Supporting Information

for

Donor free stibenium cation as efficient cyanosilylation catalyst

Nilanjana Sen[a], Prachi Gothe[a], Pallavi Sarkar[b], Shubhajit Das[b], Srinu Tothadi[c] Swapan K Pati[b*], Shabana Khan[a*]

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[S1] Crystal Data and Structure Refinement for 2-4:

Crystallography reflections were collected on a Bruker Smart Apex Duo diffractometer at 150 K using Mo Kα radiation (λ = 0.71073 Å) for 2, 3, 4. The structures were solved by direct method and refined by full-matrix least-squares methods against F2 (SHELXL-2014/6). Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC no. 2165631 (**2**) 2151271 (**3**) and 2193921 (**4**).

Table S1. Data collection parameters for compounds **2**, **3** and **4**.

	2	**3**	**4**
Chemical formula	$C_{16}H_{26}ClN_2Sb$	$C_{17}H_{26}F_3N_2O_3SSb$	$C_{16}H_{26}F_6N_2Sb_2$
Formula weight	403.59 g/mol	517.21 g/mol	603.89 g/mol
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P 2ybc*	*P 2yb*	*P 21/n*
Unit cell dimensions	*a* = 28.428(3) Å	*a* = 8.8486(6) Å	*a* = 11.2599(14) Å
	b = 11.5247(12) Å	*b* = 11.4722(9) Å	*b* = 11.4547(15) Å
	c = 16.1500(18) Å	*c* = 9.9293(8) Å	*c* = 16.001(2) Å
	α = 90°	*α* = 90°	*α* = 90°
	β = 98.154(3) °	*β* = 95.050(3) °	*β* = 92.702(3) °
	γ = 90°	*γ* = 90°	*γ* = 90°
Volume	5237.6(10) $Å^3$	1004.04(13) $Å^3$	2061.5(5) $Å^3$
Z	12	2	4
Density (calculated)	1.535 g/cm^3	1.711 g/cm^3	1.946 g/cm^3
Absorption coefficient	1.727 mm^{-1}	1.525 mm^{-1}	2.675 mm^{-1}
F(000)	2448	520	1168
Theta range for data collection	2.24 to 28.31°	2.719 to 24.997°	2.55 to 28.37°
Index ranges	-33<=h<=33, -13<=k<=13, -19<=l<=19	-10<=h<=10, -13<=k<=13, -11<=l<=11	-13<=h<=13, -13<=k<=13, -19<=l<=19
Reflections collected	192266	31749	75452
Independent reflections	9198 [R(int) = 0.0589]	3527 [R(int) = 0.0368]	3619 [R(int) = 0.0286]
Coverage of independent reflections	100%	99.8%	99.7%
Function minimized	Σ w (Fo2 - Fc2)2	Σ w (Fo2 - Fc2)2	Σ w (Fo2 - Fc2)2
Data / restraints / parameters	9198 / 0 / 560	3527/ 1 / 250	3619 / 0 / 242
Goodness-of-fit on F2	1.167	1.077	1.109

Δ/σ max	0.002	0.001	0.001
Final R indices	8282 data; [I>2σ(I)] R1 = 0.0264, wR2 = 0.0508	3409 data; [I>2σ(I)], R1 = 0.0150, wR2 = 0.0325	3425 data; [I>2σ(I)], R1 = 0.0144, wR2 = 0.0345
	all data, R1 = 0.0325, wR2 = 0.0526	all data, R1 = 0.0166, wR2 = 0.0331	all data, R1 = 0.0160, wR2 = 0.0355
Largest diff. peak and hole	0.096 and -495 eÅ-3	0.313and -0.336 eÅ-3	0.559 and -0.535 eÅ-3
R.M.S. deviation from mean	0.080 eÅ-3	0.052 eÅ-3	0.055 eÅ-3

[S2] Molecular structure of compound 2:

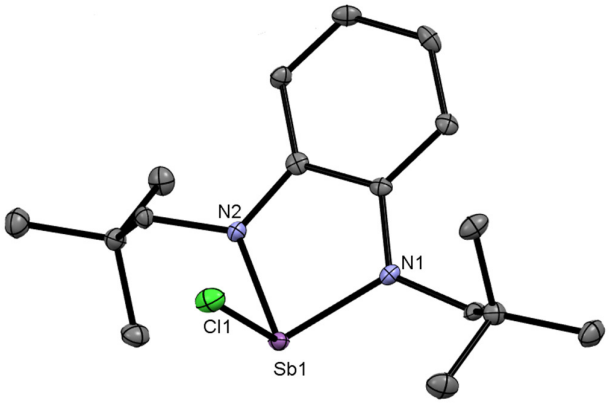


Figure S1. Molecular structure of **2** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **2:** Sb1-Cl1 2.565(1), Sb1-N1 1.988(3), Sb1-N2 1.992(3). Selected bond angles (˚) for **2:** Cl1-Sb1-N1 102.29(1), Cl1-Sb1-N2 92.28(1), N1-Sb1-N2 81.67(1).

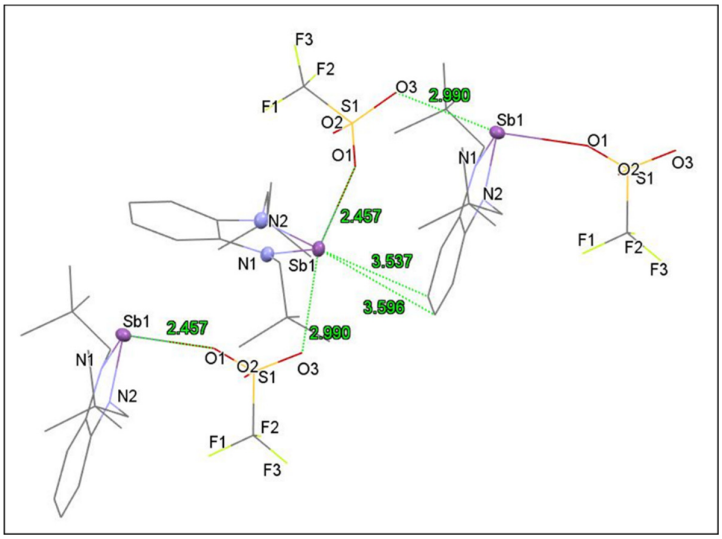


Figure S2. Representation of the extended head-to-tail cation chains observed for compound **3.** Hydrogen atoms are not shown for clarity. Short contacts are shown in green dotted lines.

Compound **3** exhibits a different pattern of cation-cation interaction in the solid-state where an extended form of zigzag chains is visible from the molecular structure (Figure S2). In this case, the cations are arranged in a head-to-tail chain-like fashion where the cations are oriented in a perpendicular direction with the antimony centre in one moiety directed towards the adjacent arene ring resulting in Sb···π interaction which is in η^2 coordination mode. Here the Sb-centroid of the arene ring separation is 3.537-3.596 Å which is slightly shorter than the sum of the van der Waals radii of both antimony and carbon. It is also observed that the antimony centre exhibits two long contacts with oxygen atoms of the triflate anions. This type of similar π interaction has been reported in the case of diamidonaphthalene stabilized phosphenium and arsenium cations where the P-arene contact is 3.426(7) Å and the As-arene distance is 3.228(6) Å.[1] Here the antimony center is in close contact with two oxygen atoms for two triflate moieties (2.457 and 2.990Å) which much shorter than that reported by Gudat and coworkers where a four membered cyclic structure is observed and Sb-O length is much greater (3.349 and 3.170Å).[2]

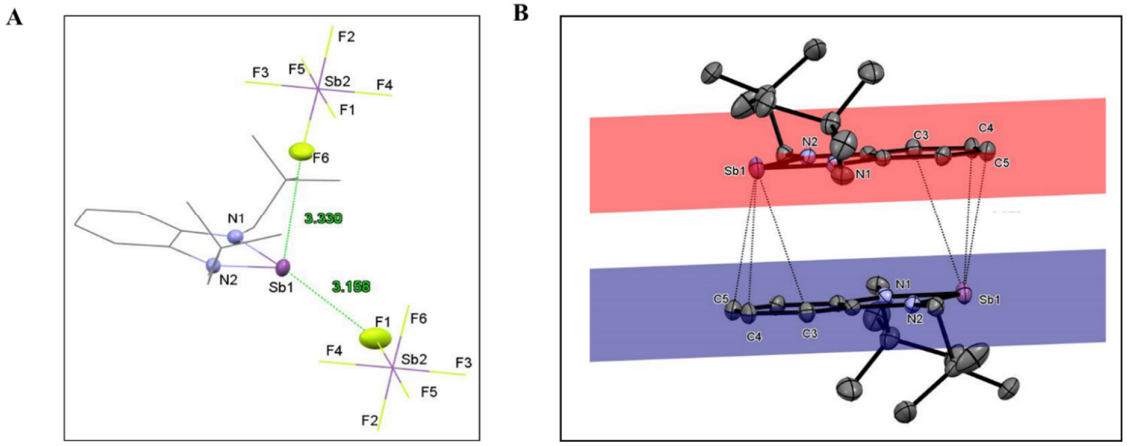


Figure S3. A) Representation of the interactions with the central cationic antimony with the adjacent fluorine atoms of compound **4**. B) Representation of π-stacked cation-cation interactions (antiparallel dimers) of compound **4**. Hydrogen atoms are not shown for clarity.

The molecular structure also reveals that the stibenium cation comprises π-stacked dimers which are antiparallel to each other in orientation (Figure S3) and the antimony centre displays an intermolecular π interaction with the arene ring of the adjacent moiety in η^3 fashion (Sb···C5 is 3.654 Å, Sb···C4 is 3.370 Å and Sb···C3 is 3.532 Å). It is also observed that the antimony centre displays two long contacts with two fluorine atoms located on two different hexafluoroantimonate anions with Sb-F distances being 3.158 and 3.330 Å respectively which is shorter than that reported compound [$(CH)_2(NtBu)_2Sb^+(OTf)^-$] (3.459Å) by Gudat and co-workers.[2] The π-stacking cation-cation contact is 3.512Å which is somewhat longer than that reported for [P(^{i}PrN)$_2$C$_{10}$H$_6$]GaCl$_4$ (3.47(1)Å) and [As(^{i}PrN)$_2$C$_{10}$H$_6$]GaCl$_4$ (3.35(1) Å).[1]

[S3]. Photophysical properties and UV-Vis absorption spectra of compounds 2, 3 and 4:

Table S2. UV-visible spectroscopic data of compounds **2**-**4**.

Compound	**Absorption Wavelength (nm)**		
	THF	DCM	ACN
2 (experimental values)	302, 354	293, 351	297, 344
2 (computed values)	302.6, 353.9	301.7, 354.1	298.2, 353.1

3 (experimental values)	296, 492	296, 496	293, 499
3 (computed values)	261.7, 451.3	261.8, 451.1	262.2, 448.4
4 (experimental values)	296, 503	293, 500	293, 502
4 (computed values)	290.6, 501.3	292.5, 489.8	293.0, 493.0

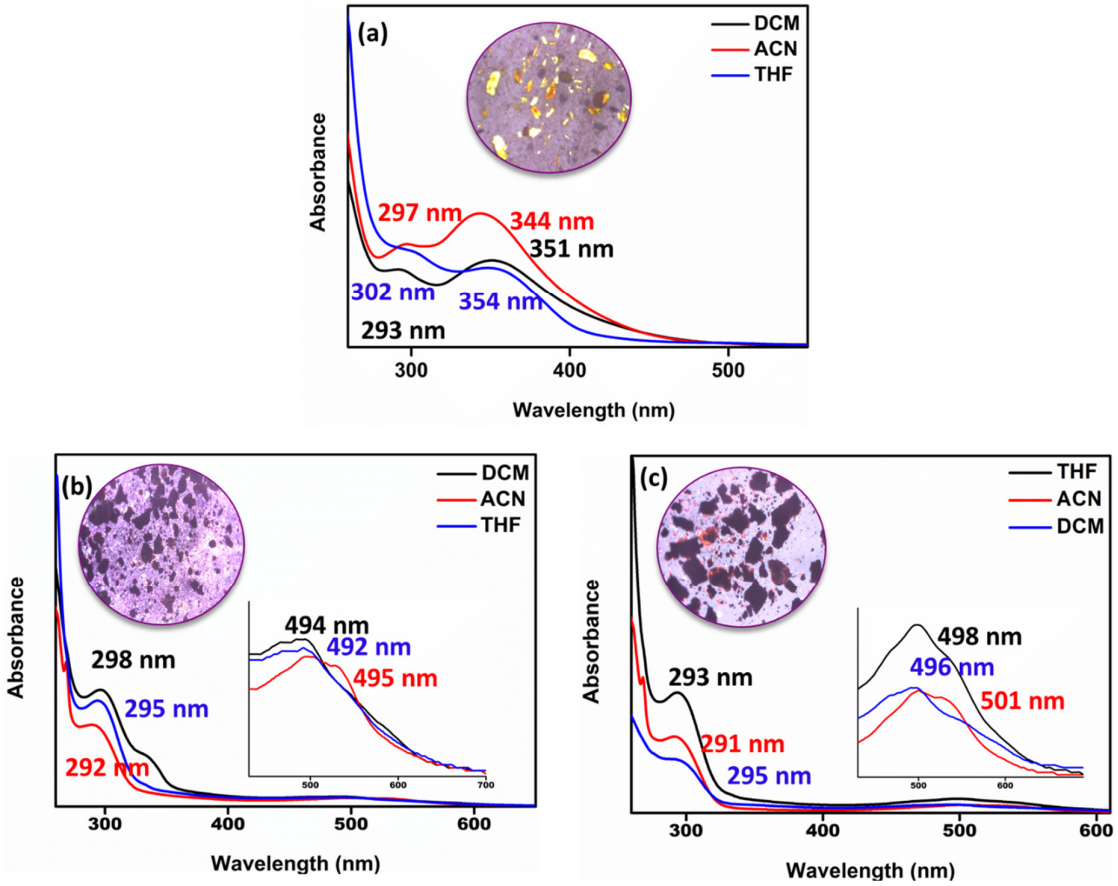


Figure S4: UV-vis absorption spectra of compounds **2** (a), **3** (b), **4** (c).

Since all the three compounds were coloured, we were interested to investigate the photophysical properties of all the three compounds **2**-**4**. To date, only a few reports are there on pnictoles and pnictenium cations where their photophysical properties have been elucidated.[3-4] All the compounds were highly soluble in polar solvents like THF, DCM and ACN, so UV-visible spectrophotometry was recorded in all the polar solvents for all the

compounds (Figure S4). Computational analysis at the TD-DFT [B3LYP-D3/def2-TZVP(Sb),6-311+G(d,p) for lighter atoms] level of theory is in good agreement with the observed visible transitions (see Table S2). Our results reveal that the absorptions are due to the charge transfer from the π electron density of the aromatic ring to vacant p orbital of the antimony atom.

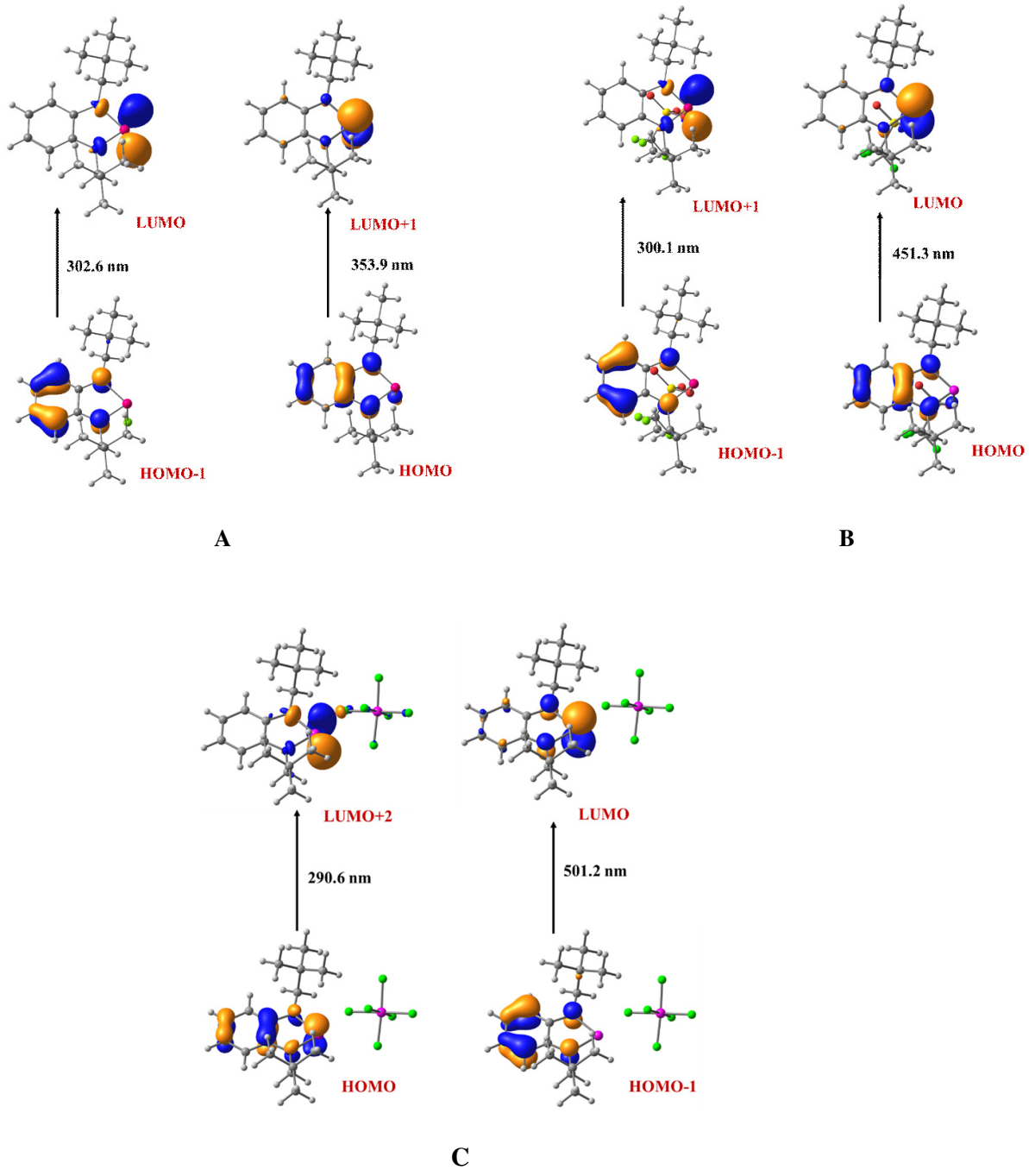


Figure S5: Calculated transitions for the main absorption of (a) **2** (b) **3** and (c) **4**. Isovalue=0.06.

[S4]. ^{1}H, ^{13}C, ^{19}F NMR spectra for compounds 2, 3 and 4:

Figure S6. ^{1}H NMR spectrum of compound **2** in $CDCl_3$**.**

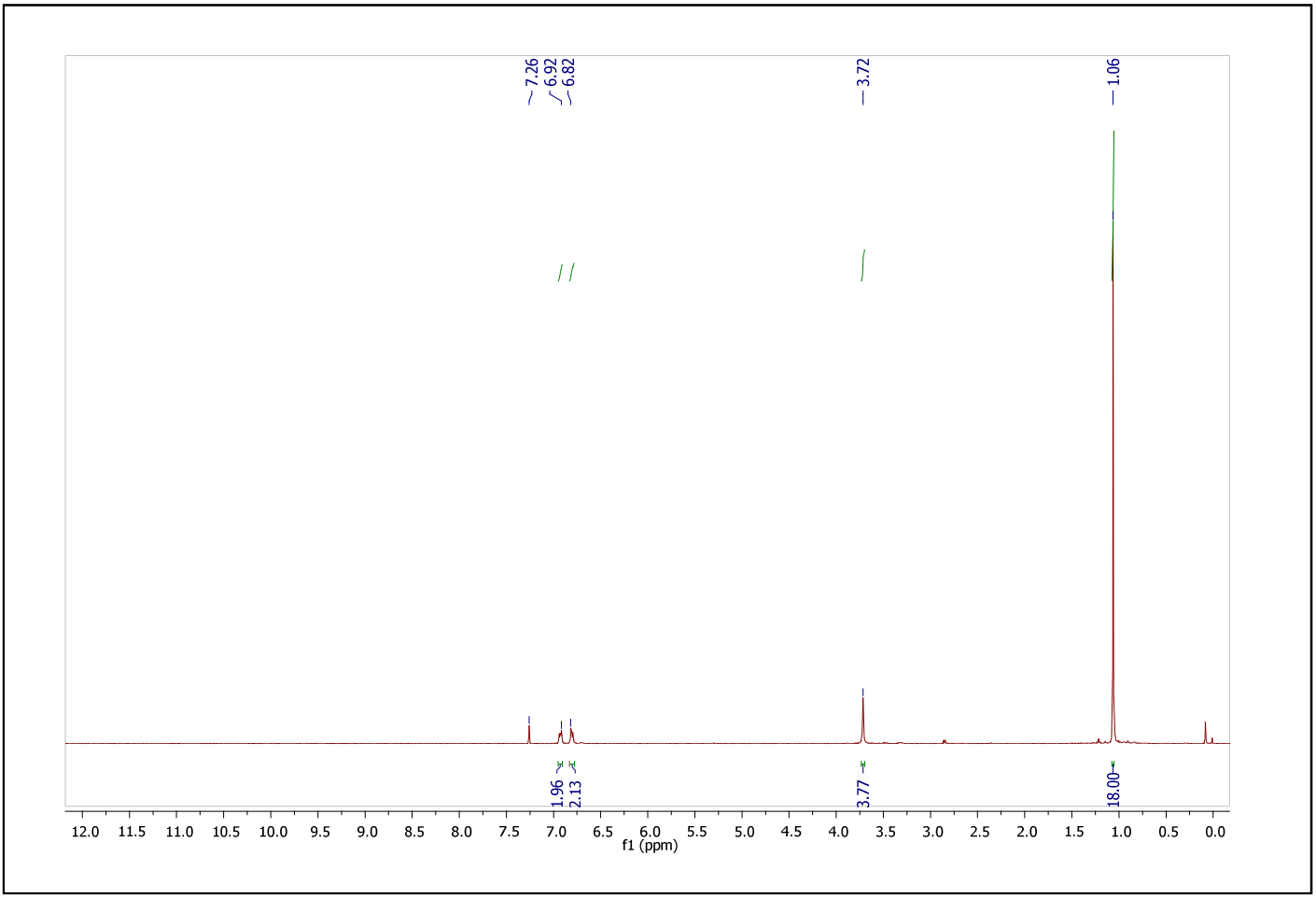


Figure S7. ^{13}C NMR spectrum of compound **2** in $CDCl_3$

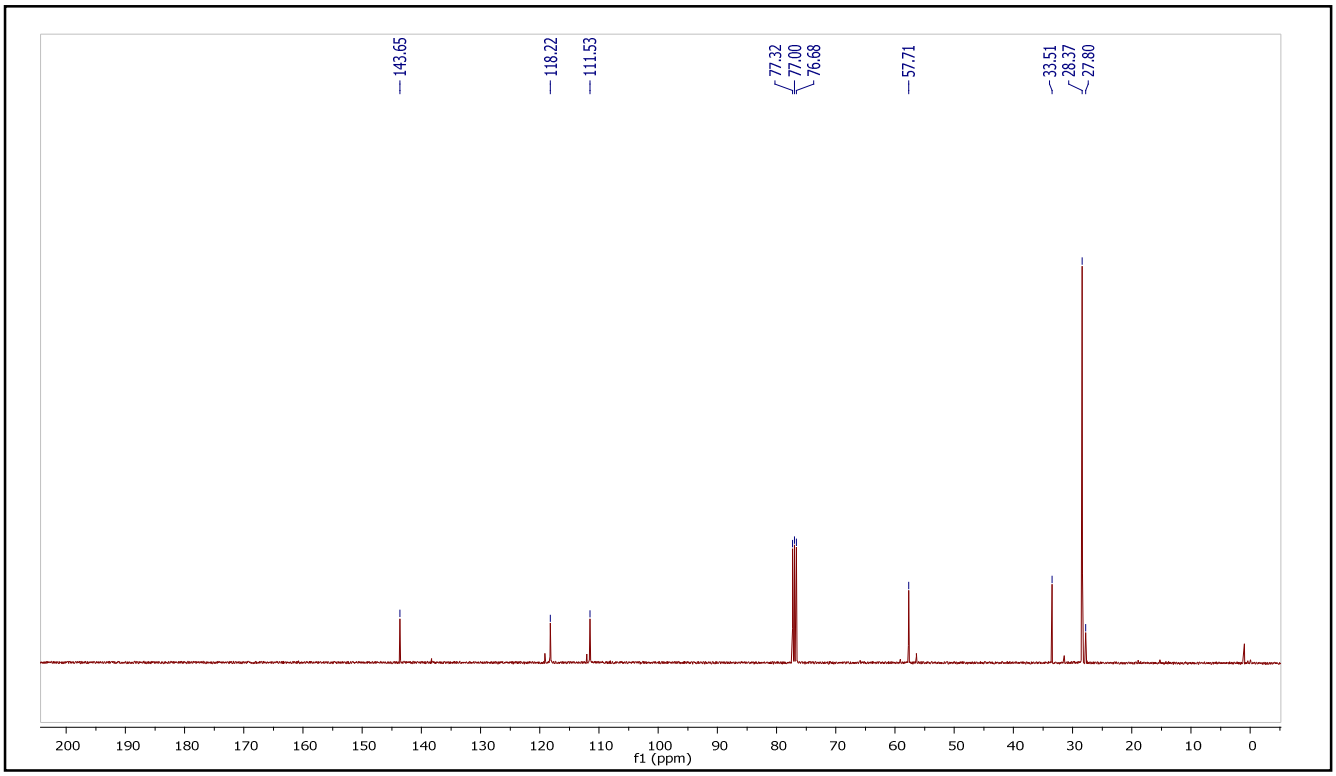


Figure S8. ^{1}H NMR spectrum of compound **3** in $CDCl_3$

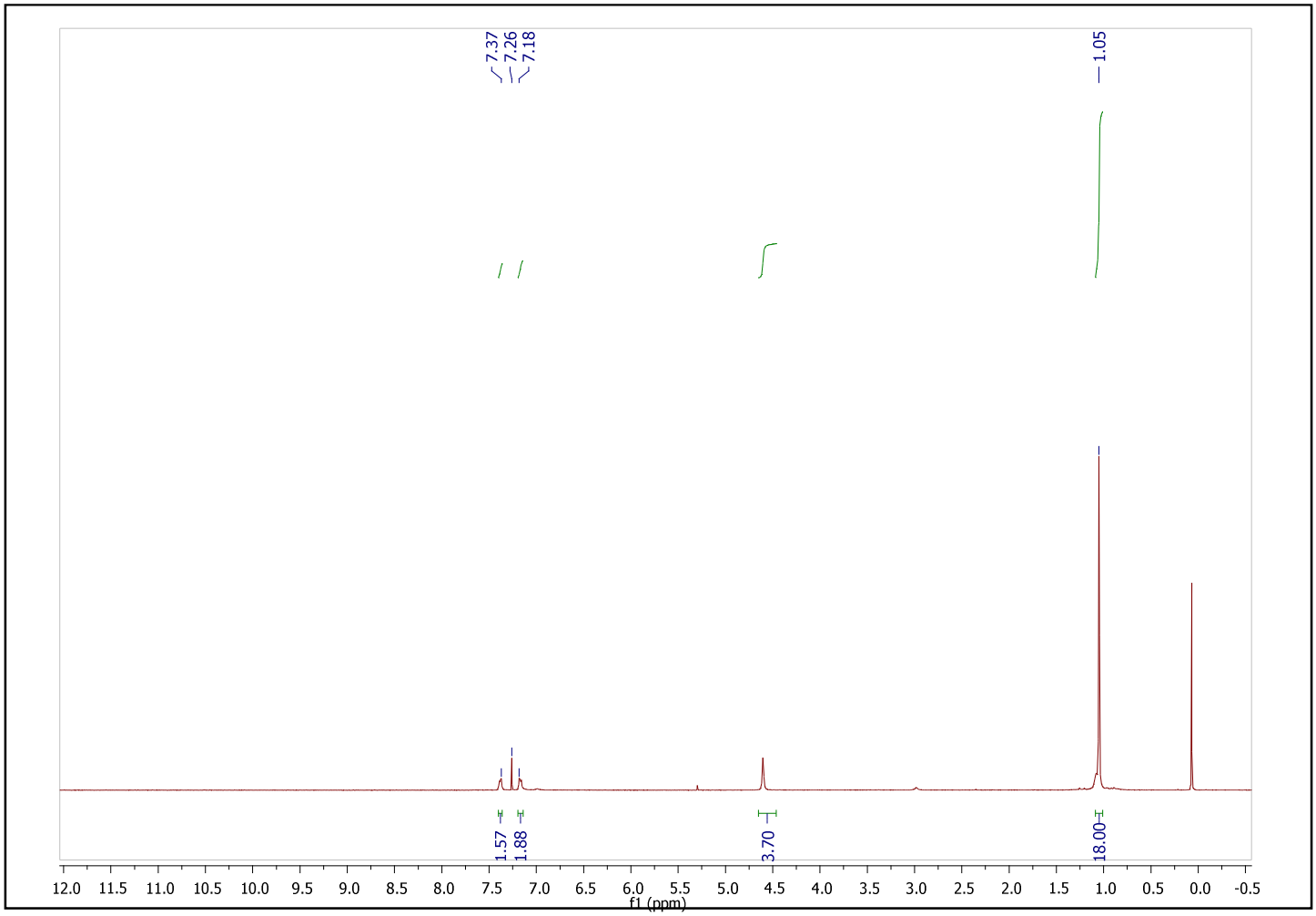


Figure S9. ^{19}F NMR spectrum of compound **3** in $CDCl_3$

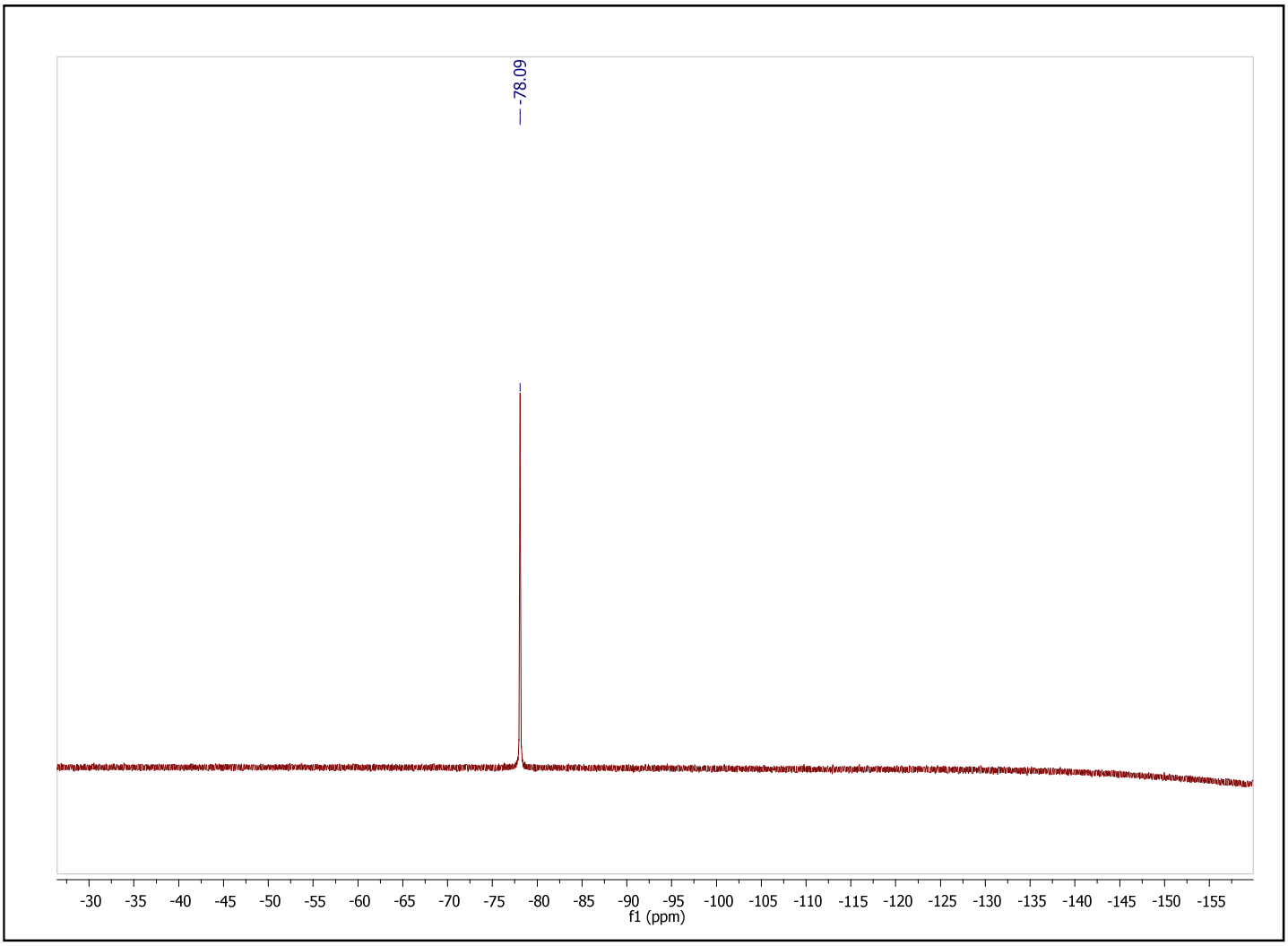


Figure S10. ^{13}C NMR spectrum of compound **3** in $CDCl_3$

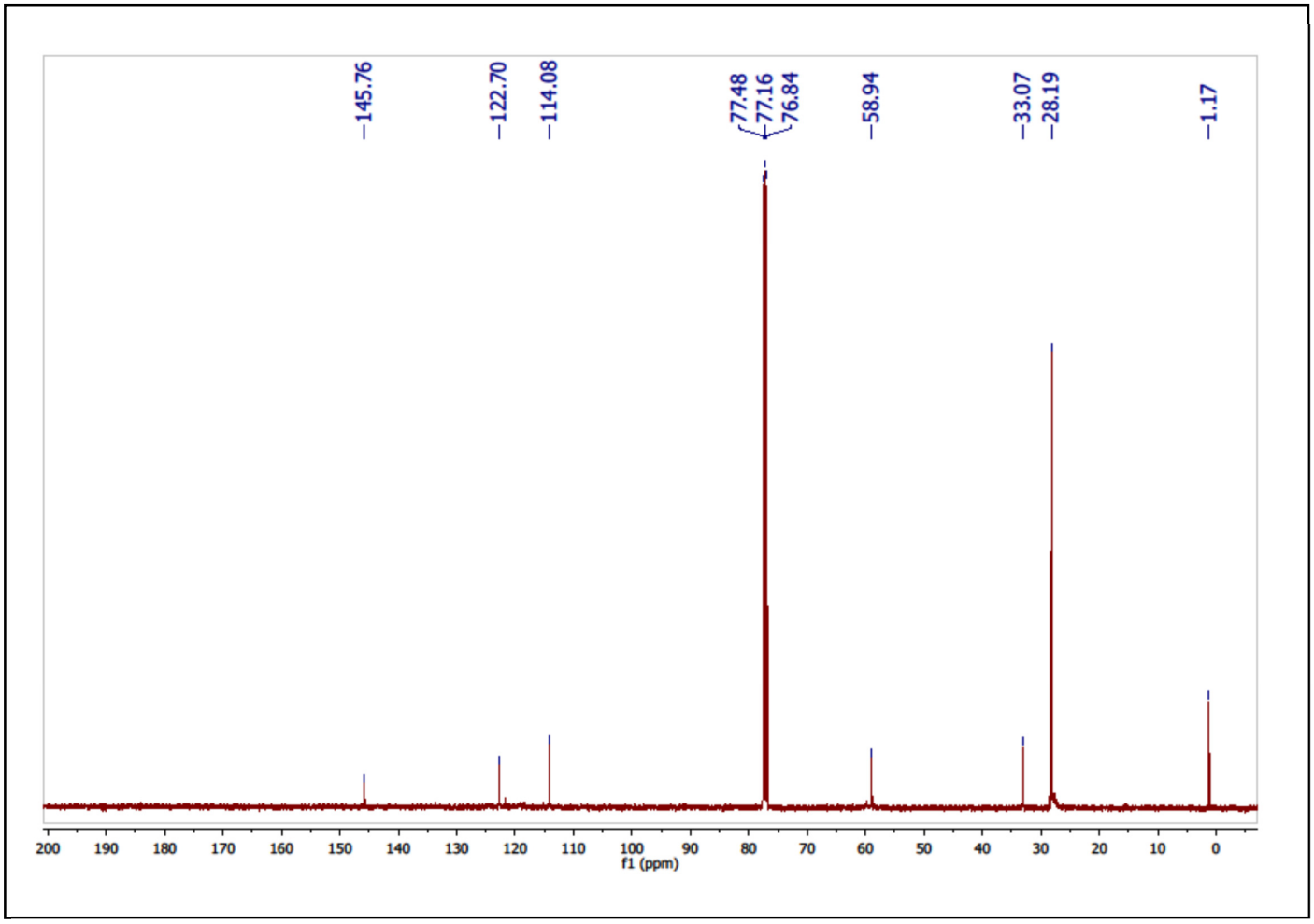


Figure S11. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

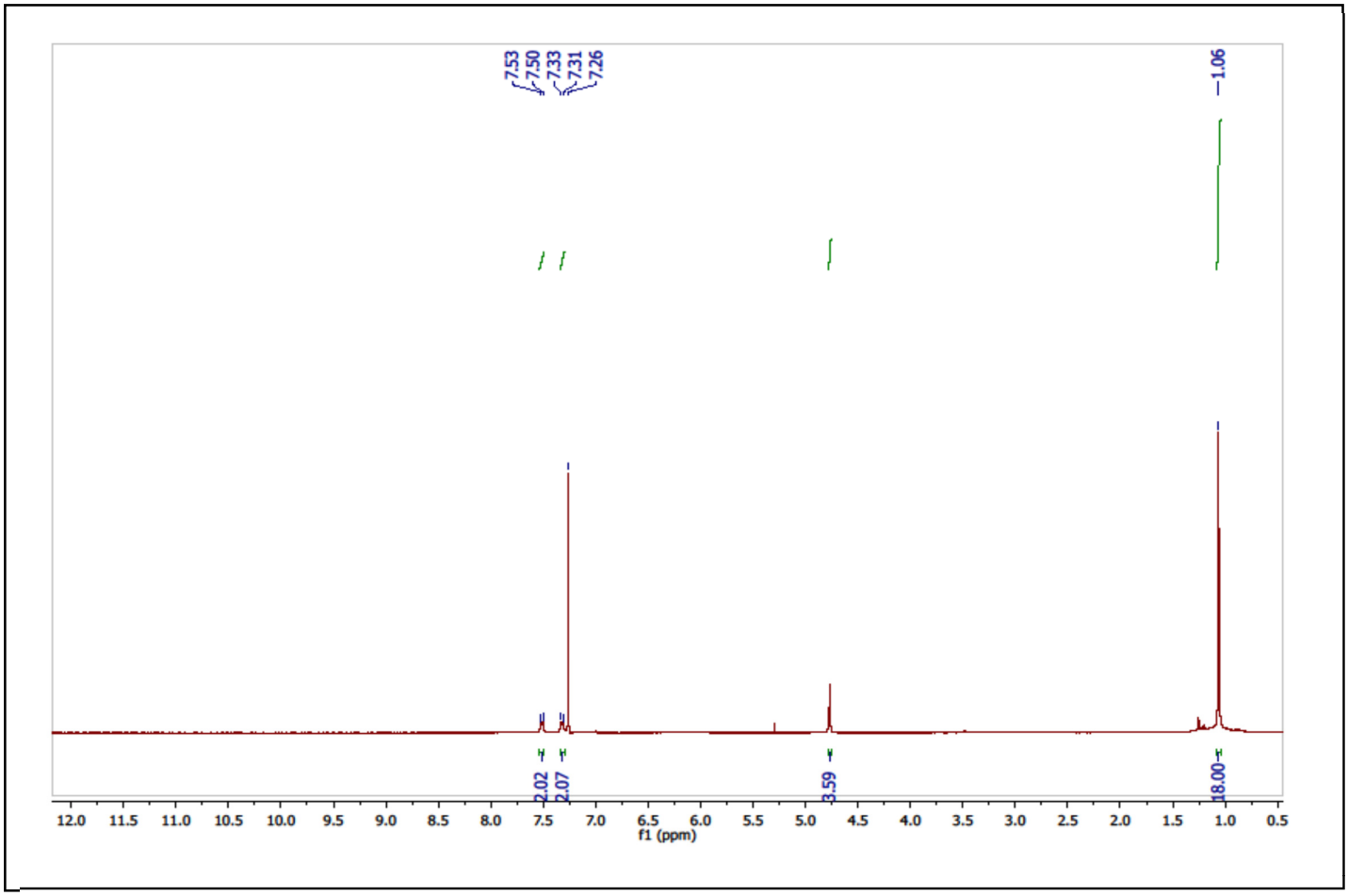


Figure S12. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

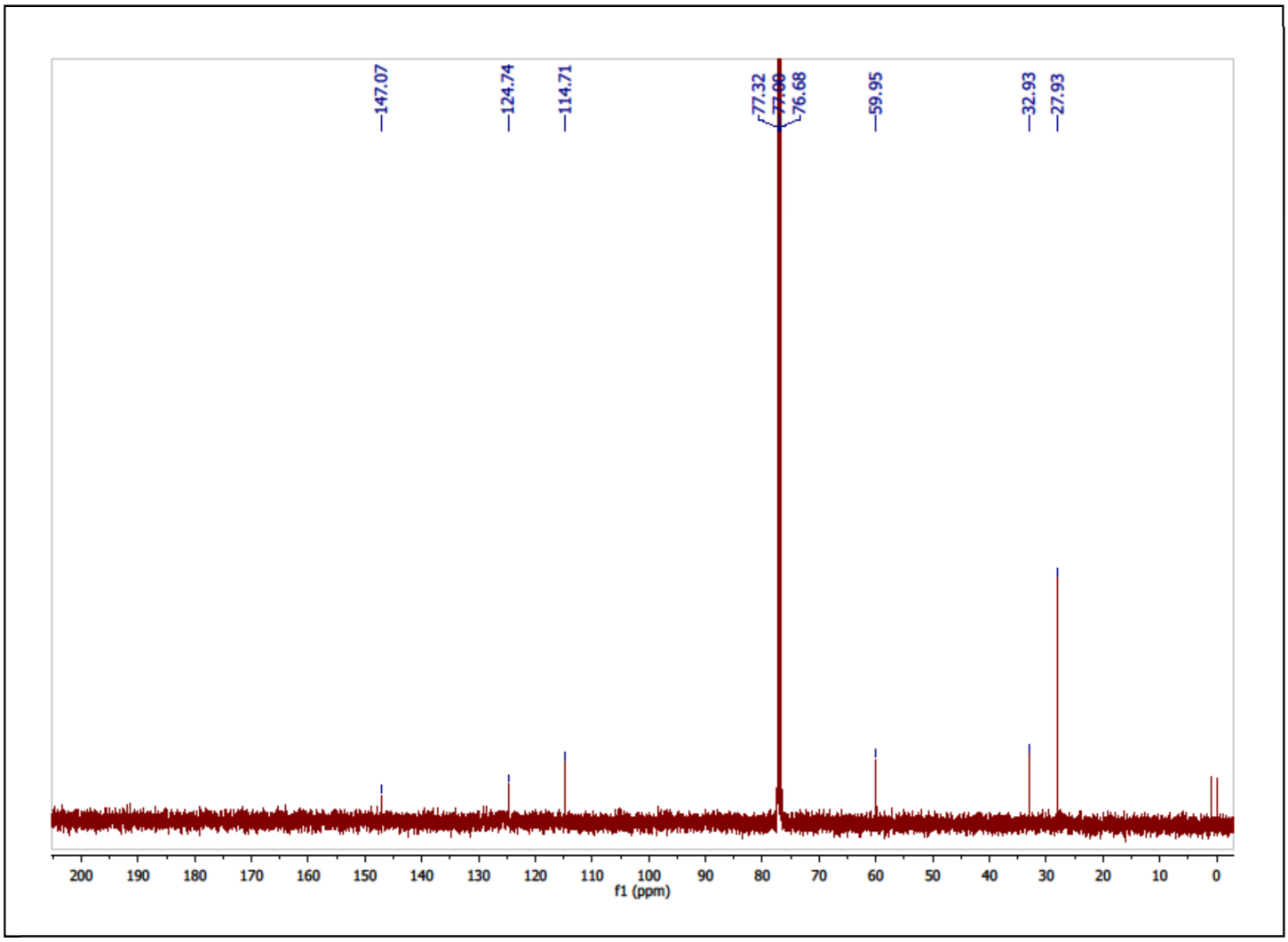
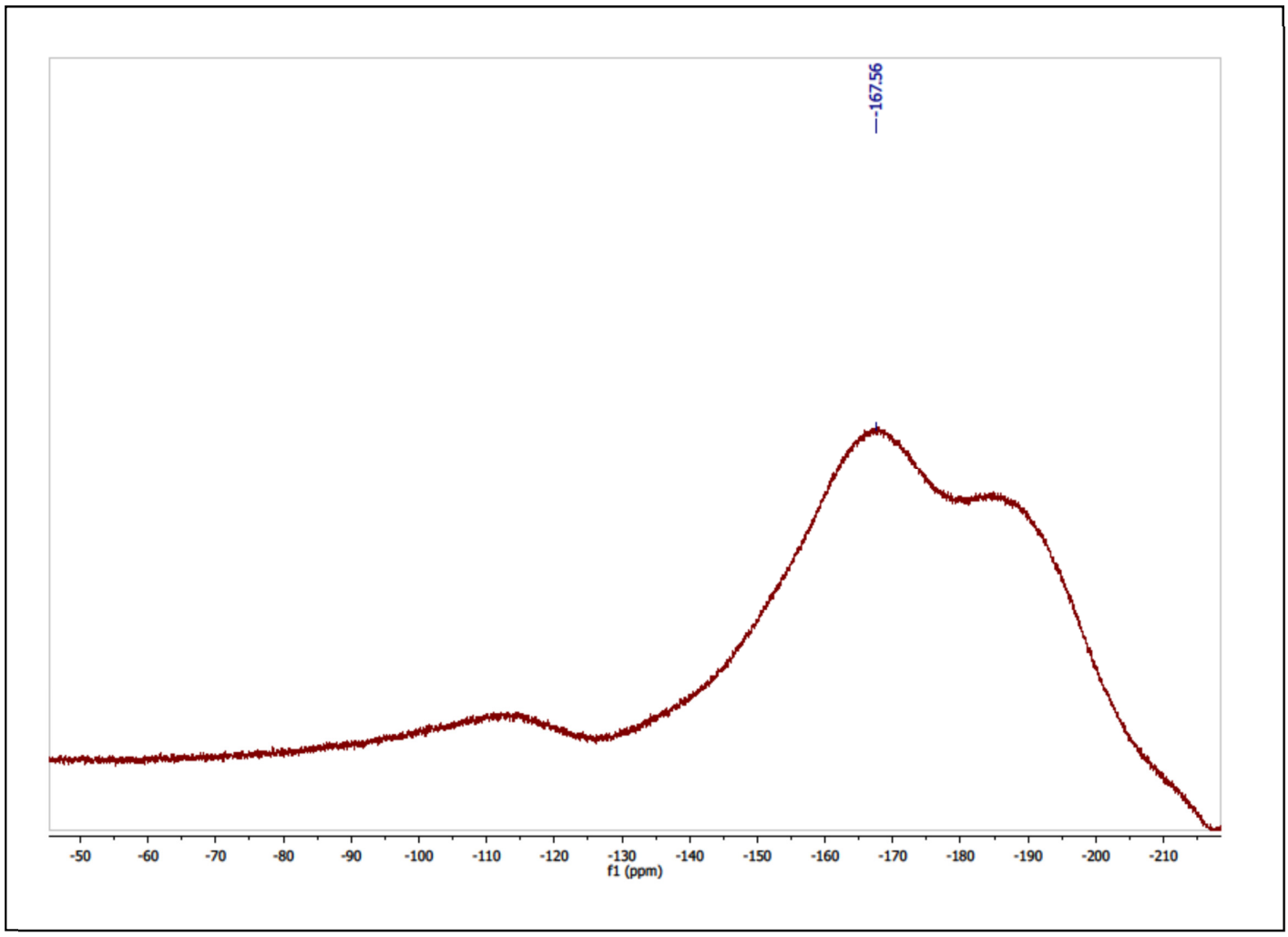


Figure S13. ^{19}F NMR spectrum of compound **4** in $CDCl_3$.



[S5]. ^{31}P NMR Spectra of 2, 3 and 4 with $OPEt_3$ (1:1 reaction).

Figure S14. ^{31}P NMR spectrum of compound **2** and $OPEt_3$ in $CDCl_3$.

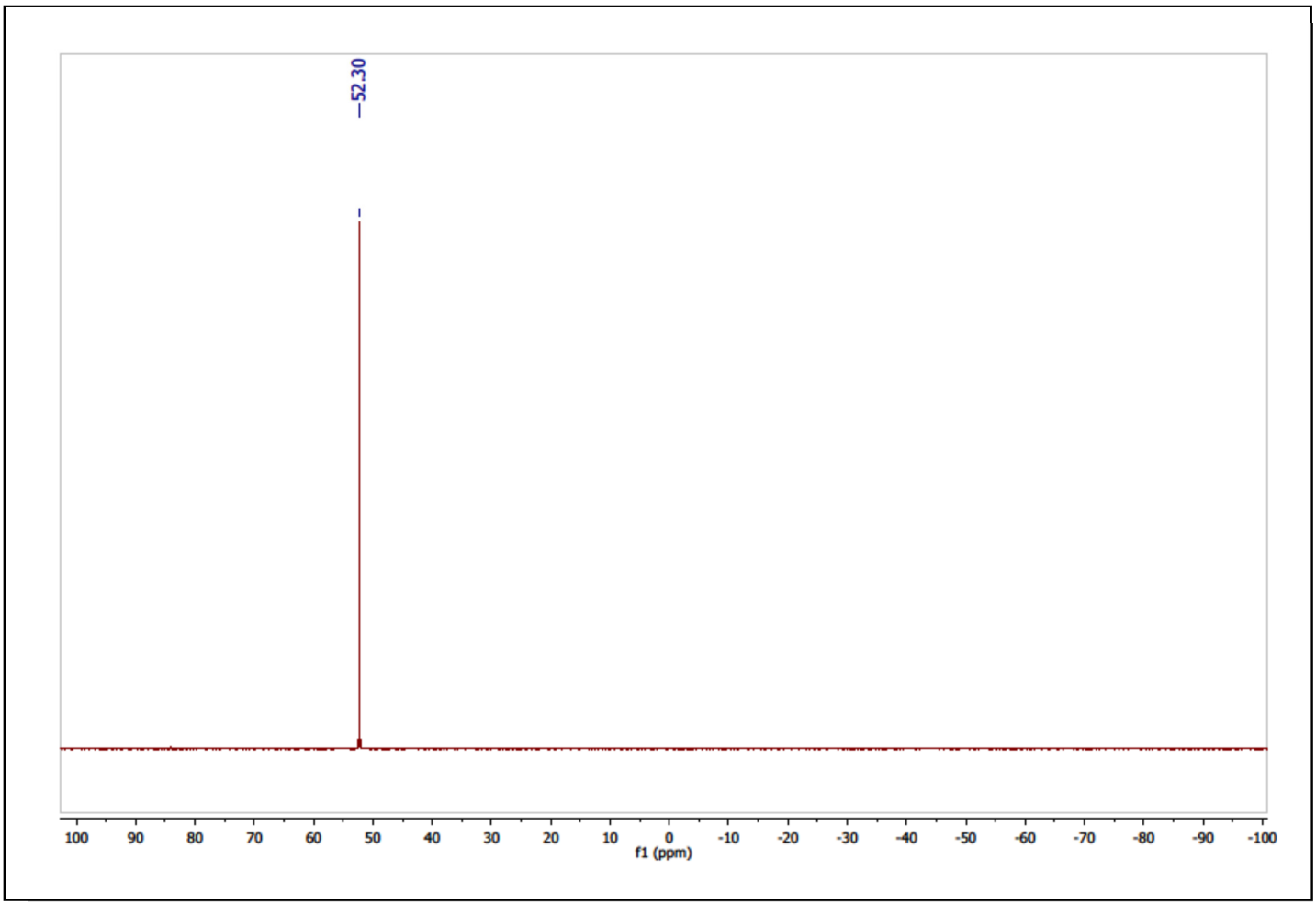


Figure S15. ^{31}P NMR spectrum of compound **3** and $OPEt_3$ in $CDCl_3$.

