Supplementary Material (ESI) for Chemical Communications

Iron-Catalyzed Aryl-Aryl Cross-Coupling Tolerating Secondary Amides and Unprotected Quinolinones

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General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in case of air- or moisture-sensitive compounds in flame-dried glassware under nitrogen. Syringes were used to transfer the reagents and the solvents were purged with nitrogen prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography.

Solutions of organomagnesium compounds were prepared, if not especially mentioned, by the reaction of Mg with aryl bromides in THF, titrated with a standard solution of I_2 in 0.5 M LiCl in THF and diluted with THF to the mentioned concentration.

Typical Procedures (TP)

Typical procedure for iron-catalyzed cross-coupling reactions (TP 1)

A dried, nitrogen flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar, was charged with the arylmagnesium reagent (3.0 equiv). Dry DME (5 mL/mmol) was added, the mixture cooled to -20 °C, CuCN·2LiCl (2.8 equiv) added dropwise and the solution stirred for 20 min. The electrophile (1.0 equiv), $Fe(acac)_3$ (10 mol%) and DME (2 mL/mmol) were added consecutively and the solution vigorously stirred at 80 °C. After complete conversion (approx. 4 h) the reaction was quenched with saturated, aqueous NH_4Cl (50 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with a saturated NH_4Cl/NH_3 (9:1) solution (50 mL), with brine (20 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification by flash chromatography on silica gel furnished the product. In cases where the isolated yields were below 80% no full conversion could be obtained.

Typical procedure for iron-catalyzed cross-coupling reactions with preceding iodine-magnesium exchange (TP 2)

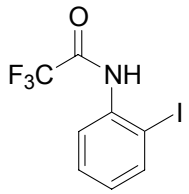
A dried, nitrogen flushed 25 mL Schlenk tube, equipped with a magnetic stirring bar, was charged with aryliodide (3.0 equiv). Dry DME (5 mL/mmol) was added, the mixture cooled to -20 °C and *i*PrMgCl (3.1 equiv) was added dropwise. The I/Mg exchange was usually complete after 30 min (checked by GC analysis of reaction aliquots) and then CuCN·2LiCl (2.8 equiv) was added dropwise and the solution stirred for 20 min. The electrophile (1.0 equiv), $Fe(acac)_3$ (10 mol%) and DME (2 mL/mmol) were added consecutively and the solution vigorously stirred at 80 °C. After complete conversion (approx. 4 h) the reaction was quenched with saturated, aqueous NH_4Cl (50 mL) and extracted with ethylacetate (3 x 20 mL). The combined organic layers were washed with a sat. NH_4Cl/NH_3 (9:1) solution (50 mL), with brine (20 mL), dried over $MgSO_4$ and the solvent removed *in vacuo.*

Purification by flash chromatography on silica gel furnished the product. In cases where the isolated yields were below 80% no full conversion could be obtained.

Typical procedure for the protection of aromatic amines with *p*-anisoylchloride (TP 3)

A dry and nitrogen flushed 100 mL flask, equipped with a magnetic stirring bar and a septum, was charged with the corresponding amine (1.0 equiv). Dry dioxane (2 mL/mmol) and dry pyridine (1 mL/mmol) were added, the mixture cooled to 0 °C and *p*-anisoyl chloride (1.05 equiv) added dropwise. After the addition, the reaction mixture was stirred at 0 °C for 30 min and then left to warm to rt and stirred vigorously until TLC analysis indicated complete conversion. Water was added to the reaction mixture as well as 1 m HCl, until the aqueous phase was at pH = 3-5. The precipitate was subsequently filtered through a glass sinter and washed with water (2 x 20 mL). Recrystallization from ethanol furnished the pure product.

2,2,2-Trifluoro-*N*-(2-iodo-phenyl)-acetamide (2a)



2-Iodoaniline (2.19 g, 10.0 mmol) was dissolved in 35 mL dry THF, followed by addition of TEA (1.6 mL). The solution was cooled to -15 °C and trifluoroacetic acid anhydride (2.52 g, 12.0 mmol) added dropwise. The reaction mixture was stirred at -15 °C for 1 h, allowed to warm to rt and stirred for 12 h. After completion of the reaction, water (30 mL) was added, the aqueous phase extracted with diethyl ether (3 x 20 mL), the combined organic layers washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by flash chromatography (pentane/diethyl ether = 5:1) and provided **2a** as a colorless solid (3.02 g, 96 %).

Mp.: 109.6-110.7 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.27 (s_br, 1H), 8.20 (dd, *J*= 8.2, 1.5 Hz, 1H), 7.84 (dd, *J*= 7.9, 1.5 Hz, 1H), 7.41 (ddd, *J*= 8.0, 7.3, 1.3 Hz, 1H), 6.97 (td, *J*= 7.7, 1.6 Hz, 1H).

^{13}C-NMR (MHz, $CDCl_3$): δ = 154.7 (q, *J*= 37.6 Hz), 139.2, 135.7, 129.6, 127.9, 122.1, 115.6 (q, *J*= 288.6 Hz), 90.2.

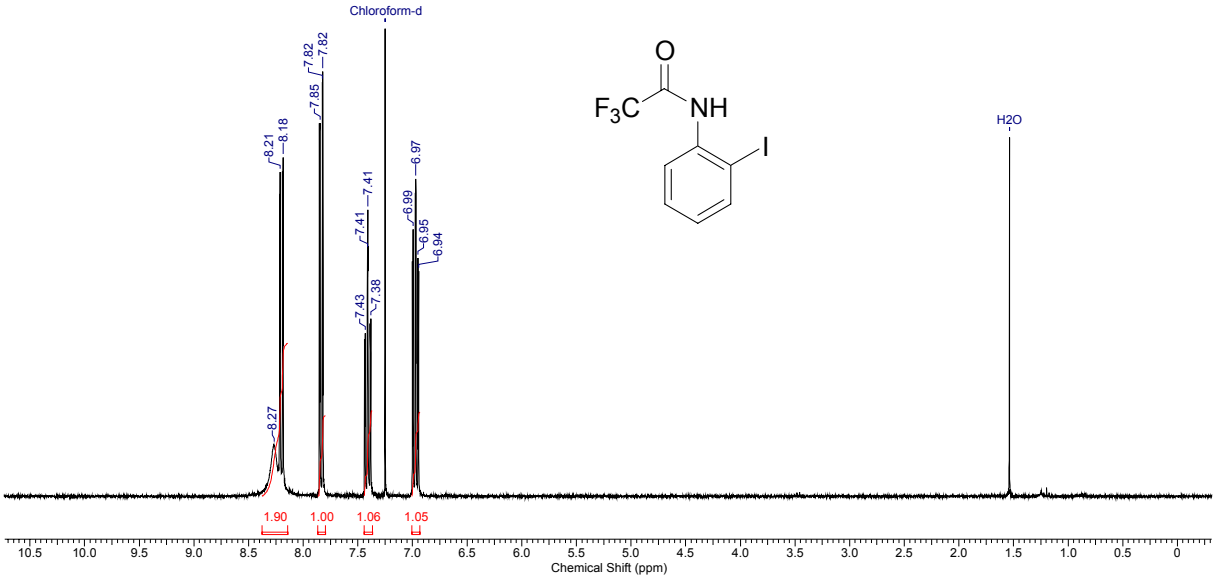
MS (70 eV, EI), *m/z* (%): 315 (24) [M^+], 188 (100), 168 (19), 119 (10), 102 (11), 91 (19).

IR (KBr): ṽ = 3853 (w), 3745 (w), 3204 (m), 3062 (w), 1707 (vs), 1545 (m), 1466 (m), 1276 (m), 1238 (m), 1202 (s), 1265, (vs), 1147 (vs), 912 (m), 758 (m), 733 (m).

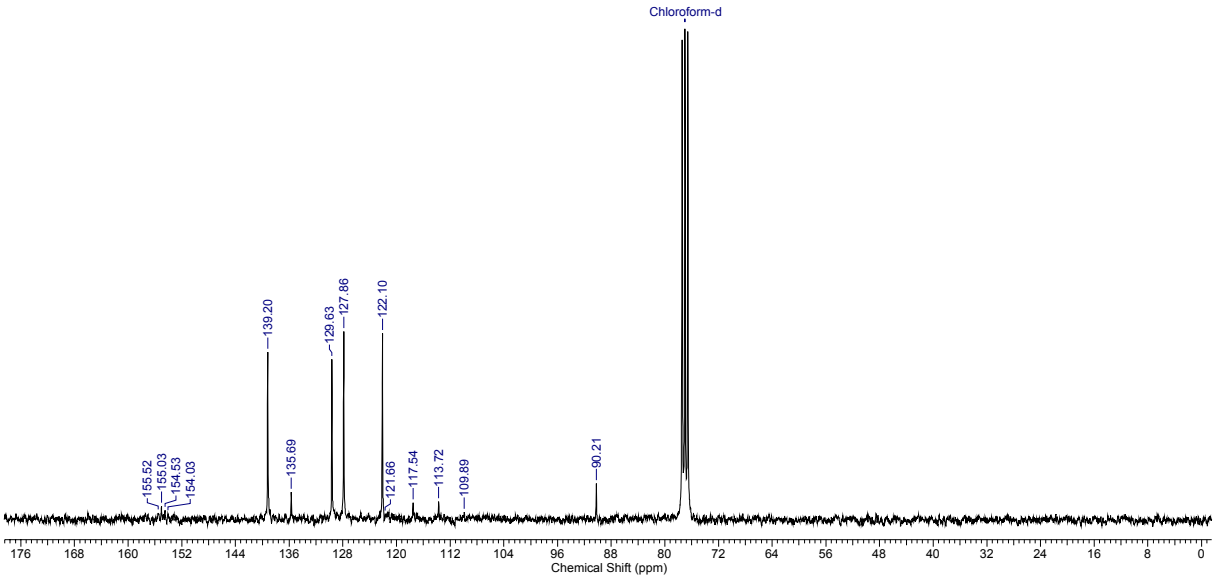
HRMS for **$C_8H_5F_3INO$** (314.9368): found: 314.9377.

2,2,2-Trifluoro-*N*-(2-iodo-phenyl)-acetamide (2a)

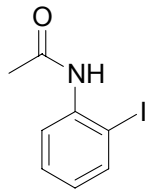
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 23 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl020_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	9849	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	4807.69
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.3005	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 23 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl020_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	2000	***Original Points Count***	23560	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



***N*-(2-Iodo-phenyl)-acetamide (2b)**



A dried 100 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 2-iodoaniline (1.10 g, 5.00 mmol), CH_2Cl_2 (37.5 mL), AgCN (0.70 g, 5.00 mmol) and MeCN (37.5 mL). Acetyl chloride (0.79 g, 10.0 mmol) was added dropwise and the reaction mixture stirred at rt for 12 h. After completion of the reaction the precipitate was filtered over celite and washed with CH_2Cl_2. The filtrate was then washed with 5% $NaHCO_3$-solution (20 mL) followed by a 1 M citric acid solution (20 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Recrystallization from ethanol yielded **2b** as colorless crystals (654 mg, 50 %).

Mp.: 110.0-110.6 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, *J*= 7.5 Hz, 1H), 7.76 (d, *J*= 7.9 Hz, 1H), 7.41 (s_br, 1H), 7.32 (t, *J*= 7.3 Hz, 1H), 6.83 (t, *J*= 7.4 Hz, 1H), 2.22 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 168.2, 138.7, 138.2, 129.2, 125.9, 122.1, 89.9, 24.8.

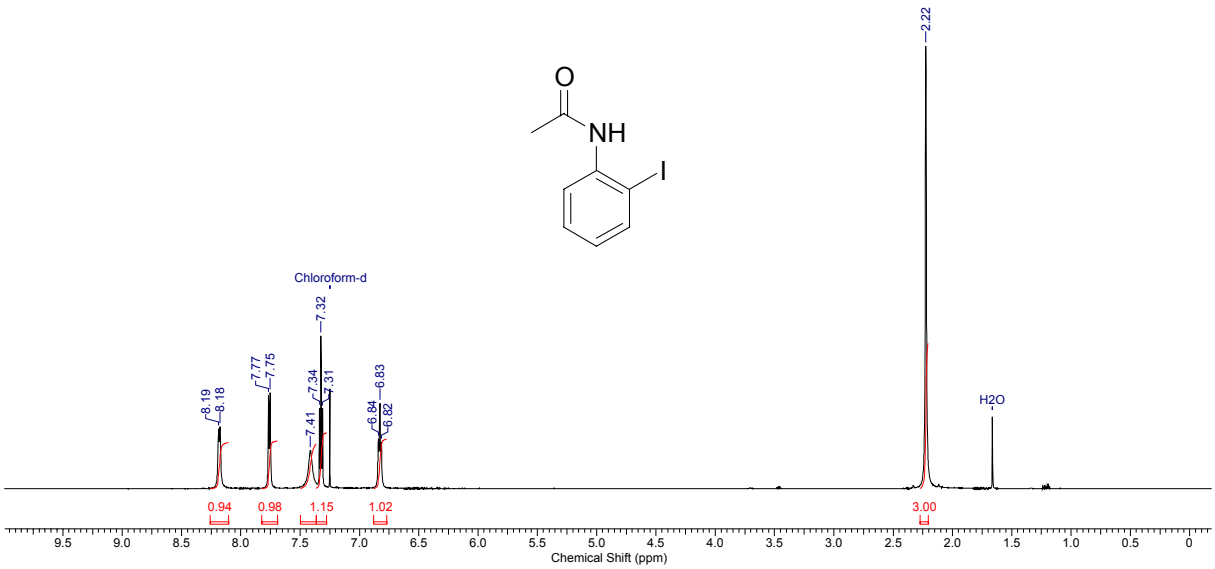
MS (70 eV, EI), *m/z* (%): 261 (15) [M^+], 219 (98), 134 (100), 92 (30), 65 (10).

IR (KBr): $\tilde{\nu}$ = 3271 (s), 1658 (m), 1573 (m), 1525 (s), 1431 (m), 1290 (s), 1013 (m), 749 (m).

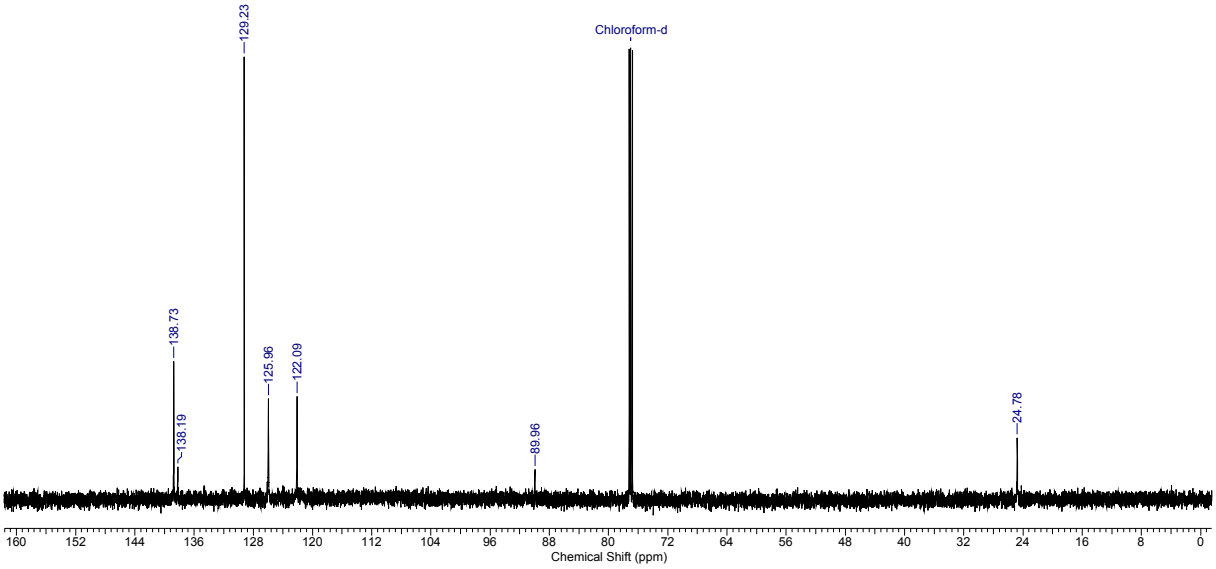
HRMS for **C_8H_8INO** (260.9651): found: 260.9640.

N-(2-Iodo-phenyl)-acetamide (2b)

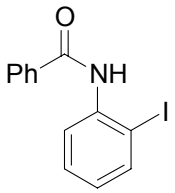
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 9 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl002_Proton_01					***Frequency (MHz)***	599.71
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	28902	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	7225.43
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 9 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl002_Carbon_01					***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	512	***Original Points Count***	58824	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	36764.71
Temperature (degree C)	27.000						



***N*-(2-Iodo-phenyl)-benzamide (2c)**



A dried 100 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 2-iodoaniline (1.10 g, 5.00 mmol), CH_2Cl_2 (37.5 mL), AgCN (0.700 g, 5.00 mmol) and MeCN (37.5 mL). Benzoyl chloride (1.41 g, 10.0 mmol) was added dropwise and the reaction mixture stirred at rt for 12 h. After completion of the reaction the precipitate was filtered over celite and washed with CH_2Cl_2. The filtrate was then washed with 5% $NaHCO_3$-solution (20 mL) followed by a 1 M citric acid solution (20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Recrystallization from ethanol yielded **2c** as colorless crystals (1.25 g, 77 %).

Mp.: 139.0-139.8 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.46 (dd, *J*= 8.2, 1.5 Hz, 1H), 8.28 (s_br, 1H), 7.98-7.97 (m, 2H), 7.81 (dd, *J*= 8.0, 1.4 Hz, 1H), 7.58 (m, 1H), 7.52 (t, *J*= 7.5 Hz, 2H), 7.40 (m, 1H), 6.88 (td, *J*= 7.6, 1.5 Hz, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 165.3, 138.8, 138.3, 134.5, 132.2, 129.4, 128.9, 127.2, 126.0, 121.8, 90.2.

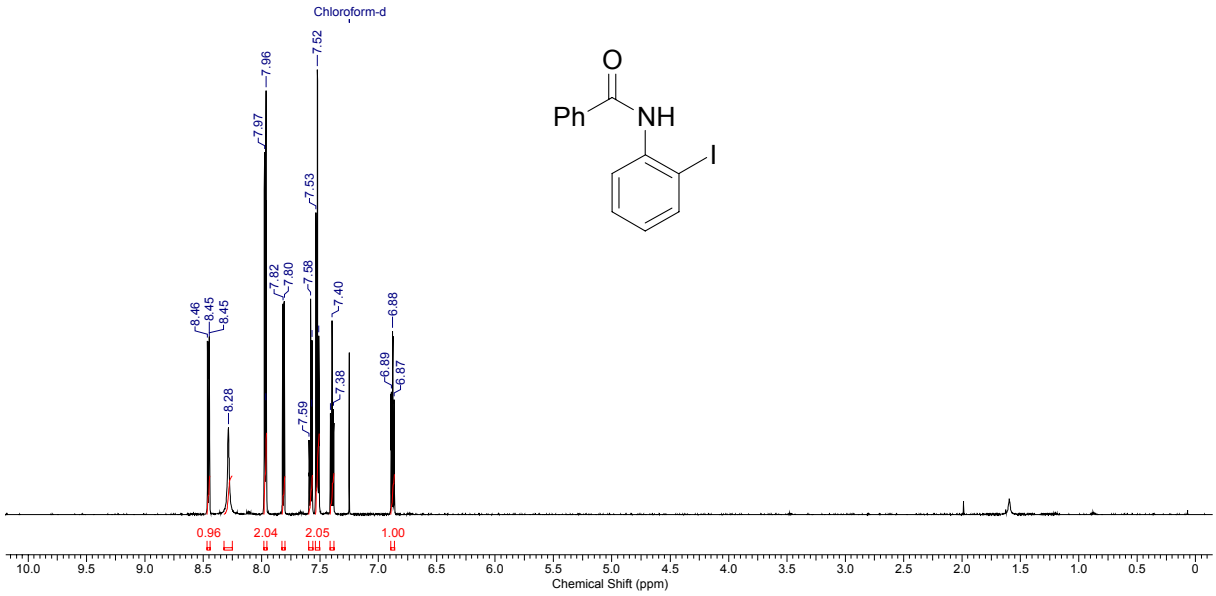
MS (70 eV, EI), *m/z* (%): 322 (5) [M^+], 196 (100), 167 (3), 105 (78), 91 (5), 77 (36).

IR (KBr): ṽ = 3210 (w), 1647 (m), 1571 (w), 1513 (m), 1464 (s), 1425 (m), 1297 (s), 1014 (m), 912 (m), 746 (s), 708 (s).

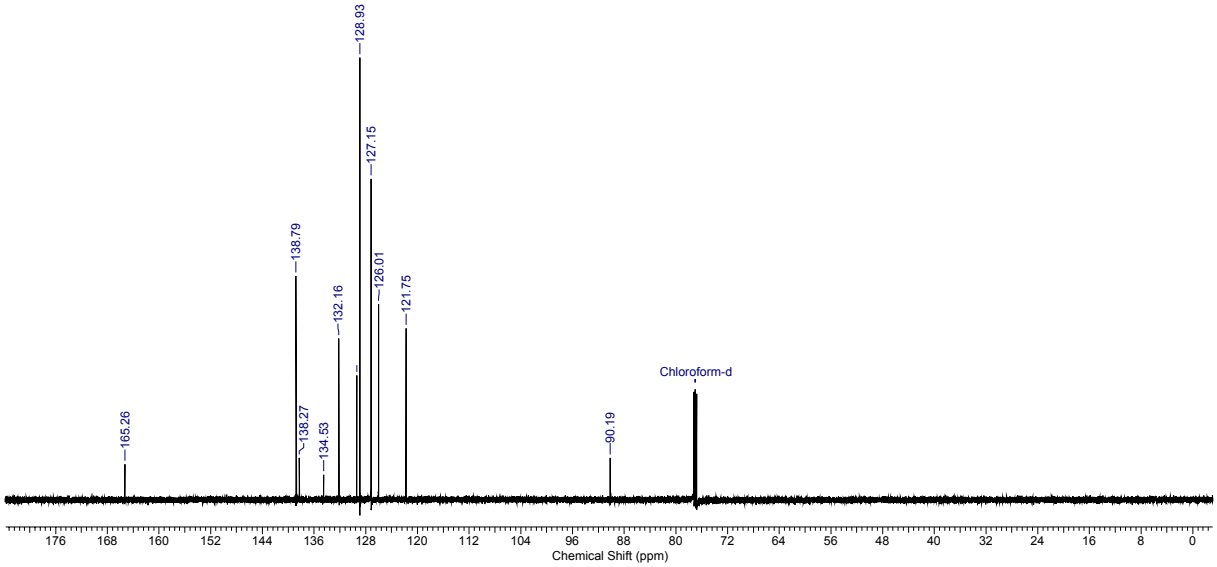
HRMS for **$C_{13}H_{10}INO$** (322.9807): found: 322.9789.

N-(2-Iodo-phenyl)-benzamide (2c)

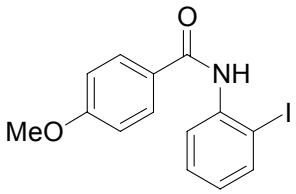
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 13 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl001_Proton_01					***Frequency (MHz)***	599.71
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	38462	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	9615.38
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 13 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl001_Carbon_01					***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	1000	***Original Points Count***	58824	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	36764.71
Temperature (degree C)	27.000						



***N*-(2-Iodo-phenyl)-4-methoxy-benzamide (2d)**



4-Methoxybenzoyl chloride (2.56 g, 15.0 mmol) diluted in 10 mL CH_2Cl_2 was added dropwise to a vigorously stirred solution of 2-iodoaniline (2.19 g, 10.0 mmol) in CH_2Cl_2 (90 mL) and TEA (1.4 mL, 10 mmol). On completion of the addition, the reaction mixture was stirred for 2 d at rt. The reaction mixture was washed with 1 M HCl (2 x 100 mL), the aqueous phase extracted with CH_2Cl_2 (3 x 20 mL), the combined organic layers washed with sat. $NaHCO_3$-solution (20 mL), with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by flash chromatography (pentane/diethyl ether = 4:1) and provided **2d** as a pale yellow solid (872 mg, 25 %).

Mp.: 154.4-155.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.4 (dd, *J*= 8.2, 1.6 Hz, 1H), 8.21 (s_br, 1H), 7.96-7.90 (m, 2H), 7.80 (dd, *J*= 8.0, 1.6 Hz, 1H), 7.41-7.35 (m, 1H), 7.03-6.98 (m, 2H), 6.86 (td, *J*= 7.6, 1.7 Hz, 1H), 3.88 (s, 3H).

^{13}C-NMR (MHz, $CDCl_3$): δ = 164.8, 162.8, 138.7, 138.5, 129.4, 129.1, 126.8, 125.8, 121.6, 114.2, 90.1, 55.5.

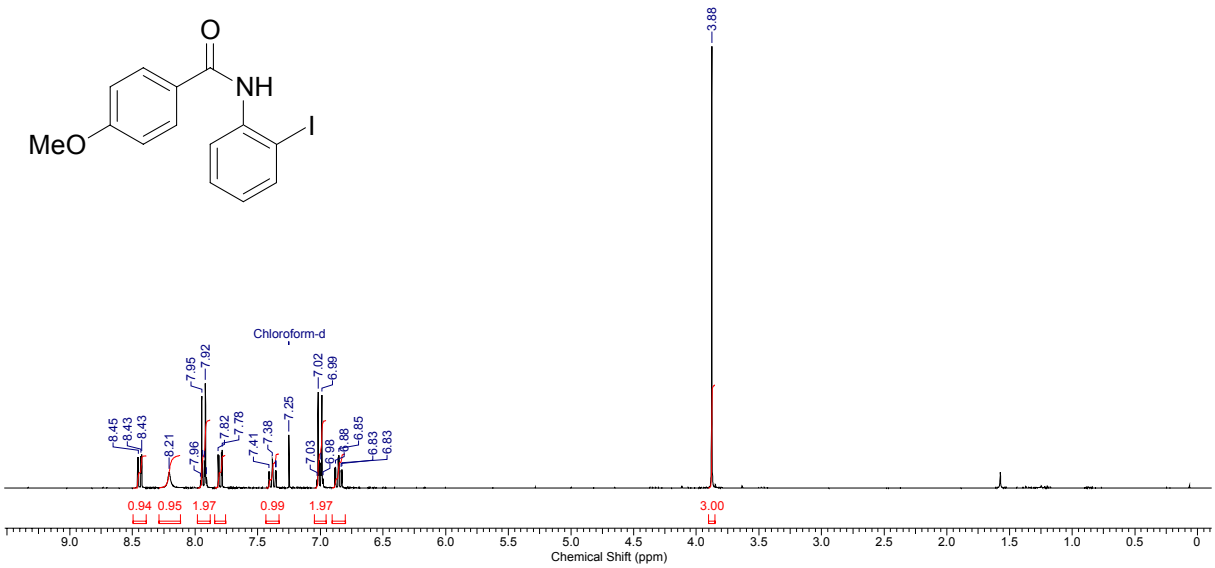
MS (70 eV, EI), *m/z* (%): 353 (3) [M^+], 226 (42), 135 (100), 107 (8), 92 (10), 77 (12).

IR (KBr): ṽ = 3258 (m), 3018 (w), 2838 (w), 1642 (s), 1605 (s), 1573 (m), 1501 (vs), 1430 (s), 1295 (s), 1252 (vs), 1176 (vs), 1103 (m), 1015 (s), 907 (w), 840 (m), 750 (vs).

