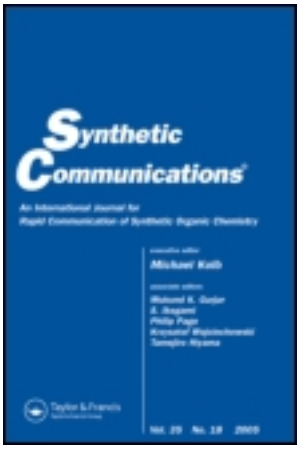

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Synthesis of 1-Tetralone Derivatives Using a Stille Cross Coupling/Friedel Crafts Acylation Sequence

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Synthesis of 1-Tetralone Derivatives Using a Stille Cross Coupling/Friedel Crafts Acylation Sequence

Johnny Vercouillie,[1] Mohamed Abarbri,[1] Jean-Luc Parrain,[2] Alain Duchêne,[1] and Jérôme Thibonnet[1,*]

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ABSTRACT

An efficient method of synthesis of 1-tetralones has been achieved featuring a Stille cross-coupling reaction as the key step.

Key Words: Friedel–Crafts acylation; Stille cross-coupling reaction; 1-Tetralone.

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The efficient preparation of functionalized cyclic structures is important in the search for small bioactive molecules. In particular, 1-tetralones constitute an important class of starting materials and intermediates for the synthesis of biologically active substances,[1] and they are also found in natural products.[2]

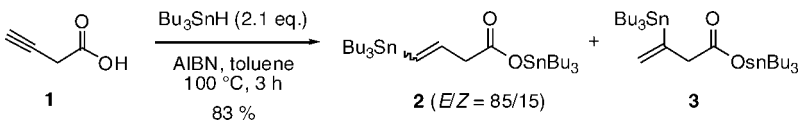
Numerous methods have been reported over a period of time for the synthesis of these structures. Classical means for the synthesis of 1-tetralones include intramolecular Friedel–Crafts reaction of 4-arylbutyric acids and its variants.[3] 1-Tetralones can also be prepared by radical cyclization, in the presence of stoichiometric amounts of lauryl peroxide,[4] or by palladium-catalyzed cyclization of appropriately substituted ω-(2-iodoaryl)alkanenitriles.[5]

We previously described the synthesis of **2** and demonstrated its efficiency in transferring but-3-enoic-d_4 acid synthons onto miscellaneous substrates.[6] To broaden the use of **2** in synthesis, we planned to prepare 1-tetralones from aryl halides using Stille and intramolecular Friedel–Crafts acylation.

The required organotin precursor **2** was easily obtained by radical hydrostannation[7] of but-3-ynoic acid **1** (prepared via carbonation of the corresponding allenylmagnesium bromide)[8] as a thermodynamic mixture ($E/Z = 85/15$) with 83% yield (Sch. 1). It should be noted that the radical hydrostannation conducted at a lower temperature (e.g., in benzene) led to a 50/50 mixture of **2** and its internal isomer **3**. Our investigation began with the coupling of **2** with organic halides under standard Stille conditions (Sch. 2).[9]

Various catalysts were tested in order to find optimal experimental conditions, and we found that *tetrakis*(triphenylphosphine)palladium was the most efficient for **2**. Good yields of homocinnamic acids (**4a–m**) were obtained with aryl halides (55–92%). When the thermodynamic mixture of $E/Z = 85/15$ was used for cross-coupling with organic halides, the crude mixture was found to contain a small amount of Z (<12%) that was eliminated during the crystallization process. The temporary protection of the carboxylic acid function was removed by simple hydrolysis at room temperature with 1 M HCl/water or by stirring on silica gel. These results demonstrate the efficiency of **2** to obtain the homocinnamyl skeleton cleanly.

Taking into account the numerous applications of compounds **4**, we decided to report an alternative and fairly general route to substituted 1-tetralones involving intramolecular Friedel–Crafts acylation (Sch. 3). Selective reduction of the double bond of the crude products **4** was accomplished



Scheme 1.

