Copper-Catalyzed Silylation of C(sp^3)–H Bonds Adjacent to Amide Nitrogen Atoms

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Supporting Information

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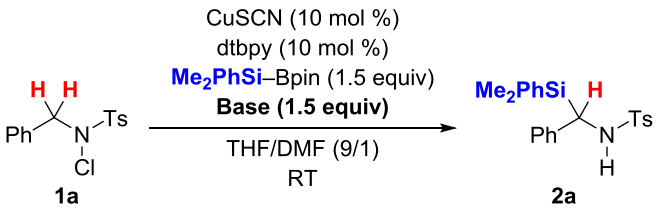
1 General Information

All reactions were performed in flame-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes. Silicon nucleophiles {$Me_2PhSiBpin$,[1] $MePh_2SiBpin$,[1] and $Et_3SiBpin$[2]} and *t*BuOCl[3] were prepared according to reported procedures. Copper(I) thiocyanate (CuSCN, 96%, *ABCR*), 4,4'-di-*tert*-butyl- 2,2'-bipyridine (dtbpy, 98%, *Sigma-Aldrich*), and 4,4'-dimethoxy-2,2'-bipyridine (4,4'-$(OMe)_2$bpy, >98%, TCI) were purchased from commercial suppliers and used as received. Acetonitrile (CH_3CN) and *N,N*-dimethylformamide (DMF) were purchased from *Acros* (99.8%, extra dry) and used as received. All other solvents (1,4-dioxane, CH_2Cl_2, *n*-hexane, toluene, Et_2O, and THF) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (cyclohexane, CH_2Cl_2, ethyl acetate, and *n*-pentane) were distilled prior to use. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ^1H, ^{13}C, ^{29}Si, ^{19}F and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker AV400 and AV500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: $\delta = 7.26$ ppm for ^1H NMR and $CDCl_3$: $\delta = 77.0$ ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplett, q = quartet, m = multiplet, m_c = centrosymmetric multiplet, br = broad signal), coupling constants (Hz), and integration. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

2 Optimization Study

General procedure for the optimization reactions: To a flame-dried Schlenk tube purged with N_2 are subsequently added copper salt (15 µmol, 10 mol%), ligand (15 µmol, 10 mol%), base (0.225 mmol, 1.5 equiv) and solvent (0.8 mL) at room temperature. After stirring the resulting suspension for 15 min, $Me_2PhSiBpin$ (65 µL, 0.225 mmol, 1.5 equiv) and a solution of *N*-chlorosulfonamide **1a** (45 mg, 0.15 mmol, 1.0 equiv) in corresponding solvent (0.8 mL) are successively added. The reaction mixture is stirred at room temperature overnight. The reaction mixture is then subjected to ^1H NMR analysis with CH_2Br_2 as an internal standard after a short pipette filtration over silica gel.

Table S1. Screening of bases in the silylation of *N*-chlorosulfonamide **1a**.

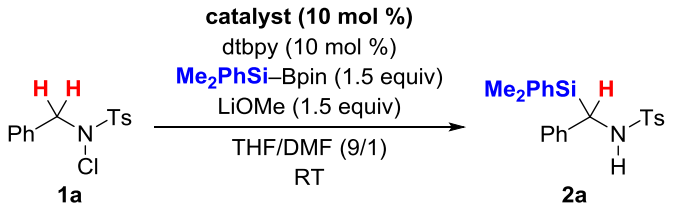


Entry	Base	Yield [%][a]
1	LiO*t*Bu	22
2	NaO*t*Bu	4
3	KO*t*Bu	18
4	NaOEt	0
5	KOEt	47
6	**LiOMe**	**60**
7	NaOMe	39
8	KOMe	2

[a] NMR yield with CH_2Br_2 as an internal standard.

dtbpy = 4,4'-di-tert-butyl-2,2'-bipyridine

Table S2. Screening of catalysts in the silylation of *N*-chlorosulfonamide **1a**.

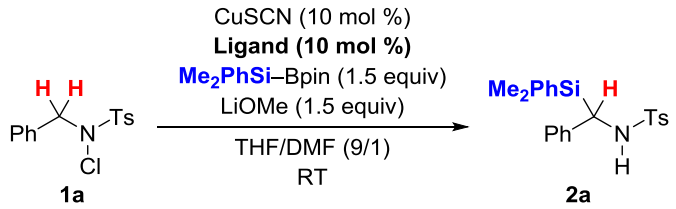


Entry	Catalyst	Yield [%][a]
1	**CuSCN**	**60**
2	CuI	21
3	CuBr	47
4	CuCl	58
5	CuTc	52
6	CuCN	45
7	CuOAc	37
8	$[Cu(MeCN)_4]^+PF_6^-$	20
9	$[Cu(MeCN)_4]^+BF_4^-$	3
10	$(CuOTf)_2 \cdot C_6H_6$	28
11	$Cu(OTf)_2$	30
12	$Cu(OAc)_2$	47
13	$(CuOTf)_2 \cdot C_6H_6$	12
14	$CuSO_4$	41
15	CuF_2	50
16	$CuCl_2$	58
17	$CuBr_2$	17
18	$Cu(acac)_2$	3
19	$Fe(OTf)_2$	3
20	$FeCl_2$	3
21	$CoCl_2$	4
22	$NiBr_2 \cdot$diglyme	0

[a] NMR yield with CH_2Br_2 as an internal standard.

TC = thiophene-2-carboxylate; dtbpy = 4,4'-di-tert-butyl-2,2'-bipyridine.

Table S3. Screening of ligands in the silylation of *N*-chlorosulfonamide **1a**.



Entry	Ligand	Yield [%][a]
1	L1	53
2	L2	63
3	L3	60
4	**L4**	**65**
5	L5	49
6	L6	48
7	L7	48
8	L8	55
9	L9	53
10	L10	57
11	L11	43
12	L12	44
13	L13	28
14	L14	51
15	L15	36
16	L16	48
17	L17	50

[a] NMR yield with CH_2Br_2 as an internal standard.

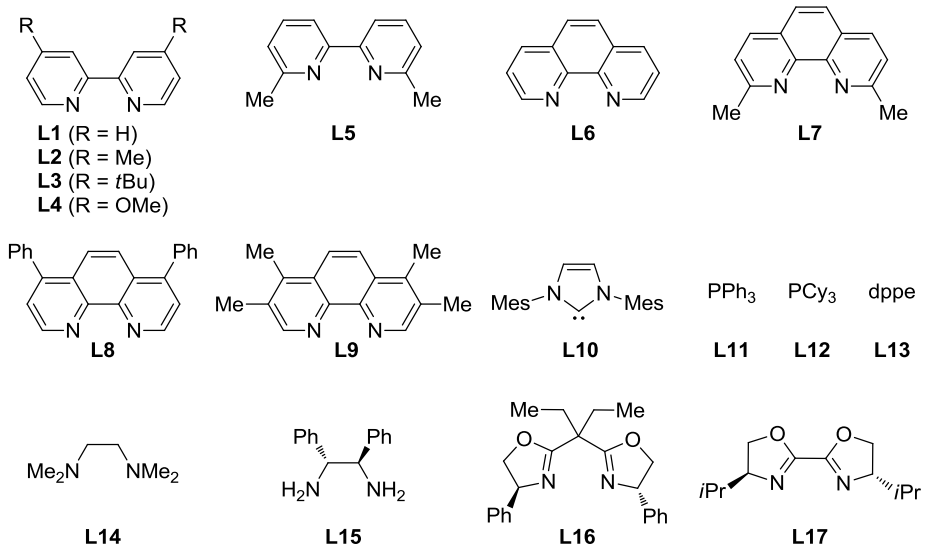
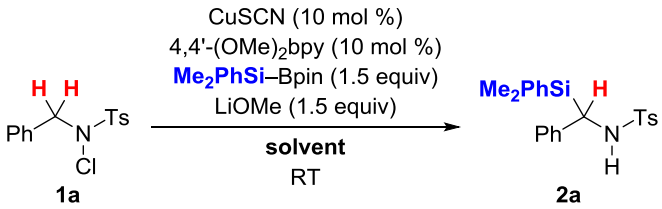


Table S4. Screening of solvents in the silylation of *N*-chlorosulfonamide **1a**.

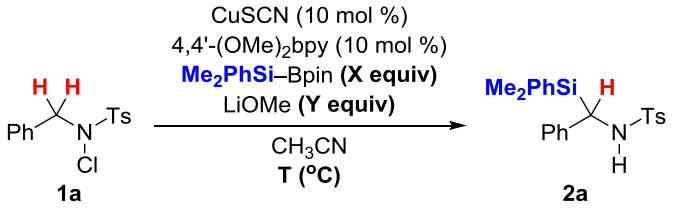


Entry	Solvent	Yield [%][a]
1	THF	37
2	1,4-dioxane	67
3	glyme	63
4	diglyme	69
5	**CH_3CN**	**78**
6	*i*PrCN	64
7	toluene	40
8	DMF	33
9	CH_2Cl_2	31
10	THF/DMF (9/1)	65
11	THF/DMA (9/1)	62
12	THF/NMP (9/1)	61
13	1,4-dioxane/DMF (9/1)	76
14	1,4-dioxane/DMF (8/2)	72
15	Et_2O/DMF (9/1)	62
16	2-MeTHF/DMF (9/1)	50
17	CH_3CN/DMF (9/1)	71
18	CH_3CN/DMF (8/2)	47
19	1,4-dioxane/CH_3CN (9/1)	49
20	1,4-dioxane/CH_3CN (8/2)	55
21	1,4-dioxane/CH_3CN (7/3)	66
22	1,4-dioxane/CH_3CN (6/4)	73

[a] NMR yield with CH_2Br_2 as an internal standard.

4,4'-$(OMe)_2$bpy = 4,4'-dimethoxy-2,2'-bipyridine.

Table S5. Screening of reaction temperature and Si-B reagent/base ratios in the silylation of *N*-chlorosulfonamide **1a**.

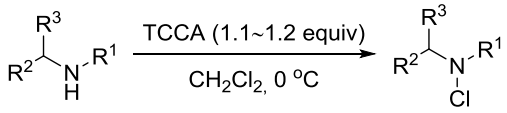


Entry	**X**	**Y**	**T** (°C)	Yield [%][a]
1	1.5	1.5	0 [b]	73
2	**1.5**	**1.5**	**25**	**78**
3	1.5	1.5	40	57
4	2.0	1.5	RT	76
5	2.5	1.5	RT	62
6	1.5	1.0	RT	73
7	1.5	2.5	RT	78
8	1.5	3.0	RT	75

[a] NMR yield with CH_2Br_2 as an internal standard. [b] The reaction mixture was stirred at 0 °C for 4 h, then it was stirred at room temperature overnight. 4,4'-$(OMe)_2$bpy = 4,4'-dimethoxy-2,2'-bipyridine.

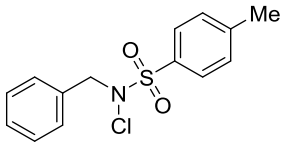
3 Experimental Details for the Preparation of *N*-Chloroamides

3.1 General Procedure for the Preparation of *N*-Chloroamides (GP1) [4]



To an ice-cooled solution of sulfonamide (4.18 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) is added trichloroisocyanuric acid (TCCA, 1.07 g, 4.60 mmol, 1.1 equiv.). Then the white mixture is stirred for about 3 h at 0 °C (as judged by TLC analysis) before quenched by water (50 mL). The organic layer is separated and the aqueous layer is extracted with CH_2Cl_2 (15 mL × 3). The combined organic phase is washed with brine (30 mL), and then dried over $MgSO_4$. After filtration, the solvent is concentrated in *vacuo*. The crude product is purified by flash chromatography on silica gel using cyclohexane/EtOAc as eluent or recrystallization afforded the desired *N*-chloroamides.

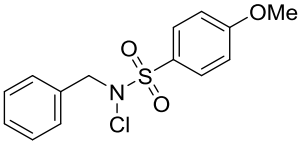
3.2 Characterization Data of the *N*-Chloroamides



1a
$C_{14}H_{14}ClNO_2S$
M = 295.78 g/mol

***N*-Benzyl-*N*-chloro-4-methylbenzenesulfonamide** (**1a**): Prepared from *N*-benzyl-4-methylbenzenesulfonamide (1.0 g, 3.82 mmol, 1.0 equiv) and TCCA (1.1 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (10/1) afforded **1a** as a white solid (1.12 g, 99% yield).

R_f = 0.45 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.51 (s, 3H), 4.36 (s, 2H), 7.32–7.38 (m, 5H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.7, 60.5, 128.56, 128.59, 129.1, 129.6, 129.8, 129.9, 133.7, 145.6 ppm. **HRMS** (EI) for $C_{14}H_{14}ClNO_2S$ $[M]^+$: calculated 295.04283, found 295.04257.

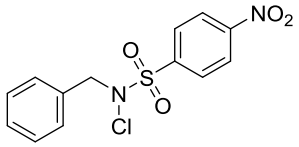


1b
$C_{14}H_{14}ClNO_3S$
M = 311.78 g/mol

***N*-Benzyl-*N*-chloro-4-methoxybenzenesulfonamide** (**1b**): Prepared from *N*-benzyl-4-methoxybenzenesulfonamide (1.16 g, 4.18 mmol, 1.0 equiv) and TCCA (1.1 equiv) according

to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (5/1) afforded **1b** as a white solid (1.24 g, 95% yield).

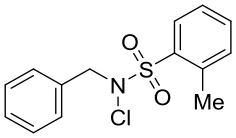
R_f = 0.46 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.93 (s, 3H), 4.36 (s, 2H), 7.09 (d, *J* = 9.0 Hz, 2H), 7.32–7.38 (m, 5H), 7.95 (d, *J* = 9.0 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 55.8, 60.5, 114.4, 124.1, 128.5, 128.6, 129.1, 131.9, 133.7, 164.3 ppm. **HRMS** (EI) for $C_{14}H_{14}ClNO_3S$ $[M]^+$: calculated 311.03774, found 311.03791.



1c
$C_{13}H_{11}ClN_2O_4S$
M = 326.75 g/mol

***N*-Benzyl-*N*-chloro-4-nitrobenzenesulfonamide** (**1c**): Prepared from *N*-benzyl-4-nitrobenzenesulfonamide (1.22 g, 4.18 mmol, 1.0 equiv) and TCCA (1.1 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc/DCM (5/1/2) afforded **1c** as a white solid (1.28 g, 94% yield).

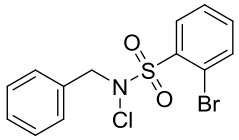
R_f = 0.80 (cyclohexane/EtOAc/DCM = 5/1/2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.43 (s, 2H), 7.32–7.40 (m, 5H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.48 (d, *J* = 8.8 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 60.4, 124.3, 128.8, 129.0, 129.1, 130.8, 132.8, 138.8, 151.1 ppm. **HRMS** (EI) for $C_{13}H_{11}ClN_2O_4S$ $[M]^+$: calculated 326.01226, found 326.01298.



1d
$C_{14}H_{14}ClNO_2S$
M = 295.78 g/mol

***N*-Benzyl-*N*-chloro-2-methylbenzenesulfonamide** (**1d**): Prepared from *N*-benzyl-2-methylbenzenesulfonamide (1.09 g, 4.18 mmol, 1.0 equiv) and TCCA (1.1 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (10/1) afforded **1d** as a white solid (1.00 g, 81% yield).

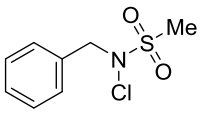
R_f = 0.47 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.77 (s, 3H), 4.61 (s, 2H), 7.35–7.42 (m, 7H), 7.56–7.59 (m, 1H), 8.11 (d, *J* = 7.5 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 20.9, 57.8, 126.3, 128.57, 128.62, 129.3, 132.2, 132.5, 132.9, 133.9, 134.4, 139.8 ppm. **HRMS** (EI) for $C_{14}H_{14}ClNO_2S$ $[M]^+$: calculated 295.04283, found 295.04243.



1e
$C_{13}H_{11}BrClNO_2S$
M = 360.65 g/mol

***N*-Benzyl-2-bromo-*N*-chlorobenzenesulfonamide** (**1e**): Prepared from *N*-benzyl-2-bromobenzenesulfonamide (0.40 g, 1.23 mmol, 1.0 equiv) and TCCA (1.1 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (10/1) afforded **1e** as a white solid (0.39 g, 88% yield).

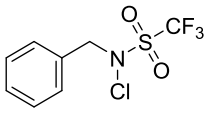
R_f = 0.36 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.75 (s, 2H), 7.35–7.44 (m, 5H), 7.49–7.55 (m, 2H), 7.83–7.85 (m, 1H), 8.24–8.26 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 58.1, 121.6, 127.6, 128.6, 129.2, 133.9, 134.1, 134.3, 135.1, 136.1 ppm. **HRMS** (EI) for $C_{13}H_{11}BrClNO_2S$ $[M]^+$: calculated 358.93769, found 358.93941.



1f
$C_8H_{10}ClNO_2S$
M = 219.68 g/mol

***N*-Benzyl-*N*-chloromethanesulfonamide** (**1f**): Prepared from *N*-benzylmethanesulfonamide (0.77 g, 4.18 mmol, 1.0 equiv) and TCCA (1.1 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (5/1) afforded **1f** as a white solid (0.83 g, 91% yield).

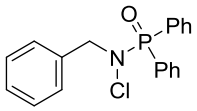
R_f = 0.32 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.10 (s, 3H), 4.58 (s, 2H), 7.36–7.41 (m, 5H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 34.6, 59.4, 128.7, 128.8, 129.3, 133.4 ppm. **HRMS** (EI) for $C_8H_{10}ClNO_2S^{37}$ $[M]^+$: calculated 221.00858, found 221.00772.



1g
$C_8H_7ClF_3NO_2S$
M = 273.65 g/mol

***N*-Benzyl-*N*-chloro-1,1,1-trifluoromethanesulfonamide** (**1g**): Prepared from *N*-benzyl-1,1,1-trifluoromethanesulfonamide (1.0 g, 4.18 mmol, 1.0 equiv) and TCCA (1.1 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (10/1) afforded **1g** as a colorless oil (0.99 g, 87% yield).

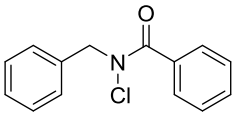
R_f = 0.60 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.77 (s, 2H), 7.38–7.45 (m, 5H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 60.8, 119.9 (q, *J* = 323.8 Hz), 127.9, 129.0, 129.3, 132.5 ppm. **^{19}F NMR** (188 MHz, $CDCl_3$): δ -70.6 ppm. **HRMS** (EI) for $C_8H_7ClF_3NO_2S$ $[M]^+$: calculated 272.98326, found 272.98355.



1h
$C_{19}H_{17}ClNOP$
M = 341.77 g/mol

***N*-Benzyl-*N*-chloro-*P*,*P*-diphenylphosphinic amide** (**1h**): Prepared from *N*-benzyl-*P*,*P*-diphenylphosphinic amide (1.0 g, 3.25 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc/CH_2Cl_2 (6/6/1) afforded **1h** as a colorless oil (1.04 g, 94% yield).

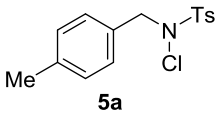
R_f = 0.49 (cyclohexane/EtOAc/CH_2Cl_2 = 6/6/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.38 (d, *J* = 4.4 Hz, 2H), 7.33–7.38 (m, 5H), 7.48–7.59 (m, 6H), 8.00–8.05 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 56.6, 128.0, 128.5, 128.6, 128.7 (d, $J_{C\text{-}P}$ = 12.9 Hz), 129.7 (d, $J_{C\text{-}P}$ = 127.2 Hz), 132.4, 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 135.9 (d, $J_{C\text{-}P}$ = 10.0 Hz) ppm. **HRMS** (ESI) for $C_{19}H_{18}ClNOP$ $[M+H]^+$: calculated 342.08090, found 342.08085.



1i
$C_{14}H_{12}ClNO$
M = 245.71 g/mol

***N*-Benzyl-*N*-chlorobenzamide** (**1i**): Prepared from *N*-benzylbenzamide (1.0 g, 4.73 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (5/1) afforded **1i** as a white solid (0.91 g, 78% yield).

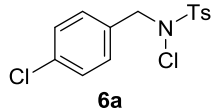
R_f = 0.7 (cyclohexane/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.92 (s, 2H), 7.32-7.50 (s, 8H), 7.58–7.60 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 58.1, 127.80, 127.84, 127.9, 128.2, 128.4, 128.7, 131.0, 133.5, 135.2, 171.3 ppm. **HRMS** (ESI) for $C_{14}H_{13}ClNO$ $[M+H]^+$: calculated 246.06802, found 246.06737.



5a
$C_{15}H_{16}ClNO_2S$
M = 309.81 g/mol

***N*-Chloro-4-methyl-*N*-(4-methylbenzyl)benzenesulfonamide** (**5a**): Prepared from 4-methyl-*N*-(4-methylbenzyl)benzenesulfonamide (1.0 g, 3.63 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Recrystallization from CH_2Cl_2 afforded **5a** as a white solid (0.98 g, 87% yield).

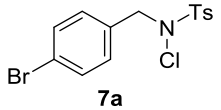
R_f = 0.45 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.50 (s, 3H), 4.31 (s, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.2, 21.7, 60.3, 129.1, 129.3, 129.6, 129.8, 130.6, 138.5, 145.5 ppm. **HRMS** (ESI) for $C_{15}H_{15}ClNO_2S$ $[M-H]^+$: calculated 308.05065, found 308.05057.



6a
$C_{14}H_{13}Cl_2NO_2S$
M = 330.22 g/mol

***N*-Chloro-*N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide** (**6a**): Prepared from *N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide (0.5 g, 1.69 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Recrystallization from cyclohexane/EtOAc afforded **6a** as a white solid (0.49 g, 88% yield).

R_f = 0.48 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 4.26 (s, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.8, 59.8, 128.8, 129.6, 129.9, 130.4, 132.2, 134.5, 145.7 ppm. **HRMS** (ESI) for $C_{14}H_{13}ClNO_2S$ $[M-Cl]^+$: calculated 294.03500, found 294.03497.

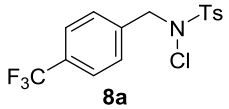


7a
$C_{14}H_{13}BrClNO_2S$
M = 374.68 g/mol

***N*-(4-Bromobenzyl)-*N*-chloro-4-methylbenzenesulfonamide** (**7a**): Prepared from *N*-(4-bromobenzyl)-4-methylbenzenesulfonamide (0.3 g, 0.88 mmol, 1.0 equiv) and TCCA (1.2

equiv) according to the **GP1**. Recrystallization from cyclohexane/EtOAc afforded **7a** as a white solid (0.31 g, 94% yield).

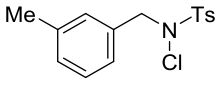
R_f = 0.55 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.50 (s, 3H), 4.30 (s, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.7, 59.8, 122.7, 129.6, 129.9, 130.7, 131.8, 132.7, 145.7 ppm. **HRMS** (ESI) for $C_{14}H_{13}BrNO_2S$ $[M\text{-}Cl]^+$: calculated 337.98449, found 337.98401.



8a
$C_{15}H_{13}ClF_3NO_2S$
M = 363.78 g/mol

***N*-Chloro-4-methyl-*N*-(4-(trifluoromethyl)benzyl)benzenesulfonamide** (**8a**): Prepared from 4-methyl-*N*-(4-(trifluoromethyl)benzyl)benzenesulfonamide (0.6 g, 1.82 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Recrystallization from CH_2Cl_2 afforded **8a** as a white solid (0.65 g, 98% yield).

R_f = 0.33 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 4.42 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.8, 59.9, 123.9 (d, $J_{C\text{-}F}$ = 272.0 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 129.2, 129.60, 129.63, 129.9, 130.8 (d, $J_{C\text{-}F}$ = 32.5 Hz), 137.7, 145.9 ppm. **^{19}F NMR** (188 MHz, $CDCl_3$): δ -62.7 ppm. **HRMS** cannot be detected by EI, ESI and APCI.

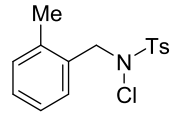


9a
$C_{15}H_{16}ClNO_2S$
M = 309.81 g/mol

***N*-Chloro-4-methyl-*N*-(3-methylbenzyl)benzenesulfonamide** (**9a**): Prepared from 4-methyl-*N*-(3-methylbenzyl)benzenesulfonamide (1.0 g, 3.63 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Recrystallization from cyclohexane/CH_2Cl_2 afforded **9a** as a white solid (1.1 g, 98% yield).

R_f = 0.45 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.51 (s, 3H), 4.32 (s, 2H), 7.11–7.16 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.3, 21.7, 60.5, 126.1, 128.4, 129.3,

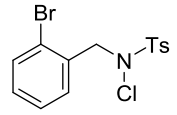
129.6, 129.7, 129.8, 133.5, 138.4, 145.5 ppm. **HRMS** (ESI) for $C_{15}H_{18}NO_2S$ $[M+2H-Cl]^+$: calculated 276.10528, found 276.10471.



10a
$C_{15}H_{16}ClNO_2S$
M = 309.81 g/mol

***N*-Chloro-4-methyl-*N*-(2-methylbenzyl)benzenesulfonamide** (**10a**): Prepared from 4-methyl-*N*-(2-methylbenzyl)benzenesulfonamide (1.0 g, 3.63 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Recrystallization from CH_2Cl_2 afforded **10a** as a white solid (1.05 g, 93% yield).

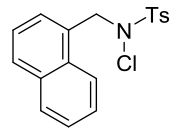
R_f = 0.46 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 2.51 (s, 3H), 4.37 (s, 2H), 7.14–7.21 (m, 3H), 7.25–7.29 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.0, 21.8, 58.7, 125.8, 128.9, 129.66, 129.70, 129.8, 130.7, 131.0, 131.3, 138.1, 145.6 ppm. **HRMS** (ESI) for $C_{15}H_{18}NO_2S$ $[M+2H-Cl]^+$: calculated 276.10528, found 276.10462.



11a
$C_{14}H_{13}BrClNO_2S$
M = 374.68 g/mol

***N*-(2-Bromobenzyl)-*N*-chloro-4-methylbenzenesulfonamide** (**11a**): Prepared from *N*-(2-bromobenzyl)-4-methylbenzenesulfonamide (1.23 g, 3.63 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using cyclohexane/EtOAc (10/1) afforded **11a** as a white solid (1.26 g, 93% yield).

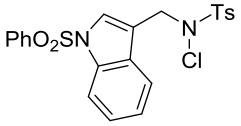
R_f = 0.50 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.50 (s, 3H), 4.55 (s, 2H), 7.18–7.22 (m, 1H), 7.32–7.36 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.50 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.56 (dd, *J* = 8.0 and 1.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.8, 59.8, 124.1, 127.6, 129.6, 129.88, 129.94, 130.9, 132.97, 133.03, 145.7 ppm. **HRMS** (ESI) for $C_{14}H_{13}BrNO_2S$ $[M-Cl]^+$: calculated 337.98449, found 337.98457.



12a
$C_{18}H_{16}ClNO_2S$
M = 345.84 g/mol

***N*-Chloro-4-methyl-*N*-(naphthalen-1-ylmethyl)benzenesulfonamide**(**12a**): Prepared from 4-methyl-N-(naphthalen-1-ylmethyl)benzenesulfonamide (0.6 g, 1.93 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Recrystallization from CH_2Cl_2 afforded **12a** as a white solid (0.62 g, 90% yield).

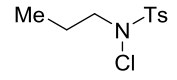
R_f = 0.34 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 4.80 (s, 2H), 7.34–7.42 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.52–7.56 (m, 1H), 7.59–7.64 (m, 1H), 7.87–7.90 (m, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.8, 58.8, 123.8, 124.8, 126.1, 126.9, 128.6, 128.7, 129.3, 129.6, 129.7, 129.87, 129.91, 131.9, 133.8, 145.7 ppm. **HRMS** (ESI) for $C_{18}H_{16}NO_2S$ $[M\text{-}Cl]^+$: calculated 310.08963, found 310.08923.



13a
$C_{22}H_{19}ClN_2O_4S_2$
M =474.97 g/mol

***N*-Chloro-4-methyl-*N*-((1-(phenylsulfonyl)-1*H*-indol-3-yl)methyl)benzenesulfonamide** (**13a**): Prepared from 4-methyl-*N*-((1-(phenylsulfonyl)-1*H*-indol-3-yl)methyl)-benzenesulfonamide (0.13 g, 0.3 mmol, 1.0 equiv) and *t*BuOCl (80 µL, 0.72 mmol, 2.4 equiv) in CH_3CN at room temperature in dark for 24 h.[5] Recrystallization from cyclohexane/EtOAc afforded **13a** as a yellow solid (0.12 g, 83% yield).

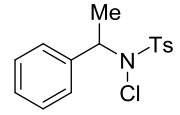
R_f = 0.7 (cyclohexane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.50 (s, 3H), 4.49 (s, 2H), 7.28–7.44 (m, 6H), 7.51–7.54 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.82–7.85 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.7, 52.1, 113.6, 115.3, 120.1, 123.7, 125.3, 126.5, 126.7, 129.3, 129.4, 129.5, 129.6, 129.9, 134.0, 135.2, 137.9, 145.8 ppm. **HRMS** (ESI) for $C_{22}H_{19}ClN_2O_4S_2Na$ $[M+Na]^+$: calculated 497.03670, found 497.03570.



14a
$C_{10}H_{14}ClNO_2S$
M = 247.74 g/mol

***N*-Chloro-4-methyl-*N*-propylbenzenesulfonamide** (**14a**): Prepared from 4-methyl-*N*-propylbenzenesulfonamide (1.0 g, 4.69 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (10/1) afforded **14a** as a white solid (1.10 g, 95% yield).

R_f = 0.45 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.65–1.74 (m, 2H), 2.47 (s, 3H), 3.18 (t, *J* = 6.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 10.6, 20.5, 21.7, 58.2, 129.5, 129.6, 129.8, 145.3 ppm. **HRMS** (EI) for $C_{10}H_{14}ClNO_2S$ $[M]^+$: calculated 247.04283, found 247.04211.



15a
$C_{15}H_{16}ClNO_2S$
M = 309.81 g/mol

***N*-Chloro-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide** (**15a**): Prepared from 4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (1.3 g, 4.69 mmol, 1.0 equiv) and TCCA (1.2 equiv) according to the **GP1**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (10/1) afforded **15a** as a white solid (1.16 g, 80% yield).

R_f = 0.48 (cyclohexane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.52 (d, *J* = 6.8 Hz, 3H), 2.45 (s, 3H), 5.55 (q, *J* = 6.4 Hz, 1H), 7.31–7.36 (m, 5H), 7.39–7.42 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.3, 21.7, 60.6, 127.7, 128.2, 128.3, 129.0, 129.6, 133.3, 138.6, 145.0 ppm. **HRMS** (EI) for $C_{15}H_{16}ClNO_2S$ $[M]^+$: calculated 309.05848, found 309.05857.

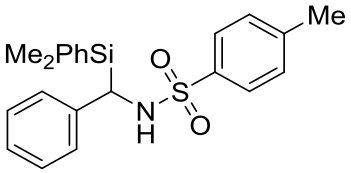
4 Experimental Details for the Silylation of *N*-Adjacent C(sp^3)–H Bonds

4.1 General Procedure for the Silylation of *N*-Adjacent C(sp^3)–H Bonds (GP2)

A flame-dried Schlenk tube equipped with a stir bar is charged with the CuSCN (2.4 mg, 20 µmol, 10 mol%), 4,4'-dimethoxy-2,2'-bipyridine (4.4 mg, 20 µmol, 10 mol%) and MeOLi (12 mg, 0.3 mmol, 1.5 equiv). The tube is evacuated and backfilled with N_2 (3 times) followed by the addition of the CH_3CN (0.7 mL). After stirring for 15 min, $Me_2PhSiBpin$ (88 µL, 0.3 mmol, 1.5 equiv) is added. Then, the reaction mixture is stirred for 5 min, a solution of the corresponding *N*-chlorosulfonamide (0.2 mmol, 1.0 equiv) in CH_3CN (1.8 mL) is added dropwise by a springe. The green mixture is stirred at room temperature for 18 h. Filtration through a small pad of silica gel using EtOAc (10 mL) and evaporation of the solvents under reduced pressure afforded the crude title compound. Purification by flash column chromatography using the indicated mixtures of solvents as eluent yields the analytical pure *α*-silylated amines.

Characterization Data of the *α*-Silylated Amines:

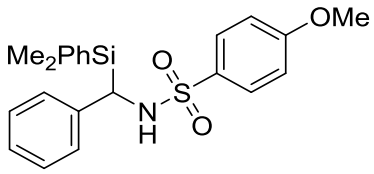
4.2 C-Si Bond Formation between *N*-Chloroamides and Me_2PhSi–Bpin



2a
$C_{22}H_{25}NO_2SSi$
M = 395.59 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-4-methylbenzenesulfonamide** (**2a**): Prepared from *N*-benzyl-*N*-chloro-4-methylbenzenesulfonamide (**1a**, 59.2 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **2a** as a white solid (61.0 mg, 77% yield).

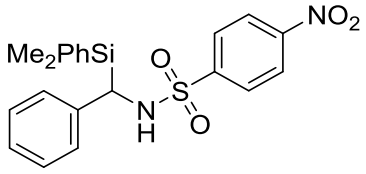
R_f = 0.50 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.21 (s, 3H), 0.28 (s, 3H), 2.29 (s, 3H), 4.12 (d, *J* = 8.0 Hz, 1H), 4.90 (d, *J* = 7.5 Hz, 1H), 6.70–6.71 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.00–7.03 (m, 3H), 7.28–7.33 (m, 4H), 7.37–7.42 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.7, –4.9, 21.3, 49.7, 125.5, 126.3, 127.2, 127.8, 128.0, 129.0, 130.0, 133.8, 134.3, 137.2, 138.8, 142.7 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.4 ppm. **HRMS** (ESI) for $C_{22}H_{26}NO_2SSi$ $[M+H]^+$: calculated 396.14480, found 396.14447.



2b
$C_{22}H_{25}NO_3SSi$
M = 411.59 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-4-methoxybenzenesulfonamide** (**2b**): Prepared from *N*-benzyl-*N*-chloro-4-methoxybenzenesulfonamide (**1b**, 63.0 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **2b** as a white solid (65.8 mg, 80% yield).

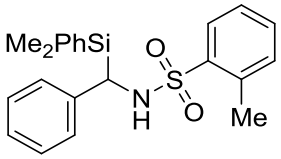
R_f = 0.42 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.21 (s, 3H), 0.29 (s, 3H), 3.76 (s, 3H), 4.12 (d, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.70–6.71 (m, 2H), 6.98–7.04 (m, 3H), 7.29–7.34 (m, 4H), 7.39–7.43 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.7, –4.9, 49.7, 55.4, 113.6, 125.6, 126.3, 127.8, 128.1, 129.3, 130.0, 131.9, 133.8, 134.3, 138.8, 162.4 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.4 ppm. **HRMS** (ESI) for $C_{22}H_{26}NO_3SSi$ $[M+H]^+$: calculated 412.13972, found 412.13921.



2c
$C_{21}H_{22}N_2O_4SSi$
M = 426.56 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-4-nitrobenzenesulfonamide** (**2c**): Pre- pared from *N*-benzyl-*N*-chloro-4-nitrobenzenesulfonamide (**1c**, 66.0 mg, 0.20 mmol) according to the **GP2** (Note: The reaction was performed in 1,4-dioxane/DMF (9:1) instead of CH_3CN for better solubility). Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **2c** as a white solid (42.1 mg, 50% yield).

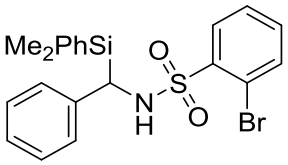
R_f = 0.45 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.23 (s, 3H), 0.34 (s, 3H), 4.26 (d, *J* = 8.5 Hz, 1H), 5.14 (d, *J* = 8.5 Hz, 1H), 6.62–6.64 (m, 2H), 6.94–7.00 (m, 3H), 7.32–7.36 (m, 4H), 7.41–7.45 (m, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.8, –4.9, 50.0, 123.5, 126.1, 126.4, 128.0, 128.2, 128.3, 130.2, 133.3, 134.3, 137.9, 146.4, 149.4 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.2 ppm. **HRMS** cannot be detected by EI, ESI and APCI.



2d
$C_{22}H_{25}NO_2SSi$
M = 395.59 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-2-methylbenzenesulfonamide** (**2d**): Prepared from *N*-benzyl-*N*-chloro-2-methylbenzenesulfonamide (**1d**, 59.2 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **2d** as a colorless oil (63.3mg, 80% yield).

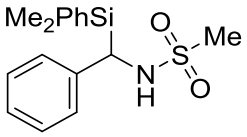
R_f = 0.50 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.21 (s, 3H), 0.28 (s, 3H), 2.33 (s, 3H), 4.04 (d, *J* = 7.5 Hz, 1H), 4.76 (broad s, 1H), 6.71–6.73 (m, 2H), 6.97–7.06 (m, 5H), 7.22–7.26 (m, 1H), 7.33–7.37 (m, 4H), 7.41–7.45 (m, 1H), 7.64 (dd, *J* = 7.5 and 1.0 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.8, –4.8, 20.2, 49.8, 125.7, 125.8, 126.2, 127.8, 128.2, 129.7, 130.1, 132.0, 132.3, 133.8, 134.3, 136.7, 138.0, 138.8 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.3 ppm. **HRMS** (ESI) for $C_{22}H_{26}NO_2SSi$ $[M+H]^+$: calculated 396.14480, found 396.14519.



2e
$C_{21}H_{22}BrNO_2SSi$
M = 460.46 g/mol

2-Bromo-*N*-((dimethyl(phenyl)silyl)(phenyl)methyl)benzenesulfonamide (**2e**): Prepared from *N*-benzyl-2-bromo-*N*-chlorobenzenesulfonamide (**1e**, 73.0 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (10/1) afforded **2e** as a colorless oil (66.4 mg, 72% yield).

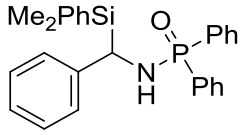
R_f = 0.35 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.21 (s, 3H), 0.38 (s, 3H), 4.18 (d, *J* = 9.0 Hz, 1H), 5.42 (d, *J* = 9.0 Hz, 1H), 6.66–6.68 (m, 2H), 6.88–6.90 (m, 3H), 7.06–7.13 (m, 2H), 7.35–7.46 (m, 6H), 7.66 (dd, *J* = 7.5 and 2.0 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.5, –4.7, 50.3, 119.7, 125.9, 126.5, 127.2, 127.7, 128.1, 130.1, 130.9, 132.8, 133.6, 134.3, 134.4, 137.8, 140.1 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.7 ppm. **HRMS** (APCI) for $C_{21}H_{23}BrNO_2SSi$ $[M+H]^+$: calculated 460.03967, found 460.03952.



2f
$C_{16}H_{21}NO_2SSi$
M = 319.49 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)methanesulfonamide** (**2f**): Prepared from *N*-benzyl-*N*-chloromethanesulfonamide (**1f**, 43.9 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **2f** as a colorless oil (42.2 mg, 66% yield).

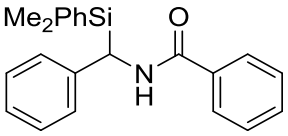
R_f = 0.22 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.26 (s, 3H), 0.41 (s, 3H), 2.44 (s, 3H), 4.29 (d, *J* = 8.5 Hz, 1H), 4.74 (broad s, 1H), 6.96–6.97 (m, 2H), 7.17–7.21 (m, 1H), 7.25–7.28 (m, 2H), 7.35–7.45 (m, 5H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.4, –4.9, 41.8, 49.4, 126.4, 126.5, 128.1, 128.5, 130.2, 133.6, 134.4, 139.6 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.2 ppm. **HRMS** (ESI) for $C_{16}H_{22}NO_2SSi$ $[M+H]^+$: calculated 320.11350, found 320.11311.



2h
$C_{27}H_{28}NOPSi$
M = 441.59 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-*P*,*P*-diphenylphosphinic amide** (**2h**): Prepared from *N*-benzyl-*N*-chloro-*P*,*P*-diphenylphosphinic amide (**1h**, 68.4 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (1/1) afforded **2h** as a white solid (68.9 mg, 78% yield).

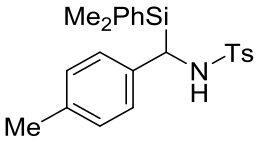
R_f = 0.25 (*n*-pentane/EtOAc = 1/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.22 (s, 3H), 0.44 (s, 3H), 3.22 (dd, *J* = 9.5 Hz, $J_{H,P}$ = 9.5 Hz, 1H), 3.94 (dd, *J* = 11.0 Hz, $J_{H,P}$ = 11.0 Hz, 1H), 6.79–6.81 (m, 2H), 7.07–7.10 (m, 1H), 7.12–7.16 (m, 2H), 7.19–7.23 (m, 2H), 7.32–7.46 (m, 9H), 7.58–7.66 (m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.3, –4.8, 46.9 (d, $J_{C,P}$ = 4.4 Hz), 125.4, 126.2, 127.8, 127.9, 128.0 (d, $J_{C,P}$ = 13.0 Hz), 128.3 (d, $J_{C,P}$ = 13.0 Hz), 129.8, 131.5 (d, $J_{C,P}$ = 2.3 Hz), 131.6 (d, $J_{C,P}$ = 2.3 Hz), 131.7 (d, $J_{C,P}$ = 9.4 Hz), 131.8 (d, $J_{C,P}$ = 99 Hz), 132.5 (d, $J_{C,P}$ = 9.5 Hz), 132.7 (d, $J_{C,P}$ = 126 Hz), 134.6, 134.7, 142.4 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.0 (d, $J_{Si,P}$ = 10 Hz) ppm. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 24.5 ppm. **HRMS** (ESI) for $C_{27}H_{29}NOPSi$ $[M+H]^+$: calculated 442.17505, found 442.17577.



2i
$C_{22}H_{23}NOSi$
M = 345.52 g/mol

***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)benzamide** (**2i**): Prepared from *N*-benzyl-*N*-chlorobenzamide (**1i**, 49.1 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (1/10) afforded **2i** as a white solid (41.7 mg, 60% yield).

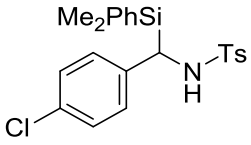
R_f = 0.33 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.30 (s, 3H), 0.44 (s, 3H), 5.04 (d, *J* = 8.8 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 6.98-7.00 (m, 2H), 7.13–7.17 (m, 1H), 7.22–7.26 (m, 2H), 7.38–7.50 (m, 8H), 7.61–7.64 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ –4.8, –4.5, 45.9, 125.8, 126.0, 126.7, 128.1, 128.2, 128.5, 129.9, 131.3, 134.3, 134.76, 134.77, 140.9, 167.0 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.5 ppm. **HRMS** (ESI) for $C_{22}H_{23}NOSiNa$ $[M+Na]^+$: calculated 368.14411, found 368.14367.



16a
$C_{23}H_{27}NO_2SSi$
M = 409.62 g/mol

***N*-((Dimethyl(phenyl)silyl)(*p*-tolyl)methyl)-4-methylbenzenesulfonamide** (**16a**): Prepared from *N*-chloro-4-methyl-*N*-(4-methylbenzyl)benzenesulfonamide (**5a**, 62.0 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **16a** as a white solid (62.6 mg, 76% yield).

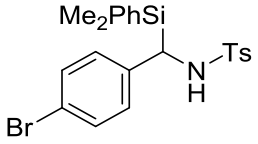
R_f = 0.48 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.20 (s, 3H), 0.27 (s, 3H), 2.23 (s, 3H), 2.31 (s, 3H), 4.05 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.30–7.34 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.39–7.43 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.7, –4.8, 20.9, 21.3, 49.4, 126.3, 127.2, 128.0, 128.5, 128.9, 129.9, 134.0, 134.3, 135.1, 135.7, 137.3, 142.6 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.7 ppm. **HRMS** (ESI) for $C_{23}H_{28}NO_2SSi$ $[M+H]^+$: calculated 410.16045, found 410.15999.



17a
$C_{22}H_{24}ClNO_2SSi$
M = 430.03 g/mol

***N*-((4-Chlorophenyl)(dimethyl(phenyl)silyl)methyl)-4-methylbenzenesulfonamide** (**17a**): Prepared from *N*-chloro-*N*-(4-chlorobenzyl)-4-methylbenzenesulfonamidefon amide (**6a**, 66.1 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **17a** as a white solid (61.0 mg, 71% yield).

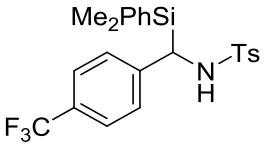
R_f = 0.48 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.22 (s, 3H), 0.28 (s, 3H), 2.34 (s, 3H), 4.08 (d, *J* = 7.5 Hz, 1H), 4.86 (broad s, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.27–7.34 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.40–7.44 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.8, –5.1, 21.4, 49.2, 127.2, 127.6, 127.9, 128.2, 129.1, 130.2, 131.3, 133.3, 134.3, 137.1, 137.5, 143.1 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.2 ppm. **HRMS** (ESI) for $C_{22}H_{25}ClNO_2SSi$ $[M+H]^+$: calculated 430.10583, found 430.10505.



18a
$C_{22}H_{24}BrNO_2SSi$
M = 474.49 g/mol

***N*-((4-Bromophenyl)(dimethyl(phenyl)silyl)methyl)-4-methylbenzenesulfonamide** (**18a**): Prepared from *N*-(4-bromobenzyl)-*N*-chloro-4-methylbenzenesulfonamide (**7a**, 74.9 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **18a** as a white solid (48.1 mg, 51% yield).

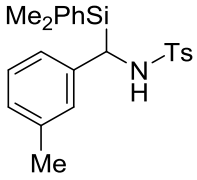
R_f = 0.28 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.21 (s, 3H), 0.28 (s, 3H), 2.34 (s, 3H), 4.06 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.27–7.33 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.40–7.43 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.8, –5.1, 21.4, 49.3, 119.3, 127.2, 128.0, 128.2, 129.1, 130.2, 130.8, 133.3, 134.3, 137.1, 138.0, 143.2 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.3 ppm. **HRMS** (ESI) for $C_{22}H_{25}BrNO_2SSi$ $[M+H]^+$: calculated 474.05532, found 474.05515.



19a
$C_{23}H_{24}F_3NO_2SSi$
M = 463.59 g/mol

***N*-((Dimethyl(phenyl)silyl)(4-(trifluoromethyl)phenyl)methyl)-4-methylbenzenesulfonamide** (**19a**): Prepared from *N*-chloro-4-methyl-*N*-(4-(trifluoromethyl)benzyl)-benzenesulfonamide (**8a**, 72.8 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **19a** as a white solid (51.9 mg, 56% yield).

R_f = 0.34 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.23 (s, 3H), 0.31 (s, 3H), 2.28 (s, 3H), 4.19 (d, *J* = 7.5 Hz, 1H), 5.01 (d, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.27–7.36 (m, 6H), 7.41–7.44 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.8, –5.1, 21.2, 49.7, 124.1 (d, $J_{C\text{-}F}$ = 270.0 Hz), 124.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.5, 127.2, 127.7 (d, $J_{C\text{-}F}$ = 32.1 Hz), 128.2, 129.1, 130.3, 133.0, 134.2, 137.0, 143.2 (d, $J_{C\text{-}F}$ = 6.4 Hz) ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –0.8 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): δ –62.4 ppm. **HRMS** (ESI) for $C_{23}H_{25}F_3NO_2SSi$ $[M+H]^+$: calculated 464.13219, found 464.13259.

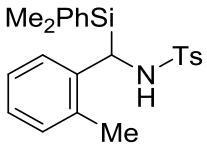


20a
$C_{23}H_{27}NO_2SSi$
M = 409.62 g/mol

***N*-((Dimethyl(phenyl)silyl)(m-tolyl)methyl)-4-methylbenzenesulfonamide** (**20a**): Prepared from *N*-chloro-4-methyl-*N*-(3-methylbenzyl)benzenesulfonamide (**9a**, 62.0 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **20a** as a white solid (56.2 mg, 69% yield).

R_f = 0.30 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.20 (s, 3H), 0.29 (s, 3H), 2.08 (s, 3H), 2.29 (s, 3H), 4.10 (d, *J* = 8.5 Hz, 1H), 4.79 (broad s, 1H), 6.37 (s, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.91 (dd, *J* = 7.5 and 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.29–7.34 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.39–7.42 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.7, –4.9, 21.1, 21.3, 49.6, 123.6, 126.3, 127.1, 127.2, 127.7, 128.0, 128.9,

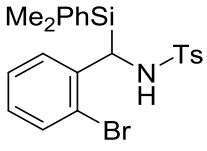
129.9, 133.9, 134.4, 137.1, 137.4, 138.5, 142.6 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.6 ppm. **HRMS** (ESI) for $C_{23}H_{28}NO_2SSi$ $[M+H]^+$: calculated 410.16045, found 410.16101.



21a
$C_{23}H_{27}NO_2SSi$
M = 409.62 g/mol

***N*-((Dimethyl(phenyl)silyl)(*o*-tolyl)methyl)-4-methylbenzenesulfonamide** (**21a**): Prepared from *N*-chloro-4-methyl-*N*-(2-methylbenzyl)benzenesulfonamide (**10a**, 62.0 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **21a** as a white solid (51.3 mg, 63% yield).

R_f = 0.48 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.26 (s, 3H), 0.30 (s, 3H), 2.01 (s, 3H), 2.25 (s, 3H), 4.42 (d, *J* = 9.0 Hz, 1H), 4.95 (d, *J* = 9.0 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.78–6.81 (m, 1H), 6.84–6.89 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.29–7.32 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.38–7.42 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.7, –4.8, 19.7, 21.3, 44.8, 125.4, 125.6, 126.3, 127.0, 128.0, 128.9, 129.87, 129.93, 134.0, 134.1, 134.4, 137.2, 137.3, 142.6 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.6 ppm. **HRMS** (ESI) for $C_{23}H_{28}NO_2SSi$ $[M+H]^+$: calculated 410.16045, found 410.16066.

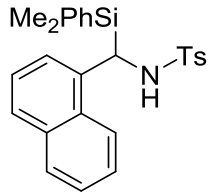


22a
$C_{22}H_{24}BrNO_2SSi$
M = 474.49 g/mol

***N*-((2-Bromophenyl)(dimethyl(phenyl)silyl)methyl)-4-methylbenzenesulfonamide** (**22a**): Prepared from *N*-(2-bromobenzyl)-*N*-chloro-4-methylbenzenesulfonamide (**11a**, 74.9 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **22a** as a white solid (57.1 mg, 60% yield).

R_f = 0.26 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.23 (s, 3H), 0.32 (s, 3H), 2.29 (s, 3H), 4.71 (d, *J* = 8.0 Hz, 1H), 4.86 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.86–6.89 (m, 1H), 6.95–6.97 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.31–7.35 (m, 5H), 7.40–7.43 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –6.0, –4.5, 21.4, 47.5,

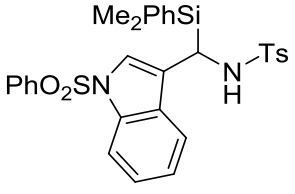
122.5, 126.9, 127.0, 127.3, 127.9, 128.1, 129.1, 130.1, 132.4, 133.5, 134.4, 136.4, 139.1, 142.9 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –0.04 ppm. **HRMS** (ESI) for $C_{22}H_{25}BrNO_2SSi$ $[M+H]^+$: calculated 474.05532, found 474.05537.



23a
$C_{26}H_{27}NO_2SSi$
M = 445.65 g/mol

***N*-((Dimethyl(phenyl)silyl)(naphthalen-1-yl)methyl)-4-methylbenzenesulfonamide** (**23a**): Prepared from *N*-chloro-4-methyl-*N*-(naphthalen-1-ylmethyl)benzene- sulfonamide (**12a**, 71.0 mg, 0.20 mmol) according to the **GP2** (Note: The reaction was performed in 1,4-dioxane/DMF (9:1) instead of CH_3CN for better solubility). Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **23a** as a white solid (61.5 mg, 69% yield).

R_f = 0.28 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.12 (s, 3H), 0.33 (s, 3H), 2.12 (s, 3H), 5.02 (d, *J* = 9.0 Hz, 1H), 5.07 (broad s, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.70 (broad s, 1H), 7.06 (dd, *J* = 7.5 and 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.30–7.43 (m, 7H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.82 (broad s, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.4, –4.4, 21.1, 43.8, 122.8, 123.7, 124.8, 125.3, 125.5, 126.0, 127.0, 128.1, 128.5, 128.6, 130.0, 130.6, 133.4, 133.9, 134.5, 135.4, 136.8, 142.4 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –0.8 ppm. **HRMS** (ESI) for $C_{26}H_{28}NO_2SSi$ $[M+H]^+$: calculated 446.16054, found 446.16077.

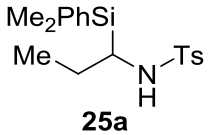


24a
$C_{30}H_{30}N_2O_4S_2Si$
M = 574.79 g/mol

***N*-((Dimethyl(phenyl)silyl)(1-(phenylsulfonyl)-1*H*-indol-3-yl)methyl)-4-methylbenzene-sulfonamide** (**24a**): Prepared from *N*-chloro-4-methyl-*N*-((1-(phenylsulfonyl)-1*H*- indol-3-yl)methyl)benzenesulfonamide (**13a**, 95.0 mg, 0.20 mmol) according to the **GP2**. Purification

by flash chromatography on silica gel using *n*-pentane/EtOAc (3/1) afforded **24a** as a white solid (57.1 mg, 50% yield).

R_f = 0.30 (*n*-pentane/EtOAc = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.18 (s, 3H), 0.31 (s, 3H), 2.16 (s, 3H), 4.32 (d, *J* = 8.0 Hz, 1H), 4.80 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 6.97–7.02 (m, 2H), 7.17–7.29 (m, 7H), 7.38–7.47 (m, 3H), 7.53–7.58 (m, 1H), 7.78–7.81 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ –5.5, –4.7, 21.2, 41.3, 113.2, 120.0, 121.1, 122.5, 122.8, 124.4, 126.7, 127.0, 128.1, 128.7, 129.2, 129.3, 130.2, 133.6, 133.8, 134.2, 134.6, 136.4, 138.2, 143.0 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.4 ppm. **HRMS** (ESI) for $C_{30}H_{30}N_2O_4S_2SiNa$ $[M+Na]^+$: calculated 597.13085, found 597.12973.



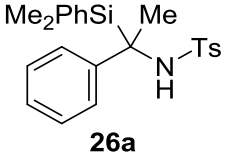
25a

$C_{18}H_{25}NO_2SSi$

M = 347.55 g/mol

***N*-(1-(Dimethyl(phenyl)silyl)propyl)-4-methylbenzenesulfonamide** (**25a**): Prepared from *N*-chloro-4-methyl-*N*-propylbenzenesulfonamide (**14a**, 49.6 mg, 0.20 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **25a** as a white solid (20.5 mg, 29% yield).

