Supporting Information

for

Highly bulky and stable geometry-constrained iminopyridines: Synthesis, structure and application in Pd-catalyzed Suzuki coupling of aryl chlorides

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NMR spectra of palladium complexes and products

1. NMR spectrum of iminopyridine–palladium complexes

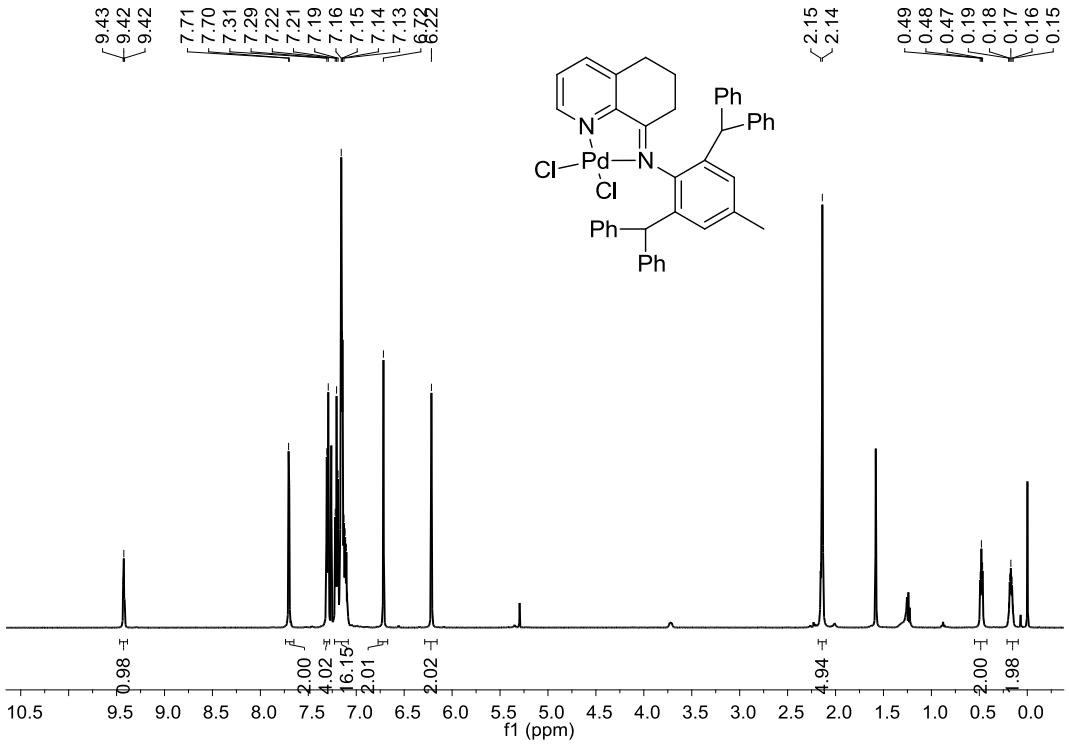


Figure S1 ^{1}H NMR of complex **Pd2** in $CDCl_3$

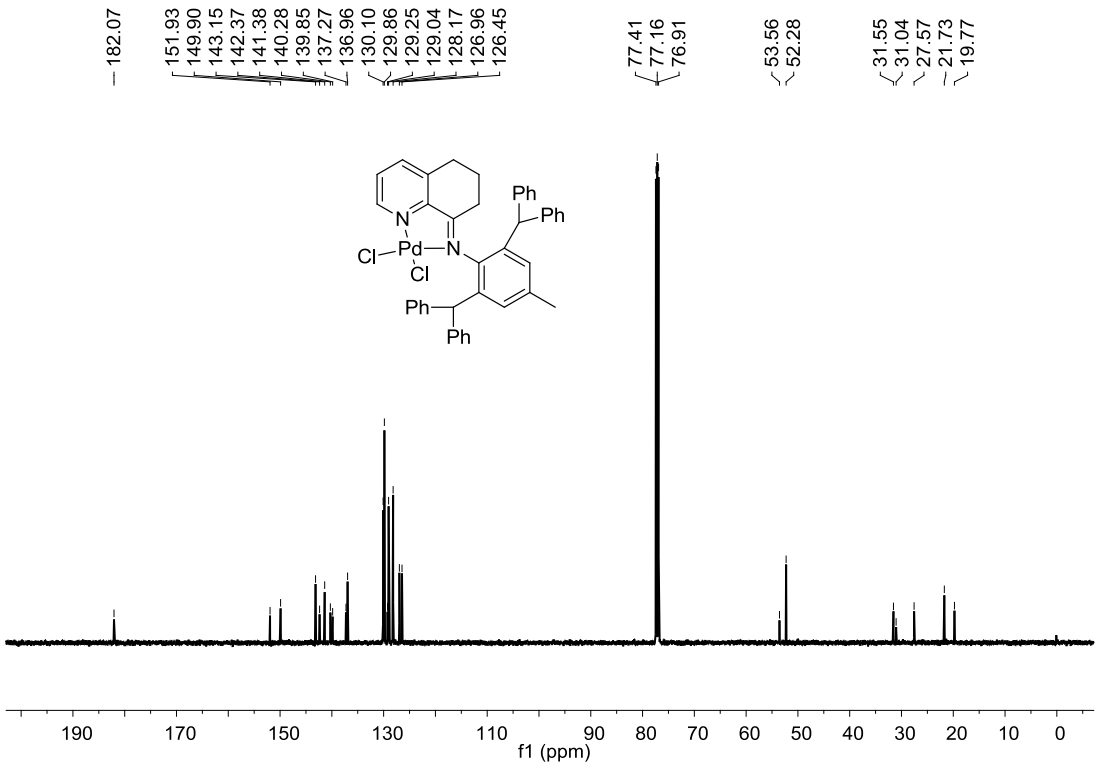


Figure S2 ^{13}C NMR of complex **Pd2** in DMSO-d_6.

