

Supporting Information

An Unusual Autocatalysis with Air-stable Pd Complex to Promote Enantioselective Synthesis of Si- Stereogenic Enynes

Fang-Ying Ling, Fei Ye, Xiao-Jun Fang, Xiao-Hua Zhou, Wei-Sheng Huang, Zheng Xu, and Li-Wen Xu*

liwenxu@hznu.edu.cn

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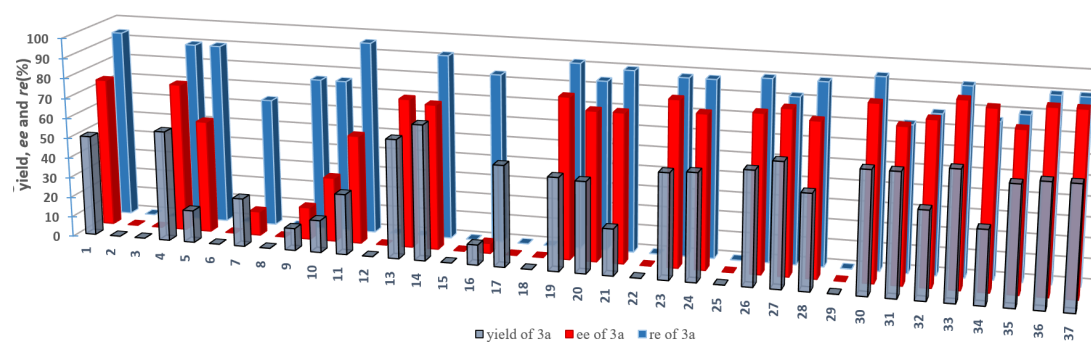
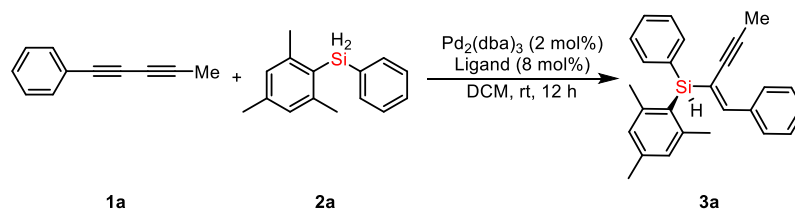
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1. General Information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. Dichloromethane (DCM), toluene, were freshly distilled from CaH₂, Ether (Et₂O), tetrahydrofuran (THF), 1,4-dioxane and Cyclohexane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh). NMR spectra were recorded on a Bruker 400-, 500- (400 MHz for ¹H; 100 MHz for ¹³C, 500 MHz for ¹⁹F, 400MHz and 500MHz for ²⁹Si). The chemical shifts (δ , ppm) were quoted in parts per million (ppm) referenced to TMS (0.00 ppm for ¹H NMR) and CDCl₃ (77.16 ppm for ¹³C NMR) The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublets of doublet, t = triplet, q = quartet, m = multiplets. Coupling constants, J, were reported in Hertz unit (Hz). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC analyses were carried out with an Agilent 1260 infinity, Waters AcQuity HPLC or Waters AcQuity UPLC using a chiralcel AD-H column, a chiralcel ND column, a chiralcel OX column, a chiralcel AS-H column and a chiral Phenomenex column.

2.Evaluation of Reaction Parameters

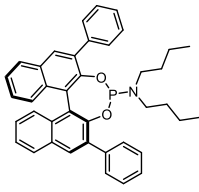
Table S1. Screening of the Chiral Phosphine Ligands ^a



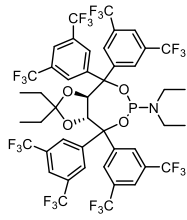
Entry	Ligand	Yield of 3a (%) ^b	<i>rr</i> of 3a ^c	<i>ee</i> of 3a (%) ^d
1	L1	50	97:3	74
2	L2	nr	-	-
3	L3	nr	-	-
4	L4	55	95:5	74
5	L5	16	95:5	56
6	L6	nr	-	-
7	L7	24	82:18	12
8	L8	trace	-	-
9	L9	11	88:12	16
10	L10	16	88:12	32
11	L11	30	98:2	-54
12	L12	nr	-	-
13	L13	59	-	74
14	L14	67	96:4	72
15	L15	nr	-	-
16	L16	10	92:8	5
17	L17	50	-	race
18	L18	trace	-	-
19	L19	46	96:4	80

20	L20	45	92:8	74
21	L21	23	95:5	74
22	L22	nr	-	-
23	L23	52	94:6	82
24	L24	53	94:6	76
25	L25	nr	-	-
26	L26	56	95:5	78
27	L27	61	91:9	81
28	L28	47	95:5	76
29	L29	trace	-	-
30	L30	60	97:3	86
31	L31	60	86:14	76
32	L32	43	89:11	80
33	L33	63	96:4	90
34	L34	36	88:12	87
35	L35	58	90:10	78
36	L36	60	95:5	89
37	L37	60	95:5	89
38 ^e	L12	48	95:5	73

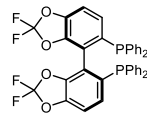
^aUnless otherwise noted, reactions were conducted under N₂ on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (0.2 mmol), Pd₂(dba)₃ (2 mol%), Ligand (8 mol%), DCM (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by GC-MS. ^dDetermined by HPLC. ^e**1a** (0.2 mmol), **2a** (0.2 mmol), Pd₂(dba)₃ (2 mol%), L12 (8 mol%), DCM (2 mL), 40 °C.



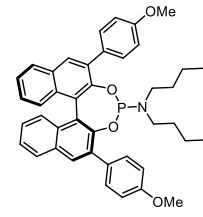
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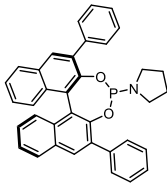
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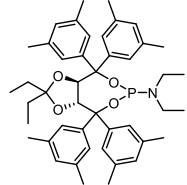
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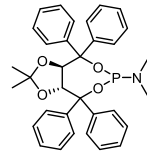
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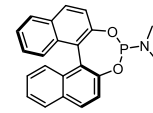
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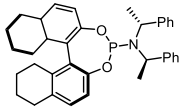
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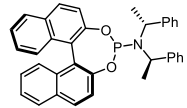
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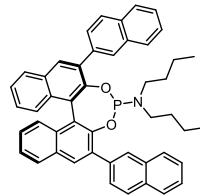
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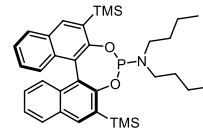
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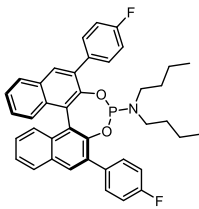
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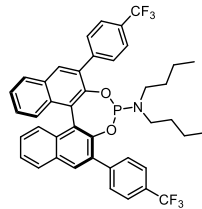
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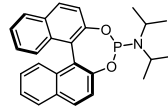
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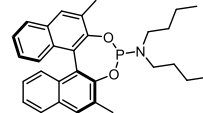
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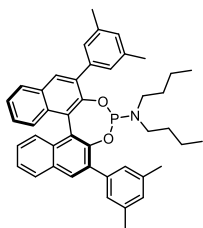
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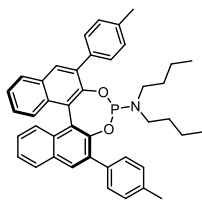
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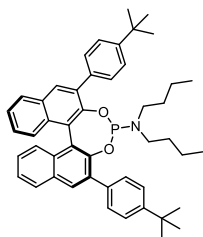
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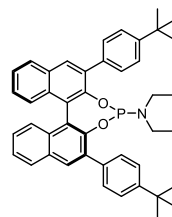
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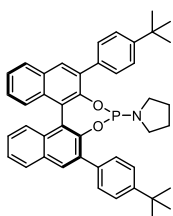
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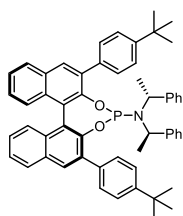
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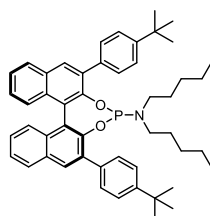
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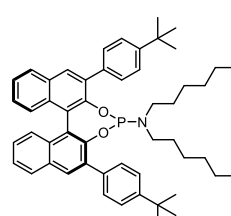
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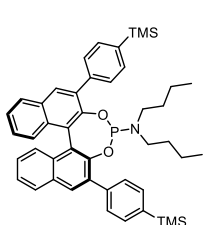
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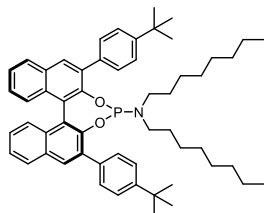
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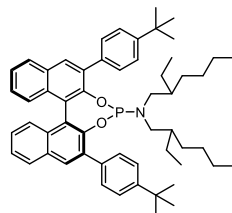
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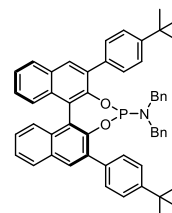
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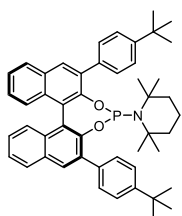
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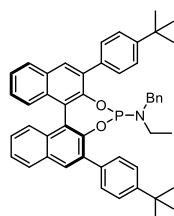
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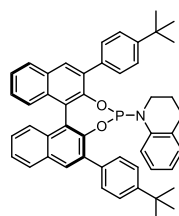
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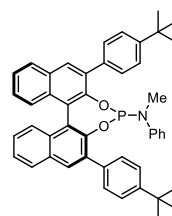
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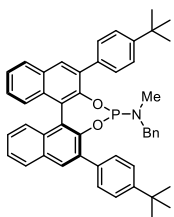
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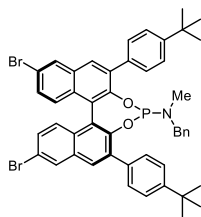
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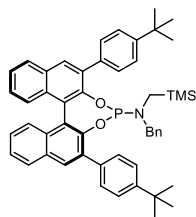
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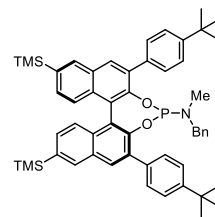
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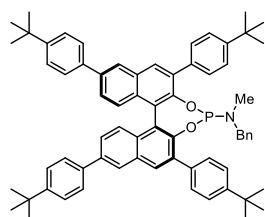
L34



L35



L36



L37

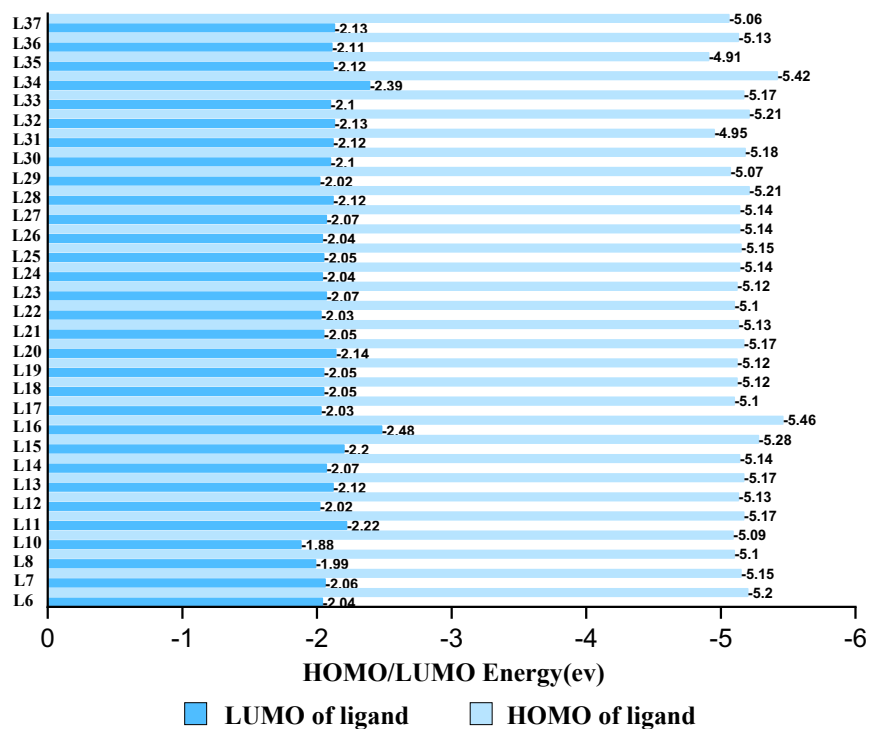
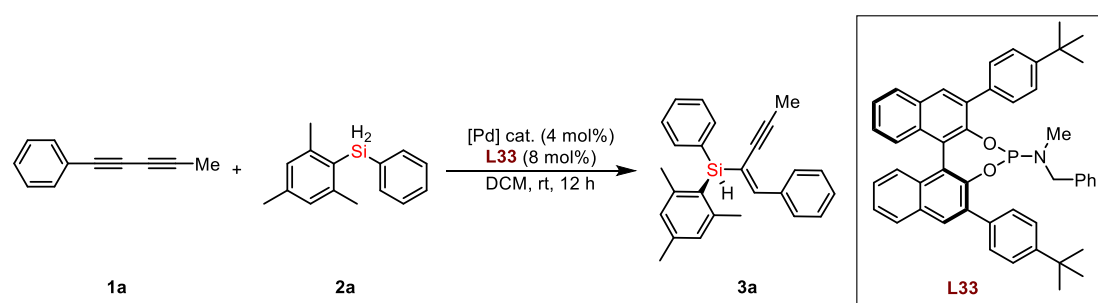


Figure S1. Frontline Orbital Analysis of L6-L37

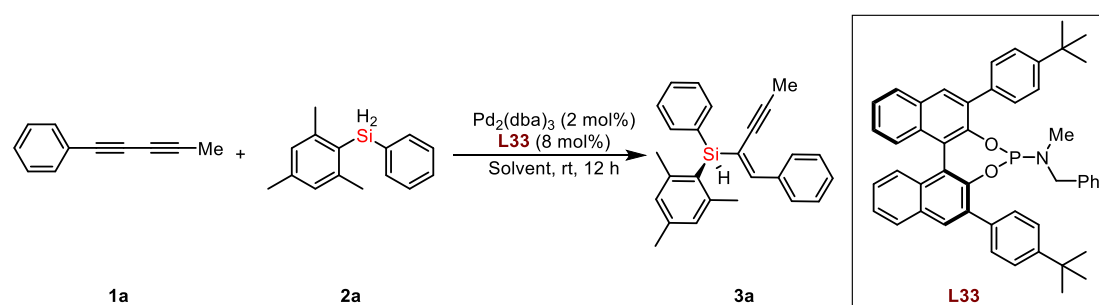
Table S2 . Screening of the Pd Catalysts ^a



Entry	[Pd] cat	Yield of 3a (%) ^b	<i>rr</i> of 3a ^c	<i>ee</i> of 3a (%) ^d
1	Pd ₂ (dba) ₃ ·CHCl ₃	59	91:9	91
2	Pd(dba) ₂	62	92:8	91
3	Pd(C ₃ H ₅) ₂ Cl ₂	10	86:14	91
4	Pd(OAc) ₂	56	88:12	91
5	Pd(cod) ₂ Cl ₂	nr	-	-
6	Pd(nbd) ₂ Cl ₂	nr	-	-
7	Pd(acac) ₂	trace	-	-
8	Pd(TFA) ₂	trace	-	-
9	Pd(PPh ₃) ₄	56	85:15	81
11	PdCl ₂	trace	-	-
12	PdBr ₂	nr	-	-
13	PdI ₂	nr	-	-
14	Pd(CN) ₂ Cl	nr	-	-
15	[PdCl(2-Me-C ₃ H ₄) ₂] ₂	52	87:13	91
16	Pd ₂ (dba) ₃	63	96:4	90

^aUnless otherwise noted, reactions were conducted under N₂ on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (0.2 mmol), [Pd] cat. (4 mol%), Ligand (8 mol%), DCM (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by GC-MS. ^dDetermined by HPLC.

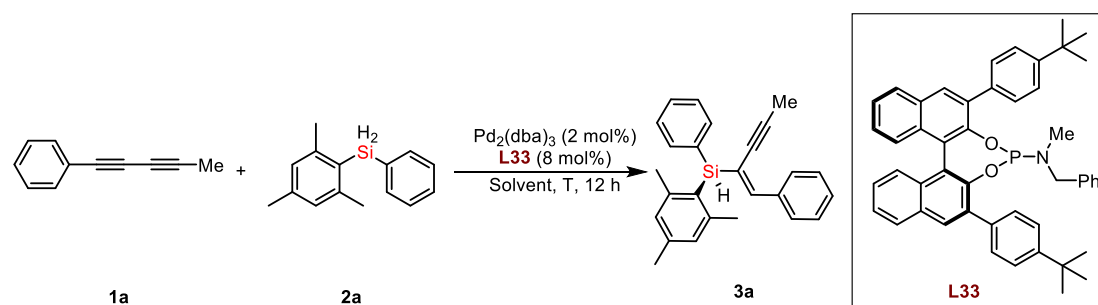
Table S3 . Screening of the Solvents ^a



Entry	Solvent	Yield of 3a (%) ^b	<i>rr</i> of 3a ^c	<i>ee</i> of 3a (%) ^d
1	Toluene	62	97:3	85
2	THF	68	97:3	89
3	DCE	60	95:5	90
4	Dioxane	60	96:4	90
5	Hexane	60	98:2	91
6	2-Me-THF	70	97:3	88
7	Et ₂ O	69	97:3	89
8	CH ₃ CN	19	97:3	86
9	THF : Hexane (1:1)	66	96:4	90
10 ^e	Hexane	62	98:2	91
11	Cyclohexane	65	98:2	91
12	Heptane	60	98:2	91
13	CHCl ₃	trace	-	-

^aUnless otherwise noted, reactions were conducted under N₂ on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (0.2 mmol), Pd₂(dba)₃ (2 mol%), Ligand (8 mol%), Solvent (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by GC-MS. ^dDetermined by HPLC. ^e5Å MS (50 mg).

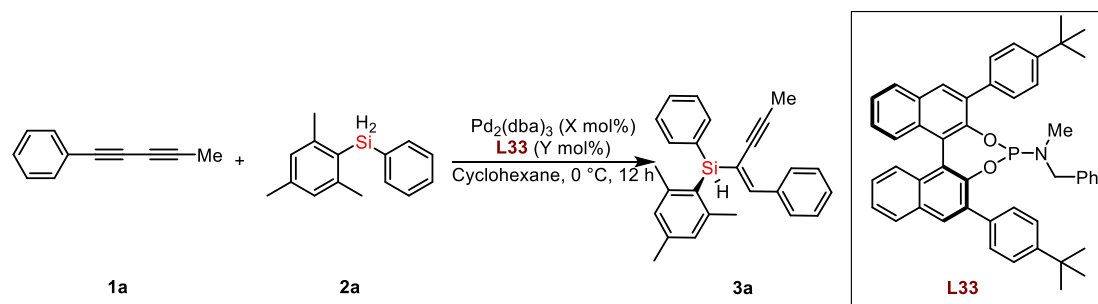
Table S4. The Effect of the Temperature on the Pd -catalyzed Hydrosilylation ^a



Entry	Solvent	T (°C)	Yield of 3a (%) ^b	<i>rr</i> of 3a ^c	<i>ee</i> of 3a (%) ^d
1	Cyclohexane	40	63	97:3	89
2	Cyclohexane	0	70	99:1	93
3 ^e	Cyclohexane	25	77	98:2	91
4	Cyclohexane	25	65	98:2	91
5	DCM	0	48	98:2	90
6	DCM	-20	trace	-	-
7	DCM	-40	nr	-	-
8	Hexane	0	62	98:2	92
9	Hexane	-20	trace	-	-
10	Cyc:Hex (1:1)	0	65	98:2	93
11	Cyc:Hex (1:1)	-20	nr	-	-

^aUnless otherwise noted, reactions were conducted under N₂ on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (0.2 mmol), Pd₂(dba)₃ (2 mol%), Ligand (8 mol%), Solvent (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by GC-MS. ^dDetermined by HPLC. ^e5Å MS (50 mg).

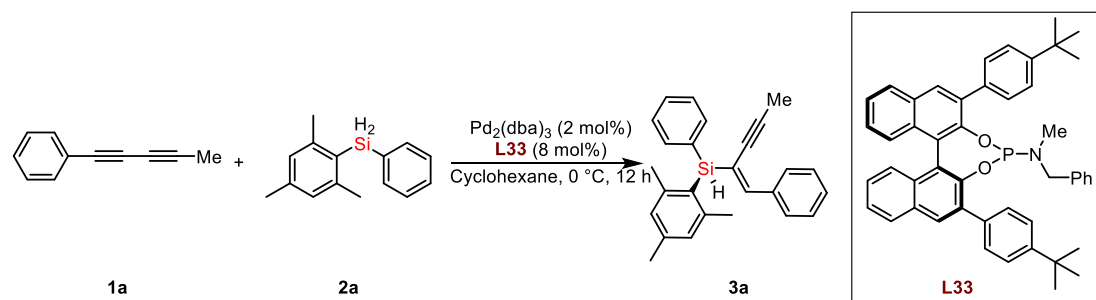
Table S5. The Effect of the Loading of the Ligand/Catalyst on the Pd - catalyzed Hydrosilylation ^a



Entry	X (mol%)	Y (mol%)	Yield of 3a (%) ^b	<i>rr</i> of 3a ^c	<i>ee</i> of 3a (%) ^d
1	2	12	69	99:1	94
2	1	4	60	99:1	93
3	2	4	53	99:1	93
4	2	8	70	99:1	93

^aUnless otherwise noted, reactions were conducted under N₂ on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (0.2 mmol), Pd₂(dba)₃ (2 mol%), Ligand (8 mol%), Solvent (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by GC-MS. ^dDetermined by HPLC.

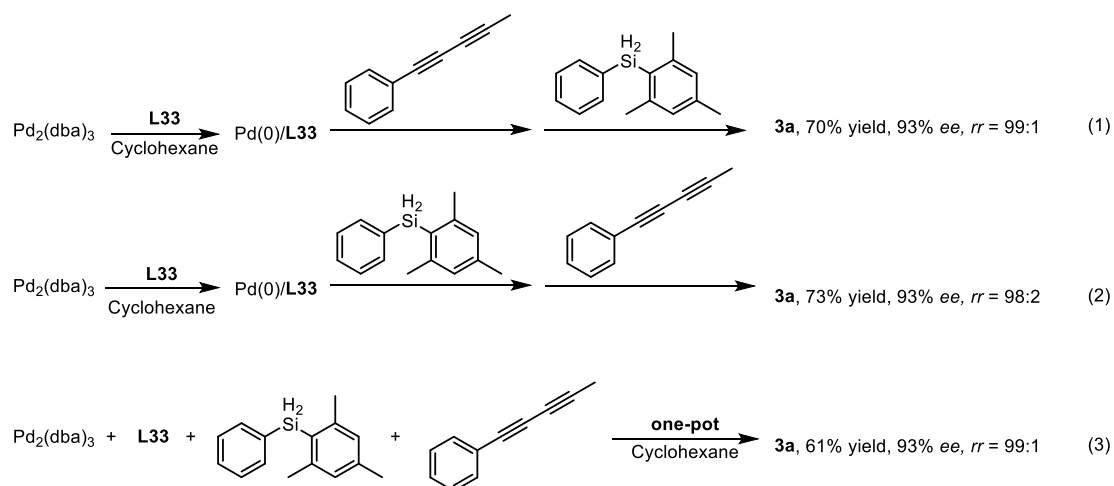
Table S6. The Effect of the Ratio of two Substrates on this Reaction ^a



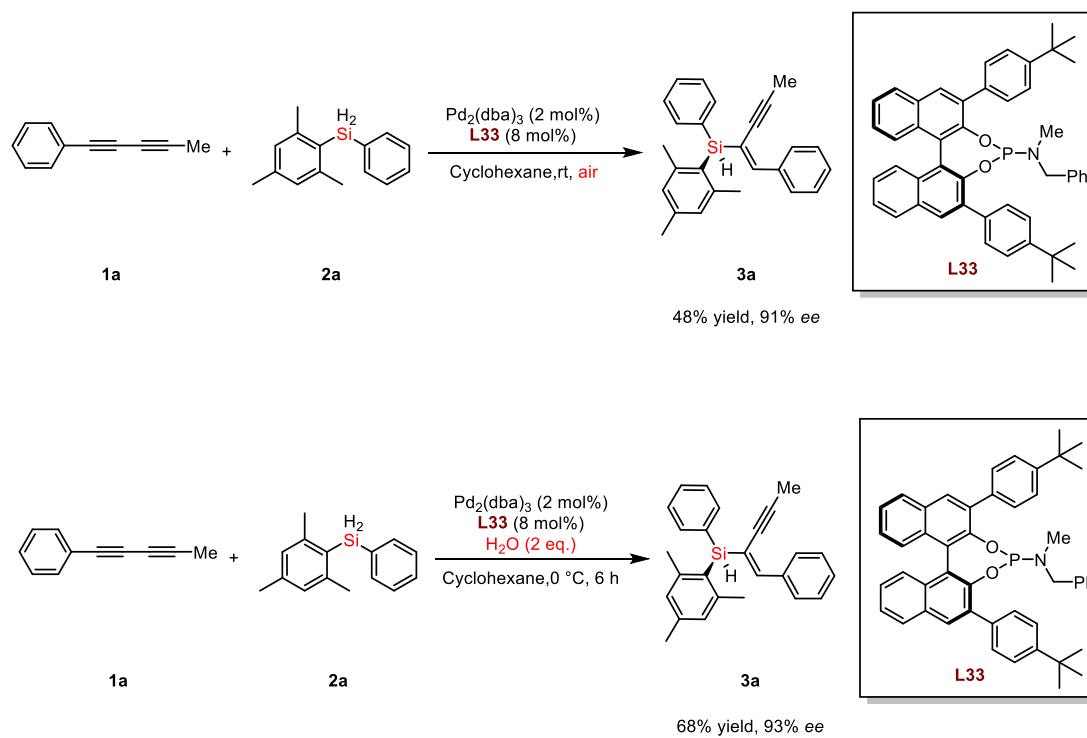
Entry	1a : 2a	Yield of 3a (%) ^b	<i>rr</i> of 3a ^c	<i>ee</i> of 3a (%) ^d
1	1:2	67	99:1	93
2	2:1	65	99:1	93
3	1:1	70	99:1	93

^aUnless otherwise noted, reactions were conducted under N₂ on 0.2 mmol scale: **1a** (x mmol), **2a** (y mmol), Pd₂(dba)₃ (2 mol%), Ligand (8 mol%), Cyclohexane (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by GC-MS. ^dDetermined by HPLC.

Table S7.^a The Reaction Result by Different Experimental Operation on the Reaction during Pre-mixing of Catalyst and Substrate ^a

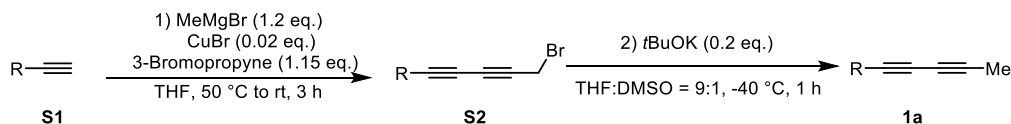


Scheme S1. Pd-catalyzed hydrosilylation of 1a and 2a under an air atmosphere or in water



3. Experimental Section

3.1 Preparation of Substrates

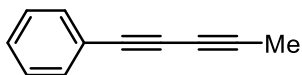


General procedure A for the synthesis of 1,3-diyne^[1-3]:

To a solution of MeMgBr (1.2 eq., 1 M in THF) was added phenylacetylene **S1** (1.0 eq.) dropwise within 2 minutes at 50 °C under nitrogen, leading to evolution of methane. After stirred at 50 °C for 1 h, the reaction mixture was allowed to cool to room temperature. CuBr (0.02 equiv.) was added quickly to the above suspension and the reaction mixture was stirred for another 15 minutes and heated to 50 °C. Then adding propargyl bromide (1.15 eq.) into the reaction mixture and keeping stirring for 90 minutes. The reaction mixture was cooled to 0 °C using an external ice-water bath and quenched by addition of a saturated solution of ammonium chloride. The phases were separated, and the aqueous phase was extracted with ethyl acetate. The collected organic phases were dried over Na₂SO₄; the solvent was evaporated, affording the crude 1,4-pentadiyn-1-benzenes, which were used without further purification.

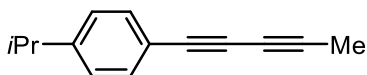
A solution of the corresponding 1,4-pentadiyn-1-benzenes in a mixture (0.3 M, 9:1 of THF and DMSO) was cooled to -40 °C. After the addition of *t*BuOK (0.02 eq.) in small portions, the reaction mixture immediately turned dark purple. Stirring was continued for 60 minutes at -40 °C. The reaction was quenched with water at -40 °C, and the resulting dark brown suspension was vigorously stirred for an additional 10 minutes. The phases were separated and the organic phase extracted three times with ether. The collected organic phases were dried over Na₂SO₄, and the solvents were evaporated under reduced pressure. After purification by column chromatography using PE as the eluent the product **1** was isolated.

penta-1, 3-diyn-1-ylbenzene



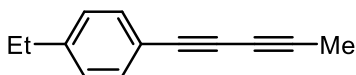
1a was synthesized following the general procedure A. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.0$ Hz, 2H), 7.37 – 7.30 (m, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.5, 128.9, 128.4, 122.1, 80.4, 74.5, 74.2, 64.4, 4.6.; HRMS (APCI) m/z Calcd for C_{11}H_8 $[\text{2M}+\text{H}]^+$: 281.1325, found: 281.1328

1-isopropyl-4-(penta-1,3-diyn-1-yl)benzene



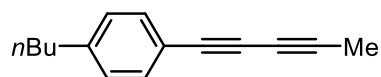
1c was synthesized following the general procedure A. White solid, mp 45.1 - 46.2 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 2.81 (m, 1H), 1.93 (s, 3H), 1.15 (d, $J = 4.0$ Hz, 6H).; ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 132.7, 126.7, 119.4, 80.0, 74.6, 73.8, 64.6, 34.3, 23.9, 4.8.; HRMS (APCI) m/z Calcd for $\text{C}_{14}\text{H}_{14}$ $[\text{M}+\text{H}]^+$: 183.1169, found: 183.1159

1-ethyl-4-(penta-1,3-diyn-1-yl)benzene



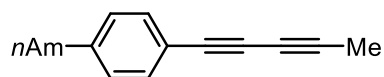
1d was synthesized following the general procedure A. Clorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 2.68 (q, $J = 8.0, 4.0$ Hz, 2H), 2.05 (s, 3H), 1.27 (t, $J = 8.0$ Hz, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 132.6, 128.0, 119.2, 80.0, 74.5, 73.9, 64.6, 28.9, 15.3, 4.6.; HRMS (ESI) m/z Calcd for $\text{C}_{13}\text{H}_{12}$ $[\text{2M}+\text{H}]^+$: 337.1951, found: 337.1729

1-butyl-4-(penta-1,3-diyn-1-yl)benzene



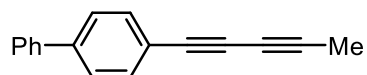
1e was synthesized following the general procedure A. Yellow solid, mp 41.6 – 43.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.02 (s, 3H), 1.60 (d, *J* = 8.0 Hz, 1H), 1.54 (d, *J* = 8.0 Hz, 1H), 1.38 – 1.28 (m, 2H), 0.91 (t, *J* = 8.0 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 132.6, 128.6, 119.2, 80.0, 77.45, 73.84, 64.57, 35.8, 33.5, 22.4, 14.1, 4.8; HRMS (APCI) *m/z* Calcd for C₁₅H₁₆[M+H]⁺ : 197.1325, found: 197.1306

1-(penta-1,3-diyne-1-yl)-4-pentylbenzene



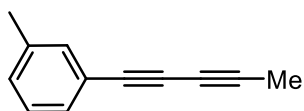
1g was synthesized following the general procedure A. White solid, mp 41.6 – 43.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 2.46 (t, *J* = 8.0 Hz, 2H), 1.86 (s, 3H), 1.51 – 1.42 (m, 2H), 1.24 – 1.14 (m, 4H), 0.77 (t, *J* = 6.7 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 132.6, 128.6, 128.6, 119.2, 80.0, 77.5, 77.2, 76.8, 74.6, 73.8, 64.58, 36.1, 31.6, 31.0, 22.7, 14.2, 4.8.; HRMS (APCI) *m/z* Calcd for C₁₅H₁₆[M+H]⁺ : 233.1481, found: 233.1202

4-(penta-1,3-diyne-1-yl)-1,1'-biphenyl



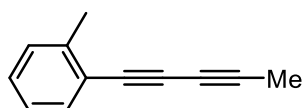
1h was synthesized following the general procedure A. White solid, mp 90.4 – 90.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.56 (m, 2H), 7.54 (s, 4H), 7.44 (m, 2H), 7.38 – 7.34 (m, 1H), 2.04 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 141.7, 140.3, 133.1, 129.0, 127.9, 127.2, 121.0, 80.8, 75.2, 74.2, 64.5, 4.8.; HRMS (ESI) *m/z* Calcd for C₁₇H₁₂[M+H]⁺ : 217.1012, found: 217.1169

1-methyl-3-(penta-1,3-diyne-1-yl)benzene



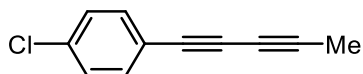
1i was synthesized following the general procedure A. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.22 – 7.16 (m, 2H), 7.13 – 7.02 (m, 2H), 2.22 (s, 3H), 1.92 (s, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 138.2, 133.1, 129.9, 129.7, 128.3, 121.9, 80.2, 74.5, 74.2, 64.5, 21.3, 4.7.; HRMS (APCI) m/z Calcd for $\text{C}_{12}\text{H}_{10}[\text{2M}+\text{H}]^+$: 309.1638, found: 309.1638

1-methyl-2-(penta-1,3-diyn-1-yl)benzene



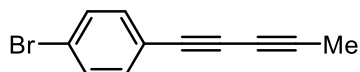
1j was synthesized following the general procedure A. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.0$ Hz, 1H), 7.22 – 7.14 (m, 2H), 7.12 – 7.07 (m, 1H), 2.42 (s, 3H), 1.99 (s, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 133.0, 129.6, 128.9, 125.7, 121.9, 81.0, 78.09, 77.5, 77.2, 76.8, 73.3, 64.5, 20.8, 4.8.; HRMS (ESI) m/z Calcd for $\text{C}_{12}\text{H}_{10}[\text{2M}+\text{H}]^+$: 309.1638, found: 309.1638

1-chloro-4-(penta-1,3-diyn-1-yl)benzene



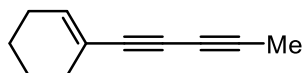
1k was synthesized following the general procedure A. White solid. mp 73.1 – 76.9 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.02 (s, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 135.1, 133.9, 128.9, 120.7, 81.1, 75.5, 73.1, 64.3, 4.8.; HRMS (ESI) m/z Calcd for $\text{C}_{12}\text{H}_{10}[\text{2M}+\text{H}]^+$: 349.0545, found: 349.0592

1-bromo-4-(penta-1,3-diyn-1-yl)benzene



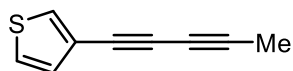
11 was synthesized following the general procedure A. White solid. mp 60.0 – 68.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 134.0, 131.8, 123.4, 121.2, 81.2, 75.7, 73.1, 64.3, 4.8.; HRMS (ESI) *m/z* Calcd for C₁₂H₁₀[2M+H]⁺ : 436.9535, found: 436.9546

1-(penta-1,3-diyn-1-yl)cyclohex-1-ene

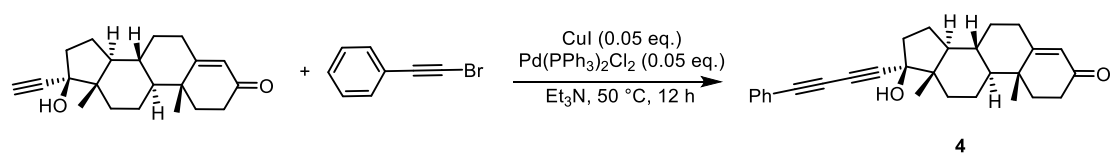


1n was synthesized following the general procedure A. Yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.27 – 6.06 (m, 1H), 2.11 – 2.02 (m, 4H), 1.93 (s, 3H), 1.62 – 1.50 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 138.0, 119.8, 79.0, 76.2, 71.8, 64.5, 28.8, 25.9, 22.2, 21.4, 4.5.; HRMS (ESI) *m/z* Calcd for C₁₂H₁₀[M+Na]⁺ : 167.0831, found: 167.0790

3-(penta-1,3-diyn-1-yl)thiophene



1o was synthesized following the general procedure A. Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 4.0 Hz, 1H), 7.16 (t, *J* = 4.0 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 1.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 130.9, 130.3, 125.5, 121.1, 80.3, 77.5, 77.2, 76.8, 74.1, 69.4, 64.4, 4.7.; HRMS (APCI) *m/z* Calcd for C₁₂H₁₀[M+H]⁺ : 147.0263, found: 147.0256

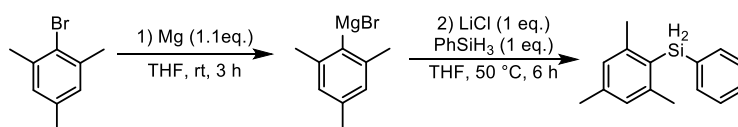


A reaction flask was charged with CuI (9.6 mg, 0.10 mmol), Pd(PPh₃)₂Cl₂ (30.4 mg, 0.10 mmol), ethisterone (138 mg, 2 mmol) and degassed Et₃N (5.0 mL) under nitrogen. The bromoethynyl benzene (4 mmol) was then added to the reaction mixture

and stirred 12 h at 50 °C.

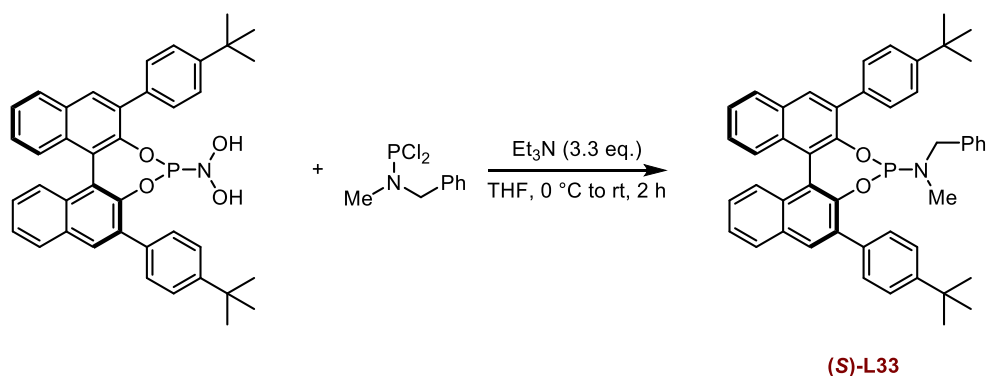
After completion of the reaction, the mixture was passed through a short celite pad using DCM as a solvent. The mixture was then concentrated in vacuo and purified by column chromatography using Petroleum ether-EtOAc (8:1) to give the desired product **4** in good yields^[4].

General procedure B for the synthesis of dihydrosilanes and chiral phosphoramidite ligand.



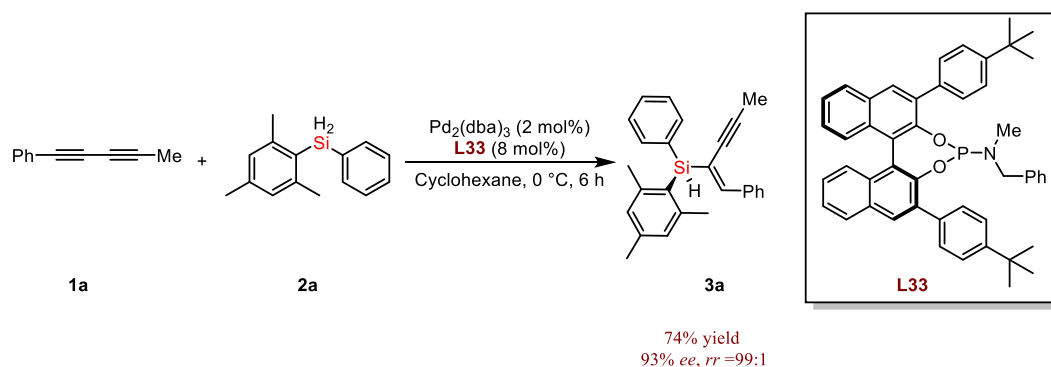
A flame dried 200 mL, round bottom flask equipped with a water-cooled condenser were added magnesium turnings (1.1 eq.), three pieces of iodine partials, THF under nitrogen. 2-bromo-1,3-diethyl-5-methylbenzene (1.0 eq.) was added slowly over 15 minutes to the refluxing mixture of THF and magnesium turnings. Following that, the mixture was refluxed for an additional 2 hour. The resulting Grignard reagent was cooled to 25 °C for the following procedure. To a suspension of LiCl (2.0 eq., 0.5 M in THF) was added the Grignard reagent (0.97 M in THF), followed by the addition of phenylsilane (1 eq.), at room temperature under argon. After the reaction mixture was stirred in an oil bath maintained at 50 °C for 6 h, the reaction was quenched by the addition of an aqueous solution of NH₄Cl (10 mL) at room temperature. The resulting mixture was filtered through Celite and washed with ethyl acetate (20 mL * 3). The organic phase was dried over Na₂SO₄ and concentrated in vacuum to give the crude product, which was purified by chromatography on silica gel eluting with PE to afford the title compound (2.6g, 51% yield) as colorless oil^[5].

(11bS)-N-benzyl-2,6-bis(4-(tert-butyl)phenyl)-N-methyldinaphtho[2,1-d:1',2'f][1,3,2]-dioxaphosphin-4-amine



To a solution of *N*-methyl-1-phenylmethanamine (484.7 mg, 4.0 mmol) in dry THF (3 mL) was added *n*BuLi (2.5 M in hexanes, 1.6 mL, 4 mmol) dropwise at 0 °C over 3 min under argon atmosphere and the mixture was stirring at 0 °C for 30 minutes. PCl₃ (1.05 mL, 12.0 mmol) was added to the reaction mixture in one portion. The resulting mixture was warmed to room temperature, stirred for 1 h, and then concentrated at room temperature. The remaining PCl₃ was removed under vacuum. Dry THF (6 mL) was then added to the resulting residue. After stirring for 10 min, the mixture was cooled to 0 °C, followed by addition of a solution of *N*-((11*b*S)-2,6-bis(4-(tert-butyl)phenyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-*N*-hydroxyhydroxylamine (1255.4 mg, 2.0 mmol) and Et₃N (667.9 mg, 6.6 mmol) in dry THF (15 mL) over 2 min. The mixture was warmed to room temperature and stirred 2 h. Then it was filtered and the solid was washed with DCM. The residue was purified by chromatography on silica gel, eluting with PE: EA = 100:1 to afford the products as white solid. White solid, mp 145.1 - 146.2 °C, $[\alpha]_D^{25} = +175.7$ (*c* = 0.32, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 12.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.70 (d, *J* = 8.0 Hz, 4H), 7.52 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.49 – 7.37 (m, 4H), 7.32 – 7.21 (m, 2H), 7.17 – 7.13 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.56 – 3.45 (m, 1H), 3.33 – 3.19 (m, 1H), 1.77 (d, *J* = 8.0 Hz, 3H), 1.40 (d, *J* = 4.0 Hz, 18H).; ¹³C NMR (100 MHz, CDCl₃) δ 150.5, 150.4, 147.5, 147.3, 138.4, 138.3, 135.4, 135.1, 135.0, 134.2, 132.5, 132.3, 131.4, 131.1, 130.4, 130.0, 130.0, 129.9, 129.8, 128.5, 128.5, 128.2, 127.5, 127.2, 127.0, 126.9, 126.1, 126.0, 125.2, 125.1, 125.0, 124.4, 50.7, 34.8, 31.6, 31.6, 31.3, 31.1.; ³¹P NMR (162 MHz, CDCl₃) δ 143.78. HRMS (ESI) *m/z* Calcd for C₄₈H₄₆NO₂P [M+H]⁺ : 700.3339, found: 700.3346

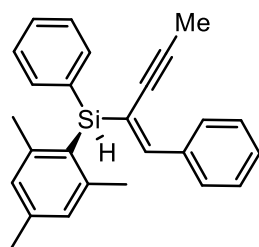
General Procedure C for the Synthesis of **3a** by Hydrosilylation of 1,3-Diynes:



In a flame dried Schlenk tube, $\text{Pd}_2(\text{dba})_3$ (3.7 mg, 0.004 mmol, 2 mol%), **L33** (11.2 mg, 0.016 mmol, 8 mol%) in cyclohexane (1 mL, 0.2M) was stirred at room temperature for 30 min under nitrogen atmosphere. Then diyne (0.2 mmol, 1 equiv.), dihydrosilanes were added sequentially to the reaction mixture, and the reaction tube was cooled at 0 °C and then stirred for 6 h. After completion of the reaction, the mixture was passed through a short celite pad using DCM as a solvent. The mixture was then concentrated in vacuo and purified by column chromatography using Petroleum ether-EtOAc (300:1) to give the desired product **3a** in good yields.

3.2 Synthesis of hydrosilylation of 1,3-Diynes

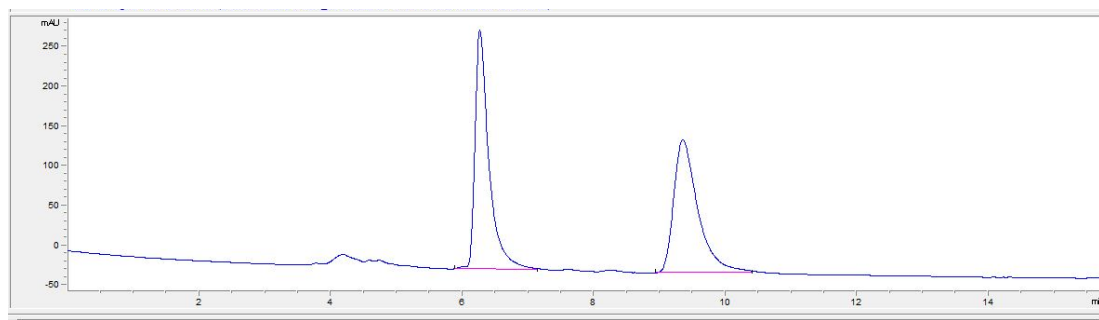
(*S,E*)-mesityl(phenyl)(1-phenylpent-1-en-3-yn-2-yl)silane:



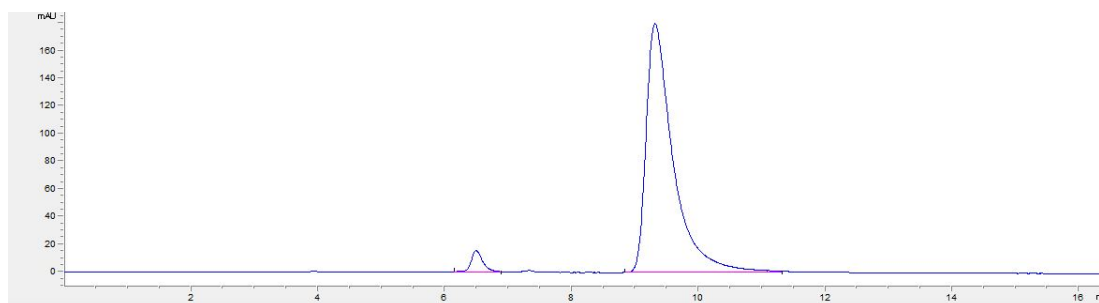
3a was synthesized following the general procedure C. Yellow liquid (51.2 mg, 70% yield). purified by column chromatography (Al_2O_3 , PE/EA= 300:1). $[\alpha]_{25}^D = 7.54$ ($c = 0.14$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.32 – 7.16 (m, 6H), 7.32 – 7.17 (m, 3H), 2.30 (s, 6H), 2.22 (s, 3H), 1.95 (s, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 145.8, 140.1, 137.7, 135.7, 134.0, 129.5, 128.9, 128.8, 128.7, 128.3, 128.1, 126.6, 118.8, 99.0, 80.6, 24.5, 21.4, 5.4.; ^{29}Si

NMR(500MHz, CDCl₃) δ 21.9.; IR (KBr, cm⁻¹): 2928.3, 2852.9, 2147.3, 1450.6, 1258.7, 1029.1, 847.9, 795.5, 739.3. HRMS (APCI) m/z Calcd for C₂₆H₂₆Si [M+H]⁺: 367.1877, found: 367.1864.

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 93% ee). tR = 9.317 min (major), tR = 6.497 min (minor).

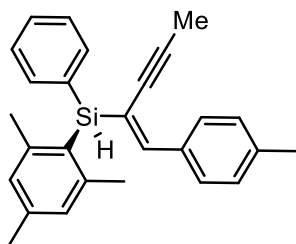


	Time/min	Area	Height	Area%
1	6.267	4425.5	300.8	50.623
2	9.352	4316.5	167.6	49.377



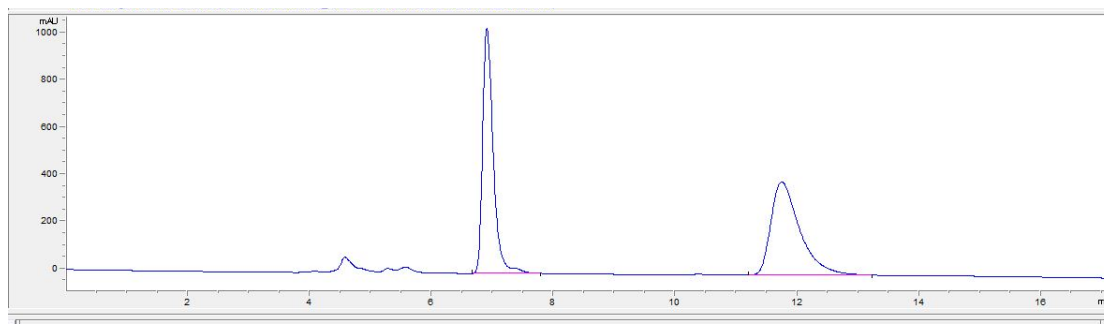
	Time/min	Area	Height	Area%
1	6.497	203.8	15.6	3.670
2	9.317	5348.9	179.7	96.330

(*S,E*)-mesityl(phenyl)(1-(*p*-tolyl)pent-1-en-3-yn-2-yl)silane

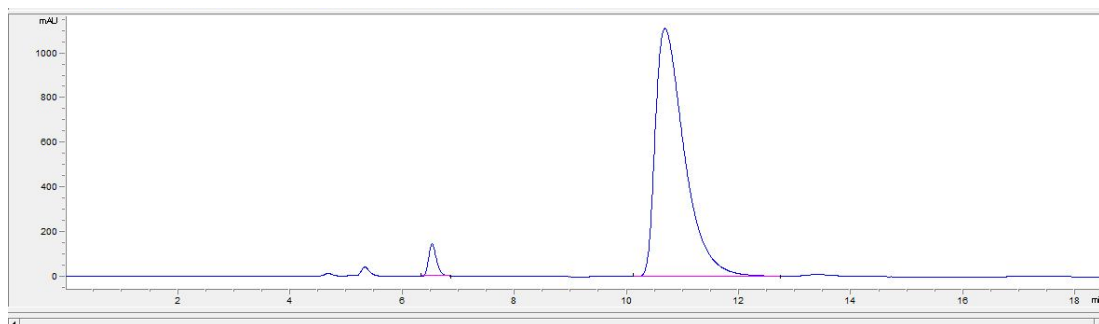


3b was synthesized following the general procedure C. Yellow liquid (66.2 mg, 87% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). [α]₂₅^D = 3.52 (c = 0.38, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.45 - 7.35 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 2H), 6.88 (s, 1H), 5.55 (s, 1H), 2.42 (s, 6H), 2.38 (s, 3H), 2.34 (s, 3H), 2.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 145.8, 140.1, 138.8, 135.7, 135.2, 134.1, 129.5, 129.0, 128.9, 128.8, 128.0, 126.7, 117.3, 98.5, 80.8, 24.5, 21.6, 21.4, 5.4; IR (KBr, cm⁻¹): 2927.3, 2859.5, 2147.3, 1612.4, 1432.2, 1258.7, 1025.2, 855.6, 787.8, 735.5, 622.1. HRMS (ESI) *m/z* Calcd for C₂₇H₂₈Si [M+H]⁺: 381.2034, found: 381.2255.

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 93% *ee*). tR = 10.682 min (major), tR = 6.53 min (minor).

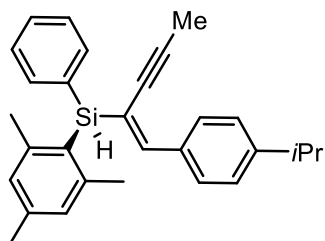


	Time/min	Area	Height	Area%
1	6.908	12708.7	1037.3	49.250
2	11.748	13095.7	394.6	50.750



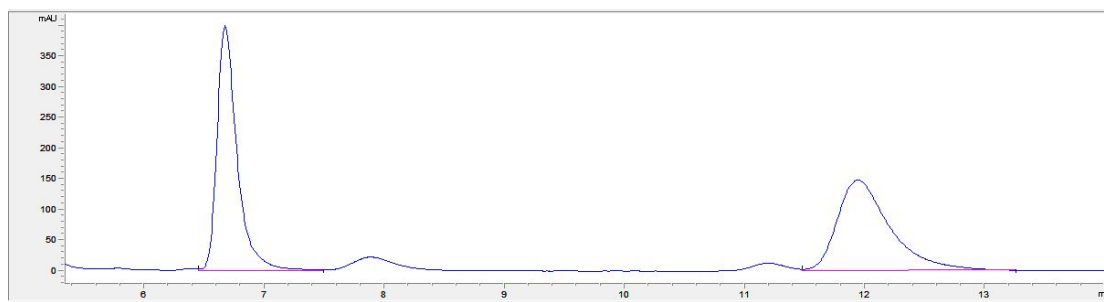
	Time/min	Area	Height	Area%
1	6.53	1444.3	144.8	3.490
2	10.682	39941.6	1112.6	96.510

(*S,E*)-(1-(4-isopropylphenyl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

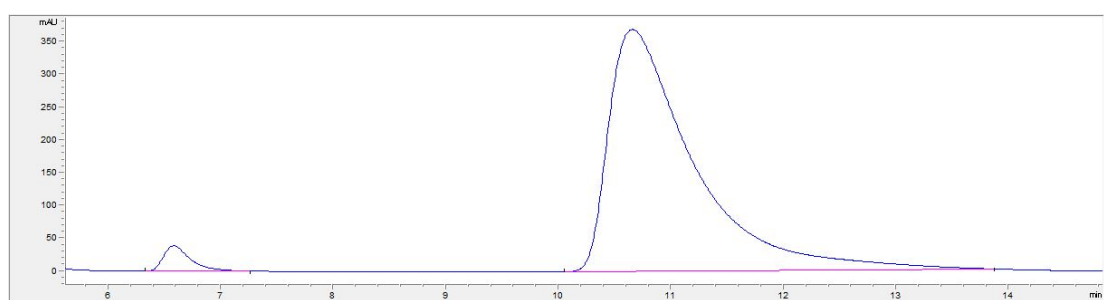


3c was synthesized following the general procedure C. White liquid (67.0 mg, 82% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). [α]₂₅^D = 0.8(c = 0.531, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.80 (m, 2H), 7.73 – 7.54 (m, 21H), 7.44 – 7.28 (m, 3H), 7.23 – 7.18 (m, 2H), 6.86 (s, 1H), 6.84 (s, 2H), 5.49 (s, 1H), 2.98 – 2.77 (m, 1H), 2.37 (s, 6H), 2.30 (s, 3H), 2.03 (s, 3H), 1.24 (d, J = 8.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 147.4, 145.9, 140.1, 135.7, 135.6, 134.2, 129.5, 128.9, 128.0, 126.7, 126.4, 117.3, 98.5, 80.8, 34.2, 29.9, 24.5, 24.0, 21.4, 5.4.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.3.; IR (KBr, cm⁻¹): 2968.0, 1416.7, 1266.5, 1076.6, 1013.6, 791.7, 705.4, 659.8. HRMS (ESI) m/z Calcd for C₂₉H₃₂Si [M+Na]⁺ : 431.2165 , found: 431.2172

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 93% ee). tR = 10.656 min (major), tR = 6.58 min (minor).

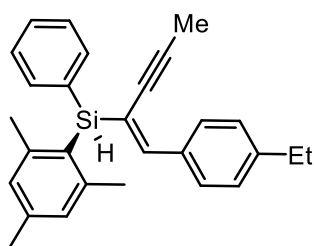


	Time/min	Area	Height	Area%
1	6.674	11847.5	974.3	49.816
2	11.941	11935.2	388	50.184



	Time/min	Area	Height	Area%
1	6.58	654.3	38.8	3.261
2	10.656	19414.3	369	96.739

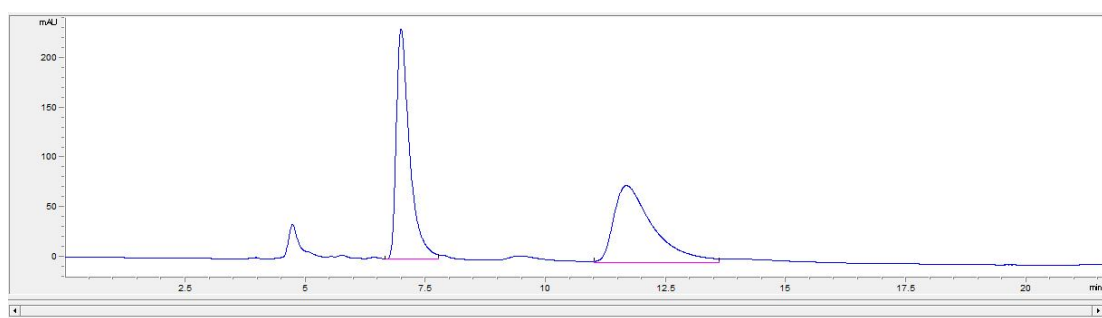
(*S,E*)-1-(4-ethylphenyl)pent-1-en-3-yn-2-yl(mesityl)(phenyl)silane



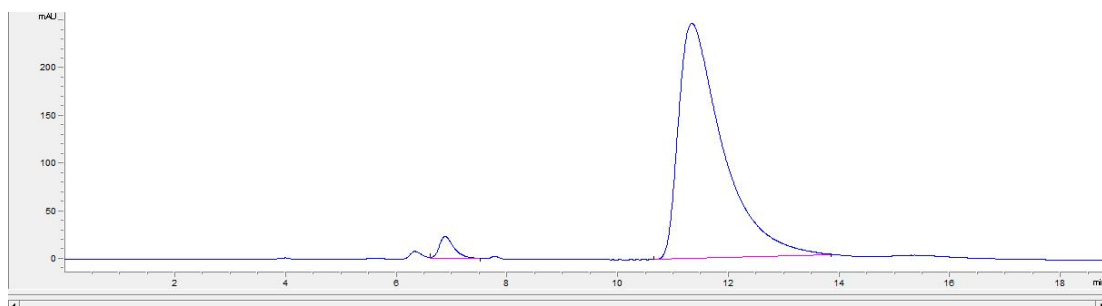
3d was synthesized following the general procedure C. White liquid (53.7 mg, 68% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 2.49$ (c = 0.42, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 4.0 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 2H), 6.85 (s, 1H), 5.51 (s, 1H), 2.66 (q, *J* = 8.0 Hz, *J* = 16.0 Hz, 2H), 2.38 (s, 6H), 2.31 (s, 3H), 2.05 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 145.8, 145.2, 140.1,

135.7, 135.4, 134.2, 129.5, 128.9, 128.0, 127.8, 126.7, 117.3, 98.5, 80.8, 29.9, 28.9, 24.5, 21.4, 15.6, 5.4.; ^{29}Si NMR(500MHz, CDCl_3) δ 26.9.; IR (KBr, cm^{-1}):2961.2, 2923.4, 2859.5, 2147.3, 1458.3, 1021.3, 851.7, 791.7, 729.7, 620.2. HRMS (APCI) m/z Calcd for $\text{C}_{28}\text{H}_{30}\text{Si}$ $[\text{M}+\text{H}]^+$: 395.2190 , found: 395.2163

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 94% *ee*). t_R = 11.334 min (major), t_R = 6.876 min (minor).

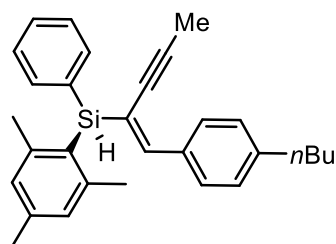


	Time/min	Area	Height	Area%
1	6.988	4461.3	231.3	50.255
2	11.68	4421.5	77.6	49.775

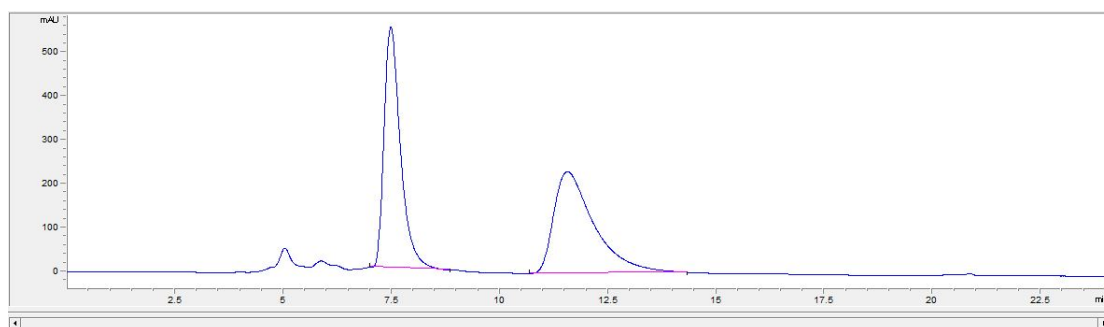


	Time/min	Area	Height	Area%
1	6.876	466.7	23.9	3.298
2	11.334	13684.4	246.5	96.702

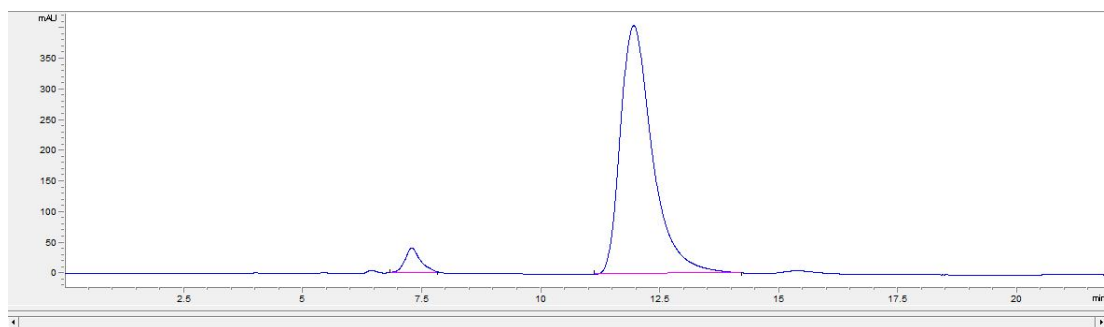
(*S,E*)-(1-(4-butylphenyl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



3e was synthesized following the general procedure C. White liquid (46.4 mg, 55% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). [α]₂₅^D = 1.52 (c = 0.21, CHCl₃) ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.93 (s, 2H), 6.91 (s, 1H), 5.58 (s, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 6H), 2.36 (s, 3H), 2.10 (s, 3H), 1.71 – 1.61 (m, 2H), 1.41 (dd, *J* = 12.0, 8.0 Hz, 2H), 0.99 (t, *J* = 8.0 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 145.8, 143.8, 140.0, 135.6, 135.4, 134.2, 129.5, 128.9, 128.8, 128.4, 128.0, 126.7, 117.2, 98.5, 80.8, 35.7, 33.6, 24.5, 22.5, 21.3, 14.1, 5.4.; IR (KBr, cm⁻¹): 2955.4, 2930.2, 2859.5, 2143.4, 1462.2, 1104.7, 1025.2, 795.5, 739.3, 610.5. HRMS (ESI) *m/z* Calcd for C₃₀H₃₄Si [M+Na]⁺ : 445.2322 , found: 445.2256
HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 91% *ee*). tR = 11.95 min (major), tR = 7.282 min (minor).



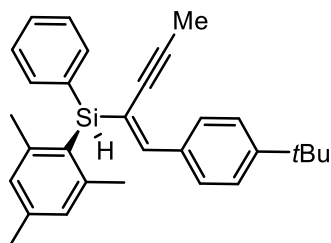
	Time/min	Area	Height	Area%
1	7.485	14549.2	548.7	49.222
2	11.566	15008.8	231.8	50.778



	Time/min	Area	Height	Area%
1	7.282	14549.2	548.7	49.222
2	11.95	15008.8	231.8	50.778

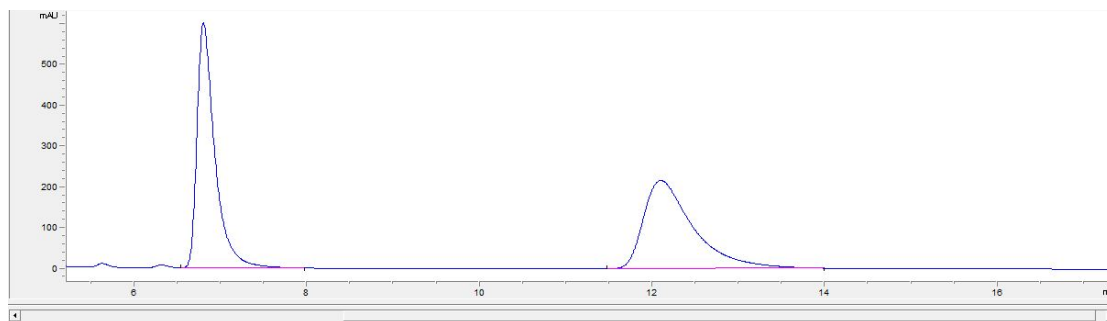
1	7.282	953.9	40.4	4.781
2	11.95	18996.4	404.8	95.219

(*S,E*)-(1-(4-(*tert*-butyl)phenyl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

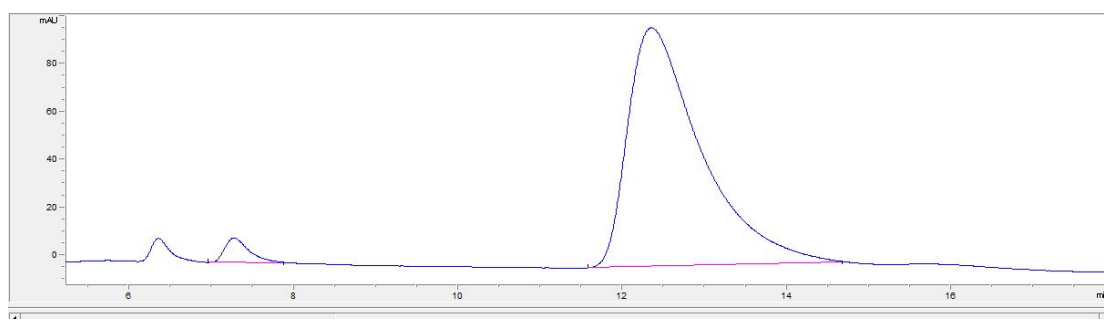


3f was synthesized following the general procedure C. White liquid (35.5 mg, 42% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 1.06$ (c = 0.29, CHCl₃) ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.46 - 7.32 (m, 5H), 6.89 (s, 2H), 6.87 (s, 1H), 5.52 (s, 1H), 2.39 (s, 6H), 2.32 (s, 3H), 2.06 (s, 3H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 151.9, 147.2, 145.9, 140.1, 135.7, 135.1, 134.2, 129.5, 128.9, 128.6, 128.0, 126.7, 125.3, 117.5, 98.6, 80.8, 34.9, 31.4, 24.5, 21.4, 5.4.; IR (KBr, cm⁻¹): 3367.2, 2961.2, 2923.4, 2855.6, 2147.3, 1612.4, 1270.3, 1107.6, 1021.3, 794.6, 607.6. HRMS (APCI) *m/z* Calcd for C₃₀H₃₄Si [M+H]⁺ : 423.2530 , found: 423.2462

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 93% *ee*). *t*R = 11.07 min (major), *t*R = 6.597 min (minor).