R_f = 0.45 (*n*-pentane/EtOAc = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.24 (s, 3H), 0.29 (s, 3H), 0.69 (t, *J* = 7.5 Hz, 3H), 1.28–1.37 (m, 1H), 1.52–1.61 (m, 1H), 2.41 (s, 3H), 2.91–2.95 (m, 1H), 4.08 (d, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.31–7.35 (m, 2H), 7.37–7.42 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –4.8, –4.4, 11.5, 21.5, 24.8, 45.4, 127.0, 128.1, 129.5, 129.6, 134.0, 135.5, 138.4, 142.9 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –1.8 ppm. **HRMS** (ESI) for $C_{18}H_{26}NO_2SSi$ $[M+H]^+$: calculated 348.14480, found 348.14457.



26a

$C_{23}H_{27}NO_2SSi$

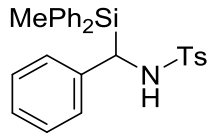
M = 409.62 g/mol

***N*-(1-(Dimethyl(phenyl)silyl)-1-phenylethyl)-4-methylbenzenesulfonamide** (**26a**): Prepared from *N*-chloro-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (**15a**, 62.0 mg, 0.20

mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (5/1) afforded **26a** as a white solid (28.4 mg, 35% yield).

R_f = 0.25 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.16 (s, 3H), 0.29 (s, 3H), 1.70 (s, 3H), 2.34 (s, 3H), 4.95 (s, 1H), 6.92–6.94 (m, 2H), 7.05–7.13 (m, 5H), 7.24–7.26 (m, 2H), 7.32–7.35 (m, 2H), 7.42–7.45 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –6.2, –6.1, 20.4, 21.4, 52.5, 125.4, 125.9, 126.8, 127.5, 128.0, 129.1, 130.1, 133.4, 134.8, 140.4, 142.5, 143.1 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ 3.1 ppm. **HRMS** (ESI) for $C_{23}H_{28}NO_2SSi$ $[M+H]^+$: calculated 410.16045, found 410.16008.

4.3 C-Si Bond Formation between *N*-Chloroamide 1a and $MePh_2Si$–Bpin

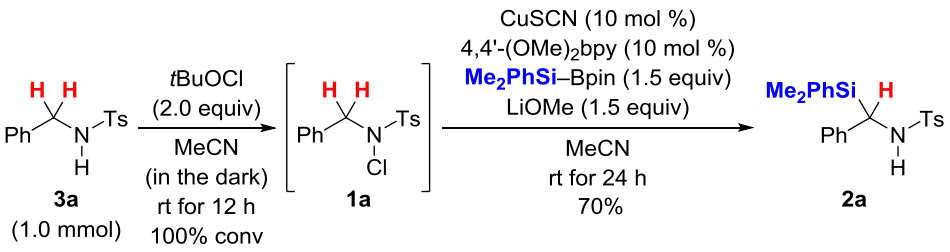


$C_{27}H_{27}NO_2SSi$
M = 457.66 g/mol

4-Methyl-*N*-((methyldiphenylsilyl)(phenyl)methyl)benzenesulfonamide: Prepared from *N*-benzyl-*N*-chloro-4-methylbenzenesulfonamide (**1a**, 59.2 mg, 0.20 mmol) and $MePh_2SiBpin$ (97.32 mg, 0.30 mmol) according to the **GP2**. Purification by flash chromatography on silica gel using *n*-pentane/EtOAc (10/1) afforded as a white solid (64.0 mg, 70% yield).

R_f = 0.25 (*n*-pentane/EtOAc = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.40 (s, 3H), 2.29 (s, 3H), 4.58 (d, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 6.64–6.66 (m, 2H), 6.94–7.00 (m, 5H), 7.30–7.46 (m, 12H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ –5.9, 21.3, 48.3, 125.7, 126.8, 127.3, 127.7, 128.0, 128.2, 129.0, 130.0, 130.3, 131.9, 132.8, 135.0, 135.4, 137.3, 138.3, 142.8 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ –8.2 ppm. **HRMS** (ESI) for $C_{27}H_{28}NO_2SSi$ $[M+H]^+$: calculated 458.16045, found 458.16093.

4.4 Procedure for the Oxidative Coupling of Sulfonamide with Si–B Reagent



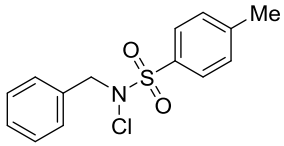
A flame-dried Schlenk tube equipped with a stir bar is charged with *N*-benzyl-4-methylbenzenesulfonamide **3a** (247 mg, 1.0 mmol, 1.0 equiv) and CH_3CN (6 mL). Then *t*BuOCl (0.2 mL, 2.0 mmol, 2.0 equiv) is added dropwise by a springe. The mixture is allowed to stir in the dark at room temperature for 12 h under a nitrogen atmosphere. After the

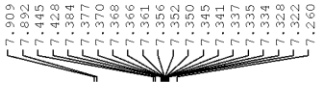
reaction is complete (as judged by TLC analysis), the solvent is removed under reduced pressure to afford the crude *N*-chlorosulfonamide **1a**.

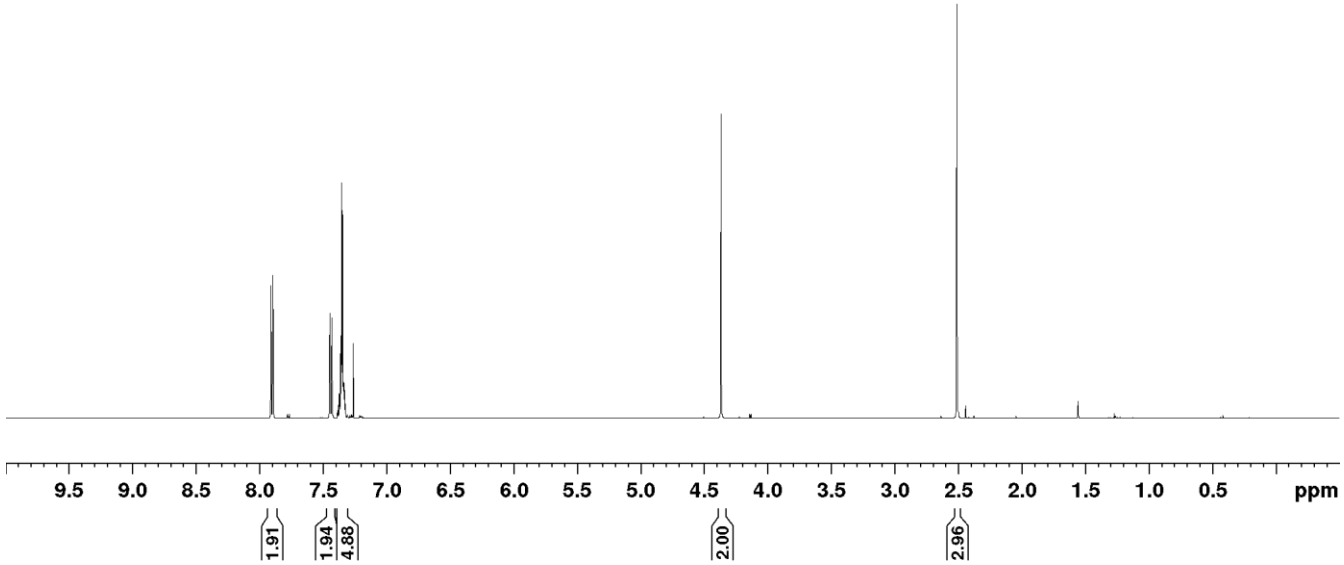
Another flame-dried Schlenk tube equipped with a stir bar is charged with the CuSCN (13 mg, 0.1 mmol, 10 mol%), 4,4'-dimethoxy-2,2'-bipyridine (22 mg, 0.1 mmol, 10 mol%) and MeOLi (57 mg, 1.5 mmol, 1.5 equiv). The tube is evacuated and backfilled with N_2 (3 times) followed by the addition of the CH_3CN (5 mL). After stirring for 15 min, $Me_2PhSiBpin$ (393 mg, 1.5 mmol, 1.5 equiv) is added. Then, the reaction mixture is stirred for 5 min, a solution of the crude *N*-chlorosulfonamide **1a** in CH_3CN (10 mL) is added dropwise by a springe. The reaction mixture is stirred at room temperature for 24 h. Filtration through a small pad of silica gel using EtOAc (10 mL) and evaporation of the solvents under reduced pressure afforded the crude title compound. Purification by flash column chromatography using *n*-pentane/EtOAc (10/1) afford **2a** as a white solid (275 mg, 70% yield).

5 NMR Spectra

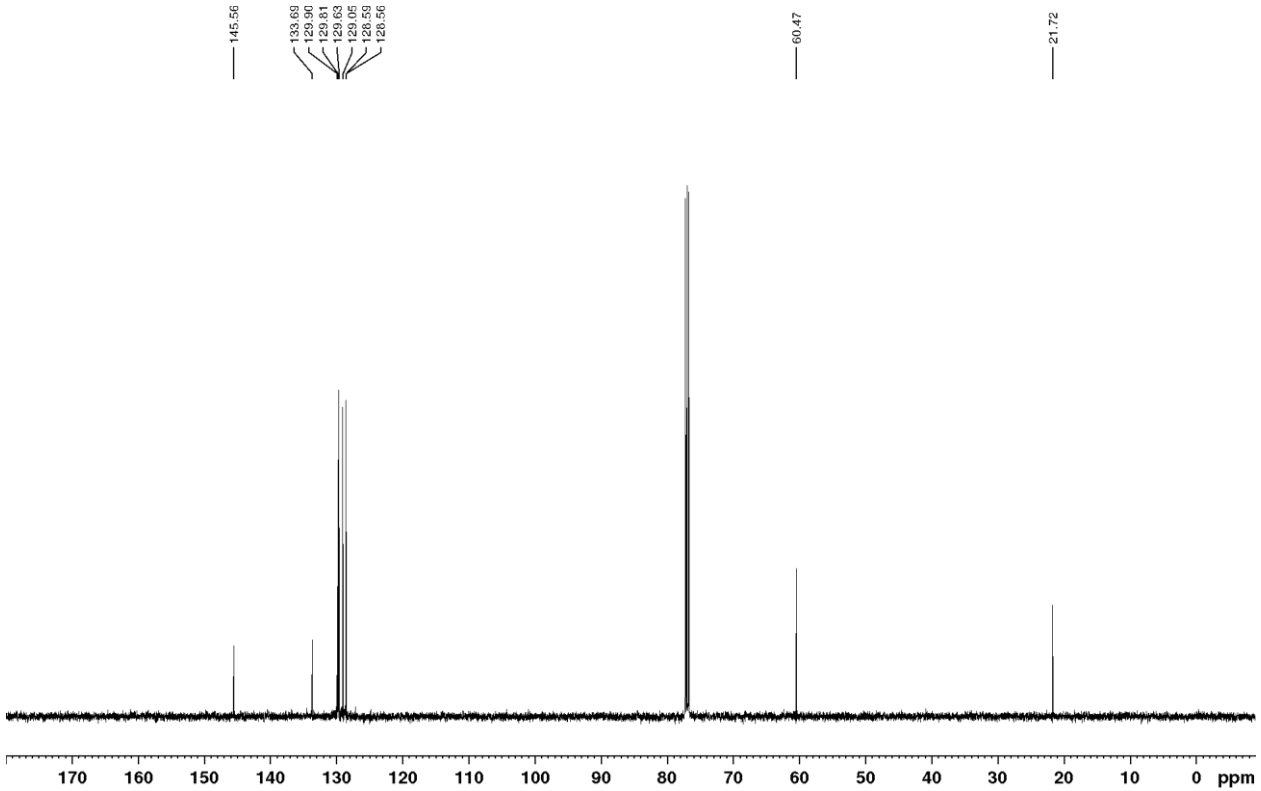
***N*-Benzyl-*N*-chloro-4-methylbenzenesulfonamide** (**1a**): ^{1}H NMR (500 MHz, $CDCl_3$)



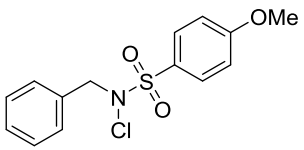


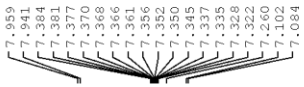


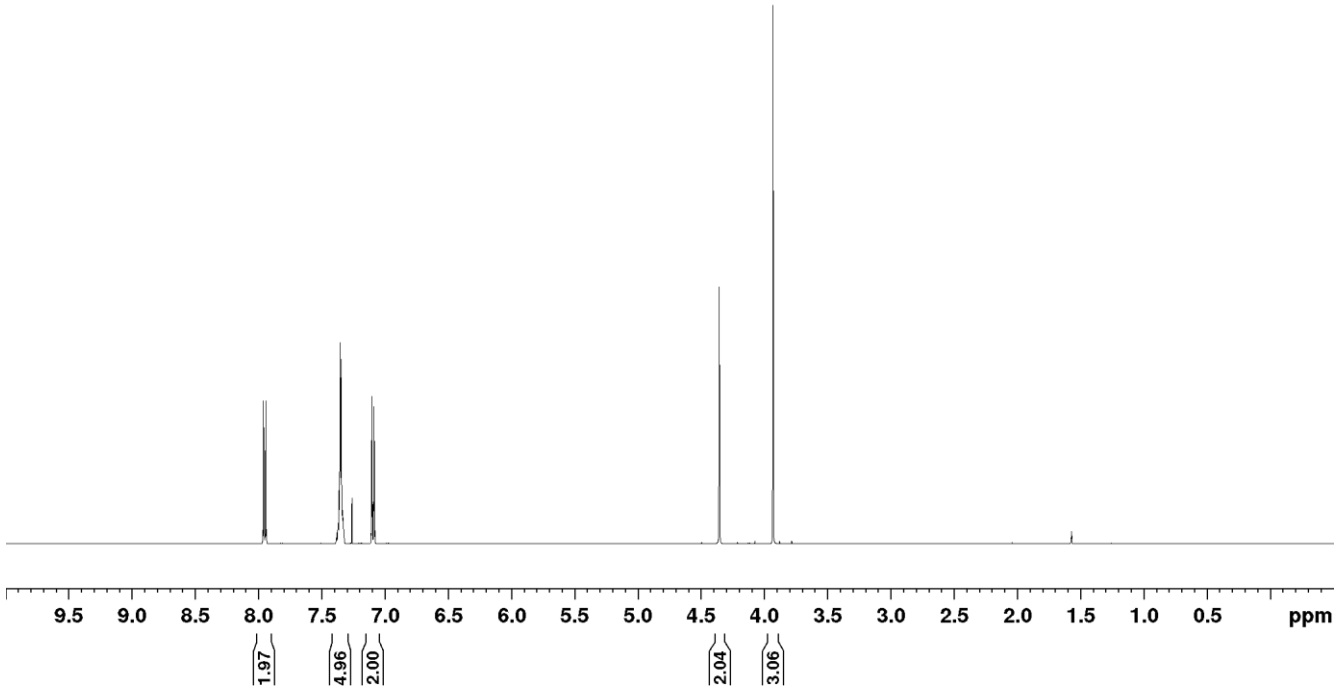
^{13}C NMR (125 MHz, $CDCl_3$)



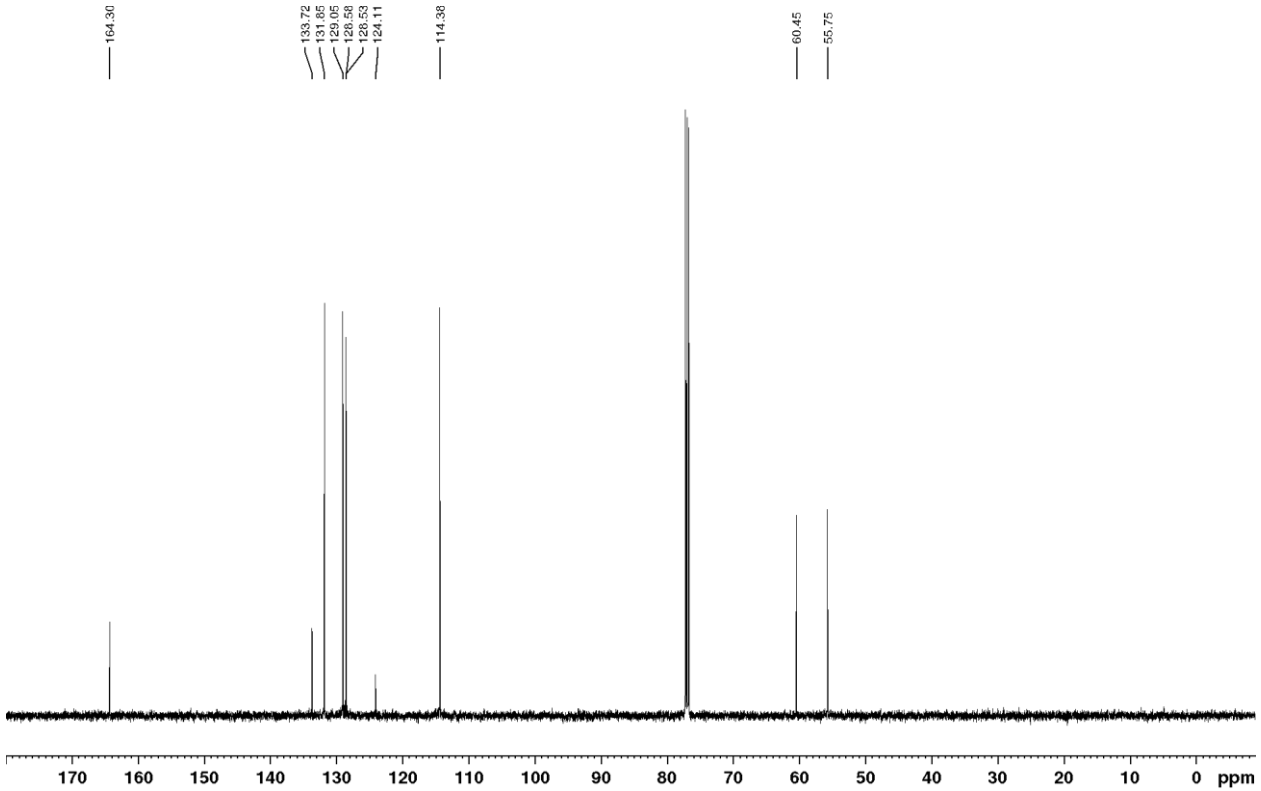
***N*-Benzyl-*N*-chloro-4-methoxybenzenesulfonamide** (**1b**): ^{1}H NMR (500 MHz, $CDCl_3$)



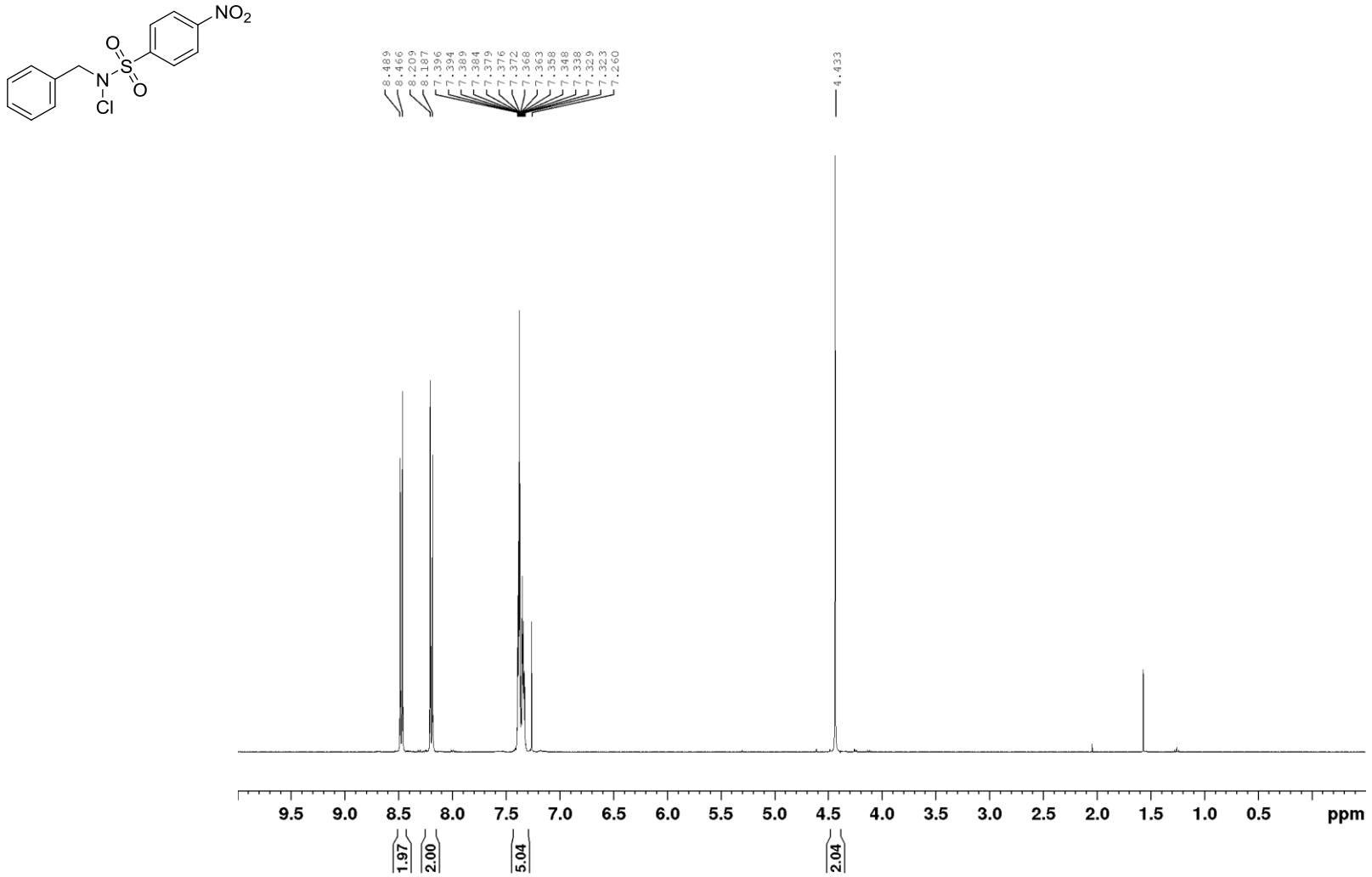




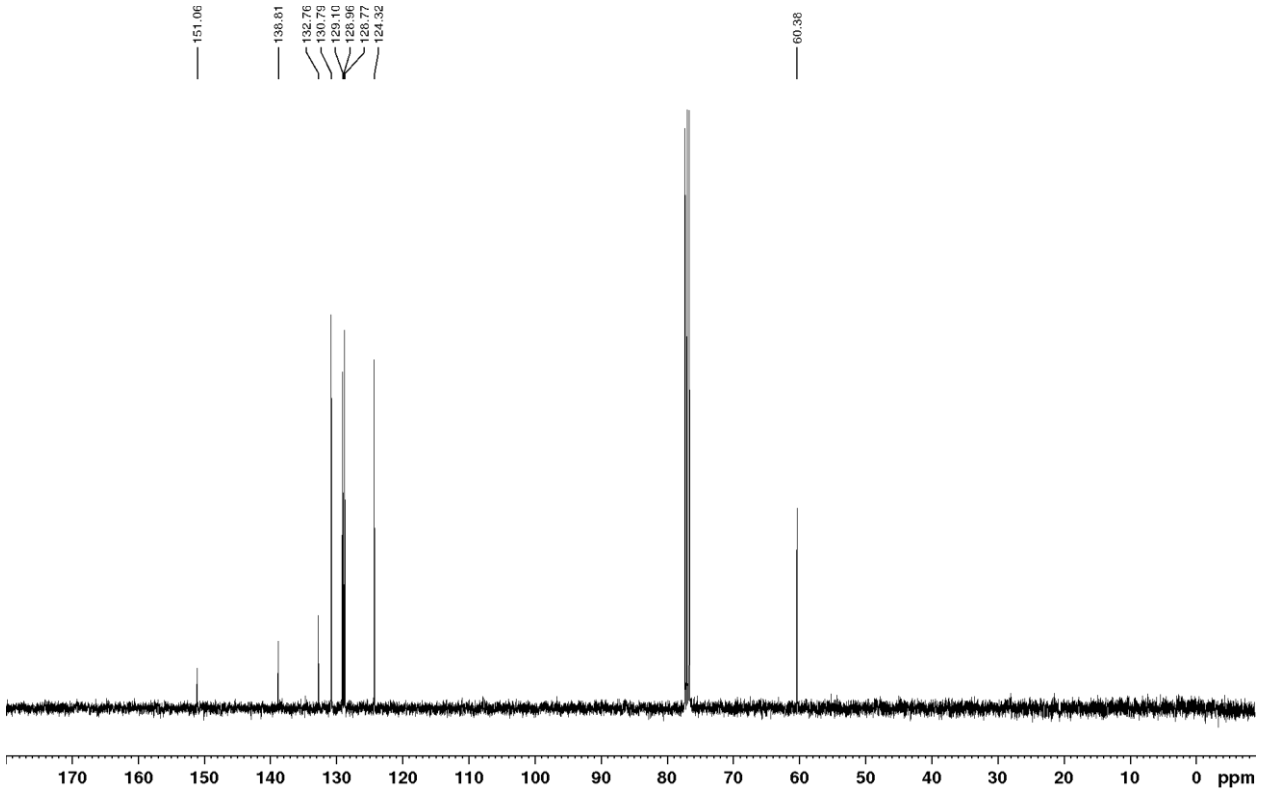
^{13}C NMR (125 MHz, $CDCl_3$)



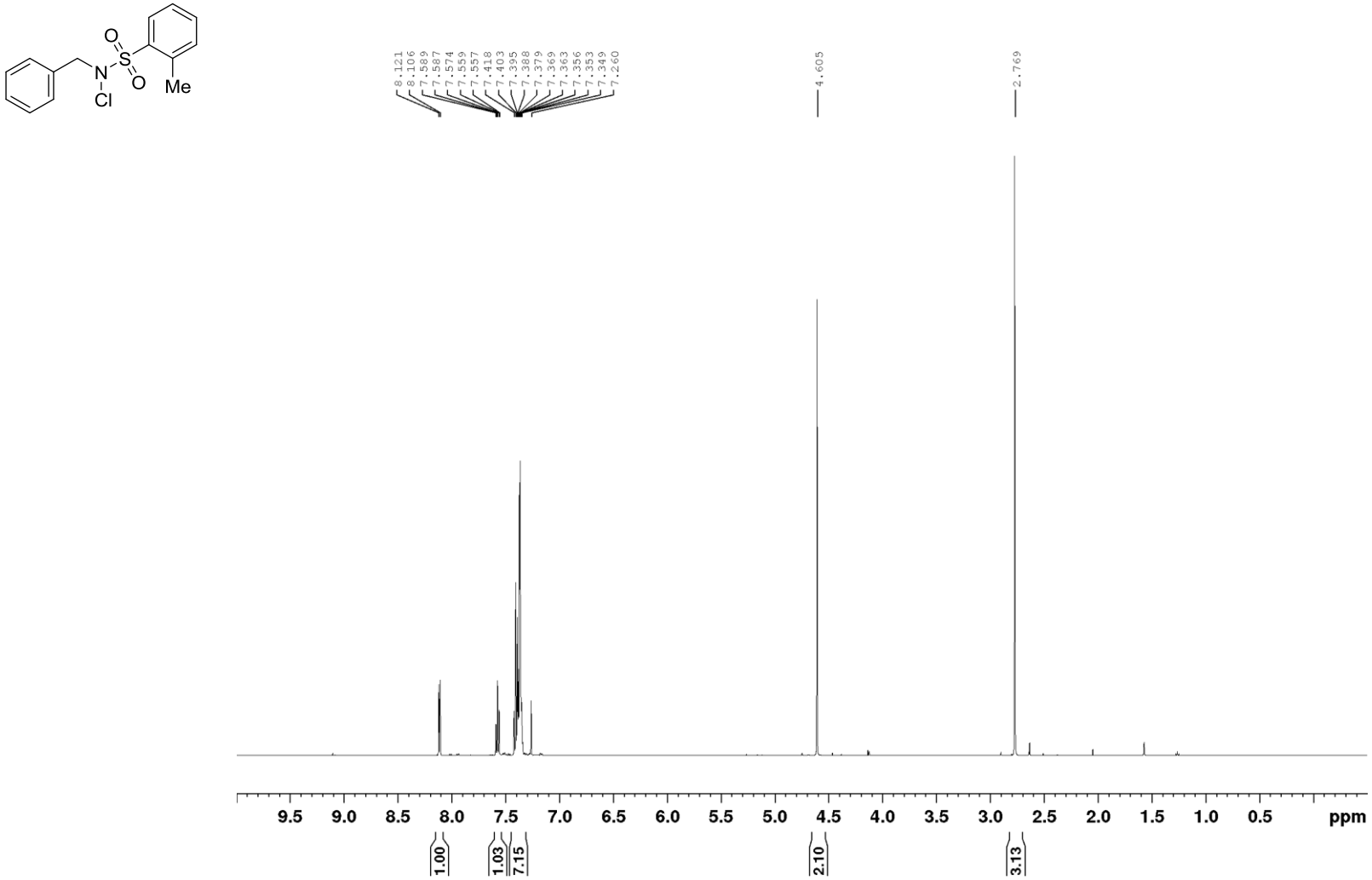
***N*-Benzyl-*N*-chloro-4-nitrobenzenesulfonamide** (**1c**): ^{1}H NMR (400 MHz, $CDCl_3$)



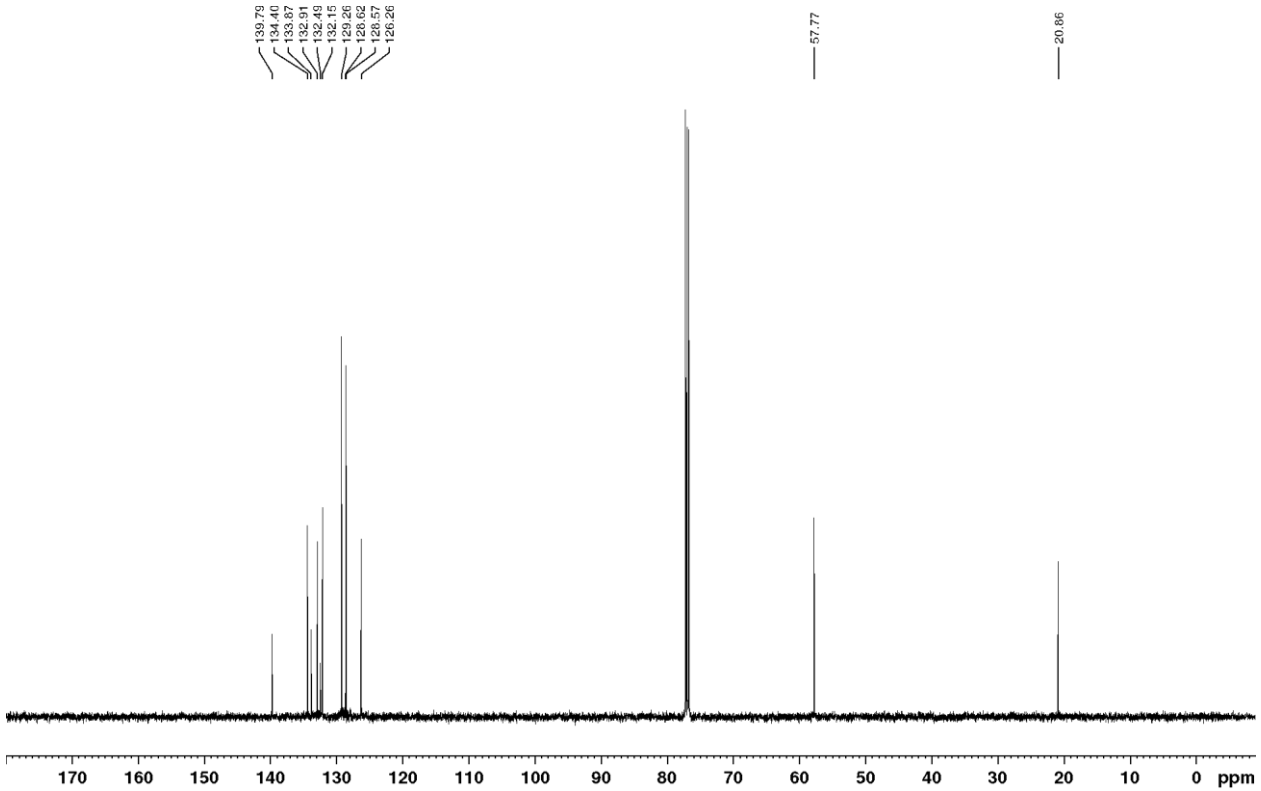
^{13}C NMR (100 MHz, $CDCl_3$)



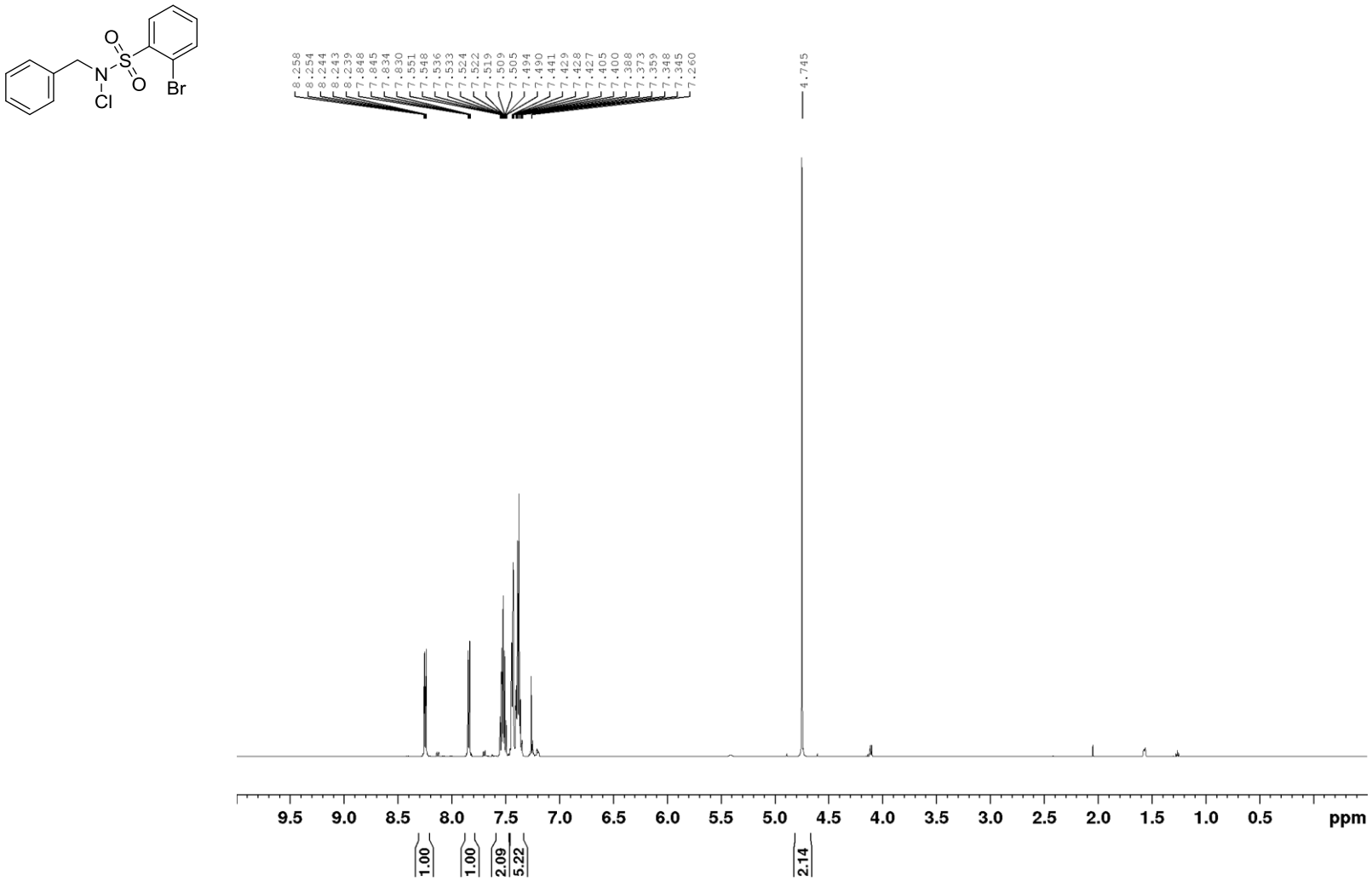
***N*-Benzyl-*N*-chloro-2-methylbenzenesulfonamide** (**1d**): ^{1}H NMR (500 MHz, $CDCl_3$)



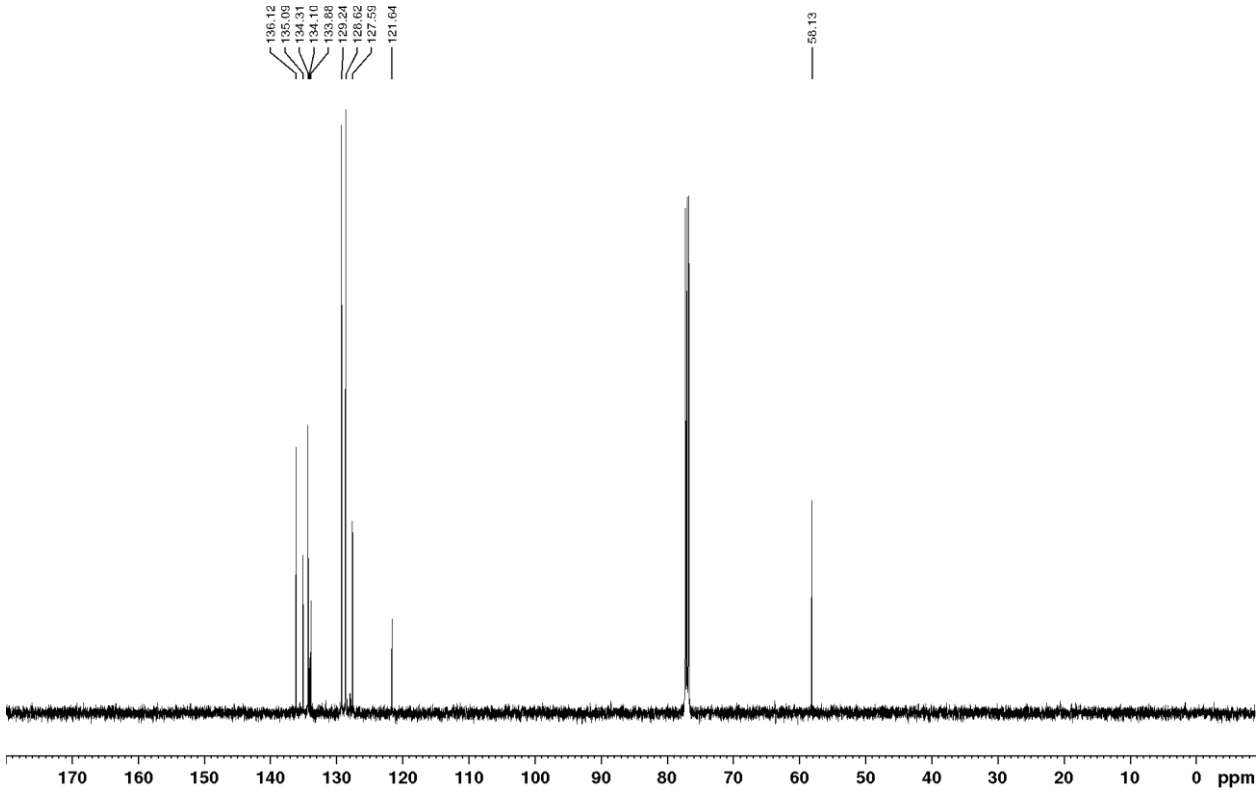
^{13}C NMR (125 MHz, $CDCl_3$)



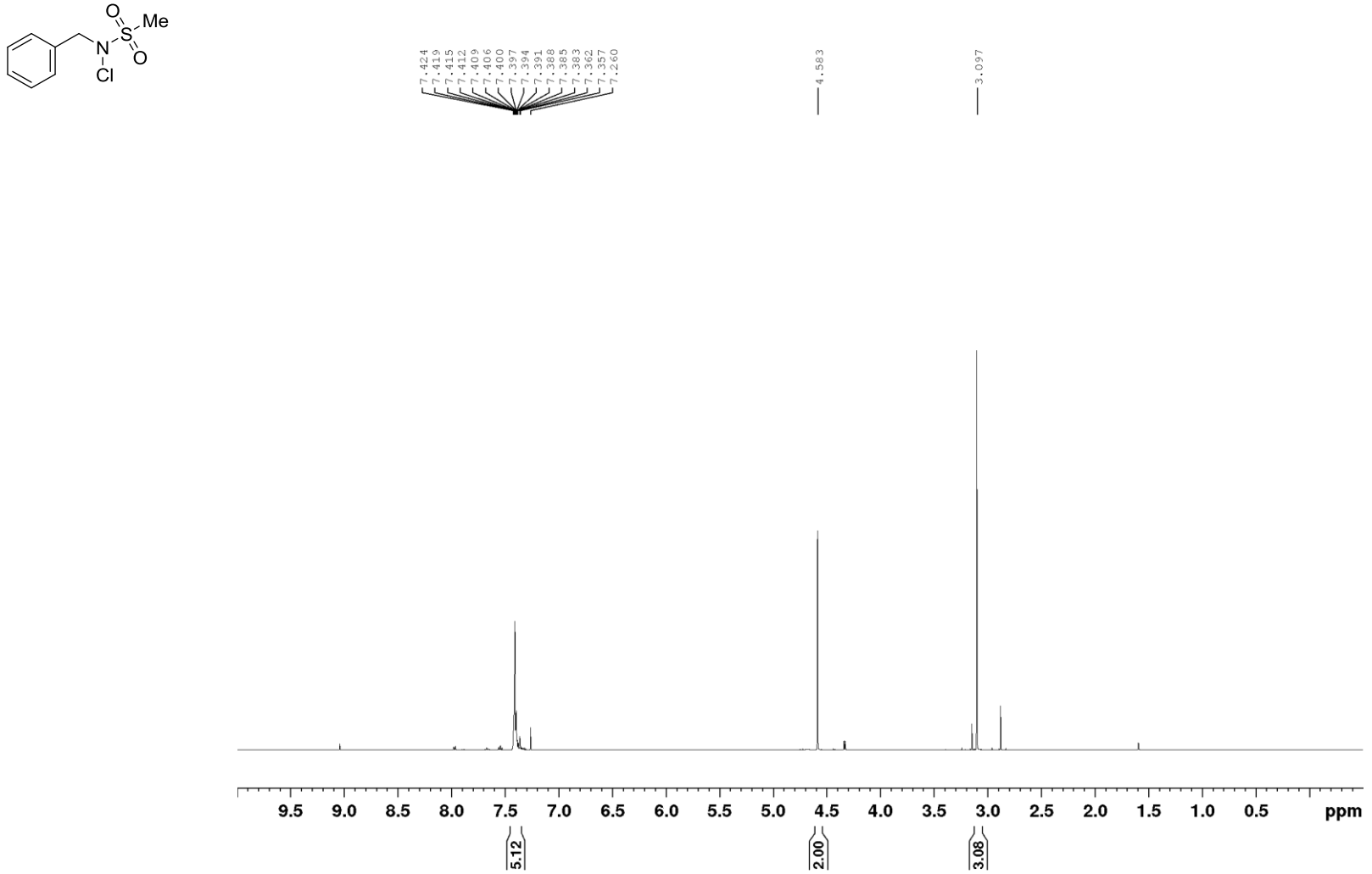
***N*-Benzyl-2-bromo-*N*-chlorobenzenesulfonamide** (**1e**): ^{1}H NMR (500 MHz, $CDCl_3$)



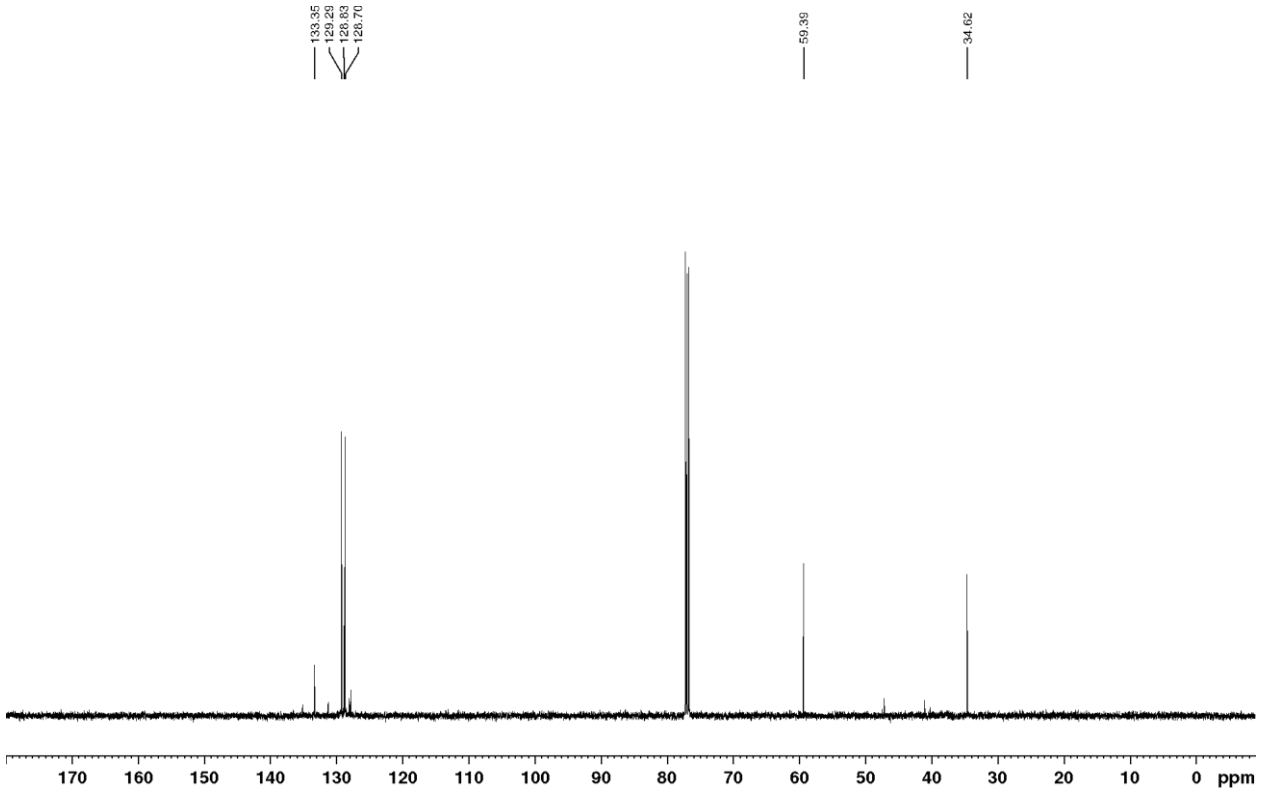
^{13}C NMR (125 MHz, $CDCl_3$)



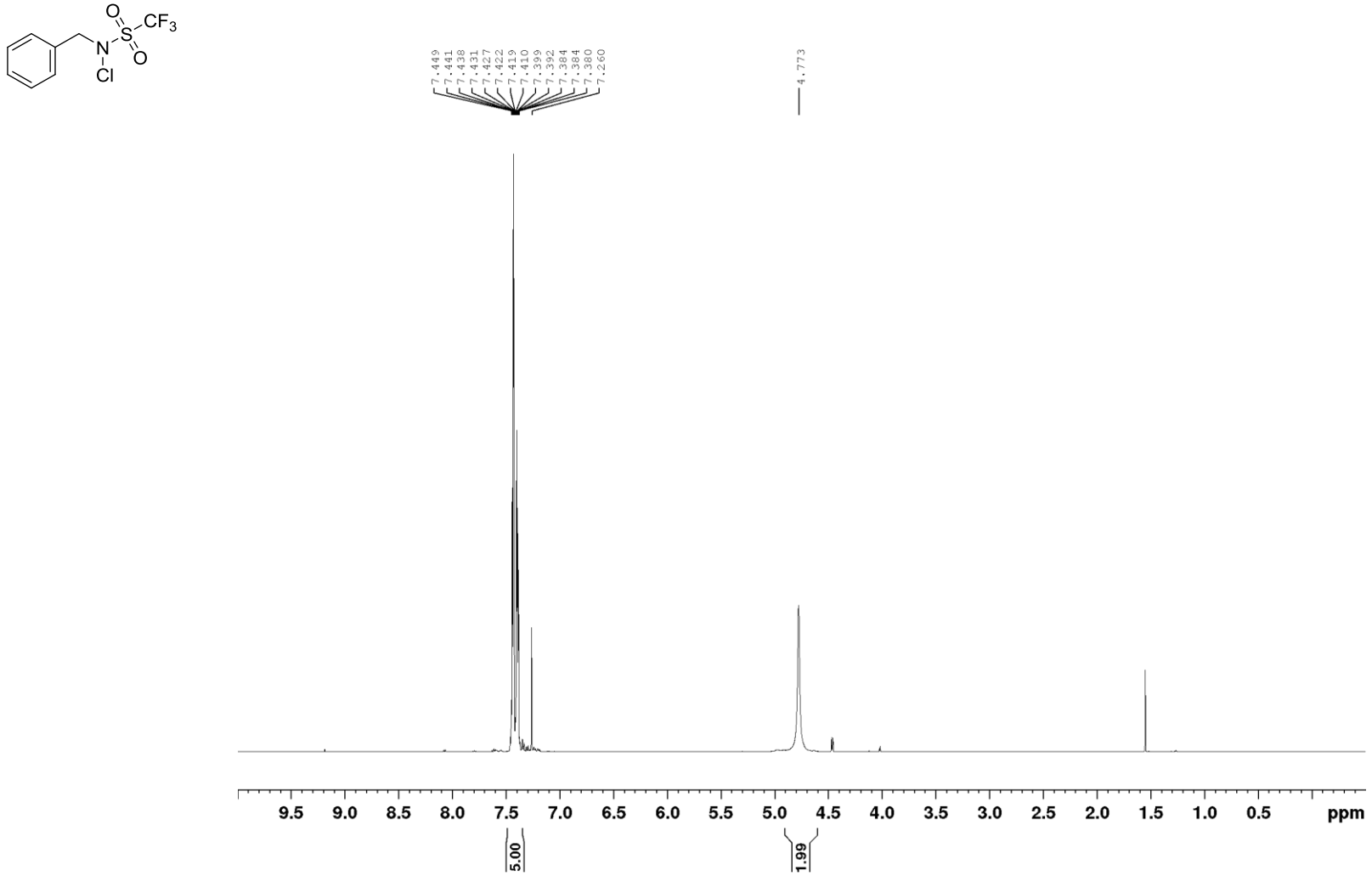
***N*-Benzyl-*N*-chloromethanesulfonamide** (**1f**): ^{1}H NMR (500 MHz, $CDCl_3$)



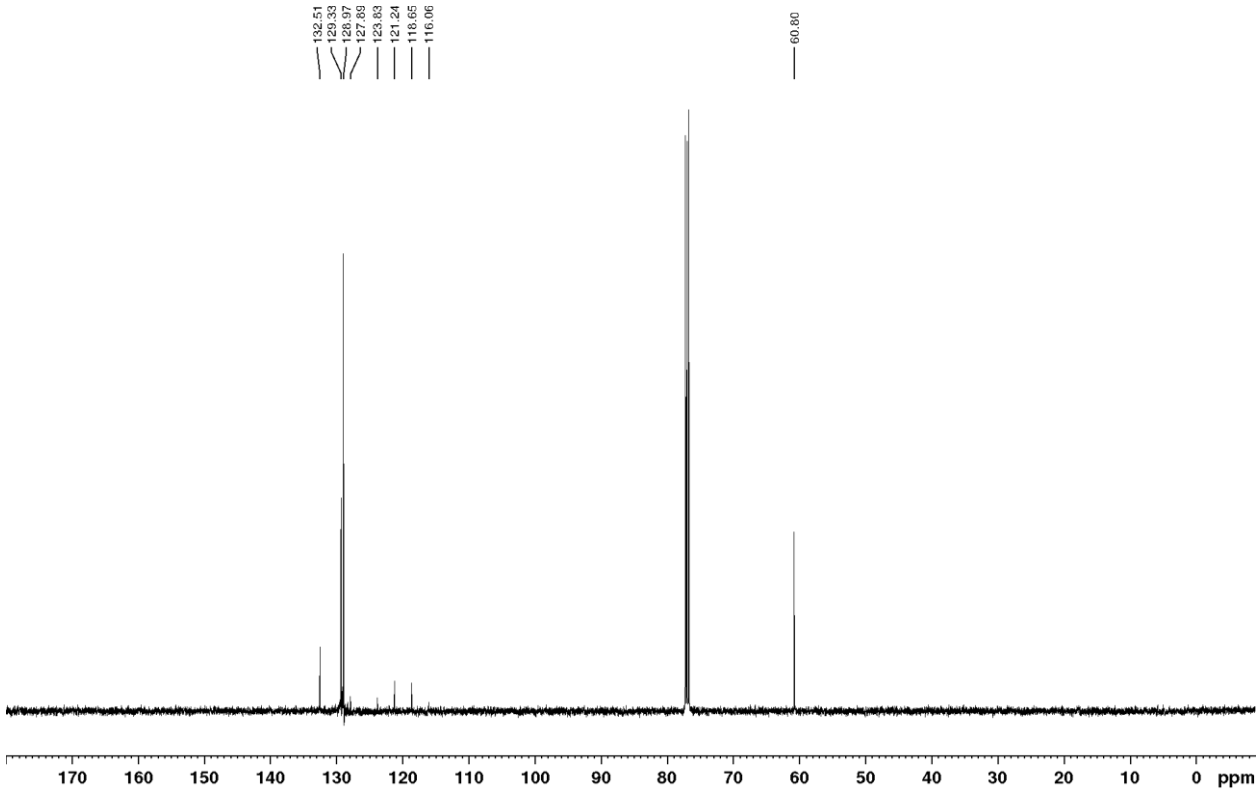
^{13}C NMR (125 MHz, $CDCl_3$)



