Supplementary information

Suzuki-Miyaura cross coupling reactions with Phenoldiazonium salts

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A General Remarks

All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ with $CHCl_3$ (δ = 7.26 ppm) as an internal standard, or in methanol-d_4 with CD_2HOD (δ = 3.31 ppm) as an internal standard. Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ with $CDCl_3$ (δ = 77.0 ppm) as an internal standard or in methanol-d_4 with CD_3OD (δ = 49.2 ppm) as an internal standard. The number of coupled protons was analyzed by DEPT- or APT-experiments and is denoted by a number in parantheses following the chemical shift value. Whenever signal assignments in ^{1}H- or ^{13}C-NMR spectra are given, these are based on H,H- and H,C-correlation spectroscopy, and NOE-spectroscopy if necessary. ^{19}F NMR spectra were recorded at 282 MHz in $CDCl_3$ with C_6F_6 (δ = –163 ppm) as an internal standard. IR spectra were recorded in substance on NaCl or KBr plates. Wavenumbers (ν) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV.

B General experimental procedures

B1 General procedure: basic conditions

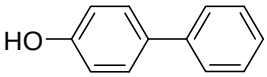
To a solution of the appropriate diazonium salt **4** (0.5 mmol) in methanol (5.0 mL) were added NaOAc (123 mg, 1.5 mmol) and $Pd(OAc)_2$ (2.8 mg, 2.5 mol%). The mixture was stirred at ambient temperature for 10 minutes, and the appropriate potassium trifluoroborate **5** (0.5 mmol) was added. Stirring at ambient temperature was continued for 12 hours, and active charcoal (100 mg) was added. All volatiles were removed in vacuo, ethyl acetate (25 mL) or MTBE (100 mL) was added and the mixture was immersed in an ultrasonic bath. It was then filtered through celite, the solvent was evaporated and the residue was purified by chromatography on silica using the eluents stated for the individual examples.

B2 General procedure: base-free conditions

To a solution of the appropriate diazonium salt **4** (0.5 mmol) in methanol (5.0 mL) was added $Pd(OAc)_2$ (2.8 mg, 2.5 mol%). The mixture was stirred for 10 minutes, and the appropriate potassium trifluoroborate **5** (0.5 mmol) was added. Stirring at ambient temperature was continued for 12 hours, and active charcoal (100 mg) was added. All volatiles were removed in vacuo, ethyl acetate (25 mL) or MTBE (100 mL) was added and the mixture was immersed in an ultrasonic bath. It was then filtered through celite, the solvent was evaporated and the residue was purified by chromatography on silica using the eluents stated for the individual examples.

C Specific details, analytical data and copies of spectra for individual compounds

*C1 Biphenyl-4-ol (**6aa**)*

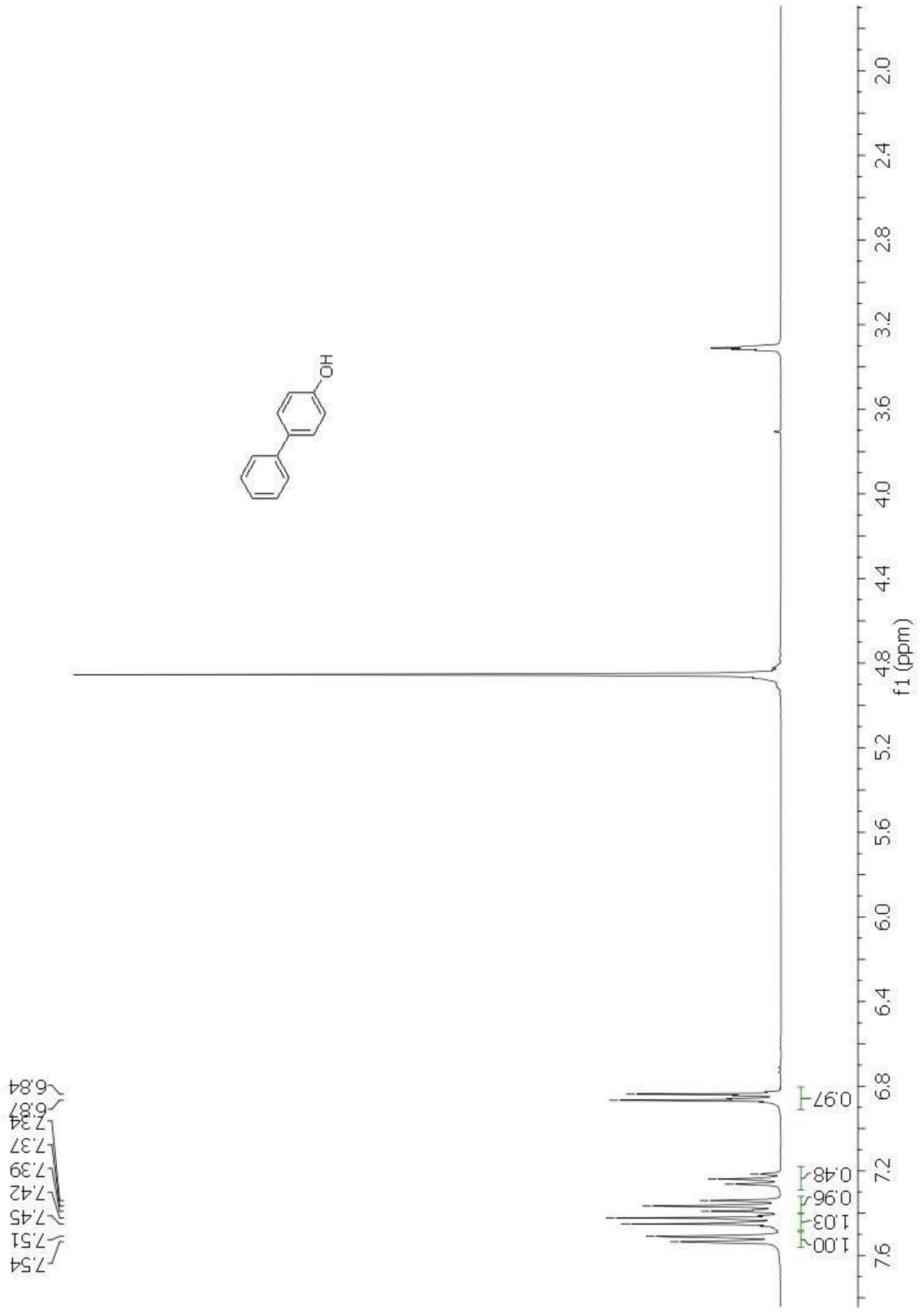


6aa

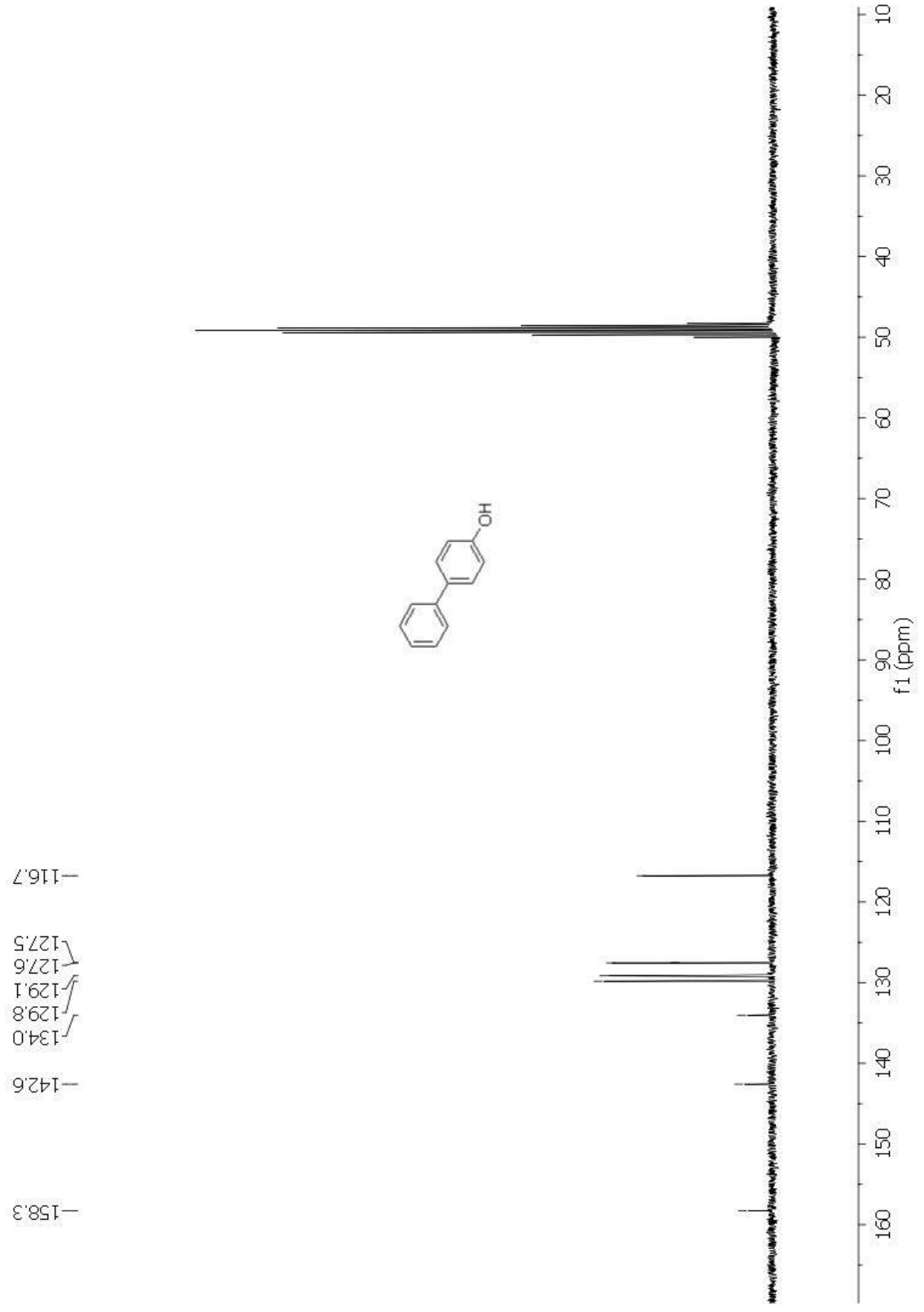
Procedure:	B1 (basic conditions)		
*Ar-N_2BF_4 (**4**):*	**4a**	0.5 mmol	104 mg
*Ar'-BF_3K (**5**):*	**5a**	0.5 mmol	92 mg
*Ar-Ar' (**6**):*	**6aa**	82%	70 mg
eluent for chromatography:	hexanes/MTBE (5 : 1, v/v)		
Aggregate state:	colourless solid, mp 162-164°C[1]		

^{1}H NMR (300 MHz, MeOD-d_4) δ 7.55 – 7.50 (2H), 7.44 (d, J = 8.7, 2H), 7.40 – 7.33 (2H), 7.24 (m, 1H), 6.85 (d, J = 8.7, 2H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 158.3 (0), 142.6 (0), 134.0 (0), 129.8 (1), 129.2 (1), 127.6 (1), 127.5 (1), 116.8 (1); IR (neat) ν 3421 (w), 1598 (w), 1534 (w), 1489 (w), 1263 (w); MS (ESI): *m/z* 170 ([M]$^+$, 10), 122 (100); HRMS (ESI): calcd. for $C_{12}H_{11}O[M+H]^+$: 171.0810, found: 171.0819; Anal. calcd. for $C_{12}H_{10}O$: C, 84.7; H, 5.9. Found: C, 84.2; H, 5.8.

[1] G. Lu, R. Franzén, Q. Zhang and Y. Xu, *Tetrahedron Lett.*, 2005, **46**, 4255-4259.

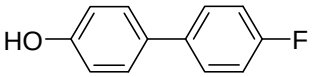


^{1}H NMR (300 MHz, MeOD-d_4) of **6aa**



^{13}C NMR (75 MHz, MeOD-d_4) of **6aa**

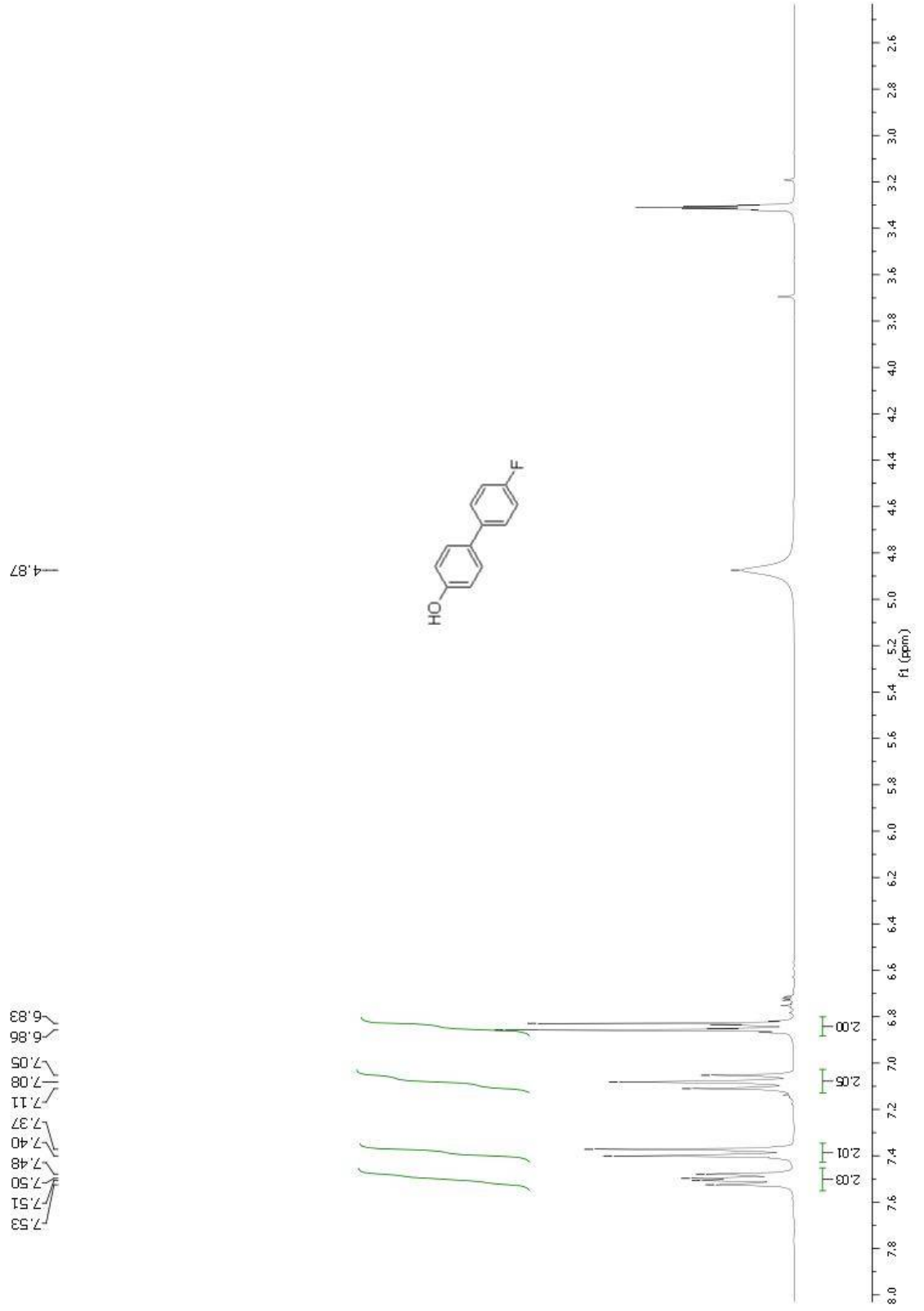
C2 4'-Fluorobiphenyl-4-ol ***(6ab)***



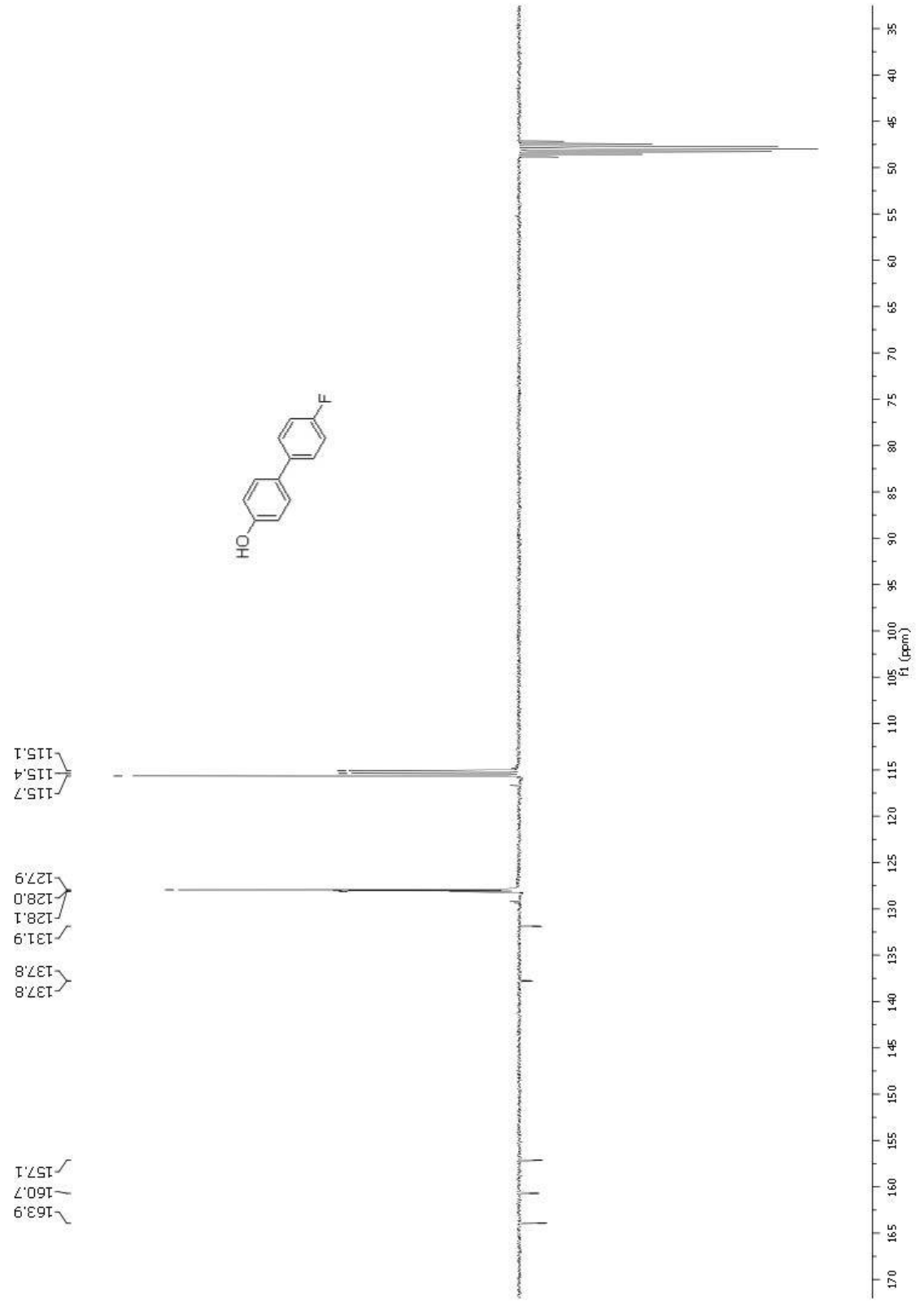
Procedure:	B1 (basic conditions)		
Ar-N_2BF_4 (**4**):	**4a**	0.5 mmol	104 mg
Ar'-BF_3K (**5**):	**5b**	0.5 mmol	101 mg
Ar-Ar' (**6**):	**6ab**	74%	69 mg
eluent for chromatography:	hexanes/MTBE (5 : 1, v/v)		
Aggregate state:	colourless solid, mp 167-170°C[2]		

^{1}H NMR (300 MHz, MeOD-d_4) δ 7.50 (dd, J = 8.2, 5.6, 2H), 7.39 (d, J = 8.5, 2H), 7.10 (d, J = 8.7, 1H), 7.06 (d, J = 8.7, 1H), 6.84 (d, J = 8.7, 2H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 162.6 (d, J = 242.3, 0), 157.1 (0), 137.8 (d, J = 3.0, 0), 131.9 (0), 128.1 (d, J = 8.3, 1), 127.9 (1), 115.7 (1), 115.3 (d, J = 21.0, 1); ^{19}F NMR (282 MHz, MeOD-d_4) δ −117.2 (tt, J = 8.8, 5.3); IR (neat): ν 3406 (w), 1600 (w), 1500 (m), 1450 (w), 1375 (w), 1246 (m), 1164 (w); MS (ESI): *m/z* 188 ([M]$^+$, 100), 159 (27), 133 (22); HRMS (ESI): calcd. for $C_{12}H_{10}FO[M+H]^+$: 189.0716, found: 189.0734; Anal. calcd. for $C_{12}H_9FO$: C, 76.6; H, 4.8. Found: C, 76.4; H, 4.8.

