

Electronic Supplementary Information

Iron-catalyzed trifluoromethylation with concomitant C–C bond formation via 1,2-migration of an aryl group

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1. General

^1H , ^{19}F NMR spectra were measured on a JEOL JNM-ECS-400 spectrometer at 400 and 376 MHz, respectively. ^{13}C NMR spectra were recorded on a JEOL JNM-ECS-400 spectrometer at 100 MHz. Chemical shifts were reported downfield from TMS (= 0) or CDCl_3 for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to CDCl_3 . For ^{19}F NMR, chemical shifts were reported in the scale relative to a CFCl_3 external standard (0 ppm). Infrared spectra were measured on a Thermo Nicolet iS5, and only diagnostic absorptions are listed below. ESI- and APCI-MS were taken on Bruker micrOTOF-QII_{-RSL}. Column chromatography was performed with silica gel N-60 (40-100 μm) purchased from Kanto Chemical Co., Inc. In some cases, purification was carried out using JIA recycling preparative HPLC system [LC-918R; column, JAIGEL-H; chloroform]. TLC analysis was performed on Silica gel 60 F_{254} -coated glass plates (Merck). Visualization was accomplished by means of ultraviolet (UV) irradiation at 254 nm or by spraying 12-molybdo(VI)phosphoric acid ethanol solution as the developing agent.

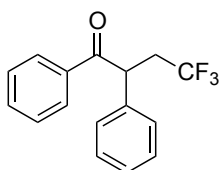
Dehydrated 1,4-dioxane was purchased from Kanto Chemical Co., Inc. $\text{Fe}(\text{OAc})_2$, FeCl_2 , CuI , CuOAc , CuCl_2 were obtained from commercial sources and were used as received. Other reagents were purified by usual methods. Substrates were prepared according to literature procedures.^[1] Togni reagent was prepared according to literature procedures.^[2]

2. Carbotrifluoromethylation via 1,2-migration of an aryl group (Tables 1, 2 and 3)

2.1. Typical experimental procedure for the 1,2-migration driven trifluoromethylation

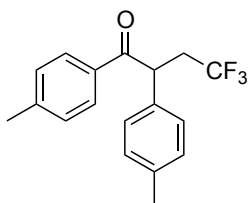
Fe(OAc)₂ (5.2 mg, 15 mol %), K₂CO₃ (27.6 mg, 1 equiv.) and Togni's reagent **1** (126.4 mg, 2 equiv.) were added into a Schlenk flask, which was flame-dried under vacuum. The flask was evacuated and backfilled with nitrogen. Then, degassed 1,4-dioxane (1 ml) and **2a** (42 mg, 0.2 mmol) were added to the tube. After stirring for 12 h at 23 °C, the reaction mixture was diluted with EtOAc (5 ml) and the organic solution was washed with aqueous NaHCO₃. The mixture was extracted with EtOAc. The organic layer was washed with brine and dried over MgSO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give the trifluoromethylated product **3a** (45.6 mg, 82%) as a colorless oil.

2.2.1. 4,4,4-trifluoro-1,2-diphenylbutan-1-one (**3a**)



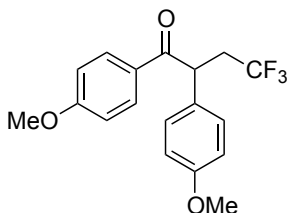
Colorless solid; 45.6 mg, 82%; ¹H NMR (400 MHz, CDCl₃): δ = 2.48-2.61 (m, 1H), 3.24-3.38 (m, 1H), 4.91 (dd, *J* = 5.3, 7.6 Hz, 1H), 7.22-7.27 (m, 1H), 7.29-7.34 (m, 4H), 7.39-7.43 (m, 2H), 7.51 (tt, *J* = 1.4, 7.4 Hz, 1H), 7.95-7.97 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 37.3 (q, *J* = 27.9 Hz), 47.2 (q, *J* = 2.9 Hz), 126.4 (q, *J* = 277.4 Hz), 127.8, 128.0, 128.6, 128.8, 129.3, 133.4, 135.6, 137.4, 196.7; ¹⁹F NMR (376 MHz, CDCl₃): δ = -64.5 (t, *J* = 10.4 Hz); IR (neat): 1686, 1598, 1449, 1260, 1139, 759, 698 cm⁻¹; HRMS (ESI): Calcd. for [C₁₆H₁₃F₃O+Na]⁺: *m/z* = 301.0811, Found: 301.0820.