Scheme 2.

under catalytic hydrogenation conditions using 10% Pd-C[10] at 14.7 psi of hydrogen at room temperature. 4-Phenylbutyric acids **5** were converted to 1-tetralones **6** by Friedel–Crafts acylation using trifluoroacetic anhydride[11] (2.0 mole equivalent) in 1,2-dichloroethane (DCE) or methanesulfonic acid and P_2O_5.[12] The results are summarized in Table 1.

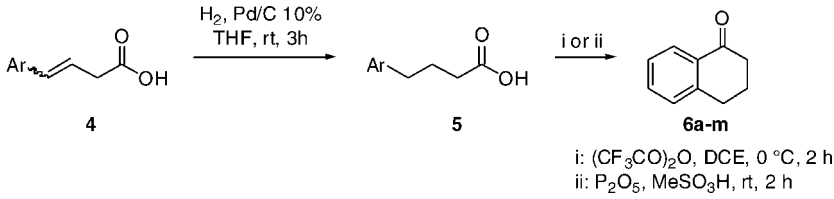
Finally, 6,7-methylenedioxy-1-tetralone **6h**, which is a key intermediate in the synthesis of ABT 200 {(±) 1′R*, 3R*)-3-phenyl-1-[1′, 2′, 3′, 4′-tetrahydro-5′,6′-methylene-dioxy-1′-naphthalenyl-methyl]-pyrrolidine}, an α-2 antagonist and a norepinephrine uptake inhibitor (3e), was synthesized by this procedure (Fig. 1).

In conclusion, a convenient procedure has been developed for the synthesis of 1-tetralones using the Stille cross-coupling between a functional vinyltin reagent and aryl halides as key step. The method appears to be general and compatible with different substitution patterns in the aromatic moiety.

EXPERIMENTAL SECTION

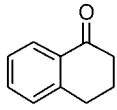
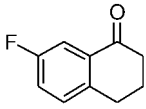
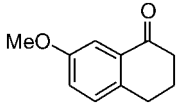
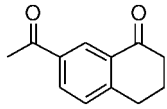
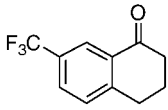
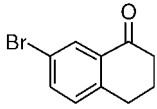
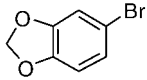
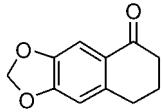
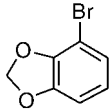
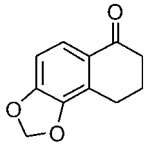
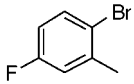
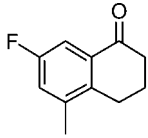
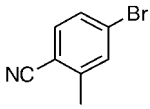
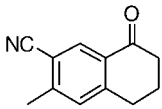
General Methods

All reactions were performed in oven-dried glassware under positive argon pressure. Toluene was dried and freshly distilled from sodium. ^{1}H-NMR spectra were recorded at 200 MHz or at 300 MHz using $CDCl_3$



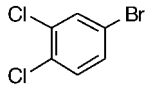
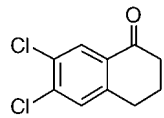
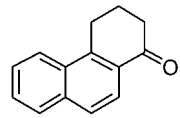
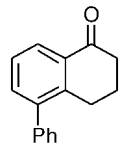
Scheme 3.

Table 1. Synthesis of 1-tetralones.

Entry	Organic Halide	1-Tetralone	Number	Yield (%)
1	Ph-I		**6a**	90[a]
2	*p*-F-Ph-Br		**6b**	89[a]
3	*p*-MeO-Ph-Br		**6c**	94[a]
4	*p*-Acetyl-Ph-Br		**6d**	90[a]
5	*p*-CF_3-Ph-Br		**6e**	87[b]
6	*p*-Br-Ph-Br		**6f**[a]	75[b]
7			**6g**	85[a]
8			**6h**	78[a]
9			**6i**	80[b]
10			**6j**	83[b]

(*continued*)

Table 1. Continued.