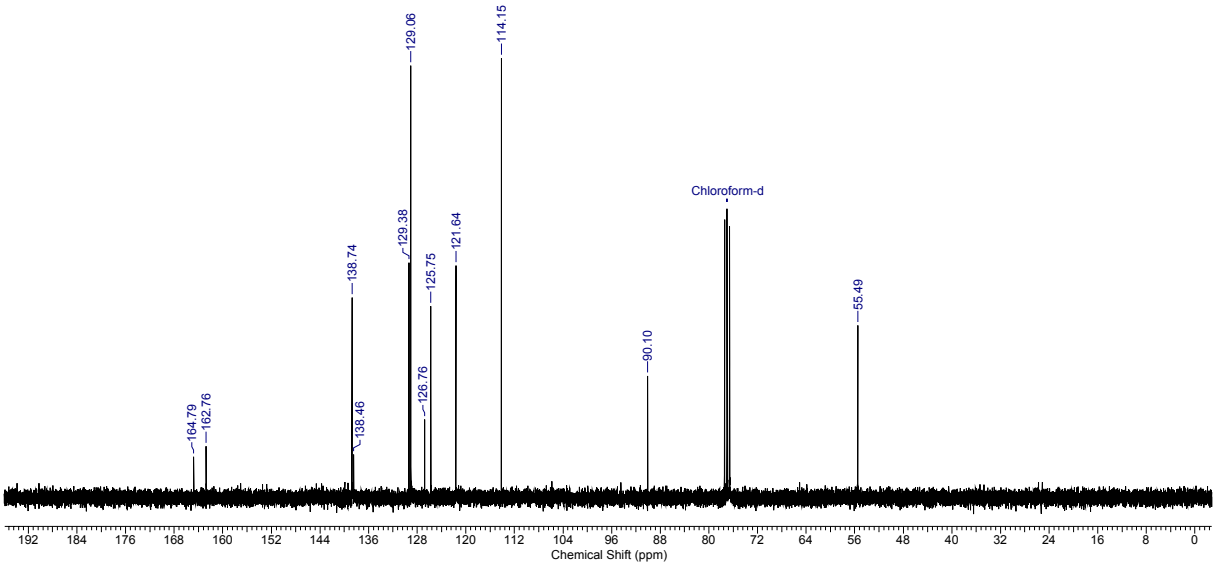
HRMS for **$C_{14}H_{12}INO_2$** (352.9913): found: 352.9925.

N-(2-Iodo-phenyl)-4-methoxy-benzamide (2d)

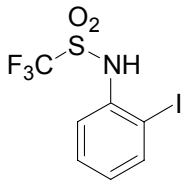
Acquisition Time (sec)	4.1943	***Comment***	Benoit Blank, AK Knochel			***Date***	Mar 14 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl035_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	16384	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	3906.25
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6010	***Comment***	Benoit Blank, AK Knochel			***Date***	Mar 14 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl035_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	1024	***Original Points Count***	29004	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



1,1,1-Trifluoro-*N*-(2-iodophenyl)methanesulfonamide (2e)



2-Iodoaniline (2.19 g, 10.0 mmol) was dissolved in 30 mL dry CH_2Cl_2 under N_2, followed by addition of TEA (1.6 mL). The solution was cooled to 0 °C and trifluoromethanesulfonic acid anhydride (3.39 g, 12.0 mmol) added dropwise. The reaction mixture was stirred at 0 °C for 2 h, allowed to warm to rt. After completion of the reaction, water (20 mL) was added, the aqueous phase extracted with CH_2Cl_2 (3 x 20 mL), the combined organic layers washed with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude black oil was distilled at 90 °C (0.2 mbar) to give a pale yellow liquid that was subsequently purified by flash chromatography (pentane/ethyl acetate = 2:1) and provided **2e** as pale yellow crystals (915 mg, 26 %).

Mp.: 53.8-55.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J*= 8.2, 1.4 Hz, 1H), 7.59 (dd, *J*= 8.3, 1.3 Hz, 1H), 7.38 (ddd, 8.5, 7.0, 1.4 Hz, 1H), 7.03-6.98 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 139.8, 135.8, 130.0, 128.9, 123.7, 120.0 (q, *J*= 322 Hz), 93.1.

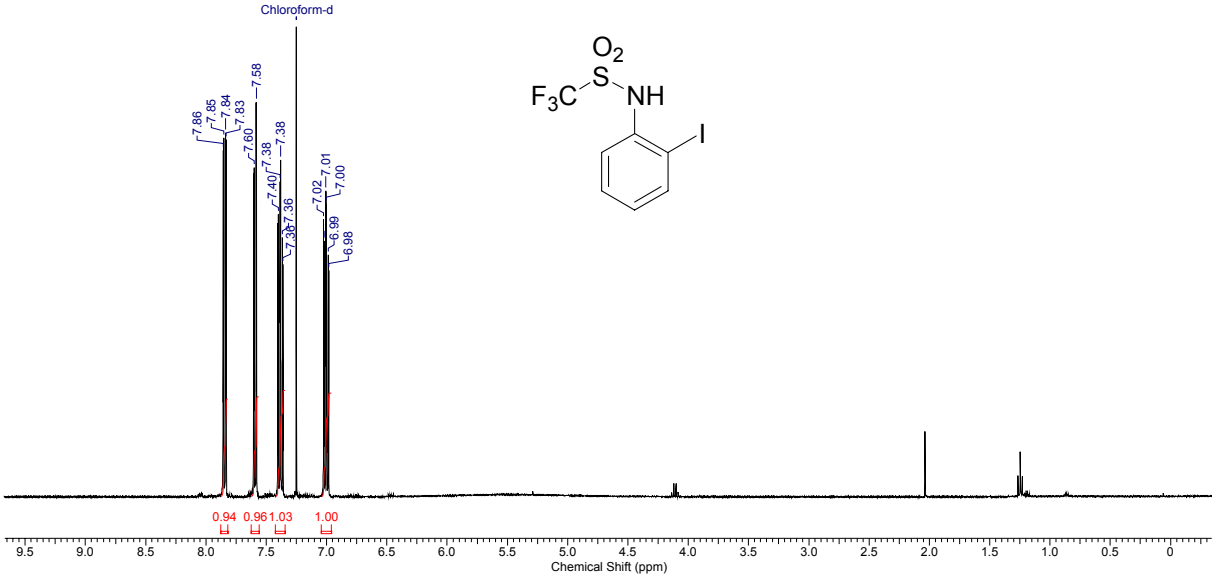
MS (70 eV, EI), *m/z* (%): 351 (100) [M^+], 218 (94), 91 (43), 64 (8).

IR (KBr): ṽ = 3269 (m), 1469 (m),1413 (s), 1363 (m), 1204 (vs), 1179 (s), 1114 (vs), 1018 (m), 925 (m), 816 (m), 753 (vs), 709 (s), 648 (m), 631 (vs).

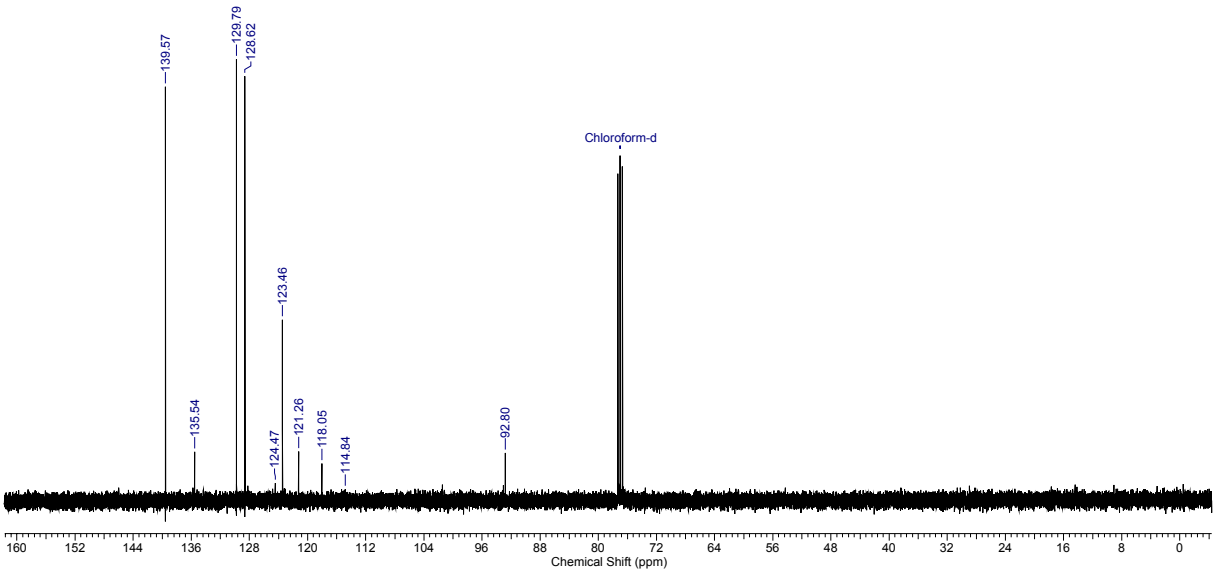
HRMS for **$C_7H_5F_3INO_2S$** (350.9038): found: 350.9049.

1,1,1-Trifluoro-*N*-(2-iodophenyl)methanesulfonamide (2e)

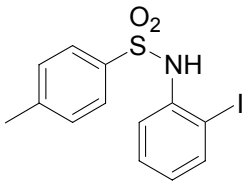
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Apr 18 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\400 MHz\bbl065_Proton_01					***Frequency (MHz)***	399.94
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	20797	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	5199.19
Temperature (degree C)	30.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Apr 18 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\400 MHz\bbl065_Carbon_01					***Frequency (MHz)***	100.58
Nucleus	13C	***Number of Transients***	4096	***Original Points Count***	38612	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24132.73
Temperature (degree C)	30.000						



***N*-(2-Iodo-phenyl)-4-methyl-benzenesulfonamide (2f)**



2-Iodoaniline (2.19 g, 10.0 mmol) was dissolved in dry THF (20 mL) under N_2, followed by addition of pyridine (2.5 mL) and *p*-tosyl chloride (2.10 g, 11.0 mmol). The reaction mixture was stirred for 2 d at rt. After completion of the reaction, EtOAc (30 mL) was added and the solution washed twice with 1 M HCl (20 mL), the aqueous phase extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with sat. $NaHCO_3$ solution (20 mL), with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by flash chromatography (pentane/diethyl ether = 7:1) and provided **2f** as a yellow solid (2.72 g, 73 %).

Mp.: 92.0-92.9 °C.

^{1}H-NMR (MHz, $CDCl_3$): δ = 7.66-7.60 (m, 4H), 7.32-7.25 (m, 1H), 7.20 (d, *J*= 7.9 Hz, 2H), 6.81 (td, *J*= 7.7, 1.6 Hz, 2H), 2.37 (s, 3H).

^{13}C-NMR (MHz, $CDCl_3$): δ = 144.2, 139.1, 137.5, 135.9, 129.6, 129.5, 127.4, 126.8, 122.4, 92.3, 21.6.

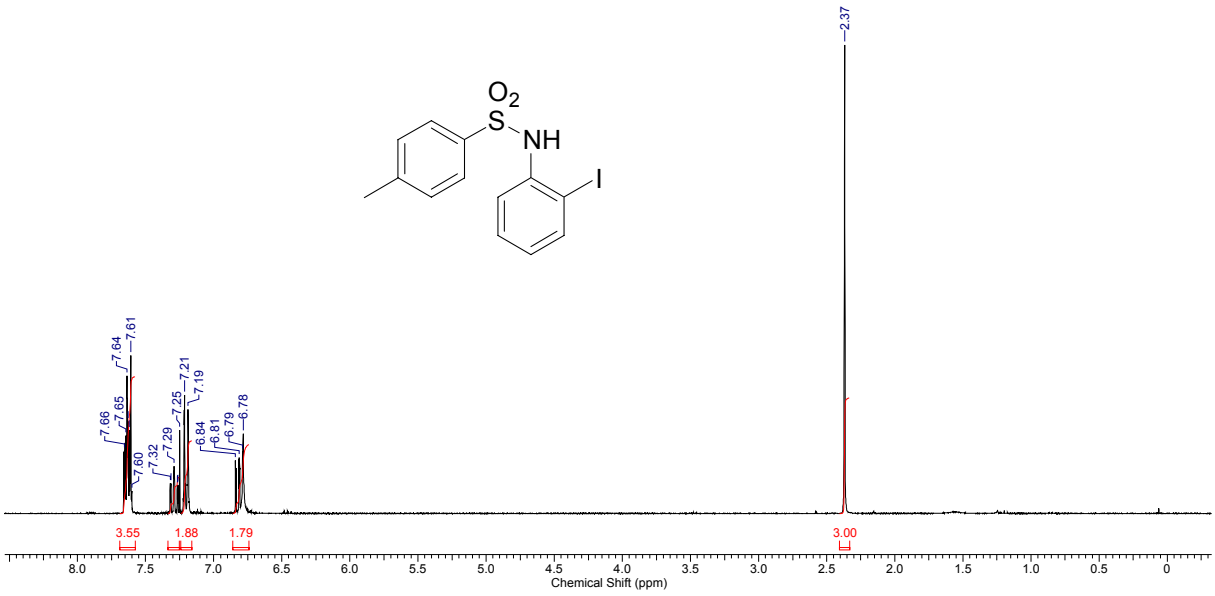
MS (70 eV, EI), *m/z* (%): 372 (85) [M^+], 218 (45), 155 (38), 139 (27), 91 (100), 65 (17).

IR (KBr): $\tilde{\nu}$ = 3284 (vs), 1593 (w), 1472 (vs), 1392 (m), 1328 (vs), 1155 (vs), 1086 (s), 1014 (m), 909 (m), 817 (m), 708 (m), 659 (m).

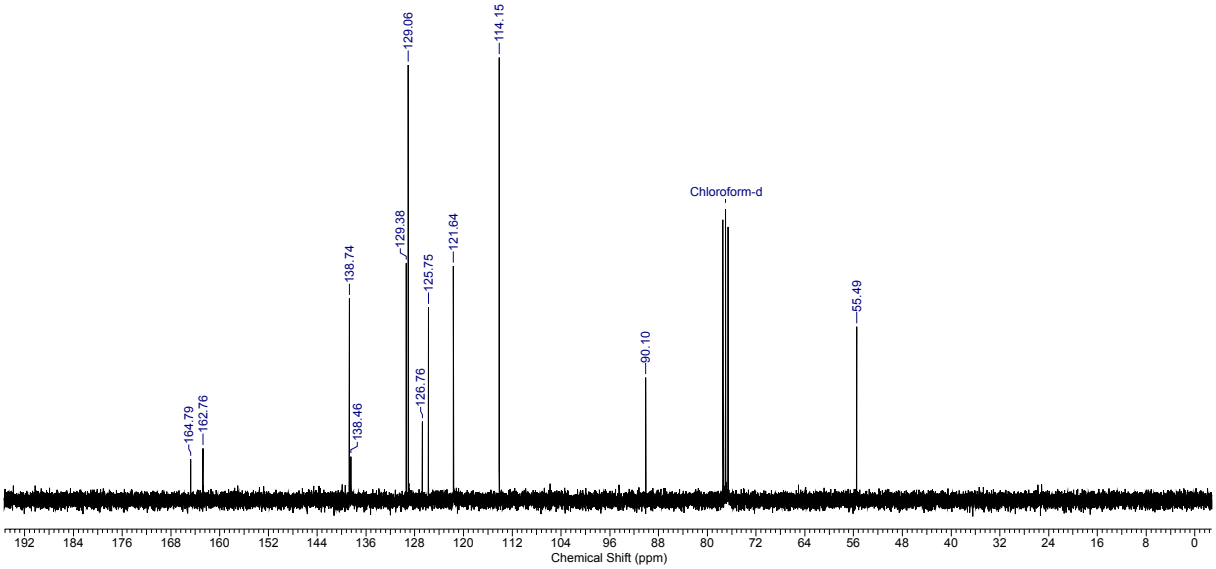
HRMS for **$C_{13}H_{12}INO_2S$** (372.9633): found: 372.9649.

N-(2-Iodo-phenyl)-4-methyl-benzenesulfonamide (2f)

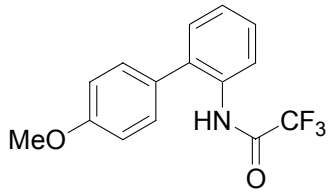
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 23 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl018_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	9849	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	4807.69
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6010	***Comment***	Benoit Blank, AK Knochel			***Date***	Mar 14 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl035_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	1024	***Original Points Count***	29004	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



2,2,2-Trifluoro-*N*-(4'-methoxybiphenyl-2-yl)acetamide (3a)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and 2,2,2-trifluoro-*N*-(2-iodo-phenyl)-acetamide (315 mg, 1.00 mmol). Reaction time: 5 h. Purification by flash chromatography (pentane/diethyl ether = 39:1) yielded biphenyl **3a** as a pale ocher solid (174 mg, 55 %).

Mp.: 86.3-87.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, *J*= 8.2 Hz, 1H), 8.00 (s_br, 1H), 7.44-7.33 (m, 1H), 7.28 (d, *J*= 8.2 Hz, 4H), 7.03 (d, *J*= 8.2 Hz, 2H), 3.87 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.8, 154.5 (q, *J*= 37.0 Hz), 132.8, 132.3, 130.4, 130.2, 128.7, 128.4, 126.1, 121.1, 115.6 (q, *J*= 299.6 Hz), 114.8, 55.4.

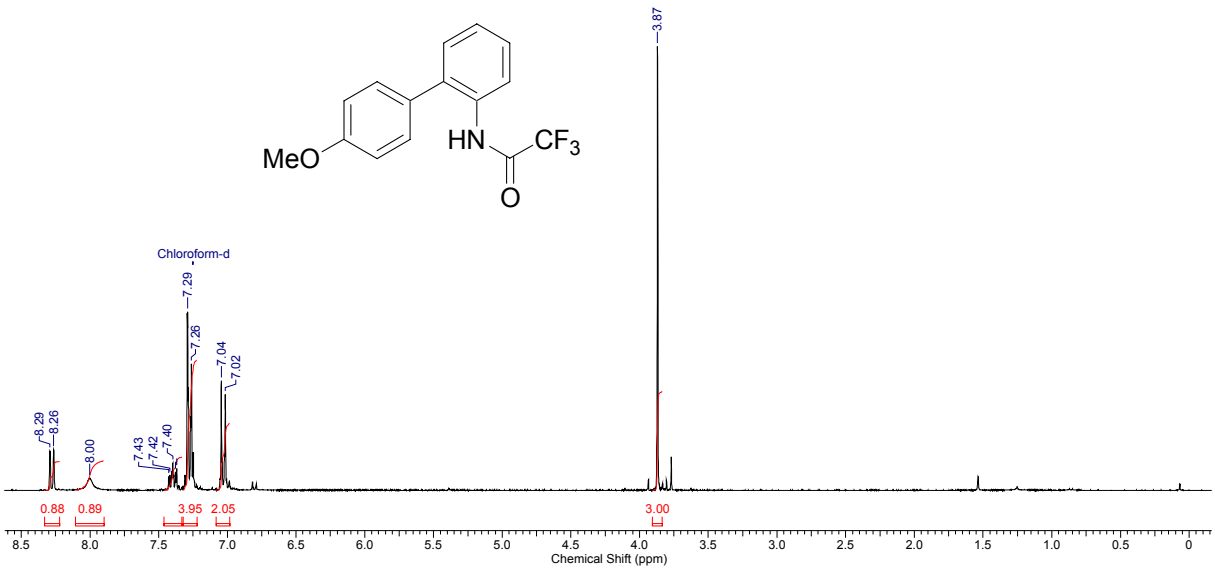
MS (70 eV, EI), *m/z* (%): 295 (100) [M^+], 226 (12), 208 (10), 183 (16), 154 (15), 127 (5).

IR (KBr): $\tilde{\nu}$ = 3286 (w), 2838 (w), 1722 (m), 1606 (w), 1541 (w), 1516 (w), 1441 (w), 1273 (m), 1239 (m), 1201 (m), 1183 (m), 1144 (vs), 1034 (m), 1018 (m), 906 (m), 832 (m), 765 (vs), 729 (m).

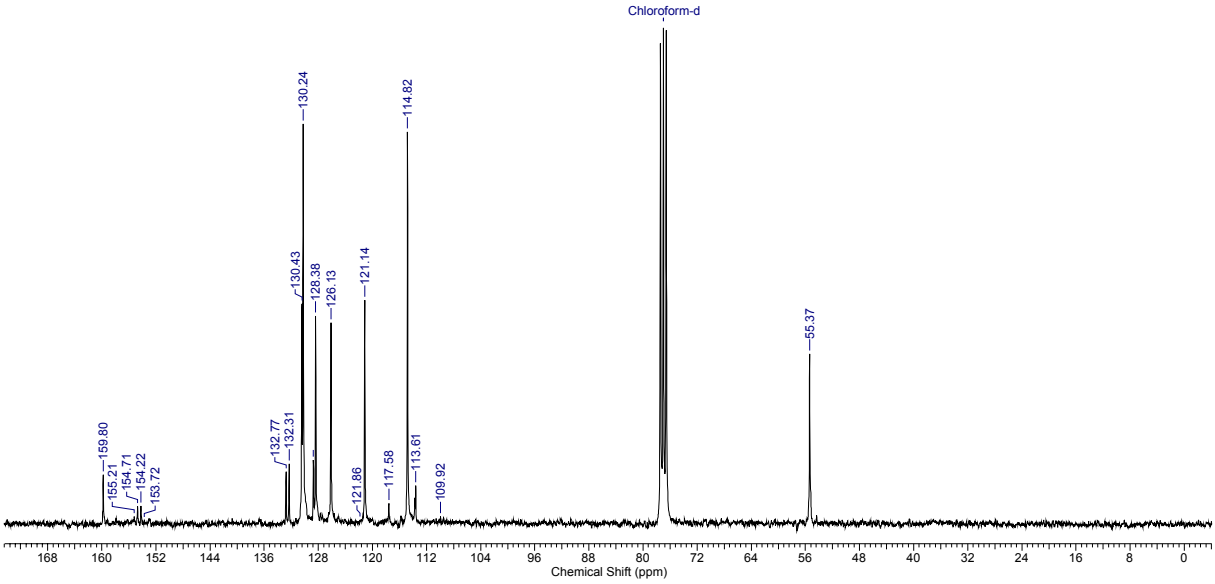
HRMS for **$C_{15}H_{12}F_3NO_2$** (295.0820): found: 295.0802.

2,2,2-Trifluoro-*N*-(4'-methoxybiphenyl-2-yl)acetamide (3a)

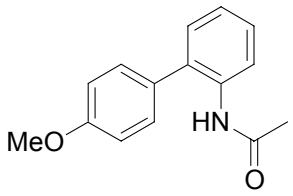
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 27 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl024_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	9849	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	4807.69
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.3005	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 27 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl024_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	5000	***Original Points Count***	23560	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



***N*-(4'-Methoxy-biphenyl-2-yl)-acetamide (3b)**



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(2-iodo-phenyl)-acetamide (261 mg, 1.00 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/diethyl ether = 1:3) yielded biphenyl **3b** as a yellow solid (179 mg, 74 %).

Mp.: 133.9-135.1 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J*= 7.9 Hz, 1H), 7.34 (dd, *J*= 7.6, 2.0 Hz, 1H), 7.28 (td, *J*= 8.8, 2.5 Hz, 2H), 7.23-7.11 (m, 3H), 7.00 (td, *J*= 8.8, 2.5 Hz, 2H), 3.86 (s, 3H), 2.01 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.1, 159.3, 134.9, 131.8, 130.4, 130.2, 130.1, 128.1, 124.2, 121.5, 114.5, 55.3, 24.6.

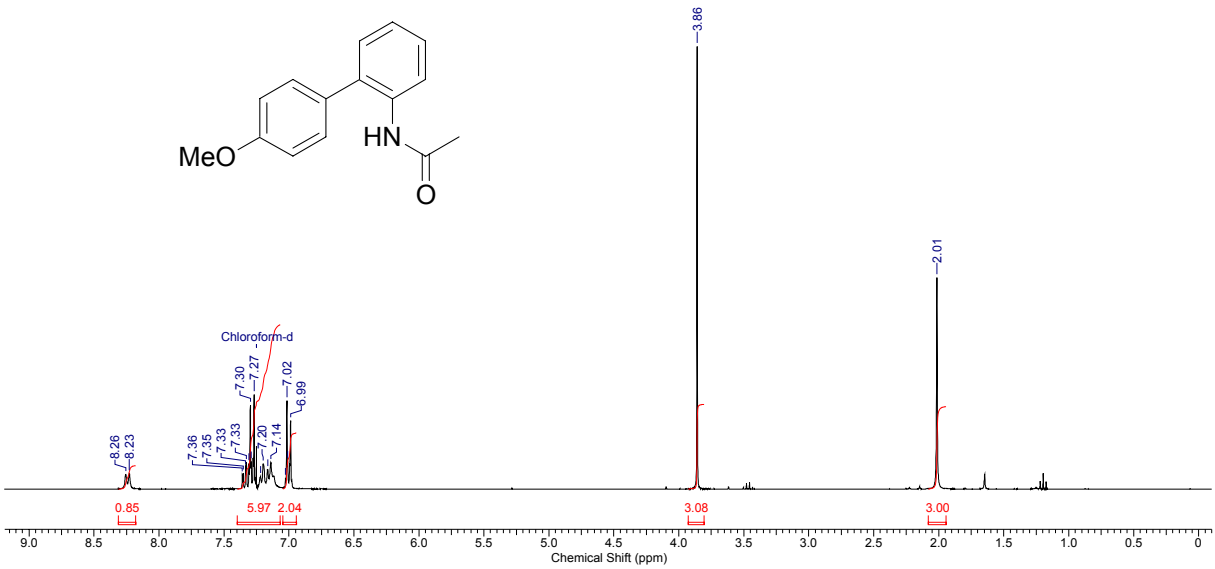
MS (70 eV, EI), *m/z* (%): 241 (65) [M^+], 199 (100), 184 (28), 167 (7), 154 (12), 128 (5).

IR (KBr): $\tilde{\nu}$ = 3350 (m), 3012 (w), 2841 (w), 1690 (m), 1609 (w), 1512 (s), 1472 (m), 1439 (m), 1362 (m), 1294 (m), 1239 (s), 1031 (m), 1015 (m), 832 (m), 773 (vs), 663 (m).

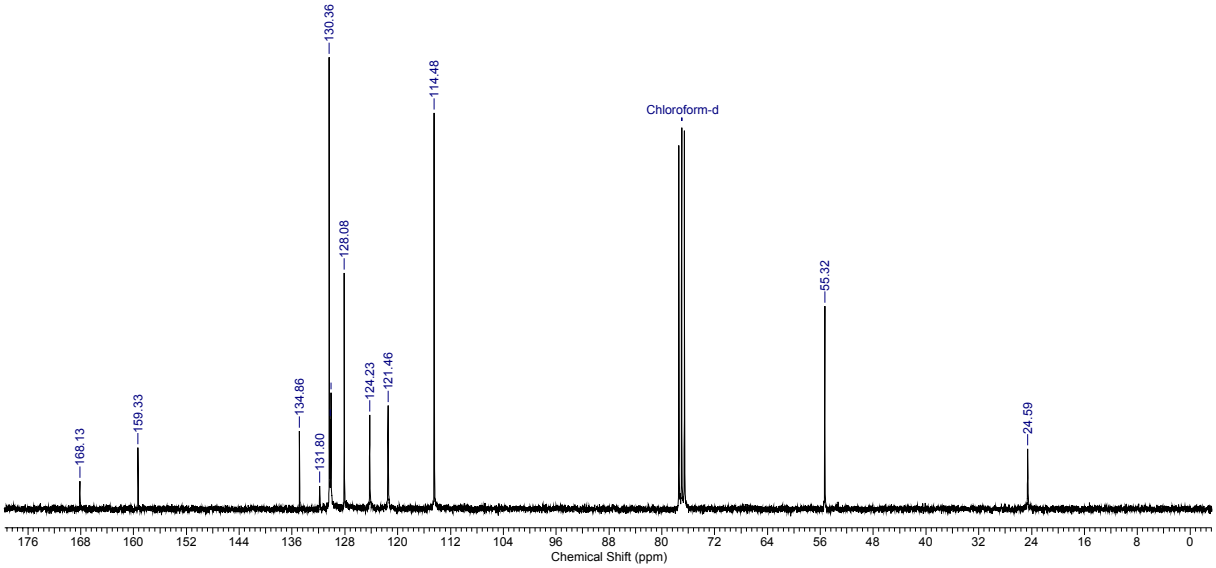
HRMS for **$C_{15}H_{15}NO_2$** (241.1103): found: 241.1089.

N-(4'-Methoxy-biphenyl-2-yl)-acetamide (3b)

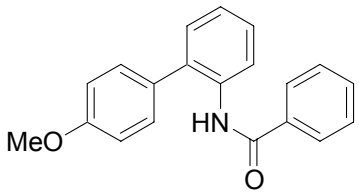
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 23 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl011_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	9849	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	4807.69
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.3005	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 23 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl011_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	2000	***Original Points Count***	23560	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



***N*-(4'-Methoxy-biphenyl-2-yl)-benzamide (3c)**



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(2-iodo-phenyl)-benzamide (323 mg, 1.00 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded biphenyl **3c** as a yellow solid (257 mg, 85 %).

