Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Stannylene Cyanide and its Use as Cyanosilylation Catalyst

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CONTENTS

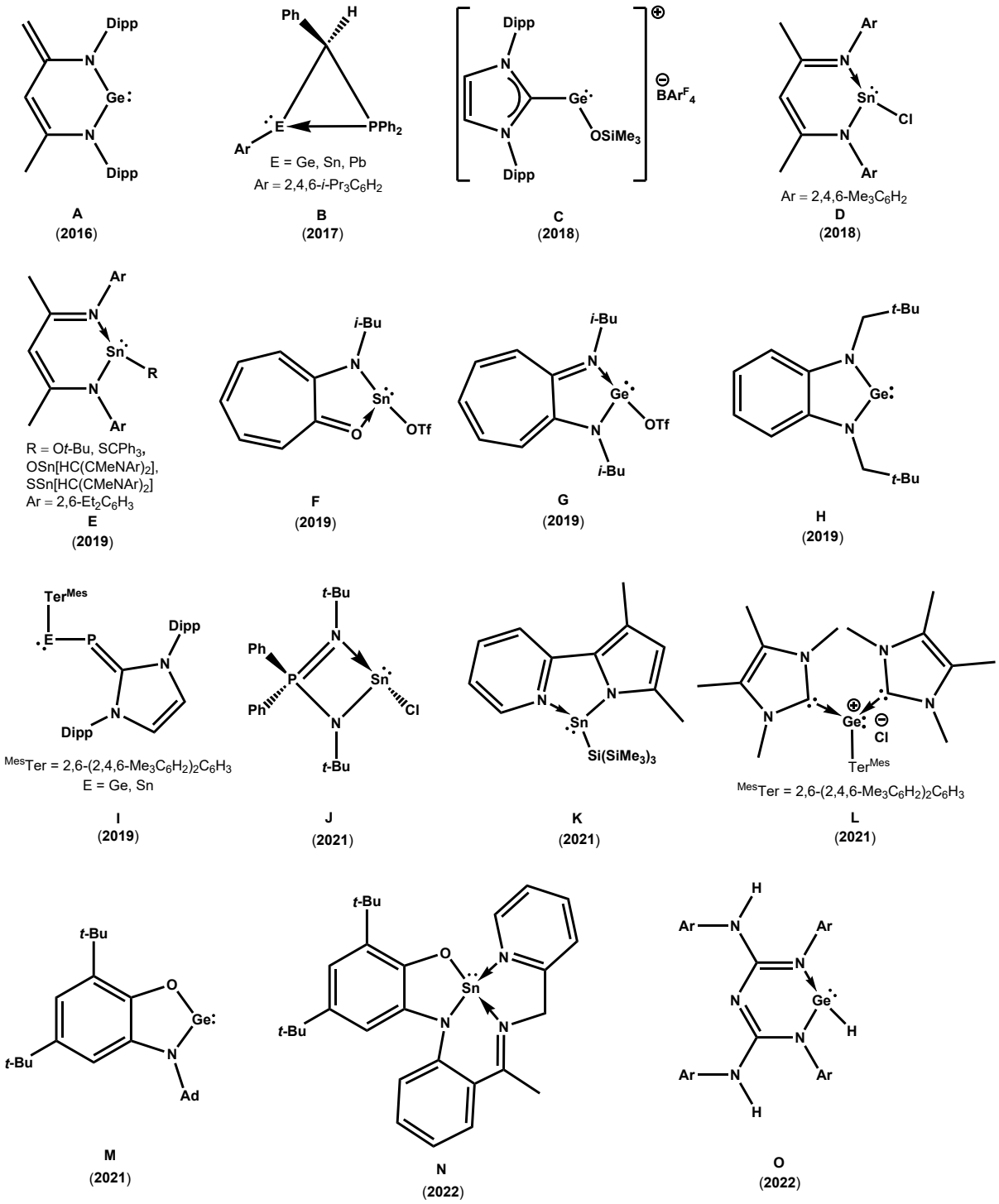


Chart S1. Low-valent main group catalysts for the hydroboration of carbonyl compounds.

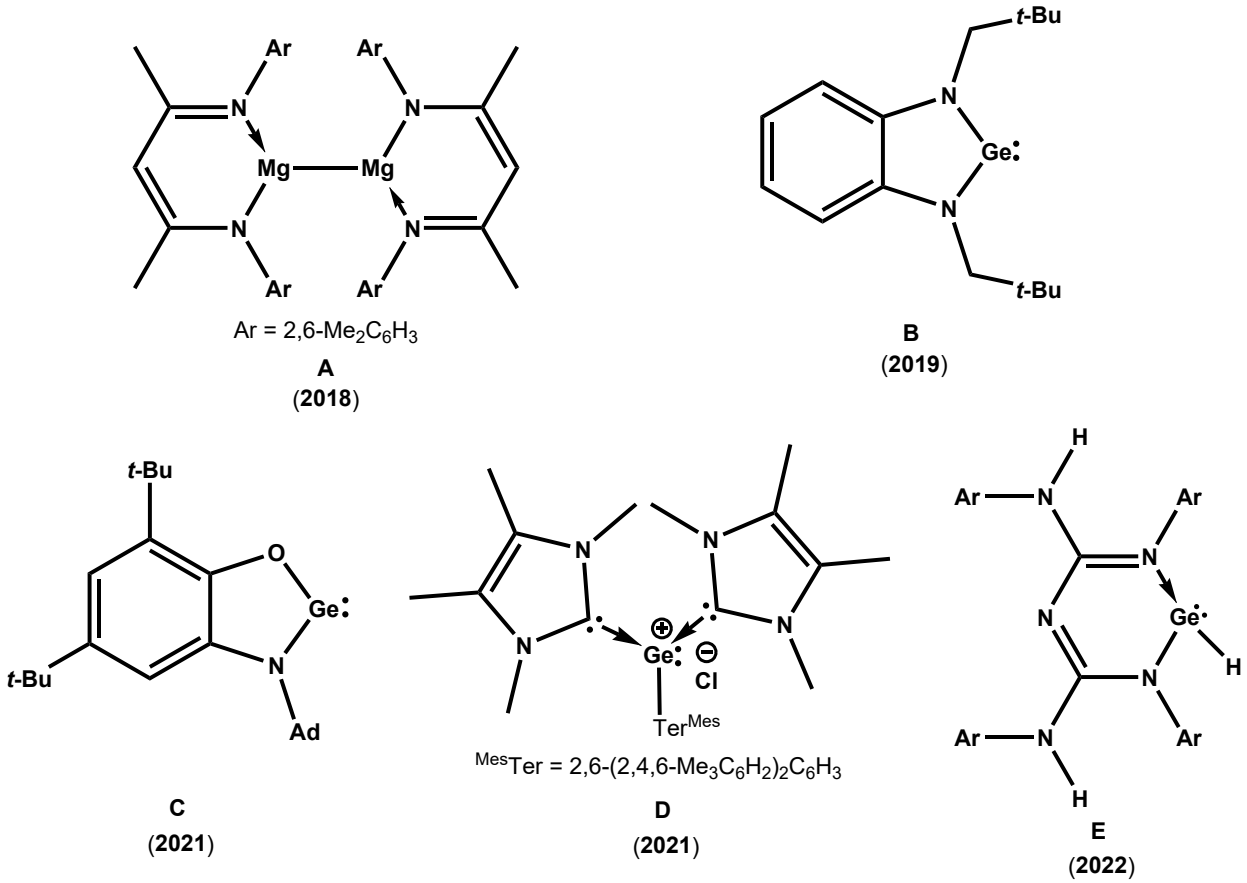


Chart S2. Low-valent main group catalysts for the cyanosilylation of carbonyl compounds.

NMR spectra of compounds 2-6

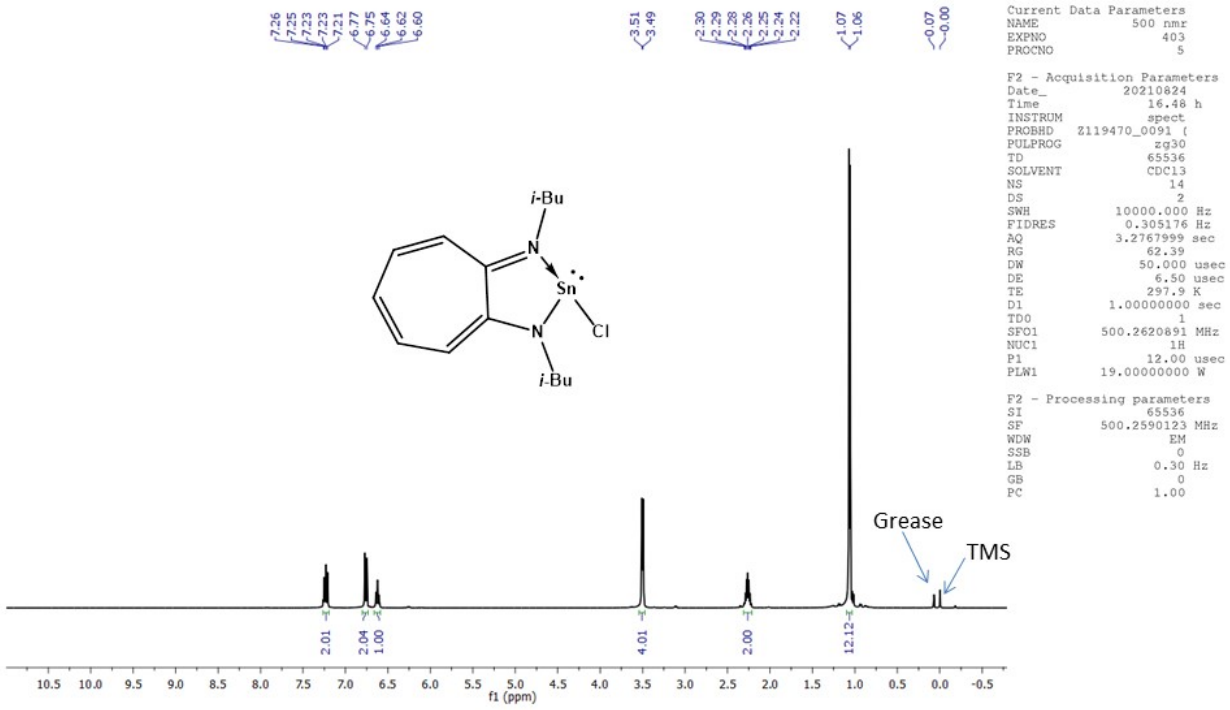


Figure S1. ^{1}H NMR spectrum of compound **2**.

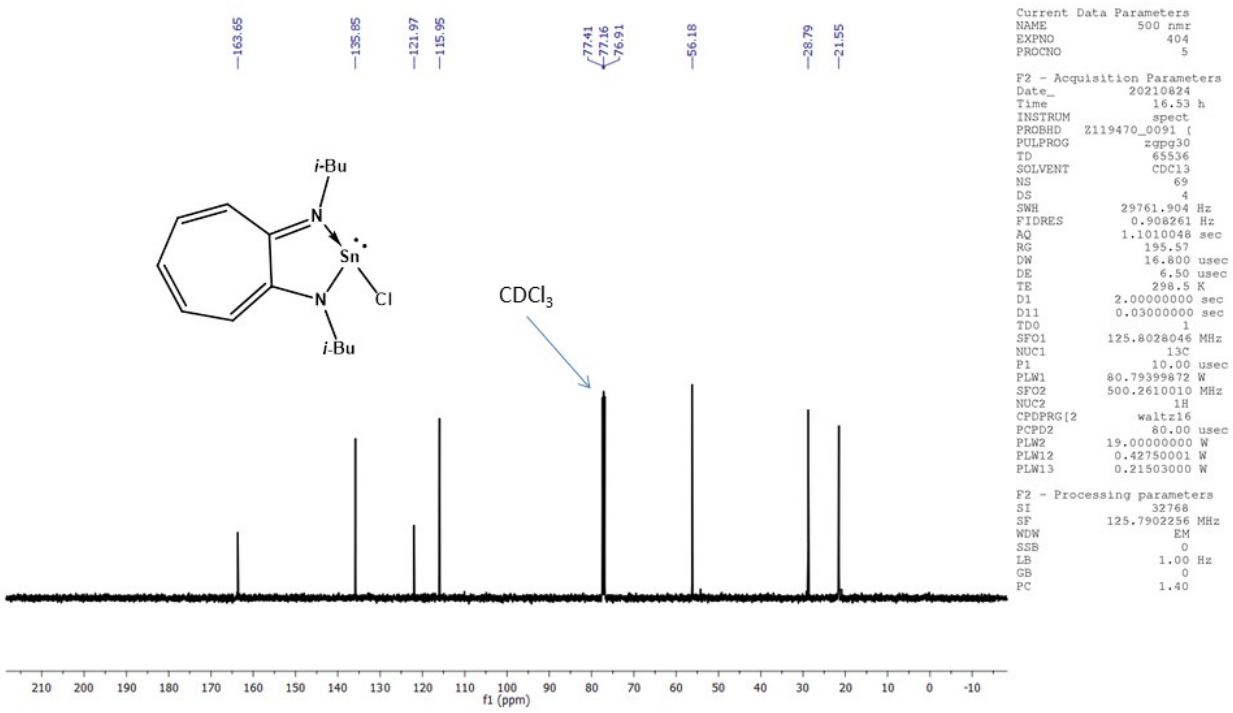


Figure S2. ^{13}C NMR spectrum of compound **2**.

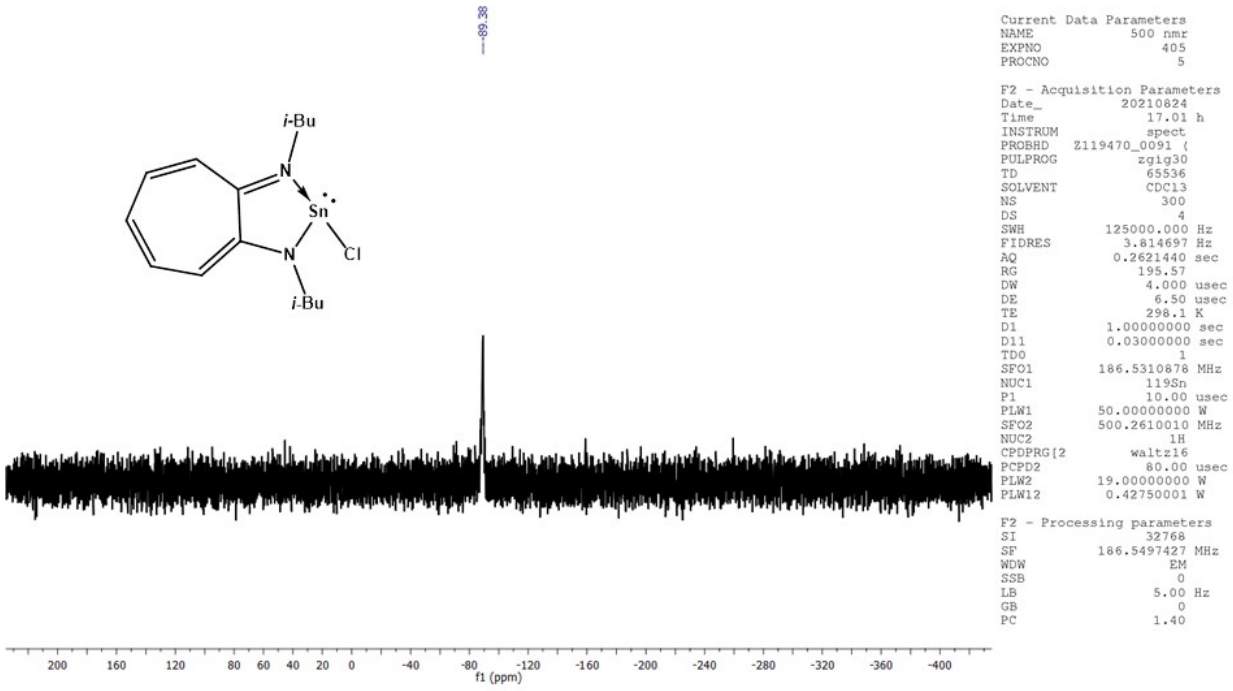


Figure S3. ^{119}Sn NMR spectrum of compound **2**.

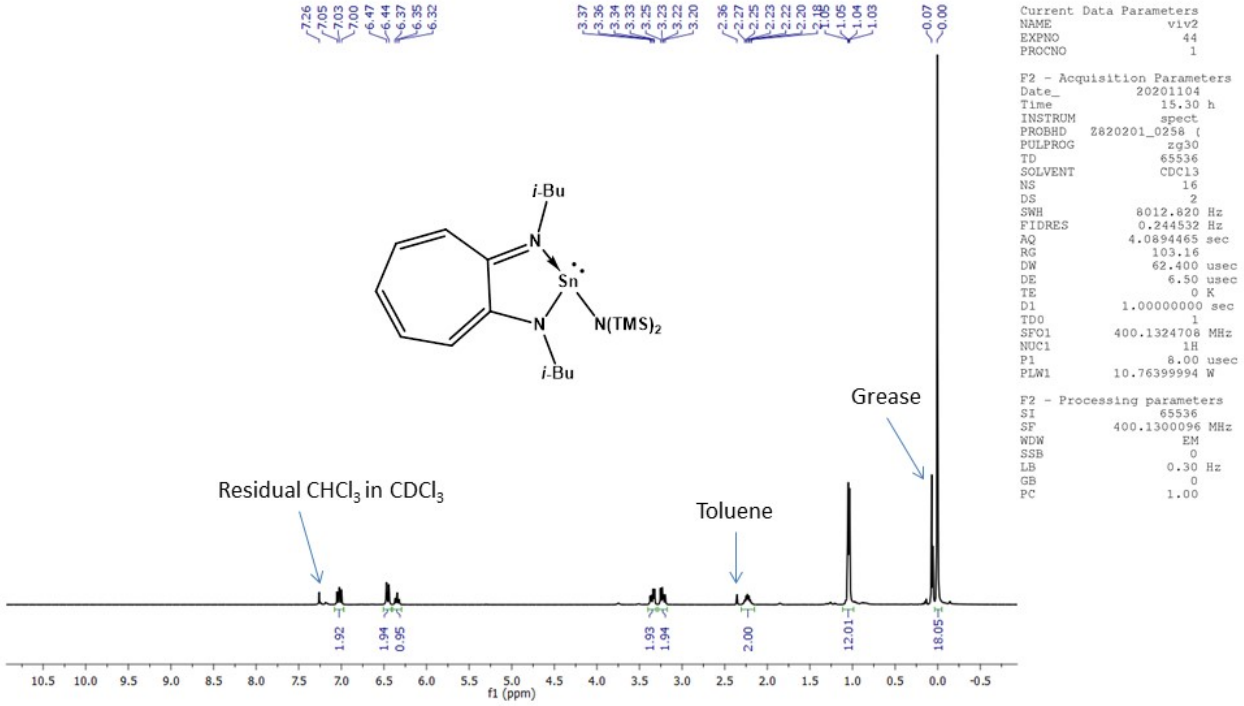


Figure S4. ^{1}H NMR spectrum of compound **3**.

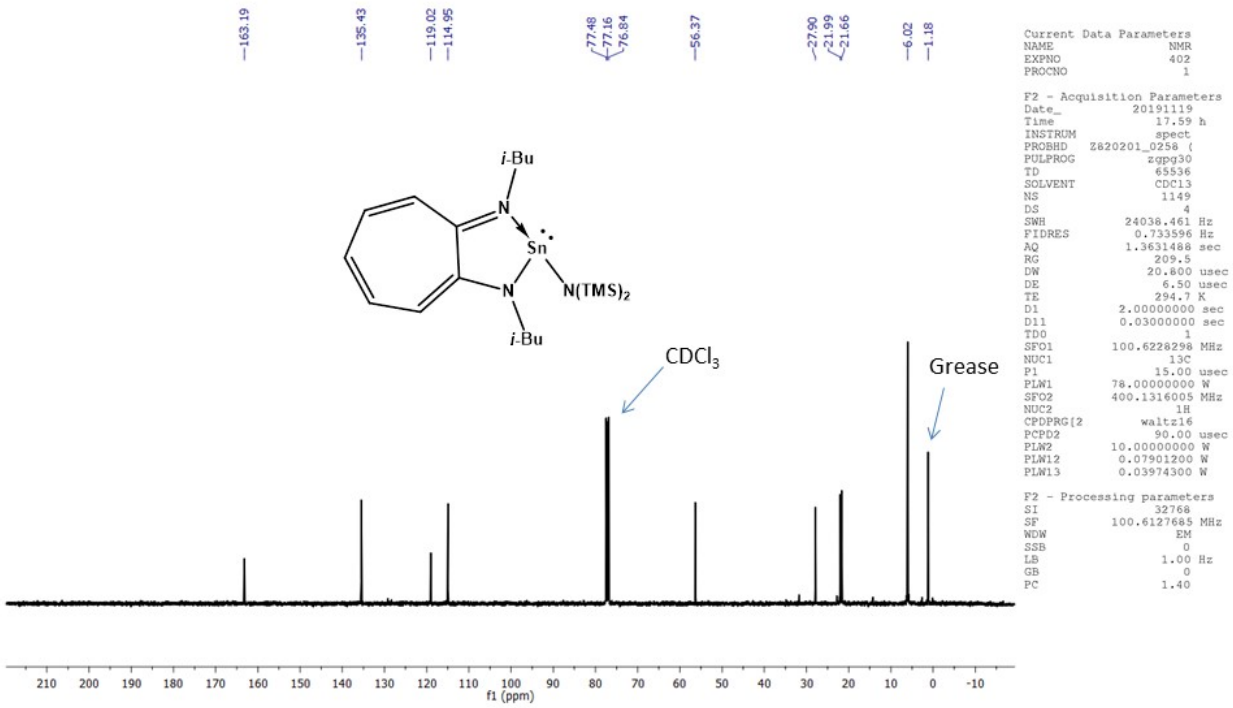


Figure S5. ^{13}C NMR spectrum of compound **3**.

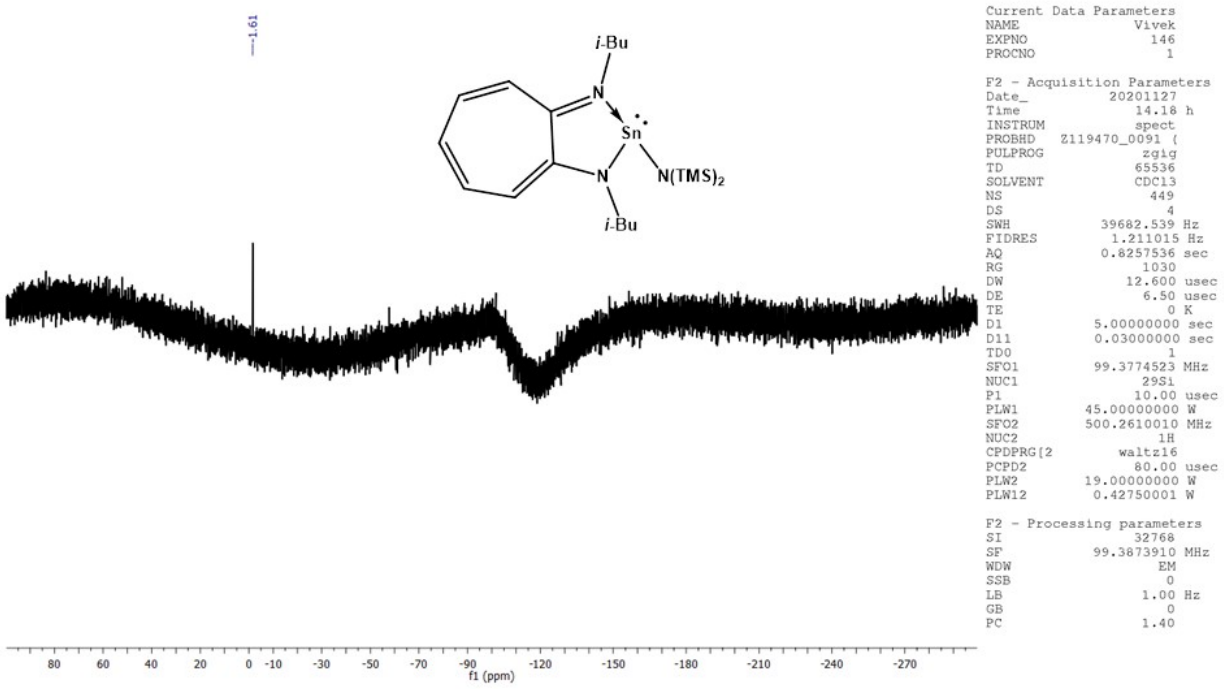


Figure S6. ^{29}Si NMR spectrum of compound **3**.

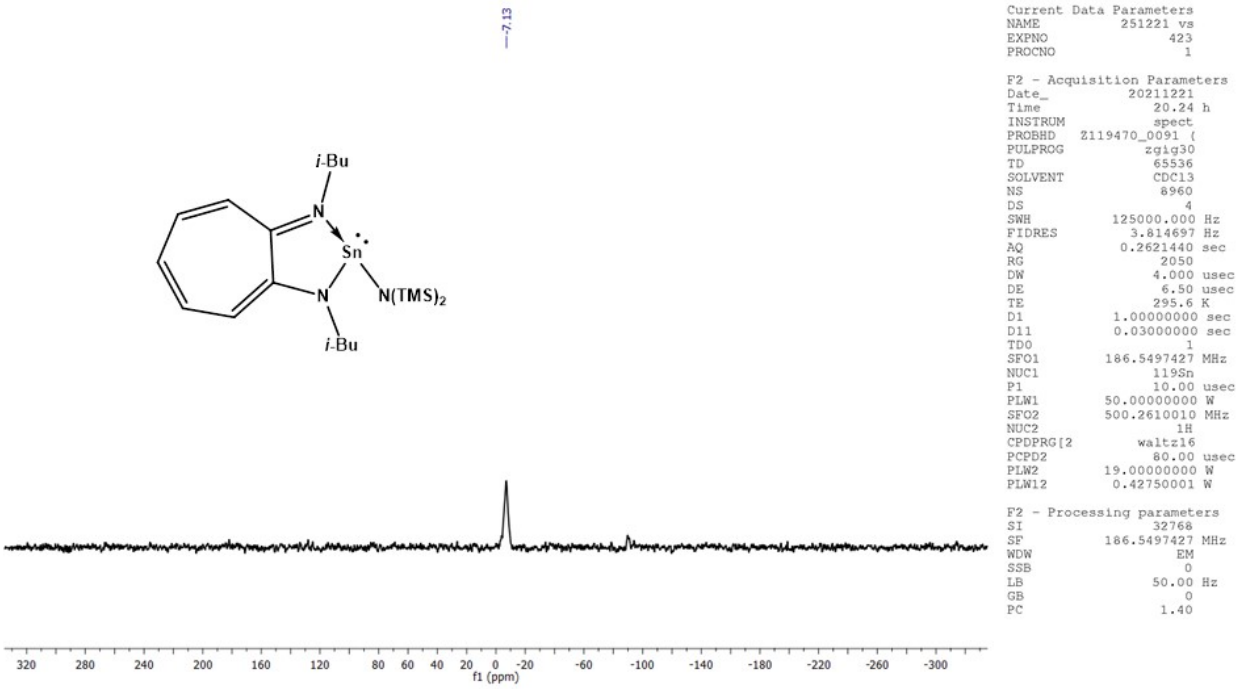


Figure S7. ^{119}Sn NMR spectrum of compound **3**.

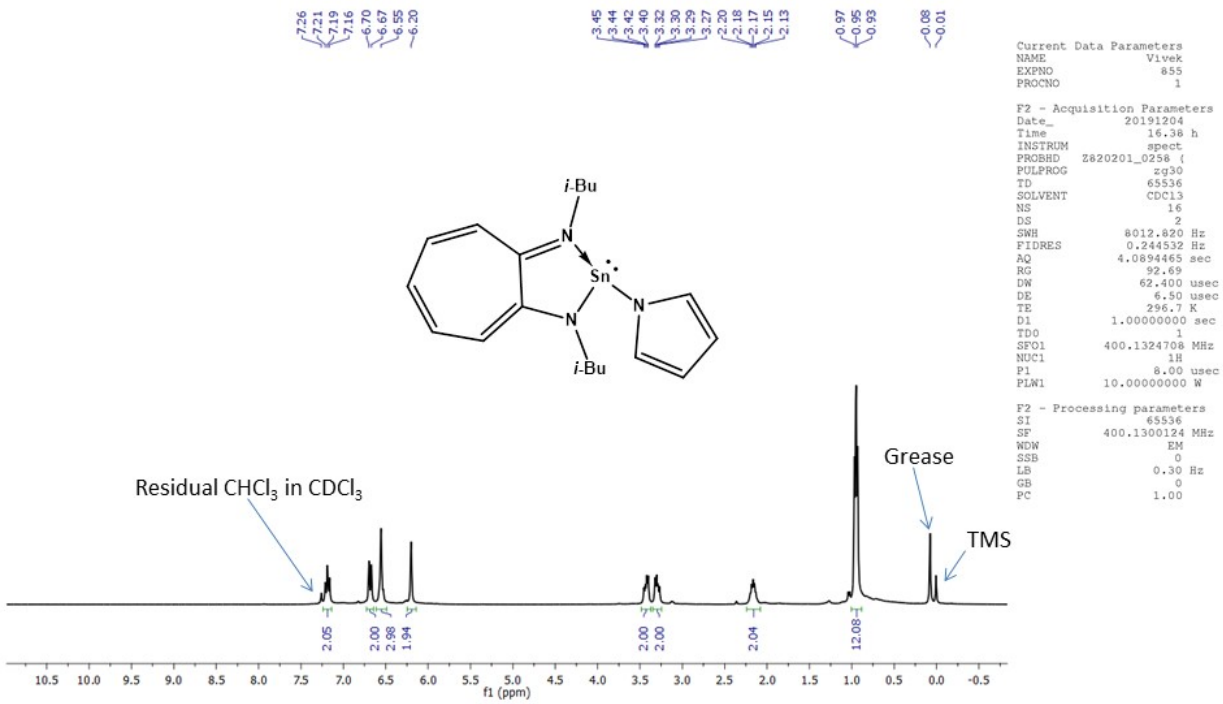


Figure S8. ^{1}H NMR spectrum of compound **4**.

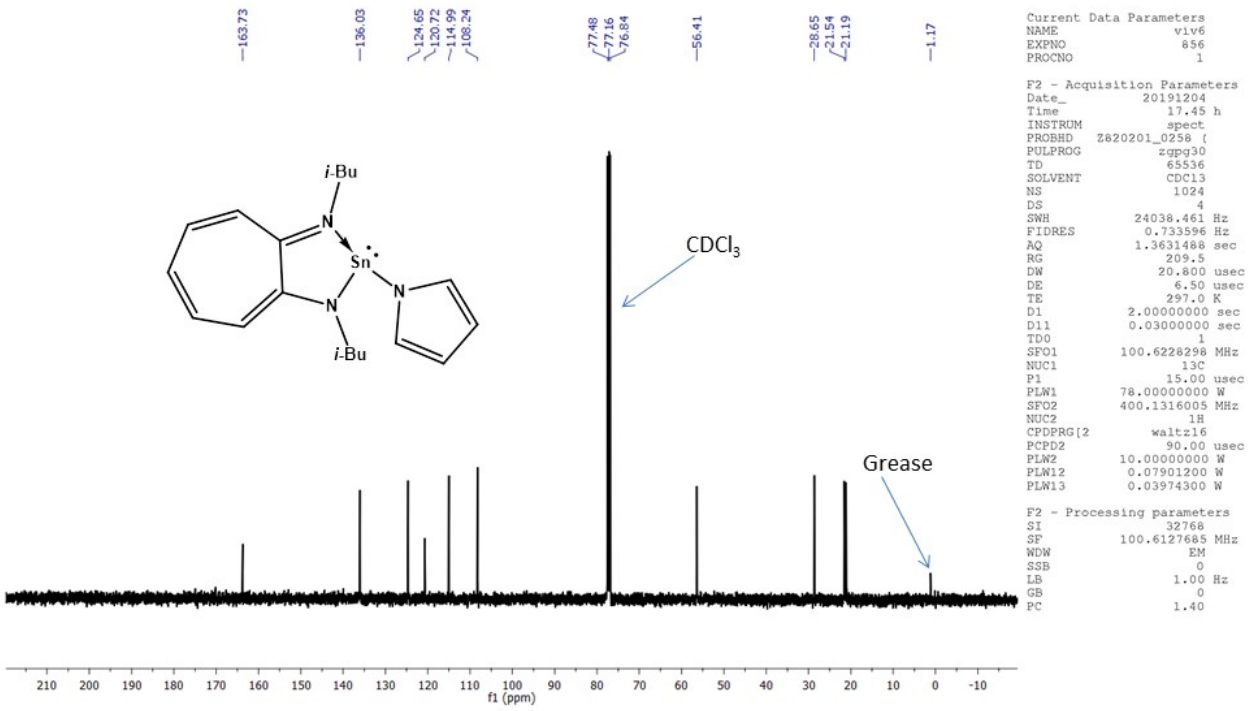


Figure S9. ^{13}C NMR spectrum of compound **4**.

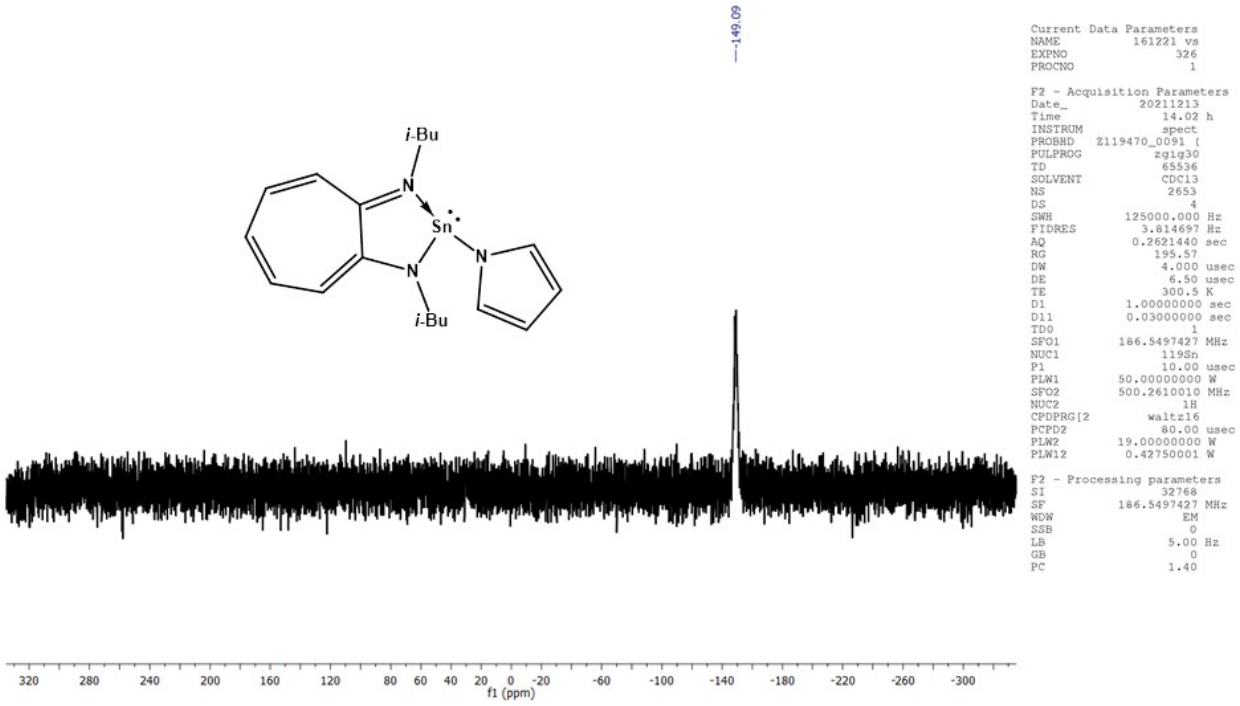


Figure S10. ^{119}Sn NMR spectrum of compound **4**.

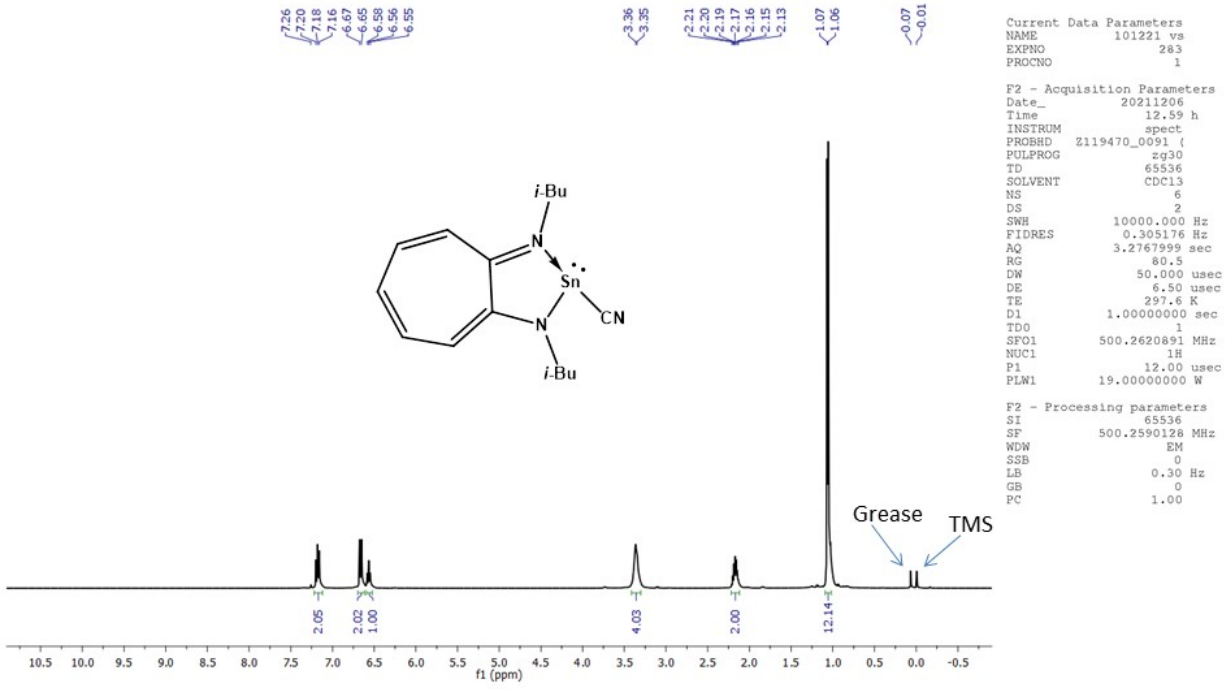


Figure S11. ^{1}H NMR spectrum of compound **5**.