2.2.2. 4,4,4-trifluoro-1,2-di-*p*-tolylbutan-1-one (3b)



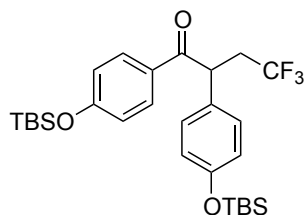
Colorless oil; 44.0 mg, 72%; ^1H NMR (400 MHz, CDCl_3): δ = 2.27 (s, 3H), 2.35 (s, 3H), 2.44-2.57 (m, 1H), 3.20-3.34 (m, 1H), 4.84 (dd, J = 6.0, 7.4 Hz, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 20.9, 21.5, 37.3 (q, J = 27.9 Hz), 46.6 (q, J = 1.9 Hz), 126.5 (q, J = 277.4 Hz), 127.8, 128.9, 129.3, 129.9, 133.1, 134.6, 137.5, 144.2, 196.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.5 (t, J = 10.4 Hz); IR (neat): 1679, 1512, 1379, 1258, 1136, 1099 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{18}\text{H}_{13}\text{F}_3\text{O}+\text{Na}]^+$: m/z = 329.1124, Found: 329.1120.

2.2.3. 4,4,4-trifluoro-1,2-bis(4-methoxyphenyl)butan-1-one (3c)



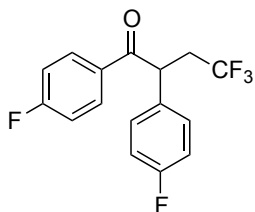
Colorless oil; 52.9 mg, 78%; ^1H NMR (400 MHz, CDCl_3): δ = 2.44-2.56 (m, 1H), 3.17-3.30 (m, 1H), 3.75 (s, 3H), 3.82 (s, 3H), 4.80 (dd, J = 6.2, 7.1 Hz, 1H), 6.83 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 9.2 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.94 (d, J = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.3 (q, J = 27.9 Hz), 45.9 (q, J = 1.9 Hz), 55.1, 55.4, 113.8, 114.6, 126.5 (q, J = 277.4 Hz), 128.5, 129.0, 129.8, 131.1, 159.0, 163.6, 195.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.3 (t, J = 10.4 Hz); IR (neat): 1674, 1600, 1510, 1249, 1029, 754 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_3+\text{Na}]^+$: m/z = 361.1022, Found: 361.1021.

2.2.4. 4,4,4-trifluoro-1,2-bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl) butan-1-one (3d)



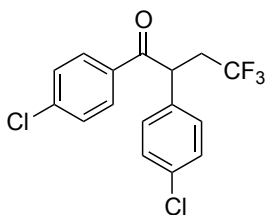
Colorless oil; 86.0 mg, 80%; ^1H NMR (400 MHz, CDCl_3): δ = 0.15 (s, 6H), 0.20 (s, 6H), 0.94 (s, 9H), 0.96 (s, 9H), 2.42-2.56 (m, 1H), 3.16-3.30 (m, 1H), 4.77 (dd, J = 6.0, 7.4 Hz, 1H), 6.75 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = -4.5, -4.4, 18.1, 18.2, 25.5, 25.6, 37.4 (q, J = 27.9 Hz), 46.0, 119.9, 120.7, 126.5 (q, J = 277.4 Hz), 129.0, 129.2, 130.4, 131.1, 155.2, 160.4, 195.5; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.5 (t, J = 10.4 Hz); IR (neat): 1677, 1598, 1509, 1256, 1138, 911, 838 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{28}\text{H}_{41}\text{F}_3\text{O}_3\text{Si}_2+\text{Na}]^+$: m/z = 561.2439, Found: 561.2443.