Mp.: 90.1-92.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.42 (d, *J*= 8.2 Hz, 1H), 7.92 (s_br, 1H), 7.54 (d, *J*= 6.8 Hz, 2H), 7.39-7.25 (m, 6H), 7.18 (dd, *J*= 7.6, 2.2 Hz, 1H), 7.09 (t, *J*= 7.5 Hz, 1H), 6.93 (d, *J*= 8.2 Hz, 2H), 3.77 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.9, 159.5, 135.1, 134.8, 132.0, 131.7, 131.3, 130.5, 130.1, 128.7, 128.3, 126.8, 124.3, 121.1, 114.6, 55.4.

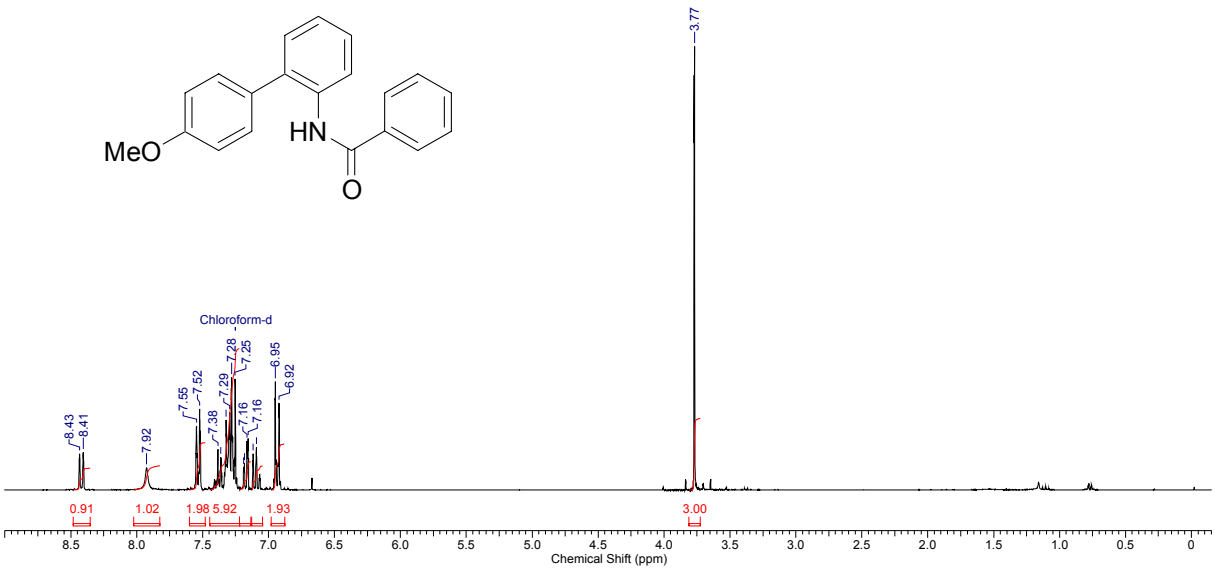
MS (70 eV, EI), *m/z* (%): 303 (73) [M^+], 286 (2), 198 (3), 154 (5), 105 (100), 77 (25).

IR (KBr): ṽ = 3235 (m), 3056 (w), 3001 (w), 2836 (w), 1648 (m), 1635 (vs), 1571 (m), 1529 (s), 1514 (vs), 1491 (m), 1449 (s), 1311 (m), 1295 (m), 1255 (vs), 1176 (m), 1036 (m), 829 (m), 752 (m), 694 (m).

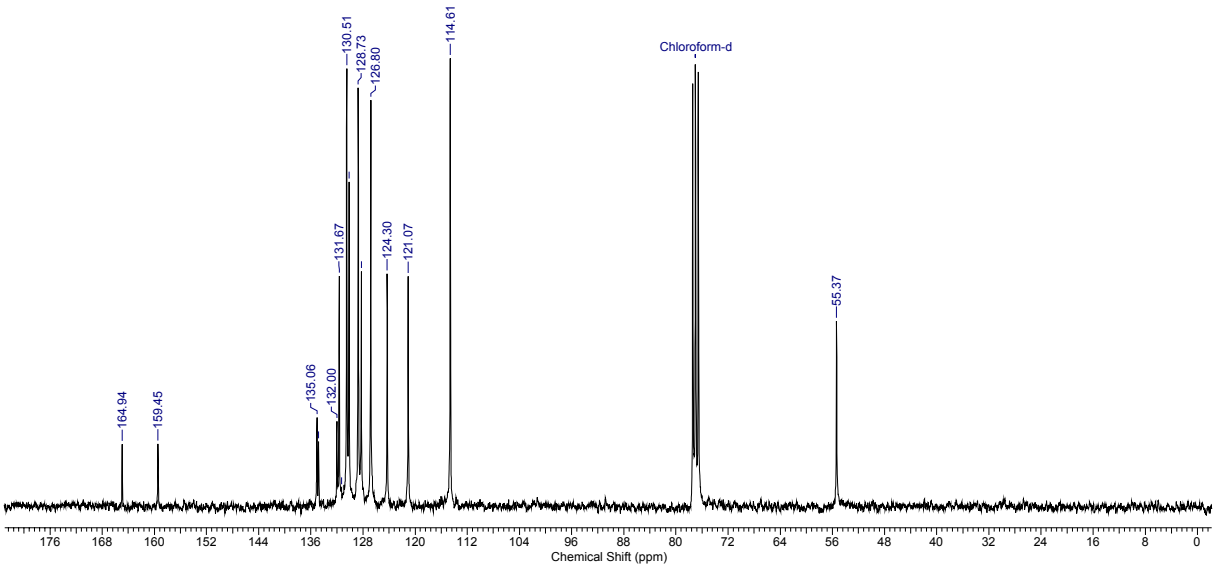
HRMS for **$C_{20}H_{17}NO_2$** (303.1259): found: 303.1263.

N-(4'-Methoxy-biphenyl-2-yl)-benzamide (3c)

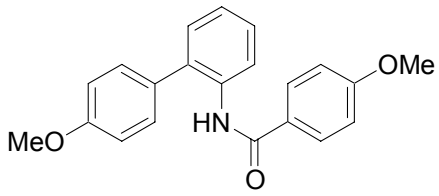
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 28 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl022_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	9849	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	4807.69
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.3005	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 28 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl022_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	2000	***Original Points Count***	23560	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



4-Methoxy-*N*-(4'-methoxybiphenyl-2-yl)benzamide (3d)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(2-iodo-phenyl)-4-methoxy-benzamide (353 mg, 1.00 mmol). Reaction time: 7 h. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded biphenyl **3d** as a colorless solid (305 mg, 92 %).

Mp.: 149.1-149.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, *J*= 8.1 Hz, 1H), 7.94 (s_br, 1H), 7.59 (d, *J*= 8.8 Hz, 2H), 7.43-7.33 (m, 3H), 7.27-7.24 (m, 1H), 7.17 (td, *J*= 7.4, 1.0 Hz, 1H), 7.03 (d, *J*= 8.8 Hz, 2H), 6.88 (d, *J*= 8.8 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.5, 162.3, 159.4, 135.2, 131.8, 130.5, 130.3, 130.1, 128.7, 128.2, 127.1, 124.0, 121.0, 114.6, 113.9, 55.4, 55.3.

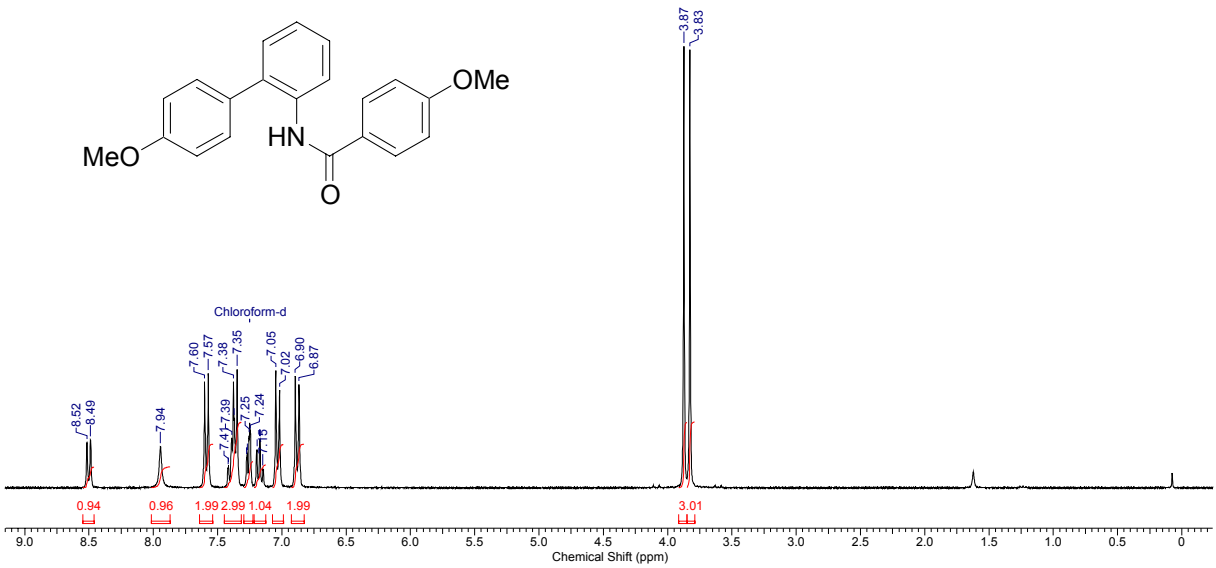
MS (70 eV, EI), *m/z* (%): 333 (32) [M^+], 135 (100), 92 (4), 77 (6).

IR (KBr): $\tilde{\nu}$ = 3301 (w), 3015 (w), 2961 (w), 2836 (w), 1638 (m), 1607 (m), 1519 (m), 1494 (s), 1463 (m), 1438 (m), 1291 (m), 1241 (vs), 1176 (s), 1023 (s), 1001 (m), 913 (w), 833 (s), 800 (w), 758 (vs).

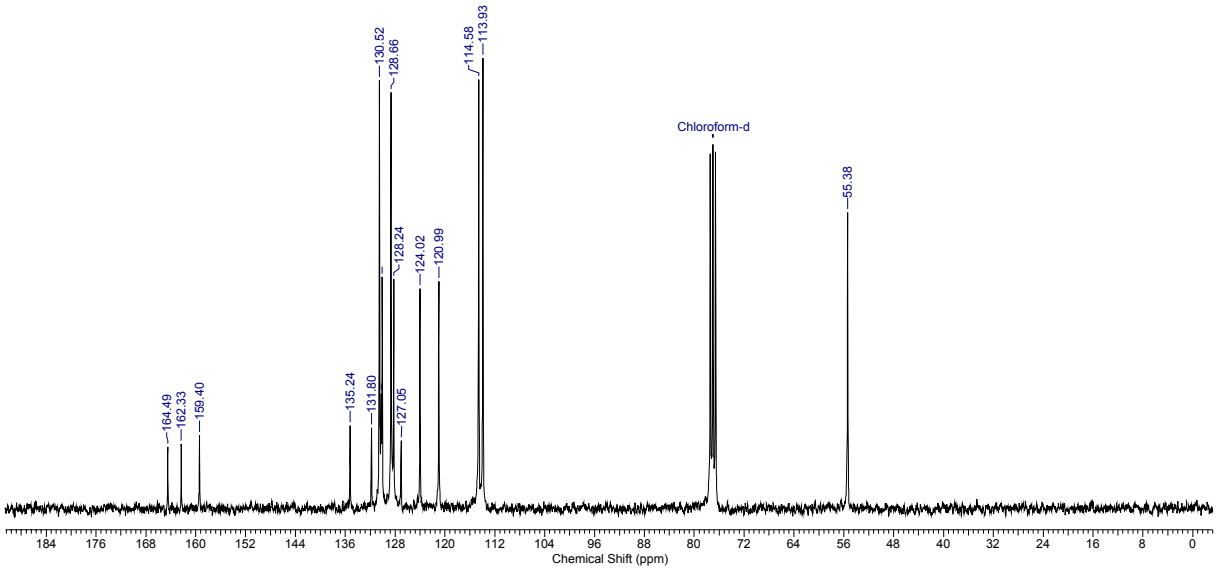
HRMS for **$C_{21}H_{19}NO_3$** (333.1365): found: 333.1340.

4-Methoxy-*N*-(4'-methoxybiphenyl-2-yl)benzamide (3d)

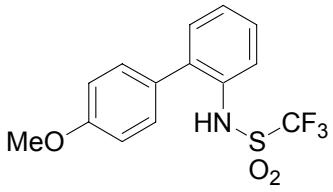
Acquisition Time (sec)	4.1943	***Comment***	Benoit Blank, AK Knochel			***Date***	Mar 27 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl041_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	16384	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	3906.25
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6010	***Comment***	Benoit Blank, AK Knochel			***Date***	Mar 27 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl041_Carbon2k_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	2048	***Original Points Count***	29004	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



1,1,1-Trifluoro-*N*-(4'-methoxybiphenyl-2-yl)methanesulfonamide (3e)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.3 mL, 3.0 mmol, 0.9 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and 1,1,1-trifluoro-*N*-(2-iodophenyl)methanesulfonamide (351 mg, 1.00 mmol). Reaction time: 5 h. Purification by flash chromatography (pentane/diethyl ether = 5:1) yielded biphenyl 3**e** as a brown solid (225 mg, 68 %).

Mp.: 78.3-79.9 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 (dt, *J*= 8.1, 0.9 Hz, 1H), 7.38-7.32 (m, 1H), 7.26 (dd, *J*= 1.8, 0.8 Hz, 1H), 7.25 (s, 1H), 7.24-7.20 (m, 2H), 7.02-6.98 (m, 2H), 3.86 (s, 3H).

^{13}C-NMR (MHz, $CDCl_3$): δ = 159.8, 134.2, 131.8, 130.9, 130.3, 128.7, 126.4, 123.7, 121.1, 116.9 (q, *J*= 192.6 Hz), 114.8, 55.4.

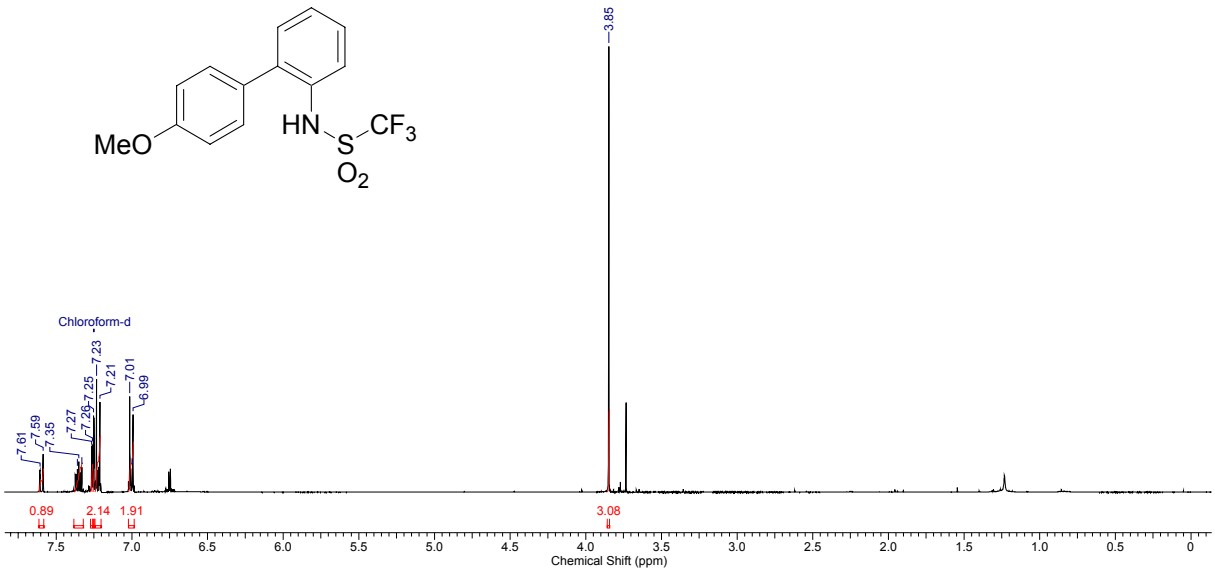
MS (70 eV, EI), *m/z* (%): 331 (73) [M^+], 198 (100), 183 (30), 167 (30), 154 (23), 127 (5).

IR (KBr): $\tilde{\nu}$ = 3158 (w), 1615 (w), 1604 (w), 1519 (w), 1486 (m), 1433 (m), 1372 (m), 1238 (m), 1229 (m), 1189 (vs), 1139 (s), 1108 (m), 1018 (m), 943 (m), 833 (m), 755 (m), 745 (m).

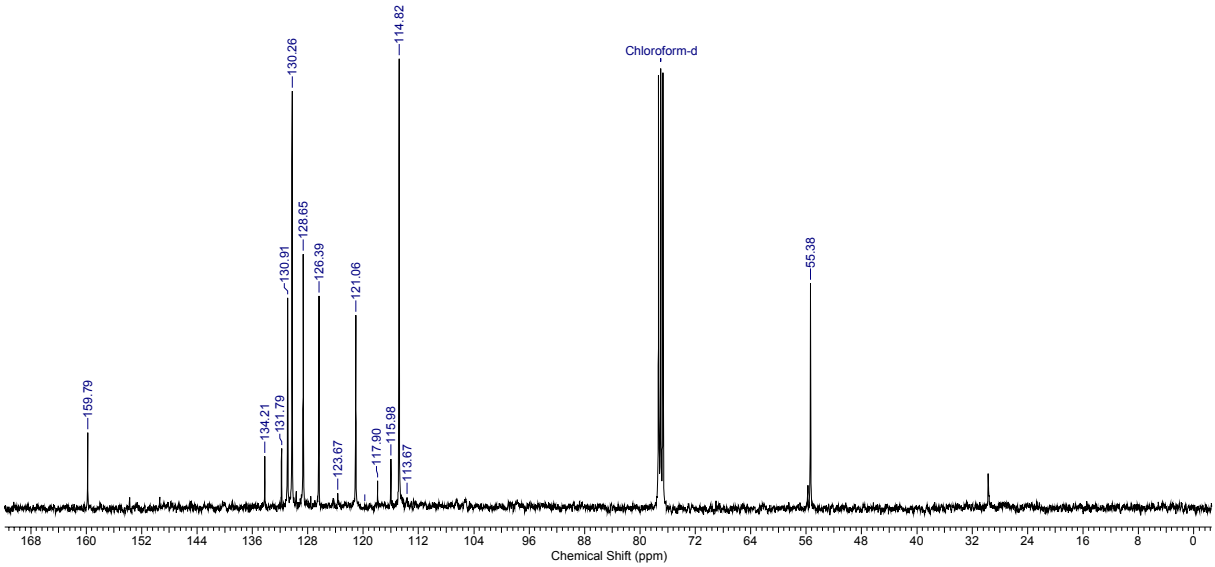
HRMS for **$C_{14}H_{12}F_3NO_3S$** (331.0490): found: 331.0493.

1,1,1-Trifluoro-*N*-(4'-methoxybiphenyl-2-yl)methanesulfonamide (3e)

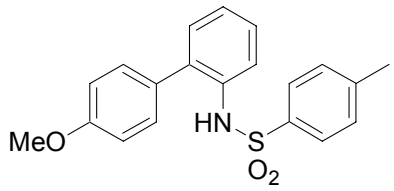
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Apr 21 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\400 MHz\bbl073_Proton_01					***Frequency (MHz)***	399.94
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	20797	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	5199.19
Temperature (degree C)	30.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Apr 21 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\400 MHz\bbl073_Carbon_01					***Frequency (MHz)***	100.58
Nucleus	13C	***Number of Transients***	8192	***Original Points Count***	38612	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24132.73
Temperature (degree C)	30.000						



***N*-(4'-Methoxybiphenyl-2-yl)-4-methylbenzenesulfonamide (3f)**



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(2-iodo-phenyl)-4-methyl-benzenesulfonamide (373 mg, 1.00 mmol). Reaction time: 5 h. Purification by flash chromatography (pentane/diethyl ether = 19:1) yielded biphenyl **3f** as a pale brown solid (297 mg, 84 %).

Mp.: 107.2-109.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, *J*= 7.6, 1.2 Hz, 1H), 7.49 (dt, *J*= 8.5, 1.9 Hz, 2H), 7.32-7.25 (m, 1H), 7.19 (d, *J*= 8.5 Hz, 2H), 7.13-7.05 (m, 2H), 6.82 (m, 4H), 6.57 (s_br, 1H), 3.84 (s, 3H), 2.39 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.4, 143.8, 136.2, 134.0, 133.4, 130.4, 130.1, 129.5, 129.3, 128.4, 127.2, 124.7, 120.9, 114.5, 55.4, 21.5.

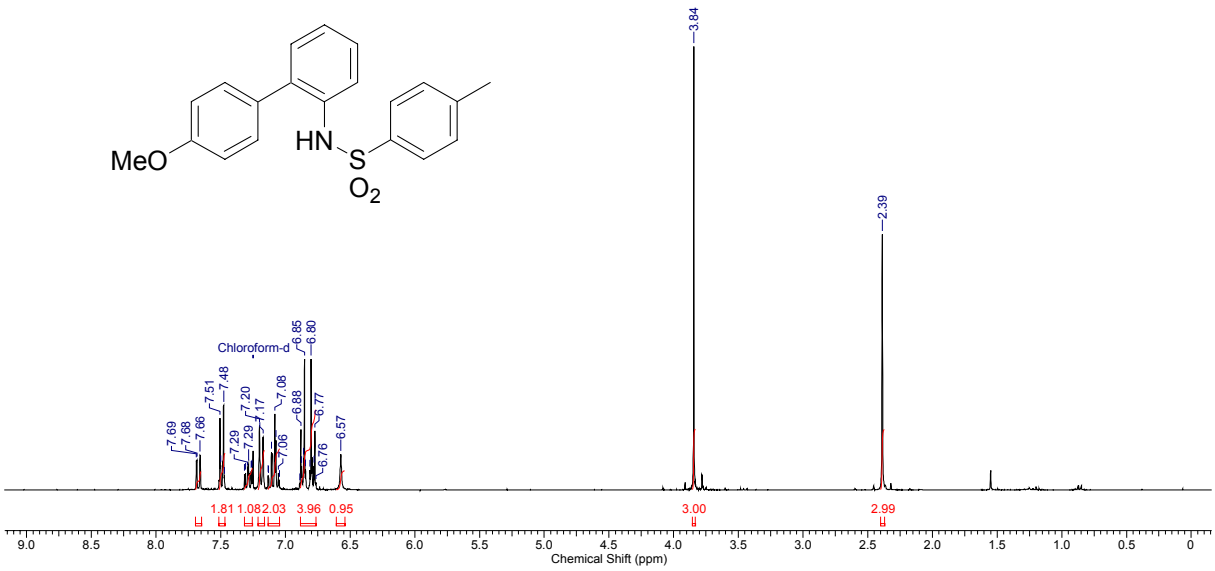
MS (70 eV, EI), *m/z* (%): 353 (30) [M^+], 198 (100), 183 (25), 167 (20), 154 (15), 91 (4).

IR (KBr): ṽ = 3250 (m), 3039 (w), 1600 (m), 1511 (m), 1485 (m), 1398 (m), 1332 (m), 1300 (m), 1241 (s), 1150 (vs), 1089 (s), 1031 (m), 907 (s), 827 (s), 810 (s), 749 (vs), 665 (vs).

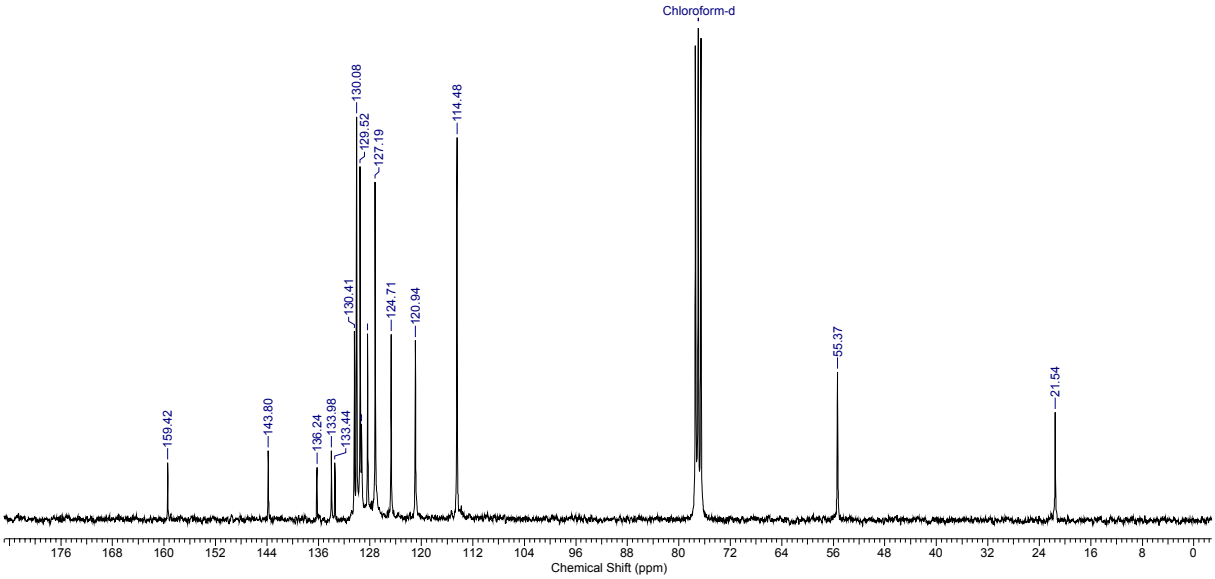
HRMS for **$C_{20}H_{19}NO_3S$** (353.1086): found: 353.1083.

N-(4'-Methoxybiphenyl-2-yl)-4-methylbenzenesulfonamide (3f)

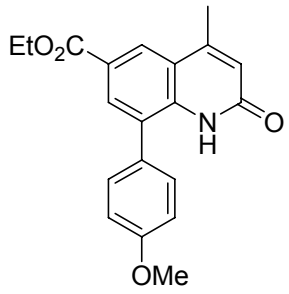
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 27 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl023_Proton_01					***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	9849	***Points Count***	16384
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	4807.69
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.3005	***Comment***	Benoit Blank, AK Knochel			***Date***	Feb 27 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl023_Carbon_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	5000	***Original Points Count***	23560	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



Ethyl 8-(4-methoxyphenyl)-4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (5a)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (1.88 mL, 1.5 mmol, 0.8 M in THF), CuCN·2LiCl (1.4 mL, 1.4 mmol, 1.0 M in THF), $Fe(acac)_3$ (18 mg, 5 mol %) and ethyl 8-iodo-4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (178 mg, 0.50 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/EtOAc/MeOH = 4:1:0.1) yielded biphenyl **5a** as a yellow solid (154 mg, 91 %).

Mp.: 168-169 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.71 (s_br, 1H), 8.37 (d, *J*= 1.8 Hz, 1H), 8.04 (d, *J*= 1.9 Hz, 1H), 7.32 (d, *J*= 8.8 Hz, 2H), 7.05 (d, *J*= 8.7 Hz, 2H), 6.54 (d, *J*= 1.0 Hz, 1H), 4.40 (q, *J*= 7.2 Hz, 2H), 3.02 (s, 3H), 2.57 (d, *J*= 1.2 Hz, 3H), 1.40 (t, *J*= 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.0, 161.9, 160.1, 149.3, 138.5, 131.9, 130.5, 128.6, 127.3, 126.0, 124.2, 121.5, 120.3, 115.1, 61.2, 55.5, 19.5, 14.4.

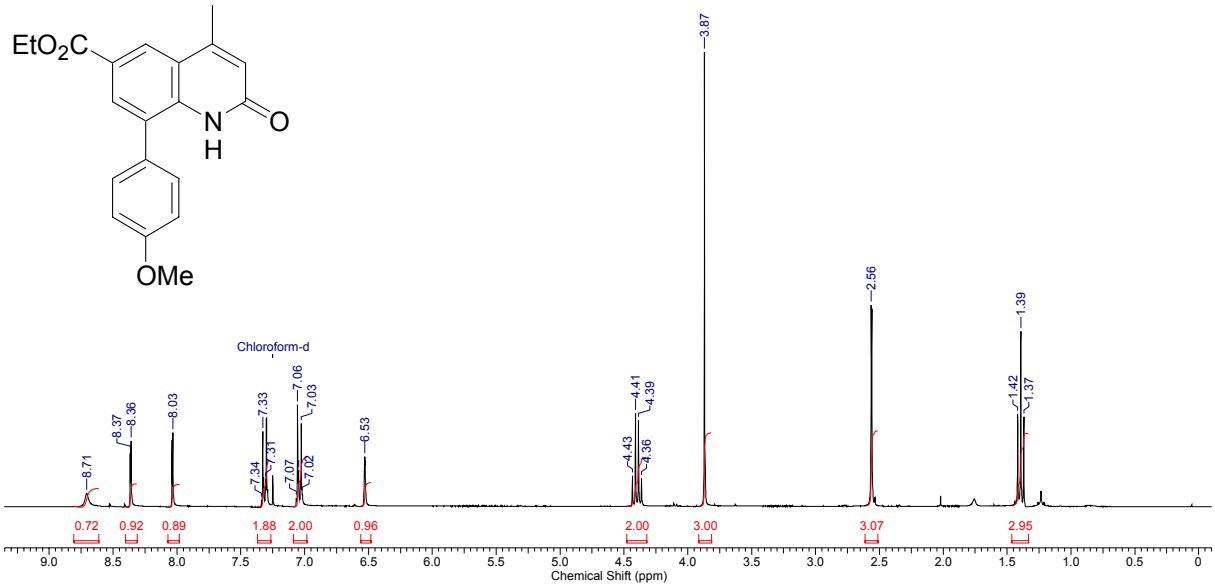
MS (70 eV, EI), *m/z* (%): 337 (100) [M^+], 336 (56), 322 (8), 308 (13), 292 (14).

