

Supporting Information for:

Ligand-Controlled Regiodivergence in Cobalt-Catalyzed Hydrosilylation of Isoprene

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1. General experimental details

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. Unless otherwise stated, all reactions were conducted under inert atmosphere using standard Schlenk techniques or in a nitrogen-filled glove-box. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature in CDCl_3 on 400 MHz or 700 MHz instrument with tetramethylsilane (TMS) as internal standard. ^{29}Si NMR spectra were recorded at room temperature with no solvent on Solid-state NMR. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

2. Screening of reaction conditions

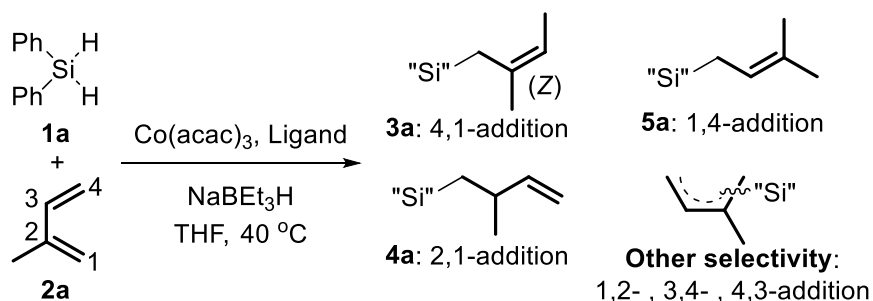
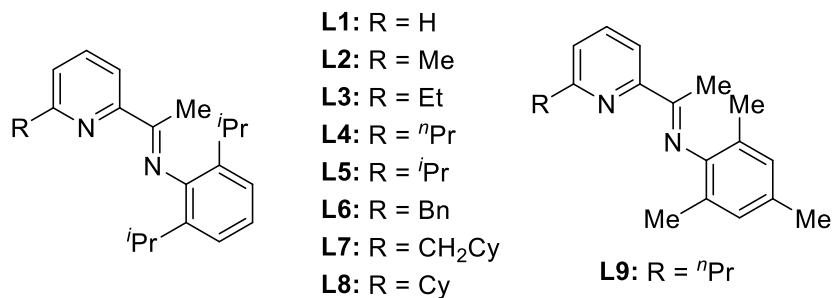


Table S1. Effect of ligands

Entry ^a	Ligand	Total yield ^b	Selectivity ^b (%)			
			3a	4a	5a	other
1	L1	76%	93	0	0	7
2	L2	74%	5	81	0	14
3	L3	89%	5	81	5	9
4	L4	90%	4	92	0	4
5	L5	37%	11	70	5	14
6	L6	65%	2	91	3	4
7	L7	15%	46	34	20	0
8	L8	30%	23	67	10	0
9	L9	62%	19	81	0	0



^a Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), Co(acac)₃ (5 mol%), Ligand (5 mol%), NaBEt₃H (10 mol%, 1.0 M in THF), THF (0.5 mL), 40 °C, 2 h, N₂. ^b Determined by ¹H NMR with 1,3,5-trimethylbenzene as the internal standard.

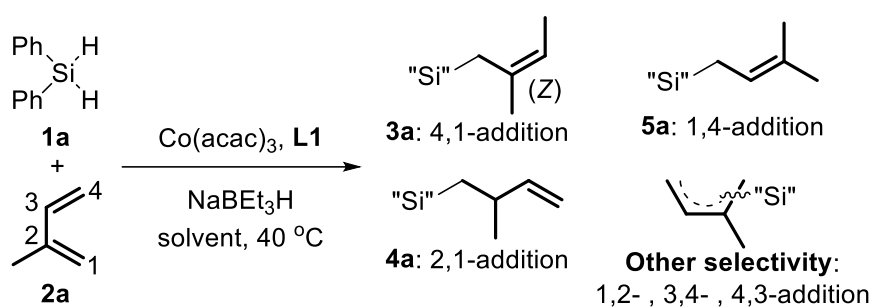


Table S2. Effect of solvent for 4,1-hydrosilylation

Entry ^a	solvent	Total yield ^b	Selectivity ^b (%)			
			3a	4a	5a	other
1	THF	76%	93	0	0	7
2	1,4-dioxane	75%	91	0	4	5
3	hexane	86%	94	0	2	4
4	toluene	47%	93	0	0	7
5	CH ₃ CN	7%	71	0	29	0

^a Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), Co(acac)₃ (5 mol%), **L1** (5 mol%), NaBEt₃H (10 mol%, 1.0 M in THF), solvent (0.5 mL), 40 °C, 2 h, N₂. ^b Determined by ¹H NMR with 1,3,5-trimethylbenzene as the internal standard.

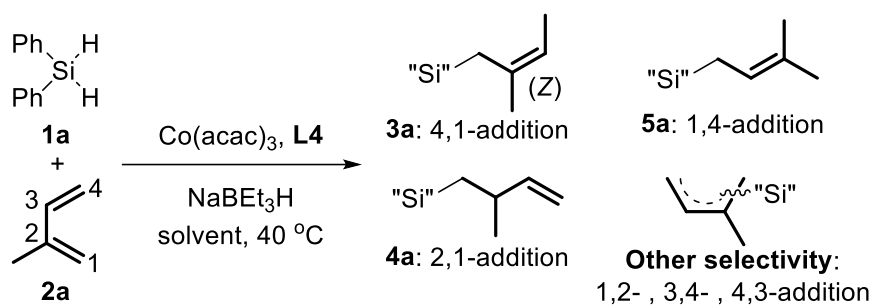
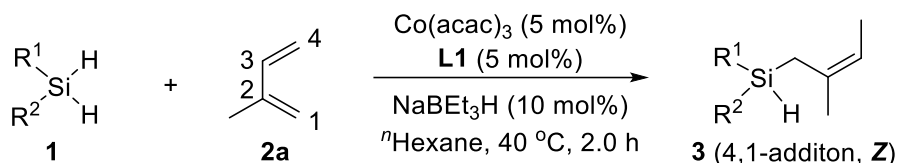


Table S3. Effect of reductant for 2,1-hydrosilylation

Entry ^a	reductant	Total yield ^b	Selectivity ^b (%)			
			3a	4a	5a	other
1	NaBEt_3H	90%	4	92	0	4
2	AlMe_3	44%	7	73	9	11
3	ZnEt_2	57%	7	93	0	0
4	PhMgBr	73%	5	84	5	6
5	AlMe_2Cl	NR	-	-	-	-
6	^t BuOK	14	14	72	14	0

^a Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), $\text{Co}(\text{acac})_3$ (5 mol%), **L4** (5 mol%), reductant (10 mol%), THF (0.5 mL), 40 °C, 2 h, N₂. ^b Determined by ¹H NMR with 1,3,5-trimethylbenzene as the internal standard.

3. Typical procedure for Co-catalyzed 4,1-hydrosilylation of isoprene

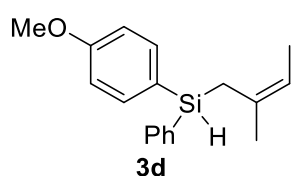


In glove box, $Co(acac)_3$ (0.01 mmol, 3.6 mg, 5 mol%), **L1** (0.01 mmol, 2.8 mg, 5 mol%) and anhydrous n-hexane (0.5 mL) were added to a sealed tube. The mixture was stirred for 5 minutes at room temperature. Then $NaBEt_3H$ (20 μ L, 1M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1** (0.20 mmol, 1.0 eq.) and **2a** (0.30 mmol, 20.4 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 $^\circ$ C for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding product **3**. The regioselectivity was determined by 1H NMR.

(Z)-(2-Methylbut-2-en-1-yl)diphenylsilane (3a): Known compound¹, colorless oil, 41.0 mg, 81% total yield, **3a:4a:5a:others** = 97:0:3:0, R_f = 0.8 (PE/EtOAc = 100/1). 1H NMR (700 MHz, $CDCl_3$) δ 7.61 (d, J = 6.4 Hz, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.3 Hz, 4H), 5.16 (q, J = 6.8 Hz, 1H), 4.93 (t, J = 4.0 Hz, 1H), 2.12 (d, J = 4.0 Hz, 2H), 1.65 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 135.3, 134.6, 132.3, 129.8, 128.1, 117.9, 25.9, 18.8, 13.8. ^{29}Si NMR (79 MHz, solid-state) δ -12.90.

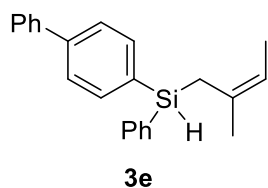
(Z)-(2-Methylbut-2-en-1-yl)(phenyl)(p-tolyl)silane (3b): Known compound¹, colorless oil, 35.6 mg, 67% total yield, **3b:4b:5b:others** = 95:0:2:3, R_f = 0.8 (PE/EtOAc = 100/1). 1H NMR (700 MHz, $CDCl_3$) δ 7.60 (d, J = 7.3 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H), 5.15 (q, J = 6.8 Hz, 1H), 4.92 (t, J = 4.0 Hz, 1H), 2.38 (s, 3H), 2.11 (d, J = 4.0 Hz, 2H), 1.65 (s, 3H), 1.41 (d, J = 6.8 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 139.7, 135.4, 135.3, 134.9, 132.5, 130.8, 129.7, 128.9, 128.0, 117.8, 25.9, 21.7, 18.9, 13.8.

(Z)-(4-(tert-Butyl)phenyl)(2-methylbut-2-en-1-yl)(phenyl)silane (3c): Known compound¹, colorless oil, 33.5 mg, 54% total yield, **3c:4c:5c:others** = 98:0:2:0, R_f = 0.8 (PE/EtOAc = 100/1). 1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.45 – 7.33 (m, 5H), 5.15 (q, J = 6.8 Hz, 1H), 4.91 (t, J = 4.0 Hz, 1H), 2.11 (d, J = 4.0 Hz, 2H), 1.65 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 135.4, 135.2, 134.8, 132.5, 130.9, 129.7, 128.0, 125.1, 117.8, 34.9, 31.4, 25.9, 18.9, 13.8.



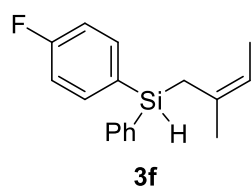
(Z)-(4-Methoxyphenyl)(2-methylbut-2-en-1-yl)(phenyl)silane

(3d): Known compound¹, colorless oil, 19.6 mg, 33% total yield, **3d:4d:5d:others** = 96:0:4:0. Accompanied by an inseparable **1d**, the yield of product has been adjusted accordingly. $R_f = 0.6$ (PE/EtOAc = 100/1). ¹H NMR (700 MHz, CDCl₃) δ 7.58 (d, $J = 7.1$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.42 – 7.38 (m, 1H), 7.36 (t, $J = 7.1$ Hz, 2H), 6.92 (d, $J = 8.1$ Hz, 2H), 5.13 (d, $J = 6.8$ Hz, 1H), 4.89 (t, $J = 4.0$ Hz, 1H), 3.82 (s, 3H), 2.08 (d, $J = 4.0$ Hz, 2H), 1.63 (s, 3H), 1.38 (d, $J = 6.8$ Hz, 3H). ¹³C NMR (175 MHz, CDCl₃) δ 161.1, 136.8, 135.3, 132.5, 129.7, 128.0, 125.2, 117.7, 113.9, 55.2, 31.7, 25.9, 19.0, 13.8.



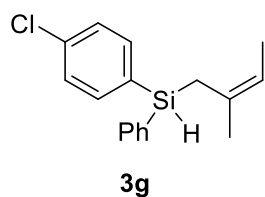
(Z)-[1,1'-Biphenyl]-4-yl(2-methylbut-2-en-1-yl)(phenyl)silane (3e):

Known compound¹, colorless oil, 52.0 mg, 79% total yield, **3e:4e:5e:others** = 94:0:3:3, $R_f = 0.6$ (PE). ¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.59 (m, 8H), 7.52 – 7.35 (m, 6H), 5.22 (q, $J = 6.8$ Hz, 1H), 4.99 (t, $J = 4.0$ Hz, 1H), 2.17 (d, $J = 4.0$ Hz, 2H), 1.70 – 1.68 (m, 3H), 1.44 (d, $J = 6.8$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 141.0, 135.8, 135.3, 134.5, 133.3, 132.3, 129.8, 128.9, 128.1, 127.6, 127.3, 126.8, 118.0, 25.9, 18.8, 13.9.



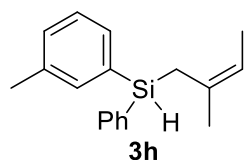
(Z)-(4-Fluorophenyl)(2-methylbut-2-en-1-yl)(phenyl)silane (3f):

Known compound¹, colorless oil, 13.4 mg, 25% total yield, **3f:4f:5f:others** = 96:0:4:0, $R_f = 0.8$ (PE/EtOAc = 100/1). ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.50 (m, 4H), 7.46 – 7.31 (m, 3H), 7.11 – 7.00 (m, 2H), 5.14 (q, $J = 6.6$ Hz, 1H), 4.90 (t, $J = 4.0$ Hz, 1H), 2.08 (d, $J = 4.0$ Hz, 2H), 1.62 (s, 3H), 1.36 (d, $J = 6.6$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.3 (d, $J = 248.9$ Hz), 137.3 (d, $J = 7.6$ Hz), 135.2, 134.3, 132.1, 129.9, 128.1, 118.1, 115.4, 115.2, 25.8, 18.8, 13.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.92.



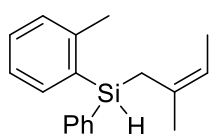
(Z)-(4-Chlorophenyl)(2-methylbut-2-en-1-yl)(phenyl)silane (3g):

Known compound¹, colorless oil, 37.1 mg, 65% total yield, **3g:4g:5g:others** = 95:0:2:3, $R_f = 0.8$ (PE/EtOAc = 100/1). ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.55 (m, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.44 – 7.33 (m, 5H), 5.16 (q, $J = 6.8$ Hz, 1H), 4.91 (t, $J = 4.0$ Hz, 1H), 2.10 (d, $J = 4.0$ Hz, 2H), 1.64 (s, 3H), 1.39 (d, $J = 6.8$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 136.1, 135.1, 133.8, 132.8, 131.8, 129.9, 128.2, 128.1, 118.1, 25.7, 18.6, 13.7.



(Z)-(2-Methylbut-2-en-1-yl)(phenyl)(m-tolyl)silane (3h):

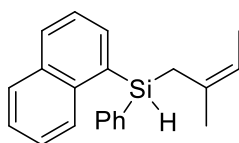
Known compound¹, colorless oil, 35.4 mg, 66% total yield, **3h:4h:5h:others** = 95:0:2:3, $R_f = 0.8$ (PE/EtOAc = 100/1). ¹H NMR (700 MHz, CDCl₃) δ 7.60 (d, $J = 8.0$ Hz, 2H), 7.43 – 7.39 (m, 3H), 7.37 (t, $J = 7.3$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.23 (d, $J = 7.7$ Hz, 1H), 5.15 (q, $J = 6.8$ Hz, 1H), 4.90 (t, $J = 4.0$ Hz, 1H), 2.36 (s, 3H), 2.11 (d, $J = 4.0$ Hz, 2H), 1.65 (s, 3H), 1.41 (d, $J = 6.8$ Hz, 3H). ¹³C NMR (175 MHz, CDCl₃) δ 137.4, 135.9, 135.3, 134.8, 134.3, 132.4, 132.3, 130.6, 129.7, 128.0, 127.97, 117.8, 25.9, 21.6, 18.8, 13.8.



3i

(Z)-(2-Methylbut-2-en-1-yl)(phenyl)(o-tolyl)silane (3i): Known compound¹, colorless oil, 35.2 mg, 61% total yield, **3i:4i:5i:others** = 93:0:3:4, Accompanied by an inseparable **1i**, the yield of product has been adjusted accordingly). $R_f = 0.8$ (PE/EtOAc = 100/1). ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.53 (m, 2H), 7.41 – 7.31 (m, 5H), 7.23 – 7.16 (m, 2H),

5.16 (q, $J = 6.7$ Hz, 1H), 5.02 (t, $J = 4.0$ Hz, 1H), 2.38 (s, 3H), 2.19 (dd, $J = 13.8, 4.2$ Hz, 1H), 2.12 (dd, $J = 13.7, 4.0$ Hz, 1H), 1.65 (s, 3H), 1.40 (d, $J = 6.7$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 136.1, 135.2, 134.9, 133.4, 132.6, 130.1, 129.8, 129.6, 128.0, 125.2, 118.0, 25.8, 22.9, 18.4, 13.8.

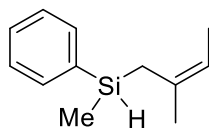


3k

(Z)-(2-Methylbut-2-en-1-yl)(naphthalen-1-yl)(phenyl)silane (3k): Known compound¹, colorless oil, 39.6 mg, 65% total yield,

3k:4k:5k:others = 88:0:9:3, $R_f = 0.8$ (PE/EtOAc 100/1). ¹H NMR (700 MHz, CDCl₃) δ 8.09 (d, $J = 8.3$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 6.7$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 2H), 7.51 – 7.47 (m, 2H), 7.47 – 7.43 (m, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.4$

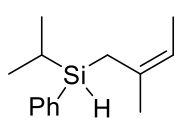
Hz, 2H), 5.33 (t, $J = 4.0$ Hz, 1H), 5.15 (q, $J = 6.8$ Hz, 1H), 2.33 (dd, $J = 13.7, 4.0$ Hz, 1H), 2.26 (dd, $J = 13.7, 4.0$ Hz, 1H), 1.65 (s, 3H), 1.38 (d, $J = 6.8$ Hz, 3H). ¹³C NMR (175 MHz, CDCl₃) δ 137.3, 135.8, 135.3, 134.8, 133.4, 132.8, 132.5, 130.7, 129.7, 129.0, 128.3, 128.1, 126.1, 125.8, 125.3, 118.2, 25.8, 18.8, 13.9.



3l

(Z)-Methyl(2-methylbut-2-en-1-yl)(phenyl)silane (3l): Known compound¹, Colorless oil, 14.6 mg, 38% total yield, **3l:4l:5l:others** = 96:0:1:3, $R_f = 0.8$ (PE). ¹H NMR (700 MHz, CDCl₃) δ 7.62–7.51 (m, 2H), 7.45–7.31 (m, 3H), 5.16 (q, $J = 6.3$ Hz, 1H), 4.45 (h, $J = 3.8$ Hz, 1H), 1.82 (d, $J = 3.8$ Hz, 2H), 1.67–1.66 (m, 3H), 1.47 – 1.44 (m, 3H), 0.39 (d, $J = 3.8$ Hz, 3H). ¹³C NMR

(175 MHz, CDCl₃) δ 136.7, 134.4, 132.9, 129.5, 128.0, 117.2, 25.9, 19.9, 13.9, -5.3.

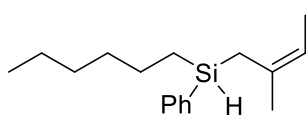


3m

(Z)-Isopropyl(2-methylbut-2-en-1-yl)(phenyl)silane (3m): Unknown compound,

colorless oil, 9.0 mg, 21% total yield, **3i:4i:5i:others** = 87:0:9:4, $R_f = 0.7$ (PE). ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.50 (m, 2H), 7.40 – 7.30 (m, 3H), 5.12 – 5.04 (m, 1H), 4.17 (dt, $J = 4.4, 2.9$ Hz, 1H), 1.89 (dd, $J = 13.7, 3.2$ Hz, 1H), 1.79 (dd, $J = 13.6, 4.3$ Hz, 1H), 1.65 – 1.60 (m, 3H), 1.44 (d, $J = 6.9$ Hz, 3H), 1.20 – 1.11 (m,

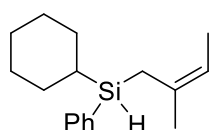
1H), 1.08 (d, $J = 6.6$ Hz, 3H), 1.01 (d, $J = 7.0$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.2, 135.0, 133.1, 129.4, 127.8, 117.1, 25.8, 18.50, 18.46, 16.8, 13.9, 12.3. HRMS calculated for C₁₄H₂₃Si [M+H]⁺ 219.1564, found 219.1568.



3n

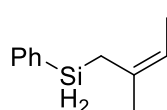
(Z)-Hexyl(2-methylbut-2-en-1-yl)(phenyl)silane (3n): Known compound¹, colorless oil, 24.7 mg, 47% total yield, **3i:4i:5i:others** = 93:0:4:3, $R_f = 0.7$ (PE). ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.51 (m, 2H), 7.41 – 7.31 (m, 3H), 5.12 (q, $J = 6.8$ Hz, 1H), 4.33 (p, $J = 3.6$ Hz, 1H), 1.84 (dd, $J = 13.7, 3.6$ Hz, 1H), 1.78 (dd, $J = 13.7, 3.6$

Hz, 1H), 1.67 – 1.64 (m, 3H), 1.44 (d, $J = 6.6$, 3H), 1.42 – 1.16 (m, 8H), 0.94 – 0.83 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.0, 134.8, 133.1, 129.4, 127.9, 117.1, 33.1, 31.6, 25.9, 24.6, 22.7, 18.7, 14.2, 13.9, 12.3.



3o

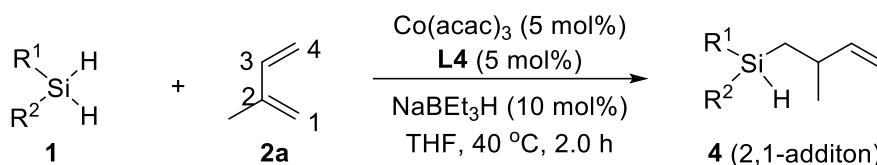
(Z)-Cyclohexyl(2-methylbut-2-en-1-yl)(phenyl)silane (3o): Known compound ¹, colorless oil, 21.4 mg, 41% total yield, **3o:4o:5o:others** = 90:0:4:6, $R_f = 0.7$ (PE). ^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.49 (m, 2H), 7.41 – 7.30 (m, 3H), 5.08 (q, $J = 6.8$ Hz, 1H), 4.15 (dt, $J = 4.5, 3.0$ Hz, 1H), 1.94 – 1.66 (m, 7H), 1.64 – 1.62 (m, 3H), 1.44 (d, $J = 6.8$ Hz, 3H), 1.36 – 1.09 (m, 5H), 1.07 – 0.95 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.3, 135.1, 133.2, 129.4, 127.8, 117.0, 28.5, 28.4, 28.01, 27.97, 26.9, 25.9, 24.0, 16.5, 13.9.



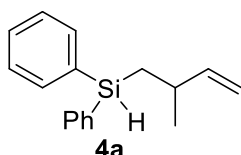
3p

(Z)-(2-methylbut-2-en-1-yl)(phenyl)silane (3p): Known compound ¹, colorless oil, 15.0 mg, 43% total yield, **3o:4o:5o:others** = 92:0:4:4, $R_f = 0.9$ (PE). ^1H NMR (700 MHz, CDCl_3) δ 7.59 (d, $J = 7.2$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.36 (t, $J = 7.3$ Hz, 2H), 5.16 (q, $J = 6.8$ Hz, 1H), 4.33 (t, $J = 4.0$ Hz, 2H), 1.88 (t, $J = 4.0$ Hz, 2H), 1.71 (s, 3H), 1.47 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.4, 132.7, 132.4, 129.8, 128.1, 117.7, 25.4, 16.5, 13.7.

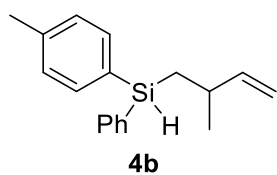
4. Typical procedure for Co-catalyzed 2,1-hydrosilylation of isoprene



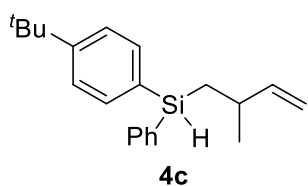
In glove box, $\text{Co}(\text{acac})_3$ (0.01 mmol, 3.6 mg, 5 mol%), **L4** (0.01 mmol, 3.2 mg, 5 mol%) and anhydrous THF (0.5 mL) were added to a sealed tube. The mixture was stirred for 5 minutes at room temperature. Then NaBEt_3H (20 μL , 1M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1** (0.20 mmol, 1.0 eq.) and **2a** (0.30 mmol, 20.4 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 °C for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding product **4**. The regioselectivity was determined by GC-FID or ^1H NMR.



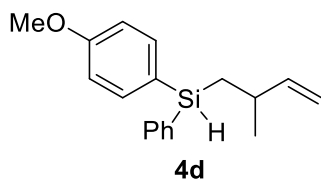
(2-Methylbut-3-en-1-yl)diphenylsilane (4a): Unknown compound, colorless oil, 43.5 mg, 86% total yield, **3a:4a:5a:others** = 3:94:0:3, $R_f = 0.8$ (PE /EtOAc = 100/1). ^1H NMR (700 MHz, CDCl_3) δ 7.59 (d, $J = 7.1$ Hz, 4H), 7.42 – 7.36 (m, 6H), 5.83 (ddd, $J = 17.2, 10.2, 7.1$ Hz, 1H), 4.98 – 4.91 (m, 2H), 4.88 (d, $J = 10.2$ Hz, 1H), 2.42 (hept, $J = 7.0$ Hz, 1H), 1.33 (ddd, $J = 14.9, 6.9, 4.0$ Hz, 1H), 1.23 (ddd, $J = 14.9, 7.6, 4.0$ Hz, 1H), 1.10 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (175 MHz, CDCl_3) δ 146.1, 135.3, 134.9, 134.8, 129.6, 128.1, 111.7, 34.2, 23.2, 20.4. ^{29}Si NMR (79 MHz, solid-state) δ -10.95. HRMS calculated for $\text{C}_{17}\text{H}_{21}\text{Si}$ $[\text{M}+\text{H}]^+$ 253.1407, found 253.1400.



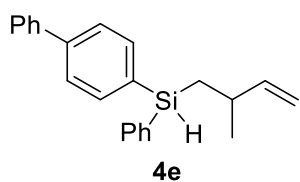
(2-Methylbut-3-en-1-yl)(phenyl)(p-tolyl)silane (4b): Unknown compound, colorless oil, 38.3 mg, 1:1 *dr*, 72% total yield, **3b:4b:5b:others** = 2:94:1:3, $R_f = 0.8$ (PE /EtOAc = 100/1). $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.59 – 7.56 (m, 2H), 7.49 – 7.47 (m, 2H), 7.42 – 7.34 (m, 3H), 7.21 (d, $J = 7.6$ Hz, 2H), 5.85 – 5.80 (m, 1H), 4.99 – 4.90 (m, 2H), 4.88 (dt, $J = 10.2, 1.4$ Hz, 1H), 2.44 – 2.39 (m, 1H), 2.38 (s, 3H), 1.34 – 1.29 (m, 1H), 1.23 – 1.19 (m, 1H), 1.09 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 146.19, 146.16, 139.56, 135.30, 135.23, 135.16, 135.11, 131.08, 131.01, 129.53, 128.95, 128.05, 111.62, 111.59, 34.22, 34.20, 23.17, 23.11, 21.66, 20.49, 20.48. HRMS calculated for $\text{C}_{18}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$ 267.1569, found 267.1581.



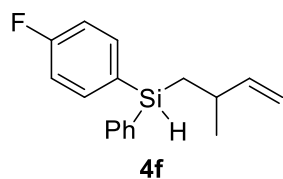
(4-(tert-Butyl)phenyl)(2-methylbut-3-en-1-yl)(phenyl)silane (4c): Unknown compound, colorless oil, 40.9 mg, 1:1 *dr*, 66% total yield, **3c:4c:5c:others** = 1:95:1:3, $R_f = 0.8$ (PE /EtOAc = 100/1). $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.61 – 7.58 (m, 2H), 7.53 – 7.50 (m, 2H), 7.42 – 7.34 (m, 5H), 5.86 – 5.80 (m, 1H), 4.97 – 4.91 (m, 2H), 4.90 – 4.85 (m, 1H), 2.46 – 2.38 (m, 1H), 1.36 – 1.29 (m, 10H), 1.23 – 1.19 (m, 1H), 1.11 – 1.08 (m, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 152.6, 146.3, 146.2, 135.3, 135.1, 131.2, 131.15, 129.6, 128.1, 125.1, 111.6, 111.58, 34.8, 34.2, 34.17, 31.4, 23.2, 23.1, 20.5. HRMS calculated for $\text{C}_{21}\text{H}_{29}\text{Si}$ $[\text{M}+\text{H}]^+$ 309.2039, found 309.2044.



(4-Methoxyphenyl)(2-methylbut-3-en-1-yl)(phenyl)silane (4d): Unknown compound, colorless oil, 40.0 mg, 1:1 *dr*, 71% total yield, **3d:4d:5d:others** = 2:93:1:4, $R_f = 0.6$ (PE /EtOAc 100/1). $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.57 – 7.55 (m, 2H), 7.51 – 7.48 (m, 2H), 7.39 – 7.34 (m, 3H), 6.94 – 6.91 (m, 2H), 5.84 – 5.79 (m, 1H), 4.96 – 4.90 (m, 2H), 4.89 – 4.84 (m, 1H), 3.82 (s, 3H), 2.44 – 2.36 (m, 1H), 1.32 – 1.27 (m, 1H), 1.22 – 1.16 (m, 1H), 1.08 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 160.8, 146.1, 146.07, 137.3, 136.7, 135.6, 135.2, 135.19, 135.1, 129.8, 129.4, 128.1, 128.0, 127.9, 125.4, 125.3, 114.0, 113.8, 111.5, 111.47, 55.0, 34.1, 34.09, 23.1, 23.0, 20.52, 20.51. HRMS calculated for $\text{C}_{18}\text{H}_{23}\text{OSi}$ $[\text{M}+\text{H}]^+$ 283.1518, found 283.1529.

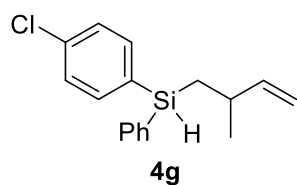


[1,1'-Biphenyl]-4-yl(2-methylbut-3-en-1-yl)(phenyl)silane (4e): Unknown compound, colorless oil, 58.4 mg, 1:1 *dr*, 89% total yield, **3e:4e:5e:others** = 1:95:0:4, $R_f = 0.6$ (PE), $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.69 – 7.67 (m, 2H), 7.64 – 7.62 (m, 6H), 7.49 – 7.45 (m, 2H), 7.44 – 7.36 (m, 4H), 5.86 (ddd, $J = 17.1, 10.3, 7.1$ Hz, 1H), 5.02 (t, $J = 4.0$ Hz, 1H), 5.00 – 4.95 (m, 1H), 4.91 (d, $J = 10.3$ Hz, 1H), 2.47 (hept, $J = 7.1$ Hz, 1H), 1.40 – 1.36 (m, 1H), 1.31 – 1.25 (m, 1H), 1.15 – 1.12 (m, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 146.1, 142.4, 141.1, 135.8, 135.3, 134.82, 134.76, 133.6, 133.5, 129.7, 128.9, 128.2, 127.6, 127.3, 126.8, 111.8, 34.2, 23.2, 20.4. HRMS calculated for $\text{C}_{23}\text{H}_{25}\text{Si}$ $[\text{M}+\text{H}]^+$ 329.1726, found 329.1752.



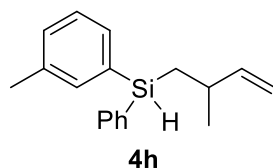
(4-Fluorophenyl)(2-methylbut-3-en-1-yl)(phenyl)silane (4f):

Unknown compound, colorless oil, 10.6 mg, 1:1 *dr*, 20% total yield, **3f:4f:5f:others** = 2:92:1:5, $R_f = 0.8$ (PE /EtOAc = 100/1). **$^1\text{H NMR}$** (700 MHz, CDCl_3) δ 7.55 – 7.51 (m, 4H), 7.40 – 7.38 (m, 1H), 7.38 – 7.34 (m, 2H), 7.08 – 7.04 (m, 2H), 5.81 – 5.75 (m, 1H), 4.93 – 4.88 (m, 2H), 4.85 (d, $J = 10.2$ Hz, 1H), 2.37 (hept, $J = 6.9$ Hz, 1H), 1.32 – 1.25 (m, 1H), 1.22 – 1.16 (m, 1H), 1.07 (d, $J = 6.7$ Hz, 3H). **$^{13}\text{C NMR}$** (175 MHz, CDCl_3) δ 164.2 (d, $J = 249.0$ Hz), 145.9, 137.2 (d, $J = 7.2$ Hz), 137.19 (d, $J = 7.2$ Hz), 135.2, 134.6, 134.56, 129.8, 128.2, 115.4, 115.3, 111.8, 34.2, 34.21, 23.2, 20.5. **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -111.17. HRMS calculated for $\text{C}_{17}\text{H}_{20}\text{FSi}$ $[\text{M}+\text{H}]^+$ 271.1318, found 271.1325.



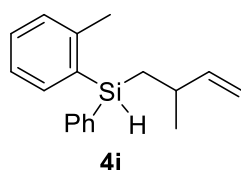
(4-Chlorophenyl)(2-methylbut-3-en-1-yl)(phenyl)silane (4g):

Unknown compound, colorless oil, 45.1 mg, 1:1 *dr*, 79% total yield, **3g:4g:5g:others** = 3:91:1:5, $R_f = 0.8$ (PE /EtOAc = 100/1). **$^1\text{H NMR}$** (700 MHz, CDCl_3) δ 7.56 – 7.53 (m, 2H), 7.50 – 7.48 (m, 2H), 7.42 – 7.39 (m, 1H), 7.39 – 7.33 (m, 4H), 5.82 – 5.76 (m, 1H), 4.96 – 4.90 (m, 2H), 4.88 – 4.85 (m, 1H), 2.39 (hept, $J = 6.7$ Hz, 1H), 1.33 – 1.27 (m, 1H), 1.24 – 1.18 (m, 1H), 1.08 (d, $J = 6.7$ Hz, 3H). **$^{13}\text{C NMR}$** (175 MHz, CDCl_3) δ 145.7, 136.5, 135.9, 135.1, 134.2, 134.1, 133.1, 133.09, 129.7, 128.3, 128.1, 111.8, 34.12, 34.10, 23.13, 23.12, 20.2. HRMS calculated for $\text{C}_{17}\text{H}_{20}\text{ClSi}$ $[\text{M}+\text{H}]^+$ 287.1023, found 287.1038.



