Dabco as an Inexpensive and Highly Efficient Ligand for Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reaction

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Supporting Information

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(A) General

^{1}H and ^{13}C NMR spectra were recorded on an INOVA-400 (Varian) spectrometer.

(B) Materials

All reagents were directly used as obtained commercially. All products are known.[1-6]

(C) Typical experimental procedures

(1) Typical experimental procedure for the palladium-catalyzed Suzuki-Miyaura cross-coupling reaction (Tables 1 and 2)

A mixture of aryl halide **1** (0.5 mmol), arylboronic acid **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol%), Dabco (6 mol%), K_2CO_3 (3 equiv), and acetone (5 mL) was added to a sealed tube, and stirred at 110 ^{o}C for desired time which monitored by TLC. After usual workup, the residue was purified by flash column chromatography to afford **3** (hexane/ethyl acetate).

Caution: Be careful because the reaction proceeded at higher boiling point with higher pressure

(2) Typical experimental procedure for 0.0001 mol% of Pd and 0.0002 mol% of Dabco-catalyzed coupling of 1-iodo-4-nitro-benzene (1a) with phenylboronic acid (2a) (Entry 4 in Table 3)

Firstly, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) was dissolved in 200 mL of acetone, and Dabco (4.5 mg, 0.04 mmol) was also dissolved in another 200 mL of acetone. Then 50 μL of $Pd(OAc)_2$ acetone solution and 50 μL of Dabco acetone solution were added to a mixture of 1-iodo-4-nitro-benzene **1a** (5 mmol), phenylboronic acid **2a** (7 mmol), and K_2CO_3 (3 equiv), and acetone (about 50 mL) in a sealed tube, respectively (by syringe). The mixture was stirred at 110 ^{o}C for 48 h, which monitored by TLC. After usual workup, the residue was purified by flash column chromatography (hexane) to afford 90% yield of **3a** (about 89 mg, TONs: 900 000).

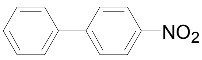
(3) Typical experimental procedure for 0.0001 mol% of Pd and 0.0002 mol% of Dabco-catalyzed coupling of iodobenzene (1d) with *p*-chlorophenylboronic acid (2d) (Entry 5 in Table 3)

Firstly, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) was dissolved in 200 mL of acetone, and Dabco (4.5 mg, 0.04 mmol) was also dissolved in another 200 mL of acetone. Then 5 μL of $Pd(OAc)_2$ acetone solution and 5 μL of Dabco acetone solution were added to a mixture of iodobenzene **1d** (0.5 mmol), *p*-chlorophenylboronic acid **2d** (0.7 mmol), and K_2CO_3 (3 equiv), and acetone (about 5 mL) in a sealed tube, respectively (by syringe). The mixture was stirred at 110 ^oC for 14 h, which monitored by TLC. After usual workup, the residue was purified by flash column chromatography (hexane) to afford 95% yield of **3f** (about 89 mg, TONs: 950 000).

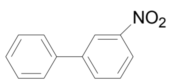
(4) Typical experimental procedure for 0.001 mol% of Pd and 0.002 mol% of Dabco-catalyzed coupling of 1-bromo-4-methoxybenzene (1h) with phenylboronic acid (2a) (Entry 14 in Table 3)

Firstly, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) was dissolved in 200 mL of acetone, and Dabco (4.5 mg, 0.04 mmol) was also dissolved in another 200 mL of acetone. Then 50 μL of $Pd(OAc)_2$ acetone solution and 50 μL of Dabco acetone solution were added to a mixture of 1-bromo-4-methoxybenzene **1h** (0.5 mmol), phenylboronic acid **2a** (0.7 mmol), and K_2CO_3 (3 equiv), and acetone (about 5 mL) in a sealed tube, respectively (by syringe). The mixture was stirred at 110 ^oC for 48 h, which monitored by TLC. After usual workup, the residue was purified by flash column chromatography (hexane/ethyl acetate) to afford 9% yield of **3g** (about 8 mg, TONs: 9 000), and >85% of 1-bromo-4-methoxybenzene **1h** was recovered.

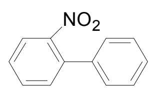
(D) Analytical data for 3

4-Nitro-biphenyl (3a)[1-3] 

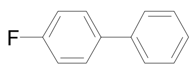
Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.53—7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 147.1, 138.8, 129.2, 128.91, 127.8, 127.4, 124.1.

3-Nitro-biphenyl (3b)[2] 

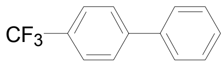
White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.21 (d, *J* = 8 Hz, 1H), 7.91 (d, *J* = 8 Hz, 1H), 7.65—7.60 (m, 3H), 7.51 (t, *J* = 8 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 129.0, 128.9, 127.9, 126.8.

2-Nitro-biphenyl (3c)[1] 

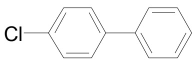
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51—7.40 (m, 5H), 7.34—7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 140.3, 137.3, 128.8, 128.7, 128.6, 127.3, 127.0, 115.7, 115.5.

4-Fluoro-biphenyl (3d)[1] 

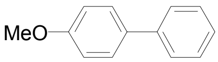
White solid; ^{1}H NMR (400 MHz), $CDCl_3$): δ 7.57—7.53 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, *J* = 244.9 Hz), 161.2, 140.2, 137.3, 128.8, 127.2, 115.6 (d, *J* = 21.8 Hz).

4-Trifluoromethyl-biphenyl (3e)[3] 

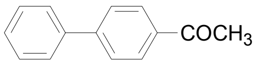
White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 4H), 7.60 (d, *J* = 8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 139.8, 129.0, 128.2, 127.6, 127.4, 127.3, 125.9 125.7.

4-Chloro-biphenyl (3f)[1, 2] 

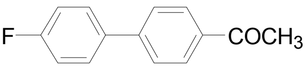
White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57—7.49 (m, 4H), 7.46—7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 139.6, 133.3, 129.0, 128.9, 128.4, 127.6, 127.0.

4-Methoxy-biphenyl (3g)[1, 4] 

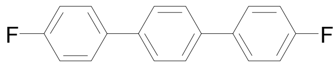
White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 8.8 Hz, 4H), 7.42 (t, *J* = 8 Hz, 2H), 7.31 (t, *J* = 7.2, 1H), 6.99 (d, J=12, 2H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

1-Biphenyl-4-yl-ethanone (3h)[4] 

White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 145.8, 139.9, 135.8, 128.9, 128.9, 128.2, 127.3, 127.2, 26.7.

1-(4'-Fluoro-biphenyl-4-yl)-ethanone (3i)[5] 

White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8 Hz, 2H), 7.64 (d, *J* = 8 Hz, 2H), 7.60—7.58 (m, 2H), 7.17 (t, J = 8.4 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 163.0 (J = 306.9 Hz), 144.7, 135.9, 135.8, 129.0, 128.9, 127.1, 116.0 (d, J = 21.1 Hz), 26.7.

4, 4′′-Difluoro-[1,1';4',1'']terphenyl (3j)[6] 

White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51—7.48 (m, 6H), 7.14—7.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, J = 244.7 Hz), 136.4, 131.9, 128.6, 128.5, 115.7(d, J = 21.8 Hz).

(E) References

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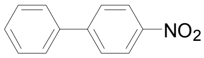
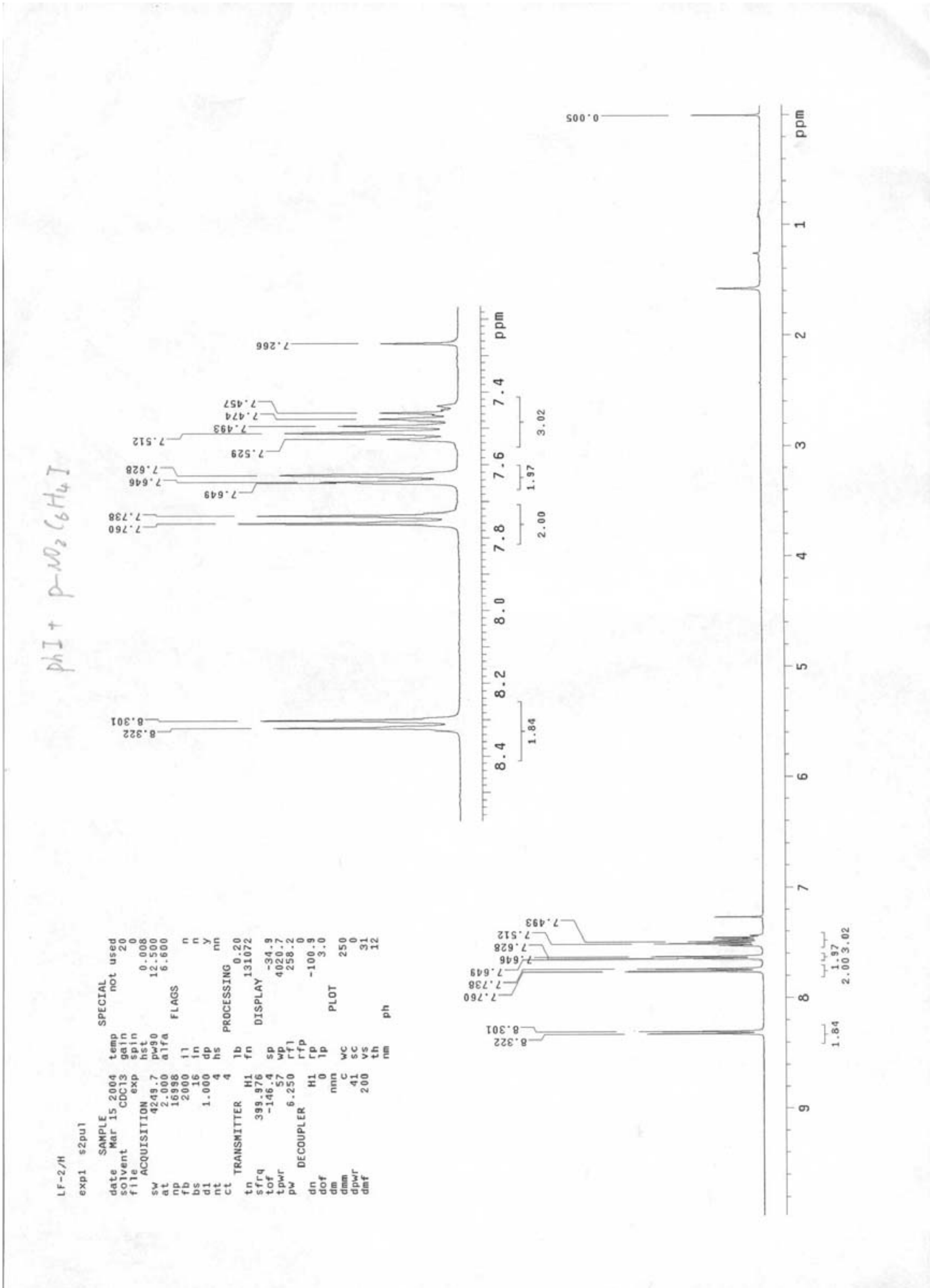
(5) Marie, F.; Dorothee, L.; Henri, D.; Maurice, S. *Synthesis*, **2001**, 2320.