IR (KBr): $\tilde{\nu}$ = 2982 (w), 1715 (m), 1660 (s), 1597 (m), 1514 (m), 1464 (w), 1395 (w), 1297 (m), 1250 (s), 1179 (w), 1072 (w), 1028 (w), 964 (w), 909 (w), 865 (w), 834 (w), 766 (w), 592 (w).

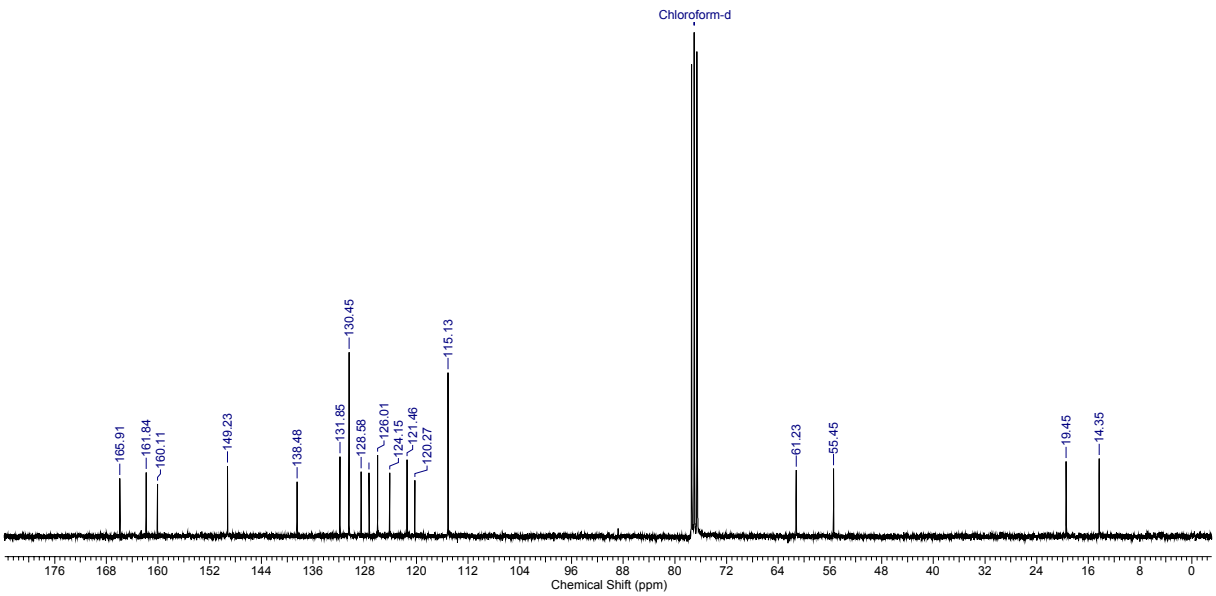
HRMS for **$C_{20}H_{19}NO_4$** (337.1314): found: 337.1307.

Ethyl 8-(4-methoxyphenyl)-4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (5a)

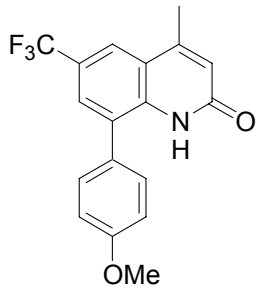
Acquisition Time (sec)	2.2610	***Comment***	Ak Knochel User Kofink Bruker ARX 300			***Date***	14 Nov 2005 07:36:32
File Name	I:\Supporting Information - Paper\cko_ng4\cko_ng4_001000fid			***Frequency (MHz)***	300.13	***Nucleus***	1H
Number of Transients	64	***Original Points Count***	8192	***Points Count***	8192	***Pulse Sequence***	zg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	3623.19	***Temperature (degree C)***	17.000



Acquisition Time (sec)	1.7039	***Comment***	Ak Knochel User Kofink Bruker ARX 300			***Date***	14 Nov 2005 09:06:08
File Name	I:\Supporting Information - Paper\cko_ng4\cko_ng4_002000fid			***Frequency (MHz)***	75.48	***Nucleus***	13C
Number of Transients	1563	***Original Points Count***	32768	***Points Count***	32768	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	19230.77	***Temperature (degree C)***	27.000



8-(4-Methoxyphenyl)-4-methyl-6-(trifluoromethyl)quinolin-2(1*H*)-one (5b)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (1.88 mL, 1.5 mmol, 0.8 M in THF), DME (3.5 mL), CuCN·2LiCl (1.4 mL, 1.4 mmol, 1.0 M in THF), $Fe(acac)_3$ (18 mg, 5 mol %) and 8-iodo-4-methyl-6-(trifluoromethyl)quinolin-2(1*H*)-one (177 mg, 0.50 mmol). Reaction time: 12 h. Purification by flash chromatography (pentane/EtOAc = 4:1) yielded biphenyl **5b** as a colorless solid (140 mg, 84 %).

Mp.: 142-143 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.71 (s_br, 1H), 7.90 (d, *J*= 0.9 Hz, 1H), 7.61 (d, *J*= 1.8 Hz, 1H), 7.32 (d, *J*= 8.9 Hz, 2H), 7.06 (d, *J*= 9.1 Hz, 2H), 6.58 (d, *J*= 1.3 Hz, 1H), 3.88 (s, 3H), 2.57 (d, *J*= 1.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 161.7, 160.3, 148.6, 137.6, 130.4, 129.4, 127.6 (q, *J*= 3.2) 126.8, 125.8, 124.3 (q, *J*= 33.0 Hz), 122.2, 121.2 (q, *J*= 4.1 Hz), 120.4, 115.3, 55.5, 19.3.

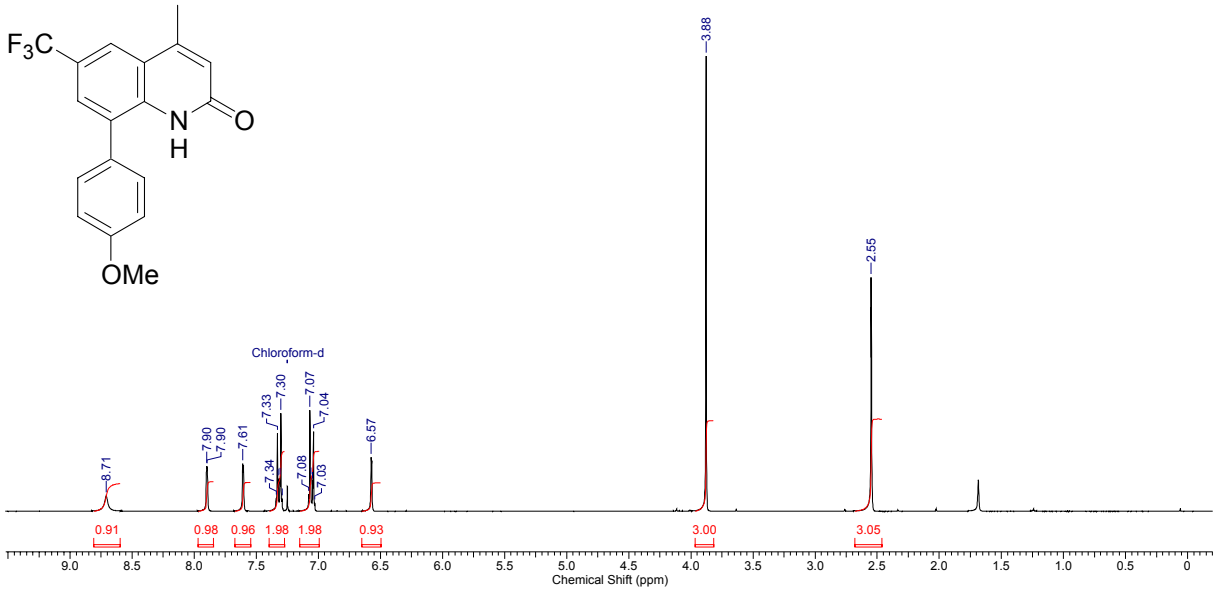
MS (70 eV, EI), *m/z* (%):333 (95) [M^+], 332 (100), 318 (14), 317 (8), 290 (7).

IR (KBr): ṽ = 3387 (w), 3169 (w), 3047 (w), 2954 (w), 2837 (w), 1667 (s), 1607 (s), 1515 (m), 1464 (w), 1402 (s), 1318 (s), 1271 (s), 1214 (w), 1152 (m), 1114 (s), 1066 (m), 892 (m), 832 (w), 784 (w), 662 (w), 592 (w), 491 (w).

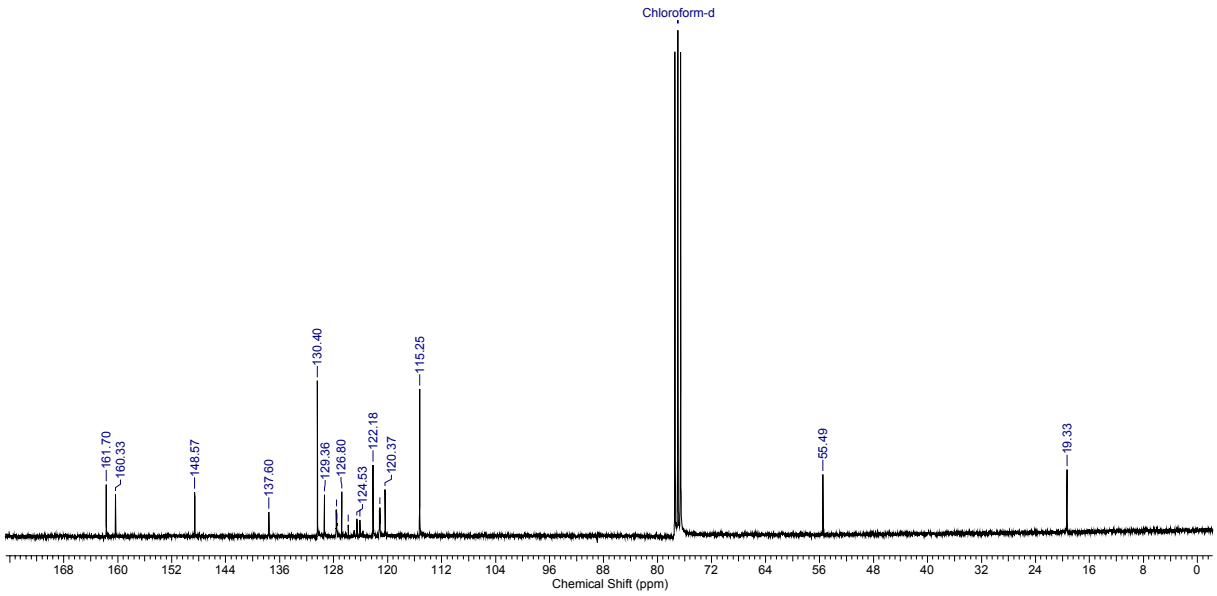
HRMS for **$C_{18}H_{14}F_3NO_2$** (333.0977): found: 333.0961.

8-(4-Methoxyphenyl)-4-methyl-6-(trifluoromethyl)quinolin-2(1*H*)-one (5b)

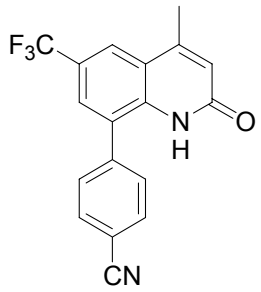
Acquisition Time (sec)	2.2610	***Comment***	Ak Knochel User Kofink Bruker ARX 300			***Date***	10 Oct 2005 06:21:52
File Name	I:\Supporting Information - Paper\cko_sp31\cko_sp31_001000fid			***Frequency (MHz)***	300.13	***Nucleus***	1H
Number of Transients	64	***Original Points Count***	8192	***Points Count***	8192	***Pulse Sequence***	zg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	3623.19	***Temperature (degree C)***	17.000



Acquisition Time (sec)	1.7039	***Comment***	Ak Knochel User Kofink Bruker ARX 300			***Date***	10 Oct 2005 09:21:04
File Name	I:\Supporting Information - Paper\cko_sp31\cko_sp31_002000fid			***Frequency (MHz)***	75.48	***Nucleus***	13C
Number of Transients	4096	***Original Points Count***	32768	***Points Count***	32768	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	19230.77	***Temperature (degree C)***	27.000



4-[4-Methyl-2-oxo-6-(trifluoromethyl)-1,2-dihydroquinolin-8-yl]benzonitrile (5c)



Prepared according to **TP 2** from 4-iodobenzonitrile (343 mg, 1.50 mmol), DME (3.5 mL), *i*PrMgCl (1.7 mL, 1.55 mmol, 0.9 M in THF), CuCN·2LiCl (1.4 mL, 1.4 mmol, 1.0 M in THF), $Fe(acac)_3$ (18 mg, 5 mol %) and 8-iodo-4-methyl-6-(trifluoromethyl)quinolin-2(1*H*)-one (177 mg, 0.50 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/EtOAc/MeOH = 4:1:0.1) yielded biphenyl **5c** as a colorless solid (122 mg, 74 %).

Mp.: 230.1-231.8 °C

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.02 (s_br, 1H), 7.98 (s, 1H), 7.84 (d, *J*= 8.1 Hz, 2H), 7.60 (s, 1H), 7.55 (d, *J*= 8.1 Hz, 2H), 6.55 (s, 1H), 2.57 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 161.7, 148.6, 139.9, 137.3, 133.4, 130.2, 127.6, 127.5 (q, *J*= 4 Hz), 124.6 (q, *J*= 28 Hz), 123.8 (q, *J*= 277 Hz), 122.6 (q, *J*= 4 Hz), 122.5, 120.8, 118.0, 113.3, 19.4.

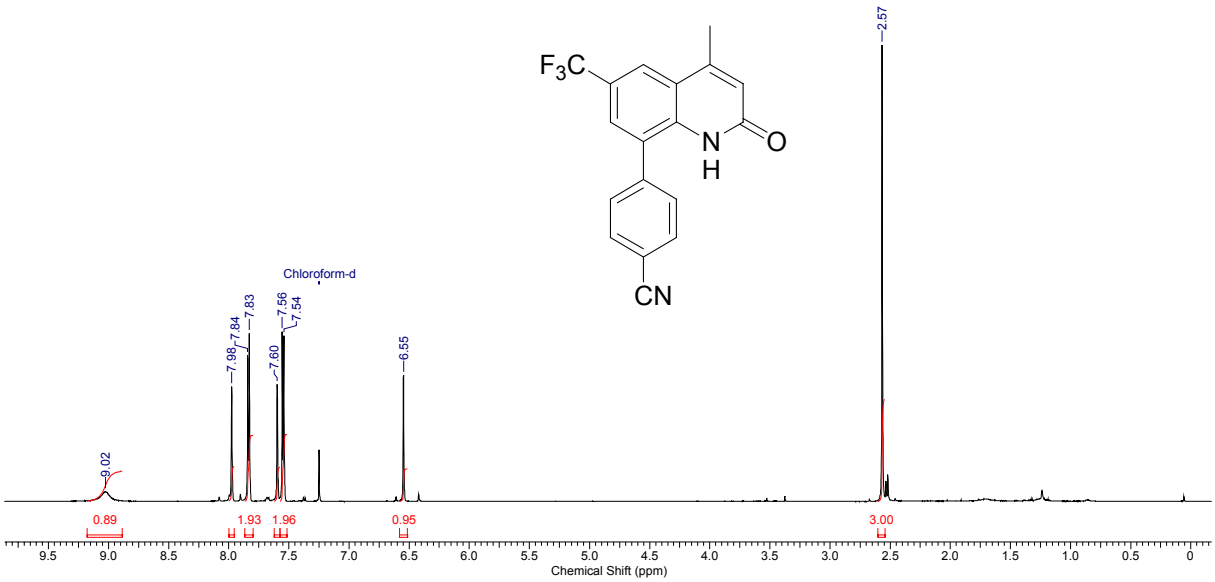
MS (70 eV, EI), *m/z* (%): 327 (100) [M-H$^+$], 299 (4), 279 (2), 115 (2).

IR (KBr): $\tilde{\nu}$ = 3189 (w), 2231 (w), 1667 (s), 1605 (m), 1395 (w), 1316 (s), 1261 (m), 1180 (m), 1098 (vs), 1059 (m), 896 (s), 833 (s), 780 (m), 632 (m).

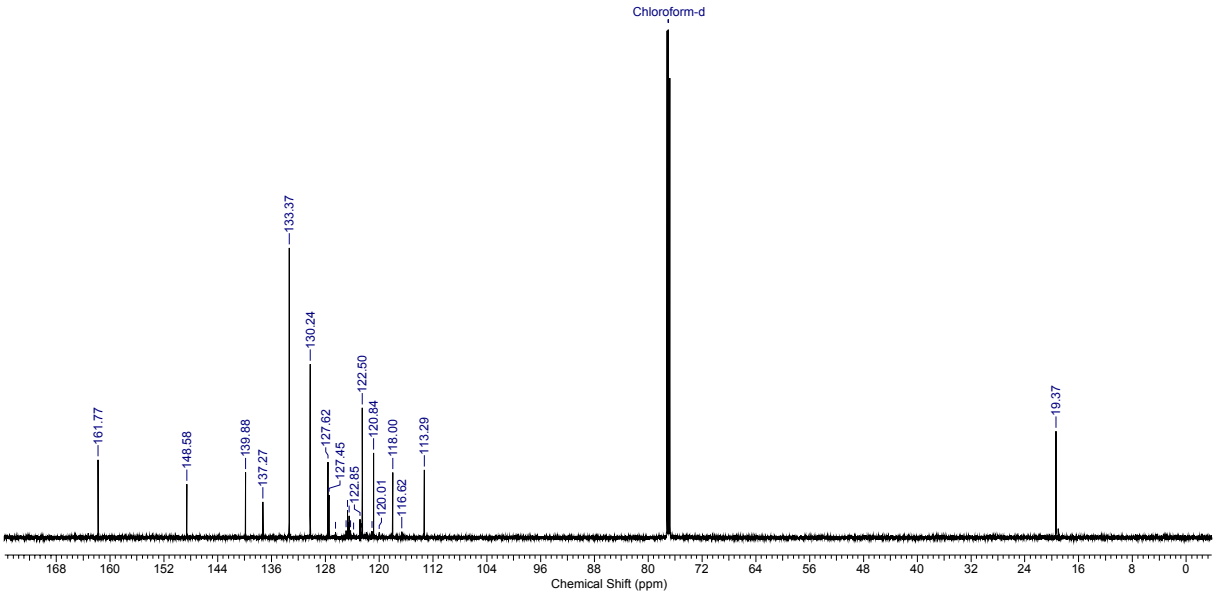
HRMS for **$C_{18}H_{11}F_3N_2O$** (328.0823): found: 328.0797.

4-[4-Methyl-2-oxo-6-(trifluoromethyl)-1,2-dihydroquinolin-8-yl]benzonitrile (5c)

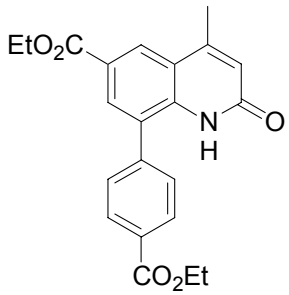
Acquisition Time (sec)	2.0972	***Comment***	Ak Knochel User C. Kofink Bruker AMX600	***Date***	13 Dec 2005 09:36:00
File Name	I:\Supporting Information - Paper\cko_ng11\cko_ng11_001000fid	***Frequency (MHz)***	599.70	***Nucleus***	1H
Number of Transients	64	***Original Points Count***	16384	***Points Count***	16384	***Pulse Sequence***	zg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	7812.50	***Temperature (degree C)***	27.000



Acquisition Time (sec)	0.8520	***Comment***	Ak Knochel User C. Kofink Bruker AMX600	***Date***	13 Dec 2005 07:25:52
File Name	I:\Supporting Information - Paper\cko_ng11\cko_ng11_002000fid	***Frequency (MHz)***	150.81	***Nucleus***	13C
Number of Transients	2277	***Original Points Count***	32768	***Points Count***	32768	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D	***Sweep Width (Hz)***	38461.54	***Temperature (degree C)***	27.000		



Ethyl 8-[4-(ethoxycarbonyl)phenyl]-4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (5d)



Prepared according to **TP 2** from ethyl 4-iodobenzoate (428 mg, 1.50 mmol), DME (3.5 mL), *i*PrMgCl (1.7 mL, 1.55 mmol, 0.9 M in THF), CuCN·2LiCl (1.4 mL, 1.4 mmol, 1.0 M in THF), $Fe(acac)_3$ (18 mg, 5 mol %) and ethyl 8-iodo-4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (178 mg, 0.50 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/EtOAc/MeOH = 4:1:0.1) yielded biphenyl **5d** as a colorless solid (158 mg, 88 %).

Mp.: 212.0-213.8 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.63 (s_br, 1H), 8.41 (d, *J*= 1.8 Hz, 1H), 8.20 (dt, *J*= 8.4, 1.8 Hz, 2H), 8.06 (d, *J*= 1.8 Hz, 1H), 7.50 (dt, *J*= 8.3, 1.8 Hz, 2H), 6.55 (d, *J*= 0.9 Hz, 1H), 4.47-4.37 (m, 4H), 2.57 (d, *J*= 1.3 Hz, 3H), 1.45-1.37 (m, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.8, 165.7, 161.7, 149.2, 139.9, 138.0, 131.7, 131.1, 130.8, 129.4, 127.7, 126.8, 124.3, 121.7, 120.5, 61.4, 61.3, 19.5, 14.4, 14.3.

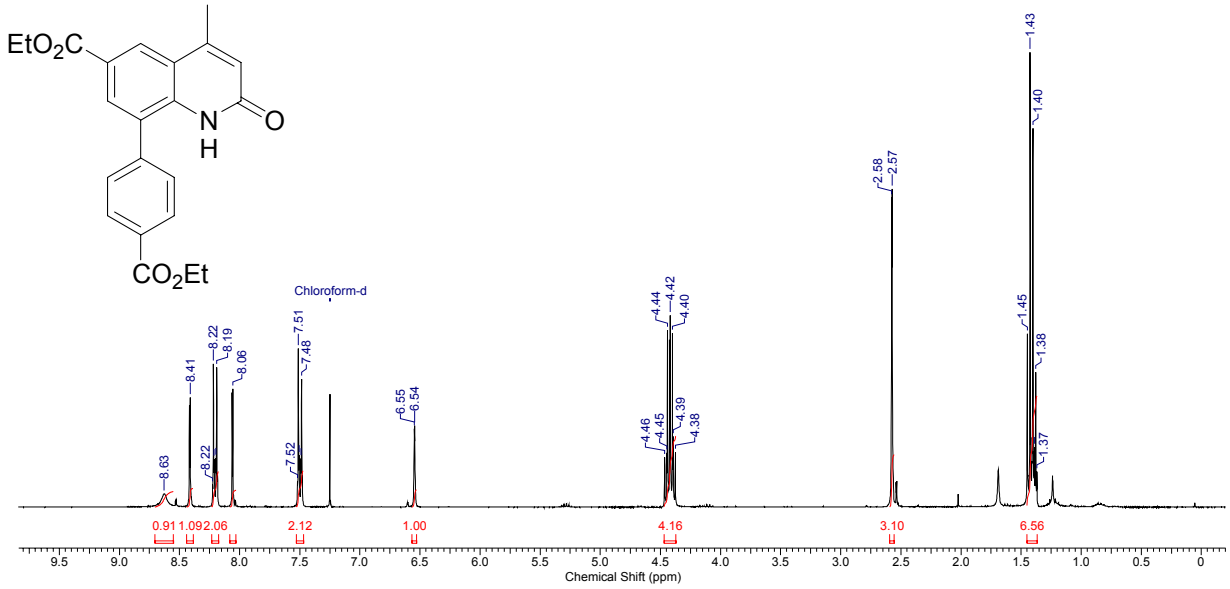
MS (70 eV, EI), *m/z* (%): 379 (100) [M^+], 350 (16), 334 (31), 306 (12), 278 (7), 233 (8), 204 (11).

IR (KBr): ṽ = 3296 (w), 2980 (w), 1710 (s), 1672 (vs), 1596 (s), 1365 (m), 1287 (m), 1253 (m), 1239 (vs), 1207 (s), 1177 (s), 1101 (s), 1029 (m), 957 (m), 855 (m), 767 (s), 716 (m).

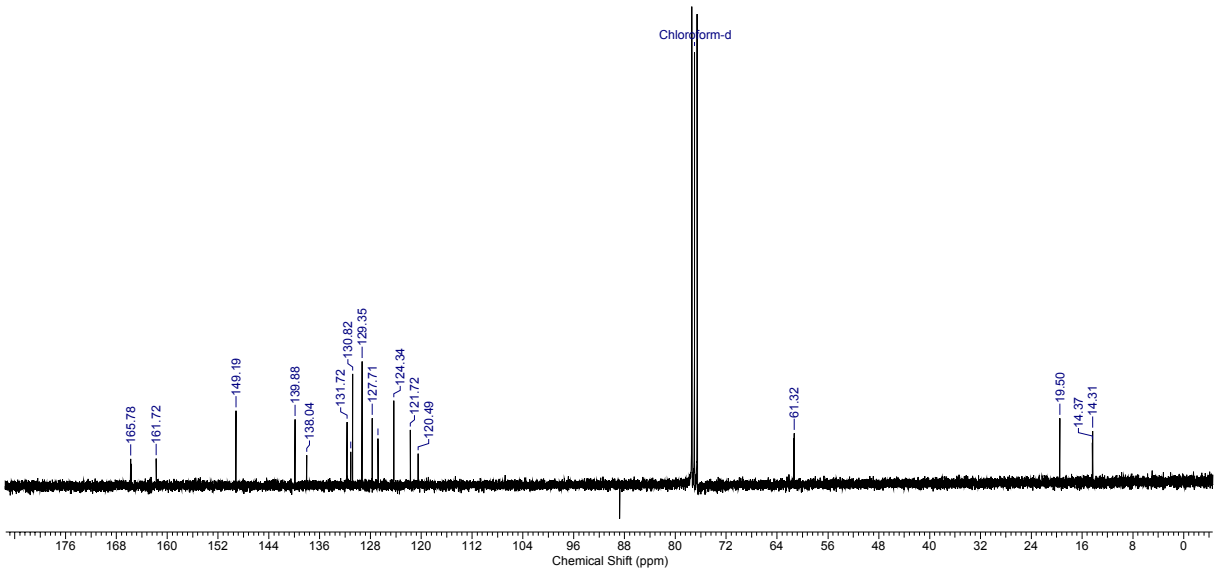
HRMS for **$C_{22}H_{21}NO_5$** (379.1420): found: 379.1411.