Entry	Organic Halide	1-Tetralone	Number	Yield (%)
11			**6k**	72[b]
12	1-Bromonaphthalene		**6l**	82[b]
13	2-Bromobiphenyl		**6m**	70[b]

[a]$(CF_3CO)_2O$, DCE, 0 °C, 2 h.
[b]P_2O_5, $MeSO_3H$, rt, 2 h.

as solvent. Results, reported using the residual proton resonance of $CDCl_3$ ($\delta_H = 7.25$ ppm) as the internal reference, were as follows (in order): chemical shift (δ in ppm relative to Me_4Si), multiplicity (s, d, t, q, quint, m, b for singlet, doublet, triplet, quartet, quintuplet, multiplet and broad), and coupling constants (J in Hz). ^{13}C-NMR spectra were recorded at 50 MHz or 75 MHz using $CDCl_3$ solvent peak at $\delta_C = 77.0$ ppm as the reference. Electron impact mass spectra were measured at 70 eV by gas chromatography-mass spectrometry (GC-MS) or direct introduction mode. Raman spectra were recorded on a Bruker RFS 100 and excitation with a laser Nd: YAG

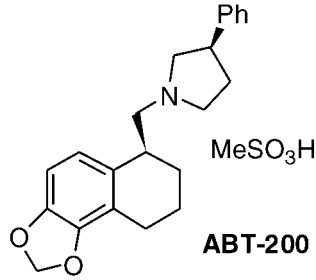


Figure 1. Structure of ABT-200: an alpha-2 antagonist and a norepinephrine uptake inhibitor.

(1064 nm, 130 mW). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum One Fourier transform infrared (FT-IR) spectrophotometer. Melting points were taken on a Büchi B-540 and are uncorrected. Standard column chromatography was performed on Merck silica gel (60 Å, 230–400 mesh silica gel) by flash column chromatography techniques. Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} plates. Tributyltin hydride was commercialy available (from Aldrich). Acid **1** was prepared by a previously reported procedure.[8] The preparation of tributylstannyl-4-tributylstannylbut-3-enoate **2** has already been described.[6c]

General Procedure for the Preparation of Substituted Homocinnamic Acids 3a–m

Toluene (20 mL), **2** (7 mmol), aryl bromide (5.8 mmol), and *tetrakis*(triphenylphosphine)palladium (3 mol%) were introduced into a 50 mL flask. The mixture was degassed under vacuum and stirred overnight at 100°C. After cooling, the stannyl ester was hydrolyzed with 10 mL of 1 M HCl solution. After extraction with diethylether, the organic layer was treated with 1 M NaOH solution. The aqueous layer was washed with Et_2O and then acidified with 1 M HCl solution and extracted with Et_2O. After removal of the solvents under reduced pressure, compounds **4** were obtained by crystallization from petroleum ether/Et_2O (95/5) or by column chromatography on silica gel with first petroleum ether/Et_2O (99/1) as eluent, then elution with petroleum ether/Et_2O (80/20).

(*E*)-4-[(8,9-Methylenedioxy)phenyl]but-3-enoic acid (**4g**)

Mp: 115°C. IR (KBr): 3018, 1689, 1604, 1257, 1230. RAMAN: 1617, 1603. ^{1}H-NMR (δ ppm): 3.30 (d, $J = 7$ Hz, 2H), 6.00 (s, 2H), 6.14 (dt, $J = 15.8$ Hz, $J = 7$ Hz, 1H), 6.46 (d, $J = 15.8$ Hz, 1H), 6.76–6.86 (m, 2H), 6.96–7.00 (m, 1H), 8.55 (bs, 1H). ^{13}C-NMR (δ ppm): 38.3, 101.5, 106, 108.7, 119.4, 121.4, 131.5, 133.9, 147.7, 148.4, 178.4. MS (70 eV, EI) m/z: 206 (M^+, 91), 161 (32), 132 (11), 131 (100), 104 (10), 103 (85), 102 (15), 77 (32), 51 (15), 45 (12).