(6) Kamata, M.; Satoh, C.; Kim, H.-S.; Wataya, Y. *Tetrahedron Lett.* **2002**, *43*, 8313.

(F) NMR spectra

4-Nitro-biphenyl (3a) 



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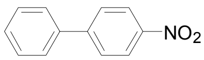
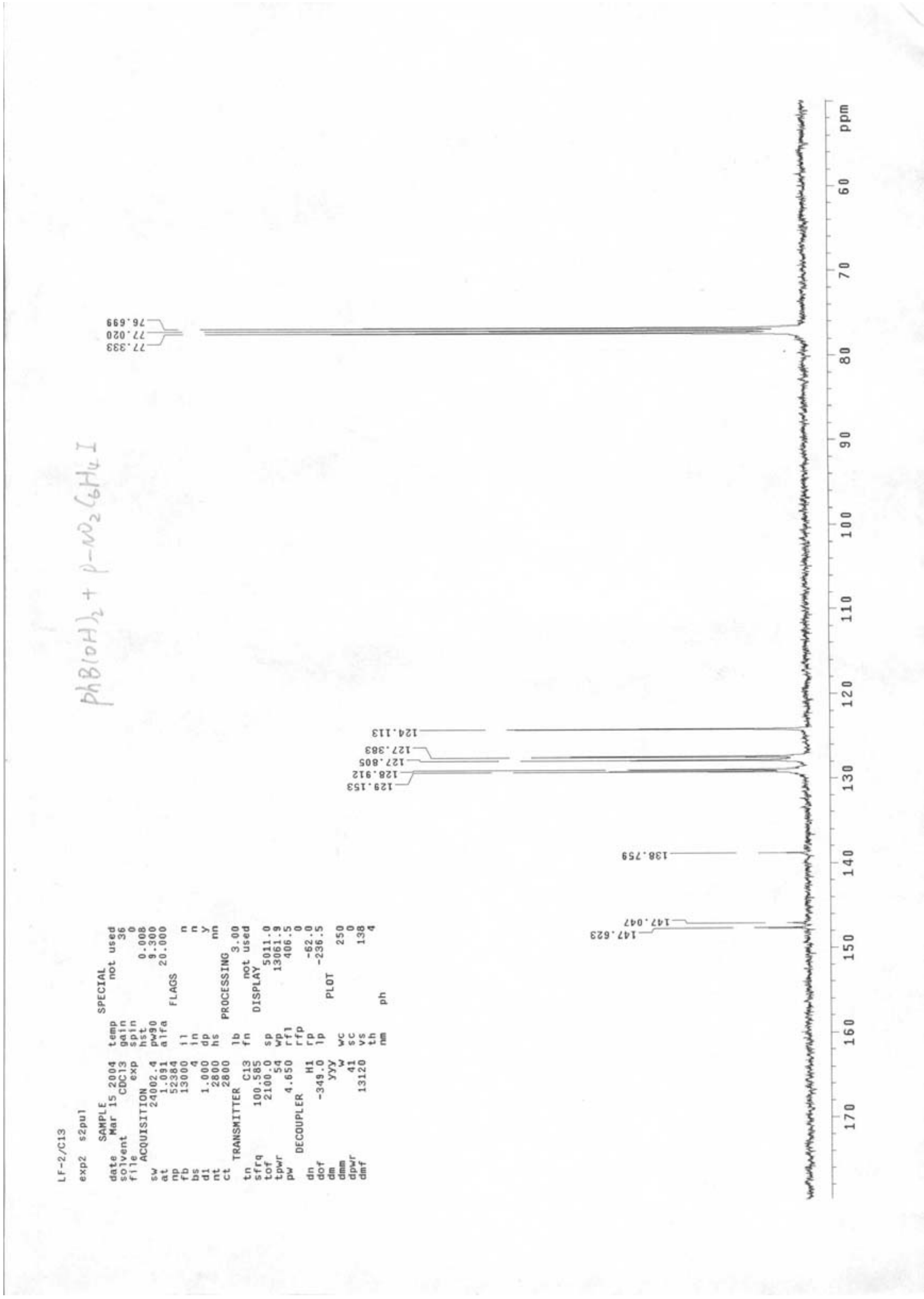
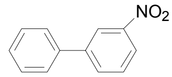
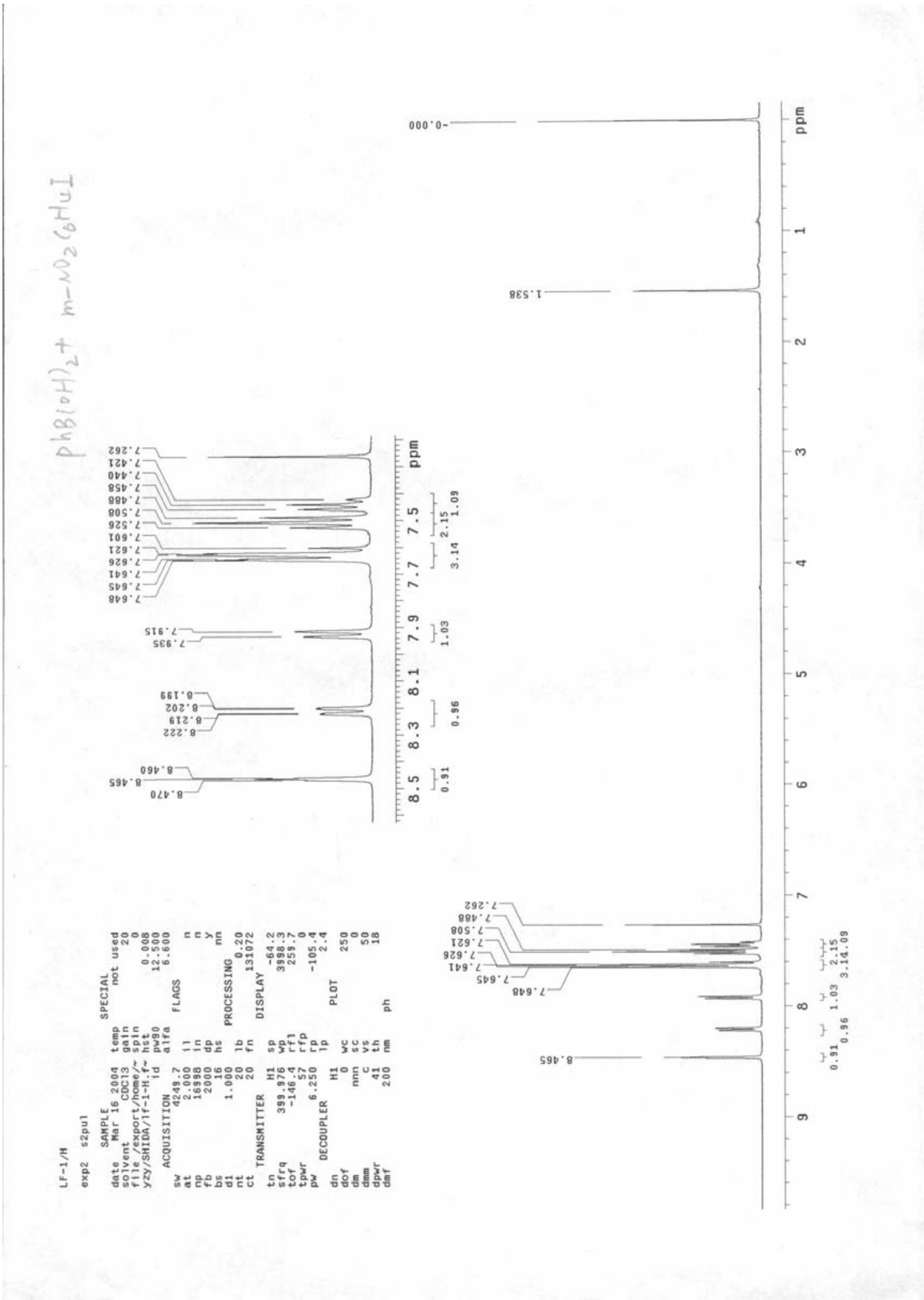
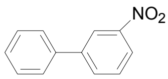
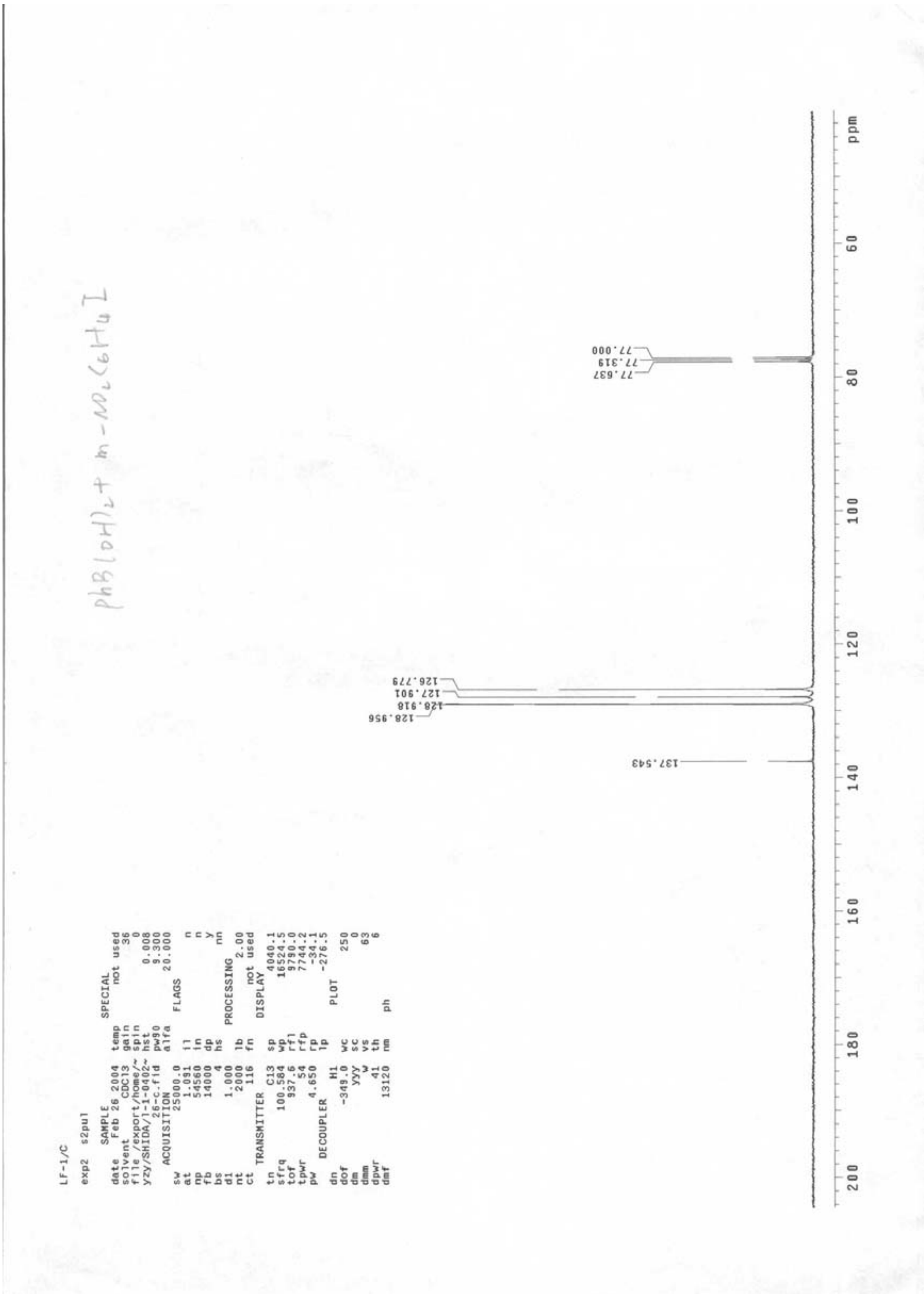