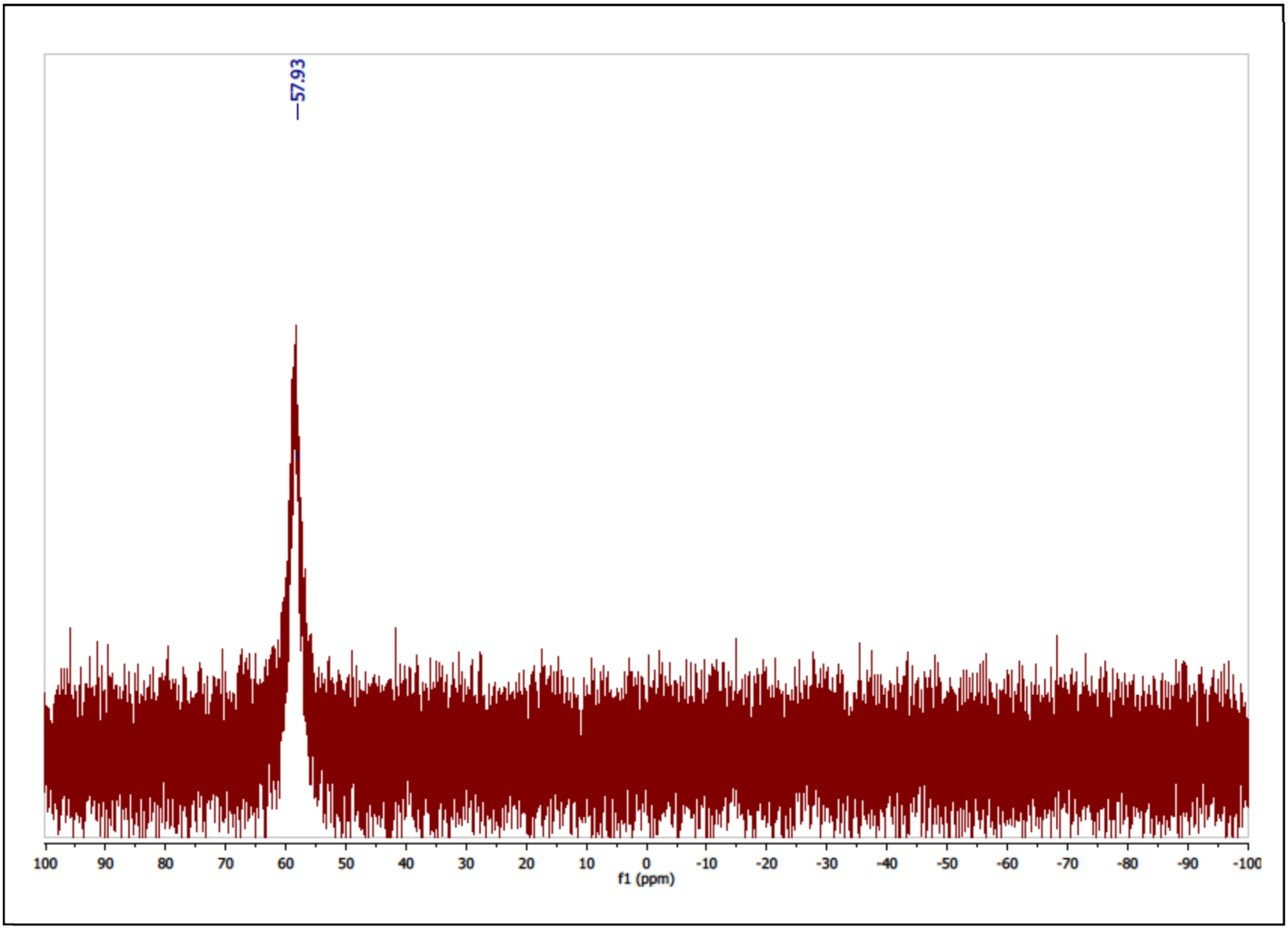
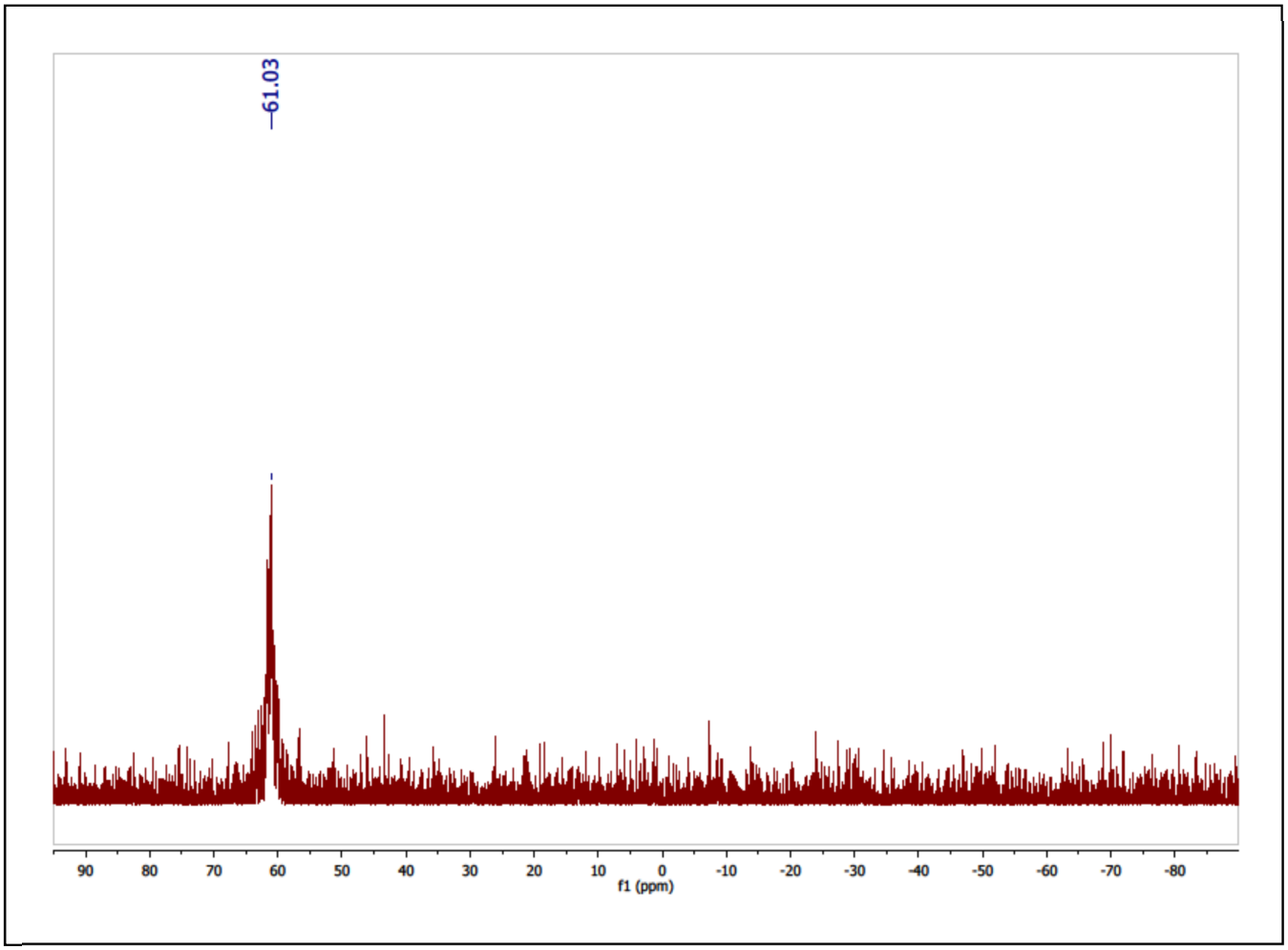


Figure S16. ^{31}P NMR spectrum of compound **4** and $OPEt_3$ in $CDCl_3$.



[S6]: General procedure for the cyanosilylation of aldehydes/ketones:

Aldehyde/ketone (0.25 mmol), TMSCN (0.25mmol), and catalyst (**2**-**4**) (1 mol%) were charged in Schlenk tube under an inert atmosphere. The reaction mixture was allowed to run at room temperature for 30 mins. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the disappearance of the aldehyde proton and the appearance of a new CH peak. Upon completion of the reaction, the reaction was dried under a high vacuum in the Schlenk line and mesitylene (0.25mmol) as an internal standard, was added while performing the NMR in $CDCl_3$.

[S7]. Standardization of reaction conditions for cyanosilylation reaction of aldehydes with trimethyl silyl cyanide using catalyst 4:

Entry	Catalyst	Mol (%)	Reaction time	TMSCN (equiv.)	Temperature	Yield (%)
1	**4**	1	8 hrs	1.5 equ	60˚C	>99
					RT	>99
2	**4**	1	4 hrs	1.5	60˚C	96
					RT	94
3	**4**	1	2 hrs	1.5	60˚C	98
					RT	93
4	**4**	1	30 mins	1.5	60˚C	>99
	4	1	30 mins	1.5	RT	>99
5	**4**	0.5	30 mins	1.5	RT	<50
6	**4**	1	30 mins	1	RT	64
7	No catalyst		30 mins	1.5	RT	Trace amount

Figure S17. ^{1}H NMR spectra for cyanosilylation of Benzaldehyde with TMSCN with catalyst loading 1 mol% for 8 hrs at 60˚C

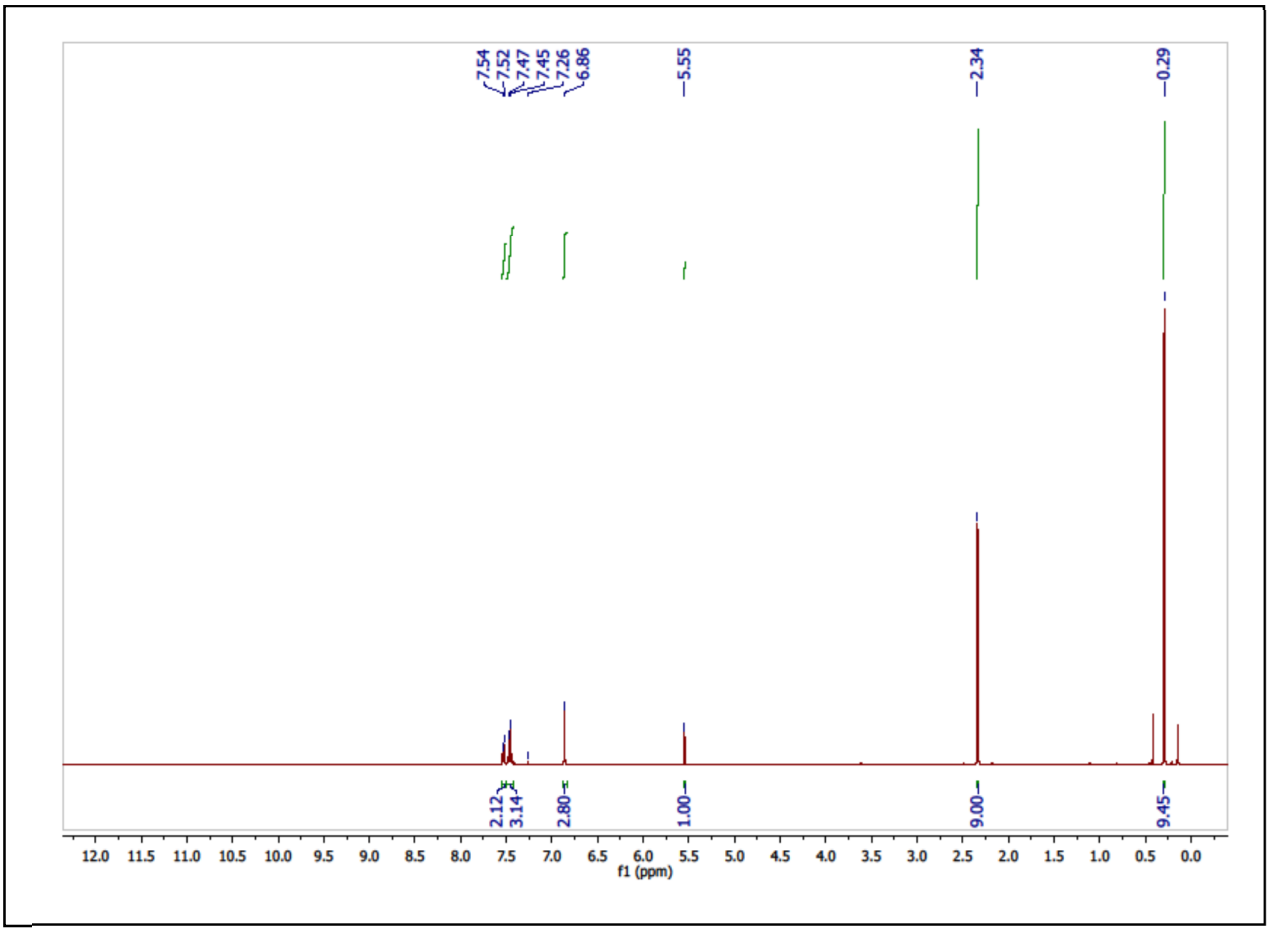


Figure S18. ^{1}H NMR spectra for cyanosilylation of Benzaldehyde with TMSCN with catalyst loading 1 mol% for 8 hrs at room temperature.

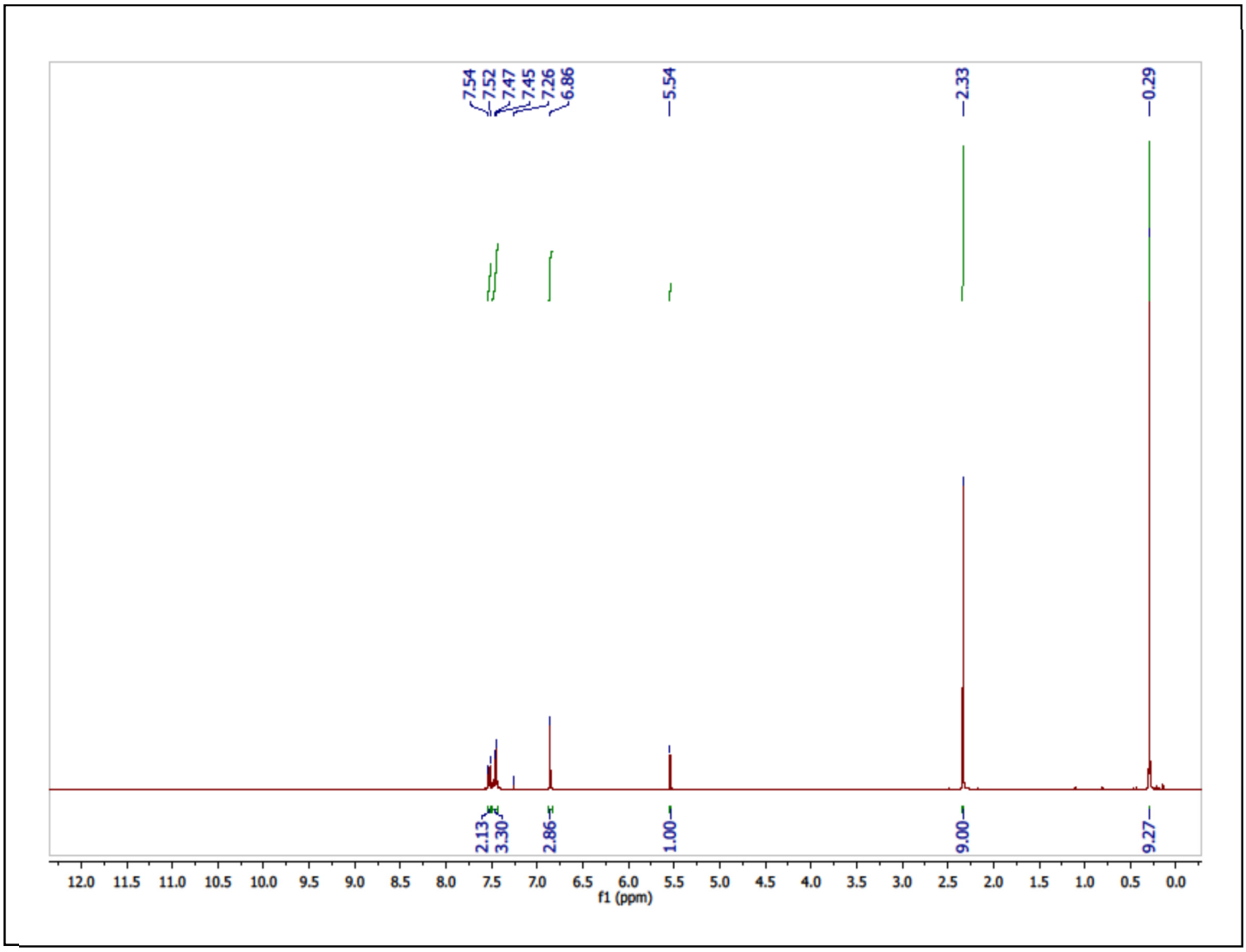


Figure S19. ^{1}H NMR spectra for cyanosilylation of Benzaldehyde with TMSCN with catalyst loading 1 mol% for 4 hrs at 60˚C.

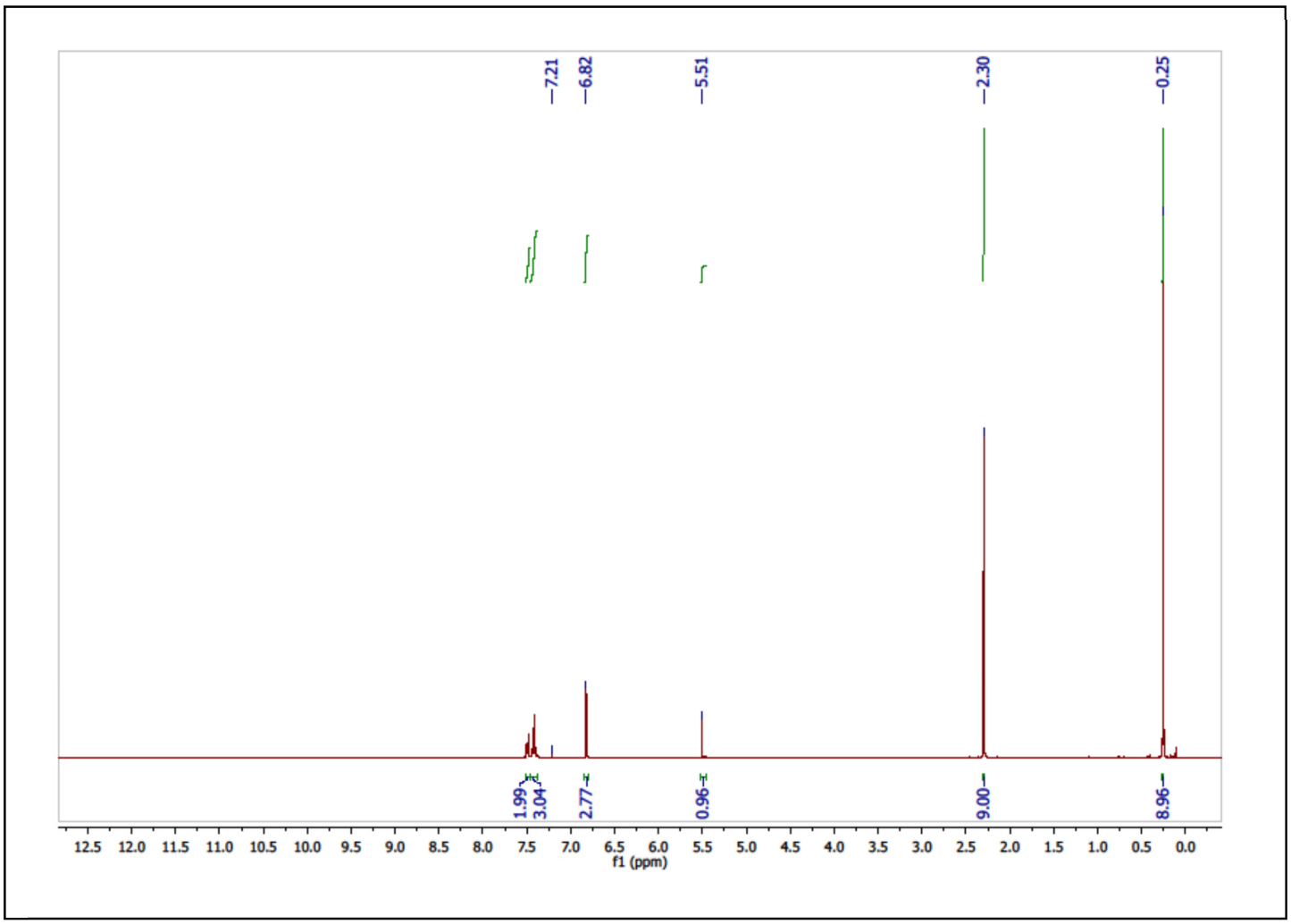


Figure S20. ^{1}H NMR spectra for cyanosilylation of Benzaldehyde with TMSCN with catalyst loading 1 mol% for 4 hrs at room temperature.

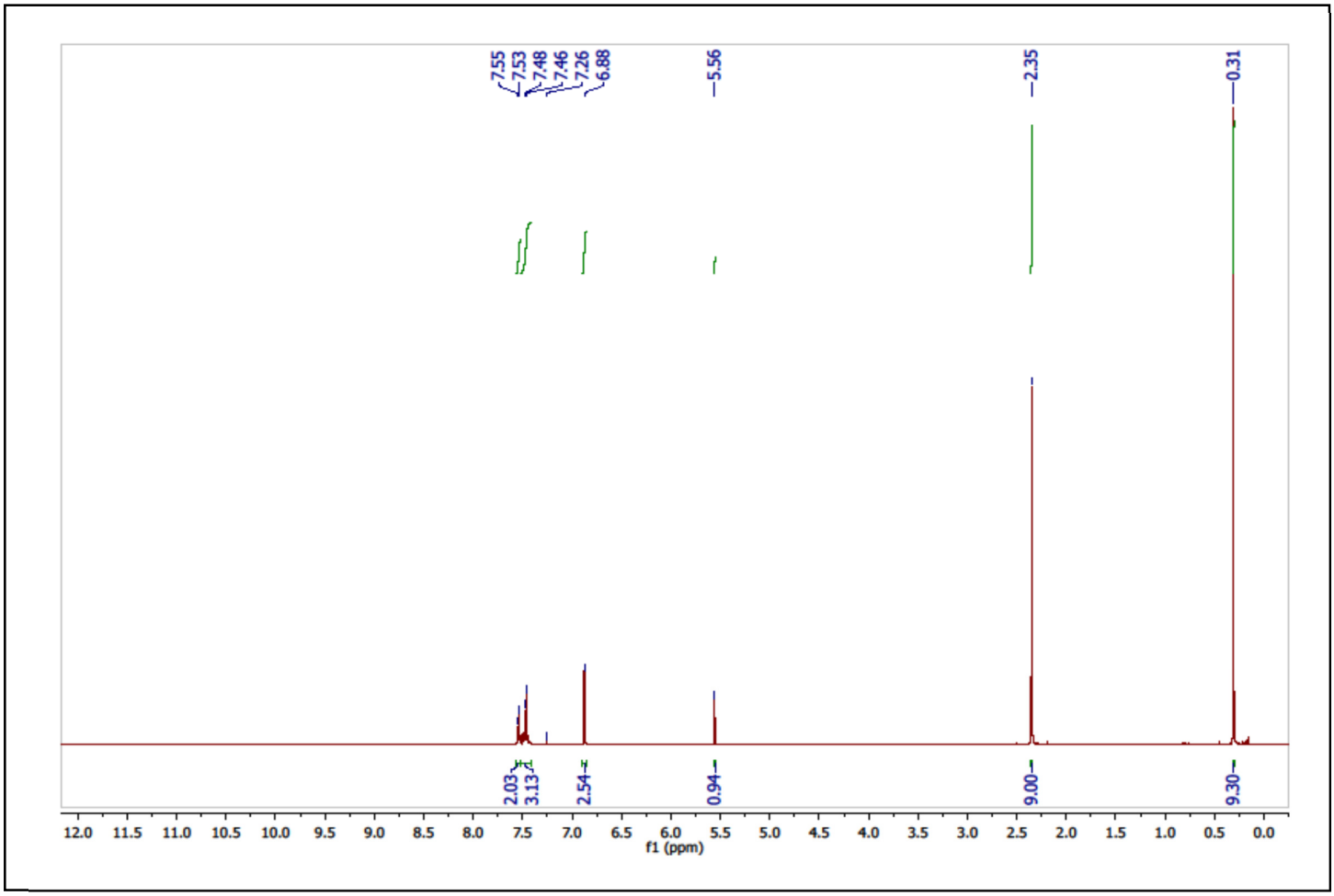


Figure S21. ^{1}H NMR spectra for cyanosilylation of Benzaldehyde with TMSCN with catalyst loading 1 mol% for 2 hrs at 60˚C.

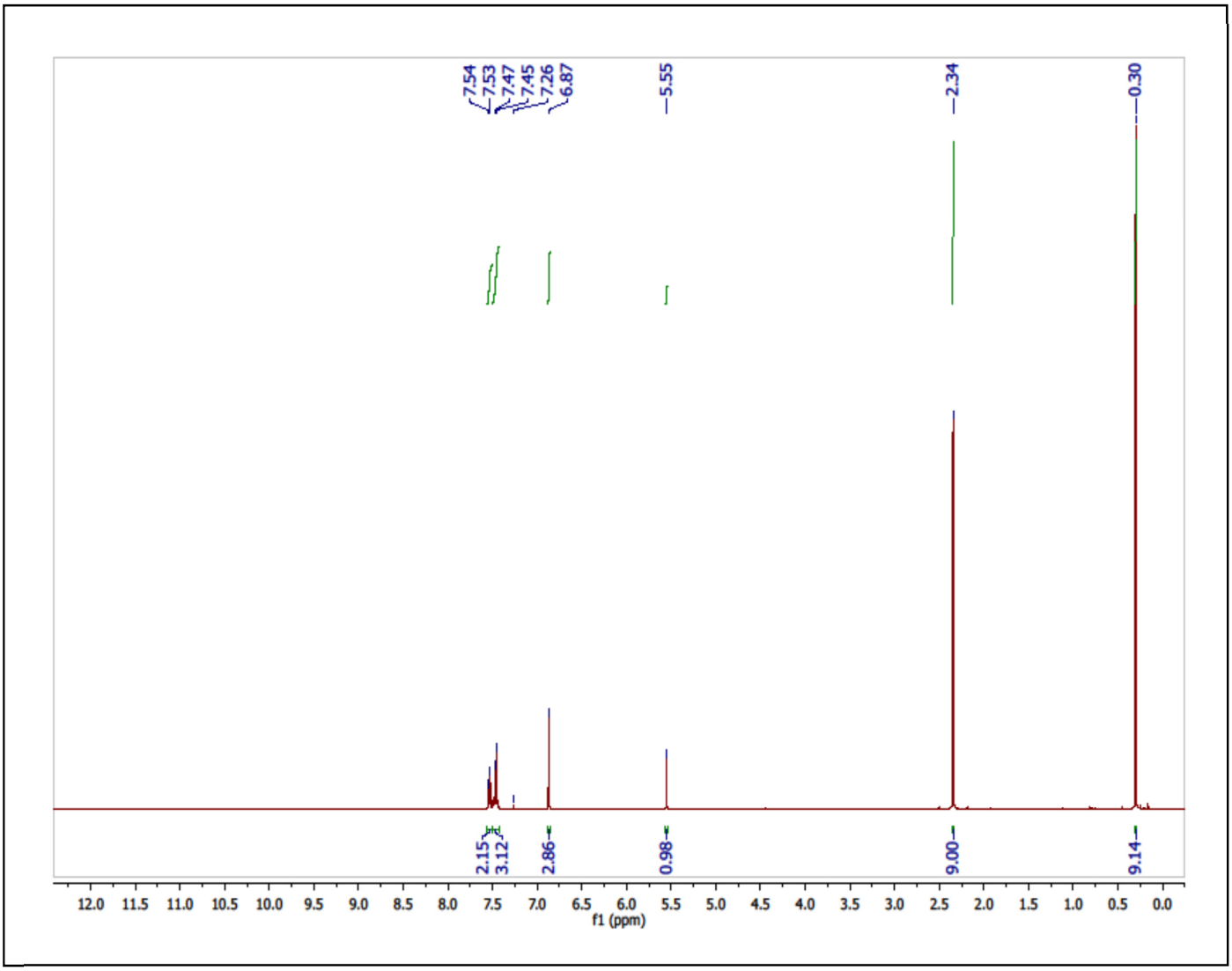


Figure S22. ^{1}H NMR spectra for cyanosilylation of Benzaldehyde with TMSCN with catalyst loading 1 mol% for 2 hrs at room temperature.

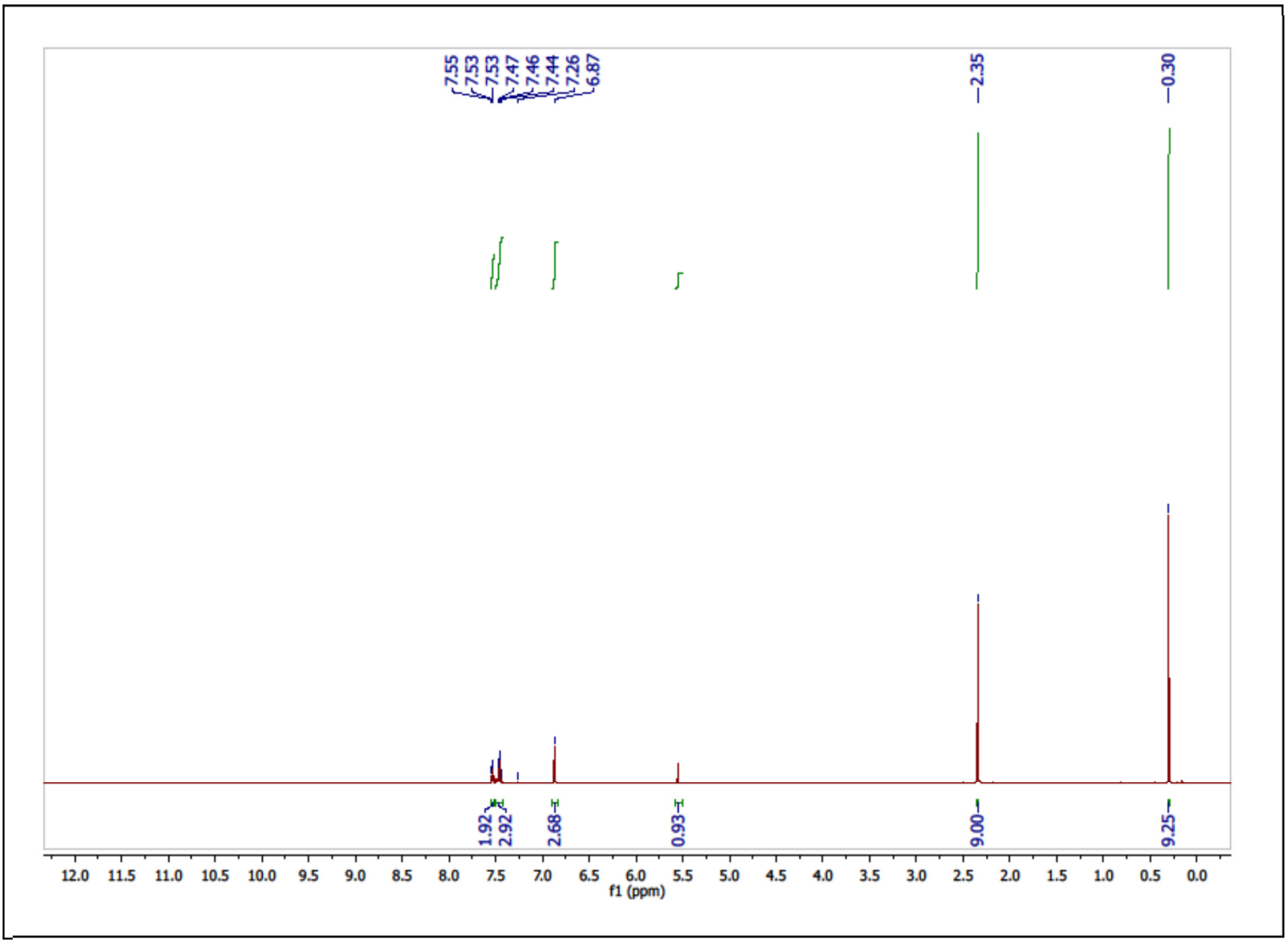


Figure S23. [1]H NMR spectrum of controlled cyanosilylation reaction of benzaldehyde in absence of catalyst **4**.

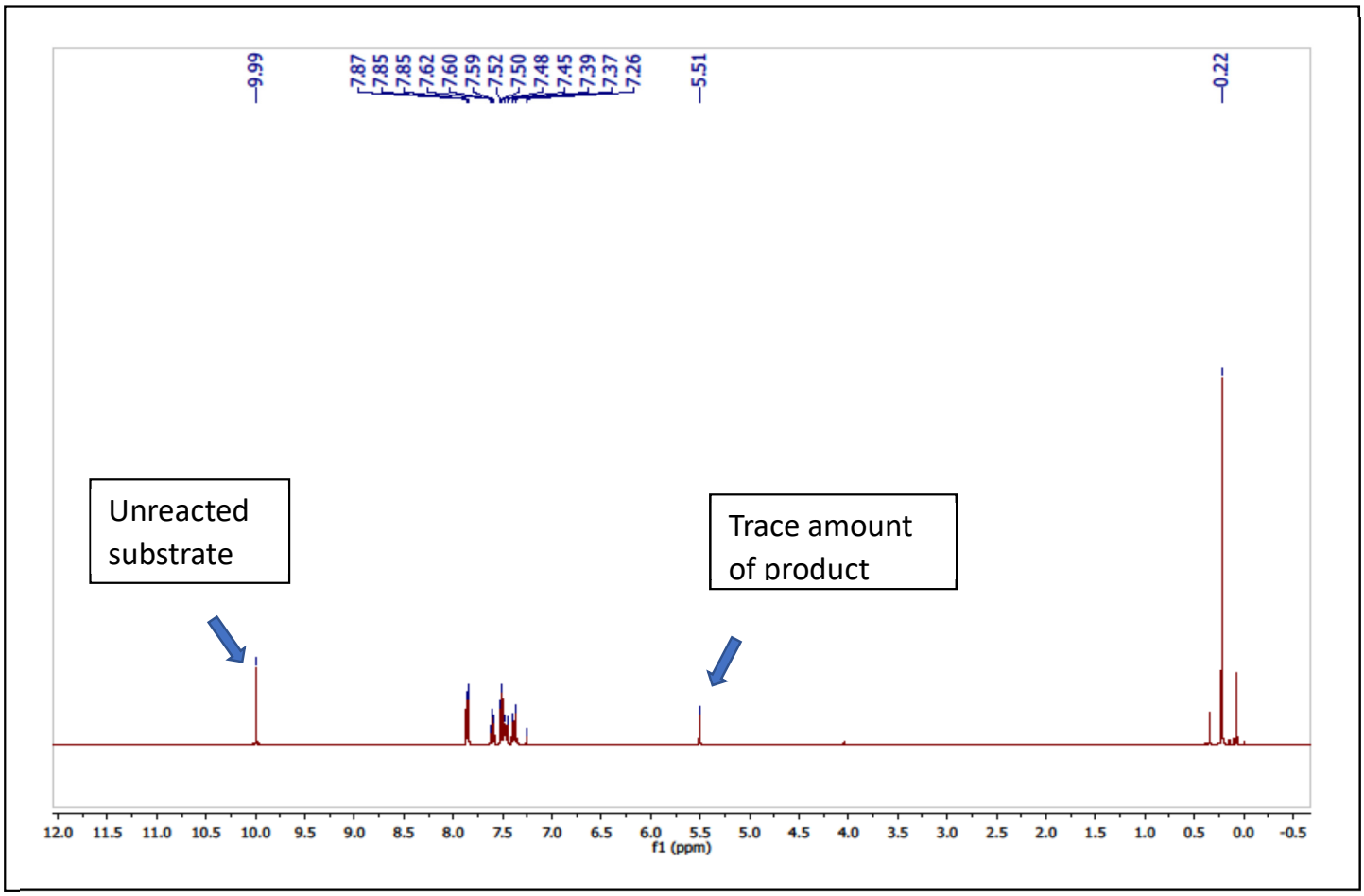
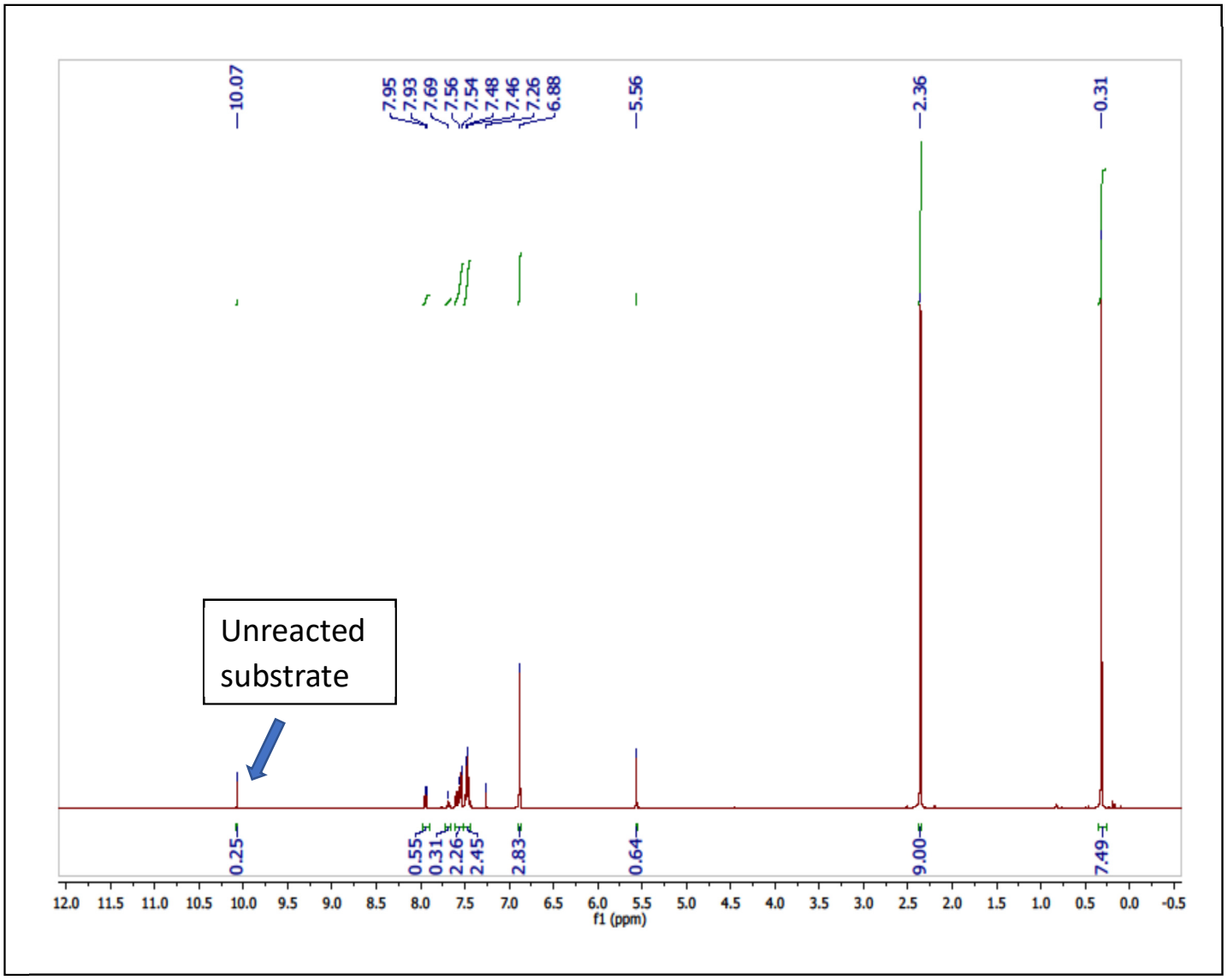


Figure S24. ^{1}H NMR spectrum of cyanosilylation of benzaldehyde with 1 eqv of TMSCN and 1 mol% of catalyst **4**.



[S8]. Comparison of catalysts 2-4:

^{1}H NMR spectra for cyanosilylation products of aldehydes/ketones by 2 and 3.

Comparison of **2**-**4** as catalysts for cyanosilylation

Entry	**Catalyst**	**Mol** (%)	**Aldehyde/Ketone**	**Yield** (%)
1	**2**	1	Benzaldehyde	82
2	**2**	1	p-Tolualdehyde	50
3	**2**	1	3-bromobenzaldehyde	50
4	**3**	1	Benzaldehyde	90
5	**3**	1	p-Tolualdehyde	99
6	**3**	1	3-bromobenzaldehyde	92
7	**3**	1	Acetophenone	89
8	**3**	1	2-Bromoacetophenone	83
9	**3**	1	4-Methylacetophenone	77
10	**4**	1	Benzaldehyde	>99
11	**4**	1	p-Tolualdehyde	>99
12	**4**	1	3-bromobenzaldehyde	>99
13	**4**	1	4-Methylacetophenone	>99

Figure S25. ^{1}H NMR of cyanosilylation of benzaldehyde by compound **3**.

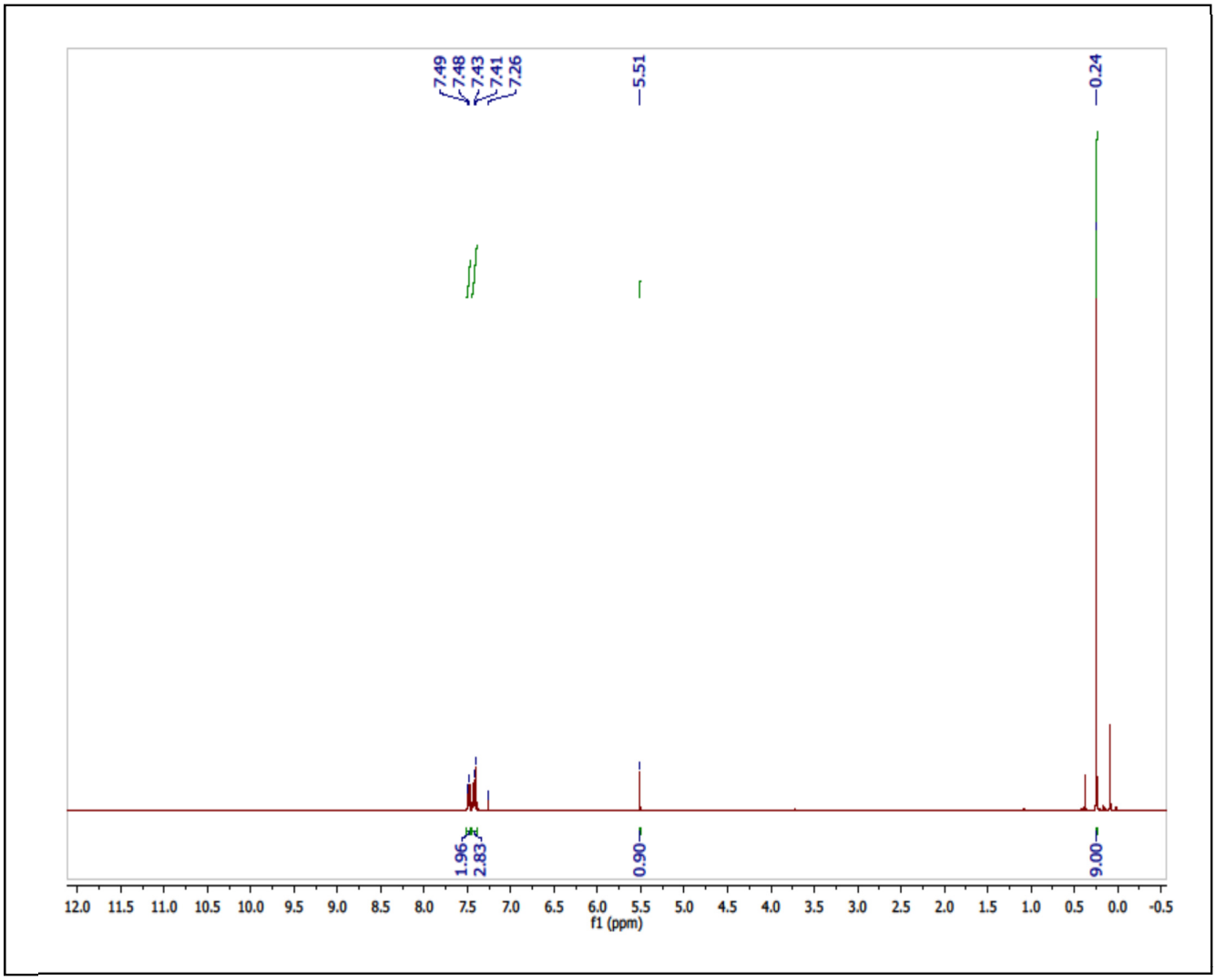


Figure S26. ^{1}H NMR of cyanosilylation of p-tolualdehyde by compound **3**.

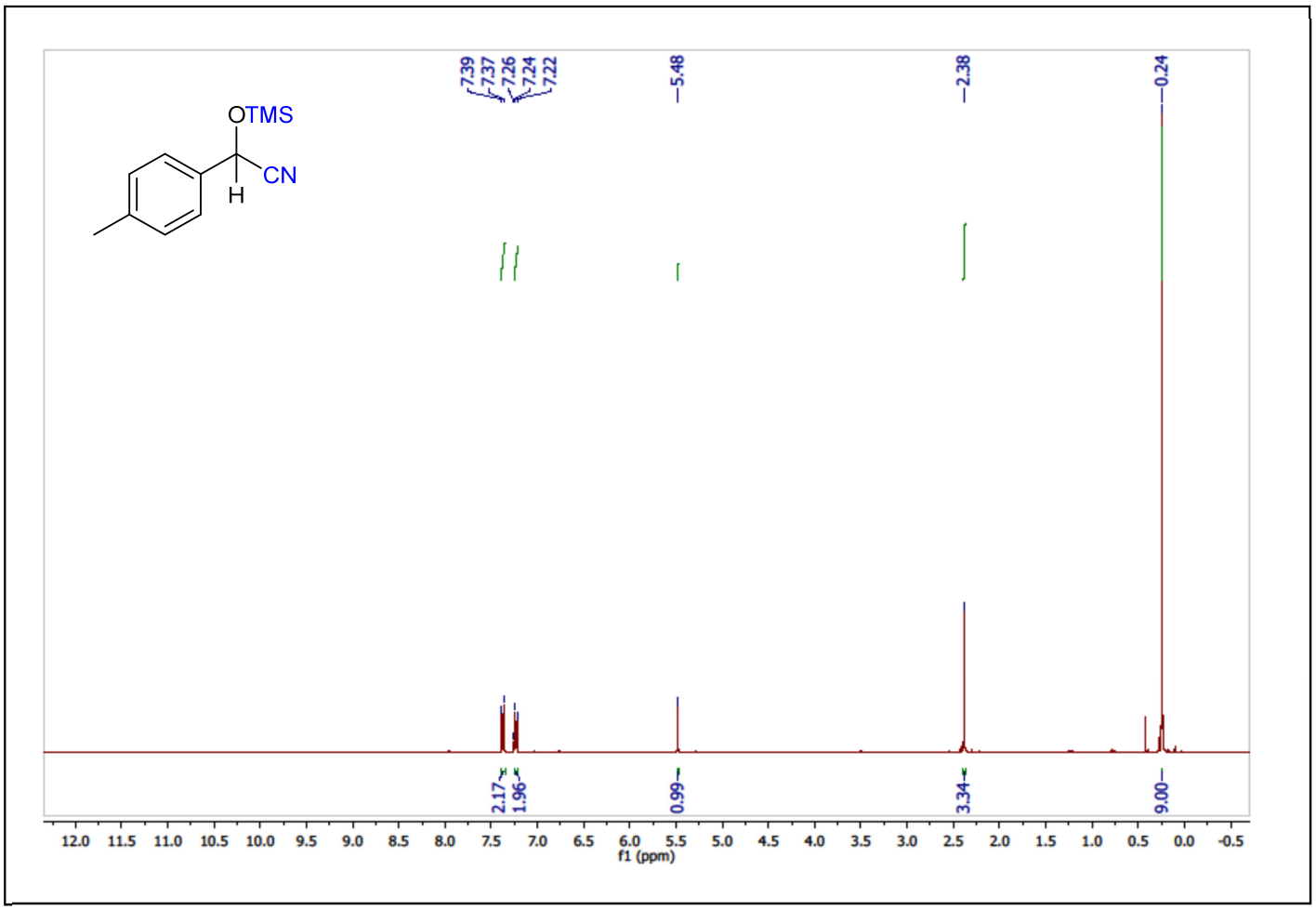


Figure S27. ^{1}H NMR of cyanosilylation of 3-bromobenzaldehyde by compound **3**.

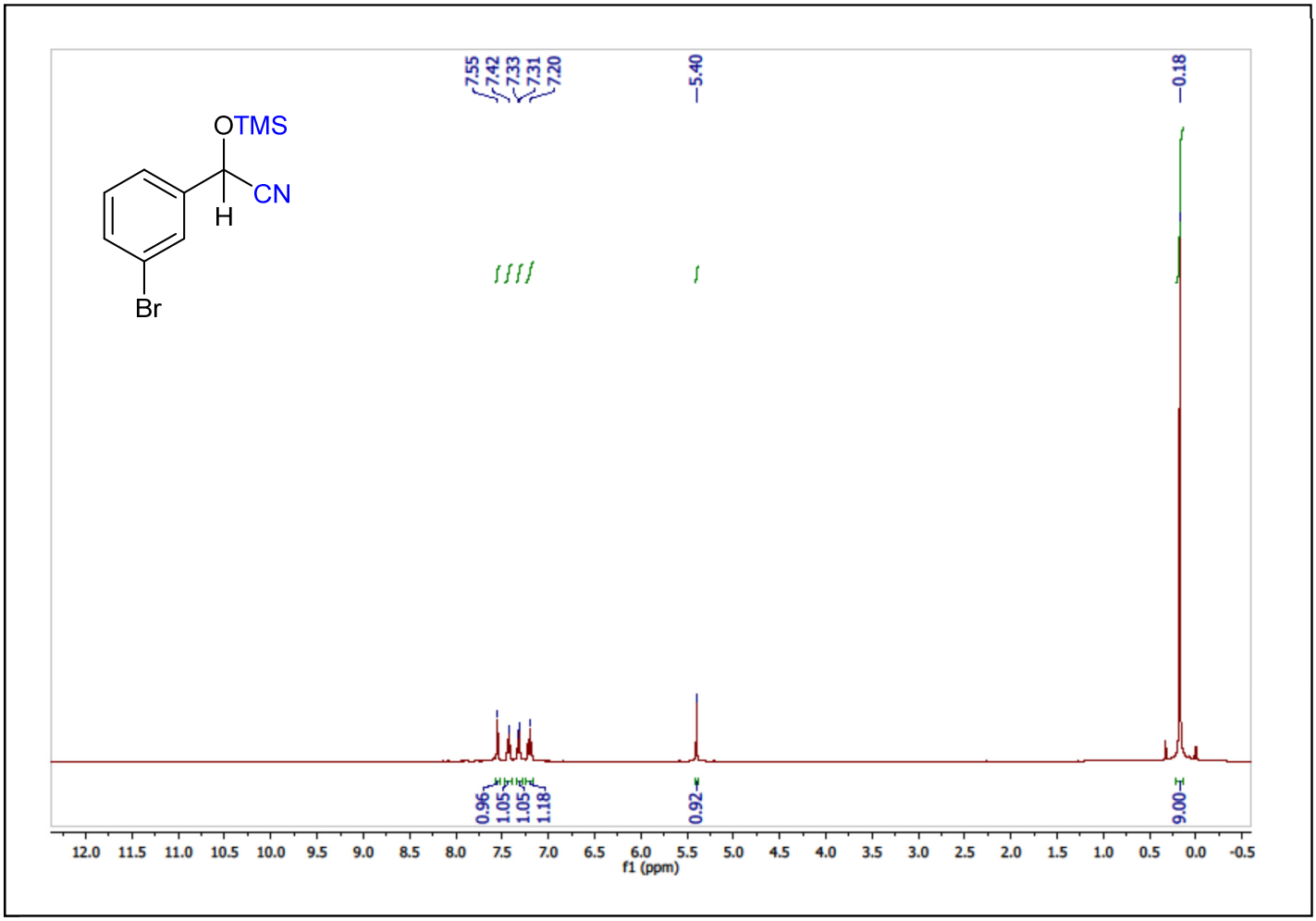


Figure S28. ^{1}H NMR of cyanosilylation of acetophenone by compound **3**.

