Supporting Information

$CoBr_2$(Bpy) : An Efficient Catalyst for the Direct Conjugated Addition of Aryl Halides or Triflates onto Activated Olefins

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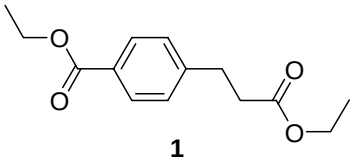
Experimental Section

GC analysis was carried out using a gas chromatograph provided with a 25-m capillary column. Mass spectra were recorded with a spectrometer coupled to a gas chromatograph (25-m /MS capillary column). Column chromatography was performed on silica gel 60, 70-230 mesh with pentane/ether as eluent. ^{1}H, and ^{13}C spectra were recorded in $CDCl_3$ on a 400 MHz. All solvents and reagents were purchased and used without further purification. No inert atmosphere was required.

Typical procedure for conjugate addition of aryl halides and triflates onto deficient electron olefins. To a solution of DMF (9 mL) and pyridine (1 mL) are successively added $CoBr_2$ (0.075 mmol, 164 mg), 2,2'-bipyridine (0.075 mmol, 117 mg), LiBr (7.5 mmol, 651 mg) and manganese powder (15 mmol, 824 mg). Aryl halide or triflate (7.5 mmol) and activated olefin are then introduced into the solution. Mn dust is activated by traces of trifluoroacetic acid (100 μL), H_2O (7.5 mmol, 135 μL) is added and the medium is stirred at 50°C or 80°C until aryl halide or triflate is consumed. The amount of the corresponding coupling product is measured by GC using an internal reference (dodecane, 200 μL). The reaction mixture is poured into a solution of 2N HCl and extracted with diethylether or methylene chloride. The organic layer is washed with brine and dried over $MgSO_4$. Evaporation of solvant and purification by column chromatography on silica gel (pentane/diethylether) afford the conjugate adducts that are characterized by NMR (^{1}H, ^{13}C) and mass spectrometry.

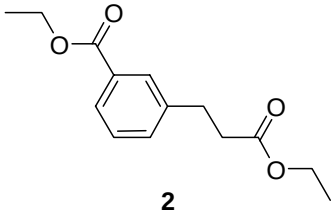
Compound Characterization

Benzenepropanoic acid, 4-(ethoxycarbonyl)-, ethyl ester (1) $C_{14}H_{18}O_4$, CAS registry number 38628-52-3. Isolated as a yellow oil (80 and 72%): IR(ν_{max}/cm^{-1}) 2980, 1713, 1611, 1272; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.01 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.6, 166.6, 145.9, 129.8 (2C), 128.6, 128.3 (2C), 60.9, 60.6, 35.4, 30.9, 14.3, 14.2; EI-MS *m/z* (rel. intensity) 250 (M, 35), 205 (36), 179 (25), 176 (100), 149 (19), 148 (75), 131 (39).



1

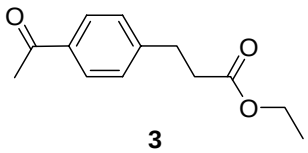
Benzenepropanoic acid, 3-(ethoxycarbonyl)-, ethyl ester (2) $C_{14}H_{18}O_4$, CAS registry number 10036-21-2. Isolated as a yellow oil (72%): IR(ν_{max}/cm^{-1}) 2980, 1715, 1588, 1277; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.87 (m, 2H), 7.37 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.6, 166.6, 140.8, 132.9, 130.6, 129.3, 128.5, 127.5, 60.9, 60.5, 35.7, 30.7, 14.3, 14.2; EI-MS *m/z* (rel. intensity) 250 (M, 12), 205 (32), 204 (100), 176 (15), 149 (12), 148 (33), 131 (77).



