Supplementary information for

Rhodium-catalyzed (*E*)-selective cross-dimerization of terminal alkynes

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General. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for $CDCl_3$ solutions. MS data were obtained by EI or CI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m). The hydroxy complex $[Rh(OH)(cod)]_2$,[S1] iodo complex $[RhI(cod)]_2$[S2] and alkyne **4**[S3] were prepared according to the published methods.

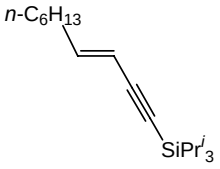
Rhodium-catalyzed reaction of triisopropylsilylacetylene (1) with 1-octyne (2a) (Entry 10 in Table 1): A mixture of $[RhI(cod)]_2$ (0.0075 mmol, 5.1 mg), Xantphos (0.015 mmol, 8.7 mg), **1** (0.50 mmol, 91 mg), **2a** (0.60 mmol, 66 mg) and 1-methylnaphthalene (ca. 50 mg) as internal standard in *o*-xylene (5 mL) was refluxed with stirring for 8 h under N_2, and then the solvent was evaporated to dryness. The residue was purified by silica gel column chromatography using hexane as eluent to afford **3a** as an oil (131 mg, 90% yield).

Rhodium-catalyzed reaction of 1-trimethylsilyloxy-1,1-diphenyl-2-propyne (4) with 1-octyne (2a) (Scheme 2): A mixture of $[RhI(cod)]_2$ (0.0075 mmol, 5.1 mg), Xantphos (0.015 mmol, 8.7 mg), **4** (0.50 mmol, 140 mg), **2a** (0.60 mmol, 66 mg) and 1-methylnaphthalene (ca. 50 mg) as internal standard in *o*-xylene (5 mL) was refluxed with stirring for 12 h under N_2, and then the solvent was evaporated to dryness. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (v/v = 99.5/0.5) as eluent to afford **5** as an oil (116 mg, 60% yield).

Rhodium-catalyzed reaction of 1-trimethylsilyloxy-1,1-diphenyl-2-propyne (4) with 1,6-heptadiyne (9) (Scheme 3): A mixture of $[RhI(cod)]_2$ (0.0075 mmol, 5.1 mg), Xantphos (0.015 mmol, 8.7 mg), **4** (0.50 mmol, 140 mg), **9** (1.0 mmol, 92 mg) and 1-methylnaphthalene (ca. 50 mg) as internal standard in *o*-xylene (5 mL) was refluxed

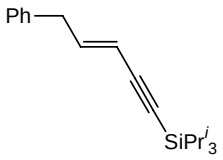
with stirring for 8 h under N_2, and then the solvent was evaporated to dryness. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (v/v = 99.7/0.3) as eluent to afford **10** as an oil (121 mg, 52% yield).

(*E*)-(Dec-3-en-1-ynyl)triisopropylsilane (3a)



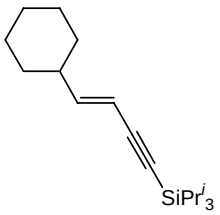
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.08 (m, 21H), 1.19-1.44 (m, 8H), 2.10 (ddt, ^4J = 1.5 Hz, *J* = 7.7 Hz, *J* = 7.0 Hz, 2H), 5.52 (dt, ^4J = 1.5 Hz, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8 Hz, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.34, 14.06, 18.62, 22.57, 28.59, 28.85, 31.66, 33.09, 88.52, 106.10, 109.84, 145.85. HRMS (EI) *m/z* calcd for $C_{19}H_{36}Si$: 292.2586 (M^+); found: 292.2590.

(*E*)-Triisopropyl(5-phenylpent-3-en-1-ynyl)silane (3b)



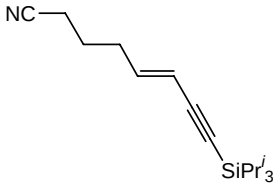
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04-1.09 (m, 21H), 3.43 (dd, ^4J = 1.5 Hz, *J* = 7.0 Hz, 2H), 5.54 (dt, ^4J = 1.5 Hz, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8 Hz, *J* = 7.0 Hz, 1H), 7.15-7.26 (m, 3H), 7.27-7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.32, 18.63, 39.30, 89.74, 105.56, 111.25, 126.42, 128.56, 28.80, 138.80, 143.66. HRMS (EI) *m/z* calcd for $C_{20}H_{30}Si$ (M^+): 298.2117 (M^+); found: 298.2113.

