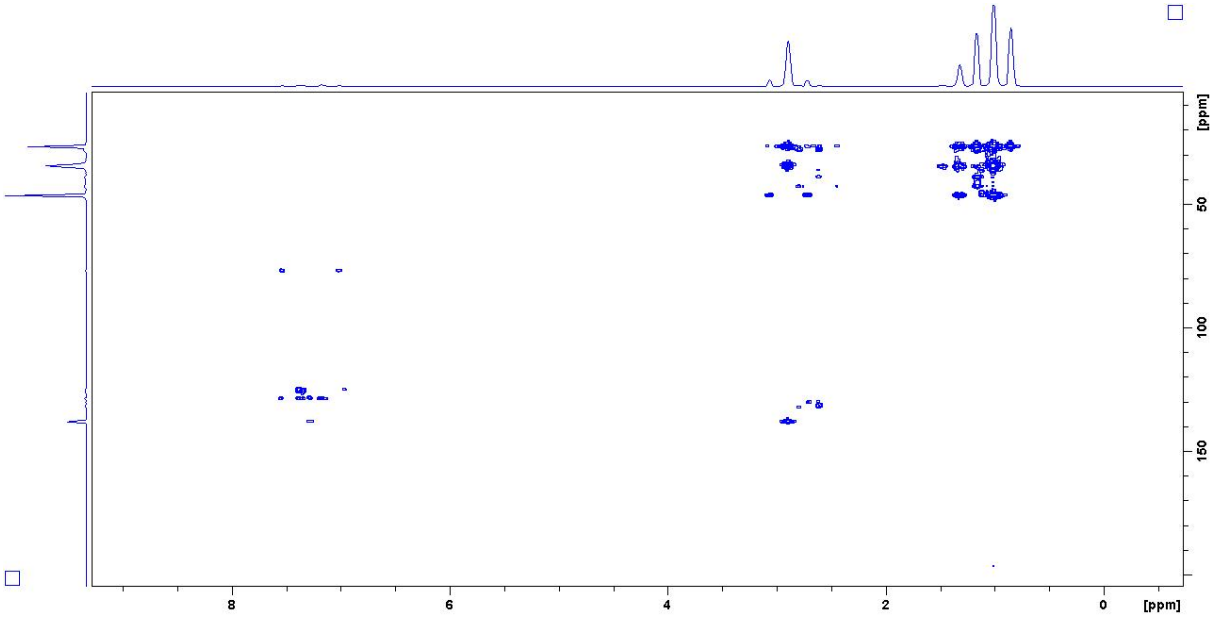


Figure 4. HMBC NMR experiment for dimer **3**

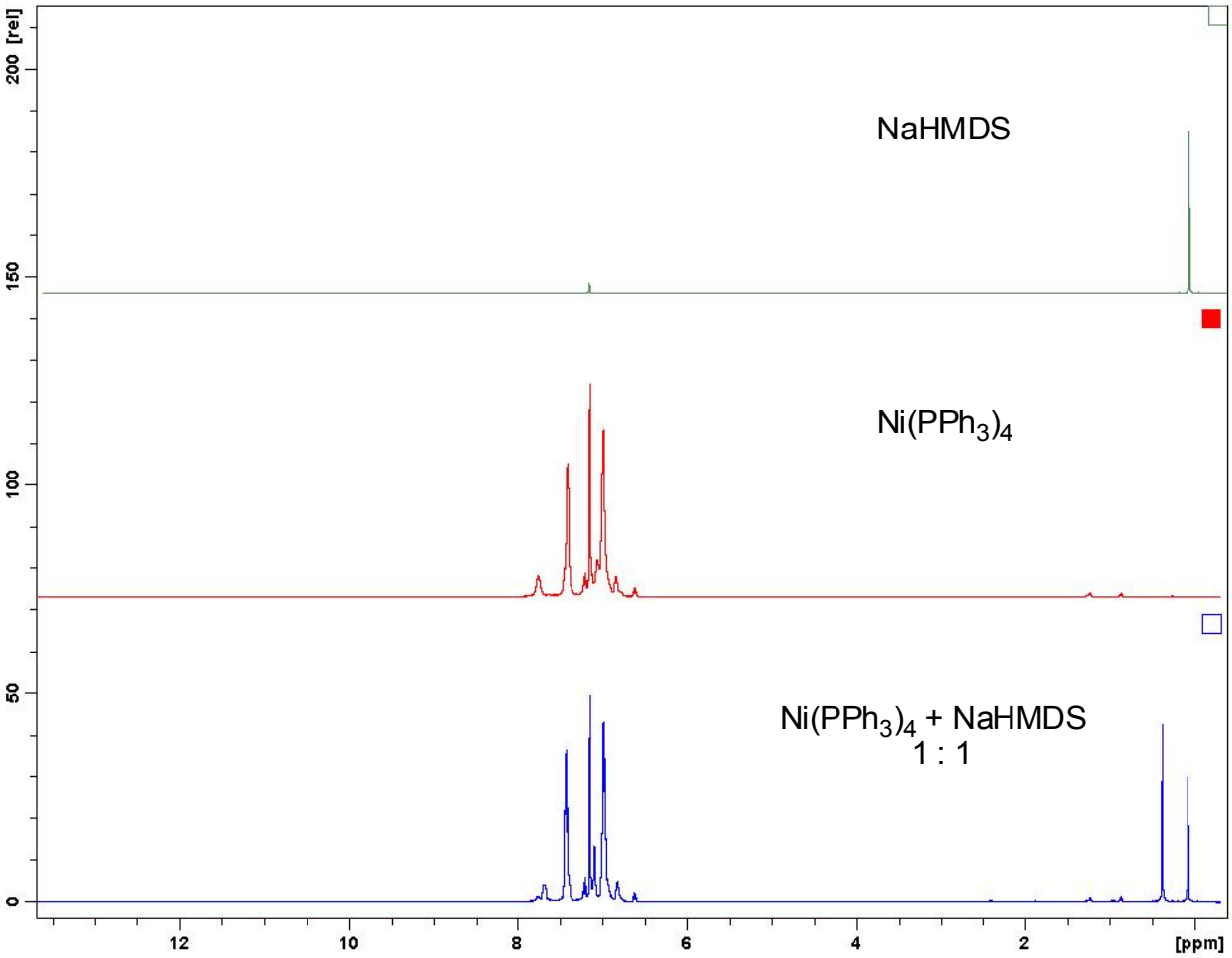


Figure 5. ^{1}H NMR study in presence of equimolar amounts of $Ni(PPh_3)_4$ and NaHMDS at 70 °C in C_6D_6

DOSY NMR

DOSY is a 2D NMR experiment measuring the diffusion coefficients of molecules in a solution, which are reported on one axis, while the typical chemical shift information is presented on the other. This technique allows the deduction of the hydrodynamic radii of molecules in solution from their diffusion coefficient according to the Stokes-Einstein equation.[12]

Despite the well-established association of anionic ligands with Pd(0) complexes,[13] the corresponding interactions with Ni(0) complexes are scarcely known.[14] One particularly relevant study describes the formation of an anionic complex between $LiAlH_4$ and (bpy)Ni(COD) in the course of the hydrodesulfurization of organosulfur heterocycles via an SET mechanism.[15]