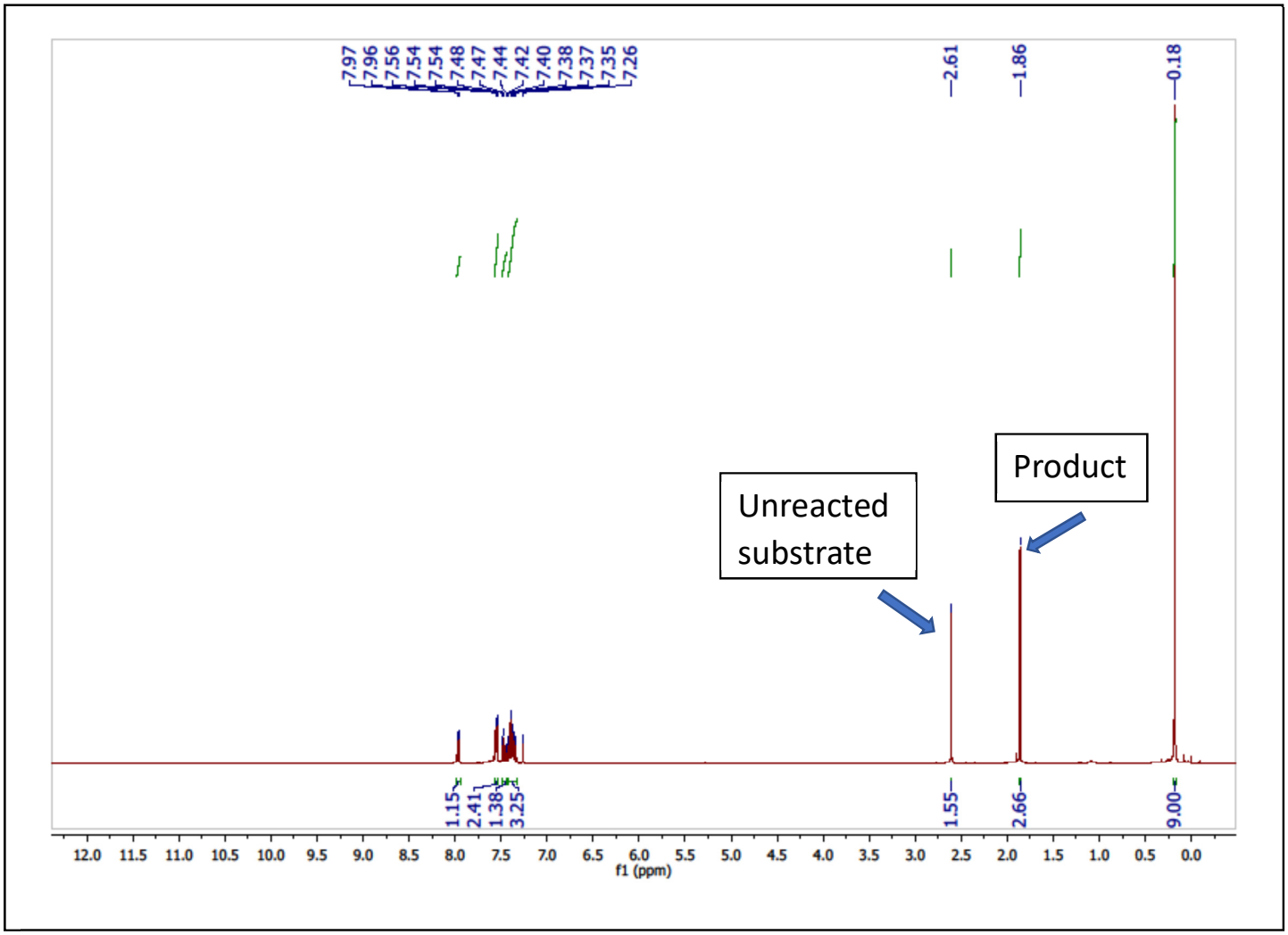


Figure S29. ^{1}H NMR of cyanosilylation of 2-bromoacetophenone by compound **3**.

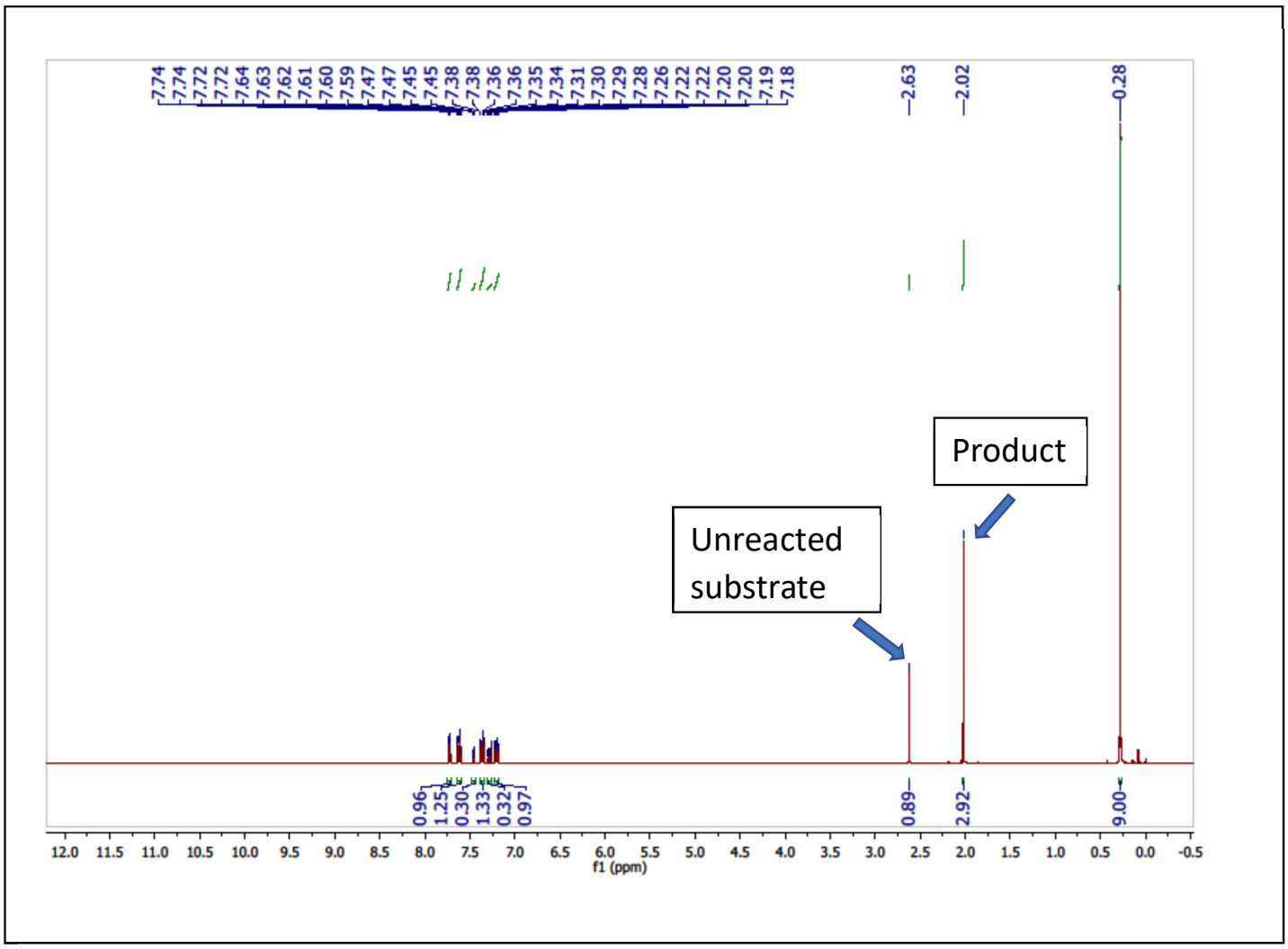


Figure S30. ^{1}H NMR of cyanosilylation of 4-methylacetophenone by compound **3**.

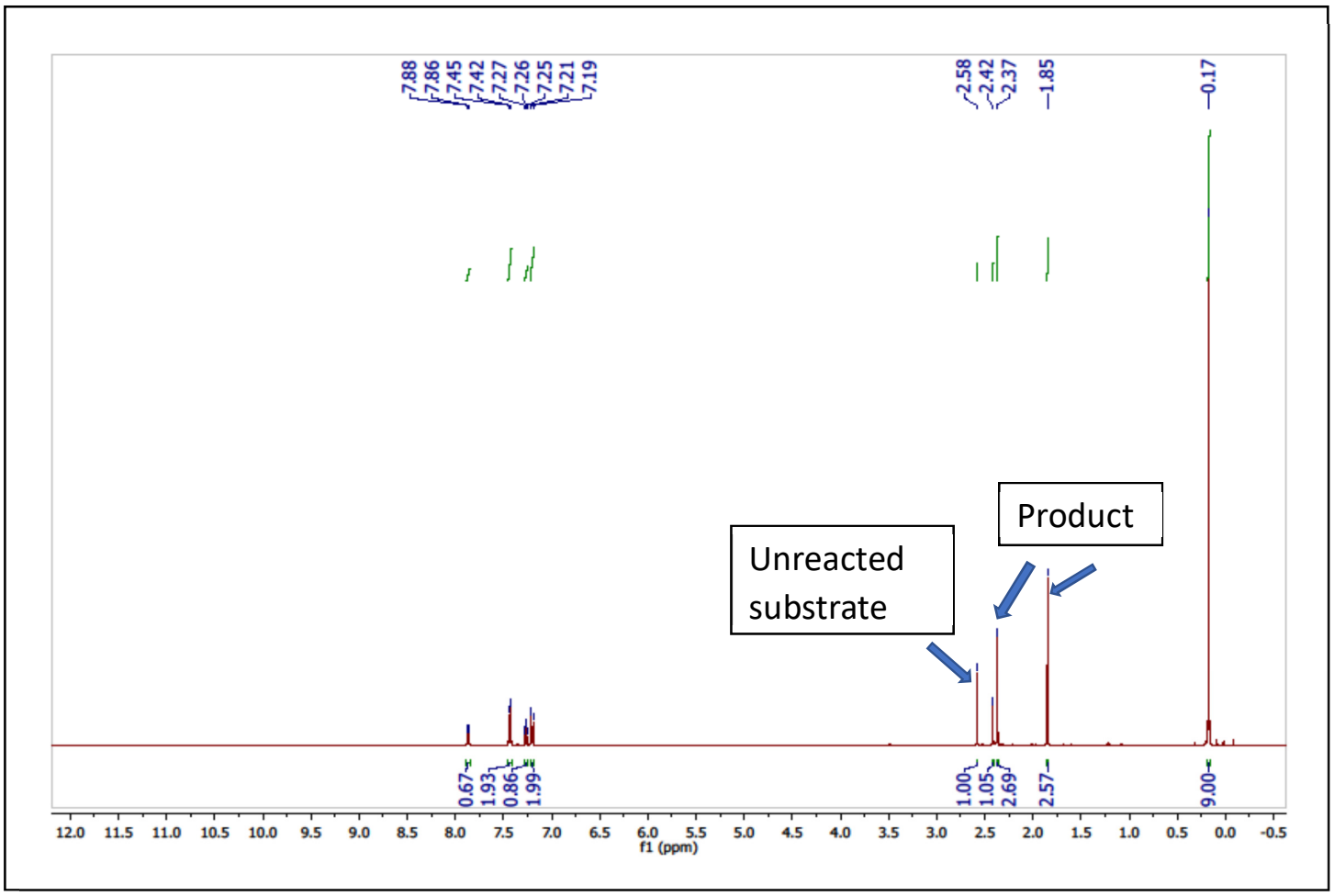


Figure S31. ^{1}H NMR of cyanosilylation of benzaldehyde by compound **2**.

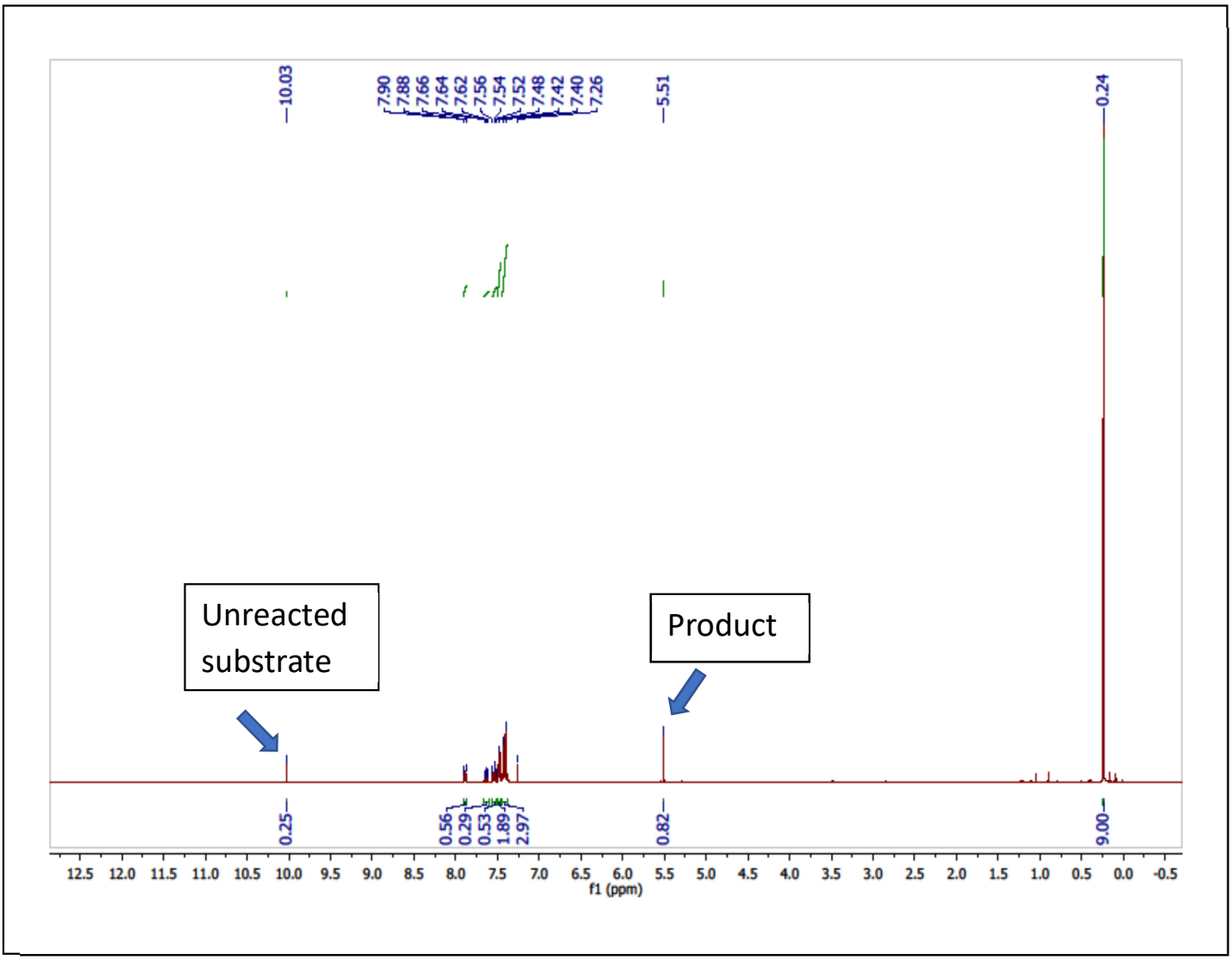


Figure S32. ^{1}H NMR of cyanosilylation of 3-bromobenzaldehyde by compound **2**.

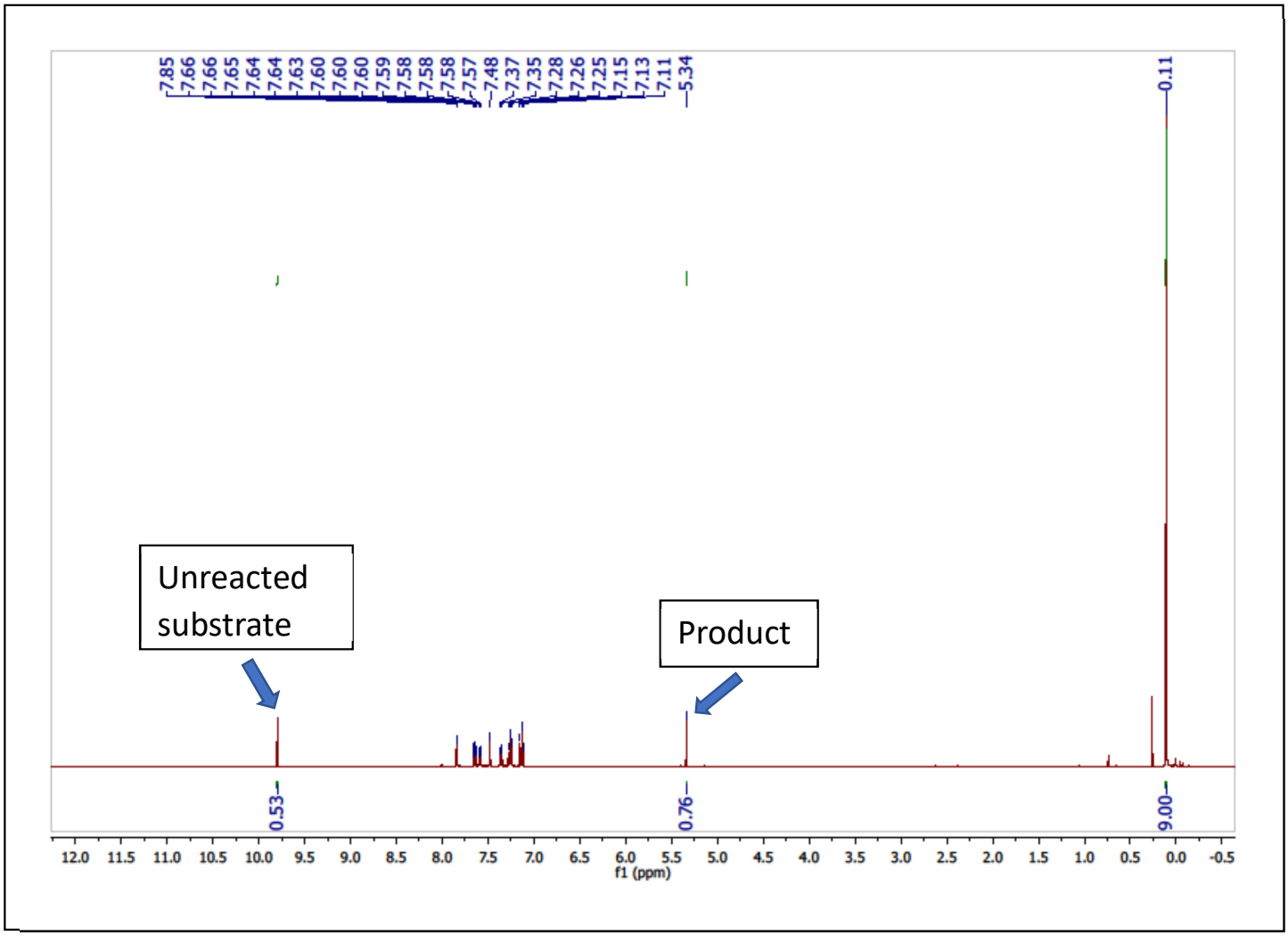
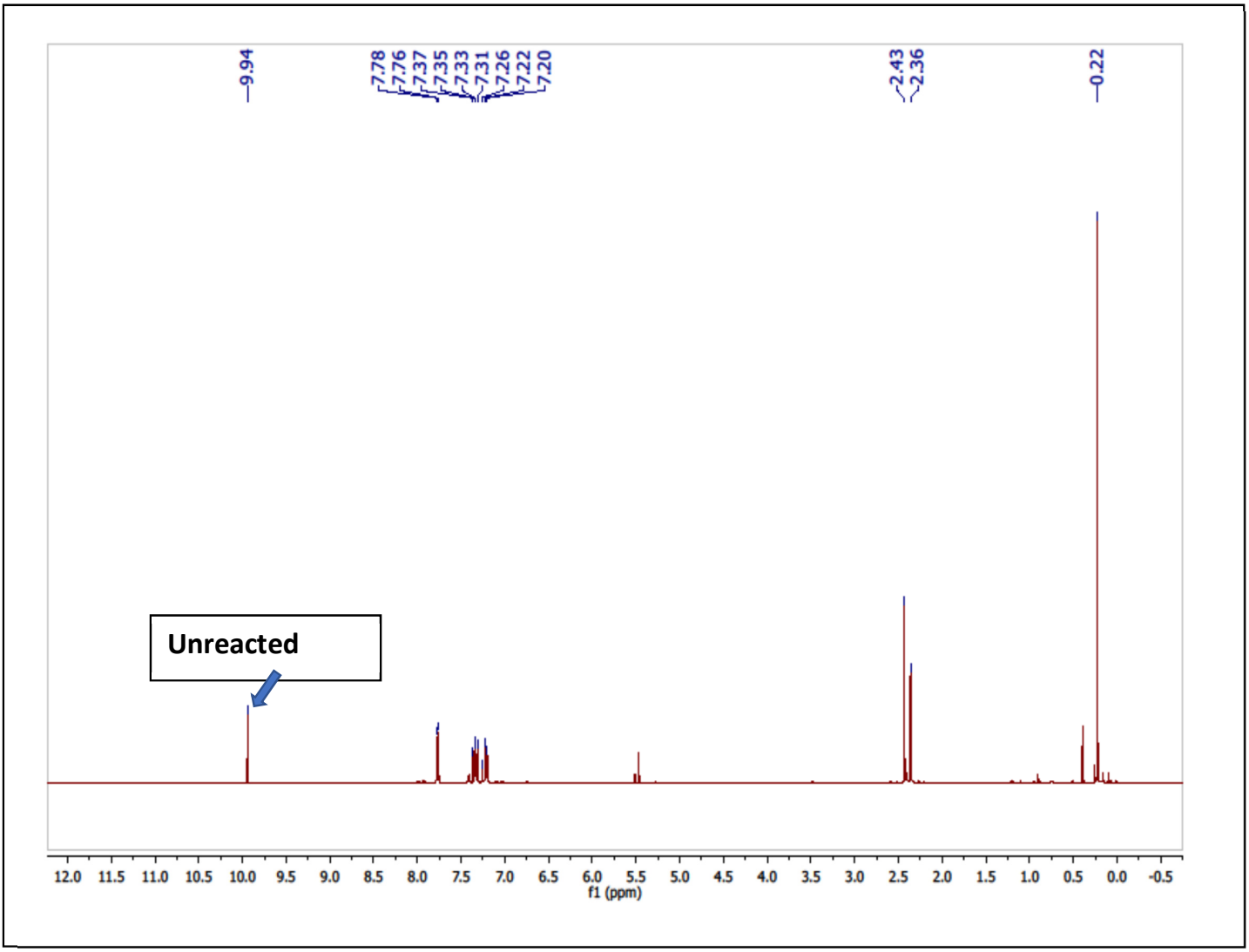


Figure S33. ^{1}H NMR of cyanosilylation of *p*-tolualdehyde by compound **2**.



[S9]. (a) NMR data for cyanosilylated products of aldehydes by catalyst 4.

(i) 4-CH_3PhCHCNOSi(CH_3)$_3$ (5a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.34(m, 4H, *Ph*), 5.42(s, 1H, TMSO-C*H*CN), 0.20(s, 9H, Si(*CH_3*)$_3$), 2.34(s, 3H, 4-C*H_3*PhCHCNOSi(CH_3)$_3$ 2.26 (s, 9H, Ph(C*H_3*)$_3$), 6.78 (s, 3H C_6*H_3*(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.29 (s, Si(*C*H_3)$_3$), 21.14(s, 4-*C*H_3PhCHCNOSi(CH_3)$_3$), 63.53(s, *C*H(CN)OSi(CH_3)$_3$), 119.27(s, CH(*C*N)OSi(CH_3)$_3$), 126.35, 126.86, 129.54, 133.40, 137.64, 139.29 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for [4-CH_3PhCHCNOSi(CH_3)$_3$]: *m/z* 219.1079. Found: *m/z* 220.1124 $[M+H]^+$.

(ii) 2,6-(CH_3)$_2$PhCHCNOSi(CH_3)$_3$ (5b) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.26(m, 3H, *Ph*), 5.98(s, 1H, TMSO-C*H*CN), 0.27 (s, 9H, Si(*CH_3*)$_3$), 2.58 (s, 6H, 2,6-C*H_3*), 2.35 (s, 9H, Ph(C*H_3*)$_3$), 6.88 (s, 3H C_6*H_3*(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.40 (s, Si(CH_3)$_3$), 19.96, 21.13(s, 2,6-(CH_3)$_2$PhCHCNOSi(CH_3)$_3$), 59.00(s, *C*H(CN)OSi(CH_3)$_3$), 118.98(s, CH(CN)OSi(CH_3)$_3$), 129.23, 129.34, 132.51, 136.79, 137.62 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for 2,6-(CH_3)$_2$PhCHCNOSi(CH_3)$_3$ *m/z* 233.1236 . Found: *m/z* 232.1199 $[M]^+$

iii) 4-(CH_3)$_3$CPhCHCOSi(CH_3)$_3$ (5c) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.51(m, 4H, *Ph*), 5.53(s, 1H, TMSO-C*H*CN), 0.30(s, 9H, Si(*CH_3*)$_3$), 1.39(s, 9H, 4-(C*H_3*)$_3$CPhCHCNOSi(CH_3)$_3$ 2.35 (s, 9H, Ph(C*H_3*)$_3$), 6.87 (s, 3H C_6*H_3*(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.30 (s, Si(*C*H_3)$_3$), 21.14(s, Ph(*C*H_3)$_3$), 31.19 4-(*C*H_3)$_3$CPhCHCNOSi(CH_3)$_3$, 34.63 4-(CH_3)$_3$*C*PhCHCNOSi(CH_3)$_3$ 63.43(s, *C*H(CN)OSi(CH_3)$_3$), 119.25(s, CH(*C*N)OSi(CH_3)$_3$), 125.83, 126.13, 133.28, 137.63, 152.48 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for 4-(CH_3)$_3$CPhCHCOSi(CH_3)$_3$ *m/z* 261.1549. Found *m/z* 262.1798 $[M+H]^+$.

iv) 3-(OCH_3)PhCHCNOSi(CH_3)$_3$ (5d) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.5-39(m, 4H, *Ph*), 5.51(s, 1H, TMSO-C*H*CN), 0.29(s,9H, Si(*CH_3*)$_3$), 3.87(s, 3H, 3-(OC*H_3*)PhCHCNOSi(CH_3)$_3$

2.33 (s, 9H, Ph(C*H*$_3$)$_3$), 6.86 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ -0.32 (s, Si(*C*H$_3$)$_3$), 21.12(s, Ph(*C*H$_3$)$_3$), 55.23 (s, 3-(O*C*H$_3$)PhCHCNOSi(CH$_3$)$_3$, 63.47(s, *C*H(CN)OSi(CH$_3$)$_3$) 118.44(s, CH(*C*N)OSi(CH$_3$)$_3$), 111.82, 114.81, 119.06, 129.95, 137.70, 159.98 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for **3**-(OCH$_3$)PhCHCNOSi(CH$_3$)$_3$ *m/z* 235.1029. Found *m/z* 236.1073 [M+H]$^+$.

v) 4-(OCOCH$_3$)PhCHCNOSi(CH$_3$)$_3$ (5e) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18-7.54(m, 4H, *Ph*), 5.53(s, 1H, TMSO-C*H*CN), 0.29(s,9H, Si(*CH$_3$)$_3$*), 2.34(s, 3H, 4-(OCOC*H$_3$*)PhCHCNOSi(CH$_3$)$_3$, 2.32 (s, 9H, Ph(C*H*$_3$)$_3$), 6.85 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ -0.39 (s, Si(*C*H$_3$)$_3$), 20.95(s, Ph(*C*H$_3$)$_3$), 21.09(s, 4-(OCOCH$_3$)PhCHCNOSi(CH$_3$)$_3$, 62.96(s, *C*H(CN)OSi(CH$_3$)$_3$), 118.90(s, CH(*C*N)OSi(CH$_3$)$_3$), 122.08, 126.82, 127.45, 133.75, 137.60, 151.23, 169.05 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for 4-(OCOCH$_3$)PhCHCNOSi(CH$_3$)$_3$ *m/z* 247.1029. Found *m/z* 248.0315 [M+H]$^+$

vi) 2-BrPhCHCNOSi(CH$_3$)$_3$ (5f) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26-7.80(m, 4H, *Ph*), 5.84(s, 1H, TMSO-C*H*CN), 0.33(s, 9H, Si(*CH$_3$)$_3$*), 2.34 (s, 9H, Ph(C*H*$_3$)$_3$), 6.87 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ -0.35 (s, Si(*C*H$_3$)$_3$), 21.13(s, Ph(*C*H$_3$)$_3$), 63.14(s, *C*H(CN)OSi(CH$_3$)$_3$), 118.25(s, CH(*C*N)OSi(CH$_3$)$_3$), 121.65, 126.84, 128.09, 130.92, 135.44, 137.60 (represents carbon atom of the aromatic phenyl ring).

vii) 4-BrPhCHCNOSi(CH$_3$)$_3$ (5g) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26-7.60(m, 4H, *Ph*), 5.48(s, 1H, TMSO-C*H*CN), 0.29(s, 9H, Si(*CH$_3$)$_3$*), 2.32 (s, 9H, Ph(C*H*$_3$)$_3$), 6.85 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ -0.34 (s, Si(*C*H$_3$)$_3$), 21.14(s, Ph(*C*H$_3$)$_3$), 62.97(s, *C*H(CN)OSi(CH$_3$)$_3$), 118.67(s, CH(*C*N)OSi(CH$_3$)$_3$), 123.43, 126.85, 127.89, 132.06, 135.33, 137.63 (represents carbon atom of the aromatic phenyl ring).

viii) 3-BrPhCHCNOSi(CH$_3$)$_3$ (5h) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26-7.67(m, 4H, *Ph*), 5.50(s, 1H, TMSO-C*H*CN), 0.30(s, 9H, Si(*CH$_3$)$_3$*), 2.33 (s, 9H, Ph(C*H*$_3$)$_3$), 6.85 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ -0.36 (s, Si(*C*H$_3$)$_3$), 21.13(s, Ph(*C*H$_3$)$_3$), 62.76(s, *C*H(CN)OSi(CH$_3$)$_3$), 118.60(s, CH(*C*N)OSi(CH$_3$)$_3$), 122.90, 124.77, 126.85, 130.42, 132.40, 137.62, 138.35 (represents carbon atom of the aromatic phenyl ring) .

ix) 4-FPhCHCNOSi(CH$_3$)$_3$ (5i) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12-7.52(m, 4H, *Ph*), 5.51(s, 1H, TMSO-C*H*CN), 0.29(s, 9H, Si(*CH$_3$)$_3$*), 2.33 (s, 9H, Ph(C*H*$_3$)$_3$), 6.85 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ -0.34 (s, Si(*C*H$_3$)$_3$), 21.13(s, Ph(*C*H$_3$)$_3$), 62.94(s,

*C*H(CN)OSi(CH_3)$_3$), 118.95(s, CH(*C*N)OSi(CH_3)$_3$), 115.80, 116.02, 128.19, 132.21, 137.65, 164.35 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for 4-FPhCHCNOSi(CH_3)$_3$ *m/z* 223.0829. Found : *m/z* 224.1278 $[M+H]^+$

x) 4-NO_2PhCHCNOSi(CH_3)$_3$ (5j) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-8.32(m, 4H, *Ph*), 5.64(s, 1H, TMSO-C*H*CN), 0.33(s, 9H, Si(*CH*$_3$)$_3$), 2.31 (s, 9H, Ph(C*H*$_3$)$_3$), 6.84 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.43 (s, Si(*C*H_3)$_3$), 21.10(s, Ph(*C*H_3)$_3$), 62.55(s, *C*H(CN)OSi(CH_3)$_3$), 118.11(s, CH(*C*N)OSi(CH_3)$_3$), 124.07, 126.82, 127.03, 137.61, 142.82, 148.33 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for 4-NO_2PhCHCNOSi(CH_3)$_3$ *m/z* 250.0774. Found: *m/z* 250.0972 $[M]^+$.

xi) 4-CNPhCHCNOSi(CH_3)$_3$ (5k) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-8.32(m, 4H, *Ph*), 5.64(s, 1H, TMSO-C*H*CN), 0.33(s, 9H, Si(*CH*$_3$)$_3$), 2.31 (s, 9H, Ph(C*H*$_3$)$_3$), 6.84 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.48 (s, Si(*C*H_3)$_3$), 21.12(s, Ph(*C*H_3)$_3$), 62.69(s, *C*H(CN)OSi(CH_3)$_3$), 118.15(s, CH(*C*N)OSi(CH_3)$_3$), 113.17, 117.99, 126.78, 132.62, 137.54, 141.05 (represents carbon atom of the aromatic phenyl ring).

xii) C_8H_8CHCNOSi(CH_3)$_3$ (5l) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-8.32(m, 4H, *Ph*), 5.64(s, 1H, TMSO-C*H*CN), 0.33(s, 9H, Si(*CH*$_3$)$_3$), 2.31 (s, 9H, Ph(C*H*$_3$)$_3$), 6.84 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.48 (s, Si(*C*H_3)$_3$), 21.12(s, Ph(*C*H_3)$_3$), 62.69(s, *C*H(CN)OSi(CH_3)$_3$), 118.15(s, CH(*C*N)OSi(CH_3)$_3$), 113.17, 117.99, 126.78, 132.62, 137.54, 141.05 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for C_8H_8CHCNOSi(CH_3)$_3$ *m/z* 233.1236. Found *m/z* 233.2010 $[M]^+$.

xiii) 4-(NHCOCH_3)PhCHCNOSi(CH_3)$_3$ (5m) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-8.32(m, 4H, *Ph*), 5.64(s, 1H, TMSO-C*H*CN), 0.33(s, 9H, Si(*CH*$_3$)$_3$), 2.31 (s, 9H, Ph(C*H*$_3$)$_3$), 6.84 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.48 (s, Si(*C*H_3)$_3$), 21.12(s, Ph(*C*H_3)$_3$), 62.69(s, *C*H(CN)OSi(CH_3)$_3$), 118.15(s, CH(*C*N)OSi(CH_3)$_3$), 113.17, 117.99, 126.78, 132.62, 137.54, 141.05 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for 4-(NHCOCH_3)PhCHCNOSi(CH_3)$_3$ *m/z* 262.1138. Found *m/z* 263.2112 $[M+H]^+$.

xiv) C_6H_{11}CHCNOSi(CH_3)$_3$ (5n) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13-1.90(m, 10H, C_6H_{10}), 4.17, 4.19(d, 1H, TMSO-C*H*CN), 0.24(s, 9H, Si(*CH*$_3$)$_3$), 2.31 (s, 9H, Ph(C*H*$_3$)$_3$), 6.84 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.51 (s, Si(*C*H_3)$_3$), 21.13(s, Ph(*C*H_3)$_3$), 66.49(s, *C*H(CN)OSi(CH_3)$_3$), 119.40(s, CH(*C*N)OSi(CH_3)$_3$), 126.85, 137.63(s, *Ph*(CH_3)$_3$) 25.48, 26.00,

27.88, 28.09, 42.91 (represents carbon atom of the aliphatic cyclohexane ring) ESI-MS: Calcd for $C_6H_{11}CHCNOSi(CH_3)_3$ *m/z* 211.1392. Found *m/z* 212.1437 $[M+H]^+$.

xv) $C_{10}H_7CHCNOSi(CH_3)_3$ (5o) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-8.28(m, 7H, $C_{10}H_7$), 6.13(s, 1H, TMSO-C*H*CN), 0.29 (s, 9H, Si(CH_3)$_3$), 2.36 (s, 9H, Ph(CH_3)$_3$), 6.89 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.24 (s, Si(CH_3)$_3$), 21.13(s, Ph(CH_3)$_3$), 62.65(s, *C*H(CN)OSi(CH_3)$_3$), 119.05(s, CH(*C*N)OSi(CH_3)$_3$),123.12, 125.01, 125.39, 126.24, 126.85, 126.92, 128.90, 129.89, 130.38, 131.33, 133.91 (represents carbon atom of the aromatic phenyl ring) ESI-MS: Calcd for $C_{10}H_7CHCNOSi(CH_3)_3$ *m/z* 255.1079. Found *m/z* 256.1805 $[M+H]^+$.

[S9]. (b) NMR data for cyanosilylated products of ketones by catalyst 4.

(i) 4-$CH_3PhCCH_3CNOSi(CH_3)_3$ (6a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.51(m, 4H, *Ph*), 1.91(s, 3H, TMSO-C*H3*CN), 0.25(s, 9H, Si(CH_3)$_3$), 2.43(s, 3H, 4-CH_3PhCHCNOSi(CH_3)$_3$ 2.35 (s, 9H, Ph(CH_3)$_3$), 7.25 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.03 (s, Si(*C*H_3)$_3$), 20.98(s, 4-*C*H_3PhCCH$_3$CNOSi(CH_3)$_3$), 21.13(s, Ph(*C*H_3)$_3$), 71.48(s, *C*CH$_3$(CN)OSi(CH_3)$_3$), 121.73(s, CCH$_3$(*C*N)OSi(CH_3)$_3$), 124.55, 129.22, 138.49, 139.05 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for 4-$CH_3PhCCH_3CNOSi(CH_3)_3$: *m/z* 233.1236. Found : 235.1684 $[M+2H]^+$

(ii) 4-$OCH_3PhCCH_3CNOSi(CH_3)_3$ (6b) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94-7.52 (m, 4H, *Ph*), 1.89(s, 3H, TMSO-C*H3*CN), 0.21(s,9H, Si(CH_3)$_3$), 3..85(s, 3H, 4-OCH_3PhCHCNOSi(CH_3)$_3$ 2.32 (s, 9H, Ph(CH_3)$_3$), 6.84 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.02(s, Si(*C*H_3)$_3$), 21.14(s, Ph(*C*H_3)$_3$), 33.37(s, 4-OCH$_3$PhC*C*H$_3$CNOSi(CH_3)$_3$), 55.24(s, 4-O*C*H_3PhCCH$_3$CNOSi(CH_3)$_3$), 71.24(s, *C*CH$_3$(CN)OSi(CH_3)$_3$), 121.65(s, CCH$_3$(*C*N)OSi(CH_3)$_3$), 113.83, 125.00, 126.84, 134.00, 137.65, 159.75 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for 4-$OCH_3PhCCH_3CNOSi(CH_3)_3$ *m/z* 249.1185. Found: *m/z* 249.1580 $[M]^+$

(iii) $PhCCH_3CNOSi(CH_3)_3$ (6c) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.51 (m, 4H, *Ph*), 1.91(s, 3H, TMSO-C*H3*CN), 0.24(s, 9H, Si(CH_3)$_3$), 2.33 (s, 9H, Ph(CH_3)$_3$), 6.86 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.01(s, Si(*C*H_3)$_3$), 21.15(s, Ph(*C*H_3)$_3$), 33.53(s, PhC*C*H$_3$CNOSi(CH_3)$_3$), 71.59(s, *C*CH$_3$(CN)OSi(CH_3)$_3$), 121.60(s, CCH$_3$(*C*N)OSi(CH_3)$_3$), 124.58, 126.87, 128.60, 137.65, 141.12, 141.98 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for $PhCCH_3CNOSi(CH_3)_3$ *m/z* 219.0107. Found *m/z* 220.1233 $[M+H]^+$

(iv) 4-OHPhCCH$_3$CNOSi(CH$_3$)$_3$ (6d) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91-7.94 (m, 4H, *Ph*), 2.58(s, 3H, TMSO-C*H3*CN), 0.35(s, 9H, Si(*CH$_3$)$_3$*), 2.32 (s, 9H, Ph(C*H*$_3$)$_3$), 6.85 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.12(s, Si(*C*H$_3$)$_3$), 21.09(s, Ph(*C*H$_3$)$_3$), 33.17(s, 4-OHPhC*C*H$_3$CNOSi(CH$_3$)$_3$), 71.27(s, *C*CH$_3$(CN)OSi(CH$_3$)$_3$), 119.96(s, CCH$_3$(*C*N)OSi(CH$_3$)$_3$), 119.73, 126.82, 130.46, 137.58, 159.72 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for 4-OHPhCCH$_3$CNOSi(CH$_3$)$_3$ *m/z* 235.1029. Found *m/z* 235.9781[M]$^+$

(v) 2-BrPhCCH$_3$CNOSi(CH$_3$)$_3$ (6e) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.80(m, 4H, *Ph*), 2.08(s, 3H, TMSO-C*H3*CN), 0.35(s, 9H, Si(*CH$_3$)$_3$*), 2.33 (s, 9H, Ph(C*H*$_3$)$_3$), 6.86 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.14(s, Si(*C*H$_3$)$_3$), 21.14(s, Ph(*C*H$_3$)$_3$), 29.82(s, 2-BrPhC*C*H$_3$CNOSi(CH$_3$)$_3$), 71.42(s, *C*CH$_3$(CN)OSi(CH$_3$)$_3$), 126.85(s, CCH$_3$(*C*N)OSi(CH$_3$)$_3$), 127.25, 127.58, 130.06, 135.20, 137.62, 139.22 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for 2-BrPhCCH$_3$CNOSi(CH$_3$)$_3$ *m/z* 297.0185. Found *m/z* 299.1816 [M+2H]$^+$

(vi) 4-BrPhCCH$_3$CNOSi(CH$_3$)$_3$ (6f) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.59 (m, 4H, *Ph*), 1.88(s, 3H, TMSO-C*H3*CN), 0.26(s, 9H, Si(*CH$_3$)$_3$*), 2.33 (s, 9H, Ph(C*H*$_3$)$_3$), 6.86 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.02(s, Si(*C*H$_3$)$_3$), 21.14(s, Ph(*C*H$_3$)$_3$), 33.42(s, 4-BrPhC*C*H$_3$CNOSi(CH$_3$)$_3$), 71.06(s, *C*CH$_3$(CN)OSi(CH$_3$)$_3$), 121.11(s, CCH$_3$(*C*N)OSi(CH$_3$)$_3$), 122.69, 126.32, 126.86, 131.76, 137.76, 141.22 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for 4-BrPhCCH$_3$CNOSi(CH$_3$)$_3$ *m/z* 297.0185. Found *m/z* 299.1817 [M+2H]$^+$

(vii) 4-NO$_2$PhCCH$_3$CNOSi(CH$_3$)$_3$ (6g) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-8.30 (m, 4H, *Ph*), 1.91(s, 3H, TMSO-C*H3*CN), 0.29(s, 9H, Si(*CH$_3$)$_3$*), 2.31 (s, 9H, Ph(C*H*$_3$)$_3$), 6.83 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.95(s, Si(*C*H$_3$)$_3$), 21.09(s, Ph(*C*H$_3$)$_3$), 33.33(s, 4-NO$_2$PhC*C*H$_3$CNOSi(CH$_3$)$_3$), 70.86(s, *C*CH$_3$(CN)OSi(CH$_3$)$_3$), 120.86(s, CCH$_3$(*C*N)OSi(CH$_3$)$_3$), 123.91, 125.64, 126.82, 137.59, 147.97, 149.88 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for 4-NO$_2$PhCCH$_3$CNOSi(CH$_3$)$_3$ *m/z* 262.1012. Found *m/z* 261.2281 [M]$^+$

(viii) Ph$_2$CCNOSi(CH$_3$)$_3$ (6h) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.62 (m, 4H, *Ph*), 0.25(s,9H, Si(*CH$_3$)$_3$*), 2.37 (s, 9H, Ph(C*H*$_3$)$_3$), 6.90 (s, 3H C$_6$*H*$_3$(CH$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.87(s, Si(*C*H$_3$)$_3$), 21.14(s, Ph(*C*H$_3$)$_3$), 76.42(s, *C*Ph$_2$(CN)OSi(CH$_3$)$_3$), 120.66(s, CPh$_2$(*C*N)OSi(CH$_3$)$_3$), 125.85, 128.51, 128.61, 137.61, 141.92(represents carbon atom of the

aromatic phenyl ring) HRMS: Calcd for $Ph_2CCNOSi(CH_3)_3$ *m/z* 281.1236. Found *m/z* 282.1304 $[M+H]^+$.

(ix) $C_5H_8CNOSi(CH_3)_3$ (6i) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82-2.18 (m, 8H, *Cp*), 0.30(s,9H, $Si(CH_3)_3$), 2.33 (s, 9H, $Ph(CH_3)_3$), 6.86 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.02(s, $Si(CH_3)_3$), 22.54(s, $Ph(CH_3)_3$), 74.40(s, $CC_4H_8(CN)OSi(CH_3)_3$), 122.54(s, $C_5H_8(CN)OSi(CH_3)_3$), 41.65(s, C_4H_8) HRMS: Calcd for $C_5H_8CNOSi(CH_3)_3$ *m/z* 225.1549. Found *m/z* 224.1255 $[M]^+$.

x) $PhCCH_2BrCNOSi(CH_3)_3$ (6j) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.64 (m, 4H, *Ph*), 3.60-3.70(dd, 2H, TMSO-C*H3*CN), 0.26(s, 9H, $Si(CH_3)_3$), 2.34 (s, 9H, $Ph(CH_3)_3$), 6.87 (s, 3H $C_6H_3(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.75(s, $Si(CH_3)_3$), 21.13(s, $Ph(CH_3)_3$), 40.85(s, $PhCCH_2BrCNOSi(CH_3)_3$), 75.32(s, $CCH_3(CN)OSi(CH_3)_3$), 118.95(s, $CCH_3(CN)OSi(CH_3)_3$), 125.36, 126.85, 128.80, 129.65, 137.61, 138.26 (represents carbon atom of the aromatic phenyl ring) HRMS: Calcd for $PhCCH_2BrCNOSi(CH_3)_3$ r*m/z* 297.0185. Found *m/z* 299.1786 $[M+2H]^+$.

[S9]. (c) ^{1}H and ^{13}C NMR data for cyanosilylated products of aldehydes and ketones by catalyst 4.

Figure S34. ^{1}H NMR of **5a** (Solvent: $CDCl_3$, IS: Mesitylene).

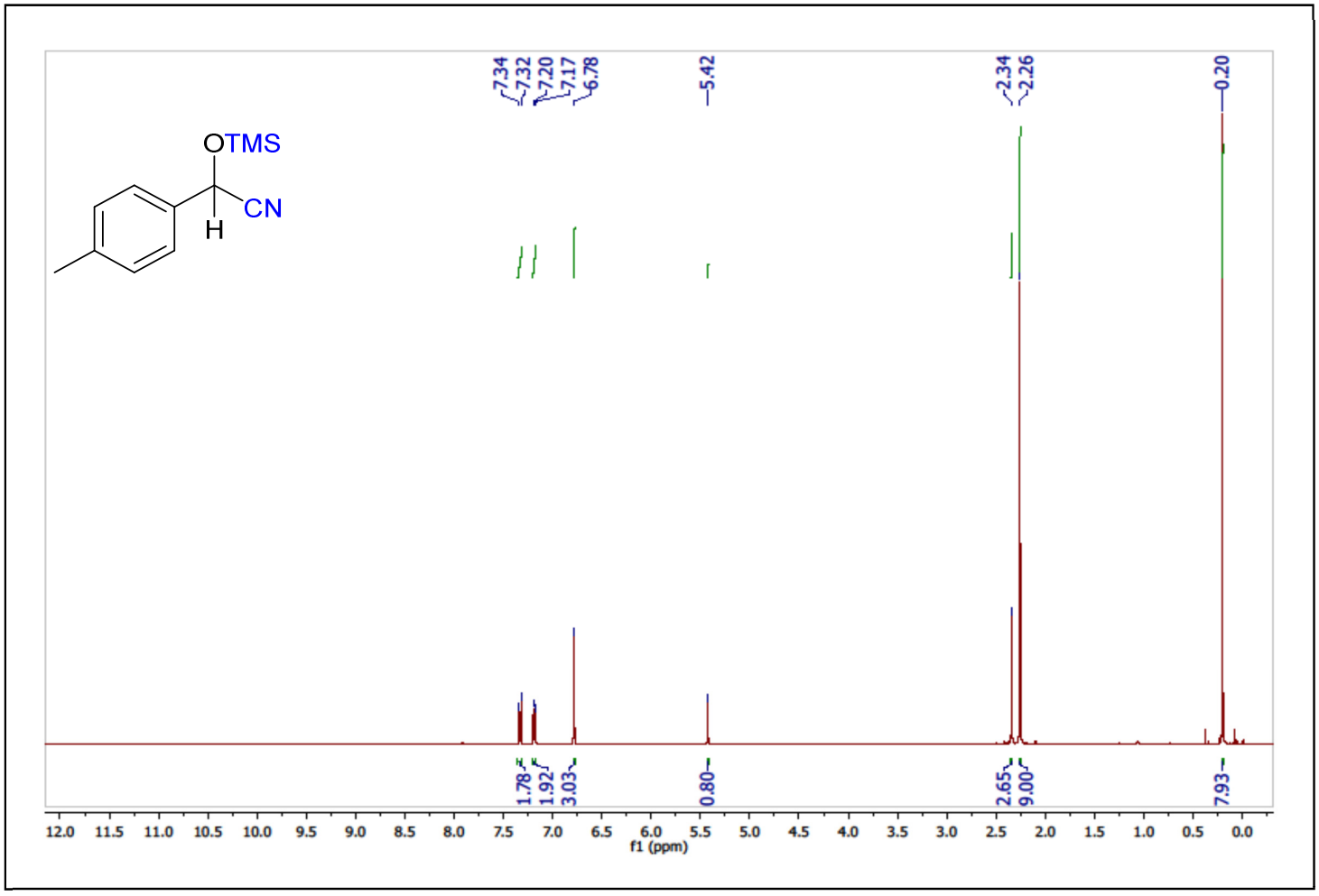


Figure S35. ^{13}C NMR of **5a** (Solvent: $CDCl_3$, IS: Mesitylene).

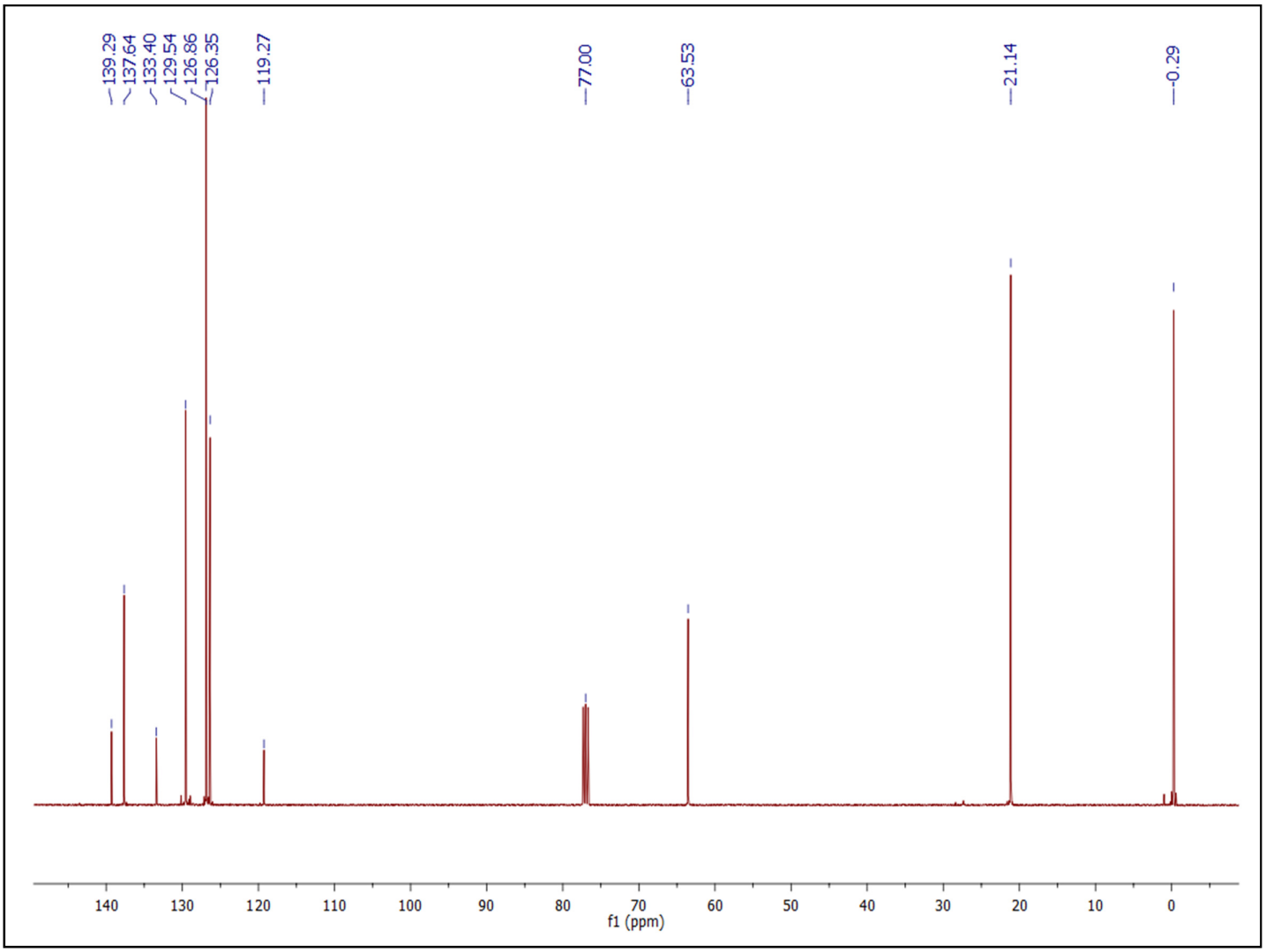


Figure S36. ^{1}H NMR of **5b** (Solvent: $CDCl_3$, IS: Mesitylene).

