Cross-coupling reaction of cyclic quaternary ammonium salts with arylzinc reagents, arylboron reagents, and silylboronate

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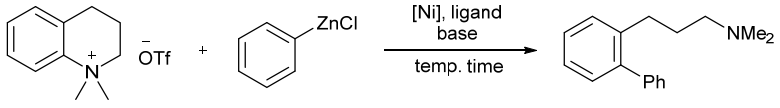
Contents

1. Screening of reaction conditions

(1) Condition optimization of the reaction of cyclic quaternary ammonium salts with arylzinc reagents

Table S1. Optimization of conditions for the reaction of cyclic quaternary ammonium salt (**1a**) with phenylzinc chloride (**2a**)[a]



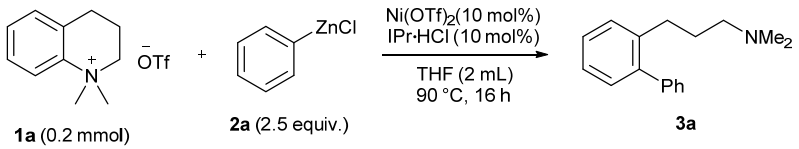
1a (0.2 mmol) **2a** (x equiv.) **3a**

Entry	[Ni] (mol%)	Ligand (mol%)	x	Temp. (°C)	Time (h)	Solvent (2 mL)	Base (10 mol%)	Yield[b] (%
1	$NiCl_2$(DME) (10)		2.0	80	12	THF		19
2	$NiCl_2$(TMEDA) ·0.2CH_2Cl_2 (10)		2.0	80	12	THF		33
3	$Ni(acac)_2$ (10)		2.0	80	12	THF		18
4	$NiCl_2(PPh_3)_3$ (10)		2.0	80	12	THF		15
5	$NiCl_2(PCy_3)_2$ (10)		2.0	80	12	THF		27
6	$NiCl_2$(dppe) (10)		2.0	80	12	THF		35
7	$NiCl_2$(dppp) (10)		2.0	80	12	THF		15
8	$NiCl_2$(dppf) (10)		2.0	80	12	THF		20
9	NiF_2 (10)		2.0	80	12	THF		15
10	$Ni(OTf)_2$ (10)		2.0	80	12	THF		41
11	$Ni(COD)_2$ (10)		2.0	80	12	THF		trace
12	$Ni(OTf)_2$ (10)	PPh_3 (20)	2.0	80	12	THF		7
13	$Ni(OTf)_2$ (10)	X-Phos (20)	2.0	80	12	THF		40
14	$Ni(OTf)_2$ (10)	dppm (10)	2.0	80	12	THF		12
15	$Ni(OTf)_2$ (10)	dppe (10)	2.0	80	12	THF		70
16	$Ni(OTf)_2$ (10)	dppf (10)	2.0	80	12	THF		33
17	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.0	80	12	THF		70
18	$Ni(OTf)_2$ (10)	IMes·HCl(10)	2.0	80	12	THF		64
19	$Ni(OTf)_2$ (10)	SIMes·HCl (10)	2.0	80	12	THF		64
20	$Ni(OTf)_2$ (10)	SIPr·HCl (10)	2.0	80	12	THF		50
21	$Ni(OTf)_2$ (5)	IPr·HCl (10)	2.0	80	12	THF		48
22	$Ni(OTf)_2$ (10)	IPr·HCl (20)	2.0	80	12	THF		36
23	$Ni(OTf)_2$ (10)	IPr·HCl (10)	1.5	80	12	THF		25

24	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	80	12	THF		75
25	$Ni(OTf)_2$ (10)	IPr·HCl (10)	3.0	80	12	THF		65
26	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	70	12	THF		73
27	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	12	THF		81
28	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	100	12	THF		78
29	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	10	THF		73
30	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	14	THF		83
31	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF		90
32	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	18	THF		90
33	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	dioxane		30
34	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	toluene		nr
35	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	NMP		46
36	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	DMF		5
37	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	DME		25
38	$Ni(OTf)_2$ (5)	IPr·HCl (5)	2.5	90	16	THF		65
39	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	NaH	82
40	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	NaO*t*Bu	85
41	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	LiO*t*Bu	86
42	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	Cs_2CO_3	95
43	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	K_2CO_3	95
44	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	K_3PO_4	88
45	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	CsF	82
46	$Ni(OTf)_2$ (10)	IPr·HCl (10)	2.5	90	16	THF	DBu	95 (93[c])
47	none	IPr·HCl (10)	2.5	90	16	THF	DBu	np

[a] Preparation method of PhZnCl: PhMgBr + $ZnCl_2$ + 2 LiCl. [b] NMR yields using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yields.

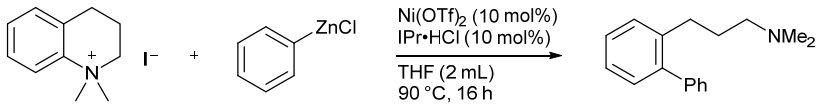
Table S2. Preparation method of PhZnCl



1a (0.2 mmol) **2a** (2.5 equiv.) **3a**

Entry	Preparation method of ArZnCl	Yield (%)
1	PhMgBr + $ZnCl_2$	19
2	PhMgBr + $ZnCl_2$ + LiCl	75
3	PhMgBr + $ZnCl_2$ + 2 LiCl	90
4	PhMgBr + $ZnCl_2$ + 3 LiCl	68
5	PhLi + $ZnCl_2$	40
6	PhLi + $ZnCl_2$ + $MgCl_2$	trace
7	PhLi + $ZnCl_2$ + $MgCl_2$ + LiCl	trace

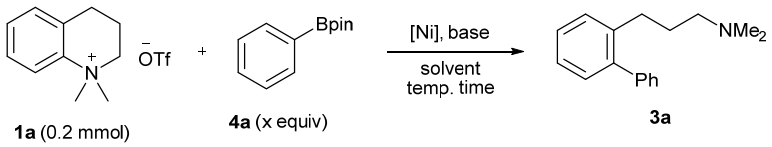
Reaction of 1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium iodide



1a' (0.2 mmol) **2a** (2.5 equiv) **3a** 70%

(2) Condition optimization of the reaction of cyclic quaternary ammonium salts with arylboron reagents

Table S3. Optimization of conditions for the reaction of quaternary ammonium salt (**1a**) with 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (**4a**)



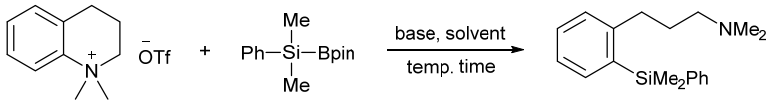
1a (0.2 mmol) **4a** (x equiv) **3a**

Entry	[Ni] (mol%)	x	Solvent	Base (2 equiv.)	Temp. (°C)	Time (h)	Yield [a] (%)
1	$NiCl_2$ (10)	2.0	THF	NaO*t*Bu	80	16	29
2	NiF_2 (10)	2.0	THF	NaO*t*Bu	80	16	nr
3	$Ni(OTf)_2$ (10)	2.0	THF	NaO*t*Bu	80	16	41
4	$NiCl_2$(DME) (10)	2.0	THF	NaO*t*Bu	80	16	27
5	$NiCl_2(PCy_3)_2$ (10)	2.0	THF	NaO*t*Bu	80	16	70
6	$NiCl_2(PPh_3)_2$ (10)	2.0	THF	NaO*t*Bu	80	16	14
7	$NiCl_2$(dppe) (10)	2.0	THF	NaO*t*Bu	80	16	18
8	$NiCl_2$(dppp) (10)	2.0	THF	NaO*t*Bu	80	16	18
9	$NiCl_2$(dppf) (10)	2.0	THF	NaO*t*Bu	80	16	28
10	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	NaO*t*Bu	80	16	80 (78[b])
11	$NiCl_2(PCy_3)_2$ (10)	2.0	DME	NaO*t*Bu	80	16	23
12	$NiCl_2(PCy_3)_2$ (10)	2.0	toluene	NaO*t*Bu	80	16	42
13	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	NaO*t*Bu	90	16	75
14	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	NaO*t*Bu	70	16	70
15	$NiCl_2(PCy_3)_2$ (10)	2.5	dioxane	NaO*t*Bu	80	16	77
16	$NiCl_2(PCy_3)_2$ (10)	1.5	dioxane	NaO*t*Bu	80	16	31
17	$NiCl_2(PCy_3)_2$ (15)	2.0	dioxane	NaO*t*Bu	80	16	46
18	$NiCl_2(PCy_3)_2$ (5)	2.0	dioxane	NaO*t*Bu	80	16	55
19	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	NaO*t*Bu	80	18	78
20	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	KO*t*Bu	80	16	42
21	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	LiO*t*Bu	80	16	12
22	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	NaOH	80	16	nr
23	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	KOH	80	16	nr
24	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	Cs_2CO_3	80	16	nr
25	$NiCl_2(PCy_3)_2$ (10)	2.0	dioxane	KF	80	16	nr

[a] NMR yields using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yields.

(3) Condition optimization of the reaction of cyclic quaternary ammonium salts with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane

Table S4. Optimization of conditions for the reaction of quaternary ammonium salt (**1a**) with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (**5**)

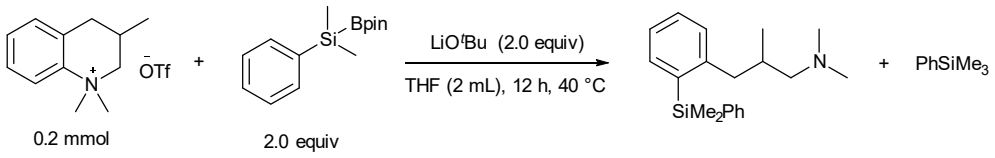


1a (0.2 mmol) **5** (x equiv) **6a**

Entry	x	T/°C	time/h	Solvent/2ml	Base (2.0 equiv)	Yield[a] (%)
1	2.0	60	12	THF	LiO*t*Bu	88
2	2.0	60	12	THF	NaO*t*Bu	78
3	2.0	60	12	THF	KO*t*Bu	64
4	2.0	60	12	THF	NaHMDS	74
4	2.0	60	12	THF	CsF	65
5	2.0	60	12	THF	KOH	nr
6	2.0	60	12	THF	NaOH	nr
7	2.0	40	12	THF	LiO*t*Bu	95(95[b])
8	2.0	25	12	THF	LiO*t*Bu	88
9	2.0	40	8	THF	LiO*t*Bu	74
10	2.0	40	12	Et_2O	LiO*t*Bu	70
11	2.0	40	12	DME	LiO*t*Bu	nr
12	2.0	40	12	1,4-dioxane	LiO*t*Bu	nr
13	2.5	40	10	THF	LiOtBu	95

[a] NMR yields using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yields.

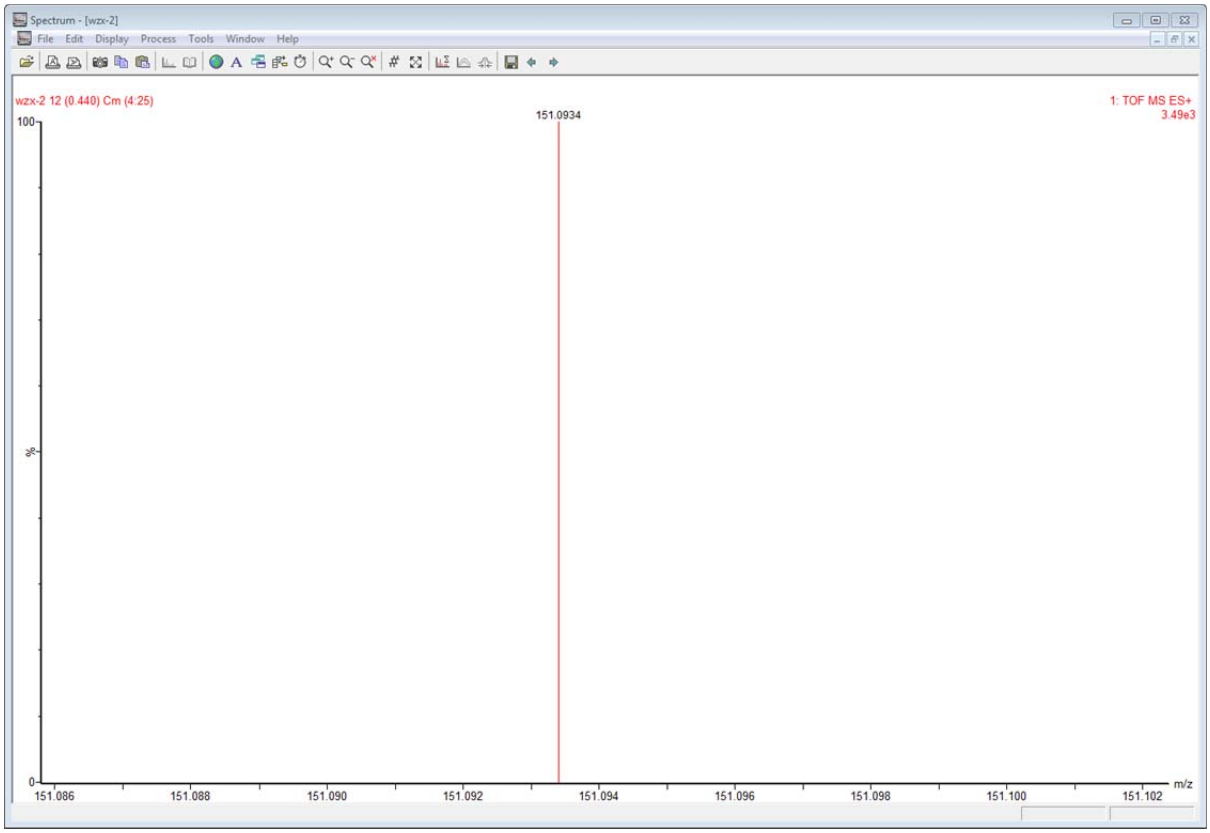
2. Detection of $PhSiMe_3$



0.2 mmol

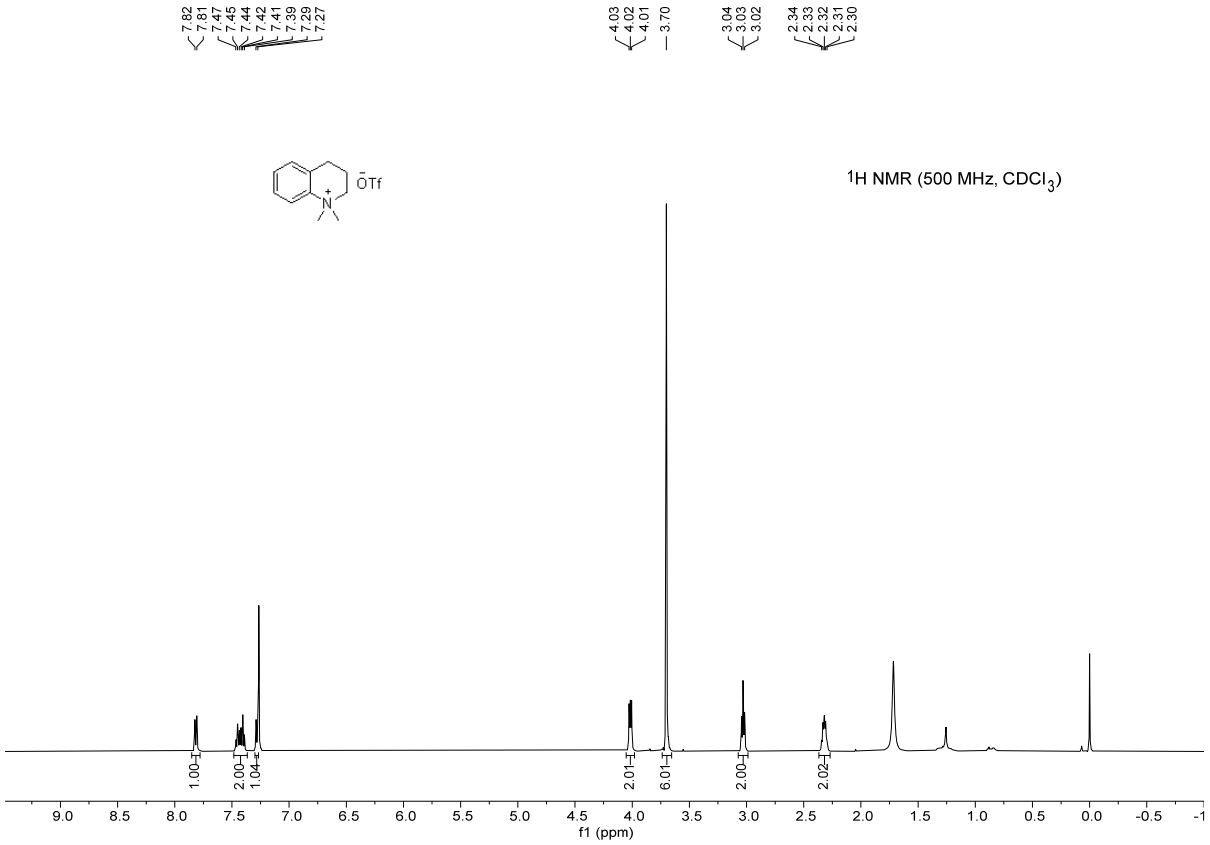
2.0 equiv

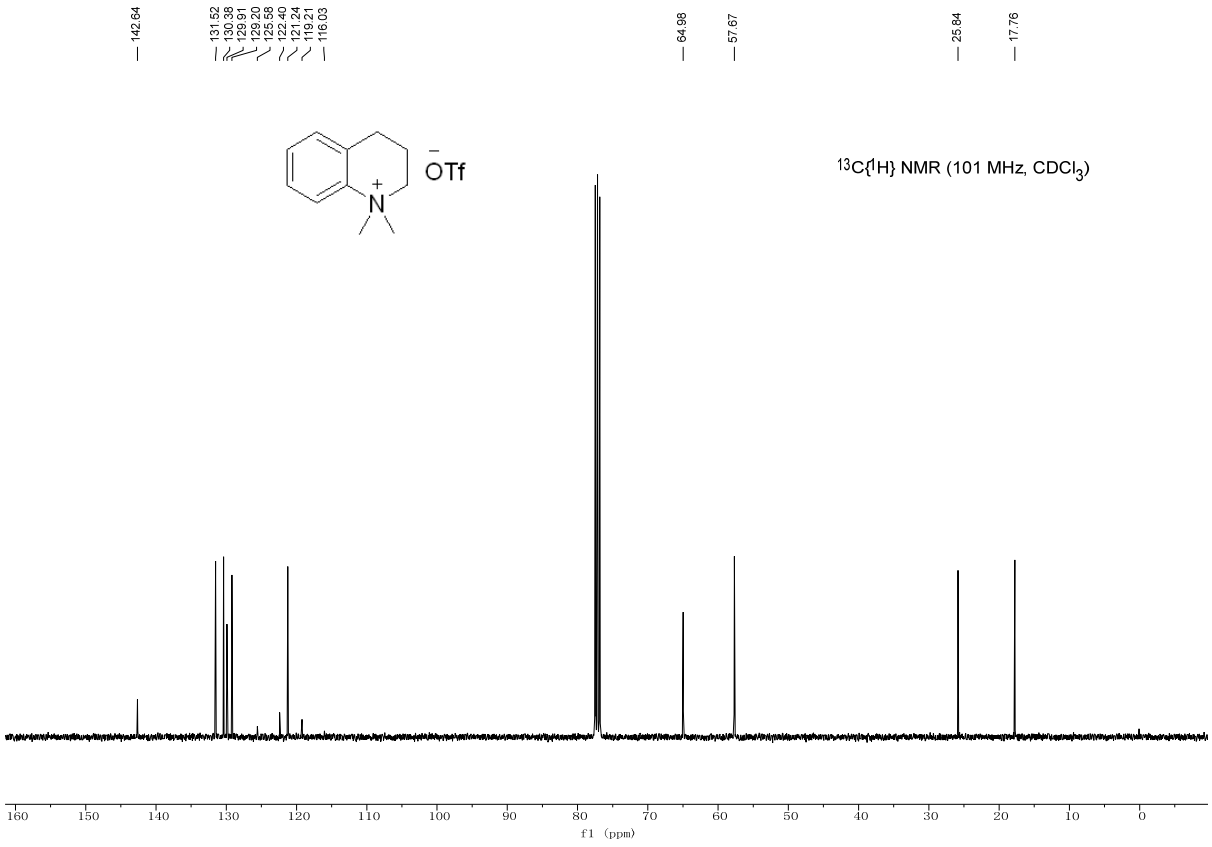
calcd. for $C_9H_{15}Si^+$ 151.0938 $[M+H]^+$
HRMS (ESI) found 151.0934



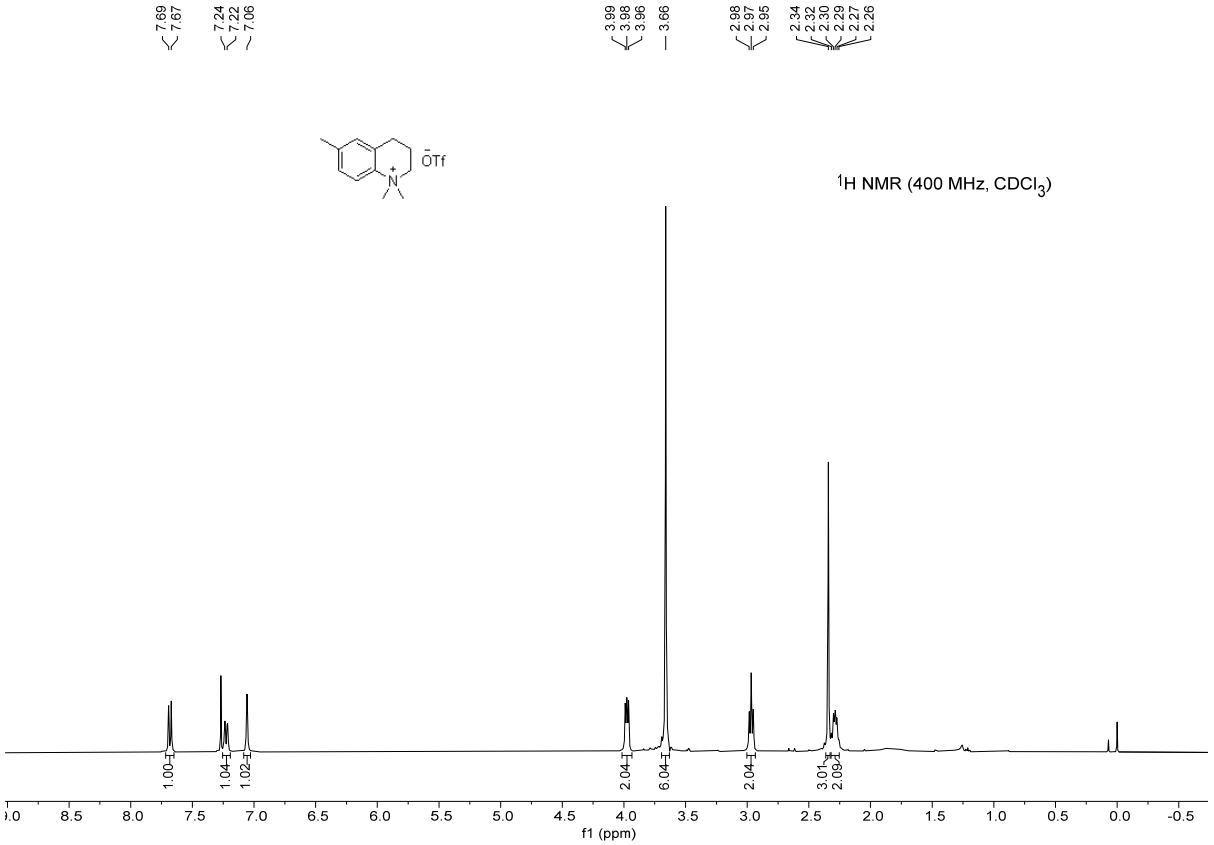
3. Spectral copies of the products

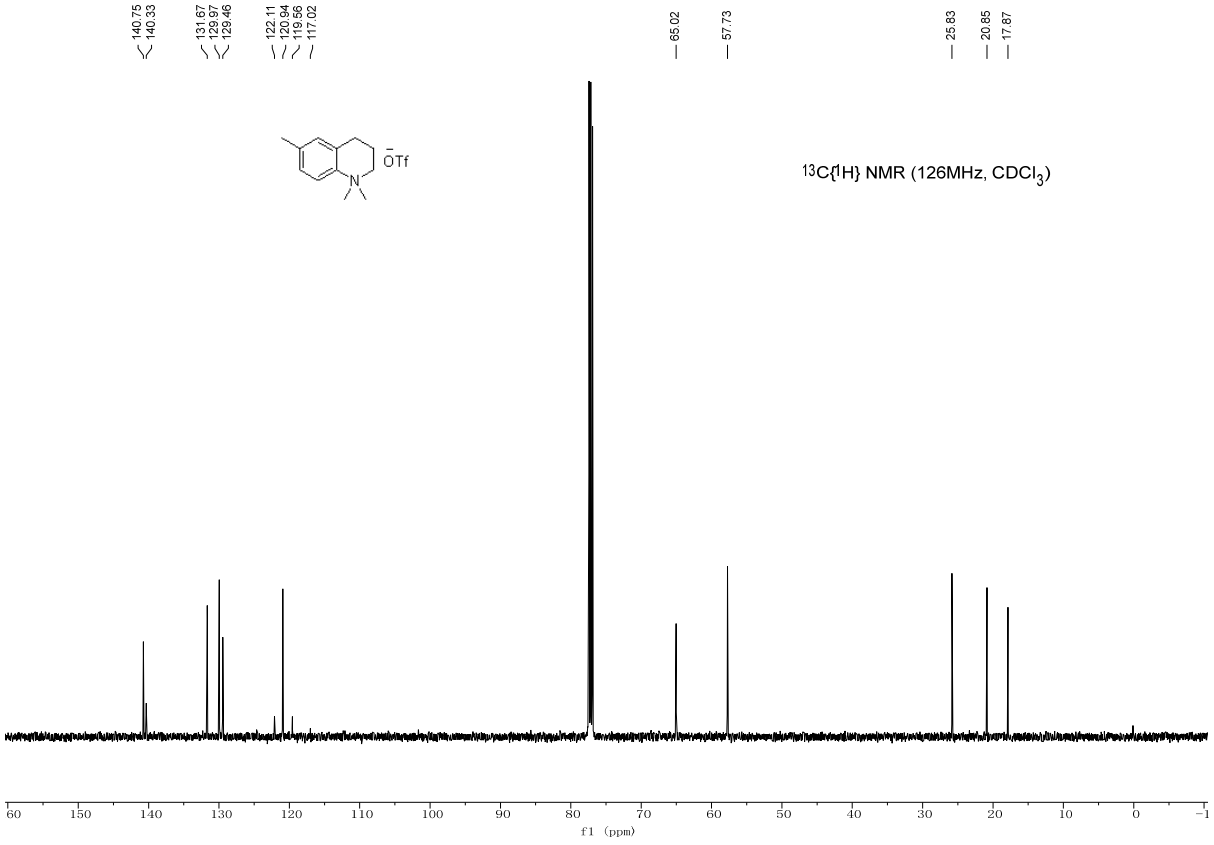
(1) 1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1a**)



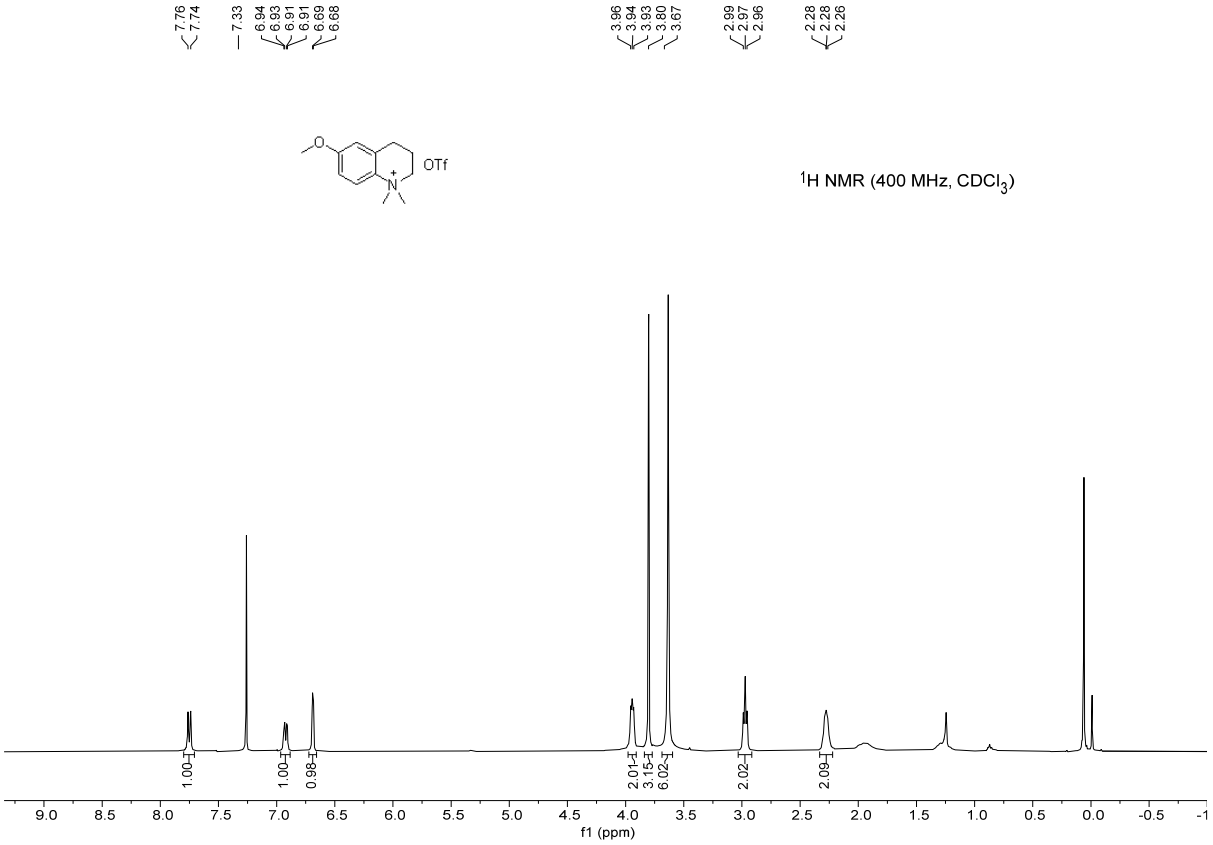


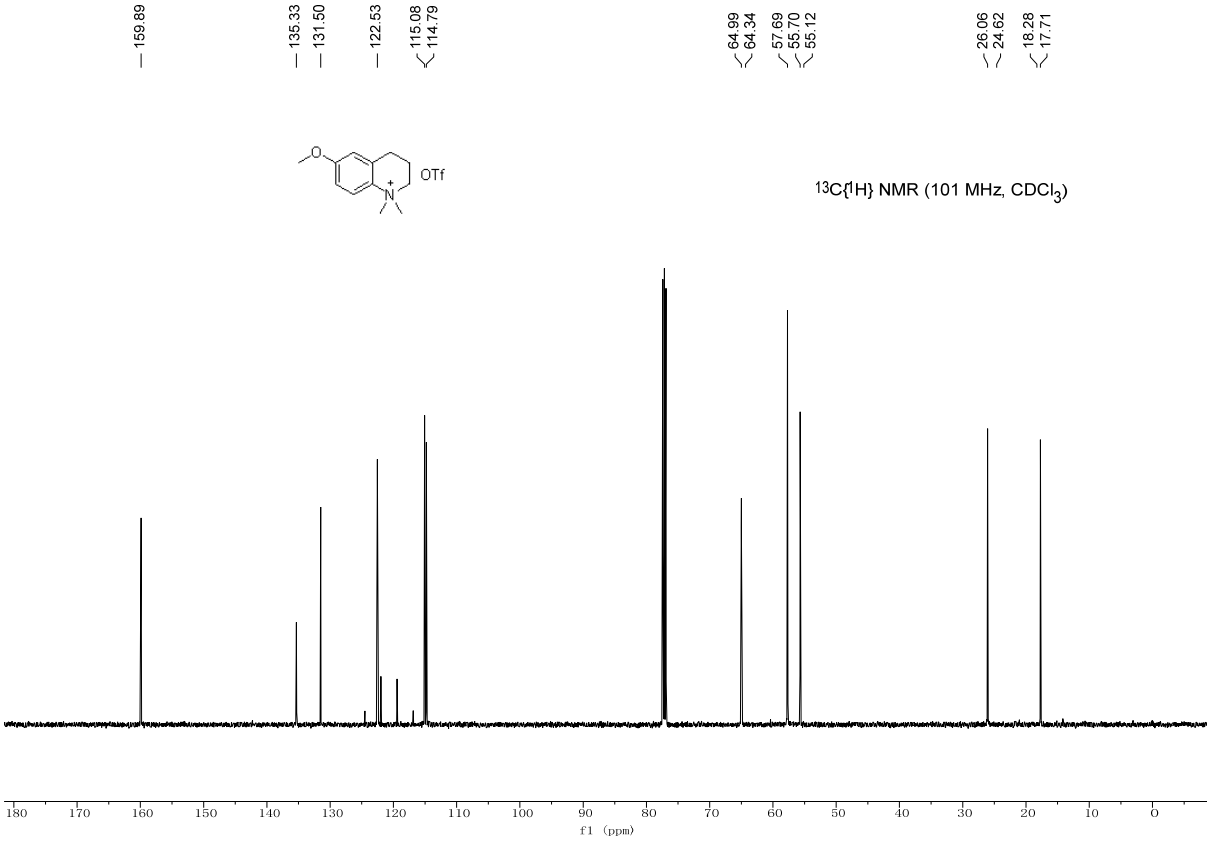
(2) 1,1,6-trimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1b**)



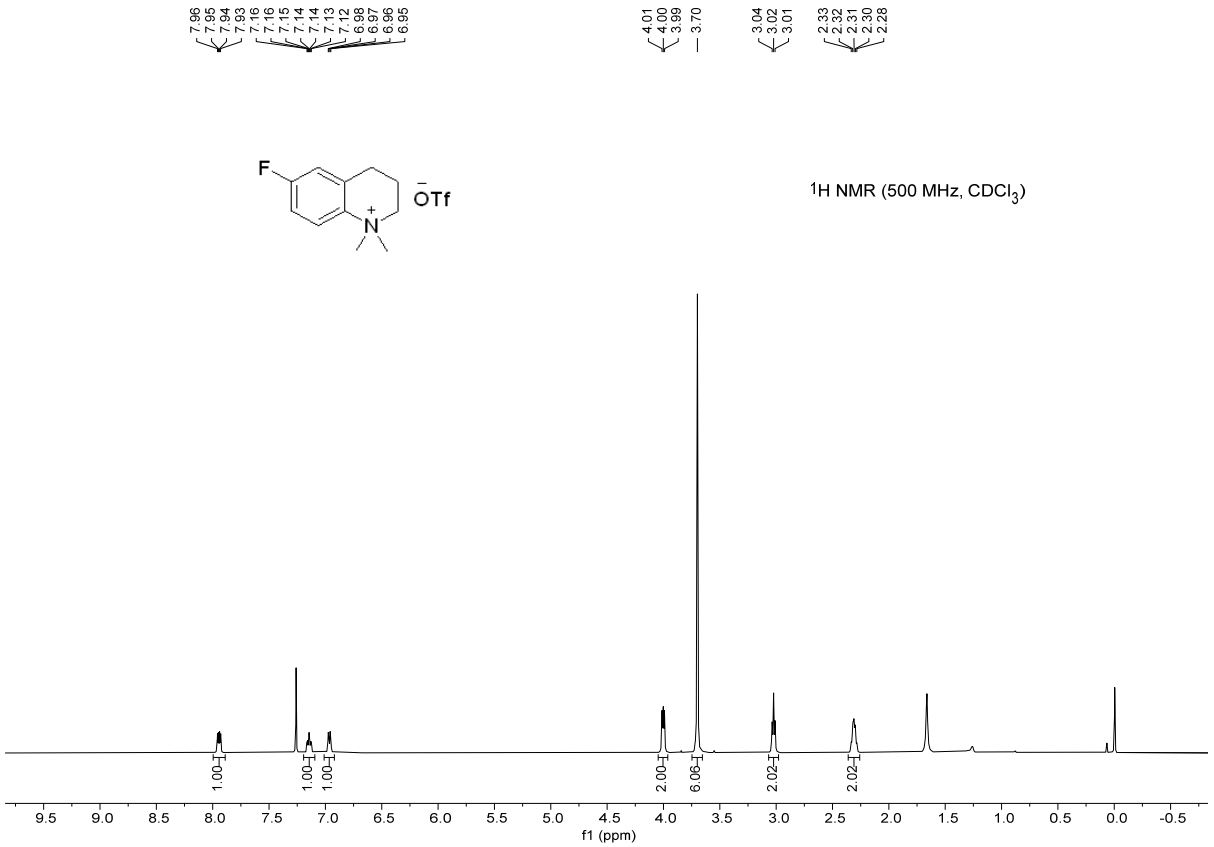


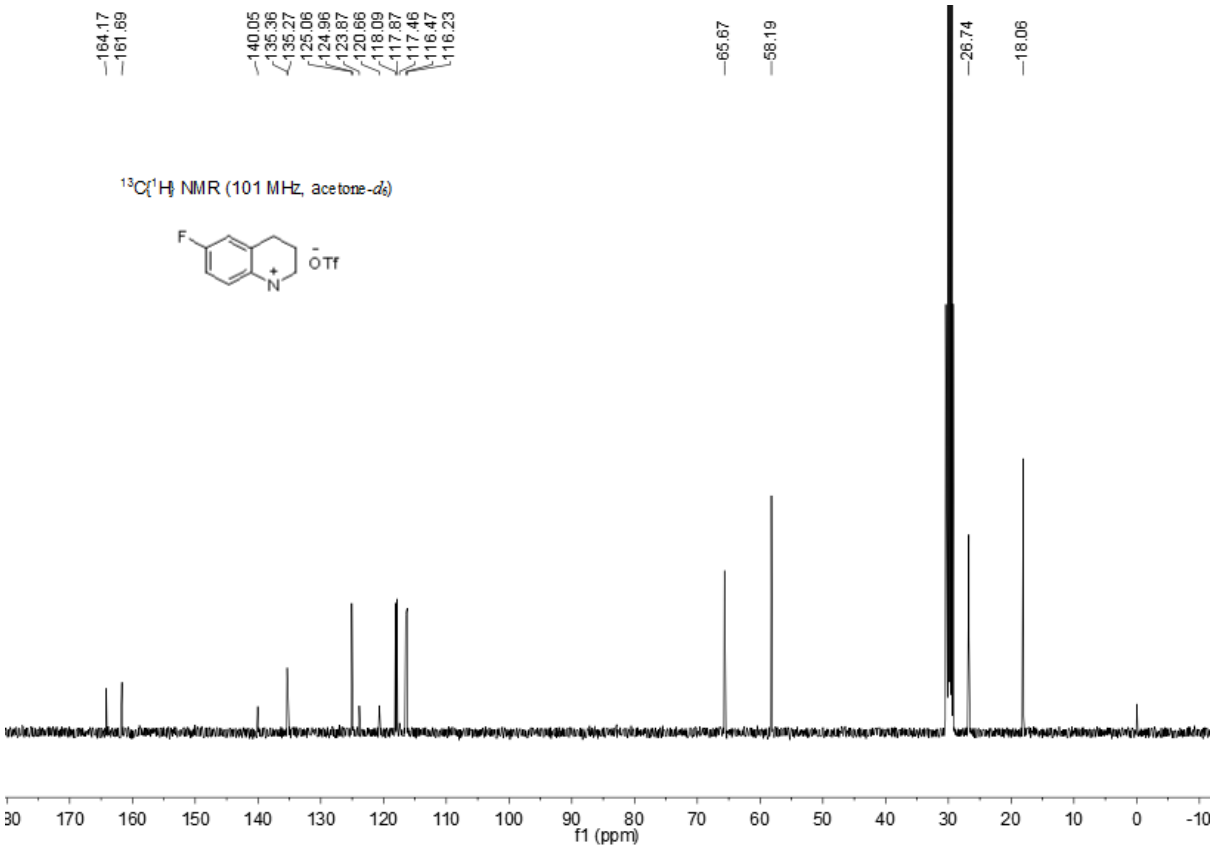
(3) 6-methoxy-1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1c**)