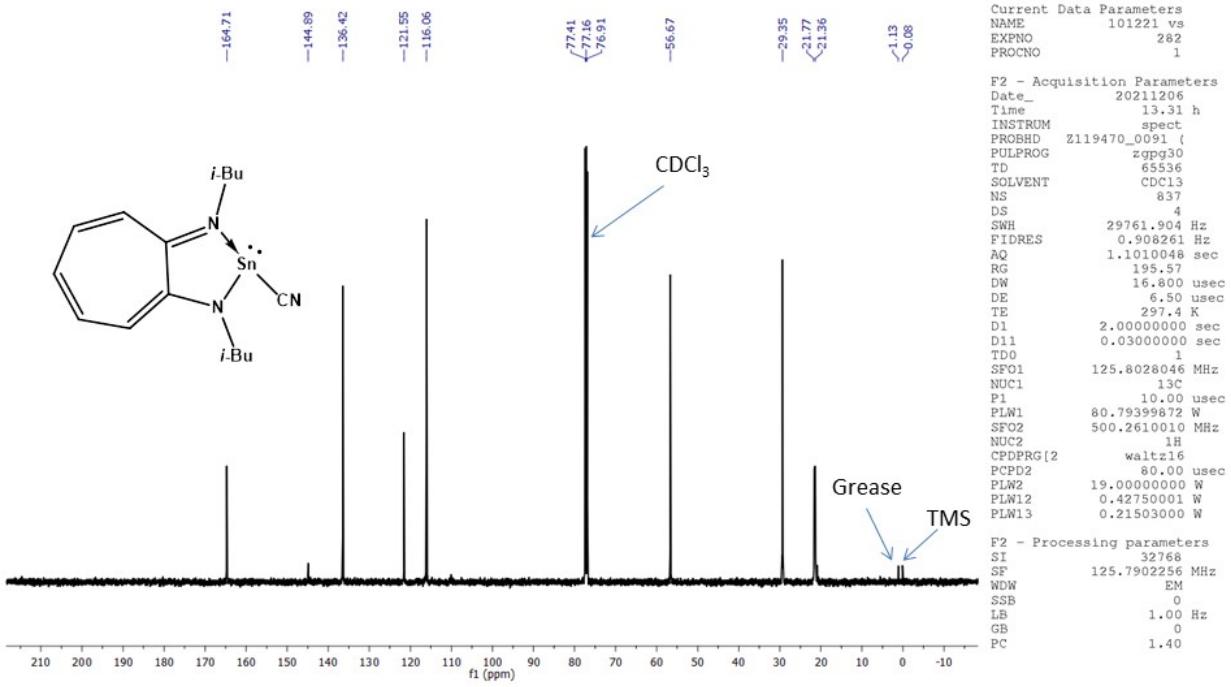


Figure S12. ^{13}C NMR spectrum of compound **5**.

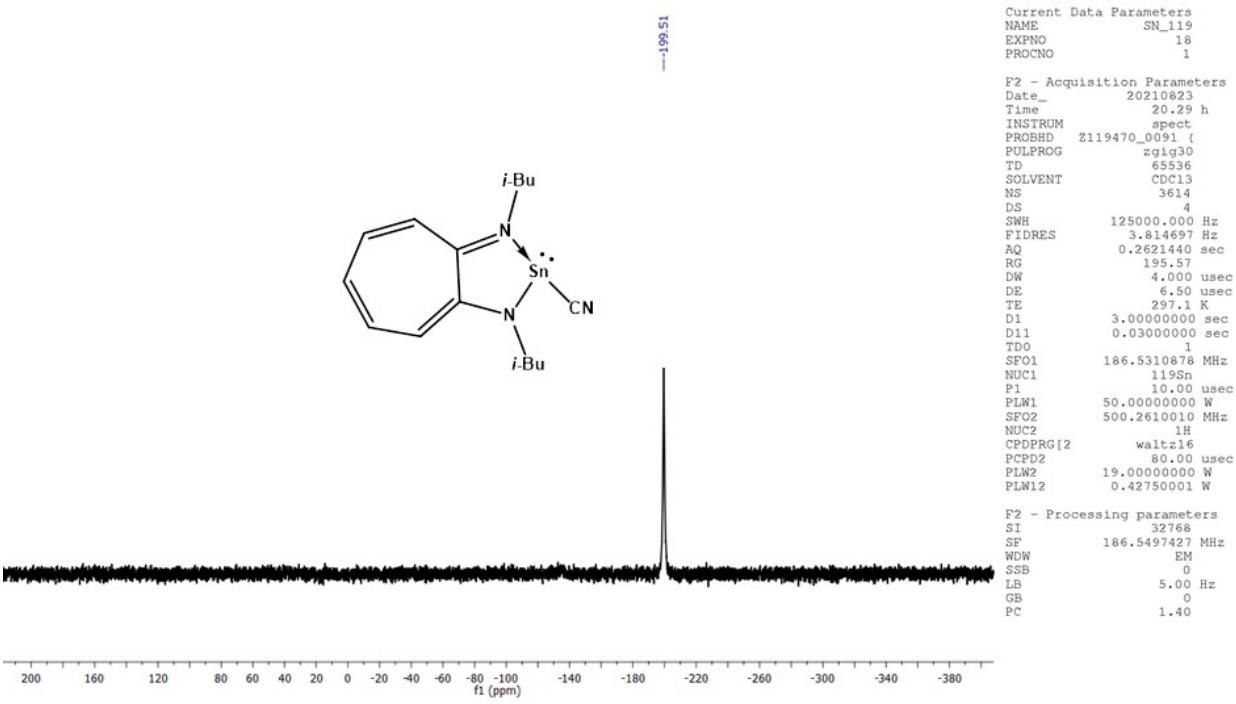


Figure S13. ^{119}Sn NMR spectrum of compound **5**.

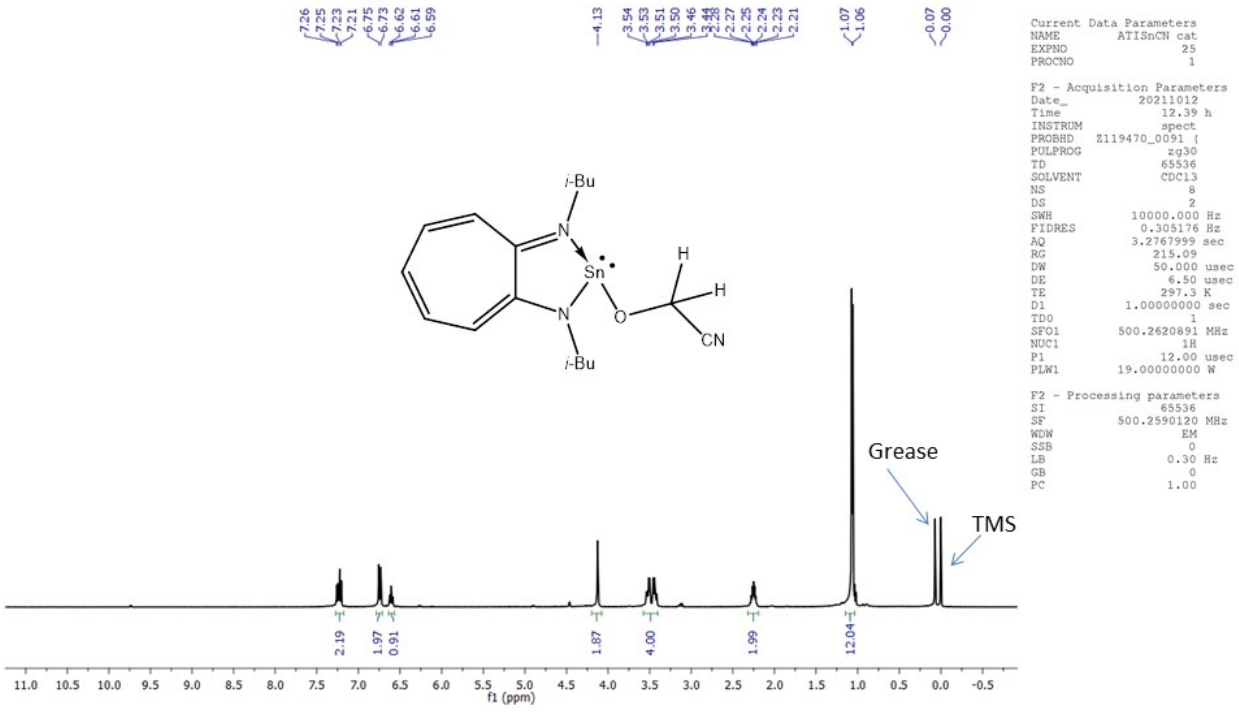


Figure S144. ^{1}H NMR spectrum of compound **6**.

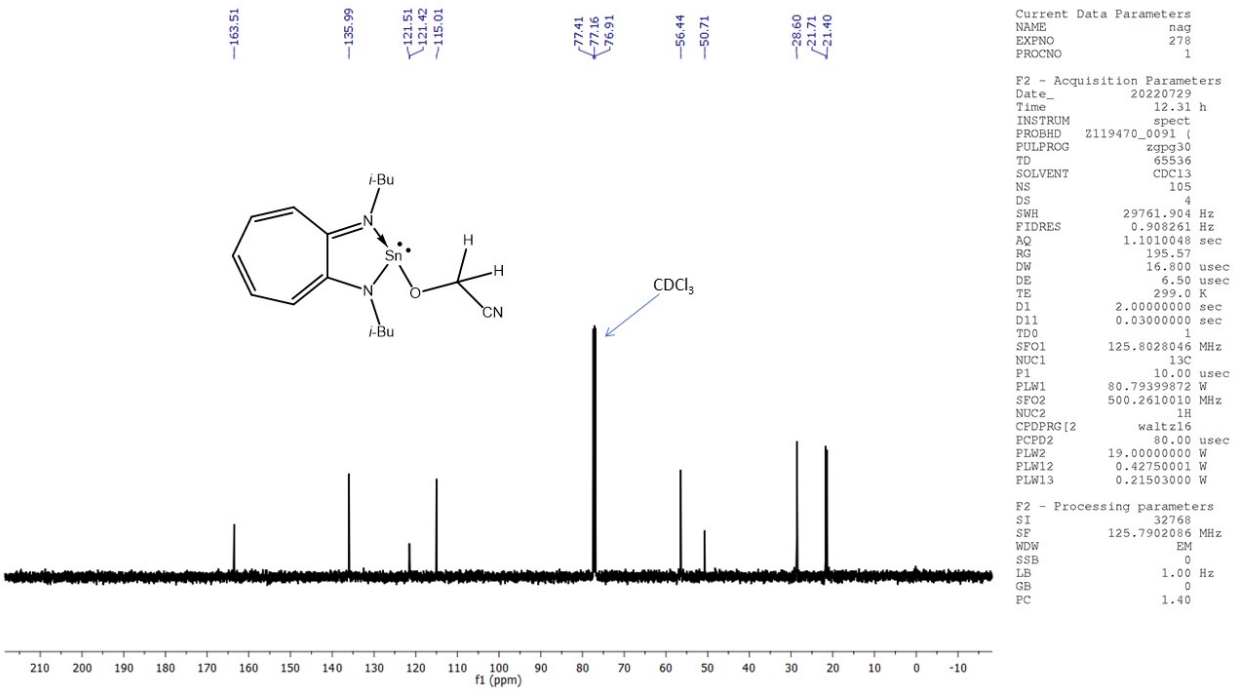


Figure S155. ^{13}C NMR spectrum of compound **6**.

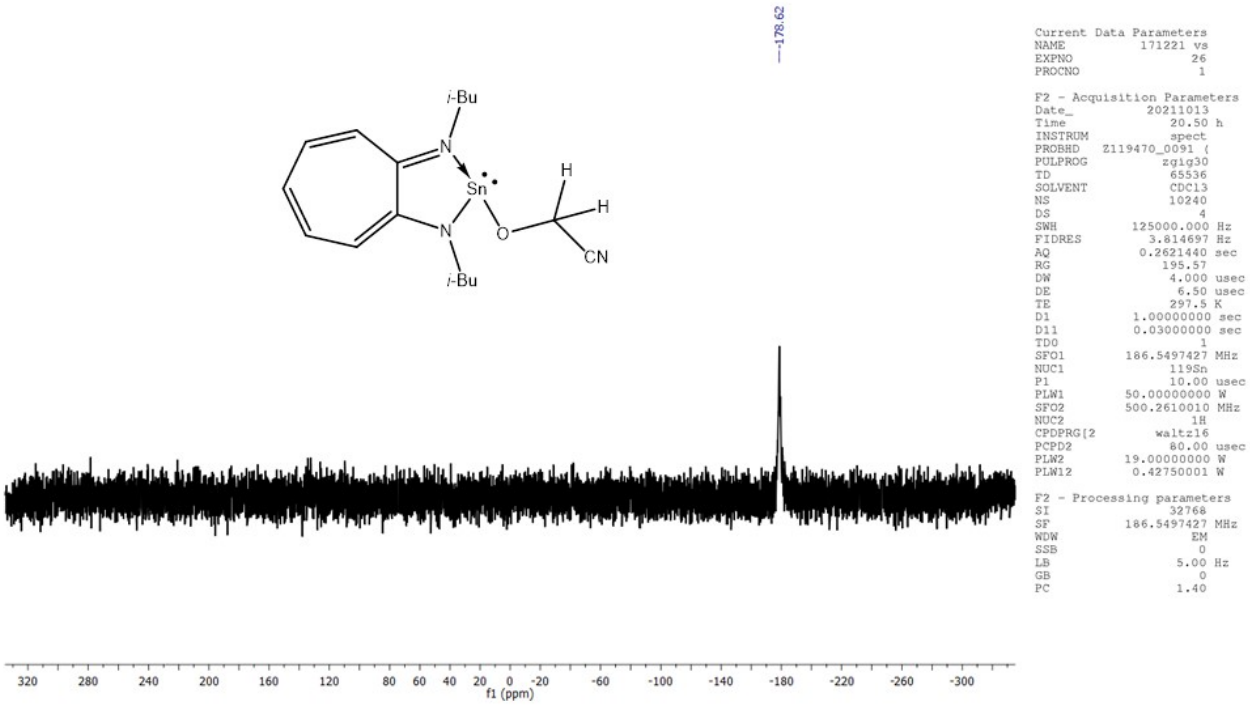


Figure S166. ^{119}Sn NMR spectrum of compound **6**.

IR spectrum of compound 5

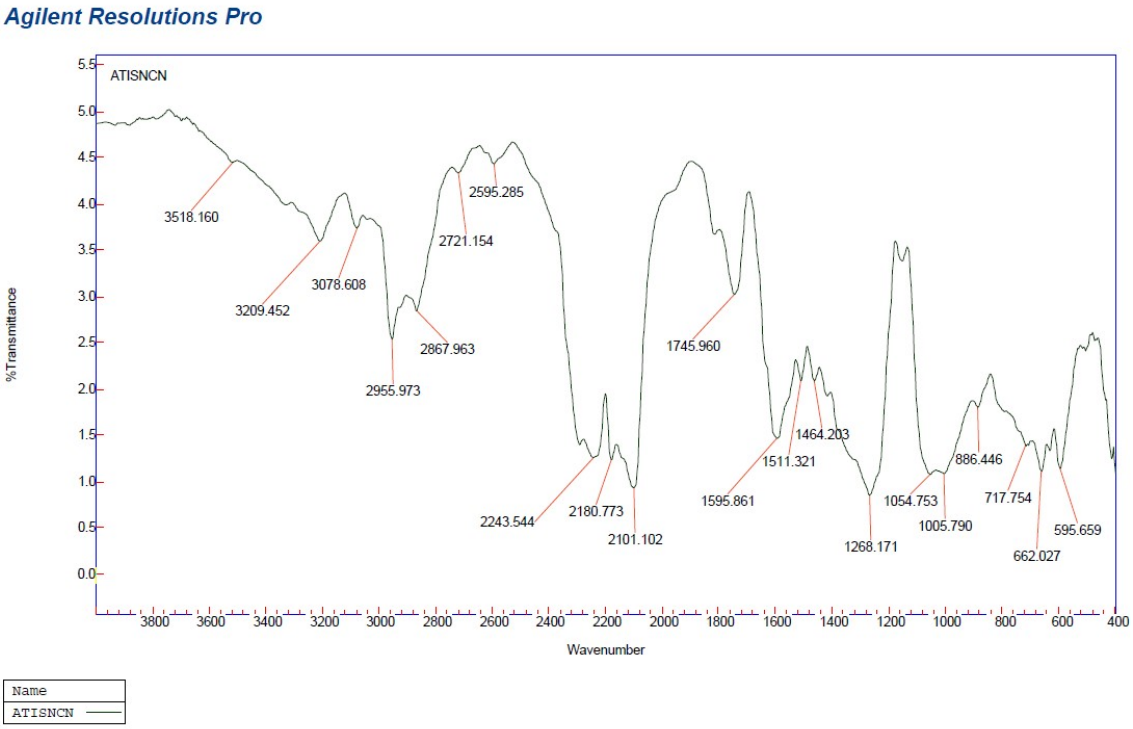


Figure S177. IR spectrum of compound **5**.

Table S1. Crystal data and structure refinement for compounds 2-4 and 6

	2	**3**	**4**	**6**
Empirical formula	$C_{15}H_{23}ClN_2Sn$	$C_{21}H_{41}N_3Si_2Sn$	$C_{19}H_{27}N_3Sn$	$C_{17}H_{25}N_3OSn$
Formula weight	385.49	510.461	416.16	812.22
Temperature, K	273(2)	100(2)	100(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	P-1	P-1	$Pbca$
Unit cell dimensions	a = 11.035(2) Å b = 11.668(2) Å c = 13.378(2) Å α = 90° β = 98.890(6)° γ = 90°	a = 8.6894(4) Å b = 11.1113(5) Å c = 15.0434(7) Å α = 96.817(3)° β = 105.219(2)° γ = 107.753(2)°	a = 9.766(2) Å b = 10.098(2) Å c = 10.208(2) Å α = 97.537(7)° β = 106.002(7)° γ = 96.018(7)°	a = 7.1880(8) Å b = 18.634(2) Å c = 27.924(3) Å α = 90° β = 90° γ = 90°
Volume, Å^3	1701.8(5)	1303.18(11)	948.8(3)	3740.2(7)
Z	4	2	2	4
Density (calculated), Mg/m^3	1.505	1.301	1.457	1.442
Absorption coefficient, mm^{-1}	1.649	1.083	1.350	1.372
F(000)	776.0	532.0	422.9	1648.0
Crystal size, mm^3	0.32 × 0.21 × 0.12	0.36 × 0.24 × 0.18	0.43 x 0.21 x 0.12	0.48 × 0.23 × 0.17

θ range for data collection, °	4.46 to 56.772	3.94 to 56.68	4.22 to 56.72	4.6 to 56.6
Limiting indices	-14 ≤ *h* ≤ 14, -15 ≤ *k* ≤ 15, -17 ≤ *l* ≤ 17	-11 ≤ *h* ≤ 11, -14 ≤ *k* ≤ 14, -20 ≤ *l* ≤ 20	-13 ≤ *h* ≤ 13, -13 ≤ *k* ≤ 13, -13 ≤ *l* ≤ 13	-9 ≤ *h* ≤ 9, -24 ≤ *k* ≤ 24, -37 ≤ *l* ≤ 37
Reflections collected	29101	33549	26574	81165
Independent reflections	4256 [R_{int} = 0.0943, R_{sigma} = 0.0776]	6526 [R_{int} = 0.0387, R_{sigma} = 0.0279]	4707 [R_{int} = 0.0548, R_{sigma} = 0.0357]	4656 [R_{int} = 0.0586, R_{sigma}= 0.0232]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4256/0/176	6526/0/254	4707/0/212	4656/0/203
Goodness-of-fit on F^2	0.983	1.055	1.036	1.060
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0444, wR_2 = 0.0637	R_1 = 0.0257, wR_2 = 0.0602	R_1 = 0.0250, wR_2 = 0.0703	R_1 = 0.0311, wR_2 = 0.0649
R indices (all data)	R_1 = 0.1299, wR_2 = 0.0795	R_1 = 0.0304, wR_2 = 0.0631	R_1 = 0.0260, wR_2 = 0.0717	R_1 = 0.0558, wR_2 = 0.0766
Largest diff. peak and hole, eÅ^{-3}	0.38 and -0.34	0.70 and -0.68	0.55 and -0.45	1.23 and -0.90

General procedure for the cyanosilylation of aldehydes using compound 5 as a catalyst

Aldehyde (1 mmol), TMSCN (1.1 mmol), and [(*i*-Bu)$_2$ATISnCN] (**5**) (0.1–2 mol%) were taken in a Schlenk flask. The reaction mixture was stirred at room temperature/50 °C for the required period (see table 2). The progress of the reaction was monitored by ^{1}H NMR spectroscopy; after the completion of the reaction, the cyanosilylated product was also characterized by ^{13}C NMR spectroscopic techniques.

^{1}H NMR spectra for the entries in Table 1

Entry 1

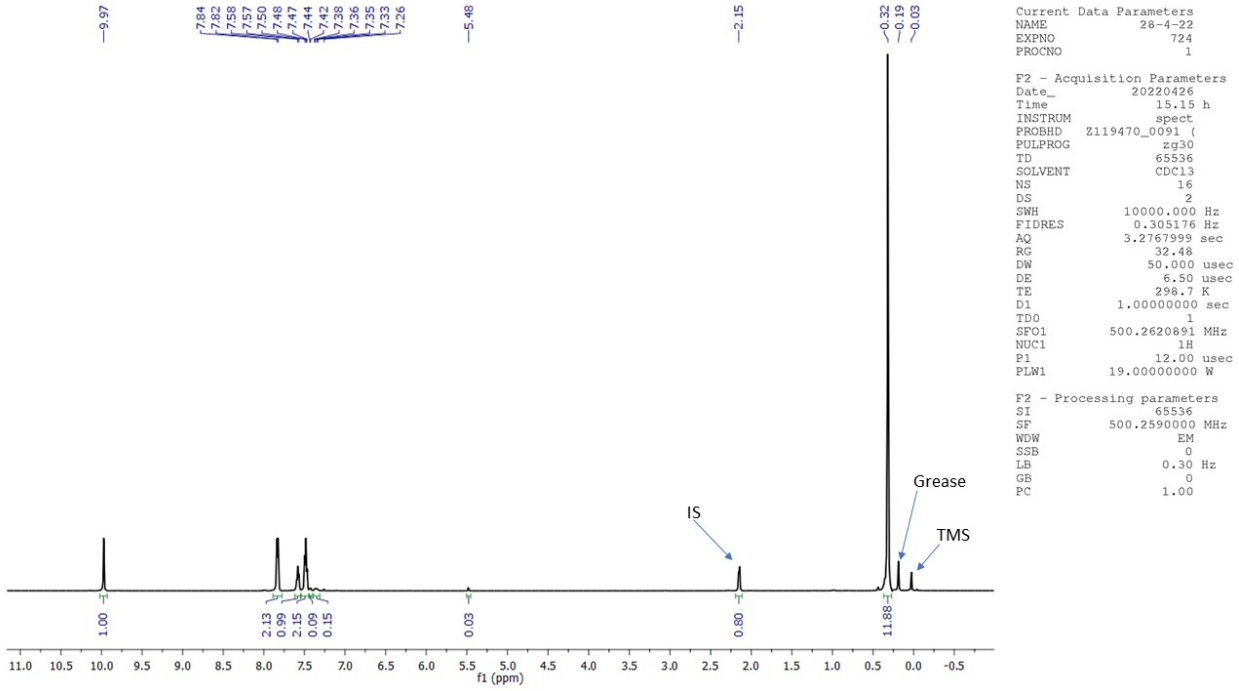


Figure S18. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN without a catalyst for 6 h at rt [IS (Internal standard) = hexamethyl benzene].

Entry 2

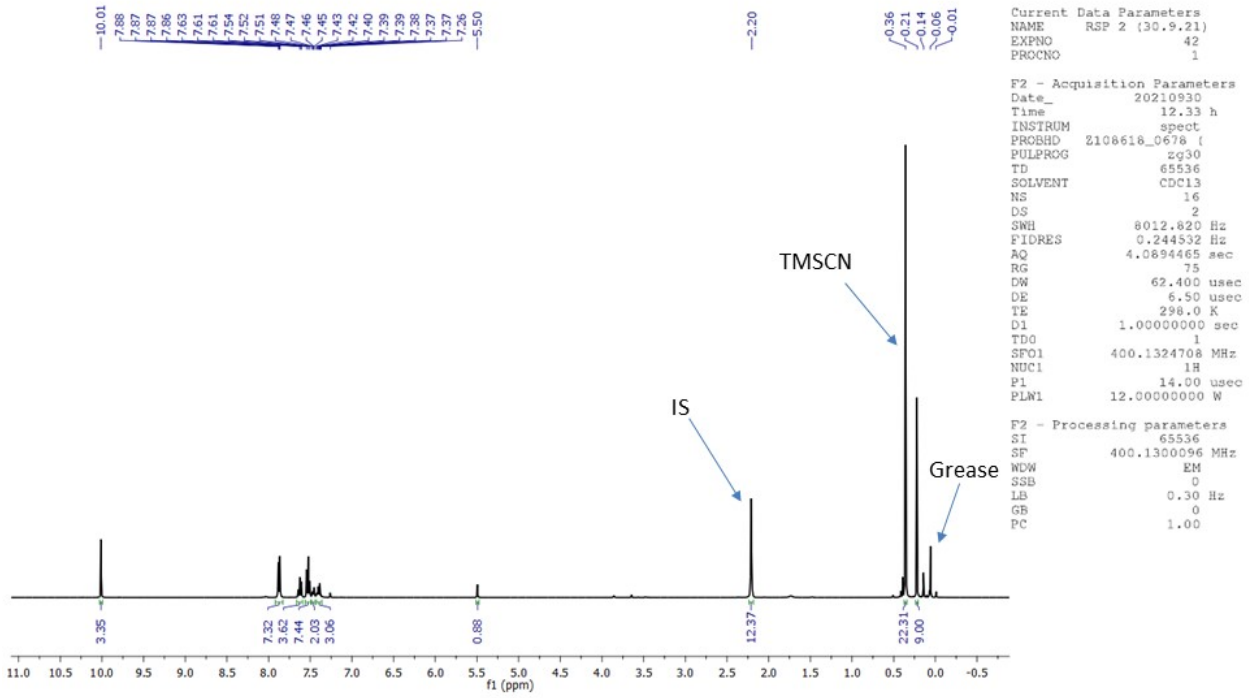


Figure S19. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN without a catalyst for 4 h at 50 °C.

Entry 3

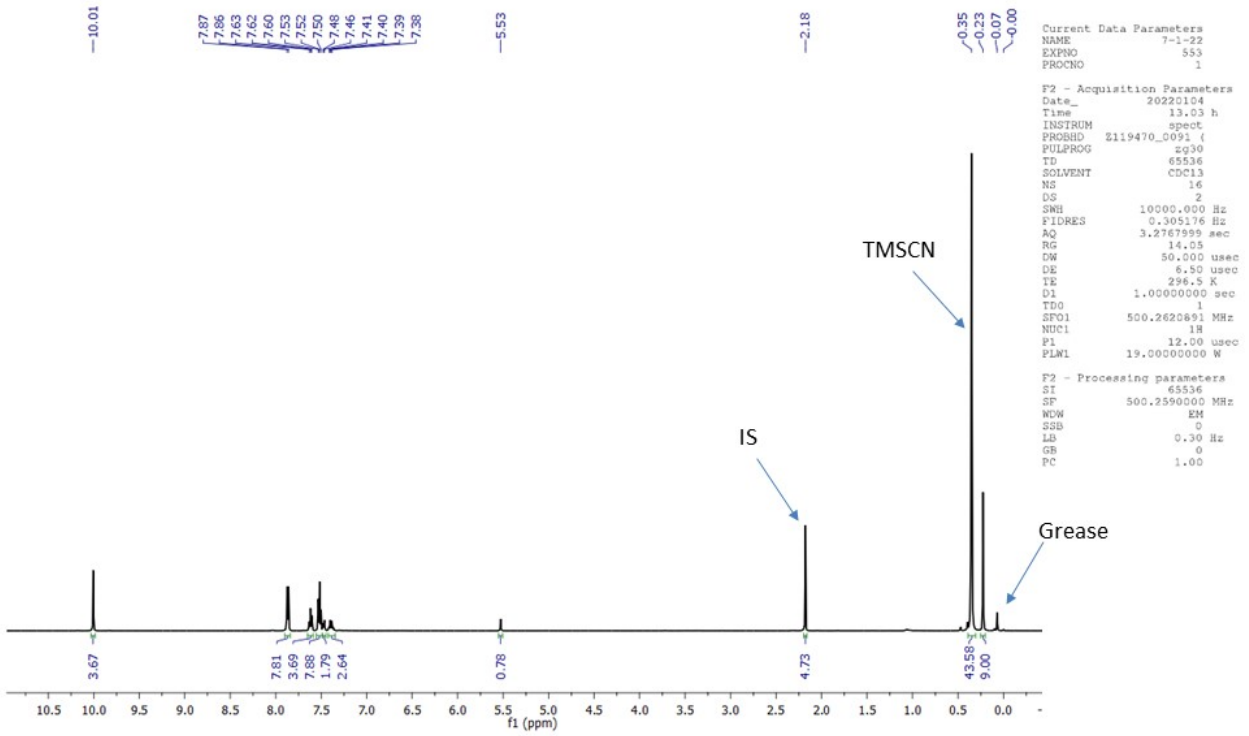


Figure S20. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 0.5 mol% for 0.33 h at rt.

Entry 4

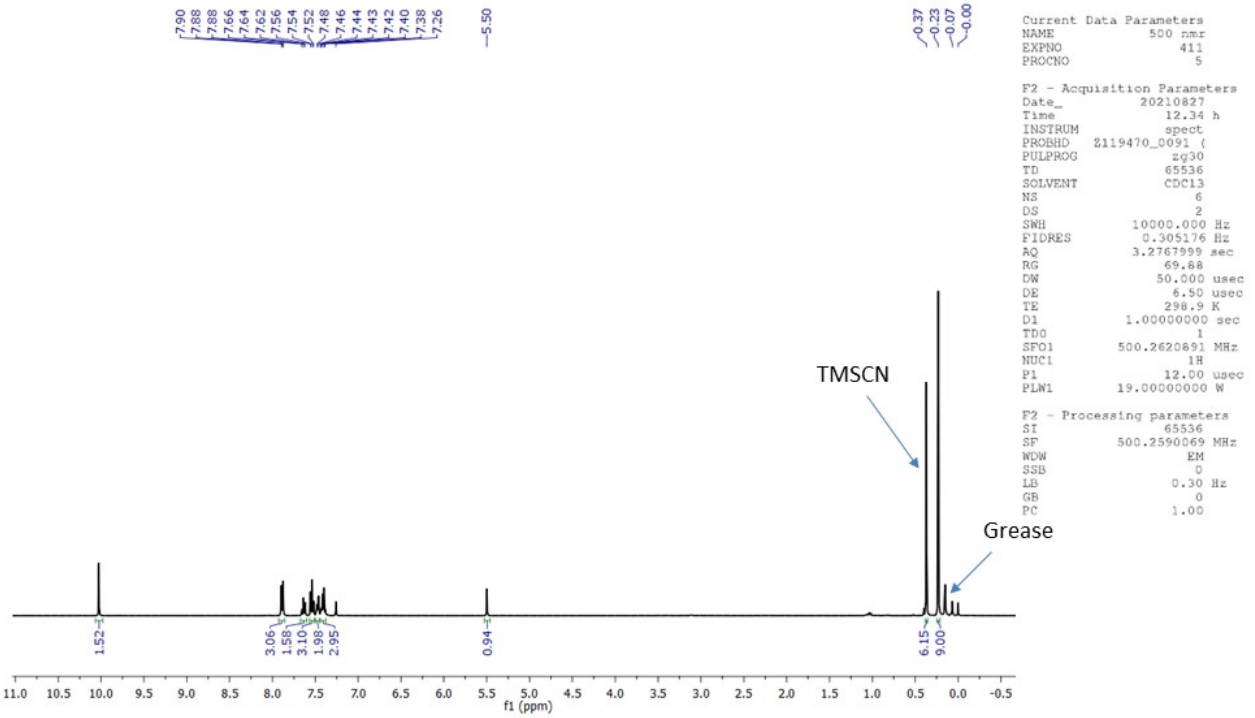


Figure S21. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 0.5 mol% for 1 h at rt.

Entry 5

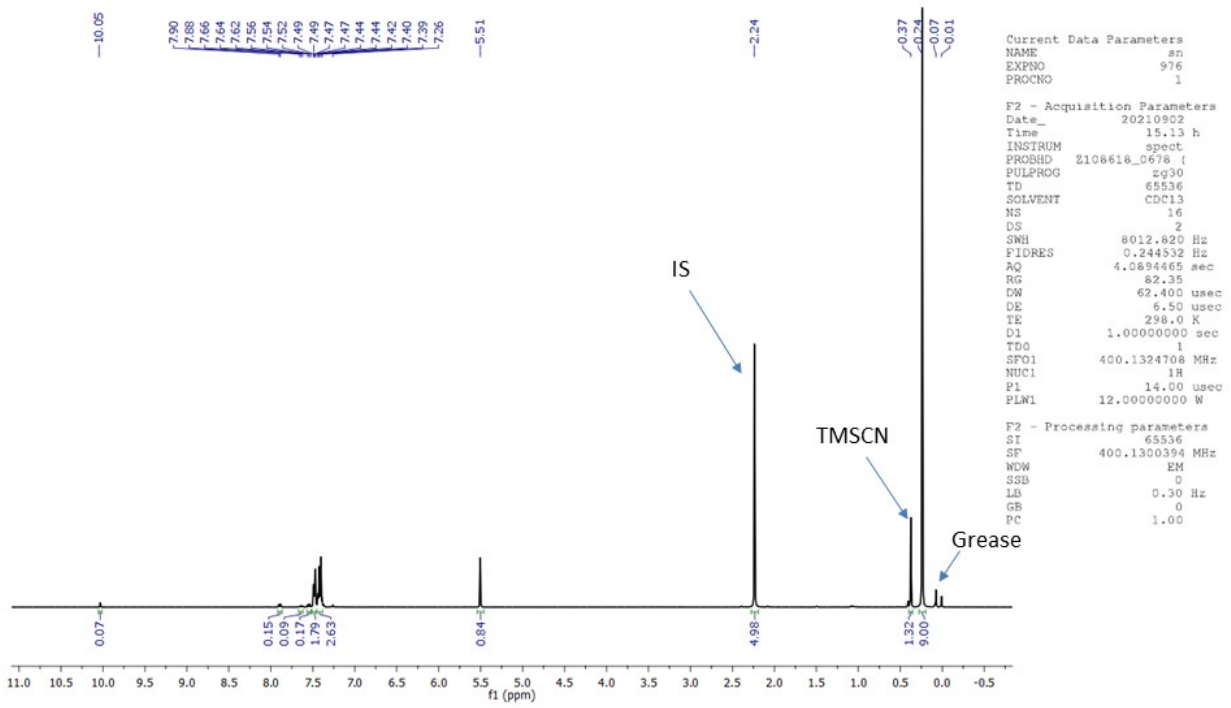


Figure S22. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 2.0 mol% for 1 h at rt.

Entry 6

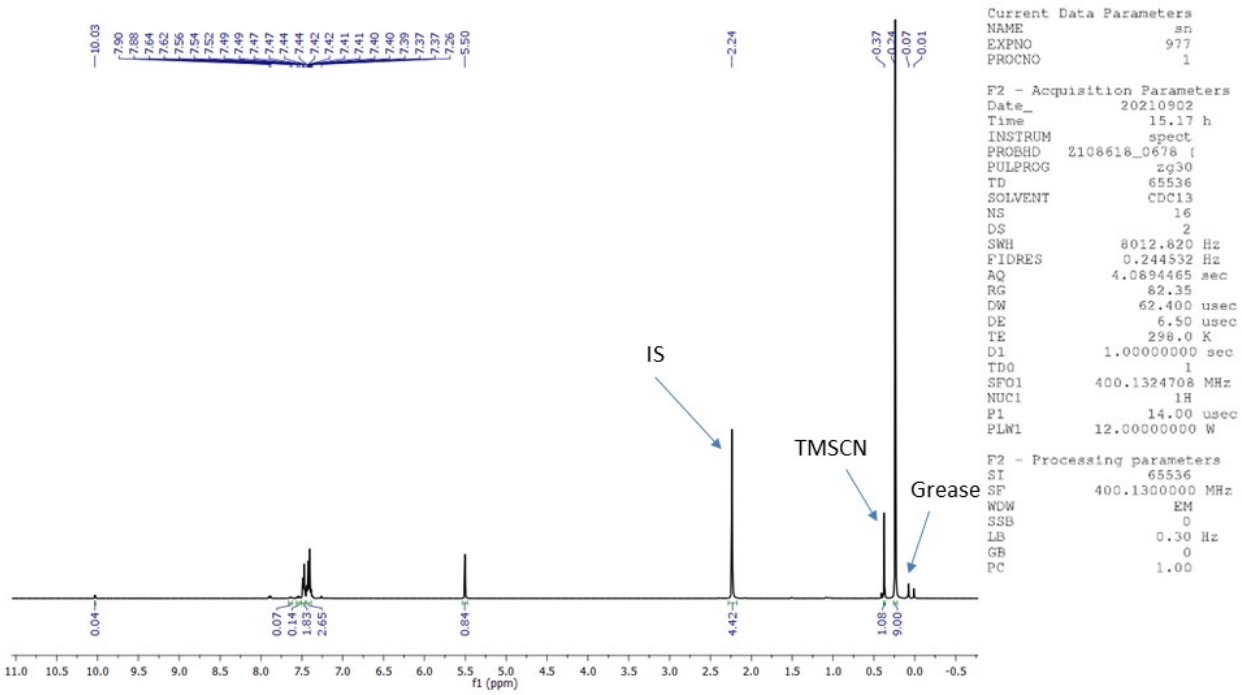


Figure S23. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 2.0 mol% for 2 h at rt.

Entry 7

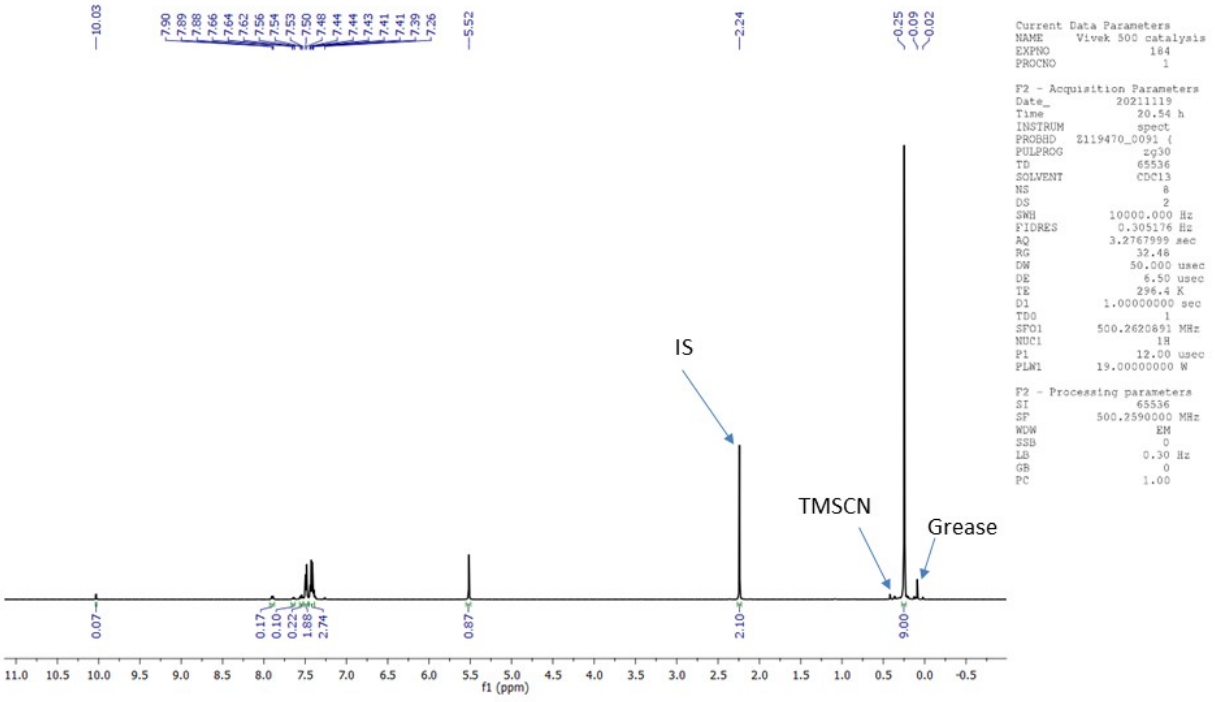


Figure S24. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 0.5 mol% for 0.25 h at 50 °C.