Ethyl 8-[4-(ethoxycarbonyl)phenyl]-4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (5d)

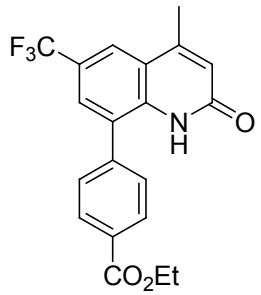
Acquisition Time (sec)	2.2610	***Comment***	Ak Knochel User Kofink Bruker ARX 300			***Date***	14 Nov 2005 09:53:04
File Name	I:\Supporting Information - Paper\cko_ng5\cko_ng5_001000fid			***Frequency (MHz)***	300.13	***Nucleus***	1H
Number of Transients	64	***Original Points Count***	8192	***Points Count***	8192	***Pulse Sequence***	zg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	3623.19	***Temperature (degree C)***	17.000



Acquisition Time (sec)	1.7039	***Comment***	Ak Knochel User Kofink Bruker ARX 300			***Date***	14 Nov 2005 10:48:32
File Name	I:\Supporting Information - Paper\cko_ng5\cko_ng5_002000fid			***Frequency (MHz)***	75.48	***Nucleus***	13C
Number of Transients	1537	***Original Points Count***	32768	***Points Count***	32768	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	19230.77	***Temperature (degree C)***	27.000



Ethyl 4-[4-methyl-2-oxo-6-(trifluoromethyl)-1,2-dihydroquinolin-8-yl]benzoate (5e)



Prepared according to **TP 2** from ethyl 4-iodobenzoate (428 mg, 1.50 mmol), DME (3.5 mL), *i*PrMgCl (1.7 mL, 1.55 mmol, 0.9 M in THF), CuCN·2LiCl (1.4 mL, 1.4 mmol, 1.0 M in THF), $Fe(acac)_3$ (18 mg, 5 mol %) and 8-Iodo-4-methyl-6-(trifluoromethyl)quinolin-2(1*H*)-one (177 mg, 0.50 mmol). Reaction time: 12 h. Purification by flash chromatography (pentane/EtOAc = 4:1) yielded biphenyl **5e** as a colorless solid (158 mg, 88 %).

Mp.: 222-224 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.76 (s_br, 1H), 8.21 (d, *J*= 8.5 Hz, 2H), 7.95 (d, *J*= 1.0 Hz, 1H), 7.62 (d, *J*= 1.7 Hz, 1H), 7.49 (d, *J*= 8.5 Hz, 2H), 6.57 (d, *J*= 1.0 Hz, 1H), 4.43 (q, *J*= 7.2 Hz, 2H), 2.55 (d, *J*= 1.1 Hz, 3H), 1.42 (t, *J*= 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.7, 161.6, 148.5, 139.3, 137.3 131.3, 130.9, 129.3, 128.5, 127.4 (q, *J*= 3.5 Hz), 125.7, 124.4 (q, *J*= 33.5) 122.4, 122.0 (q, *J*= 3.8 Hz), 120.6, 61.4, 19.3, 14.3.

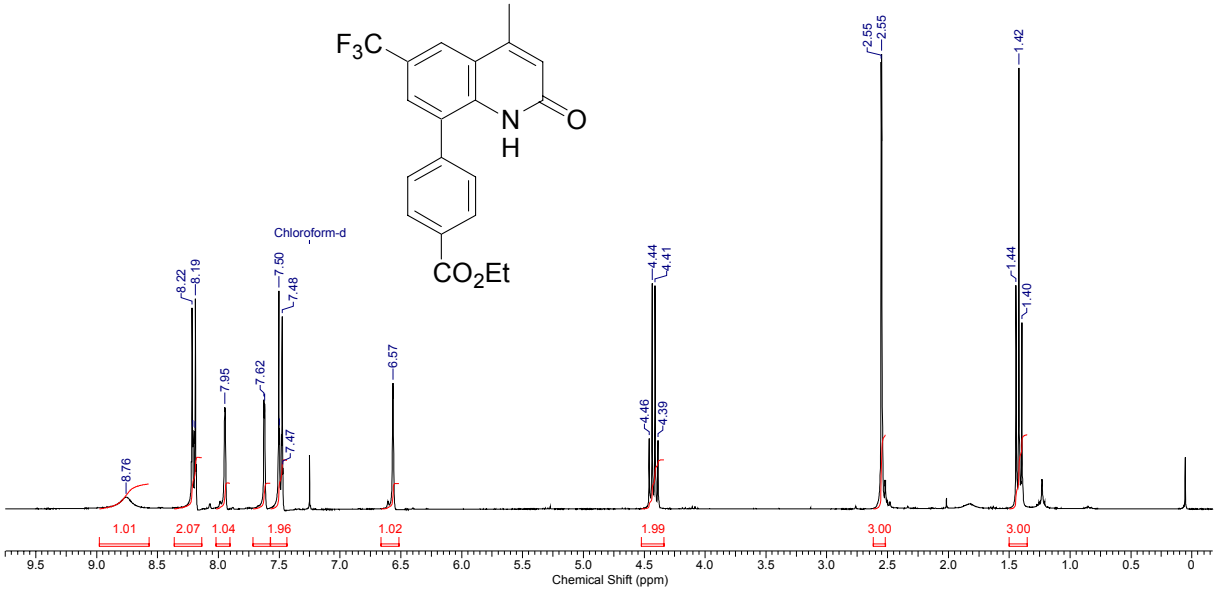
MS (70 eV, EI), *m/z* (%): 375 (100) [M^+], 374 (56), 347 (10), 346 (38), 330 (37), 303 (14), 302 (58) 272 (20), 204 (15), 164 (12).

IR (KBr): $\tilde{\nu}$ = 2986 (w), 1716 (m), 1668 (s), 1608 (m) 1401 (w), 1317 (m), 1276 (m), 1190 (w), 1157 (w), 1108 (m), 1062 (w), 1022 (w), 894 (w), 774 (w), 708 (w), 494 (w).

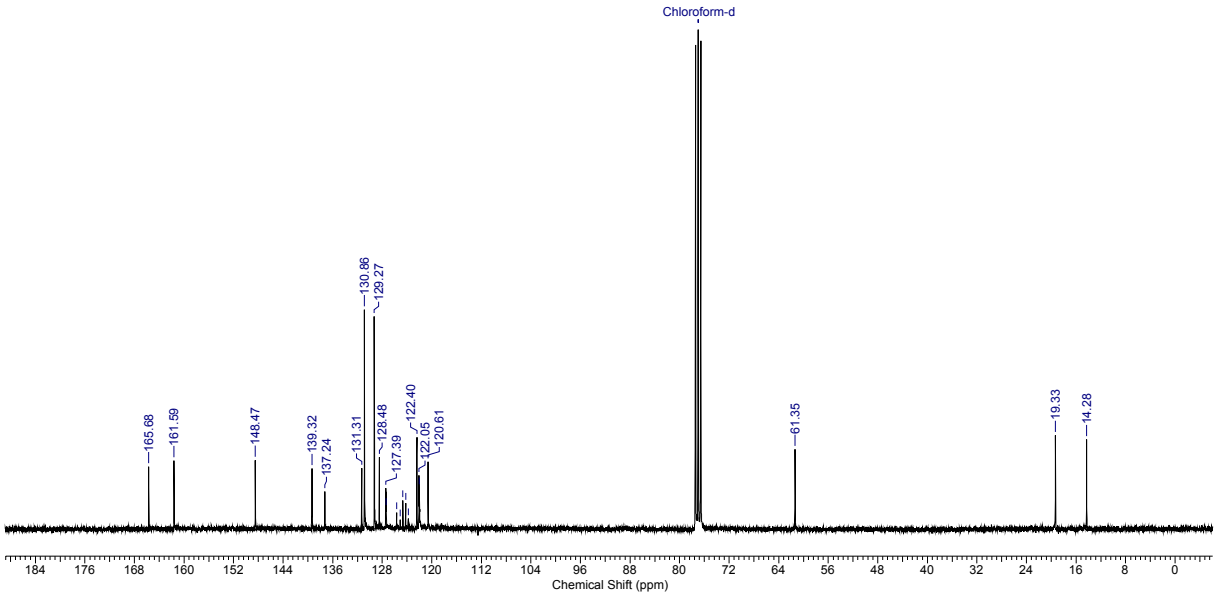
HRMS for **$C_{20}H_{16}F_3NO_3$** (375.1082): found: 375.1059.

Ethyl 4-[4-methyl-2-oxo-6-(trifluoromethyl)-1,2-dihydroquinolin-8-yl]benzoate (5e)

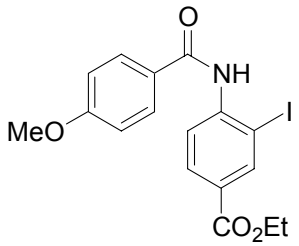
Acquisition Time (sec)	2.2610	***Comment***	Ak Knochel User Kofink Bruker ARX 300	***Date***	13 Oct 2005 04:35:12
File Name	I:\Supporting Information - Paper\cko-sp34\cko-sp34_001000fid	***Frequency (MHz)***	300.13	***Nucleus***	1H
Number of Transients	64	***Original Points Count*** 8192	***Points Count***	8192	***Pulse Sequence*** zg30
Solvent	CHLOROFORM-D		***Sweep Width (Hz)***	3623.19	***Temperature (degree C)*** 17.000



Acquisition Time (sec)	1.7039	***Comment***	Ak Knochel User Kofink Bruker ARX 300	***Date***	13 Oct 2005 05:28:32
File Name	I:\Supporting Information - Paper\cko-sp34\cko-sp34_002000fid	***Frequency (MHz)***	75.48	***Nucleus***	13C
Number of Transients	2048	***Original Points Count*** 32768	***Points Count***	32768	***Pulse Sequence*** zgpg30
Solvent	CHLOROFORM-D		***Sweep Width (Hz)***	19230.77	***Temperature (degree C)*** 27.000



Ethyl 3-iodo-4-[(4-methoxybenzoyl)amino]benzoate (6a)



Prepared according to **TP 3** from ethyl 4-amino-3-iodobenzoate (1.30 g, 4.47 mmol) and *p*-anisoyl chloride (0.6 mL, 4.5 mmol) in dioxane (20 mL) and pyridine (10 mL). Reaction time: 12 h. Purification by recrystallization from ethanol furnished **6a** as a pink solid (1.35 g, 71 %).

Mp.: 138.4-140.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.59 (d, *J*= 8.6 Hz, 1H), 8.47 (t, *J*= 2.1 Hz, 1H), 8.42 (s_br, 1H), 8.04 (d, *J*= 8.7 Hz, 1H), 7.93 (d, *J*= 6.6 Hz, 2H), 7.01 (d, *J*= 6.7 Hz, 2H), 4.36 (q, *J*= 7.1 Hz, 2H), 3.88 (s, 3H), 1.39 (t, *J*= 7.1 Hz, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.8, 164.7, 163.0, 142.2, 140.1, 130.9, 129.2, 127.2, 126.3, 119.8, 114.3, 88.6, 61.2, 55.5, 14.3.

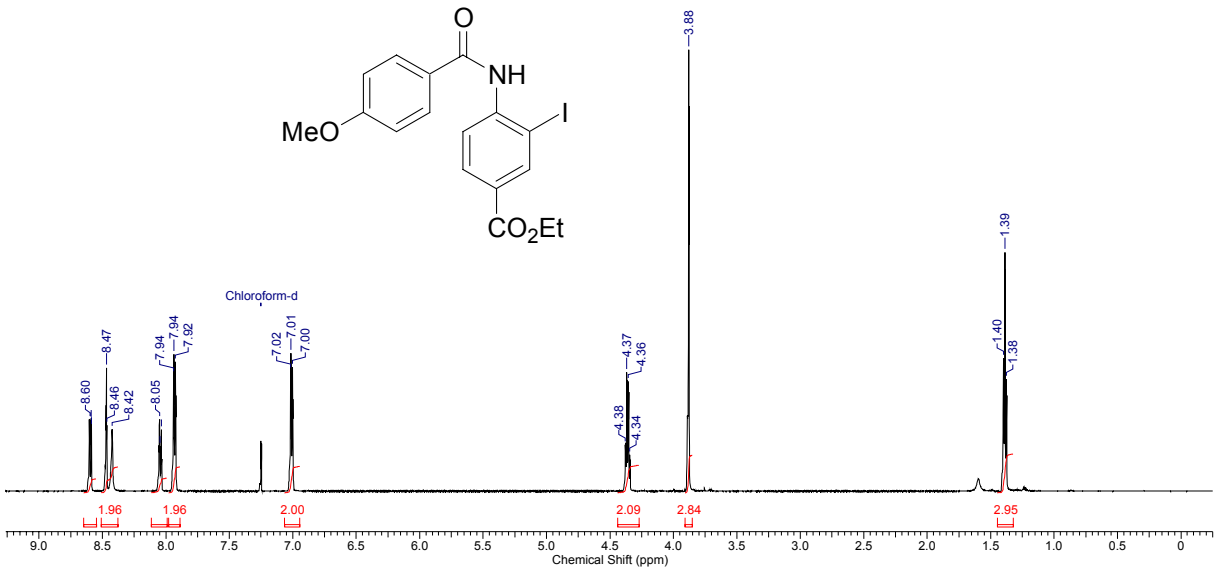
MS (70 eV, EI), *m/z* (%): 425 (4) [M^+], 298 (40), 135 (100), 92 (4), 77 (5).

IR (KBr): ṽ = 3403 (w), 2984 (w), 1708 (m), 1692 (m), 1589 (m), 1503 (vs), 1237 (s), 1263 (vs), 1173 (vs), 1113 (m), 1091 (s), 1023 (s), 842 (m), 763 (s), 751 (s), 684 (s), 633 (m).

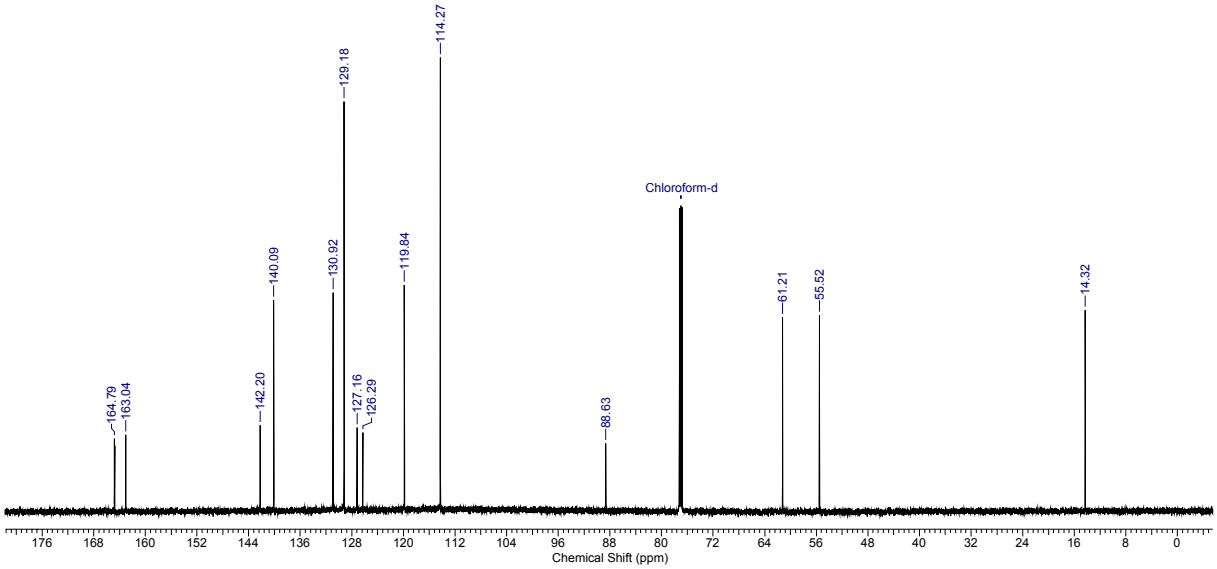
HRMS for **$C_{17}H_{16}INO_4$** (425.0124): found: 425.0137.

Ethyl 3-iodo-4-[(4-methoxybenzoyl)amino]benzoate (6a)

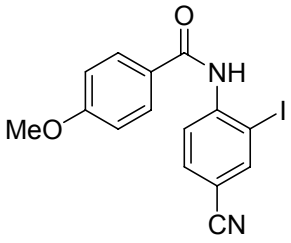
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 2 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\BBI102_Proton_01			***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	7225.43
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 2 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\BBI102_Carbon2048_01			***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	4096	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	27.000				



N-(4-Cyano-2-iodophenyl)-4-methoxybenzamide (6b)



Prepared according to **TP 3** from 4-amino-3-iodo-benzonitrile (1.28 g, 5.26 mmol) and *p*-anisoyl chloride (0.7 mL, 5.3 mmol) in dioxane (20 mL) and pyridine (10 mL). Reaction time: 12 h. Purification by recrystallization from ethanol furnished **6b** as a colorless solid (1.27 g, 64 %).

Mp.: 206.6-208.7 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.67 (d, *J*= 8.6 Hz, 1H), 8.43 (s_br, 1H), 8.08-8.06 (m, 1H), 7.93-7.90 (m, 2H), 7.66 (dd, *J*= 8.7, 1.9 Hz, 1H), 7.03-7.00 (m, 2H), 3.89 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 165.1, 163.5, 142.8, 142.2, 133.6, 129.5, 126.1, 120.6, 117.4, 114.6, 108.7, 88.7, 55.8.

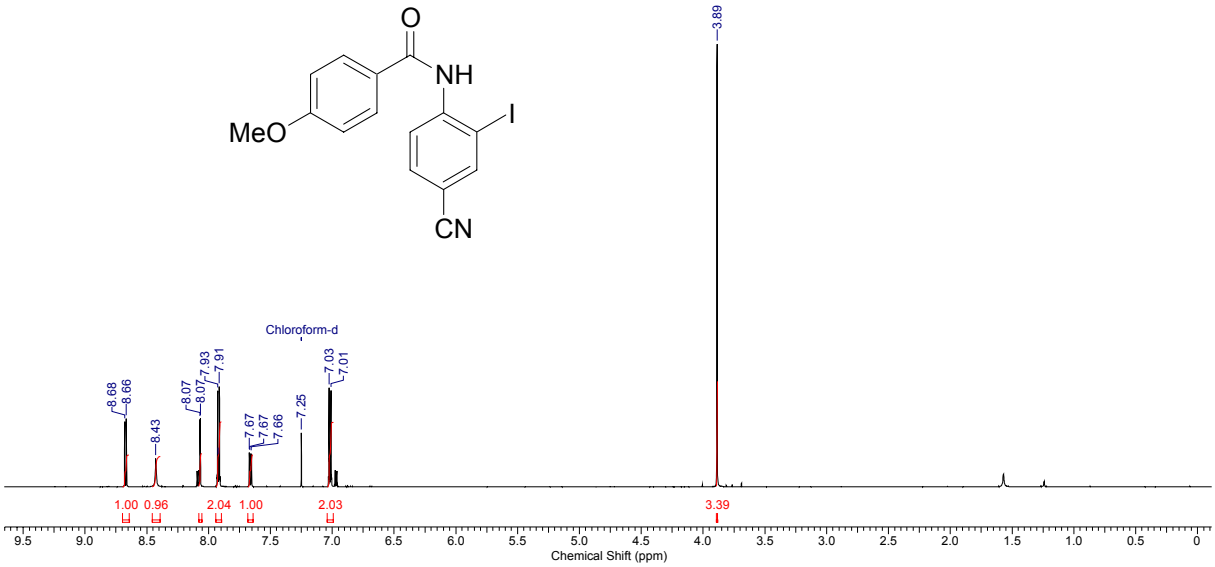
MS (70 eV, EI), *m/z* (%): 377 (4) [M^+], 251 (4), 135 (100), 92 (4), 77 (5).

IR (KBr): ṽ = 3380 (w), 2228 (w), 1787 (w), 1668 (m), 1607 (m), 1568 (m), 1502 (s), 1443 (m), 1383 (m), 1298 (m), 1258 (s), 1235 (s), 1181 (s), 1118 (m), 1023 (s), 886 (m), 843 (vs).

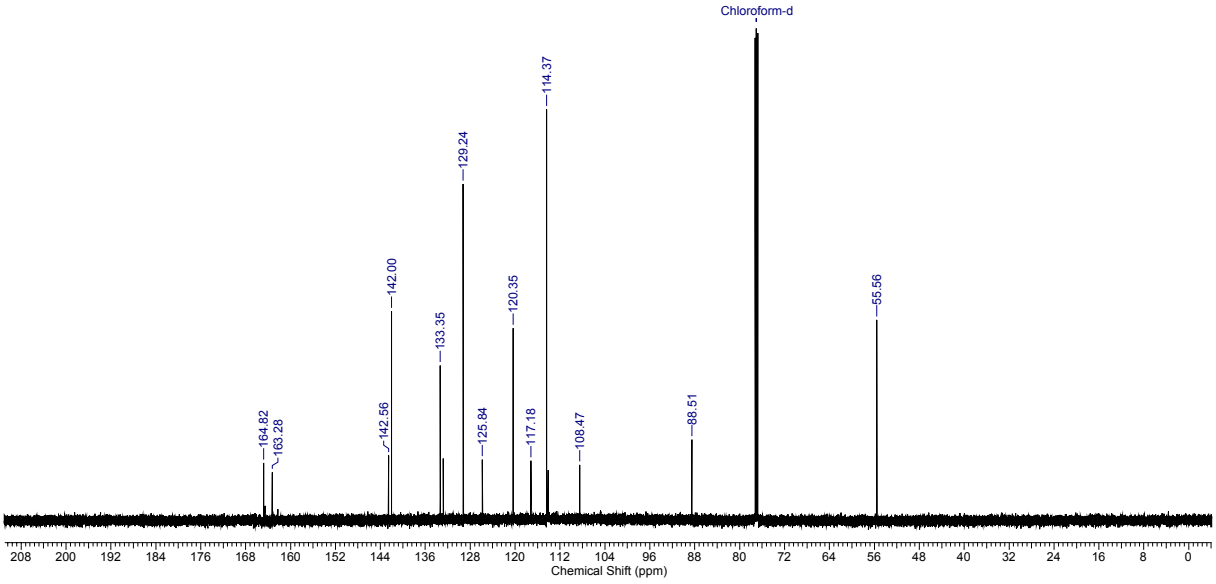
HRMS for **$C_{15}H_{11}IN_2O_2$** (377.9865): found: 377.9842.

_N_-(4-Cyano-2-iodophenyl)-4-methoxybenzamide (6b)

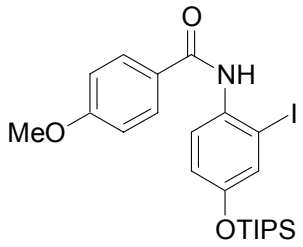
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 2 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl101_Proton_01			***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 28902	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 7225.43
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 1 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\BBl101_Carbon2048_01			***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	4096	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	27.000				



***N*-{2-Iodo-4-[(triisopropylsilyl)oxy]phenyl}-4-methoxybenzamide (6c)**



Prepared according to **TP 3** from 2-iodo-4-[(triisopropylsilyl)oxy]aniline (3.38 g, 8.63 mmol) and *p*-anisoyl chloride (1.2 mL, 8.8 mmol) in dioxane (30 mL) and pyridine (10 mL). Reaction time: 2 h. Purification by recrystallization from ethanol furnished **6c** as a colorless solid (3.43 g, 76 %).

Mp.: 106.8-108.0 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J*= 9.3 Hz, 1H), 7.99 (s_br, 1H), 7.93-7.88 (m, 2H), 7.34 (d, *J*= 2.7 Hz, 1H), 7.01-6.96 (m, 2H), 6.91 (dd, *J*= 8.8, 2.7 Hz, 1H), 3.87 (s, 3H), 1.30-1.18 (m, 3H), 1.09 (d, *J*= 7.1 Hz, 18H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.7, 162.6, 153.0, 132.2, 129.6, 129.0, 126.9, 122.4, 120.3, 114.1, 90.5, 55.5, 17.9, 12.6.

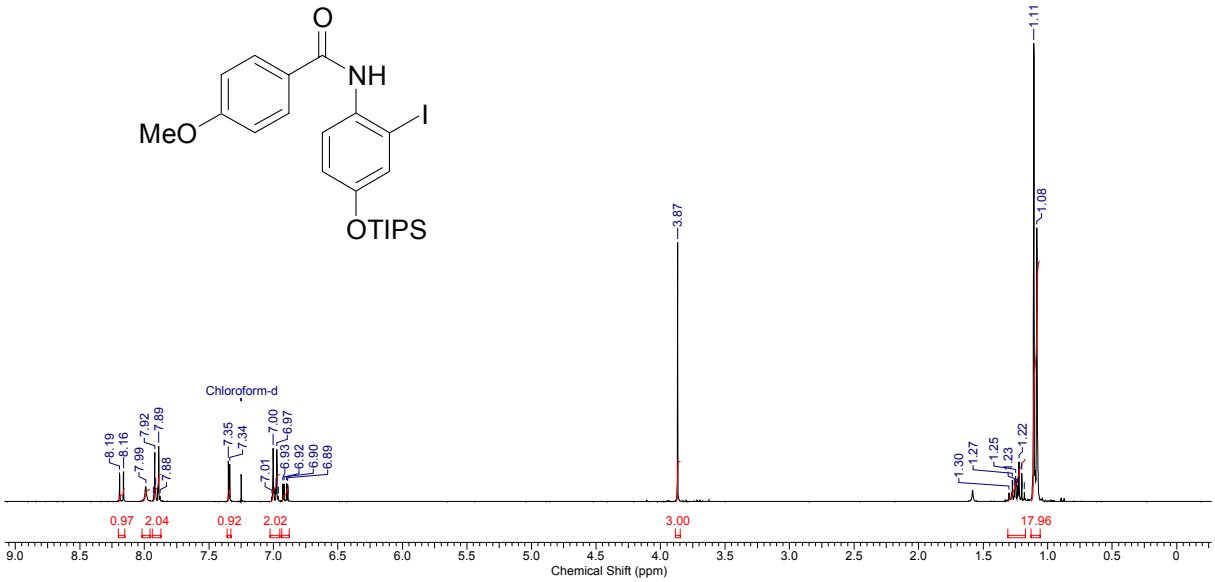
MS (70 eV, EI), *m/z* (%): 525 (97) [M^+], 482 (42), 454 (27), 426 (18), 398 (97), 355 (41), 298 (20), 135 (100).

IR (KBr): ṽ = 3393 (w), 2942 (w), 2863 (w), 1652 (m), 1606 (m), 1564 (m), 1501 (m), 1463 (m), 1382 (m), 1247 (m), 1180 (m), 1021 (m), 922 (s), 881 (s), 855 (vs), 824 (vs), 790 (m), 726 (s), 689 (vs).

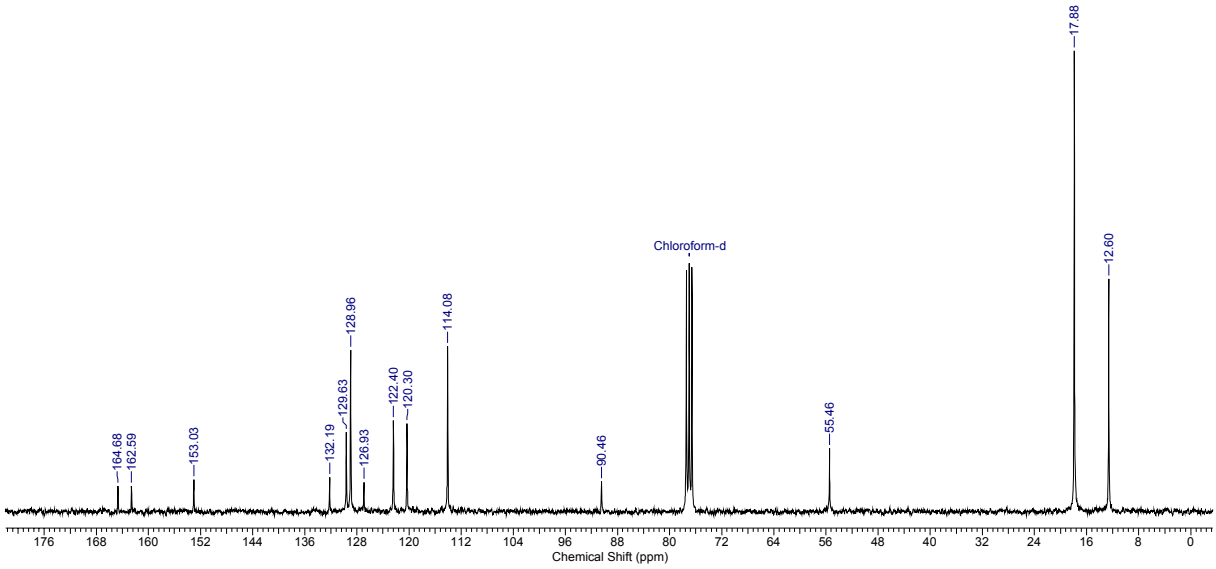
HRMS for **$C_{23}H_{32}INO_3Si$** (525.1196): found: 525.1172.