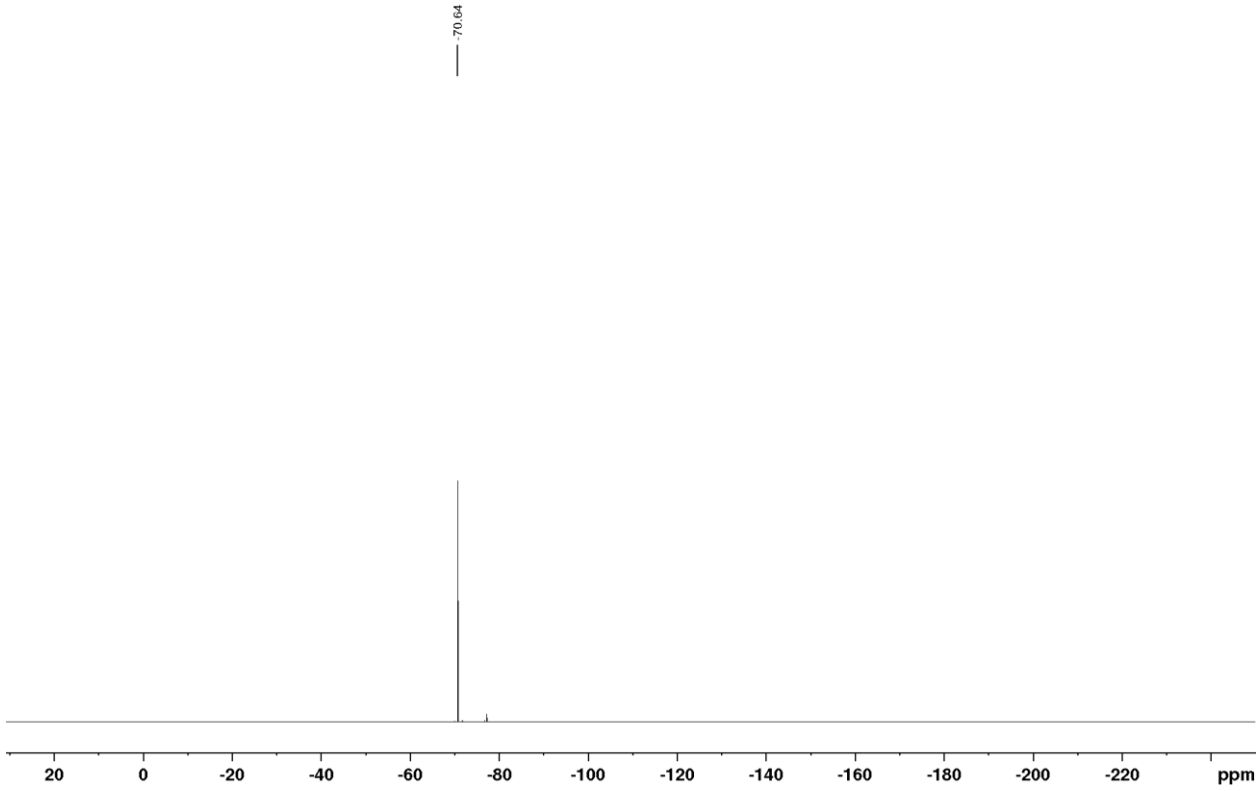
***N*-Benzyl-*N*-chloro-1,1,1-trifluoromethanesulfonamide** (**1g**): ^{1}H NMR (500 MHz, $CDCl_3$)



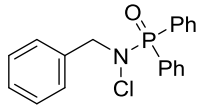
^{13}C NMR (125 MHz, $CDCl_3$)

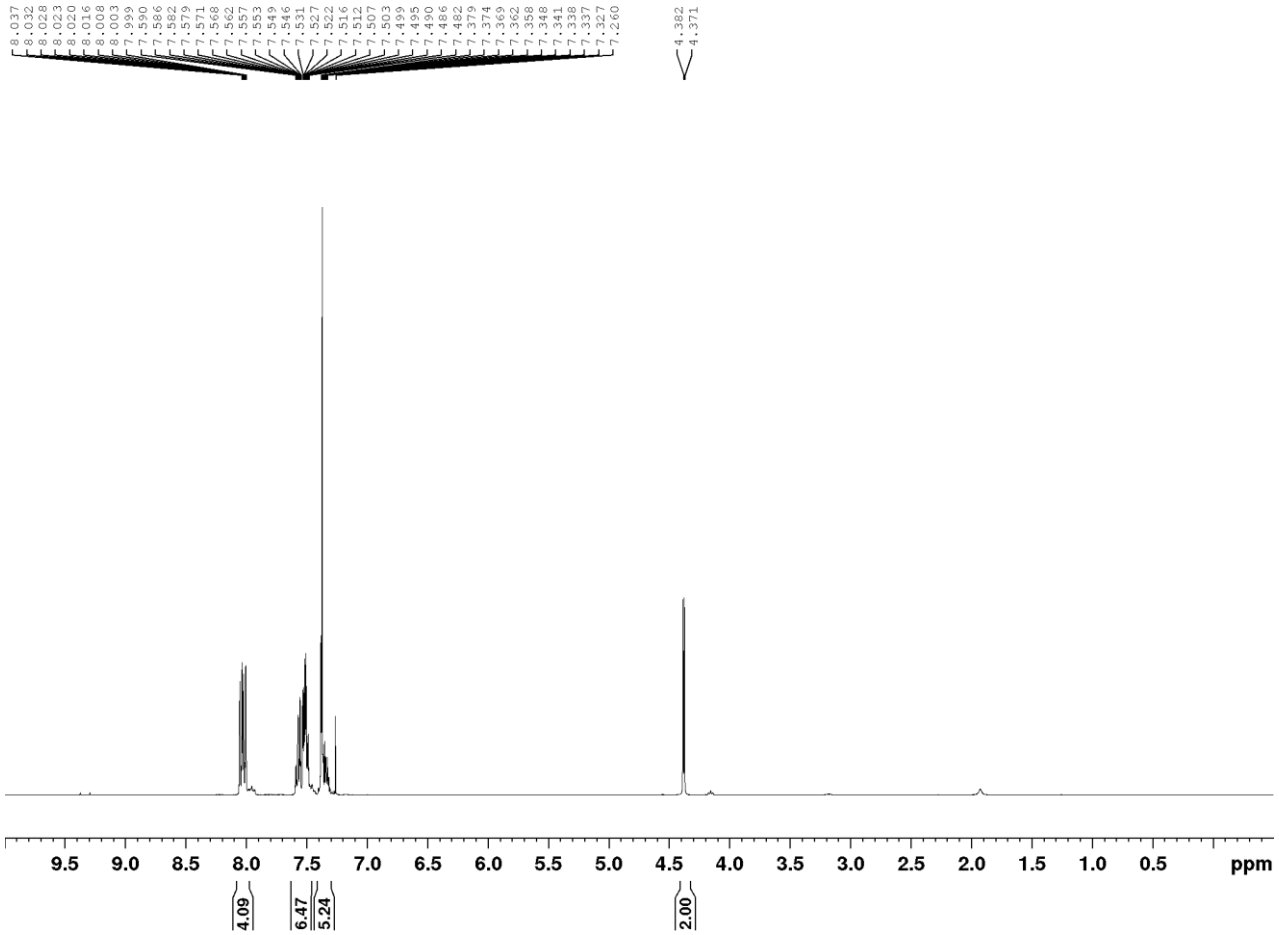


^{19}F NMR (188 MHz, $CDCl_3$)

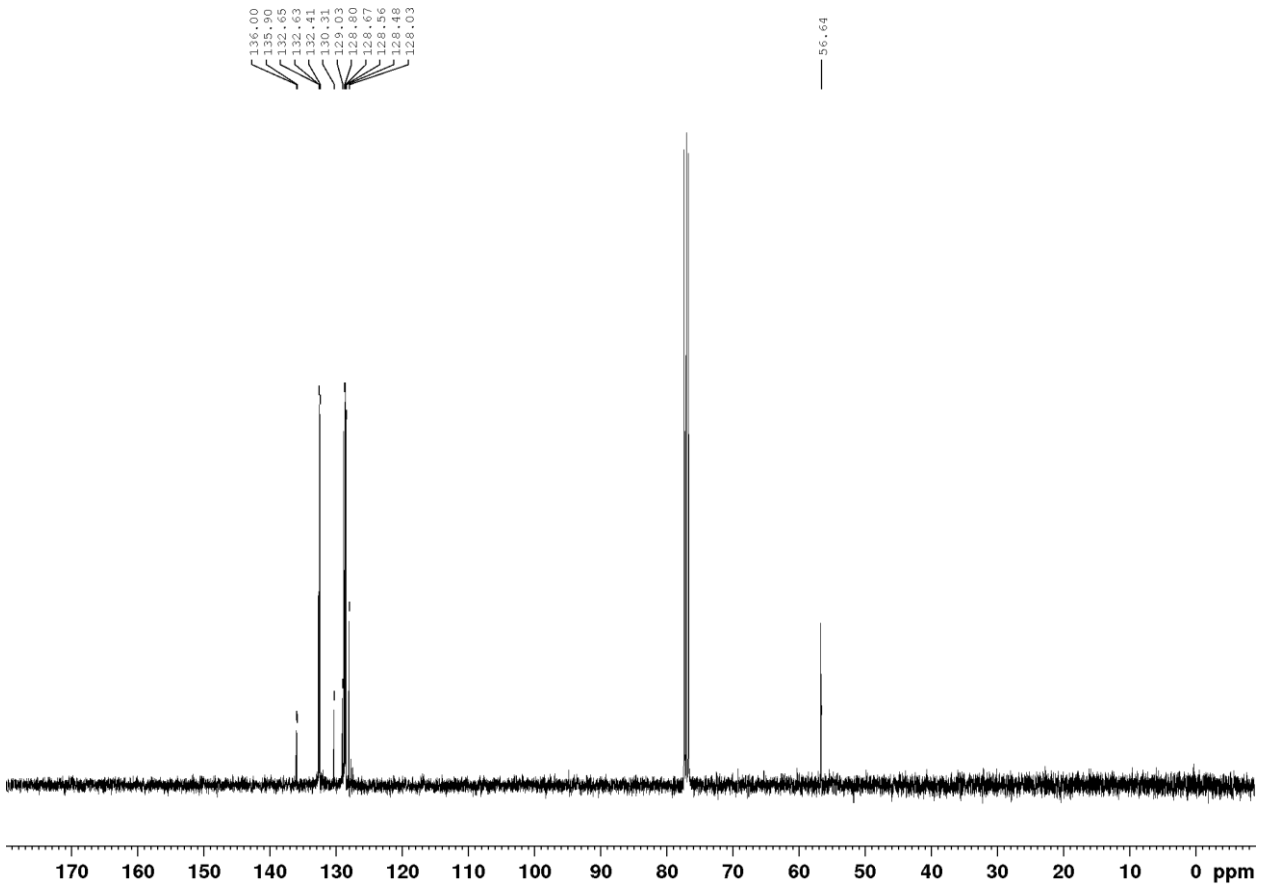


***N*-Benzyl-*N*-chloro-*P*,*P*-diphenylphosphinic amide** (**1h**): ^{1}H NMR (400 MHz, $CDCl_3$)

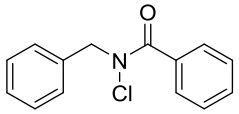


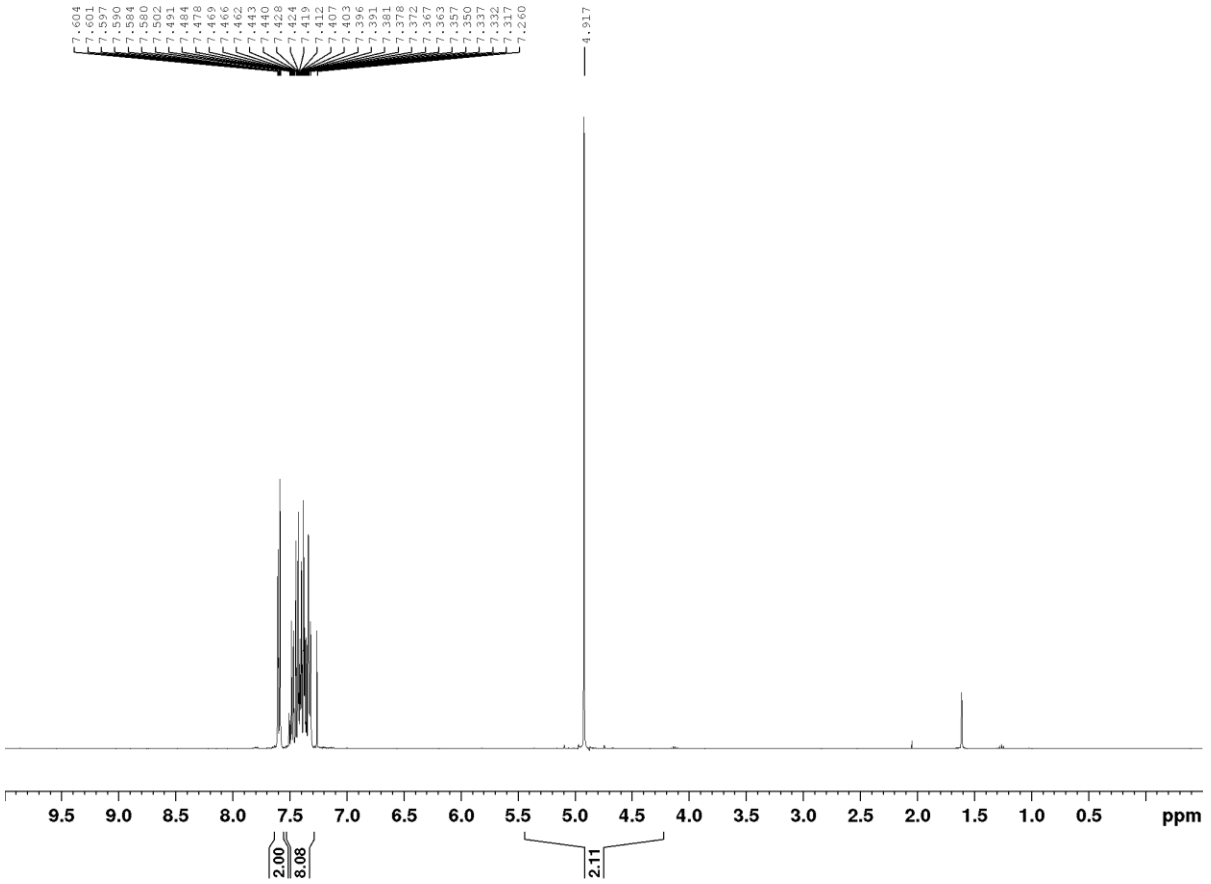


^{13}C NMR (100 MHz, $CDCl_3$)

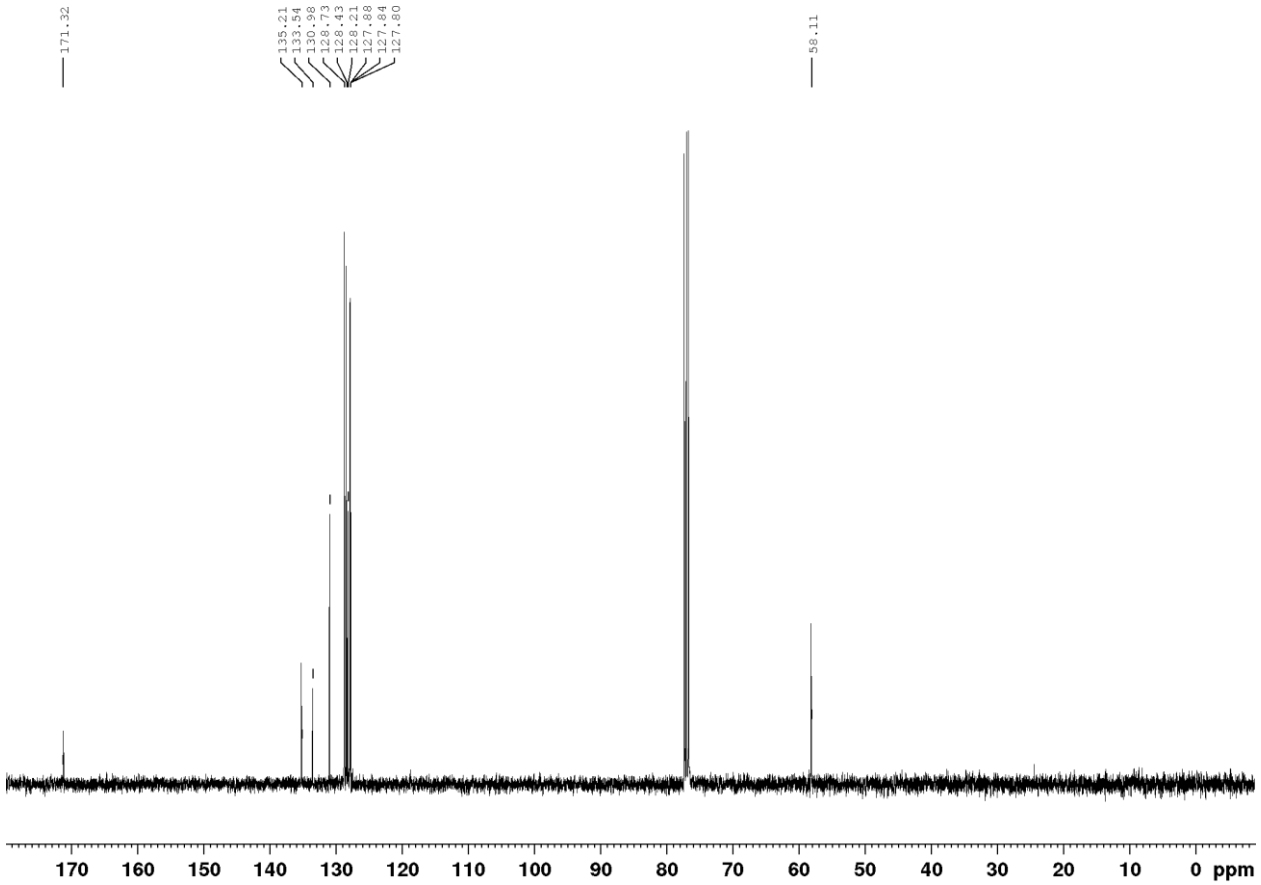


***N*-Benzyl-*N*-chlorobenzamide** (**1i**): ^{1}H NMR (400 MHz, $CDCl_3$)

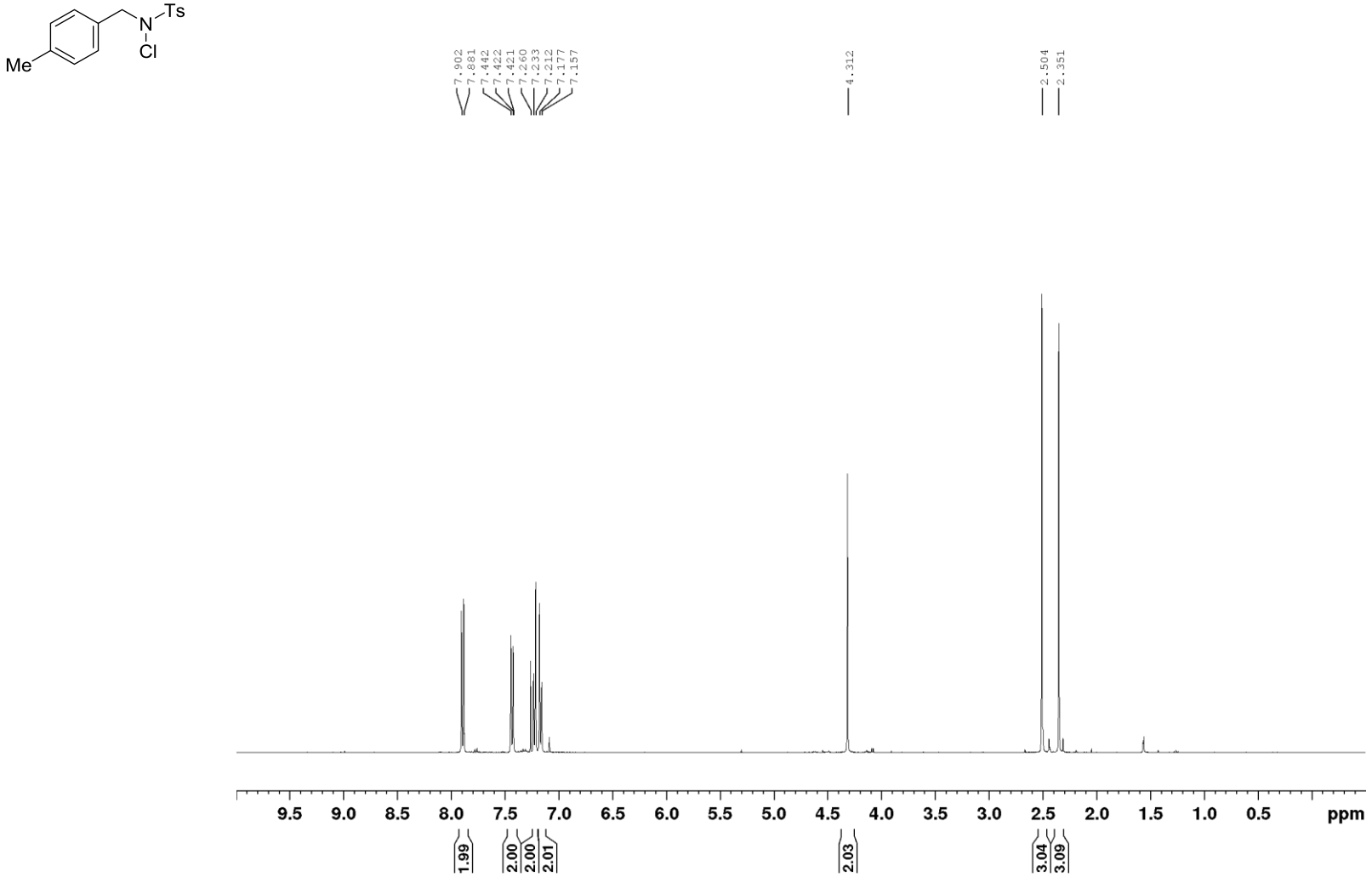




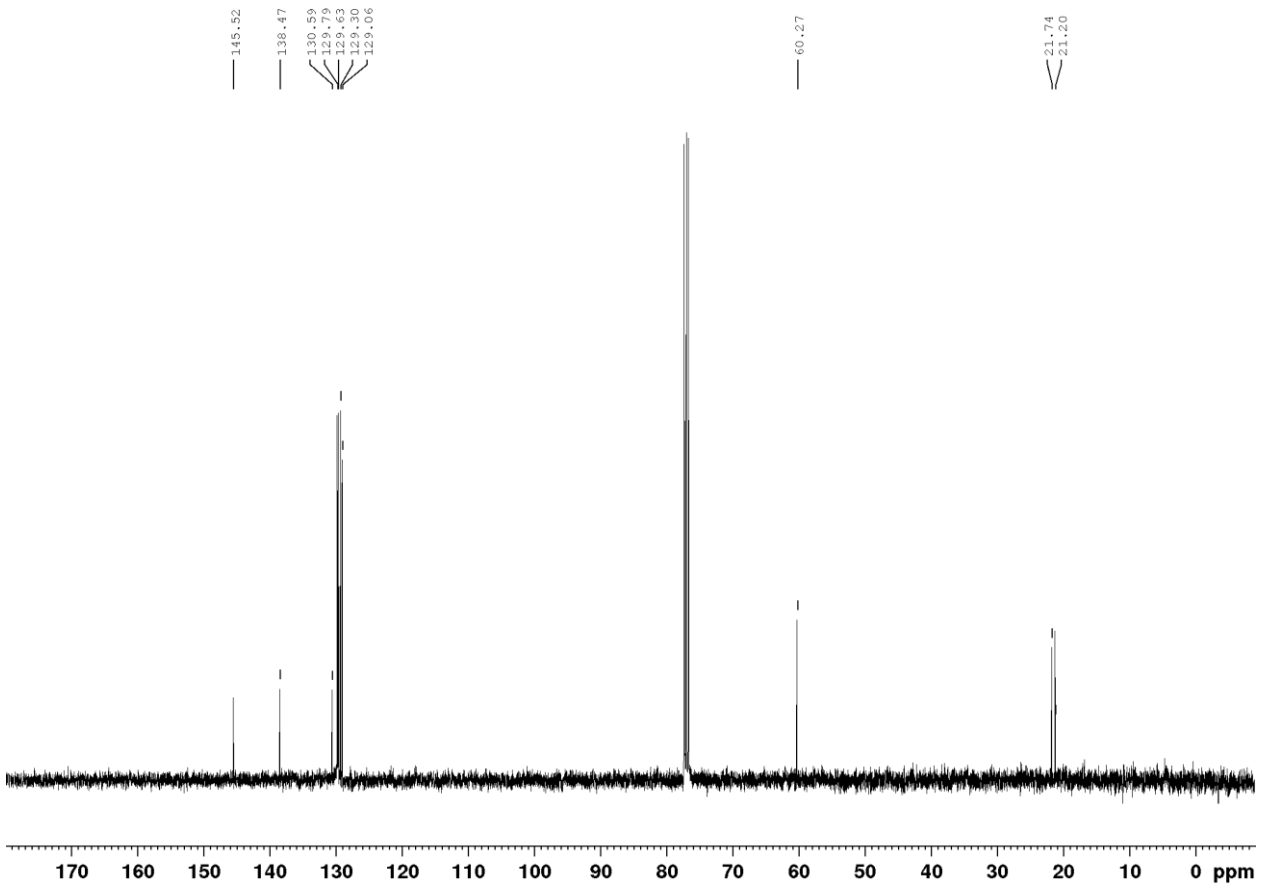
^{13}C NMR (100 MHz, $CDCl_3$)



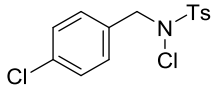
***N*-Chloro-4-methyl-*N*-(4-methylbenzyl)benzenesulfonamide** (**5a**): ^{1}H NMR (400 MHz, $CDCl_3$)

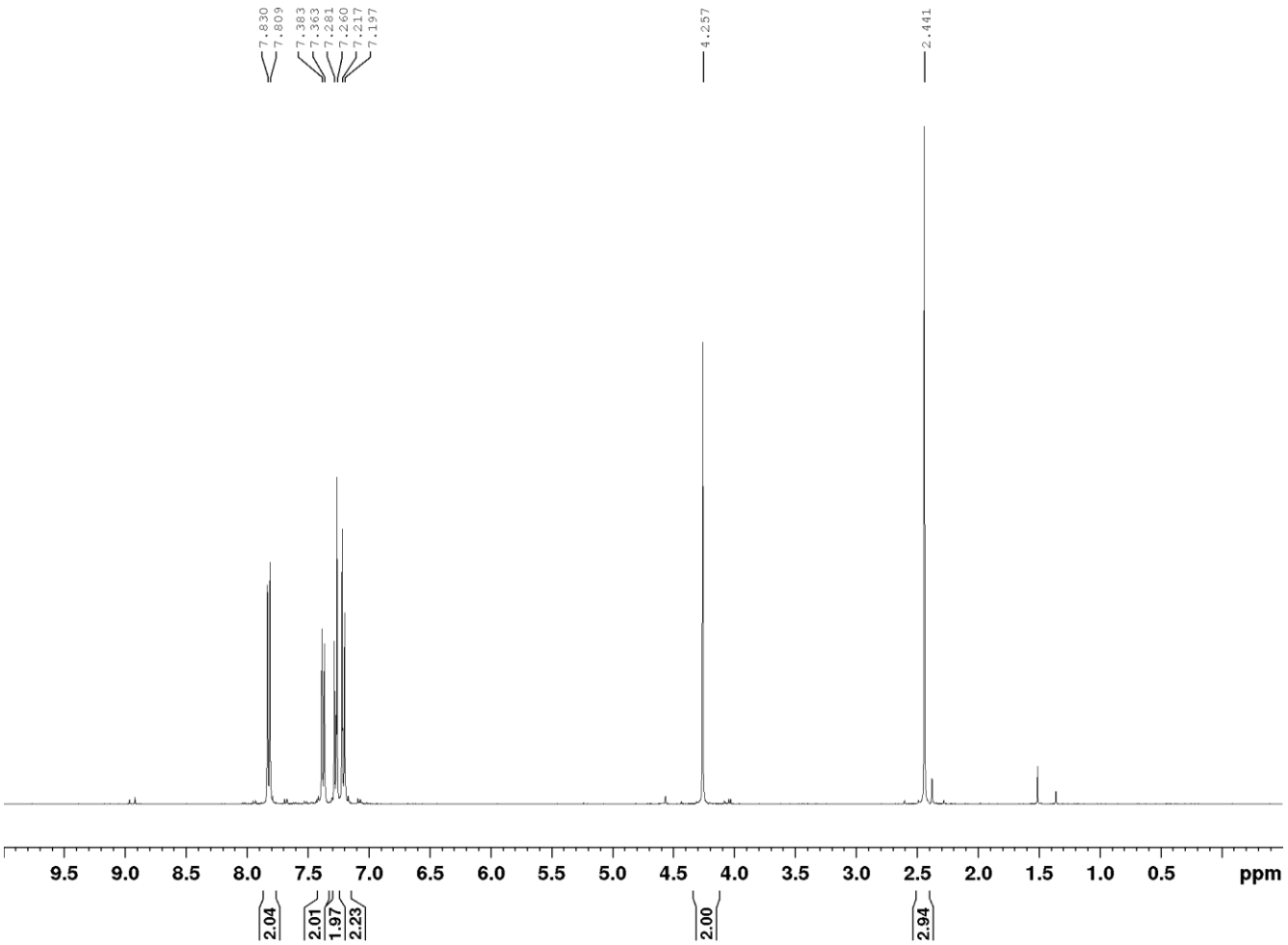


^{13}C NMR (100 MHz, $CDCl_3$)

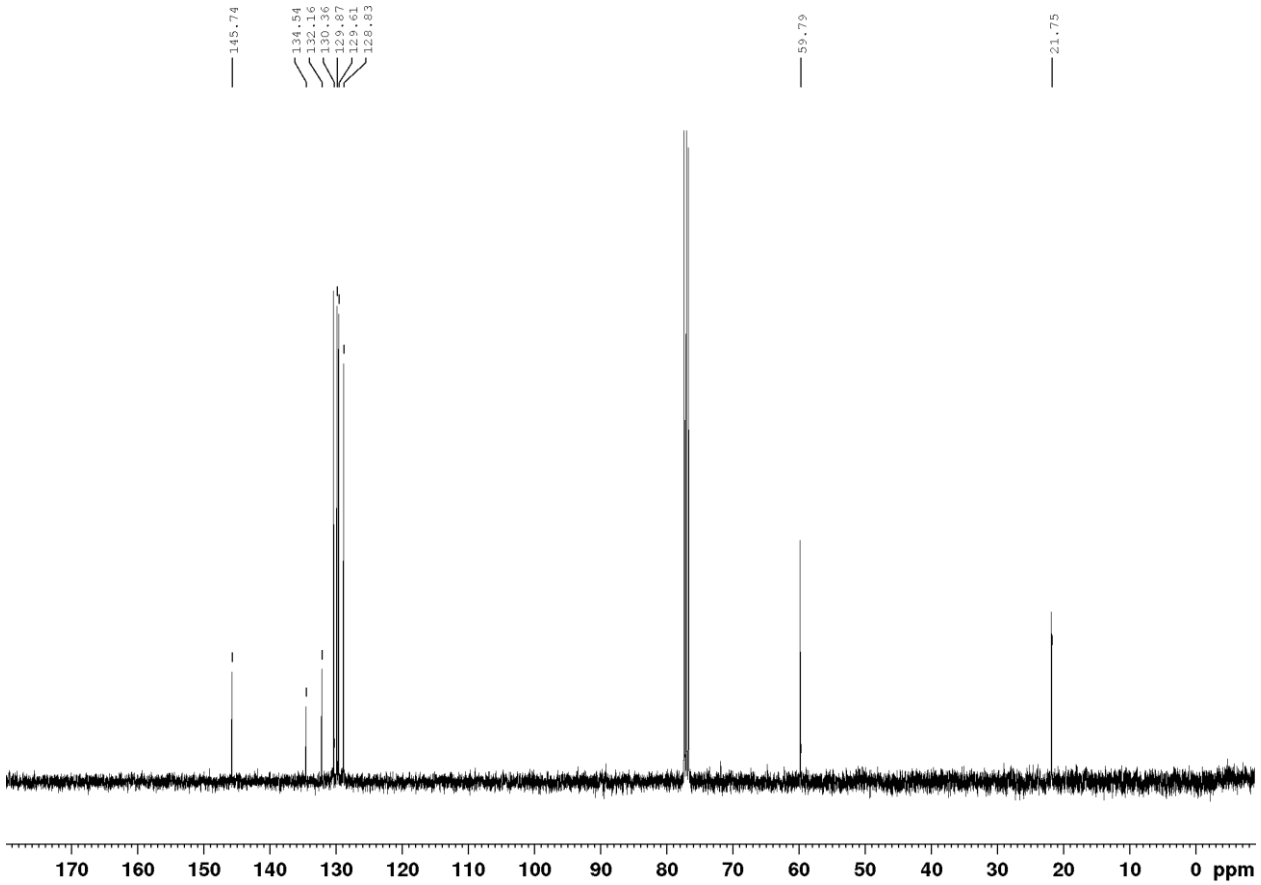


***N*-Chloro-*N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide** (**6a**): ^{1}H NMR (400 MHz, $CDCl_3$)

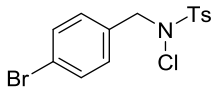


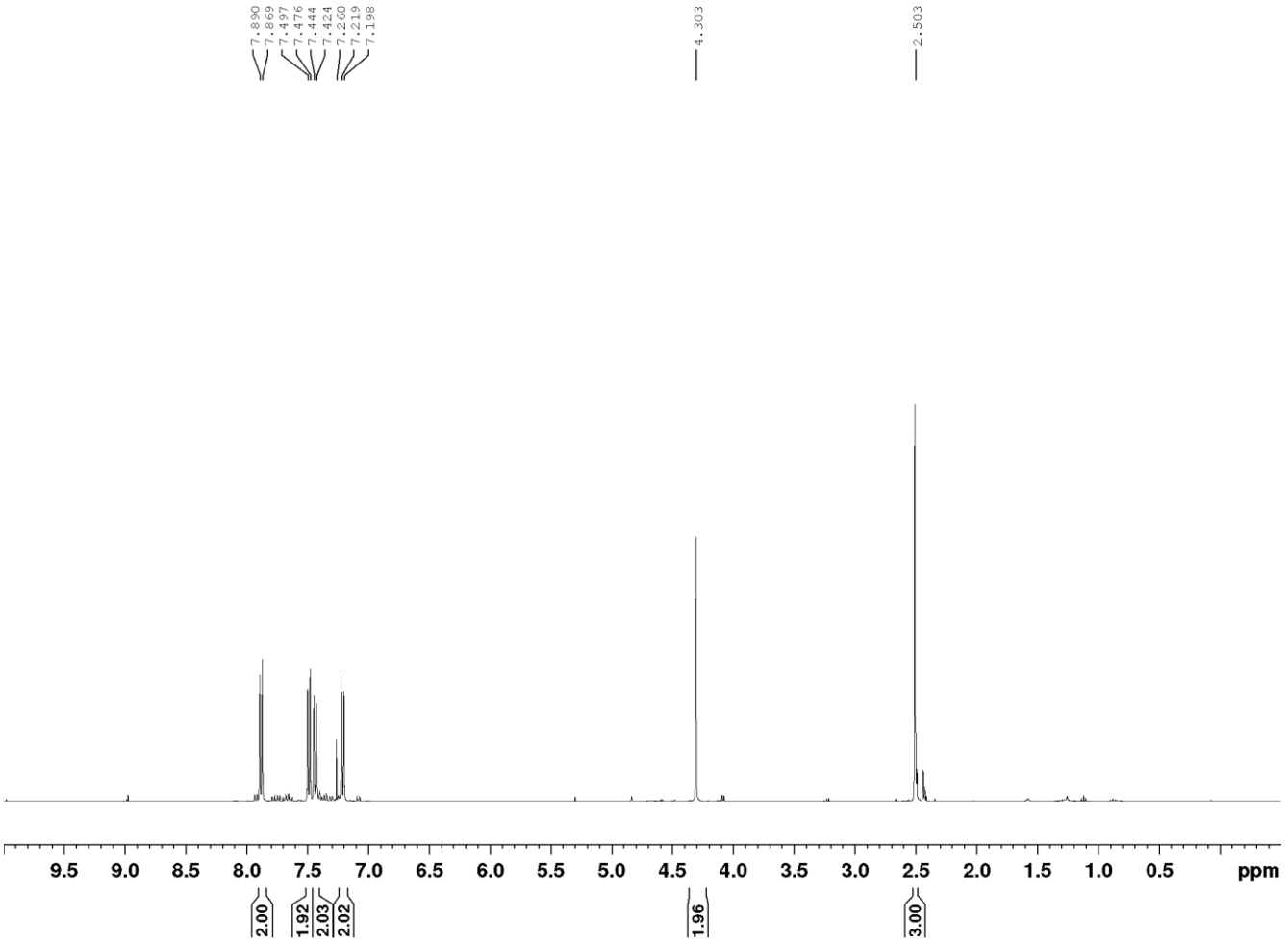


^{13}C NMR (100 MHz, $CDCl_3$)

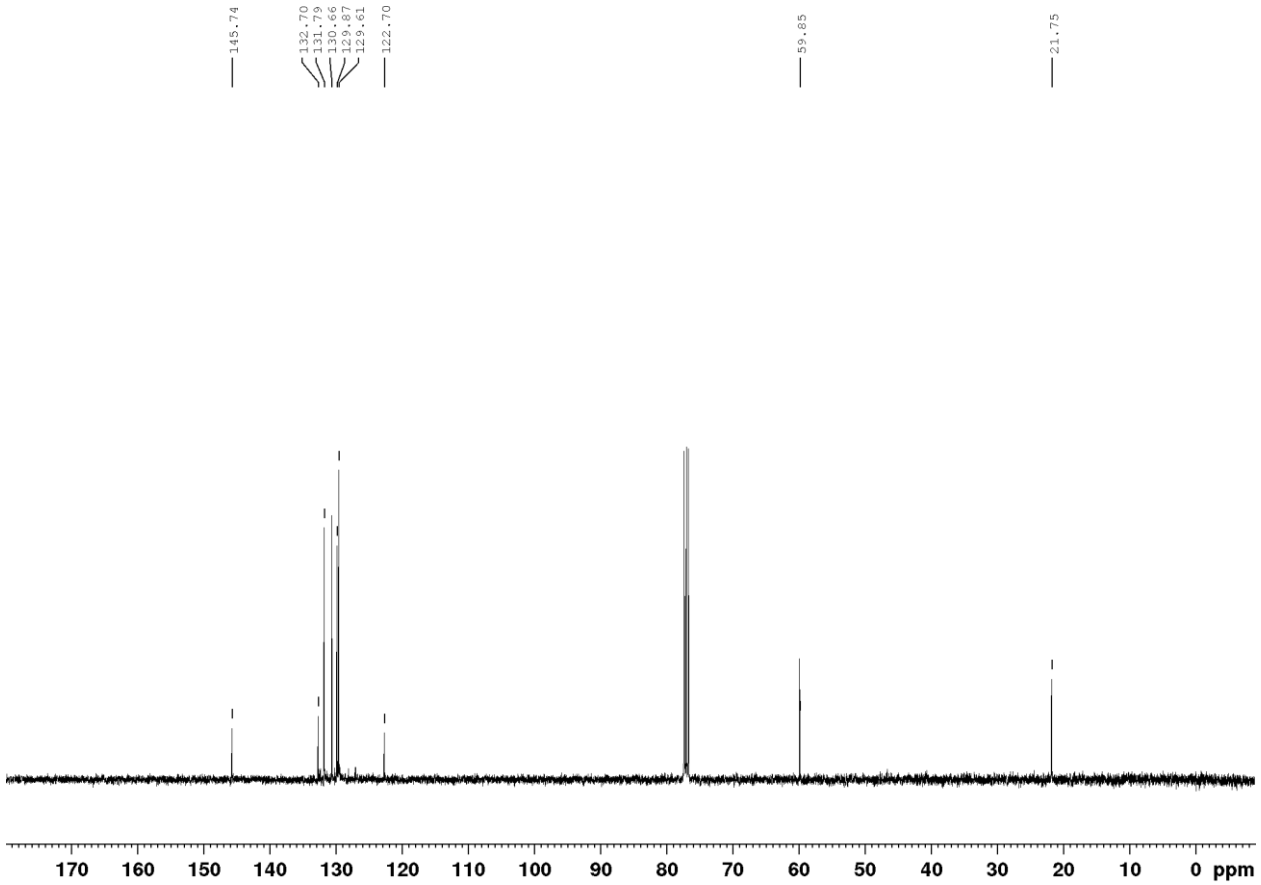


***N*-(4-Bromobenzyl)-*N*-chloro-4-methylbenzenesulfonamide** (**7a**): ^{1}H NMR (400 MHz, $CDCl_3$)

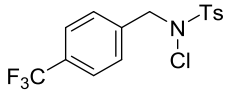


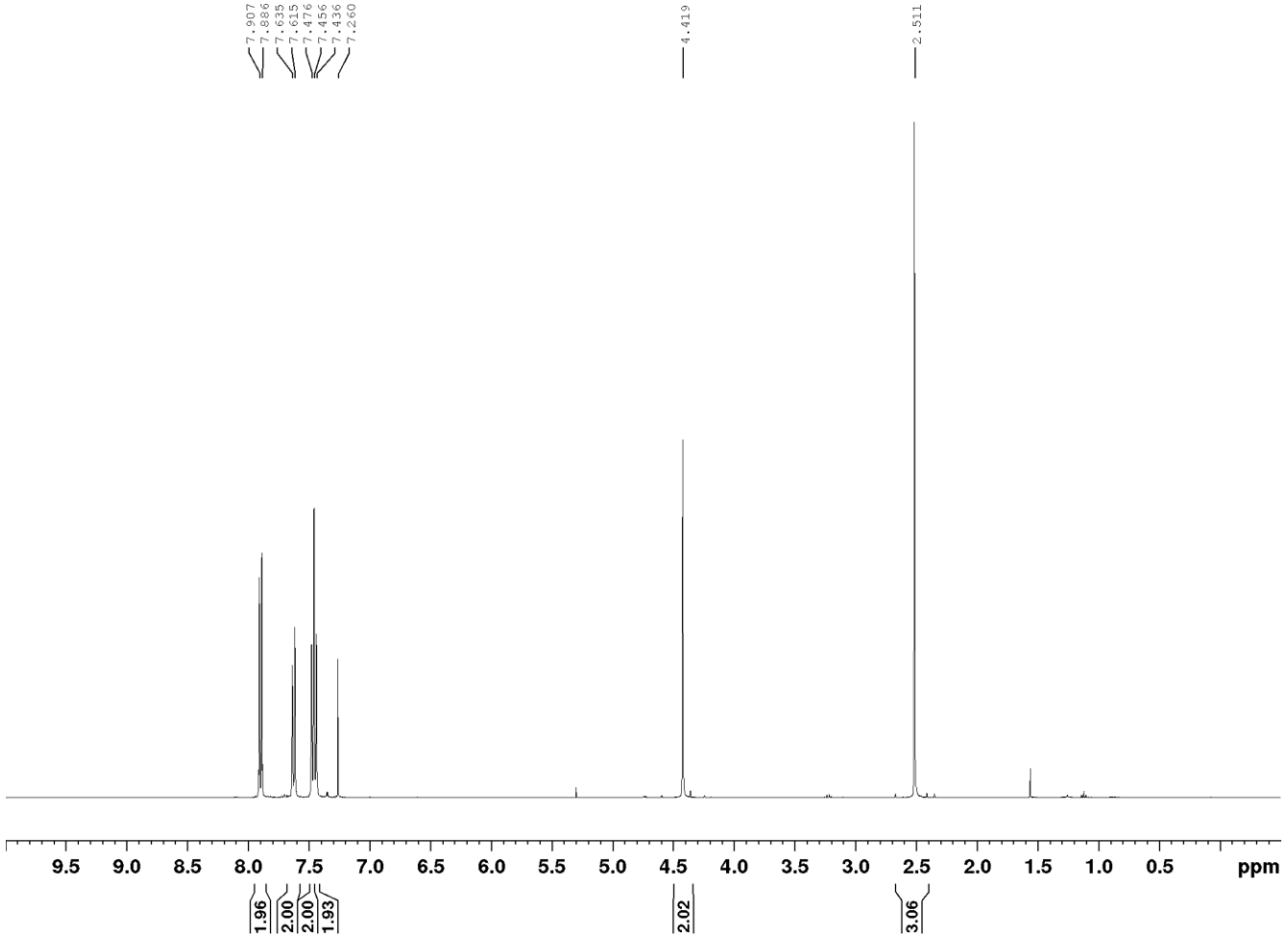


^{13}C NMR (100 MHz, $CDCl_3$)

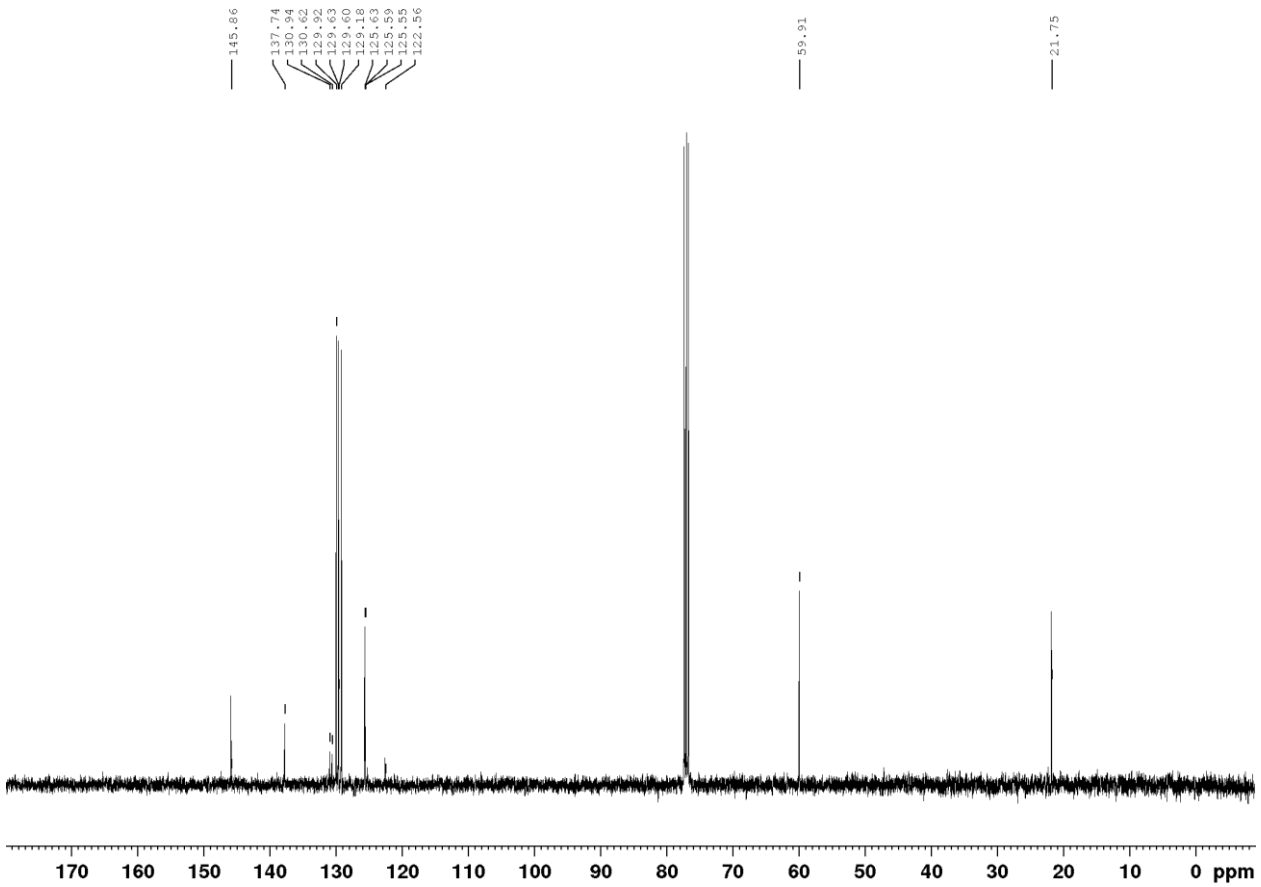


***N*-Chloro-4-methyl-*N*-(4-(trifluoromethyl)benzyl)benzenesulfonamide** (**8a**): ^{1}H NMR (400 MHz, $CDCl_3$)

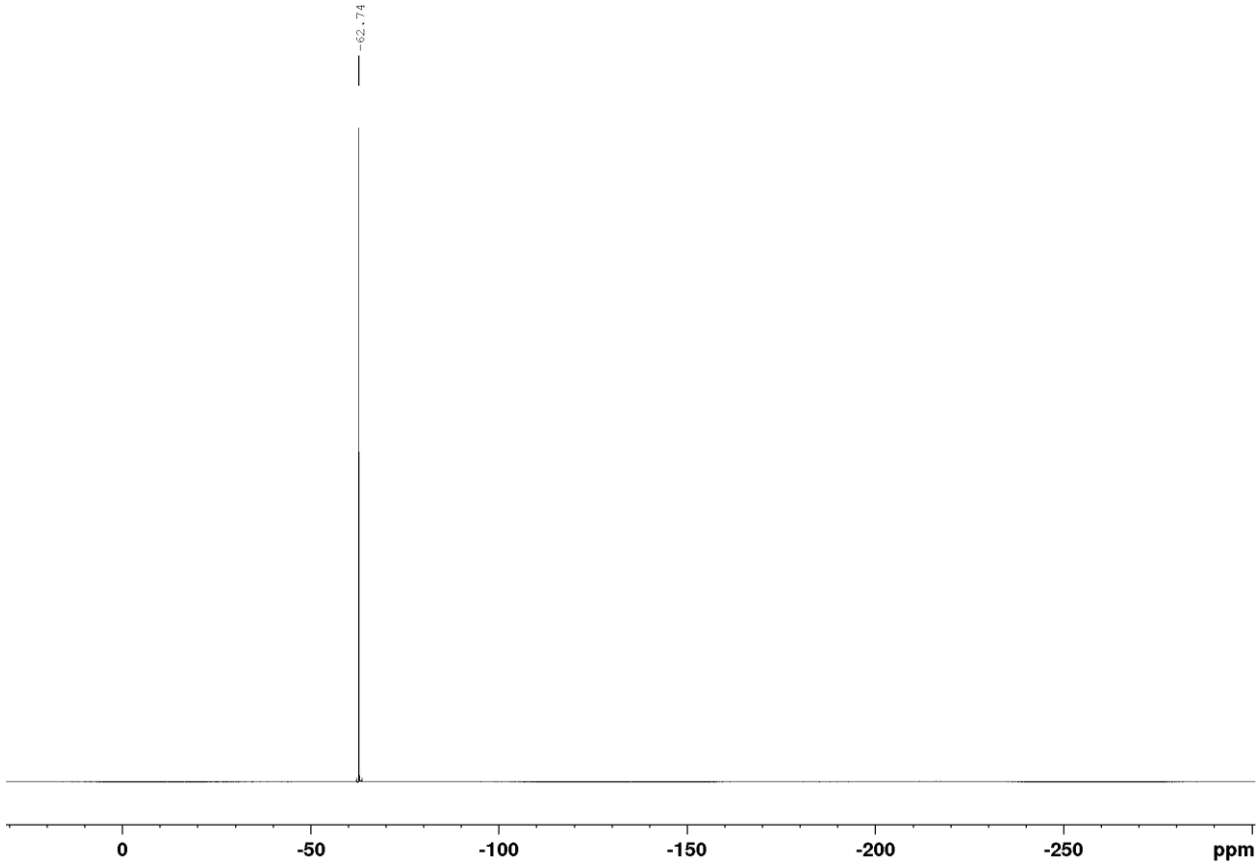




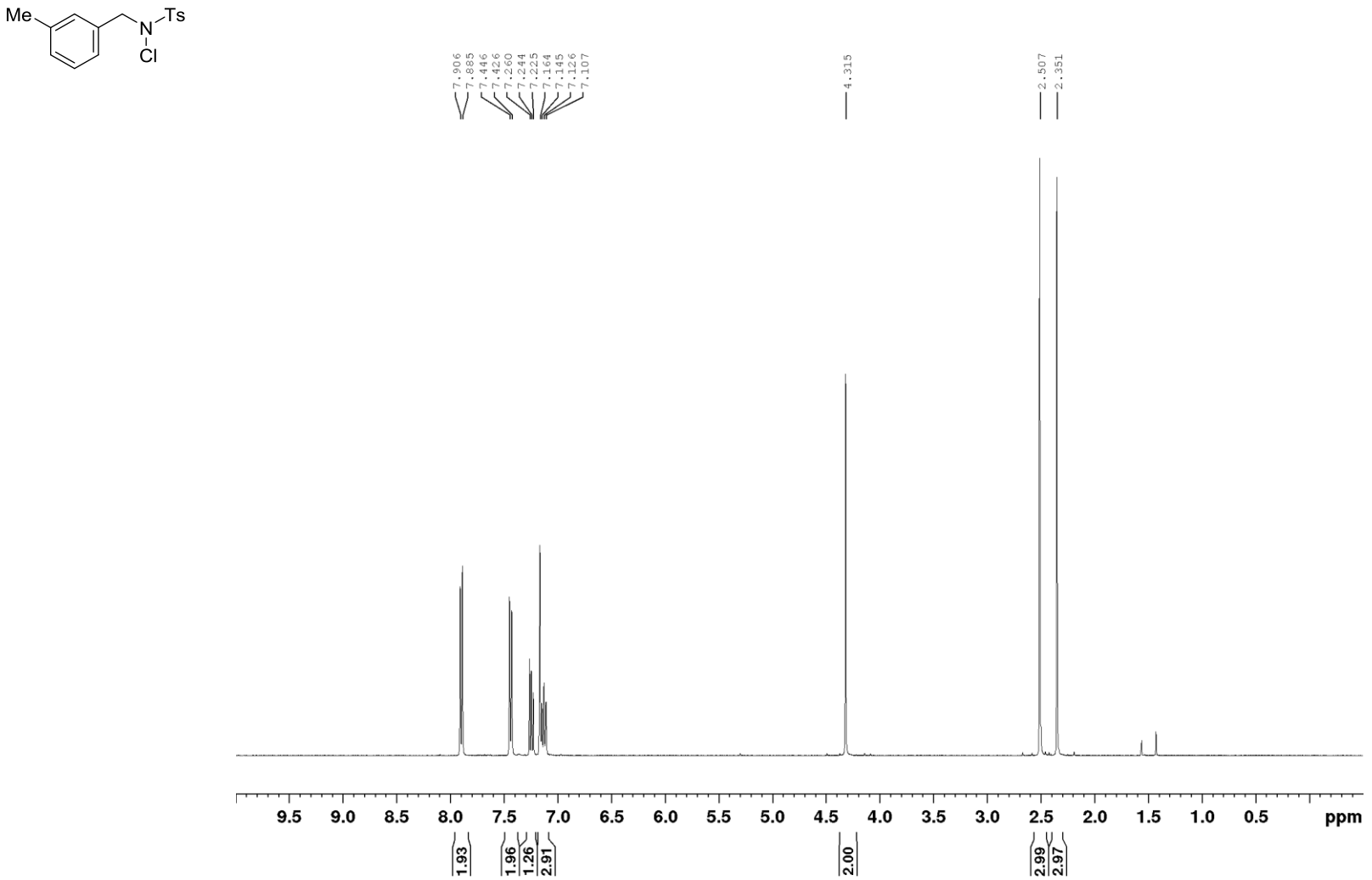
^{13}C NMR (100 MHz, $CDCl_3$)