2.2.5. 4,4,4-trifluoro-1,2-bis(4-fluorophenyl)butan-1-one (3e)



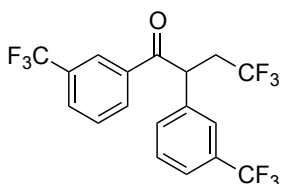
Colorless oil; 50.3 mg, 80%; ^1H NMR (400 MHz, CDCl_3): δ = 2.46-2.59 (m, 1H), 3.17-3.30 (m, 1H), 4.84 (dd, J = 6.7, 6.7 Hz, 1H), 6.99-7.03 (m, 2H), 7.07-7.11 (m, 2H), 7.24-7.28 (m, 2H), 7.95-7.98 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.4 (q, J = 27.9 Hz), 46.3 (q, J = 1.9 Hz), 115.9 (d, J = 22.2 Hz), 116.4 (d, J = 21.2 Hz), 126.2 (q, J = 277.4 Hz), 129.6 (d, J = 7.7 Hz), 131.5 (d, J = 9.6 Hz), 131.8 (d, J = 2.9 Hz), 132.9 (d, J = 2.9 Hz), 162.3 (d, J = 247.6 Hz), 165.8 (d, J = 256.2 Hz), 195.1; ^{19}F NMR (376 MHz, CDCl_3): δ = -113.7--113.6 (m, 1F), -103.9--103.8 (m, 1F), -64.4 (t, J = 10.8 Hz, 3F); IR (neat): 1684, 1597, 1508, 1258, 1225, 832 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{11}\text{F}_5\text{O}+\text{H}]^+$: m/z = 315.0803, Found: 315.0805.

2.2.6. 4,4,4-trifluoro-1,2-bis(4-chlorophenyl) butan-1-one (3f)



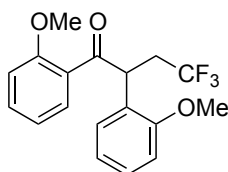
Colorless oil; 63.6 mg, 92%; ^1H NMR (400 MHz, CDCl_3): δ = 2.46-2.59 (m, 1H), 3.17-3.30 (m, 1H), 4.81 (dd, J = 6.7, 6.7 Hz, 1H), 7.21 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.1 (q, J = 27.9 Hz), 46.5 (q, J = 1.9 Hz), 126.2 (q, J = 277.4 Hz), 129.1, 129.3, 129.6, 130.1, 133.6, 134.1, 135.4, 140.1, 195.2; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.4 (t, J = 10.4 Hz); IR (neat): 1685, 1590, 1491, 1257, 1093 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{F}_3\text{O}+\text{H}]^+$: m/z = 347.0212, Found: 347.0210.

2.2.7. 4,4,4-trifluoro-1,2-bis(3-(trifluoromethyl)phenyl)butan-1-one (3g)



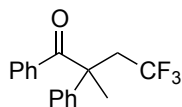
Colorless oil; 75.4 mg, 91%; ^1H NMR (400 MHz, CDCl_3): δ = 2.54-2.67 (m, 1H), 3.25-3.38 (m, 1H), 4.94-4.97 (m, 1H), 7.46-7.61 (m, 5H), 7.80 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.20 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.3 (q, J = 28.9 Hz), 47.1 (q, J = 1.9 Hz), 123.4 (q, J = 272.6 Hz), 123.6 (q, J = 272.6 Hz), 124.8 (q, J = 3.8 Hz), 125.2 (q, J = 3.8 Hz), 125.7 (q, J = 3.8 Hz), 126.0 (q, J = 277.4 Hz), 129.6, 130.1, 130.1 (q, J = 3.8 Hz), 131.4, 131.6 (q, J = 32.7 Hz), 131.8, 132.0 (q, J = 32.7 Hz), 135.7, 137.6, 194.9; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.4 (t, J = 10.8 Hz, 3F), -63.0 (s, 3F), -62.7 (s, 3F); IR (neat): 1694, 1613, 1438, 1328, 1127, 1074 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{18}\text{H}_{11}\text{F}_9\text{O}+\text{H}]^+$: m/z = 415.0739, Found: 415.0747.