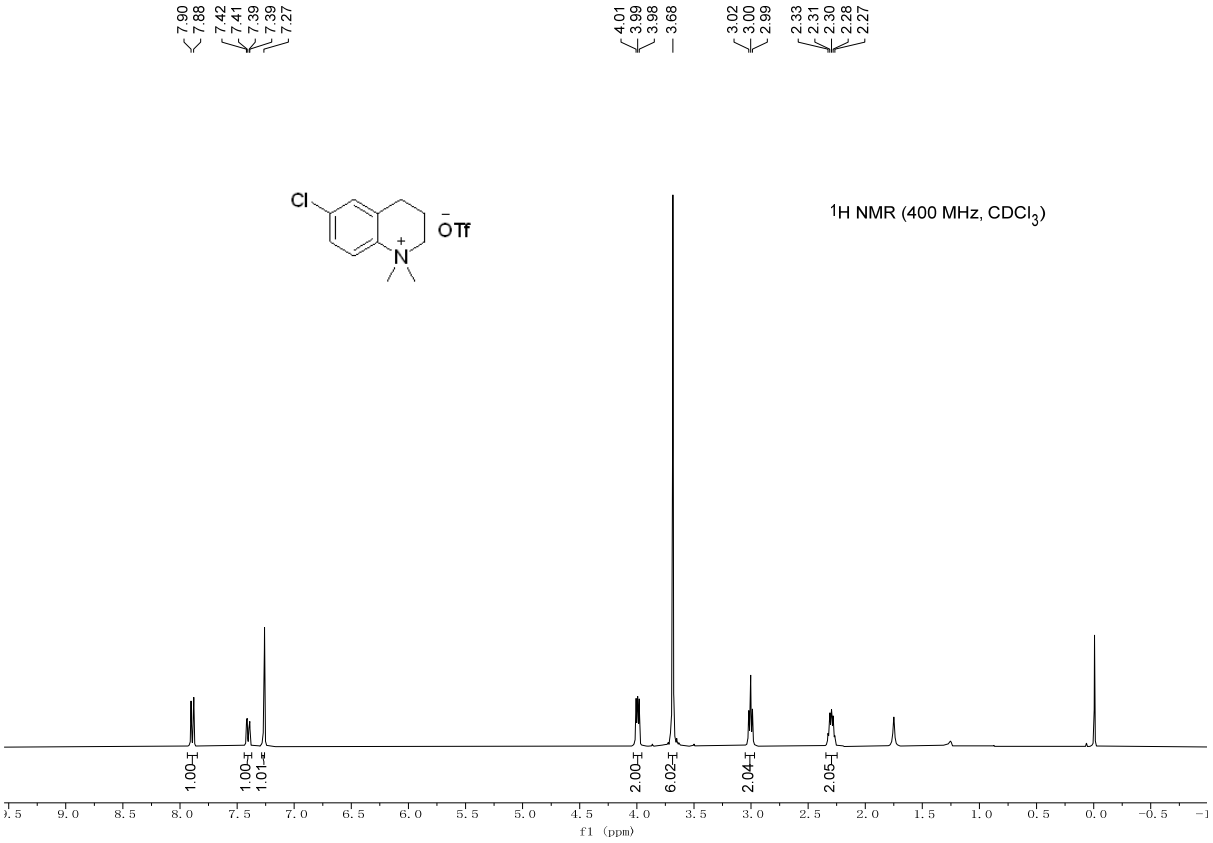


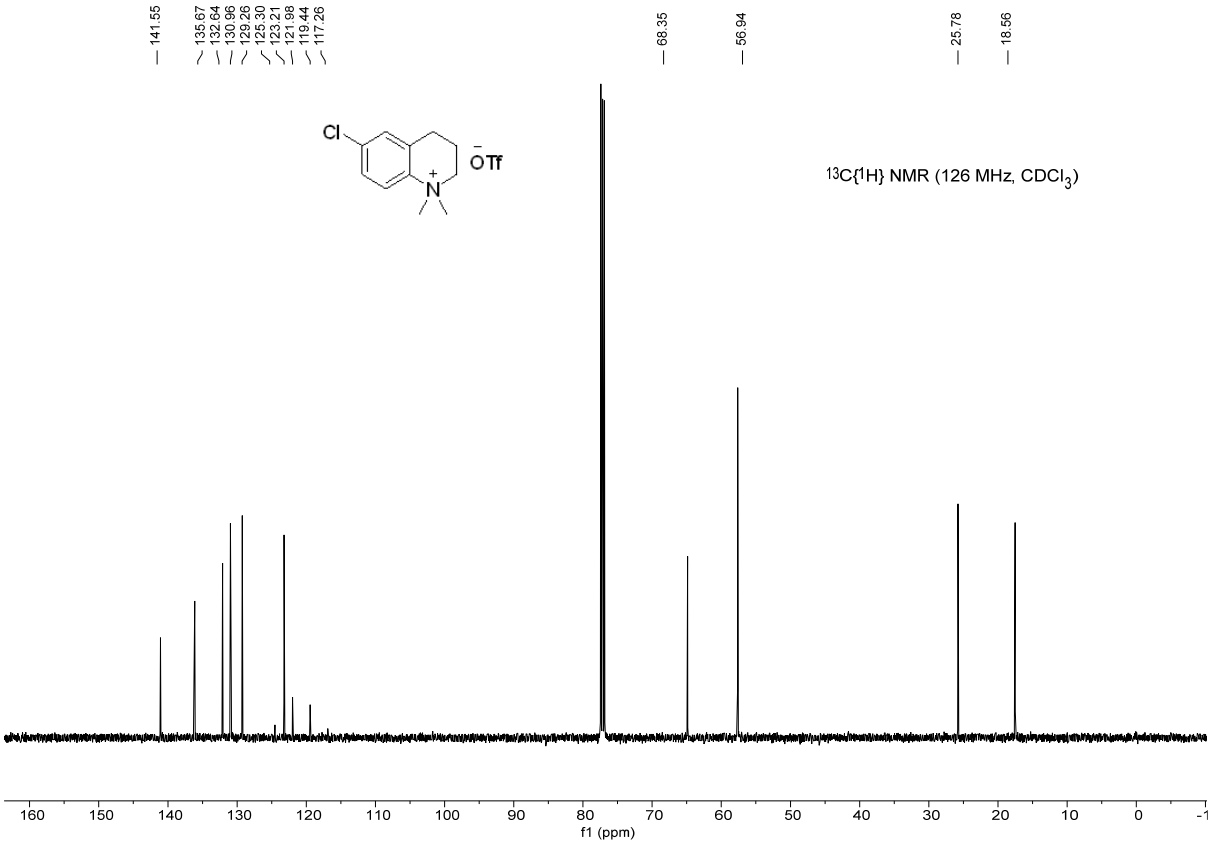
(4) 6-fluoro-1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1d**)



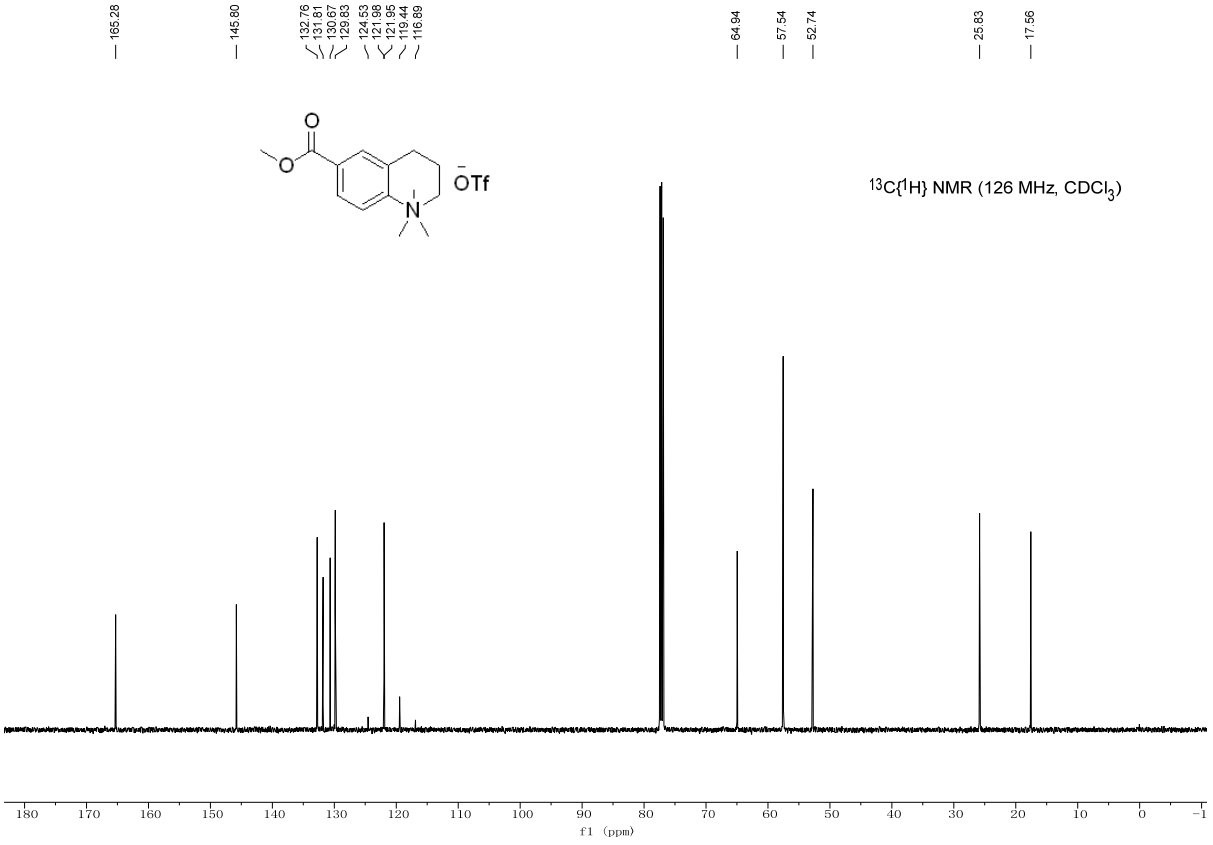


(5) 6-chloro-1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1e**)

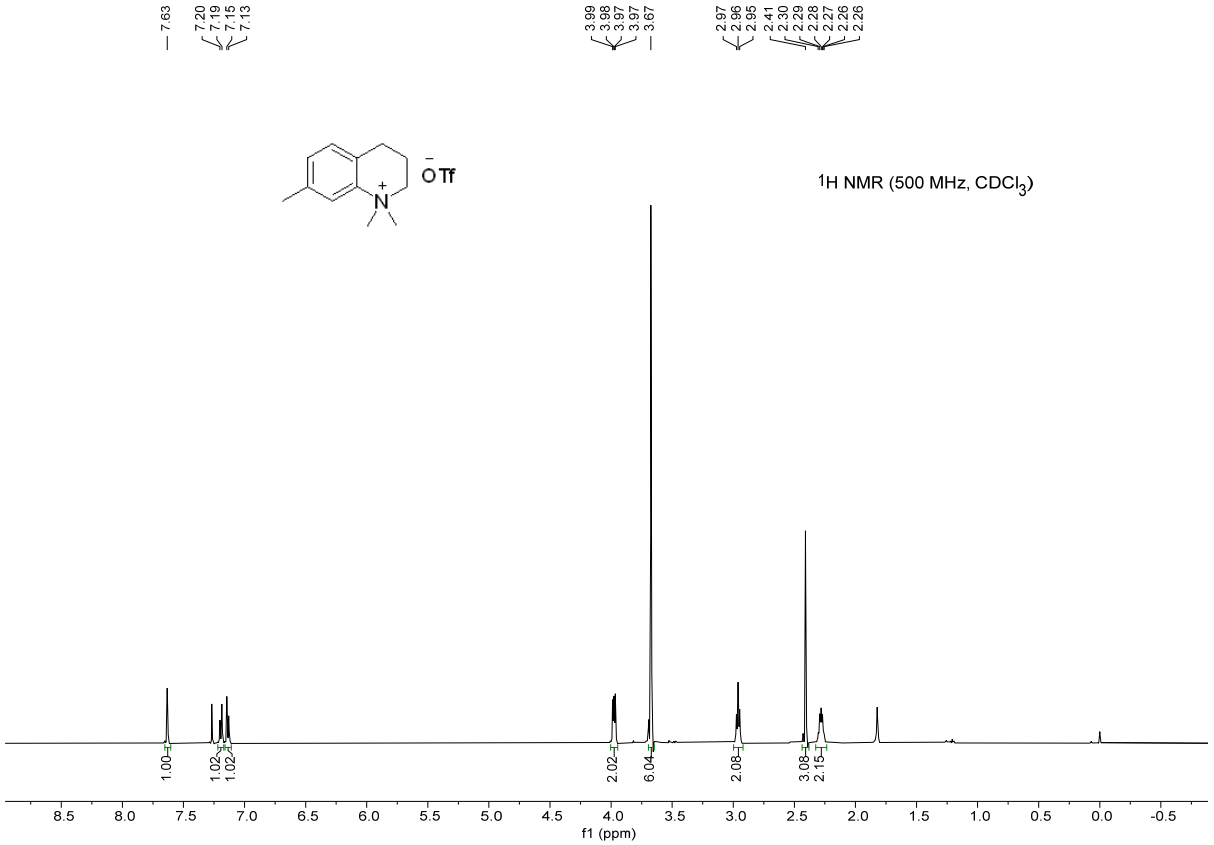


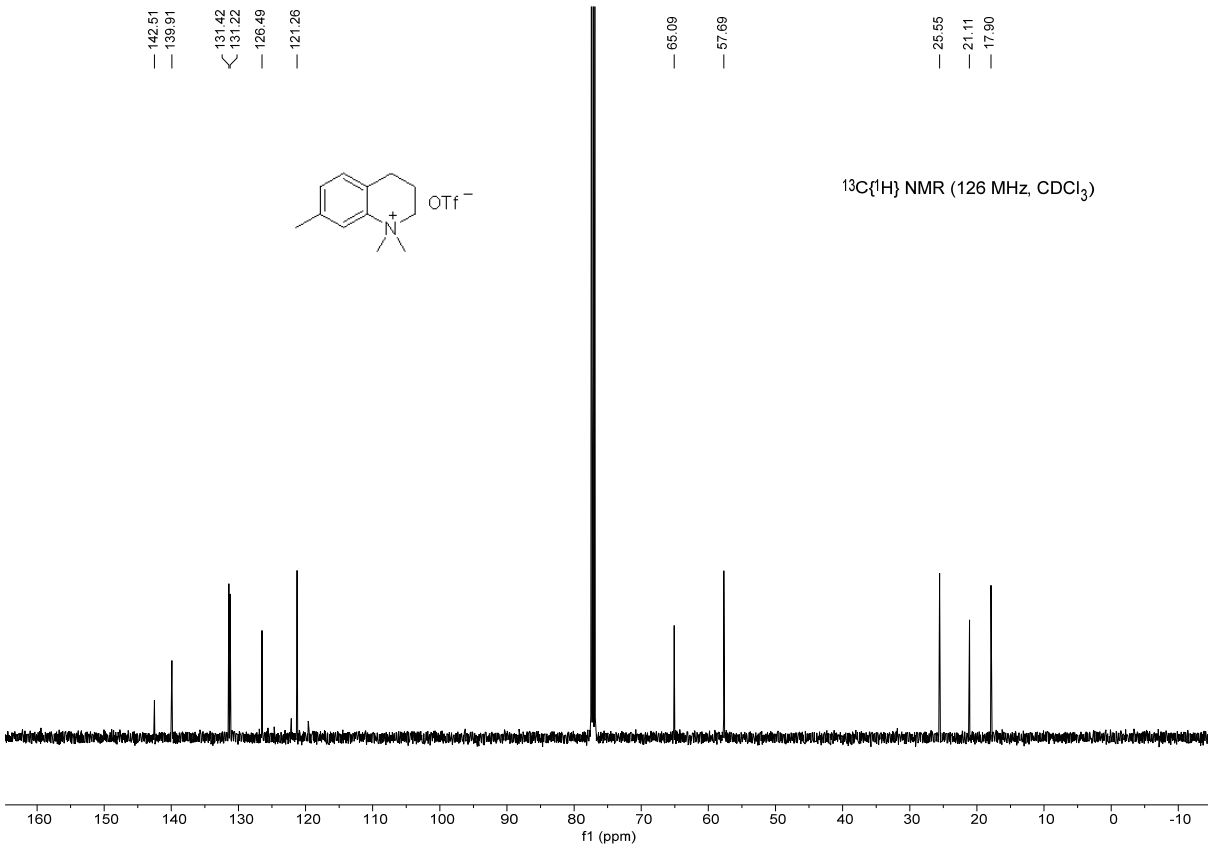


(6) 6-(methoxycarbonyl)-1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1f**)

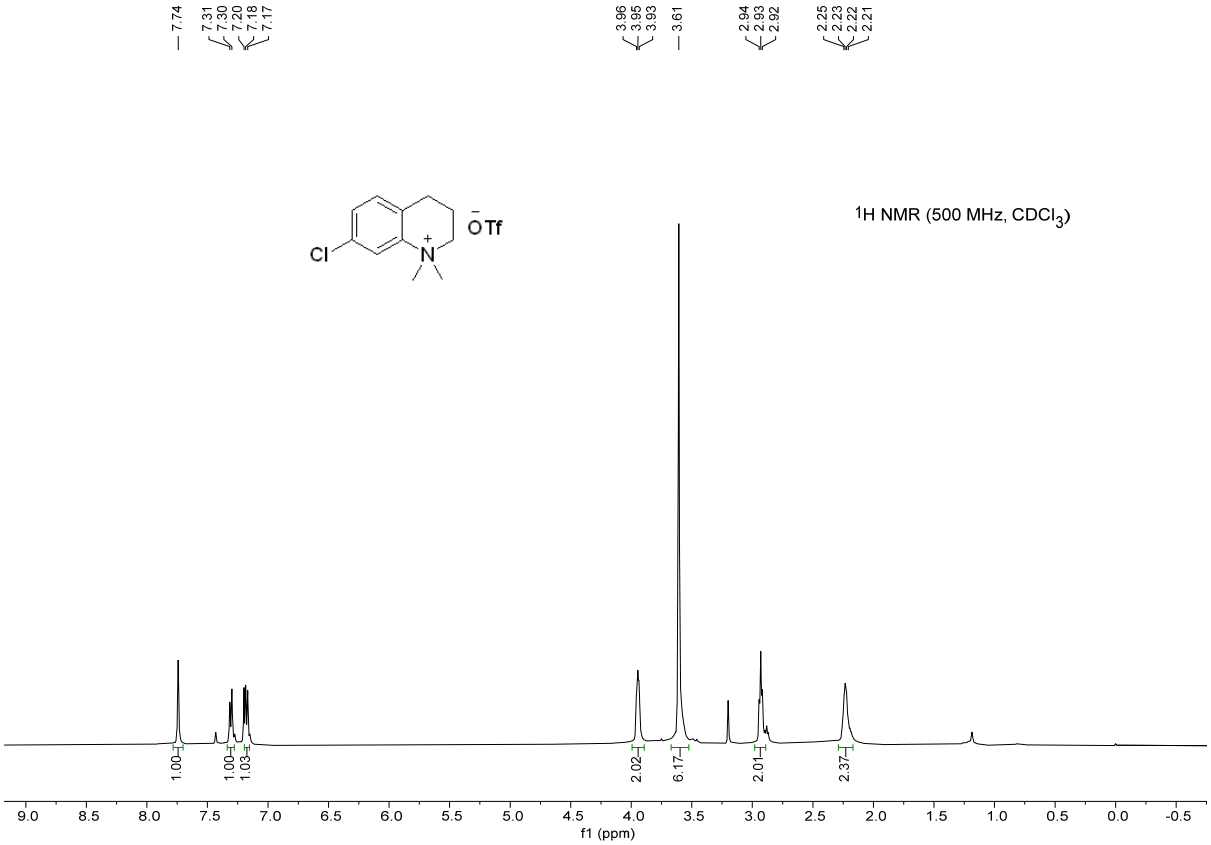


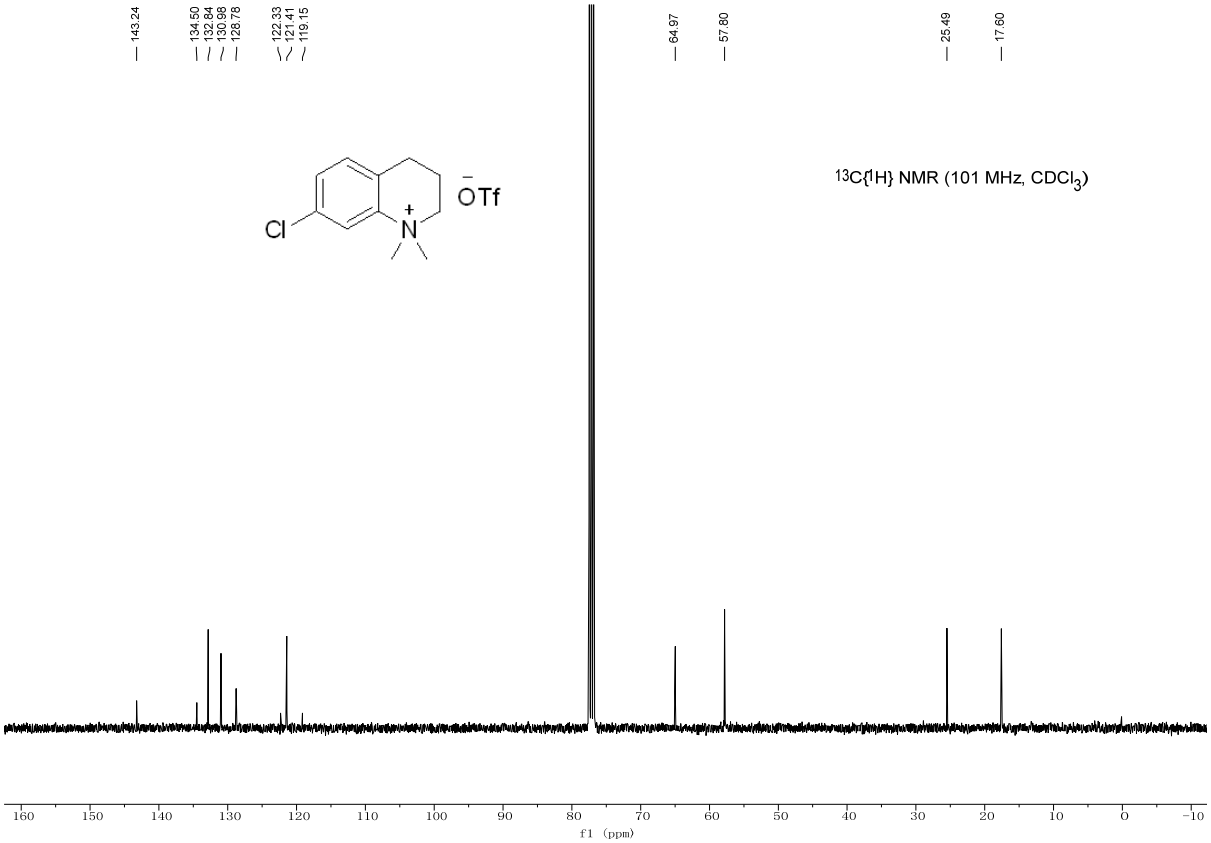
(7) 1,1,7-trimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1g**)



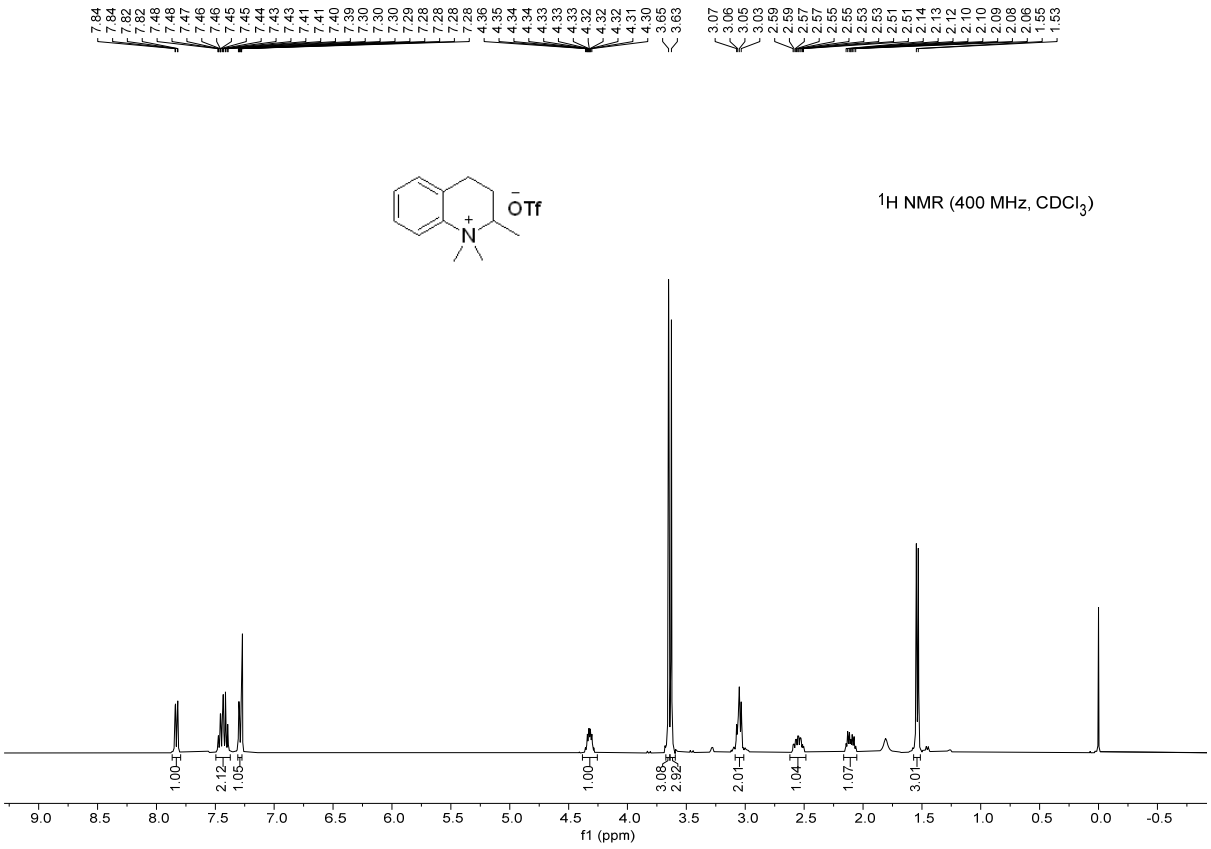


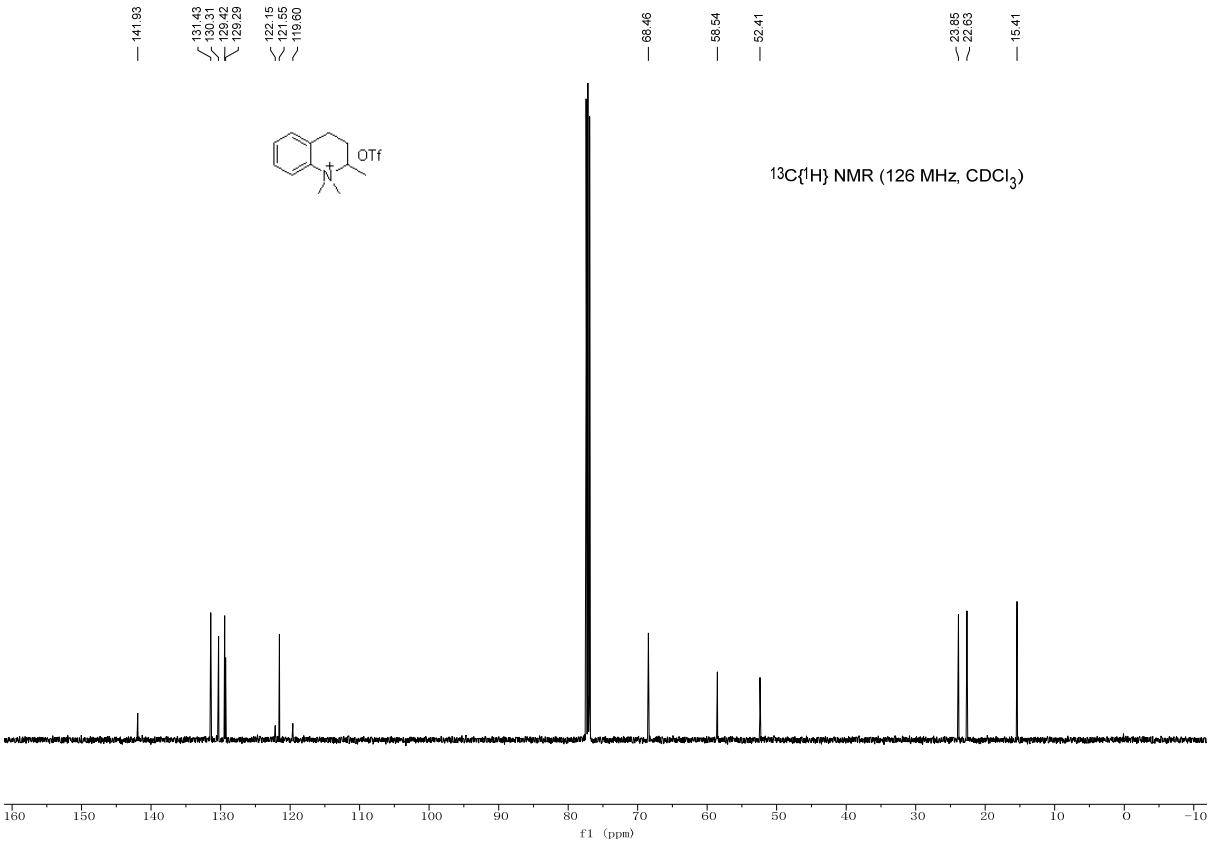
(8) 7-chloro-1,1-dimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1h**)



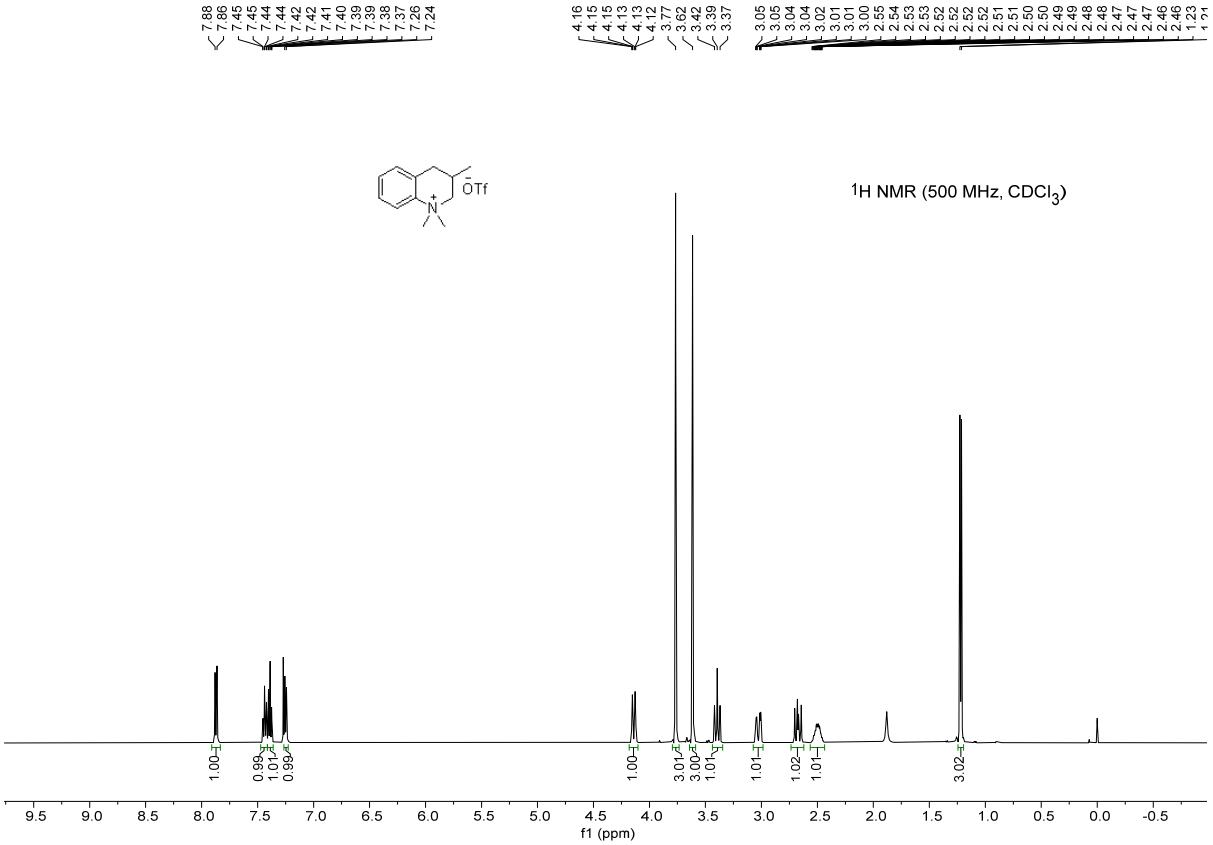


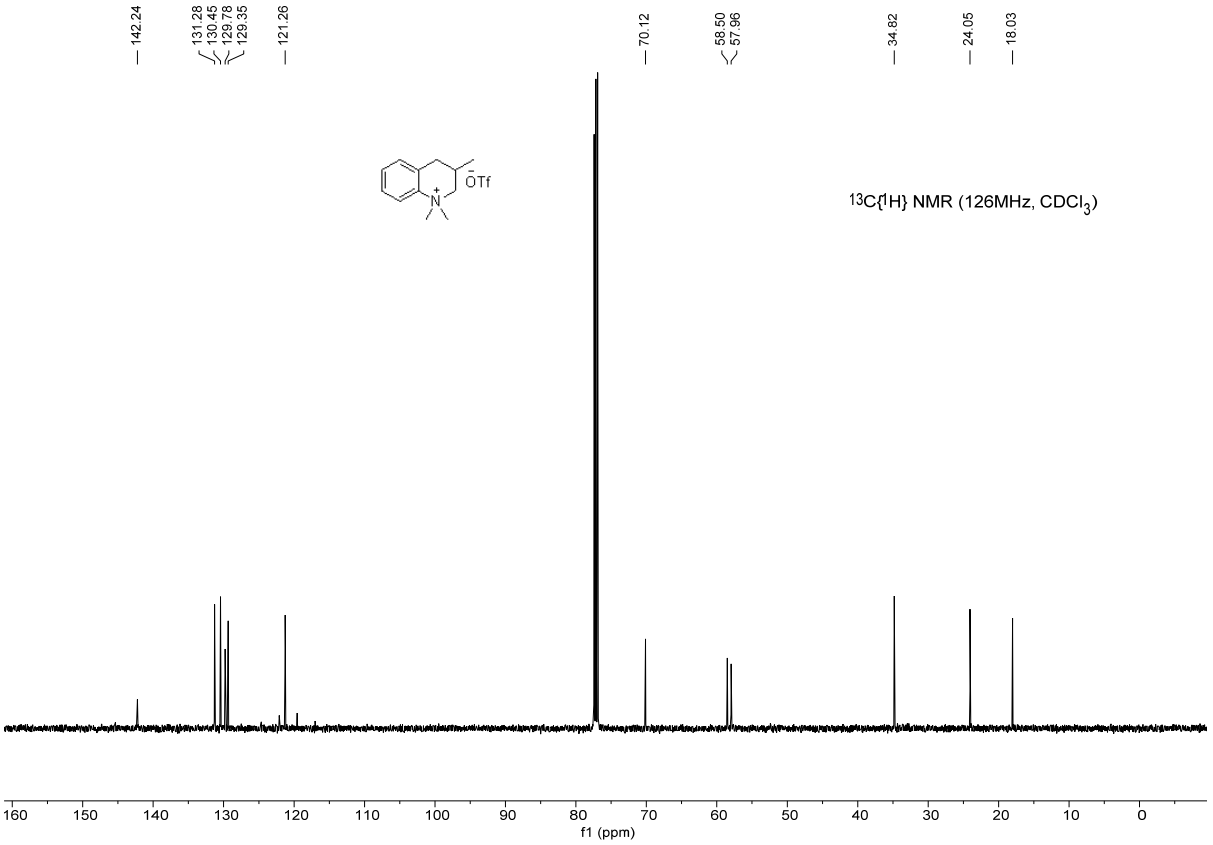
(9) 1,1,2-trimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1i**)



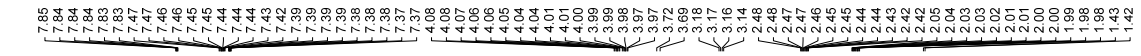


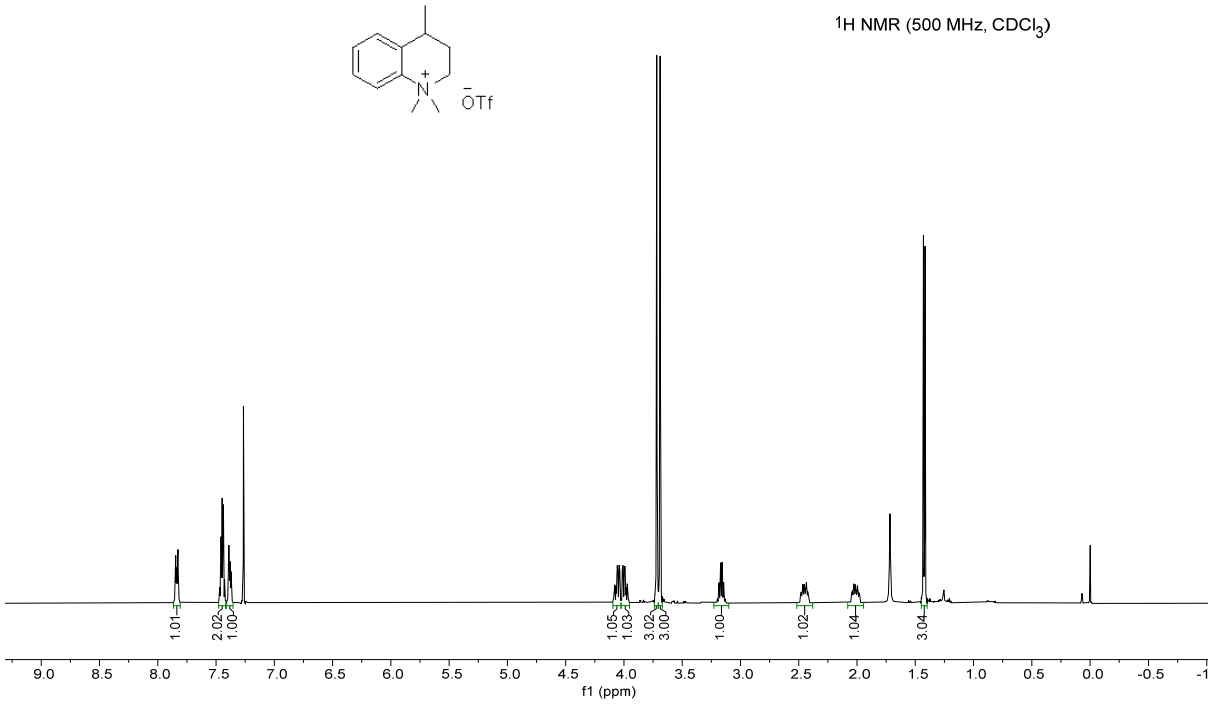
(10) 1,1,3-trimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1j**)