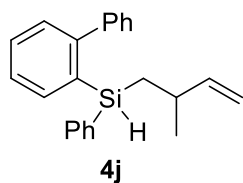
(2-Methylbut-3-en-1-yl)(phenyl)(m-tolyl)silane (4h):

Unknown compound, colorless oil, 1:1 *dr*, 38.1 mg, 71% total yield, **3h:4h:5h:others** = 2:92:1:5, $R_f = 0.8$ (PE /EtOAc 100/1). **$^1\text{H NMR}$** (700 MHz, CDCl_3) δ 7.57 – 7.54 (m, 2H), 7.39 – 7.32 (m, 5H), 7.24 (d, $J = 7.7$ Hz, 1H), 7.19 (d, $J = 7.7$ Hz, 1H), 5.83 – 5.77 (m, 1H), 4.93 – 4.88 (m, 2H), 4.86 – 4.83 (m, 1H), 2.39 (hept, $J = 6.9$, 1H), 2.33 (s, 3H), 1.30 (ddd, $J = 14.9, 6.8, 4.0$ Hz, 1H), 1.21 – 1.17 (m, 1H), 1.09 – 1.03 (m, 3H). **$^{13}\text{C NMR}$** (175 MHz, CDCl_3) δ 146.19, 146.17, 137.5, 135.9, 135.3, 135.0, 134.97, 134.7, 134.6, 132.3, 130.5, 129.6, 128.1, 128.0, 34.2, 23.2, 23.1, 21.6, 20.4. HRMS calculated for $\text{C}_{18}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$ 267.1569, found 267.1581.



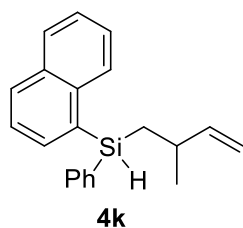
(2-Methylbut-3-en-1-yl)(phenyl)(o-tolyl)silane (4i):

Unknown compound, colorless oil, 45.3 mg, 1:1 *dr*, 85% total yield, **3i:4i:5i:others** = 4:90:0:6, $R_f = 0.8$ (PE /EtOAc = 100/1). **$^1\text{H NMR}$** (700 MHz, CDCl_3) δ 7.57 – 7.53 (m, 3H), 7.42 – 7.30 (m, 4H), 7.23 – 7.17 (m, 2H), 5.86 – 5.80 (m, 1H), 5.05 (t, $J = 4.0$ Hz, 1H), 4.96 – 4.91 (m, 1H), 4.89 – 4.86 (m, 1H), 2.44 – 2.39 (m, 1H), 2.38 (d, $J = 4.2$ Hz, 3H), 1.39 – 1.34 (m, 1H), 1.28 – 1.23 (m, 1H), 1.12 – 1.08 (m, 3H). **$^{13}\text{C NMR}$** (175 MHz, CDCl_3) δ 146.13, 146.12, 144.39, 144.36, 136.21, 136.18, 135.21, 135.20, 135.03, 134.97, 133.56, 133.47, 130.03, 130.01, 129.79, 129.48, 128.08, 128.07, 125.19, 111.64, 34.41, 34.39, 23.16, 23.06, 22.87, 22.85, 20.10, 20.09. HRMS calculated for $\text{C}_{18}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$ 267.1569, found 267.1585.



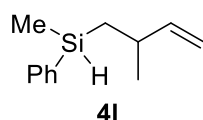
(1,1'-Biphenyl)-2-yl(2-methylbut-3-en-1-yl)(phenyl)silane (4j):

Unknown compound, colorless oil, 61.4 mg, 1:1 *dr*, 93% total yield, **3j:4j:5j:others** = 0:72:18:10, $R_f = 0.8$ (PE /EtOAc = 100/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 7.64 (m, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.29 (m, 9H), 7.24 – 7.22 (m, 2H), 5.71 – 5.59 (m, 1H), 4.86 – 4.73 (m, 3H), 2.17 (hept, $J = 6.9$ Hz, 1H), 1.07 – 0.69 (m, 5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.97, 149.86, 146.13, 146.04, 143.57, 137.49, 136.68, 136.64, 135.89, 135.67, 135.19, 135.17, 133.58, 132.44, 130.95, 130.22, 129.62, 129.59, 129.47, 129.42, 129.28, 129.17, 128.16, 128.00, 127.93, 127.40, 127.25, 126.68, 126.53, 111.38, 111.31, 34.22, 34.19, 22.85, 22.81, 20.14, 20.04. HRMS calculated for $\text{C}_{23}\text{H}_{25}\text{Si}$ $[\text{M}+\text{H}]^+$ 329.1720, found 329.1716.



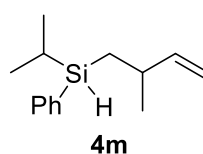
(2-Methylbut-3-en-1-yl)(naphthalen-1-yl)(phenyl)silane (4k):

Unknown compound, colorless oil, 43.5 mg, 1:1 *dr*, 72% total yield, **3k:4k:5k:others** = 6:89:0:5, $R_f = 0.8$ (PE /EtOAc = 100/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 – 8.04 (m, 1H), 7.93 (d, $J = 8.2$ Hz, 1H), 7.91 – 7.86 (m, 1H), 7.82 – 7.78 (m, 1H), 7.63 – 7.58 (m, 2H), 7.53 – 7.43 (m, 3H), 7.43 – 7.32 (m, 3H), 5.90 – 5.79 (m, 1H), 5.39 – 5.35 (m, 1H), 4.99 – 4.84 (m, 2H), 2.46 (hept, $J = 6.9$ Hz, 1H), 1.54 – 1.45 (m, 1H), 1.43 – 1.35 (m, 1H), 1.13 – 1.11 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.1, 146.0, 137.3, 135.83, 135.78, 135.3, 134.92, 134.87, 133.4, 133.0, 132.9, 130.6, 129.6, 129.0, 128.2, 128.1, 126.18, 126.17, 125.8, 125.3, 111.79, 111.72, 34.6, 34.5, 23.2, 23.1, 20.64, 20.58. HRMS calculated for $\text{C}_{21}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$ 303.1564, found 303.1574.



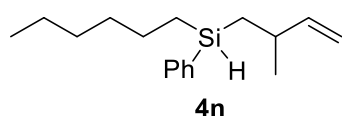
Methyl-2-methylbut-3-en-1-yl(phenyl)silane (4l):

Unknown compound, colorless oil, 10.4 mg, 1:1 *dr*, 27% total yield, **3l:4l:5l:others** = 9:83:0:8, $R_f = 0.8$ (PE). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 – 7.48 (m, 2H), 7.43 – 7.32 (m, 3H), 5.85 – 5.74 (m, 1H), 4.97 – 4.91 (m, 1H), 4.88 – 4.83 (m, 1H), 4.45 – 4.38 (m, 1H), 2.45 – 2.29 (m, 1H), 1.09 – 1.05 (m, 3H), 1.04 – 0.82 (m, 2H), 0.38 – 0.33 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.4, 146.3, 136.9, 134.4, 129.3, 128.0, 111.5, 34.5, 34.4, 23.33, 23.30, 21.8, 21.7, -4.79, -4.84. HRMS calculated for $\text{C}_{12}\text{H}_{19}\text{Si}$ $[\text{M}+\text{H}]^+$ 191.1251, found 191.1250.



Isopropyl(2-methylbut-3-en-1-yl)(phenyl)silane (4m):

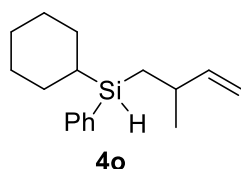
Unknown compound, colorless oil, 19.9 mg, 1:1 *dr*, 46% total yield, **3l:4l:5l:others** = 7:87:3:3, $R_f = 0.7$ (PE). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 – 7.43 (m, 2H), 7.43 – 7.30 (m, 3H), 5.83 – 5.71 (m, 1H), 4.97 – 4.79 (m, 2H), 4.22 – 4.16 (m, 1H), 2.37 – 2.26 (m, 1H), 1.16 – 0.85 (m, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.7, 146.2, 135.28, 135.27, 135.22, 135.0, 129.30, 129.28, 127.87, 127.85, 111.5, 111.2, 34.5, 34.2, 23.5, 22.8, 18.50, 18.45, 18.3, 12.21, 12.17. HRMS calculated for $\text{C}_{14}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$ 219.1564, found 219.1562



Hexyl(2-methylbut-3-en-1-yl)(phenyl)silane (4n):

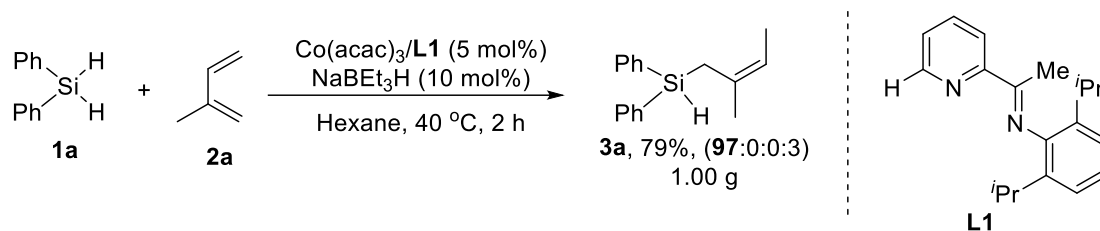
Unknown compound, colorless oil, 24.6 mg, 1:1 *dr*, 47% total yield, **3n:4n:5n:others** = 6:89:0:5, $R_f = 0.7$ (PE). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.45 (m, 2H), 7.41 – 7.31 (m, 3H), 5.79 (ddd, $J =$

17.3, 10.2, 7.1 Hz, 1H), 4.97 – 4.89 (m, 1H), 4.88 – 4.83 (m, 1H), 4.36 – 4.30 (m, 1H), 2.34 (hept, $J = 7.0$ Hz, 1H), 1.43 – 1.18 (m, 8H), 1.07 – 1.03 (m, 3H), 1.02 – 0.72 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 136.3, 134.9, 129.3, 127.9, 111.5, 111.4, 34.5, 34.3, 33.0, 31.6, 24.6, 23.4, 23.1, 22.7, 20.3, 20.2, 14.2, 12.6. HRMS calculated for $\text{C}_{17}\text{H}_{29}\text{Si}$ $[\text{M}+\text{H}]^+$ 261.2039, found 261.2057.

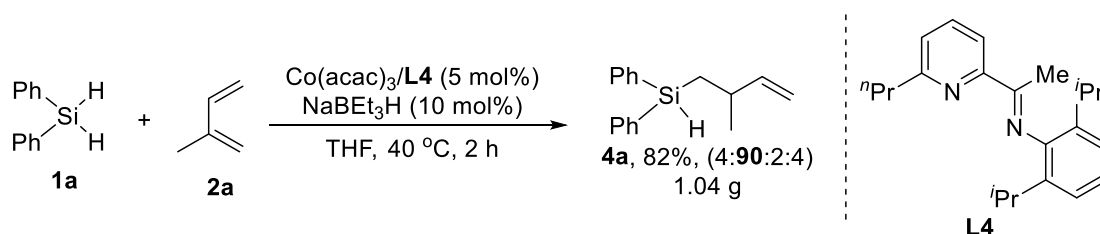


Cyclohexyl(2-methylbut-3-en-1-yl)(phenyl)silane (4o): Unknown compound, colorless oil, 23.3 mg, 1:1 *dr*, 45% total yield, **3o:4o:5o:others** = 5:88:4:3, $R_f = 0.7$ (PE). ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.48 (m, 2H), 7.39 – 7.31 (m, 3H), 5.82 – 5.72 (m, 1H), 4.95 – 4.79 (m, 2H), 4.20 – 4.13 (m, 1H), 2.35 – 2.24 (m, 1H), 1.80 – 1.62 (m, 6H), 1.30 – 1.12 (m, 5H), 1.10 – 0.85 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 146.3, 135.33, 135.30, 135.28, 135.1, 129.3, 129.2, 127.9, 127.83, 127.78, 111.5, 111.2, 34.5, 34.1, 28.49, 28.48, 28.43, 28.42, 28.02, 28.00, 26.9, 24.02, 23.98, 23.5, 22.7, 18.2, 18.01. HRMS calculated for $\text{C}_{17}\text{H}_{27}\text{Si}$ $[\text{M}+\text{H}]^+$ 259.1877, found 259.1884.

5. Gram-scale experiment.



In glove box, $\text{Co}(\text{acac})_3$ (0.25 mmol, 89.1 mg, 5 mol%), **L1** (0.25 mmol, 70.1 mg, 5 mol%) and anhydrous hexane (15.0 mL) were added to a sealed tube. The mixture was stirred for 5 minutes at room temperature. Then NaBEt_3H (0.5 mL, 1 M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1a** (5.00 mmol, 921.5 mg, 1.0 eq.) and **2a** (7.50 mmol, 510.8 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 °C for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding product **3a** (1.00 g, 79% yield). The regioselectivity was determined by ^1H NMR.

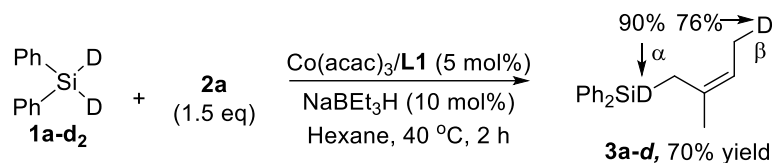


In glove box, a sealed tube was charged with $\text{Co}(\text{acac})_3$ (0.25 mmol, 89.1 mg, 5 mol%), and **L4** (0.25 mmol, 80.6 mg, 5 mol%) in anhydrous THF (15.0 mL). Then, NaBEt_3H (0.5 mL, 1 M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, **1a** (5.00 mmol, 921.5 mg, 1.0 eq.) and **2a** (7.50 mmol, 510.8 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 °C for 2 hours. After cooling to room temperature, the

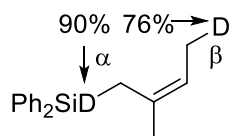
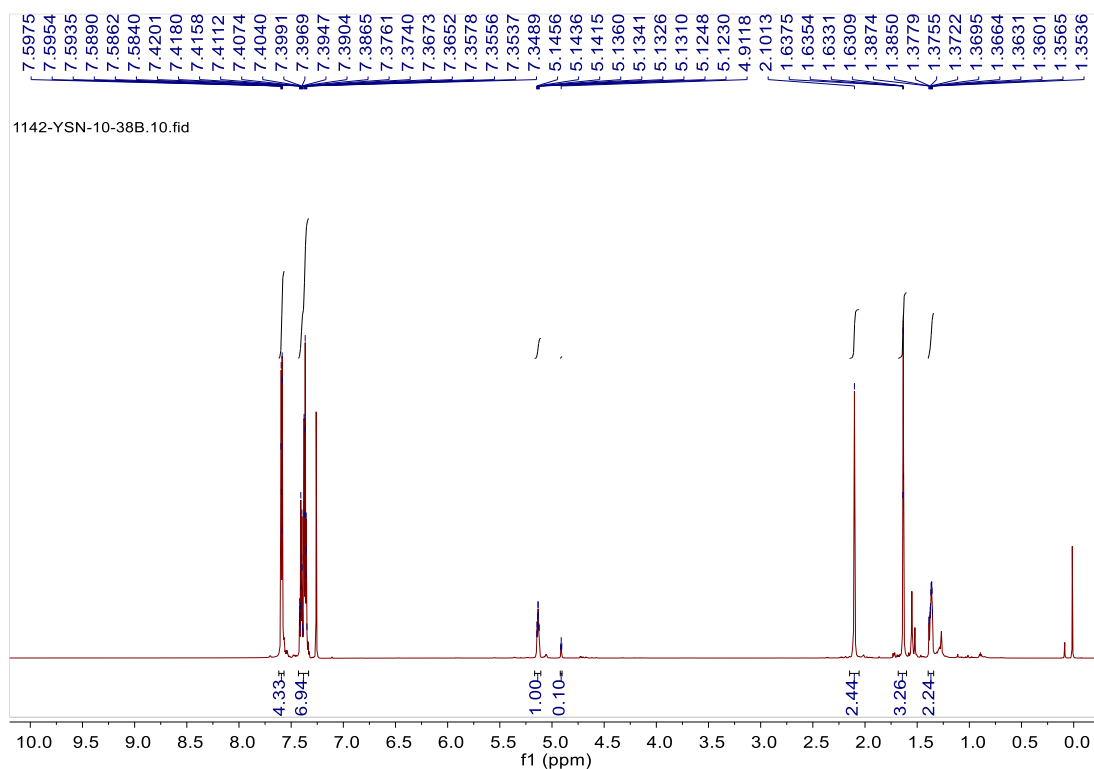
reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding product 1.04 g of **4a** (82% yield). The regioselectivity was determined by ¹H NMR.

6. Mechanistic studies

6.1. Deuterium labelling experiments: isoprene effect



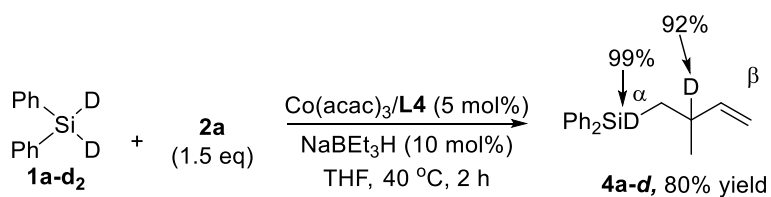
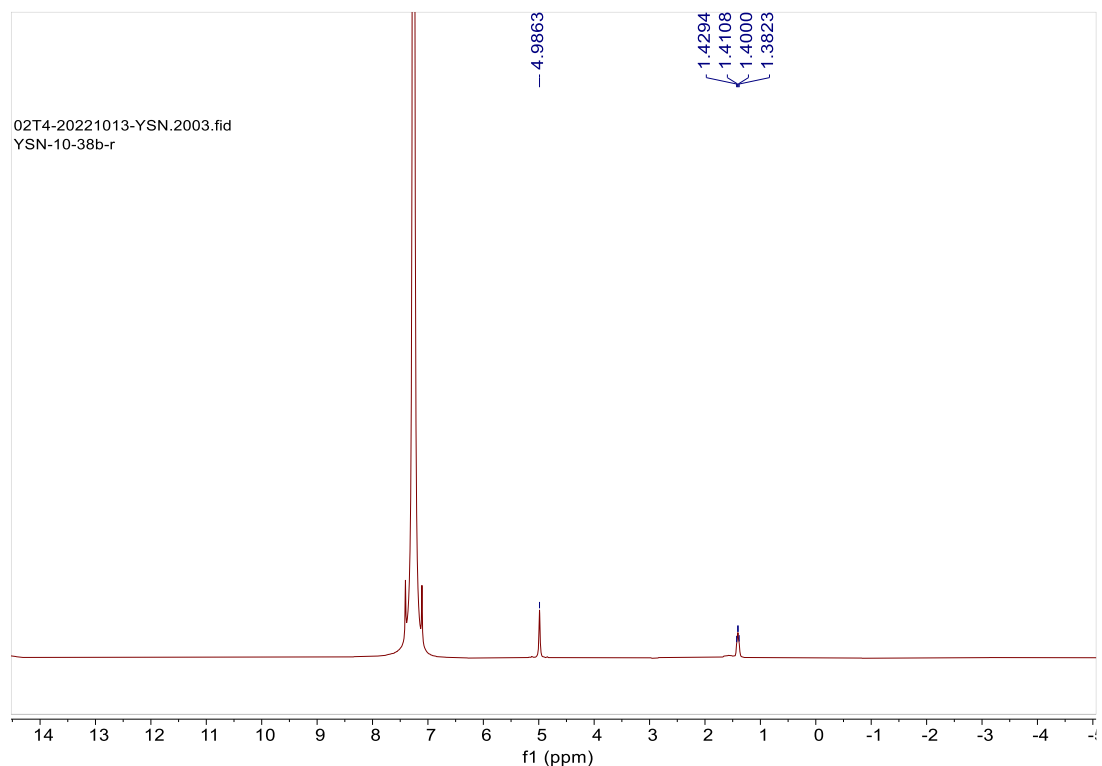
In glove box, a sealed tube was charged with Co(acac)_3 (0.01 mmol, 3.6 mg, 5 mol%) and **L1** (0.01 mmol, 2.8 mg, 5 mol%) in anhydrous hexane (0.5 mL). Then, NaBEt_3H (20 μL , 1 M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1a-d₂** (0.20 mmol, 37.3 mg, 1.0 eq.) and **2a** (0.30 mmol, 20.4 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 $^\circ\text{C}$ for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding product of **3a-d** (70% yield).



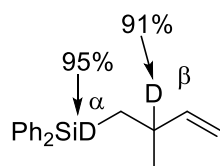
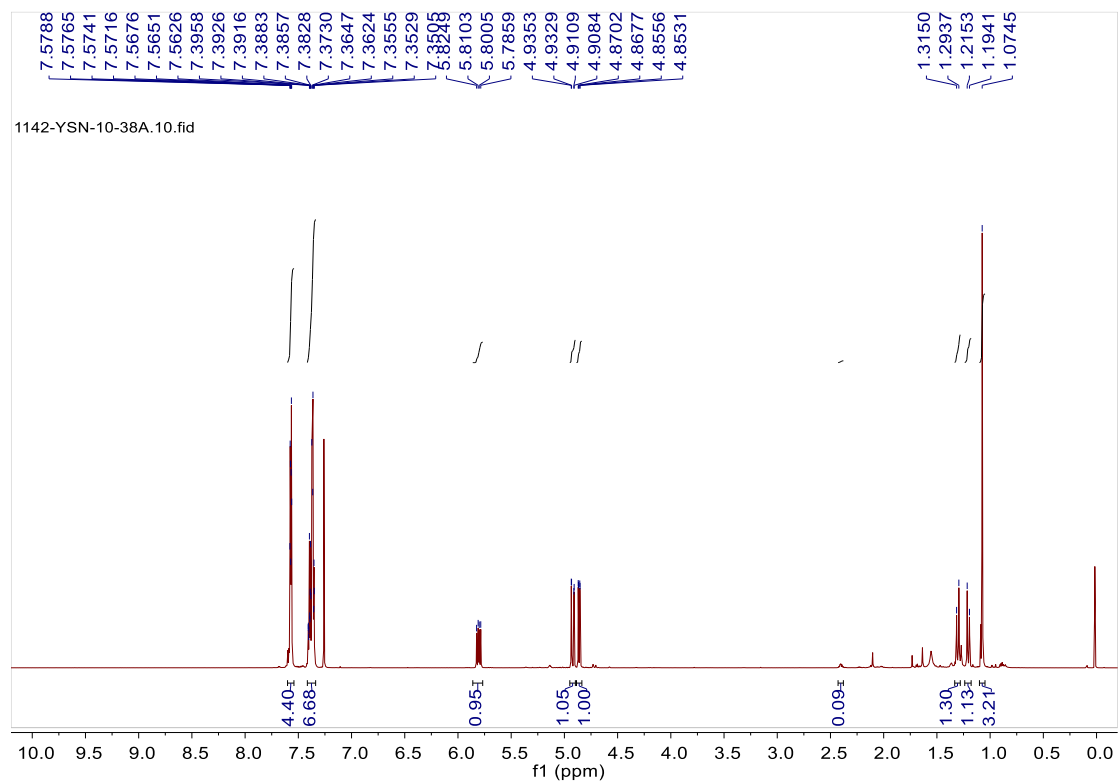
3a-d

$^1\text{H NMR}$ (700 MHz, CDCl_3)

$^2\text{D NMR}$ (700 MHz, CDCl_3)



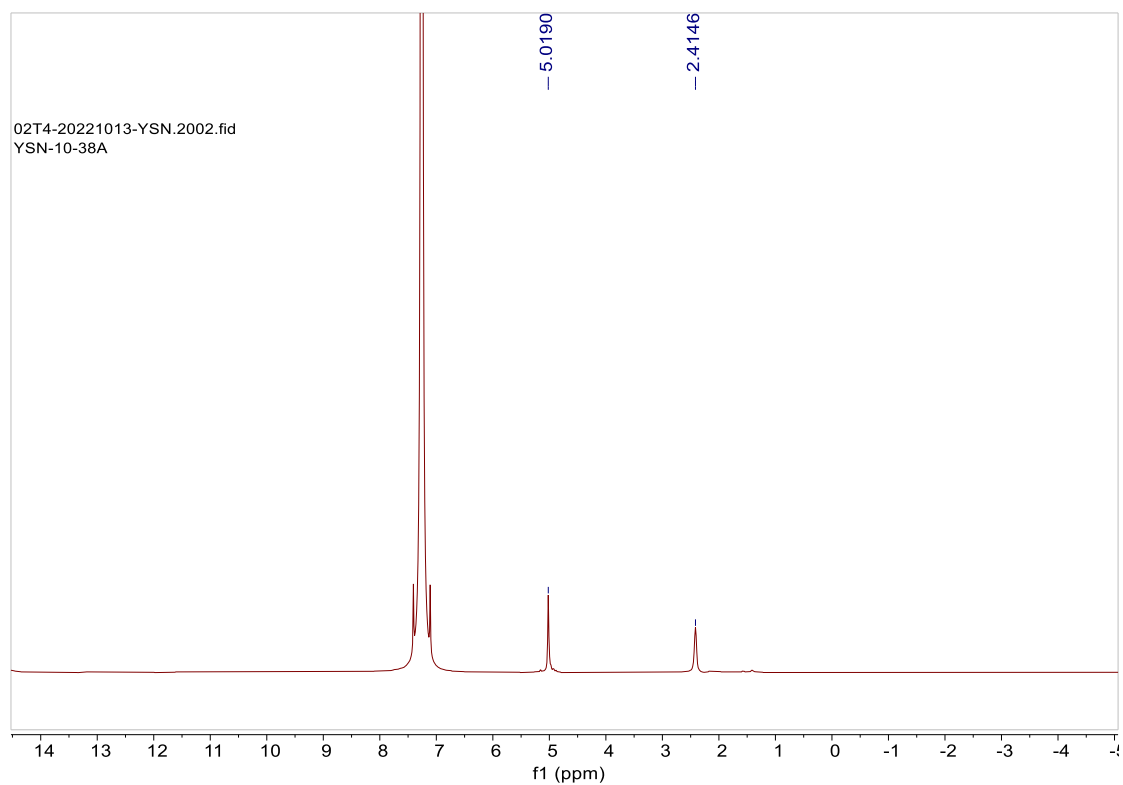
In glove box, a sealed tube was charged with $\text{Co}(\text{acac})_3$ (0.01 mmol, 3.6 mg, 5 mol%) and **L4** (0.01 mmol, 3.2 mg, 5 mol%) in anhydrous THF (0.5 mL). Then, NaBEt_3H (20 μL , 1M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1a-d₂** (0.20 mmol, 37.3 mg, 1.0 eq.) and **2a** (0.30 mmol, 20.4 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 $^\circ\text{C}$ for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding product of **4a-d** (80% yield).

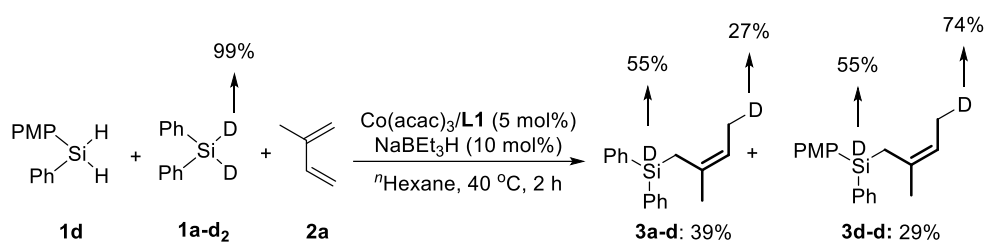


4a-d

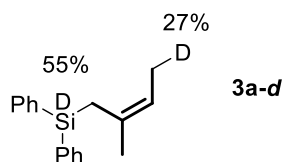
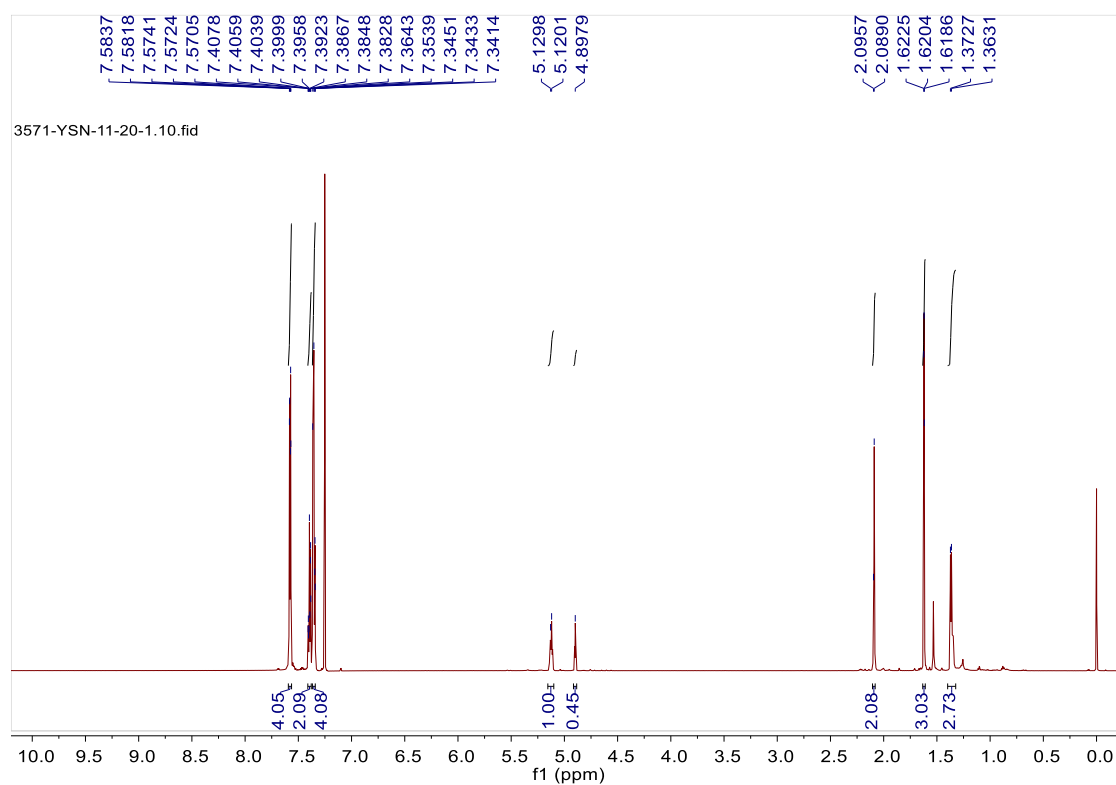
^1H NMR (700 MHz, CDCl_3)

^2D NMR (700 MHz, CDCl_3)

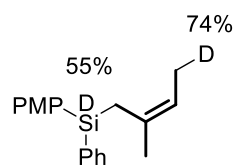
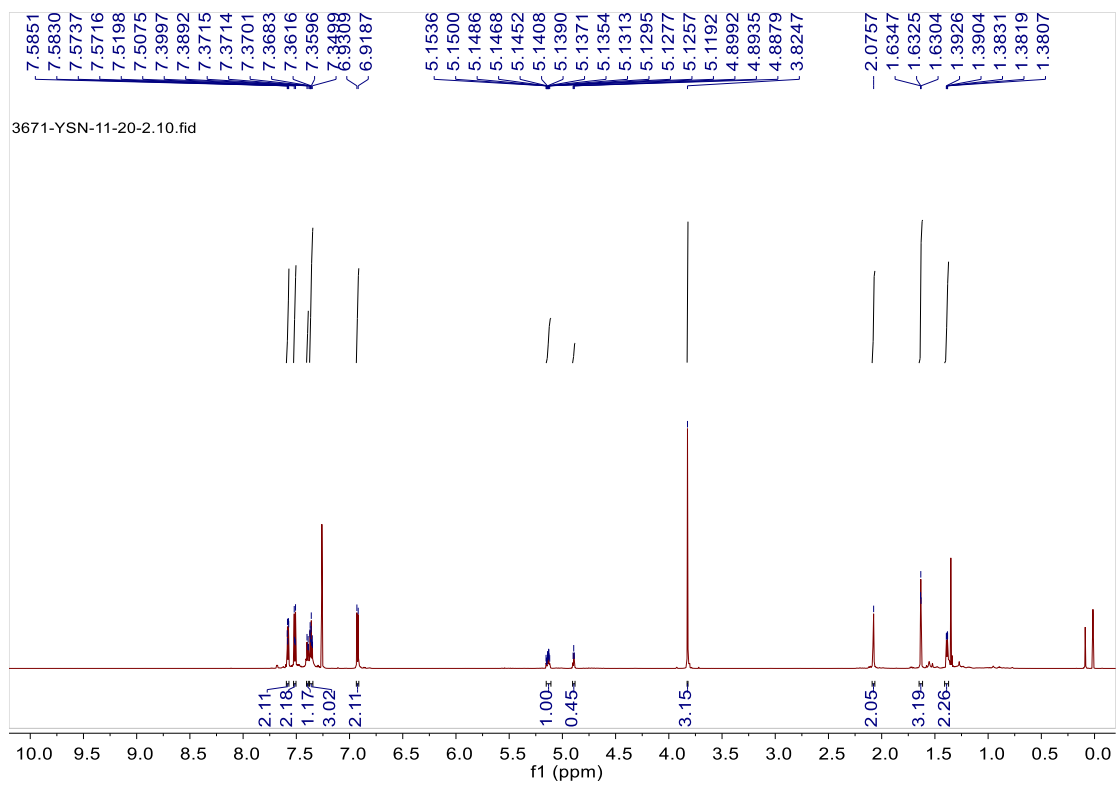
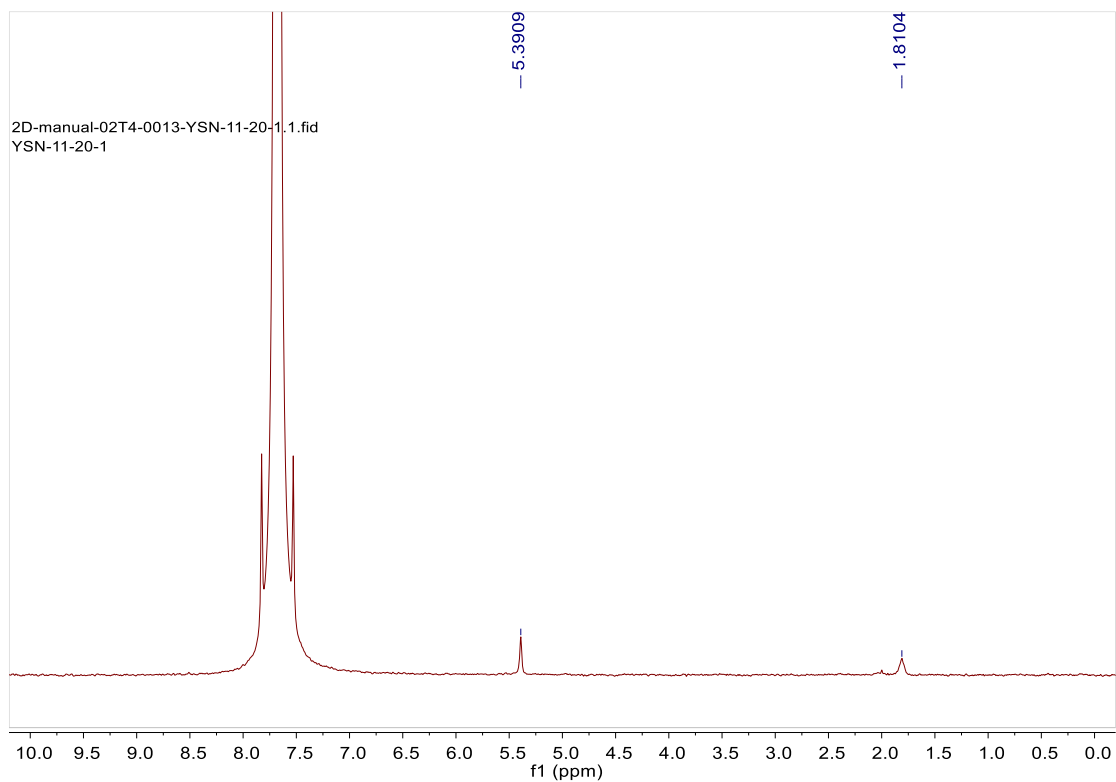




In glove box, a sealed tube was charged with Co(acac)_3 (0.01 mmol, 3.6 mg, 5 mol%) and **L1** (0.01 mmol, 2.8 mg, 5 mol%) in anhydrous hexane (0.5 mL). Then, NaBEt_3H (20 μL , 1 M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1a-d₂** (0.10 mmol, 18.6 mg, 1.0 eq.), **1d** (0.10 mmol, 21.4 mg, 1.0 eq.), and **2a** (0.30 mmol, 20.4 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 $^\circ\text{C}$ for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding products of **3a-d** (39% yield) and **3d-d** (29% yield).