(*E*)-(4-Cyclohexylbut-3-en-1-ynyl)triisopropylsilane (3c)



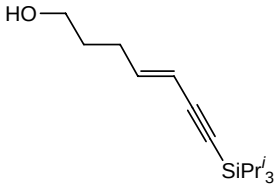
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02-1.32(m, 27H), 1.60-1.76 (m, 4H), 1.97-2.07 (m, 1H), 5.48 (dt, ^4J = 1.5 Hz, *J* = 16.1 Hz, 1H), 6.15 (dd, *J* = 7.0 Hz, *J* = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.35, 18.64, 25.86, 26.04, 32.18, 41.21, 88.74, 106.33, 107.61, 151.01. HRMS (EI) *m/z* calcd for $C_{19}H_{34}Si$ (M^+): 290.2430; found: 290.2438.

(*E*)-8-(Triisopropylsilanyl)oct-5-en-7-ynenitrile (3d)



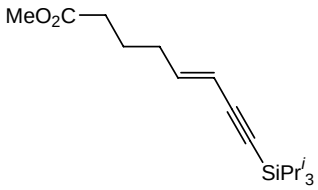
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03-1.10 (m, 21H), 1.78 (tt, *J* = 7.3 Hz, 2H), 2.28 (ddt, ^4J = 1.5 Hz, *J* = 7.3 Hz, *J* = 7.3 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 5.61 (dt, ^4J = 1.5 Hz, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8 Hz, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.27, 16.48, 18.60, 24.40, 31.58, 90.16, 105.03, 112.30, 119.21, 141.96. HRMS (CI) *m/z* calcd for $C_{17}H_{30}NSi$ (M+H): 276.2148; found: 276.2141.

(*E*)-7-(Triisopropylsilanyl)hept-4-en-6-yn-1-ol (3e)



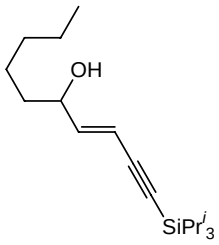
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05-1.10 (m, 21H), 1.63-1.72 (m, 2H), 2.16-2.24 (m, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 5.58 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8Hz, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.31, 18.62, 29.31, 31.50, 62.16, 89.10, 105.71, 110.61, 144.62. HRMS (EI) *m/z* calcd for $C_{16}H_{30}OSi$ (M^+): 266.2066; found: 266.2075.

(*E*)-8-(Triisopropylsilanyl)oct-5-en-7-ynoic acid methyl ester (3f)



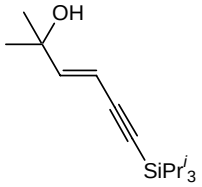
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04-1.09 (m, 21H), 1.74 (tt, *J* = 7.3 Hz, 2H), 2.11-2.18 (m, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 3.66 (s, 3H), 5.54 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 7.0 Hz , *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.32, 18.59, 23.82, 32.26, 33.28, 51.47, 89.23, 105.63, 111.04, 143.97, 173.68. HRMS (EI) *m/z* calcd for $C_{18}H_{32}O_2Si$ (M^+): 308.2172; found: 308.2170.

(*E*)-1-(Triisopropylsilanyl)dec-3-en-1-yn-5-ol (3g)



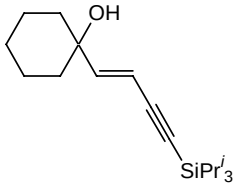
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.06-1.09 (m, 21H), 1.25-1.36 (m, 6H), 1.49-1.60 (m, 2H), 4.14 (dt, *J* = 6.2 Hz, *J* = 5.9 Hz, 1H), 5.75 (dd, ^4J = 1.5 Hz, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 6.2 Hz, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.28, 14.01, 18.60, 22.55, 24.97, 31.70, 36.90, 72.37, 91.44, 104.94, 110.21, 146.40. HRMS (CI) *m/z* calcd for $C_{19}H_{37}OSi$ (M+H): 309.2614; found: 309.2609.

(*E*)-2-Methyl-6-(triisopropylsilanyl)hex-3-en-5-yn-2-ol (3h)



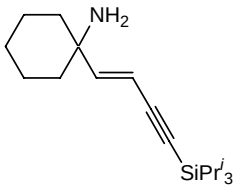
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04-1.10 (m, 21H), 1.33 (s, 6H), 5.77 (d, *J* = 16.1 Hz, 1H), 6.30 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.32, 18.61, 29.44, 70.94, 91.20, 105.17, 107.39, 151.04. HRMS (EI) *m/z* calcd for $C_{16}H_{30}OSi$ (M^+): 266.2066; found: 266.2062.