N-{2-Iodo-4-[(triisopropylsilyl)oxy]phenyl}-4-methoxybenzamide (6c)

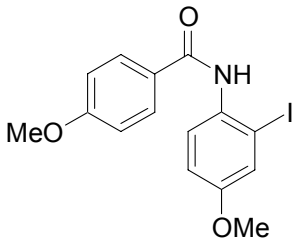
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 22 2006	
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl119_Proton_01					***Frequency (MHz)***	300.10	***Nucleus*** 1H
Number of Transients	8	***Original Points Count***	7401	***Points Count***	8192	***Pulse Sequence***	s2pul	
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	3612.72	***Temperature (degree C)***	27.000	



Acquisition Time (sec)	1.6010	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 22 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\300 MHz\bbl119_Carbon2k_01					***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	2048	***Original Points Count***	29004	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	18115.94
Temperature (degree C)	27.000						



N-(2-Iodo-4-methoxyphenyl)-4-methoxybenzamide (6d)



Prepared according to **TP 3** from 2-iodo-4-methoxyaniline (2.02 g, 8.10 mmol) and *p*-anisoyl chloride (1.1 mL, 8.2 mmol) in dioxane (25 mL) and pyridine (10 mL). Reaction time: 2 h. Purification by recrystallization from ethanol furnished **6d** as a colorless solid (2.75 g, 89 %).

Mp.: 185.8-187.0 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J*= 8.8 Hz, 1H), 7.97 (s_br, 1H), 7.94-7.88 (m, 2H), 7.34 (d, *J*= 2.7 Hz, 1H), 7.01-6.93 (m, 3H), 3.87 (s, 3H), 3.78 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.7, 162.6, 156.6, 132.0, 129.0, 126.8, 123.8, 123.0,

114.8, 114.1, 91.2, 55.7, 55.5.

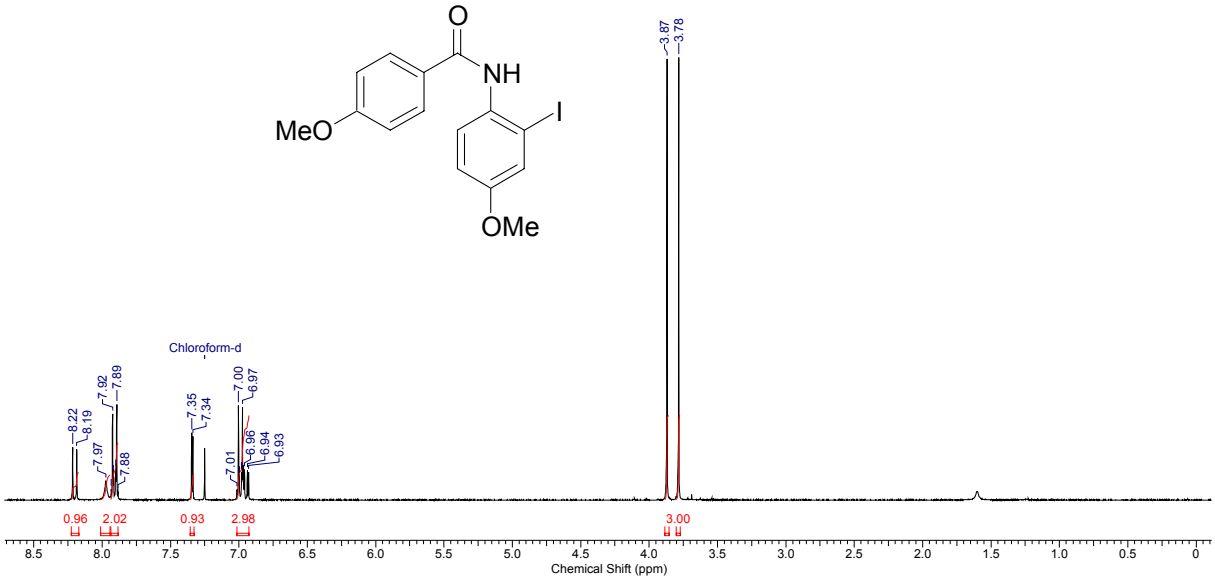
MS (70 eV, EI), *m/z* (%): 383 (29) [M^+], 256 (77), 240 (5), 135 (100), 107 (7), 92 (7), 77 (10).

IR (KBr): $\tilde{\nu}$ = 3278 (w), 2835 (w), 1644 (m), 1603 (m), 1491 (s), 1458 (m), 1312 (m), 1284 (m), 1253 (s), 1216 (s), 1173 (s), 1021 (vs), 869 (m), 7841 (s), 763 (m), 640 (m), 606 (s).

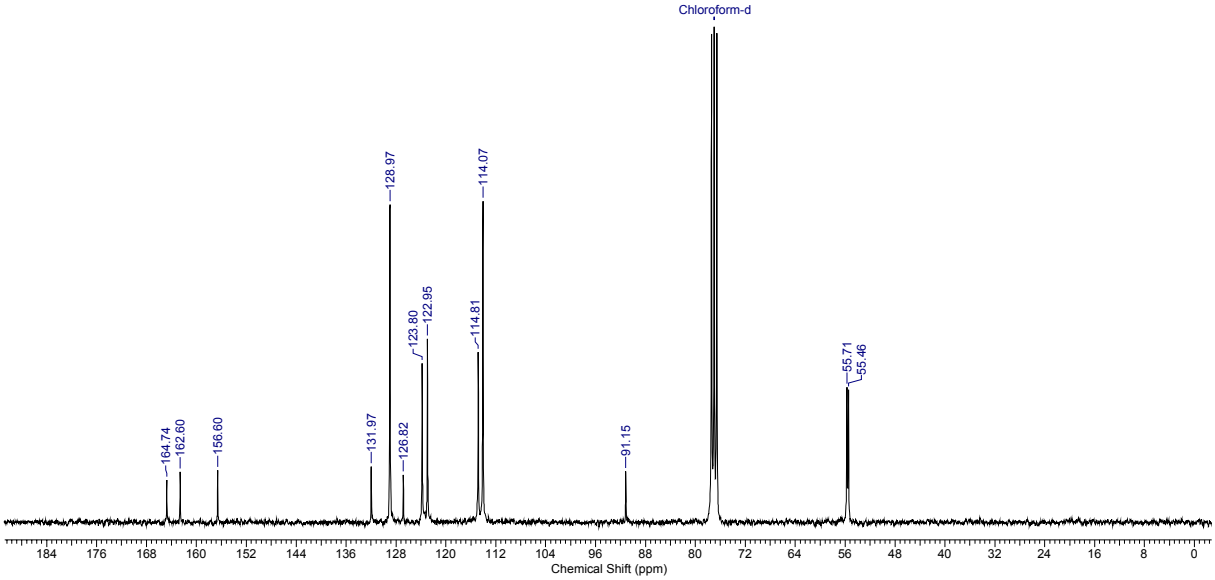
HRMS for **$C_{15}H_{14}INO_3$** (383.0018): found: 382.9995.

N-(2-Iodo-4-methoxyphenyl)-4-methoxybenzamide (6d)

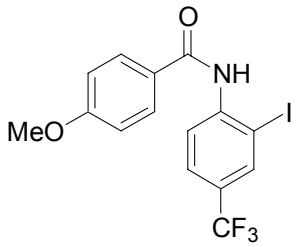
Acquisition Time (sec)	2.0486	***Comment***	Benoit Blank, AK Knochel	***Date***	Jul 12 2006
File Name	\\141.84.254.80\NMR_Roh\300MHz\Knochel\Blank\bbl_117_Proton_01			***Frequency (MHz)***	300.10
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 7401	***Points Count*** 8192
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 3612.72
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6010	***Comment***	Benoit Blank, AK Knochel	***Date***	Jul 12 2006
File Name	\\141.84.254.80\NMR_Roh\300MHz\Knochel\Blank\bbl_117_Carbon2k_01			***Frequency (MHz)***	75.47
Nucleus	13C	***Number of Transients***	8192	***Original Points Count*** 29004	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 18115.94
Temperature (degree C)	27.000				



***N*-[2-Iodo-4-(trifluoromethyl)phenyl]-4-methoxybenzamide (6e)**



Prepared according to **TP 3** from 2-iodo-4-(trifluoromethyl)aniline (2.12 g, 7.37 mmol) and *p*-anisoyl chloride (1.0 mL, 7.4 mmol) in dioxane (20 mL) and pyridine (10 mL). Reaction time: 18 h. Purification by recrystallization from ethanol furnished **6e** as a colorless solid (1.96 g, 63 %).

Mp.: 158.9-160.1 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.63 (d, *J*= 8.6 Hz, 1H), 8.37 (s_br, 1H), 8.04 (d, *J*= 1.3 Hz, 1H), 7.95-7.92 (m, 2H), 7.64 (dd, *J*= 8.7, 1.9 Hz, 1H), 7.02 (d, *J*= 8.8 Hz, 2H), 3.89 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.9, 163.1, 141.6, 135.7 (q, *J*= 3.5 Hz), 129.2, 127.1 (q, *J*= 33.6 Hz), 126.6 (q, *J*= 3.5 Hz), 126.1, 122.9 (q, *J*= 272.1 Hz), 120.6, 114.3, 88.7, 55.5.

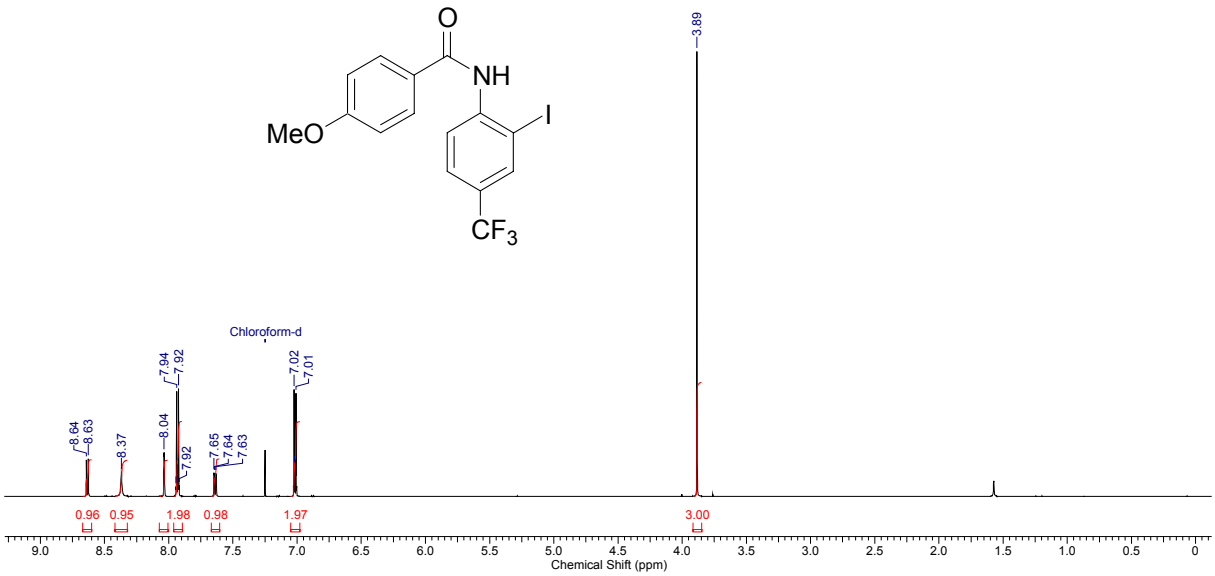
MS (70 eV, EI), *m/z* (%): 421 (3) [M^+], 284 (18), 135 (100), 92 (4), 77 (5).

IR (KBr): ṽ = 3279 (w), 2835 (w), 1647 (m), 1602 (m), 1525 (m), 1508 (s), 1389 (m), 1311 (s), 1245 (s), 1157 (s), 1135 (s), 1102 (vs), 1074 (s), 1031 (s), 888 (m), 831 (s), 759 (s).

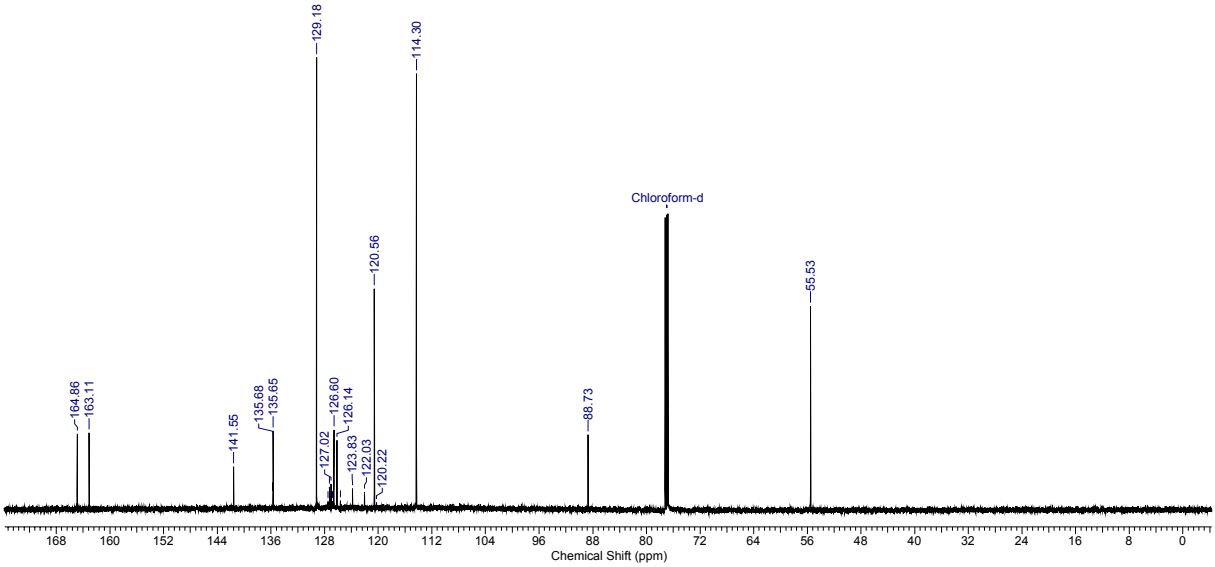
HRMS for **$C_{15}H_{11}F_3INO_2$** (420.9787): found: 420.9797.

N-[2-Iodo-4-(trifluoromethyl)phenyl]-4-methoxybenzamide (6e)

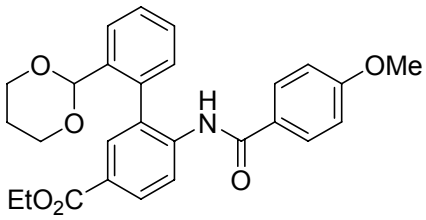
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 19 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl103_Proton_01			***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 28902	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 7225.43
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 19 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl103_Carbon2048_01			***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	4096	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	27.000				



Ethyl 3'-(1,3-dioxan-2-yl)-6-[(4-methoxybenzoyl)amino]biphenyl-3-carboxylate (7a)



Prepared according to **TP 1** from bromo[3-(1,3-dioxan-2-yl)phenyl]magnesium (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and ethyl 3-iodo-4-[(4-methoxybenzoyl)amino]benzoate (425 mg, 1.00 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded **7a** as a pale yellow solid (348 mg, 75 %).

Mp.: 142.5-144.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.73 (d, *J*= 8.6 Hz, 1H), 8.19 (s_br, 1H), 8.08 (dd, *J*= 8.6, 2.0 Hz, 1H), 7.98 (d, *J*= 2.0 Hz, 1H), 7.67 (t, *J*= 1.8 Hz, 1H), 7.63-7.58 (m, 3H), 7.54 (t, *J*= 7.6 Hz, 1H), 7.42 (dt, *J*= 7.6, 1.6 Hz, 1H), 6.87-6.83 (m, 2H), 5.58 (s, 1H), 4.37 (q, *J*= 7.1 Hz, 2H), 4.27 (ddd, *J*= 12.0, 4.9, 1.2 Hz, 2H), 4.01 (td, *J*= 12.2, 2.5 Hz, 2H), 3.81 (s, 3H), 2.26-2.18 (m, 1H), 1.49-1.45 (m, 1H), 1.38 (t, *J*= 7.2 Hz, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 166.2, 164.6, 162.6, 140.2, 139.3, 137.1, 131.4, 131.0, 130.3, 129.8, 129.5, 129.0, 127.1, 126.6, 126.3, 125.5, 119.6, 113.9, 101.0, 67.4, 60.9, 55.4, 25.8, 14.4.

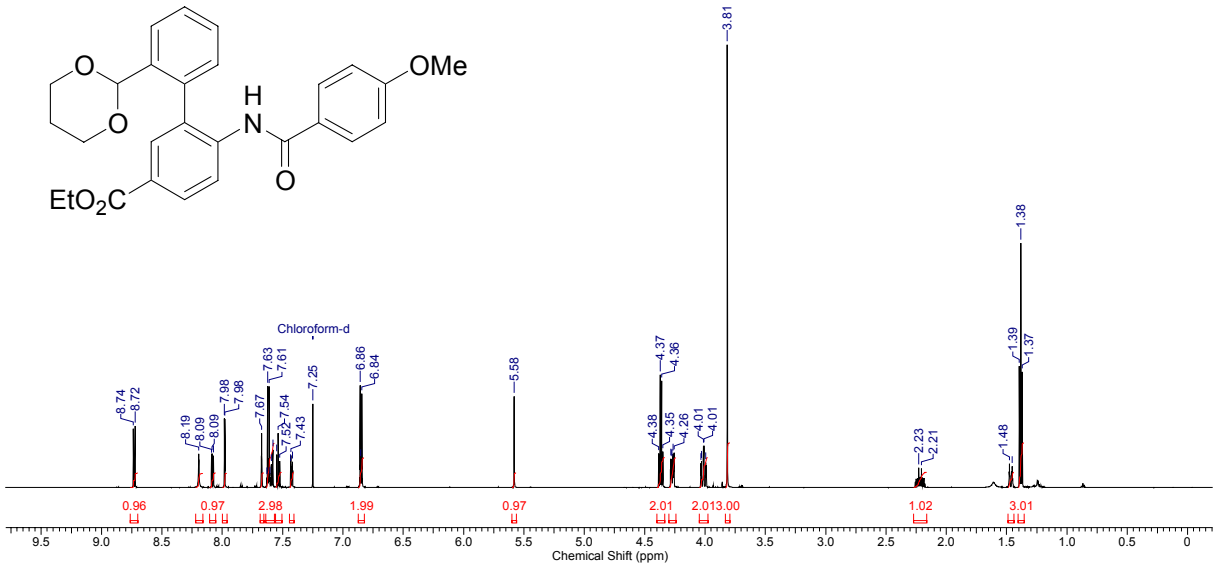
MS (70 eV, EI), *m/z* (%): 461 (37) [M^+], 416 (5), 326 (10), 268 (6), 193 (19), 135 (100).

IR (KBr): $\tilde{\nu}$ = 3426 (w), 2977 (w), 1723 (s), 1684 (m), 1585 (m), 1509 (s), 1376 (m), 1302 (m), 1239 (s), 1179 (s), 1093 (vs), 1020 (s); 904 (m), 841 (m), 767 (m), 740 (m).

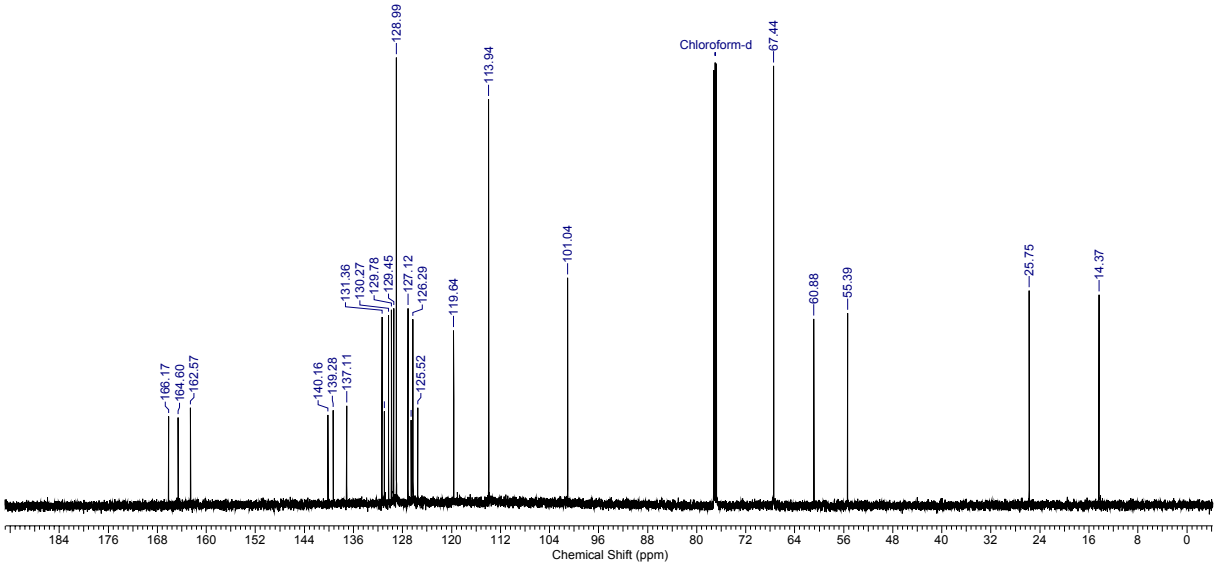
HRMS for **$C_{27}H_{27}NO_6$** (461.1838): found: 461.1846.

Ethyl 3'-(1,3-dioxan-2-yl)-6-[(4-methoxybenzoyl)amino]biphenyl-3-carboxylate (7a)

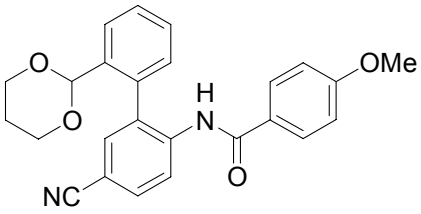
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 19 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl100_2_Proton_01					***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	28902	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	7225.43
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 19 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl100_2_Carbon2048_01					***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	4096	***Original Points Count***	58824	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	36764.71
Temperature (degree C)	27.000						



***N*-[3'-(1,3-Dioxan-2-yl)-5-isocyanobiphenyl-2-yl]-4-methoxybenzamide (7b)**



Prepared according to **TP 1** from bromo[3-(1,3-dioxan-2-yl)phenyl]magnesium (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(4-cyano-2-iodophenyl)-4-methoxybenzamide (378 mg, 1.00 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 3:1) yielded **7b** as a colorless solid (292 mg, 70 %).

Mp.: 145.2-146.8 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.80 (d, *J*= 8.6 Hz, 1H), 8.21 (s_br, 1H), 7.68 (dd, *J*= 8.6,

2.0 Hz, 1H), 7.66 (s, 1H), 7.62-7.59 (m, 3H), 7.58-7.54 (m, 2H), 7.40-7.37 (m, 1H), 7.87-7.84 (m, 2H), 5.58 (s, 1H), 4.29-4.25 (m, 2H), 4.02 (td, *J*= 12.3, 2.5 Hz, 2H), 3.82 (s, 3H), 2.26-2.18 (m, 1H), 1.48 (d, *J*= 13.5 Hz, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.6, 162.8, 140.5, 139.4, 135.8, 133.6, 132.7, 131.8, 129.7, 129.5, 129.0, 126.9, 126.8, 126.1, 120.4, 118.8, 114.0, 106.8, 100.8, 67.5, 55.4, 25.7.

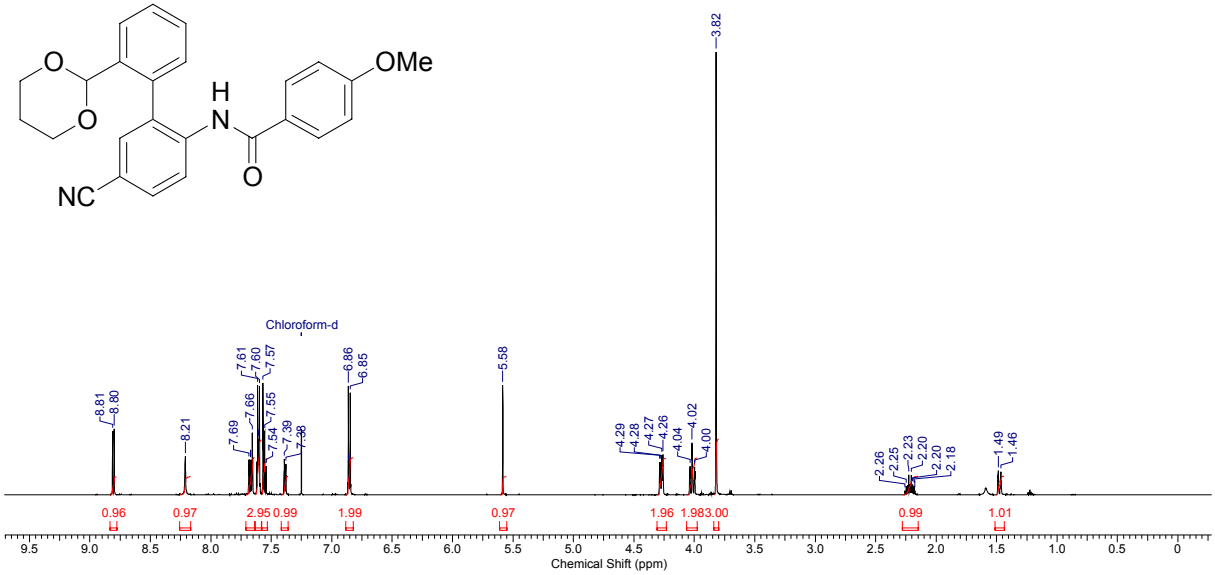
MS (70 eV, EI), *m/z* (%): 414 (14) [M^+], 279 (8), 193 (14), 135 (100), 107 (5), 77 (6).

IR (KBr): ṽ = 3420 (w), 2953 (w), 2839 (w), 2222 (m), 1679 (m), 1581 (m), 1504 (s), 1465 (s), 1308 (m), 1245 (s), 1167 (s), 1147 (s), 1095 (vs), 1023 (s), 1005 (s), 988 (s), 828 (vs), 757 (s), 708 (s), 612 (s).

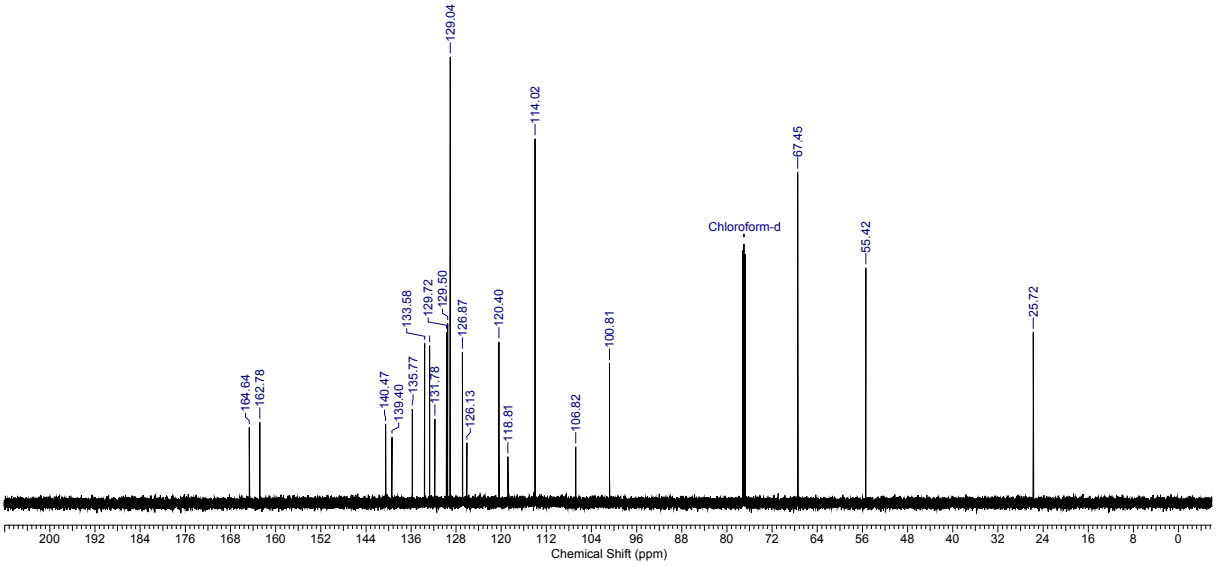
HRMS for **$C_{25}H_{22}N_2O_4$** (414.1580): found: 414.1587.

