Supplementary Material

Carboxylic acid as a traceless directing group for palladium-catalyzed proaromatic C(alkenyl)–H arylation

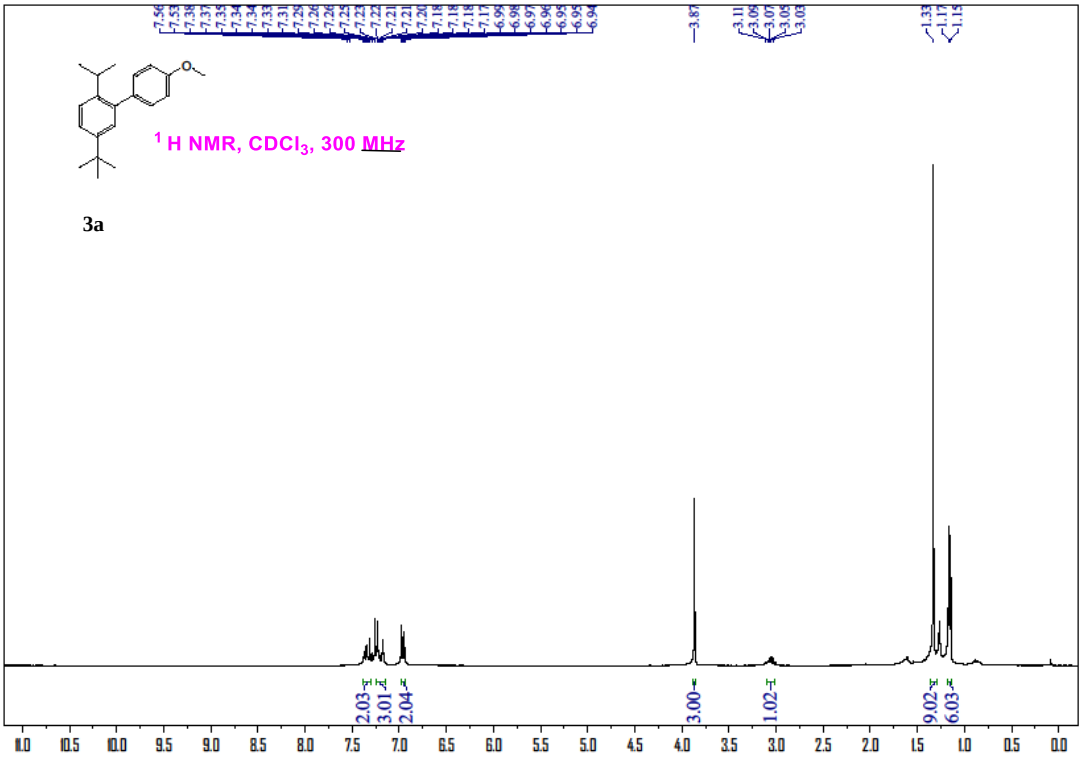
Veerabhushanam Kadiyala, Hsiao-Fen Hsu, and Chih-Ming Chou*

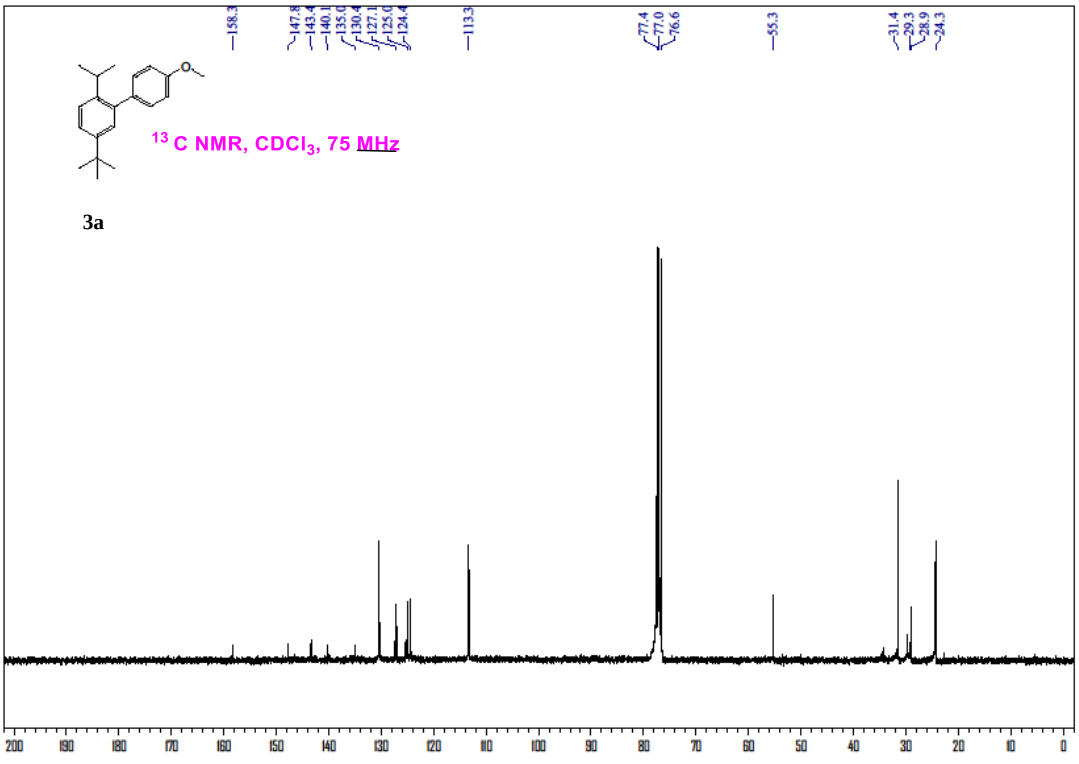
Department of Applied Chemistry, National University of Kaohsiung 700, Kaohsiung University Road Nanzih District, 81148 Kaohsiung, Taiwan
Email: cmchou@nuk.edu.tw

Table of Contents

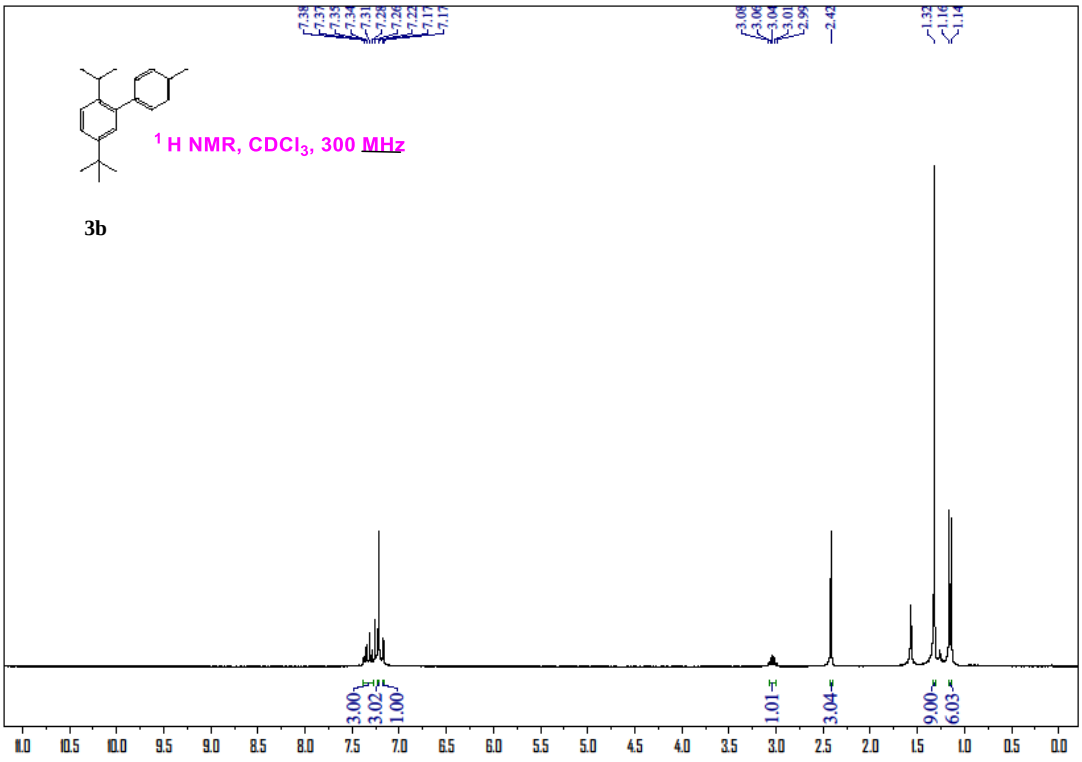
Copies of ^{1}H and ^{13}C NMR spectra (**3a-3t**)

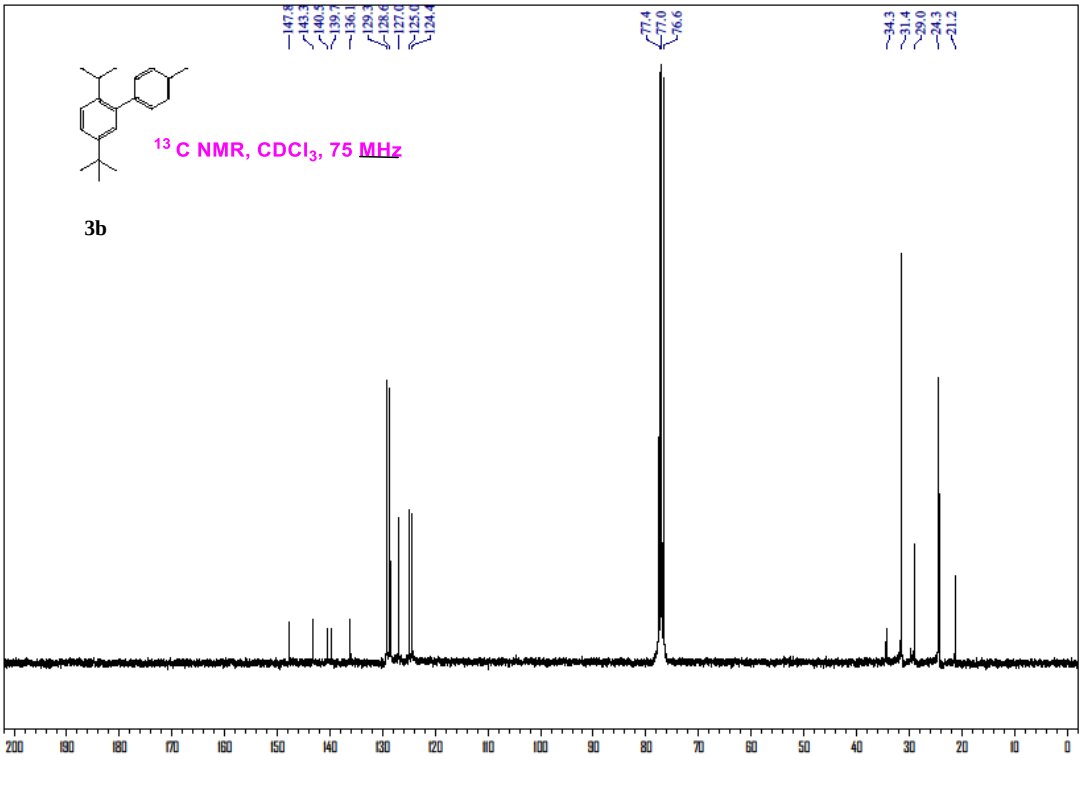
5-(*tert*-butyl)-2-isopropyl-4'-methoxy-1,1'-biphenyl (3a)



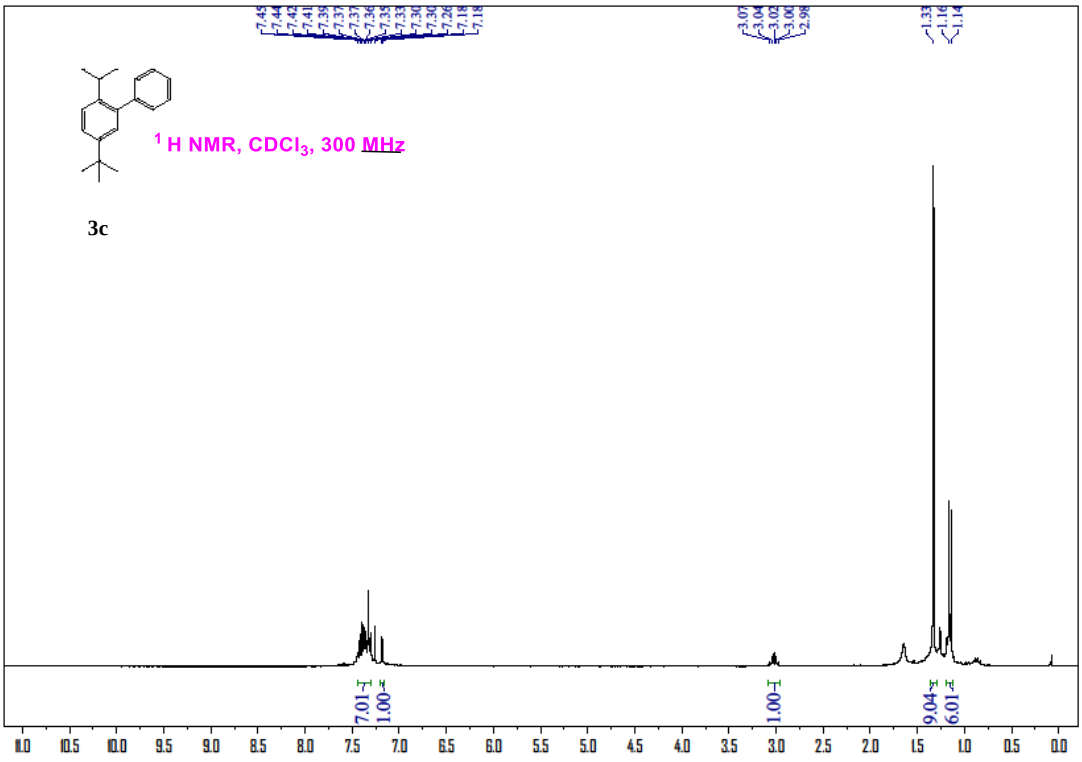


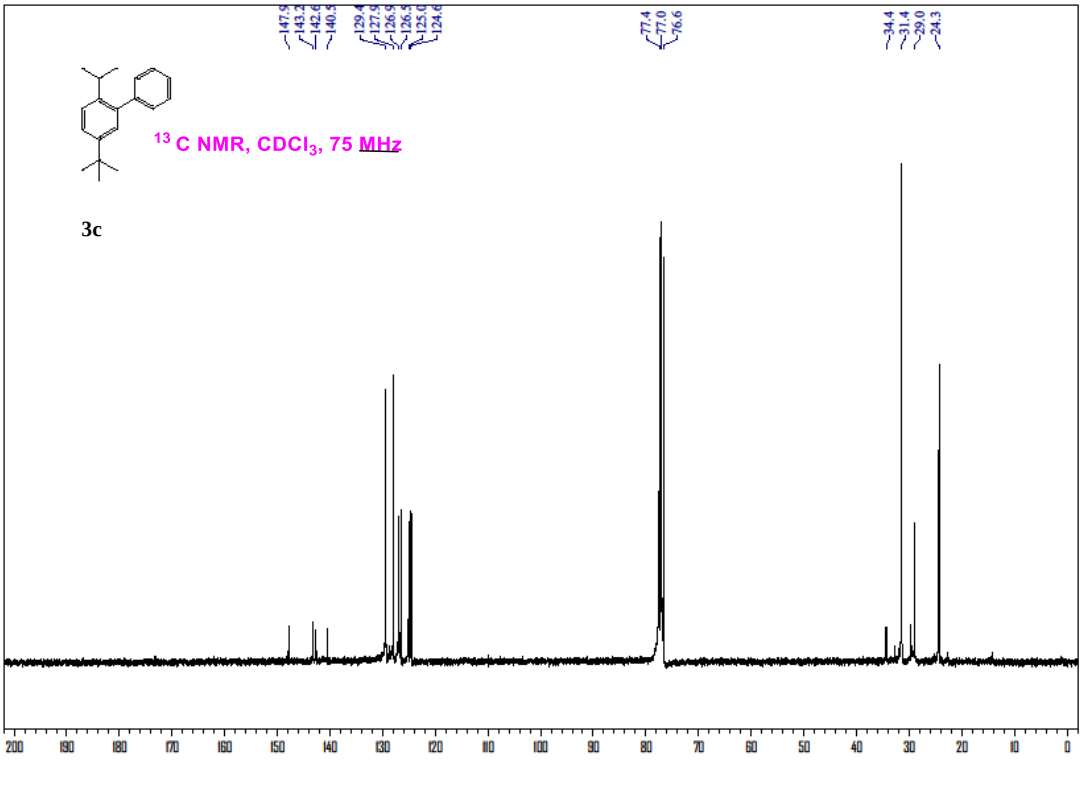
5-(*tert*-butyl)-2-isopropyl-4'-methyl-1,1'-biphenyl (3b)