(*E*)-1-(4-Triisopropylsilanylbut-1-en-3-ynyl)cyclohexanol (3i)



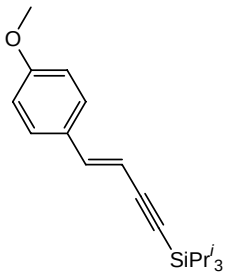
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05-1.09 (m, 21H), 1.23-1.32 (m, 2H), 1.48-1.69 (m, 8H), 5.81 (d, *J* = 16.1 Hz, 1H), 6.30 (d, *J* = 16.1, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.28, 18.59, 21.79, 25.32, 37.44, 71.76, 91.12, 105.42, 107.79, 151.07. HRMS (EI) *m/z* calcd for $C_{19}H_{34}OSi$ (M^+): 306.2379; found: 306.2375.

(*E*)-1-(4-Triisopropylsilanylbut-1-en-3-ynyl)cyclohexylamine (3j)



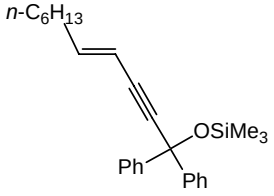
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02-1.11 (m, 23H), 1.30-1.64 (m, 8H), 5.69 (d, *J* = 16.1 Hz, 1H), 6.23 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.34, 18.63, 22.05, 25.66, 38.27, 52.68, 90.37, 105.91, 107.03, 153.37. HRMS (EI) *m/z* calcd for $C_{19}H_{35}NSi$ (M^+): 305.2539; found: 305.2533.

(*E*)-Triisopropyl-[4-(4-methoxyphenyl)but-3-en-1-ynyl]silane (3k)



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09-1.13 (m, 21H), 3.79 (s, 3H), 6.07 (d, *J* = 16.1 Hz, 1H), 6.82-6.87 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 16.1 Hz, 1H), 7.28-7.33 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.40, 18.69, 55.28, 92.24, 106.06, 106.71, 114.14, 127.58, 129.14, 141.64, 160.11. HRMS (EI) *m/z* calcd for $C_{20}H_{30}OSi$ (M^+): 314.2066; found: 314.2070.

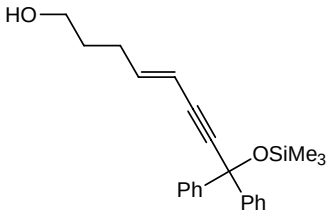
(*E*)-(1,1-Diphenylundec-4-en-2-ynyloxy)trimethylsilane (5)



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.24-1.34 (m, 6H), 1.36-1.43 (m, 2H), 2.13 (dt, ^4J = 1.5 Hz,

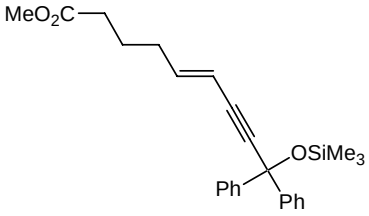
J = 7.3 Hz, 2H), 5.60 (dt, ^4J = 1.5 Hz, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 7.3 Hz, *J* = 15.8 Hz, 1H), 7.16-7.21 (m, 2H), 7.23-7.29 (m, 4H), 7.53-7.57 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.51, 14.08, 22.59, 28.62, 28.81, 31.65, 33.17, 75.92, 87.17, 90.34, 109.05, 126.07, 127.05, 127.92, 145.51, 146.95. HRMS (EI) *m/z* calcd for $C_{26}H_{34}OSi$ (M^+): 390.2379; found: 390.2366.

(*E*)-8,8-Diphenyl-8-trimethylsilanyloxyoct-4-en-6-yn-1-ol (6)



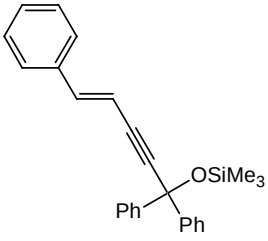
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 2.23-2.30 (m, 2H), 2.27 (ddt, ^4J = 1.5 Hz, *J* = 7.0 Hz, *J* = 6.6 Hz, 2H), 3.67 (t, *J* = 6.6 Hz, 2H), 5.69 (dt, ^4J = 1.5 Hz, *J* = 16.1 Hz, 1H), 6.23 (dt, *J* = 16.1 Hz, *J* = 7.0 Hz, 1H), 7.20-7.25 (m, 2H), 7.26-7.33 (m, 4H), 7.56-7,61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.55, 29.42, 31.54, 62.08, 75.94, 86.88, 90.77, 109.79, 126.08, 127.12, 127.96, 144.34, 146.87. HRMS (EI) *m/z* calcd for $C_{23}H_{28}O_2Si$ (M^+): 364.1859; found: 364.1867.