2.2.8. 4,4,4-trifluoro-1,2-bis(2-methoxyphenyl)butan-1-one (3h)



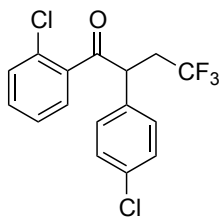
Colorless oil; 62.0 mg, 92%; ^1H NMR (400 MHz, CDCl_3): δ = 2.38-2.52 (m, 1H), 3.24-3.38 (m, 1H), 3.70 (s, 3H), 3.77 (s, 3H), 5.11 (dd, J = 6.4, 6.4 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.81-6.88 (m, 2H), 7.12-7.16 (m, 2H), 7.28-7.32 (m, 1H), 7.44 (dd, J = 1.8, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 34.6 (q, J = 27.9 Hz), 46.4 (q, J = 1.9 Hz), 55.1, 55.1, 110.4, 110.9, 120.2, 120.4, 126.4, 127.0 (q, J = 277.4 Hz), 128.1, 128.7, 129.9, 130.3, 132.8, 156.6, 157.3, 200.6; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.3 (t, J = 10.4 Hz); IR (neat): 1688, 1598, 1492, 1465, 1436, 1250, 1125, 752 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_3+\text{Na}]^+$: m/z = 361.1022, Found: 361.1030.

2.2.9. 4,4,4-trifluoro-2-methyl-1,2-diphenylbutan-1-one (3i)



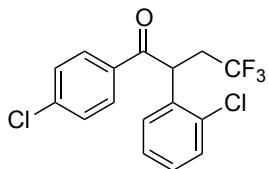
Colorless oil; 44.1 mg, 75%; ^1H NMR (400 MHz, CDCl_3): δ = 1.82 (s, 3H), 2.83 (qd, J = 11.0, 15.6 Hz, 1H), 3.06 (qd, J = 11.0, 15.6 Hz, 1H), 7.20-7.23 (m, 2H), 7.31-7.43 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3): δ = 22.0, 43.4 (q, J = 27.0 Hz), 51.9, 126.3, 126.4 (q, J = 278.4 Hz), 127.8, 128.1, 129.2, 129.3, 131.8, 136.0, 140.8, 201.4; ^{19}F NMR (376 MHz, CDCl_3): δ = -58.5 (t, J = 11.0 Hz); IR (neat): 1677, 1598, 1447, 1366, 1259, 1117, 698 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}+\text{Na}]^+$: m/z = 315.0967, Found: 315.0970.

2.2.10. 4,4,4-trifluoro-1-(2-chlorophenyl)-2-(4-chlorophenyl)butan-1-one (5a)



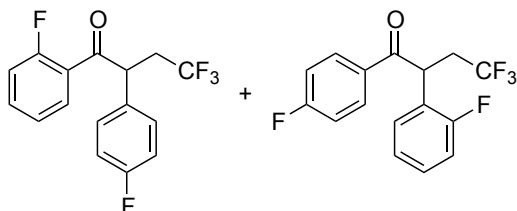
Colorless oil; 55.4 mg, 80%; ^1H NMR (400 MHz, CDCl_3): δ = 2.52-2.65 (m, 1H), 3.19-3.32 (m, 1H), 4.79 (dd, J = 6.7, 6.7 Hz, 1H), 7.10-7.16 (m, 3H), 7.79-7.23 (m, 1H), 7.25-7.27 (m, 2H), 7.31-7.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 36.1 (q, J = 28.9 Hz), 50.8 (q, J = 1.9 Hz), 126.3 (q, J = 277.4 Hz), 126.9, 129.3, 129.5, 129.9, 130.6, 130.9, 132.1, 134.3, 137.9, 199.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.0 (t, J = 10.4 Hz); IR (neat): 1705, 1590, 1942, 1434, 1254, 1139, 1094, 741 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{F}_3\text{O}+\text{H}]^+$: m/z = 347.0212, Found: 347.0195.