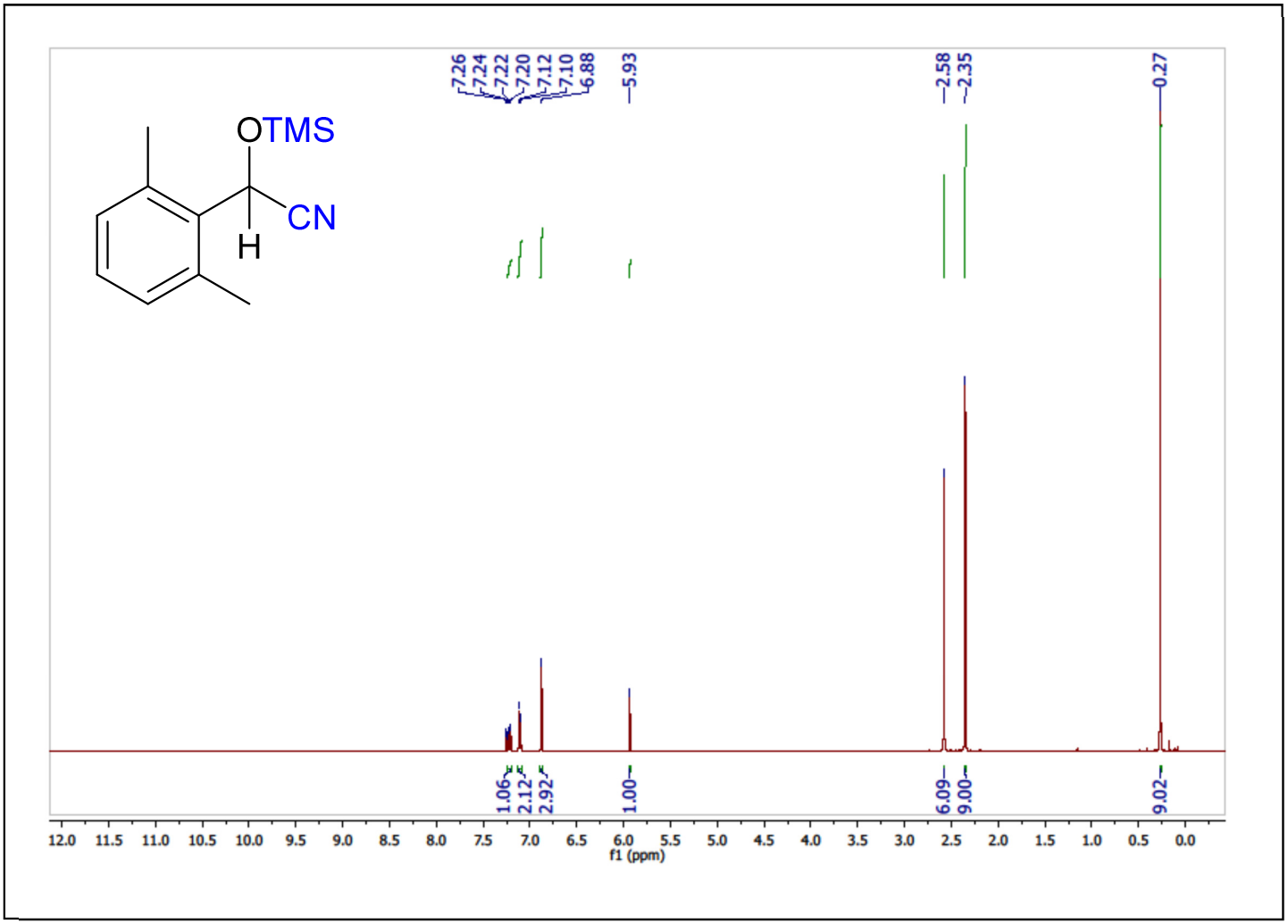


Figure S37. ^{13}C NMR of **5b** (Solvent: $CDCl_3$, IS: Mesitylene).

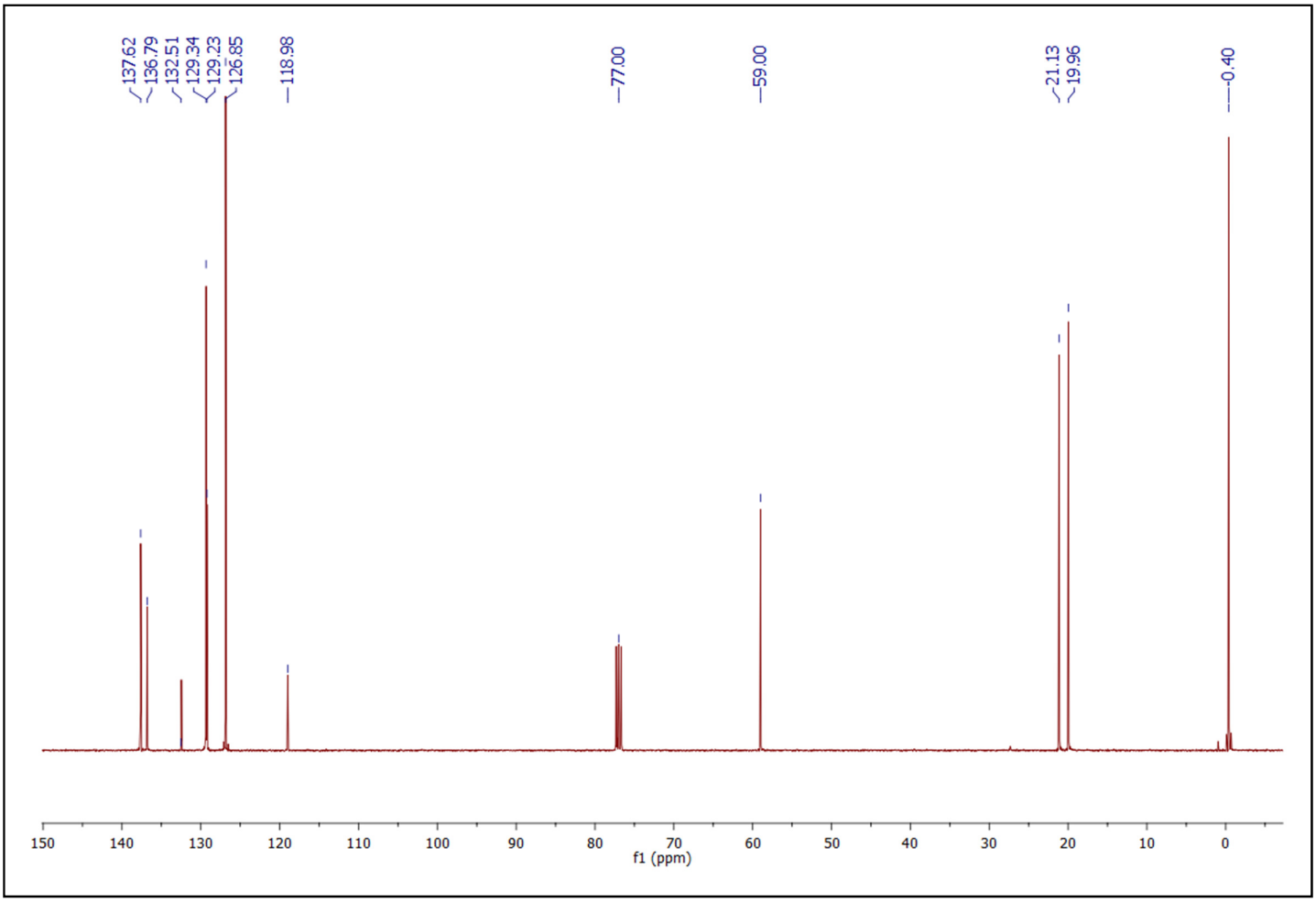


Figure S38. ^{1}H NMR of **5c** (Solvent: $CDCl_3$, IS: Mesitylene).

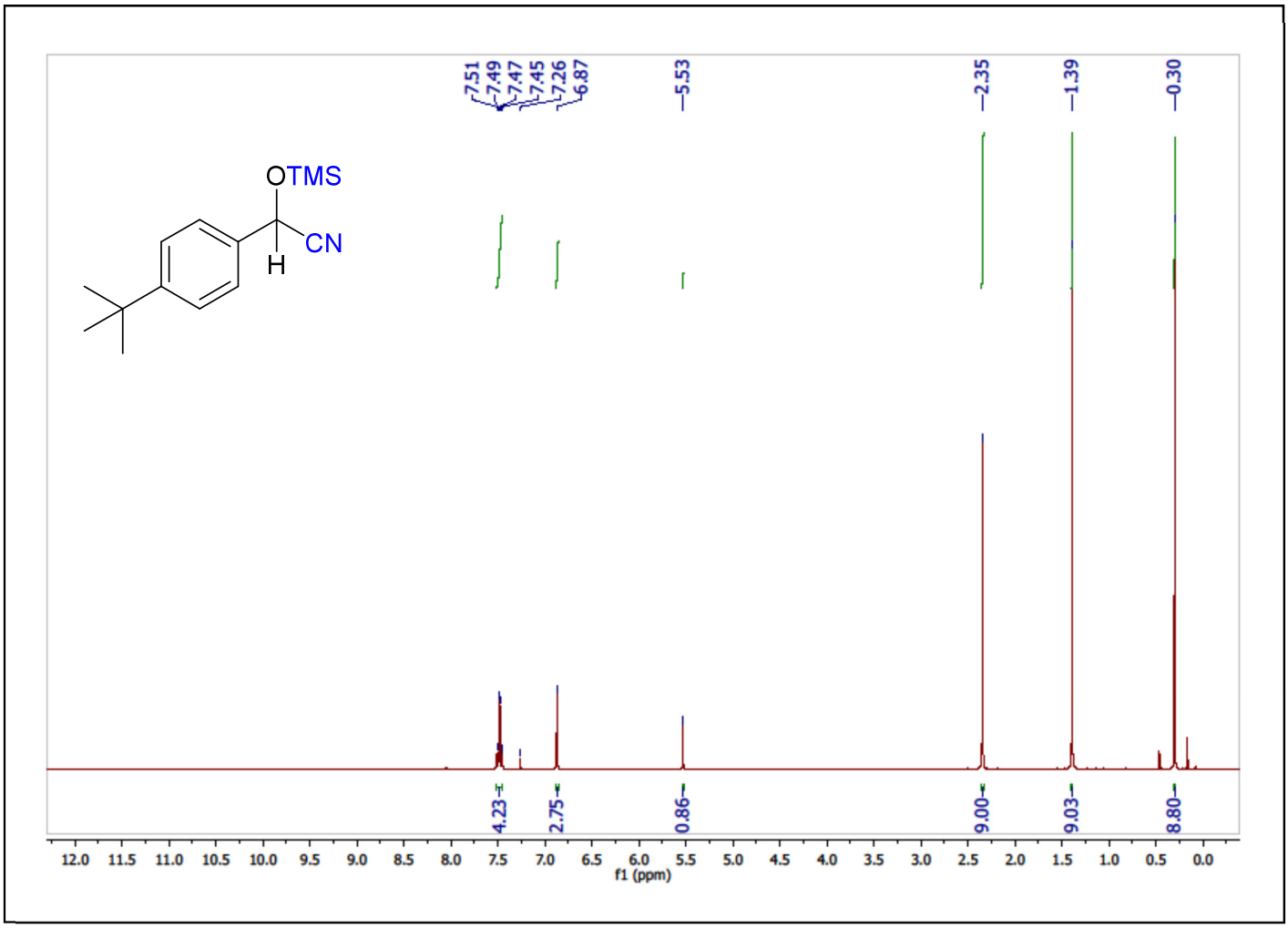


Figure S39. ^{13}C NMR of **5c** (Solvent: $CDCl_3$, IS: Mesitylene).

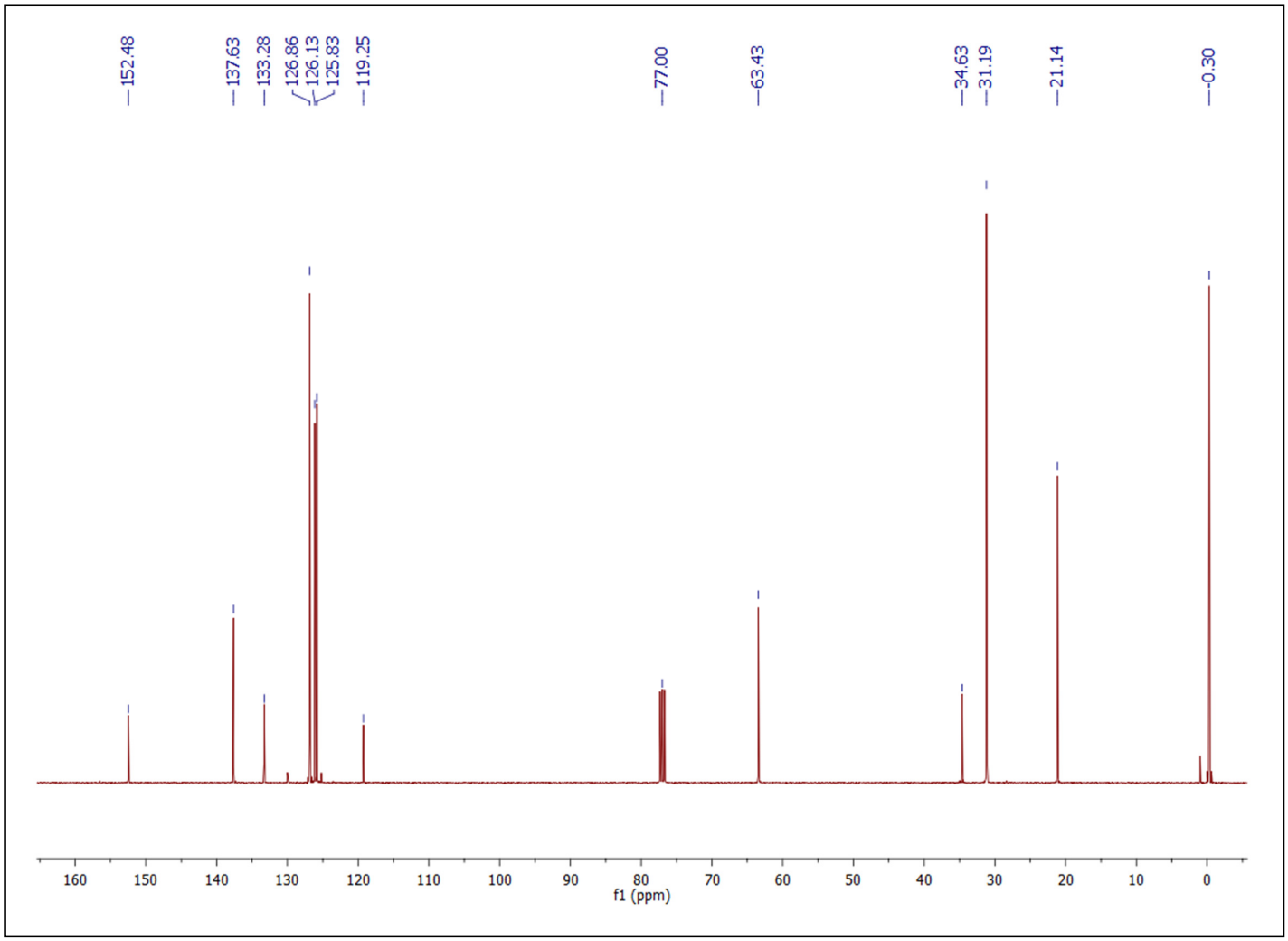


Figure S40. ^{1}H NMR of **5d** (Solvent: $CDCl_3$, IS: Mesitylene).

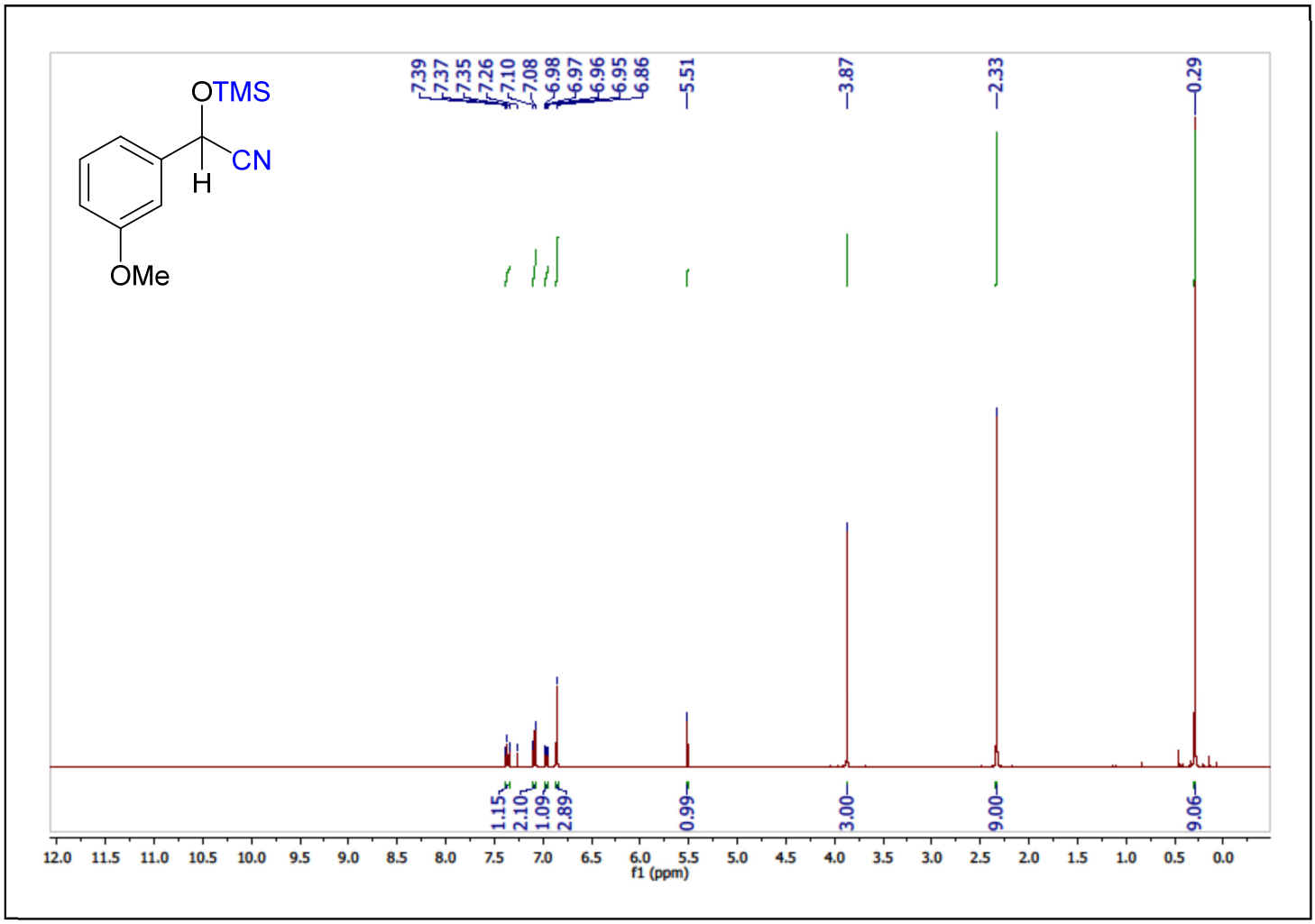


Figure S41. ^{13}C NMR of **5d** (Solvent: $CDCl_3$, IS: Mesitylene).

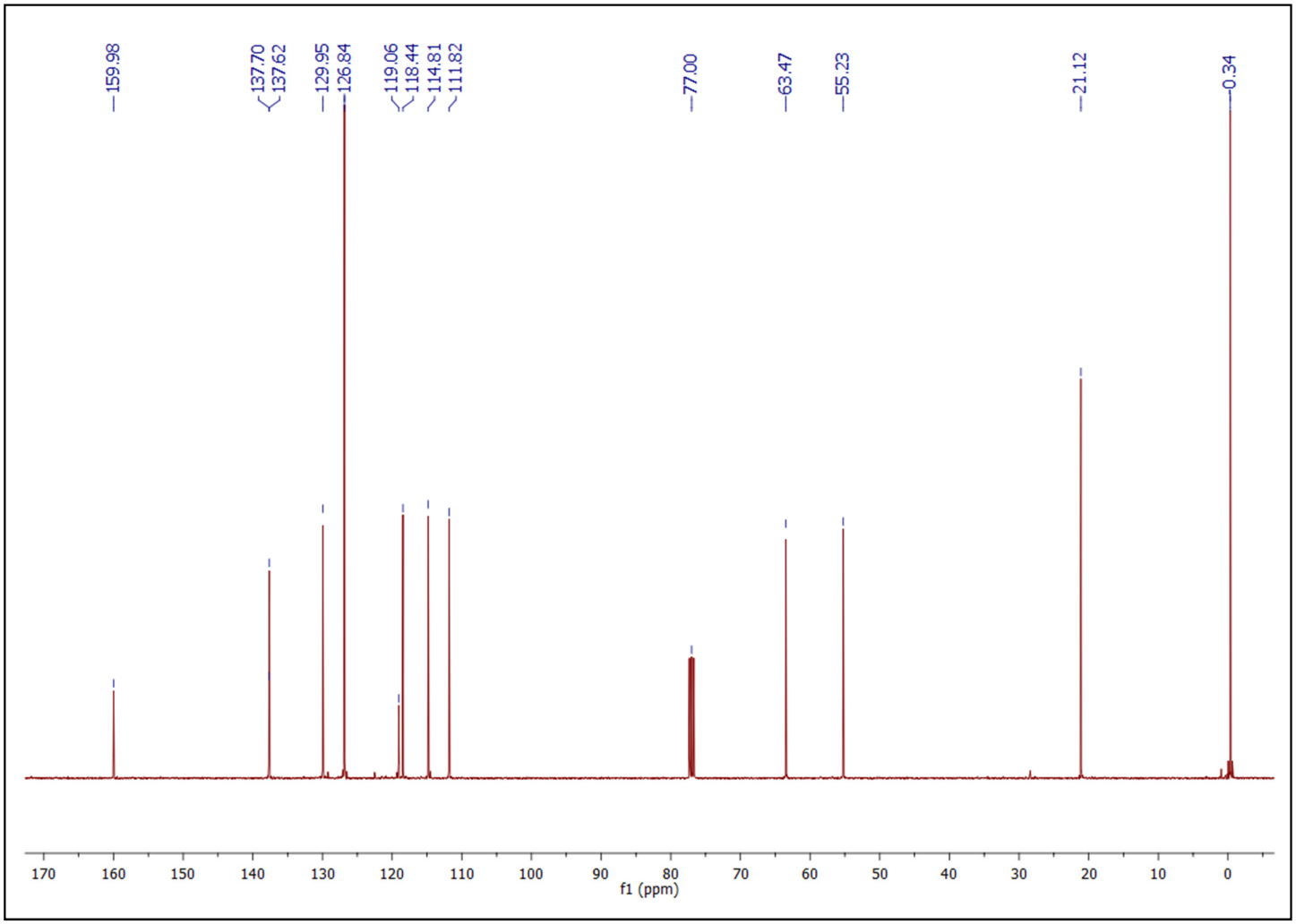


Figure S42. ^{1}H NMR of **5e** (Solvent: $CDCl_3$, IS: Mesitylene).

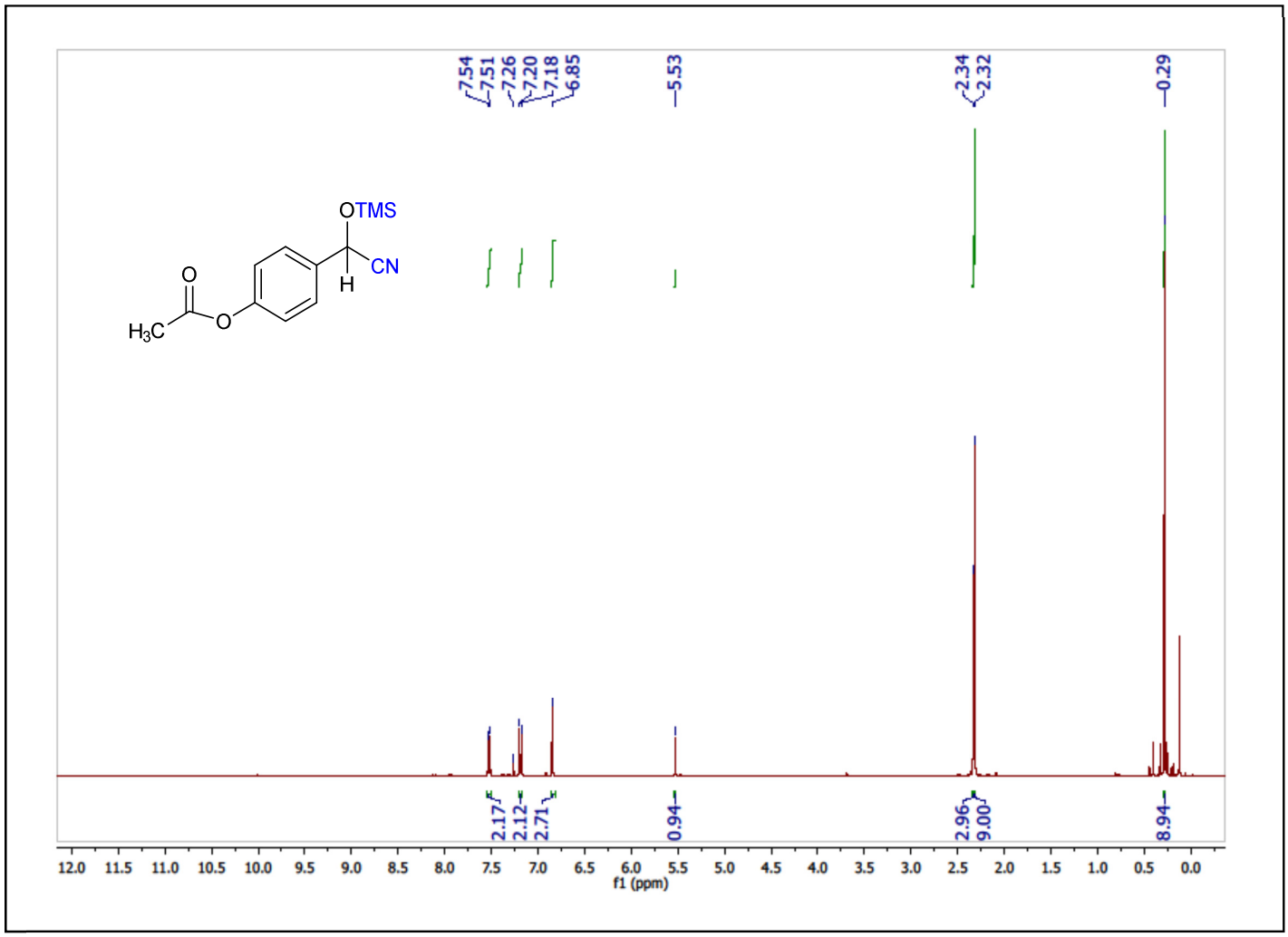


Figure S43. ^{13}C NMR of **5e** (Solvent: $CDCl_3$, IS: Mesitylene).

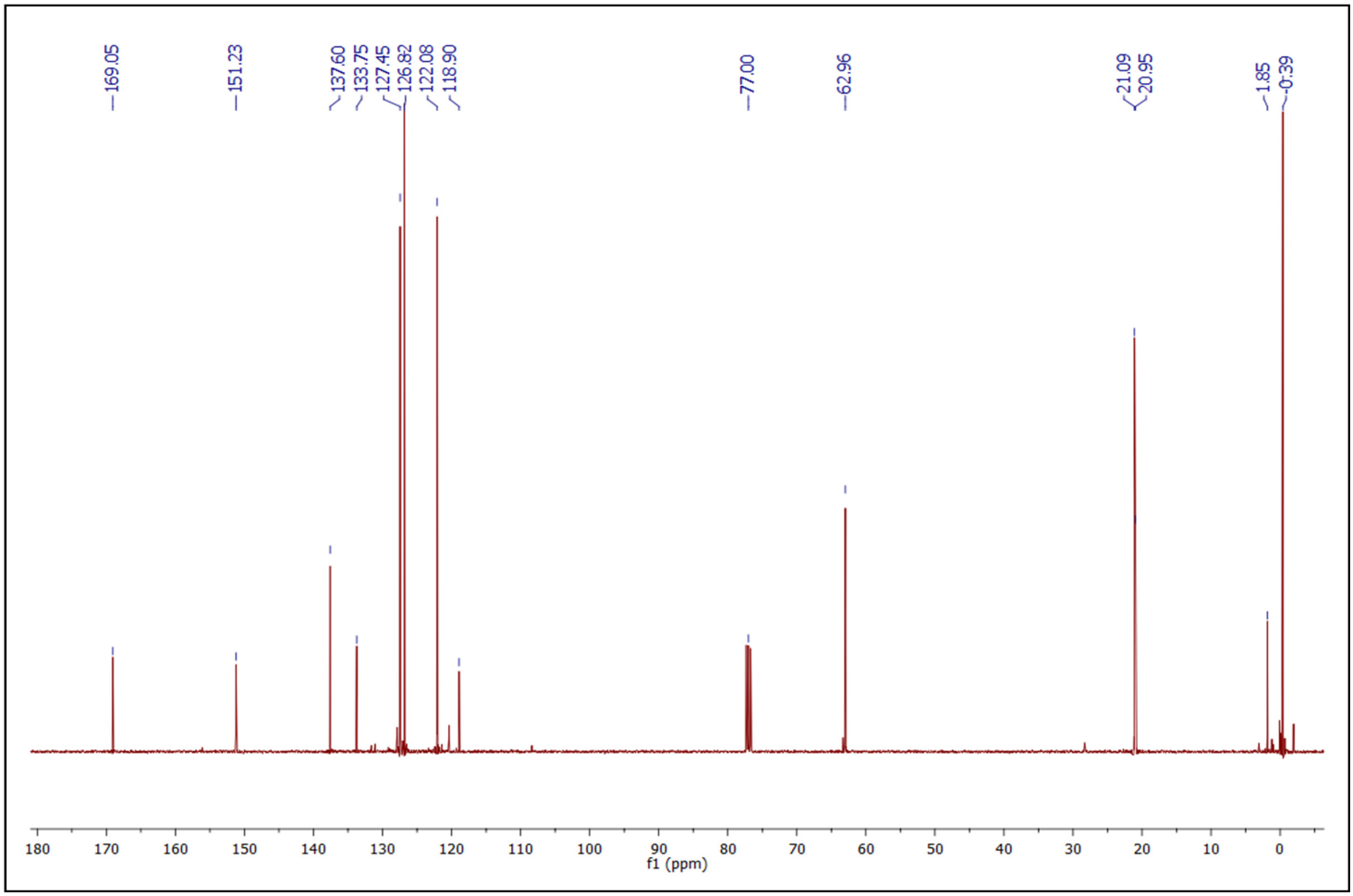


Figure S44. ^{1}H NMR of **5f** (Solvent: $CDCl_3$, IS: Mesitylene).

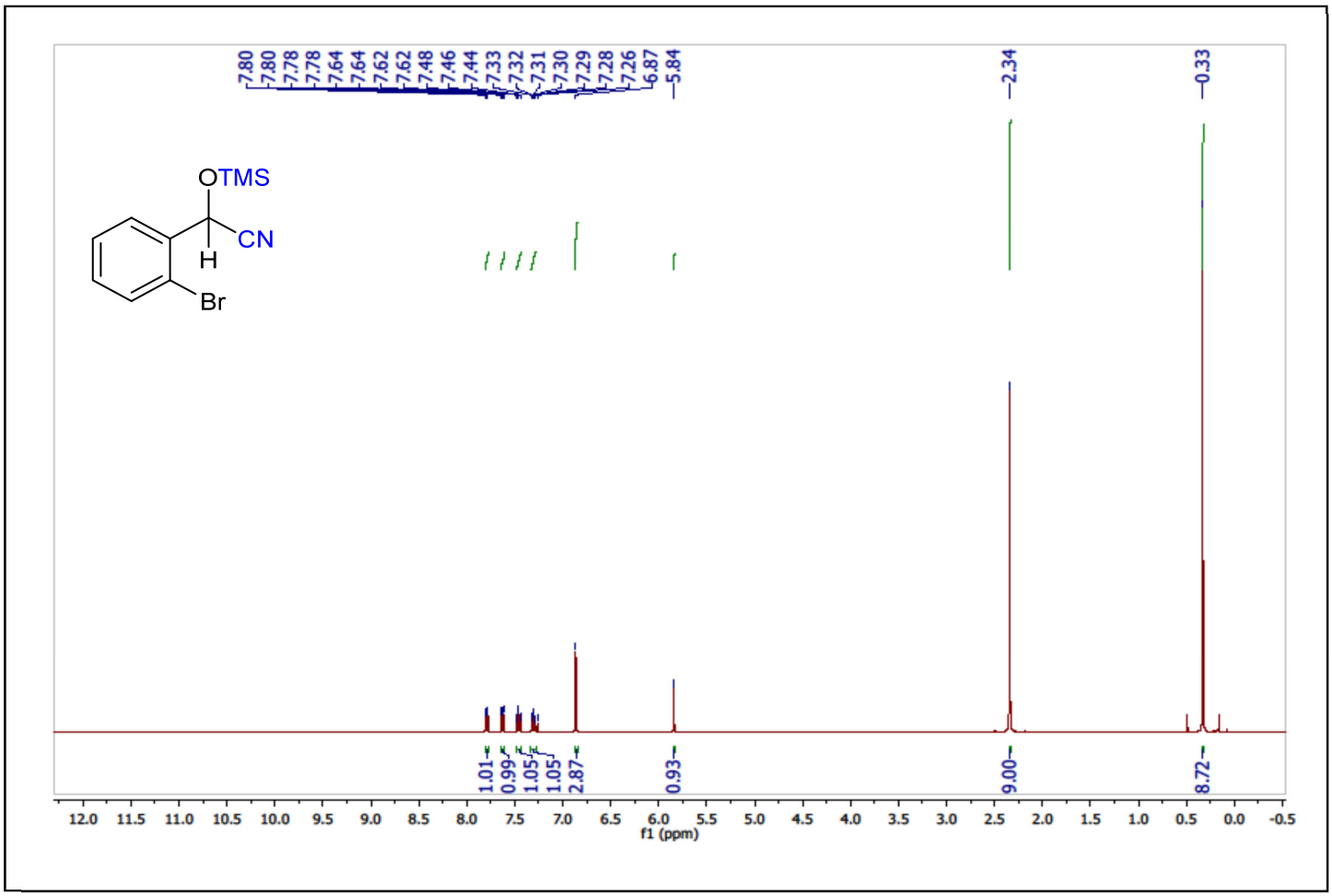


Figure S45. ^{13}C NMR of **5f** (Solvent: $CDCl_3$, IS: Mesitylene).

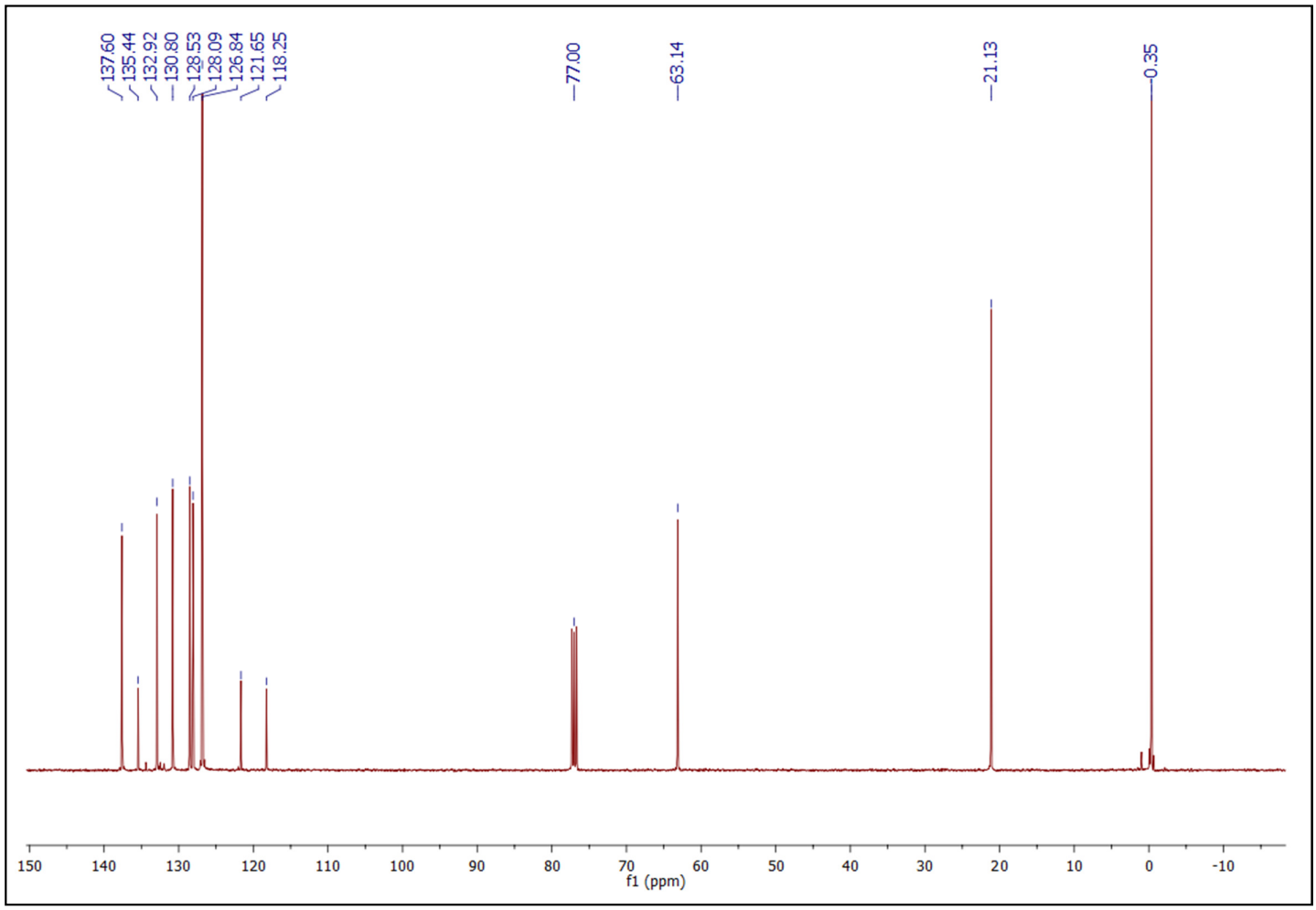


Figure S46. ^{1}H NMR of **5g** (Solvent: $CDCl_3$, IS: Mesitylene).

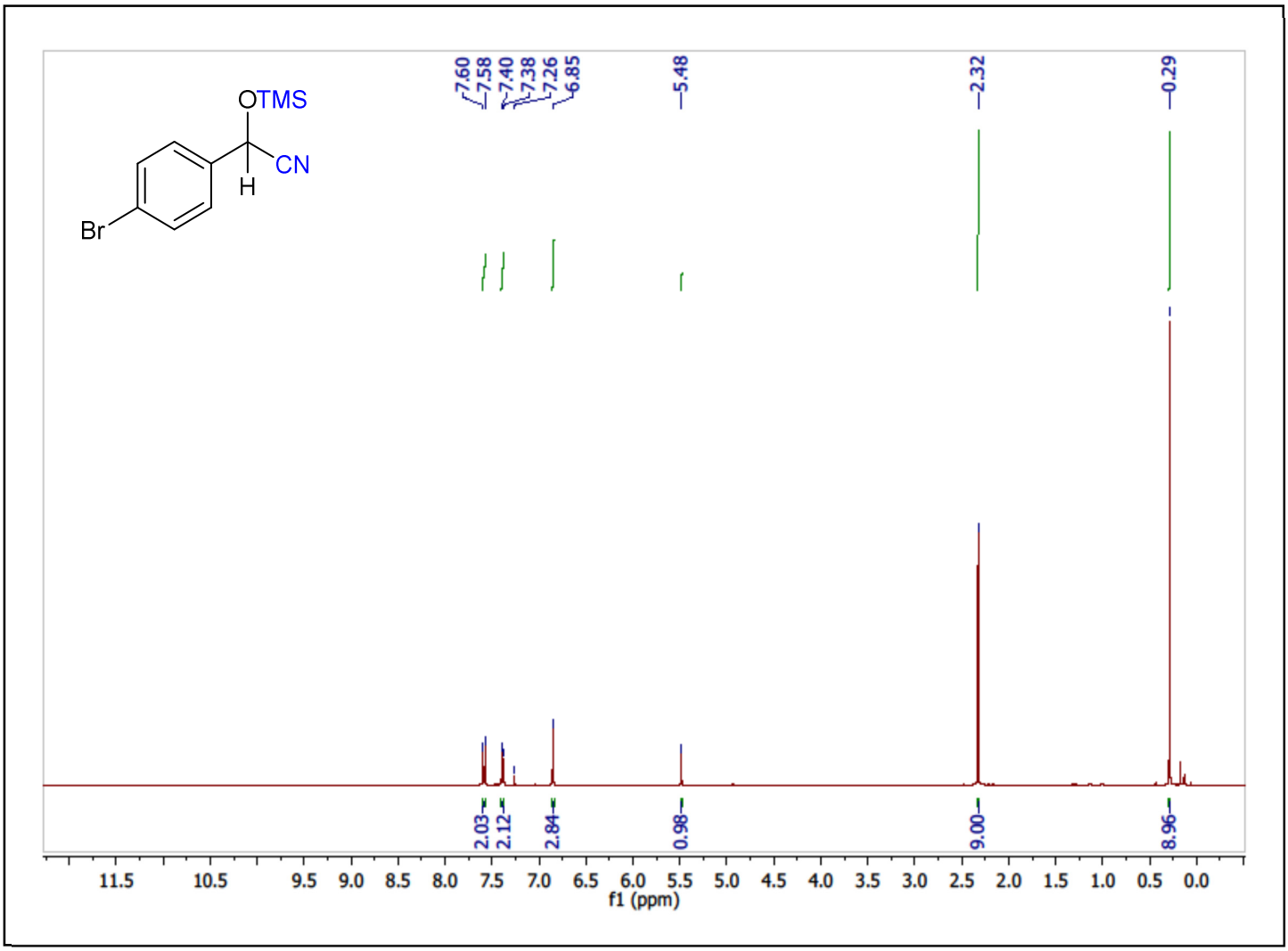


Figure S47. ^{13}C NMR of **5g** (Solvent: $CDCl_3$, IS: Mesitylene).

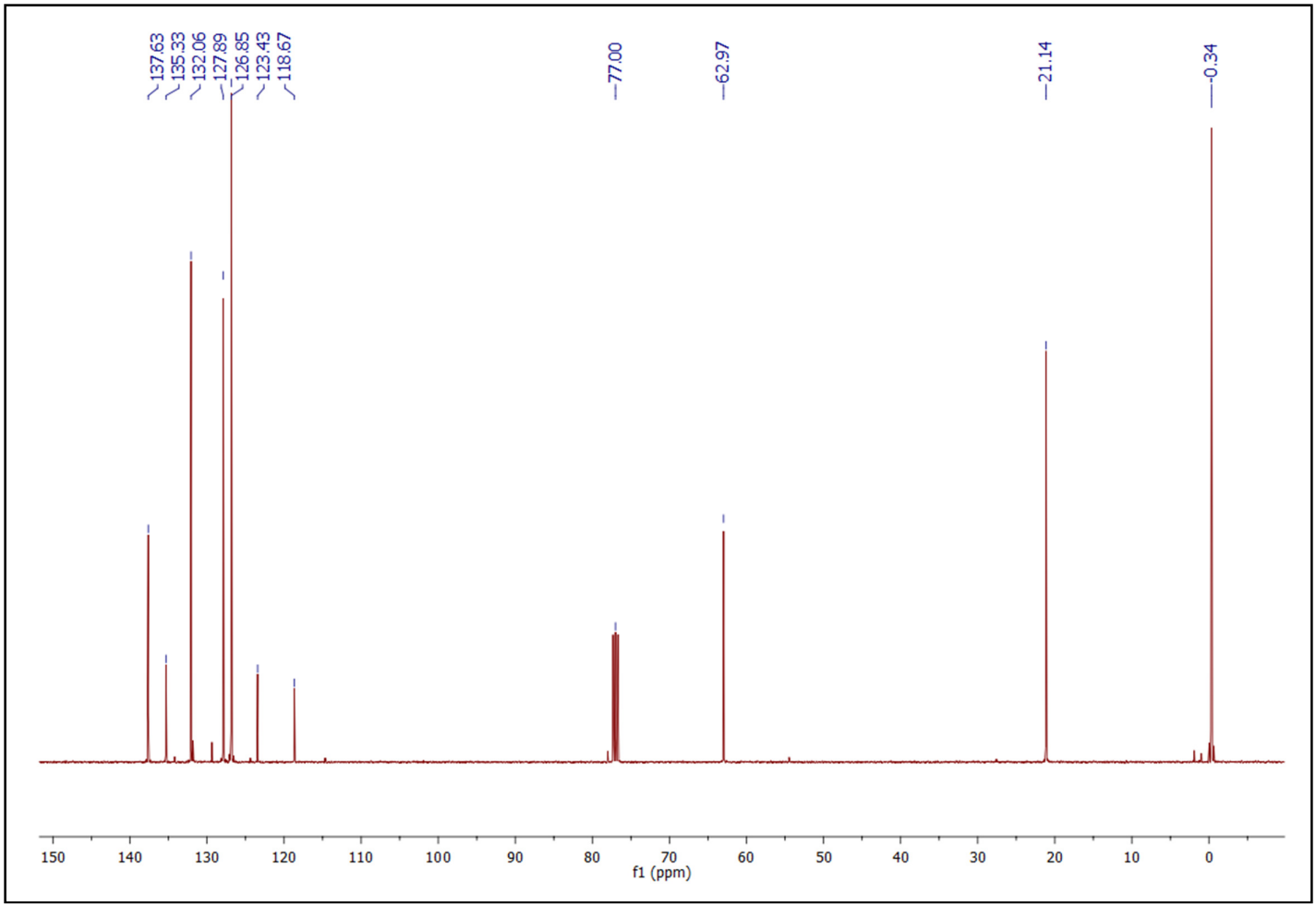


Figure S48. ^{1}H NMR of **5h** (Solvent: $CDCl_3$, IS: Mesitylene).

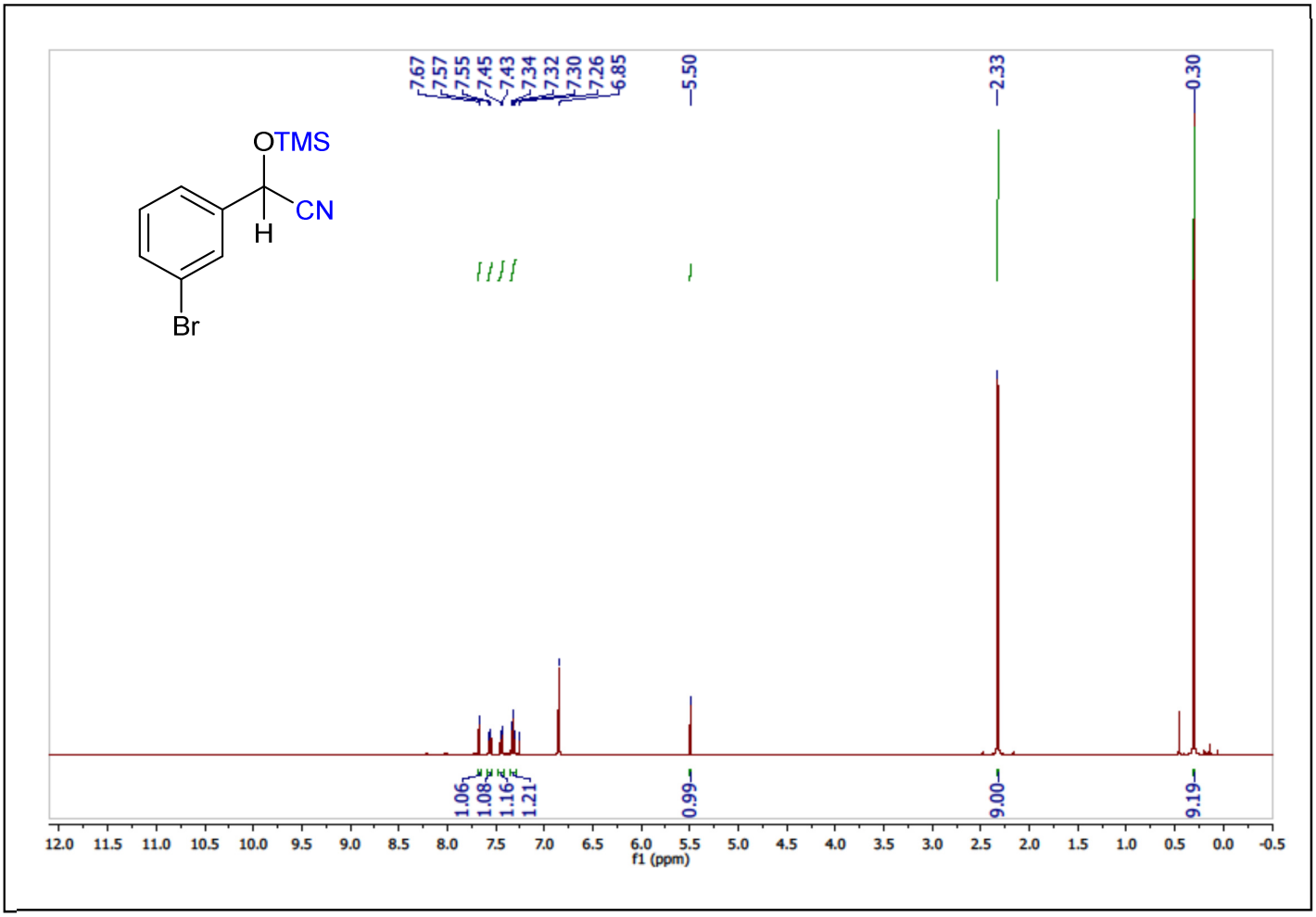


Figure S49. ^{13}C NMR of **5h** (Solvent: $CDCl_3$, IS: Mesitylene).

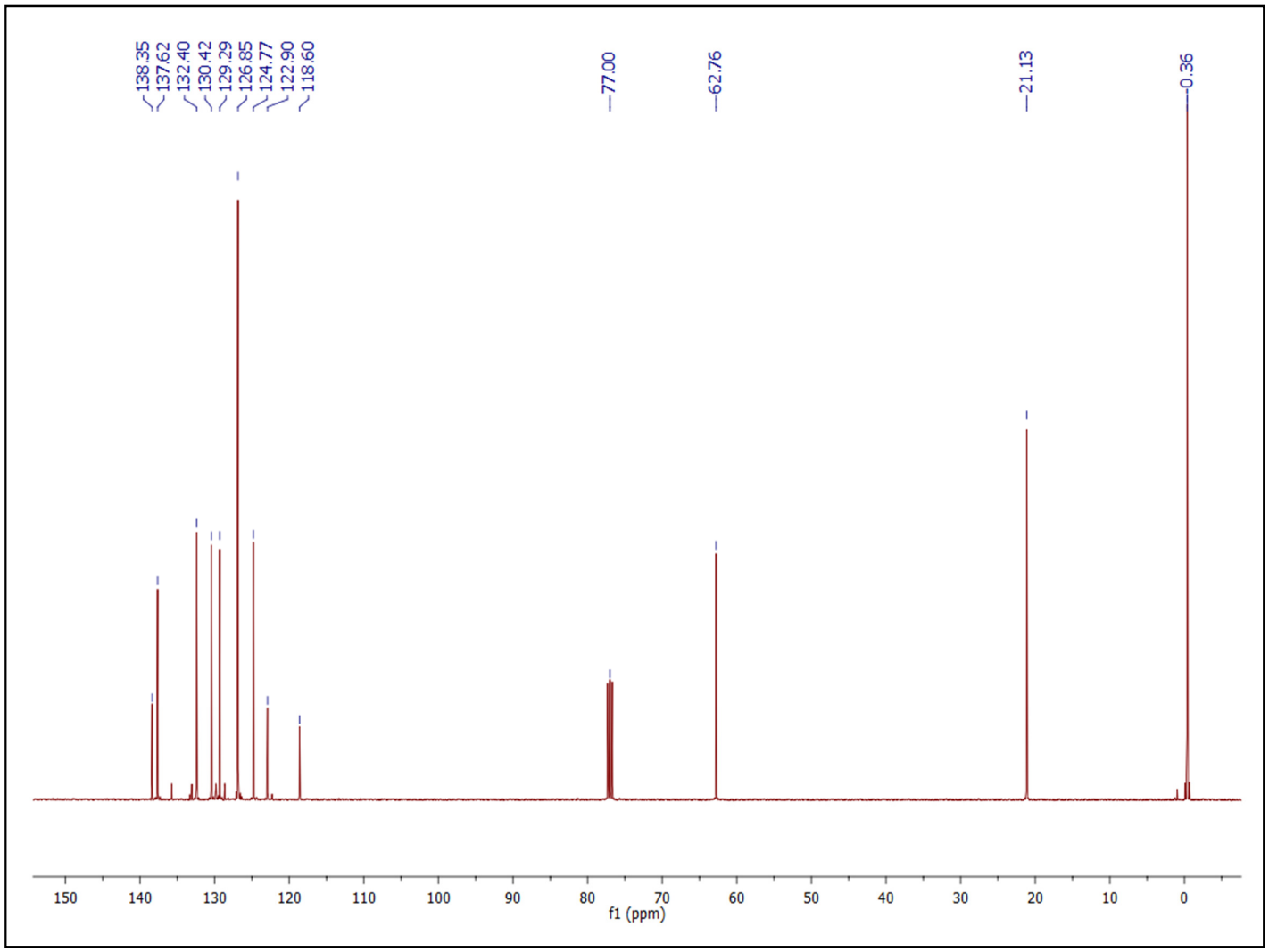


Figure S50. ^{1}H NMR of **5i** (Solvent: $CDCl_3$, IS: Mesitylene).