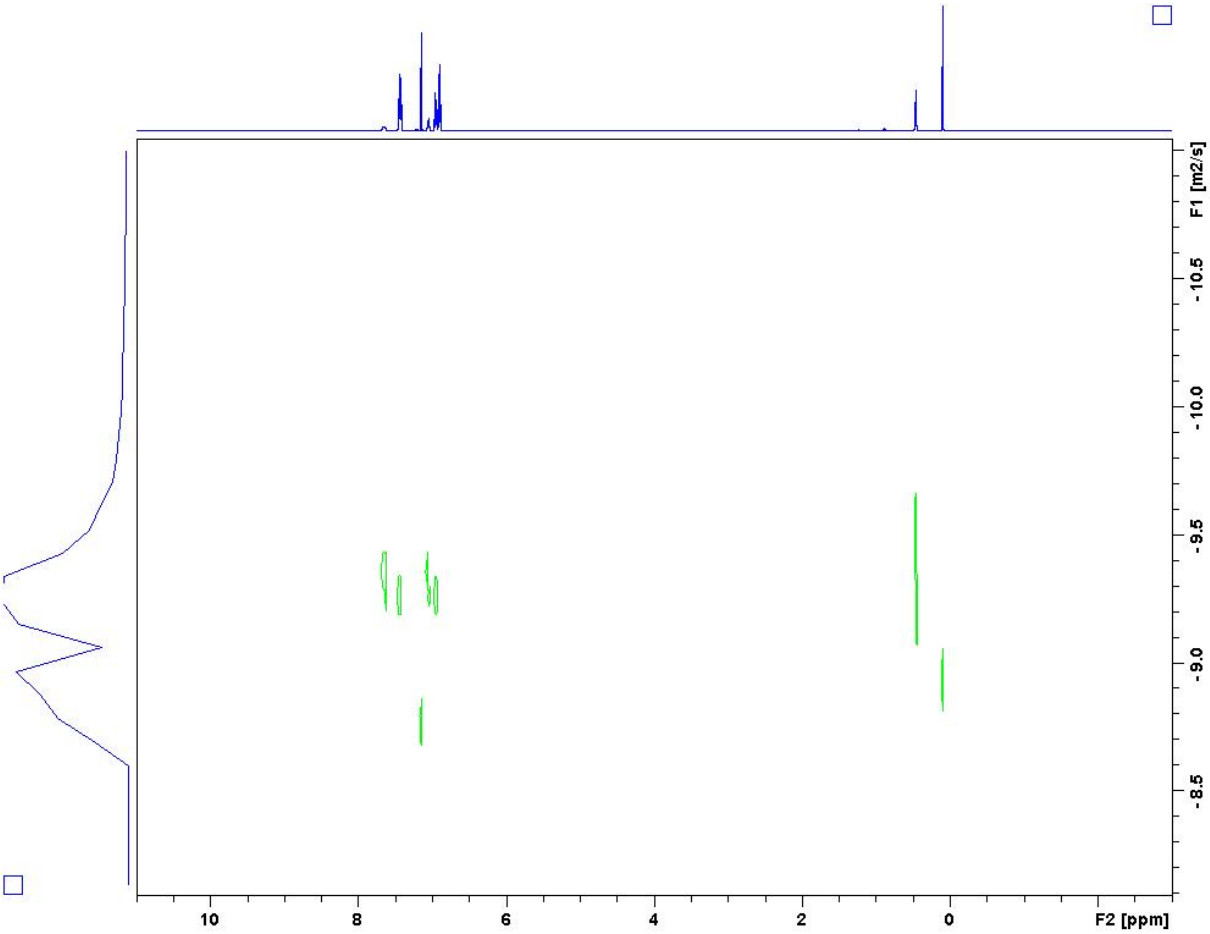


Figure 6. DOSY ^{1}H NMR experiment using equimolar amounts of $Ni(PPh_3)_4$ and NaHMDS at 25 °C in C_6D_6.

Since we observe diffusion coefficients of the same order of magnitude for the NMR signals attributed to $Ni(PPh_3)_4$ and those associated with a mixture of $Ni(PPh_3)_4$, NaHMDS and **4a**, we can conclude that an adduct is formed between these three components (**Figures 7** and **9**). Upon filtration and concentration of a similarly prepared mixture, the signals for this adduct disappear in the ^{1}H NMR spectrum, thus indicating that the signals attributed to the adduct do not correspond to a reaction by-product (**Figure 8**).

