

**Supporting Information**

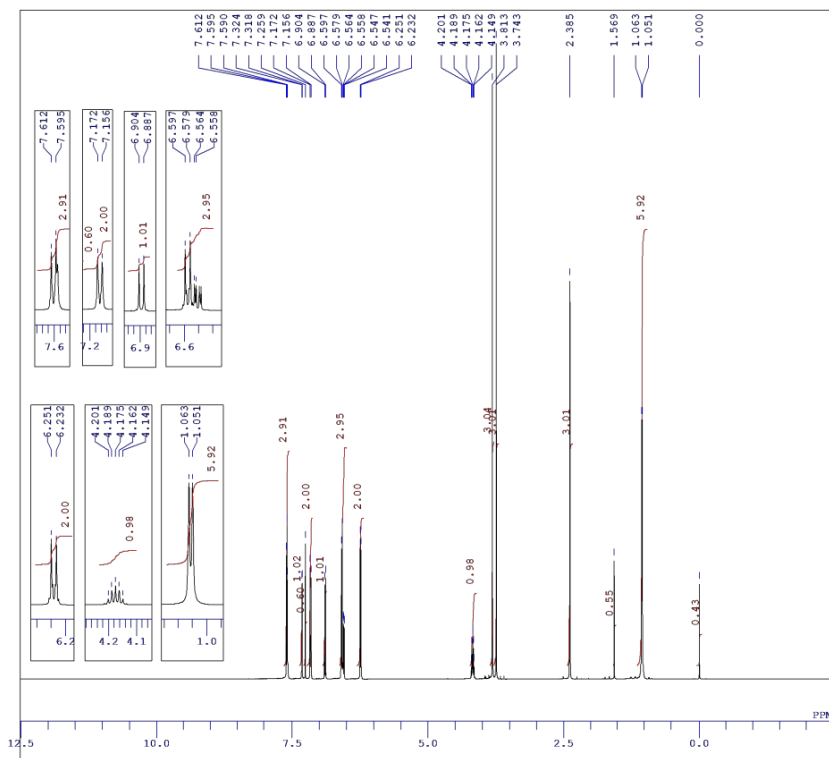
**DIRHODIUM(II)-CATALYZED *ORTHO* C–H AMINATION OF *N*-  
ALKYLDIARYLAMINES**

Motoki Ito,<sup>\*</sup> Mamiko Mori, Tomoya Nakagawa, Miki Hori, Kazuhiro Higuchi, and Shigeo  
Sugiyama<sup>\*</sup>

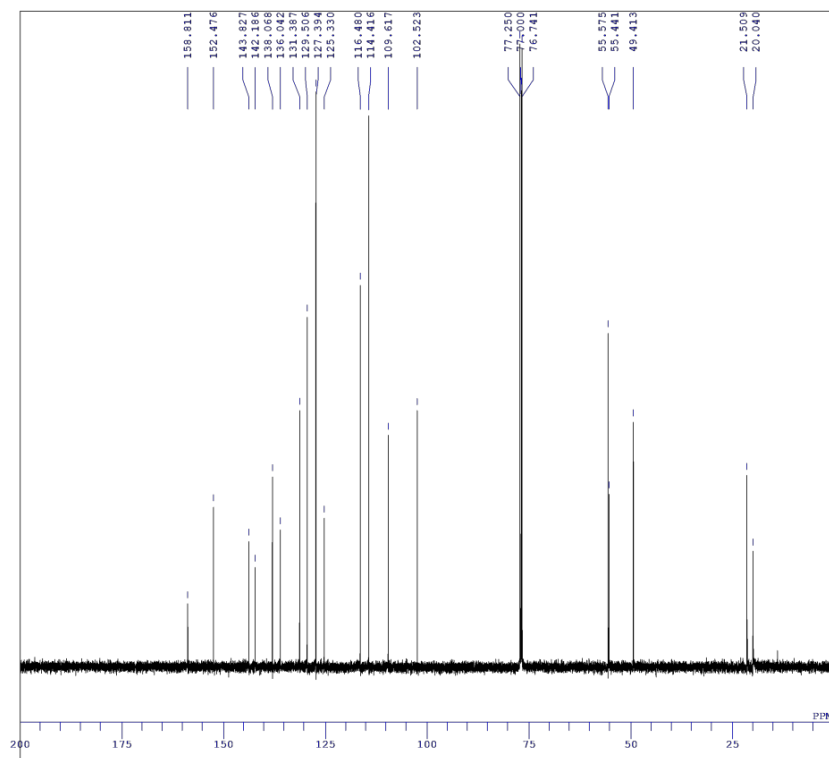
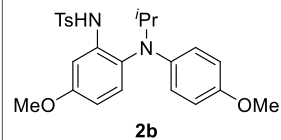
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# N-Isopropyl-4-methoxy-N-(4-methoxyphenyl)-2-(tosylamido)aniline (2b)