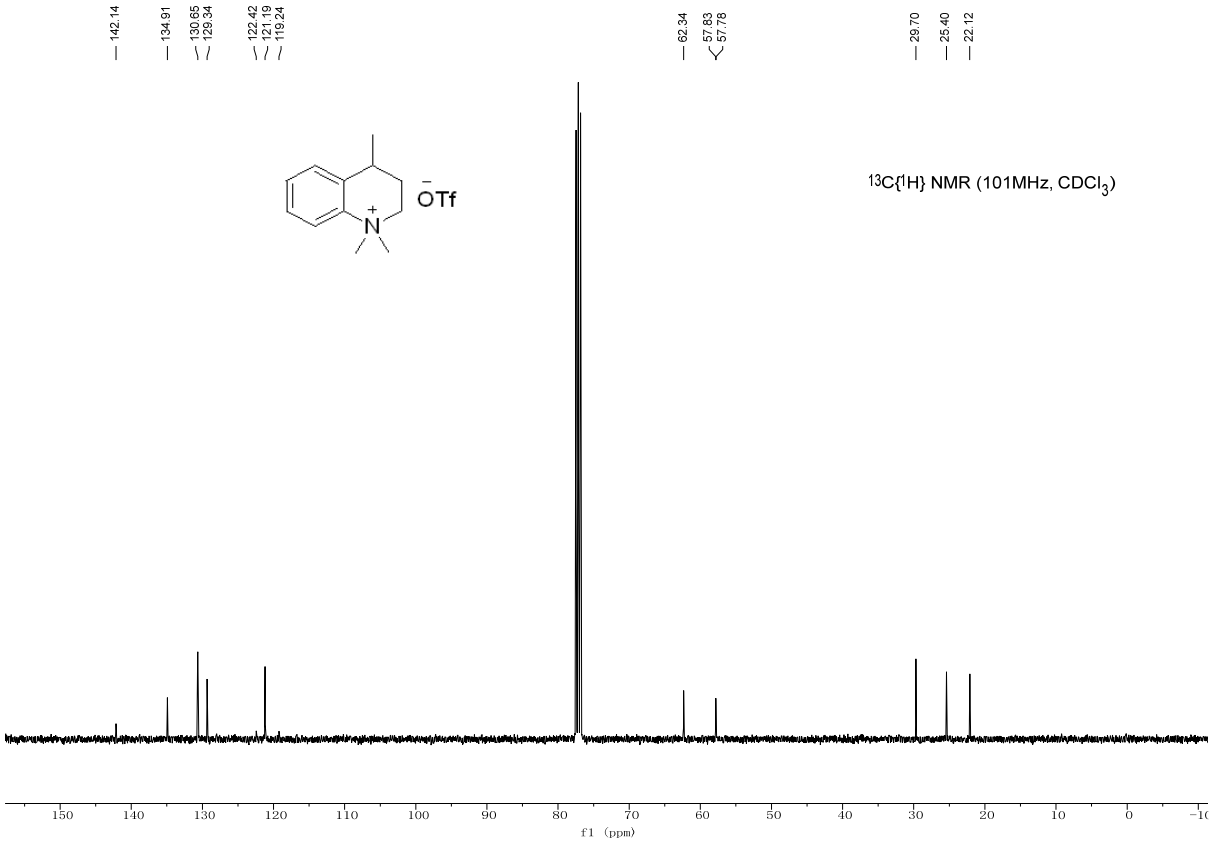




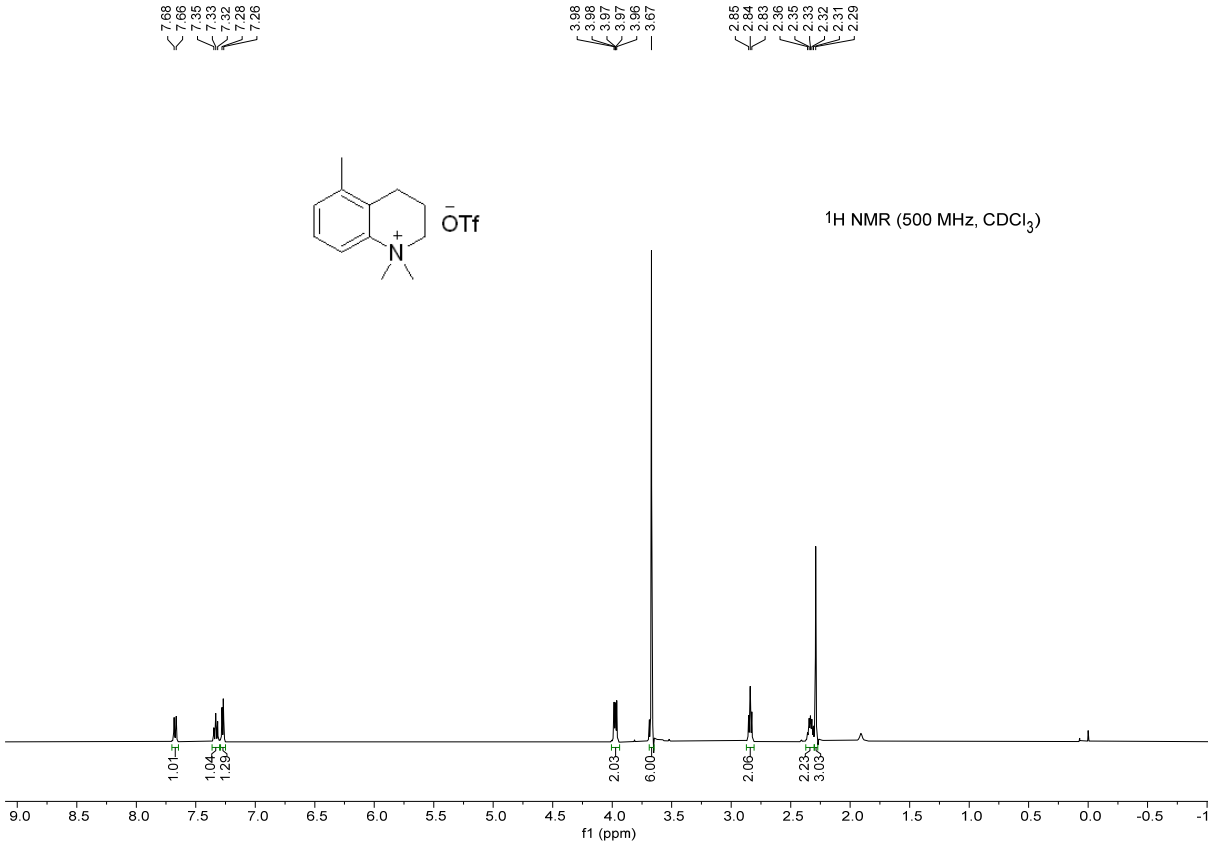
(11) 1,1,4-trimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1k**)

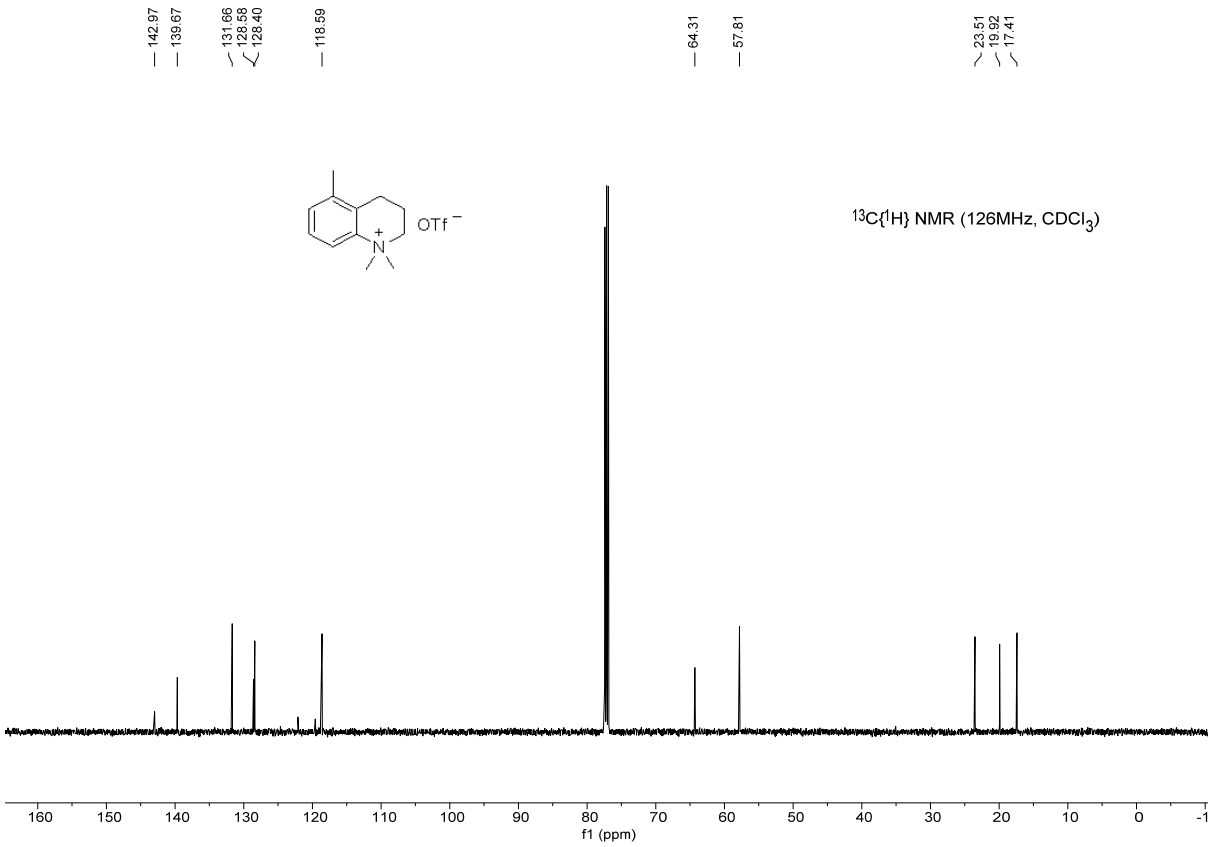




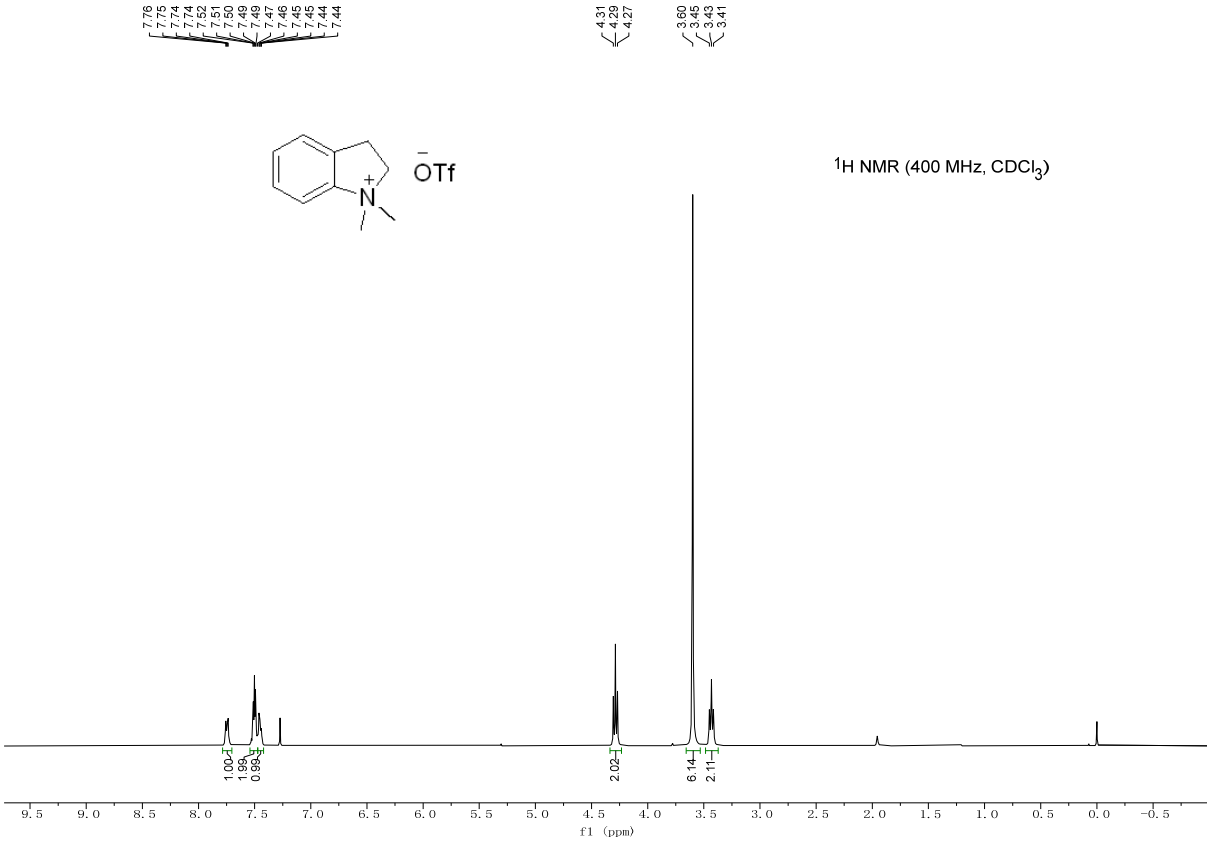


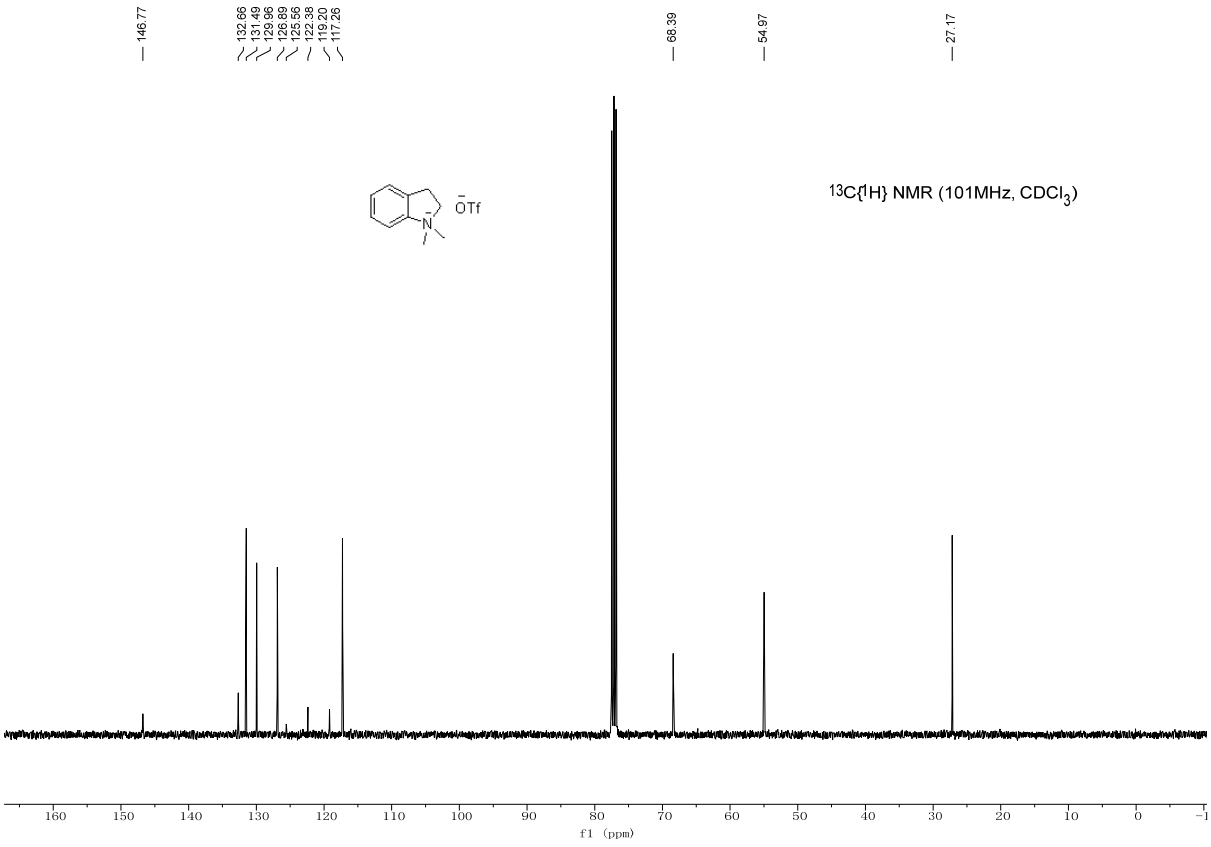
(12) 1,1,5-trimethyl-1,2,3,4-tetrahydroquinolin-1-ium triflate (**1l**)



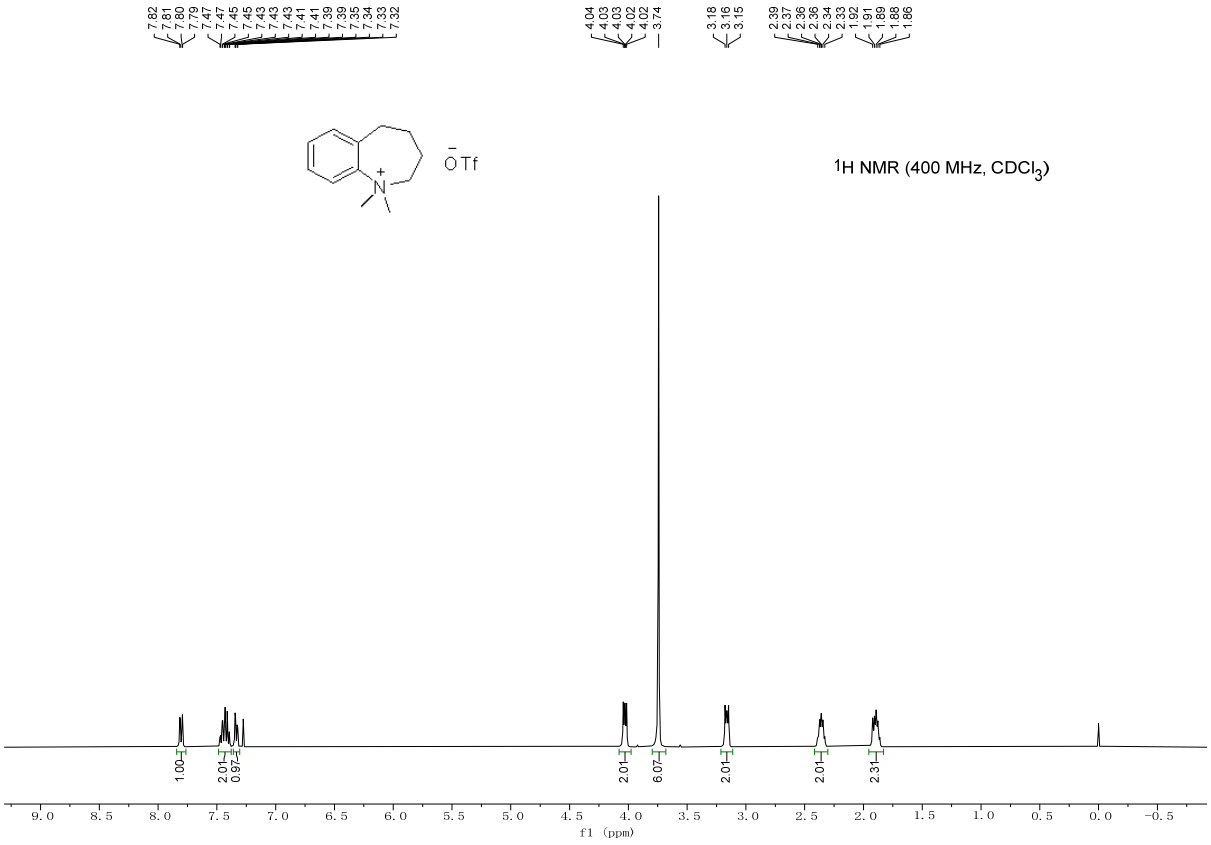


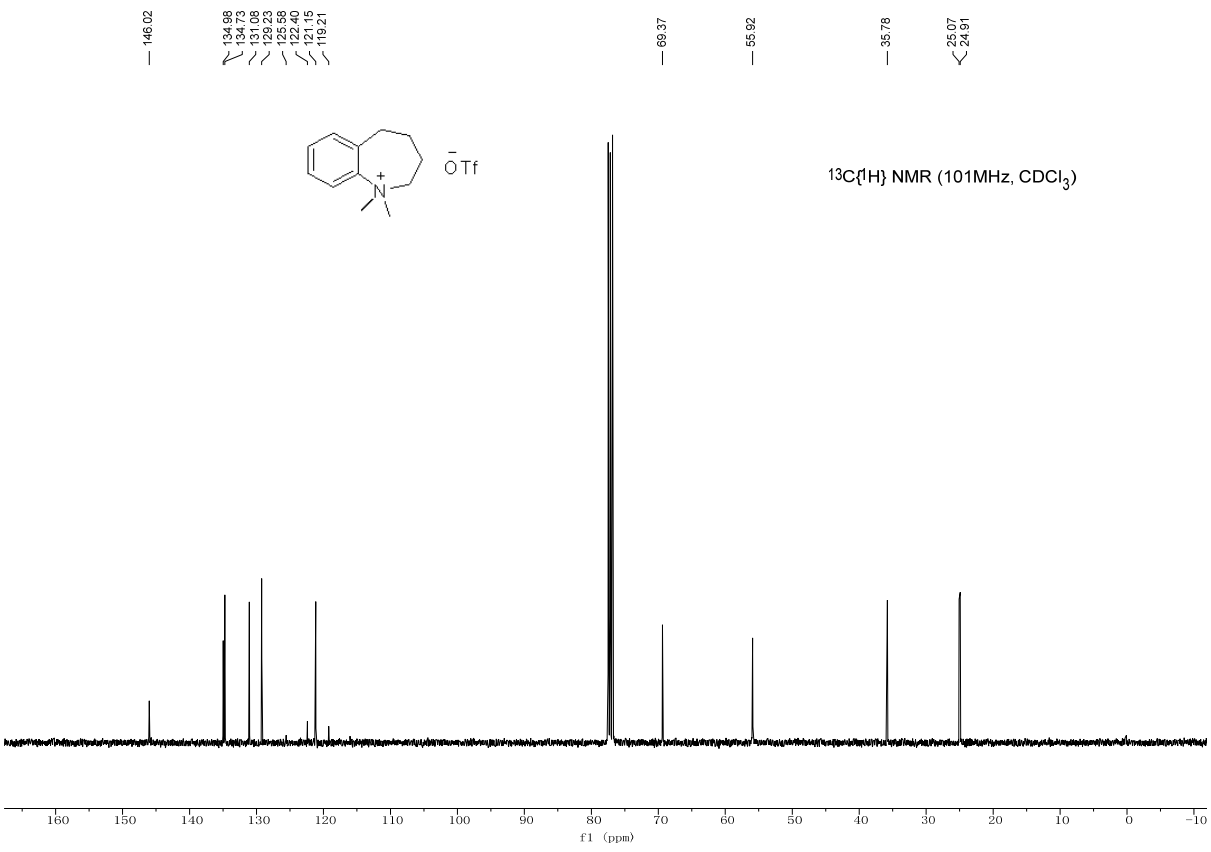
(13) 1,1-dimethylindolin-1-ium triflate (**1m**)





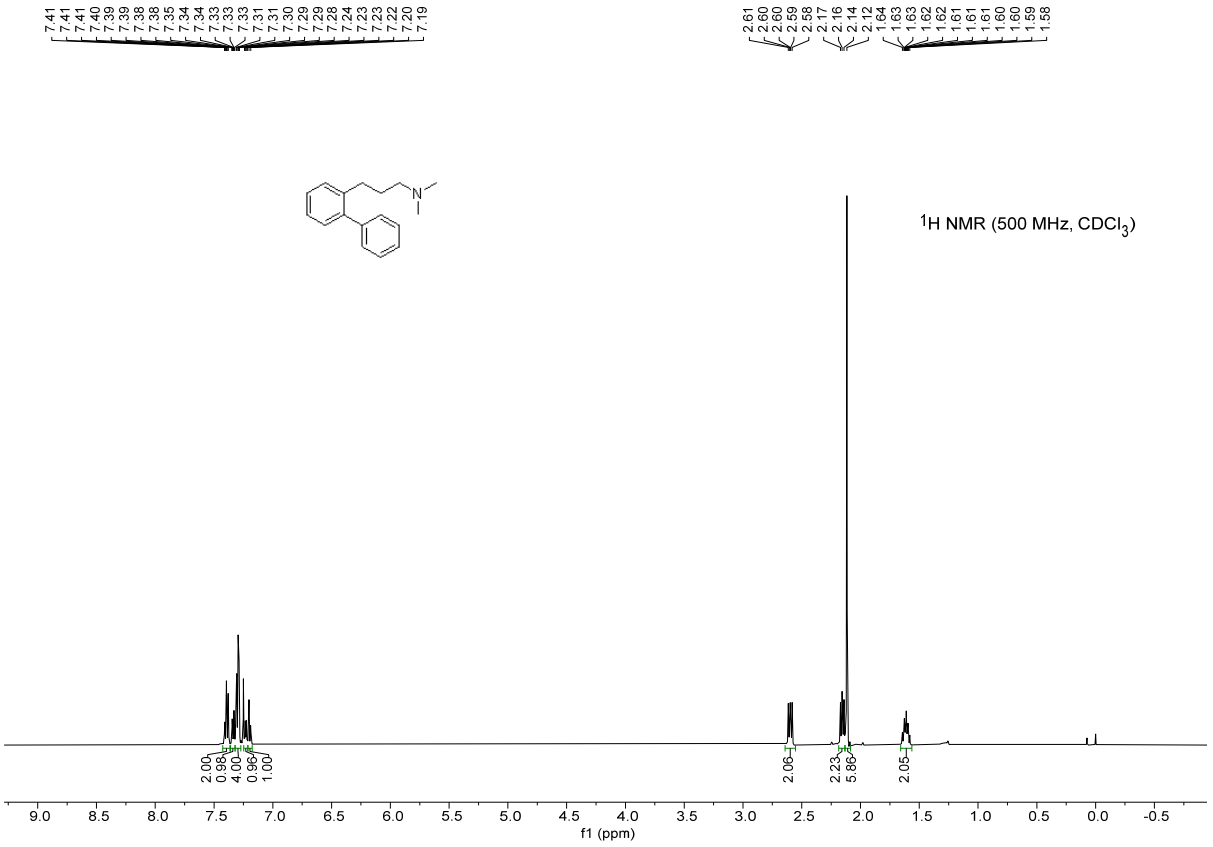
(14) 1,1-dimethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-ium triflate (**1n**)

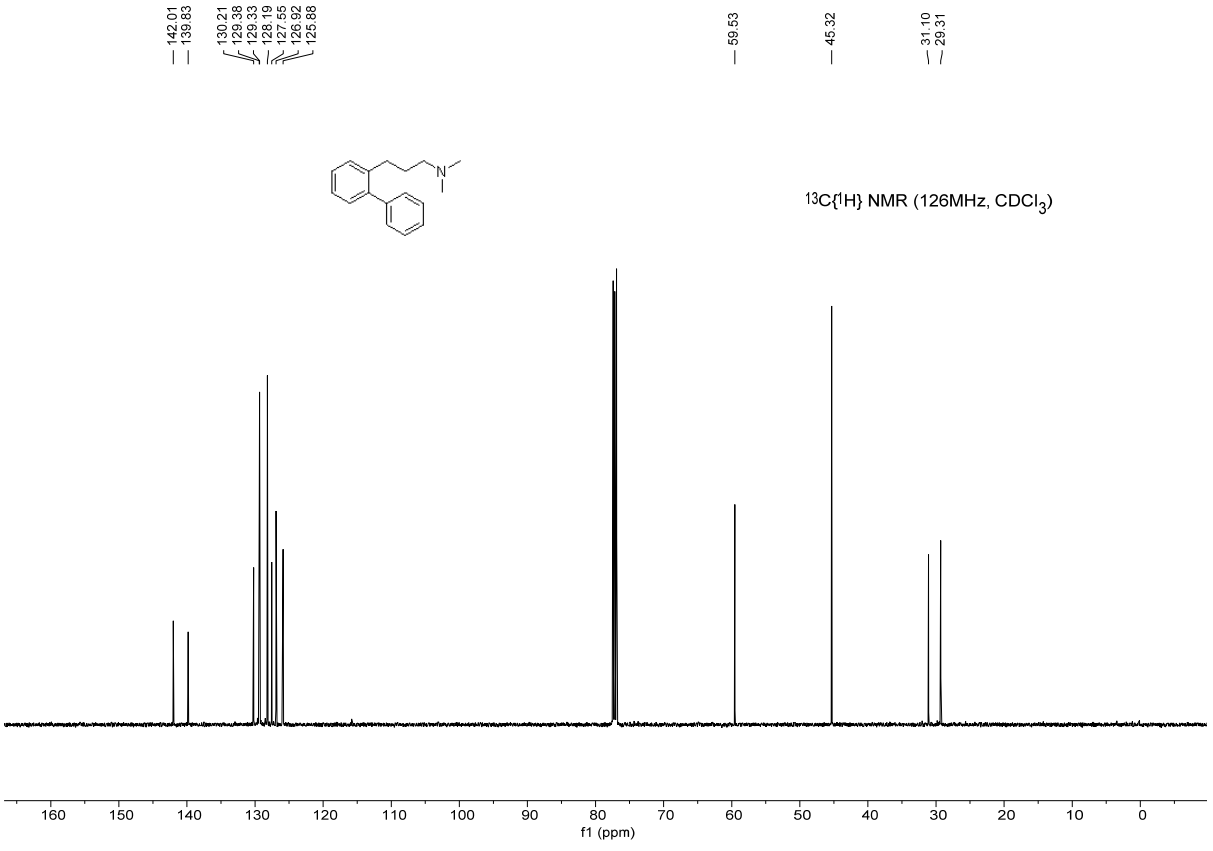




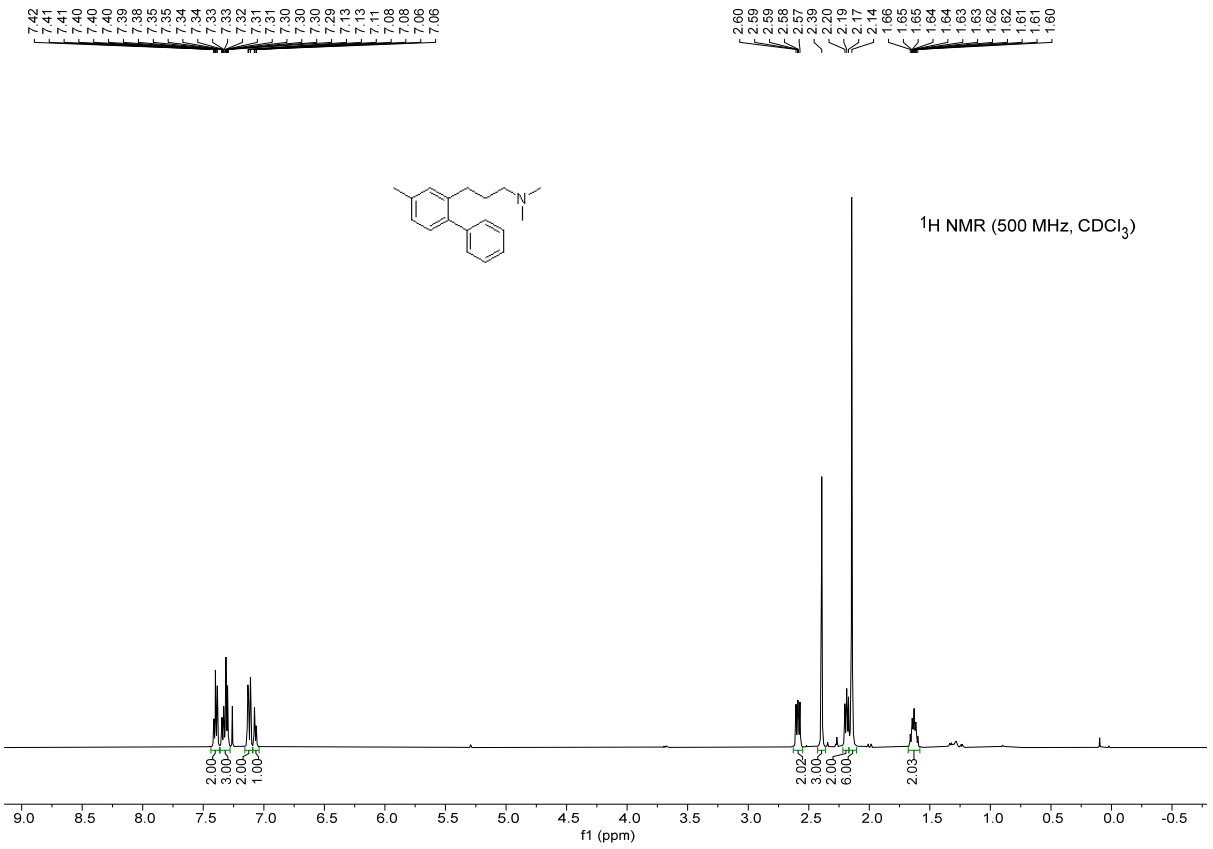
2. NMR spectral copies of the coupling products

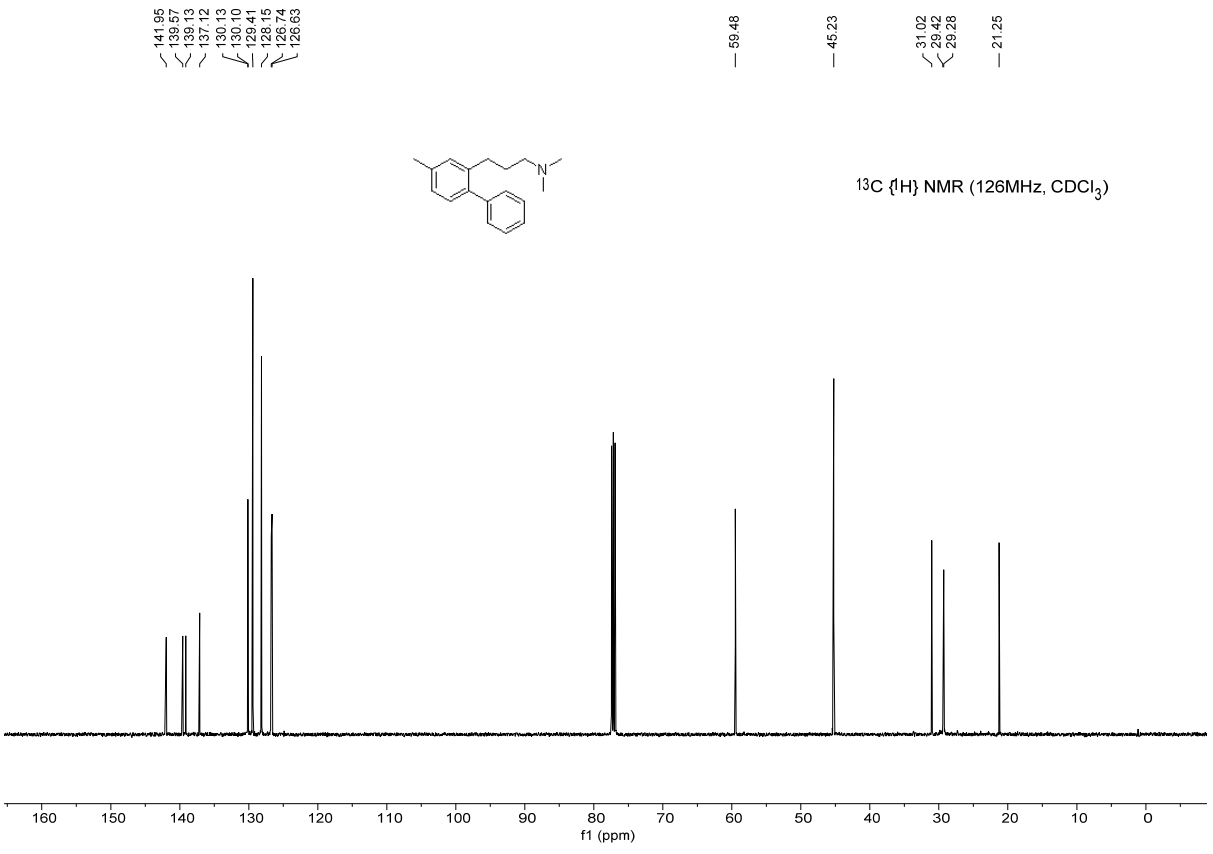
(1) 3-([1,1'-biphenyl]-2-yl)-N,N-dimethylpropan-1-amine (**3a**)