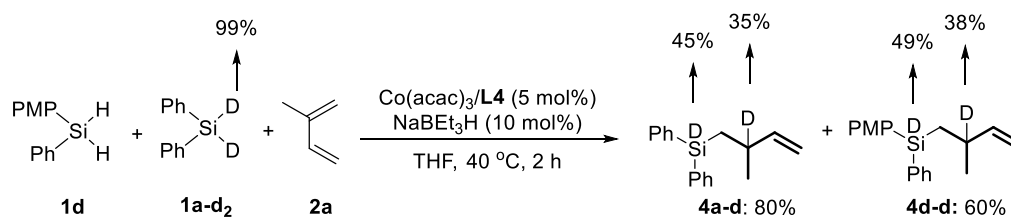
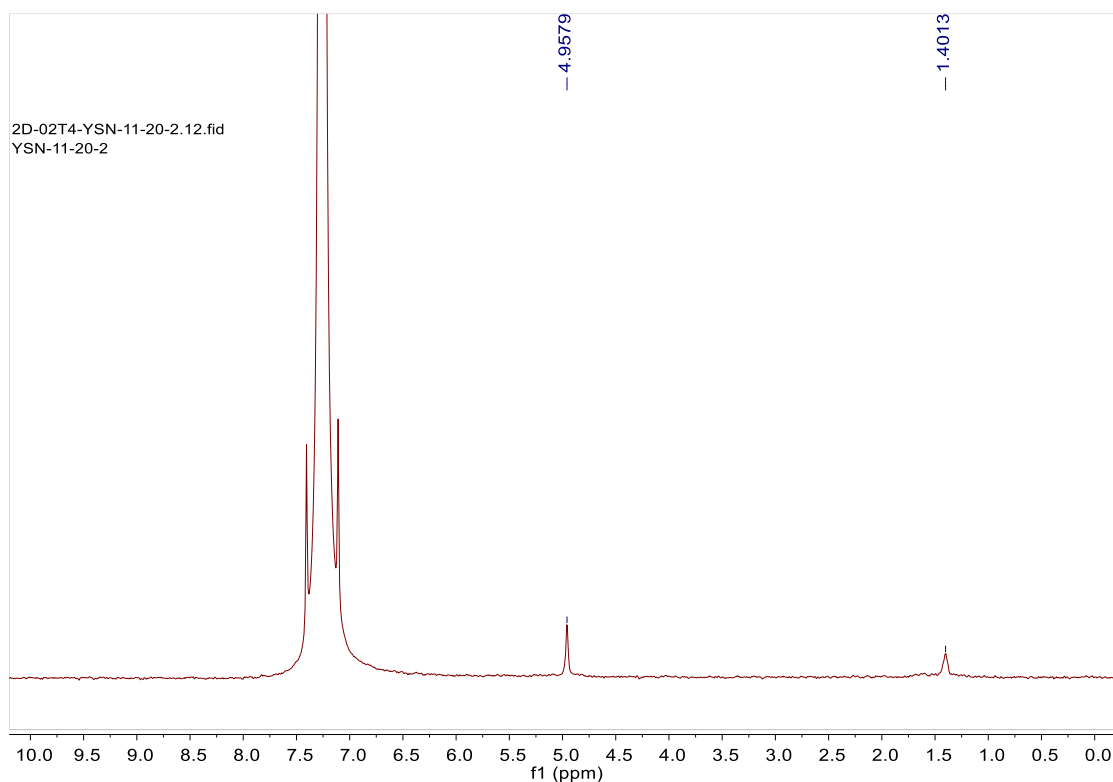
$^1\text{H NMR}$ (700 MHz, CDCl_3)
 $^2\text{D NMR}$ (700 MHz, CDCl_3)



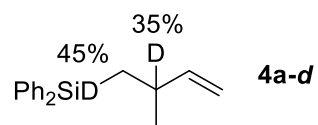
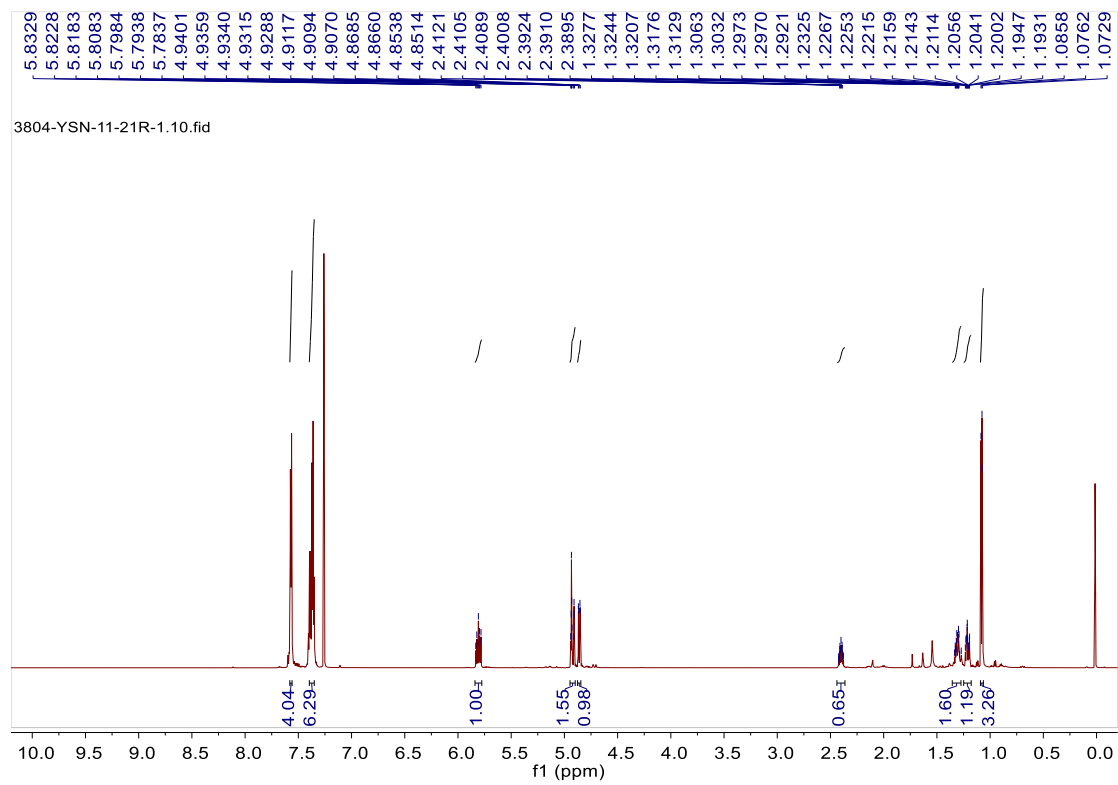
3d-d

¹H NMR (700 MHz, CDCl₃)

²D NMR (700 MHz, CDCl₃)

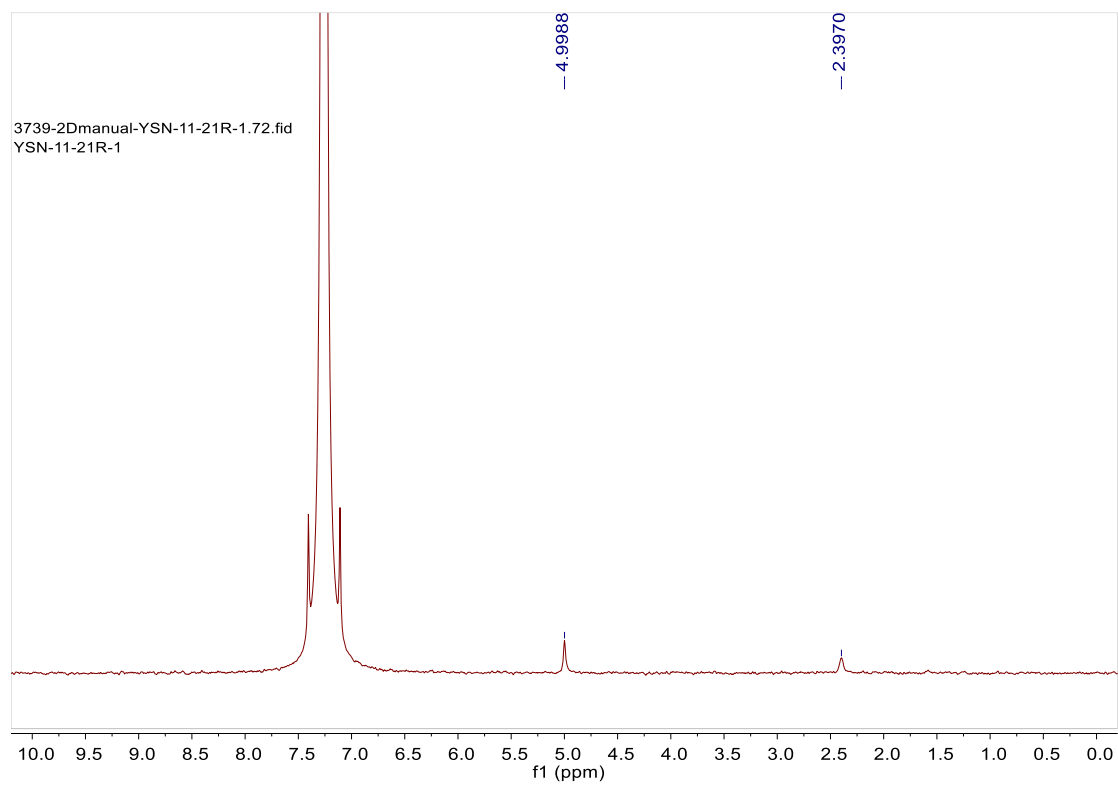


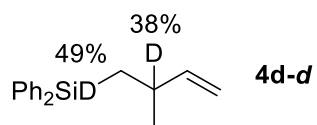
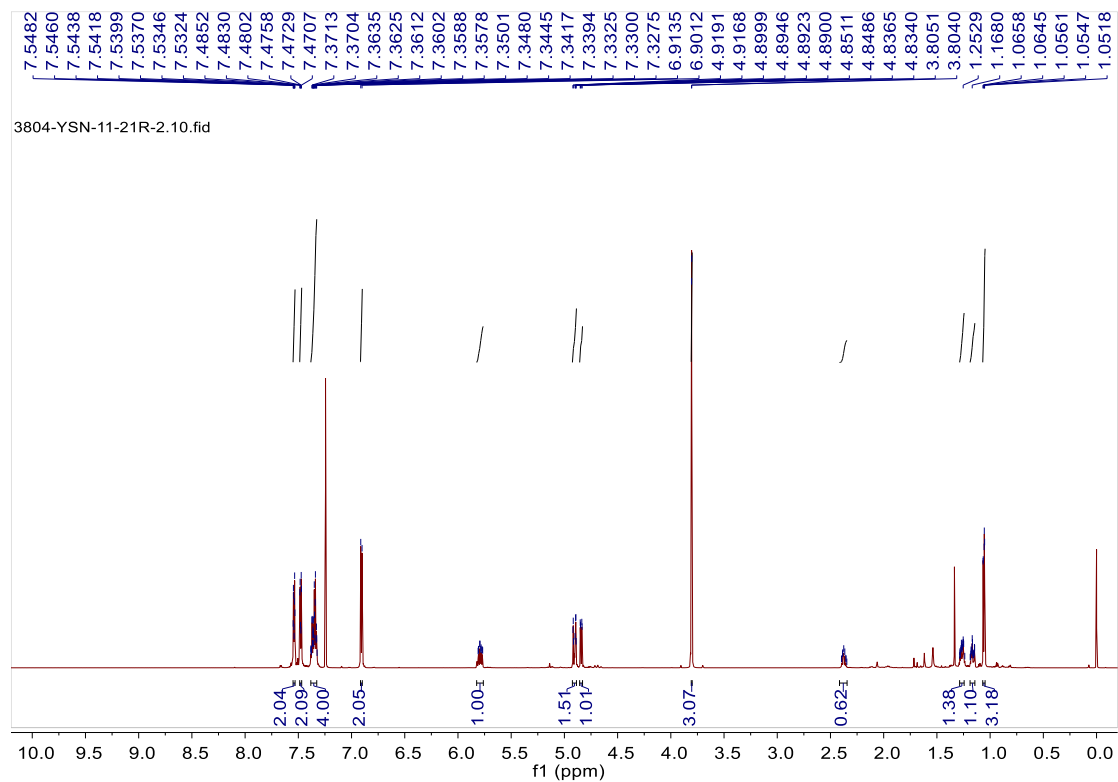
In glove box, a sealed tube was charged with $\text{Co}(\text{acac})_3$ (0.01 mmol, 3.6 mg, 5 mol%) and **L4** (0.01 mmol, 3.2 mg, 5 mol%) in anhydrous THF (0.5 mL). Then, NaBEt_3H (20 μL , 1M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, silane **1a-d₂** (0.10 mmol, 18.6 mg, 1.0 eq.), **1d** (0.10 mmol, 21.4 mg, 1.0 eq.), and **2a** (0.30 mmol, 20.4 mg, 1.5 eq.) were added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 $^\circ\text{C}$ for 2 hours. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using petroleum and ethyl acetate to afford the corresponding products of **3a-d** (80% yield) and **3d-d** (60% yield).



¹H NMR (700 MHz, CDCl₃)

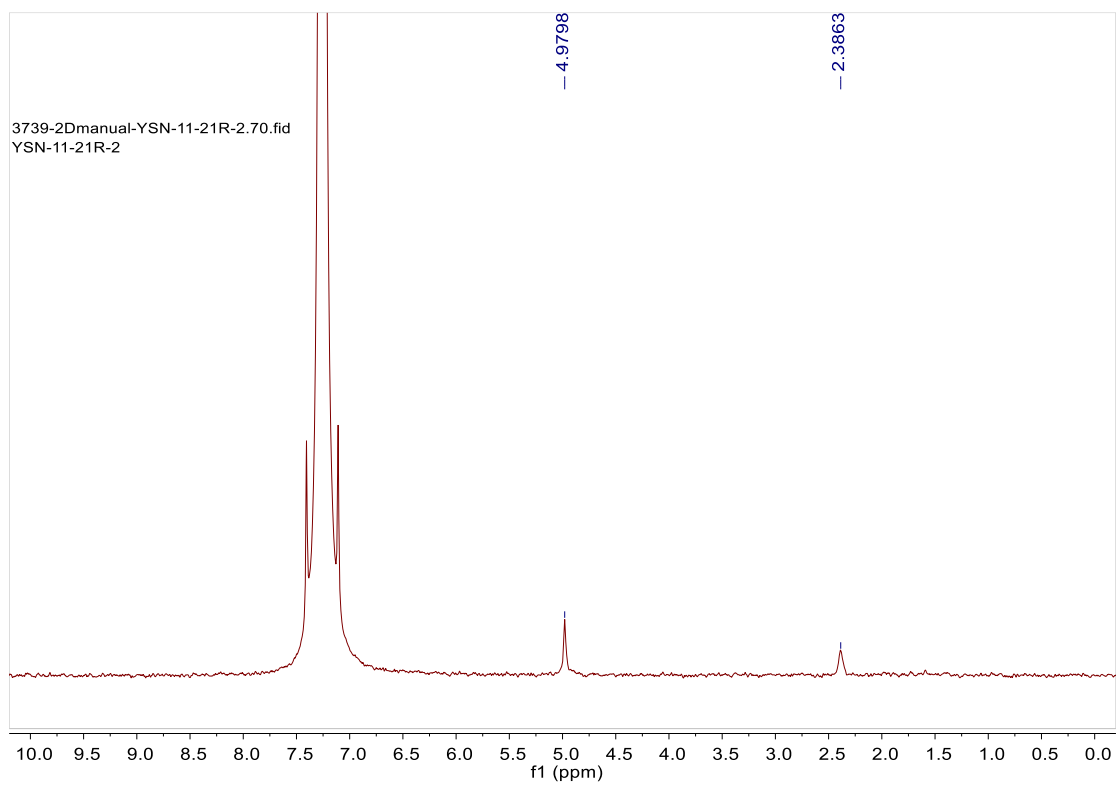
²D NMR (700 MHz, CDCl₃)



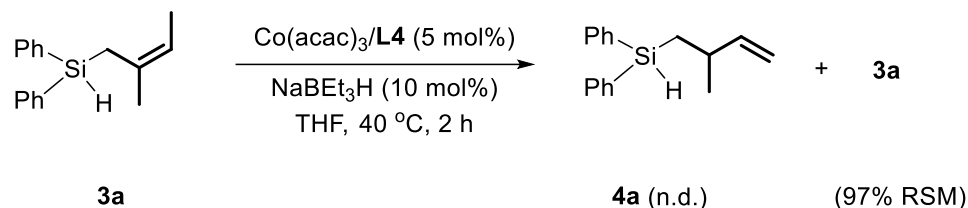


¹H NMR (700 MHz, CDCl₃)

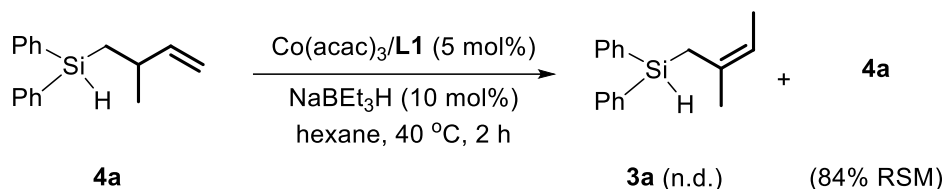
²D NMR (700 MHz, CDCl₃)



6.2. Inter-isomerization experiment of hydrosilylation products



In glove box, a sealed tube was charged with $\text{Co}(\text{acac})_3$ (0.01 mmol, 3.6 mg, 5 mol%) and **L4** (0.01 mmol, 3.2 mg, 5 mol%) in anhydrous THF (0.5 mL). Then, NaBEt_3H (20 μL , 1M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, **3a** (0.20 mmol, 50.5 mg, 1.0 eq.) was added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 °C for 2 hours. The yields were determined by ^1H NMR with mesitylene (0.10 mmol, 12.0 mg) as the internal standard (IS). **4a** was not detected and 97% yield of **3a** (49.0 mg) was recovered.

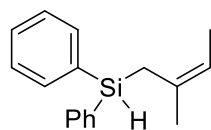
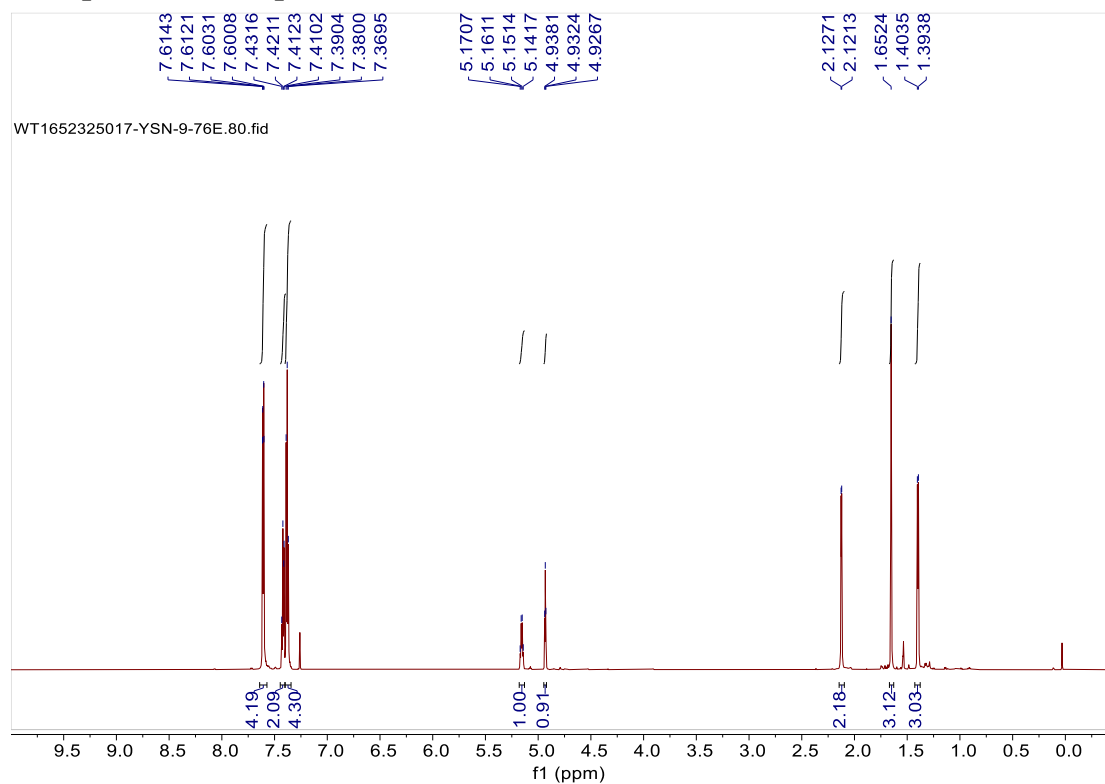


In glove box, a sealed tube was charged with $\text{Co}(\text{acac})_3$ (0.01 mmol, 3.6 mg, 5 mol%) and **L1** (0.01 mmol, 2.8 mg, 5 mol%) in anhydrous hexane (0.5 mL). Then, NaBEt_3H (20 μL , 1 M solution in THF, 10 mol%) was added and stirred for 1 minute at room temperature. After that, **4a** (0.20 mmol, 50.5 mg, 1.0 eq.) was added at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 40 °C for 2 hours. The yields were determined by ^1H NMR with mesitylene (0.10 mmol) as the internal standard (IS). **3a** was not detected and 84% yield of **4a** (42.4 mg) was recovered.

7. Reference

[1] C. S. Kuai, D. W. Ji, C. Y. Zhao, H. Liu, Y. C. Hu, Q. A. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 19115.

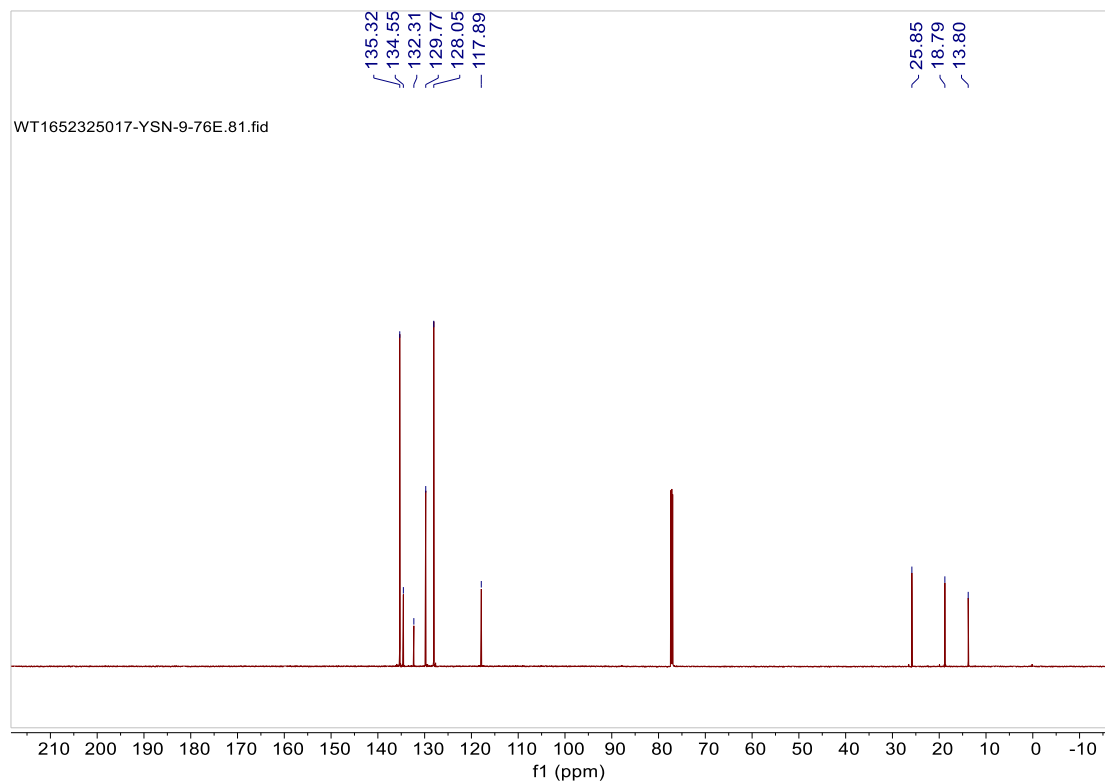
8. Copies of NMR spectra

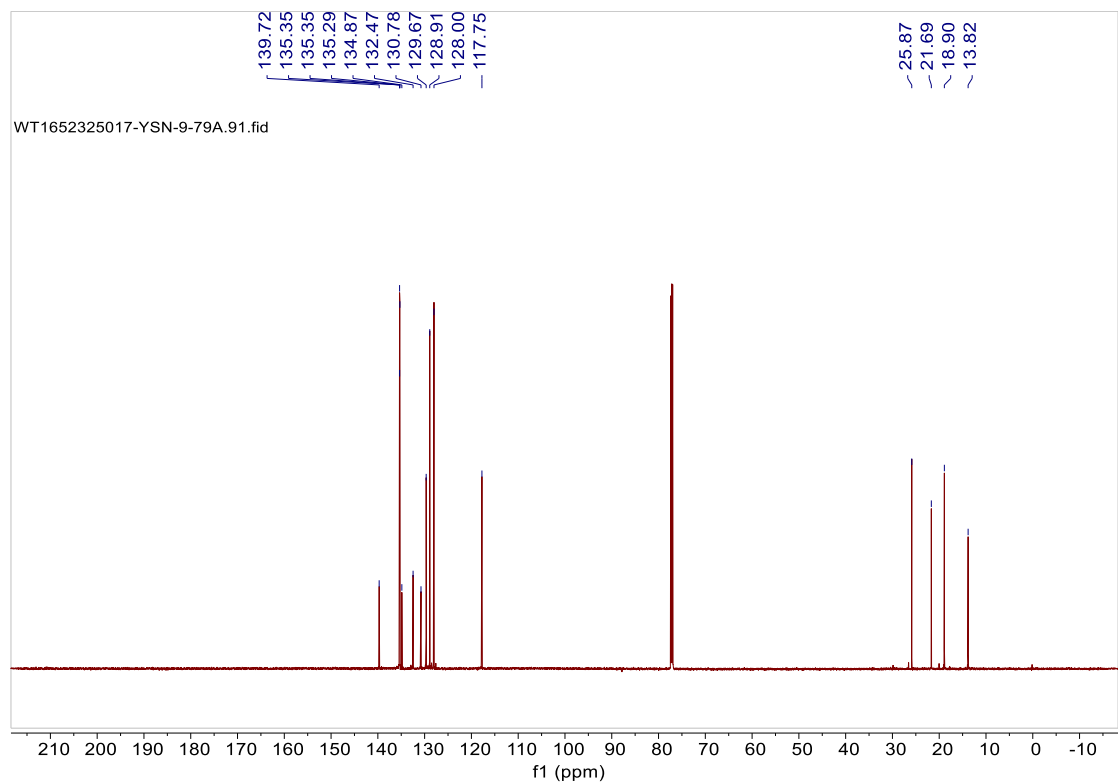
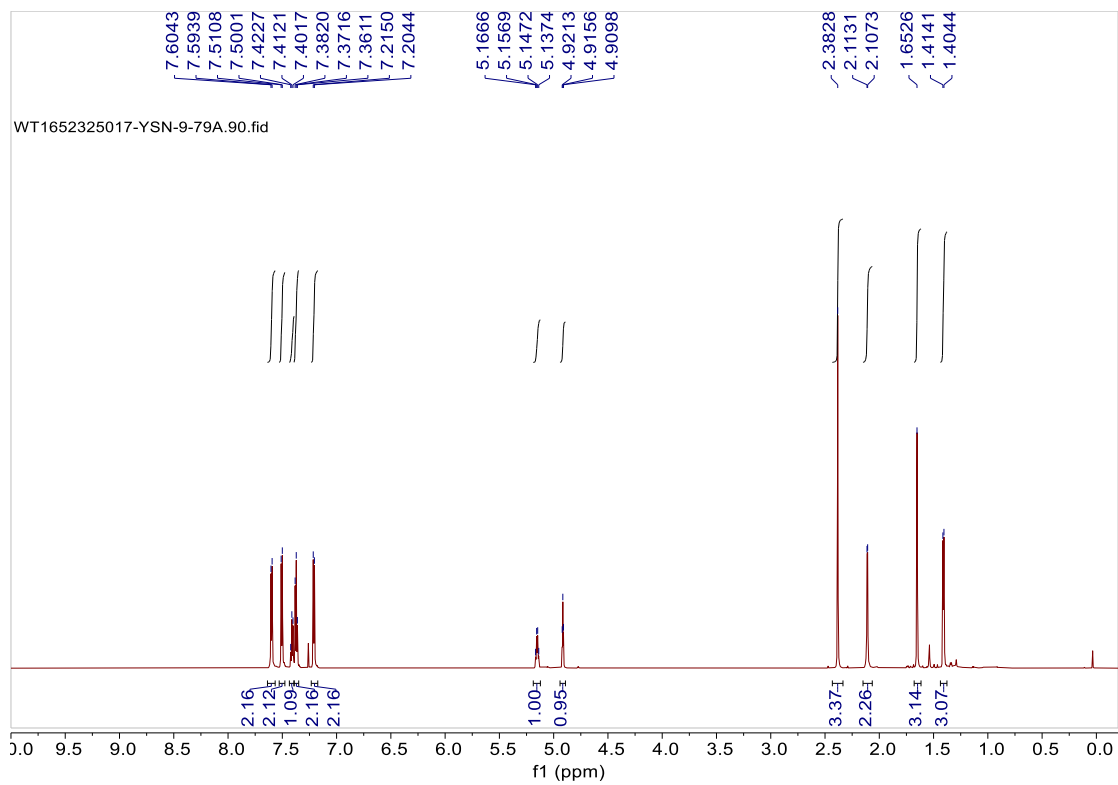