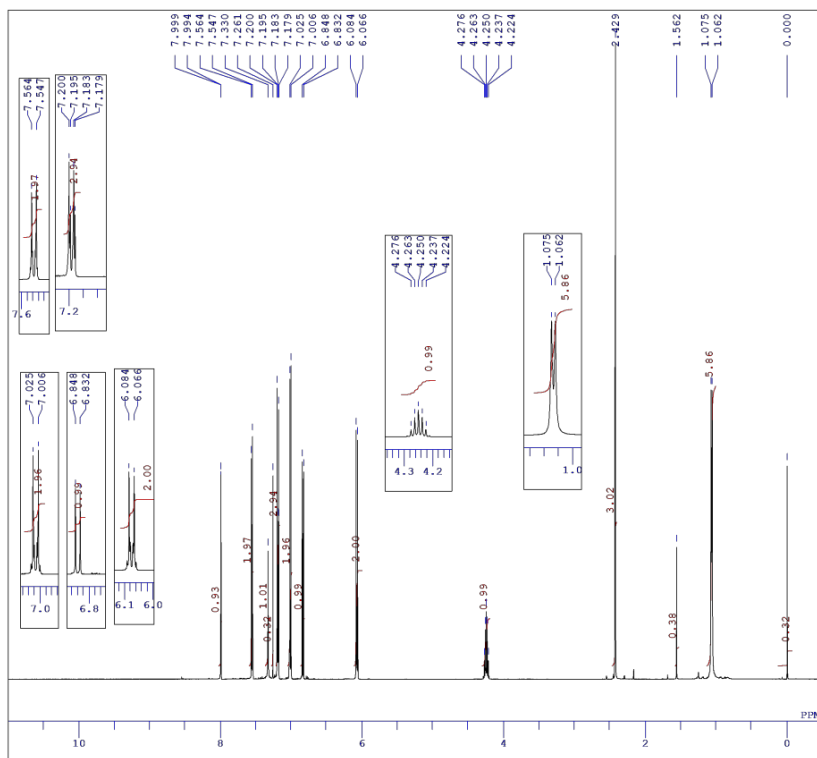


DFILE (4-MeOC6H4)2NiPr+TsNlPh.p  
 COMNT single pulse  
 DATIM 2020-04-02 10:31:05  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFREQ 500.16 MHz  
 OBSETE 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 26214  
 FREQU 7507.51 Hz  
 SCANS 16  
 ACQTM 3.4918 sec  
 PD 5.0000 sec  
 PW 3.00 usec  
 IRNUC 1H  
 CTEMP 24.0 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 REGAIN 46

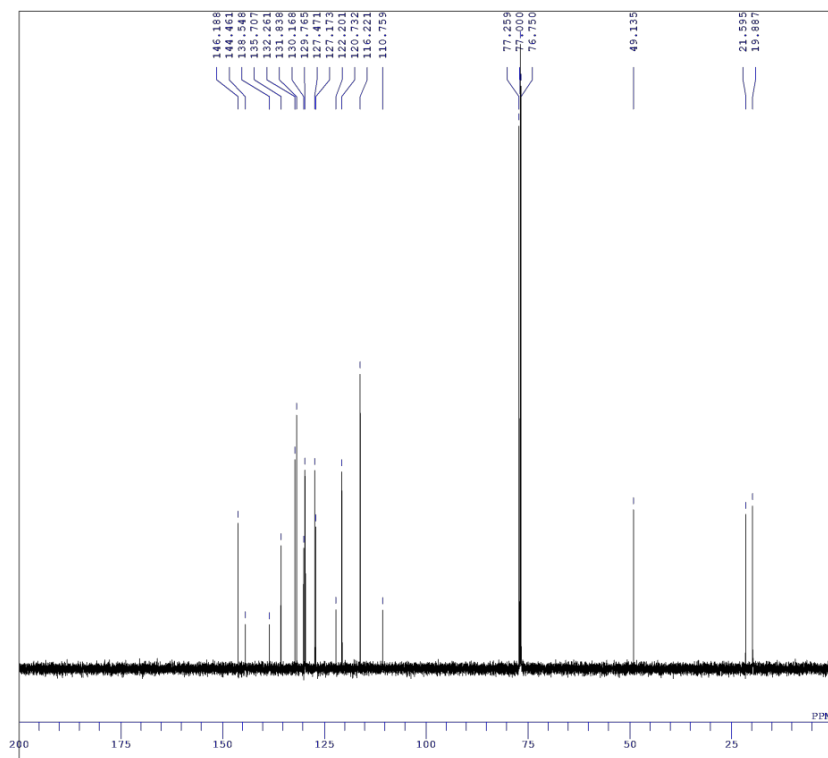
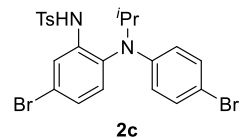


DFILE (4-MeOC6H4)2NiPr+TsNlPh.c  
 COMNT single pulse decoupled ga  
 DATIM 2020-04-02 09:42:20  
 OBNUC 13C  
 EXMOD carbon.jxp  
 OBFREQ 125.77 MHz  
 OBSETE 7.87 KHz  
 OBFIN 4.21 Hz  
 POINT 26214  
 FREQU 31645.57 Hz  
 SCANS 512  
 ACQTM 0.8284 sec  
 PD 2.0000 sec  
 PW 3.46 usec  
 IRNUC 13H  
 CTEMP 24.0 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 0.12 Hz  
 REGAIN 36