2.2.11. 4,4,4-trifluoro-2-(2-chlorophenyl)-1-(4-chlorophenyl)butan-1-one (6a)



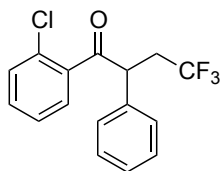
Colorless oil; 2.8 mg, 4%; ^1H NMR (400 MHz, CDCl_3): δ = 2.38-2.51 (m, 1H), 3.20-3.34 (m, 1H), 5.37 (dd, J = 5.1, 7.8 Hz, 1H), 7.13-7.23 (m, 3H), 7.38 (d, J = 8.7 Hz, 2H), 7.43-7.45 (m, 1H), 7.90 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 36.4 (q, J = 28.9 Hz), 43.2 (q, J = 1.9 Hz), 126.1 (q, J = 277.4 Hz), 127.8, 128.6, 129.1, 129.4, 130.1, 130.5, 133.3, 133.6, 134.9, 140.2, 195.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.8 (t, J = 10.4 Hz); IR (neat): 1720, 1689, 1591, 1491, 1257, 1136, 757 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{F}_3\text{O}+\text{H}]^+$: m/z = 347.0212, Found: 347.0204.

2.2.12. 4,4,4-trifluoro-1-(2-fluorophenyl)-2-(4-fluorophenyl)butan-1-one (5b) + 4,4,4-trifluoro-2-(2-fluorophenyl)-1-(4-fluorophenyl)butan-1-one (6b)



Colorless oil; 52.9 mg, 84% (1:1); ^1H NMR (400 MHz, CDCl_3): δ = 2.43-2.62 (m, 2H), 3.17-3.34 (m, 2H), 4.86 (t, J = 6.7, 6.7 Hz, 1H), 5.23 (t, J = 6.7, 6.7 Hz, 1H), 6.95-7.25 (m, 12H), 7.45-7.50 (m, 1H), 7.76 (dt, J = 1.8, 7.3 Hz, 1H), 7.98-8.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 36.5 (q, J = 28.9 Hz), 37.1 (q, J = 28.9 Hz), 38.9 (q, J = 2.9 Hz), 50.3 (q, J = 1.9 Hz), 116.0 (d, J = 8.7 Hz), 116.2 (d, J = 7.7 Hz), 116.2 (d, J = 22.2 Hz), 116.8 (d, J = 24.1 Hz), 124.5 (d, J = 22.2 Hz), 124.6 (d, J = 22.2 Hz), 124.7 (d, J = 2.9 Hz), 125.1 (d, J = 3.8 Hz), 126.3 (q, J = 276.5 Hz), 126.4 (q, J = 276.5 Hz), 128.7 (d, J = 2.9 Hz), 129.5 (d, J = 8.7 Hz), 130.2 (d, J = 7.7 Hz), 131.4 (d, J = 2.9 Hz), 131.5 (d, J = 3.8 Hz), 131.6 (d, J = 2.9 Hz), 132.2 (d, J = 3.8 Hz), 135.1 (d, J = 9.6 Hz), 159.7 (d, J = 246.6 Hz), 161.1 (d, J = 254.3 Hz), 162.4 (d, J = 254.3 Hz), 166.1 (d, J = 255.3 Hz), 194.7, 195.6 (d, J = 3.8 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -118.0--117.9 (m), -114.0 (m), -109.2--109.2 (m), -103.8--103.8 (m), -64.6 (t, J = 10.4 Hz), -64.8 (t, J = 10.4 Hz), -64.4 (t, J = 10.4 Hz); IR (neat): 1687, 1609, 1598, 1509, 1493, 1482, 1453, 1228, 1137, 828, 756 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{11}\text{F}_5\text{O}+\text{H}]^+$: m/z = 315.0803, Found: 315.0797.

