Iron-Catalyzed Acylation of Polyfunctionalized Aryl- and Benzylzinc Halides with Acid Chlorides

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Table of contents:

General Considerations: All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes, which were used to transfer anhydrous solvents or reagents, were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H-NMR (25 °C) and GC-analysis. Chemical shifts are reported as δ-values in ppm relative to the solvent peak. NMR spectra were recorded on solutions in $CDCl_3$ (residual chloroform: $\delta = 7.25$ ppm for ^{1}H-NMR and $\delta = 77.0$ ppm for ^{13}C-NMR). For the characterization of the observed signal multiplicities the following abbreviations were used: s (singulet), d (doublet), t (triplet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), dq (doublet of quartet), q (quartet), qn (quintet), m (multiplet) as well as br (broad). All reagents obtained from commercial sources were used without any further purification unless otherwise stated.

Typical Procedure for the Preparation of Benzylzinc(II) Chlorides (1a-g) (TP 1):

A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with LiCl (0.53 g, 12.5 mmol, 1.25 equiv) and heated up to ca. 450 °C for 5 min under high vacuum using a heat gun. After cooling to room temperature under vigorous stirring, $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv) was added under argon, the *Schlenk*-tube was heated to ca. 320 °C for 5 min using a heatgun, cooled to room temperature and charged with magnesium turnings (0.58 g, 24.0 mmol, 2.40 equiv). Freshly distilled THF (10-15 mL) and the corresponding benzylic chloride (10.0 mmol, 1.00 equiv) were added and the reaction mixture was stirred at room temperature for a given time until full conversion of the starting material was observed. The completion of the metalation was monitored by GC-analysis of hydrolyzed and iodolyzed aliquots. When the oxidative insertion was complete, the solution of the corresponding benzylzinc(II) chloride was separated from the resulting salts *via* a syringe equipped with a filter and transferred to another pre-dried and argon-flushed *Schlenk*-tube, before being titrated against iodine.

Typical Procedure for the Preparation of Arylzinc(II) Chlorides (4a-f) (TP 2):

A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with the corresponding aryl iodide (10.0 mmol, 1.00 equiv) and dissolved in freshly distilled THF (10 mL). The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for a given time at the prior adjusted temperature until full conversion of the starting material was observed. The completion of the metalation was monitored by GC-analysis of hydrolyzed and iodolyzed aliquots with regard to an internal standard, transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.00 M in THF, 1.20 equiv) and finally titrated against iodine.

Typical Procedure for the Iron-Catalyzed Acylation of Benzylic Zinc Chlorides (1a-g) with Acid Chlorides (TP 3):

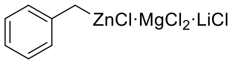
A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), the selected acid chloride (1.00 mmol, 1.00 equiv) and freshly distilled THF (1 mL). The corresponding prior prepared benzylic zinc chloride solution (1.25 mmol, 1.25 equiv) was dropwise added and the reaction mixture was stirred for a given time at room temperature. Subsequently, the reaction mixture was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude products by flash column chromatography afforded the desired products.

Typical Procedure for the Iron-Catalyzed Acylation of Arylzinc Chlorides (4a-f) with Acid Chlorides (TP 4):

A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), the selected acid chloride (1.00 mmol, 1.00 equiv) and freshly distilled THF (1 mL). The corresponding prior prepared arylzinc chloride (1.25 mmol, 1.25 equiv) was dropwise added and the reaction mixture was stirred for a given time at 50 °C. Subsequently, the reaction mixture was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude products by flash column chromatography afforded the desired products.

Preparation of the Benzylzinc(II) chlorides (1a-g)

Preparation of benzylzinc(II) chloride (1a)

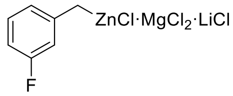


According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (10 mL) were used. Benzyl chloride (1.27 g, 1.16 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 1 h at room temperature. The concentration of benzylzinc(II) chloride (**1a**) was determined by titration with iodine in THF (0.80 M, 80%).

Preparation of 3-(trifluoromethyl)benzylzinc(II) chloride (1b)

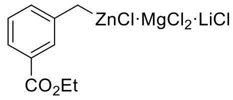
According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (10 mL) were used. 3-(Trifluoromethyl)benzyl chloride (1.95 g, 1.56 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 2 h at room temperature. The concentration of 3-(trifluoromethyl)benzylzinc(II) chloride (**1b**) was determined by titration with iodine in THF (0.72 M, 72%).

Preparation of 3-fluorobenzylzinc(II) chloride (1c)



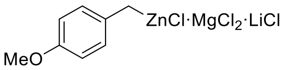
According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (10 mL) were used. 3-Fluorobenzyl chloride (1.45 g, 1.21 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 2 h at room temperature. The concentration of 3-fluorobenzylzinc(II) chloride (**1c**) was determined by titration with iodine in THF (0.65 M, 65%).

Preparation of 3-(ethoxycarbonyl)benzylzinc(II) chloride (1d)



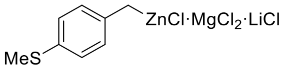
According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (15 mL) were used. Ethyl 3-(chloromethyl)benzoate (1.99 g, 1.70 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 1.5 h at room temperature. The concentration of 3-(ethoxycarbonyl)-benzylzinc(II) chloride (**1d**) was determined by titration with iodine in THF (0.38 M, 57%).

Preparation of 4-methoxybenzylzinc(II) chloride (1e)



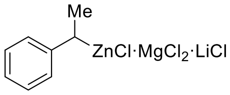
According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (10 mL) were used. 4-Methoxybenzyl chloride (1.57 g, 1.36 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 1 h at room temperature. The concentration of 4-methoxybenzylzinc(II) chloride (**1e**) was determined by titration with iodine in THF (0.60 M, 60%).

Preparation of 4-(methylthio)benzylzinc(II) chloride (1f)



According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (15 mL) were used. 4-(Methylthio)benzyl chloride (1.73 g, 1.48 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 1 h at room temperature. The concentration of 4-(methylthio)benzylzinc(II) chloride (**1f**) was determined by titration with iodine in THF (0.35 M, 53%).

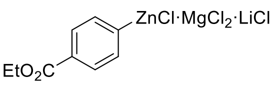
Preparation of (1-phenylethyl)zinc(II) chloride (1g)



According to **TP1**, LiCl (0.53 g, 12.5 mmol, 1.25 equiv), $ZnCl_2$ (1.51 g, 11.0 mmol, 1.10 equiv), Mg turnings (0.58 g, 24.0 mmol, 2.40 equiv) and freshly distilled THF (10 mL) were used. (1-Chloroethyl)benzene (1.41 g, 1.33 mL, 10.0 mmol, 1.00 equiv) was dropwise added and the reaction mixture was stirred for 2 h at room temperature. The concentration of (1-phenylethyl)zinc(II) chloride (**1g**) was determined by titration with iodine in THF (0.56 M, 56%).

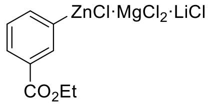
Preparation of the Arylzinc(II) Chlorides (4a-f)

Preparation of (4-(ethoxycarbonyl)phenyl)zinc(II) chloride (4a)



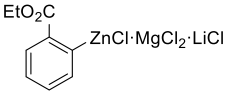
According to **TP2**, ethyl 4-iodobenzoate (2.76 g, 1.68 mL, 10.0 mmol, 1.00 equiv), tetradecane (500 µL) and freshly distilled THF (10 mL) were used. The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for 0.5 h at the prior adjusted temperature and subsequently transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.0 M in THF, 1.20 equiv). The concentration of (4-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4a**) was determined by titration with iodine in THF (0.32 M, >90%).

Preparation of (3-(ethoxycarbonyl)phenyl)zinc(II) chloride (4b)



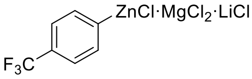
According to **TP2**, ethyl 3-iodobenzoate (2.76 g, 1.68 mL, 10.0 mmol, 1.00 equiv), tetradecane (500 µL) and freshly distilled THF (10 mL) were used. The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for 0.5 h at the prior adjusted temperature and subsequently transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.0 M in THF, 1.20 equiv). The concentration of (3-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4b**) was determined by titration with iodine in THF (0.31 M, >90%).

Preparation of (2-(ethoxycarbonyl)phenyl)zinc(II) chloride (4c)



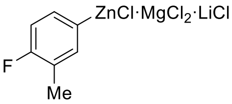
According to **TP2**, ethyl 2-iodobenzoate (2.76 g, 1.68 mL, 10.0 mmol, 1.00 equiv), tetradecane (500 µL) and freshly distilled THF (10 mL) were used. The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for 0.5 h at the prior adjusted temperature and subsequently transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.0 M in THF, 1.20 equiv). The concentration of (2-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4c**) was determined by titration with iodine in THF (0.34 M, >90%).

Preparation of (4-(trifluoromethyl)phenyl)zinc(II) chloride (4d)



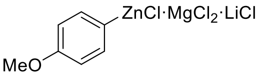
According to **TP2**, 4-iodobenzotrifluoride (2.72 g, 1.47 mL, 10.0 mmol, 1.00 equiv), tetradecane (250 µL) and freshly distilled THF (5.0 mL) were used. The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for 0.5 h at the prior adjusted temperature and subsequently transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.0 M in THF, 1.20 equiv). The concentration of (4-(trifluoromethyl)-phenyl)zinc(II) chloride (**4d**) was determined by titration with iodine in THF (0.42 M, >90%).

Preparation of (4-fluoro-3-methylphenyl)zinc(II) chloride (4e)



According to **TP2**, 2-fluoro-5-iodotoluene (2.36 g, 10.0 mmol, 1.00 equiv), tetradecane (500 µL) and freshly distilled THF (10 mL) were used. The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for 0.5 h at the prior adjusted temperature and subsequently transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.0 M in THF, 1.20 equiv). The concentration of (4-fluoro-3-methylphenyl)zinc(II) chloride (**4e**) was determined by titration with iodine in THF (0.33 M, >90%)

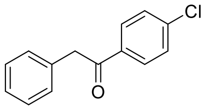
Preparation of (4-methoxyphenyl)zinc(II) chloride (4f)



According to **TP2**, 4-iodoanisole (2.34 g, 10.0 mmol, 1.00 equiv), tetradecane (500 µL) and freshly distilled THF (10 mL) were used. The solution was cooled to – 20 °C and *i*PrMgCl·LiCl (10.0 mL, 12.0 mmol, 1.21 M in THF, 1.20 equiv) was dropwise added. The reaction mixture was stirred for 0.5 h at the prior adjusted temperature and subsequently transmetalated with $ZnCl_2$ (12.0 mL, 12.0 mmol, 1.0 M in THF, 1.20 equiv). The concentration of (4-methoxyphenyl)zinc(II) chloride (**4f**) was determined by titration with iodine in THF (0.36 M, >90%).

Iron-Catalyzed Acylation of Benzylic Zinc Chlorides (1a-g) with Acid Chlorides

Preparation of 1-(4-chlorophenyl)-2-phenylethan-1-one (3a)



Based on **TP 3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The benzylzinc(II) chloride solution (**1a**, 1.56 mL, 1.25 mmol, 0.80 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 0.5 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, $R_f = 0.45$) afforded the desired product **3a** (208 mg, 0.90 mmol, 90%) as a white solid.

M.p.: 80.2 °C

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ = 7.93 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.33-7.31 (m, 2H), 7.26-7.23 (m, 3H), 4.24 (s, 2H).

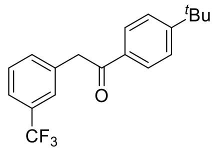
^{13}C-NMR (150 MHz, $CDCl_3$, ppm) δ = 196.3, 139.6, 134.8, 134.1, 130.0, 129.3, 128.9, 128.7, 127.0, 45.5.

IR (ATR, cm^{-1}) ṽ = 3028, 2901, 1723, 1686, 1588, 1571, 1496, 1485, 1452, 1395, 1336, 1320, 1271, 1217, 1201, 1169, 1104, 1088, 1072, 1004, 991, 961, 824, 795, 749, 711, 694, 661.

MS (EI, 70 eV, %) m/z = 230 (10), 141 (30), 139 (100), 111 (19), 91 (14), 57 (20), 43 (26), 41 (11)

HRMS (EI, 70 eV) m/z: calc. for **$C_{14}H_{11}ClO$**: 230.0498; found 230.0484.

Preparation of 1-(4-(*tert*-butyl)phenyl)-2-(3-(trifluoromethyl)phenyl)ethan-1-one (3b)



According to **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 3-(trifluoromethyl)-benzylzinc(II) chloride solution (**1b**, 1.74 mL, 1.25 mmol, 0.72 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 0.5 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, R_f = 0.15) leading to the desired product **3b** (208 mg, 0.65 mmol, 65%) (38% isolated yield without catalyst after prolonged reaction time of 2 h at room temperature) as a white solid.

M.p.: 68.3°C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.96 (d, J = 8.7 Hz, 2H), 7.56-7.43 (m, 6H), 4.33 (s, 2H), 1.35 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 196.1, 157.2, 135.4, 133.6, 132.9 (q, ^3J(C,F) = 4.0 Hz), 130.7 (q, ^2J(C,F) = 32 Hz), 128.8, 128.3, 126.2 (q, ^3J(C,F) = 3.8 Hz), 125.6, 123.9 (q, ^1J(C,F) = 271 Hz), 123.6 (q, ^3J(C,F) = 3.8 Hz), 44.7, 35.0, 30.9.

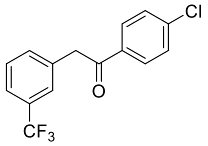
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 62.6.

IR (ATR, cm^{-1}) ṽ = 2964, 1725, 1711, 1678, 1641, 1603, 1451, 1406, 1366, 1331, 1268, 1223, 1160, 1110, 1092, 1075, 1004, 992, 915, 880, 841, 829, 786, 720, 701, 658.

MS (EI, 70 eV, %) m/z = 320 (1), 305 (10), 162 (12), 161 (100), 118 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{19}H_{19}F_3O$**: 320.1388; found 320.1386.

Preparation of 1-(4-chlorophenyl)-2-(3-(trifluoromethyl)phenyl)ethan-1-one (3c)



According to **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 3-(trifluoromethyl)-benzylzinc(II) chloride solution (**1b**, 1.74 mL, 1.25 mmol, 0.72 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 0.5 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.22) furnished the product **3c** (212 mg, 0.71 mmol, 71%) as a white solid.

M.p.: 54.5°C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.95 (d, *J* = 8.7 Hz, 2H), 7.57-7.39 (m, 6H), 4.32 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 195.8, 140.5, 135.5, 135.1, 133.5 (q, ^4J(C,F) = 2.0 Hz), 131.4 (q, ^2J(C,F) = 32 Hz), 130.3, 129.6, 129.5, 126.8 (q, ^3J(C,F) = 3.8 Hz), 124.5 (q, ^1J(C,F) = 270 Hz), 124.4 (q, ^3J(C,F) = 3.8 Hz), 45.3.

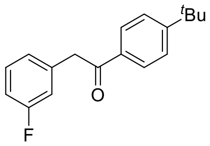
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 62.6.

IR (ATR, cm^{-1}) $\tilde{\nu}$ = 2916, 1726, 1694, 1681, 1587, 1570, 1488, 1454, 1400, 1330, 1209, 1185, 1156, 1120, 1092, 1074, 1013, 1003, 990, 902, 878, 848, 812, 784, 700, 676, 657.

MS (EI, 70 eV, %) m/z = 298 (1), 141 (31), 140 (10), 139 (100), 111 (22), 75 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{15}H_{10}ClF_3O$**: 298.0372; found 298.0359.

Preparation of 1-(4-(*tert*-butyl)phenyl)-2-(3-fluorophenyl)ethan-1-one (3d)



Based on **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 3-fluorobenzylzinc(II) chloride (**1c**, 1.92 mL, 1.25 mmol, 0.65 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 0.5 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.50) leading to the desired product **3d** (237 mg, 0.88 mmol, 88%) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.91 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.27-7.18 (m, 1H), 7.02-6.85 (m, 3H), 4.21 (s, 2H), 1.29 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 196.3, 162.7 (d, ^1J(C,F) = 245 Hz), 157.0, 137.0 (d, ^3J(C,F) = 7.7 Hz), 133.7, 129.8 (d, ^3J(C,F) = 8.4 Hz), 128.4, 125.5, 125.0 (d, ^4J(C,F) = 2.9 Hz), 116.3 (d, ^2J(C,F) = 22 Hz), 113.6 (d, ^2J(C,F) = 21 Hz), 44.8, 35.0, 30.9.

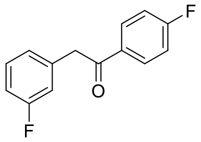
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 113.1.

IR (ATR, cm^{-1}) ṽ = 3062, 2964, 2906, 2870, 1679, 1604, 1590, 1488, 1449, 1406, 1364, 1329, 1299, 1268, 1254, 1218, 1192, 1141, 1108, 994, 948, 850, 828, 774, 754, 711, 681.

MS (EI, 70 eV, %) m/z = 272 (1), 272 (3), 162 (10), 161 (55), 70 (11), 61 (16), 45 (15), 43 (100).

HRMS (EI, 70 eV) m/z: calc. for **$C_{18}H_{19}FO$**: 270.1420; found 270.1413.

Preparation of 2-(3-fluorophenyl)-1-(4-fluorophenyl)ethan-1-one (3e)



According to **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-fluorobenzoyl chloride (**2c**, 159 mg, 0.12 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 3-fluorobenzylzinc(II) chloride (**1c**, 1.92 mL, 1.25 mmol, 0.65 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 0.5 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.38) afforded the product **3e** (172 mg, 0.74 mmol, 74%) as a colourless oil.

M.p.: 48.6 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.96 (dd, J = 9.0, 5.4 Hz, 2H), 7.26-7.18 (m, 1H), 7.10-7.03 (m, 2H), 6.99-6.85 (m, 3H), 4.18 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 195.4, 166.0 (d, ^1J(C,F) = 254 Hz), 163.0 (d, ^1J(C,F) = 245 Hz), 136.8 (d, ^3J(C,F) = 7.7 Hz), 132.9 (d, ^4J(C,F) = 3.0 Hz), 131.3 (d, ^3J(C,F) = 9.4 Hz), 130.3 (d, ^3J(C,F) = 8.4 Hz), 125.3 (d, ^4J(C,F) = 2.9 Hz), 116.6 (d, ^2J(C,F) = 22 Hz), 116.0 (d, ^2J(C,F) = 22 Hz), 114.1 (d, ^2J(C,F) = 21 Hz), 45.1.

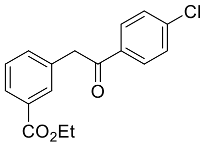
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 104.6, – 112.9.

IR (ATR, cm^{-1}) $\tilde{v}$ = 3061, 2927, 2854, 1680, 1591, 1507, 1488, 1448, 1412, 1327, 1298, 1250, 1236, 1207, 1156, 1144, 1100, 1008, 994, 954, 941, 886, 831, 815, 769, 738, 684.

MS (EI, 70 eV, %) m/z = 233 (8), 232 (1), 124 (10), 123 (100), 95 (28), 70 (10), 61 (13), 45 (11), 42 (79).

HRMS (EI, 70 eV) m/z: calc. for **$C_{14}H_{10}F_2O$**: 232.0700; found 232.0694.

Preparation of ethyl 3-(2-(4-chlorophenyl)-2-oxoethyl)benzoate (3f)



Based on **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 3-(ethoxycarbonyl)-benzylzinc(II) chloride (**1d**, 3.30 mL, 1.25 mmol, 0.38 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 9 : 1, R_f = 0.21) leading to the product **3f** (151 mg, 0.50 mmol, 50%) as pale yellow solid.

M.p.: 77.1 °C.

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ = 7.94-7.92 (m, 4H), 7.44-7.38 (m, 4H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.30 (s, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).

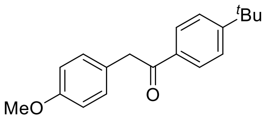
^{13}C-NMR (150 MHz, $CDCl_3$, ppm) δ = 195.8, 166.3, 139.8, 134.7, 134.4, 133.9, 130.9, 129.9, 129.0, 128.7, 128.3, 61.0, 45.1, 14.3.

IR (ATR, cm^{-1}) ṽ = 2982, 2915, 2853, 1703, 1693, 1606, 1587, 1570, 1483, 1444, 1396, 1365, 1332, 1280, 1170, 1106, 1087, 1029, 1000, 990, 831, 815, 796, 755, 721, 672.

MS (EI, 70 eV, %) m/z = 302 (5), 141 (30), 139 (100), 111 (15).

HRMS (EI, 70 eV) m/z: calc. for **$C_{17}H_{15}ClO_3$**: 302.0710; found 302.0698.

Preparation of 1-(4-(*tert*-butyl)phenyl)-2-(4-methoxyphenyl)ethan-1-one (3g)



According to **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 4-methoxybenzylzinc(II) chloride (**1e**, 2.10 mL, 1.25 mmol, 0.60 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 0.5 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.28) gave the product **3g** (164 mg, 0.58 mmol, 58%) as a pale yellow solid.

M.p.: 109.7 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.89 (d, *J* = 6.7 Hz, 2H), 7.40 (d, *J* = 6.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.13 (s, 2H), 3.71 (s, 3H), 1.27 (s, 9H).

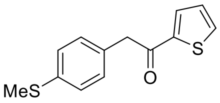
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 197.5, 158.5, 156.8, 134.0, 130.4, 128.6, 126.8, 125.6, 114.1, 55.3, 44.6, 35.1, 31.1.

IR (ATR, cm^{-1}) ṽ = 2952, 2901, 2869, 2829, 1721, 1683, 1601, 1511, 1462, 1404, 1360, 1332 (w), 1300, 1268, 1241, 1174, 1104, 1040, 1022, 994, 860, 824, 794, 692.

MS (EI, 70 eV, %) m/z = 283 (1), 282 (5), 163 (12), 161 (100), 120 (17).

HRMS (EI, 70 eV) m/z: calc. for **$C_{19}H_{22}O_2$**: 282.1620; found 282.1615.

Preparation of 2-(4-(methylthio)phenyl)-1-(thiophen-2-yl)ethan-1-one (3h)



Based on **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 2-thiophenecarbonyl chloride (**2d**, 147 mg, 0.11 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The 4-(methylthio)-benzylzinc(II) chloride (**1f**, 3.60 mL, 1.25 mmol, 0.35 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.35) leading to the product **3h** (149 mg, 0.60 mmol, 60%) as pale yellow solid.

M.p.: 106.2 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.69 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 4.8 Hz, 1H), 7.16 (s, 4H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.08 (s, 2H), 2.39 (s, 3H).

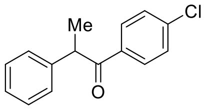
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 190.3, 143.8, 137.2, 134.1, 132.6, 131.1, 130.0, 128.2, 127.0, 45.8, 16.0.

IR (ATR, cm^{-1}) ṽ = 3070, 2920, 1660, 1602, 1516, 1494, 1412, 1402, 1354, 1326, 1224, 1198, 1116, 1084, 1060, 956, 940, 916, 854, 796, 760, 744, 658.

MS (EI, 70 eV, %) m/z = 248 (14), 138 (12), 137 (100), 122 (12), 111 (48).

HRMS (EI, 70 eV) m/z: calc. for **$C_{13}H_{12}OS_2$**: 248.0330; found 248.0330.

Preparation of 1-(4-chlorophenyl)-2-phenylpropan-1-one (3i)



According to **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (1-phenylethyl)-zinc(II) chloride (**1g**, 2.25 mL, 1.25 mmol, 0.56 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, R_f = 0.34) afforded the product **3i** (192 mg, 0.78 mmol, 78%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.81 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.25-7.10 (m, 5H), 4.55 (q, *J* = 6.8 Hz, 1H), 1.47 (d, *J* = 6.8 Hz, 3H).

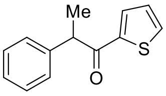
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 199.0, 141.2, 139.2, 134.8, 130.2, 129.1, 128.8, 127.7, 127.1, 48.1, 19.4.

IR (ATR, cm^{-1}) ṽ = 3062, 3028, 2975, 2931, 2871, 1681, 1587, 1569, 1490, 1451, 1400, 1373, 1332, 1248, 1217, 1174, 1091, 1063, 1013, 1000, 950, 847, 786, 754, 731, 698.

MS (EI, 70 eV, %) m/z = 244 (2), 139 (100), 138 (48), 105 (24).

HRMS (EI, 70 eV) m/z: calc. for **$C_{15}H_{13}ClO$**: 244.0655; found 244.0652.

Preparation of 2-phenyl-1-(thiophen-2-yl)propan-1-one (3j)



According to **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 2-thiophenecarbonyl chloride (**2d**, 147 mg, 0.11 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (1-phenylethyl)-zinc(II) chloride (**1g**, 2.25 mL, 1.25 mmol, 0.56 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.45) leading to the product **3j** (141 mg, 0.65 mmol, 65%) as pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.61 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.48 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.30-7.21 (m, 4H), 7.20-7.13 (m, 1H), 6.97 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.45 (q, *J* = 6.9 Hz, 1H), 1.49 (d, *J* = 6.9 Hz, 3H).

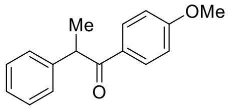
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 193.3, 143.8, 141.3, 133.6, 132.4, 128.9, 128.0, 127.8, 127.1, 49.4, 19.2.

IR (ATR, cm^{-1}) ṽ = 3087, 3027, 2975, 2930, 2870, 1657, 1600, 1517, 1491, 1451, 1412, 1372, 1354, 1253, 1234, 1216, 1182, 1053, 1031, 942, 906, 854, 798, 719, 697.

MS (EI, 70 eV, %) m/z = 217 (3), 216 (5), 111 (100), 105 (28), 69 (12), 57 (12).

HRMS (EI, 70 eV) m/z: calc. for **$C_{13}H_{12}OS$**: 216.0609; found 216.0598.

Preparation of 1-(4-methoxyphenyl)-2-phenylpropan-1-one (3k)



Based on **TP3**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-methoxybenzoyl chloride (**2e**, 171 mg, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (1-phenylethyl)-zinc(II) chloride (**1g**, 2.25 mL, 1.25 mmol, 0.56 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.28) furnished the product **3k** (190 mg, 0.79 mmol, 79%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.89 (d, *J* = 9.0 Hz, 2H), 7.28-7.19 (m, 4H), 6.79 (d, *J* = 9.0 Hz, 2H), 4.58 (q, *J* = 6.9 Hz, 1H), 3.73 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 198.8, 163.2, 142.0, 131.1, 129.5, 128.9, 127.7, 126.8, 113.7, 55.4, 47.5, 19.6.

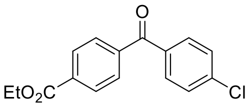
IR (ATR, cm^{-1}) ṽ = 2972, 2931, 2840, 1710, 1671, 1598, 1573, 1510, 1493, 1452, 1418, 1372, 1333, 1314, 1248, 1224, 1166, 1115, 1062, 1028, 951, 845, 795, 772, 751, 699.

MS (EI, 70 eV, %) m/z = 241 (1), 136 (10), 135 (100), 77 (13).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{16}O_2$**: 240.1150; found 241.1148.

Iron-Catalyzed Acylation of Arylzinc Chlorides (4a-f) with Acid Chlorides

Preparation of ethyl 4-(4-chlorobenzoyl)benzoate (5a)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4a**, 3.90 mL, 1.25 mmol, 0.32 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, R_f = 0.35) afforded the product **5a** (179 mg, 0.62 mmol, 62%) (34% isolated yield without catalyst after prolonged reaction time of 12 h at 50 °C) as a white solid.

M.p.: 108.4 °C

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ = 8.14 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

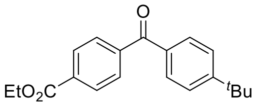
^{13}C-NMR (150 MHz, $CDCl_3$, ppm) δ = 194.8, 165.7, 140.8, 139.5, 135.2, 133.8, 131.4, 129.5 (2C), 128.8, 61.5, 14.3.

IR (ATR, cm^{-1}) ṽ = 1714, 1648, 1586, 1568, 1401, 1368, 1301, 1268, 1144, 1105, 1091, 1010, 978, 931, 875, 853, 841, 783, 737, 708, 668.

MS (EI, 70 eV, %) m/z = 290 (19), 289 (11), 288 (56), 260 (14), 245 (18), 243 (51), 180 (11), 177 (59), 152 (11), 149 (17), 14 (34), 139 (100), 111 (25), 76 (11), 75 (10), 71 (34), 70 (14), 57 (46), 56 (28), 43 (82), 42 (47), 41 (40).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{13}ClO_3$**: 288.0553; found 282.0549.

Preparation of ethyl 4-(4-(*tert*-butyl)benzoyl)benzoate (5b)



Based on **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4a**, 3.90 mL, 1.25 mmol, 0.32 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.29) leading to the desired product **5b** (203 mg, 0.65 mmol, 65%) as a pale yellow solid.

M.p.: 87.8 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 9H).

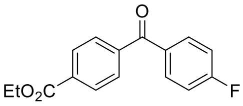
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 195.7, 165.9, 156.8, 141.6, 134.2, 133.4, 130.2, 129.6, 129.4, 125.4, 61.4, 35.2, 31.1, 14.3.

IR (ATR, cm^{-1}) ṽ = 2966, 2906, 2871, 1712, 1651, 1605, 1476, 1462, 1364, 1278, 1265, 1191, 1120, 1106, 1015, 932, 874, 843, 791, 759, 745, 715, 702, 673.

MS (EI, 70 eV, %) m/z = 311 (21), 310 (100), 297 (14), 296 (68), 266 (16), 265 (39), 178 (10), 177 (42), 145 (11), 125 (12), 121 (13), 118 (12), 115 (10), 111 (35), 104 (14), 76 (12), 65 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{20}H_{22}O_3$**: 310.1569; found 310.1558.

Preparation of ethyl 4-(4-fluorobenzoyl)benzoate (5c)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-fluorobenzoyl chloride (**2c**, 159 mg, 0.12 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4a**, 3.90 mL, 1.25 mmol, 0.32 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.33) gave the product **5c** (227 mg, 0.83 mmol, 83%) (21% isolated yield without catalyst after prolonged reaction time of 12 h at 50 °C) as a white solid.

M.p.: 75.7 °C

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ = 8.14 (d, *J* = 8.6 Hz, 2H), 7.83 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$, ppm) δ = 194.5, 165.6 (d, ^1J(C,F) = 254 Hz), 165.7, 141.1, 133.6, 133.2, 132.7 (d, ^3J(C,F) = 9.1 Hz), 130.1, 129.5, 127.2, 115.7 (d, ^2J(C,F) = 22 Hz), 61.4, 14.3.

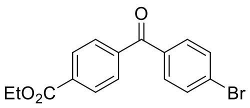
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 105.0.

IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3069, 2989, 1712, 1647, 1596, 1500, 1407, 1370, 1308, 1269, 1232, 1180, 1148, 1100, 1020, 1008, 978, 960, 934, 872, 856, 817, 787, 742, 718, 702, 672.

MS (EI, 70 eV, %) m/z = 273 (2), 272 (11), 253 (11), 226 (12), 123 (25), 70 (13), 61 (17), 45 (15), 42 (100).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{13}FO_3$**: 272.0849; found 272.0837.

Preparation of ethyl 4-(4-bromobenzoyl)benzoate (5d)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-bromobenzoyl chloride (**2f**, 220 mg, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4a**, 3.90 mL, 1.25 mmol, 0.32 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.22) affording the product **5d** (227 mg, 0.68 mmol, 68%) as a white solid.

M.p.: 108.2 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 8.15 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.73-7.58 (m, 4H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

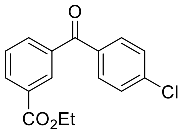
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 194.9, 165.7, 140.7, 135.7, 133.8, 131.8, 131.5, 129.6, 129.5, 128.1, 61.4, 14.3.

IR (ATR, cm^{-1}) ṽ = 2984, 2958, 2932, 1712, 1648, 1582, 1478, 1460, 1396, 1368, 1266, 1182, 1142, 1102, 1068, 1022, 978, 928, 838, 782, 732, 704, 664.

MS (EI, 70 eV, %) m/z = 335 (12), 334 (54), 333 (12), 332 (57), 289 (10), 287 (44), 185 (99), 183 (100), 178 (12), 177 (98), 157 (20), 149 (26), 76 (50), 75 (24).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{13}BrO_3$**: 332.0048; found 332.0043.

Preparation of ethyl 3-(4-chlorobenzoyl)benzoate (5e)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (3-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4b**, 4.00 mL, 1.25 mmol, 0.31 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 9 : 1, R_f = 0.36) furnished product **5e** (217 mg, 0.75 mmol, 75%) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 8.33 (t, *J* = 1.7 Hz, 1H), 8.19 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.88 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

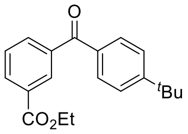
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 194.5, 165.7, 139.3, 137.6, 135.6, 133.8, 133.6, 131.4, 130.9, 130.8, 128.8, 128.7, 61.4, 14.3.

IR (ATR, cm^{-1}) ṽ = 2982, 1716, 1660, 1601, 1584, 1486, 1399, 1367, 1302, 1287, 1239, 1170, 1150, 1088, 1014, 974, 960, 874, 844, 775, 734, 700.

MS (EI, 70 eV, %) m/z = 290 (16), 289 (10), 288 (40), 245 (13), 243 (36), 177 (40), 148 (12), 141 (33), 139 (100), 111 (259, 76 (12), 75 (10), 44 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{13}ClO_3$**: 288.0553; found 288.0547.

Preparation of ethyl 3-(4-(*tert*-butyl)benzoyl)benzoate (5f)



Based on **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (3-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4b**, 4.00 mL, 1.25 mmol, 0.31 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.16) gave the product **5f** (224 mg, 0.72 mmol, 72%) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 8.38 (t, *J* = 1.5 Hz, 1H), 8.17 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.90 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 9H).

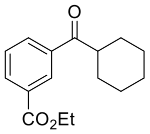
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 195.5, 165.9, 156.6, 138.3, 134.3, 133.9, 132.9, 130.8, 130.7, 130.1, 128.4, 125.4, 61.3, 35.1, 31.1, 14.3.

IR (ATR, cm^{-1}) ṽ = 2965, 2255, 1719, 1659, 1605, 1464, 1407, 1367, 1317, 1304, 1286, 1246, 1193, 1154, 1102, 1081, 1022, 975, 909, 876, 850, 781, 746, 730, 707, 675.

MS (EI, 70 eV, %) m/z = 312 (14), 311 (69), 310 (30), 298 (13), 296 (19), 295 (100), 267 (35), 265 (14), 253 (19), 176 (14), 161 (70), 148 (30), 146 (10), 145 (11), 118 (12), 111 (13).

HRMS (EI, 70 eV) m/z: calc. for **$C_{20}H_{22}O_3$**: 310.1569; found 310.1563.

Preparation of ethyl 4-(cyclohexanecarbonyl)benzoate (5g)



Based on **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), cyclohexanecarbonyl chloride (**2h**, 145 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (3-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4b**, 4.00 mL, 1.25 mmol, 0.31 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 9 : 1, $R_f = 0.50$) leading to the product **5g** (155 mg, 0.60 mmol, 60%) as a colourless oil.

^{1}H-NMR (800 MHz, $CDCl_3$, ppm) δ = 8.59 (t, *J* = 1.6 Hz, 1H), 8.24 (dt, *J* = 7.7, 1.4 Hz, 1H), 8.14 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.32 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.93-1.89 (m, 2H), 1.87 (dt, *J* = 13.4, 3.5 Hz, 2H), 1.79-1.73 (m, 1H), 1.52 (qd, *J* = 13.0, 3.2 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.30 (dtd, *J* = 12.9, 9.1, 4.6 Hz, 2H).

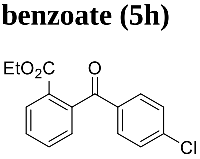
^{13}C-NMR (200 MHz, $CDCl_3$, ppm) δ = 203.3, 166.1, 136.8, 133.6, 132.5, 131.2, 129.4, 128.9, 61.5, 45.8, 29.5, 26.1, 25.9, 14.5.

IR (ATR, cm^{-1}) ṽ = 2929, 2853, 1719, 1681, 1601, 1447, 1367, 1295, 1276, 1238, 1198, 1172, 1135, 1100, 1077, 1022, 990, 981, 892, 864, 821, 760, 714, 693.

MS (EI, 70 eV, %) m/z = 260 (1), 215 (11), 187 (24), 178 (12), 177 (100), 149 (14), 83 (11), 55 (13).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{20}O_3$**: 260.1412; found 260.1407.

Preparation of ethyl 2-(4-chlorobenzoyl)benzoate (5h)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (2-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4c**, 3.70 mL, 1.25 mmol, 0.34 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.18) afforded product **5h** (213 mg, 0.74 mmol, 74%) as a white solid.

M.p.: 78.2 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.67-7.52 (m, 2H), 7.42-7.34 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H).