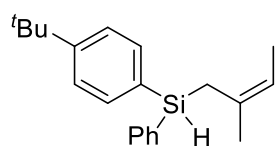
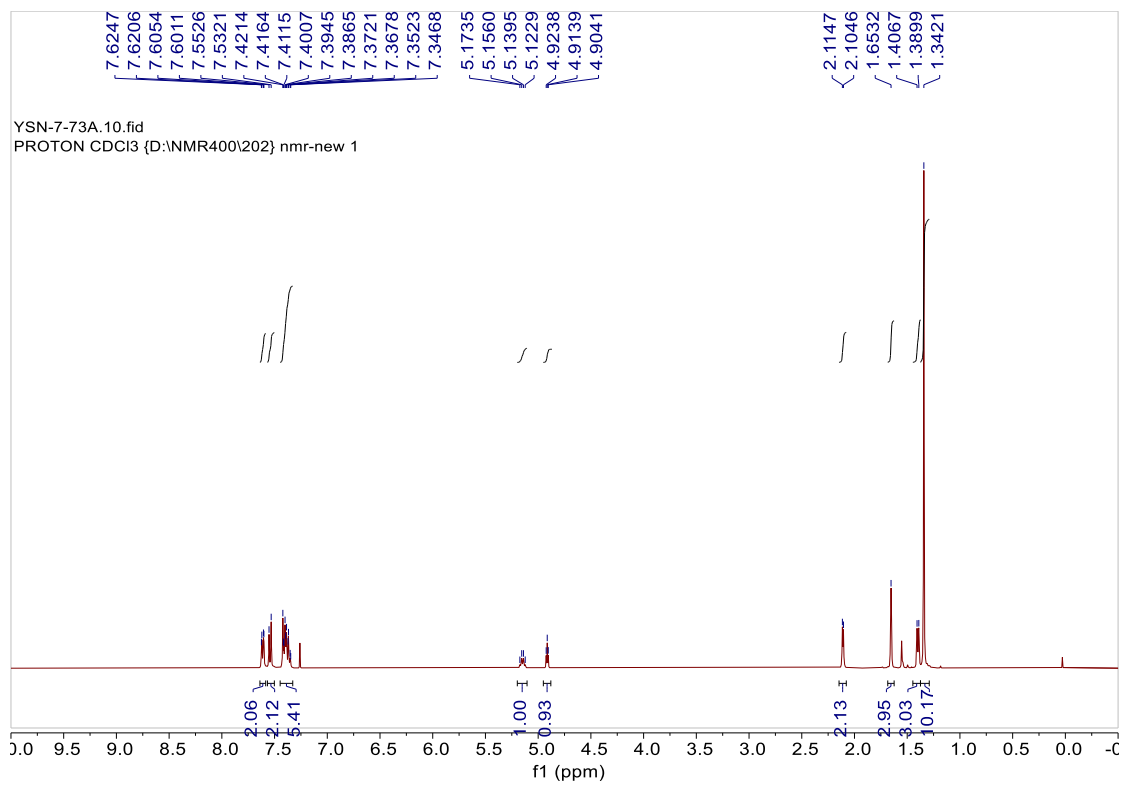
3a

^1H NMR (700 MHz, CDCl_3)

^{13}C NMR (175 MHz, CDCl_3)



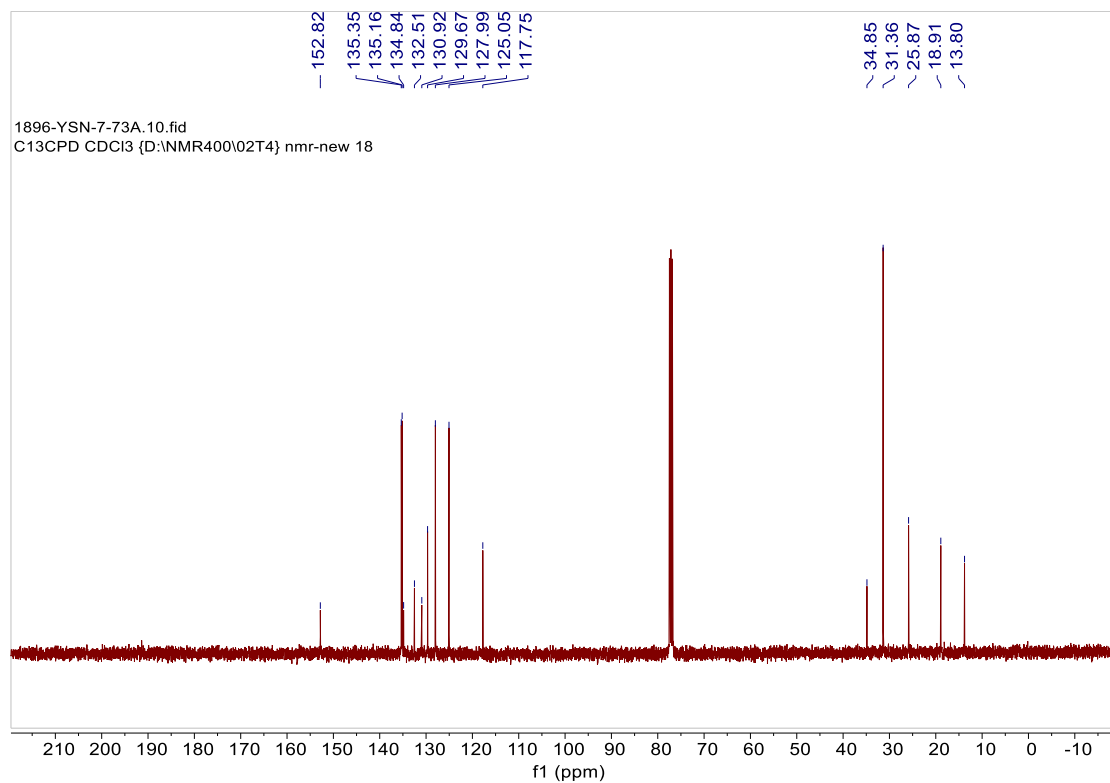


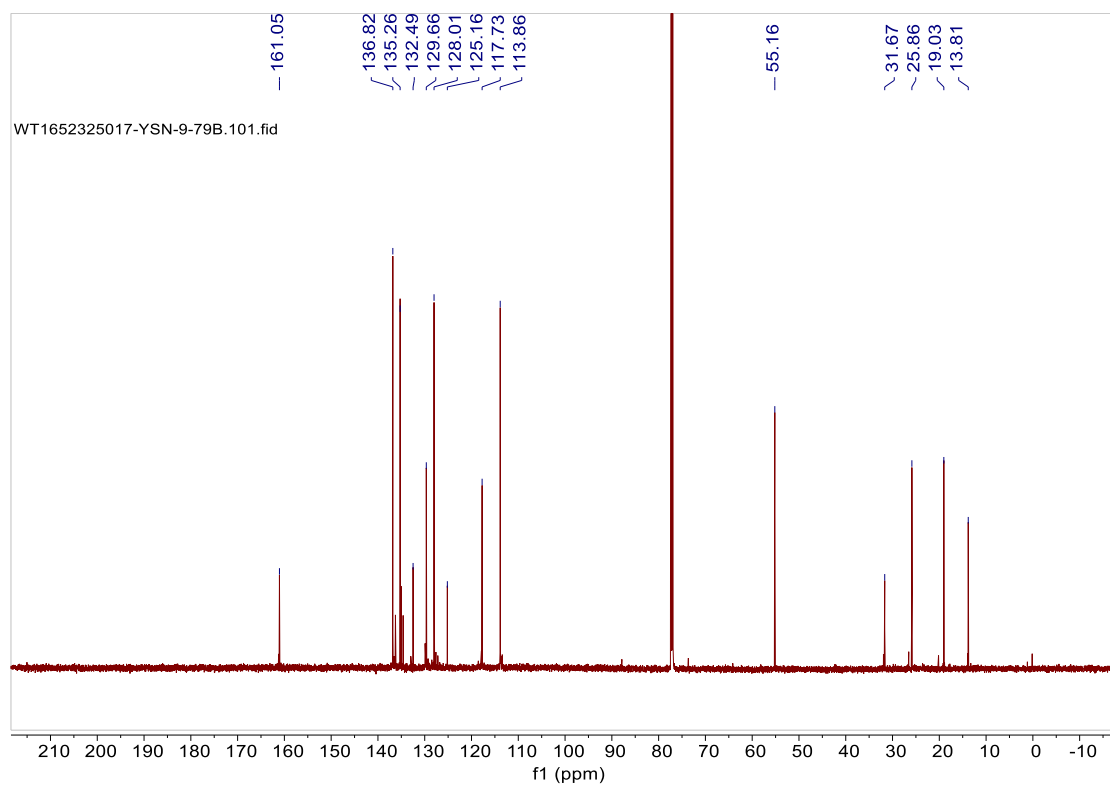
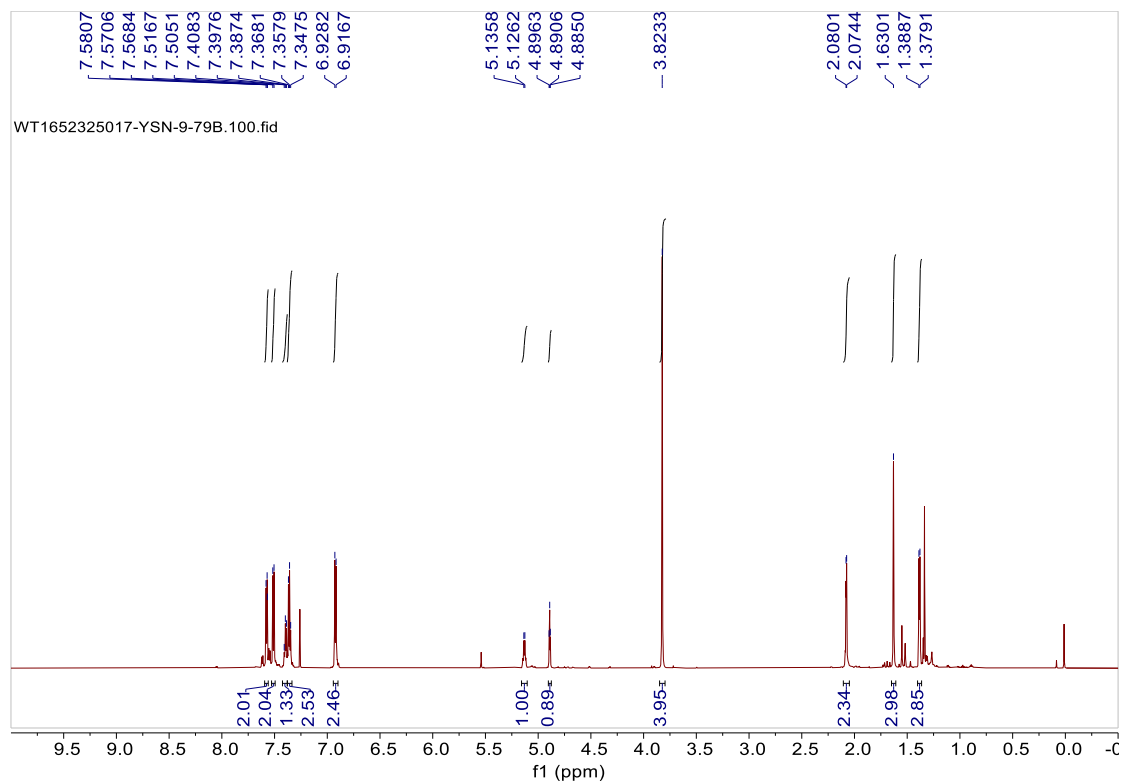


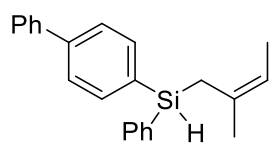
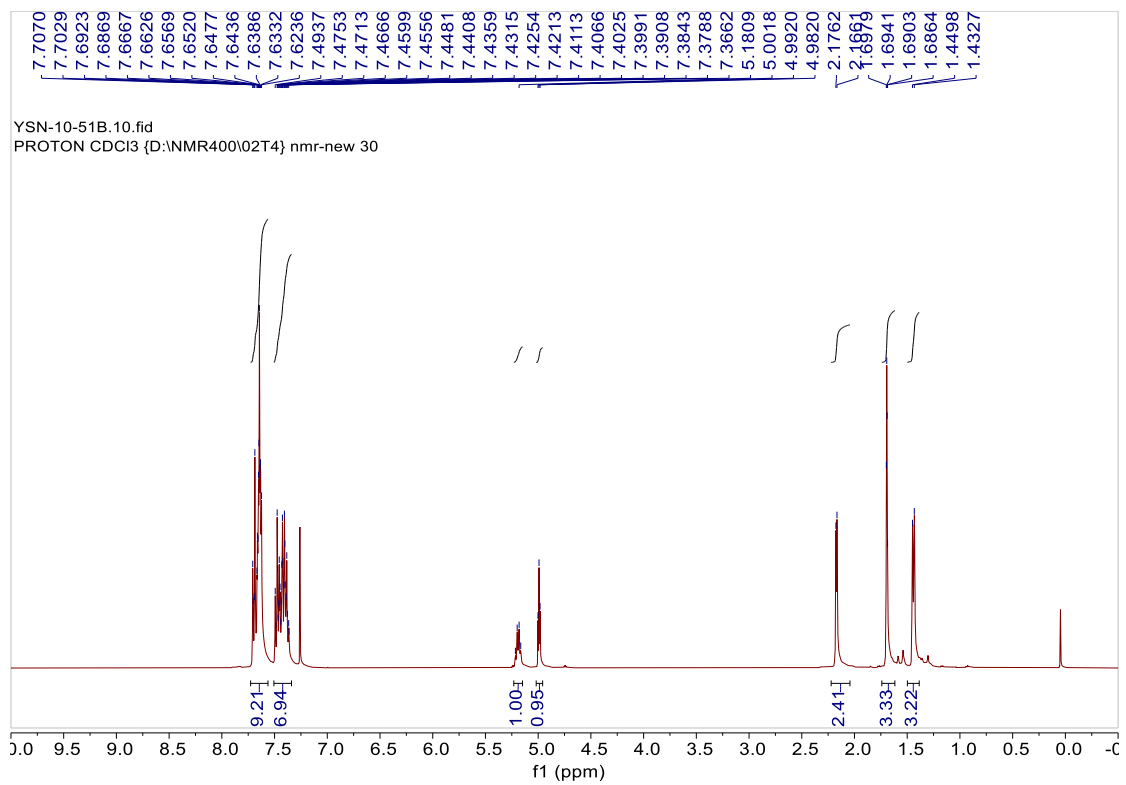
3c

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)



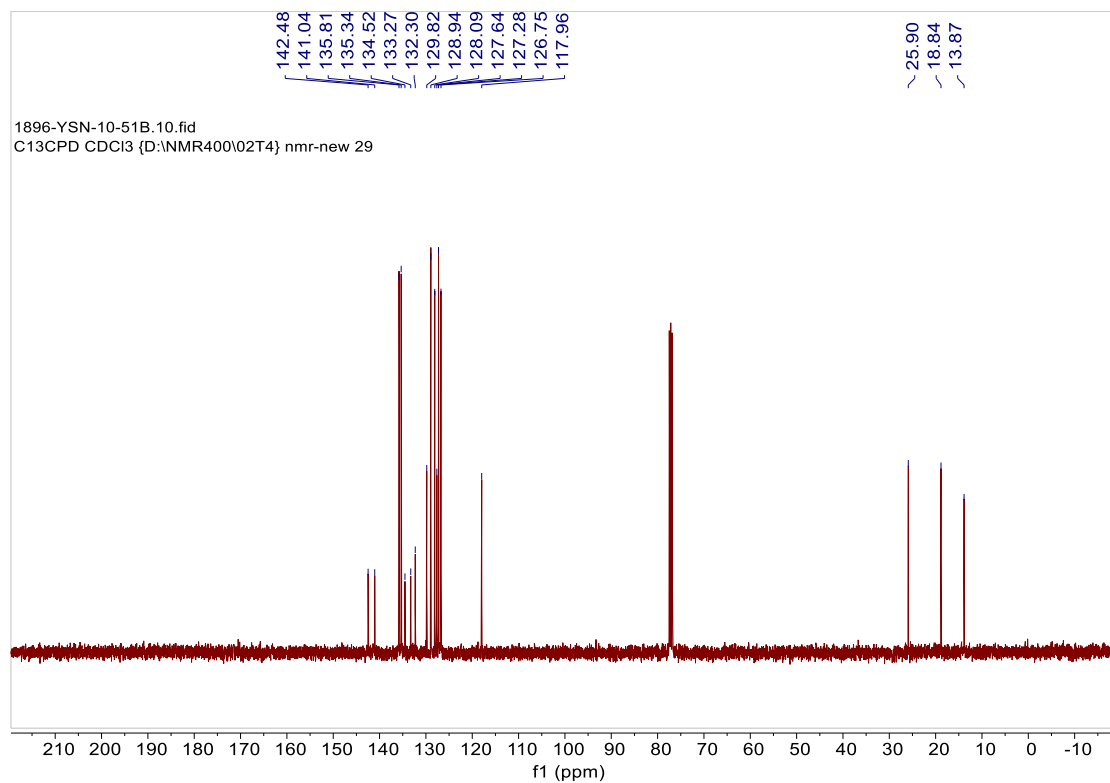


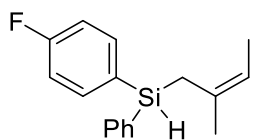
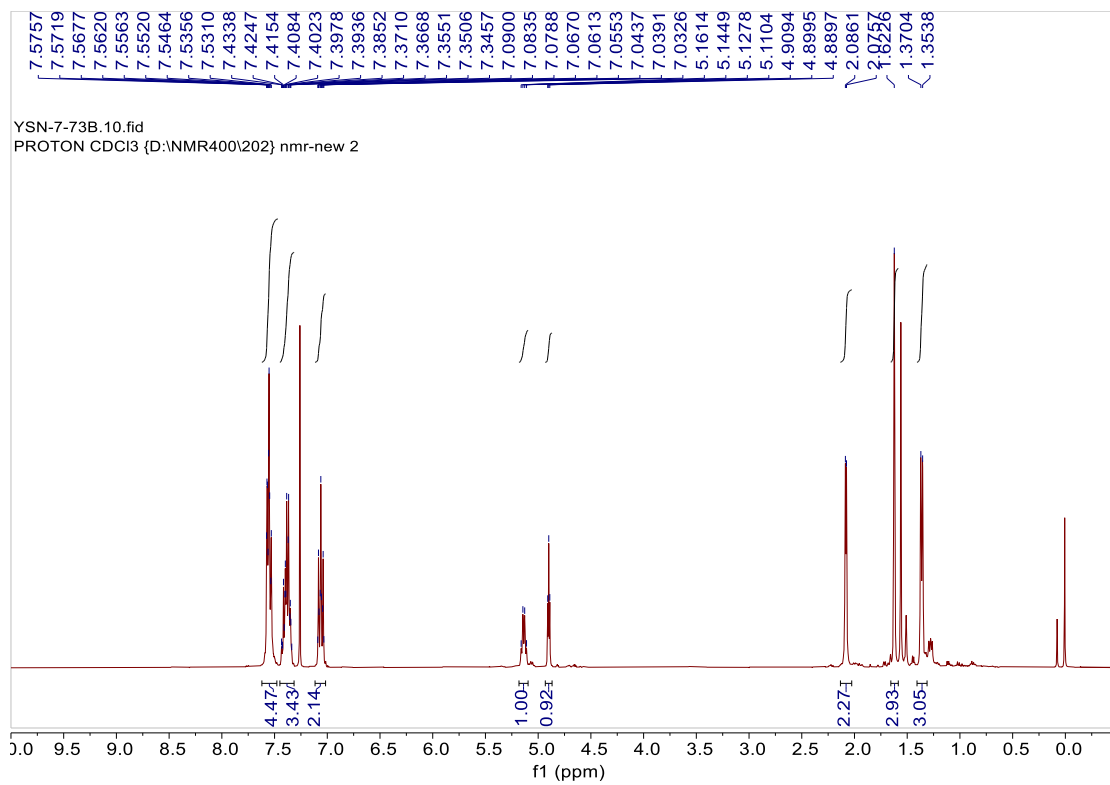


3e

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

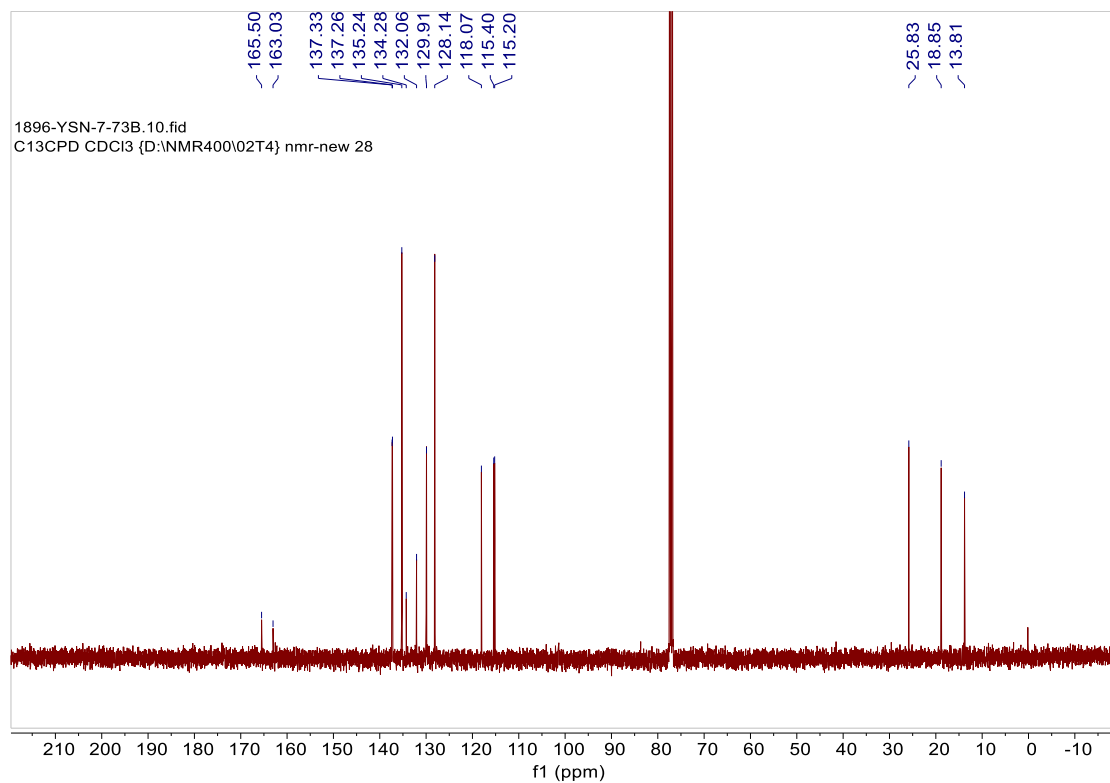


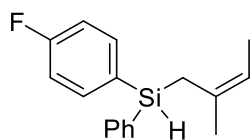


3f

¹H NMR (400 MHz, CDCl₃)

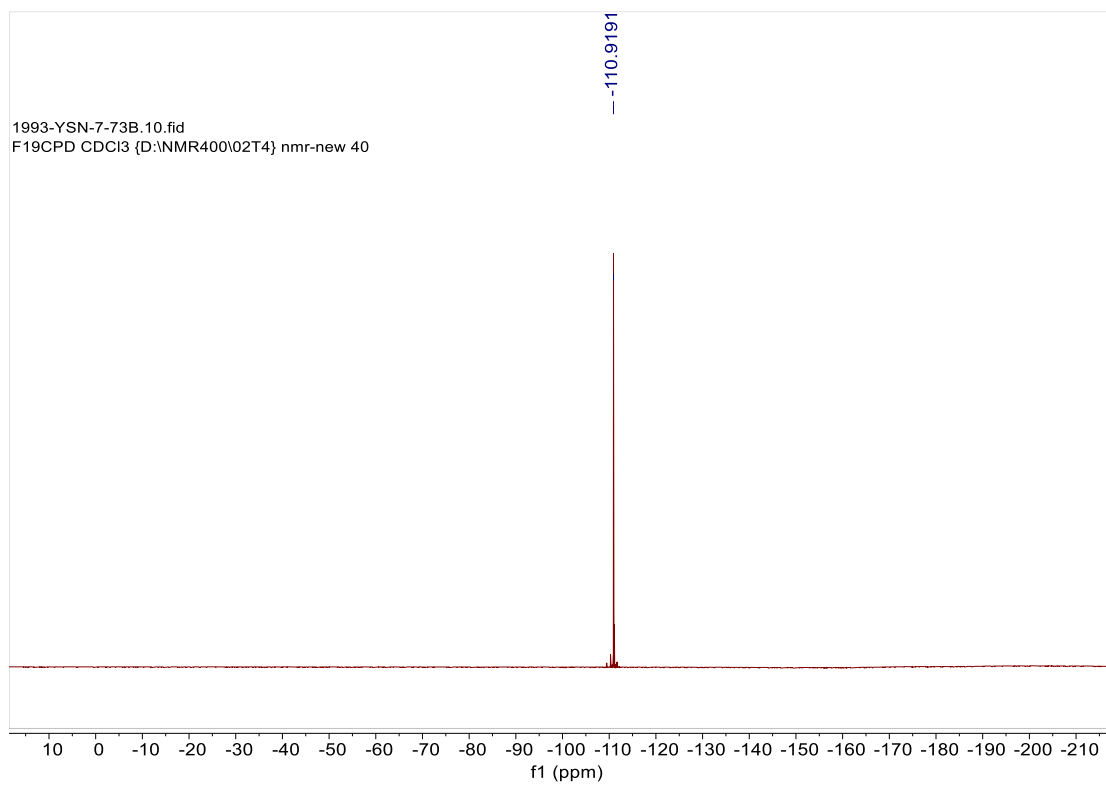
¹³C NMR (100 MHz, CDCl₃)

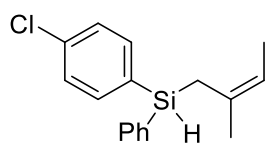
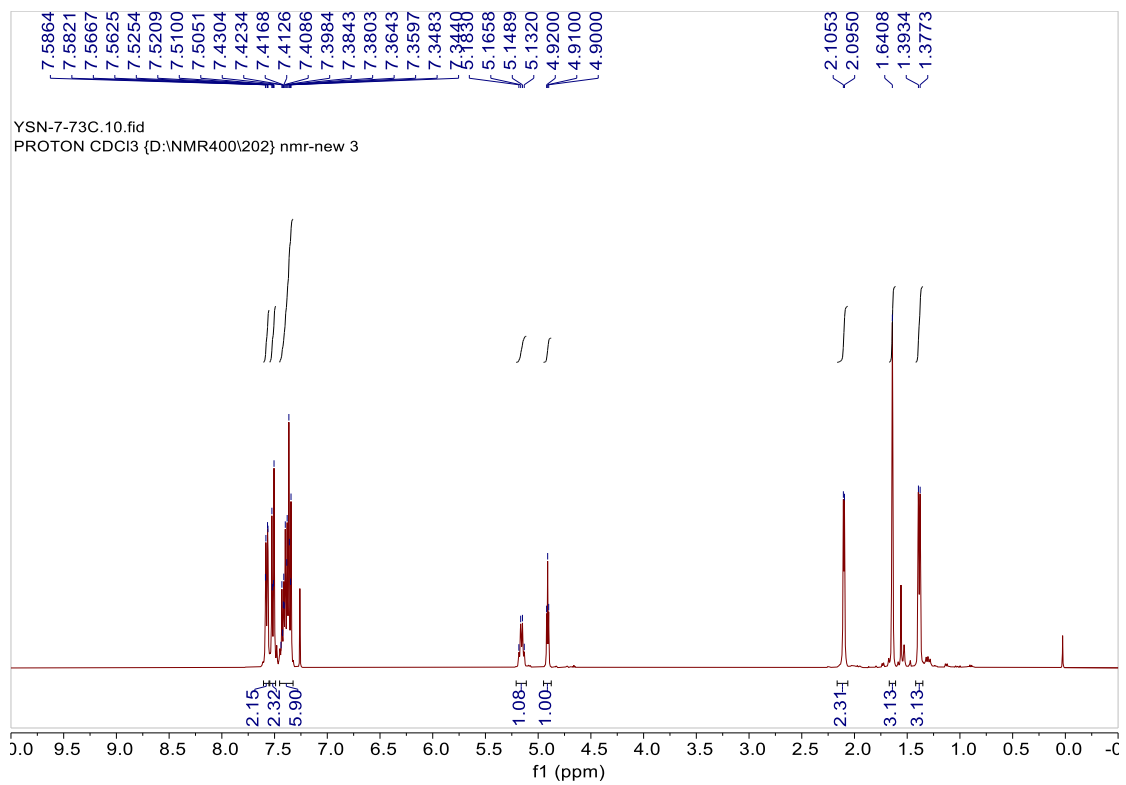




3f

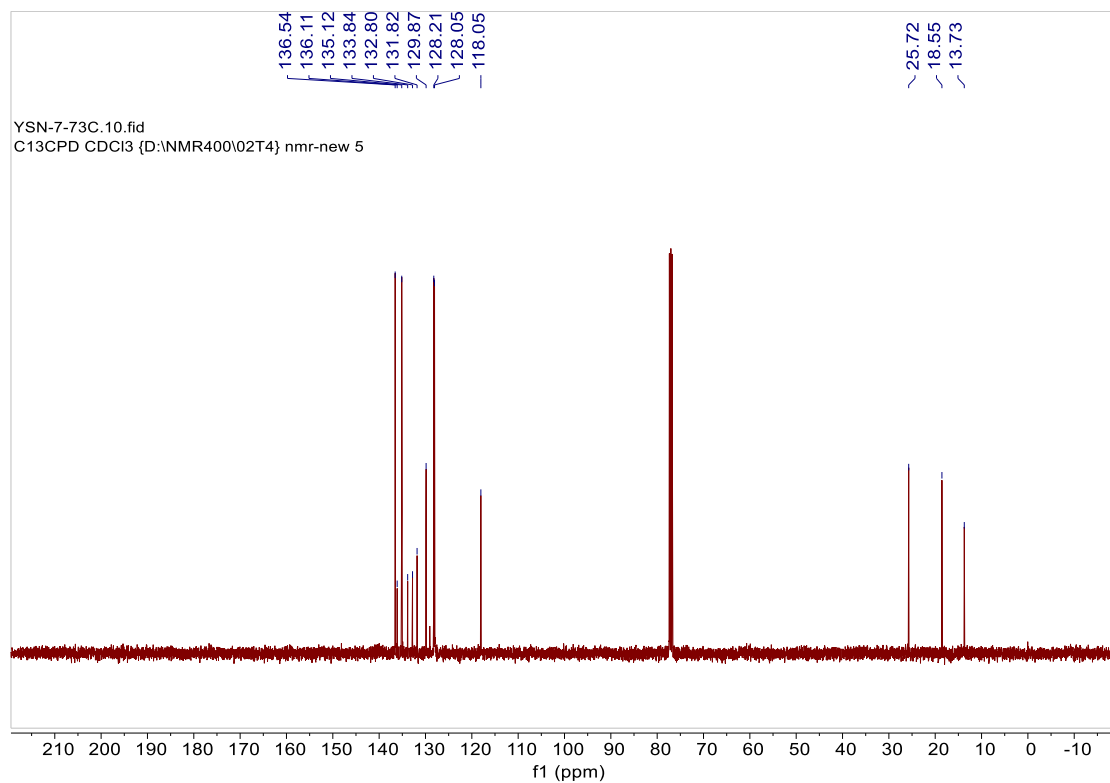
^{19}F NMR (376 MHz, CDCl_3)

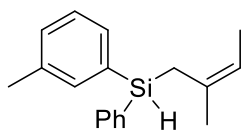
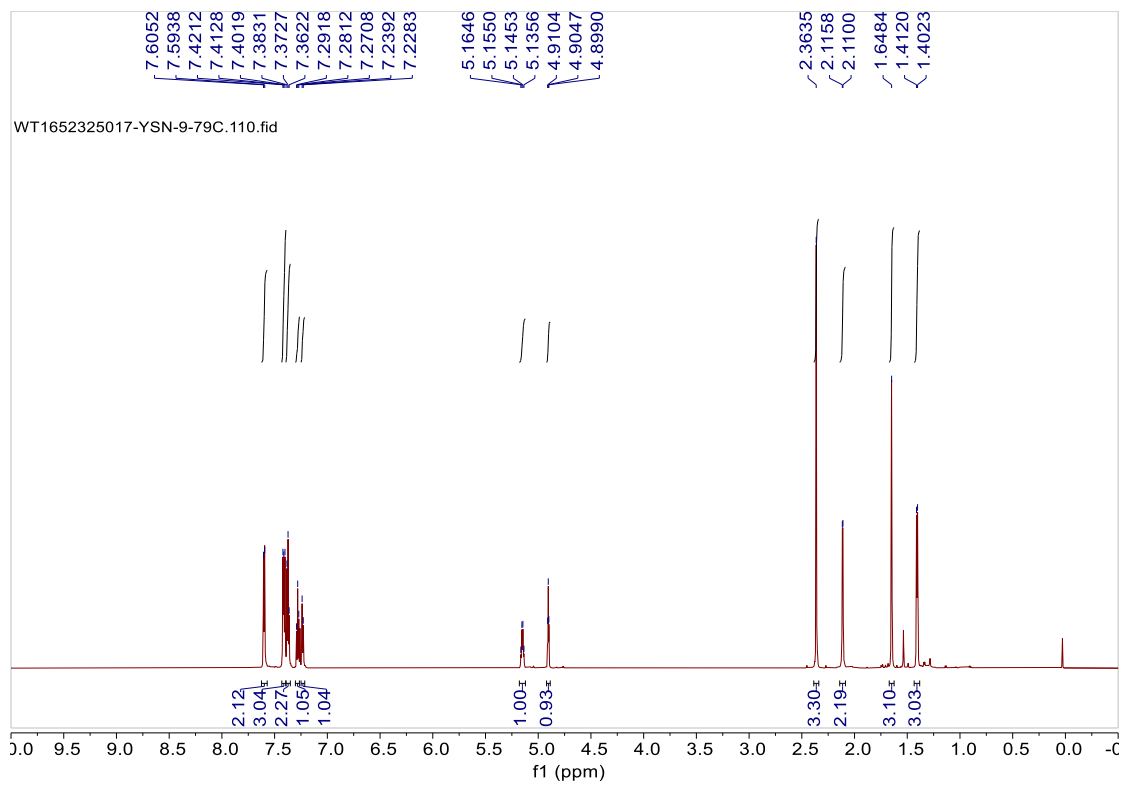