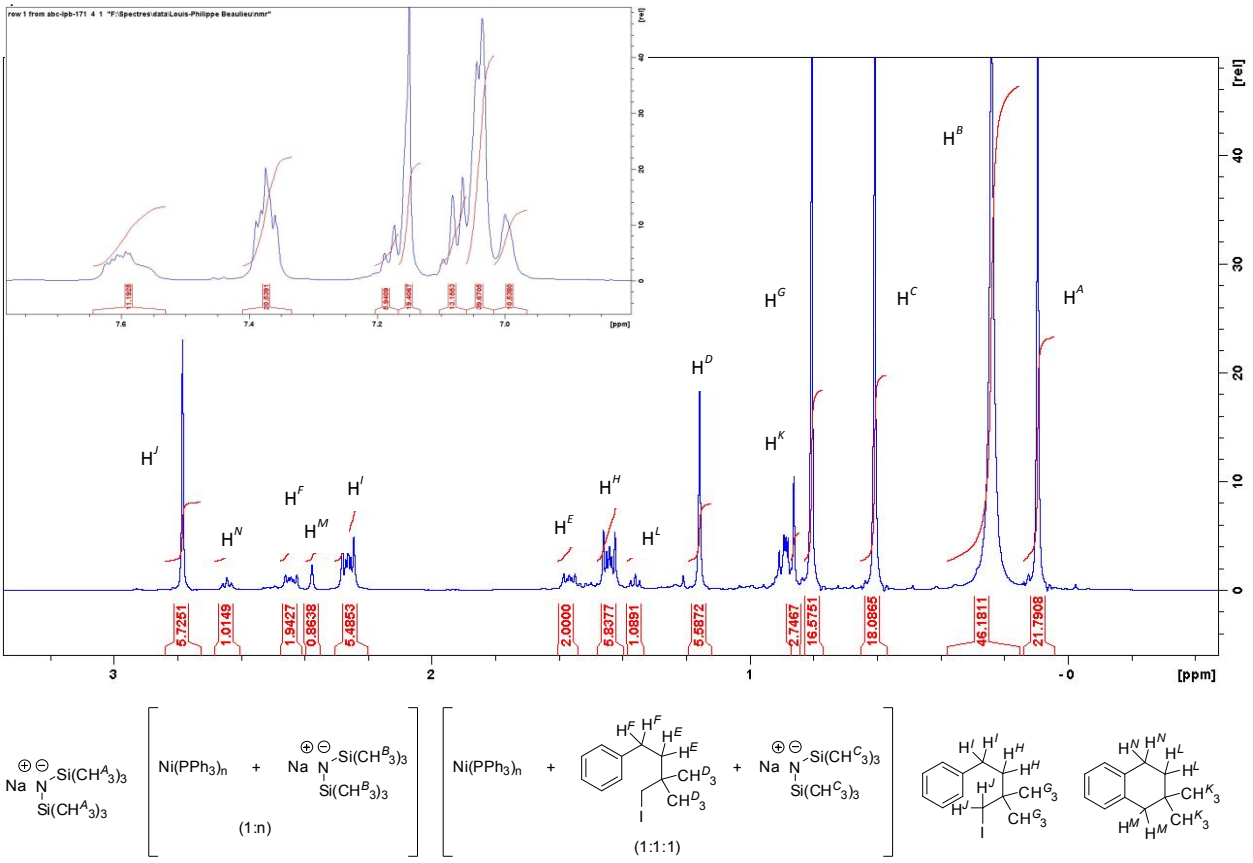


Figure 7. DOSY ^{1}H NMR experiment involving a solution of $Ni(PPh_3)_4$ (55.4 mg, 0.05 mmol), **4a** (28.8 mg, 0.1 mmol), NaHMDS (27.5 mg, 0.15 mmol) in 0.75 mL of C_6D_6, performed at 25 °C with a gradient of 52.1 G.cm^{-1}