Entry 8

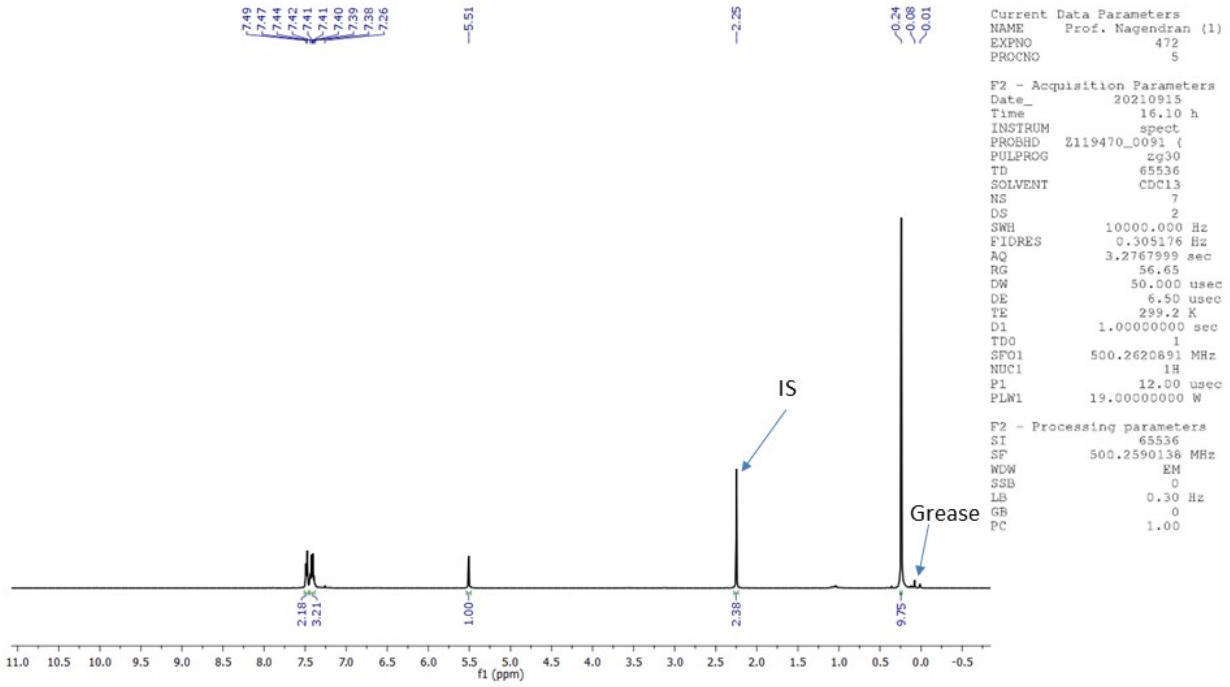


Figure S25. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 0.5 mol% for 0.33 h at 50 °C.

Entry 9

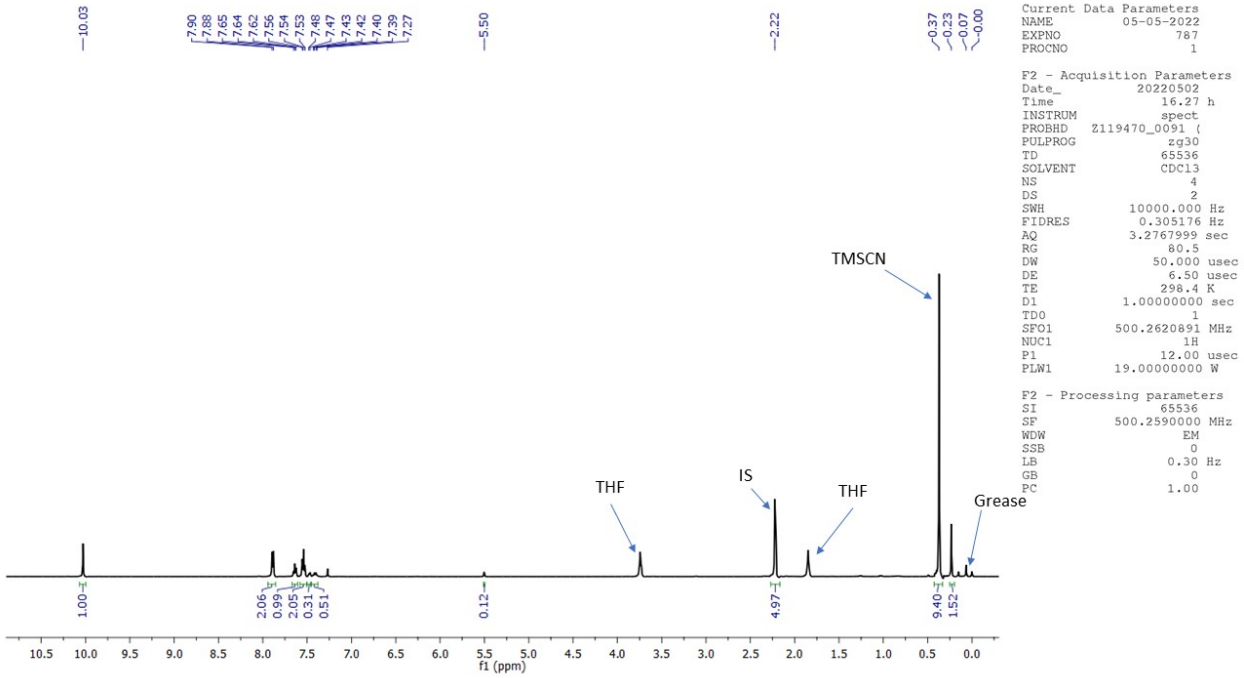


Figure S26. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**ATIH**) loading of 0.5 mol% for 0.33 h at rt.

Entry 10

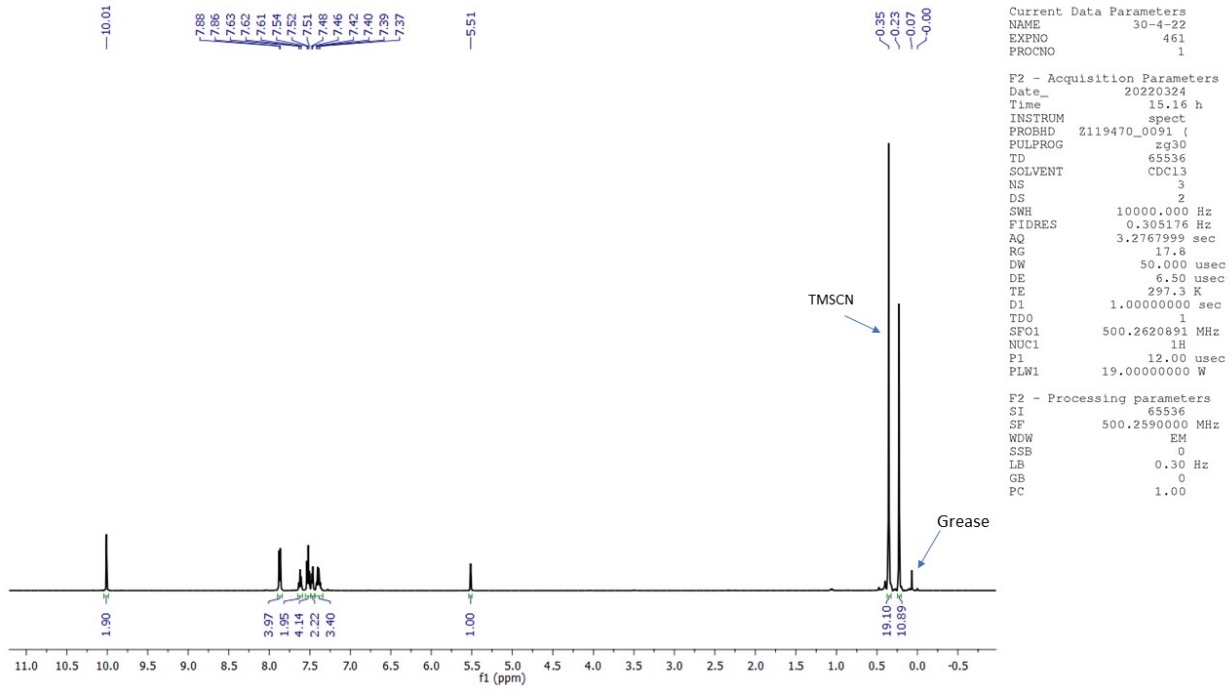


Figure S27. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**2**) loading of 0.5 mol% for 0.33 h at rt.

Entry 11

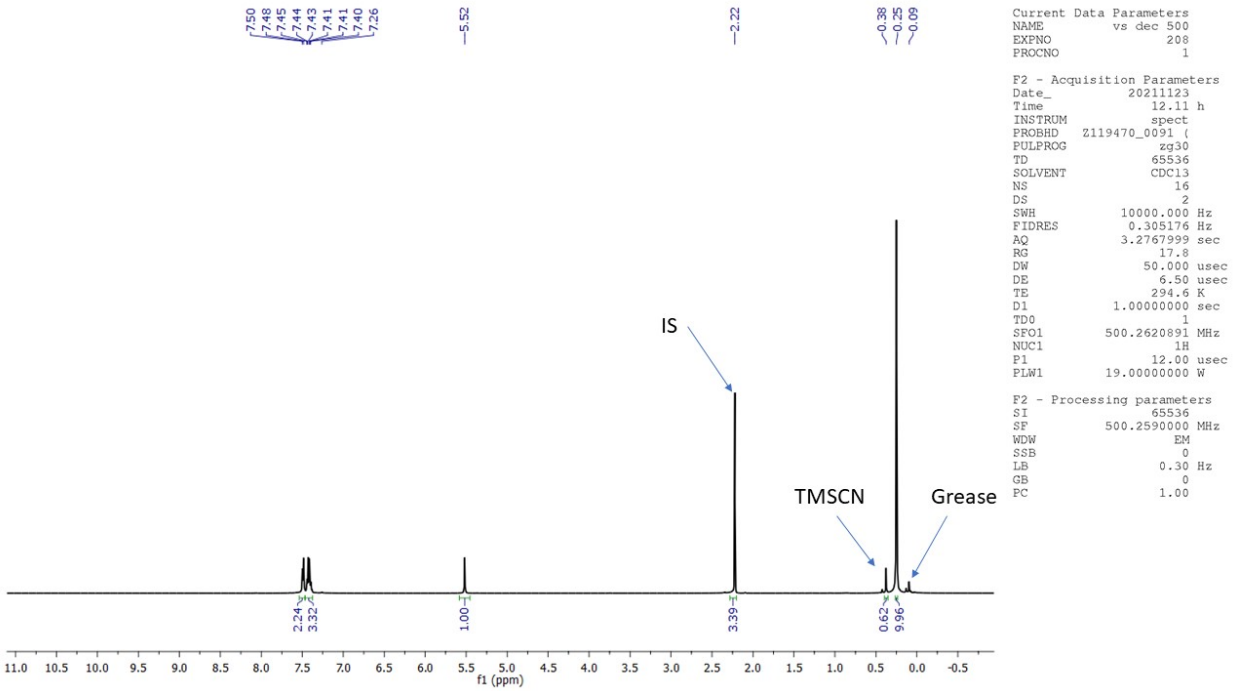


Figure S28. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**3**) loading of 0.5 mol% for 0.33 h at 50 °C.

Entry 12

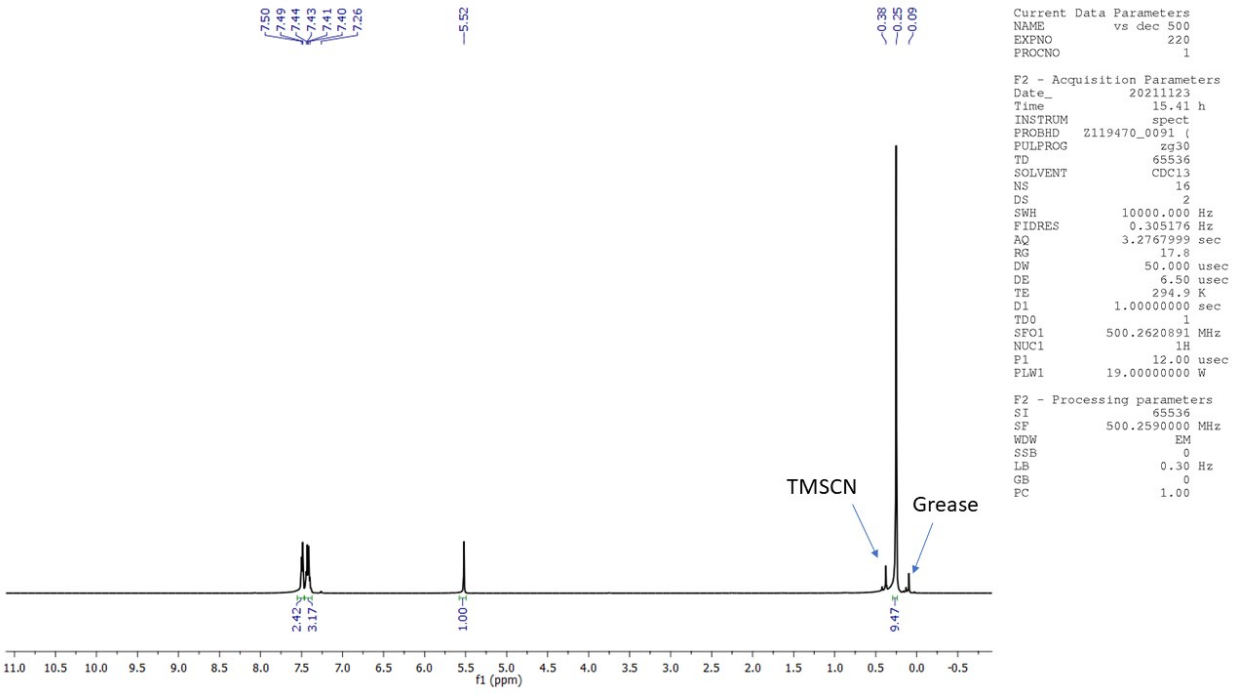


Figure S29. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**4**) loading of 0.5 mol% for 0.33 h at 50 °C.

Entry 13

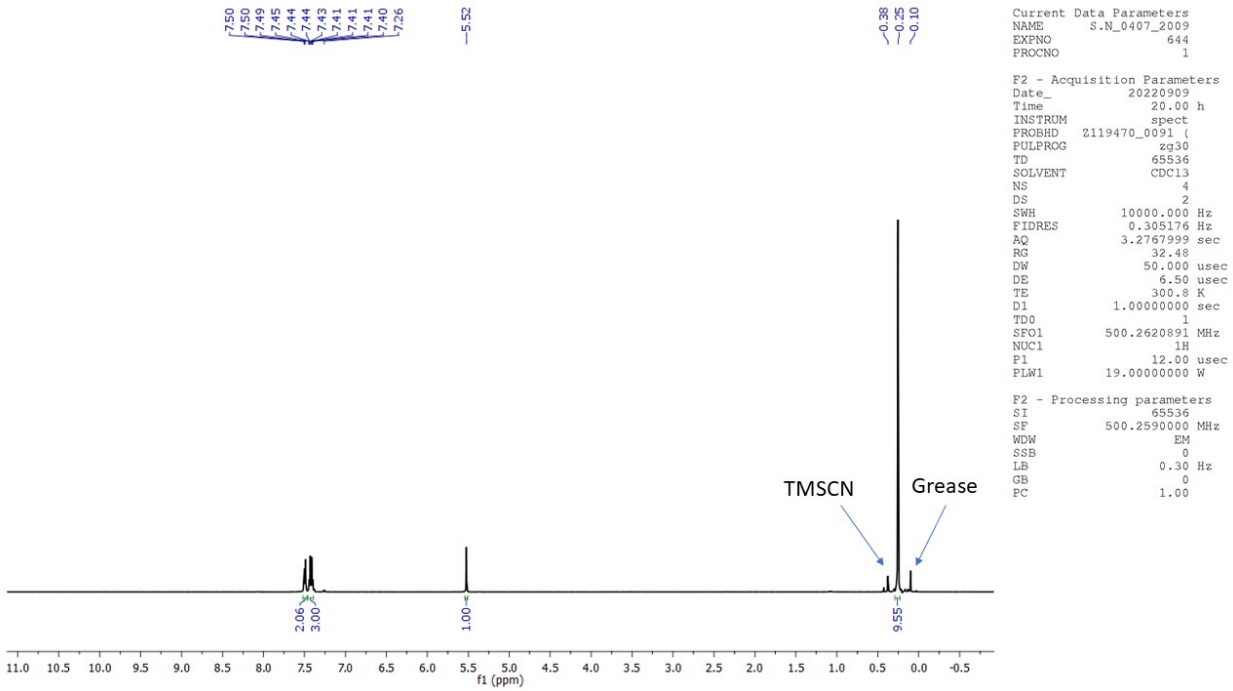


Figure S30. ^{1}H NMR spectrum for the cyanosilylation of C_6H_5CHO with TMSCN using a catalyst (**5**) loading of 0.5 mol% for 0.33 h at 50 °C. This reaction was carried out on a large scale; benzaldehyde (5.0 mmol) and TMSCN (5.5 mmol).

NMR data for the cyanosilylated products reported in Table 2

Entry 1. $CH_2(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.21 (s, 9H, Si(CH_3)$_3$), 2.24 (s, C_6(CH_3)$_6$), 4.35 (s, 2H, CH_2OSi(CH$_3$)$_3$) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.78 (Si(*C*H$_3$)$_3$), 16.93 C_6(*C*H$_3$)$_6$), 48.97 (*C*H$_2$OSi(CH$_3$)$_3$), 117.65 (*C*N) 132.14 *C*$_6$(CH$_3$)$_6$) ppm.

Entry 2. $CH_3(CH_2)_4(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.20 (s, 9H, Si(CH_3)$_3$), 0.89 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_2$CH_3), 1.31-1.35 (m, 4H, (CH_2)$_2$CH$_3$), 1.42-1.48 (m, 2H, (CH$_2$)$_2$CH_2), 1.75-1.79 (q, $^3J_{HH}$ = 6.75 Hz, 2H, CH$_2$CH_2), 2.21 (s, C_6(CH_3)$_6$), 4.38 (t, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OSi(CH$_3$)$_3$)) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.26 (Si(*C*H$_3$)$_3$), 14.05 (*C*H$_3$), 16.91 C_6(*C*H$_3$)$_6$), 22.51 (*C*H$_2$), 24.35 (*C*H$_2$), 31.21 (*C*H$_2$), 36.32 (*C*H$_2$), 61.62 (*C*HOSi(CH_3)$_3$), 120.28 (*C*N), 132.13 *C*$_6$(CH$_3$)$_6$) ppm.

Entry 3. $CH_3(CH_2)_6(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 9H, Si(CH_3)$_3$), 0.87 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_2$CH_3), 1.26-1.30 (m, 8H, (CH_2)$_4$CH$_3$), 1.40-1.44 (m, 2H, (CH$_2$)$_2$CH_2), 1.74-1.78 (q, $^3J_{HH}$ = 6.45 Hz, 2H, CH$_2$CH_2), 2.17 (s, C_6(CH_3)$_6$), 4.37 (t, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OSi(CH$_3$)$_3$) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.31 (Si(*C*H$_3$)$_3$), 14.13 (*C*H$_3$), 16.85 C_6(*C*H$_3$)$_6$), 22.68 (*C*H$_2$), 24.64 (*C*H$_2$), 28.99 (*C*H$_2$), 29.14 (*C*H$_2$), 31.78 (*C*H$_2$), 36.33 (*C*H$_2$), 61.57 (*C*HOSi(CH_3)$_3$), 120.21 (*C*N), 132.07 *C*$_6$(CH$_3$)$_6$) ppm.

Entry 4. $C_6H_5CH_2CH_2CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.23 (s, 9H, Si(CH_3)$_3$), 2.12-2.16 (m, 2H, CH_2), 2.26 (s, C_6(CH_3)$_6$), 2.82 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, CH_2), 4.39 (t, $^3J_{H,H}$ = 6.55 Hz, 1H, C*H*OSi(CH$_3$)$_3$), 7.21-7.26 (m, 3H, Ar), 7.31-7.34 (m, 2H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.36 (Si(*C*H$_3$)$_3$), 16.88 C_6(*C*H$_3$)$_6$), 30.71

(CH_2), 37.72 (CH_2), 60.71 ($CHOSi(CH_3)_3$), 119.97 (*C*N), 126.49 (C_{Ar}), 128.48 (C_{Ar}), 128.70 (C_{Ar}), 132.10 $C_6(CH_3)_6$), 140.04 (C_{Ar}) ppm.

Entry 5. $C_6H_5CHCHCH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.24 (s, 9H, $Si(CH_3)_3$), 2.19 (s, $C_6(CH_3)_6$), 5.09 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, C*H*), 6.14 (dd, $^3J_{H,H}$ = 6.0 and 16.0 Hz, 1 H, C*H*), 6.77 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H, C*H*), 7.27-7.38 (m, 5H, Ar) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = -0.07 ($Si(CH_3)_3$), 16.72, $C_6(CH_3)_6$), 62.27, ($CHOSi(CH_3)_3$), 118.48 (*C*N), 123.62 (C_{Ar}), 127.02 (C_{Ar}), 128.80 (*C*H), 128.84 (C_{Ar}), 132.00 $C_6(CH_3)_6$), 133.97 (C_{Ar}), 135.08 (*C*H), ppm.

Entry 6. $C_6H_5CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.25 (s, 9H, $Si(CH_3)_3$), 2.22 (s, $C_6(CH_3)_6$), 5.52 (s, 1H, C*H*$OSi(CH_3)_3$), 7.38-7.50 (m, 5H, Ph) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.18 ($Si(CH_3)_3$), 16.72, $C_6(CH_3)_6$), 63.73 ($CHOSi(CH_3)_3$), 119.29 (*C*N), 126.44 (C_{Ar}), 129.02 (C_{Ar}), 129.42 (C_{Ar}), 132.02 $C_6(CH_3)_6$), 136.36 (C_{Ar}).

Entry 7. 4-$FC_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.23 (s, 9H, $Si(CH_3)_3$), 2.22 (s, $C_6(CH_3)_6$), 5.49 (s, 1 H, C*H*$OSi(CH_3)_3$), 7.08-7.12 (m, 2 H, Ar), 7.45-7.47 (m, 2 H, Ar) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ -0.24 ($Si(CH_3)_3$), 16.84 $C_6(CH_3)_6$), 63.06 ($CHOSi(CH_3)_3$), 115.94 (d, $^1J_{C\text{-}F}$ = 20.0 Hz, *p*-*C*F), 119.12 (*C*N), 128.34 (d, $^2J_{C\text{-}F}$ = 9.0 Hz, *m*-*C*H), 132.02 $C_6(CH_3)_6$), 132.38 (d, $^2J_{C\text{-}F}$ = 3.0 Hz, *m*-*C*H), 162.24 (C_{Ar}), 164.22 (C_{Ar}) ppm.

Entry 8. 4-$ClC_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.24 (s, 9H, $Si(CH_3)_3$), 2.22 (s, $C_6(CH_3)_6$), 5.47 (s, 1H, C*H*$OSi(CH_3)_3$), 7.38-7.42 (m, 4H, Ar) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ -0.15 ($Si(CH_3)_3$), 16.89 $C_6(CH_3)_6$),

63.12 (*C*HOSi$(CH_3)_3$), 118.93 (*C*N), 127.82 (C_{Ar}), 129.30 (C_{Ar}), 132.08 $C_6(CH_3)_6$), 134.99 (C_{Ar}), 135.47 (C_{Ar}) ppm.

Entry 9. 4-BrC_6H_4CH(CN)(OTMS):

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.24 (s, 9H, Si(C$H_3)_3$), 2.21 (s, C_6(C$H_3)_6$), 5.45 (s, 1H, C*H*OSi$(CH_3)_3$), 7.34 (d, $^3J_{H,H}$ = 10.5 Hz, 2H, Ar), 7.54 (d, $^3J_{H,H}$ = 10.5 Hz, 2H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.13 (Si(*C*$H_3)_3$), 16.86 C_6(*C*$H_3)_6$), 63.17 (*C*HOSi$(CH_3)_3$), 118.85 (*C*N), 123.63 (C_{Ar}), 128.08 (C_{Ar}), 132.07 $C_6(CH_3)_6$), 132.26 (C_{Ar}), 135.50 (C_{Ar}) ppm.

Entry 10. 3-BrC_6H_4CH(CN)(OTMS):

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.26 (s, 9H, Si(C$H_3)_3$), 2.21 (s, C_6(C$H_3)_6$), 5.46 (s, 1H, C*H*OSi$(CH_3)_3$), 7.29 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, Ar), 7.39 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, Ar), 7.52 (d, $^3J_{H,H}$ = 9.8 Hz, 1H, Ar), 7.63 (s, 1H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.16 (Si(*C*$H_3)_3$), 17.08 C_6(*C*$H_3)_6$), 62.96 (*C*HOSi$(CH_3)_3$), 118.82 (*C*N), 123.10 (C_{Ar}), 124.97 (C_{Ar}), 129.49 (C_{Ar}), 130.63 (C_{Ar}), 132.16 $C_6(CH_3)_6$), 132.58 (C_{Ar}), 138.47 (C_{Ar}) ppm.

Entry 11. 4-CNC_6H_4CH(CN)(OTMS):

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.24 (s, 9H, Si(C$H_3)_3$), 2.19 (s, C_6(C$H_3)_6$), 5.56 (s, 1H, C*H*OSi$(CH_3)_3$), 7.58-7.71 (m, 4H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.35 (Si(*C*$H_3)_3$), 16.88 C_6(*C*$H_3)_6$), 62.64 (*C*HOSi$(CH_3)_3$), 113.34 (C_{Ar}), 118.14 (*C*N), 118.32 (*C*N), 126.90 (C_{Ar}), 131.99 $C_6(CH_3)_6$), 132.88 (C_{Ar}), 141.20 (C_{Ar}) ppm.

Entry 12. 4-$NO_2C_6H_4$CH(CN)(OTMS):

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.28 (s, 9H, Si(C$H_3)_3$), 2.22 (s, C_6(C$H_3)_6$), 5.60 (s, 1H, C*H*OSi$(CH_3)_3$), 7.66 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar), 8.27 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):

δ -0.21 (Si(CH$_3$)$_3$), 16.90 C$_6$(CH$_3$)$_6$), 62.76 (CHOSi(CH$_3$)$_3$), 118.27 (CN), 124.31 (C_{Ar}), 127.24 (C_{Ar}), 132.12 C_6(CH$_3$)$_6$), 143.01 (C_{Ar}), 148.57 (C_{Ar}) ppm.

Entry 13. 3-$NO_2C_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.28 (s, 9H, Si(CH_3)$_3$), 2.20 (s, C$_6$(CH_3)$_6$), 5.61 (s, 1H, CHOSi(CH$_3$)$_3$), 7.63 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, Ar), 7.82 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, Ar), 8.24 (d, $^3J_{H,H}$ = 8.1 Hz, 1H, Ar), 8.34 (s, 1H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ -0.36 (Si(CH$_3$)$_3$), 16.91 C$_6$(CH$_3$)$_6$), 62.62 (CHOSi(CH$_3$)$_3$), 118.39 (CN), 121.37 (C_{Ar}), 124.33 (C_{Ar}), 130.23 (C_{Ar}), 132.06 C_6(CH$_3$)$_6$), 132.16 (C_{Ar}), 138.53 (C_{Ar}), 148.58 (C_{Ar}) ppm.

Entry 14. 2-$NO_2C_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.27 (s, 9H, Si(CH_3)$_3$), 2.19 (s, C$_6$(CH_3)$_6$), 6.21 (s, 1H, CHOSi(CH$_3$)$_3$), 7.59 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, Ar), 7.77 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, Ar), 8.01 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, Ar), 8.14(d, $^3J_{H,H}$ = 8.2 Hz, 1H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ -0.36 (Si(CH$_3$)$_3$), 16.80 C$_6$(CH$_3$)$_6$), 60.27 (CHOSi(CH$_3$)$_3$), 117.99 (CN), 125.42 (C_{Ar}), 128.60 (C_{Ar}), 130.40 (C_{Ar}), 132.01 C_6(CH$_3$)$_6$), 132.22 (C_{Ar}), 134.60 (C_{Ar}), 146.47 (C_{Ar}) ppm.

Entry 15. 2,6-$Cl_2C_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.21 (s, 9H, Si(CH_3)$_3$), 2.25 (s, C$_6$(CH_3)$_6$), 6.28 (s, 1H, CHOSi(CH$_3$)$_3$), 7.28-7.38 (m, 3H Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ -0.19 (Si(CH$_3$)$_3$), 16.85 C$_6$(CH$_3$)$_6$), 59.61 (CHOSi(CH$_3$)$_3$), 117.66 (CN), 129.50 (C_{Ar}), 131.32 (C_{Ar}), 131.50 (C_{Ar}), 132.18 C_6(CH$_3$)$_6$), 135.64 (C_{Ar}) ppm.

Entry 16. 2,5-$(CH_3O)_2C_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.23 (s, 9H, Si(CH_3)$_3$), 2.20 (s, C$_6$(CH_3)$_6$), 3.79 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.77 (s, 1H, CHOSi(CH$_3$)$_3$), 6.82-6.87 (m, 2H, Ar), 7.16 (s, 1H, Ar) ppm; ^{13}C{^{1}H} NMR (125

MHz, $CDCl_3$): δ -0.25 (Si(CH_3)$_3$), 16.81 C_6(CH_3)$_6$), 55.89 (OCH_3), 56.03 (OCH_3), 58.27 ($CHOSi(CH_3)_3$), 111.84 (C_{Ar}), 113.21 (C_{Ar}), 115.21 (C_{Ar}), 119.34 (CN), 125.64 (C_{Ar}), 132.02 $C_6(CH_3)_6$), 150.02 (C_{Ar}), 153.95 (C_{Ar}) ppm.

Entry 17. 4-$OCH_3C_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.21 (s, 9H, Si(CH_3)$_3$), 2.22 (s, C_6(CH_3)$_6$), 3.81 (s, 3H, OCH_3), 5.43 (s, 1H, $CHOSi(CH_3)_3$), 6.91-6.93 (m, 2H, Ar), 7.37-7.39 (m, 2H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.08 (Si(CH_3)$_3$), 16.91 C_6(CH_3)$_6$), 55.49 (OCH_3), 63.52 ($CHOSi(CH_3)_3$), 114.45 (C_{Ar}), 119.46 (CN), 128.08 (C_{Ar}), 128.66 (C_{Ar}), 132.13 $C_6(CH_3)_6$), 160.53 (C_{Ar}) ppm.

Entry 18. 4-$CH_3C_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.23 (s, 9H, Si(CH_3)$_3$), 2.22 (s, C_6(CH_3)$_6$), 2.38 (s, 3H, CH_3), 5.47 (s, 1H, $CHOSi(CH_3)_3$), 7.22 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, Ar), 7.35 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.18 (Si(CH_3)$_3$), 16.87 C_6(CH_3)$_6$), 21.32 (CH_3), 63.57 ($CHOSi(CH_3)_3$), 119.43 (CN), 126.52 (C_{Ar}), 129.72 (C_{Ar}), 132.10 $C_6(CH_3)_6$), 133.56 (C_{Ar}), 139.49 (C_{Ar}) ppm.

Entry 19. 4-$C_5H_4NCH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.21 (s, 9H, Si(CH_3)$_3$), 2.15 (s, C_6(CH_3)$_6$), 5.48 (s, 1H, $CHOSi(CH_3)_3$), 7.34 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, $CH_{pyridine}$), 8.60 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, $CH_{pyridine}$) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.41 (Si(CH_3)$_3$), 16.72 C_6(CH_3)$_6$), 62.23 ($CHOSi(CH_3)_3$), 118.08 (CN), 120.55 ($CH_{pyridine}$), 131.93 $C_6(CH_3)_6$), 144.88 ($C_{pyridine}$), 150.38 ($CH_{pyridine}$) ppm.

Entry 20. 2-$C_5H_4NCH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.22 (s, 9H, Si(CH_3)$_3$), 2.18 (s, C_6(CH_3)$_6$), 5.56 (s, 1H, $CHOSi(CH_3)_3$), 7.26-7.28 (m, 1H, $CH_{pyridine}$), 7.54-7.57 (m, 1H, $CH_{pyridine}$), 7.73-7.76 (m, 1H, $CH_{pyridine}$), 8.54-8.55 (m, 1H, $CH_{pyridine}$) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.35 (Si(CH_3)$_3$), 16.75 C_6(CH_3)$_6$), 65.10

(*C*HOSi(CH_3)$_3$), 118.72 (*C*N), 120.47 (*C*$H_{pyridine}$), 124.01 (*C*$H_{pyridine}$), 131.96 *C*$_6$(CH_3)$_6$), 137.51 (*C*$H_{pyridine}$), 149.38 (*C*$H_{pyridine}$), 155.42 (*C*$_{pyridine}$) ppm.

Entry 21. 2-C_4H_4NCH(CN)(OTMS):

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 9H, Si(C*H*$_3$)$_3$), 2.26 (s, C$_6$(C*H*$_3$)$_6$), 5.58 (s, 1H, C*H*OSi(CH_3)$_3$), 6.18 (br, 1H, C*H*$_{pyrrole}$), 6.29 (br, 1H, C*H*$_{pyrrole}$), 6.84 (br, 1H, C*H*$_{pyrrole}$), 8.66 (bs, 1H, N*H*$_{pyrrole}$) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.31 (Si(*C*H$_3$)$_3$), 16.85 C$_6$(*C*H$_3$)$_6$), 57.86 (*C*HOSi(CH_3)$_3$), 108.49 (*C*H$_{pyrrole}$), 108.84 (*C*H$_{pyrrole}$), 118.47 (*C*N), 120.04 (*C*H$_{pyrrole}$), 125.52(*C*$_{pyrrole}$), 132.07 *C*$_6$(CH_3)$_6$) ppm.

Entry 22. $CH_3CONHC_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.21 (s, 9H, Si(C*H*$_3$)$_3$), 2.16 (s, 3H, NHCOC*H*$_3$), 2.24 (s, C$_6$(C*H*$_3$)$_6$), 5.45 (s, 1H, C*H*OSi(CH_3)$_3$), 7.38 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, Ar), 7.56 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, Ar), 7.74 (bs, 1H, N*H*) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.11 (Si(*C*H$_3$)$_3$), 16.93 C$_6$(*C*H$_3$)$_6$), 24.68 (NHCO*C*H$_3$), 63.43 (*C*HOSi(CH_3)$_3$), 119.37 (*C*N), 120.14 (*C*Ar), 127.32 (*C*$_{Ar}$), 131.94 (*C*$_{Ar}$), 132.15 *C*$_6$(CH_3)$_6$), 139.16 (*C*$_{Ar}$), 168.80 (NH*C*OCH$_3$) ppm.

Entry 23. $CH_3COC_6H_4CH(CN)(OTMS)$:

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.26 (s, 9H, Si(C*H*$_3$)$_3$), 2.22 (s, C$_6$(C*H*$_3$)$_6$), 2.62 (s, 3H, COC*H*$_3$), 5.55 (s, 1H, C*H*OSi(CH_3)$_3$), 7.57 (d, $^3J_{H,H}$ = 8.15 Hz, 2H, Ar), 8.00 (d, $^3J_{H,H}$ = 8.15 Hz, 2H, Ar) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ -0.13 (Si(*C*H$_3$)$_3$), 16.76 C$_6$(*C*H$_3$)$_6$), 26.98 (CO*C*H$_3$), 63.31 (*C*HOSi(CH_3)$_3$), 118.75 (*C*N), 126.61 (*C*$_{Ar}$), 129.10 (*C*$_{Ar}$), 132.13 *C*$_6$(CH_3)$_6$), 137.97 (*C*$_{Ar}$), 141.11 (*C*$_{Ar}$), 197.47 (*C*OCH$_3$) ppm.

^{1}H and ^{13}C NMR spectra of the cyanosilylated products in Table 2

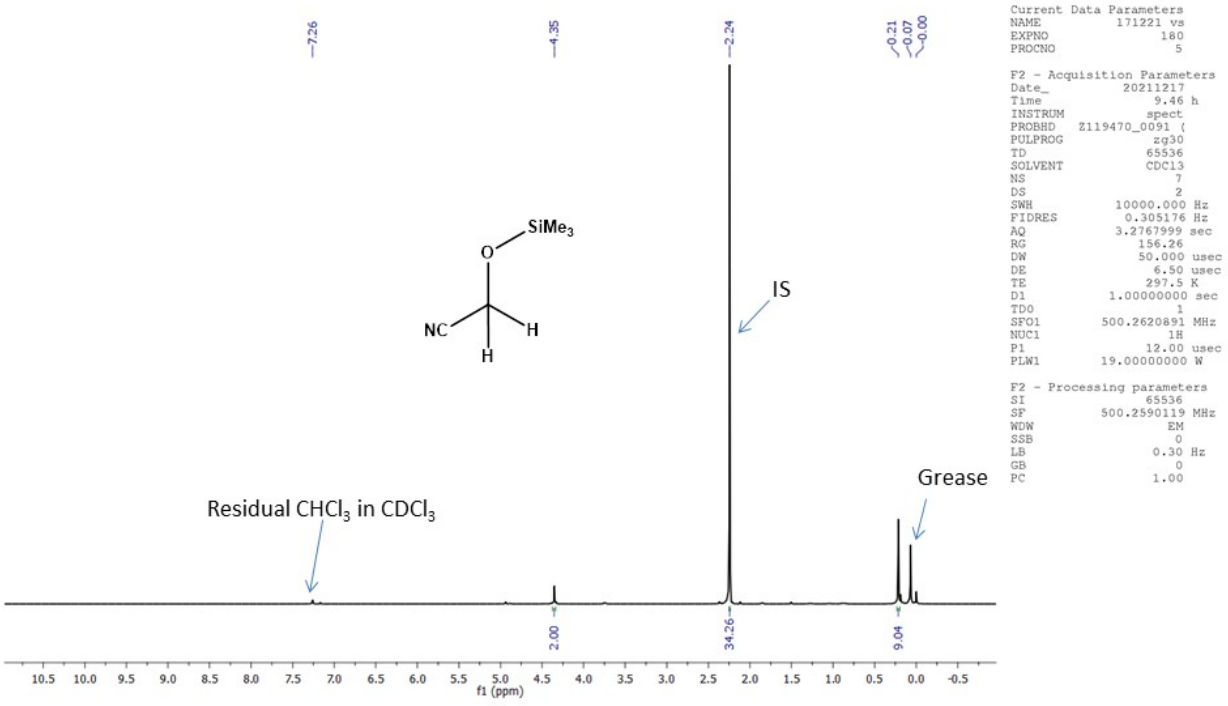


Figure S28. ^{1}H NMR spectrum of the cyanosilylated product of *p*-formaldehyde.