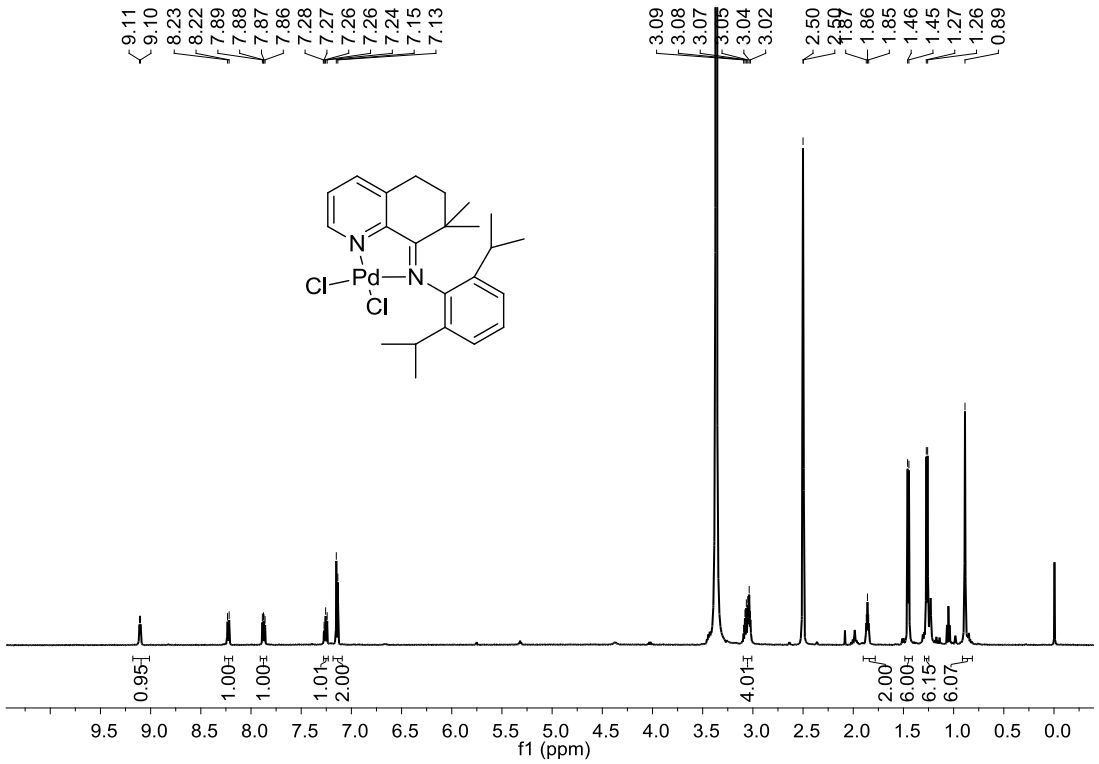


Figure S3 ^{1}H NMR of complex **Pd3** in DMSO-d_6

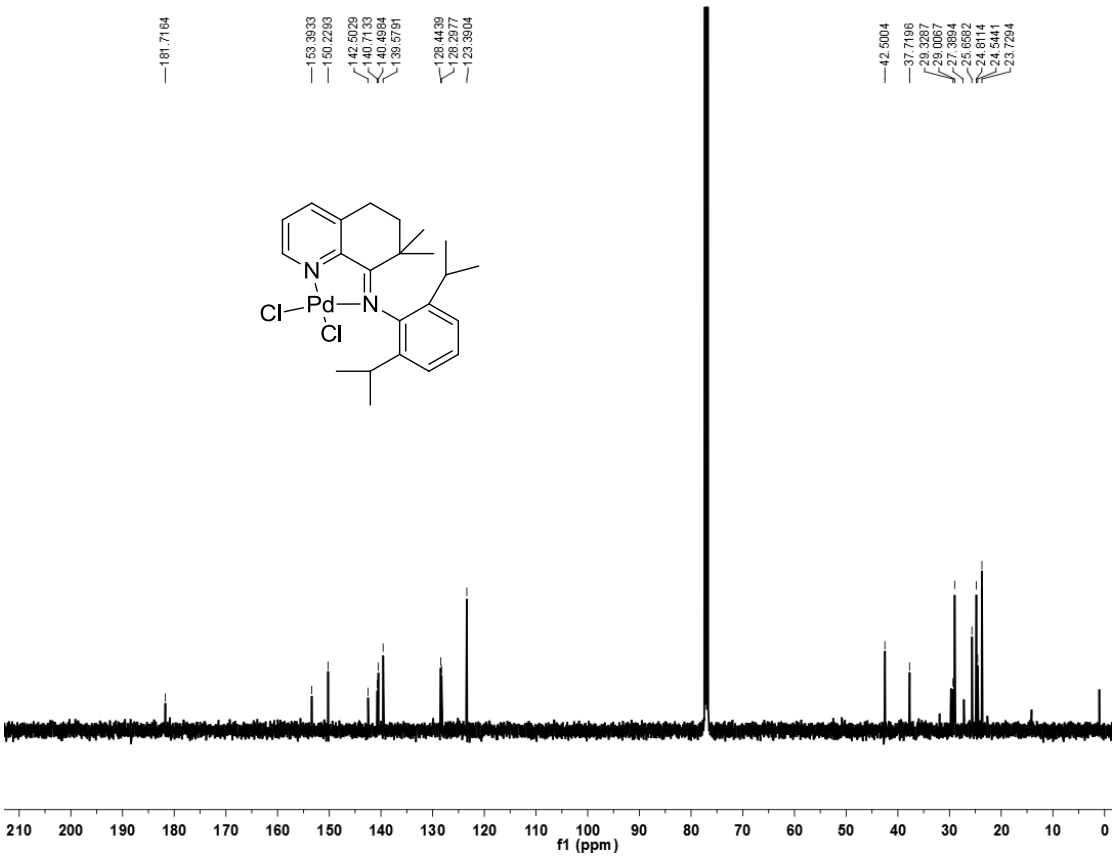


Figure S4 ^{13}C NMR of complex **Pd3** in DMSO-d_6.

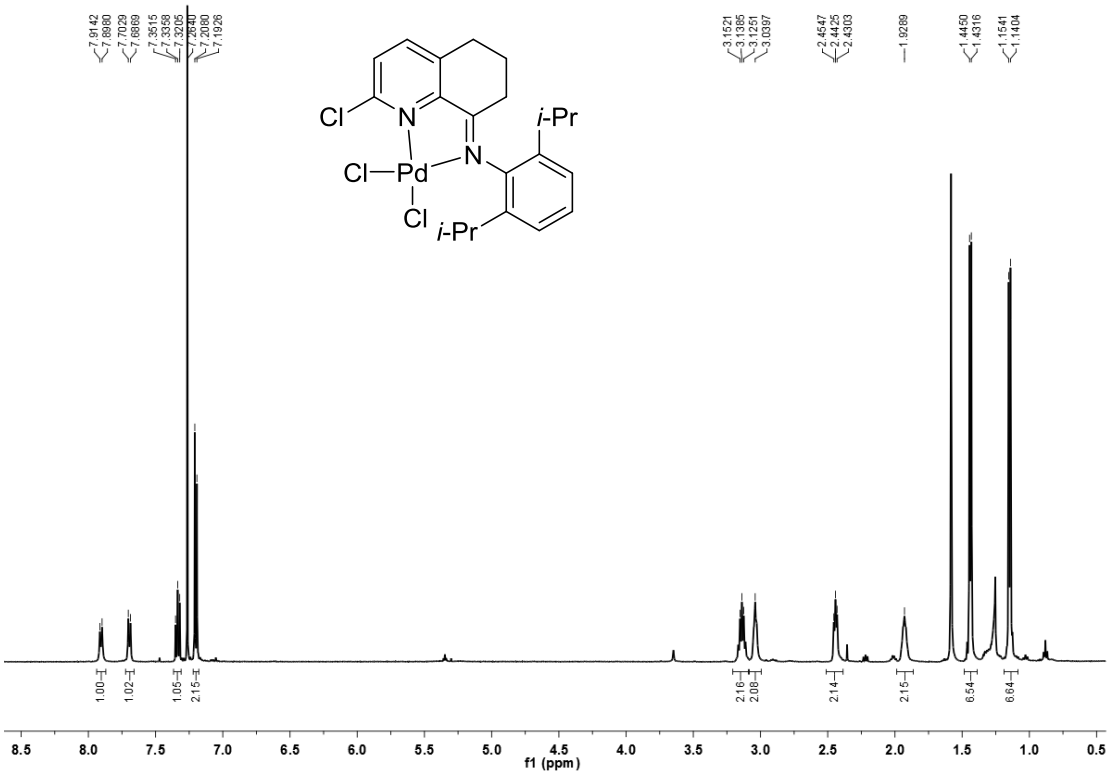


Figure S5 ^{1}H NMR of complex **Pd4** in $CDCl_3$.

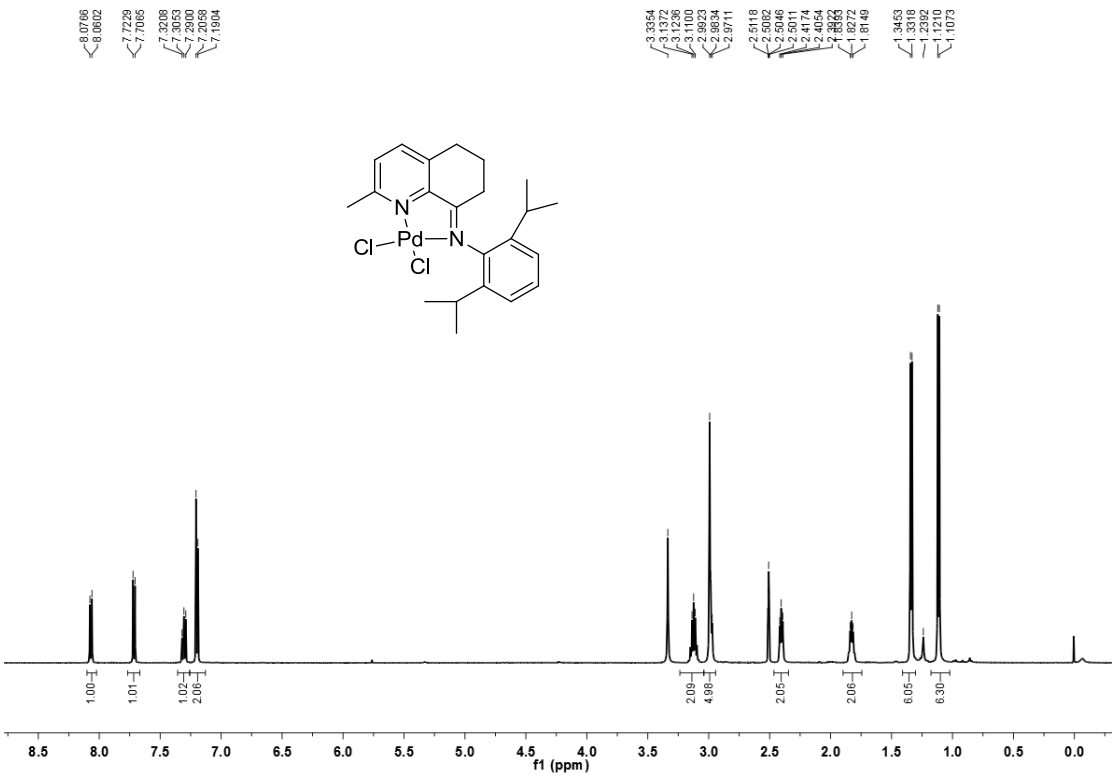


Figure S6 1H NMR of complex **Pd5** in DMSO-d_6.

