Monoalkylation of acetonitrile by primary alcohols catalyzed by iridium complexes

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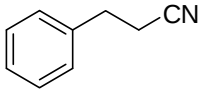
General experimental methods

All reactions were run under an atmosphere of argon. Microwave tube were dried in an oven overnight and cooled under a stream of argon. Commercially available acetonitrile (>99.9%), cesium carbonate and $[IrcodCl]_2$ were purchased from Aldrich and were used directly without further purification. The reactions were carried in the C.E.M. microwave Discover. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 at 400 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane as internal standard, multiplicity (s = singulet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances, integration). ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 at 100 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as internal standard ($CDCl_3$, δ 77.0 ppm or DMSO-d_6, δ 40.4 ppm), multiplicity with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH2, q = CH3). Mass spectra with electronic impact (MS-EI) were recorded from a Hewlett-Packard tandem 5890A GC (12 m capillary column) -5971 MS (70 eV). Infrared (IR) spectra were recorded on a Bruker TENSOR^{TM} 27 (IRFT), wave-numbers are indicated in cm^{-1}. TLC was performed on Merck $60F_{254}$ silica gel plates and visualized with a UV lamp (254 nm), or by using solutions of $KMnO_4/K_2CO_3$/NaOH in water followed by heating. Column chromatography was performed with Merck Geduran Si 60 silica gel (40–63 µm). High resolution mass spectra (HRMS) were performed by the centre regional de microanalyse (Université Pierre et Marie Curie Paris VI).

General procedure for α-alkylation of acetonitrile by aryl- and heteroaryl-methanol (Table 2 and 3)

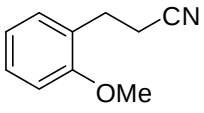
To a solution of alcohol (1 equiv) in acetonitrile (10 equiv) was added Cs_2CO_3 (0.2 equiv). The mixture was heated at 180 °C during 20 min under microwave irradiations. $[IrcodCl]_2$ (1 mol %) was added and the mixture was heated during 20 min at 180 °C under microwave irradiations. The procedure was repeated until the complete conversion of the alcohol was observed. The mixture was filtered, concentrated under reduced pressure and purified by flash chromatography on silica gel using a mixture of petroleum ether and Et_2O as the eluant to afford the desired nitrile.

3-phenylpropanenitrile (3a)[a]



An orange oil. IR (neat): 3030, 2933, 2246, 1496, 1454, 1424, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.24 (m, 5H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2 (s), 128.9 (d), 128.3 (d), 127.2 (d), 119.2 (s), 31.6 (t), 19.3 (t). MS *m/z* (%): 131 ($M^{+\cdot}$, 22), 92 (7), 91 (100), 65 (14), 51 (9). HRMS (ESI) calculated for C_9H_9NNa [M+Na^+]: 154.06272; found 154.06205.

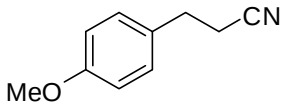
3-(2-methoxyphenyl)propanenitrile (3b)[b]



A yellow oil. IR (neat): 2939, 2244, 1601, 1493, 1463, 1438, 1290, 1243, 1114, 1028 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (ddd, *J* = 9.4, 7.9, 1.7 Hz, 1H), 7.16 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.90 (ddd, *J*

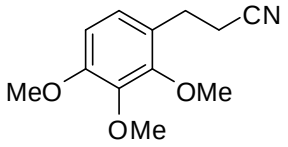
= 8.3, 7.5, 0.8 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 3H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3 (s), 130.2 (d), 128.7 (d), 126.4 (s), 120.7 (d), 119.8 (s), 110.4 (d), 55.2 (q), 27.1 (t), 17.5 (t). MS *m/z* (%): 161 ($M^{+\cdot}$, 23), 121 (92), 93 (19), 91 (100), 78 (14), 76 (16), 65 (22), 63 (10), 51 (17). HRMS (ESI) calculated for $C_{10}H_{11}NONa$ [M+Na^+]: 184.07329; found 184.07343.

3-(4-methoxyphenyl)propanenitrile (3c)[c]



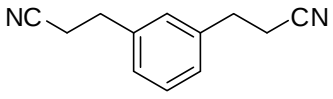
A yellow oil. IR (neat): 2934, 2213, 1603, 1511, 1463, 1300, 1245, 1176, 1110, 1030 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8 (s), 130.2 (s), 129.4 (d), 119.4 (s), 114.3 (d), 55.4 (q), 30.9 (t), 19.8 (t). MS *m/z* (%): 161 ($M^{+\cdot}$, 10), 121 (100), 91 (11), 78 (13), 77 (17). HRMS (ESI) calculated for $C_{10}H_{11}NONa$ [M+Na^+]: 184.07329; found 184.07335.