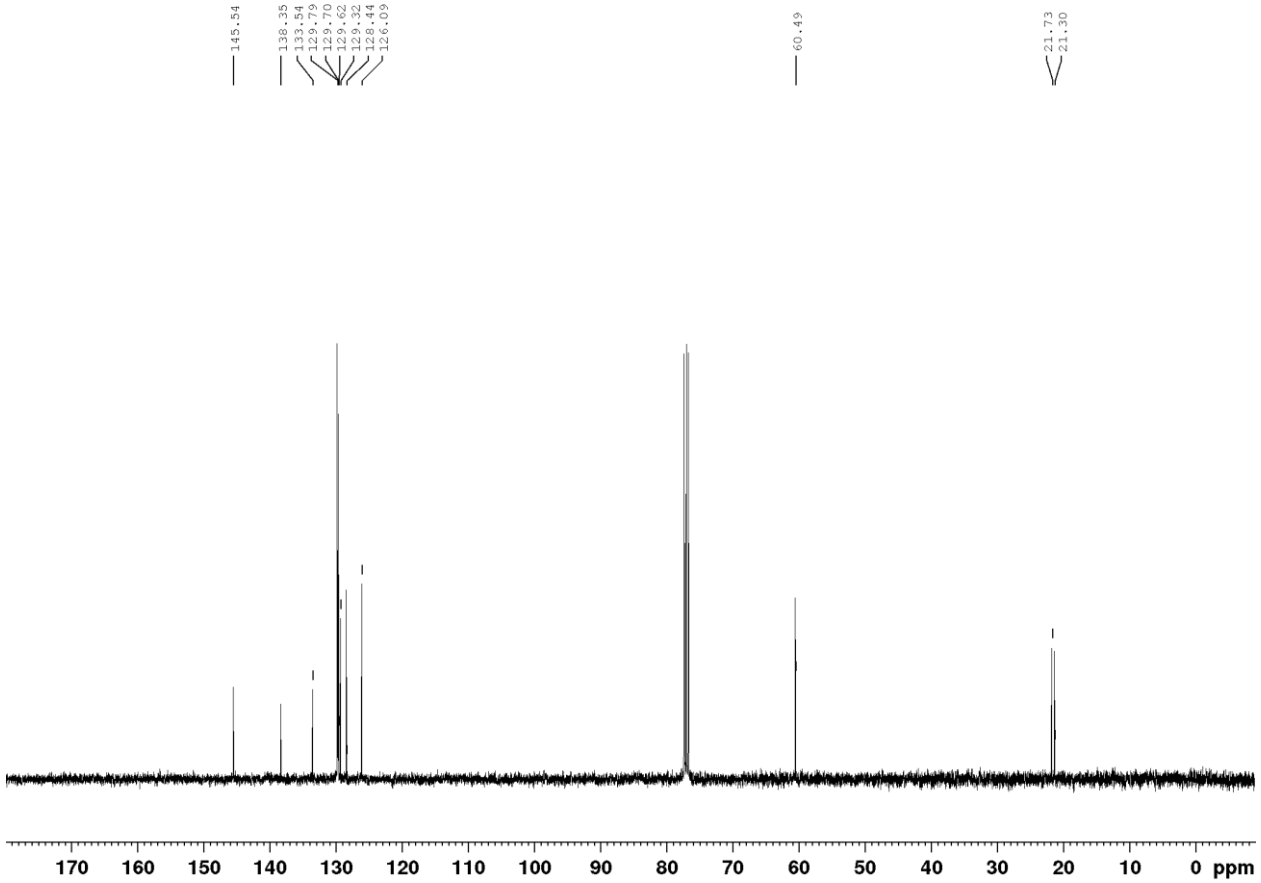
^{19}F NMR (188 MHz, $CDCl_3$)



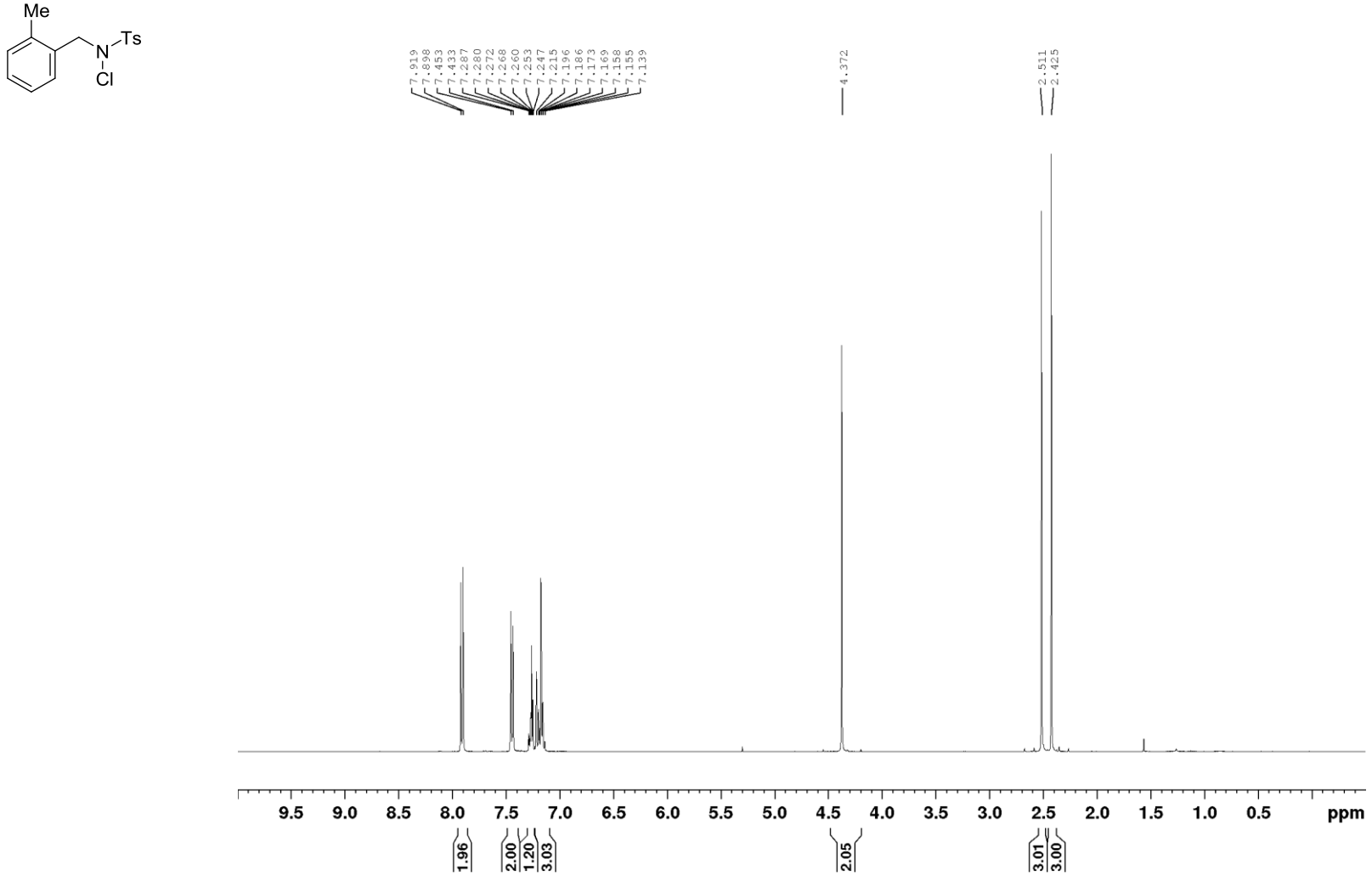
***N*-Chloro-4-methyl-*N*-(3-methylbenzyl)benzenesulfonamide** (**9a**): ^{1}H NMR (400 MHz, $CDCl_3$)



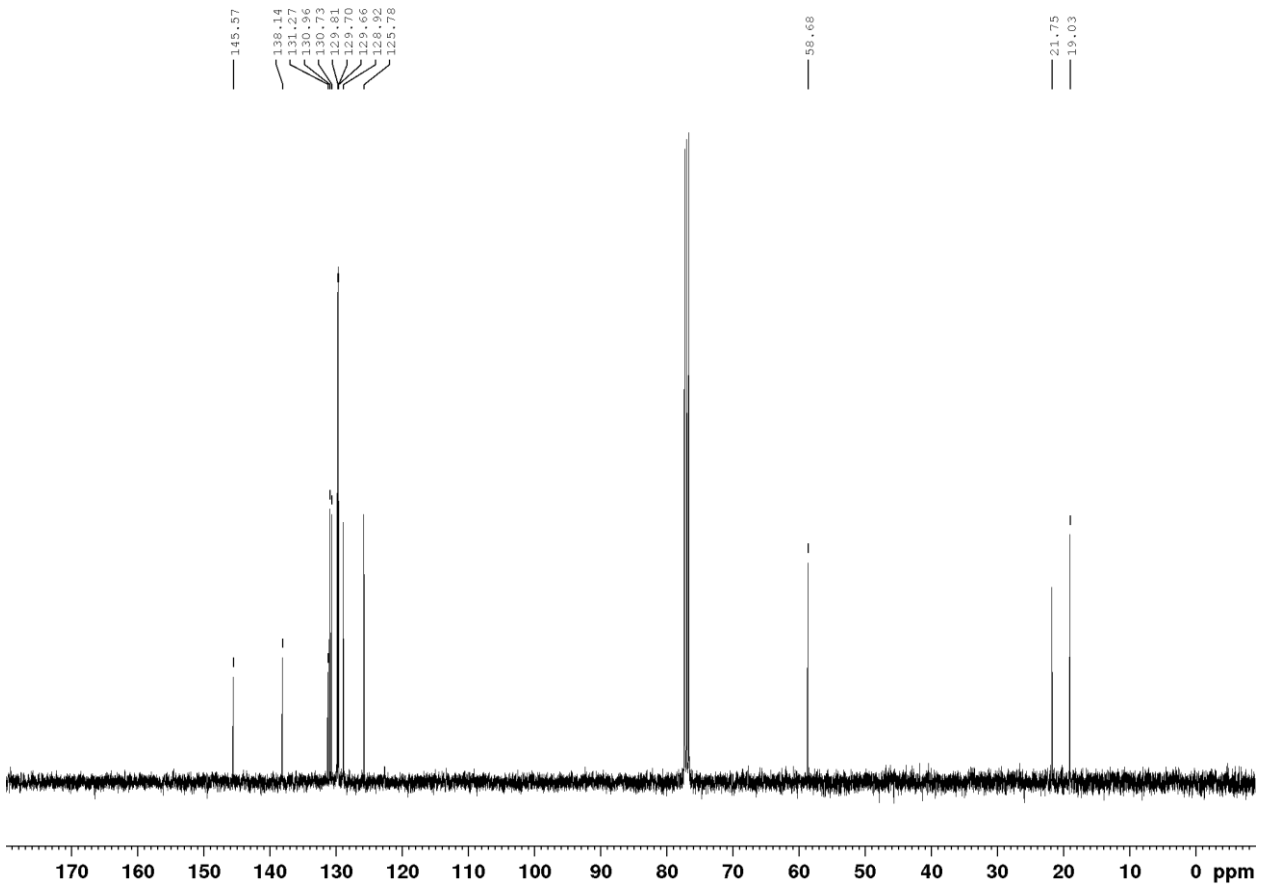
^{13}C NMR (100 MHz, $CDCl_3$)



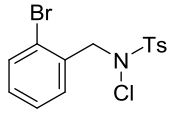
***N*-Chloro-4-methyl-*N*-(2-methylbenzyl)benzenesulfonamide** (**10a**): ^{1}H NMR (400 MHz, $CDCl_3$)

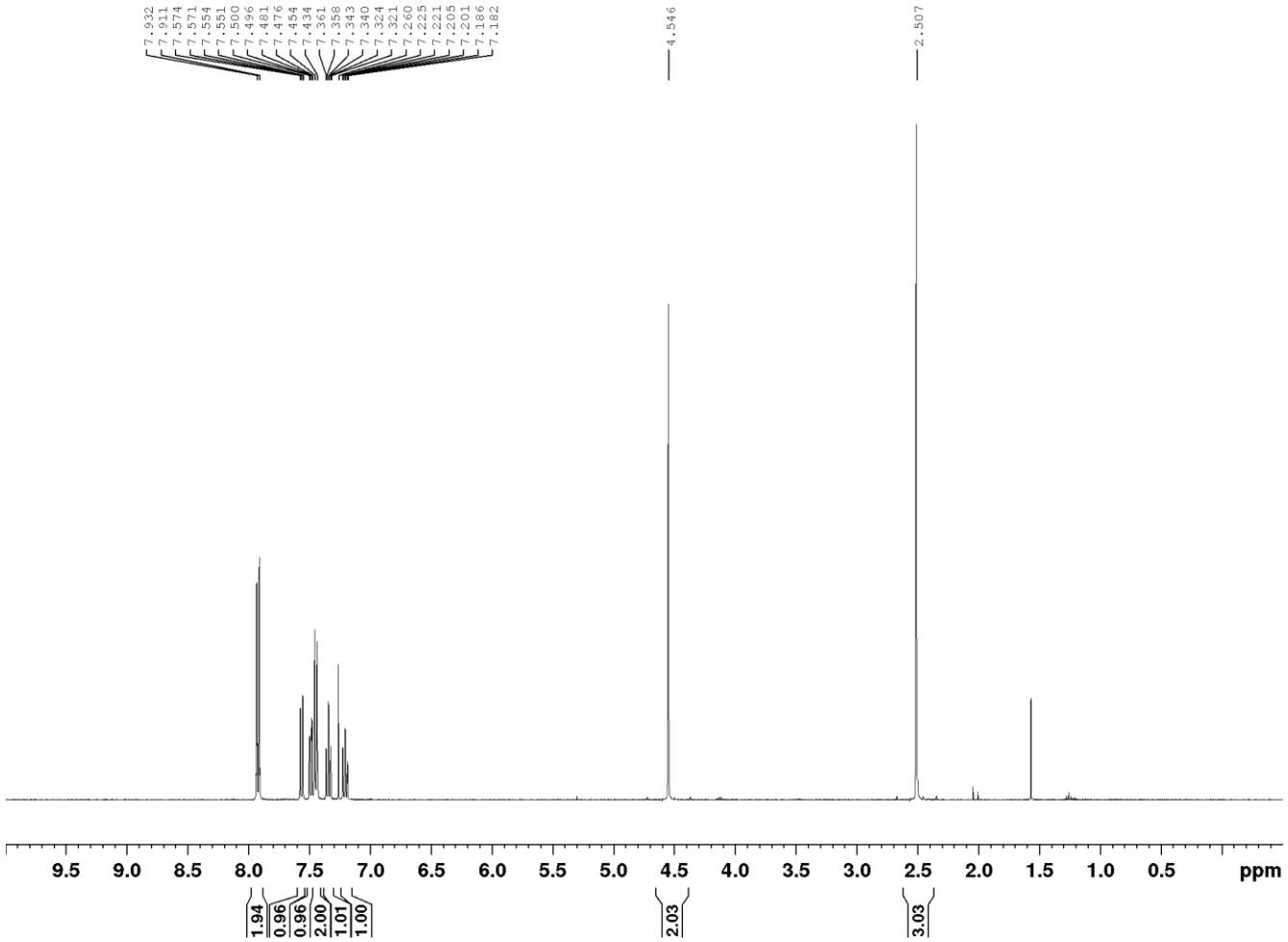


^{13}C NMR (100 MHz, $CDCl_3$)

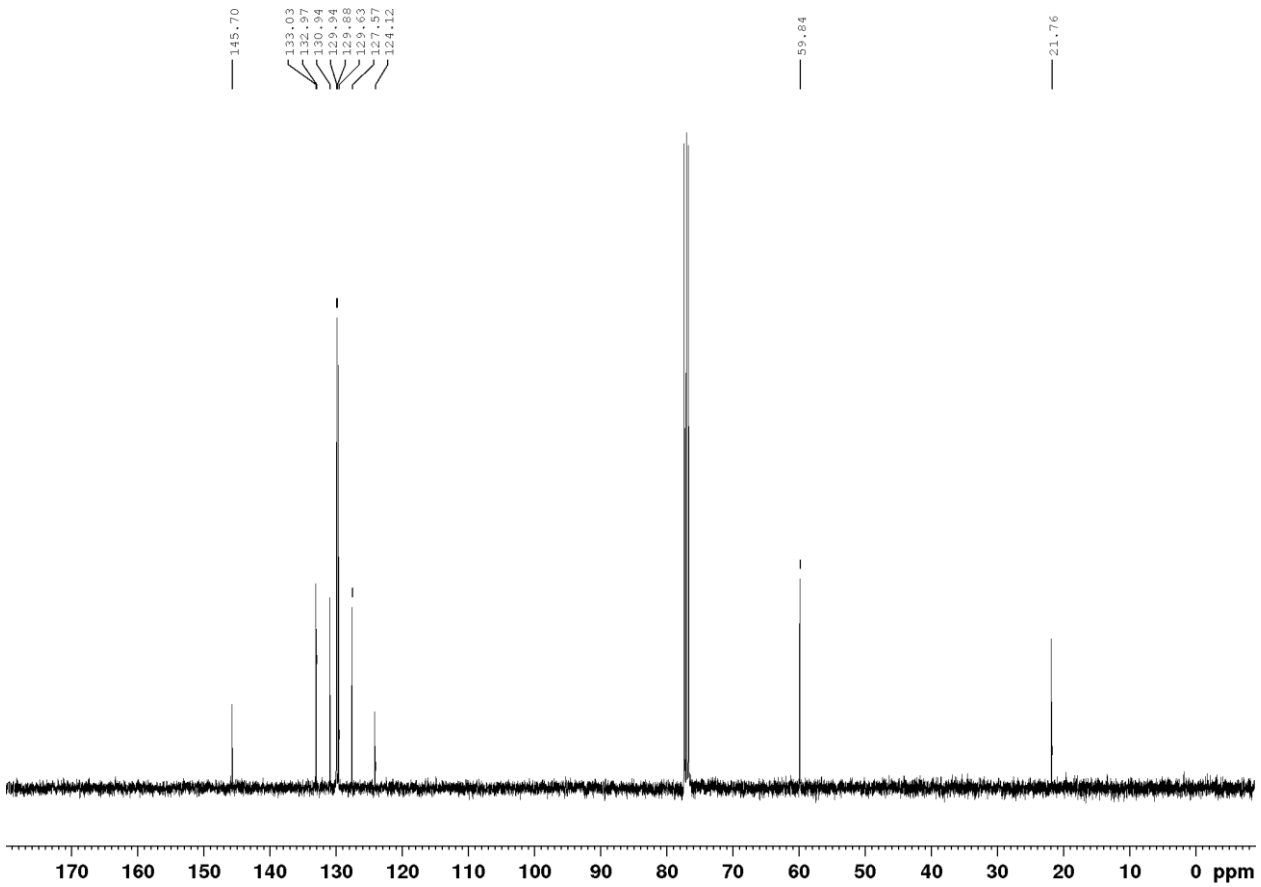


***N*-(2-Bromobenzyl)-*N*-chloro-4-methylbenzenesulfonamide** (**11a**): ^{1}H NMR (400 MHz, $CDCl_3$)

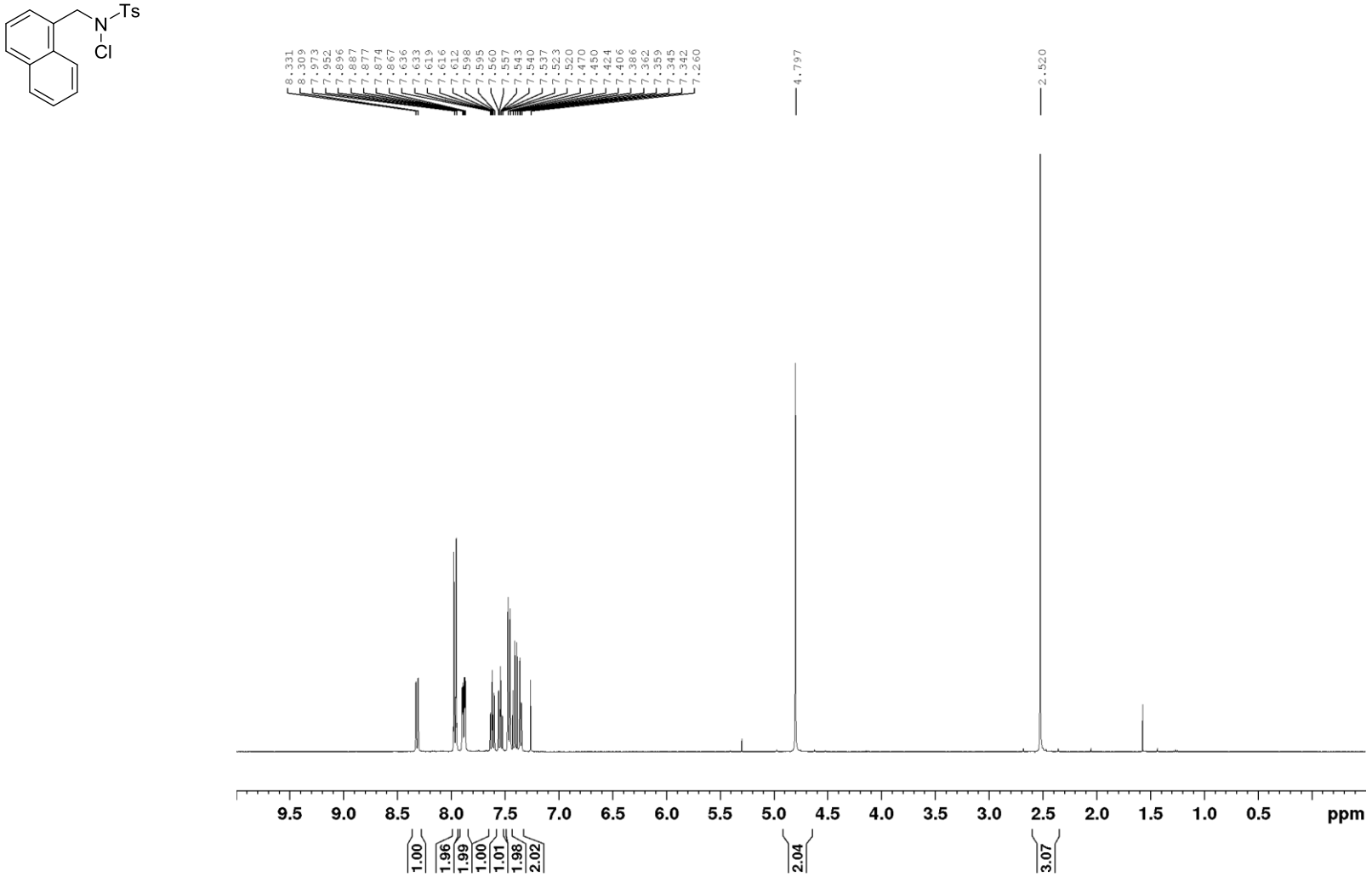




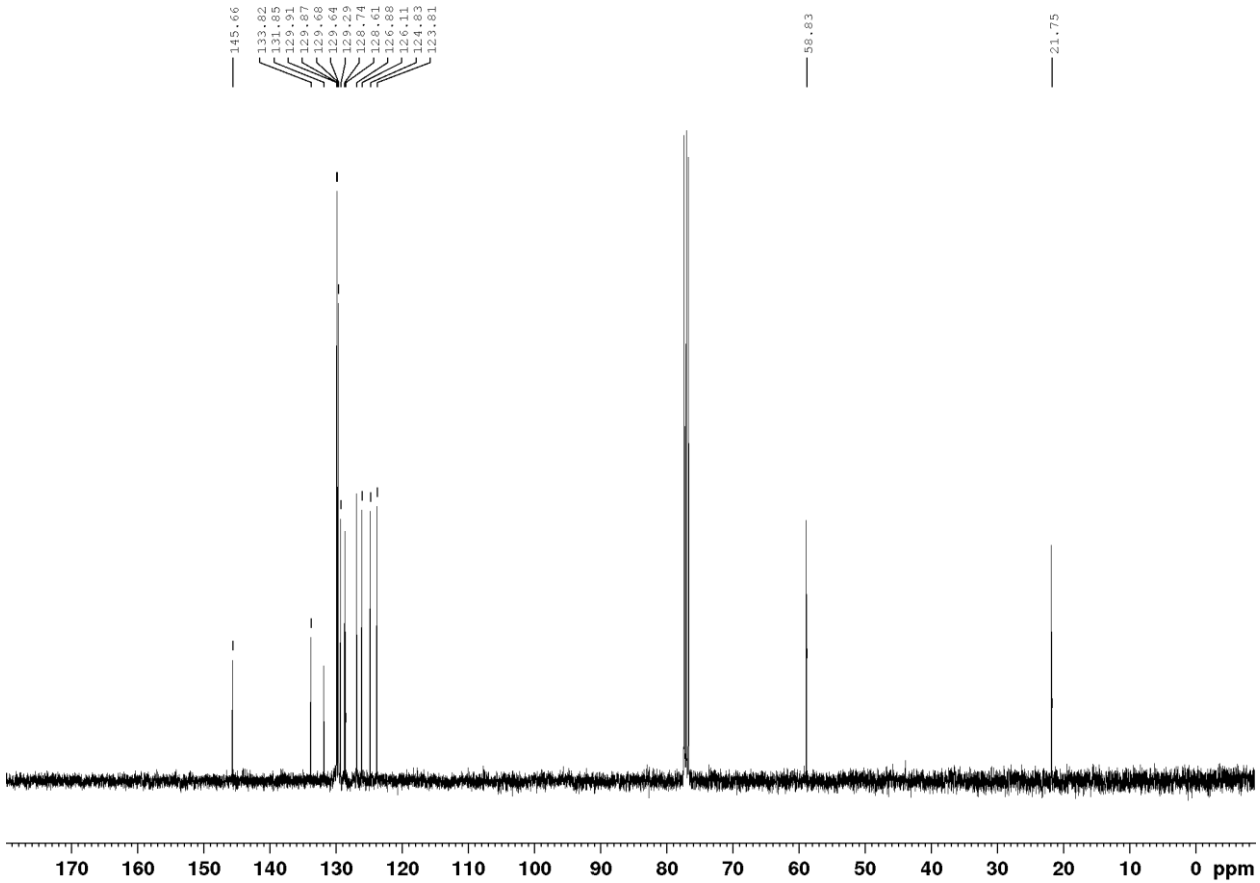
^{13}C NMR (100 MHz, $CDCl_3$)



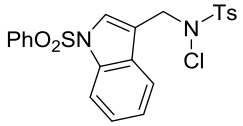
***N*-Chloro-4-methyl-*N*-(naphthalen-1-ylmethyl)benzenesulfonamide** (**12a**): ^{1}H NMR (400 MHz, $CDCl_3$)

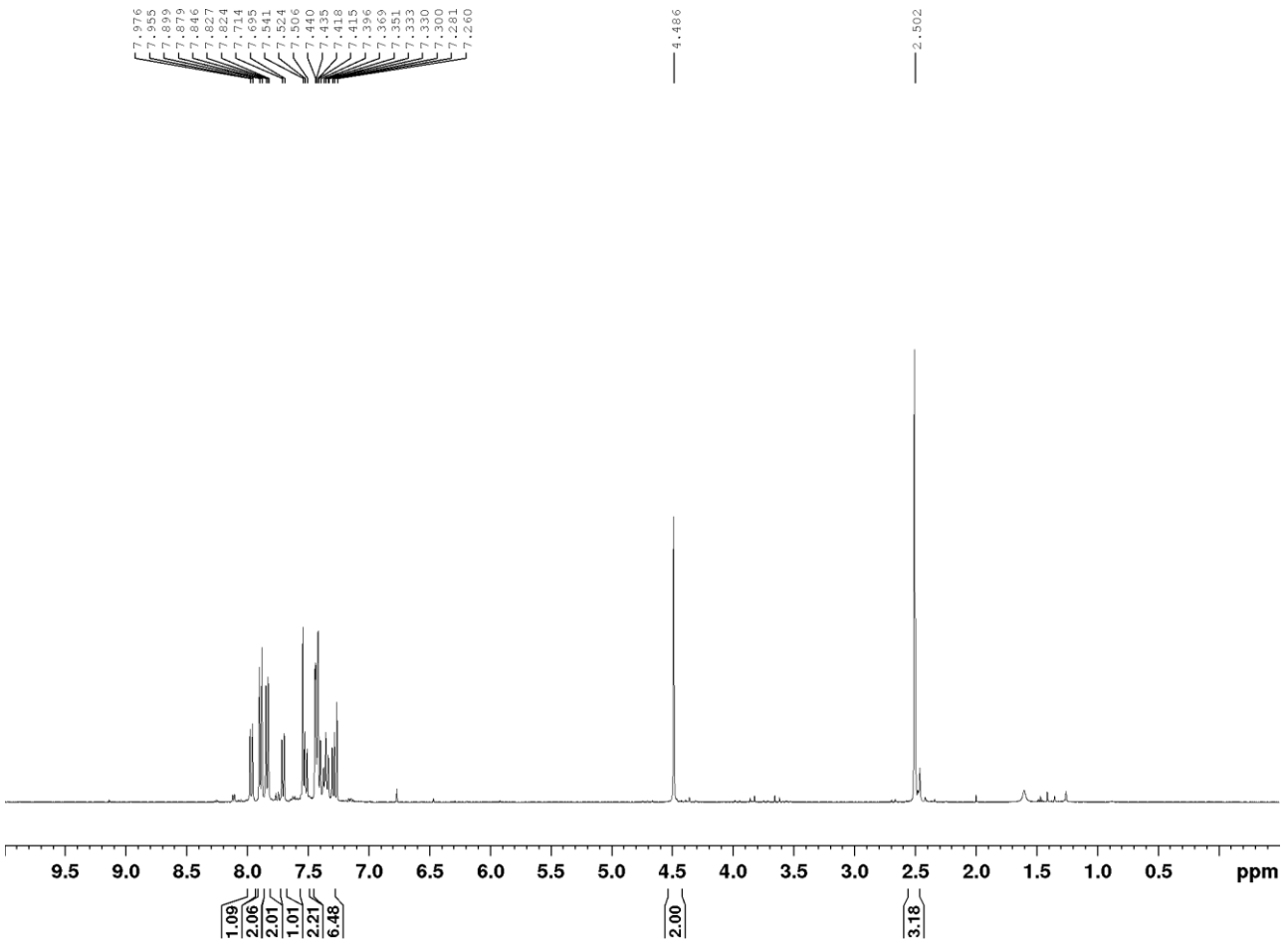


^{13}C NMR (100 MHz, $CDCl_3$)

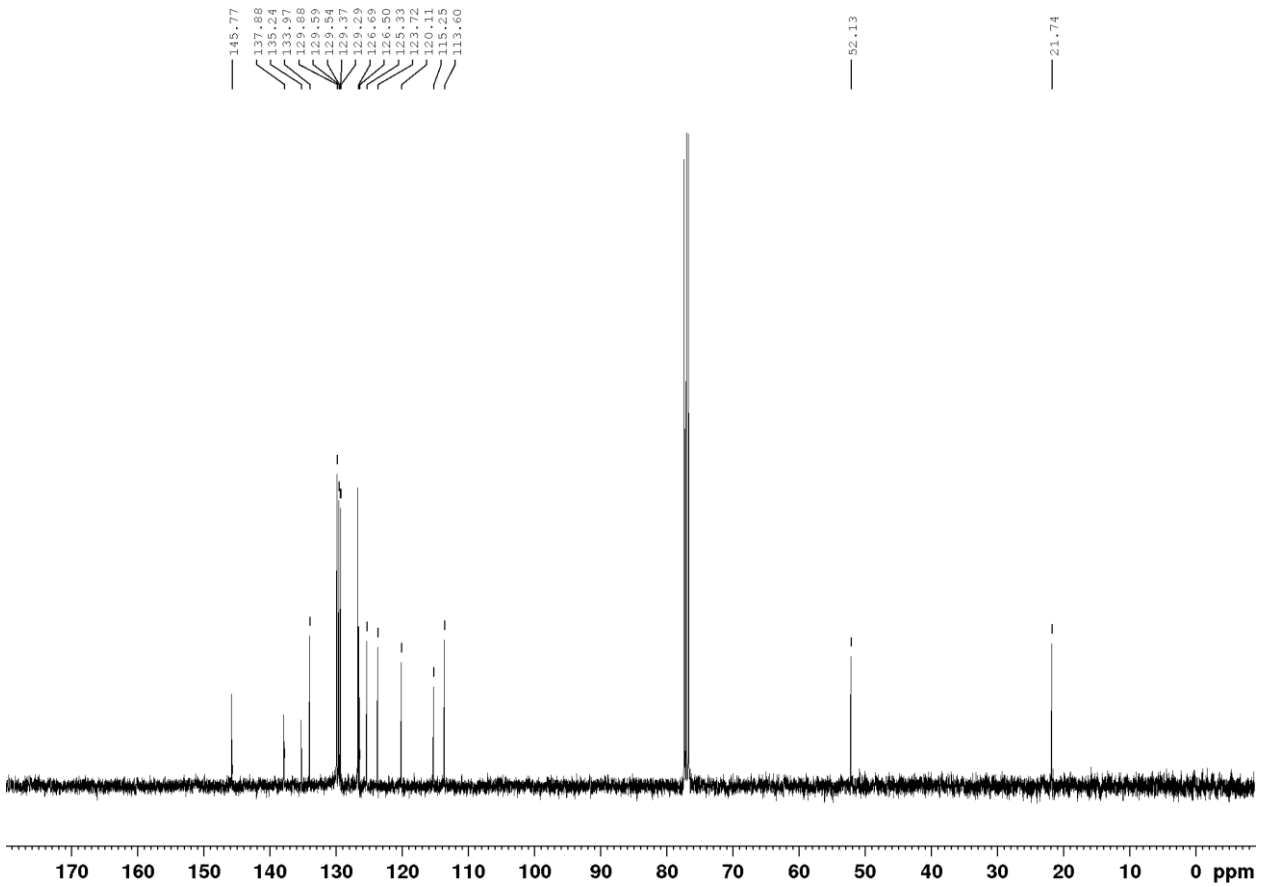


***N*-Chloro-4-methyl-*N*-((1-(phenylsulfonyl)-1*H*-indol-3-yl)methyl)benzenesulfonamide** (**13a**): ^{1}H NMR (400 MHz, $CDCl_3$)

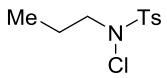


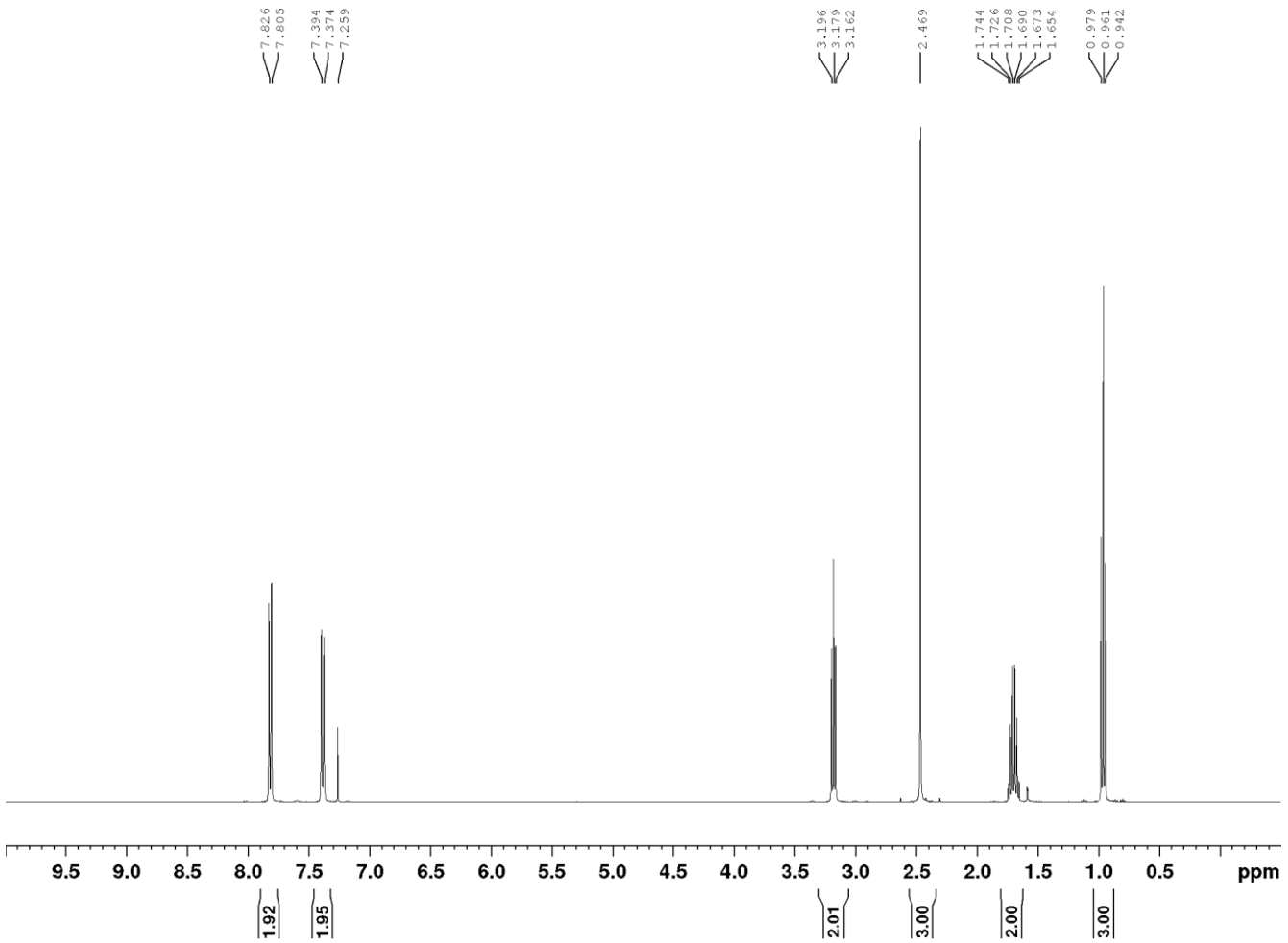


^{13}C NMR (100 MHz, $CDCl_3$)

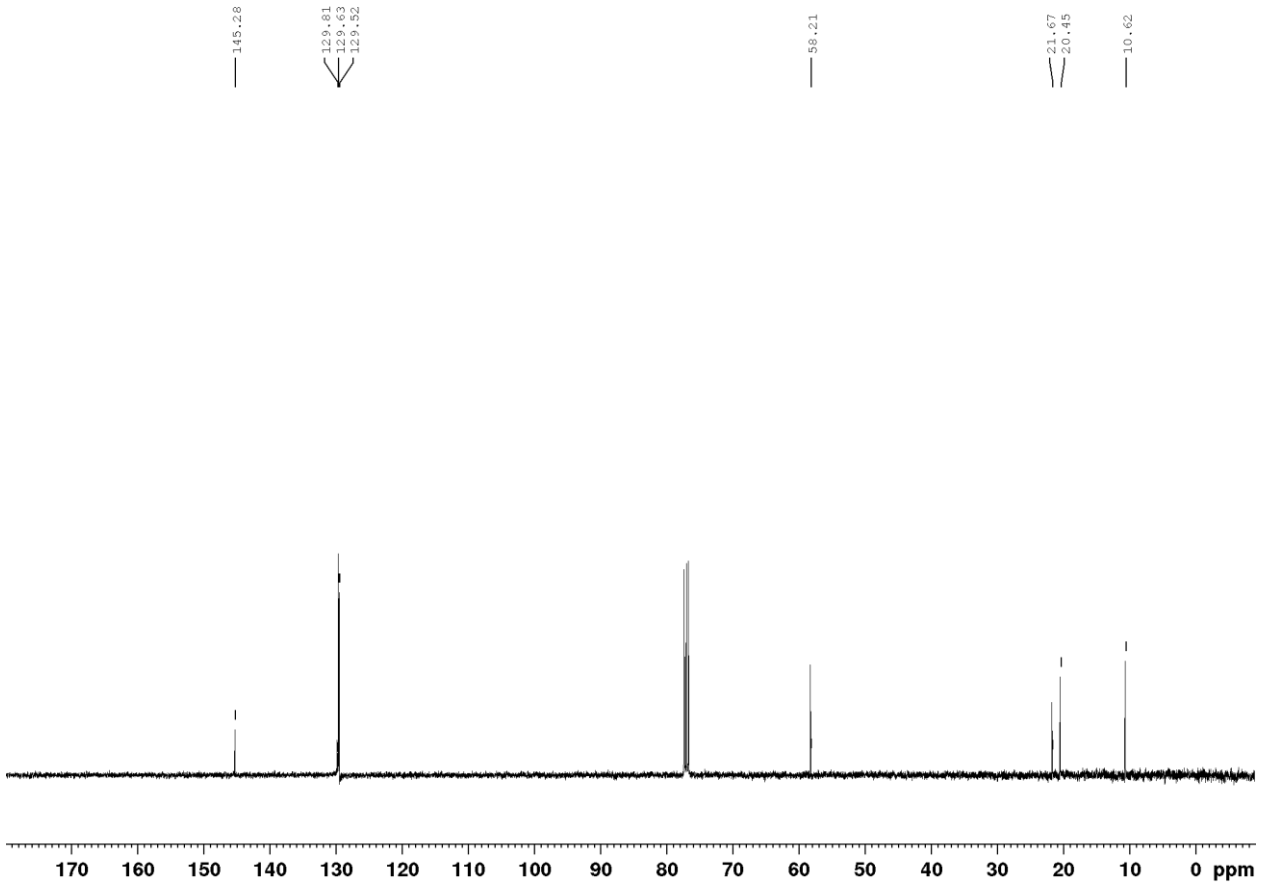


***N*-Chloro-4-methyl-*N*-propylbenzenesulfonamide** (**14a**): ^{1}H NMR (400 MHz, $CDCl_3$)

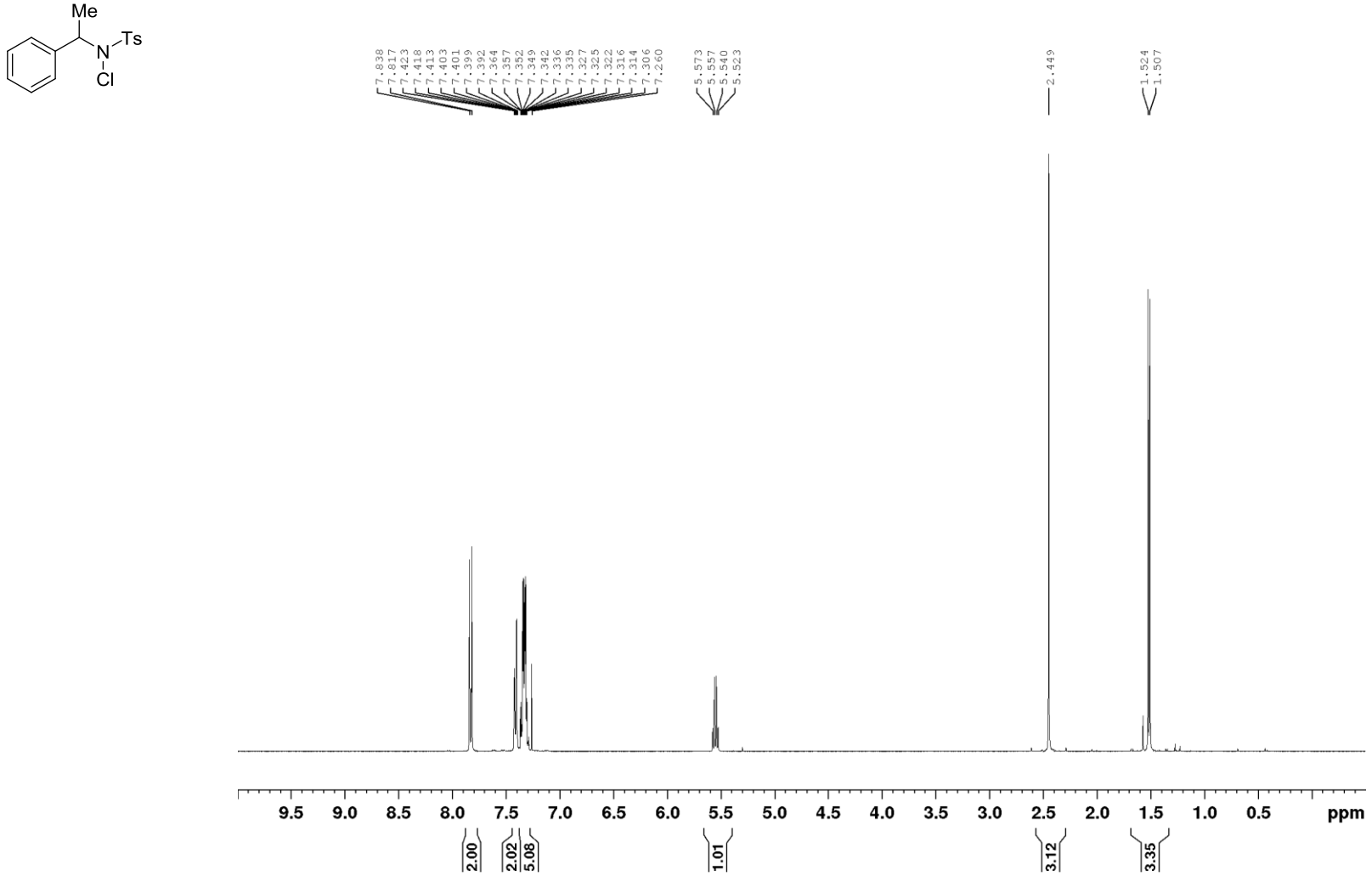




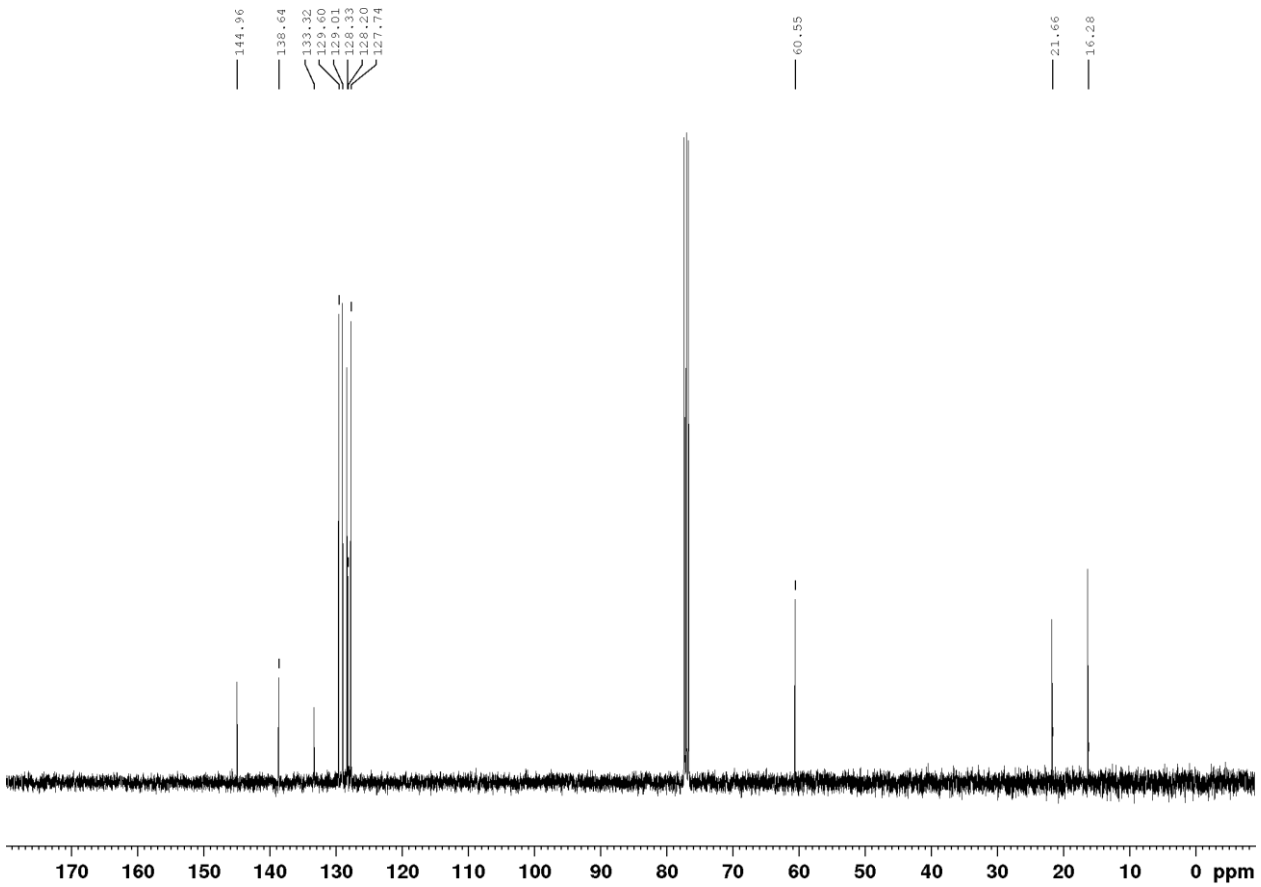
^{13}C NMR (100 MHz, $CDCl_3$)



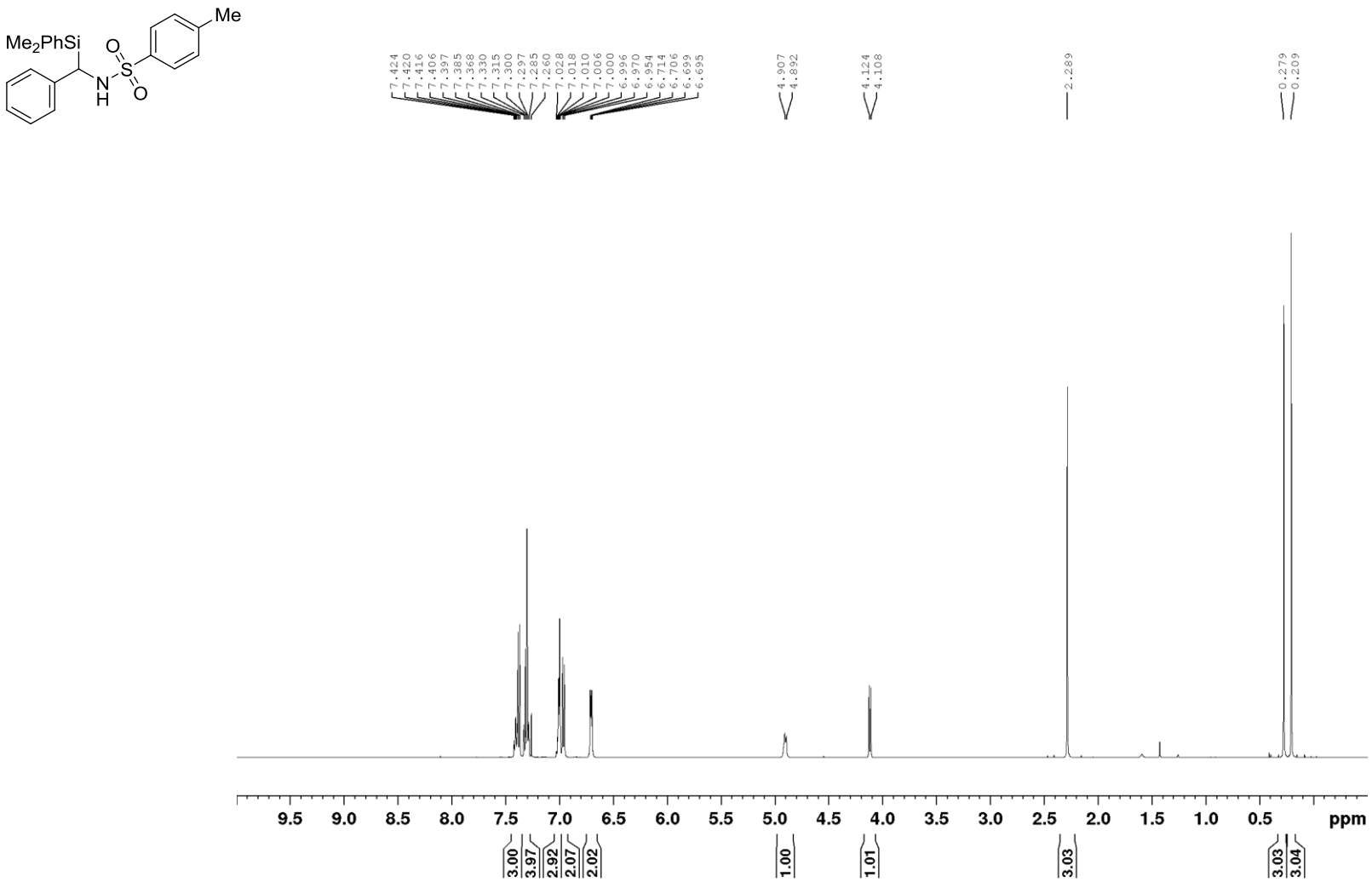
***N*-Chloro-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide** (**15a**): ^{1}H NMR (400 MHz, $CDCl_3$)