(*E*)-9,9-Diphenyl-9-(trimethylsilanyloxy)non-5-en-7-ynoic acid methyl ester (7)



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.74-1.82 (m, 2H), 2.17-2.24 (m, 2H), 2.35 (t, *J* = 7.7 Hz, 2H), 3.69 (s, 3H), 5.67 (dt, ^4J = 1.5 Hz, *J* = 16.1 Hz, 1H), 6.20 (dt, *J* = 7.0 Hz, *J* = 16.1 Hz, 1H), 7.19-7.24 (m, 2H), 7.27-7.32 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.48, 23.84, 32.34, 33.23, 51.49, 75.90, 86.75, 90.89, 110.19, 126.04, 127.06, 127.90, 143.66, 146.81, 173.64. HRMS (EI) *m/z* calcd for $C_{25}H_{30}O_3Si$ (M^+): 406.1964; found: 406.1956.

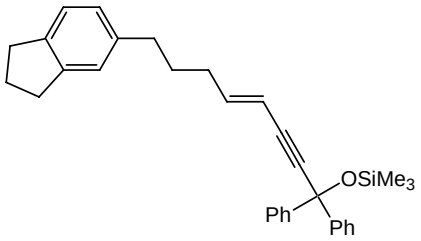
(*E*)-Trimethyl-(1,1,5-triphenylpent-4-en-2-ynyloxy)silane (8)



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 6.31 (d, *J* = 16.1 Hz, 1H), 7.02 (d, *J* = 16.1 Hz, 1H), 7.19-7.24 (m, 2H), 7.26-7.36 (m, 7H), 7.39-7.42 (m, 2H), 7.57-7.61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.55, 76.04, 87.43, 94.22, 107.61, 126.07, 126.32, 127.16, 127.98, 128.73, 128.76, 136.07, 141.70, 146.71. HRMS (EI) *m/z* calcd for

$C_{26}H_{26}OSi$ (M^+): 382.1753; found: 382.1759.

(8-Indan-5-yl-1,1-diphenyloct-4-en-2-ynyloxy)trimethylsilane (10)



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.72-1.83 (m, 2H), 2.05-2.14 (m, 2H), 2.18-2.56 (m, 2H), 2.64 (t, J = 7.7 Hz, 2H), 2.87-2.95 (m, 4H), 5.66 (dt, ^4J = 1.5 Hz, J = 15.8 Hz, 1H), 6.27 (dt, J = 7.0 Hz, J = 15.8 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 7.09 (s, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.20-7.34 (m, 6H), 7.57-7.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.49, 25.51, 30.62, 32.47, 32.63, 32.81, 35.12, 75.93, 87.06, 90.58, 109.49, 124.15, 124.43, 126.05, 126.23, 127.03, 127.90, 139.83, 141.67, 144.41, 144.93, 146.91. HRMS (EI) *m/z* calcd for $C_{32}H_{36}OSi$ (M^+): 464.2535; found: 464.2537.

The ^{1}H and ^{13}C NMR spectra of **3a**, **5** and **10** are included as the representative (*E*)-enyne products.