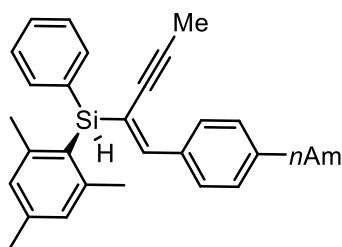


	Time/min	Area	Height	Area%
1	6.801	8715.7	602	50.127
2	12.099	8671.6	216.4	49.873



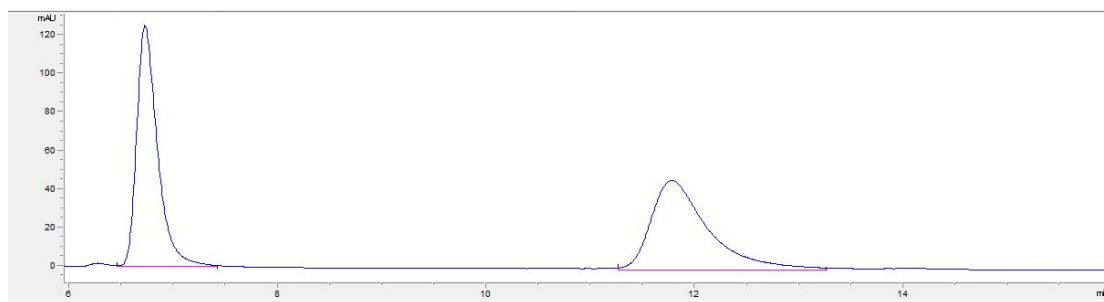
	Time/min	Area	Height	Area%
1	6.597	500.6	25.9	3.645
2	11.07	13234	226.8	96.355

(*S,E*)-mesityl(1-(4-pentylphenyl)pent-1-en-3-yn-2-yl)(phenyl)silane

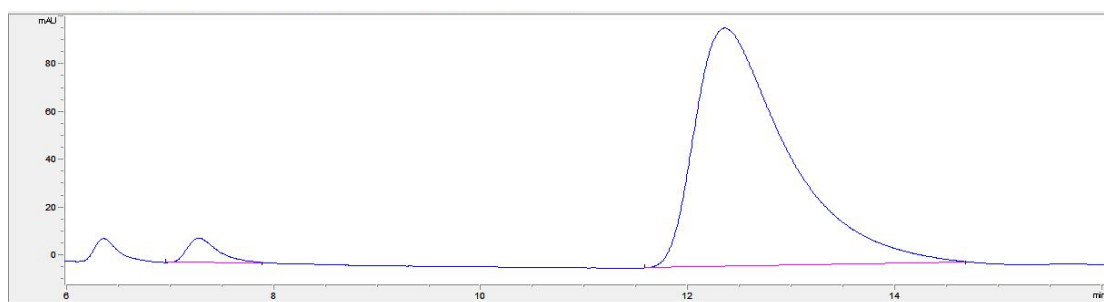


3g was synthesized following the general procedure C. Yellow liquid (34.9 mg, 40% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 2.68$ (c = 0.40, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.23 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 2H), 6.76 (s, 1H), 5.42 (s, 1H), 2.56 - 2.43 (m, 2H), 2.29 (s, 6H), 2.21 (s, 3H), 1.95 (s, 3H), 1.57 - 1.49 (m, 2H), 1.26 - 1.20 (m, 4H), 0.80 (t, *J* = 6.0 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 145.8, 143.9, 140.1, 135.7, 135.4, 134.2, 129.5, 128.9, 128.8, 128.4, 128.0, 126.7, 117.2, 98.6, 80.8, 77.5, 77.2, 76.8, 36.0, 31.6, 31.2, 24.5, 22.7, 21.4, 14.2, 5.4.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.4.; IR (KBr, cm⁻¹): 2930.2, 2851.7, 2151.2, 1466.1, 1021.3, 791.7, 742.2, 622.1. HRMS (ESI) *m/z* Calcd for C₃₁H₃₆Si [M+H]⁺ : 437.2659, found: 437.2335

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 ml/min, 230 nm, 93% *ee*). *t*R = 12.355 min (major), *t*R = 7.273 min (minor).

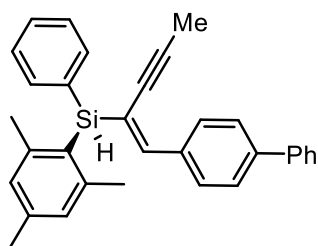


	Time/min	Area	Height	Area%
1	6.727	1738.2	125.3	49.005
2	11.78	1808.7	46.8	50.995



	Time/min	Area	Height	Area%
1	7.273	214.1	10.3	3.341
2	12.355	6195.8	99.8	96.659

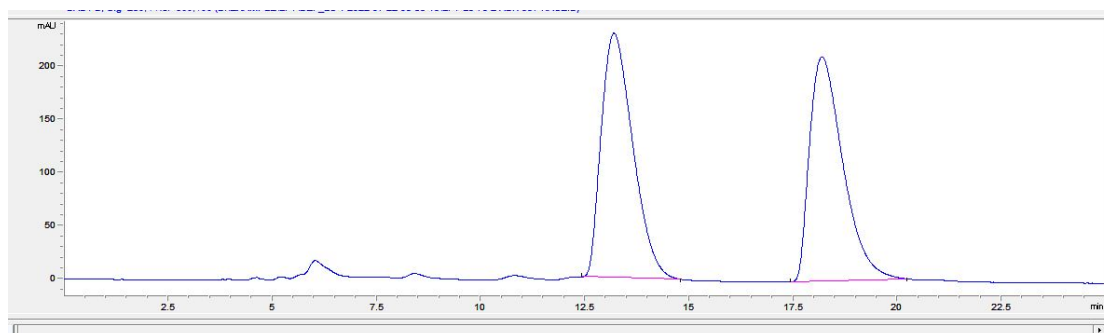
(*S,E*)-(1-([1,1'-biphenyl]-4-yl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



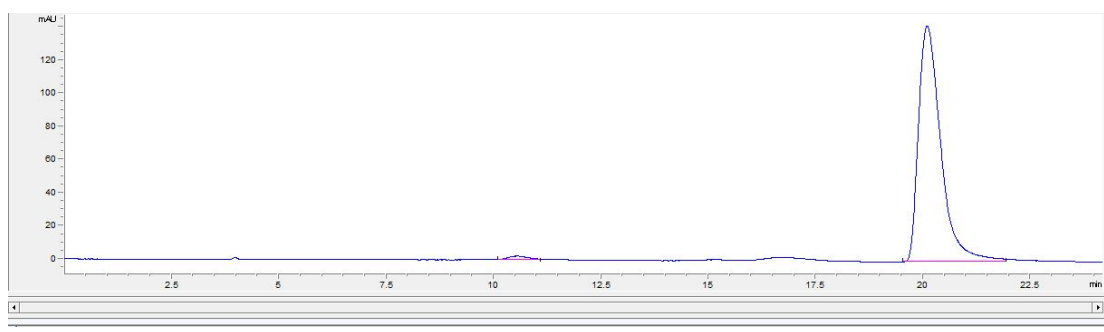
3h was synthesized following the general procedure C. Yellow liquid (77.8 mg, 88% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 39.9$ (c = 4.47, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 8.0 Hz, 4H), 7.49 – 7.42 (m, 3H), 7.41 – 7.35 (m, 3H), 6.92 (s,

1H), 6.91 (s, 2H), 5.55 (s, 1H), 2.42 (s, 6H), 2.33 (s, 3H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 145.9, 141.3, 140.8, 140.2, 136.8, 135.7, 134.0, 129.6, 129.2, 128.9, 128.9, 128.1, 127.6, 127.2, 127.0, 126.6, 118.9, 99.4, 80.8, 24.6, 21.4, 5.5.; IR (KBr, cm⁻¹): 2964.1, 2927.3, 2855.6, 2142.4, 1462.2, 1266.5, 1009.7, 791.7; HRMS (ESI) m/z Calcd for C₃₂H₃₀Si [M+H]⁺ : 443.219, found: 443.2007

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 98% ee). tR = 20.097min (major), tR = 10.2546 min (minor).

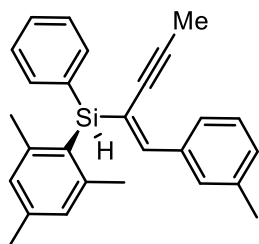


	Time/min	Area	Height	Area%
1	13.199	12108.1	229.8	50.610
2	18.194	11816.1	211.4	49.390



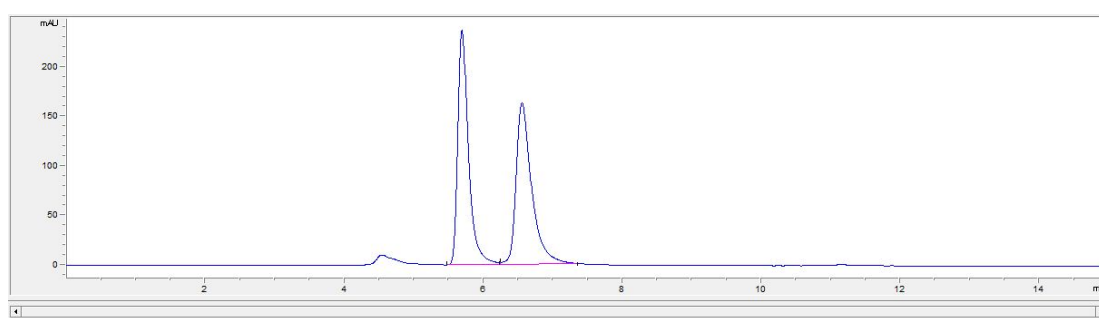
	Time/min	Area	Height	Area%
1	10.546	63	2	1.220
2	20.097	5102.7	141.9	98.780

(*S,E*)-mesityl(phenyl)(1-(*m*-tolyl)pent-1-en-3-yn-2-yl)silane

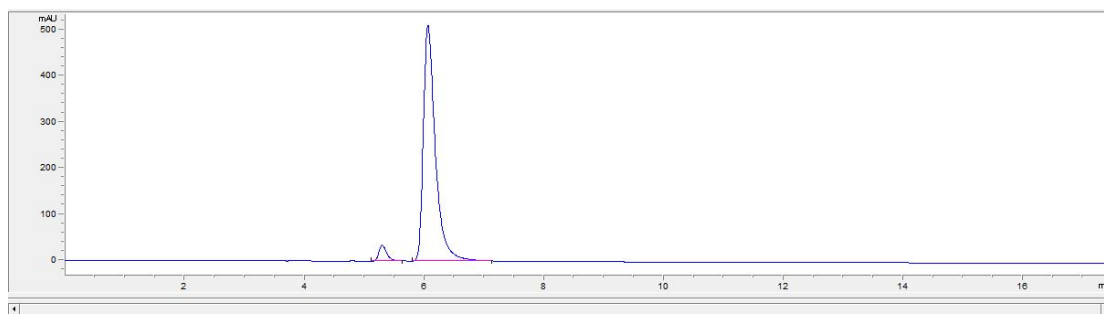


3i was synthesized following the general procedure C. Yellow liquid (36.5 mg, 48% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 4.01$ (c = 0.48, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 2H), 6.85 (s, 1H), 5.52 (s, 1H), 2.38 (s, 6H), 2.34 (s, 3H), 2.30 (s, 3H), 2.04 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 145.8, 140.1, 137.7, 137.7, 135.7, 134.0, 129.6, 129.5, 128.9, 128.2, 128.0, 126.6, 125.8, 118.4, 98.8, 80.8, 29.9, 24.5, 21.6, 21.4, 5.4.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.4.; IR (KBr, cm⁻¹):2927.3, 2850.8, 2151.2, 1612.4, 1266.5, 1025.2, 915.7, 791.7, 723.8, 689.9. HRMS (ESI) m/z Calcd for C₃₀H₃₄Si [M+H]⁺ : 423.2503, found: 423.2692

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 91% *ee*). tR = 6.063 min (major), tR = 5.299 min (minor).

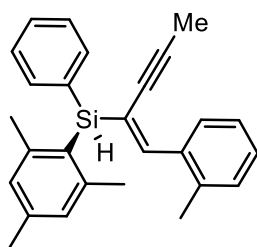


	Time/min	Area	Height	Area%
1	5.595	2527.9	236.9	49.540
2	6.557	2574.9	163.3	50.460

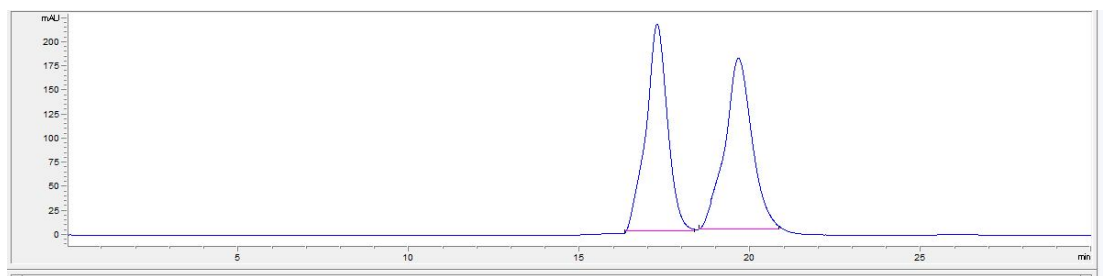


	Time/min	Area	Height	Area%
1	5.299	319.5	34.2	4.300
2	6.063	7110.4	510.7	95.700

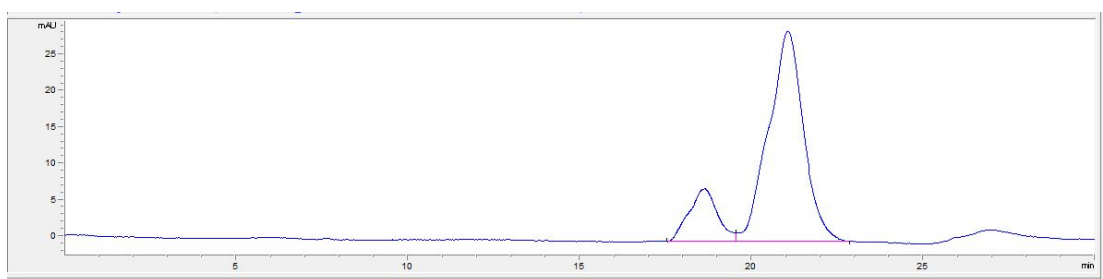
(*S,E*)-mesityl(phenyl)(1-(*o*-tolyl)pent-1-en-3-yn-2-yl)silane



3j was synthesized following the general procedure C. Yellow liquid (23.6 mg, 31% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). [α]₂₅^D = 39.9 (c = 4.47, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.60 (m, 2H), 7.43 – 7.31 (m, 3H), 7.31 – 7.23 (m, 1H), 7.19 – 7.12 (m, 2H), 7.12 – 7.05 (m, 1H), 6.86 (s, 2H), 6.41 (m, 1H), 5.49 (s, 1H), 2.38 (s, 6H), 2.29 (s, 3H), 2.23 (s, 3H), 2.10 (d, J = 8.0 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 145.8, 143.9, 140.1, 135.7, 135.4, 134.2, 129.5, 128.9, 128.8, 128.4, 128.0, 126.7, 117.2, 98.6, 80.8, 77.5, 77.2, 76.8, 36.0, 31.6, 31.2, 24.5, 22.7, 21.4, 14.2, 5.4.; IR (KBr, cm⁻¹): 2964.1, 2859.5, 1253.9, 1077.5, 1006.8, 791.7, 699.6. HRMS (ESI) m/z Calcd for C₂₇H₂₈Si [M+H]⁺ : 423.2503, found: 423.2201
HPLC: Chiralpak Phenomenex column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 76% ee). tR = 21.053 min (major), tR = 18.638 min (minor).

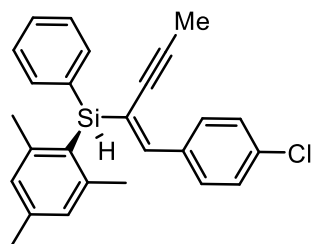


	Time/min	Area	Height	Area%
1	17.265	9454	215.7	49.135
2	19.656	9786.8	177.3	50.865



	Time/min	Area	Height	Area%
1	18.638	427.8	7.3	17.241
2	21.053	2053.3	2.9	82.759

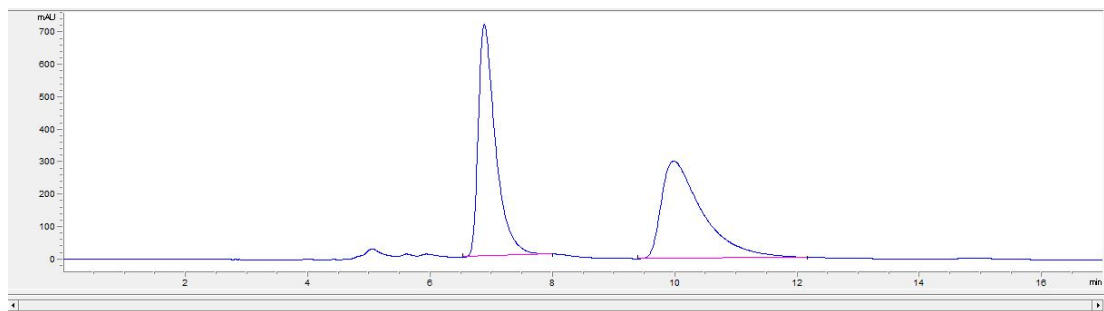
(*S,E*)-(1-(4-chlorophenyl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



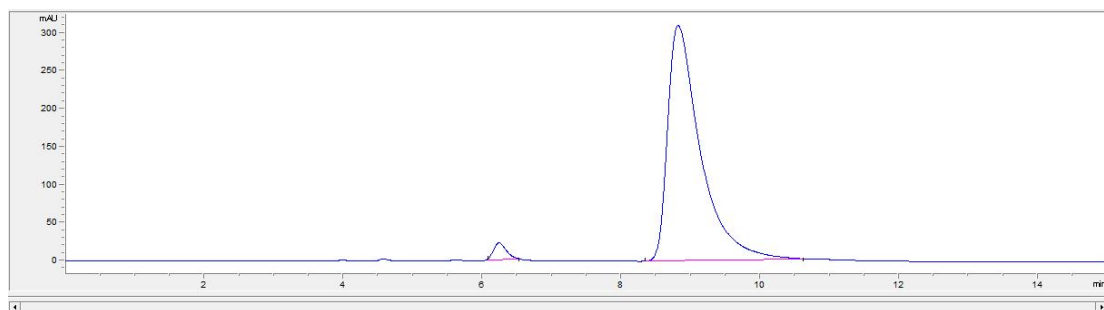
3k was synthesized following the general procedure C. Yellow liquid (56.0 mg, 70% yield). purified by column chromatography (Al_2O_3 , PE/EA= 300:1). $[\alpha]_{25}^D = 1.01$ ($c = 0.27$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.36 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.90 (s, 2H), 6.83 (s, 1H), 5.53 (s, 1H), 2.40 (s, 6H), 2.33 (s, 3H), 2.06 (s, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 145.8, 145.8, 140.2, 136.2, 135.6, 134.1, 133.7, 130.0, 129.6, 128.9, 128.5, 128.1, 126.4, 119.8,

99.8, 80.4, 24.5, 21.4, 5.4.; IR (KBr, cm^{-1}): 2927.3, 2147.3, 1604.7, 1492.2, 1428.3, 1093.0, 919.6, 791.7, 736.2. HRMS (ESI) m/z Calcd for $\text{C}_{30}\text{H}_{34}\text{Si}$ $[\text{M}+\text{Na}]^+$: 423.1414, found: 423.1448

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 94% *ee*). t_R = 8.822 min (major), t_R = 6.241 min (minor).

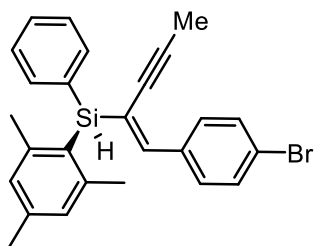


	Time/min	Area	Height	Area%
1	6.881	14063.4	716.4	50.057
2	9.978	14031.6	300.2	49.943



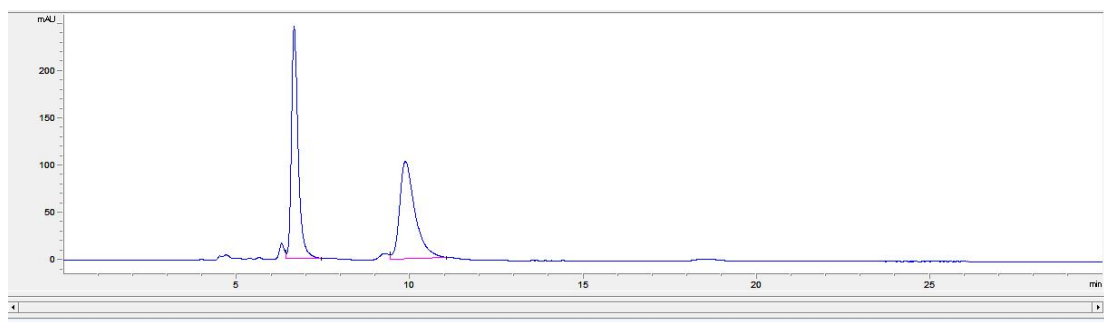
	Time/min	Area	Height	Area%
1	6.241	314.6	23.4	2.995
2	8.822	10190	310.5	97.005

(*S,E*)-(1-(4-bromophenyl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

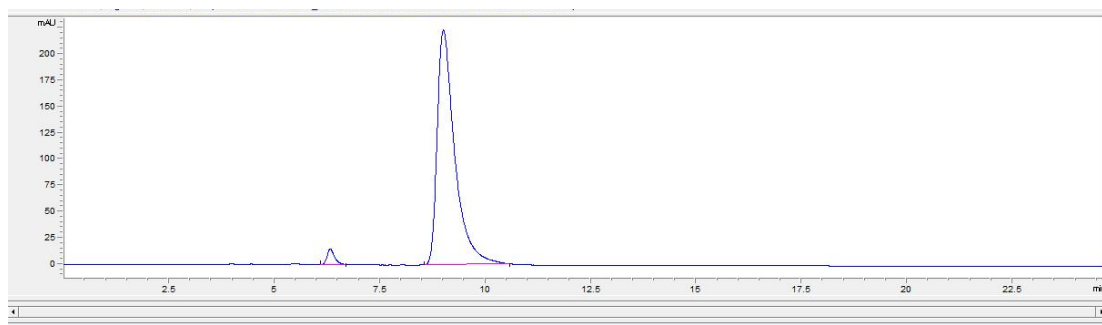


3I was synthesized following the general procedure C. Yellow liquid (30.3 mg, 34% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 0.88$ (c = 0.37, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.43 - 7.35 (m, 3H), 6.90 (s, 2H), 6.81 (s, 1H), 5.52 (s, 1H), 2.40 (s, 6H), 2.32 (s, 3H), 2.05 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 140.2, 136.5, 135.6, 133.7, 131.4, 130.2, 129.6, 128.9, 128.1, 126.3, 122.4, 120.1, 100.0, 80.4, 29.9, 24.5, 21.4, 5.4.; IR (KBr, cm⁻¹): 2927.3, 2855.1, 2147.3 1462.2, 1077.5, 1013.6, 791.7, 739.3. HRMS (APCI) *m/z* Calcd for C₂₆H₂₅BrSi [M+H]⁺ : 445.0982, found: 445.2832

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 95% *ee*). *t*_R = 9.006 min (major), *t*_R = 6.324 min (minor).

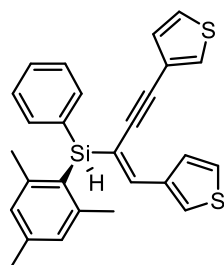


	Time/min	Area	Height	Area%
1	6.654	3289.7	246.6	50.826
2	9.865	3182.8	103.3	49.174



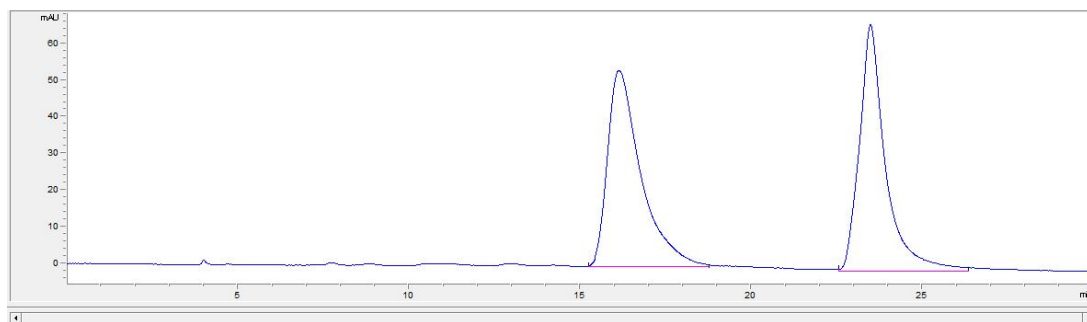
	Time/min	Area	Height	Area%
1	6.324	184.1	14.8	2.753
2	9.006	6503.3	223.9	97.247

(*S,E*)-(1,4-di(thiophen-3-yl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

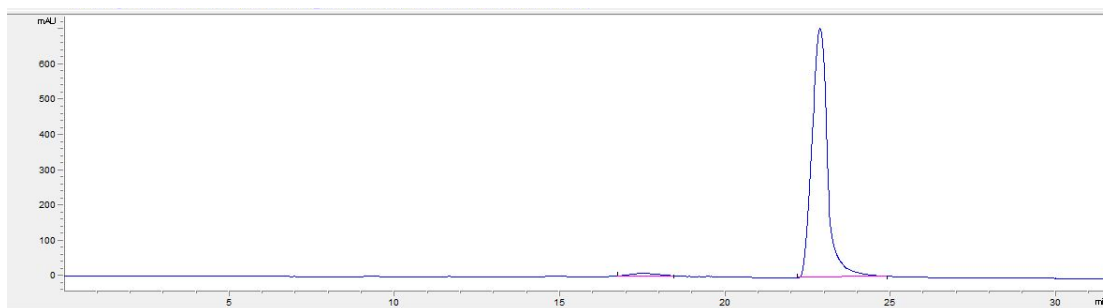


3m was synthesized following the general procedure C. Yellow liquid (58.2 mg, 66% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = -4.72$ (c = 2.03, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.87 (m, 1H), 7.78 – 7.73 (m, 1H), 7.72 – 7.65 (m, 2H), 7.45 – 7.33 (m, 3H), 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 7.01 (s, 1H), 7.00 – 6.95 (m, 1H), 6.89 (s, 2H), 5.59 (s, 1H), 2.41 (s, 6H), 2.30 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 141.6, 140.4, 140.2, 135.7, 133.6, 129.6, 129.6, 128.9, 128.2, 128.2, 128.1, 126.45, 126.4, 125.4, 125.2, 123.1, 115.5, 96.3, 90.8, 24.7, 21.4.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.8.; IR (KBr, cm⁻¹): 3102.7, 2921.6, 2851.7, 2147.3, 1428.3, 1104.7, 843.9, 773.3, 735.5. HRMS (ESI m/z Calcd for C₂₇H₂₄S₂Si [M+Na]⁺ : 463.0981 found: 463.0949

HPLC: Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 95% ee). tR =22.864 min (major), tR = 17.53 min (minor).

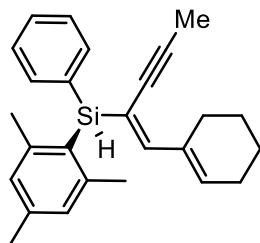


	Time/min	Area	Height	Area%
1	16.136	3659.3	53.9	50.443
2	23.485	3595.1	67.5	49.557



	Time/min	Area	Height	Area%
1	17.53	575.5	8.9	2.444
2	22.864	22970.2	706.5	97.556

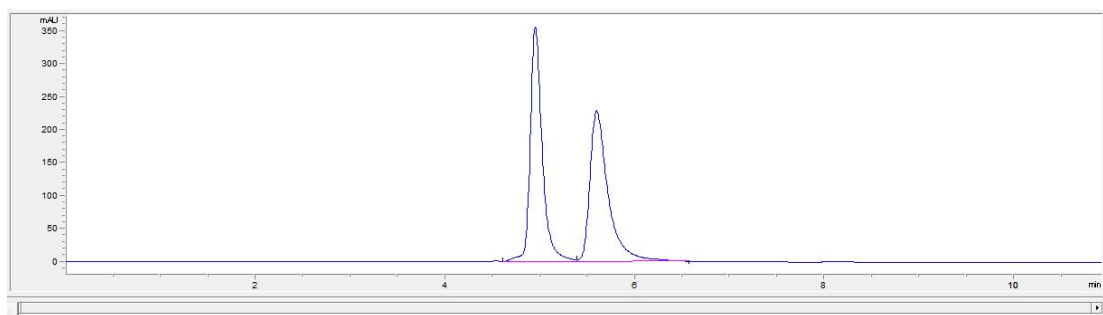
(*S,E*)-(1-(cyclohex-1-en-1-yl)pent-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



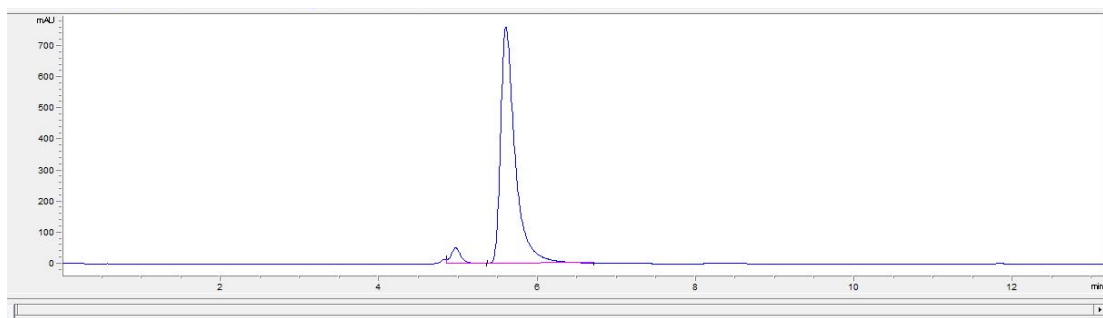
3n was synthesized following the general procedure C. Brown liquid (47.4 mg, 64% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 1.20$ (c = 0.48, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 - 7.31 (m,

3H), 6.85 (s, 2H), 6.36 (s, 1H), 5.98 – 5.89 (m, 1H), 5.41 (s, 1H), 2.70 - 2.61 (m, 2H), 2.35 (s, 6H), 2.29 (s, 3H), 1.95 – 1.91 (m, 2H), 1.94 (s, 3H), 1.70 - 1.63 (m, 2H), 1.61 – 1.55 (m, 2H).; ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 145.7, 139.9, 138.7, 135.6, 134.6, 133.6, 129.3, 128.8, 127.9, 127.1, 113.5, 96.4, 81.0, 27.3, 26.3, 24.5, 22.9, 22.1, 21.3, 5.2.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.1.; IR (KBr, cm⁻¹): 2964.1, 2863.4, 1262.6, 1080.4, 1009.7, 783.9. HRMS (APCI) m/z Calcd for C₂₆H₃₀Si [M+H]⁺ : 371.2190 found: 371.2174

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 91% *ee*). tR =5.602 min (major), tR = 4.965 min (minor).

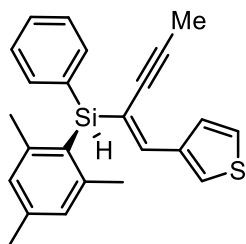


	Time/min	Area	Height	Area%
1	4.951	3162.4	356.3	50.633
2	5.599	3083.4	229.2	49.367



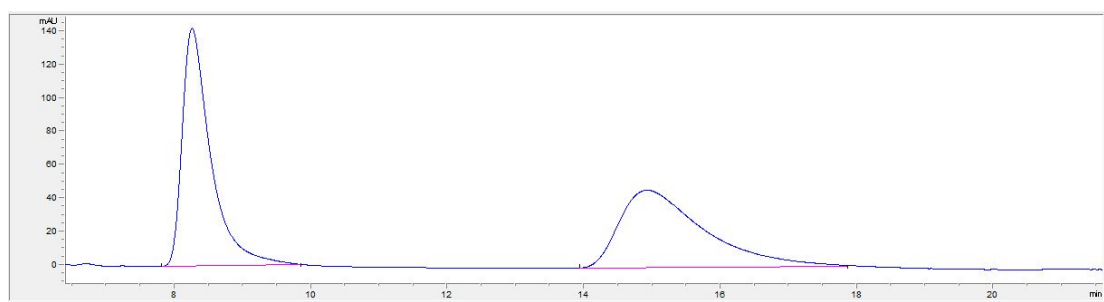
	Time/min	Area	Height	Area%
1	4.965	445.3	51	4.389
2	5.602	760.3	760.3	95.611

(*S,E*)-mesityl(phenyl)(1-(thiophen-3-yl)pent-1-en-3-yn-2-yl)silane

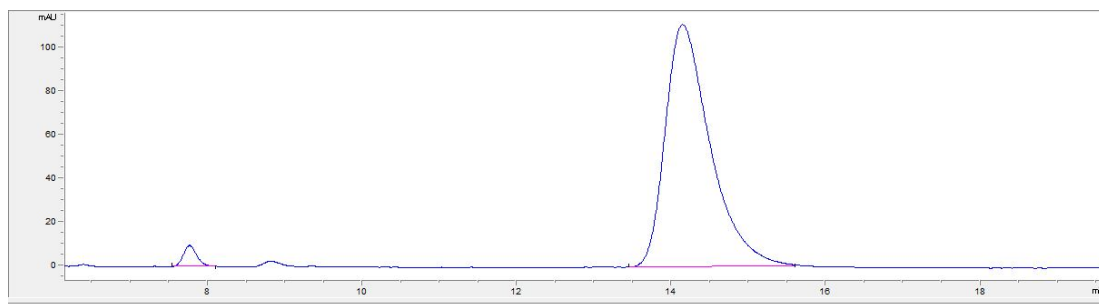


3o was synthesized following the general procedure C. White solid (48.4 mg, 65% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). [α]₂₅^D = 5.52 (c = 0.56, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 4.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 8.0, 4.0Hz, 2H), 7.41 – 7.31 (m, 3H), 7.27 – 7.22 (m, 1H), 6.88 (s, 1H), 6.87 (s, 2H), 5.49 (s, 1H), 2.36 (s, 6H), 2.29 (s, 3H), 2.05 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 145.7, 139.9, 138.7, 135.6, 134.6, 133.6, 129.3, 128.8, 127.9, 127.1, 113.5, 96.4, 81.0, 27.3, 26.3, 24.5, 22.9, 22.1, 21.3, 5.2.; IR (KBr, cm⁻¹): 2927.3, 2859.5, 2147.3, 1428.3, 1021.3, 847.9, 791.7, 739.3. HRMS (APCI) *m/z* Calcd for C₂₄H₂₄SSi [M+H]⁺ : 373.1441 found: 373.1439

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 95% *ee*). t_R = 5.602 min (major), t_R = 4.965 min (minor).

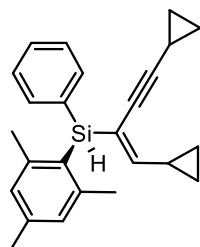


	Time/min	Area	Height	Area%
1	8.26	4185.3	142.5	50.769
2	14.926	4085.5	46.6	49.231

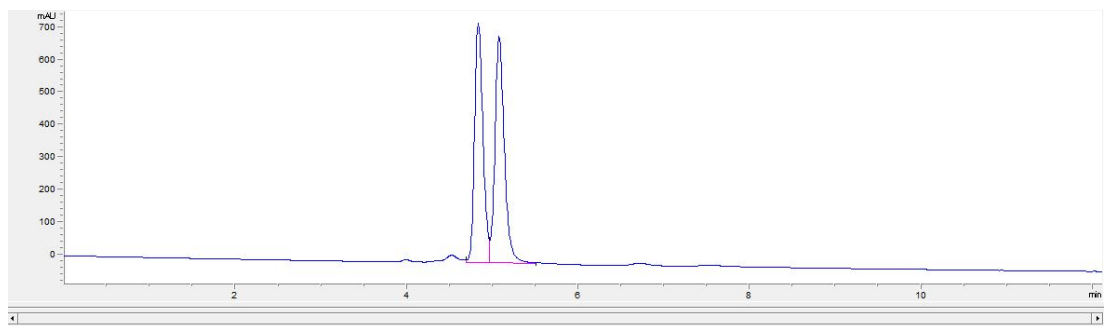


	Time/min	Area	Height	Area%
1	7.767	119.6	9.8	2.589
2	14.148	4500.4	111.1	97.411

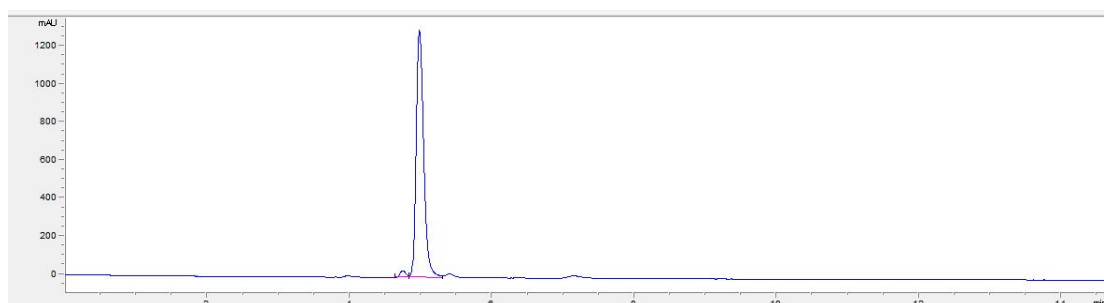
(*S,E*)-(1,4-dicyclopropylbut-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



3p was synthesized following the general procedure C. Yellow liquid (37.1 mg, 52% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 6.47$ (c = 1.65, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 4.0 Hz, 2H), 7.40 – 7.29 (m, 3H), 6.85 (s, 2H), 5.51 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 1H), 2.35 (s, 6H), 2.30 (s, 3H), 2.25 – 2.14 (m, 1H), 1.40 – 1.33 (m, 1H), 0.95 – 0.86 (m, 2H), 0.79 – 0.71 (m, 2H), 0.61 – 0.55 (m, 2H), 0.52 – 0.46 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 145.7, 139.9, 135.5, 134.4, 129.3, 128.7, 127.9, 127.0, 115.0, 101.3, 75.5, 24.5, 21.3, 15.6, 8.9, 8.25, 0.8.; IR (KBr, cm⁻¹): 3013.6, 2919.6, 2151.2, 1604.7, 1428.3, 1104.7, 905.0, 855.6, 735.5, 705.4. HRMS (ESI *m/z* Calcd for C₂₅H₂₈Si [M+H]⁺ : 357.2034 found: 357.2100 HPLC: Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 96% *ee*). *t*_R = 4.98 min (major), *t*_R = 4.747 min (minor)

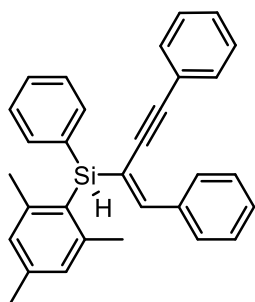


	Time/min	Area	Height	Area%
1	4.833	5049.3	738.3	48.530
2	5.076	5355.3	697.3	51.470



	Time/min	Area	Height	Area%
1	4.747	214.2	35.9	2.176
2	4.98	9630.4	1299.3	97.824

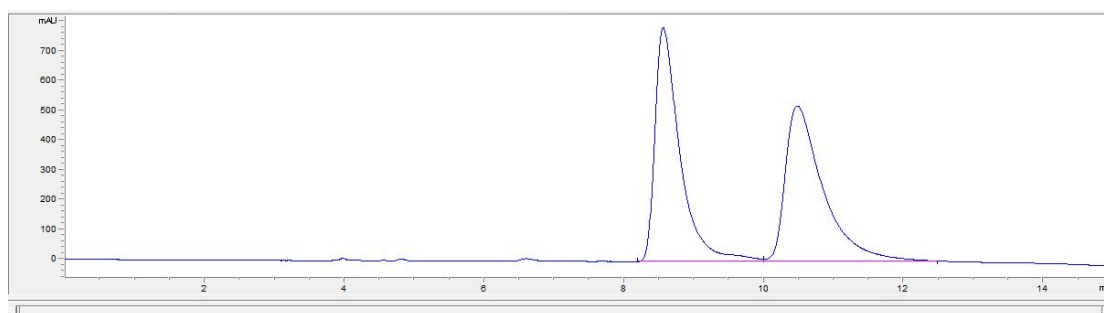
(*S,E*)-(1,4-diphenylbut-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



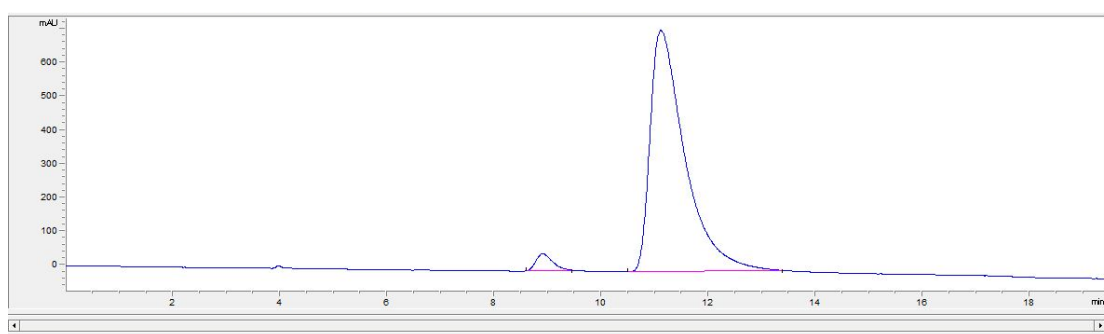
3q was synthesized following the general procedure C. White liquid (51.4 mg, 60% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = -4.69$ (c = 0.90, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.39 (m, 1H), 7.39 – 7.34 (m, 5H), 7.34 – 7.30 (m, 5H), 7.08 (s, 1H),

6.94 (s, 2H), 5.68 (s, 1H), 2.49 (s, 6H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.2, 145.9, 140.3, 137.7, 135.7, 133.6, 131.5, 129.7, 129.2, 129.0, 128.9, 128.4, 128.4, 128.2, 128.1, 126.5, 124.1, 117.7, 101.5, 90.8, 24.7, 21.4.; IR (KBr, cm⁻¹): 3055.2, 2923.4, 2851.7, 2147.3, 1608.5, 1438.9, 843.0, 735.5, 693.8. HRMS (APCI) m/z Calcd for C₃₁H₂₈Si [M+H]⁺ : 429.2034 found: 429.2008

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 210 nm, 93% ee). tR =10.557 min (major), tR = 8.332 min (minor).

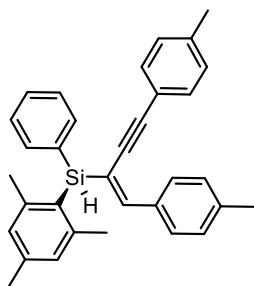


	Time/min	Area	Height	Area%
1	8.564	19698.9	787.3	49.852
2	10.484	19815.9	523.3	50.148



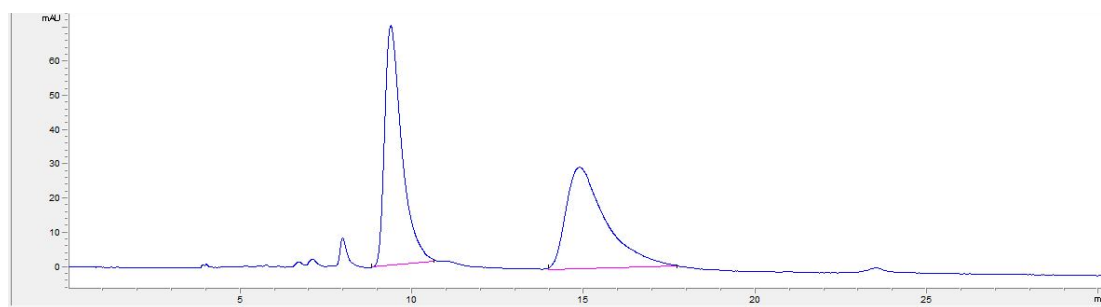
	Time/min	Area	Height	Area%
1	8.332	889	52	3.523
2	10.557	24346.2	686.8	96.477

(S,E)-(1,4-di-p-tolylbut-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

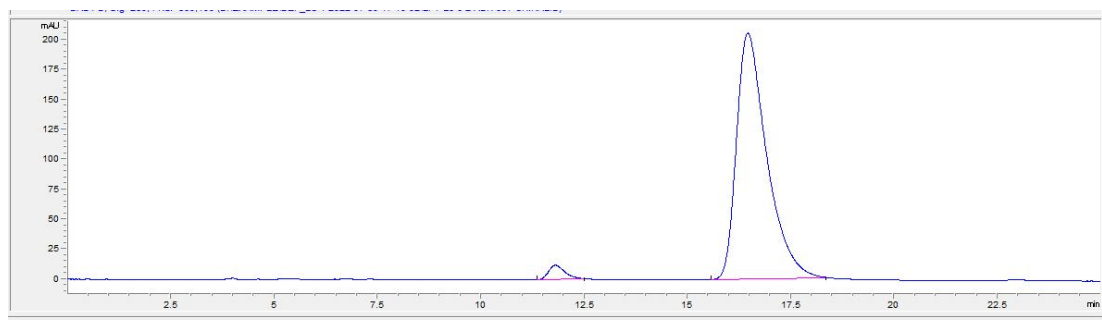


3r was synthesized following the general procedure C. Yellow liquid (70.3 mg, 77% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = -7.63$ (c = 0.80, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.20 – 7.13 (m, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 1H), 6.87 (s, 2H), 5.62 (s, 1H), 2.42 (s, 6H), 2.34 (s, 3H), 2.29 (d, *J* = 8.0 Hz, 6H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 145.8, 140.1, 139.1, 138.2, 135.7, 135.2, 133.8, 131.3, 129.6, 129.1, 129.1, 128.9, 128.1, 126.7, 121.2, 116.3, 101.5, 90.5, 77.5, 21.6, 21.6, 21.4.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.5.; IR (KBr, cm⁻¹): 3029.1, 2930.2, 2855.6, 2143.4, 1608.5, 1111.4, 841.1, 817.6, 733.1, 700.4. HRMS (APCI) *m/z* Calcd for C₃₃H₃₂Si [M+H]⁺ : 457.2347 found: 457.2337

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 93% *ee*). tR =16.459min (major), tR = 11.802 min (minor).

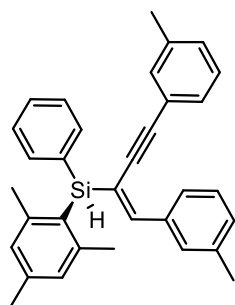


	Time/min	Area	Height	Area%
1	9.379	2407.6	70.1	50.027
2	14.853	2405	29.7	49.973



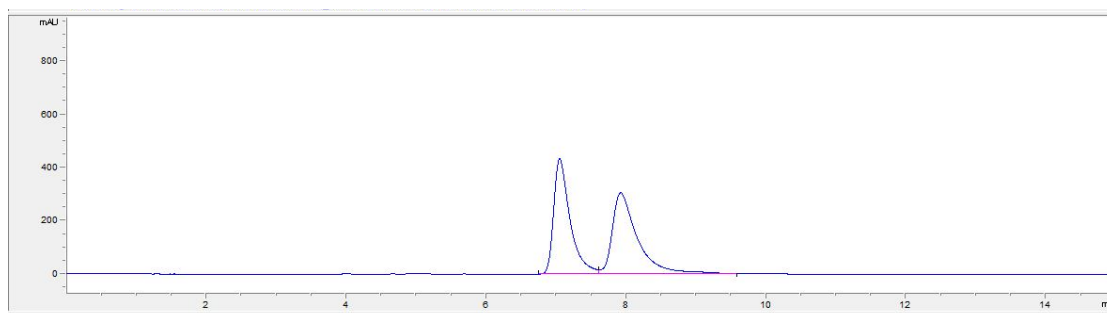
	Time/min	Area	Height	Area%
1	11.802	333.7	12	3.083
2	16.459	10491.5	205.6	95.917

(*S,E*)-(1,4-di-*m*-tolylbut-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

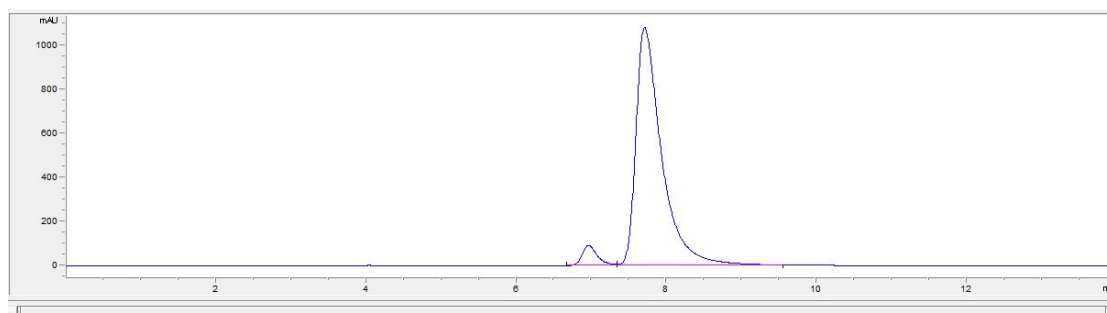


3s was synthesized following the general procedure C. White liquid (83.1mg, 91% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = -1.54$ (c = 0.78, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.45 – 7.32 (m, 3H), 7.27 (t, J = 8.0 Hz, 1H), 7.15 (m, 5H), 6.98 (s, 1H), 6.89 (s, 2H), 5.62 (s, 1H), 2.43 (s, 6H), 2.37 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 148.2, 145.8, 140.2, 138.0, 137.8, 137.7, 135.8, 133.7, 132.1, 129.8, 129.8, 129.6, 129.1, 128.9, 128.5, 128.3, 128.3, 128.1, 126.6, 126.4, 124.0, 117.4, 101.8, 90.7, 29.9, 24.7, 21.6, 21.4.; IR (KBr, cm⁻¹): 2928.3, 2859.5, 2249.0, 2151.2, 1599.8, 1454.4, 905.0, 787.8, 731.6, 697.7. HRMS (APCI) m/z Calcd for C₃₃H₃₂Si [M+H]⁺ : 457.2346 found: 457.2391

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 91% *ee*). tR = 7.711 min (major), tR = 6.966 min (minor).

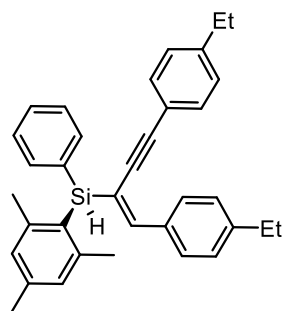


	Time/min	Area	Height	Area%
1	7.049	7189.4	434.7	48.433
2	7.922	7654.7	305.4	51.567



	Time/min	Area	Height	Area%
1	6.966	1312.9	92.4	4.858
2	7.711	25709.6	1082.9	95.142

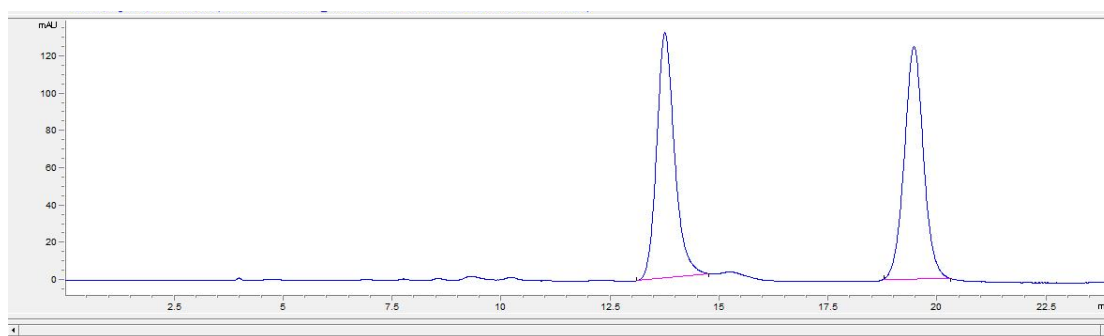
(*S,E*)-(1,4-bis(4-ethylphenyl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



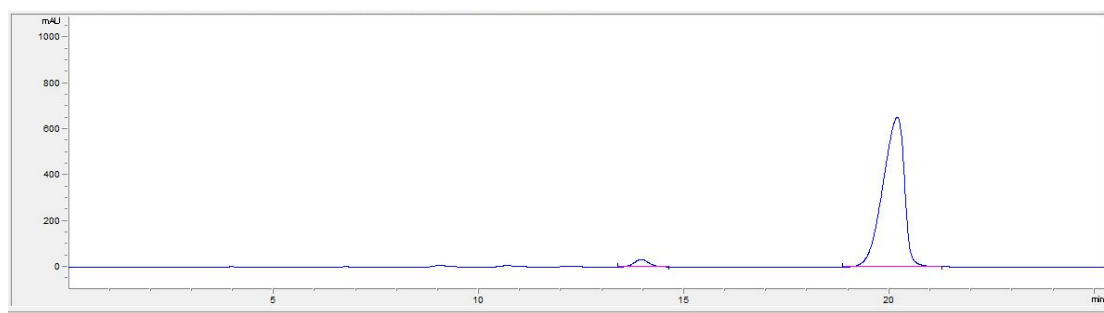
3t was synthesized following the general procedure C. White liquid (77.6mg, 80% yield). purified by column chromatography (Al_2O_3 , PE/EA= 300:1). $[\alpha]_{25}^D = -0.95$ (c = 2.46, $CHCl_3$). 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.35 (m, 3H), 7.19 (d, $J = 8.0$ Hz, 4H), 7.11 – 7.06 (m, 2H), 6.99 (s, 1H), 6.87

(s, 2H), 5.63 (s, 1H), 2.61 (dq, $J = 12.0, 8.0$ Hz, 4H), 2.43 (s, 6H), 2.28 (s, 3H), 1.24 – 1.14 (m, 6H).; ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 145.8, 145.4, 144.5, 140.1, 135.7, 135.5, 133.8, 131.4, 129.6, 129.2, 128.9, 128.1, 128.0, 127.9, 126.7, 121.5, 116.3, 101.6, 90.5, 29.0, 24.7, 21.4, 15.6, 15.5.; IR (KBr, cm^{-1}): 3065.9, 2964.1, 2155.0, 1604.7, 1424.4, 1115.3, 907.9, 829.5, 7316, 697.7. HRMS (ESI) m/z Calcd for $\text{C}_{35}\text{H}_{30}\text{Si}$ $[\text{M}+\text{Na}]^+$: 501.2009 found: 501.2088

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 93% *ee*). $t_R = 19.242$ min (major), $t_R = 13.674$ min (minor).

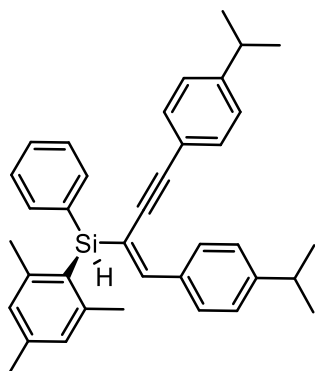


	Time/min	Area	Height	Area%
1	13.751	3764.1	131.7	49.341
2	19.463	3864.8	125.3	50.659



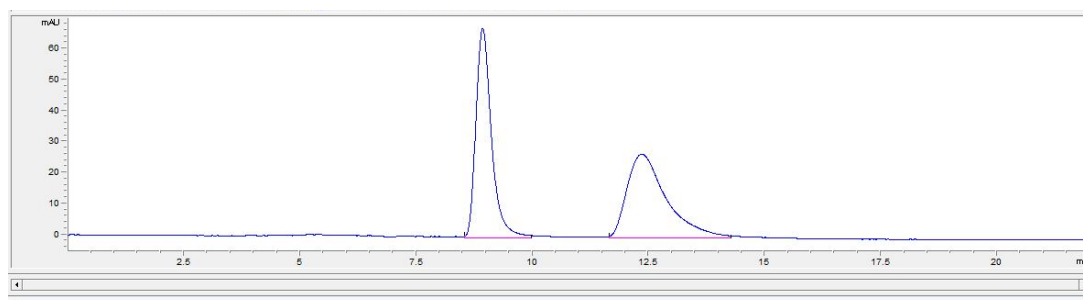
	Time/min	Area	Height	Area%
1	13.674	217.6	8.2	3.368
2	19.242	6241.9	196.8	96.632

(*S,E*)-(1,4-bis(4-isopropylphenyl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

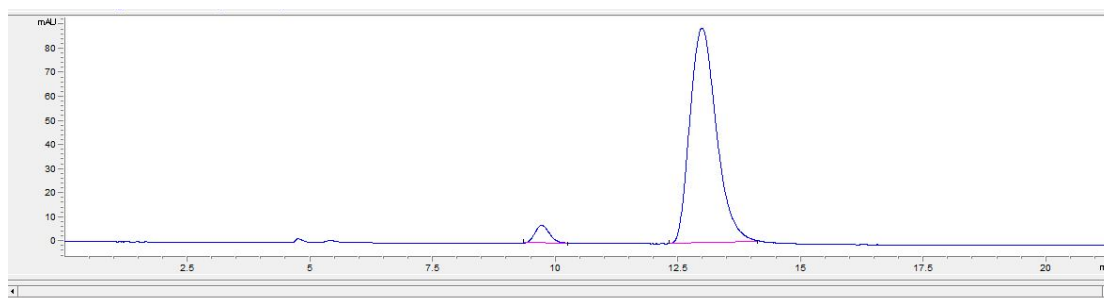


3u was synthesized following the general procedure C. White liquid (71.8 mg, 80% yield). purified by column chromatography (Al_2O_3 , PE/EA= 300:1). $[\alpha]_{25}^D = -5.99$ ($c = 2.99$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.41 – 7.32 (m, 3H), 7.25 – 7.18 (m, 4H), 7.16 – 7.11 (m, 2H), 6.98 (s, 1H), 6.88 (s, 2H), 5.61 (s, 1H), 2.98 – 2.78 (m, 2H), 2.42 (s, 6H), 2.29 (s, 3H), 1.23 (dd, $J = 12.0, 8.0$ Hz, 12H).; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.0, 149.1, 147.8, 145.8, 140.1, 135.7, 135.6, 133.9, 131.5, 129.6, 129.3, 128.9, 128.1, 126.7, 126.5, 126.5, 121.7, 116.4, 101.6, 90.4, 34.2, 24.7, 24.0, 23.9, 21.4.; IR (KBr, cm^{-1}): 2961.2, 2923.4, 2151.2, 1604.6, 1462.2, 911.8, 829.5, 731.6. HRMS (ESI) m/z Calcd for $\text{C}_{37}\text{H}_{40}\text{Si}$ $[\text{M}+\text{H}]^+$: 513.2972 found: 513.2903

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 254 nm, 91% *ee*). $t_R = 12.987$ min (major), $t_R = 9.717$ min (minor).

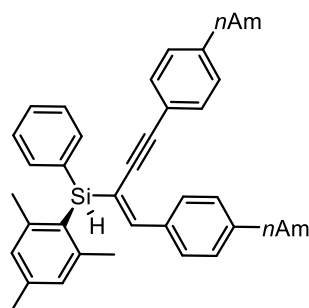


	Time/min	Area	Height	Area%
1	8.931	1610.6	68	49.991
2	12.352	1611.2	27.2	50.009



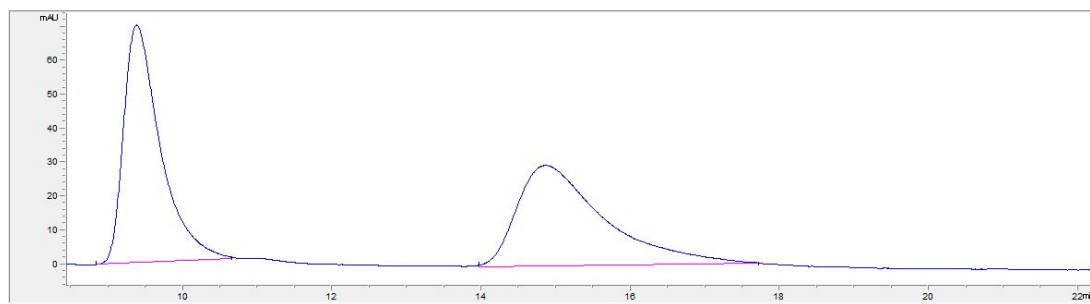
	Time/min	Area	Height	Area%
1	9.717	154.9	7.5	4.405
2	12.987	3361.4	89.3	95.595

(*S,E*)-(1,4-bis(4-pentylphenyl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane

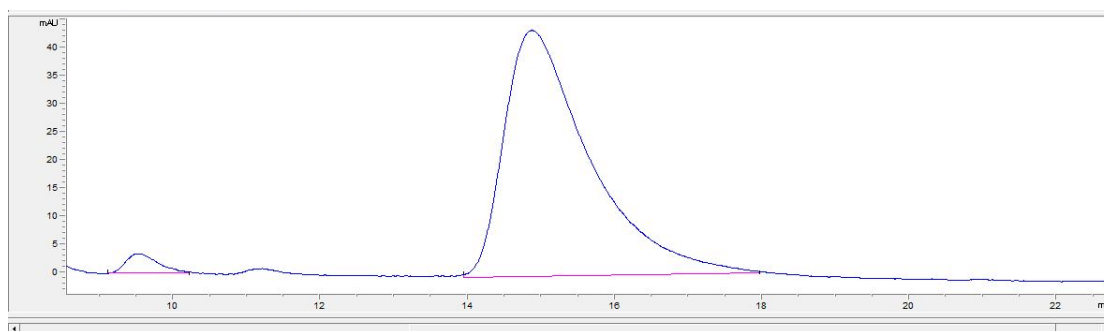


3v was synthesized following the general procedure C. White liquid (77.4 mg, 68% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_D^{25} = -6.35$ (c = 2.43, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0, 1.5 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 1H), 6.88 (s, 2H), 5.61 (s, 1H), 2.66 – 2.50 (m, 4H), 2.42 (s, 6H), 2.29 (s, 3H), 1.67 – 1.53 (m, 4H), 1.35 – 1.24 (m, 8H), 0.88 (d, *J* = 8.0 Hz, 6H).; ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 145.9, 144.2, 143.3, 140.1, 135.7, 135.5, 133.89, 131.4, 129.6, 129.2, 128.9, 128.5, 128.5, 128.1, 126.7, 121.5, 116.3, 101.6, 36.0, 31.6, 31.6, 31.2, 31.1, 24.7, 22.7 21.4, 14.2.; ²⁹Si NMR(500MHz, CDCl₃) δ 26.4.; IR (KBr, cm⁻¹): 3025.2, 2930.2, 2143.4, 1424.4, 1102.7, 847.9, 795.5, 729.7, 693.8. HRMS (APCI) *m/z* Calcd for C₄₁H₄₈Si [M+H]⁺ : 569.3599 found: 569.3589

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 254 nm, 94% *ee*). tR =14.875 min (major), tR = 9.52 min (minor).