Entry	Proton Label	Chemical Shift (ppm)	Diffusion Coefficient (E-10 m^2s^{-1})
1		7.65-7.54	5.7
2		7.42-7.33	8.9
3		7.20-7.17	10.3
4		7.17-7.14	16.1
5		7.11-7.02	8.2
6		7.02-6.97	6.5
7	H^J	2.82-2.75	11.0
8	H^N	2.67-2.62	12.9
9	H^F	2.48-2.41	6.3
10	H^M	2.40-2.36	12.6
11	H^I	2.32-2.21	11.0
12	H^E	1.61-1.55	6.2
13	H^H	1.48-1.41	10.8
14	H^L	1.39-1.34	11.0
15	H^D	1.19-1.13	6.0
16	H^K	0.87-0.85	12.5
17	H^G	0.84-0.78	10.9
18	H^C	0.65-0.57	5.9

19	H^B	0.33-0.15	6.0
20	H^A	0.14-0.05	13.1

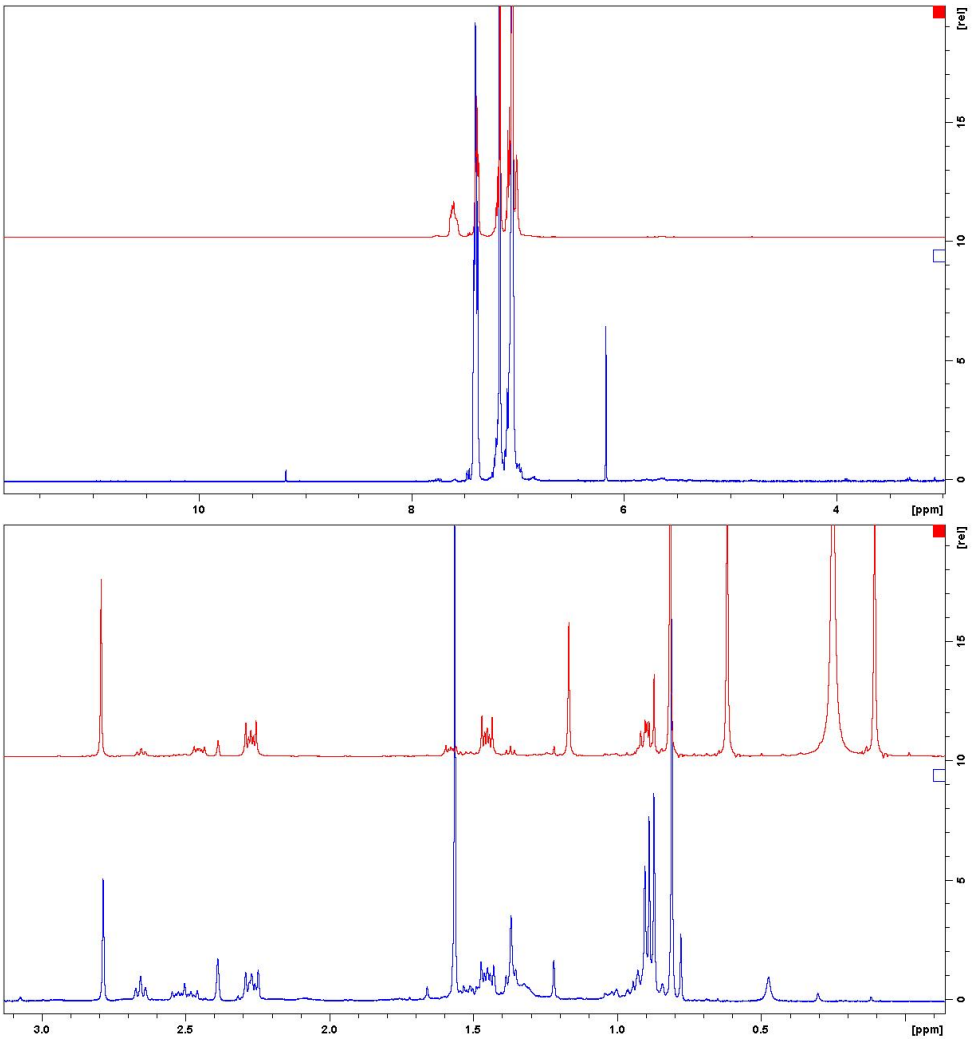


Figure 8. ^{1}H NMR spectra of a solution of $Ni(PPh_3)_4$ (55.4 mg, 0.05 mmol), **4a** (28.8 mg, 0.1 mmol), NaHMDS (27.5 mg, 0.15 mmol) in 0.75 mL of C_6D_6, performed at 25 °C (top, in red) and ^{1}H NMR spectra of a sample prepared in the same manner, then filtered over a pad of silica with hexanes, then concentrated (bottom, in blue).