# N-Isopropyl-4-bromo-N-(4-bromophenyl)-2-(tosylamido)aniline (2c)

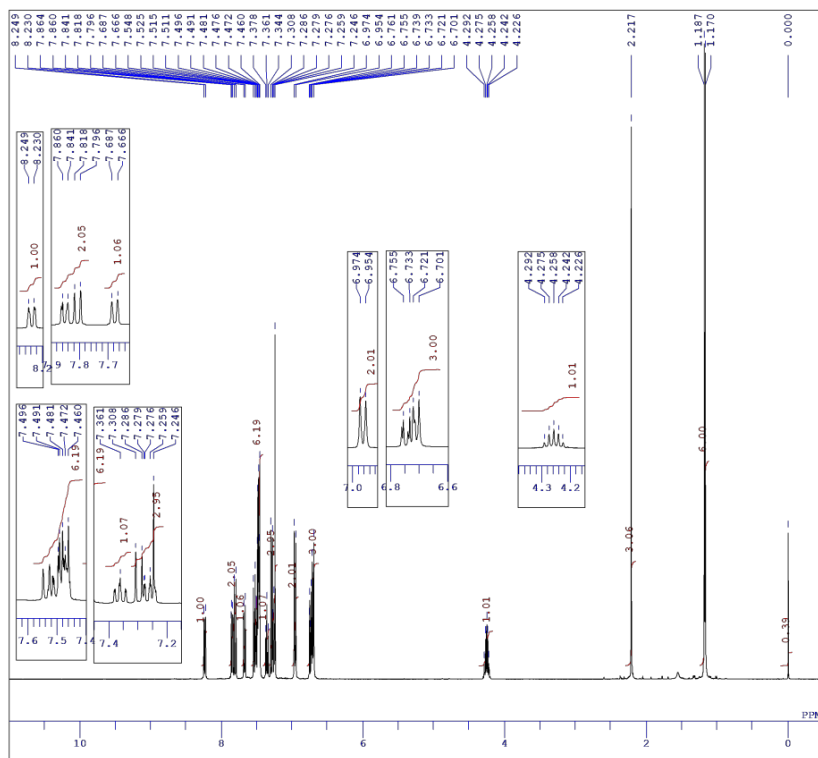


DFILE (4-BrC6H4)2NiPr+TsNIPh\_pr  
 COMNT single pulse  
 DATIM 2020-04-02 10:42:18  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFREQ 500.16 MHz  
 OBSSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 26214  
 FREQU 7507.51 Hz  
 SCANS 16  
 ACQTM 3.4918 sec  
 PD 5.0000 sec  
 PW 3.00 usec  
 IRNUC 1H  
 CTEMP 23.9 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 RGAIN 46

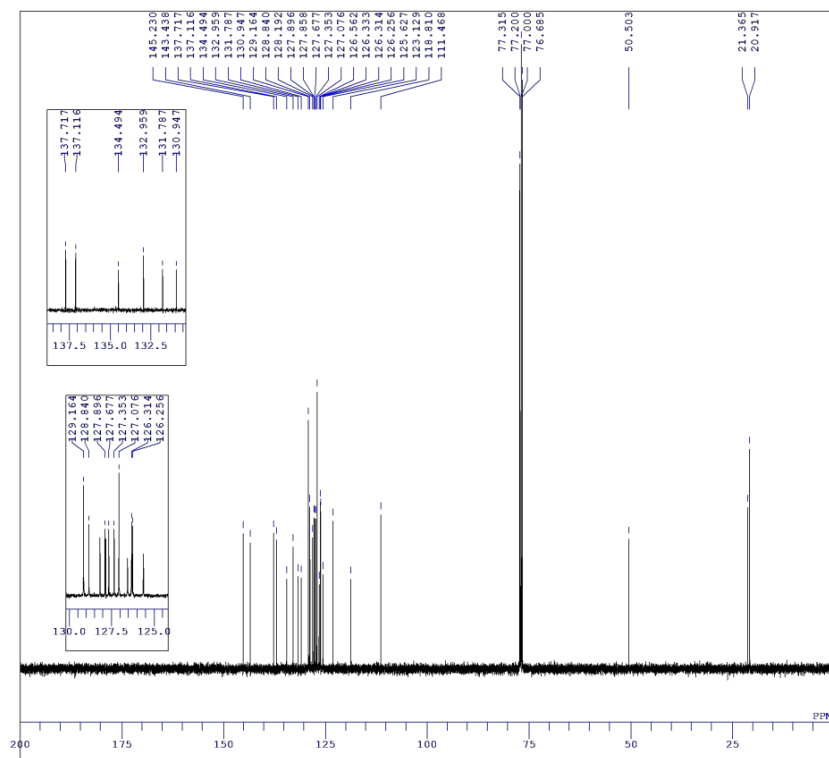
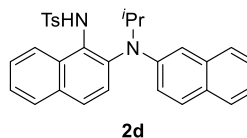


DFILE (4-BrC6H4)2NiPr+TsNIPh\_ca  
 COMNT single pulse decoupled ga  
 DATIM 2020-04-02 10:45:13  
 OBNUC 13C  
 EXMOD carbon.jxp  
 OBFREQ 125.77 MHz  
 OBSSET 7.87 KHz  
 OBFIN 4.21 Hz  
 POINT 26214  
 FREQU 31645.57 Hz  
 SCANS 512  
 ACQTM 0.8284 sec  
 PD 2.0000 sec  
 PW 3.46 usec  
 IRNUC 13C  
 CTEMP 24.0 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 0.12 Hz  
 RGAIN 36