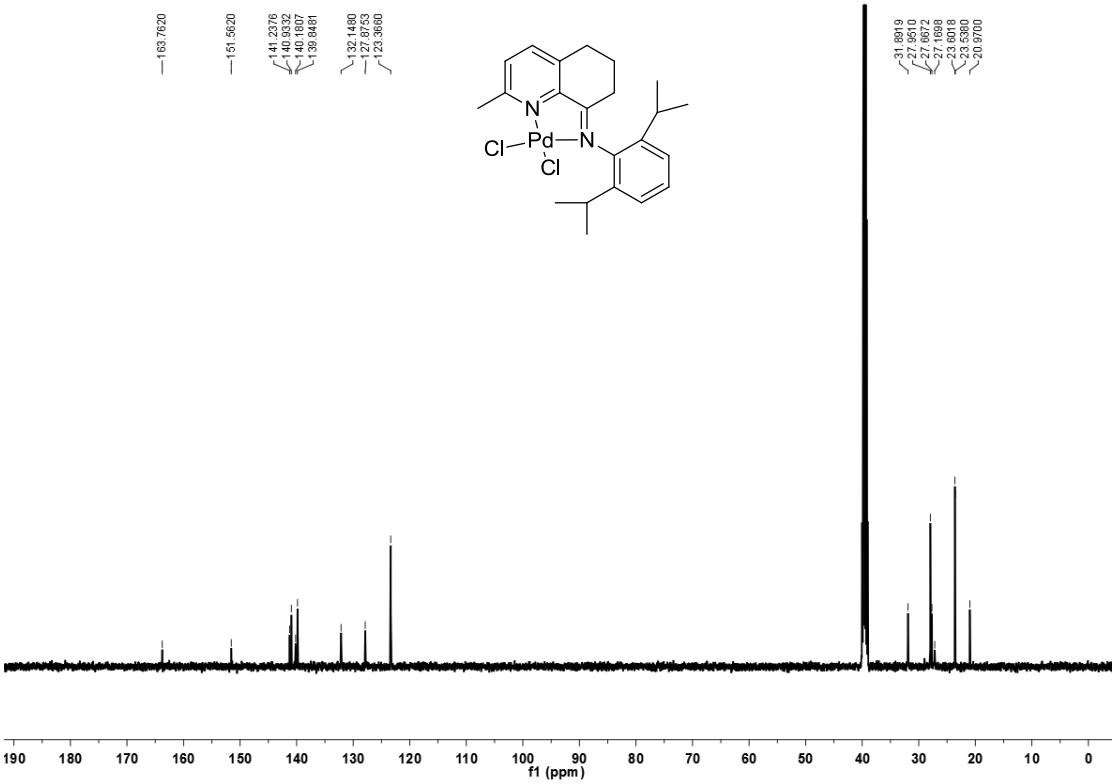
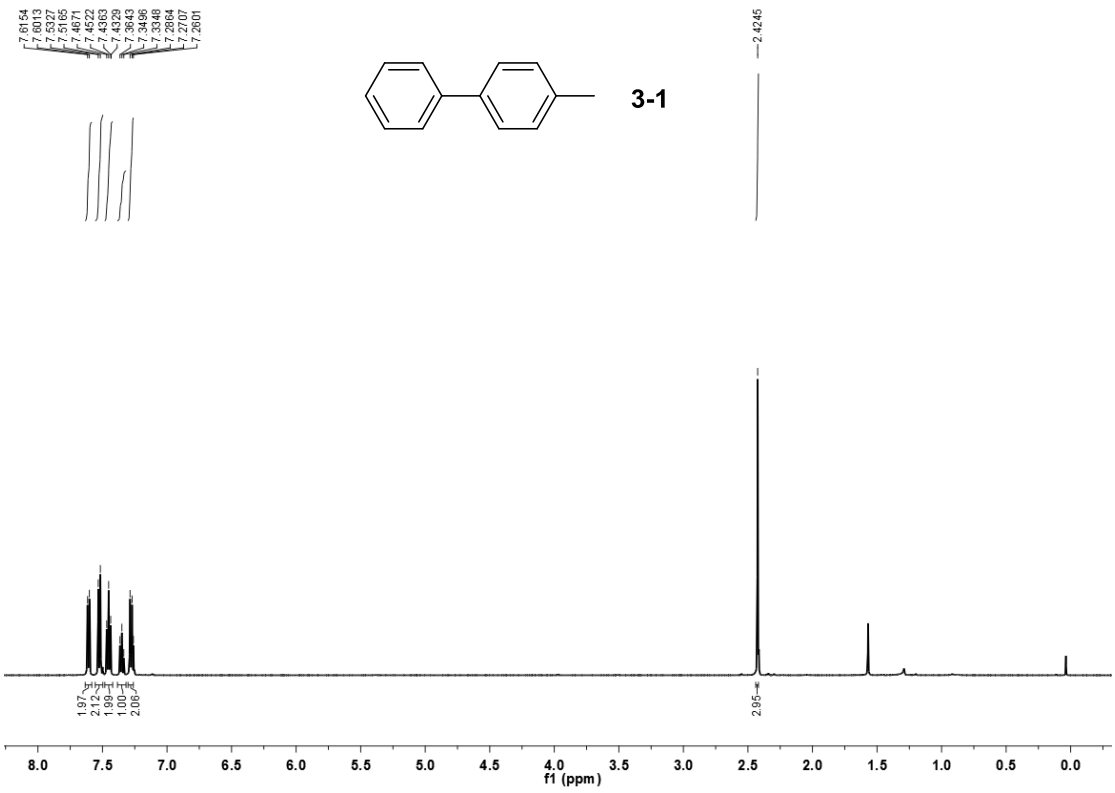


Figure S7 ^{13}C NMR of complex **Pd5** in DMSO-d_6.

2. NMR spectrum of biaryl compounds

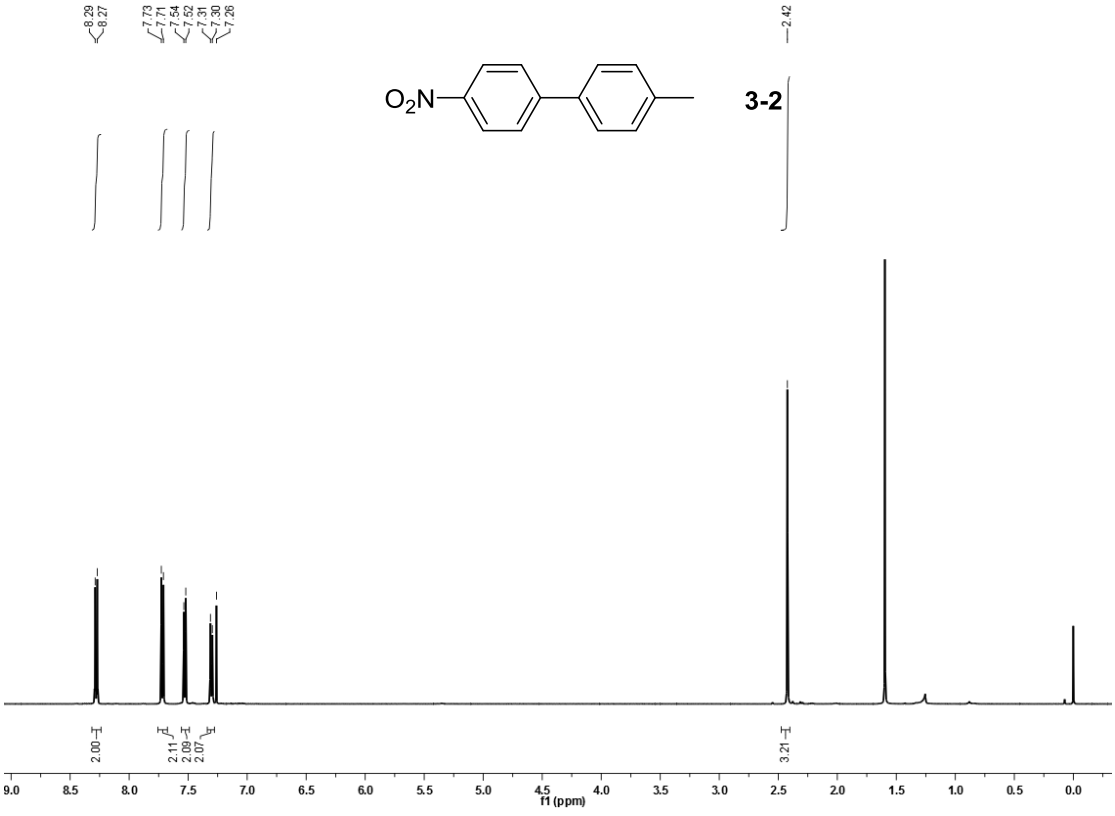
4-Methyl-biphenyl (**3-1**)[1]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (d, *J* = 8.2Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 2.42 (s, 3H).