2

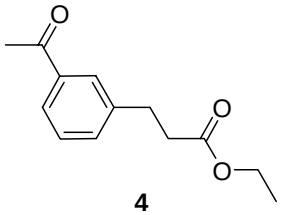
Benzenepropanoic acid, 4-carboxy-,α-ethyl ester (3) $C_{13}H_{16}O_3$, CAS registry number 267888-21-1. Isolated as a yellow oil (78, 59 and 51%): IR(ν_{max}/cm^{-1}) 2980, 1730, 1680, 1266; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5

Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.57 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 197.8, 172.5, 146.3, 135.4, 128.6 - 128.4 (4C), 60.6, 35.3, 30.8, 26.6, 14.2; EI-MS *m/z* (rel. intensity) 220 (M, 34), 205 (100), 177 (23), 146 (28), 131 (77).



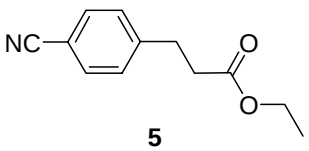
3

Benzenepropanoic acid, 3-carboxy-, α-ethyl ester (4) $C_{13}H_{16}O_3$. Isolated as a yellow oil (84%): IR(ν_{max}/cm^{-1}) 2980, 1729, 1682, 1602, 1271; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.77 (m, 2H), 7.38 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.57 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 198.2, 172.6, 141.1, 137.3, 133.2, 128.7, 128.1, 126.5, 60.5, 35.7, 30.7, 26.7, 14.2; EI-MS *m/z* (rel. intensity) 220 (M, 48), 205 (68), 177 (35), 146 (100), 131 (69); Anal. Calcd. For $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; O, 21.79; Found: C, 70.71; H, 7.41; O, 22.04.



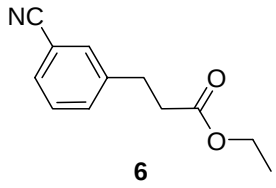
4

Benzenepropanoic acid, 4-cyano-, ethyl ester (5) $C_{12}H_{13}O_2N$, CAS registry number 116460-89-0. Isolated as a yellow oil (70, 66 and 69%): IR(ν_{max}/cm^{-1}) 2981, 2227, 1728, 1607, 1178; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.2, 146.2, 132.3 (2C), 129.2 (2C), 118.9, 110.2, 60.7, 35.1, 30.9, 14.2; EI-MS *m/z* (rel. intensity) 203 (M, 21), 130 (43), 129 (100), 116 (15), 103 (12).



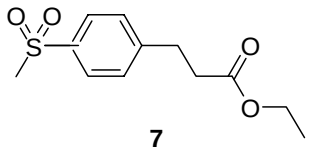
5

Benzenepropanoic acid, 3-cyano-, ethyl ester (6) $C_{12}H_{13}O_2N$, CAS registry number 10036-20-1. Isolated as a yellow oil (70 and 47%): IR(ν_{max}/cm^{-1}) 2982, 2229, 1728, 1601, 1583, 1180; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.49 (m, 1H), 7.43 (m, 1H), 7.38 (m, 2H), 4.10 (t, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.2, 141.9, 133.0, 131.9, 130.1, 129.3, 118.9, 112.5, 60.7, 35.2, 30.4, 14.2; EI-MS *m/z* (rel. intensity) 203 (M, 26), 130 (87), 129 (100), 116 (16), 103 (16).



6

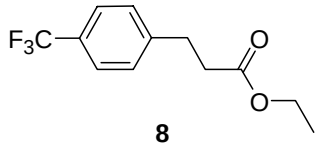
Benzenepropanoic acid, 4-(phenylmethylsulfone)-, ethyl ester (7) $C_{12}H_{16}O_4S$. Isolated as a white solid (mp = 68°C, 83 and 79%): IR(ν_{max}/cm^{-1}) 2983, 1729, 1305, 1150; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.99 (m, 5H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.2, 147.1, 138.5, 129.3, 127.6, 60.6, 44.5, 35.1, 30.7, 14.2; EI-MS *m/z* (rel. intensity) 256 (M, 54), 228 (34), 183 (87), 182 (100), 133 (14), 119 (24); Anal. Calcd. For $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29; O, 24.97; S, 12.51; Found: C, 56.55; H, 6.32; O, 24.42; S, 13.00.