# N-Isopropyl-N-(naphthalen-2-yl)-1-(tosylamido)naphthalen-2-amine (2d)

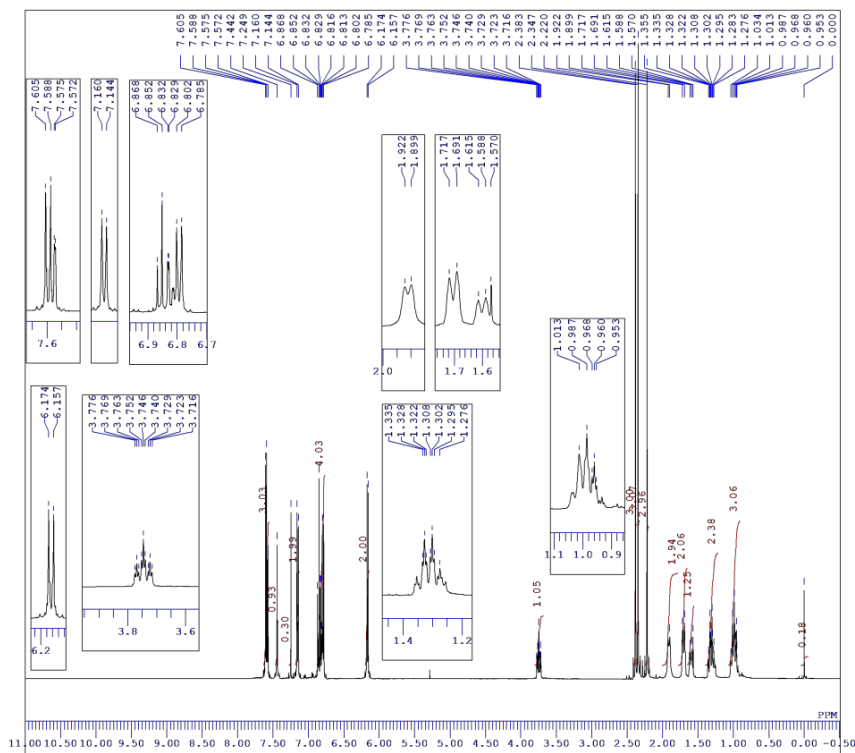


DFILE (2-Naph)2NiPr+TsNIph\_1H-  
 COMNT single pulse  
 DATIM 2020-03-12 12:54:10  
 OBNUC 1H  
 EXMOD single pulse.jxp  
 OBFREQ 399.78 MHz  
 OBSET 4.19 KHz  
 OBFIN 7.29 Hz  
 POINT 26214  
 FREQU 6002.40 Hz  
 SCANS 16  
 ACQTM 4.3673 sec  
 PD 5.0000 sec  
 PW 3.35 usec  
 IRNUC 1H  
 CTEMP 21.3 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 RGAIN 36

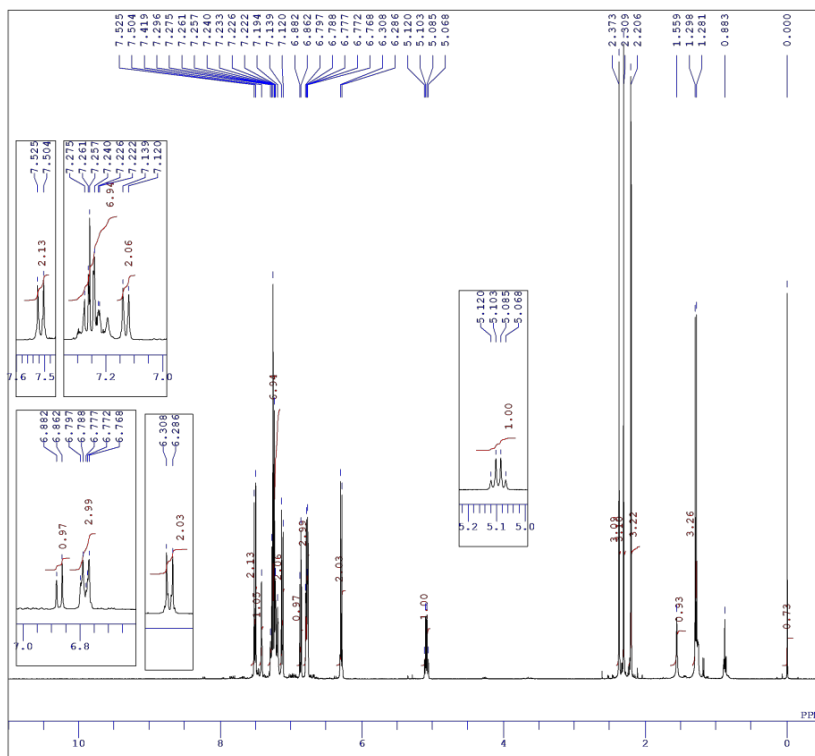


DFILE (2-Naph)2NiPr+TsNIph\_E13C  
 COMNT single pulse decoupled ga  
 DATIM 2020-03-12 12:57:11  
 OBNUC 13C  
 EXMOD single pulse dec  
 OBFREQ 100.53 MHz  
 OBSET 5.35 KHz  
 OBFIN 5.86 Hz  
 POINT 26214  
 FREQU 25125.63 Hz  
 SCANS 720  
 ACQTM 1.0433 sec  
 PD 2.0000 sec  
 PW 3.60 usec  
 IRNUC 13C  
 CTEMP 21.2 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 0.12 Hz  
 RGAIN 60