3g

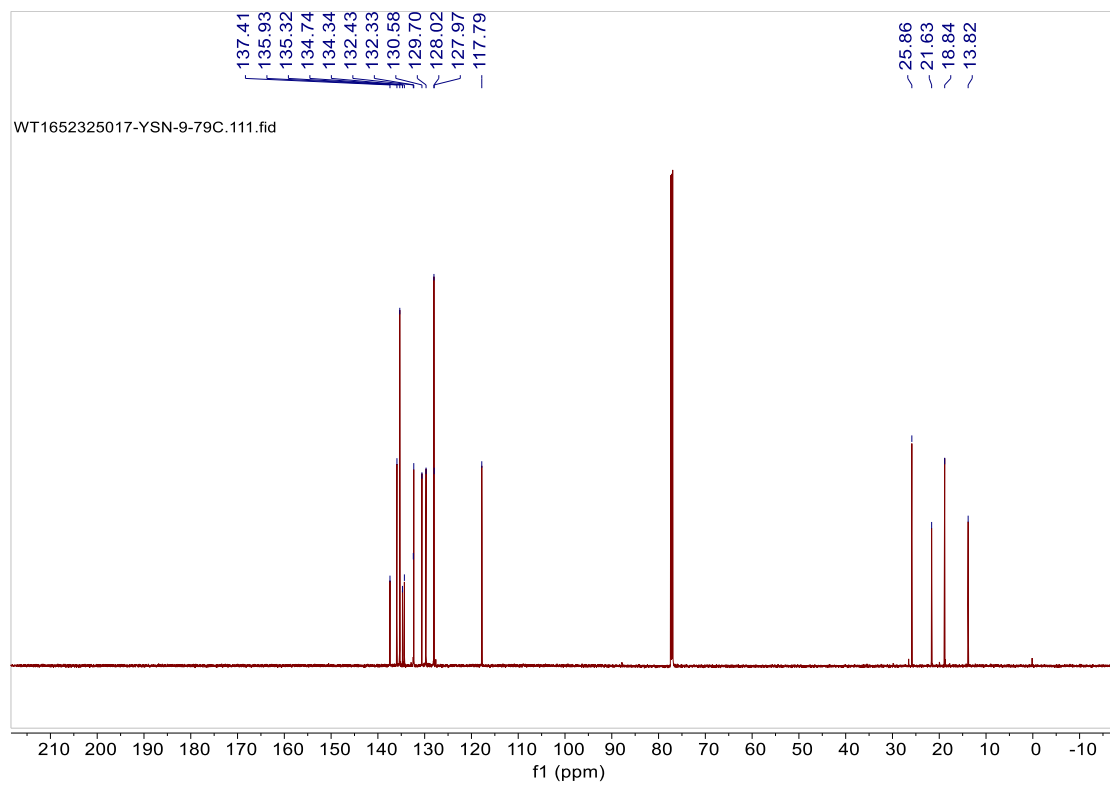
¹H NMR (400 MHz, CDCl₃)
¹³C NMR (100 MHz, CDCl₃)

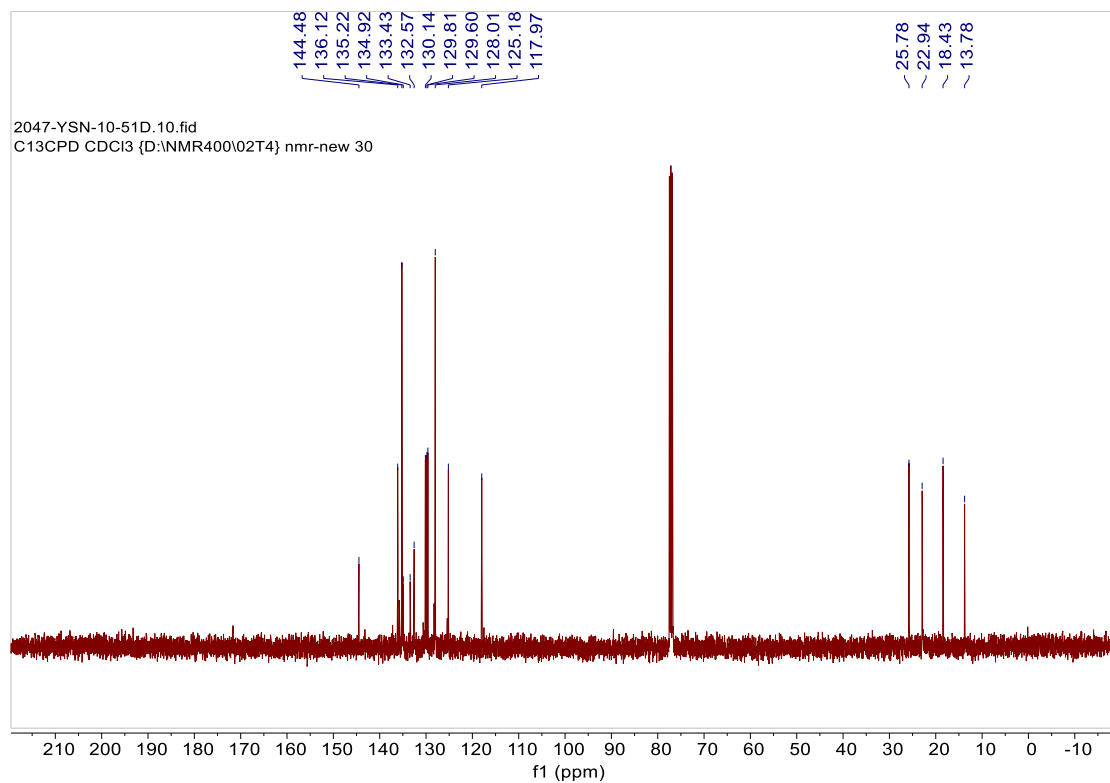
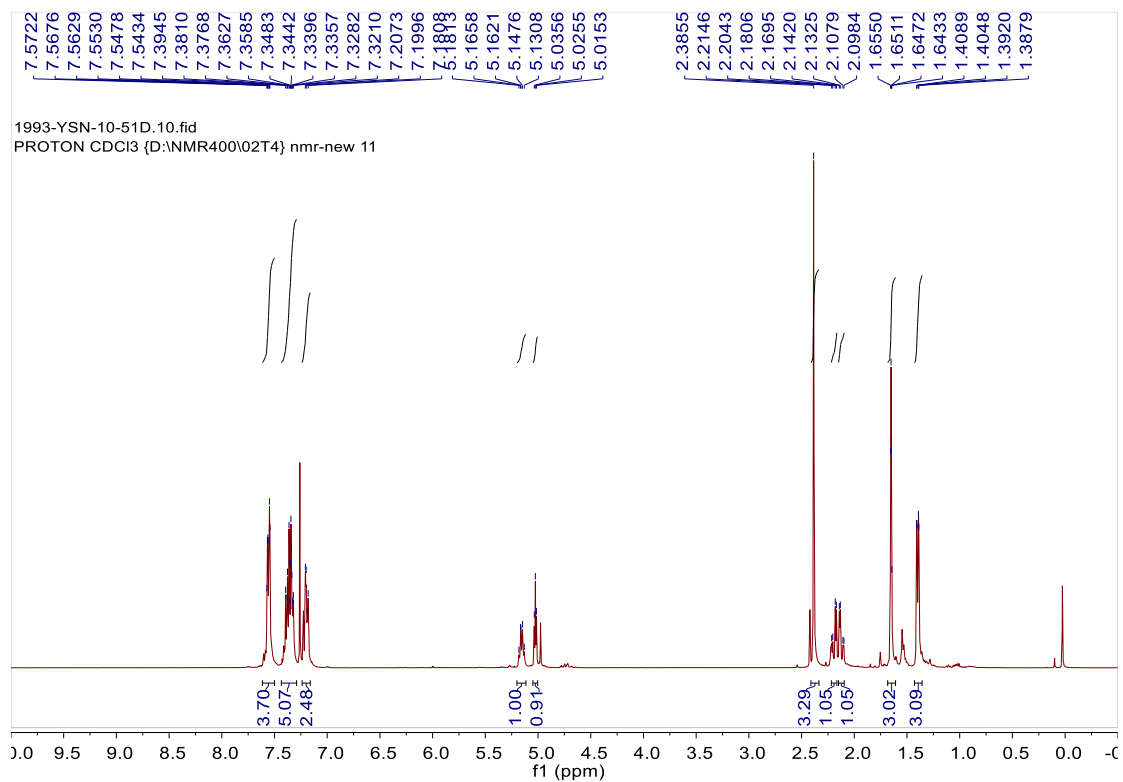


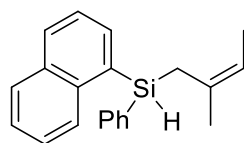
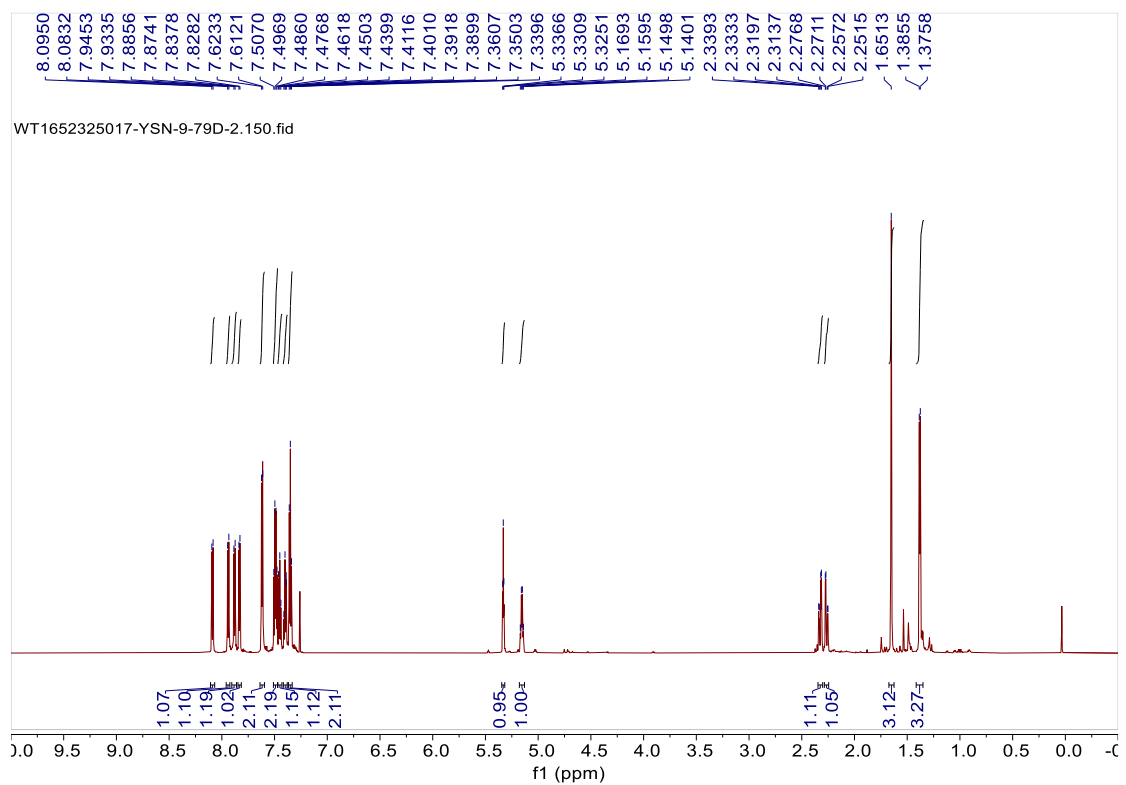


3h

¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

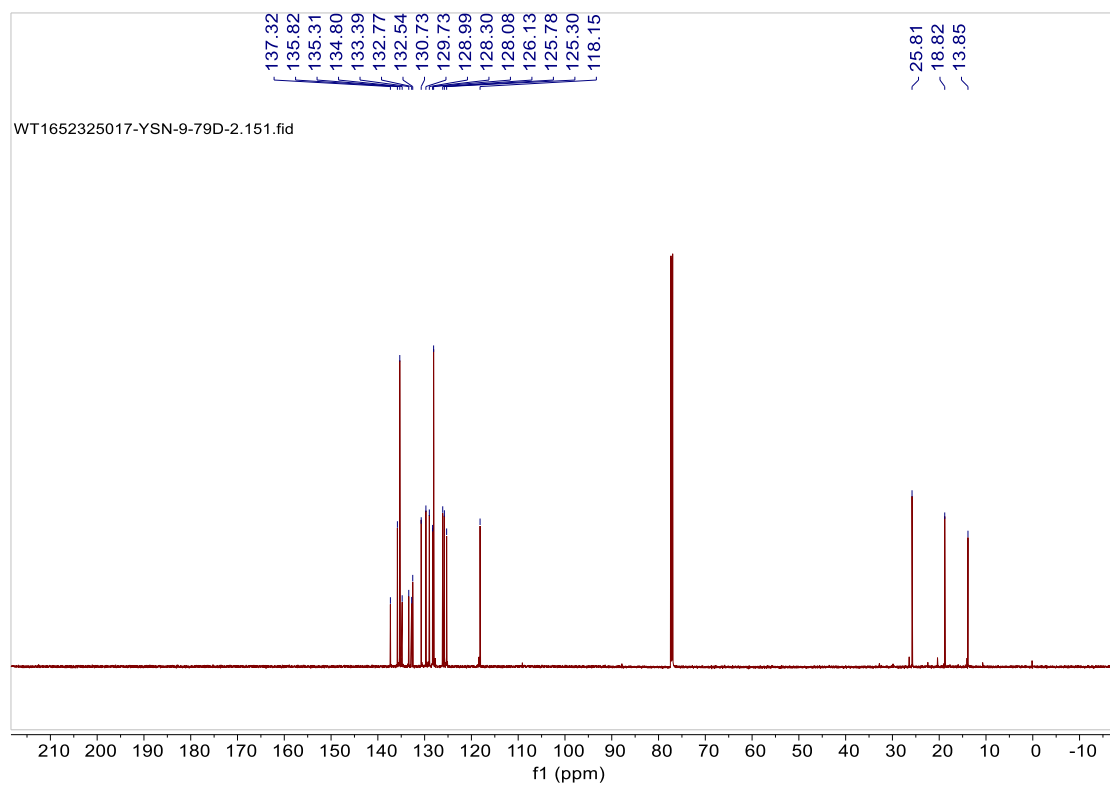


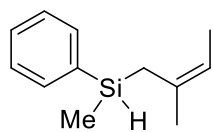
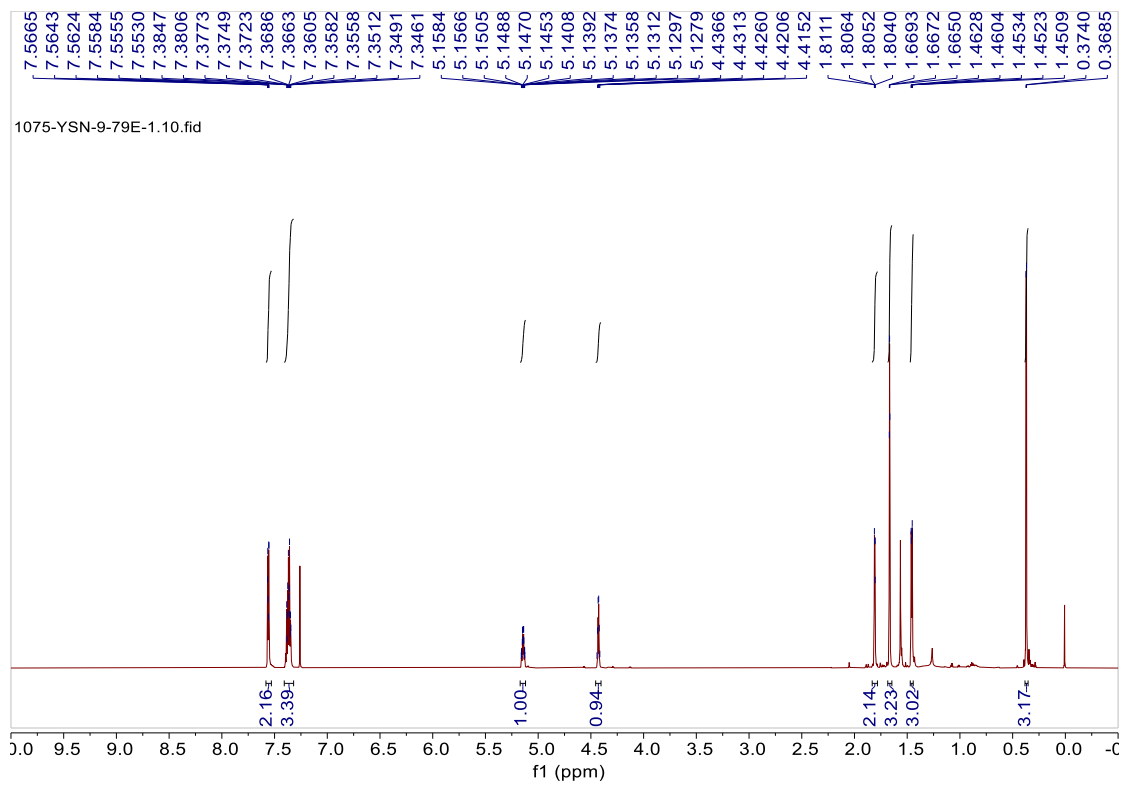




3k

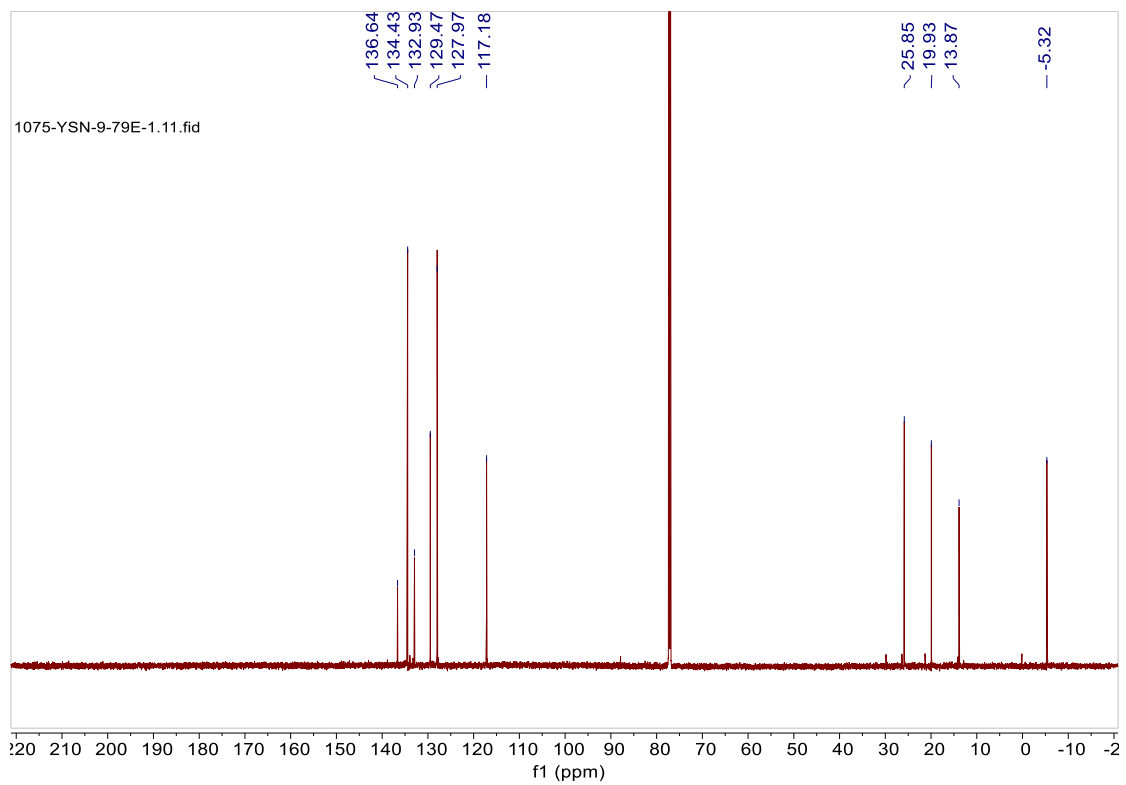
¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

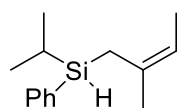
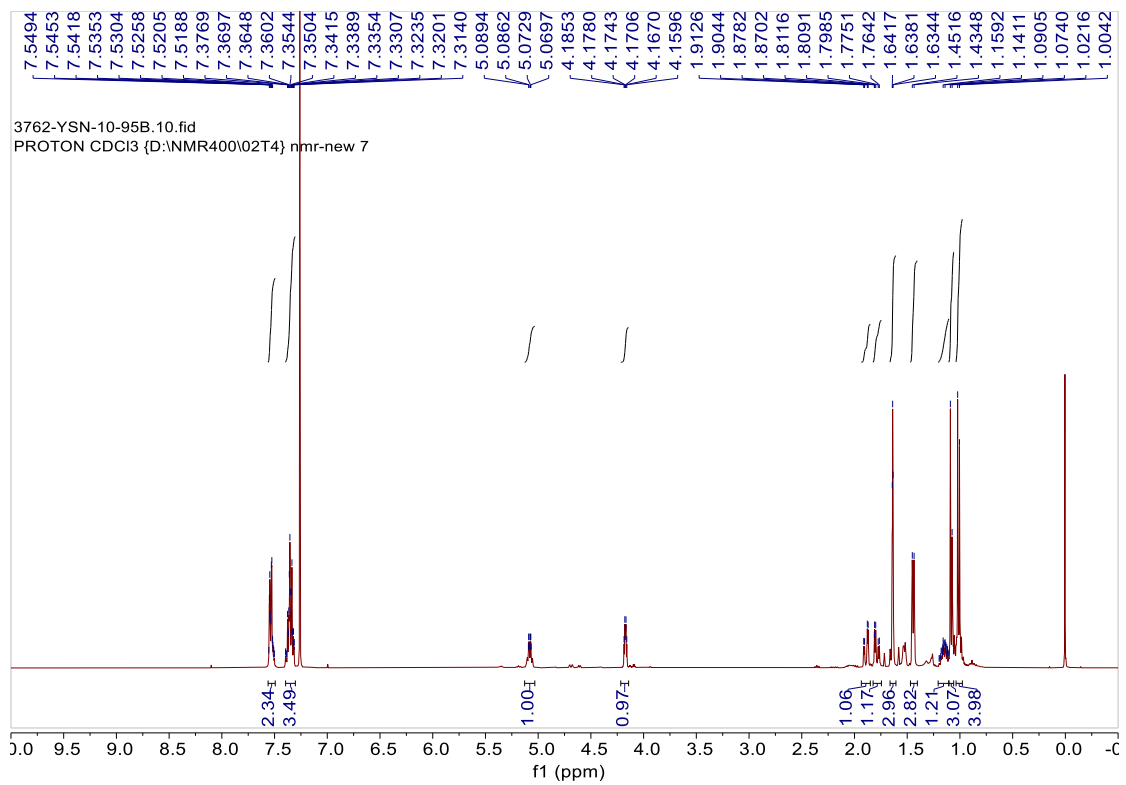




3

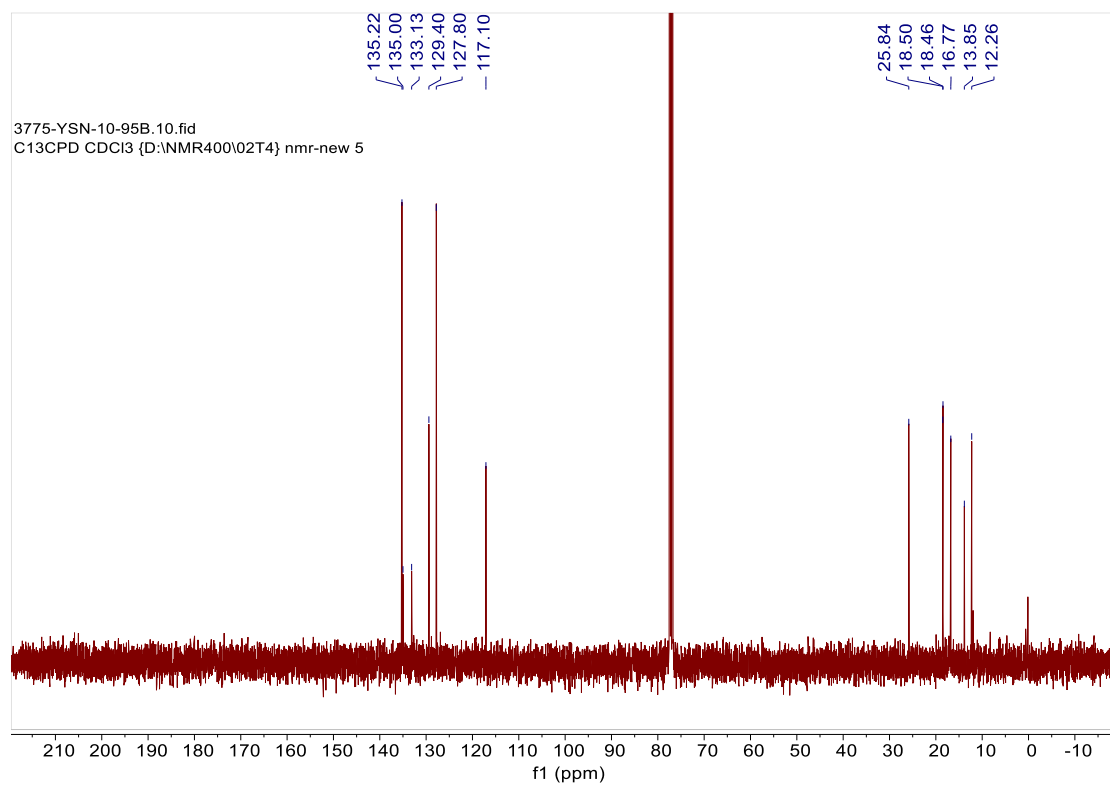
¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

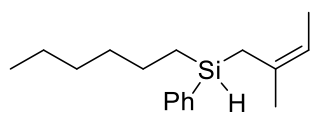
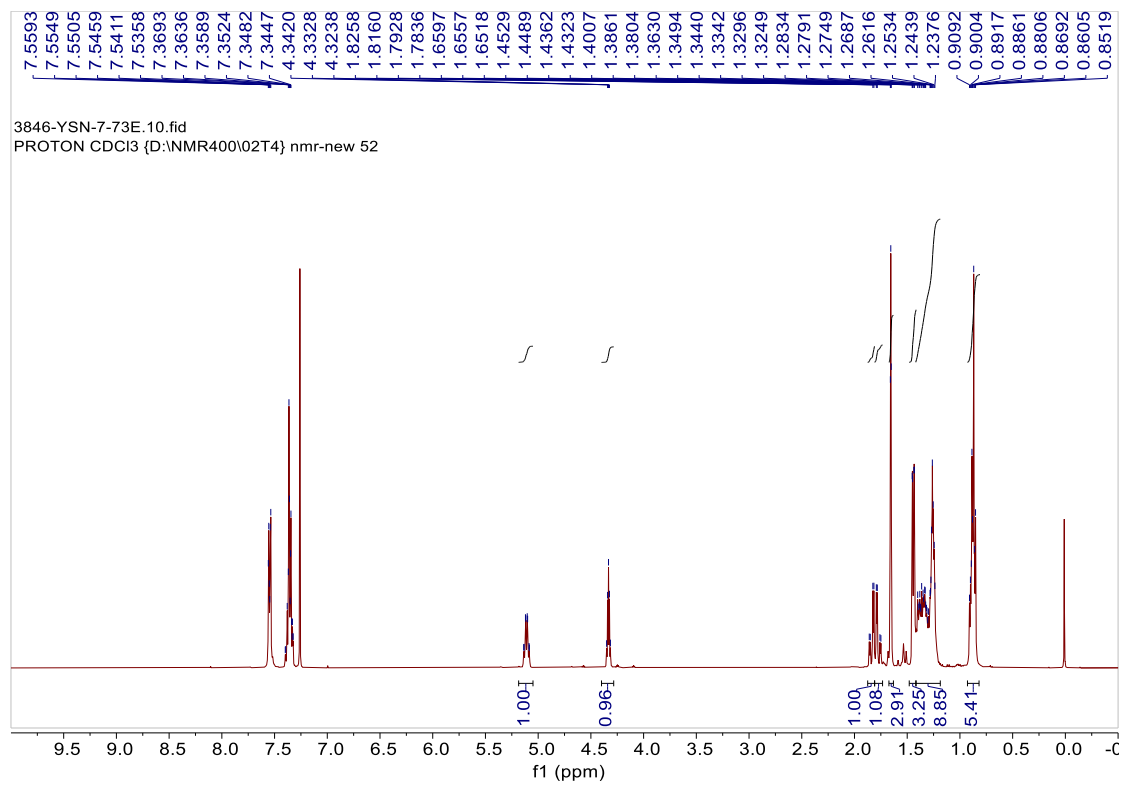




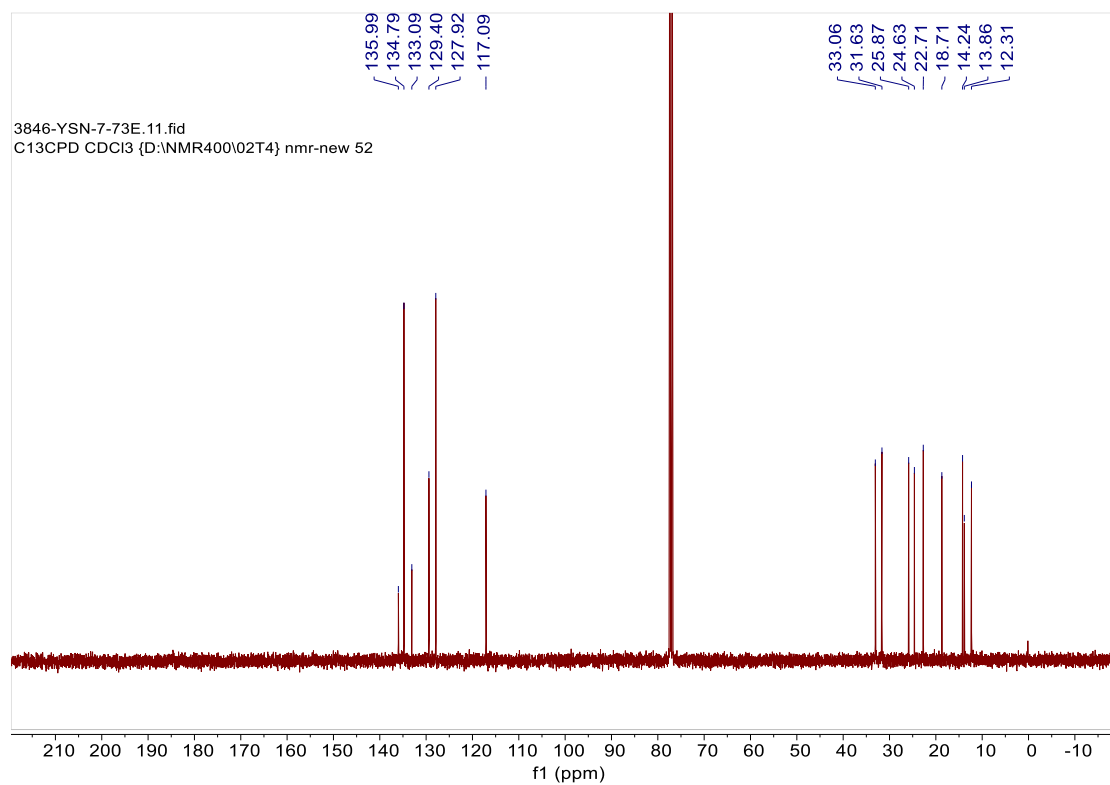
3m

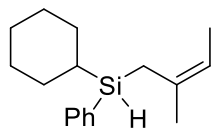
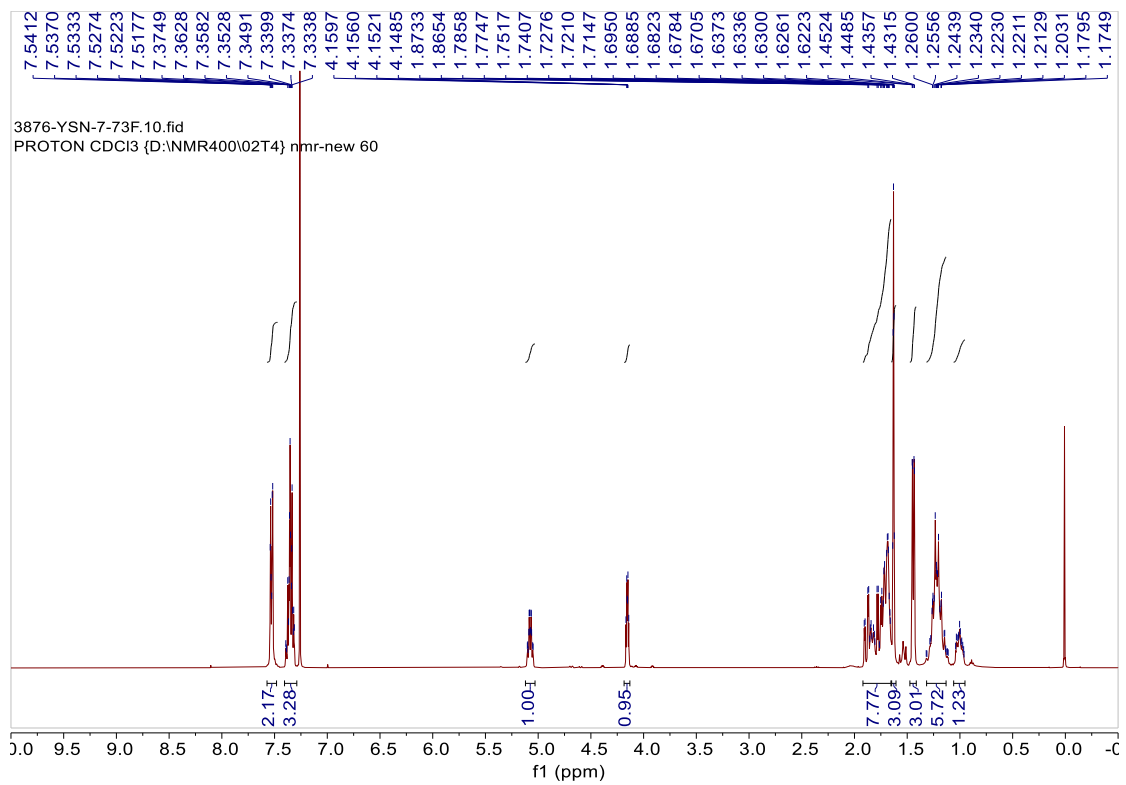
¹H NMR (400 MHz, CDCl₃)
¹³C NMR (100 MHz, CDCl₃)