7

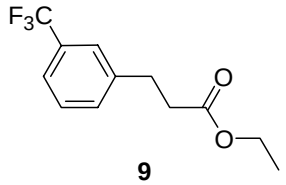
Benzenepropanoic acid, 4-(trifluoromethyl)-, ethyl ester (8) $C_{12}H_{13}O_2F_3$, CAS registry number 82989-27-3. Isolated as a yellow oil (86 and 57%): IR(ν_{max}/cm^{-1}) 2984, 1732, 1619, 1323, 1160, 1107; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.4, 144.7, 128.7,

128.6 (q, *J* = 31 Hz), 125.6 (3C), 124.4 (q, *J* = 271 Hz), 60.6, 35.4, 30.7, 14.1; ^{19}F NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ -62.8 (s, 3F); EI-MS *m/z* (rel. intensity) 246 (M, 25), 173 (40), 172 (100), 159 (19), 153 (24).



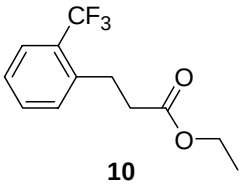
8

Benzenepropanoic acid, 3-(trifluoromethyl)-, ethyl ester (9) $C_{12}H_{13}O_2F_3$, CAS registry number 70311-33-0. Isolated as a yellow oil (83%): IR(ν_{max}/cm^{-1}) 2984, 1731, 1327, 1160, 1119; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.45 ((m, 1H), 7.41 (m, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.4, 141.5, 131.8, 130.7 (q, *J* = 32 Hz), 128.2, 124.7, 124.2 (q, *J* = 270 Hz), 123.1, 60.6, 35.6, 30.7, 14.1; ^{19}F NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ -63.0 (s, 3F); EI-MS *m/z* (rel. intensity) 246 (M, 21), 173 (36), 172 (100), 159 (23), 153 (14).



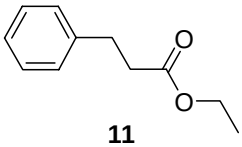
9

Benzenepropanoic acid, 2-(trifluoromethyl)-, ethyl ester (10) $C_{12}H_{13}O_2F_3$, CAS registry number 191155-80-3. Isolated as a yellow oil (20%): IR(ν_{max}/cm^{-1}) 2984, 1732, 1312, 1151, 1107; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.62 ((d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.33 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.13 (t, *J* = 7.9 Hz, 2H), 2.62 (t, *J* = 7.9 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.6, 139.3, 131.9, 130.9, 128.5 (q, *J* = 30 Hz), 126.4 (2C), 124.4 (q, *J* = 272 Hz), 60.6, 35.8, 27.8, 14.2; ^{19}F NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ -60.2 (s, 3F); EI-MS *m/z* (rel. intensity) 246 (M, 1), 226 (64), 173 (57), 172 (26), 159 (28), 154 (87), 150 (100), 133 (57).



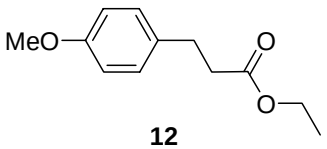
10

Benzenepropanoic acid, ethyl ester (11) $C_{11}H_{14}O_2$, CAS registry number 2021-28-5. Isolated as a colorless oil (58 and 82%): IR(ν_{max}/cm^{-1}) 2980, 1731, 1159; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.29 (m, 2H), 7.22 (m, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.9, 140.6, 128.9 - 128.3 (4C), 126.2, 60.4, 35.9, 31.0, 14.2; EI-MS *m/z* (rel. intensity) 178 (M, 36), 107 (21), 105 (40), 104 (100), 91 (31).