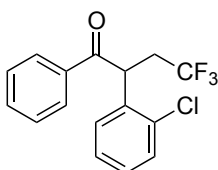
2.2.13. 4,4,4-trifluoro-1-(2-chlorophenyl)-2-phenylbutan-1-one (5c)



Colorless oil; 49.6 mg, 79%; ^1H NMR (400 MHz, CDCl_3): δ = 2.54-2.67 (m, 1H), 3.25-3.28 (m, 1H), 4.80 (dd, J = 6.7, 6.7 Hz, 1H), 7.12-7.19 (m, 4H), 7.24-7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ = 35.9 (q, J = 28.9 Hz), 51.3 (q, J = 1.9 Hz), 126.4 (q, J = 277.4 Hz), 126.6, 128.1,

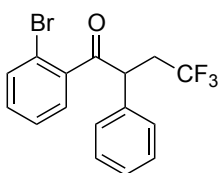
128.4, 129.1, 129.2, 130.4, 130.8, 131.7, 135.6, 138.1, 199.5; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -64.2$ (t, $J = 10.4$ Hz); IR (neat): 1704, 1590, 1433, 1254, 1136, 1070, 753, 698 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{12}\text{ClF}_3\text{O}+\text{H}]^+$: $m/z = 313.0602$, Found: 313.0613.

2.2.14. 4,4,4-trifluoro-2-(2-chlorophenyl)-1-phenylbutan-1-one (6c)



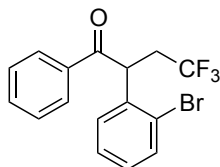
Colorless oil; 5.5 mg, 9%; ^1H NMR (400 MHz, CDCl_3): $\delta = 2.39$ -2.52 (m, 1H), 3.21-3.35 (m, 1H), 5.44 (dd, $J = 5.3, 7.3$ Hz, 1H), 7.17-7.22 (m, 3H), 7.40-7.45 (m, 3H), 7.50-7.54 (m, 1H), 7.95-7.97 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 27.9$ (q, $J = 27.9$ Hz), 43.1, 126.1 (q, $J = 276.5$ Hz), 127.7, 128.7, 128.7, 128.7, 129.2, 130.4, 133.4, 133.6, 135.2, 135.3, 196.5; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -64.8$ (t, $J = 10.4$ Hz); IR (neat): 1690, 1591, 1433, 1255, 1134, 753, 699 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{12}\text{ClF}_3\text{O}+\text{H}]^+$: $m/z = 313.0602$, Found: 313.0606.

2.2.15. 4,4,4-trifluoro-1-(2-bromophenyl)-2-phenylbutan-1-one (5d)



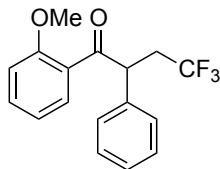
Colorless oil; 58.1 mg, 81%; ^1H NMR (400 MHz, CDCl_3): $\delta = 2.57$ -2.71 (m, 1H), 3.22-3.36 (m, 1H), 4.76 (t, $J = 6.7, 6.7$ Hz, 1H), 7.03-7.06 (m, 1H), 7.15-7.30 (m, 7H), 7.52-7.54 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 35.8$ (q, $J = 28.9$ Hz), 51.3 (q, $J = 1.9$ Hz), 119.0, 126.4 (q, $J = 277.4$ Hz), 127.1, 128.1, 128.5, 129.0, 129.1, 131.6, 133.6, 135.4, 140.2, 200.0; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -64.0$ (t, $J = 10.4$ Hz); IR (neat): 1704, 1588, 1430, 1255, 1135, 1064, 757, 698 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{12}\text{BrF}_3\text{O}+\text{H}]^+$: $m/z = 357.0096$, Found: 357.0098.

2.2.16. 4,4,4-trifluoro-2-(2-bromophenyl)-1-phenylbutan-1-one (6d)



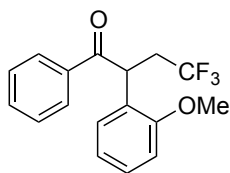
Colorless oil; 4.8 mg, 7%; ^1H NMR (400 MHz, CDCl_3): δ = 2.35-2.48 (m, 1H), 3.22-3.35 (m, 1H), 5.42 (dd, J = 4.6, 8.5 Hz, 1H), 7.09-7.13 (m, 1H), 7.16-7.23 (m, 2H), 7.40-7.43 (m, 2H), 7.50-7.55 (m, 1H), 7.63 (dd, J = 0.9, 8.4 Hz, 1H), 7.96-7.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 36.5 (q, J = 28.9 Hz), 45.9 (q, J = 1.9 Hz), 124.2, 126.0 (q, J = 277.4 Hz), 128.3, 128.7, 128.7, 129.2, 129.5, 133.6, 133.9, 135.4, 136.8, 196.5; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.0 (t, J = 10.4 Hz); IR (neat): 1719, 1689, 1491, 1258, 1140, 755 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_{12}\text{BrF}_3\text{O}+\text{H}]^+$: m/z = 357.0096, Found: 357.0099.