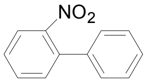


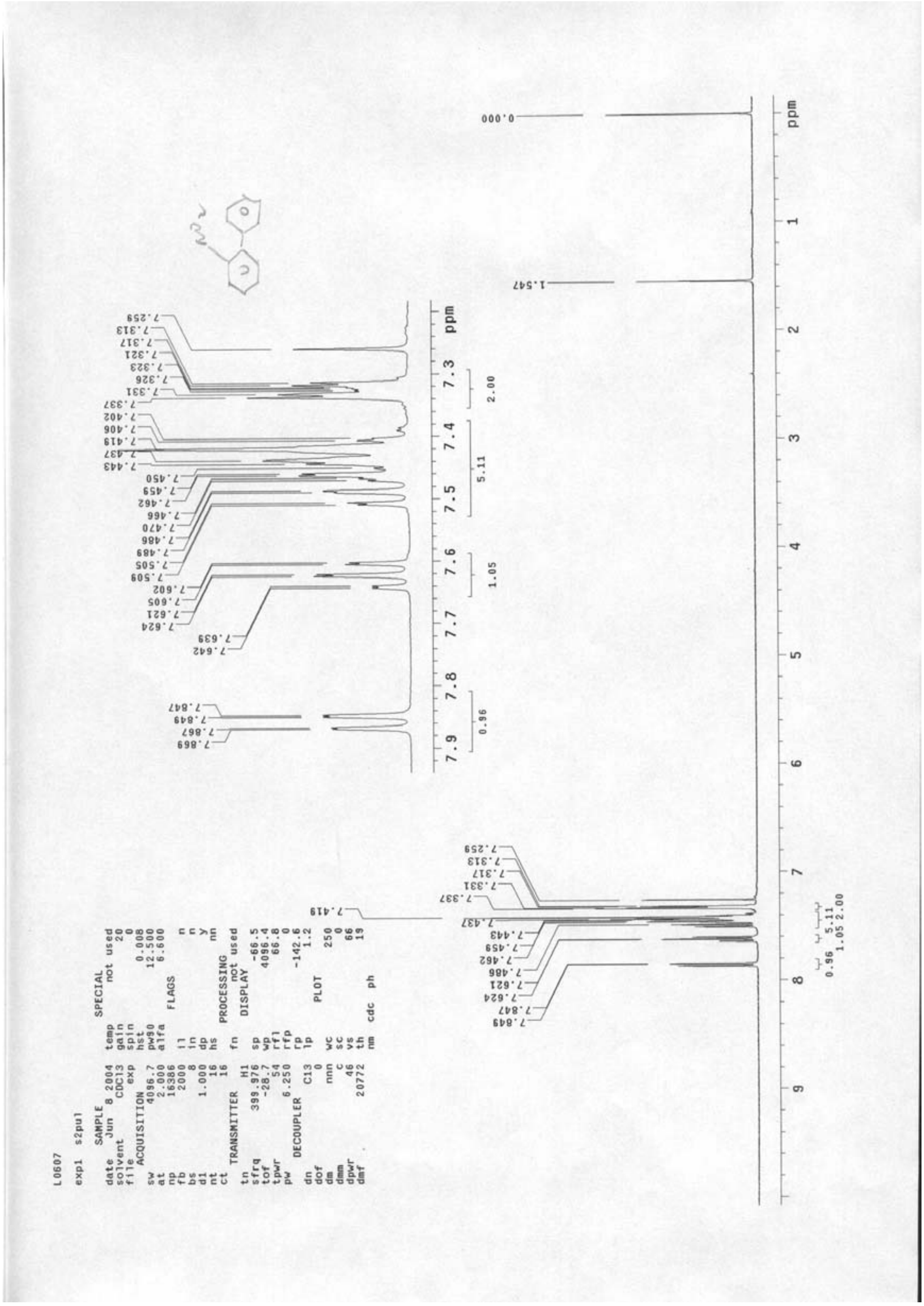
3-Nitro-biphenyl (3b) 

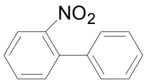


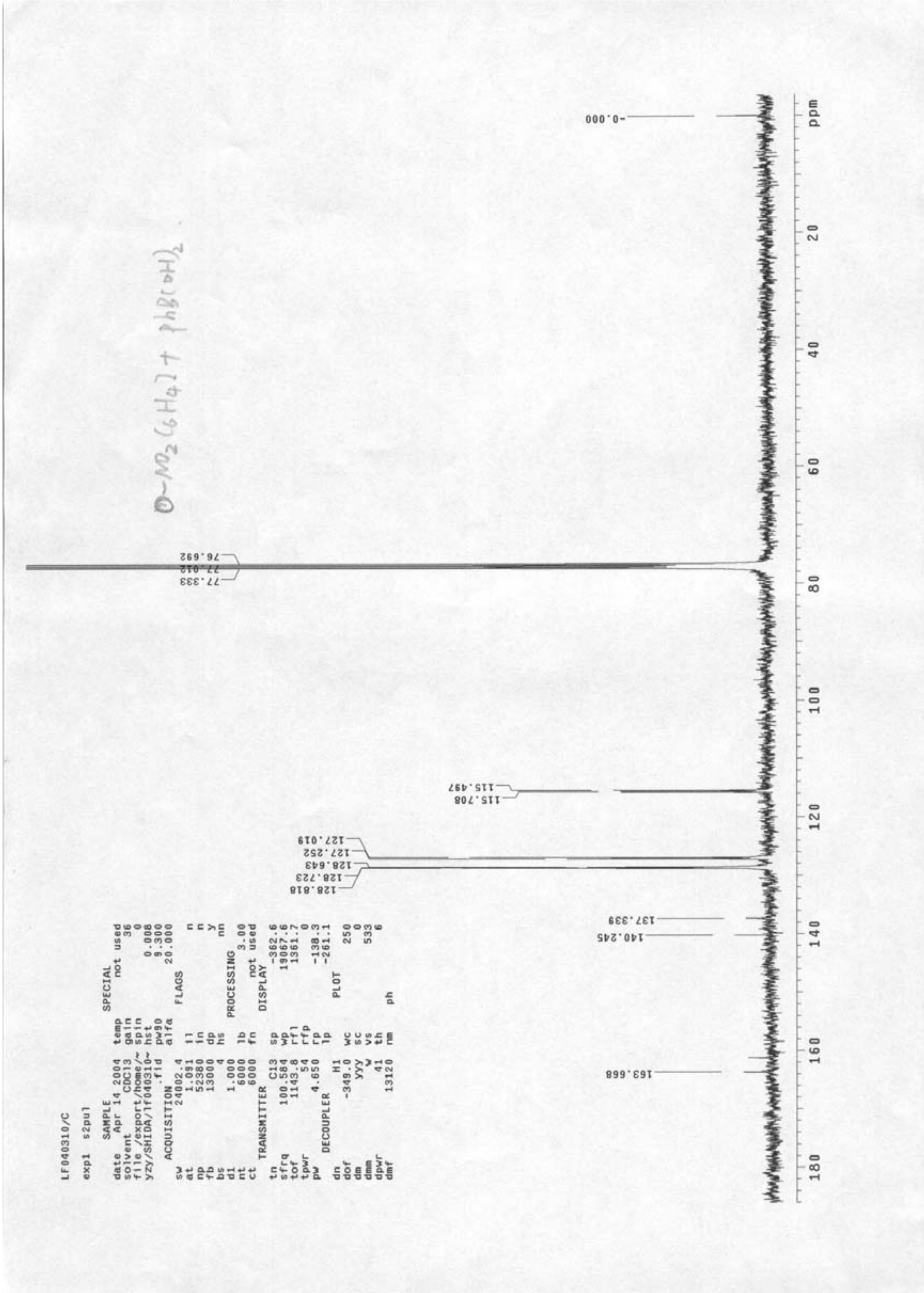
3-Nitro-biphenyl (3b) 