[2] P. J. Hajduk, G. Sheppard, D. G. Nettesheim, E. T. Olejniczak, S. B. Shuker, R. P. Meadows, D. H. Steinman, G. M. Carrera, P. A. Marcotte, J. Severin, K. Walter, H. Smith, E. Gubbins, R. Simmer, T. F. Holzman, D. W. Morgan, S. K. Davidsen, J. B. Summers and S. W. Fesik, *J. Am. Chem. Soc.*, 1997, **119**, 5818-5827.

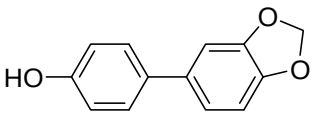


^{1}H NMR (300 MHz, MeOD-d_4) of **6ab**



^{13}C NMR (75 MHz, MeOD-d_4) of **6ab**

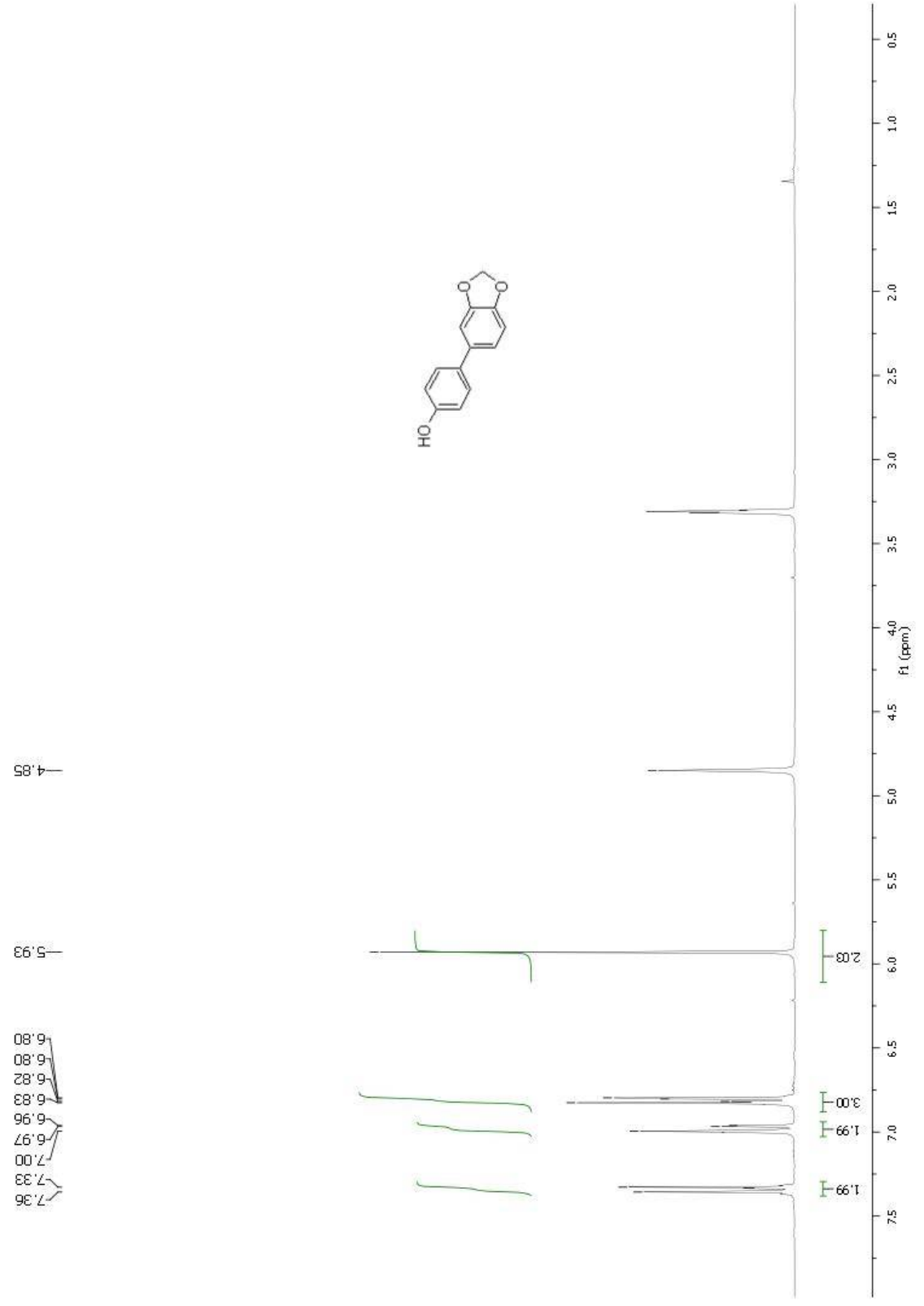
*C3 4-(Benzo[d][1,3]dioxol-5-yl)phenol (**6ac**)*



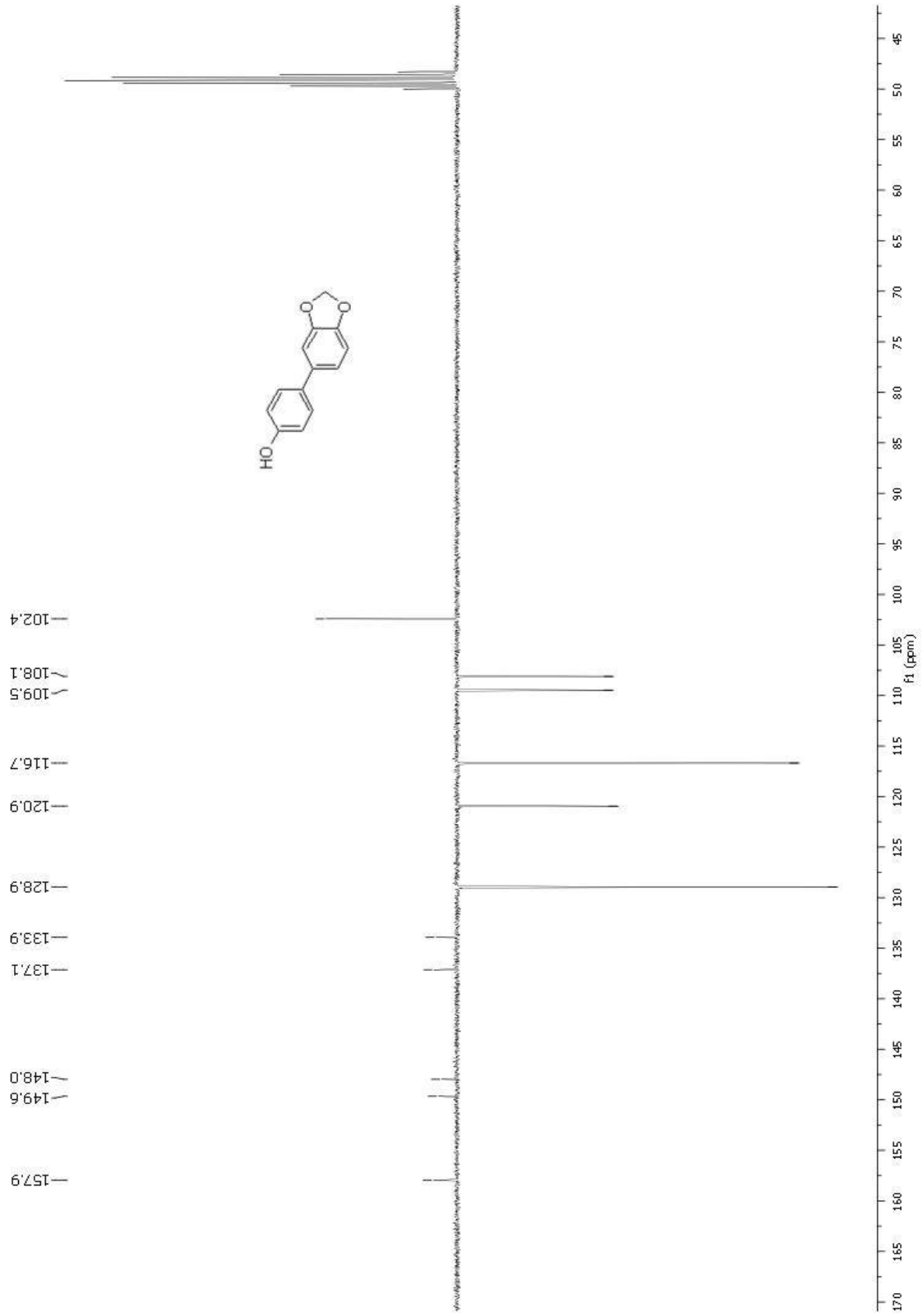
6ac

Procedure:	B1 (basic conditions)		
Ar-N_2BF_4 (**4**):	**4a**	0.5 mmol	104 mg
Ar'-BF_3K (**5**):	**5c**	0.5 mmol	114 mg
Ar-Ar' (**6**):	**6ac**	66%	71 mg
eluent for chromatography:	hexanes/MTBE (5 : 1, v/v)		
Aggregate state:	colourless solid, mp 143-144°C		

^{1}H NMR (300 MHz, MeOD-d_4) δ 7.34 (d, J = 8.7, 2H), 7.03-6.94 (2H), 6.82 (m, 1H), 6.81 (d, J = 8.7, 2H), 5.93 (s, 2H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 157.9 (0), 149.7 (0), 148.0 (0), 137.1 (0), 133.9 (0), 128.9 (1), 120.9 (1), 116.7 (1), 109.5 (1), 108.1 (1), 102.4 (2); IR (neat): ν 3420 (w), 2888 (w), 1610 (w), 1491 (m), 1239 (m), 1110 (w), 1044 (m); MS (ESI): *m/z* 214 ($[M]^+$, 28), 194 (100); HRMS (ESI): calcd. for $C_{13}H_{11}O_3[M+H]^+$: 215.0708, found: 215.0708.

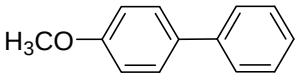


^{1}H NMR (300 MHz, MeOD-d_4) of **6ac**



^{13}C NMR (75 MHz, MeOD-d_4) of **6ac**

*C4 4-methoxybiphenyl (**6ba**)*

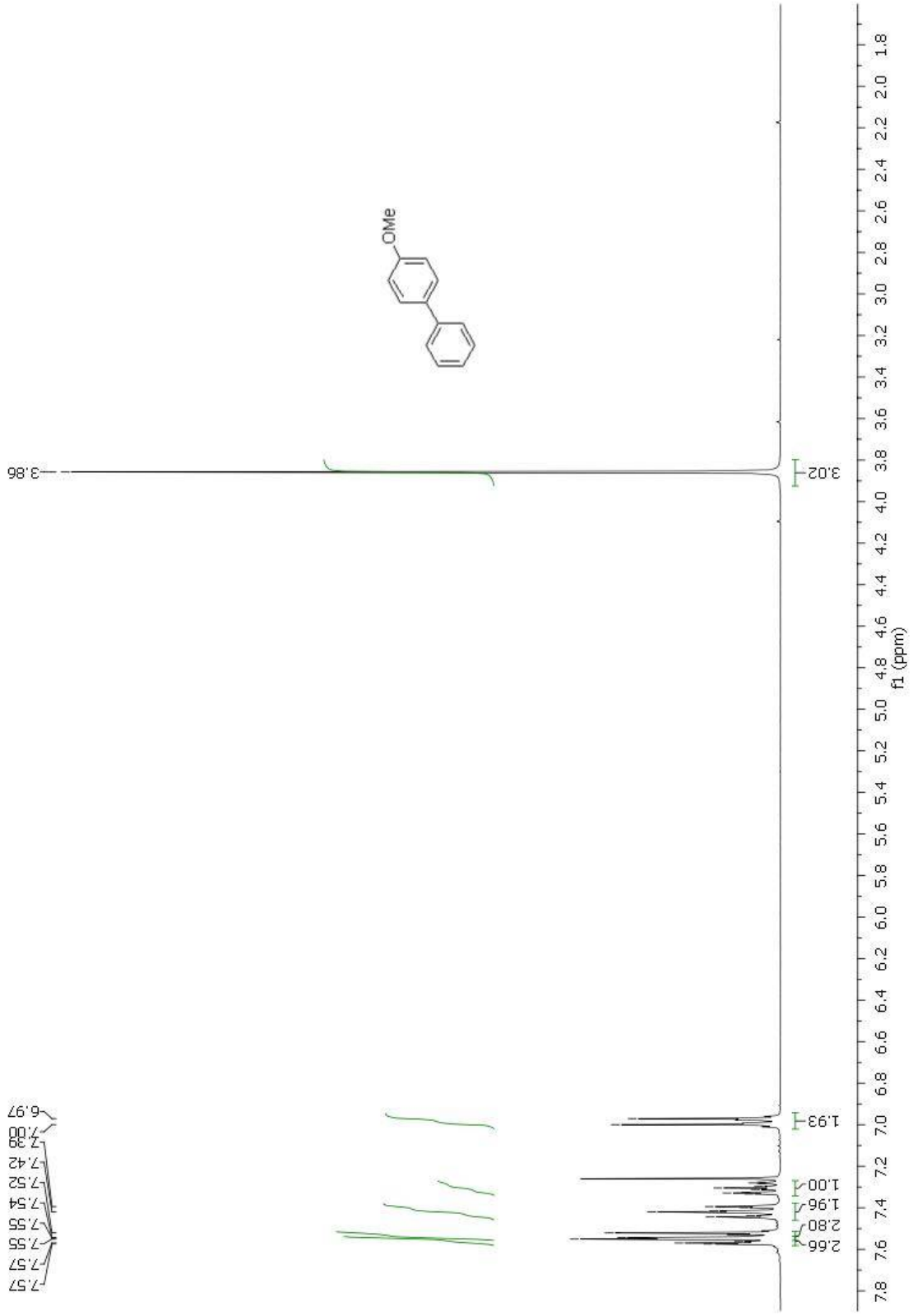


6ba

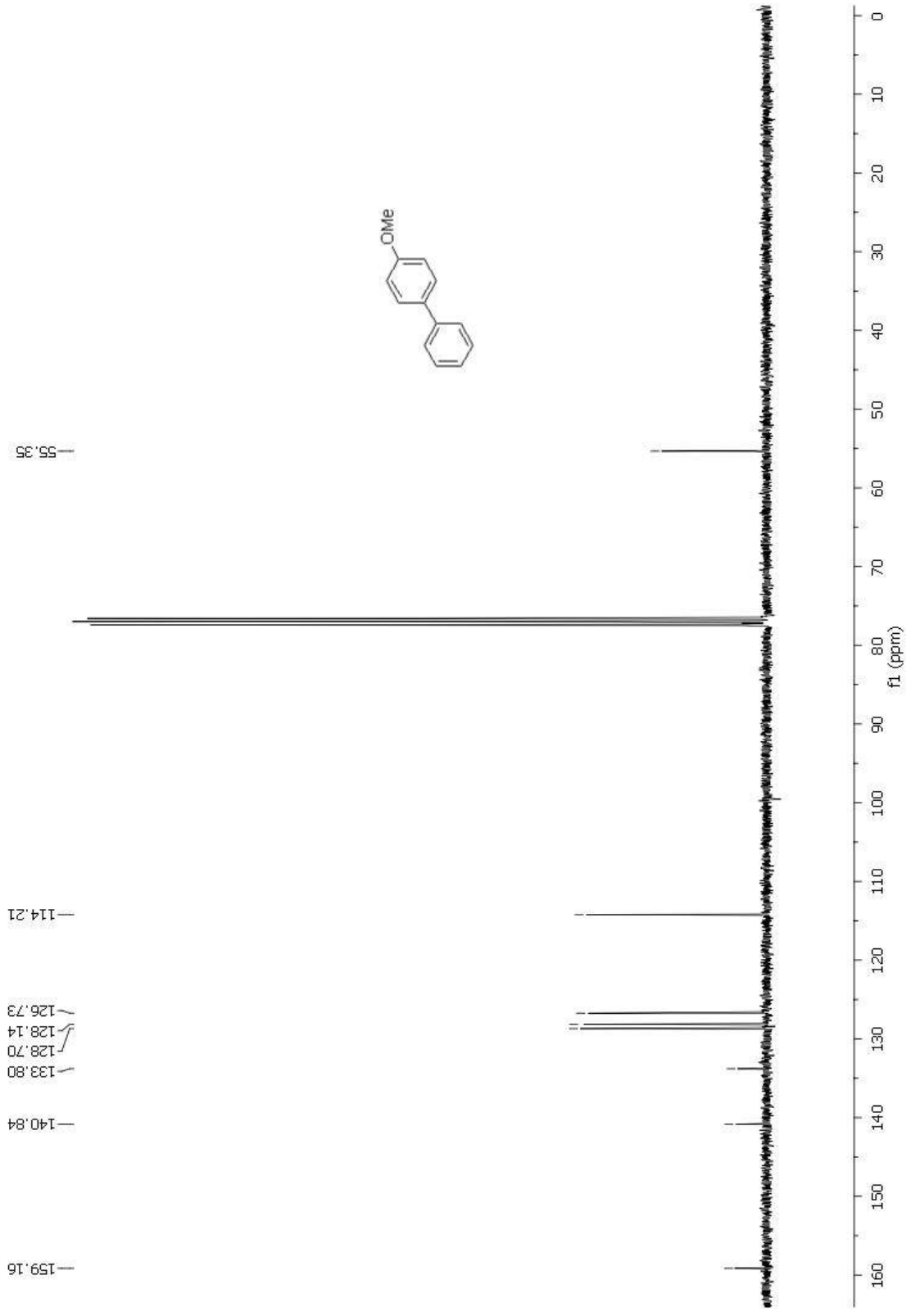
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4b**	0.5 mmol	111 mg
Ar'-BF_3K (**5**):	**5a**	0.5 mmol	92 mg
Ar-Ar' (**6**):	**6ba**	64%	58 mg
eluent for chromatography:	hexanes/MTBE (10 : 1, v/v)		
Aggregate state:	colourless solid, mp 86-87°C[3]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.56 (2H), 7.56 (d, J = 8.8, 2H), 7.48 – 7.40 (2H), 7.36 – 7.29 (m, 1H), 7.01 (d, J = 8.8, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (0), 140.8 (0), 133.8 (0), 128.7 (1), 128.1 (1), 126.7 (1), 114.2 (1), 55.4 (3); IR (neat) ν 3003 (w), 1607 (m), 1487 (m), 1250 (s); Anal. calcd. for $C_{13}H_{12}O$: C, 84.8; H, 6.6. Found: C, 84.8; H, 6.3.