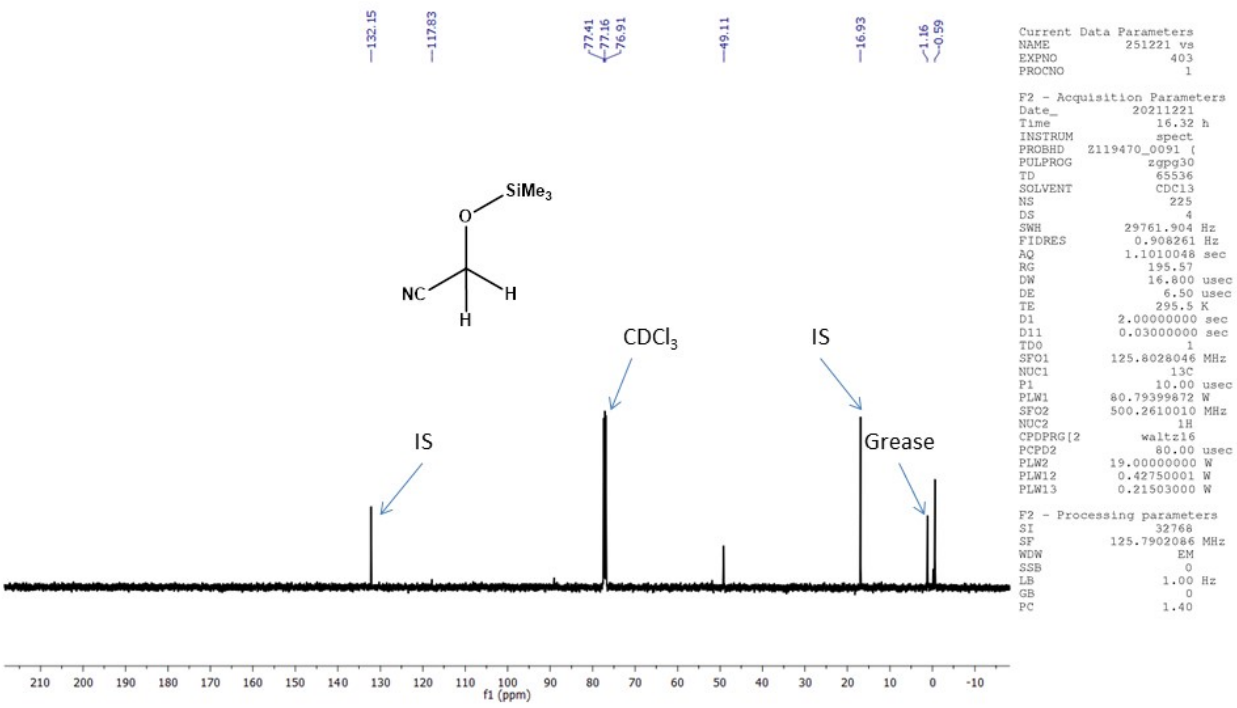


Figure S29. ^{13}C NMR spectrum of the cyanosilylated product of *p*-formaldehyde.

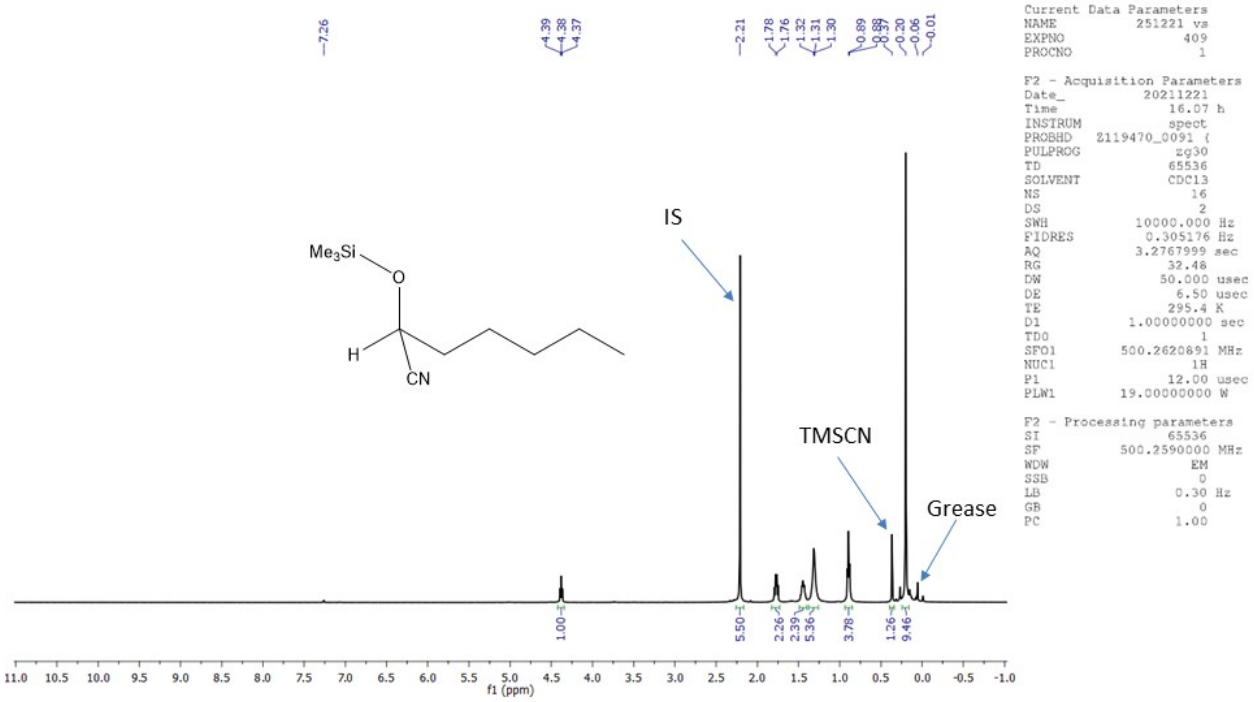


Figure S30. ^{1}H NMR spectrum of the cyanosilylated product of hexanal.

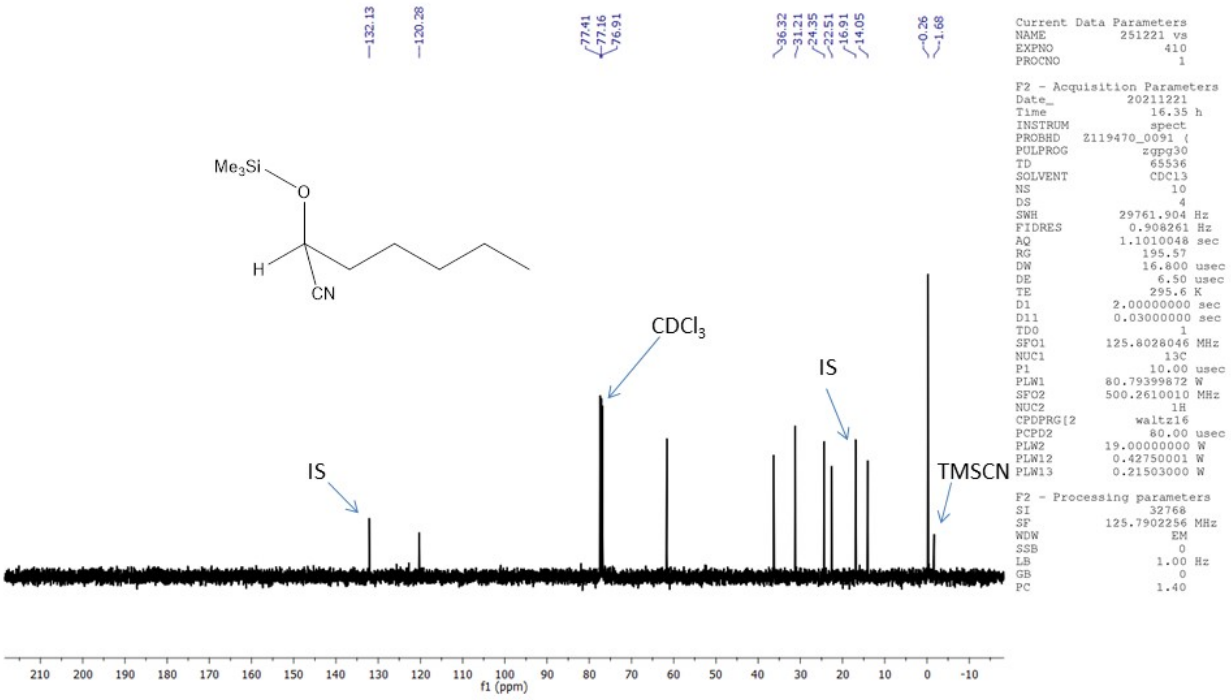


Figure S314. ^{13}C NMR spectrum of the cyanosilylated product of hexanal.

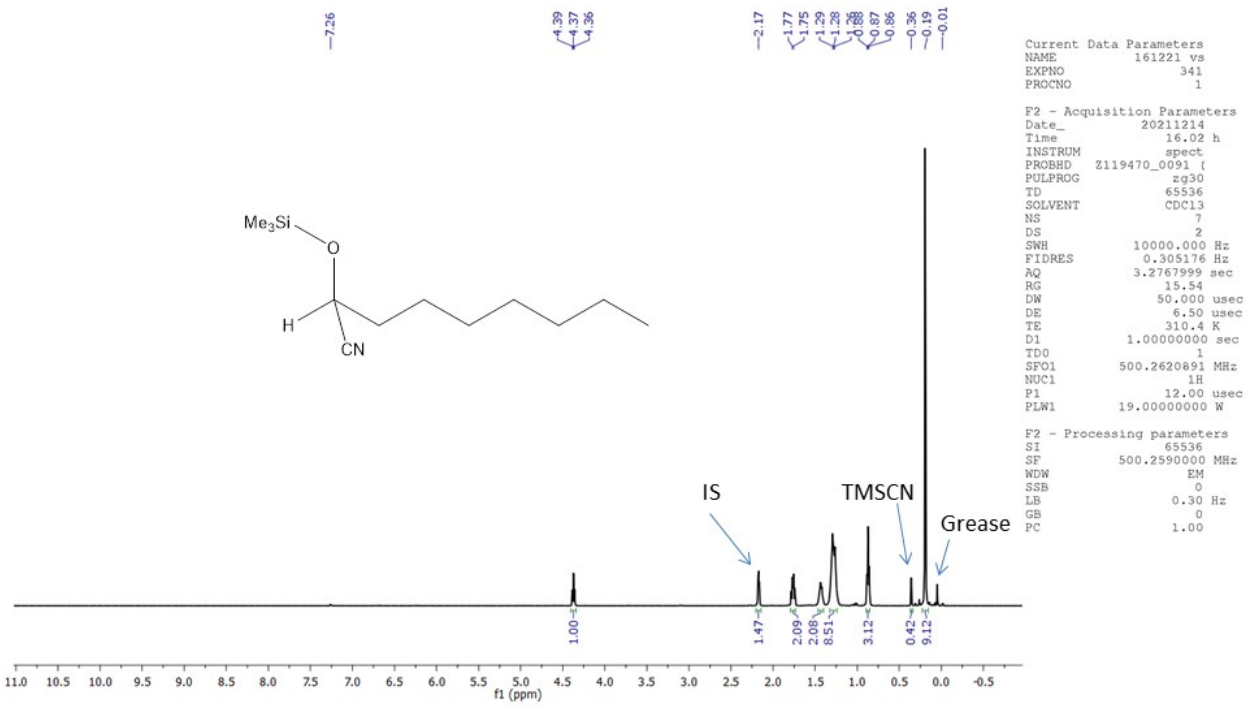


Figure S325. ^{1}H NMR spectrum of the cyanosilylated product of octanal.

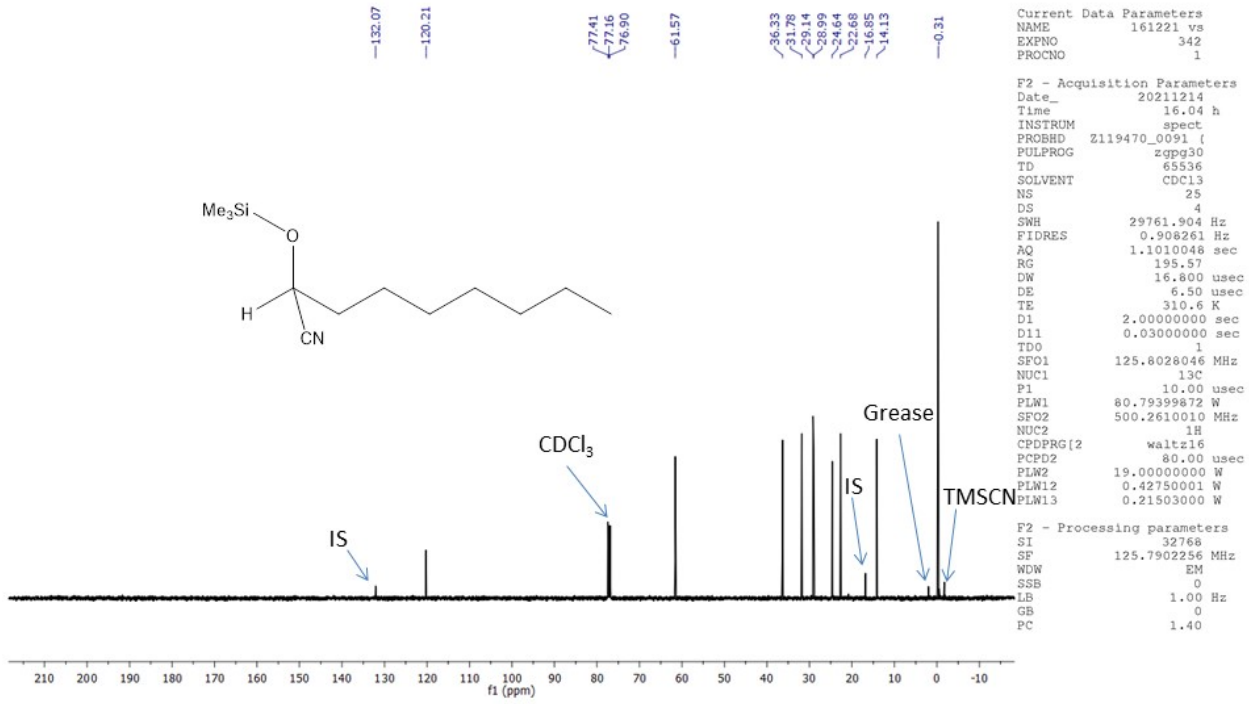


Figure S336. ^{13}C NMR spectrum of the cyanosilylated product of octanal.

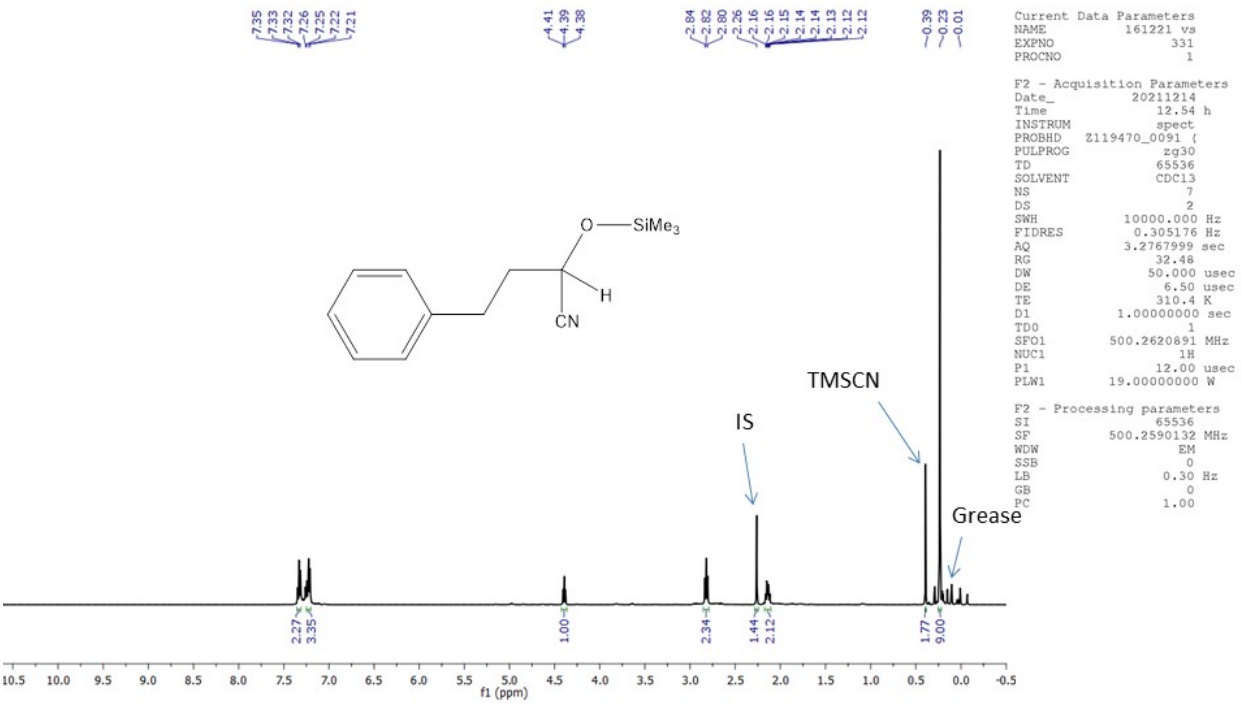


Figure S347. ^{1}H NMR spectrum of the cyanosilylated product of 3-phenylpropanal.

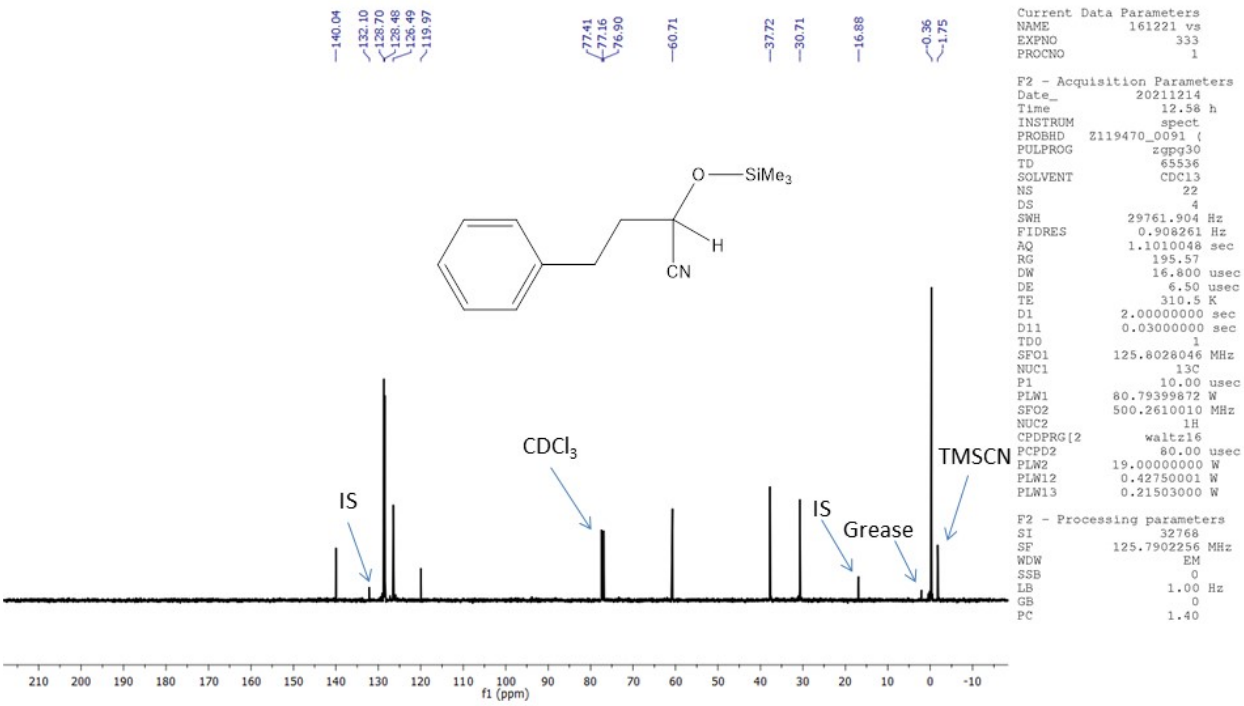


Figure S358. ^{13}C NMR spectrum of the cyanosilylated product of 3-phenylpropanal.

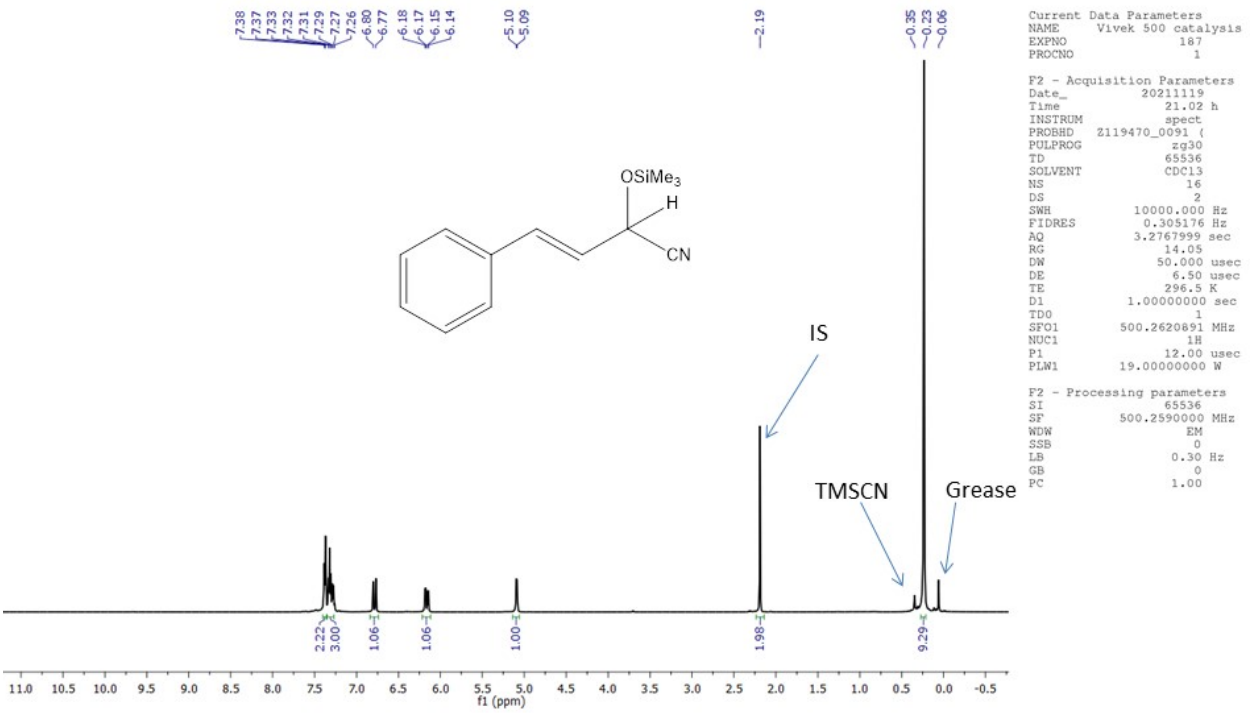


Figure S369. ^{1}H NMR spectrum of the cyanosilylated product of *trans*-cinnamaldehyde.

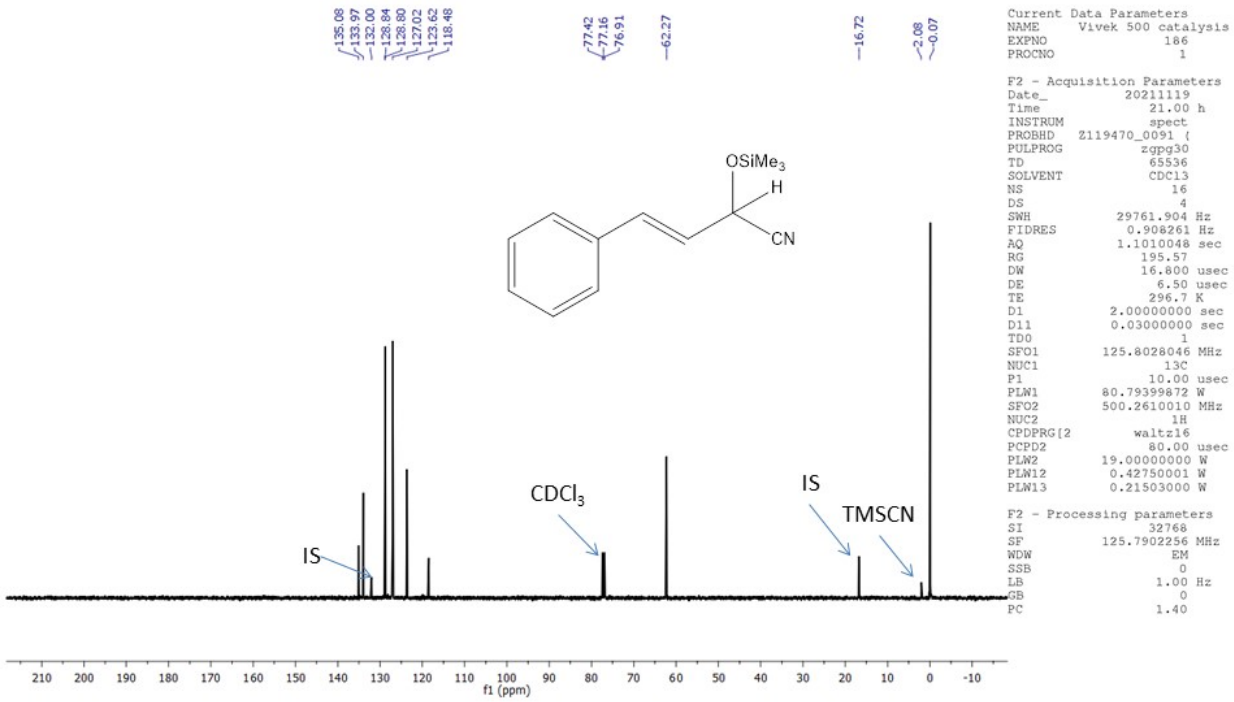


Figure S4037. ^{13}C NMR spectrum of the cyanosilylated product of *trans*-cinnamaldehyde.

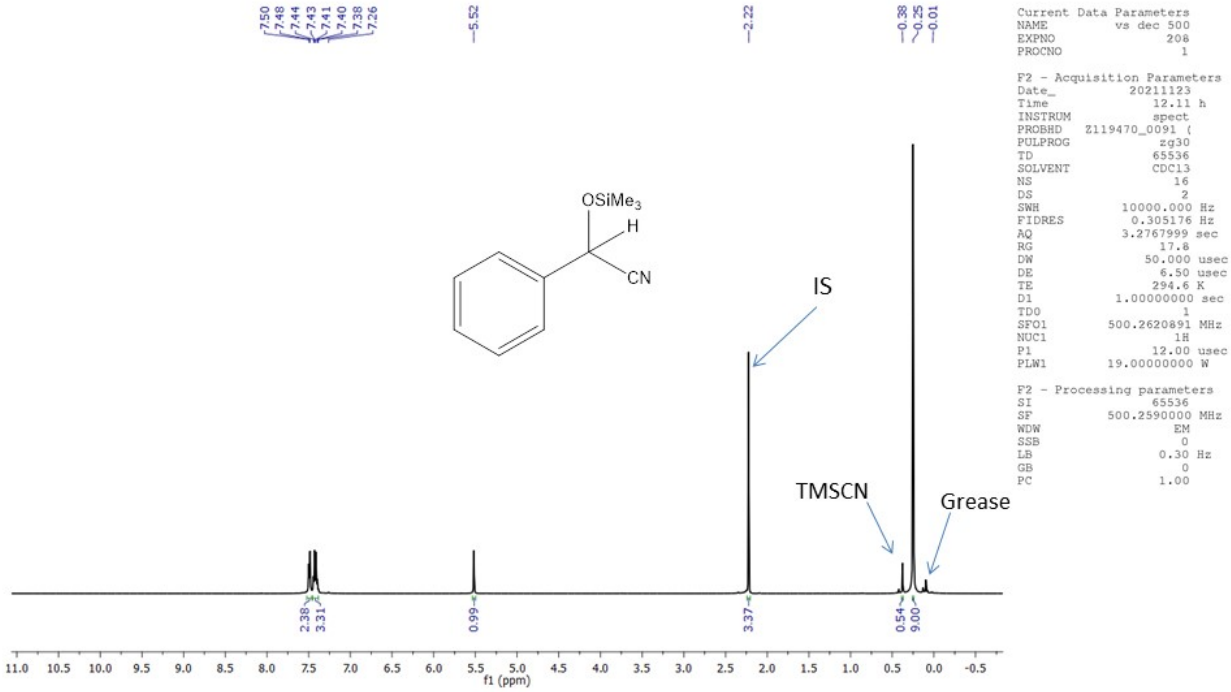


Figure S41. ^{1}H NMR spectrum of the cyanosilylated product of benzaldehyde.

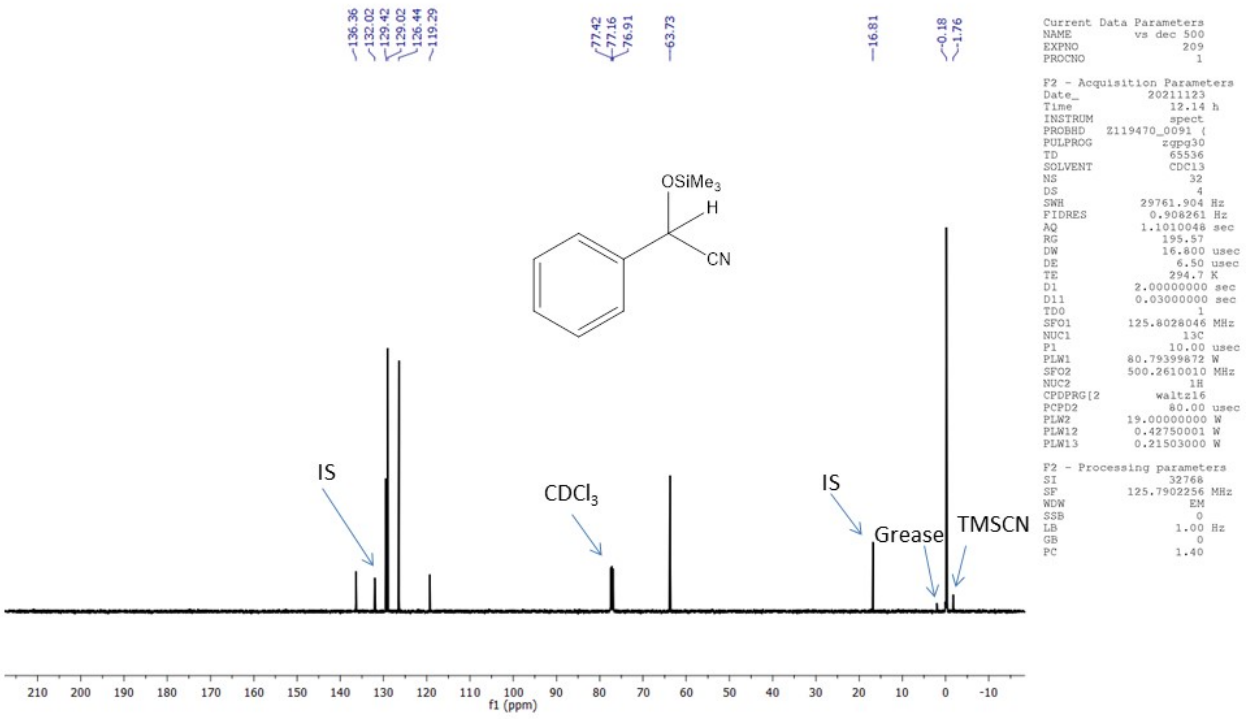


Figure S42. ^{13}C NMR spectrum of the cyanosilylated product of benzaldehyde.

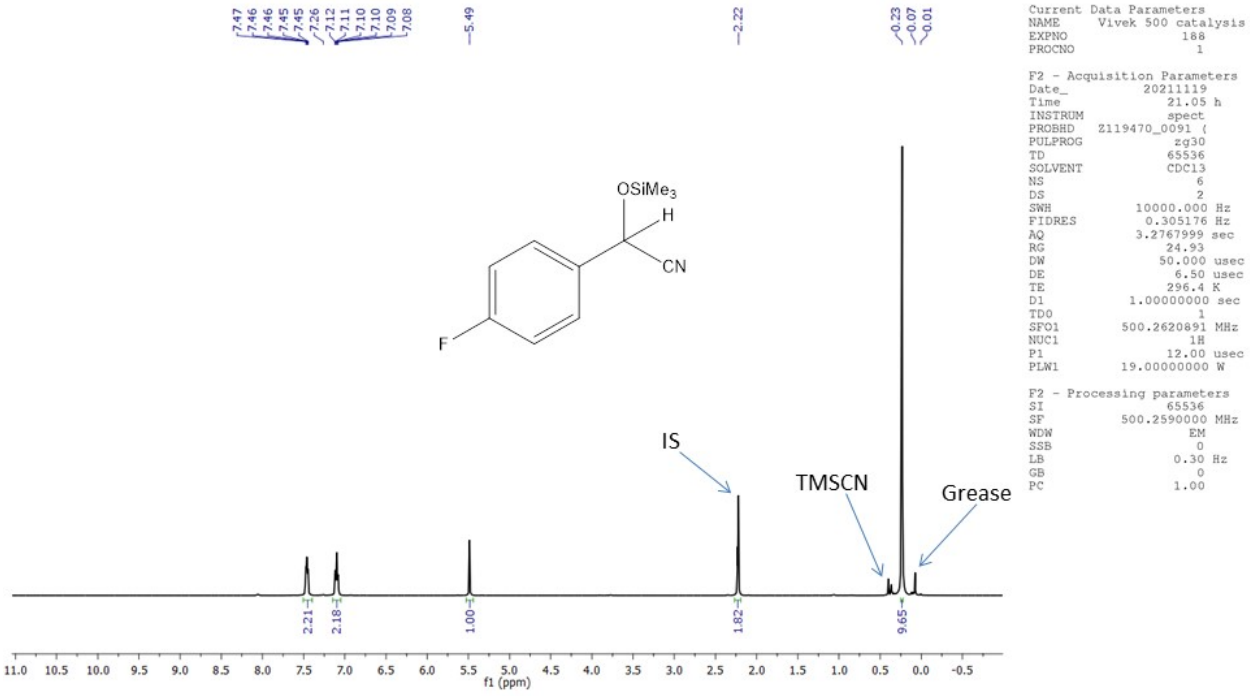


Figure S43. ^{1}H NMR spectrum of the cyanosilylated product of 4-fluorobenzaldehyde.

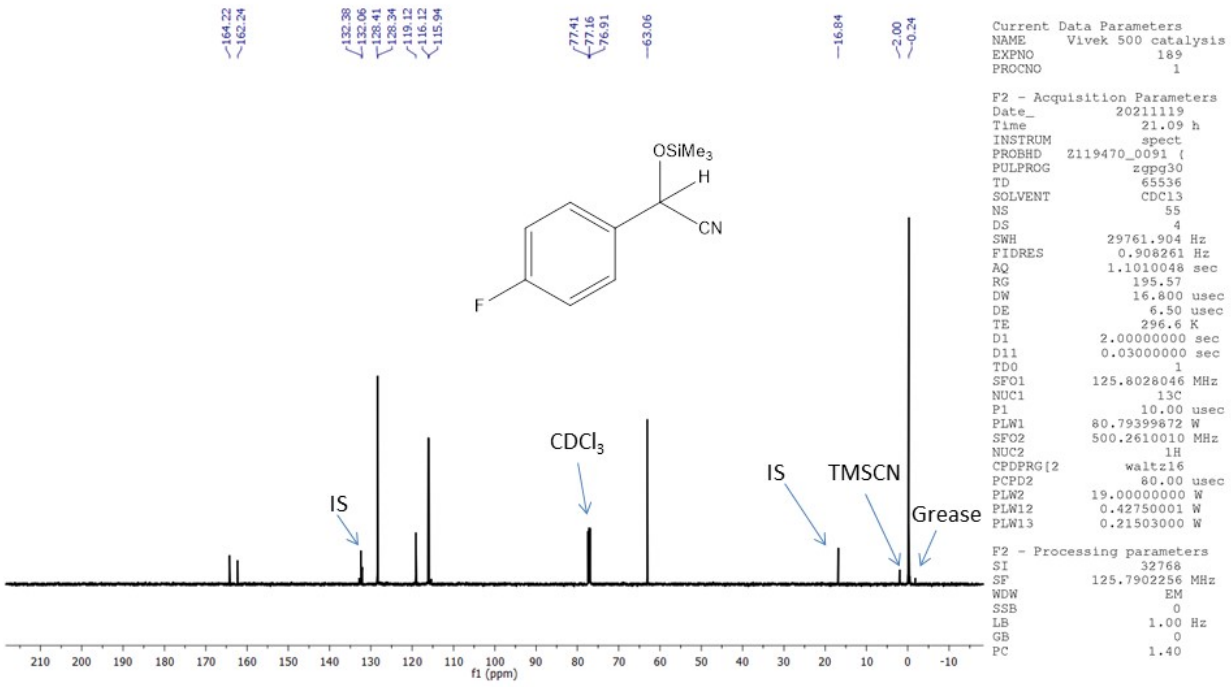


Figure S38. ^{13}C NMR spectrum of the cyanosilylated product of 4-fluorobenzaldehyde.