3-(2,3,4-trimethoxyphenyl)propanenitrile (3d)[d]



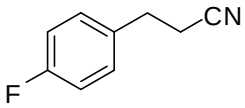
A colorless oil. IR (neat): 2938, 2836, 2213, 1601, 1494, 1466, 1416, 1275, 1234, 1200, 1094 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4 (s), 151.9 (s), 142.3 (s), 124.3 (d), 123.9 (s), 119.7 (s), 107.3 (d), 61.1 (q), 60.9 (q), 56.1 (q), 26.7 (t), 18.6 (t). MS *m/z* (%): 221 ($M^{+\cdot}$, 44), 182 (10), 181 (100), 166 (67), 138 (11), 136 (26), 123 (22), 106 (10), 95 (10), 92 (10), 91 (29), 80 (10), 77 (12), 65 (14). HRMS (ESI) calculated for $C_{12}H_{15}NO_3Na$ [M+Na^+]: 244.09441; found 244.09406.

3,3'-(1,3-phenylene)dipropanenitrile (3e)



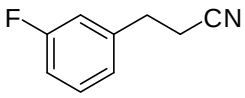
A colorless oil. IR (neat): 2930, 2246, 1609, 1589, 1489, 1449, 1423, 1339, 1094 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.8 Hz, 1H), 7.18–7.10 (m, 3H), 2.94 (t, *J* = 7.3 Hz, 4H), 2.62 (t, *J* = 7.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8 (s), 129.4 (d), 128.4 (d), 127.2 (d), 119.2 (s), 31.4 (t), 19.3 (t). MS *m/z* (%): 184 ($M^{+\cdot}$, 13), 145 (11), 144 (100), 117 (29), 116 (12), 115 (34), 104 (26), 103 (17), 91 (11), 78 (20), 77 (13), 51 (12). HRMS (ESI) calculated for $C_{12}H_{12}N_2Na$ [M+Na^+]: 207.08927; found 207.08894.

3-(4-fluorophenyl)propanenitrile (3h)[c]



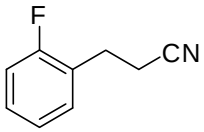
A colorless oil. IR (neat): 2935, 2247, 1601, 1509, 1425, 1222, 1158, 1097, 1016 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (m, 2H), 7.01 (m, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (ds, *J* = 245.7 Hz), 133.8 (ds, *J* = 4.0 Hz),), 129.9 (dd, *J* = 8.8 Hz), 119.0 (s), 115.7 (dd, *J* = 21.6 Hz), 30.8 (t), 19.6 (t). MS *m/z* (%): 149 ($M^{+\cdot}$, 11), 109 (100), 83 (17). HRMS (ESI) calculated for C_9H_8NFNa [$M+Na^+$]: 172.05330; found 172.05335.

3-(3-fluorophenyl)propanenitrile (3i)[e]



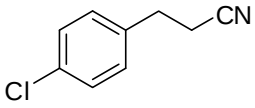
A yellow oil. IR (neat): 2938, 2248, 1587, 1488, 1450, 1255, 1141 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 1H), 7.04–6.91 (m, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (ds, *J* = 247.1 Hz), 140.4 (ds, *J* = 7.2 Hz), 130.5 (dd, *J* = 8.4 Hz), 124.0 (dd, *J* = 3.2 Hz), 118.9 (s), 115.4 (dd, *J* = 20.8 Hz), 114.4 (dd, *J* = 21.2 Hz), 31.3 (dt, *J* = 1.6 Hz),), 19.2 (t). MS *m/z* (%): 149 ($M^{+\cdot}$, 20), 109(100), 83 (16). HRMS (ESI) calculated for C_9H_8NFNa [$M+Na^+$]: 172.05330; found 172.05326.

3-(2-fluorophenyl)propanenitrile (3j)



A yellow oil. IR (neat): 2938, 2247, 1586, 1492, 1455, 1231, 1189, 1102 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.23 (m, 2H), 7.15–7.02 (m, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (ds, *J* = 246.6 Hz), 130.8 (dd, *J* = 4.0 Hz), 129.4 (dd, *J* = 8.0 Hz), 125.0 (ds, *J* = 16.0 Hz), 124.6 (dd, *J* = 3.6 Hz), 119.0 (s), 115.7 (dd, *J* = 21.6 Hz), 25.6 (dt, *J* = 2.4 Hz), 18.1 (dt, *J* = 1.6 Hz). MS *m/z* (%): 149 ($M^{+\cdot}$, 17), 109(100), 83 (17). HRMS (ESI) calculated for C_9H_8NFNa [$M+Na^+$]: 172.05330; found 172.05337.