(*E*)-4-[(6,7-Methylenedioxy)phenyl]but-3-enoic acid (**4h**)

IR: 3018, 1711, 1655, 1288. ^{1}H-NMR (δ ppm): 3.35 (d, $J = 4.8$ Hz, 2H), 6.03 (s, 2H), 6.48–6.55 (m, 2H), 6.75–6.85 (m, 3H), 11.52 (bs, 1H). ^{13}C-NMR (δ ppm): 38.4, 100.8, 107.4, 120.6, 121.5, 123.8, 128.3, 119, 144.5, 147.6, 177.9. MS (70 eV, EI) m/z: 206 (M^+, 100), 161 (40), 132 (14), 131 (91), 104 (14), 103 (94), 102 (17), 78 (10), 77 (42), 76 (12), 75 (11), 63 (14), 51 (21), 50 (10), 45 (18).

(*E*)-4-(4-Fluoro-2-methylphenyl)but-3-enoic acid (**4i**)

Mp: 96–97°C. IR (KBr): 3054, 1711, 1609, 1585, 1266. ^{1}H-NMR (δ ppm): 2.35 (s, 3H), 3.35 (dd, $J = 7.1$ Hz, $J = 1.4$ Hz, 2H), 6.14 (dt, $J = 15.7$ Hz, $J = 7.1$ Hz, 1H), 6.69 (d, $J = 15.7$ Hz, 1H), 6.85–6.95 (m, 2H), 7.44 (dd, $J = 9.3$ Hz, $J = 5.9$ Hz, 1H), 9.70 (bs, 1H). ^{13}C-NMR (δ ppm): 19.8, 38.2, 112.9 (d, $J_{C\text{-}F} = 22$ Hz), 116.7 (d, $J_{C\text{-}F} = 21$ Hz), 122.0, 121.3 (d, $J_{C\text{-}F} = 8.6$ Hz), 130.8, 137.5 (d, $J_{C\text{-}F} = 7.6$ Hz), 162.1 (d, $J_{C\text{-}F} = 246$ Hz), 177.6. MS (70 eV, EI) m/z: 194 (M^+, 52), 150 (12), 149 (100), 147 (13), 134 (32), 133 (30), 109 (41).

(*E*)-4-(4-Cyano-3-methylphenyl)but-3-enoic acid (**4j**)

Mp: 95–97°C. IR (KBr): 3056, 1713, 1606, 1266. ^{1}H-NMR (δ ppm): 2.57 (s, 3H), 3.38 (d, $J = 5.8$ Hz, 2H), 5.42 (dt, $J = 16.0$ Hz, $J = 6.3$ Hz, 1H), 6.62 (d, $J = 16.0$ z, 1H), 7.22–7.34 (m, 2H), 7.58 (d, $J = 8.0$ Hz, 1H), 8.90 (bs, 1H). ^{13}C-NMR (δ ppm): 20.4, 37.9, 111.4, 118.1, 124.0, 124.6, 127.9, 132.5, 132.7, 140.8, 142.2, 173.3. MS (70 eV, EI) m/z: 201 (M^+ 49), 159 (27), 157 (13), 156 (100), 154 (12), 142 (15), 141 (17), 140 (24), 130 (13), 129 (49), 128 (19), 127 (20), 116 (22), 115 (18), 77 (18), 51 (14), 39 (17).

(*E*)-4-(3,4-Dichlorophenyl)but-3-enoic acid (**4k**)

Mp: 70°C. IR (KBr): 3056, 1710, 1554, 1293. ^{1}H-NMR (δ ppm): 3.34 (d, $J = 6.6$ Hz, 2H), 6.32 (dt, $J = 15.9$ Hz, $J = 6.6$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 7.23 (dd, $J = 8.3$ Hz, $J = 1.8$ Hz, 1H), 7.41 (d, $J = 8.3$ Hz, 1H), 7.49 (d, $J = 1.8$ Hz, 1H), 9.25 (bs, 1H). ^{13}C-NMR (δ ppm): 37.8, 122.9, 125.5, 128.0, 130.5, 131.4, 131.7, 132.7, 136.7, 177.4. MS (70 eV, EI) m/z: 234 (M^+, 7), 232 (M^+, 39), 230 (M^+, 61), 188 (20), 187 (59), 186 (11), 185 (93), 152 (25), 151 (78), 149 (59), 116 (15), 115 (100), 114 (19), 75 (18), 74 (14), 63 (19), 39 (19).