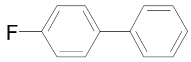


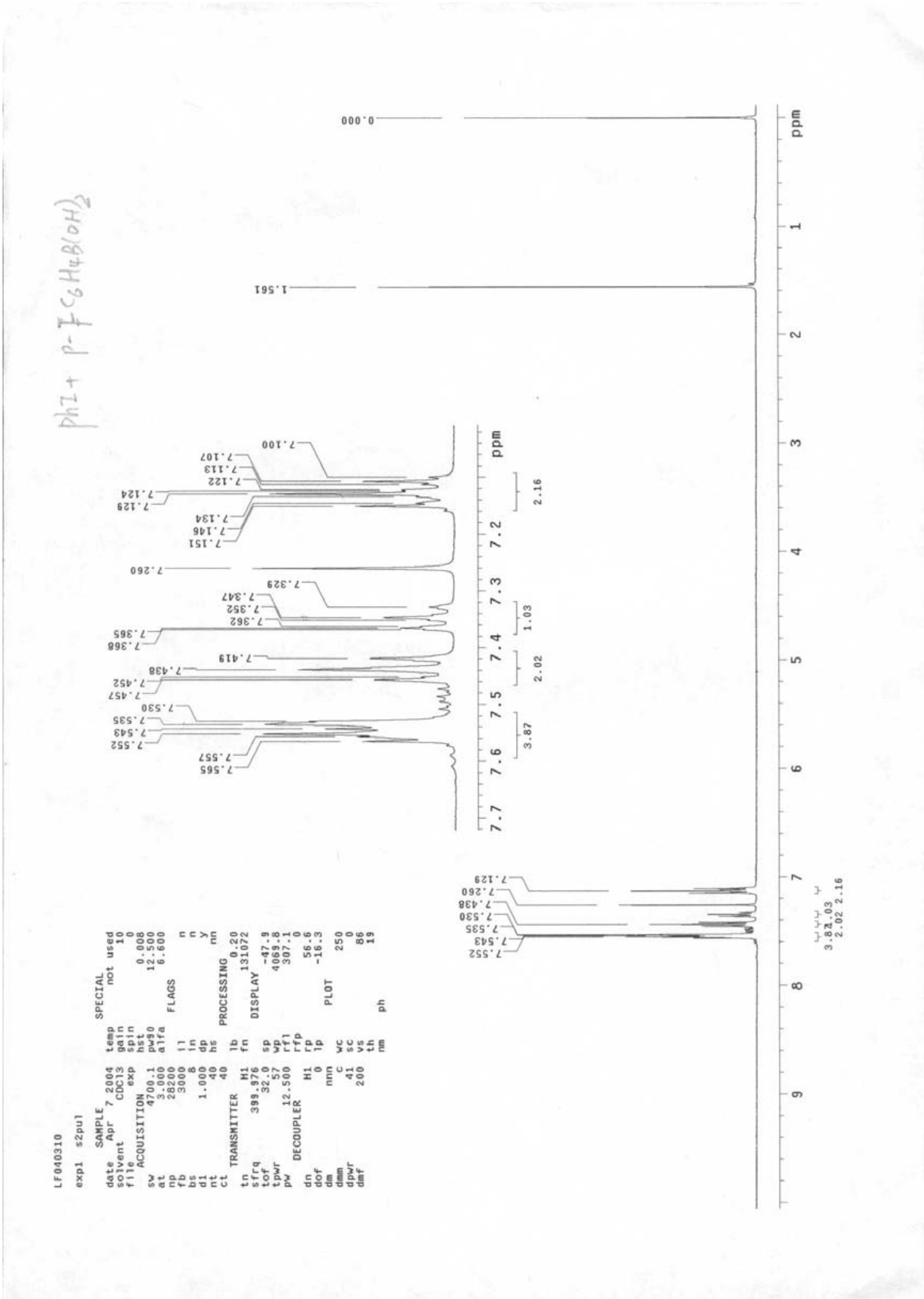
2-Nitro-biphenyl (3c) 

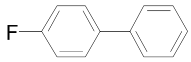


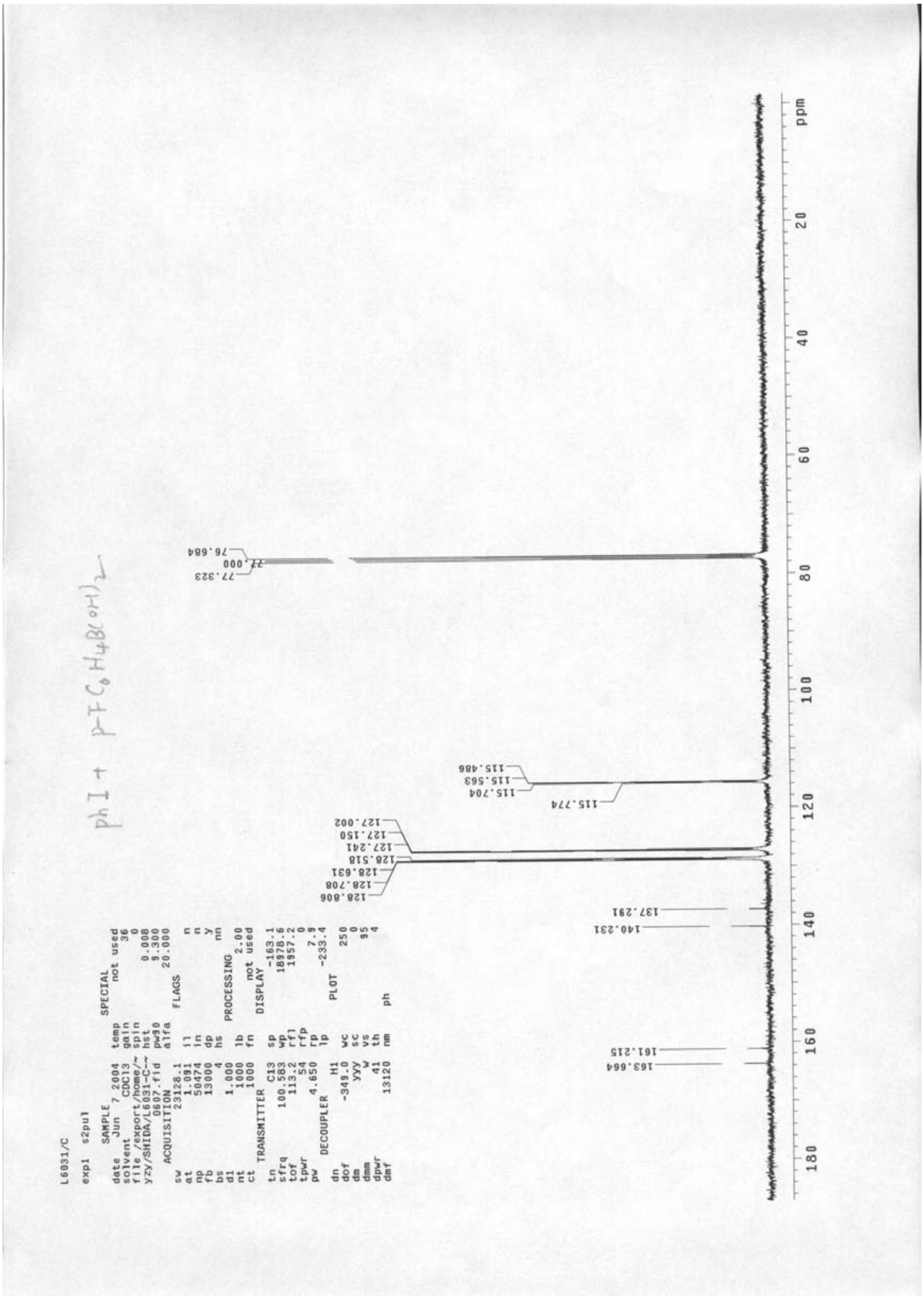
2-Nitro-biphenyl (3c) 

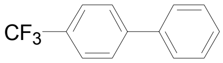


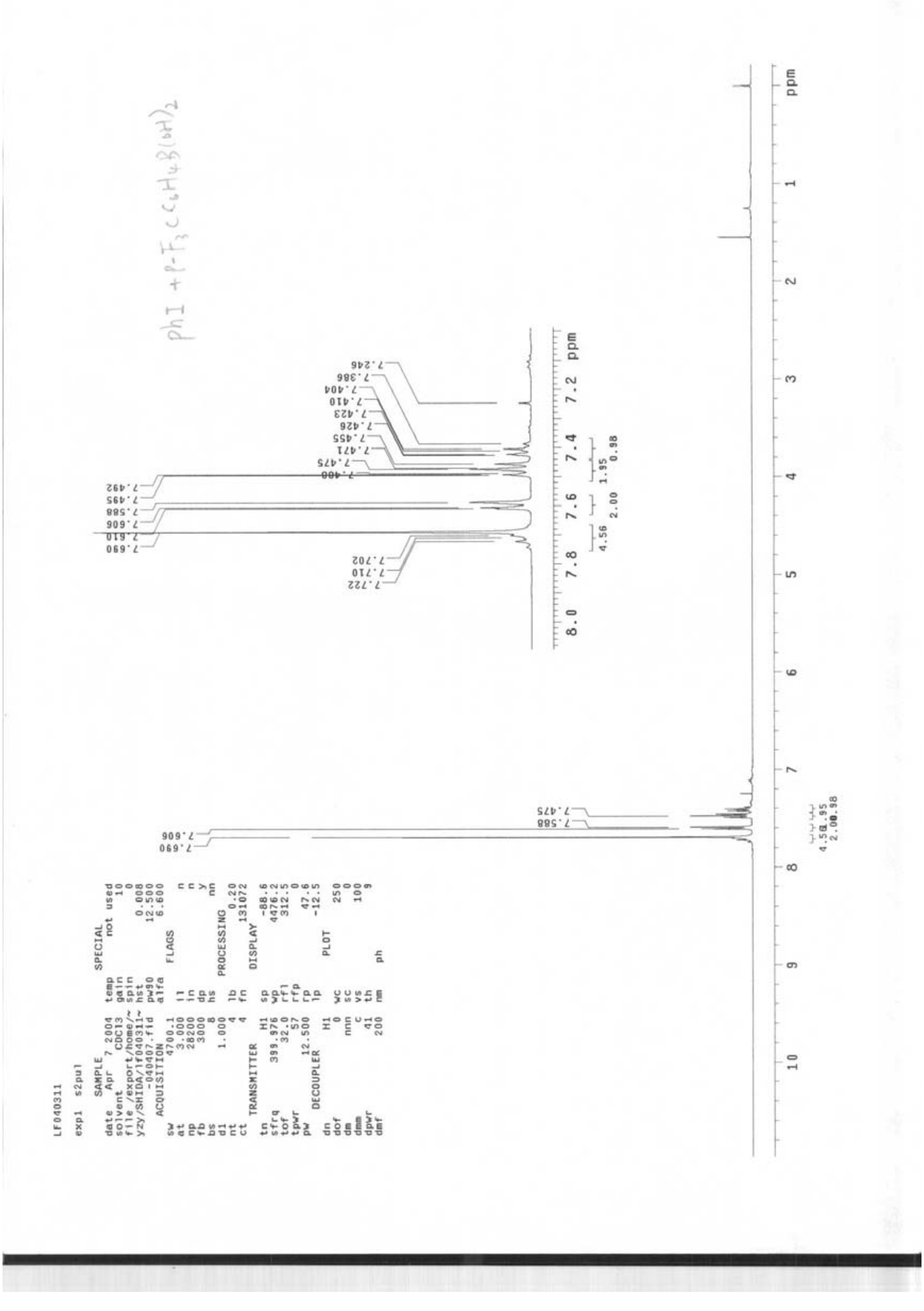
4-Fluoro-biphenyl (3d) 