11

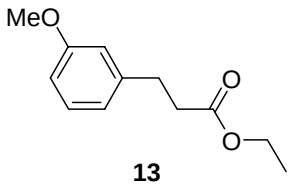
Benzenepropanoic acid, 4-methoxy-, ethyl ester (12) $C_{12}H_{16}0_3$, CAS registry number 22767-72-2. Isolated as a yellow oil (56%): IR(ν_{max}/cm^{-1}) 2980, 1730, 1612, 1584, 1244, 1176; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.12 (q, *J* = 7.3 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 173.1, 158.0, 132.6, 129.3, 113.9, 60.4, 55.2, 36.3, 30.1, 14.2; EI-MS *m/z* (rel. intensity) 208 (M, 40), 135 (11), 134 (100), 121 (85), 91 (15).



12

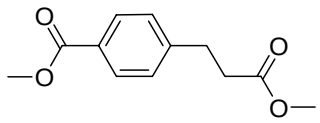
Benzenepropanoic acid, 3-methoxy-, ethyl ester (13) $C_{12}H_{16}0_3$, CAS registry number 7116-39-4. Isolated as a yellow oil (62%): IR(ν_{max}/cm^{-1}) 2979, 1730, 1601, 1584, 1257, 1152; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.21 (m, 1H), 6.79 (m, 1H), 6.75 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.24 (t, *J* =

7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 173.0, 142.2, 129.5 (2C), 120.6, 114.0, 111.6, 60.5, 55.1, 35.9, 31.0, 14.2; EI-MS *m/z* (rel. intensity) 208 (M, 41), 135 (36), 134 (100), 121 (11), 91 (10).



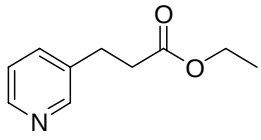
13

Benzenepropanoic acid, 4-(methoxycarbonyl)-, methyl ester (16) $C_{12}H_{14}O_4$, CAS registry number 40912-11-6. Isolated as a pasty yellow solid (64%): IR(ν_{max}/cm^{-1}) 2982, 1719, 1590, 1574, 1279, 1176; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.67 (s, 3H), 3.01 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 173.0, 167.0, 145.9, 129.8 (2C), 128.3 (3C), 52.0, 51.7, 55.1, 35.2, 30.8; EI-MS *m/z* (rel. intensity) 222 (M, 19), 191 (21), 163 (14), 162 (100), 149 (12), 131 (69), 121 (22).



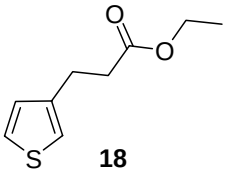
16

3-pyridinepropanoic acid, ethyl ester (17) $C_{10}H_{13}O_2N$, CAS registry number 64107-54-6. Isolated as an orange oil (68%): IR(ν_{max}/cm^{-1}) 2981, 1729, 1575, 1181; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.45 (m, 2H), 7.51 (m, 1H), 7.19 (m, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.3, 149.7, 147.7, 135.9 (2C), 123.4, 60.6, 35.4, 28.0, 14.1; EI-MS *m/z* (rel. intensity) 179 (M, 1), 150 (12), 136 (12), 134 (32), 135 (100), 106 (54), 92 (17), 79 (10), 78 (16).



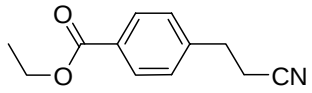
17

3-thiophenepropanoic acid, ethyl ester (18) $C_9H_{12}O_2S$, CAS registry number 99198-96-6. Isolated as an orange oil (34%): IR(ν_{max}/cm^{-1}) 3102, 2979, 1729, 1635, 1249, 1154; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.28 (m, 1H), 7.00 (m, 1H), 6.97 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 172.9, 140.8, 128.0, 125.6, 120.6, 60.5, 35.2, 25.5, 14.2; EI-MS *m/z* (rel. intensity) 184 (M, 66), 113 (25), 111 (53), 110 (100), 97 (43), 85 (11).