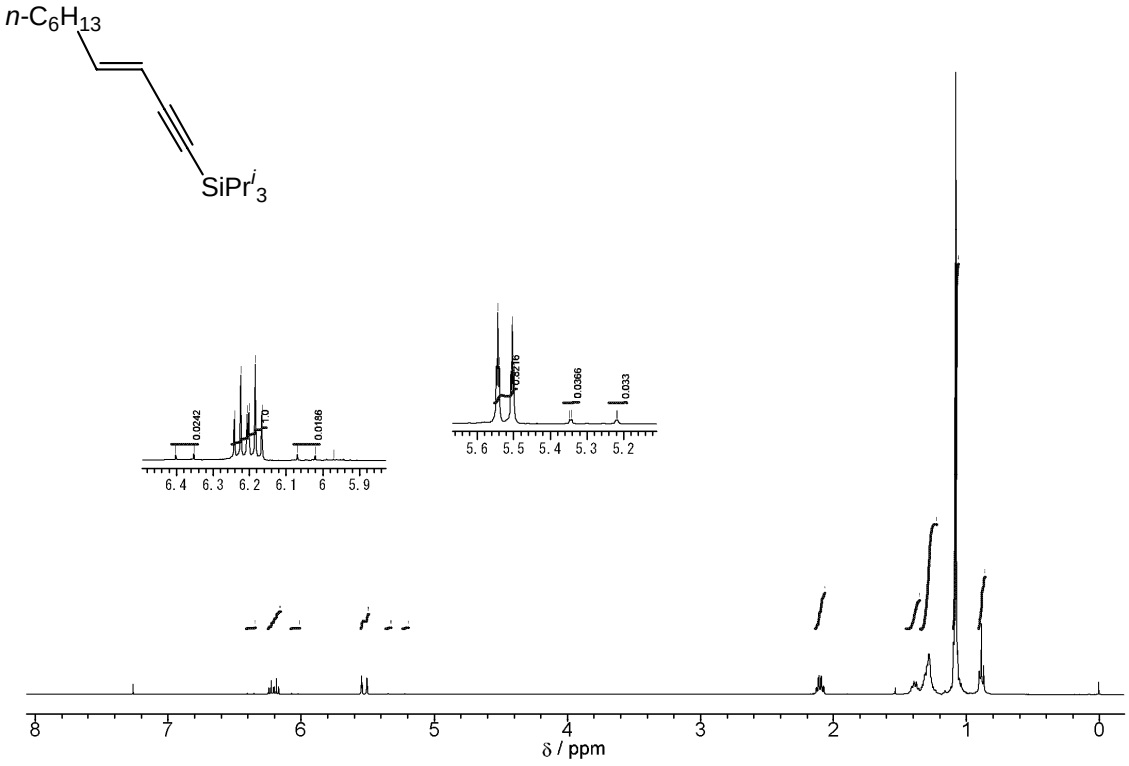
References

S1) R. Uson, L. A. Oro and J. A. Cabwza, *Inorg. Synth.*, 1985, **23**, 126.

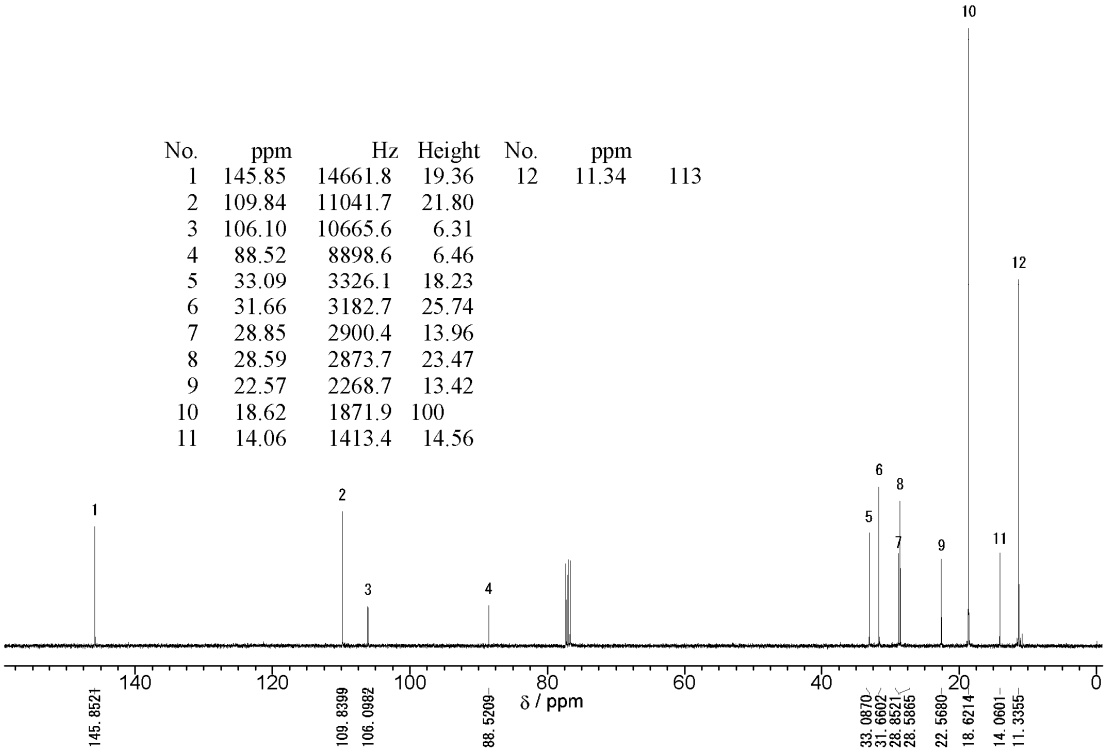
S2) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

S3) J. R. Granjja, L. Castedo and A. Mourifio, *J. Org. Chem.*, 1993, **58**, 124.