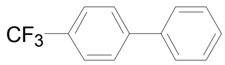


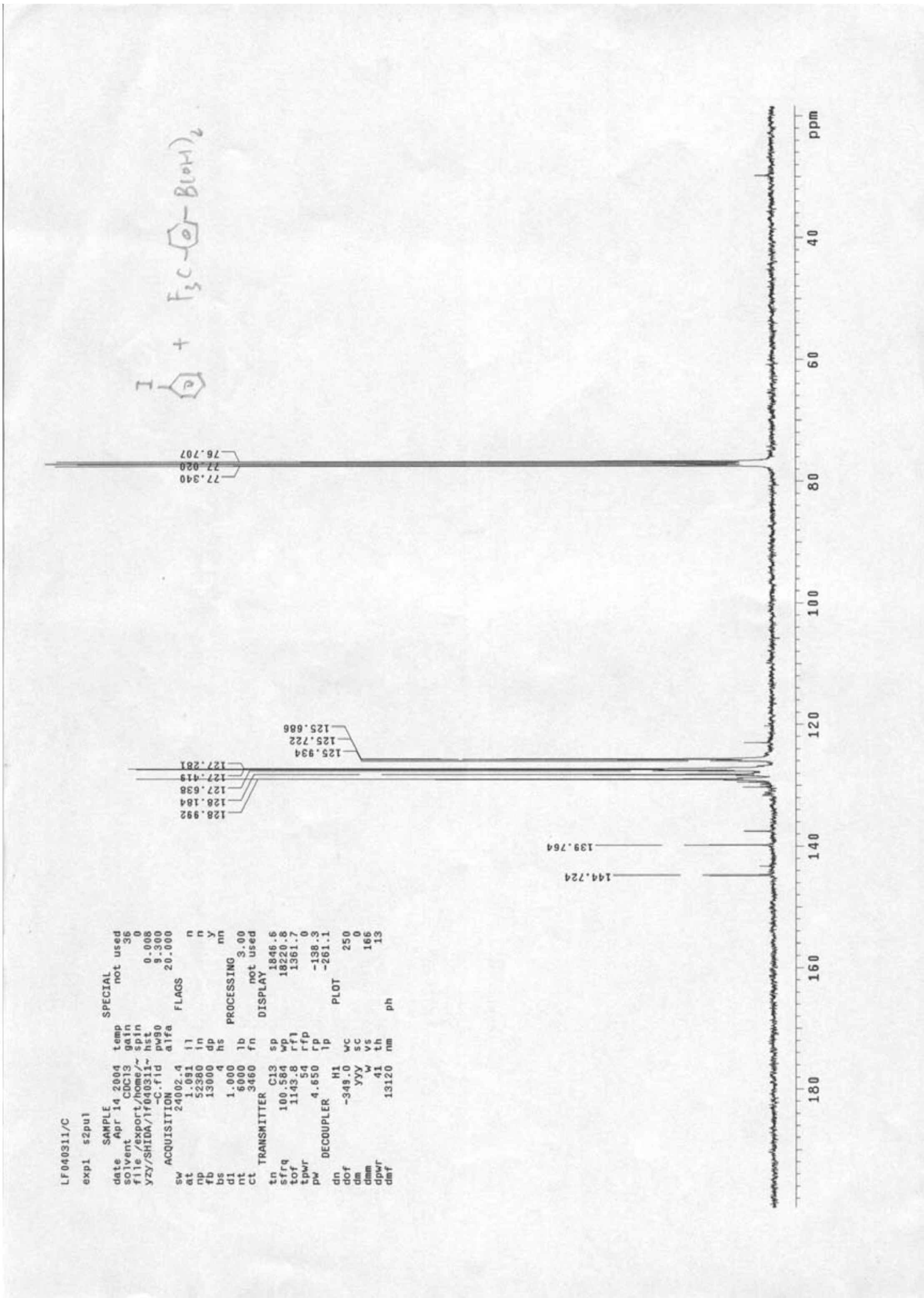
4-Fluoro-biphenyl (3d) 

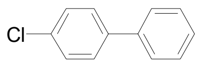


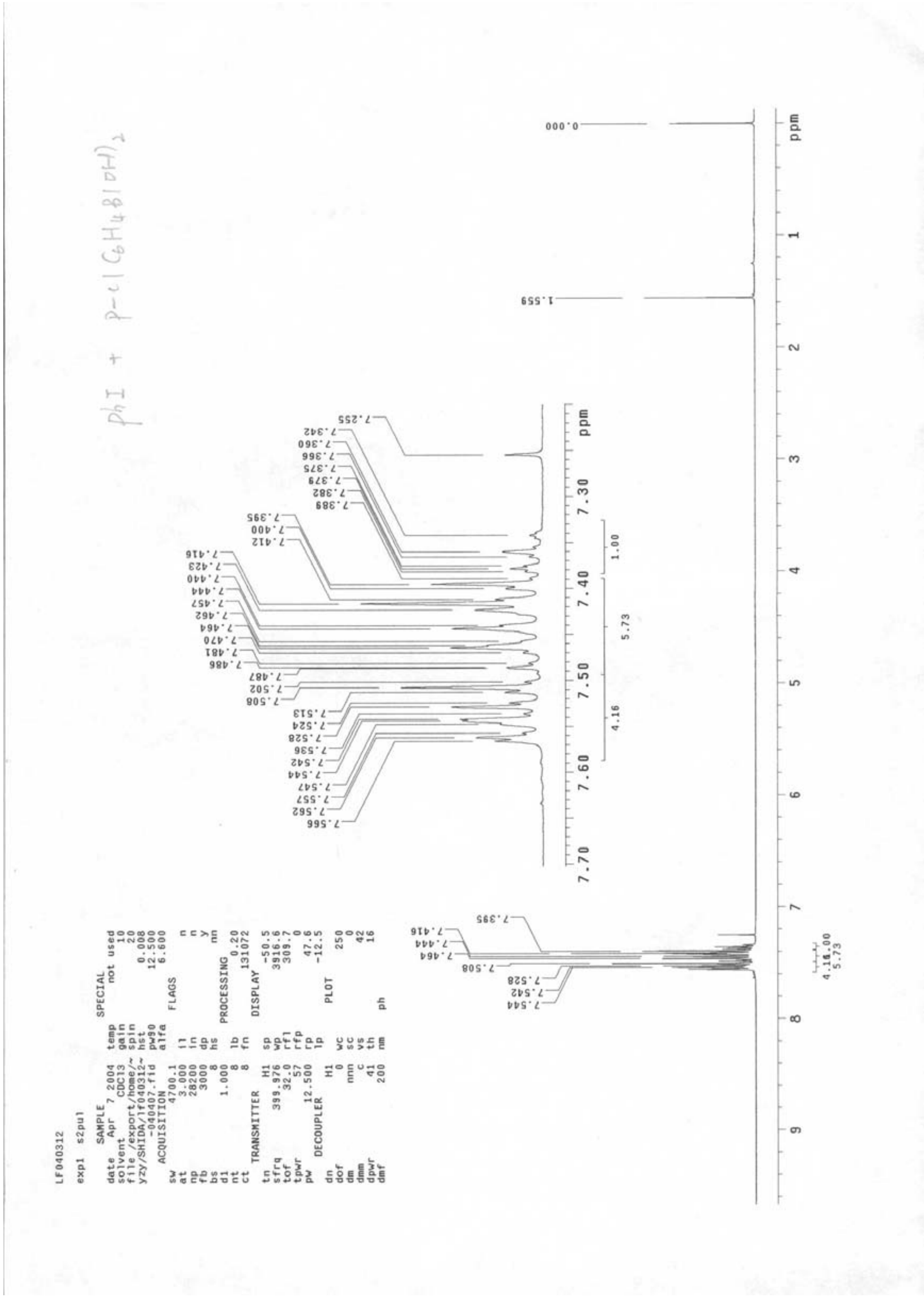
4-Trifluoromethyl-biphenyl (3e) 