18

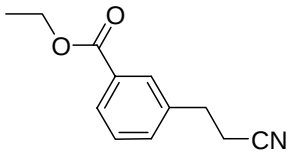
Benzoic acid, 4-(2-cyanoethyl)-, ethyl ester (19) $C_{12}H_{13}O_2N$, CAS registry number 69333-40-0. Isolated as a yellow oil (85%): IR(ν_{max}/cm^{-1}) 2982, 2246, 1711, 1612, 1275, 1180; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.36 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 166.3, 142.9, 130.2 (2C), 129.6, 128.3 (2C), 118.8, 61.0, 31.4, 19.0, 14.3; EI-MS *m/z* (rel. intensity) 203 (M, 9), 175 (61), 163 (14), 158 (100), 130 (5), 118 (17), 103 (15).



19

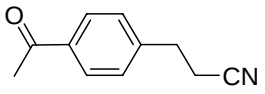
Benzoic acid, 3-(2-cyanoethyl)-, ethyl ester (20) $C_{12}H_{13}O_2N$, CAS registry number 179179-36-3. Isolated as a yellow oil (73%): IR(ν_{max}/cm^{-1}) 2984, 2251, 1713, 1588, 1279, 1197; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.94 (m, 1H), 7.88 (m, 1H), 7.42 (m, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 166.3, 138.3, 132.8, 131.1, 129.3, 128.9,

128.4, 118.8, 61.1, 31.3, 19.2, 14.3; EI-MS *m/z* (rel. intensity) 203 (M, 4), 175 (45), 163 (11), 158 (100), 135 (48), 130 (13), 119 (17), 103 (34).



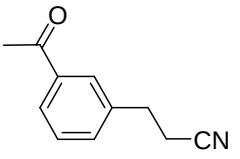
20

Benzenepropanenitrile, 4-acetyle (21) $C_{11}H_{11}ON$, CAS registry number 158613-21-9. Isolated as a yellow oil (82%): IR(ν_{max}/cm^{-1}) 2981, 2246, 1678, 1607; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 197.6, 143.3, 136.2, 129.0 (2C), 128.6 (2C), 118.7, 31.4, 26.7, 19.0; EI-MS *m/z* (rel. intensity) 173 (M, 6), 158 (100), 118 (12), 103 (15).



21

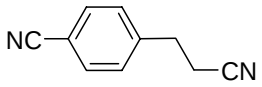
Benzenepropanenitrile, 3-acetyle (22) $C_{11}H_{11}ON$. Isolated as a yellow oil (63%): IR(ν_{max}/cm^{-1}) 2982, 2247, 1682, 1603, 1585; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.84 (2H, m), 7.45 (2H, m), 3.01 (2H, t, *J* = 7.3 Hz), 2.66 (2H, t, *J* = 7.3 Hz), 2.60 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 197.9, 138.5, 137.6, 133.1, 129.2, 128.0, 127.5, 118.8, 31.3, 26.7, 19.3; EI-MS *m/z* (rel. intensity) 173 (M, 1), 158 (100), 103 (27); Anal. Calcd. For $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09; O, 9.24; Found: C, 75.99; H, 6.60; N, 7.78; O, 9.90.



22

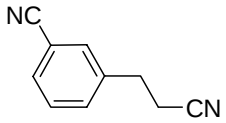
Benzenepropanenitrile, 4-cyano (23) $C_{10}H_8N_2$, CAS registry number 18176-72-2. . Isolated as a white solid (mp = 83°C, 77%): IR(ν_{max}/cm^{-1}) 2980, 2252, 2229, 1610; ^{1}H NMR

(400 MHz, $CDCl_3$, 293 K, TMS) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 143.8, 132.5 (2C), 129.4 (2C), 119.0, 118.8, 110.7, 31.2, 18.6; EI-MS *m/z* (rel. intensity) 156 (M, 22), 116 (100), 89 (18).