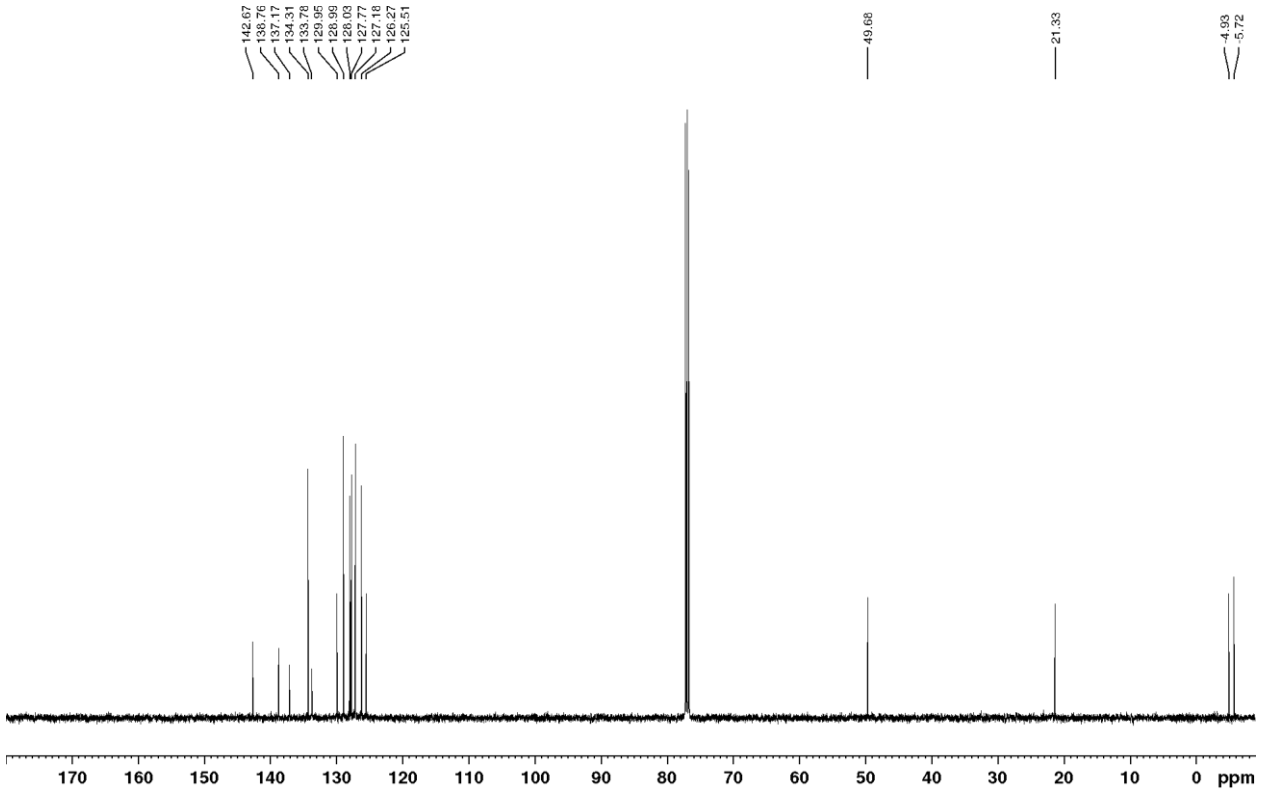
^{13}C NMR (100 MHz, $CDCl_3$)



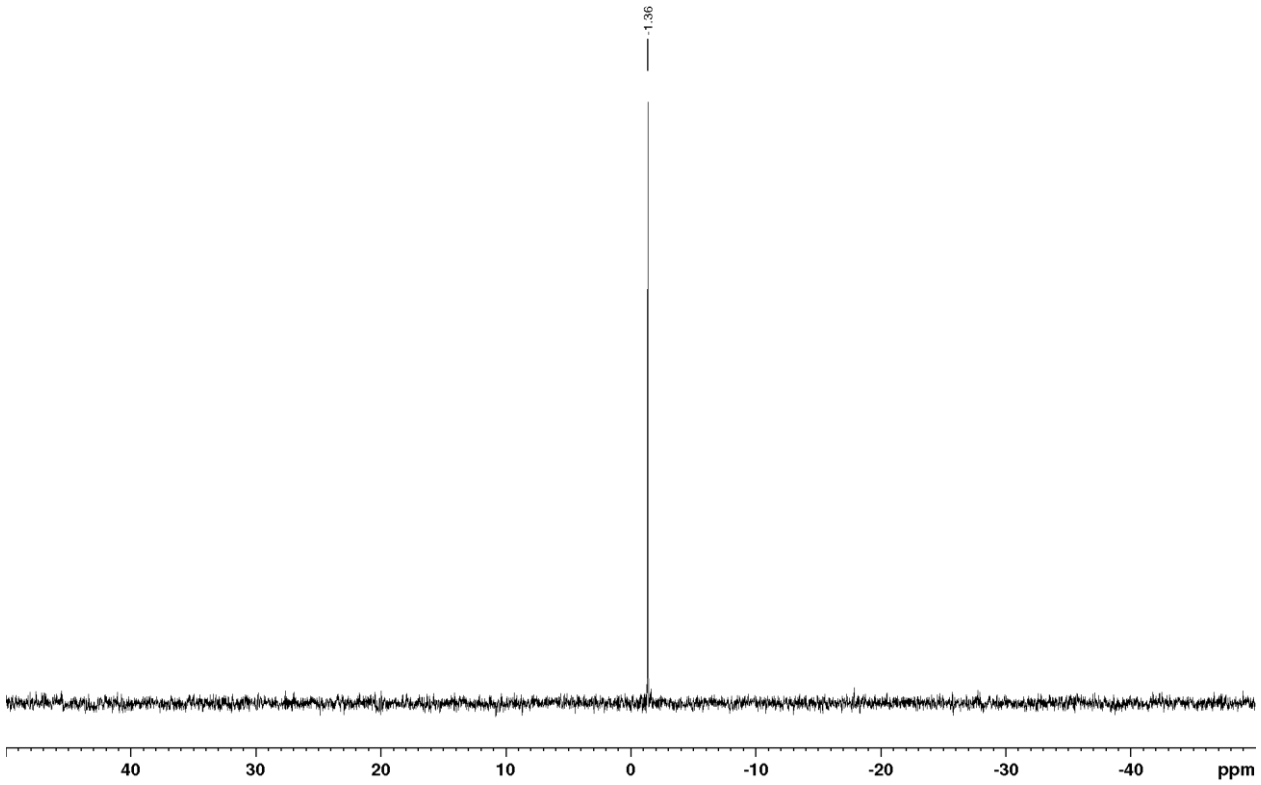
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-4-methylbenzenesulfonamide** (**2a**): ^{1}H NMR (500 MHz, $CDCl_3$)



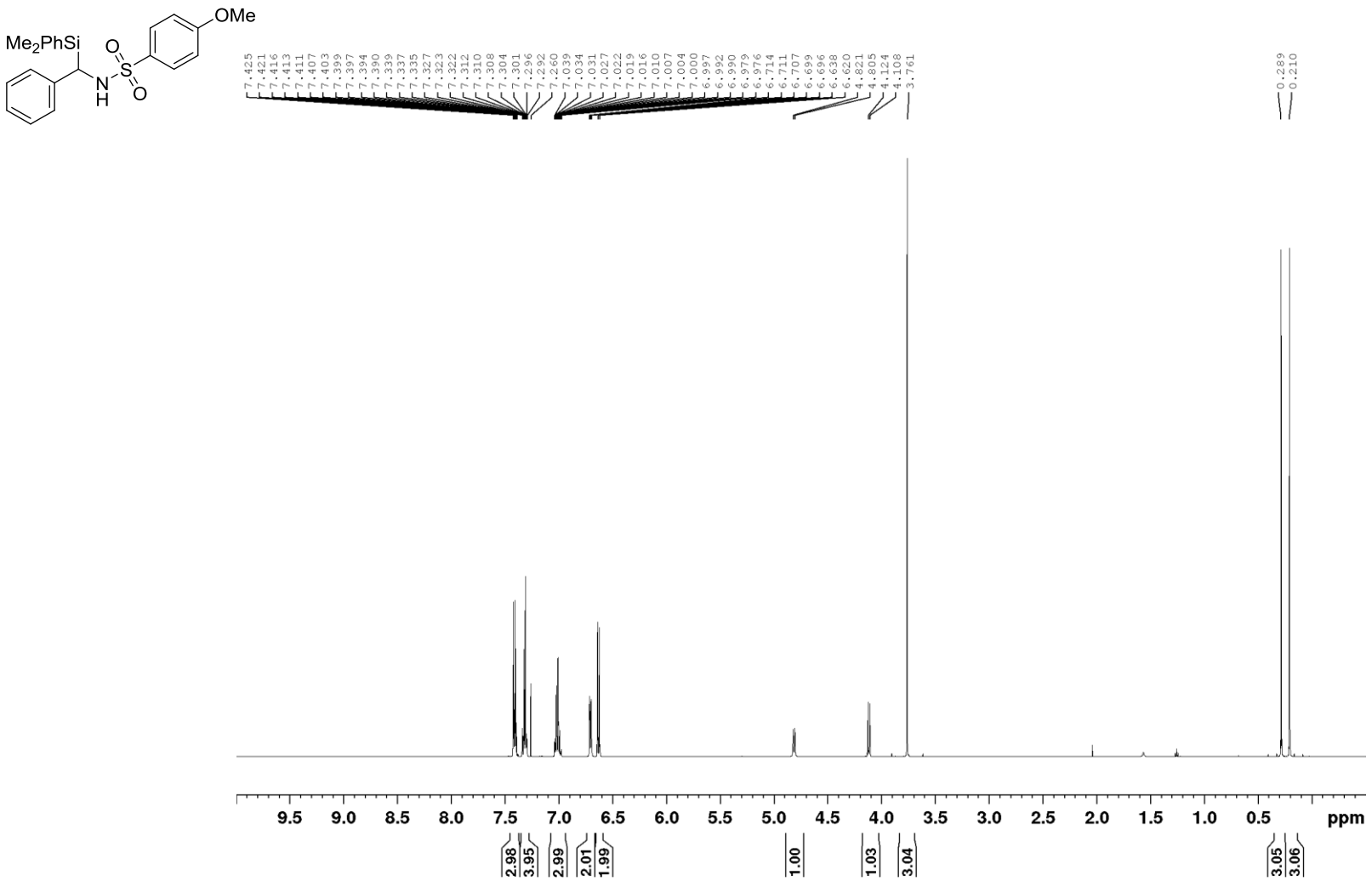
^{13}C NMR (125 MHz, $CDCl_3$)



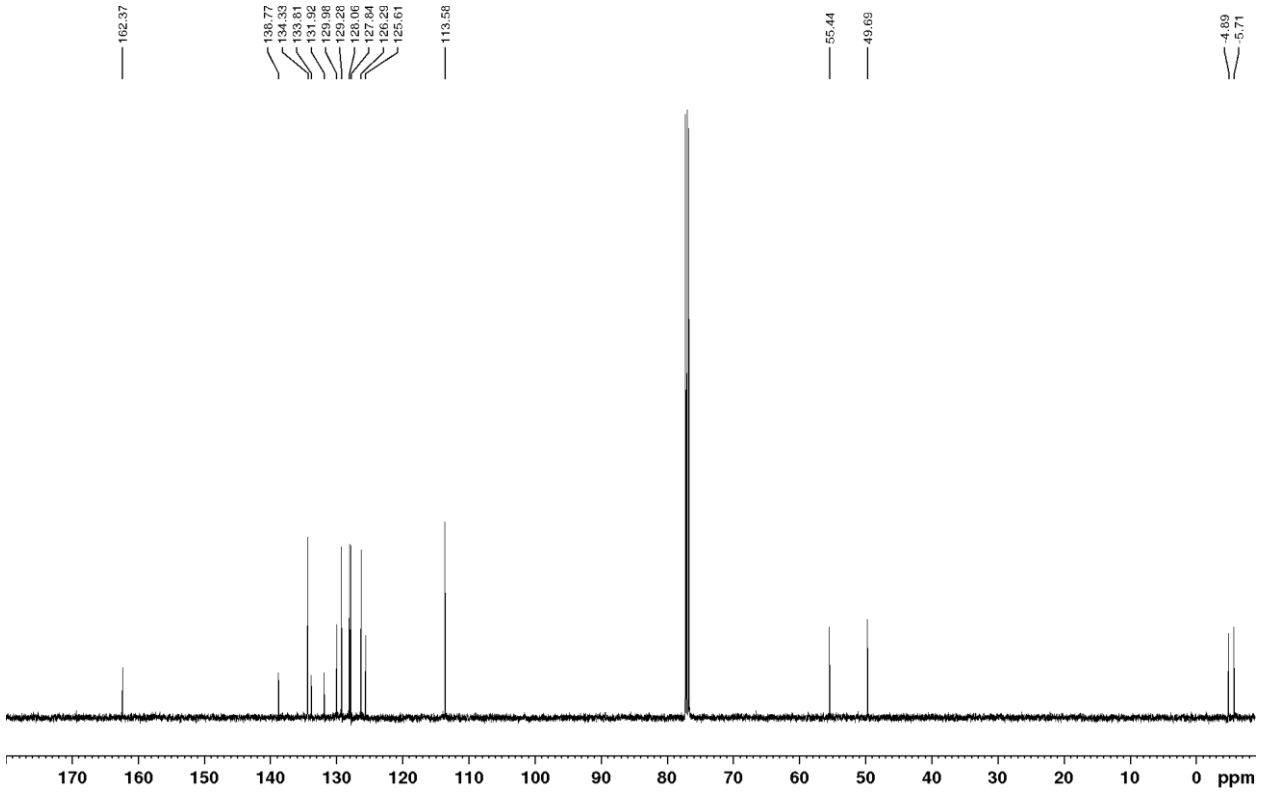
^{29}Si NMR (99 MHz, $CDCl_3$)



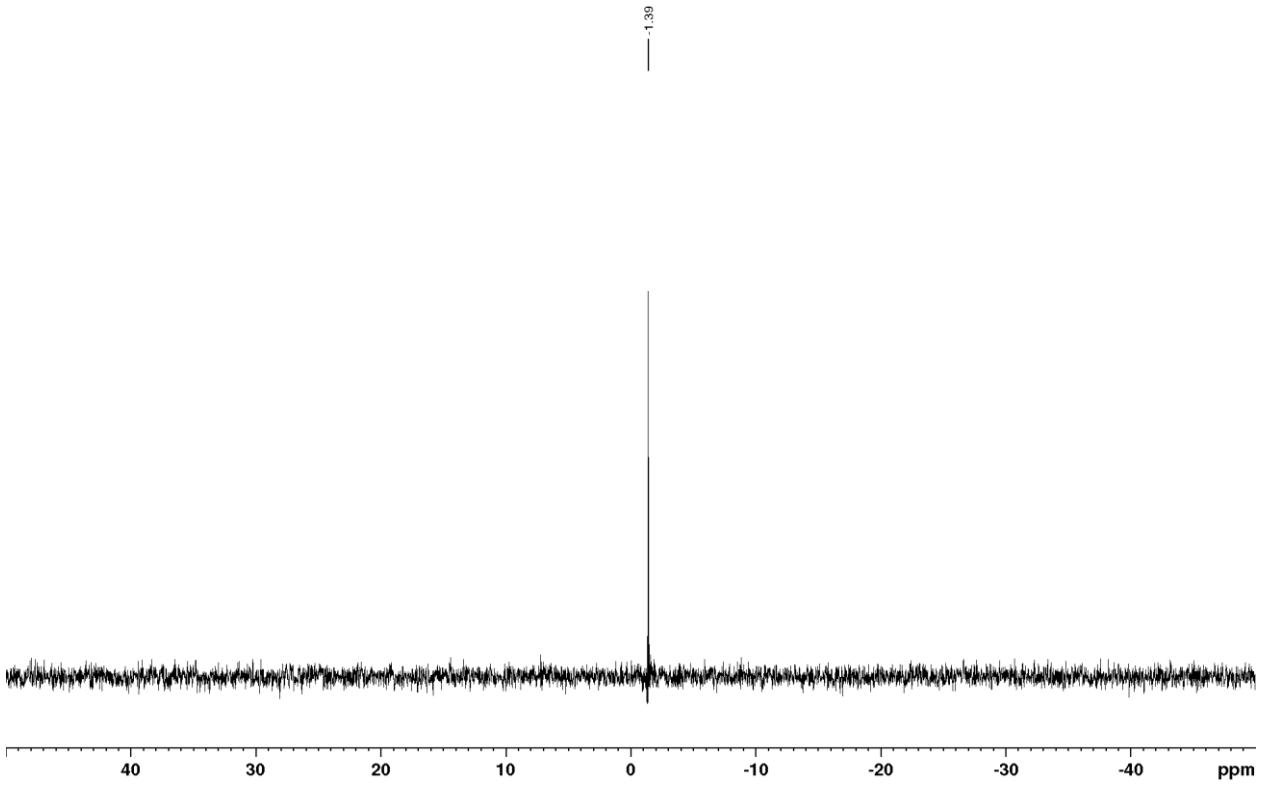
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-4-methoxybenzenesulfonamide** (**2b**): ^{1}H NMR (500 MHz, $CDCl_3$)



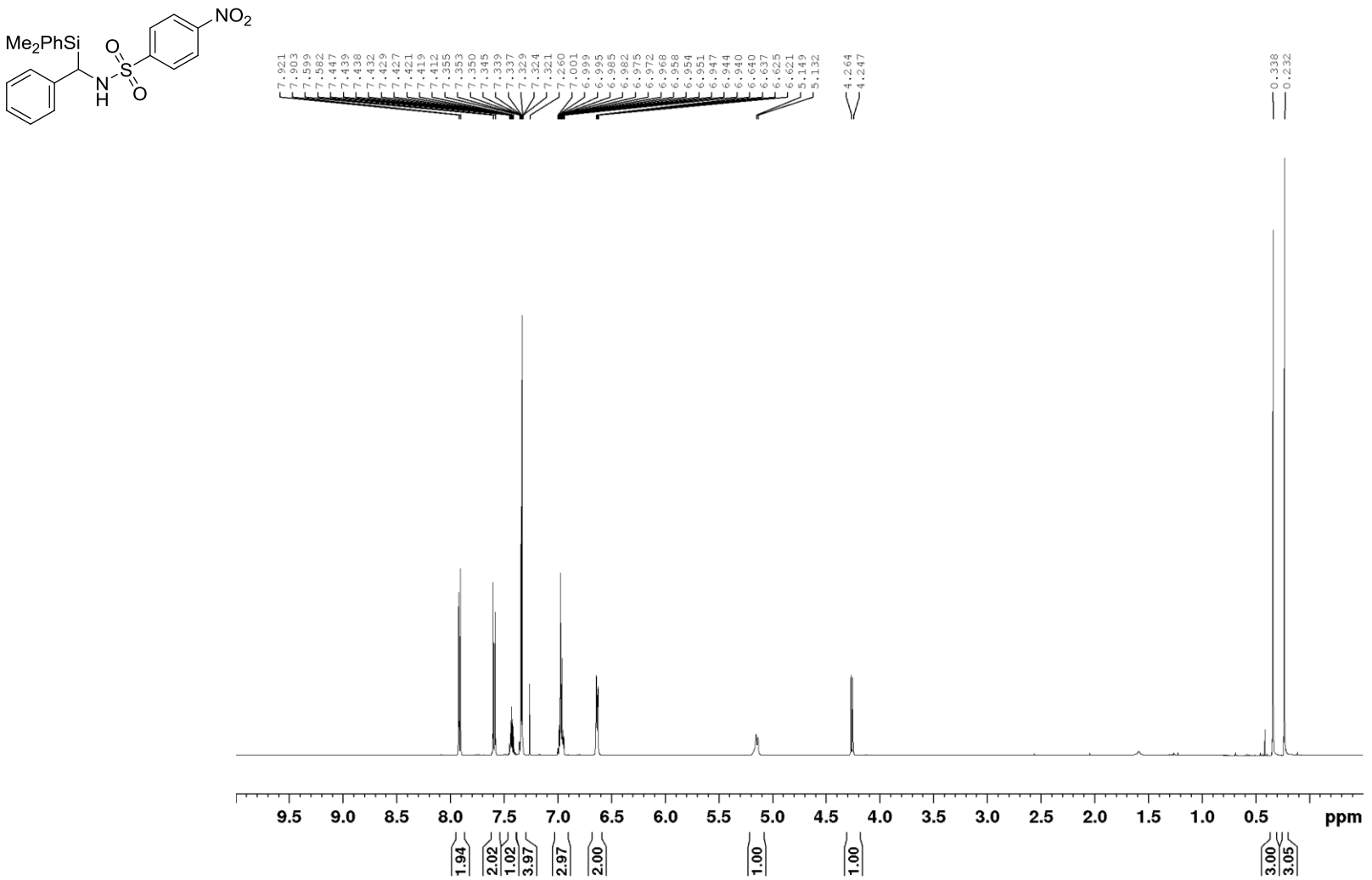
^{13}C NMR (125 MHz, $CDCl_3$)



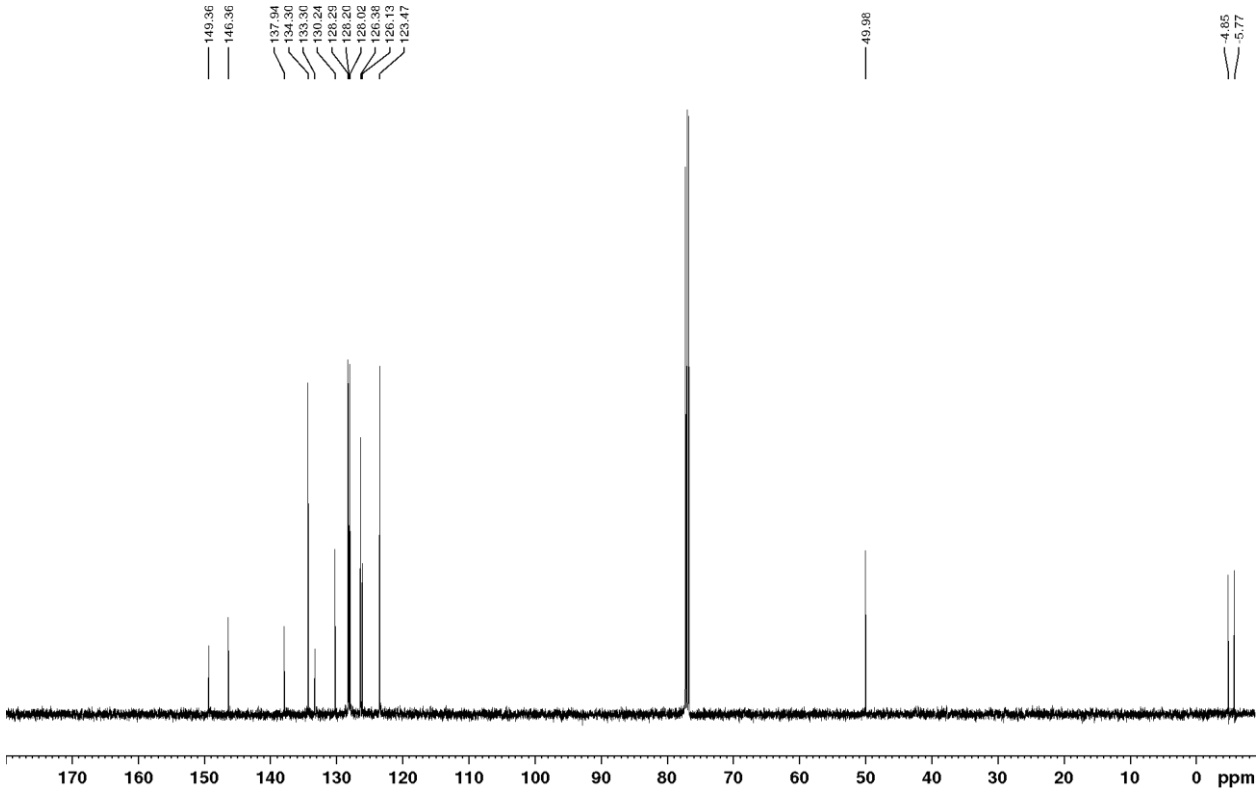
^{29}Si NMR (99 MHz, $CDCl_3$)



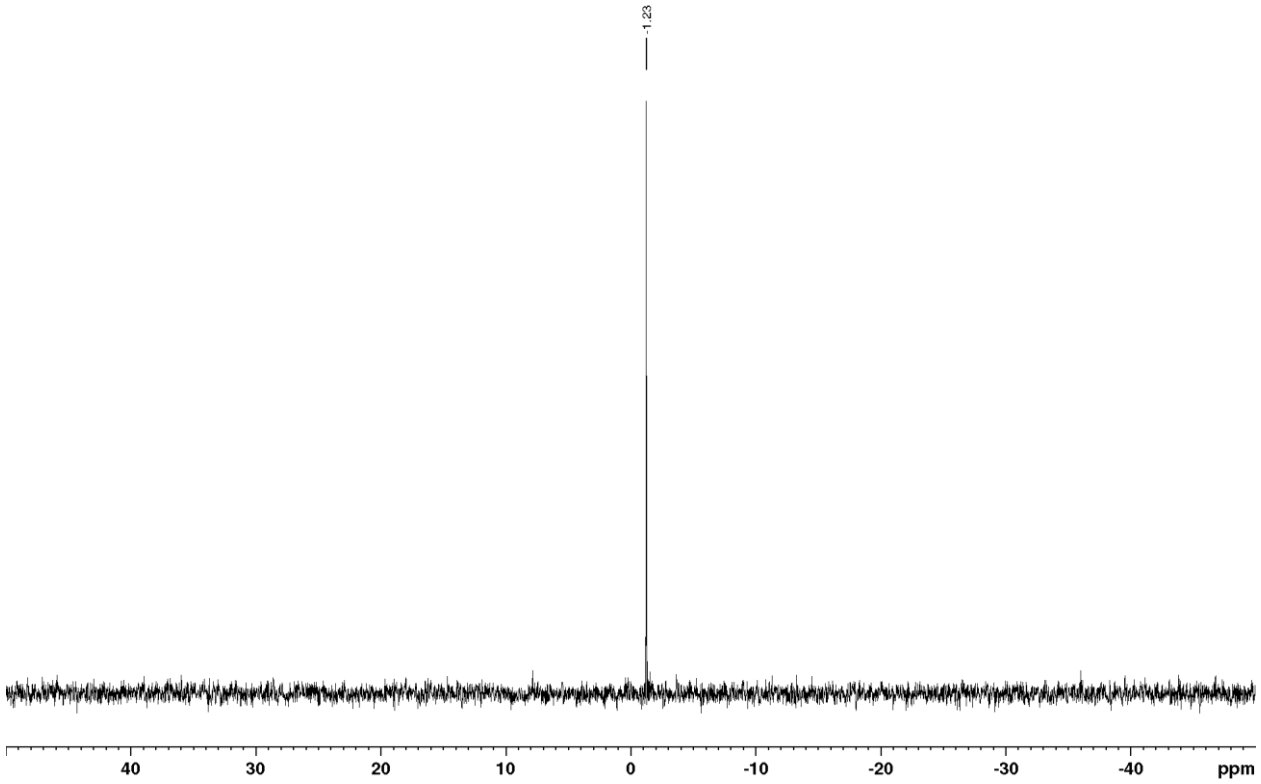
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-4-nitrobenzenesulfonamide** (**2c**): ^{1}H NMR (500 MHz, $CDCl_3$)



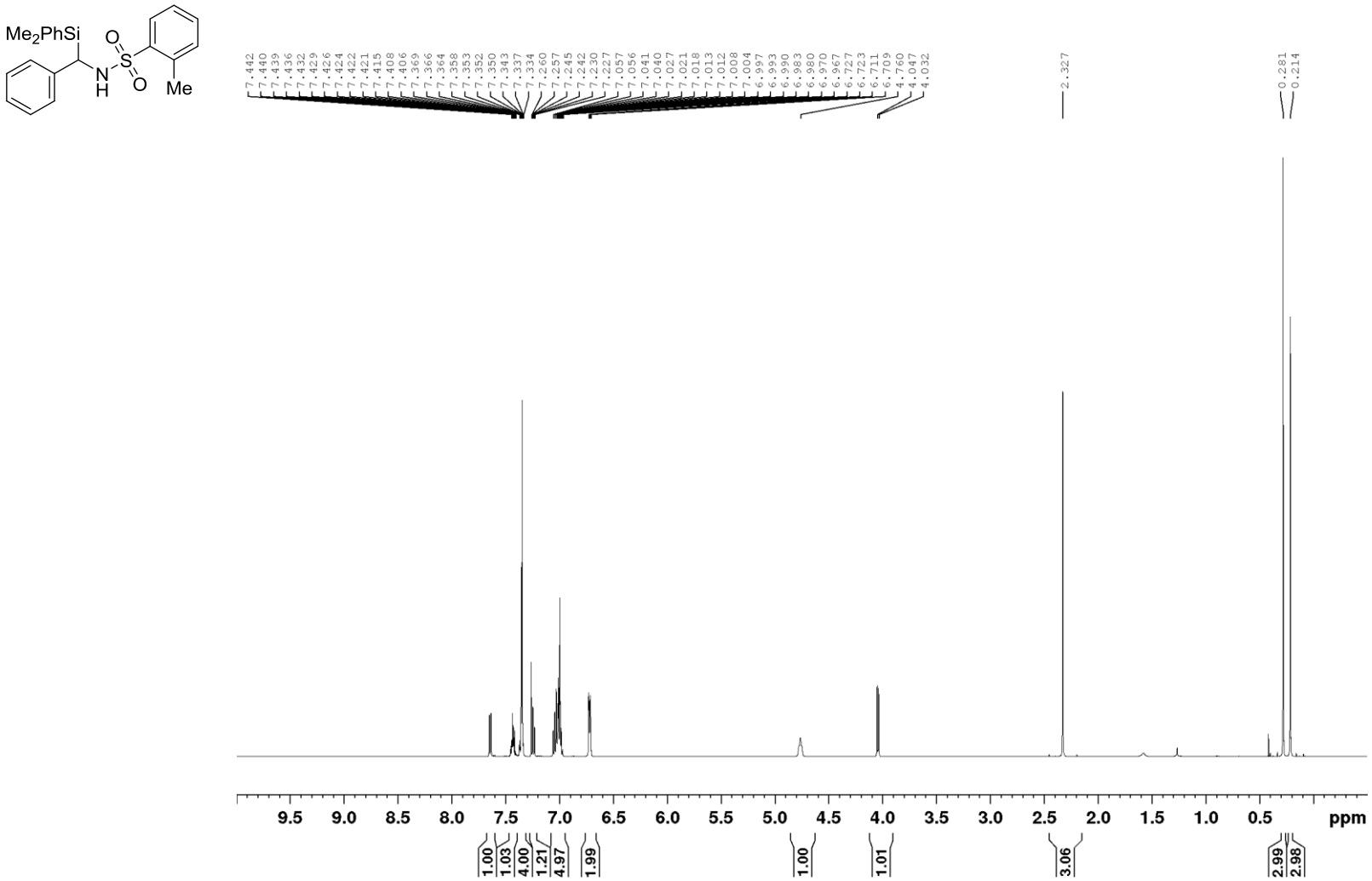
^{13}C NMR (125 MHz, $CDCl_3$)



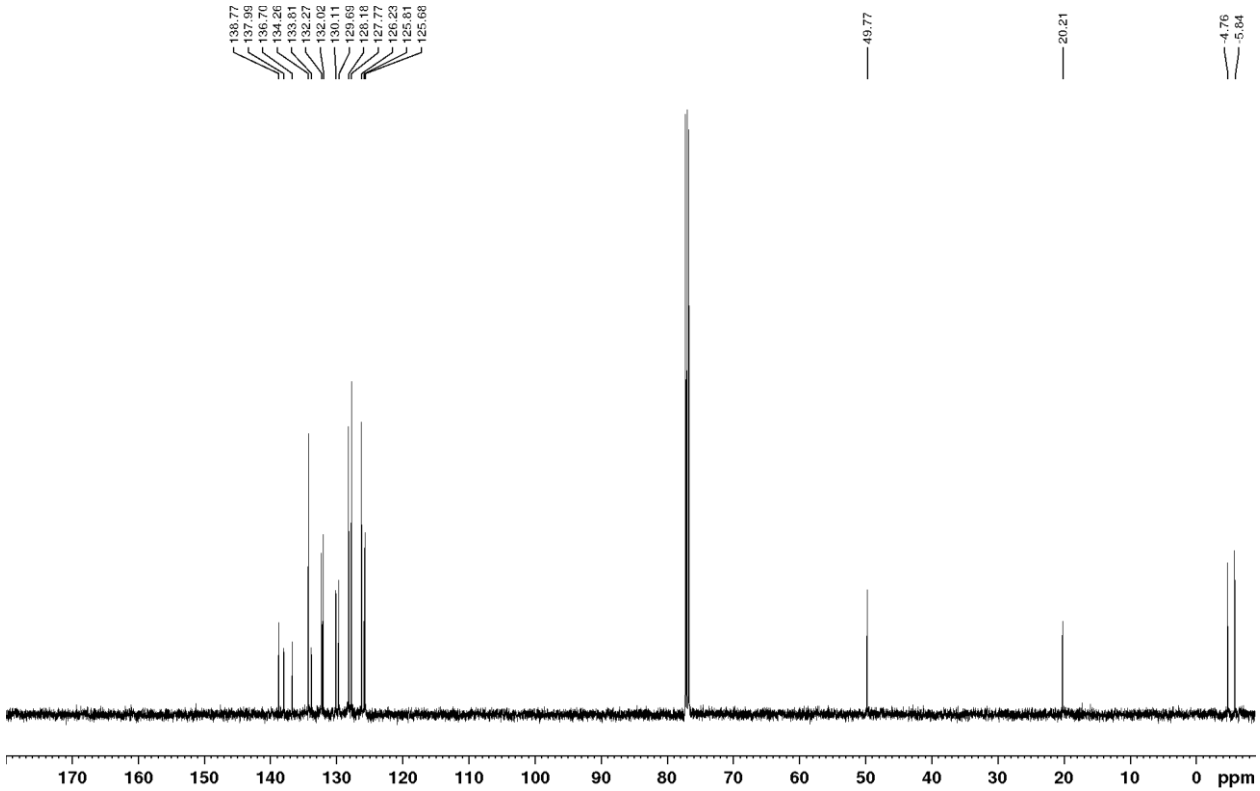
^{29}Si NMR (99 MHz, $CDCl_3$)



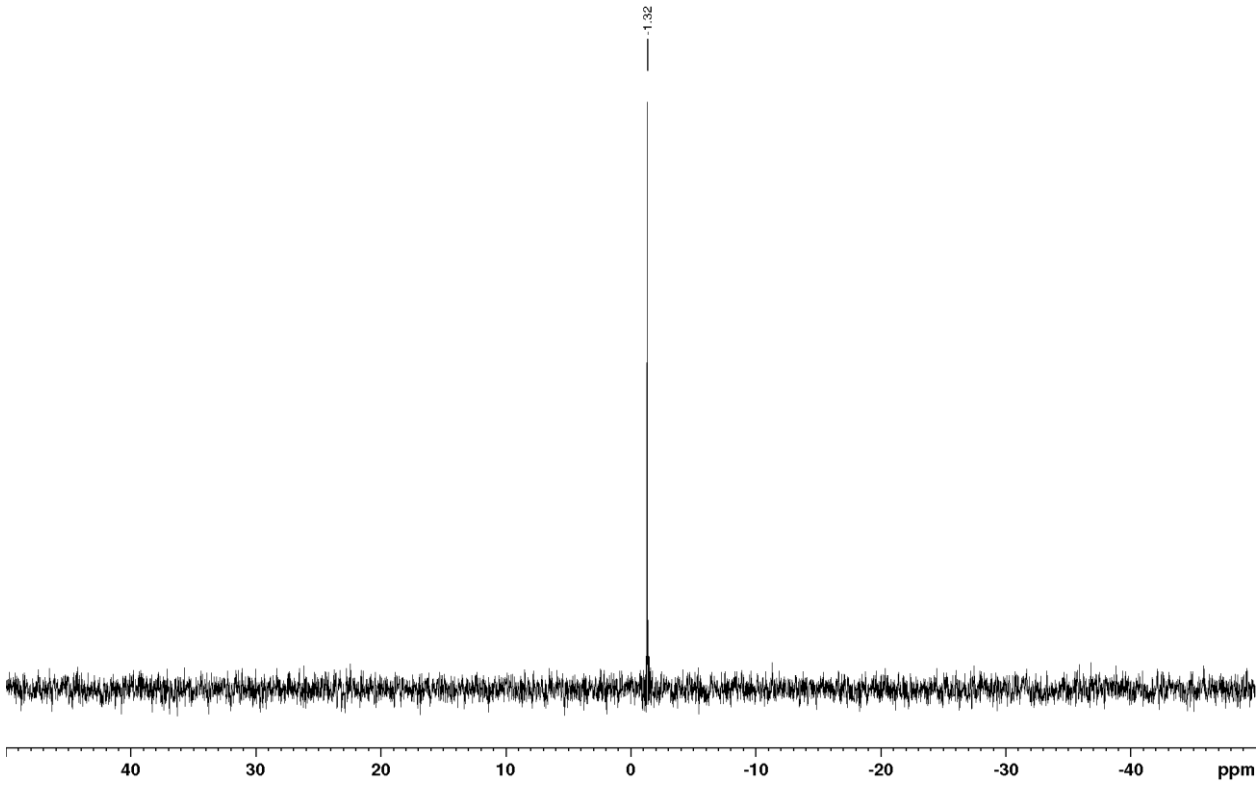
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-2-methylbenzenesulfonamide** (**2d**): ^{1}H NMR (500 MHz, $CDCl_3$)



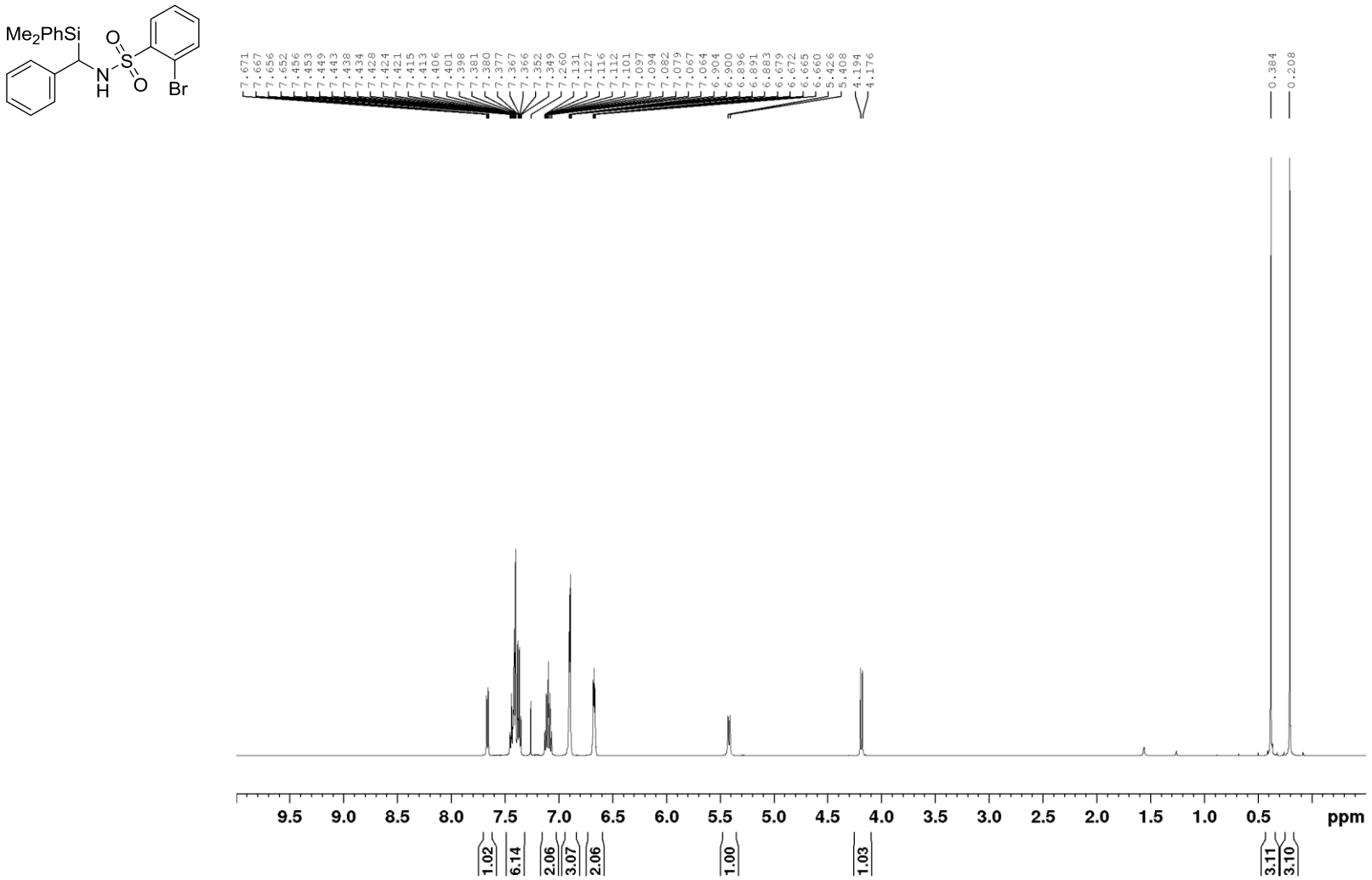
^{13}C NMR (125 MHz, $CDCl_3$)



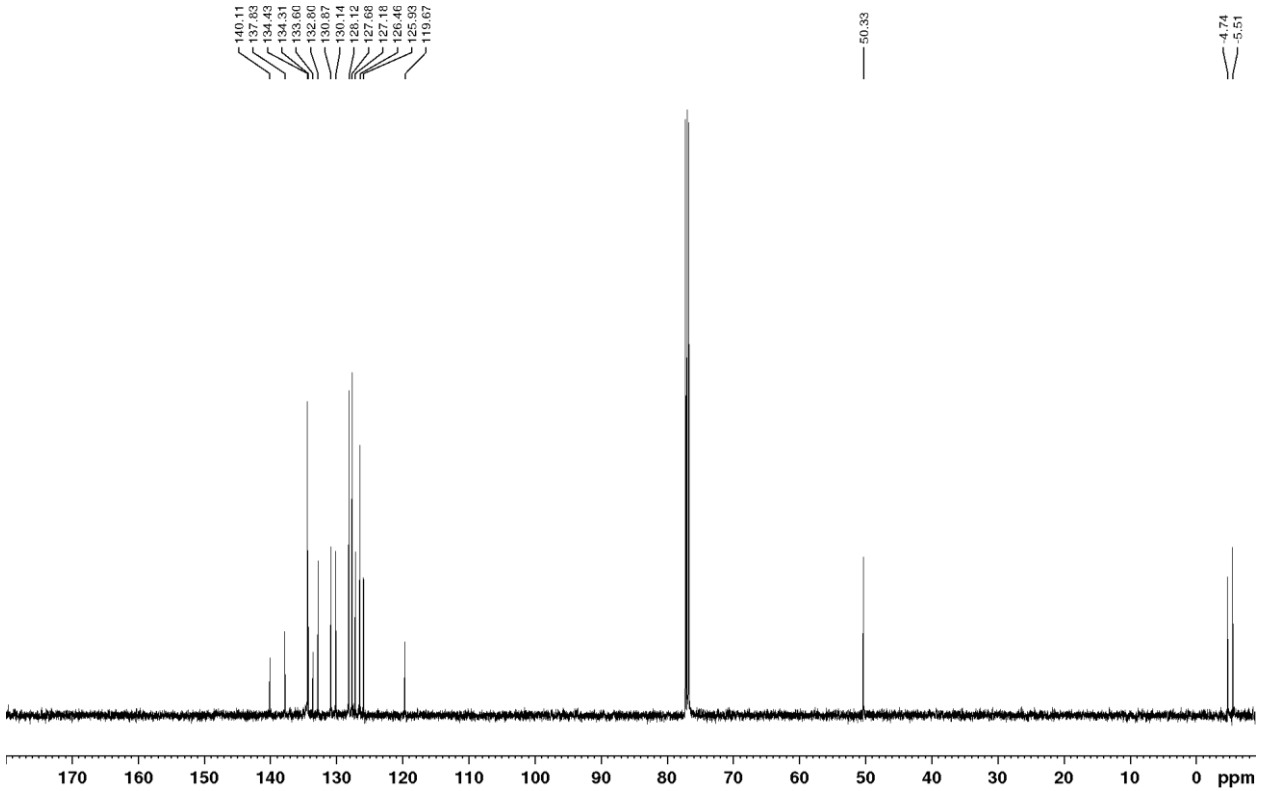
^{29}Si NMR (99 MHz, $CDCl_3$)



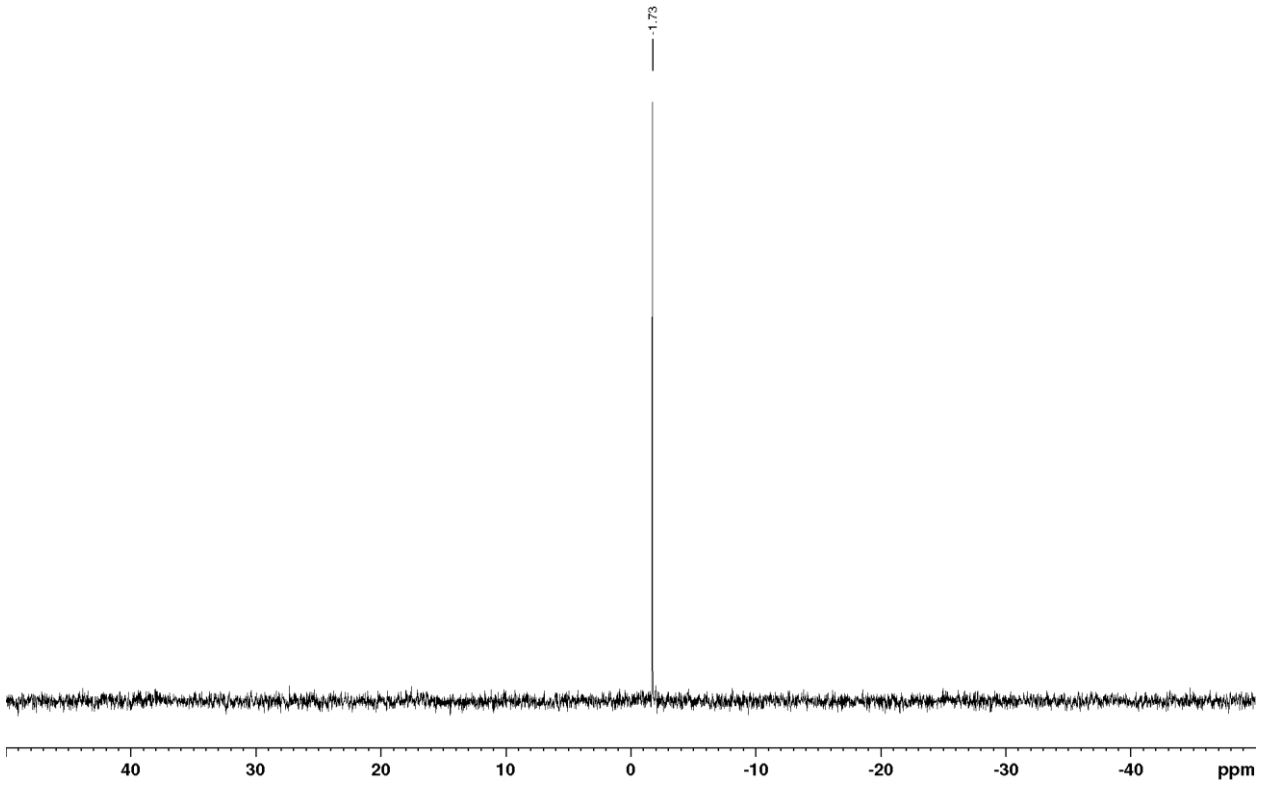
2-Bromo-*N*-((dimethyl(phenyl)silyl)(phenyl)methyl)benzenesulfonamide (**2e**): ^{1}H NMR (500 MHz, $CDCl_3$)



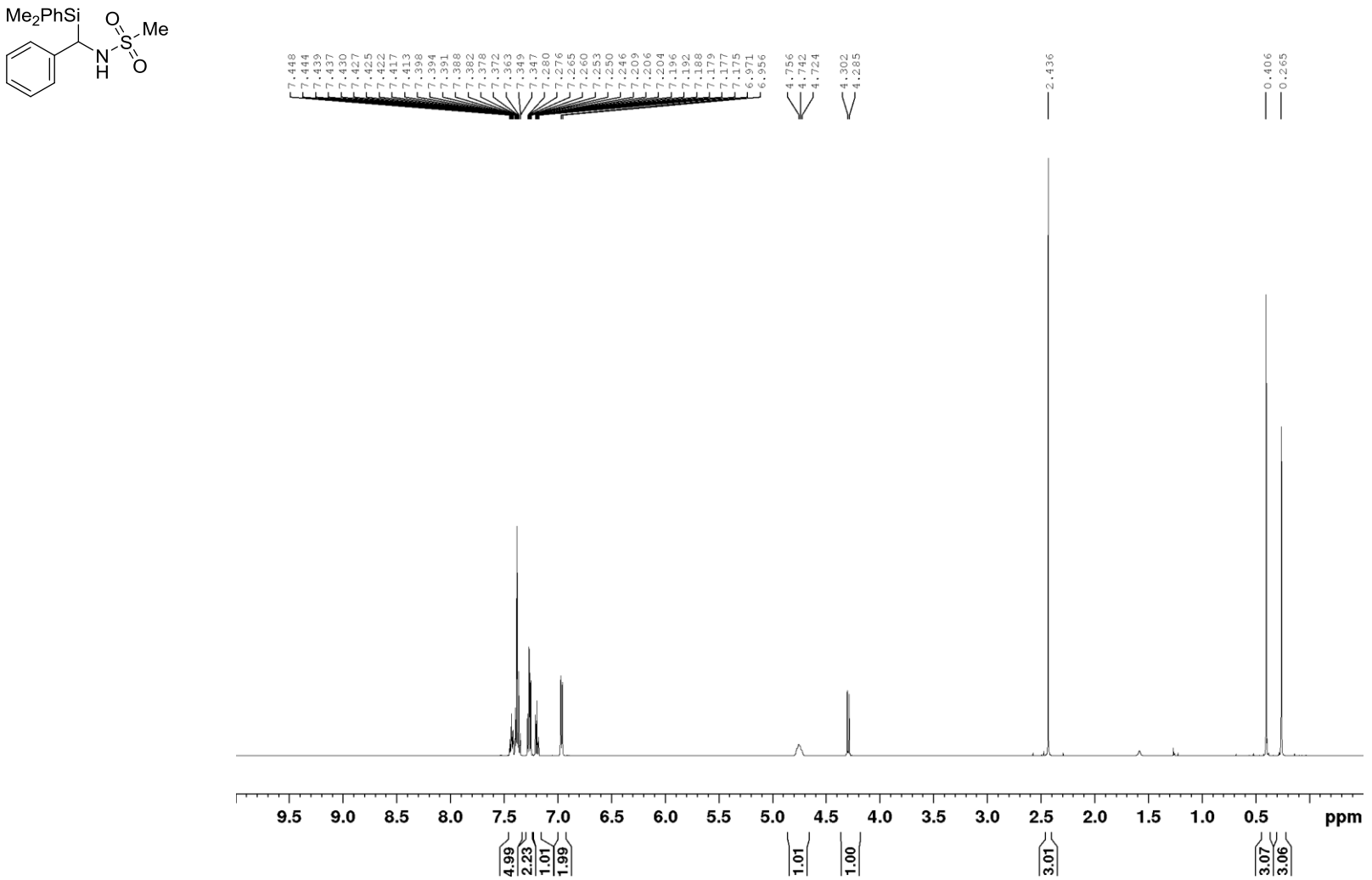
^{13}C NMR (125 MHz, $CDCl_3$)



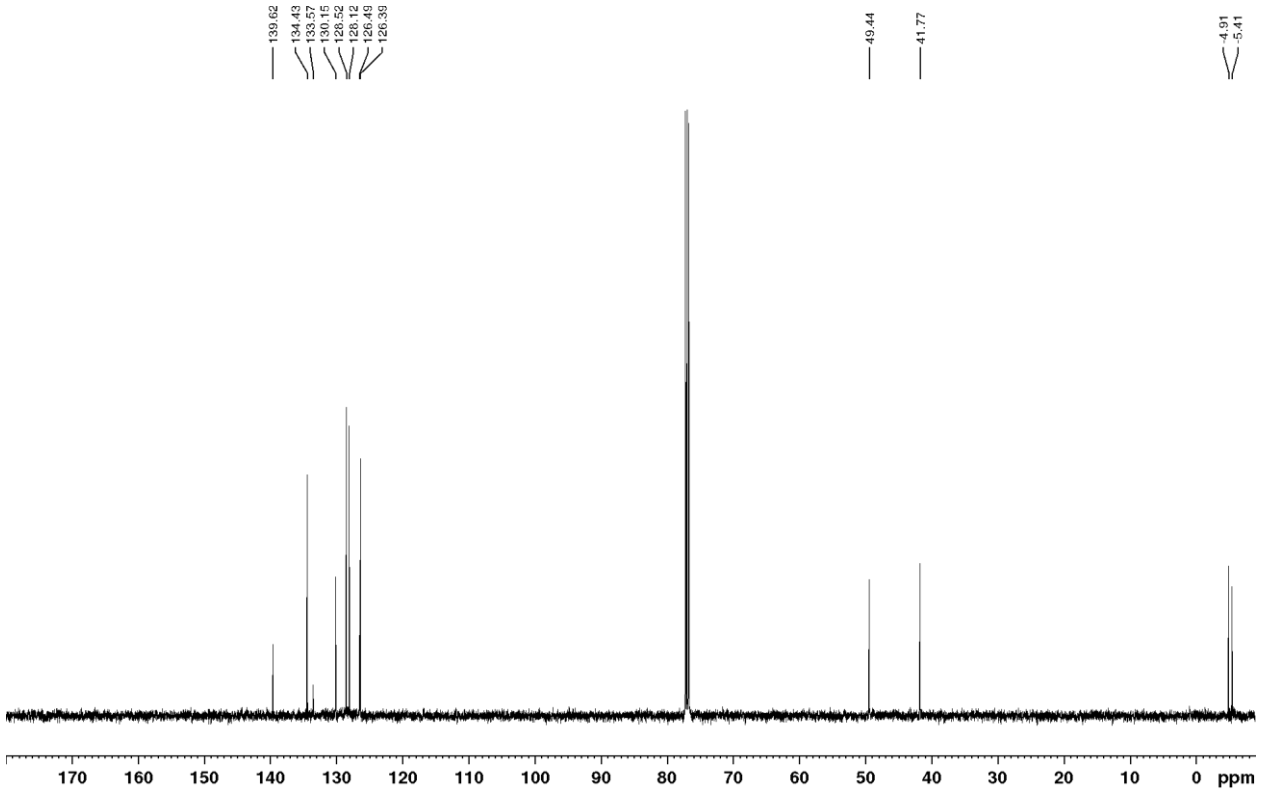
^{29}Si NMR (99 MHz, $CDCl_3$)