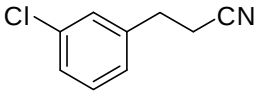
3-(4-chlorophenyl)propanenitrile (3k)[f]



A pale yellow oil. IR (neat): 3063, 2247, 1474, 1443, 1126, 1052, 1040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.28 (m, 2H), 7.20–7.14 (m, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5 (s), 133.3 (s), 129.8 (d), 129.2 (d), 118.9 (s), 31.0 (t), 19.4 (t). MS

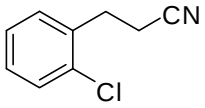
m/z (%): 167 ($M^{+\cdot}$, 4), 165 ($M^{+\cdot}$, 14), 127(31), 125 (100), 89 (21), 63 (11). HRMS (ESI) calculated for *C_9H_8NClNa* [M+Na^+]: 188.02375; found 188.02350.

3-(3-chlorophenyl)propanenitrile (3l)[e]



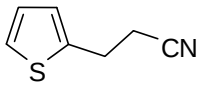
A pale yellow oil. IR (neat): 2934, 2247, 1598, 1573, 1476, 1430, 1205, 1079 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.11 (m, 3H), 7.04 (m, 1H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0 (s), 134.6 (s), 130.2 (d), 128.5 (d), 127.5 (d), 126.6 (d), 118.8 (s), 31.1 (t), 19.1 (t). MS *m/z* (%): 167 ($M^{+\cdot}$, 4), 165 ($M^{+\cdot}$, 14), 127(33), 125 (100), 89 (23), 63 (12), 51 (10). HRMS (ESI) calculated for *C_9H_8NClNa* [M+Na^+]: 188.02375; found 188.02373.

3-(2-chlorophenyl)propanenitrile (3m)[c]



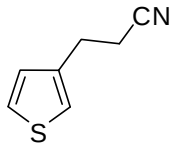
A pale yellow oil. IR (neat): 2935, 2246, 1492, 1408, 1091, 1015 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.20 (m, 4H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6 (s), 133.8 (s), 130.8 (d), 129.9 (d), 128.9 (d), 127.4 (d), 118.9 (s), 29.7 (t), 17.5 (t). MS *m/z* (%): 167 ($M^{+\cdot}$, 4), 165 ($M^{+\cdot}$, 15), 127(32), 125 (100), 89 (18), 63 (10). HRMS (ESI) calculated for *C_9H_8NClNa* [M+Na^+]: 188.02375; found 188.02388.

3-(thiophen-2-yl)propanenitrile (5a)[e]



A pale yellow oil. IR (neat): 3107, 2928, 2246, 1439, 1422, 1251, 1128, 1041 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.98–6.91 (m, 2H), 3.19 (dt, *J* = 7.3, 1.3 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0 (s), 127.2 (d), 125.7 (d), 124.6 (d), 118.7 (s), 26.0 (t), 19.9 (t). MS *m/z* (%): 137 ($M^{+\cdot}$, 20), 98 (6), 97 (100), 69 (6), 58 (5), 53 (12). HRMS (ESI) calculated for *C_7H_7NSNa* [M+Na^+]: 160.01914; found 160.01892.

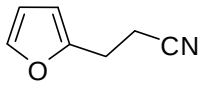
3-(thiophen-3-yl)propanenitrile (5b)[h]



A pale yellow oil. IR (neat): 2928, 2245, 1422, 1334, 1243, 1154, 1081 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.10 (m, 1H), 6.99 (dd, *J* = 5.0, 1.3 Hz, 1H), 2.99 (t, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 138.3 (s), 127.5 (d), 126.5 (d), 121.9 (d),

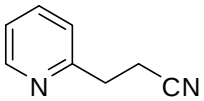
119.2 (s), 26.1 (t), 18.8 (t). MS *m/z* (%): 137 ($M^{+\cdot}$, 23), 97 (100), 53 (12). HRMS (ESI) calculated for C_7H_7NSNa [M+Na^+]: 160.01914; found 160.01896.

3-(furan-2-yl)propanenitrile (5c)[c]



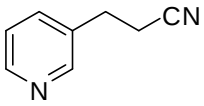
A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.17 (ddd, *J* = 3.2, 1.7, 0.8 Hz, 1H), 2.99 (t, *J* = 7.3 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3 (s), 142.1 (d), 110.5 (d), 106.8 (d), 24.3 (t), 16.6 (t). MS *m/z* (%): 121 ($M^{+\cdot}$, 18), 81 (100), 65 (7), 53 (46), 51 (9). HRMS (ESI) calculated for C_7H_7NONa [M+Na^+]: 144.04199; found 144.04174.