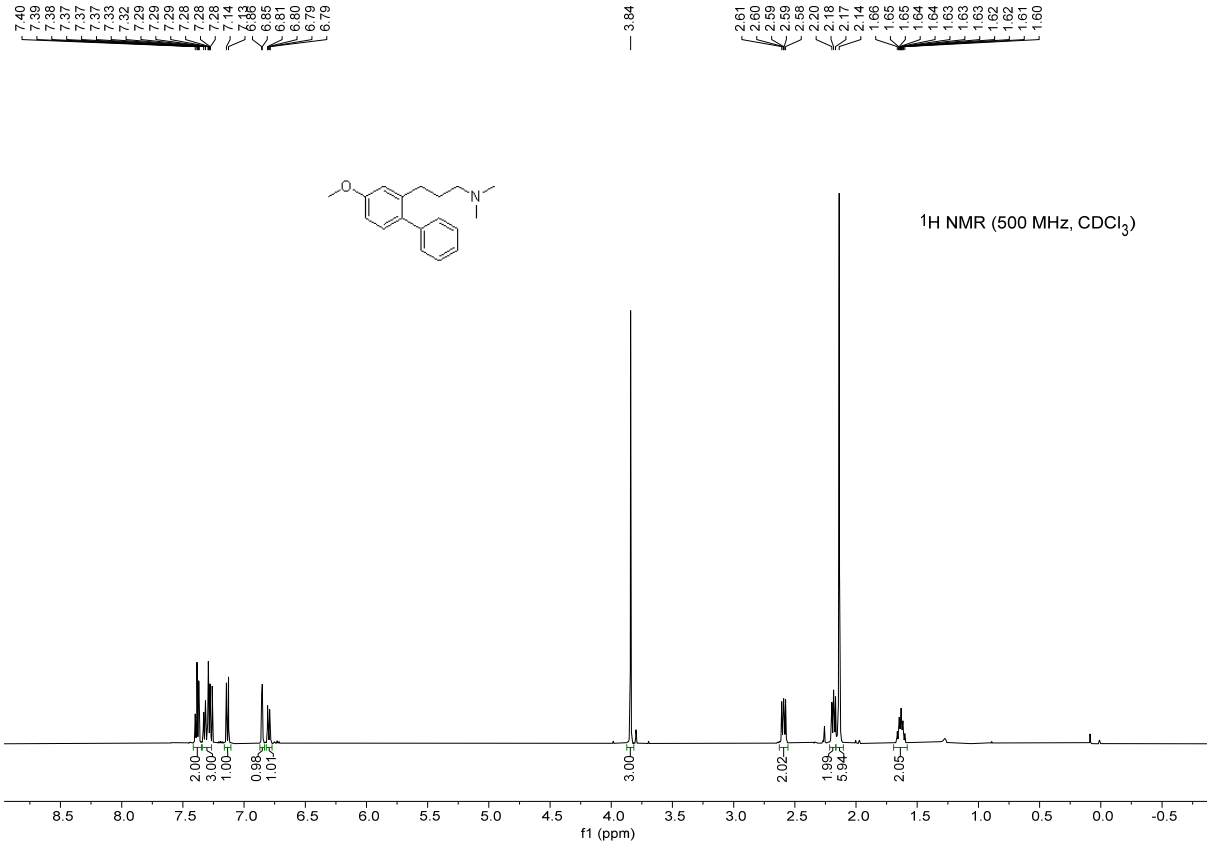


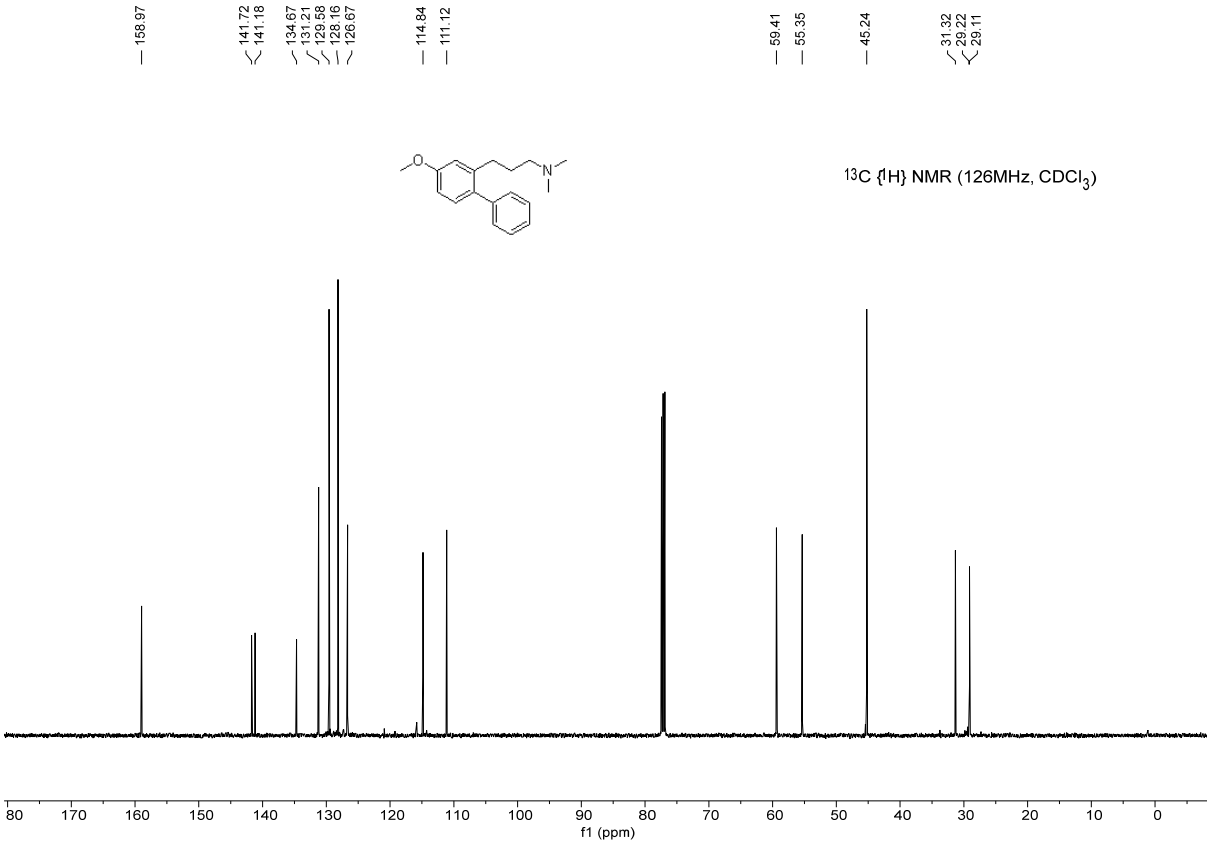
(2) N,N-dimethyl-3-(4-methyl-[1,1'-biphenyl]-2-yl)propan-1-amine (**3b**)



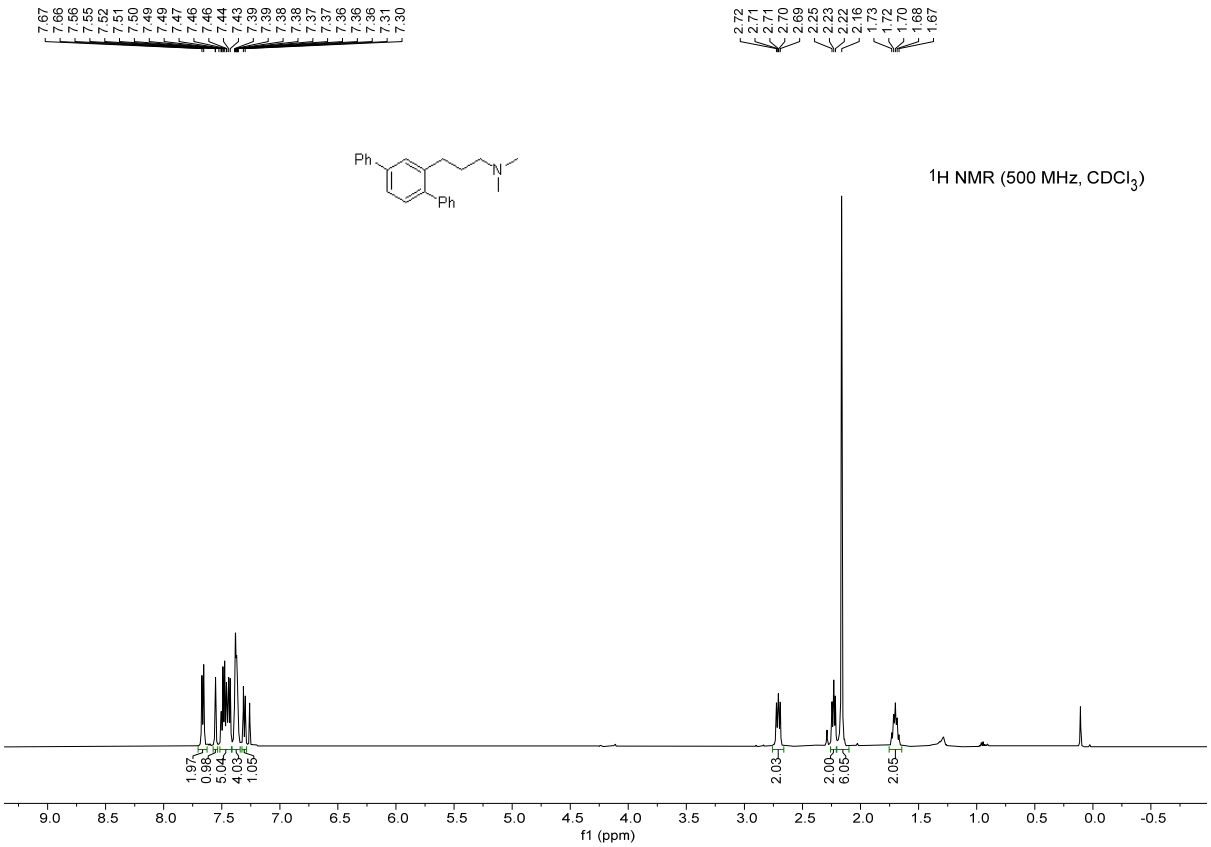


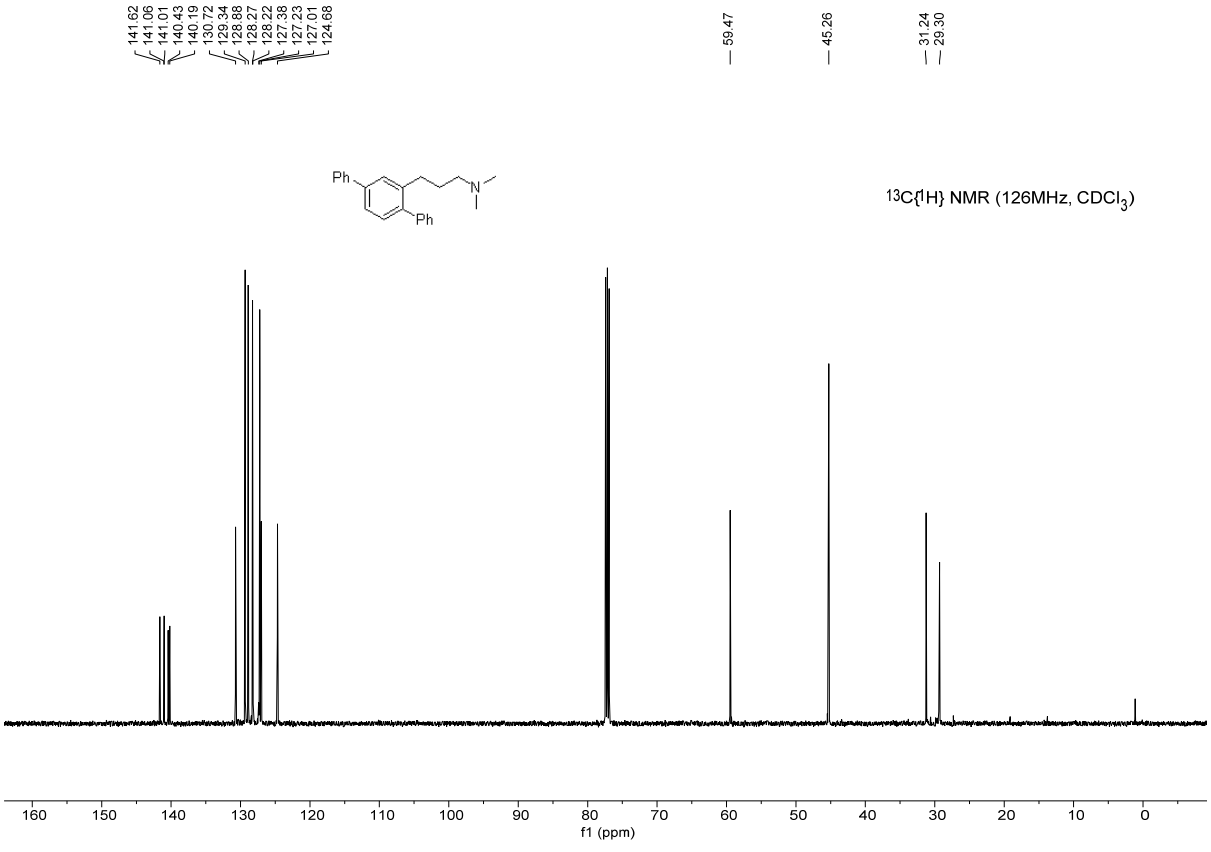
(3) 3-(4-methoxy-[1,1'-biphenyl]-2-yl)-N,N-dimethylpropan-1-amine (**3c**)



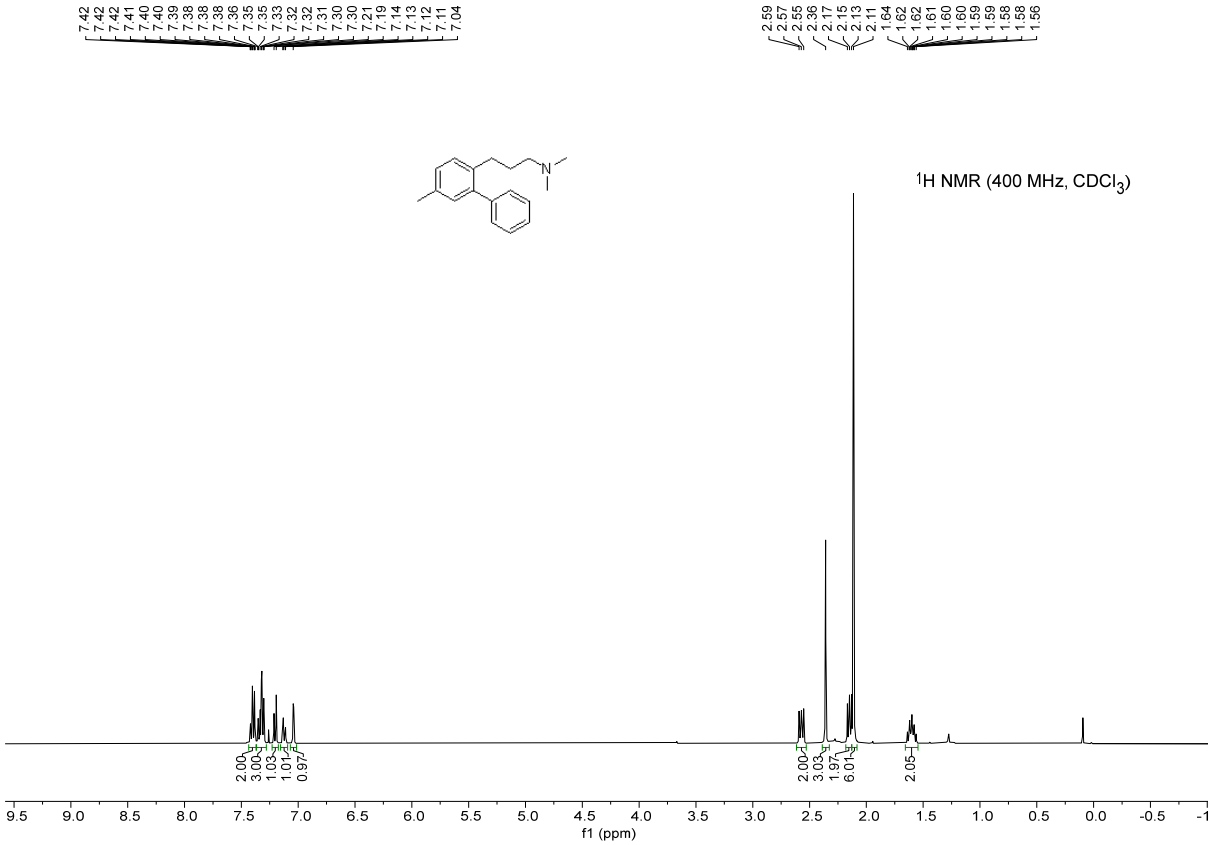


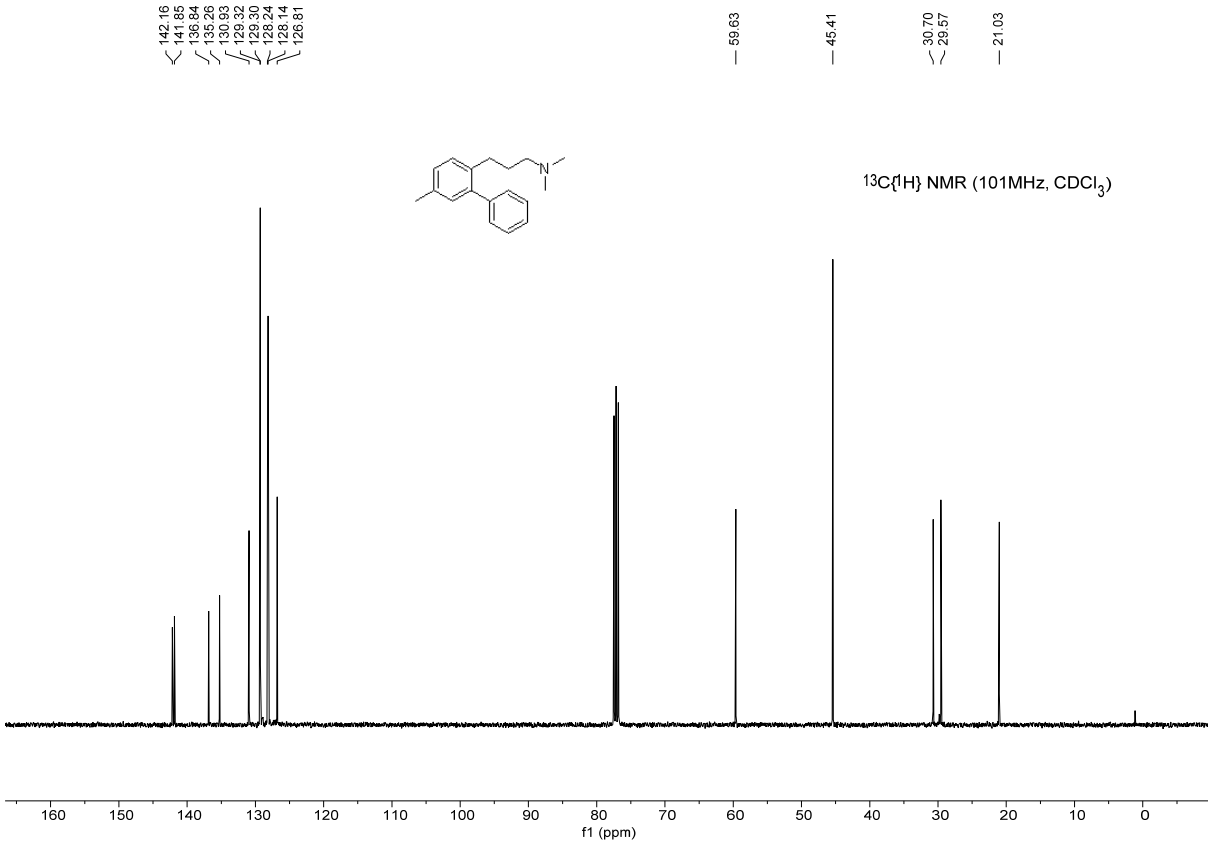
(4) 3-([1,1':4',1''-terphenyl]-2'-yl)-N,N-dimethylpropan-1-amine (**3d**)



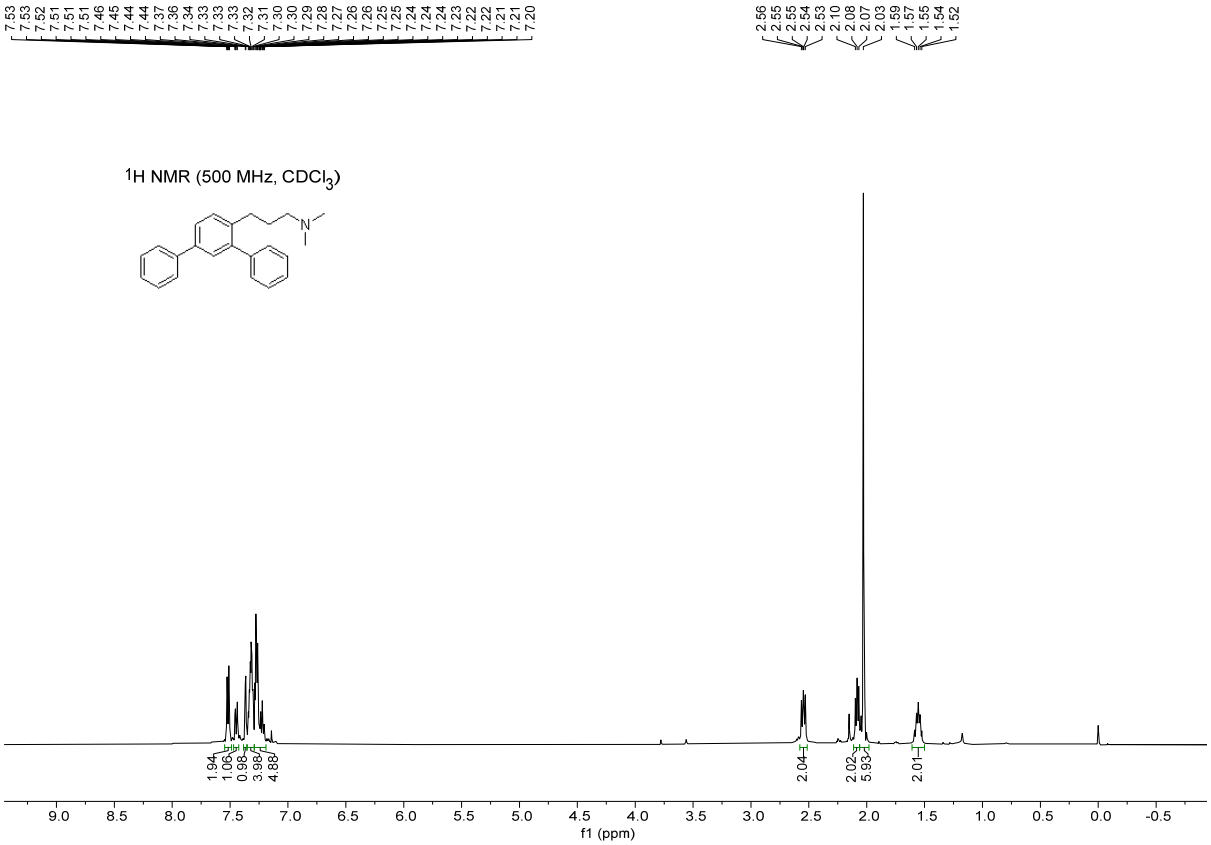


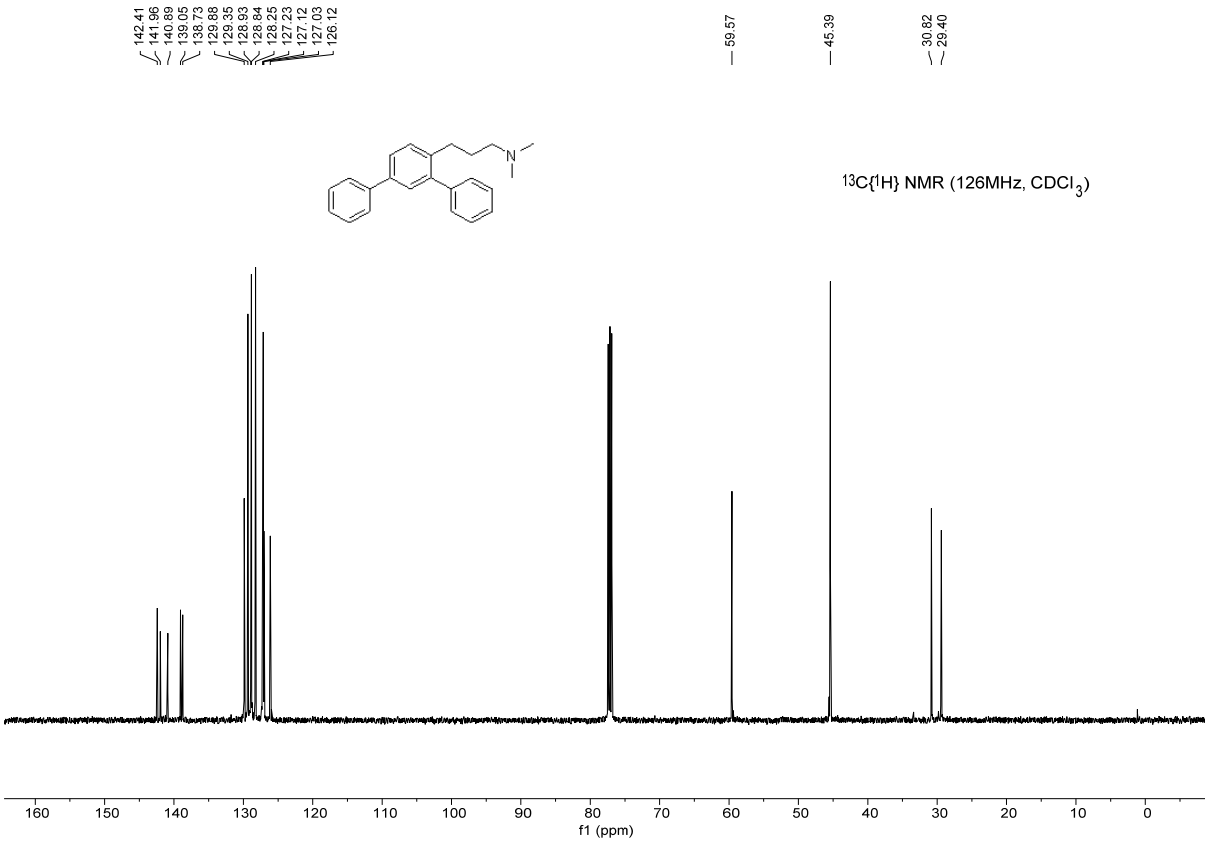
(5) N,N-dimethyl-3-(3-methyl-[1,1'-biphenyl]-2-yl)propan-1-amine (**3e**)



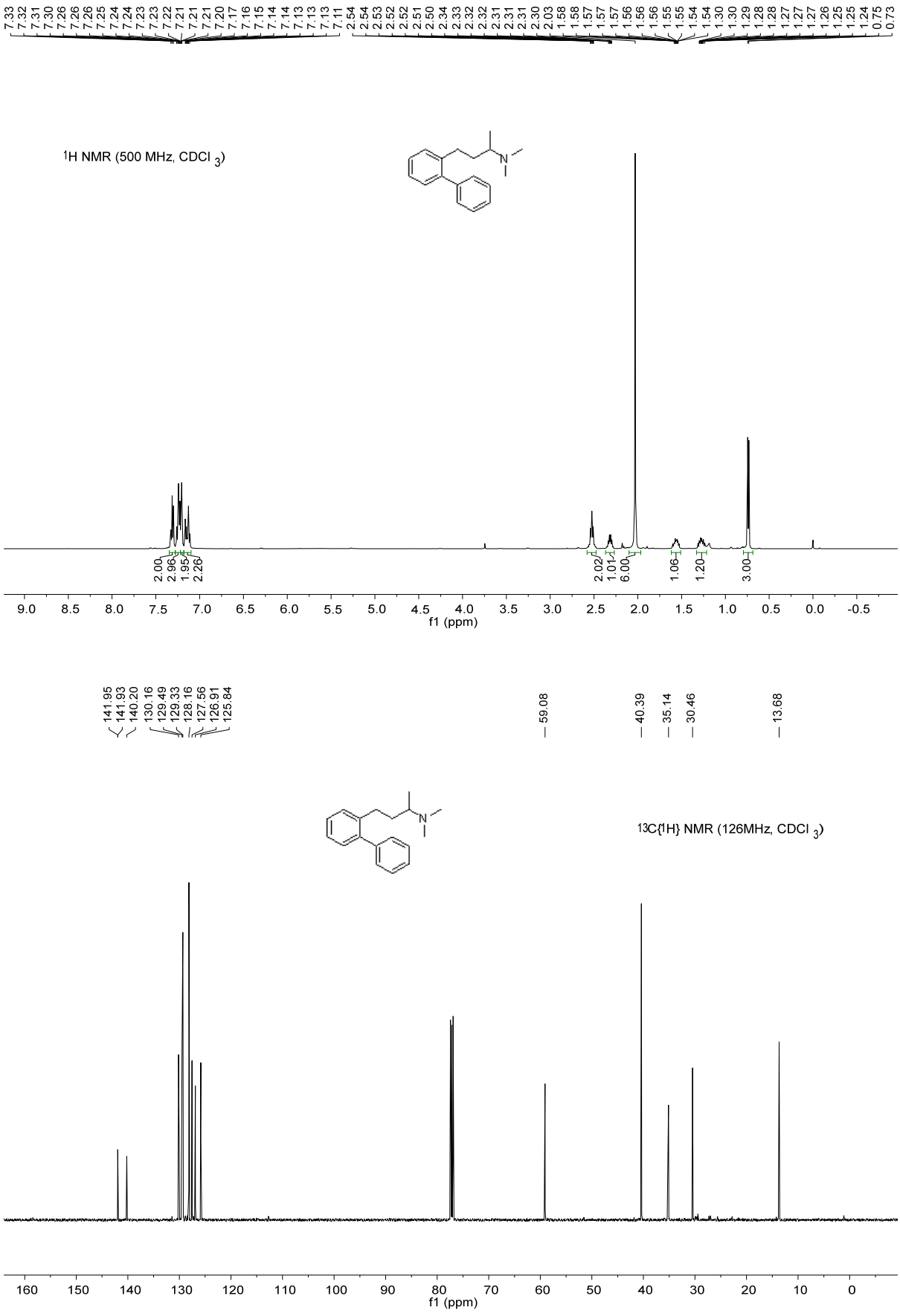


(6) 3-([1,1':3',1"-terphenyl]-4'-yl)-N,N-dimethylpropan-1-amine (**3f**)

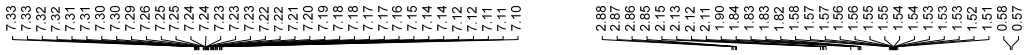


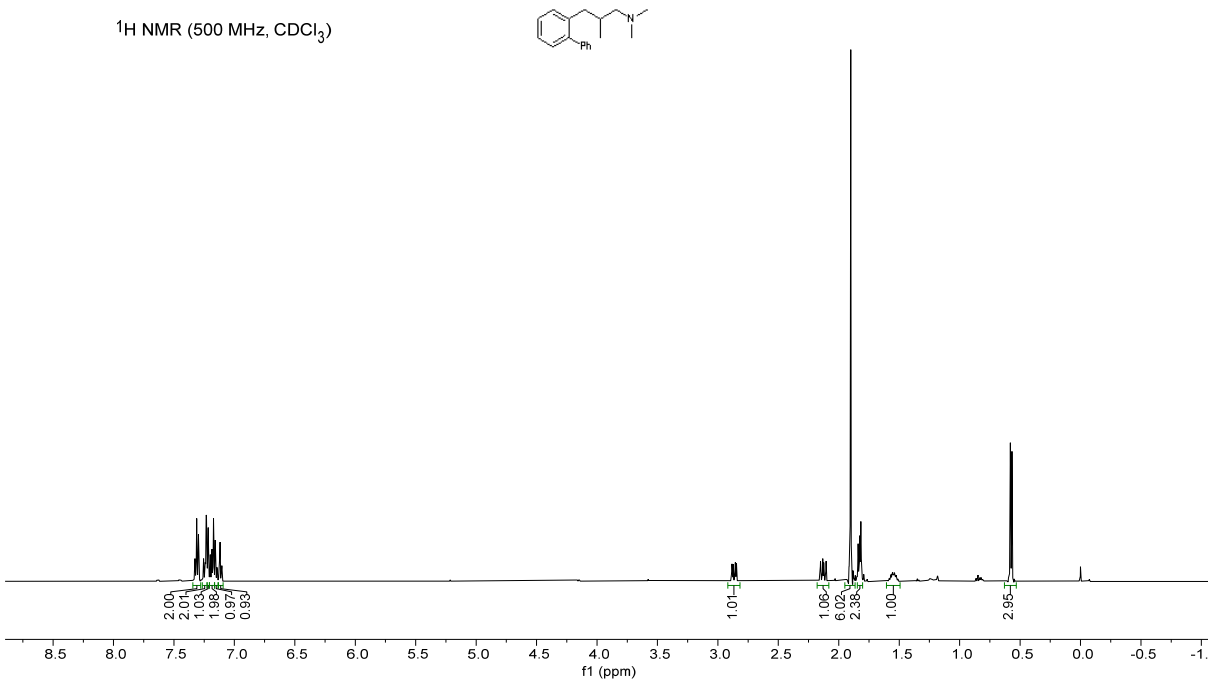


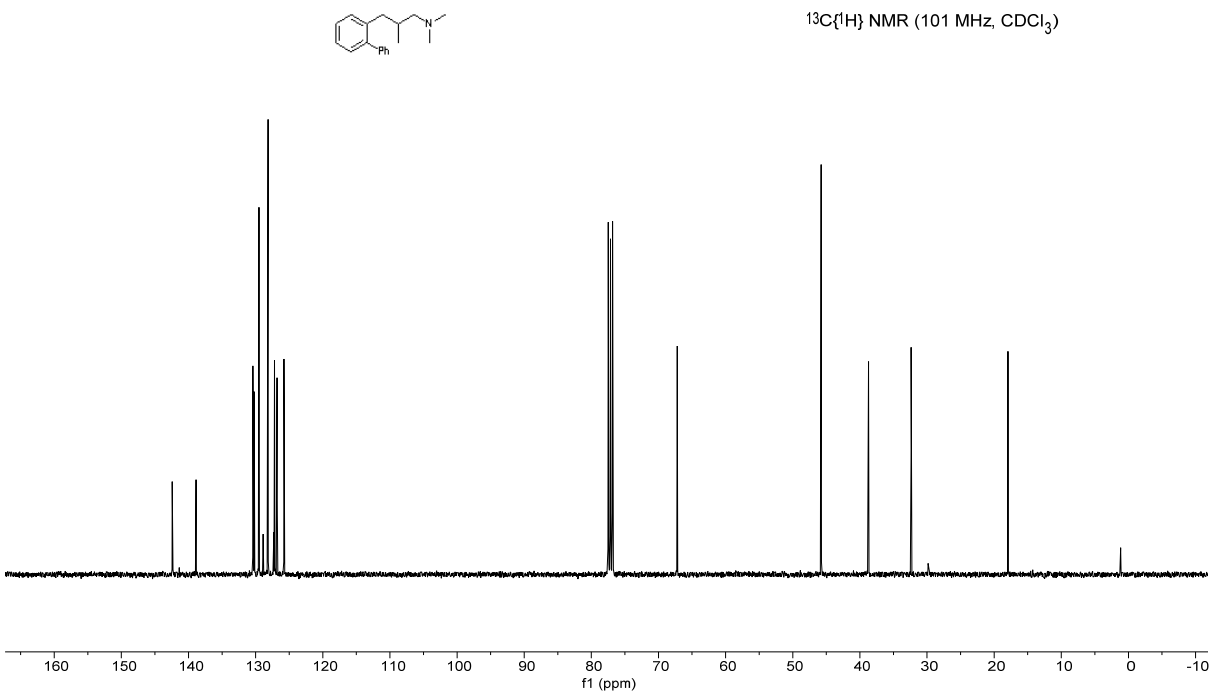
(7) 4-([1,1'-biphenyl]-2-yl)-N,N-dimethylbutan-2-amine (**3g**)



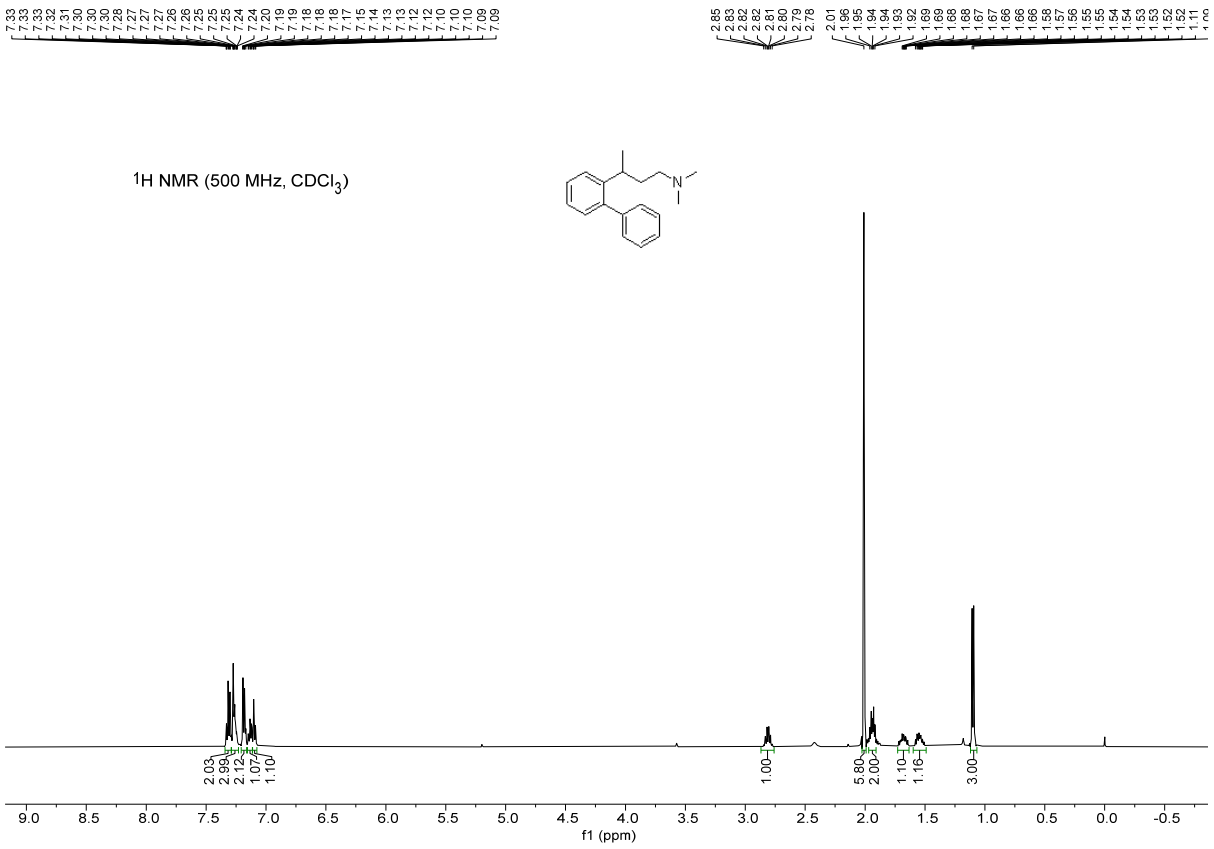
(8) 3-([1,1'-biphenyl]-2-yl)-N,N,2-trimethylpropan-1-amine (**3h**)