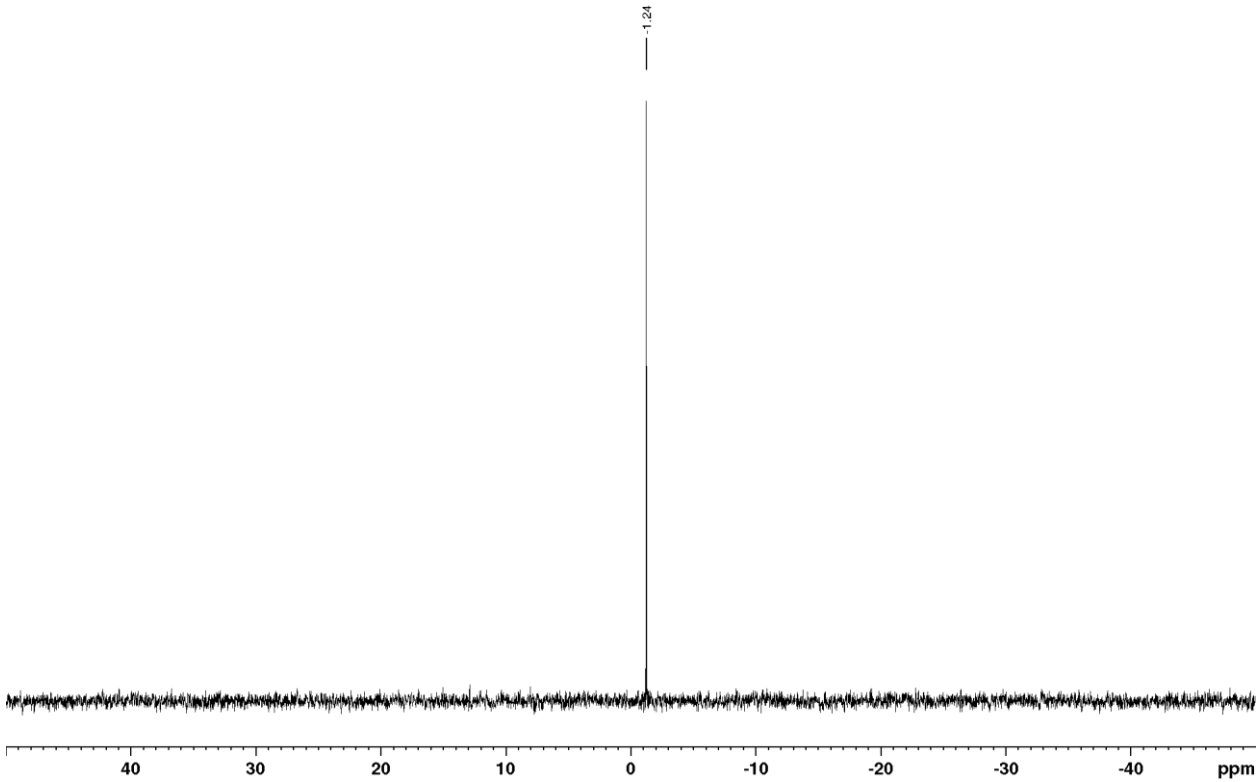
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)methanesulfonamide** (**2f**): ^{1}H NMR (500 MHz, $CDCl_3$)



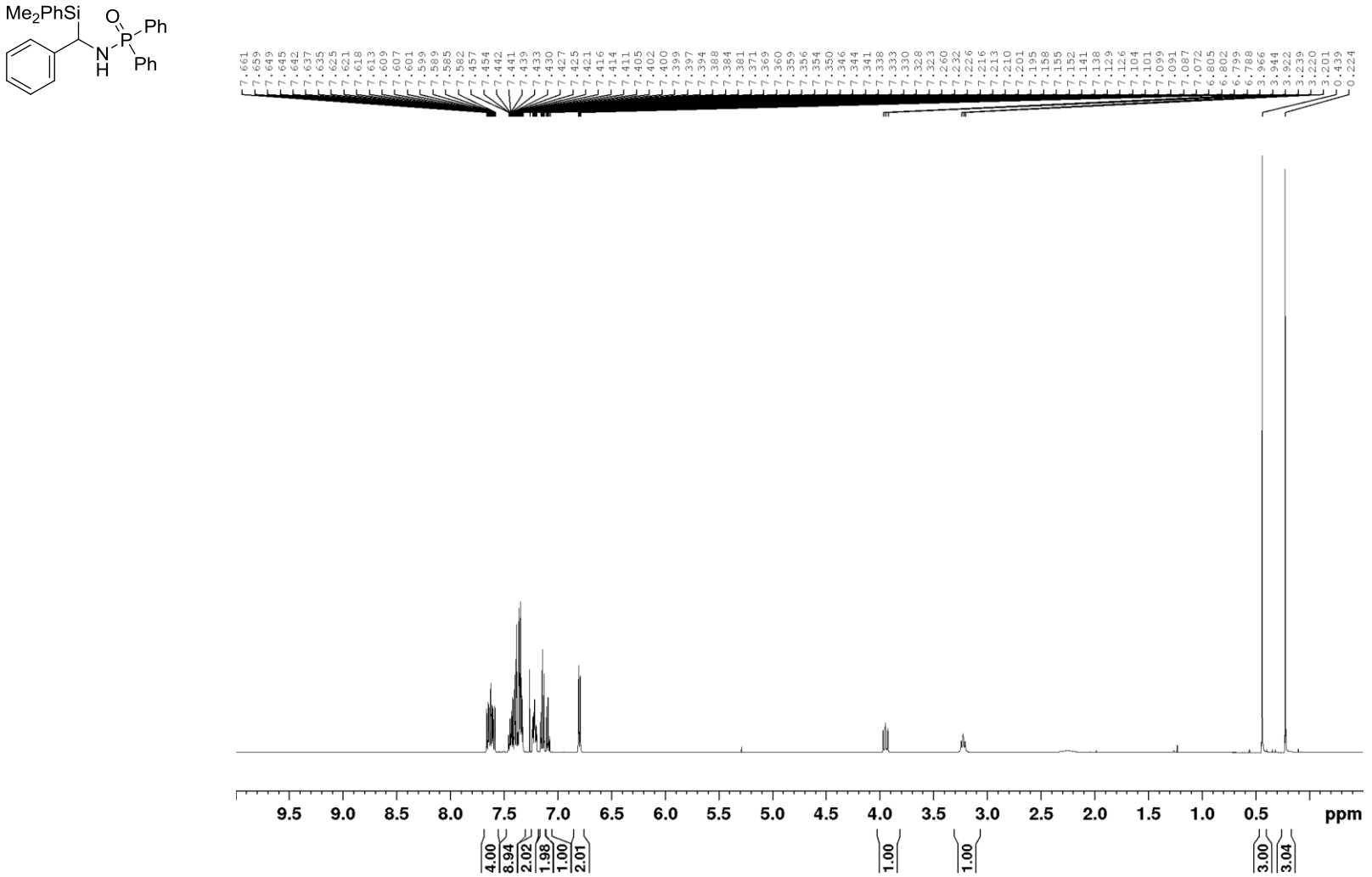
^{13}C NMR (125 MHz, $CDCl_3$)



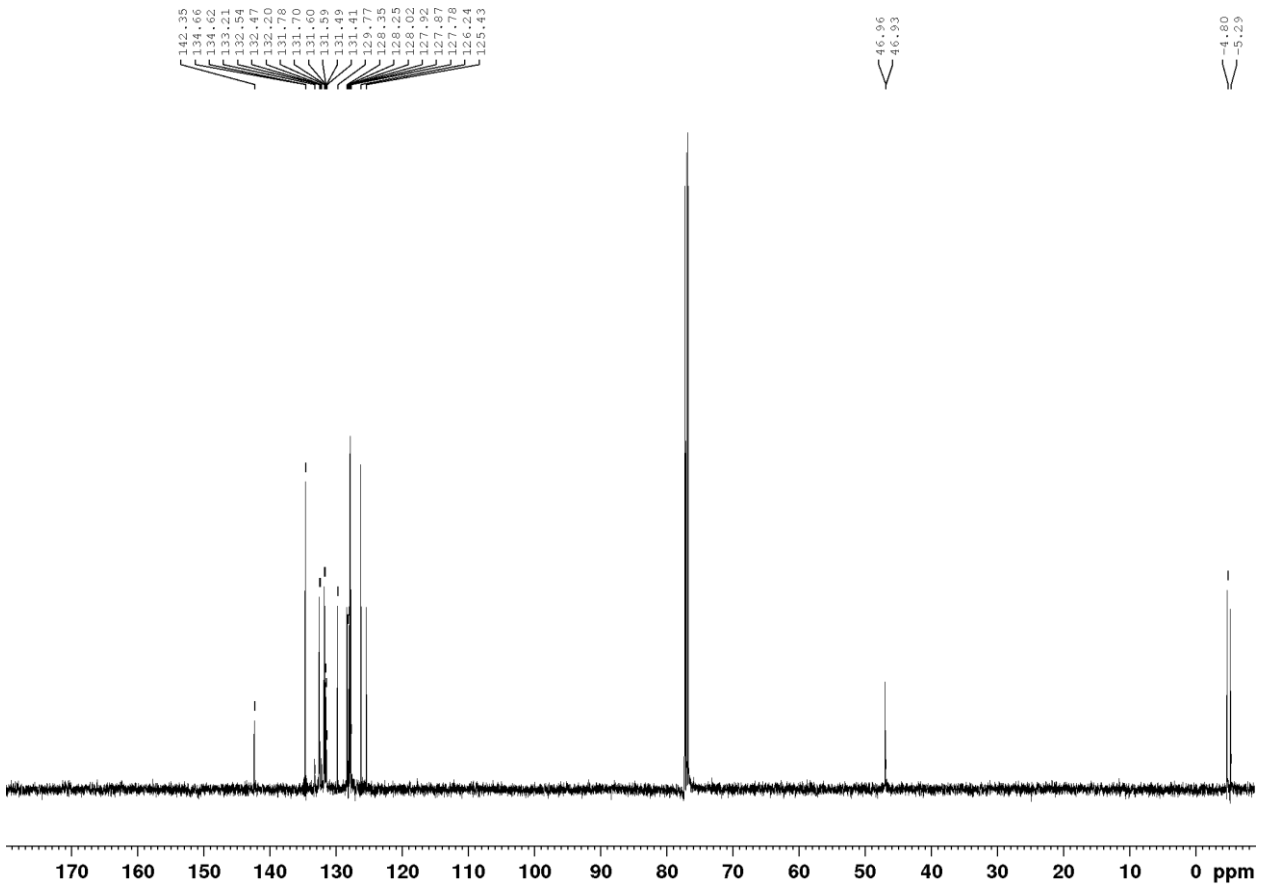
^{29}Si NMR (99 MHz, $CDCl_3$)



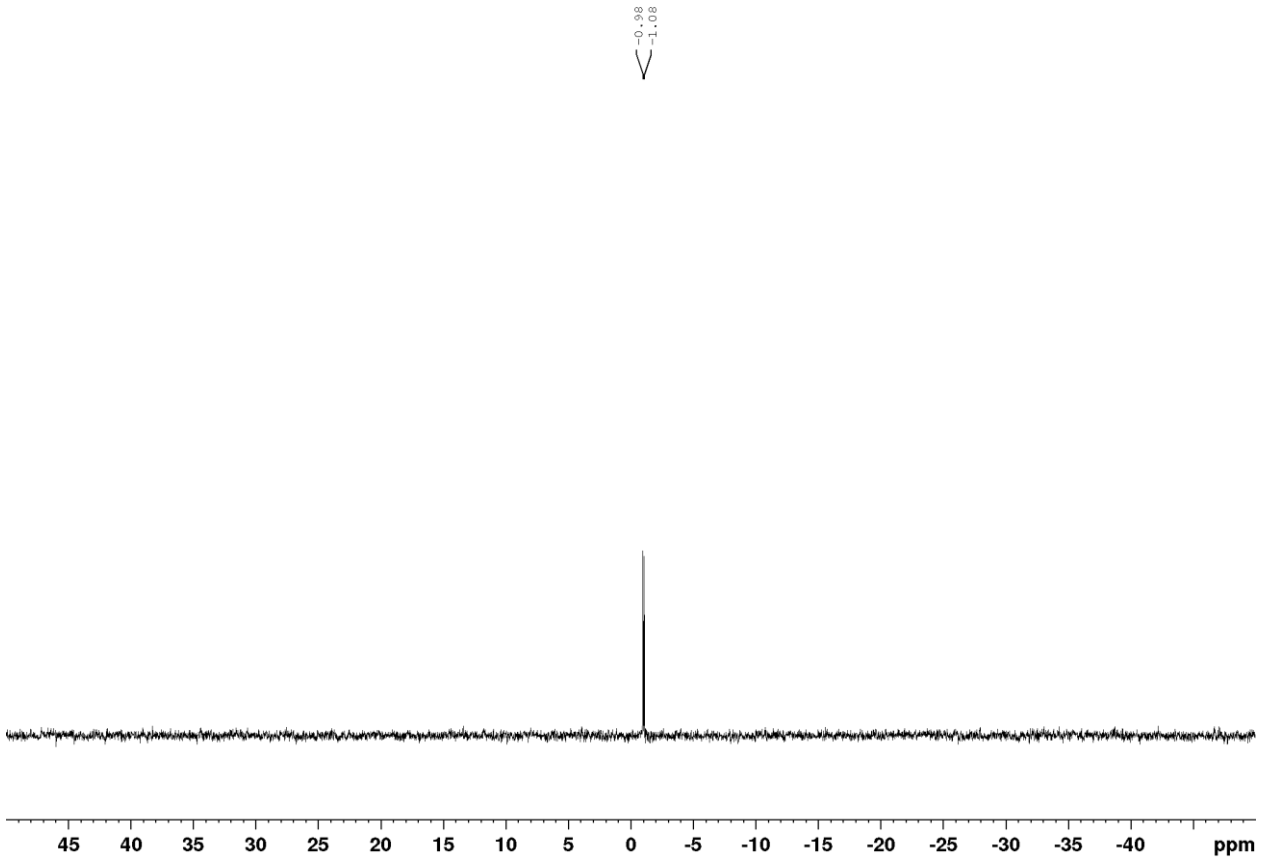
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)-*P*,*P*-diphenylphosphinic amide** (**2h**): ^{1}H NMR (500 MHz, $CDCl_3$)



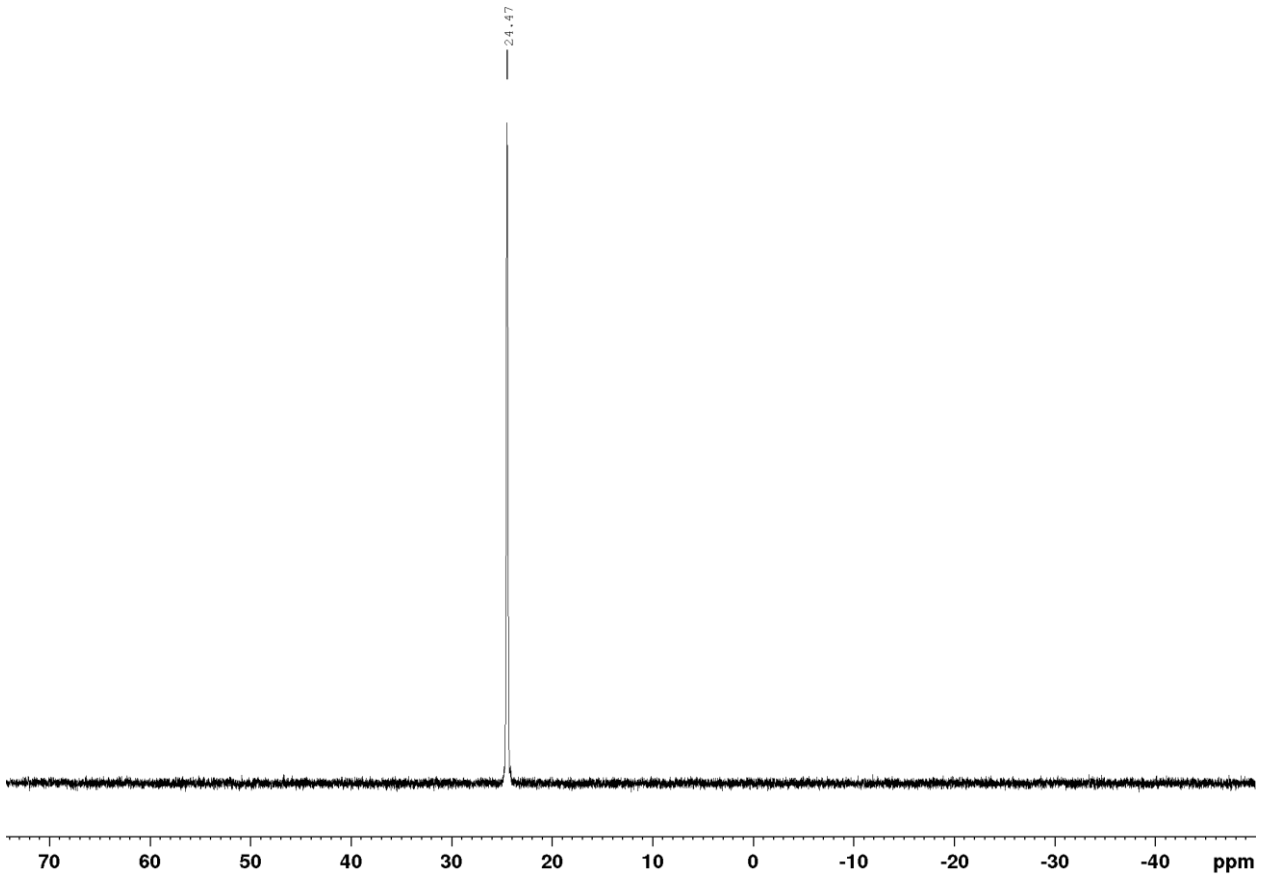
^{13}C NMR (125 MHz, $CDCl_3$)



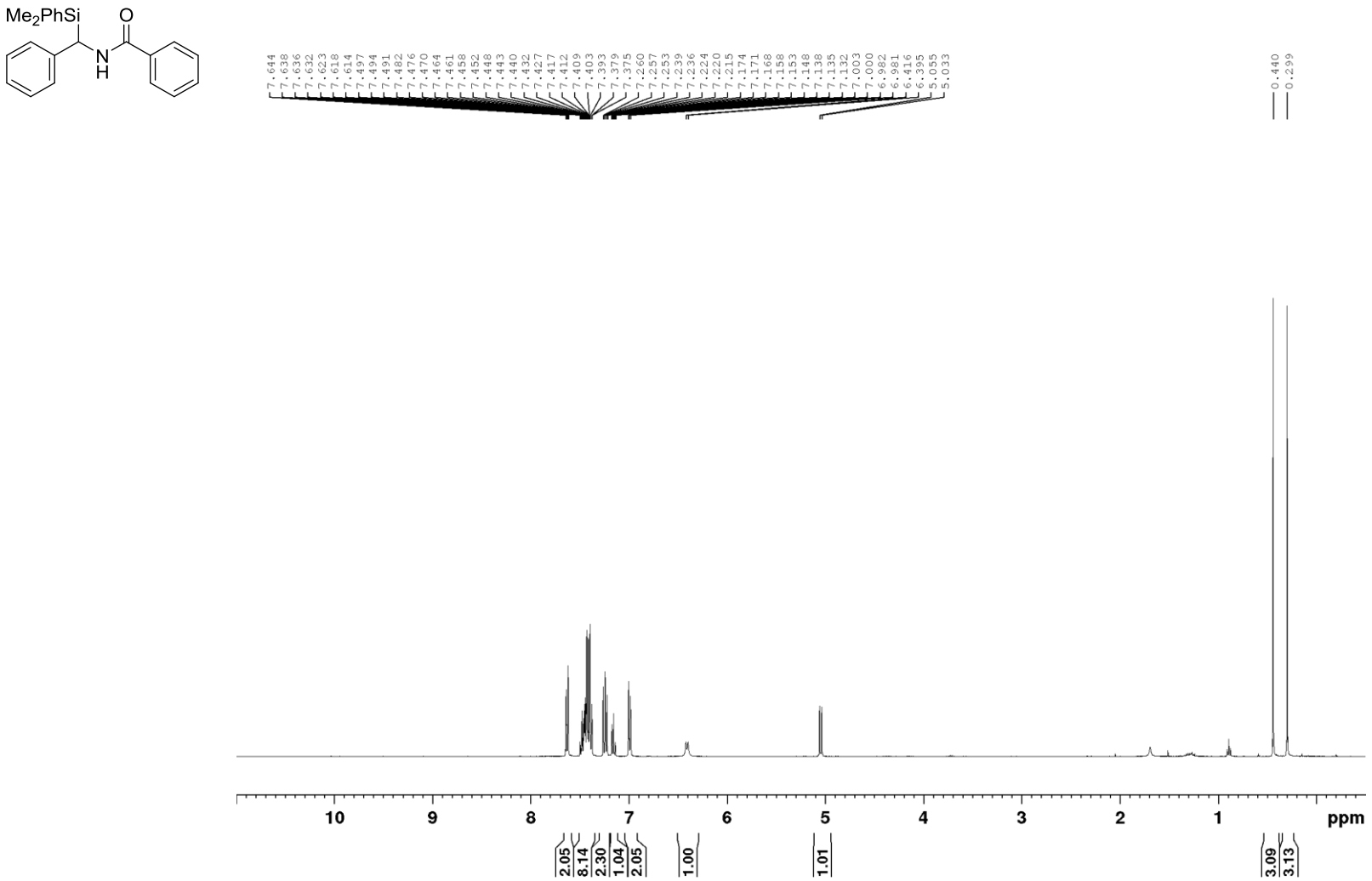
^{29}Si NMR (99 MHz, $CDCl_3$)



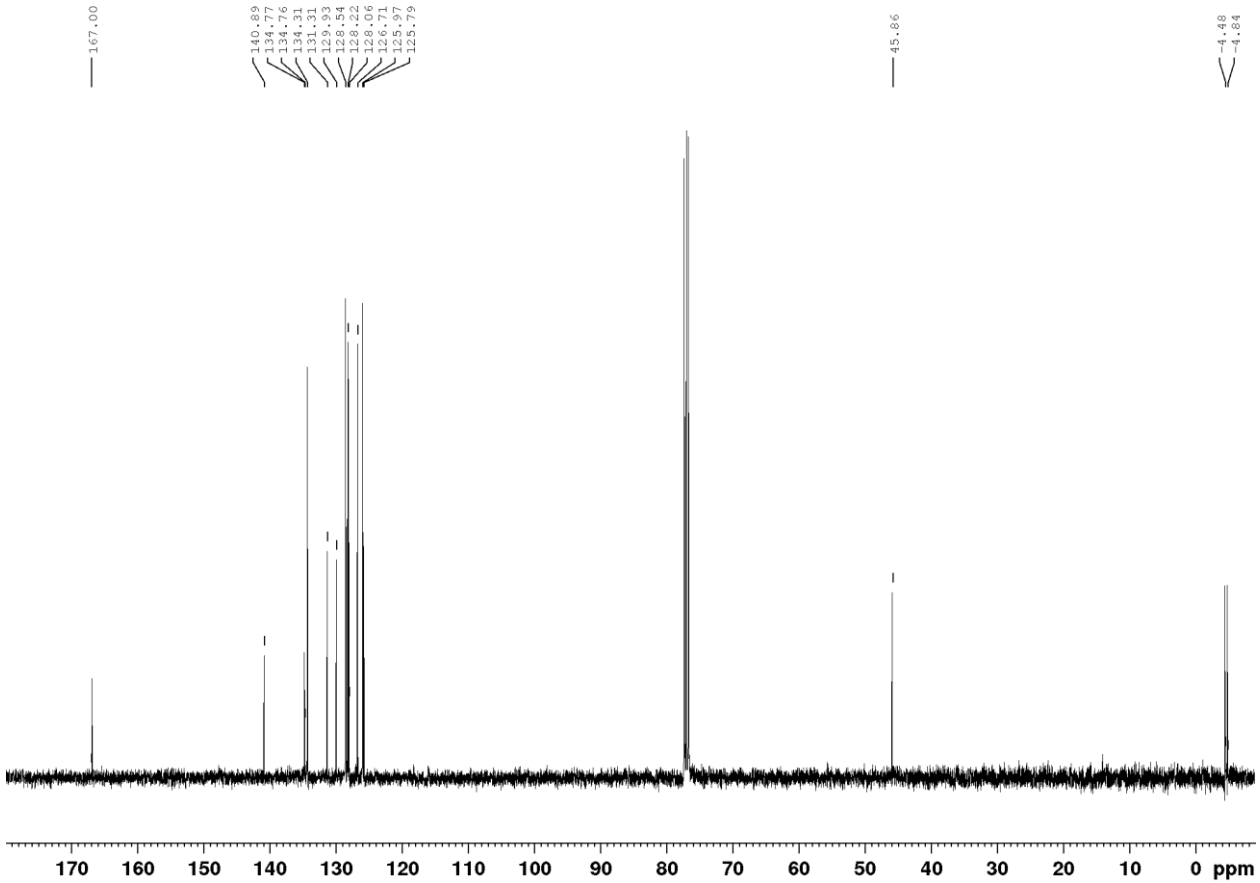
^{31}P NMR (202 MHz, $CDCl_3$)



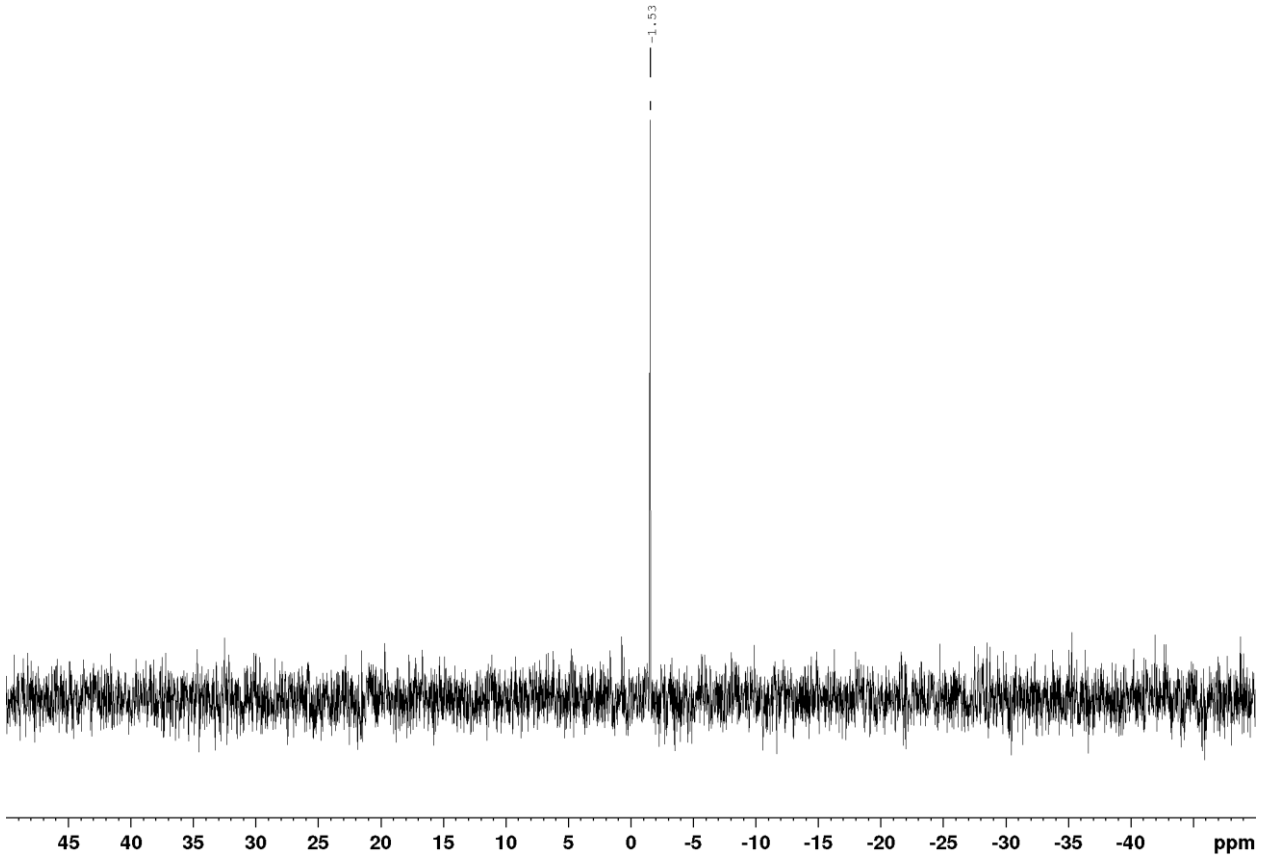
***N*-((Dimethyl(phenyl)silyl)(phenyl)methyl)benzamide** (**2i**): ^{1}H NMR (400 MHz, $CDCl_3$)



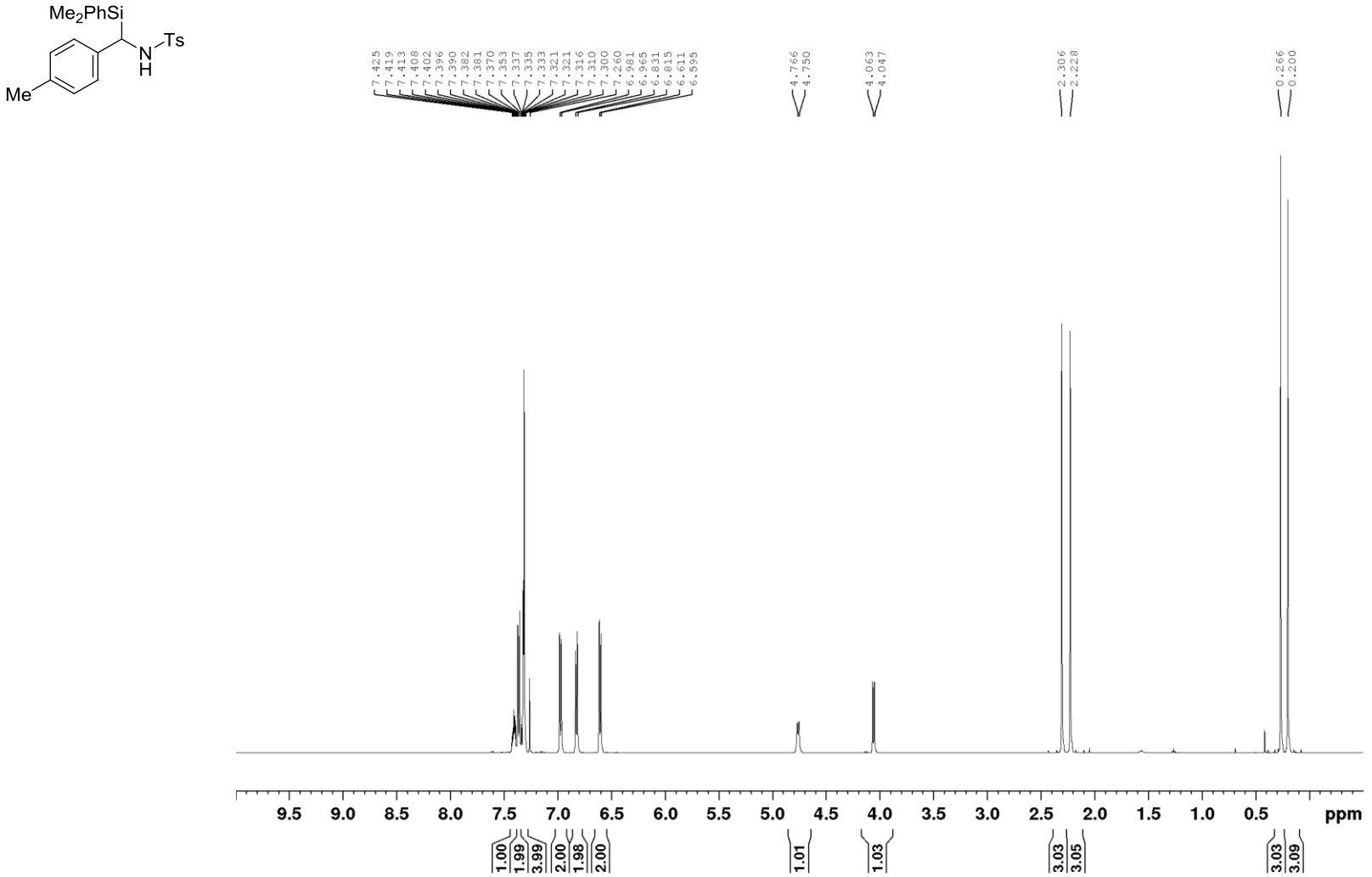
^{13}C NMR (100 MHz, $CDCl_3$)



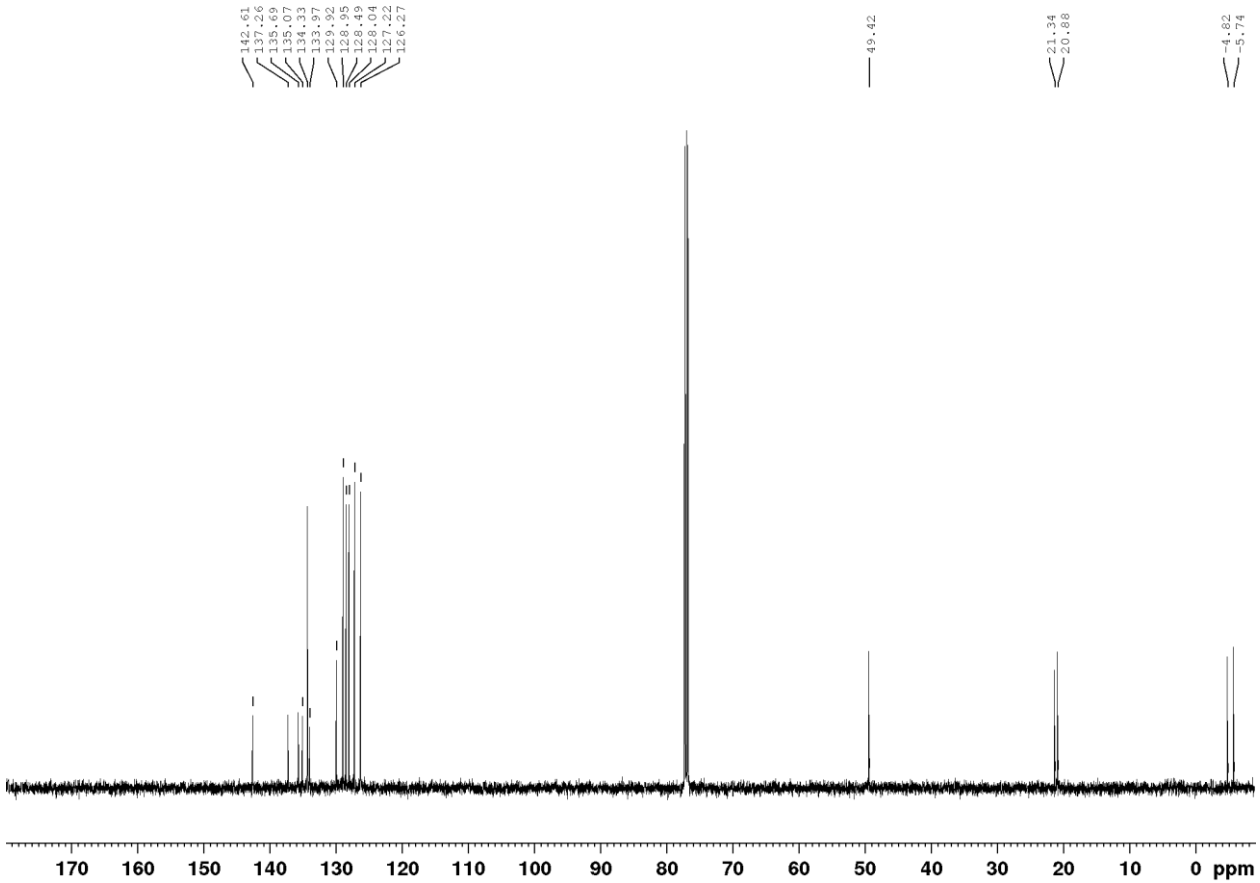
^{29}Si NMR (99 MHz, $CDCl_3$)



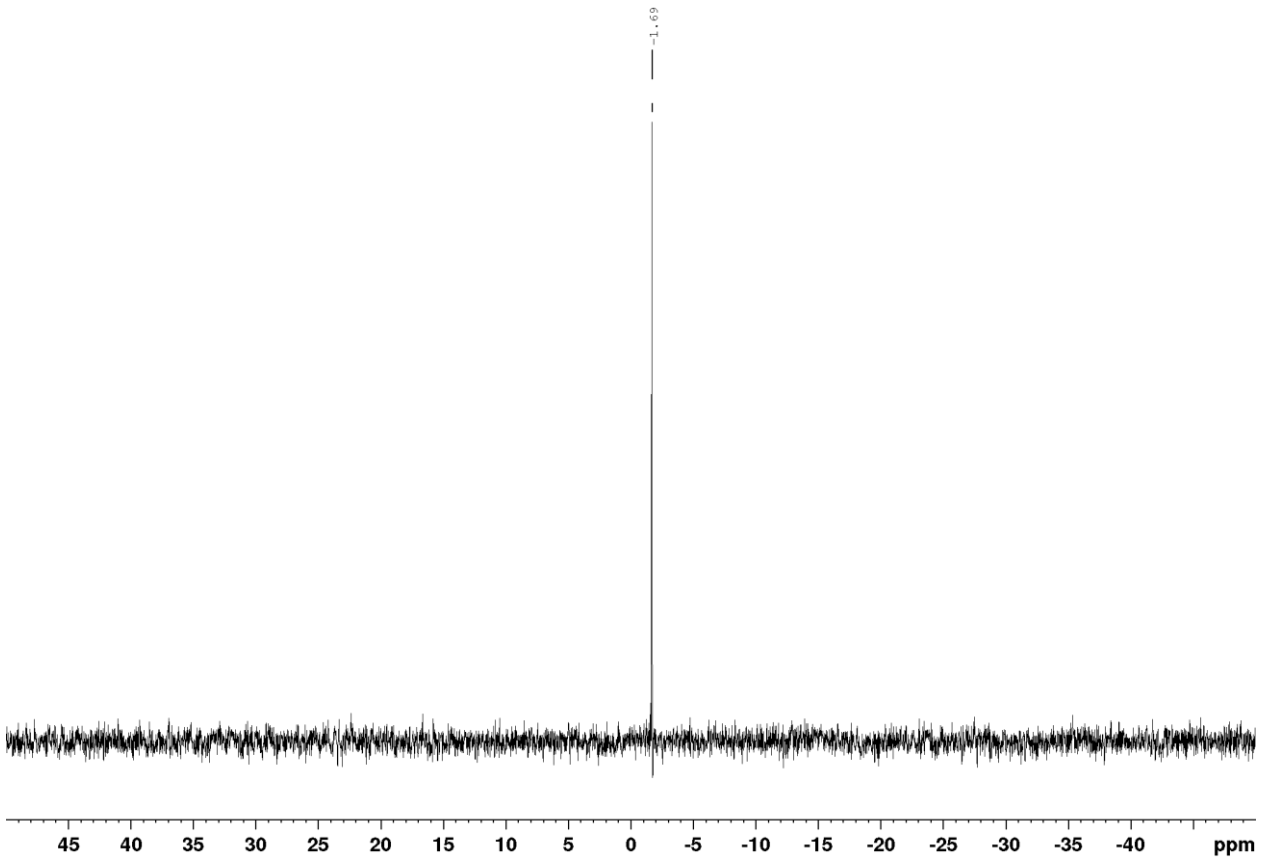
***N*-((Dimethyl(phenyl)silyl)(*p*-tolyl)methyl)-4-methylbenzenesulfonamide** (**16a**): ^{1}H NMR (500 MHz, $CDCl_3$)



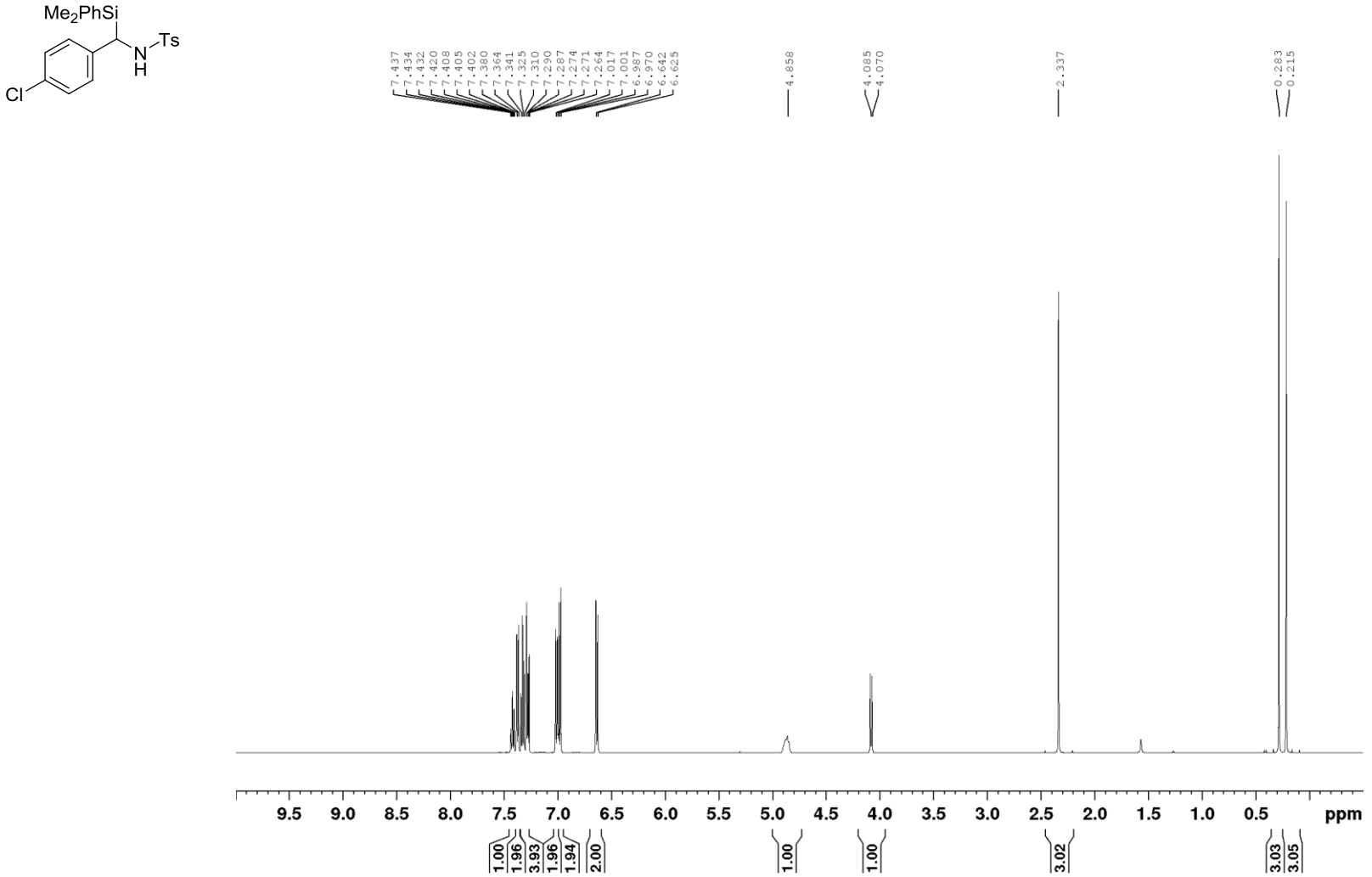
^{13}C NMR (125 MHz, $CDCl_3$)



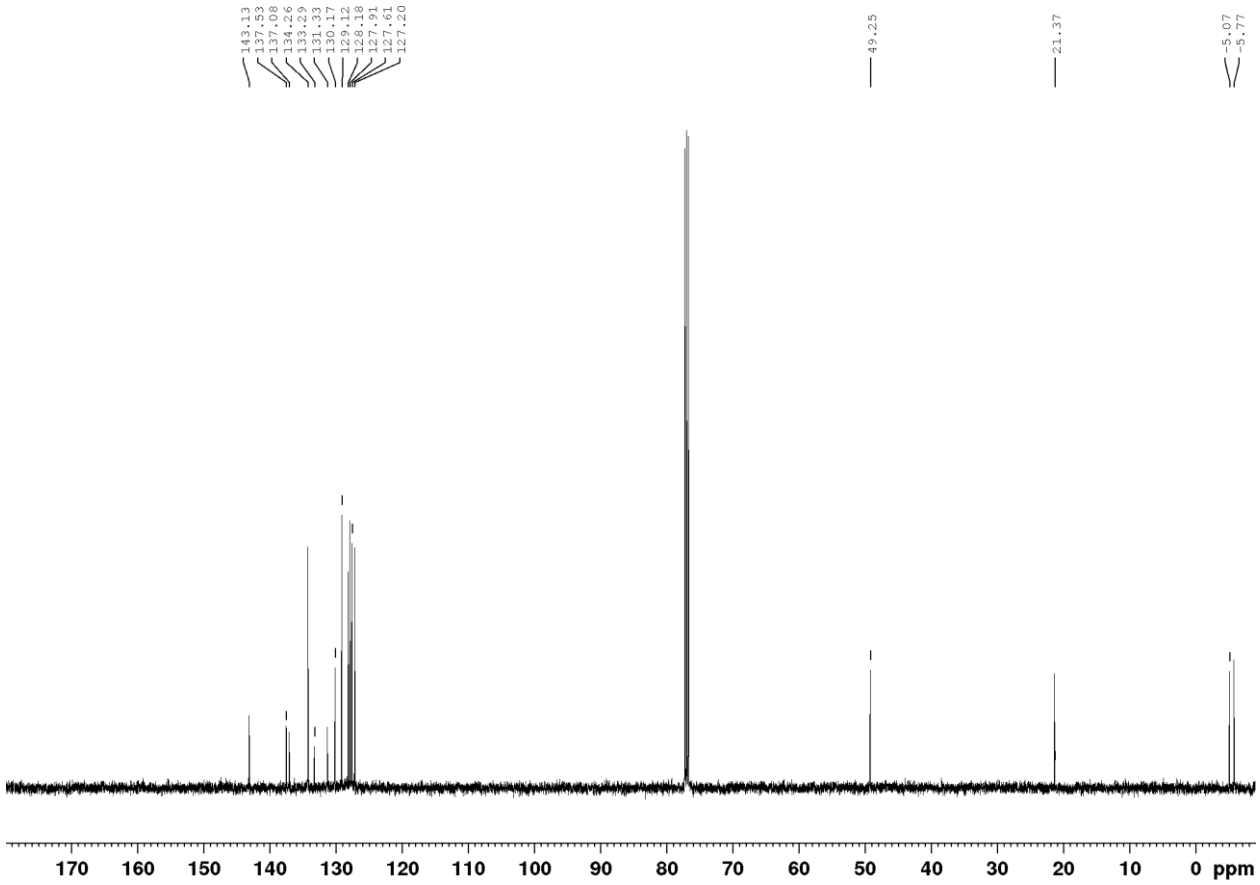
^{29}Si NMR (99 MHz, $CDCl_3$)



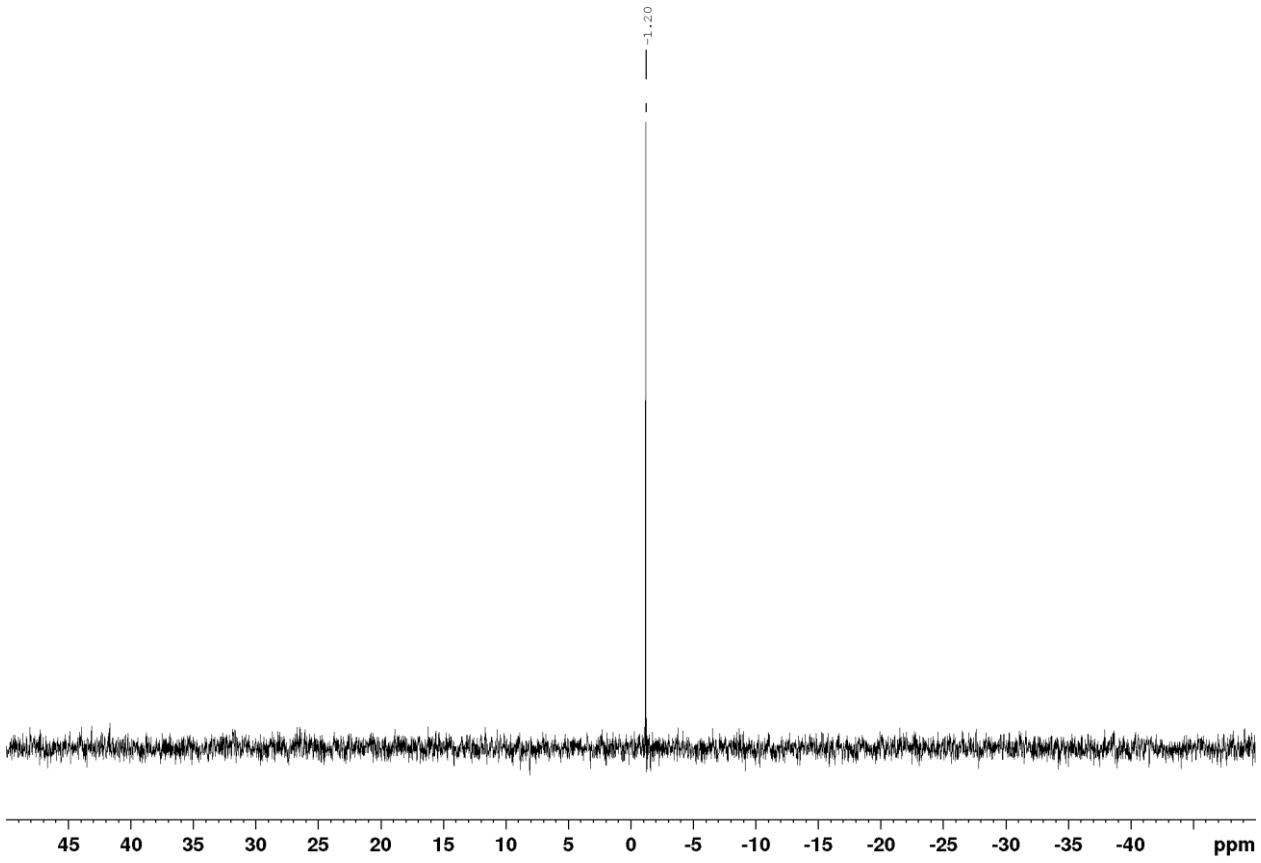
***N*-((4-Chlorophenyl)(dimethyl(phenyl)silyl)methyl)-4-methylbenzenesulfonamide** (**17a**): ^{1}H NMR (500 MHz, $CDCl_3$)



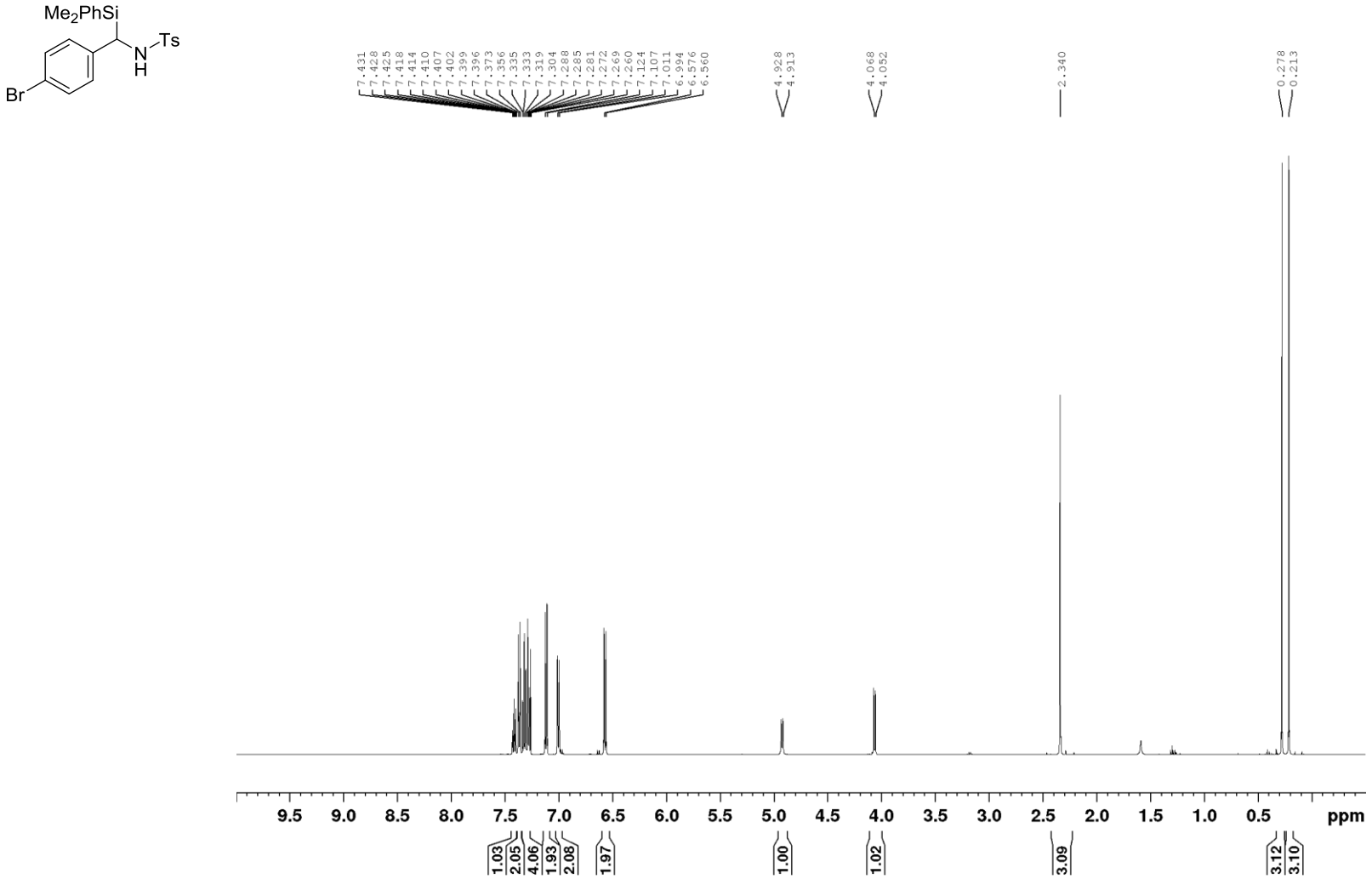
^{13}C NMR (125 MHz, $CDCl_3$)



