

Supporting Information

Synthesis of Conjugated Triynes via Alkyne Metathesis

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Table of contents

I- General.....	3
II- Reagents.....	4
III- Synthesis of diyne substrates.....	5
Synthesis of (<i>E</i>)-(4-chlorobut-3-en-1-yn-1-yl)-triisopropylsilane (12a).....	5
Synthesis of Triisopropyl(penta-1,3-diynyl)silane (13a).....	6
Synthesis of (<i>E</i>)-(4-chlorobut-3-en-1-yn-1-yl)triethylsilane (12b).....	6
Synthesis of triethyl(penta-1,3-diyn-1-yl)silane (13b).....	6
Synthesis of (<i>E</i>)-(4-chlorobut-3-en-1-yn-1-yl)triphenylsilane (12c).....	7
Synthesis of (penta-1,3-diyn-1-yl)triphenylsilane (13c).....	7
Synthesis of (<i>E</i>)-(3-chloroprop-2-ene-1,1,1-triyl)tribenzene (12d).....	8
Synthesis of hexa-2,4-diyne-1,1,1-triyltribenzene (13d).....	8
Synthesis of (<i>E</i>)-(4-chlorobut-3-en-1-yn-1-yl)-1,3,5-trimethylbenzene (12e).....	8
Synthesis of 1,3,5-trimethyl-2-(penta-1,3-diyn-1-yl)benzene (13e).....	9
IV- Mo-catalyzed self-metathesis of diynes.....	9
Self-metathesis of TIPS-diyne 13a (Table 1- Entries 1-6).....	11
Self-metathesis of TMS-diyne 13f (Table 1- Entry 7).....	17
Self-metathesis of TES-diyne 13b (Table 1- Entry 8).....	20
Self-metathesis of Ph ₃ Si-diyne 13c (Table 1, Entry 9).....	23
Synthesis of 1,1,1,8,8,8-hexaphenylocta-2,4,6-triyne (16) (Scheme 2, a).....	26
Synthesis of 1,6-dimesitylhexa-1,3,5-triyne (17) (Scheme 2, b).....	27
V- Mo-catalyzed cross-metathesis of diynes.....	30

Cross metathesis of triisopropyl(penta-1,3-diyn-1-yl)silane (13a) and 1,3,5-trimethyl-2-(penta-1,3-diyn-1-yl)benzene (13e) (Scheme 3, c)	30
Cross metathesis of triisopropyl(penta-1,3-diyn-1-yl)silane (13a) and hexa-2,4-diyne-1,1,1-triyltribenzene (13d) (Scheme 3, d).....	32
Cross metathesis of 1,3,5-trimethyl-2-(penta-1,3-diyn-1-yl)benzene (13e) and hexa-2,4-diyne-1,1,1-triyltribenzene (13d) (Scheme 3, e).....	33
VI- Stability study of 16 and 14a toward the Mo-benzylidyne catalyst Cat-2	34
Stability study of 16	34
Stability study of 14a	34
VII- Post-functionalization of dissymmetrical triyne 22	36
VIII- NMR spectra	37
IX- X-Ray Crystallographic data.....	52
X-ray structure of triyne 16	52
X-ray structure of diyne 13d	53
X-ray structure of diyne 13e	54
X-ray structure of triyne 14c	55
X-ray structure of triyne 22	56
X-ray structure of triyne 23	57

I- General

Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F254) using UV light as visualizing agent and by staining with KMnO_4 . Column chromatography was performed with silica gel (spherical, particle size 40 μm , neutral). ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra were recorded on a Bruker 400 NMR spectrometer with complete proton decoupling for nucleus other than ^1H . ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a Bruker Av I 500 MHz fitted with a TCI cryoprobe (Biosit platform - Université de Rennes 1). Chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl_3 : ^1H , δ 7.26 ppm; ^{13}C , δ 77.16 ppm). Coupling constants (J) are reported in hertz (Hz). Multiplicities are reported using following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Solvents: tetrahydrofuran and toluene were purified using MBraun MB-SPS-5 Solvent Purification System and typically contained <15 ppm of H_2O (verified by Karl Fischer titration). Solvents used for catalysis were freeze-pump-thaw degassed prior to use. All commercial chemicals were used as received unless otherwise noted. CDCl_3 was purchased from Euriso-Top company and used as received. High Resolution Mass Spectrometry (HRMS) were recorded on a Waters QToF-I spectrometer using electrospray ionization at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1 and at Institut de Chimie de Toulouse. Melting points were measured on a Stuart Melting Point Apparatus SMP3 and are uncorrected.