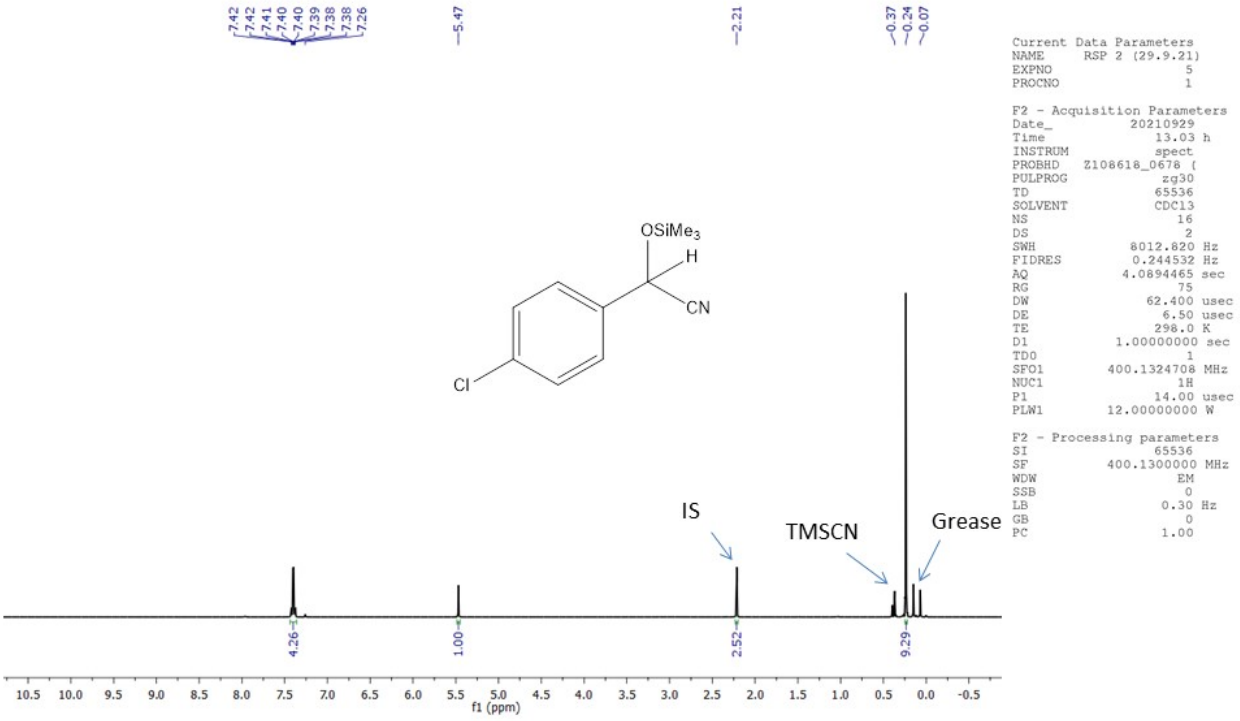


Figure S39. ^{1}H NMR spectrum of the cyanosilylated product of 4-chlorobenzaldehyde.

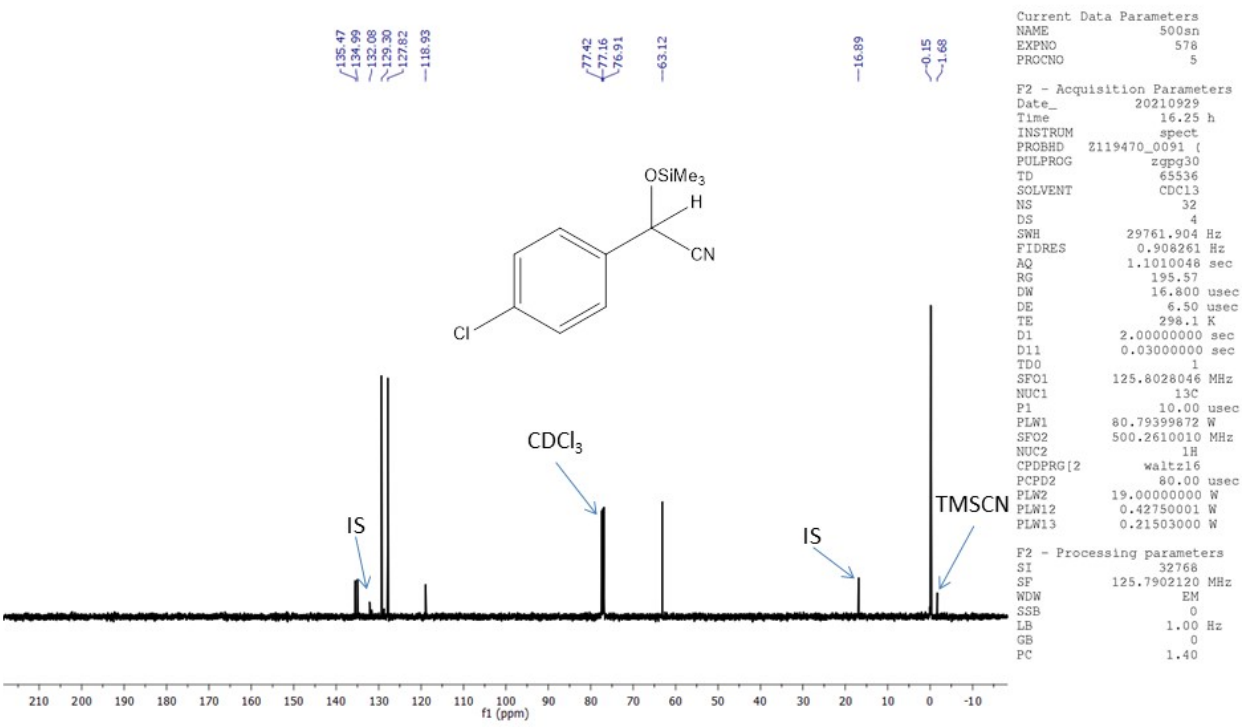


Figure S40. ^{13}C NMR spectrum of the cyanosilylated product of 4-chlorobenzaldehyde.

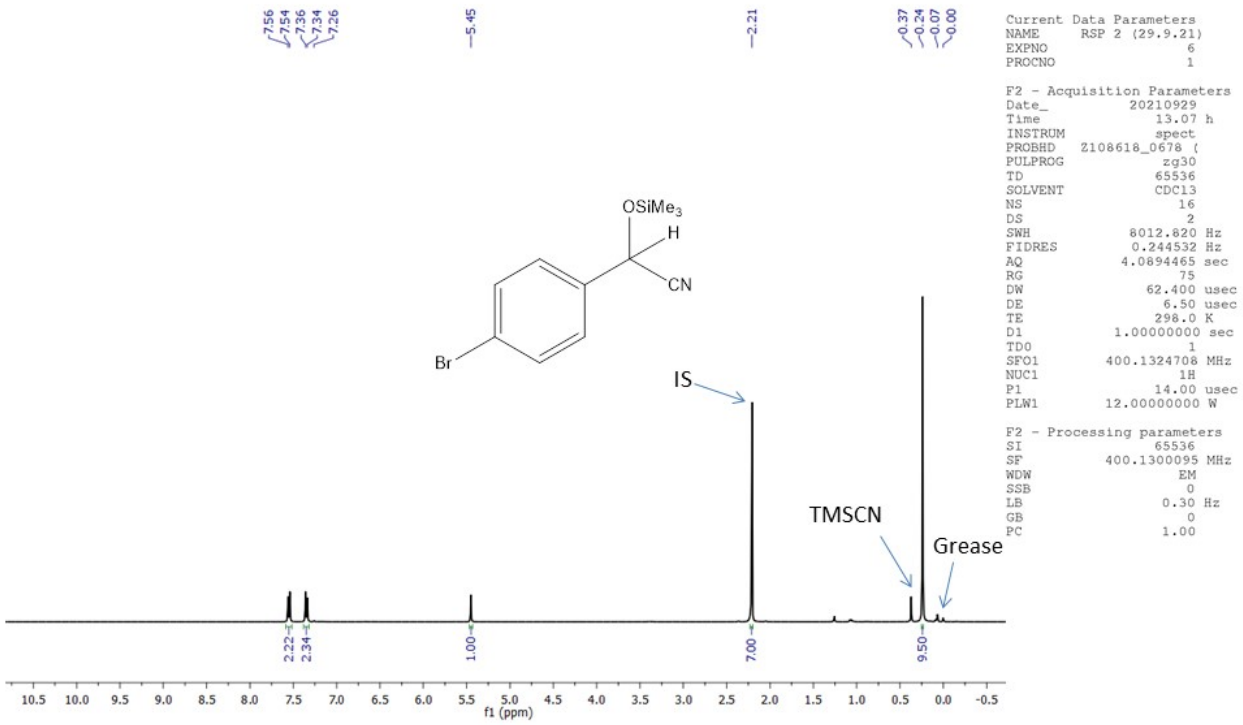


Figure S41. ^{1}H NMR spectrum of the cyanosilylated product of 4-bromobenzaldehyde.

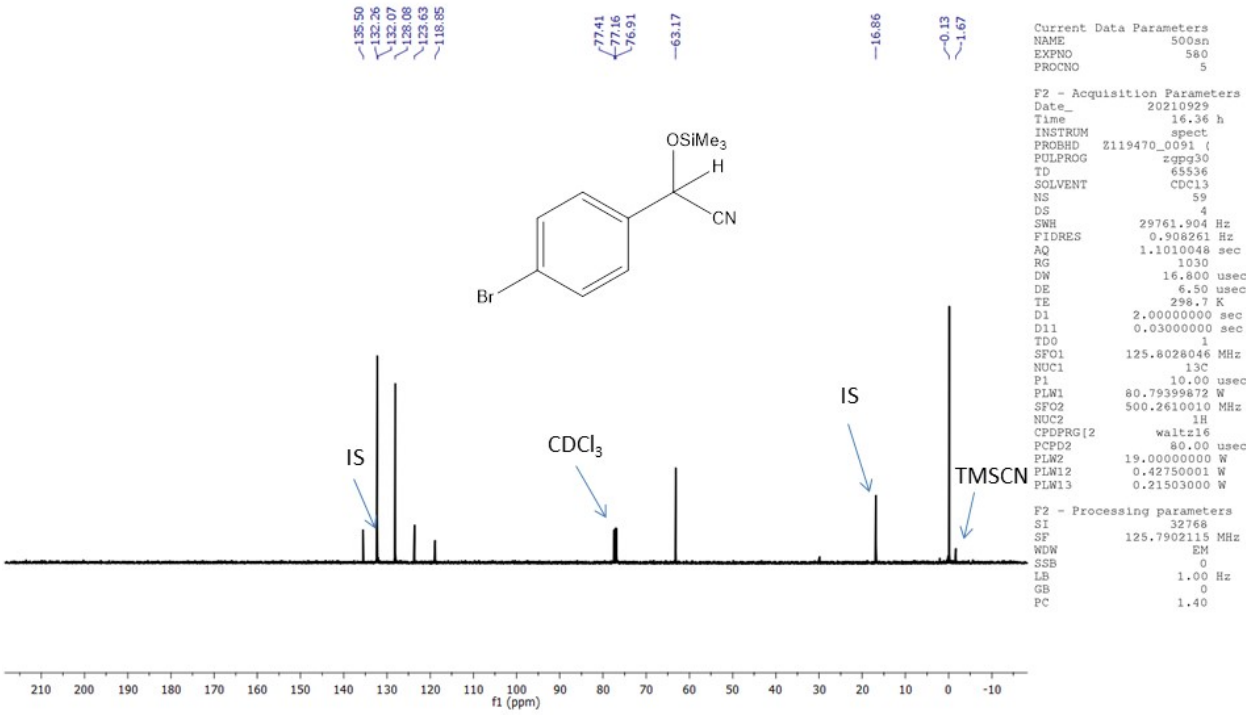


Figure S42. ^{13}C NMR spectrum of the cyanosilylated product of 4-bromobenzaldehyde.

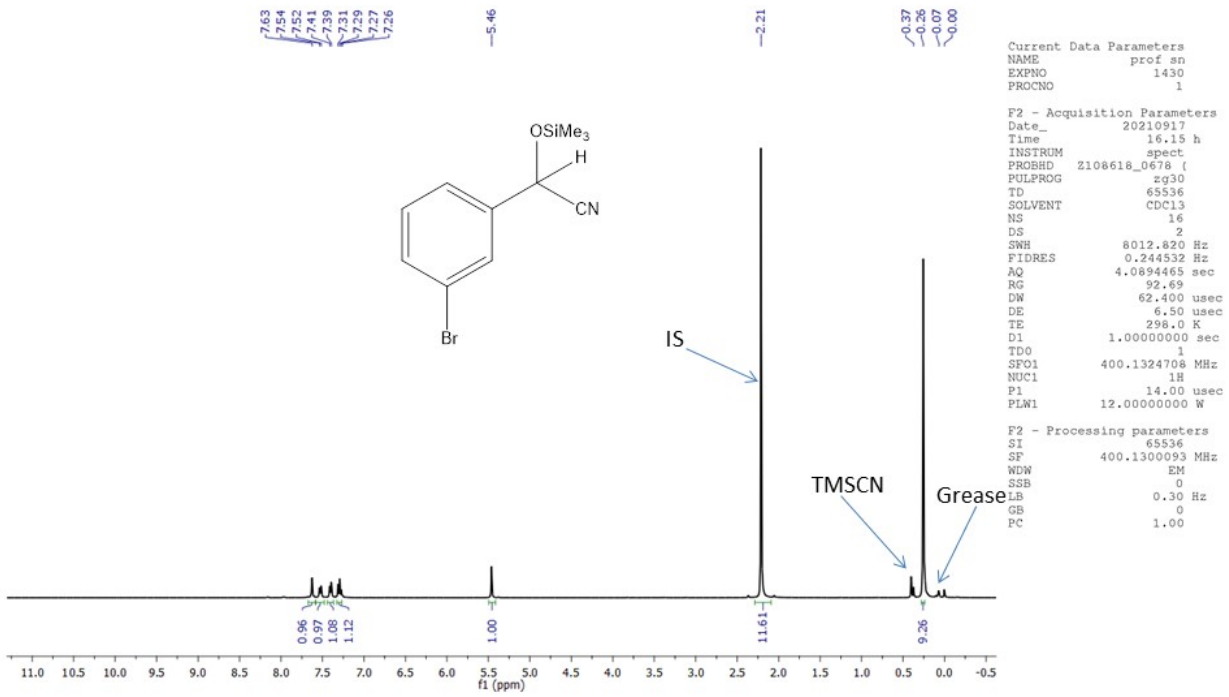


Figure S43. ^{1}H NMR spectrum of the cyanosilylated product of 3-bromobenzaldehyde.

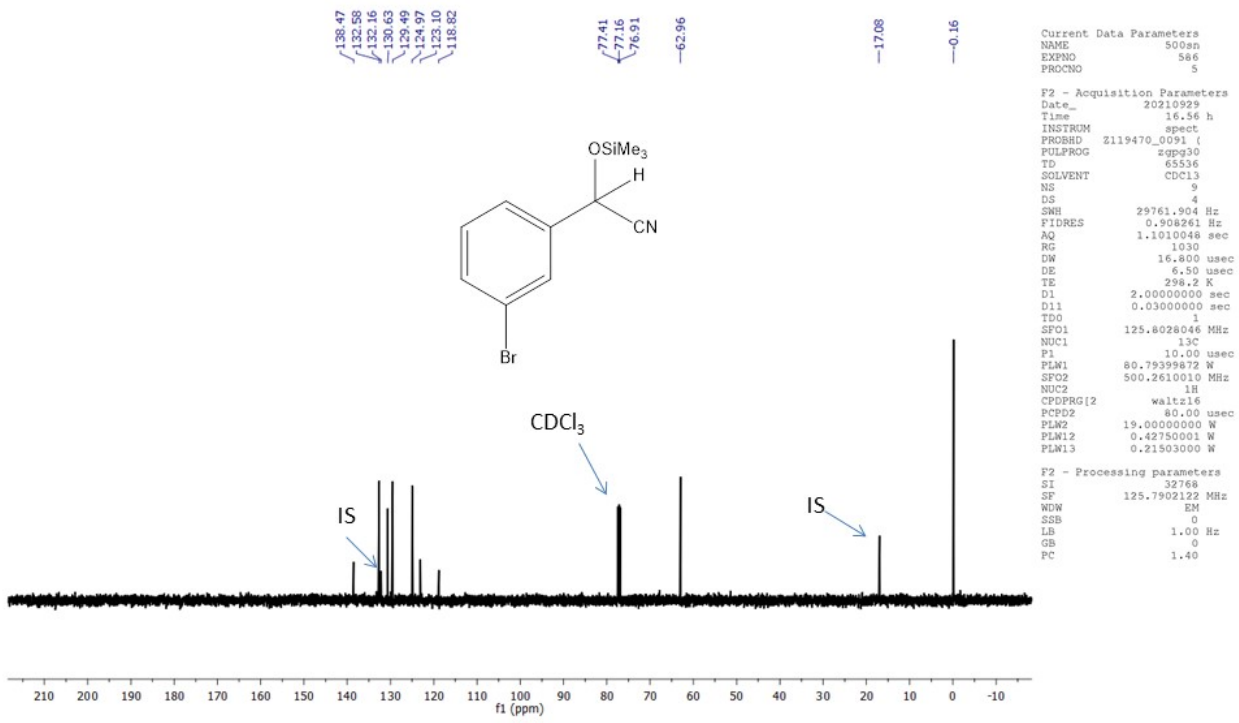


Figure S50. ^{13}C NMR spectrum of the cyanosilylated product of 3-bromobenzaldehyde.

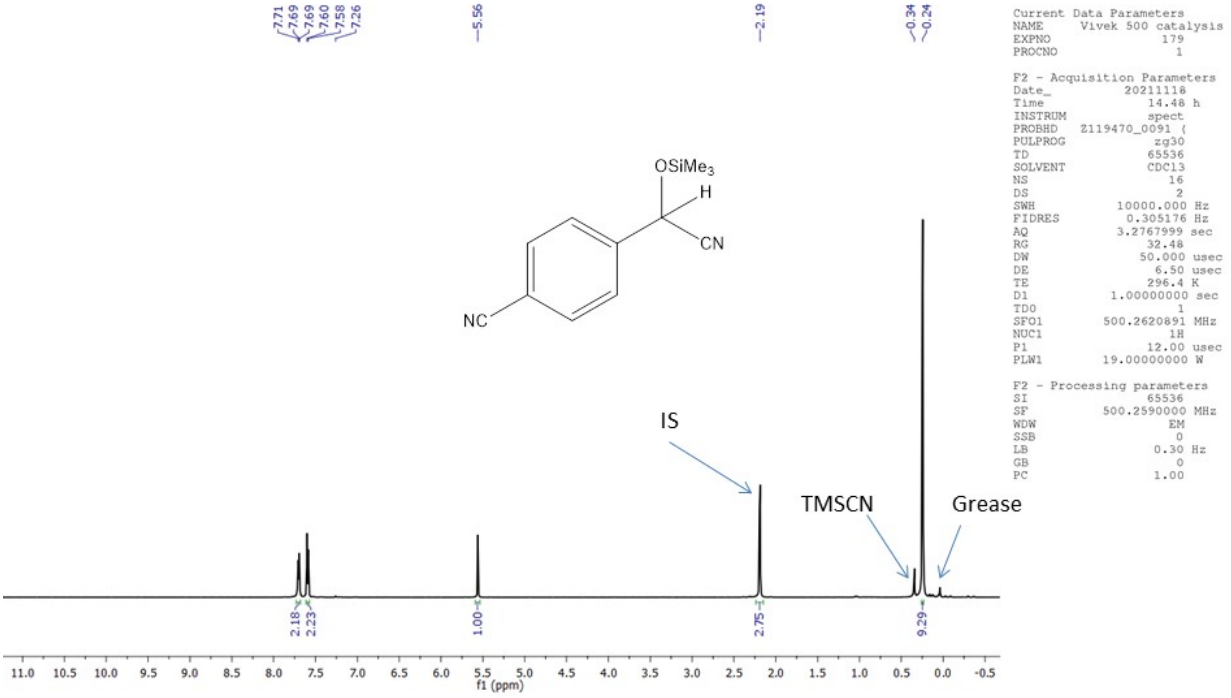


Figure S51. ^{1}H NMR spectrum of the cyanosilylated product of 4-cyanobenzaldehyde.

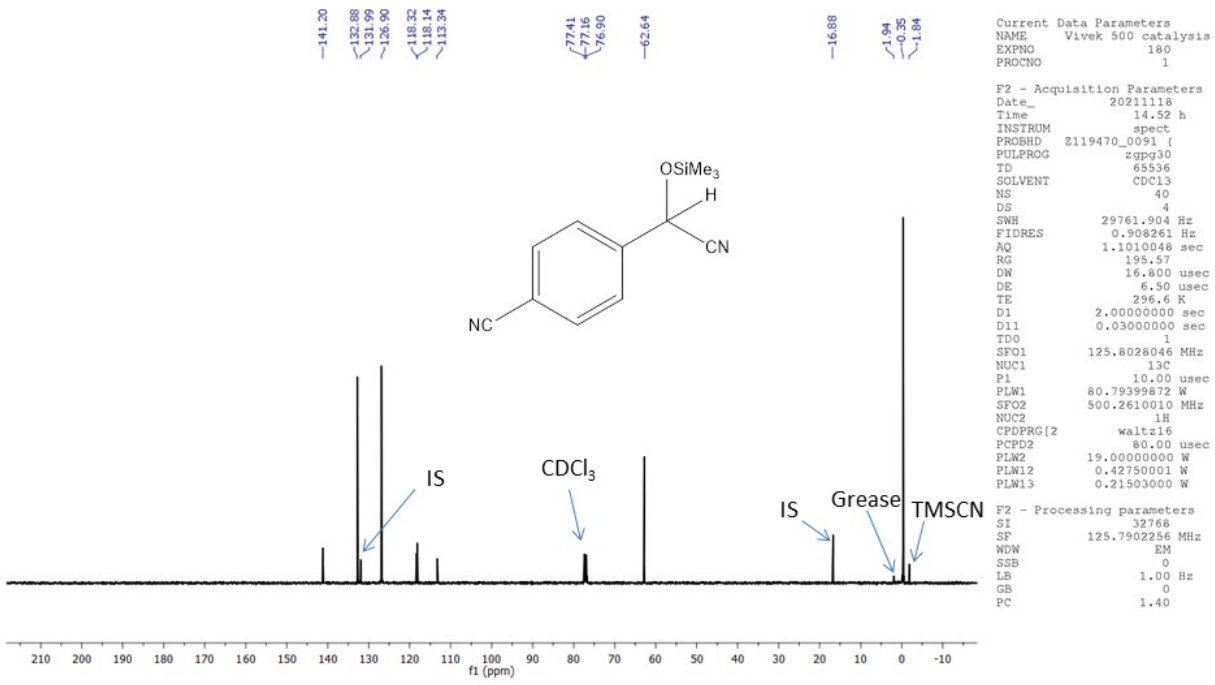


Figure S52. ^{13}C NMR spectrum of the cyanosilylated product of 4-cyanobenzaldehyde.

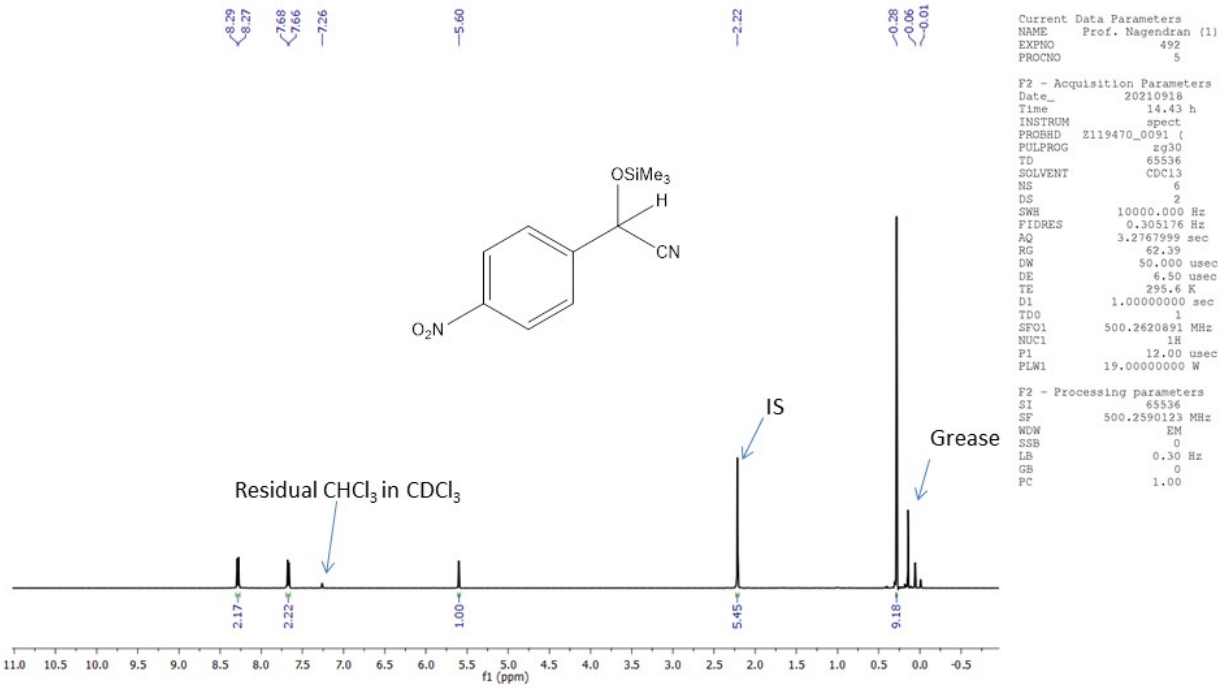


Figure S44. ^{1}H NMR spectrum of the cyanosilylated product of 4-nitrobenzaldehyde.

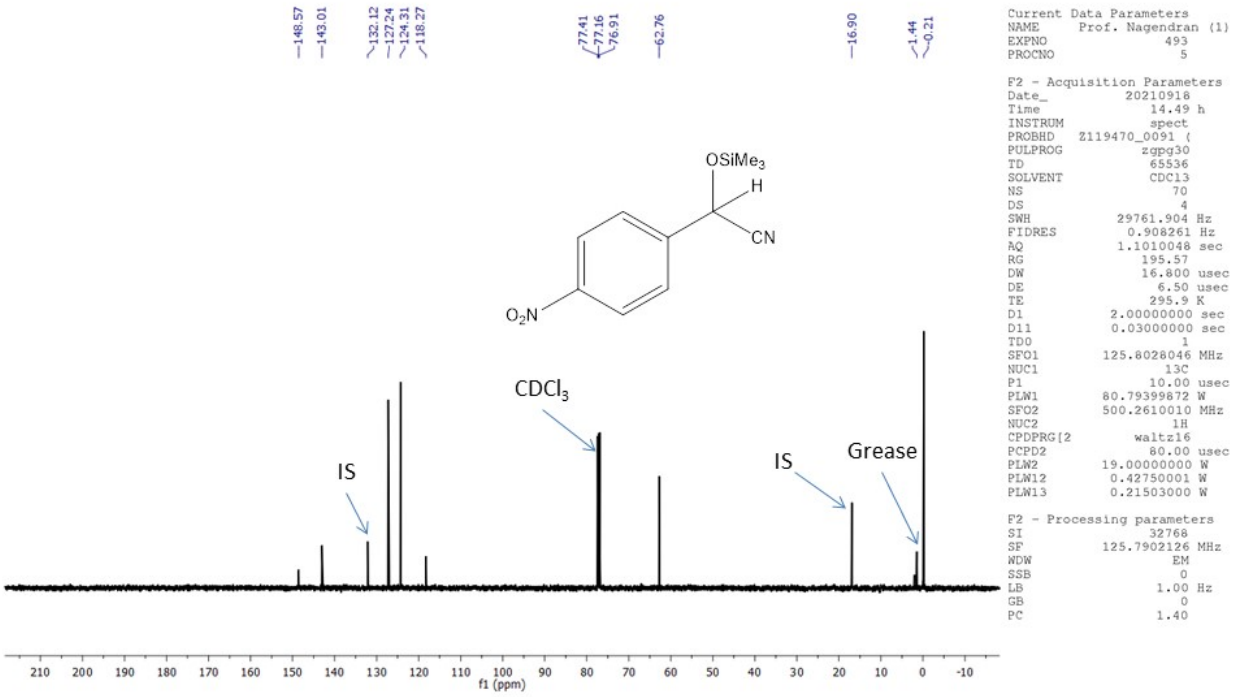


Figure S45. ^{13}C NMR spectrum of the cyanosilylated product of 4-nitrobenzaldehyde.

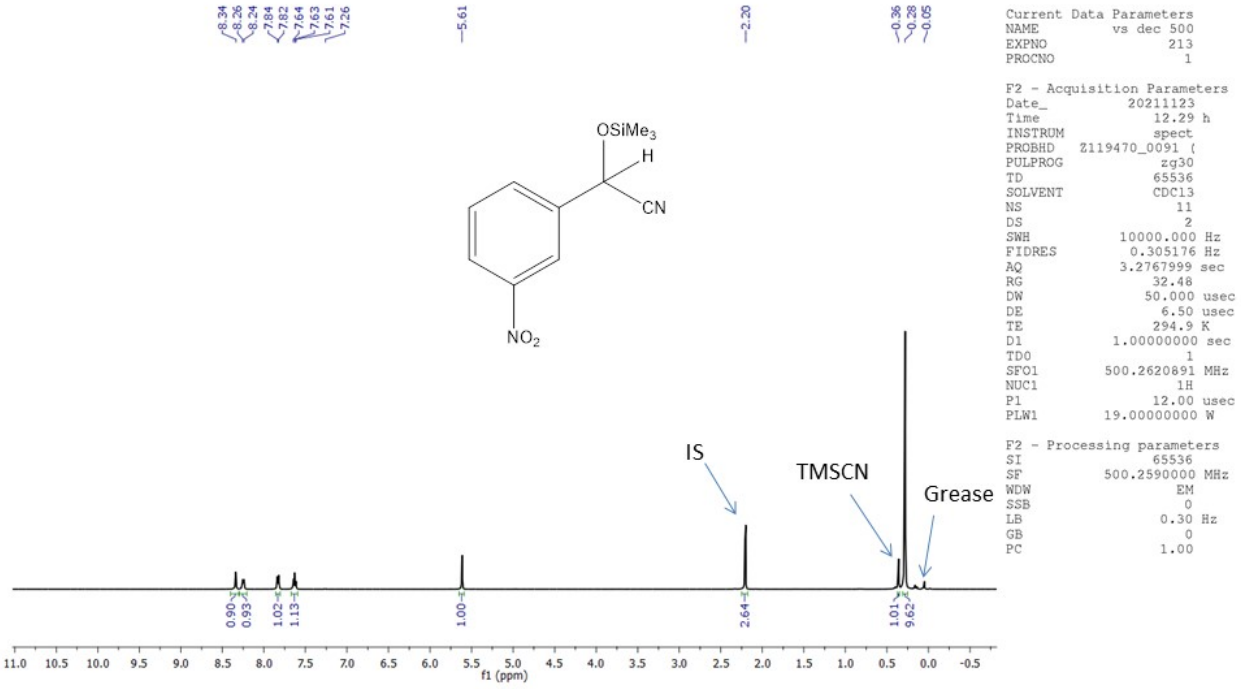


Figure S46. ^{1}H NMR spectrum of the cyanosilylated product of 3-nitrobenzaldehyde.

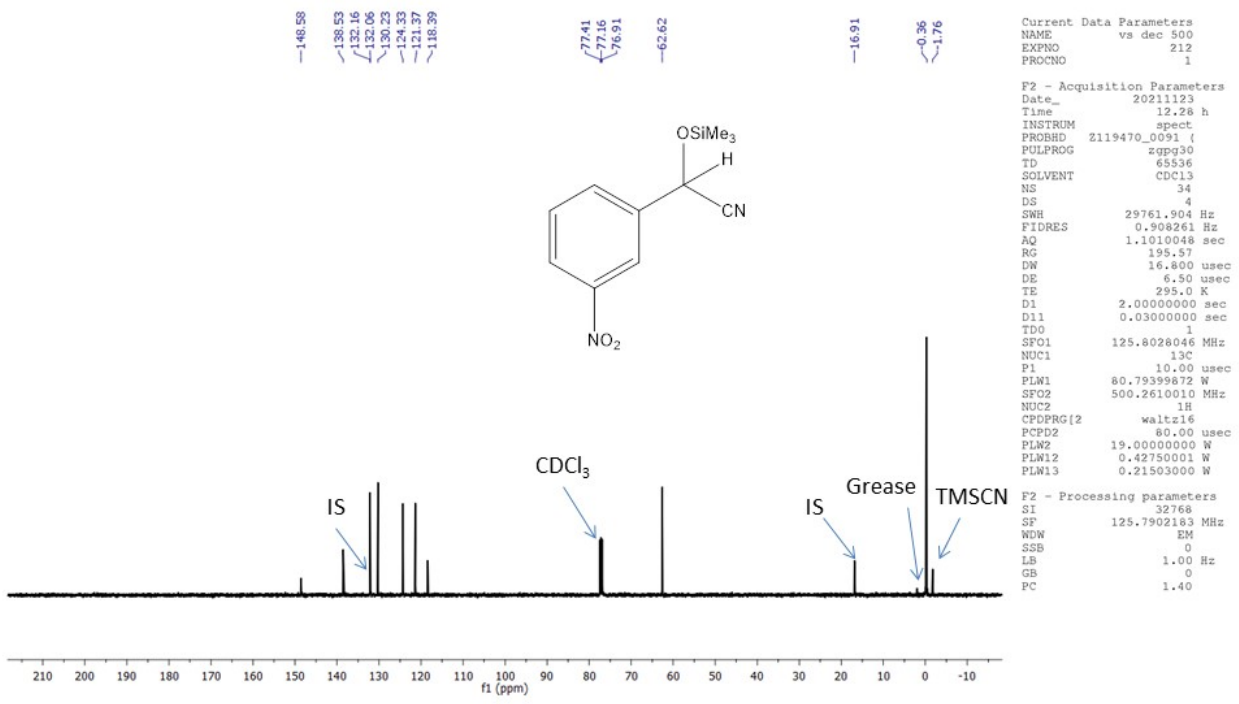


Figure S47. ^{13}C NMR spectrum of the cyanosilylated product of 3-nitrobenzaldehyde.

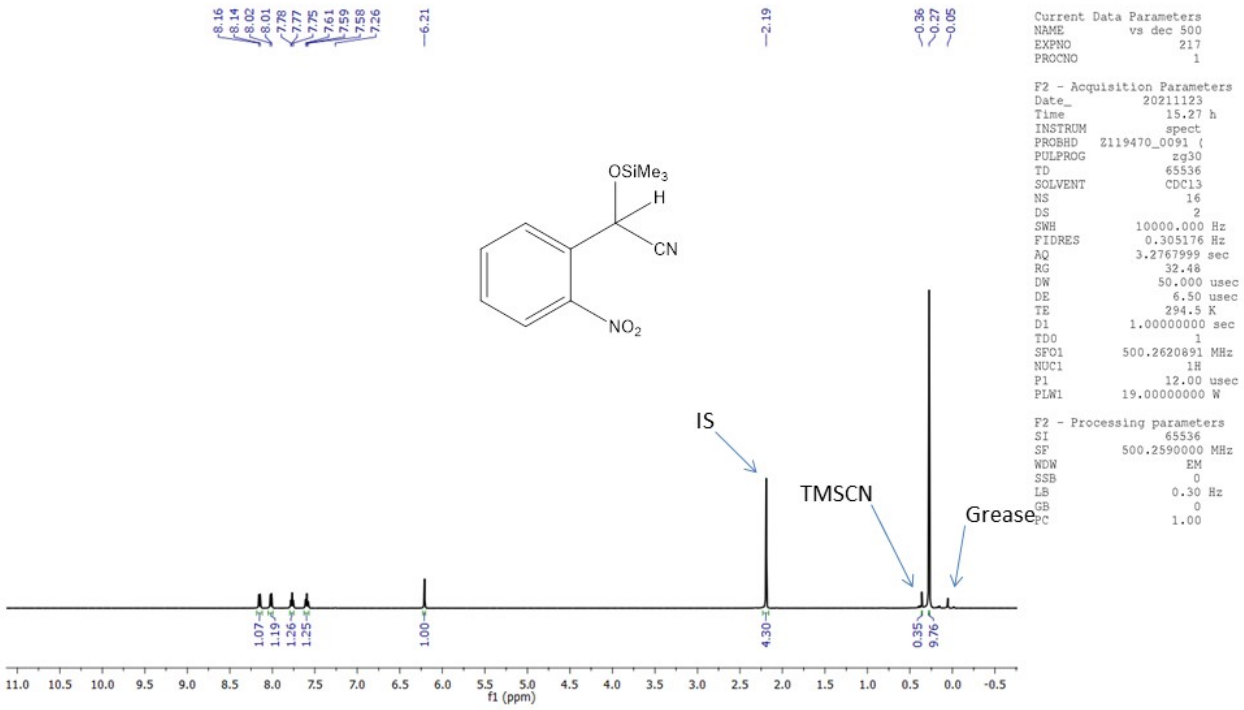


Figure S48. ^{1}H NMR spectrum of the cyanosilylated product of 2-nitrobenzaldehyde.

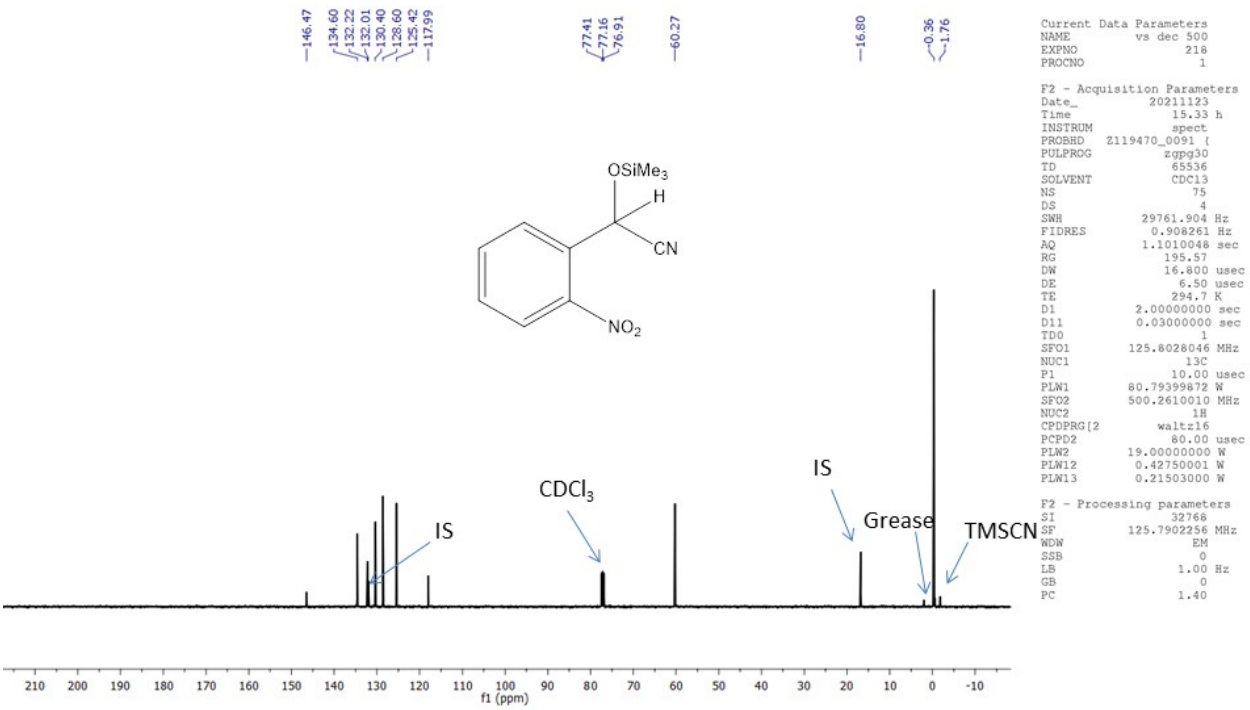


Figure S49. ^{13}C NMR spectrum of the cyanosilylated product of 2-nitrobenzaldehyde.