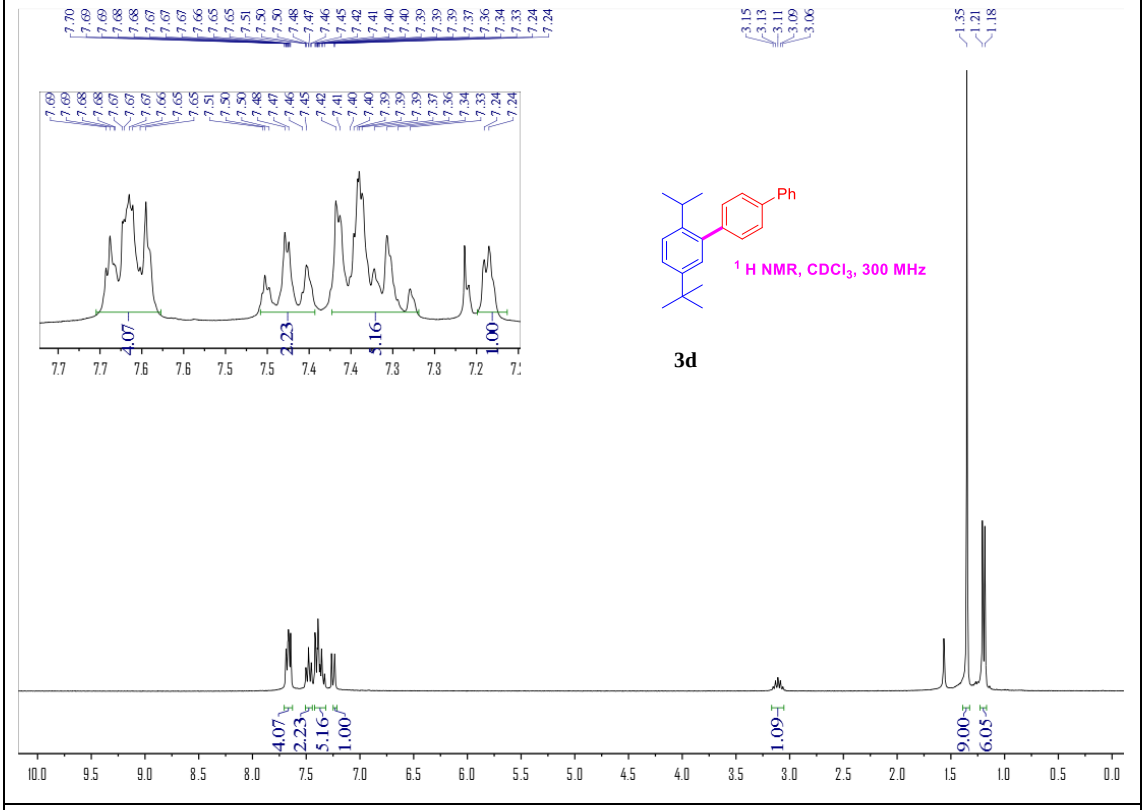


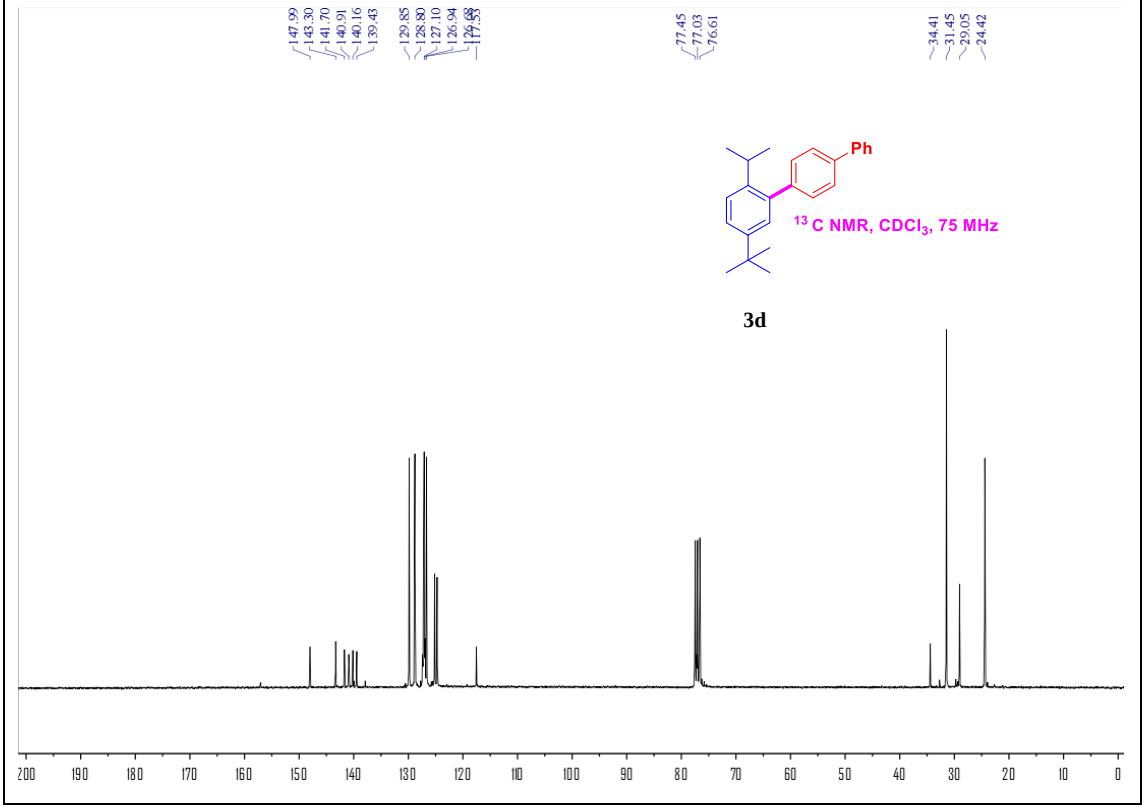
5-(*tert*-butyl)-2-isopropyl-1,1'-biphenyl (3c)



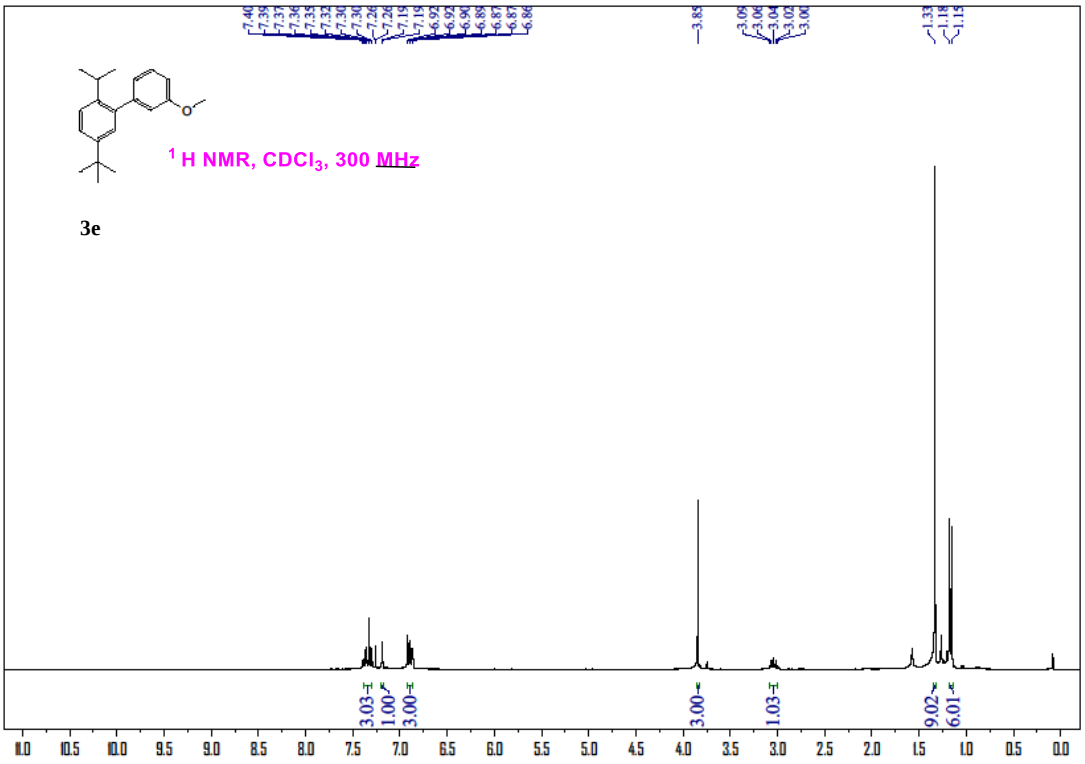


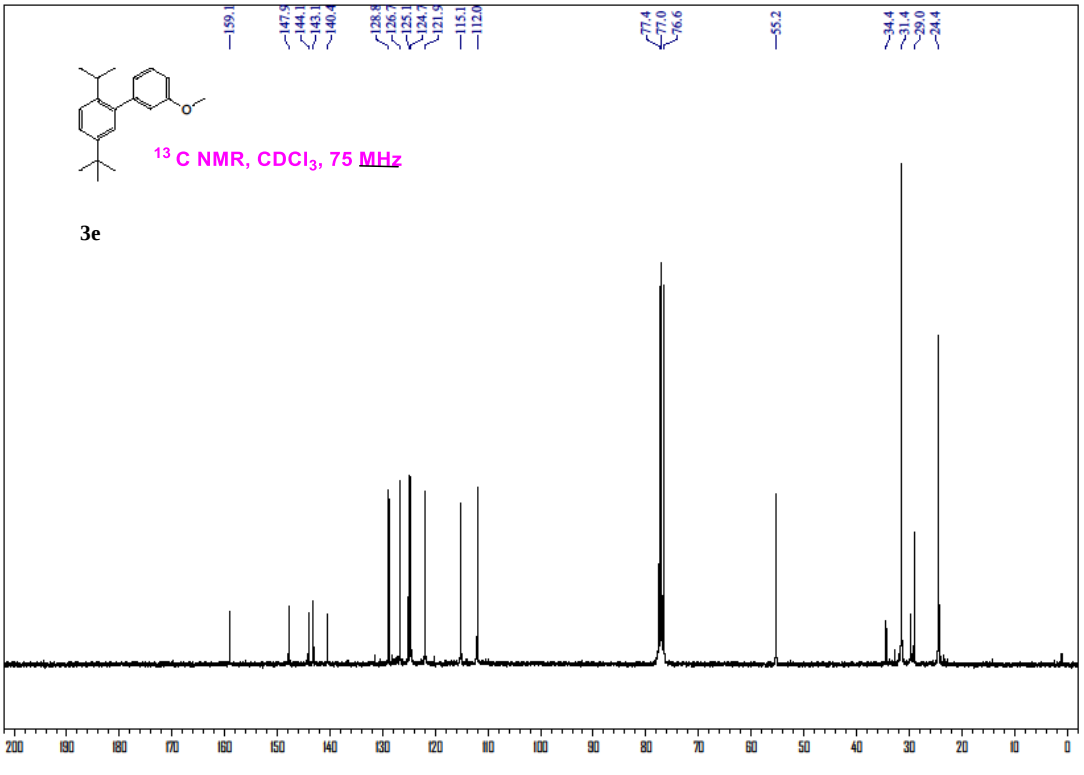
5-(*tert*-butyl)-2-isopropyl-1,1':4',1''-terphenyl (3d)



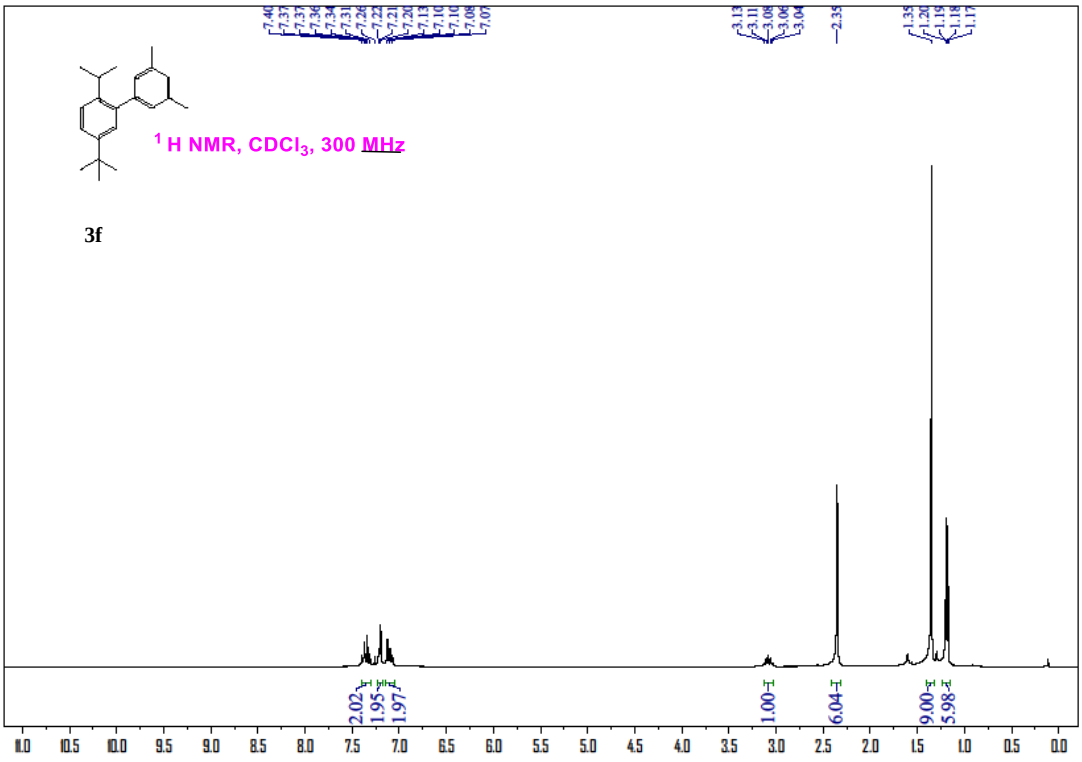


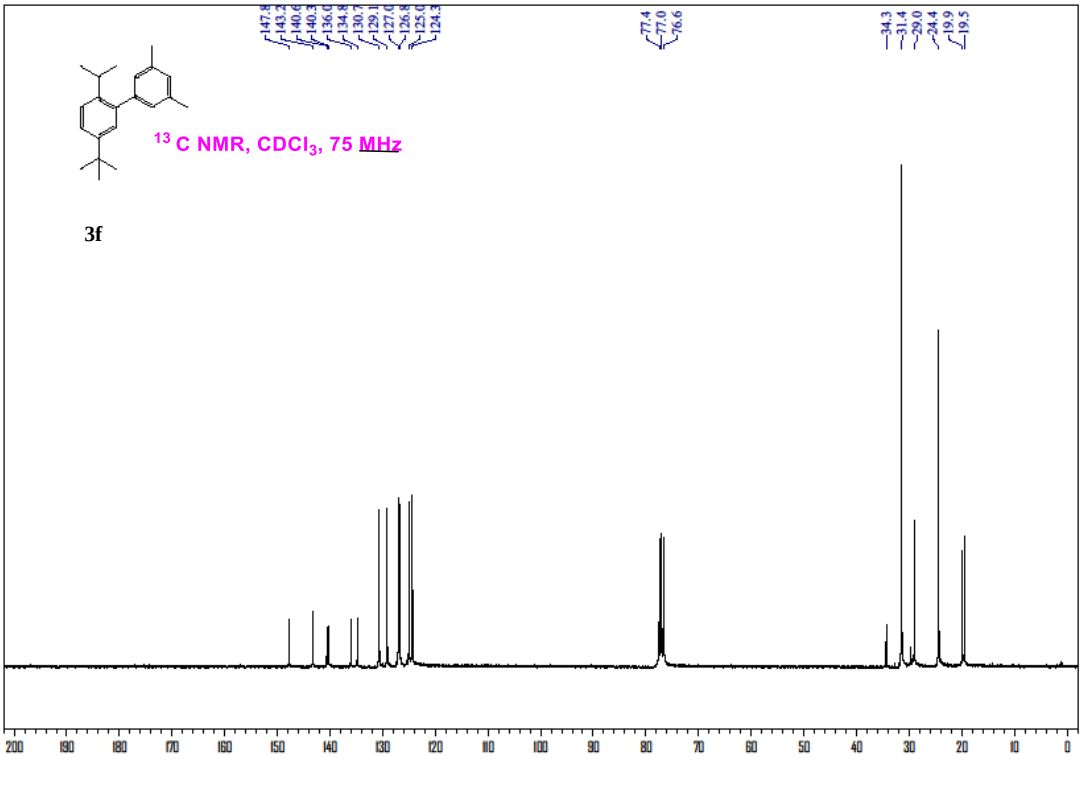
5-(*tert*-butyl)-2-isopropyl-3'-methoxy-1,1'-biphenyl (3e)