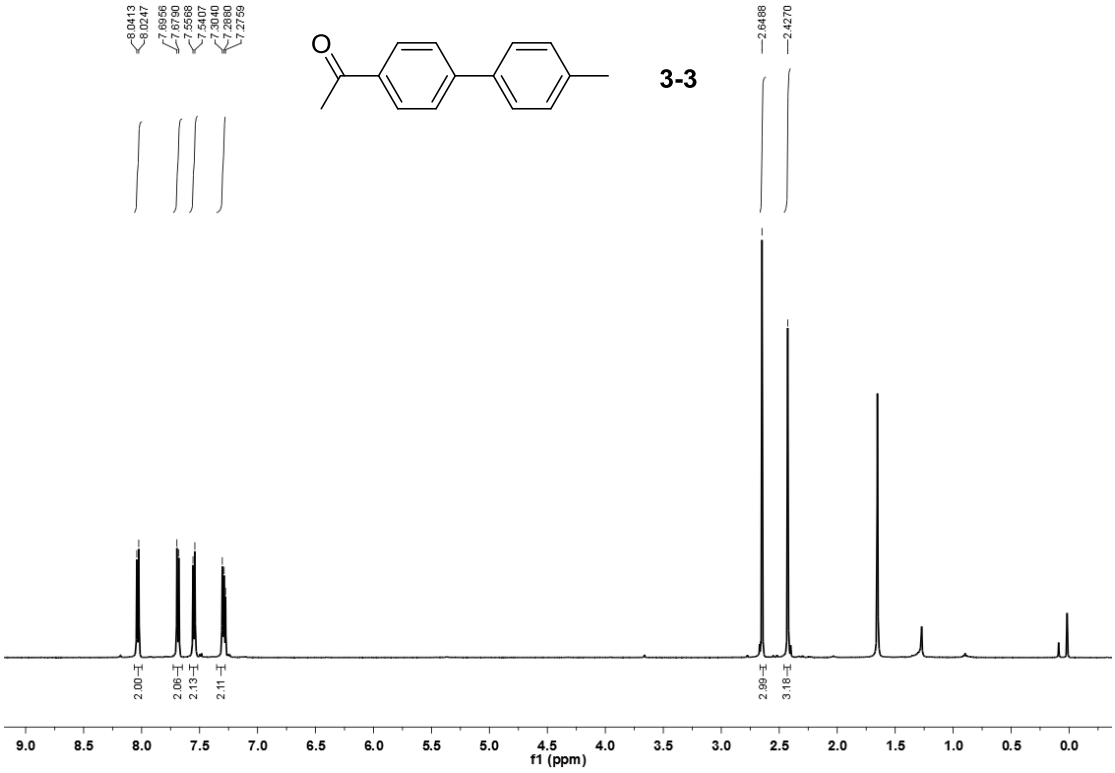
4-Methyl-4'-nitro-biphenyl (**3-2**) [2]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.28 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H).



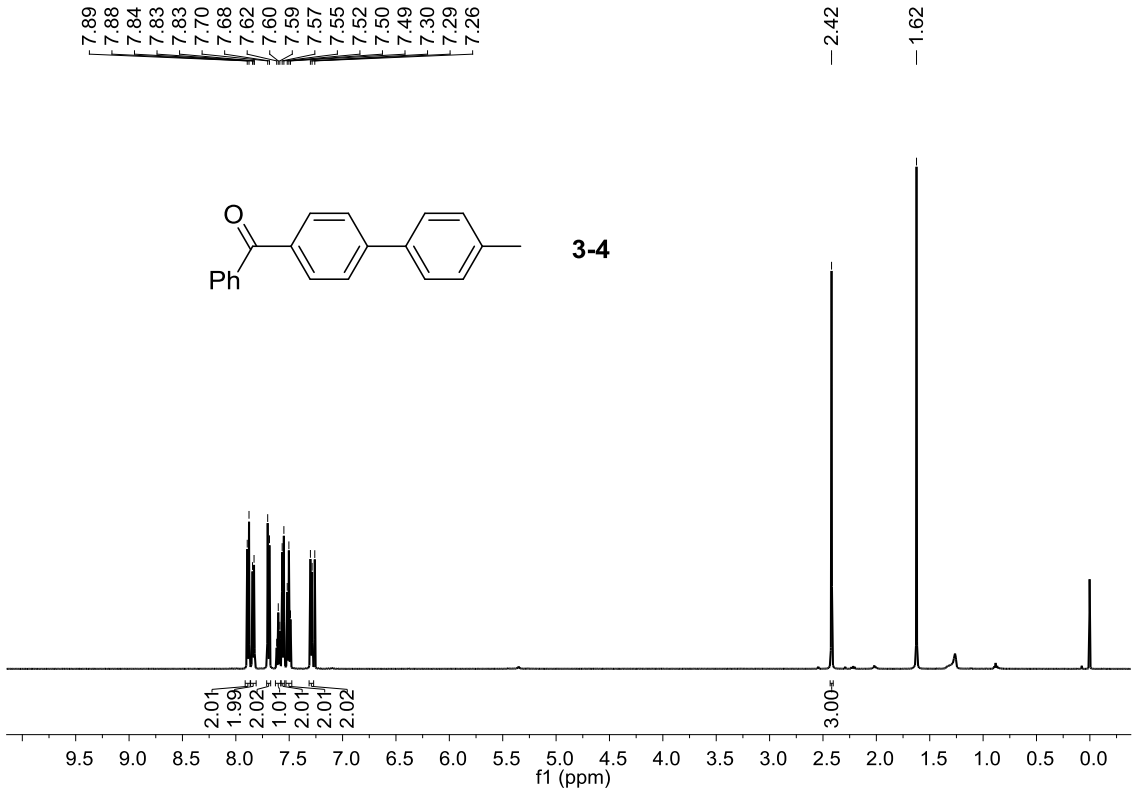
4-Methyl-4'-acetylbiphenyl (**3-3**)[3]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 2.42 (s, 3H).



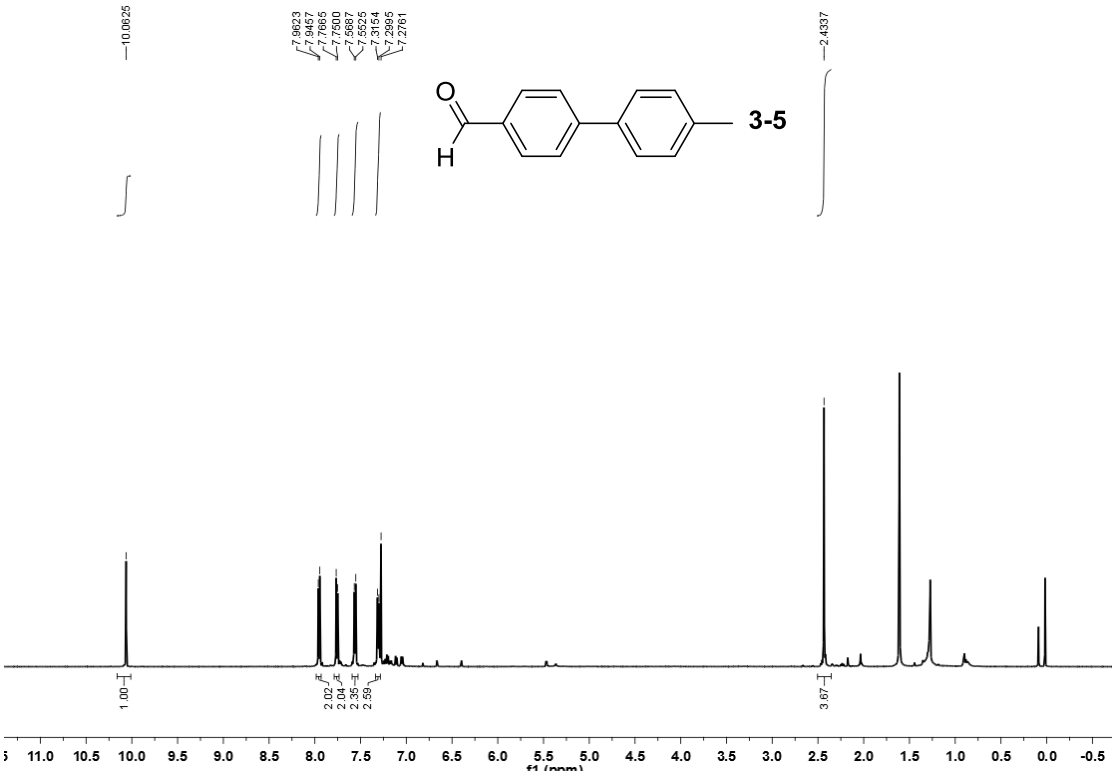
4-Benzoyl-4'-methylbiphenyl (**3d-4**)[4]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.88 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).