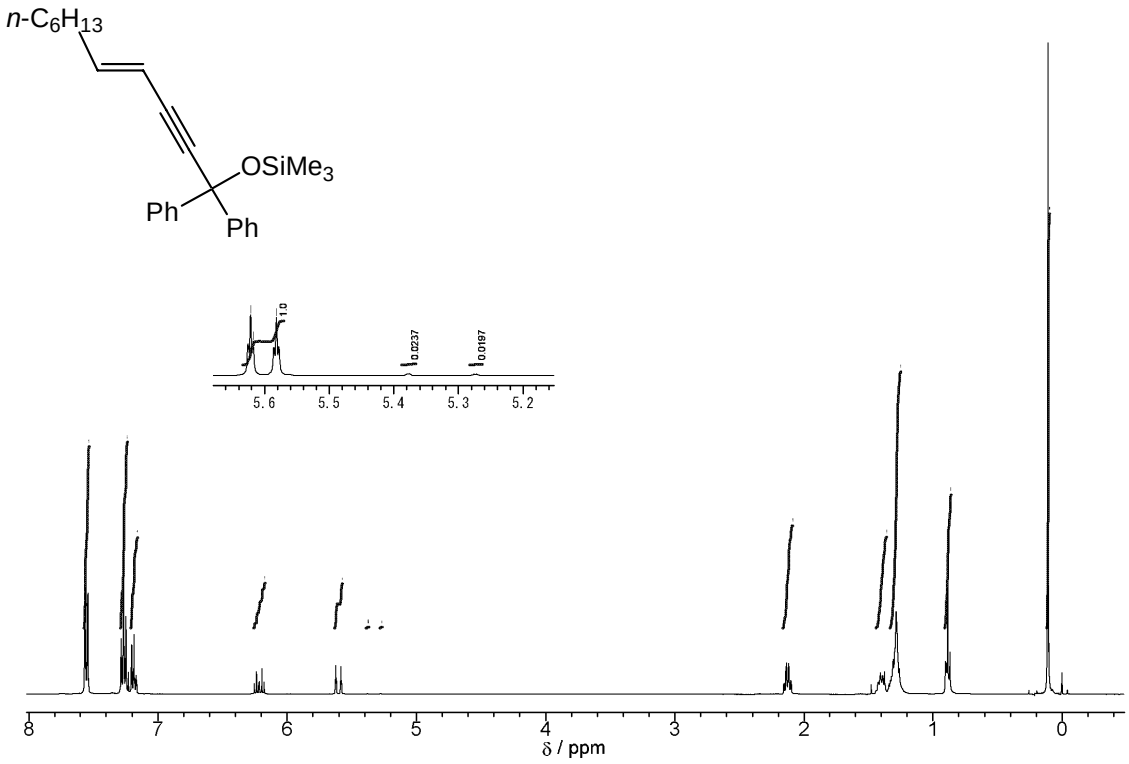
[^{1}H and ^{13}C NMR Spectra of **3a**]