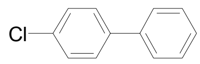


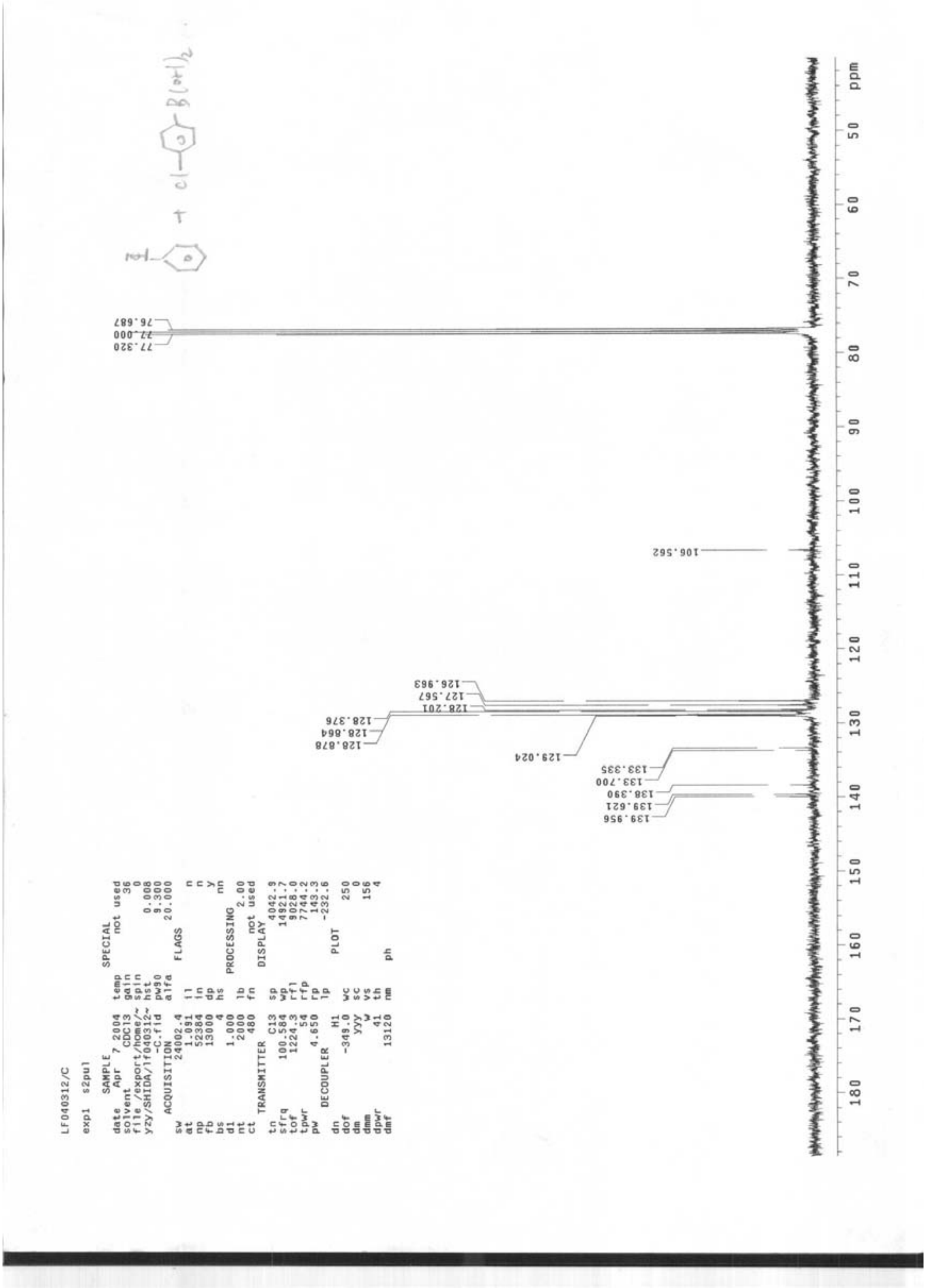
4-Trifluoromethyl-biphenyl (3e) 

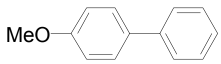


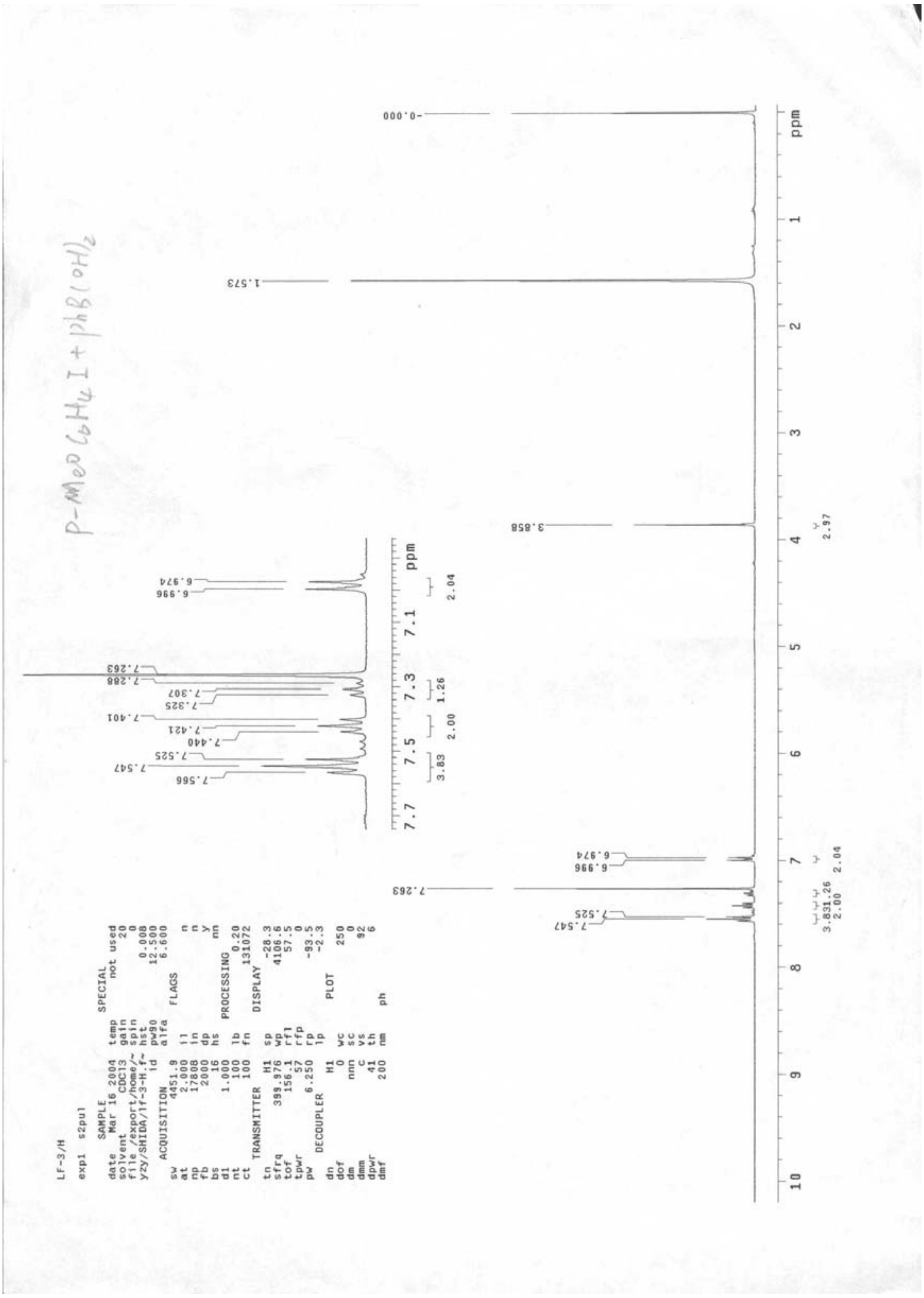
4-Chloro-biphenyl (3f) 

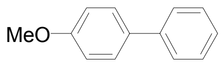


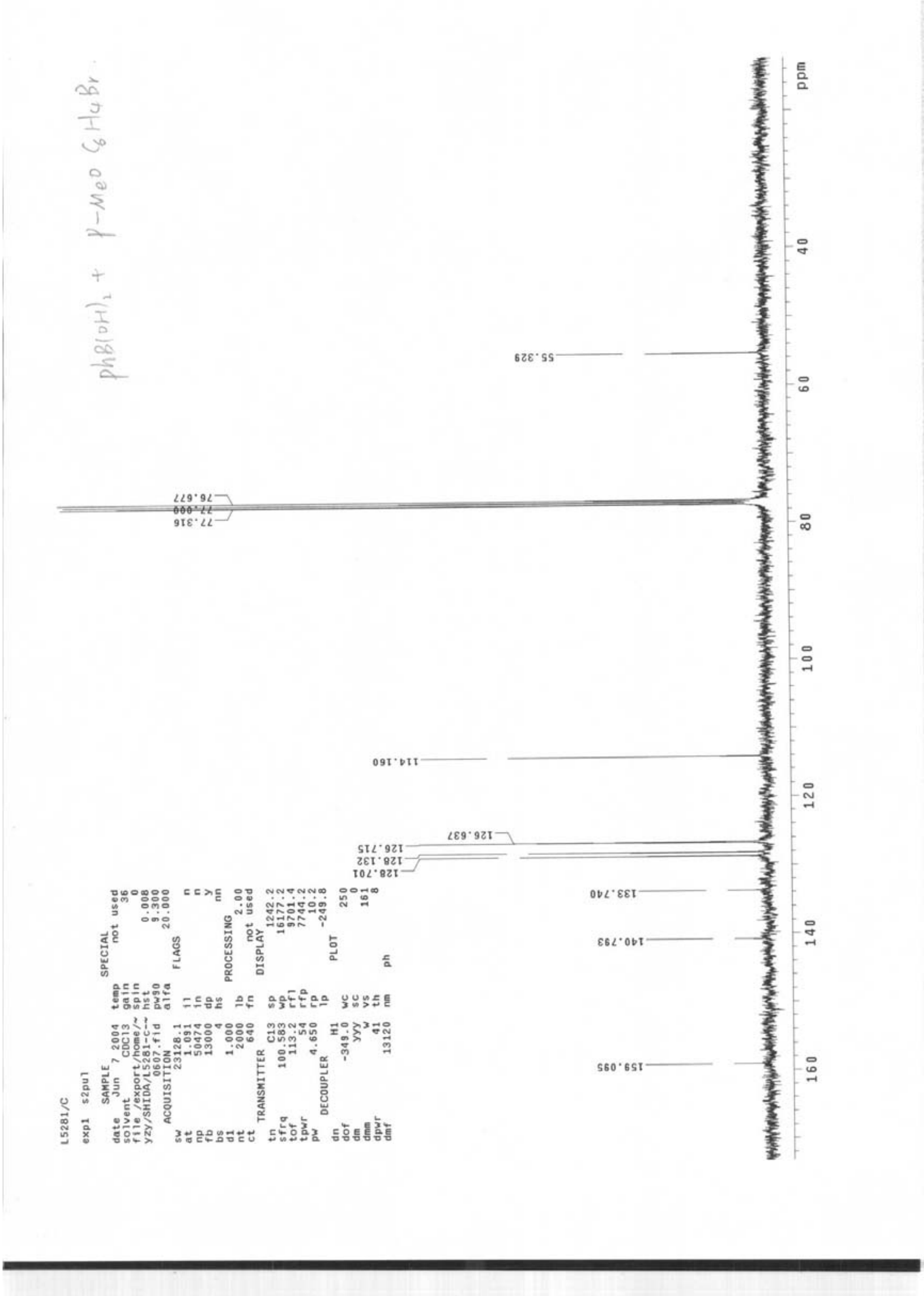
4-Chloro-biphenyl (3f) 