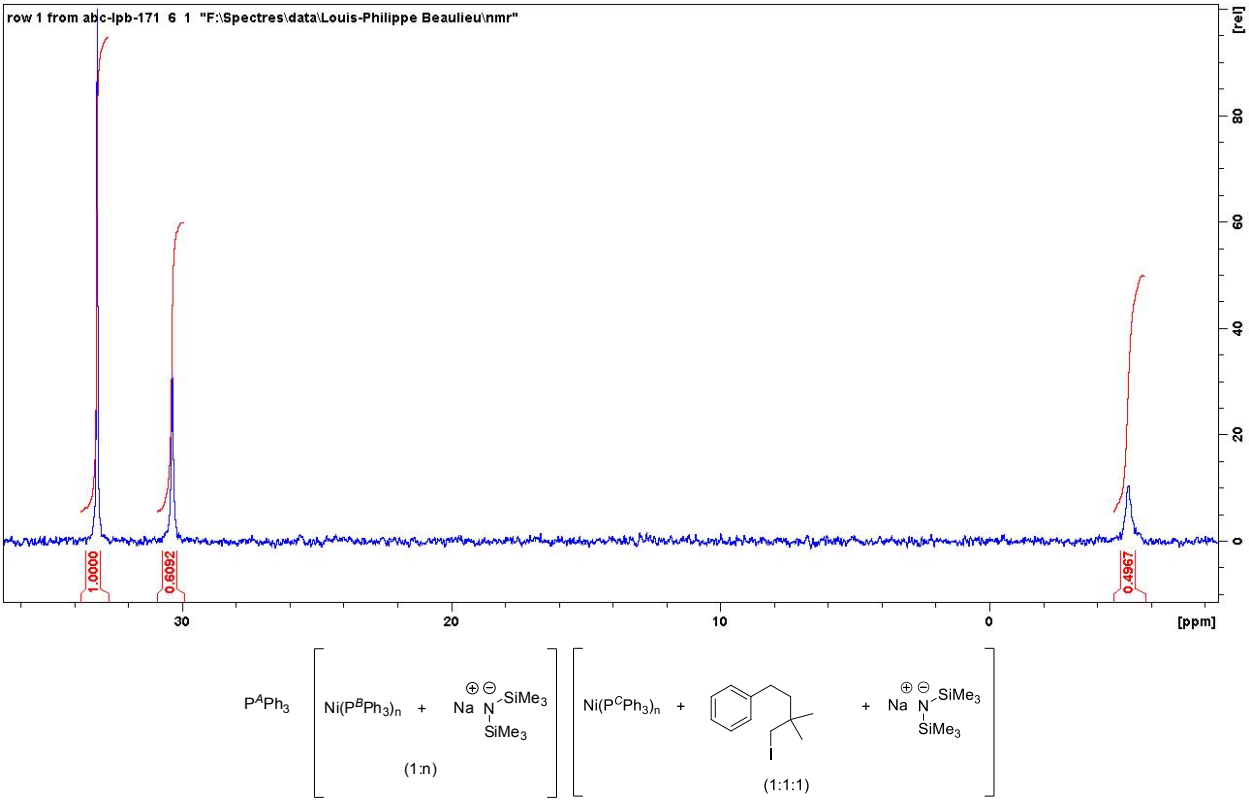


Figure 9. DOSY ^{31}P NMR experiment involving a solution of $Ni(PPh_3)_4$ (55.4 mg, 0.05 mmol), **4a** (28.8 mg, 0.1 mmol), NaHMDS (27.5 mg, 0.15 mmol) in 0.75 mL of C_6D_6, performed at 25 °C with a gradient of 49.8 G.cm^{-1}

Entry	Phosphorus Label	Chemical Shift (ppm)	Diffusion Coefficient (E-10 m^2s^{-1})
1	P^B or P^C	33.78-32.72	6.2
2	P^B or P^C	30.93-29.91	5.9
3	P^A	-4.60- -5.80	8.6

References:

1. E. Lee, C. Lee, J. S. Tae, H. S. Whang, and K. S. Li, *Tetrahedron Lett.* **1993**, 34, 2343-2346.

2. S. Phoenix, E. Bourque and P. Deslongchamps, *Org. Lett.* 2000, **2**, 4149-4152.

3. Singh, G. S. Reddy and J. C. Calabrese, *J. Org. Chem.* 1984, **49**, 5132-5136.

4. T. Fujita, S. Watanabe, K. Suga and H. Nakayama, *Synthesis* 1979, 310-311.

5. A. A. Khalaf and R. M. Roberts, *J. Org. Chem.* 1972, **37**, 4227-4235.

6. D. J. Muir and J. B. Stothers, *Can. J. Chem.* 1993, **71**, 1099-1105.

7. H. O. House, W. C. Liang and P. D. Weeks, *J. Org. Chem.* 1974, **39**, 3102-3107.

8. E. Rothstein and W. G. Schofield, *J. Chem. Soc.* 1965, 4566-4576.