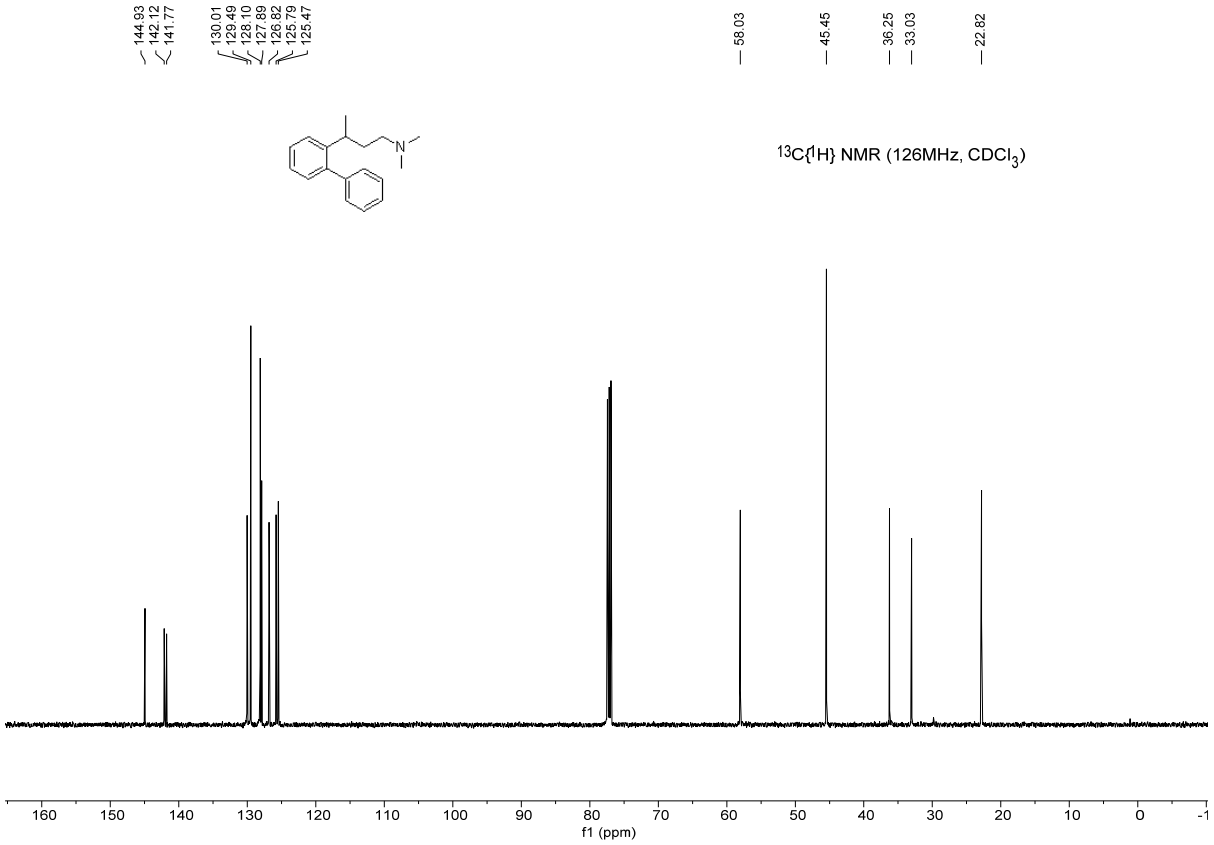




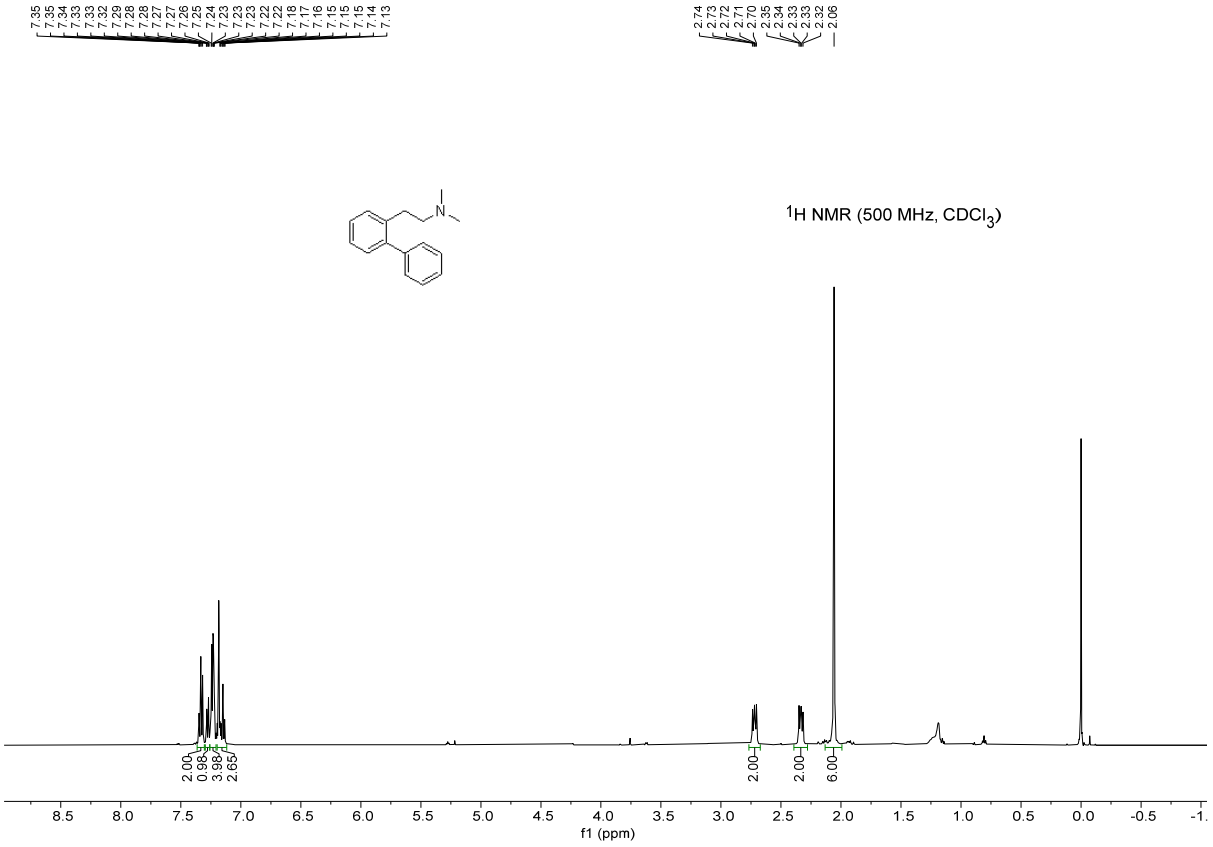


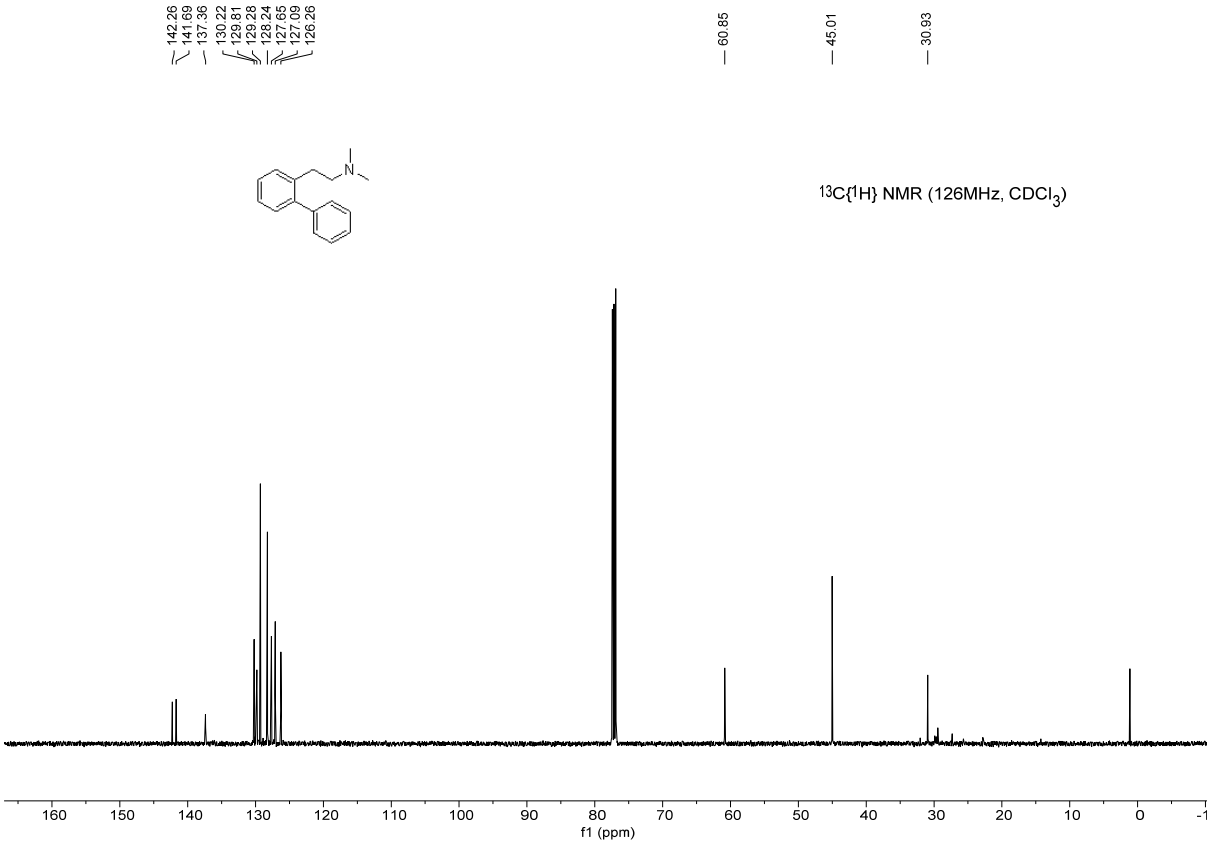
(9) 3-([1,1'-biphenyl]-2-yl)-N,N-dimethylbutan-1-amine (**3i**)



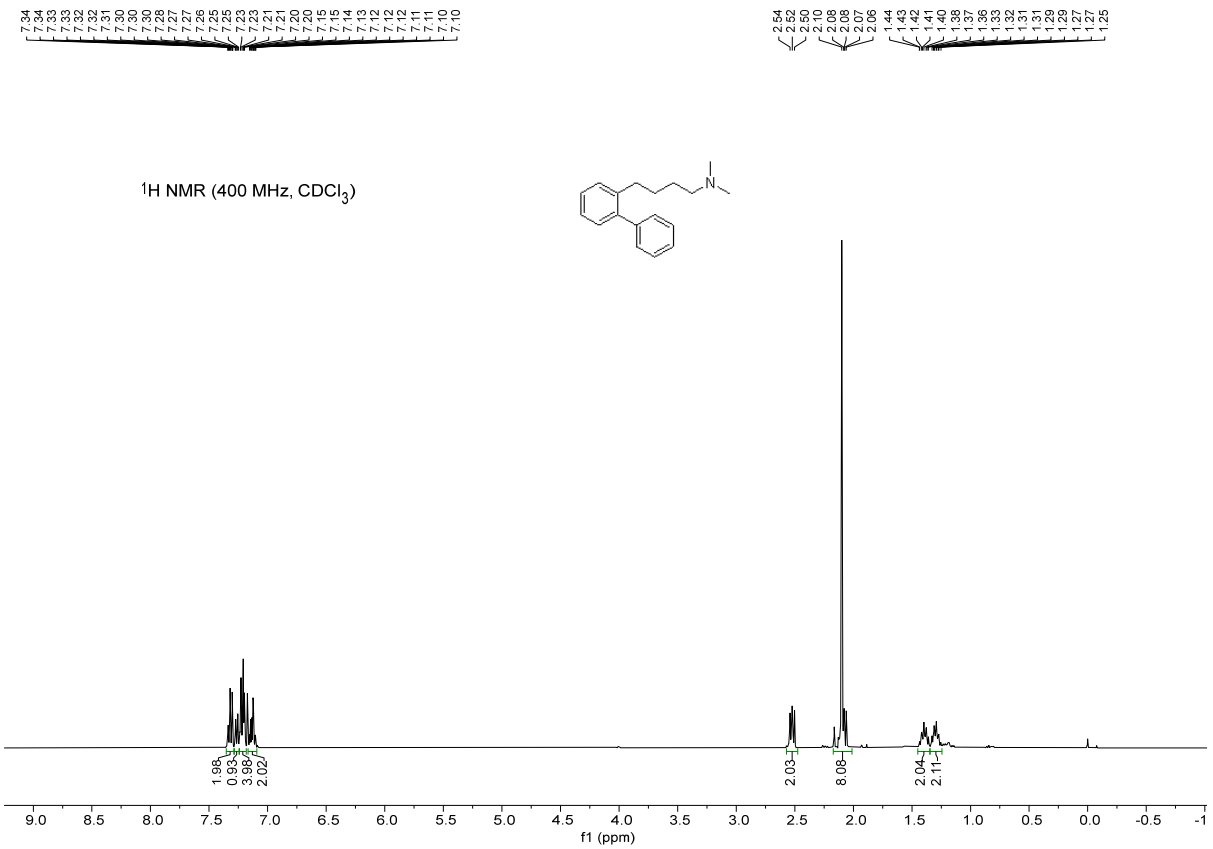


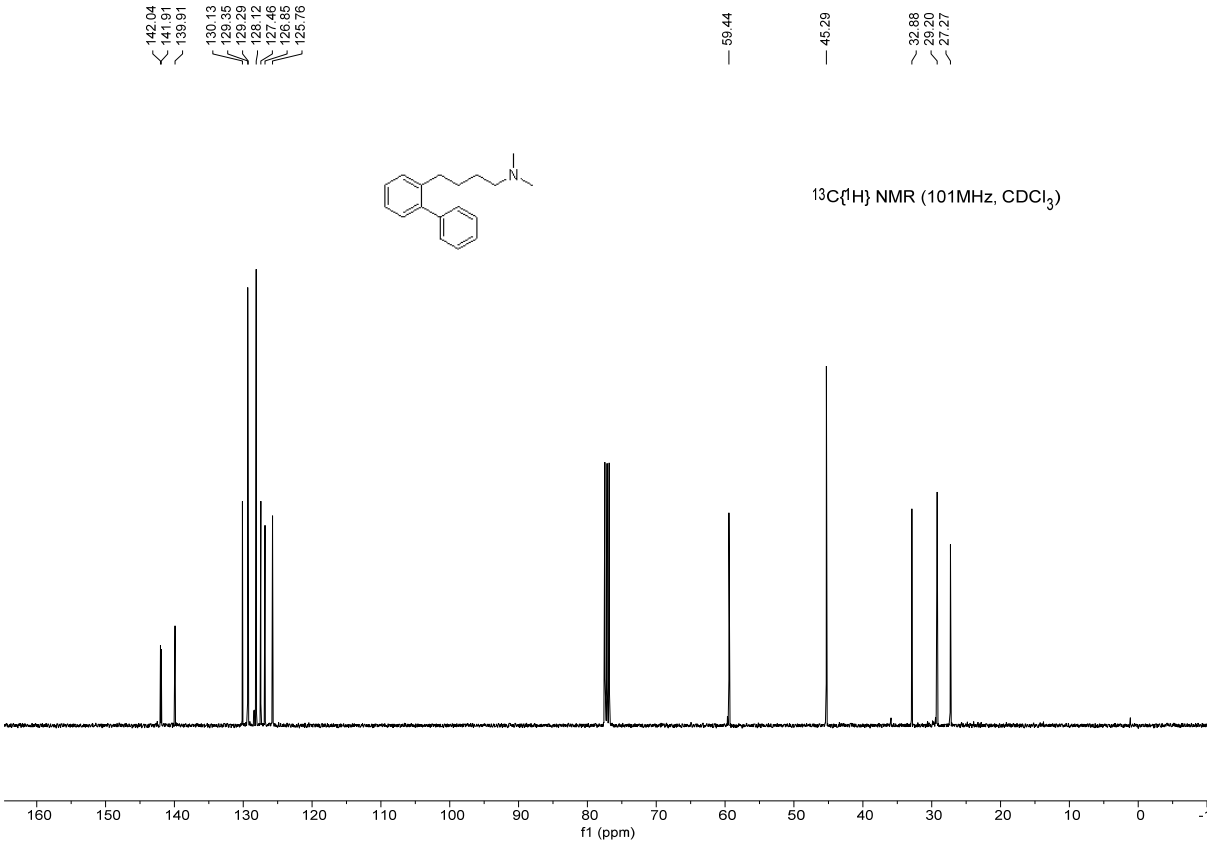
(10) 2-([1,1'-biphenyl]-2-yl)-N,N-dimethylethan-1-amine (**3j**)



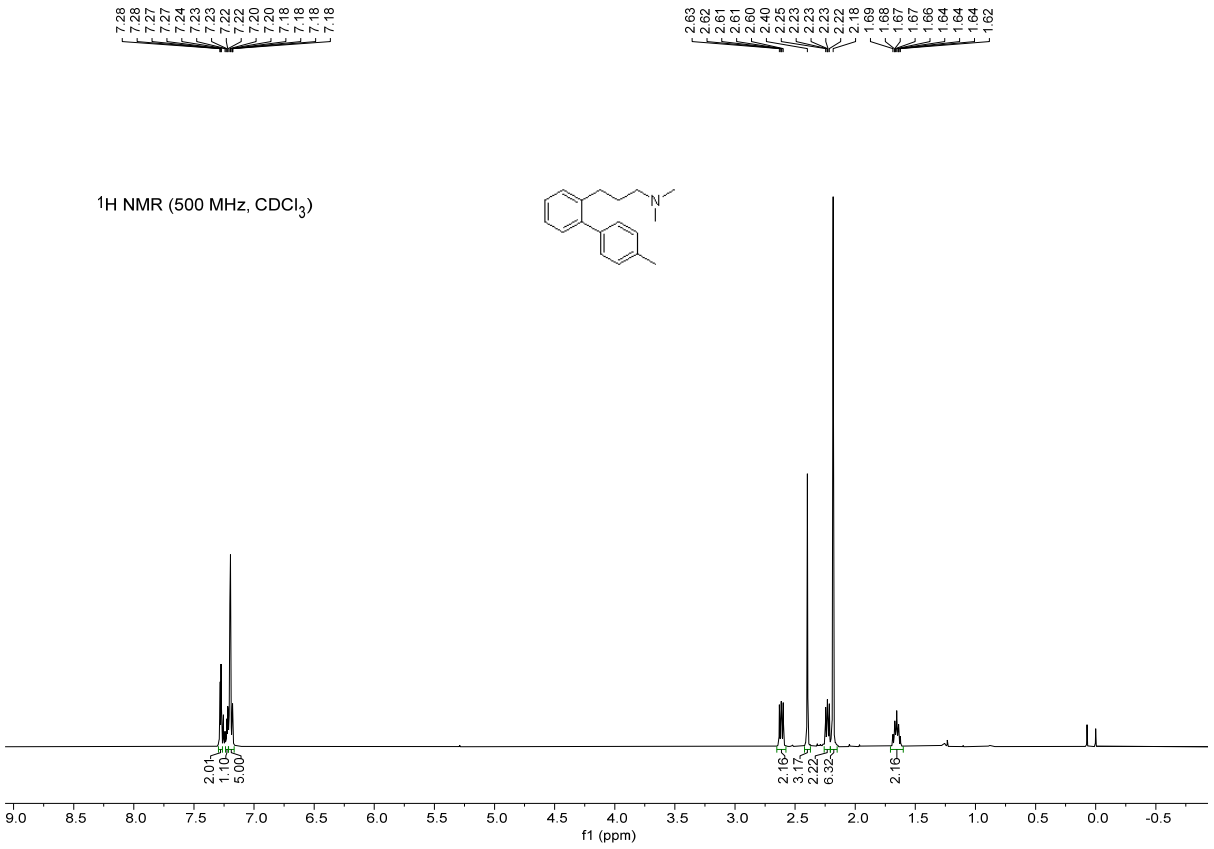


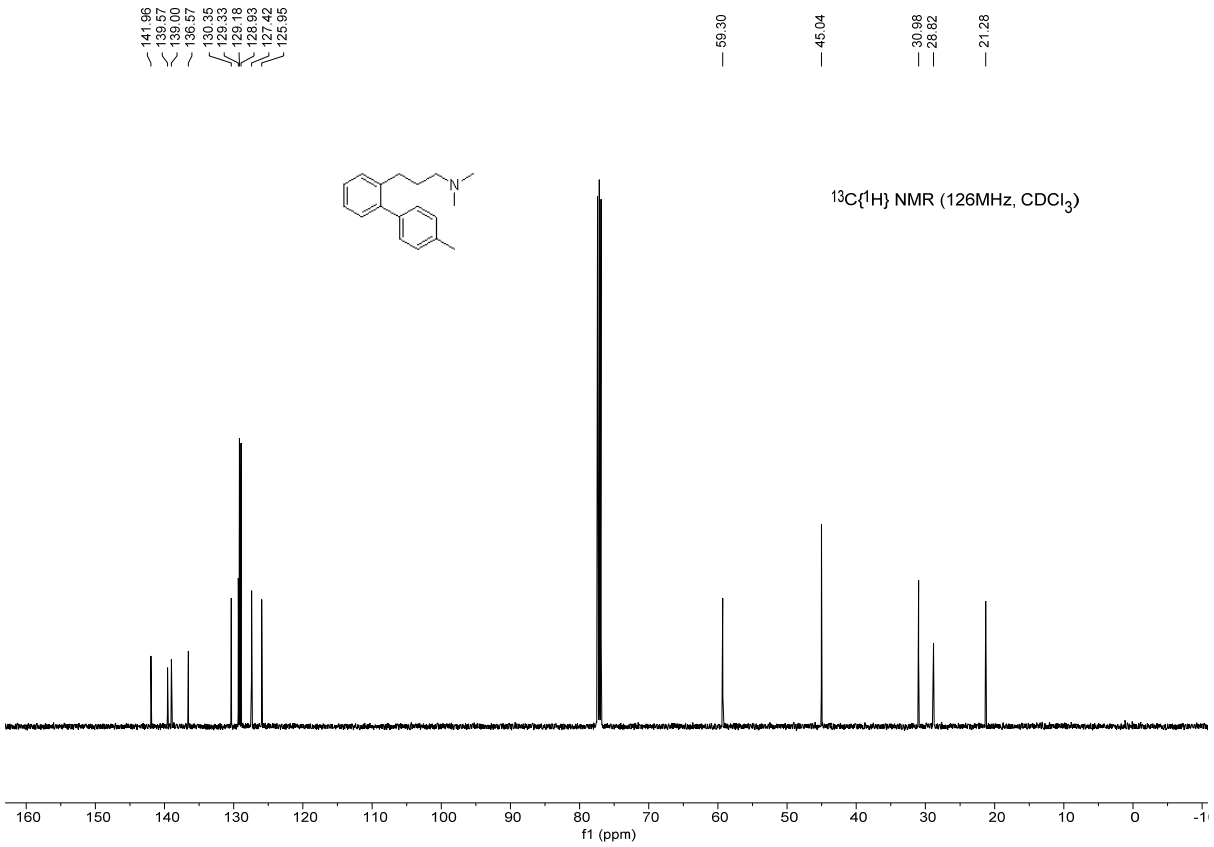
(11) 4-([1,1'-biphenyl]-2-yl)-N,N-dimethylbutan-1-amine (**3k**)



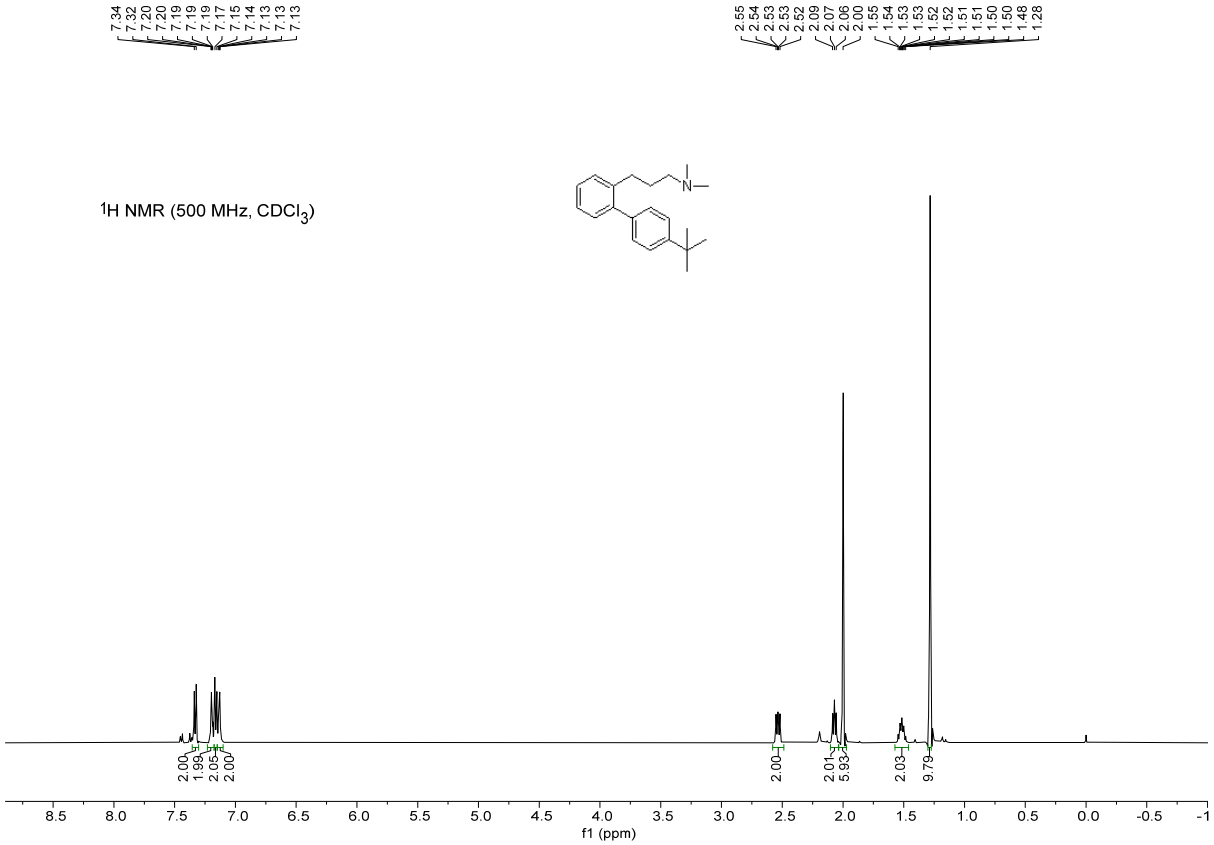


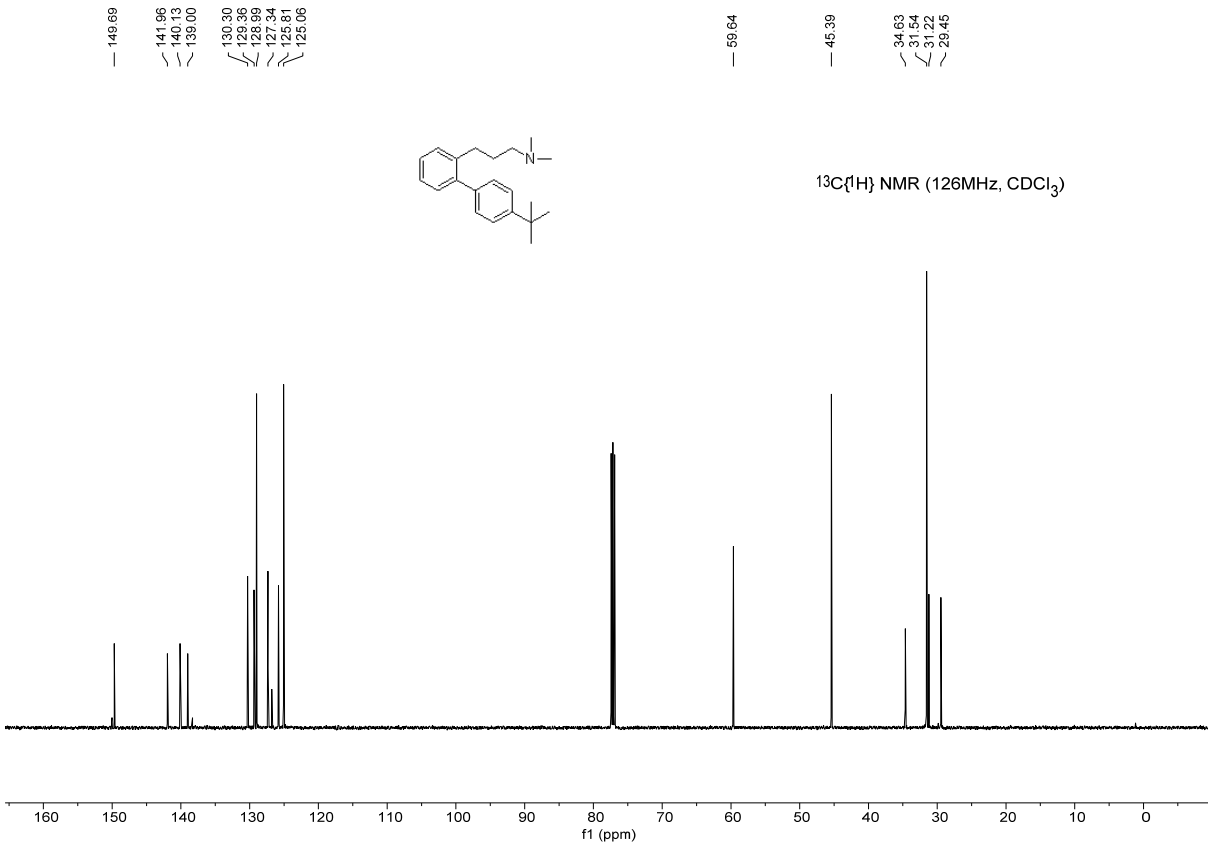
(12) N,N-dimethyl-3-(4'-methyl-[1,1'-biphenyl]-2-yl)propan-1-amine (**3l**)



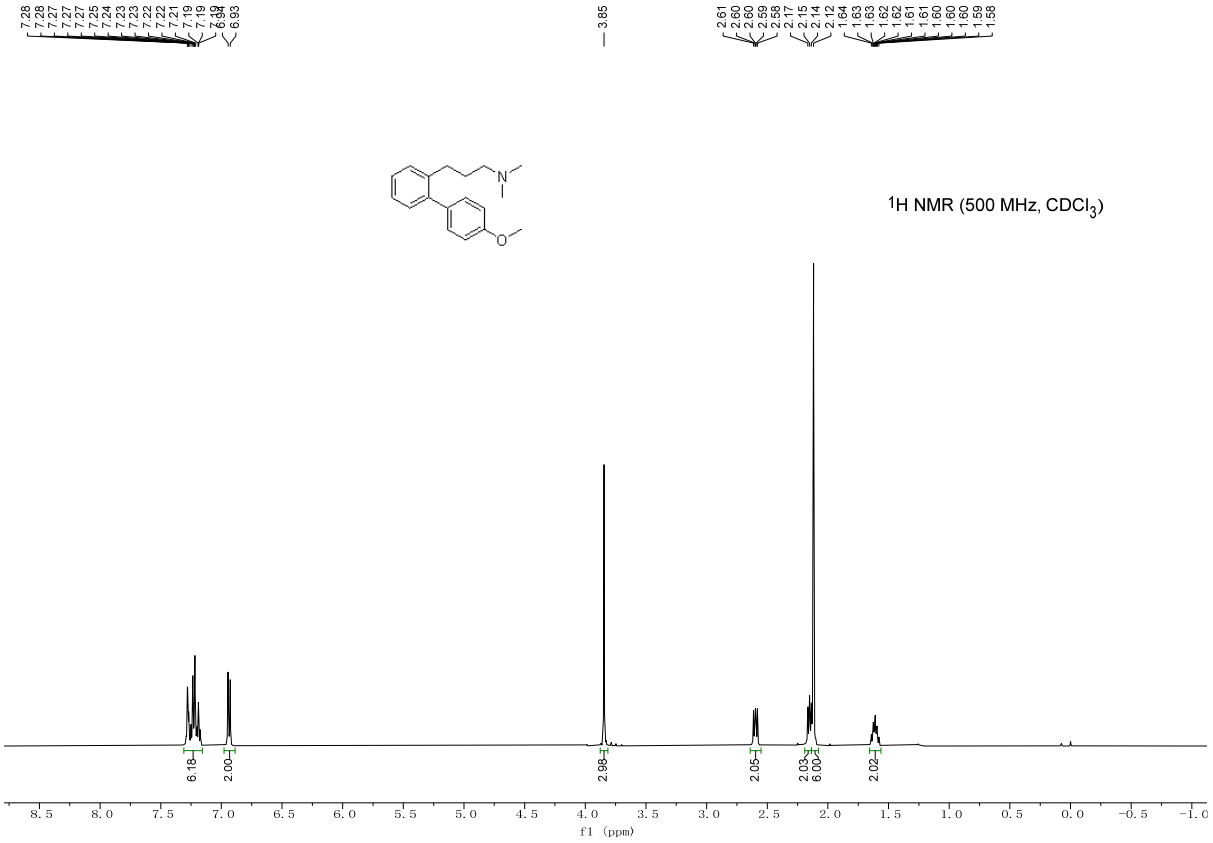


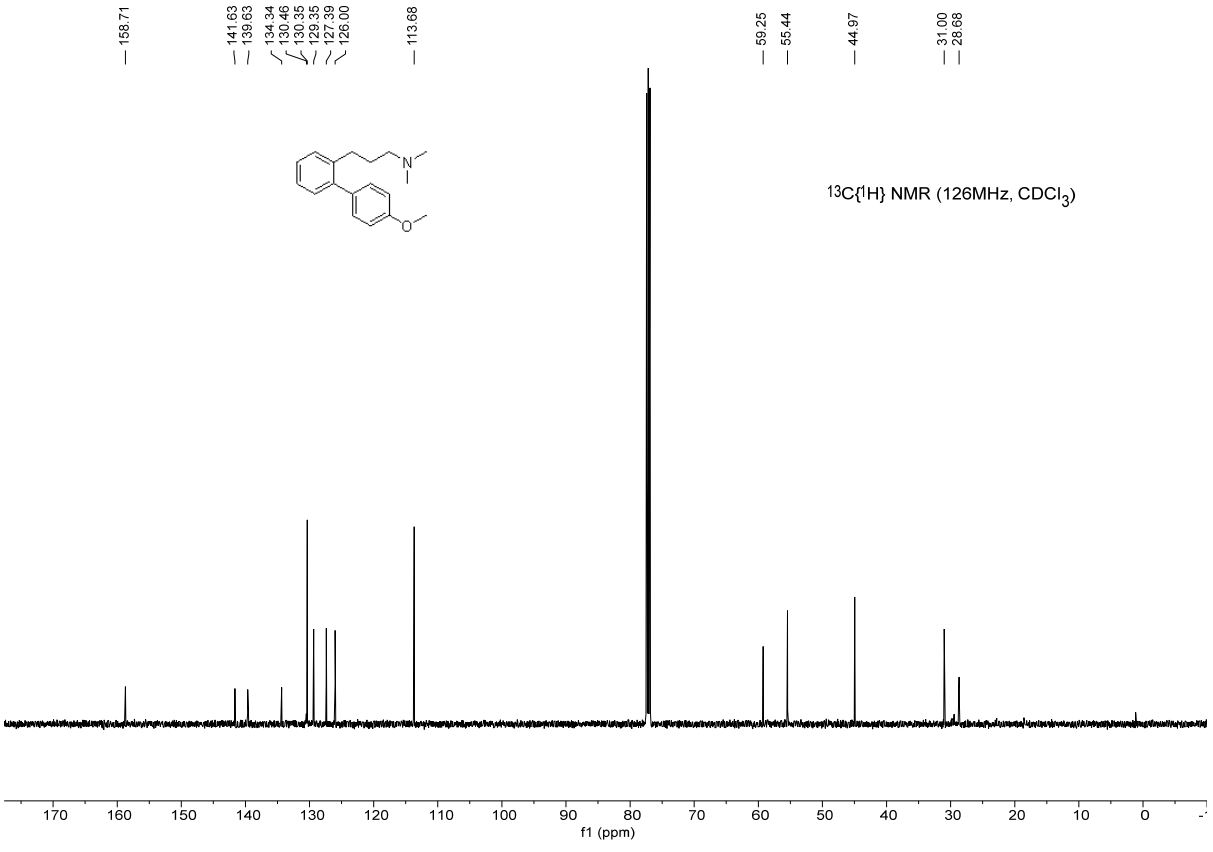
(13) 3-(4'-(tert-butyl)-[1,1'-biphenyl]-2-yl)-N,N-dimethylpropan-1-amine (**3m**)



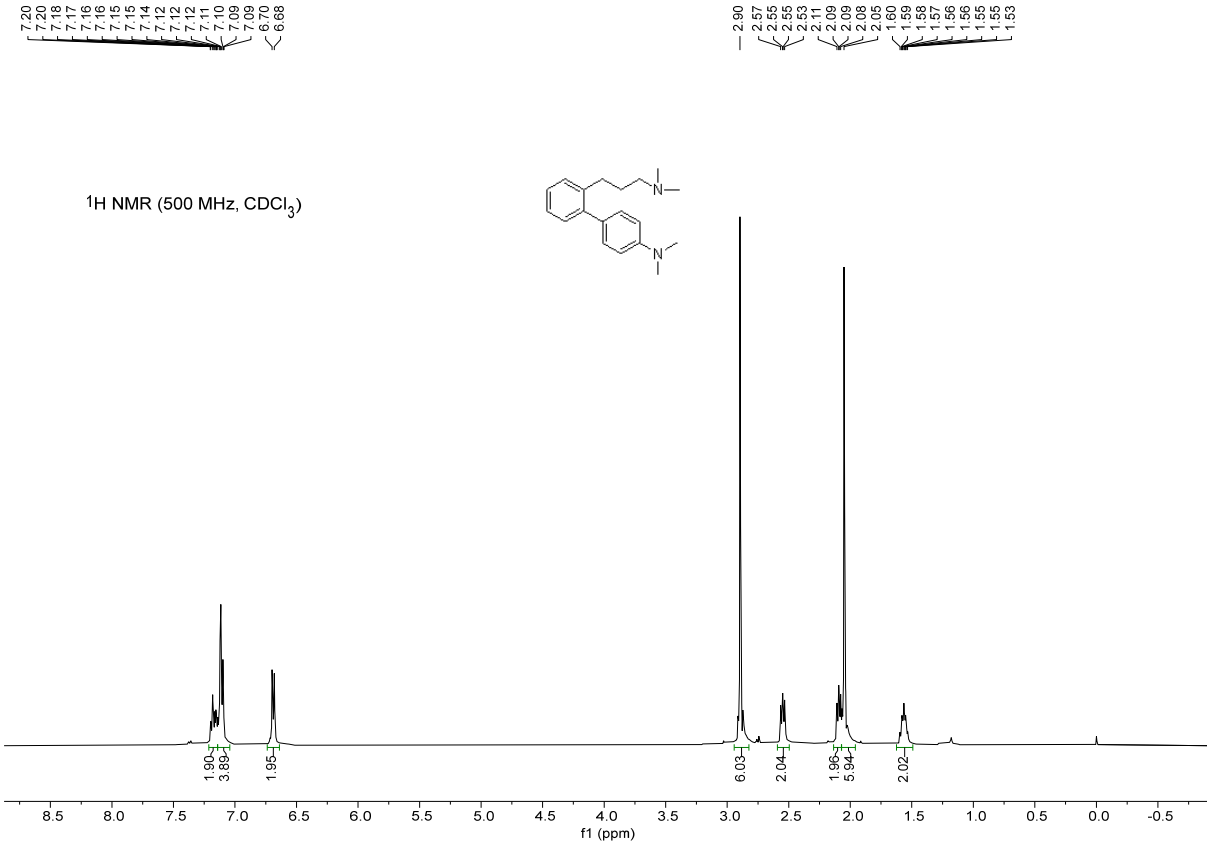


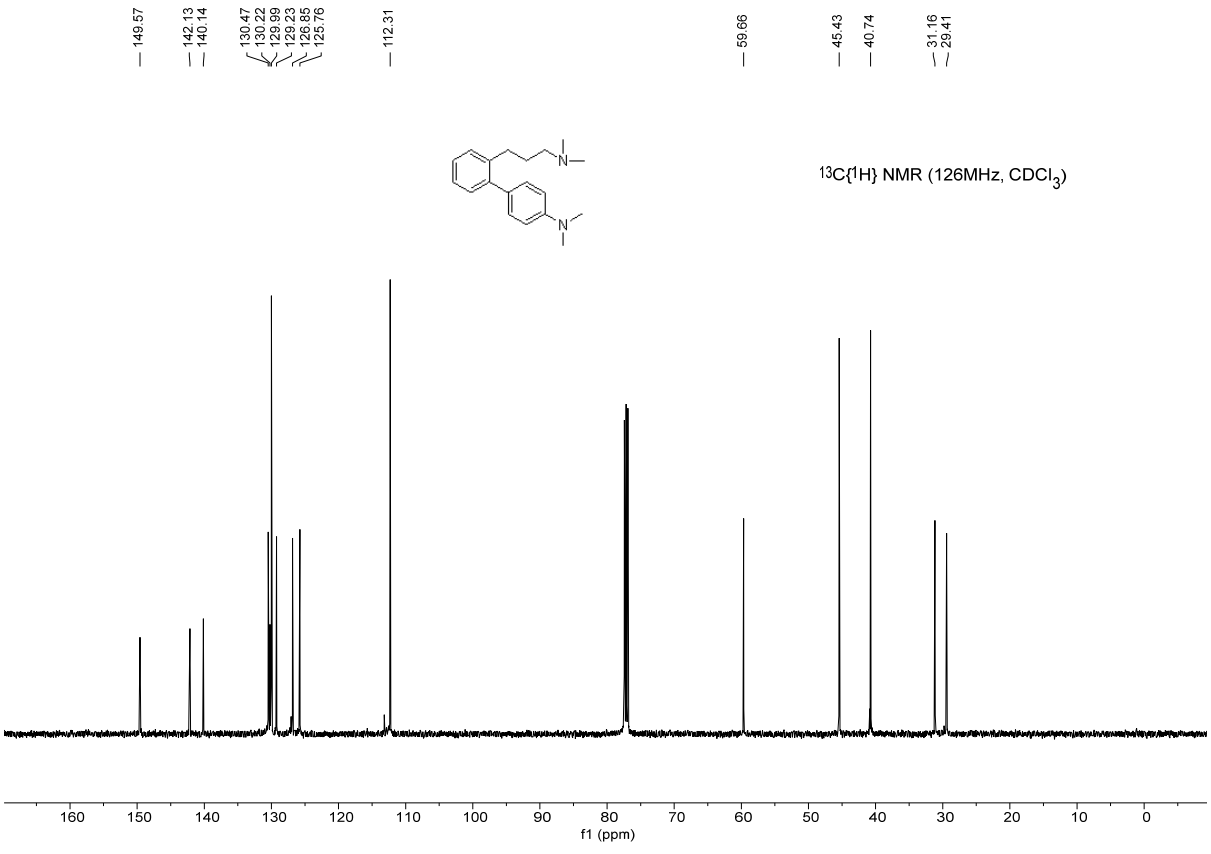
(14) 3-(4'-methoxy-[1,1'-biphenyl]-2-yl)-N,N-dimethylpropan-1-amine (**3n**)