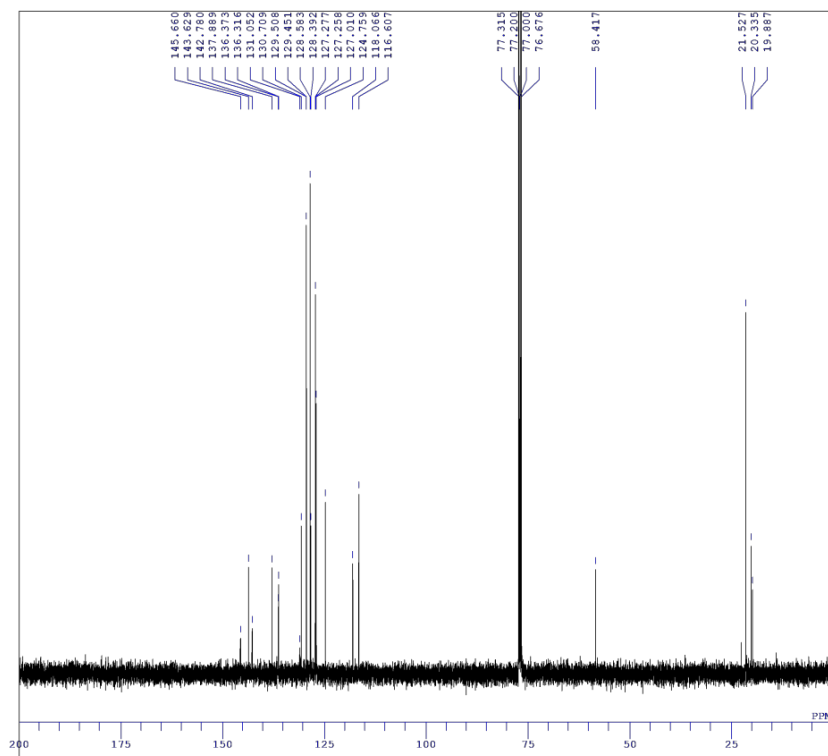
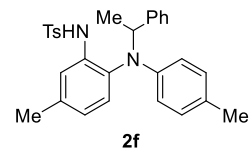
# N-Cyclohexyl-4-methyl-N-(p-tolyl)-2-(tosylamido)aniline (2e)



### 4-Methyl-N-(1-phenylethyl)-N-(p-tolyl)-2-(tosylamido)aniline (2f)

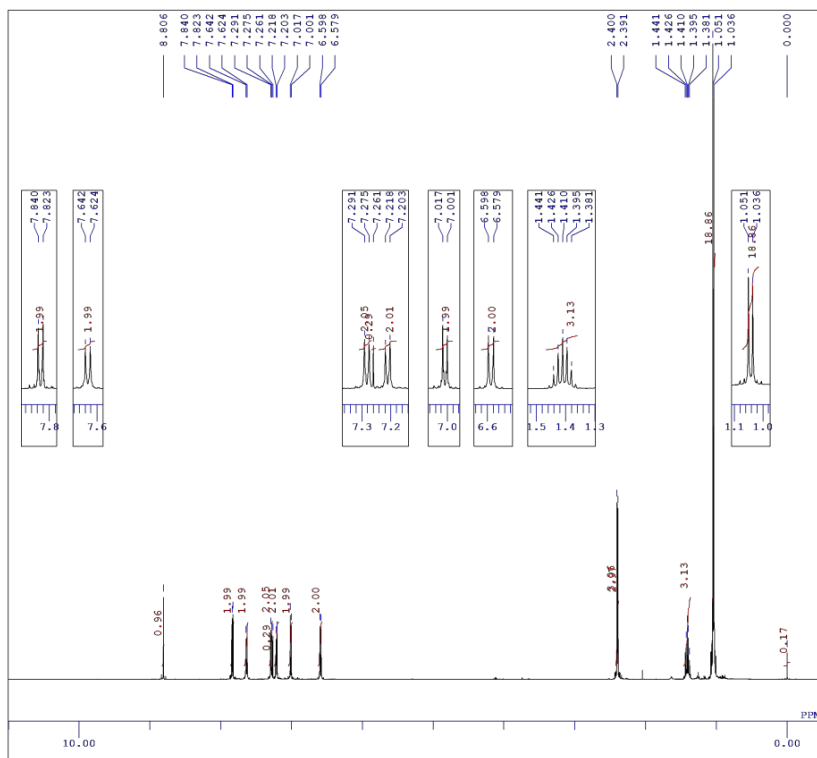


DFILE (p-Tol)2NCH(Ph)Me+TsNIPh\_  
 COMNT single pulse  
 DATIM 2020-03-12 10:36:49  
 OBNUC 1H  
 EXMOD single pulse.jxp  
 OBFREQ 399.78 MHz  
 OBSET 4.19 KHz  
 OBFIN 7.29 Hz  
 POINT 26214  
 FREQU 6002.40 Hz  
 SCANS 16  
 ACQTM 4.3673 sec  
 PD 5.0000 sec  
 PW 3.35 usec  
 IRNUC 1H  
 CTEMP 21.3 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 GAIN 40

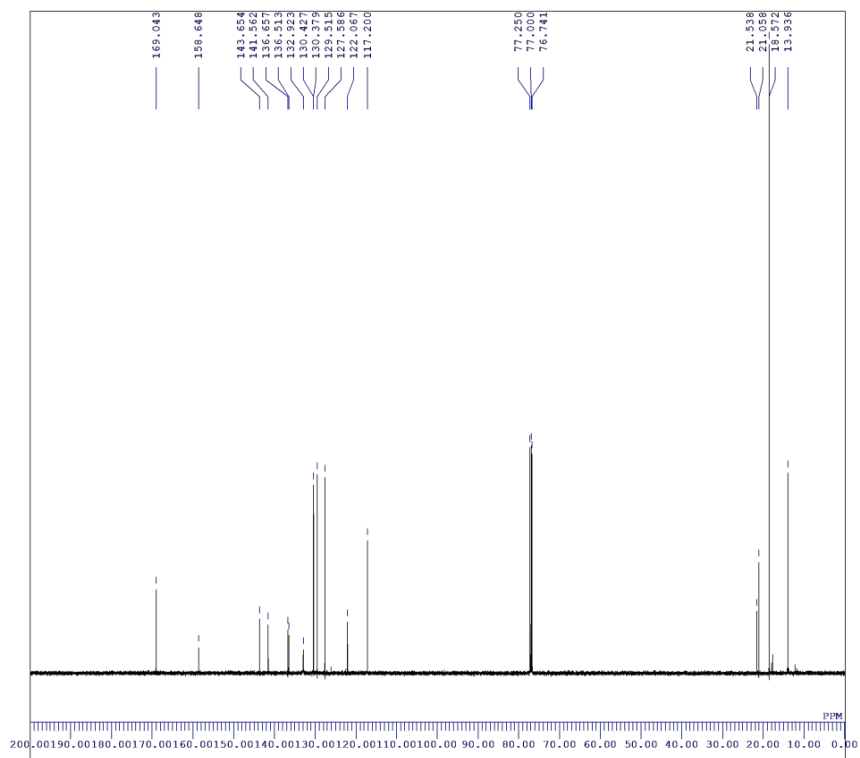
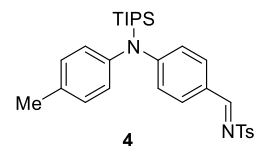