[3] M. Guo, F. Jian and R. He, *Tetrahedron Lett.*, 2005, **46**, 9017-9020.

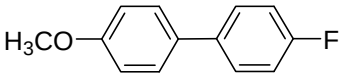


^{1}H NMR (300 MHz, $CDCl_3$) of **6ba**



^{13}C NMR (75 MHz, $CDCl_3$) of **6ba**

*C5 4-Fluoro-4'-methoxybiphenyl (**6bb**)*

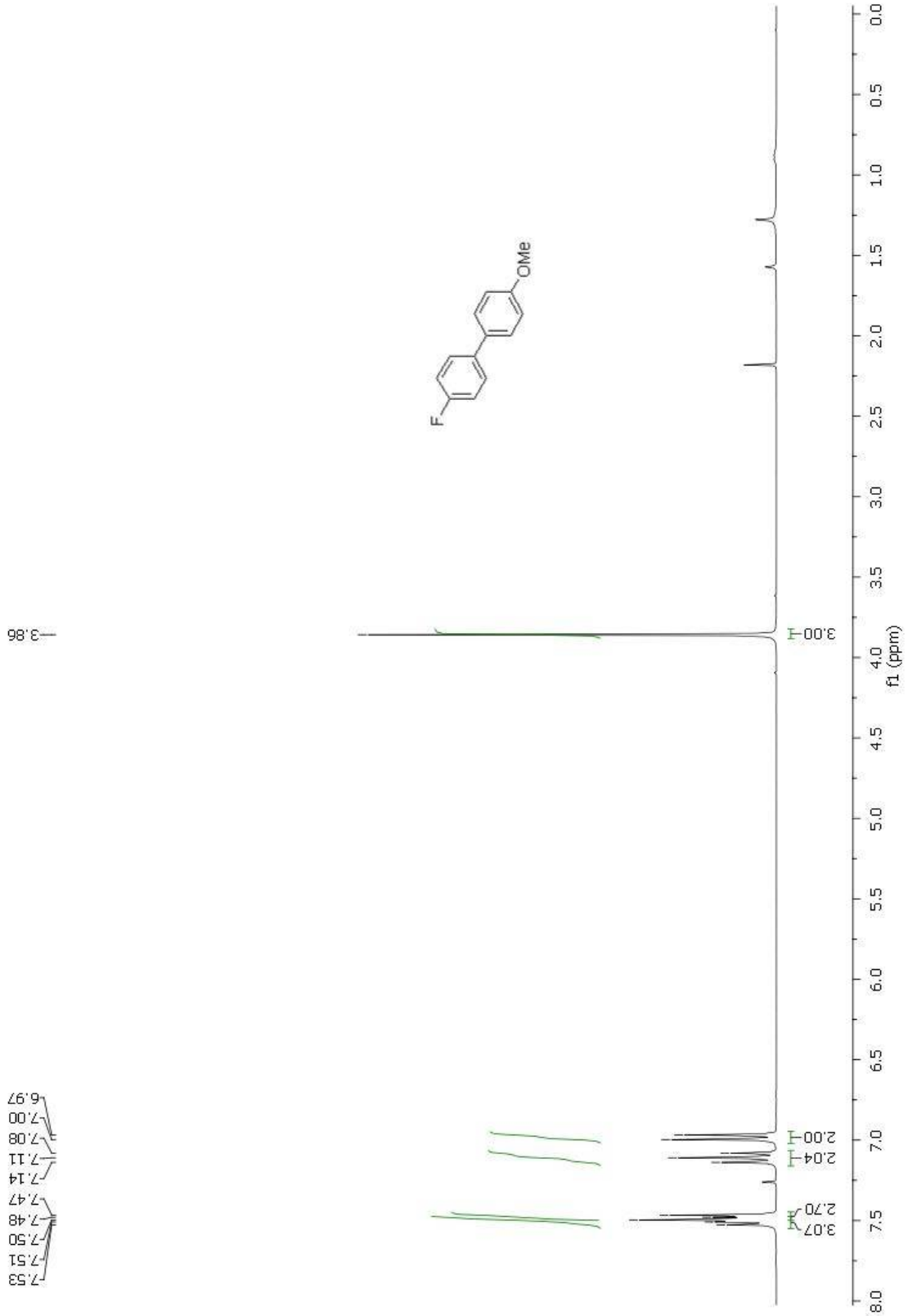


6bb

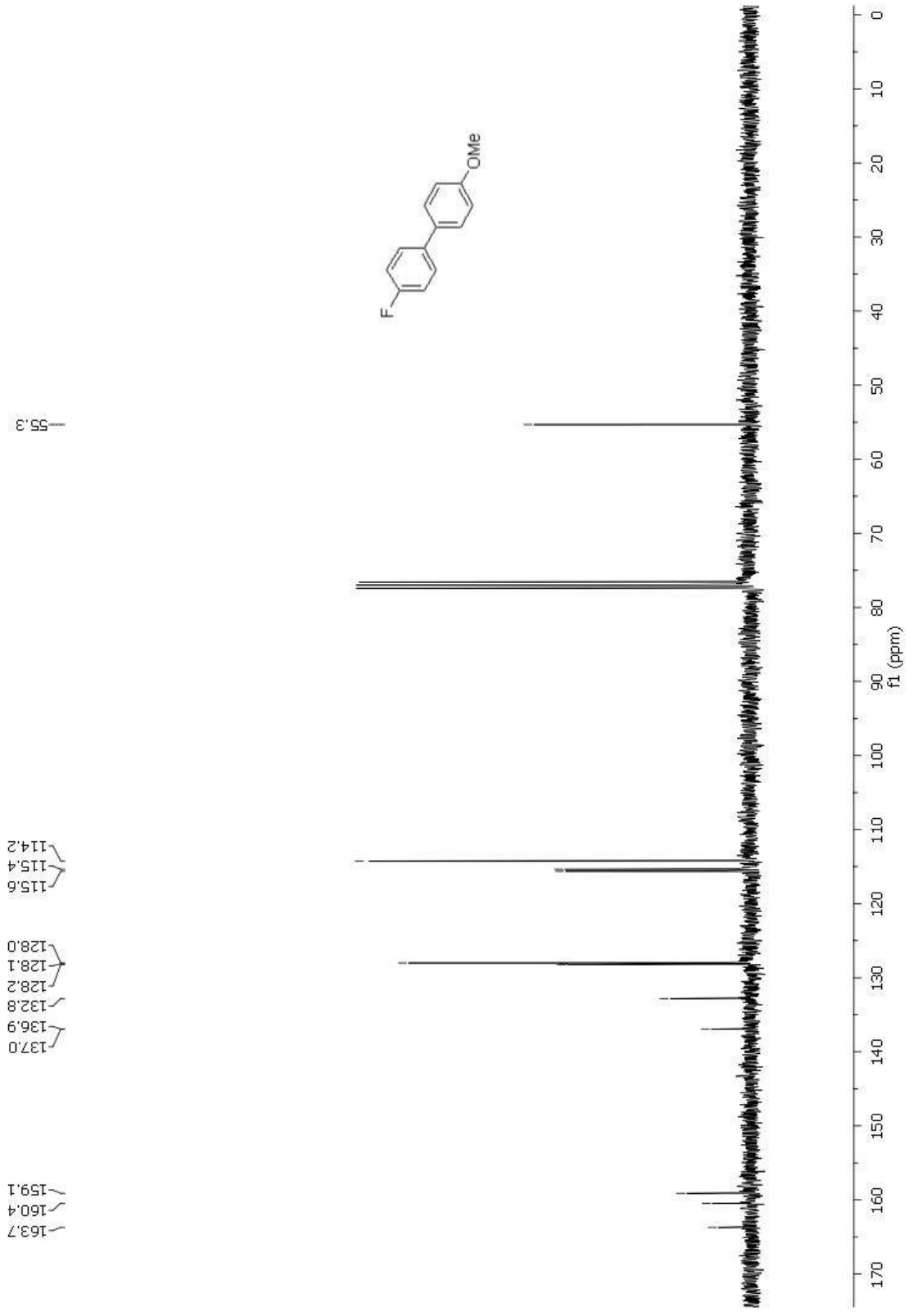
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4b**	0.5 mmol	111 mg
Ar'-BF_3K (**5**):	**5b**	0.5 mmol	101 mg
Ar-Ar' (**6**):	**6bb**	40%	40 mg
eluent for chromatography:	hexanes/MTBE (10 : 1, v/v)		
Aggregate state:	colourless solid, mp 88-91°C[4]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, J = 8.9, 5.2, 2H), 7.48 (d, J = 8.9, 2H), 7.11 (dd, J = 8.7, 8.7, 2H), 6.98 (d, J = 8.7, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1 (d, J = 245.6, 0), 159.1 (0), 132.8 (0), 137.0 (d, J = 3.2, 0), 128.2 (d, J = 7.9, 1), 128.0 (1), 115.5 (d, J = 21.4, 1), 114.2 (1), 55.3 (3); ^{19}F NMR (282 MHz, $CDCl_3$) δ –117.9 (tt, J = 5.3, 3.3); IR (neat) ν 2920 (w), 1606 (w), 1466 (m), 1235 (s); Anal. calcd. for $C_{13}H_{11}OF$: C, 77.2; H, 5.5. Found: C, 77.2; H, 5.7.

[4] S. E. Denmark, R. C. Smith, W.-T. T. Chang and J. M. Muhuhi, *J. Am. Chem. Soc.*, 2009, **131**, 3104-3118.

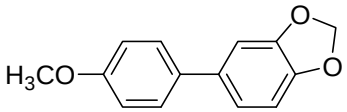


^{1}H NMR (300 MHz, $CDCl_3$) of **6bb**

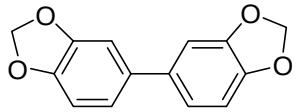


^{13}C NMR (75 MHz, $CDCl_3$) of **6bb**

*C6 4-Fluoro-4'-methoxybiphenyl (**6bc**) and 5,5'-bibenzo[d][1,3]dioxole (**7**)*



6bc

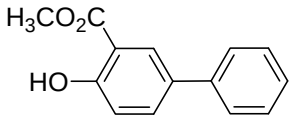


7

Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4b**	0.5 mmol	111 mg
Ar'-BF_3K (**5**):	**5c**	0.5 mmol	114 mg
Ar-Ar' (**6**):	**6bc**/**7**	--	40 mg
eluent for chromatography:	hexanes/MTBE (10 : 1, v/v)		
Aggregate state:	inseparable mixture of compounds, ratio **6bc** : **7** = 5 : 1		

NMR-spectroscopical data of **6bc** were obtained from the mixture: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 8.7, 1H), 7.05-6.99 (2H), 6.96 (d, J = 8.6, 1H), 6.86 (m, 1H), 5.99 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9 (0), 148.0 (0), 146.6 (0), 135.3 (0), 133.6 (0), 127.9 (1), 120.1 (1), 114.2 (1), 108.5 (1), 107.4 (1), 101.0 (2), 55.3 (3); MS (ESI): *m/z* 228 ($[M]^+$, 100), 213 (63); HRMS (EI): calcd. for $C_{14}H_{12}O_3[M]^+$: 228.0781; found: 228.0769.

*C7 Methyl 4-hydroxybiphenyl-3-carboxylate (**6ca**)*

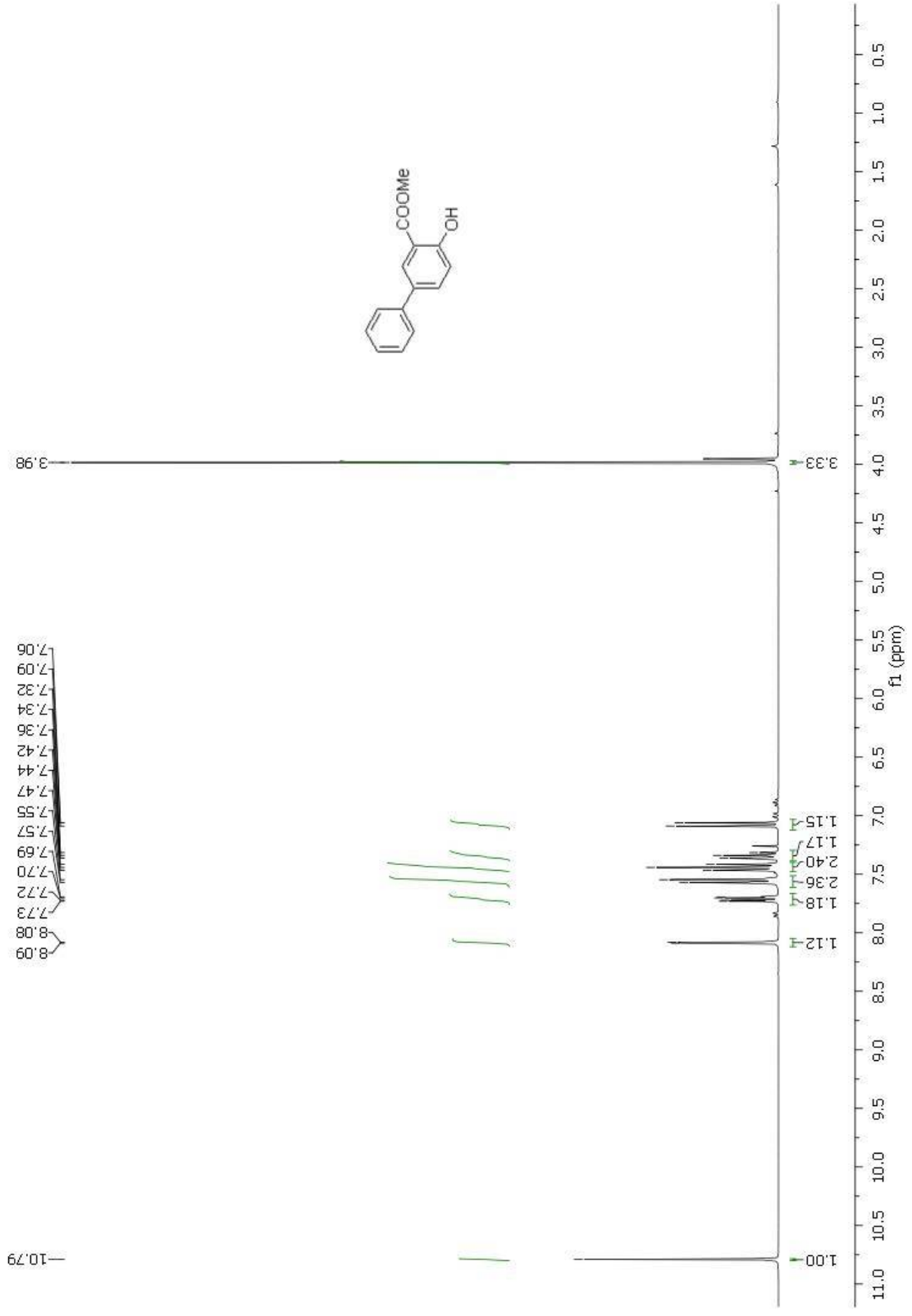


6ca

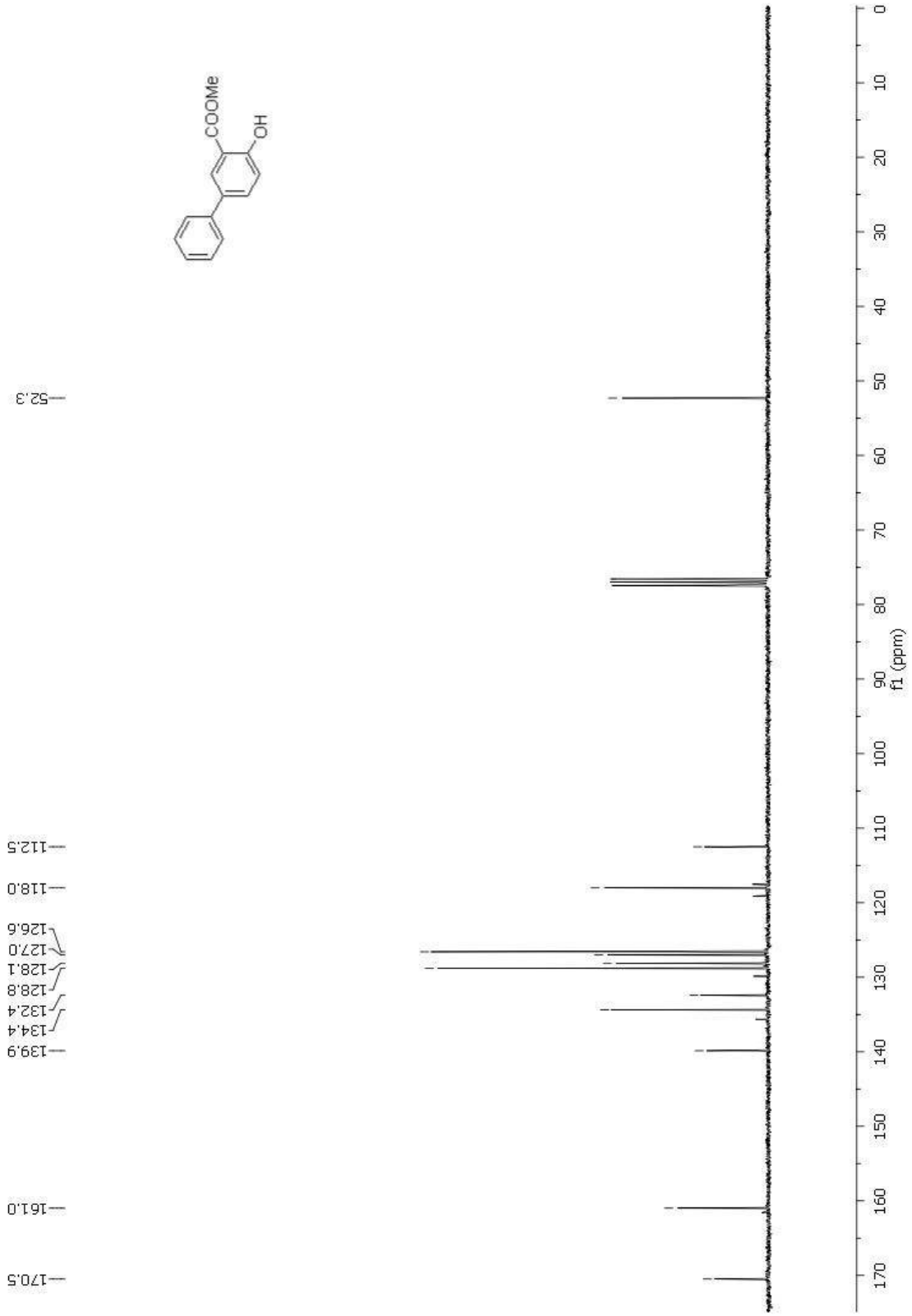
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4c**	0.5 mmol	133 mg
Ar'-BF_3K (**5**):	**5a**	0.5 mmol	92 mg
Ar-Ar' (**6**):	**6ca**	70%	80 mg
eluent for chromatography:	hexanes/MTBE (10 : 1, v/v)		
Aggregate state:	colourless solid, mp 94-95°C[5]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.08 (d, J = 2.4, 1H), 7.71 (dd, J = 8.6, 2.4, 1H), 7.58 – 7.53 (2H), 7.48 – 7.40 (2H), 7.34 (m, 1H), 7.07 (d, J = 8.6, 1H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (0), 161.0 (0), 139.9 (0), 134.4 (1), 132.4 (0), 128.8 (1), 128.1 (1), 127.0 (1), 126.6 (1), 118.0 (1), 112.5 (0), 52.3 (3); IR (neat) ν 3170 (w), 2954(w), 1676 (s), 1440 (m), 1345 (m), 1209 (s); MS (EI): *m/z* 228 ($[M]^+$, 38), 196 (100), 168 (20); HRMS (EI): calcd. for $C_{14}H_{12}O_3[M]^+$: 228.0781, found: 228.0792; Anal. calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.4; H, 5.0.