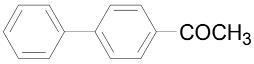


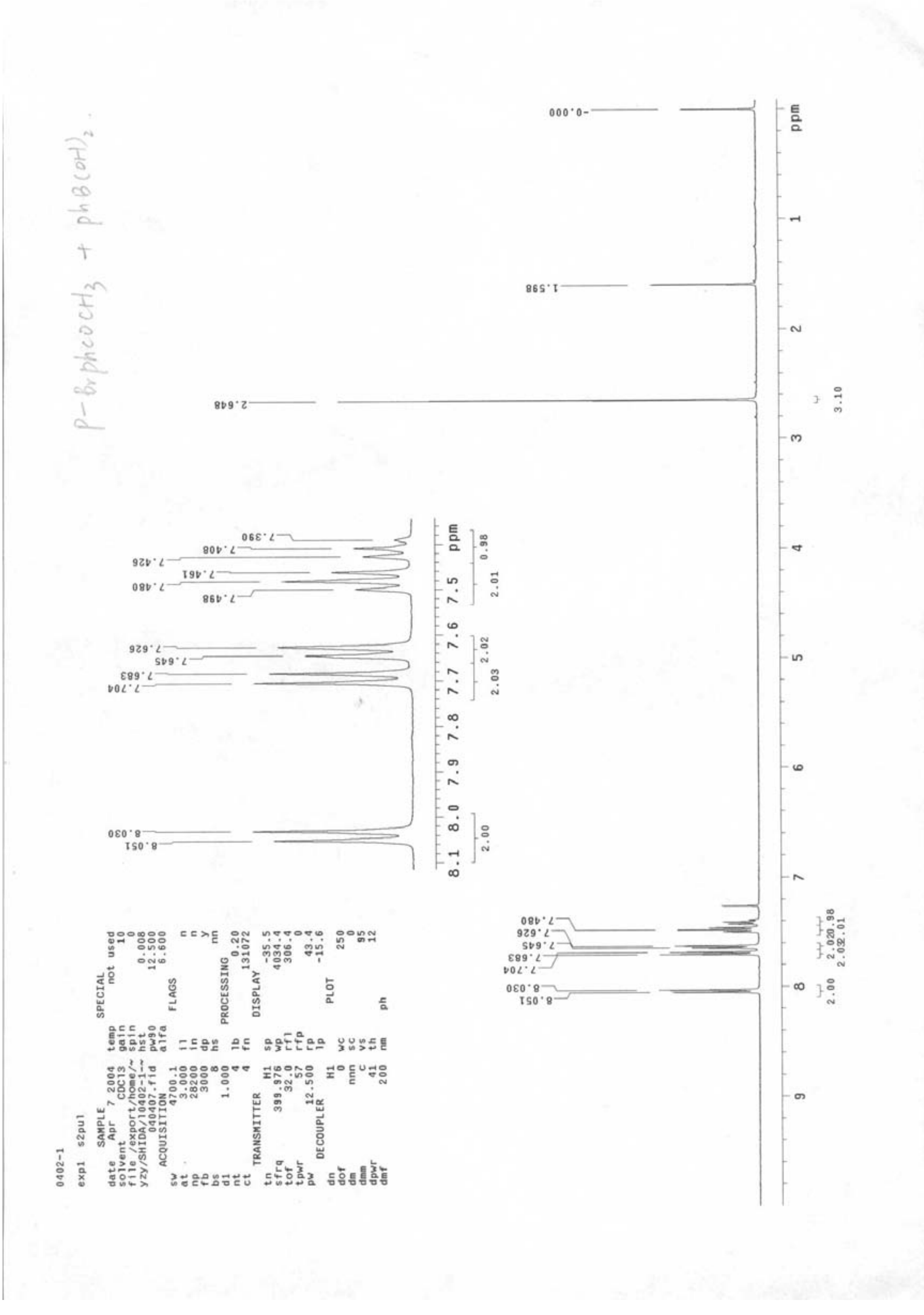
4-Methoxy-biphenyl (3g) 

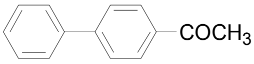


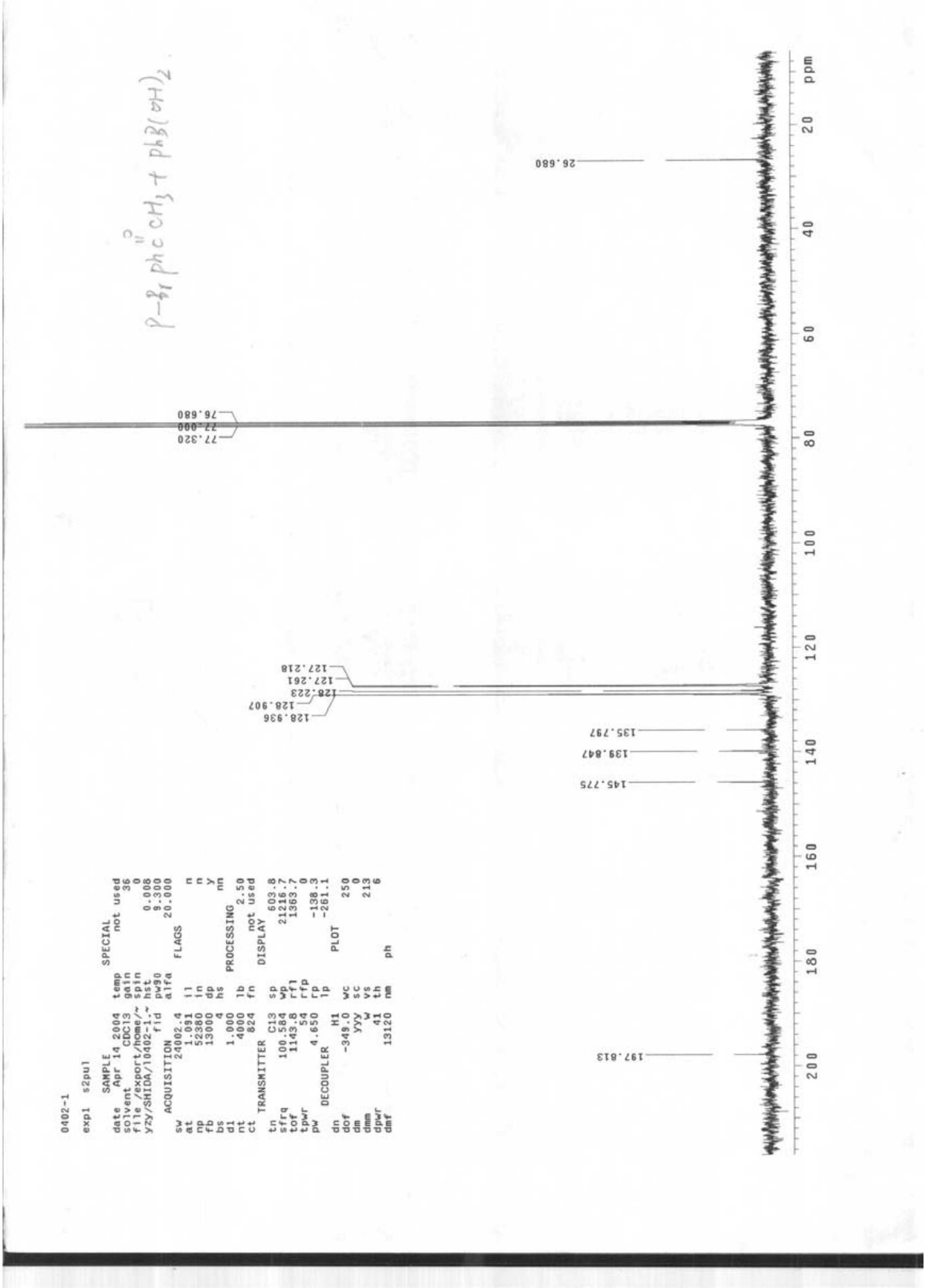
4-Methoxy-biphenyl (3g) 