DFILE (p-Tol)2NCH(Ph)Me+TsNIPh  
 COMNT single pulse decoupled ga  
 DATIM 2020-03-12 10:39:55  
 OBNUC 13C  
 EXMOD single pulse dec  
 OBFREQ 100.53 MHz  
 OBSET 5.35 KHz  
 OBFIN 5.86 Hz  
 POINT 26214  
 FREQU 25125.63 Hz  
 SCANS 1800  
 ACQTM 1.0433 sec  
 PD 2.0000 sec  
 PW 3.60 usec  
 IRNUC 13C  
 CTEMP 22.2 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 0.12 Hz  
 GAIN 60

### 4-Methyl-N-{4-[*p*-tolyl(triisopropylsilyl)amino]benzylidene}benzenesulfonamide (4)

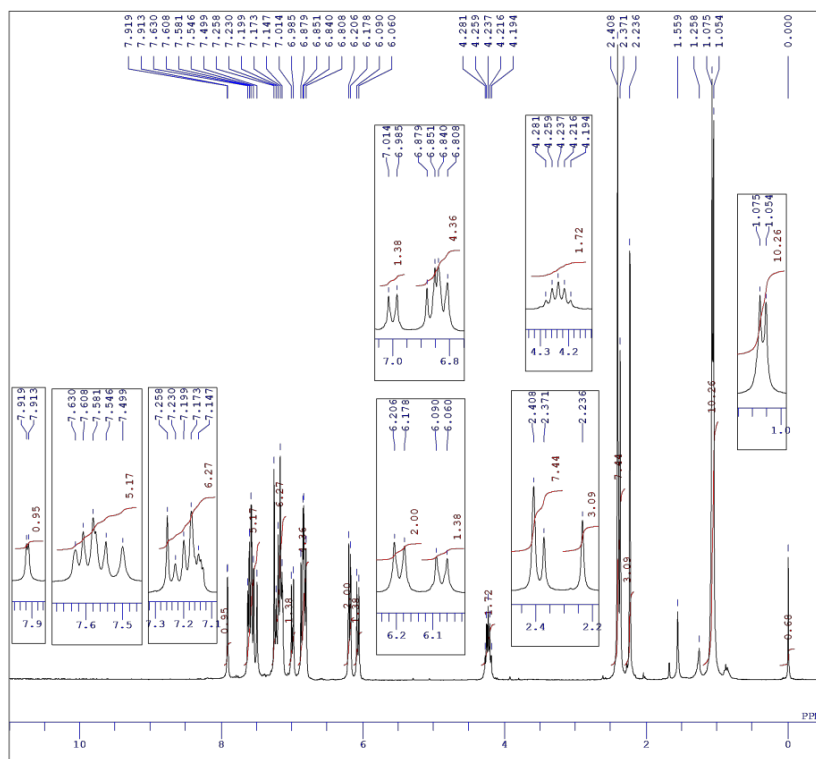


DFILE (p-Tol)2NTIPS+TsNlPh\_prot  
 COMNT single pulse  
 DATIM 2020-03-21 13:01:19  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFREQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 26214  
 FREQU 7507.51 Hz  
 SCANS 16  
 ACQTM 3.4918 sec  
 PD 5.0000 sec  
 PW 3.00 usec  
 IRNUC 1H  
 CTEMP 23.5 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 RGAIN 36

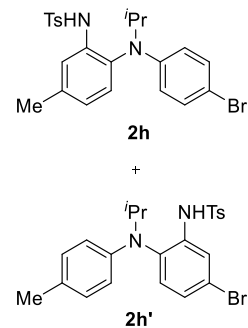


DFILE (p-Tol)2TIPS+TsNlPh\_carbo  
 COMNT single pulse decoupled ga  
 DATIM 2020-03-21 13:04:14  
 OBNUC 13C  
 EXMOD carbon.jxp  
 OBFREQ 125.77 MHz  
 OBSET 7.87 KHz  
 OBFIN 4.21 Hz  
 POINT 26214  
 FREQU 31645.57 Hz  
 SCANS 512  
 ACQTM 0.8284 sec  
 PD 2.0000 sec  
 PW 3.46 usec  
 IRNUC 13C  
 CTEMP 23.6 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 0.12 Hz  
 RGAIN 36