[5] L. F. Fieser and C. K. Bradsher, *J. Am. Chem. Soc.*, 1936, **58**, 1738-1741.

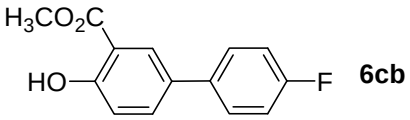


^{1}H NMR (300 MHz, $CDCl_3$) of **6ca**



^{13}C NMR (75 MHz, $CDCl_3$) of **6ca**

*C8 Methyl 4'-fluoro-4-hydroxybiphenyl-3-carboxylate (**6cb**)*

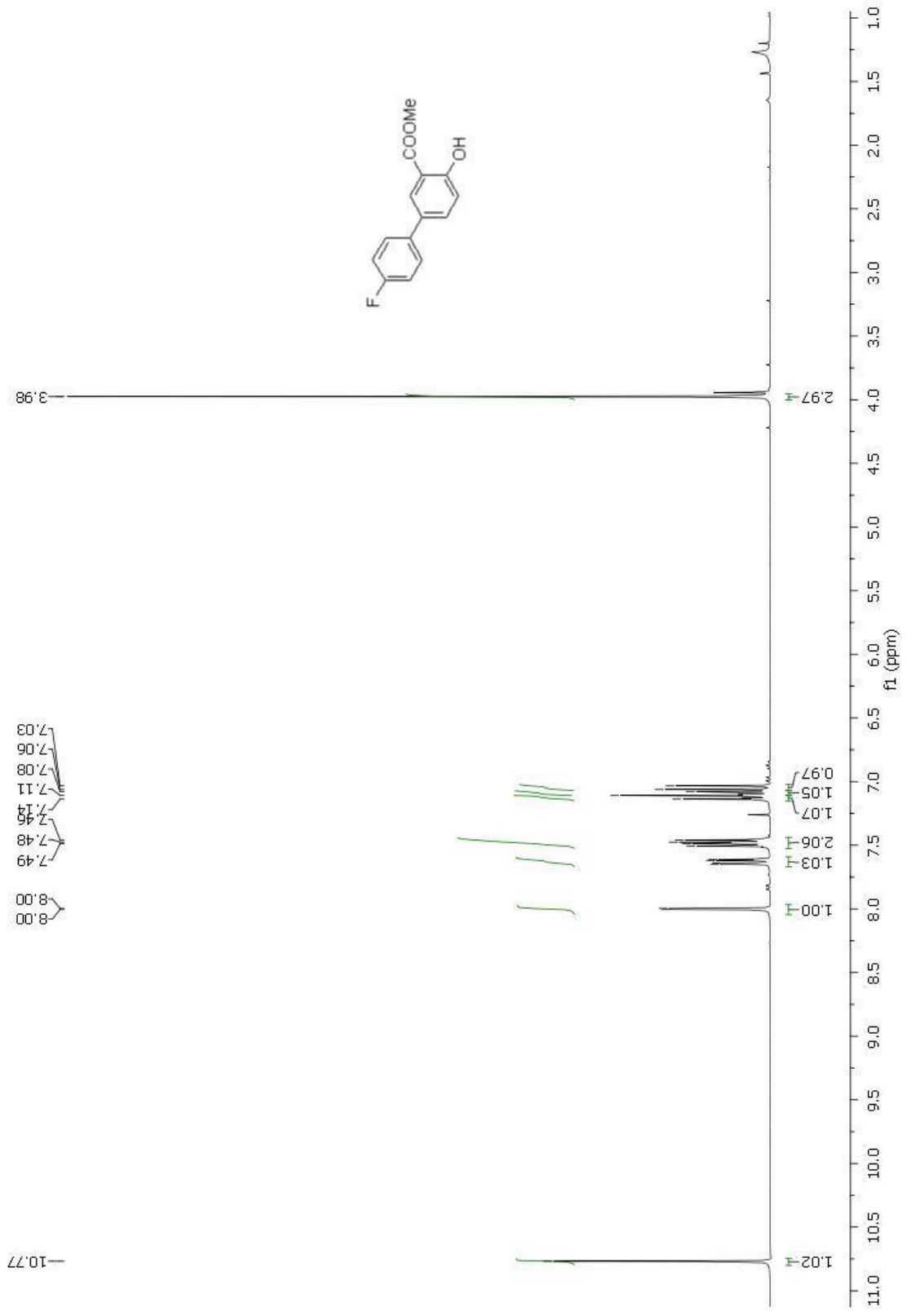


6cb

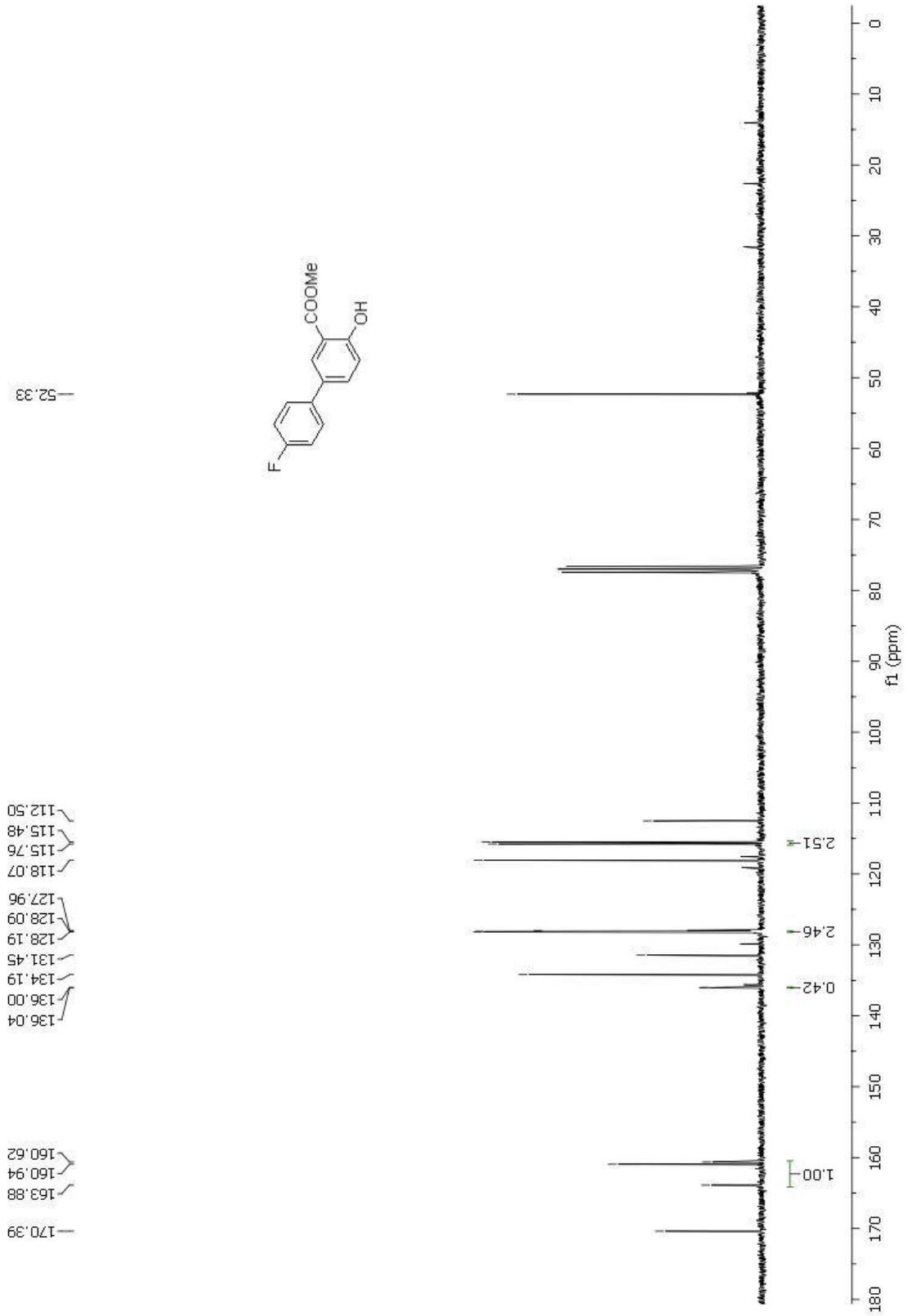
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4c**	0.5 mmol	133 mg
Ar'-BF_3K (**5**):	**5b**	0.5 mmol	101 mg
Ar-Ar' (**6**):	**6cb**	82%	100 mg
eluent for chromatography:	hexanes/MTBE (10 : 1, v/v)		
Aggregate state:	colourless solid, mp 50-52°C[6]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.77 (s, 1H), 8.00 (d, J = 2.4, 1H), 7.63 (dd, J = 8.6, 2.4, 1H), 7.49 (d, J = 8.8, 1H); 7.47 (d, J = 8.8, 1H), 7.12 (d, J = 8.7, 1H), 7.09 (d, J = 8.7, 1H), 7.05 (d, J = 8.7, 1H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4 (0), 162.3 (d, J = 246.2, 0), 136.0 (d, J = 3.2, 0), 134.2 (1),131.5 (0), 128.1 (d, J = 8.0, 1), 128.0 (1),118.1 (1), 115.6 (d, J = 21.5, 1), 112.5 (0), 52.3 (3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −117.1 (tt, J = 5.3, 3.3); IR (neat): ν 2957 (w), 1679 (m), 1483 (m), 1208 (s); Anal. calcd. for $C_{14}H_{11}O_3F$: C, 68.3; H, 4.5. Found: C, 68.2; H, 4.6.

[6] J. Hannah, W. V. Ruyle, H. Jones, A. R. Matzuk, K. W. Kelly, B. E. Witzel, W. J. Holtz, R. A. Houser and T. Y. Shen, *J. Med. Chem.*, 1978, **21**, 1093-1100.

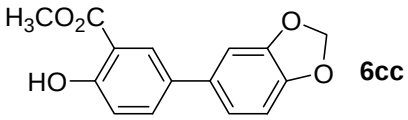


^{1}H NMR (300 MHz, $CDCl_3$) of **6cb**



^{13}C NMR (75 MHz, $CDCl_3$) of **6cb**

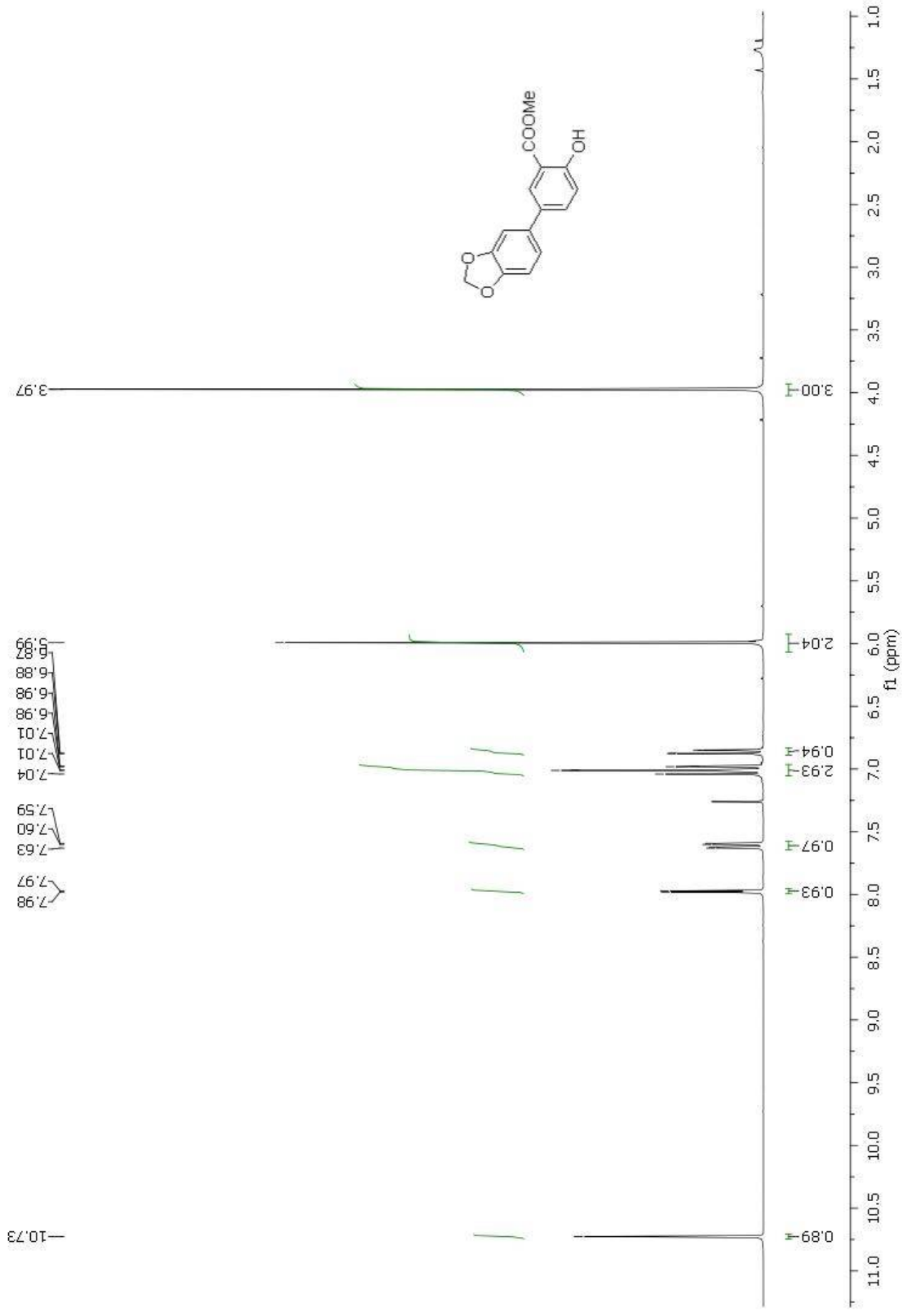
*C9 Methyl 5-(benzo[d][1,3]dioxol-5-yl)-2-hydroxybenzoate (**6cc**)*



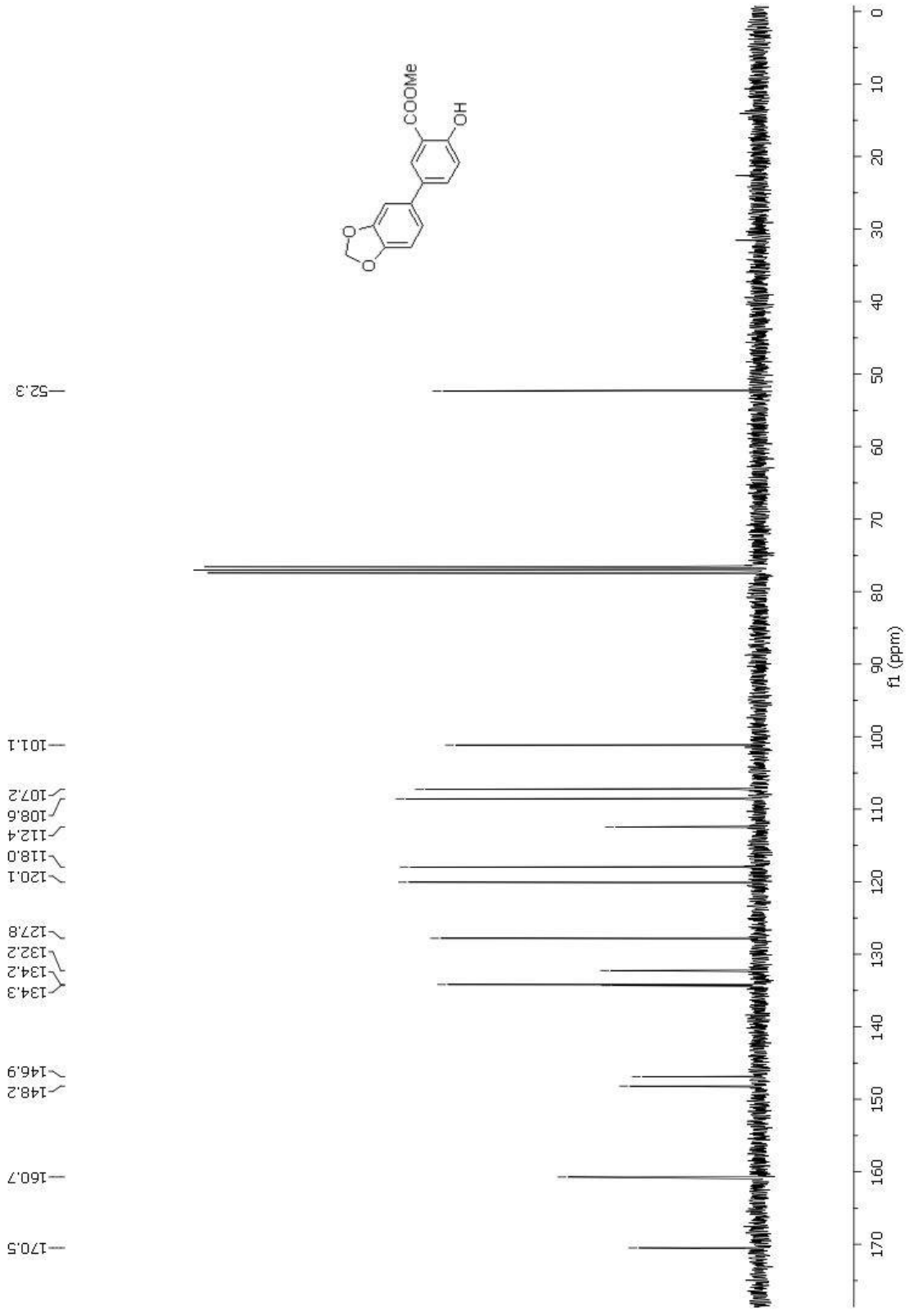
6cc

Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4c**	0.5 mmol	133 mg
Ar'-BF_3K (**5**):	**5c**	0.5 mmol	114 mg
Ar-Ar' (**6**):	**6cc**	44%	60 mg
eluent for chromatography:	hexanes/MTBE (10 : 1, v/v)		
Aggregate state:	colourless solid, mp 134-136°C		

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.73 (s, 1H), 7.98 (d, J = 2.4, 1H), 7.61 (dd, J = 8.7, 2.4, 1H), 7.06 – 6.96 (3H), 6.86 (dd, J = 7.8, 0.6, 1H), 5.99 (s, 2H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (0), 160.7 (0), 148.2 (0), 146.9 (0), 134.3 (0), 134.2 (1), 132.2 (0), 127.8 (1), 120.1 (1), 118.0 (1), 112.4 (0), 108.6 (1), 107.2 (1), 101.2 (2), 52.3 (3); IR (neat) ν 3194 (w), 2895 (w), 1628 (m), 1677 (s), 1476 (s), 1223 (s); MS (EI) *m/z* 272 ($[M]^+$, 64), 240 (100), 126 (86); HRMS (EI) calcd. for $C_{15}H_{12}O_5[M]^+$: 272.0679; found: 272.0679; Anal. calcd. for $C_{15}H_{12}O_5$: C, 66.2; H, 4.4. Found: C, 65.9; H, 4.2.