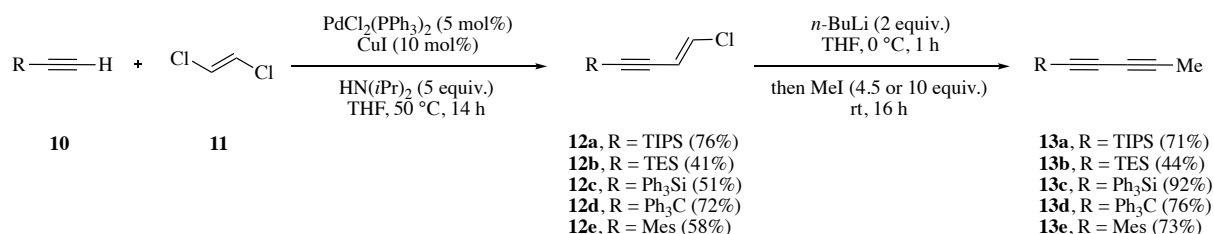
II- Reagents

Starting materials and products:

- (*E*)-(2-chlorovinyl)triisopropylsilane **12a** was prepared according to the literature.^[1]
- The synthesis of 1,4-bis(triisopropylsilyl)buta-1,3-diyne (**15a**) was described in the literature.^[2]
- Prop-2-yne-1,1,1-triyltribenzene (**10d**) was prepared according to the literature.^[3]
- Trimethyl(penta-1,3-diynyl)silane (**13f**) was prepared according to the literature.^[4]
- 1,4-bis(trimethylsilyl)buta-1,3-diyne (**15f**) is commercially available. CAS: 4526-07-2.
- 2-ethynyl-1,3,5-trimethylbenzene (**10e**) is commercially available. CAS: 769-26-6.
- The Mo-based complex **Cat-2** was synthesized by the Prof. A. Fürstner group according to the literature.^[5]

III- Synthesis of diyne substrates

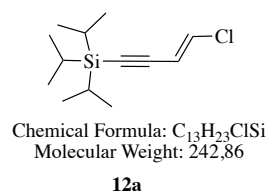
General procedure to the synthesis of diyne substrate



Argon gas was bubbled through a solution of acetylene **10** (1.0 equiv.), dichloroethylene **11** (4.0 equiv.), PdCl₂(PPh₃)₂ (0.05 or 0.1 equiv.), and diisopropylamine (5.0 equiv.) in THF (C = 0.06 M) for 10 minutes. CuI (0.1 equiv.) was added at room temperature and the mixture was heated to 50 °C for 14 hours. Then heating was stopped and once the reaction mixture reached room temperature it was filtered through a pad of silica gel and thoroughly rinsed with pentane. The desired compound **12** was obtained after distillation under reduced pressure.

To a solution of freshly prepared compound **12** (1.0 equiv.) in THF (C = 0.06 M) was added *n*-BuLi (2.0 equiv.; 1.6 M solution in hexanes) at 0 °C and the solution was stirred for 1 hour at 0 °C. Then a solution of iodomethane (4.5 or 10 equiv.) in THF (C = 1 M) was added dropwise to the reaction mixture at 0 °C. The mixture was stirred at room temperature for 16 hours and then quenched by the addition of a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted with Et₂O and the combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resultant residue was purified by flash chromatography (Pentane/DCM) to obtain diyne **13**.

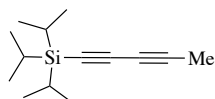
Synthesis of (*E*)-(4-chlorobut-3-en-1-yn-1-yl)-triisopropylsilane (**12a**)



Following the general procedure for the synthesis of chlorinated compound (**12**), with triisopropylacetylene (2.7 mL, 12 mmol, 1.0 equiv.), dichloroethylene (3.8 mL, 49 mmol, 4.0 equiv.), PdCl₂(PPh₃)₂ (844.8 mg, 1.2 mmol, 0.05 equiv.), diisopropylamine (8.4 mL, 60 mmol, 5.0 equiv.), CuI (232.8 mg, 1.2 mmol, 0.1 equiv.) in THF (40 mL), the desired product **12a** was isolated as a pale-yellow oil (2.21 g, **76% yield**) after distillation under reduced pressure.