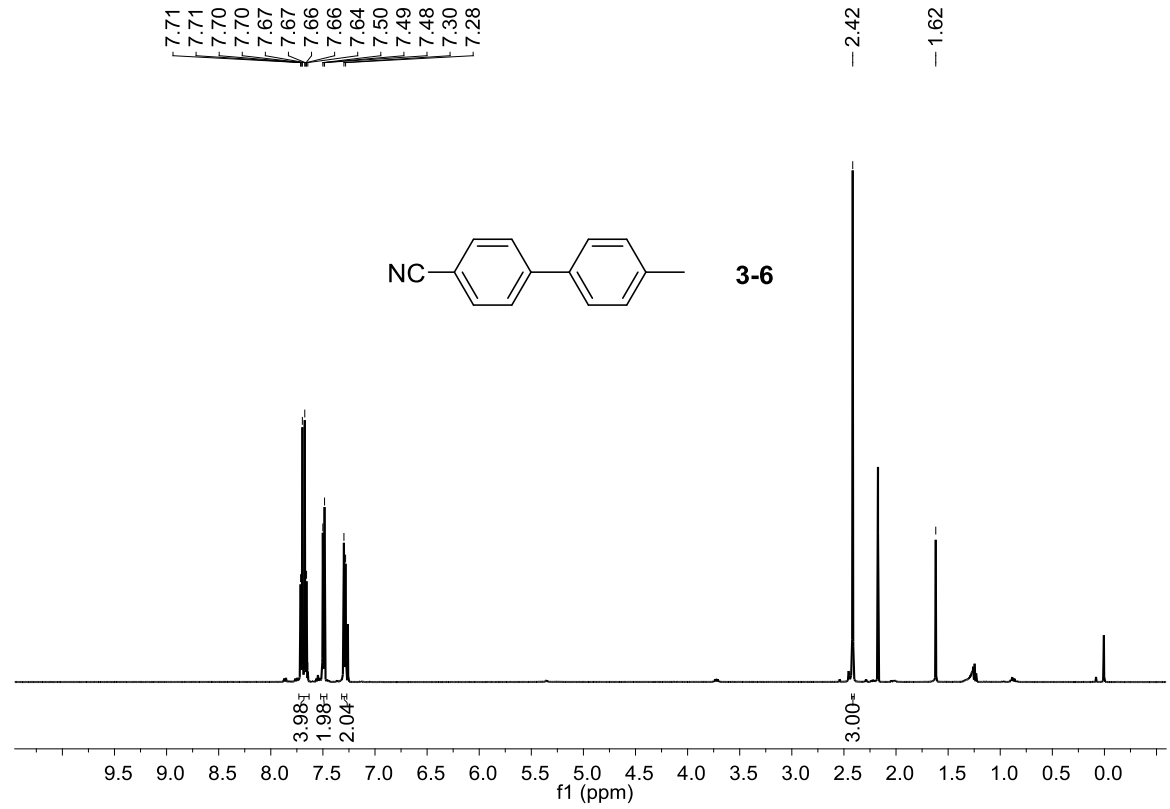
4-Formyl-4'-methylbiphenyl (**3-5**)[5]

^{1}H NMR ($CDCl_3$, 500 MHz): 10.08 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H).



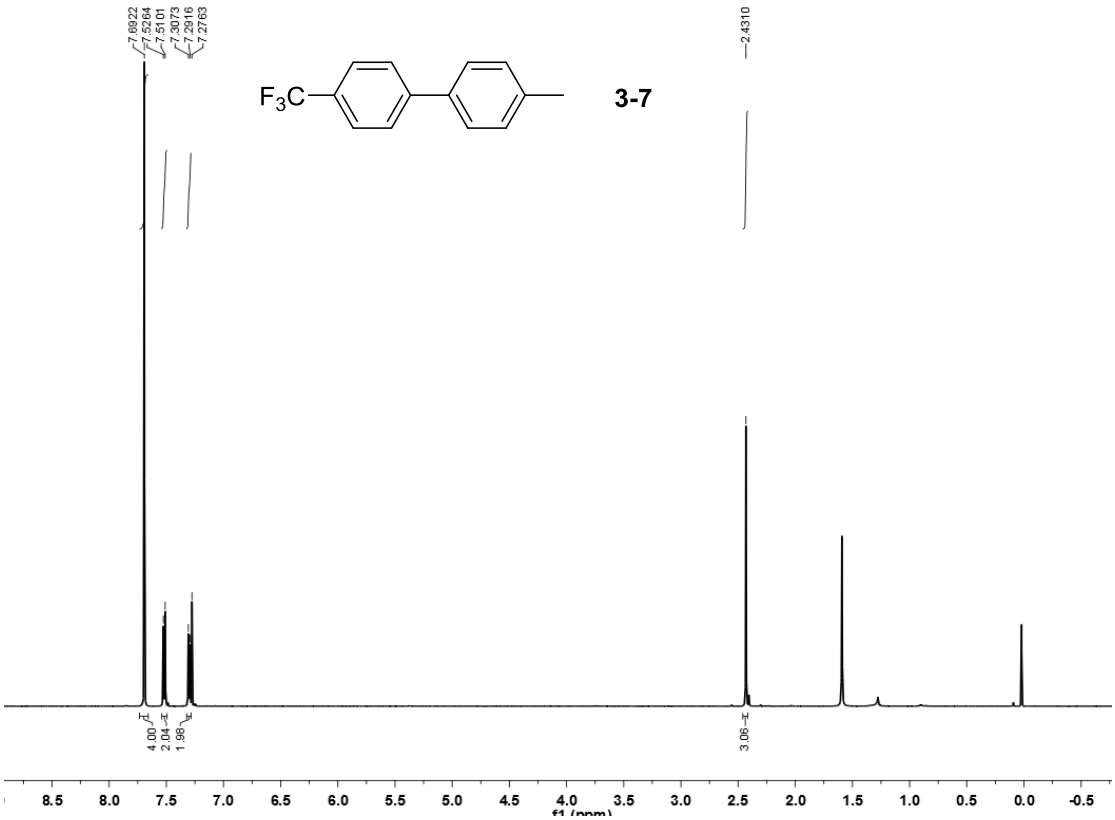
4-Cyano-4'-methylbiphenyl (**3-6**)[4]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.73-7.64 (m, 4H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).



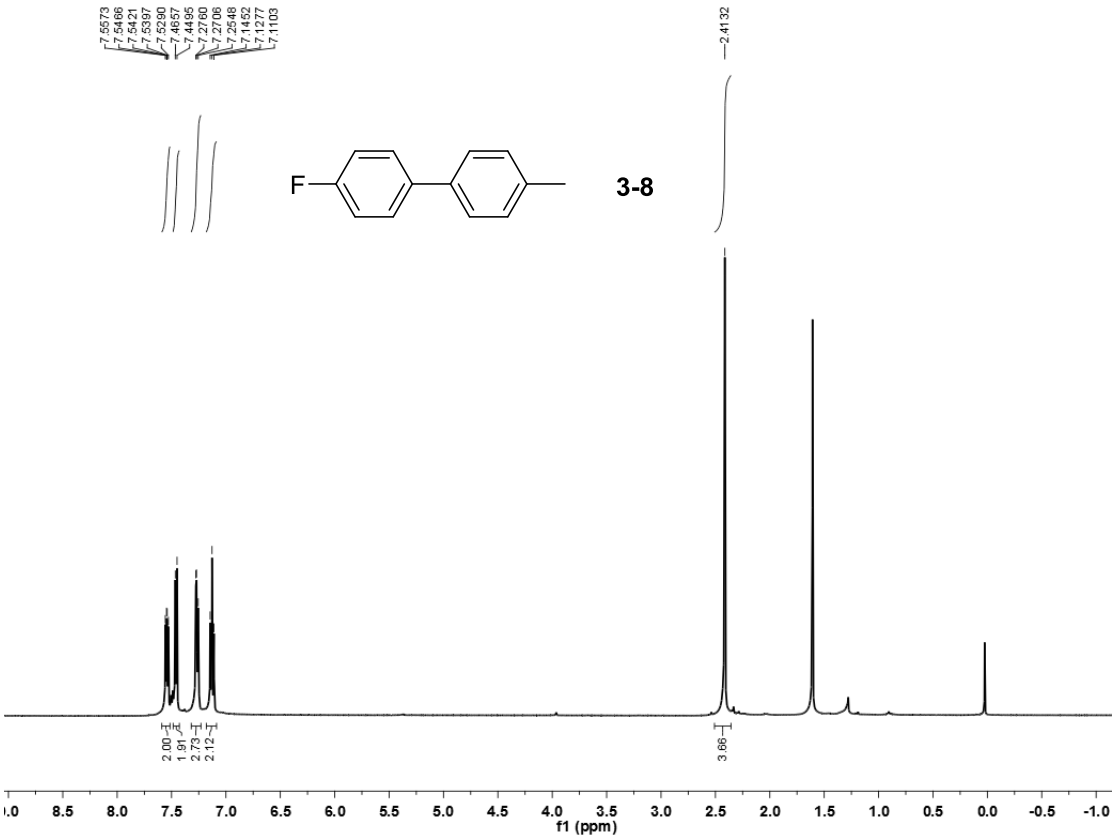
4-Trifluoromethyl-4'-methylbiphenyl (**3-7**)[6]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.69 (br, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H).