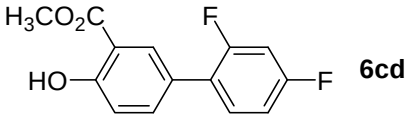
^{1}H NMR (300 MHz, $CDCl_3$) of **6cc**



^{13}C NMR (75 MHz, $CDCl_3$) of **6cc**

C10 Methyl 4',6'-difluoro-4-hydroxybiphenyl-3-carboxylate

*(Diflunisal methyl ester, **6cd**)*

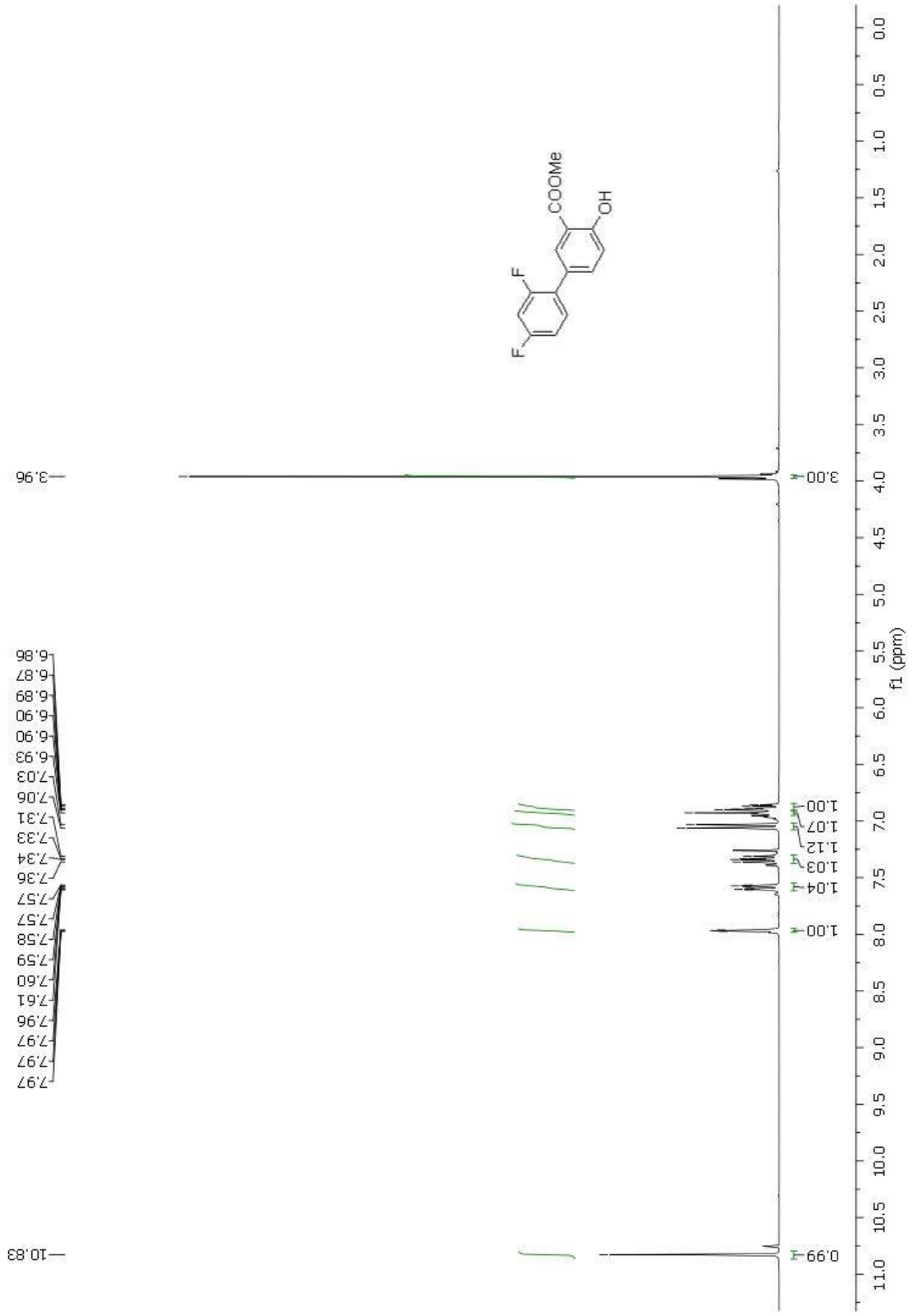


6cd

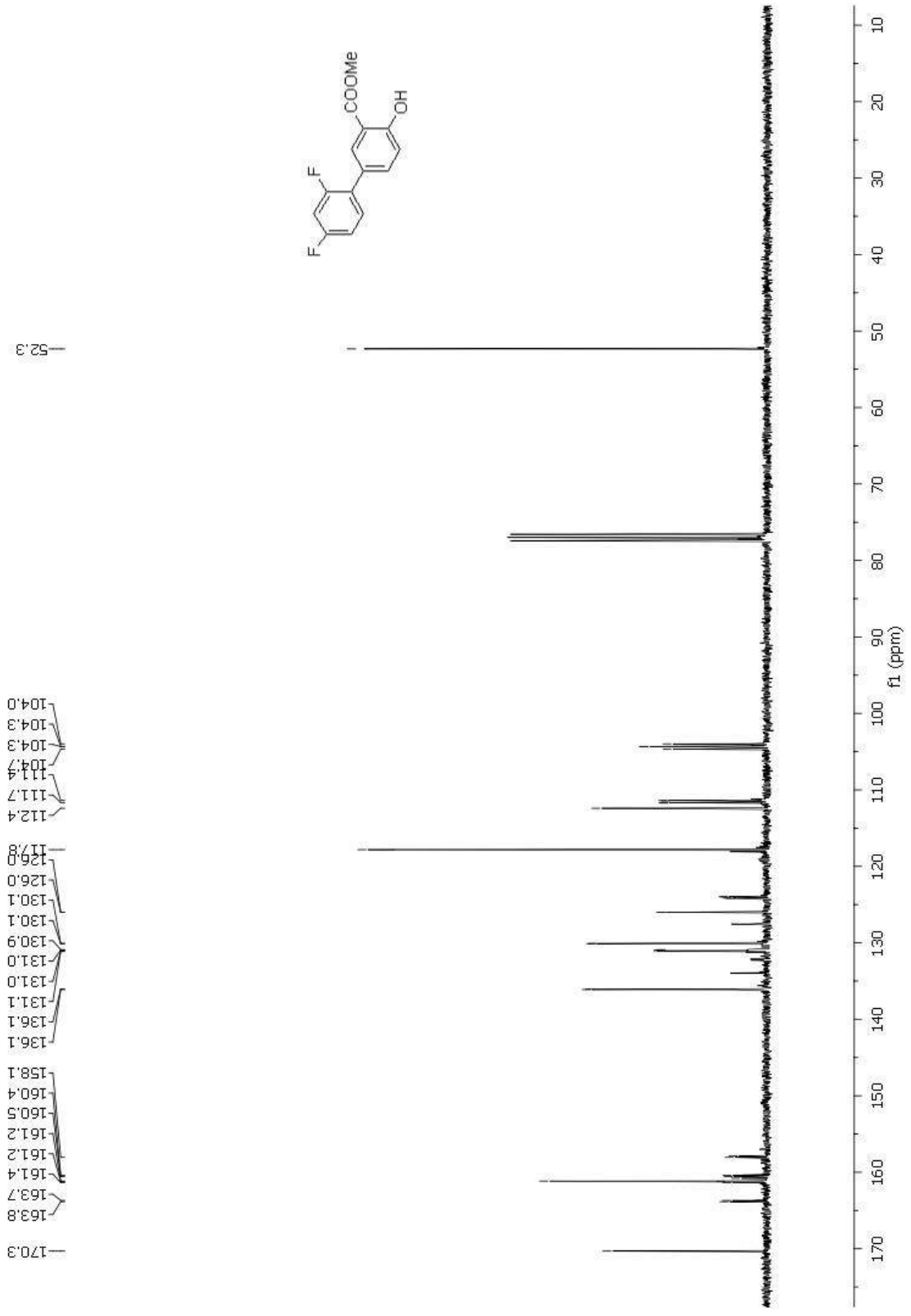
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4c**	0.5 mmol	133 mg
Ar'-BF_3K (**5**):	**5d**	0.5 mmol	110 mg
Ar-Ar' (**6**):	**6cd**	99%	130 mg
eluent for chromatography:	hexanes/MTBE (1 : 2, v/v)		
Aggregate state:	colourless solid, mp 97-99°C[7]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.97 (dd, J = 2.1, 1.3, 1H), 7.62 – 7.55 (m, 1H), 7.34 (dd, J = 8.7, 6.4, 1H), 7.05 (d, J = 8.7, 1H), 6.91 (d, J = 8.2, 1H), 6.91 – 6.84 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 (0), 162.2 (dd, J = 249.0, 11.9, 0), 161.2 (0), 159.8 (dd, J = 250.1, 11.9, 0), 136.1 (d, J = 3.1, 1), 131.0 (dd, J = 9.4, 4.8, 1), 130.1 (d, J = 6.9, 1), 126.0 (d, J = 1.1, 0), 124.1 (dd, J = 13.6, 3.8, 0), 117.8 (1), 112.4 (0), 111.5 (dd, J = 21.1, 3.8, 1), 104.3 (dd, J = 16.5 15.4, 1), 52.34 (3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.6 (m), −115.0 (m); IR (neat) ν 3135 (w), 1678 (s), 1484 (s), 1441 (m), 1212 (m); MS (EI): *m/z* 264 ($[M]^+$, 45), 232 (100); HRMS (EI) calcd. for $C_{14}H_{10}F_2O_3[M]^+$: 264.0598; found: 264.0574; Anal. calcd. for $C_{14}H_{10}F_2O_3$: C, 63.6; H, 3.8. Found: C, 63.6; H, 3.7.

[7] S. G. Küçükgüzel, A. Mazi, F. Sahin, S. Öztürk and J. Stables, *Eur. J. Med. Chem.*, 2003, **38**, 1005-1013.

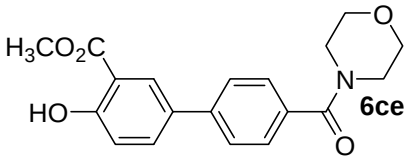


^{1}H NMR (300 MHz, $CDCl_3$) of **6cd**



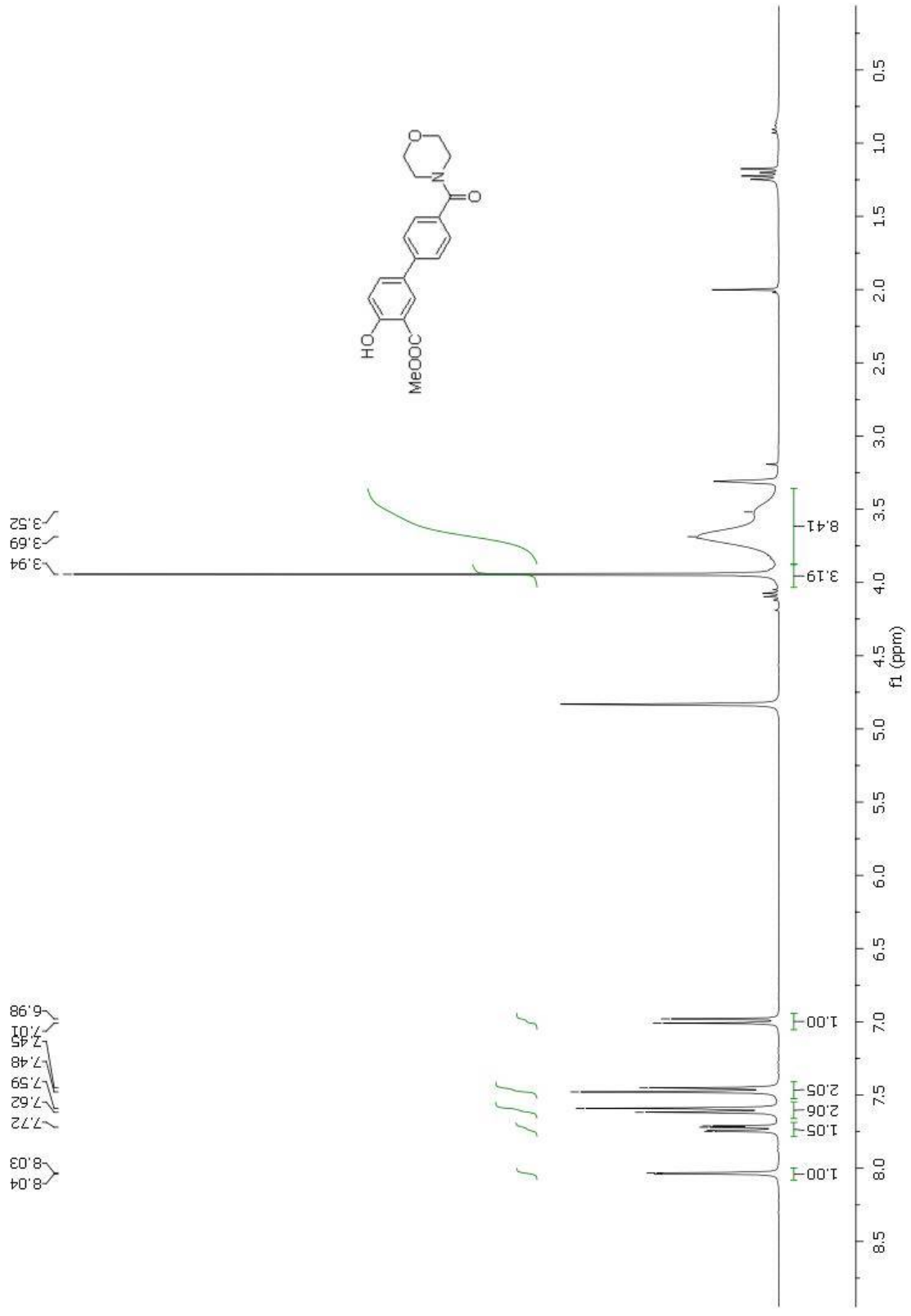
^{13}C NMR (75 MHz, $CDCl_3$) of **6cd**

*C11 Methyl 4-hydroxy-4'-(morpholine-4-carbonyl)biphenyl-3-carboxylate (**6ce**)*

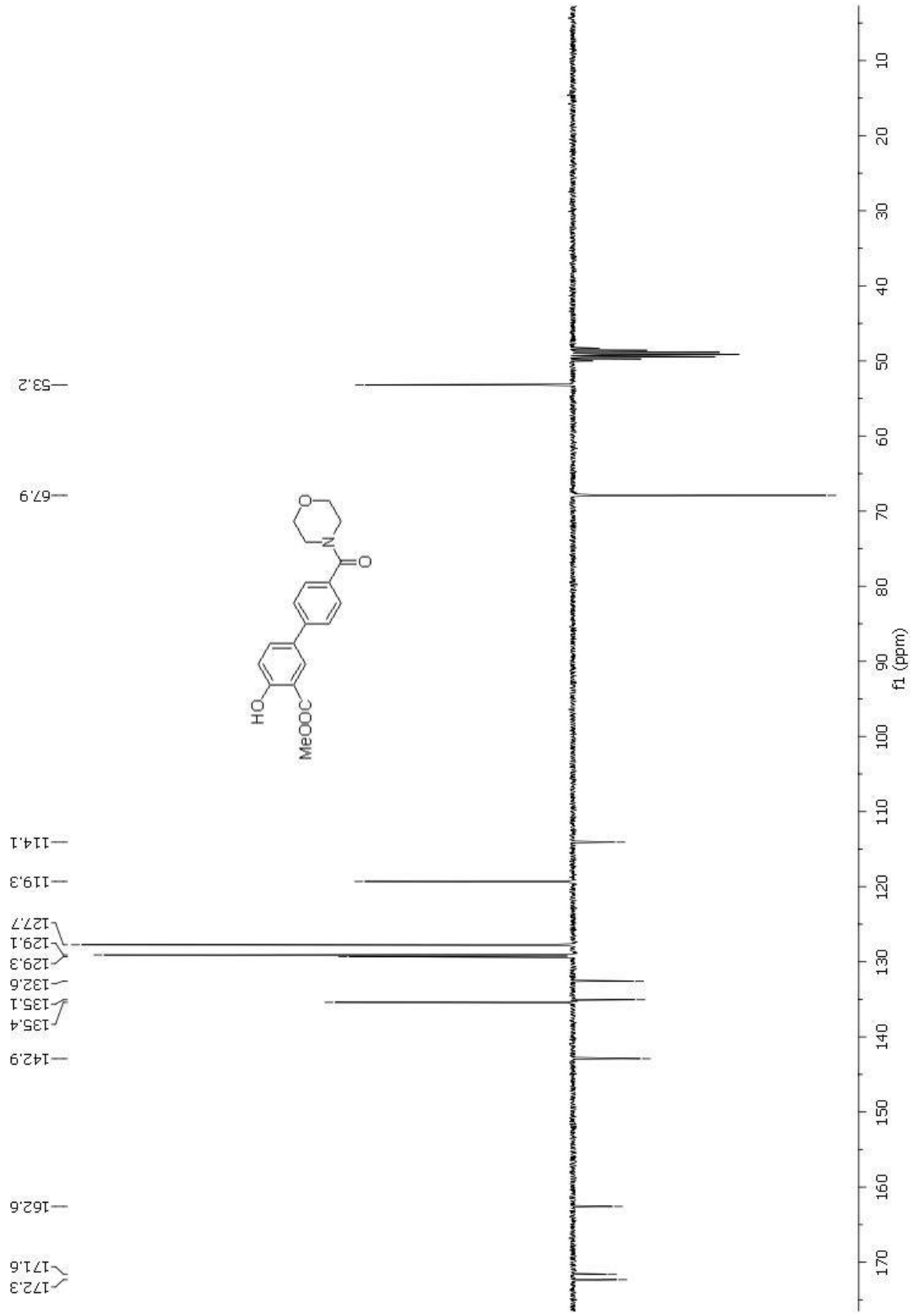


Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4c**	0.5 mmol	133 mg
Ar'-BF_3K (**5**):	**5e**	0.5 mmol	149 mg
Ar-Ar' (**6**):	**6ce**	70%	120 mg
eluent for chromatography:	MTBE/ethyl acetate (1 : 1, v/v)		
Aggregate state:	colourless solid, mp 120-122°C		

^{1}H NMR (300 MHz, MeOD-d_4) δ 8.03 (d, J = 2.4, 1H), 7.73 (dd, J = 8.7, 2.4, 1H), 7.60 (d, J = 8.3, 2H), 7.47 (d, J = 8.3, 2H), 6.99 (d, J = 8.7, 1H), 3.94 (s, 3H), 3.40 – 3.80 (broad due to hindered rotation around the amide bond, 8H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 172.3 (0), 171.6 (0), 162.6 (0), 142.9 (0), 135.4 (1), 135.1 (0), 132.6 (0), 129.3 (1), 129.1 (1), 127.7 (1), 119.3 (1), 114.1 (0), 67.9 (2), 53.2 (3), signal for *C*H_2N not observed due to hindered rotation and/or quadrupole broadening; IR (neat) ν 2957 (w), 2855 (w), 1676 (s), 1628 (s), 1429 (s), 1340 (m), 1275 (s), 1247 (s), 1209 (s); MS (EI) *m/z* 341 ([M]$^+$, 51), 255 (95), 223 (100), 139 (65); HRMS (EI) calcd. for $C_{19}H_{19}NO_5$[M]$^+$: 341.1258; found: 341.1278; Anal. calcd. for $C_{19}H_{19}NO_5$: C, 66.9; H, 5.6; N, 4.1. Found: C, 66.7; H, 5.4; N, 4.3.