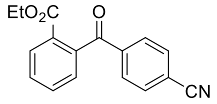
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 195.9, 165.8, 141.3, 139.6, 135.8, 132.6, 130.8, 130.4, 129.8, 129.4, 128.9, 127.6, 61.7, 13.9.

IR (ATR, cm^{-1}) ṽ = 3070, 2988, 2938, 1710, 1676, 1584, 1576, 1486, 1474, 1446, 1398, 1364, 1282, 1260, 1166, 1140, 1086, 1016, 962, 928, 876, 848, 828, 768, 750, 708, 686.

MS (EI, 70 eV, %) m/z = 290 (11), 288 (37), 245 (17), 244 (15), 177 (44), 154 (33), 149 (100), 139 (76), 111 (27).

HRMS (EI, 70 eV) m/z: calc. for **$C_{16}H_{13}ClO_3$**: 288.0553; found 288.0551.

Preparation of ethyl 2-(4-cyanobenzoyl)benzoate (5i)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-cyanobenzoyl chloride (**2g**, 166 mg, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (2-(ethoxycarbonyl)phenyl)zinc(II) chloride (**4c**, 3.70 mL, 1.25 mmol, 0.34 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 4 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 9 : 1, R_f = 0.13) yielding the product **5i** (173 mg, 0.62 mmol, 62%) as a pale yellow solid.

M.p.: 148.6 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 8.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.67 (td, *J* = 7.5, 1.4 Hz, 1H), 7.61 (td, *J* = 7.6, 1.4 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H).

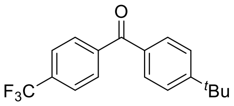
^{13}C-NMR (100 MHz, CDCl$_3$, ppm) δ = 195.6, 165.6, 140.8, 140.5, 132.9, 132.5, 130.4, 130.2, 129.6, 129.4, 127.6, 118.1, 116.3, 61.8, 13.9.

IR (ATR, cm^{-1}) ṽ = 3096, 2992, 2230, 1956, 1708, 1680, 1602, 1574, 1476, 1408, 1368, 1276, 1262, 1144, 1114, 1084, 1018, 932, 854, 760, 710, 690.

MS (EI, 70 eV, %) m/z = 279 (13), 235 (17), 234 (59), 177 (62), 149 (100), 130 (23), 102 (22).

HRMS (EI, 70 eV) m/z: calc. for **$C_{17}H_{13}NO_3$**: 279.0895; found 279.0890.

Preparation of (4-(*tert*-butyl)phenyl)(4-(trifluoromethyl)phenyl)methanone (5j)



Based on **TP4**, FeCl$_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-(trifluoromethyl)phenyl)zinc(II) chloride (**4d**, 3.00 mL, 1.25 mmol, 0.42 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 3 h at 50 °C. The reaction was quenched with a saturated aqueous NH$_4$Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over MgSO$_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO$_2$, *i*-hexane : EtOAc = 99 : 1, R$_f$ = 0.50) gave the product **5j** (255 mg, 0.83 mmol, 83%) as a white solid.

M.p.: 76.0 °C

^{1}H-NMR (400 MHz, CDCl$_3$, ppm) δ = 7.82 (d, *J* = 8.0 Hz, 2H), 7.74-7.64 (m, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 1.31 (s, 9H).

^{13}C-NMR (100 MHz, CDCl$_3$, ppm) δ = 195.2, 157.0, 141.0 (q, ^4J(C,F) = 2.0 Hz), 134.0, 133.5 (q, ^2J(C,F) = 32 Hz), 130.2, 130.0, 125.5, 125.3 (q, ^3J(C,F) = 3.8 Hz), 123.7 (q, ^1J(C,F) = 271 Hz), 35.2, 31.1.

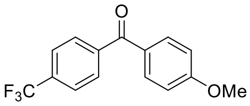
^{19}F-NMR (376 MHz, CDCl$_3$, ppm) δ = – 63.0.

IR (ATR, cm^{-1}) ṽ = 2969, 1651, 1604, 1408, 1324, 1310, 1280, 1163, 1122, 1105, 1064, 1016, 972, 932, 860, 838, 774, 734, 698, 677.

MS (EI, 70 eV, %) m/z = 306 (2), 291 (15), 162 (13), 161 (100).

HRMS (EI, 70 eV) m/z: calc. for $\mathbf{C_{18}H_{17}F_3O}$: 306.1231; found 306.1233.

Preparation of (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (5k)



Based on **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-methoxybenzoyl chloride (**2e**, 171 mg, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-(trifluoromethyl)phenyl)zinc(II) chloride (**4d**, 3.00 mL, 1.25 mmol, 0.42 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 3 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.25) leading to the product **5k** (173 mg, 0.62 mmol, 62%) as a white solid.

M.p.: 124.1 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.78-7.74 (m, 4H), 7.67 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 194.3, 163.7, 141.5 (q, ^4J(C,F) = 2.0 Hz), 133.3 (q, ^2J(C,F) = 33 Hz), 132.6, 129.8, 129.4, 125.3 (q, ^3J(C,F) = 4.0 Hz), 123.7 (q, ^1J(C,F) = 271Hz), 113.8, 55.6.

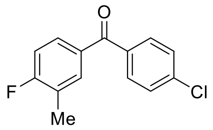
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 63.0.

IR (ATR, cm^{-1}) ṽ = 1643, 1600, 1573, 1504, 1407, 1328, 1306, 1286, 1262, 1165, 1127, 1108, 1067, 1029, 1016, 972, 930, 861, 843, 770, 736, 700, 686.

MS (EI, 70 eV, %) m/z = 280 (26), 145 (14), 135 (100), 92 (13), 77 (16)

HRMS (EI, 70 eV) m/z: calc. for $\mathbf{C_{15}H_{11}F_3O_2}$: 280.0711; found 280.0707.

Preparation of (4-chlorophenyl)(4-fluoro-3-methylphenyl)methanone (5l)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-fluoro-3-methylphenyl)zinc(II) chloride (**4e**, 3.80 mL, 1.25 mmol, 0.33 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 2 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, R_f = 0.40) afforded product **5l** (188 mg, 0.76 mmol, 76%) as a white solid.

M.p.: 124.8 °C

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ = 7.70 (d, *J* = 8.6 Hz, 2H), 7.66 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.58 (ddd, *J* =7.4, 4.8, 2.1 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.08 (t, *J* = 8.8 Hz, 1H), 2.32 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$, ppm) δ = 194.3, 164.1 (d, ^1J(C,F) = 253 Hz), 138.8, 135.9, 133.6 (d, ^3J(C,F) = 6.0 Hz), 133.2, 131.2, 129.9 (d, ^3J(C,F) = 9.0 Hz), 128.6, 125.4 (d, ^2J(C,F) = 18 Hz), 115.0 (d, ^2J(C,F) = 23 Hz), 14.5.

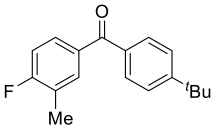
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 109.6.

IR (ATR, cm^{-1}) ṽ = 2959, 2927, 2870, 1724, 1647, 1605, 1582, 1486, 1398, 1300, 1281, 1262, 1238, 1190, 1176, 1134, 1113, 1086, 1007, 972, 915, 858, 842, 828, 759, 751, 684.

MS (EI, 70 eV, %) m/z = 250 (24), 249 (12), 248 (76), 213 (13), 141 (13), 139 (42), 137 (100), 111 (14), 109 (18).

HRMS (EI, 70 eV) m/z: calc. for **$C_{14}H_{10}ClFO$**: 248.0404; found 248.0396.

Preparation of (4-(*tert*-butyl)phenyl)(4-fluoro-3-methylphenyl)methanone (5m)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-fluoro-3-methylphenyl)zinc(II) chloride (**4e**, 3.80 mL, 1.25 mmol, 0.33 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 2 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.34) furnished product **5m** (189 mg, 0.70 mmol, 70%) as a colourless oil.

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ = 7.73-7.70 (m, 2H), 7.65-7.59 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 1H), 2.34 (s, 3H), 1.37 (s, 9H).

^{13}C-NMR (150 MHz, $CDCl_3$, ppm) δ = 195.4, 164.0 (d, ^1J(C,F) = 252 Hz), 156.3, 135.0, 134.0, 133.8 (d, ^3J(C,F) = 5.4 Hz), 130.1, 125.4, 125.1, 115.0 (d, ^2J(C,F) = 23 Hz), 35.2, 31.3, 14.7.

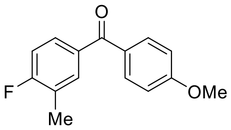
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 110.7.

IR (ATR, cm^{-1}) ṽ = 2963, 2870, 1718, 1656, 1605, 1498, 1407, 1364, 1315, 1300, 1282, 1264, 1239, 1185, 1115, 1018, 968, 905, 850, 827, 772, 757, 726, 692.

MS (EI, 70 eV, %) m/z = 271 (7), 270 (35), 256 (25), 255 (100), 137 (11).

HRMS (EI, 70 eV) m/z: calc. for **$C_{18}H_{19}FO$**: 270.1420; found 270.1419.

Preparation of (4-fluoro-3-methylphenyl)(4-methoxyphenyl)methanone (5n)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-methoxybenzoyl chloride (**2e**, 171 mg, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-fluoro-3-methylphenyl)zinc(II) chloride (**4e**, 3.80 mL, 1.25 mmol, 0.33 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 2 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, R_f = 0.26) yielding the product **5n** (194 mg, 0.79 mmol, 79%) as a white solid.

M.p.: 76.3 °C

^{1}H-NMR (600 MHz, CDCl$_3$, ppm) δ = 7.77 (d, *J* = 9.0 Hz, 2H), 7.63 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.58-7.54 (m, 1H), 7.10-7.02 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.32 (s, 3H).

^{13}C-NMR (150 MHz, CDCl$_3$, ppm) δ = 194.4, 163.6 (d, ^1J(C,F) = 251 Hz), 163.1, 134.1, 133.4 (d, ^4J(C,F) = 3.6 Hz), 132.4, 131.5, 130.2, 129.6 (d, ^3J(C,F) = 9.0 Hz), 125.1 (d, ^2J(C,F) = 18 Hz), 114.8 (d, ^2J(C,F)= 22.9 Hz), 113.6, 55.5, 14.5.

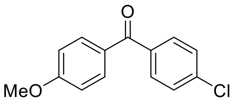
^{19}F-NMR (376 MHz, CDCl$_3$, ppm) δ = – 111.2.

IR (ATR, cm^{-1}) ṽ = 3071, 2959, 2934, 2842, 1711, 1644, 1596, 1587, 1511, 1464, 1441, 1419, 1318, 1297, 1255, 1236, 1193, 1167, 1130, 1111, 1019, 964, 902, 873, 846, 818, 795, 766, 754, 685.

MS (EI, 70 eV, %) m/z = 245 (10), 244 (42), 137 (18), 136 (10), 135 (100), 109 (11), 77 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{15}H_{13}FO_2$**: 244.0900; found 244.0893.

Preparation of (4-chlorophenyl)(4-methoxyphenyl)methanone (5o)



Based on **TP4**, FeCl$_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-methoxyphenyl)zinc(II) chloride (**4f**, 3.50 mL, 1.25 mmol, 0.36 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 3 h at 50 °C. The reaction was quenched with a saturated aqueous NH$_4$Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over MgSO$_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO$_2$, *i*-hexane : EtOAc = 19 : 1, R$_f$ = 0.30) afforded product **5o** (182 mg, 0.74 mmol, 74%) as a yellow solid.

M.p.: 118.6 °C

^{1}H-NMR (400 MHz, CDCl$_3$, ppm) δ = 7.73 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H).

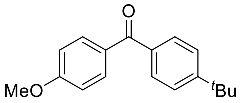
^{13}C-NMR (100 MHz, CDCl$_3$, ppm) δ = 194.2, 163.4, 138.3, 136.6, 132.4, 131.2, 129.8, 128.5, 113.7, 55.5.

IR (ATR, cm^{-1}) ṽ = 3014, 2934, 2841, 1722, 1637, 1600, 1588, 1509, 1461, 1414, 1397, 1299, 1283, 1245, 1170, 1147, 1086, 1062, 1028, 1013, 966, 950, 925, 853, 834, 759, 736, 722, 678.

MS (EI, 70 eV, %) m/z = 248 (32), 247 (14), 246 (99), 211 (16), 138 (26), 136 (22), 135 (100), 111 (22), 92 (18), 77 (22), 75 (12).

HRMS (EI, 70 eV) m/z: calc. for $\mathbf{C_{14}H_{11}ClO_2}$: 246.0448; found 246.0438.

Preparation of (4-(*tert*-butyl)phenyl)(4-methoxyphenyl)methanone (5p)



Based on **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-*tert*-butylbenzoyl chloride (**2b**, 197 mg, 0.20 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-methoxyphenyl)zinc(II) chloride (**4f**, 3.50 mL, 1.25 mmol, 0.36 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 3 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, R_f = 0.28) furnished product **5p** (219 mg, 0.82 mmol, 82%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.77 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 1.30 (s, 9H).

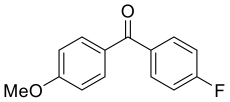
^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 195.2, 163.1, 155.6, 135.5, 132.5, 130.5, 129.8, 127.0, 113.5, 55.5, 35.1, 31.2.

IR (ATR, cm^{-1}) ṽ = 2962, 1649, 1600, 1574, 1509, 1462, 1442, 1418, 1364, 1314, 1305, 1281, 1252, 1172, 1151, 1104, 1028, 951, 929, 853, 836, 798, 772, 728, 687.

MS (EI, 70 eV, %) m/z = 269 (13), 268 (57), 254 (27), 253 (100), 161 (14), 135 (65), 77 (12), 44 (20).

HRMS (EI, 70 eV) m/z: calc. for $\mathbf{C_{18}H_{20}O_2}$: 268.1463; found 268.1447.

Preparation of (4-fluorophenyl)(4-methoxyphenyl)methanone (5q)



According to **TP4**, $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), 4-fluorobenzoyl chloride (**2c**, 159 mg, 0.12 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The (4-methoxyphenyl)zinc(II) chloride (**4f**, 3.50 mL, 1.25 mmol, 0.36 M in THF, 1.25 equiv) was added dropwise and the reaction mixture was stirred for 3 h at 50 °C. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 19 : 1, $R_f = 0.15$) leading to the product **5q** (189 mg, 0.82 mmol, 82%) as a yellow solid.

M.p.: 92.4 °C

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.73 (dt, *J* = 9.0, 2.7 Hz, 4H), 7.08 (t, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 194.1, 165.1 (d, ^1J(C,F) = 252 Hz), 163.3, 134.5 (d, ^4J(C,F) = 3.1 Hz), 132.4, 132.3 (d, ^3J(C,F) = 9.0 Hz), 127.0, 115.3 (d, ^2J(C,F) = 22 Hz), 113.6, 55.5.

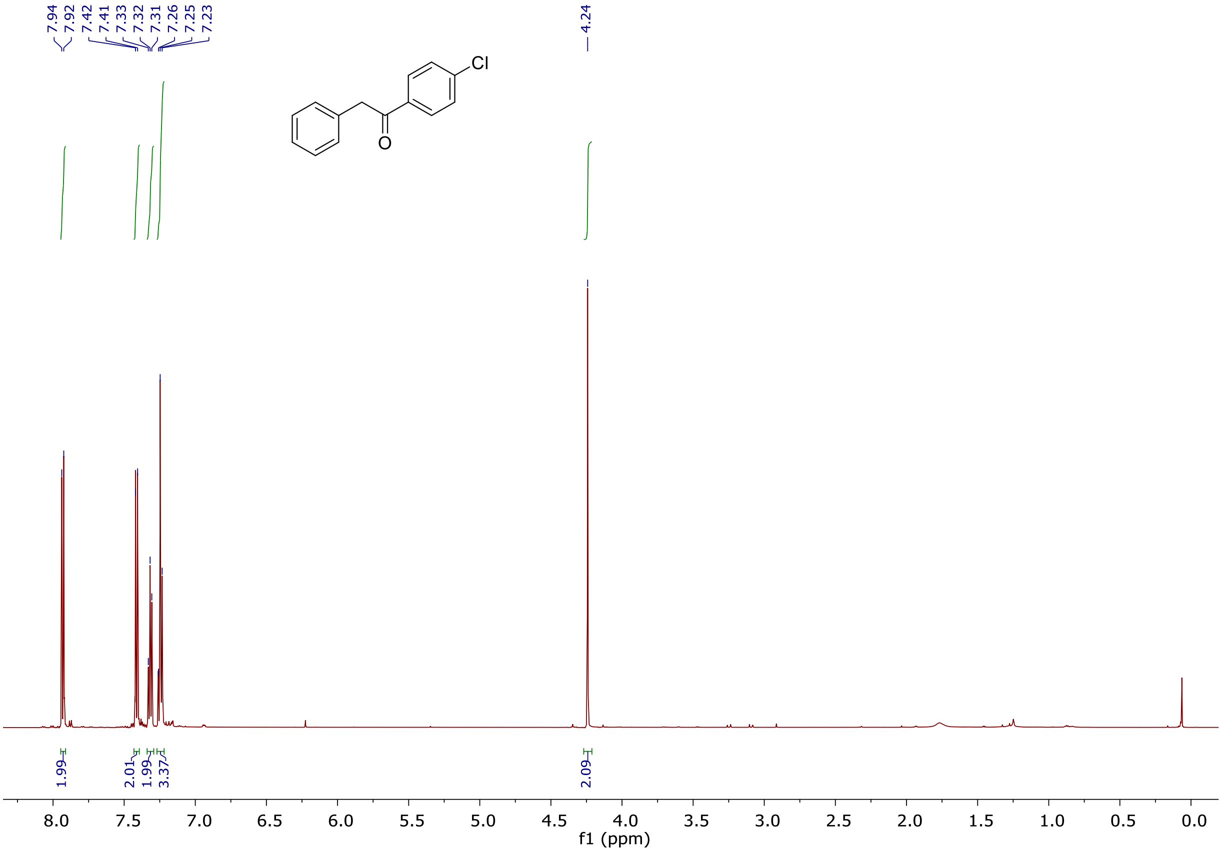
^{19}F-NMR (376 MHz, $CDCl_3$, ppm) δ = – 107.0.

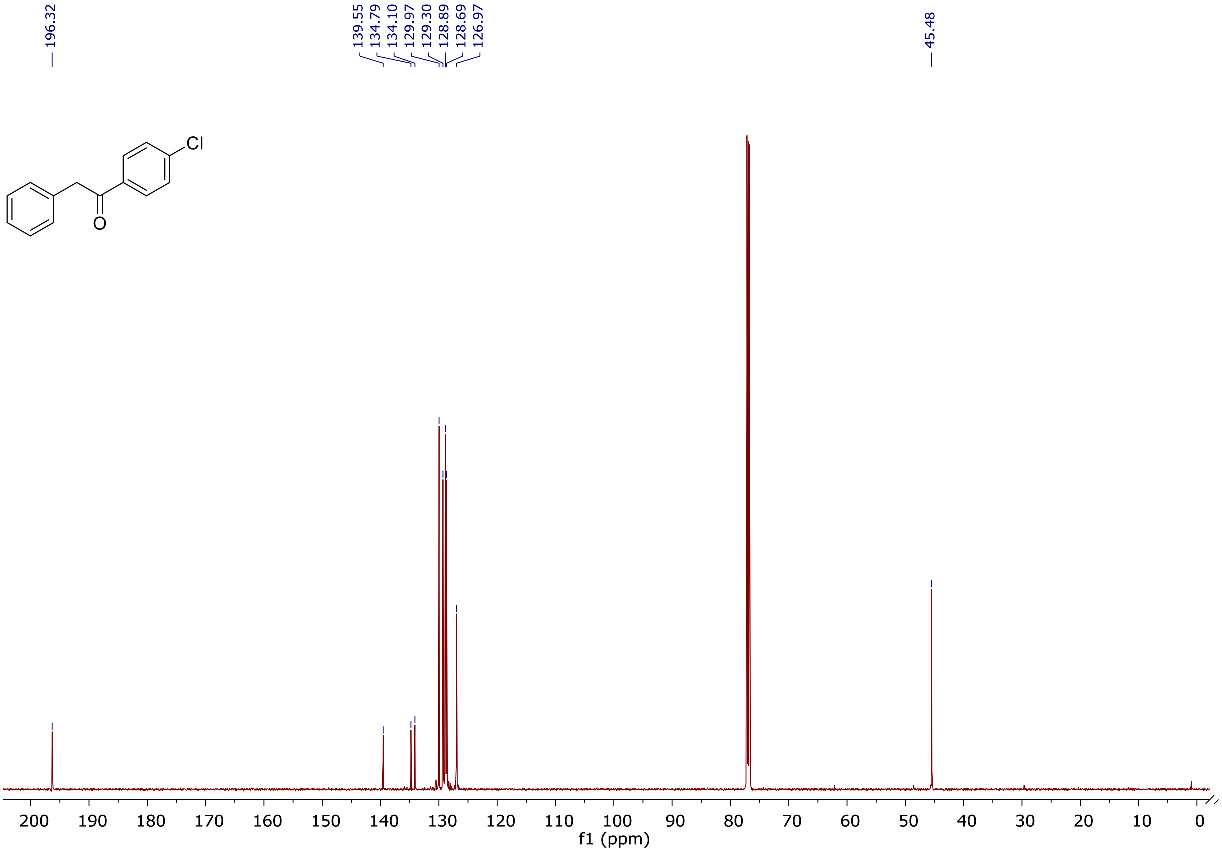
IR (ATR, cm^{-1}) ṽ = 2931, 2848, 1720, 1639, 1597, 1574, 1506, 1465, 1442, 1416, 1406, 1303, 1282, 1247, 1226, 1174, 1148, 1116, 1028, 1013, 967, 927, 856, 841, 789, 763, 681.

MS (EI, 70 eV, %) m/z = 230 (31), 135 (38), 123 (25), 95 (13), 85 (13), 83 (12), 71 (20), 57 (26), 55 (15), 44 (37), 43 (19).

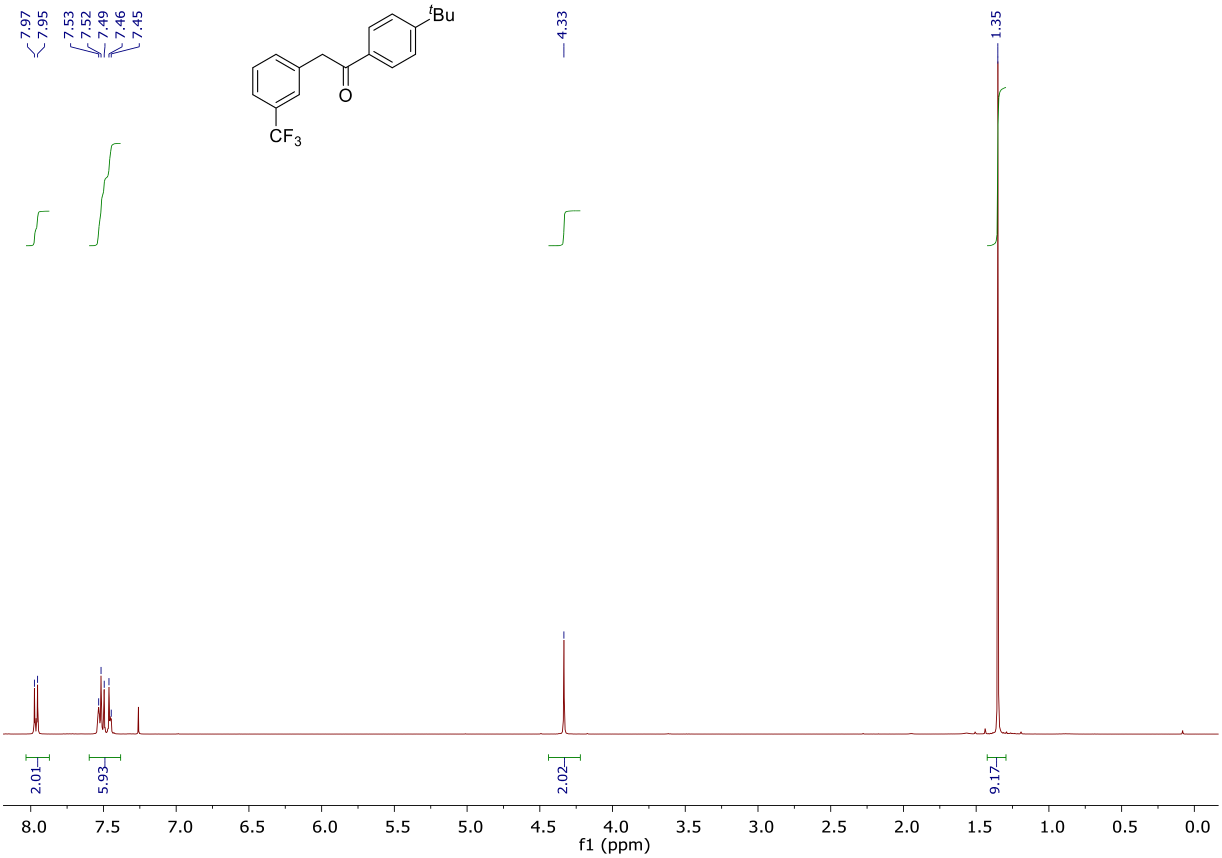
HRMS (EI, 70 eV) m/z: calc. for **$C_{14}H_{11}FO_2$**: 230.0743; found 230.0747.

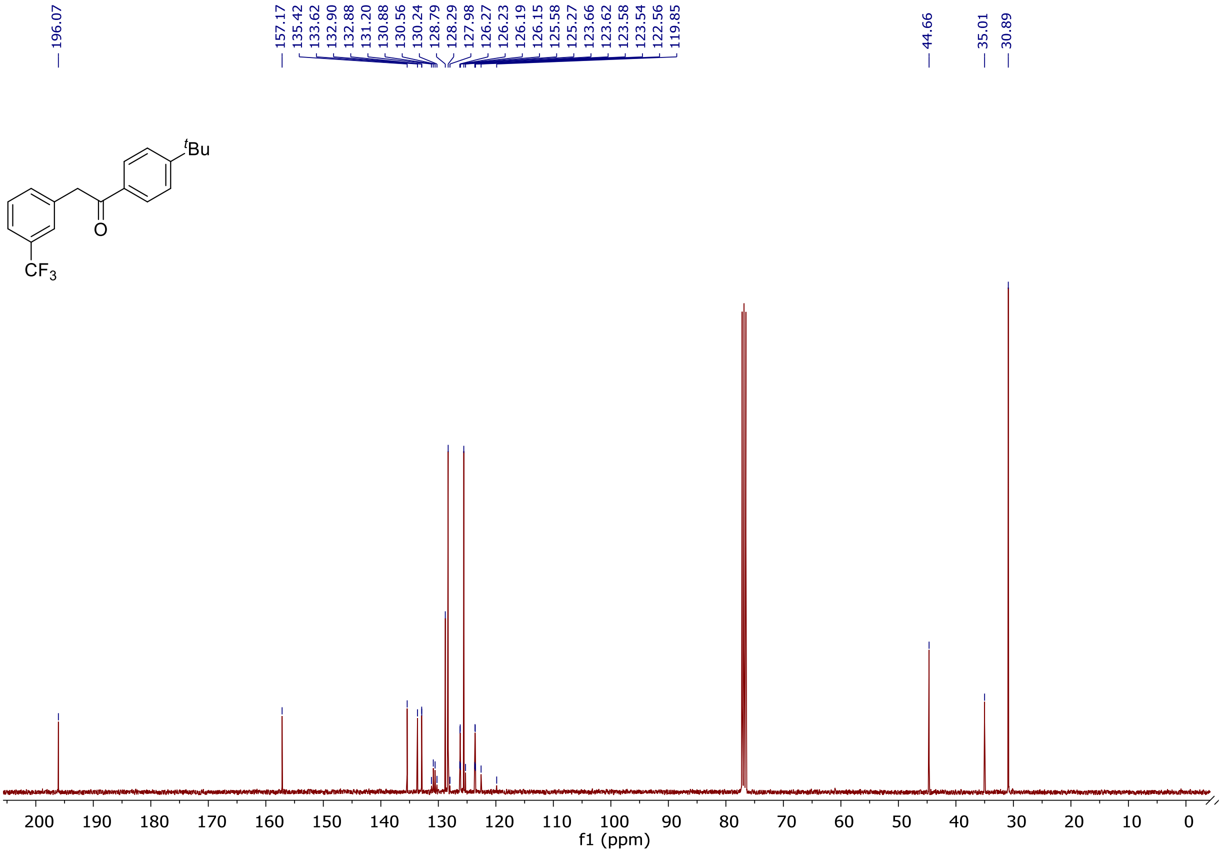
NMR-Spectra of 1-(4-chlorophenyl)-2-phenylethan-1-one (3a)

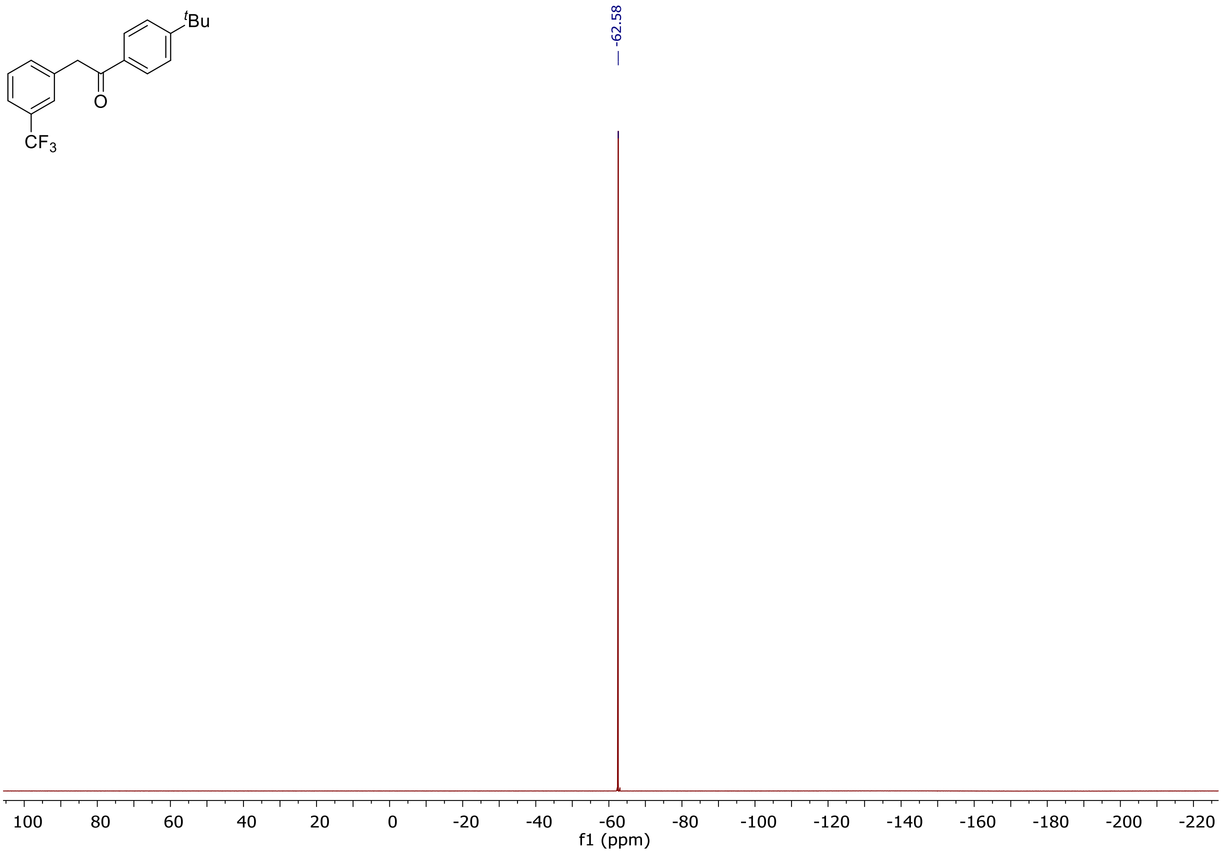




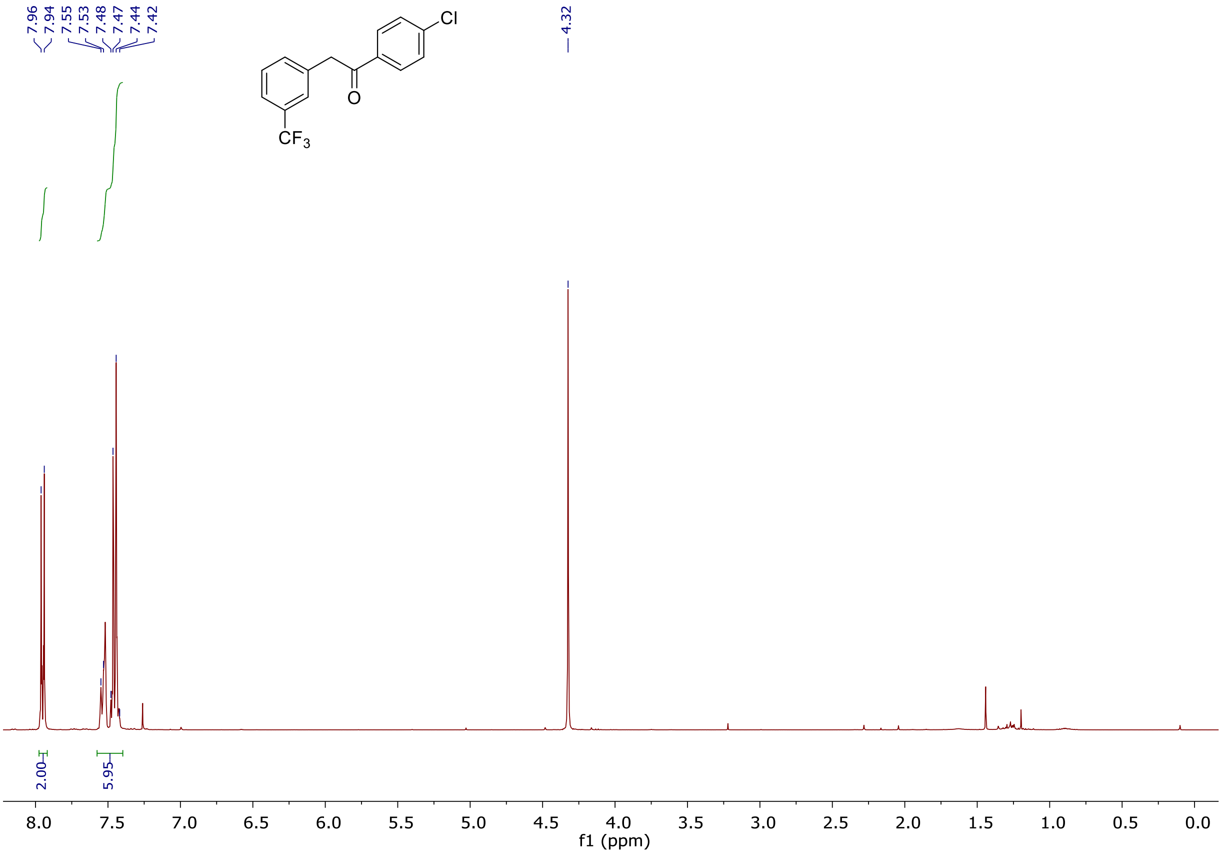
NMR-Spectra of 1-(4-(*tert*-butyl)phenyl)-2-(3-(trifluoromethyl)phenyl)ethan-1-one (3b)