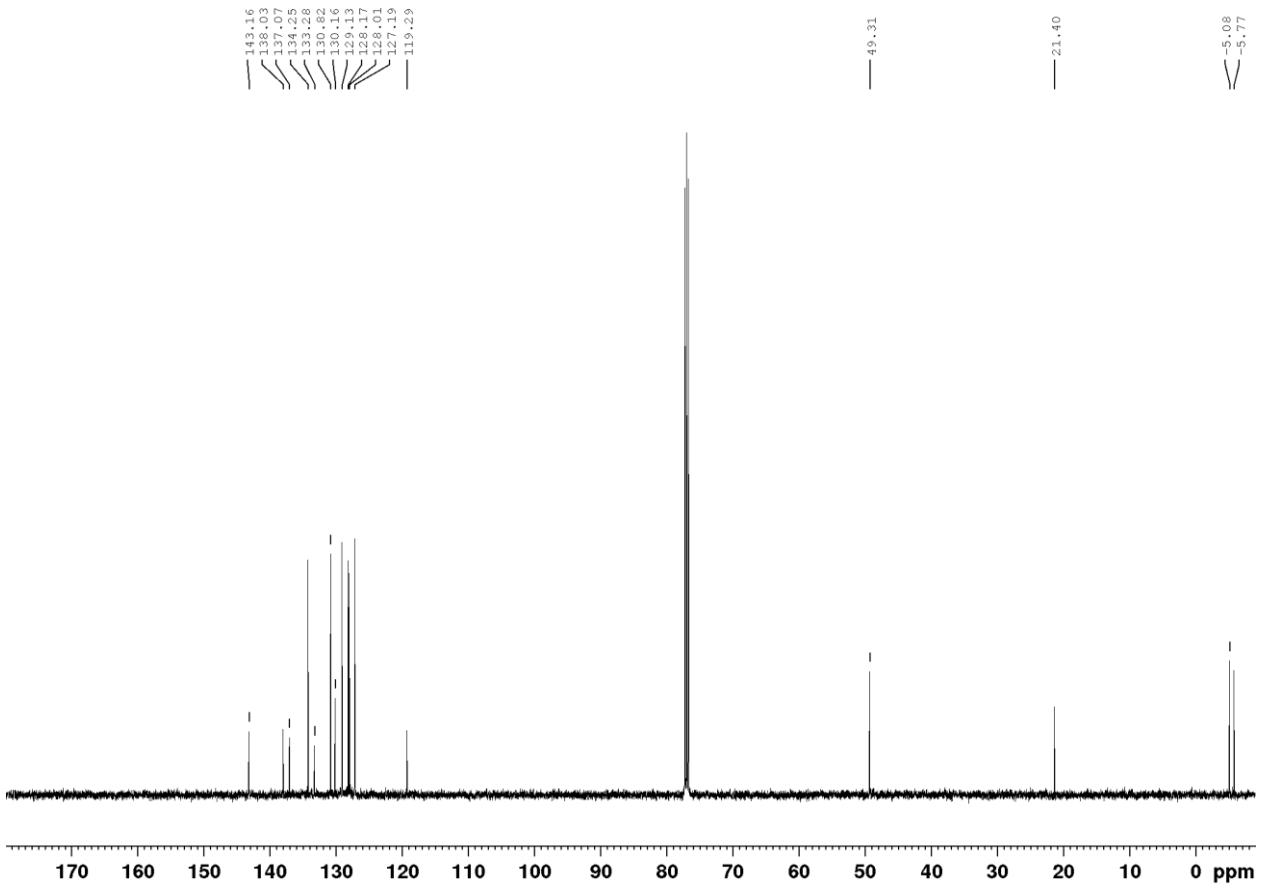
^{29}Si NMR (99 MHz, $CDCl_3$)



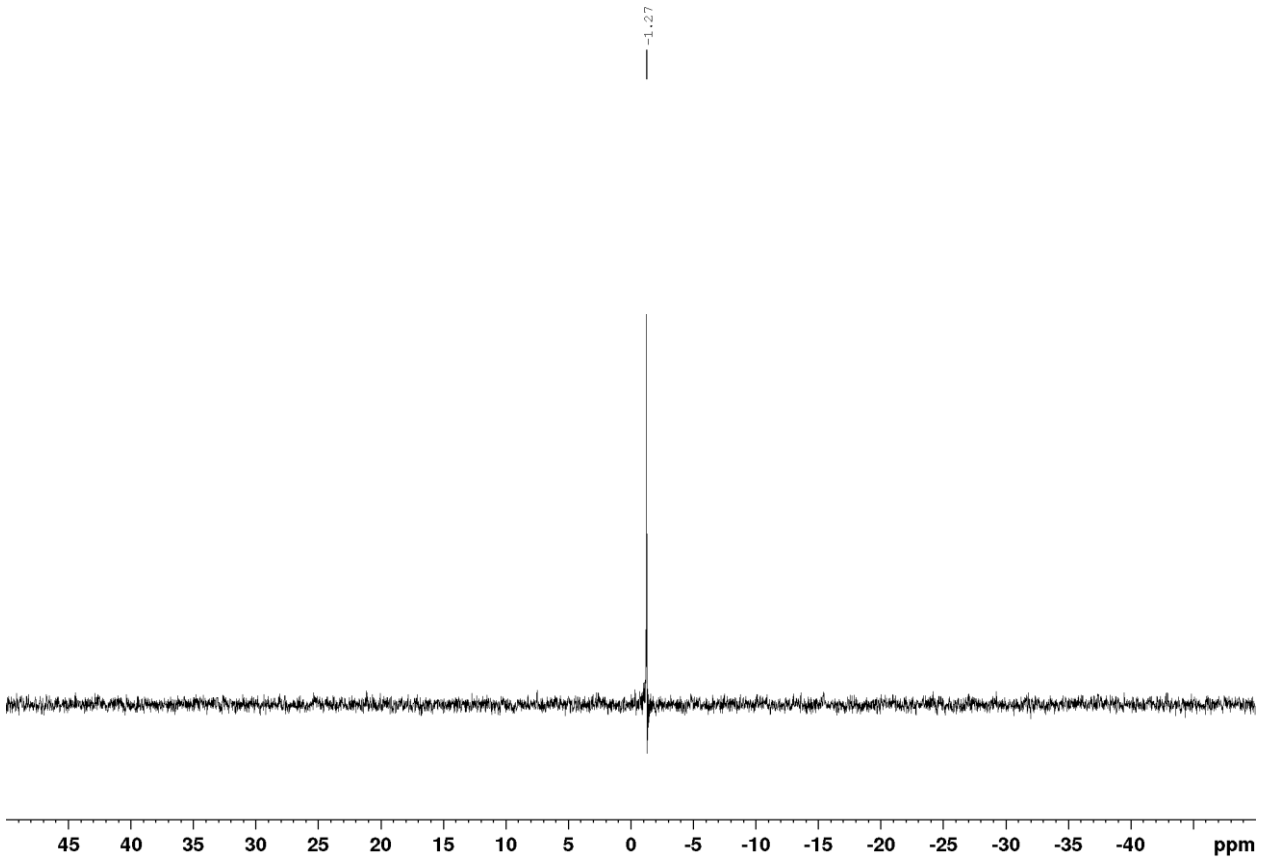
***N*-((4-Bromophenyl)(dimethyl(phenyl)silyl)methyl)-4-methylbenzenesulfonamide** (**18a**): ^{1}H NMR (500 MHz, $CDCl_3$)



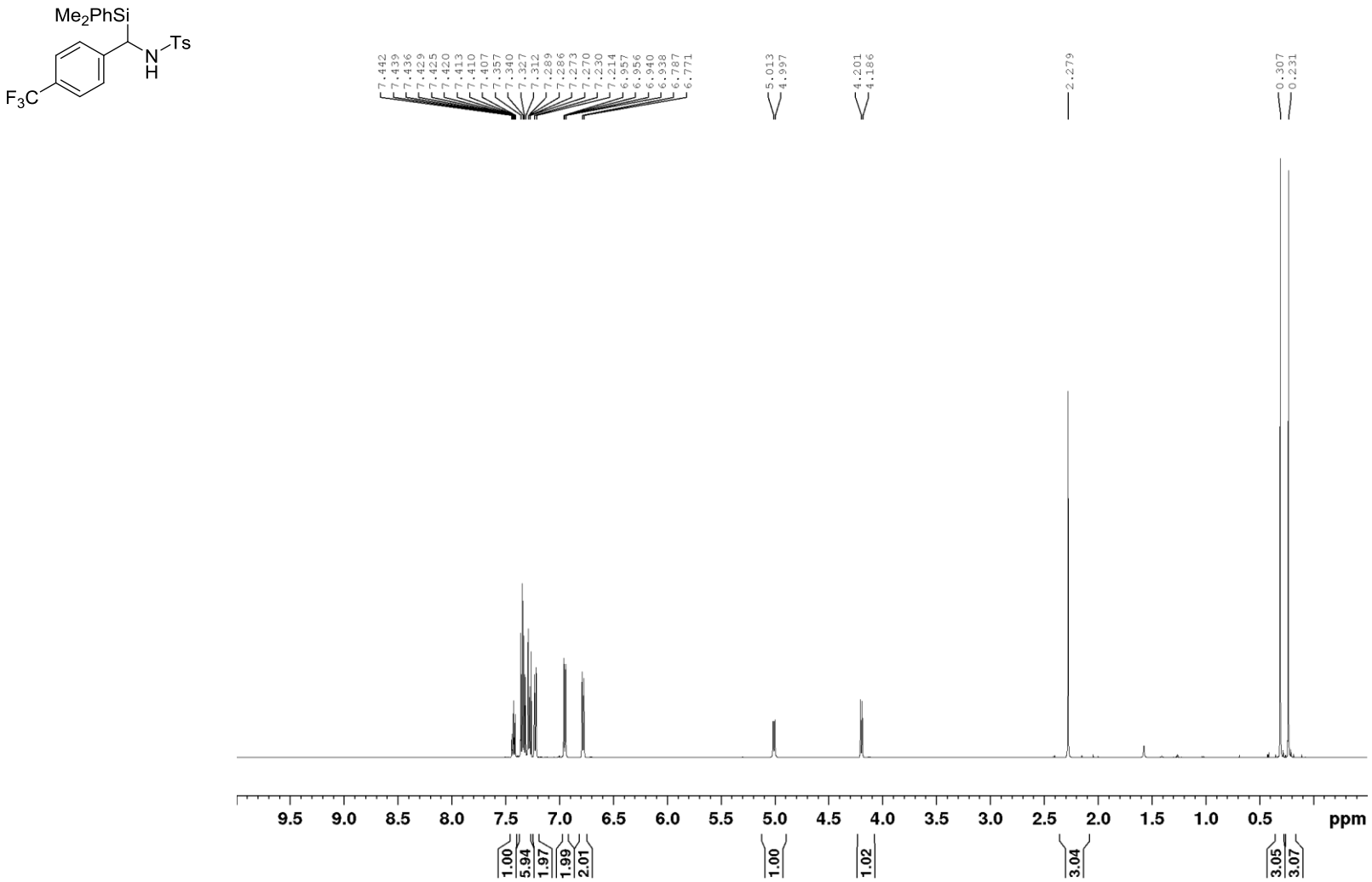
^{13}C NMR (125 MHz, $CDCl_3$)



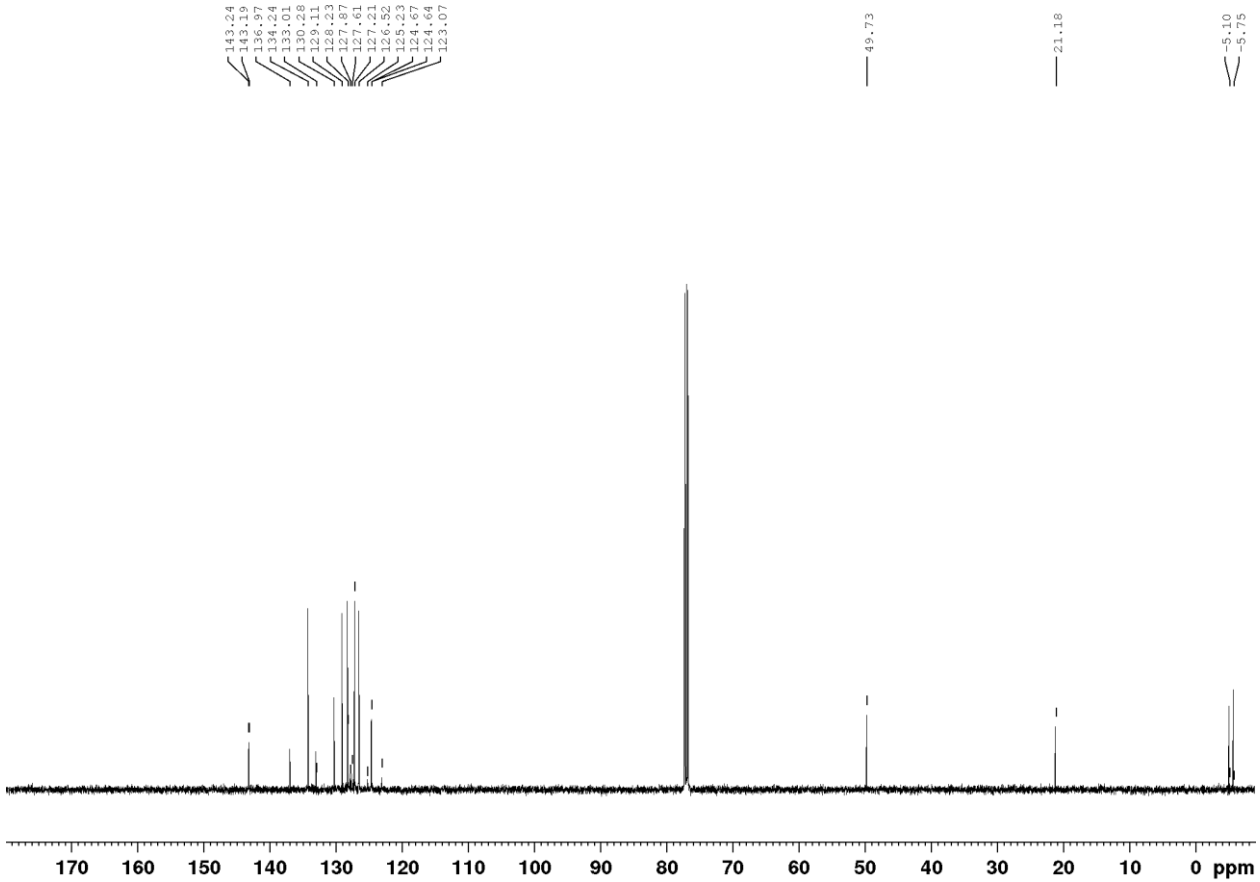
^{29}Si NMR (99 MHz, $CDCl_3$)



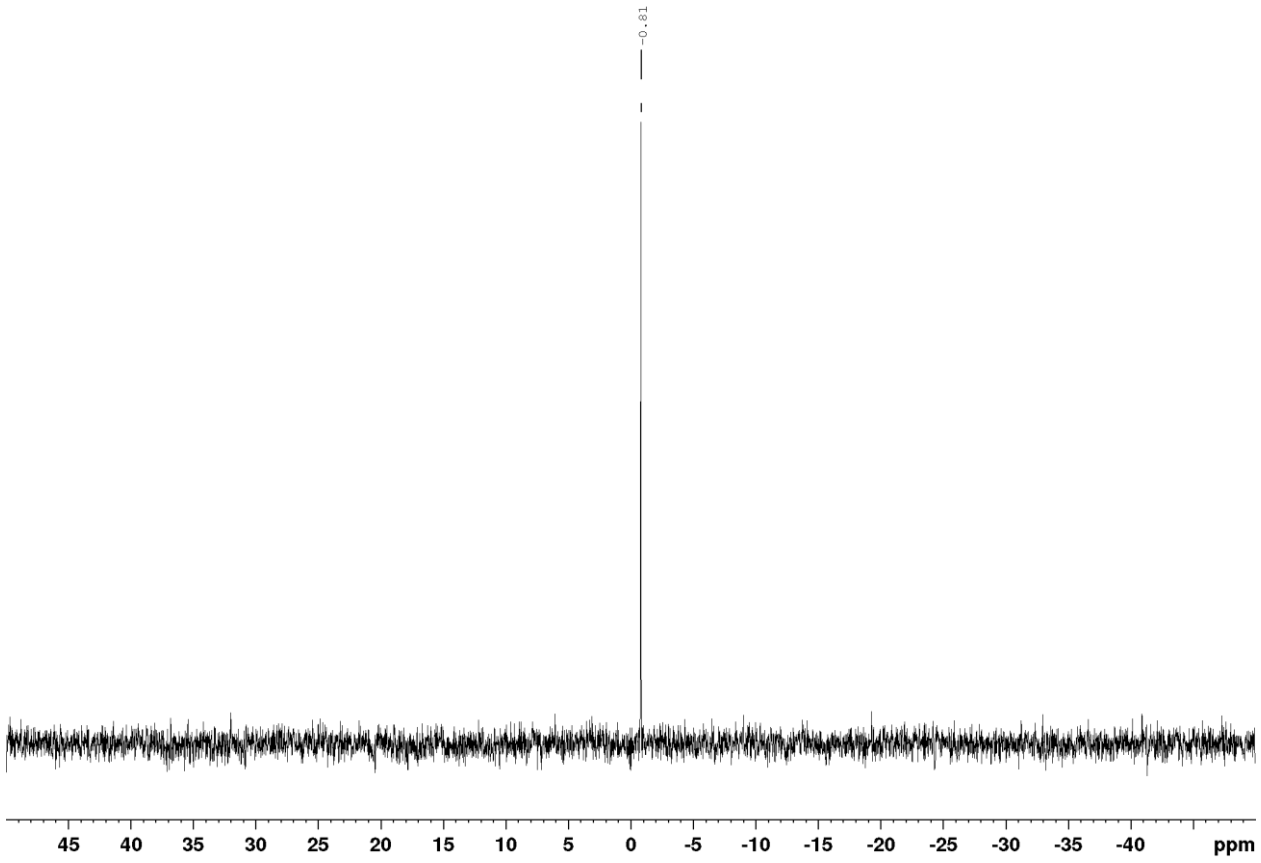
***N*-((Dimethyl(phenyl)silyl)(4-(trifluoromethyl)phenyl)methyl)-4-methylbenzenesulfonamide** (**19a**): ^{1}H NMR (500 MHz, $CDCl_3$)



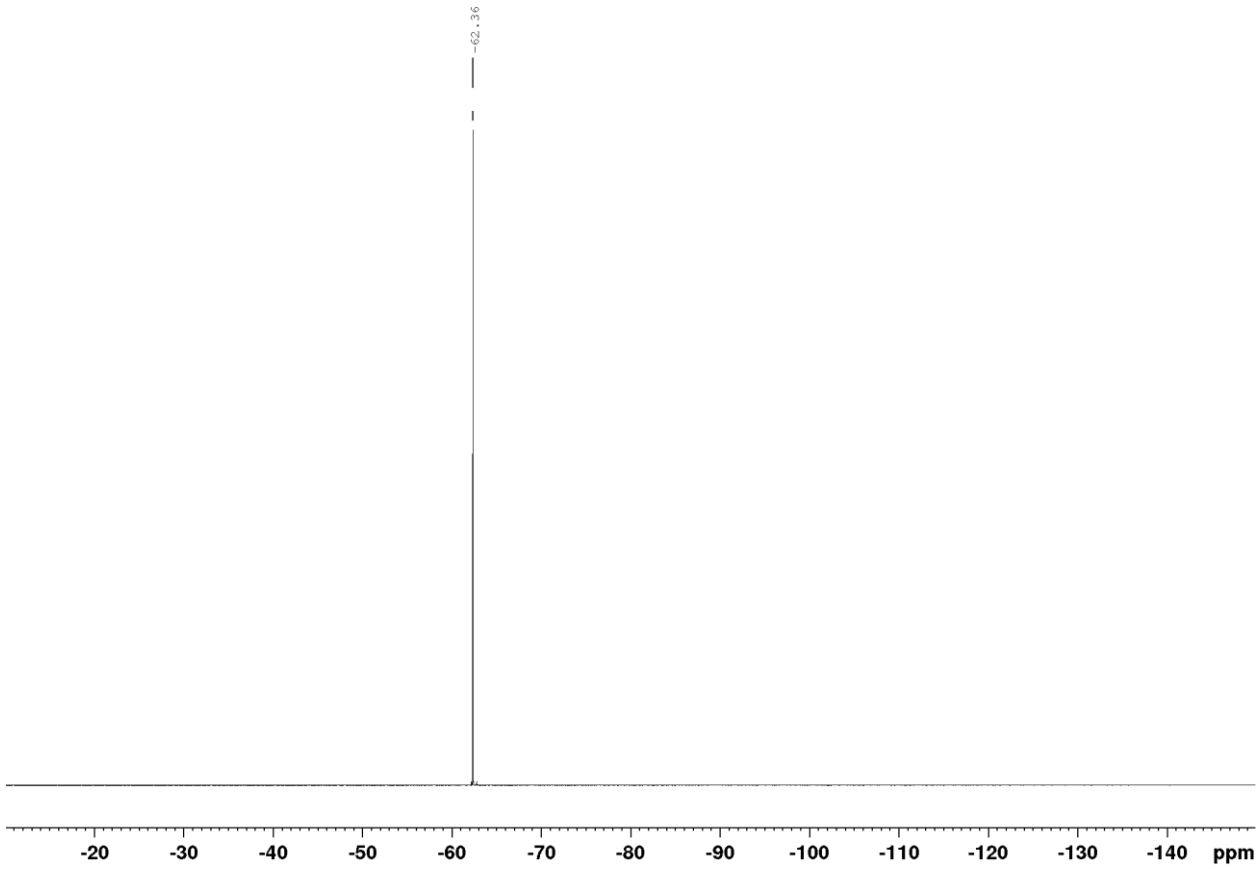
^{13}C NMR (125 MHz, $CDCl_3$)



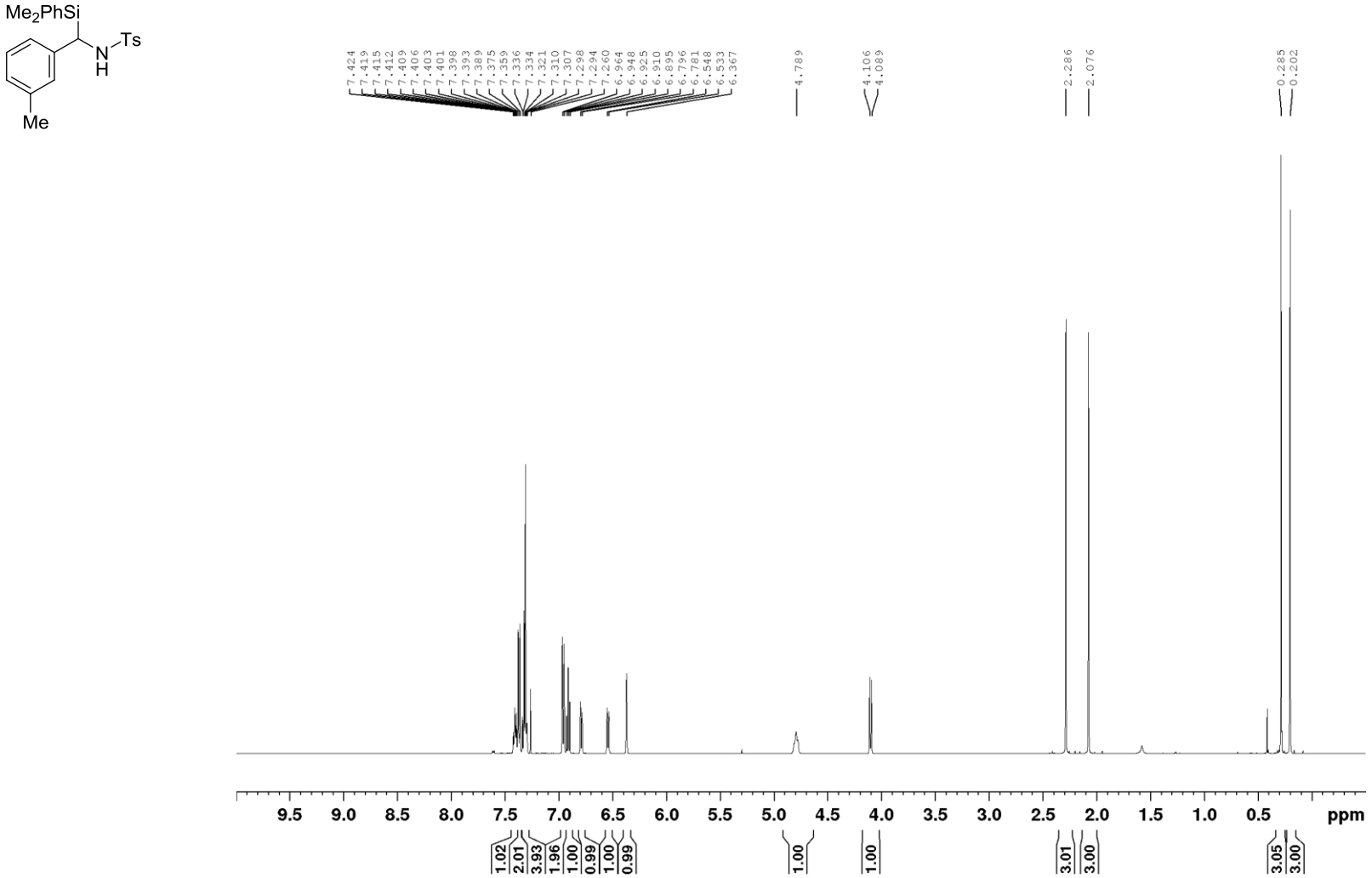
^{29}Si NMR (99 MHz, $CDCl_3$)



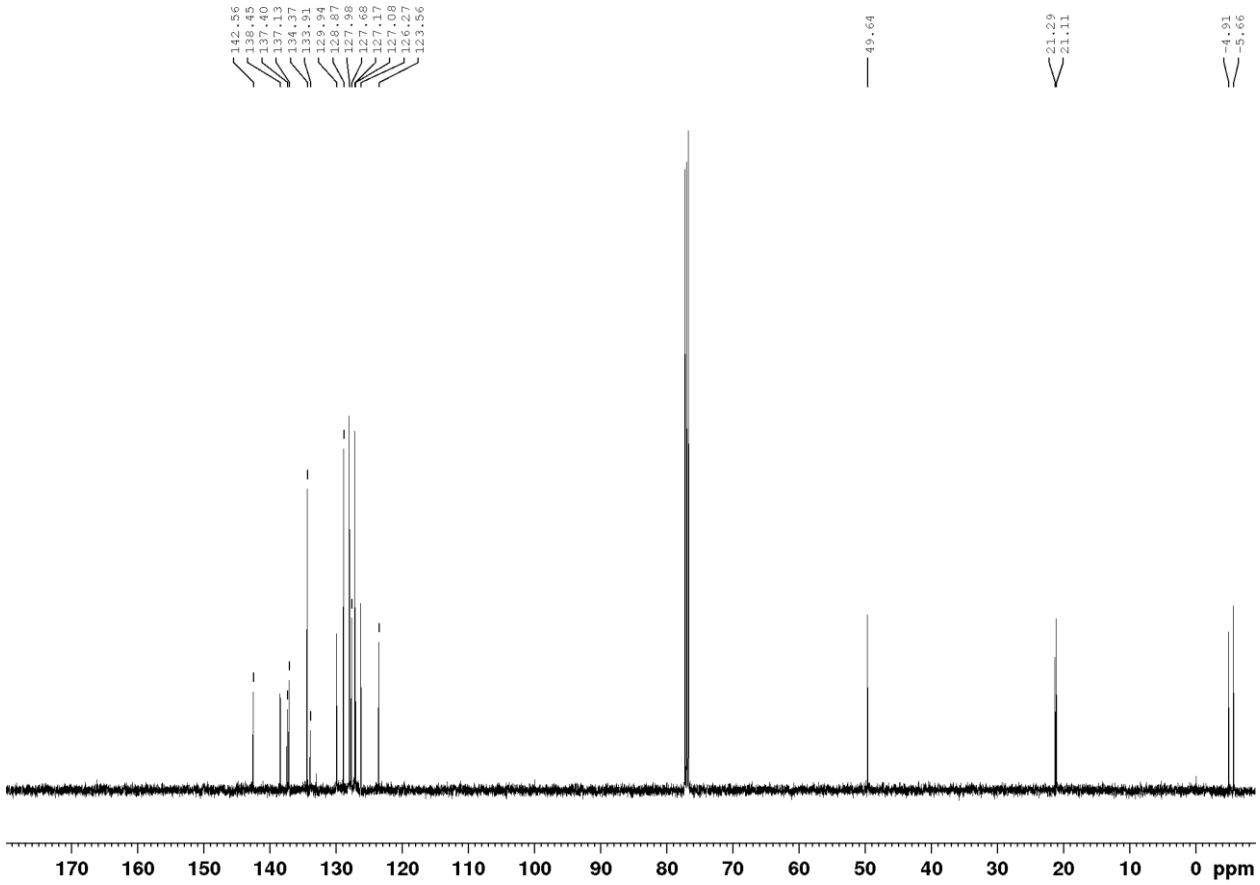
^{19}F NMR (470 MHz, $CDCl_3$)



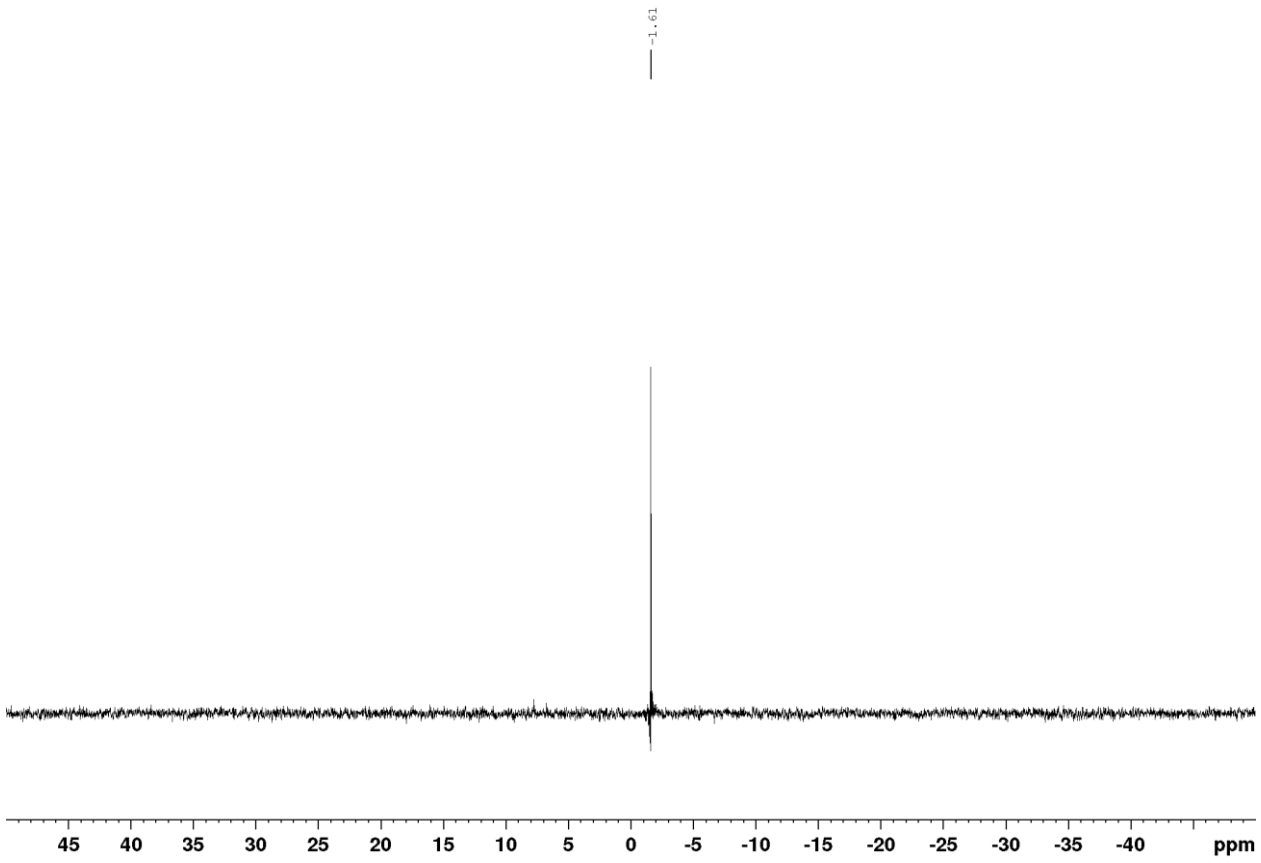
***N*-((Dimethyl(phenyl)silyl)(m-tolyl)methyl)-4-methylbenzenesulfonamide** (**20a**): ^{1}H NMR (500 MHz, $CDCl_3$)



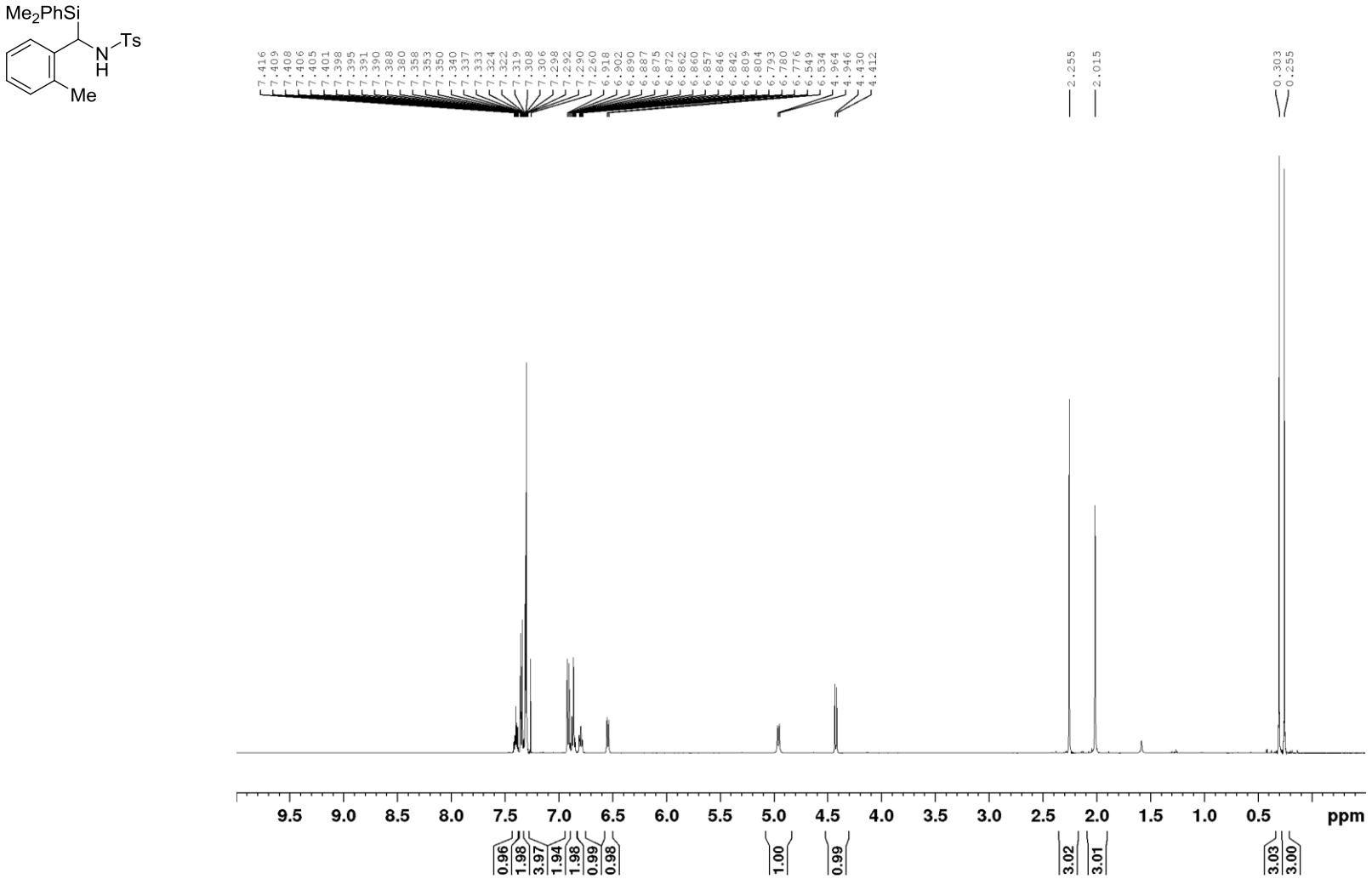
^{13}C NMR (125 MHz, $CDCl_3$)



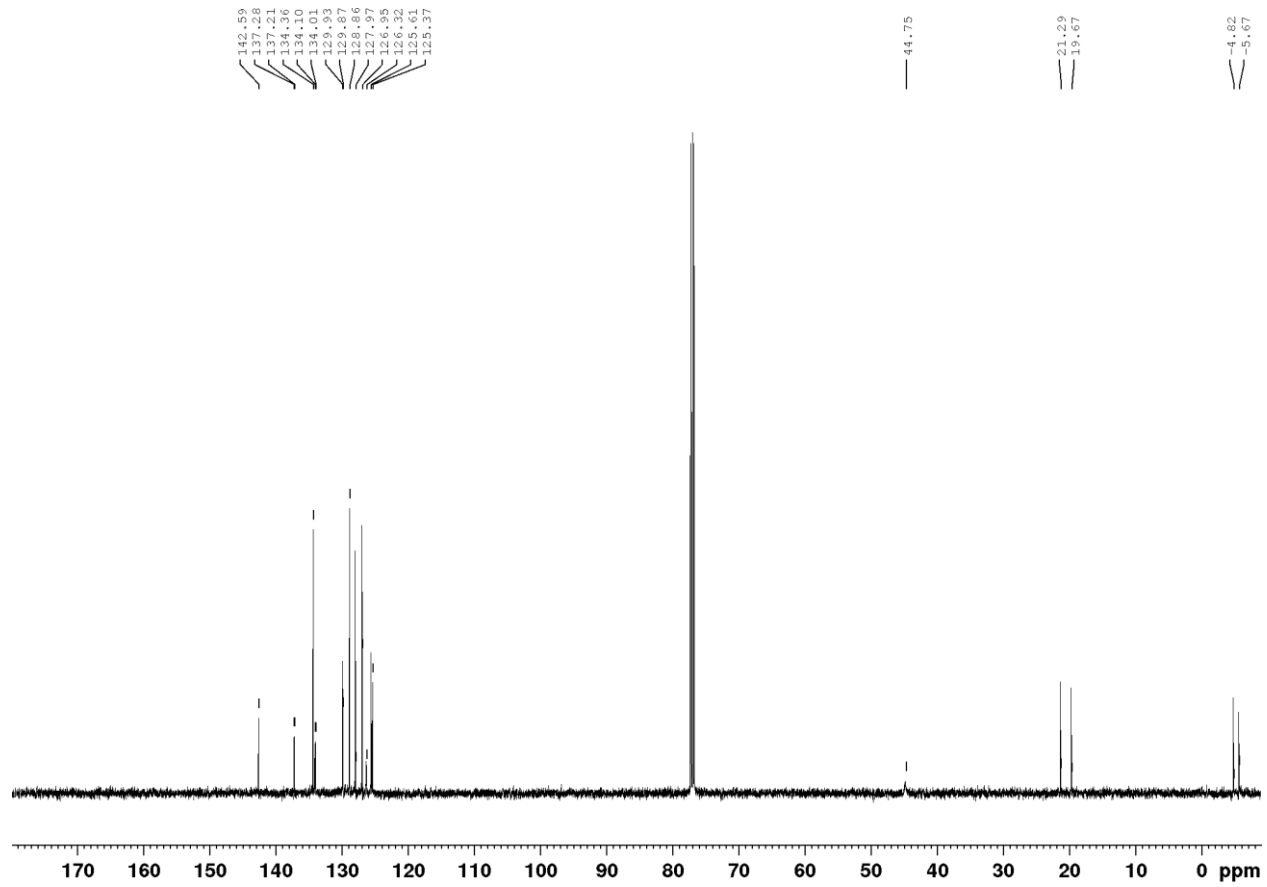
^{29}Si NMR (99 MHz, $CDCl_3$)



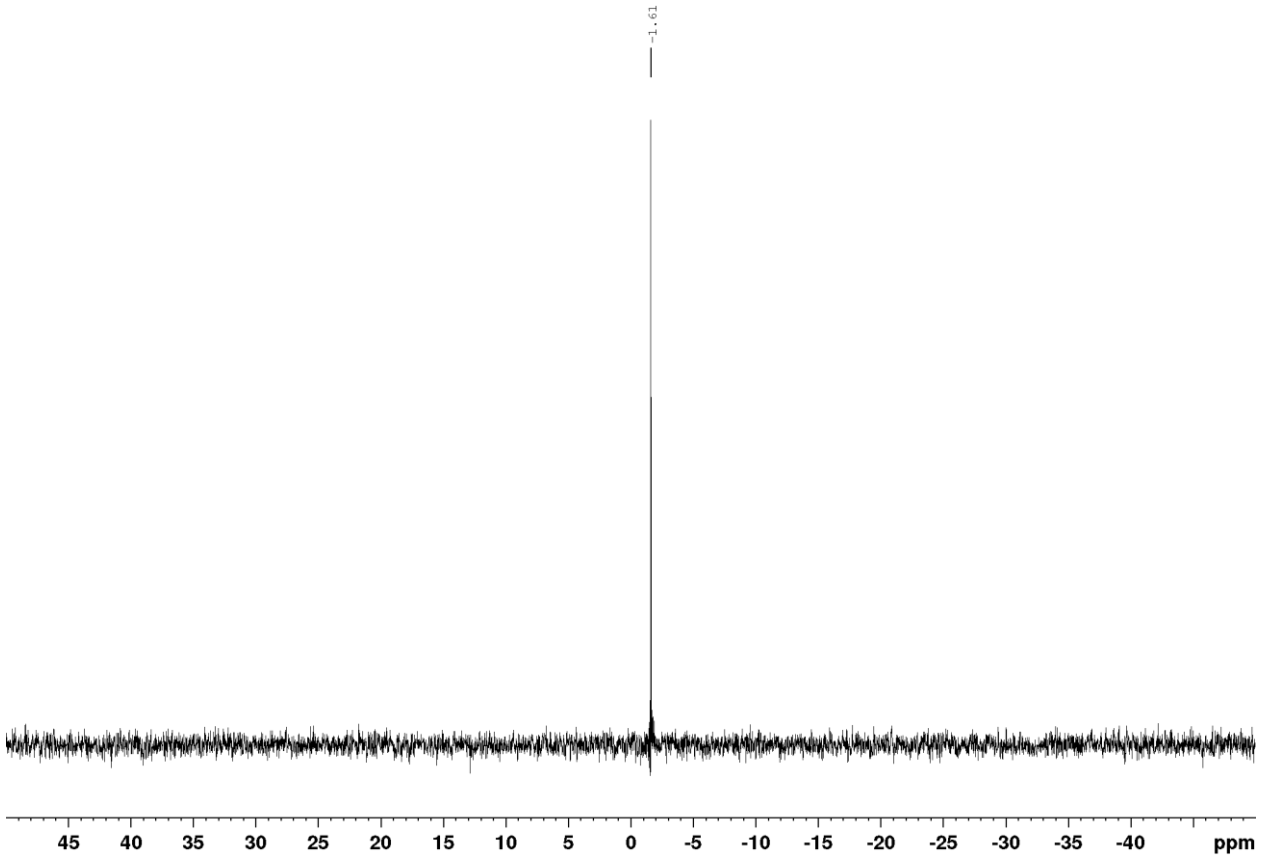
***N*-((Dimethyl(phenyl)silyl)(*o*-tolyl)methyl)-4-methylbenzenesulfonamide** (**21a**): ^{1}H NMR (500 MHz, $CDCl_3$)



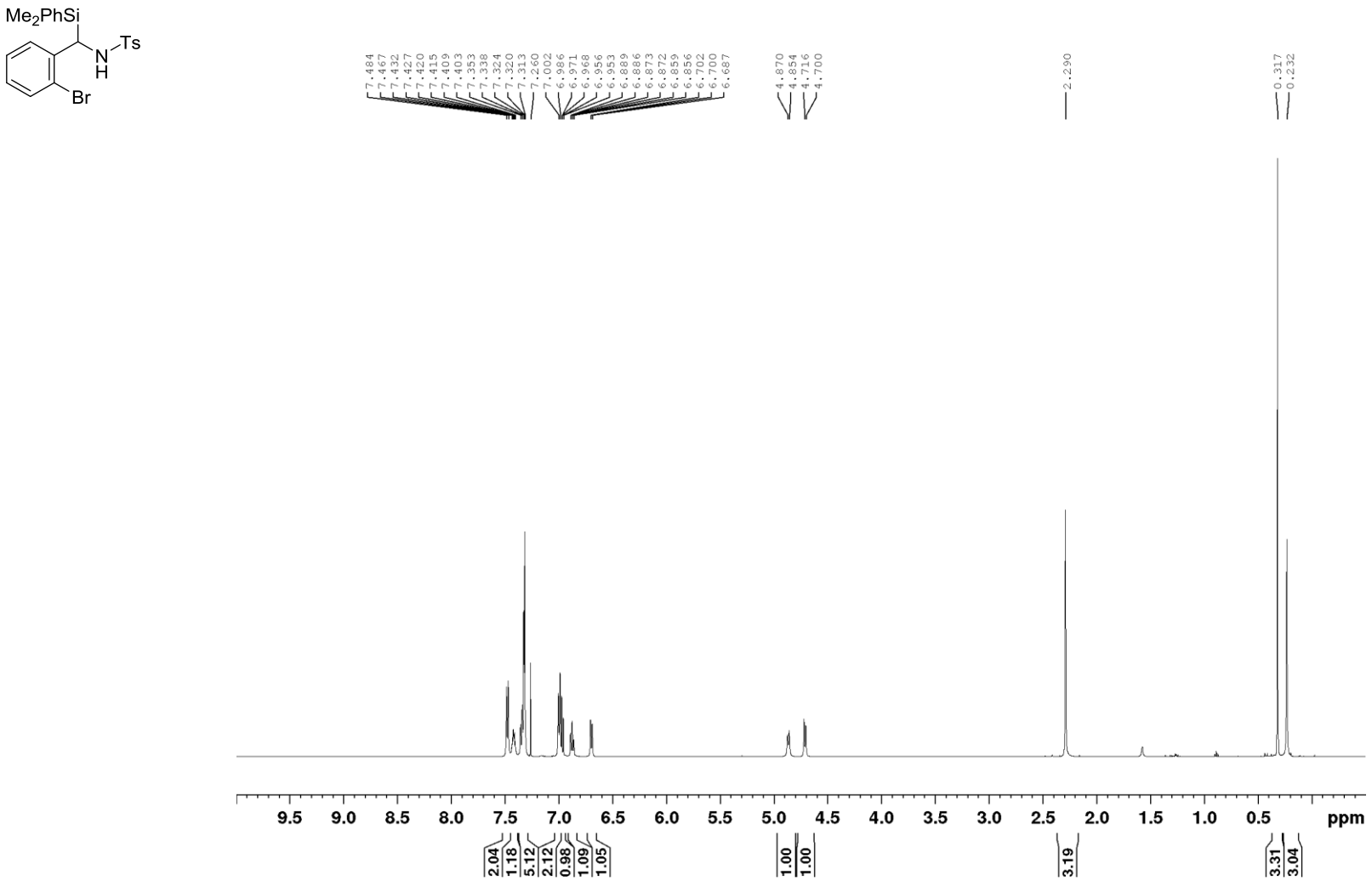
^{13}C NMR (125 MHz, $CDCl_3$)



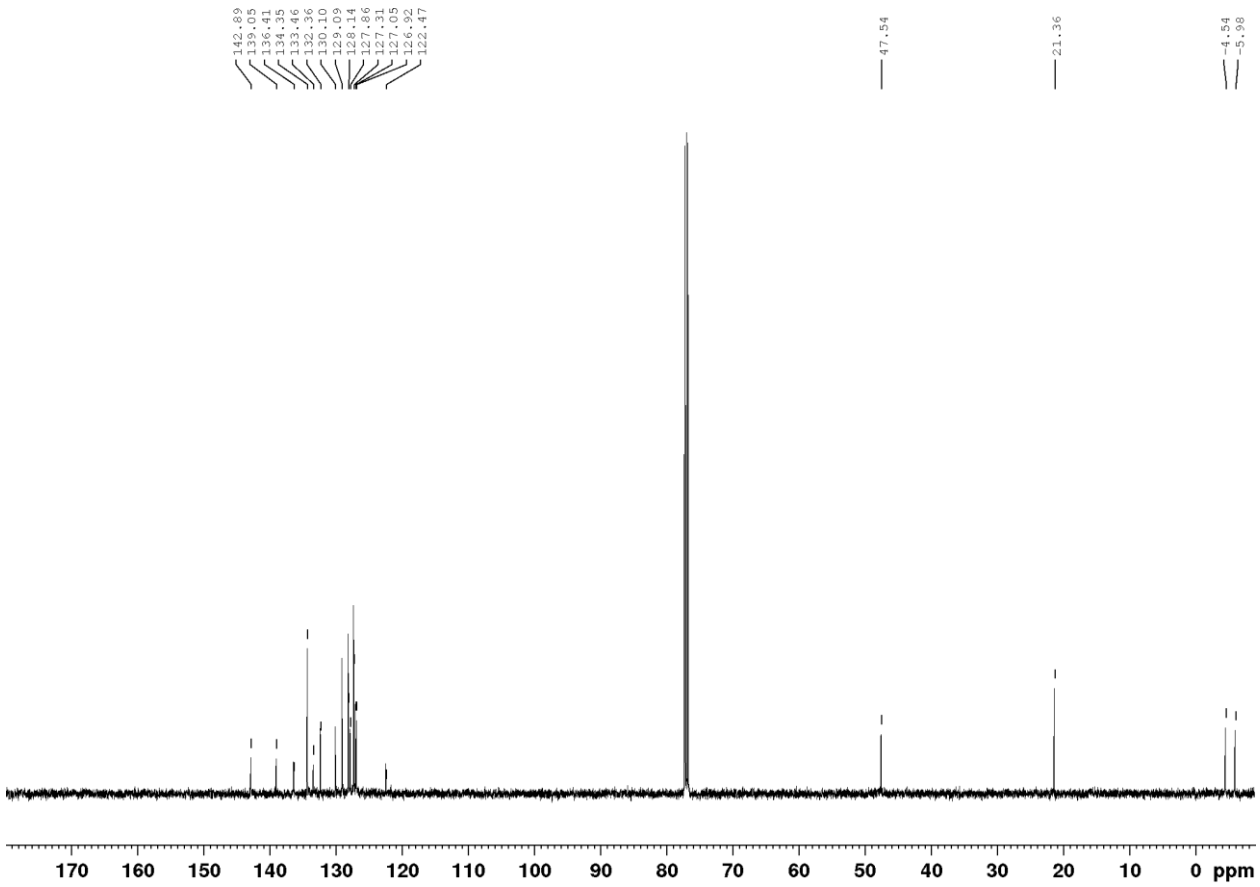
^{29}Si NMR (99 MHz, $CDCl_3$)



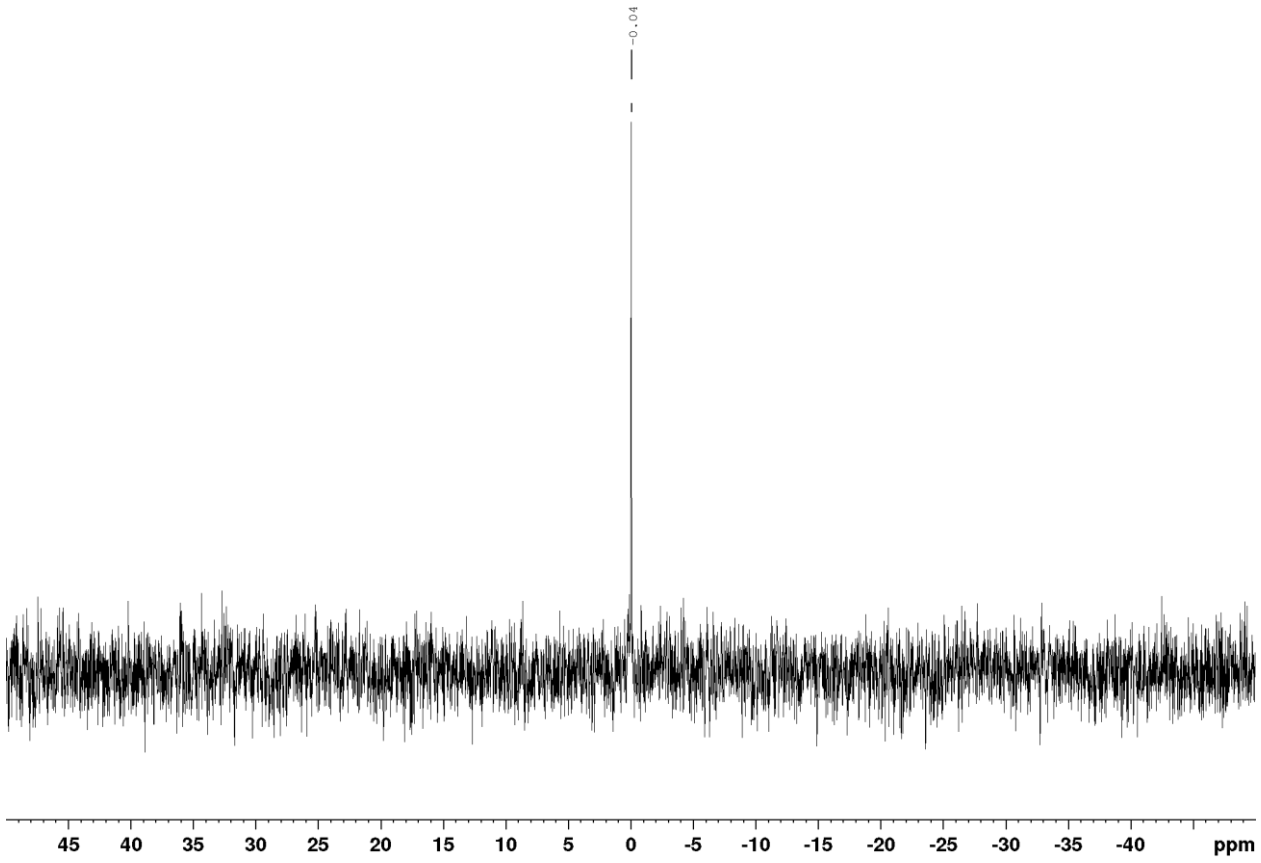
***N*-((2-Bromophenyl)(dimethyl(phenyl)silyl)methyl)-4-methylbenzenesulfonamide** (**22a**): ^{1}H NMR (500 MHz, $CDCl_3$)