General Procedure for the Hydrogenation Acids 4a–m

Pd/C (0.24 mmol, 10% mol) was added to a solution of **4** (2.4 mmol) in dry tetrahydrofuran (THF) (20 mL) in a dried, two-necked, 50 mL round-bottomed flask equipped with a magnetic stir bar, rubber septum cap, and H_2-filled balloon. The resulting suspension was stirred at room temperature for 3 h under a current of hydrogen. Insoluble materials were removed by filtration, and the filtrate was concentrated in vacuo to give a residue that was purified by column chromatography (silica gel, petroleum ether/Et_2O = 90/10) to give **5**.

4-[(7,8-Methylenedioxy)phenyl]butanoic acid (**5g**)

IR: 3034, 1706, 1602, 1257. ^{1}H-NMR (δ ppm): 1.96 (tt, $J = 7.2$ Hz, $J = 7.5$ Hz, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 2.63 (t, $J = 7.5$ Hz, 2H), 5.96 (s, 2H), 6.69–6.79 (m, 3H), 10.15 (bs, 1H). ^{13}C-NMR (δ ppm): 26.3, 33.1, 34.6, 100.7, 108.1, 108.8, 121.2, 134.9, 145.7, 147.5, 180. MS (70 eV, EI) m/z: 208 (M^+, 36), 148 (58), 136 (11), 135 (100), 105 (10), 79 (12), 77 (42), 63 (10), 51 (33), 50 (10), 45 (12).

4-[(6,7-Methylenedioxy)phenyl]butanoic acid (**5h**)

IR: 3084, 3043, 1703, 1631, 1278, 1259. ^{1}H-NMR (δ ppm): 2.02 (tt, $J = 7.3$ Hz, $J = 7.4$ Hz, 2H), 2.44 (t, $J = 7.3$ Hz, 2H), 2.70 (t, $J = 7.4$ Hz, 2H), 5.97 (s, 2H), 6.68–6.84 (m, 3H), 10.5 (bs, 1H). ^{13}C-NMR (δ ppm): 24.3, 28.5, 33.2, 100.4, 106.6, 121.4, 122.4, 128.2, 145.6, 145.9, 179.5. MS (70 eV, EI) m/z: 208 (M^+, 65), 149 (10), 148 (100), 136 (10), 135 (59), 105 (16), 91 (18), 79 (17), 78 (11), 77 (54), 51 (41), 50 (12), 45 (21).

4-(4-Fluoro-2-methylphenyl)butanoic acid (**5i**)

Mp: 54°C. IR (KBr): 3055, 1709, 1612, 1591, 1266. ^{1}H-NMR (δ ppm): 1.94 (quint, $J = 7.3$ Hz, 2H), 2.34 (s, 3H), 2.46 (t, $J = 7.3$ Hz, 2H), 2.67 (t, $J = 7.3$ Hz, 2H), 6.78–6.96 (m, 2H), 7.11 (dd, $J = 6.1$ Hz, $J = 7.8$ Hz, 1H), 10.50 (bs, 1H). ^{13}C-NMR (δ ppm): 19.3, 25, 31.6, 33.5, 112.9 (d, $J_{C\text{-}F} = 22$ Hz), 116.7 (d, $J_{C\text{-}F} = 21$ Hz), 122.0, 121.3 (d, $J_{C\text{-}F} = 9$ Hz), 130.8, 137.5 (d, $J_{C\text{-}F} = 8$ Hz), 162.1 (d, $J_{C\text{-}F} = 246$ Hz), 177.6. MS (70 eV, EI) m/z: 196 (M^+, 27), 137 (13), 136 (81), 135 (22), 124 (11), 123 (100), 103 (15), 77 (16).