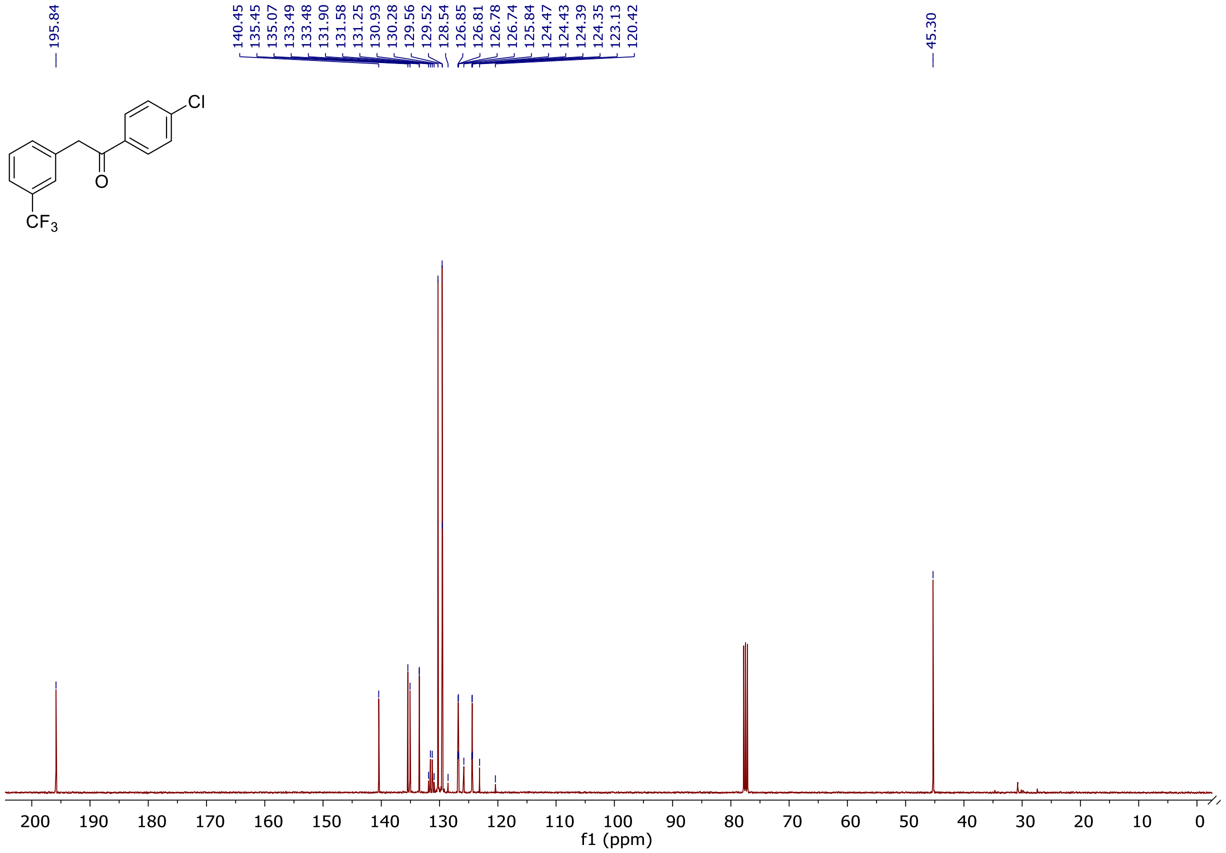


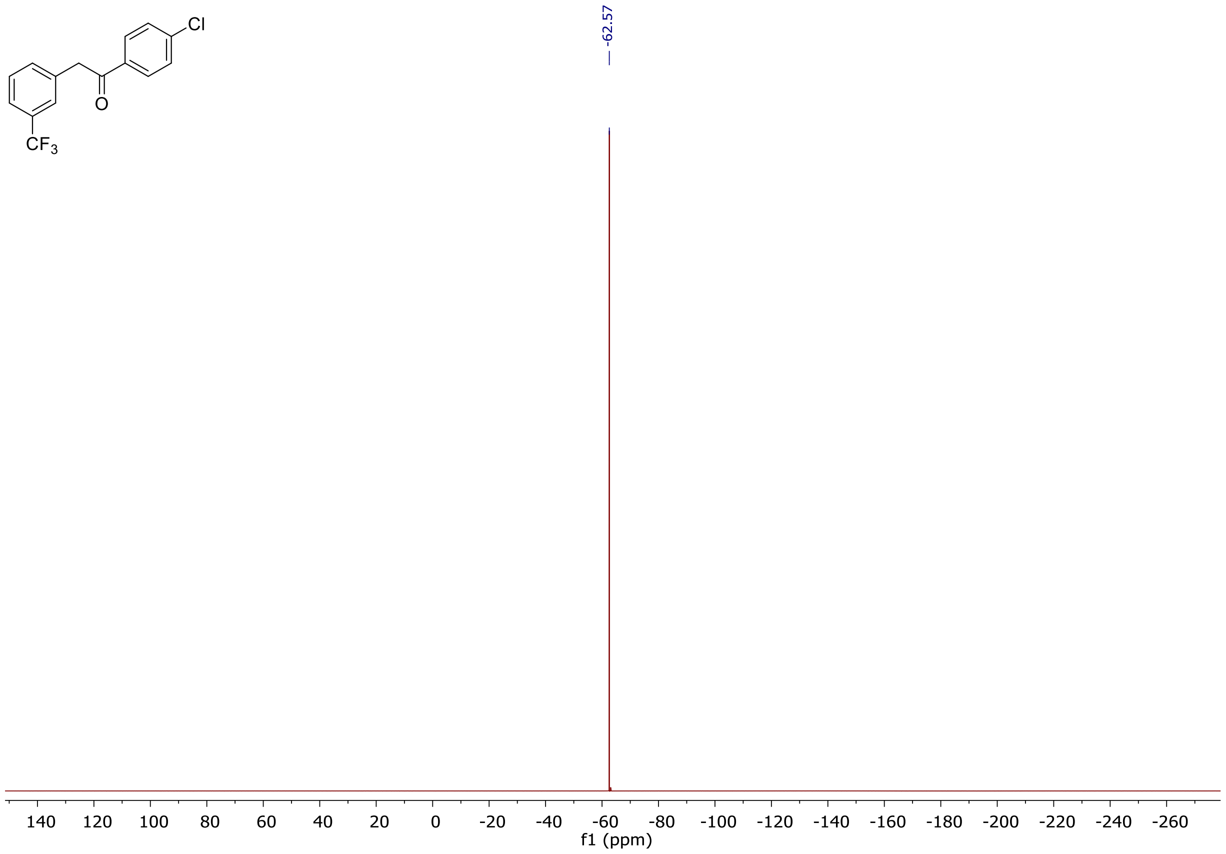




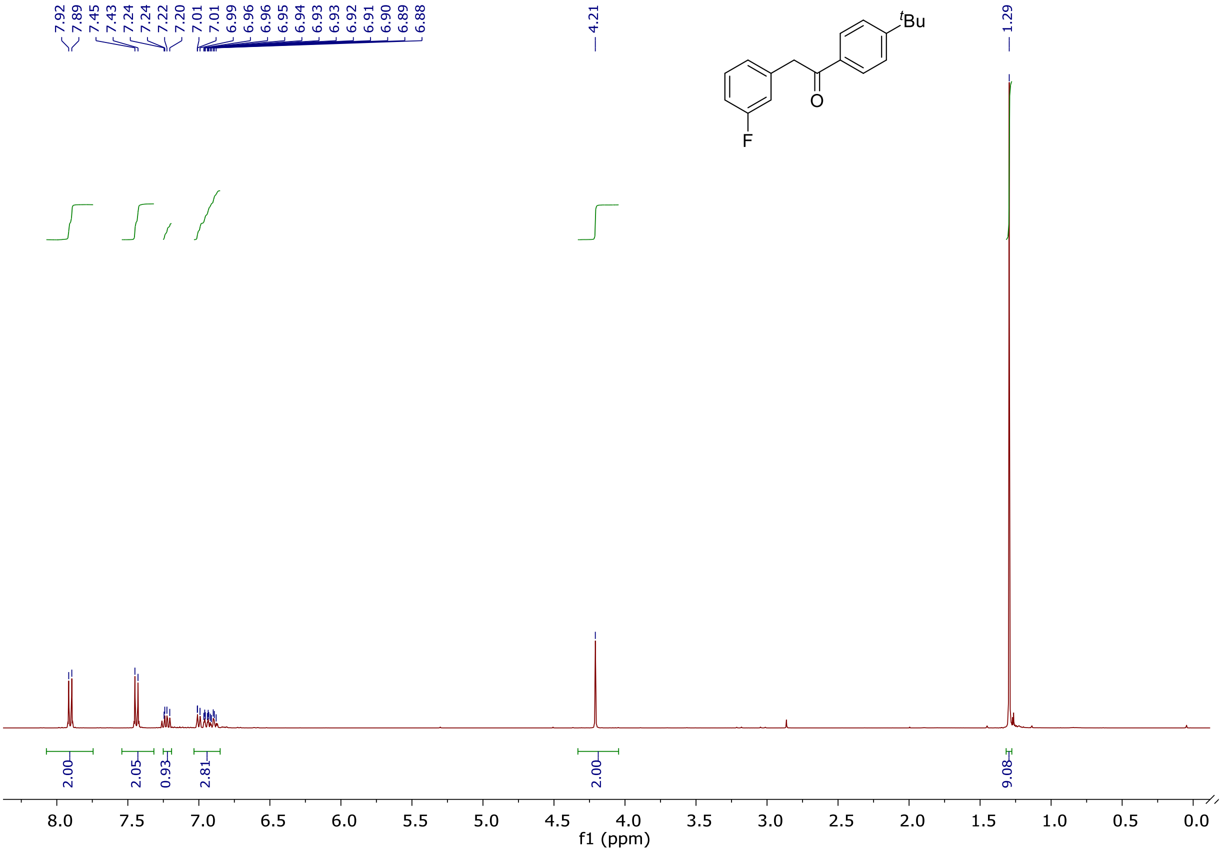
NMR-Spectra of 1-(4-chlorophenyl)-2-(3-(trifluoromethyl)phenyl)ethan-1-one (3c)

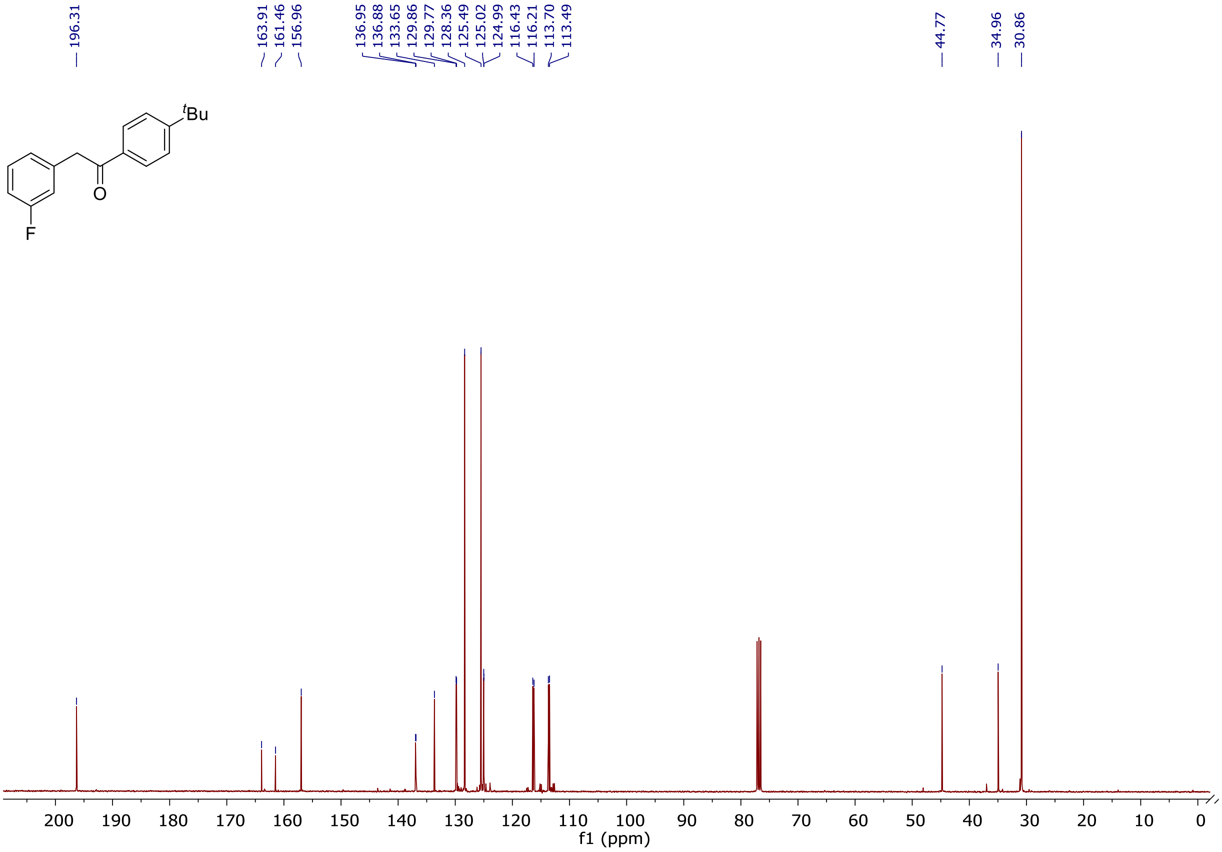


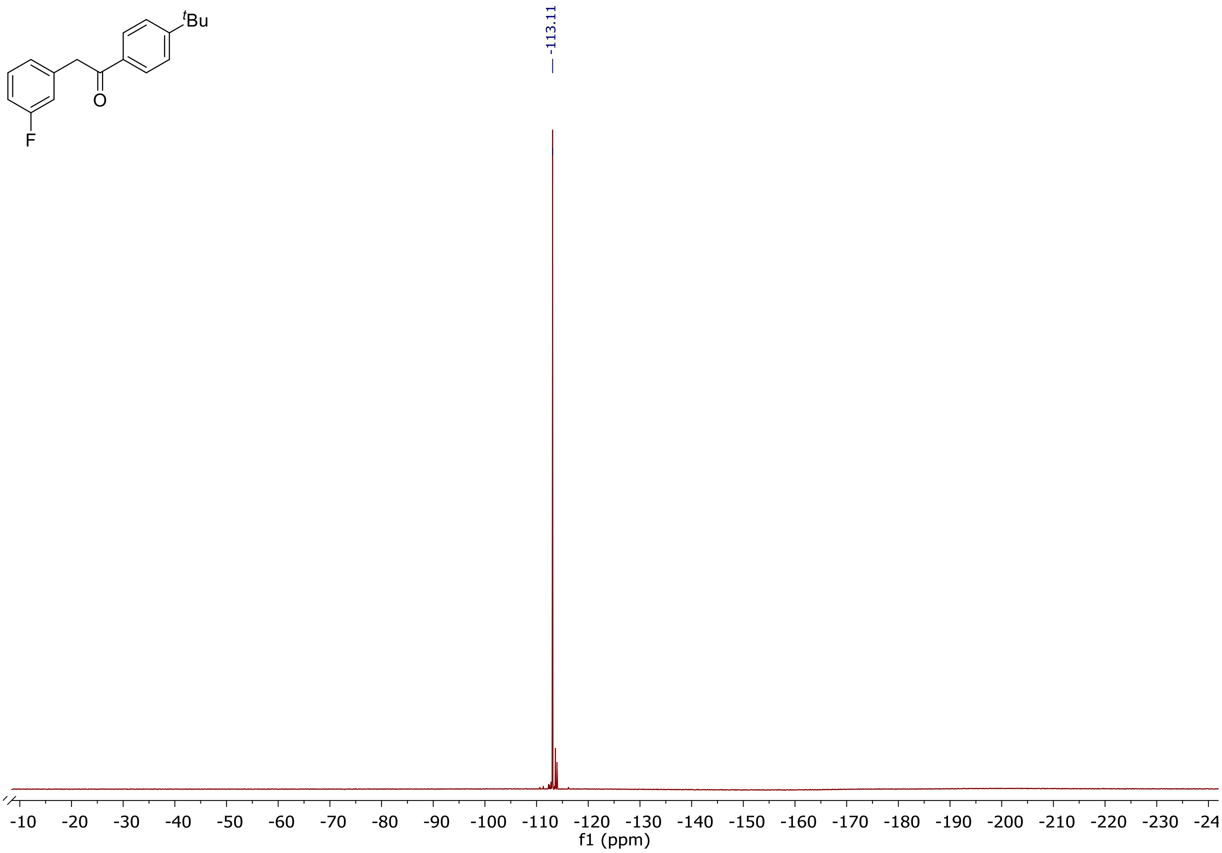

195.84
140.45
135.45
135.07
133.49
133.48
131.90
131.58
131.25
130.93
130.28
129.56
129.52
128.54
126.85
126.81
126.78
126.74
125.84
124.47
124.43
124.39
124.35
123.13
120.42
45.30
Cl
O
CF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.57
Cl
O
CF3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

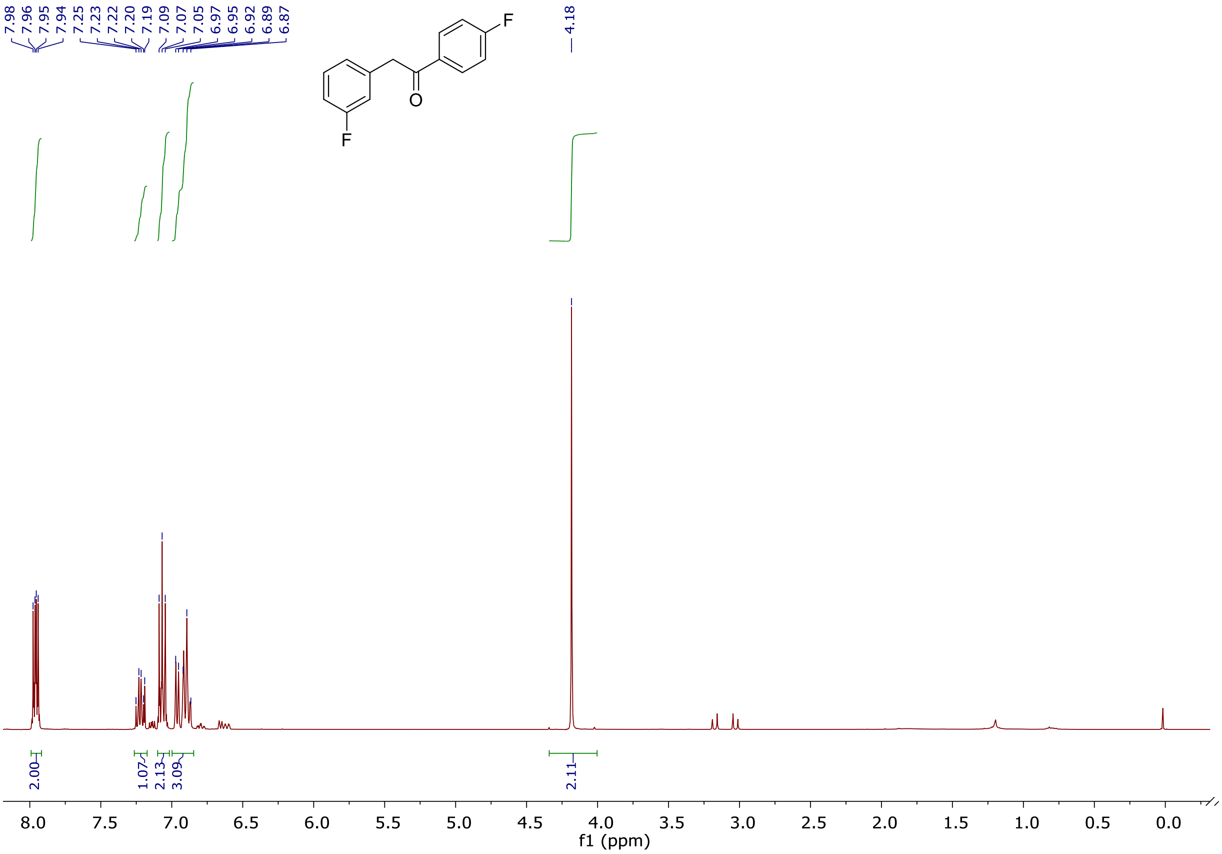
NMR-Spectra of 1-(4-(*tert*-butyl)phenyl)-2-(3-fluorophenyl)ethan-1-one (3d)

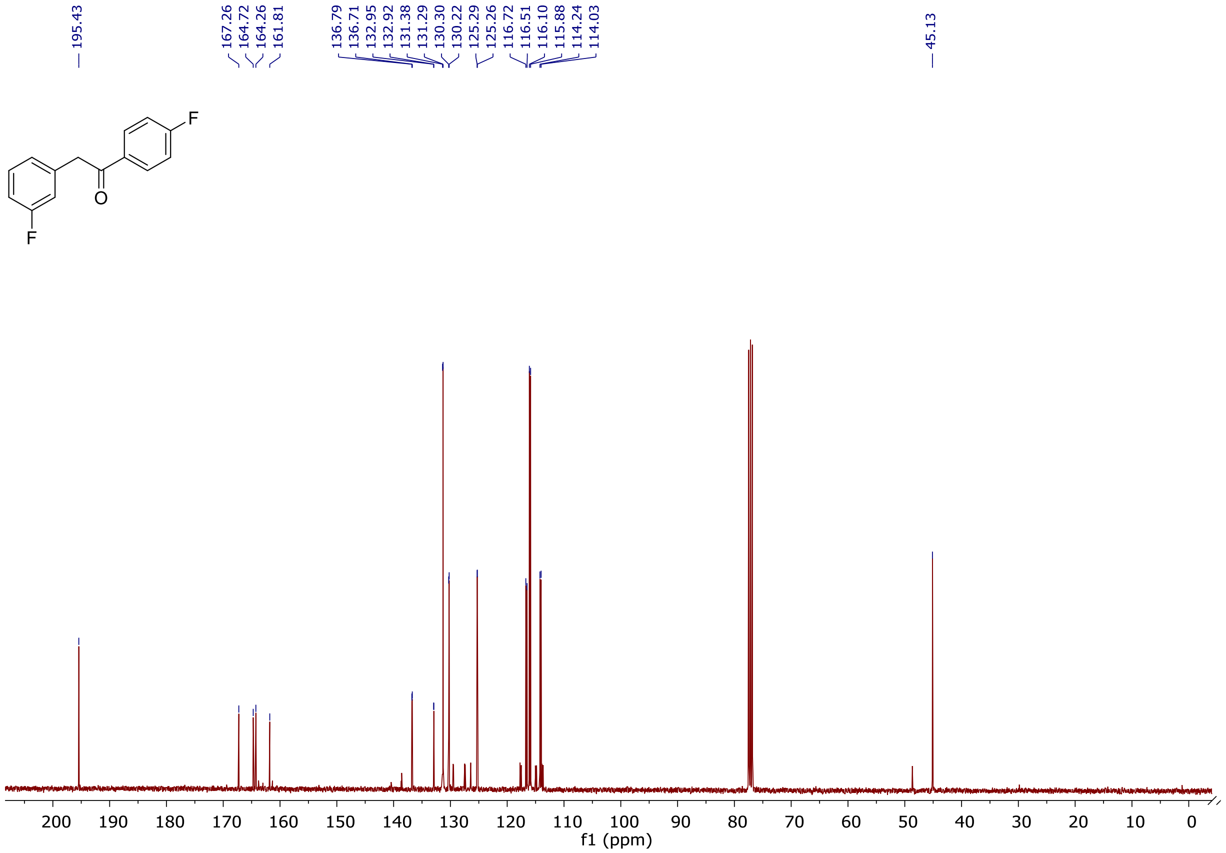


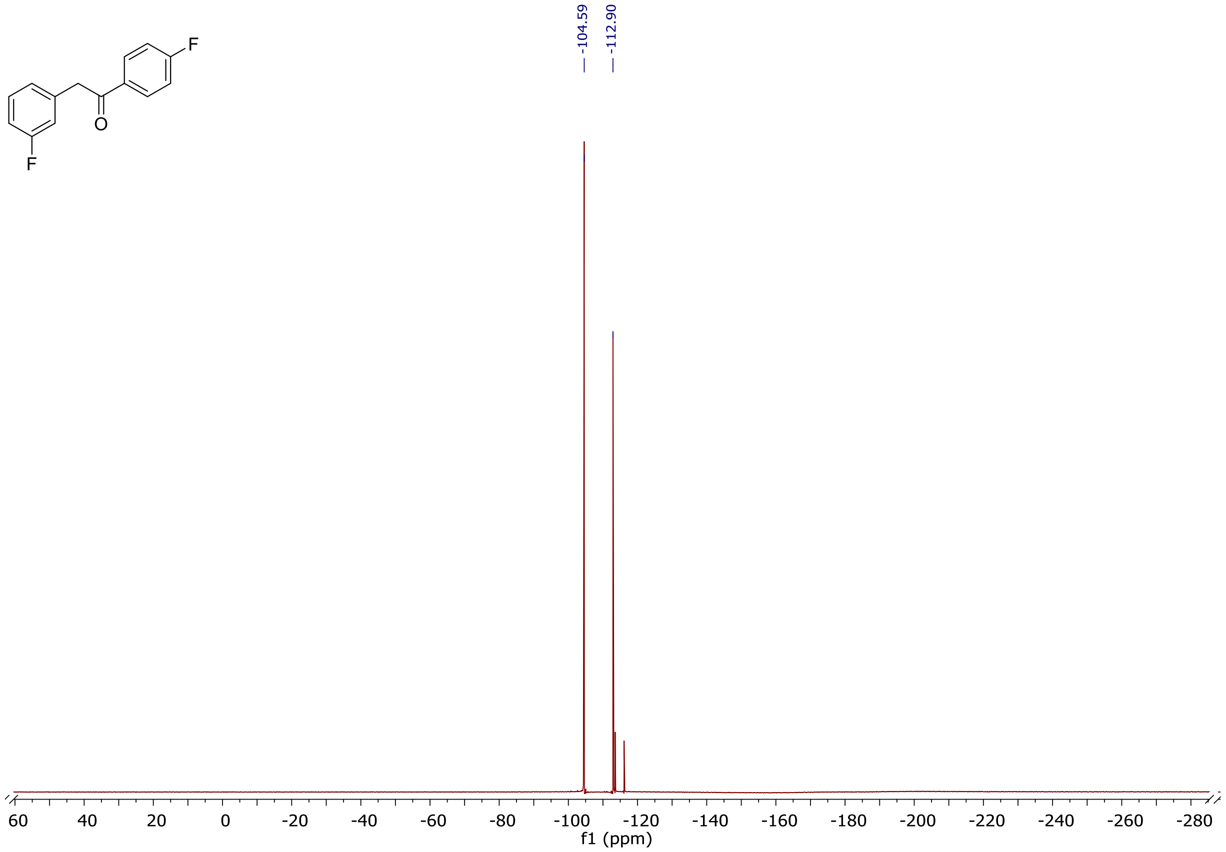




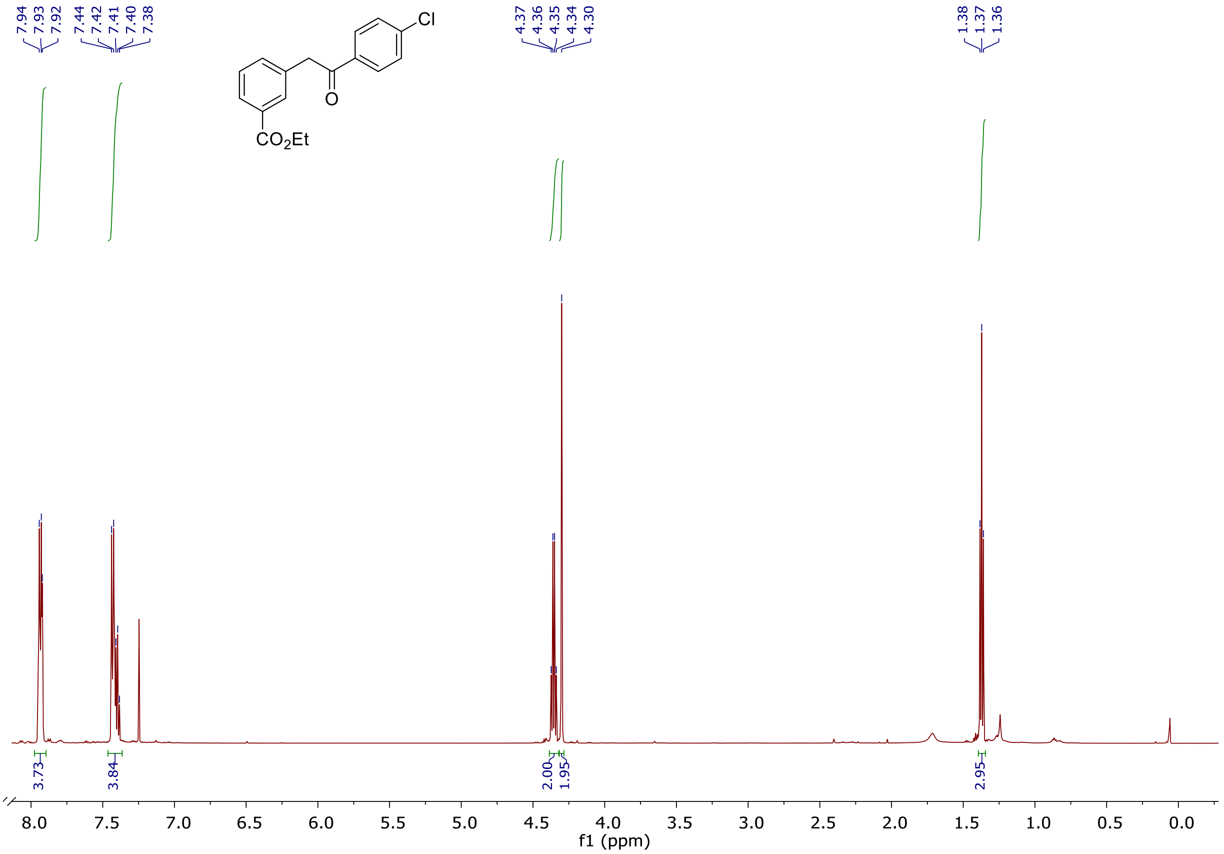
NMR-Spectra of 2-(3-fluorophenyl)-1-(4-fluorophenyl)ethan-1-one (3e)

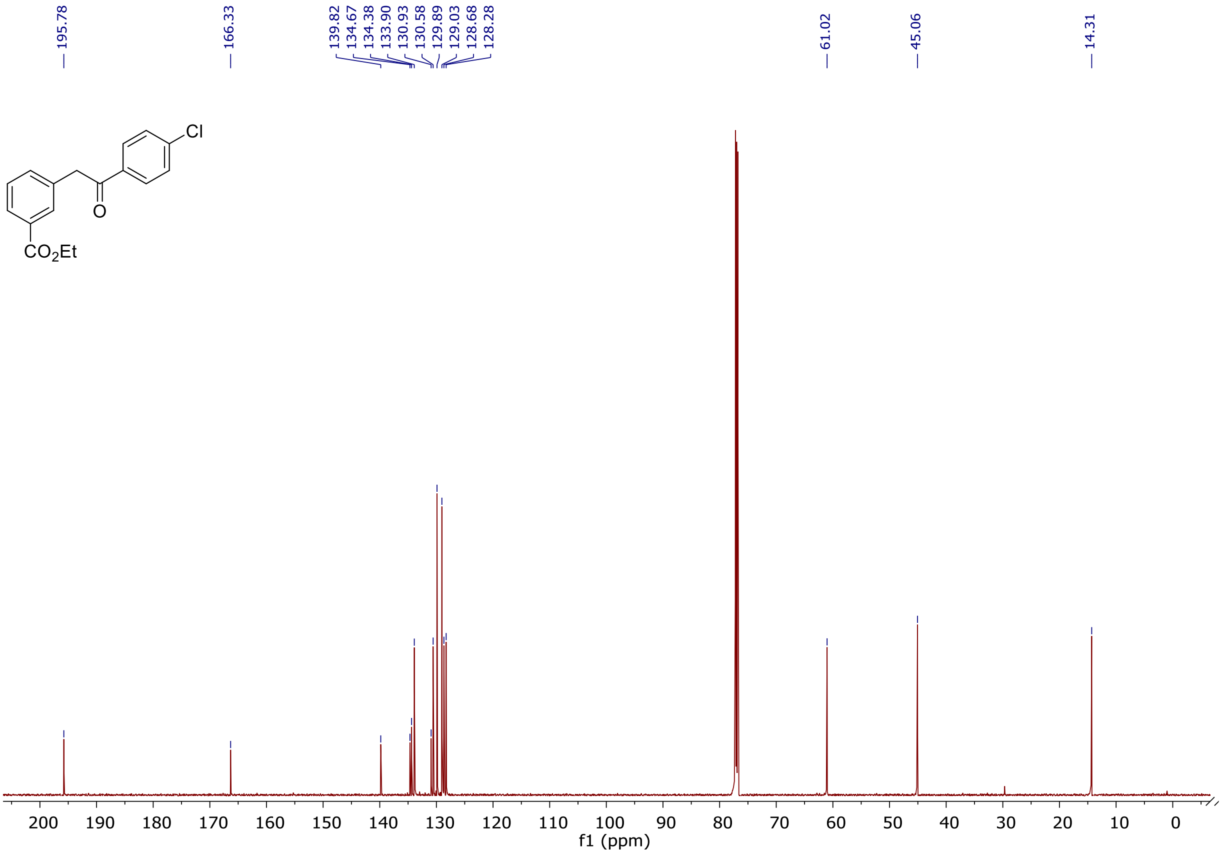



195.43
167.26
164.72
164.26
161.81
136.79
136.71
132.95
132.92
131.38
131.29
130.30
130.22
125.29
125.26
116.72
116.51
116.10
115.88
114.24
114.03
45.13
F
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

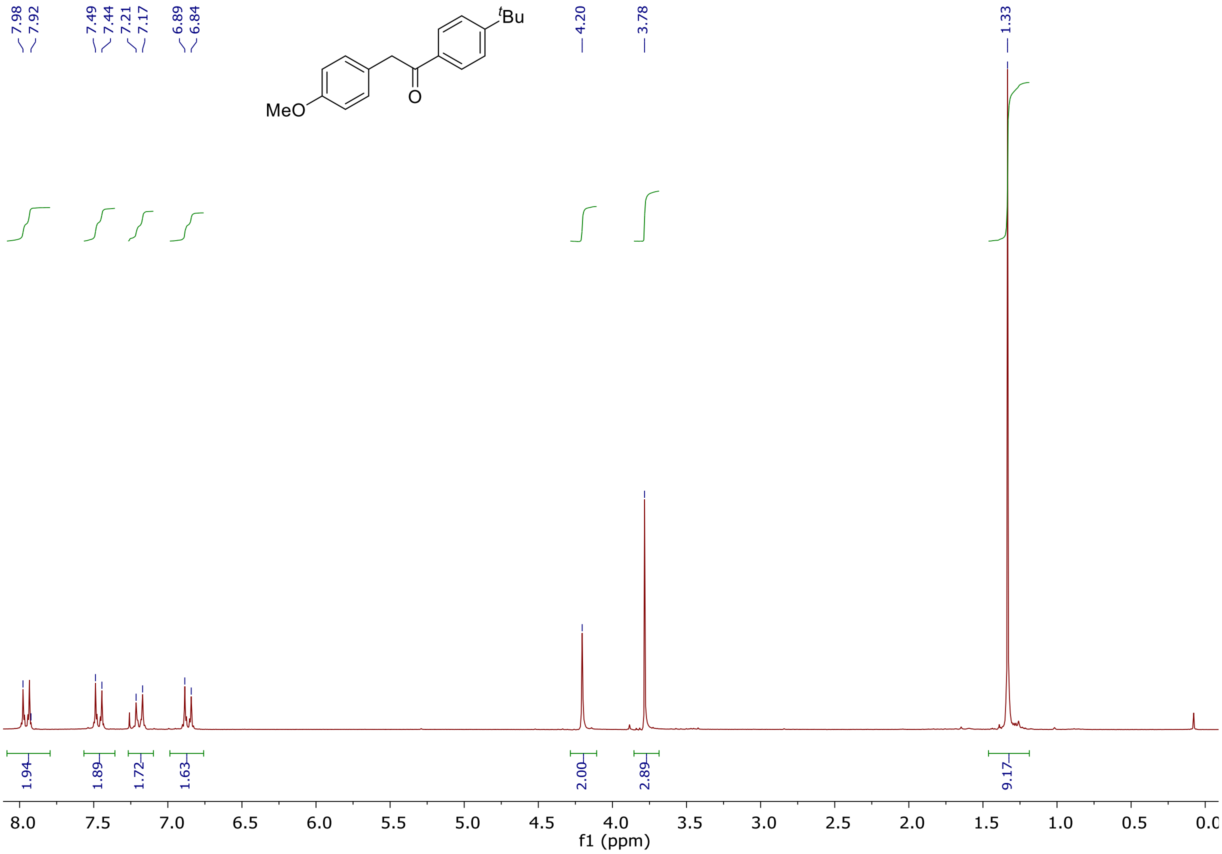

-104.59
-112.90
F
O
F
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

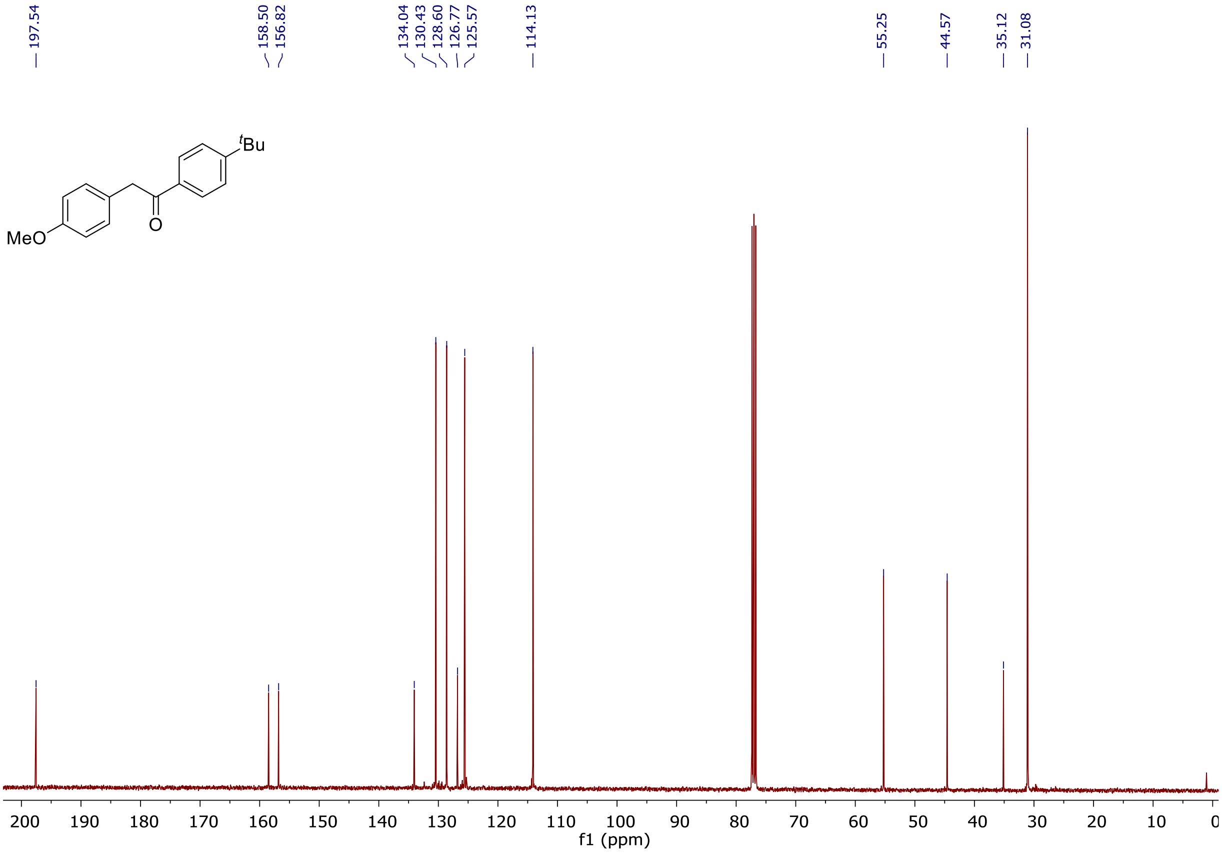
NMR-Spectra of ethyl 3-(2-(4-chlorophenyl)-2-oxoethyl)benzoate (3f)