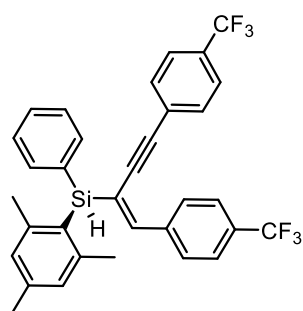


	Time/min	Area	Height	Area%
1	9.379	2407.6	70.1	50.027
2	14.853	2405	29.7	49.973



	Time/min	Area	Height	Area%
1	9.52	107	3.5	2.940
2	14.875	3531.5	43.8	97.060

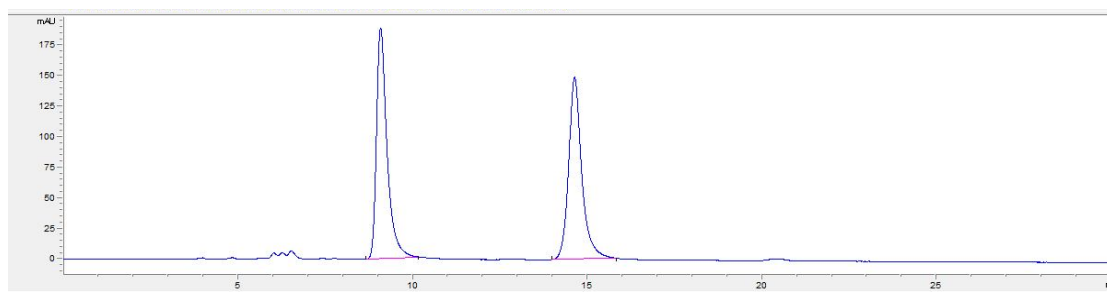
(*S,E*)-(1,4-bis(4-(trifluoromethyl)phenyl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



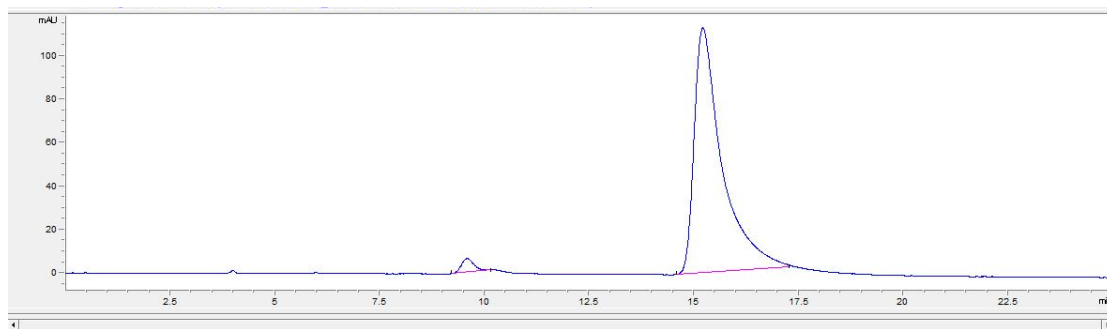
3w was synthesized following the general procedure C. Yellow liquid (50.8 mg, 45% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 7.42$ (c = 2.57, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.33

(d, $J = 8.0$ Hz, 2H), 7.12 (s, 1H), 6.95 (s, 2H), 5.68 (s, 1H), 2.47 (s, 6H), 2.35 (s, 3H);
 ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 145.82, 140.7, 140.5, 135.8, 132.8, 131.7,
 130.8, 130.0, 129.9(q, $J = 28.0$ Hz), 129.9, 129.2, 129.1, 128.3, 127.4, 125.8, 125.4(q,
 $J = 3.0$ Hz), 122.8, 122.7, 121.1, 101.1, 92.3, 24.7, 21.4. ^{19}F NMR (500 MHz, CDCl_3)
 δ -62.64, -62.83 (d).; ^{29}Si NMR(500MHz, CDCl_3) δ 26.3.; IR (KBr, cm^{-1}): 2923.4,
 2855.6, 2147.3, 1608.5, 1428.3, 1107.6, 787.8, 731.6, 697.7. HRMS (ESI m/z Calcd
 for $\text{C}_{33}\text{H}_{26}\text{F}_6\text{Si}$ $[\text{M}+\text{H}]^+$: 565.1781 found: 565.1167

HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 254 nm,
 94% *ee*). $t_R = 15.213$ min (major), $t_R = 9.587$ min (minor).

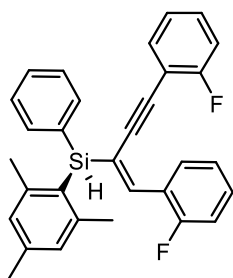


	Time/min	Area	Height	Area%
1	9.633	3551	138.1	50.232
2	15.602	3518.2	84.6	49.768

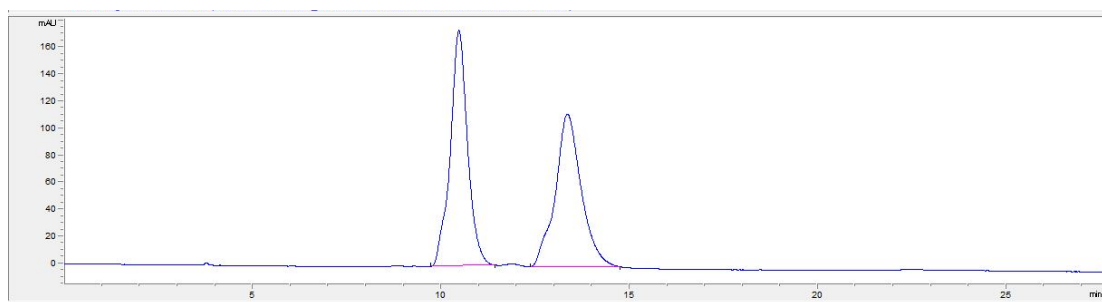


	Time/min	Area	Height	Area%
1	9.587	138.6	6.4	2.940
2	15.213	5207.9	112.9	97.060

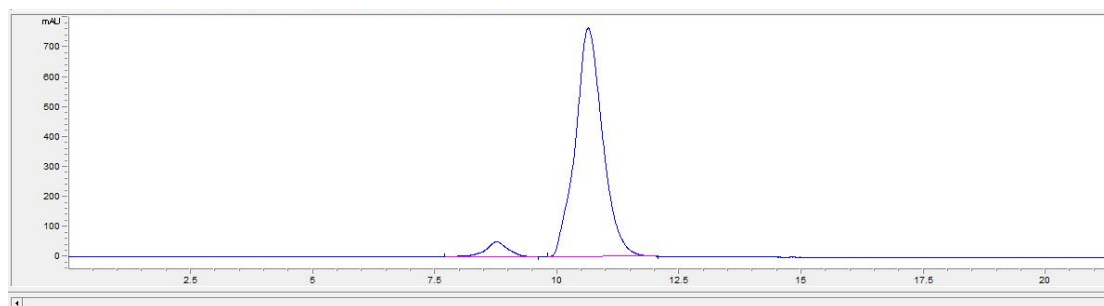
(*S,E*)-(1,4-bis(2-fluorophenyl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



3x was synthesized following the general procedure C. White liquid (53.9 mg, 58% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = -4.29$ (c = 1.26, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.83 (t, *J* = 8.0 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.41 – 7.35 (m, 3H), 7.29 – 7.15 (m, 3H), 7.13 – 7.06 (m, 1H), 7.05 – 6.97 (m, 3H), 6.89 (s, 2H), 5.66 (s, 1H), 2.44 (s, 6H), 2.29 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 162.7(d, *J* = 241.0 Hz), 160.2(d, *J* = 241.0 Hz), 145.8, 140.4, 140.0, 139.9, 135.7, 133.5, 133.2, 130.7(d, *J* = 80.0 Hz), 130.1(d, *J* = 80.0 Hz), 129.8, 129.2, 129.0, 128.2, 126.1, 125.5, 125.4, 124.0(d, *J* = 40.0 Hz),, 123.9(d, *J* = 40.0 Hz), 119.5, 115.5(d, *J* = 40.0 Hz),, 115.3(d, *J* =22.0 Hz), 112.6, 112.4, 95.4, 77.5, 77.2, 76.8, 24.7, 21.4. ¹⁹F NMR (500 MHz, CDCl₃) δ -109.10 - -116.90 (m).; ²⁹Si NMR(500MHz, CDCl₃) δ 26.3.; IR (KBr, cm⁻¹): 2923.4, 2146.3, 1604.7, 1500.1, 1458.3, 1096.9, 757.8, 731.6, 697.7. HRMS (ESI m/z Calcd for C₃₁H₂₆F₂Si [M+Na]⁺ : 487.1664 found: 487.1662 HPLC: Chiralpa Phenomenex column (hexanes: isopropanol = 99.9:0.1, 0.8 mL/min, 230 nm, 90% *ee*). tR =10.636 min (major), tR = 8.765 min (minor).

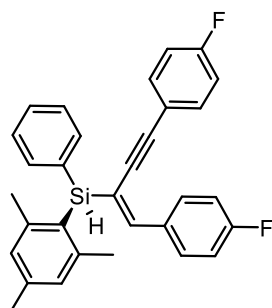


	Time/min	Area	Height	Area%
1	10.471	5589.4	174.4	50.707
2	13.355	5433.6	113.3	49.293

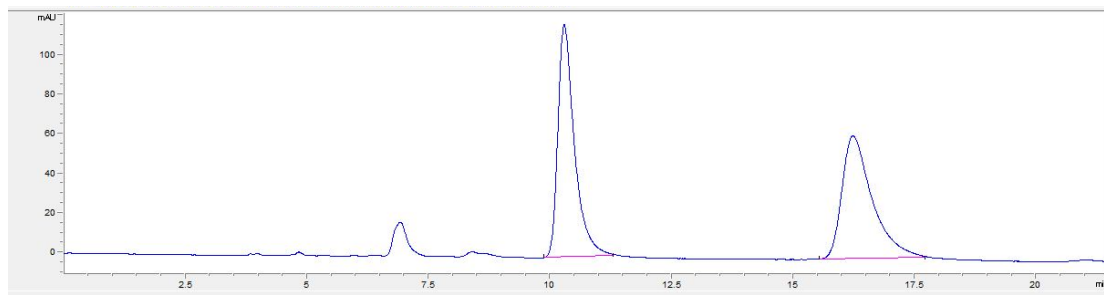


	Time/min	Area	Height	Area%
1	8.765	1619.3	50.2	5.175
2	10.636	29673.5	764.1	94.825

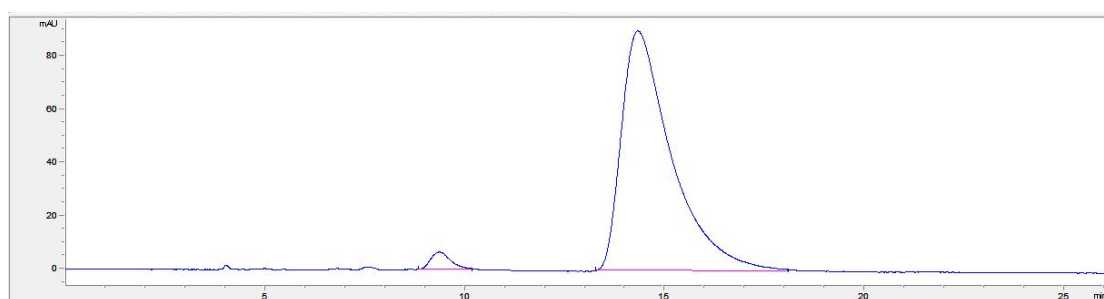
(*S,E*)-(1,4-bis(4-fluorophenyl)but-1-en-3-yn-2-yl)(mesityl)(phenyl)silane



3y was synthesized following the general procedure C. White liquid (53.9 mg, 58% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = -4.70$ (c = 3.32, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.84 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.12 – 7.07 (m, 2H), 7.00 – 6.93 (m, 2H), 6.89 – 6.83 (m, 3H), 6.80 (s, 2H), 5.52 (s, 1H), 2.33 (s, 6H), 2.21 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 163.9 (d, *J* = 28.0 Hz), 161.48(d, *J* = 28.0 Hz), 146.7, 145.8, 140.4, 135.7, 134.0(d, *J* = 3.0 Hz), 133.41, 133.3(d, *J* = 8.0 Hz), 130.9(d, *J* = 8.0 Hz), 129.8, 129.0, 128.2, 126.3, 120.0(d, *J* = 3.0 Hz), 117.1(d, *J* = 3.0 Hz), 115.7(d, *J* = 22.0 Hz), 115.4(d, *J* = 22.0 Hz), 100.4, 90.2, 77.5, 77.2, 76.84, 2.64, 21.4. ¹⁹F NMR (500 MHz, CDCl₃) δ -110.76 - -111.04 (m).; IR (KBr, cm⁻¹): 3065.9, 2915.7, 2155.0, 1601.7, 1506.8, 1227.7, 837.2, 735.5. HRMS (ESI *m/z* Calcd for C₃₁H₂₆F₂Si [M+H]⁺ : 465.1845 found: 465.1857
HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 95% *ee*). *t*R =14.325min (major), *t*R = 9.347 min (minor).

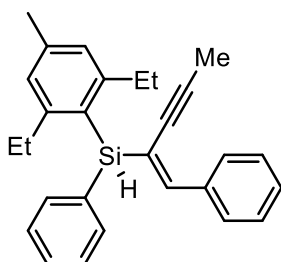


	Time/min	Area	Height	Area%
1	10.292	2788.7	117.6	50.851
2	16.236	2695.4	62.1	49.149



	Time/min	Area	Height	Area%
1	9.347	222.2	6.5	2.731
2	14.325	7913.7	90.2	97.269

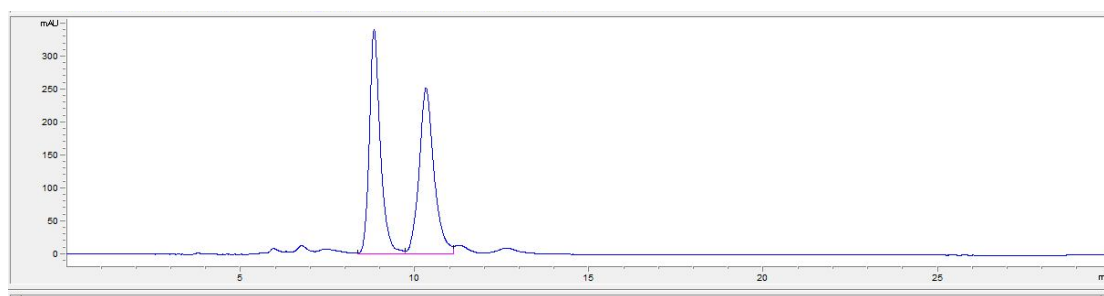
(*R,E*)-(2,6-diethyl-4-methylphenyl)(phenyl)(1-phenylpent-1-en-3-yn-2-yl)silane



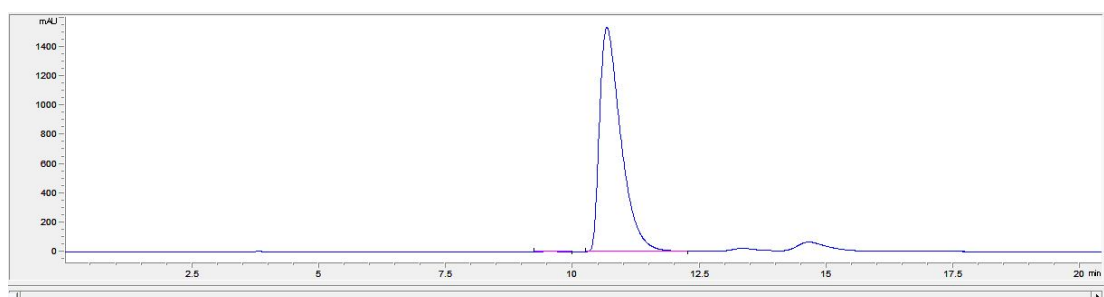
3aa was synthesized following the general procedure C. White liquid (37.9 mg, 48% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 1.56$ (c = 1.47, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0

Hz, 2H), 7.43 – 7.35 (m, 5H), 7.34 – 7.29 (m, 1H), 6.98 (s, 2H), 6.91 (s, 1H), 5.55 (s, 1H), 2.86 – 2.77 (m, 4H), 2.39 (s, 3H), 2.09 (s, 3H), 1.10 (t, $J = 8.0$ Hz, 6H).; ^{13}C NMR (100 MHz, CDCl_3) δ 152.4, 147.5, 140.4, 137.8, 135.8, 134.3, 129.4, 128.8, 128.6, 128.3, 127.9, 127.6, 125.2, 119.2, 99.1, 80.8, 30.7, 21.6, 16.9, 5.4. IR (KBr, cm^{-1}): 3059.1, 2961.2, 2866.3, 2151.2, 1595.9, 1428.3, 1104.7, 915.7, 807.2, 727.7, 693.8. HRMS (APCI m/z Calcd for $\text{C}_{28}\text{H}_{30}\text{Si}$ $[\text{M}+\text{H}]^+$: 395.2190 found: 395.2064

HPLC: Chiralpa Phenomenex column (hexanes: isopropanol = 99.9:0.1, 0.8 mL/min, 230 nm, >99% *ee*). $t_R = 10.673$ min (major), $t_R = 9.558$ min (minor)

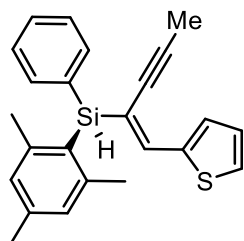


	Time/min	Area	Height	Area%
1	8.824	7453.5	340.5	49.874
2	10.313	252.2	252.2	50.126



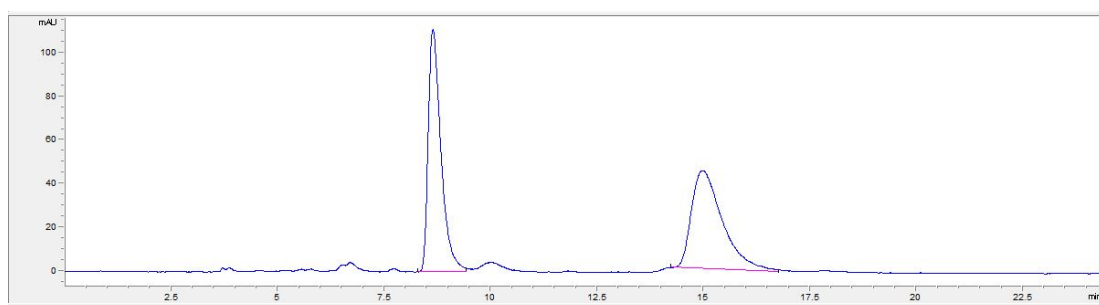
	Time/min	Area	Height	Area%
1	9.558	36.3	1.8	0.081
2	10.673	44696.1	1531.2	99.919

(*S,E*)-mesityl(phenyl)(1-(thiophen-2-yl)pent-1-en-3-yn-2-yl)silane

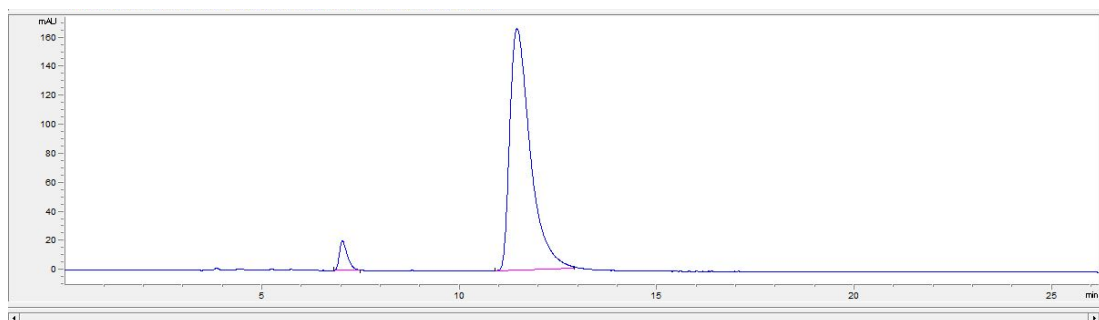


3ab was synthesized following the general procedure C. White liquid (48.4 mg, 65% yield). purified by column chromatography (Al_2O_3 , PE/EA= 300:1). $[\alpha]_{25}^{\text{D}} = 12.35$ ($c = 0.17$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 2H), 7.42 – 7.29 (m, 4H), 7.19 (d, $J = 3.5$ Hz, 1H), 7.10 (s, 1H), 7.01 (d, $J = 3.8$ Hz, 1H), 6.88 (s, 2H), 5.51 (s, 1H), 2.37 (s, 6H), 2.31 (s, 3H), 2.13 (s, 3H).; ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 142.5, 141.1, 140.2, 135.6, 133.9, 129.7, 129.6, 128.9, 128.1, 126.9, 126.4, 126.3, 115.2, 101.6, 81.4, 24.6, 21.4, 5.7. HRMS (ESI m/z Calcd for $\text{C}_{24}\text{H}_{24}\text{SSi}$ $[\text{M}+\text{H}]^+$: 373.1441 found: 373.1438

HPLC: Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 360 nm, 91% *ee*). $t_{\text{R}} = 11.453$ min (major), $t_{\text{R}} = 7.028$ min (minor)

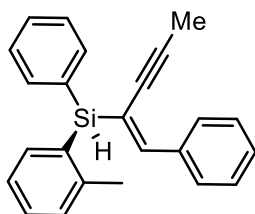


	Time/min	Area	Height	Area%
1	8.646	2316.5	110.8	50.381
2	14.992	2281.5	44.9	49.619

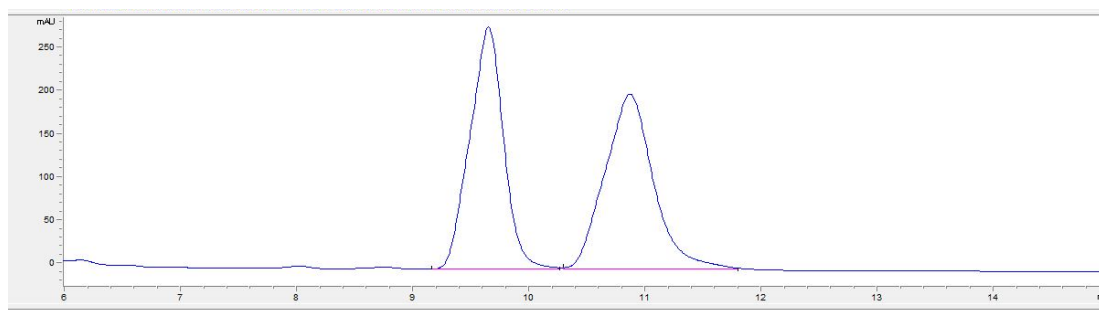


	Time/min	Area	Height	Area%
1	7.028	294.4	20.4	4.655
2	11.453	6030.1	166.6	95.345

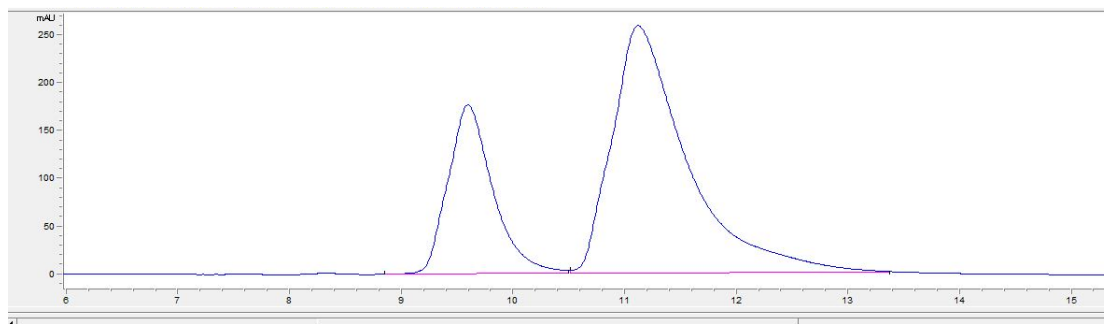
(*R,E*)-phenyl(1-phenylpent-1-en-3-yn-2-yl)(*o*-tolyl)silane



3ac was synthesized following the general procedure C. White liquid (36.6 mg, 54% yield). purified by column chromatography (Al_2O_3 , PE/EA= 300:1). $[\alpha]_{25}^D = -1.55$ ($c = 1.61$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.43 – 7.30 (m, 6H), 7.29 – 7.23 (m, 1H), 7.22 – 7.14 (m, 2H), 6.86 (s, 1H), 5.35 (s, 1H), 2.41 (s, 3H), 2.01 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.0, 144.9, 137.6, 137.0, 135.9, 132.9, 131.6, 130.4, 129.9, 129.8, 128.8, 128.3, 128.1, 125.2, 118.1, 99.3, 80.4, 77.5, 77.2, 76.8, 29.8, 22.8, 5.4.; HRMS (APCI m/z Calcd for $\text{C}_{24}\text{H}_{22}\text{Si}$ $[\text{M}+\text{H}]^+$:339.1491 found:339.1455 HPLC:Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 40% ee). $t_R = 11.117$ min (major), $t_R = 9.593$ min (minor)

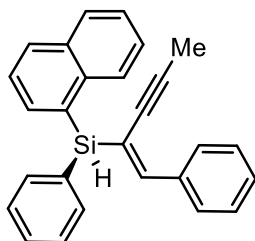


	Time/min	Area	Height	Area%
1	9.649	5704.8	280.3	48.745
2	10.868	5998.6	203.3	51.255



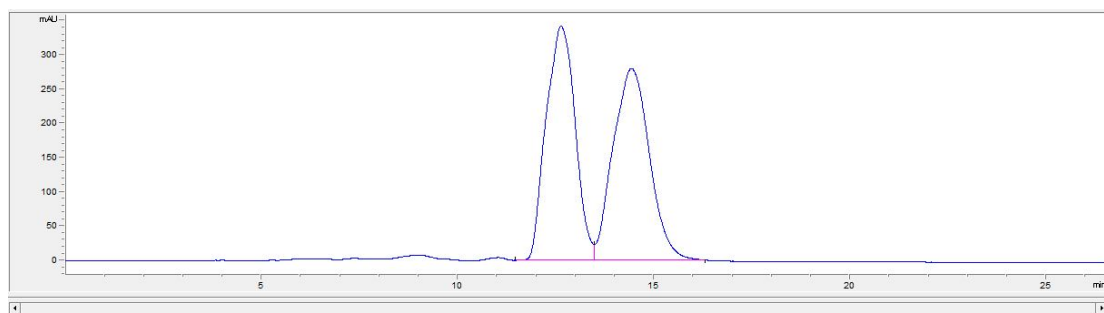
	Time/min	Area	Height	Area%
1	9.593	4969.3	177	29.098
2	11.117	12108.7	258.9	70.902

(*R,E*)-naphthalen-1-yl(phenyl)(1-phenylpent-1-en-3-yn-2-yl)silane

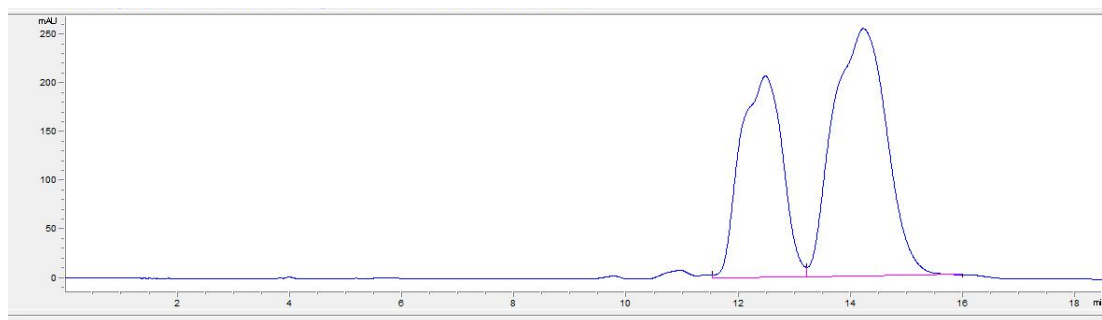


3ad was synthesized following the general procedure C. Yellow liquid (40.5 mg, 54% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). [α]₂₅^D = -2.37 (c = 1.69, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 12.0 Hz, 1H), 7.94 – 7.88 (m, 3H), 7.87 – 7.80 (m, 2H), 7.70 – 7.64 (m, 2H), 7.48 – 7.37 (m, 5H), 7.37 – 7.26 (m, 4H), 6.92 (s, 1H), 5.67 (s, 1H), 1.98 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 148.4, 137.5, 137.5, 136.9, 136.0, 133.4, 132.8, 131.0, 130.9, 130.0, 128.9, 128.8, 128.4, 128.3, 128.2, 126.3, 125.8, 125.4, 118.1, 99.5, 80.5, 29.8, 5.4.; HRMS (APCI *m/z* Calcd for C₂₇H₂₂Si [M+H]⁺ :375.1491 found:375.1014

HPLC: Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 230 nm, 22% *ee*). tR =22.864 min (major), tR = 17.53 min (minor)

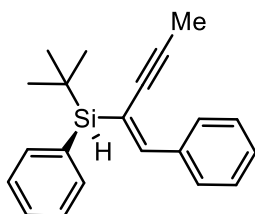


	Time/min	Area	Height	Area%
1	12.622	17652.3	342.3	49.329
2	14.426	18132.2	2280.5	50.671



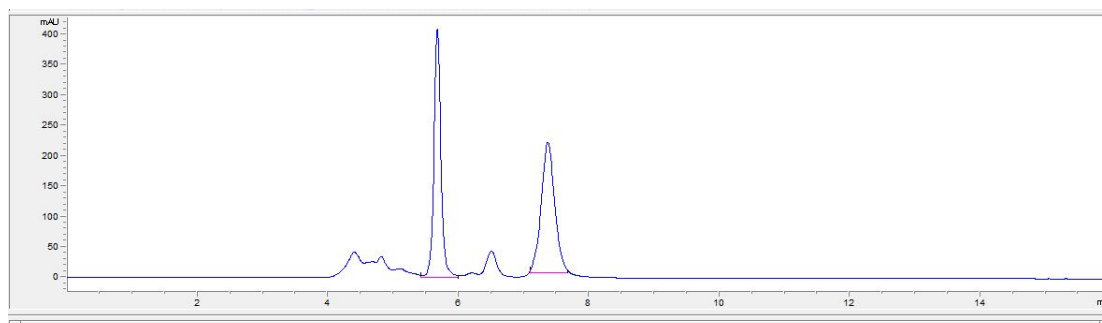
	Time/min	Area	Height	Area%
1	12.475	10762.7	207.1	39.028
2	14.222	16813.9	254.4	60.972

(*R,E*)-tert-butyl(phenyl)(1-phenylpent-1-en-3-yn-2-yl)silane

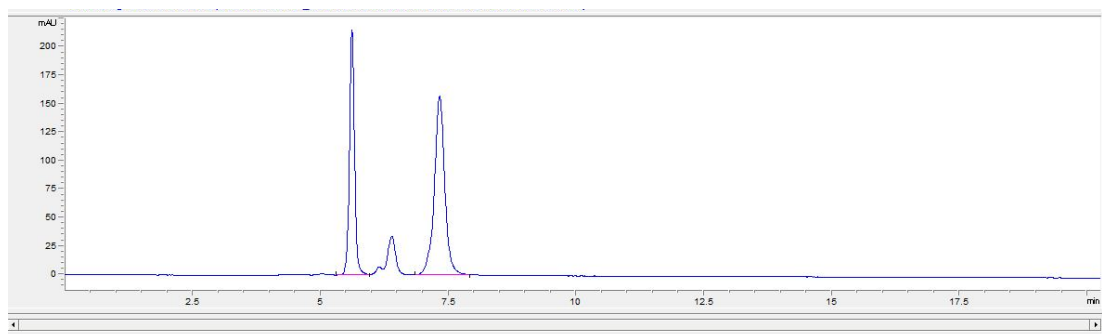


3ae was synthesized following the general procedure C. Yellow liquid (26.2 mg, 43% yield). purified by column chromatography (Al₂O₃, PE/EA= 300:1). $[\alpha]_{25}^D = 1.67$ (c = 1.50, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.22 – 7.14 (m, 1H), 6.94 (s, 1H), 4.33 (s, 1H), 2.07 (s, 3H), 1.03 (s, 9H).; ¹³C NMR (100 MHz, CDCl₃) δ 148.0, 137.7, 135.7, 133.9, 129.7, 128.8, 128.6, 128.3, 127.8, 118.4, 98.9, 81.1, 27.6, 18.5, 5.4.; HRMS (ESI *m/z* Calcd for C₂₁H₂₄Si [M+H]⁺ :305.1647 found:305.1678

HPLC:Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 254 nm, 20% *ee*). tR =7.331 min (major), tR = 5.674 min (minor)

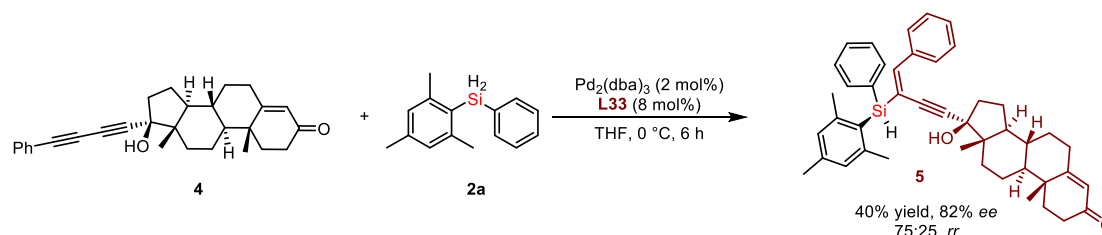


	Time/min	Area	Height	Area%
1	5.674	3037.4	408.8	49.596
2	7.37	3086.9	215.1	50.404



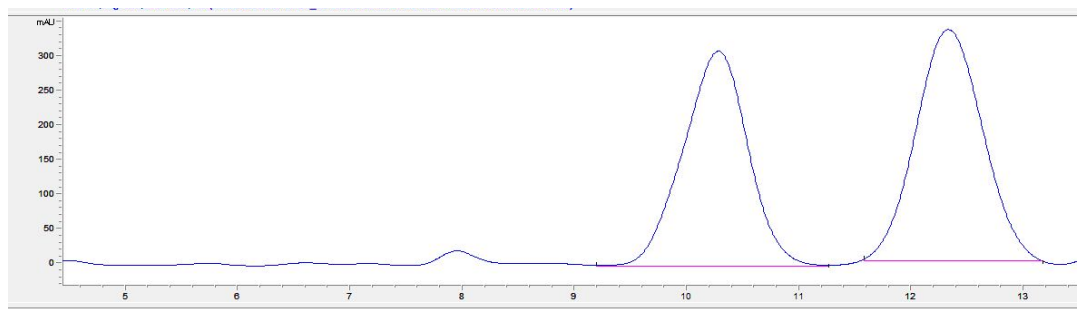
	Time/min	Area	Height	Area%
1	5.614	1490.8	215.1	39.931
2	7.331	2242.6	157.1	60.069

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-hydroxy-17-((*E*)-3-(mesityl(phenyl)silyl)-4-phenylbut-3-en-1-yn-1-yl)-13-methyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one

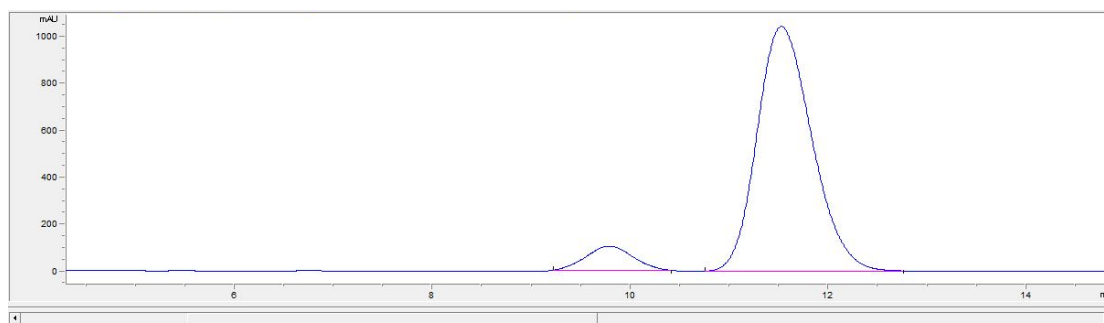


5 was synthesized following the general procedure C. White liquid (51.1 mg, 40% yield). purified by column chromatography (Al₂O₃, PE/EA= 8:1). $[\alpha]_{25}^D = 38.58$ (c = 1.2, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.31 (m, 3H), 7.31 – 7.22 (m, 3H), 7.24 – 7.13 (m, 1H), 6.87 (s, 2H), 6.38 (s, 1H), 5.74 (s, 1H), 5.51 (s, 1H), 3.86 (s, 21H), 2.47 – 2.41 (m, 1H), 2.38 (s, 6H), 2.36 – 2.32 (m, 1H), 2.28 (s, 3H), 2.19 – 2.09 (m, 1H), 2.06 – 1.91 (m, 2H), 1.88 – 1.79 (m, 1H), 1.71 (m, 3H), 1.62 – 1.54 (m, 2H), 1.47 – 1.36 (m, 2H), 1.33 – 1.22 (m, 24H), 1.18 (s, 3H), 1.16 – 1.06 (m, 1H), 0.98 (s, 3H), 0.95 – 0.83 (m, 1H), 0.82 – 0.71 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 199.7, 171.3, 158.6, 145.7, 140.4, 135.5, 133.4, 131.3, 129.8, 128.9, 128.6, 128.4, 128.2, 126.1, 124.0, 123.1, 116.5, 102.2, 87.7, 87.2, 54.1, 50.7, 48.9, 38.7, 37.1, 36.5, 36.0, 34.1, 32.9, 32.3, 31.9, 24.7, 23.7, 21.4, 20.9, 17.6, 14.4. HRMS (ESI *m/z*) Calcd for C₄₄H₅₀O₂Si [M+Na]⁺: 639.3653 found: 639.3714

HPLC: Chiralpa AD-H column (hexanes: isopropanol = 90:10, 1 mL/min, 230 nm, 83% *ee*). $t_R = 19.012$ min (major), $t_R = 14.047$ min (minor)

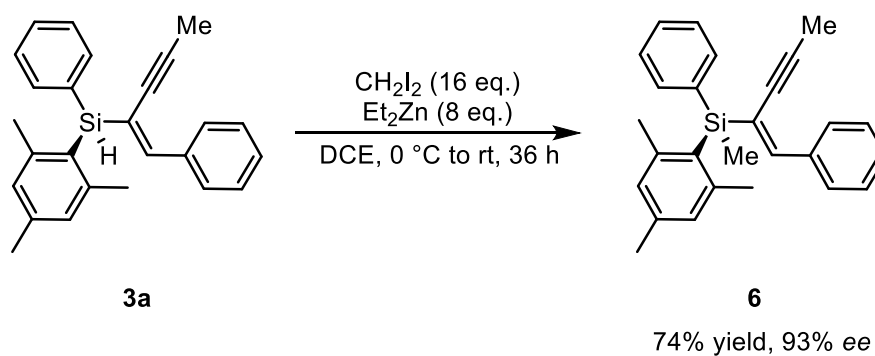


	Time/min	Area	Height	Area%
1	10.282	12521.6	311	47.327
2	12.331	13936.2	335	52.673



	Time/min	Area	Height	Area%
1	9.795	3690	106.7	8.317
2	11.526	40676.9	1047.1	91.683

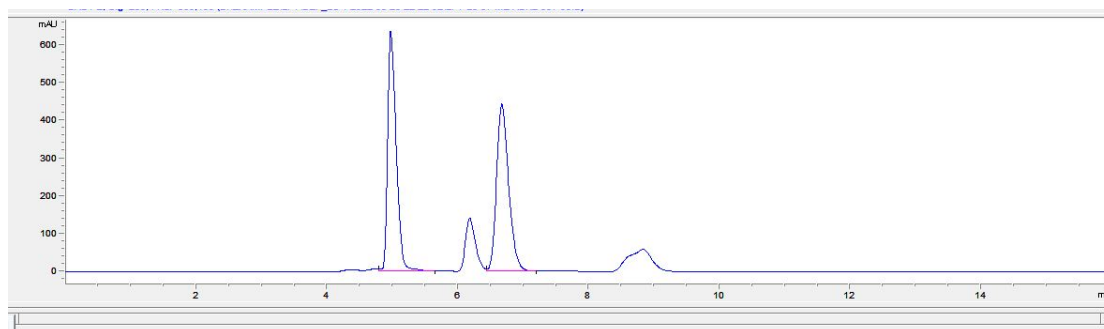
3.3 Synthetic Applications of Chiral Monohydrosilanes



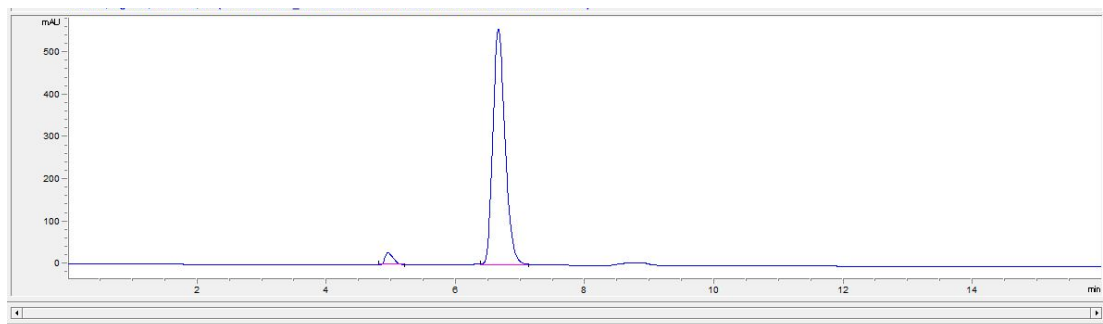
The procedure was followed the known literature. To a flame dried 25 mL Schlenk tube, a solution of 3a (36.3 mg, 0.1 mmol, 1M) in DCE (4 ml) was cooled to 0 °C, and

Et₂Zn (0.8 mL, 0.8 mmol) was added to the solution under N₂ atmosphere. After that, CH₂I₂ (428.5 mg, 1.6 mmol) was added dropwise. The reaction was kept at 0 °C for 20 min and warmed to room temperature for 36 h. After the reaction was completed, the reaction mixture was cooled to 0 °C and the saturated aqueous solution of NH₄Cl was added. The aqueous phase was then extracted by DCM. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. The resulting solution was concentrated and purified by preparative thin-layer chromatography using petroleum ether as the eluent to afford colorless liquid **6** (28.2 mg, 74% yield, 93% *ee*). [α]₂₅^D = 34.3 (c = 0.14, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.29 (m, 6H), 6.84 (s, 2H), 6.67 (s, 1H), 2.28 (s, 6H), 2.05 (s, 3H), 1.25 (s, 3H), 0.85 (s, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 145.9, 145.6, 139.4, 138.6, 138.0, 134.8, 129.4, 129.1, 128.7, 128.7, 128.4, 128.3, 128.0, 124.2, 98.7, 80.8, 25.3, 21.2, 5.4, 1.1.; HRMS (ESI *m/z* Calcd for C₂₁H₂₄Si [M+Na]⁺: 403.1853 found: 403.2353

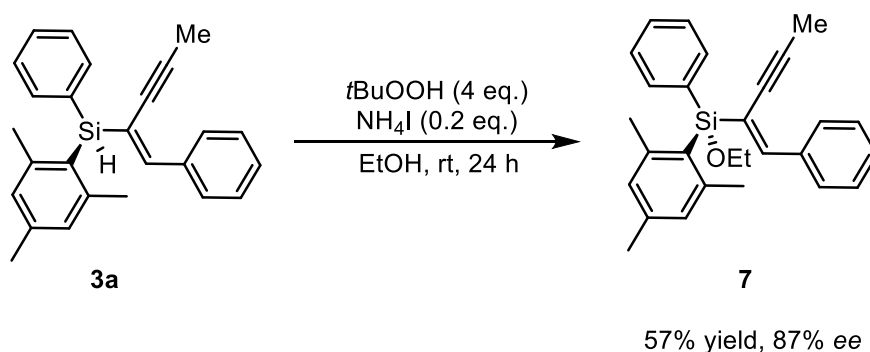
HPLC: Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 280 nm, 93% *ee*). t_R = 6.659 min (major), t_R = 4.951 min (minor)



	Time/min	Area	Height	Area%
1	4.972	5822.4	636.8	50.561
2	6.672	5693.1	443.4	49.439



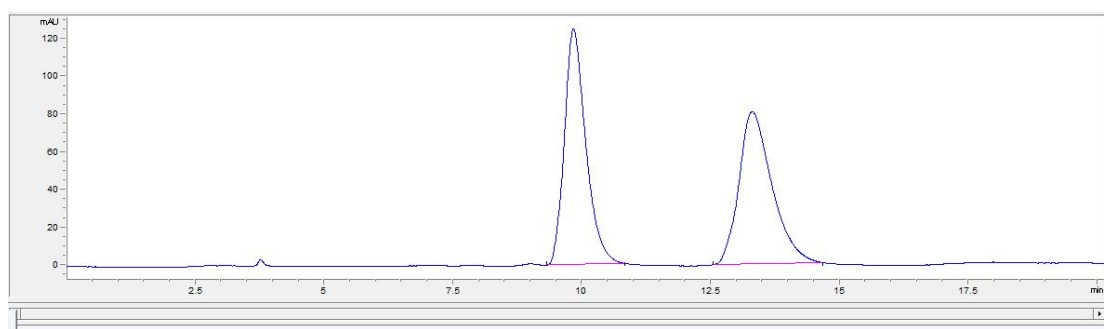
	Time/min	Area	Height	Area%
1	4.951	253.6	28.8	3.334
2	6.659	7353	558.7	96.666



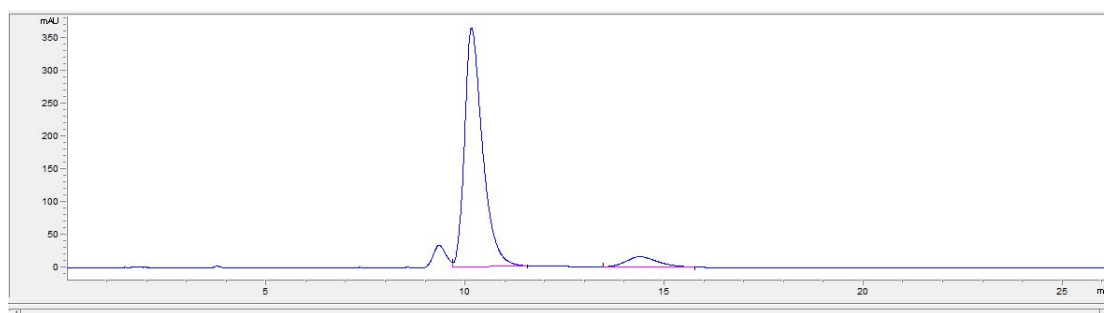
The procedure was followed the known literature. To a flame 25 mL Schlenk tube, a solution of **3a** (36.3 mg, 0.1 mmol, 1M) and ammonium iodide (2.9 mg, 0.02 mmol) in alcohol (1 mL) and 70% aqueous TBHP (36 mg, 0.4 mmol) was dropped wisely over a period of 10 min and stirred at room temperature for 24 h. Progress of the reaction was monitored by TLC, and after completion of the reaction, the mixture was quenched with saturated aq. $\text{Na}_2\text{S}_2\text{O}_3$. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The resulting solution was concentrated and purified by preparative thin-layer chromatography using petroleum ether as the eluent to afford colorless liquid **7** (23.4 mg, 57% yield, 87% ee). $[\alpha]_{25}^D = 1.2$ (c = 0.99, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.40 – 7.26 (m, 6H), 6.87 (s, 1H), 6.83 (s, 1H), 3.95 – 3.82 (m, 2H), 2.35 (s, 6H), 2.28 (s, 3H), 2.03 (s, 3H), 1.25

(t, $J = 4.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 146.1, 139.8, 137.8, 136.5, 135.1, 129.7, 129.3, 129.0, 128.7, 128.3, 127.9, 127.6, 121.8, 98.8, 80.8, 77.5, 76.8, 59.9, 24.7, 21.3, 18.5, 5.4.; HRMS (ESI m/z Calcd for $\text{C}_{28}\text{H}_{30}\text{OSi}$ $[\text{M}+\text{H}]^+$: 411.2034 found: 411.0838

HPLC: Chiralpa AD-H column (hexanes: isopropanol = 99.7:0.3, 0.8 mL/min, 280 nm, 87% ee). $t_R = 10.156$ min (major), $t_R = 14.37$ min (minor)

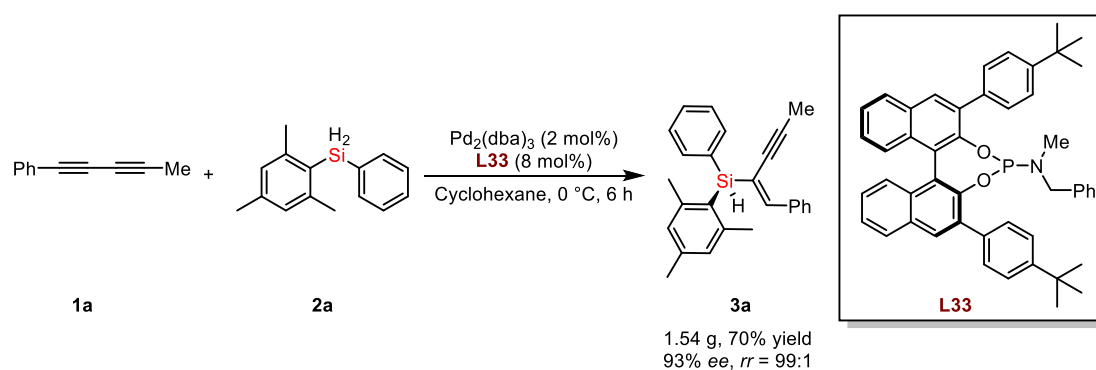


	Time/min	Area	Height	Area%
1	9.836	3624.9	125	49.922
2	13.307	3636.2	81	50.078



	Time/min	Area	Height	Area%
1	10.156	11450.3	364.6	92.779
2	14.37	891.2	15.8	7.221

3.4 Gram-Scale Synthesis of **3a**



In a flame 100 mL dried Schlenk tube, Pd₂(dba)₃ (109.9 mg, 0.12 mmol, 2 mol%), **L33** (335.9 mg, 0.48 mmol, 8 mol%) in cyclohexane (30 mL, 0.5M) was stirred at room temperature for 30 min under nitrogen atmosphere. Then diyne (6 mmol, 1 equiv.), dihydrosilanes (6 mmol, 1 equiv.) were added sequentially to the reaction mixture, and the reaction tube was cooled for 4 h at 0 °C. After completion of the reaction, the mixture was passed through a short celite pad using DCM as a solvent. The mixture was then concentrated in vacuo and purified by column chromatography using Petroleum ether-EtOAc (300:1) to give the desired product **3a** (1.54 g, 70% yield, 93% ee, rr = 99:1) in good yields.

3.5 Kinetic Study for the Pd-catalyzed Hydrosilylation

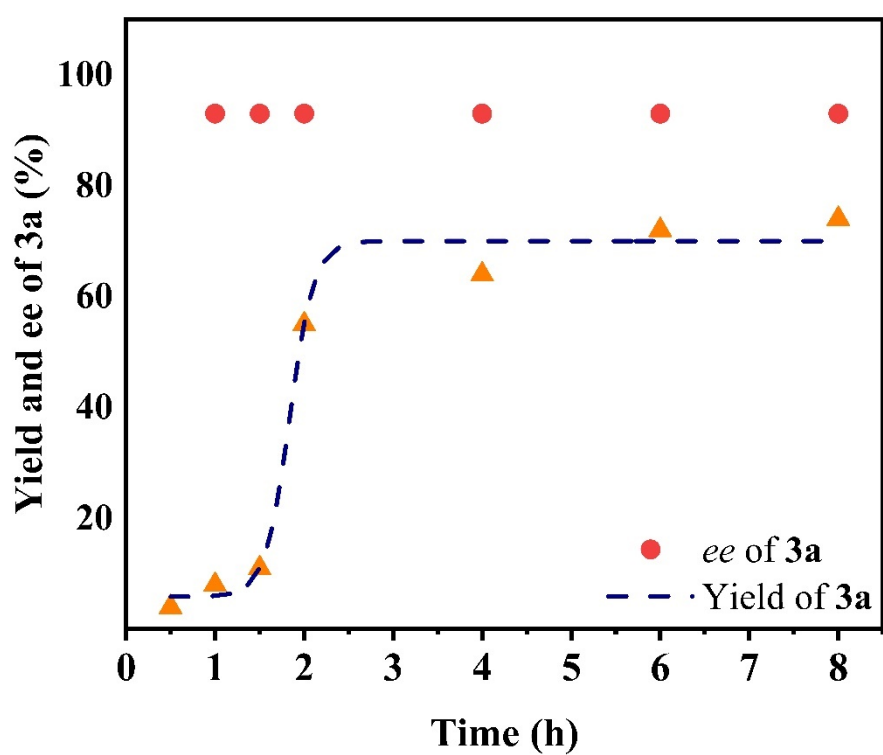
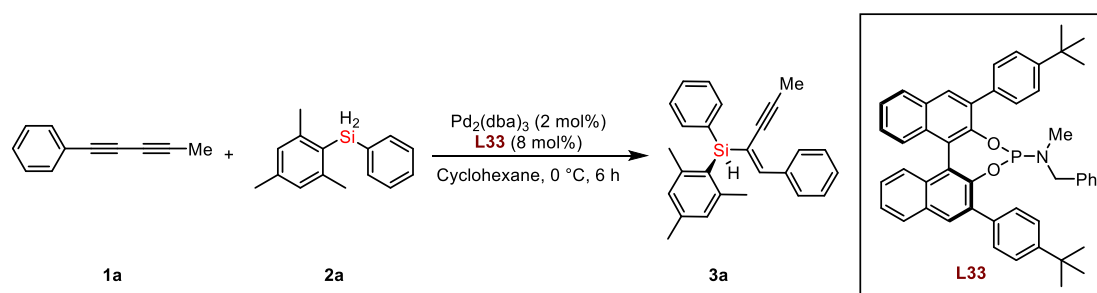


Figure S2. Kinetic Study for the Pd-catalyzed hydrosilylation of **1a**

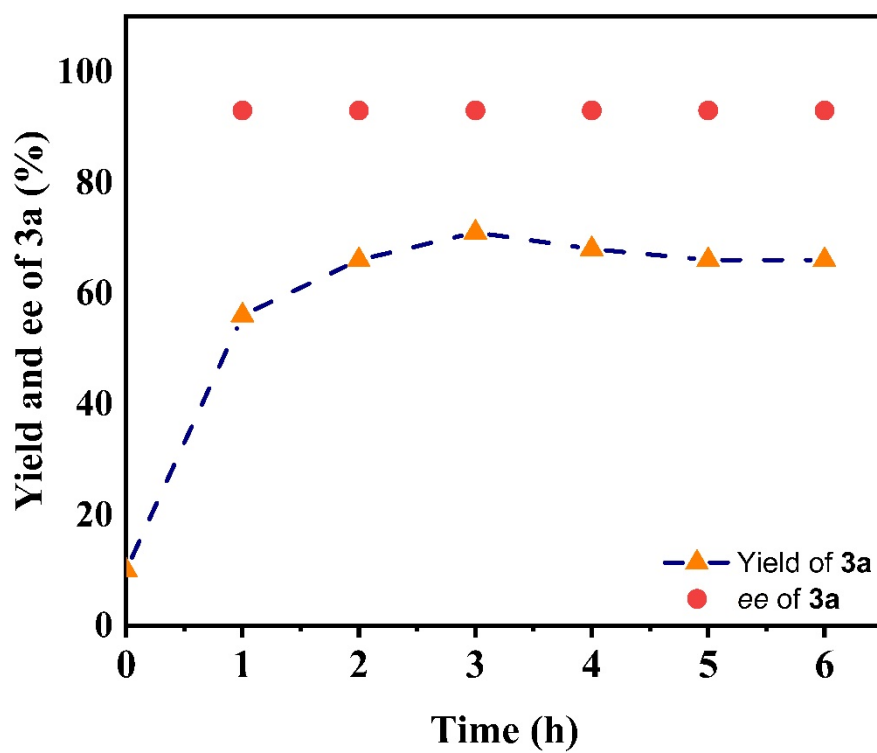
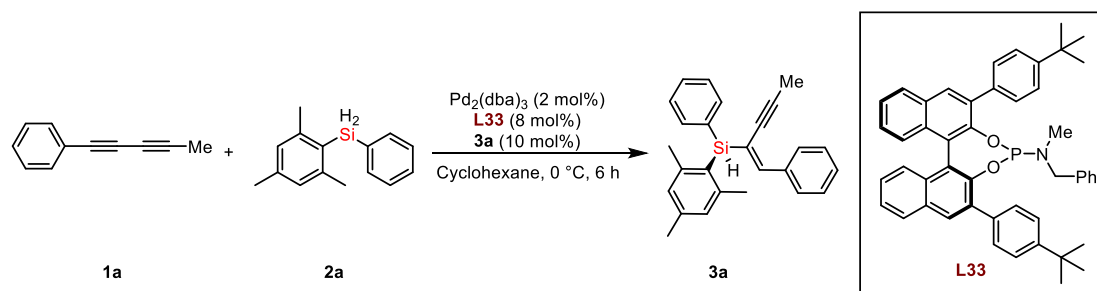


Figure S3. Kinetic Study for the Pd-catalyzed hydrosilylation of **1a** with **3a** (10 mol%) as additive

3.6 Experiments for Mechanistic Study

3.6.1 Kinetic Study for the KIE

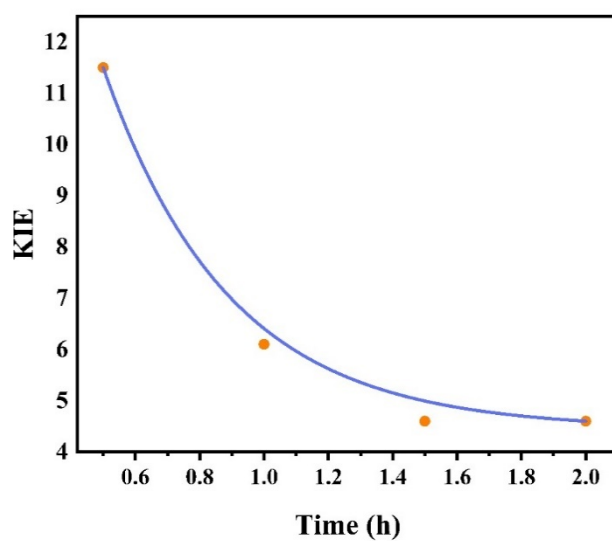
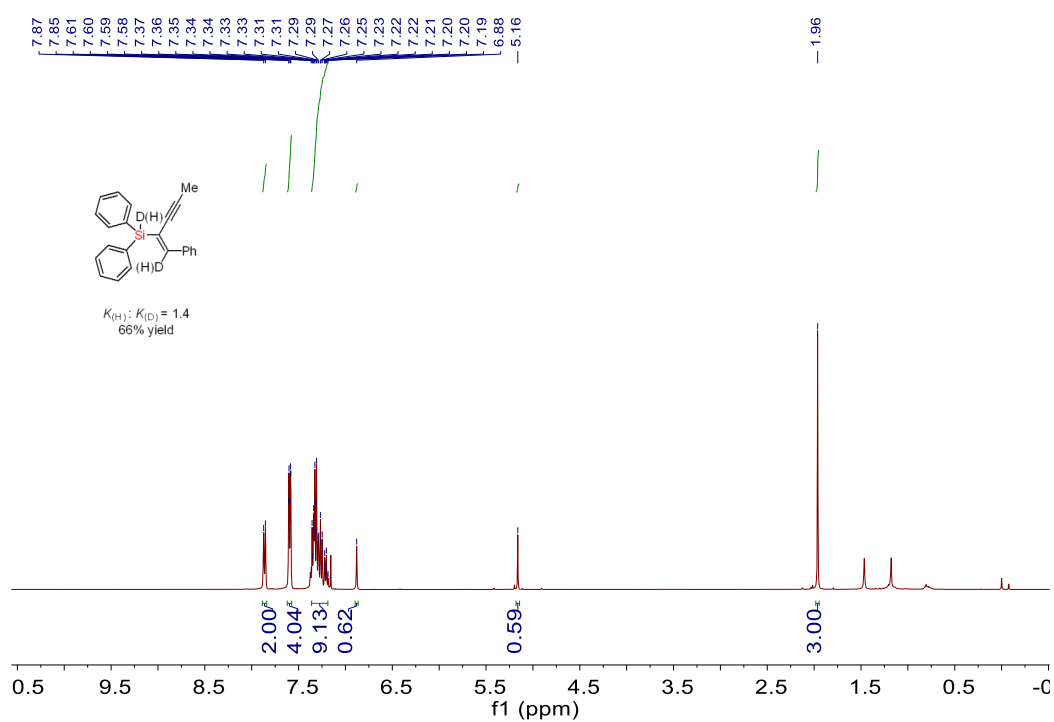
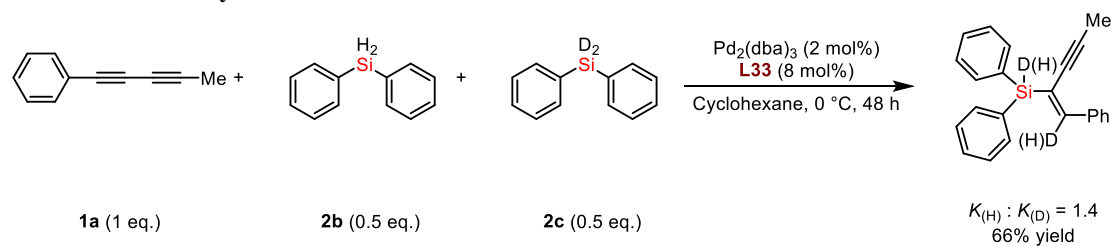


Figure S4. KIE analysis of the Pd-catalyzed hydrosilylation of **1a** for 2 h

3.6.2 The NLE study of the Pd-catalyzed Hydrosilylation of 1a

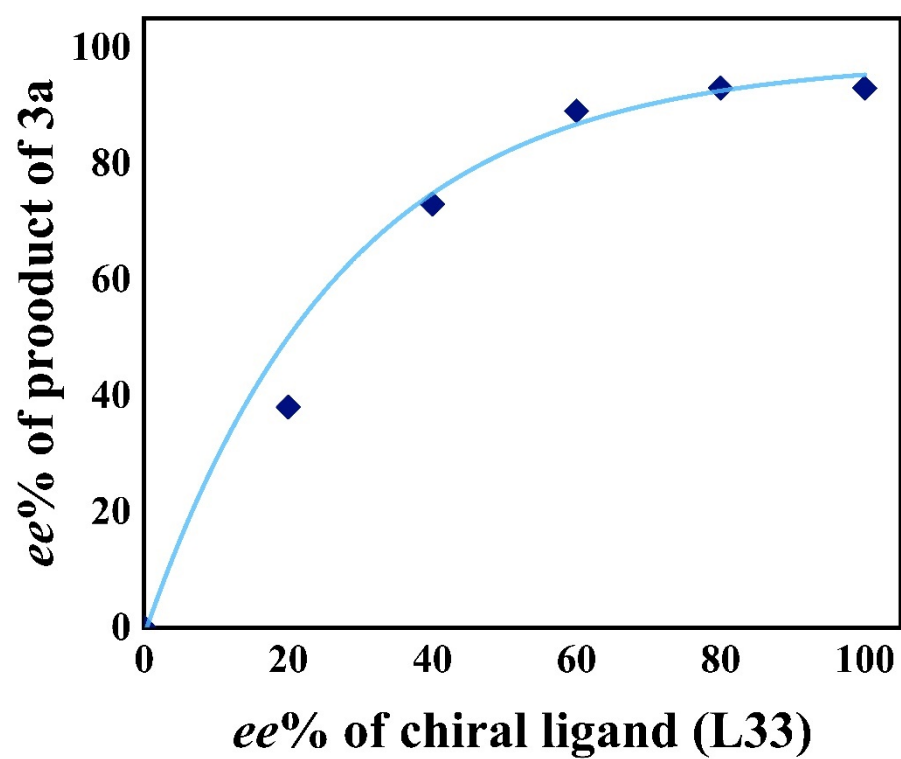
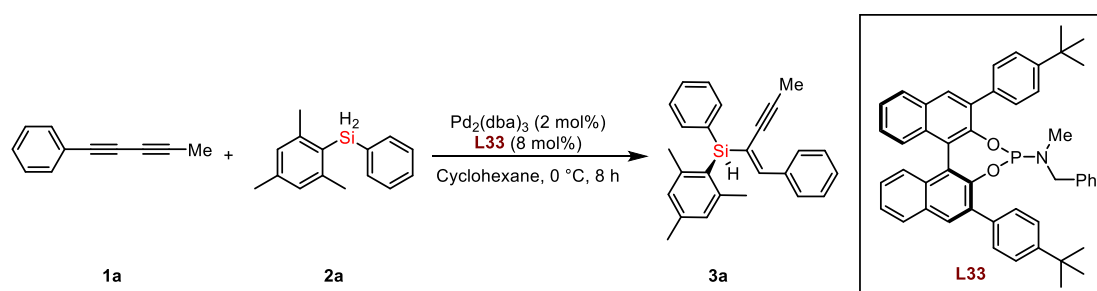


Figure S5. The study of possible NLE in the Pd-catalyzed hydrosilylation of 1a

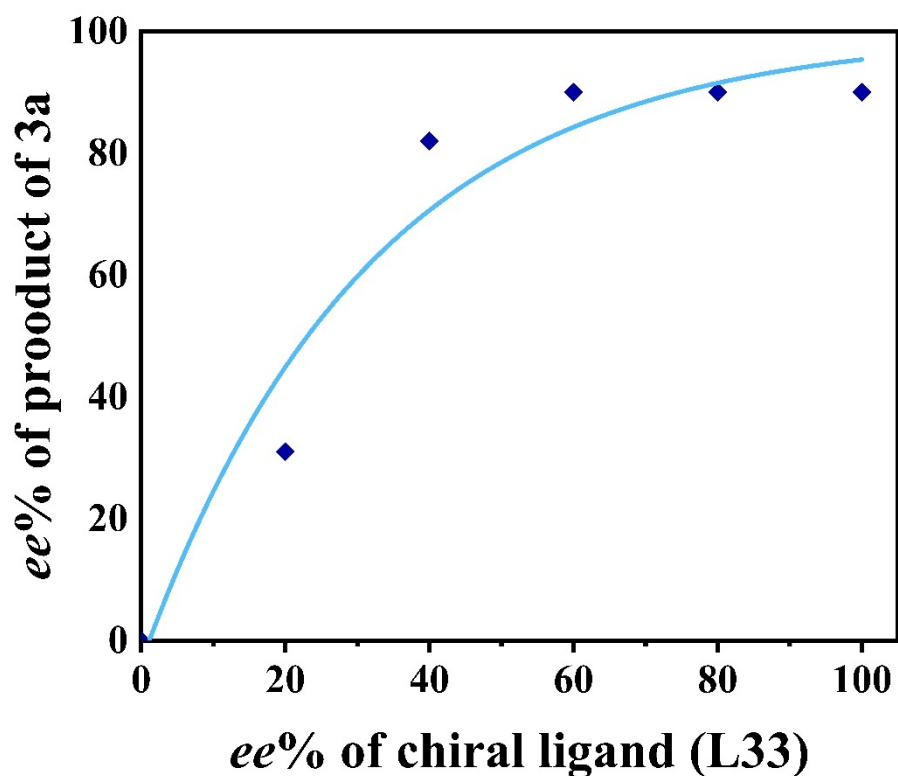


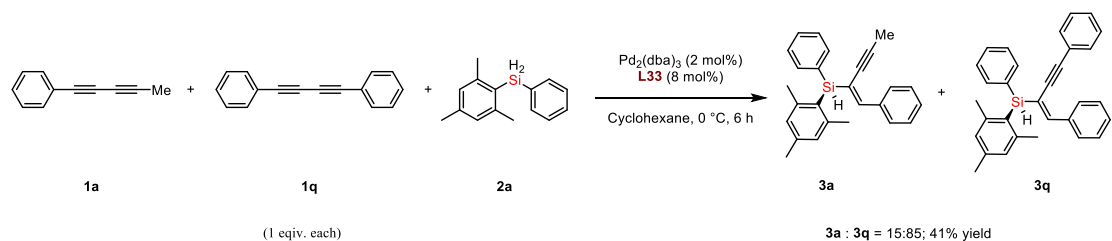
Figure S6. The study of possible NLE in the Pd-catalyzed hydrosilylation of **1a** with DCM as solvent.