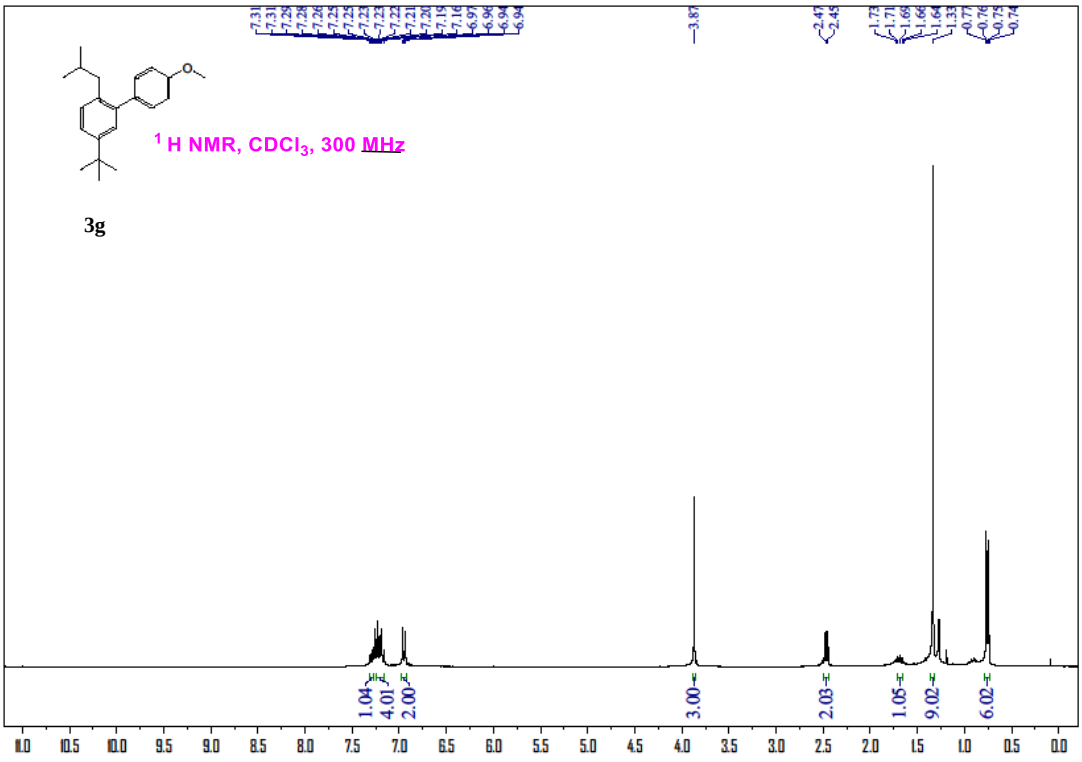


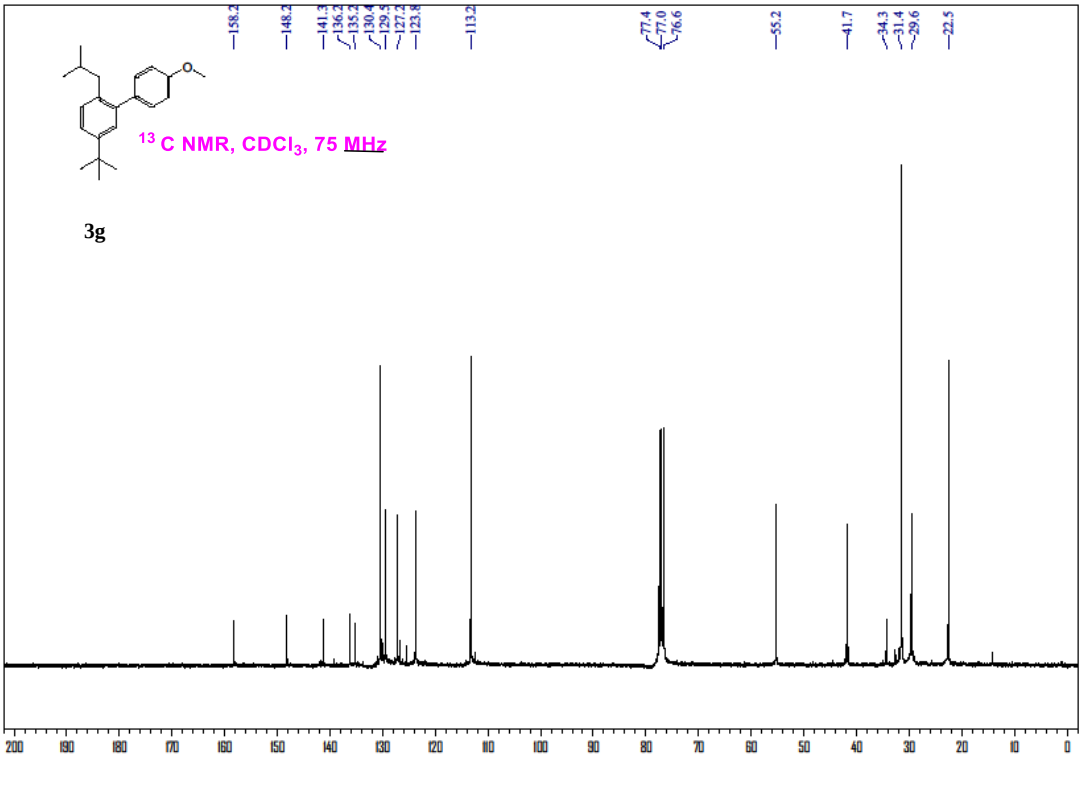
5-(*tert*-butyl)-2-isopropyl-3',5'-dimethyl-1,1'-biphenyl (3f)



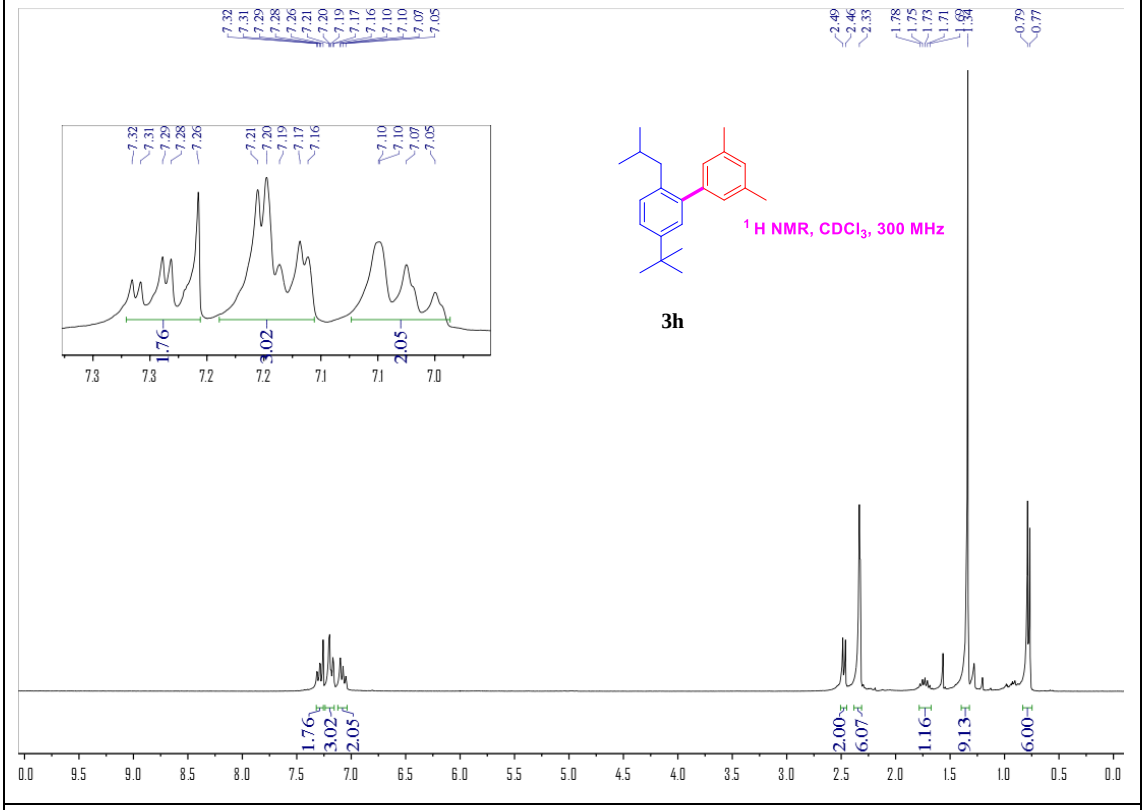


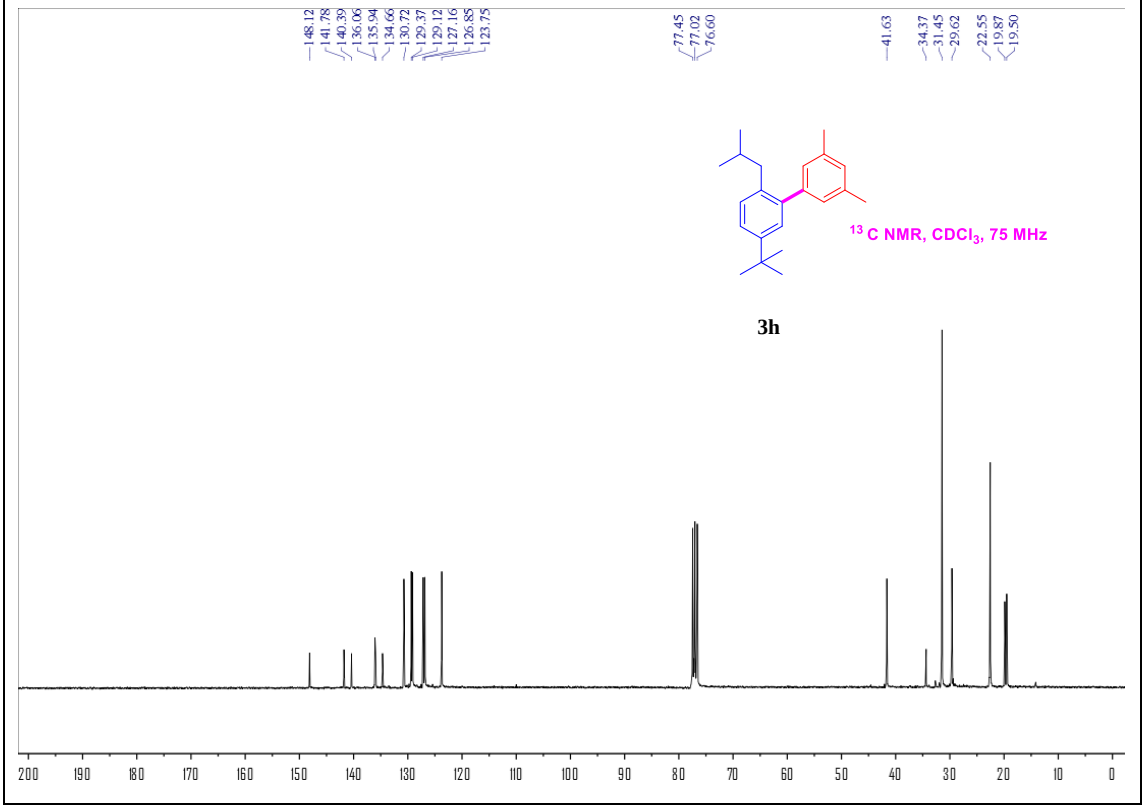
5-(*tert*-butyl)-2-isobutyl-4'-methoxy-1,1'-biphenyl (3g)



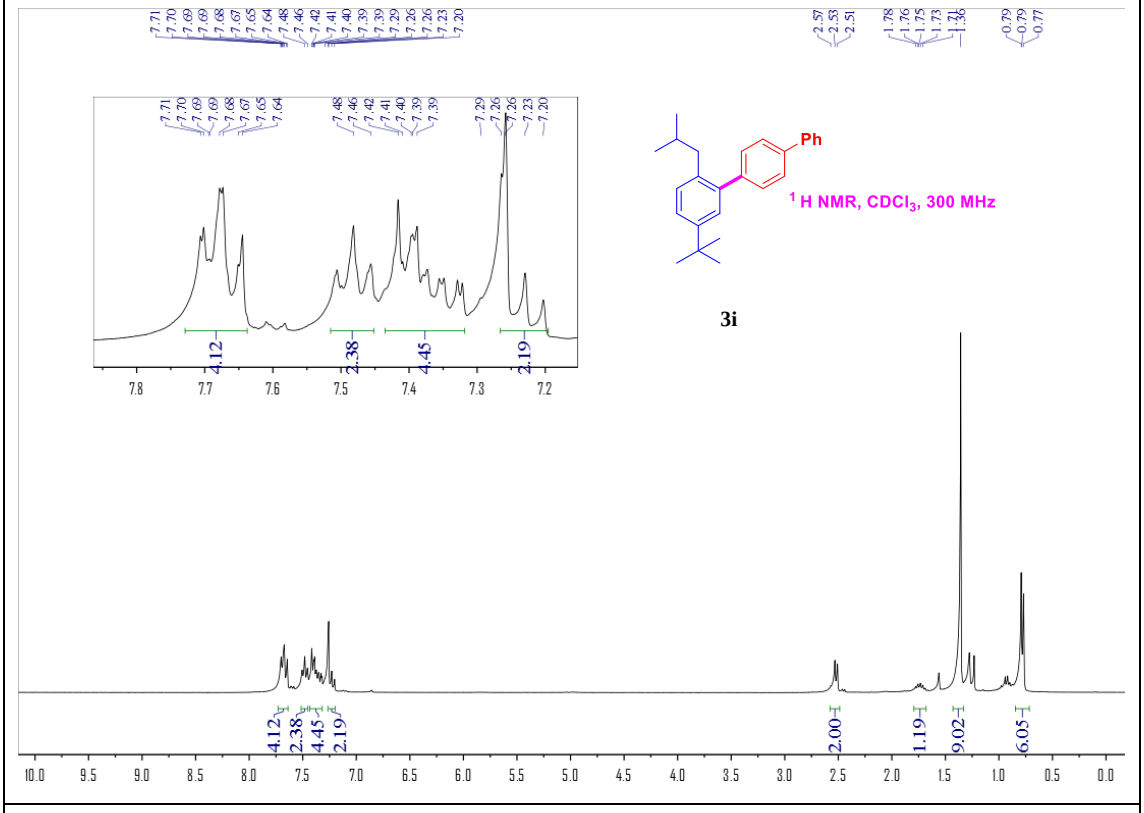


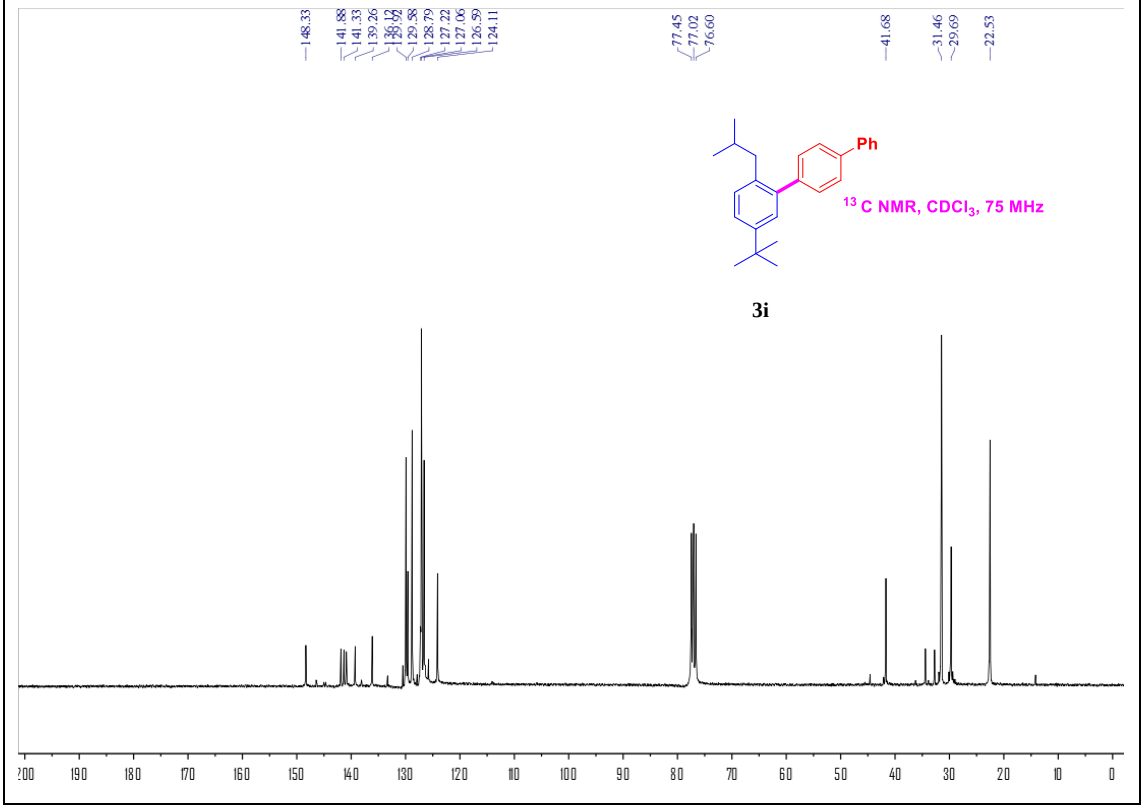
5-(*tert*-butyl)-2-isobutyl-3',5'-dimethyl-1,1'-biphenyl (3h)