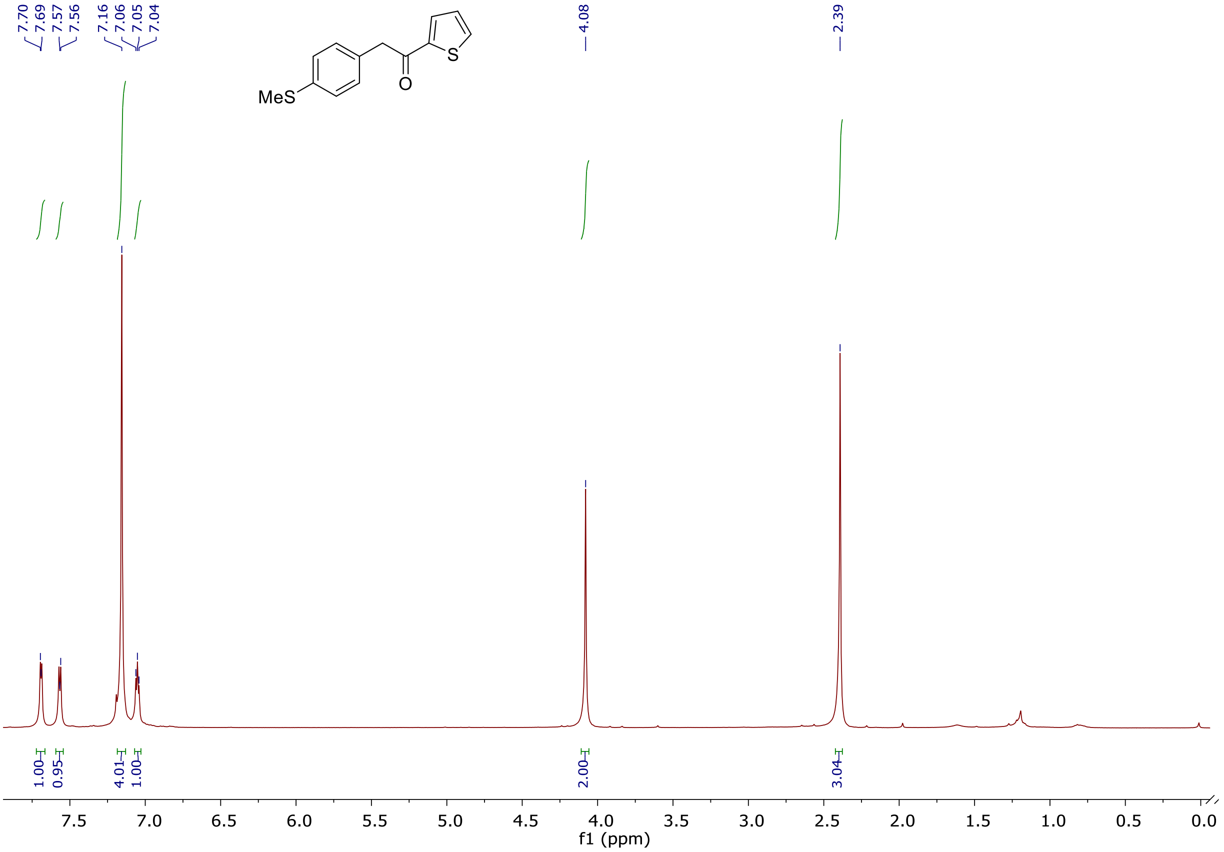


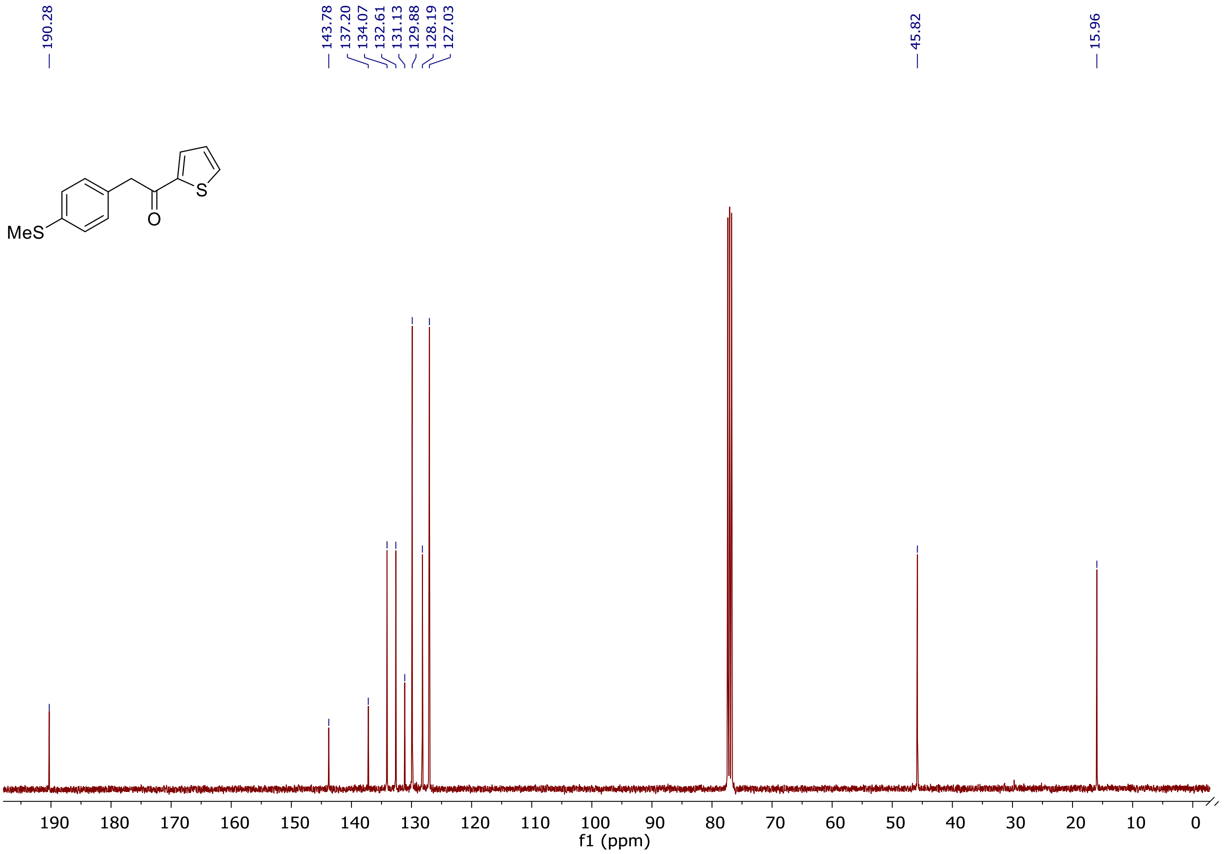
NMR-Spectra of 1-(4-(*tert*-butyl)phenyl)-2-(4-methoxyphenyl)ethan-1-one (3g)



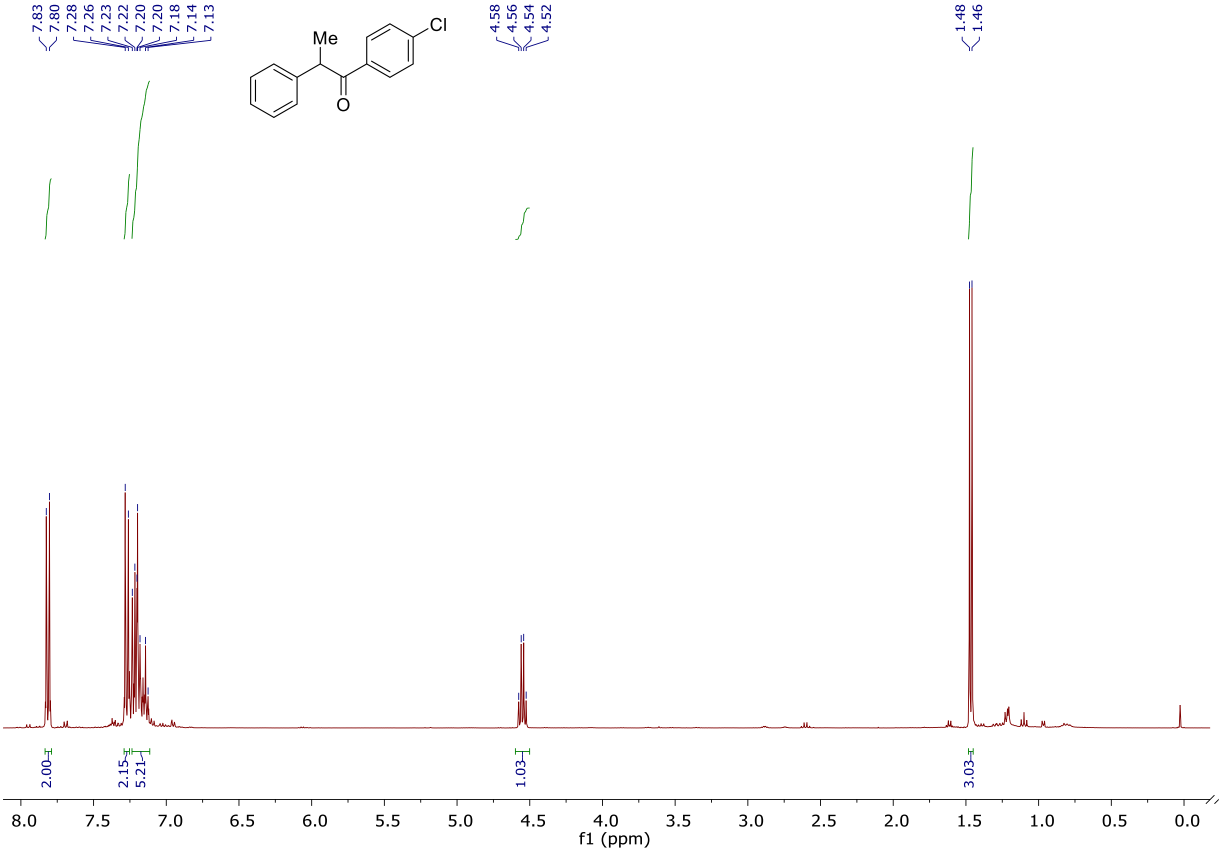


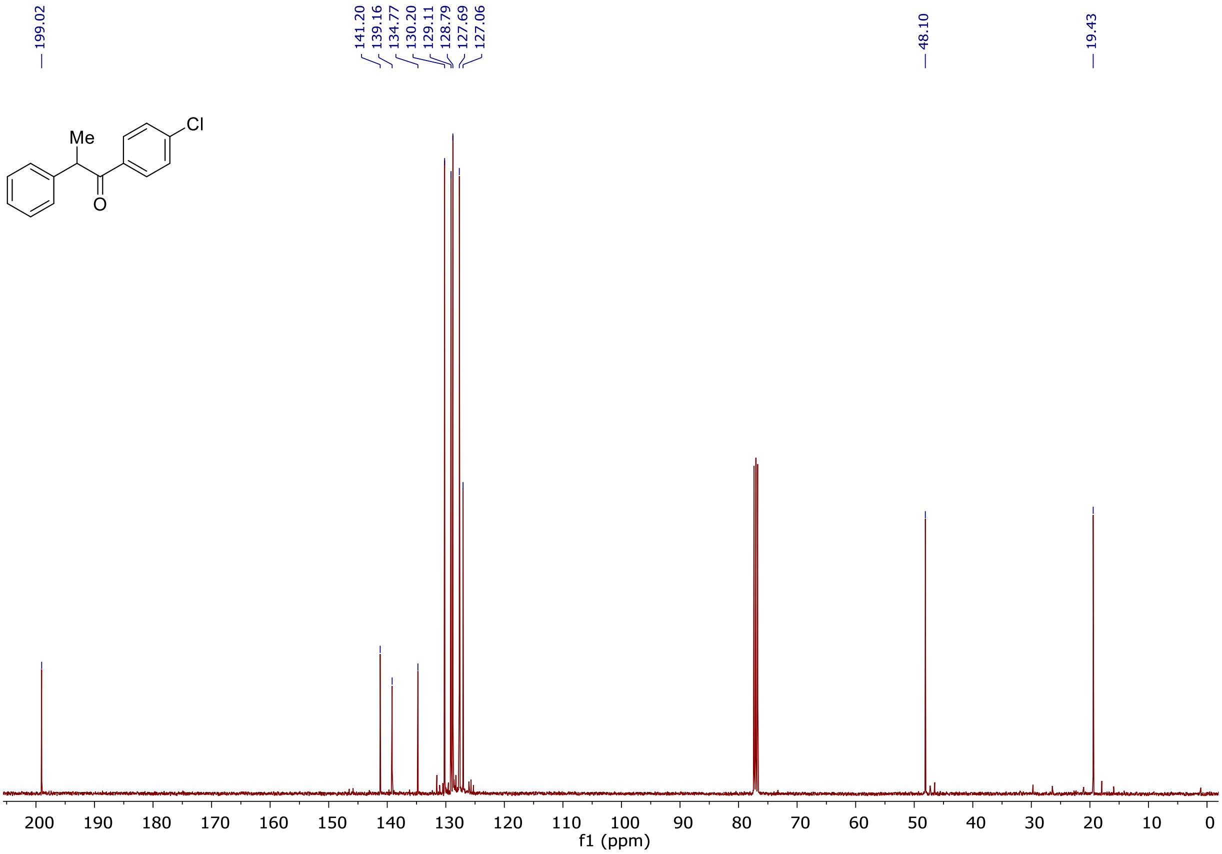
NMR-Spectra of 2-(4-(methylthio)phenyl)-1-(thiophen-2-yl)ethan-1-one (3h)



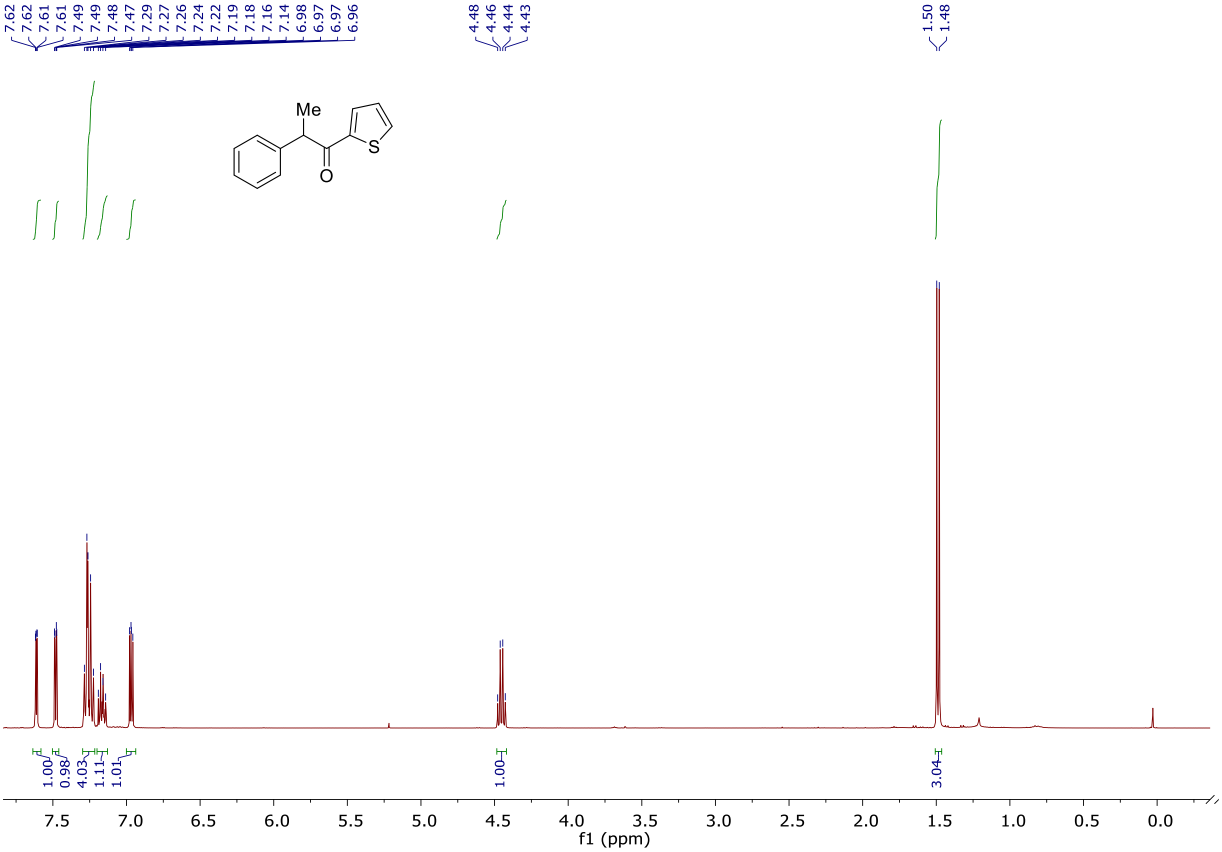


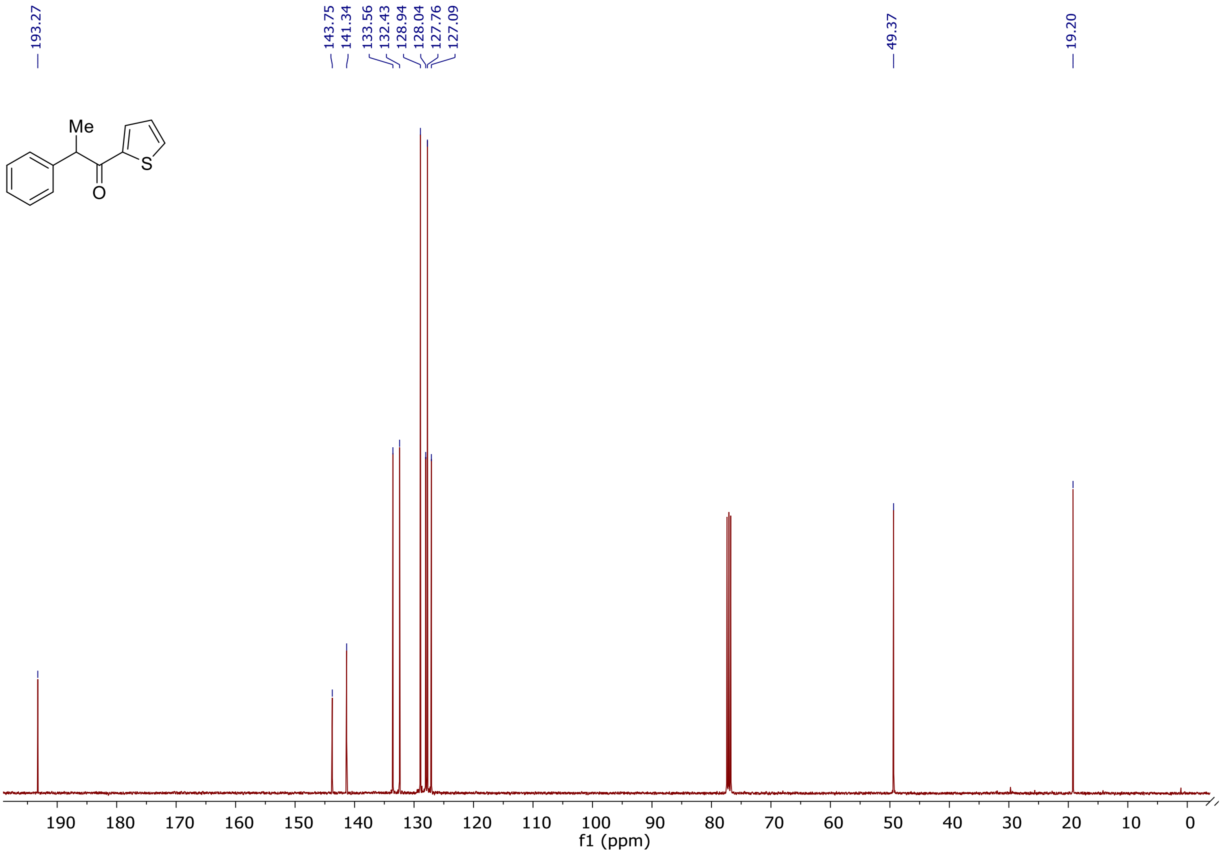
NMR-Spectra of 1-(4-chlorophenyl)-2-phenylpropan-1-one (3i)



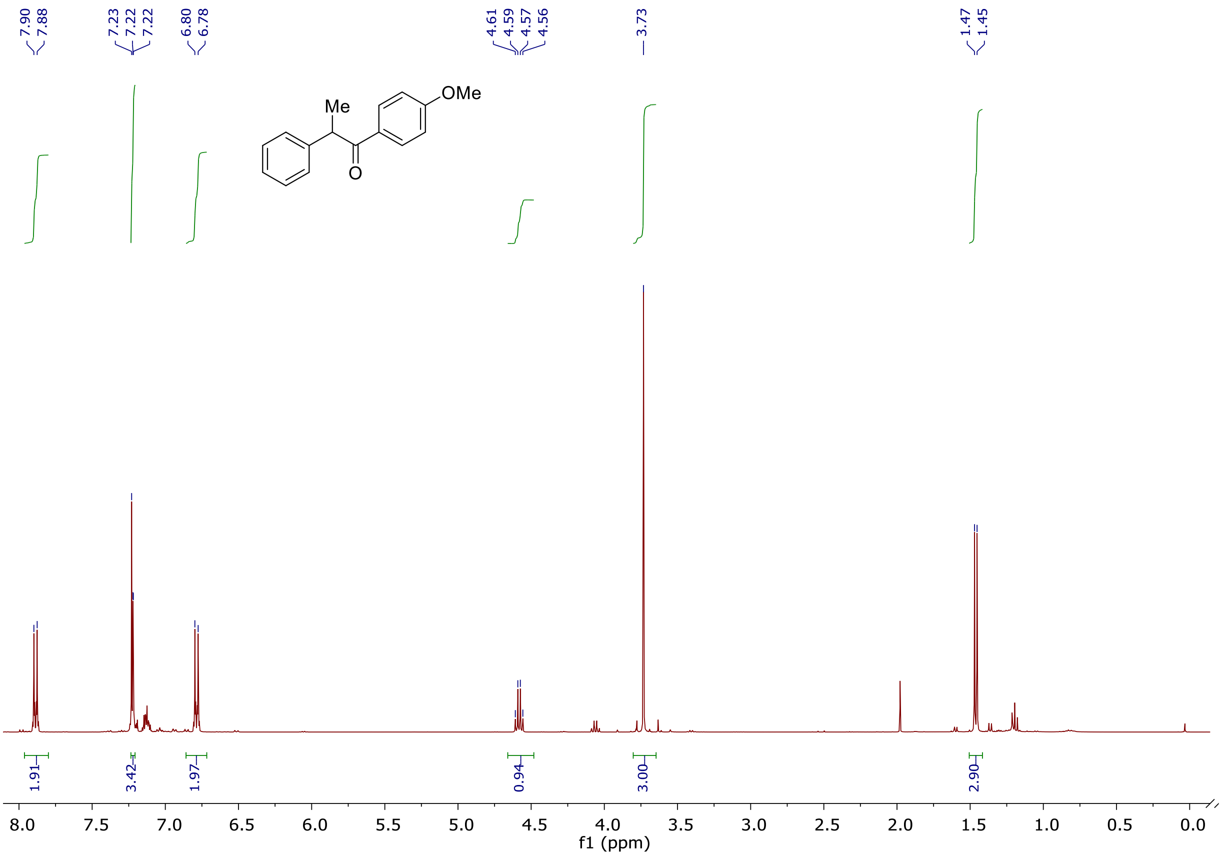


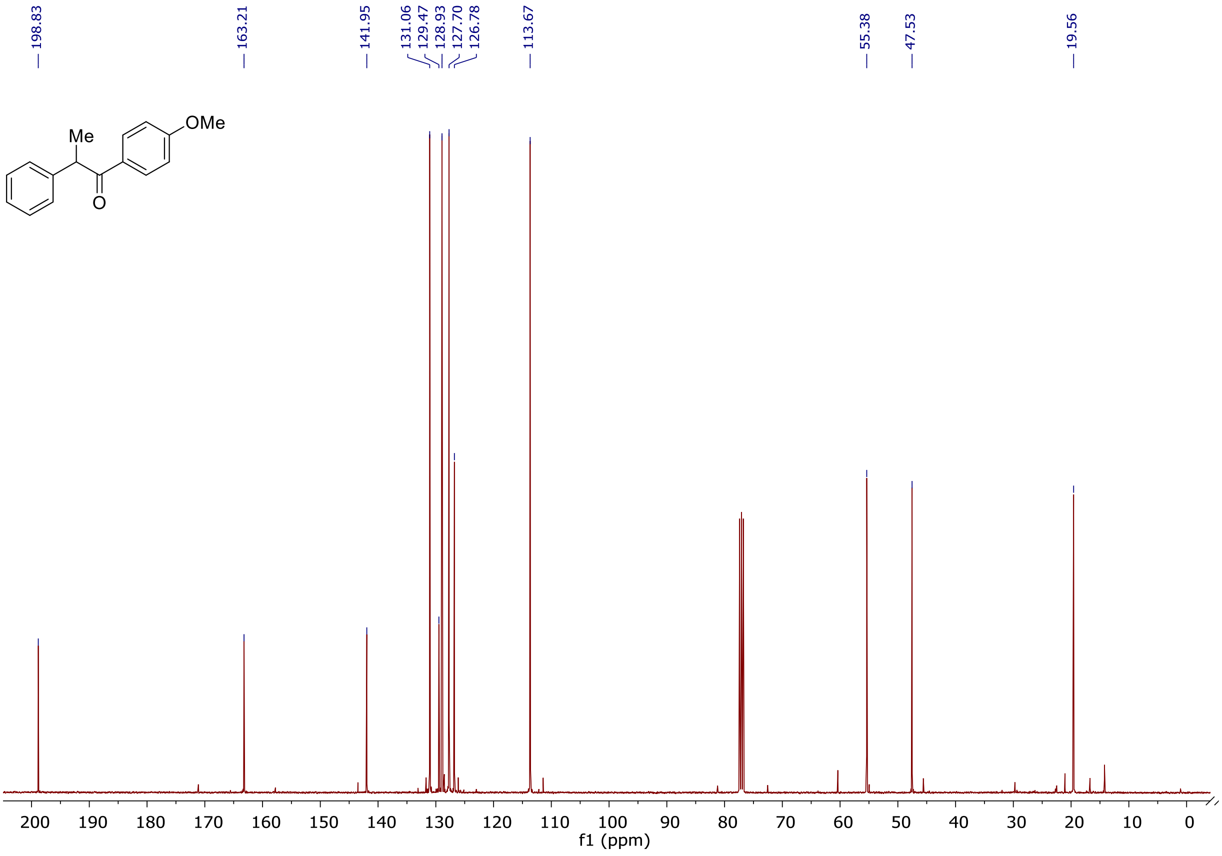
NMR-Spectra of 2-phenyl-1-(thiophen-2-yl)propan-1-one (3j)



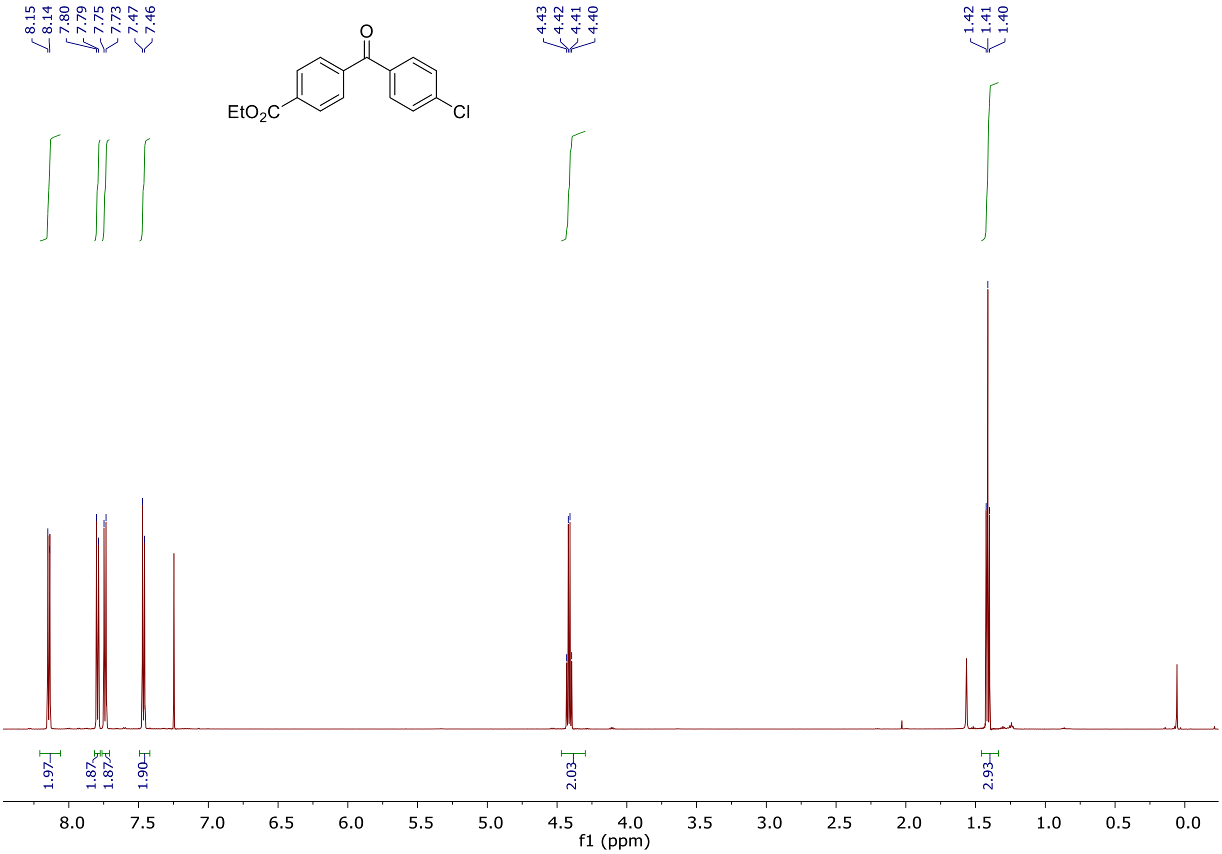


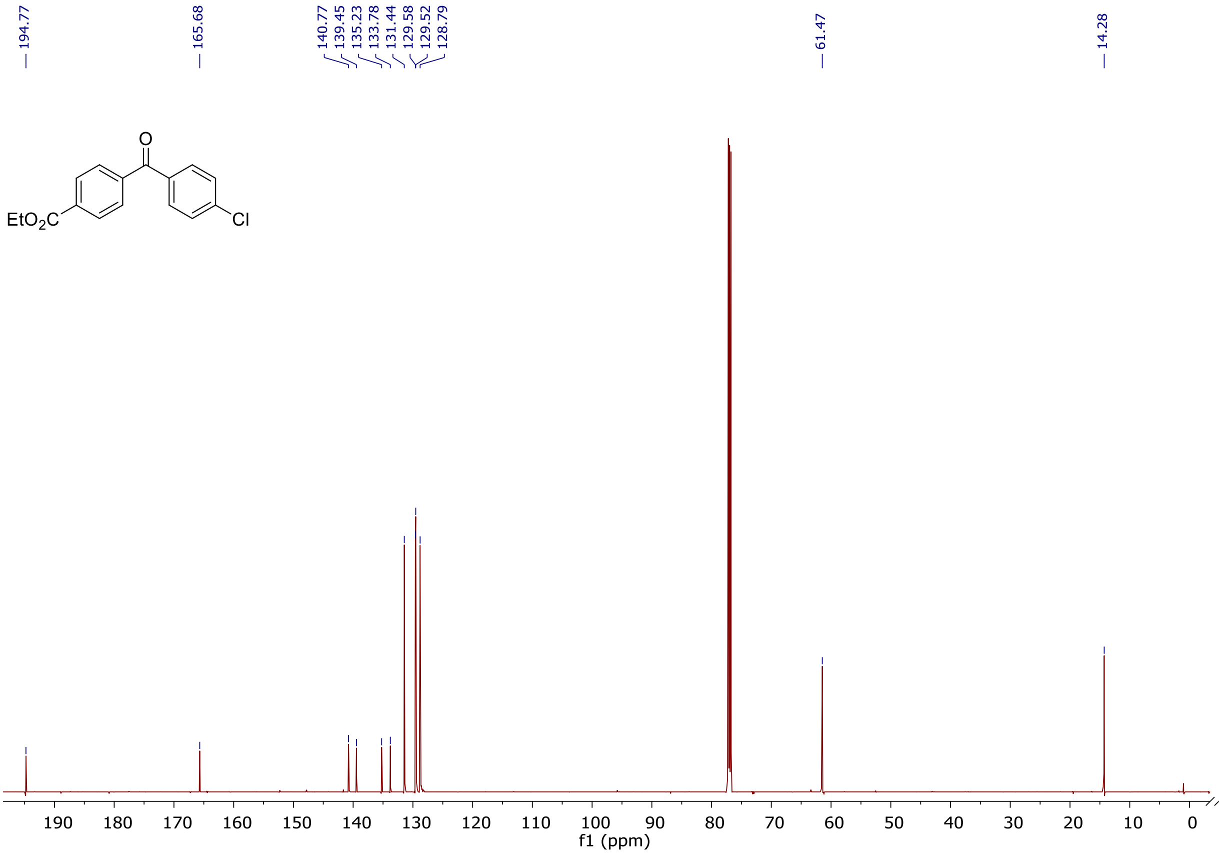
NMR-Spectra of 1-(4-methoxyphenyl)-2-phenylpropan-1-one (3k)



