Nickel-Catalyzed Cross-Coupling of Functionalized Organomanganese Reagents with Aryl and Heteroaryl Halides promoted by 4-Fluorostyrene

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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. Methyl tert-butyl ether (MTBE) was 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: δ = 7.25 ppm for $^1$H-NMR and δ = 77.0 ppm for $^{13}$C-NMR). For the characterization of the observed signal multiplicities the following abbreviations were used: s (singlet), 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.
1. Preparation of Benzylic Manganese(II) Chlorides (1a-i):

Typical Procedure TP1:

A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), followed by freshly distilled THF (3.0 mL) or MTBE (1.9 mL) and a solution of MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF). The mixture was cooled to 0 °C, the corresponding benzylic chloride (3.0 mmol, 1.00 equiv) was added at once and maintained at 0 °C until a complete conversion of starting material was observed. The completion of the metalation was monitored by GC-analysis of hydrolysed and iodolysed aliquots. When the oxidative insertion was complete, the solution of benzylic manganese 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 with an iodine solution in THF.

1.1 Preparation of benzylmanganese(II) chloride (1a)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), THF (3.0 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. Benzyl chloride (2a, 0.38 g, 0.35 mL, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of benzylmanganese(II) chloride (1a) was determined by titration with iodine in THF (0.31 M, 70%).

1.2 Preparation of (4-(tert-butyl)benzyl)manganese(II) chloride (1b)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), THF (3.0 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. Subsequently, 1-(tert-butyl)-4-(chloromethyl)benzene (2b, 0.55 g, 0.58 mL, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of (4-(tert-butyl)benzyl)manganese(II) chloride (1b) was determined by titration with iodine in THF (0.37 M, 84%).
1.3 Preparation of (3-methoxybenzyl)manganese(II) chloride (1c)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), THF (3.0 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. 1-(Chloromethyl)-3-methoxybenzene (2c, 0.47 g, 0.44 mL, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of (3-methoxy-benzyl)manganese(II) chloride (1c) was determined by titration with iodine in THF (0.32 M, 73%).

1.4 Preparation of (2-chlorobenzyl)manganese(II) chloride (1d)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), MTBE (1.80 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. 1-Chloro-2-(chloromethyl)benzene (2d, 0.48 g, 0.38 mL, 3.0 mmol, 1.0 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of (2-chloro-benzyl)manganese(II) chloride (1d) was determined by titration with iodine in THF (0.22 M, 41%).

1.5 Preparation of (3-fluorobenzyl)manganese(II) chloride (1e)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), THF (3.0 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. 1-(Chloromethyl)-3-fluorobenzene (2e, 0.43 g, 0.36 mL, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 0.5 h at the given temperature. The concentration of (3-fluoro-benzyl)manganese(II) chloride (1e) was determined by titration with iodine in THF (0.30 M, 68%).
1.6 Preparation of (3-(trifluoromethyl)benzyl)manganese(II) chloride (1f)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), MTBE (1.80 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. 1-(Chloromethyl)-3-(trifluoromethyl)benzene (2f, 0.58 g, 0.46 mL, 3.0 mmol, 1.0 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of (3-(trifluoromethyl)benzyl)manganese(II) chloride (1f) was determined by titration with iodine in THF (0.31 M, 58%).

1.7 Preparation (4-bromobenzyl)manganese(II) chloride (1g)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), THF (3.0 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. 1-Bromo-4-(chloromethyl)benzene (2g, 0.62 g, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 2.0 h at the given temperature. The concentration of (4-bromobenzyl)manganese(II) chloride (1g) was determined by titration with iodine in THF (0.22 M, 50%).

1.8 Preparation of (3-chlorobenzyl)manganese(II) chloride (1h)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), MTBE (1.8 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. 1-Chloro-3-(chloromethyl)benzene (2h, 0.48 g, 0.40 mL, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of (3-chlorobenzyl)manganese(II) chloride (1h) was determined by titration with iodine in THF (0.47 M, 88%).
1.9 Preparation of (4-(methylthio)benzyl)manganese(II) chloride (1i)

According to TP1, magnesium turnings (0.18 g, 7.20 mmol, 2.40 equiv), THF (3.0 mL) and MnCl$_2$·2LiCl (3.80 mL, 3.80 mmol, 1.25 equiv, 1.0 M in THF) were used. (4-(Chloromethyl)phenyl)(methyl)sulfane (2i, 0.68 g, 0.58 mL, 3.00 mmol, 1.00 equiv) was added at once at 0 °C and the reaction mixture was stirred for 1.0 h at the given temperature. The concentration of (4-(methylthio)benzyl)manganese(II) chloride (1i) was determined by titration with iodine in THF (0.22 M, 50%).