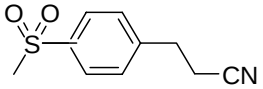
23

Benzenepropanenitrile, 3-cyano (24) $C_{10}H_8N_2$, CAS registry number 18153-17-8. . Isolated as a white solid (mp = 89°C, 71%): IR(ν_{max}/cm^{-1}); 2979, 2246, 2225, 1583; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.52 (m, 4H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 139.4, 133.1 (2C), 131.9, 131.1, 129.8, 118.6, 112.8, 30.9, 19.0; EI-MS *m/z* (rel. intensity) 156 (M, 25), 116 (100), 89 (18).



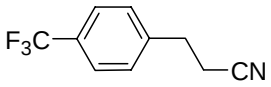
24

Benzenepropanitrile, 4-(phenylmethylsulfone)-, (25) $C_{12}H_{16}O_4S$, CAS registry number 858217-61-5. Isolated as a white solid (mp = 96°C, 82%): IR(ν_{max}/cm^{-1}) 2982, 2246, 1598, 1292, 1144; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 2.99 (m, 5H), 2.65 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 144.0, 139.4, 129.5 (2C), 127.9 (2C), 44.5, 31.2, 18.8; EI-MS *m/z* (rel. intensity) 209 (M, 26), 194 (36), 169 (22), 146 (79), 130 (63), 107 (100), 103 (72), 77 (23).



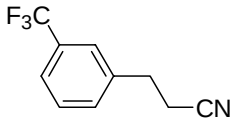
25

Benzenepropanenitrile, 4-trifluoromethyl (26) $C_{10}H_8F_3N$. Isolated as a yellow oil (79%): IR(ν_{max}/cm^{-1}) 2980, 2248, 1619, 1323; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 142.1, 129.5 (q, *J* = 32 Hz), 128.8 (2C), 125.8 (2C), 124.1 (q, *J* = 270 Hz), 118.7, 31.2, 19.0; ^{19}F NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ -63.0 (s, 3F); ; EI-MS *m/z* (rel. intensity) 199 (M, 32), 159 (100), 109 (25); Anal. Calcd. For $C_{10}H_8F_3N$: C, 60.30; H, 4.05; F, 28.62; N, 7.03; Found: C, 60.59; H, 4.31; F, 27.58; N, 6.98.



26

Benzenepropanenitrile, 3-trifluoromethyl (27) $C_{10}H_8F_3N$, CAS registry number 95096-06-3. Isolated as a yellow oil (78%): IR(ν_{max}/cm^{-1}) 2981, 2249, 1324; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.56 (m, 1H), 7.48 (m, 3H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 138.9, 131.8, 131.1 (q, *J* = 32 Hz), 129.4, 125.1, 124.2, 123.9 (q, *J* = 271 Hz), 118.7, 31.2, 19.0; ^{19}F NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ -63.1 (s, 3F); EI-MS *m/z* (rel. intensity) 199 (M, 14), 159 (100), 109 (24);



27

4-(2-dimethylcarbamoyl-ethyl)-benzoic acid ethyl ester (28) $C_{14}H_{19}O_3N$. Isolated as a yellow oil (60%): IR(ν_{max}/cm^{-1}) 2983, 1711, 1644, 1610, 1271, 1177; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.8 Hz, 2H), 2.94 (s, 3H), 2.93 (s, 3H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K, TMS) δ 171.7, 166.5, 146.9, 129.7 (2C),

128.4 (3C), 60.8, 37.1, 35.5, 34.7, 31.2, 14.3; EI-MS *m/z* (rel. intensity) 249 (M, 100), 220 (14), 24 (25), 177 (19), 149 (20), 148 (10), 131 (36)); Anal. Calcd. For $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62; O, 19.25 Found: C, 67.54; H, 7.96; N, 5.24; O, 19,26.

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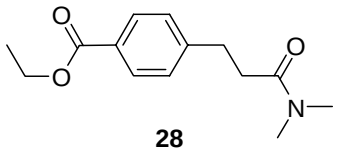

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