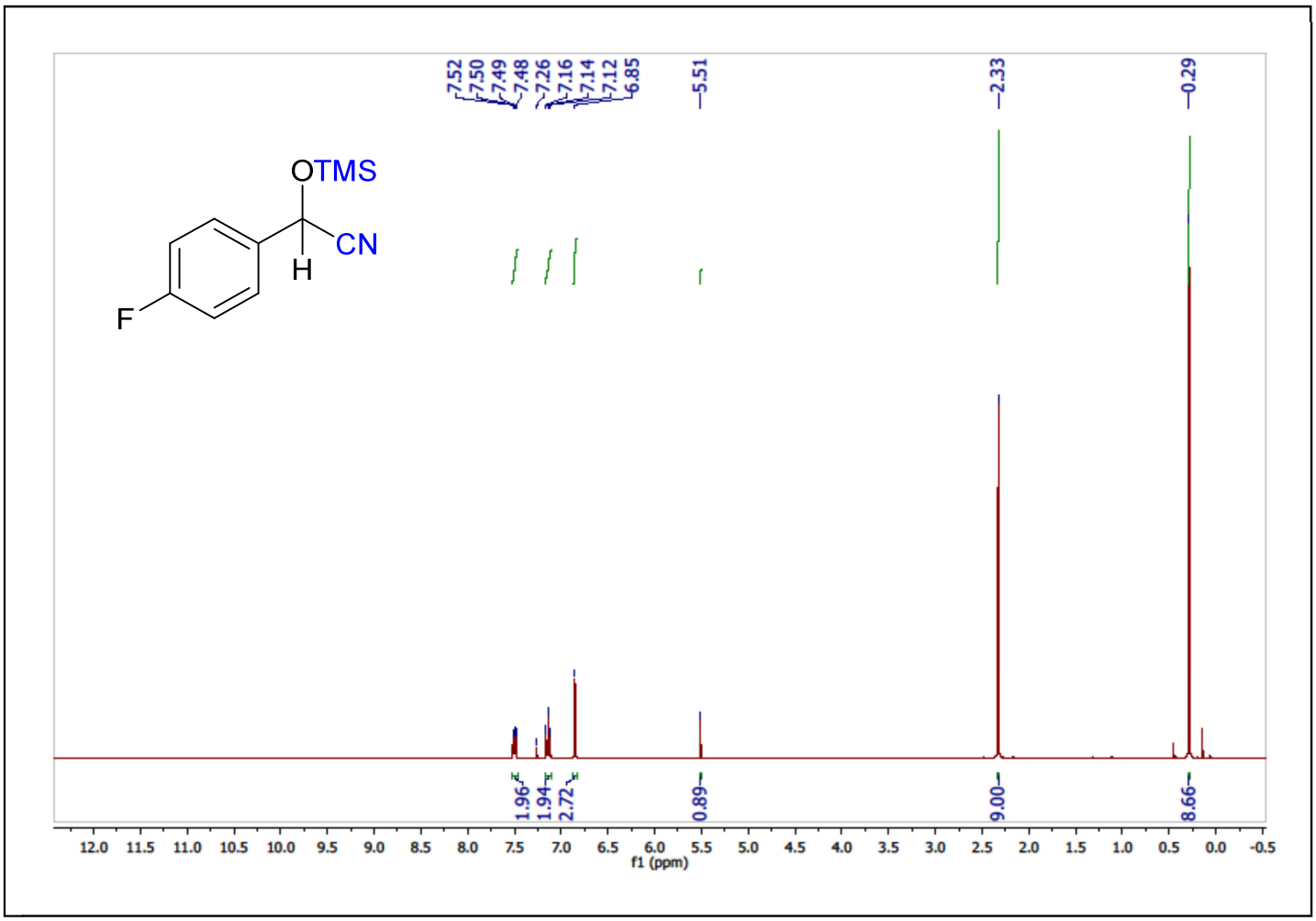


Figure S51. ^{13}C NMR of **5i** (Solvent: $CDCl_3$, IS: Mesitylene).

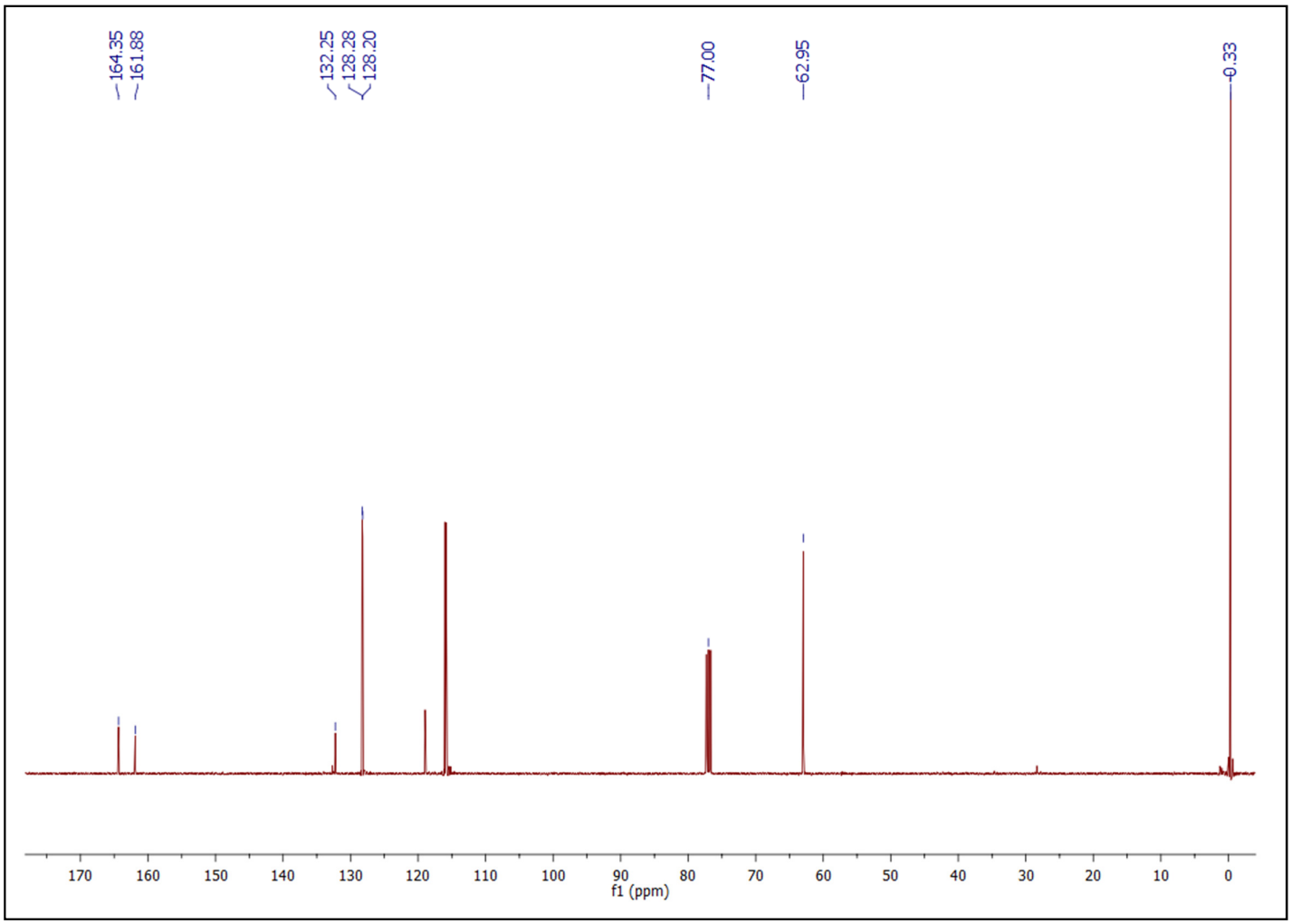


Figure S52. ^{1}H NMR of **5j** (Solvent: $CDCl_3$, IS: Mesitylene).

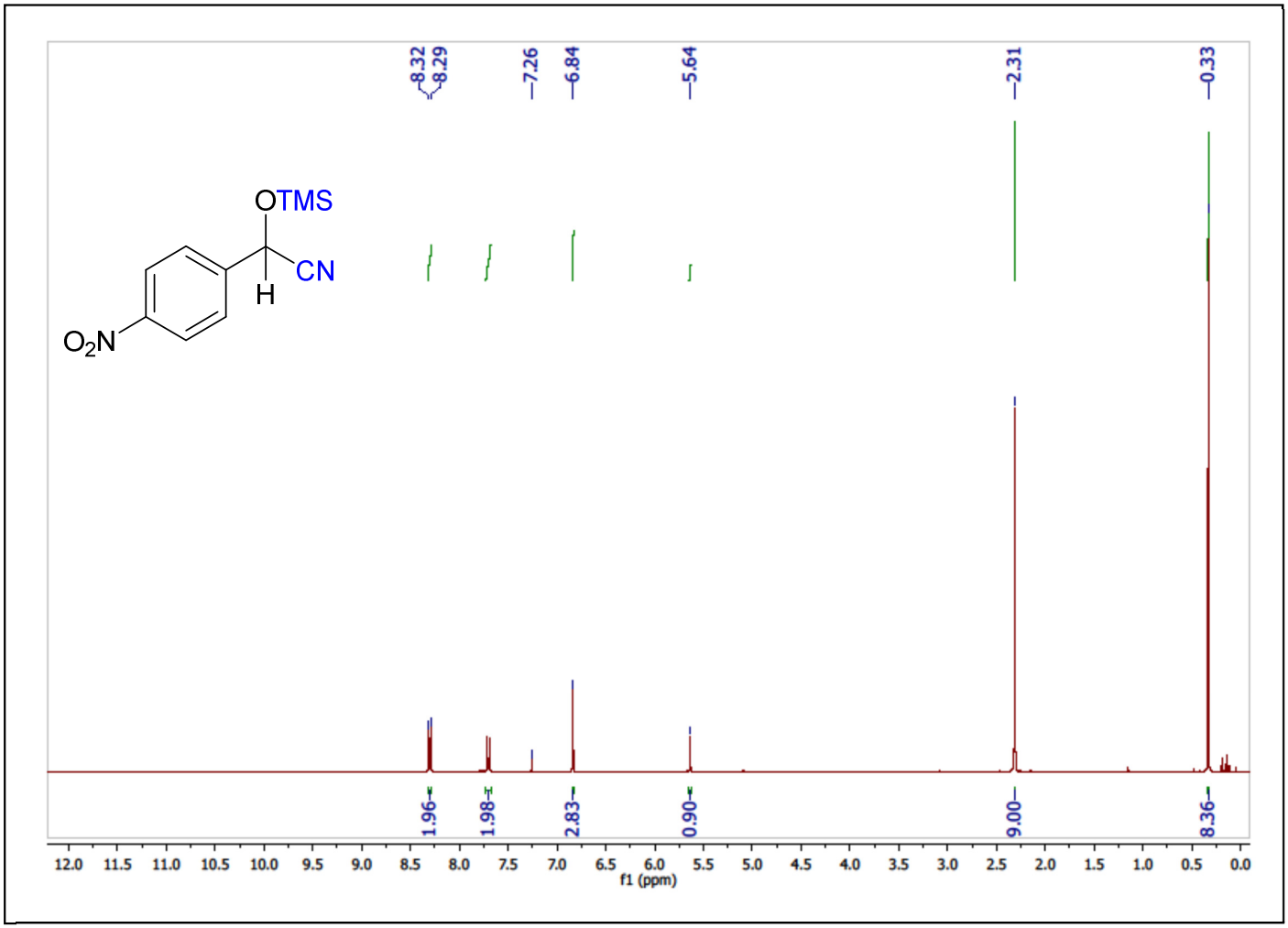


Figure S53. ^{13}C NMR of **5j** (Solvent: $CDCl_3$, IS: Mesitylene).

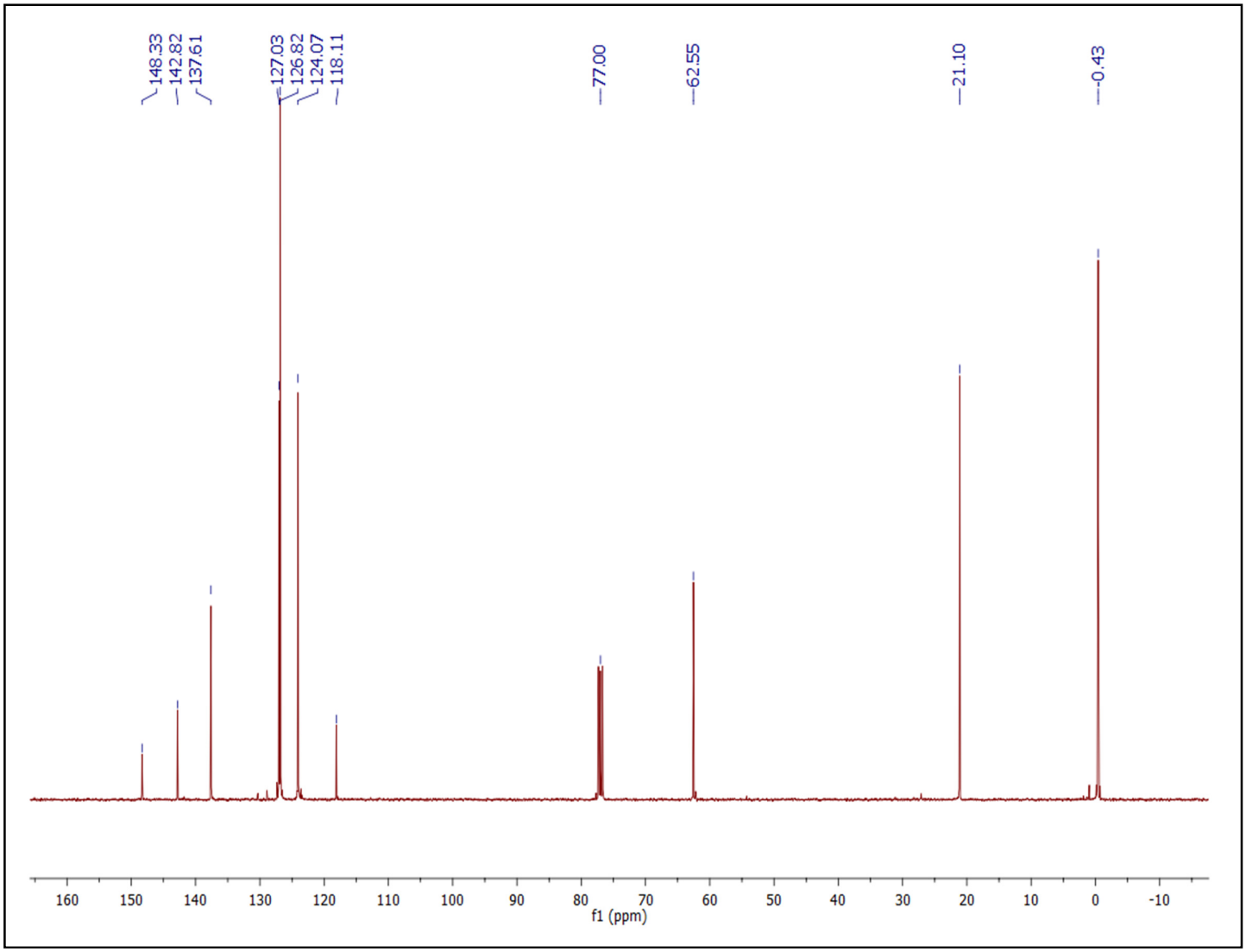


Figure S54. ^{1}H NMR of **5k** (Solvent: $CDCl_3$, IS: Mesitylene).

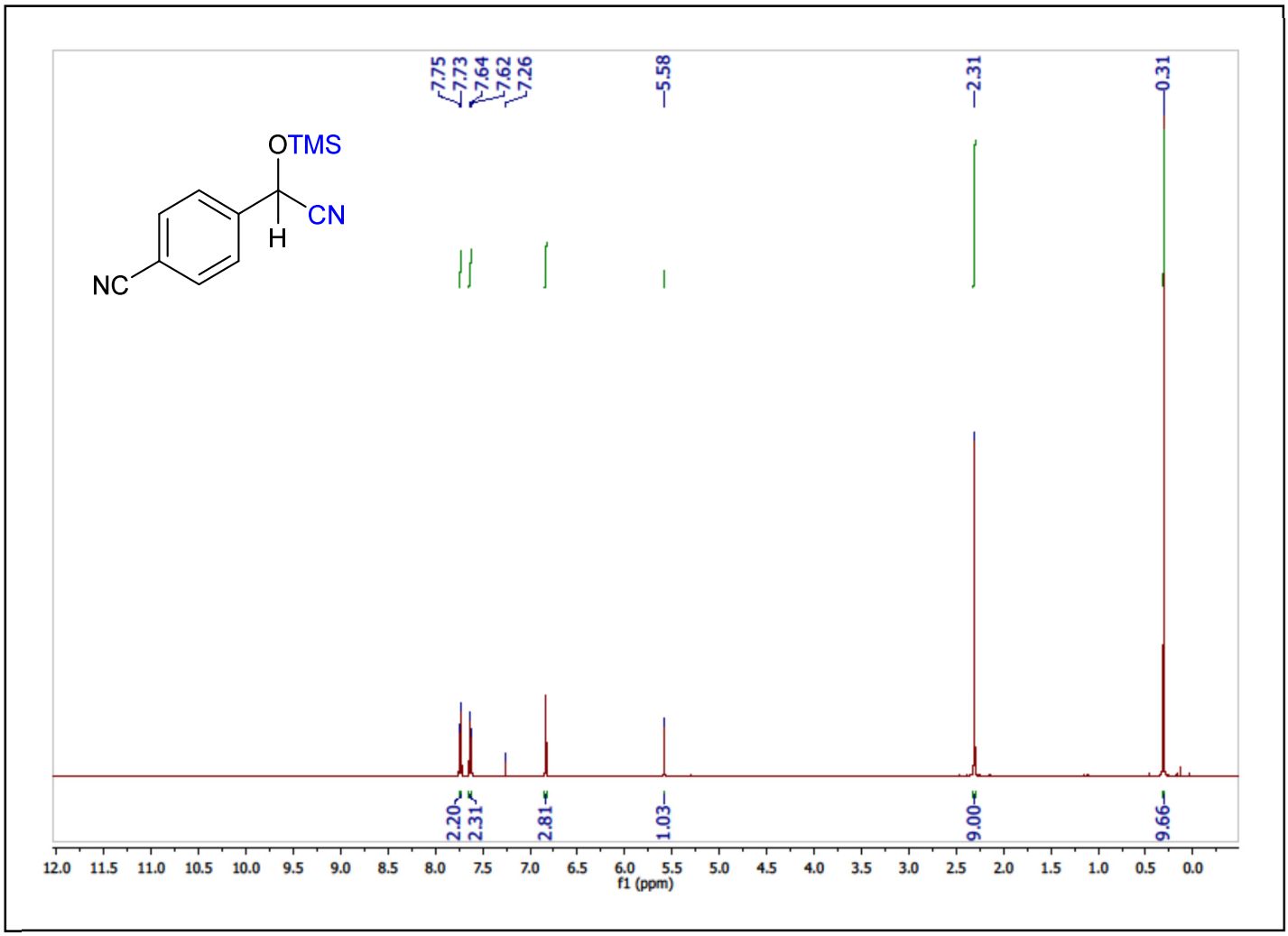


Figure S55. ^{13}C NMR of **5k** (Solvent: $CDCl_3$, IS: Mesitylene).

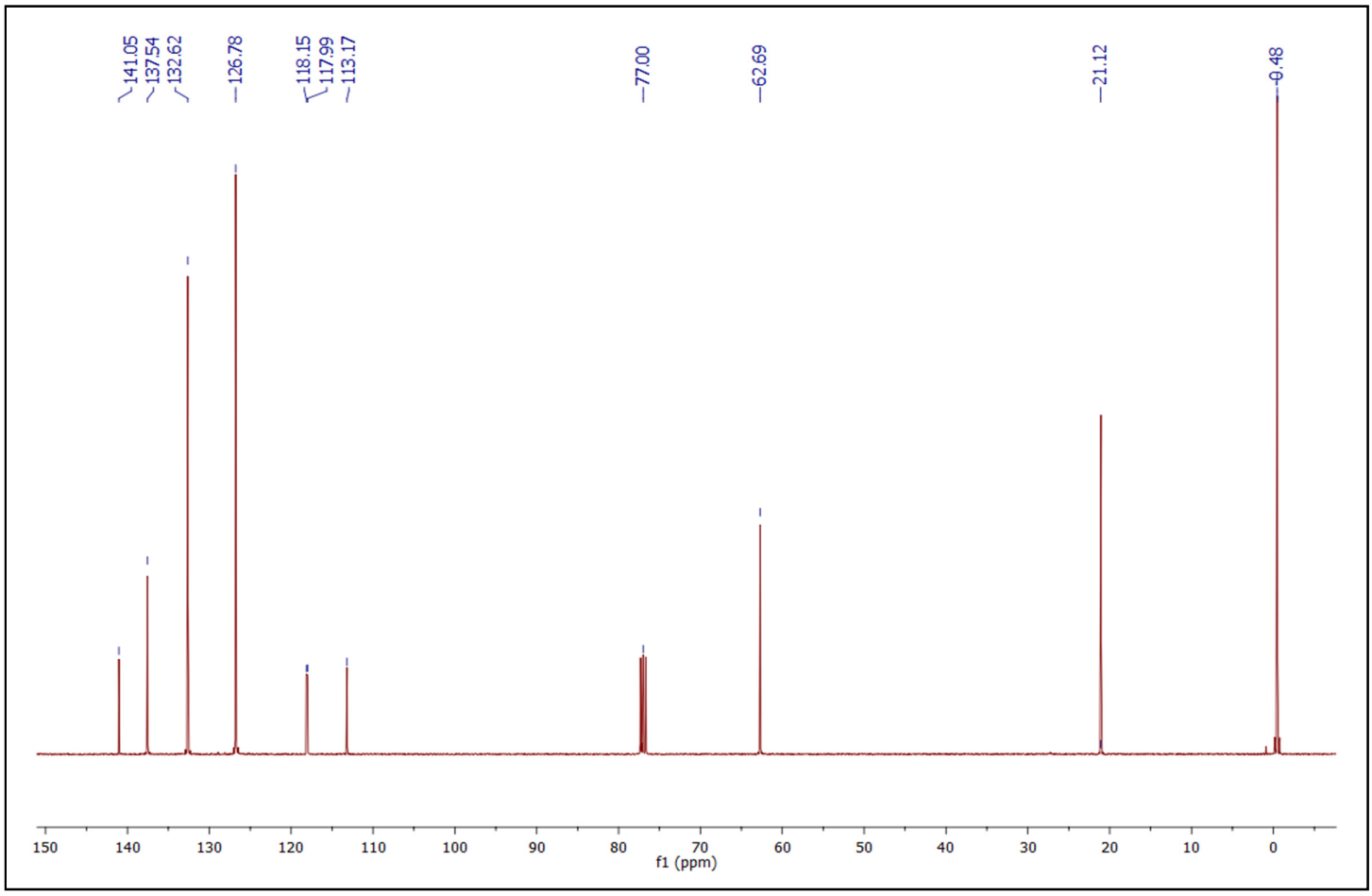


Figure S56. ^{1}H NMR of **5l** (Solvent: $CDCl_3$, IS: Mesitylene).

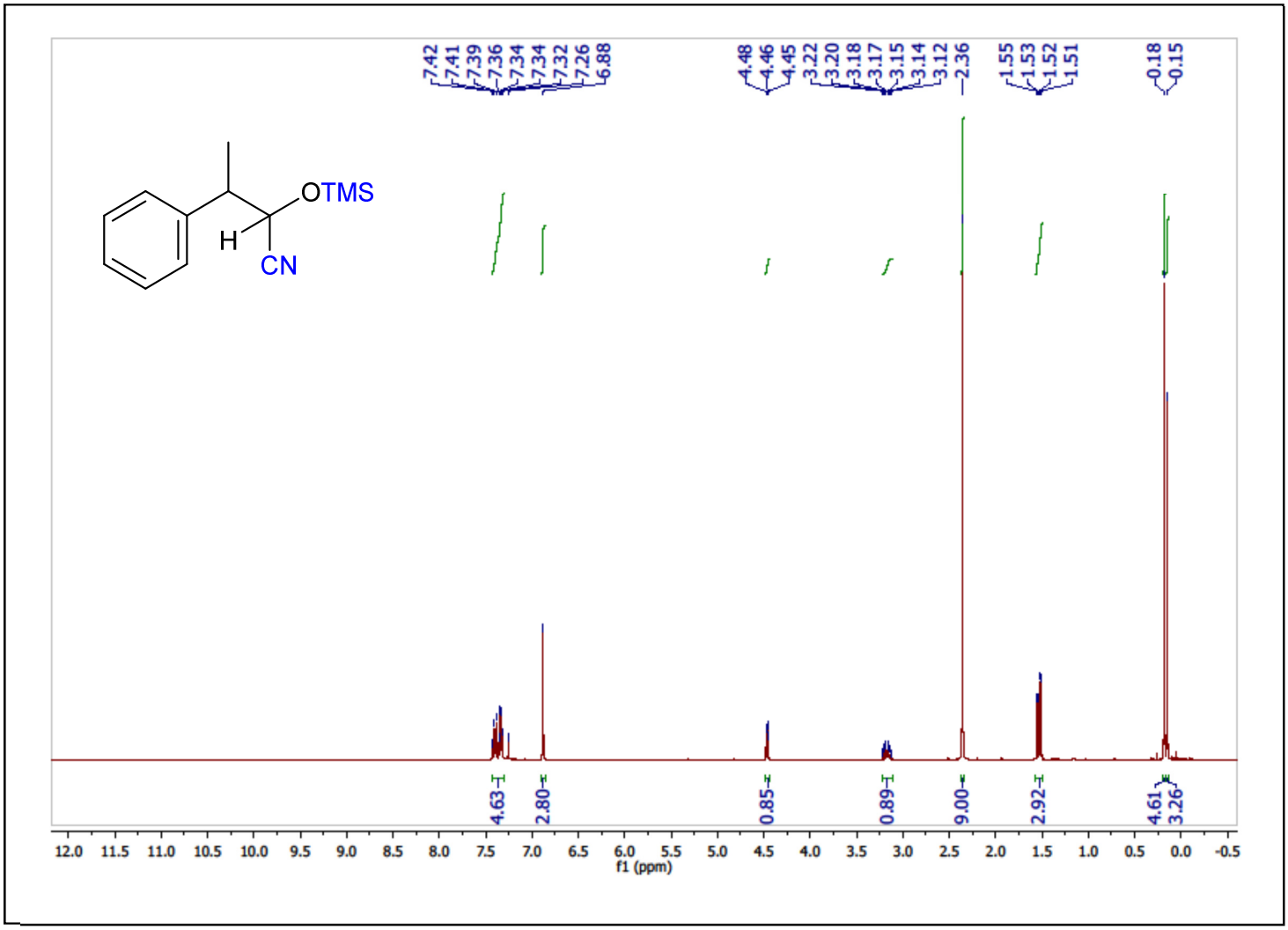


Figure S57. ^{13}C NMR of **5l** (Solvent: $CDCl_3$, IS: Mesitylene).

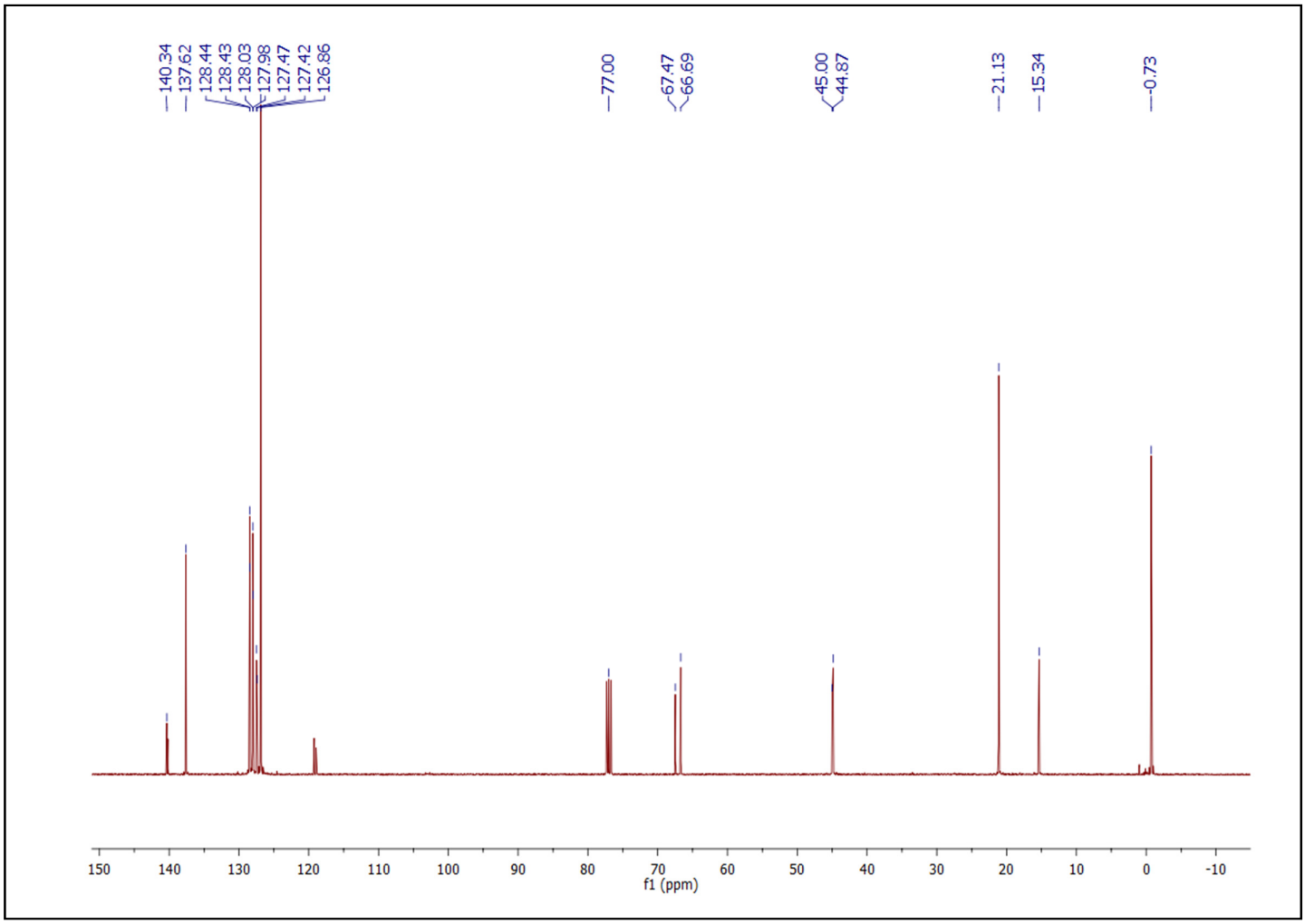


Figure S58. ^{1}H NMR of **5m** (Solvent: $CDCl_3$, IS: Mesitylene).

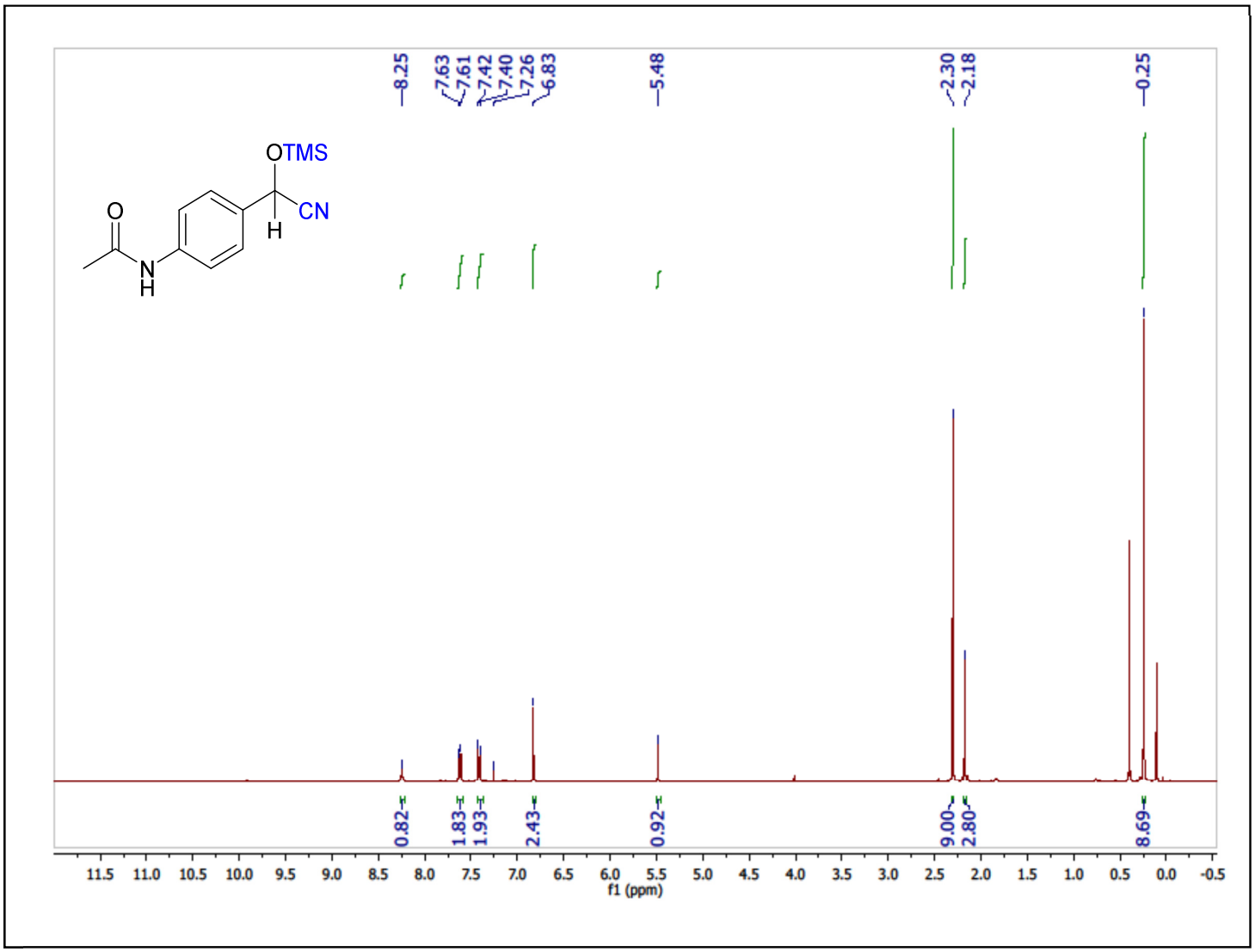


Figure S59. ^{13}C NMR of **5m** (Solvent: $CDCl_3$, IS: Mesitylene).

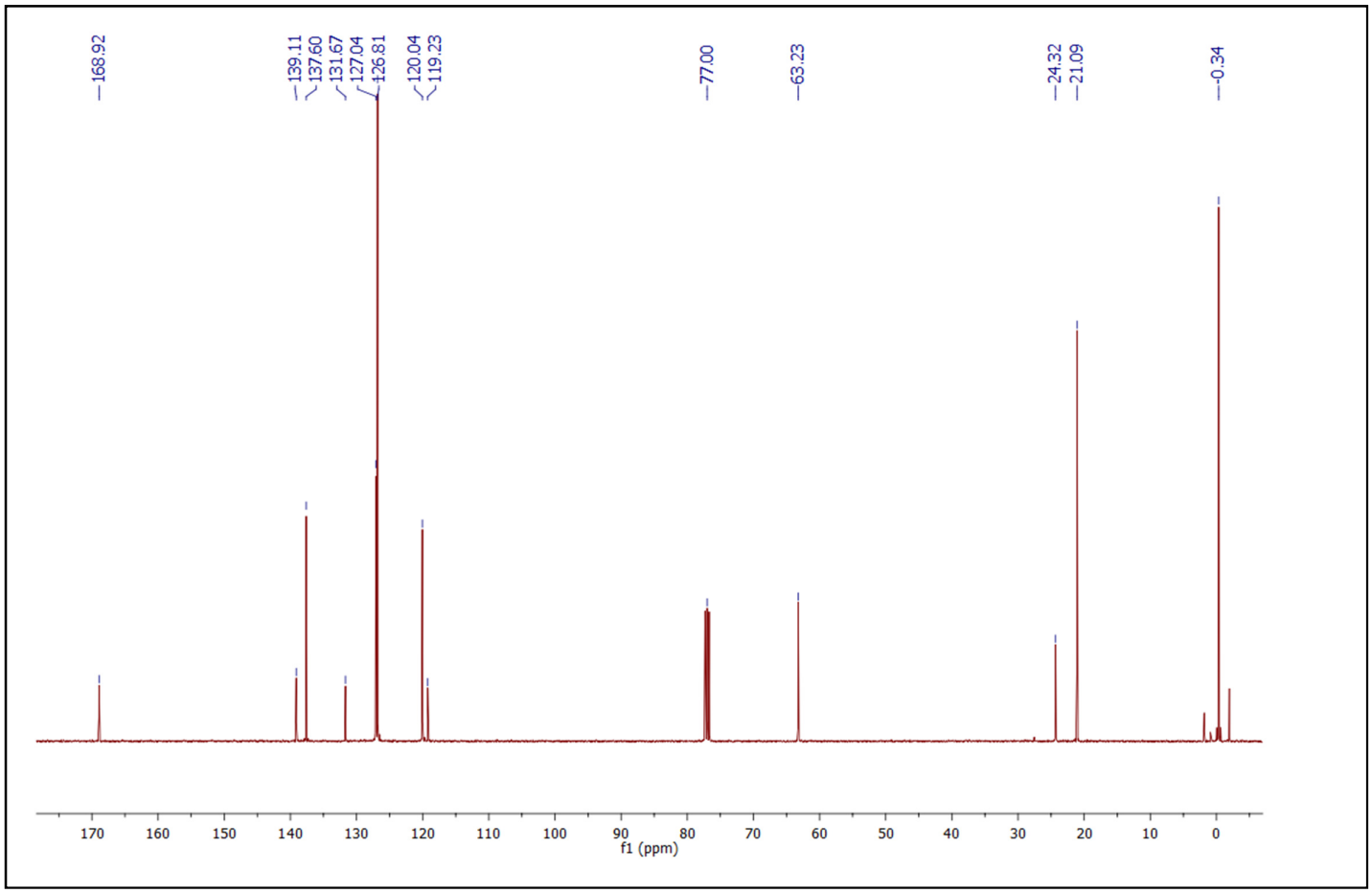


Figure S60. ^{1}H NMR of **5n** (Solvent: $CDCl_3$, IS: Mesitylene).

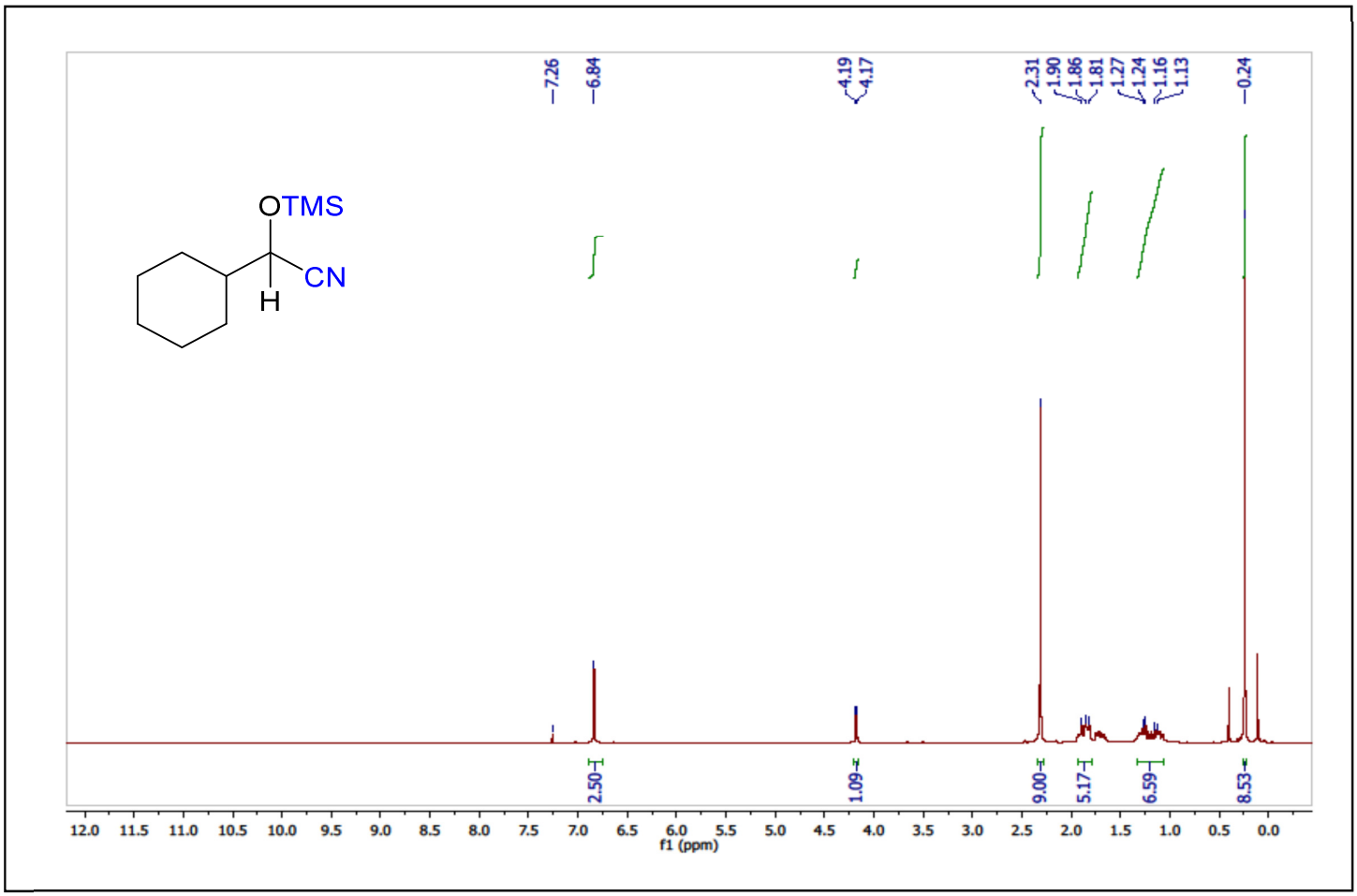


Figure S61. ^{13}C NMR of **5n** (Solvent: $CDCl_3$, IS: Mesitylene).

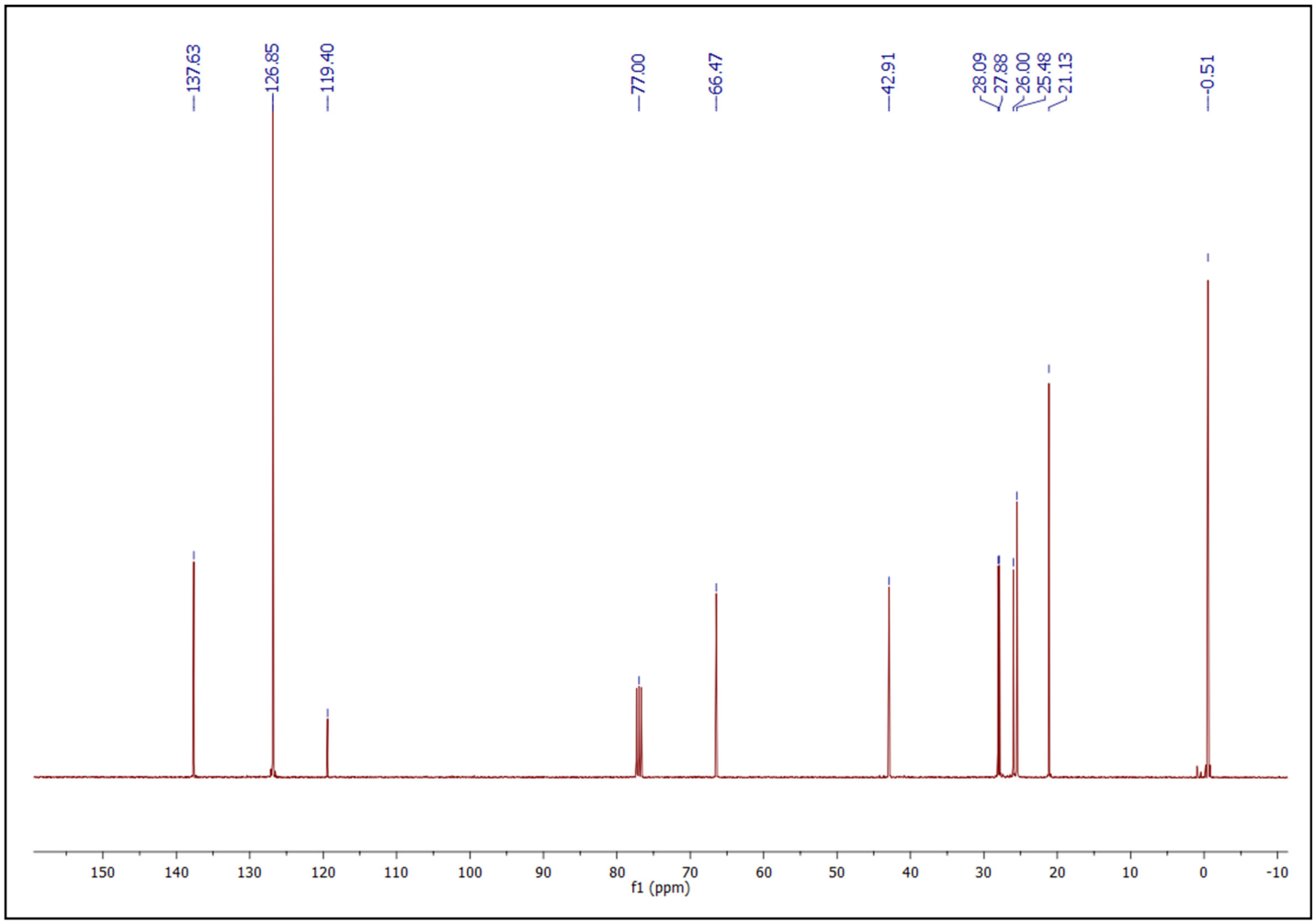


Figure S62. ^{1}H NMR of **5o** (Solvent: $CDCl_3$, IS: Mesitylene).

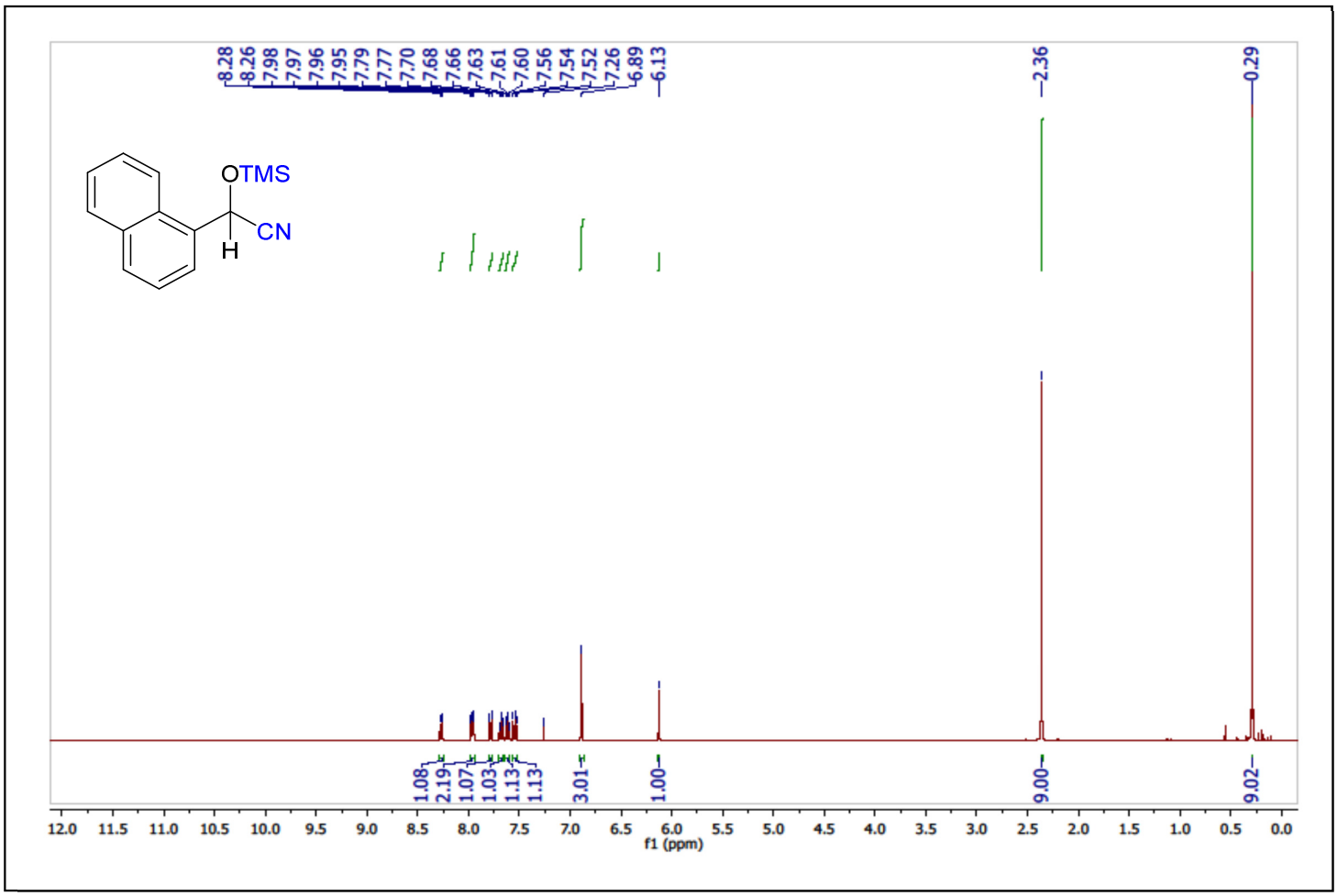


Figure S63. ^{13}C NMR of **5o** (Solvent: $CDCl_3$, IS: Mesitylene).

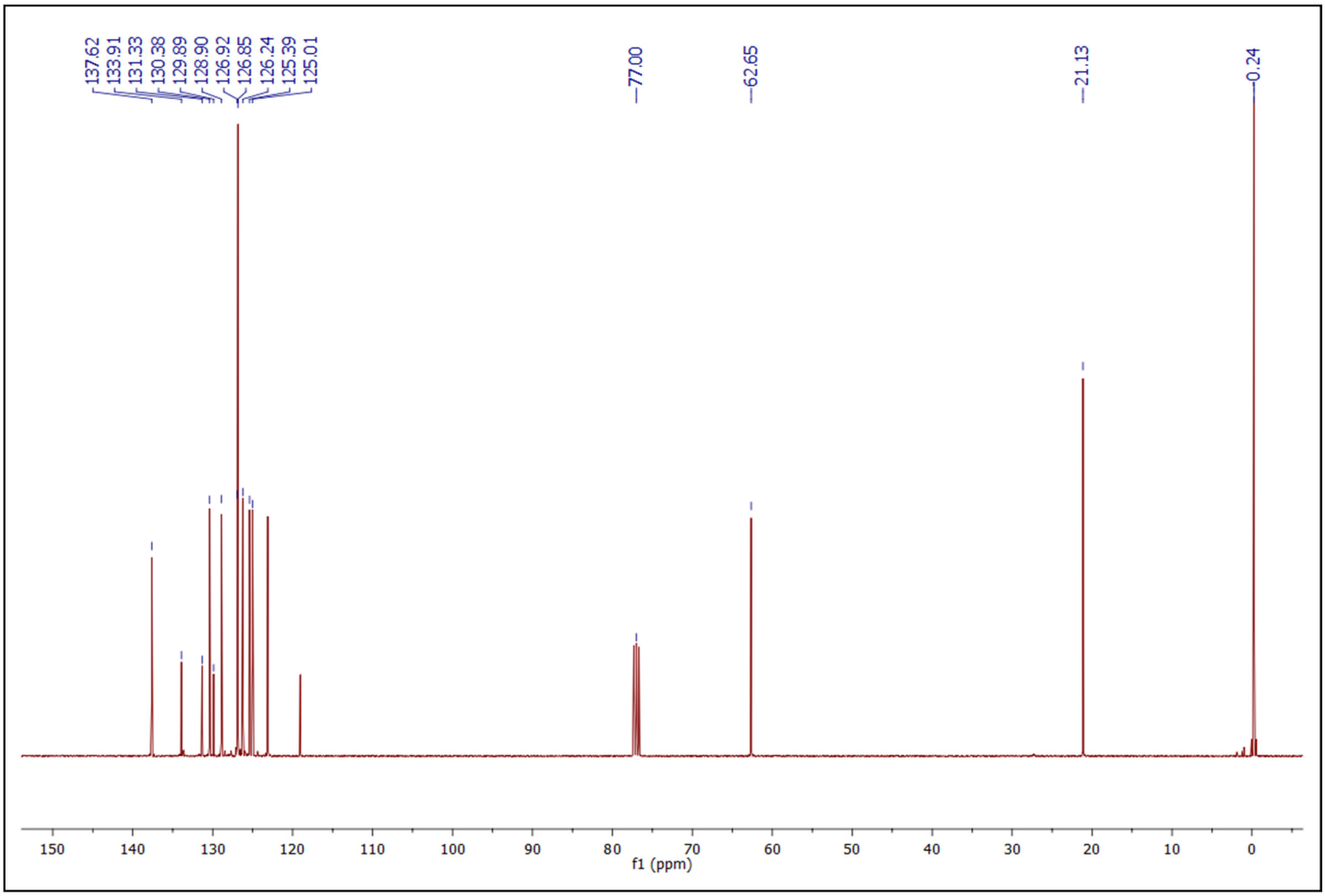


Figure S64. ^{1}H NMR of **6a** (Solvent: $CDCl_3$, IS: Mesitylene).