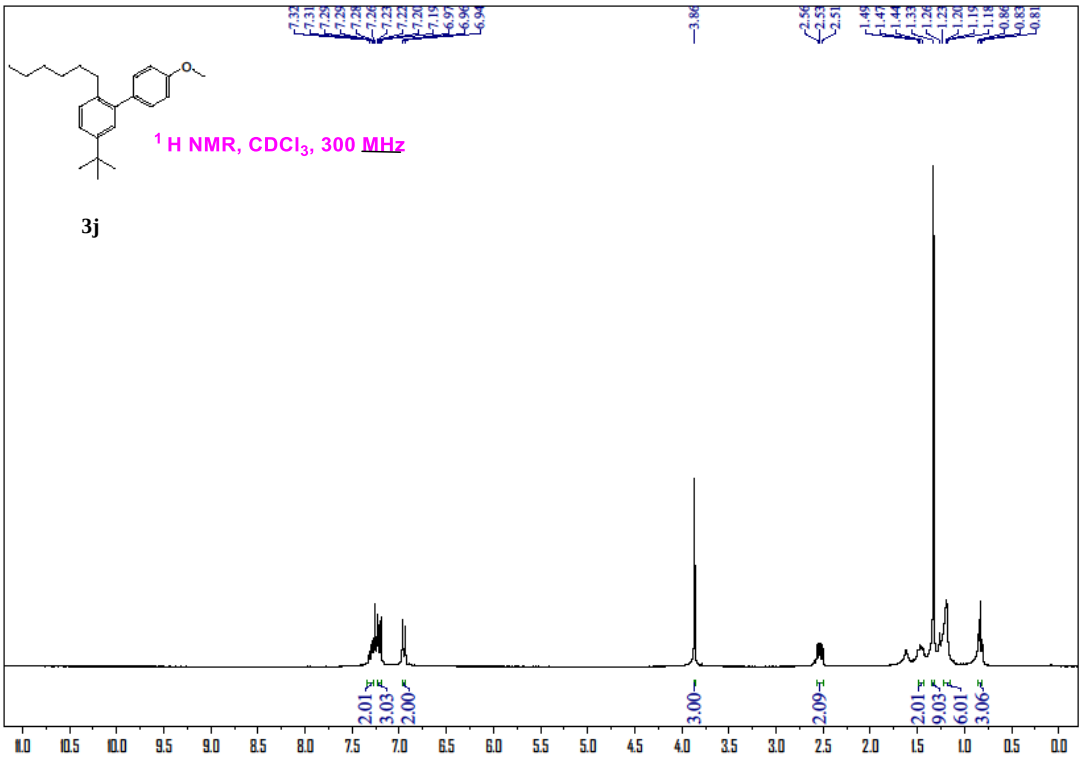


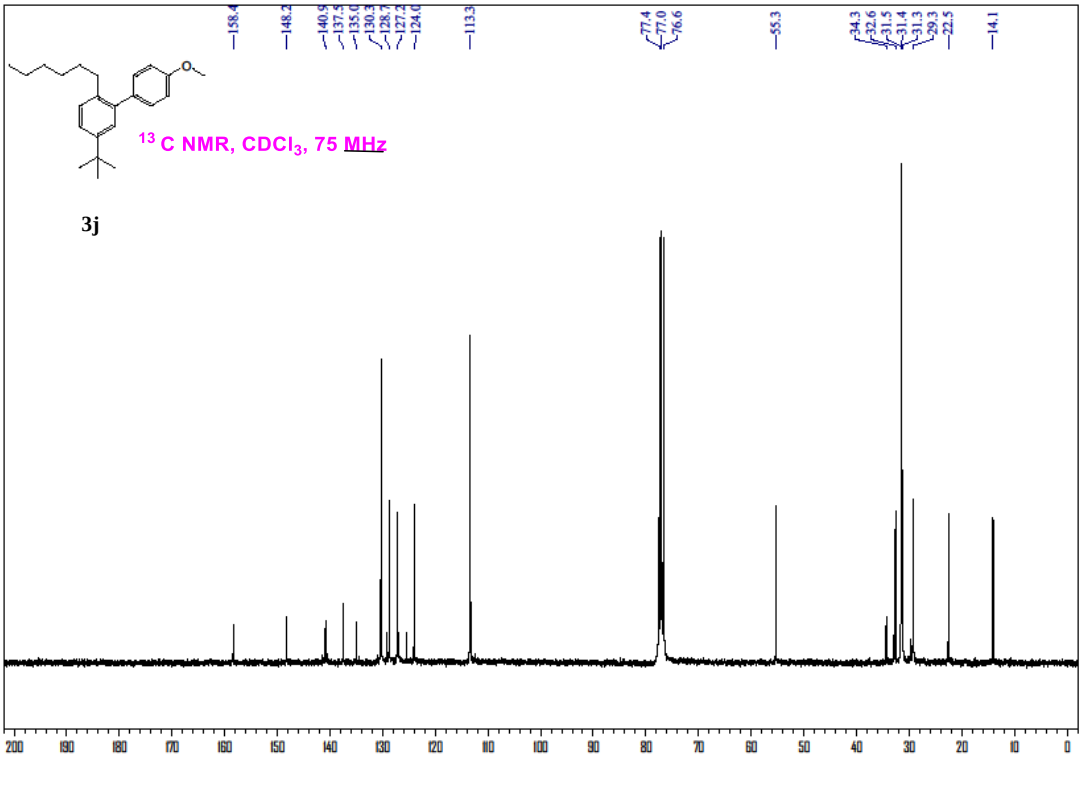
5-(*tert*-butyl)-2-isobutyl-1,1':4',1''-terphenyl (3i)



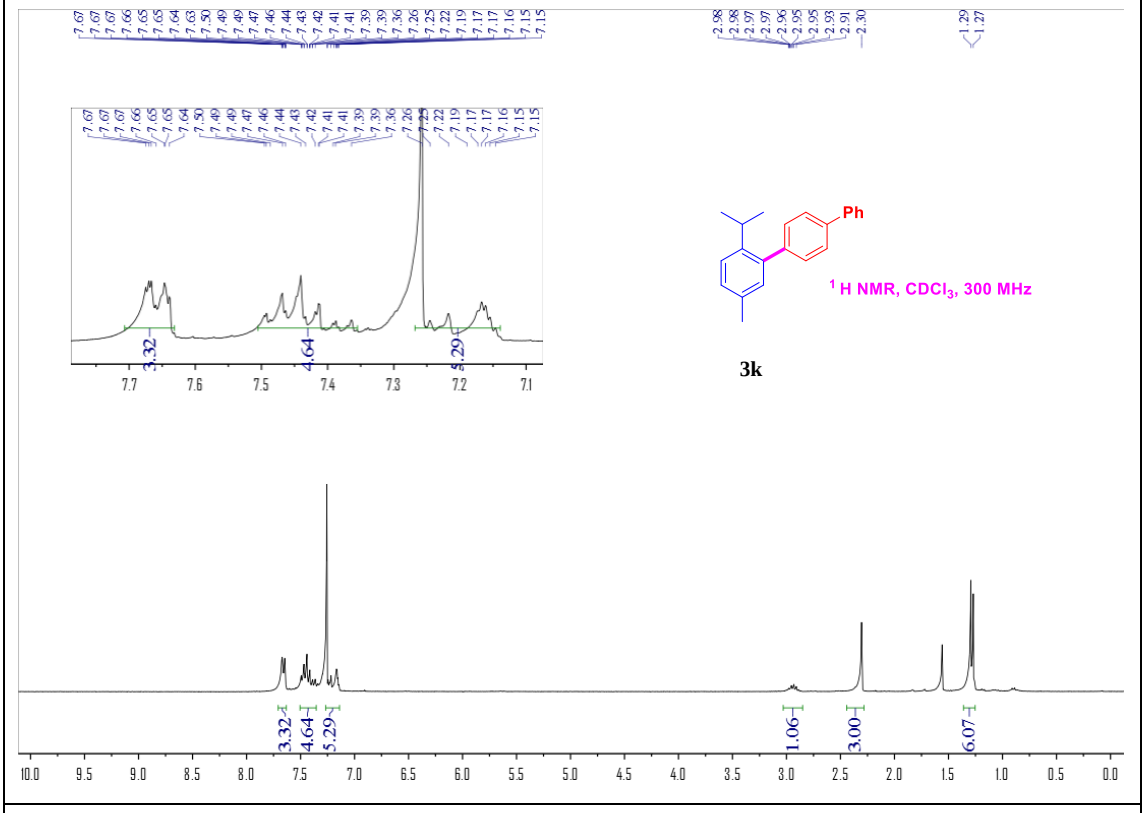


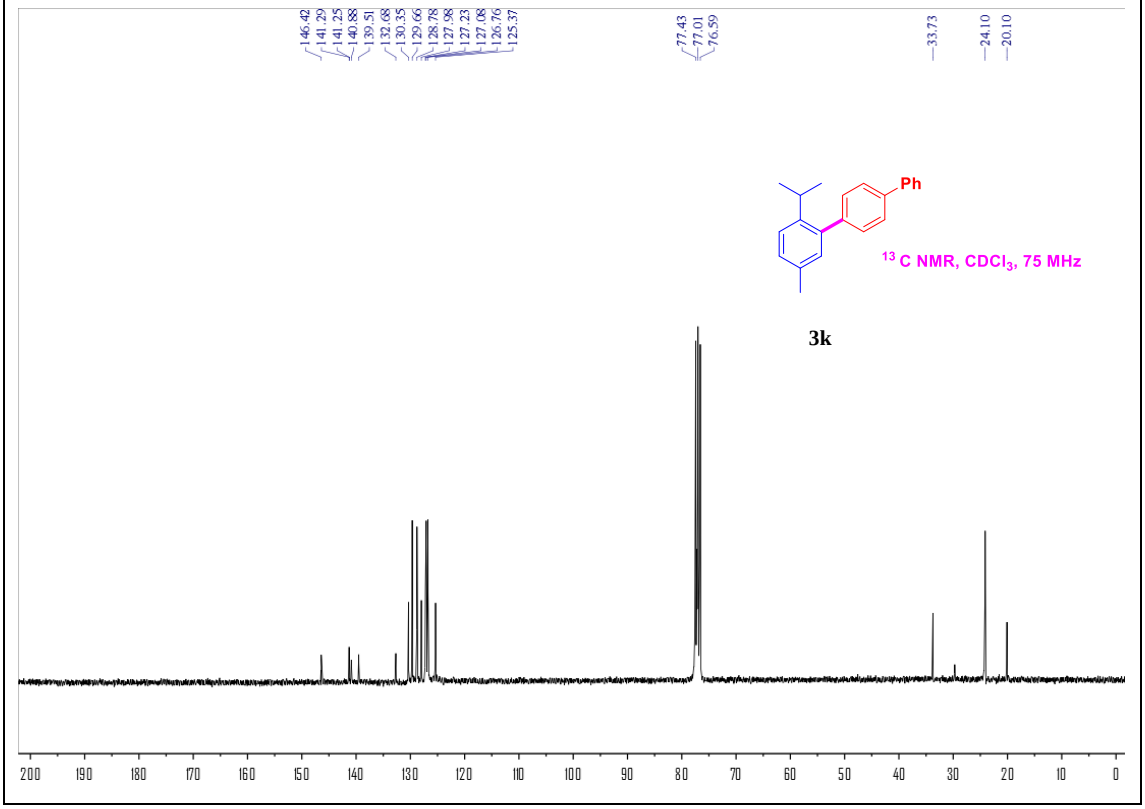
5-(*tert*-butyl)-2-hexyl-4'-methoxy-1,1'-biphenyl (3j)