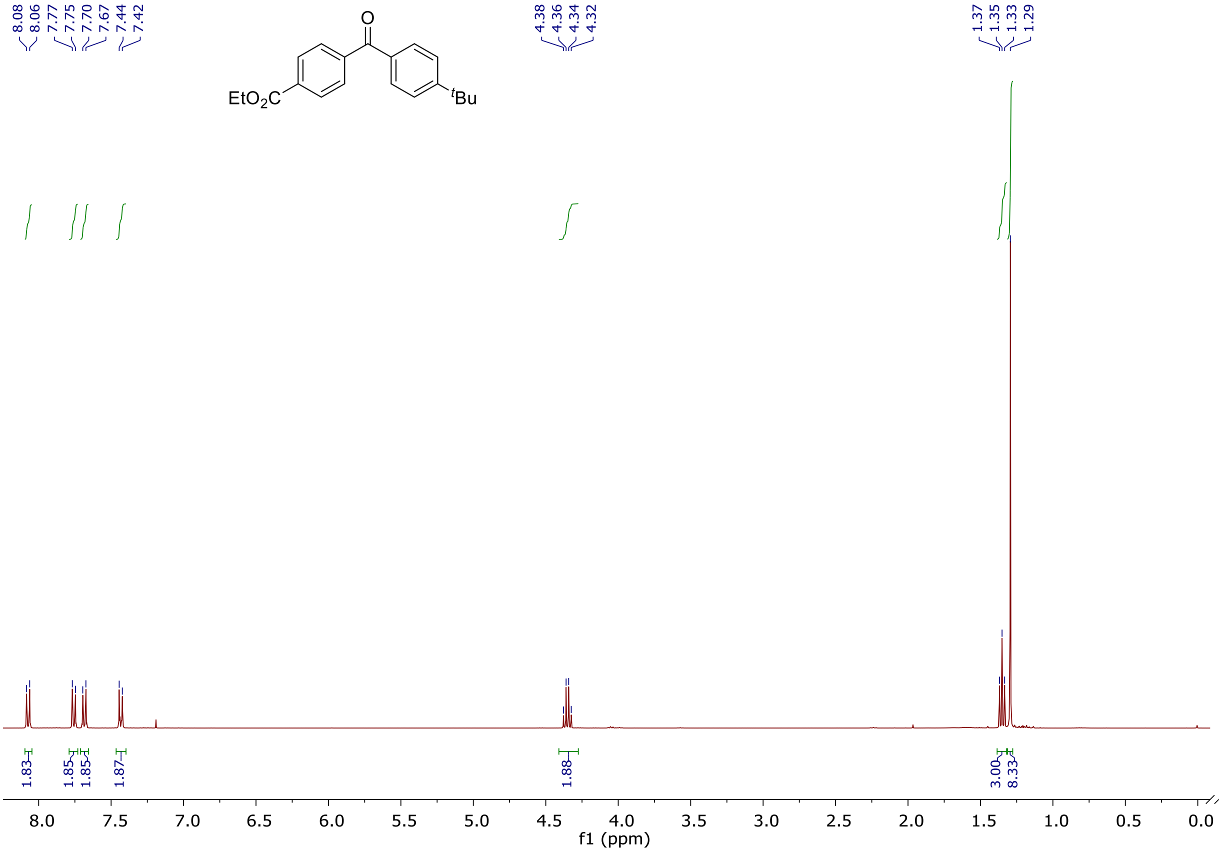


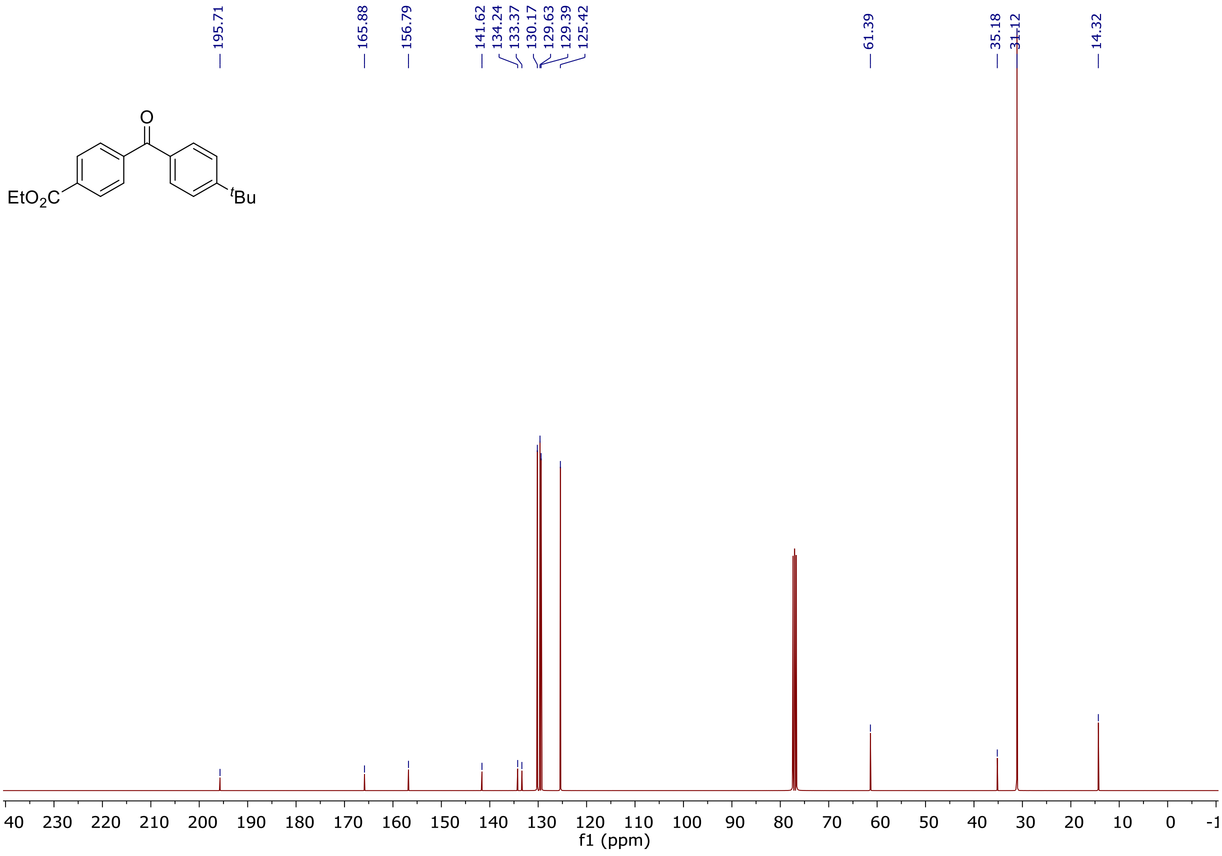
NMR-Spectra of ethyl 4-(4-chlorobenzoyl)benzoate (5a)



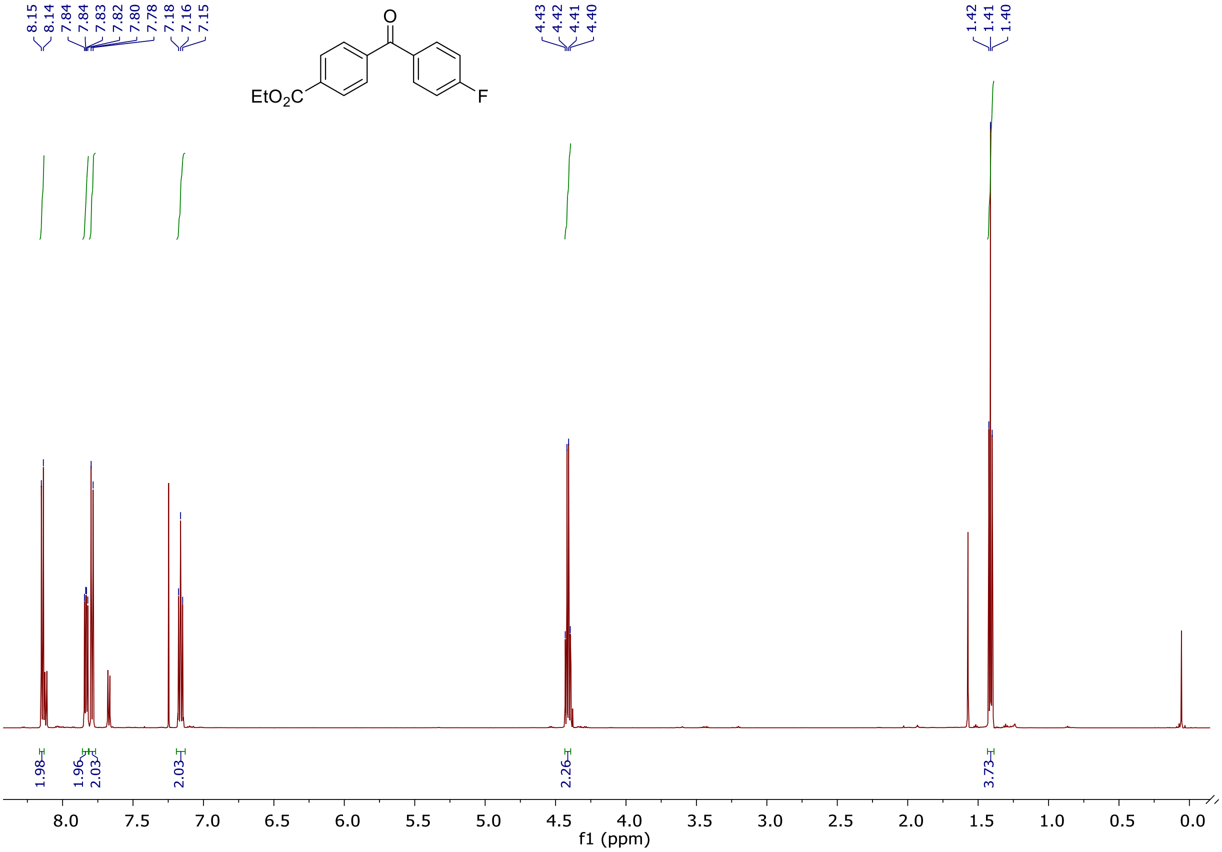


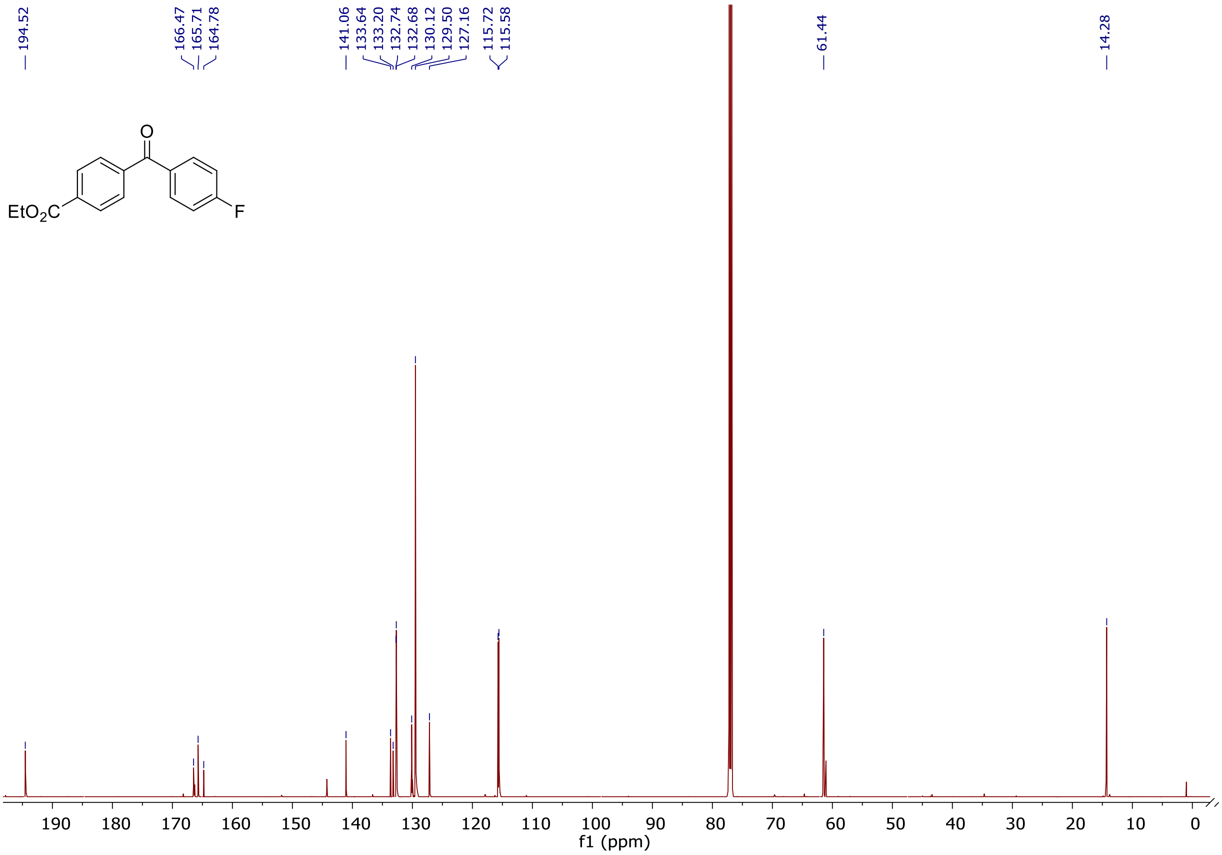
NMR-Spectra of ethyl 4-(4-(*tert*-butyl)benzoyl)benzoate (5b)

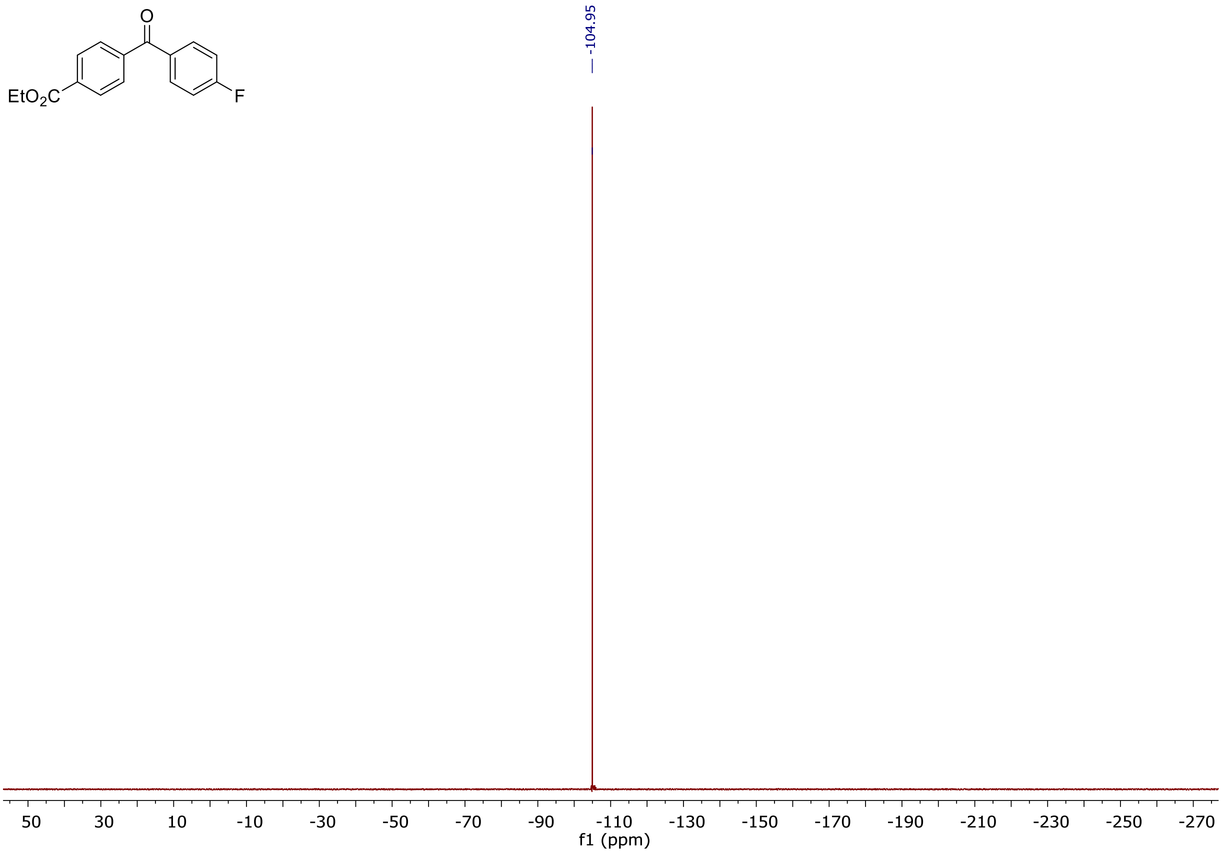




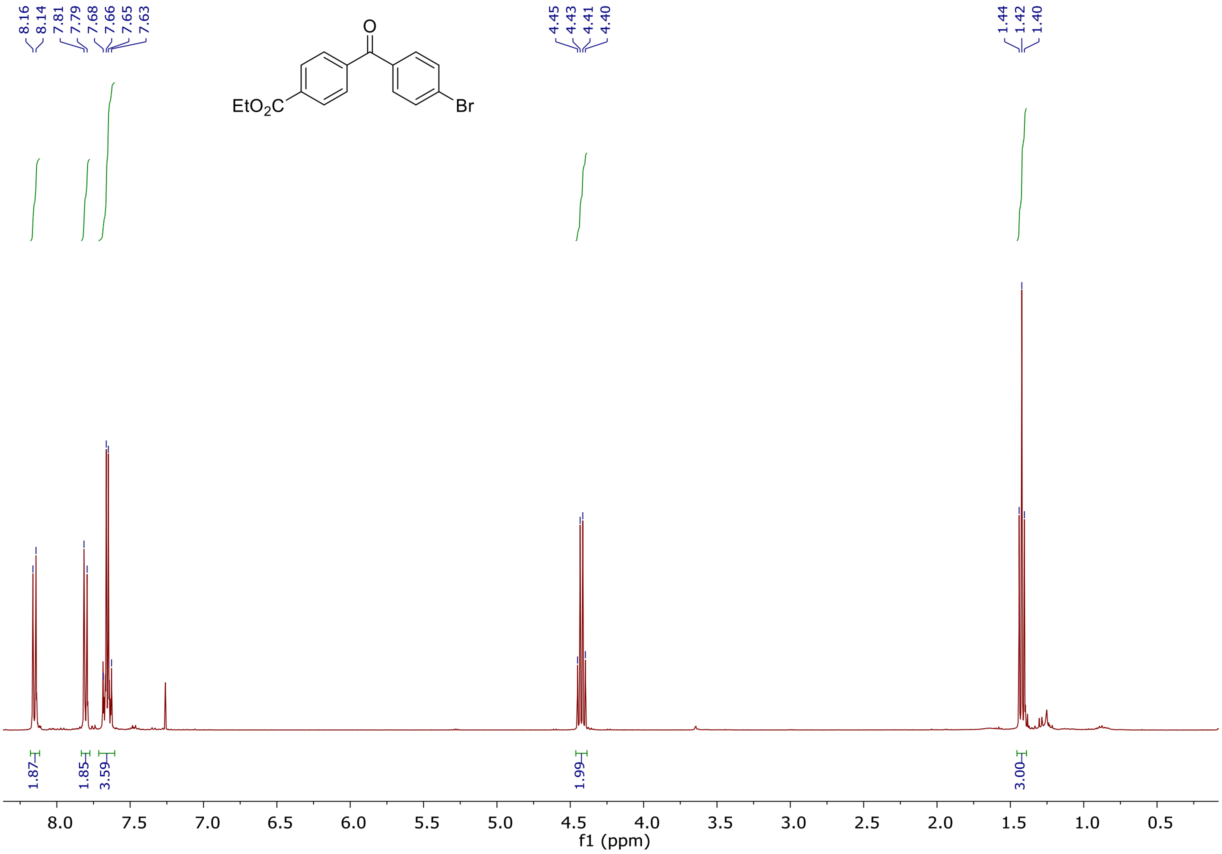
NMR-Spectra of ethyl 4-(4-fluorobenzoyl)benzoate (5c)

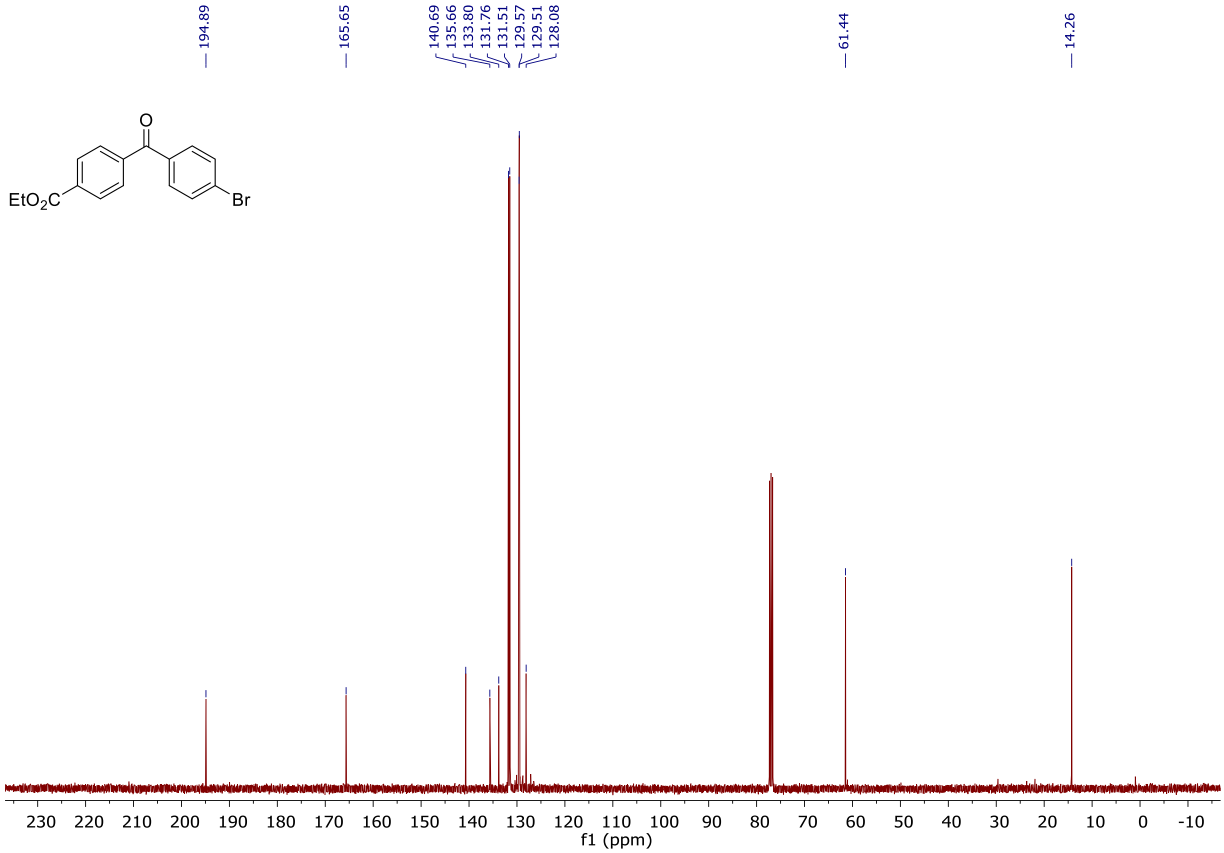




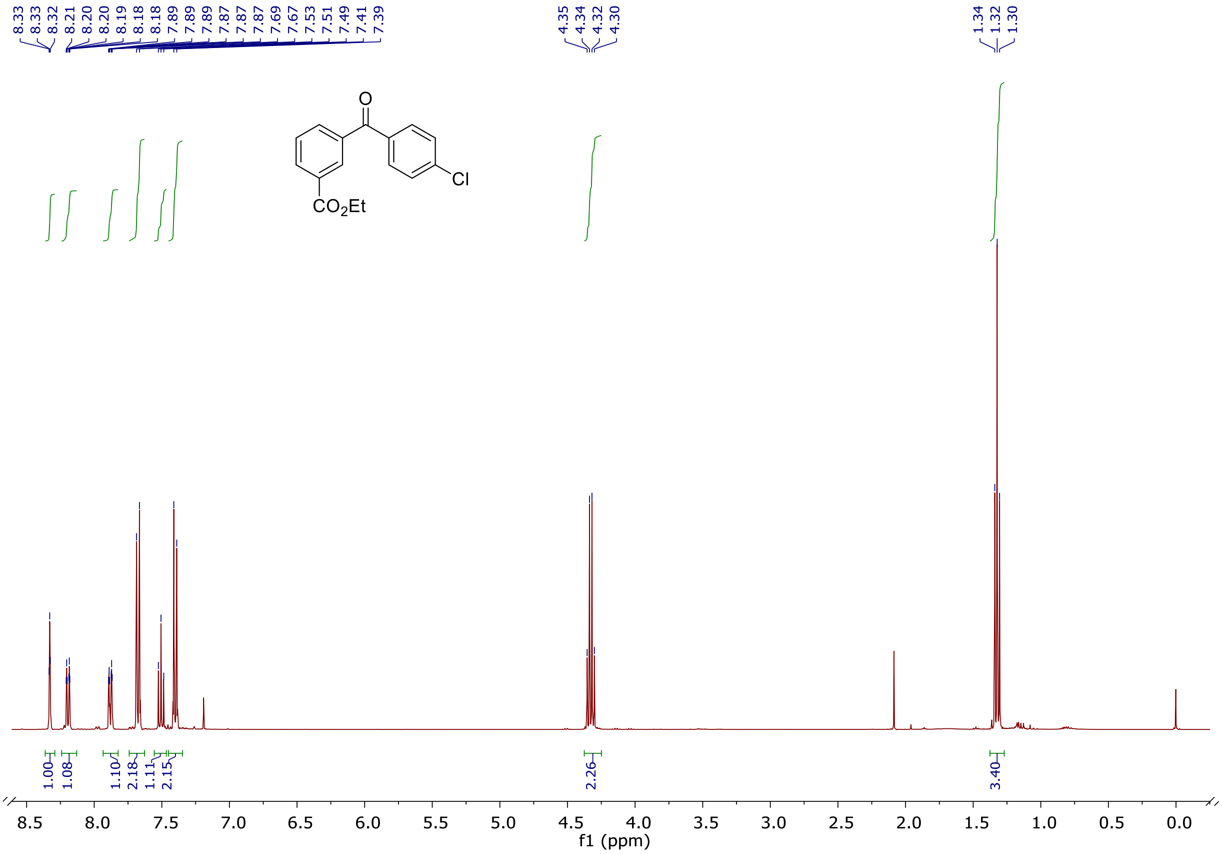


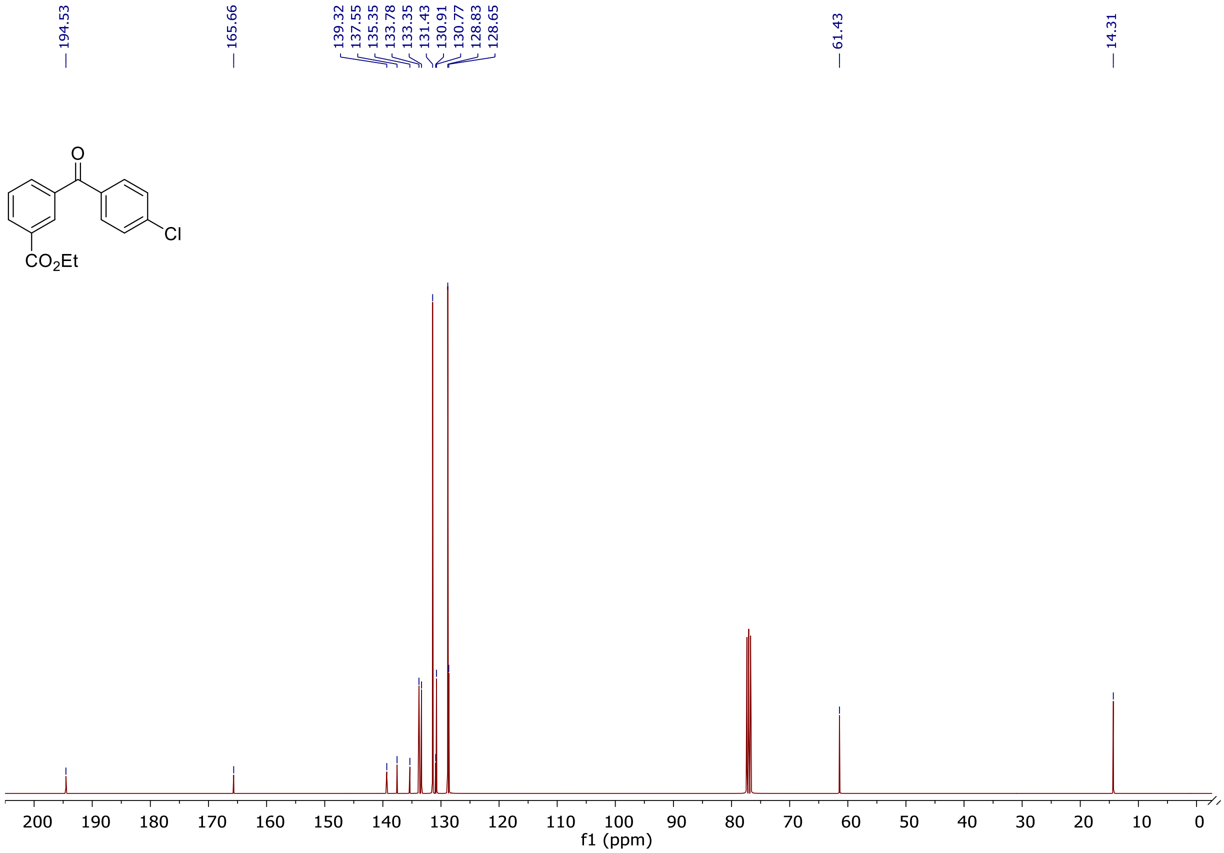
NMR-Spectra of ethyl 4-(4-bromobenzoyl)benzoate (5d)



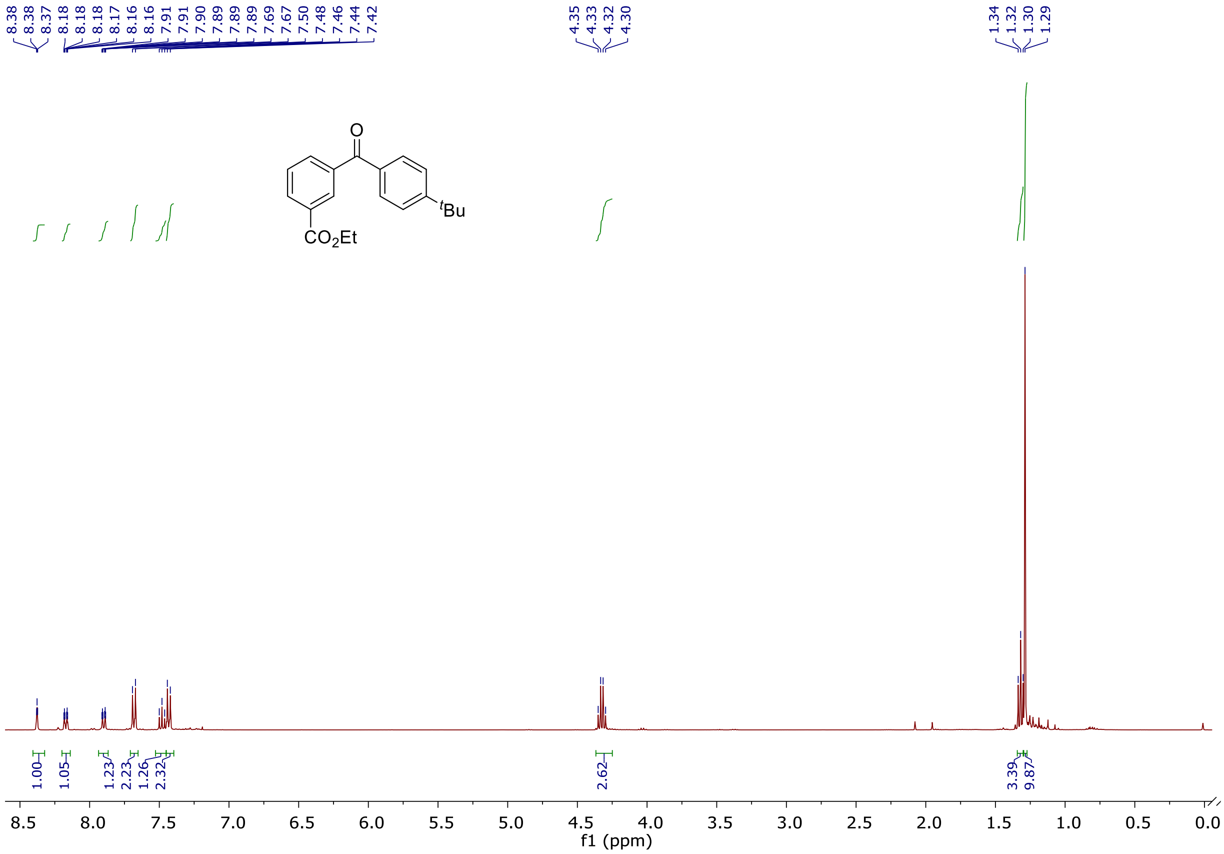


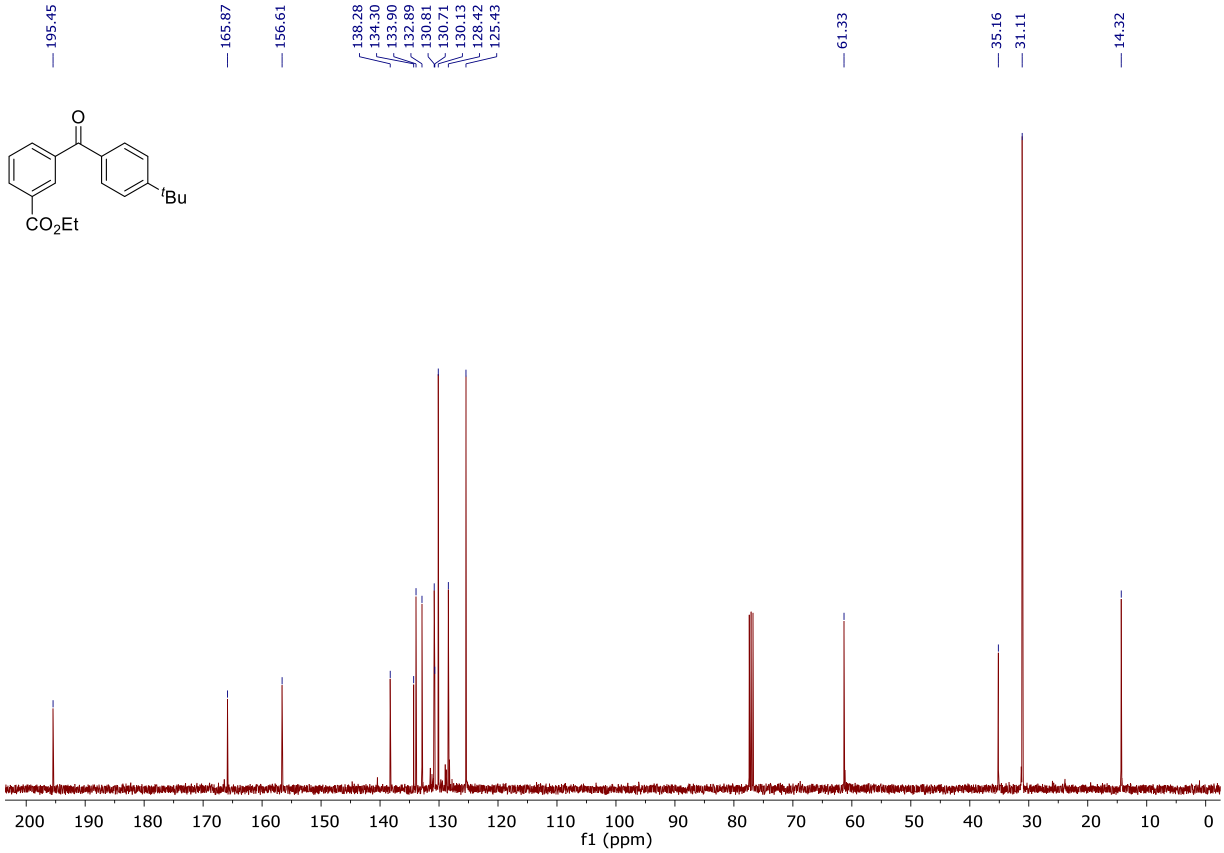
NMR-Spectra of ethyl 3-(4-chlorobenzoyl)benzoate (5e)