Table S8. The effect of water on Pd-catalyzed hydrosilylation ^a

Entry	water content (%)	Yield of 3a (%) ^b	<i>ee</i> of 3a (%) ^c
1	10	44	90
2	20	48	90
3	30	36	90
4	40	36	90
5	50	42	90

^aUnless otherwise noted, reactions were conducted under N₂ on 0.1 mmol scale: **1a** (0.1 mmol), **2a** (0.1 mmol), Pd₂(dba)₃ (2 mol%), L33 (8 mol%), THF : H₂O (2 mL). ^bDetermined by ¹H NMR using dibromomethane as an internal standard. ^cDetermined by HPLC.

3.6.3 Competitive Experiment for the Different Reactivity of Aliphatic and Aromatic diynes.



3.6.4 Comparison of ^{31}P NMR of Ligand and Pd/L33 Complex in the Reaction of 1a and 2a.

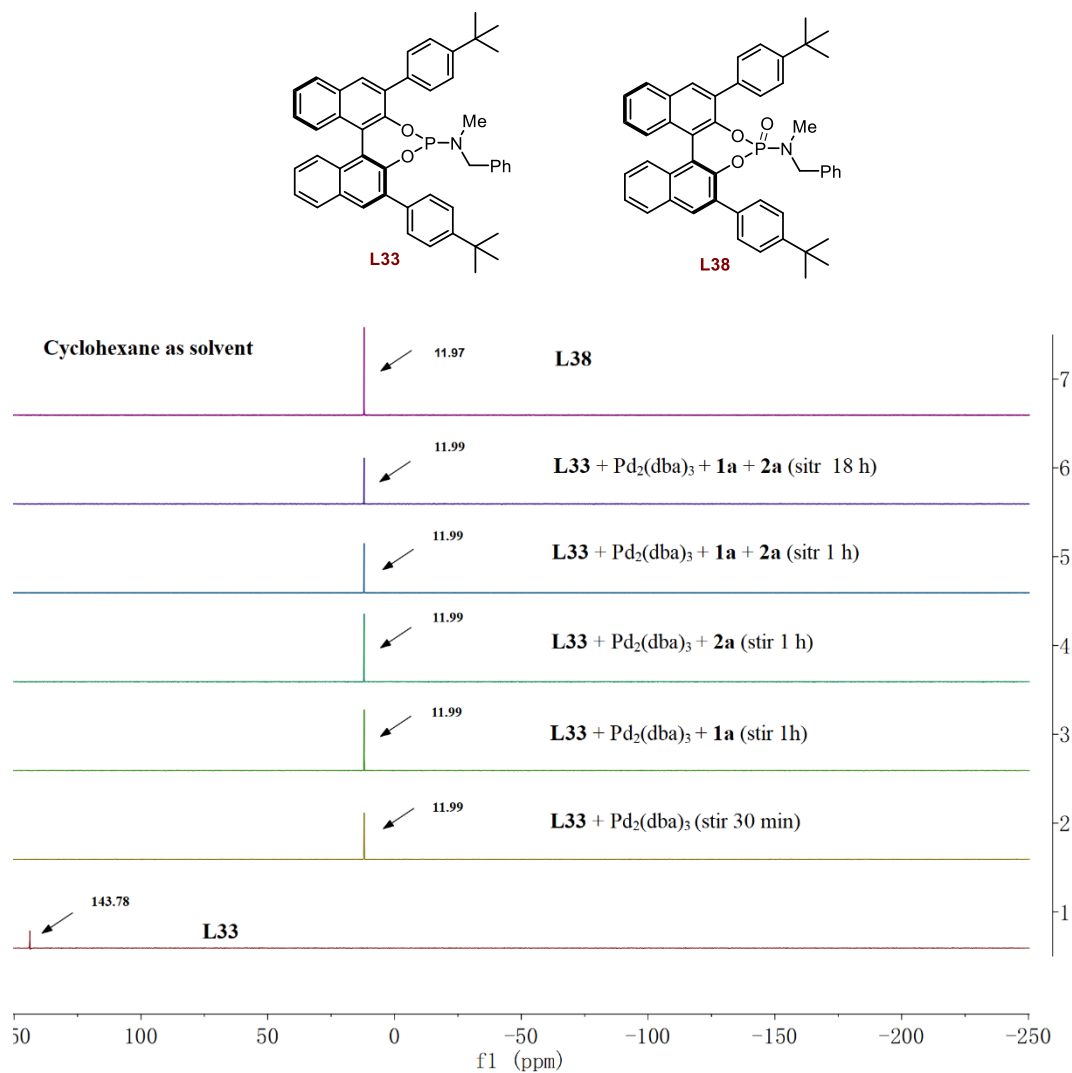


Figure S7. Comparison of ^{31}P NMR of ligand and Pd/L33 complex in the reaction with **1a** and **2a**.

3.6.5 Comparison of ^1H NMR of L33, Pd/L33 Complex in the Reaction of 1a and 2a.

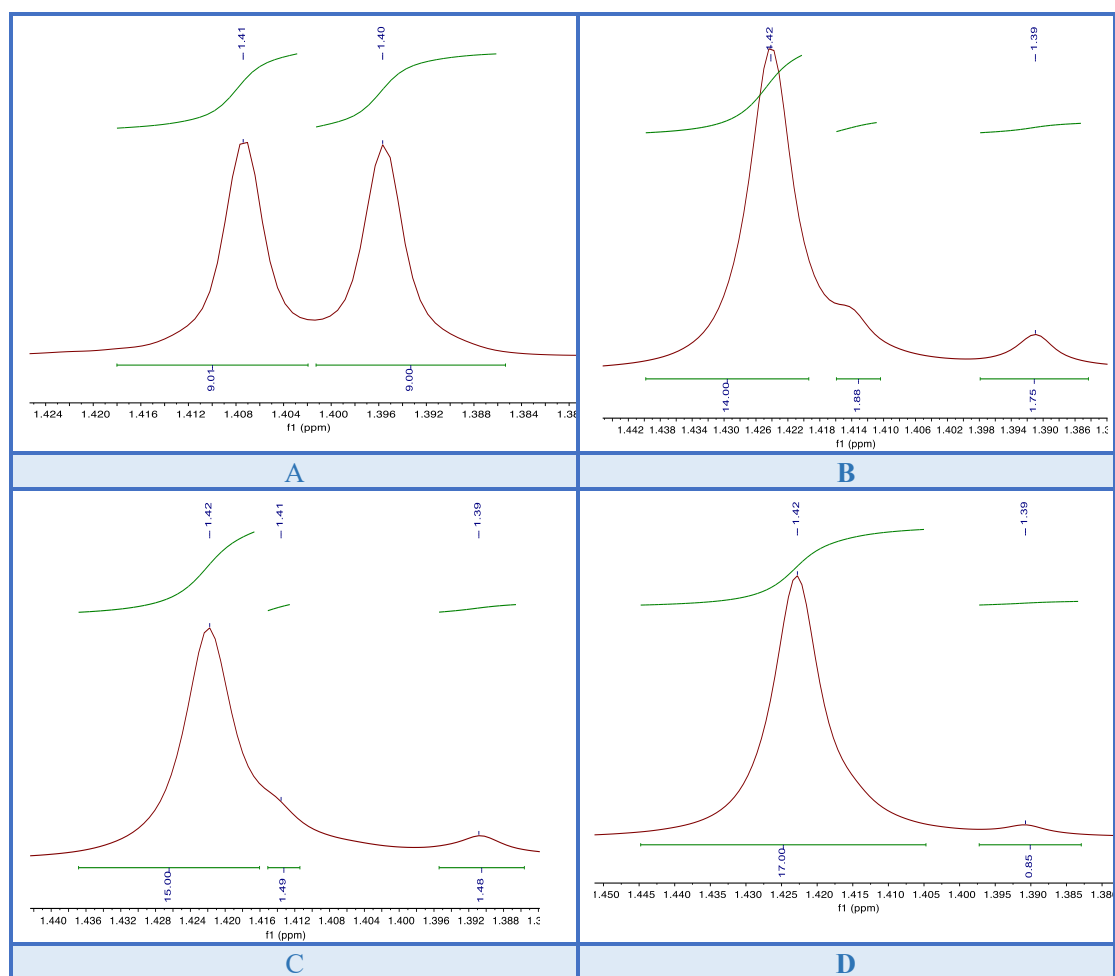
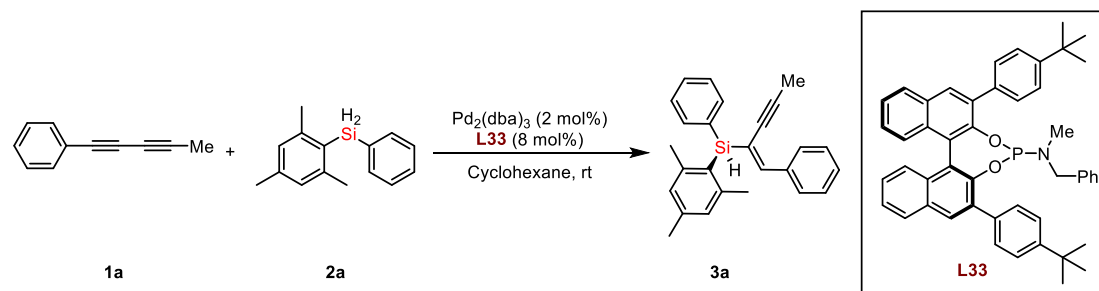


Figure S8. ^1H NMR (A) L33; (B) $\text{Pd}_2(\text{dba})_3 + \text{L33} + 2\text{a}$, stir 1 h; (C) $\text{Pd}_2(\text{dba})_3 + \text{L33} + 1\text{a} + 2\text{a}$, stir 1 h; (D) $\text{Pd}_2(\text{dba})_3 + \text{L33} + 1\text{a} + 2\text{a}$, stir 18 h.

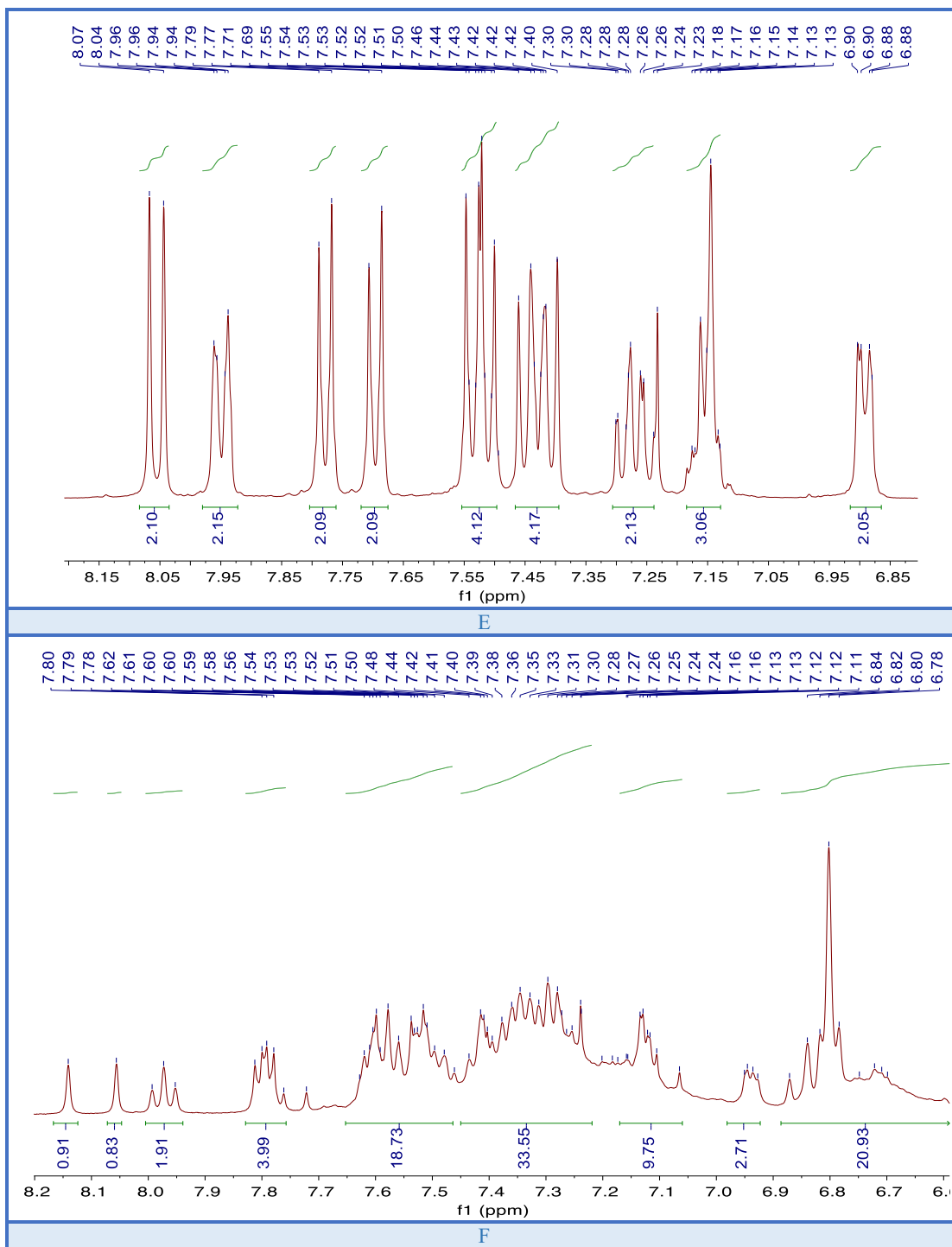
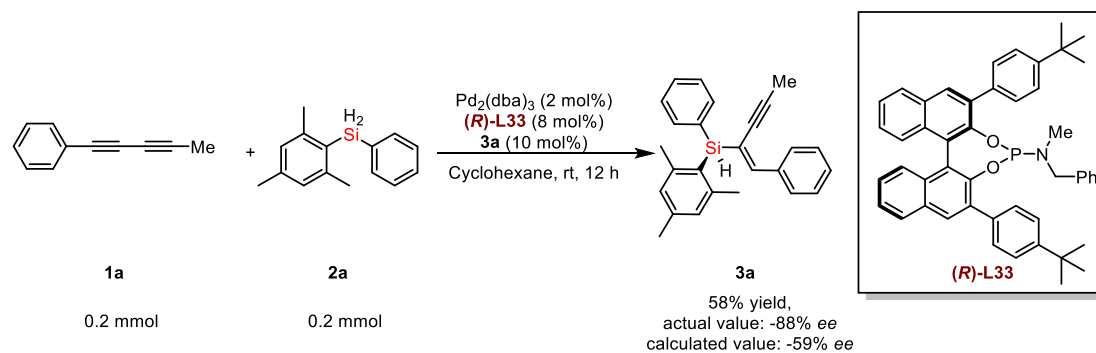


Figure S9. ^1H NMR (E) L33; (F) $\text{Pd}_2(\text{dba})_3 + \text{L33} + \text{2a}$, stir 1 h.

3.6.6 The determination of product-promoted palladium catalysis (autocatalysis) by chirality matching between chiral additive (3a) and chiral ligand in the Pd-catalyzed hydrosilylation



	Ratio of 3	<i>R</i>	<i>S</i>
<i>(R)</i> - 3a	48%	95.5	4.5
<i>(S)</i> - 3a	10%	4	97

method of calculated value : $48\% \times 95.5 + 10\% \times 4 : 48\% \times 4.5 + 10\% \times 97$
 79.6 : 20.4

3.6.7 CD Spectra

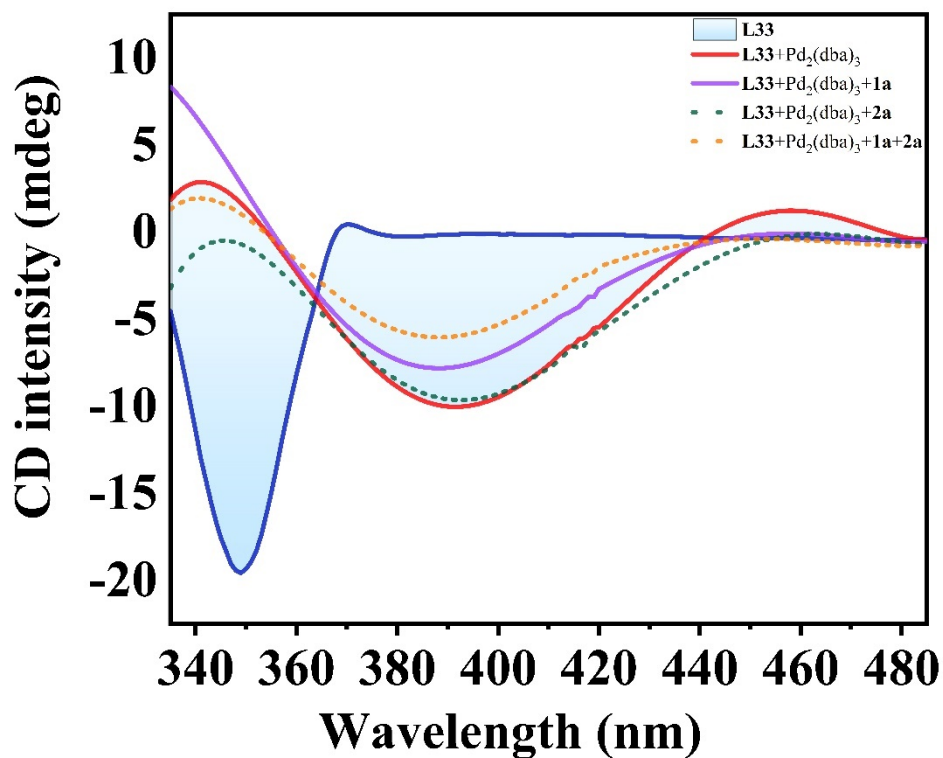


Figure S10. Circular dichroism spectroscopy analysis CD (1.00×10^{-2} mol/L) intensity spectra of the Pd-catalyzed hydrosilylation of **1a**.

3.6.8 UV Spectra

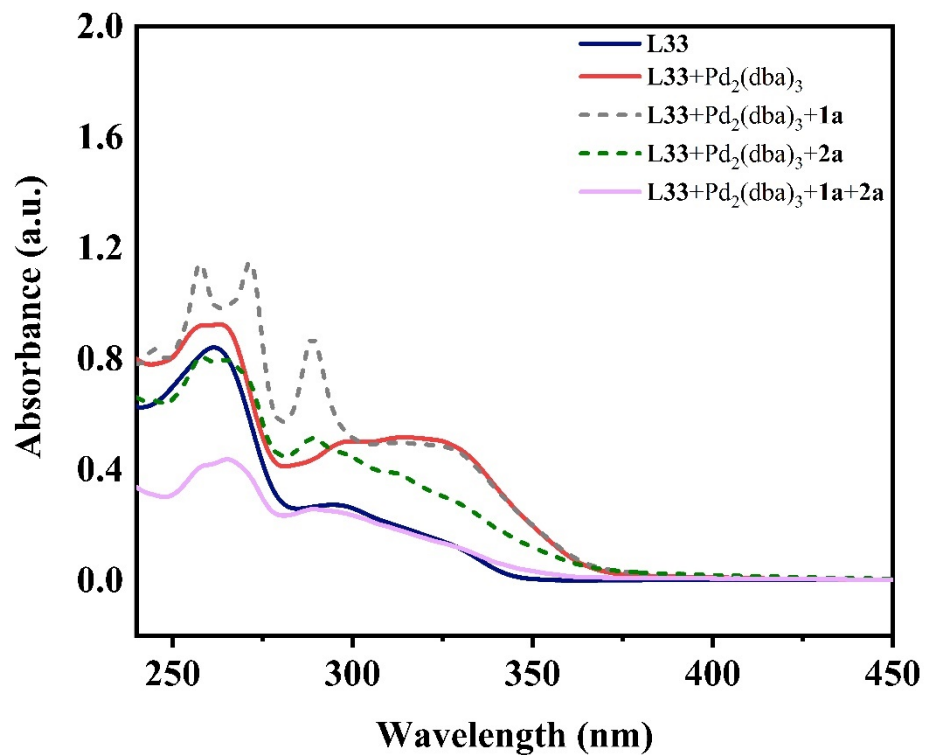


Figure S11. 2D UV-vis absorption spectrum of L33, Pd₂(dba)₃, 1a and 2a in CHCl₃ (2.5×10^{-5} mol/L).

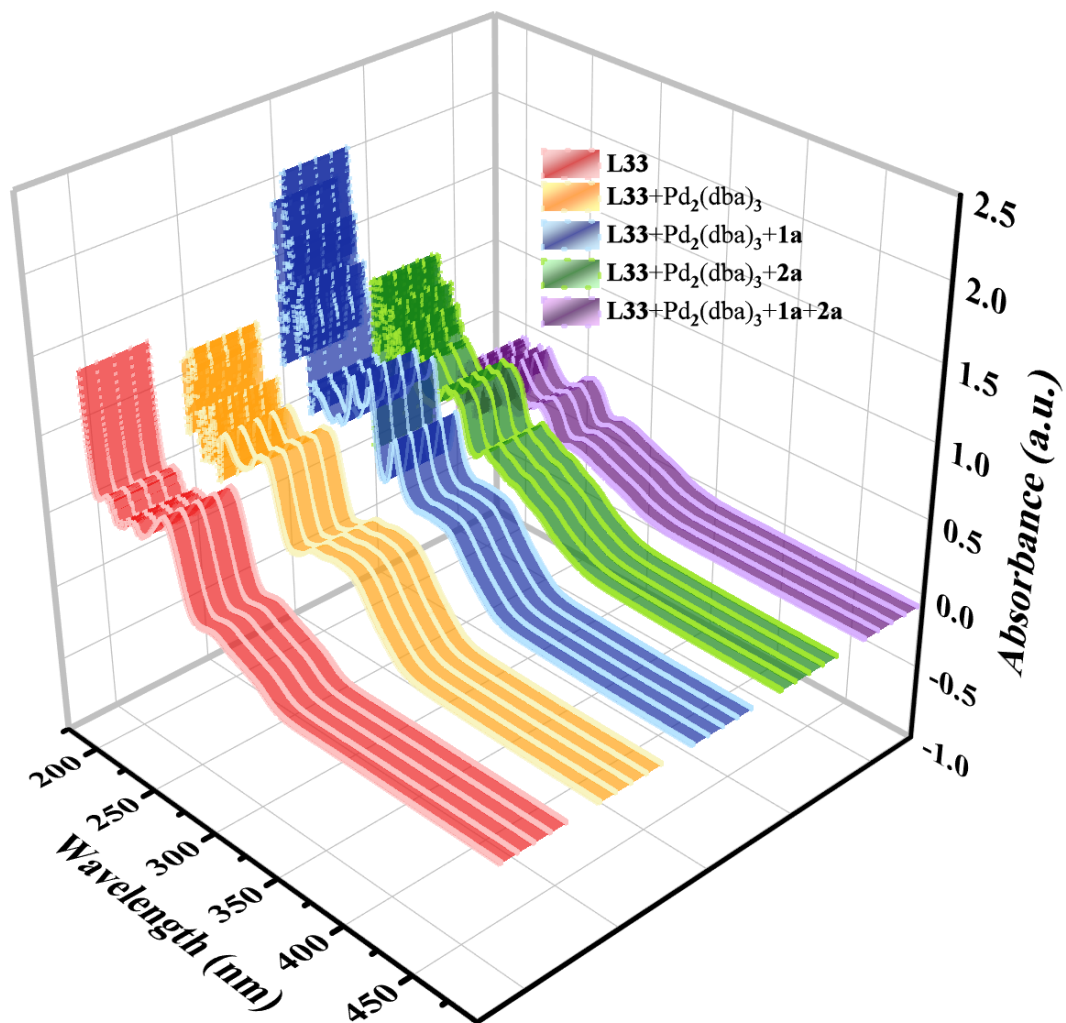
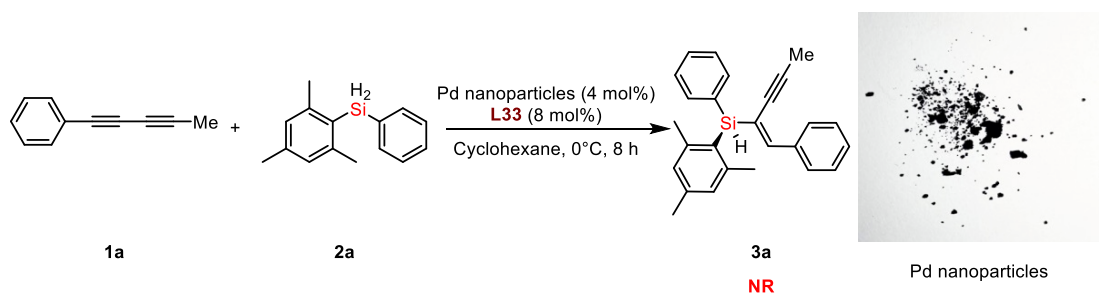


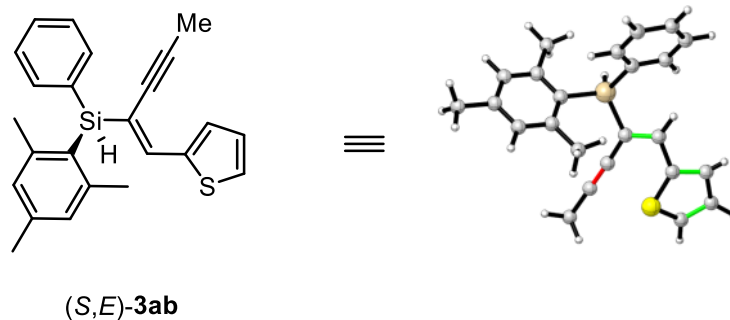
Figure S12. 3D UV-vis absorption spectrum of **L33**, $\text{Pd}_2(\text{dba})_3$, **1a** and **2a** in CHCl_3 (2.5×10^{-5} mol/L).

3.6.9 Pd-nanoparticles catalyzed hydrosilylation^[7]



3.7 X-Ray Structure of 3ab

Single crystals of **3ab** were obtained by recrystallization from PE/EA. The molecular structure and X-ray diffraction data/refinement of **3ab** were shown below

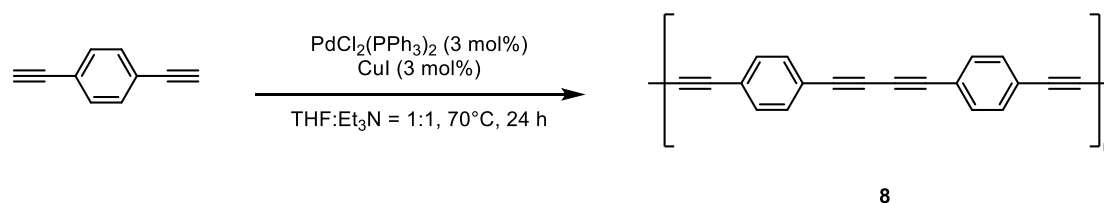


(CCDC 2209523)

Empirical formula	C ₄₈ H ₄₈ S ₂ Si ₂
Formula weight	745.16
Temperature	293(2) K
Crystal system	Monoclinic
space group	P2(1)
a/Å	9.1046(7)
b/Å	7.8073(6)
c/Å	15.4040(11)
α/°	90
β/°	101.618
γ/°	90
Volume/ Å ³	1072.53(14)
Z	1
Calculated density mg/m ³	1.154
Absorption coefficient mm ⁻¹	1.886
F(000)	396
Crystal size/ mm ³	0.120 x 0.120 x 0.110
Theta range for data collection/°	2.929 to 67.169 deg.
Limiting indices	-10<=h<=6, -9<=k<=8, -18<=l<=17
Reflections collected / unique	3868 / 2808 [R(int) = 0.0257
Completeness to theta	99.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2808 / 1 / 243
Goodness-of-fit on F ²	0.995
Final R indices [I>2σ(I)]	R1 = 0.0412, wR2 = 0.1002
R indices (all data)	R1 = 0.0483, wR2 = 0.1058
Absolute structure parameter	0.04(2)
Extinction coefficient	n/a
Largest diff. peak and hole / e. Å ⁻³	0.142 and -0.209

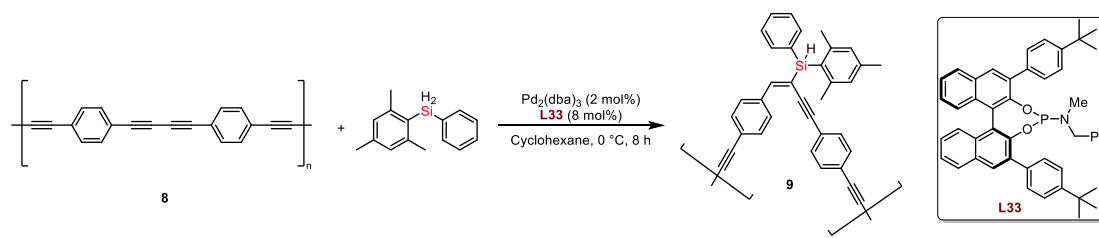
3.8 Synthesis of Polydiyne **9** by Pd-catalyzed Hydrosilylation

3.8.1 Preparation of Polydiyne **8**



A flame dried 25 mL Schlenk tube, 1,4-diethynylbenzene (252 mg, 2 mmol), Pd(PPh₃)₂Cl₂ (41 mg, 3 mol%) and CuI (11 mg, 3 mol%) were dissolved in the mixture of THF (2 mL) and Et₃N (2 mL). The mixture solution was heated to 70 °C and stirred 24 h. After that, the mixture was cooled to temperature and washed 3 times with methanol, chloroform and acetone. Being dried in vacuum for overnight at 70 °C to give 344 mg of product **8**.

3.8.2 Pd-catalyzed Hydrosilylation of Polydiyne **8**



In a flame dried Schlenk tube, Pd₂(dba)₃ (1.8 mg, 0.003 mmol, 2 mol%), **L33** (5.6 mg, 0.008 mmol, 8 mol%) in Cyclohexane (1 mL, 0.2M) was stirred at room temperature for 30 min under nitrogen atmosphere. Then **8** (0.1 mmol, 1 equiv.), dihydrosilanes (0.1 mmol, 1 equiv.) were added sequentially to the reaction mixture, and the reaction tube was cooled for 8 h at 0 °C. After completion of the reaction, the mixture was warmed to temperature and washed with methanol and chloroform. The product 15 mg of product **9** was dried in vacuum.

3.8.3 CD Spectra of Polyenyne 9

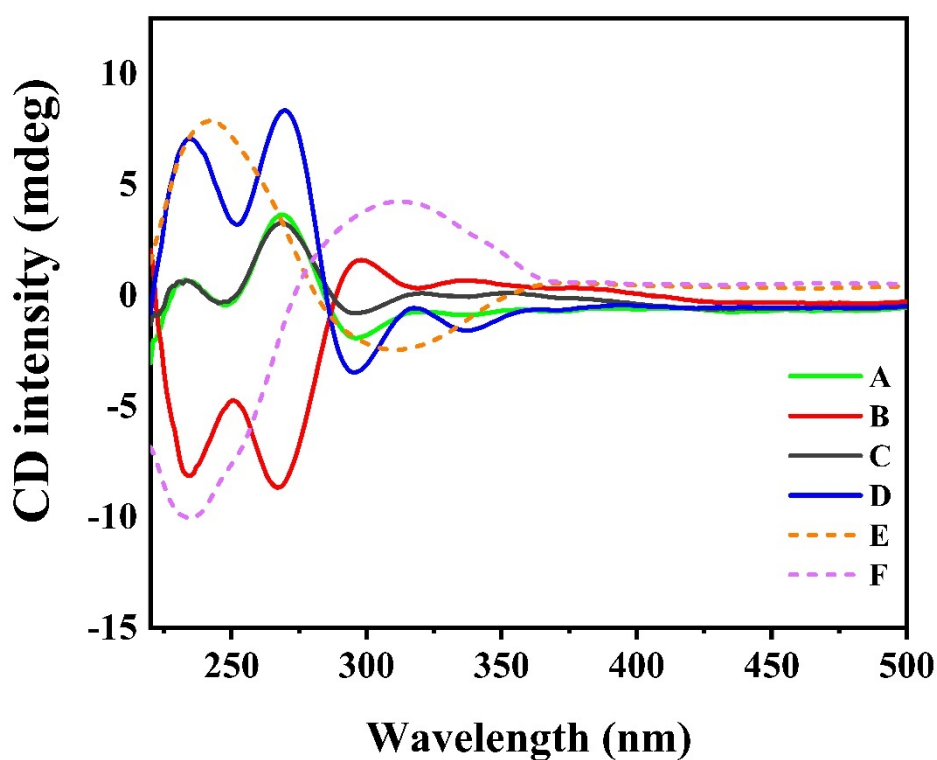
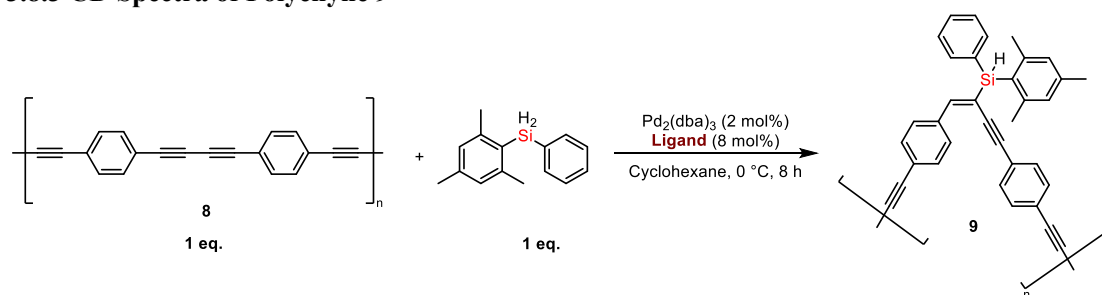


Figure S13. Circular dichroism spectroscopy analysis intensity spectra of (A) a diluted THF solution of the **9** with (*S*)-**L33** (2 g/L in THF); (B) a diluted THF solution of the **9** with (*R*)-**L33** (2 g/L in THF); (C) a diluted THF solution of the the **9** with (*S*)-**L33** and 0.5 eq. [Si-H] (2 g/L in THF); (D) a diluted THF solution of the the **9** with (*S*)-**L14** (2 g/L in THF); (E) a diluted THF solution of the (*R*)-**3q** (0.3 g/L in THF); (F) a diluted THF solution of the (*S*)-**3q** (0.3 g/L in THF).

3.8.4 FTIR spectra

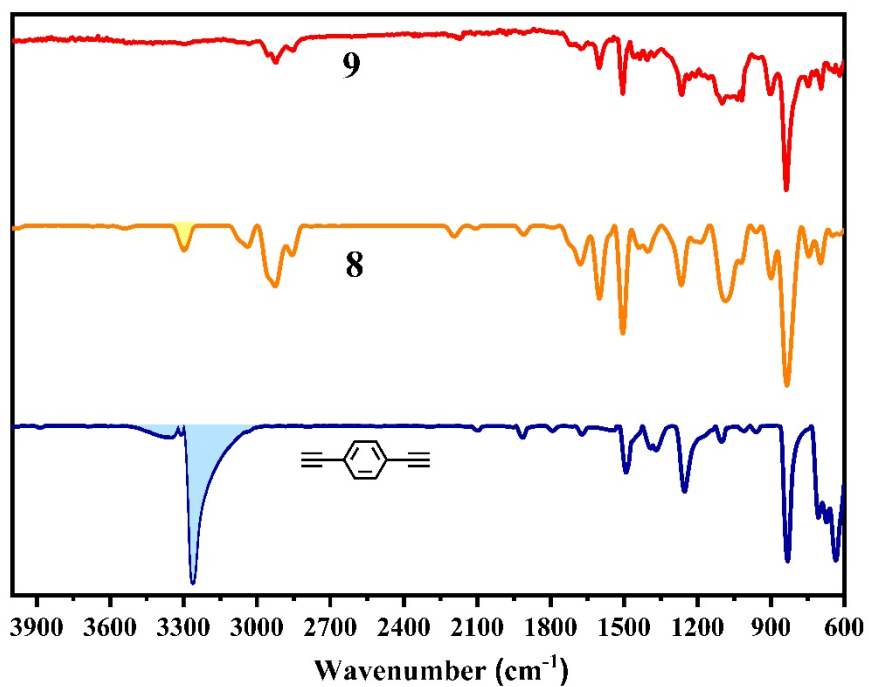


Figure S14. FTIR spectra of pyrolysis products of 1,4-Diethynylbenzene, **8** and **9**.
1,4-Diethynylbenzene(area): 3.07; **8** (area): 57.62. $M_w = 4736$.

3.8.5 SEM images

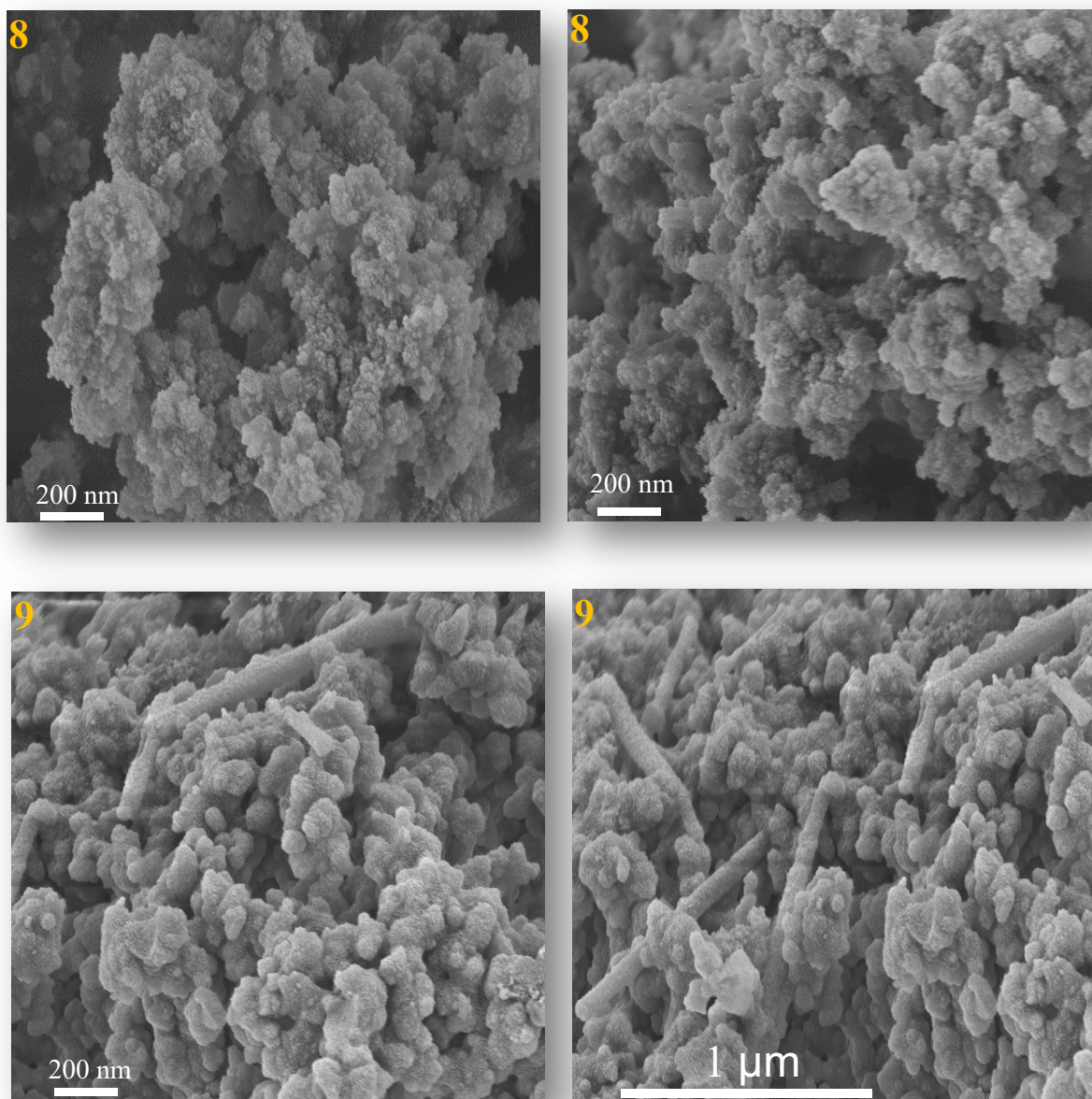


Figure S15. SEM images of **8** and **9**.

3.8.6 TG Analysis of Polydiyne 8 and Polyenyne 9

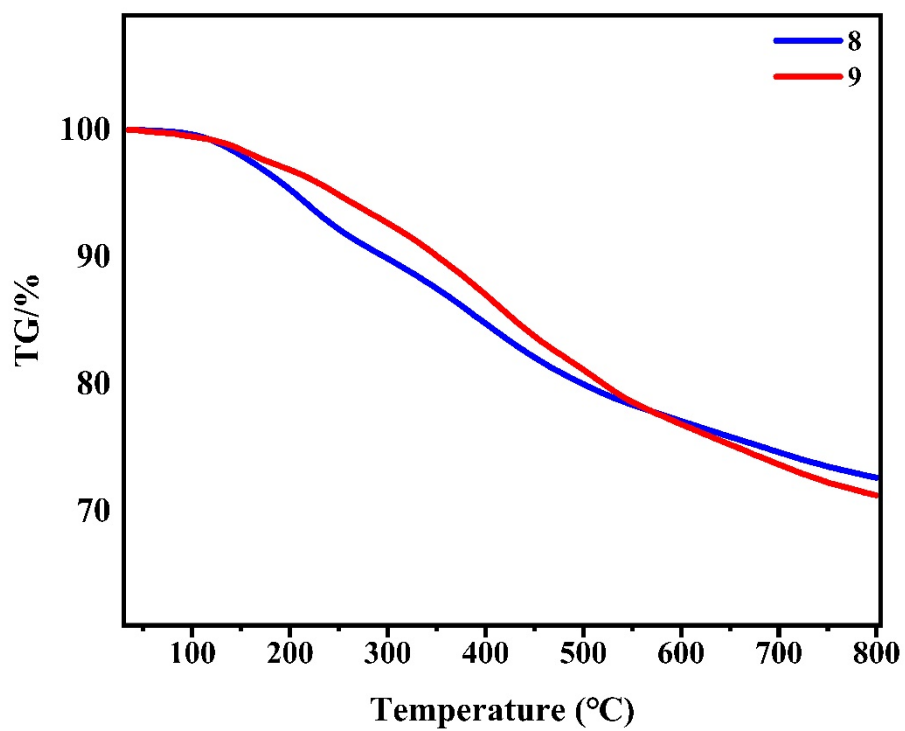
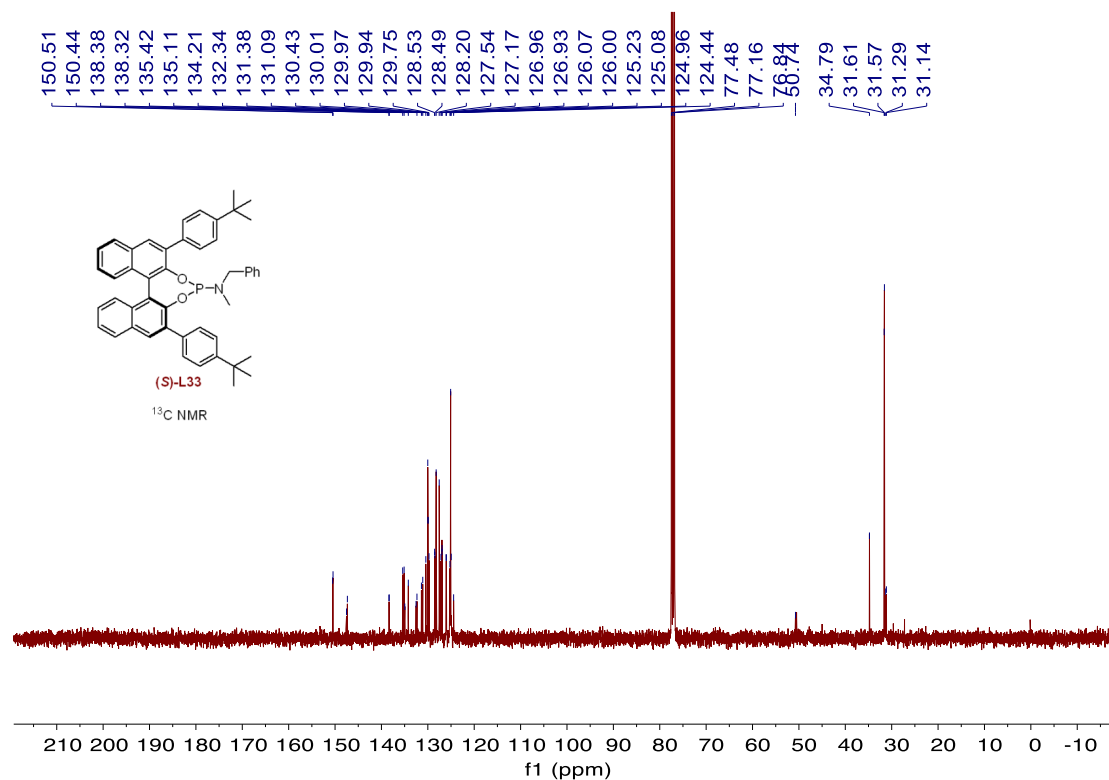
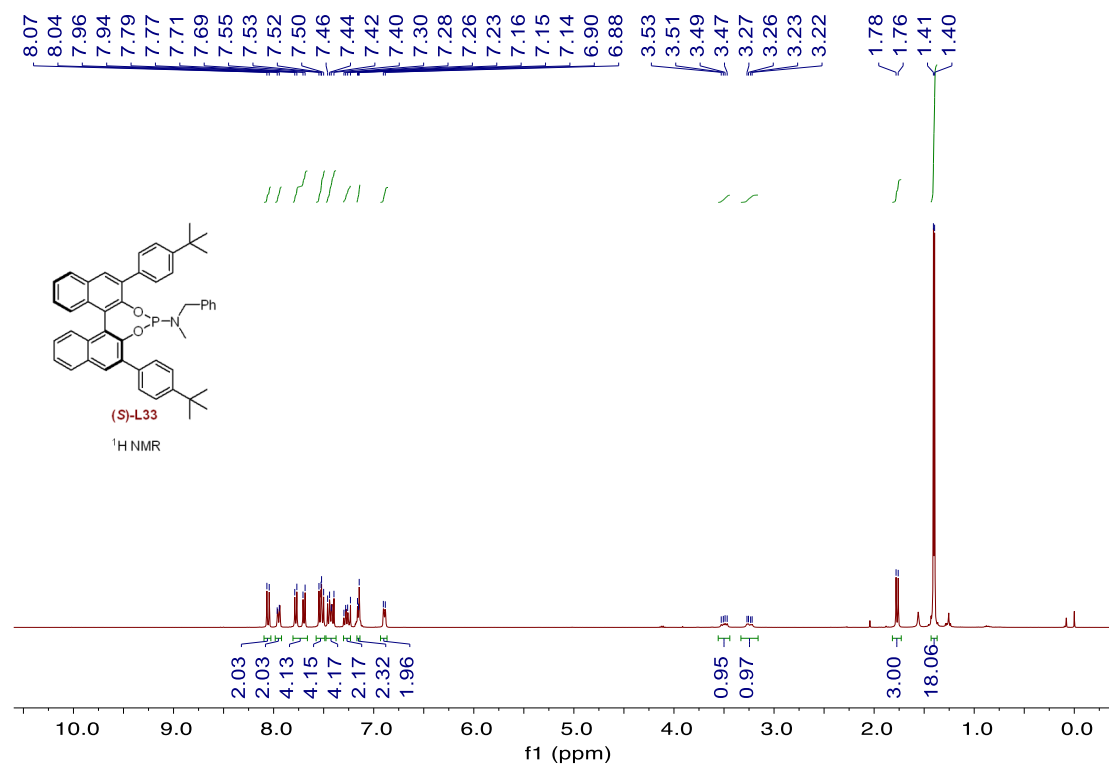
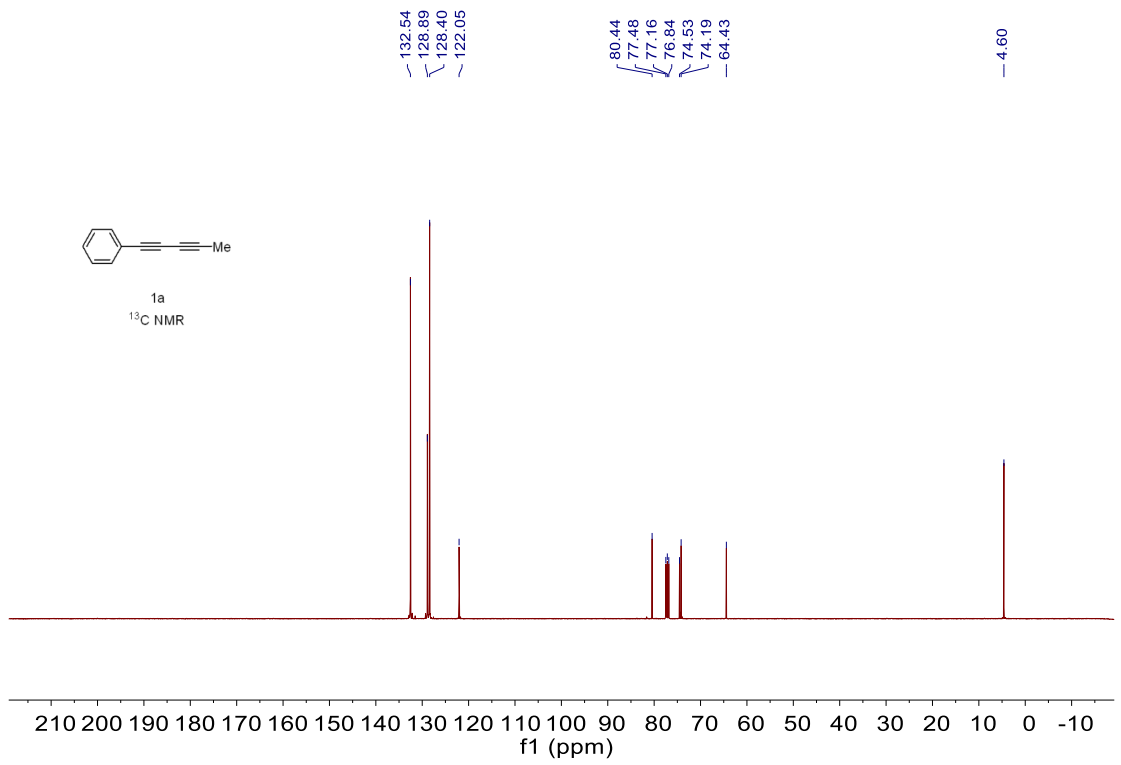
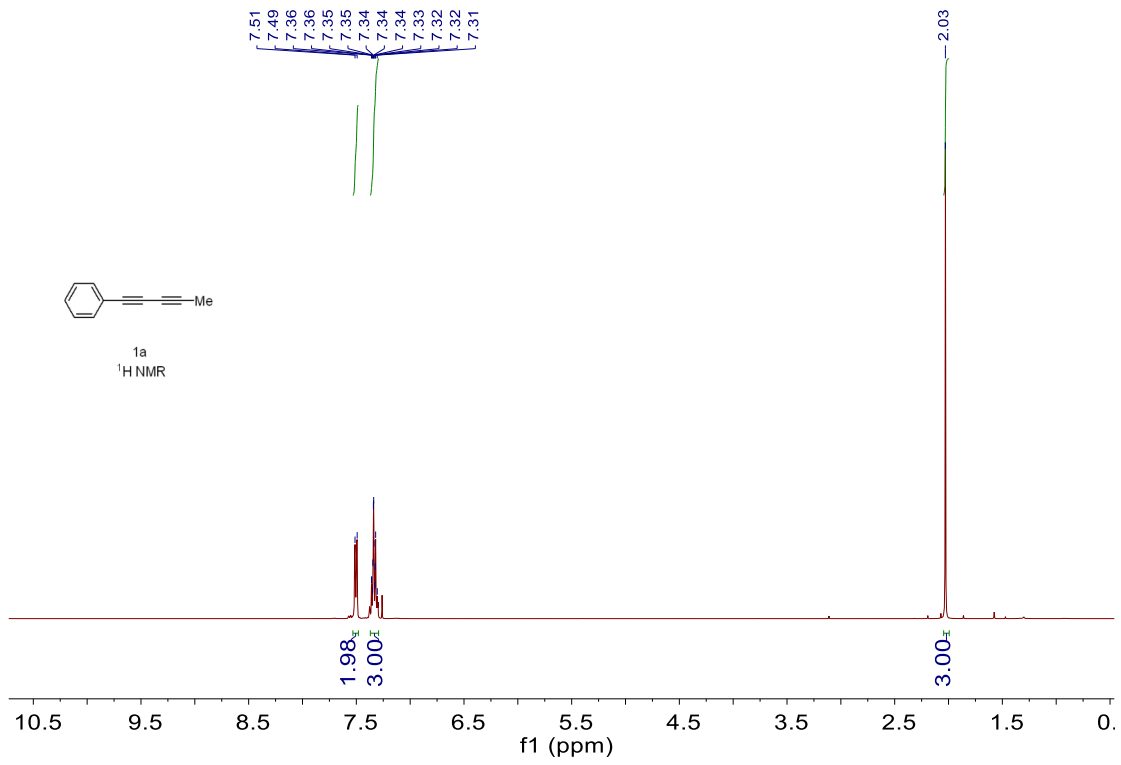
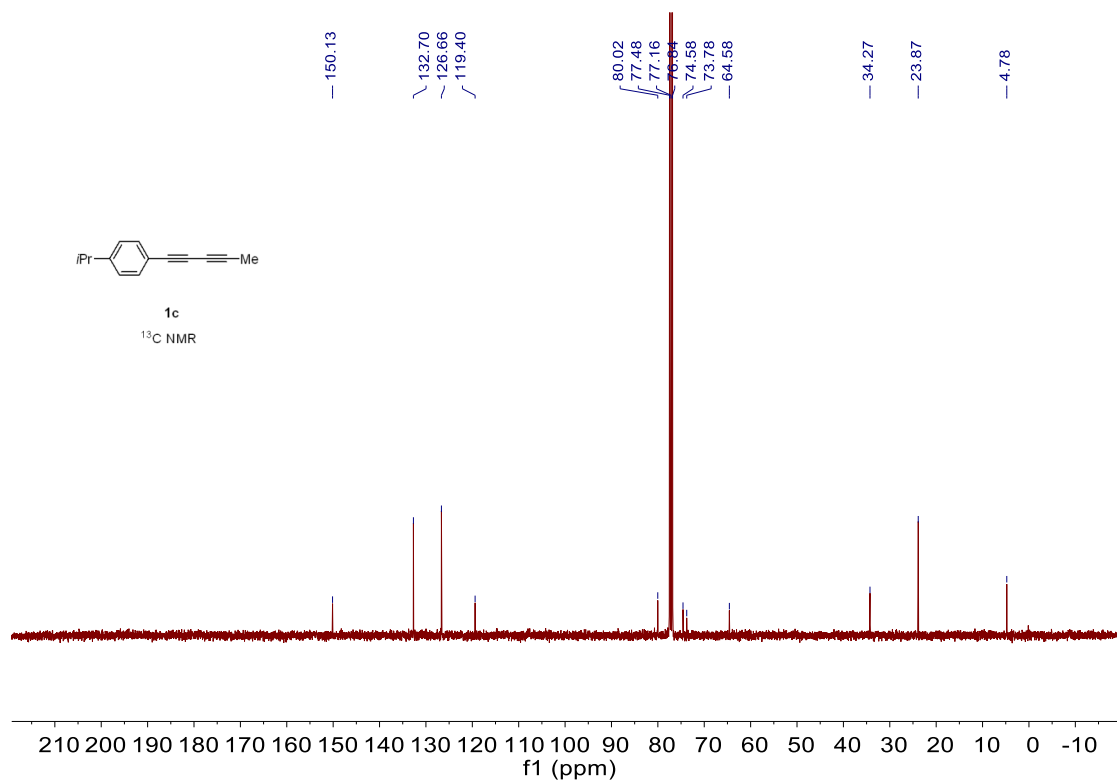
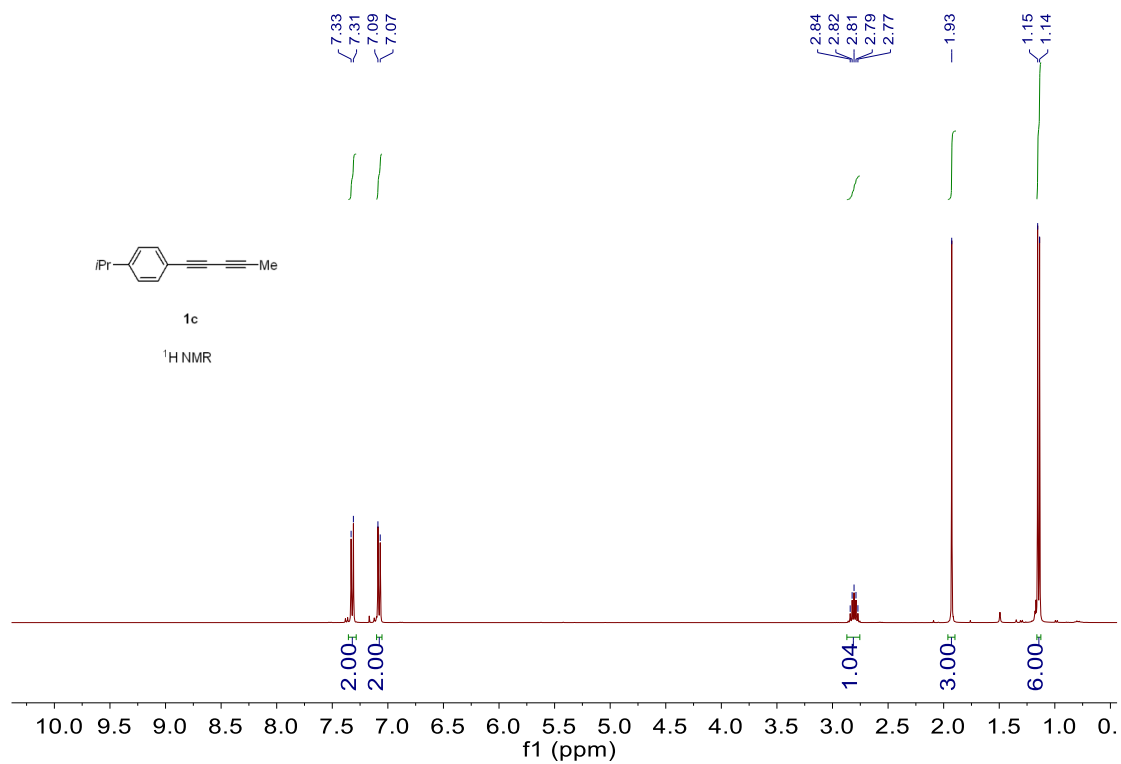


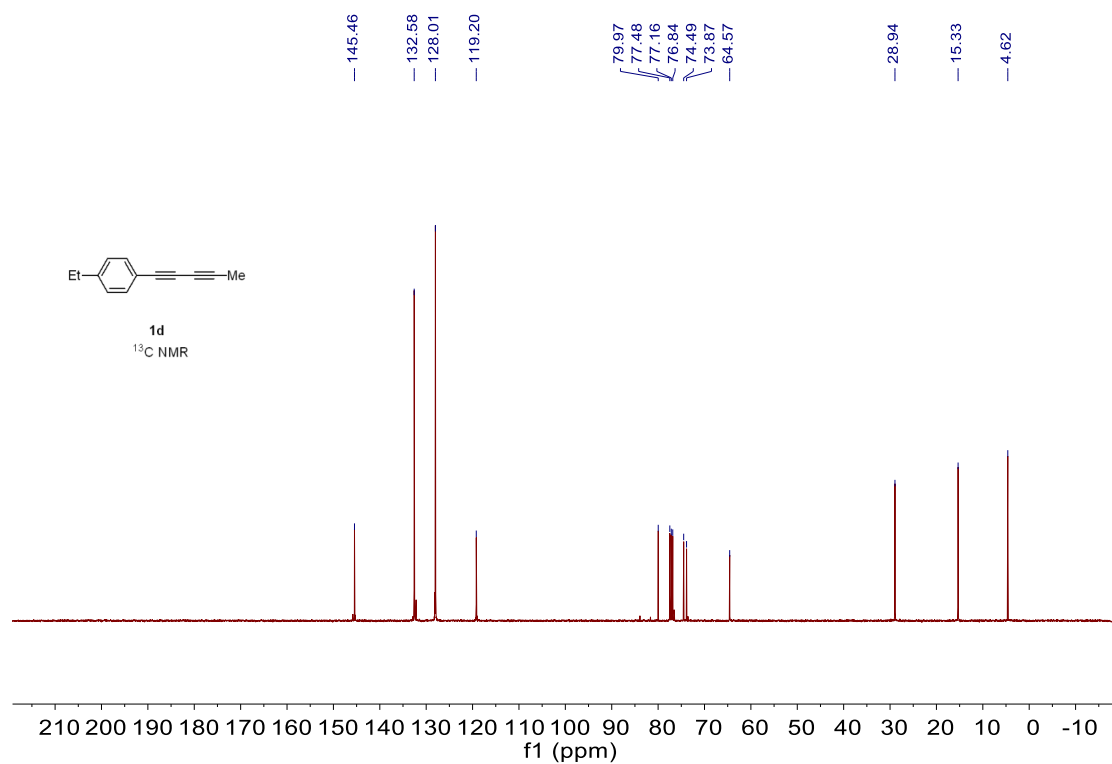
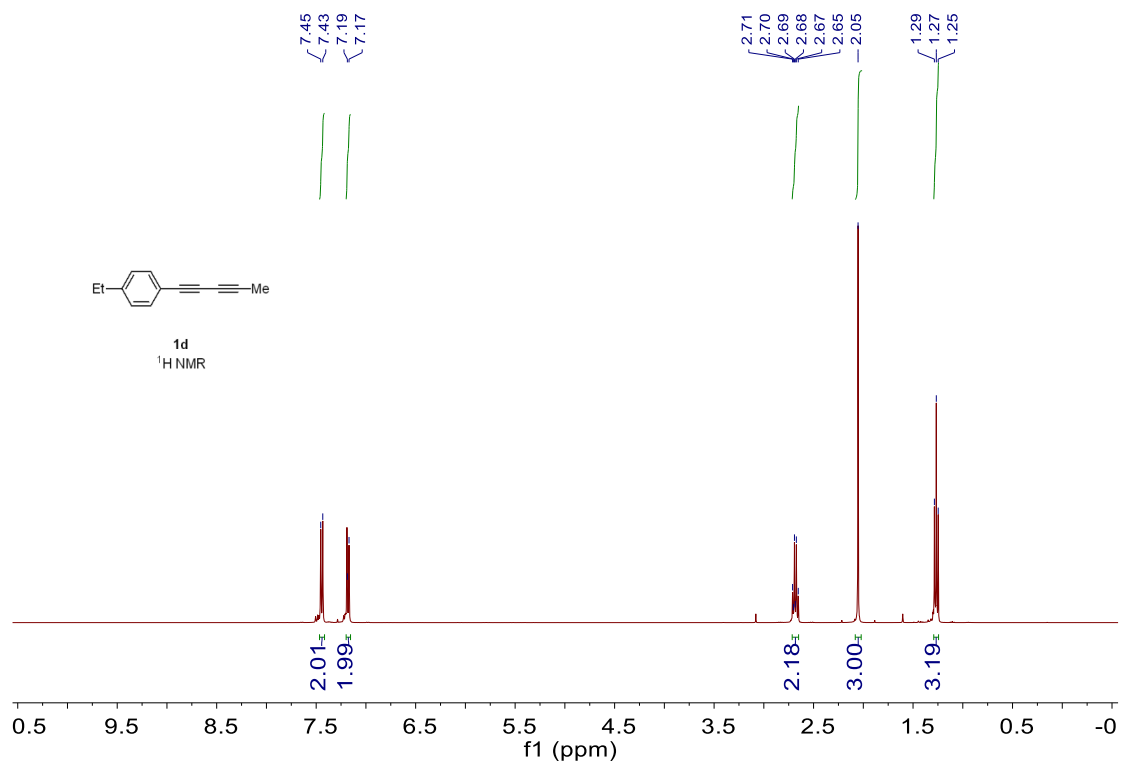
Figure S16. TG (solid line) curves of **8** and **9** with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 .