¹H NMR (400 MHz, CDCl₃): δ 6.58 (d, *J* = 13.6 Hz, 1 H), 5.98 (d, *J* = 13.6 Hz, 1 H), 1.08 (s, 3 H), 1.07 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃): δ 131.4, 114.3, 101.6, 94.4, 18.7, 11.4. Spectral data were consistent with those previously reported.^[6]

Synthesis of Triisopropyl(penta-1,3-diynyl)silane (**13a**)



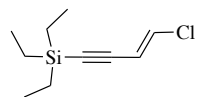
Chemical Formula: C₁₄H₂₄Si
Molecular Weight: 220.43

13a

Following the general procedure for the synthesis of diyne (**13**), with (*E*)-(2-chlorovinyl)triisopropylsilane **12a** (2.21 g, 9.1 mmol, 1.0 equiv.), *n*BuLi (12.8 mL, 18.2 mmol, 2.0 equiv.; 1.42 M solution in hexanes), THF (130 mL), solution of MeI (2.6 mL, 41 mmol, 4.5 equiv.) in THF (9 mL), the desired product **13a** was obtained as a pale-yellow oil (1.43 g, **71% yield**) after purification by column chromatography (Pentane/DCM from 100:0 to 95:5).

¹H NMR (400 MHz, CDCl₃): δ 1.92 (s, 3 H), 1.06 (s, 21 H). **¹³C NMR** (101 MHz, CDCl₃): δ 90.3, 79.4, 74.5, 65.3, 18.6, 11.4, 4.3. Spectral data were consistent with those previously reported.^[7]

Synthesis of (*E*)-(4-chlorobut-3-en-1-yn-1-yl)triethylsilane (**12b**)



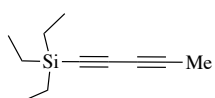
Chemical Formula: C₁₀H₁₇ClSi
Molecular Weight: 200.78

12b

Following the general procedure for the synthesis of chlorinated compound (**12**), with triethyl(ethynyl)silane (2.2 mL, 12.2 mmol, 1.0 equiv.), dichloroethylene (3.8 mL, 49 mmol, 4.0 equiv.), PdCl₂(PPh₃)₂ (845.2 mg, 1.2 mmol, 0.1 equiv.), diisopropylamine (8.4 mL, 59.9 mmol, 4.9 equiv.), CuI (229.7 mg, 1.2 mmol, 0.1 equiv.) in THF (40 mL), the desired product **12b** was isolated as a pale-yellow solid (1.01 g, **41% yield**) after distillation under reduced pressure.

¹H NMR (400 MHz, CDCl₃): δ 6.58 (d, *J* = 13.6 Hz, 1 H), 5.96 (d, *J* = 13.6 Hz, 1 H), 1.02-0.97 (m, 9H), 0.65-0.59 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 131.6, 114.2, 100.8, 95.4, 7.5, 4.4.

Synthesis of triethyl(penta-1,3-diyn-1-yl)silane (**13b**)



Chemical Formula: C₁₁H₁₈Si
Molecular Weight: 178.35

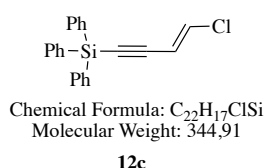
13b

Following the general procedure for the synthesis of diyne (**13**), with (*E*)-(4-chlorobut-3-en-1-yn-1-yl)triethylsilane **12b** (908.5 mg, 4.5 mmol, 1.0 equiv.), *n*BuLi (6.4 mL, 9.1 mmol, 2.0 equiv.; 1.42 M solution in hexanes), THF (68 mL), solution of MeI (2.8 mL, 45.0 mmol, 10 equiv.) in THF (4.5

mL), the desired product **13b** was obtained as a yellowish oil (350.7 mg, **44% yield**) after purification by column chromatography (Pentane).

¹H NMR (400 MHz, CDCl₃): δ 1.93 (s, 3 H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 89.6, 80.6, 75.1, 65.1, 7.5, 4.4. Spectral data were consistent with those previously reported.^[8]

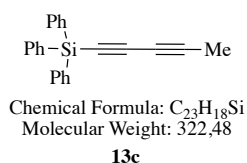
Synthesis of (*E*)-(4-chlorobut-3-en-1-yn-1-yl)triphenylsilane (**12c**)



Following the general procedure for the synthesis of chlorinated compound (**12**), with ethynyltriphenylsilane (171.0 mg, 0.6 mmol, 1.0 equiv.), dichloroethylene (241 μL, 3.1 mmol, 5.2 equiv.), PdCl₂(PPh₃)₂ (42.0 mg, 0.06 mmol, 0.1 equiv.), diisopropylamine (430 μL, 3.1 mmol, 5.1 equiv.), CuI (12 mg, 0.06 mmol, 0.1 equiv.) in THF (2 mL), the desired product **12c** was isolated as a white solid (104 mg, **51% yield**) after purification by column chromatography (Pentane/DCM from 100:0 to 95:5).