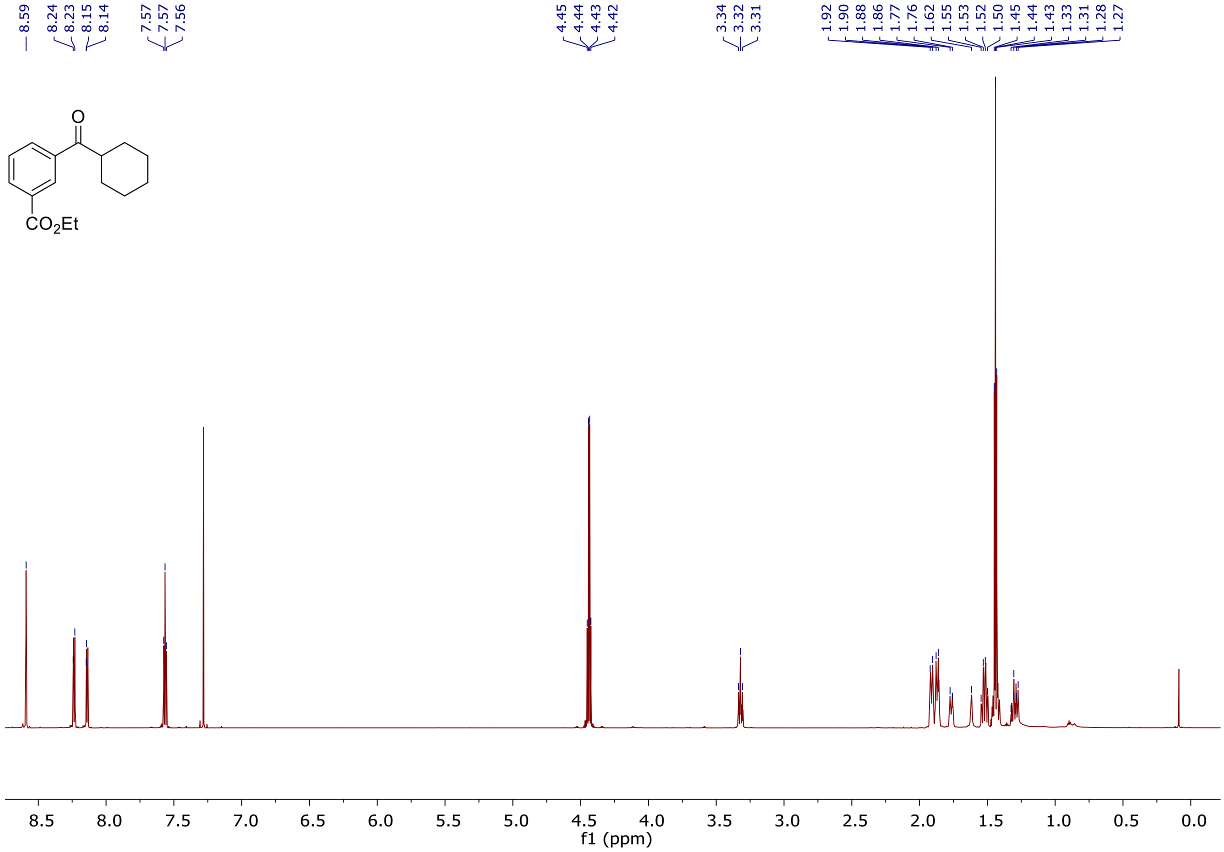


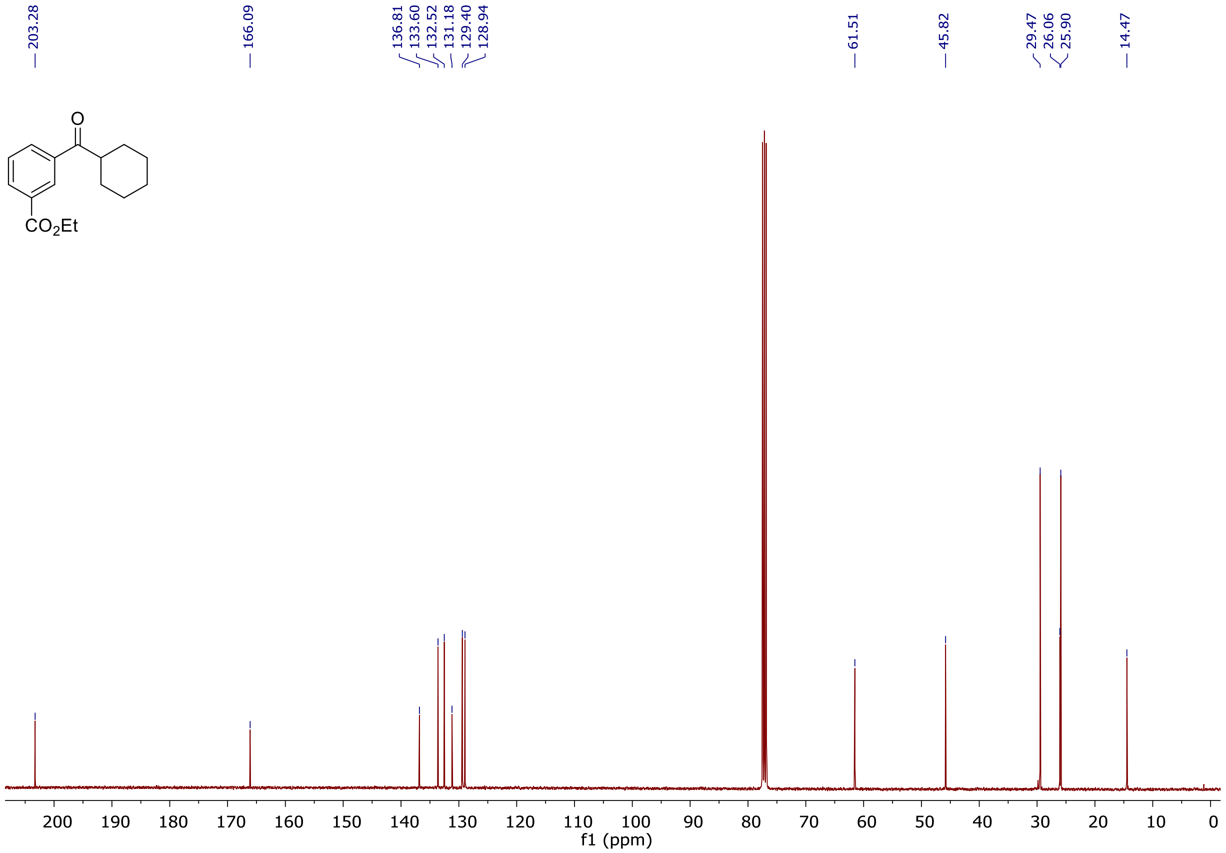
NMR-Spectra of ethyl 3-(4-(*tert*-butyl)benzoyl)benzoate (5f)



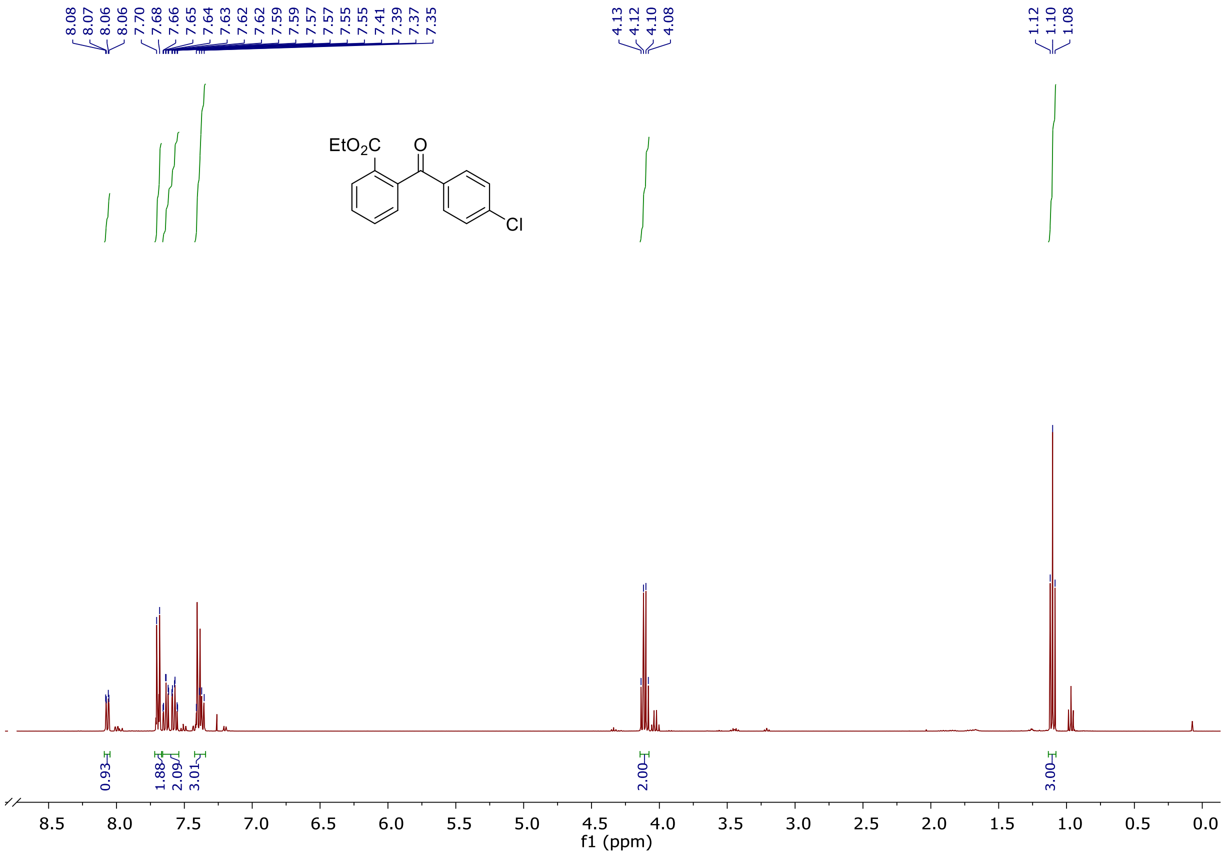


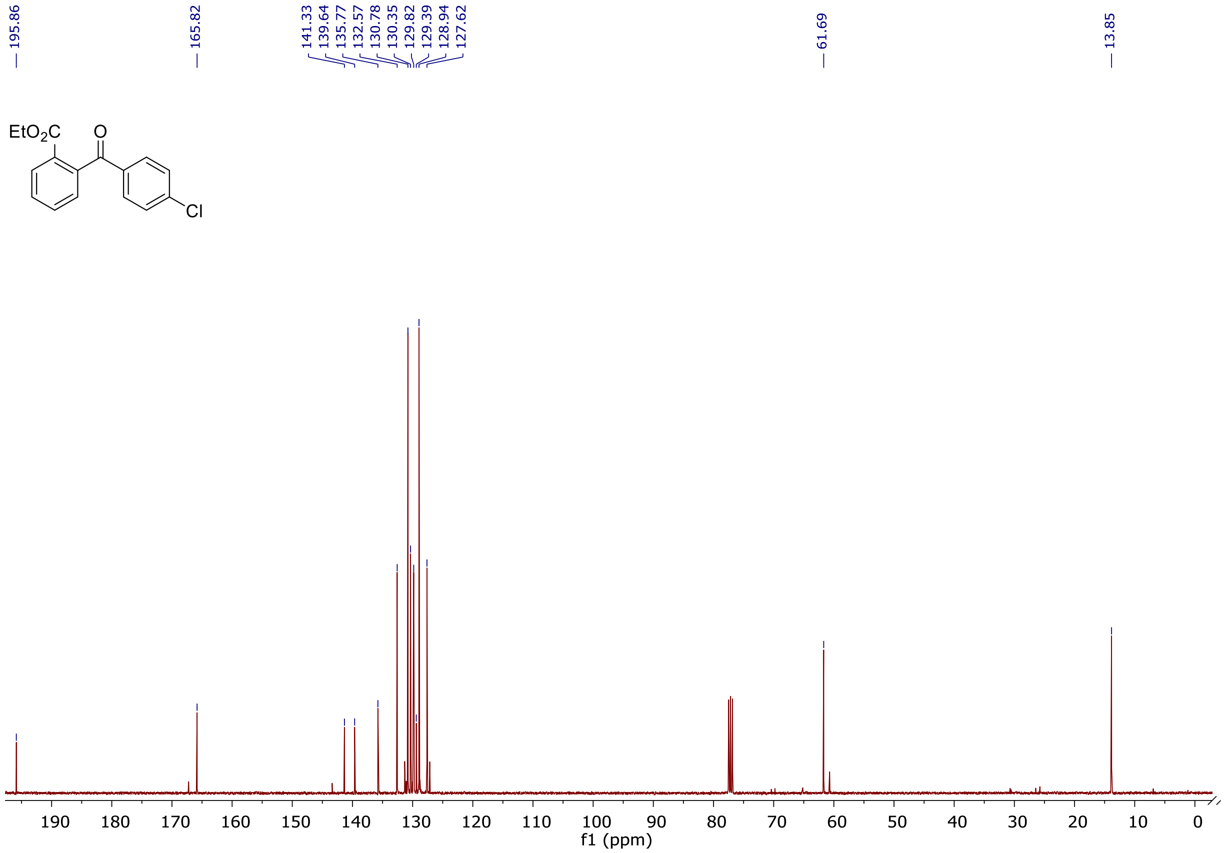
NMR-Spectra of ethyl 4-(cyclohexanecarbonyl)benzoate (5g)



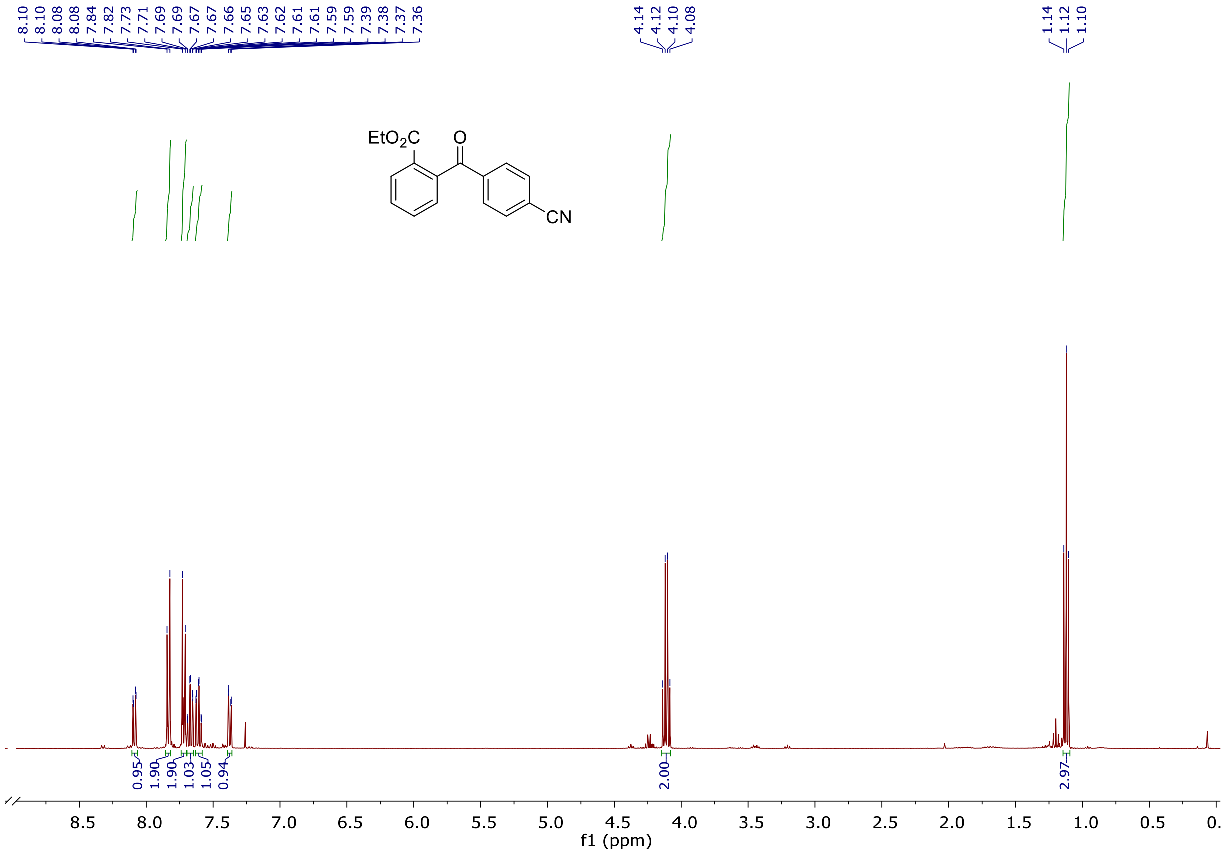


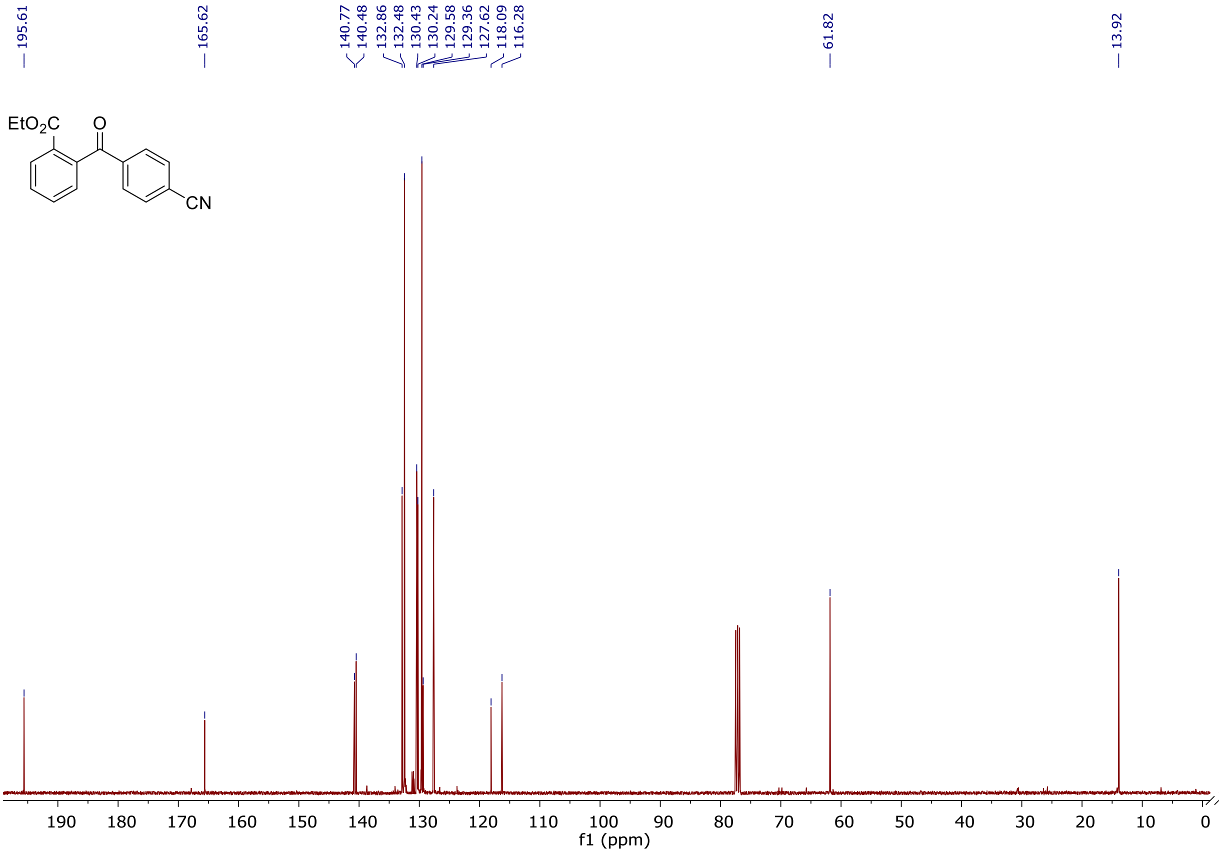
NMR-Spectra of ethyl 2-(4-chlorobenzoyl)benzoate (5h)



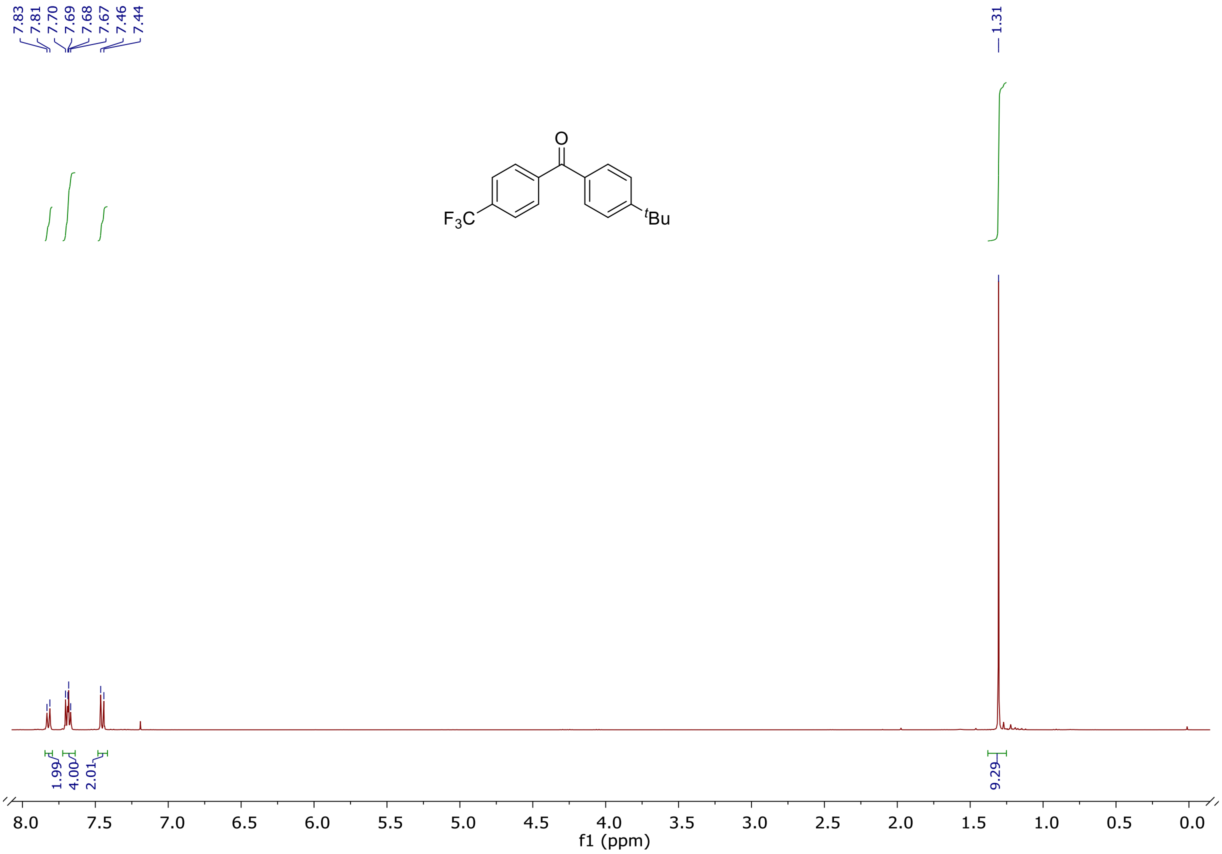


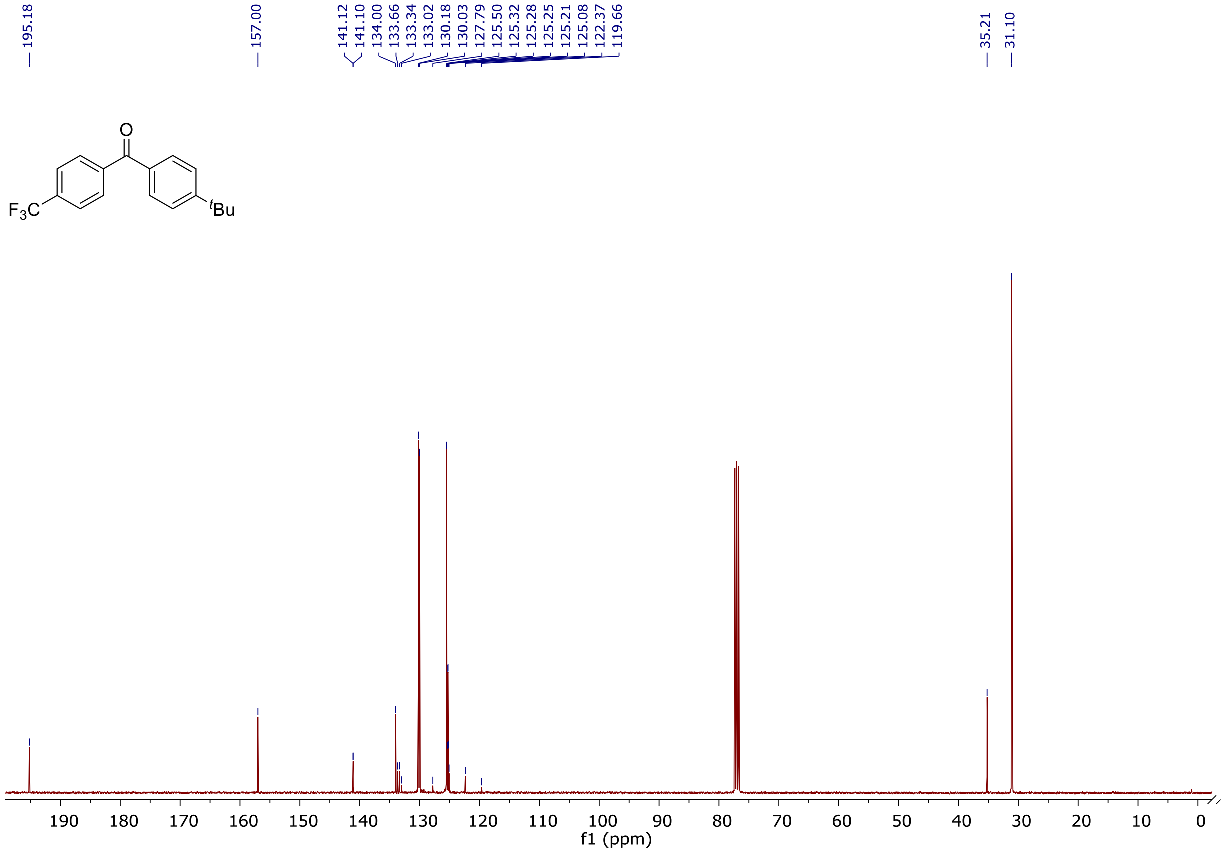
NMR-Spectra of ethyl 2-(4-cyanobenzoyl)benzoate (5i)





NMR-Spectra of (4-(*tert*-butyl)phenyl)(4-(trifluoromethyl)phenyl)methanone (5j)

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141.12
141.10
134.00
133.66
133.34
133.02
130.18
130.03
127.79
125.50
125.32
125.28
125.25
125.21
125.08
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31.10
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F3C
tBu
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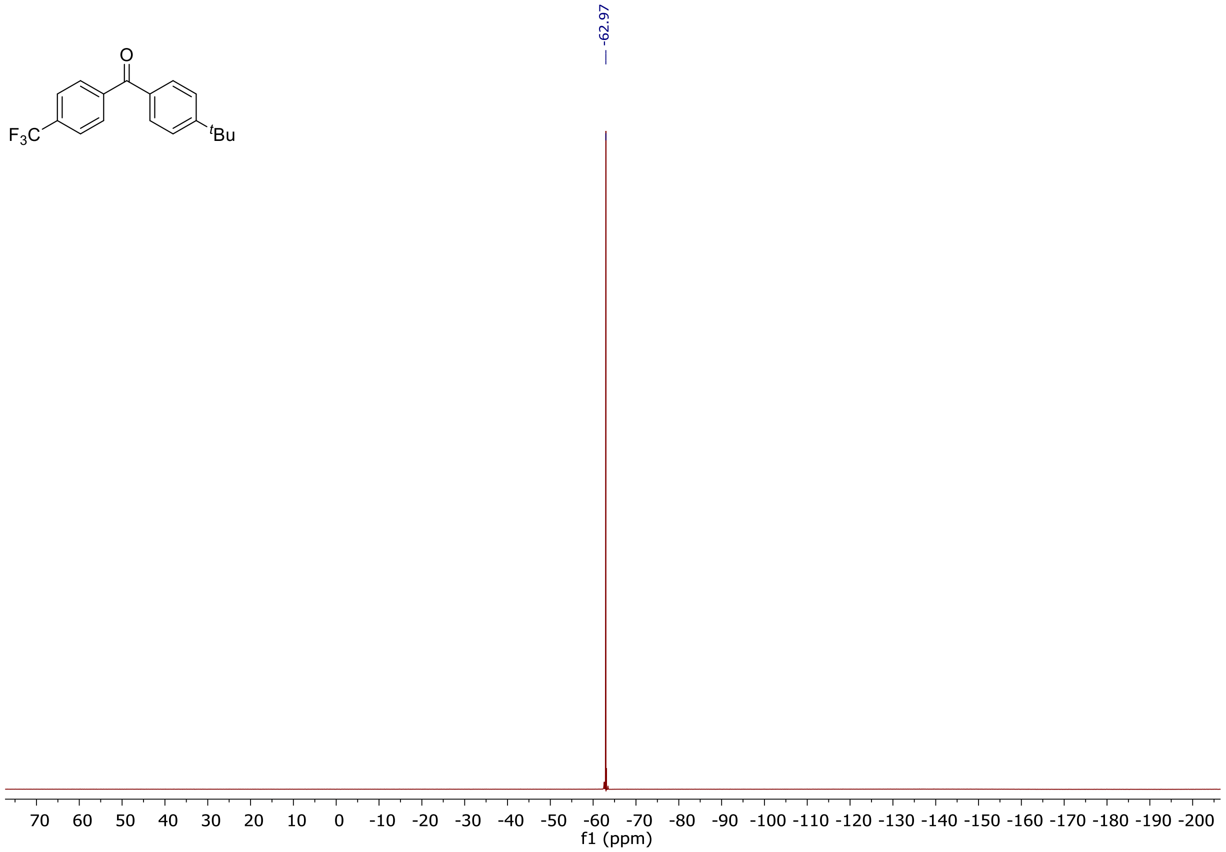
f1 (ppm)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O
F3C
tBu
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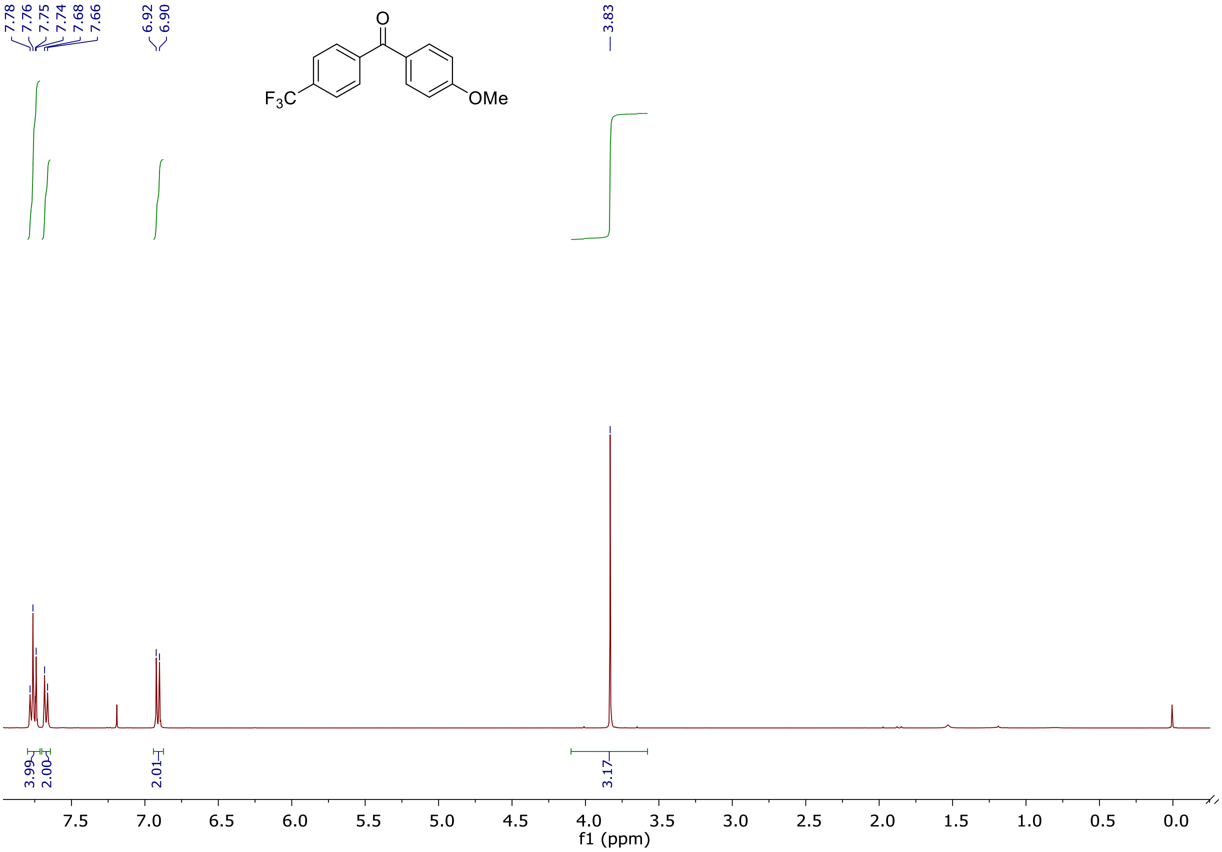
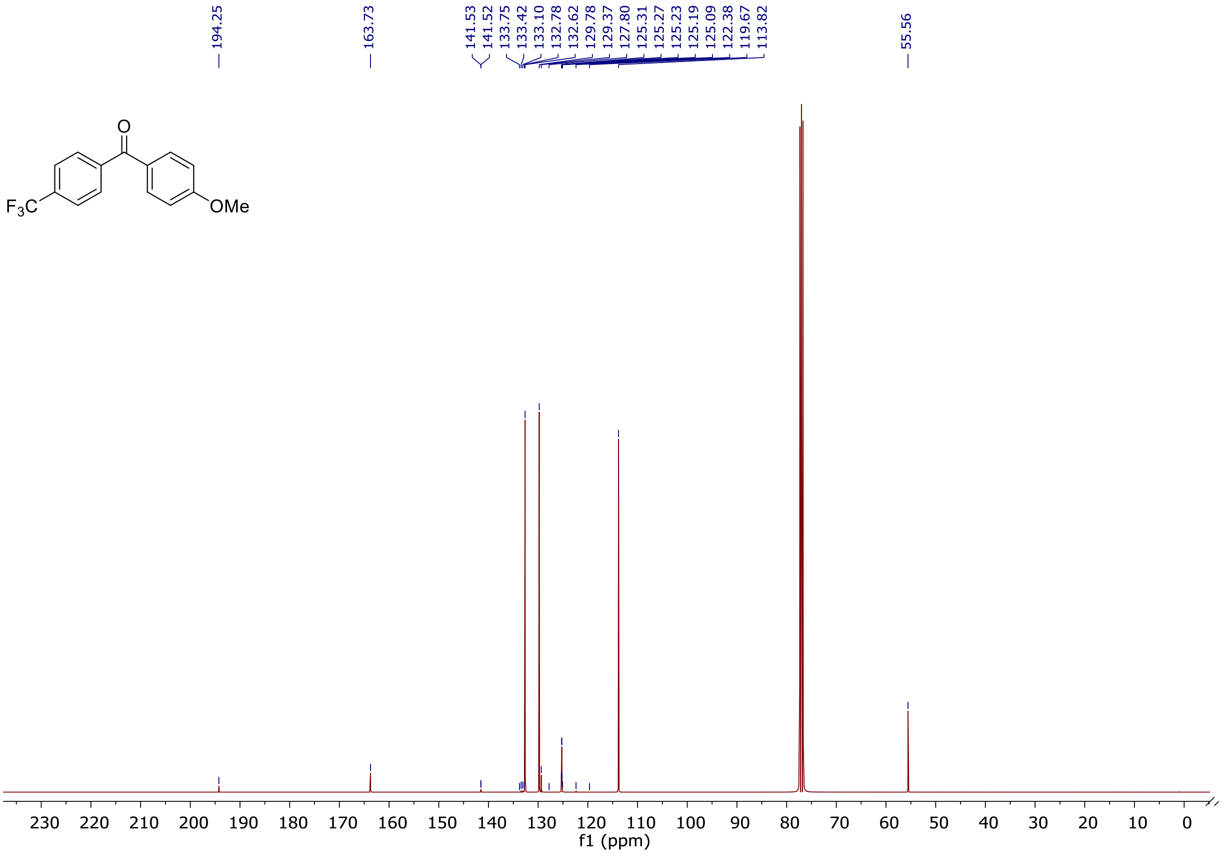
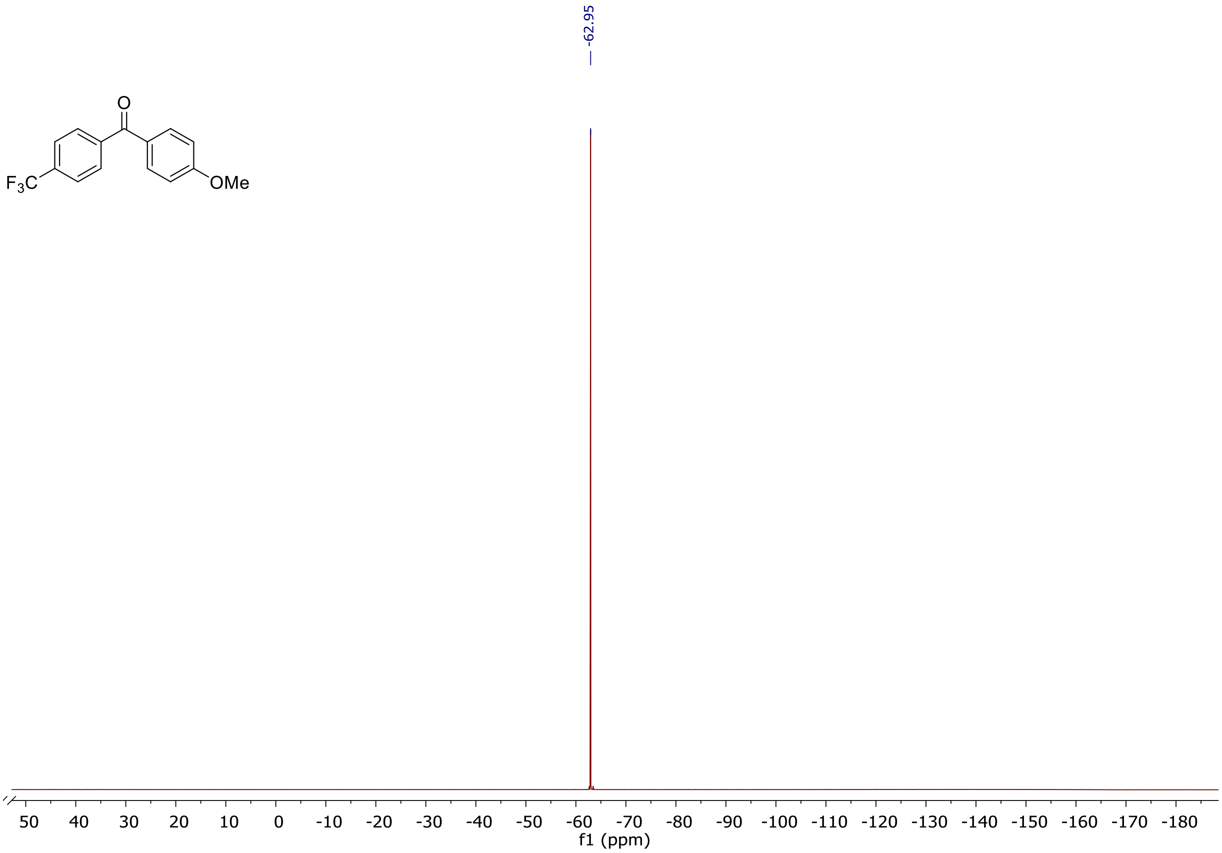
f1 (ppm)