3-(pyridin-2-yl)propanenitrile (5d)[g]



A pale yellow oil. IR (neat): 2933, 2246, 1591, 1570, 1475, 1436, 1249, 1148, 1097 1051 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (ddd, *J* = 4.8, 1.7, 0.8 Hz, 1H), 7.64 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.25–7.17 (m, 2H), 3.13 (t, *J* = 7.3 Hz, 2H), 2.85 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2 (s), 149.7 (d), 136.9 (d), 123.2 (d), 122.3 (d), 119.5 (s), 33.4 (t), 16.8 (t). MS *m/z* (%): 132 ($M^{+\cdot}$, 69), 131 (80), 105 (17), 104 (16), 92 (14), 79 (100), 78 (26), 65 (40), 52 (34), 51 (41), 50 (18). HRMS (ESI) calculated for $C_8H_8N_2Na$ [M+Na^+]: 155.05797; found 155.05765.

3-(pyridin-3-yl)propanenitrile (5e)[e]

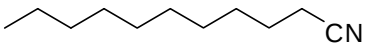


A pale yellow oil. IR (neat): 2937, 2246, 1577, 1480, 1425, 1342, 1193, 1105, 1029 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60–8.48 (m, 2H), 7.61 (dm, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8 (d), 149.0 (d), 136.0 (d), 133.5 (s), 123.8 (d), 118.6 (s), 28.9 (t), 19.3 (t). MS *m/z* (%): 132 ($M^{+\cdot}$, 1), 130 (100), 104 (46), 103 (44), 76 (64), 51 (32), 50 (46). HRMS (ESI) calculated for $C_8H_9N_2$ [M+H^+]: 133.07602; found 133.07573.

General procedure for α-alkylation of acetonitrile by alkyl-methanol (Table 4)

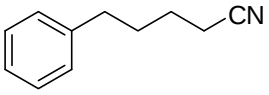
To a solution of alcohol (1 equiv) in acetonitrile (10 equiv) was added Cs_2CO_3 (0.2 equiv). The mixture was heated at 180 °C during 20 min under microwave irradiations. $[IrcodCl]_2$ (3 mol %) was added and the mixture was heated during 12 h at 180 °C under microwave irradiations. The mixture was filtered, concentrated under reduced pressure and purified by flash chromatography on silica gel using a mixture of petroleum ether and Et_2O as the eluant to afford the desired nitrile.

undecanenitrile (7a)[i]



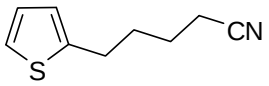
A corlorless oil. IR (neat): 2924, 2855, 2246, 1464, 1427, 1377 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.33 (t, *J* = 7.1 Hz, 2H), 1.65 (m, 2H), 1.44 (m, 2H), 1.38–1.20 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.9 (s), 31.8 (t), 29.3 (t), 29.2 (t), 28.8 (t), 28.7 (t), 25.4 (t), 22.6 (t), 17.1 (t), 14.1 (q). MS *m/z* (%): 153 ($M^{+\cdot}$, 1), 124 (23), 111 (15), 110 (60), 97 (63), 96 (87), 83 (65), 82 (100), 70 (20), 69 (66), 68 (13), 57 (48), 56 (24), 55 (69), 54 (66). HRMS (ESI) calculated for $C_{10}H_{19}NNa$ [$M+Na^+$]: 176.14097; found 176.14079.

5-phenylpentanenitrile (7b)[j]



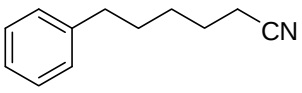
A corlorless oil. IR (neat): 2935, 2861, 2246, 1496, 1453, 1424, 1084, 1029 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23–7.06 (m, 5H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.74–1.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3 (s), 128.5 (d), 128.4 (d), 126.1 (d), 119.7 (s), 35.0 (t), 30.3 (t), 24.9 (t), 17.1 (t). MS *m/z* (%): 159 ($M^{+\cdot}$, 11), 92 (11), 91 (100), 65 (18). HRMS (ESI) calculated for $C_{11}H_{13}NNa$ [$M+Na^+$]: 182.09402; found 182.09400.