9. F. G. Morin, W. J. Horton, D. M. Grant, D. K. Dalling and R. J. Pugmire, *J. Am. Chem. Soc.* 1983, **105**, 3992-3998.

10. D. C. Harrowven and R. F. Dainty, *Tetrahedron* 1997, **53**, 15771-15786.

11. A. Radha Krishna Murthy and G. S. R. Subba Rao, *Tetrahedron* 1982, **38**, 3335-3338.

12. (a) K. F. Morris and C. S. Johnson, *J. Am. Chem. Soc.*, 1992, **114**, 3139-3141. (b) Y. Cohen, L. Avram and L. Frish, *Angew. Chem., Int. Ed.*, 2005, **44**, 520-554.

13. (a) L. Xue and Z. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1692-1705. (b) Goo, D. Koley, H. Hermann and W. Thiel, *Chem. Commun.*, 2004, 2141-2143. (c) C. Amatore, M. Azzabi and A. Jutand, *J. Am. Chem. Soc.*, 1991, **113**, 8375-8384. (d) C. Amatore, A. Jutand and A. Suarez, *J. Am. Chem. Soc.*, 1993, **115**, 9531-9541. (e) C. Amatore and A. Jutand, *J. Organomet. Chem.*, 1999, **576**, 254-278. (f) C. Amatore and A. Jutand, *Acc. Chem. Res.*, 2000, **33**, 314-321.

14. H. Hou, A. L. Rheingold and C. P. Kubiak, *Organometallics*, 2004, **24**, 231-233.

15. J. Eisch, L. E. Hallenbeck and K. I. Han, *J. Am. Chem. Soc.*, 1986, **108**, 7763-7767.