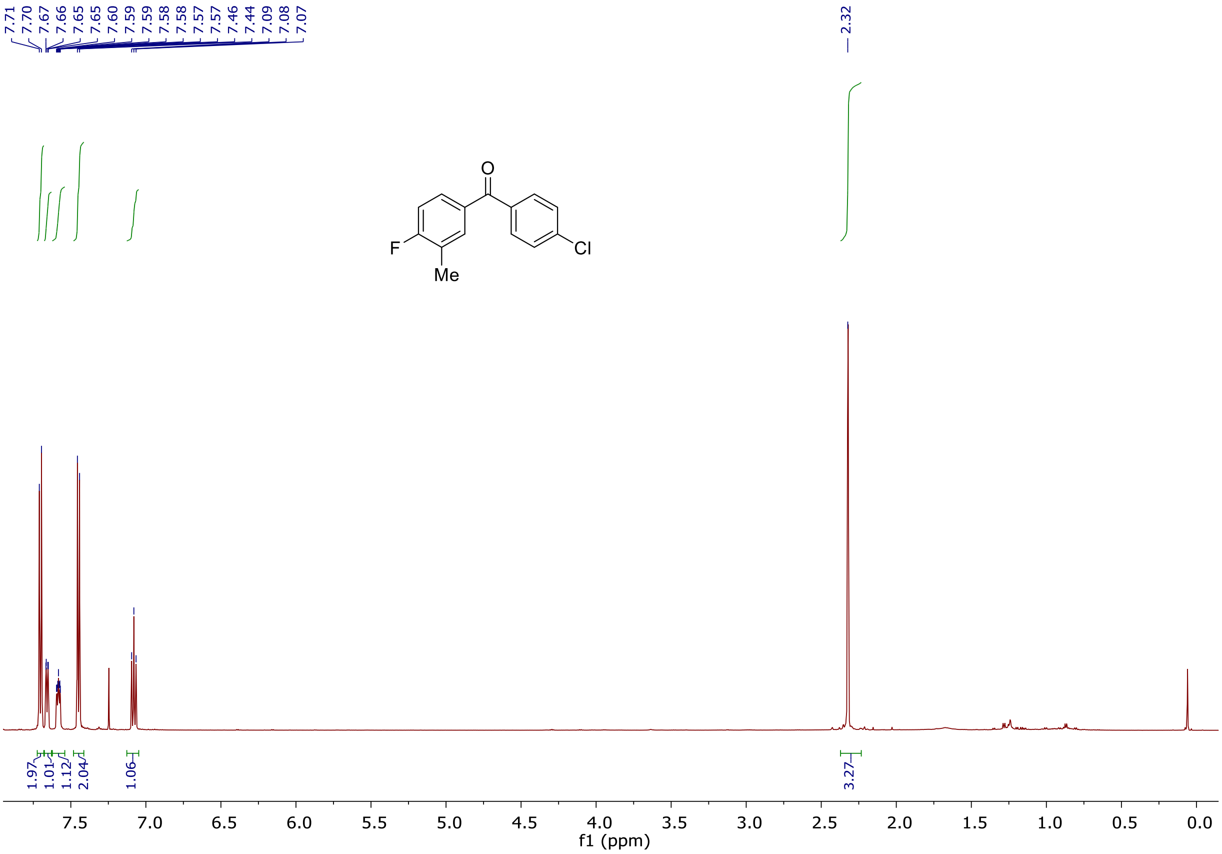
NMR-Spectra of (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (5k)

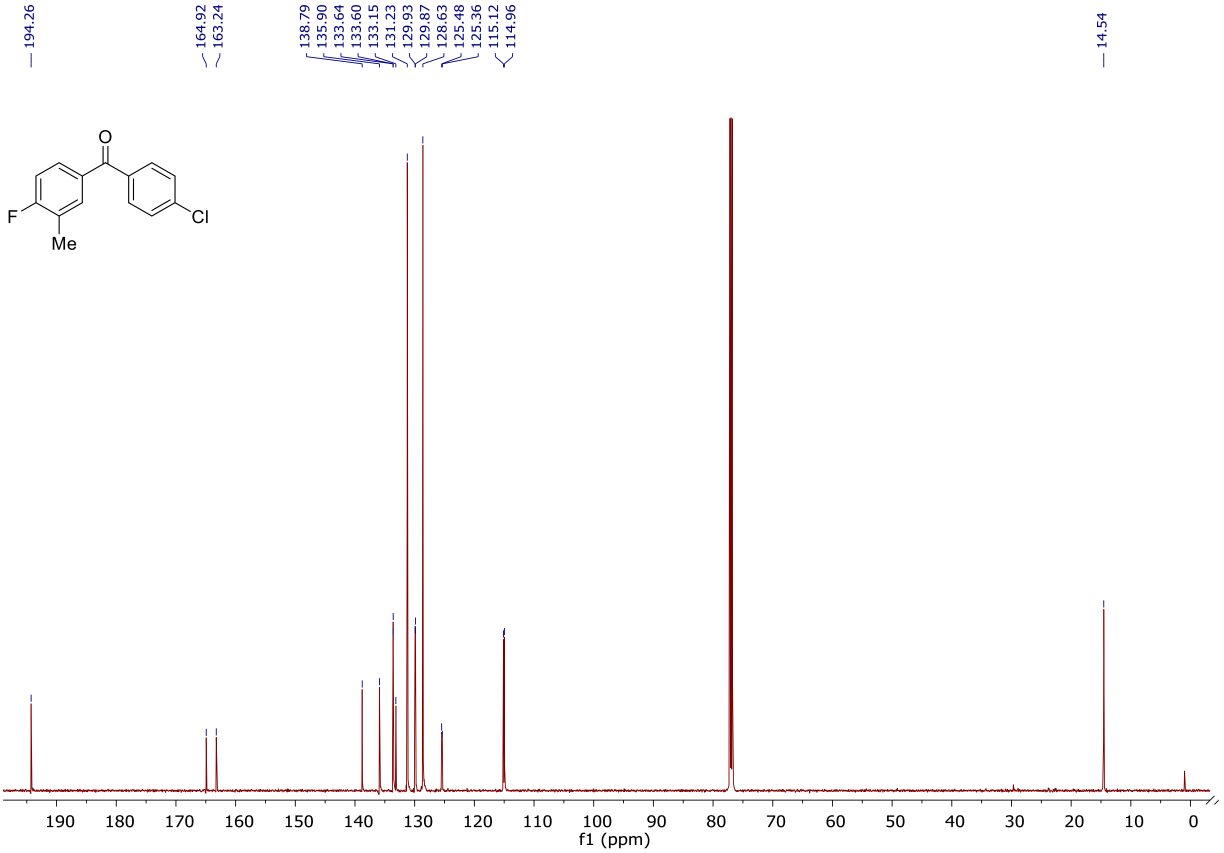


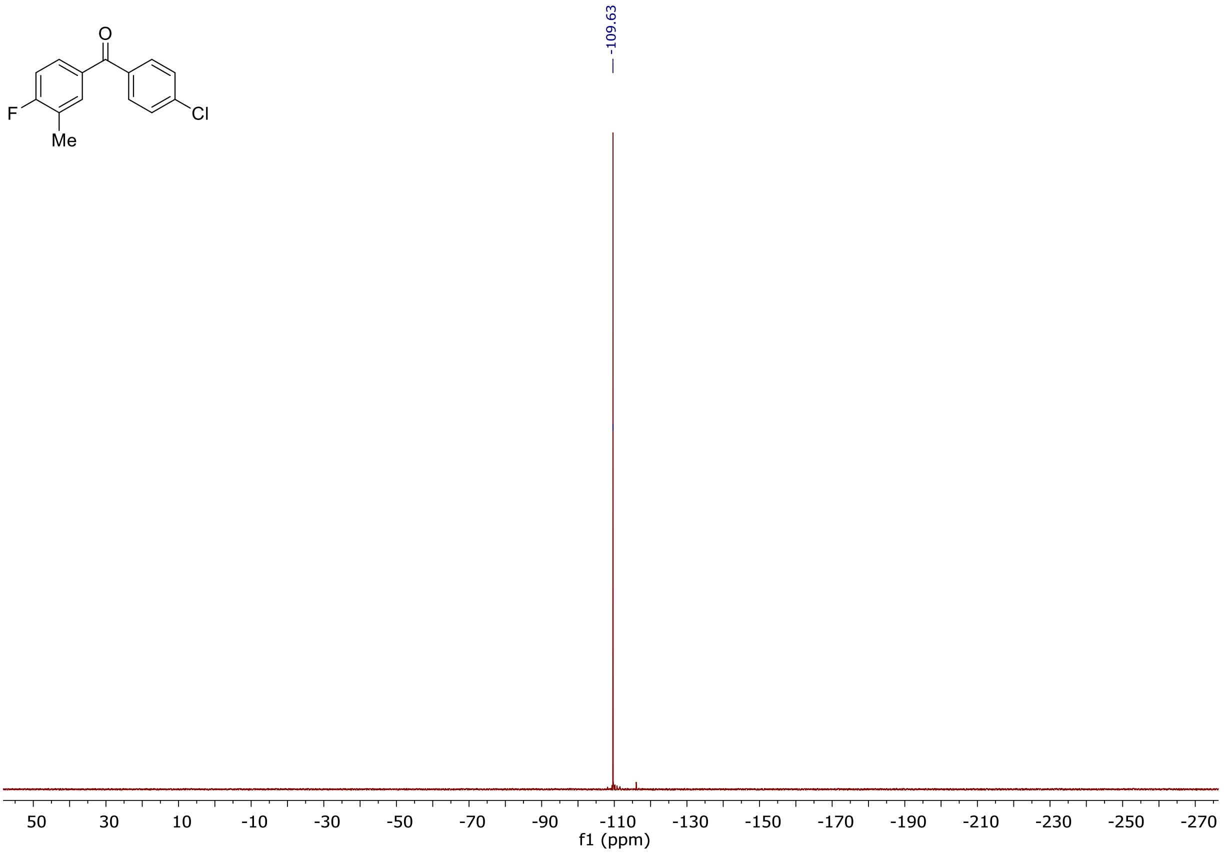




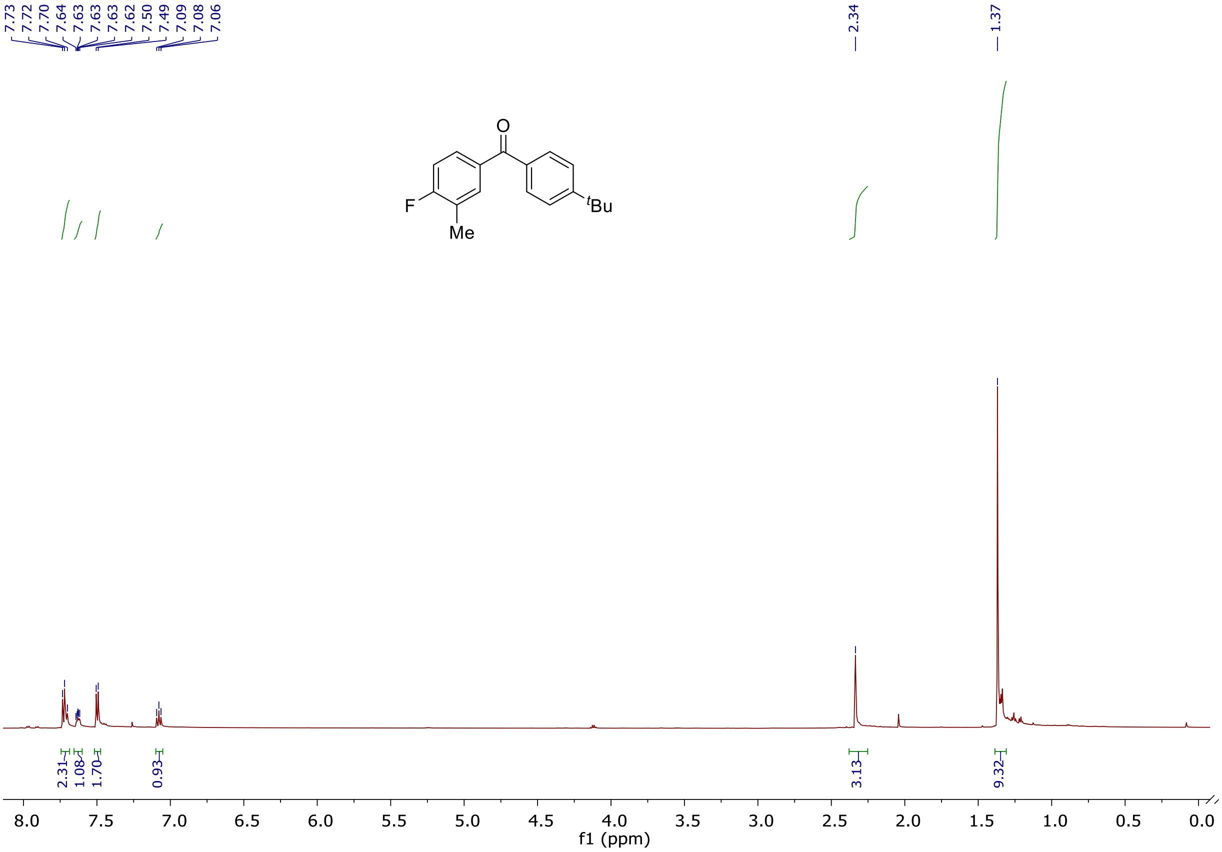
NMR-Spectra of (4-chlorophenyl)(4-fluoro-3-methylphenyl)methanone (5l)

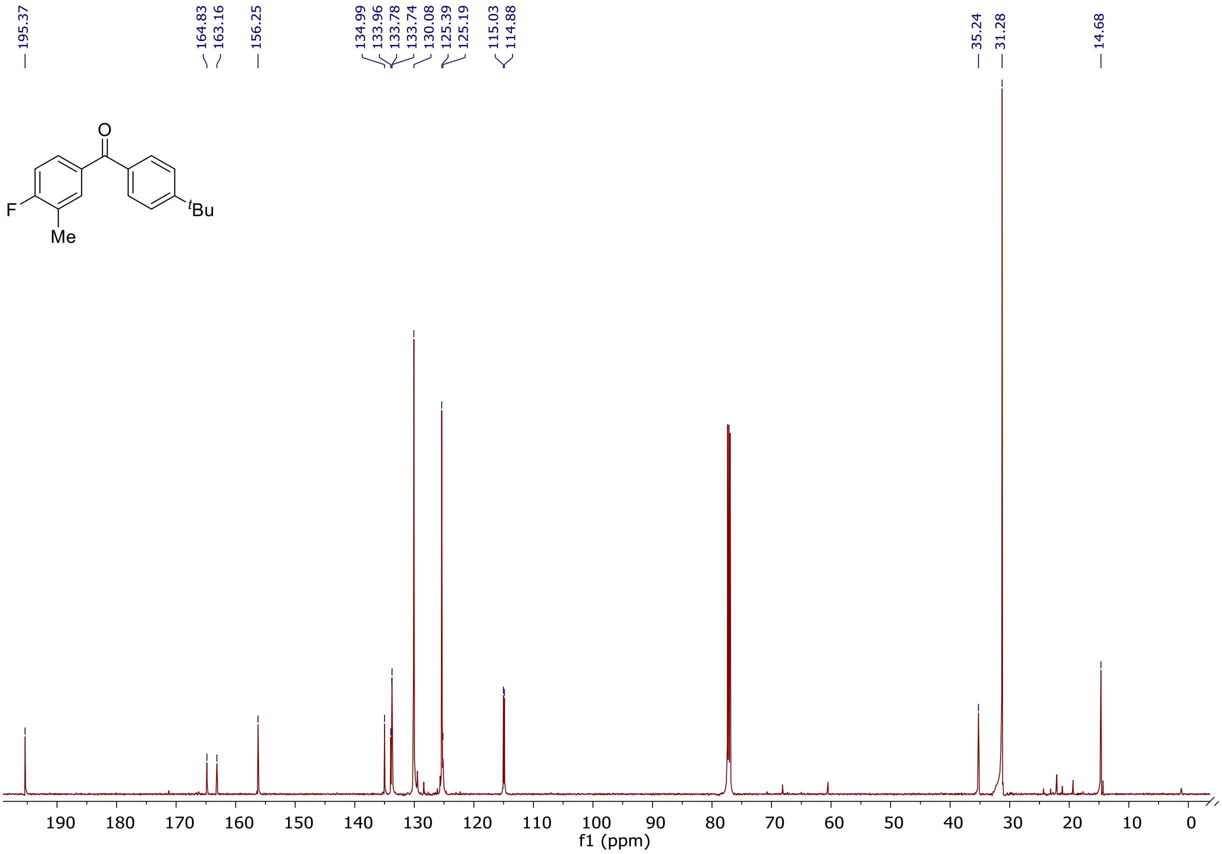


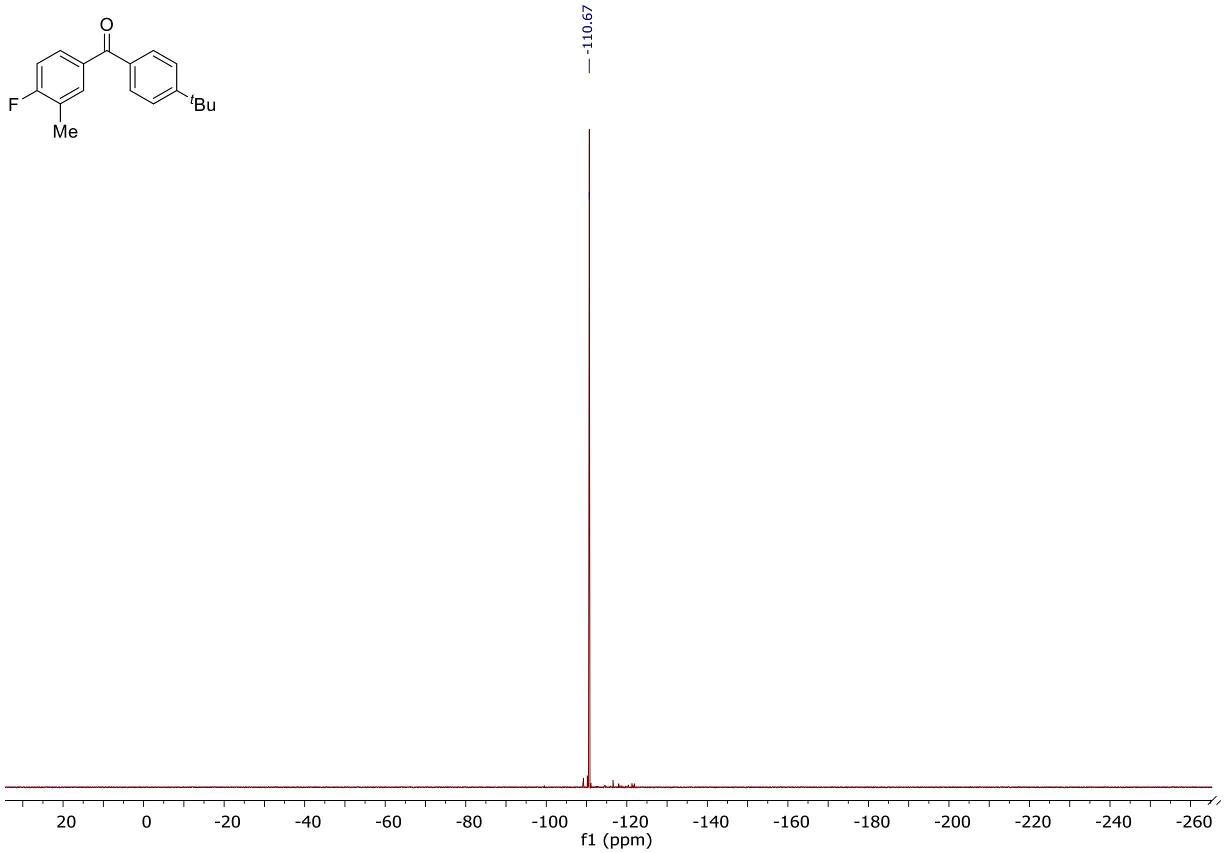

194.26
164.92
163.24
138.79
135.90
133.64
133.60
133.15
131.23
129.93
129.87
128.63
125.48
125.36
115.12
114.96
14.54
O
F
Me
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-109.63
O
F
Me
Cl
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270
f1 (ppm)

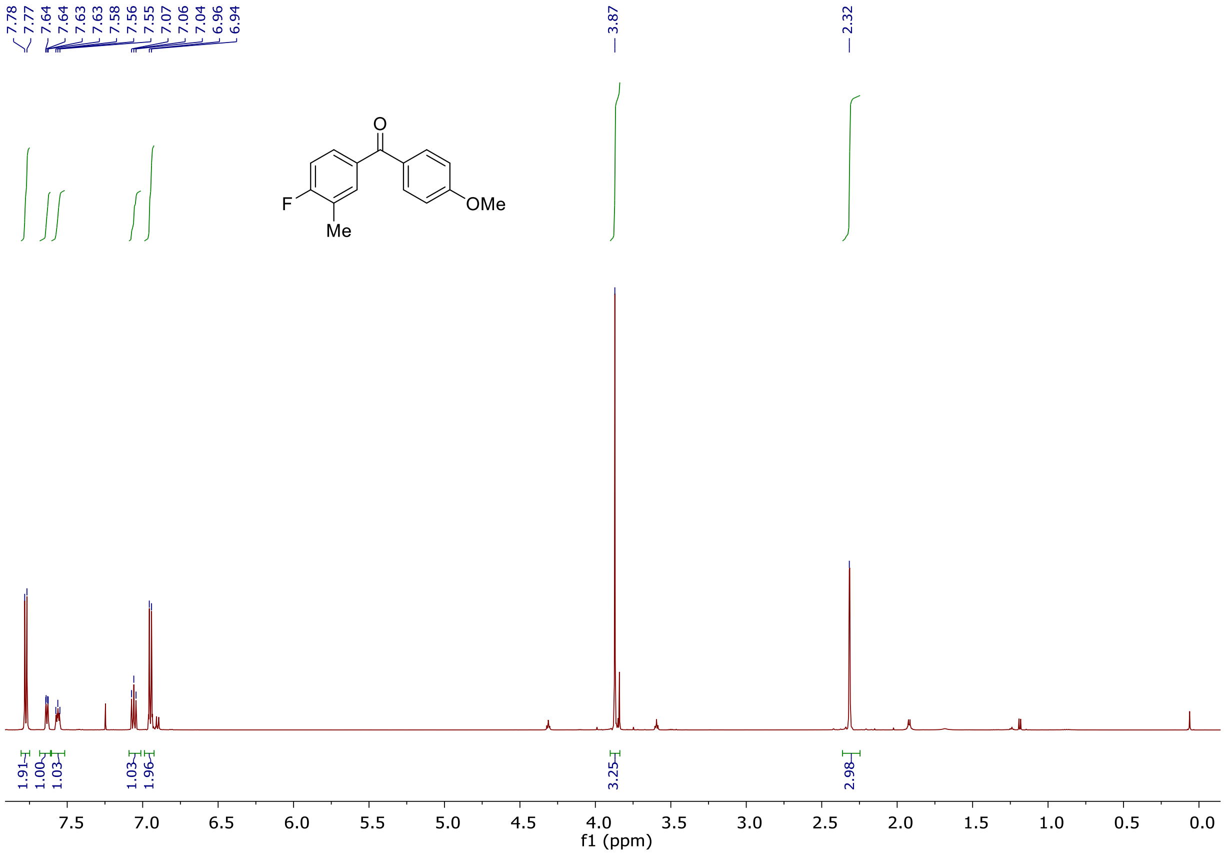
NMR-Spectra of (4-(*tert*-butyl)phenyl)(4-fluoro-3-methylphenyl)methanone (5m)

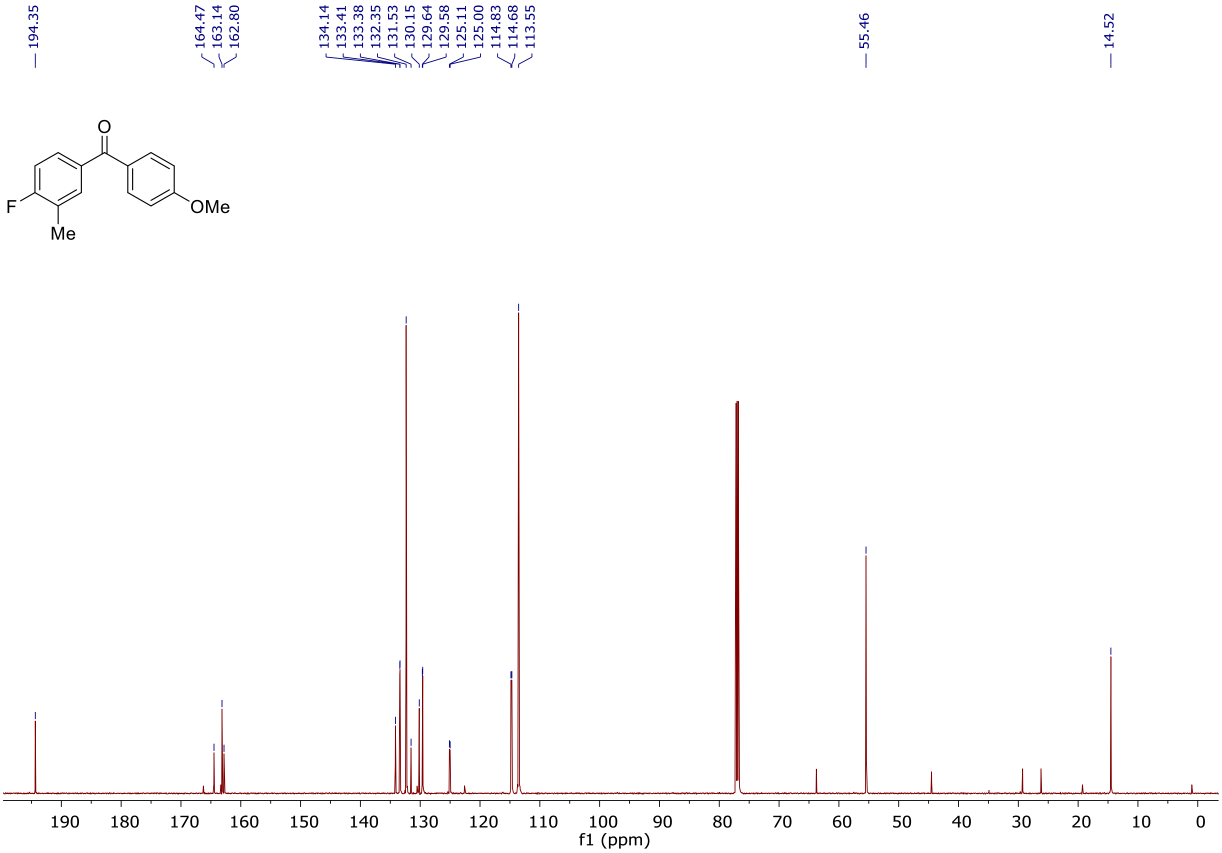






NMR-Spectra of (4-fluoro-3-methylphenyl)(4-methoxyphenyl)methanone (5n)

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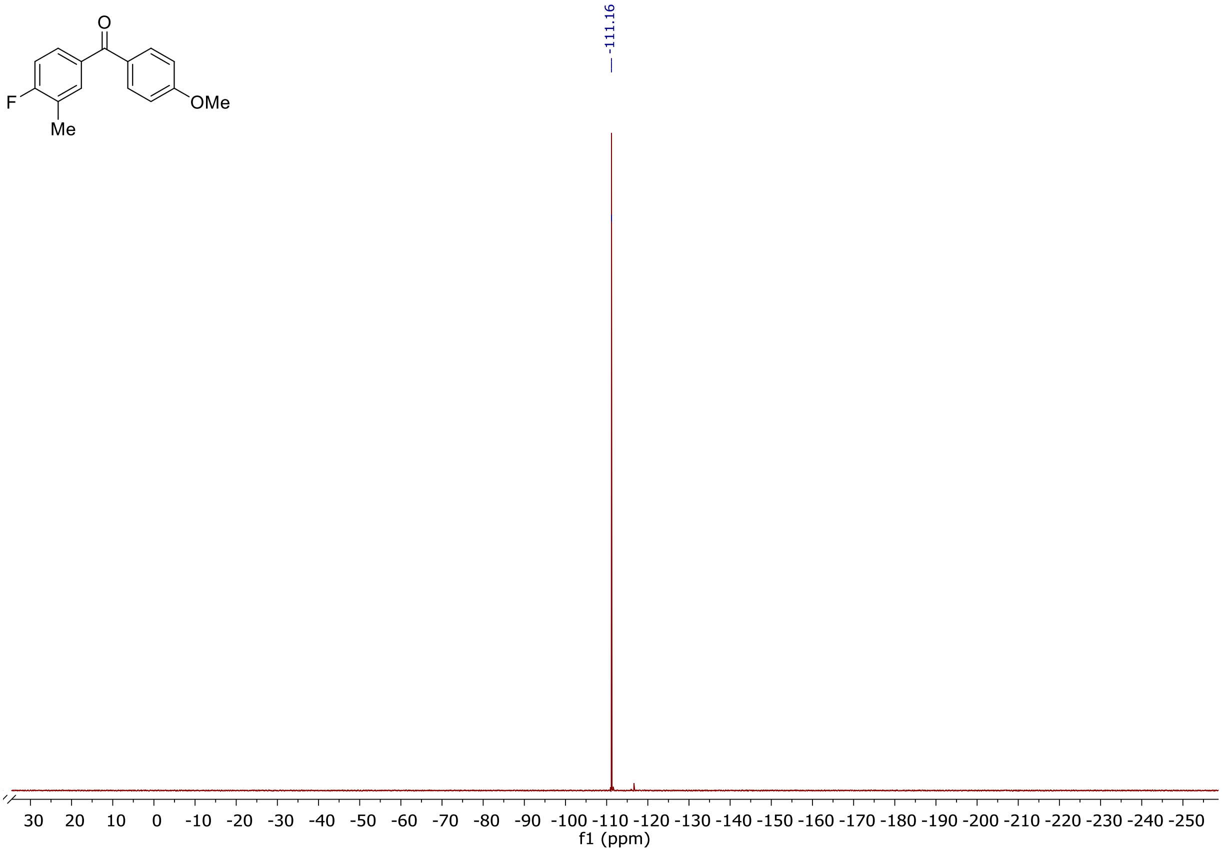
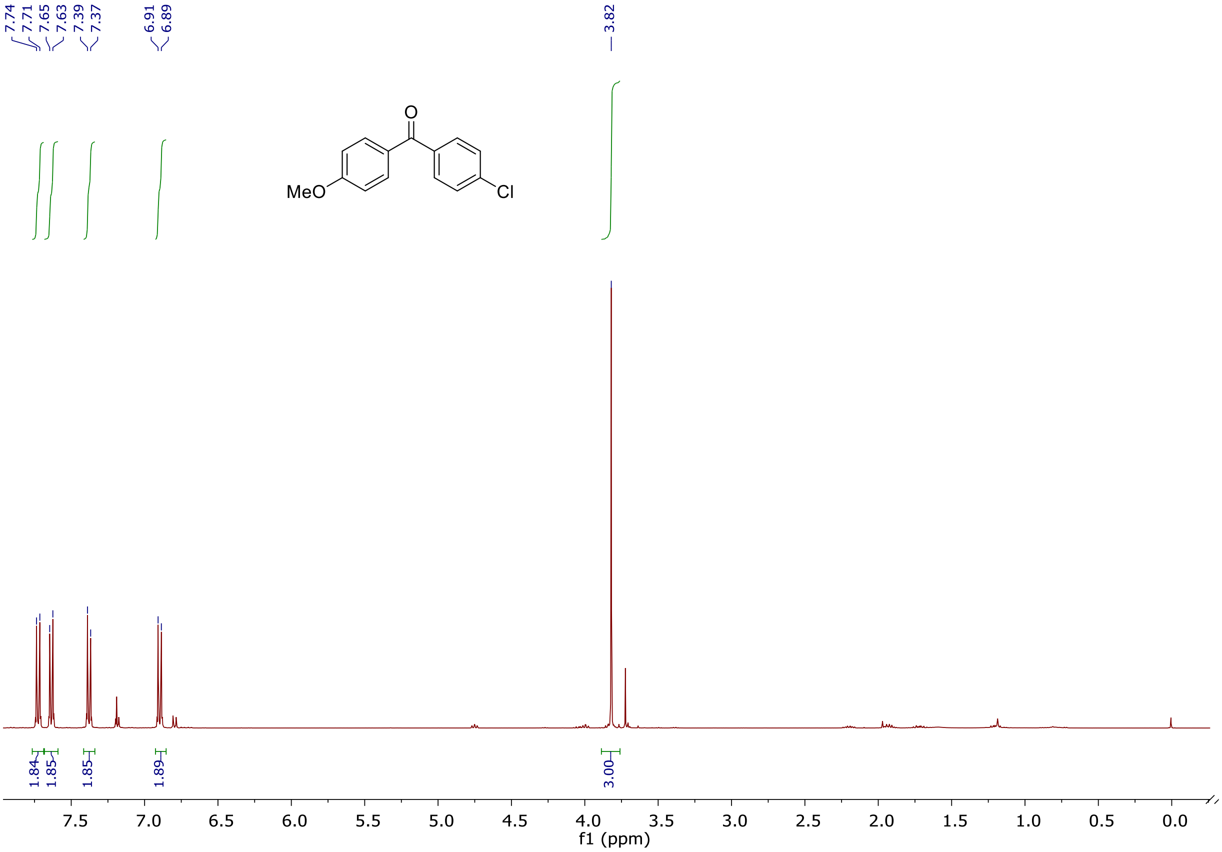
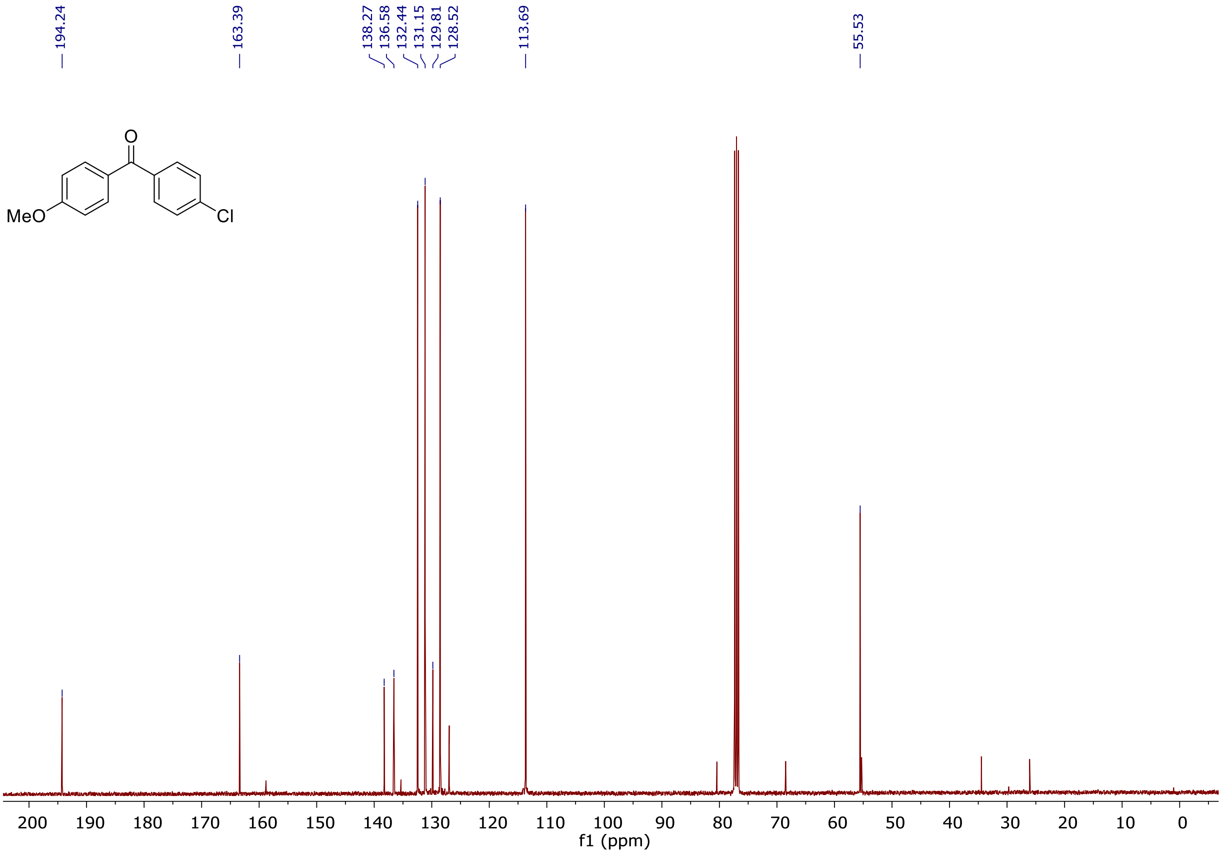
164.47
163.14
162.80
134.14
133.41
133.38
132.35
131.53
130.15
129.64
129.58
125.11
125.00
114.83
114.68
113.55
55.46
14.52
O
F
Me
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