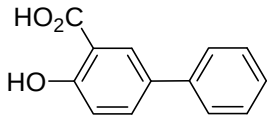


^{1}H NMR (300 MHz, MeOD-d_4) of **6ce**



^{13}C NMR (75 MHz, MeOD-d_4) of **6ce**

*C12 4-Hydroxybiphenyl-3-carboxylic acid (**6da**)*

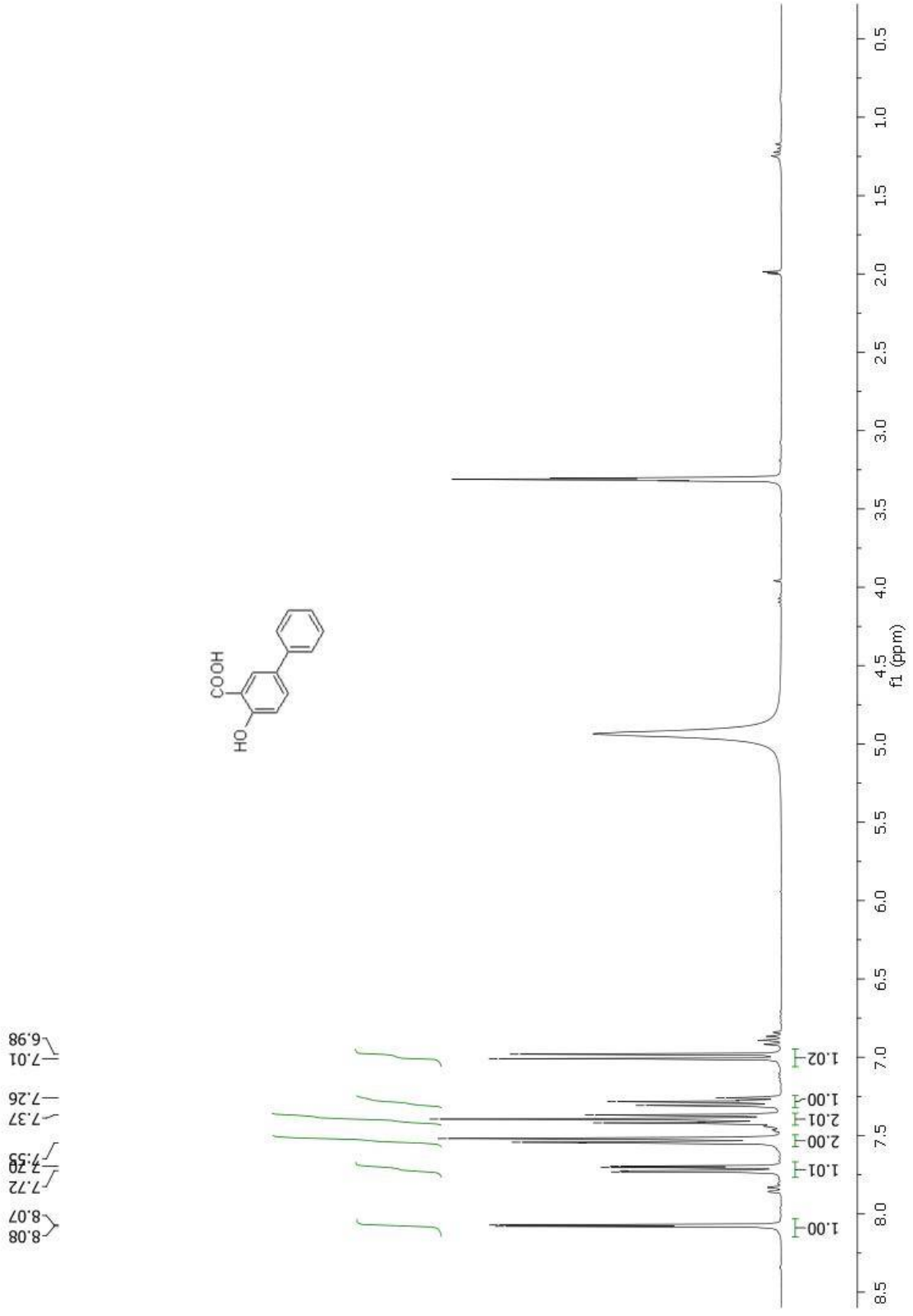


6da

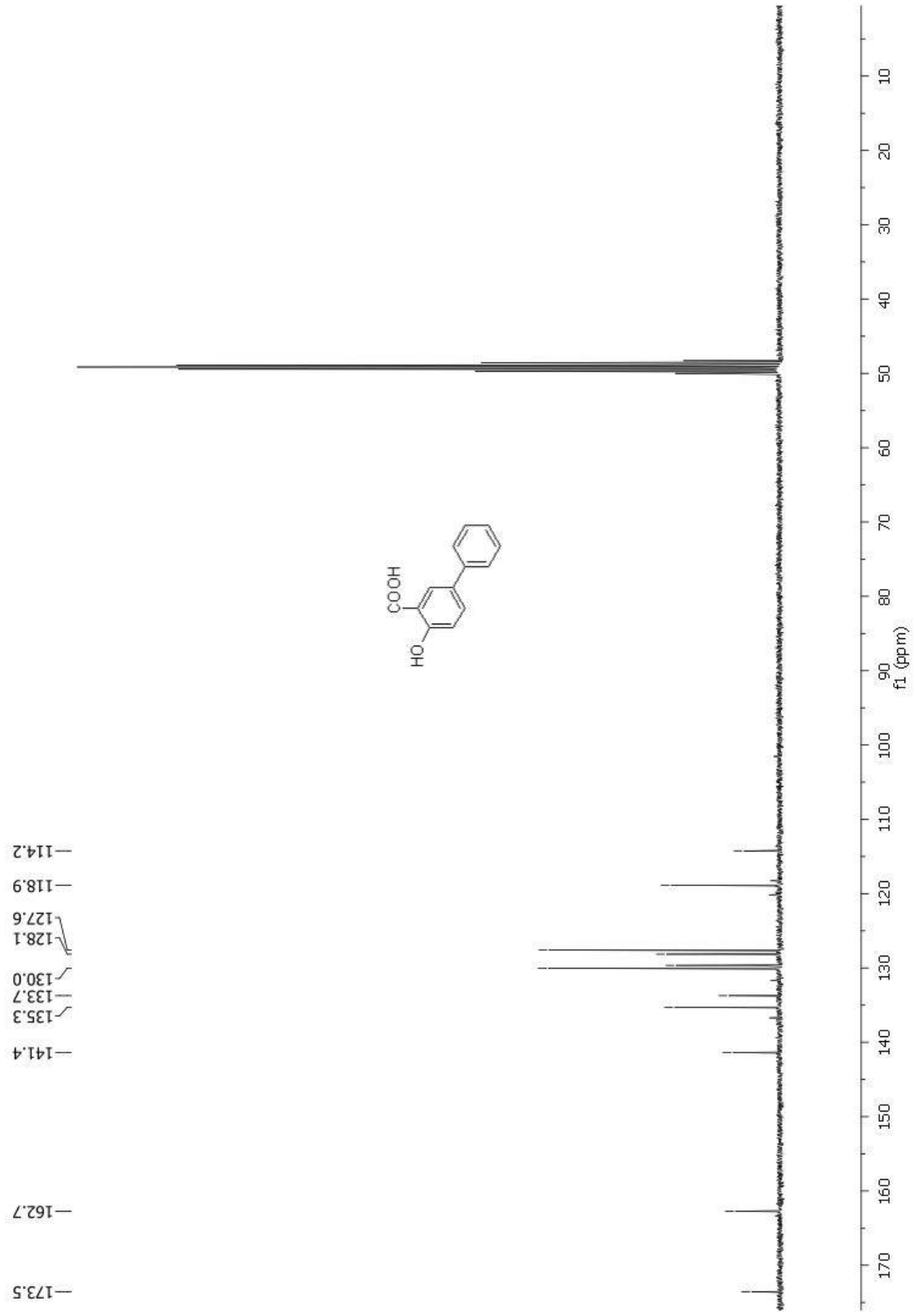
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4d**	0.5 mmol	126 mg
Ar'-BF_3K (**5**):	**5a**	0.5 mmol	92 mg
Ar-Ar' (**6**):	**6da**	59%	63 mg
eluent for chromatography:	hexanes/MTBE/acetic acid (300 : 100 : 1, v/v/v)		
Aggregate state:	colourless solid, mp 212-214°C[8]		

^{1}H NMR (300 MHz, MeOD-d_4) δ 8.07 (d, J = 2.4, 1H), 7.71 (dd, J = 8.6, 2.4, 1H), 7.57 – 7.50 (2H), 7.43 – 7.36 (2H), 7.28 (m, 1H), 6.99 (d, J = 8.6, 1H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 173.55, 162.72, 141.38, 135.29, 133.72, 130.03, 129.65, 128.15, 127.60, 118.86, 114.24; IR (neat) ν 2922 (w), 1667 (m), 1447 (m), 1237 (m); MS (ESI) *m/z* 215 ($[M+H]^+$, 42), 197 (100); HRMS (ESI) calcd. for $C_{13}H_{11}O_3[M+H]^+$: 215.0708, found: 215.0716; Anal. calcd. for $C_{13}H_{10}O_3$: C, 72.9; H, 4.7. Found: C, 72.7; H, 4.6.

[8] S. Shrestha, B. R. Bhattarai, K.-H. Lee and H. Cho, *Bioorg. Med. Chem.*, 2007, **15**, 6535-6548.

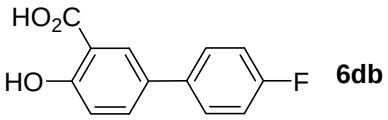


^{1}H NMR (300 MHz, MeOD-d_4) of **6da**



^{13}C NMR (75 MHz, MeOD-d_4) of **6da**

*C13 4'-Fluoro-4-hydroxybiphenyl-3-carboxylic acid (**6db**)*

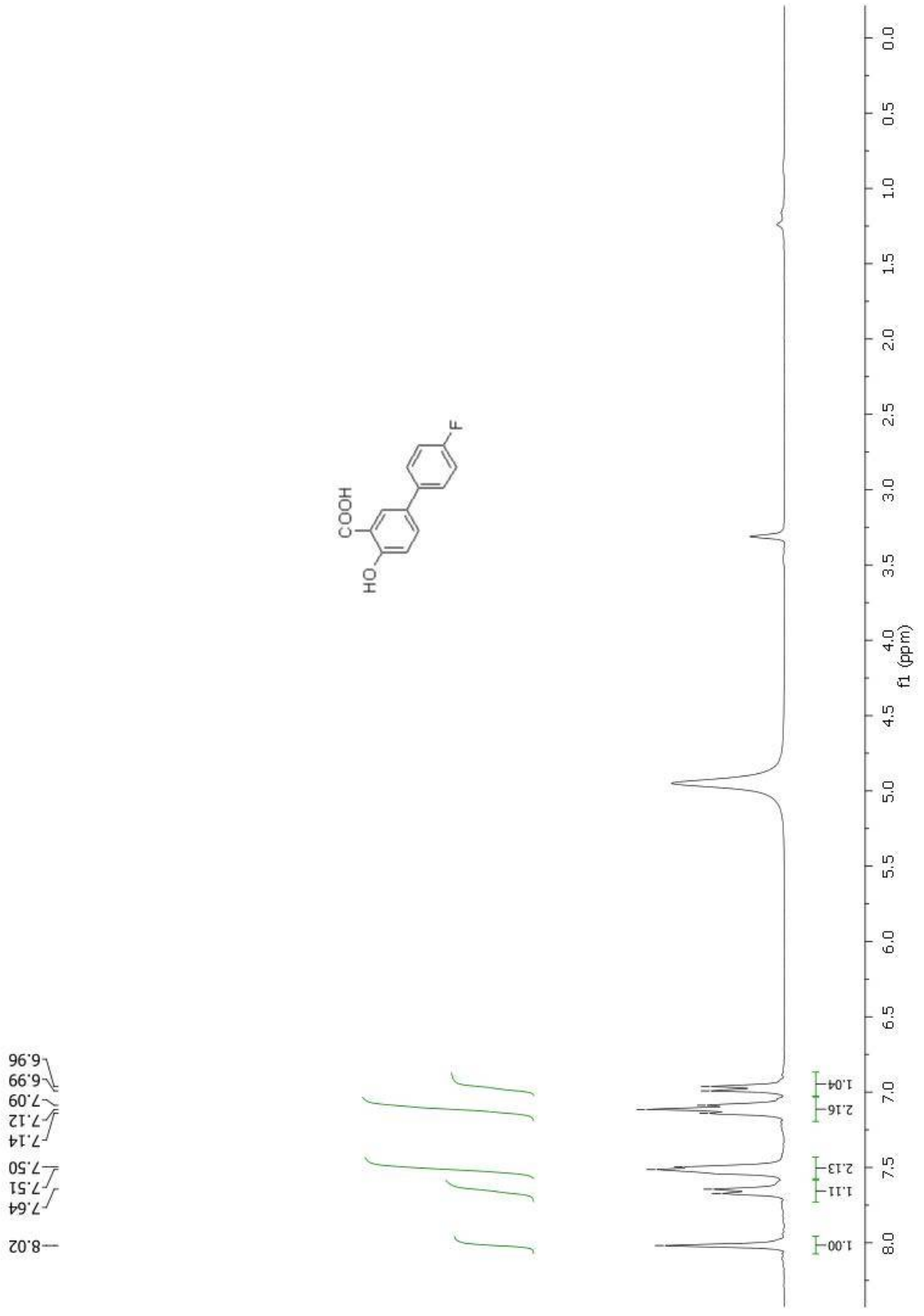


6db

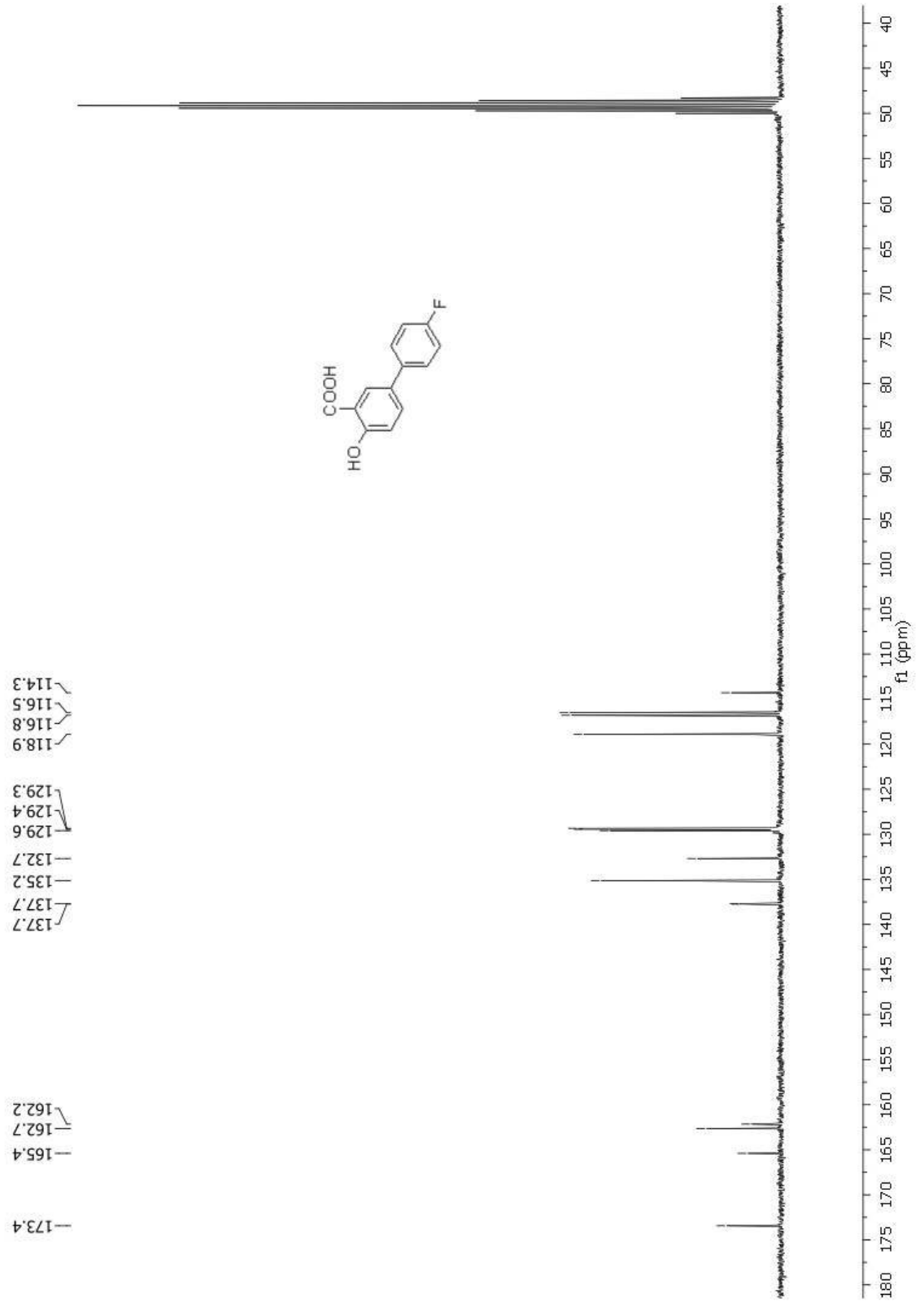
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4d**	0.5 mmol	126 mg
Ar'-BF_3K (**5**):	**5b**	0.5 mmol	101 mg
Ar-Ar' (**6**):	**6db**	34%	40 mg
eluent for chromatography:	hexanes/MTBE/acetic acid (300 : 100 : 1, v/v/v)		
Aggregate state:	colourless solid, mp 204-205°C[9]		

^{1}H NMR (300 MHz, MeOD-d_4) δ 8.02 (s, 1H), 7.66 (d, J = 8.4, 1H), 7.55 – 7.45 (2H), 7.17 – 7.07 (2H), 6.98 (d, J = 8.5, 1H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 173.4 (0), 163.8 (d, J = 244.7, 0), 162.7 (0), 137.7 (d, J = 3.1, 0), 135.2 (1), 132.7 (0), 129.6 (1), 129.4 (d, J = 8.1, 1), 118.9 (1), 116.6 (d, J = 21.7, 1), 114.3 (0); ^{19}F NMR (282 MHz, MeOD-d_4) δ –116.0 (m); IR (neat): ν 2925 (w), 1676 (w), 1516 (w), 1585 (w), 1439 (w), 1200 (m); MS (ESI): *m/z* 233 ([M+H]$^+$, 35), 215 (100); HRMS (ESI) calcd. for $C_{13}H_{10}FO_3$[M+H]$^+$: 233.0614; found: 233.0597; Anal. calcd. for $C_{13}H_9FO_3$: C, 67.2; H, 3.9. Found: C, 67.1; H, 4.0.