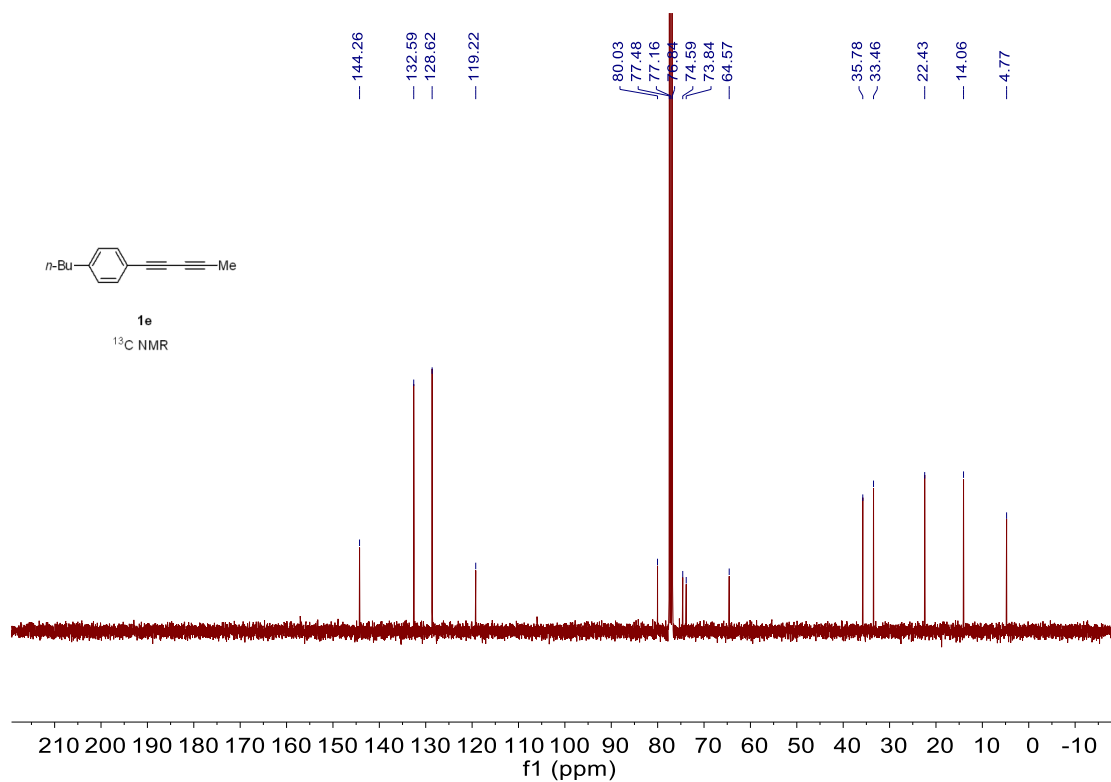
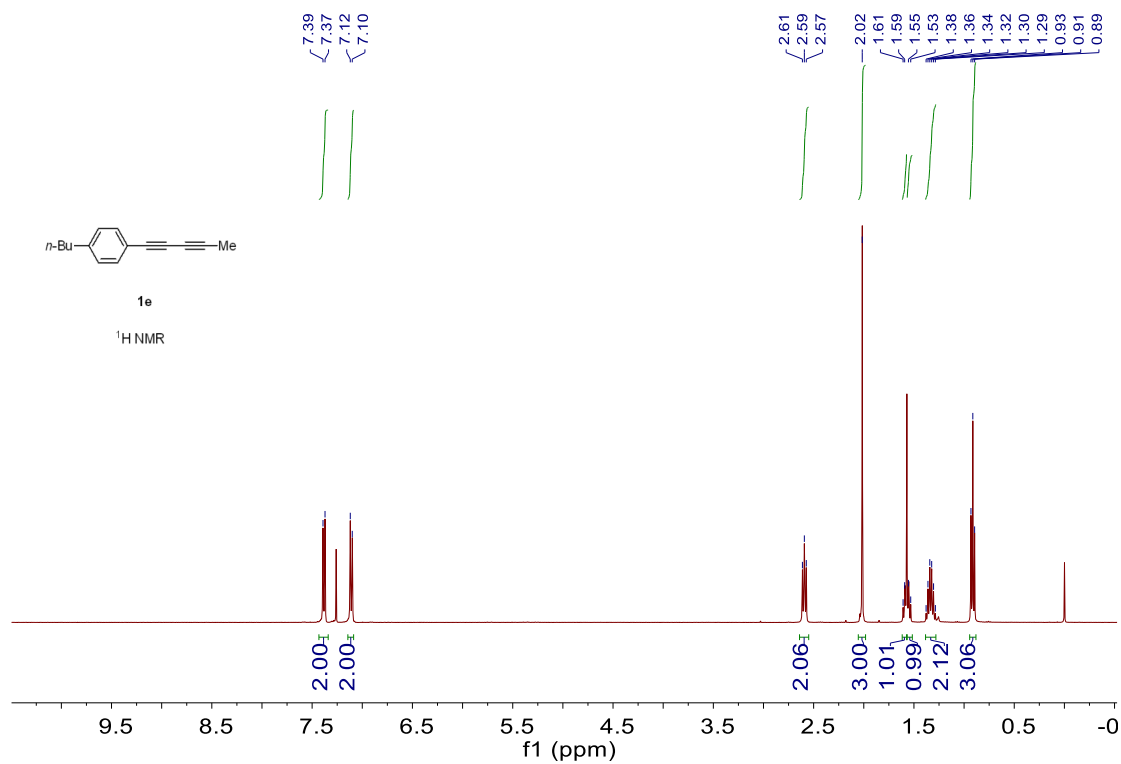
4 NMR Spectra

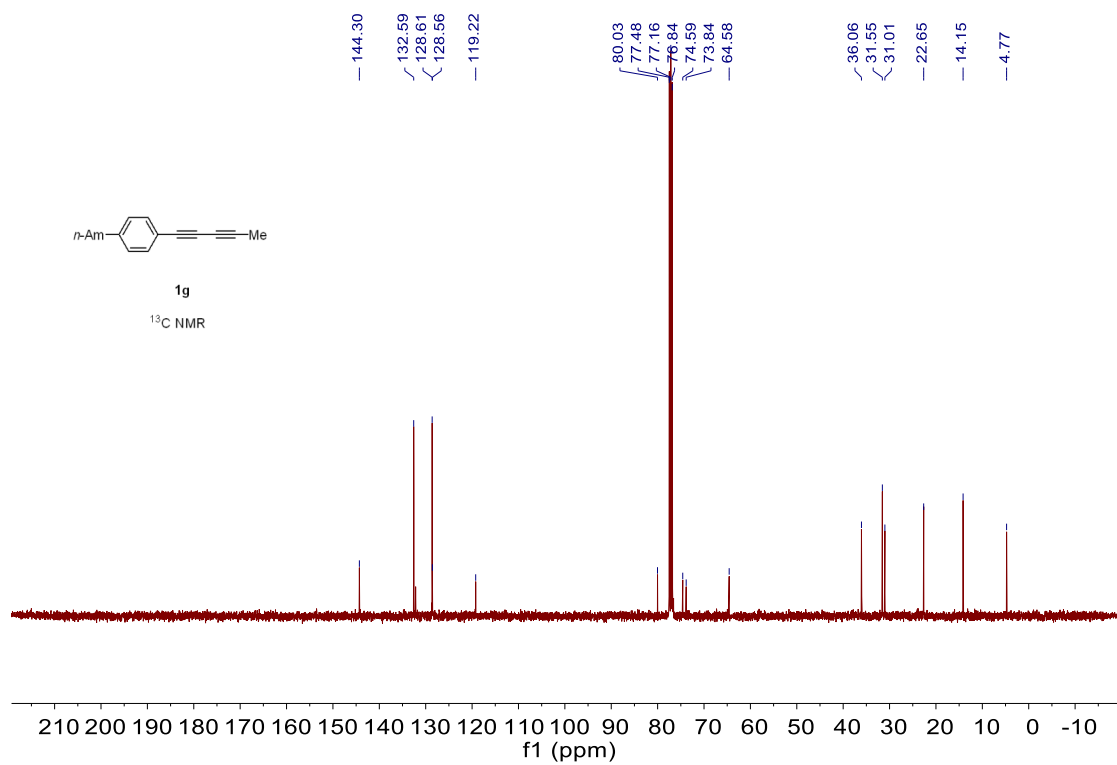
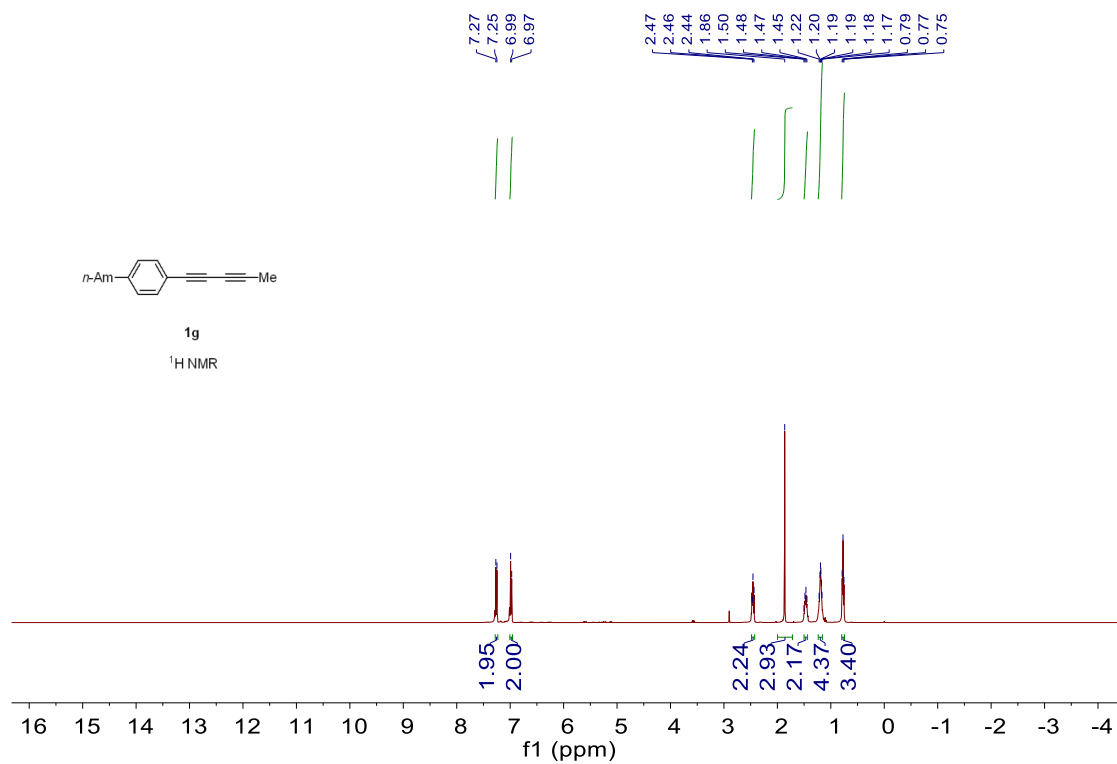


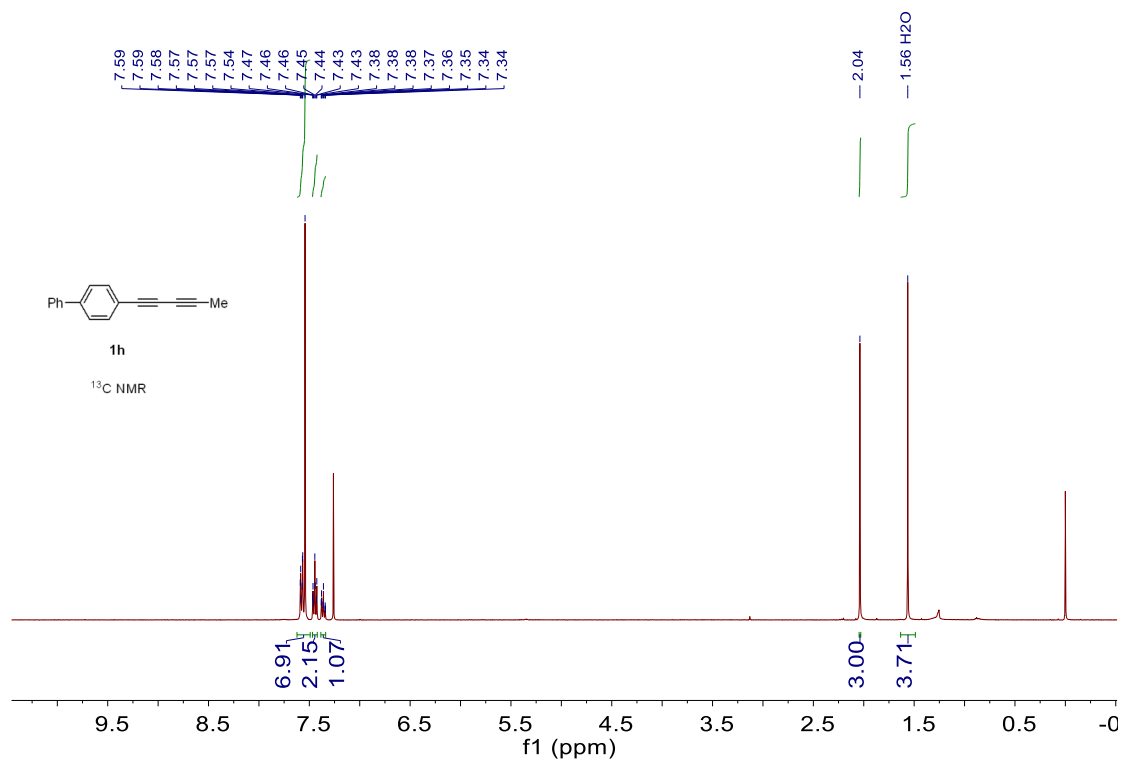
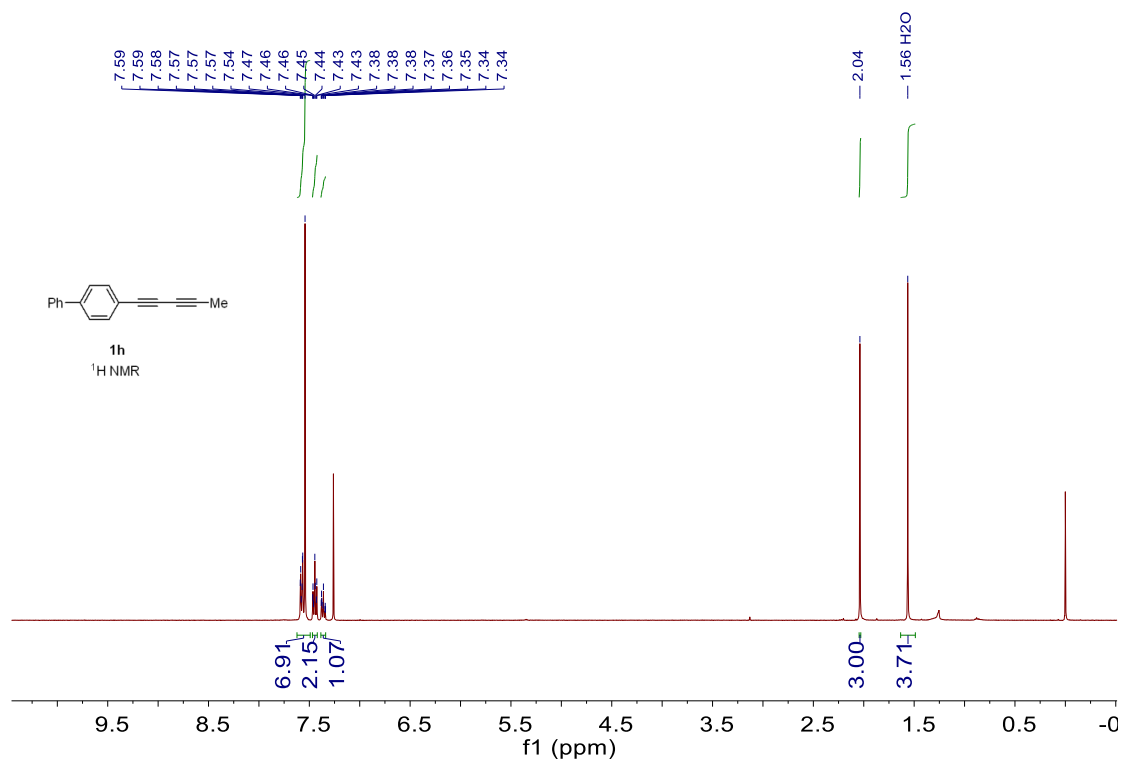


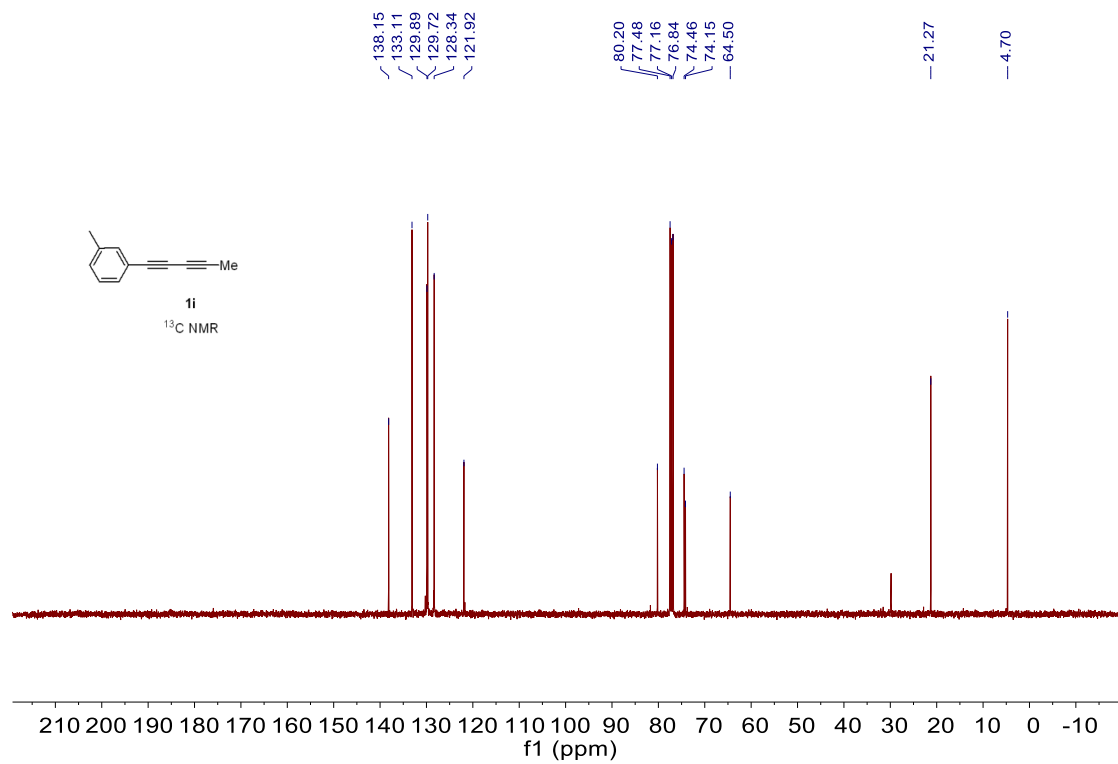
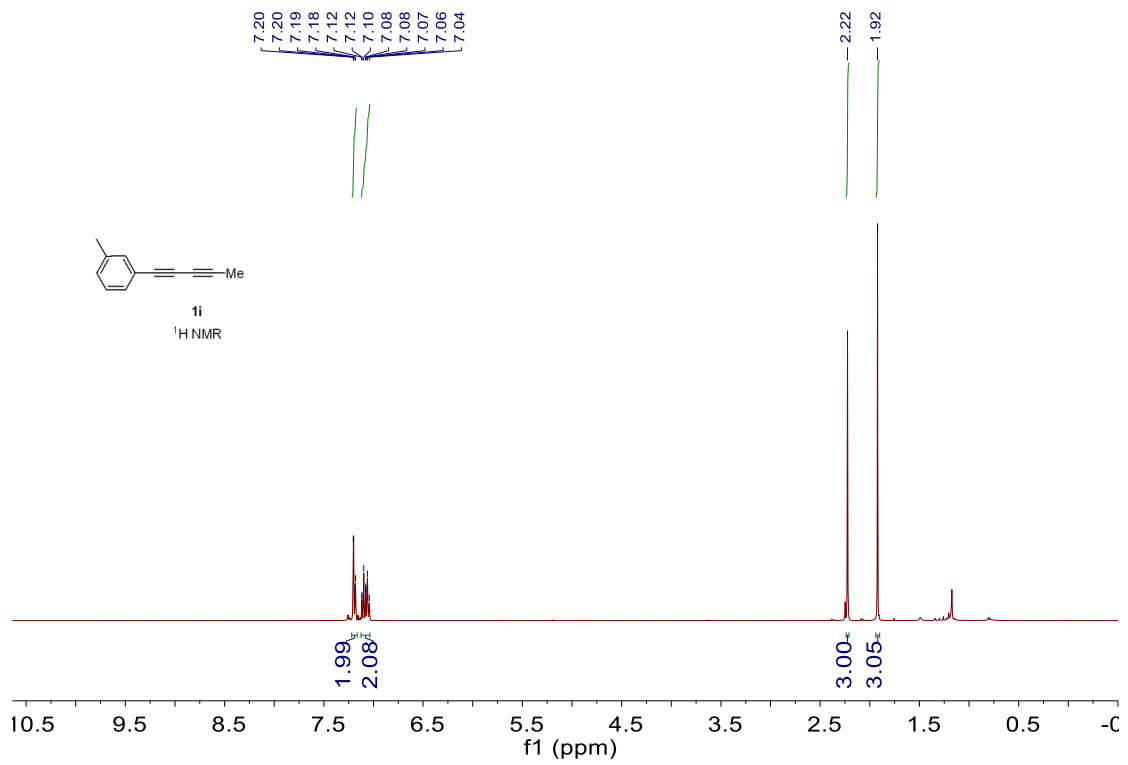


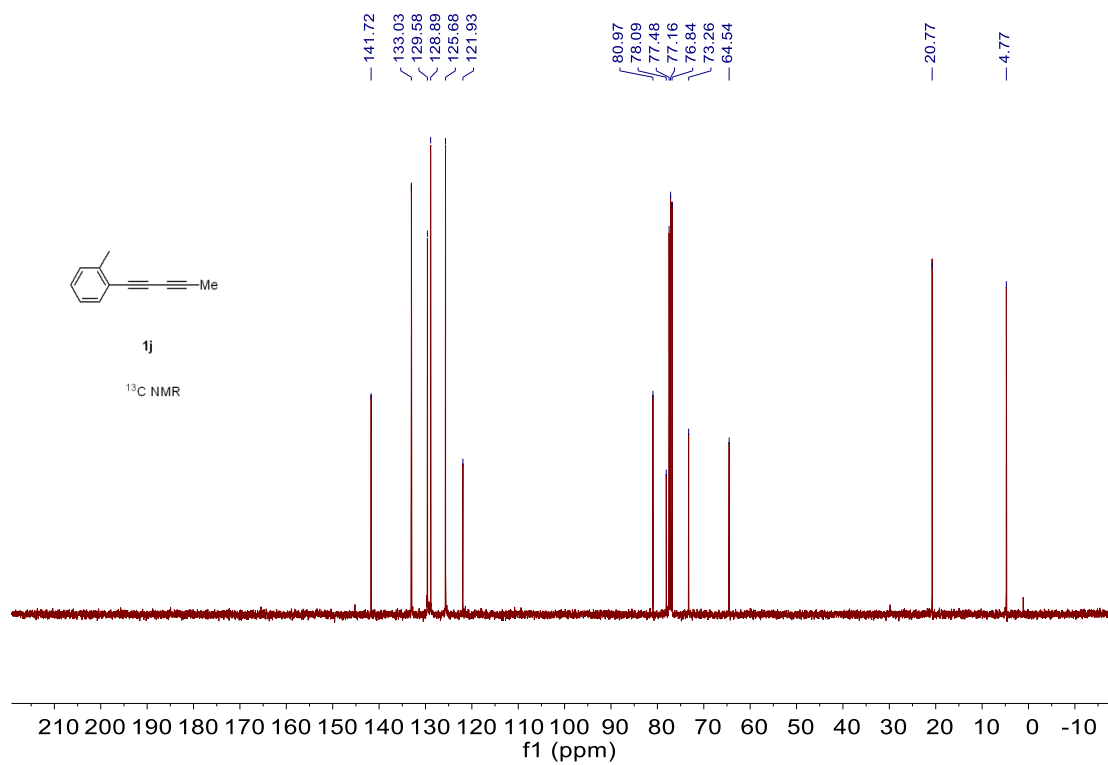
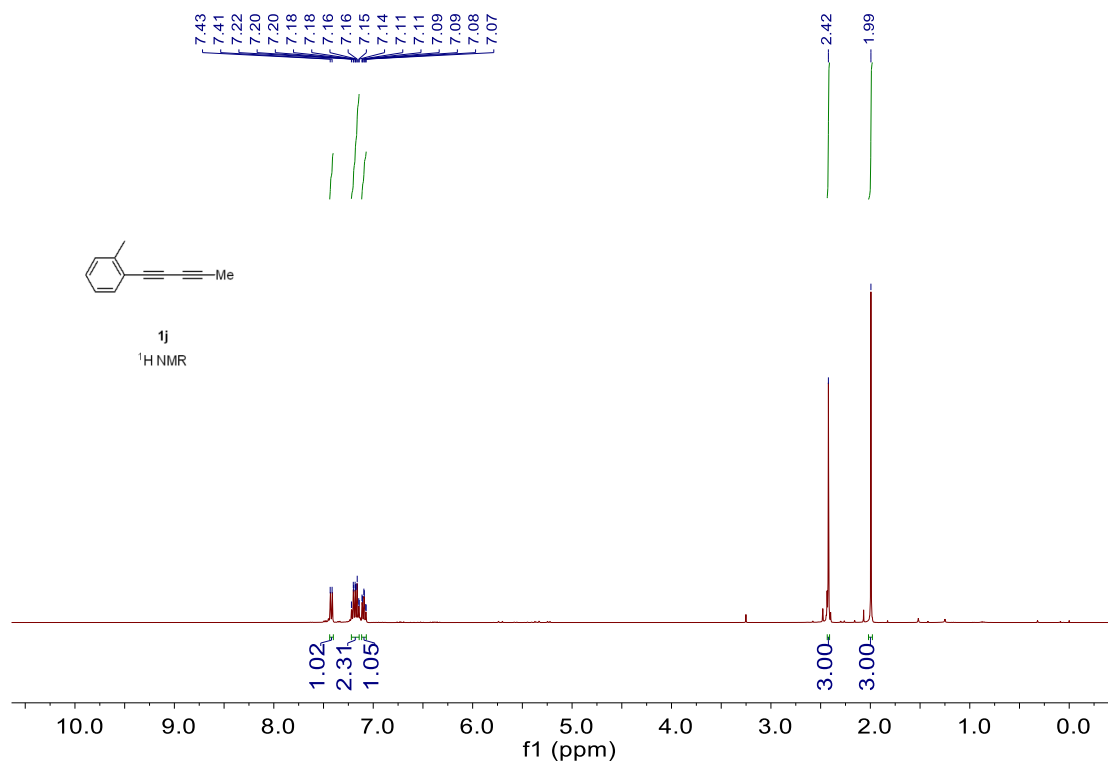


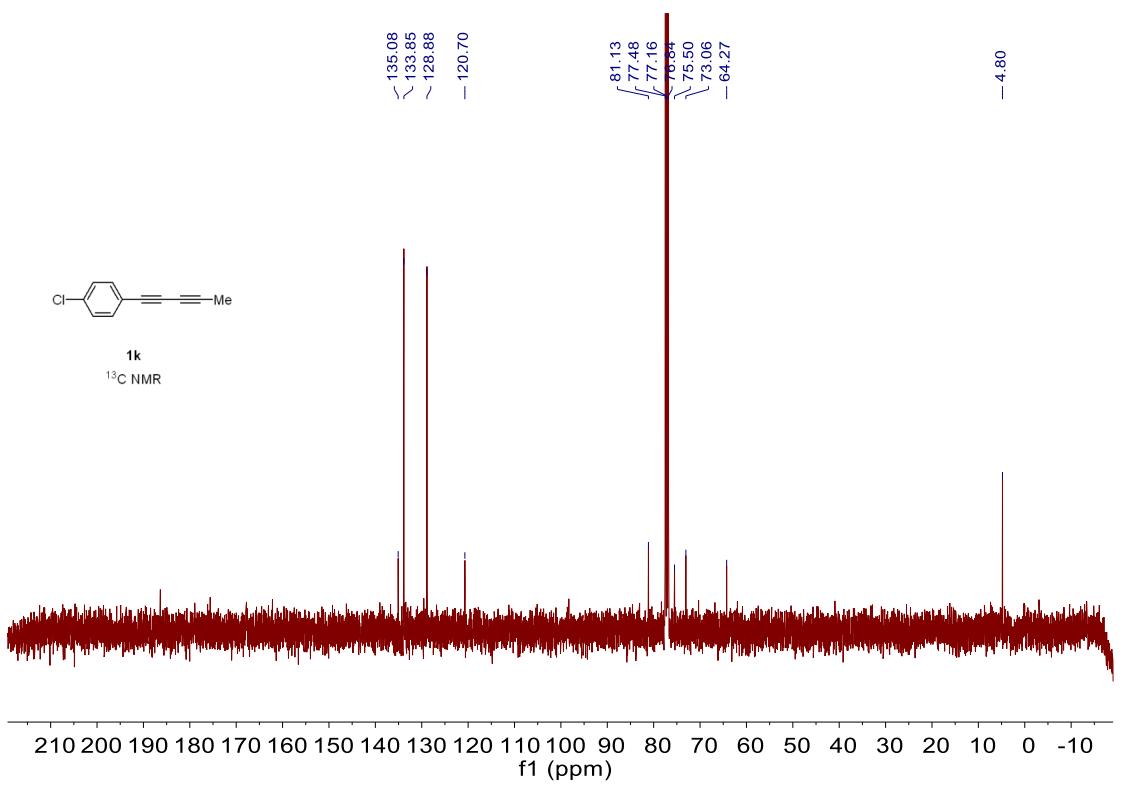
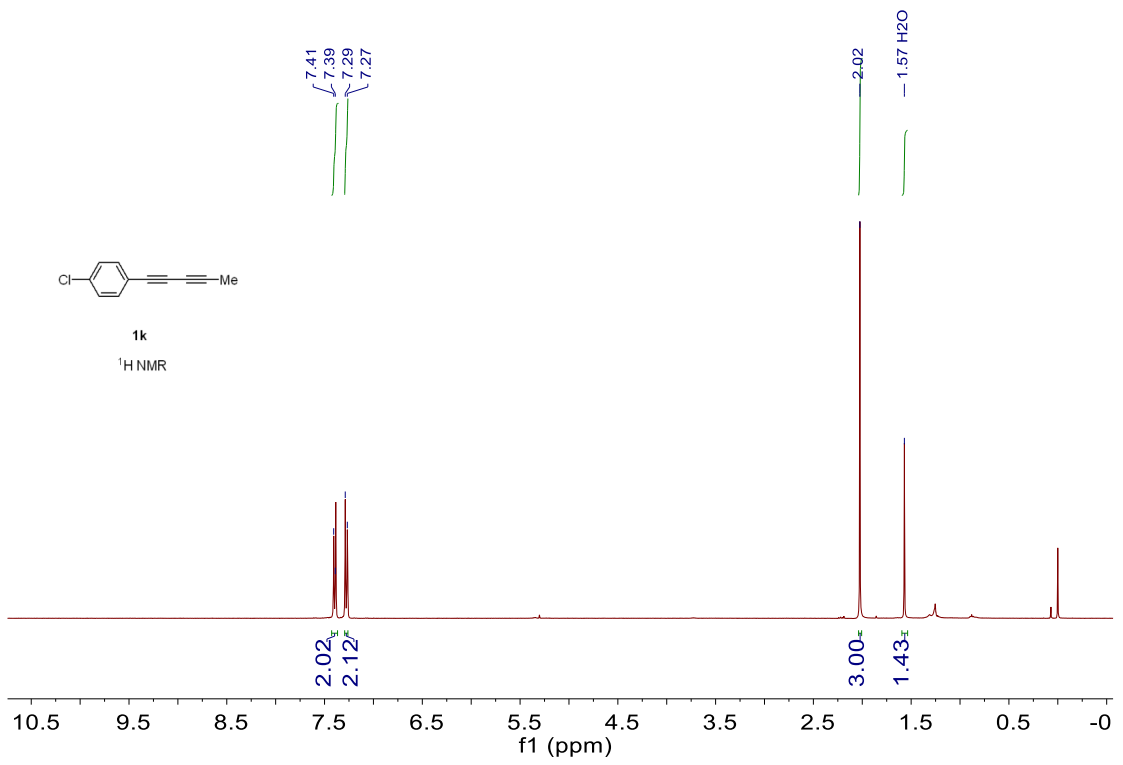


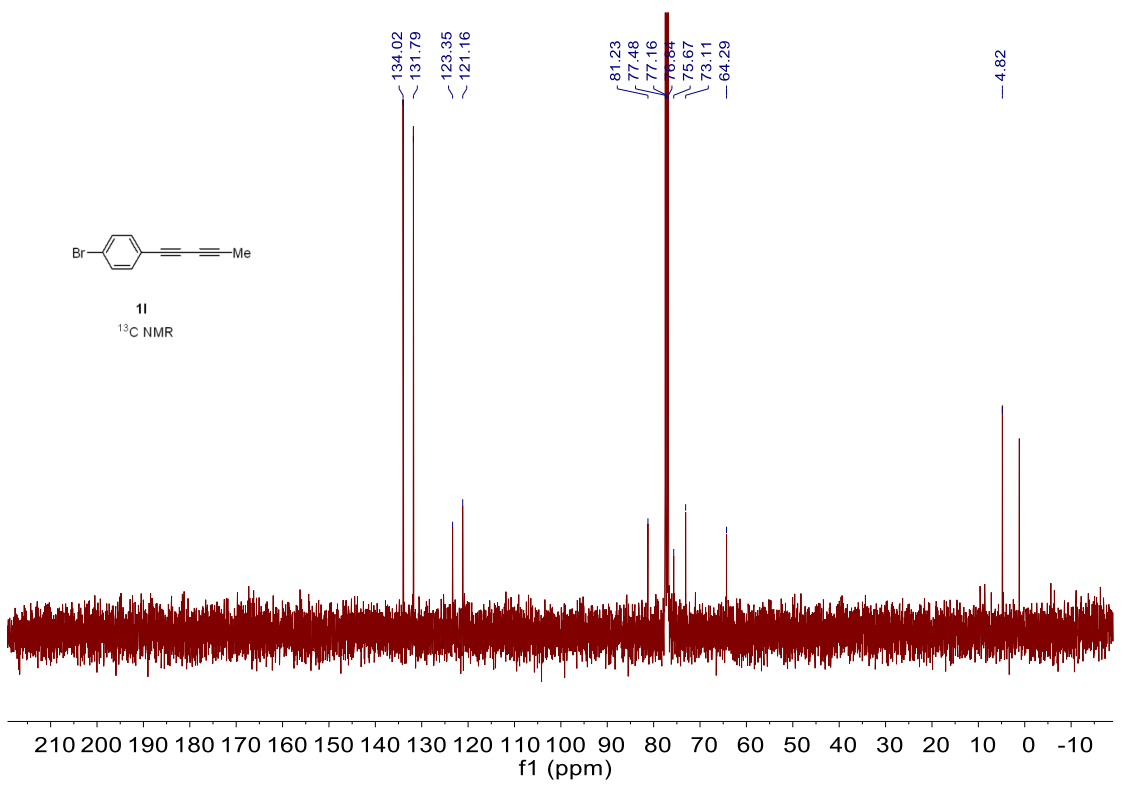
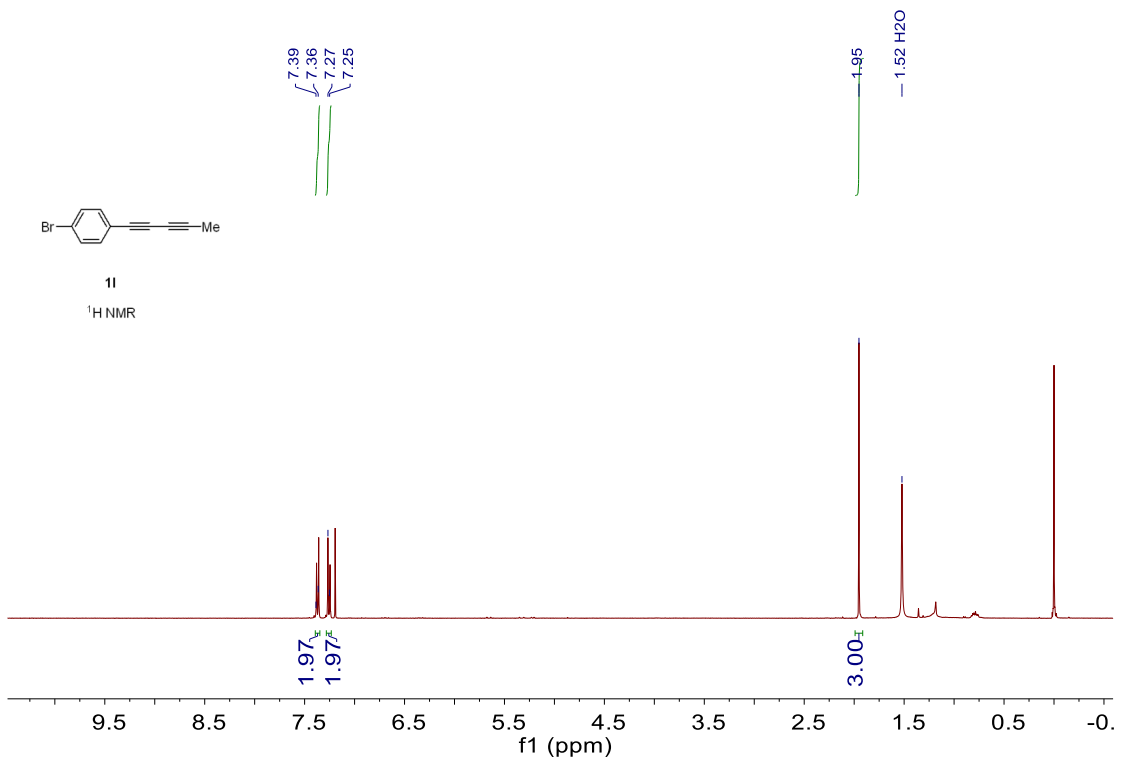


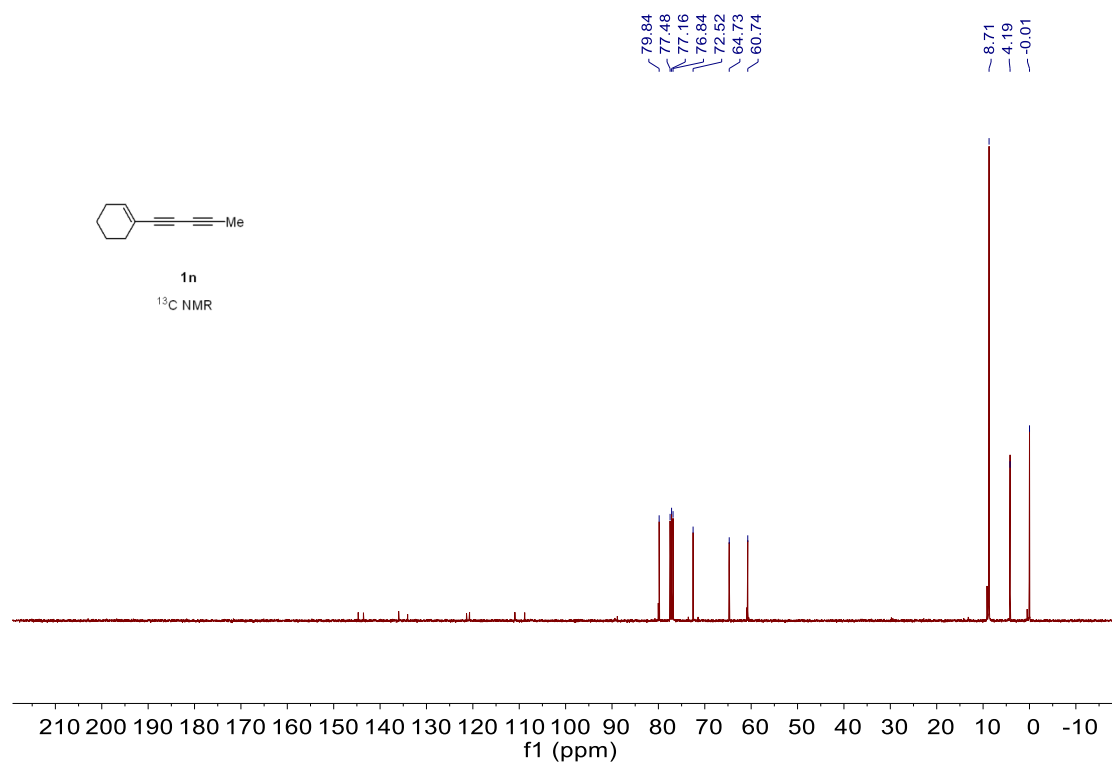
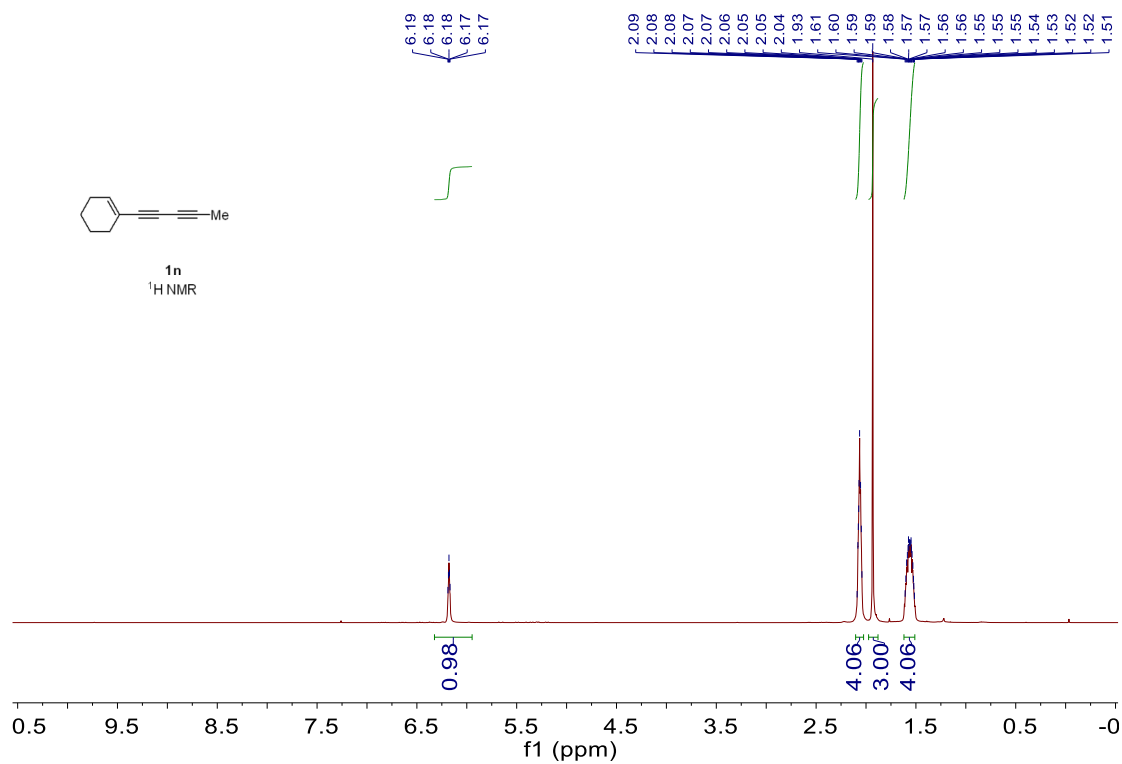


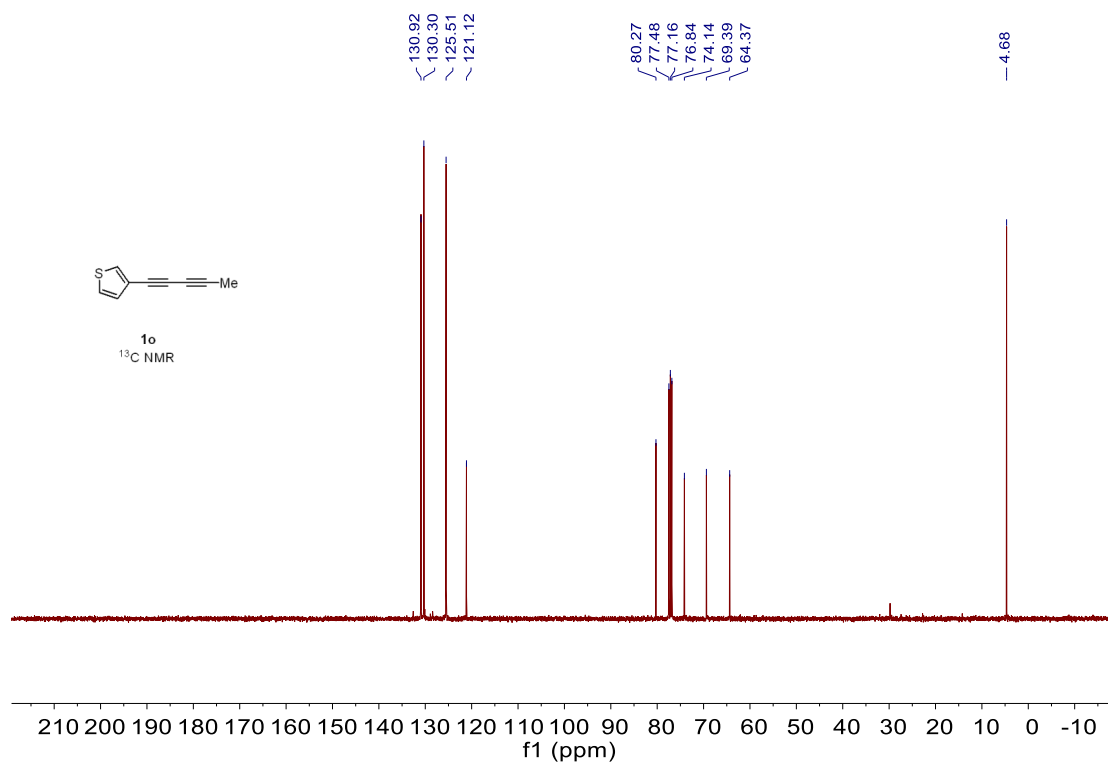
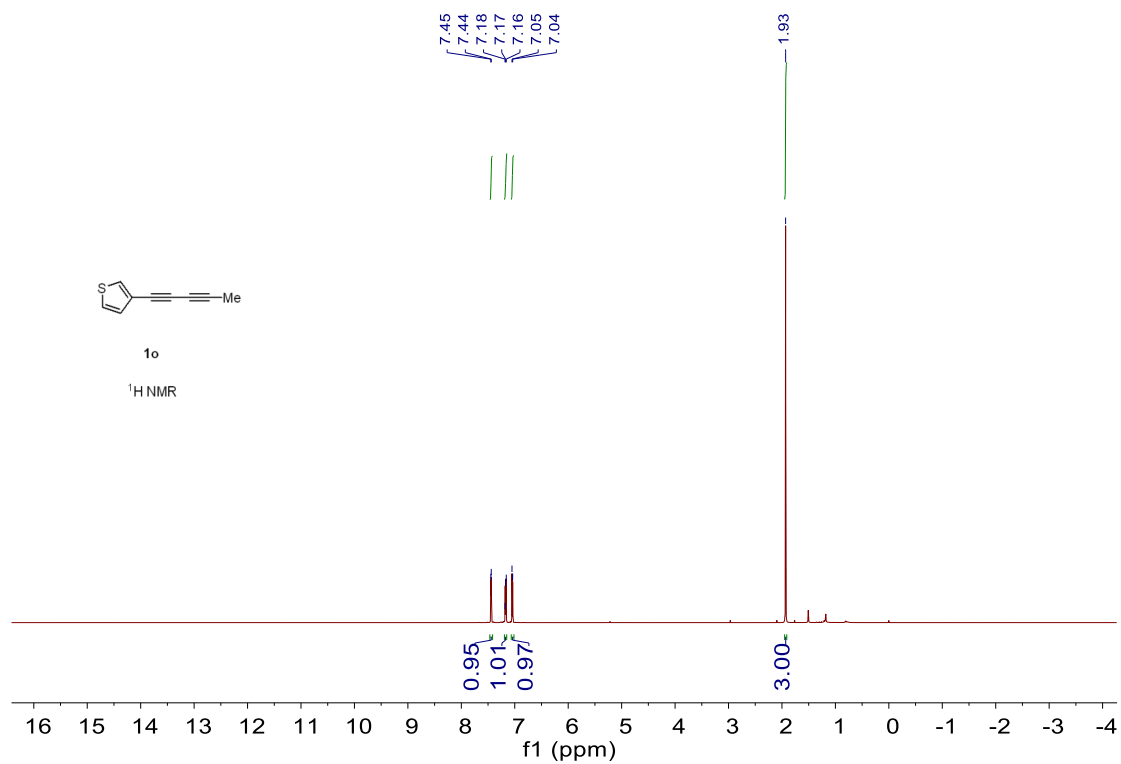


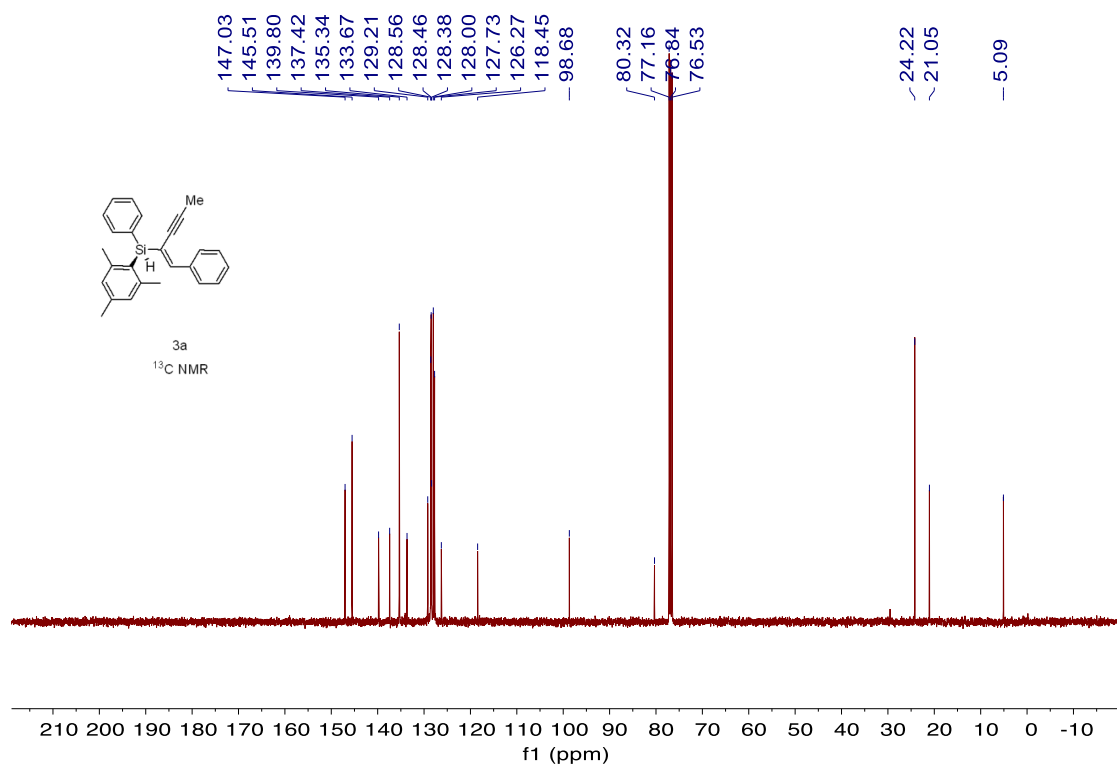
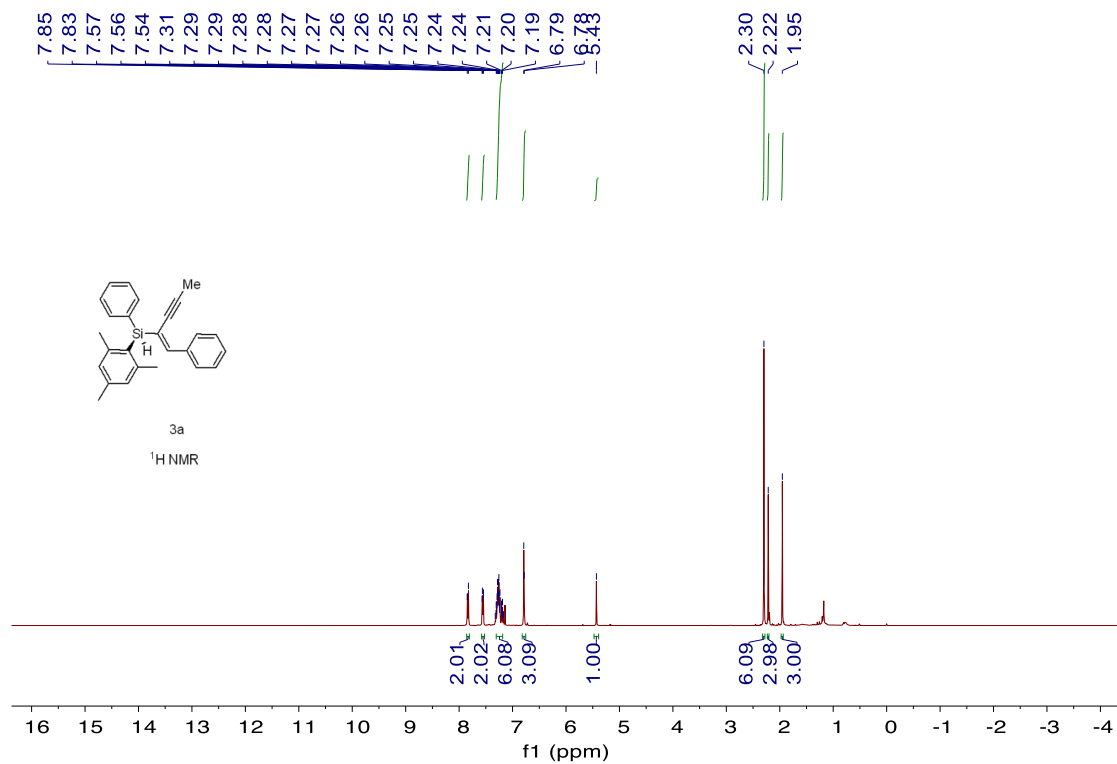


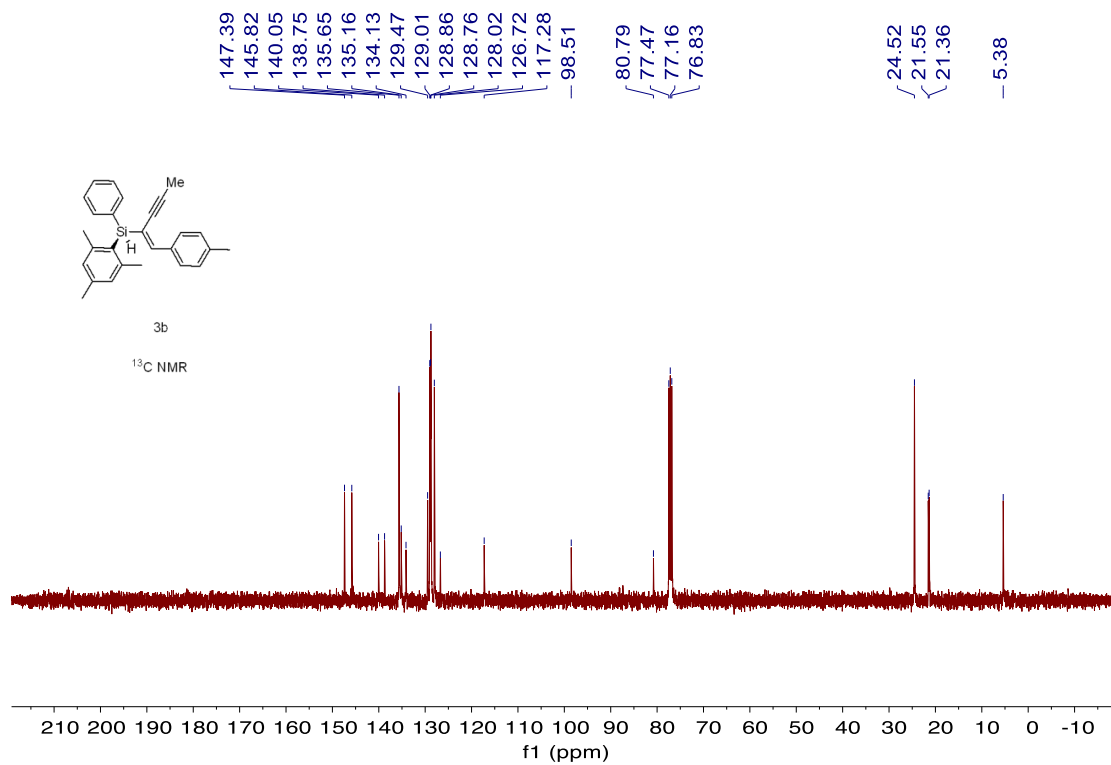
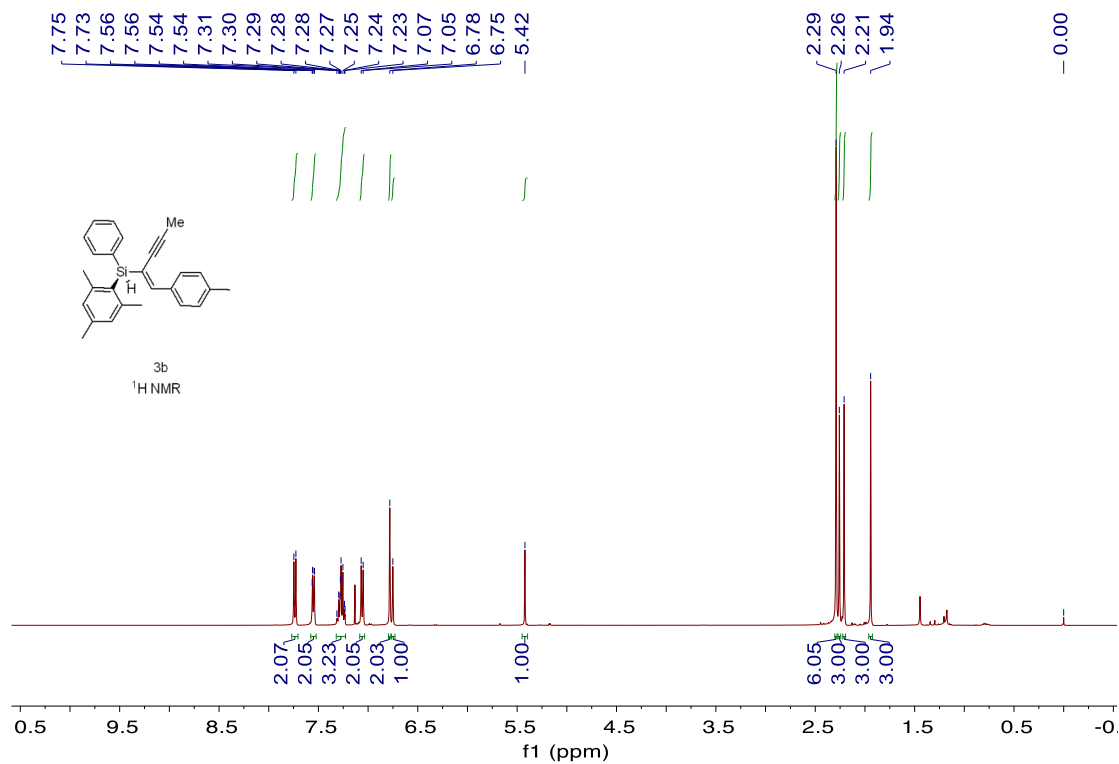


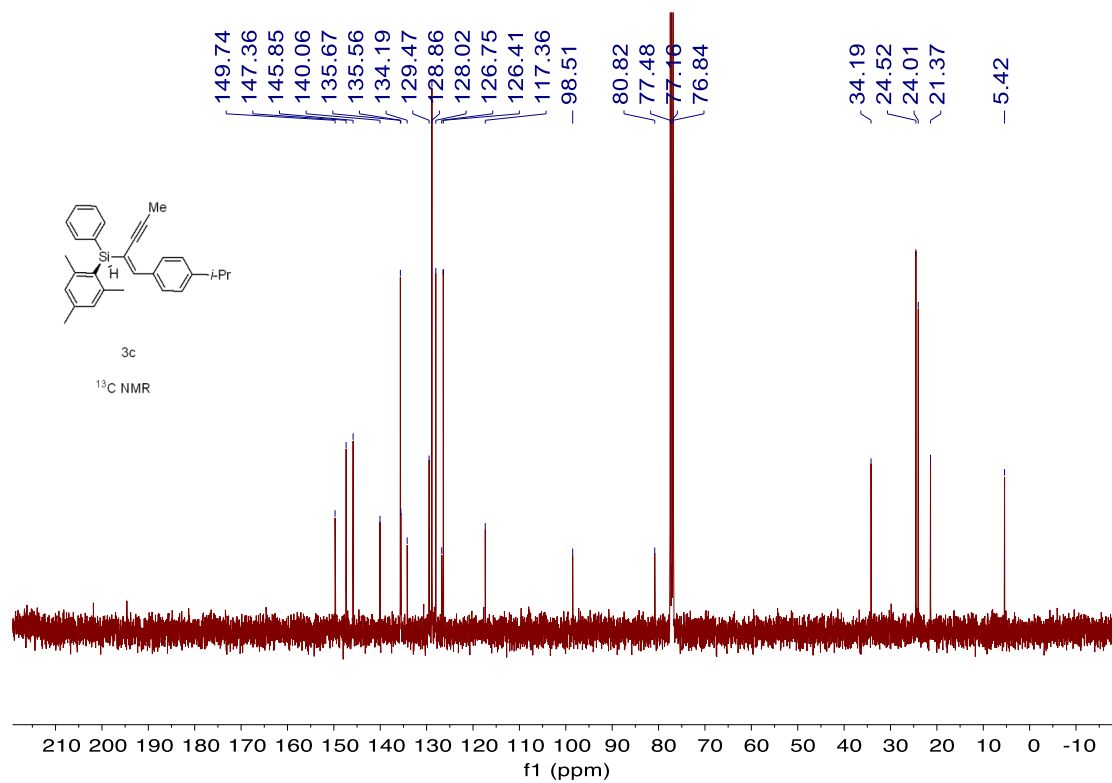
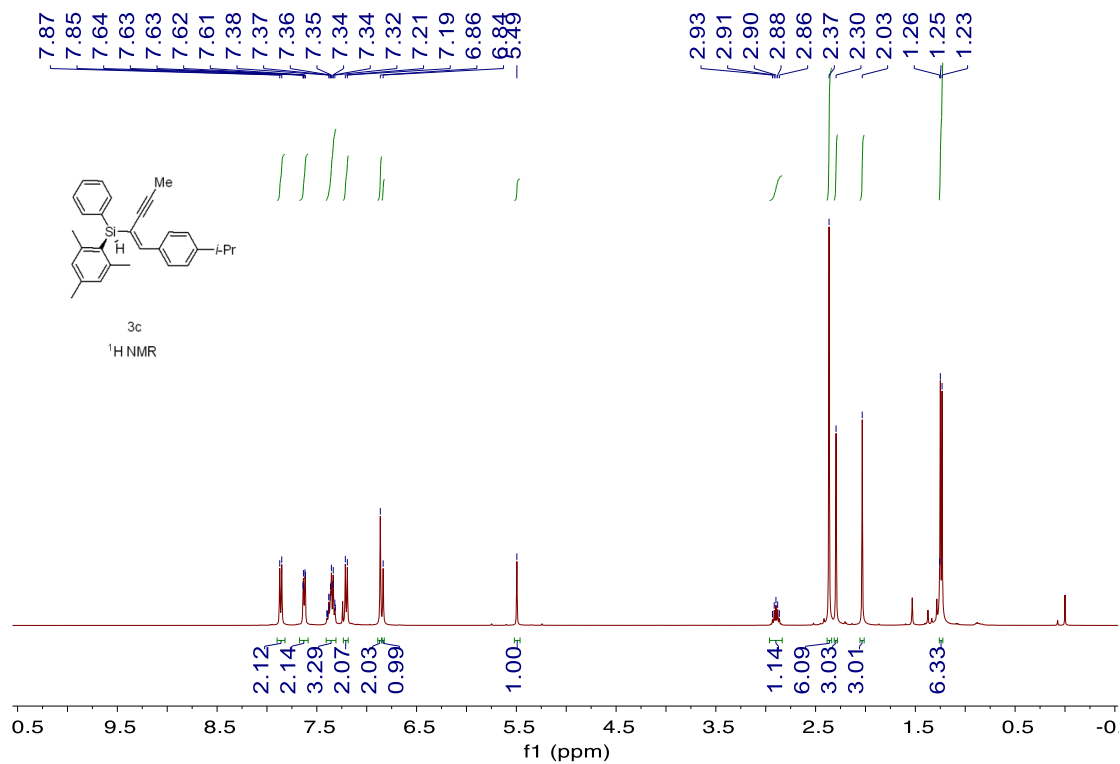