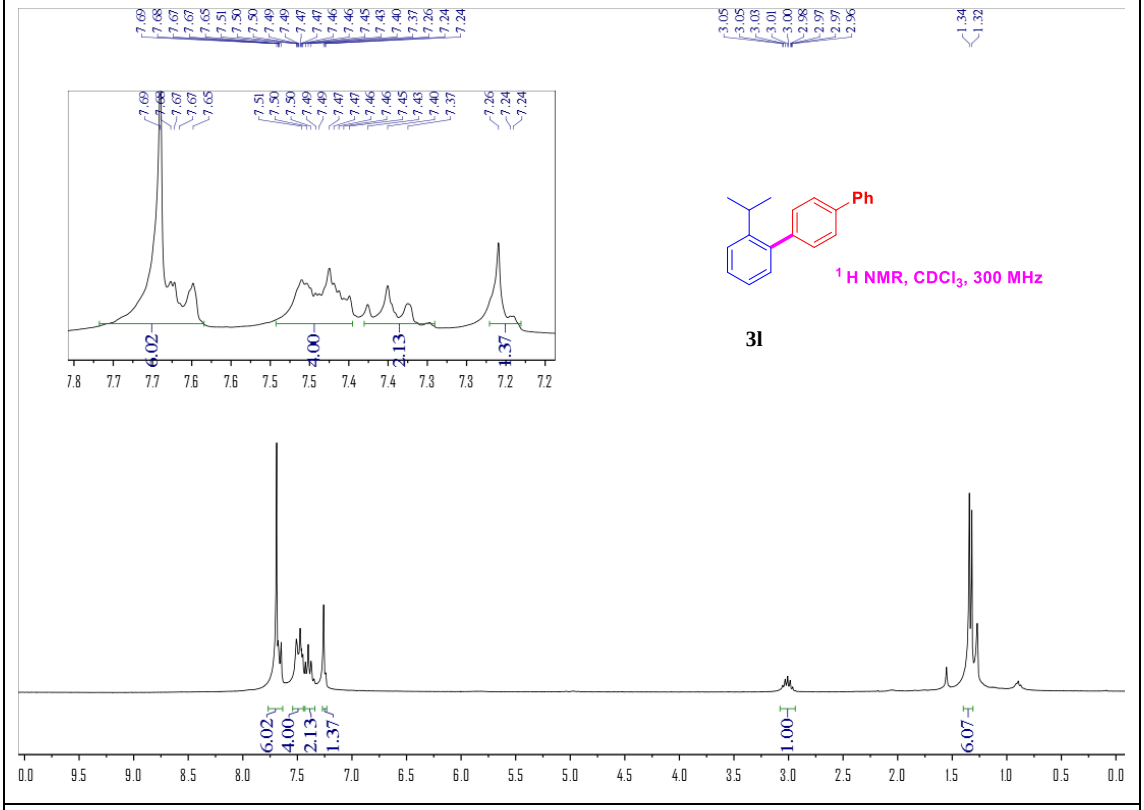


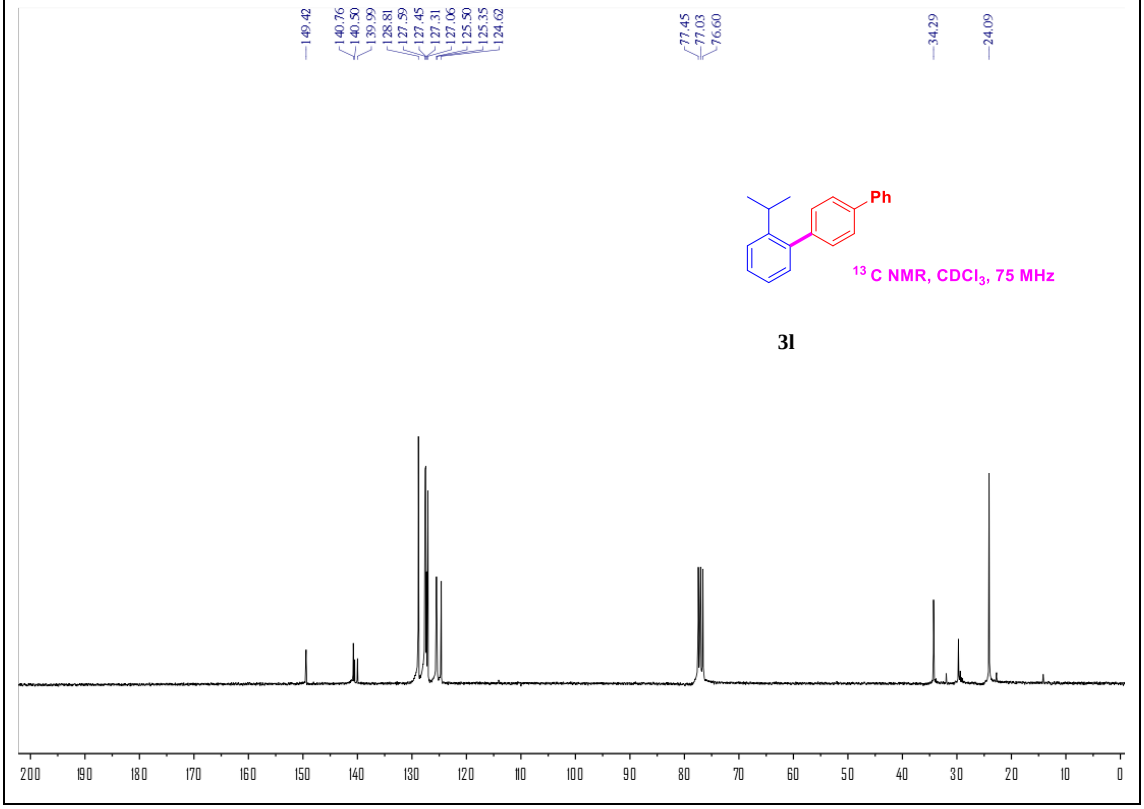
2-isopropyl-5-methyl-1,1':4',1''-terphenyl (3k)



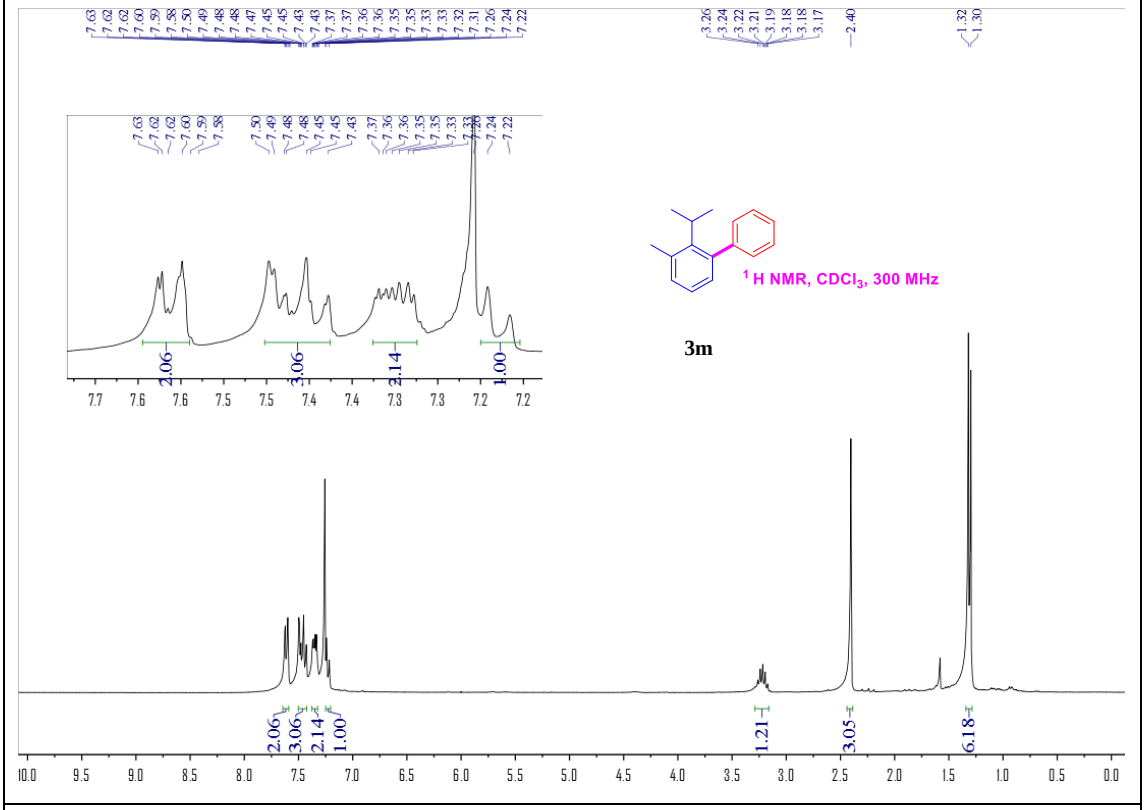


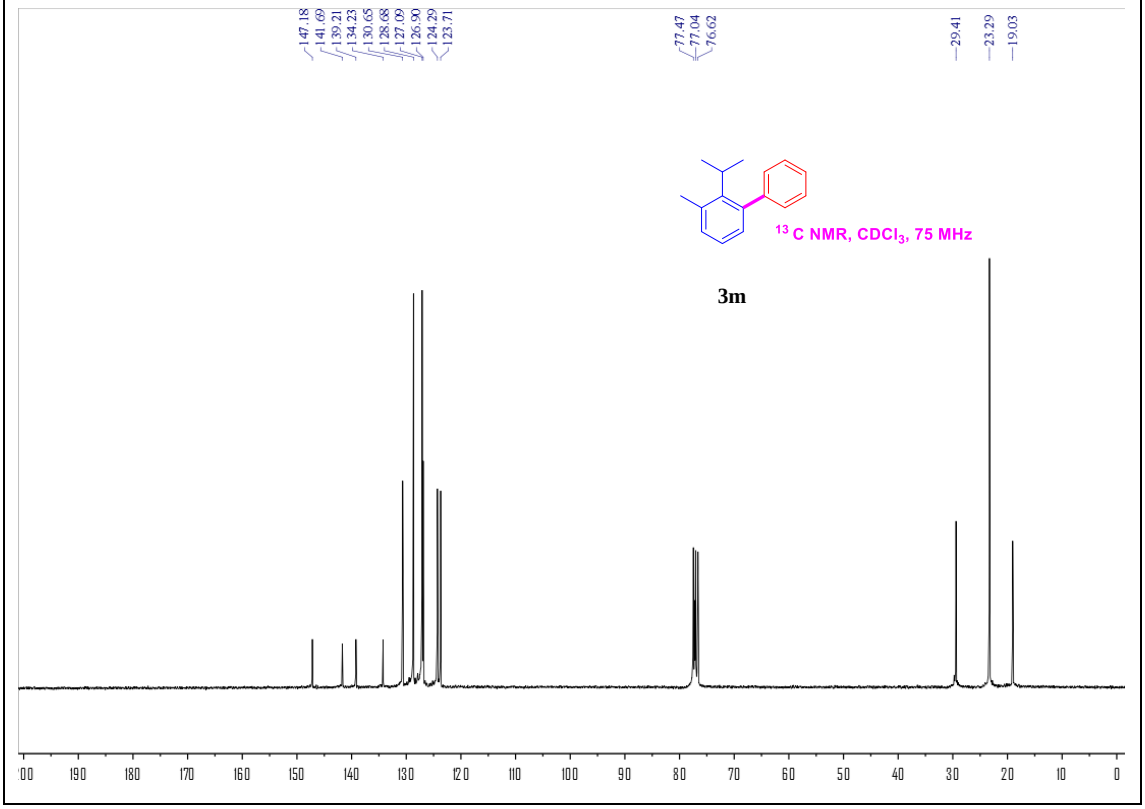
2-isopropyl-1,1':4',1''-terphenyl (3l)



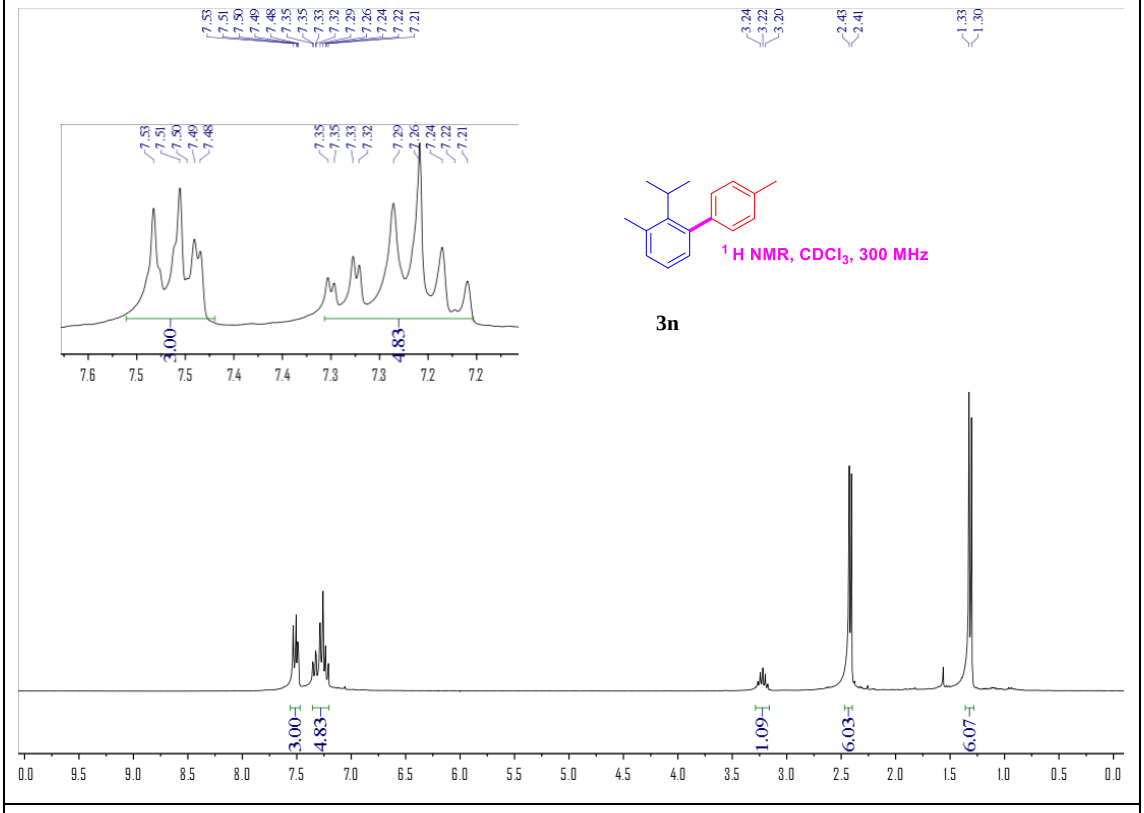


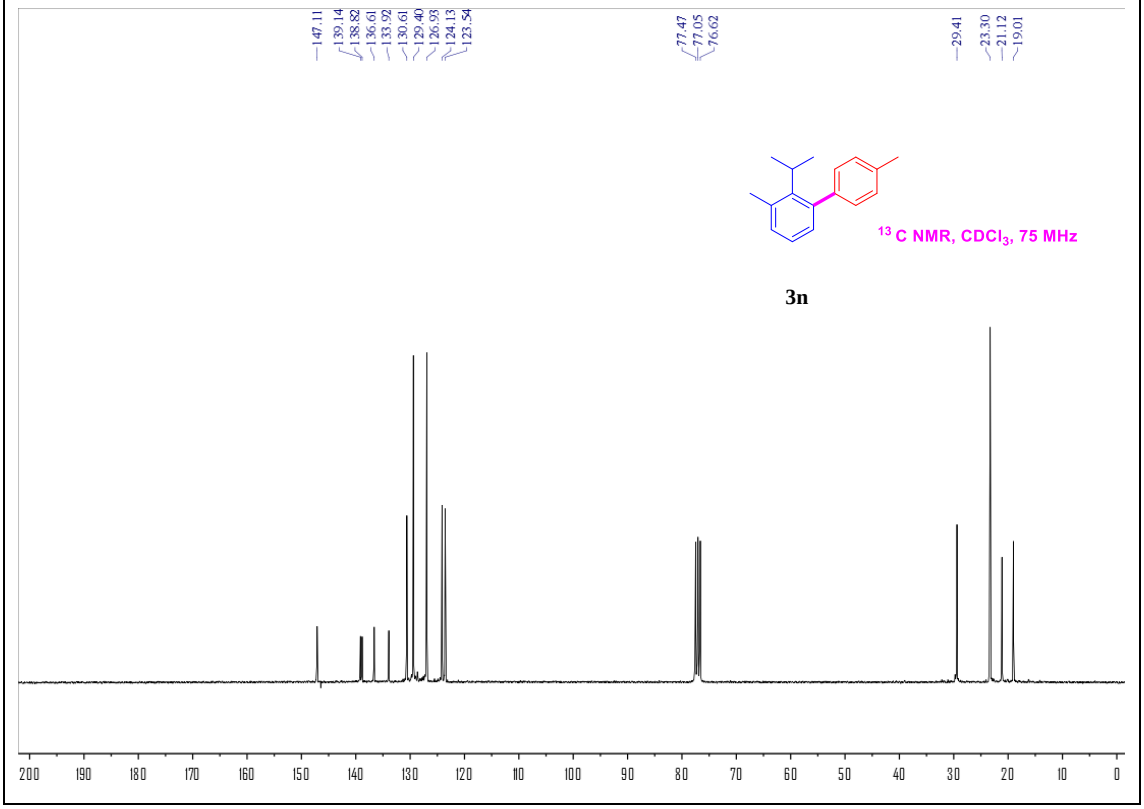
2-isopropyl-3-methyl-1,1'-biphenyl (3m)