4-(4-Cyano-3-methylphenyl)butanoic acid (**5j**)

Mp: 61–62°C. IR (KBr): 3056, 1710, 1611, 1209. ^{1}H-NMR (δ ppm): 2.00 (quint, $J = 7.3$ Hz, 2H), 2.43 (t, $J = 7.3$ Hz, 2H), 2.56 (s, 3H), 2.73 (t, $J = 7.3$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 1H), 7.18 (s, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 10.90 (bs, 1H). ^{13}C-NMR (δ ppm): 20.4, 25.6, 33.1, 35.0, 110.4, 118.3, 126.4, 130.4, 132.6, 142.1, 146.6, 179.0. MS (70 eV, EI) m/z: 203 (M^+, 16), 145 (12), 144 (100), 143 (51), 130 (23), 116 (13), 115 (13), 103 (24), 77 (31), 63 (13), 60 (45), 51 (17), 44 (28), 39 (22), 36 (18).

4-(3,4-Dichlorophenyl)butanoic acid (**5k**)

Mp: 71–72°C. IR (KBr): 3056, 3034, 1708, 1563, 1212. ^{1}H-NMR (δ ppm): 1.98 (quint, $J = 7.3$ Hz, 2H), 2.42 (t, $J = 7.3$ Hz, 2H), 2.68

(t, $J = 7.3$ Hz, 2H), 7.06 (dd, $J = 7.4$ Hz, $J = 2.0$ Hz, 1H), 7.32 (d, $J = 2.0$ Hz, 1H), 7.40 (d, $J = 7.4$ Hz, 1H), 10.75 (bs, 1H). ^{13}C-NMR (δ ppm): 25.8, 30.1, 34.0, 127.9, 130.0, 130.3, 130.4, 132.3, 141.4, 179.7. MS (70 eV, EI) m/z: 234 (M^+, 15), 232 (M^+, 20), 174 (65), 173 (20), 172 (100), 161 (21), 159 (32), 89 (17), 60 (59).

Cyclization

1. A solution of $(CF_3CO)_2O$ (1.92 mmol, 270 μL) in 1,2-dichloroethane (4 mL) was added dropwise to a solution of **5** (0.96 mmol) in dry 1,2-dichloroethane (2 mL) at 0°C. The mixture was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography (petroleum ether/Et_2O = 80/20) yielded **6**.
2. Acid **5** (3 mmol) was added to a mixture of P_2O_5 (1.09 g, 7.56 mmol) in CH_3SO_3H (10.95 g, 114 mmol). The solution was stirred at room temperature for 12 h and then poured over 37 g of ice. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **6**.

6,7-Methylenedioxy-1-tetralone (**6g**)

Mp: 133–134°C. IR (KBr): 3080, 1676, 1620, 1584, 1283. ^{1}H-NMR (δ ppm): 2.14 (quint, $J = 6.3$ Hz, 2H), 2.64 (t, $J = 6.4$ Hz, 2H), 2.87 (t, $J = 6$ Hz, 2H), 6.08 (s, 2H), 6.80 (d, $J = 8.3$ Hz, 1H), 7.72 (d, $J = 8.3$ Hz, 1H). ^{13}C-NMR (δ ppm): 22.5, 22.7, 38.7, 101.8, 106.8, 123.0, 125.2, 127.5, 144.4, 151, 196. MS (70 eV, EI) m/z: 190 (M^+, 82), 175 (13), 163 (10), 162 (100), 134 (49), 81 (11), 78 (14), 77 (14), 76 (13), 51 (12).