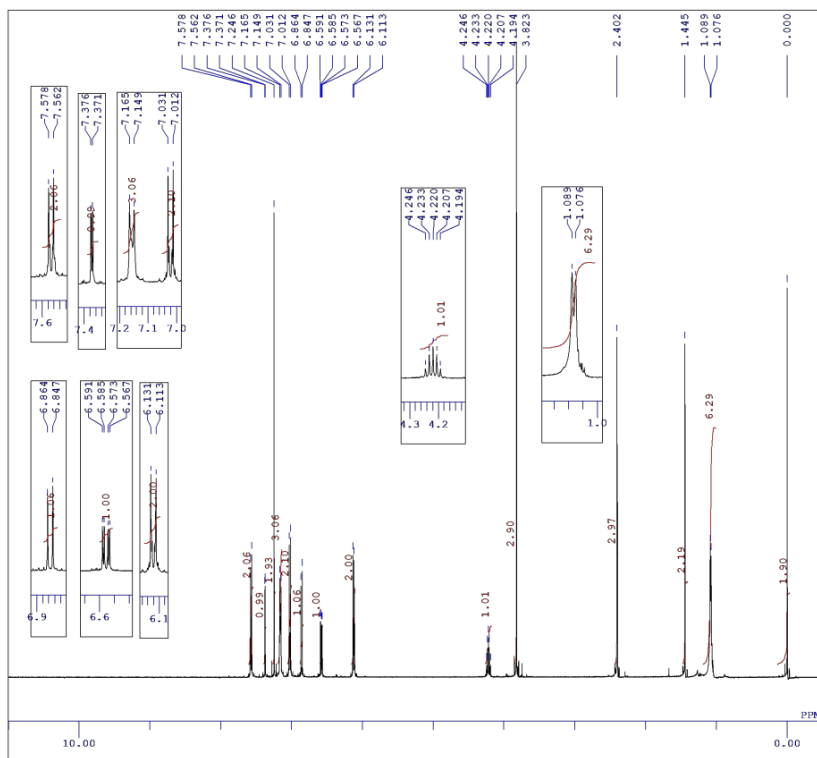
***N*-(4-Bromophenyl)-*N*-isopropyl-4-methyl-2-(tosylamido)aniline (2h) and 4-bromo-*N*-isopropyl-*N*-(*p*-tolyl)-2-(tosylamido)aniline (2h')**



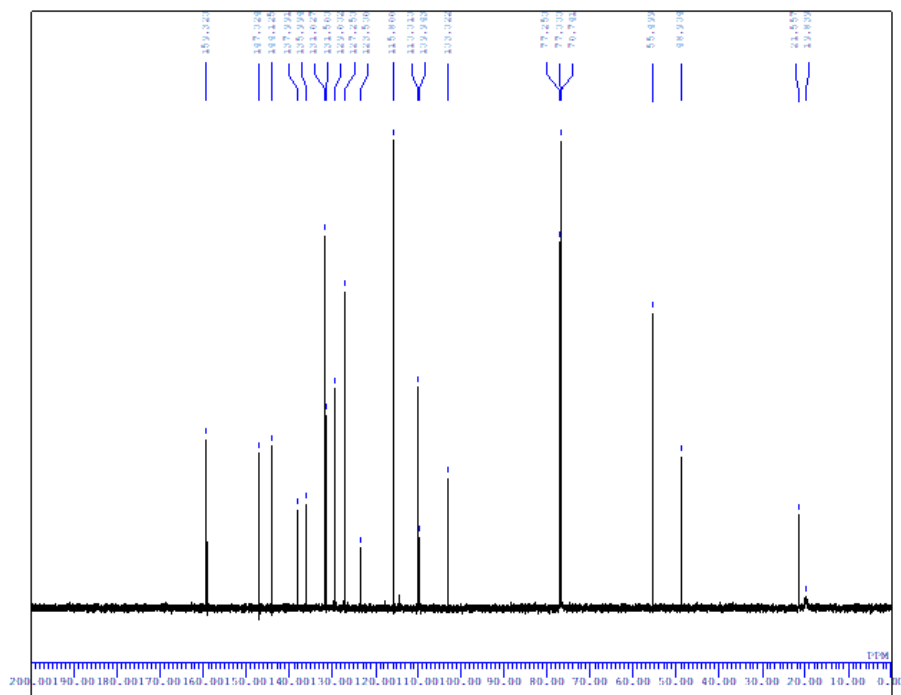
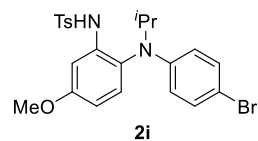
DFILE (p-Tol)(4-BrC6H4)NIPrTsN  
 CDMT (p-Tol)(4-BrC6H4)NIPrTsN  
 DATUM Wed Mar 18 14:41:36 2020  
 OBNUC 1H  
 EXMOD NON  
 OFFSET 300.40 MHz  
 OBSFQ 130.00 KHz  
 OBFIN 1150.00 Hz  
 POINT 32768  
 FREQU 6006.01 Hz  
 SCANS 16  
 ACQTM 5.4559 sec  
 PD 1.5440 sec  
 PW1 5.20 usec  
 IRNUC 1H  
 CRMP 25.7 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 1.20 Hz  
 REGAIN 17