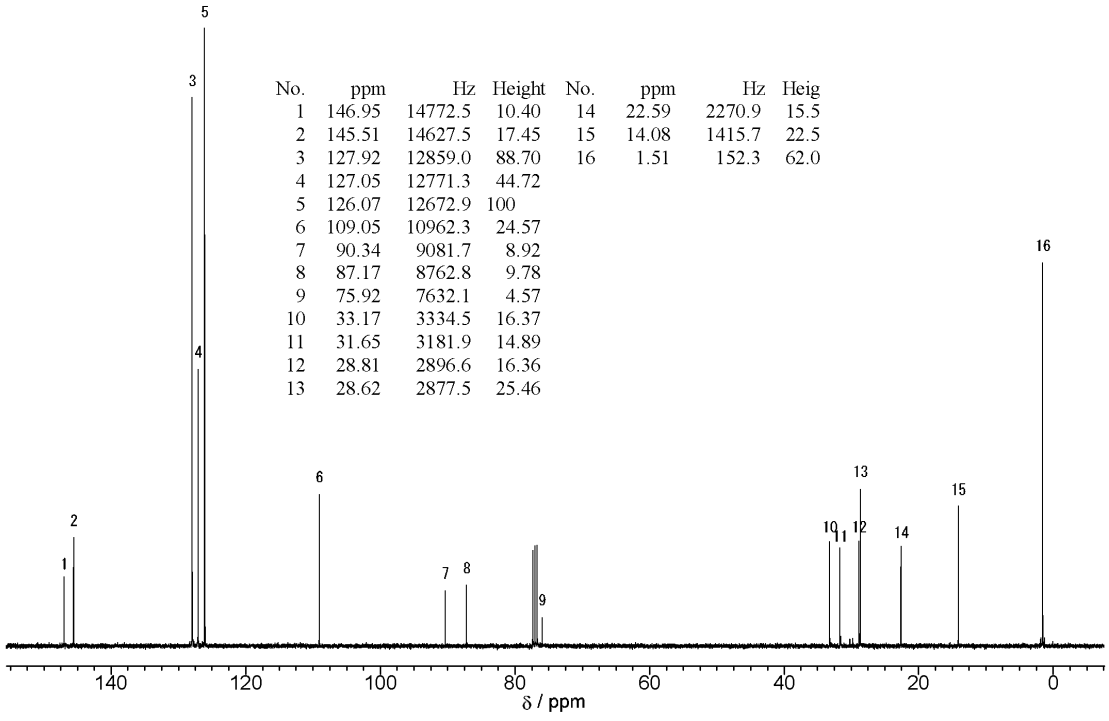


No.	ppm	Hz	Height	No.	ppm	
1	145.85	14661.8	19.36	12	11.34	113
2	109.84	11041.7	21.80			
3	106.10	10665.6	6.31			
4	88.52	8898.6	6.46			
5	33.09	3326.1	18.23			
6	31.66	3182.7	25.74			
7	28.85	2900.4	13.96			
8	28.59	2873.7	23.47			
9	22.57	2268.7	13.42			
10	18.62	1871.9	100			
11	14.06	1413.4	14.56			



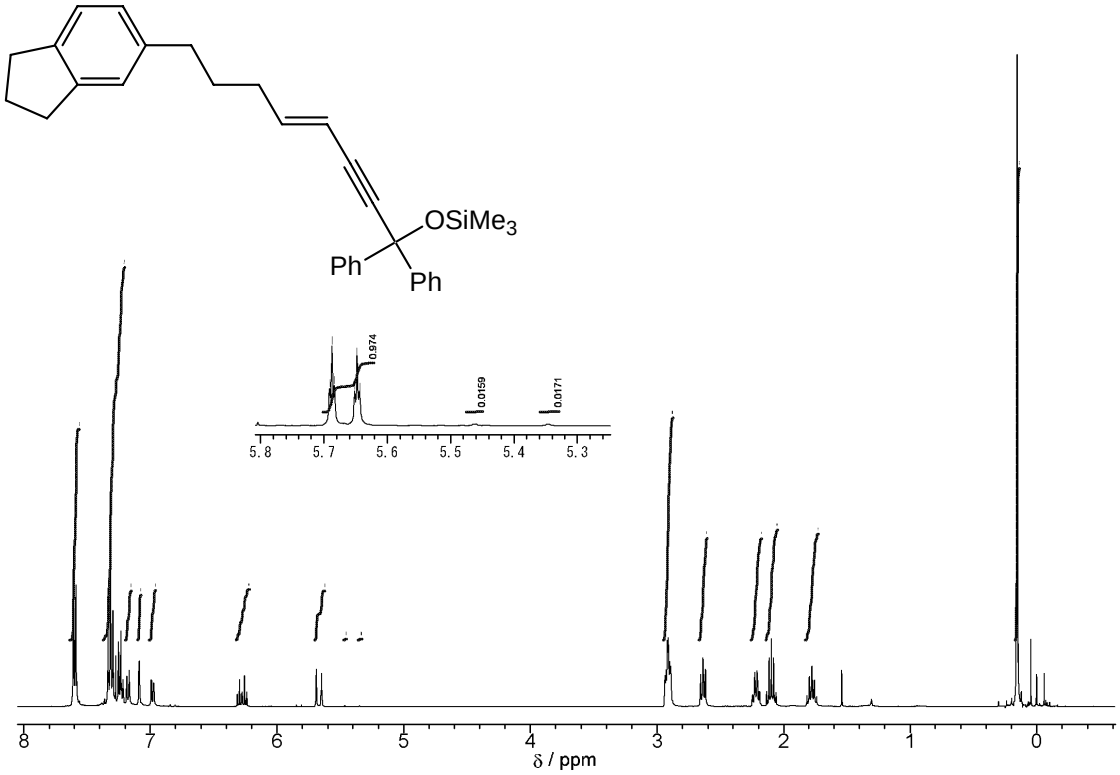
[^{1}H and ^{13}C NMR Spectra of **5**]