[9] N. A. Bumagin and V. V. Bykov, *Tetrahedron*, 1997, **53**, 14437-14450.

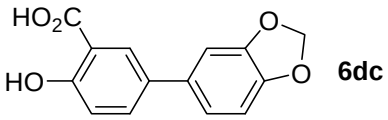


^{1}H NMR (300 MHz, MeOD-d_4) of **6db**



^{13}C NMR (75 MHz, MeOD-d_4) of **6db**

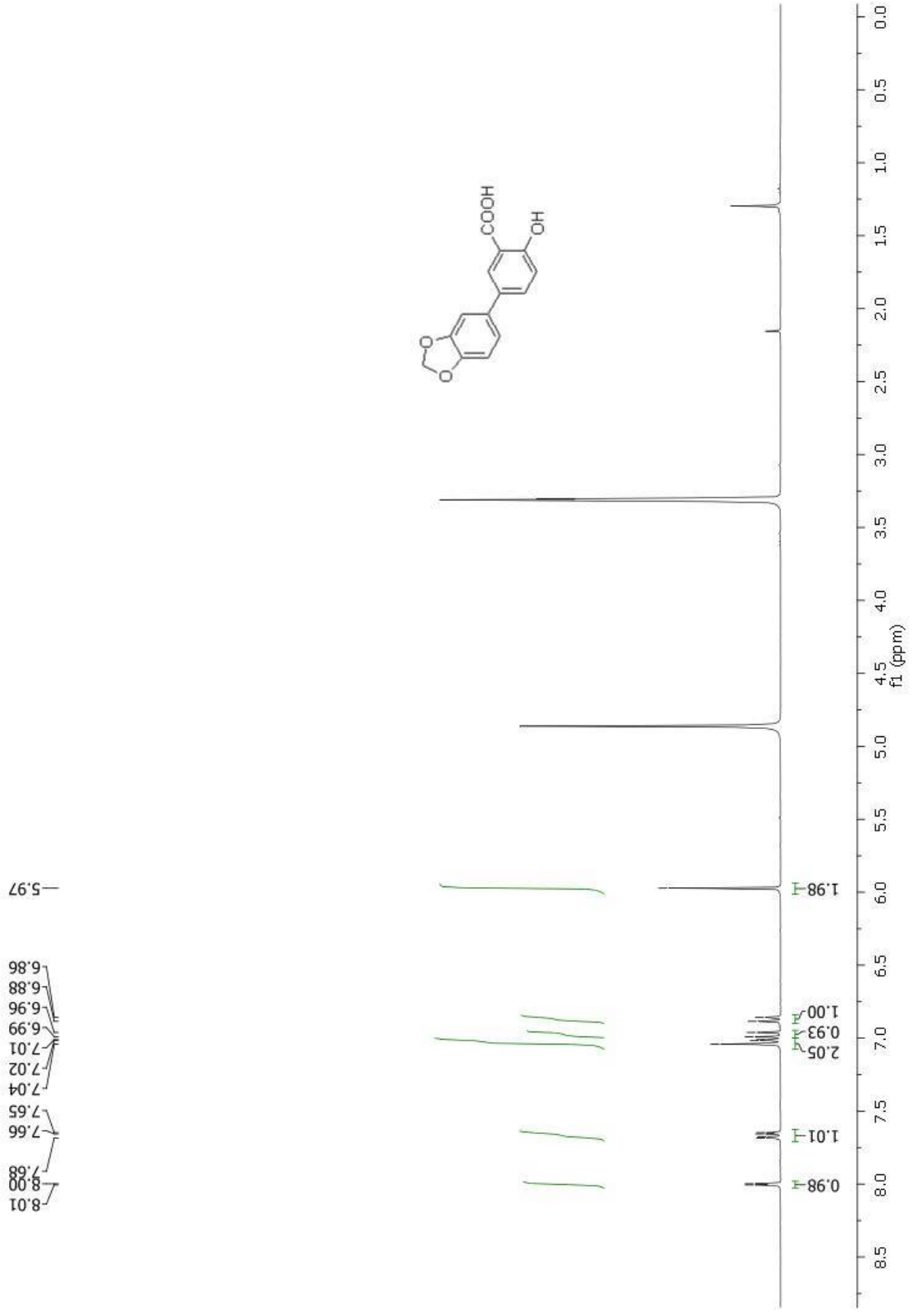
*C14 5-(Benzo[d][1,3]dioxol-5-yl)-2-hydroxybenzoic acid (**6dc**)*



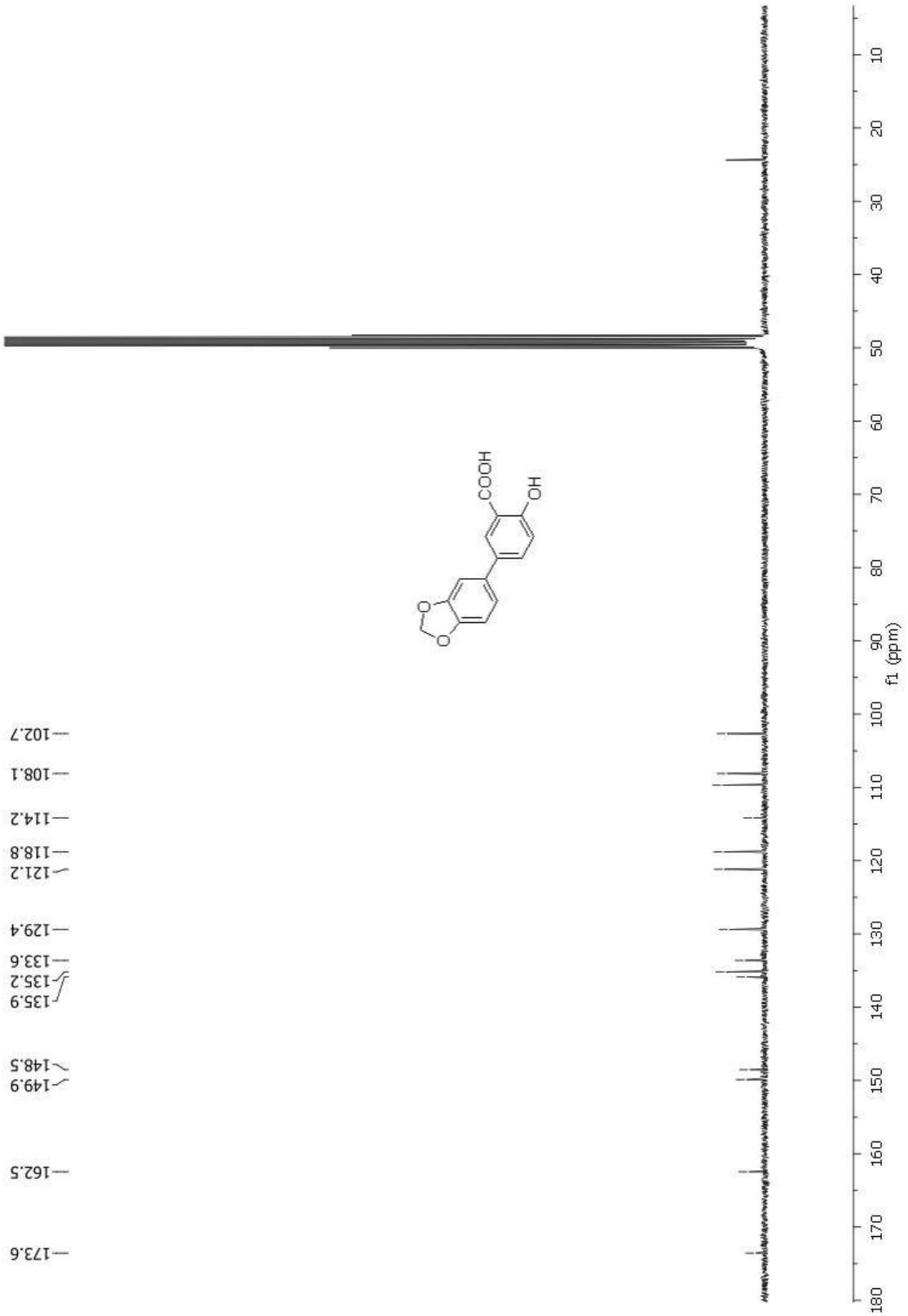
6dc

Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4d**	0.5 mmol	126 mg
Ar'-BF_3K (**5**):	**5c**	0.5 mmol	114 mg
Ar-Ar' (**6**):	**6dc**	46%	59 mg
eluent for chromatography:	hexanes/MTBE/acetic acid (300 : 100 : 1, v/v/v)		
Aggregate state:	colourless solid, mp 241-245°C		

^{1}H NMR (300 MHz, MeOD-d_4) δ 8.00 (d, J = 2.4, 1H), 7.67 (dd, J = 8.6, 2.5, 1H), 7.05 – 7.03 (2H), 6.98 (d, J = 8.6, 1H), 6.87 (d, J = 8.5, 1H), 5.97 (s, 2H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 173.6 (0), 162.5 (0), 149.9 (0), 148.5 (0), 135.9 (0), 135.2 (1), 133.6 (0), 129.4 (1), 121.2 (1), 118.8 (0), 114.2 (0), 109.7 (1), 108.1 (1), 102.7 (1); IR (neat) ν 2917 (w), 2850 (w), 1665 (m), 1455 (m), 1251 (m); MS (EI): *m/z* 258 ([M]$^+$, 43), 240 (100), 126 (73); HRMS (EI): calcd. for $C_{14}H_{10}O_5$[M]$^+$: 258.0523; found: 258.0536; Anal. calcd. for $C_{14}H_{10}O_5$: C, 65.1; H, 3.9. Found: C, 65.1; H, 3.8.

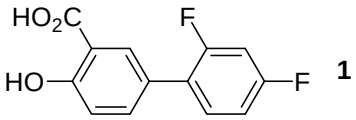


^{1}H NMR (300 MHz, MeOD-d_4) of **6dc**



^{13}C NMR (75 MHz, MeOD-d_4) of **6dc**

*C15 4',6'-Difluoro-4-hydroxybiphenyl-3-carboxylic acid (Diflunisal, **1**)*

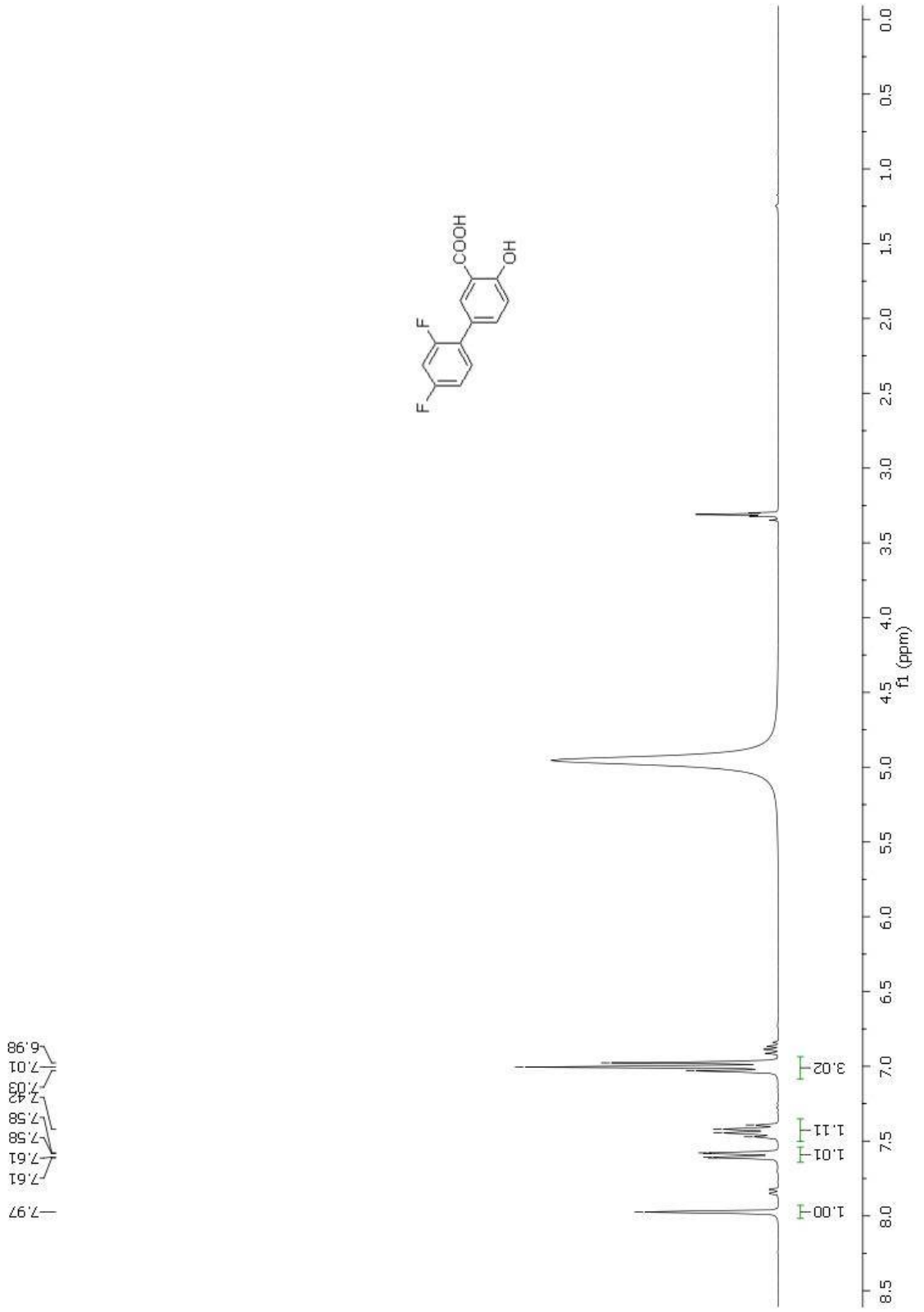


1

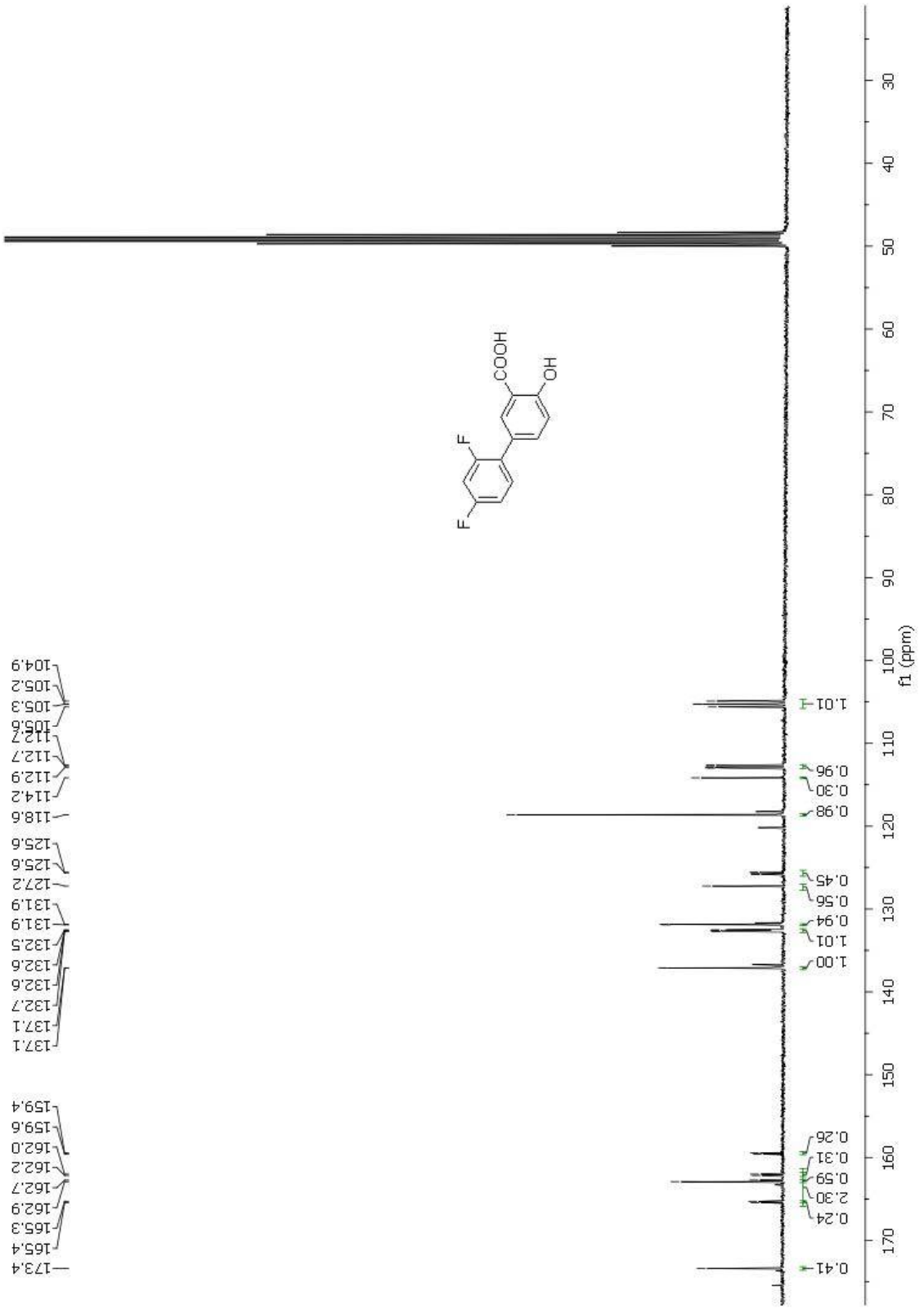
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4d**	0.5 mmol	126 mg
Ar'-BF_3K (**5**):	**5d**	0.5 mmol	110 mg
Ar-Ar' (**6**):	**1**	34%	42 mg
eluent for chromatography:	CH_2Cl_2/acetic acid (50 : 1, v/v)		
Aggregate state:	colourless solid, mp 204-206°C[10]		

^{1}H NMR (300 MHz, MeOD-d_4) δ 7.97 (s, 1H), 7.60 (dd, J = 1.5, 8.6, 1H), 7.43 (dd, J = 7.9, 15.6, 1H), 7.05 – 6.95 (3H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 173.4, 163.7 (dd, J = 247.5, 11.9), 163.0, 161.2 (dd, J = 248.7, 11.9) 137.1 (d, J = 2.9), 132.6 (dd, J = 9.5, 4.8), 131.9 (d, J = 3.1), 127.2, 125.7 (dd, J = 13.6, 3.9), 118.6 , 114.2, 112.8 (dd, J = 21.4, 3.8), 105.3 (dd, J = 27.1, 25.8); ^{19}F NMR (282 MHz, MeOD-d_4) δ –111.3 (m), –113.3 ("q", J = 9.9); IR (neat): ν 3344 (s), 2950 (w), 2838 (w), 1651 (m), 1450 (m); MS (EI) *m/z* 250 ([M]$^+$, 50), 232 (100); HRMS (EI) calcd. for $C_{13}H_8F_2O_3$[M]$^+$: 250.0442. Found: 250.0449; Anal. calcd. for $C_{13}H_8F_2O_3$: C, 62.4; H, 3.2. Found: C, 62.5; H, 3.6.