2.2.17. 4,4,4-trifluoro-1-(2-methoxyphenyl)-2-phenylbutan-1-one (5e)



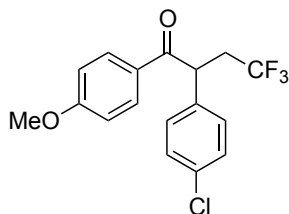
Colorless oil; 43.1 mg, 71%; ^1H NMR (400 MHz, CDCl_3): δ = 2.42-2.56 (m, 1H), 3.22-3.36 (m, 1H), 3.88 (s, 3H), 5.09 (dd, J = 6.7, 6.7 Hz, 1H), 6.88-6.92 (m, 2H), 7.19-7.27 (m, 5H), 7.36-7.41 (m, 1H), 7.47-7.49 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.0 (q, J = 27.9 Hz), 51.0 (q, J = 1.9 Hz), 55.5, 111.6, 120.8, 126.7 (q, J = 277.4 Hz), 127.5, 127.6, 128.5, 128.8, 131.1, 133.7, 137.6, 158.0, 200.0; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.4 (t, J = 10.4 Hz); IR (neat): 1686, 1598, 1494, 1259, 1136, 1094, 754, 695 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_2+\text{Na}]^+$: m/z = 331.0916, Found: 331.0909.

2.2.18. 4,4,4-trifluoro-2-(2-methoxyphenyl)-1-phenylbutan-1-one (6e)



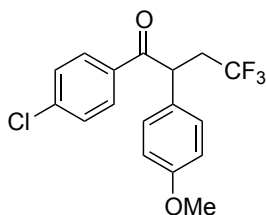
Colorless oil; 12.9 mg, 21%; ^1H NMR (400 MHz, CDCl_3): δ = 2.37-2.51 (m, 1H), 3.18-3.31 (m, 1H), 3.93 (s, 3H), 5.38 (t, J = 6.4 Hz, 1H), 6.84-6.90 (m, 2H), 7.10 (dd, J = 1.8, 7.8 Hz, 1H), 7.19-7.22 (m, 1H), 7.35-7.38 (m, 2H), 7.47 (tt, J = 1.4, 7.4 Hz, 1H), 7.95-7.98 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 36.3 (q, J = 27.9 Hz), 39.5 (q, J = 1.9 Hz), 55.7, 111.2, 121.2, 126.1, 126.6 (q, J = 277.4), 128.2, 128.4, 128.6, 129.0, 133.1, 135.7, 155.8, 197.5; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.8 (t, J = 10.4 Hz); IR (neat): 1674, 1598, 1485, 1436, 1255, 1133, 1021, 752, 699 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_2+\text{Na}]^+$: m/z = 331.0916, Found: 331.0910. The structure was determined by HMBC and HSQC analyses.

2.2.19. 4,4,4-trifluoro-2-(4-chlorophenyl)-1-(4-methoxyphenyl)butan-1-one (5f)



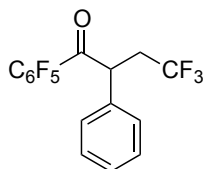
Colorless oil; 55.0 mg, 80%; ^1H NMR (400 MHz, CDCl_3): δ = 2.46-2.59 (m, 1H), 3.16-3.29 (m, 1H), 3.83 (s, 3H), 4.83 (dd, J = 6.7, 6.7 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 7.22-7.30 (m, 4H), 7.92 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.2 (q, J = 27.9 Hz), 46.0 (q, J = 1.9 Hz), 55.4, 113.9, 126.3 (q, J = 277.4 Hz), 128.2, 129.3, 129.4, 131.1, 133.7, 136.3, 163.8, 194.8; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.3 (t, J = 10.4 Hz); IR (neat): 1674, 1599, 1511, 1491, 1256, 1093, 753 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{17}\text{H}_{14}\text{ClF}_3\text{O}_2+\text{Na}]^+$: m/z = 365.0527, Found: 365.0520. The structure was determined by HMBC and HSQC analyses.