***N*-[3'-(1,3-Dioxan-2-yl)-5-isocyanobiphenyl-2-yl]-4-methoxybenzamide (7b)**

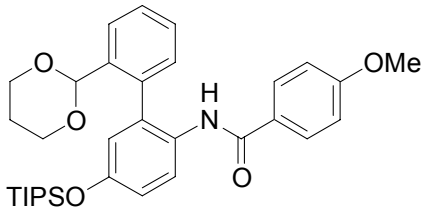
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 20 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl111_Proton_01			***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 28902	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 7225.43
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 20 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl111_Carbon2048_01			***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	4096	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	27.000				



_N_-{2'-(1,3-Dioxan-2-yl)-5-[(triisopropylsilyl)oxy]biphenyl-2-yl}-4-methoxybenzamide (7c)

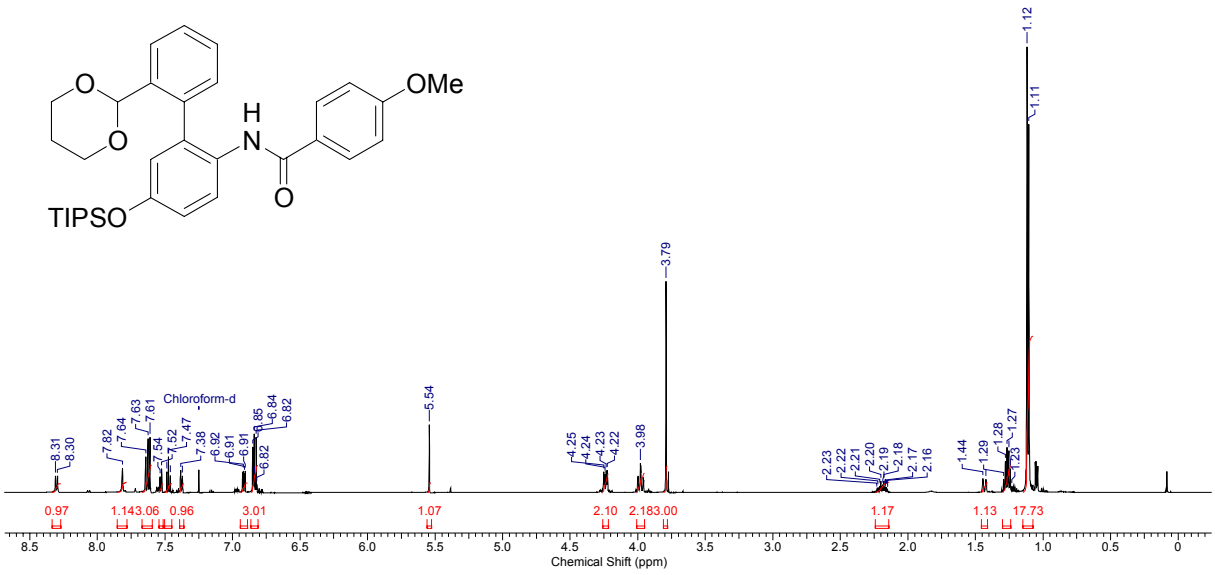


Prepared according to **TP 1** from bromo[3-(1,3-dioxan-2-yl)phenyl]magnesium (3.5 mL, 3.0 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-{2-iodo-4-[(triisopropylsilyl)oxy]phenyl}-4-methoxybenzamide (525 mg, 1.00 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 5:2) yielded **7c** as a colorless highly viscous liquid (459 mg, 82 %).

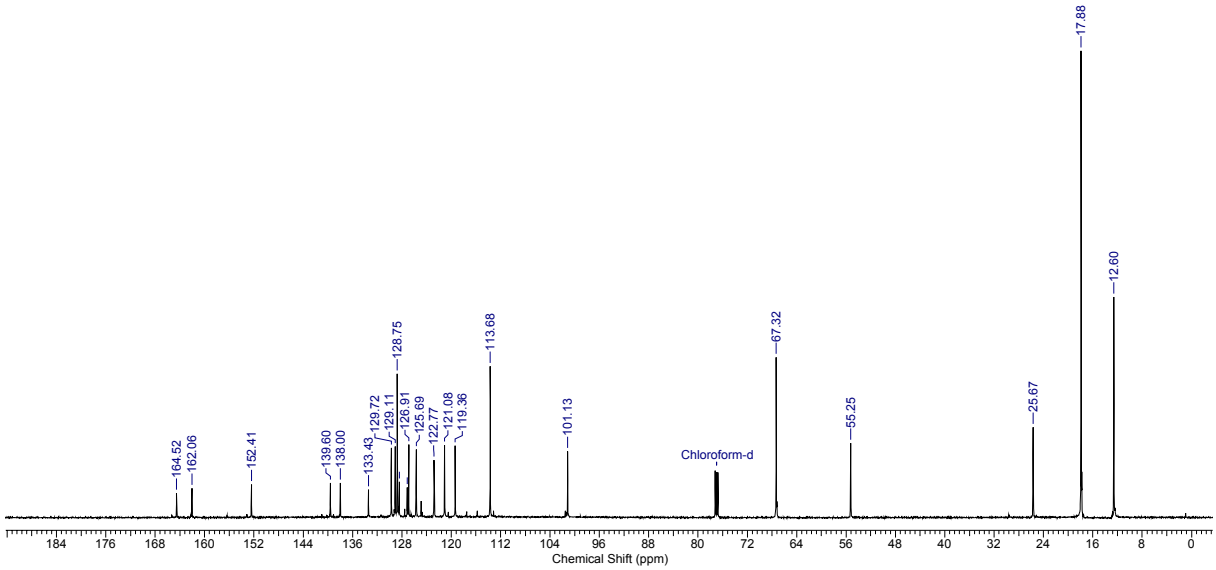
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.30 (d, *J*= 8.8 Hz, 1H), 7.82 (s_br, 1H), 7.64 (s, 1H), 7.62 (d, 8.8 Hz, 2H), 7.53 (d, *J*= 7.7 Hz, 1H), 7.47 (t, *J*= 7.6 Hz, 1H), 7.38 (d, *J*= 7.5 Hz, 1H), 6.92 (dd, *J*= 8.8, 2.9 Hz, 1H), 6.86-6.82 (m, 3H), 5.54 (s, 1H), 4.26-4.22 (m, 2H), 3.98 (d, *J*= 2.2 Hz, 2H), 3.79 (s, 3H), 2.23-2.15 (m, 1H), 1.43 (d, *J*= 13.5 Hz, 1H), 1.29-1.24 (m, 3H), 1.11 (d, *J*= 7.5 Hz, 18H).
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.5, 162.1, 152.4, 139.6, 138.0, 133.4, 129.7, 129.1, 128.8, 128.4, 127.2, 126.9, 125.7, 122.8, 121.1, 119.4, 113.7, 101.1, 67.3, 55.3, 25.7, 17.9, 12.6.
MS (70 eV, EI), *m/z* (%): 561 (90) [M^+], 518 (15), 460 (36), 432 (11), 135 (100), 87 (14).
IR (KBr): ṽ = 2944 (w), 1865 (w), 1666 (w), 1606 (m), 1504 (m), 1464 (m), 1375 (w), 1247 (m), 1208 (m), 1174 (m), 1103 (m), 995 (m), 880 (m), 794 (m), 759 (m), 683 (m).
HRMS for **$C_{33}H_{43}NO_5Si$** (561.2911): found: 561.2916.

N-{2'-(1,3-Dioxan-2-yl)-5-[(triisopropylsilyl)oxy]biphenyl-2-yl}-4-methoxybenzamide (7c)

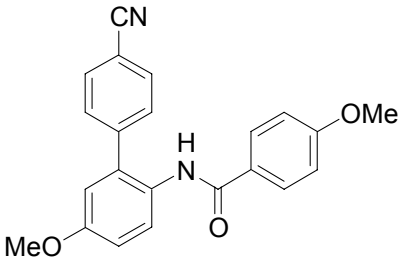
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jul 4 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl123_Proton_01					***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	28902	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	7225.43
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jul 4 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl123_Carbon2048_01					***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	4096	***Original Points Count***	58824	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	36764.71
Temperature (degree C)	27.000						



N-(4'-Isocyano-5-methoxybiphenyl-2-yl)-4-methoxybenzamide (7d)



Prepared according to **TP 2** from 4-iodobenzonitrile (687 mg, 3.00 mmol), *i*PrMgCl (4.1 mL, 3.1 mmol, 0.76 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(2-iodo-4-methoxyphenyl)-4-methoxybenzamide (383 mg, 1.00 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded **7d** as a colorless solid (263 mg, 74 %).

Mp.: 212.8-215.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.97 (t, *J*= 9.2 Hz, 1H), 7.73-7.70 (m, 2H), 7.58-7.52 (m,

4H), 7.48-7.42 (m, 1H), 7.00-6.96 (m, 1H), 6.90-6.86 (m, 2H), 6.81 (d, *J*= 2.7 Hz, 1H), 3.83 (s, 6H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 165.2, 162.5, 157.1, 143.4, 134.2, 132.6, 129.9, 128.7, 127.4, 126.4, 126.0, 118.5, 115.3, 114.5, 114.0, 111.8, 55.6, 55.4.

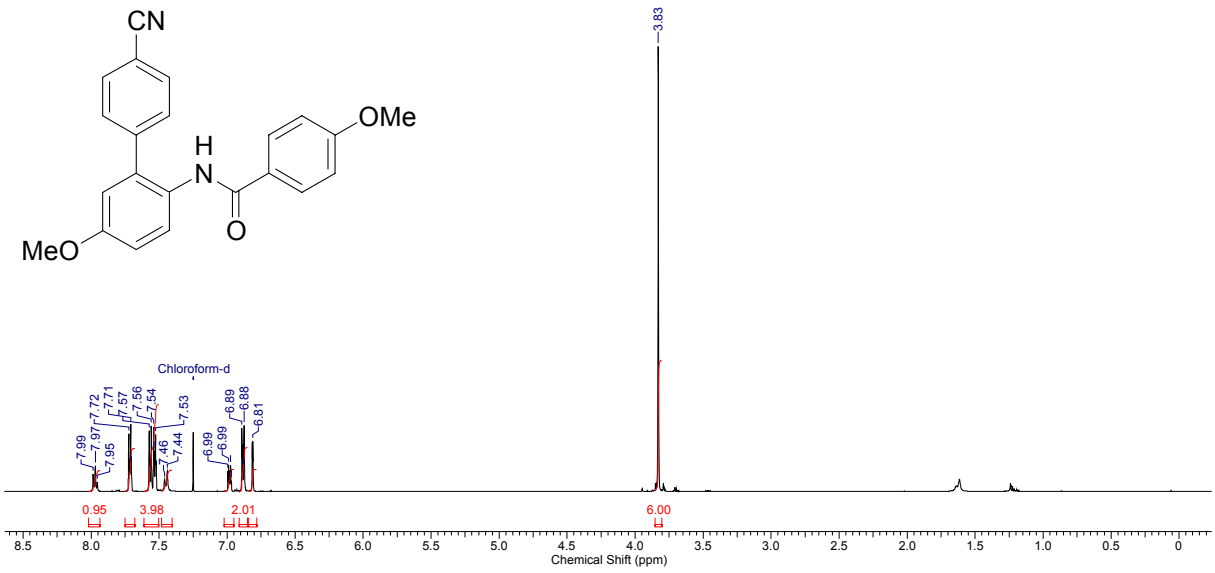
MS (70 eV, EI), *m/z* (%): 358 (22) [M^+], 135 (100), 107 (4), 77 (6).

IR (KBr): ṽ = 3245 (m), 3005 (w), 2838 (w), 2224 (m), 1624 (m), 1595 (vs), 1575 (w), 1526 (w), 1493 (s), 1315 (w), 1293 (w), 1260 (s), 1210 (s), 1172 (m), 1034 (m), 1014 (m), 841 (m), 852 (m), 802 (m), 769 (m), 658 (w).

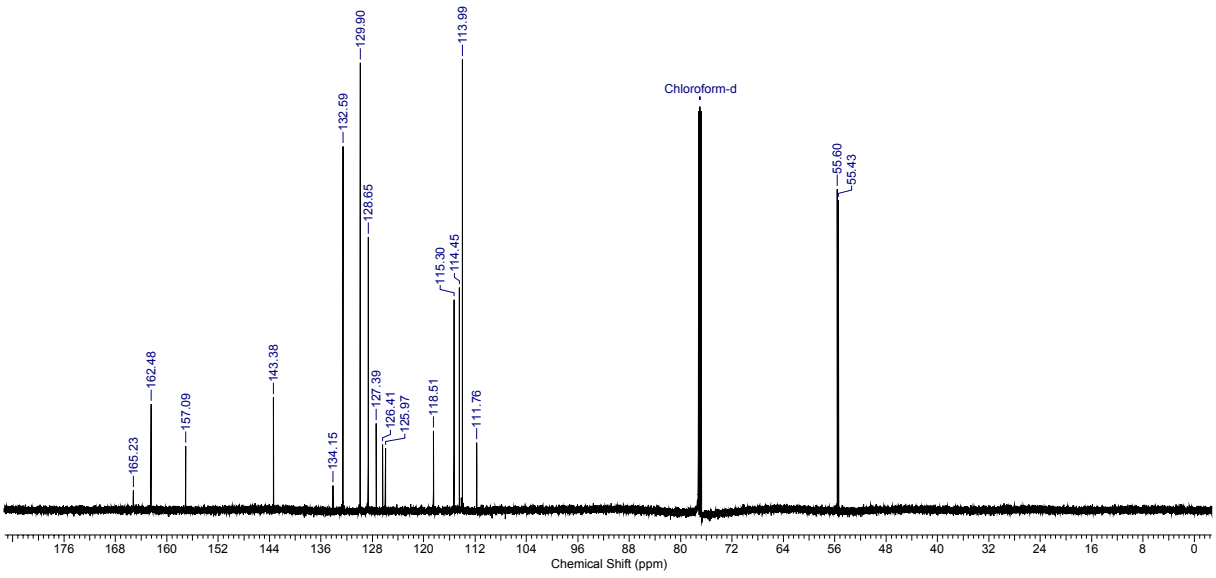
HRMS for **$C_{22}H_{18}N_2O_3$** (358.1317): found: 358.1331.

N-(4'-Isocyano-5-methoxybiphenyl-2-yl)-4-methoxybenzamide (7d)

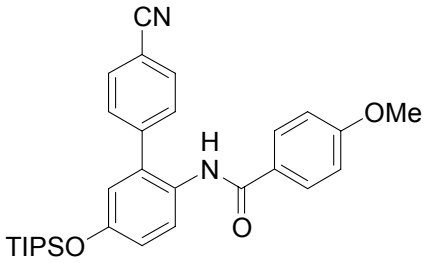
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jul 24 2006
File Name	\\141.84.254.80\NMR_Roh\600MHz\Knochel\Blank\bbl128_Proton_01x			***Frequency (MHz)***	599.67
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 28902	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 7225.43
Temperature (degree C)	25.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jul 24 2006
File Name	\\141.84.254.80\NMR_Roh\600MHz\Knochel\Blank\bbl128_Carbon2048_01			***Frequency (MHz)***	150.80
Nucleus	13C	***Number of Transients***	2048	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	DEUTERIUM OXIDE		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	25.000				



***N*-{4'-Cyano-5-[(triisopropylsilyl)oxy]biphenyl-2-yl}-4-methoxybenzamide (7e)**



Prepared according to **TP 2** from 4-iodobenzonitrile (687 mg, 3.00 mmol), *i*PrMgCl (4.10 mL, 3.10 mmol, 0.76 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-{2-iodo-4-[(triisopropylsilyl)oxy]phenyl}-4-methoxybenzamide (525 mg, 1.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded **7e** as a colorless solid (481 mg, 96 %).

Mp.: 167.0-168.2 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, *J*= 8.8 Hz, 1H), 7.73 (d, *J*= 8.6 Hz, 2H), 7.56 (d, *J*= 8.8 Hz, 2H), 7.52 (d, *J*= 8.4 Hz, 2H), 7.41 (s_br, 1H), 6.96 (dd, *J*= 8.8, 2.9 Hz, 1H), 6.89 (d, *J*= 8.8 Hz, 2H), 6.80 (d, *J*= 2.9 Hz, 1H), 3.83 (s, 3H), 1.29-1.23 (m, 3H), 1.11 (d, *J*= 7.5 Hz, 18H).

^{13}C-NMR (300 MHz, $CDCl_3$): δ = 165.0, 162.5, 153.5, 143.4, 133.6, 132.7, 129.9, 128.6, 127.7, 126.6, 125.4, 120.9, 120.5, 118.5, 114.0, 111.8, 55.4, 17.9, 12.7.

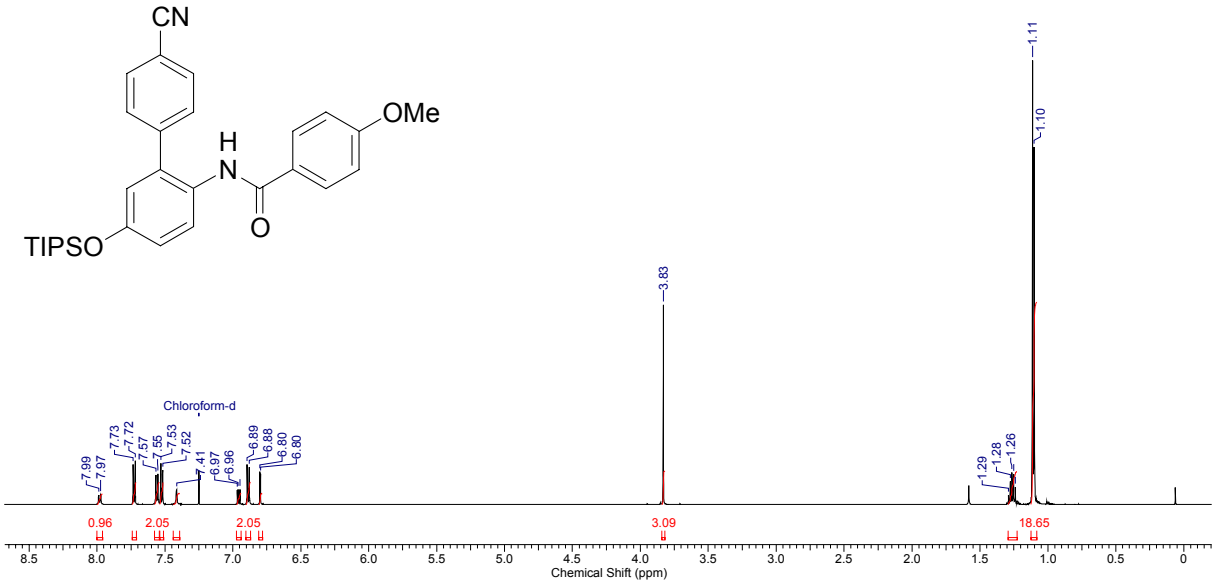
MS (70 eV, EI), *m/z* (%): 500 (62) [M^+], 457 (59), 429 (26), 401 (18), 387 (9), 135 (100).

IR (KBr): ṽ = 3208 (m), 2944 (s), 2866 (s), 2224 (m), 1641 (s), 1606 (s), 1578 (m), 1503 (s), 1485 (vs), 1463 (m), 1395 (w), 1291 (s), 1256 (s), 1208 (s), 1173 (m), 1015 (w), 943 (m), 878 (m), 835 (m), 795 (w), 676 (m).

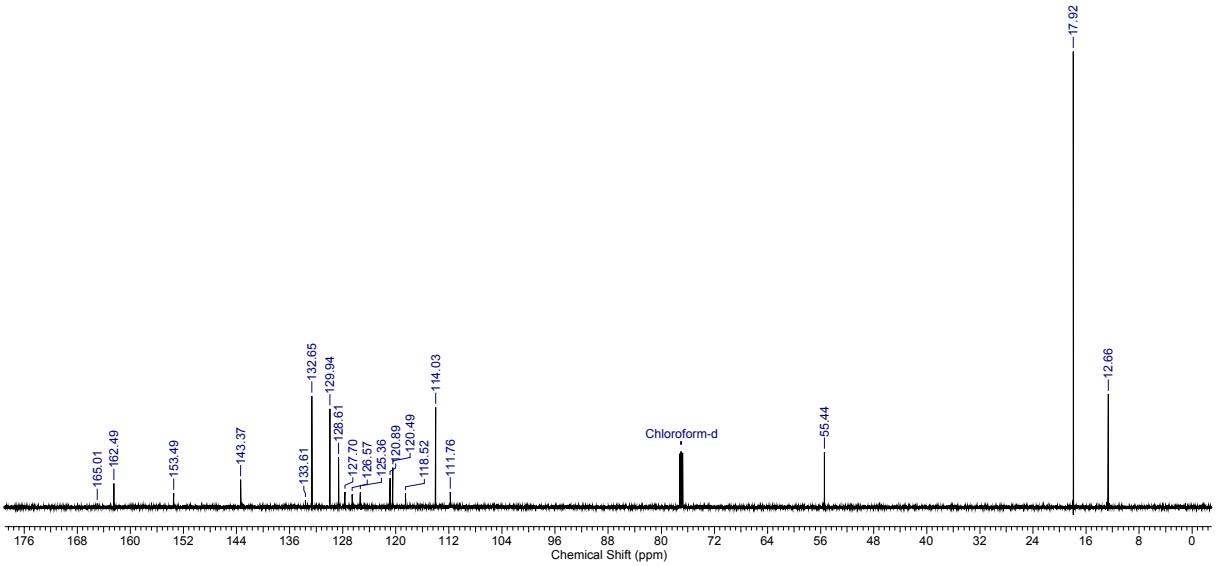
HRMS for **$C_{30}H_{36}N_2O_3Si$** (500.2495): found: 500.2497.

N-{4'-Cyano-5-[(triisopropylsilyl)oxy]biphenyl-2-yl}-4-methoxybenzamide (7e)

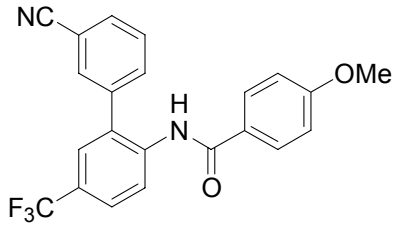
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 30 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl125_Proton_01			***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 28902	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 7225.43
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jun 30 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl125_Carbon2048_01			***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	2048	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	27.000				



***N*-[3'-Cyano-5-(trifluoromethyl)biphenyl-2-yl]-4-methoxybenzamide (7f)**



Prepared according to **TP 2** from 3-iodobenzonitrile (687 mg, 3.00 mmol), *i*PrMgCl (4.1 mL, 3.1 mmol, 0.86 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-[2-iodo-4-(trifluoromethyl)phenyl]-4-methoxybenzamide (421 mg, 1.00 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 3:2) yielded **7f** as a colorless solid (281 mg, 70 %).

Mp.: 150.9-151.7 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.60 (d, *J*= 8.6 Hz, 1H), 7.79-7.75 (m, 2H), 7.74-7.69 (m, 3H), 7.66 (d, *J*= 7.7 Hz, 1H), 7.55-7.52 (m, 2H), 7.50 (d, *J*= 2.0 Hz, 1H), 6.91-6.88 (m, 2H), 3.83 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.7, 162.9, 138.4, 138.1, 133.6, 132.7, 132.3, 130.3, 130.2, 128.7, 126.9 (q, *J*= 3.9 Hz), 126.6 (q, *J*= 3.9 Hz), 126.5 (q, *J*= 36.5 Hz), 126.0, 122.0 (q, *J*= 271.5 Hz), 121.9, 117.8, 114.2, 114.0, 55.5.

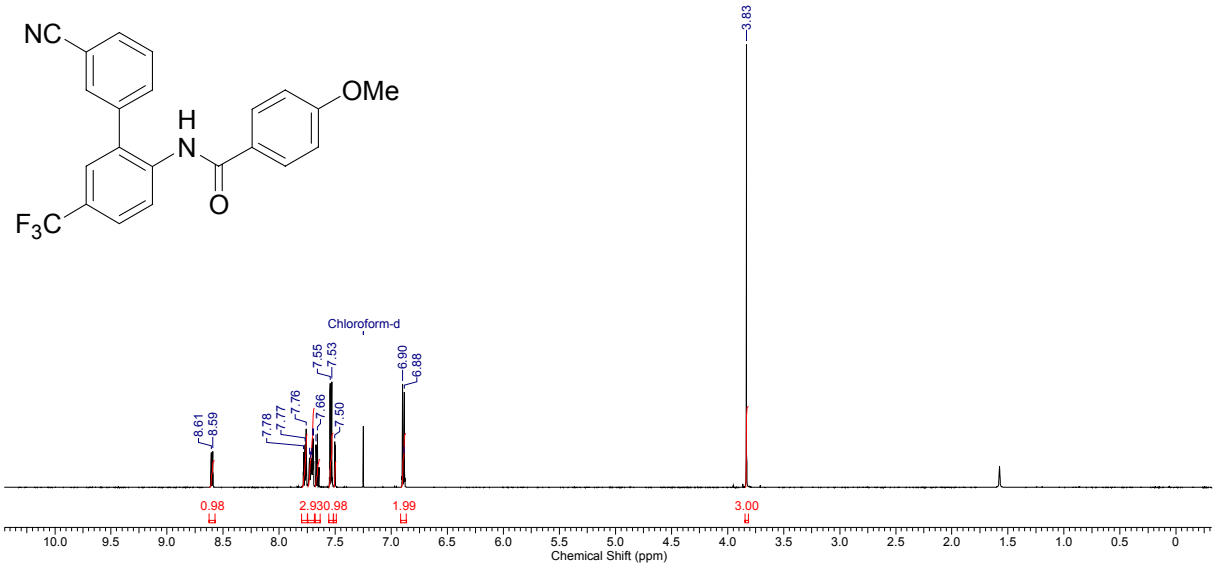
MS (70 eV, EI), *m/z* (%): 396 (5) [M^+], 135 (100), 107 (4), 77 (6).

IR (KBr): $\tilde{\nu}$ = 3257 (m), 2231 (m), 1665 (vs), 1603 (m), 1511 (s), 1488 (s), 1468 (m), 1415 (m), 1336 (s), 1314 (s), 1253 (s), 1175 (m), 1164 (m), 1109 (vs), 1078 (m), 1031 (m), 904 (w), 839 (m), 764 (w), 696 (w), 626 (w).

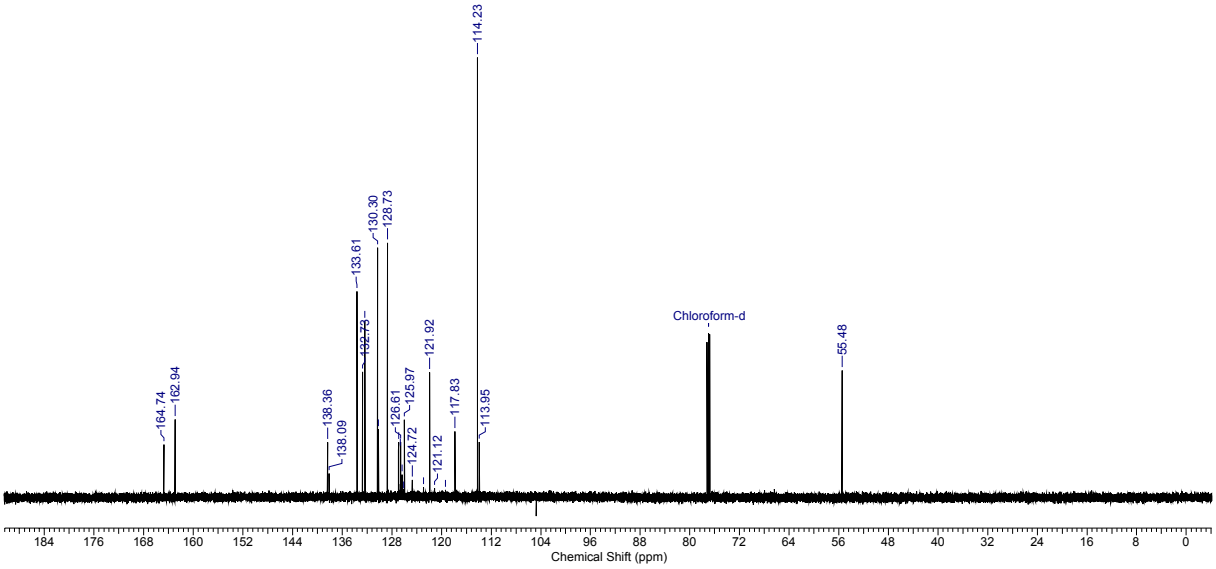
HRMS for **$C_{22}H_{15}F_3N_2O_2$** (396.1086): found: 396.1088.

N-[3'-Cyano-5-(trifluoromethyl)biphenyl-2-yl]-4-methoxybenzamide (7f)

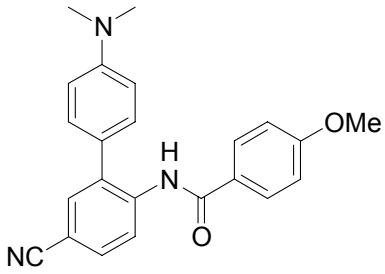
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 30 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl120_Proton_01					***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	28902	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	7225.43
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 30 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl120_Carbon2048_01					***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	2048	***Original Points Count***	58824	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	36764.71
Temperature (degree C)	27.000						



N-[4'-(Dimethylamino)-5-isocyanobiphenyl-2-yl]-4-methoxybenzamide (7g)



Prepared according to **TP 1** from 4-dimethylaminophenylmagnesium bromide (4.4 mL, 3.0 mmol, 0.68 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(4-cyano-2-iodophenyl)-4-methoxybenzamide (378 mg, 1.00 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded **7g** as a colorless solid (264 mg, 71 %).