¹H NMR (400 MHz, CDCl₃)
¹³C NMR (100 MHz, CDCl₃)

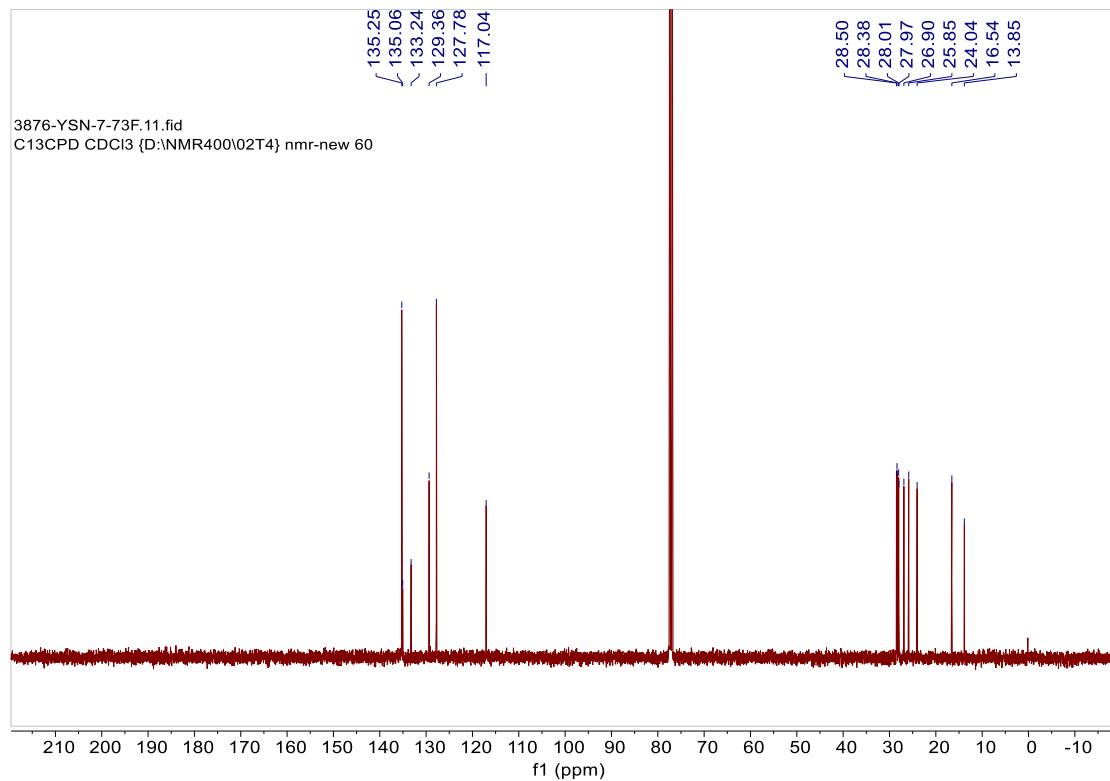


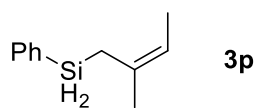
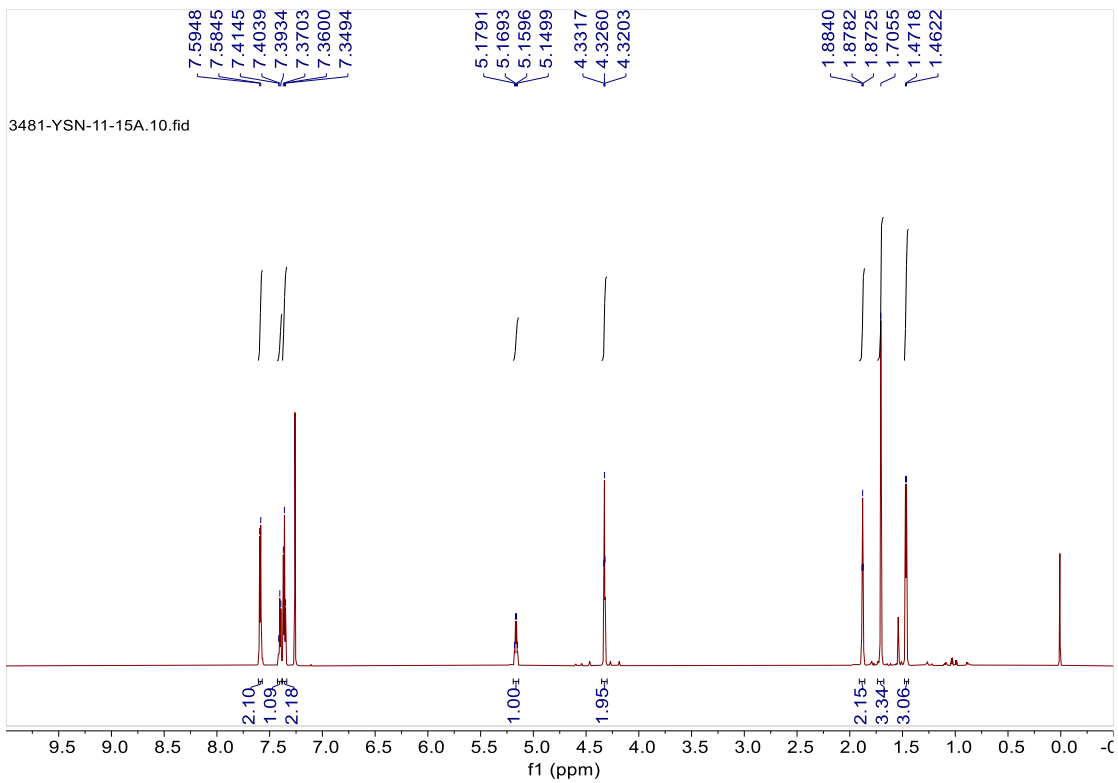


3o

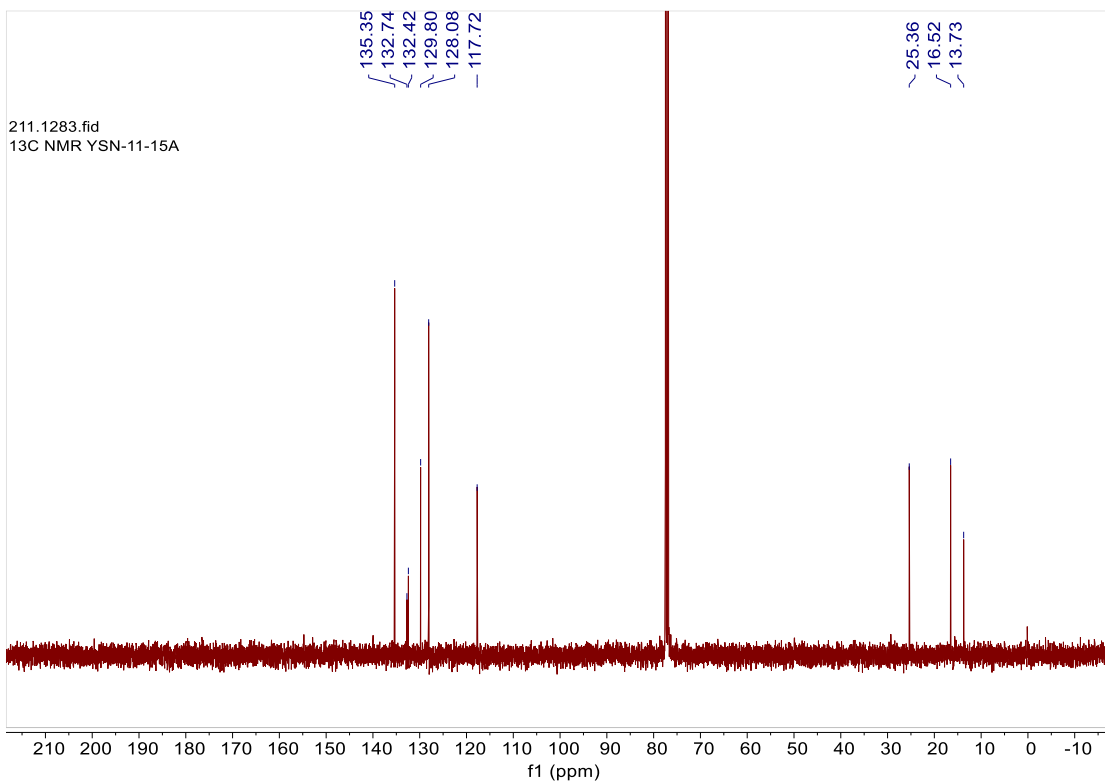
¹H NMR (400 MHz, CDCl₃)

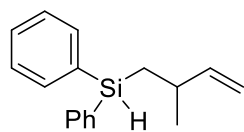
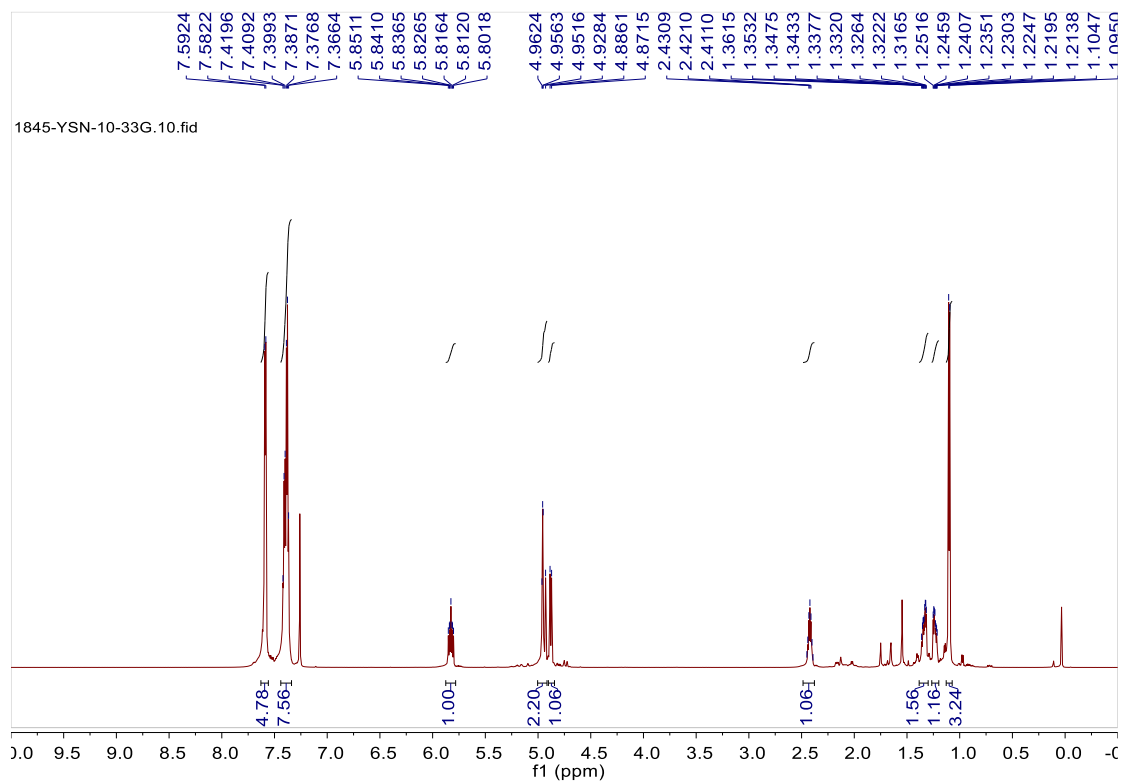
¹³C NMR (100 MHz, CDCl₃)





^1H NMR (700 MHz, CDCl_3)
 ^{13}C NMR (100 MHz, CDCl_3)

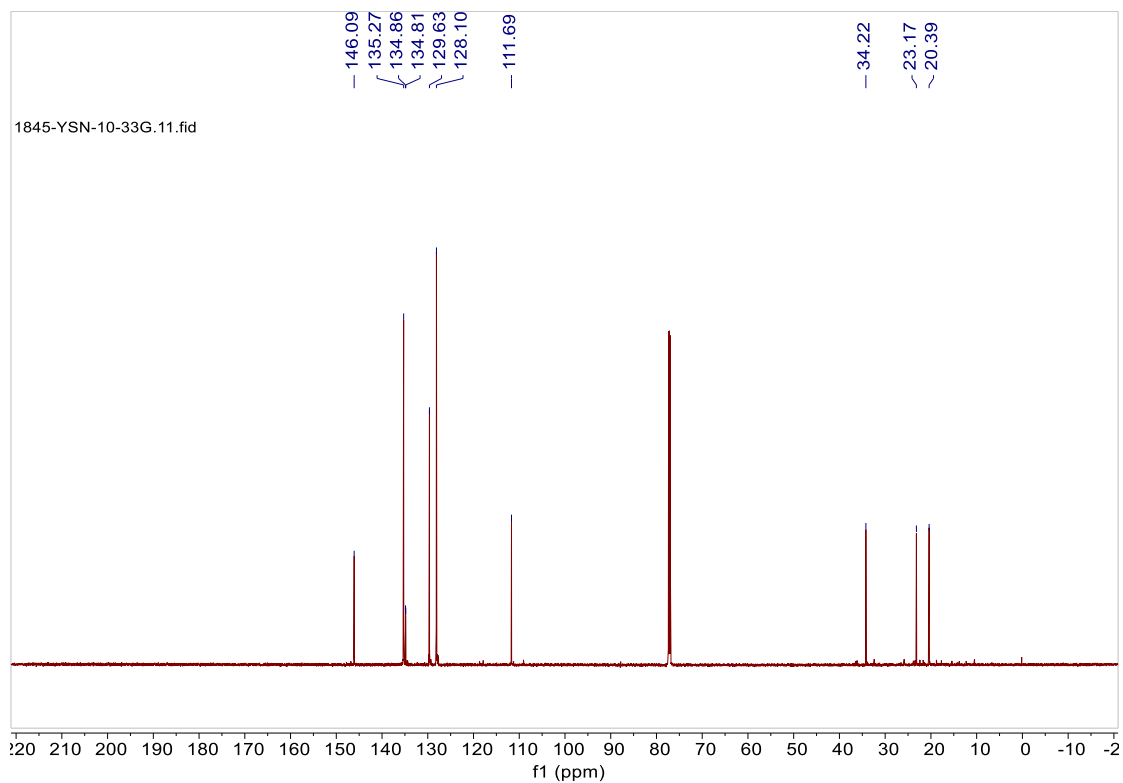


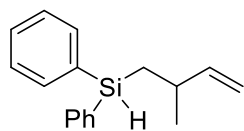


4a

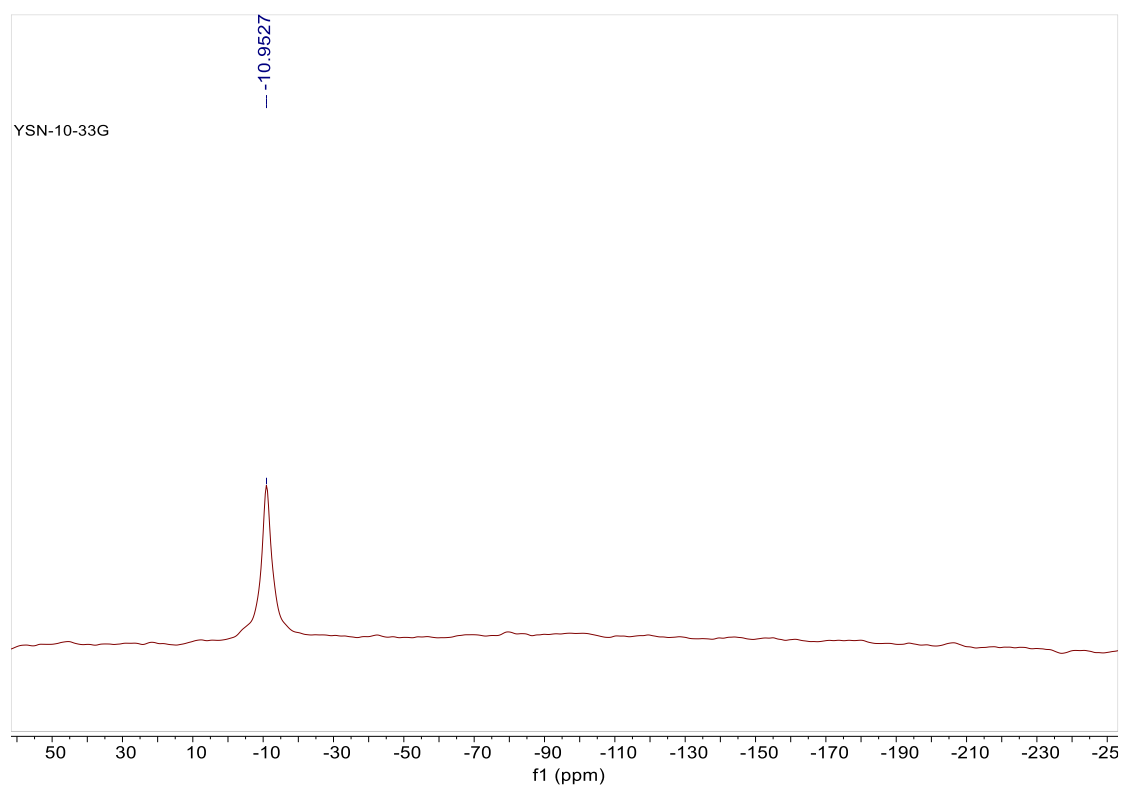
^1H NMR (700 MHz, CDCl_3)

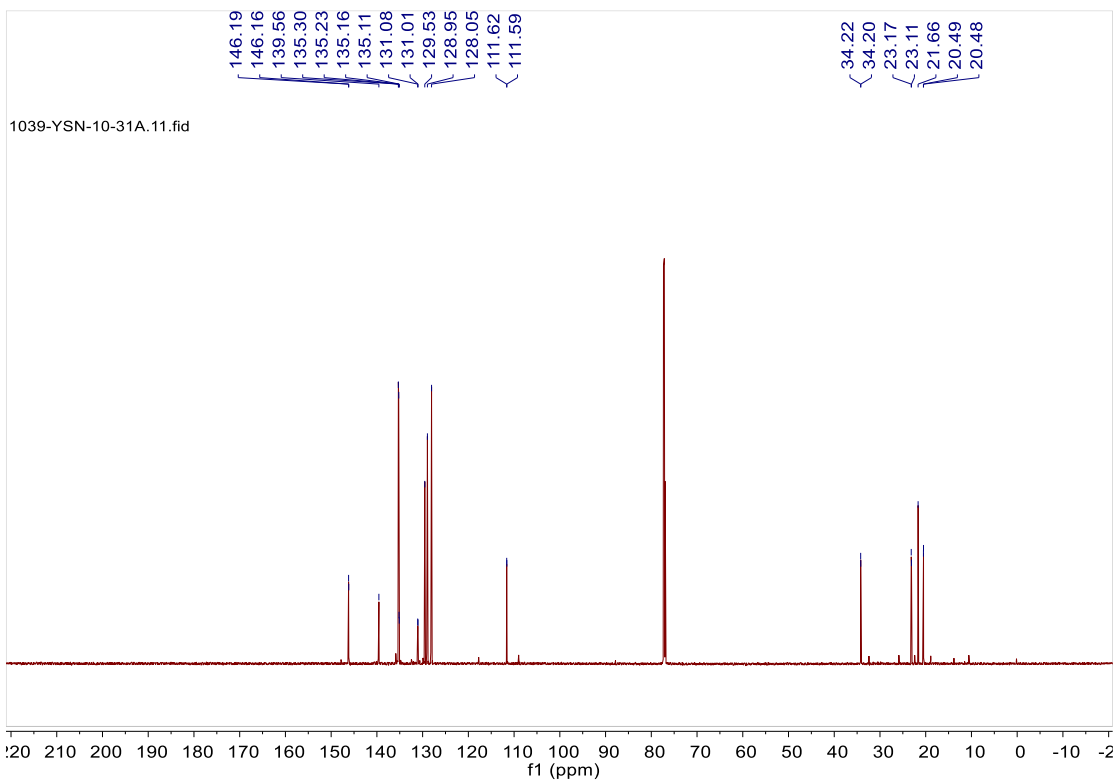
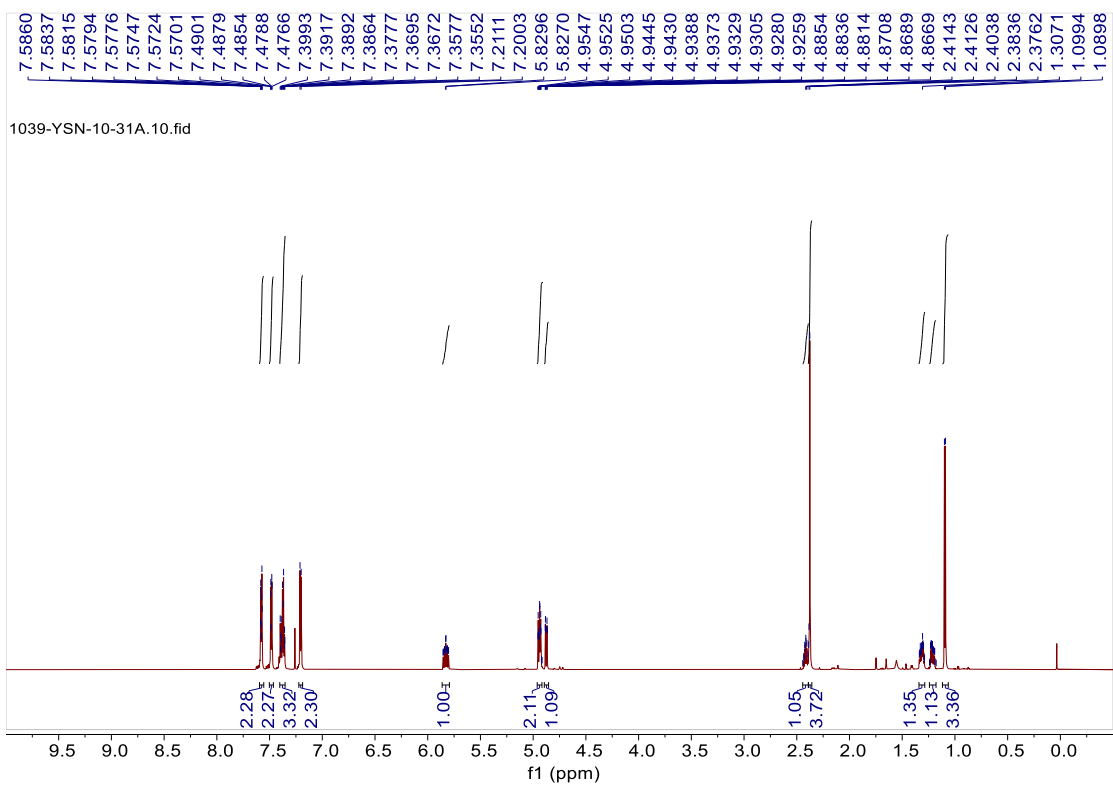
^{13}C NMR (175 MHz, CDCl_3)

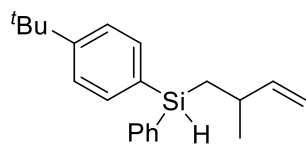
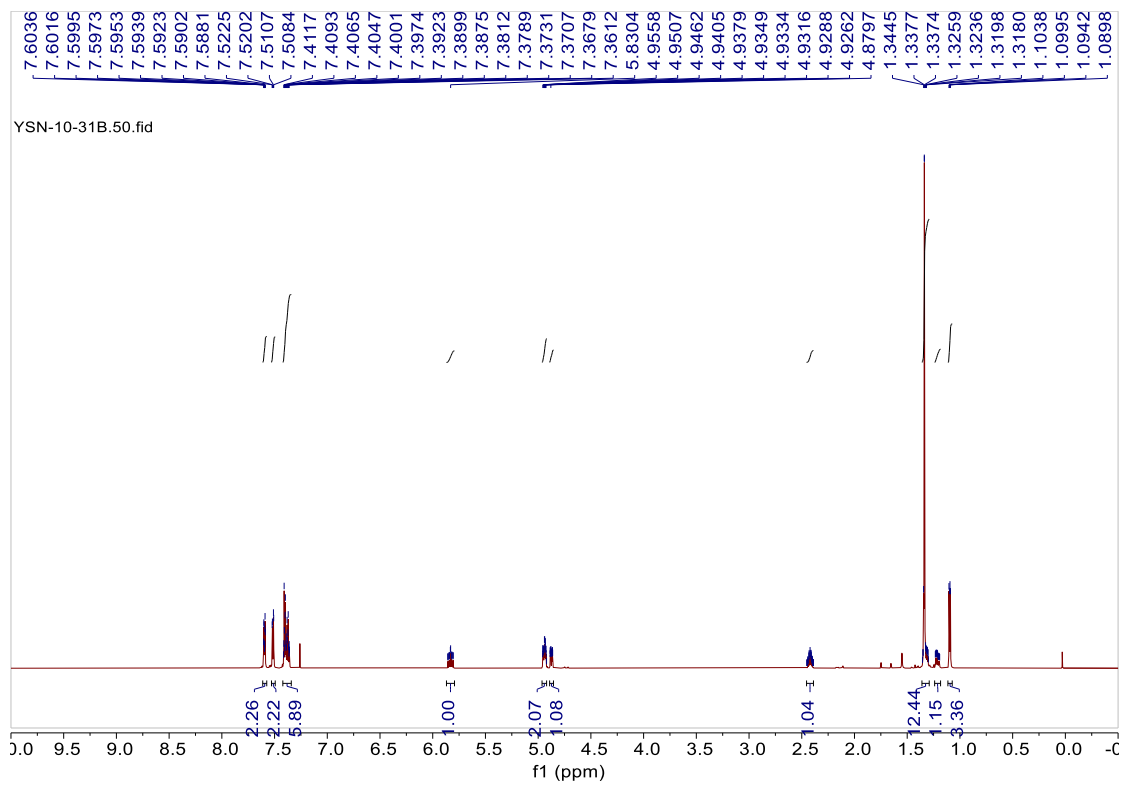




4a ^{29}Si NMR (79 MHz, solid-state)

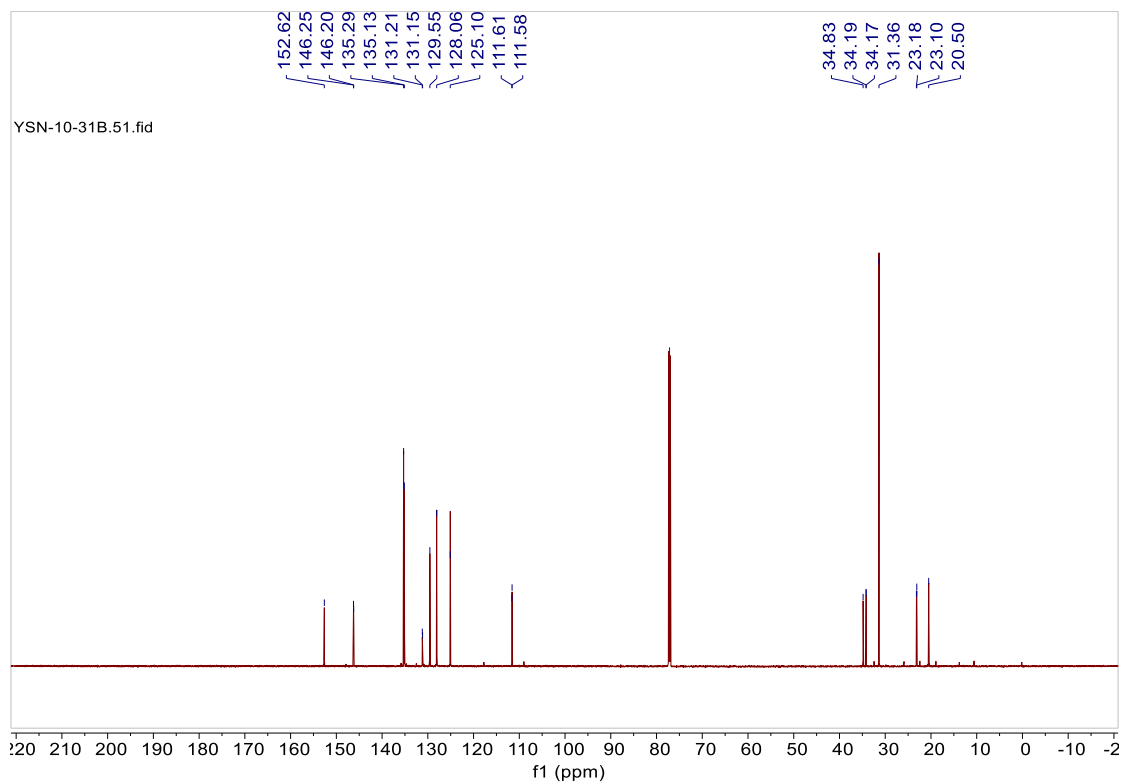


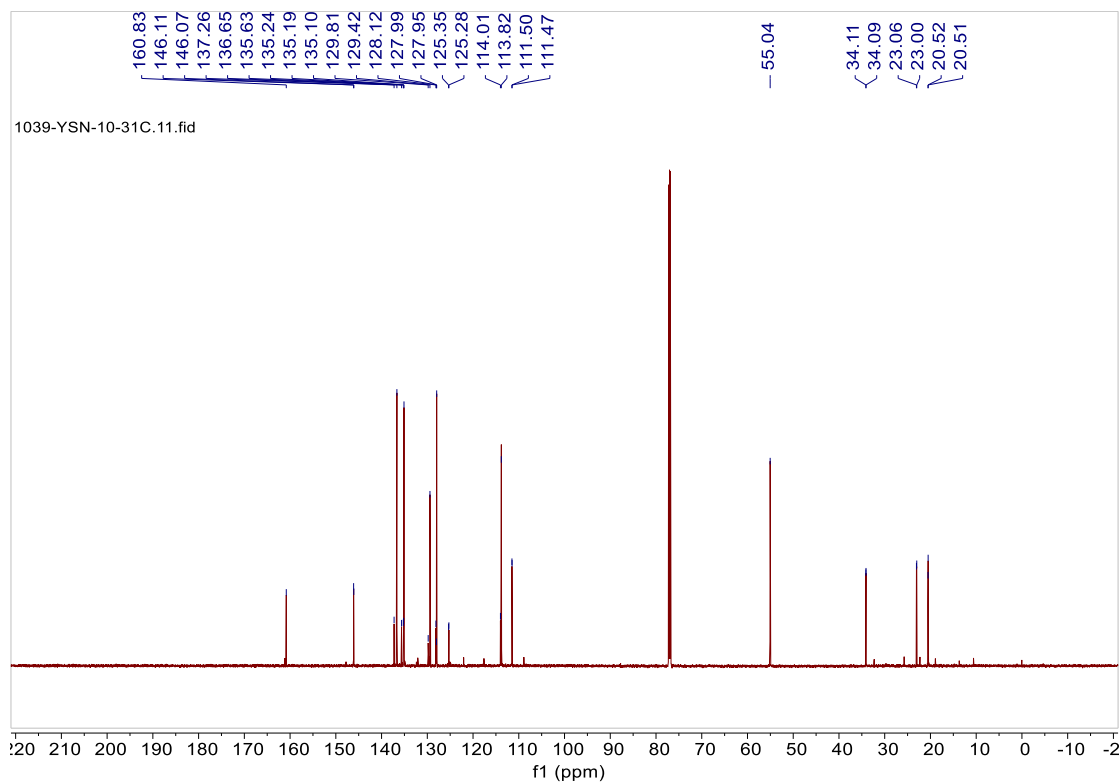
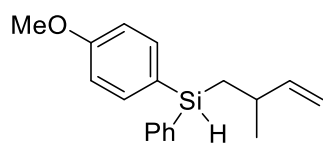
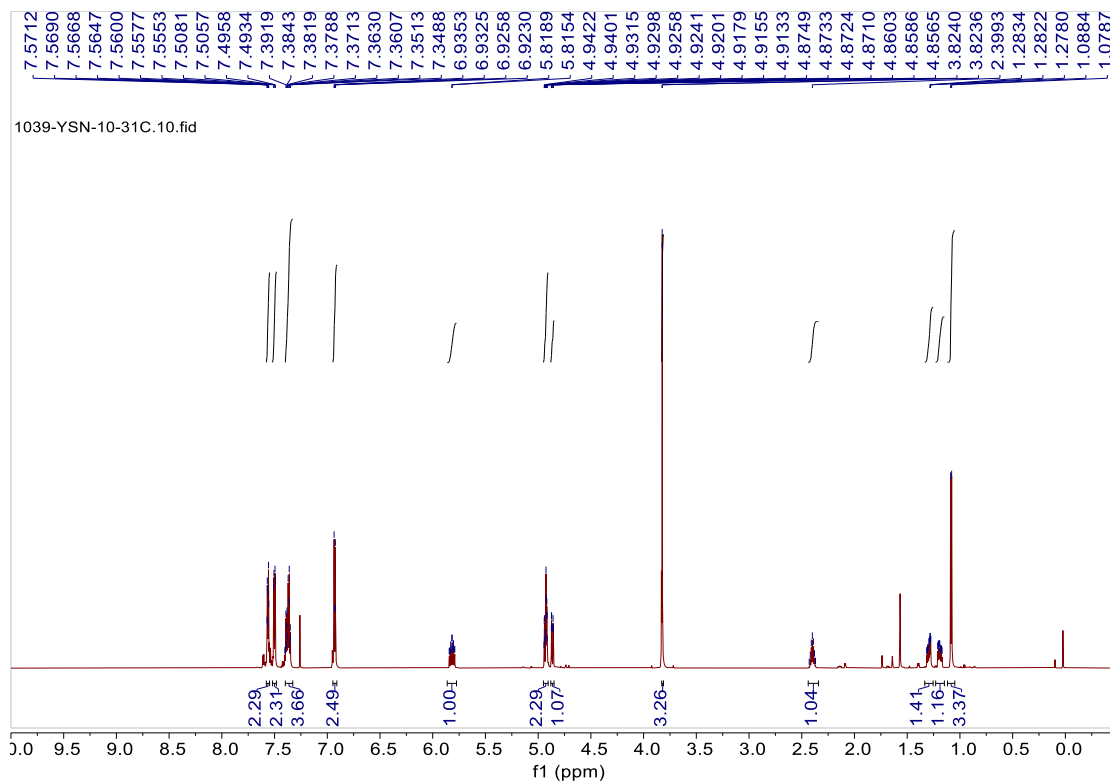