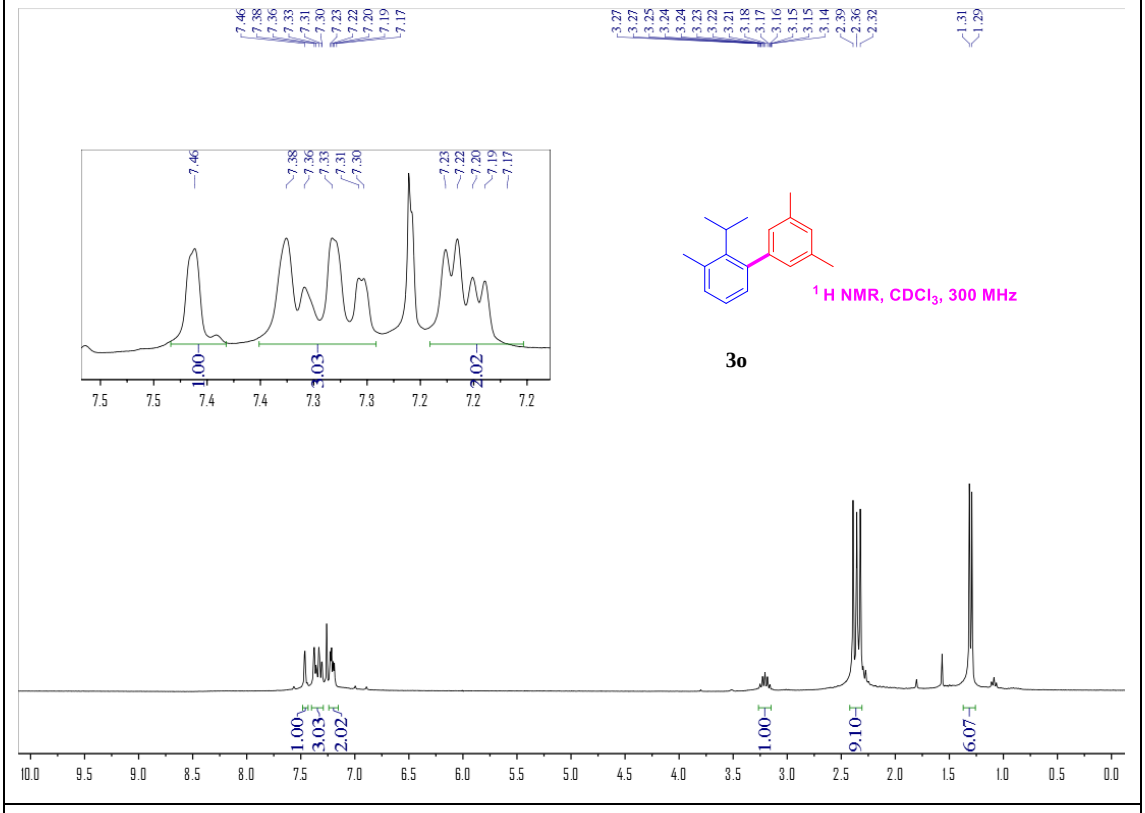


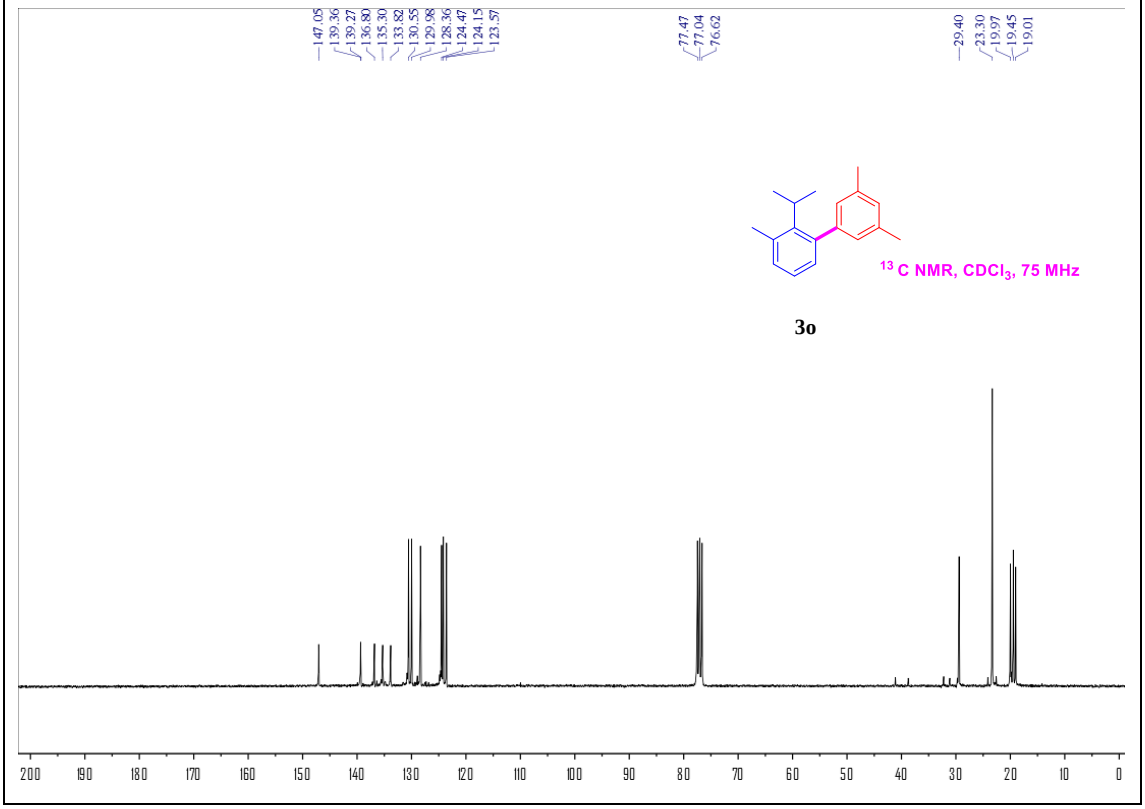
2-isopropyl-3,4'-dimethyl-1,1'-biphenyl (3n)



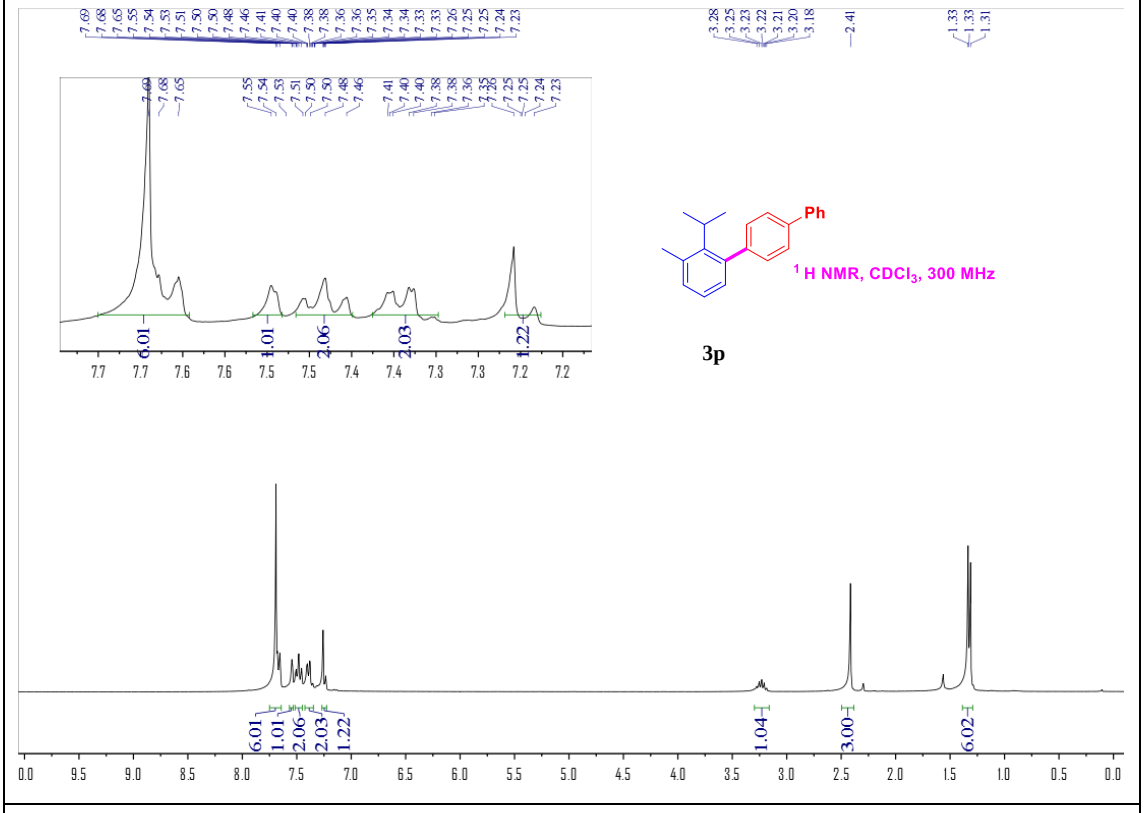


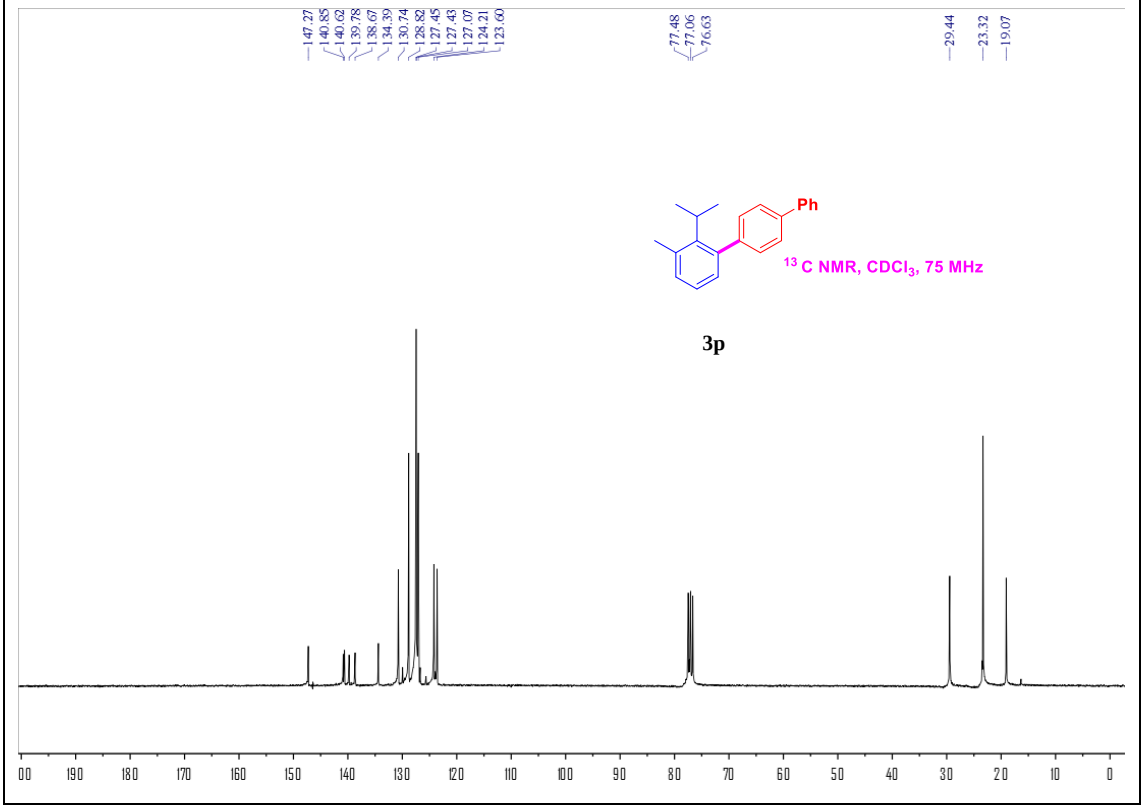
2-isopropyl-3,3',5'-trimethyl-1,1'-biphenyl (3o)



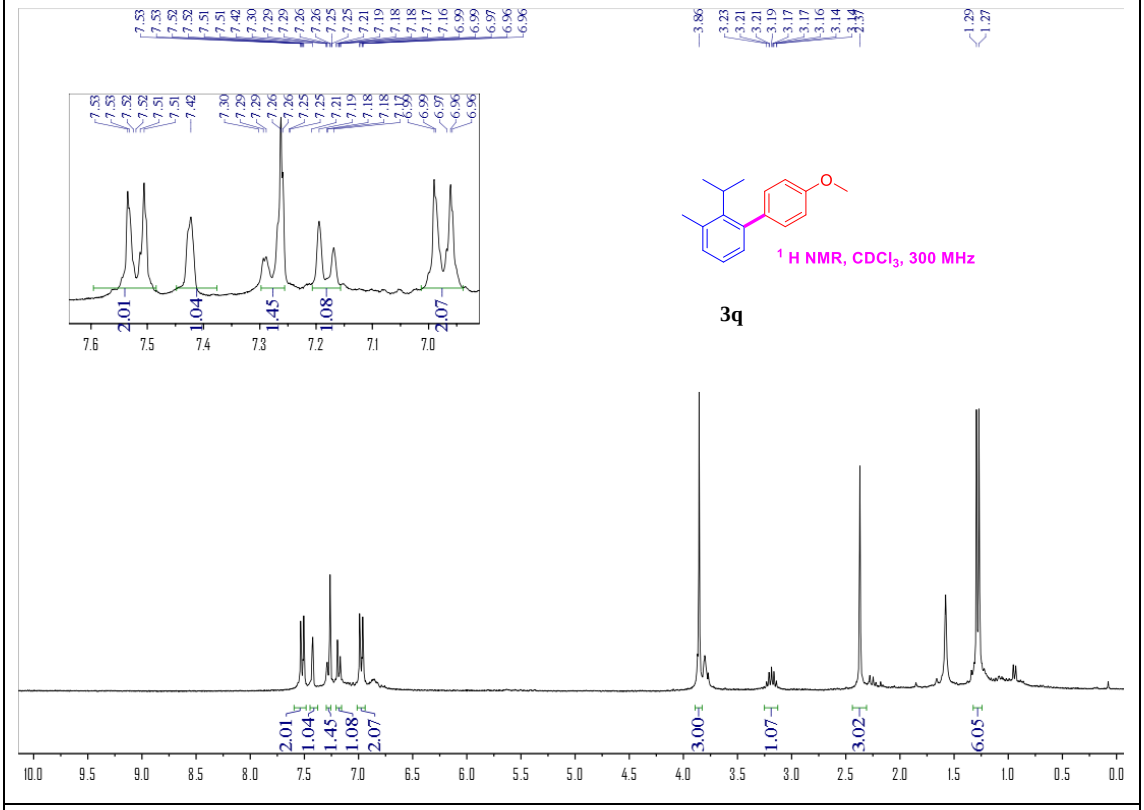


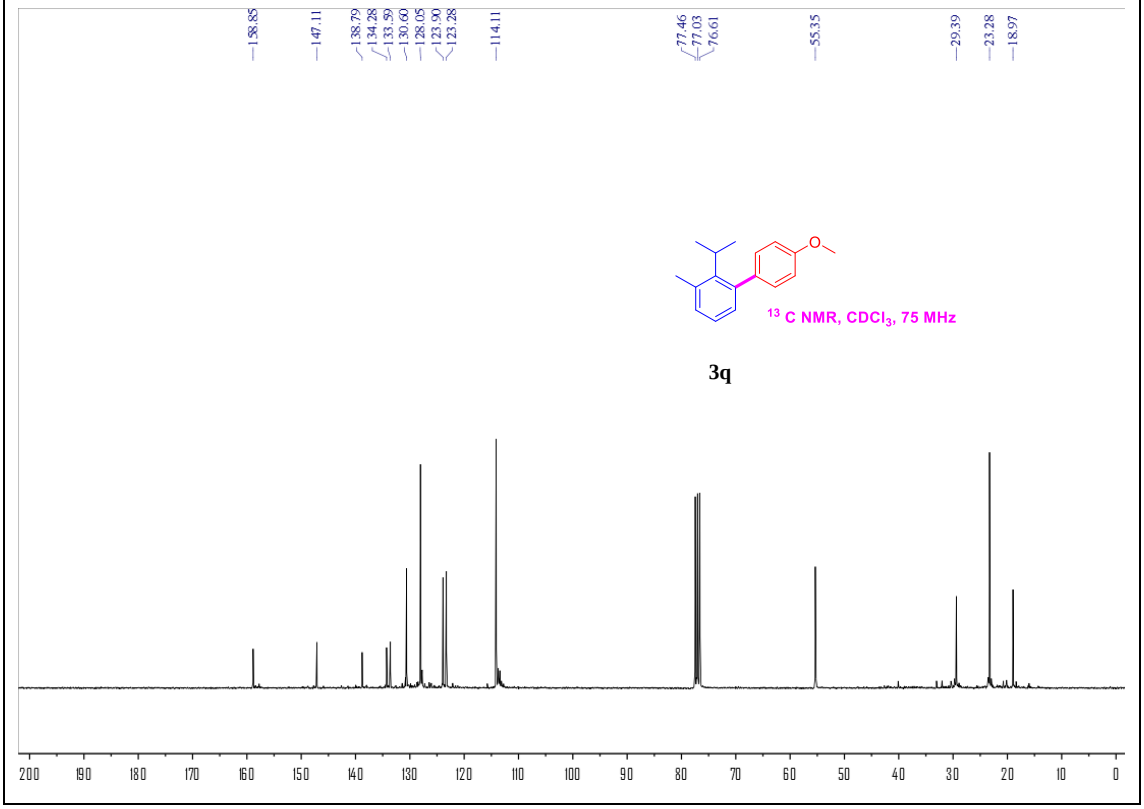
2-isopropyl-3-methyl-1,1':4',1''-terphenyl (3p)