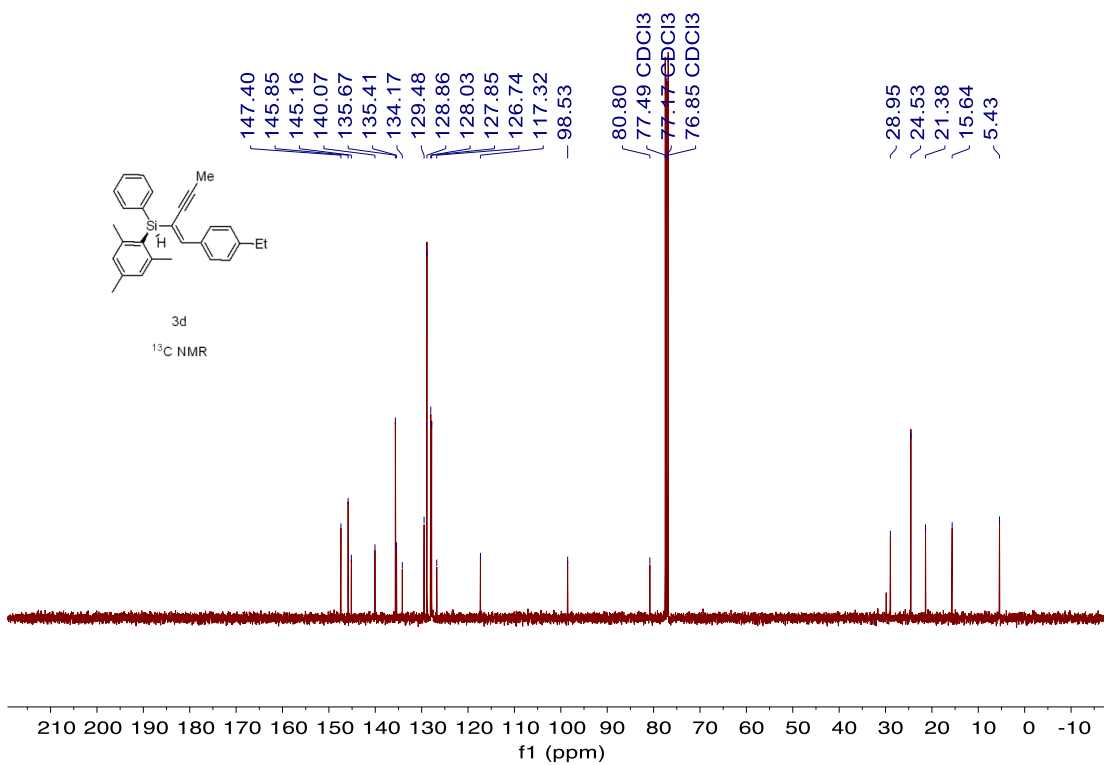
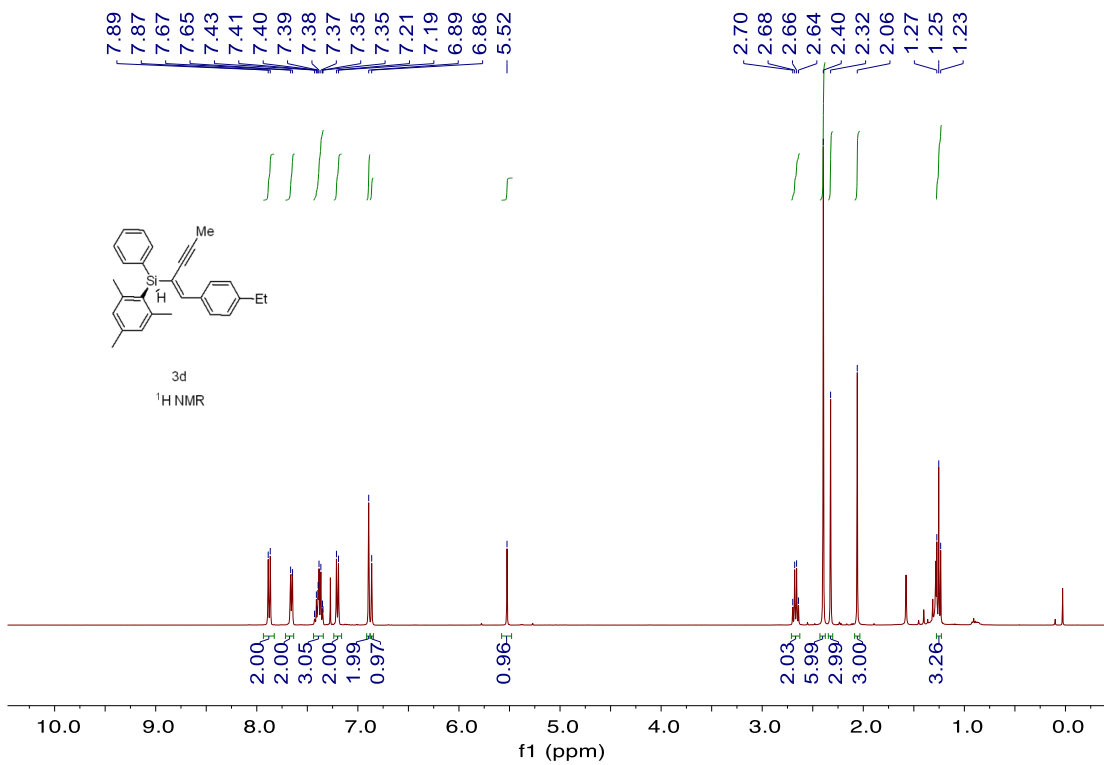


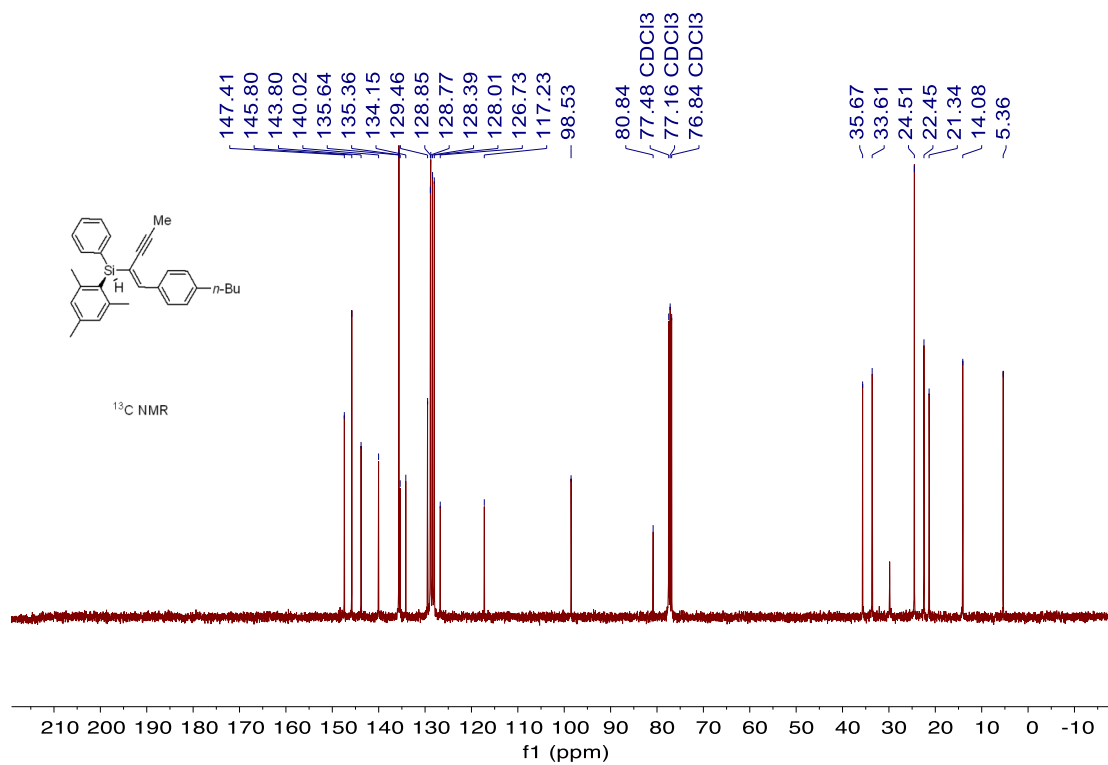
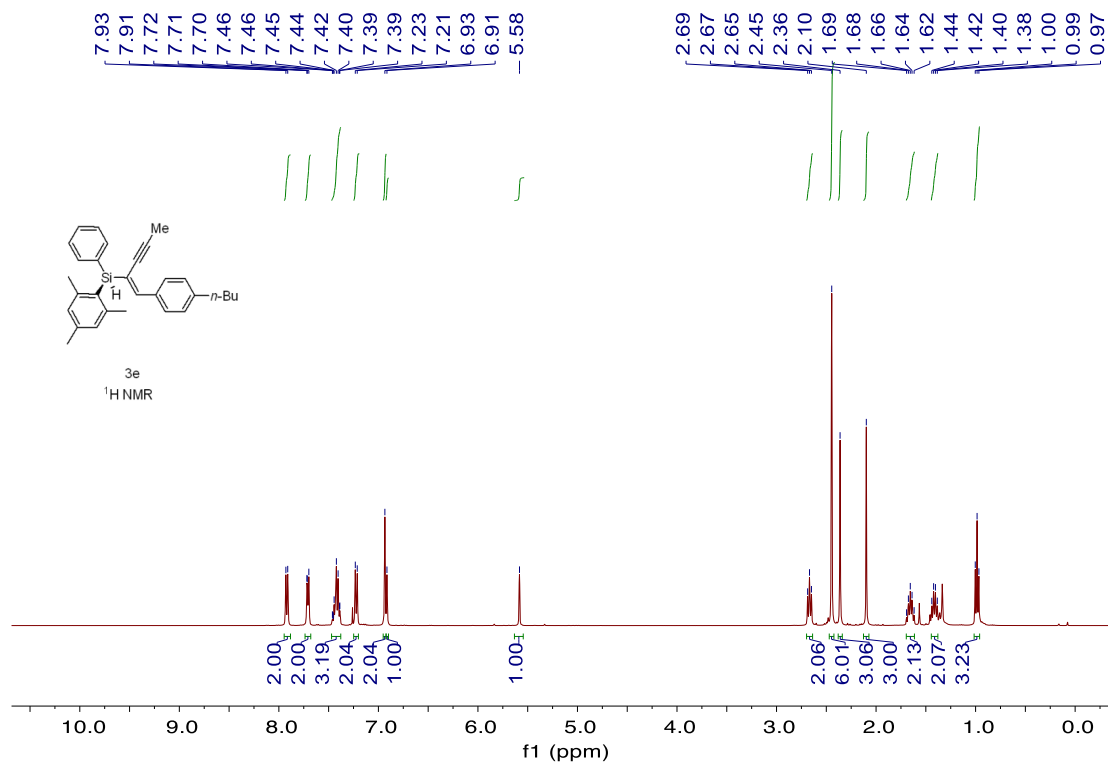


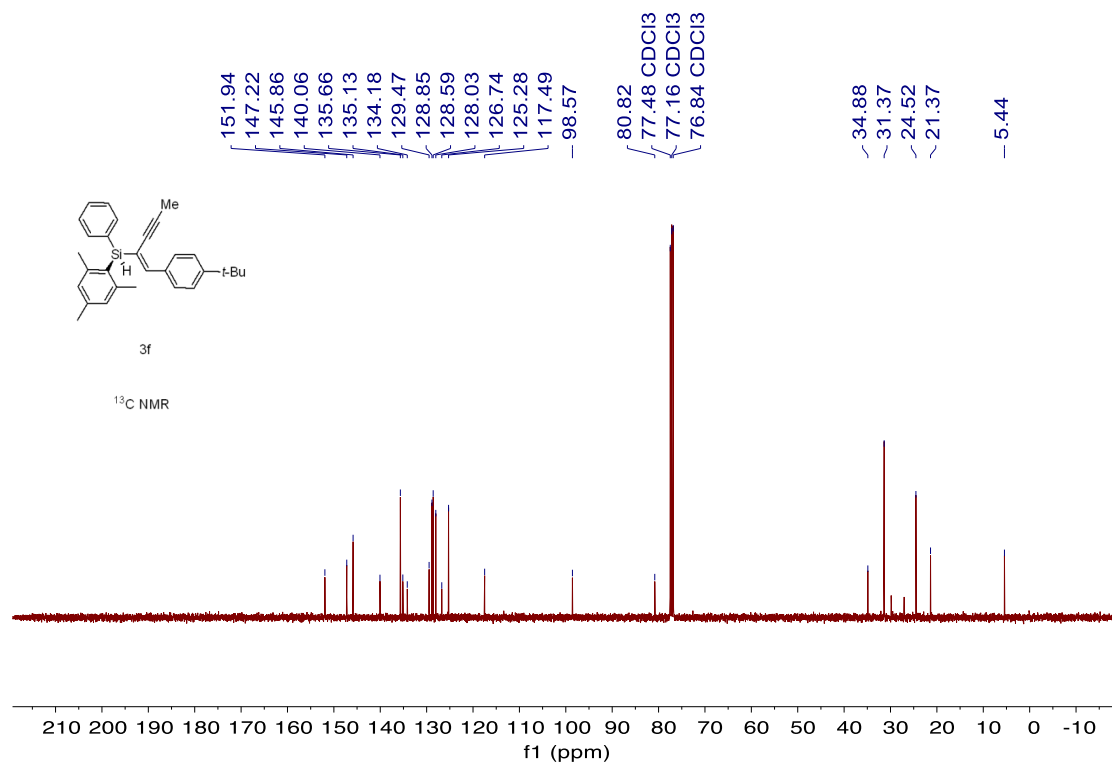
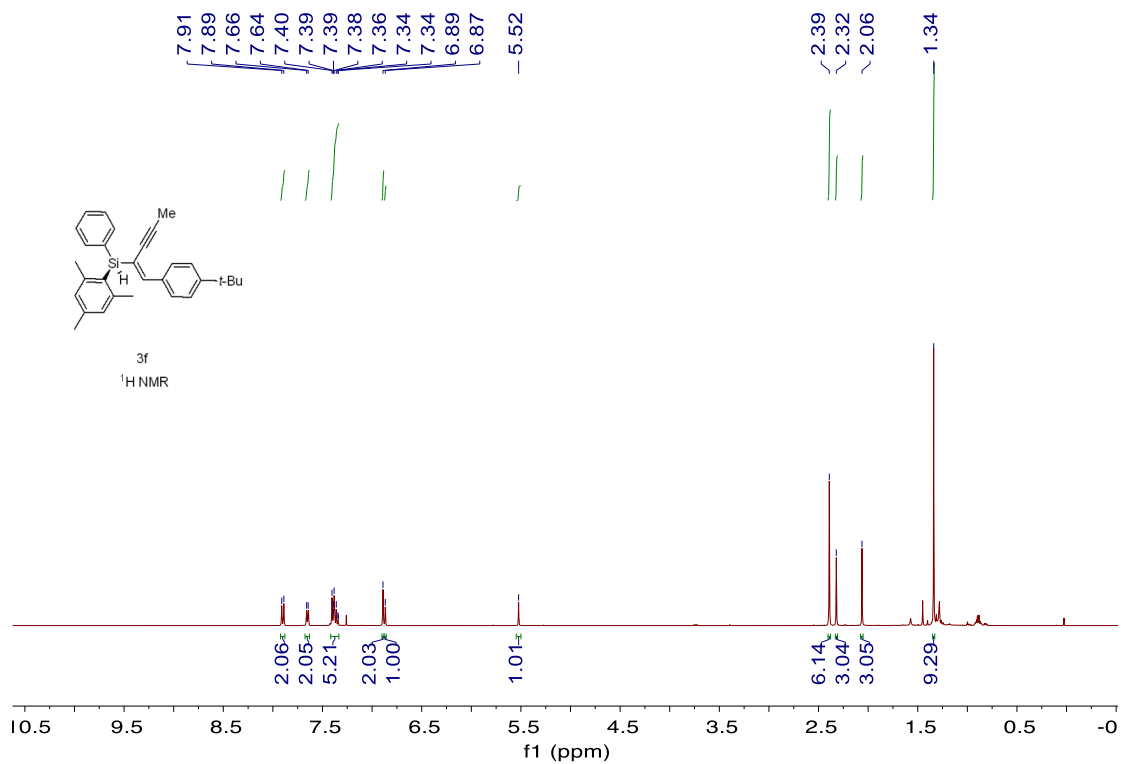


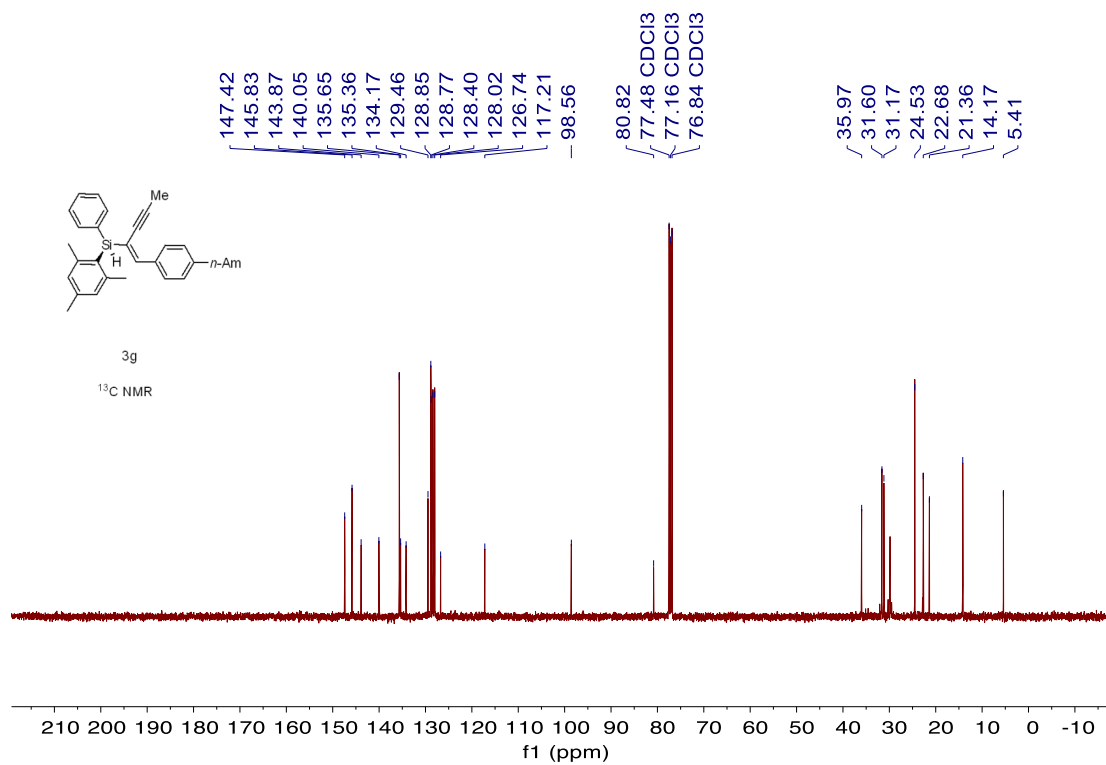
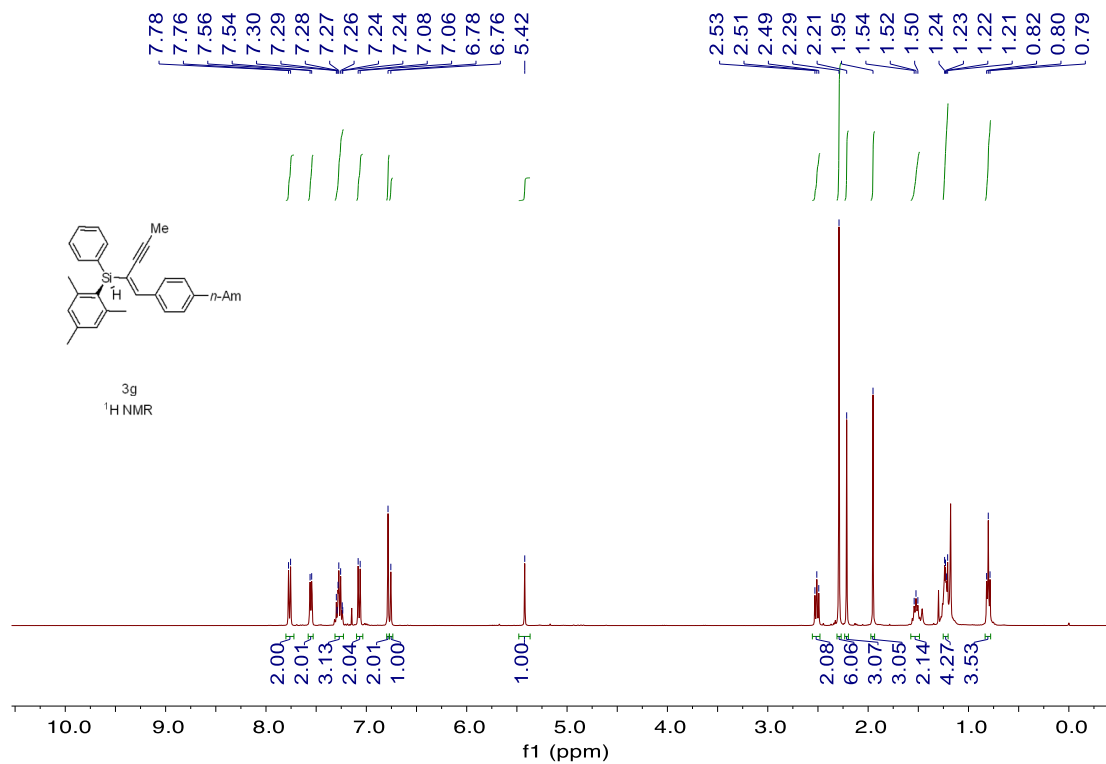


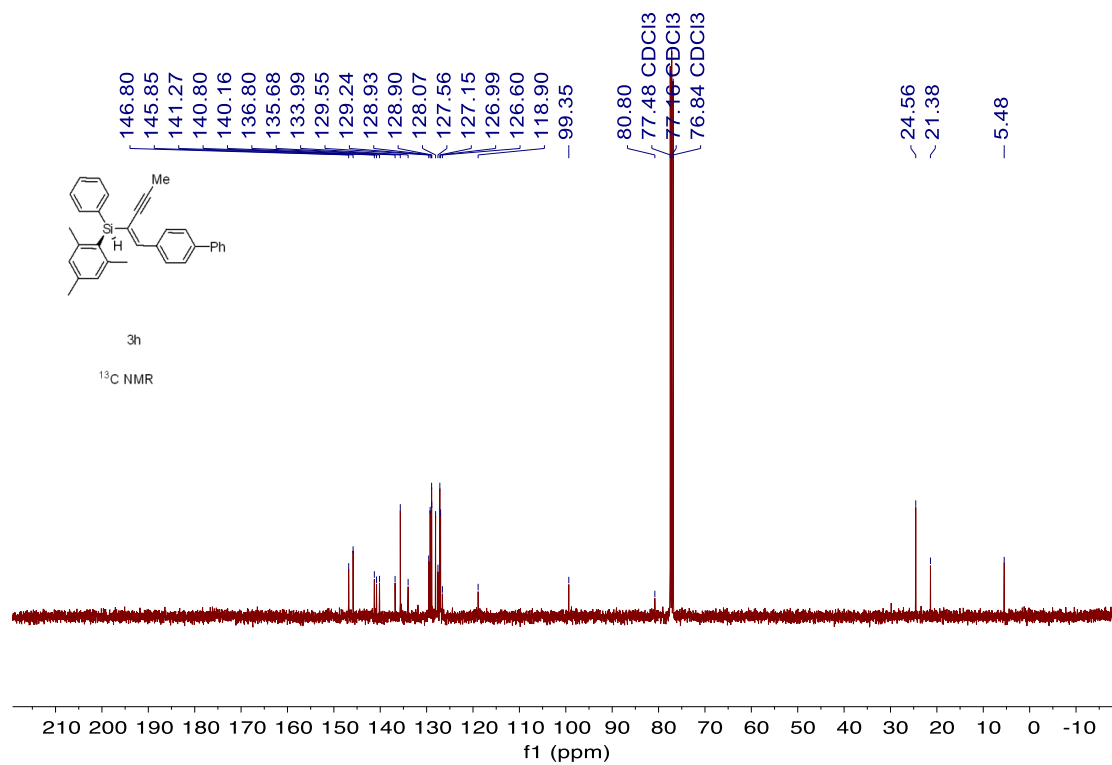
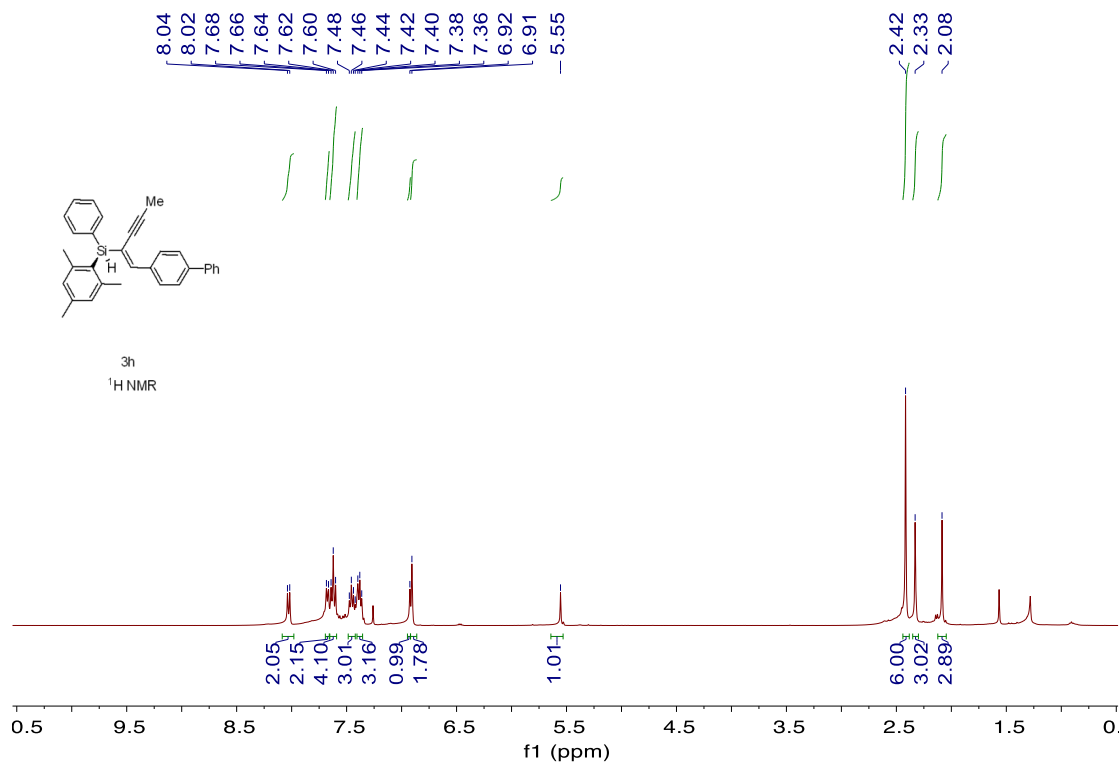


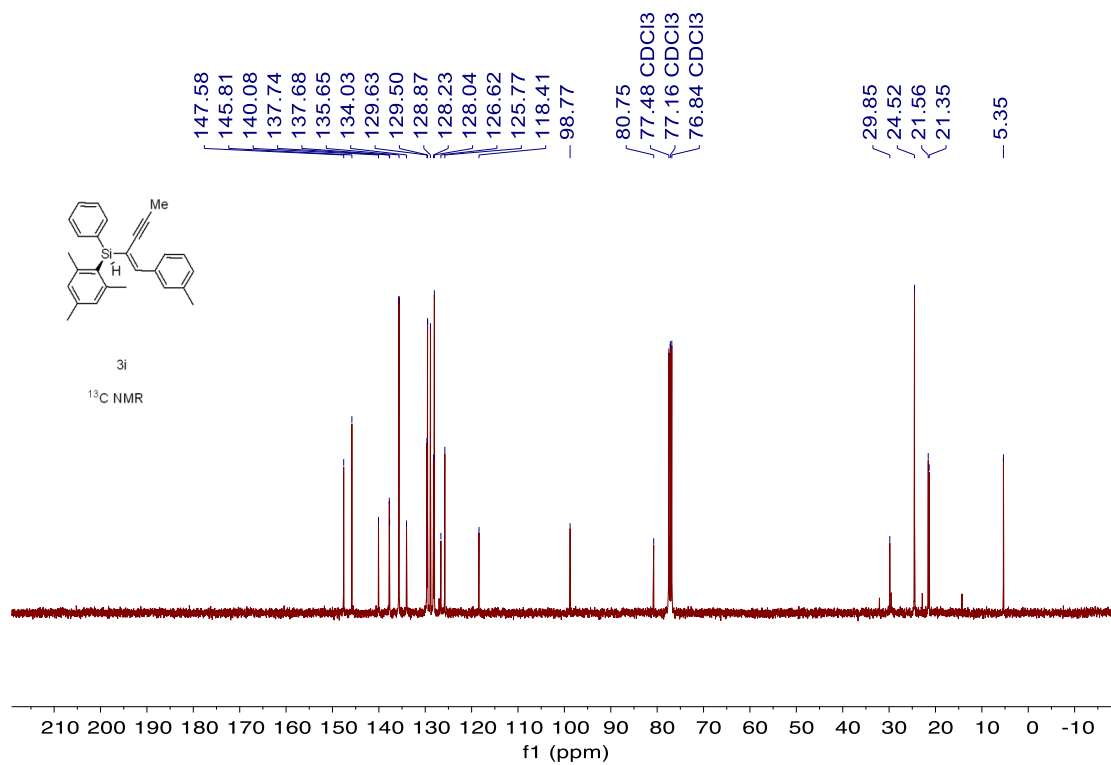
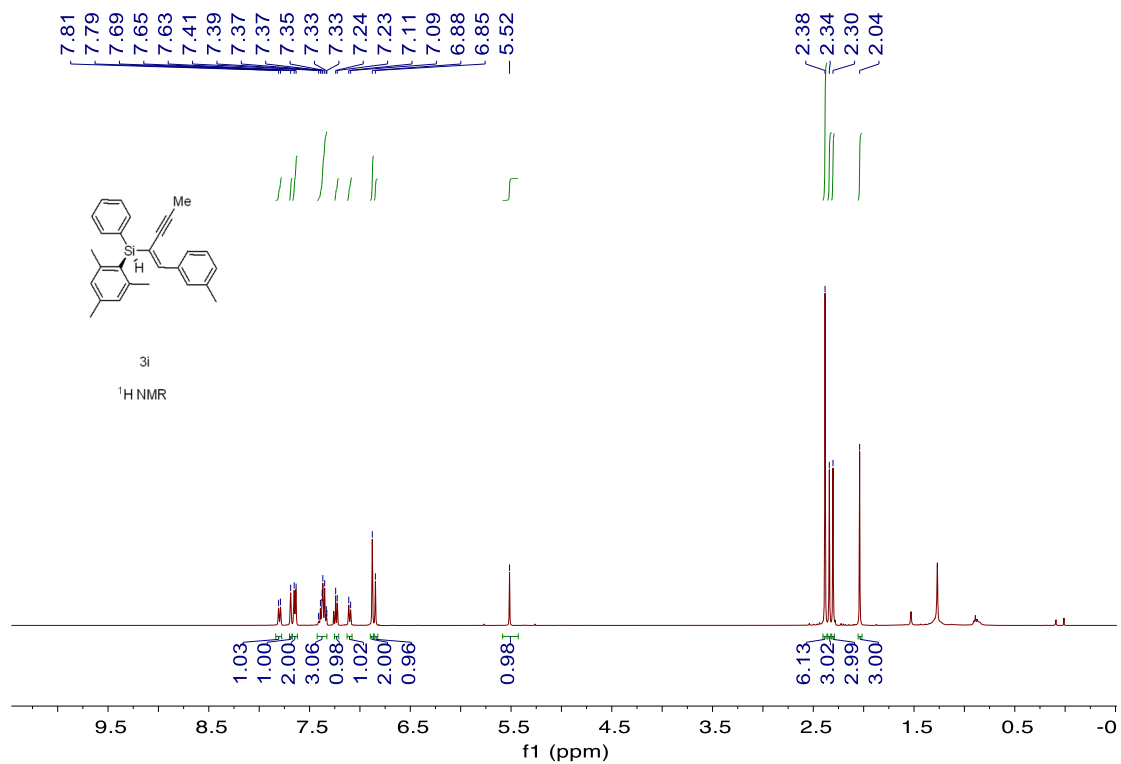


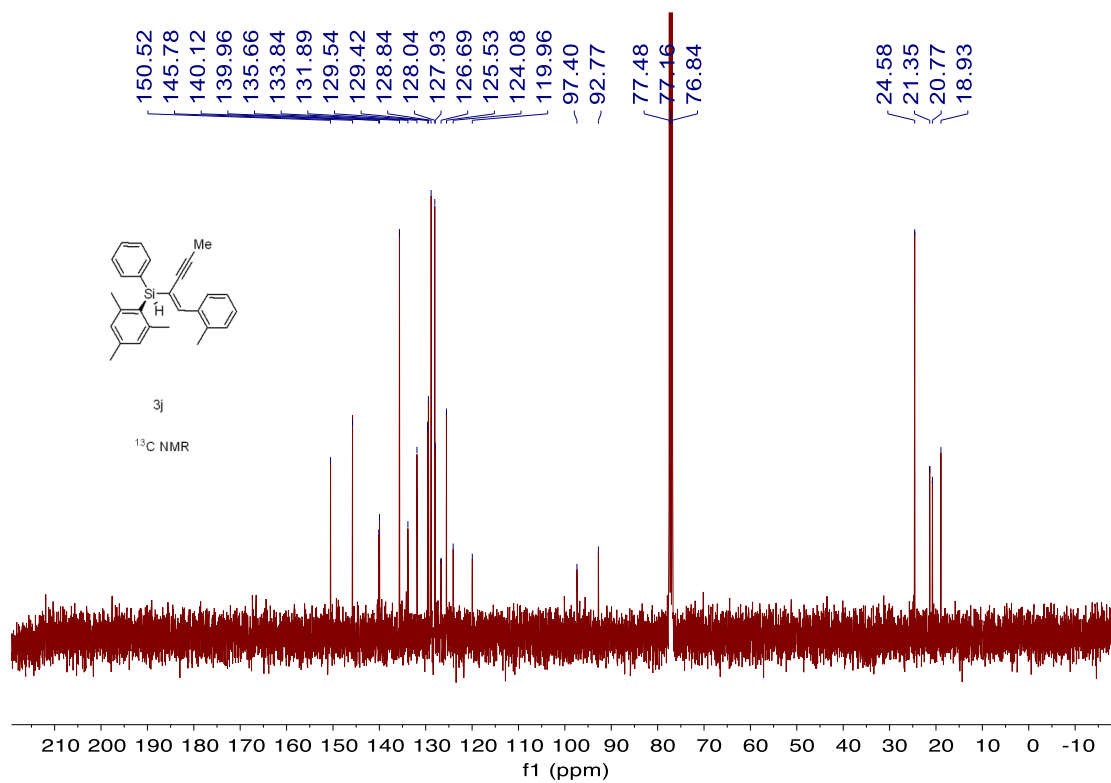
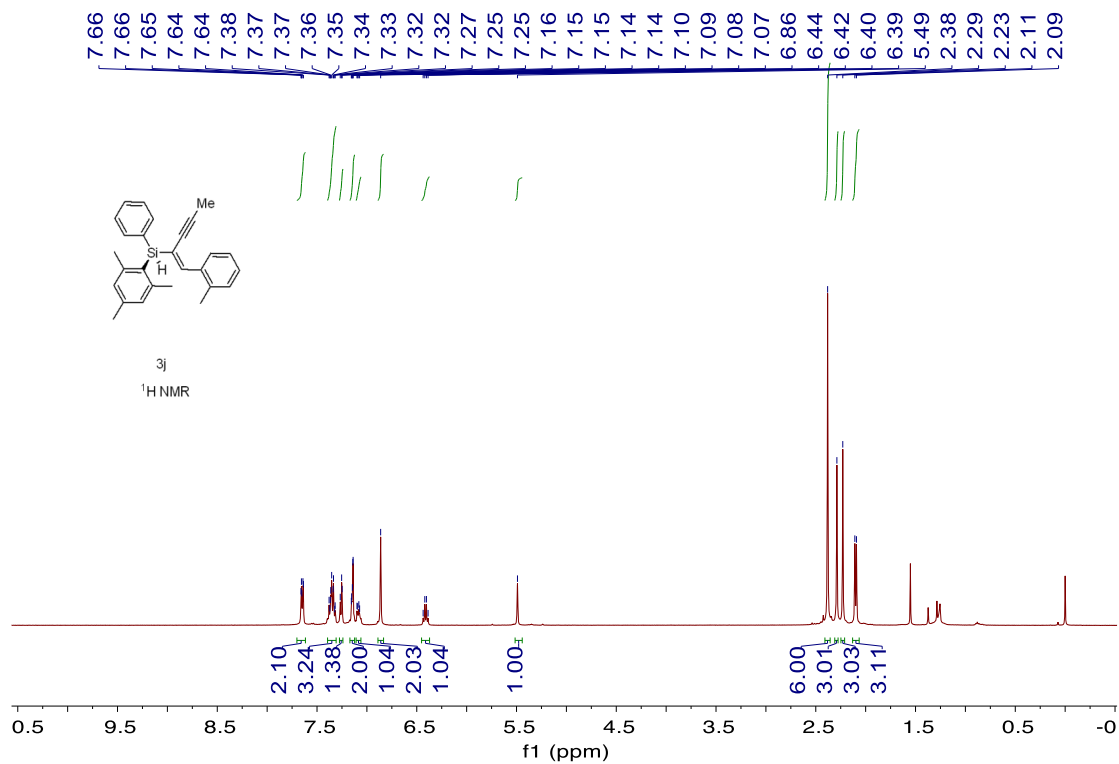


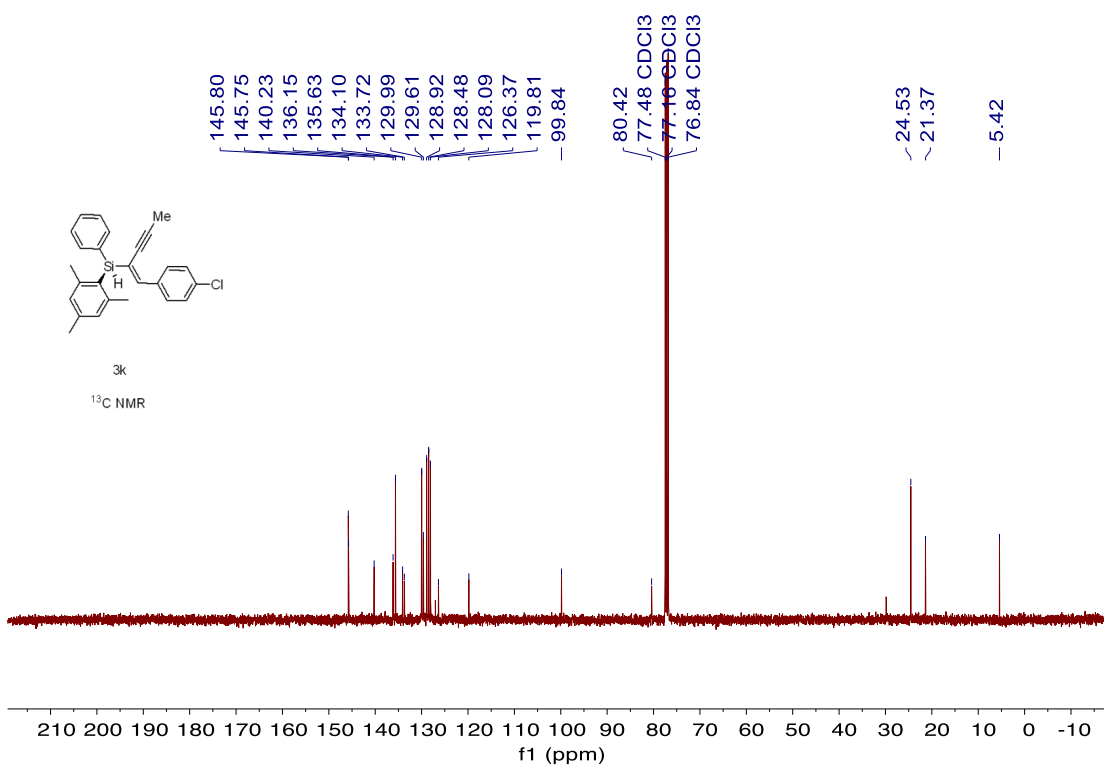
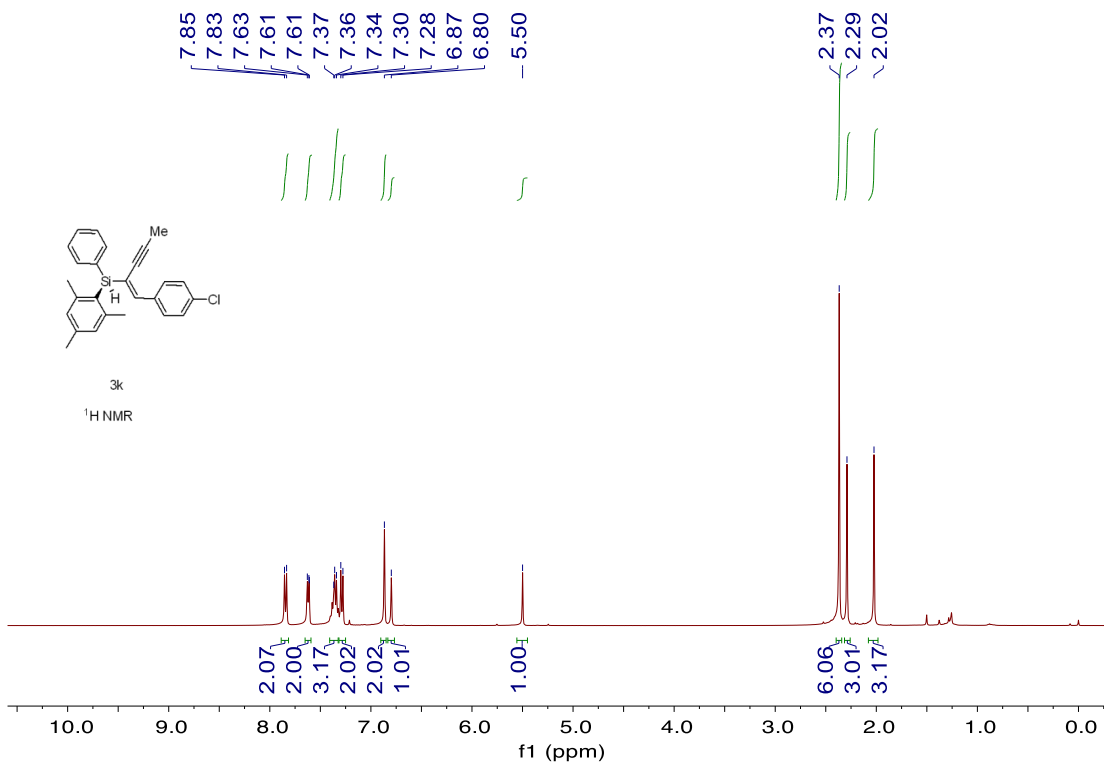


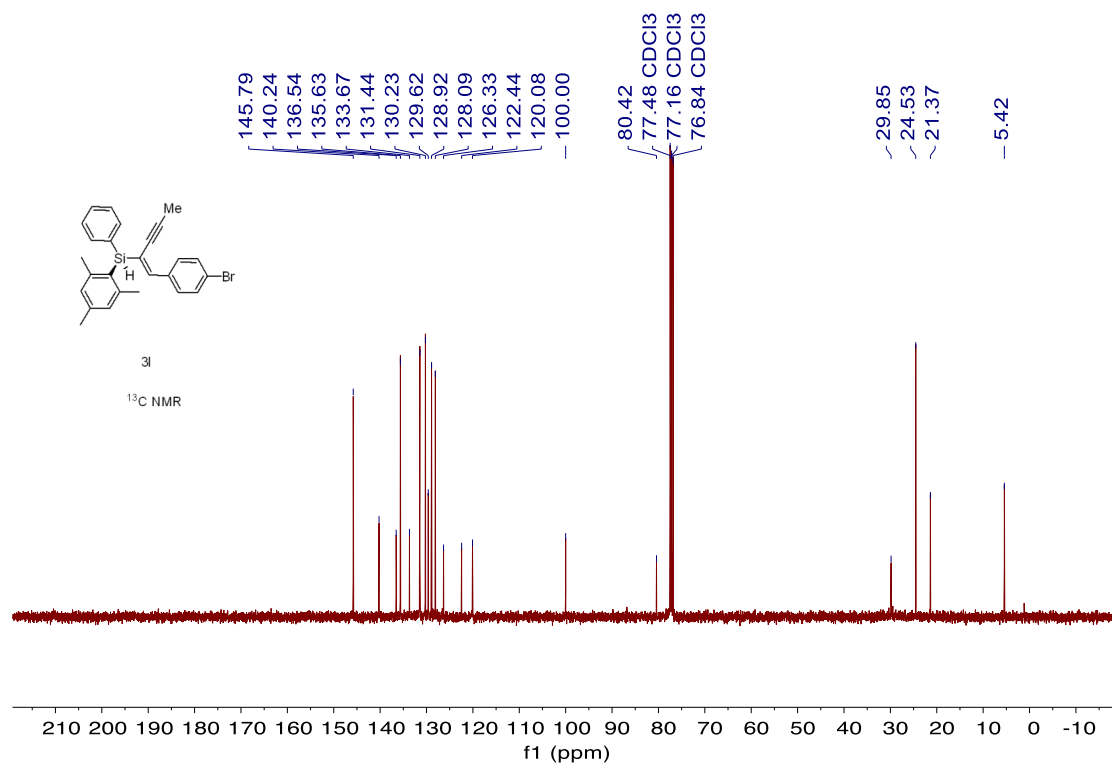
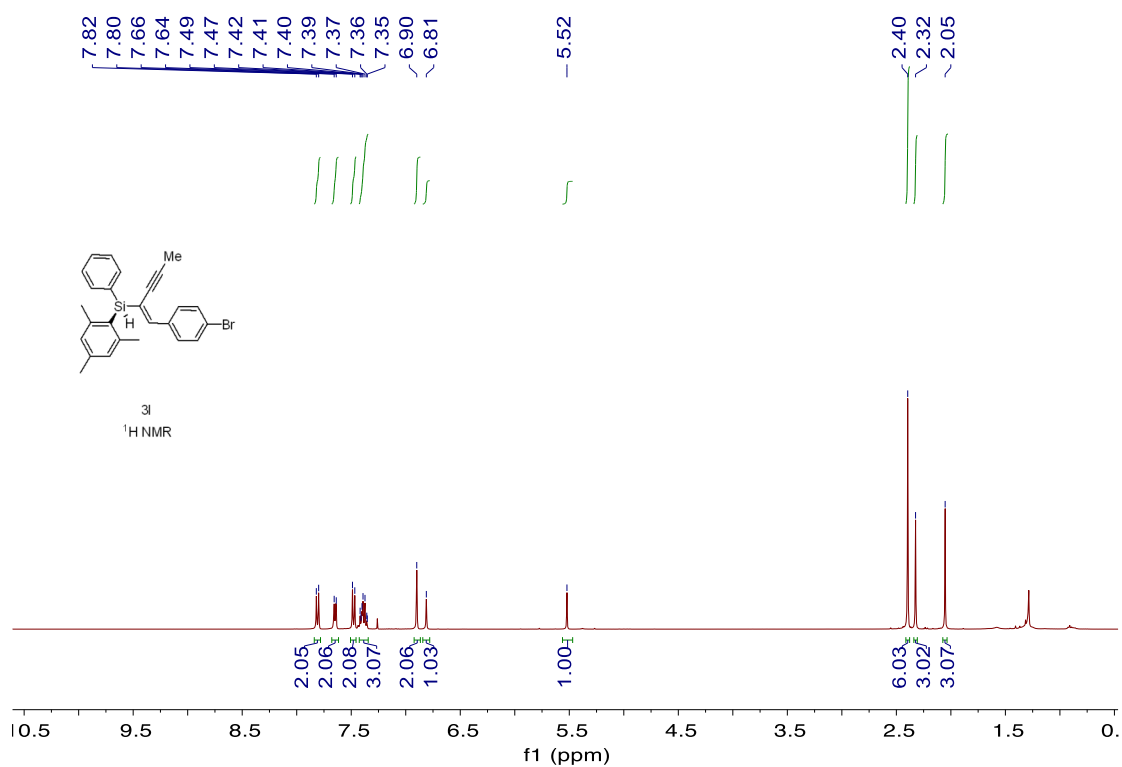


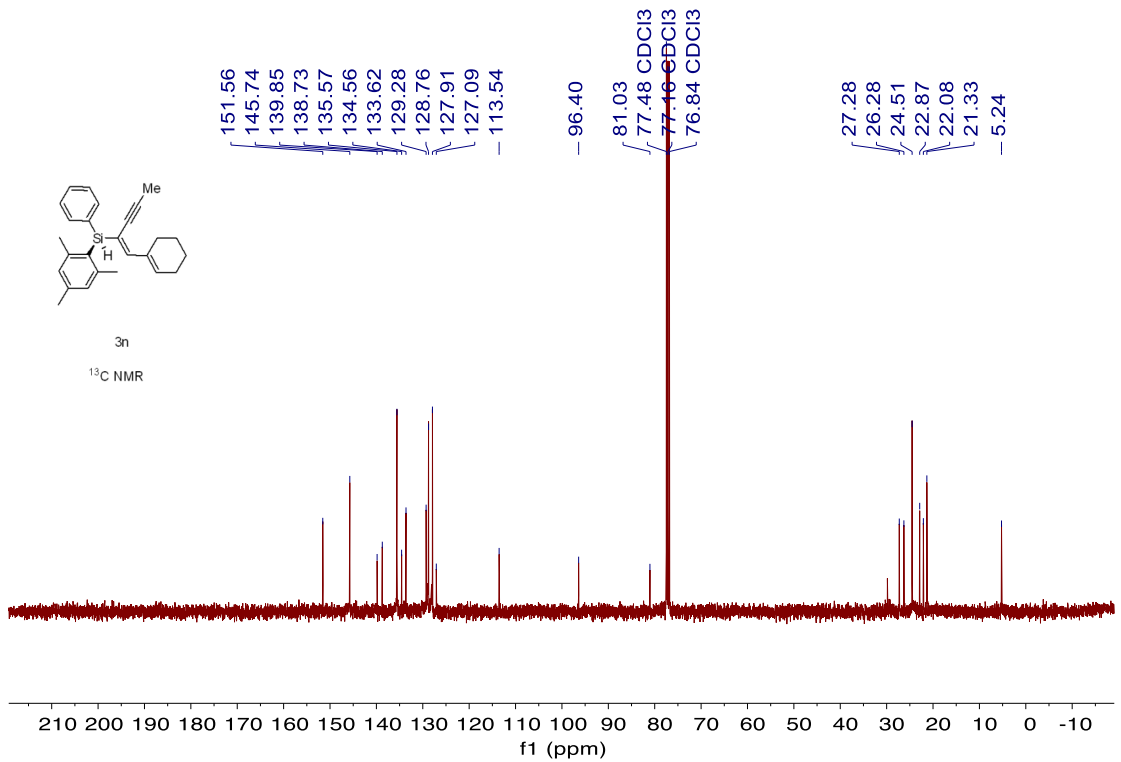
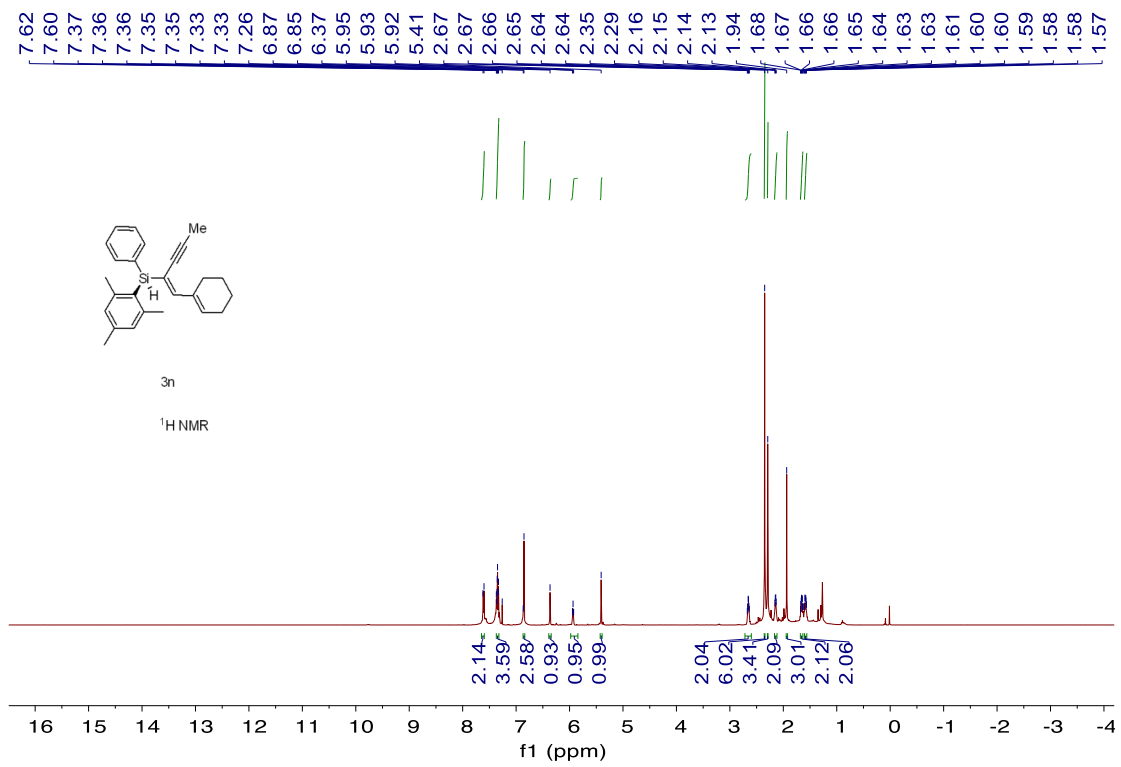


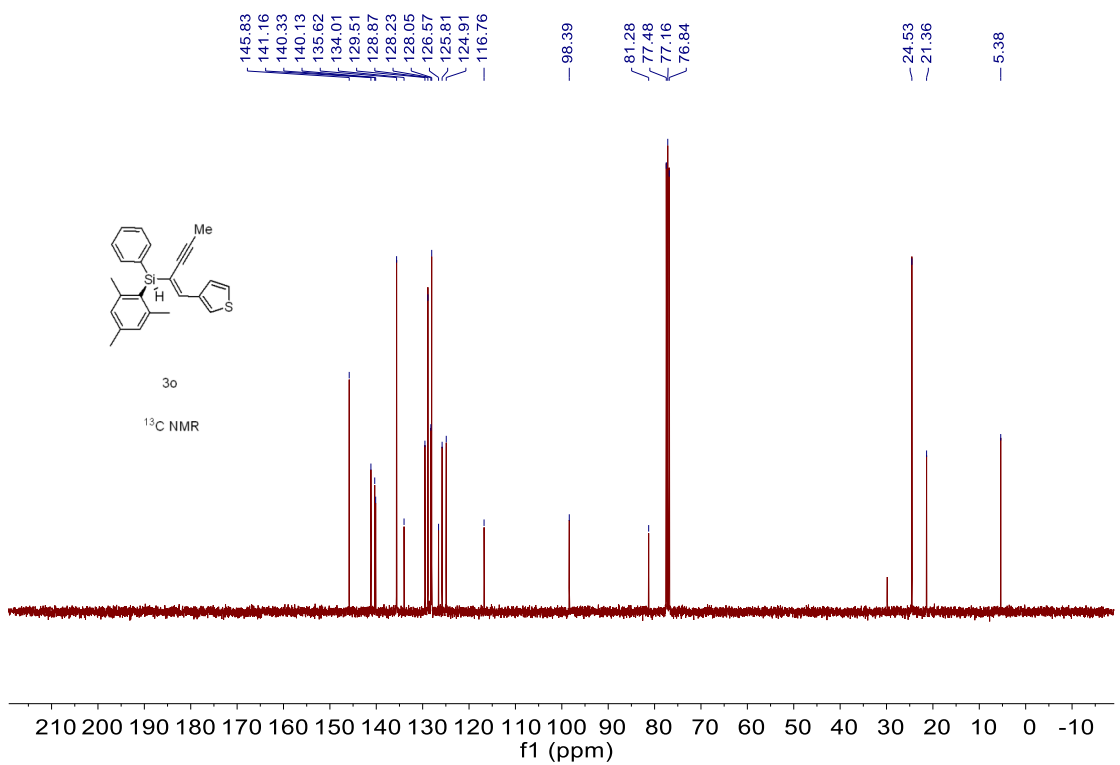
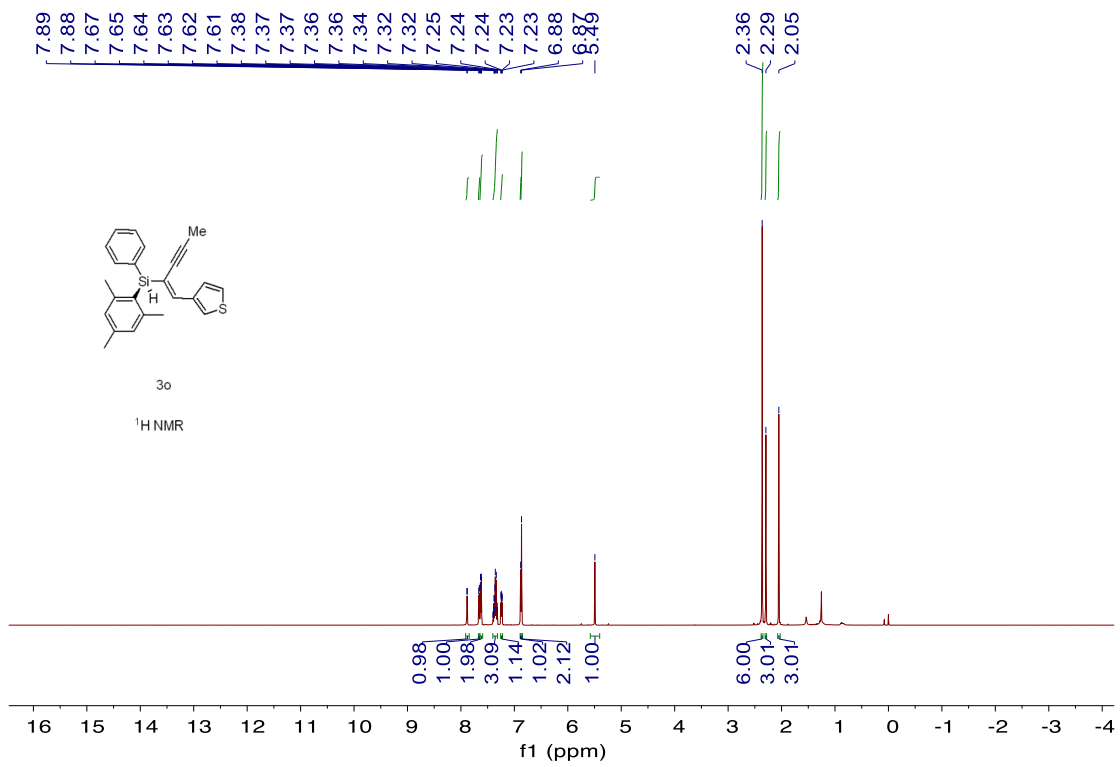


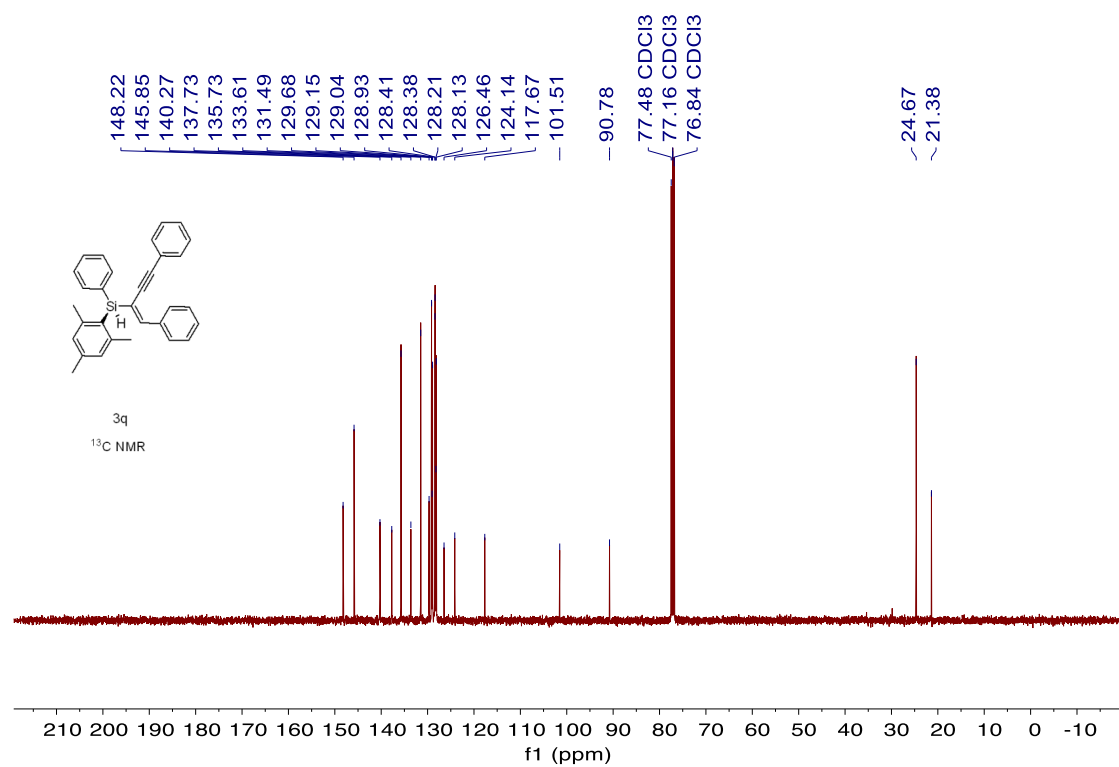
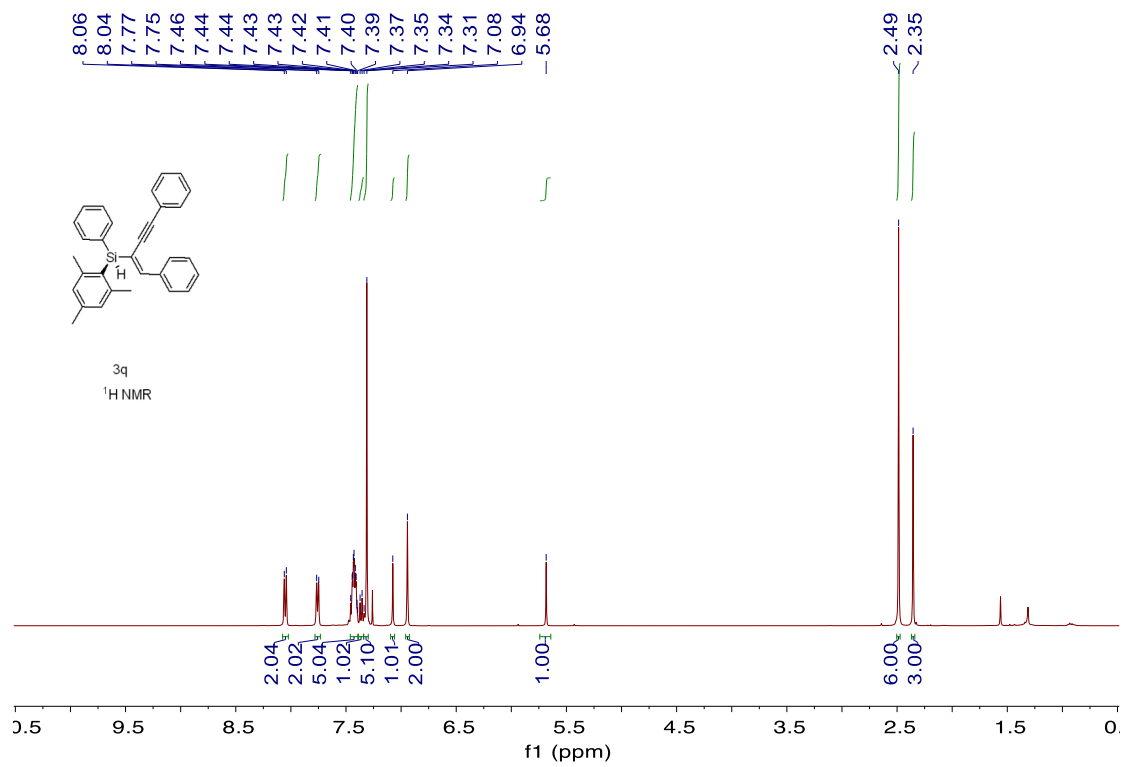


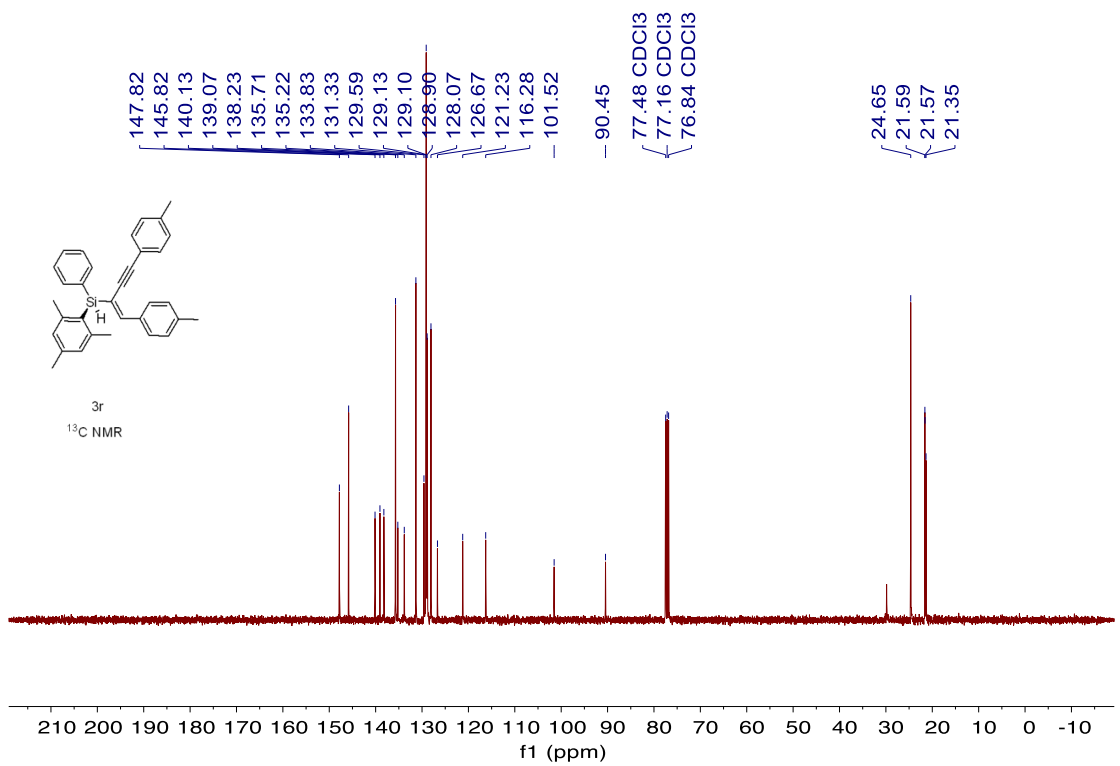
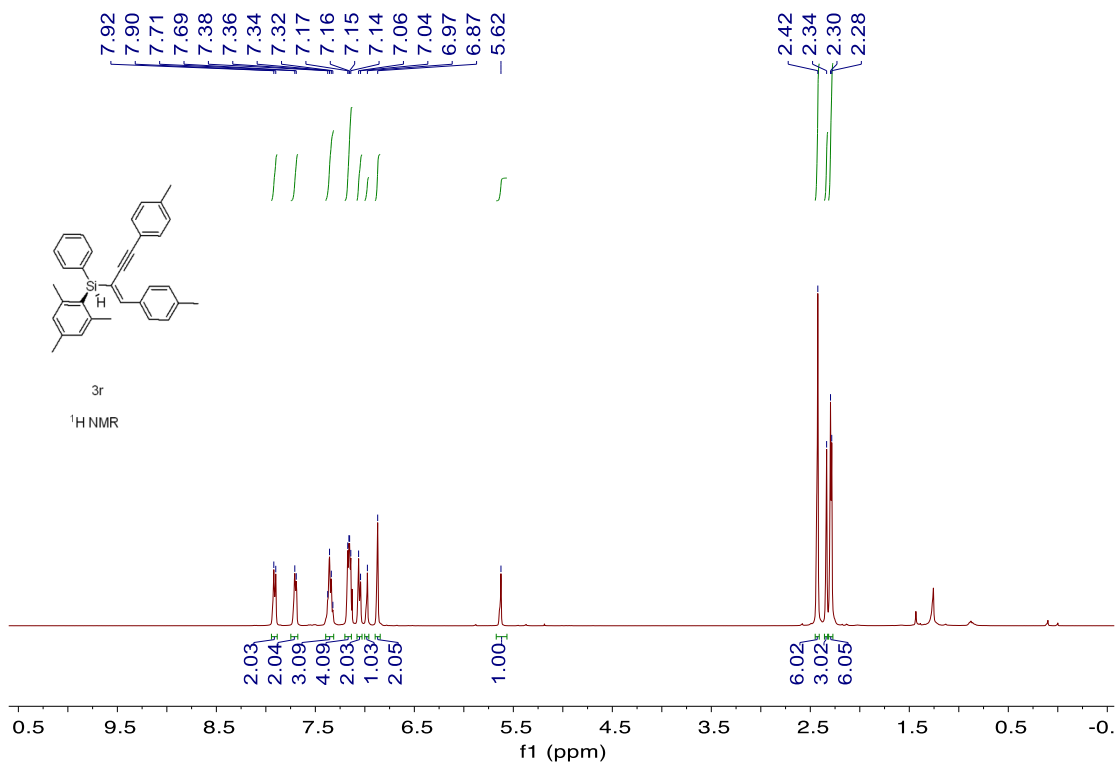