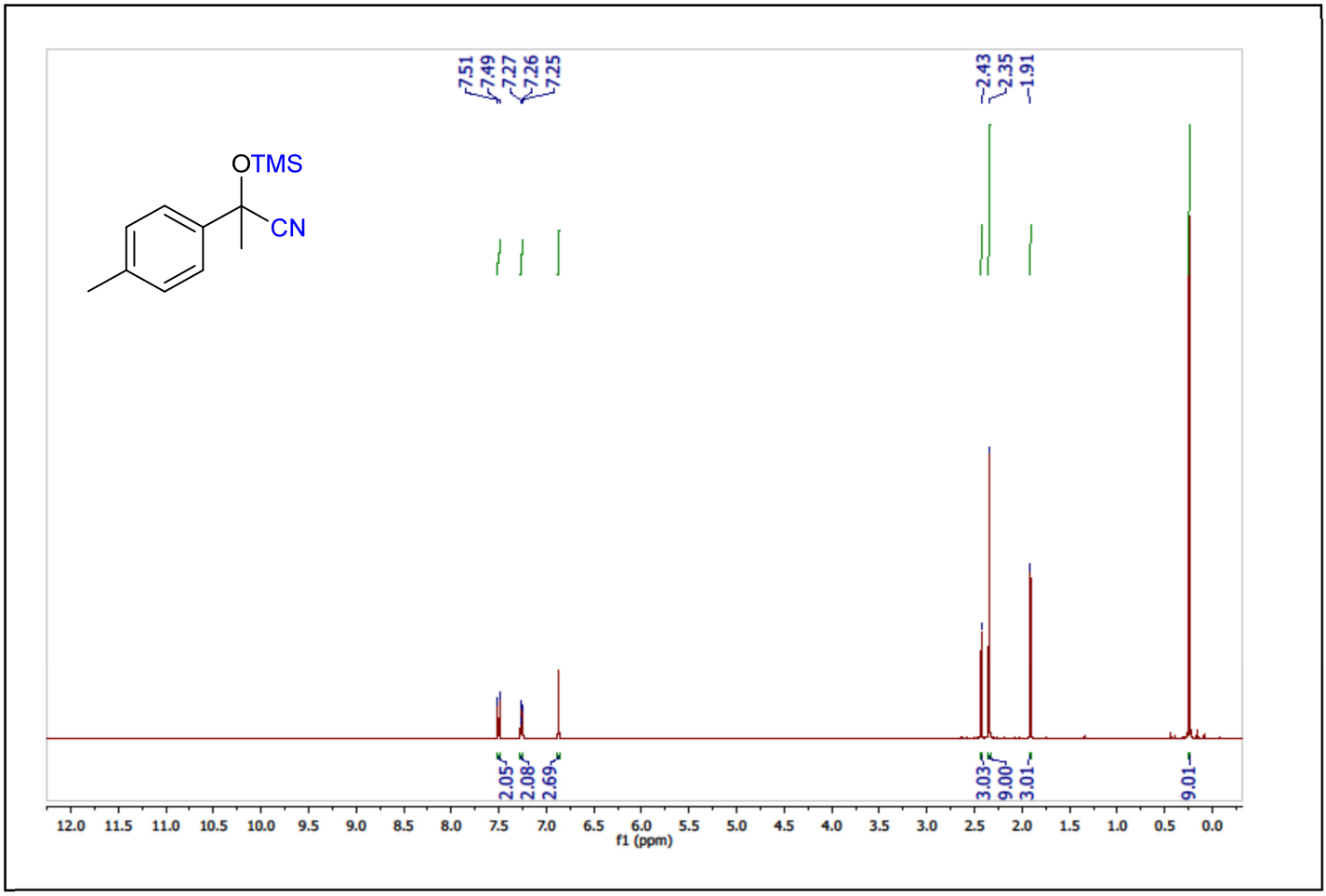


Figure S65. ^{13}C NMR of **6a** (Solvent: $CDCl_3$, IS: Mesitylene).

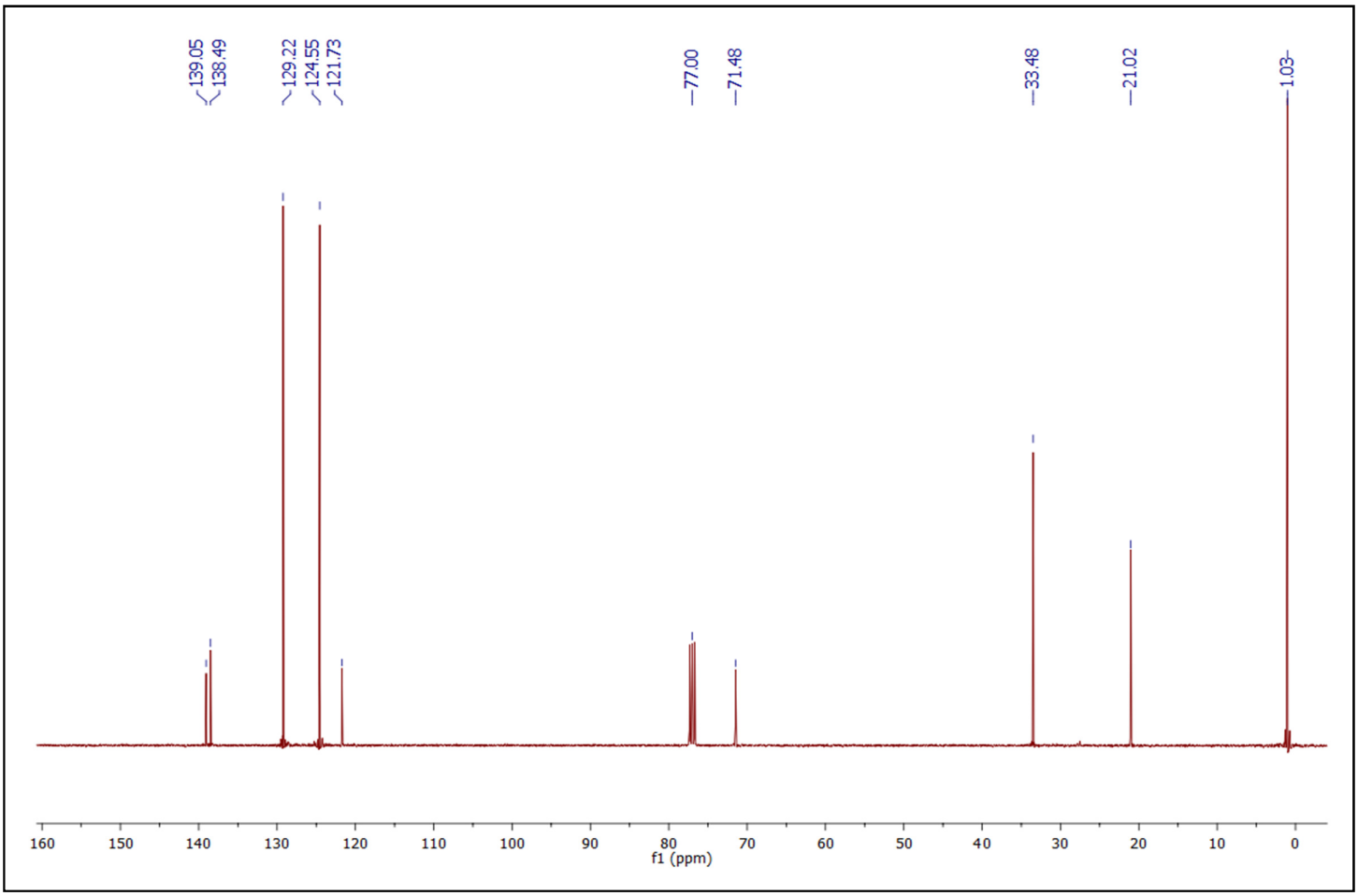


Figure S66. ^{1}H NMR of **6b** (Solvent: $CDCl_3$, IS: Mesitylene).

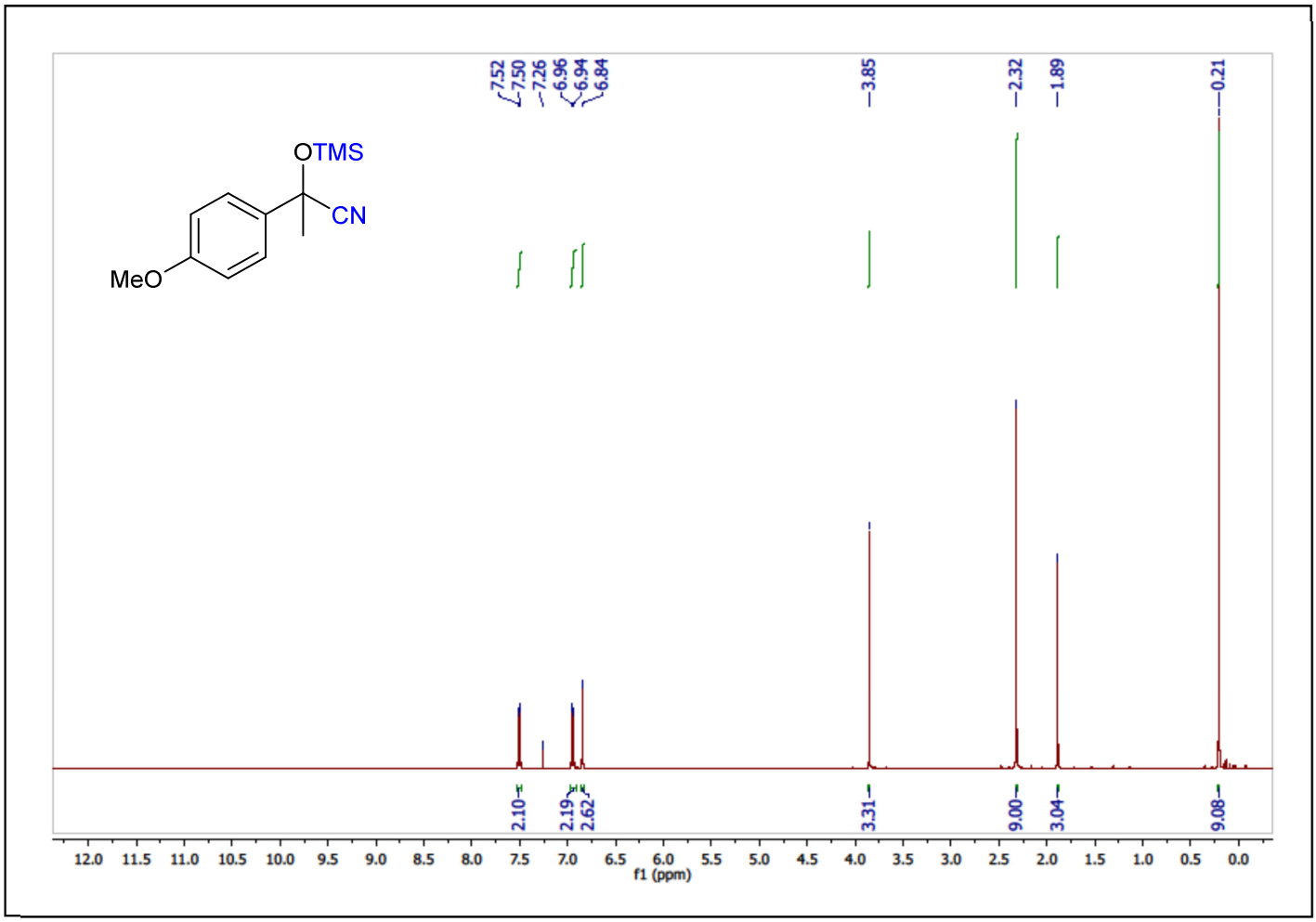


Figure S67. ^{13}C NMR of **6b** (Solvent: $CDCl_3$, IS: Mesitylene).

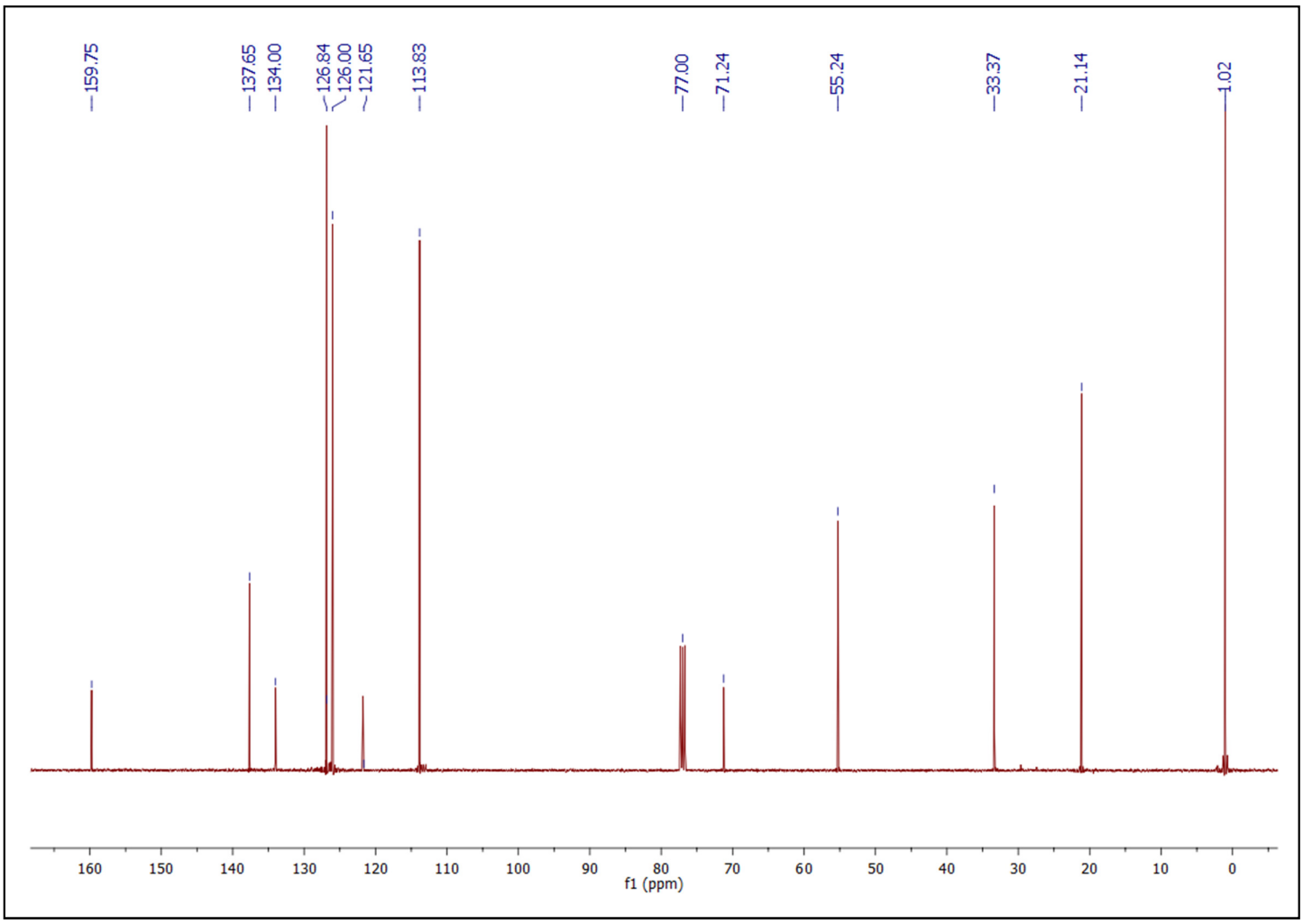


Figure S68. ^{1}H NMR of **6c** (Solvent: $CDCl_3$, IS: Mesitylene).

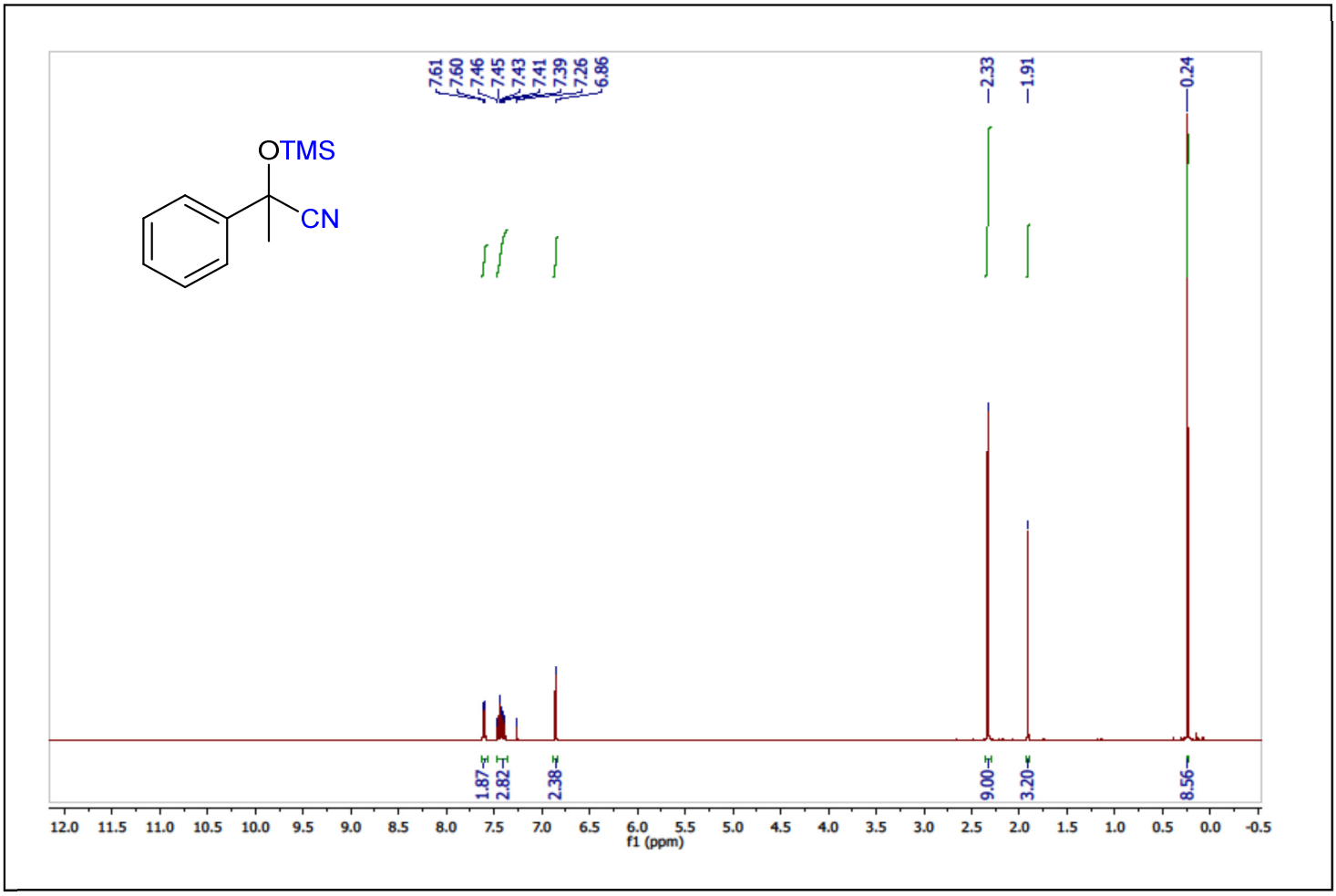


Figure S69. ^{13}C NMR of **6c** (Solvent: $CDCl_3$, IS: Mesitylene).

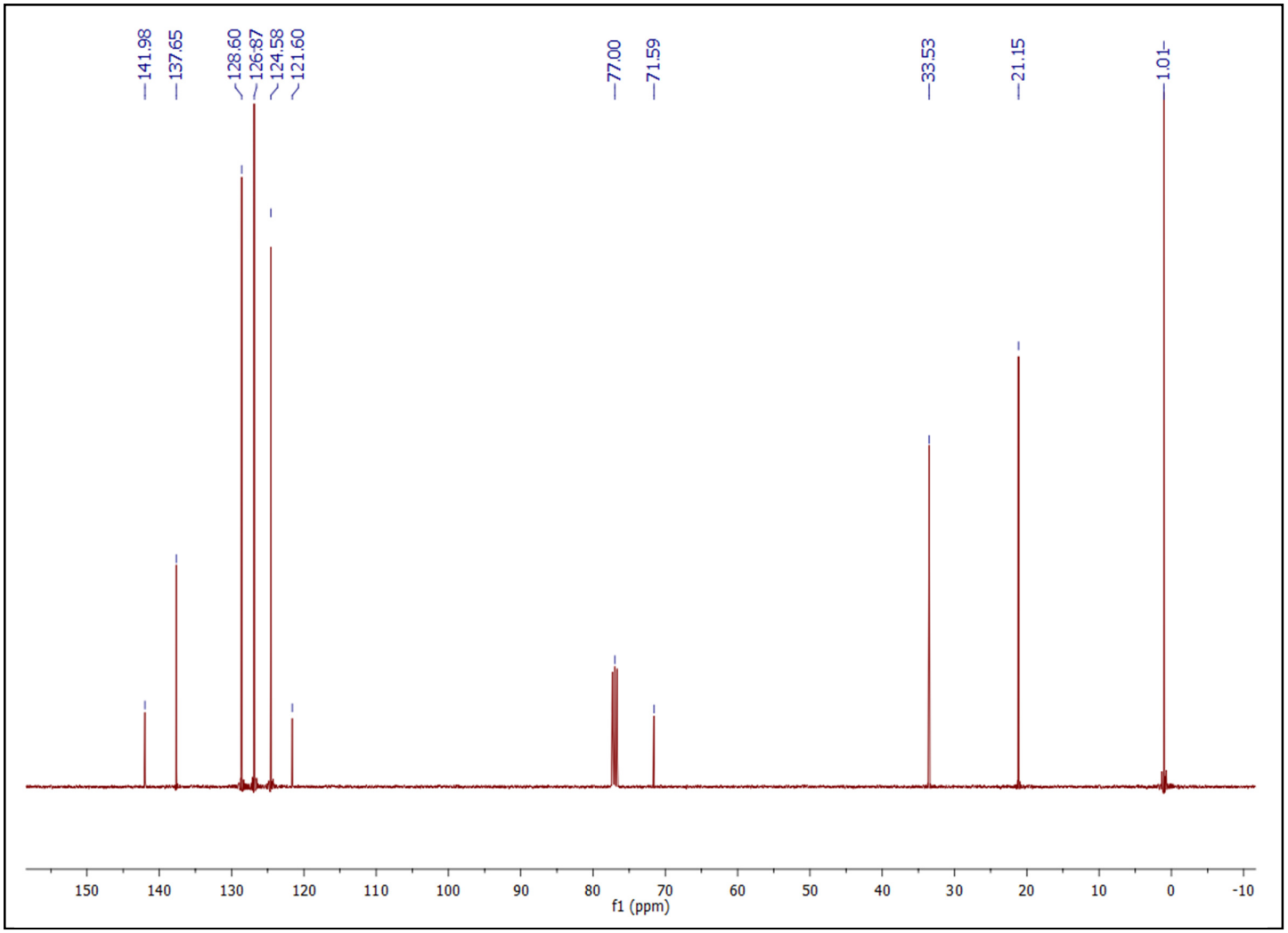


Figure S70. ^{1}H NMR of **6d** (Solvent: $CDCl_3$, IS: Mesitylene).

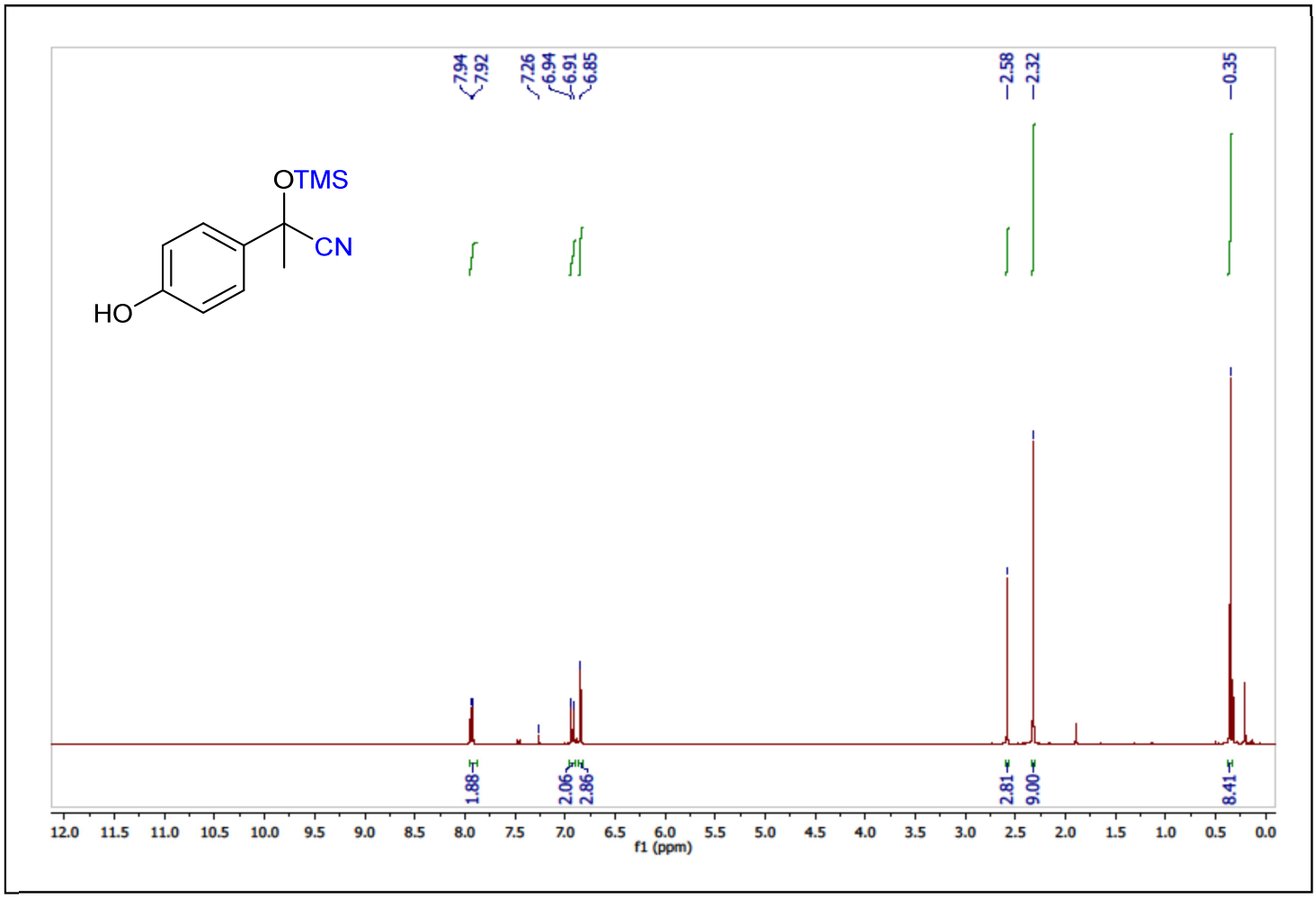


Figure S71. ^{13}C NMR of **6d** (Solvent: $CDCl_3$, IS: Mesitylene).

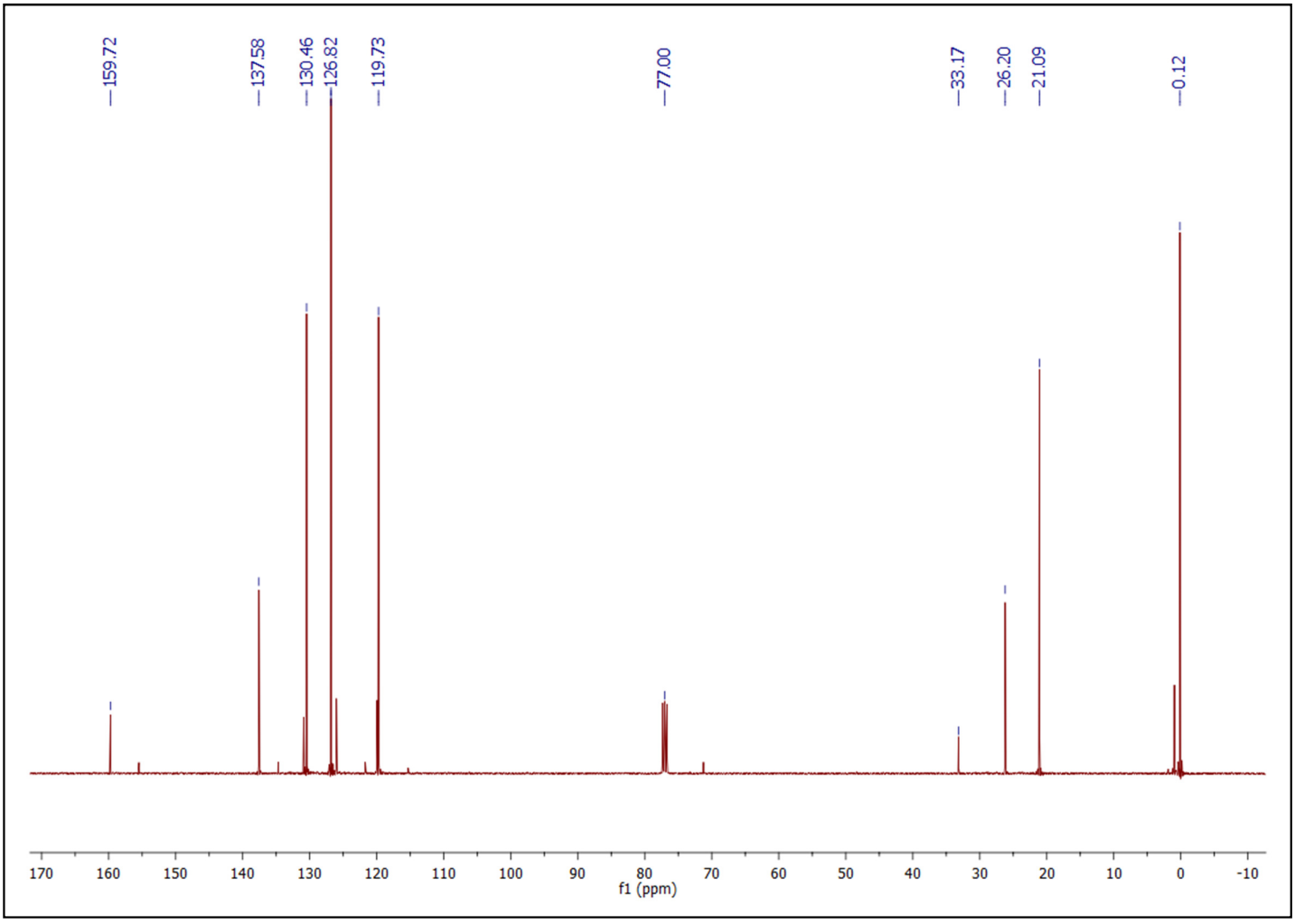


Figure S72. ^{1}H NMR of **6e** (Solvent: $CDCl_3$, IS: Mesitylene).

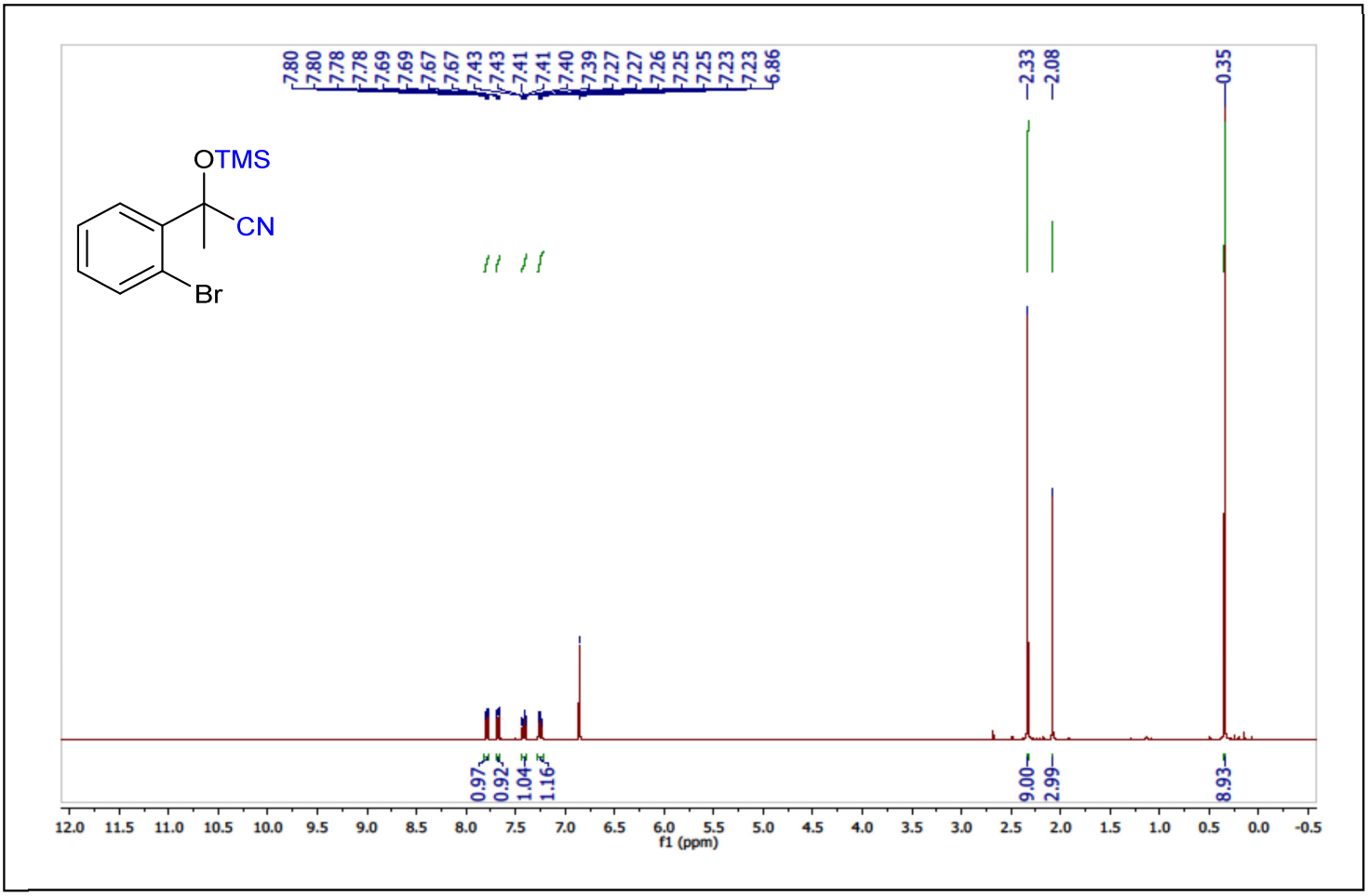


Figure S73. ^{13}C NMR of **6e** (Solvent: $CDCl_3$, IS: Mesitylene).

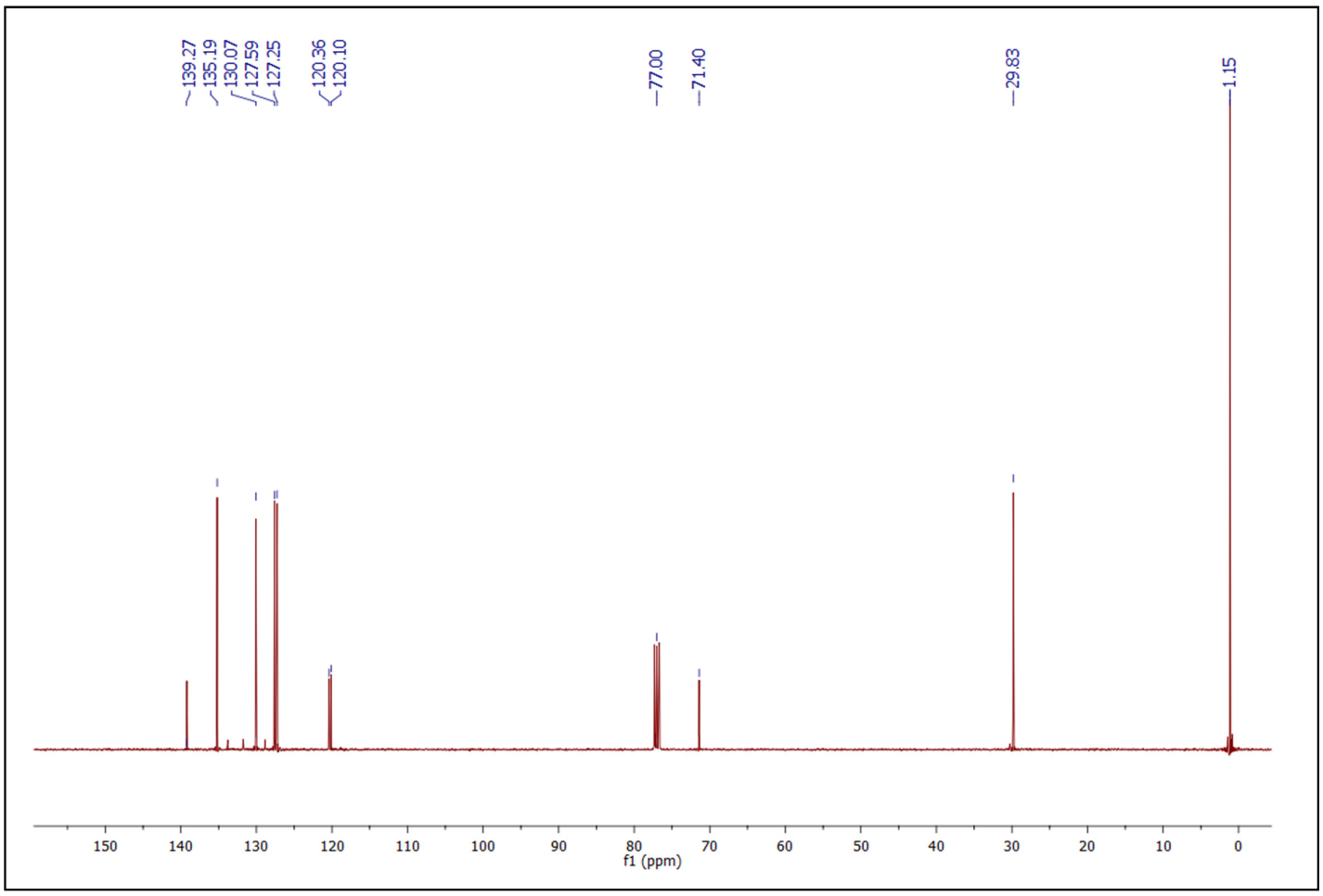


Figure S74. ^{1}H NMR of **6f** (Solvent: $CDCl_3$, IS: Mesitylene).

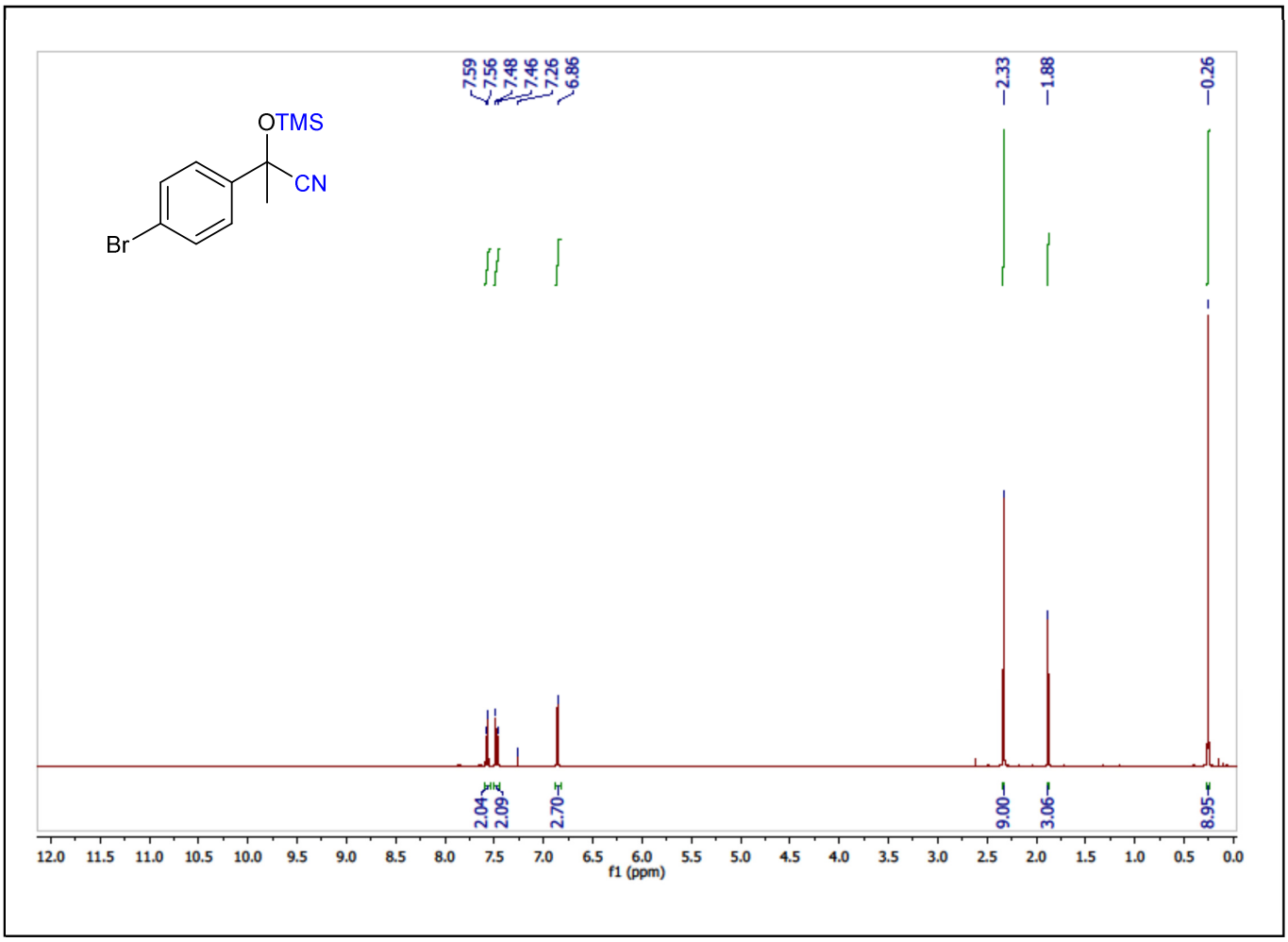


Figure S75. ^{13}C NMR of **6f** (Solvent: $CDCl_3$, IS: Mesitylene).

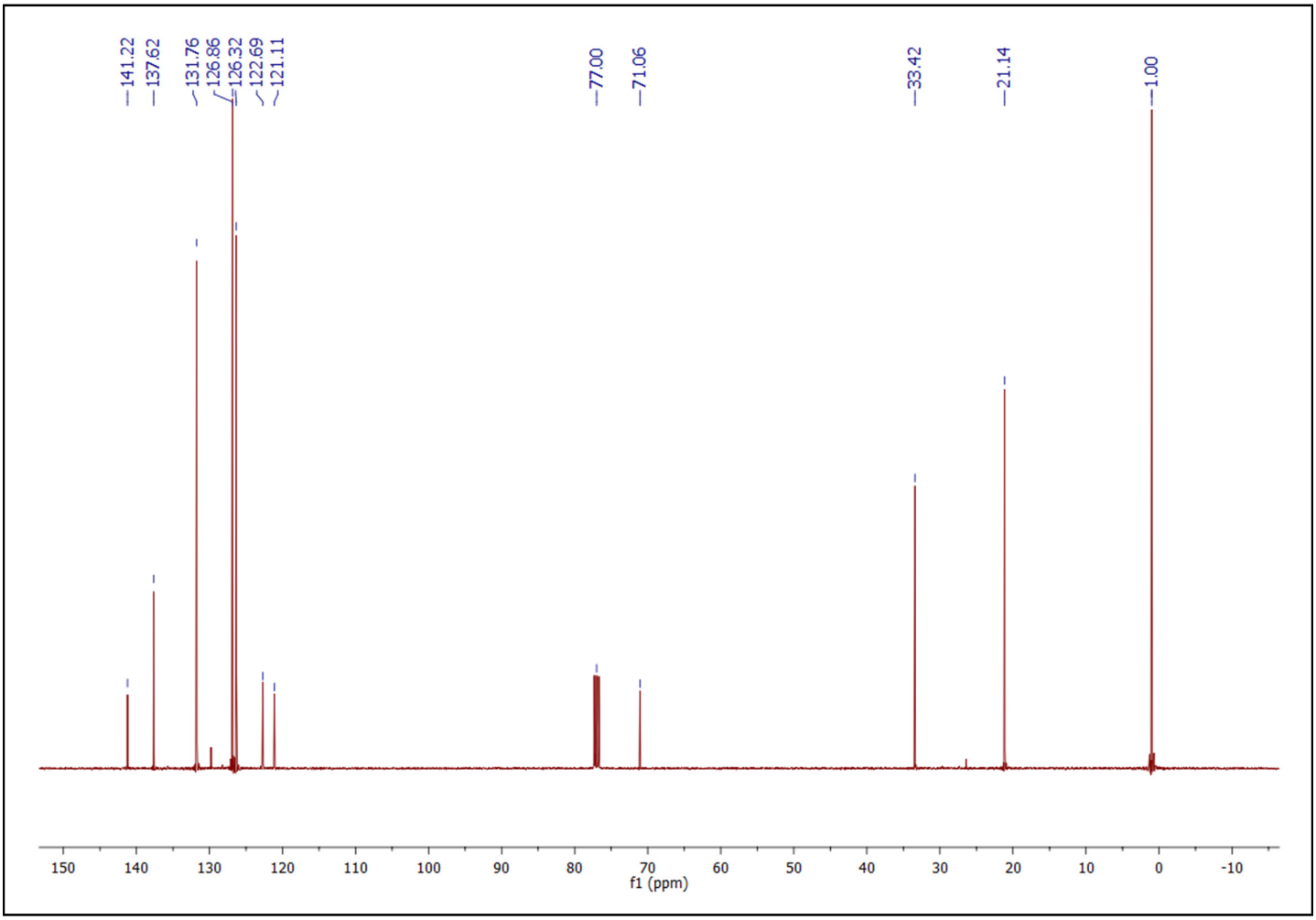


Figure S76. ^{1}H NMR of **6g** (Solvent: $CDCl_3$, IS: Mesitylene).

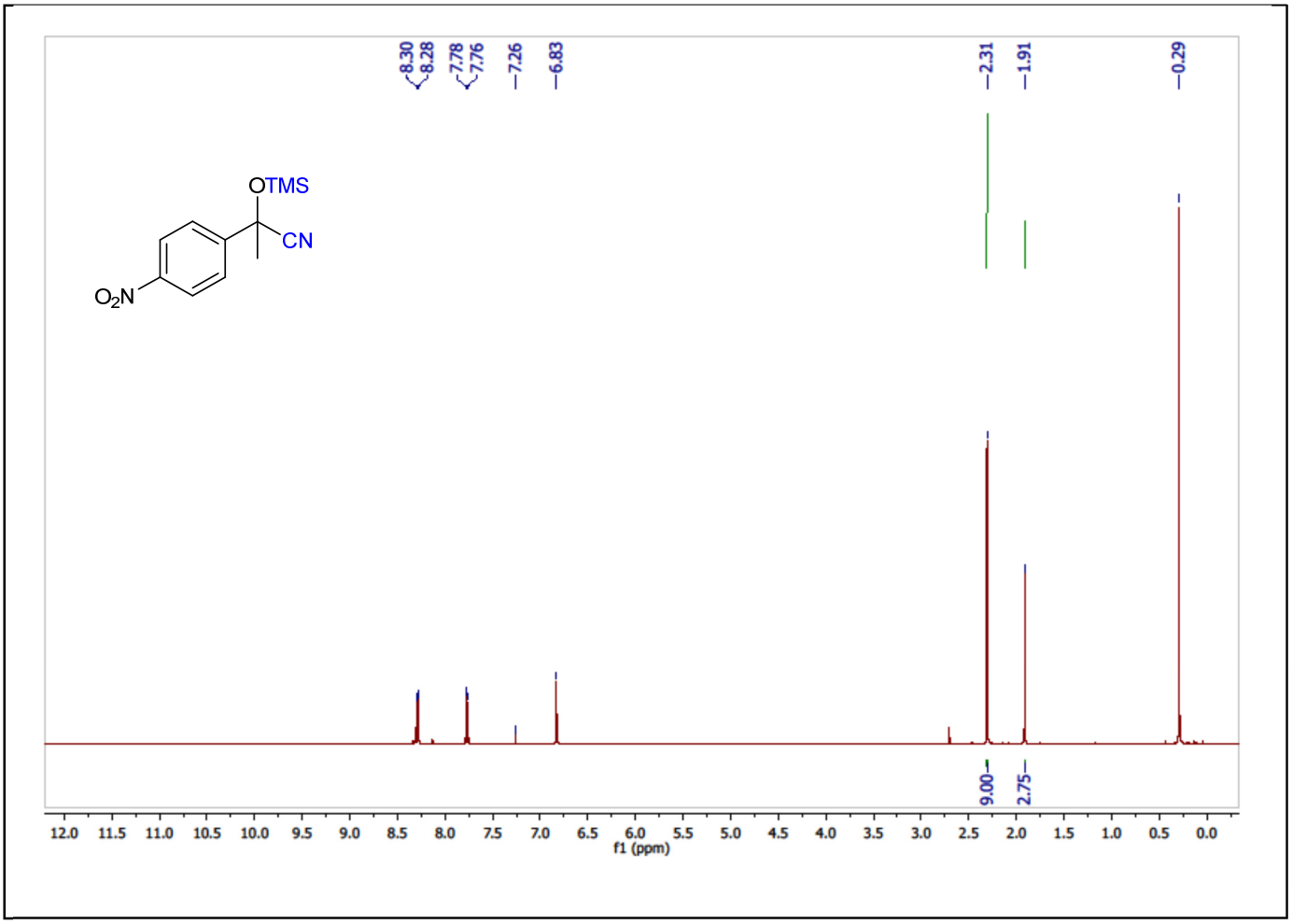


Figure S77. ^{13}C NMR of **6g** (Solvent: $CDCl_3$, IS: Mesitylene).

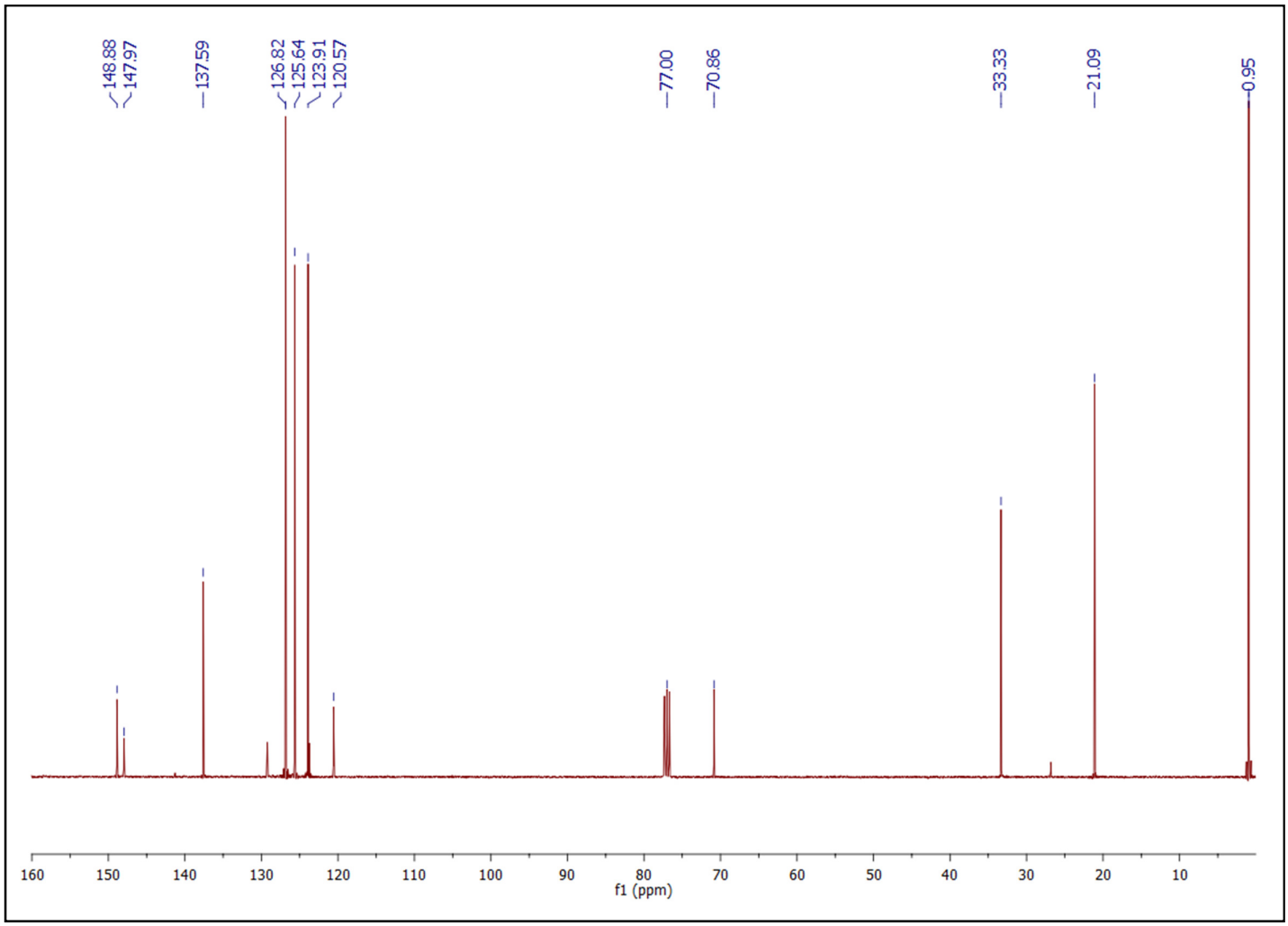


Figure S78. ^{1}H NMR of **6h** (Solvent: $CDCl_3$, IS: Mesitylene).