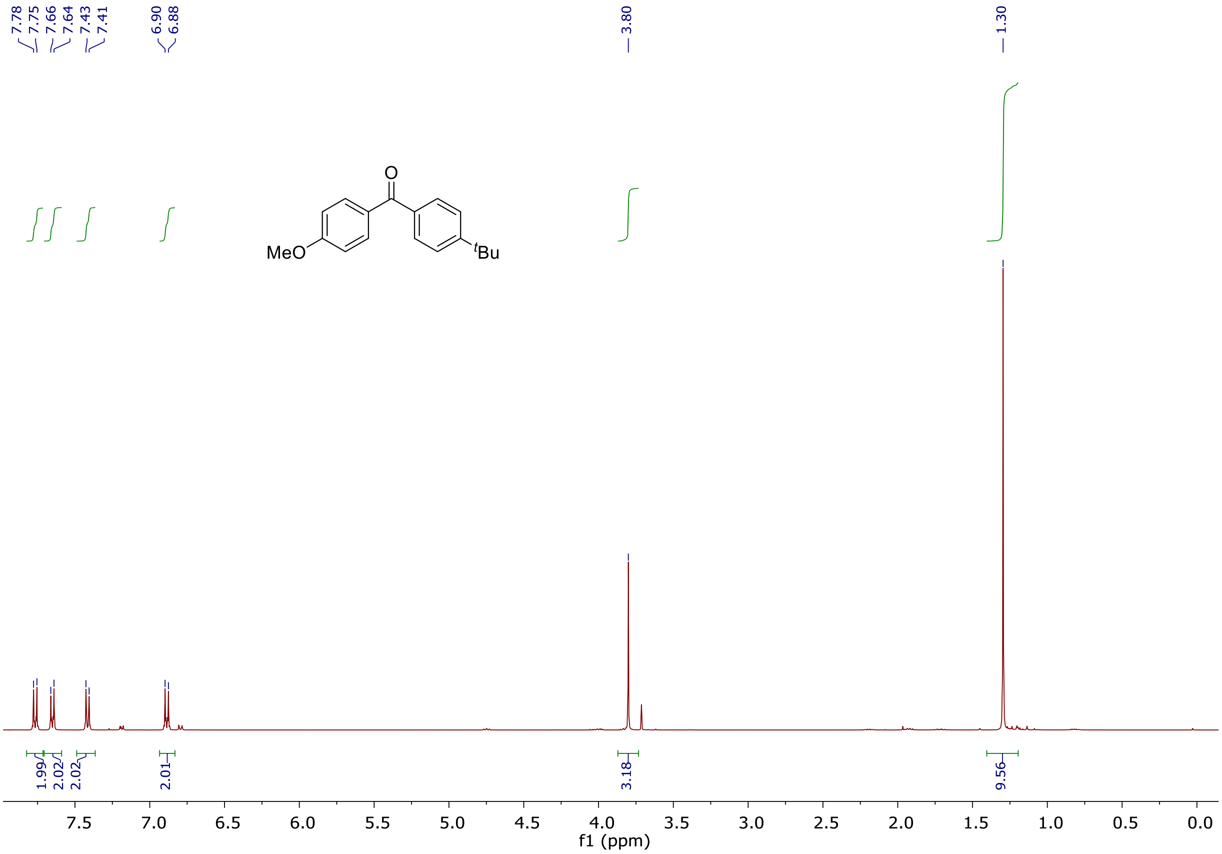

-111.16
O
F
Me
OMe
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

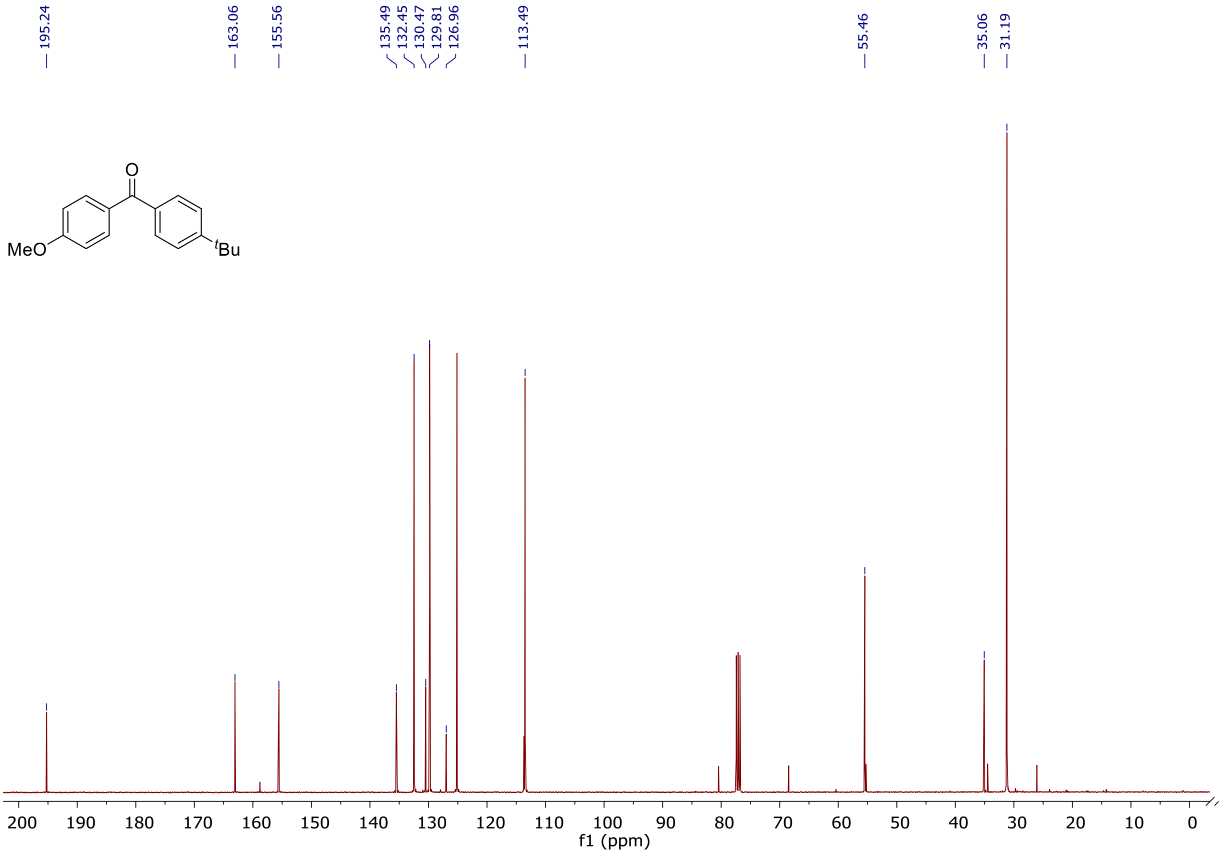
NMR-Spectra of (4-chlorophenyl)(4-methoxyphenyl)methanone (5o)



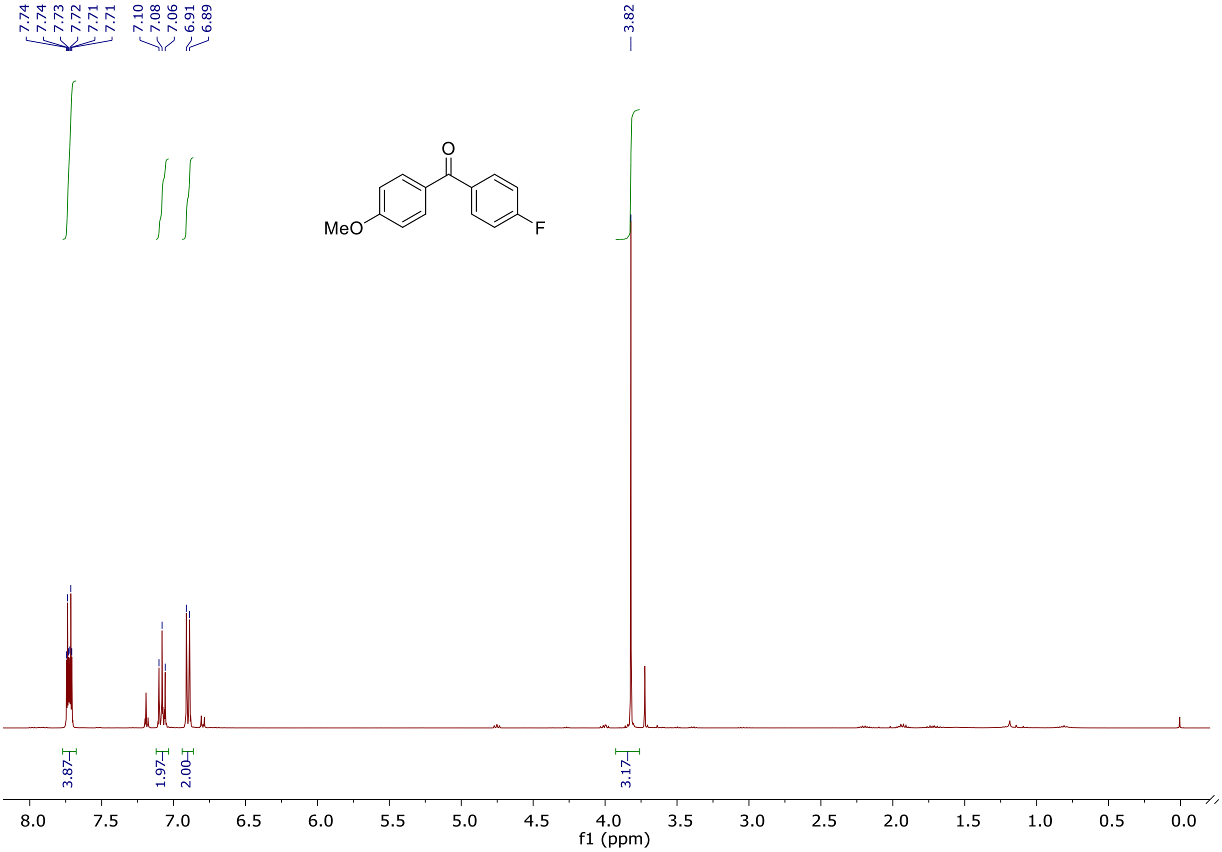


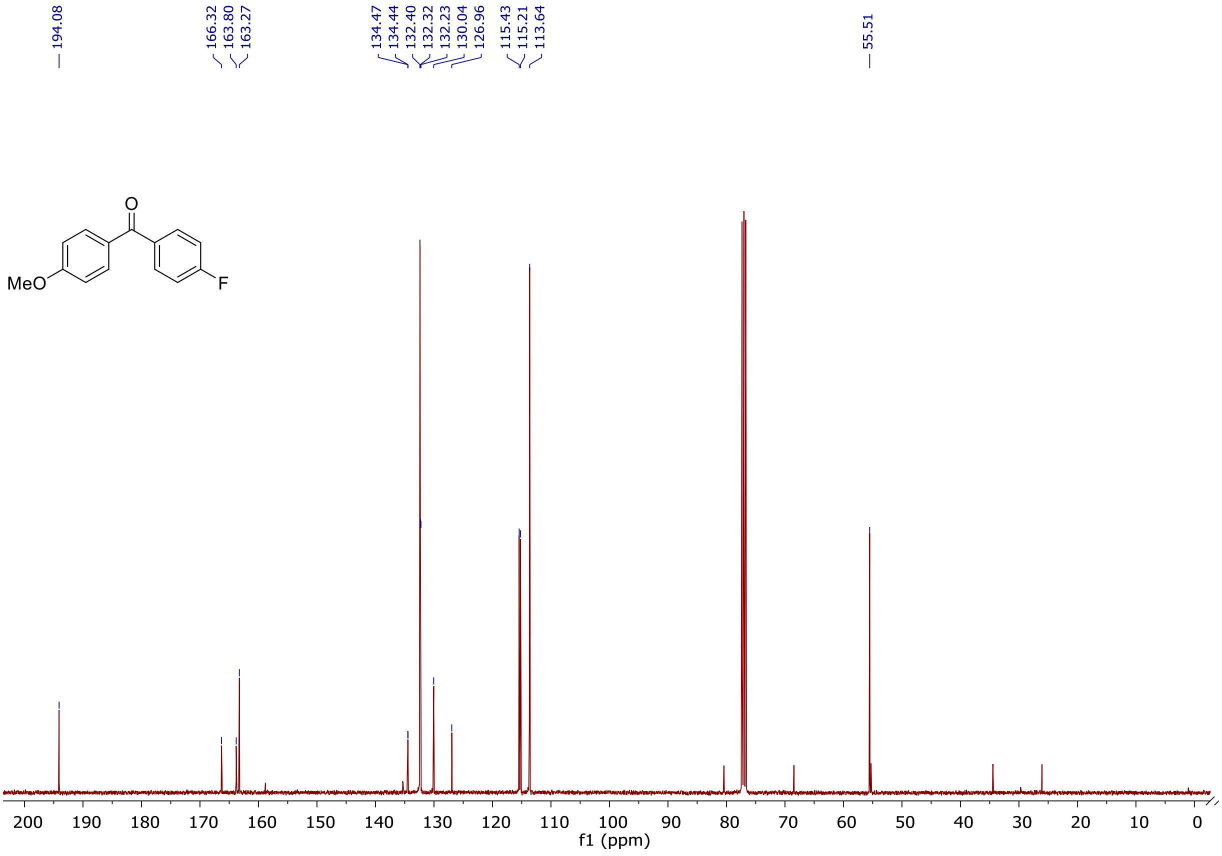
NMR-Spectra of (4-(*tert*-butyl)phenyl)(4-methoxyphenyl)methanone (5p)





NMR-Spectra of (4-fluorophenyl)(4-methoxyphenyl)methanone (5q)





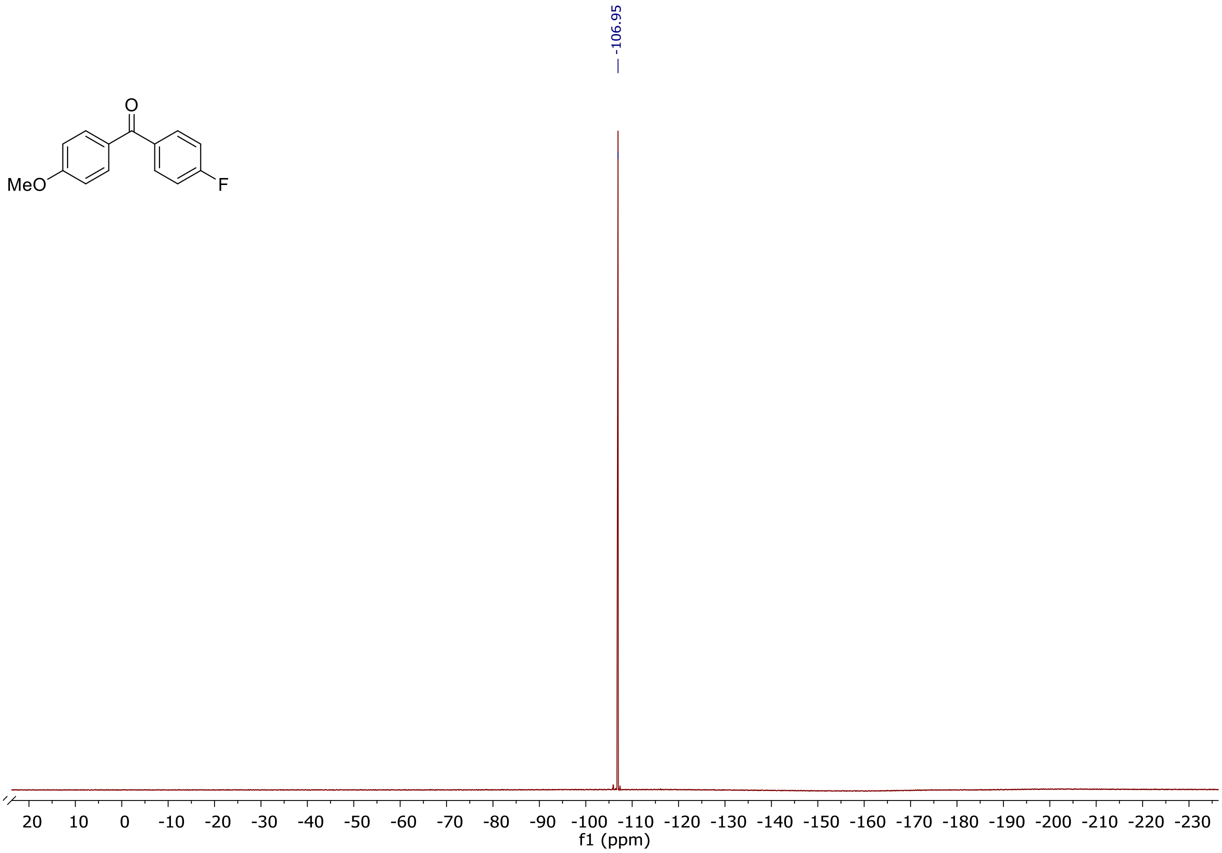
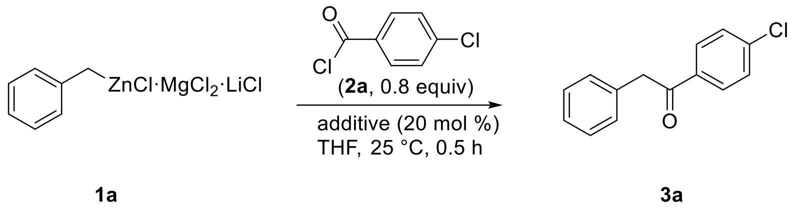

-106.95
O
MeO
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

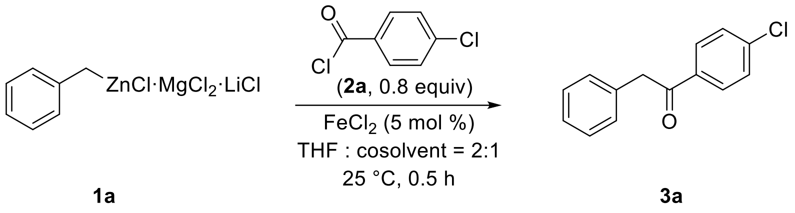
Table 1. Additional Screening of Additives for the Acylation of Benzylzinc Chloride (1a) with 4-Chlorobenzoyl Chloride (2a)



entry	additive	yield (%)[a]
1	4-DMAP	55
2	$Sc(OTf)_3$	54
3	$InCl_3$	traces
4	$TiCl_4$	traces[b]
5	$BF_3{\cdot}OEt_2$	40
6	$LaCl_3{\cdot}2LiCl$	traces

[a] Isolated yield of pure product; [b] Almost quantitative amounts of homo-coupling were observed.

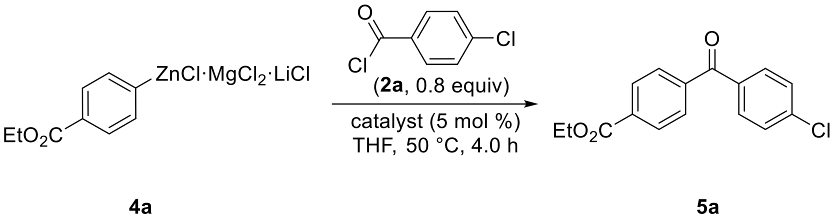
Table 2. Additional Screening of Polar Cosolvents for the Acylation of Benzylzinc Chloride (1a) with 4-Chlorobenzoyl Chloride (2a)



entry	solvent ratio	yield (%)[a]
1	THF : MeCN	87
2	THF : NMP	83
3	THF : DMPU	68
4	THF : Dioxan	64
5	THF : DMF	29
6	THF : DMAc	traces

[a] Isolated yield of pure product.

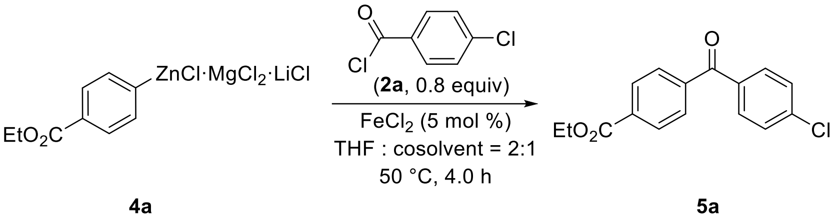
Table 3. Additional Screening of Catalysts for the Acylation of (4-(ethoxycarbonyl)phenyl)-zinc(II) chloride (4a) with 4-Chlorobenzoyl Chloride (2a)



entry	catalyst	yield (%)[a]
1	-	34
2	$Fe(OTf)_3$	34
3	$Fe(acac)_3$	36
4	$FeBr_3$	53
5	$Fe(acac)_2$	60
6	$FeBr_2$	56
7	$FeCl_2$	62

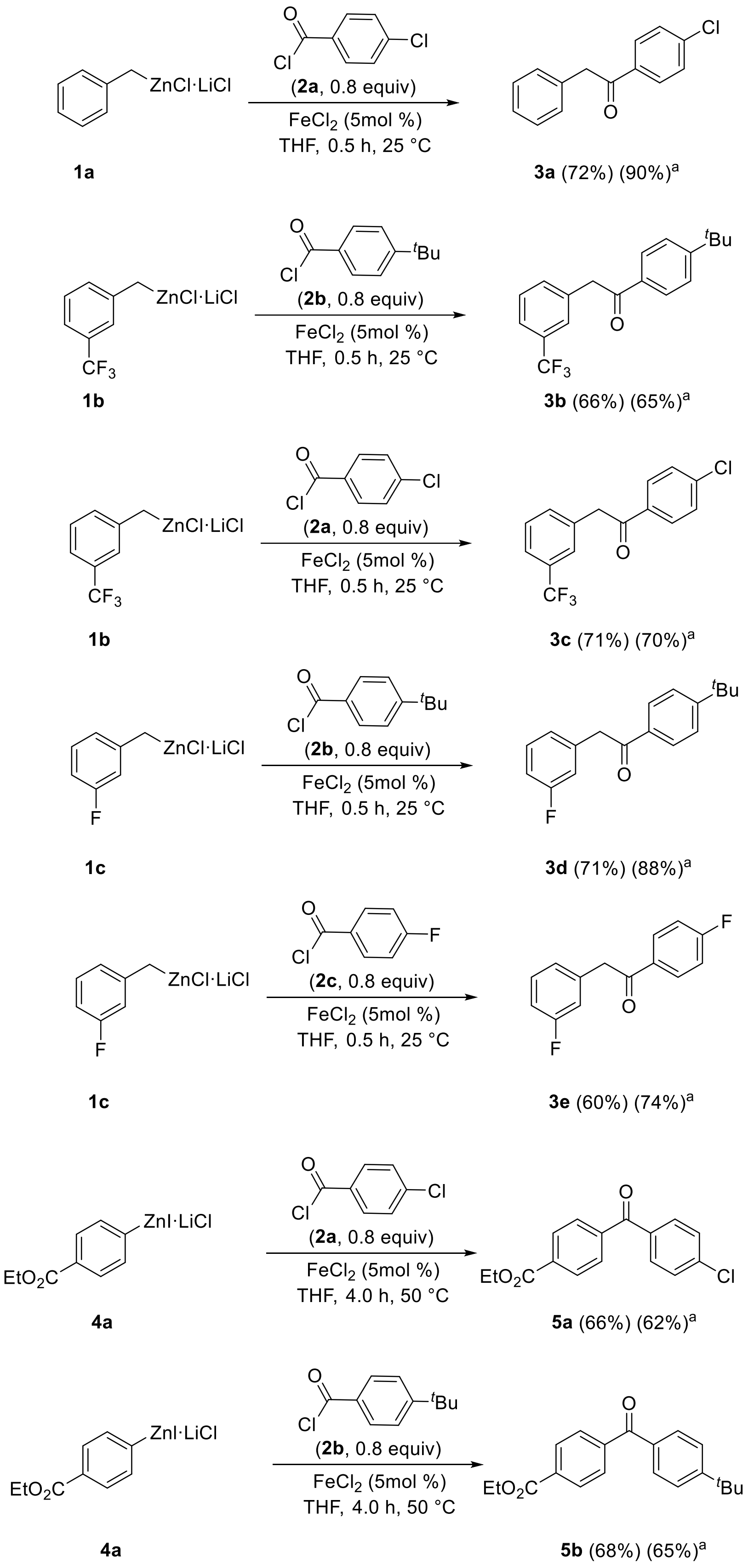
[a] Isolated yield of pure product.

Table 4. Additional Screening of Polar Cosolvents for the Acylation of (4-(ethoxycarbonyl)-phenyl)zinc(II) chloride (4a) with 4-Chlorobenzoyl Chloride (2a)



entry	solvent ratio	yield (%)[a]
1	THF : DMF	38
2	THF : NMP	42
3	THF : DMPU	45
4	THF : MeCN	60
5	THF : Dioxan	64
6	THF : DMAc	64

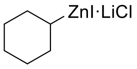
[a] Isolated yield of pure product.



Scheme 1: Iron-catalyzed acylations of aryl- and benzyl-halides (**1a-c**, **4a**), prepared by the direct oxidative insertion of zinc dust in the presence of LiCl, with acid chlorides (**2a-c**).[a] Yields refer to isolated yields of pure products obtained by using the *in situ* transmetalated organozinc species.

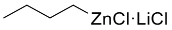
Preliminary Experiments towards Iron-Catalyzed Acylation of Alkylzinc Halides (6a,b)

Preparation of cyclohexylzinc(II) iodide (6a)



A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with LiCl (0.95 g, 22.5 mmol, 1.50 equiv) and heated up to ca. 450 °C for 5 min under high vacuum using a heat gun. After cooling to room temperature under vigorous stirring, Zn dust (2.94 g, 45.0 mmol, 3.00 equiv) was added and heated up to ca. 450 °C for 5 min one more time. Freshly distilled THF (15 mL), trimethylsilyl chloride (5 mol %) and 1,2-dibromoethane (5 mol %) were added and the suspension was heated shortly to reflux. Iodocyclohexane (3.15 g, 1.94 mL, 15.0 mmol, 1.00 equiv) was added dropwise at room temperature and the reaction mixture was stirred for additional 30 min. The completion of the metalation was monitored by GC-analysis of hydrolyzed and iodolyzed aliquots. When the oxidative insertion was complete, the solution was separated from the zinc dust *via* a syringe equipped with a filter and transferred to another pre-dried and argon-flushed *Schlenk*-tube. The concentration of cyclohexylzinc(II) iodide (**6a**) was determined by titration with iodine in THF (0.80 M).

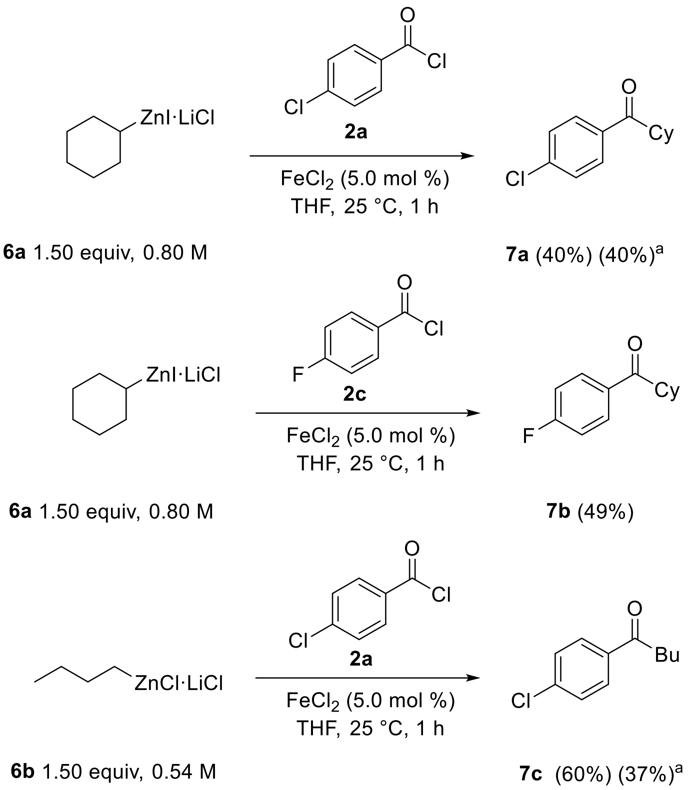
Preparartion of butylzinc(II) chloride (6b)



A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with *n*BuLi (3.85 mL, 2.60 M in hexane, 10.0 mmol) and cooled to -40 °C. $ZnCl_2$ (12.0 mL, 1.00 M in THF, 12.0 mmol) was added and to resulting solution was stirred for additional 10 min. The concentration of butylzinc(II) chloride (**6b**) was determined by titration with iodine in THF (0.54 M).

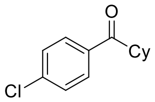
Typical Procedure for the Iron-Catalyzed Acylation of Alkylzinc Halides (6a,b) with Acid Chlorides (TP 5):

A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with $FeCl_2$ (6.34 mg, 0.05 mmol, 5.0 mol %), the selected acid chloride (1.00 mmol, 1.00 equiv) and freshly distilled THF (1 mL). The corresponding prior prepared alkylzinc halide solution (1.50 mmol, 1.50 equiv) was dropwise added and the reaction mixture was stirred for a given time at room temperature. Subsequently, the reaction mixture was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude products by flash column chromatography afforded the desired products.



Scheme 2: Iron-catalyzed acylations of alkylzinc halides (**6a**,**b**) with acid chlorides (**2a**,**c**). [a] A solvent mixture of THF:NMP = 1:1 was used, see reference 8b in the manuscript.

Preparation of cyclohexyl(4-chlorophenyl)methanone (7a)



According to **TP5**, $FeCl_2$ 6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The cyclohexylzinc(II) iodide (**6a**, 1.88 mL, 1.50 mmol, 0.80 M in THF, 1.50 equiv) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, $R_f = 0.40$) leading to the product **7a** (88 mg, 0.40 mmol, 40%) as a pale yellow oil.

The analytical data of product **7a** is consistent with the data given in the literature.[1]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 3.25-3.20 (m, 1H), 1.88-1.84 (m, 4H), 1.77-1.74 (m, 1H), 1.56-1.24 (m, 5H)

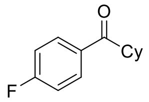
^{13}C-NMR (100 MHz, CDCl$_3$, ppm) δ = 202.4, 139.3, 134.5, 129.7, 128.9, 45.6, 29.4, 25.8, 25.7.

IR (ATR, cm^{-1}) ṽ = 2929, 2854, 1714, 1681, 1590, 1572, 1487, 1449, 1400, 1371, 1315, 1274, 1249, 1206, 1171, 1114, 1104, 1090, 1037, 1013, 974, 893, 834, 760, 738, 685.

MS (EI, 70 eV, %) m/z = 222 (5), 187 (11), 157 (16), 141 (28), 139 (100), 111 (16), 82 (14), 67 (10), 55 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{13}H_{15}ClO$**: 222.0811; found 222.0814.

Preparation of cyclohexyl(4-fluorophenyl)methanone (7b)



According to **TP5**, FeCl$_2$ 6.34 mg, 0.05 mmol, 5.0 mol %), 4-fluorobenzoyl chloride (**2c**, 159 mg, 0.12 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The cyclohexylzinc(II) iodide (**6a**, 1.88 mL, 1.50 mmol, 0.80 M in THF, 1.50 equiv) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated aqueous NH$_4$Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO$_2$, *i*-hexane : EtOAc = 99 : 1, R$_f$ = 0.44) leading to the product **7b** (101 mg, 0.49 mmol, 49%) as a pale yellow oil.

The analytical data of product **7b** is consistent with those given in the literature.[1]

^{1}H-NMR (400 MHz, CDCl$_3$, ppm) δ = 8.00-7.97 (m, 2H), 7.14 (t, *J* = 8.8 Hz, 2H), 3.26-3.19 (m, 1H), 1.90-1.85 (m, 4H), 1.77-1.73 (m, 1H), 1.55-1.26 (m, 5H).

^{13}C-NMR (100 MHz, CDCl$_3$, ppm) δ = 202.2, 165.6 (d, ^{1}J(C,F) = 252 Hz), 132.6 (d, ^{4}J(C,F) = 2.4 Hz), 130.9 (d, ^{3}J(C,F) = 8.7 Hz), 115.7 (d, ^{2}J(C,F) = 22 Hz), 45.6, 29.4, 25.9, 25.8.

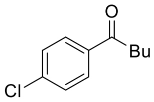
^{19}F-NMR (376 MHz, CDCl$_3$, ppm) δ = – 106.0.

IR (ATR, cm^{-1}) ṽ = 2929, 2855, 1714, 1680, 1597, 1505, 1450, 1410, 1372, 1313, 1277, 1234, 1206, 1154, 1113, 1091, 1013, 975, 894, 842, 768, 740, 675.

MS (EI, 70 eV, %) m/z = 207 (14), 206 (4), 124 (10), 123 (100), 109 (16), 95 (12), 83 (15), 55 (16), 41 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{13}H_{15}FO$**: 206.1107; found 206.1108.

Preparation of 1-(4-chlorophenyl)pentan-1-one (7c)



Based on **TP5**, $FeCl_2$ 6.34 mg, 0.05 mmol, 5.0 mol %), 4-chlorobenzoyl chloride (**2a**, 175 mg, 0.13 mL, 1.00 mmol, 1.00 equiv) and freshly distilled THF (1.0 mL) were used. The butylzinc(II) chloride (**6b**, 2.78 mL, 1.50 mmol, 0.54 M in THF, 1.50 equiv) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, *i*-hexane : EtOAc = 99 : 1, $R_f = 0.55$) leading to the product **7c** (118 mg, 0.60 mmol, 60%) as a colorless oil.

The analytical data of product **7c** is consistent with those given in the literature.[2]

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ = 7.90-7.87 (dt, *J* = 2.4, 8.8 Hz, 2H), 7.43-7.40 (dt, *J* = 2.4, 8.8 Hz, 2H), 2.94-2.91 (t, *J* = 7.2 Hz, 2H), 1.74-1.67 (m, 2H), 1.44-1.35 (m, 2H), 0.96-0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ = 199.2, 139.2, 135.2, 129.4, 128.8, 38.3, 26.3, 22.4, 13.9.

IR (ATR, cm^{-1}) ṽ = 2958, 2932, 2873, 1722, 1687, 1590, 1572, 1488, 1400, 1271, 1205, 1174, 1090, 1012, 968, 838, 810, 793, 760, 733, 685.

MS (EI, 70 eV, %) m/z = 196 (1), 156 (11), 154 (26), 141 (30), 139 (100), 111 (20), 75 (10).

HRMS (EI, 70 eV) m/z: calc. for **$C_{11}H_{13}ClO$**: 196.0655; found 196.0642.

References

(1) Zhang, X.; Wang, Z.; Fan, X.; Wang, J. *J. Org. Chem.* **2015**, *80*, 10660.

(2) Genna, D. T.; Posner, G. H. *Org. Lett.* **2011**, *13*, 5358.