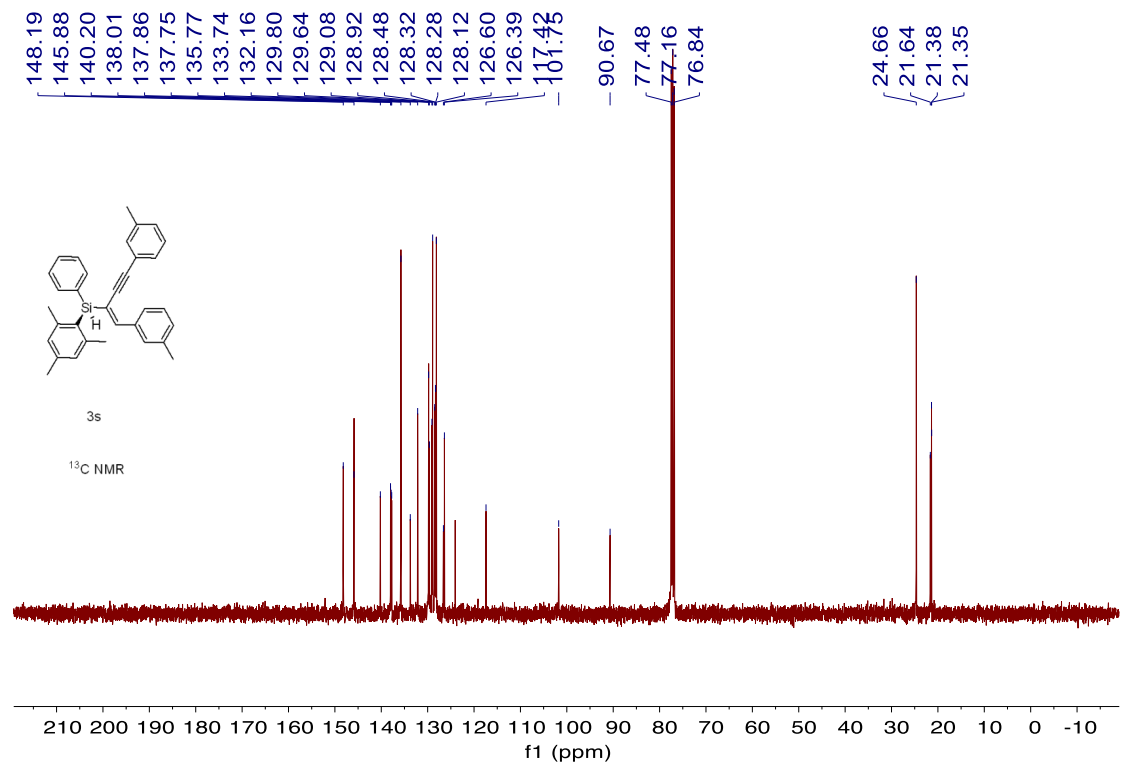
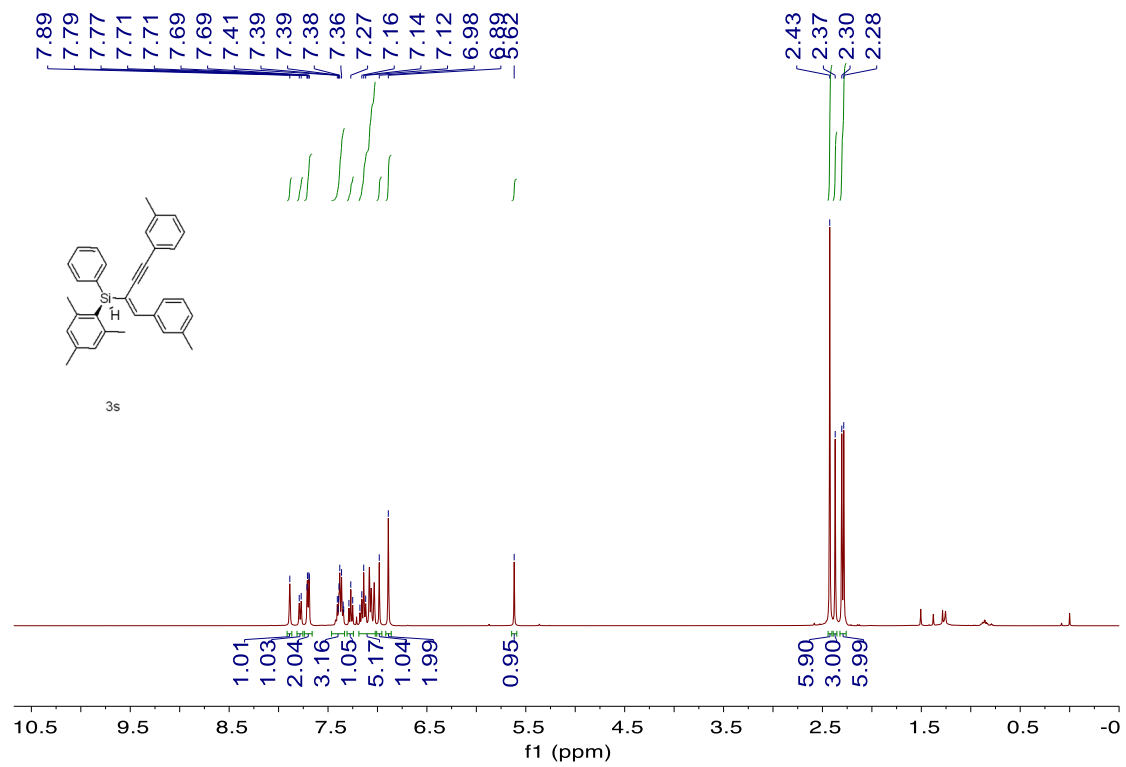


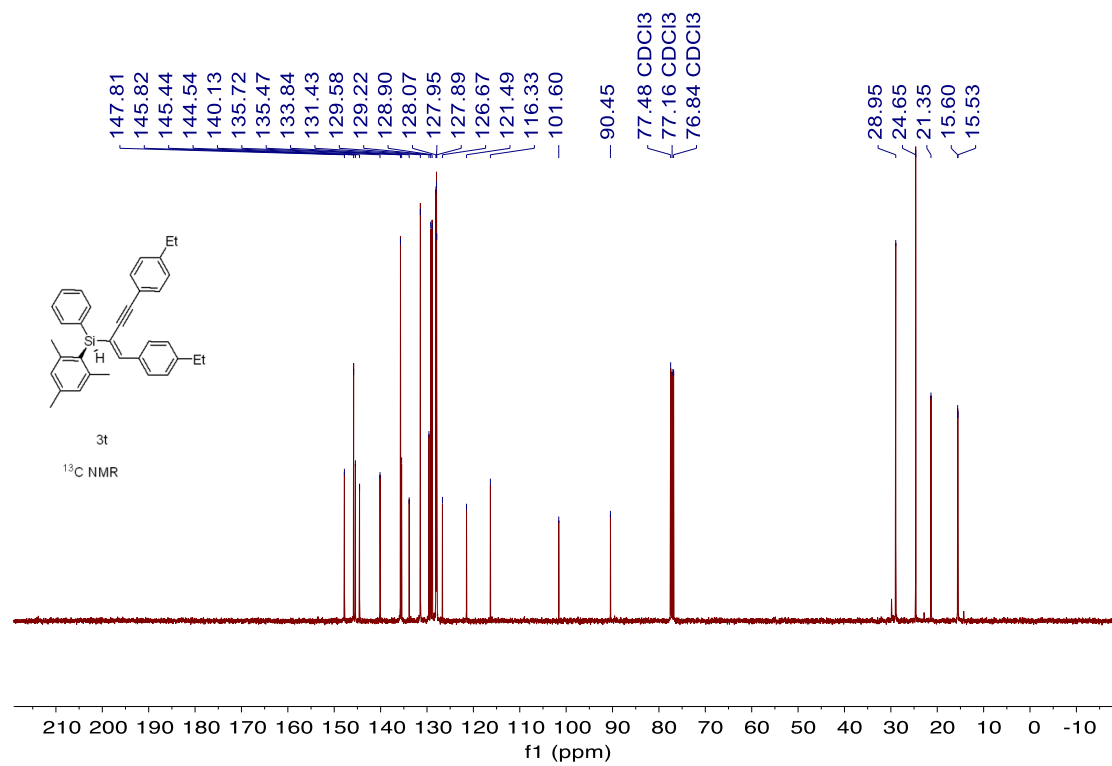
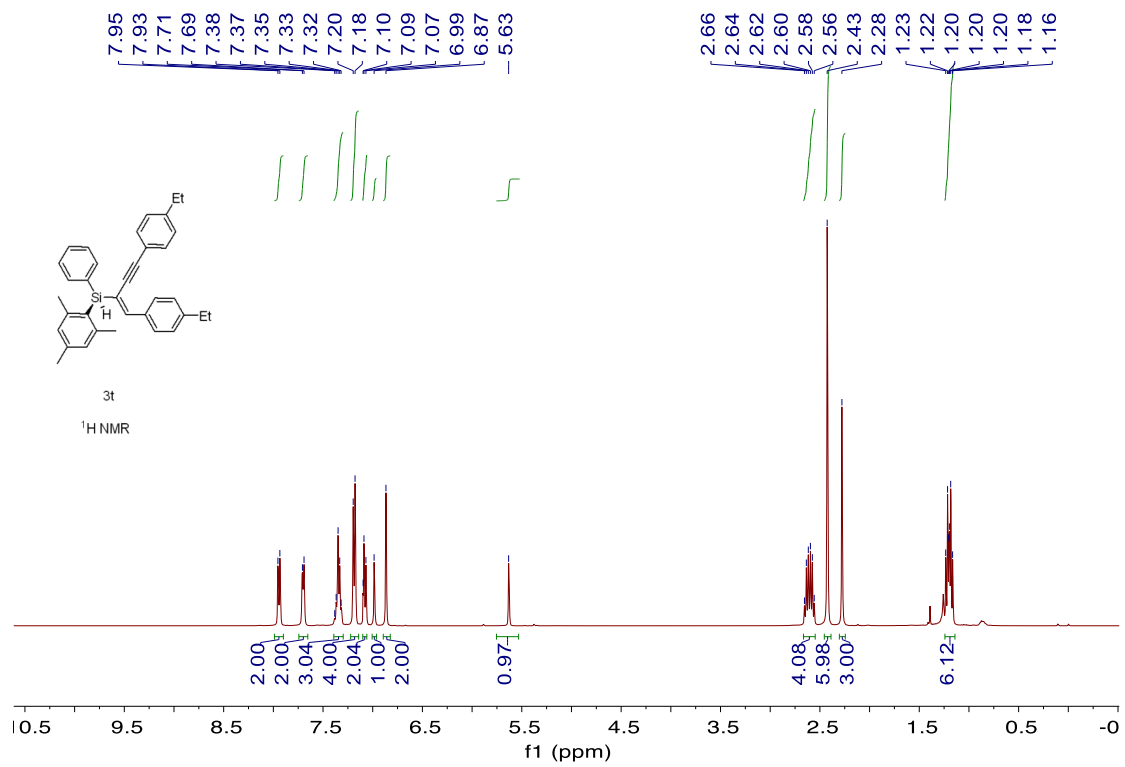


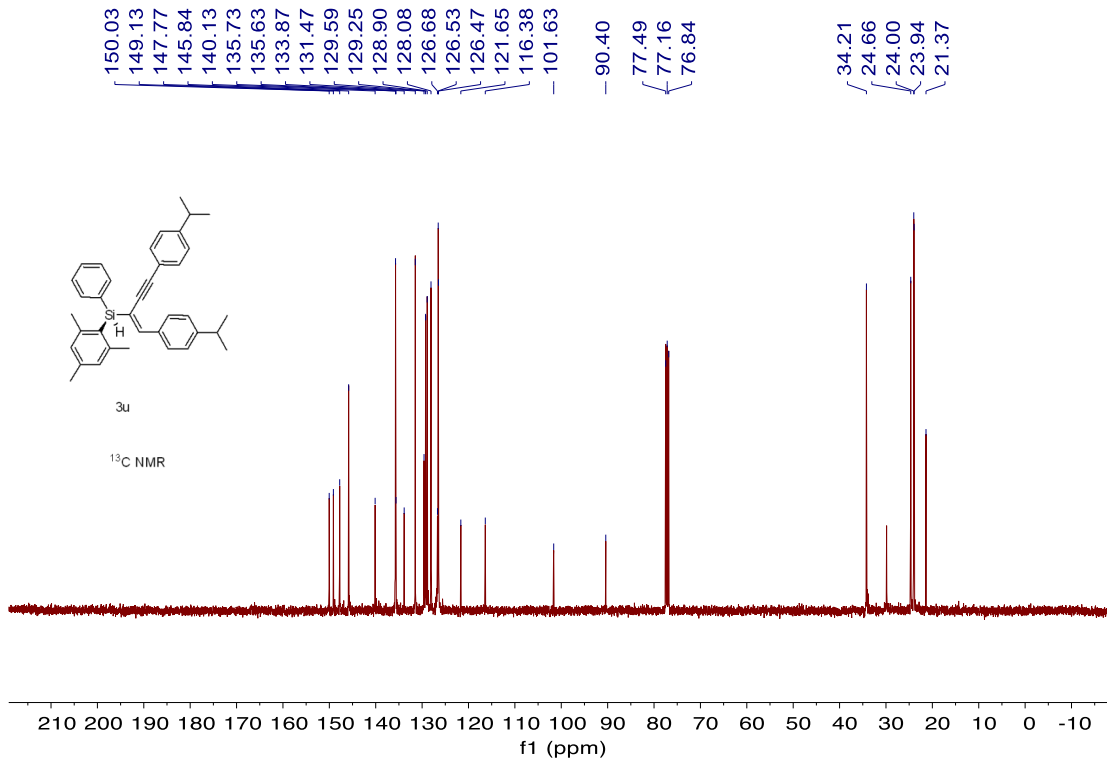
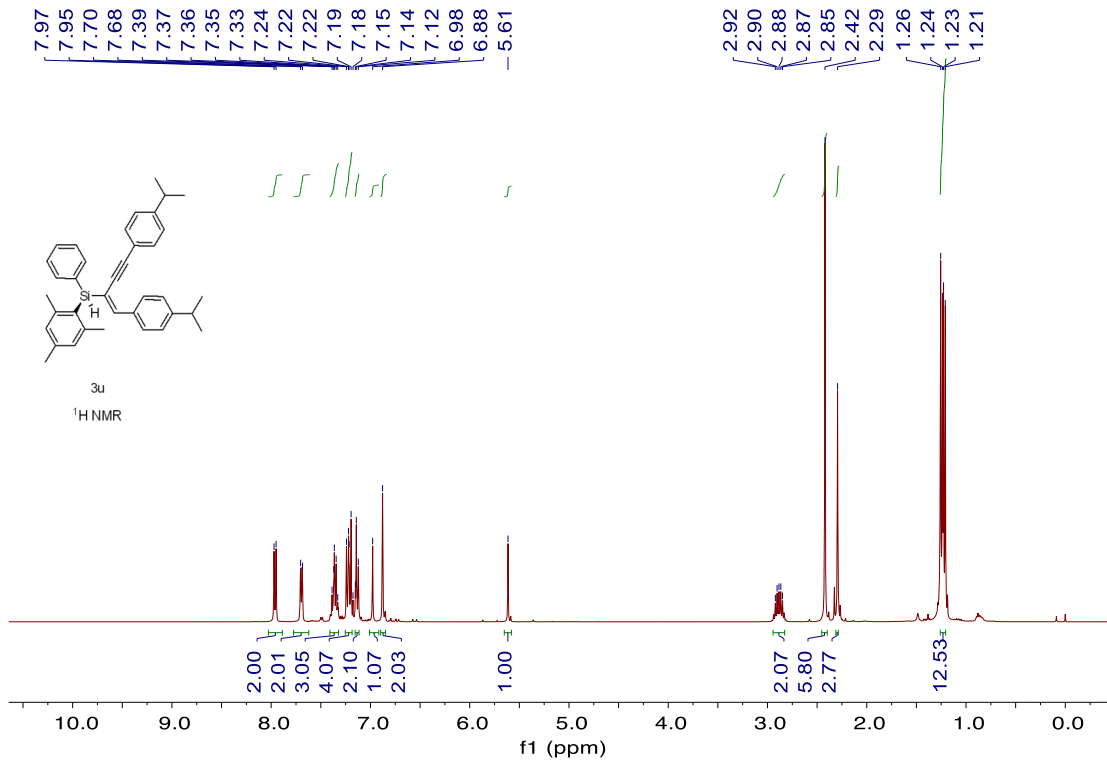


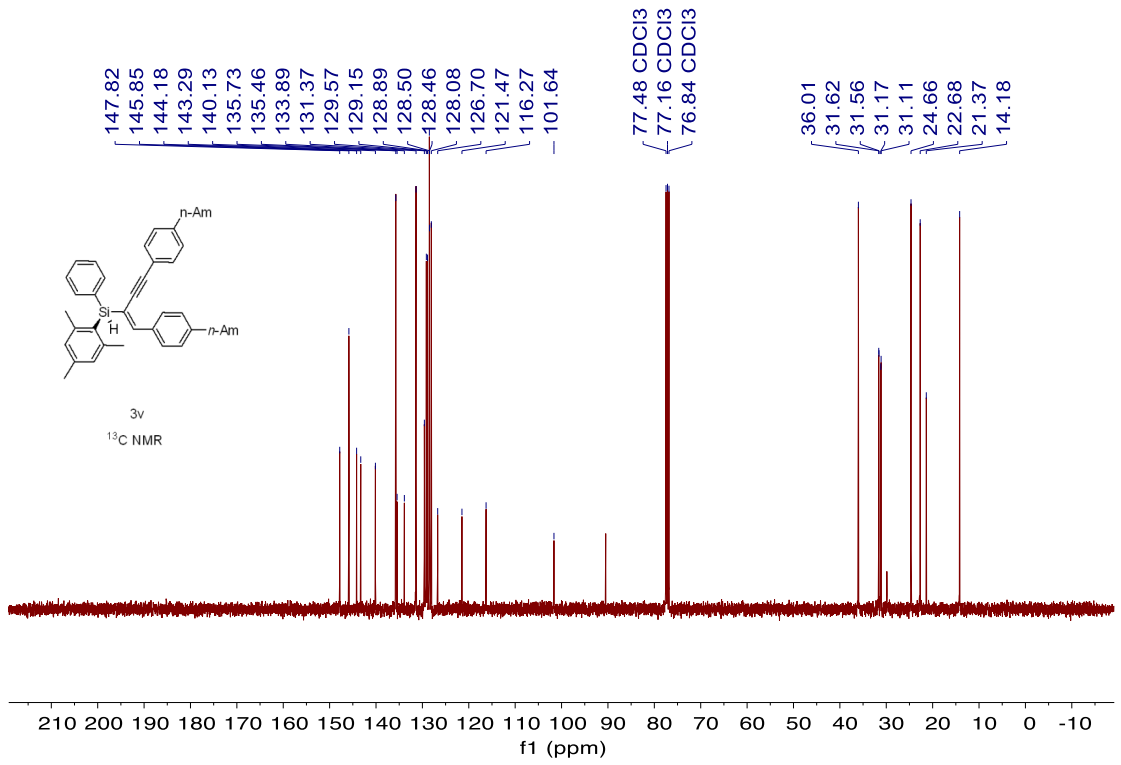
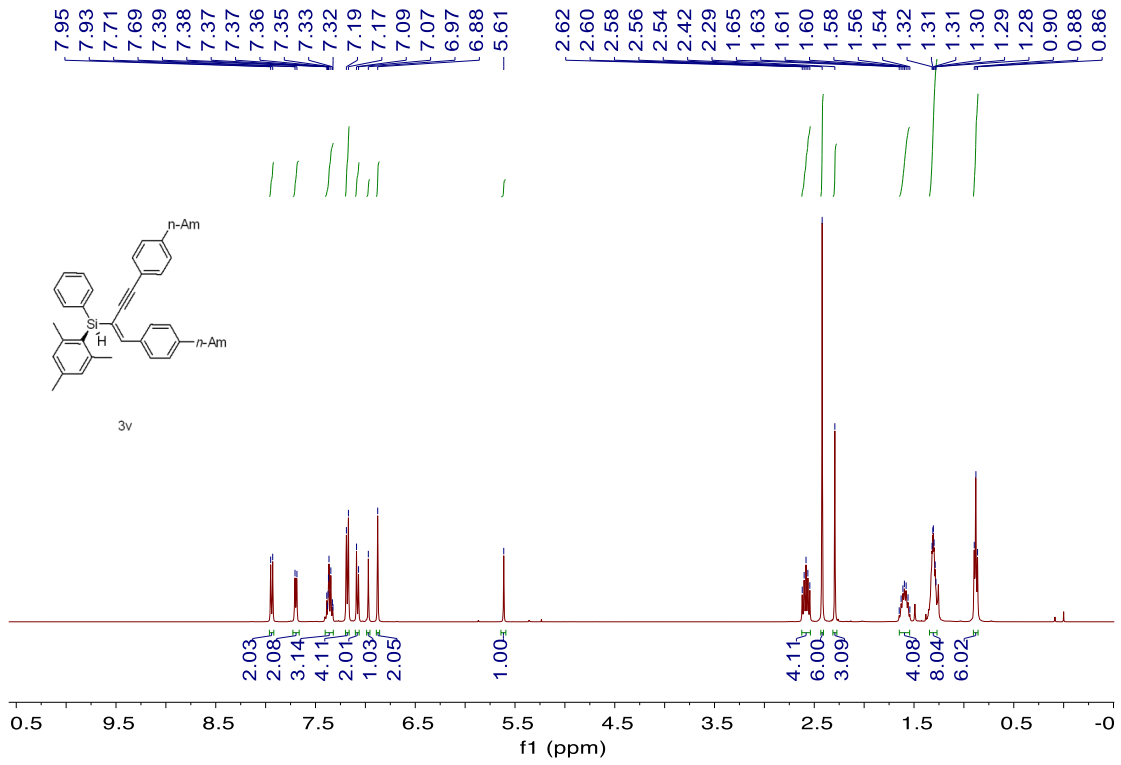


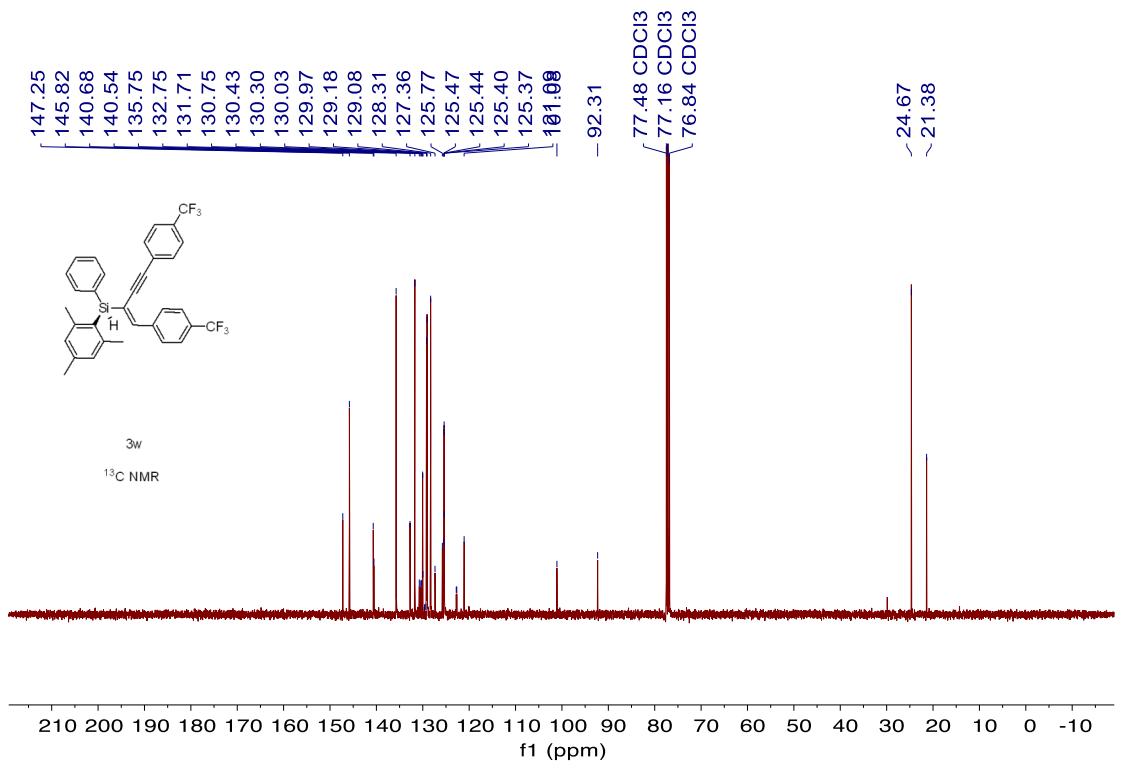
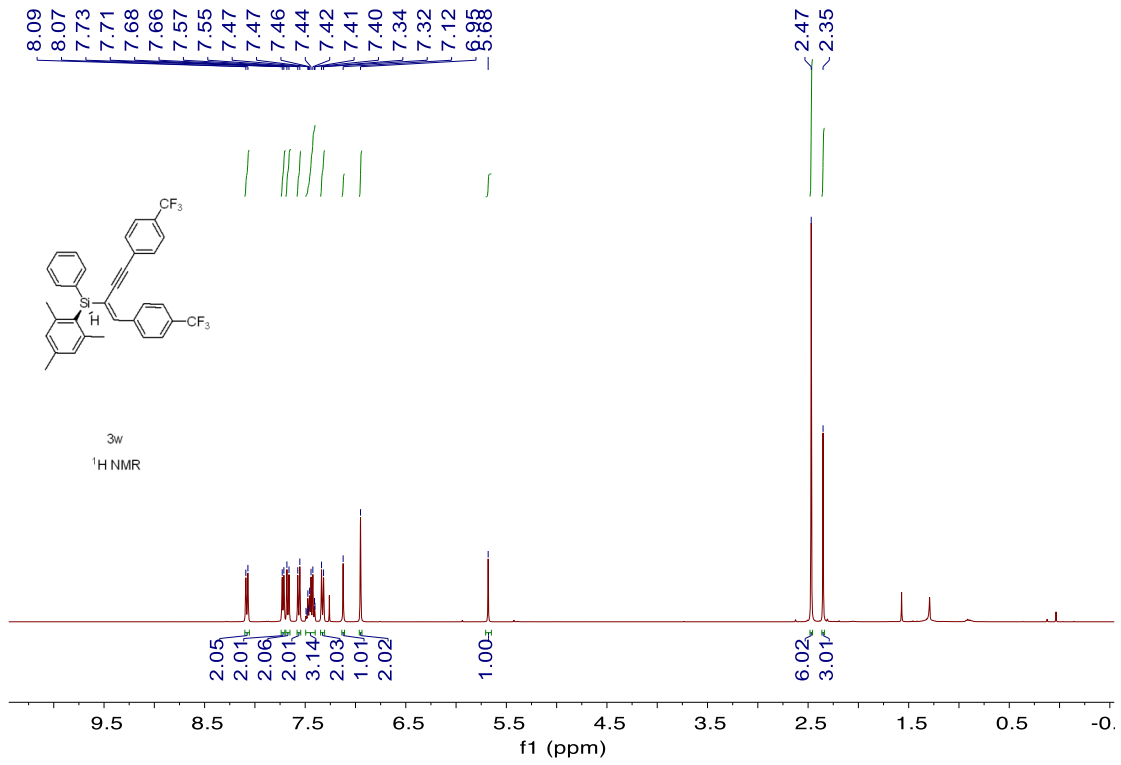


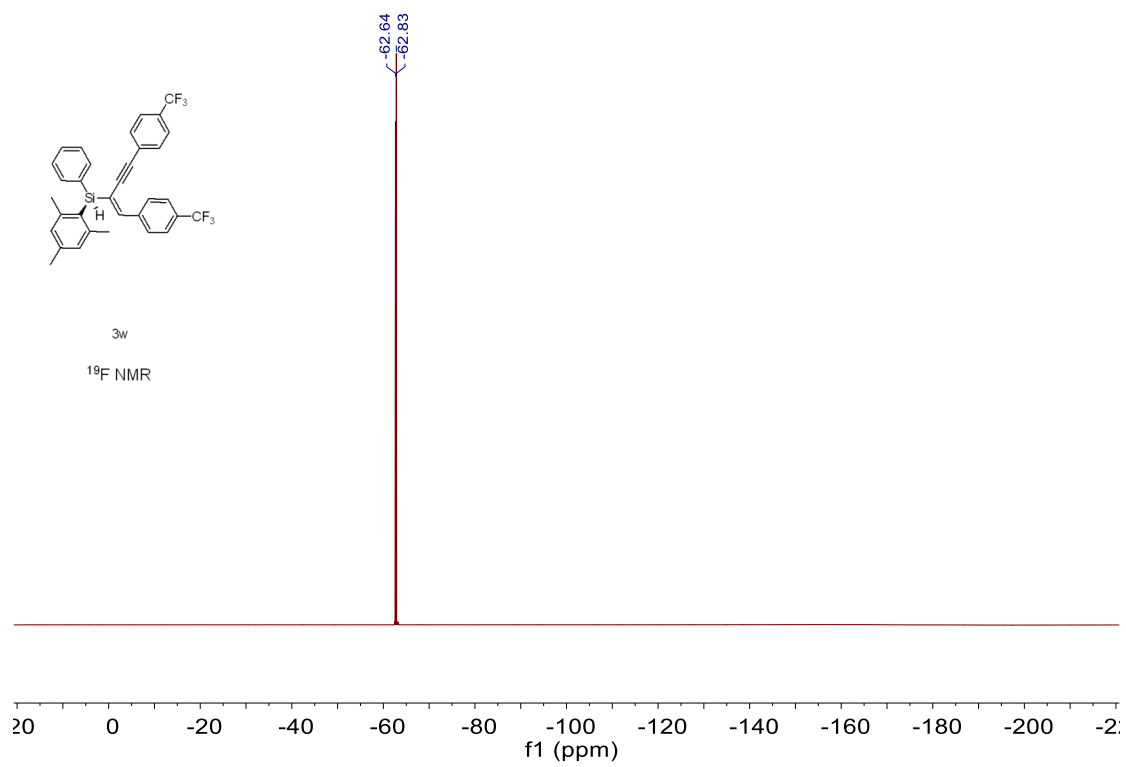


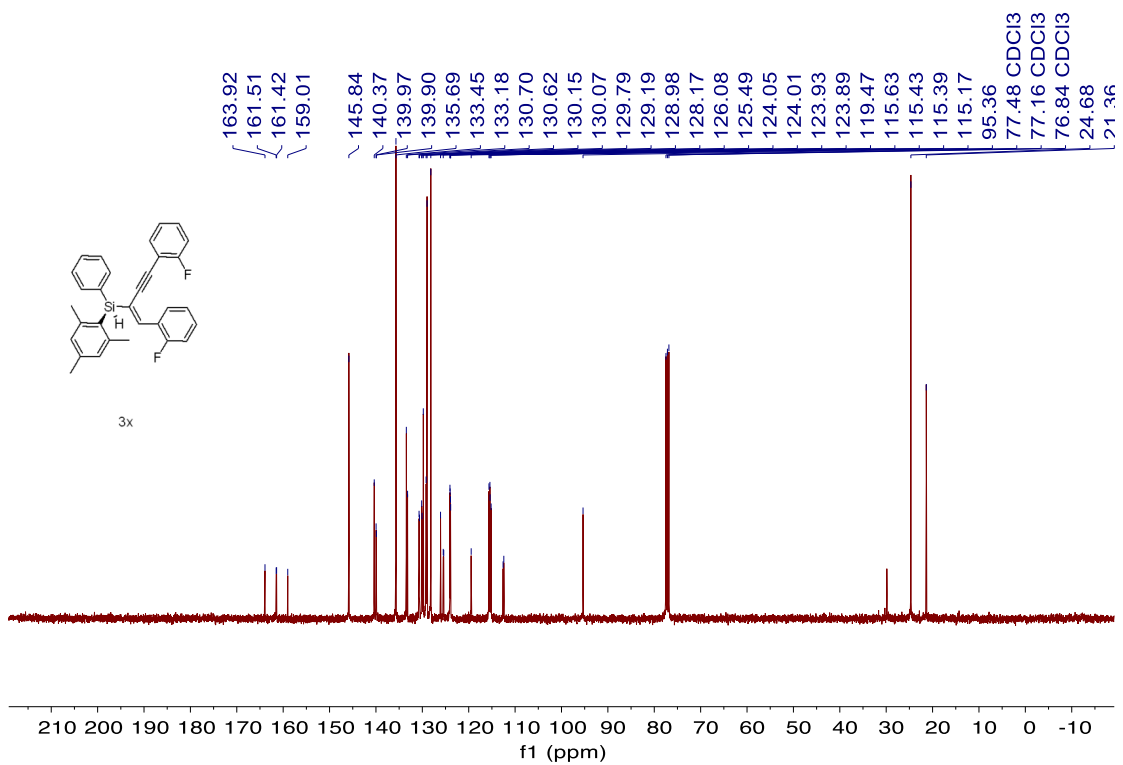
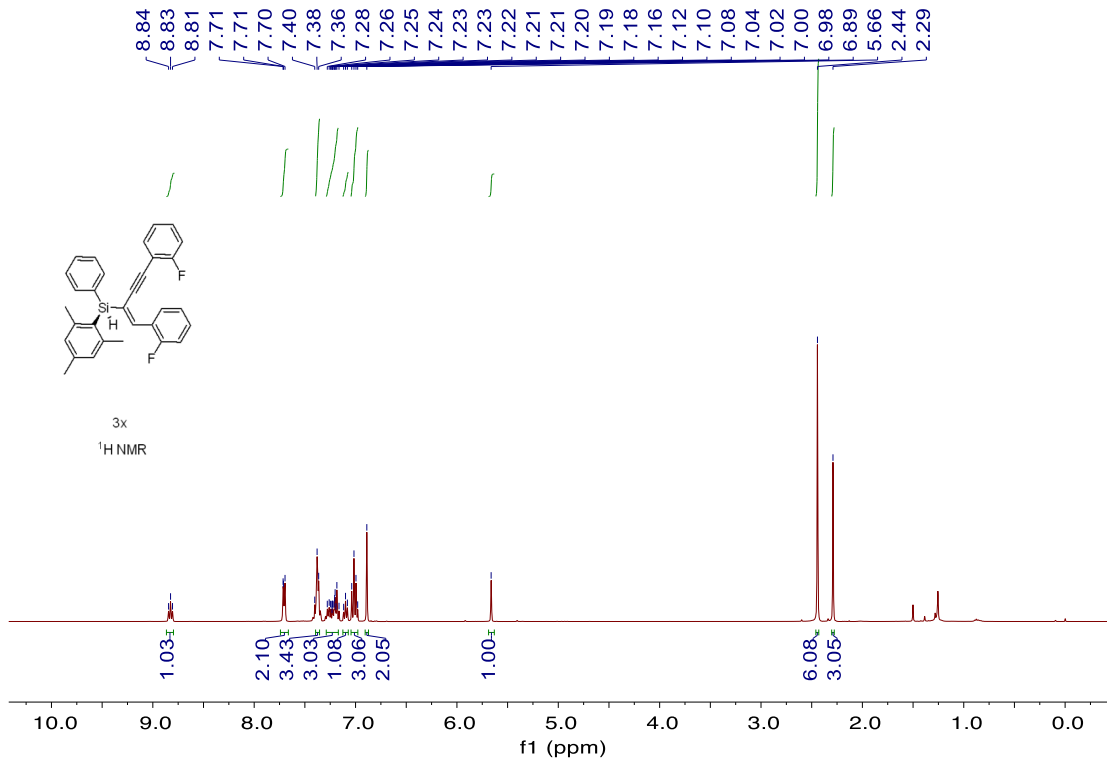


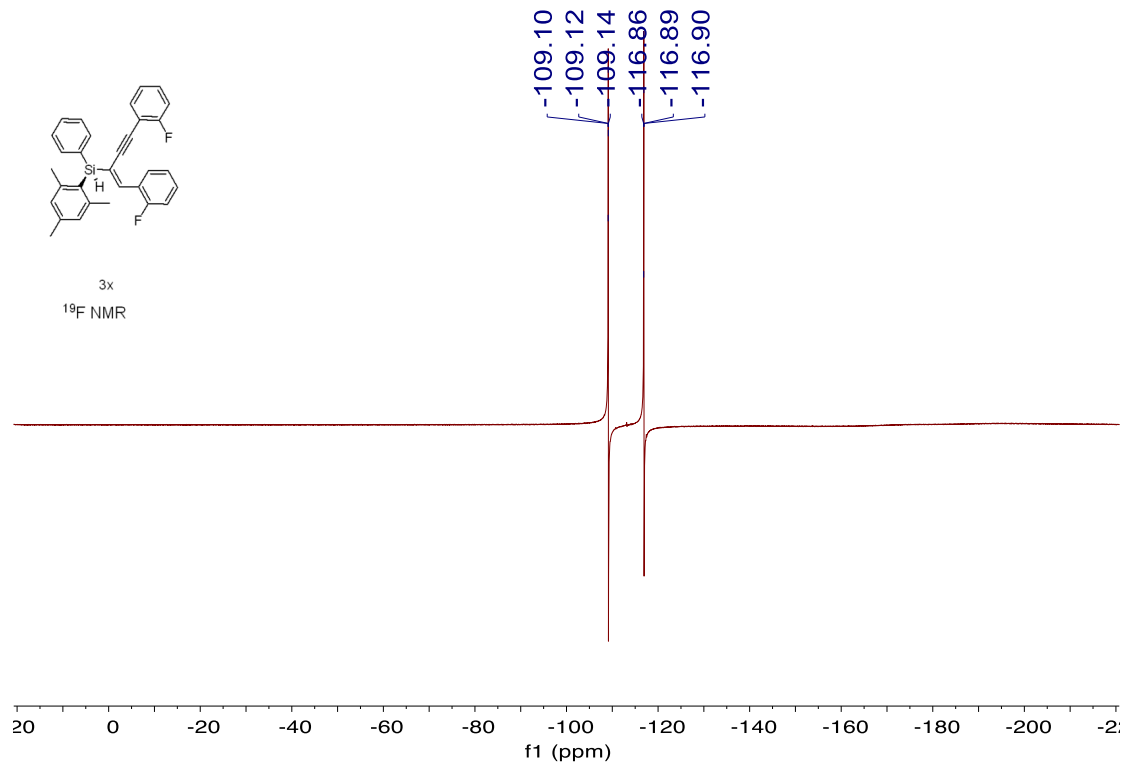


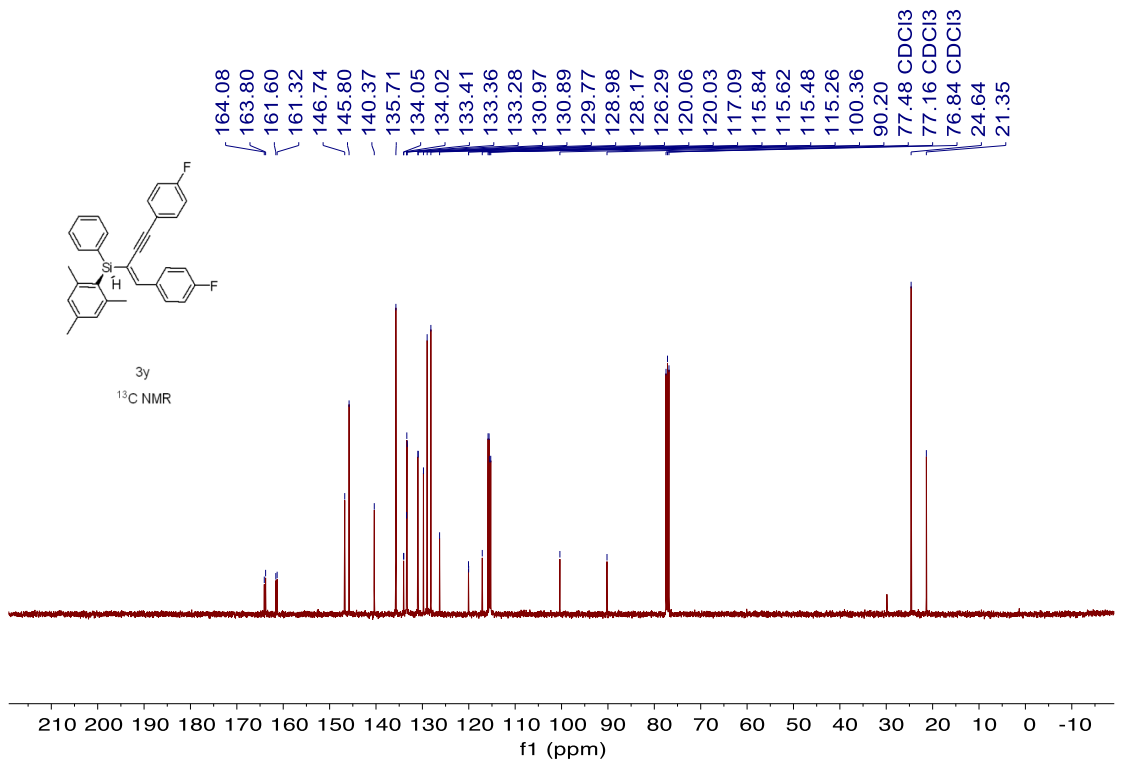
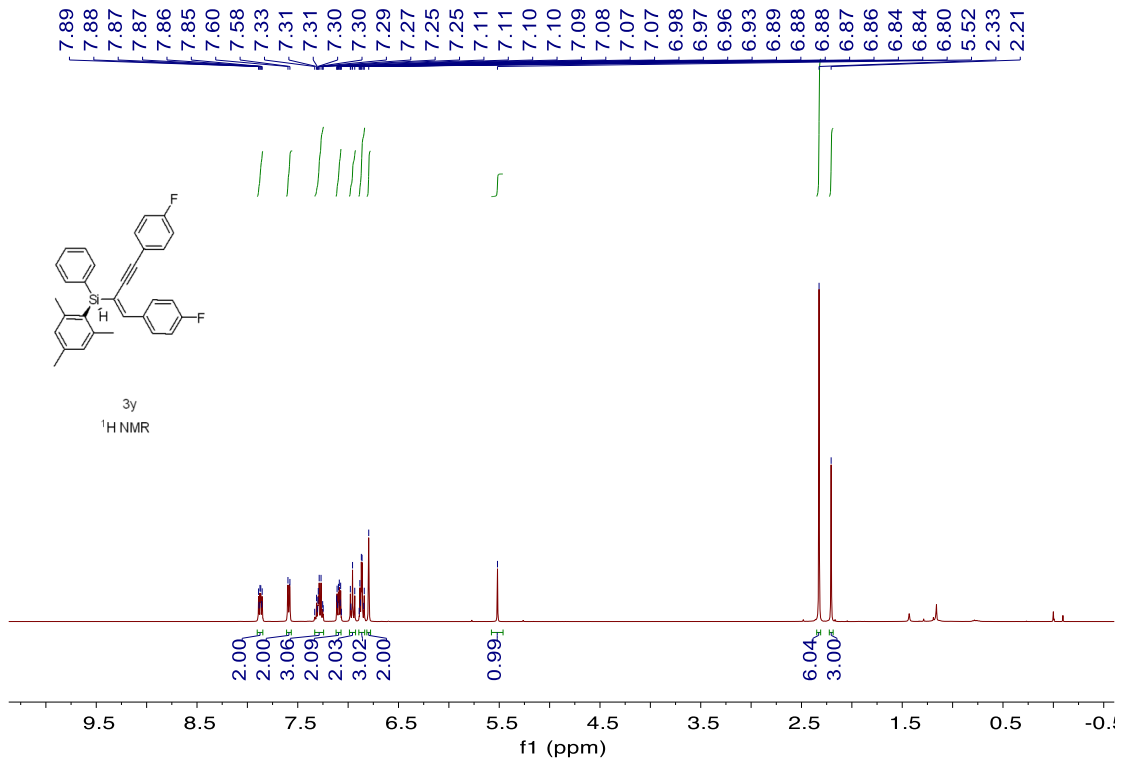


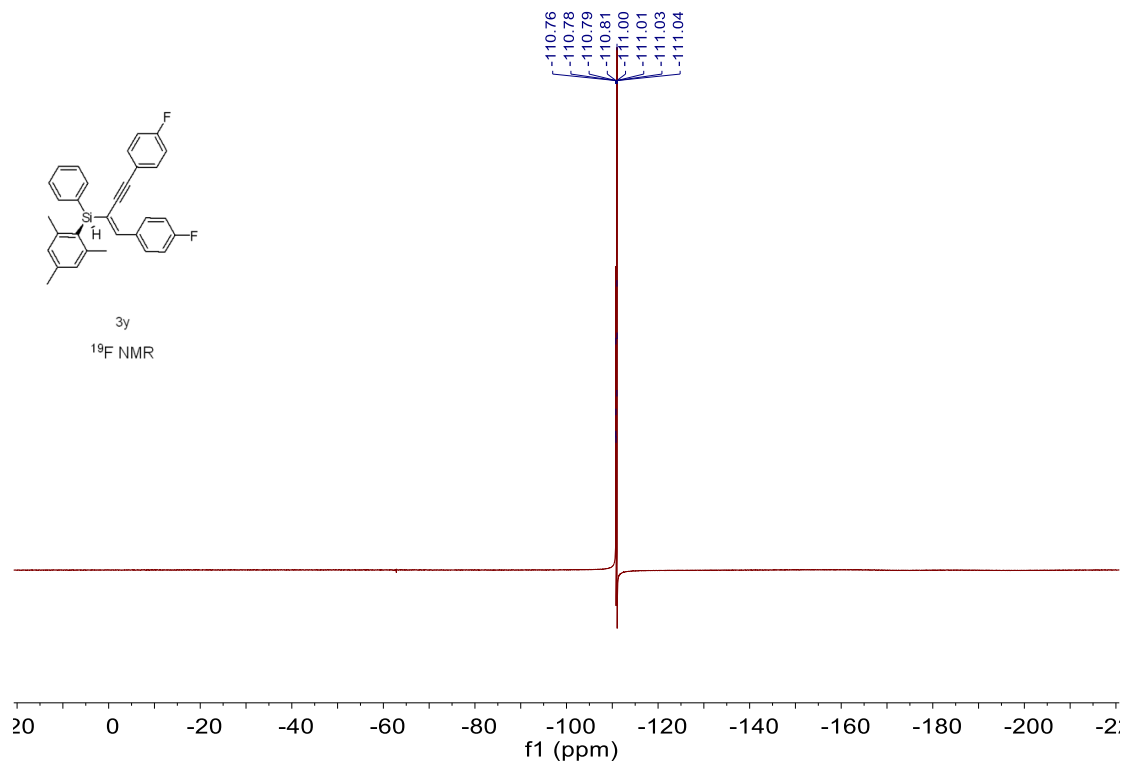


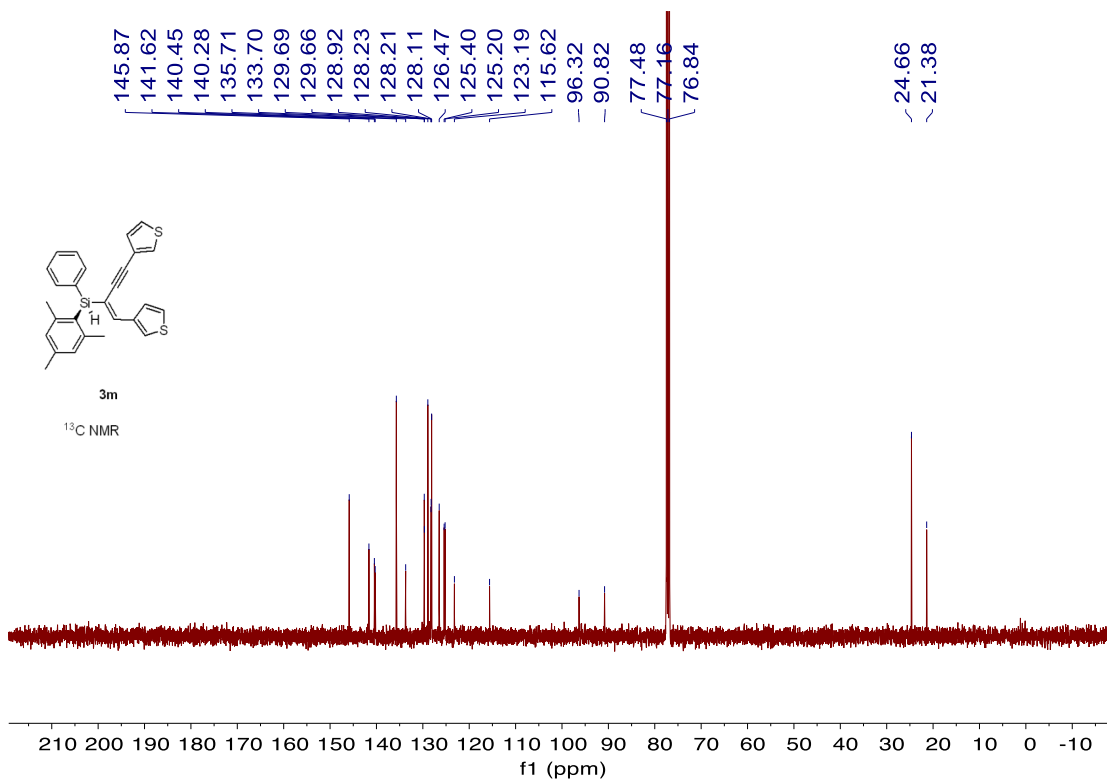
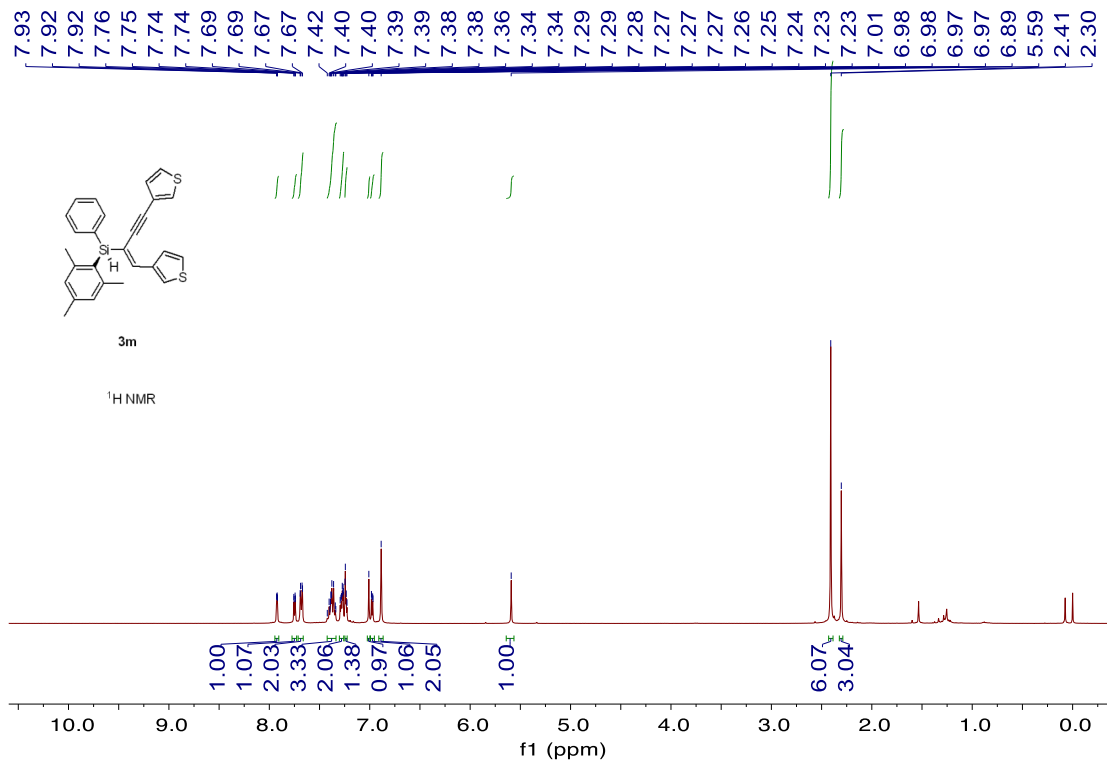


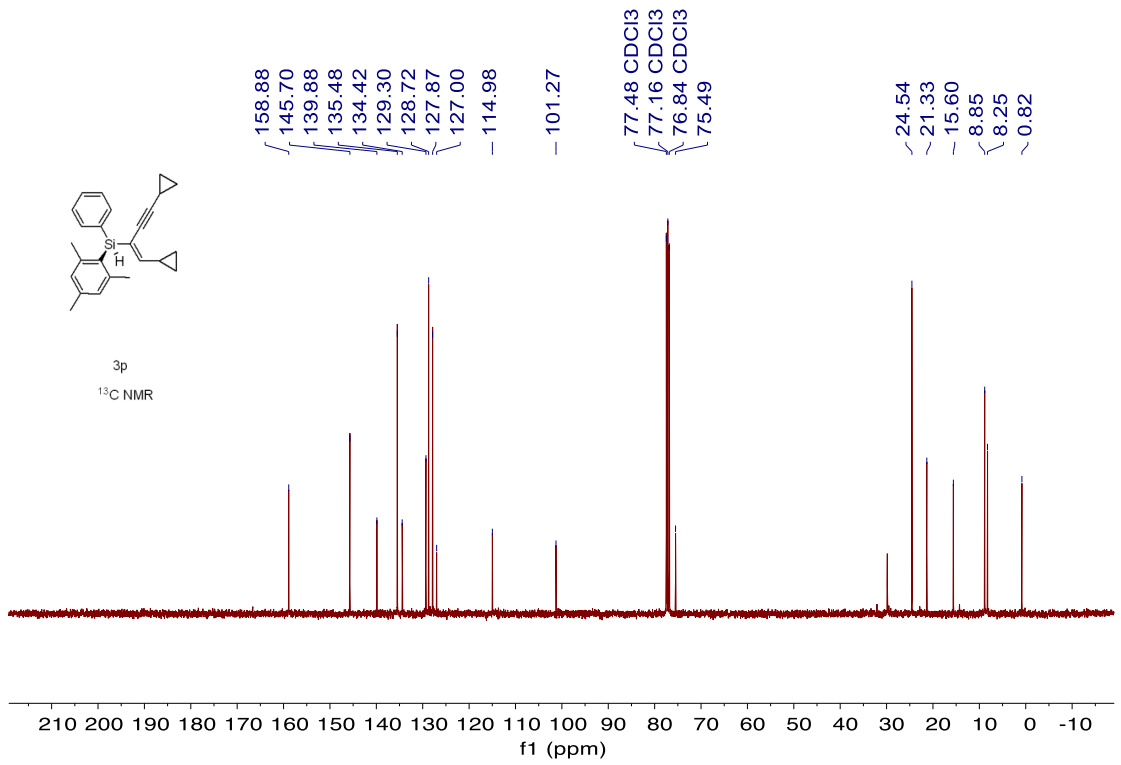
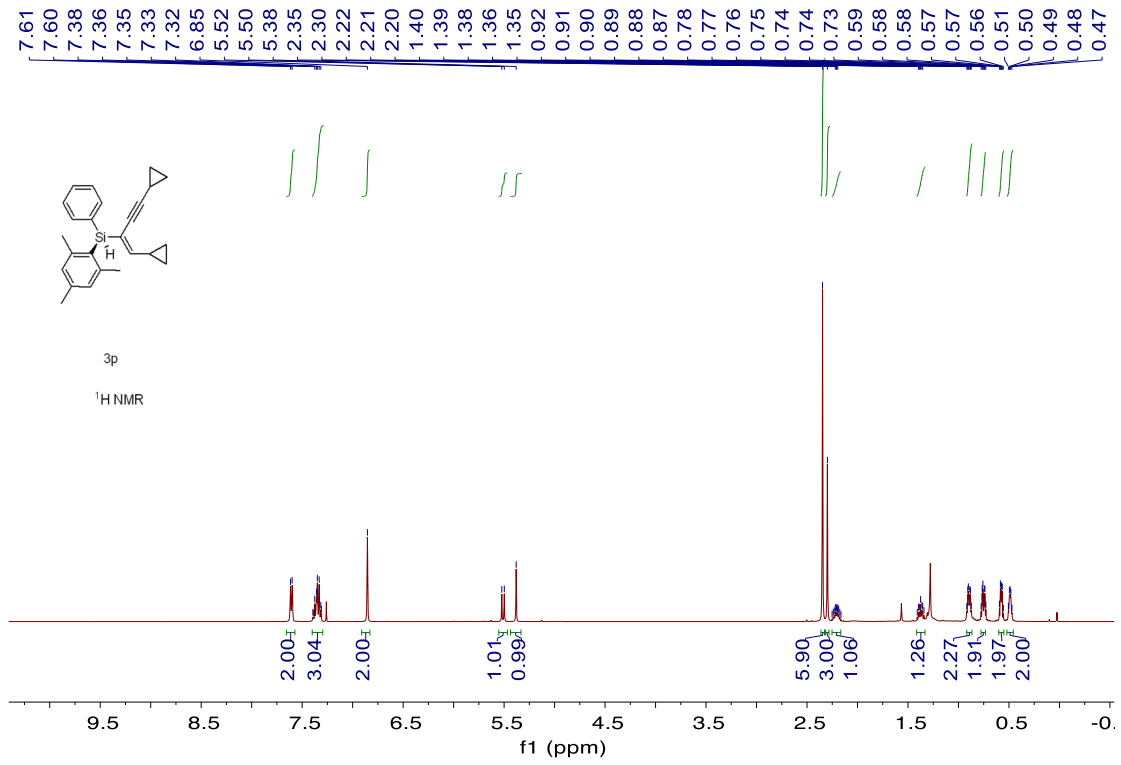


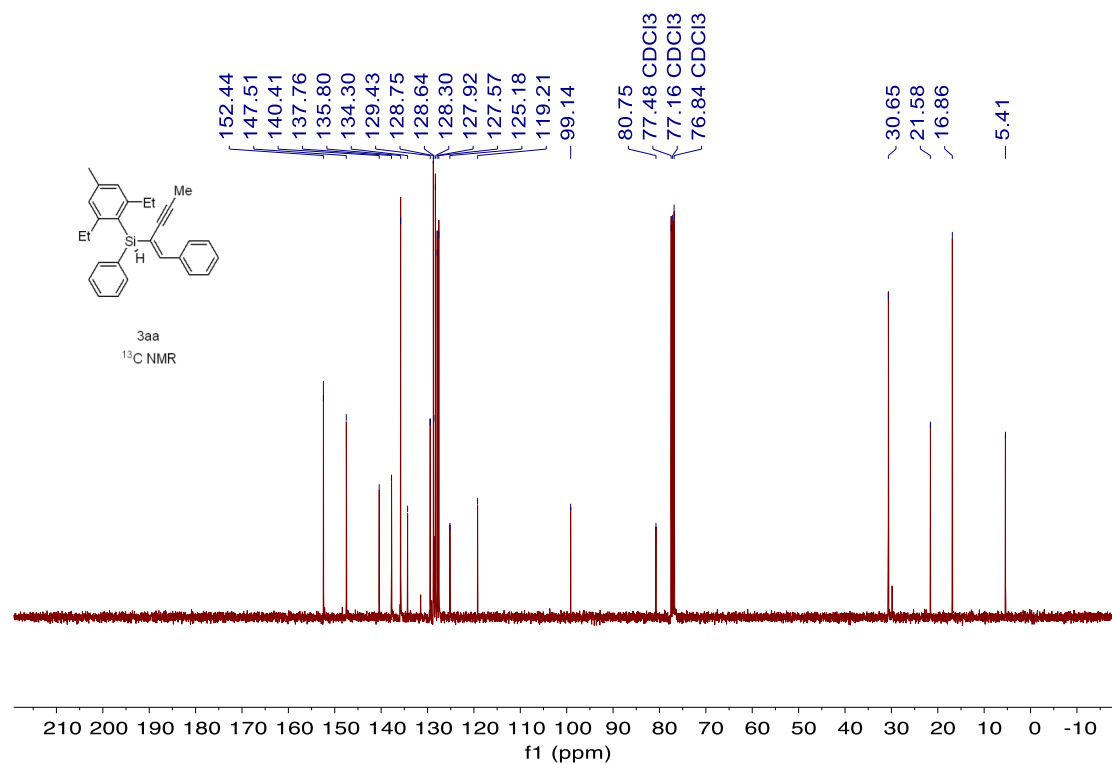
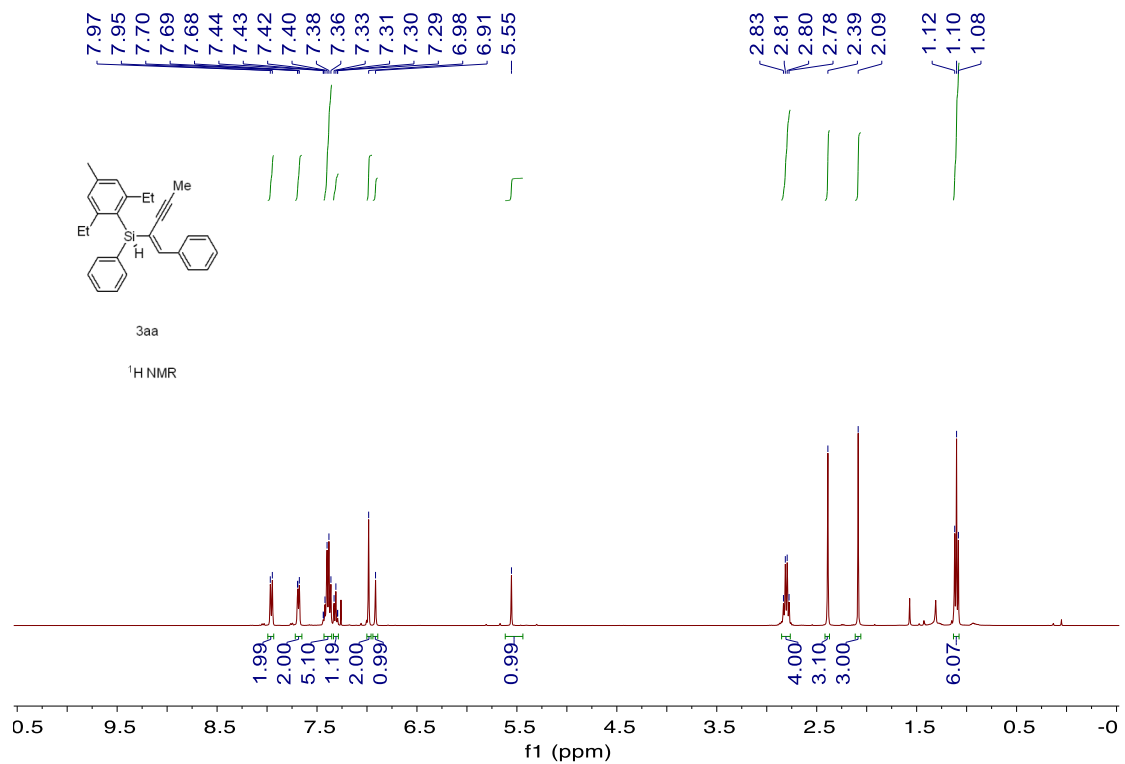