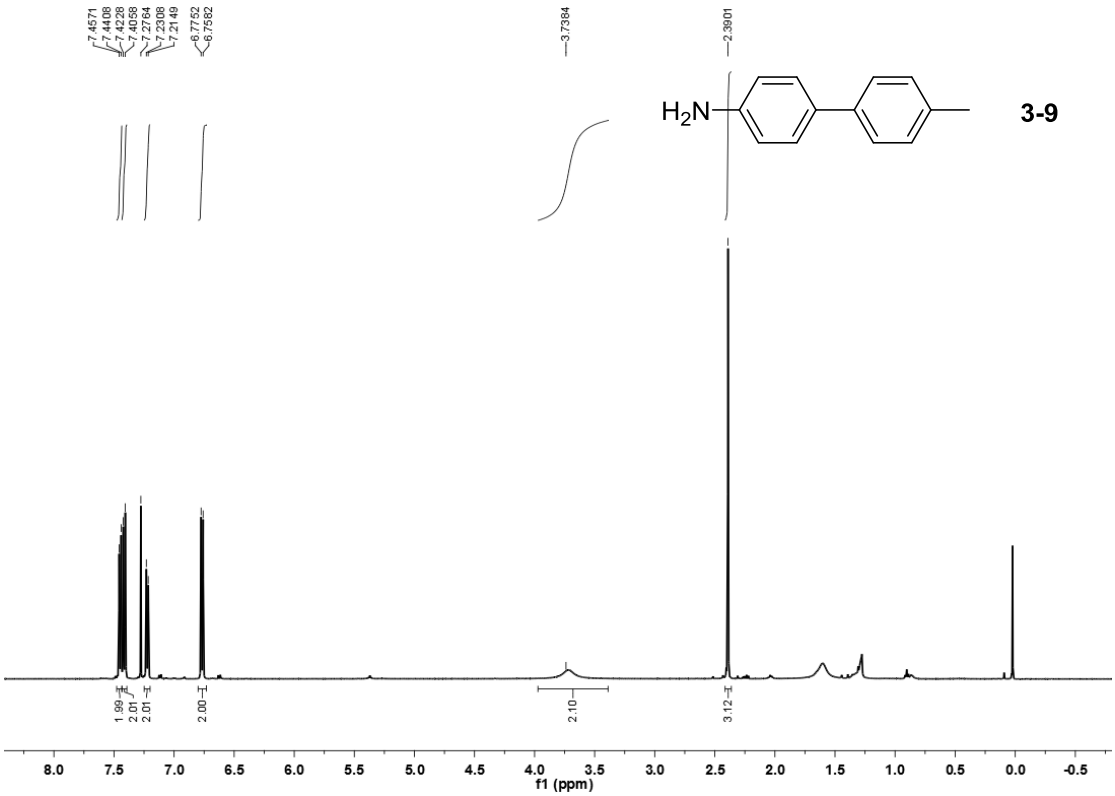
4-Fluoro-4'-methylbiphenyl (**3-8**)[7]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.58-7.51 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 8.5 Hz, 2H), 2.41 (s, 3H).



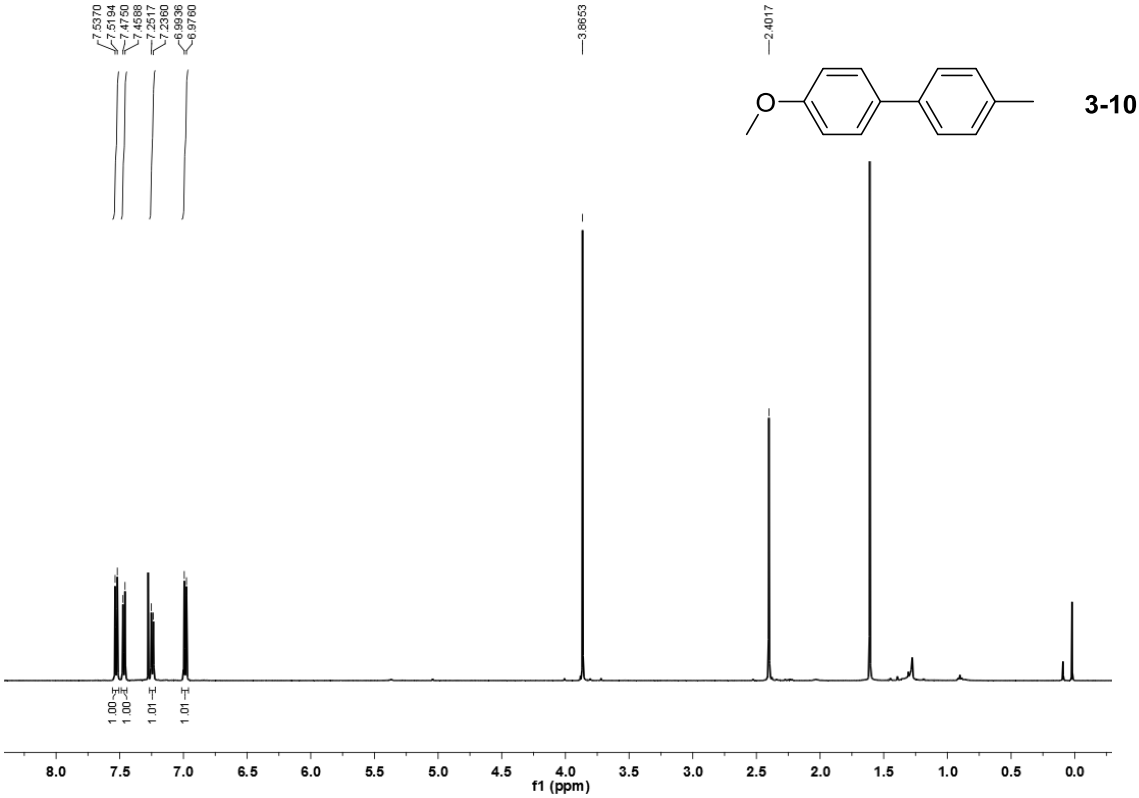
4-Amino-4'-methylbiphenyl (**3-9**)[8]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.45 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.74 (br, 2H), 2.39 (s, 3H).



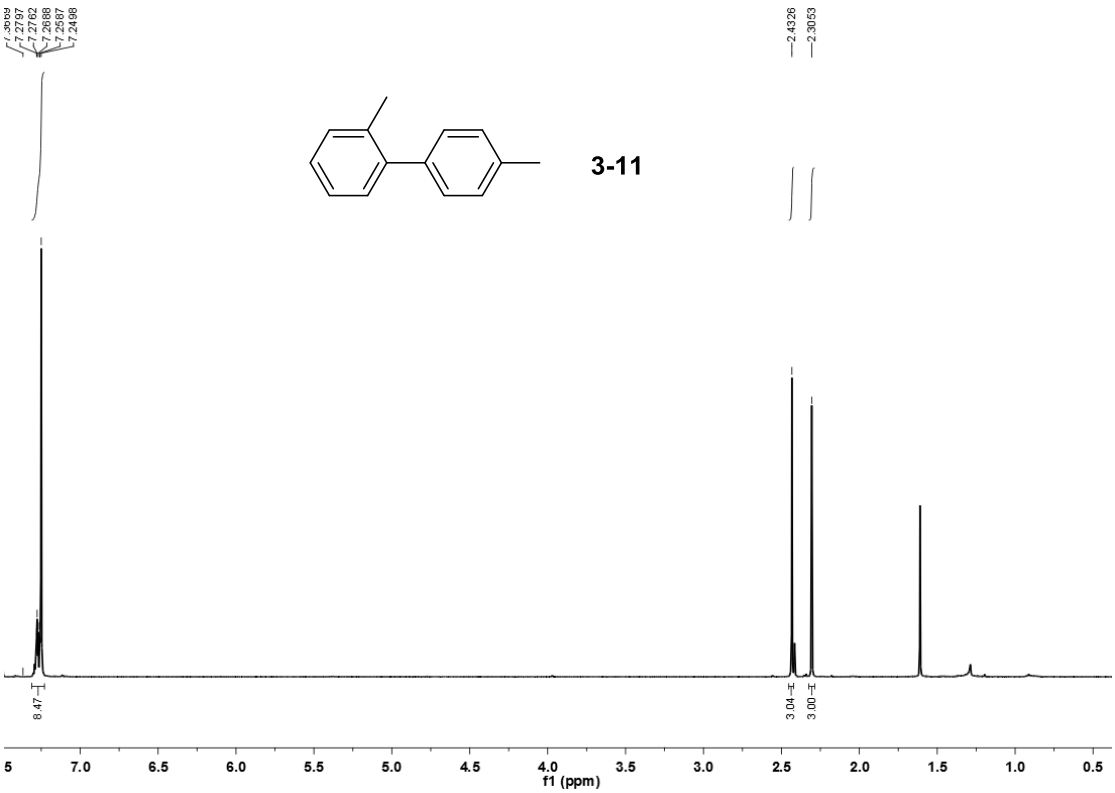
4-Methoxy-4'-methylbiphenyl (**3-10**)[4]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.52 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 2.40 (s, 3H).