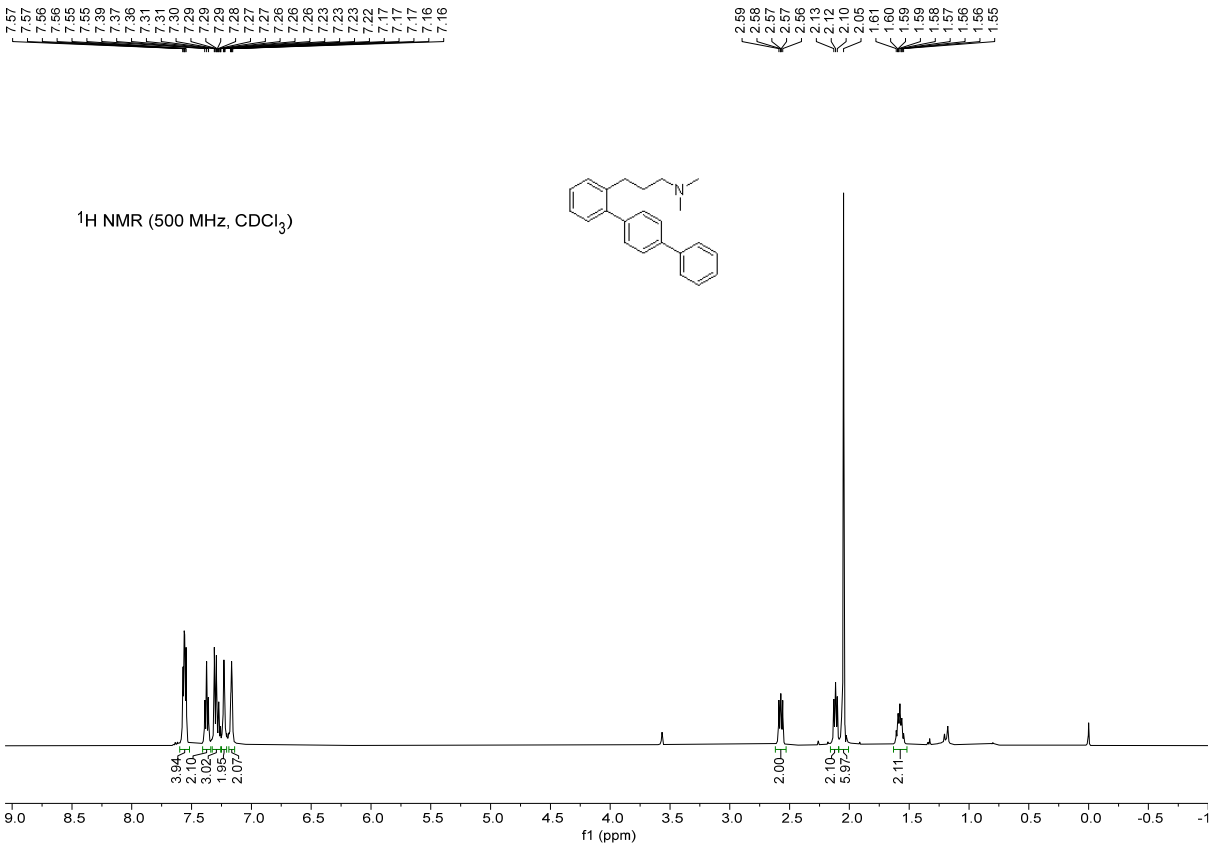


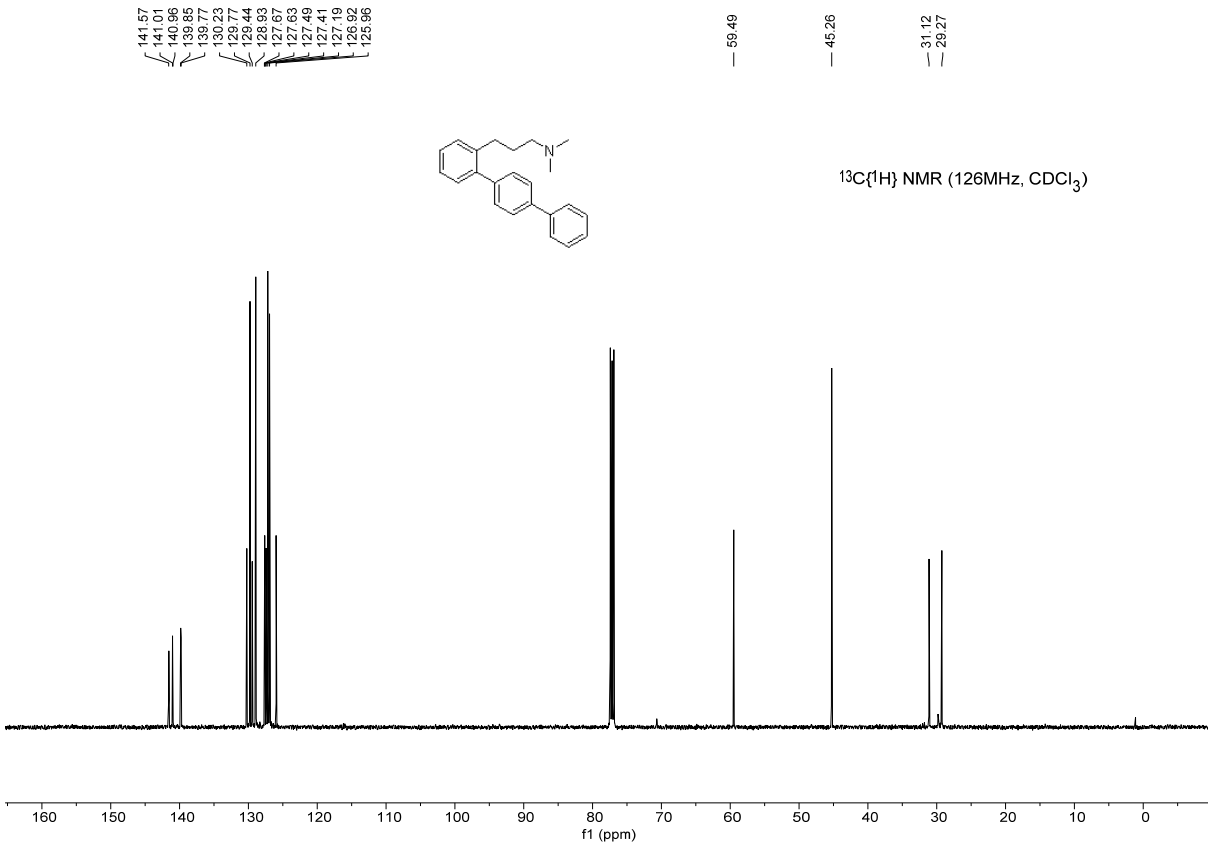
(15) 2'-(3-(dimethylamino)propyl)-N,N-dimethyl-[1,1'-biphenyl]-4-amine (**3o**)



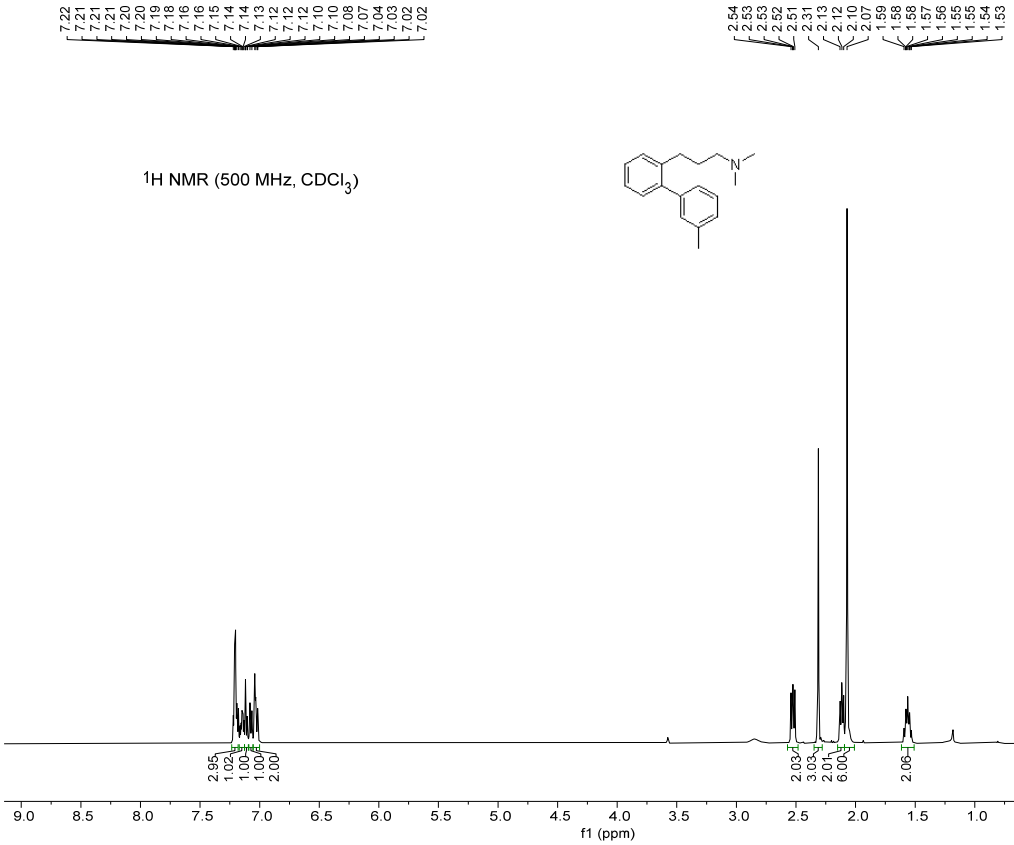


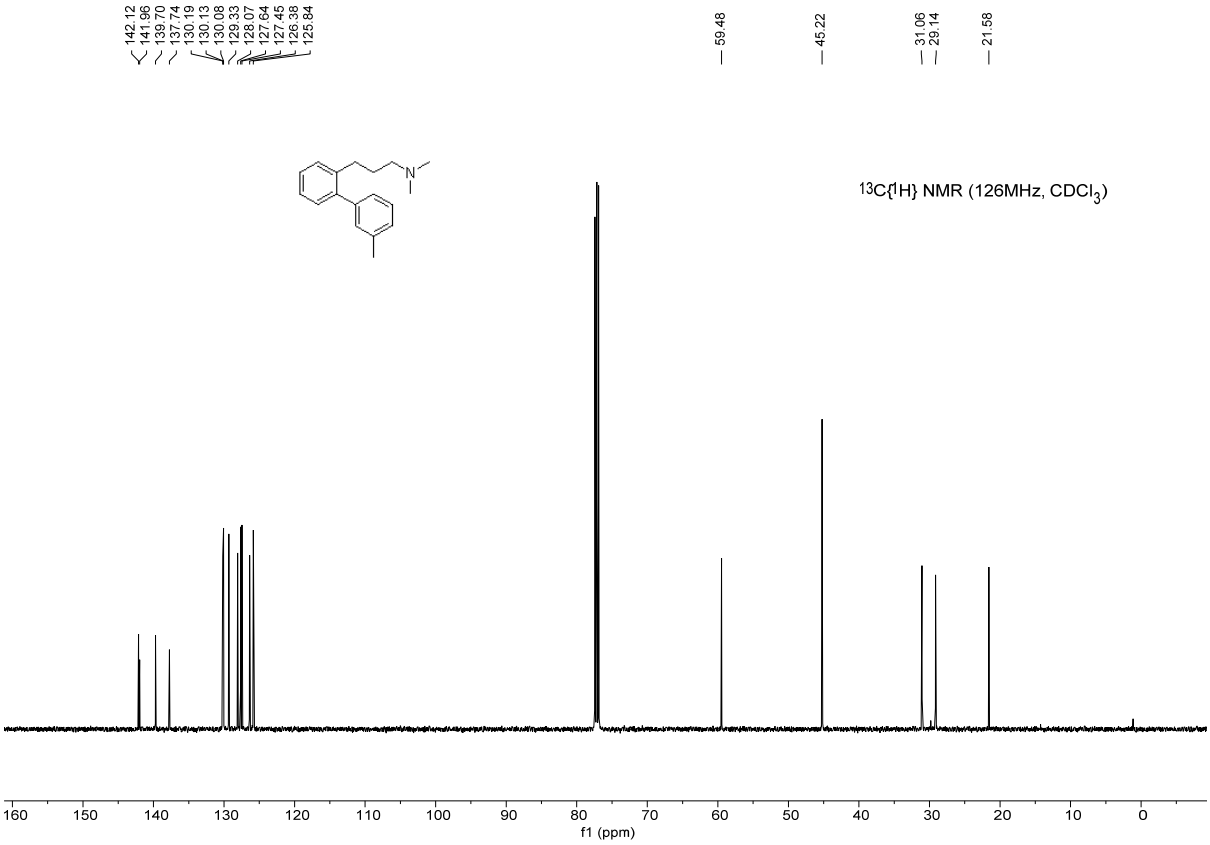
(16) 3-([1,1':4',1"-terphenyl]-2-yl)-N,N-dimethylpropan-1-amine (**3p**)



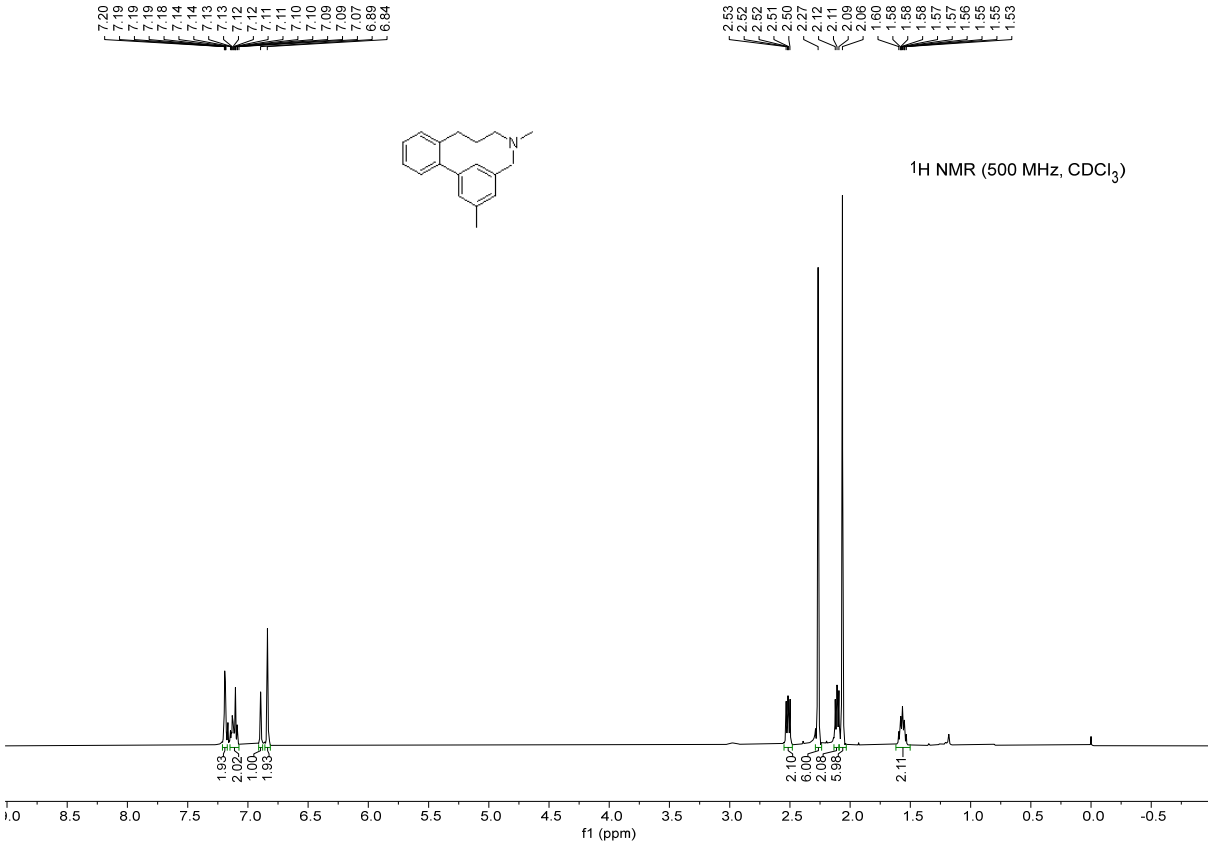


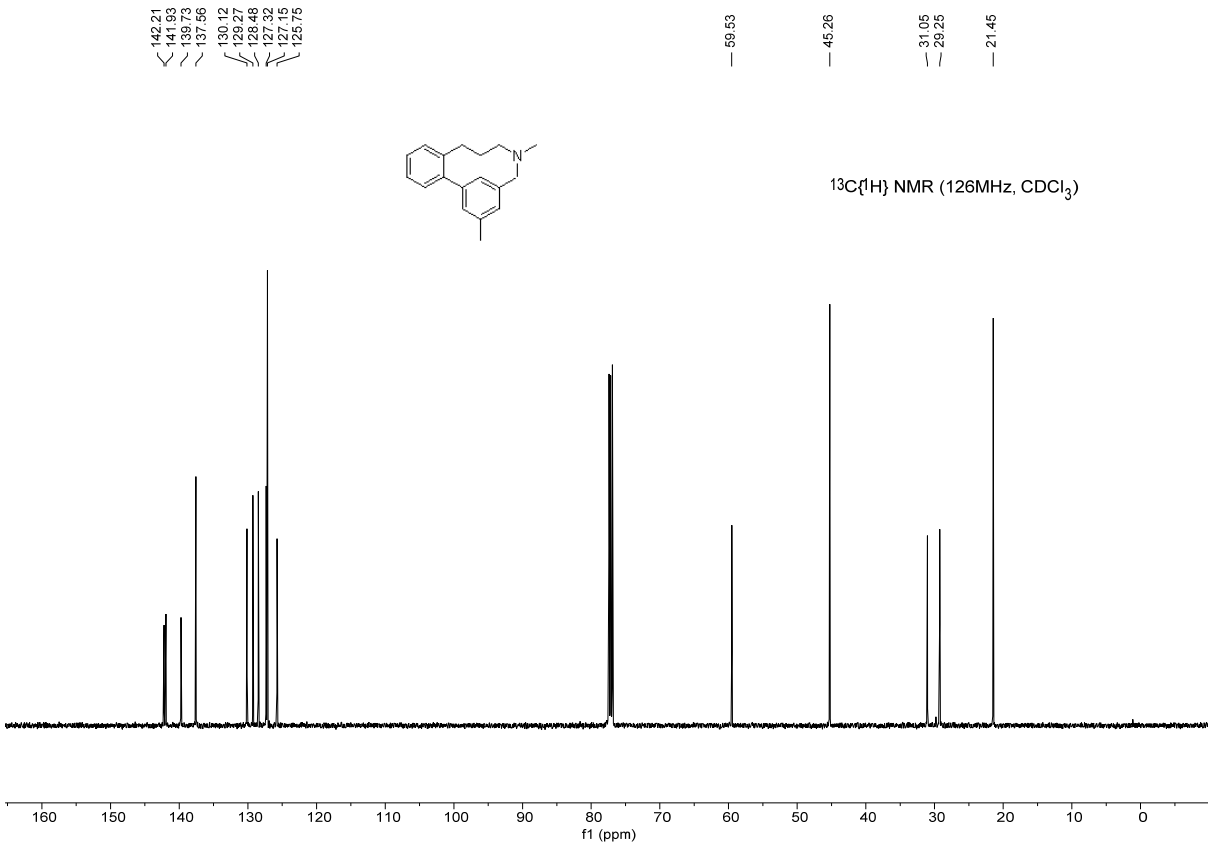
(17) N,N-dimethyl-3-(3'-methyl-[1,1'-biphenyl]-2-yl)propan-1-amine (**3q**)



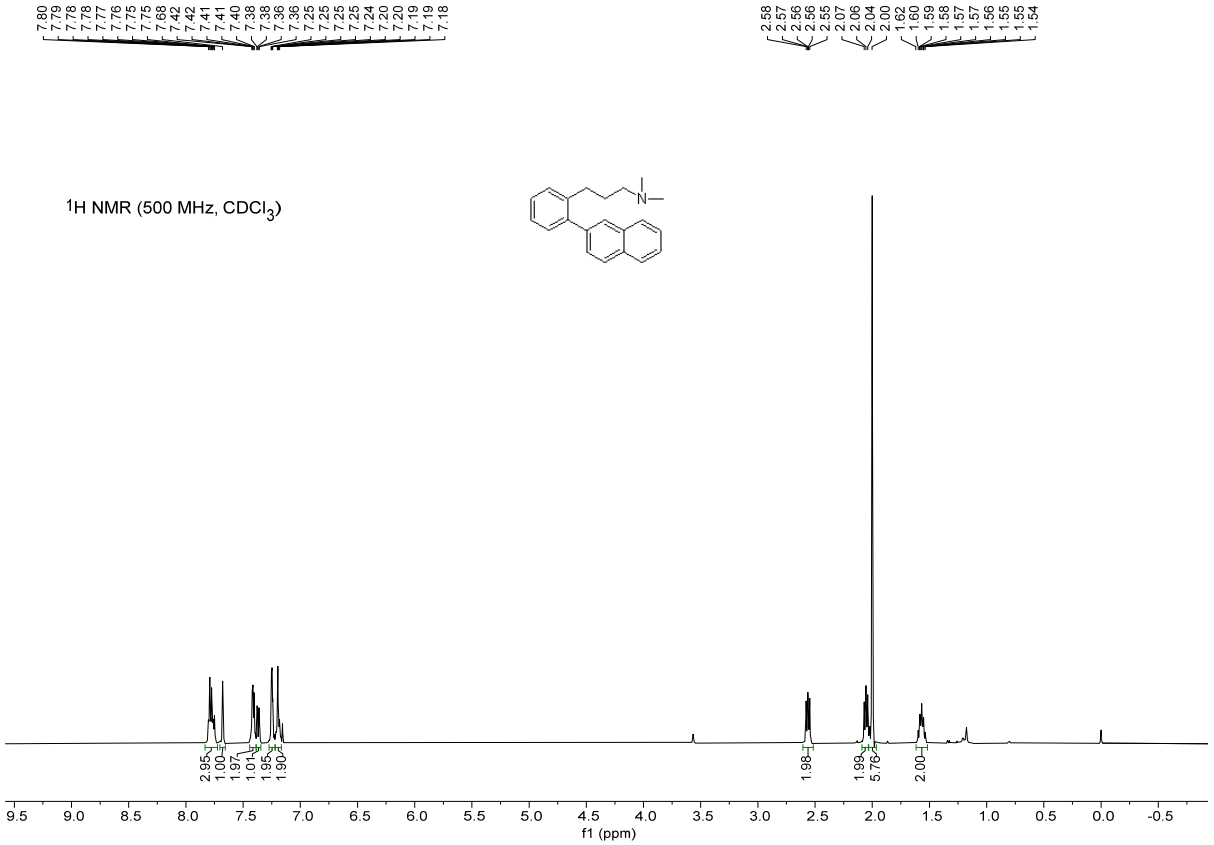


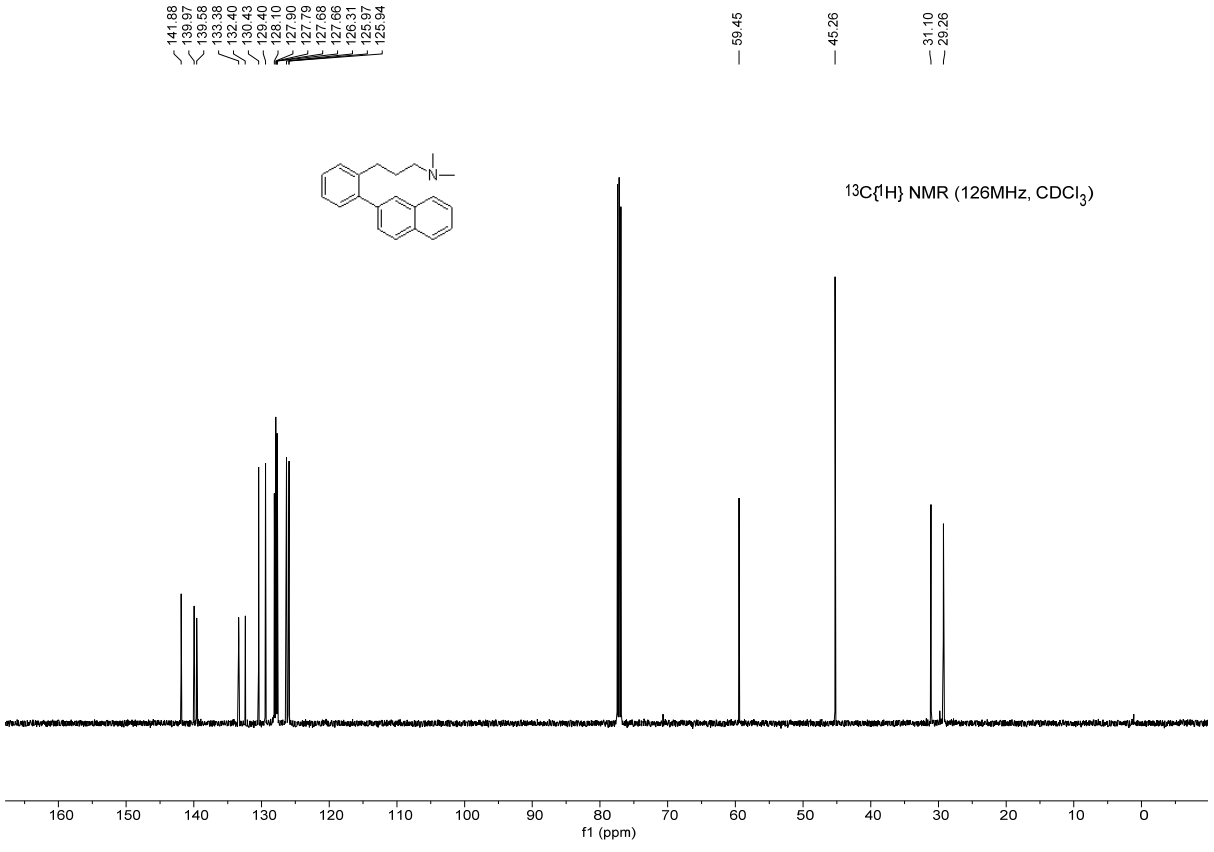
(18) 3-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)-N,N-dimethylpropan-1-amine (**3r**)



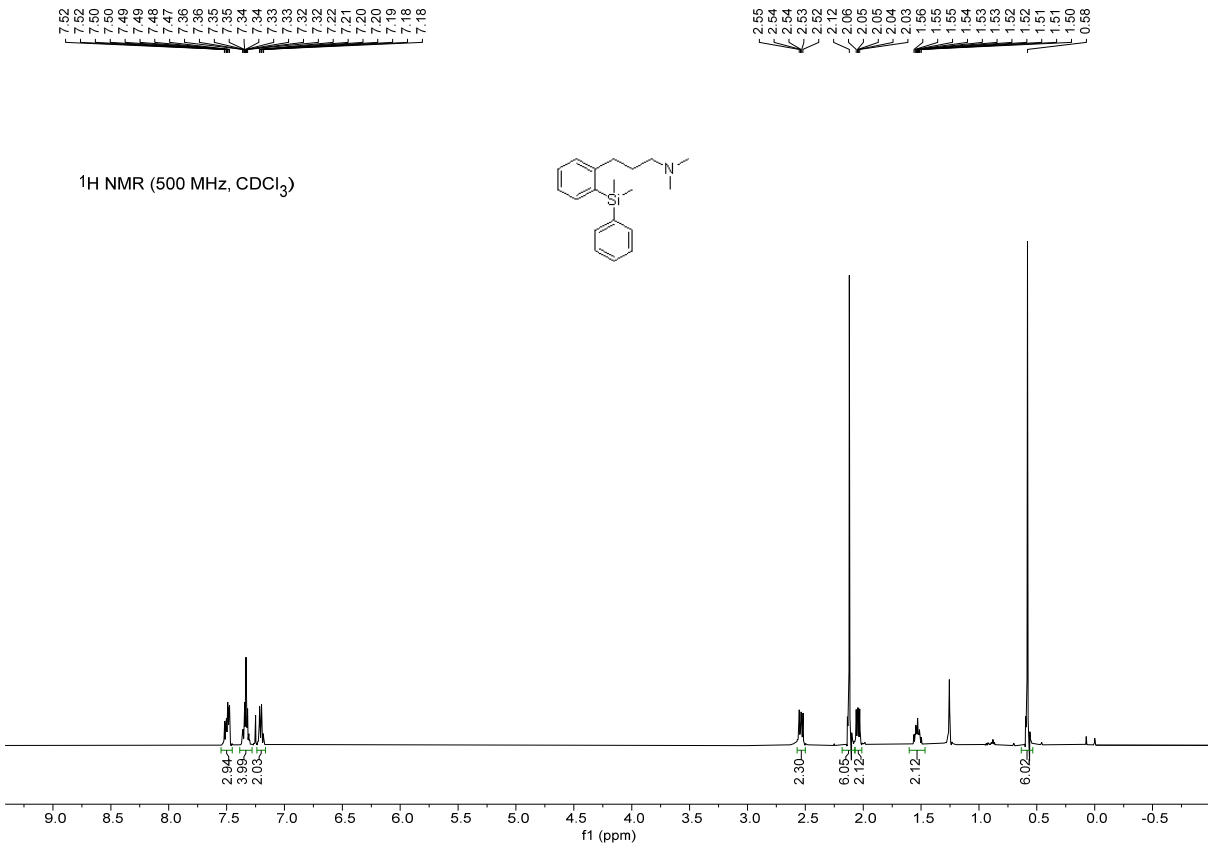


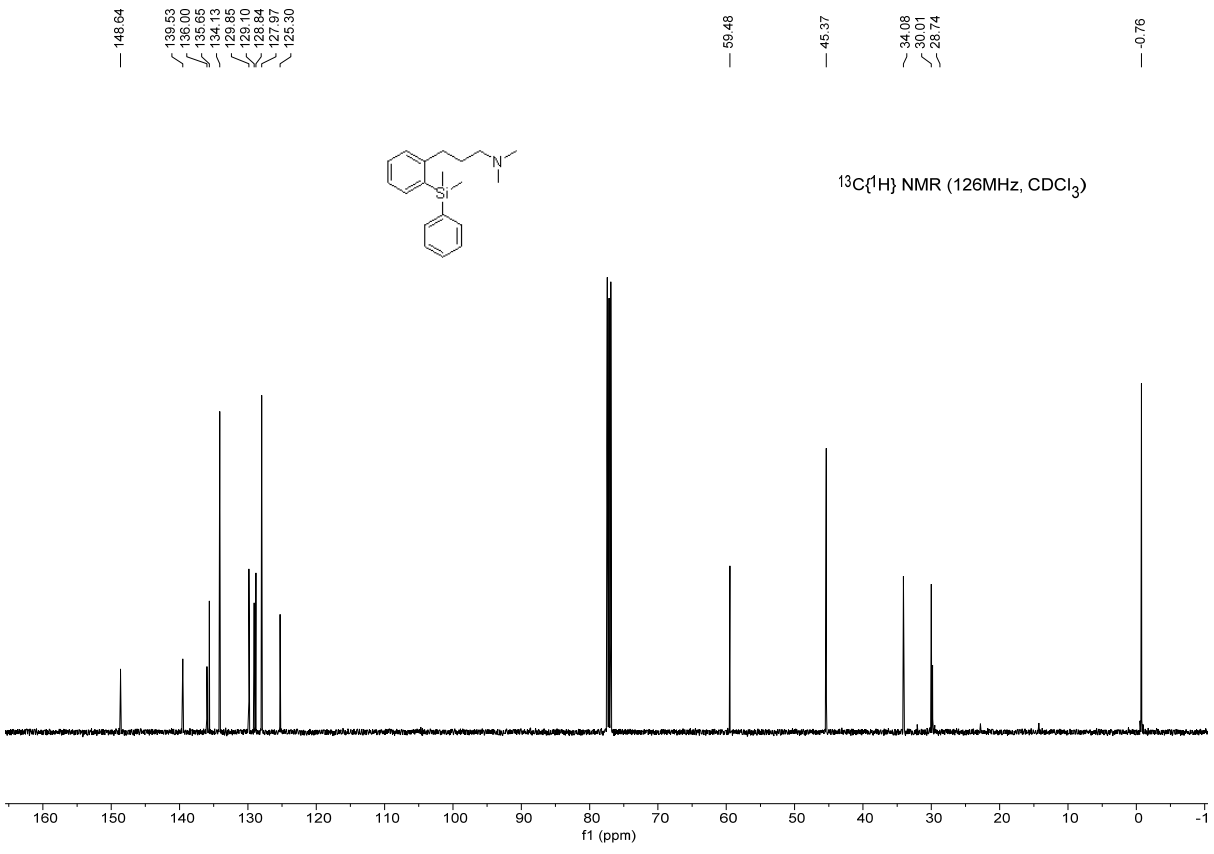
(19) N,N-dimethyl-3-(2-(naphthalen-2-yl)phenyl)propan-1-amine (**3s**)



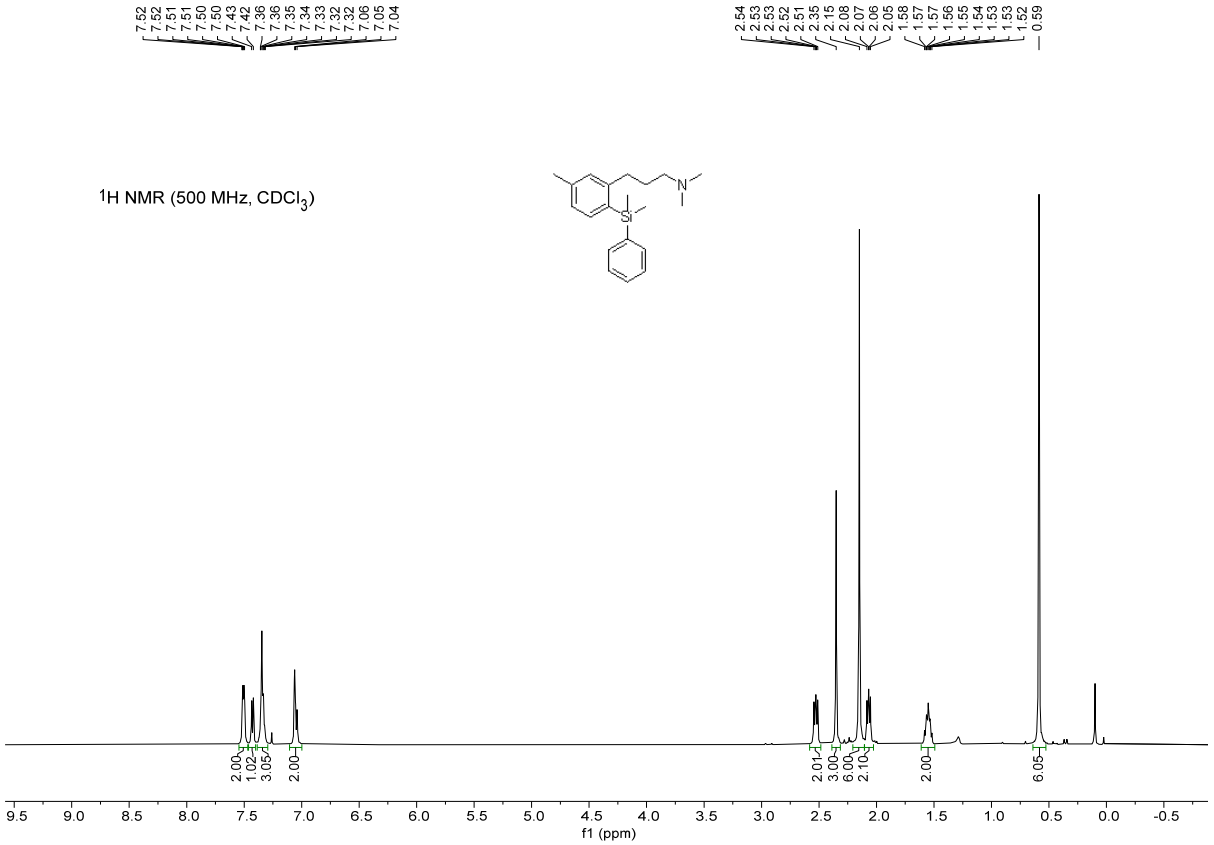


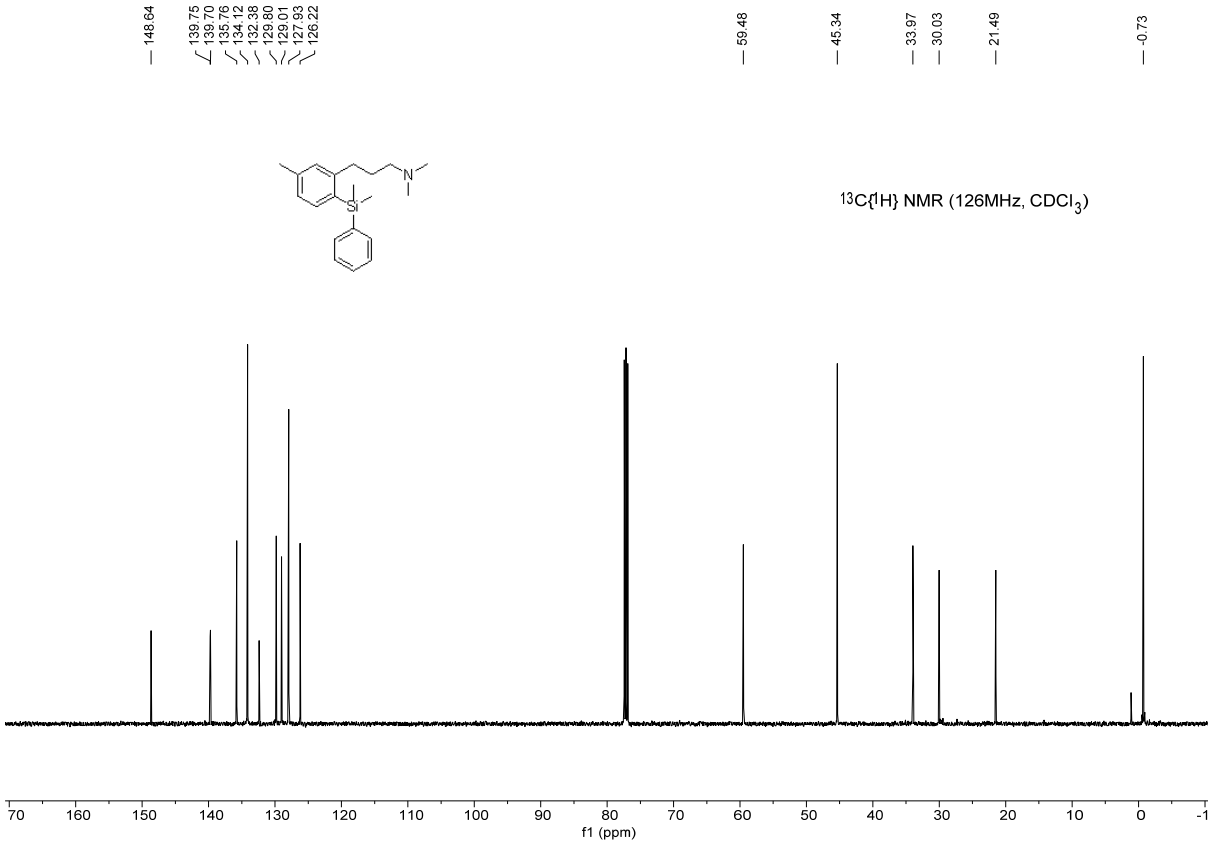
(20) 3-(2-(dimethyl(phenyl)silyl)phenyl)-N,N-dimethylpropan-1-amine (**6a**)