2. Preparation of bis-(aryl)manganese Reagents (5a-i):

Typical Procedure TP2:

A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with LiCl (0.42 g, 10.0 mmol, 1.20 equiv) and heated at 450 °C under high vacum for 5 min. After cooling down to room temperature under vigorous stirring, magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were added. The mixture was cooled to 0 °C, the corresponding aryl bromide (8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The completion of the metalation was monitored by GC-analysis of hydrolysed and iodolysed aliquots. When the oxidative insertion was complete, the solution was transferred to another pre-dried and argon-flushed Schlenk-tube, before being titrated against iodine. The remaining arylmagnesium halide was cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in THF). The resulting bis-(aryl)manganese reagent was titrated with an iodine solution one more time before being used.

2.1 Preparation of bis-(4-methoxyphenyl)manganese (5a)

Based on TP2, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 4-bromo-anisole (7a, 1.50 g, 1.00 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in THF). The
concentration of the resulting bis-(4-methoxyphenyl)manganese (5a) was determined by titration with iodine in THF (0.22 M).

2.2 Preparation of bis-(3,4,5-trimethoxyphenyl)manganese (5b)

Based on TP2, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 5-bromo-1,2,3-trimethoxybenzene (7b, 1.98 g, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting (3,4,5-trimethoxyphenyl)manganese (5b) was determined by titration with iodine in THF (0.22 M).

2.3 Preparation of bis-(4-(trifluoromethoxy)phenyl)manganese (5c)

Based on TP2, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 1-bromo-4-(trifluoromethoxy)benzene (7c, 1.93 g, 1.19 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(4-(trifluoromethoxy)phenyl)manganese (5c) was determined by titration with iodine in THF (0.22 M).

2.4 Preparation of bis-(3-(trimethylsilyl)phenyl)manganese (5d)

Based on TP2, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, (3-bromophenyl)trimethylsilane (7d, 1.83 g, 1.49 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF).
The concentration of the resulting bis-(3-(trimethylsilyl)phenyl)manganese (5d) was determined by titration with iodine in THF (0.22 M).

2.5 Preparation of bis-(4-chlorophenyl)manganese (5e)

Based on **TP2**, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 1-bromo-4-chlorobenzene (7e, 1.53 g, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(4-chlorophenyl)manganese (5e) was determined by titration with iodine in THF (0.22 M).

2.6 Preparation of bis-(4-fluorophenyl)manganese (5f)

Based on **TP2**, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 1-bromo-4-fluorobenzene (7f, 1.40 g, 0.88 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(4-fluorophenyl)manganese (5f) was determined by titration with iodine in THF (0.26 M).

2.7 Preparation of bis-(2-(trifluoromethyl)phenyl)manganese (5g)

Based on **TP2**, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 1-bromo-2-(trifluoromethyl)benzene (7g, 1.80 g, 1.09 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in
The concentration of the resulting bis-(2-(trifluoromethyl)phenyl)manganese (5g) was determined by titration with iodine in THF (0.28 M).

2.8 Preparation of bis-benzo[d][1,3]dioxol-5-ylmanganese (5h)

Based on TP2, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 5-bromobenzo[d][1,3]dioxole (7h, 1.61 g, 0.96 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-benzo[d][1,3]dioxol-5-ylmanganese (5h) was determined by titration with iodine in THF (0.28 M).

2.9 Preparation of bis-(4-(dimethylamino)phenyl)manganese (5i)

Based on TP2, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 4-bromo-N,N-dimethylaniline (7i, 1.60 g, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained arylmagnesium halide was again cooled to 0 °C and transmetalated with a solution of MnCl$_2$·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(4-(dimethylamino)phenyl)manganese (5i) was determined by titration with iodine in THF (0.22 M).

3. Preparation of bis-(alkyl)manganese Reagents (8a-c):

Typical Procedure TP3:

A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with LiCl (0.42 g, 10.0 mmol, 1.20 equiv) and heated at 450 °C under high vaccum for 5 min. After cooling down to room temperature under vigorous stirring, magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were added. The mixture was cooled to 0 °C, the corresponding alkyl bromide (8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The completion of the metalation
was monitored by GC-analysis of hydrolysed and iodolysed aliquots. When the oxidative insertion was complete, the solution was transferred to another pre-dried and argon-flushed Schlenk-tube, before being titrated with iodine. The remaining alkylmagnesium reagent was cooled to -20 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF). The resulting bis-(alkyl)manganese reagent was titrated with iodine one more time before being used.

3.1 Preparation of bis-(cyclohexyl)manganese (8a)

Based on TP3, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, bromocyclohexane (10a, 1.30 g, 0.98 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained alkylmagnesium halide was cooled to -20 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(cyclohexyl)manganese (8a) was determined by titration with iodine in THF (0.17 M).

3.2 Preparation of bis-(isopentyl)manganese (8b)

Based on TP3, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 1-bromo-3-methylbutane (10b, 1.21 g, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained alkylmagnesium halide was cooled to -20 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(isopentyl)manganese (8b) was determined by titration with iodine in THF (0.25 M).