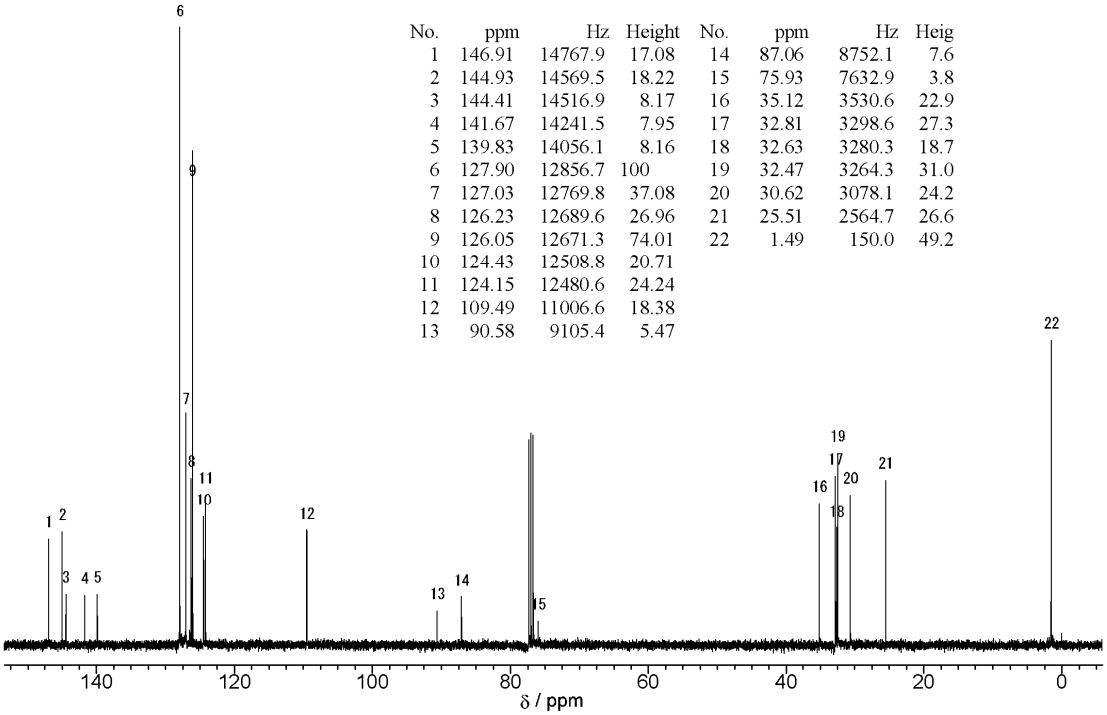




No.	ppm	Hz	Height	No.	ppm	Hz	Heig
1	146.95	14772.5	10.40	14	22.59	2270.9	15.5
2	145.51	14627.5	17.45	15	14.08	1415.7	22.5
3	127.92	12859.0	88.70	16	1.51	152.3	62.0
4	127.05	12771.3	44.72				
5	126.07	12672.9	100				
6	109.05	10962.3	24.57				
7	90.34	9081.7	8.92				
8	87.17	8762.8	9.78				
9	75.92	7632.1	4.57				
10	33.17	3334.5	16.37				
11	31.65	3181.9	14.89				
12	28.81	2896.6	16.36				
13	28.62	2877.5	25.46				

[^{1}H and ^{13}C NMR Spectra of **10**]





No.	ppm	Hz	Height	No.	ppm	Hz	Heig
1	146.91	14767.9	17.08	14	87.06	8752.1	7.6
2	144.93	14569.5	18.22	15	75.93	7632.9	3.8
3	144.41	14516.9	8.17	16	35.12	3530.6	22.9
4	141.67	14241.5	7.95	17	32.81	3298.6	27.3
5	139.83	14056.1	8.16	18	32.63	3280.3	18.7
6	127.90	12856.7	100	19	32.47	3264.3	31.0
7	127.03	12769.8	37.08	20	30.62	3078.1	24.2
8	126.23	12689.6	26.96	21	25.51	2564.7	26.6
9	126.05	12671.3	74.01	22	1.49	150.0	49.2
10	124.43	12508.8	20.71				
11	124.15	12480.6	24.24				
12	109.49	11006.6	18.38				
13	90.58	9105.4	5.47				