2.2.20. 4,4,4-trifluoro-1-(4-chlorophenyl)-2-(4-methoxyphenyl)butan-1-one (6f)



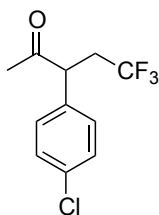
Colorless oil; 4.5 mg, 7%; ^1H NMR (400 MHz, CDCl_3): δ = 2.44-2.57 (m, 1H), 3.17-3.31 (m, 1H), 3.75 (s, 3H), 4.78 (dd, J = 6.2, 6.2 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 37.3 (q, J = 27.9 Hz), 46.5 (q, J = 1.9 Hz), 55.2, 114.8, 126.3 (q, J = 277.4 Hz), 128.9, 129.0, 129.1, 130.2, 134.0, 139.8, 159.2, 195.7; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.4 (t, J = 10.4 Hz); IR (neat): 1684, 1590, 1511, 1251, 1138, 1059 cm^{-1} ; HRMS (ESI): Calcd. for $[\text{C}_{17}\text{H}_{14}\text{ClF}_3\text{O}_2+\text{Na}]$: m/z = 365.0527, Found: 365.0527.

2.2.21. 4,4,4-trifluoro-1-(perfluorophenyl)-2-phenylbutan-1-one (5g)



Colorless oil; 58.5 mg, 79%; ^1H NMR (400 MHz, CDCl_3): δ = 2.46-2.59 (m, 1H), 3.25-3.39 (m, 1H), 4.49 (dd, J = 6.7, 6.7 Hz, 1H), 7.15-7.18 (m, 2H), 7.26-7.35 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 35.6 (q, J = 28.9 Hz), 53.6 (q, J = 1.9 Hz), 113.6-114.0 (m), 126.0 (q, J = 276.5 Hz), 128.2, 128.8, 129.6, 134.4, 136.0-138.9 (m), 141.4-144.3 (m), 142.5-145.3 (m), 190.4; ^{19}F NMR (376 MHz, CDCl_3): δ = -159.6--159.5 (m), -148.2--148.1 (m), -140.4--140.3 (m), -64.6 (t, J = 10.4 Hz); IR (neat): 1714, 1650, 1494, 1457, 1255, 1136, 983, 700 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{16}\text{H}_8\text{F}_8\text{O}+\text{H}]^+$: m/z = 369.0520, Found: 369.0539.

2.2.21. 5,5,5-trifluoro-3-(4-chlorophenyl)pentan-2-one (5h)



Colorless oil; 32.1 mg, 64%; ^1H NMR (400 MHz, CDCl_3): δ = 2.10 (s, 3H), 2.29-2.42 (m, 1H), 3.02-3.15 (m, 1H), 3.94 (dd, J = 6.7, 6.7 Hz, 1H), 7.15 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 28.7, 35.8 (q, J = 28.9 Hz), 52.1 (q, J = 2.9 Hz), 126.2 (J = 276.5 Hz), 129.4, 129.6, 134.2, 135.2, 204.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -64.5 (t, J = 10.4 Hz); IR (neat): 1718, 1491, 1358, 1254, 1136, 1092, 1015 cm^{-1} ; HRMS (APCI): Calcd. for $[\text{C}_{11}\text{H}_{10}\text{ClF}_3\text{O}+\text{H}]^+$: m/z = 251.0445, Found: 251.0444.

3. References

- [1] N. Marion, R. Gealageas and S. P. Nolan, *Org. Lett.*, 2007, **9**, 2653.
- [2] K. Stanek, R. Koller and A. Togni, *J. Org. Chem.*, 2008, **73**, 7678.

6. NMR spectra