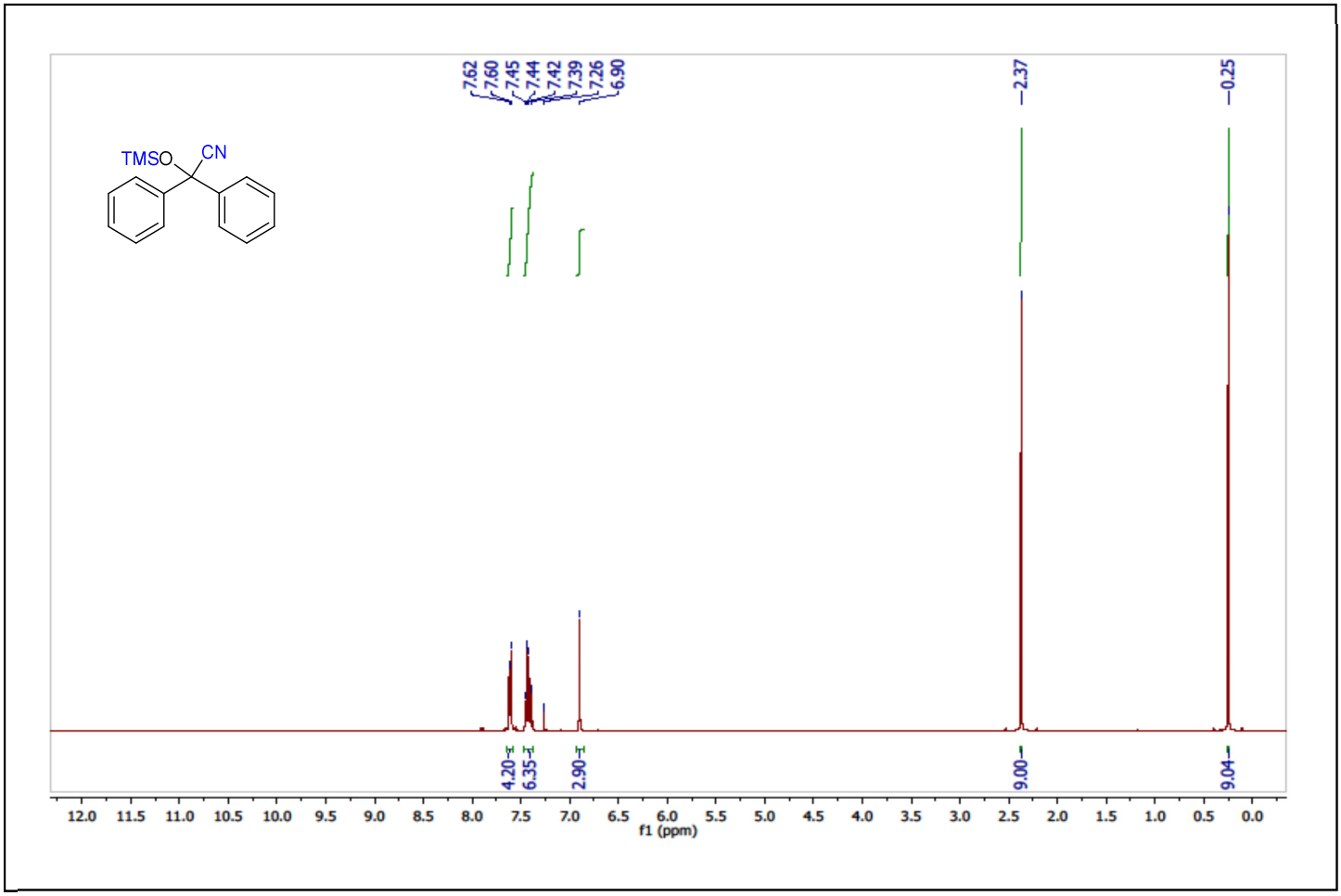


Figure S79. ^{13}C NMR of **6h** (Solvent: $CDCl_3$, IS: Mesitylene).

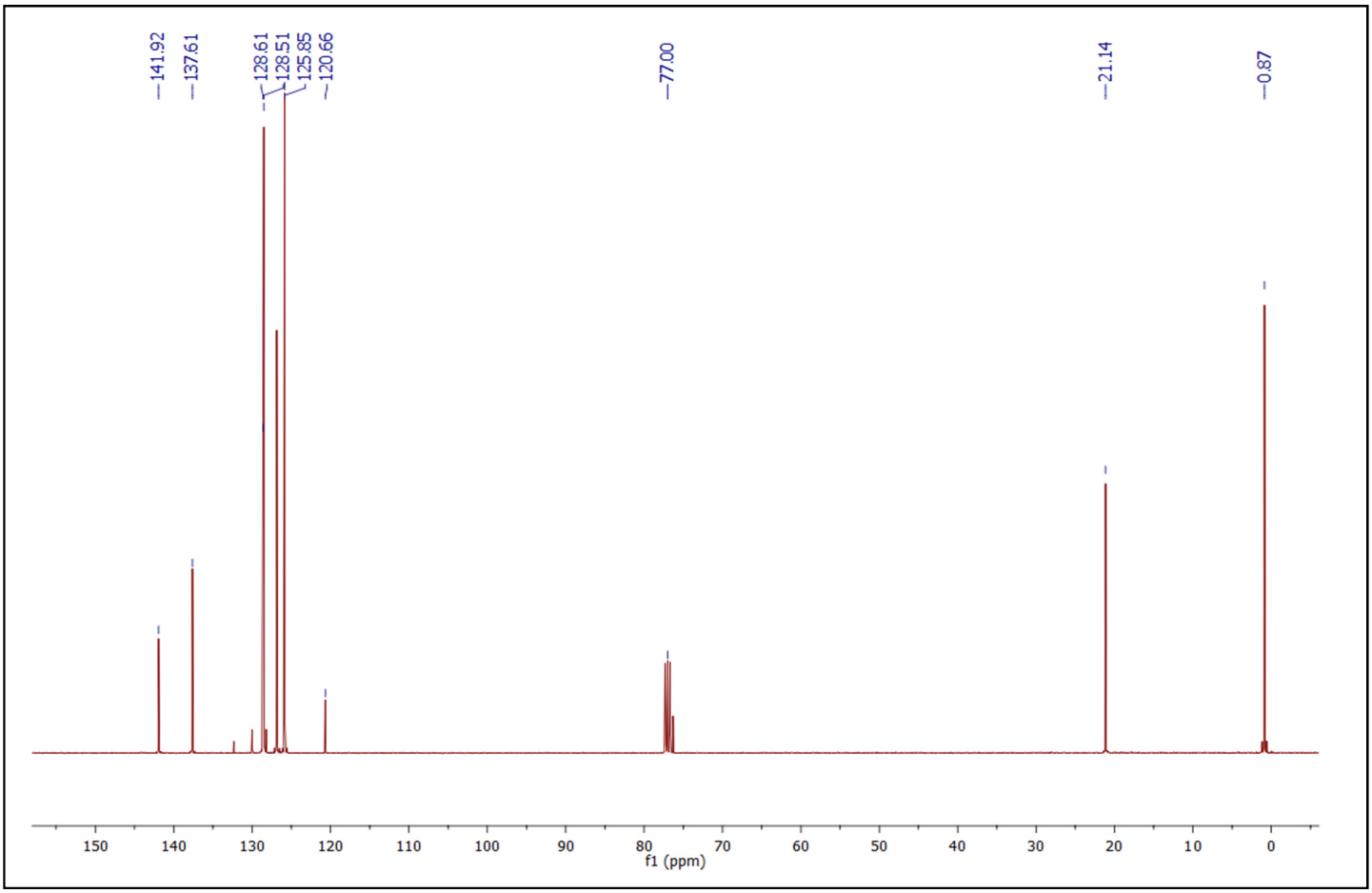


Figure S80. ^{1}H NMR of **6i** (Solvent: $CDCl_3$, IS: Mesitylene).

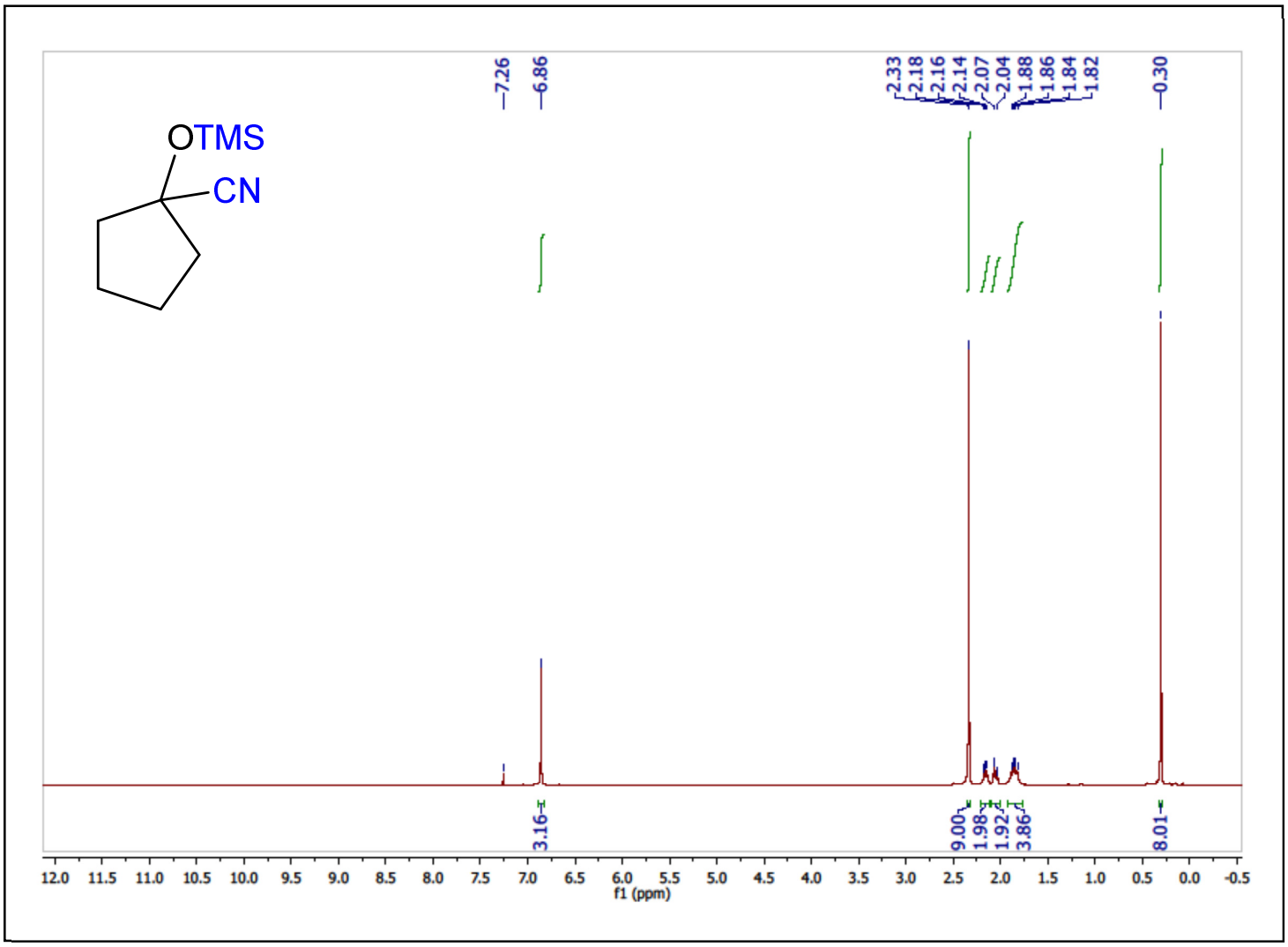


Figure S81. ^{13}C NMR of **6i** (Solvent: $CDCl_3$, IS: Mesitylene).

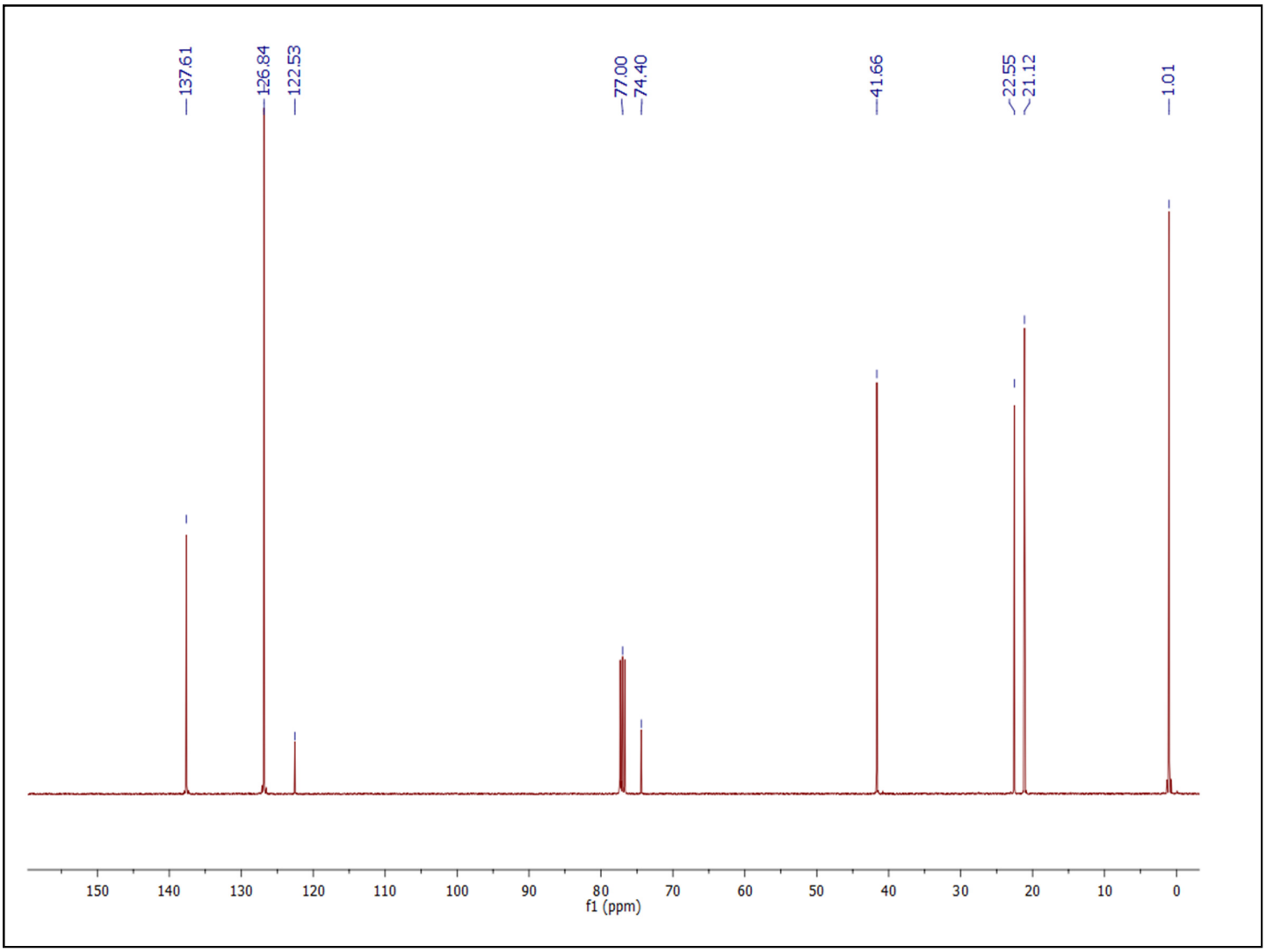


Figure S82. ^{1}H NMR of **6j** (Solvent: $CDCl_3$, IS: Mesitylene).

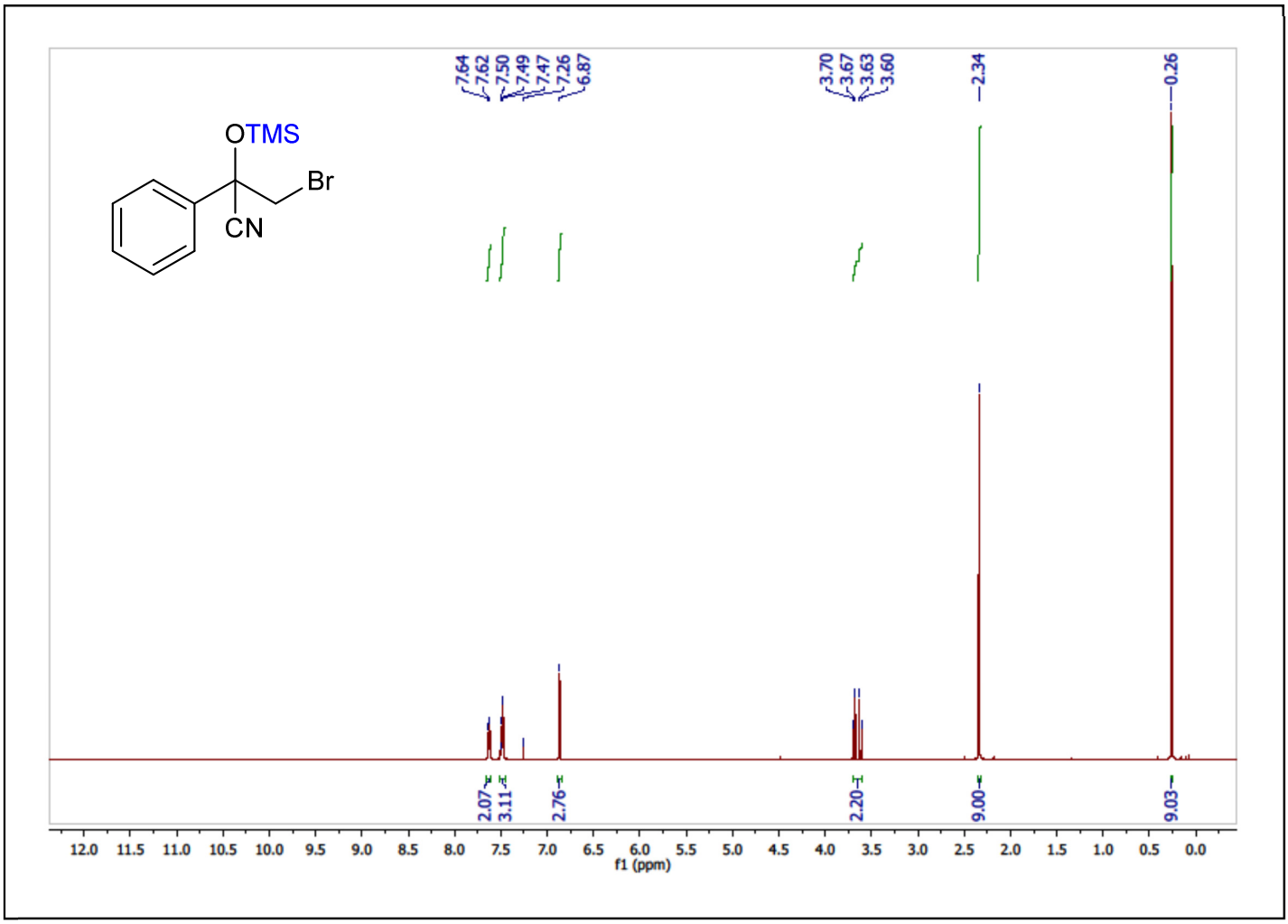
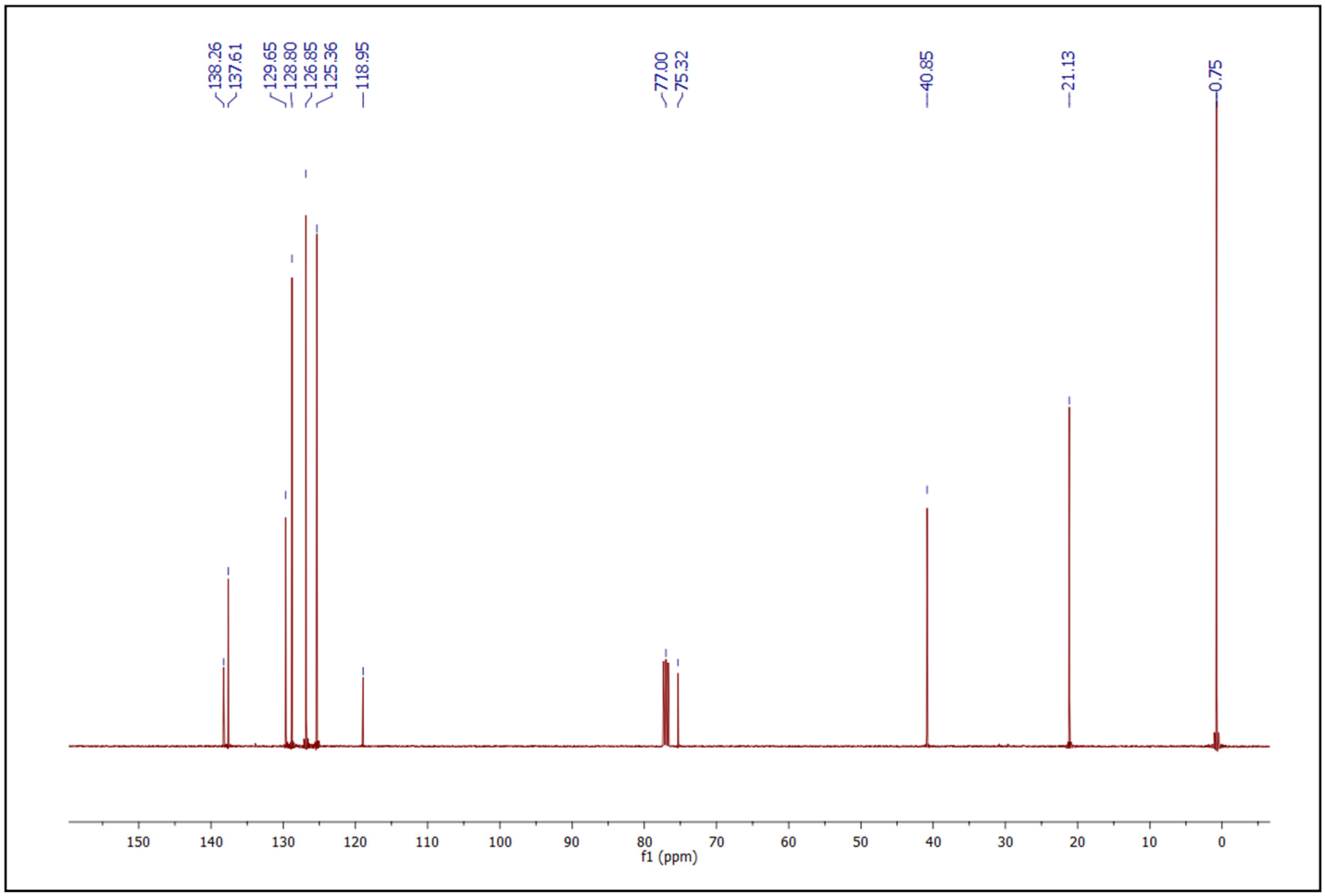


Figure S83. ^{13}C NMR of **6j** (Solvent: $CDCl_3$, IS: Mesitylene).



[S10]. Selective cyanosilylation of aldehydes using catalyst 4:

Figure S84. ^{1}H NMR of Intermolecular cyanosilylation with catalyst **4** (Solvent: $CDCl_3$, IS: Mesitylene).

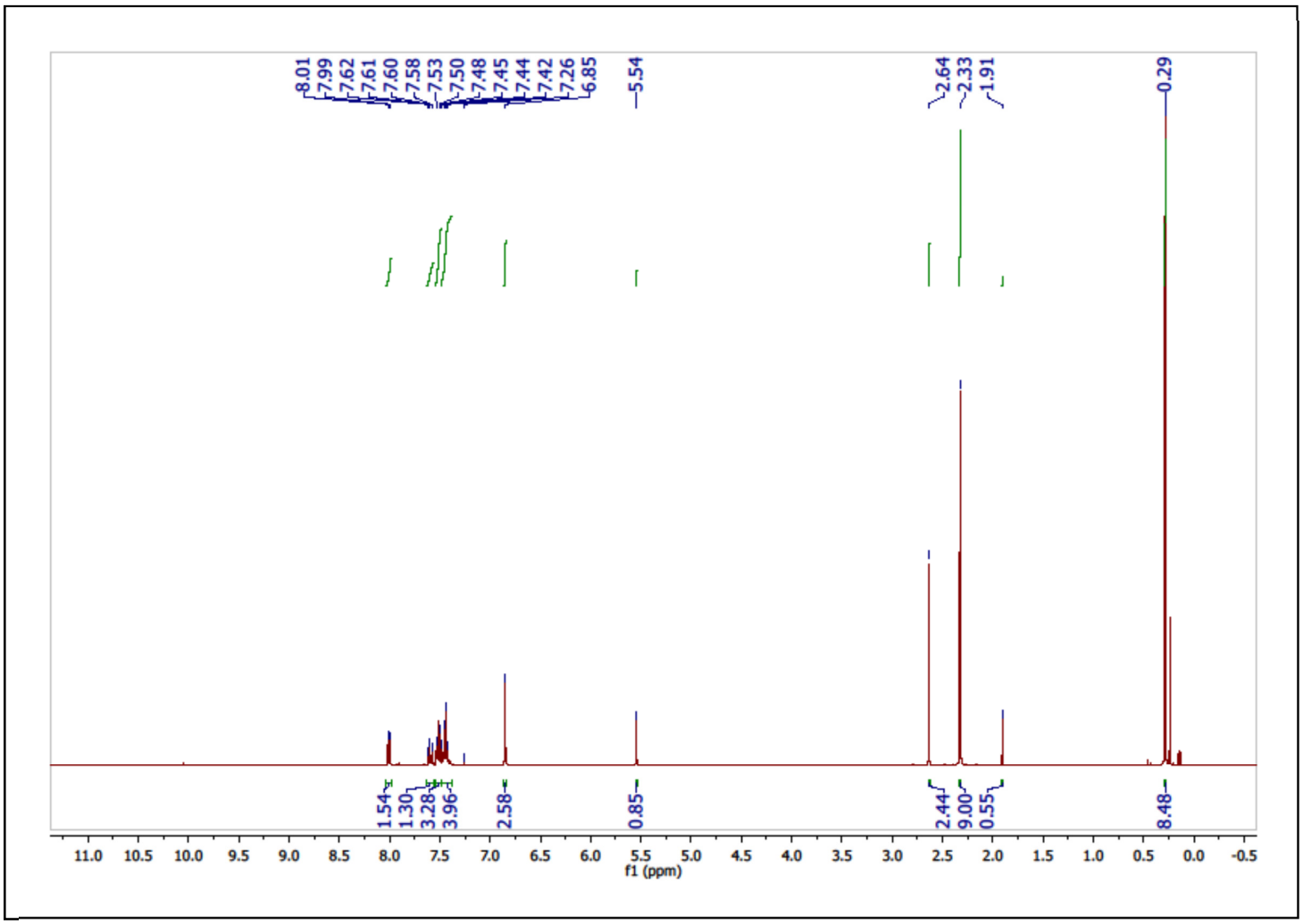
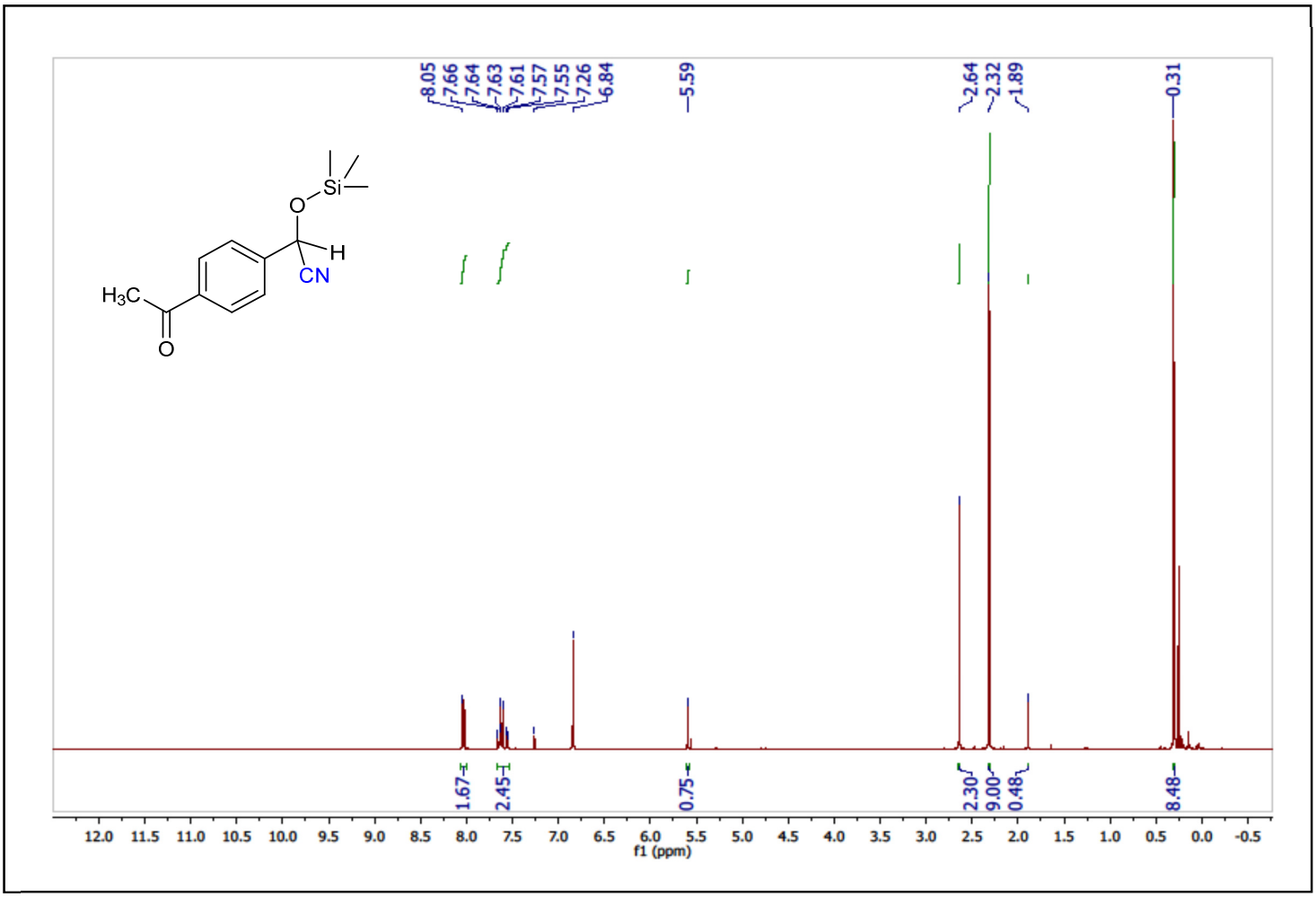


Figure S85. ^{1}H NMR of Intramolecular cyanosilylation by catalyst **4** (Solvent: $CDCl_3$, IS: Mesitylene).



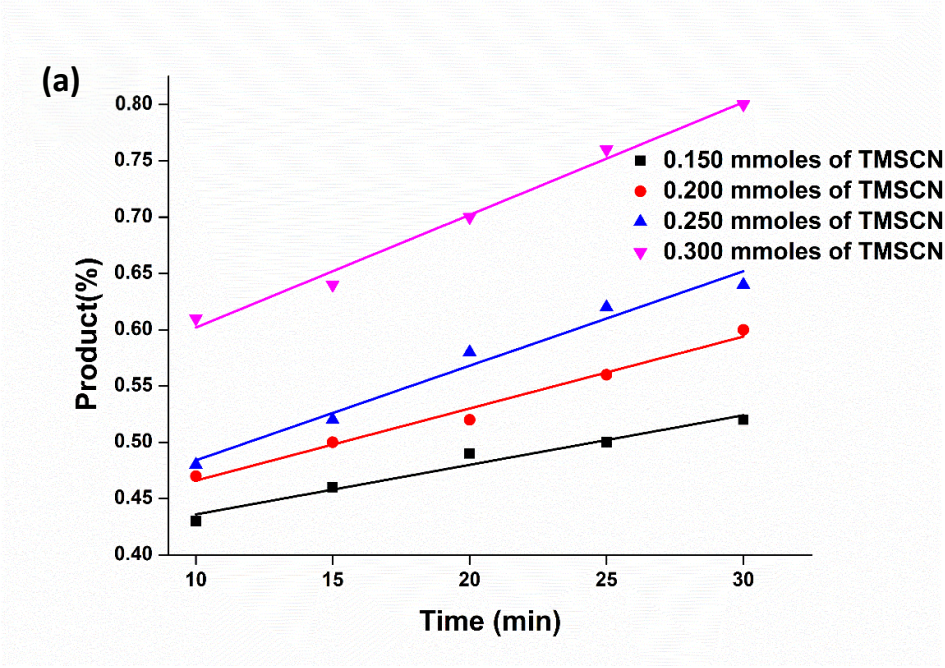
[S11]. Kinetic studies:

Representative procedure for reaction rate determination: The order of the cyanosilylation reaction catalyzed by compound **4** for aldehydes was determined by the method of initial rates.[5-6] The rate of the reaction k_{obs} was calculated from the slope of the graph that is plotted as the concentration of the product formation with respect to time while the concentration of one of the starting reactants was varied keeping the concentration of another reactant as well as the catalyst constant. The k_{obs} value for each reaction was determined using ^{1}H NMR experiment using mesitylene as the internal standard. ^{1}H NMR spectra were collected at every 5 mins interval starting from t = 0 to t = 30 mins. The value of kobs was determined from the slope of each linear best fit plot of [Product] vs. time. The plot of rate k_{obs} vs concentration of benzaldehyde indicates the order of the reaction with respect to benzaldehyde.

Firstly, the catalyst (0.0025 mmoles) was taken in the NMR tube inside the glove box and then benzaldehyde (0.25 mmoles) along with mesitylene (0.25 mmoles) was added followed by the addition of TMSCN (in different mmoles) and $CDCl_3$ (0.5 ml) was added to the NMR tube under argon. ^{1}H NMR spectra were recorded at various time intervals. The varying TMSCN concentration and concentration of catalyst and benzaldehyde are provided in Table S3 and represented graphically. The plot of k_{obs} vs concentration of TMSCN indicates that upon increasing the concentration of TMSCN it follows a linear co-relation with k_{obs}.

SI. NO.	**Catalyst (mmoles)**	**Benzaldehyde (mmoles)**	**TMSCN (mmoles)**	**K_{obs} values (10^{-3})**
1	0.0025	0.25	0.150	4.4
2	0.0025	0.25	0.200	6.4
3	0.0025	0.25	0.250	8.4
4	0.0025	0.25	0.300	10.0

Table S3. Initial rates (k_{obs}) for the cyanosilylation of aldehydes with TMSCN catalyzed by catalyst **4**, carried out under varying concentrations of TMSCN.



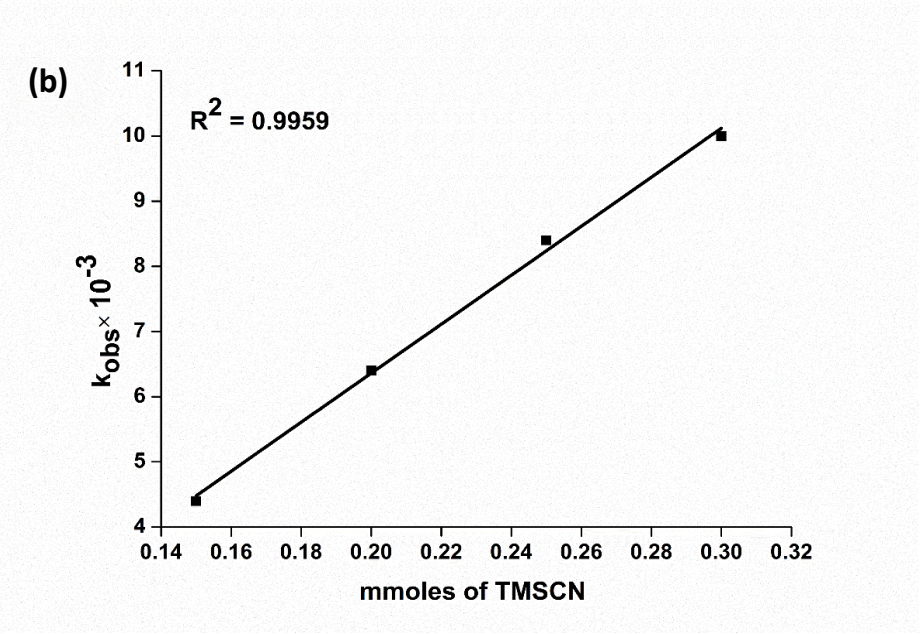


Figure S86. (a) Plot of Product (%) *vs* Time for the determination of the initial rate (k_{obs}) values. (b) Plot of k_{obs} vs mmoles of TMSCN for the determination of order of the reaction.

After this, the kinetic experiment was performed varying the concentration of benzaldehyde and keeping the concentrations of both catalyst and TMSCN constant. Catalyst (0.0025 mmoles) was taken in an NMR tube inside the glove box and benzaldehyde (in different concentrations, i.e., 0.150 mmol, 0.200 mmoles, 0.300 mmoles and 0.400 mmoles), TMSCN (0.25 moles) and mesitylene (0.25 mmoles) and $CDCl_3$ (0.5 ml) were added to the NMR tube under inert atmosphere. After this ^1H NMR spectra were recorded at 5 mins time interval. The concentration of the catalyst, varying concentration of benzaldehyde and concentration of TMSCN for each set of experiments along with the rate of each reaction k_{obs} have been given in Table S4. The plot of rate (k_{obs}) vs concentration benzaldehyde indicates that upon increase in the concentration of benzaldehyde it follows a linear co-relation with rate.

SI. NO.	**Catalyst (mmoles)**	**Benzaldehyde (mmoles)**	**TMSCN (mmoles)**	**K_{obs} values (10^{-3})**
1	**0.0025**	**0.150**	**0.25**	**3.6**
2	**0.0025**	**0.25**	**0.25**	**5.6**
3	**0.0025**	**0.300**	**0.25**	**6.4**
4	**0.0025**	**0.400**	**0.25**	**7.4**

Table S4. Initial rates (k_{obs}) for the cyanosilylation of aldehydes with TMSCN catalysed by catalyst **4**, carried out under varying concentrations of benzaldehyde.

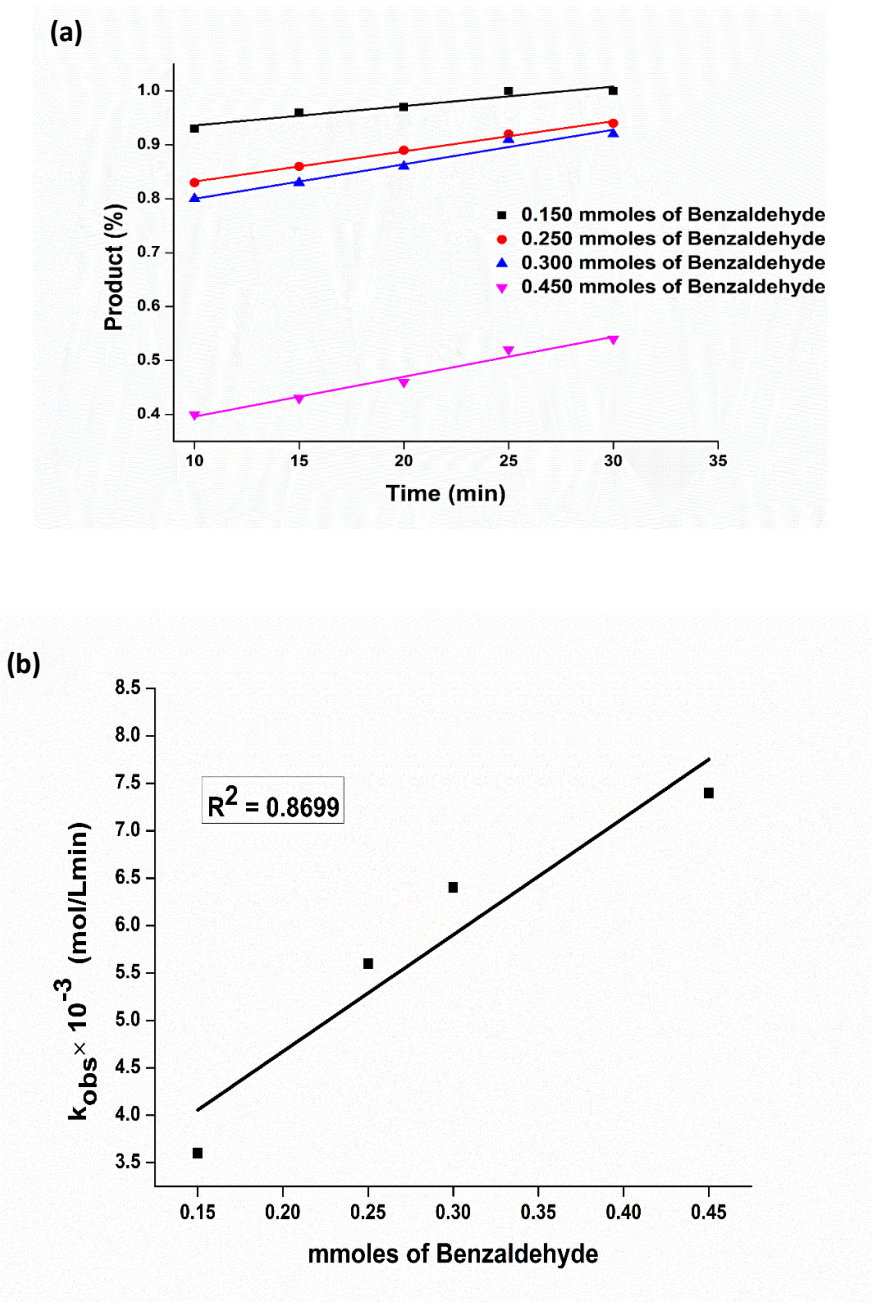


Figure S87. (a) Plot of Product (%) *vs* Time for the determination of the initial rate (k_{obs}) values. (b) Plot of k_{obs} vs mmoles of benzaldehyde for the determination of order of the reaction.

[S12]. Experimental data and theoretical calculations to propose mechanistic pathway of cyanosilylation reaction.

^{1}H, ^{13}C and ^{29}Si NMR and IR spectra's to experimentaly prove the mechanism of cyanosilylation reaction:

Figure 88. ^{29}Si NMR of 1:1 reaction of catalyst **4** and TMSCN in DMSO-d_6.

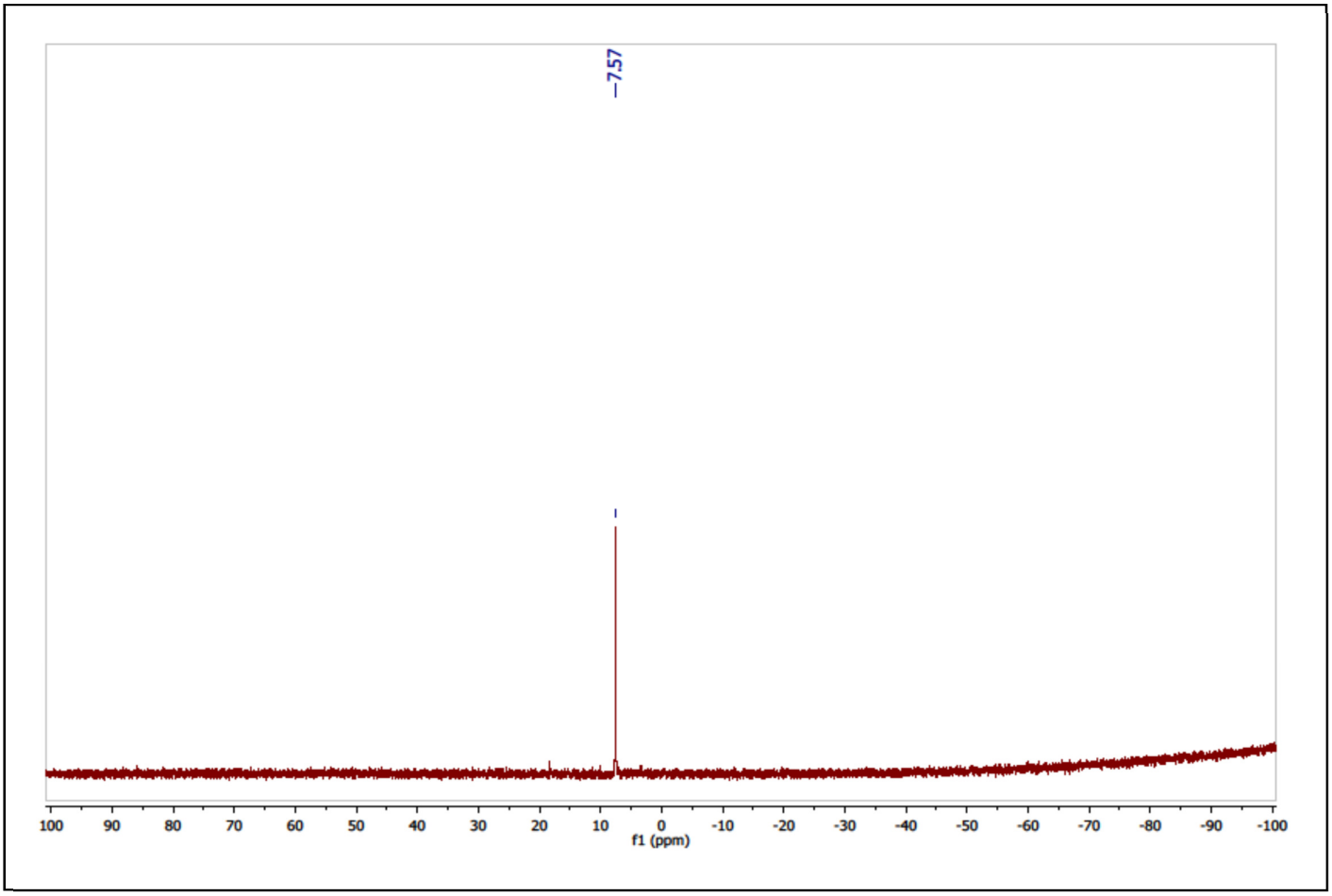


Figure 89. ^{1}H NMR of 1:1 reaction of catalyst **4** and TMSCN in DMSO-d_6.

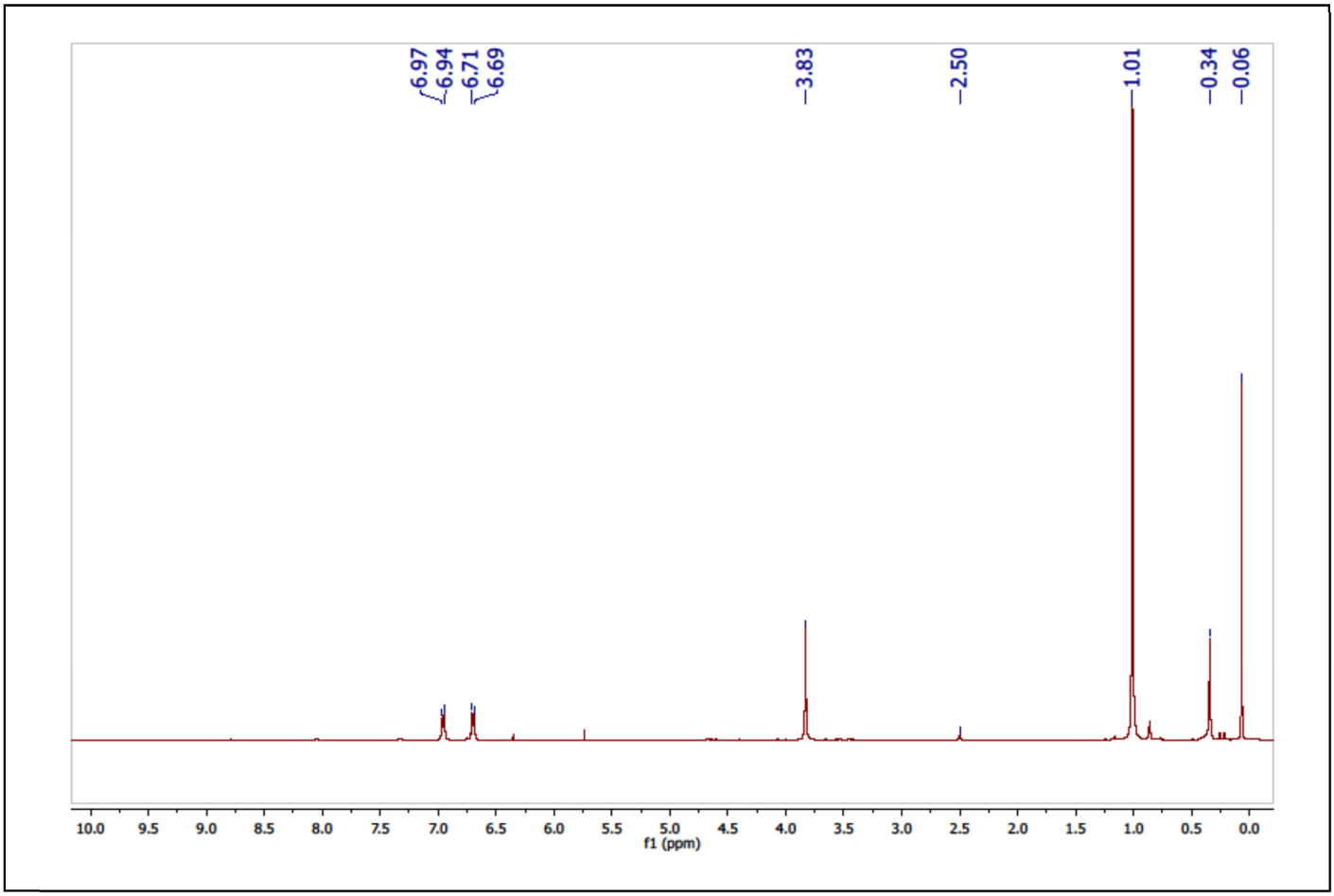
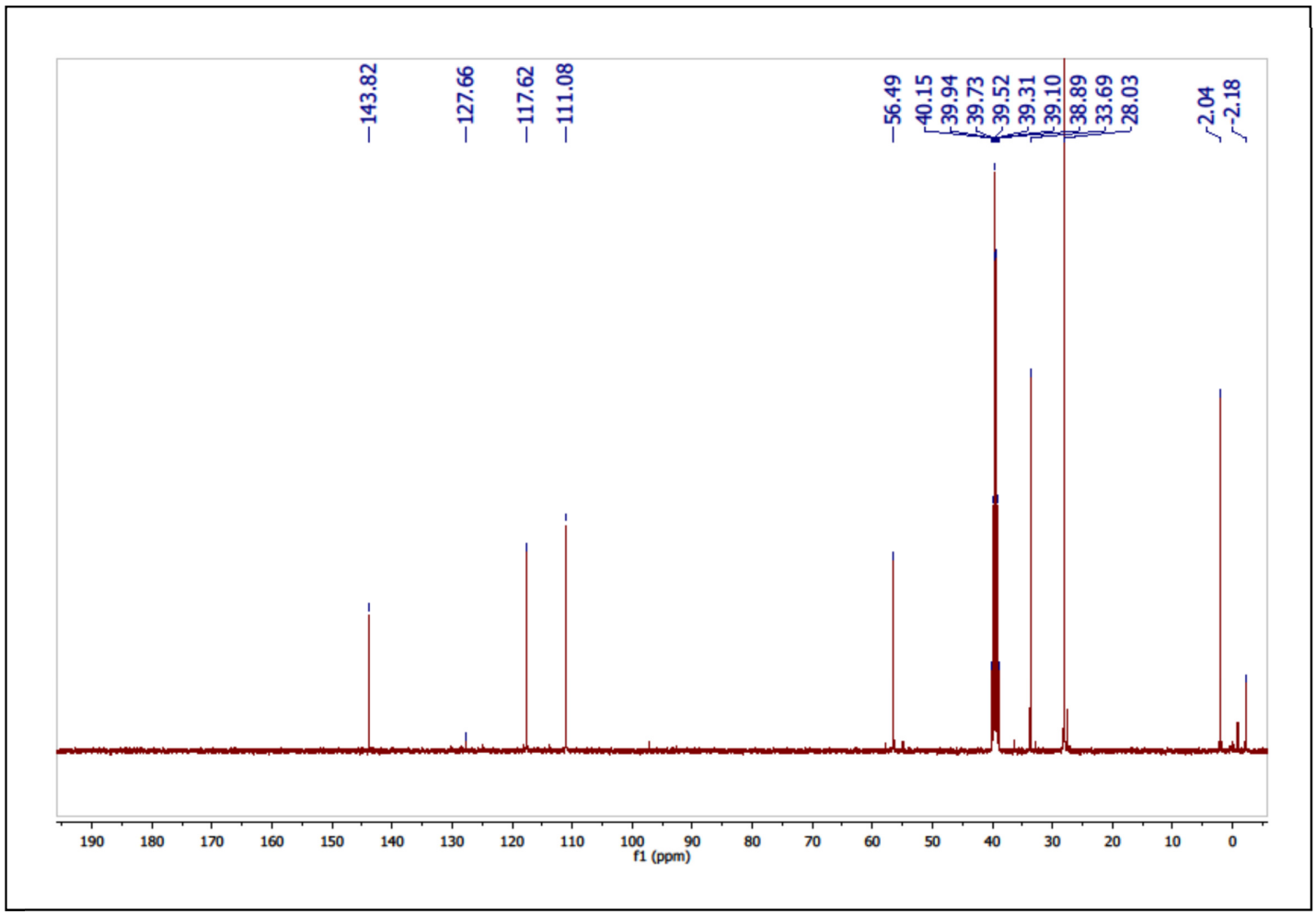


Figure 90. ^{13}C NMR of 1:1 reaction of catalyst **4** and TMSCN in DMSO-d_6.