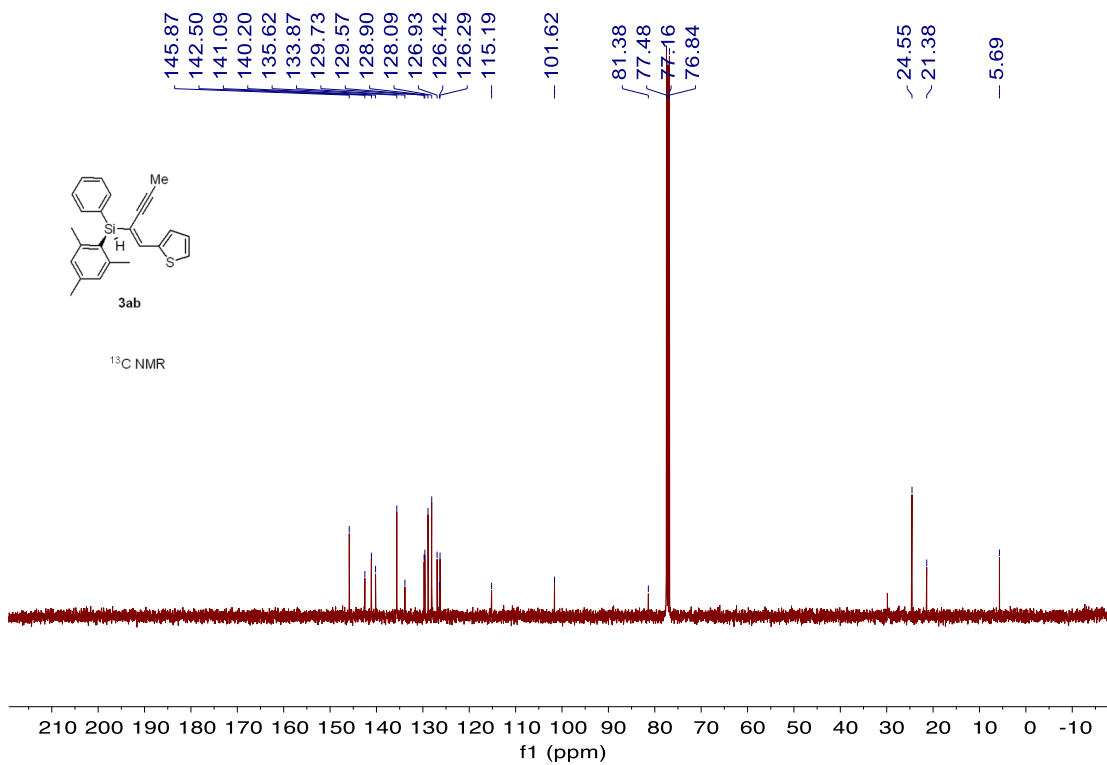
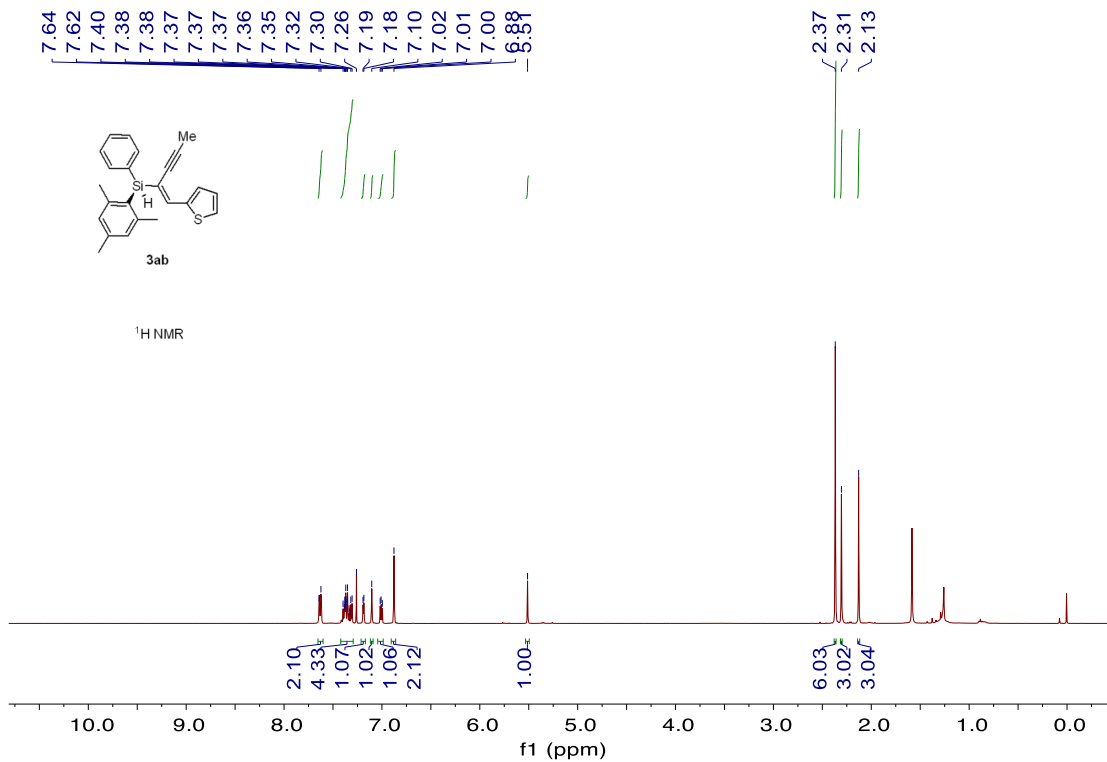


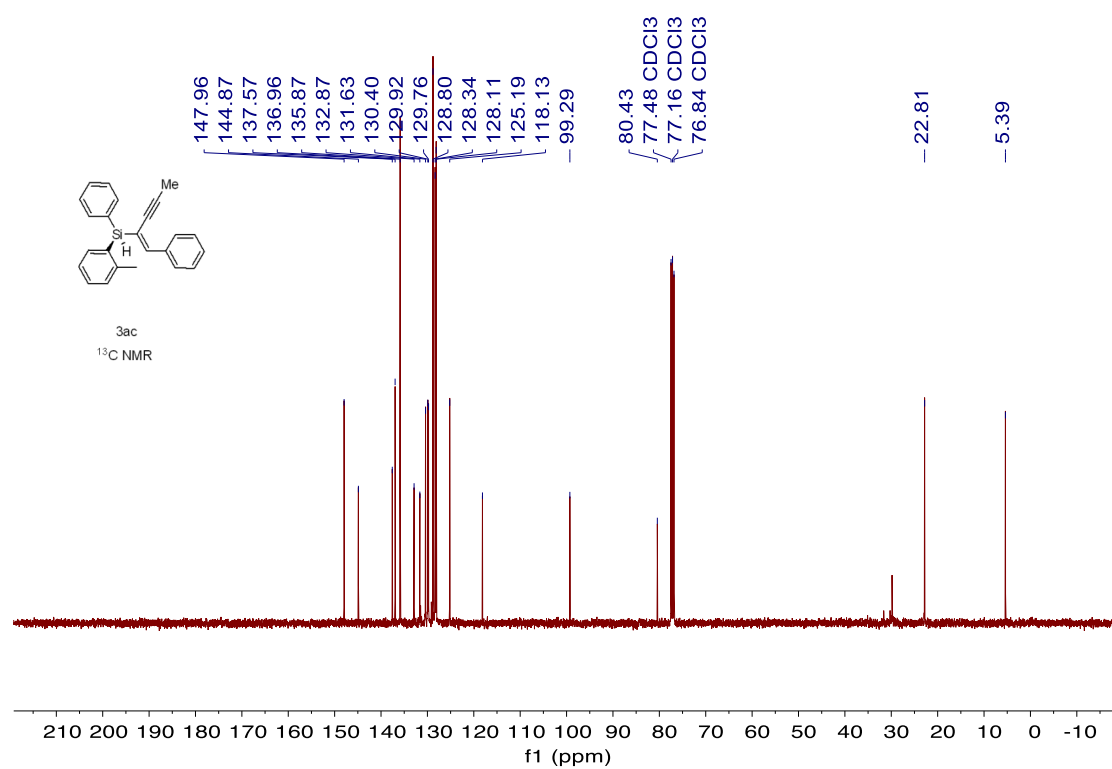
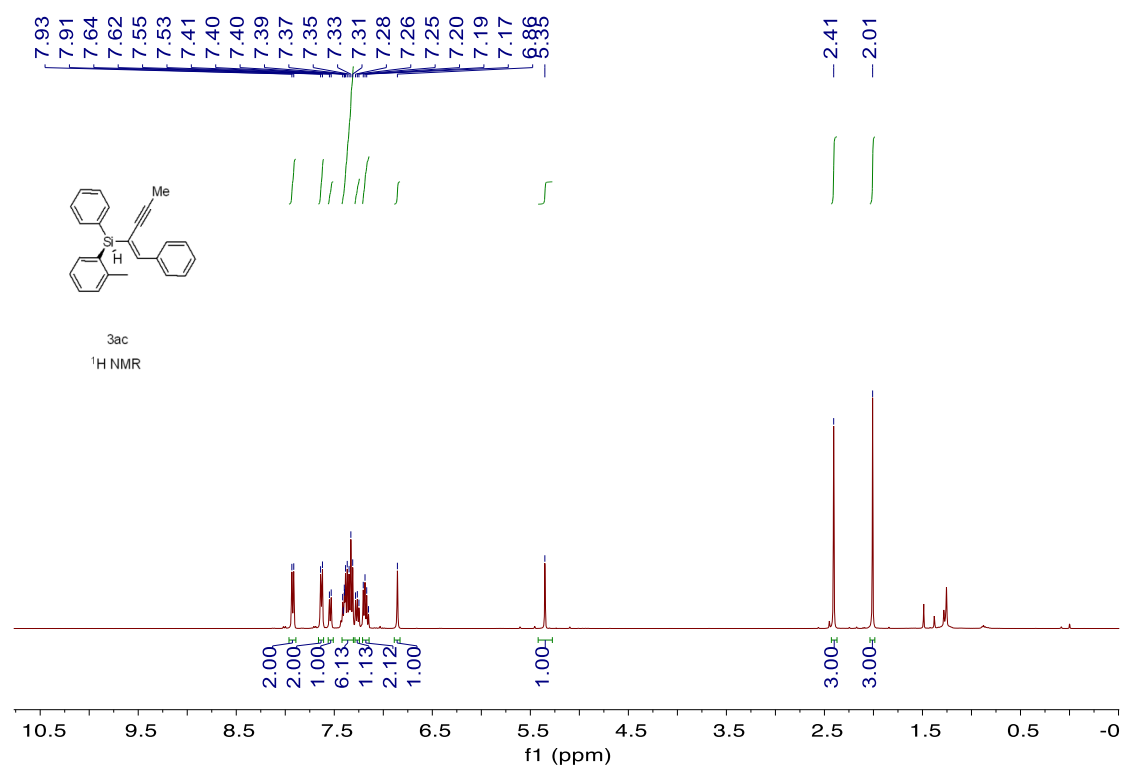


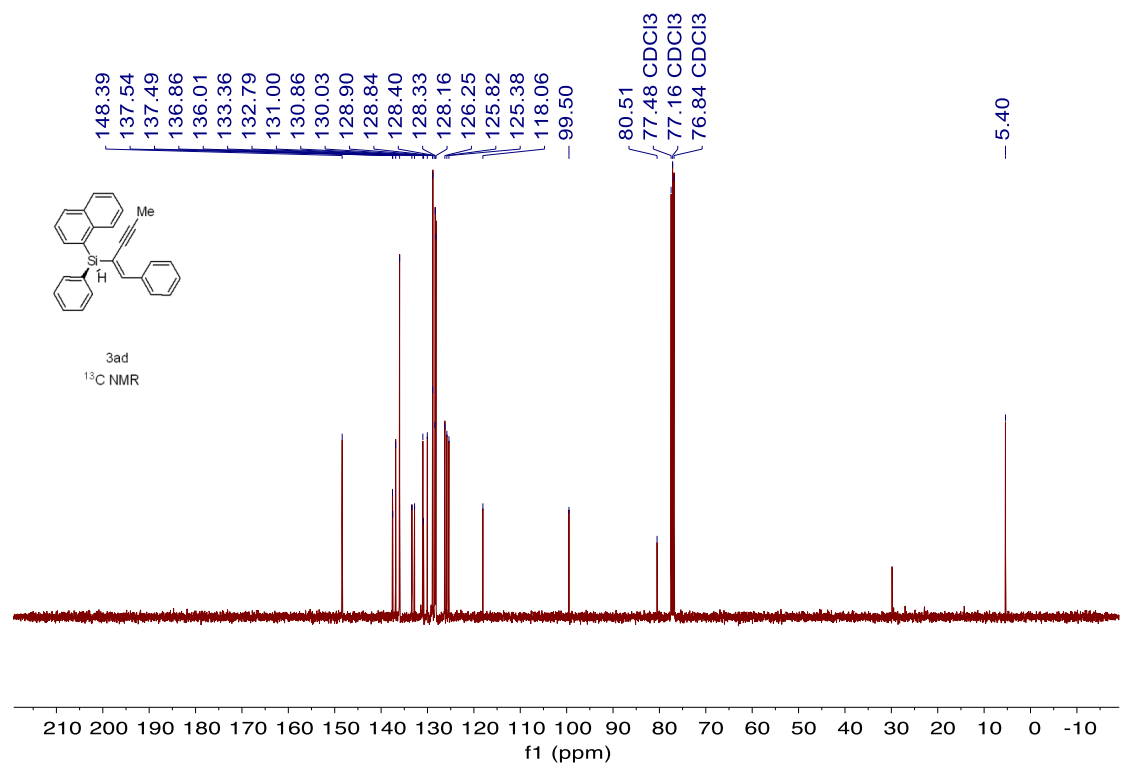
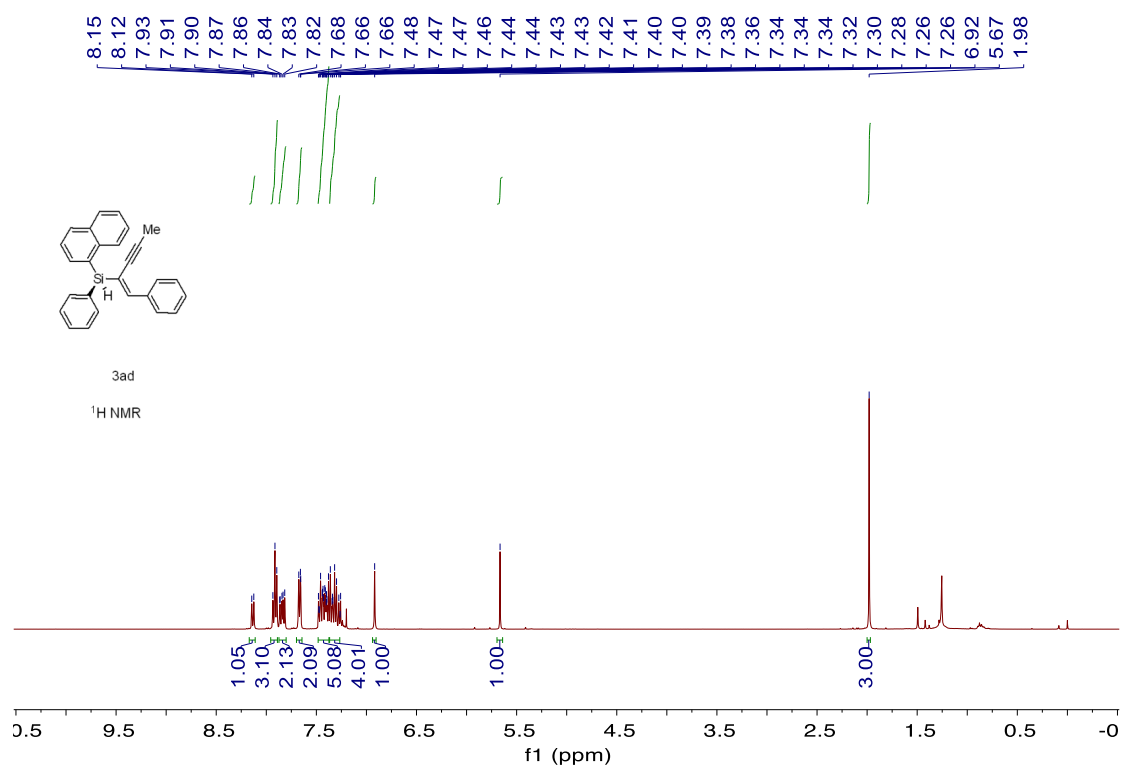


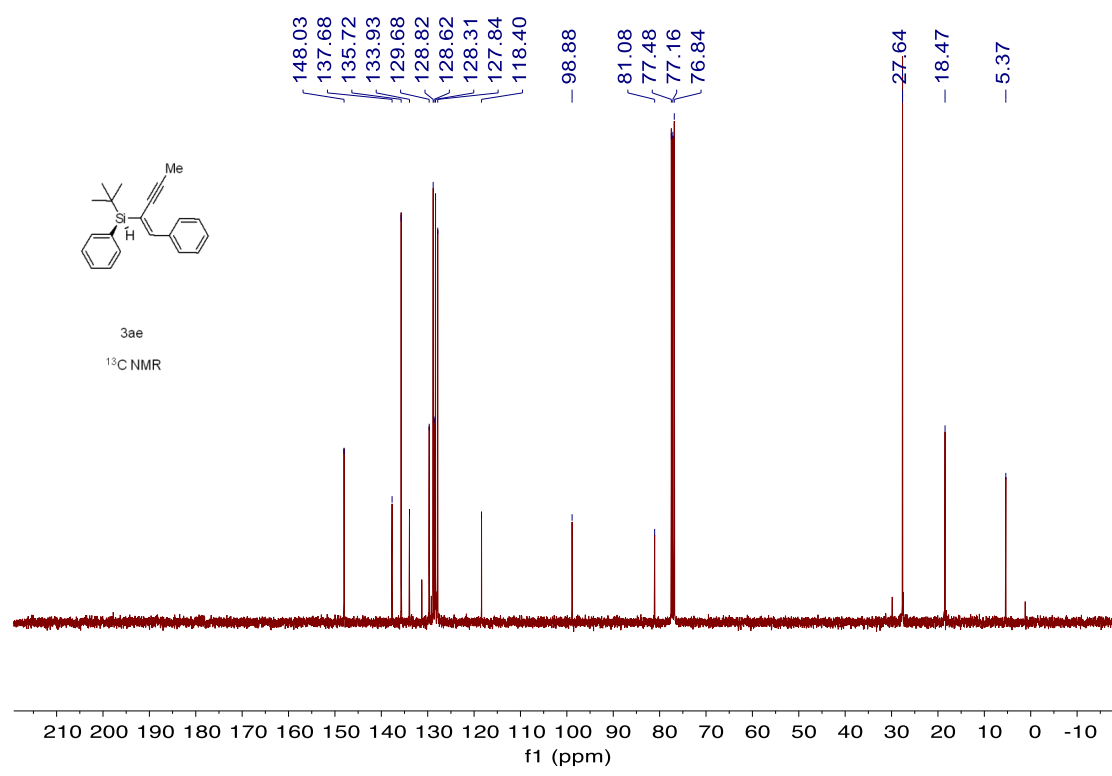
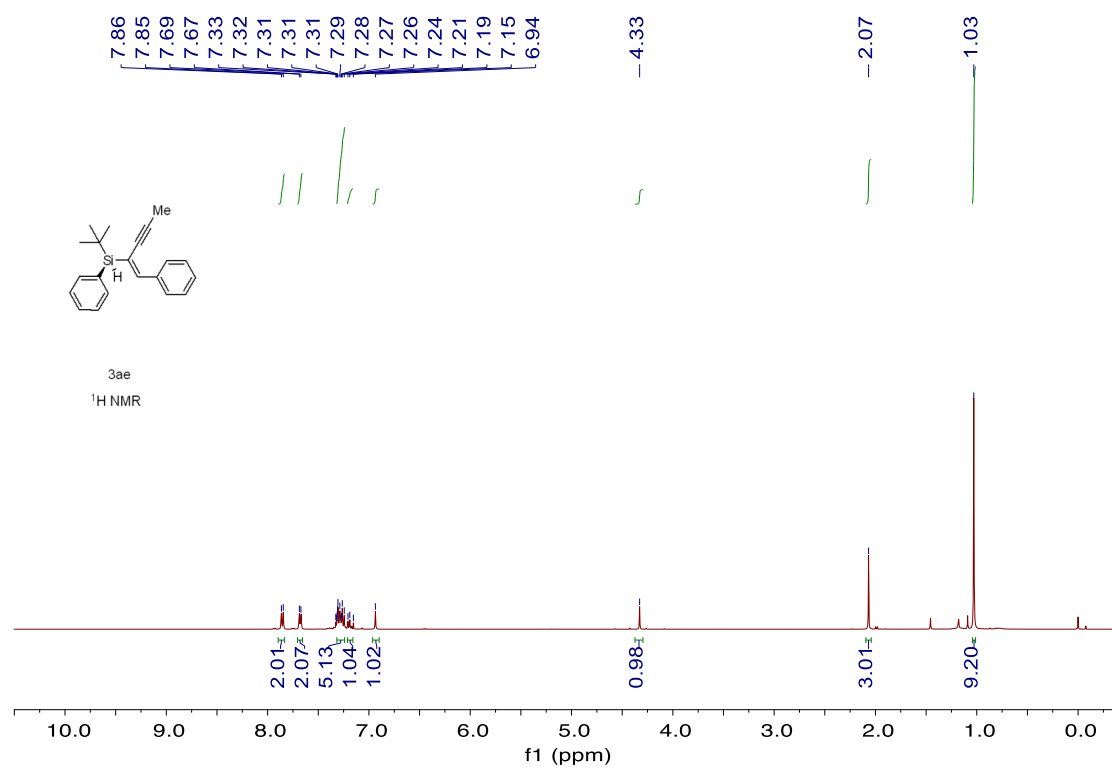


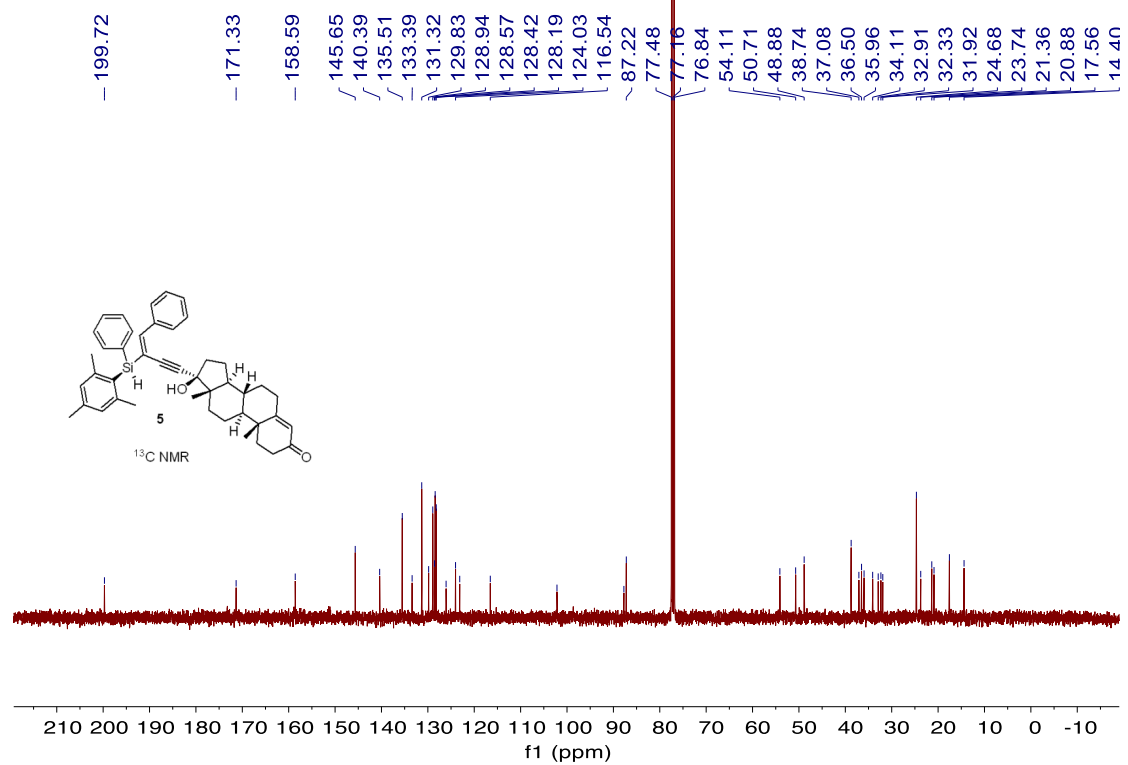
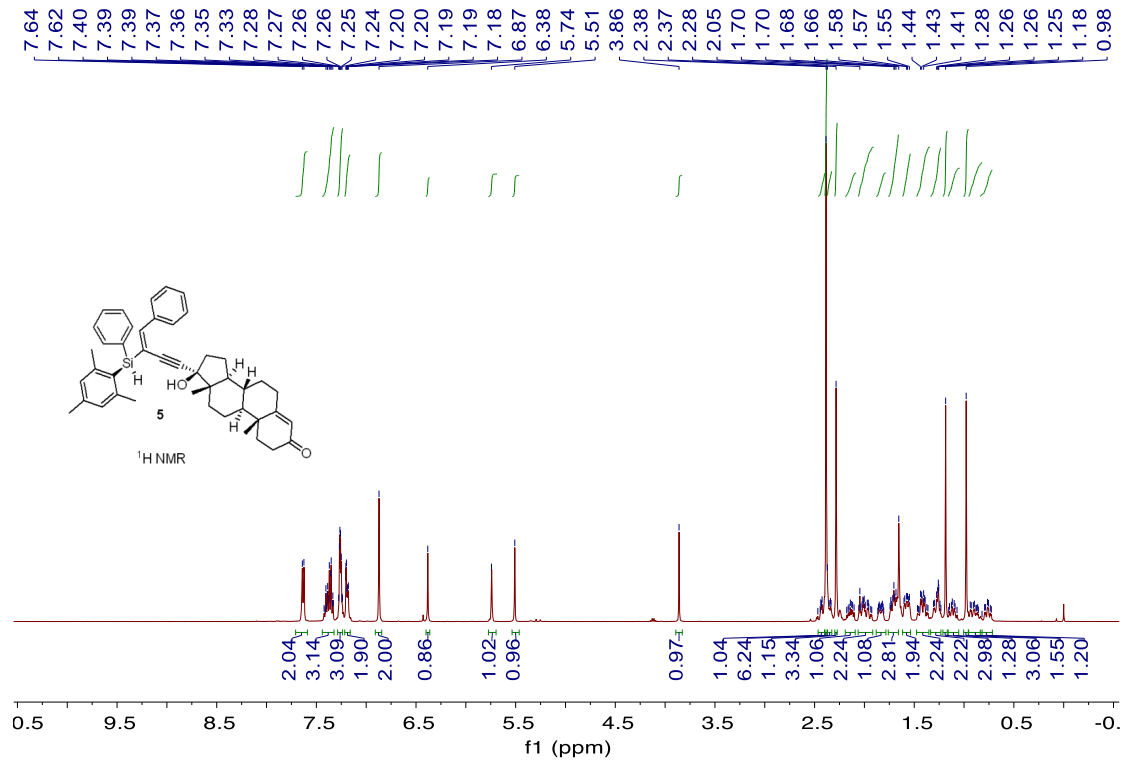


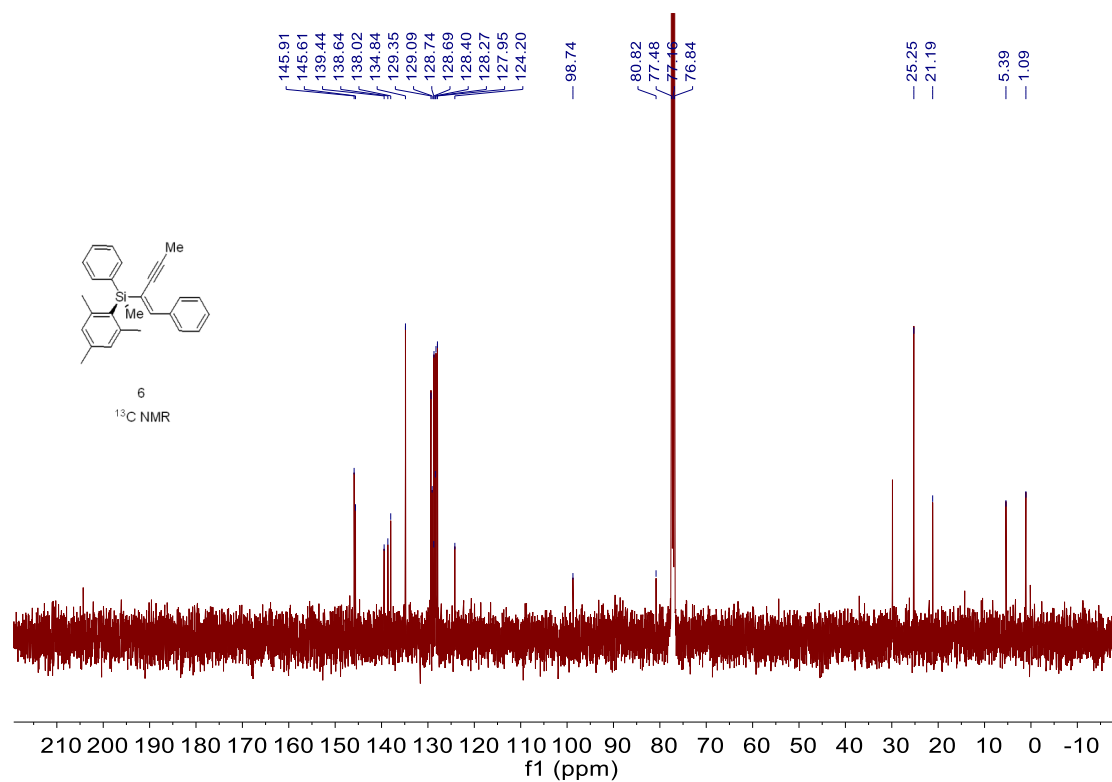
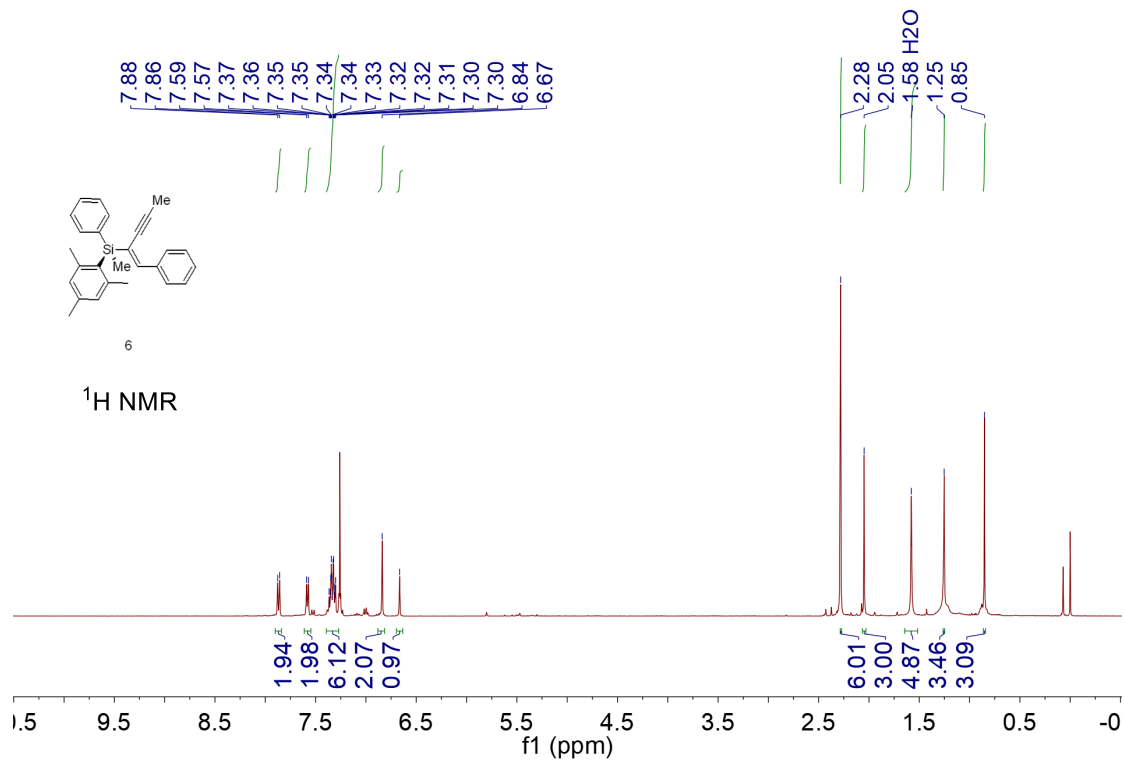


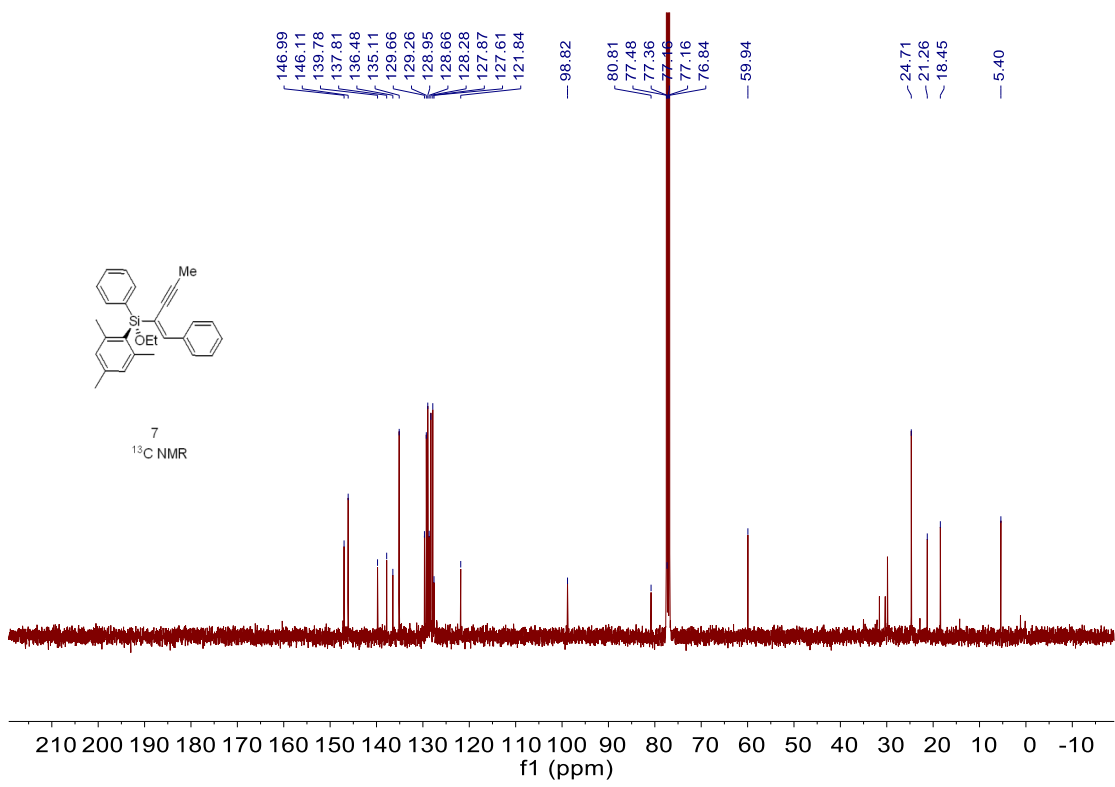
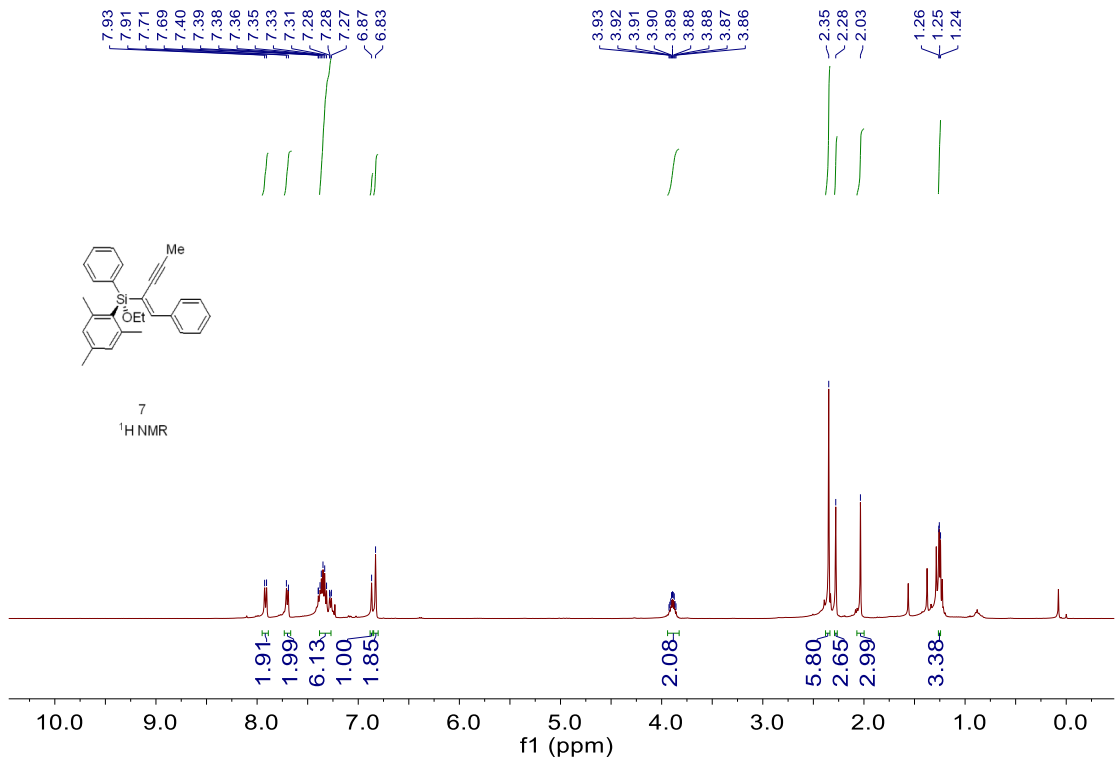


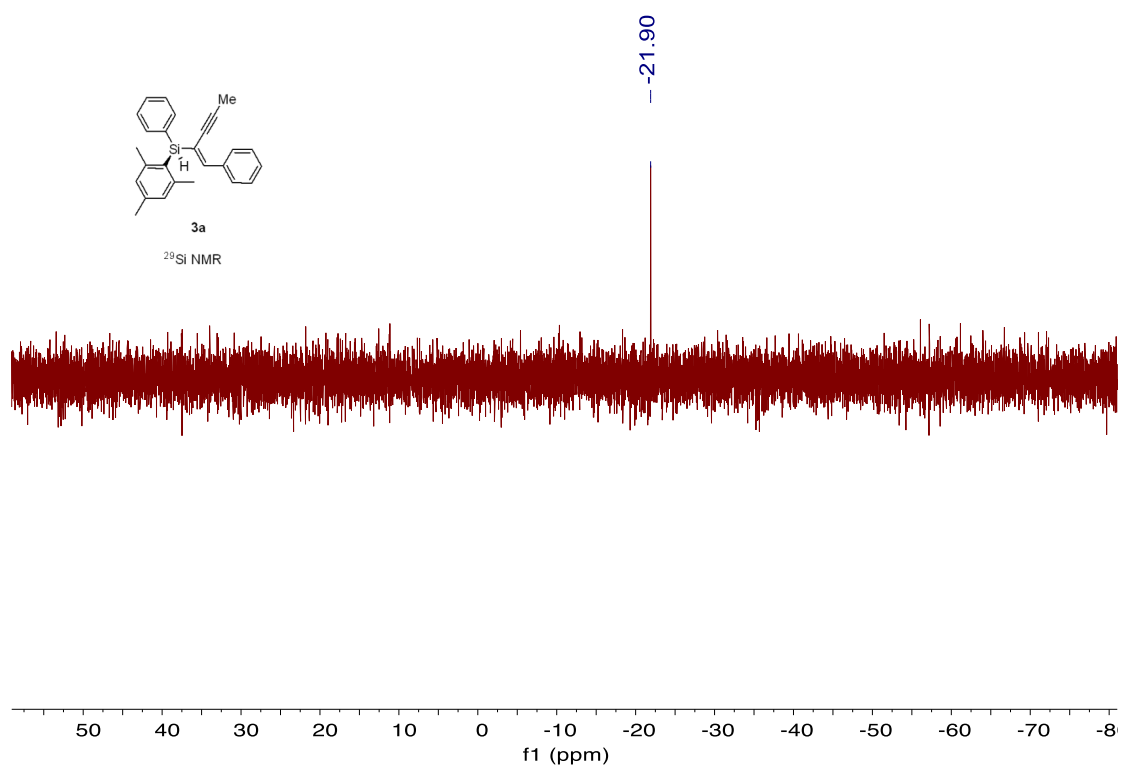
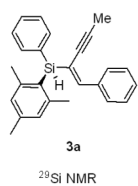


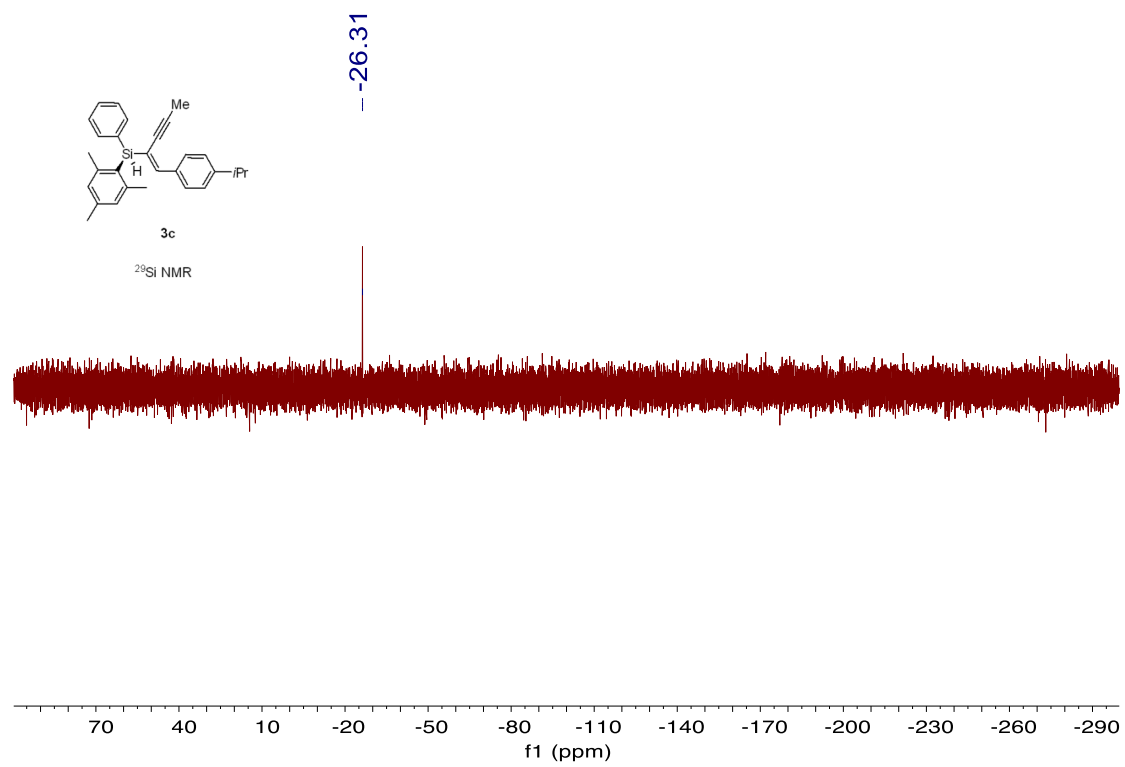




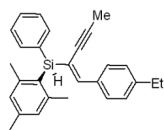






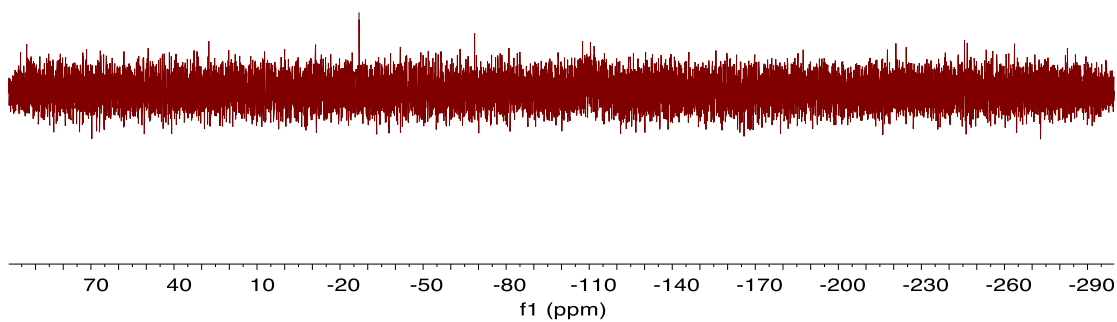


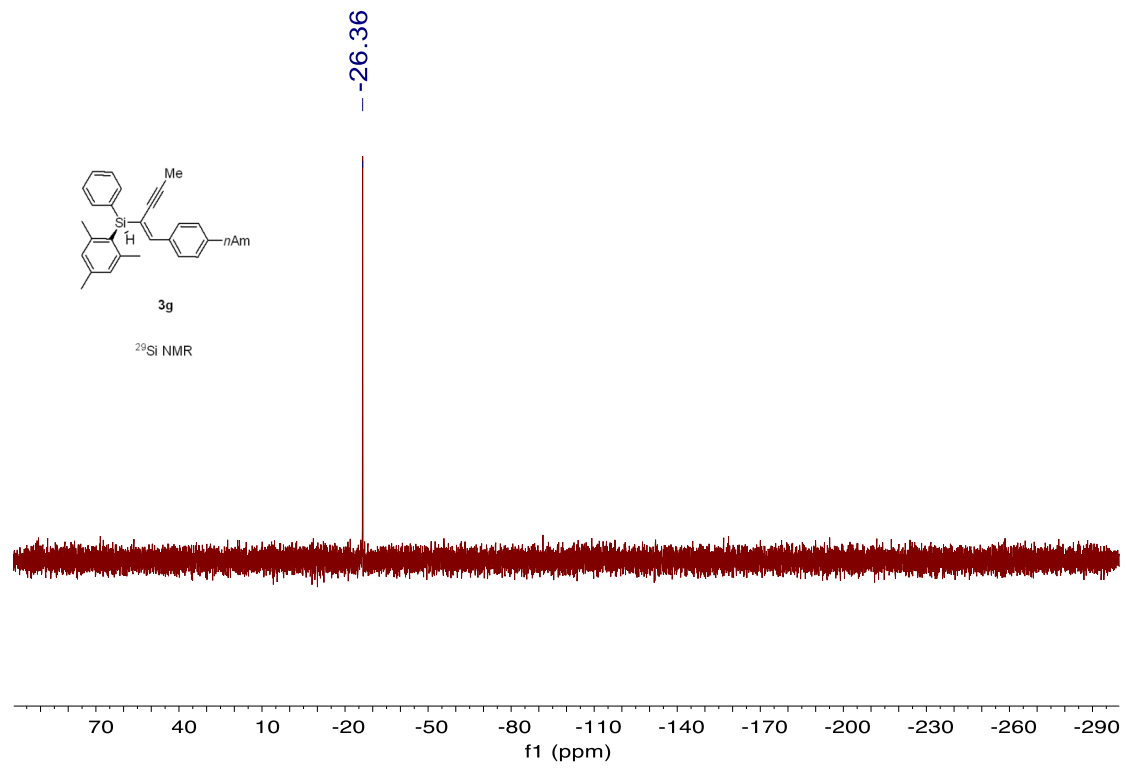
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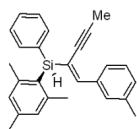


3d

²⁹Si NMR

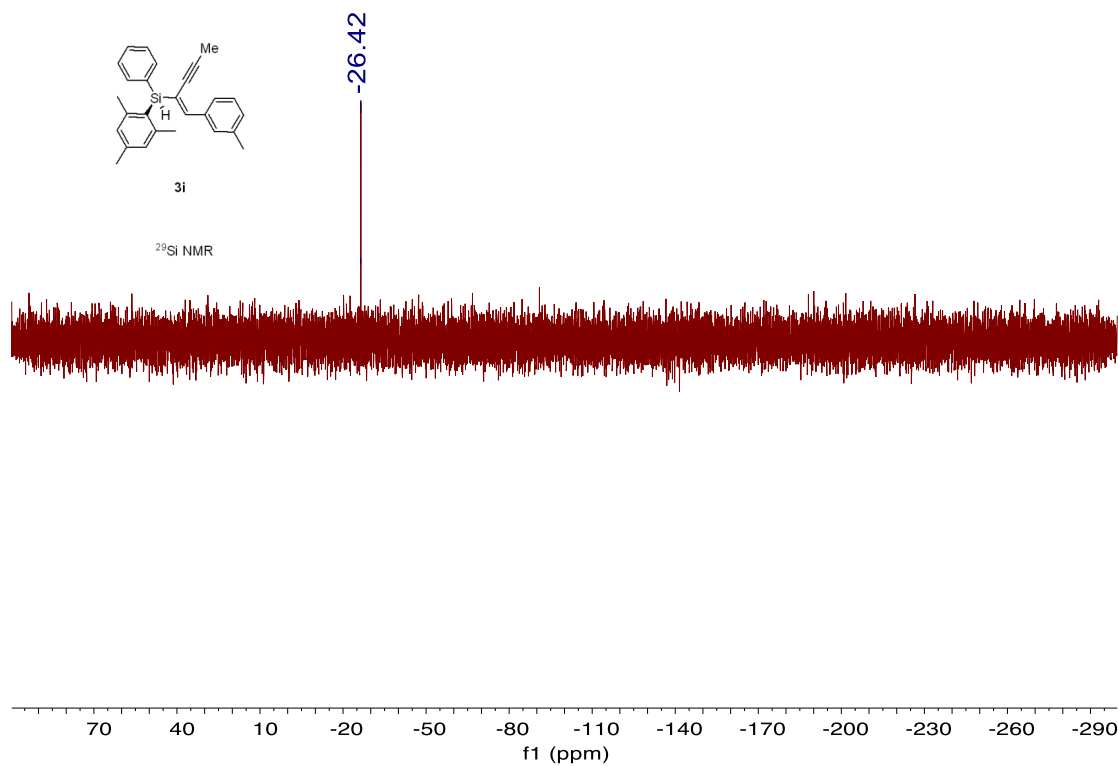


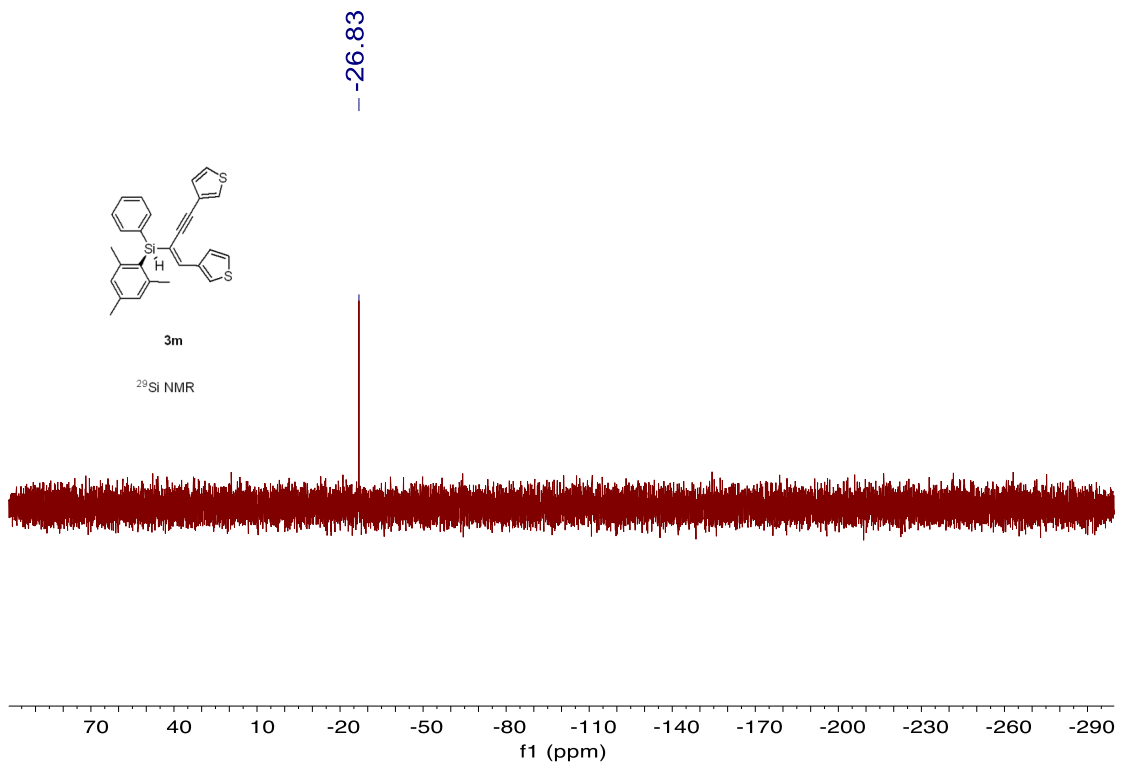


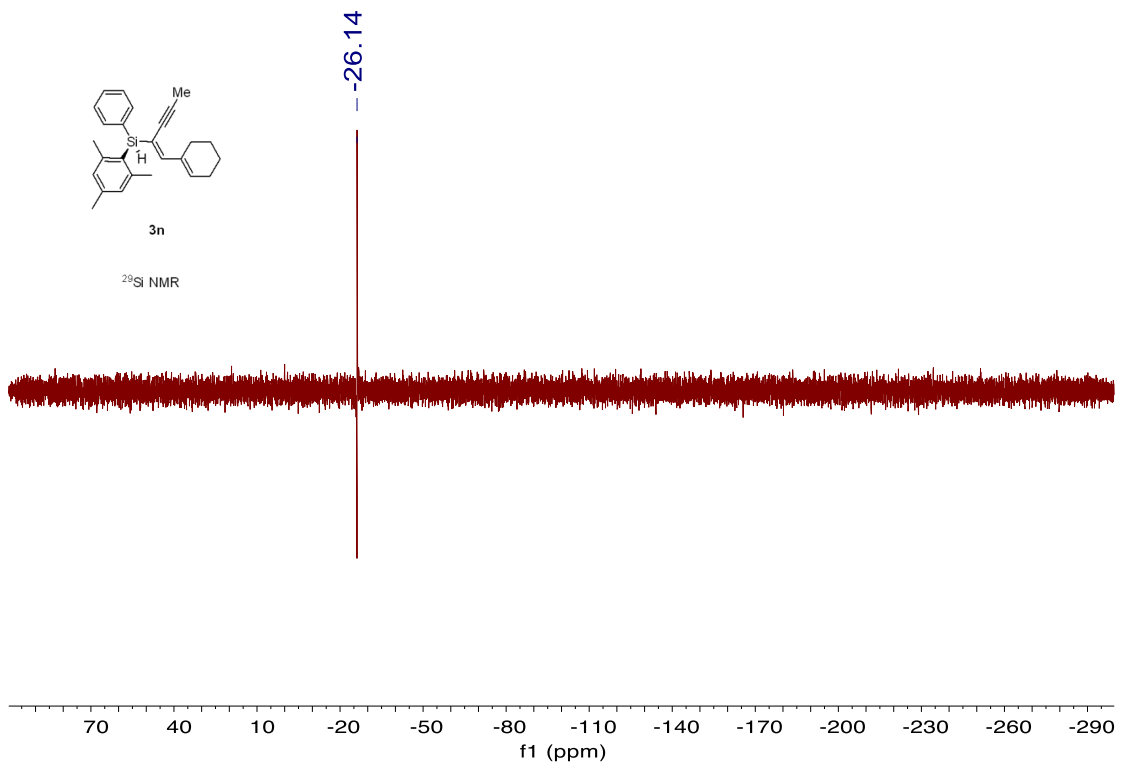


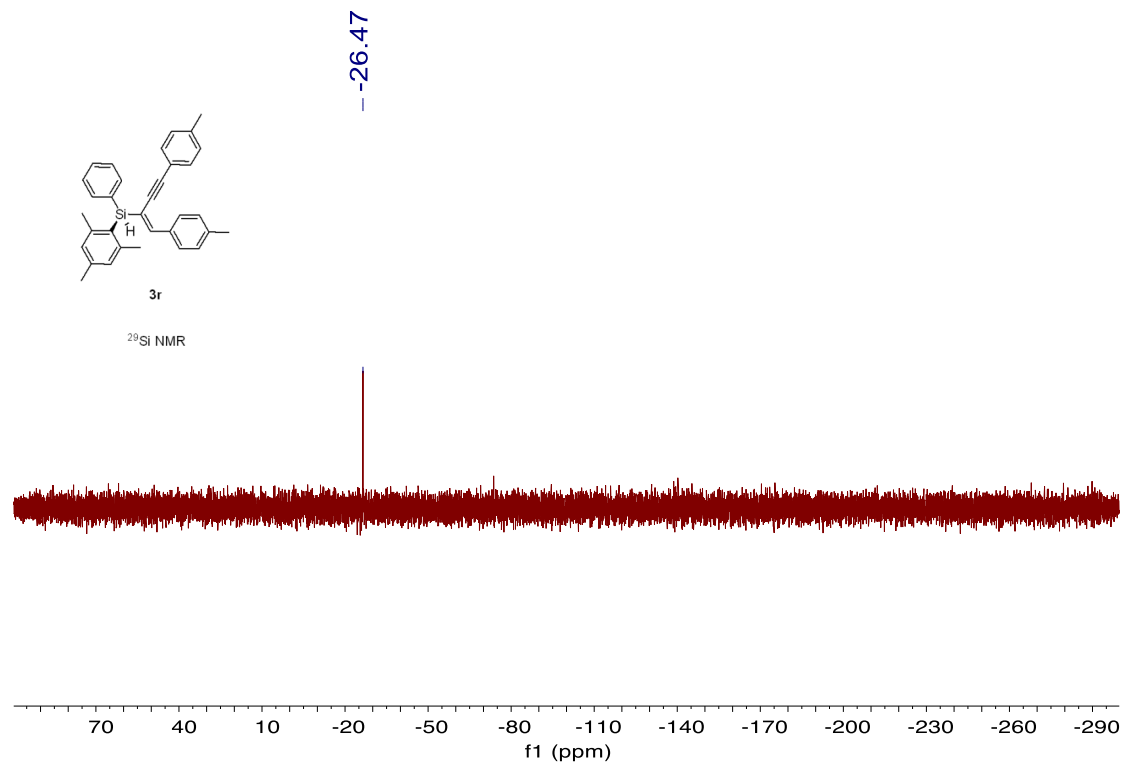
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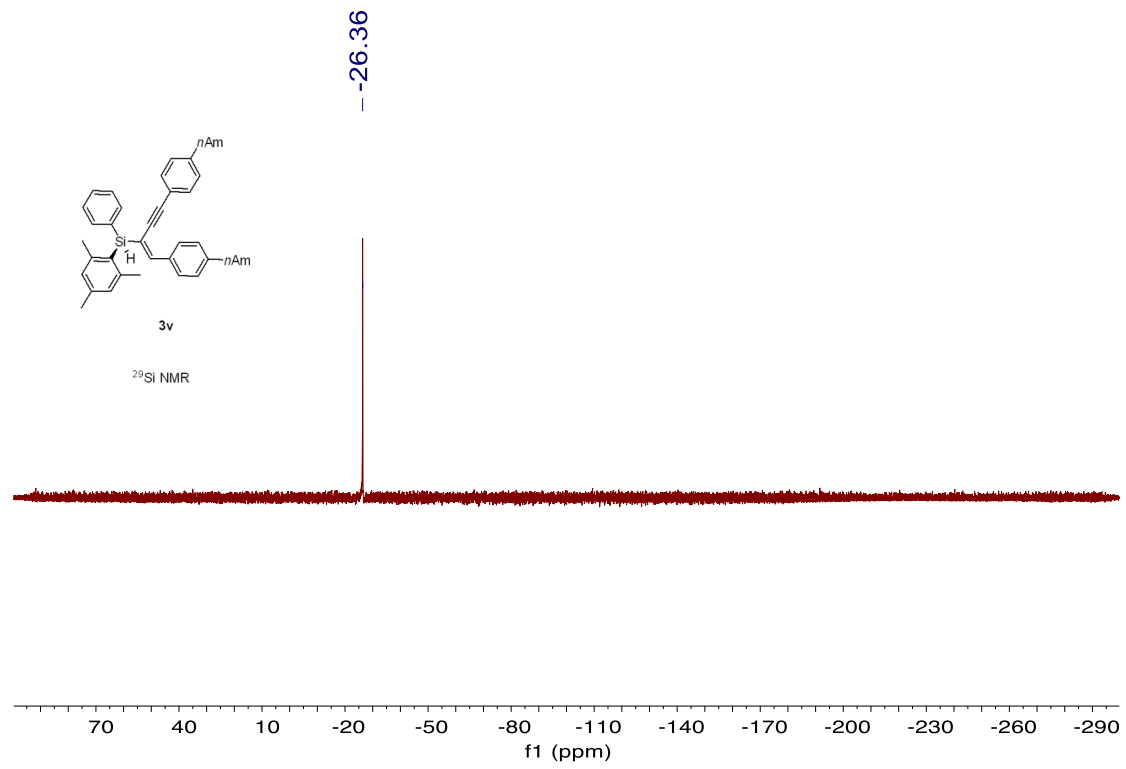
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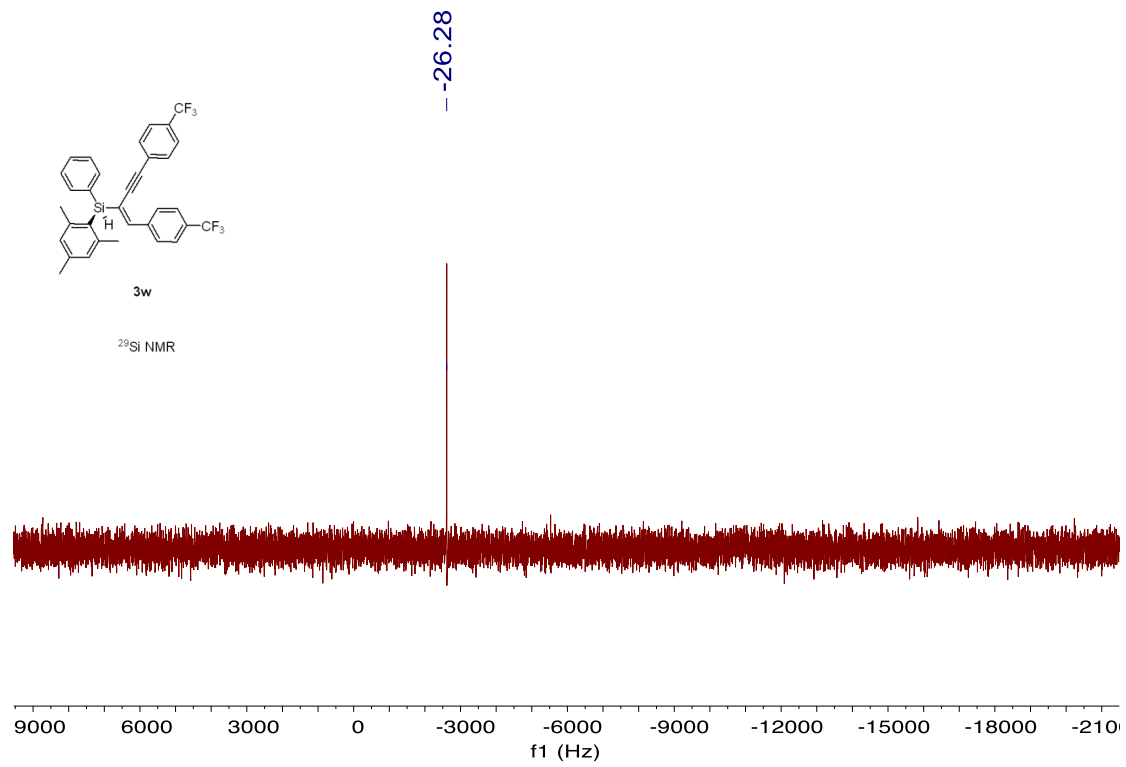


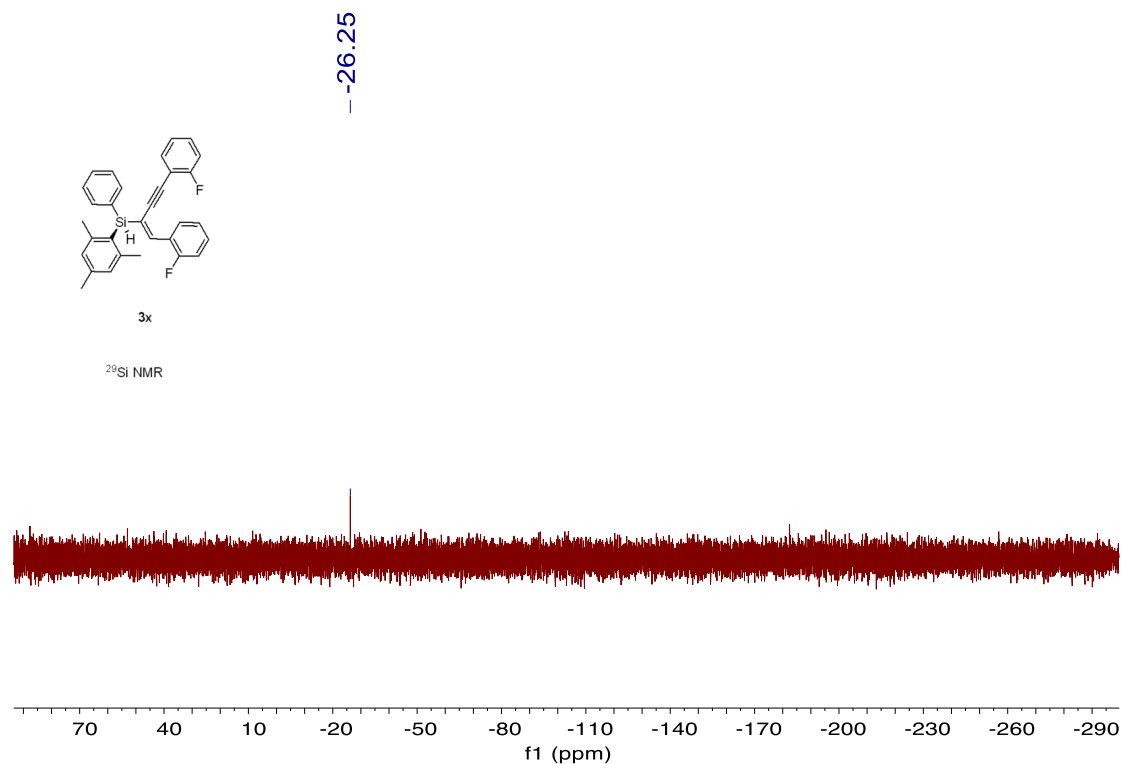












5 References

- [1] Tamm, M.; Jones, PG.; Volbeda, MJ.; Lysenko, S.; Sergej Lysenko, DC. *Angew. Chem. Int. - Ed.*, **2012**, *124*, 6861–6865.
- [2] Beller, M.; Jackstell, R.; Franke, R.; Schneider, C.; Yang, J.; Liu, JW. *Angew. Chem. Int. Ed.*, **2020**, *59*, 9032–9040.
- [3] Ohno, H.; Fujii, N.; Oishi, S.; Naoe, S.; Matsuda, Y. *Chem. Eur. J.*, **2015**, *21*, 1463–1467.
- [4] Yin, SF.; Zhou, YB.; Qiu, RH.; Sun, ML.; Liu, L.; Dong, JY.; Su, LB. *J. Am. Chem. Soc.*, **2016**, *138*, 12348–12355.
- [5] Hirokazu, U.; Takeshi, H.; Ryoichi, T.; Hiroaki, S.; Naoki, H. *Angew. Chem. Int. Ed.*, **2010**, *49*, 7762–7764.
- [6] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (<http://www.cylview.org>)
- [7] Q. Z. Yu. Preparation and application prospect of nano-palladium powder by two-step chemical method. *Precious Metals*, **2010**, *31(02)*, 57-59.