[10] P. C. Andrews, R. L. Ferrero, P. C. Junk, I. Kumar, Q. Luu, K. Nguyen and J. W. Taylor, *Dalton Trans.*, 2010, **39**, 2861-2868.

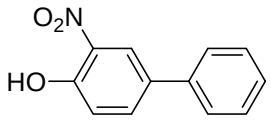


^{1}H NMR (300 MHz, MeOD-d_4) of **1**



^{13}C NMR (75 MHz, MeOD-d_4) of **1**

C16 3-Nitrobiphenyl-4-ol ***(6ea)***

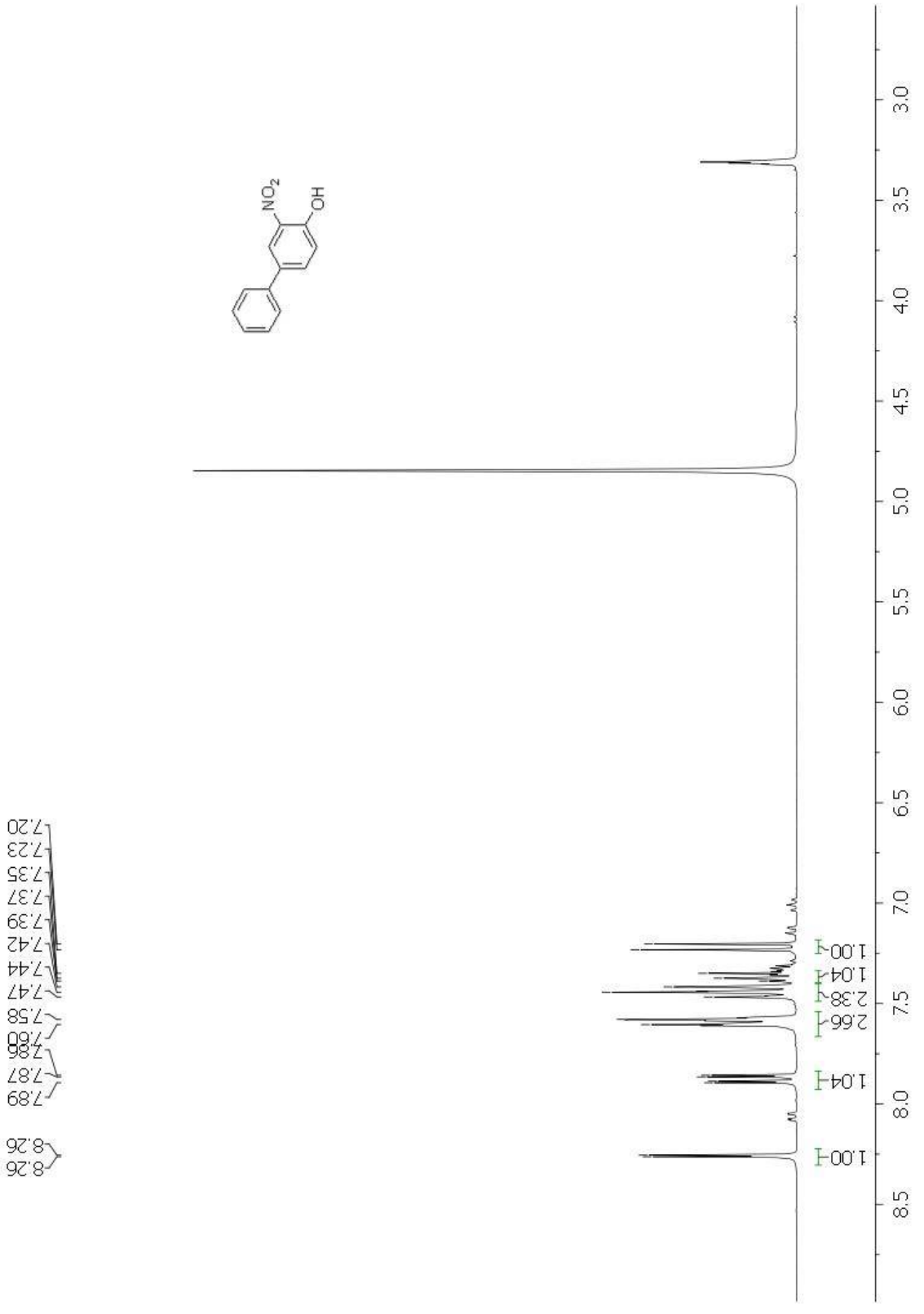


6ea

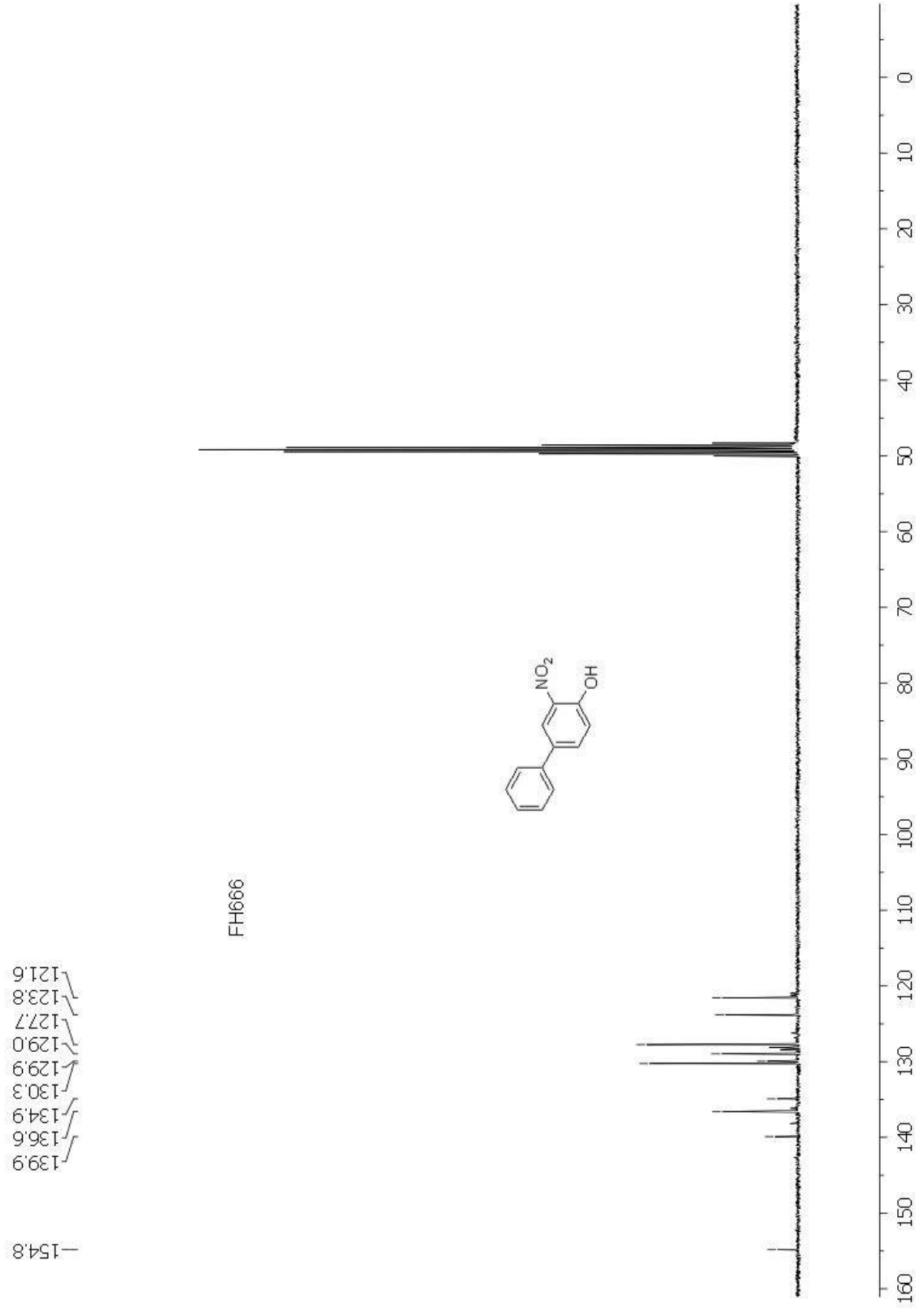
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4e**	0.5 mmol	127 mg
Ar'-BF_3K (**5**):	**5a**	0.5 mmol	92 mg
Ar-Ar' (**6**):	**6ea**	94%	100 mg
eluent for chromatography:	hexanes/MTBE (1 : 1, v/v)		
Aggregate state:	colourless solid, mp 65-67°C[11]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.33 (d, J = 2.1, 1H), 7.84 (dd, J = 8.7, 2.2, 1H), 7.50 – 7.44 (2H), 7.46 – 7.39 (2H), 7.39 (m, 1H), 7.25 (d, J = 8.7, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3 (0), 138.2 (0), 136.3 (1), 133.9 (0), 133.8 (0), 129.1 (1), 128.0 (1), 126.7 (1), 122.8 (1), 120.4 (1); IR (neat) ν 3243 (w), 3032 (w), 1628 (m), 1536 (s), 1476 (s), 1310 (s); MS (EI) *m/z* 215 ([M]$^+$, 13), 181 (100), 130 (28); HRMS (EI): calcd. for $C_{12}H_9NO_3$[M]$^+$: 215.0582; found: 215.0596; Anal. calcd. for $C_{12}H_9NO_3$: C, 67.0; H, 4.2; N, 6.5. Found: C, 67.0; H, 4.2; N, 6.4.

[11] M. J. Zabik and R. D. Schuetz, *J. Org. Chem.*, 1967, **32**, 300-307.

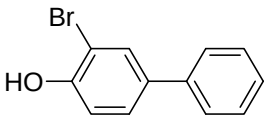


^{1}H NMR (300 MHz, $CDCl_3$) of **6ea**



^{13}C NMR (75 MHz, $CDCl_3$) of **6ea**

*C17 3-Bromobiphenyl-4-ol (**6fa**)*

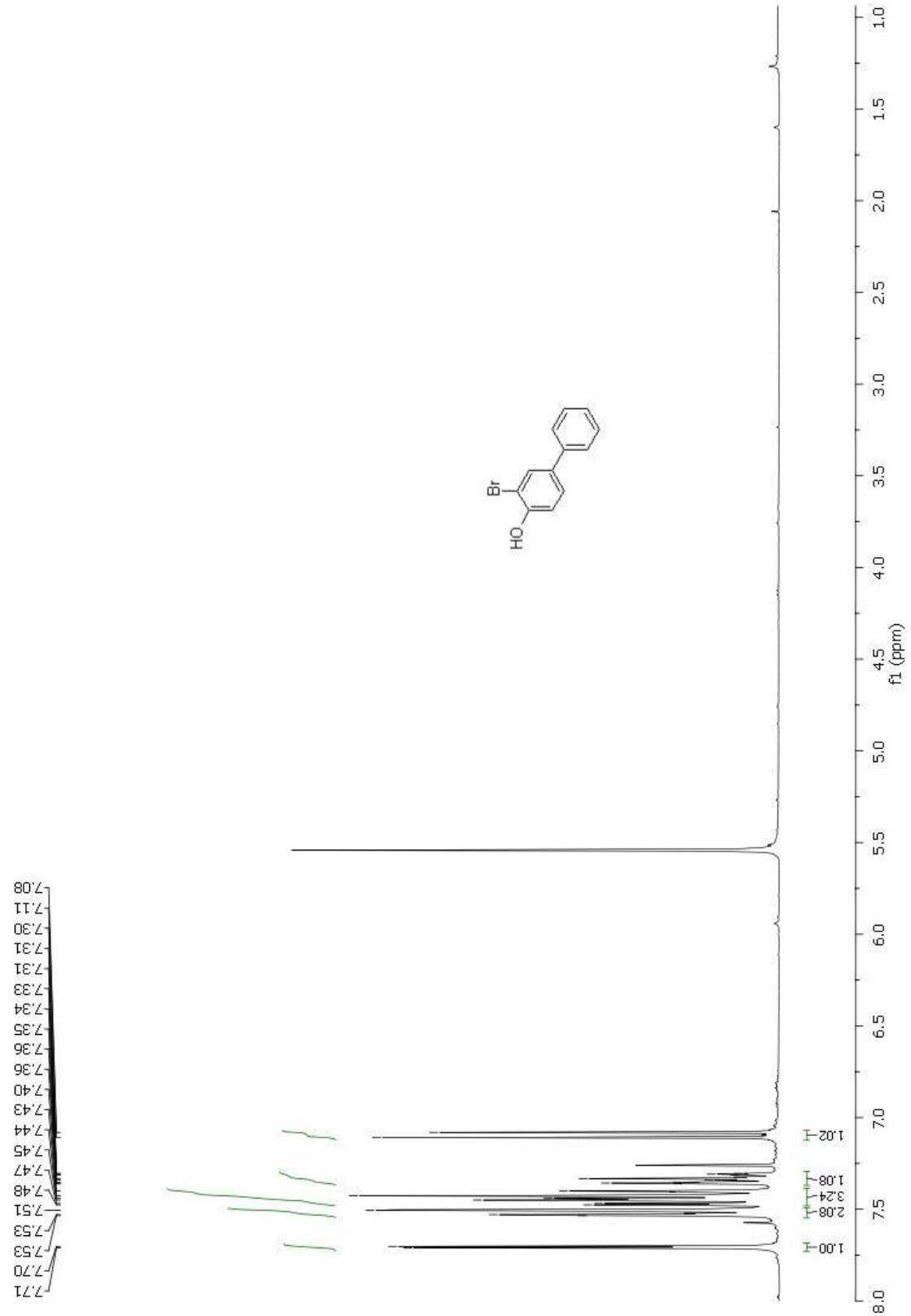


6fa

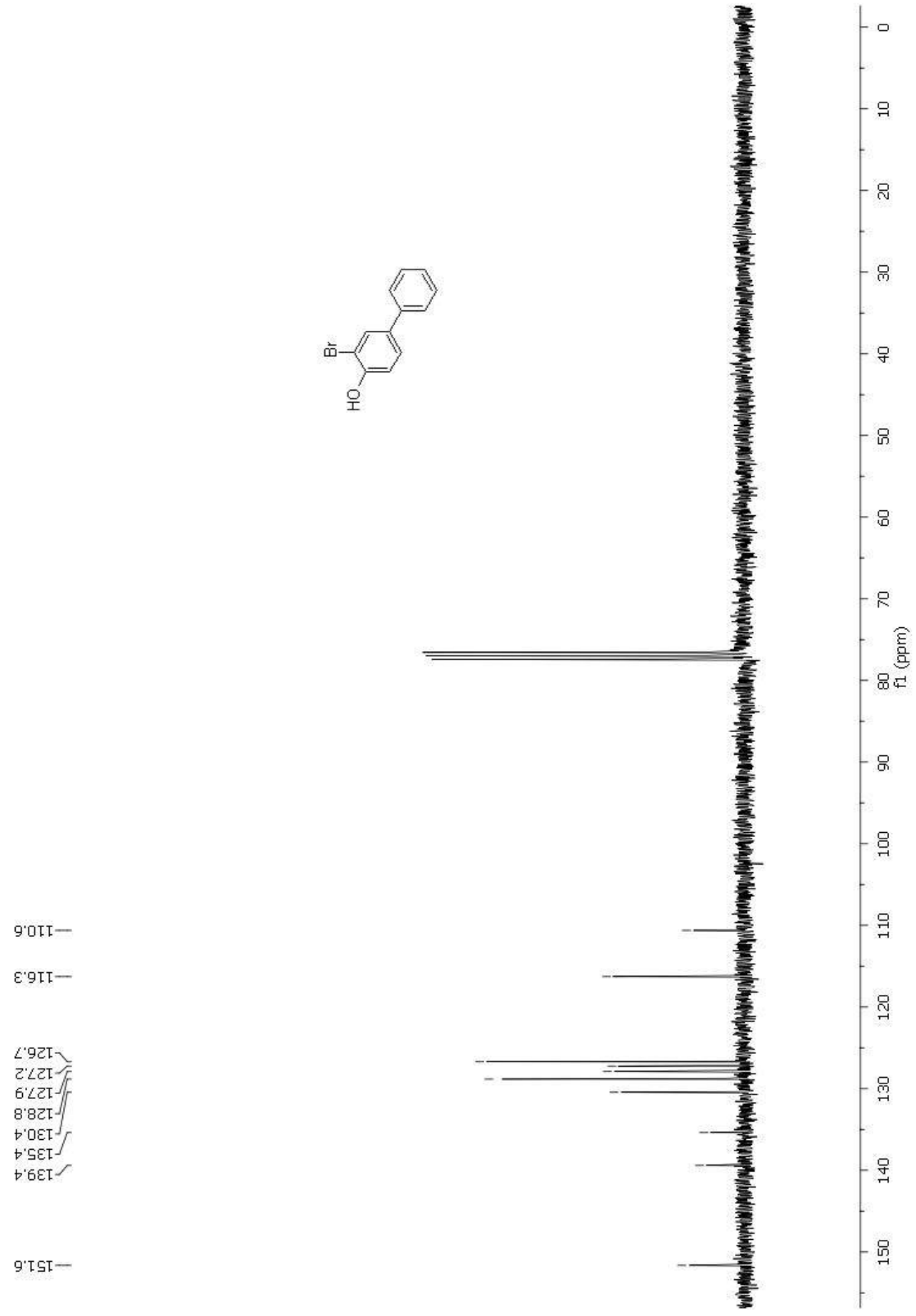
Procedure:	B2 (base-free conditions)		
Ar-N_2BF_4 (**4**):	**4f**	0.5 mmol	143 mg
Ar'-BF_3K (**5**):	**5a**	0.5 mmol	92 mg
Ar-Ar' (**6**):	**6fa**	44%	55 mg
eluent for chromatography:	hexanes/MTBE (1 : 1, v/v)		
Aggregate state:	colourless solid, mp 94-95°C[12]		

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 2.2, 1H), 7.54 – 7.49 (2H), 7.48 – 7.39 (3H), 7.33 (m, 1H), 7.09 (d, J = 8.4, 1H), 5.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6 (0), 139.4 (0), 135.4 (0), 130.4 (1), 128.8 (1), 127.9 (1), 127.2 (1), 126.7 (1), 116.3 (1), 110.6 (0); IR (neat) ν 3320 (m), 2360 (w), 1488 (m) 1450 (m) 1412 (s) 1273 (s); MS (EI) *m/z* 248 ($[M]^+$, 100), 139 (80), 115 (25); HRMS (EI) calcd. for $C_{12}H_9BrO[M]^+$: 247.9831; found: 247.9836; Anal. calcd. for $C_{12}H_9BrO$: C, 57.9; H, 3.6. Found: C, 57.6; H, 3.5.

[12] C. D. Gutsche and H. N. Kwang, *J. Org. Chem.*, 1982, **47**, 2708-2712.



^{1}H NMR (300 MHz, $CDCl_3$) of **6fa**



^{13}C NMR (75 MHz, $CDCl_3$) of **6fa**