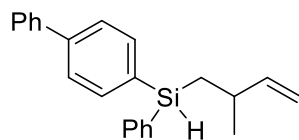
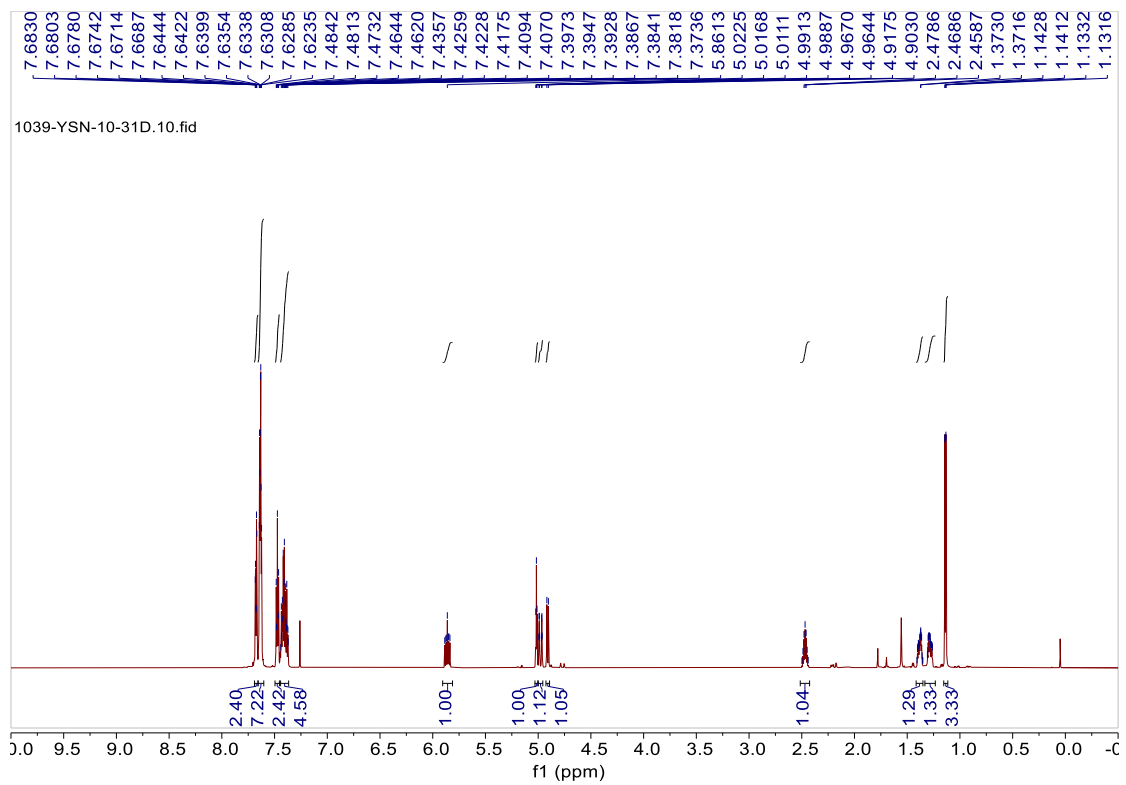


4c

¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

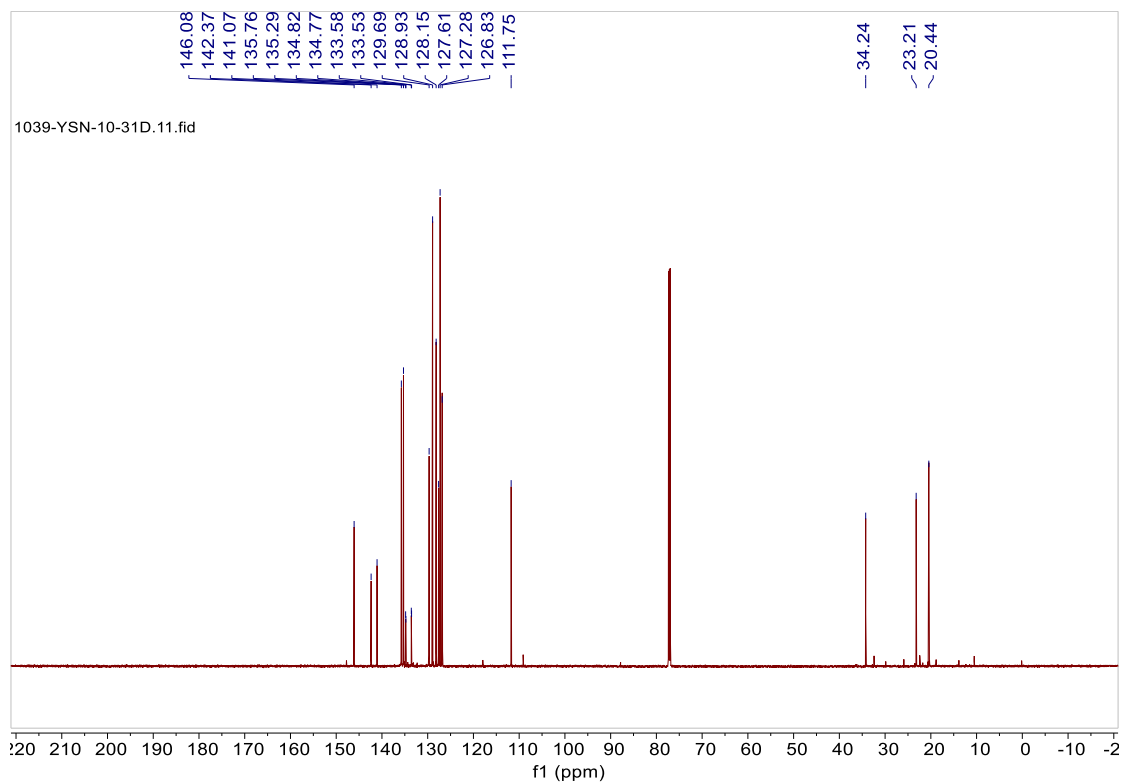


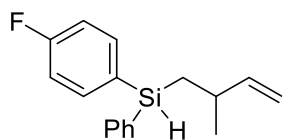
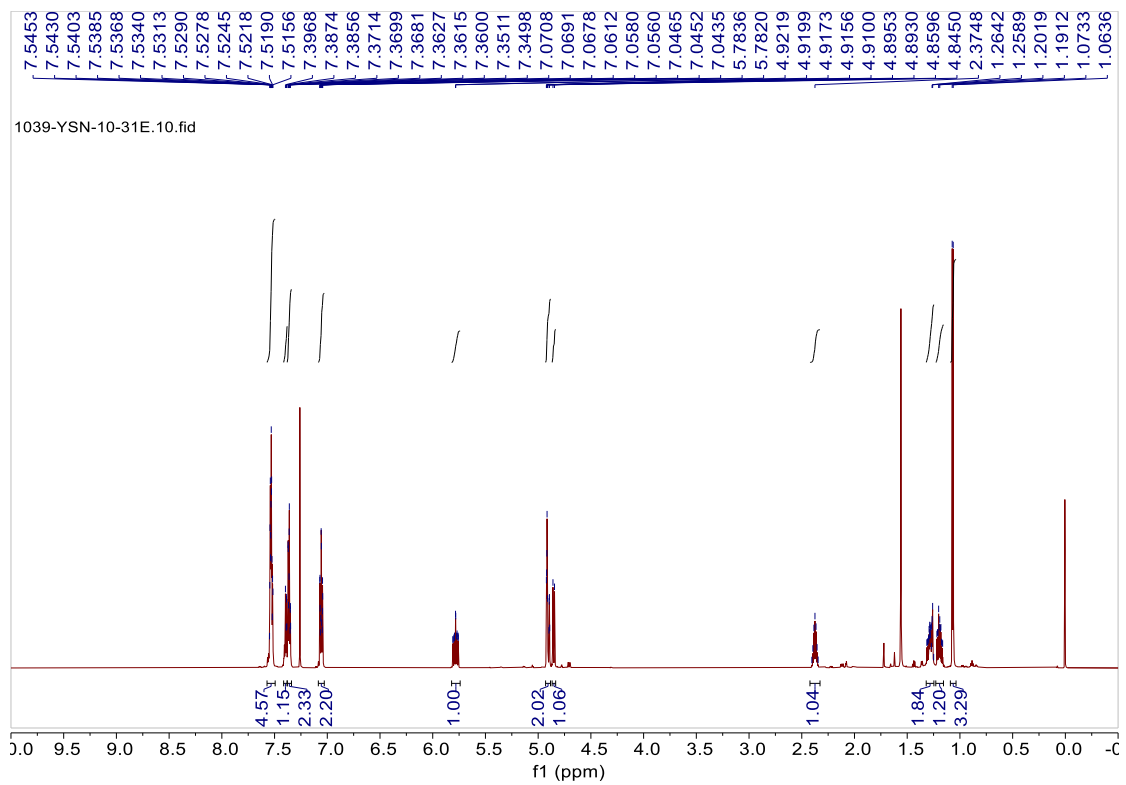




4e

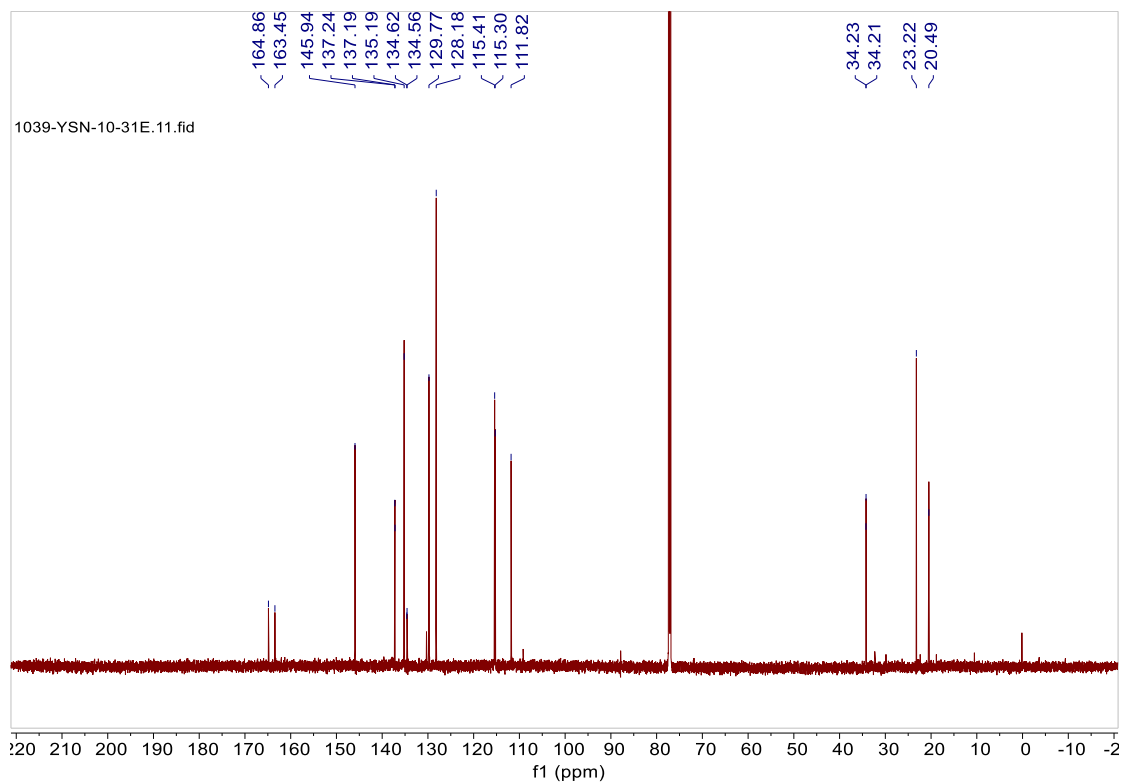
¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

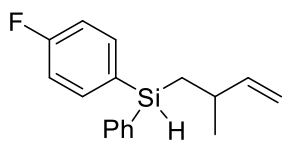




4f

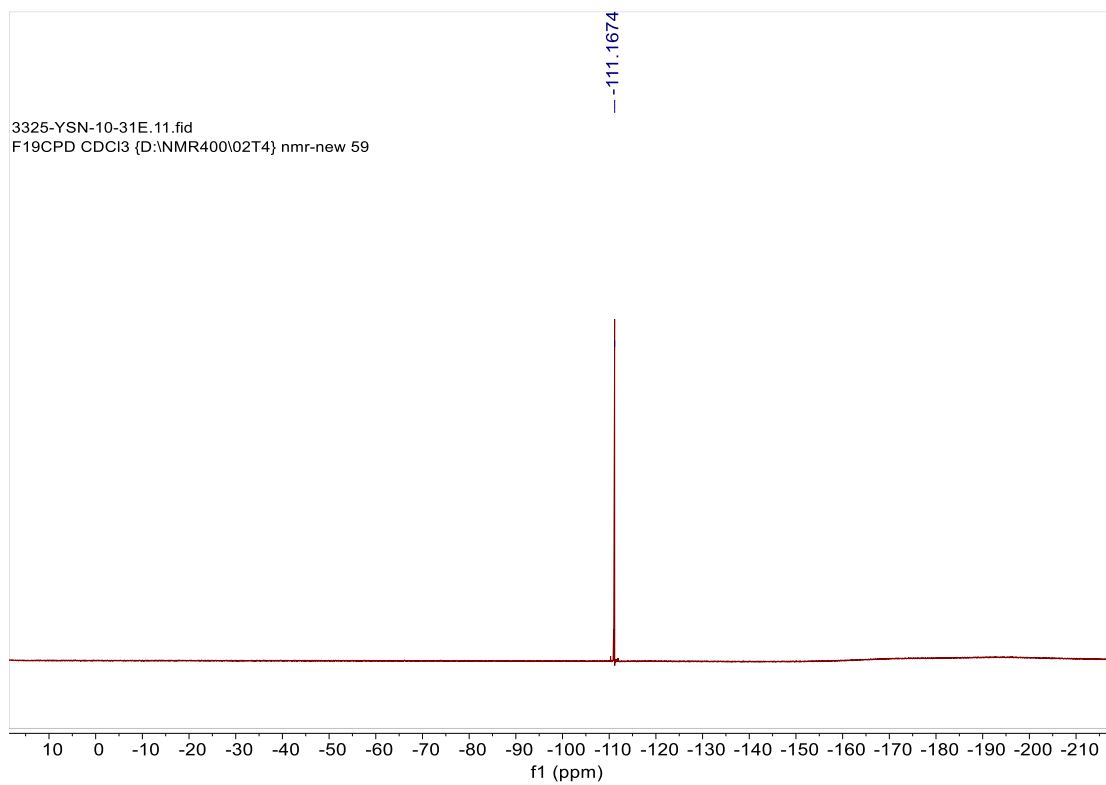
¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

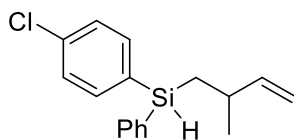
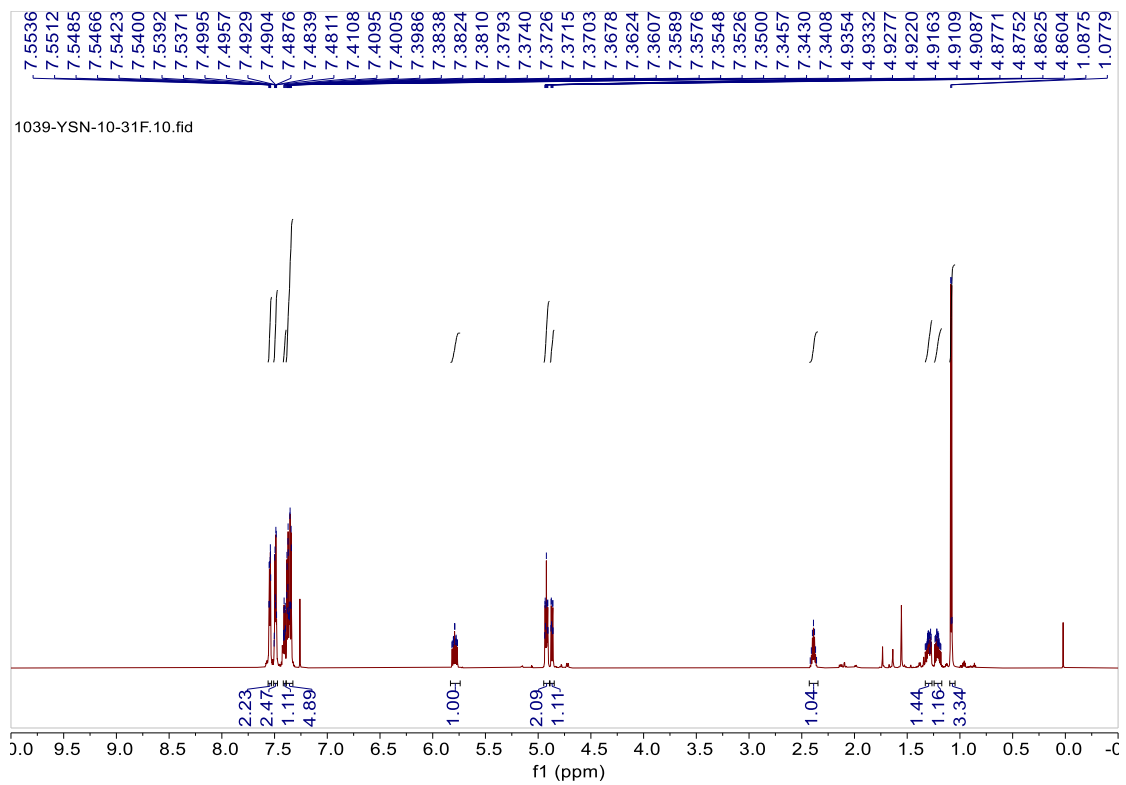




4f

¹⁹F NMR (376 MHz, CDCl₃)

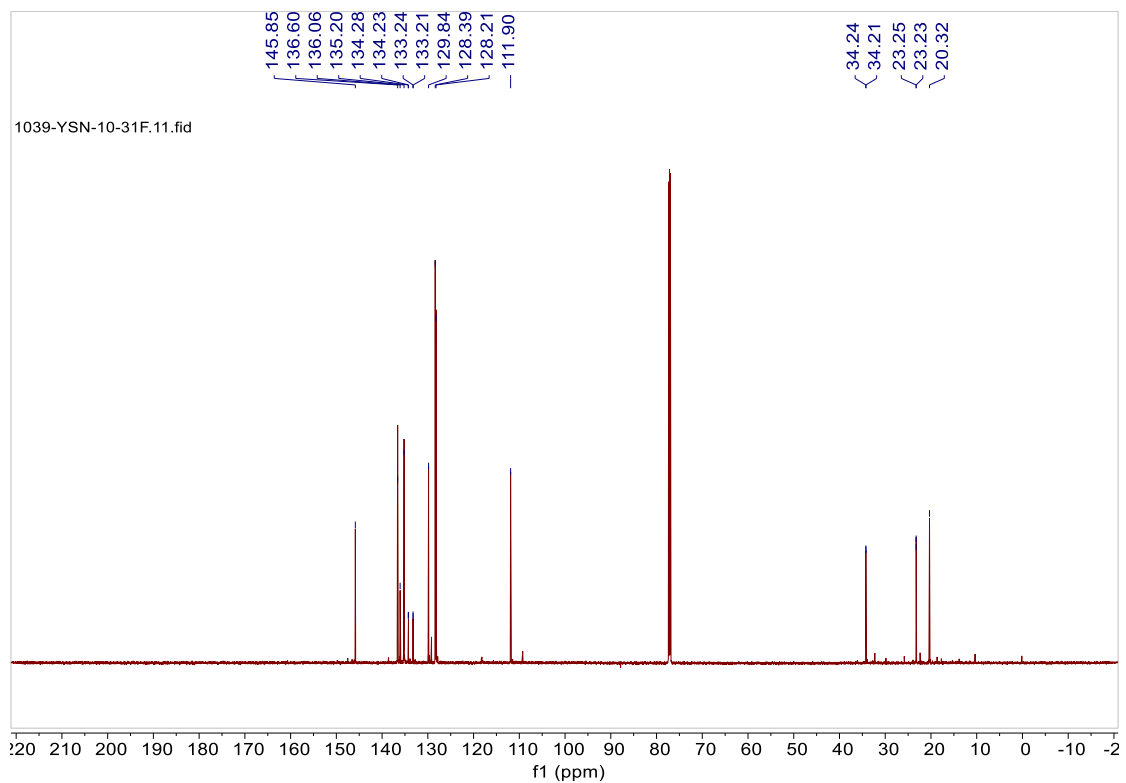


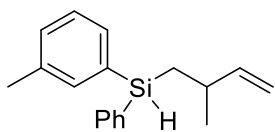
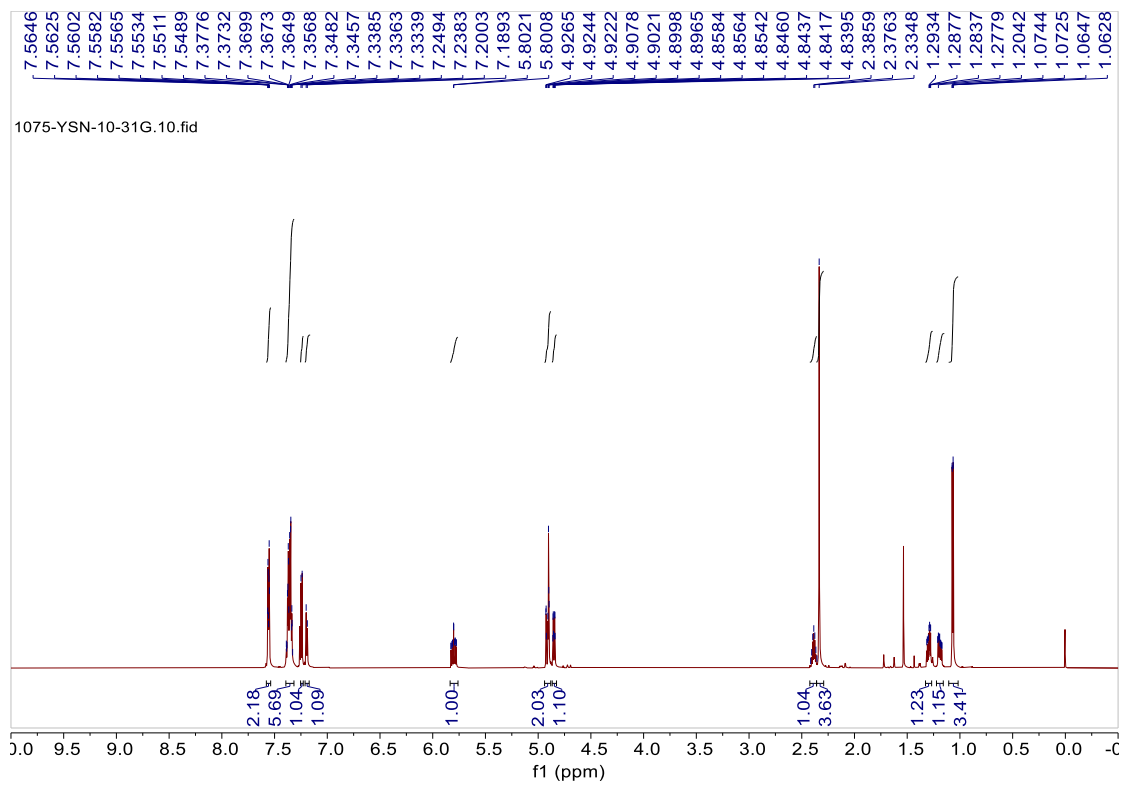


4g

¹H NMR (700 MHz, CDCl₃)

¹³C NMR (175 MHz, CDCl₃)

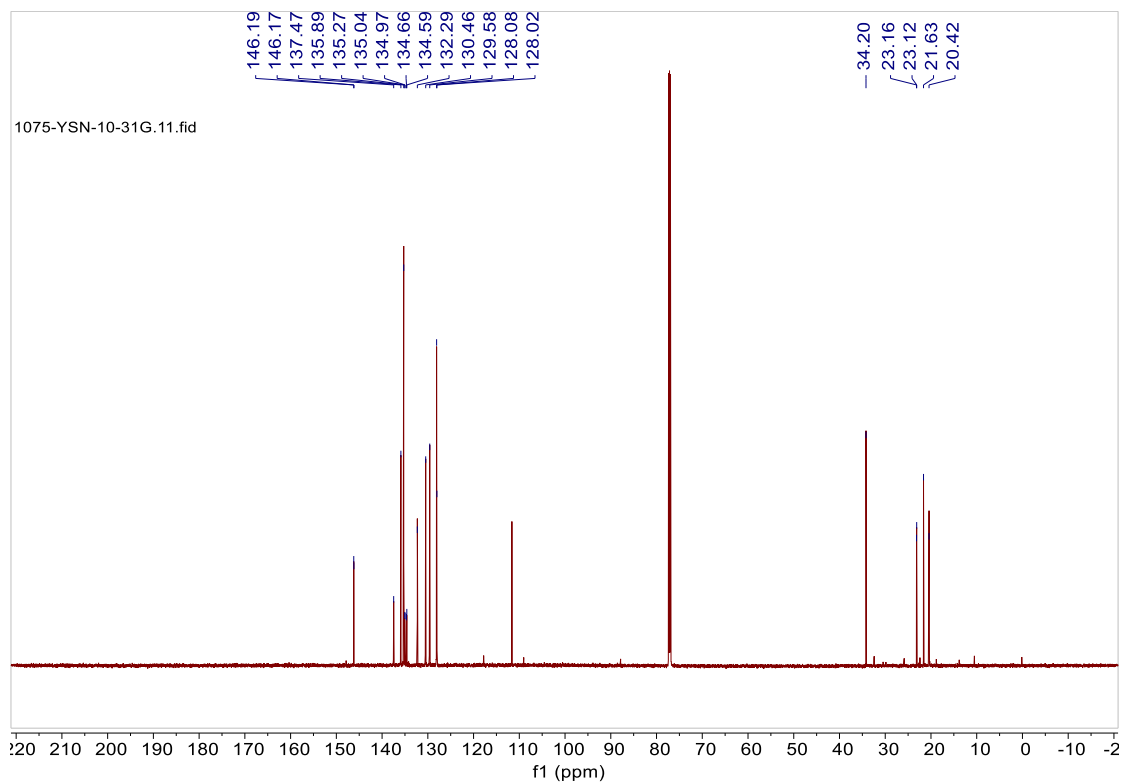


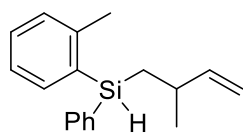
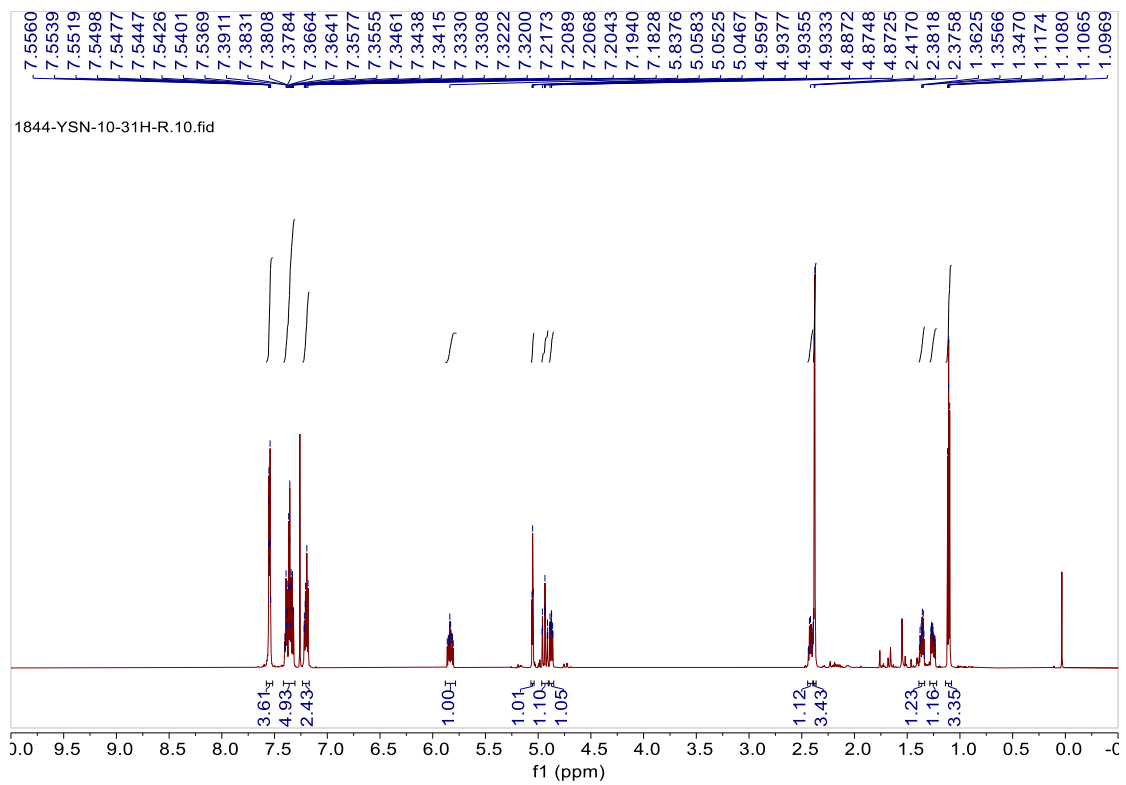


4h

¹H NMR (700 MHz, CDCl₃)