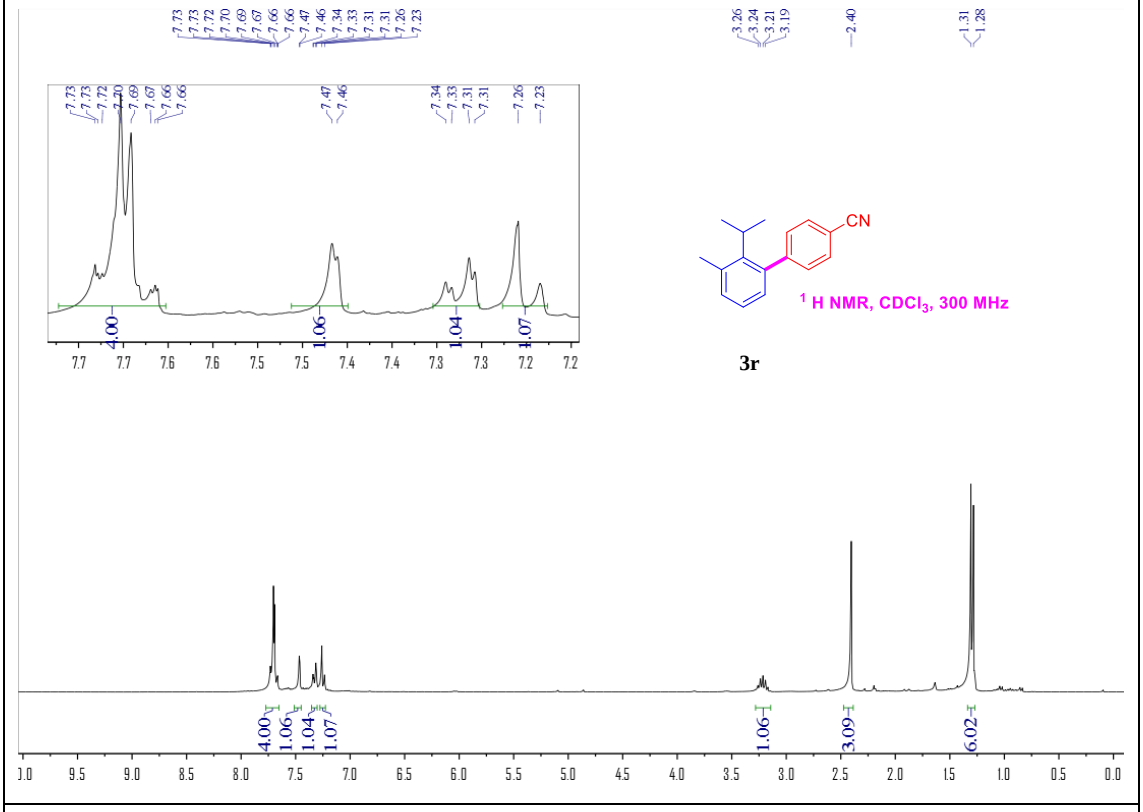


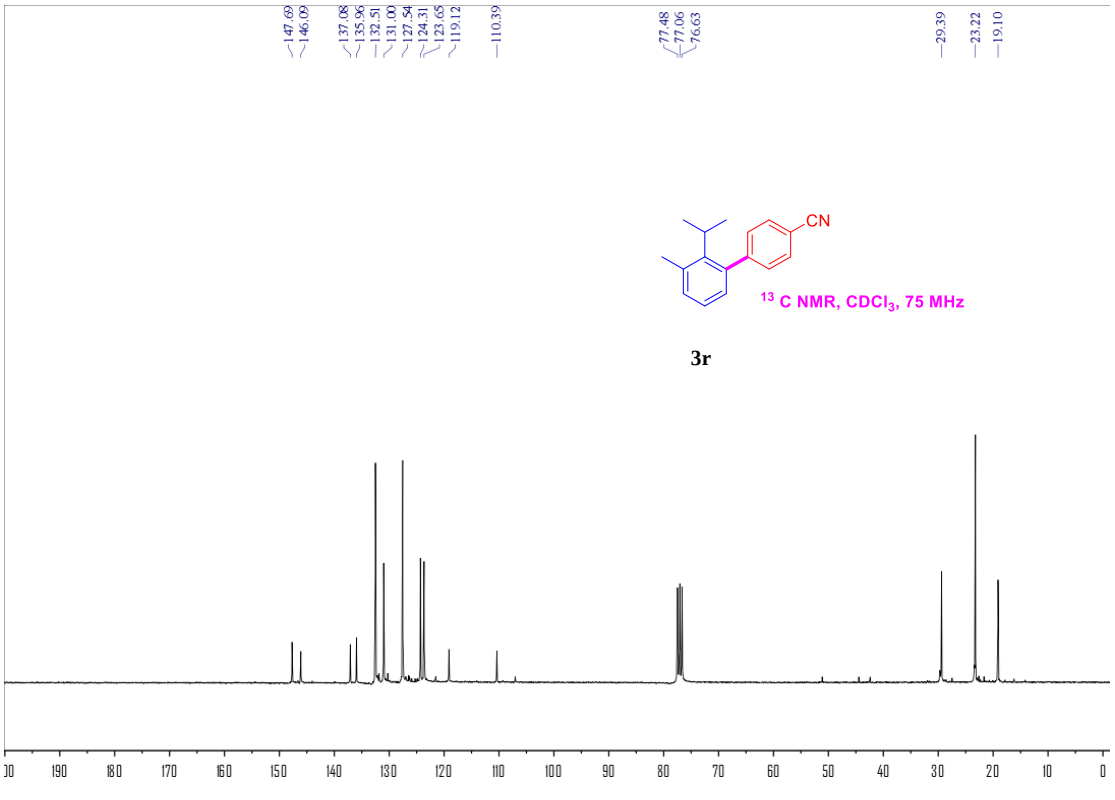
2-isopropyl-4'-methoxy-3-methyl-1,1'-biphenyl (3q)



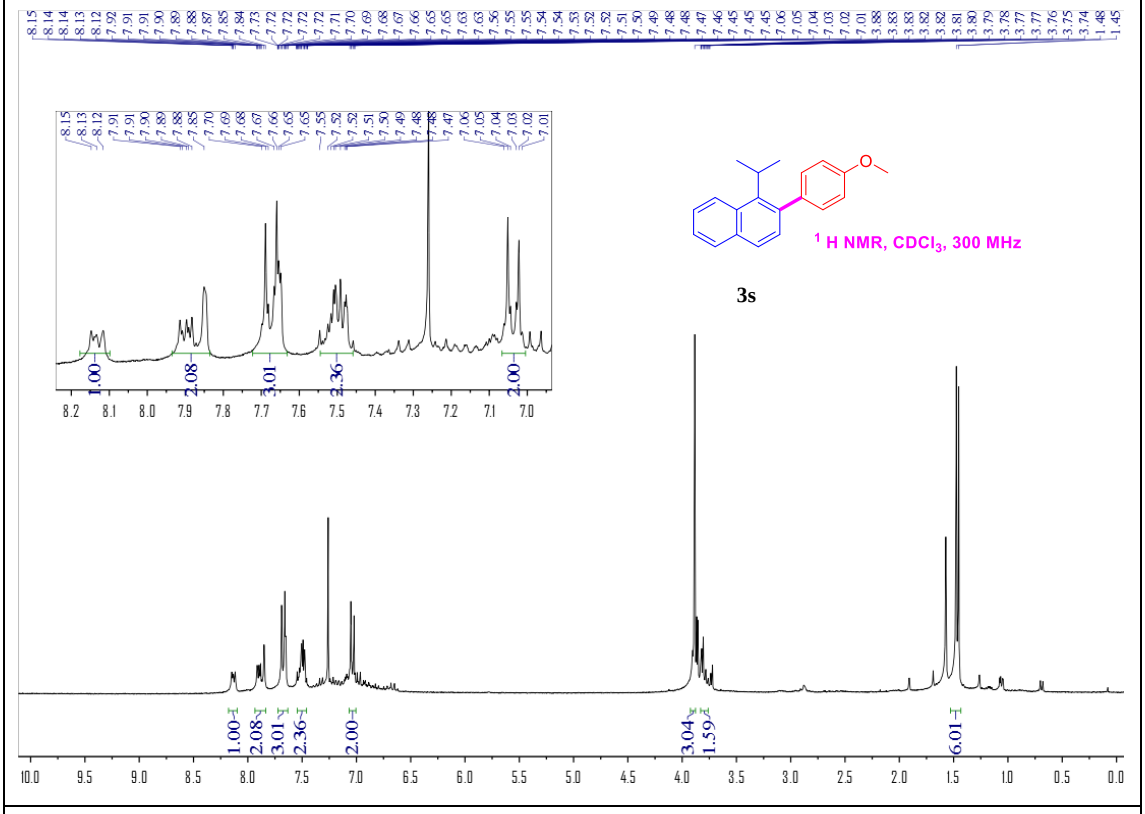


2'-isopropyl-3'-methyl-[1,1'-biphenyl]-4-carbonitrile (3r)



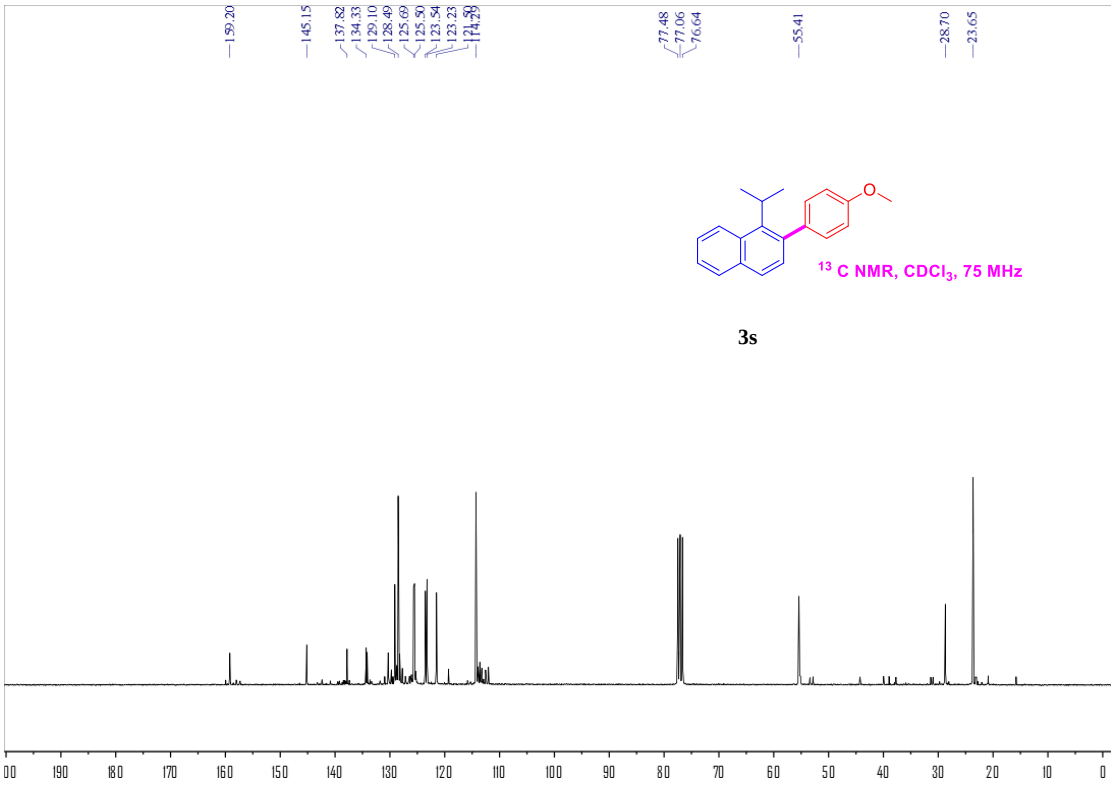


1-isopropyl-2-(4-methoxyphenyl)naphthalene (3s)



^{1}H NMR, $CDCl_3$, 300 MHz

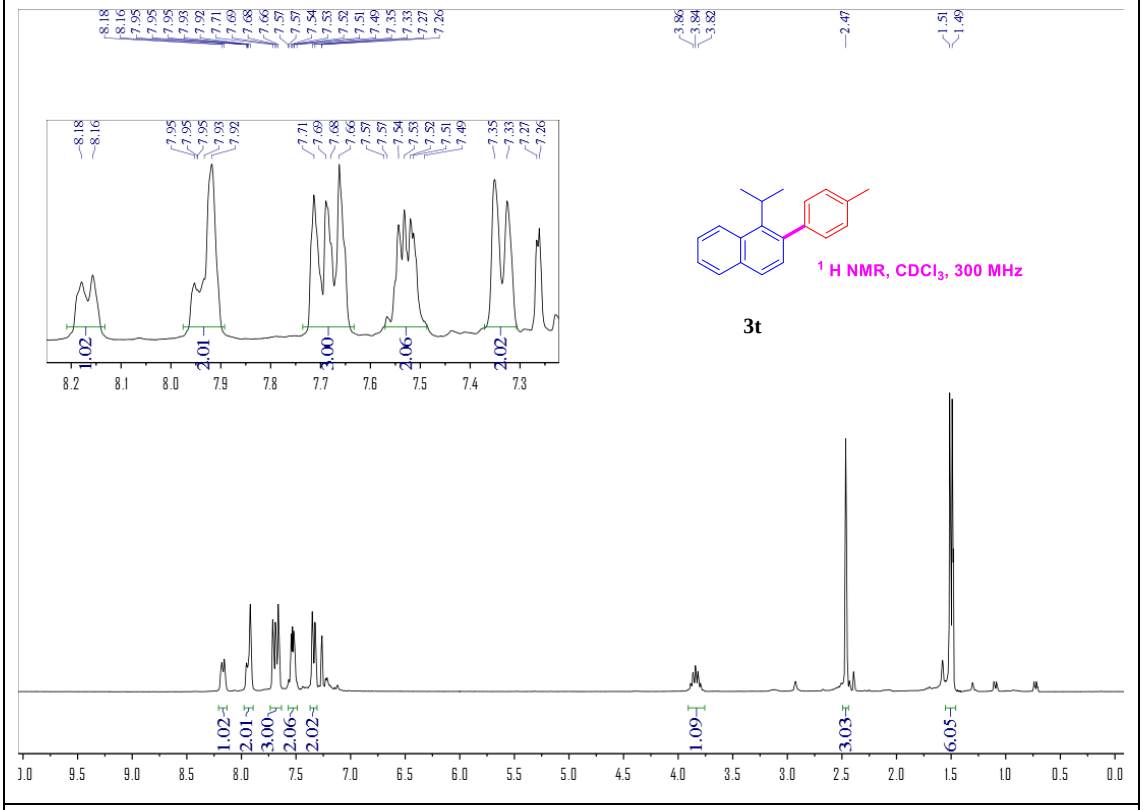
3s

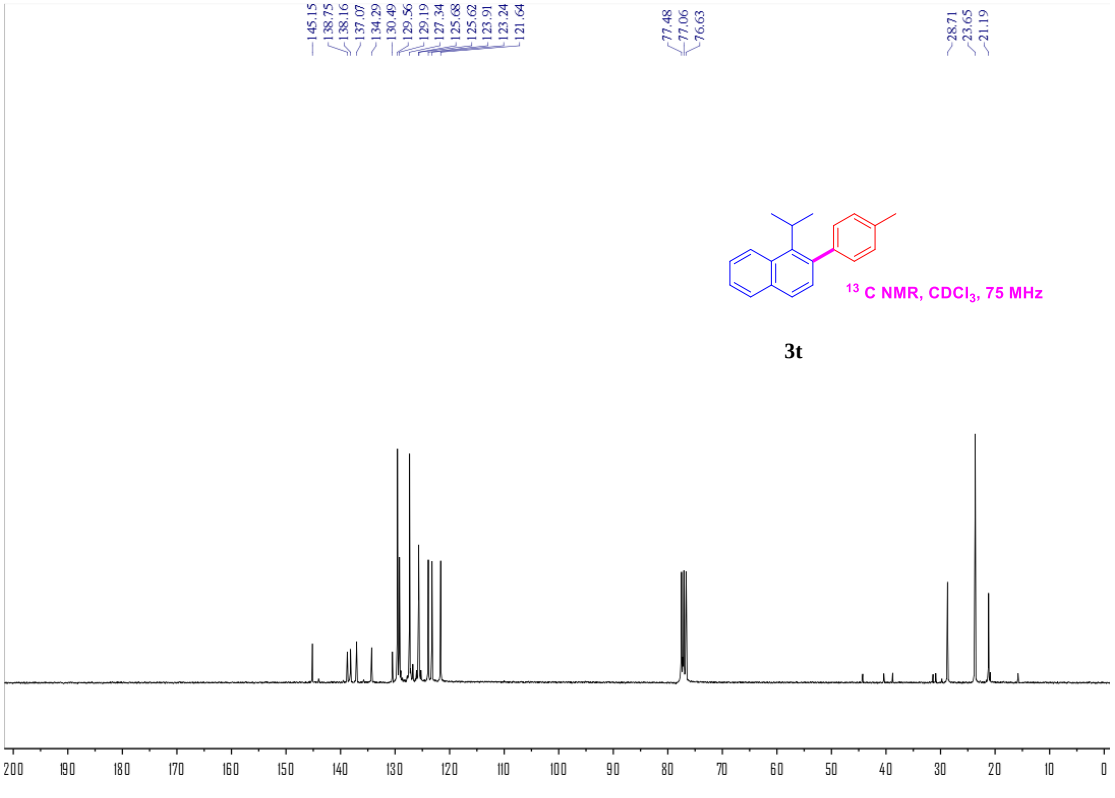


^{13}C NMR, $CDCl_3$, 75 MHz

3s

1-isopropyl-2-(*p*-tolyl)naphthalene (3t)