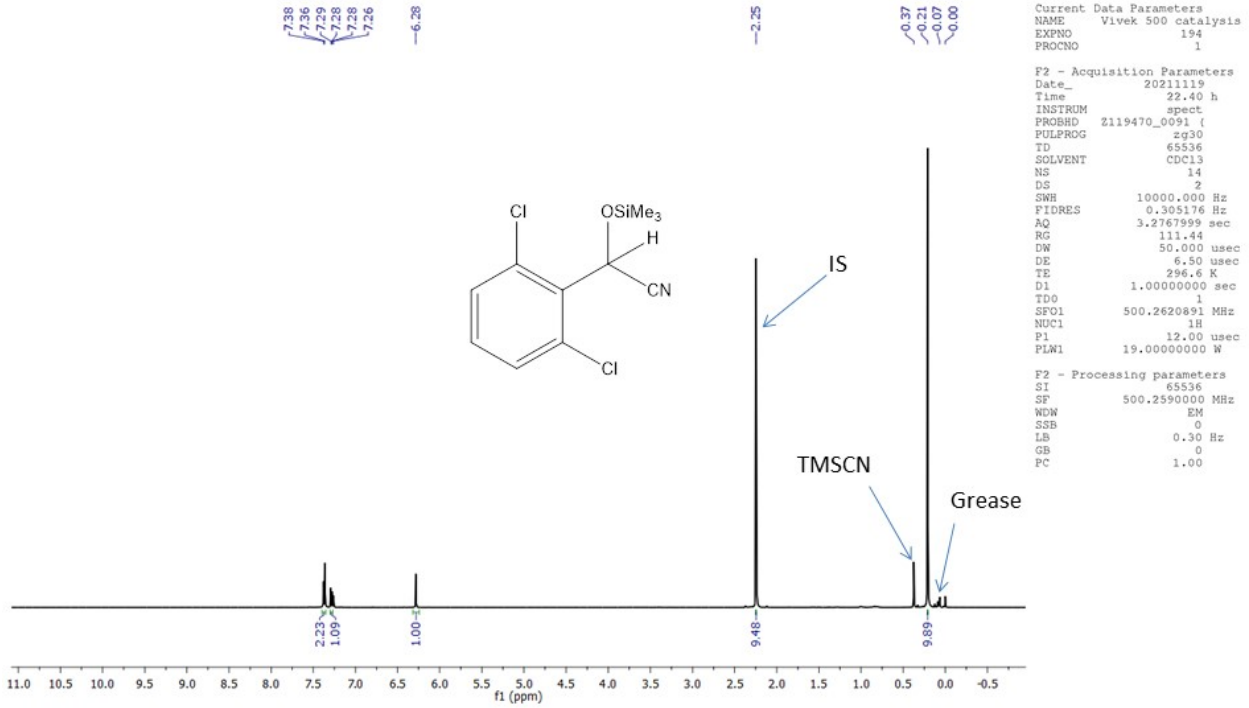


Figure S50. ^{1}H NMR spectrum of the cyanosilylated product of 2,6-dichlorobenzaldehyde.

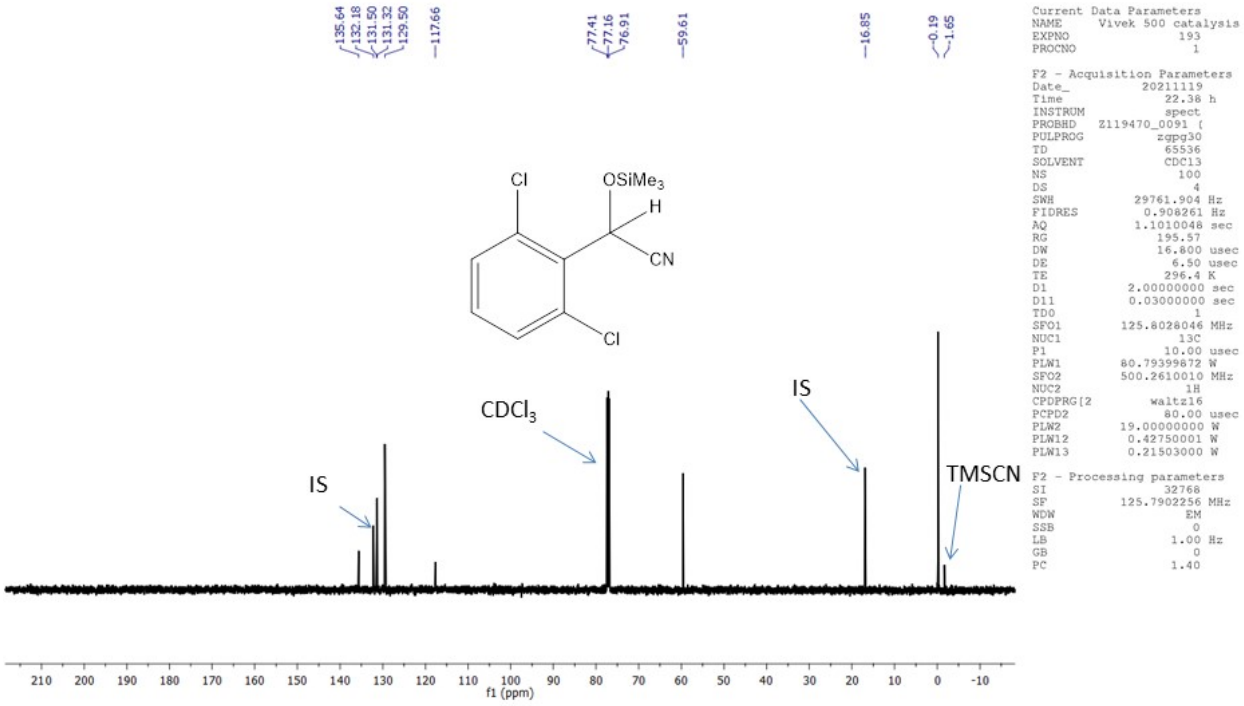


Figure S60. ^{13}C NMR spectrum of the cyanosilylated product of 2,6-dichlorobenzaldehyde.

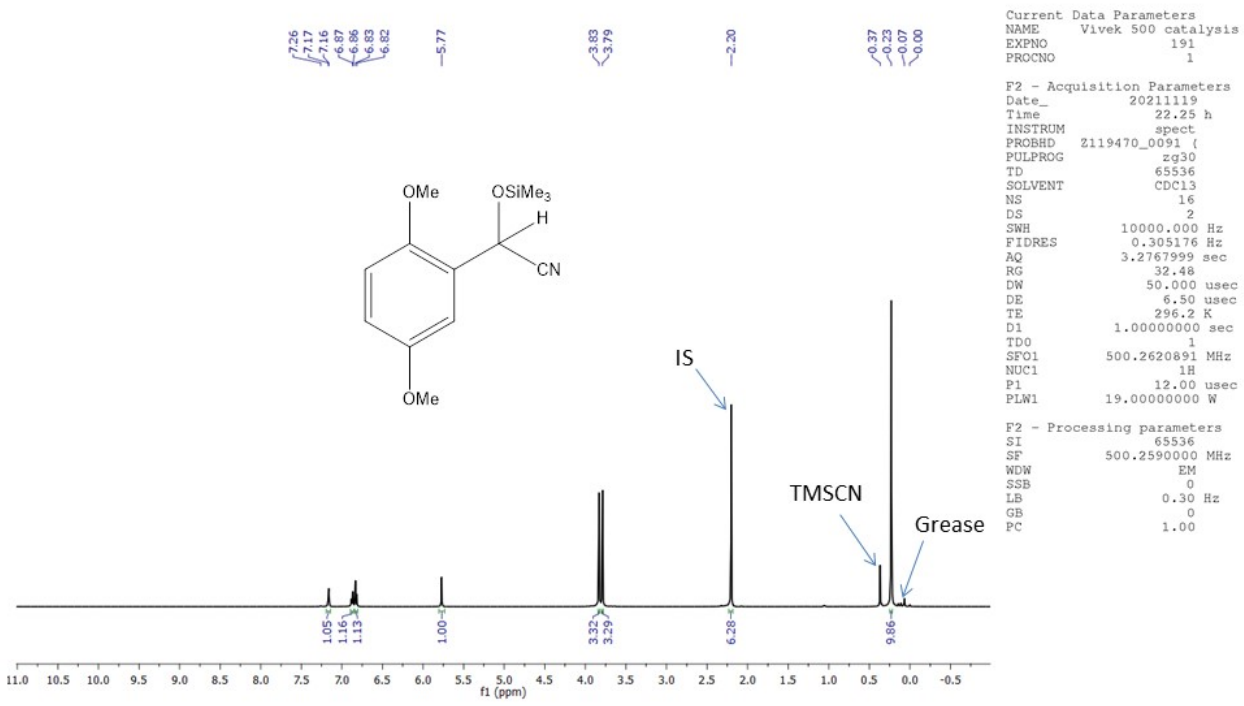


Figure S61. ^{1}H NMR spectrum of the cyanosilylated product of 2,5-dimethoxybenzaldehyde.

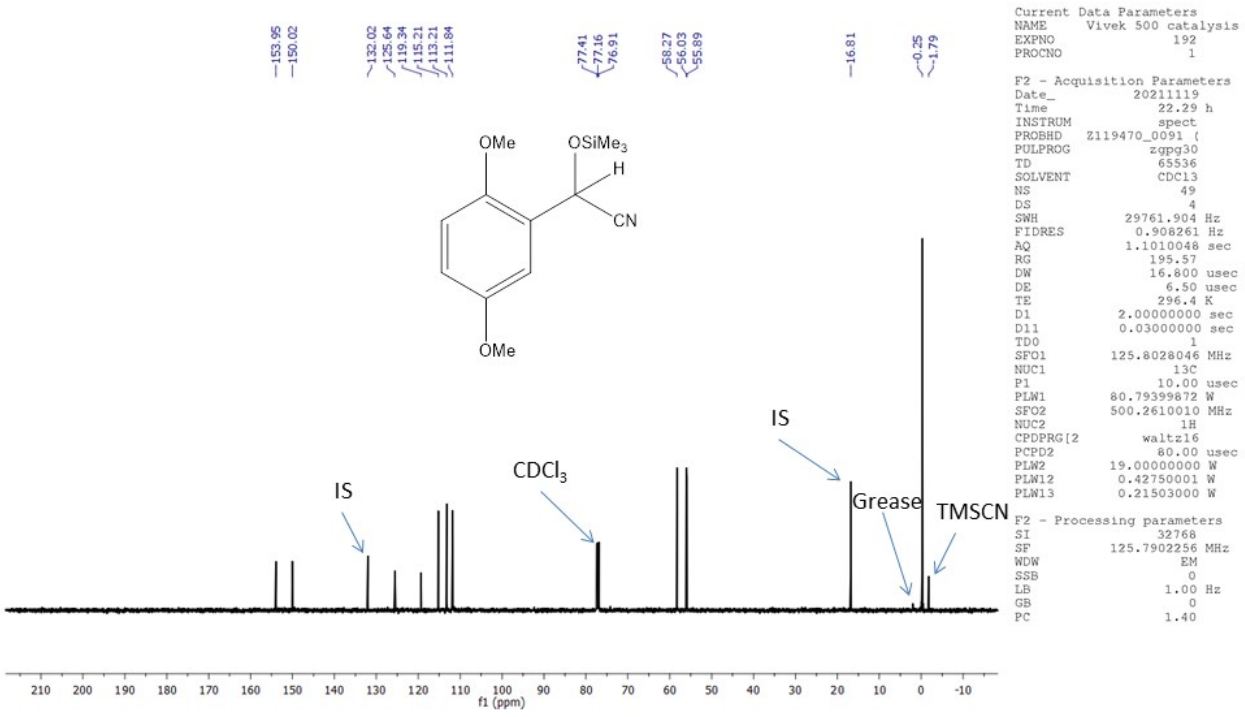


Figure S62. ^{13}C NMR spectrum of the cyanosilylated product of 2,5-dimethoxybenzaldehyde.

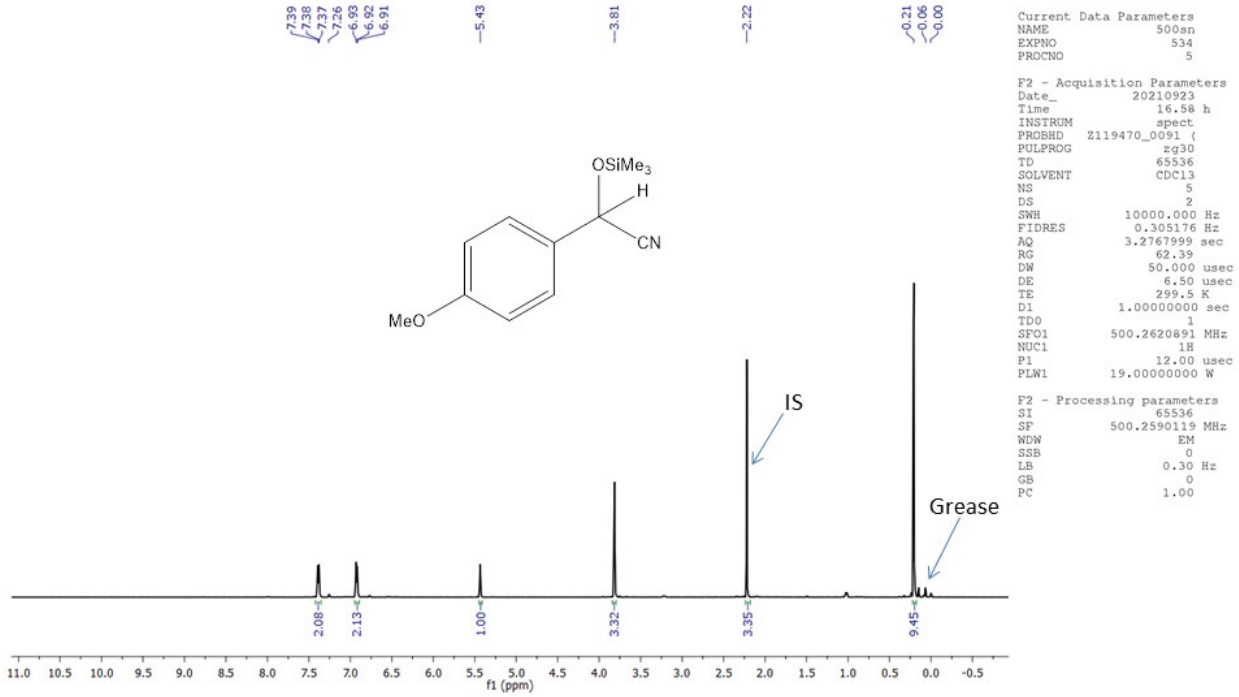


Figure S51. ^{1}H NMR spectrum of the cyanosilylated product of 4-methoxybenzaldehyde.

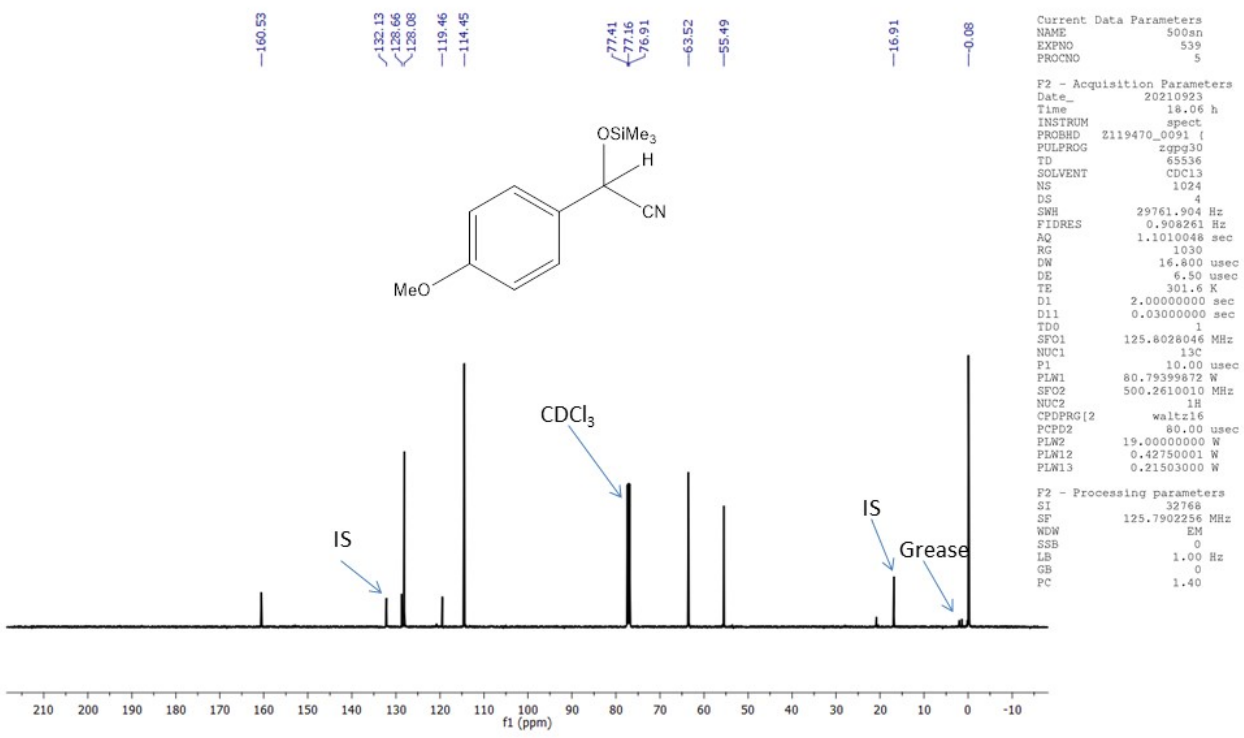


Figure S52. ^{13}C NMR spectrum of the cyanosilylated product of 4-methoxybenzaldehyde.

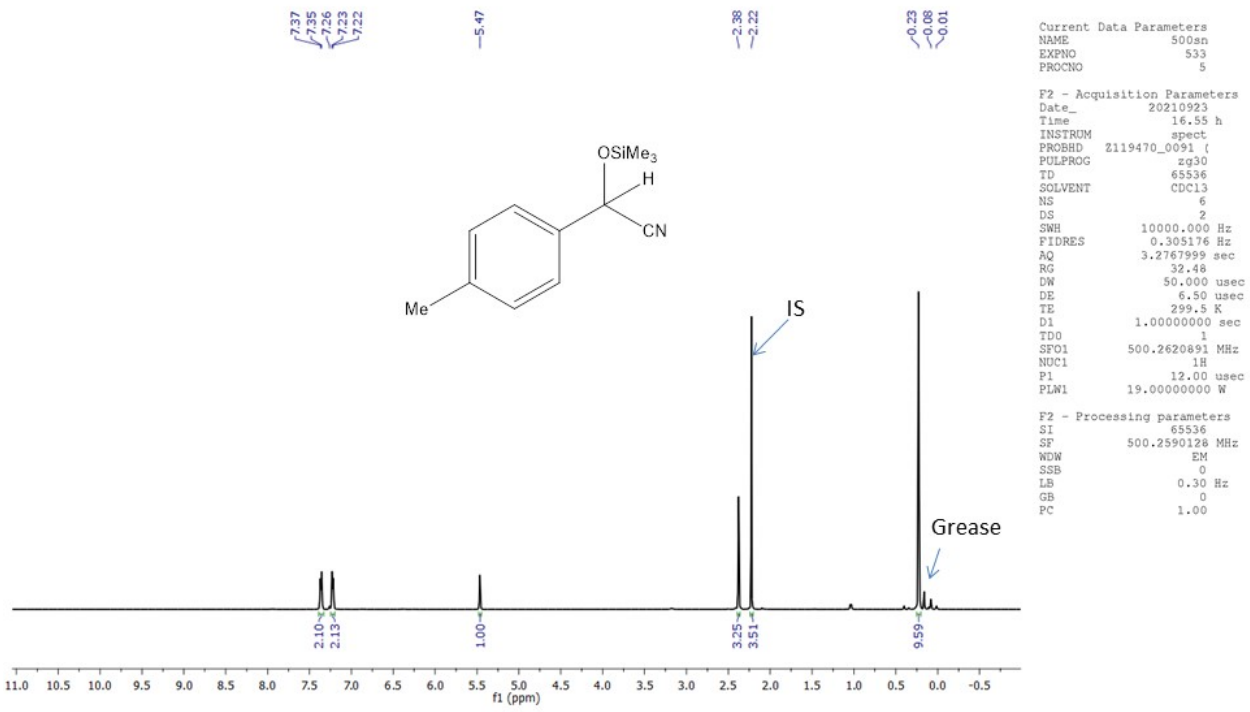


Figure S53. ^{1}H NMR spectrum of the cyanosilylated product of 4-methylbenzaldehyde.

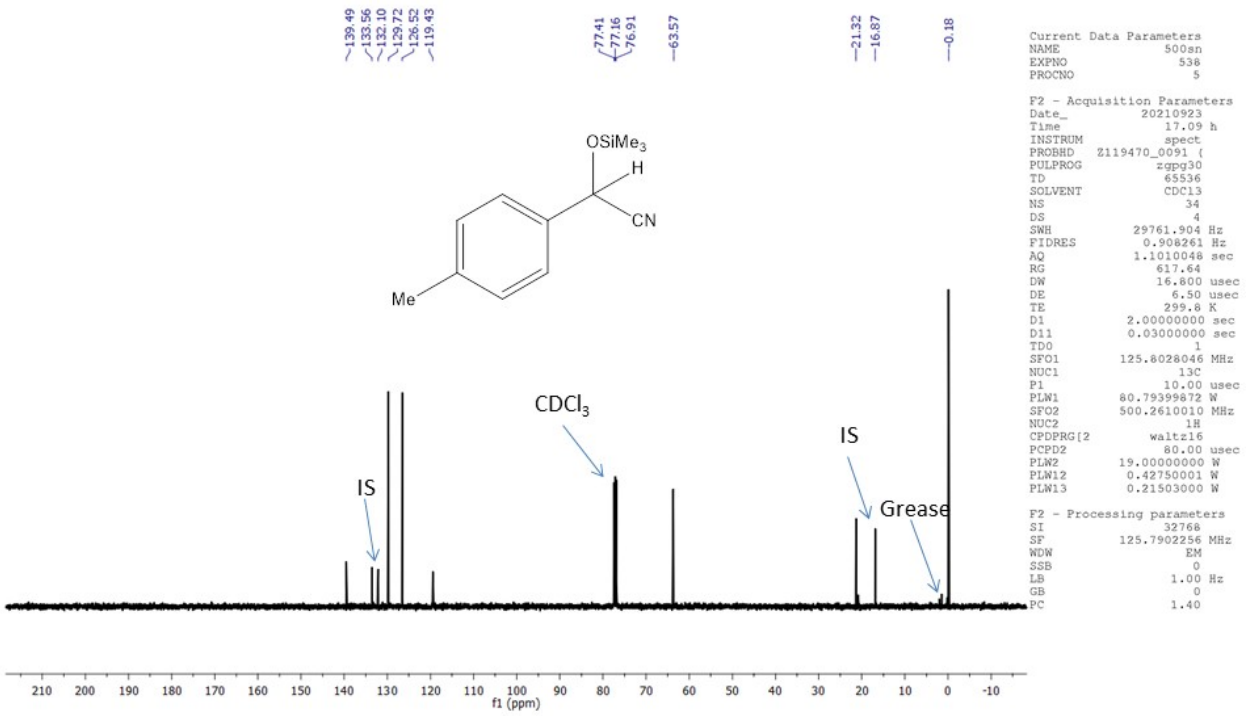


Figure S54. ^{13}C NMR spectrum of the cyanosilylated product of 4-methylbenzaldehyde.

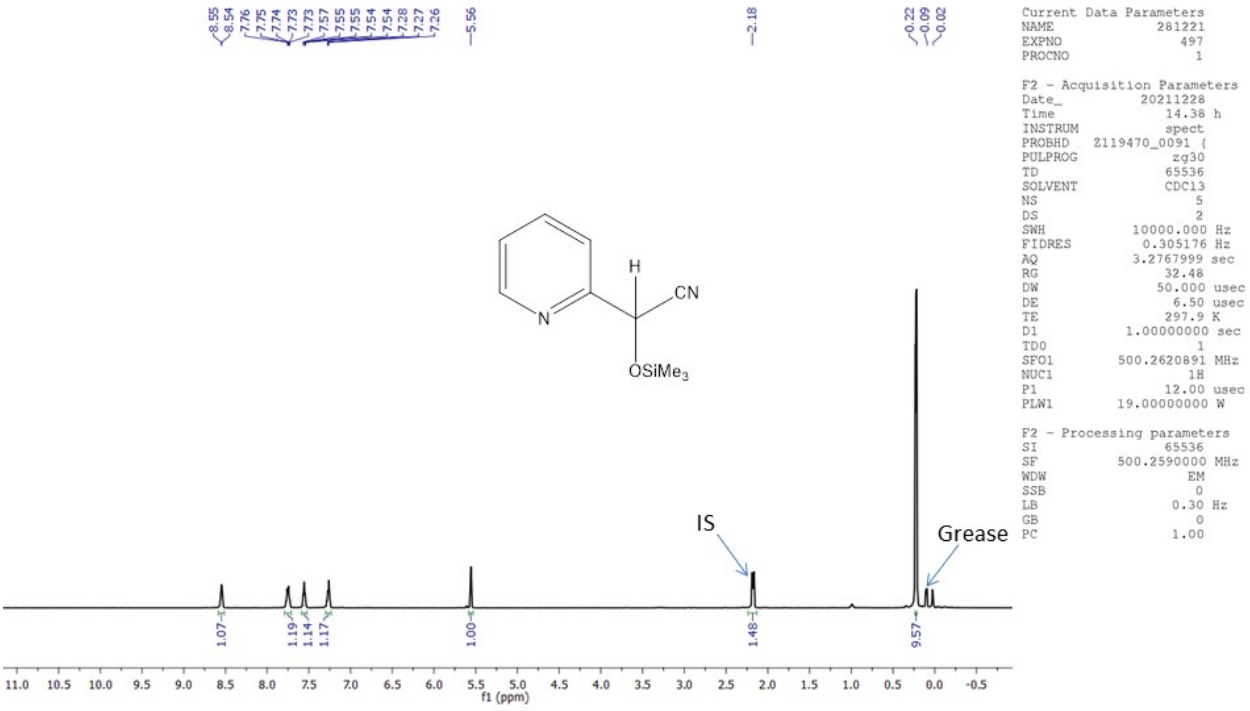


Figure S55. ^{1}H NMR spectrum of the cyanosilylated product of pyridine-2-carbaldehyde.

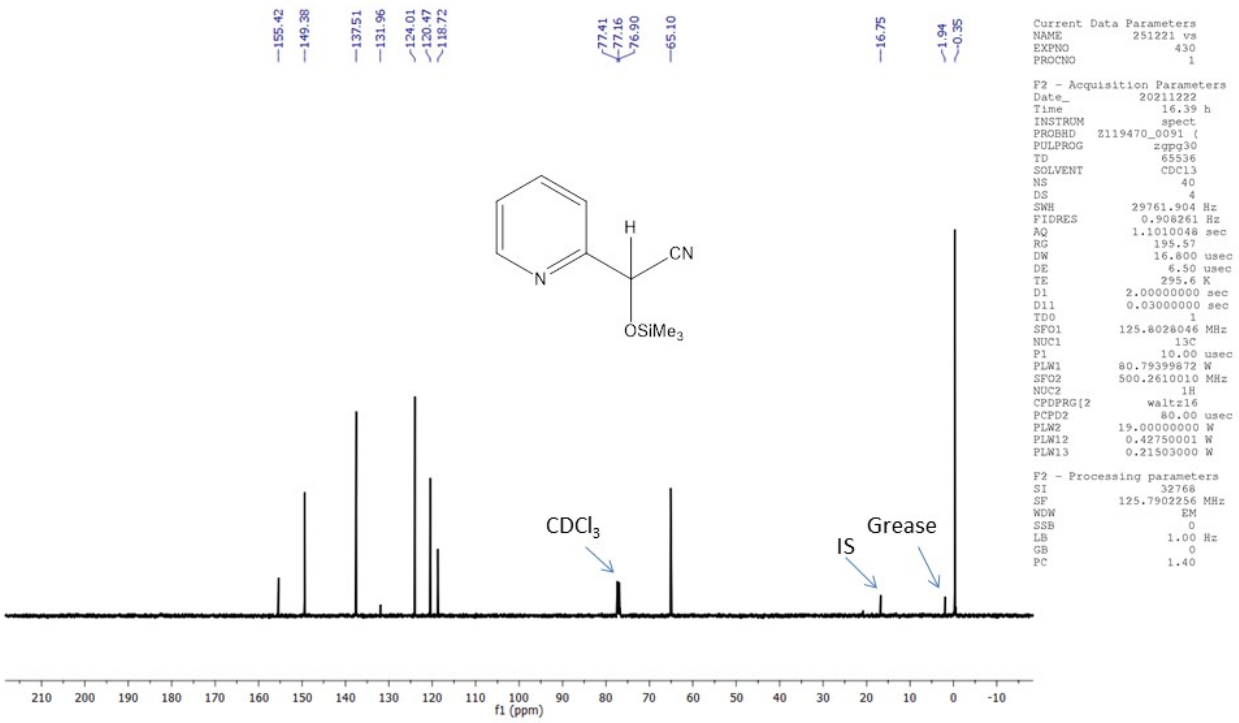


Figure S56. ^{13}C NMR spectrum of the cyanosilylated product of pyridine-2-carbaldehyde.

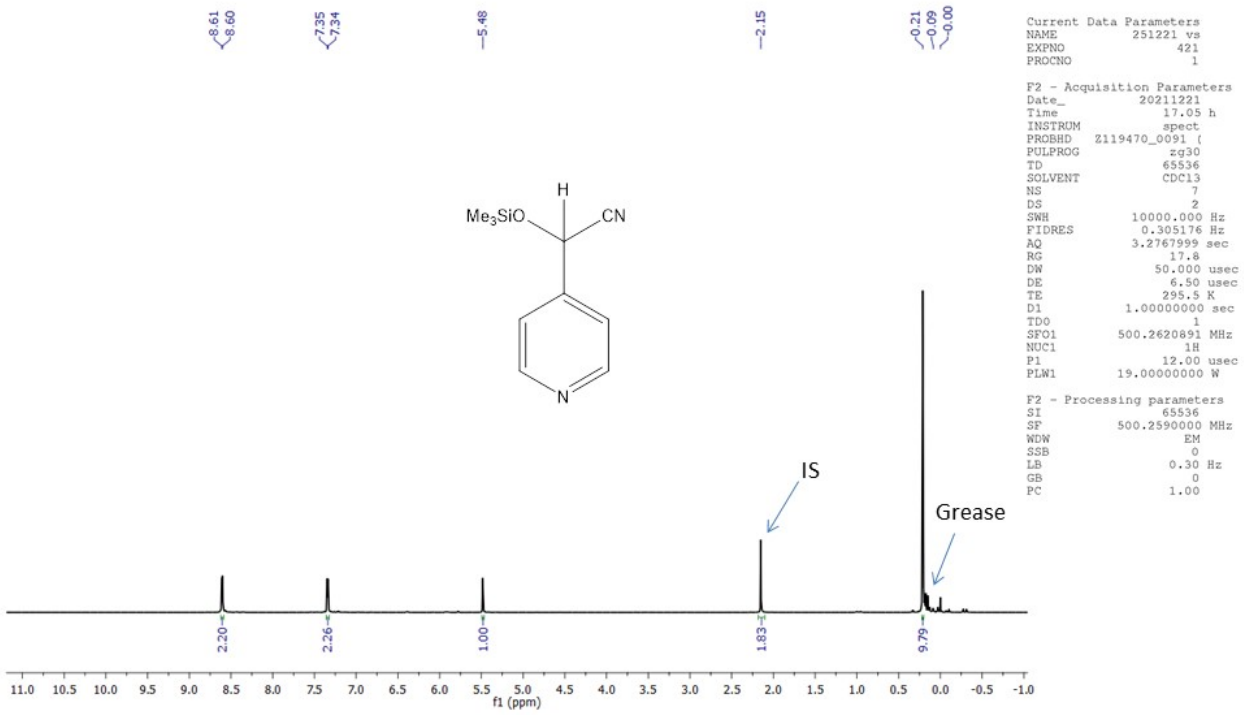


Figure S57. ^{1}H NMR spectrum of the cyanosilylated product of pyridine-4-carbaldehyde.

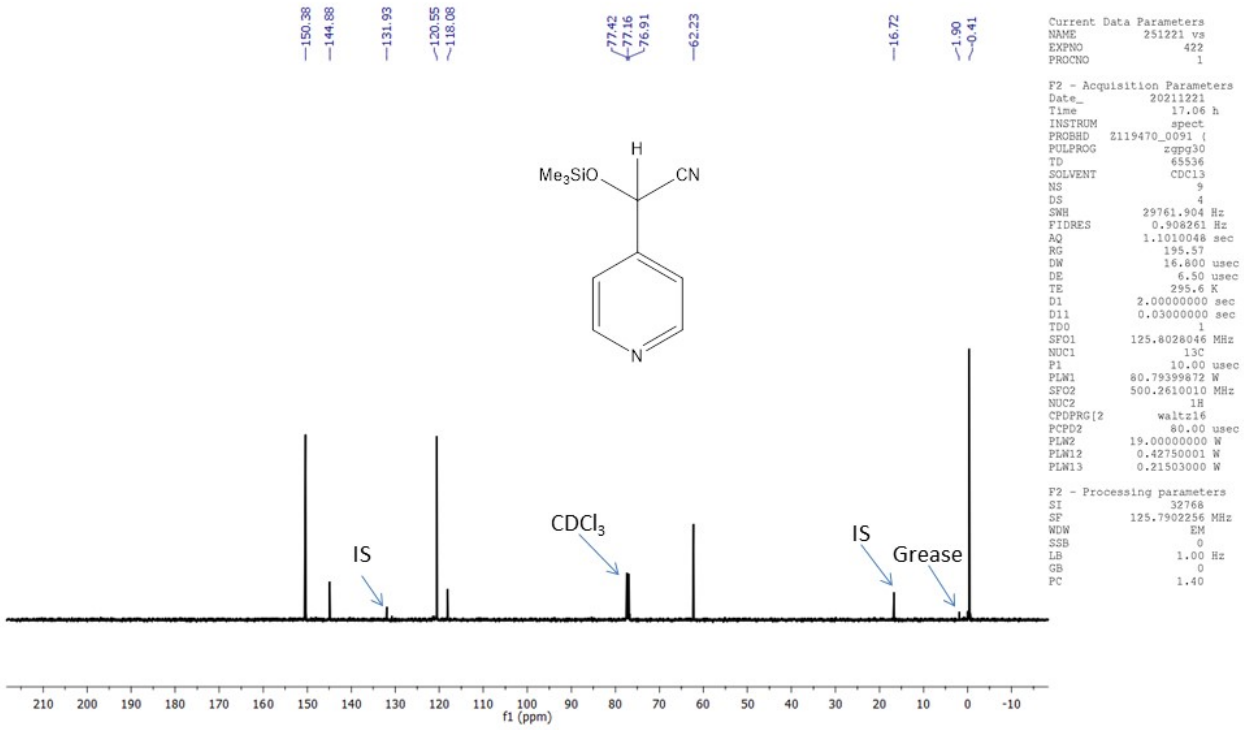


Figure S580. ^{13}C NMR spectrum of the cyanosilylated product of pyridine-4-carbaldehyde.

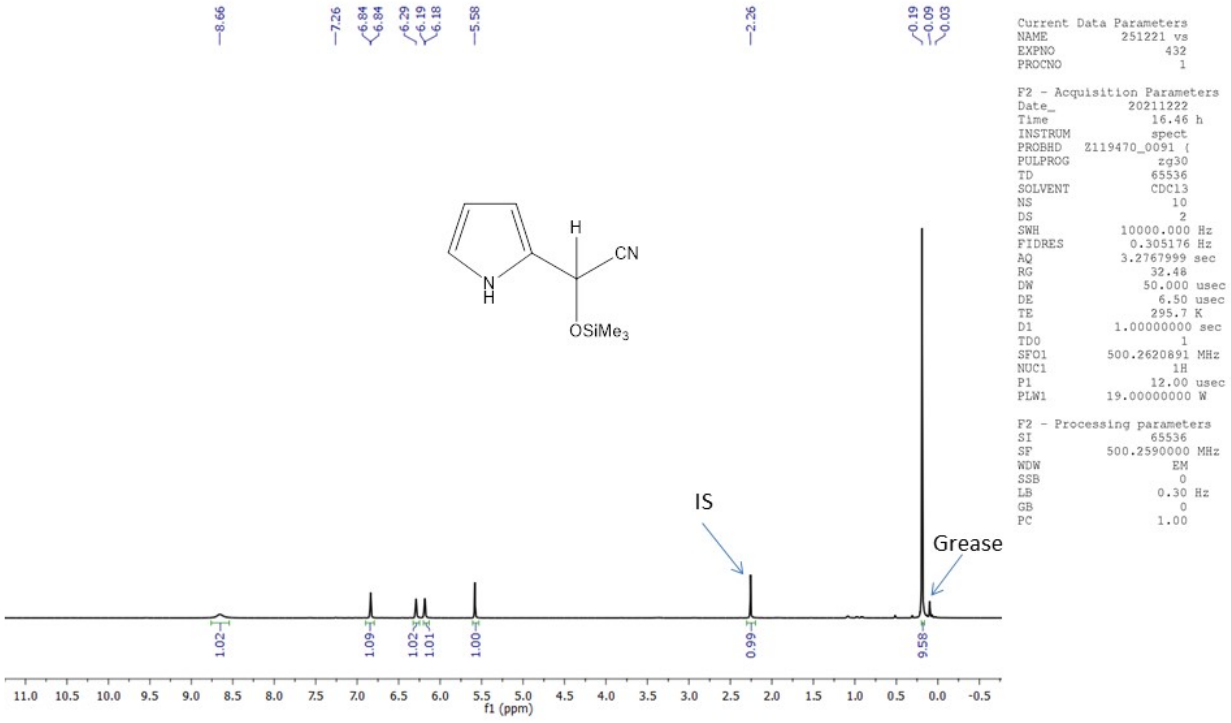


Figure S7159. ^{1}H NMR spectrum of the cyanosilylated product of pyrrole-2-carbaldehyde.