5-(thiophen-2-yl)pentanenitrile (7c)[k]



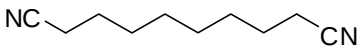
A yellow oil. IR (neat): 2934, 2246, 1439, 1236, 1078 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.79 (m, 1H), 2.88 (td, *J* = 7.3, 0.7 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.89–1.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0 (s), 127.0 (d), 124.6 (d), 123.4 (d), 119.6 (s), 30.7 (t), 29.1 (t), 24.8 (t), 17.1 (t). MS *m/z* (%): 165 ($M^{+\cdot}$, 10), 97 (100), 53 (10). HRMS (ESI) calculated for $C_9H_{11}NSNa$ [$M+Na^+$]: 188.05044; found 188.05015.

6-phenylhexanenitrile (7d)[l]



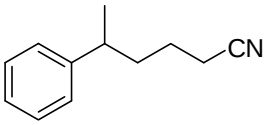
A corlorless oil. IR (neat): 2933, 2858, 2244, 1602, 1496, 1453, 1030 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.24 (m, 2H), 7.21–7.13 (m, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.73–1.61 (m, 4H), 1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1 (s), 128.5 (d), 128.4 (d), 125.9 (d), 119.8 (s), 35.6 (t), 30.7 (t), 28.3 (t), 25.4 (t), 17.2 (t). MS *m/z* (%): 173 ($M^{+\cdot}$, 12), 172 (13), 92 (15), 91 (100), 65 (14). HRMS (ESI) calculated for $C_{12}H_{15}NNa$ [M+Na^+]: 196.10967; found 196.10958.

decanedinitrile (7e)[m]



A corlorless oil. IR (neat): 2931, 2858, 2244, 1461, 1426 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.35 (t, *J* = 7.1 Hz, 4H), 1.72–1.59 (m, 4H), 1.52–1.41 (m, 4H), 1.40–1.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.8 (s), 28.7 (t), 28.6 (t), 25.4 (t), 17.2 (t). MS *m/z* (%): 124 ($M^{+\cdot}$-CH_2CN, 10), 96 (24), 83 (89), 82 (100), 79 (12), 69 (24), 55 (60), 54 (37), 53 (11). HRMS (ESI) calculated for $C_{10}H_{16}N_2Na$ [M+Na^+]: 187.12057; found 187.12061.

5-phenylhexanenitrile (7f)



A corlorless oil. IR (neat): 3027, 2959, 2871, 2245, 1493, 1452, 1242, 1025 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 2H), 7.23–7.15 (m, 3H), 2.71 (m, 1H), 2.27 (td, *J* = 7.1, 1.7 Hz, 2H), 1.80–1.44 (m, 4H), 1.27 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4 (s), 128.7 (d), 127.0 (d), 126.4 (d), 119.8 (s), 39.6 (t), 37.2 (t), 23.7 (t), 22.5 (d), 17.3 (q). MS *m/z* (%): 173 ($M^{+\cdot}$, 8), 105 (100), 91 (12), 79 (11), 77 (14). HRMS (ESI) calculated for $C_{12}H_{15}NNa$ [M+Na^+]: 196.10967; found 196.10955.

a) McNulty, J.; Nair, J. J.; Cheekoori, S.; Larichev, V.; Capretta, A.; Robertson, A. J. *Chem. Eur. J.* **2006**, *12*, 9314–9322; b) Juhnke, B.; Jas, G.; Schumann, D. *Organic Preparations and Procedures International* **1992**, *24*, 673–675; c) Kim, D.; Park, B. M.; Yun, J. *Chem. Commun.* **2005**, 1755–1757; d) Kametani, T.; Takeda, H.; Hirai, Y.; Satoh, F.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2141–2145 ; e) Montgomery, J. D.; Niwas, S.; Rose, J. D.; Secrist III, J. A.; Babu, Y. S.; Bugg, C. E.; Erion, M. D.; Guida, W. C.; Ealick, S. E. *J. Med. Chem.* **1993**, *36*, 55–69; f) Zaragoza, F. *J. Org. Chem.* **2002**, *67*, 4963–4964; g) Nakao, Y.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2010**, *132*, 10024–10026; h) Hable, C. T.; Crooks, R. M.; Valentine, J. R.; Giasson, R.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97*, 6060–6065; i) Ballini, R.; Fiorini, D.; Palmieri, A. *Synlett* **2003**, *12*, 1841–1843; j) Huo, S. *Org. Lett.* **2003**, *5*, 423–425; k) Padwa, A.; Hertzog, D. L.; Nadler, W. R. *J. Org. Chem.* **1994**, *59*, 7072–7084; l) Ackermann, L.; Kapdi, A. R.; Schulzke, C. *Org. Lett.* **2010**, *12*, 2298–2301; m) Nicolaou, K. C.; Vassilikogiannakis, G.; Kranich, R.; Baran, P. S.; Zhong, Y. L.; Natarajan, S. *Org. Lett.* **2000**, *2*, 1895–1898.