X-ray crystal of **3d** (ORTEP)

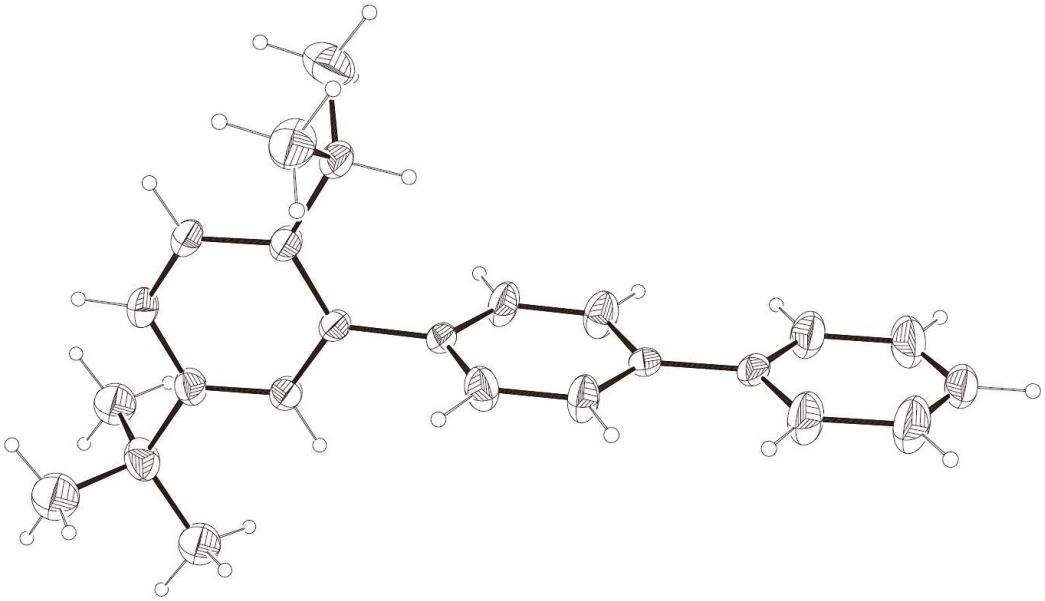


Table 1. Crystal data and structure refinement for **3d** with thermal ellipsoids at 50% probability

CCDC No.	2249903	
Identification code	d24356	
Empirical formula	C_{25} H_{28}	
Formula weight	328.47	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P 63	
Unit cell dimensions	a = 18.4162(8) Å	□= 90°.
	b = 18.4162(8) Å	□= 90°.
	c = 10.2265(6) Å	□ = 120°.
Volume	3003.7(3) $Å^3$	
Z	6	
Density (calculated)	1.090 Mg/m^3	
Absorption coefficient	0.061 mm^{-1}	
F(000)	1068	
Crystal size	0.62 x 0.09 x 0.02 mm^3	
Theta range for data collection	2.21 to 25.02°.	
Index ranges	-21<=h<=21, -21<=k<=17, -12<=l<=12	
Reflections collected	26160	
Independent reflections	3513 [R(int) = 0.0886]	
Completeness to theta = 25.02°	99.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9988 and 0.9632	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3513 / 1 / 231	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.1772	
R indices (all data)	R1 = 0.1354, wR2 = 0.2360	
Absolute structure parameter	-10(10)	
Largest diff. peak and hole	0.243 and -0.246 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for d24356. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	300(2)	1712(2)	5084(12)	77(1)
C(2)	-205(8)	1242(6)	6263(10)	114(3)
C(3)	-189(6)	1261(6)	3843(9)	102(3)
C(4)	527(2)	2623(2)	5077(10)	61(1)
C(5)	-100(2)	2835(2)	5084(11)	74(1)
C(6)	76(2)	3656(2)	5124(10)	72(1)
C(7)	891(2)	4315(2)	5091(10)	65(1)
C(8)	1081(3)	5224(2)	5083(13)	84(1)
C(9)	718(9)	5340(8)	6498(10)	99(4)
C(10)	645(9)	5394(10)	4042(13)	113(4)
C(11)	2005(5)	5863(5)	4843(12)	94(3)
C(9')	318(9)	5296(9)	5412(17)	105(5)
C(10')	1403(12)	5608(11)	3765(17)	106(5)
C(11')	1778(11)	5748(11)	6146(16)	98(5)
C(12)	1520(2)	4108(2)	5079(10)	60(1)
C(13)	1356(2)	3284(2)	5066(8)	53(1)
C(14)	2080(2)	3127(2)	5087(8)	51(1)
C(15)	2436(5)	3060(5)	3944(7)	77(2)
C(16)	3081(5)	2889(5)	3946(7)	74(2)
C(17)	3429(2)	2800(2)	5049(9)	50(1)
C(18)	3094(5)	2894(6)	6224(7)	84(2)
C(19)	2429(5)	3051(6)	6216(7)	83(3)
C(20)	4122(2)	2608(2)	5103(10)	58(1)
C(21)	4449(6)	2491(7)	3934(10)	94(3)
C(22)	5079(7)	2290(7)	3960(13)	116(4)
C(23)	5401(3)	2210(2)	5067(18)	104(2)
C(24)	5101(7)	2331(7)	6211(14)	113(3)
C(25)	4460(6)	2523(6)	6194(10)	92(3)

Table 3. Bond lengths [Å] and angles [°] for d24356.

C(1)-C(2)	1.504(14)
C(1)-C(4)	1.512(4)
C(1)-C(3)	1.538(13)
C(1)-H(1)	1.0000
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(5)	1.393(4)
C(4)-C(13)	1.398(4)
C(5)-C(6)	1.379(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.380(5)
C(6)-H(6)	0.9500
C(7)-C(12)	1.390(4)
C(7)-C(8)	1.528(5)
C(8)-C(10)	1.459(17)
C(8)-C(10')	1.50(2)
C(8)-C(9')	1.515(15)
C(8)-C(11)	1.528(9)
C(8)-C(11')	1.588(19)
C(8)-C(9)	1.653(16)
C(9)-H(9A)	0.9801
C(9)-H(9B)	0.9801
C(9)-H(9C)	0.9801
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(9')-H(99A)	0.9800
C(9')-H(99B)	0.9800
C(9')-H(99C)	0.9800

C(10')-H(10D)	0.9803
C(10')-H(10E)	0.9803
C(10')-H(10F)	0.9803
C(11')-H(10G)	0.9802
C(11')-H(10H)	0.9802
C(11')-H(10I)	0.9802
C(12)-C(13)	1.390(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.500(4)
C(14)-C(19)	1.362(11)
C(14)-C(15)	1.376(11)
C(15)-C(16)	1.372(10)
C(15)-H(15)	0.9500
C(16)-C(17)	1.347(11)
C(16)-H(16)	0.9500
C(17)-C(18)	1.401(12)
C(17)-C(20)	1.487(4)
C(18)-C(19)	1.392(10)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-C(25)	1.324(13)
C(20)-C(21)	1.402(13)
C(21)-C(22)	1.383(11)
C(21)-H(21)	0.9500
C(22)-C(23)	1.320(18)
C(22)-H(22)	0.9500
C(23)-C(24)	1.360(17)
C(23)-H(23)	0.9500
C(24)-C(25)	1.392(12)
C(24)-H(24)	0.9500
C(25)-H(25)	0.9500
C(2)-C(1)-C(4)	113.0(8)
C(2)-C(1)-C(3)	108.9(3)
C(4)-C(1)-C(3)	110.9(8)
C(2)-C(1)-H(1)	107.6
C(4)-C(1)-H(1)	108.0
C(3)-C(1)-H(1)	108.3
C(1)-C(2)-H(2A)	109.2

C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	110.1
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.7
C(1)-C(3)-H(3B)	109.8
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	108.9
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(4)-C(13)	117.0(3)
C(5)-C(4)-C(1)	120.2(3)
C(13)-C(4)-C(1)	122.9(3)
C(6)-C(5)-C(4)	122.2(3)
C(6)-C(5)-H(5)	118.9
C(4)-C(5)-H(5)	118.9
C(5)-C(6)-C(7)	121.4(3)
C(5)-C(6)-H(6)	119.3
C(7)-C(6)-H(6)	119.3
C(6)-C(7)-C(12)	116.5(3)
C(6)-C(7)-C(8)	121.2(3)
C(12)-C(7)-C(8)	122.3(3)
C(10)-C(8)-C(10')	51.2(10)
C(10)-C(8)-C(9')	60.5(10)
C(10')-C(8)-C(9')	108.8(12)
C(10)-C(8)-C(11)	103.7(10)
C(10')-C(8)-C(11)	57.8(9)
C(9')-C(8)-C(11)	133.8(7)
C(10)-C(8)-C(7)	112.9(8)
C(10')-C(8)-C(7)	110.0(9)
C(9')-C(8)-C(7)	112.3(6)
C(11)-C(8)-C(7)	113.7(4)
C(10)-C(8)-C(11')	137.2(9)
C(10')-C(8)-C(11')	108.7(11)
C(9')-C(8)-C(11')	107.4(11)
C(11)-C(8)-C(11')	52.6(9)
C(7)-C(8)-C(11')	109.6(8)

C(10)-C(8)-C(9)	107.9(7)
C(10')-C(8)-C(9)	144.6(8)
C(9')-C(8)-C(9)	48.7(8)
C(11)-C(8)-C(9)	114.1(9)
C(7)-C(8)-C(9)	104.6(8)
C(11')-C(8)-C(9)	65.1(9)
C(8)-C(9)-H(9A)	109.4
C(8)-C(9)-H(9B)	109.4
C(8)-C(9)-H(9C)	109.7
C(8)-C(10)-H(10A)	109.3
C(8)-C(10)-H(10B)	109.9
C(8)-C(10)-H(10C)	109.2
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.4
C(8)-C(9')-H(99A)	109.4
C(8)-C(9')-H(99B)	109.5
H(99A)-C(9')-H(99B)	109.5
C(8)-C(9')-H(99C)	109.6
H(99A)-C(9')-H(99C)	109.5
H(99B)-C(9')-H(99C)	109.5
C(8)-C(10')-H(10D)	109.8
C(8)-C(10')-H(10E)	109.5
H(10D)-C(10')-H(10E)	109.5
C(8)-C(10')-H(10F)	109.2
H(10D)-C(10')-H(10F)	109.4
H(10E)-C(10')-H(10F)	109.4
C(8)-C(11')-H(10G)	109.8
C(8)-C(11')-H(10H)	109.3
H(10G)-C(11')-H(10H)	109.4
C(8)-C(11')-H(10I)	109.4
H(10G)-C(11')-H(10I)	109.5
H(10H)-C(11')-H(10I)	109.5
C(7)-C(12)-C(13)	122.9(3)
C(7)-C(12)-H(12)	118.6
C(13)-C(12)-H(12)	118.5
C(12)-C(13)-C(4)	119.9(3)
C(12)-C(13)-C(14)	118.8(2)

C(4)-C(13)-C(14)	121.3(3)
C(19)-C(14)-C(15)	116.1(3)
C(19)-C(14)-C(13)	122.9(7)
C(15)-C(14)-C(13)	121.0(7)
C(14)-C(15)-C(16)	121.7(6)
C(14)-C(15)-H(15)	119.1
C(16)-C(15)-H(15)	119.2
C(17)-C(16)-C(15)	123.3(7)
C(17)-C(16)-H(16)	118.3
C(15)-C(16)-H(16)	118.4
C(16)-C(17)-C(18)	116.0(3)
C(16)-C(17)-C(20)	125.3(8)
C(18)-C(17)-C(20)	118.8(7)
C(19)-C(18)-C(17)	120.5(7)
C(19)-C(18)-H(18)	119.7
C(17)-C(18)-H(18)	119.8
C(14)-C(19)-C(18)	122.4(7)
C(14)-C(19)-H(19)	118.9
C(18)-C(19)-H(19)	118.7
C(25)-C(20)-C(21)	115.9(3)
C(25)-C(20)-C(17)	124.7(8)
C(21)-C(20)-C(17)	119.4(8)
C(22)-C(21)-C(20)	120.4(10)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(23)-C(22)-C(21)	122.0(11)
C(23)-C(22)-H(22)	119.1
C(21)-C(22)-H(22)	118.9
C(22)-C(23)-C(24)	118.5(4)
C(22)-C(23)-H(23)	120.6
C(24)-C(23)-H(23)	120.9
C(23)-C(24)-C(25)	119.8(11)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.2
C(20)-C(25)-C(24)	123.3(10)
C(20)-C(25)-H(25)	118.4
C(24)-C(25)-H(25)	118.3

Symmetry transformations used to generate equivalent atoms

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for d24356. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42(2)	50(2)	132(3)	0(6)	-4(5)	19(2)
C(2)	132(9)	76(7)	126(7)	13(6)	-5(7)	48(7)
C(3)	81(5)	70(5)	150(8)	-28(5)	-13(5)	34(5)
C(4)	44(2)	52(2)	88(2)	-3(4)	3(4)	24(1)
C(5)	43(2)	69(2)	110(3)	10(5)	6(5)	29(2)
C(6)	60(2)	80(2)	90(3)	3(5)	7(5)	47(2)
C(7)	66(2)	64(2)	76(2)	0(5)	-2(5)	41(2)
C(8)	91(3)	70(2)	108(3)	-8(6)	-11(6)	53(2)
C(12)	51(2)	52(2)	78(2)	-1(4)	1(4)	26(2)
C(13)	43(2)	48(2)	64(2)	1(4)	6(4)	21(1)
C(14)	38(2)	44(2)	67(2)	3(4)	2(4)	18(1)
C(15)	90(6)	112(7)	59(4)	14(4)	4(4)	72(6)
C(16)	75(5)	112(7)	65(4)	-5(4)	2(4)	68(5)
C(17)	38(2)	37(1)	68(2)	4(4)	2(4)	12(1)
C(18)	77(5)	137(9)	58(4)	1(4)	-2(4)	69(6)
C(19)	69(5)	141(8)	63(4)	16(4)	15(4)	72(6)
C(20)	40(2)	41(2)	86(2)	-2(4)	7(4)	15(1)
C(21)	98(6)	124(8)	95(6)	-9(5)	11(5)	81(6)
C(22)	104(8)	138(10)	144(8)	-9(7)	21(7)	89(8)
C(23)	51(2)	64(3)	202(6)	10(9)	11(9)	33(2)
C(24)	83(7)	119(9)	164(9)	5(7)	-17(7)	69(7)
C(25)	73(5)	120(8)	102(7)	3(6)	-1(5)	62(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)
for d24356.

	x	y	z	U(eq)
H(1)	833	1692	5092	92
H(2A)	-755	1202	6228	170
H(2B)	90	1540	7059	170
H(2C)	-278	677	6268	170
H(3A)	134	1565	3069	153
H(3B)	-731	1243	3840	153
H(3C)	-284	689	3829	153
H(5)	-670	2399	5060	88
H(6)	-372	3770	5175	86
H(9A)	802	5909	6556	148
H(9B)	1017	5250	7214	148
H(9C)	118	4931	6562	148
H(10A)	844	5319	3191	170
H(10B)	758	5971	4120	170
H(10C)	41	5005	4116	170
H(11A)	2203	5695	4074	141
H(11B)	2336	5887	5609	141
H(11C)	2067	6416	4691	141
H(99A)	482	5889	5490	157
H(99B)	79	5010	6242	157
H(99C)	-101	5035	4716	157
H(10D)	996	5266	3092	158
H(10E)	1938	5632	3594	158
H(10F)	1485	6176	3748	158
H(10G)	1855	6313	6208	148
H(10H)	2309	5785	5890	148
H(10I)	1601	5469	6997	148
H(12)	2087	4548	5079	72
H(15)	2230	3133	3132	93
H(16)	3292	2830	3130	89

H(18)	3323	2851	7034	101
H(19)	2211	3108	7027	100
H(21)	4236	2550	3119	113
H(22)	5286	2207	3156	139
H(23)	5833	2071	5063	125
H(24)	5329	2285	7020	136
H(25)	4255	2597	7006	110