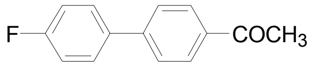


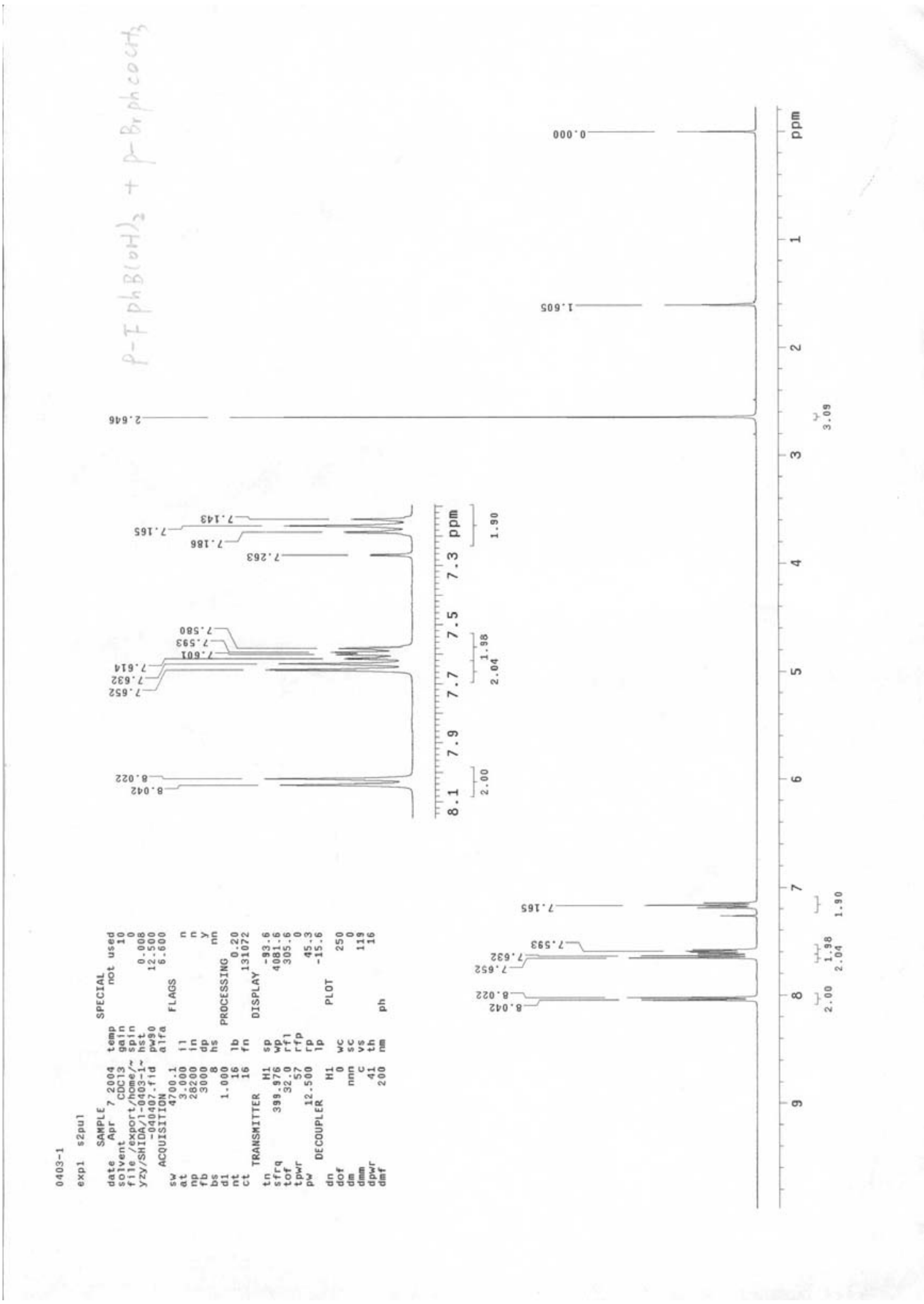
1-Biphenyl-4-yl-ethanone (3h) 



1-Biphenyl-4-yl-ethanone (3h) 



1-(4'-Fluoro-biphenyl-4-yl)-ethanone (3i) 



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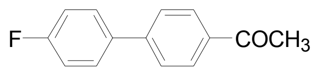
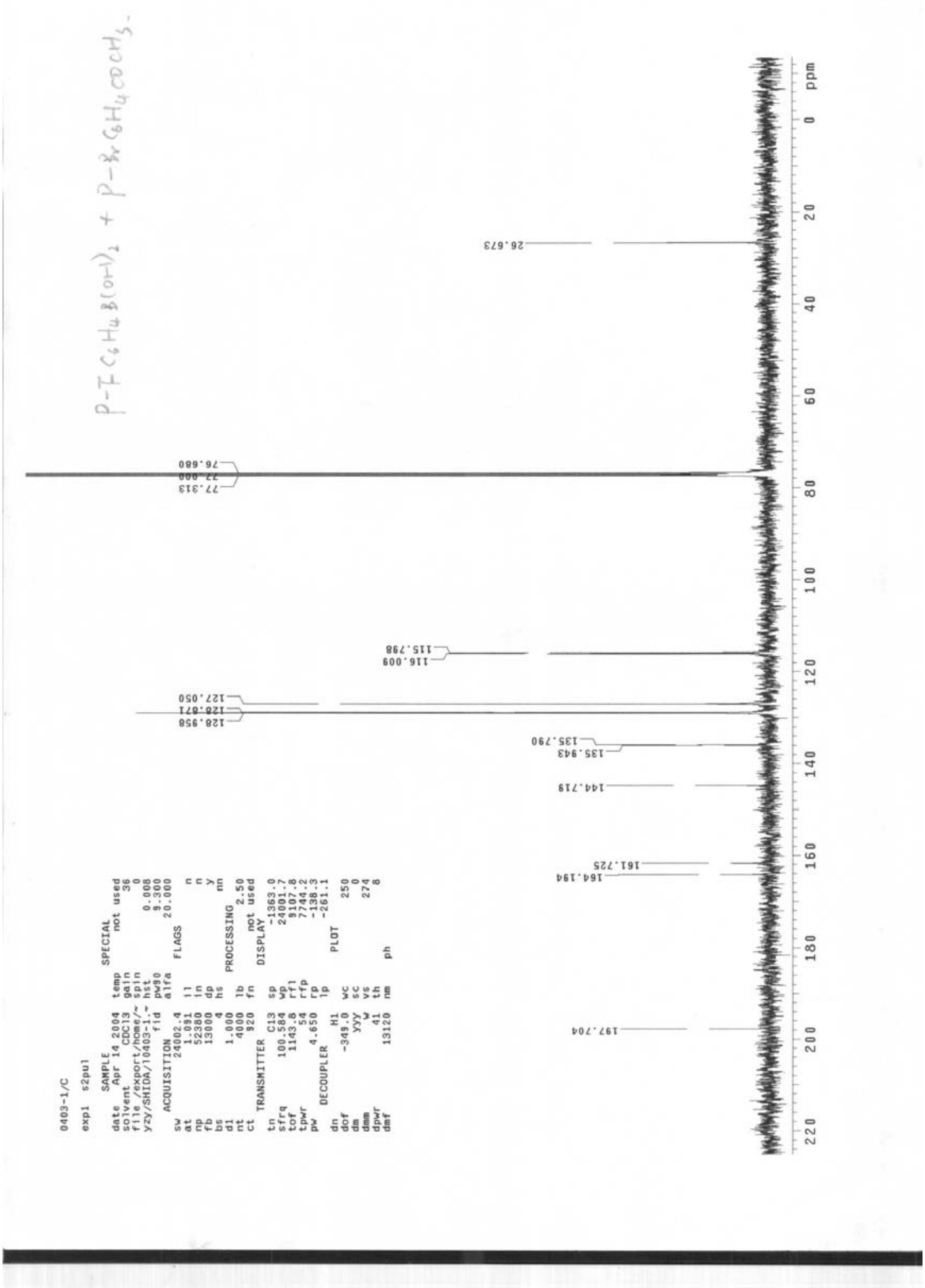
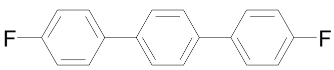
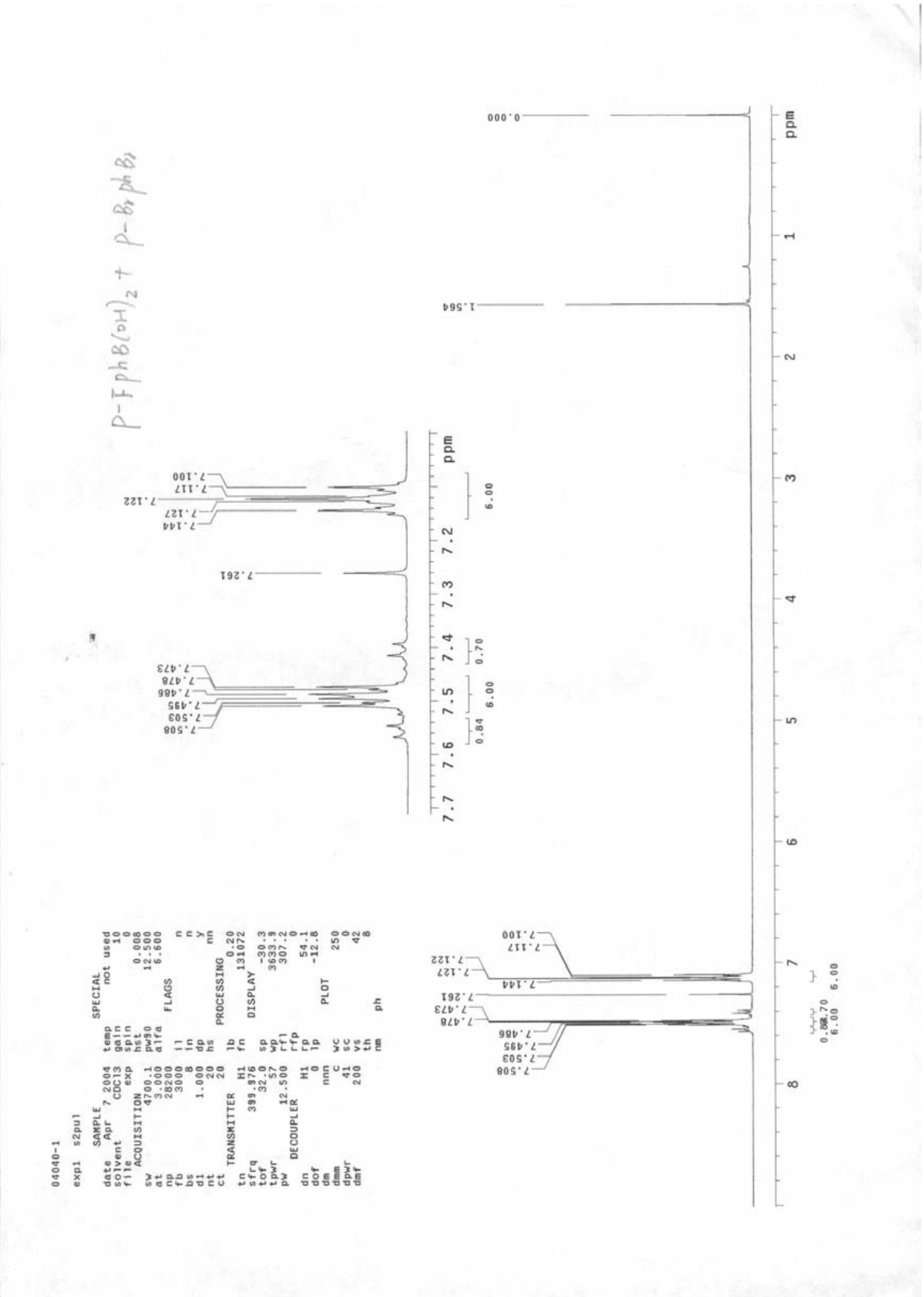




(4, 4´´)-Difluoro-[1,1';4',1'']Terphenyl (3j) 



(4, 4´´)-Difluoro-[1,1';4',1'']Terphenyl (3j)