Mp.: 174.7-175.7 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.73 (d, *J*= 8.8 Hz, 1H), 8.33 (s_br, 1H), 7.63-7.58 (m, 3H), 7.52 (d, *J*= 2.0 Hz, 1H), 7.27-7.25 (m, 2H), 6.90-6.87 (m, 2H), 6.84 (d, *J*= 8.6 Hz, 2H), 3.83 (s, 3H), 3.04 (s, 6H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.6, 162.8, 150.7, 139.7, 133.7, 132.6, 131.8, 129.9, 128.9, 126.3, 122.6, 120.2, 119.1, 114.1, 112.9, 106.7, 55.5, 40.3.

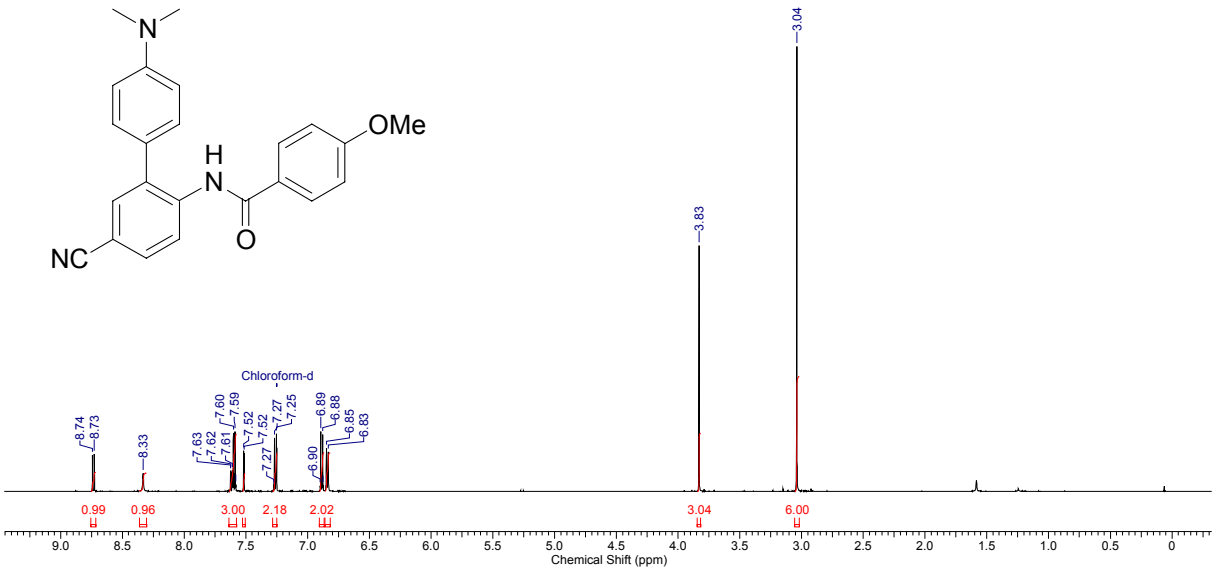
MS (70 eV, EI), *m/z* (%): 371 (58) [M^+], 135 (100), 107 (4), 77 (5).

IR (KBr): $\tilde{\nu}$ = 3407 (s), 2980 (w), 2810 (w), 2221 (m), 1678 (m), 1603 (s), 1581 (s), 1521 (m), 1498 (vs), 1463 (s), 1403 (m), 1309 (m), 1247 (s), 1177 (s), 1123 (m), 1020 (m), 835 (m), 825 (m), 755 (m), 687 (w).

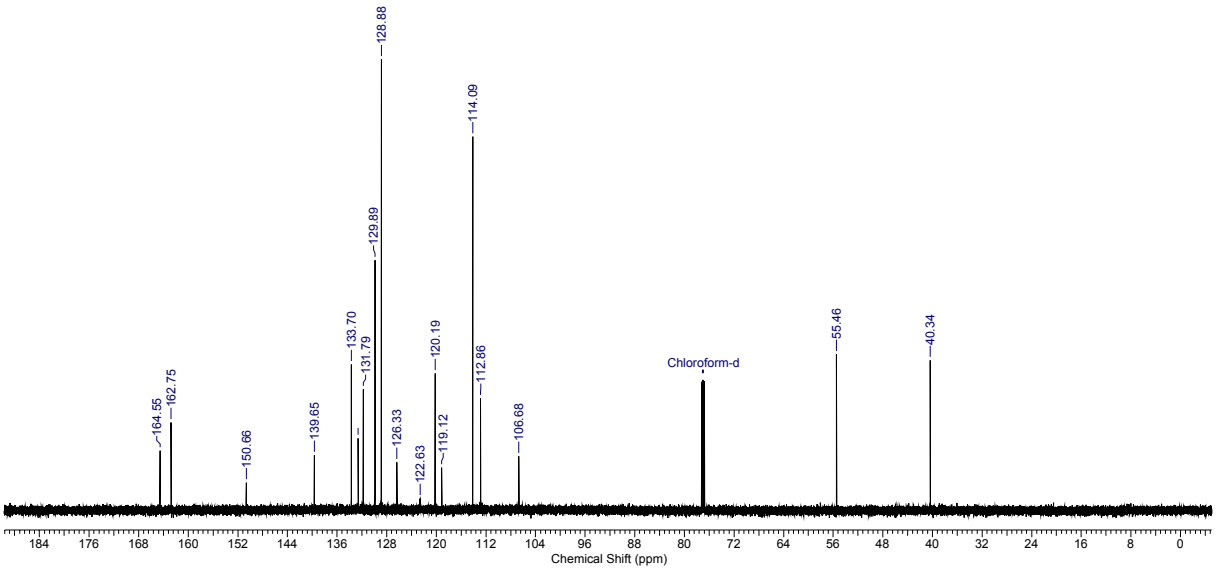
HRMS for **$C_{23}H_{21}N_3O_2$** (371.1634): found: 371.1619.

N-[4'-(Dimethylamino)-5-isocyanobiphenyl-2-yl]-4-methoxybenzamide (7g)

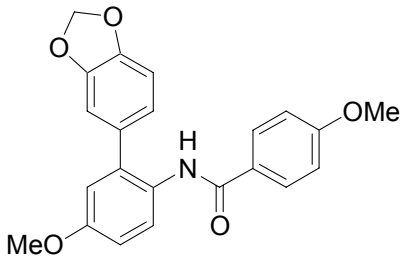
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jul 4 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl126_Proton_01			***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count*** 28902	***Points Count*** 32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 7225.43
Temperature (degree C)	27.000				



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel	***Date***	Jul 4 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl126_Carbon2048_01			***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	2048	***Original Points Count*** 58824	***Points Count*** 65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D		***Sweep Width (Hz)*** 36764.71
Temperature (degree C)	27.000				



***N*-[2-(1,3-Benzodioxol-5-yl)-4-methoxyphenyl]-4-methoxybenzamide (7h)**



Prepared according to **TP 1** from 1,3-benzodioxol-5-yl(bromo)magnesium (3.9 mL, 3.0 mmol, 0.76 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol%) and *N*-(2-iodo-4-methoxyphenyl)-4-methoxybenzamide (383 mg, 1.00 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 3:2) yielded **7h** as a colorless solid (316 mg, 84 %).

Mp.: 183.6-185.4 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.28 (d, *J*= 8.8 Hz, 1H), 7.76 (s_br, 1H), 7.62-7.58 (m, 2H), 6.94-6.87 (m, 6H), 6.80 (d, *J*= 3.1 Hz, 1H), 6.02 (s, 2H), 3.82 (s, 3H), 3.81 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 164.6, 162.3, 156.1, 148.3, 147.5, 133.8, 131.9, 128.6, 128.4, 127.2, 123.3, 122.5, 115.6, 113.9, 113.3, 109.8, 108.7, 101.4, 55.5, 55.4.

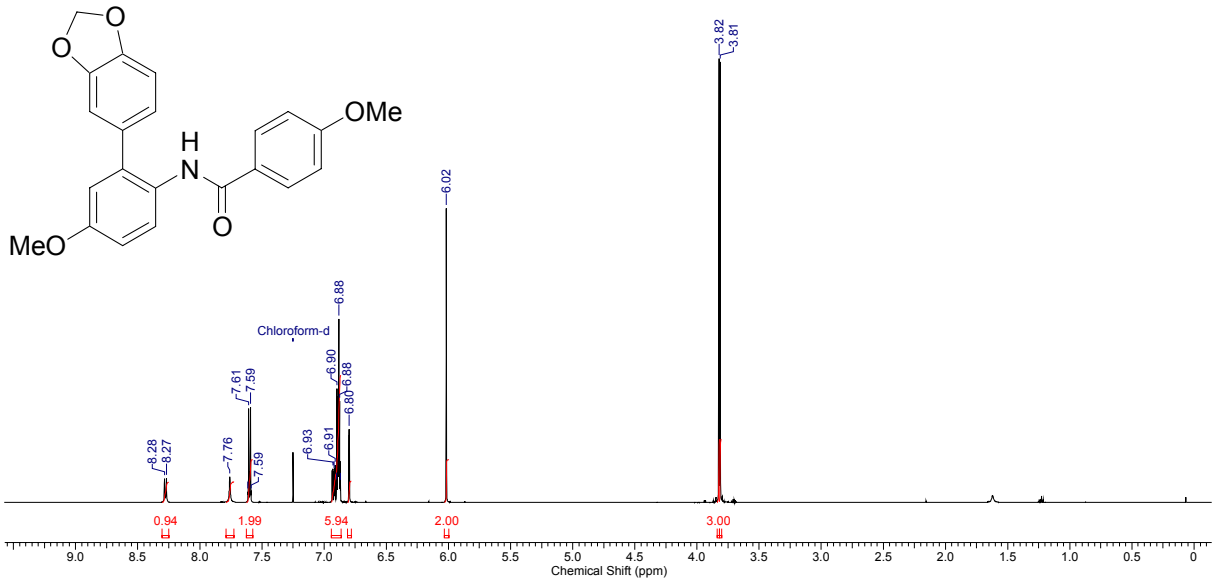
MS (70 eV, EI), *m/z* (%): 377 (59) [M^+], 135 (100), 107 (4), 77 (6).

IR (KBr): ṽ = 3324 (m), 3083 (w), 2883 (w), 2779 (w), 1633 (m), 1606 (m), 1569 (w), 1486 (vs), 1434 (m), 1285 (m), 1260 (m), 1235 (m), 1213 (m), 1173 (m), 1103 (w), 1022 (m), 935 (w), 848 (w), 817 (w), 767 (w), 614 (w).

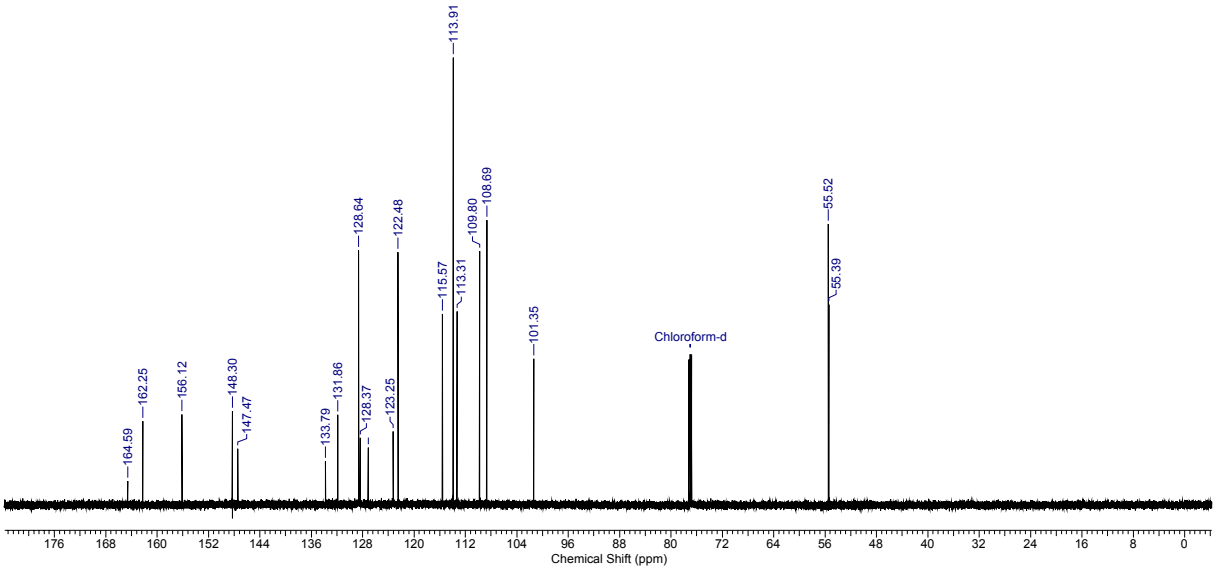
HRMS for $\mathbf{C_{22}H_{19}NO_5}$ (377.1263): found: 377.1240.

N-[2-(1,3-Benzodioxol-5-yl)-4-methoxyphenyl]-4-methoxybenzamide (7h)

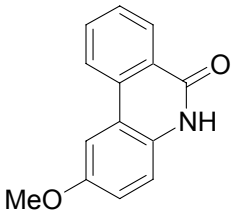
Acquisition Time (sec)	4.0000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 30 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl122_Proton_01					***Frequency (MHz)***	599.68
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	28902	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	7225.43
Temperature (degree C)	27.000						



Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel			***Date***	Jun 30 2006
File Name	\\srvknoch2\bblch\Spektren\NMR\600 MHz\bbl122_Carbon2048_01					***Frequency (MHz)***	150.81
Nucleus	13C	***Number of Transients***	2048	***Original Points Count***	58824	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	36764.71
Temperature (degree C)	27.000						



Synthesis of 2-methoxyphenanthridin-6(5*H*)-one (7i)



Prepared according to **TP 2** from ethyl 2-iodobenzoate (828 mg, 3.00 mmol), *i*PrMgCl (4.1 mL, 3.1 mmol, 0.76 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol %) and *N*-(2-iodo-4-methoxyphenyl)-4-methoxybenzamide (383 mg, 1.00 mmol). Reaction time: 2 h. After workup, the crude compound was taken in $CHCl_3$ (5 mL), cooled to 0 °C and filtered through a glass sinter, affording **7i** as a pale brown solid (207 mg, 92 %).

Mp.: 224.5-225.3 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 11.54 (s_br, 1H), 8.53 (d, *J*= 8.2 Hz, 1H), 8.31 (d, *J*= 7.2 Hz, 1H), 7.83 (m, 2H), 7.63 (t, *J*= 7.5 Hz, 1H), 7.30 (d, *J*= 9.0 Hz, 1H), 7.12 (dd, *J*= 8.9, 2.6 Hz, 1H), 3.86 (s, 3H).

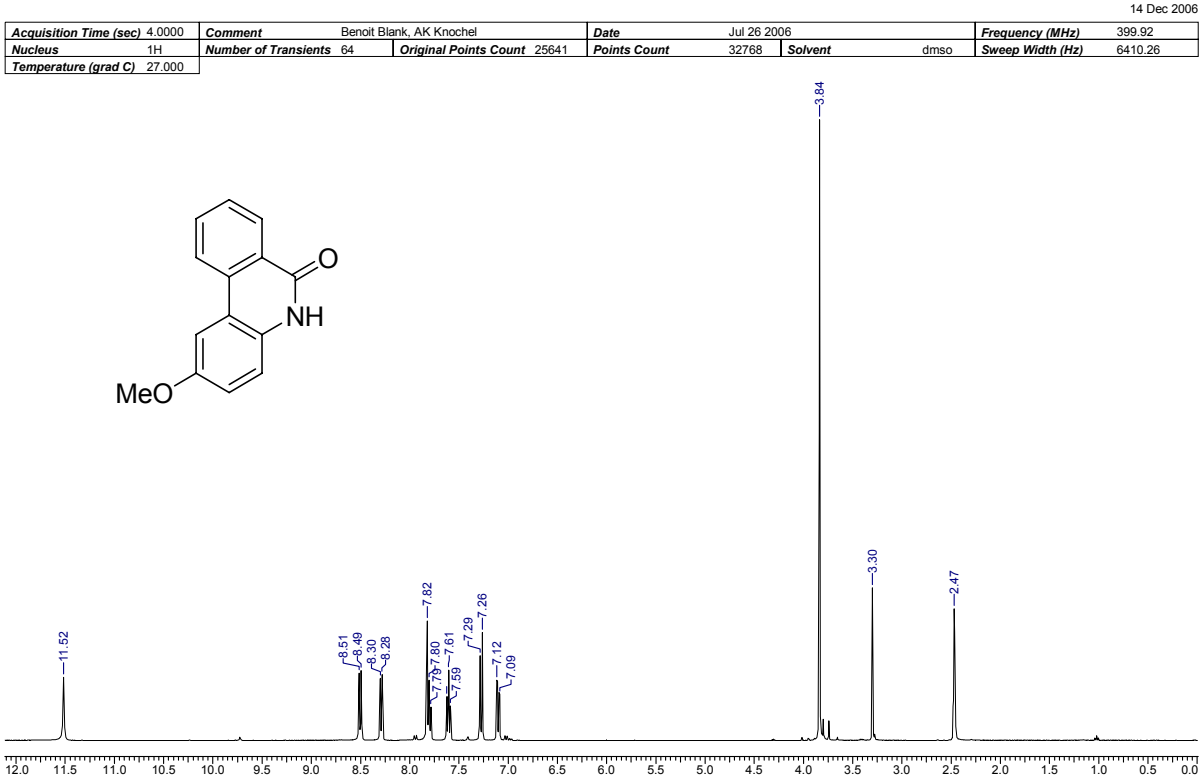
^{13}C-NMR (100 MHz, DMSO-d_6): δ = 160.3, 154.8, 134.0, 132.5, 130.7, 127.9, 127.4, 125.8, 122.9, 118.3, 117.7, 117.3, 106.2, 55.6.

MS (70 eV, ESI), *m/z* (%): 451 (100) [2M+H$^+$], 226 (20) [M+H$^+$].

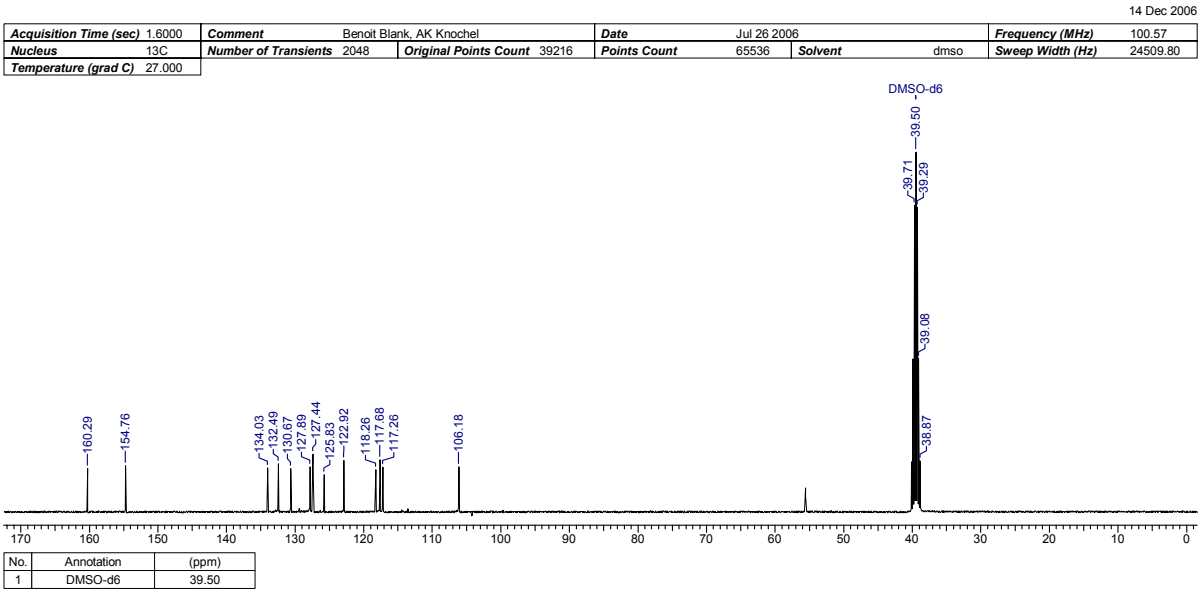
IR (KBr): ν̃ = 3016 (m), 2871 (m), 1665 (vs), 1609 (s), 1504 (s), 1472 (m), 1446 (m), 1369 (m), 1269 (m), 1205 (m), 1151 (m), 1039 (m), 804 (m), 769 (m), 716 (m), 656 (m).

HRMS for **$C_{14}H_{11}NO_2$** (225.0790): found: 225.0786.

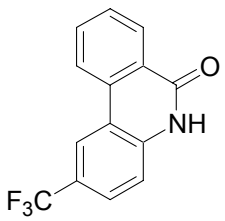
2-methoxyphenanthridin-6(5H)-one



2-methoxyphenanthridin-6(5H)-one



Synthesis of 2-(trifluoromethyl)phenanthridin-6(5*H*)-one (7j)



Prepared according to **TP 2** from ethyl 2-iodobenzoate (828 mg, 3.00 mmol), *i*PrMgCl (4.1 mL, 3.1 mmol, 0.76 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF), $Fe(acac)_3$ (35 mg, 10 mol %) and *N*-[2-iodo-4-(trifluoromethyl)phenyl]-4-methoxybenzamide (421 mg, 1.00 mmol). Reaction time: 3 h. Purification by flash chromatography (CH_2Cl_2) yielded **7j** as a colorless solid (206 mg, 78 %).

Mp.: 293.2-294.7 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 11.96 (s, 1H), 8.66 (s, 1H), 8.61 (d, *J*= 8.0 Hz, 1H), 8.32 (dd, *J*= 7.9, 1.5 Hz, 1H), 7.91-7.80 (m, 1H), 7.76 (dd, *J*= 8.6, 1.8 Hz, 1H), 7.67 (t, *J*= 7.5 Hz, 1H), 7.50 (d, *J*= 8.4 Hz, 1H).

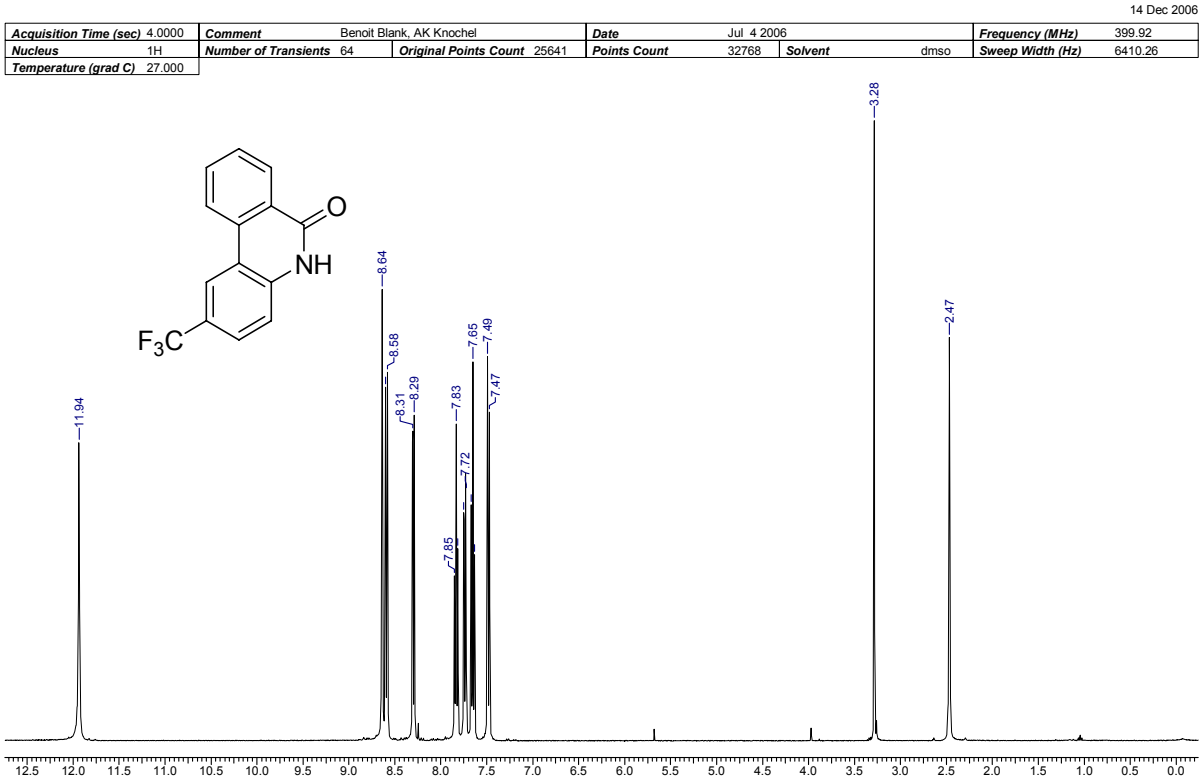
^{13}C-NMR (100 MHz, DMSO-d_6): δ = 160.9, 139.2, 133.2, 133.0, 128.7, 127.4, 125.8 (q, *J*= 3.7 Hz), 125.7, 124.4 (q, *J*= 271.1 Hz), 123.0, 122.7 (q, *J*= 32.2 Hz), 120.7 (q, *J*= 4.1 Hz), 117.6, 116.7.

MS (70 eV, EI), *m/z* (%): 263 (100) [M^+], 235 (8), 185 (2), 139 (2).

IR (KBr): ṽ = 2884 (w), 2360 (w), 2341 (w), 1684 (m), 1609 (m), 1358 (m), 1324 (m), 1296 (m), 1269 (m), 1114 (vs), 1075 (m), 1021 (w), 898 (m), 877 (m), 832 (m), 775 (s), 682 (m), 640 (s), 617 (w).

HRMS for **$C_{14}H_{18}F_3NO$** (263.0558): found: 263.0563.

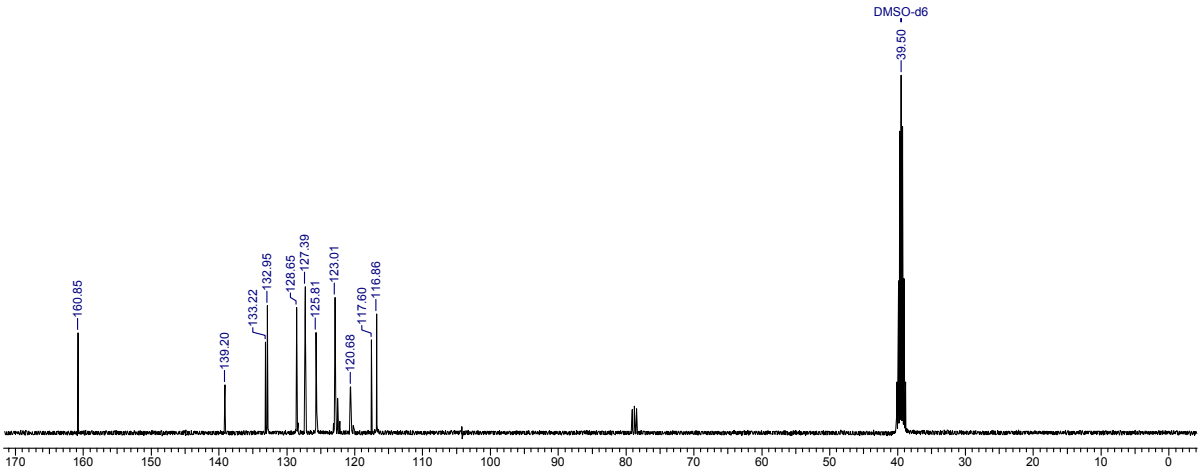
2-(trifluoromethyl)phenanthridin-6(5H)-one



2-(trifluoromethyl)phenanthridin-6(5H)-one

14 Dec 2006

Acquisition Time (sec)	1.6000	***Comment***	Benoit Blank, AK Knochel		***Date***	Jul 4 2006		***Frequency (MHz)***	100.57
Nucleus	13C	***Number of Transients***	2048	***Original Points Count*** 39216	***Points Count***	65536	***Solvent*** dmso	***Sweep Width (Hz)***	24509.80
Temperature (grad C)	27.000								



No.	Annotation	(ppm)
1	DMSO-d6	39.50