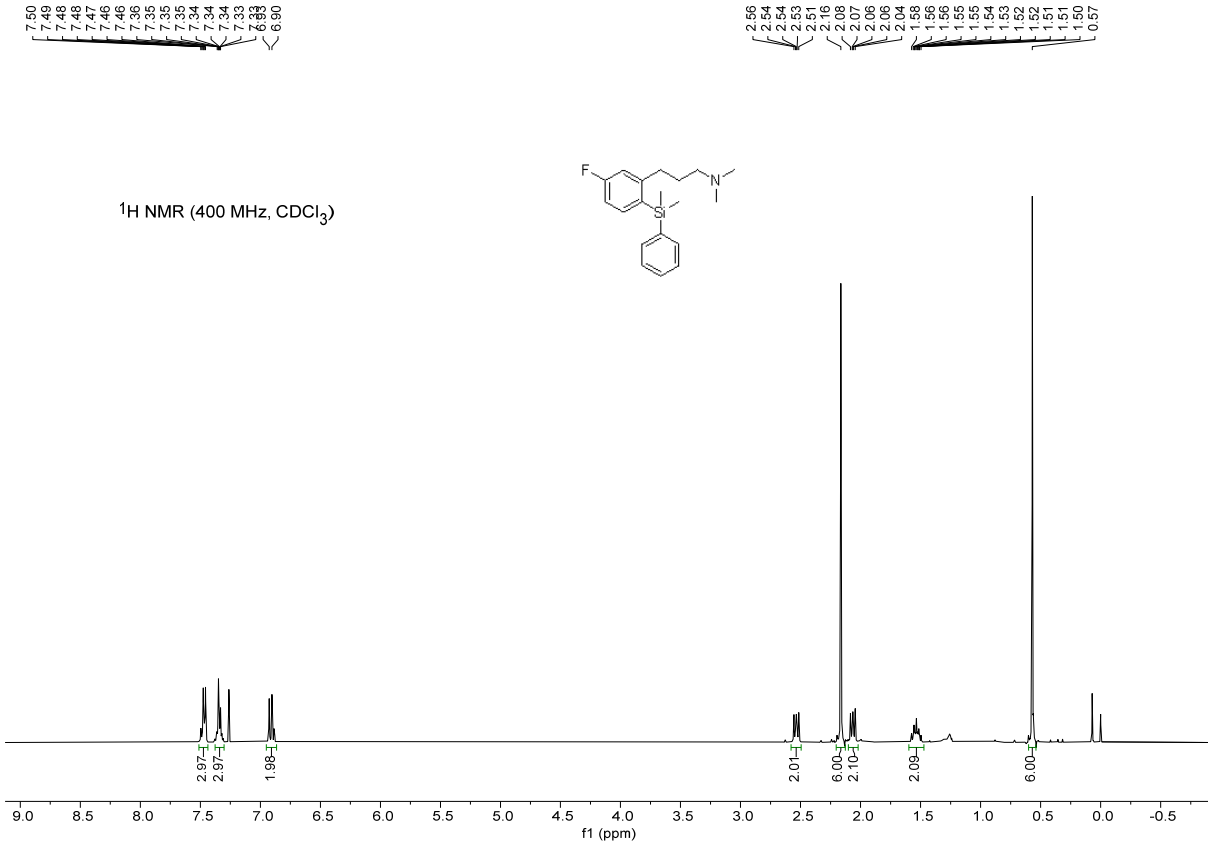


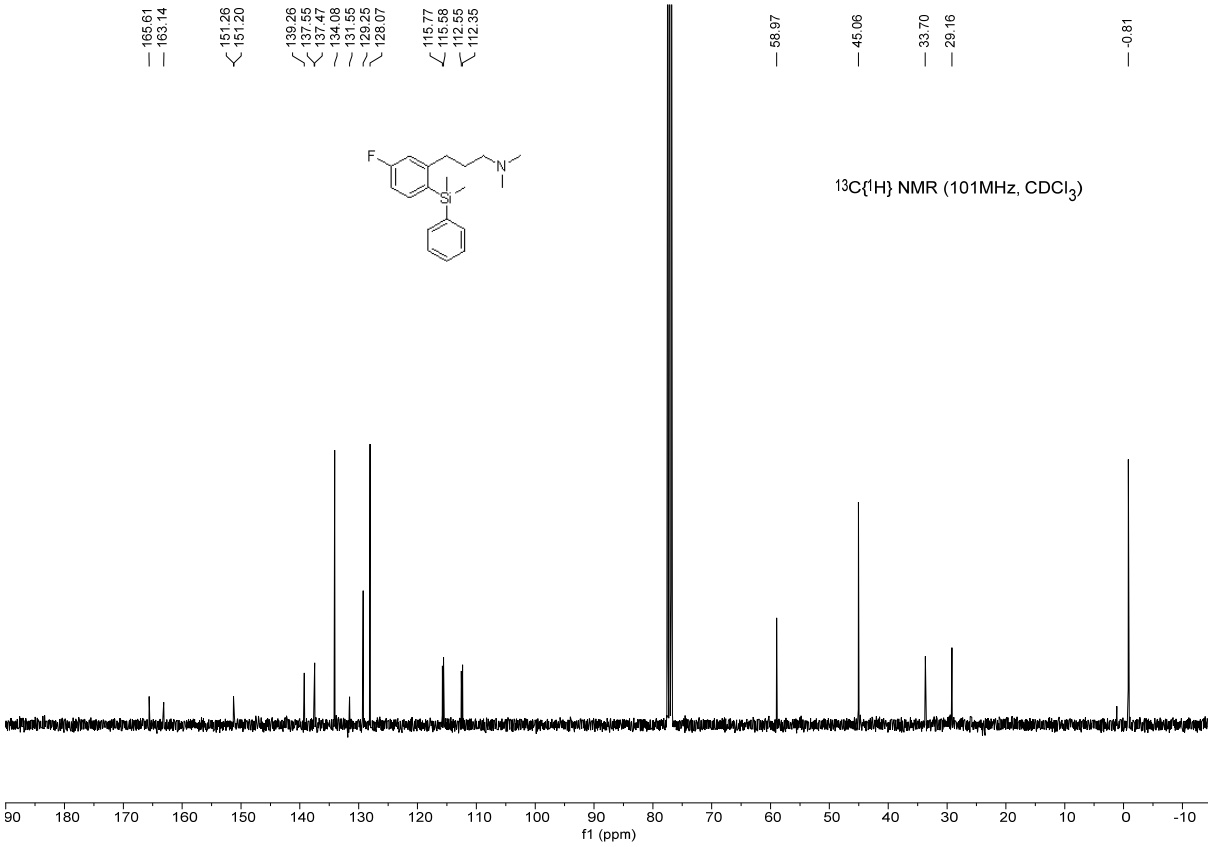
(21) 3-(2-(dimethyl(phenyl)silyl)-5-methylphenyl)-N,N-dimethylpropan-1-amine (**6b**)

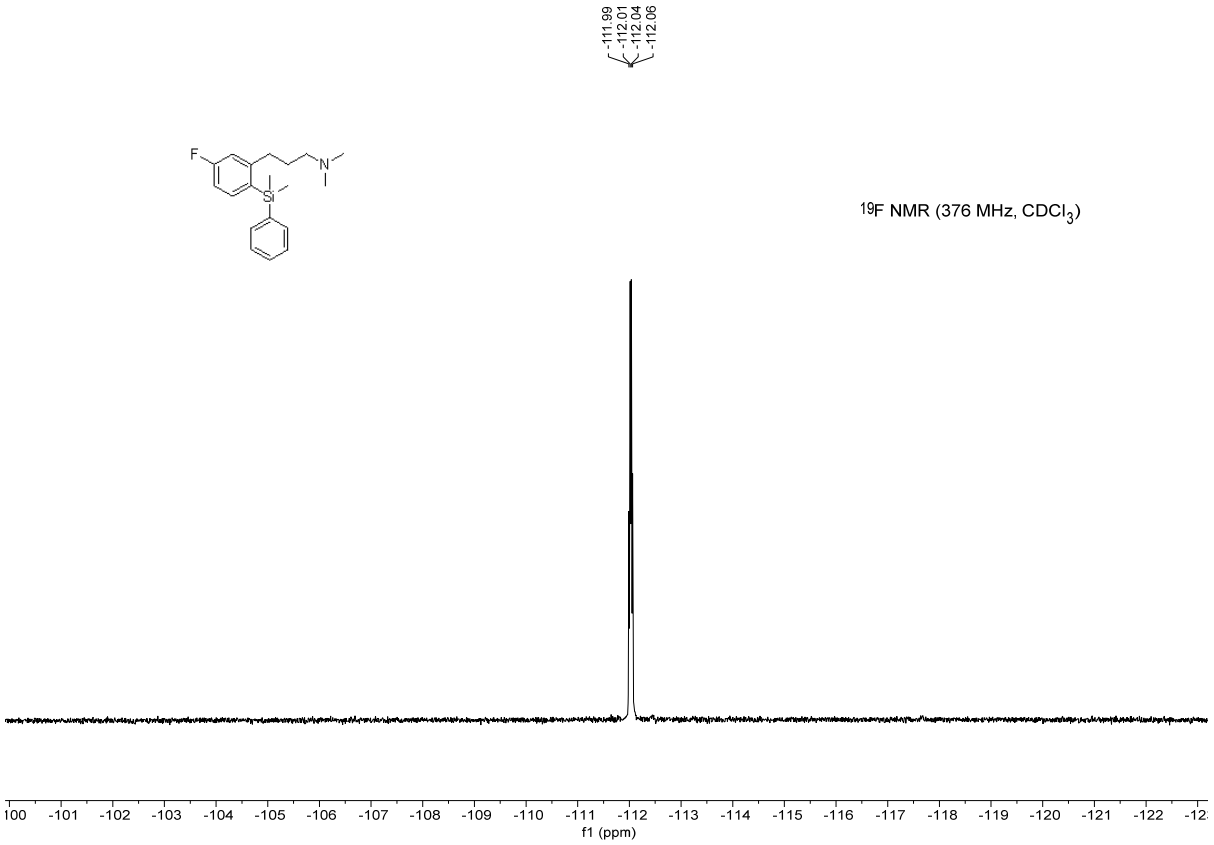




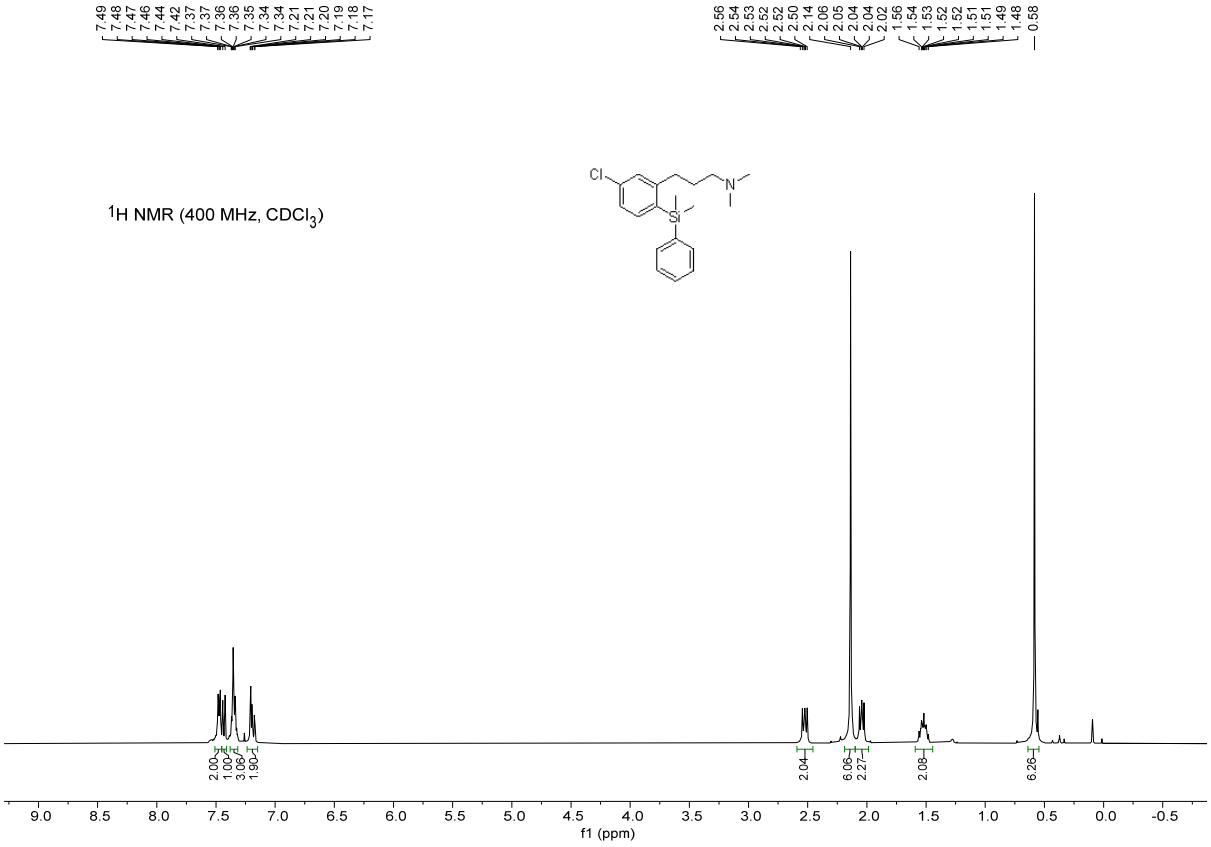
(22) 3-(2-(dimethyl(phenyl)silyl)-5-fluorophenyl)-N,N-dimethylpropan-1-amine (**6c**)

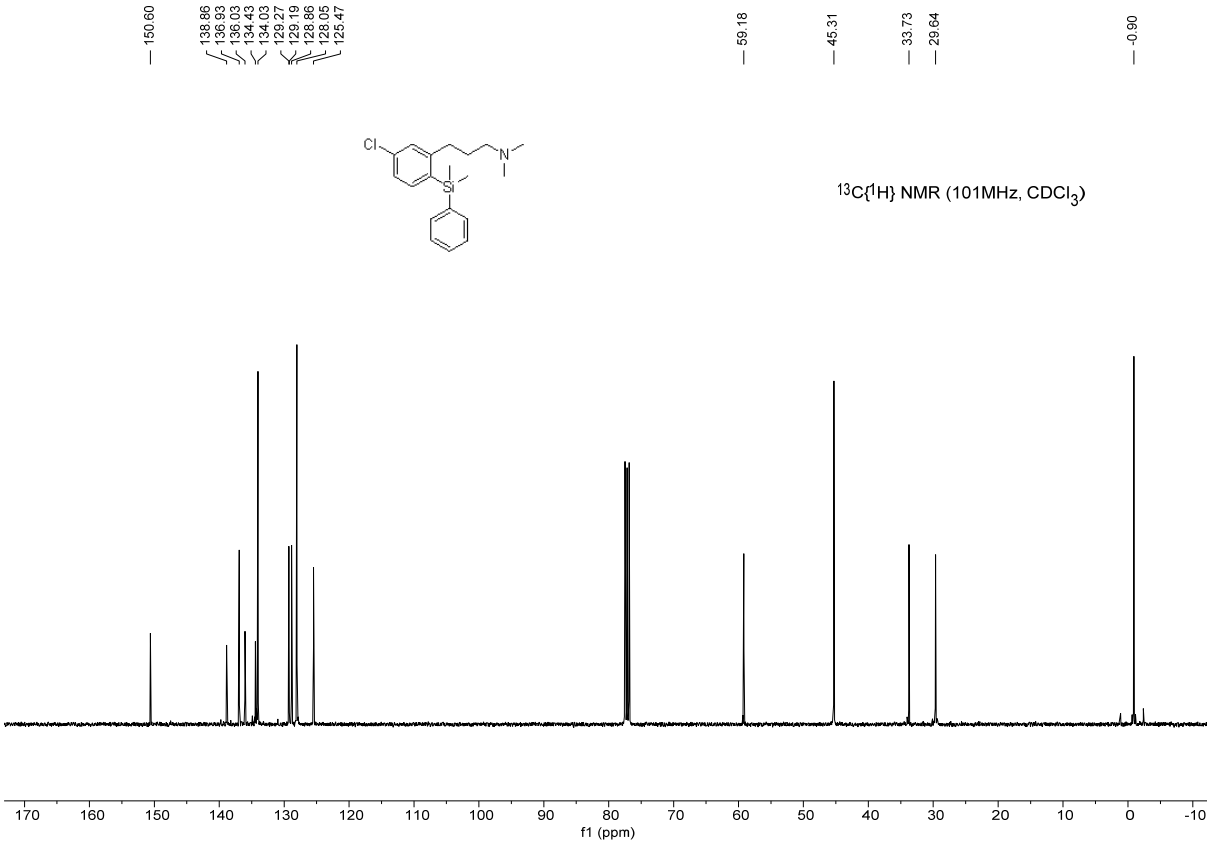




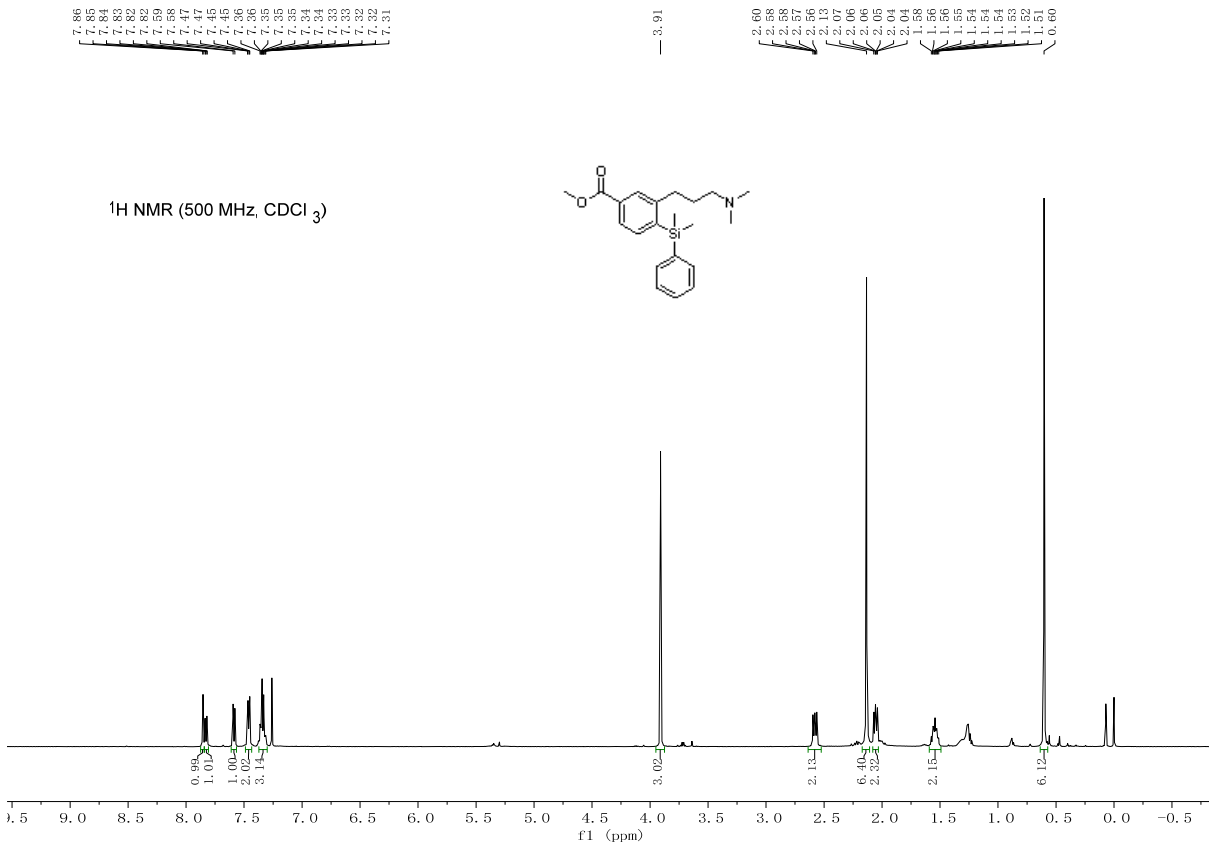

-111.99
-112.01
-112.04
-112.06
F
N
Si
^{19}F NMR (376 MHz, $CDCl_3$)
-100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122
f1 (ppm)

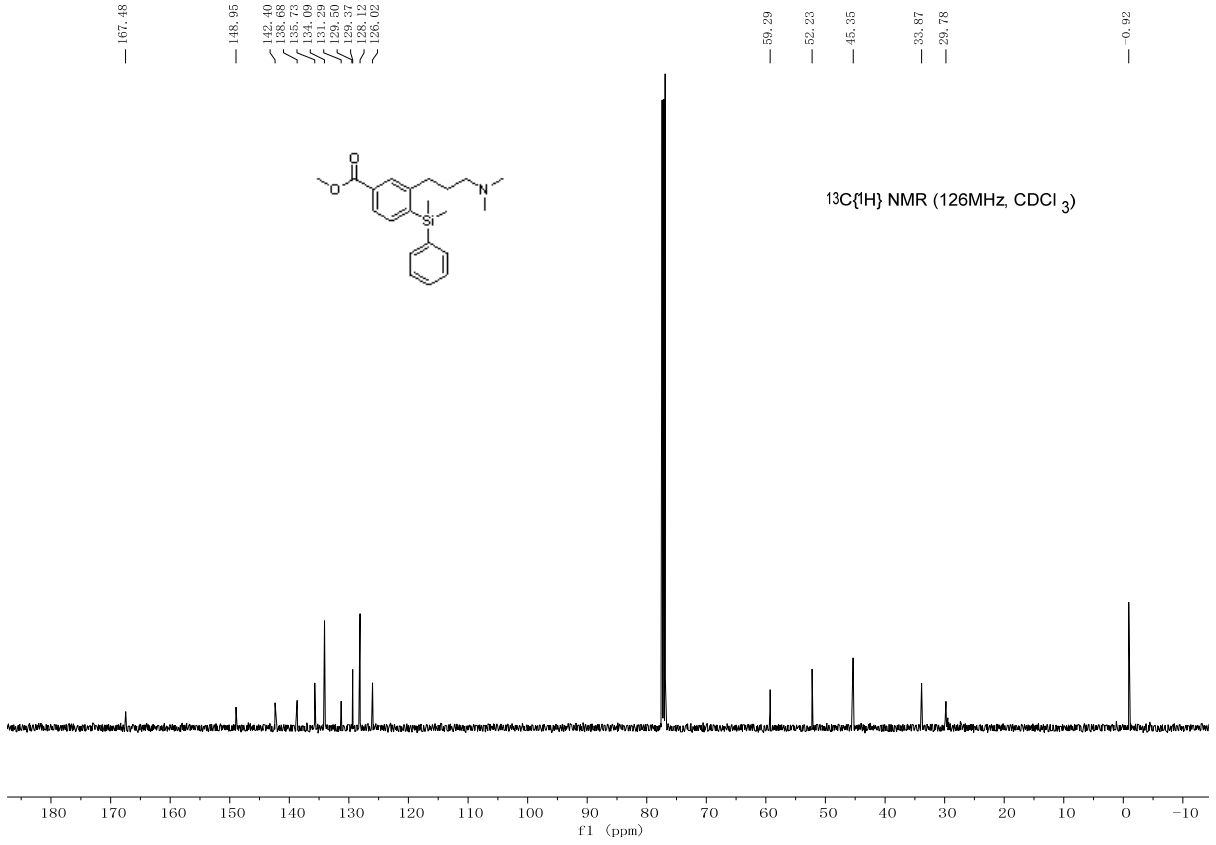
(23) 3-(5-chloro-2-(dimethyl(phenyl)silyl)phenyl)-N,N-dimethylpropan-1-amine (**6d**)



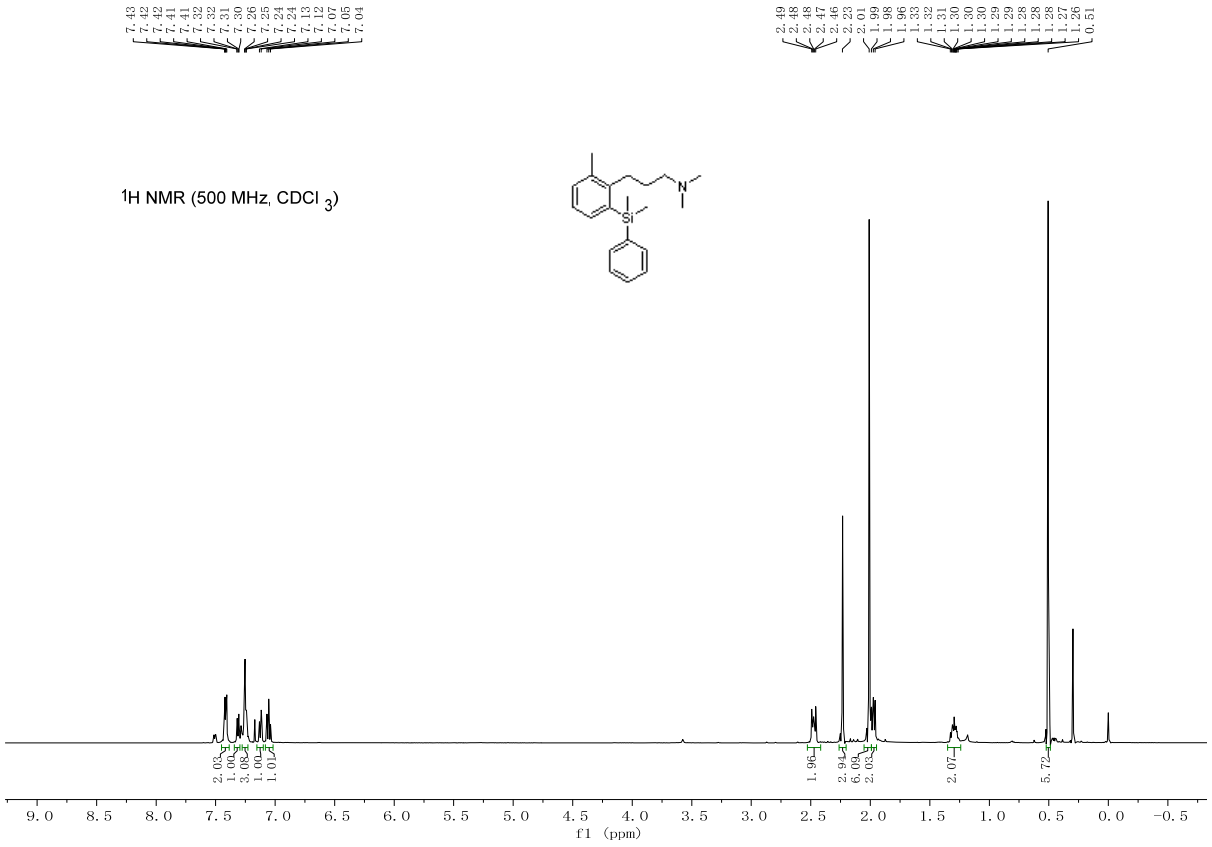


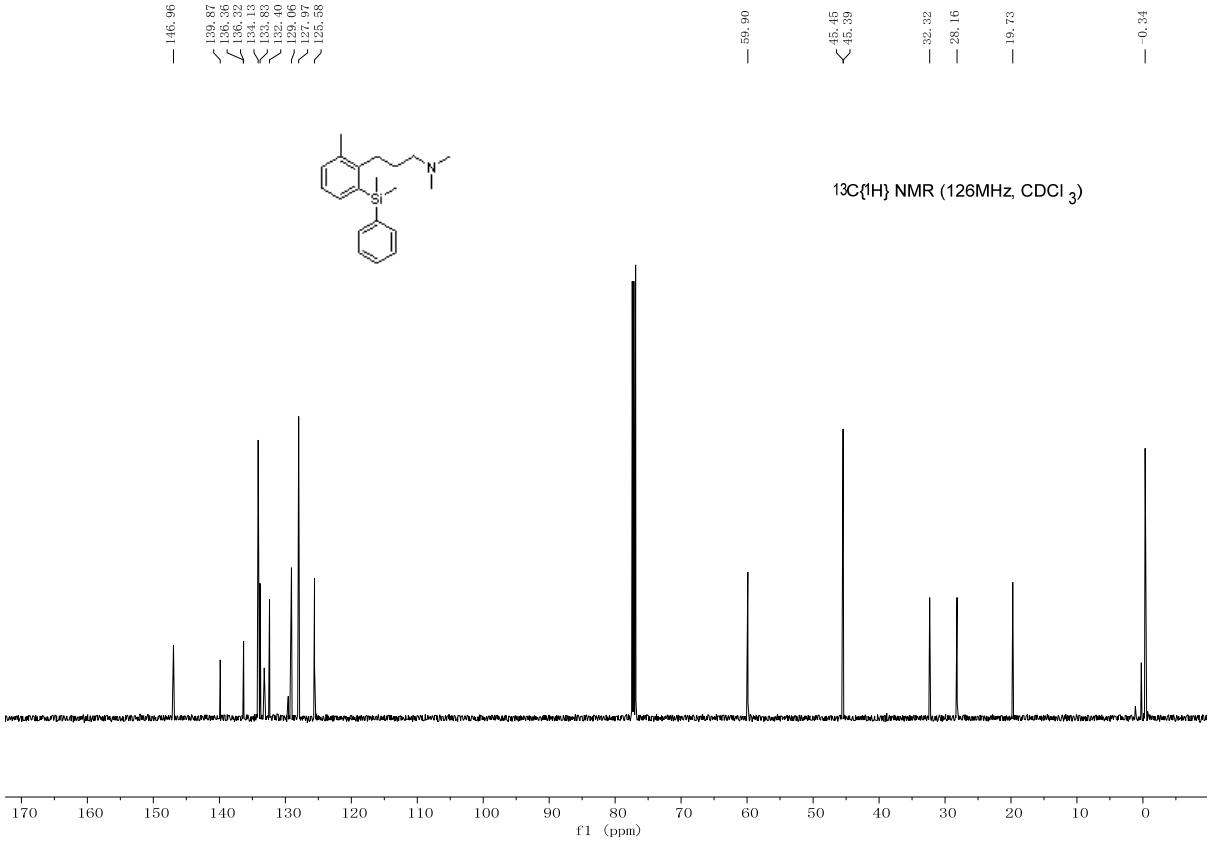
(24) methyl 4-(dimethyl(phenyl)silyl)-3-(3-(dimethylamino)propyl)benzoate (**6e**)



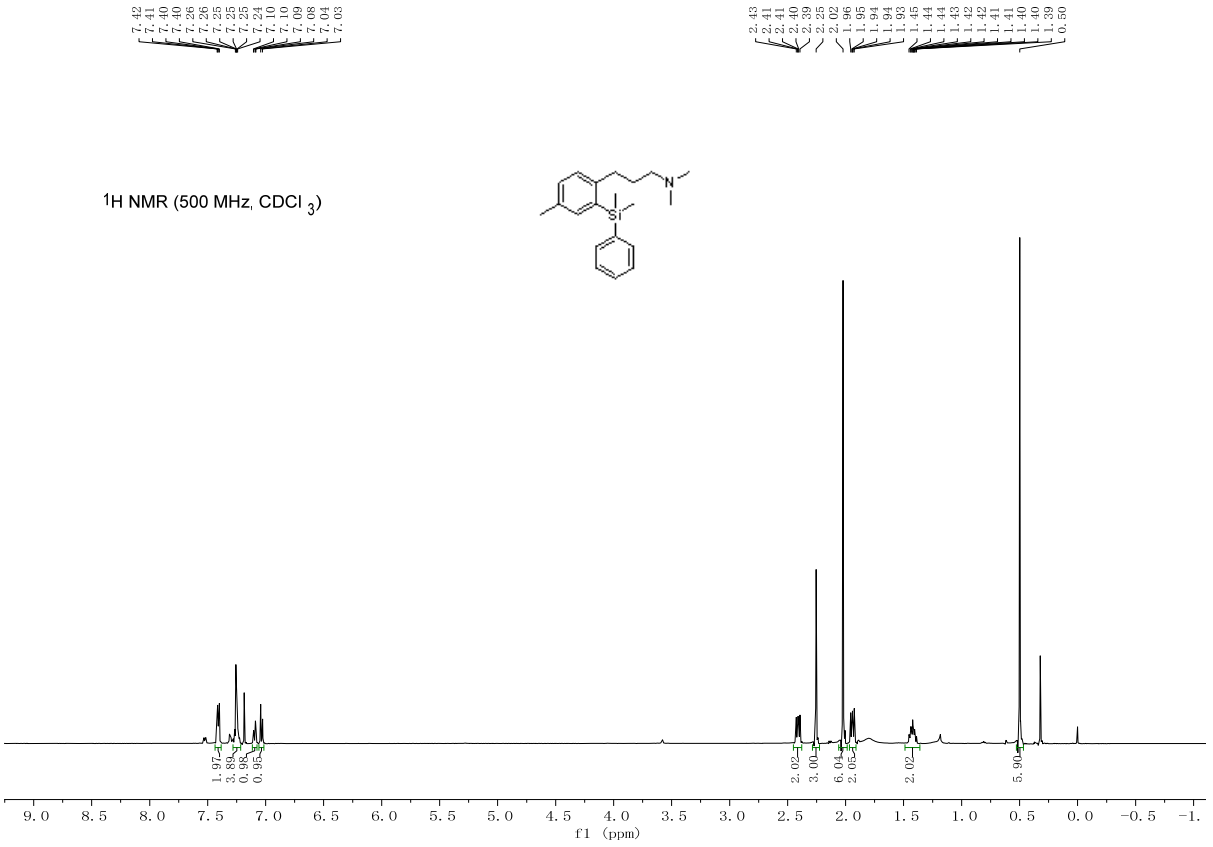


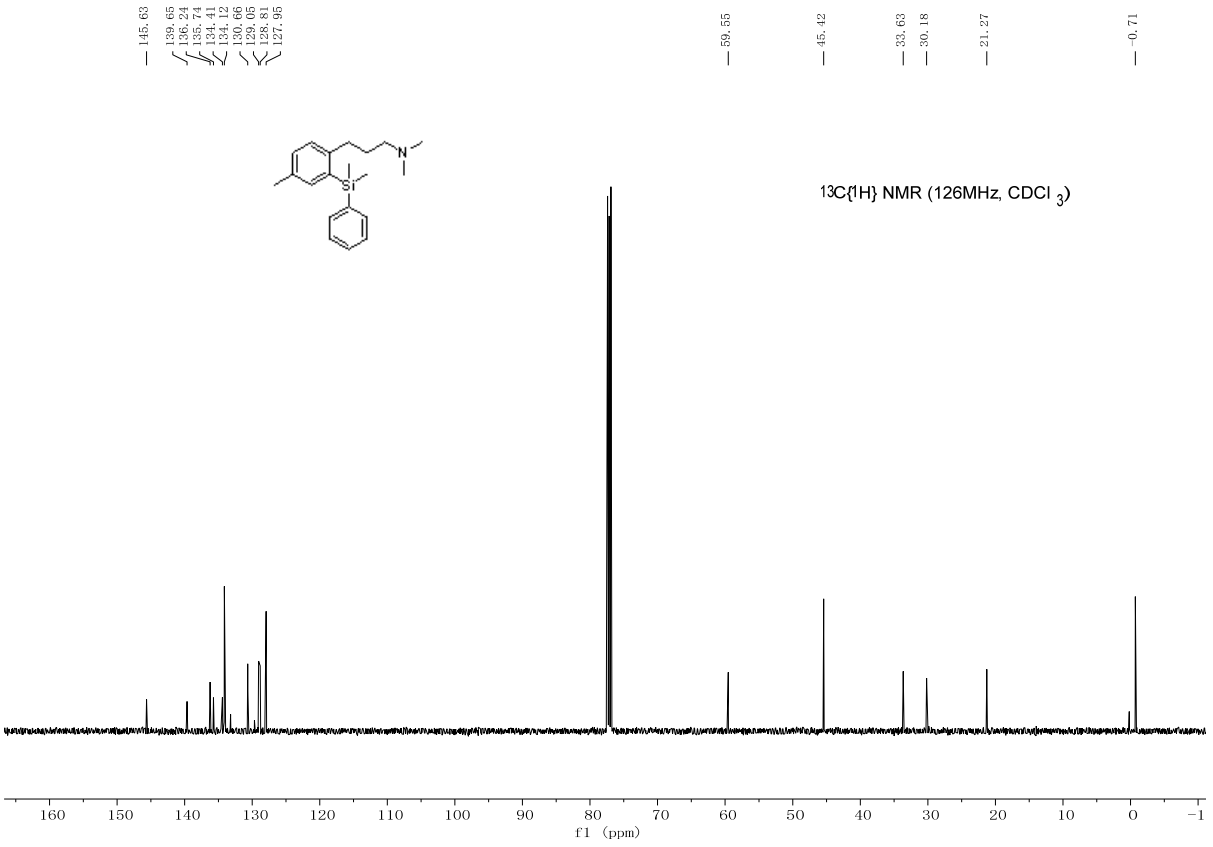
(25) 3-(2-(dimethyl(phenyl)silyl)-6-methylphenyl)-N,N-dimethylpropan-1-amine (**6f**)