¹H NMR (400 MHz, CDCl₃): δ 7.65-7.63 (m, 6 H), 7.47-7.37 (m, 9H), 6.75 (d, *J* = 13.7 Hz, 1 H), 6.10 (d, *J* = 13.7 Hz, 1 H). **¹³C NMR** (101 MHz, CDCl₃): δ 135.7, 133.1, 130.2, 128.2, 113.9, 104.0, 92.8. **HRMS** (ESI) *m/z* calcd. for C₂₂H₁₈³⁵ClSi [M+H]⁺ 345.08663, found 345.0864.

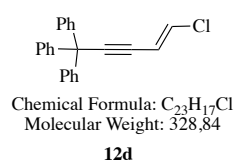
Synthesis of (penta-1,3-diyn-1-yl)triphenylsilane (**13c**)



Following the general procedure for the synthesis of diyne (**13**), with (*E*)-(4-chlorobut-3-en-1-yn-1-yl)triphenylsilane **12c** (106.2 mg, 0.31 mmol, 1.0 equiv.), *n*BuLi (450 μL, 0.64 mmol, 2.0 equiv.; 1.42 M solution in hexanes), THF (4.5 mL), solution of MeI (0.2 mL, 3.2 mmol, 10 equiv.) in THF (0.5 mL), the desired product **13c** was obtained as a yellowish solid (91.9 mg, **92% yield**) after purification by column chromatography (Pentane/DCM from 100:0 to 95:5).

¹H NMR (400 MHz, CDCl₃): δ 7.65-7.62 (m, 6 H), 7.45-7.36 (m, 9H), 1.98 (s, 3 H). **¹³C NMR** (101 MHz, CDCl₃): δ 135.7, 133.0, 130.2, 128.2, 92.9, 77.4, 77.3, 65.2, 4.5. **HRMS** (ESI) *m/z* calcd. for C₂₃H₁₈NaSi [M+Na]⁺ 345.10755, found 345.1072.

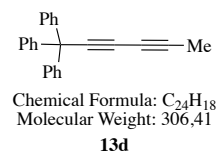
Synthesis of (E)-(3-chloroprop-2-ene-1,1,1-triyl)tribenzene (12d)



Following the general procedure for the synthesis of chlorinated compound (**12**), with prop-2-yne-1,1,1-triyltribenzene (608 mg, 2.3 mmol, 1.0 equiv.), dichloroethylene (673 mg, 6.9 mmol, 3.0 equiv.), $PdCl_2(PPh_3)_2$ (78.5 mg, 0.1 mmol, 0.05 equiv.), diisopropylamine (1.6 mL, 11.4 mmol, 5.0 equiv.), CuI (47 mg, 0.25 mmol, 0.1 equiv.) in THF (40 mL), the desired product **12d** was isolated as a colorless solid (539 mg, **72% yield**) after purification by column chromatography (Pentane/DCM from 100:0 to 95:5).

1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.21 (m, 15 H), 6.58 (d, $J = 13.6$ Hz, 1 H), 6.09 (d, $J = 13.6$ Hz, 1 H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.8, 129.9, 129.1, 128.1, 127.0, 114.0, 98.2, 93.4, 68.7. **HRMS** (ESI) m/z calcd. for $C_{23}H_{18}^{35}Cl$ $[M+H]^+$ 329.10915, found 329.1091.

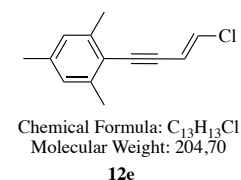
Synthesis of hexa-2,4-diyne-1,1,1-triyltribenzene (13d)



Following the general procedure for the synthesis of diyne (**13**), with (E)-(3-chloroprop-2-ene-1,1,1-triyl)tribenzene **12d** (117.9 mg, 0.36 mmol, 1.0 equiv.), *n*BuLi (0.5 mL, 0.71 mmol, 2.0 equiv.; 1.42 M solution in hexanes), THF (5 mL), solution of MeI (0.1 mL, 1.61 mmol, 4.5 equiv.) in THF (0.5 mL), the desired product **13d** was obtained as a yellowish solid (83.3 mg, **76% yield**) after purification by column chromatography (Pentane/DCM from 100:0 to 95:5).

1H -NMR (400 MHz, $CDCl_3$): δ 7.31-7.21 (m, 15 H), 1.96 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.5, 129.1, 128.1, 127.0, 80.8, 76.4, 70.2, 64.5, 56.1, 4.4. **HRMS** (ESI) m/z calcd. for $C_{24}H_{19}$ $[M+H]^+$ 307.14813, found 307.1481.