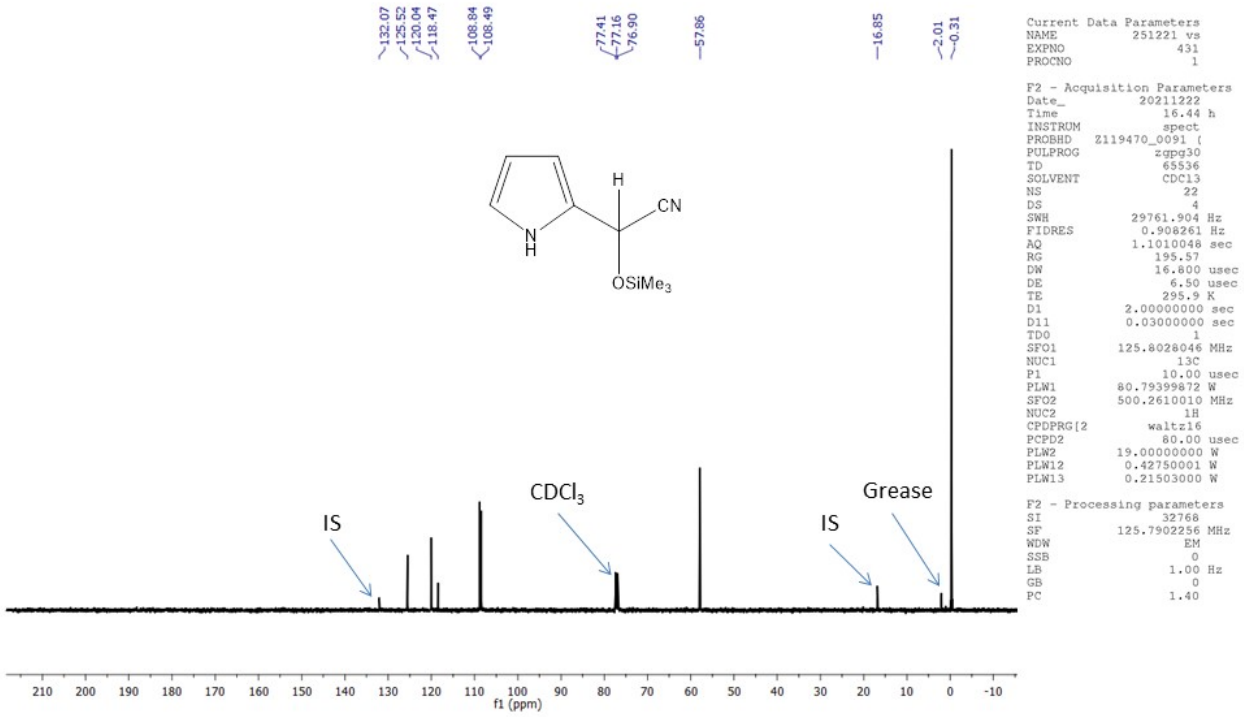


Figure S72. ^{13}C NMR spectrum of the cyanosilylated product of pyrrole-2-carbaldehyde.

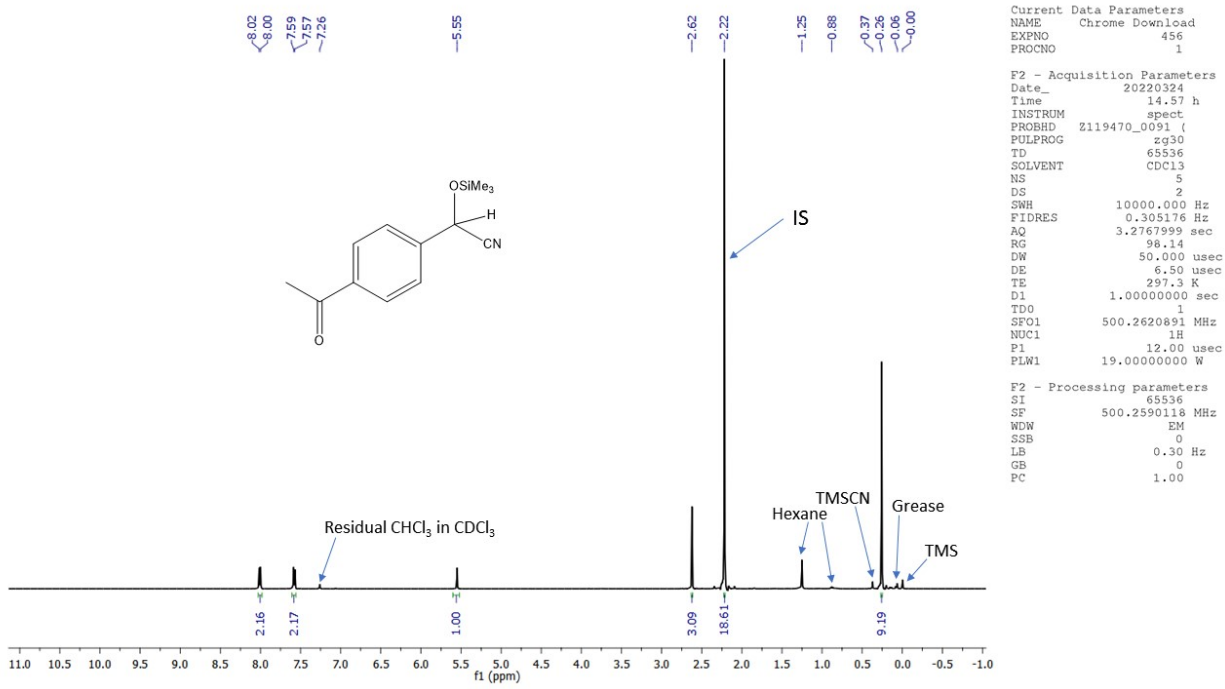


Figure S60. ^{1}H NMR spectrum of the cyanosilylated product of 4-acetylbenzaldehyde.

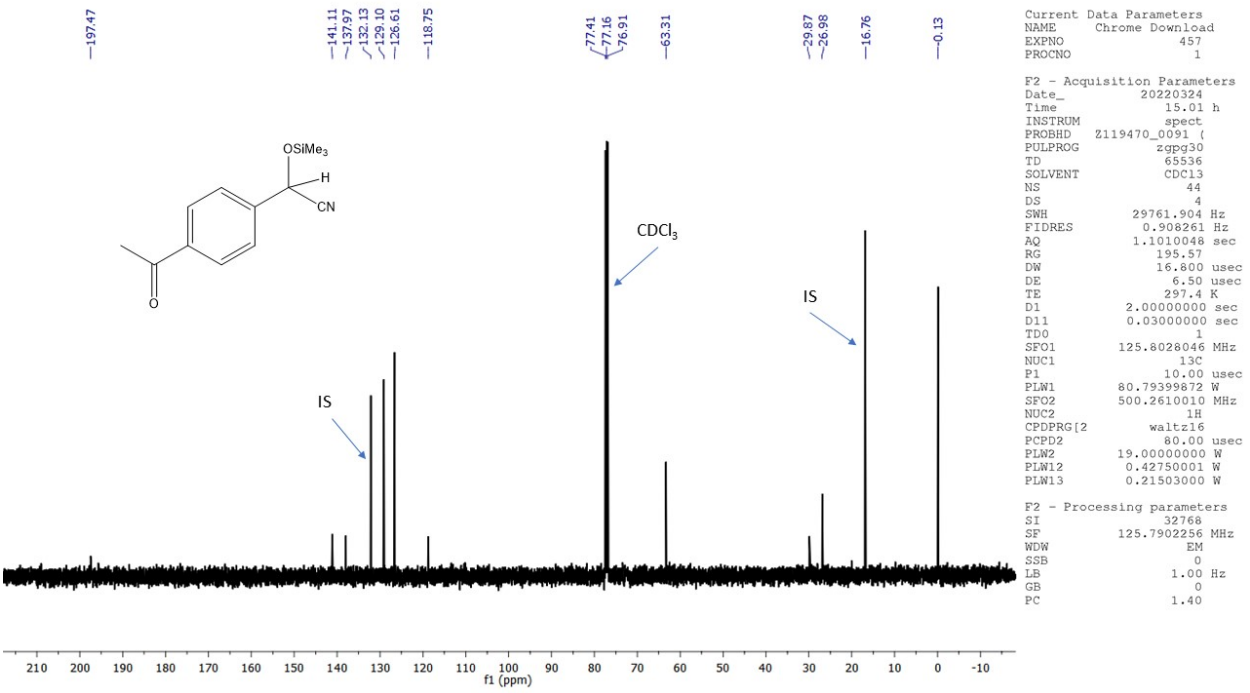


Figure S61. ^{13}C NMR spectrum of the cyanosilylated product of 4-acetylbenzaldehyde.

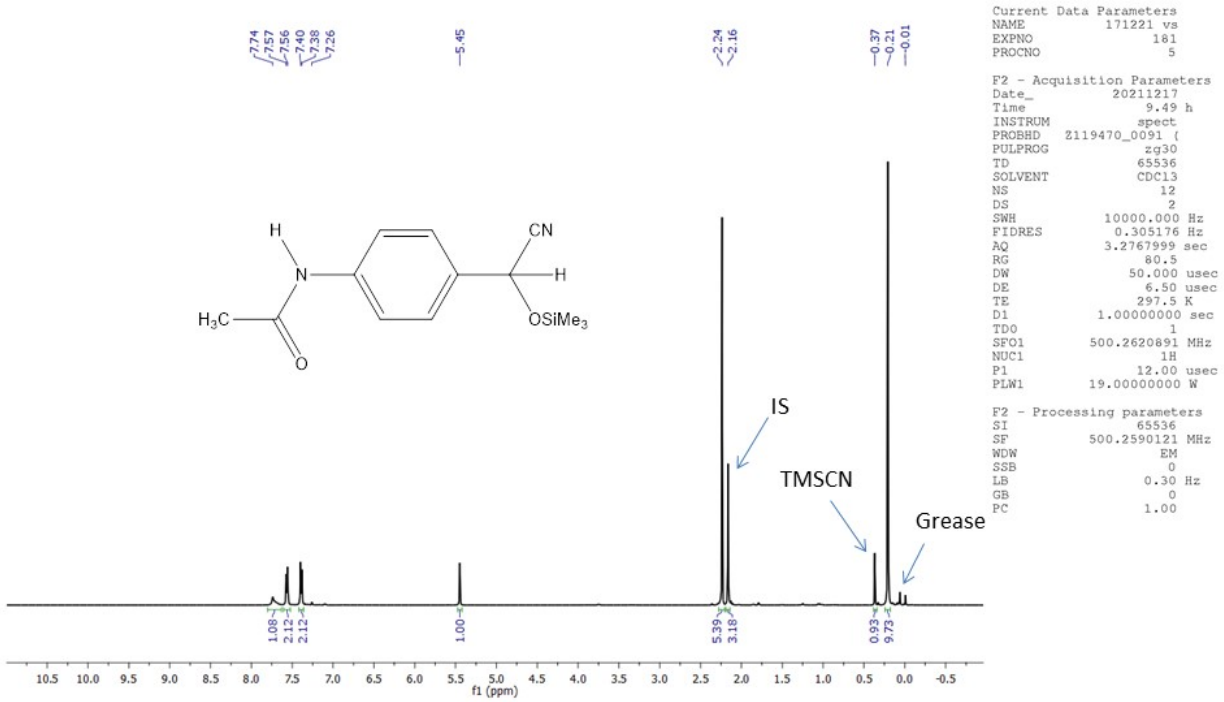


Figure S62. ^{1}H NMR spectrum of the cyanosilylated product of 4-acetamidobenzaldehyde.

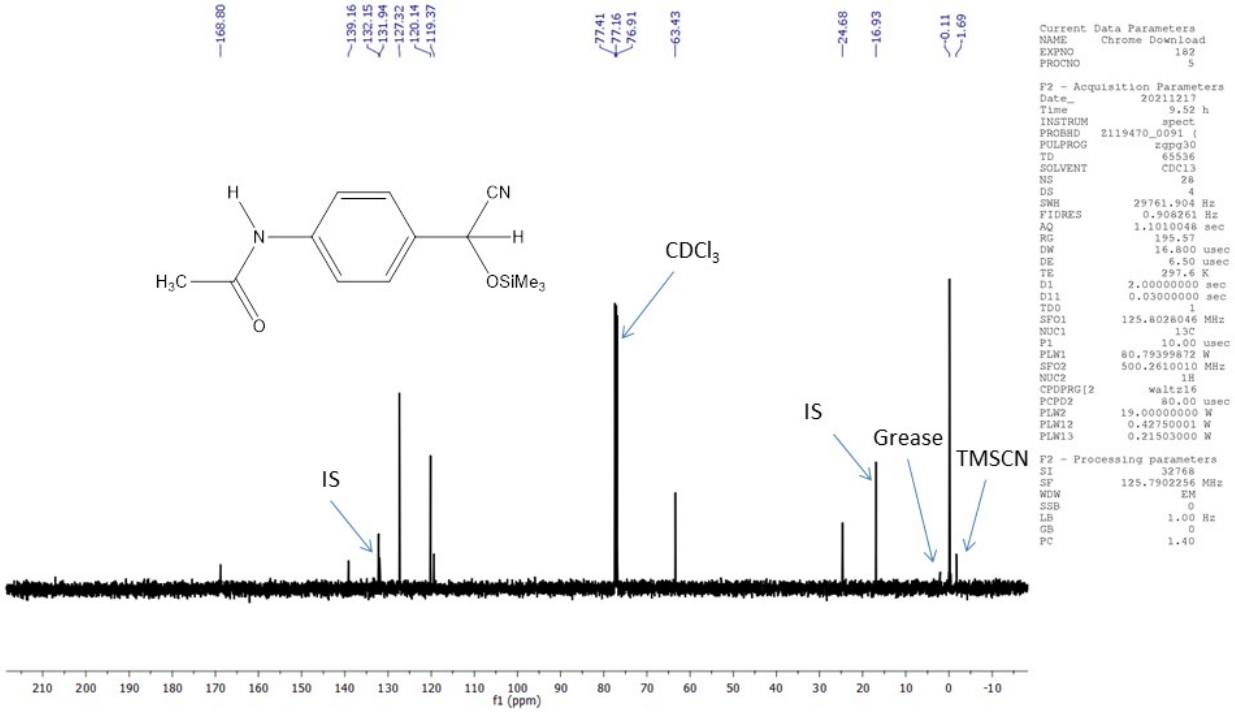


Figure S63. ^{13}C NMR spectrum of the cyanosilylated product of 4-acetamidobenzaldehyde.

General procedure for the intermolecular chemoselective cyanosilylation using catalyst 5 (eqns 1-3)

Benzaldehyde (1.0 mmol), substrate (1.0 mmol) [acetophenone (eqn 1), benzonitrile (eqn 2), and phenyl benzoate (eqn 3)], TMSCN (1.1 mmol), and catalyst **5** (0.5 mol %) were stirred at 50 °C for required period. The reaction progress was monitored by ^{1}H NMR spectroscopy; after the completion of the reaction, a ^{13}C NMR spectrum was also recorded.

^{1}H and ^{13}C NMR spectra of the reactions shown in eqns 1-3

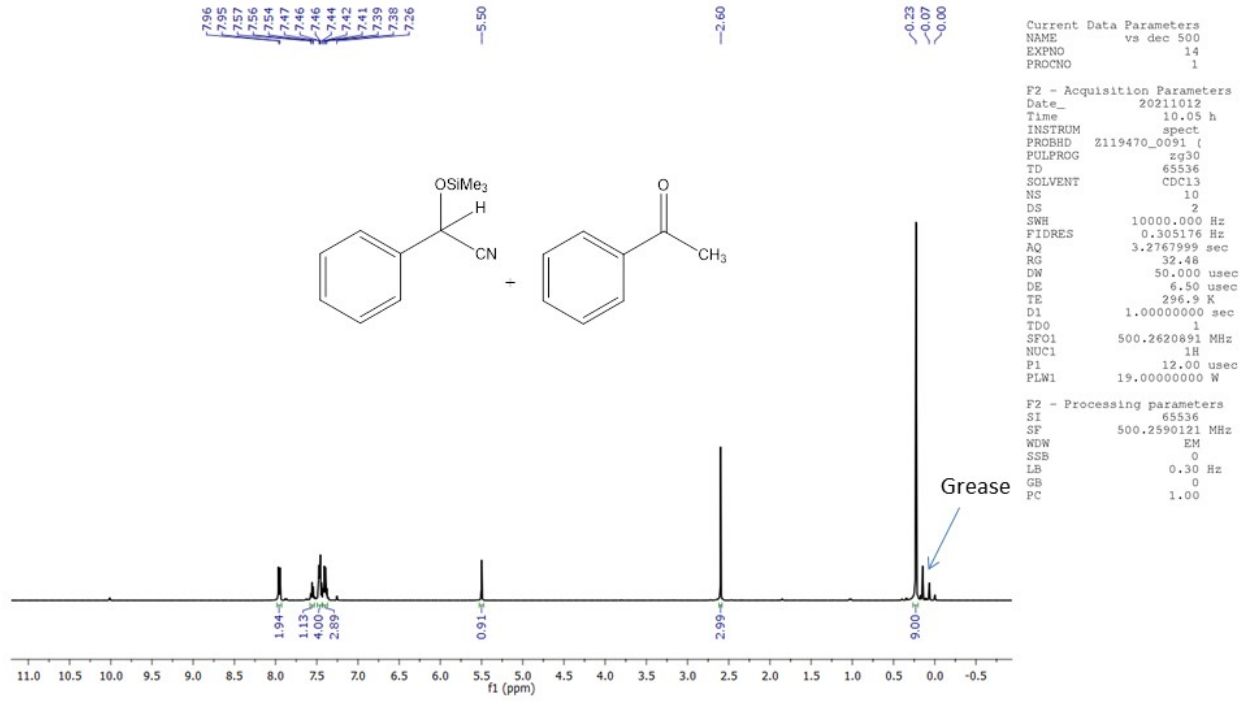


Figure S64. ^{1}H NMR spectrum of the chemoselective cyanosilylation of benzaldehyde in the presence of acetophenone (eqn 1).

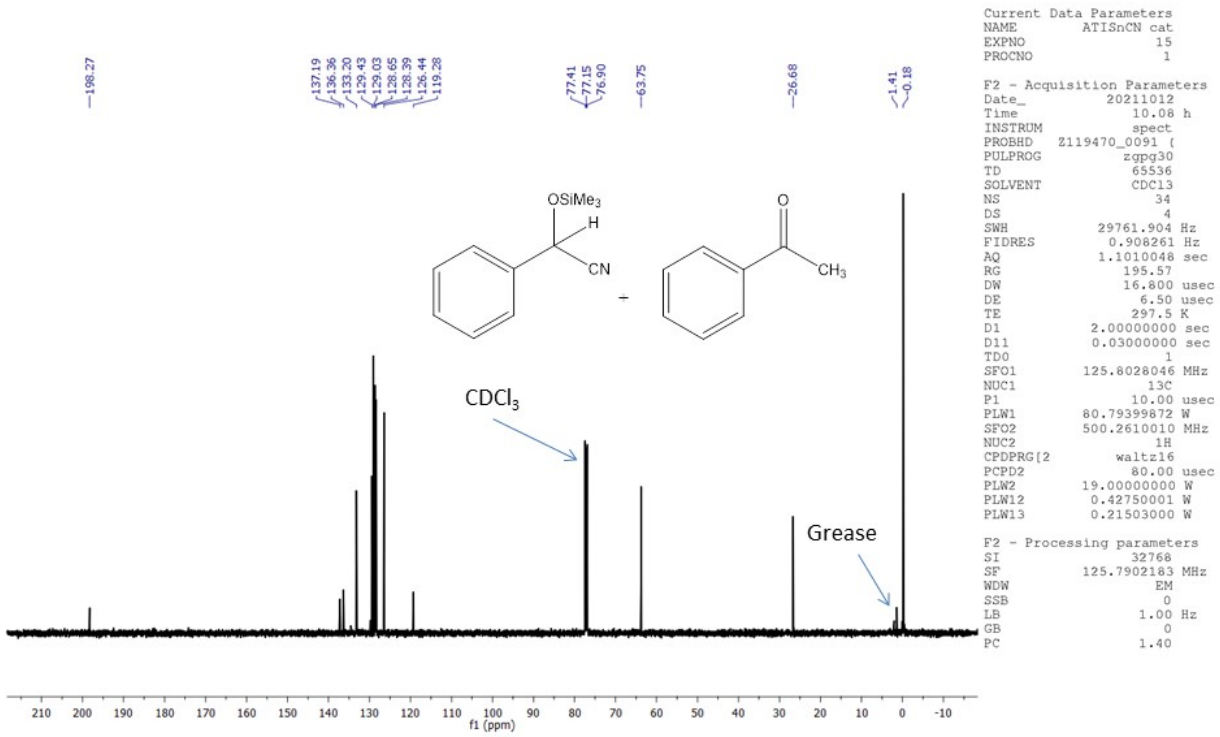


Figure S65. ^{13}C NMR spectrum of the chemoselective cyanosilylation of benzaldehyde in the presence of acetophenone (eqn 1).

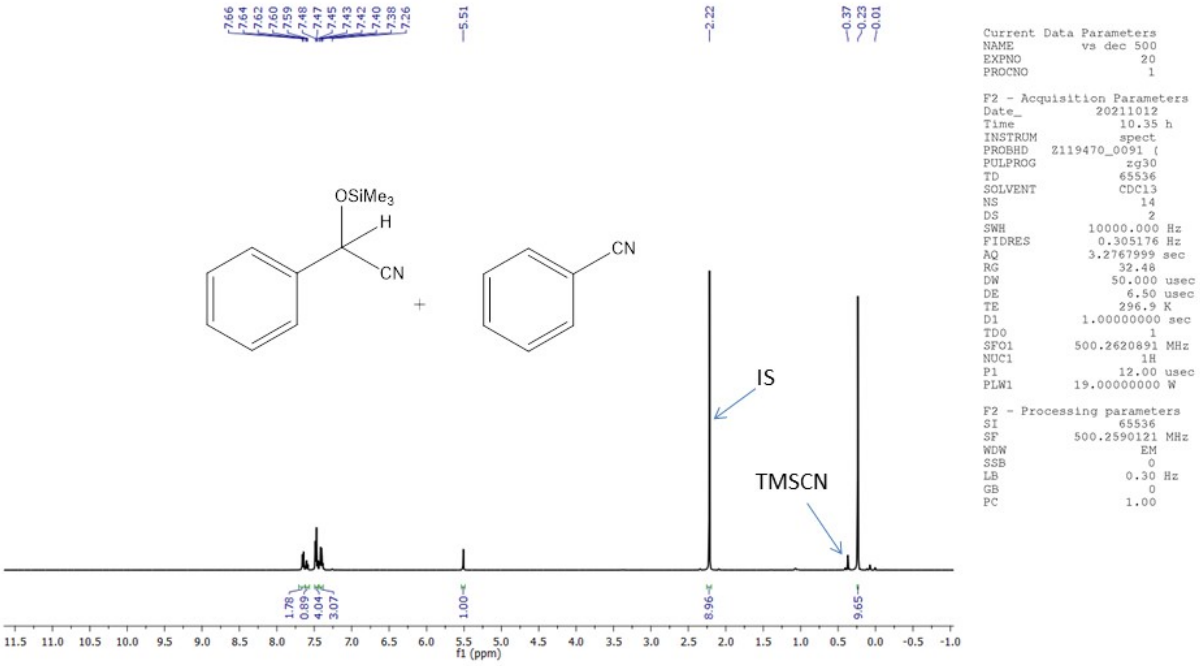


Figure S66. ^{1}H NMR spectrum of the chemoselective cyanosilylation of benzaldehyde in the presence of benzonitrile (eqn 2).

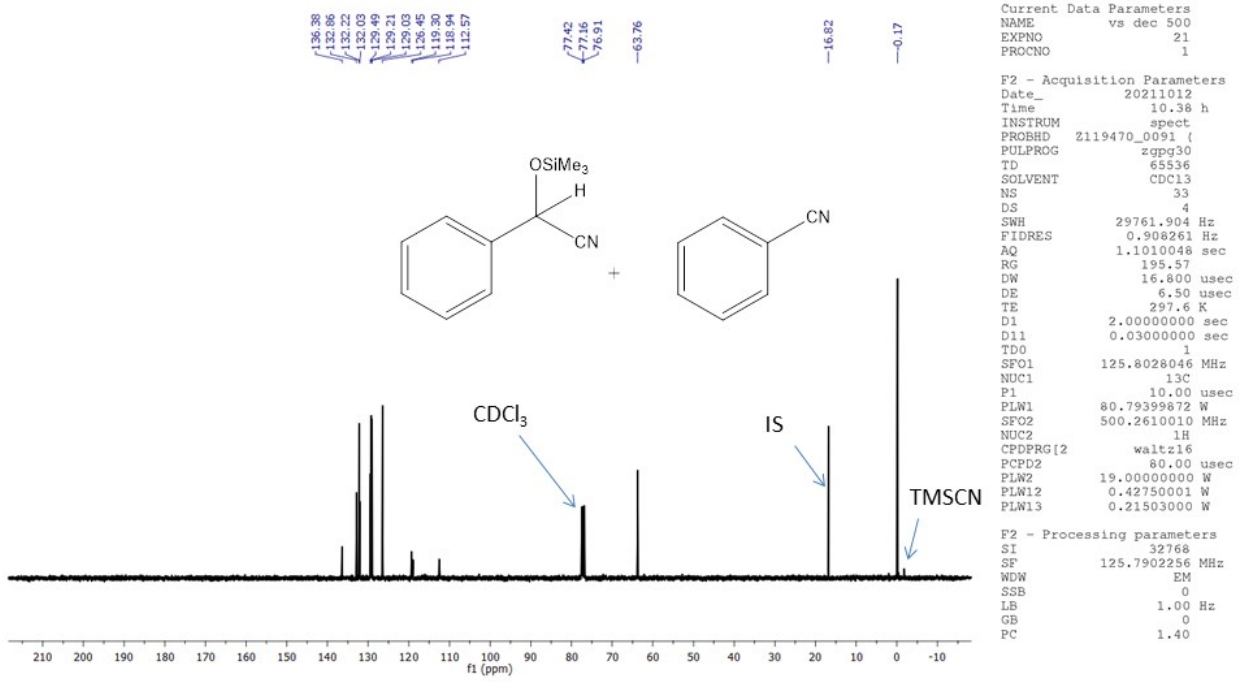


Figure S80. ^{13}C NMR spectrum of the chemoselective cyanosilylation of benzaldehyde in the presence of benzonitrile (eqn 2).

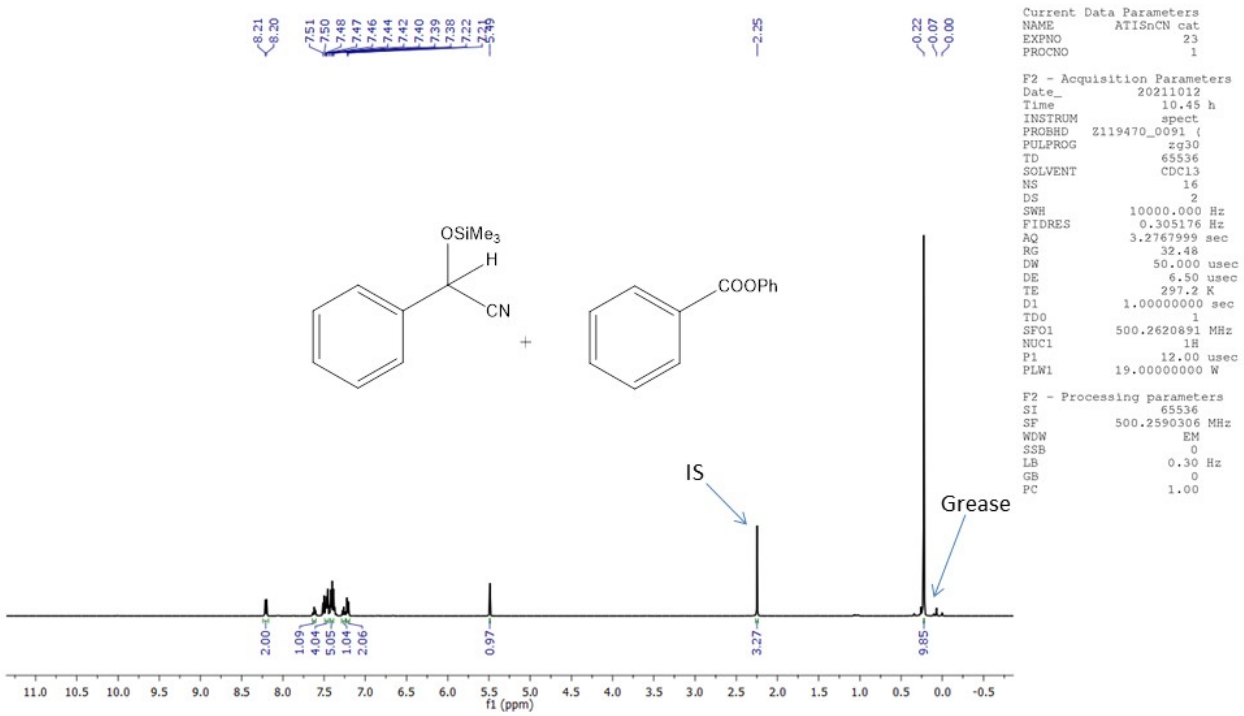


Figure S67. ^{1}H NMR spectrum of the chemoselective cyanosilylation of benzaldehyde in the presence of phenyl benzoate (eqn 3).

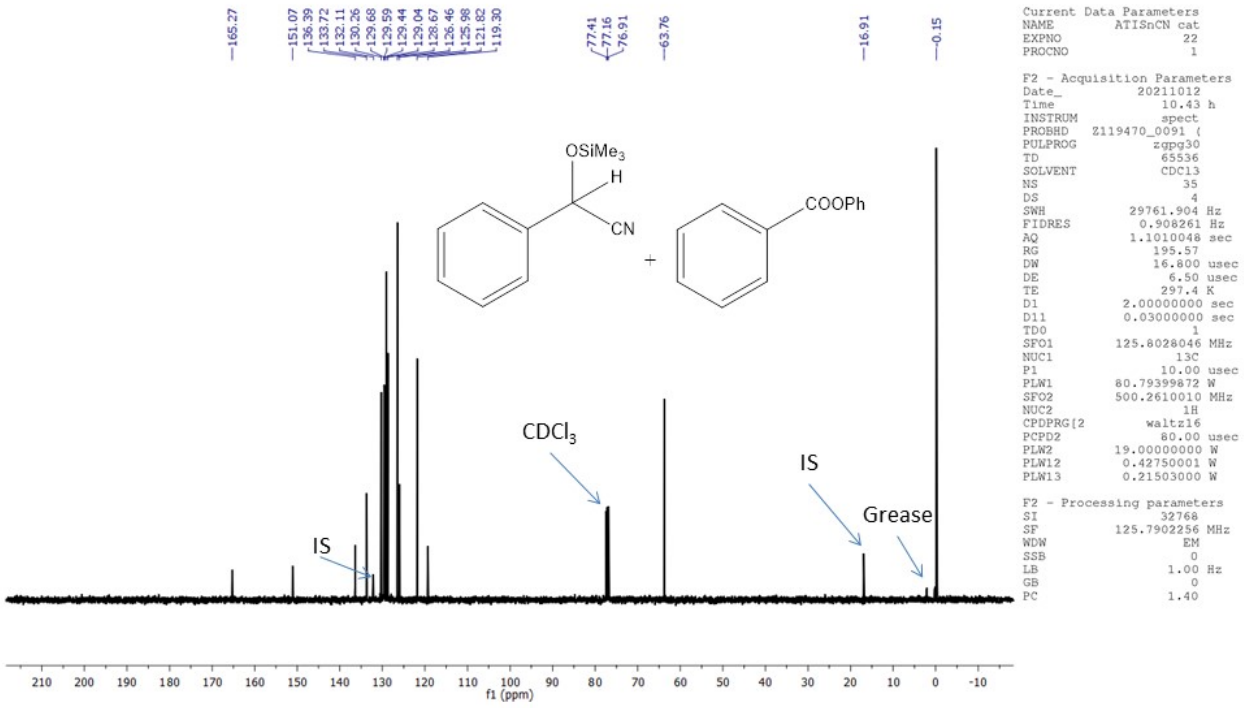


Figure S82. ^{13}C NMR spectrum of the chemoselective cyanosilylation of benzaldehyde in the presence of phenyl benzoate (eqn 3).

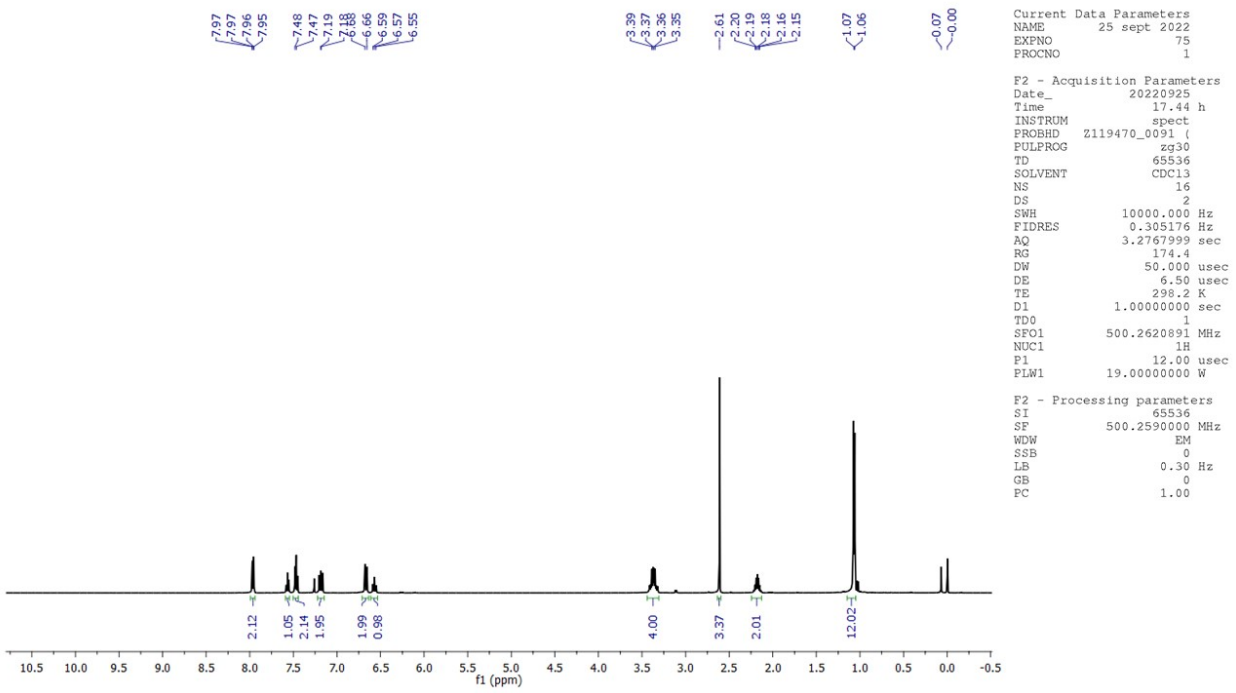
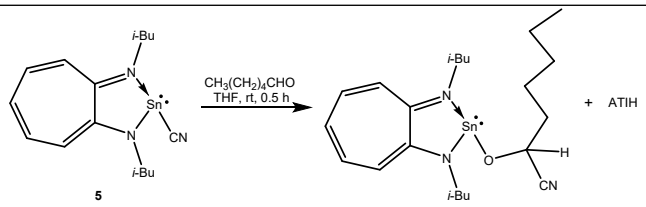
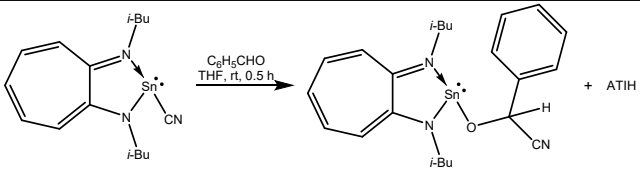
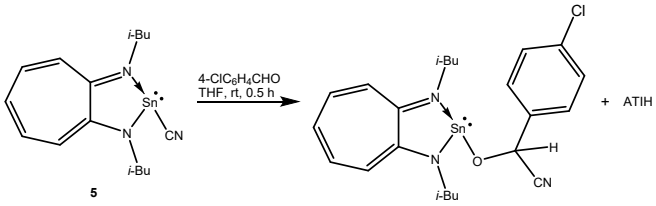
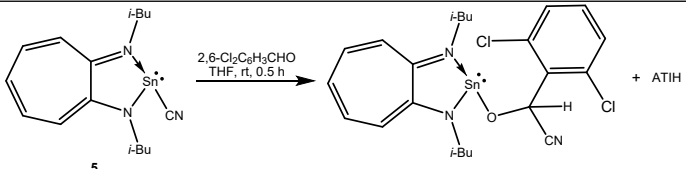


Figure S83. ^{1}H NMR spectrum of the equimolar reaction of compound **5** with acetophenone. The spectrum was recorded after 4 h of adding acetophenone.

Table S2. The equimolar reactions of catalyst 5 with hexanaldehyde, benzaldehyde, 4-chlorobenzaldehyde, and 2,6-dichlorobenzaldehyde to afford cyanostannylated products S1, S2, S3, and S4, respectively*

Entry	Reaction
1	 **S1** (^{119}Sn NMR: δ -180 ppm)
2	 **S2** (^{119}Sn NMR: δ -186 ppm)
3	 **S3** (^{119}Sn NMR: δ -188 ppm)
4	 **S4** (^{119}Sn NMR: δ -194 ppm)

*Unreacted aldehyde is also seen. The separation of the cyanostannylated products from these mixtures was predominantly not feasible as the individual components have similar solubility.

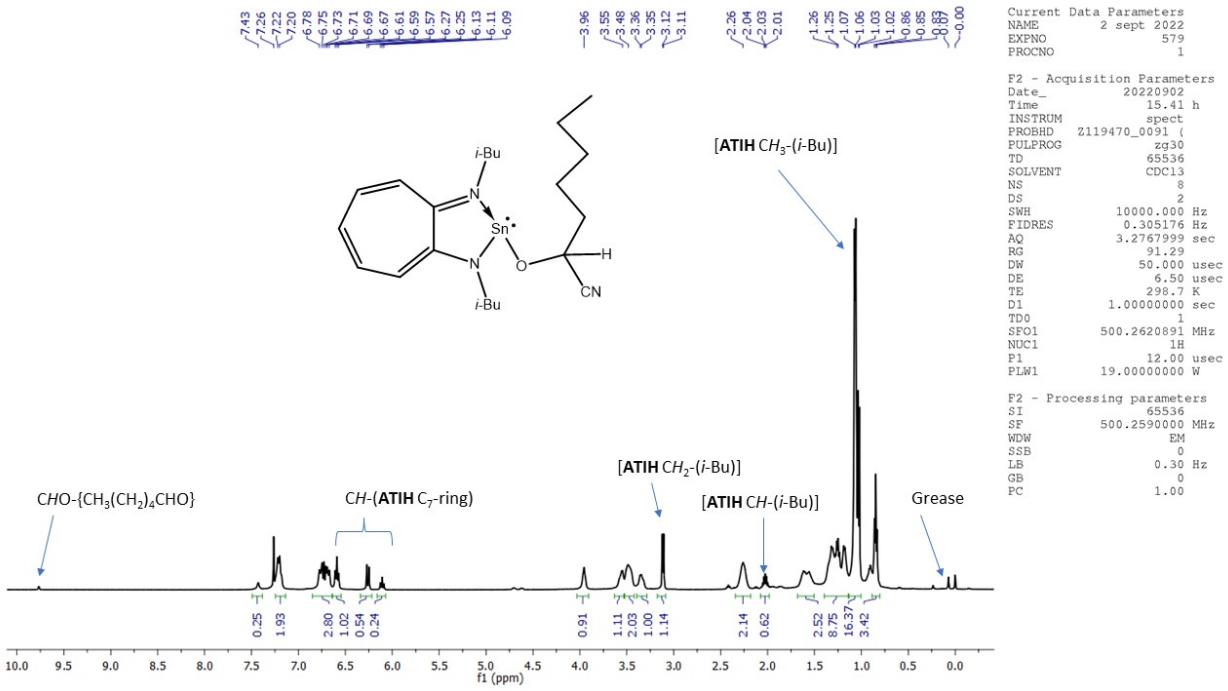


Figure S84. ^{1}H NMR spectrum of the equimolar reaction of compound **5** with hexanaldehyde. The spectrum was recorded after 0.5 h of adding hexanaldehyde.