3.3 Preparation of bis-(2-(1,3-dioxan-2-yl)ethyl)manganese (8c)

Based on TP3, LiCl (0.42 g, 10.0 mmol, 1.20 equiv), magnesium turnings (0.47 g, 19.2 mmol, 2.40 equiv) and freshly distilled THF (8 mL) were used. The mixture was cooled to 0 °C, 2-(2-bromoethyl)-1,3-dioxane (10c, 1.56 g, 1.09 mL, 8.00 mmol, 1.00 equiv) was added and the reaction was allowed to warm to room temperature. The obtained alkylmagnesium halide was
cooled to -20 °C and transmetalated with a solution of MnCl₂·2LiCl (0.55 equiv, 1.0 M in THF). The concentration of the resulting bis-(2-(1,3-dioxan-2-yl)ethyl)manganese (8c) was determined by titration with iodine in THF (0.24 M).

4. NMR-Spectra of Functionalized Diarylmethane Derivatives (4a-r)

4.1 NMR-Spectra of ethyl 4-benzylbenzoate (4a)
4.2 NMR-Spectra of ethyl 2-(4-(tert-butyl)benzyl)nicotinate (4b)
4.3 NMR-Spectra of 1-(tert-butyl)-4-(4-(trifluoromethyl)benzyl)benzene (4c)
4.4 NMR Spectra of ethyl 4-((tert-butyl)benzyl)benzoate (4d)
4.5 NMR Spectra of 4-(3-methoxybenzyl)benzonitrile (4e)
4.6 NMR-Spectra of ethyl 4-(3-methoxybenzyl)benzoate (4f)
4.7 NMR-Spectra of ethyl 3-(2-chlorobenzyl)benzoate (4g)
4.8 NMR-Spectra of 1-fluoro-3-(4-(trifluoromethyl)benzyl)benzene (4h)
4.9 NMR-Spectra of ethyl 2-(3-(trifluoromethyl)benzyl)benzoate (4i)
4.10 NMR-Spectra of ethyl 4-(4-bromobenzyl)benzoate (4j)
4.11 NMR-Spectra of 1-(4-(2-chlorobenzyl)phenyl)-2-methylpropan-1-one (4k)
4.12 NMR-Spectra of (4-(2-chlorobenzyl)phenyl)(cyclohexyl)methanone (4l)
4.13 NMR-Spectra of 1-((4-([3-fluorobenzyl]phenyl)-2-methylpropan-1-one (4m)
4.14 NMR-Spectra of cyclohexyl(4-(3-fluorobenzyl)phenyl)methanone (4n)
4.15 NMR-Spectra of 1-(4-(3-fluorobenzyl)phenyl)ethan-1-one (4o)
4.16 NMR-Spectra of 1-(4-(3-chlorobenzyl)phenyl)ethan-1-one (4p)
4.17 NMR-Spectra of 2-(3-methoxybenzyl)nicotinonitrile (4q)
4.18 NMR-Spectra of ethyl 2-(4-[(methylthio)benzyl]nicotinate (4r)
5. NMR-Spectra of Functionalized Biphenyl Derivatives (6a-o)

5.1 NMR-Spectra of ethyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate (6a)
5. NMR-Spectra of cyclohexyl(3',4',5'-trimethoxy-[1,1'-biphenyl]-4-yl)methanone (6b)
5.3 NMR-Spectra of 4-methoxy-4′-(trifluoromethoxy)-1,1′-biphenyl (6c)
5. NMR-Spectra of ethyl 4'-{(trifluoromethoxy)-[1,1'-biphenyl]4-carboxylate (6d)
5. NMR-Spectra of ethyl 3′-(trimethylsilyl)-[1,1′-biphenyl]-3-carboxylate (6e)
5. 6 NMR-Spectra of 2-methyl-1-(3'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)propan-1-one (6f)
5. 7 NMR-Spectra of ethyl 4'-chloro-[1,1'-biphenyl]-4-carboxylate (6g)
5. NMR Spectra of (4'-chloro-[1,1'-biphenyl]-4-yl)(cyclohexyl)methanone (6h)
5. NMR Spectra of ethyl 4'-fluoro-[1,1'-biphenyl]-3-carboxylate (6i)
5. 10 NMR-Spectra of ethyl 2'-((trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (6))
5. 11 NMR-Spectra of 1-(2'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (6k)
5. 12 NMR-Spectra of 4-(benzo[d][1,3]dioxol-5-yl)benzonitrile (6i)
5. 13 NMR-Spectra of 5-((trifluoromethyl)-2-(3,4,5-trimethoxyphenyl)pyridine (6m)
5.14 NMR-Spectra of ethyl 2-(benzo[d][1,3]dioxol-5-yl)nicotinate (6n)
5.15 NMR-Spectra of 2-(4-(dimethylamino)phenyl)nicotinonitrile (60)
6. NMR-Spectra of 2-Alkyl-Substituted Pyridine Derivatives

6.1 NMR-Spectra of ethyl 2-cyclohexylnicotinate (9a)
6.2 NMR-Spectra of 2-isopentynicotonitrile (9b)
6.3 NMR-Spectra of ethyl 2-((1,3-dioxan-2-yl)ethyl)nicotinate (9c)