**N-(4-Bromophenyl)-N-isopropyl-4-methoxy-2-(tosylamido)aniline (2i)**

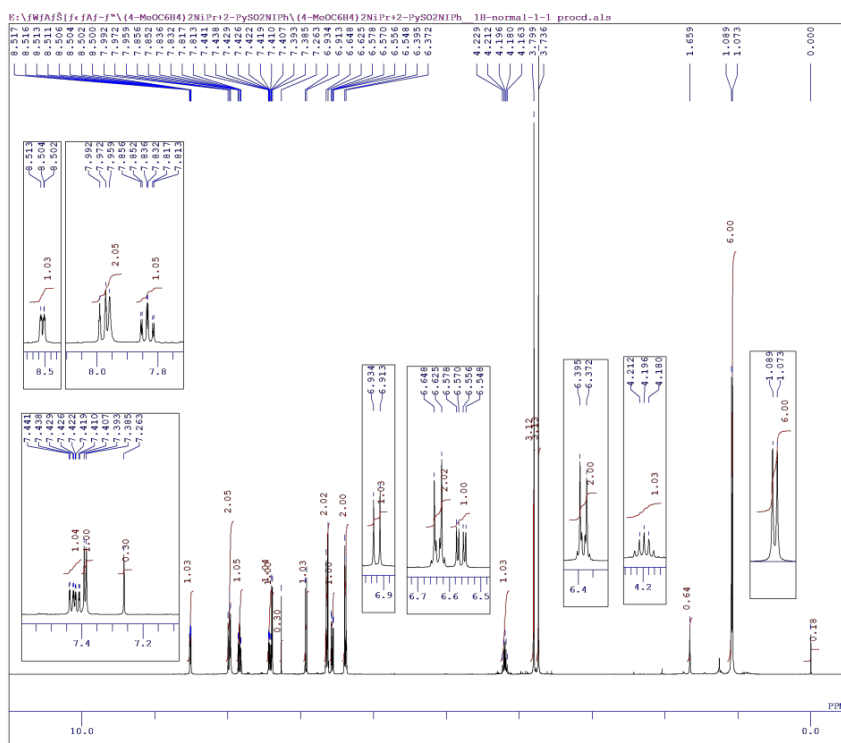


DFILE (4-MeO6H4) (4-Br6H4)NiPr+T  
 COMNT single pulse  
 DATIM 2020-03-16 11:11:24  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFRQ 500.16 MHz  
 OBSSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 26214  
 FRFQU 7507.51 Hz  
 SCANS 16  
 ACQTM 3.4918 sec  
 PD 5.0000 sec  
 PW 3.00 usec  
 TRNUC 1H  
 CTEMP 60.0 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BP 0.12 Hz  
 RGAIN 66

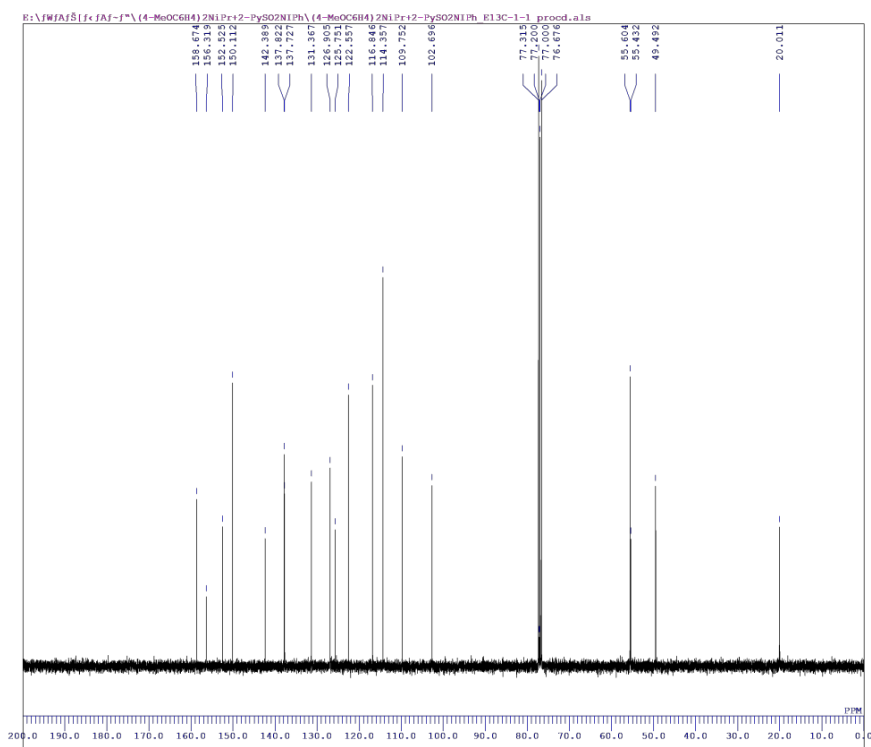




# N-Isopropyl-4-methoxy-N-(4-methoxyphenyl)-2-[(2-pyridylsulfonyl)amido]aniline (5)



OFILE (4-MeOC6H4)2NiPr+2-PyS  
 COMNT single\_pulse  
 DATIM 2020-06-01 14:08:21  
 ORNOC 1H  
 EXMOD single\_pulse.jpg  
 OFFRQ 399.78 MHz  
 ORSET 4.19 KHz  
 OFBIN 7.29 Hz  
 POINT 26214  
 FREQU 6002.40 Hz  
 SCANS 16  
 ACQTM 4.3673 sec  
 PD 5.0000 sec  
 FWI 3.35 usec  
 IRNOC 1H  
 CTZMP 22.6 c  
 SLVNF CDCL3  
 EXREF 0.00 ppm  
 BF 0.17 Hz  
 RGAIN 36



OFILE (4-MeOC6H4)2NiPr+2-PyS  
 COMNT single\_pulse\_decoupled  
 DATIM 2020-06-01 14:11:22  
 ORNOC 13C  
 EXMOD single\_pulse\_dec  
 OFFRQ 100.53 MHz  
 ORSET 5.35 KHz  
 OFBIN 5.06 Hz  
 POINT 26214  
 FREQU 25125.63 Hz  
 SCANS 512  
 ACQTM 1.0433 sec  
 PD 2.0000 sec  
 FWI 3.60 usec  
 IRNOC 13C  
 CTZMP 21.6 c  
 SLVNF CDCL3  
 EXREF 77.00 ppm  
 BF 0.17 Hz  
 RGAIN 60