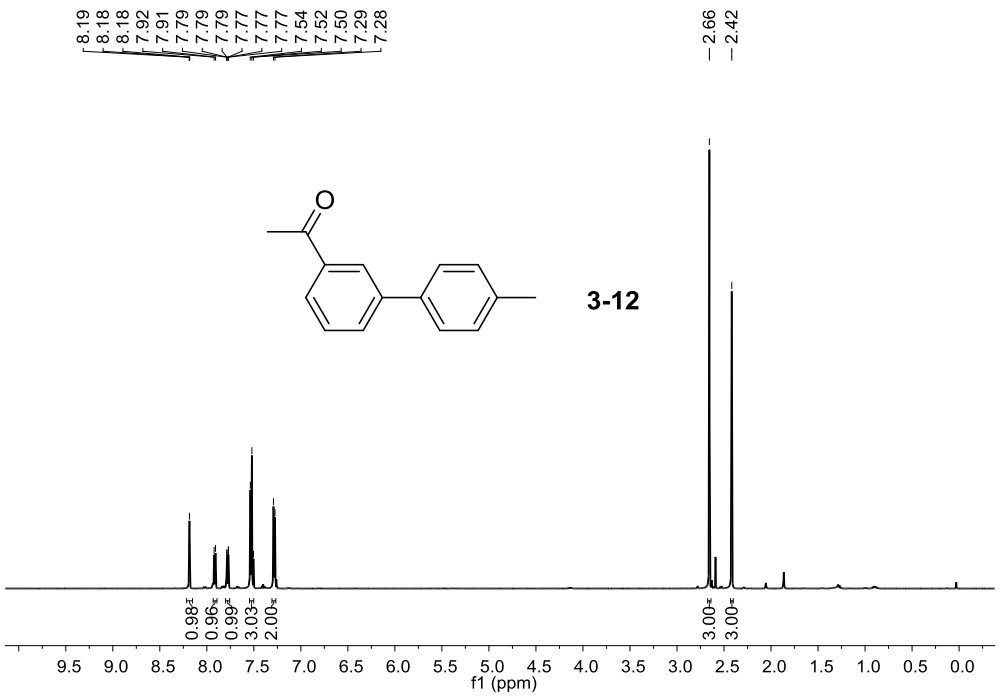
2,4'-Dimethylbiphenyl (**3-11**)[9]

^{1}H NMR ($CDCl_3$, 500 MHz): 7.33-7.21 (m, 8H), 2.43 (s, 3H), 2.31 (s, 3H).



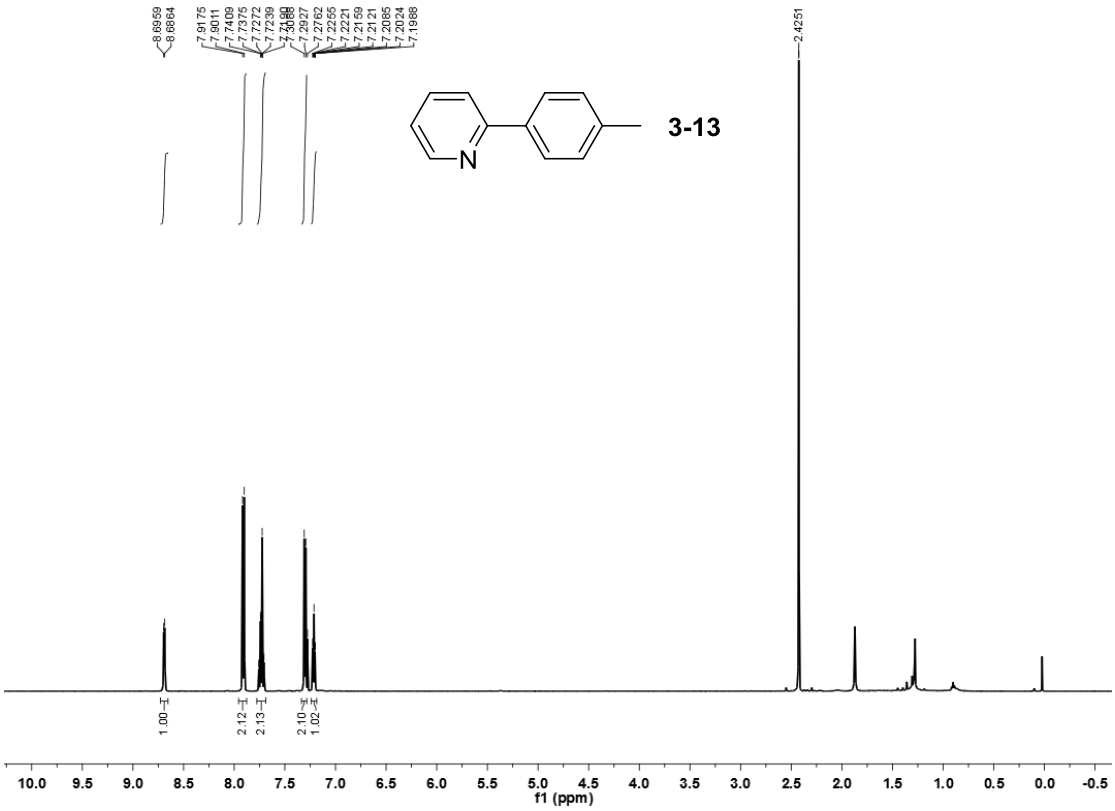
3-Acetyl-4'-methylbiphenyl (**3-12**)[10]

^{1}H NMR ($CDCl_3$, 500 MHz): 8.18 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.9Hz, 1H), 7.56-7.45 (m, 3H), 7.28 (d, *J* = 8.1Hz, 2H), 2.66 (s, 3H), 2.42 (s, 3H).



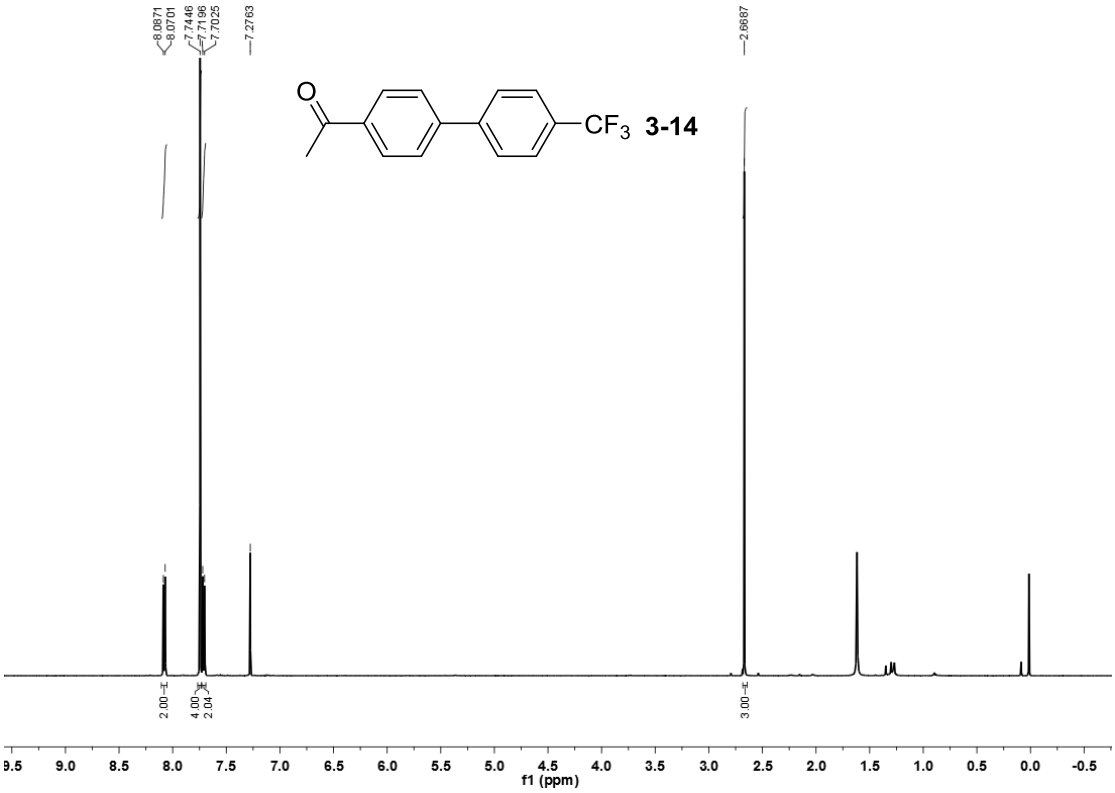
2-(*p*-Tolyl)pyridine (**3-13**)[4]

^{1}H NMR ($CDCl_3$, 500 MHz): 8.69 (d, *J* = 4.7 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.77-7.69 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J*1 = 4.7 Hz, *J*2 = 1.7 Hz, 1H), 2.43 (s, 3H).