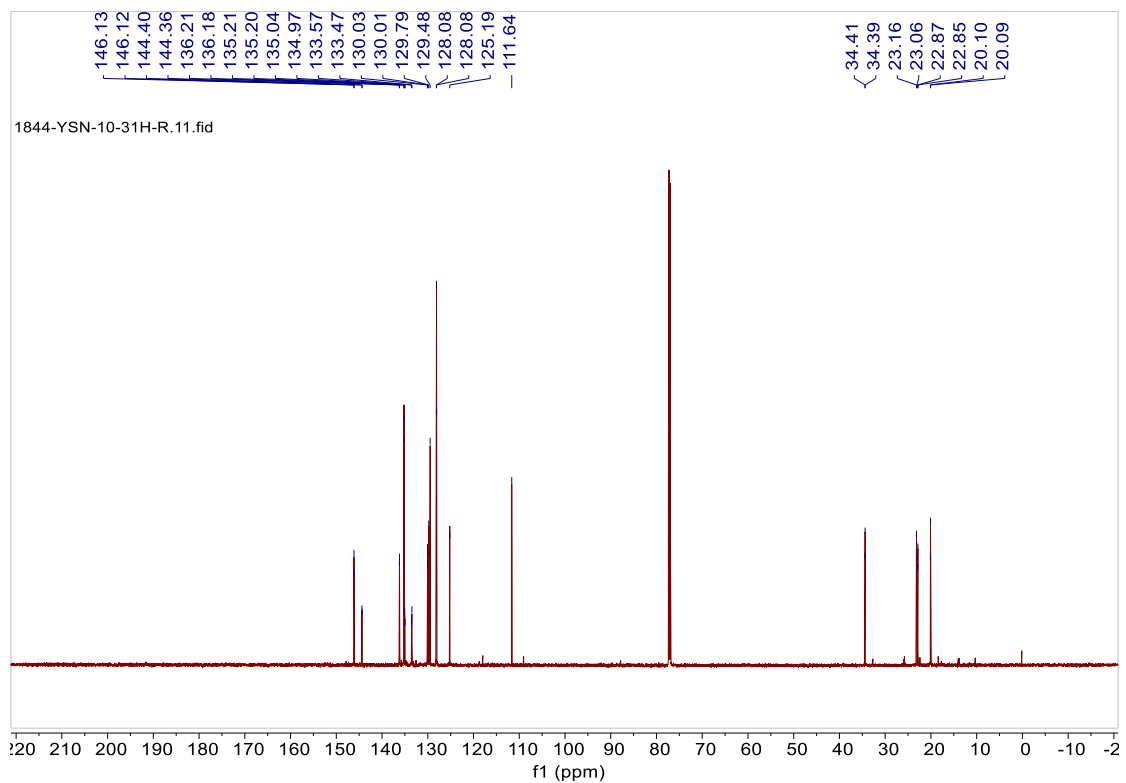
¹³C NMR (175 MHz, CDCl₃)

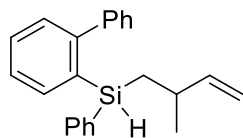
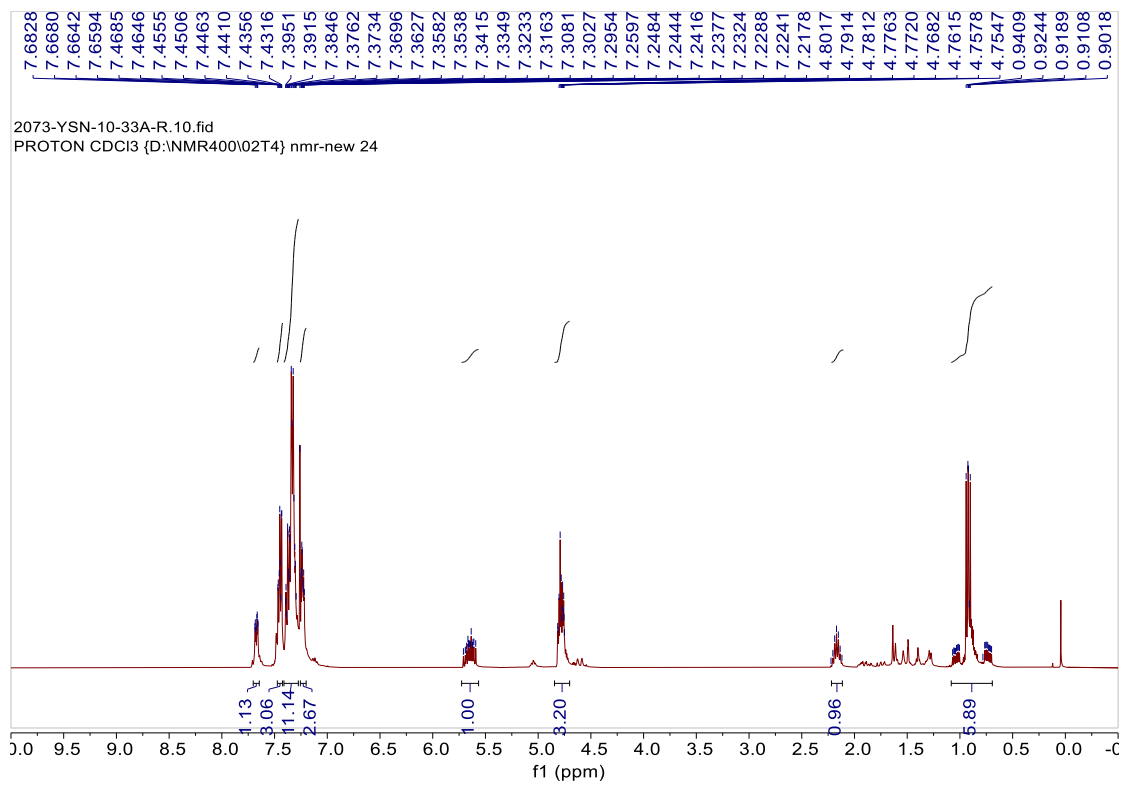




4i

¹H NMR (700 MHz, CDCl₃)
¹³C NMR (175 MHz, CDCl₃)

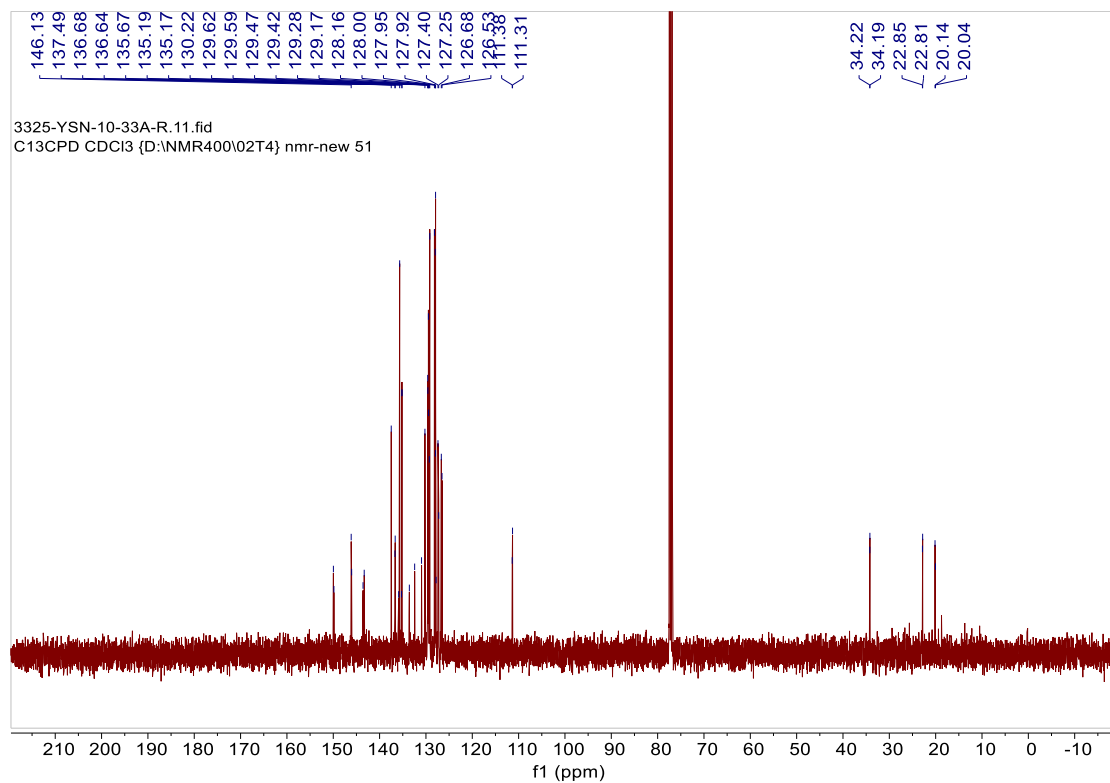


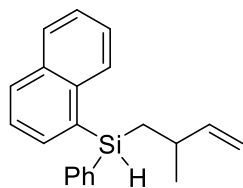
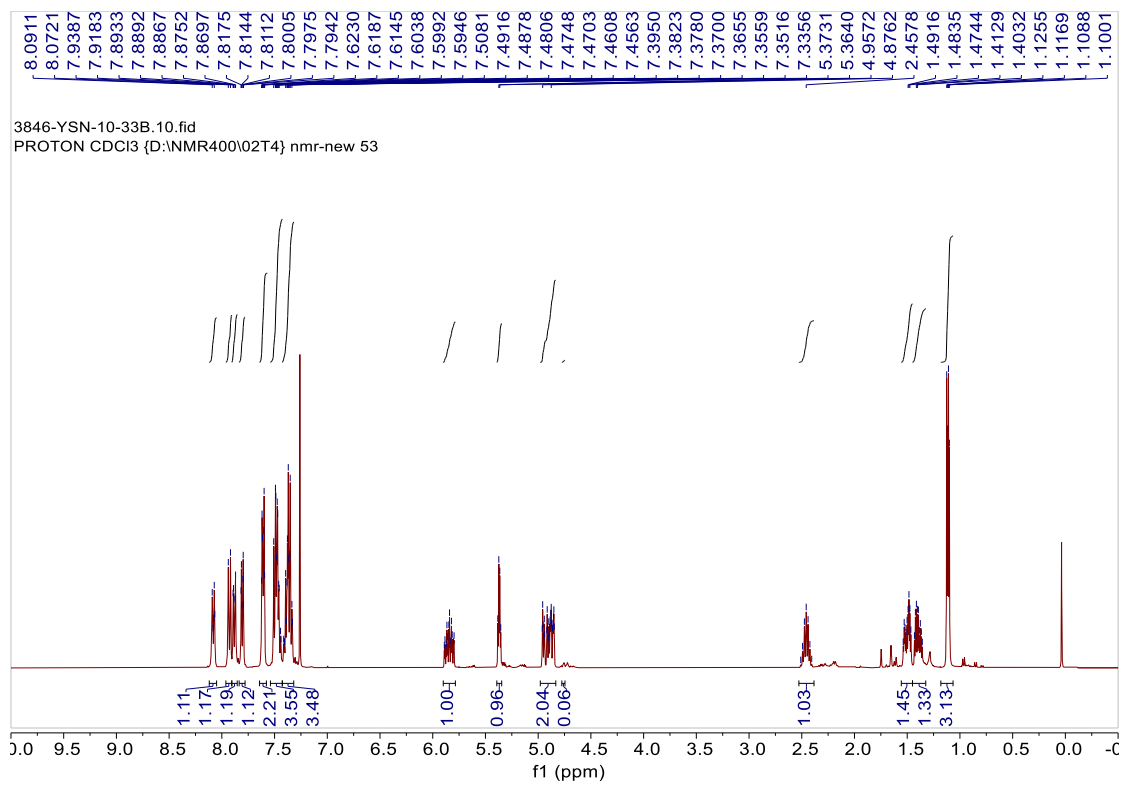


4j

^1H NMR (400 MHz, CDCl_3)

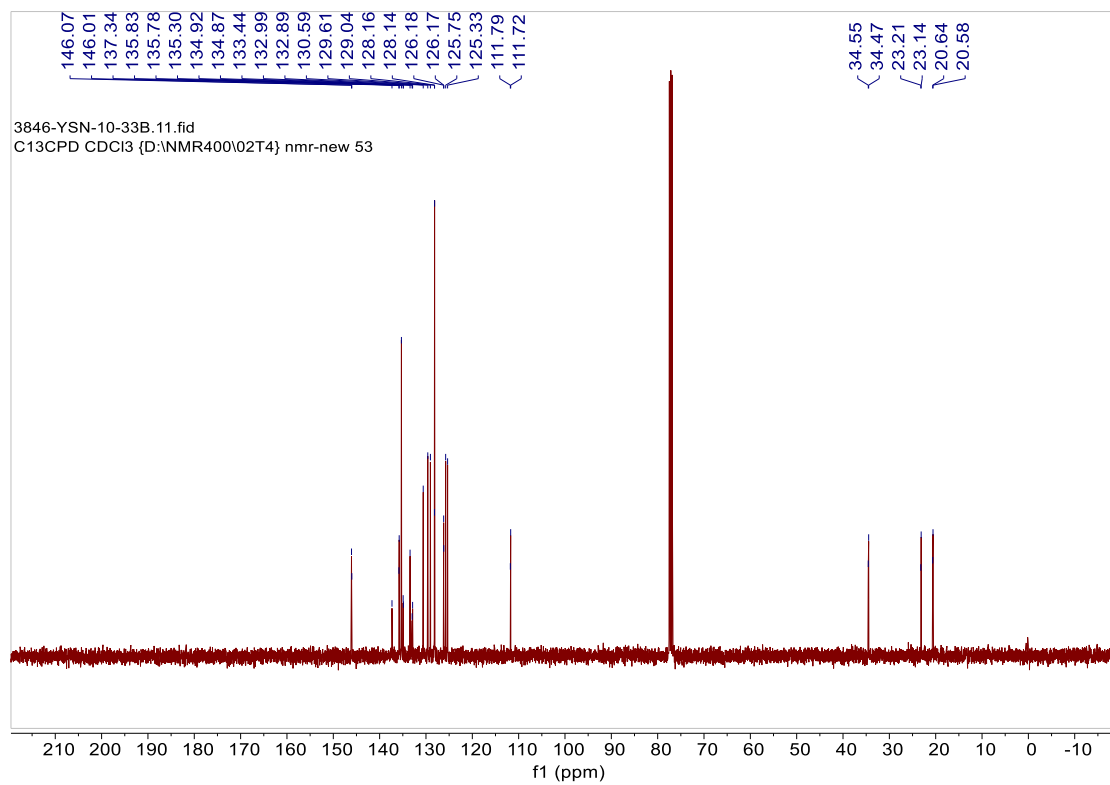
^{13}C NMR (100 MHz, CDCl_3)

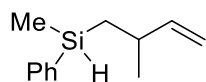
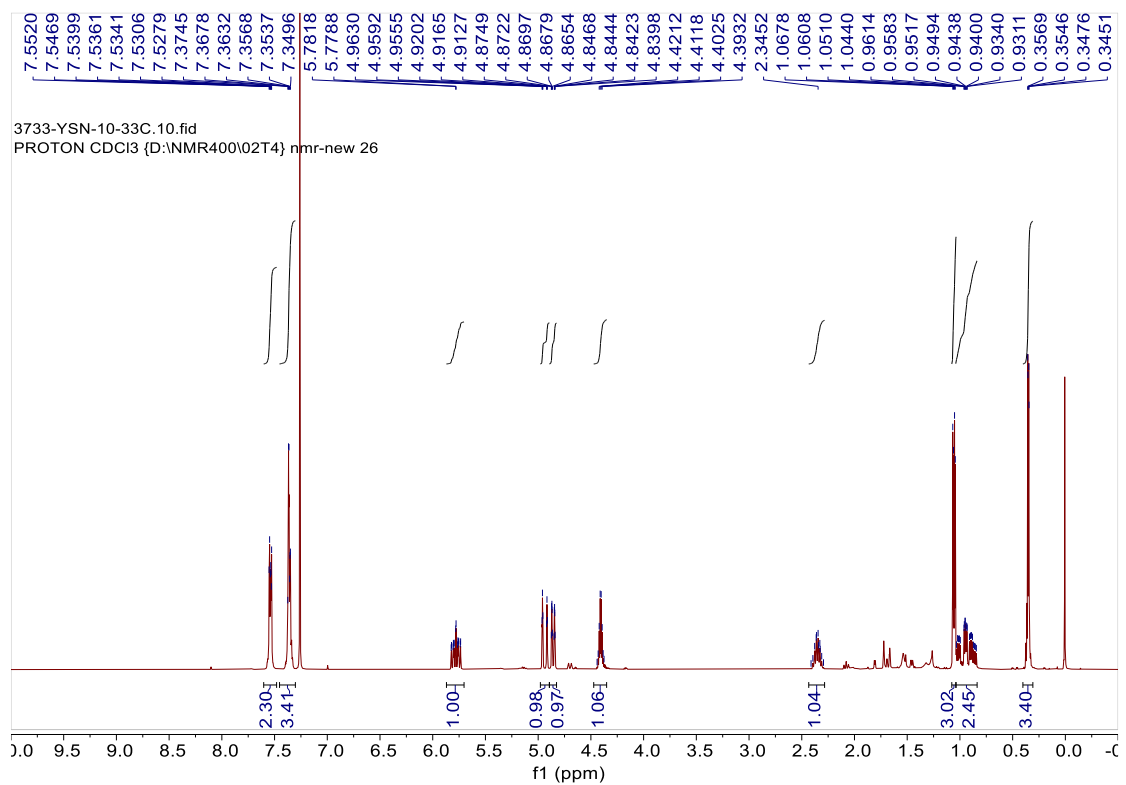




4k

¹H NMR (400 MHz, CDCl₃)
¹³C NMR (100 MHz, CDCl₃)

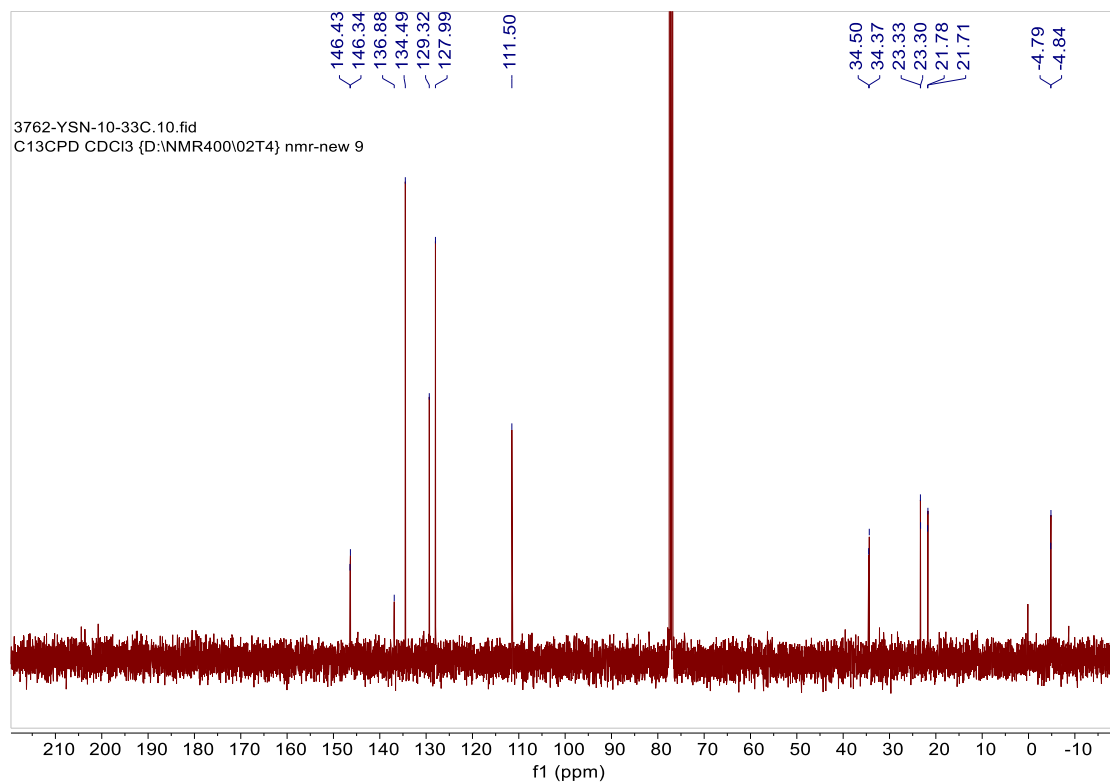


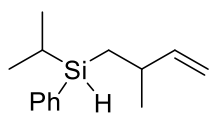
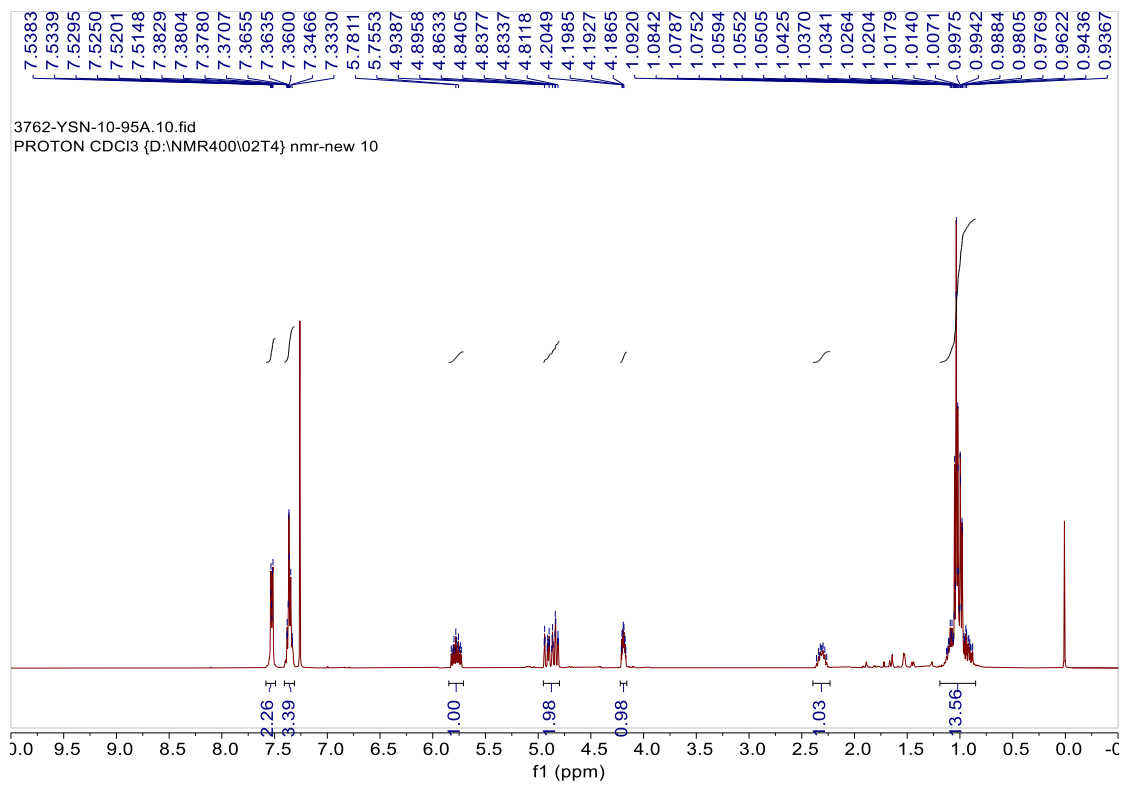


4i

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

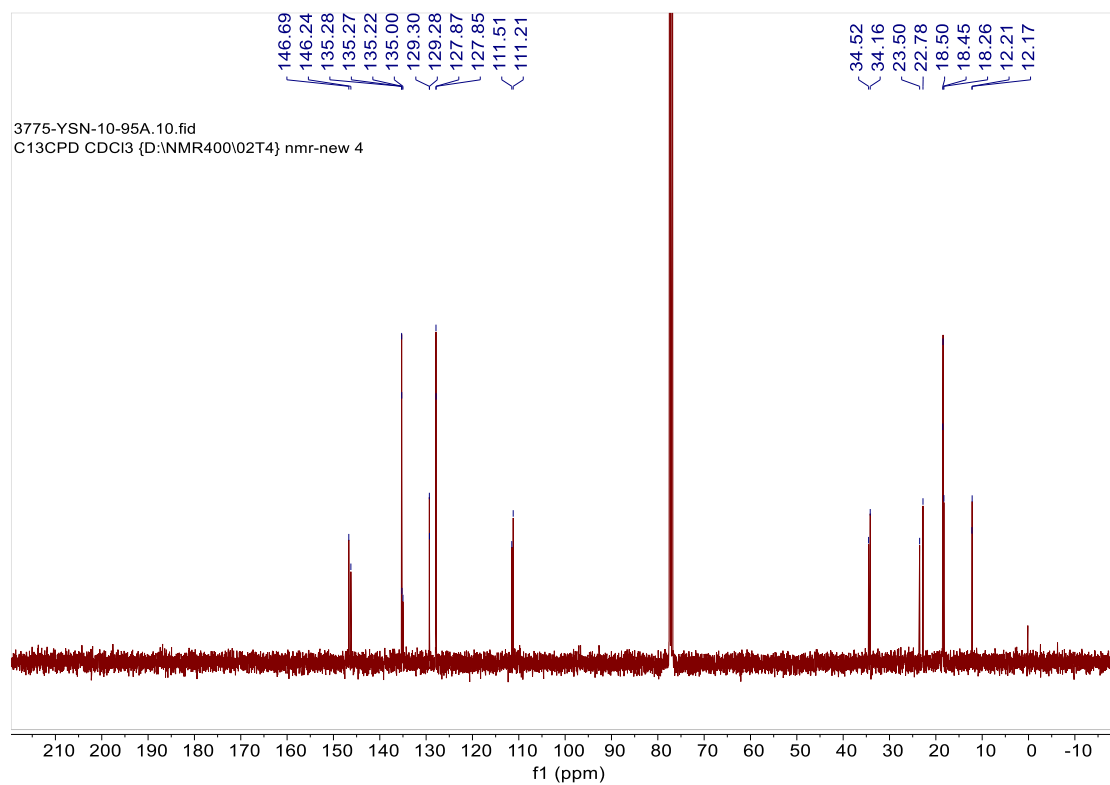


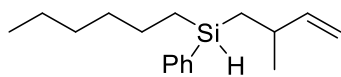
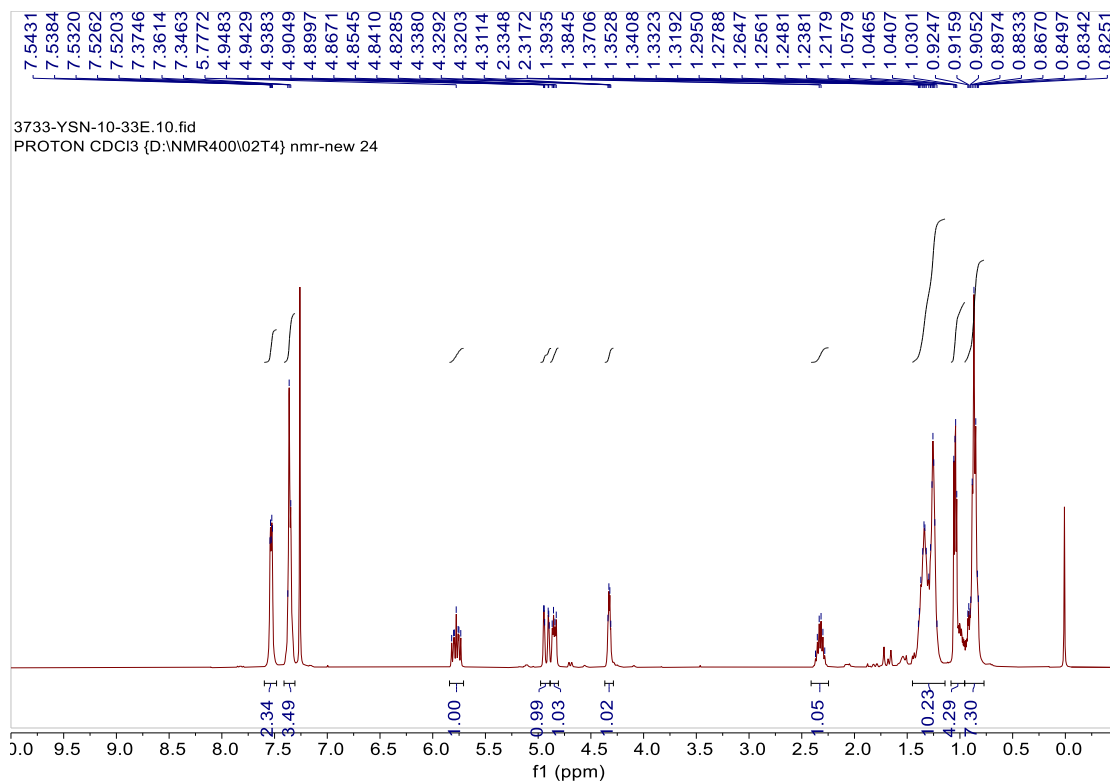


4m

^1H NMR (400 MHz, CDCl_3)

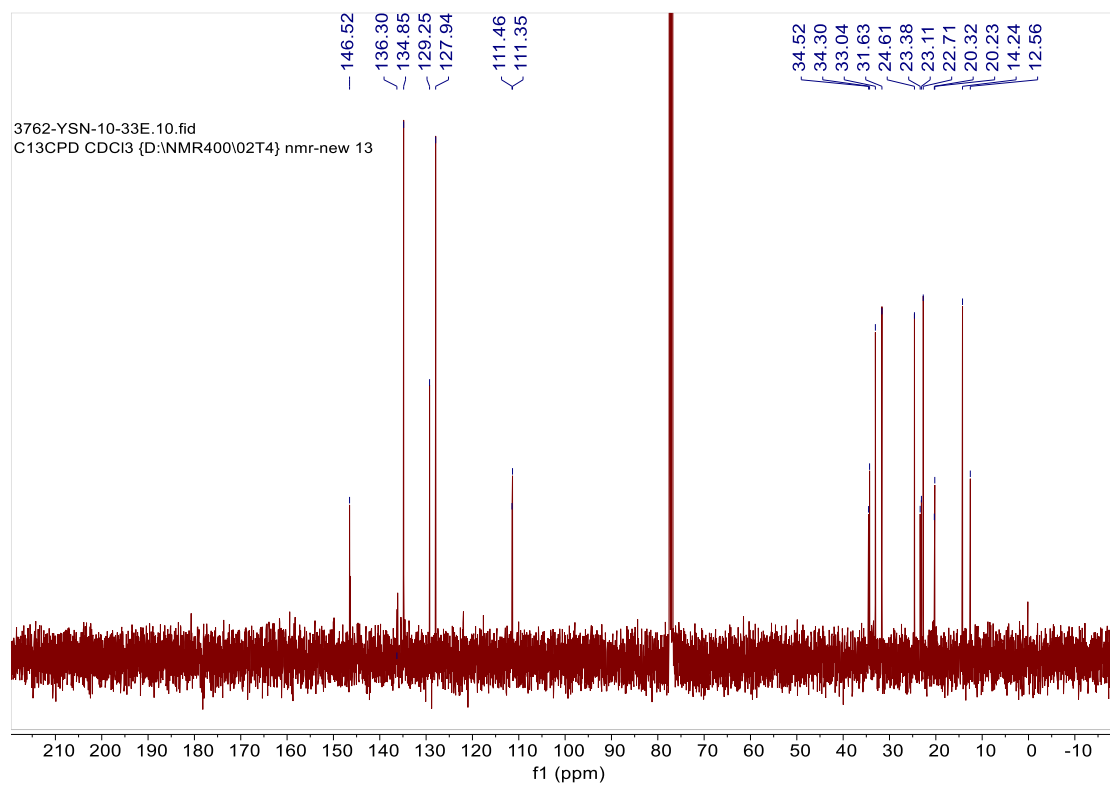
^{13}C NMR (100 MHz, CDCl_3)

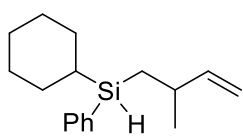
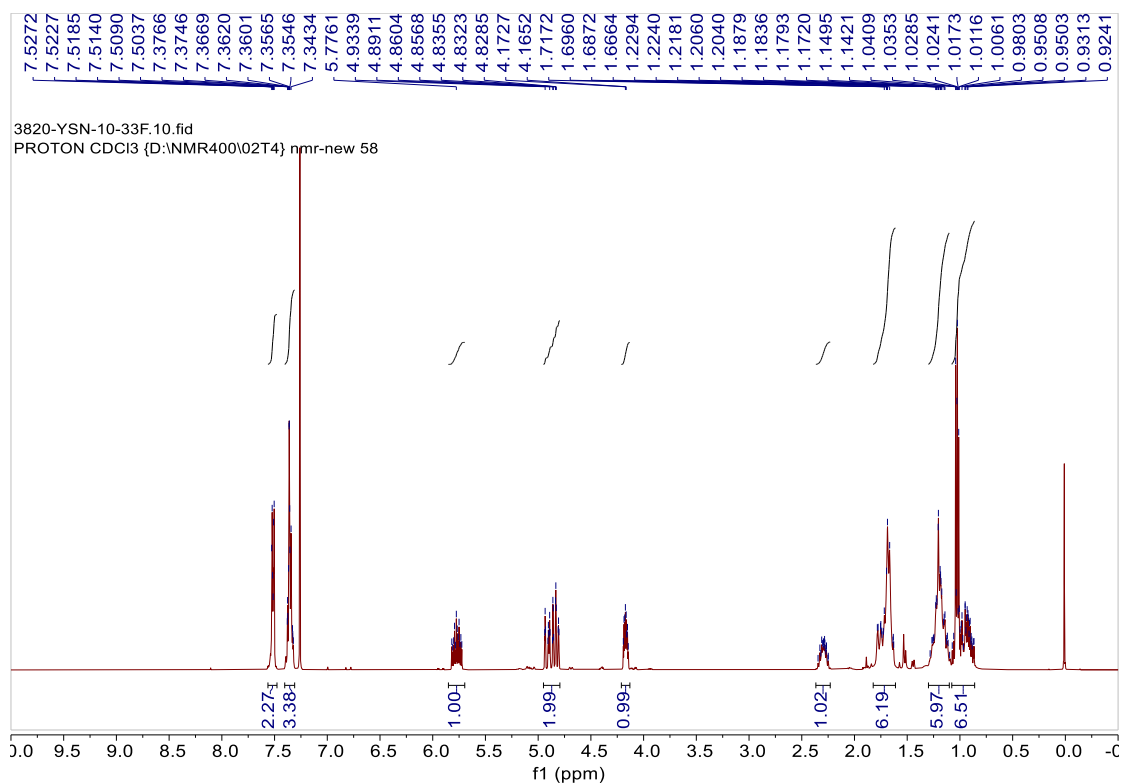




4n

¹H NMR (400 MHz, CDCl₃)
¹³C NMR (100 MHz, CDCl₃)





4o

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