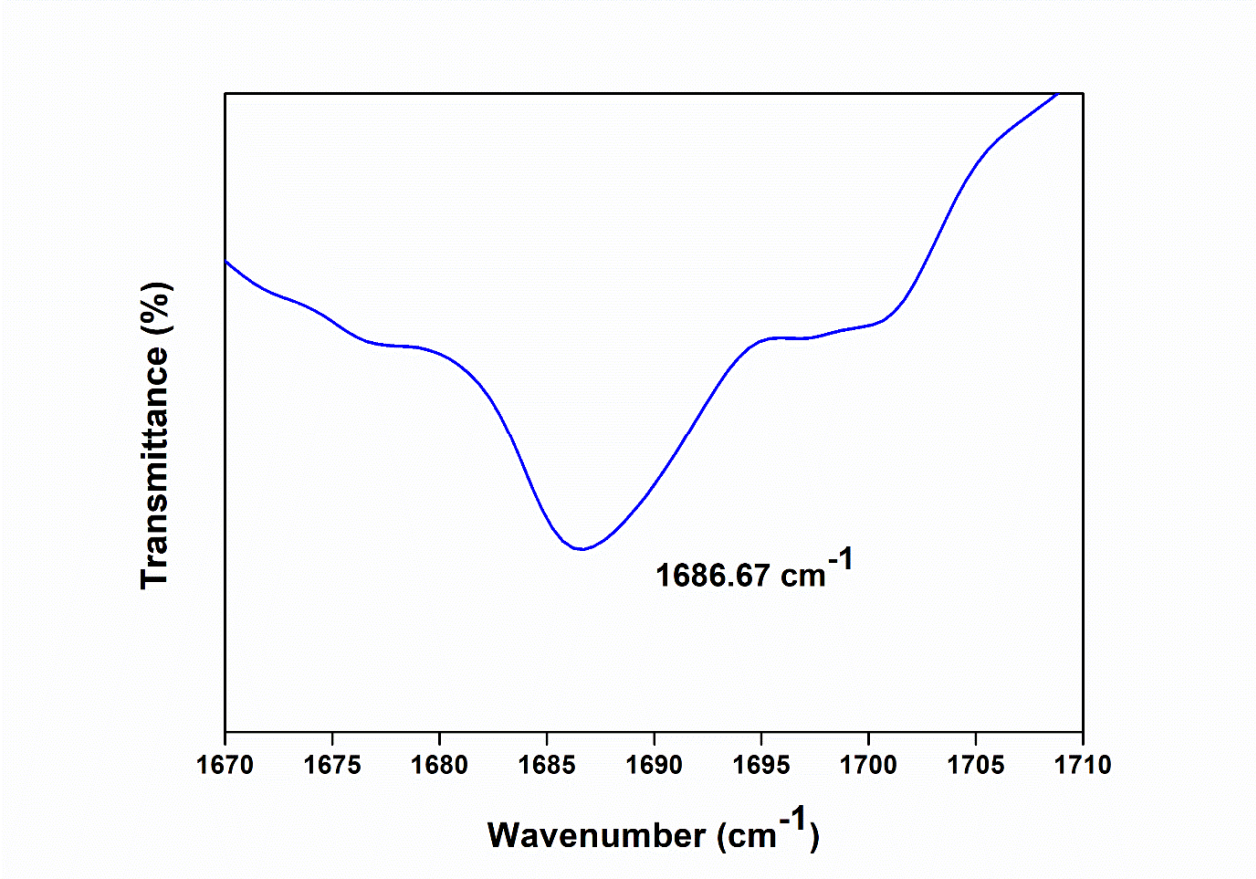


Figure 91. IR spectrum of 1:1 reaction of catalyst **4** and TMSCN.

Figure 92. ^{1}H NMR of cyanosilylation of acetophenone with $AgSbF_6$ using mesitylene as internal standard.

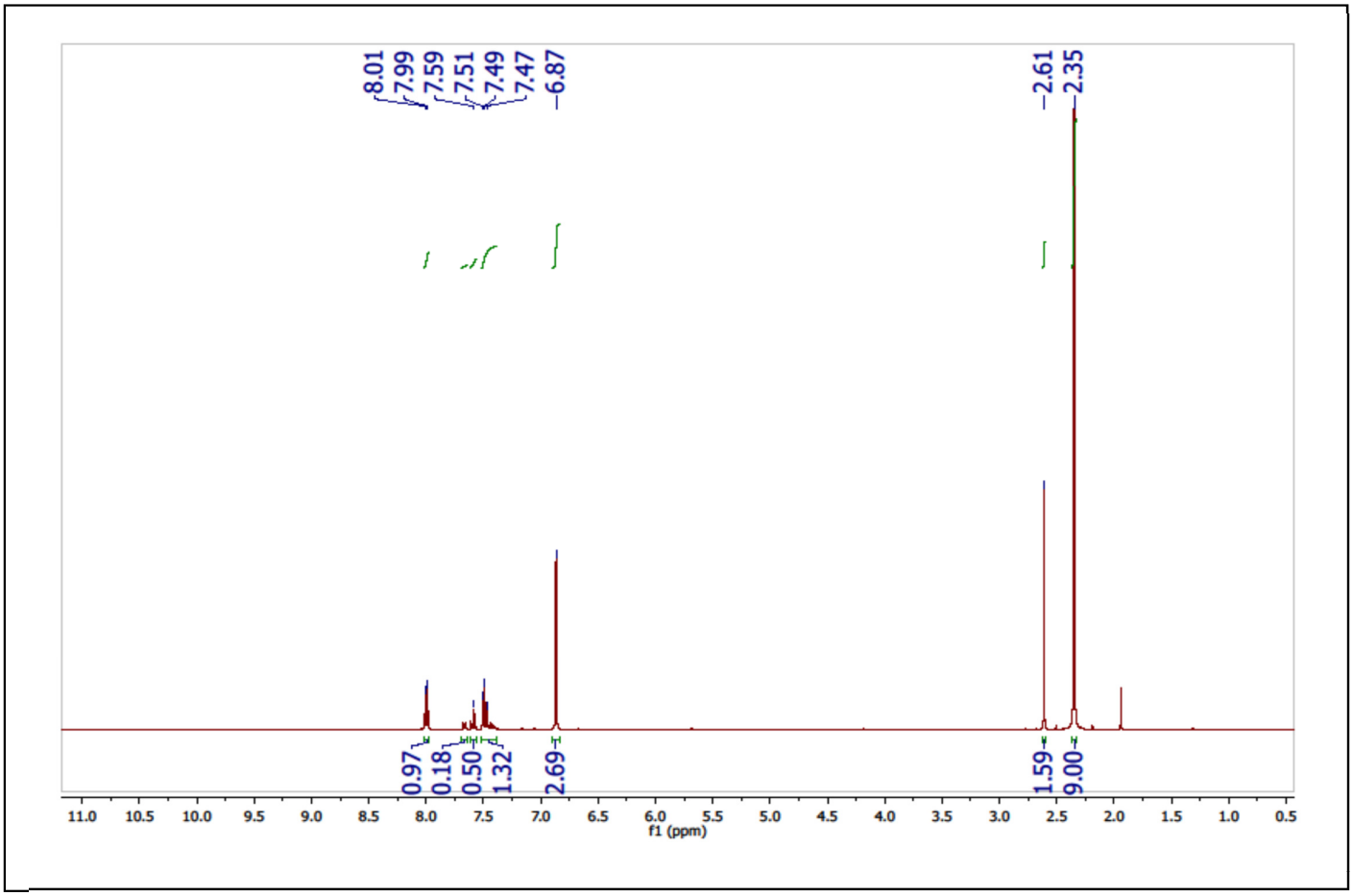
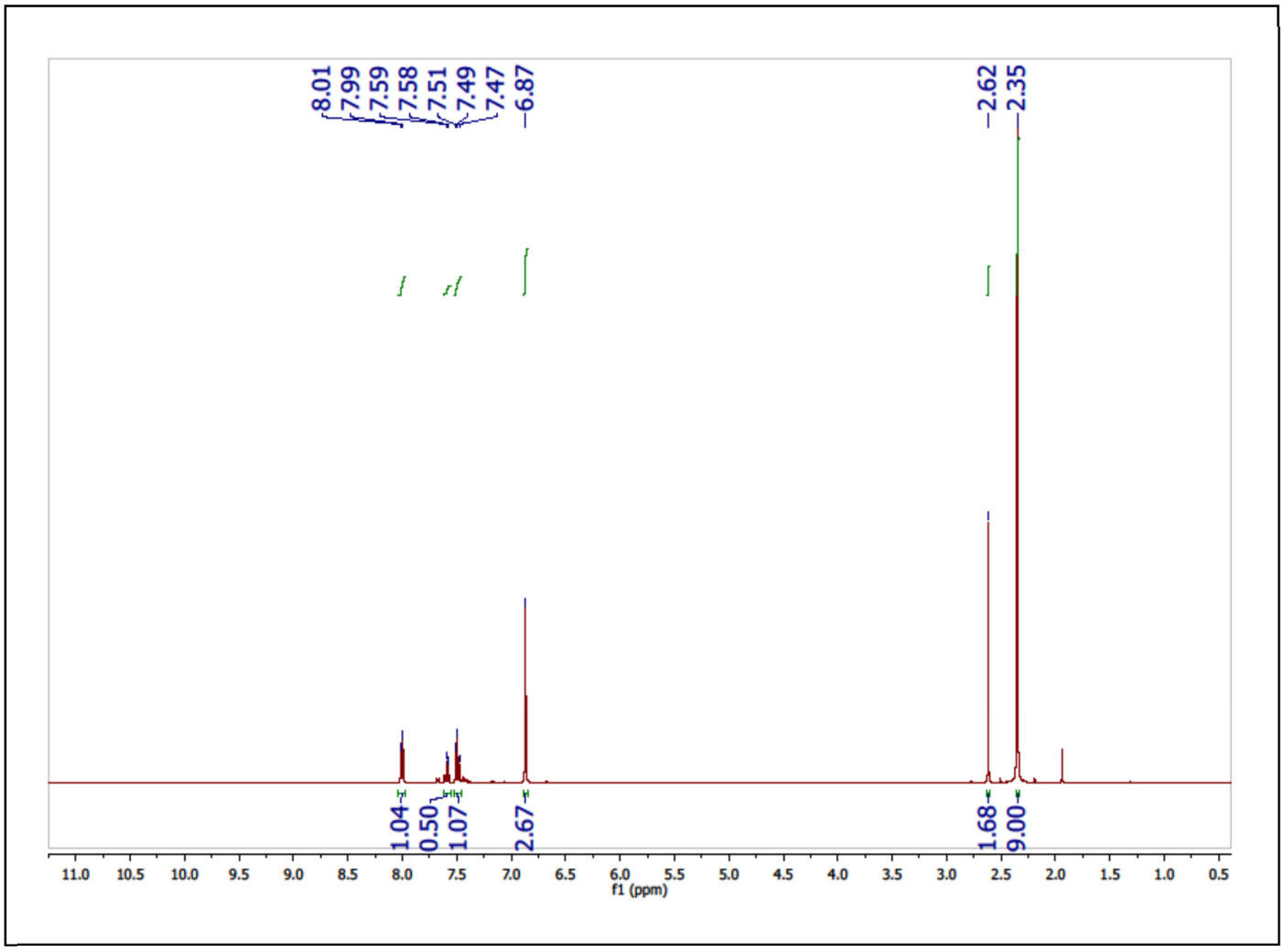


Figure 93. ^{1}H NMR of cyanosilylation of acetophenone with AgOTf using mesitylene as internal standard.



[S13]. Computational Details:
Geometry optimized structures of the all-reaction intermediates & transition states:

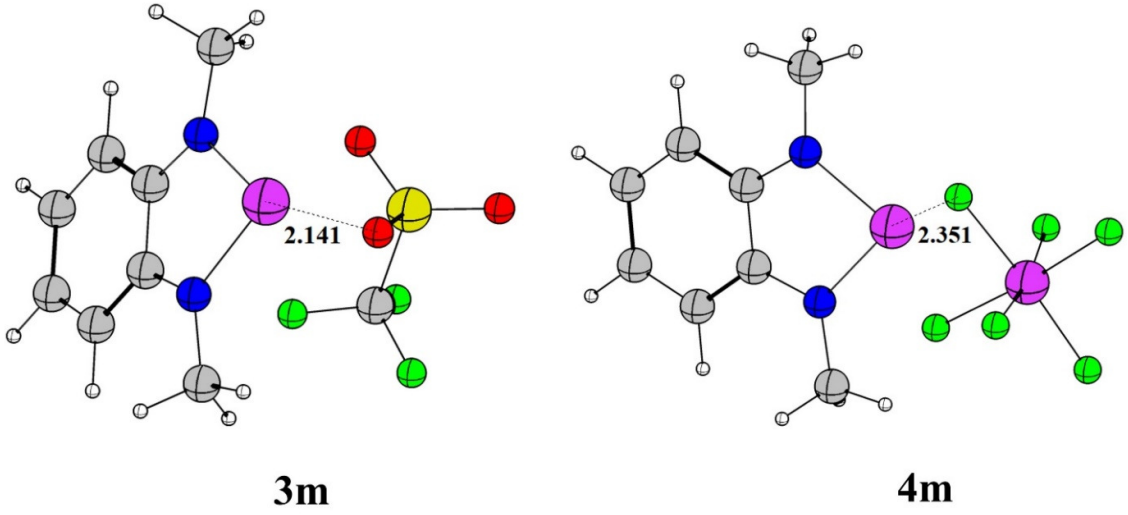


Figure S94: Geometry optimized structures of catalyst **3m** and **4m**. All distances are shown in Å unit

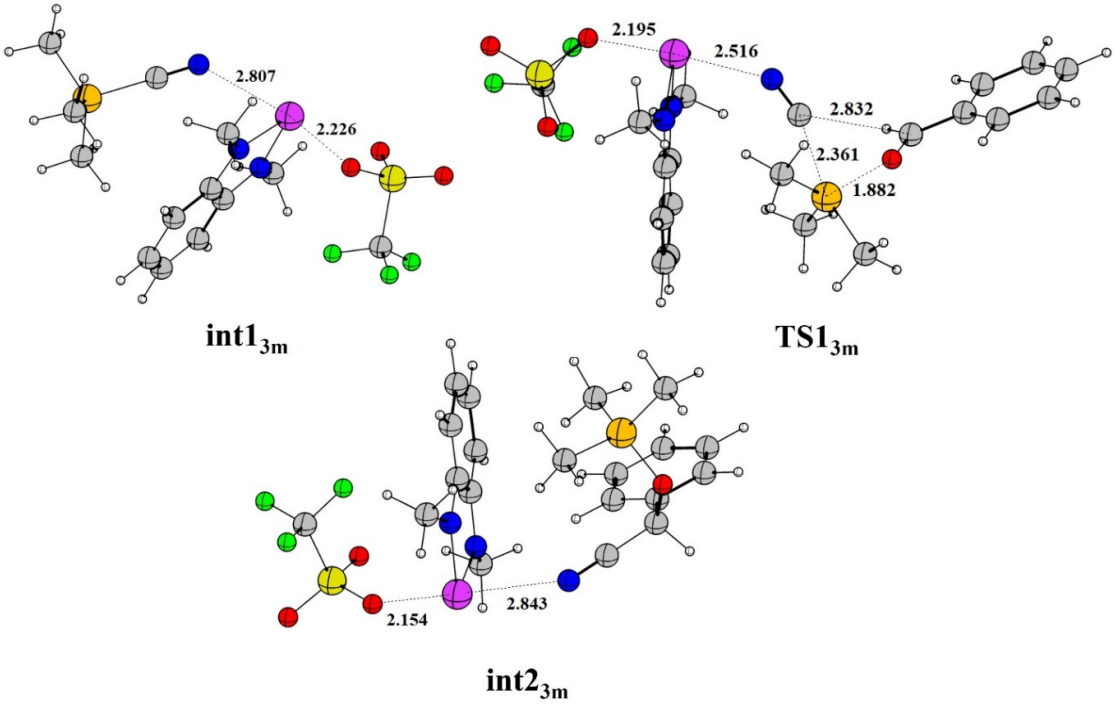


Figure S95: Geometry optimized structures of various intermediates and transition states for cyanosilylation of benzaldehyde catalysed by **3m**. All distances are shown in Å unit.

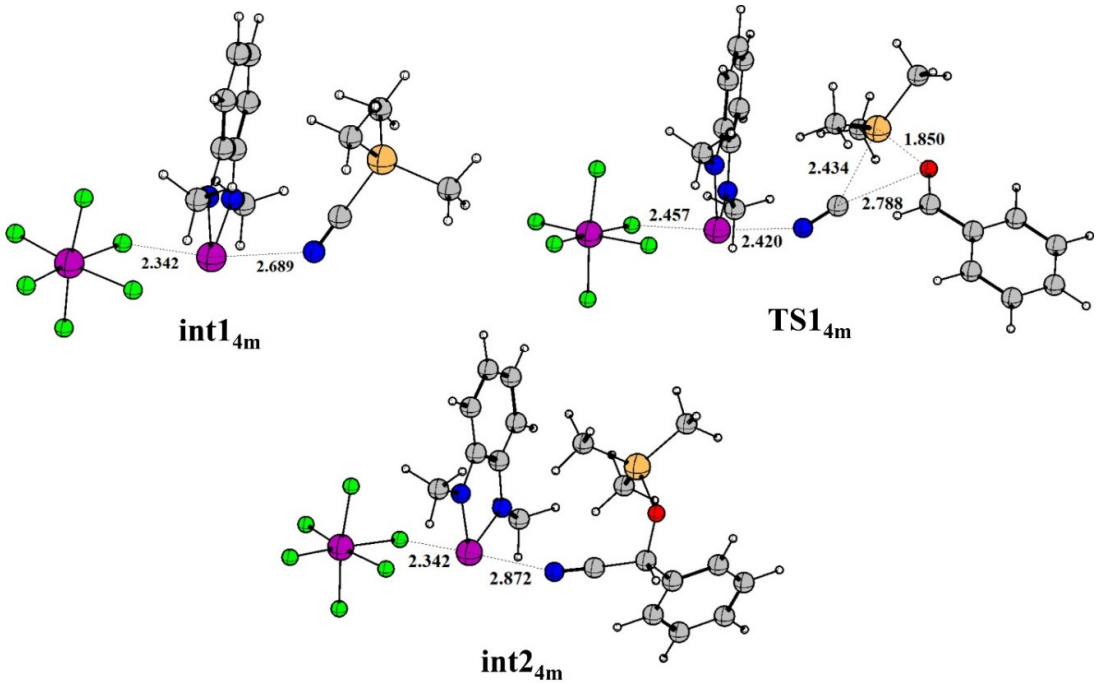


Figure S96: Geometry optimized structures of various intermediates and transition states for cyanosilylation of benzaldehyde catalysed by **4m**. All distances are shown in Å unit.

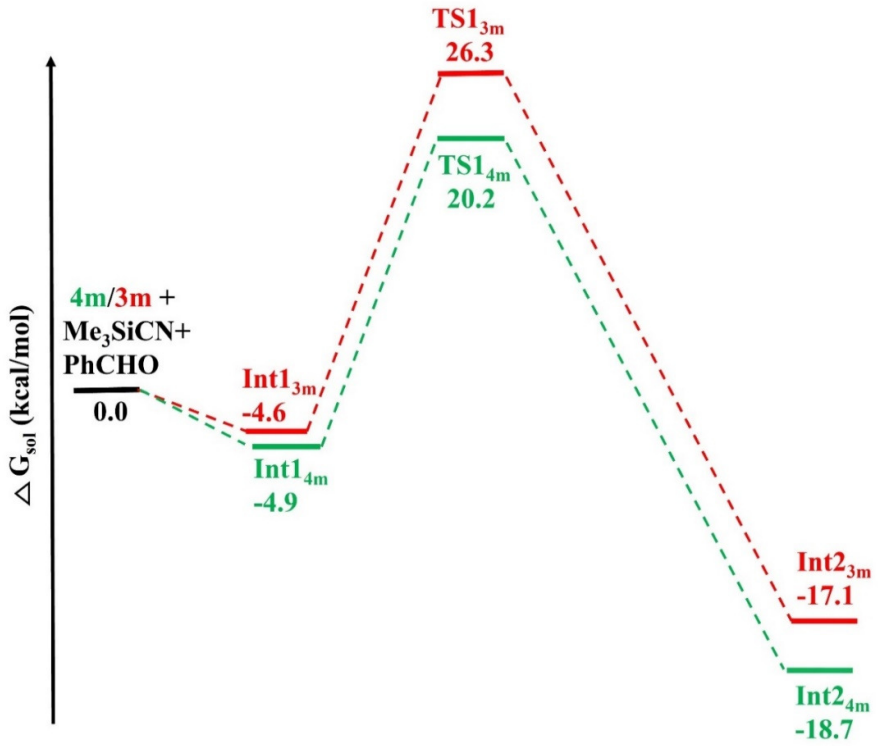


Figure S97: Relative solvent-corrected Gibbs free energy profiles for the cyanosilylation of PhCHO catalyzed by **3m** and **4m**.

Table S5: Selected NBO interaction energies (estimated at the second order perturbation level) in the reaction intermediates/transition states of cyanosilylation catalysed by 3m/4m. All the energies are in kcal/mol.

RI/TS	NBO interaction energy (kcal/mol)
INT1$_{3m}$	$\Delta E^{int}_{N(p) \rightarrow Sb(p^*1)} = 14.9$ $\Delta E^{int}_{O1(p1) \rightarrow Sb(p^*1)} = 10.1$ $\Delta E^{int}_{O1(p1) \rightarrow Sb(p^*2)} = 3.6$ $\Delta E^{int}_{O1(p2) \rightarrow Sb(p^*1)} = 2.6$ $\Delta E^{int}_{O2(p1) \rightarrow Sb(p^*1)} = 47.9$ $\Delta E^{int}_{O2(p1) \rightarrow Sb(p^*2)} = 27.5$
TS1$_{3m}$	$\Delta E^{int}_{N(p) \rightarrow Sb(p^*1)} = 39.9$ $\Delta E^{int}_{N(p) \rightarrow Sb(p^*2)} = 2.6$ $\Delta E^{int}_{O1(p1) \rightarrow Sb(p^*1)} = 20.4$ $\Delta E^{int}_{O1(p1) \rightarrow Sb(p^*2)} = 5.8$ $\Delta E^{int}_{O2(p1) \rightarrow Sb(p^*1)} = 64.8$ $\Delta E^{int}_{O2(p1) \rightarrow Sb(p^*2)} = 18.9$
INT14$_m$	$\Delta E^{int}_{N(p) \rightarrow Sb(p^*1)} = 21.4$
TS14$_m$	$\Delta E^{int}_{N(p) \rightarrow Sb(p^*1)} = 38.8$ $\Delta E^{int}_{N(p) \rightarrow Sb(p^*2)} = 15.9$

Electronic structure of all the systems studied are done by density functional theory. For geometry optimization M062X[7-8] exchange-correlation functional along with 6-311G(d,p) basis set is used for lighter atoms (C, H, B, N, O, F). For Sb, we have used def2TZVP basis set in combinatio with Stuttgart-Dresden pseudopotential.[9] All optimized geometries are characterized by harmonic vibrational analysis to recognize the structures as minima (all positive frequencies) or transition state (one negative frequency). Transition states are (TS) are verified through intrinsic reaction coordinate (IRC) calculations. All thermochemical data are estimated within the ideal gas-rigid rotor-harmonic oscillator approximation at 298.15 K and 1 atm pressure. SMD model is used to take into account solvent effects as proposed by Truhlar and Cramer. The computed entropic corrections are further scaled to 75% in order to take into

account the quenching of translational and rotational degrees of freedom in the solution phase.[10-13] Photophysical properties of these catalysts are calculated using time-dependent density functional theory (TD-DFT) methods using B3LYP-D3[14-18] exchange-correlation functional.

The model catalysts 3m and 4m are used for the mechanistic study wherein the substituent on the N centres in 3 and 4 are replaced by methyl groups, which does not impose major changes in the electronic and structural properties of the catalysts. The obvious change in the steric environment also does not affect the reactivity as found in our initial test calculations with full catalyst structures. Note that, we have previously used similar model structures to study the bonding properties of silylene chalcogenone complexes.[6]

We have also calculated the anion dissociation energies, which run as **2 >3 > 4**. Note that this trend is in agreement with the experimentally measured Lewis acidity trend (**4>3>2**). Thus, it can be said that for catalyst **4**, the anion SbF_6^- is loosely bound with the cationic Sb centre. As a consequence, **4** possess higher Lewis acidity compared to **2** and **3**. This result is also in agreement with the Natural bonding analysis (NBO) results which shows the absence of any interaction between the anion SbF_6^- and the cationic Sb centre in catalyst **4**.

Anion dissociation energies-

Compound **2** = [cationic Sb moiety] + Cl^- ΔG = 62.6 kcal/mol

Compound **3** = [cationic Sb moiety] + OTf^- ΔG = 42.0 kcal/mol

Compound **4** = [cationic Sb moiety] + SbF_6^- ΔG = 27.8 kcal/mol

[S14]. References

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Coordinates of the Intermediates and Transition states in XYZ format

2

Sb	-0.00007000	-1.38141100	0.13900400
Cl	-0.00022700	-2.01946600	2.50840000
N	1.30905200	0.14395400	0.21224200
N	-1.30905300	0.14405800	0.21203500
C	3.52365900	-0.03420300	-1.00214400
C	1.39186400	2.56371300	0.75788400
H	2.47296700	2.58085800	0.75134800
C	4.99415500	-0.32017700	-0.68380100
H	5.11669800	-1.30913600	-0.23261200
H	5.39584400	0.42222200	0.01160800
H	5.59739600	-0.28821000	-1.59451700
C	0.69295000	3.73818400	1.02543300
H	1.24161700	4.64926300	1.22897500

C	-2.98936200	-1.11549200	-1.94603700
H	-1.96561000	-0.89453500	-2.26098000
H	-3.60369600	-1.17243800	-2.84816400
H	-3.00600200	-2.10244300	-1.46992800
C	-4.99416900	-0.31970000	-0.68390800
H	-5.11692900	-1.30849800	-0.23237300
H	-5.59731600	-0.28798700	-1.59469300
H	-5.39582200	0.42298700	0.01119300
C	2.74672500	-0.07044800	0.33037500
H	2.91706800	-1.05186700	0.79299300
H	3.17011900	0.65757300	1.02869900
C	-0.69277800	3.73825900	1.02526600
H	-1.24139900	4.64940600	1.22862500
C	-3.52358600	-0.03408900	-1.00218900
C	-0.71018500	1.37904000	0.49296600
C	3.39301500	1.33388500	-1.67541400
H	3.88993800	1.32439100	-2.64939500
H	3.85824100	2.11759300	-1.07169800
H	2.34380400	1.59870500	-1.82776600
C	0.71025600	1.37896300	0.49310700
C	-3.39257800	1.33382700	-1.67570700
H	-3.85783600	2.11773400	-1.07231400
H	-3.88925800	1.32416800	-2.64981700
H	-2.34327800	1.59843200	-1.82784400

C	-2.74675200	-0.07027100	0.33033500
H	-3.17005600	0.65782200	1.02864500
H	-2.91714200	-1.05166300	0.79294400
C	-1.39174100	2.56385400	0.75754400
H	-2.47284100	2.58108400	0.75078500
C	2.98942200	-1.11533000	-1.94629800
H	3.60435200	-1.17267400	-2.84800700
H	1.96602300	-0.89380600	-2.26194800
H	3.00519100	-2.10228800	-1.47017200

3

Sb	0.18785300	-0.38254200	-1.38996700
S	0.00711800	2.88436300	-0.48584500
O	-0.33349500	1.69333100	-1.40395300
F	-1.53929100	1.70986600	1.26651400
F	-1.41338900	3.85598100	1.47241900
F	-2.58221500	2.98764600	-0.12210900
N	1.47663500	-0.43884000	0.12827800
O	1.13431200	2.57695500	0.36270200
N	-1.08477400	-0.96588800	0.03756100
C	-2.52988700	-1.02013400	-0.17259100
H	-2.79521600	-0.29846200	-0.95690500
H	-3.03614300	-0.66661800	0.73025500
C	2.84473000	0.06613100	0.01327300

H	3.09883100	0.61647800	0.92238000
H	2.87105300	0.82042200	-0.78244200
C	0.80838900	-0.87254600	3.77583900
H	1.32492100	-0.82714100	4.72631600
C	3.57818100	-1.69349600	-1.62792000
H	3.44843200	-0.96134900	-2.43329100
H	2.66884100	-2.29667400	-1.54779400
H	4.38774600	-2.36636800	-1.92138400
C	-1.20335100	-1.23405400	2.50295300
H	-2.25696900	-1.47517300	2.47724600
C	3.97847700	-2.05765900	0.80965700
H	4.68873800	-2.84352400	0.53845200
H	3.00317600	-2.52104800	0.97851000
H	4.31440200	-1.61663600	1.75161600
C	-2.82079000	-3.44387800	0.49935400
H	-1.75692300	-3.50198000	0.74287900
H	-3.14953400	-4.43015900	0.16096100
H	-3.36865200	-3.20721000	1.41519100
C	-0.51523900	-0.97548600	1.32061500
C	3.90725600	-1.00528300	-0.29928600
C	-2.42594300	-2.85217400	-1.89454500
H	-1.36457800	-3.07357100	-1.74903800
H	-2.52531800	-2.08990200	-2.67588200
H	-2.89972600	-3.76549700	-2.26260300

C	-3.08244100	-2.39845000	-0.58711300
C	0.86763100	-0.67081900	1.37018900
C	-4.58989000	-2.23847600	-0.80585100
H	-5.04114200	-3.19501900	-1.08046100
H	-4.80048500	-1.52384500	-1.60674800
H	-5.08200500	-1.88346800	0.10390200
C	-0.54313000	-1.18177900	3.72607100
H	-1.09282900	-1.38367500	4.63679100
C	1.51207500	-0.61939400	2.60338500
H	2.56496800	-0.38104500	2.65588900
C	-1.48190500	2.86024900	0.60637700
O	-0.04737900	4.12269200	-1.21205600
C	5.25438500	-0.28668000	-0.42207900
H	5.50202700	0.24030500	0.50337000
H	5.24011000	0.44529900	-1.23465700
H	6.05409700	-1.00290100	-0.62648700

4

Sb	-0.38623200	-0.48249900	-0.32968000
N	-1.11389000	1.38961200	-0.48925700
N	-2.36681600	-0.87892300	-0.55338000
C	-2.48221000	1.46781400	-0.69730400
C	-3.21330800	2.65551300	-0.87904900
C	-3.16886400	0.22364200	-0.74996100
C	-2.89274300	-2.24512200	-0.54885200

C	-0.30382100	2.61211000	-0.36450900
C	-4.55025100	0.20051800	-1.00746500
C	-0.07991900	3.10597900	1.08467300
C	-5.23952200	1.37960900	-1.19130000
C	-4.56955400	2.60737800	-1.12302200
C	-3.29016800	-2.80039300	0.83855500
C	-3.75278700	-4.24441200	0.61209800
C	0.81525200	2.13040100	1.85207700
C	-2.08256500	-2.80089000	1.78012000
C	-1.40026700	3.29108300	1.83588400
C	-4.42340600	-1.98884400	1.47057500
C	0.64474500	4.45222600	0.96866800
Sb	3.29450100	-0.49092300	-0.17126500
F	3.97656700	1.04373300	0.65574800
F	1.82275800	0.61701800	-0.85978500
F	2.11033700	-0.74397200	1.30373200
F	2.34465800	-1.90539100	-1.00500200
F	4.25729200	-0.16200600	-1.73333500
F	4.57951600	-1.62643600	0.55148200
H	0.66978900	2.41608500	-0.81156400
H	-0.77091500	3.39905600	-0.95833700
H	1.77375500	1.97777300	1.35153400
H	1.01862200	2.52109300	2.85234000
H	0.34119600	1.15343300	1.99655200

H	0.03303300	5.18591200	0.43562400
H	0.86153600	4.85196200	1.96191000
H	1.59361200	4.34161900	0.43714600
H	-1.96503200	2.35607200	1.89124100
H	-1.19882800	3.62048700	2.85828100
H	-2.03498100	4.04440400	1.36272400
H	-3.73824800	-2.31633500	-1.23809900
H	-2.11474200	-2.90151400	-0.95486400
H	-1.21506600	-3.29304600	1.32653800
H	-1.79817000	-1.78655700	2.07443200
H	-2.32222800	-3.34225000	2.69821200
H	-2.94638300	-4.85959200	0.20325500
H	-4.07186000	-4.69285700	1.55556700
H	-4.59774500	-4.28334000	-0.08104500
H	-5.33504100	-2.04095100	0.86975200
H	-4.65575600	-2.38709600	2.46154600
H	-4.14830600	-0.93762000	1.58622500
H	-2.72079700	3.61514200	-0.83048700
H	-5.11720400	3.53061400	-1.26380500
H	-6.30407600	1.35321200	-1.38655300
H	-5.07677200	-0.74220700	-1.05411300

3m

Sb	0.32413300	-1.85794000	0.38147900

S	-2.26162800	0.06735500	-0.65003900
O	-1.61759200	-0.95835900	0.30246500
F	-0.68435100	1.78296200	0.52671500
F	-2.47621200	2.64424100	-0.31842900
F	-2.58167400	1.50517700	1.51259200
N	1.26199800	-0.96730400	-1.13079500
O	-1.47384100	0.21648800	-1.85210000
N	1.22783500	-0.40690400	1.41357400
C	1.01986400	-0.10751500	2.82043200
H	0.47182100	-0.92272600	3.29655400
H	0.43827000	0.81250300	2.94030700
C	1.11364600	-1.30224700	-2.53955600
H	0.50986700	-0.54850900	-3.05039400
H	0.60616500	-2.26407700	-2.63741500
C	3.07057900	2.28480800	-1.19829500
H	3.52683800	2.97117700	-1.90044600
C	2.47922500	1.69678100	1.06593800
H	2.47088600	1.93383700	2.12211900
C	1.87901900	0.53017200	0.60615800
C	1.87938000	0.23543400	-0.77690700
C	3.07736400	2.56973600	0.15986200
H	3.54038600	3.47861600	0.52308600
C	2.47007200	1.12056900	-1.67186200
H	2.45359100	0.91115900	-2.73343800

C	-1.98579800	1.60475900	0.33322600
O	-3.68354100	-0.11858200	-0.72545200
H	2.09380800	-1.38493900	-3.01716700
H	1.97464300	0.00688800	3.34135500

4m

Sb	0.72259500	-1.39494500	0.70314200
N	1.35319300	0.41383400	1.22065800
N	2.31509600	-1.27632800	-0.49858700
C	2.41928000	0.88214400	0.45686000
C	2.98447400	2.15220100	0.57085000
C	2.93662700	-0.03215200	-0.49030800
C	2.73275700	-2.27793700	-1.46808100
C	0.76033900	1.29650700	2.22298800
C	3.99688400	0.34315800	-1.31475300
C	4.54675800	1.61186200	-1.19052500
C	4.04312100	2.50979700	-0.25312000
Sb	-2.30893100	0.35447600	-0.31792000
F	-1.20430900	1.84898900	-0.06983100
F	-1.57327100	-0.32998700	1.34578700
F	-0.69078200	-0.57318300	-0.98744800
F	-3.18941300	-1.28198400	-0.50697700
F	-3.74477900	1.15706500	0.54579700
F	-2.75822600	0.88587400	-2.04066800
H	-0.05010800	0.78101400	2.73354700

H	1.51690100	1.58924200	2.95524500
H	3.78739600	-2.53042900	-1.32943300
H	2.14430600	-3.18754800	-1.33585700
H	2.59021400	2.86060500	1.28703300
H	4.47283500	3.49971800	-0.16636400
H	5.36996400	1.90147000	-1.83128000
H	4.38906000	-0.35045600	-2.04744000
H	0.34471900	2.18329400	1.74108500
H	2.58538100	-1.91999600	-2.49075600

int13m

Sb	0.50788400	-1.44954700	-0.05132500
S	3.56073900	-0.68043900	0.00902500
O	2.40913900	-0.76070900	-0.98294400
F	2.66072800	1.73684200	0.46744000
F	4.70986800	1.40727900	1.05830400
F	4.21009200	1.62952200	-1.03021000
N	0.19685600	0.21519400	1.01042200
O	3.06147200	-1.09577200	1.31944600
N	-0.53162600	-0.40814100	-1.41843900
C	-0.94363100	-0.87653100	-2.72522200
H	-0.58998000	-1.89725900	-2.88190200
H	-0.52783700	-0.25235800	-3.52281200
C	0.58406700	0.44129300	2.39230900

H	1.25608800	1.30087000	2.47146800
H	1.11957800	-0.42808400	2.77074300
C	-1.49337800	3.38726700	0.04351000
H	-1.71161200	4.36928000	0.44478200
C	-1.60933000	1.78634500	-1.75889200
H	-1.90649900	1.53791700	-2.77069700
C	-0.90183900	0.86047500	-0.99625300
C	-0.49808900	1.20298700	0.32394500
C	-1.90390100	3.04859300	-1.23644700
H	-2.44257900	3.76441100	-1.84509300
C	-0.79660300	2.46500500	0.82792400
H	-0.47757400	2.73601800	1.82618600
C	3.80120100	1.14780100	0.13045600
O	4.79931400	-1.21458600	-0.48280900
H	-2.03669600	-0.87912600	-2.81719900
H	-0.29876500	0.62063700	3.01541800
Si	-4.65698100	-0.24996700	0.39715300
C	-4.90412400	-0.06716300	-1.43526900
C	-3.09144300	-1.29074500	0.60792300
N	-2.14407500	-1.93492600	0.73022600
C	-6.00629100	-1.25056300	1.19797200
C	-4.32763300	1.35841000	1.25186300
H	-6.95860000	-0.71928200	1.11972300
H	-6.12018500	-2.22261900	0.71373700

H	-5.79867700	-1.41780700	2.25682300
H	-5.21552200	1.99500200	1.20426700
H	-4.07344300	1.20484600	2.30288700
H	-3.50040600	1.88497000	0.76929800
H	-5.84638600	0.45197100	-1.63112300
H	-4.09332900	0.52365000	-1.86650800
H	-4.94143700	-1.03769900	-1.93468600

TS13m

S	-4.60167900	-0.43240400	-0.76952700
O	-3.47106500	-1.37884400	-1.16297800
F	-4.21089900	0.08957000	1.80553700
F	-6.08626900	-0.86287000	1.35891800
F	-4.26548000	-2.01543200	1.33966500
O	-4.19444200	0.95338600	-0.81549000
C	-4.79865300	-0.82717200	1.05104900
O	-5.84280900	-0.83710300	-1.37895900
C	6.18682400	-2.01942000	1.14616500
C	5.98807600	-0.91780800	0.30629000
C	6.99055700	-0.50205400	-0.58175000
C	8.18701700	-1.19310300	-0.62162000
C	8.38276500	-2.29279800	0.21690900
C	7.38901300	-2.70829100	1.09863900
C	4.72423800	-0.22175800	0.37401600

O	4.46601400	0.74677800	-0.35036300
Si	2.96584900	1.87867700	-0.25035600
C	2.24663800	2.05562000	1.45548000
C	1.94754900	-0.25020900	-0.18016400
N	1.14569100	-1.08108600	-0.30227100
C	4.17016500	3.33357800	-0.37389600
C	2.02946600	1.97500300	-1.85560400
H	6.81003500	0.35462300	-1.21954200
H	8.97121400	-0.88445900	-1.30091400
H	9.32264700	-2.83070500	0.17996100
H	7.55365600	-3.56312200	1.74157700
H	5.39863600	-2.32939800	1.82366900
H	3.96849400	-0.56830400	1.08748400
H	3.59178900	4.26291200	-0.34554700
H	4.88076000	3.36669700	0.45708000
H	4.73809100	3.32594200	-1.30832800
H	1.94182900	3.01793500	-2.17045000
H	2.59271700	1.43520300	-2.62374300
H	1.04389200	1.51708400	-1.77542200
H	2.32223800	3.09064900	1.79611000
H	1.20175600	1.74293900	1.48032300
H	2.79263200	1.42739000	2.16795900
N	-1.22035100	0.65514300	-1.29903100
C	-1.33654500	0.81995800	1.07813800

C	-1.07096800	2.86099400	-0.20734700
H	-0.99373500	3.36839500	-1.16150800
C	-1.20239500	1.47849500	-0.17216900
C	-1.18481400	2.95485500	2.20021600
H	-1.18310000	3.52426500	3.12165700
C	-1.32601300	1.56538200	2.25163700
H	-1.44478400	1.06959700	3.20686200
C	-1.05806600	3.59806500	0.98055800
H	-0.96205800	4.67619200	0.93808000
N	-1.48932700	-0.56357900	1.01841800
C	-1.41265800	-1.33294500	2.24219300
H	-2.23594000	-1.07804000	2.91706000
H	-1.49534600	-2.39795600	2.01642000
C	-1.59189600	1.22768600	-2.58244400
H	-1.72717700	0.42974400	-3.31637500
H	-2.53750300	1.77017700	-2.49039000
Sb	-1.30150800	-1.30054500	-0.84218800
H	-0.81844900	1.90252700	-2.96700900
H	-0.46204700	-1.15850600	2.76165400

int23m

C	-5.34563600	-1.61815500	-0.23639700
C	-4.04290700	-1.28623400	-0.60793400
C	-2.96524400	-1.93022500	-0.01200900

C	-3.19158400	-2.90122700	0.96002800
C	-4.48812500	-3.22957100	1.33275400
C	-5.56802400	-2.58659500	0.73154100
C	-3.88451700	-0.16016400	-1.61982100
O	-4.38295100	1.06119500	-1.16491600
Si	-3.83767000	2.00332800	0.11863800
C	-2.32372600	2.94059100	-0.43020200
C	-2.47270400	-0.03425900	-2.06359800
N	-1.38236900	0.06859300	-2.40621300
C	-5.26377800	3.15181500	0.43213900
C	-3.43394100	0.96858100	1.60820800
H	-1.94831300	-1.65890300	-0.28022500
H	-2.34974900	-3.39047700	1.43518400
H	-4.66007900	-3.98296000	2.09180900
H	-6.58105200	-2.84053100	1.01901600
H	-6.18000400	-1.09949200	-0.69664700
H	-4.45124900	-0.41772000	-2.52136500
H	-6.14691800	2.59664500	0.75667900
H	-5.01331800	3.87538800	1.21222400
H	-5.52419700	3.70553900	-0.47275800
H	-3.24659100	1.63175800	2.45862300
H	-4.24523400	0.28593300	1.87503800
H	-2.52365600	0.37990300	1.46322500
H	-1.99222500	3.60086800	0.37744700

H	-1.49984100	2.25976700	-0.66150900
H	-2.52819100	3.55330400	-1.31194700
S	4.27283200	-0.84892800	-0.05656400
O	3.45858500	-0.24485700	-1.20903500
F	3.21948500	0.97902700	1.49004200
F	5.20487000	0.35260800	2.06218700
F	4.92792800	1.65369000	0.36158100
O	3.49446600	-1.81087200	0.68962700
C	4.41825900	0.63131800	1.03658500
O	5.60997400	-1.16561600	-0.47819400
N	0.62239100	-1.28020400	-0.26220800
C	0.44805700	0.84133400	0.80399600
C	-0.10663100	-1.13691400	2.09498800
H	-0.17868300	-2.21364100	2.18342100
C	0.30556300	-0.56533500	0.89615100
C	-0.25469900	1.05003600	3.10234700
H	-0.46603100	1.67771700	3.95931200
C	0.16248900	1.63759500	1.90743700
H	0.29027900	2.71135600	1.84616600
C	-0.38811900	-0.32631700	3.19571300
H	-0.70226100	-0.78271500	4.12598700
N	0.92855900	1.31568700	-0.41920100
C	1.35970200	2.69964500	-0.52608900
H	2.13114300	2.92448900	0.21776300

H	1.77992900	2.87994600	-1.51761700
C	0.70388500	-2.73140300	-0.20152600
H	1.01342400	-3.12317800	-1.17289800
H	1.44265900	-3.04386800	0.54076500
Sb	1.37041200	-0.13750800	-1.72681800
H	-0.27106700	-3.17125800	0.03581800
H	0.52114500	3.38893000	-0.38838200

int14m

Sb	0.08999800	-0.81031800	1.03559900
N	-0.49301600	-0.03657300	-0.70466100
N	-0.91997200	0.76945000	1.73795400
C	-1.28850100	1.09467300	-0.57763300
C	-1.85018000	1.79958400	-1.64151300
C	-1.50368200	1.55029500	0.75037800
C	-1.06675700	1.14726100	3.13137400
C	-0.28141300	-0.60442100	-2.02849300
C	-2.24113500	2.71052900	0.97411700
C	-2.78246700	3.41099500	-0.10284700
C	-2.59435600	2.95419600	-1.40062500
Sb	3.39800500	-0.03823200	-0.35312100
F	2.37119000	0.87267500	-1.63107100
F	2.15481000	-1.50842800	-0.53772600
F	2.03188300	0.49798200	0.97637600

F	4.21214600	-0.99259000	1.03310800
F	4.54830800	-0.72640800	-1.64298800
F	4.39359400	1.48807400	0.02175500
H	0.34175700	-1.49284300	-1.95369500
H	-1.24002000	-0.87754100	-2.48430400
H	-2.12252900	1.17372300	3.42093800
H	-0.55860300	0.42010800	3.76720700
H	-1.67435700	1.47213200	-2.65837100
H	-3.00973600	3.50281500	-2.23683000
H	-3.35040800	4.31470500	0.08014600
H	-2.38773100	3.07231500	1.98399800
H	-0.62499100	2.12977700	3.32273400
H	0.23958000	0.11202100	-2.66748300
C	-3.32553000	-1.52595500	0.33198000
N	-2.36733900	-1.88829800	0.86006400
Si	-4.90006600	-0.93827700	-0.54956100
C	-5.30417200	0.70948200	0.19040400
H	-4.50359600	1.42570700	-0.01100300
H	-6.22881500	1.09651200	-0.24672600
H	-5.44228200	0.63805300	1.27139900
C	-4.46612200	-0.85070300	-2.35261600
H	-4.06844700	-1.79989700	-2.71799800
H	-5.36099000	-0.61196800	-2.93404300
H	-3.72726100	-0.06580800	-2.52681200

C	-6.16430600	-2.25117100	-0.17946300
H	-6.33790300	-2.34277700	0.89460200
H	-7.11446100	-1.99268700	-0.65455400
H	-5.84978400	-3.22480300	-0.56070200

TS14m

C	-6.21251400	-2.98294600	-0.39291900
C	-6.28855000	-1.60124800	-0.17789100
C	-7.47248800	-1.01060700	0.28926900
C	-8.57325300	-1.80883400	0.53554500
C	-8.49452000	-3.18694200	0.32005900
C	-7.32086000	-3.77627100	-0.14161900
C	-5.11736600	-0.80525200	-0.44494500
O	-5.10123700	0.42312500	-0.27241900
Si	-3.71866300	1.59777600	-0.63644500
C	-2.62835600	1.05968400	-2.05104200
C	-2.47350000	-0.21693900	0.40360000
N	-1.46041800	-0.66861200	0.75156100
C	-4.94111700	2.78719000	-1.43482000
C	-3.11777100	2.45841800	0.89528000
H	-7.50376600	0.06041600	0.44760600
H	-9.49464800	-1.36956500	0.89556800
H	-9.36110800	-3.80708200	0.51643700
H	-7.27409700	-4.84548700	-0.30175300

H	-5.28740000	-3.42291500	-0.74921900
H	-4.21477300	-1.30364200	-0.80992300
H	-4.39627400	3.68566300	-1.74290600
H	-5.41848100	2.37073700	-2.32616600
H	-5.72441700	3.09936800	-0.73910300
H	-3.43257700	3.50371200	0.89875500
H	-3.48586600	1.96372900	1.79515900
H	-2.02641200	2.41193300	0.90705400
H	-2.63419200	1.82256300	-2.83337200
H	-1.60788700	0.88989400	-1.70940900
H	-2.99036800	0.12441200	-2.49130300
Sb	0.95436000	-0.53314900	0.83461000
N	0.88329000	0.67085100	-0.76750100
N	0.70186800	1.21889400	1.78437700
C	0.60722300	2.00056100	-0.45151500
C	0.39637500	3.01209900	-1.38313900
C	0.53458000	2.30311200	0.93470600
C	0.60650700	1.41062400	3.21648600
C	1.12830900	0.31335400	-2.15903400
C	0.28702200	3.60984700	1.34385600
C	0.07207500	4.61178200	0.39560600
C	0.12024600	4.31383400	-0.95687600
Sb	4.48410700	-1.05086800	-0.30516400
F	4.13381100	0.36148300	-1.49272600

F	2.77926600	-1.79935600	-0.81176100
F	3.37110100	-0.12233600	1.00441500
F	4.65246900	-2.43737300	0.94481400
F	5.37517700	-2.02426800	-1.62431900
F	6.01273200	-0.20208200	0.34296300
H	1.33961800	-0.75123100	-2.23360500
H	0.25802500	0.54185900	-2.78409500
H	-0.37134600	1.82202500	3.49449600
H	0.72873500	0.45381500	3.72789400
H	0.46193400	2.79345800	-2.44144300
H	-0.03464200	5.09245200	-1.69370100
H	-0.12441600	5.62444100	0.72572300
H	0.25207700	3.84775500	2.39965700
H	1.38654000	2.08727600	3.58056300
H	1.99868500	0.85406500	-2.53827100

int24m

Sb	4.37387600	-0.58066200	-0.02996000
F	5.77313100	-0.61891400	-1.25432700
F	4.48533400	-2.41404500	0.31977500
F	3.05192600	-0.99608000	-1.37947300
F	2.73420000	-0.58847600	1.08360300
F	5.40744500	-0.16630800	1.45995900
F	4.01439000	1.22981500	-0.35969300

C	-6.34959800	-1.30302600	-0.23964500
C	-5.04835400	-1.67227700	-0.57552200
C	-4.44568700	-2.74686600	0.06931600
C	-5.13817400	-3.44465700	1.05461000
C	-6.43169700	-3.07132500	1.39621200
C	-7.03702000	-2.00033600	0.74509600
C	-4.35127800	-0.87403900	-1.67553500
O	-4.68673200	0.47609800	-1.66445700
Si	-4.14299700	1.63583600	-0.56519900
C	-2.65079600	2.46401200	-1.29112200
C	-2.87681000	-1.05728300	-1.60570500
N	-1.73563700	-1.16180100	-1.53651800
C	-5.57385600	2.80407500	-0.37947000
C	-3.69653700	0.81663600	1.04866600
H	-3.43233900	-3.04024400	-0.18254600
H	-4.66109700	-4.27656900	1.55808000
H	-6.96728200	-3.61167000	2.16708200
H	-8.04662000	-1.70669200	1.00565500
H	-6.80926300	-0.46106500	-0.74380700
H	-4.65293600	-1.27837400	-2.64877300
H	-6.43007100	2.30678100	0.08277600
H	-5.29723300	3.65533200	0.24779200
H	-5.88777200	3.19031400	-1.35201700
H	-3.34684400	1.59265000	1.73700300

H	-4.53828200	0.29272400	1.50717600
H	-2.87056400	0.11028700	0.91748800
H	-2.24693100	3.20242400	-0.59106400
H	-1.85557000	1.73840000	-1.48824200
H	-2.89292600	2.97227700	-2.22783400
N	-0.19209500	0.20085600	1.38252300
C	0.45026900	2.03283400	0.02514000
C	-0.63740500	2.51337300	2.14317400
H	-1.08576800	2.17625800	3.06976200
C	-0.14782700	1.58649100	1.22724600
C	0.06212500	4.31357000	0.69613800
H	0.15462300	5.37359800	0.49518200
C	0.55760400	3.39710600	-0.22763700
H	1.02931900	3.74429300	-1.13732200
C	-0.53763700	3.87624000	1.87062400
H	-0.91461800	4.59295600	2.58953300
N	0.88183200	1.02683100	-0.83800500
C	1.46435600	1.39720200	-2.12276600
H	1.71970100	0.49967600	-2.68267600
H	0.74698400	1.98631000	-2.70190200
C	-0.62142300	-0.35802800	2.65437700
H	-0.55859300	-1.44767400	2.61822300
H	0.01578600	-0.00527900	3.47102000
Sb	0.71992800	-0.80595600	-0.09057700

H	-1.65897700	-0.08854000	2.87334000
H	2.38101700	1.97151500	-1.97189700