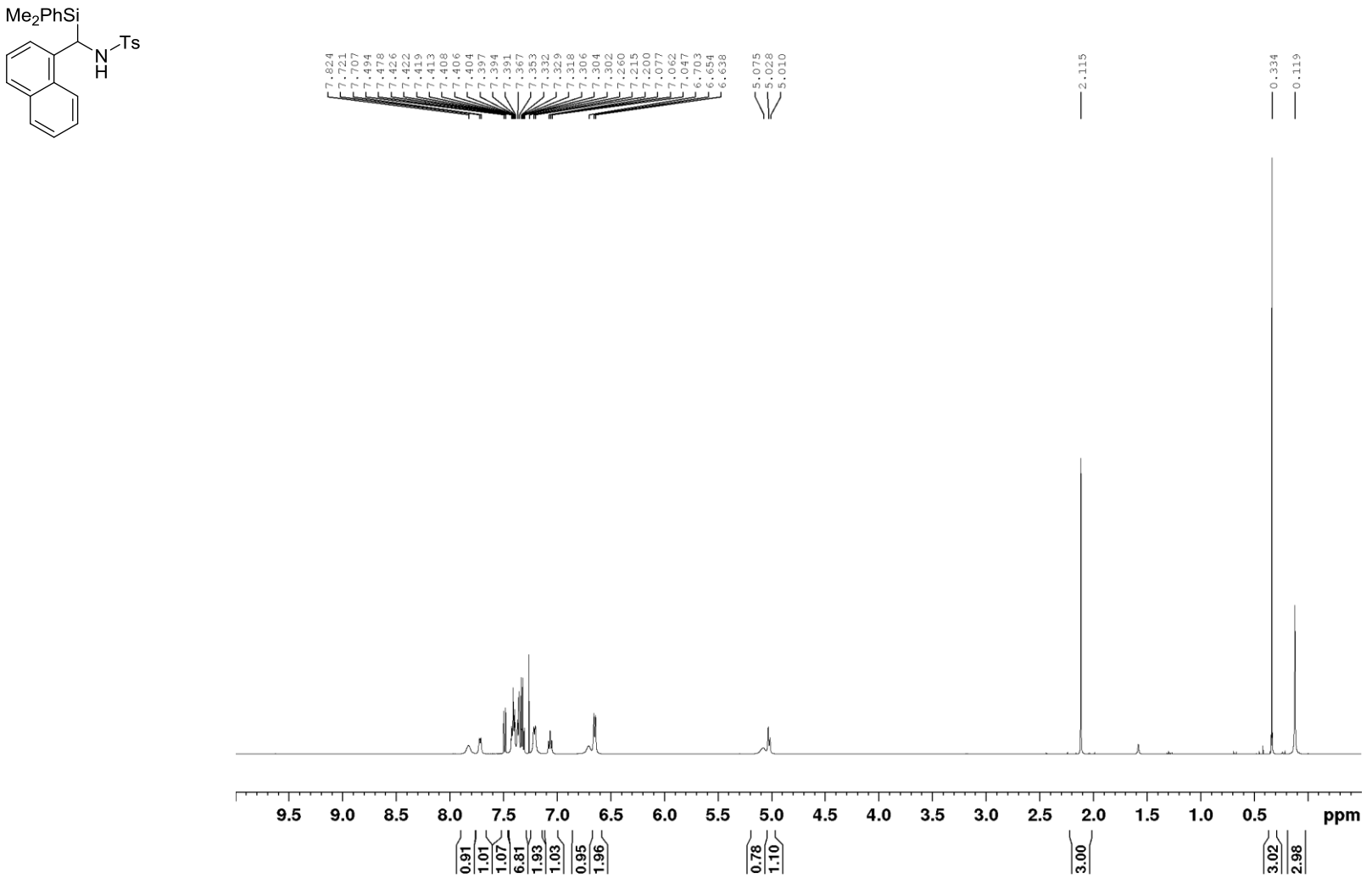
^{13}C NMR (125 MHz, $CDCl_3$)



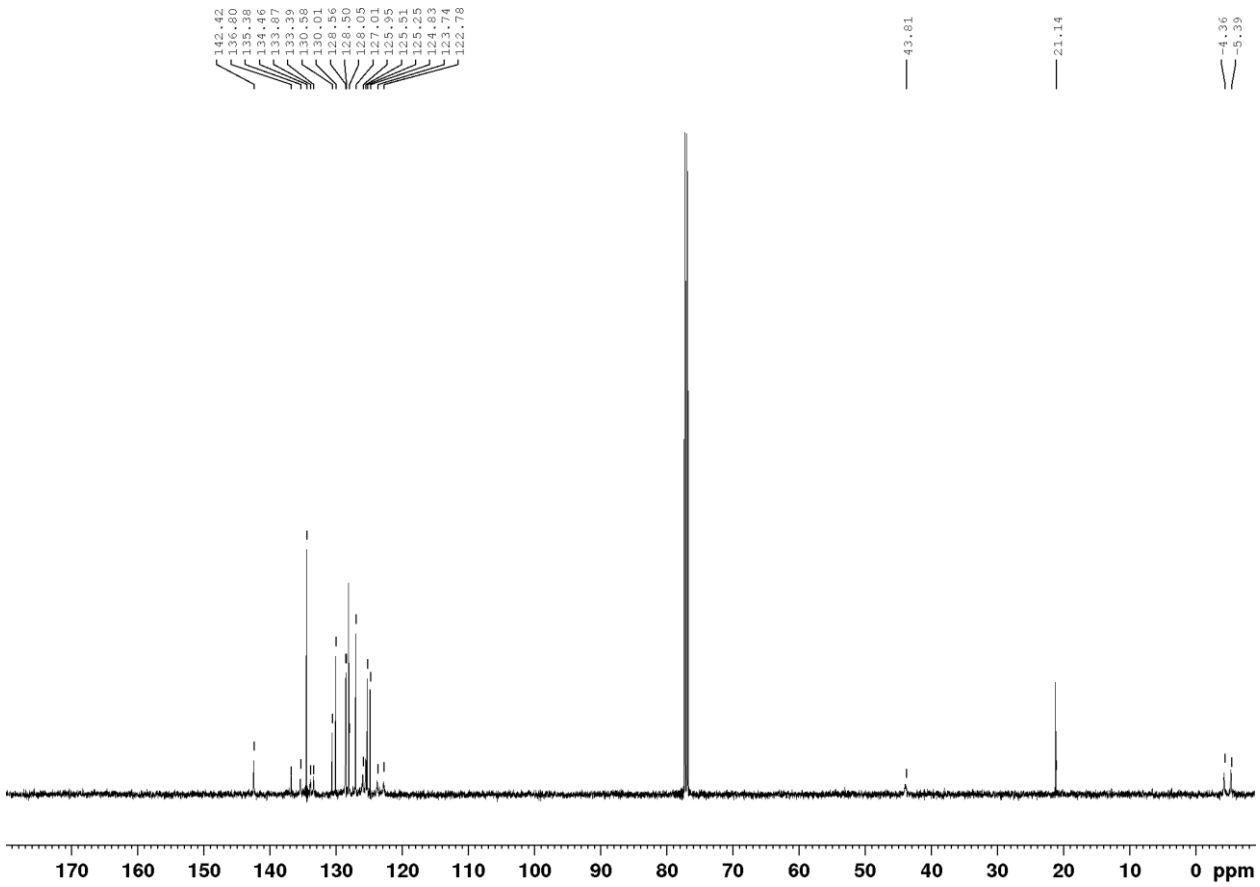
^{29}Si NMR (99 MHz, $CDCl_3$)



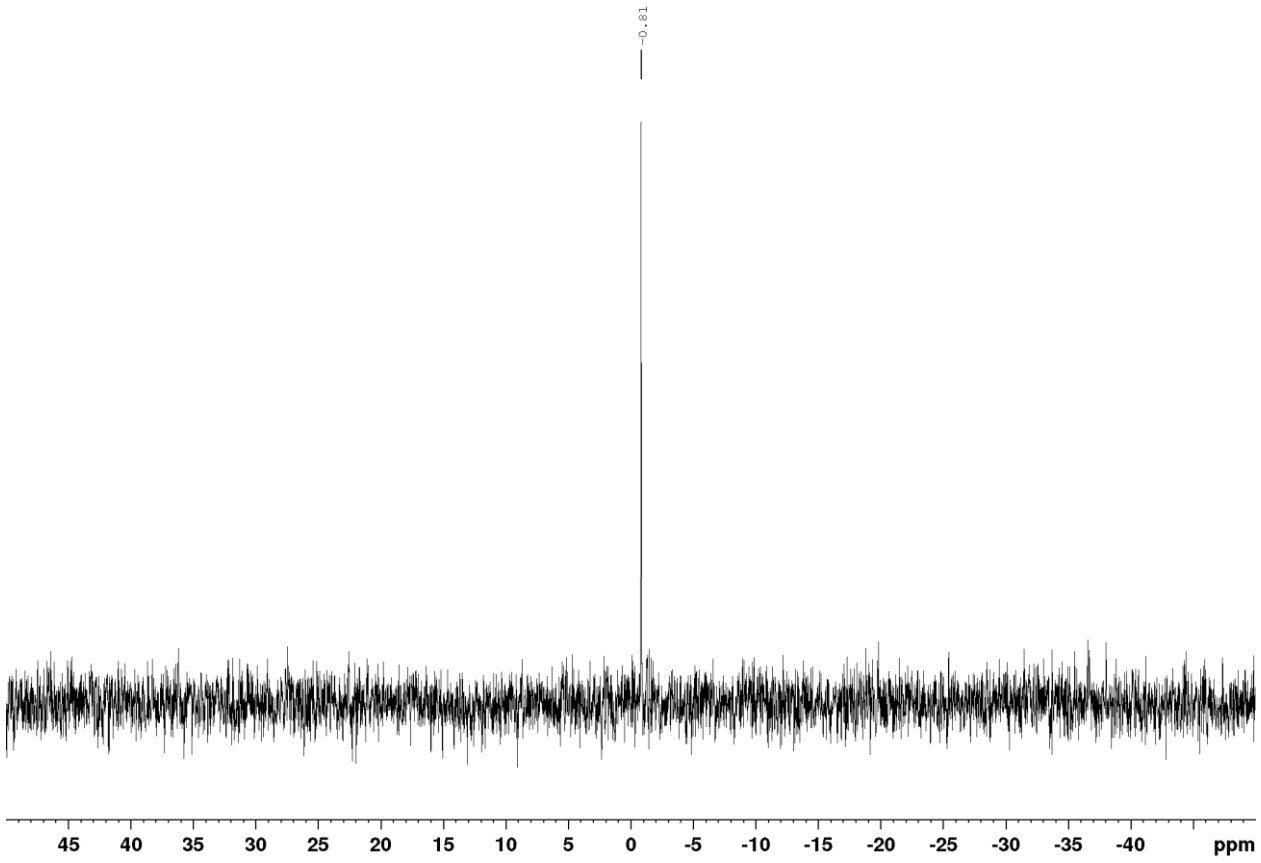
***N*-((Dimethyl(phenyl)silyl)(naphthalen-1-yl)methyl)-4-methylbenzenesulfonamide** (**23a**): ^{1}H NMR (500 MHz, $CDCl_3$)



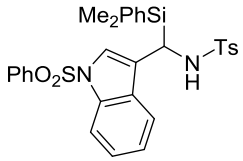
^{13}C NMR (125 MHz, $CDCl_3$)

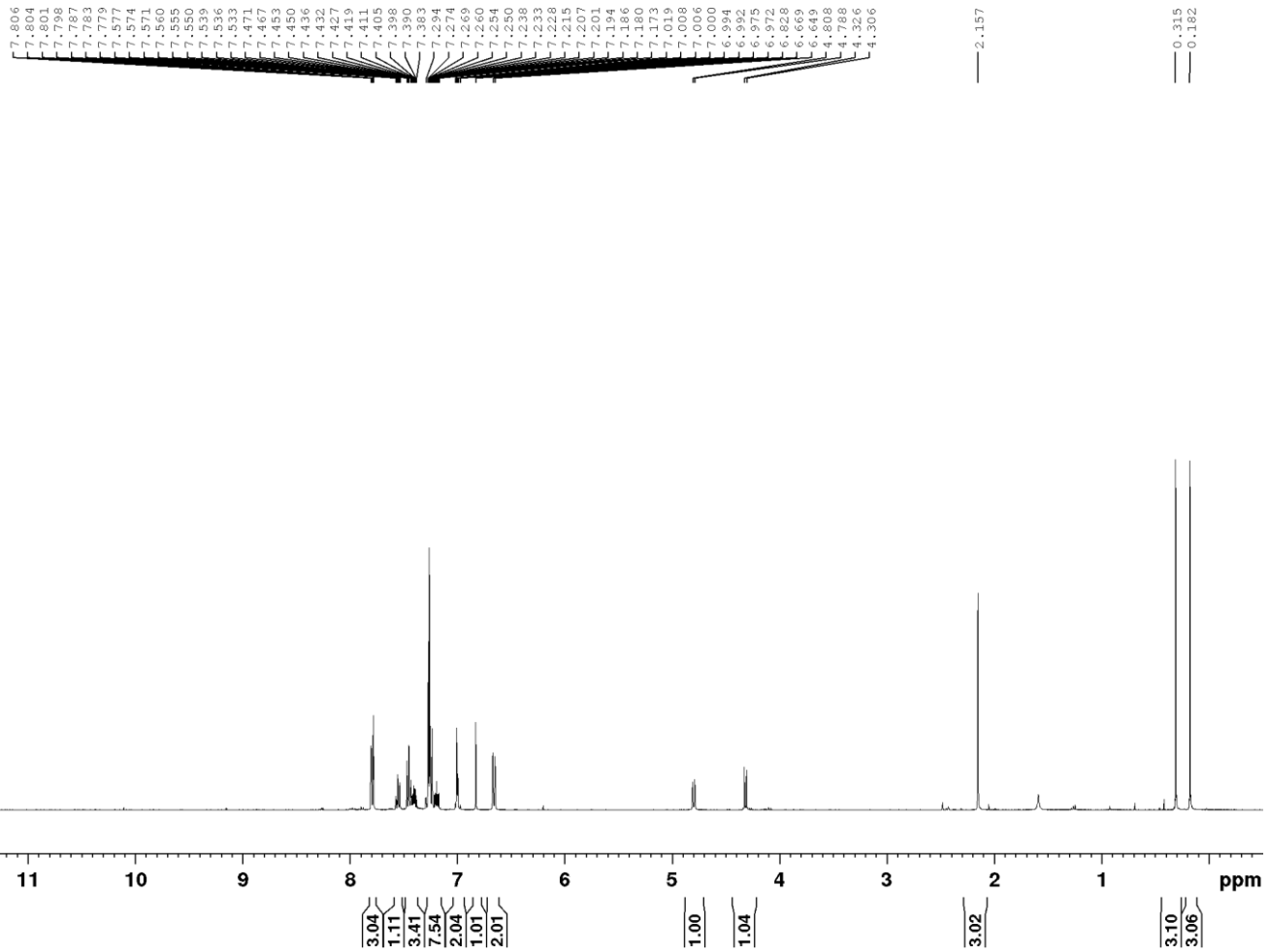


^{29}Si NMR (99 MHz, $CDCl_3$)

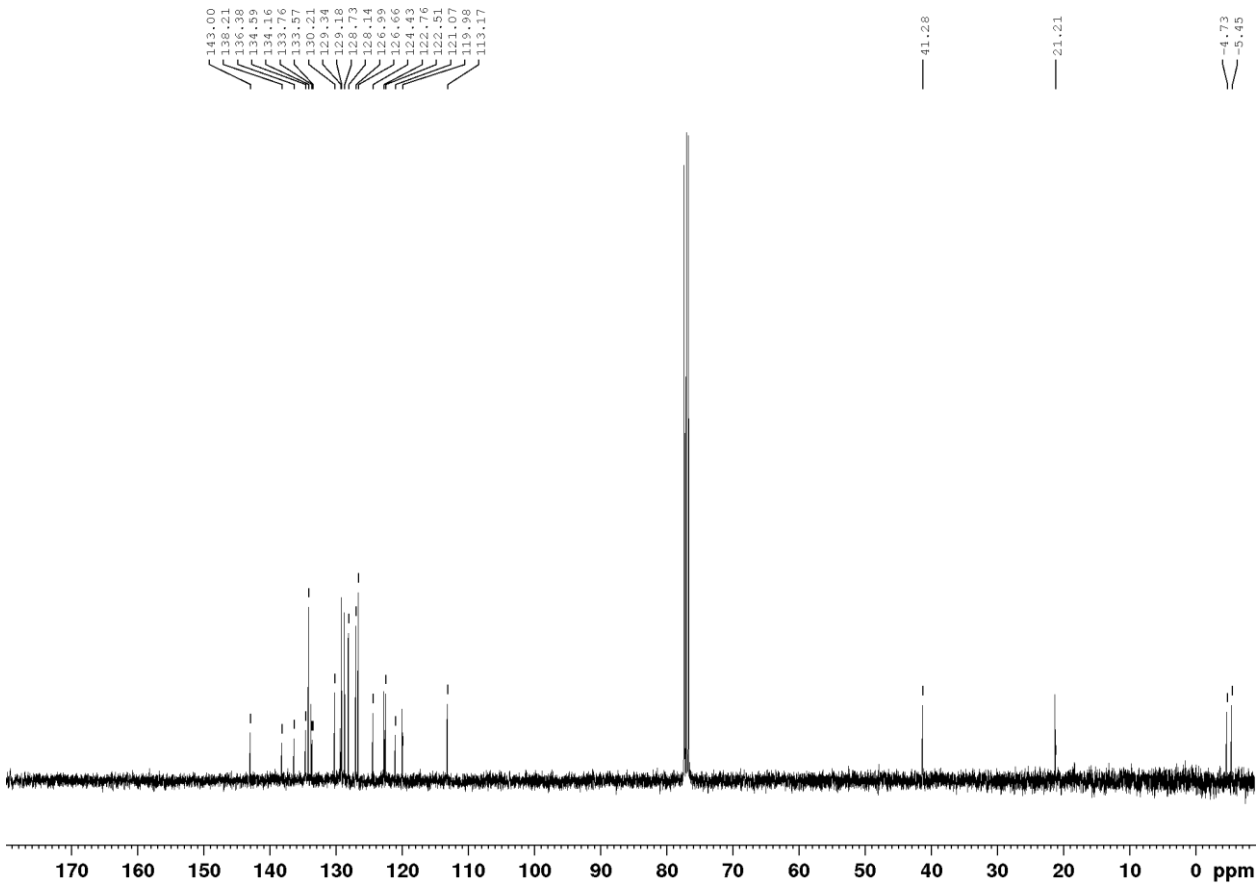


***N*-((Dimethyl(phenyl)silyl)(1-(phenylsulfonyl)-1*H*-indol-3-yl)methyl)-4-methylbenzenesulfonamide** (**24a**): ^{1}H NMR (400 MHz, $CDCl_3$)

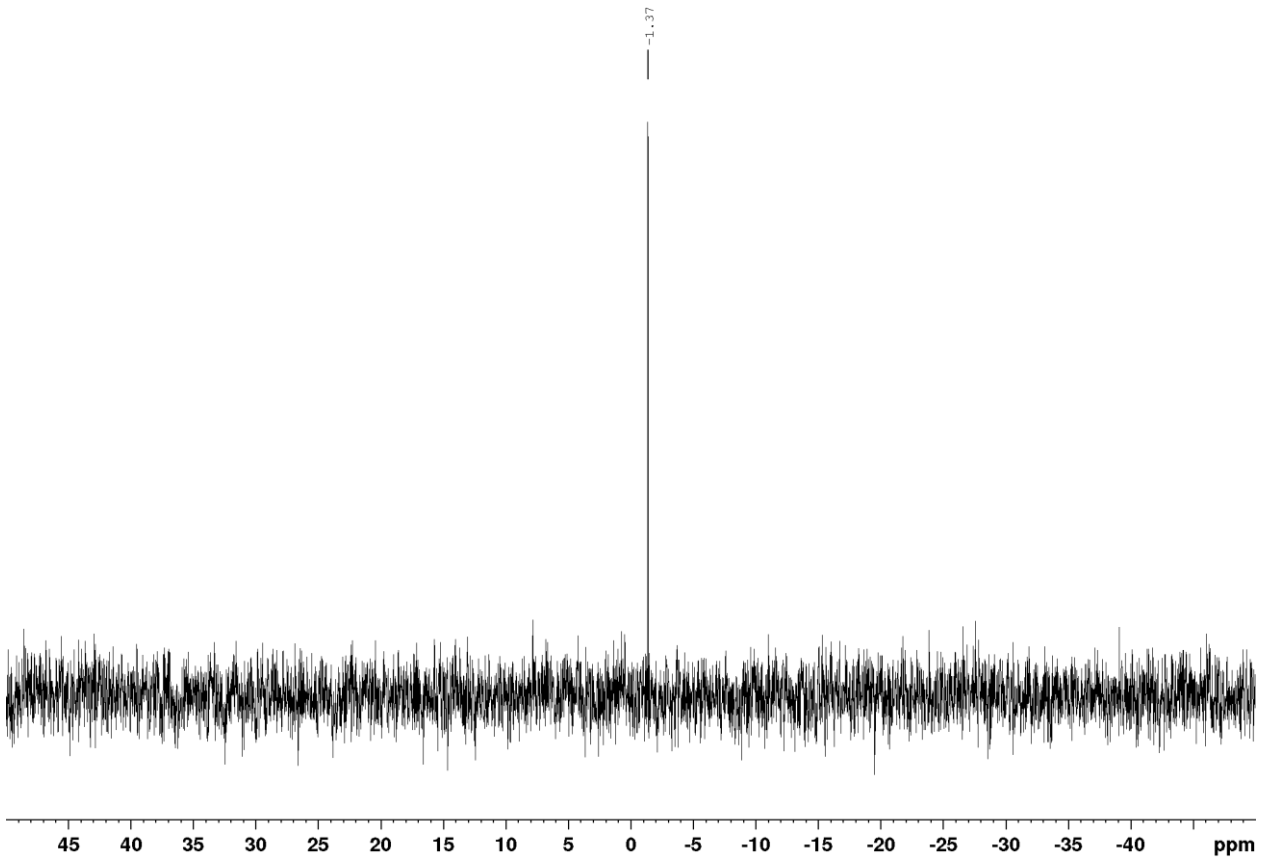




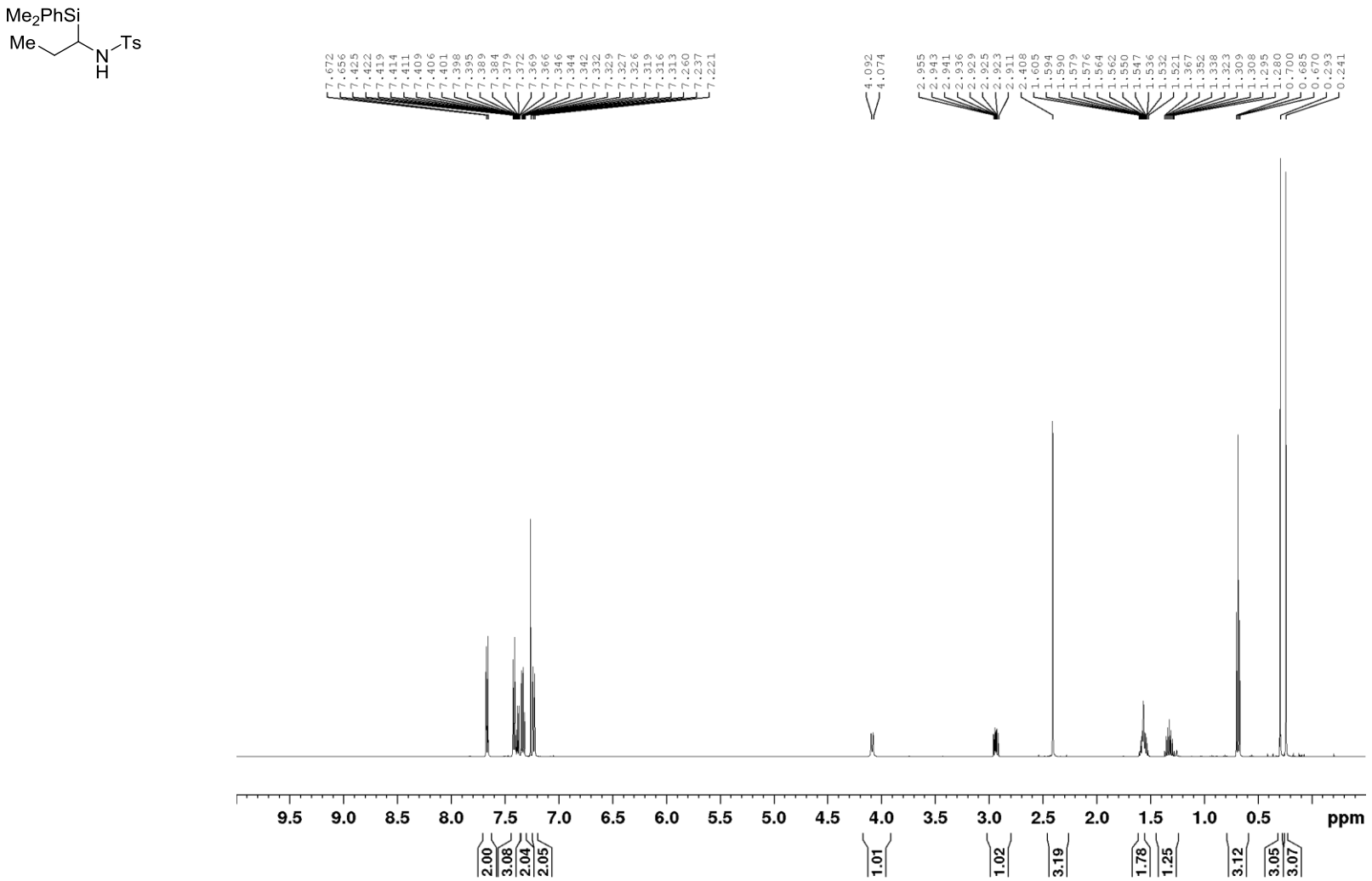
^{13}C NMR (125 MHz, $CDCl_3$)



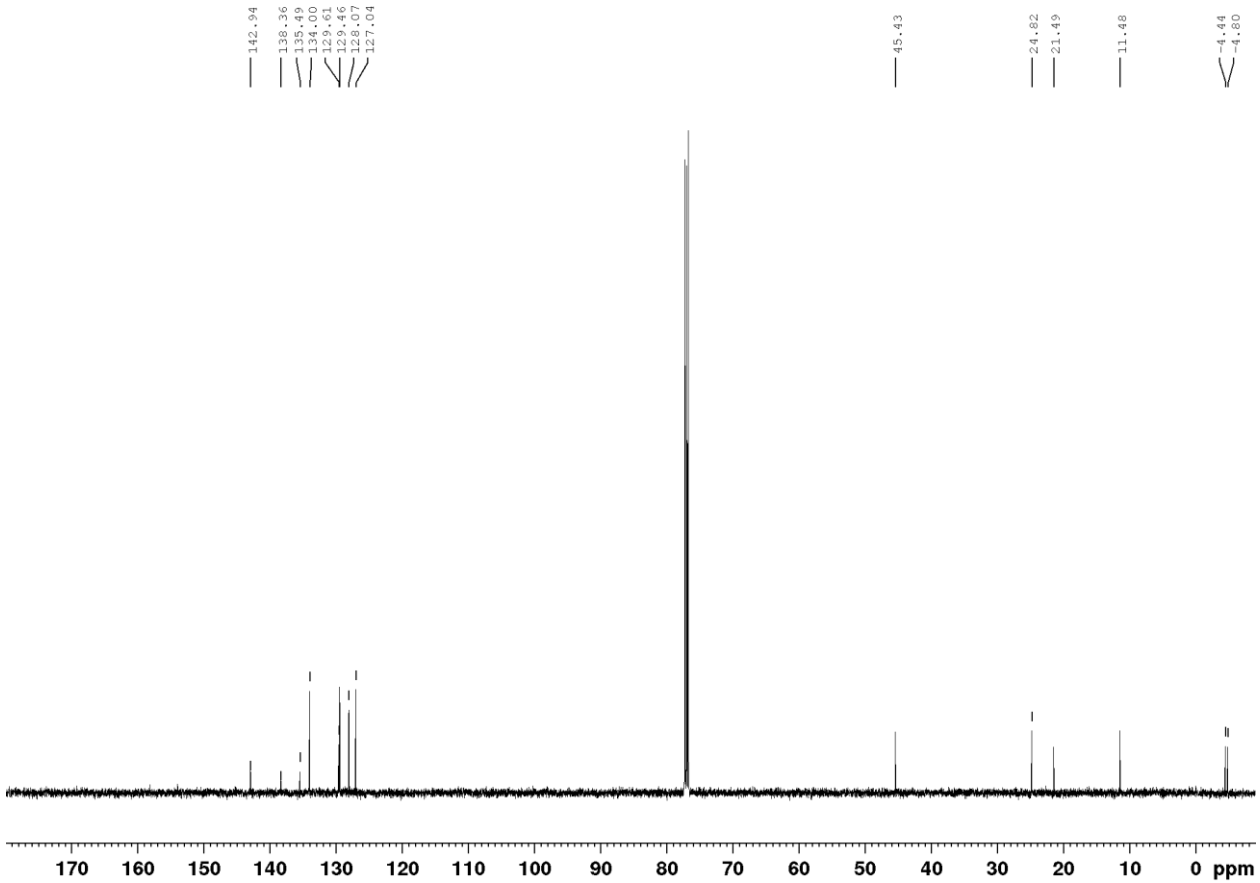
^{29}Si NMR (99 MHz, $CDCl_3$)



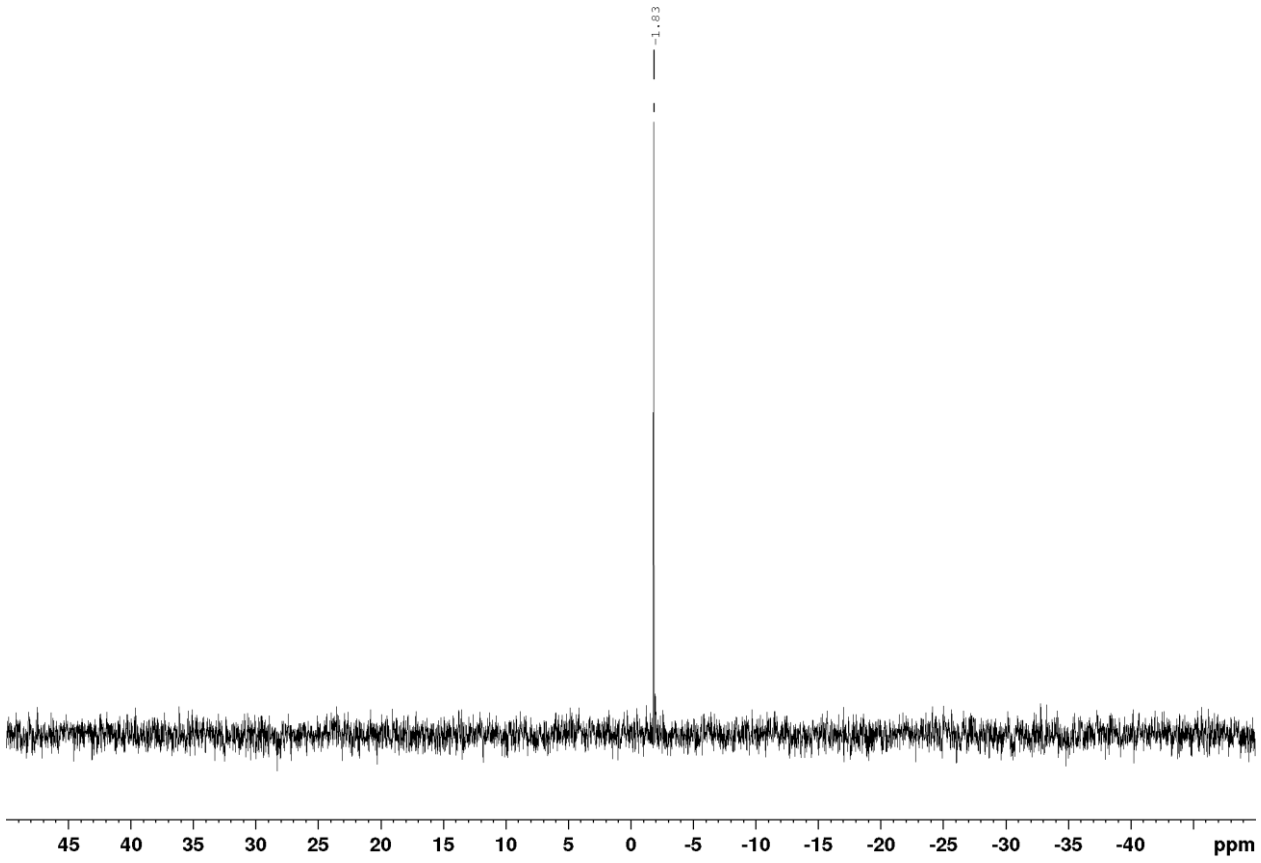
***N*-(1-(Dimethyl(phenyl)silyl)propyl)-4-methylbenzenesulfonamide** (**25a**): ^{1}H NMR (500 MHz, $CDCl_3$)



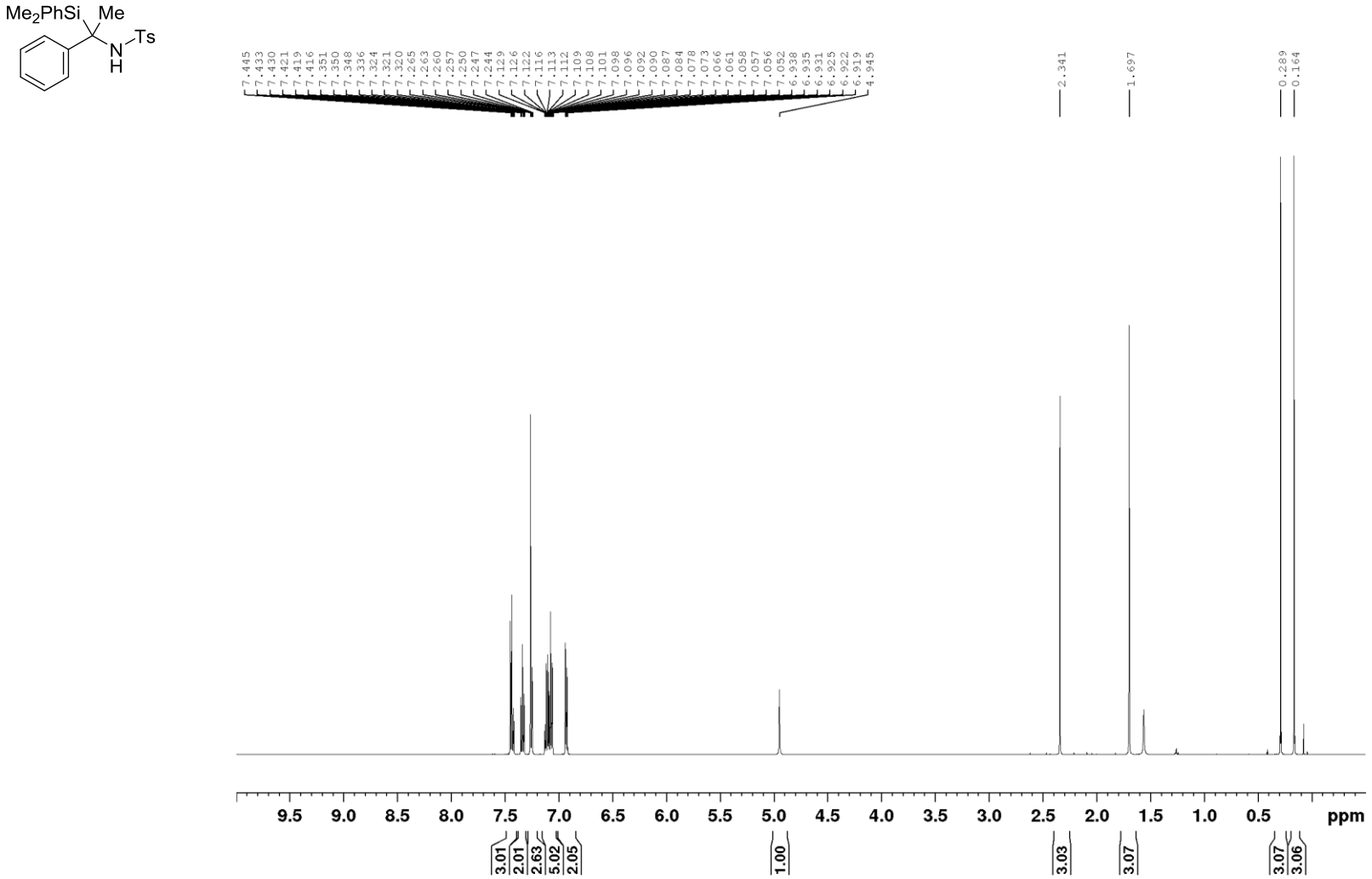
^{13}C NMR (125 MHz, $CDCl_3$)



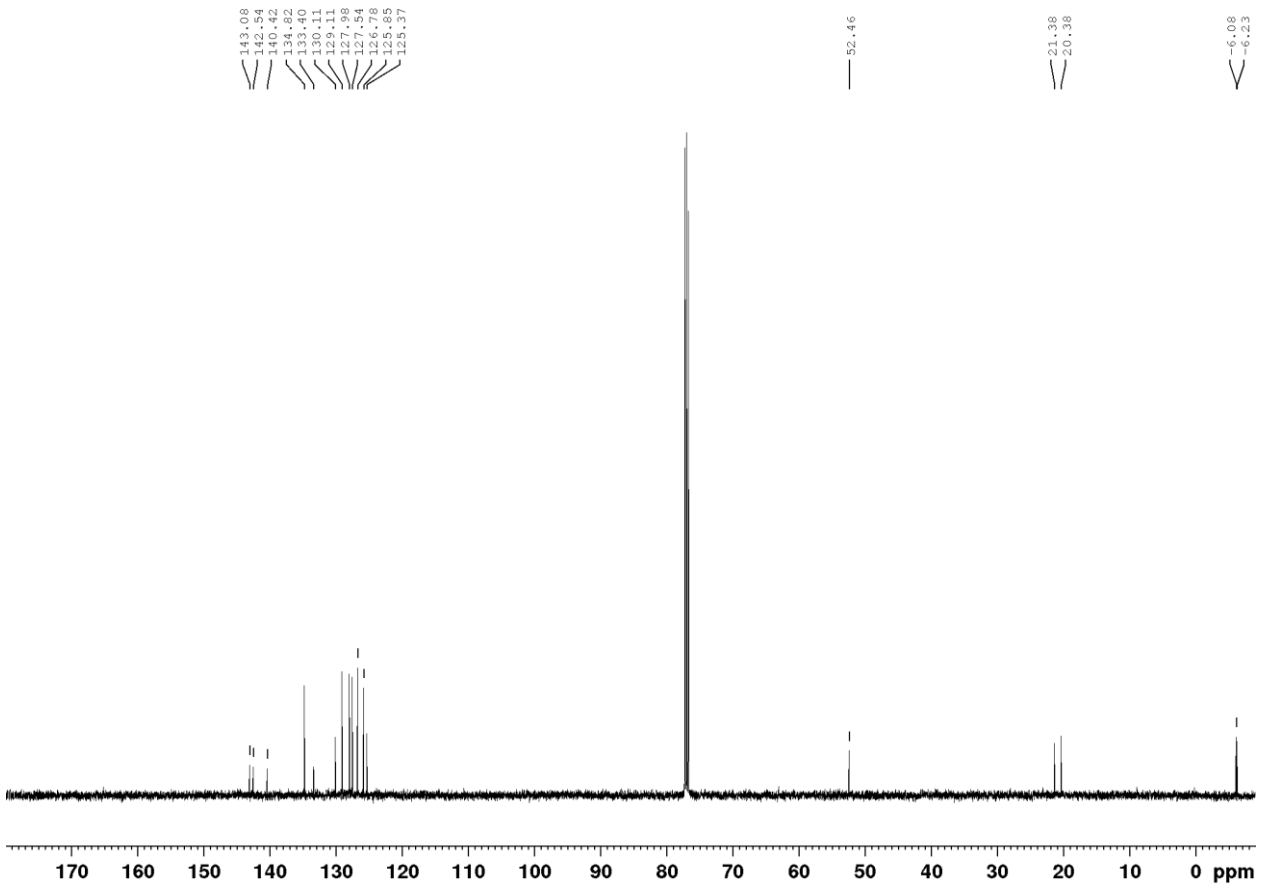
^{29}Si NMR (99 MHz, $CDCl_3$)



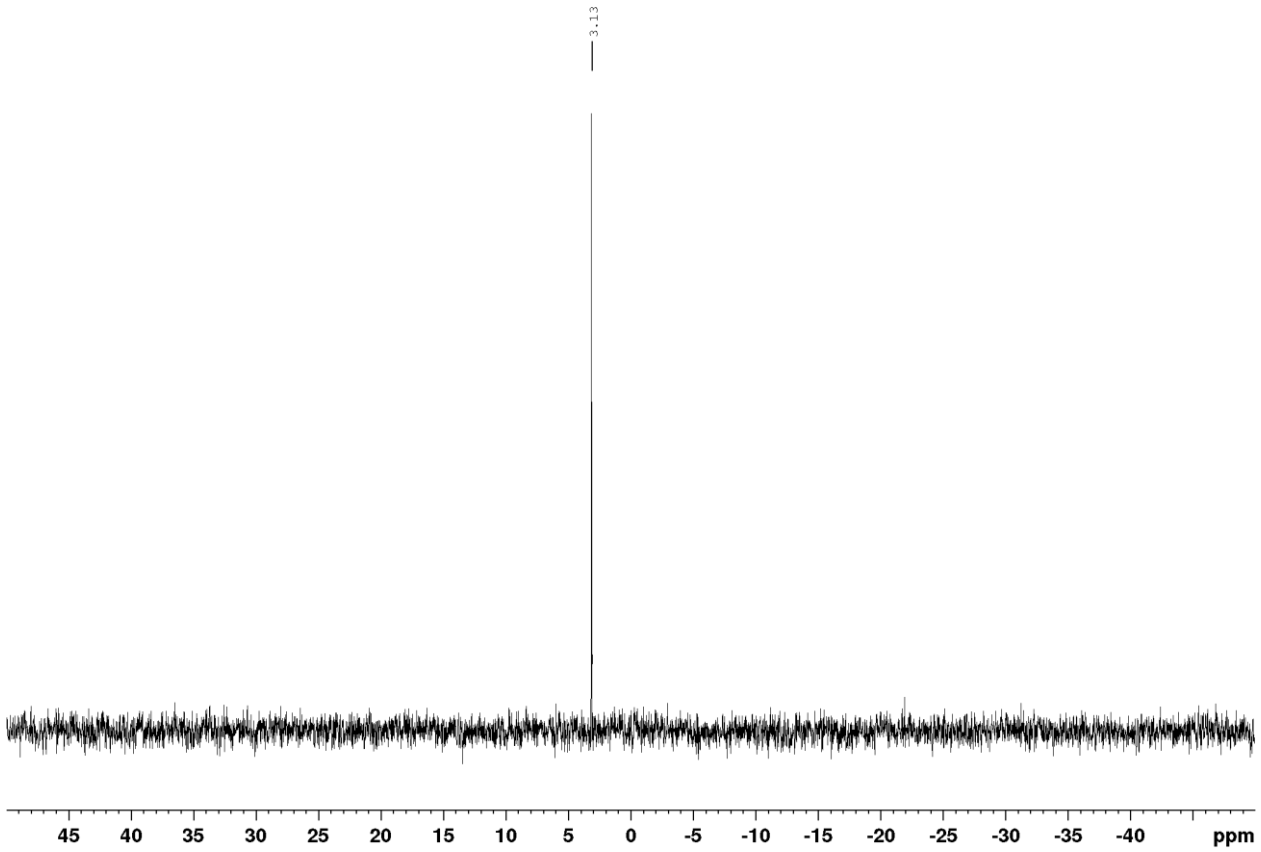
***N*-(1-(Dimethyl(phenyl)silyl)-1-phenylethyl)-4-methylbenzenesulfonamide** (**26a**): ^{1}H NMR (500 MHz, $CDCl_3$)



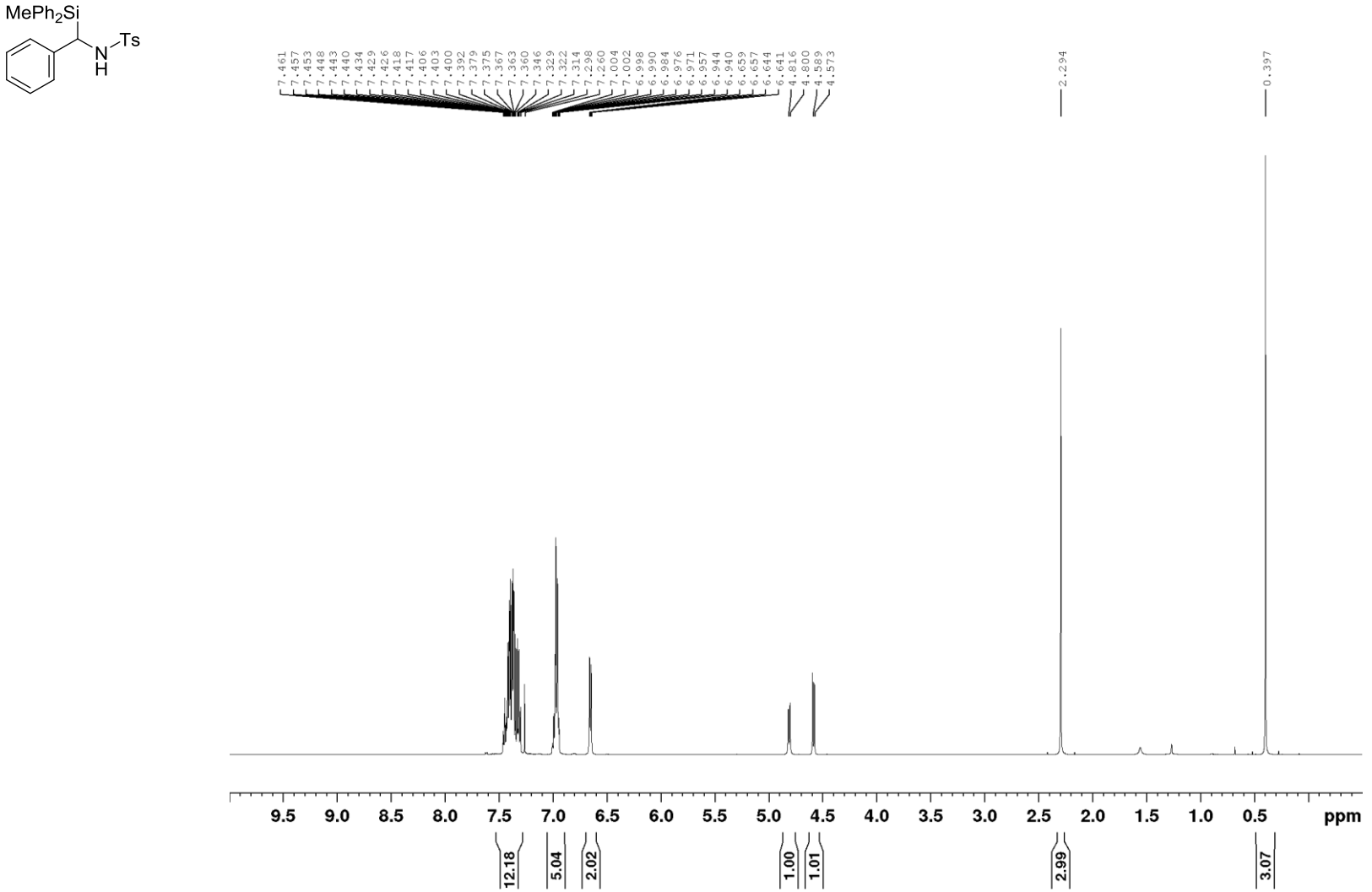
^{13}C NMR (125 MHz, $CDCl_3$)



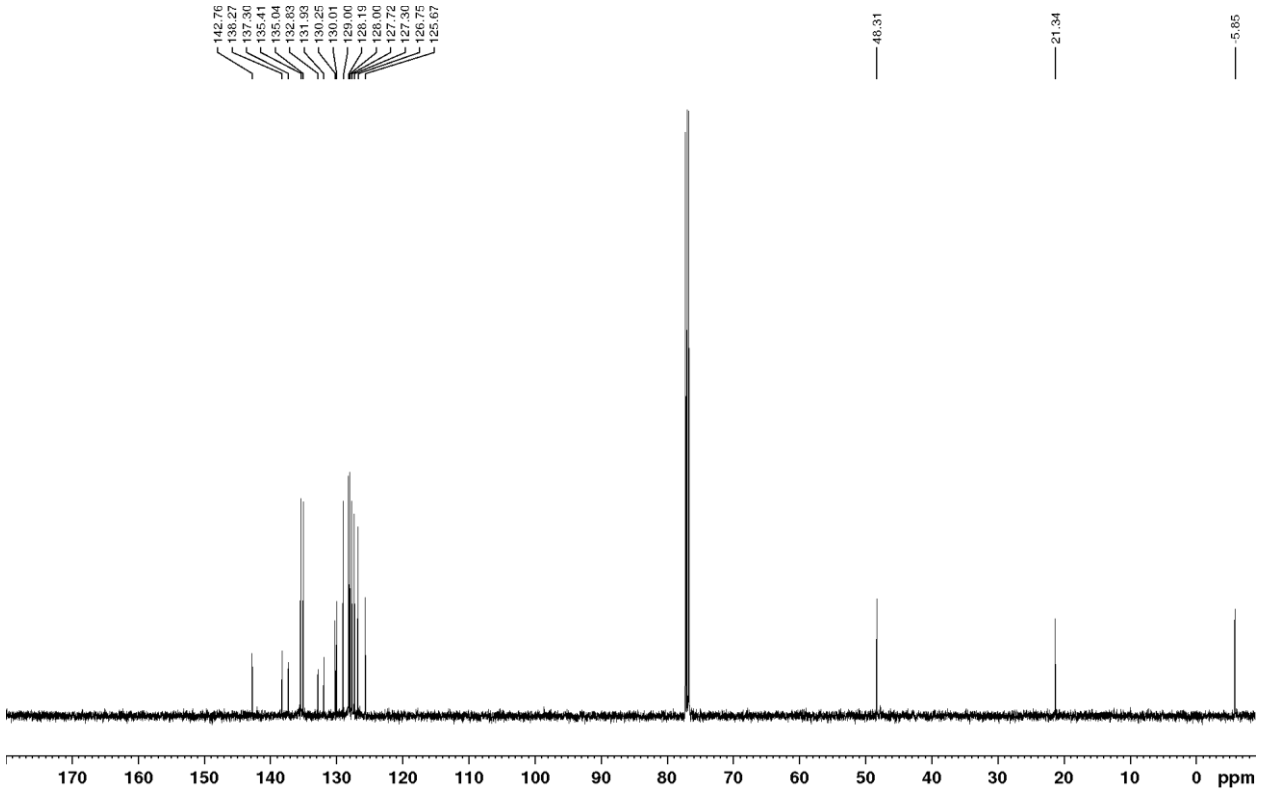
^{29}Si NMR (99 MHz, $CDCl_3$)



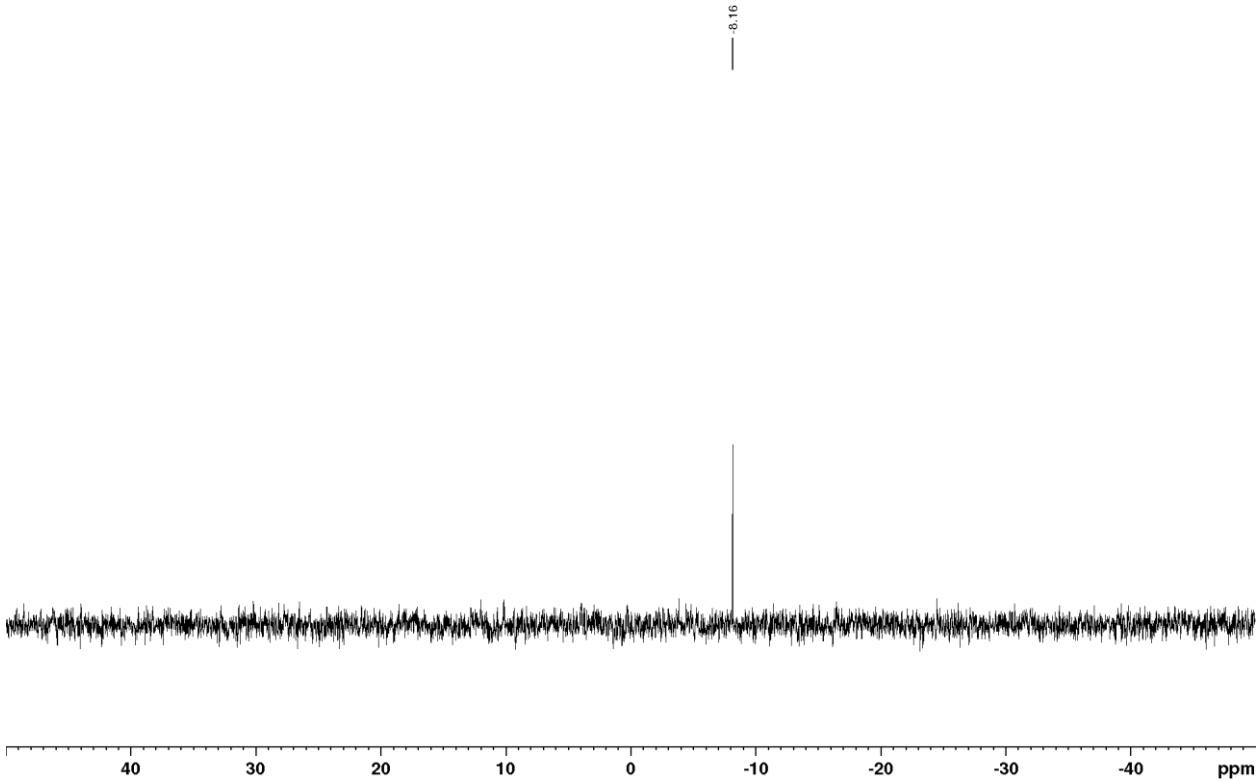
4-Methyl-*N*-((methyldiphenylsilyl)(phenyl)methyl)benzenesulfonamide: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{29}Si NMR (99 MHz, $CDCl_3$)



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[2] Boebel, T. A.; Hartwig, J. F. *Organometallics* **2008**, *27*, 6013–6019.

[3] Mintz, M. J.; Walling, C. *Organic Synthesis* Coll. Vol. 5, 184–187.

[4] Qin, Q.; Yu, S. *Org. Lett*. **2015**, *17*, 1894–1897.

[5] Minakata, S.; Kano, D.; Oderaotoshi, Y.; Komatsu, M. *Org. Lett*. **2002**, *4*, 2097–2099.