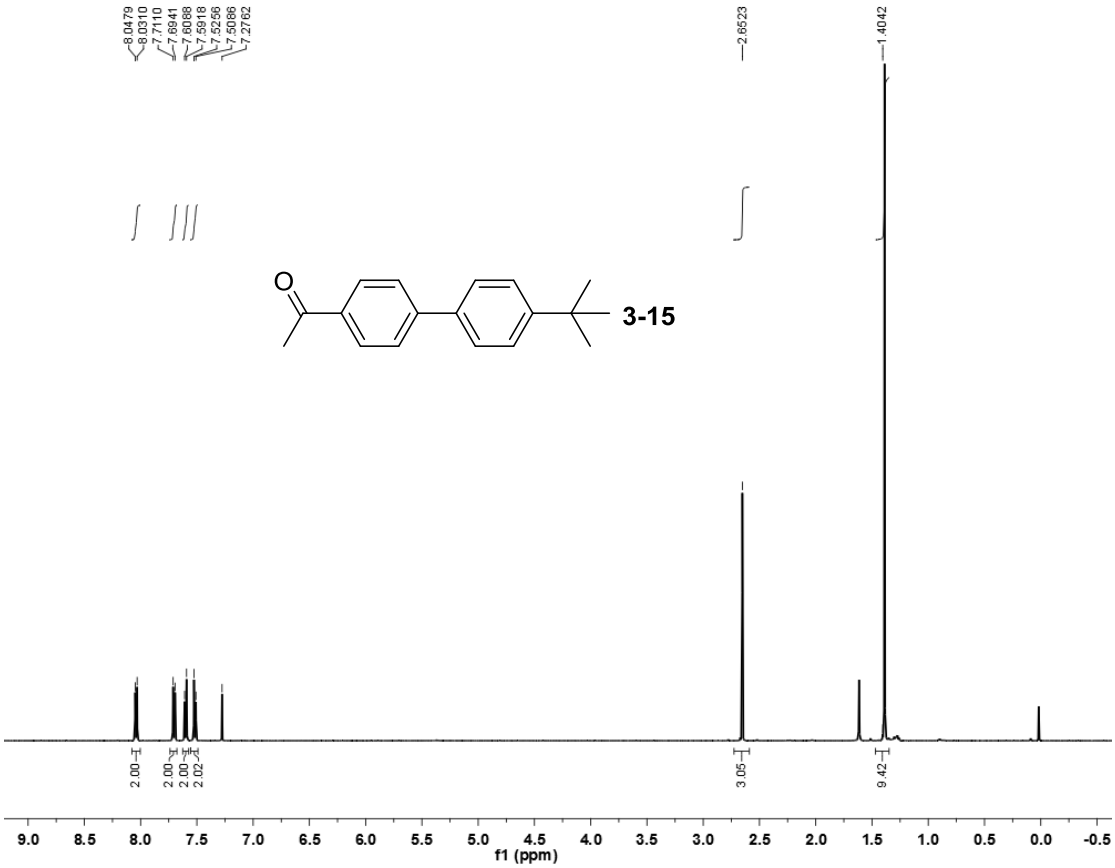
4-Acetyl-4'-trifluoromethylbiphenyl (**3-14**)[11]

^{1}H NMR ($CDCl_3$, 500 MHz): 8.08 (d, *J* = 8.5 Hz, 2H), 7.74 (br, 4H), 7.71 (d, *J* = 8.5 Hz, 2H), 2.69 (s, 3H).



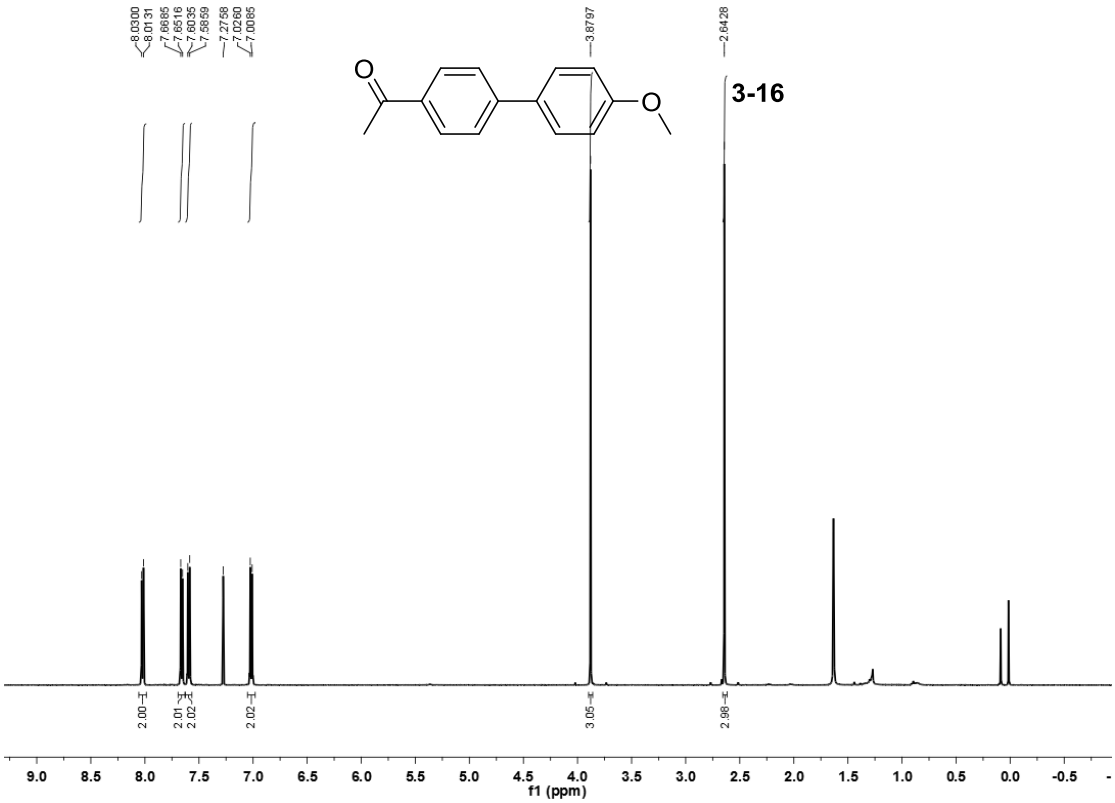
4-Acetyl-4'-(*tert*-butyl)biphenyl (**3-15**)[12]

^{1}H NMR ($CDCl_3$, 500 MHz): 8.04 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 2.65 (s, 3H), 1.40 (s, 9H).



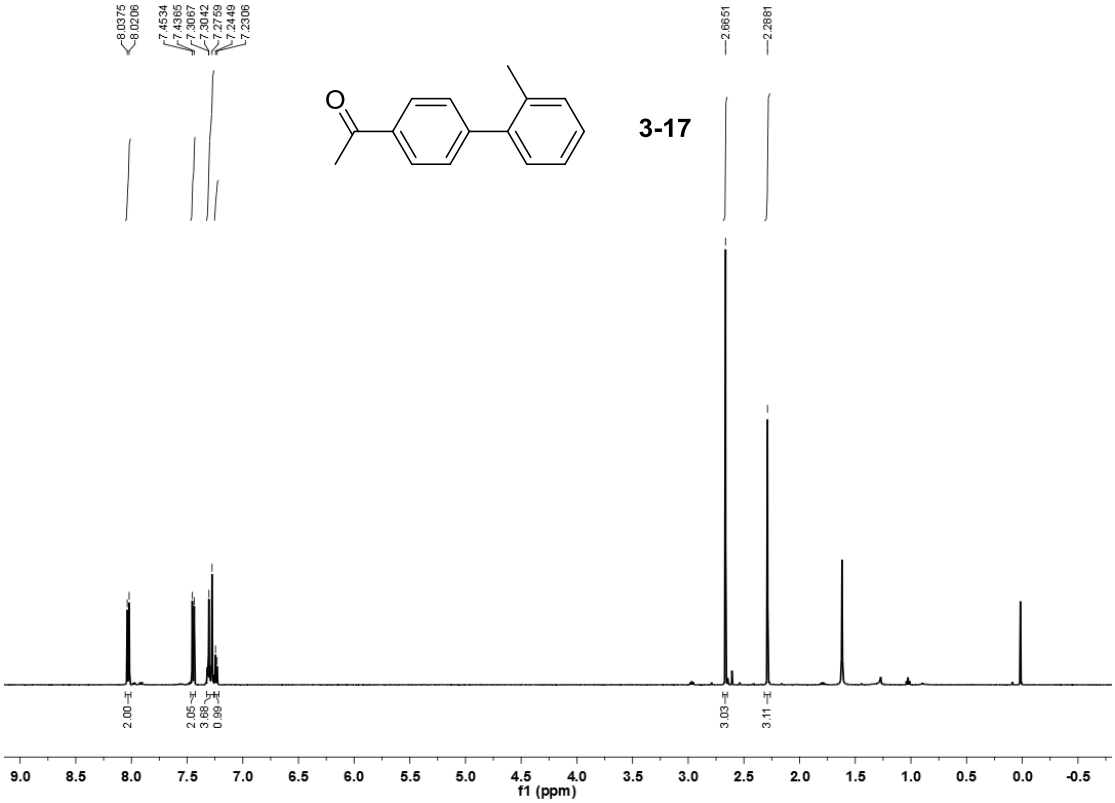
4-Acetyl-4'-methoxylbiphenyl (**3-16**)[10]

^{1}H NMR ($CDCl_3$, 500 MHz): 8.02 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H).



4-Acetyl-2'-methylbiphenyl (**3-17**)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): 8.02 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.32-7.26 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 2.67 (s, 3H), 2.29 (s, 3H).



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