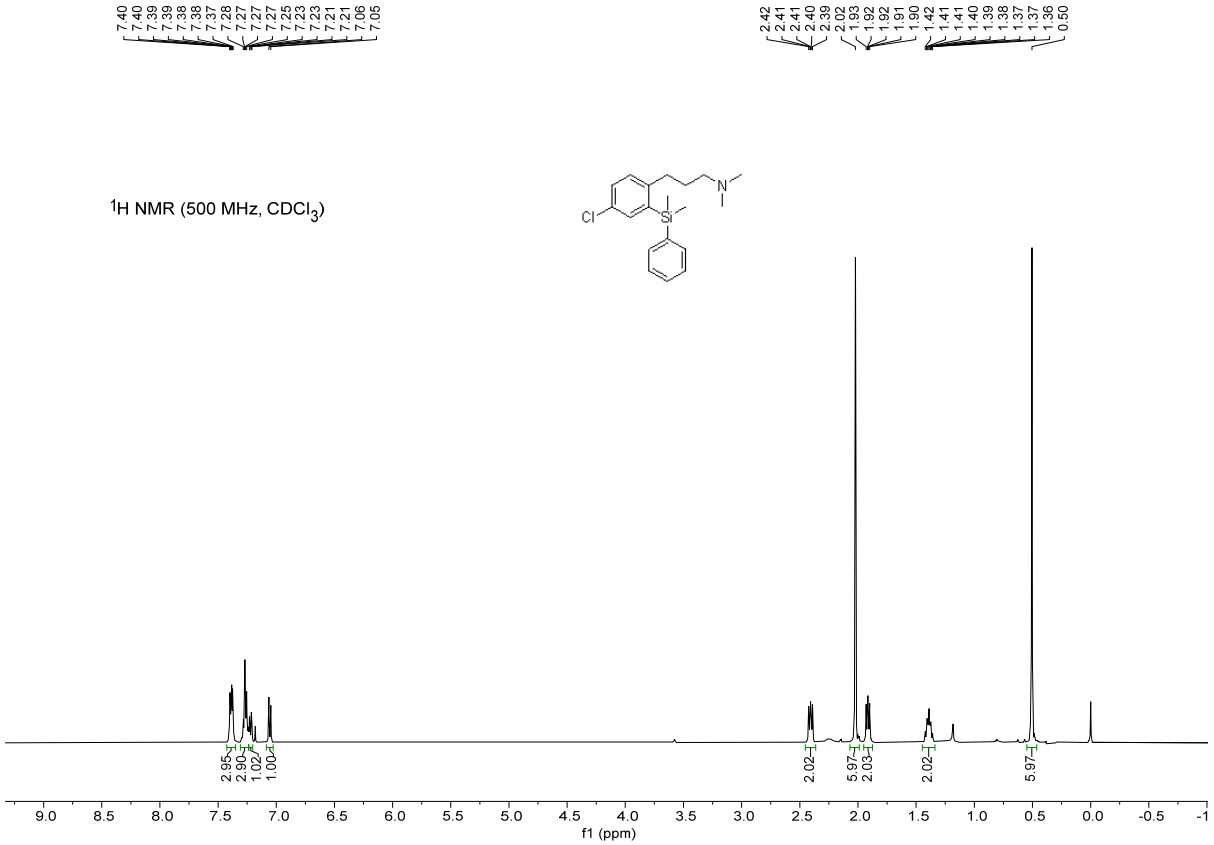


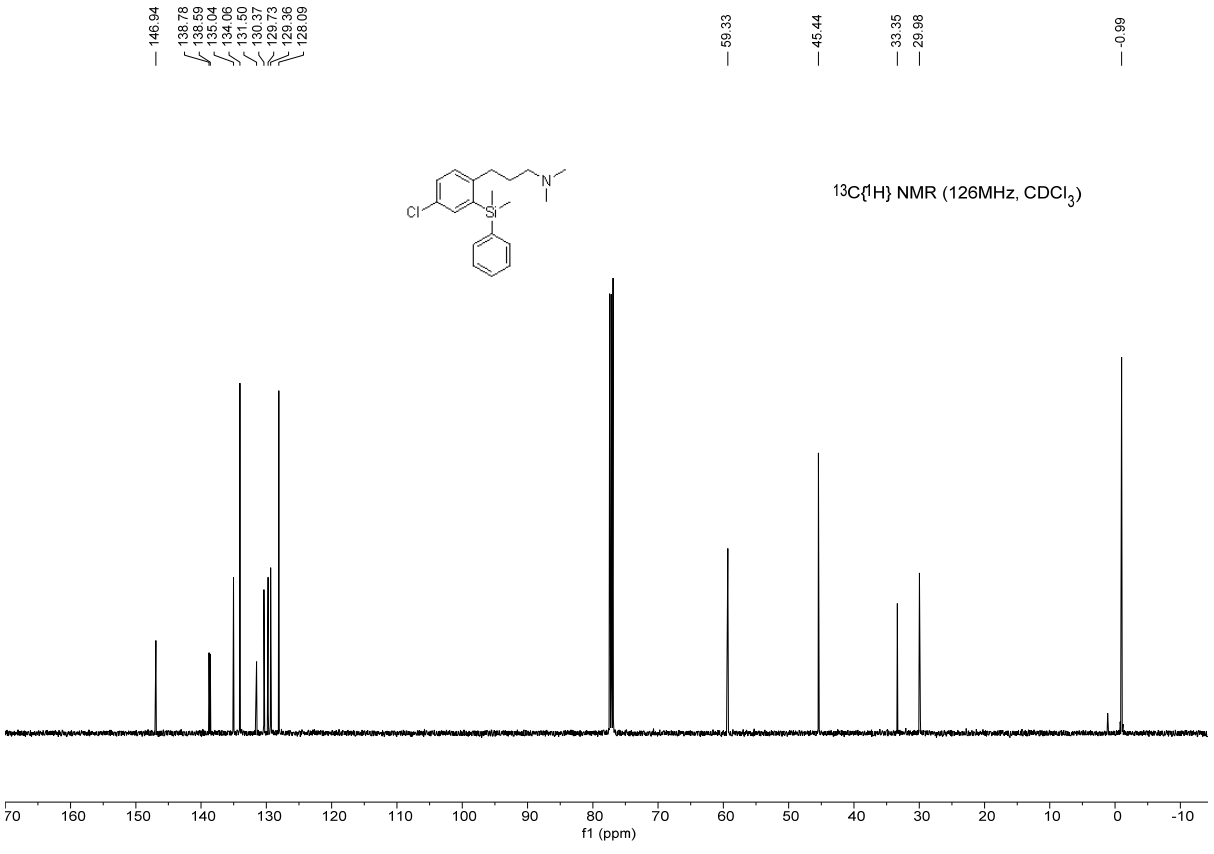
(26) 3-(2-(dimethyl(phenyl)silyl)-4-methylphenyl)-N,N-dimethylpropan-1-amine (**6g**)



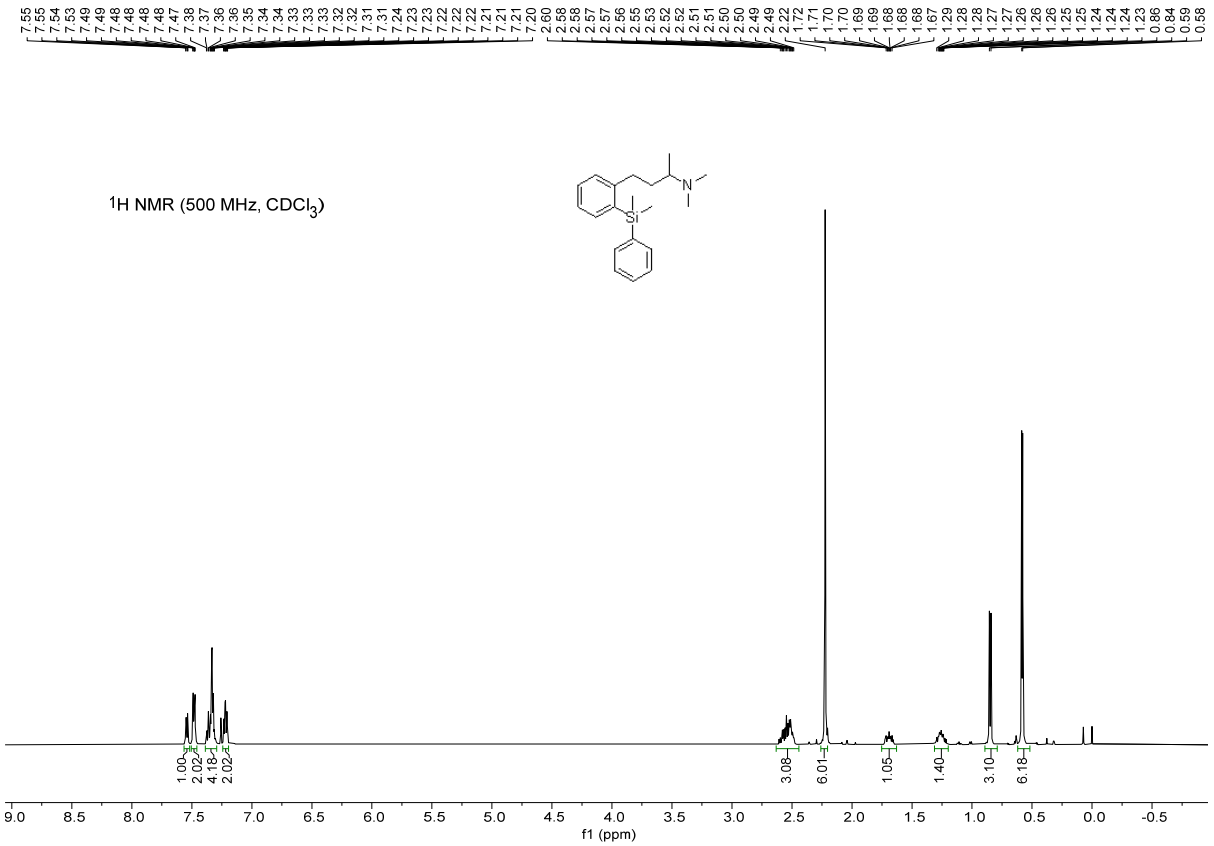


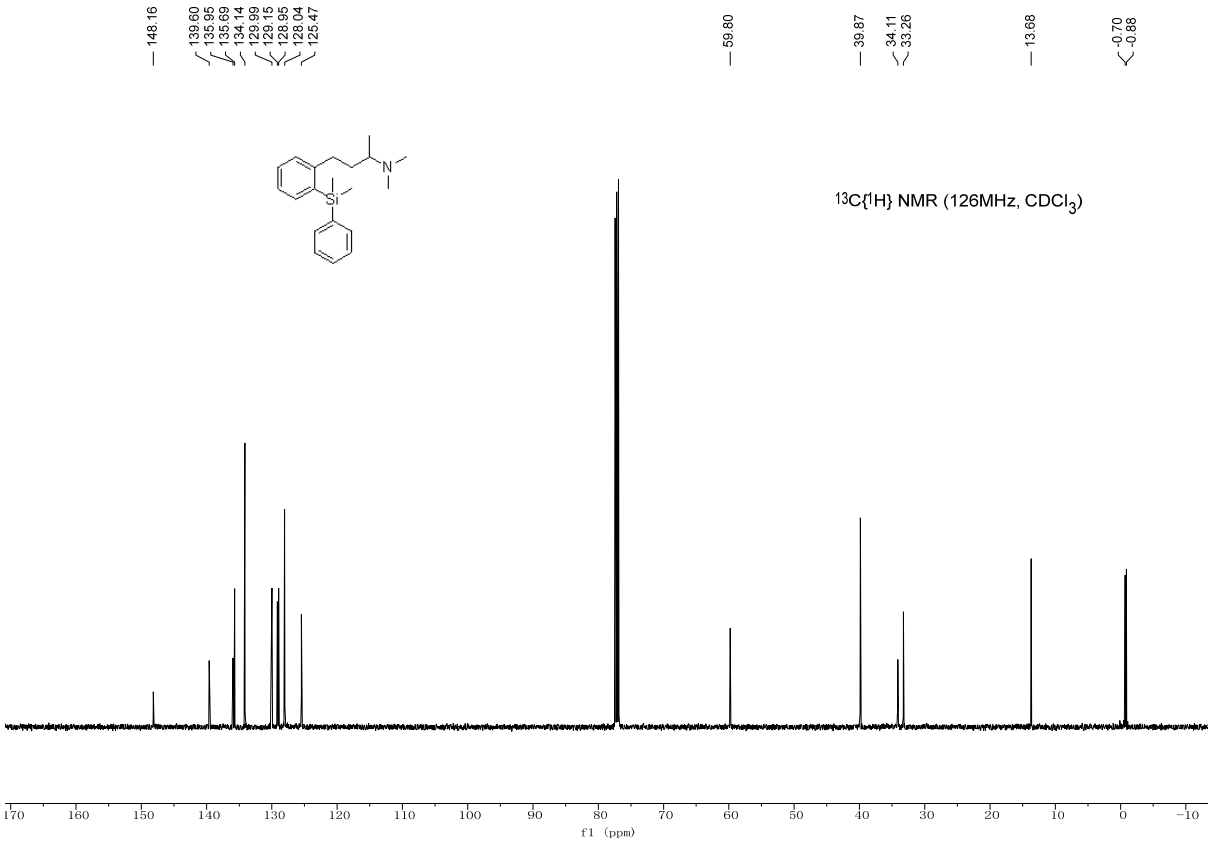
(27) 3-(4-chloro-2-(dimethyl(phenyl)silyl)phenyl)-N,N-dimethylpropan-1-amine (**6h**)



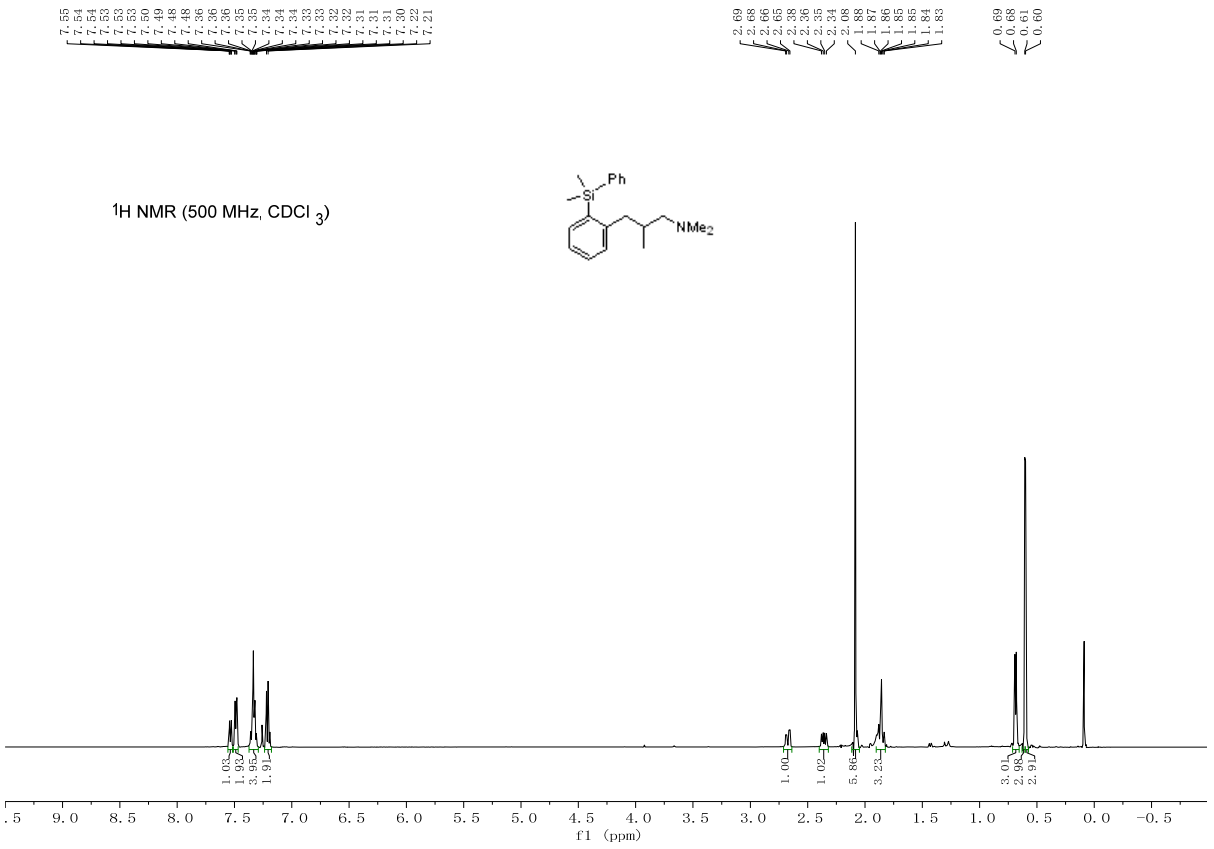


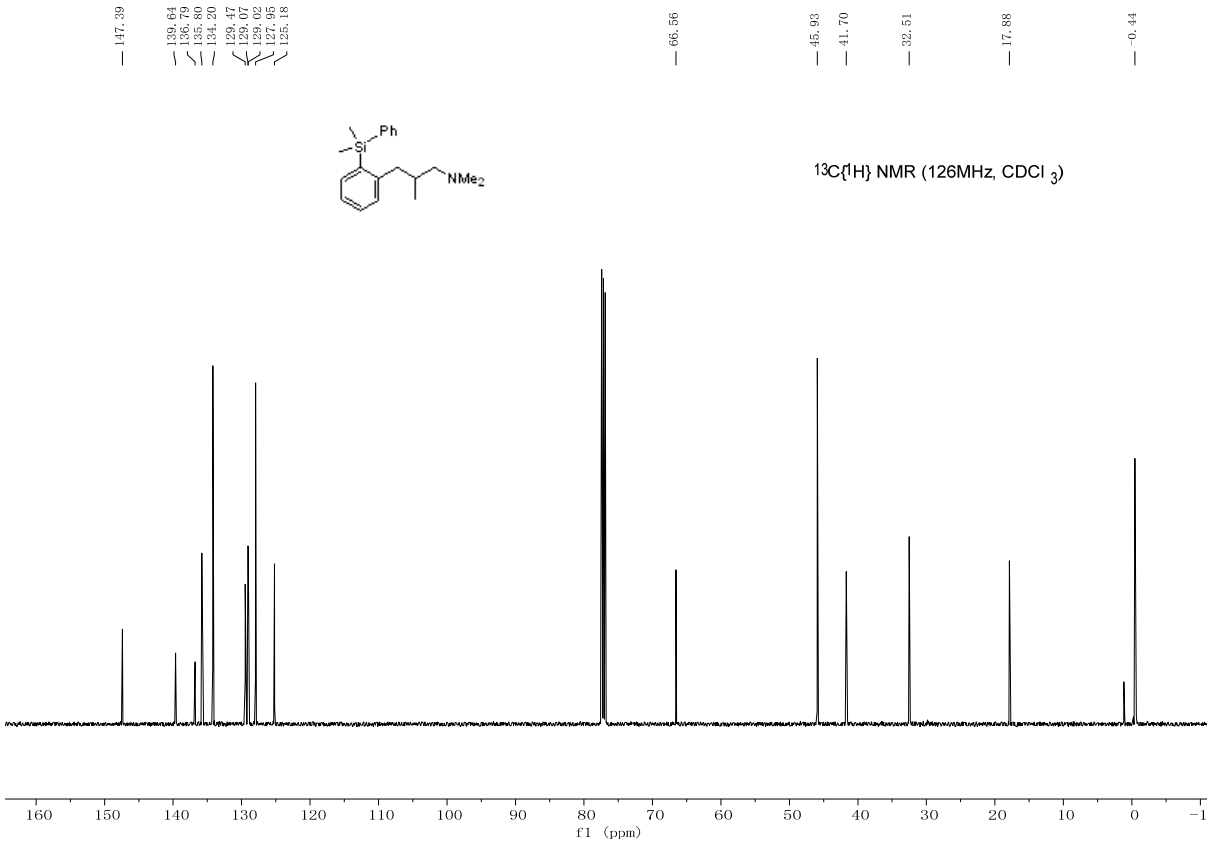
(28) 4-(2-(dimethyl(phenyl)silyl)phenyl)-N,N-dimethylbutan-2-amine (**6i**)



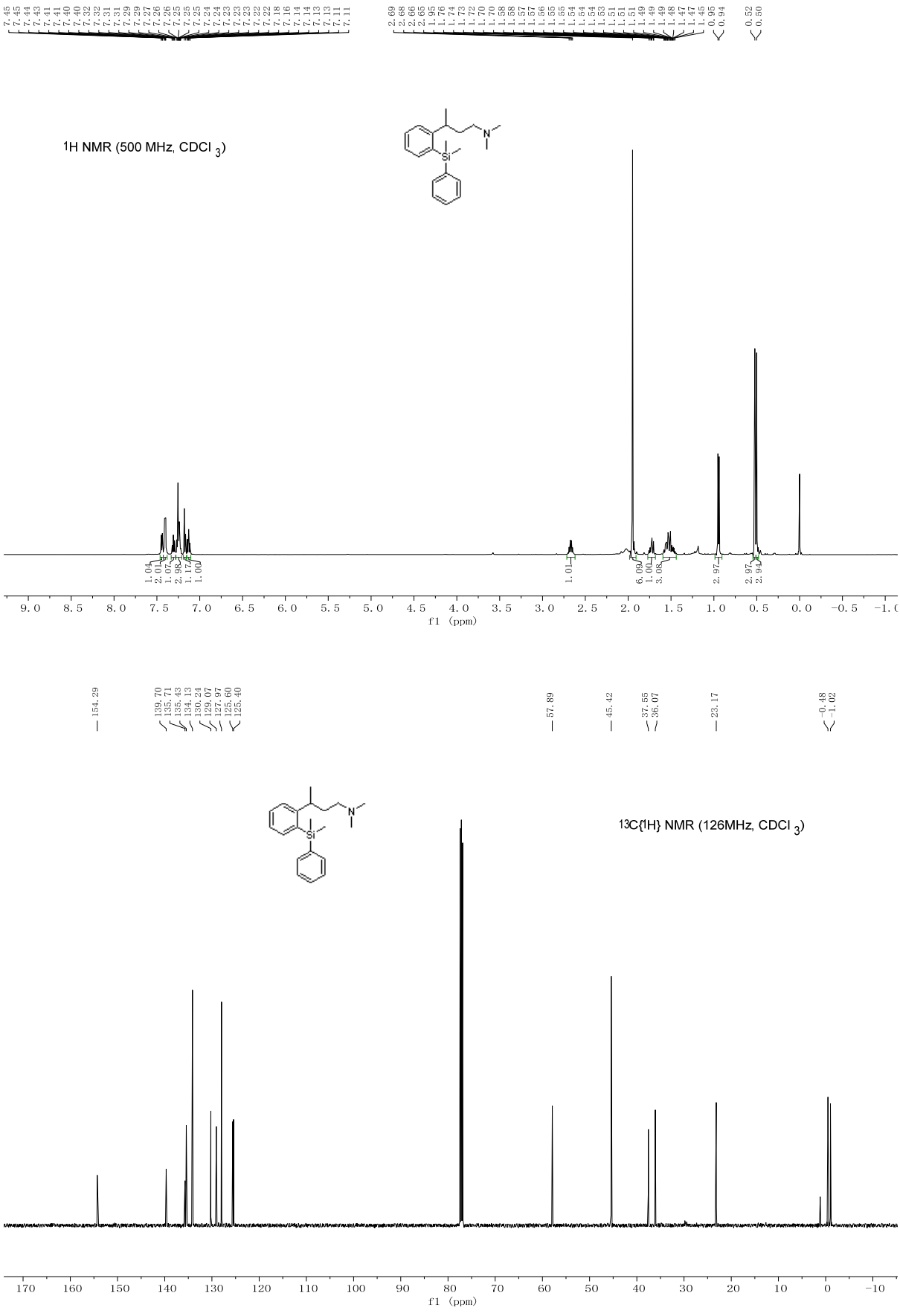


(29) 3-(2-(dimethyl(phenyl)silyl)phenyl)-N,N,2-trimethylpropan-1-amine (**6j**)

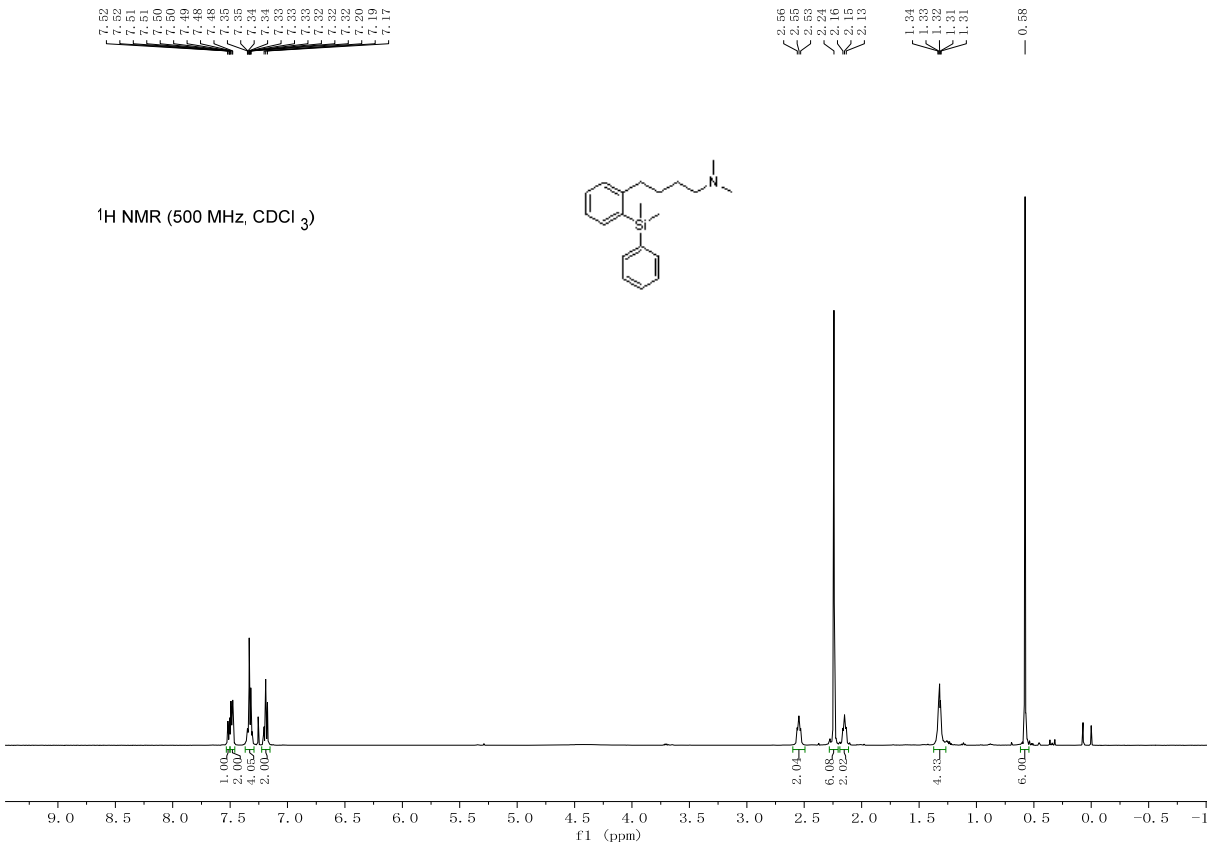


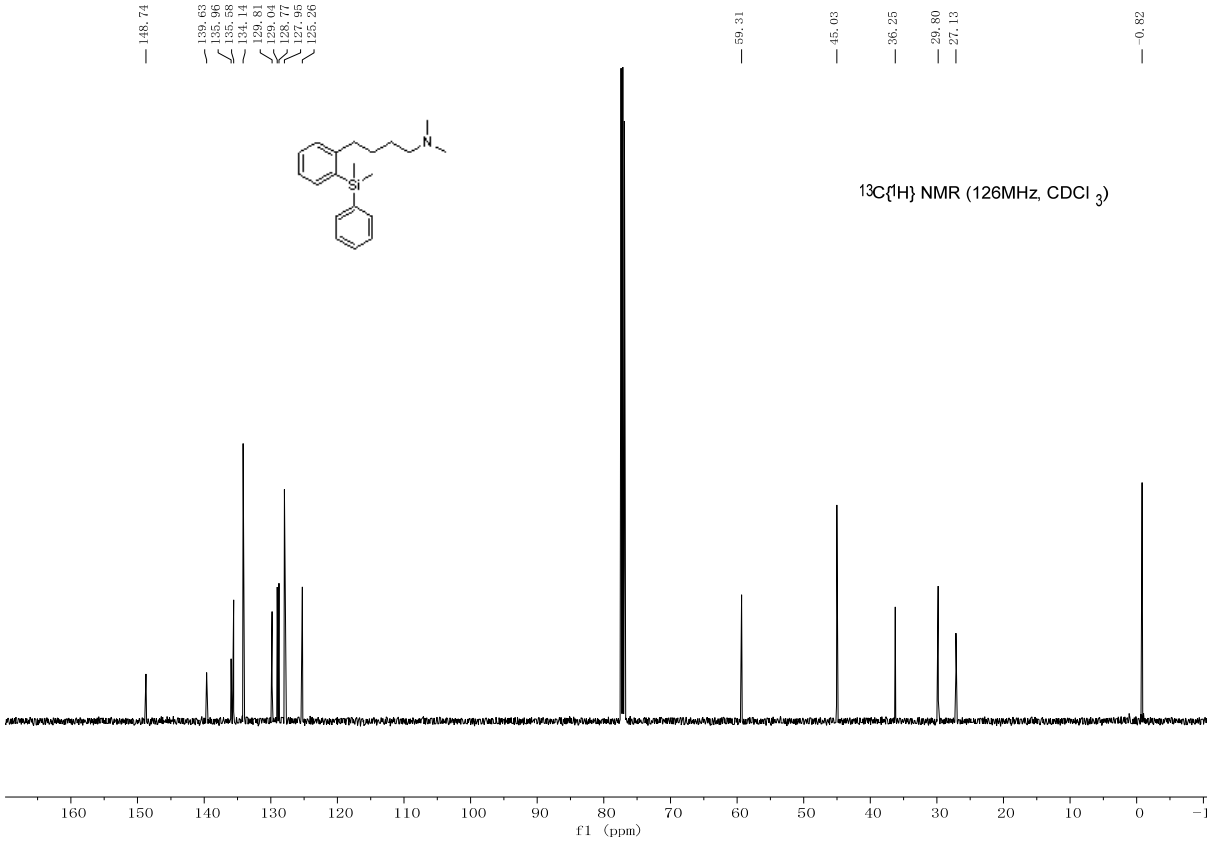


(30) 3-(2-(dimethyl(phenyl)silyl)phenyl)-N,N-dimethylbutan-1-amine (**6k**)

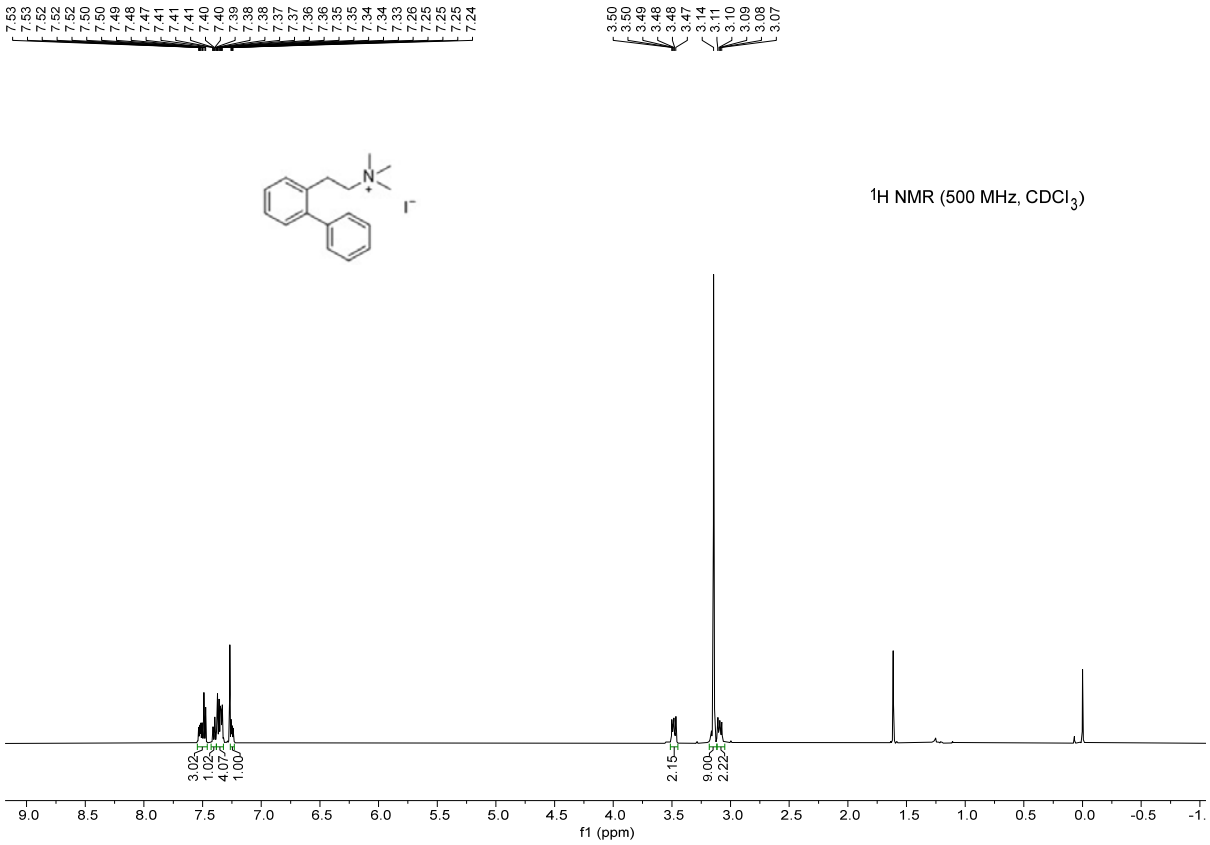


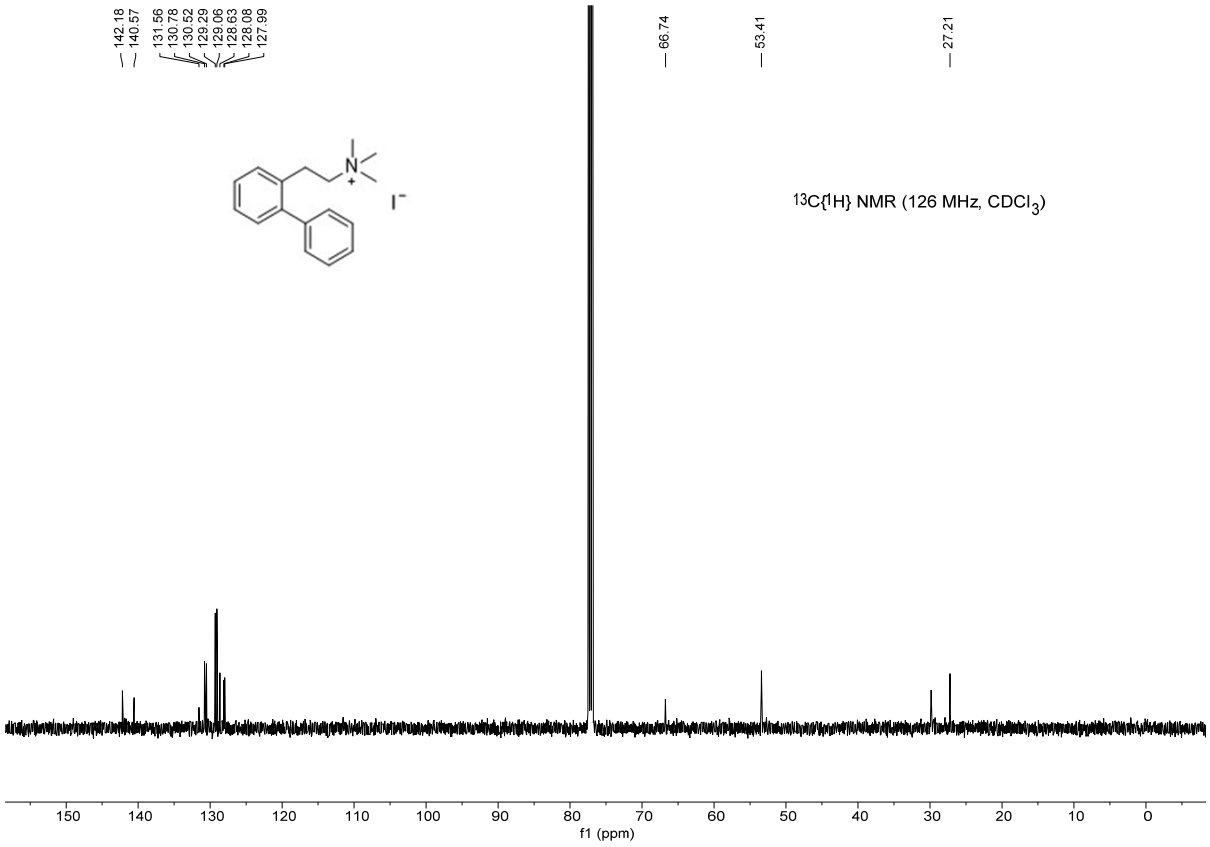
(31) 4-(2-(dimethyl(phenyl)silyl)phenyl)-N,N-dimethylbutan-1-amine (**6l**)



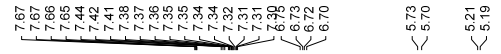


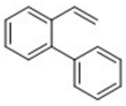
(32) 2-([1,1'-biphenyl]-2-yl)-N,N,N-trimethylethan-1-aminium iodide



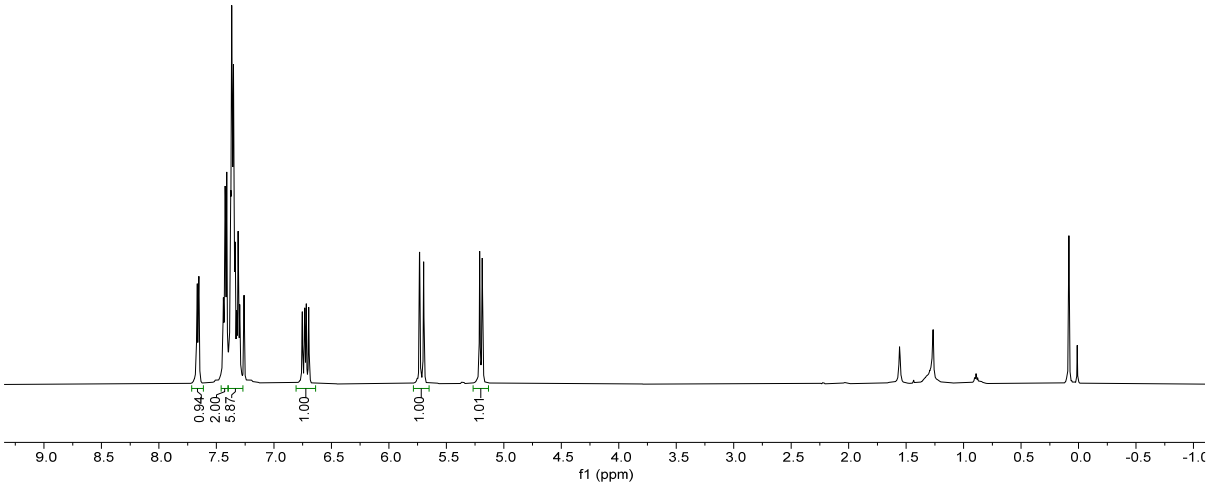


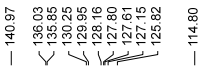
(33) 2-vinyl-1,1'-biphenyl

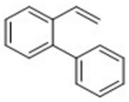




^{1}H NMR (500 MHz, $CDCl_3$)







^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)