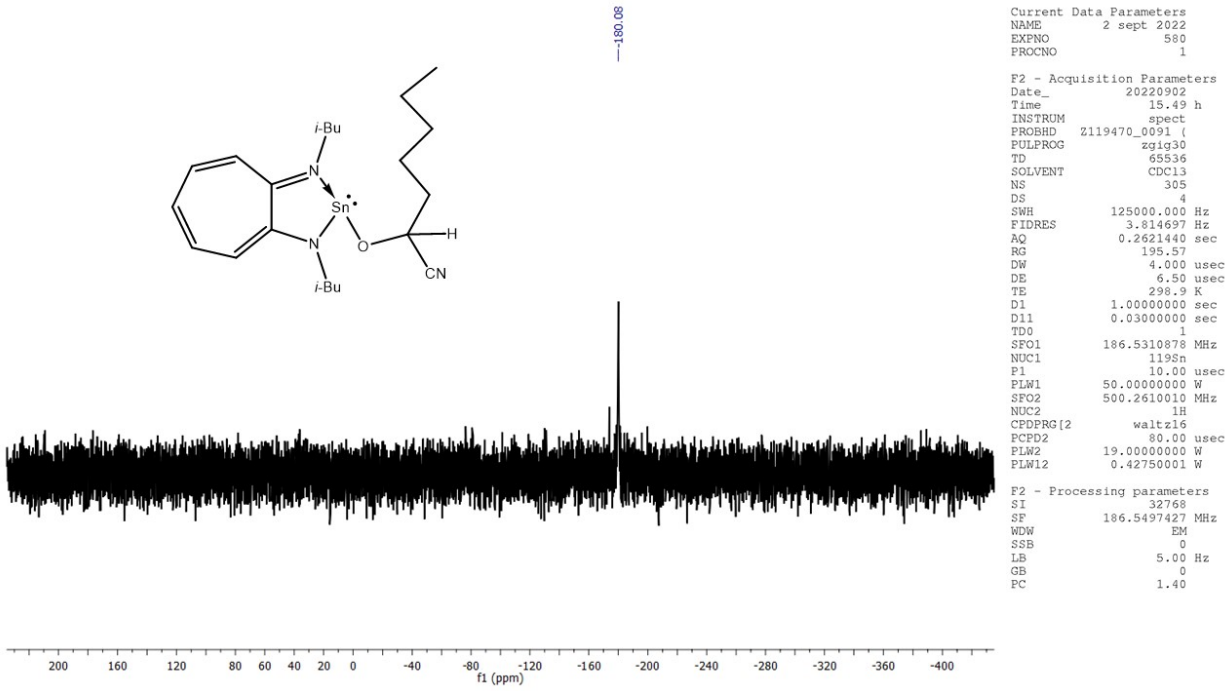


Figure S85. ^{119}Sn NMR spectrum of the equimolar reaction of compound **5** with hexanaldehyde. The spectrum was recorded after 0.5 h of adding hexanaldehyde.

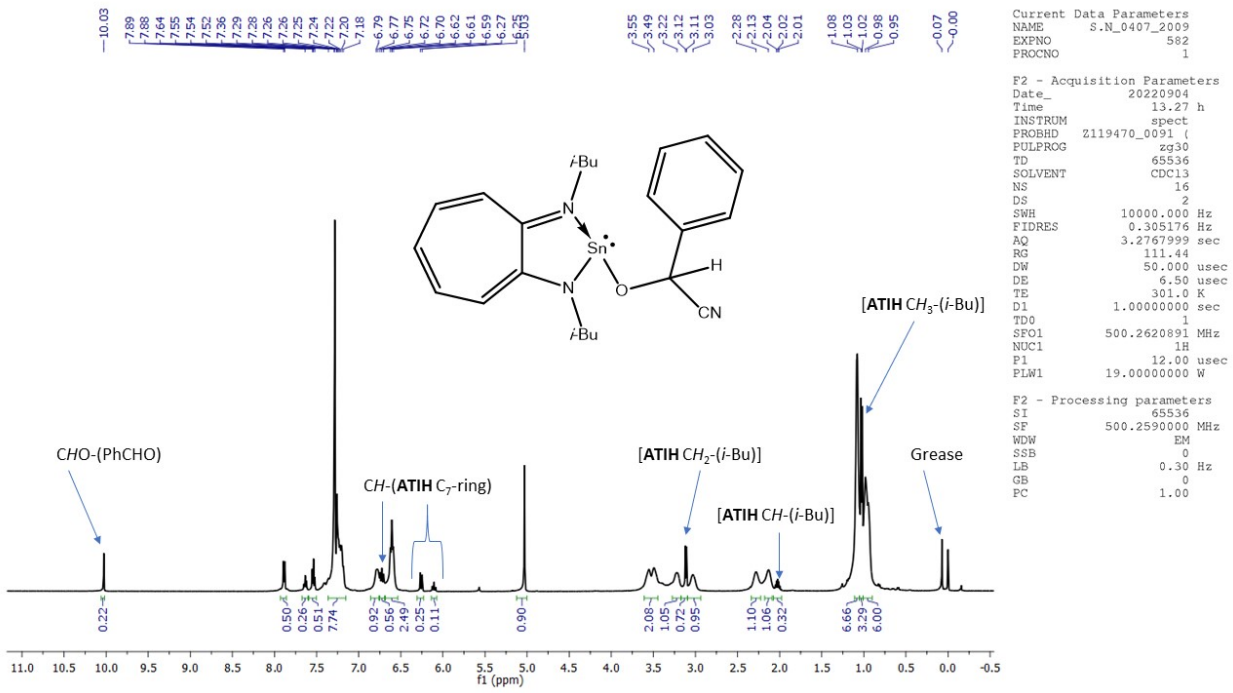


Figure S86. ^{1}H NMR spectrum of the equimolar reaction of compound **5** with benzaldehyde. The spectrum was recorded after 0.5 h of adding benzaldehyde.

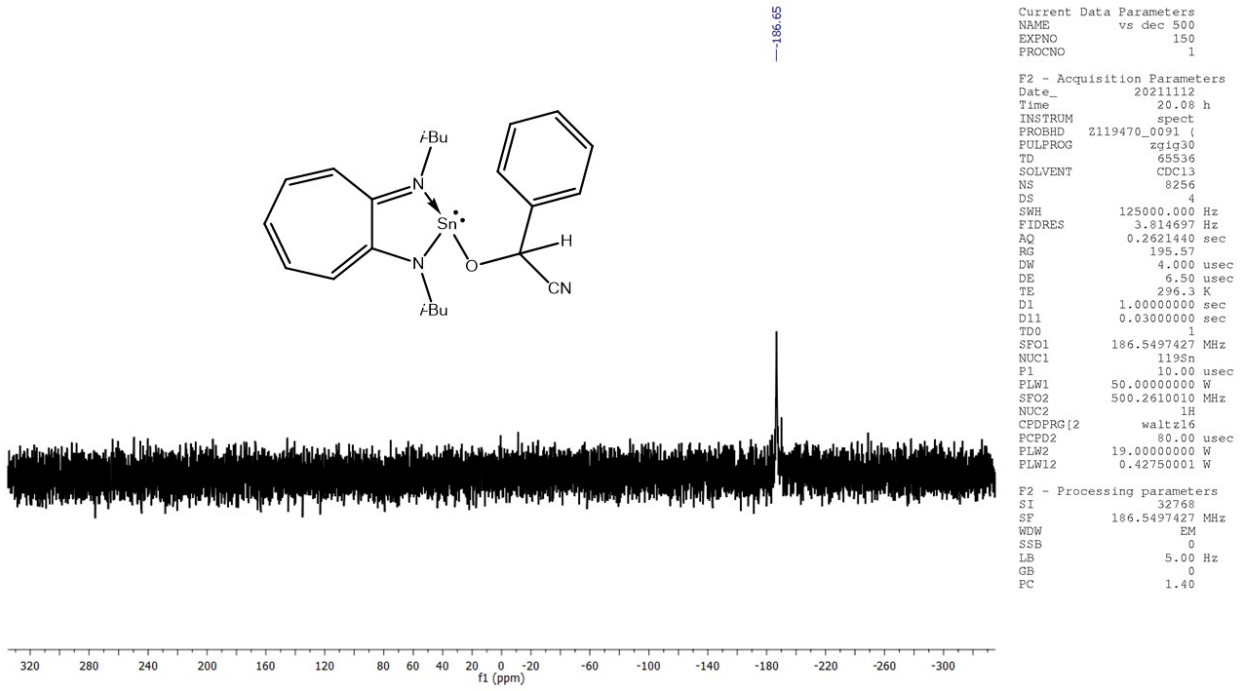


Figure S87. ^{119}Sn NMR spectrum of the equimolar reaction of compound **5** with benzaldehyde. The spectrum was recorded after 0.5 h of adding benzaldehyde.

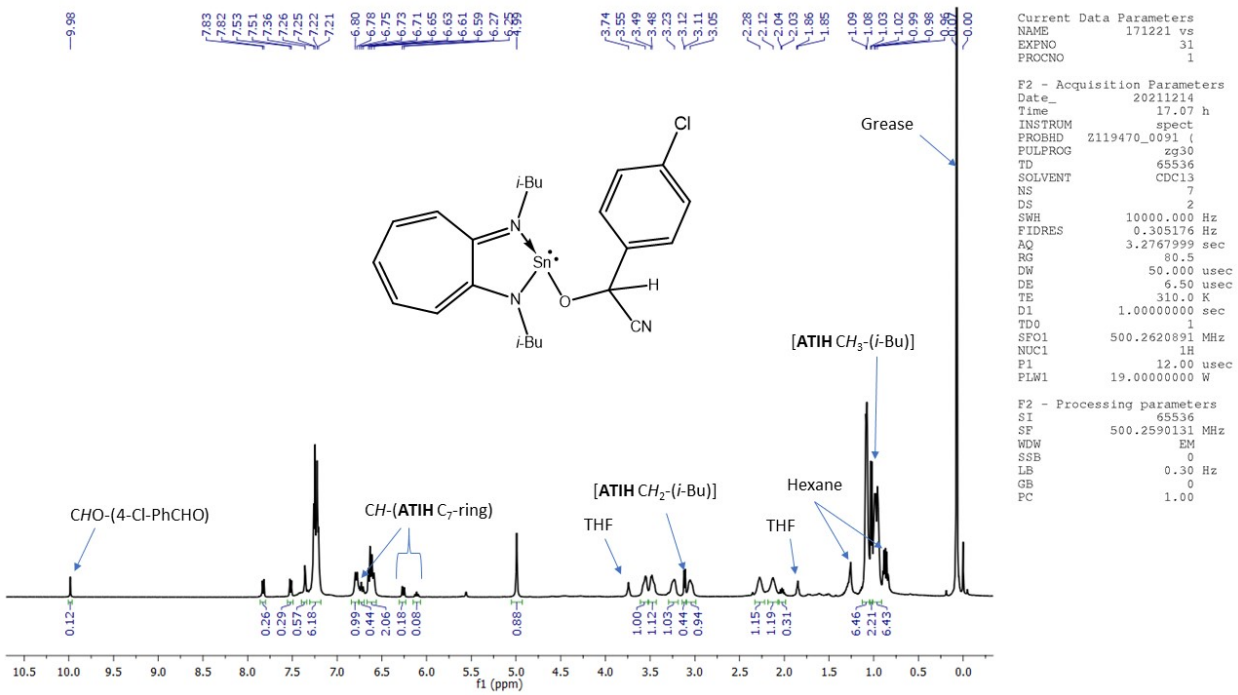


Figure S88. ^{1}H NMR spectrum of the equimolar reaction of compound **5** with 4-chlorobenzaldehyde. The spectrum was recorded after 0.5 h of adding 4-chlorobenzaldehyde.

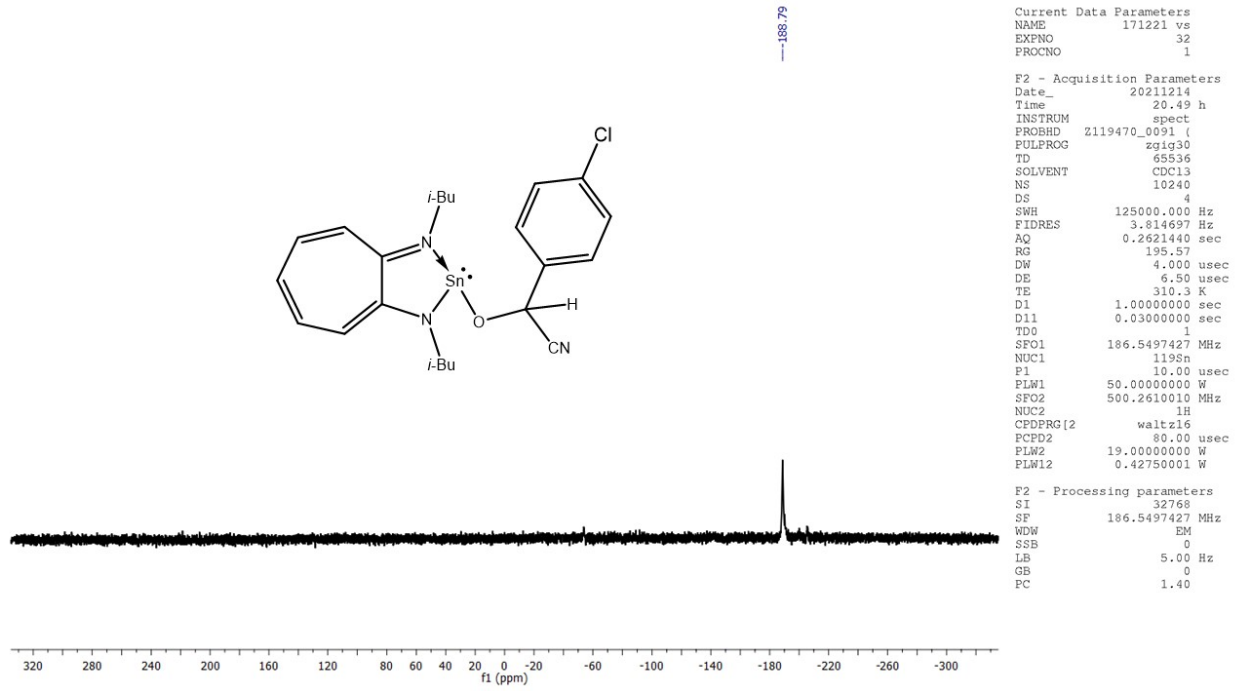


Figure S89. ^{119}Sn NMR spectrum of the equimolar reaction of compound **5** with 4-chlorobenzaldehyde. The spectrum was recorded after 0.5 h of adding 4-chlorobenzaldehyde.

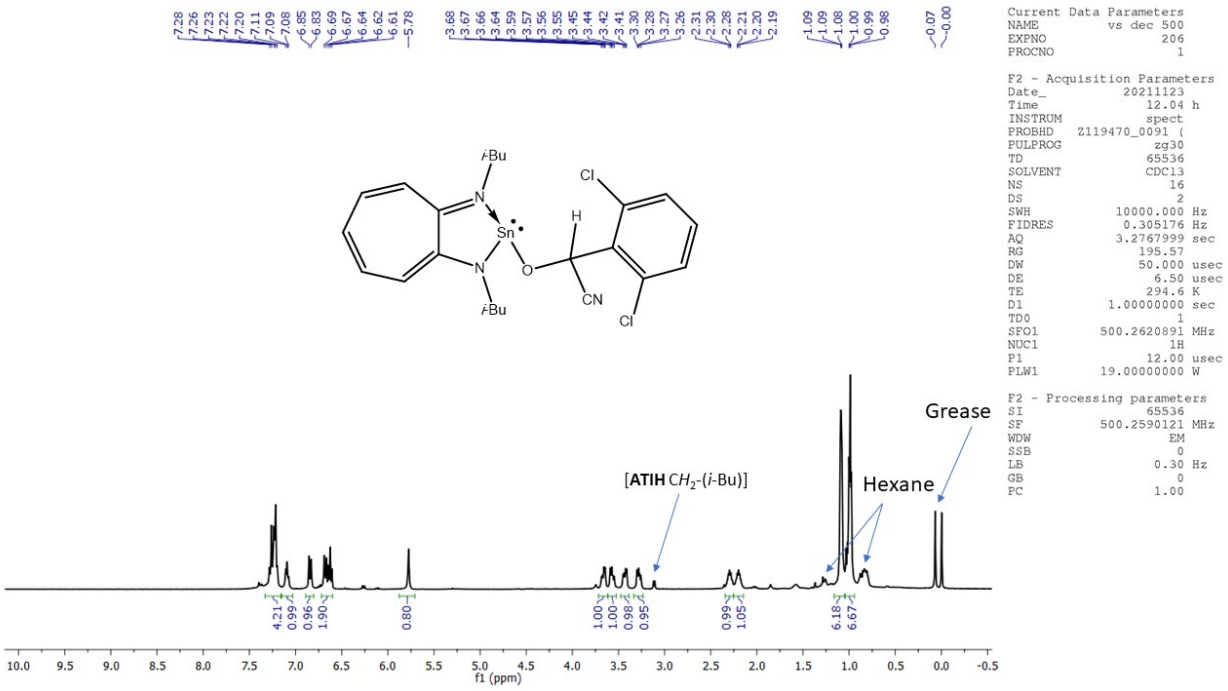


Figure S90. ^{1}H NMR spectrum of the equimolar reaction of compound **5** with 2,6-dichlorobenzaldehyde. The spectrum was recorded after 0.5 h of adding 2,6-dichlorobenzaldehyde.

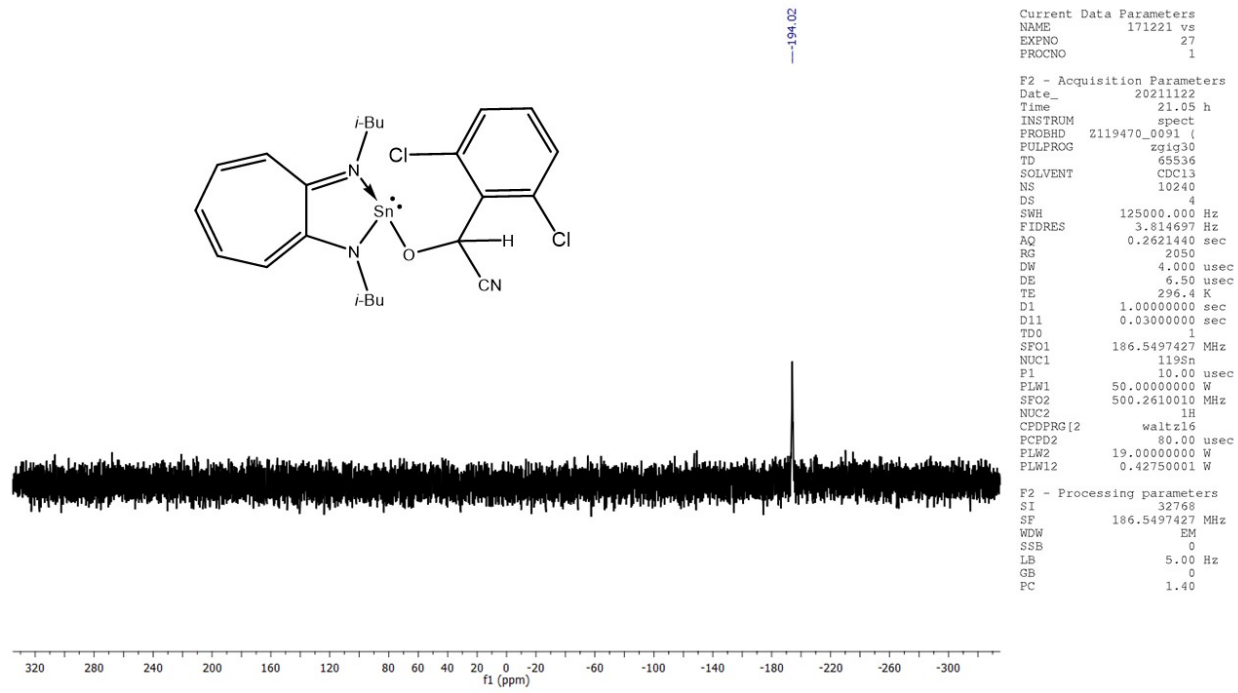


Figure S91. ^{119}Sn NMR spectrum of the equimolar reaction of compound **5** with 2,6-dichlorobenzaldehyde. The spectrum was recorded after 0.5 h of adding 2,6-dichlorobenzaldehyde.

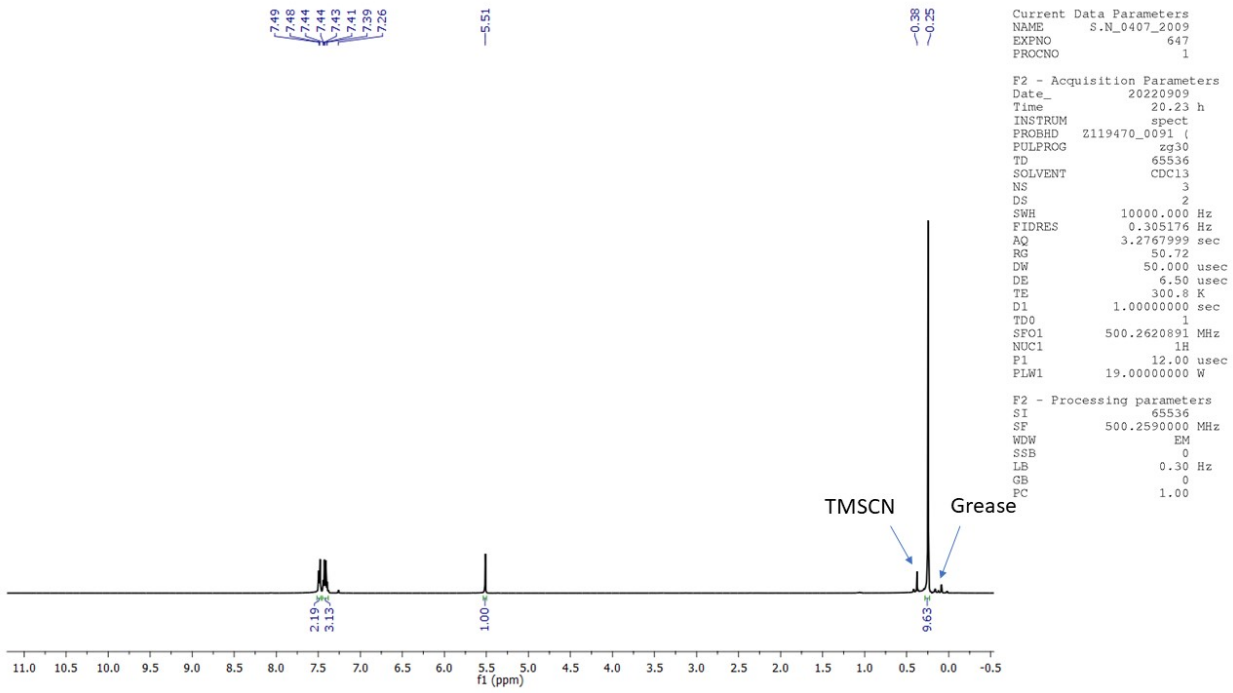


Figure S92. The ^{1}H NMR spectrum of the reaction of benzaldehyde with TMSCN at 50 °C in the presence of 0.5 mol% of compound **6**

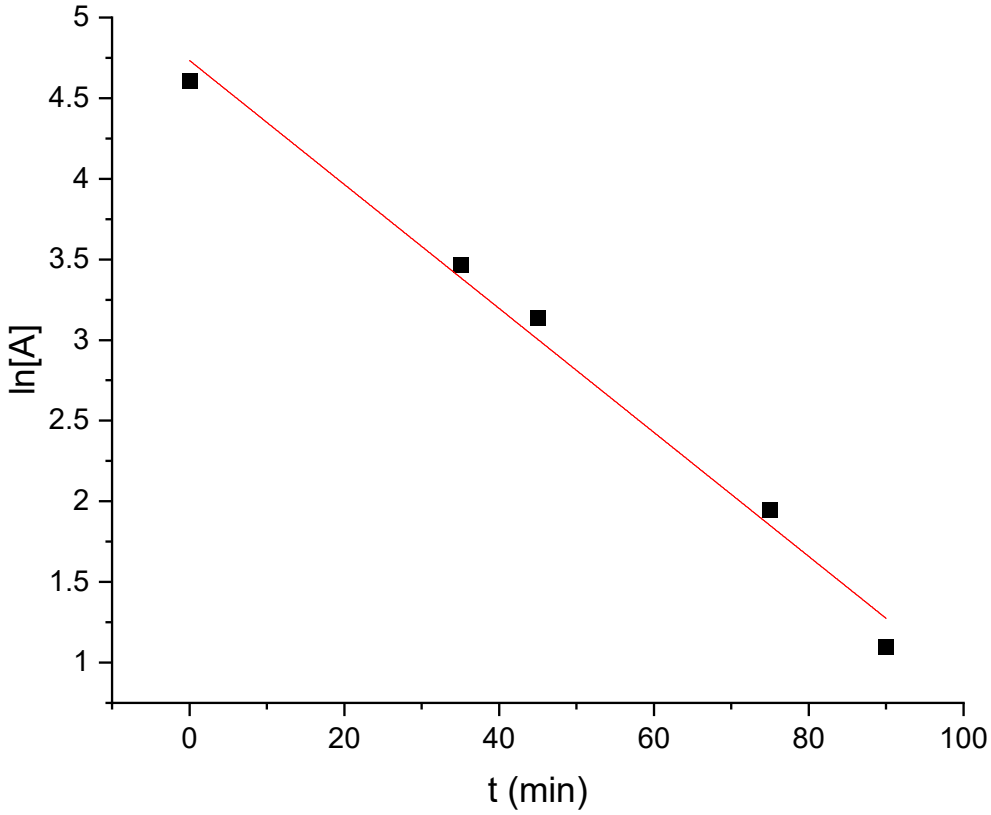


Figure S93. Plot of ln[*A*] versus *t* for the benzaldehyde cyanosilylation done at 40 °C.

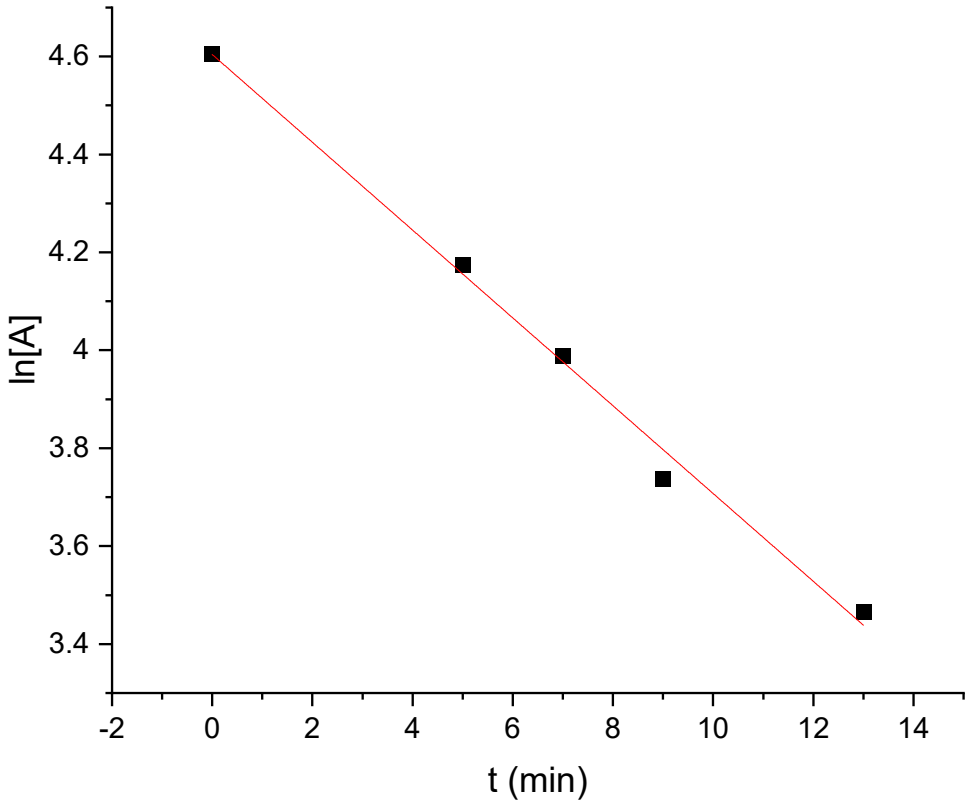


Figure S94. Plot of ln[*A*] versus *t* for the benzaldehyde cyanosilylation done at 50 °C.

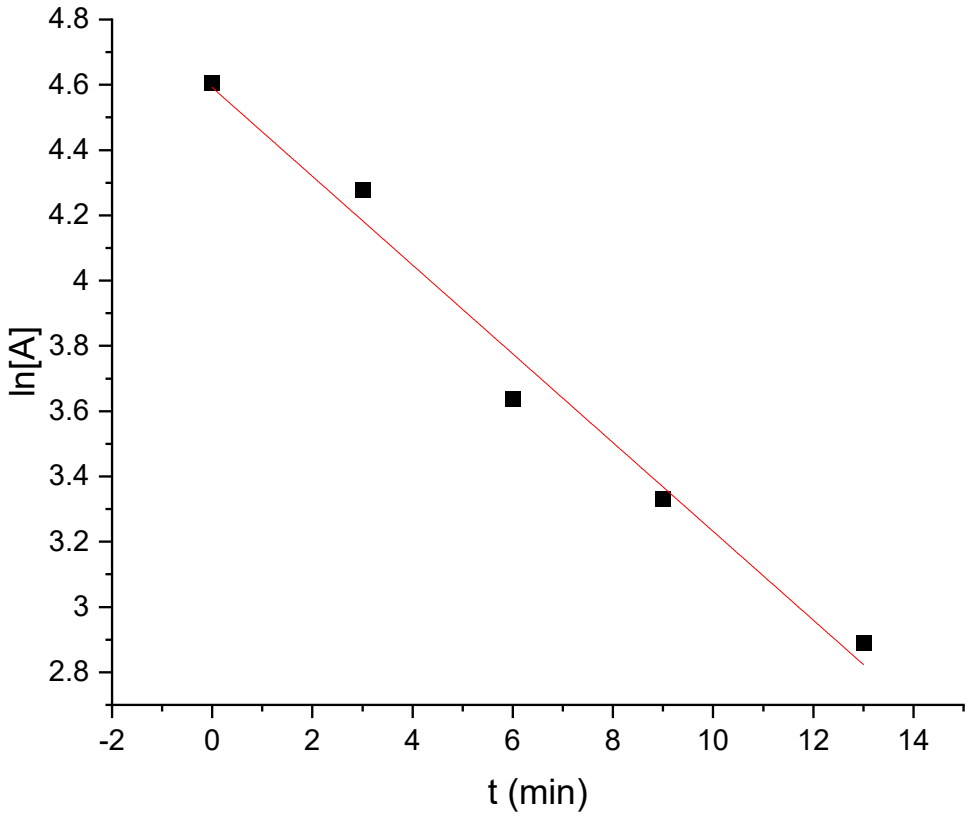


Figure S95. Plot of ln[*A*] versus *t* for the benzaldehyde cyanosilylation done at 60 °C.

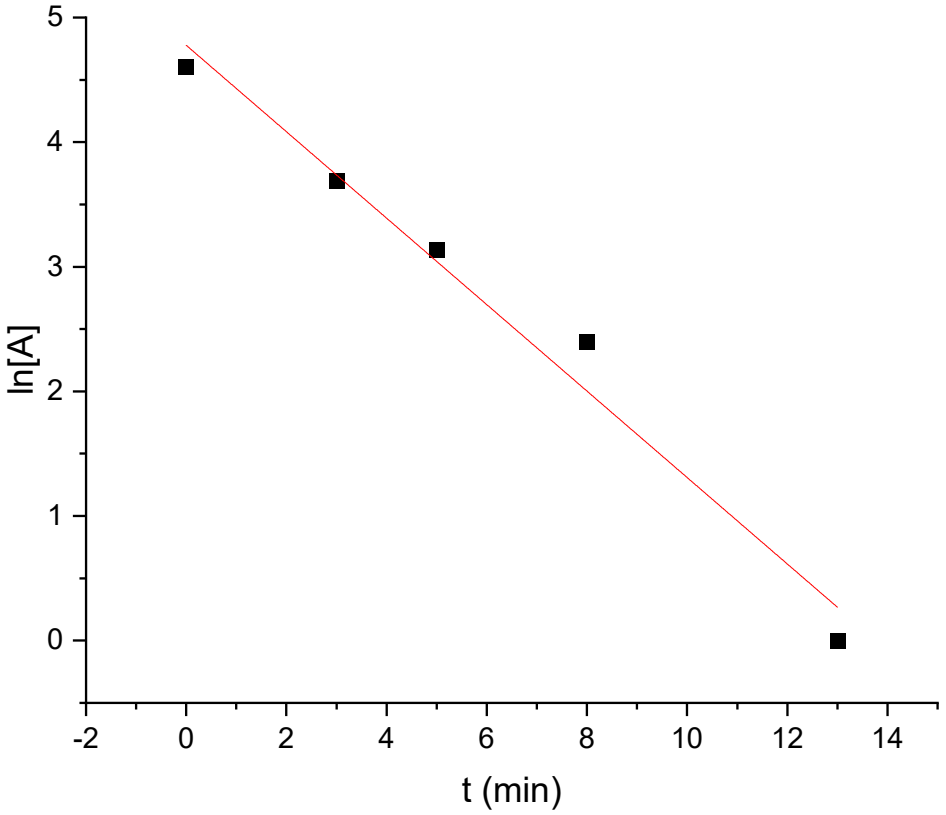


Figure S96. Plot of ln[*A*] versus *t* for the benzaldehyde cyanosilylation done at 70 °C.

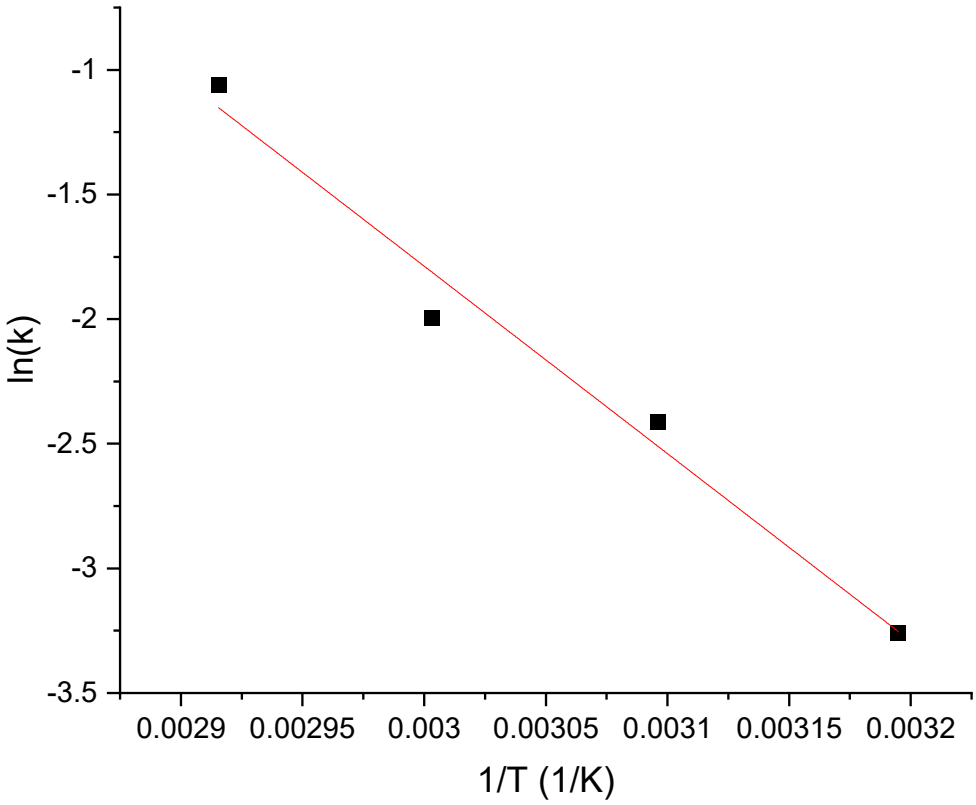
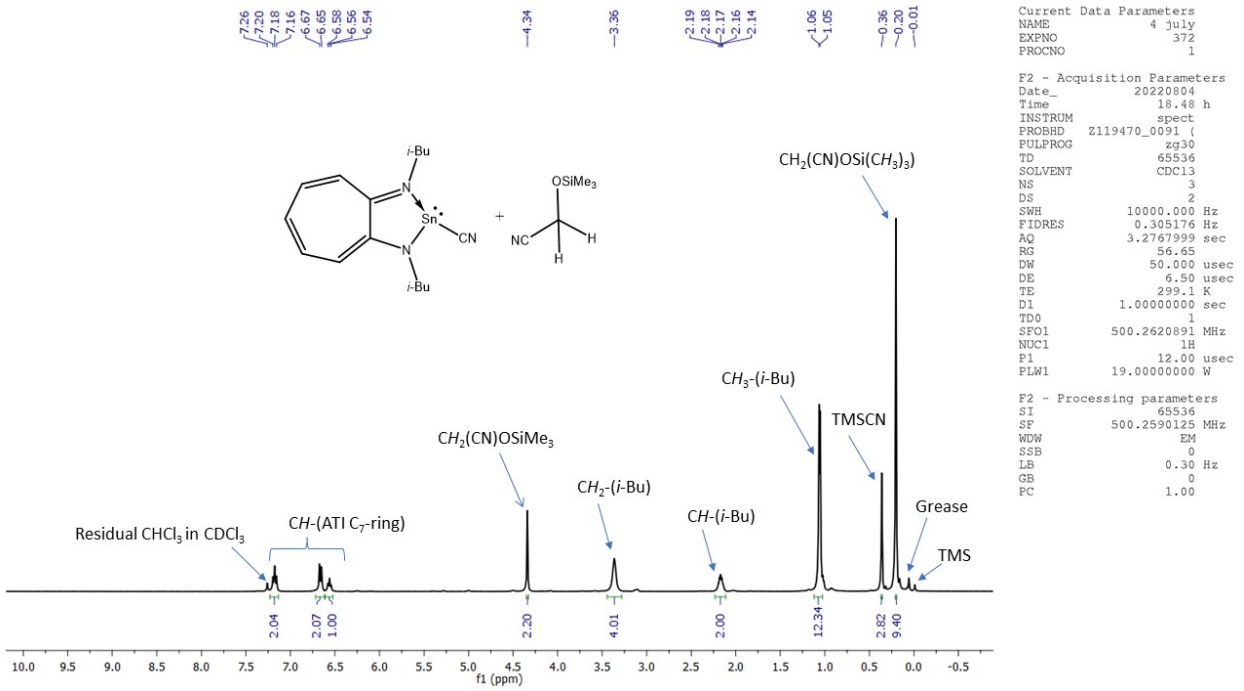


Figure S97. The Arrhenius plot of ln(*k*) versus 1/*T*. From the slope, the activation energy was found to be 62(6) kJ/mol.

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PROCNO                   1

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DS                      2
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DE                 6.50 usec
TE                 299.1 K
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NUC1                   1H
P1                  12.00 usec
PLW1          19.00000000 W

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PC                   1.00
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Figure S98. ^{1}H NMR spectrum of the reaction of compound **6** with TMSCN to afford cyanosilylated product **7** and catalyst **5**. The spectrum was recorded after 0.5 h from adding a slight excess TMSCN to compound **6**.