7,8-Methylenedioxy-1-tetralone (**6h**)

Mp: 74–75°C. IR (KBr): 3067, 1672, 1620, 1500, 1265, 1248. ^{1}H-NMR (δ ppm): 2.16 (quint, $J = 6.4$ Hz, 2H), 2.68 (t, $J = 6.9$ Hz, 2H), 2.96 (t, $J = 6.1$ Hz, 2H), 5.92 (s, 2H), 6.57 (s, 1H), 7.35 (s, 1H). ^{13}C-NMR (δ ppm): 23.3, 29.8, 38.4, 101.4, 105.8, 107.7, 127.1, 141.2, 146.6, 151.8, 196.4. MS (70 eV, EI) m/z: 190 (M^+, 100), 175 (10), 162 (64), 148 (11), 134 (94), 104 (19), 77 (15), 76 (26), 51 (13).

5-Methyl-7-fluoro-1-tetralone (**6i**)

IR: 3055, 3022, 1686, 1606, 1266. ^{1}H-NMR (δ ppm): 2.17 (quint, $J = 6.7$ Hz, 2H), 2.34 (s, 3H), 2.70 (t, $J = 6.1$ Hz, 2H), 2.85 (t, $J = 6.1$ Hz, 2H), 7.12 (dd, $J = 9$ Hz, $J = 2.8$ Hz, 1H), 7.60 (dd, $J = 9$ Hz, $J = 2.8$ Hz, 1H). ^{13}C-NMR (δ ppm): 19.5, 22.4, 25.8, 38.2, 110.7 (d, $J_{C\text{-}F} = 22$ Hz), 122.1 (d, $J_{C\text{-}F} = 22$ Hz), 134.0 (d, $J_{C\text{-}F} = 6.5$ Hz), 139.0 (d, $J_{C\text{-}F} = 7$ Hz), 139.2, 160.9 (d, $J_{C\text{-}F} = 246$ Hz), 199. MS (70 eV, EI) m/z: 178 (M^+, 56), 163 (26), 149 (54), 136 (21), 135 (18), 133 (20), 123 (12), 122 (11), 121 (21), 109 (12), 101 (22), 96 (30), 75 (19), 63 (14), 51 (23), 39 (23).

6-Methyl-7-cyano-1-tetralone (**6j**)

Mp: 131–132°C. IR (KBr): 3055, 2226, 1688, 1610, 1266. ^{1}H-NMR (δ ppm): 2.17 (quint, $J = 6$ Hz, 2H), 2.58 (s, 3H), 2.70 (t, $J = 6$ Hz, 2H), 2.85 (t, $J = 6$ Hz, 2H), 7.27 (s, 1H), 8.26 (s, 1H). ^{13}C-NMR (δ ppm): MS (70 eV, EI) m/z: 185 (M^+, 41), 157 (100), 129 (51), 128 (19), 103 (16), 102 (25), 101 (11), 77 (19), 76 (14), 63 (20), 51 (26), 50 (14), 39 (30).

6,7-Dichloro-1-tetralone (**6k**)

Mp: 95°C. IR (KBr): 3054, 1690, 1591, 1267. ^{1}H-NMR (δ ppm): 2.15 (quint, $J = 6.3$ Hz, 2H), 2.65 (t, $J = 6.3$ Hz, 2H), 2.93 (t, $J = 6.3$ Hz, 2H), 7.37 (s, 1H), 8.05 (s, 1H). ^{13}C- NMR (δ ppm): 22.8, 28.8, 38.5, 128.9, 130.6, 131.2, 132, 137.5, 143.7, 196.1. MS (70 eV, EI) m/z: 218 (M^+, 7), 216 (M^+, 43), 214 (M^+, 67), 201 (90), 199 (30), 188 (60), 187 (14), 186 (96), 79 (27), 160 (50), 158 (82), 151 (16), 149 (16), 125 (33), 123 (100), 116 (27), 115 (52), 114 (15), 99 (17), 97 (22), 89 (19), 88 (15), 87 (34), 86 (24), 85 (14), 75 (43), 74 (45), 73 (43), 63 (62), 62 (47), 57 (35), 56 (15), 55 (28), 51 (27), 50 (29), 39 (60).

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