Synthesis of (E)-(4-chlorobut-3-en-1-yn-1-yl)- 1,3,5-trimethylbenzene (12e)

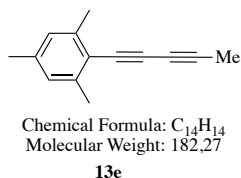


Following the general procedure for the synthesis of chlorinated compound (**12**), with 2-ethynyl-1,3,5-trimethylbenzene (0.8 mL, 5.1 mmol, 1.0 equiv.), dichloroethylene (1.9 mL, 24.5 mmol, 4.8 equiv.), $PdCl_2(PPh_3)_2$ (423.3 mg, 0.6 mmol, 0.1 equiv.), diisopropylamine (4.2 mL, 30 mmol, 5.8 equiv.), CuI (116.2 mg, 0.6 mmol, 0.1 equiv.) in THF (20 mL), the desired product **12e** was isolated as a pale-yellow oil (603.5 mg, **58% yield**) after distillation under reduced pressure.

1H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 2 H), 6.62 (d, $J = 13.6$ Hz, 1 H), 6.28 (d, $J = 13.6$ Hz, 1 H), 2.42 (s, 6 H), 2.32 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.3, 138.3, 128.9, 127.8,

119.5, 114.5, 91.9, 90.1, 21.5, 21.0. **HRMS** (ESI) m/z calcd. for $C_{13}H_{14}^{35}Cl$ $[M+H]^+$ 205.07785, found 205.0782.

Synthesis of 1,3,5-trimethyl-2-(penta-1,3-diyn-1-yl)benzene (**13e**)



Following the general procedure for the synthesis of diyne (**13**), with (*E*)-(2-chlorovinyl)triisopropylsilane **12e** (603.5 mg, 2.9 mmol, 1.0 equiv.), *n*BuLi (4.3 mL, 6.1 mmol, 2.0 equiv.; 1.42 M solution in hexanes), THF (45 mL), solution of MeI (1.8 mL, 29 mmol, 10 equiv.) in THF (3 mL), the desired product **13e** was obtained as a yellow solid (394.7 mg, **73% yield**).

1H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 2 H), 2.40 (s, 6 H), 2.28 (s, 3 H), 2.05 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.9, 138.5, 127.8, 118.9, 81.5, 81.2, 72.4, 64.8, 21.5, 21.0, 4.9 **HRMS** (ESI) m/z calcd. for $C_{14}H_{15}$ $[M+H]^+$ 183.1168, found 183.1168.

IV- Mo-catalyzed self-metathesis of diynes

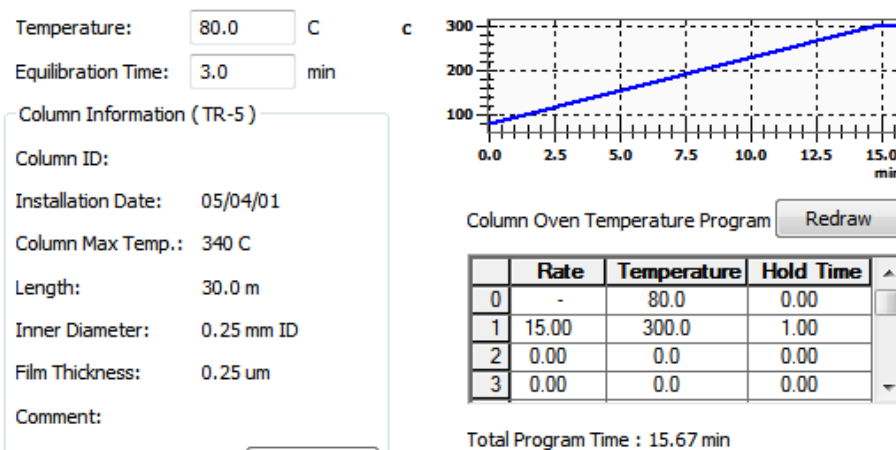
Note: All reactions were carried out in a glove-box with degassed solvents. The powdered molecular sieves Molecular sieves 4 Å (CAS: 70955-01-0; Ref. No. 11424553 Alfa Aesar™) and 5 Å (CAS : 69912-79-4; Ref. No. 10296980 Acros Organics™) were heated with a heatgun (~ 300 °C for 10 min at 1 mbar) prior to introduction into the glove box.

• GC-analysis:

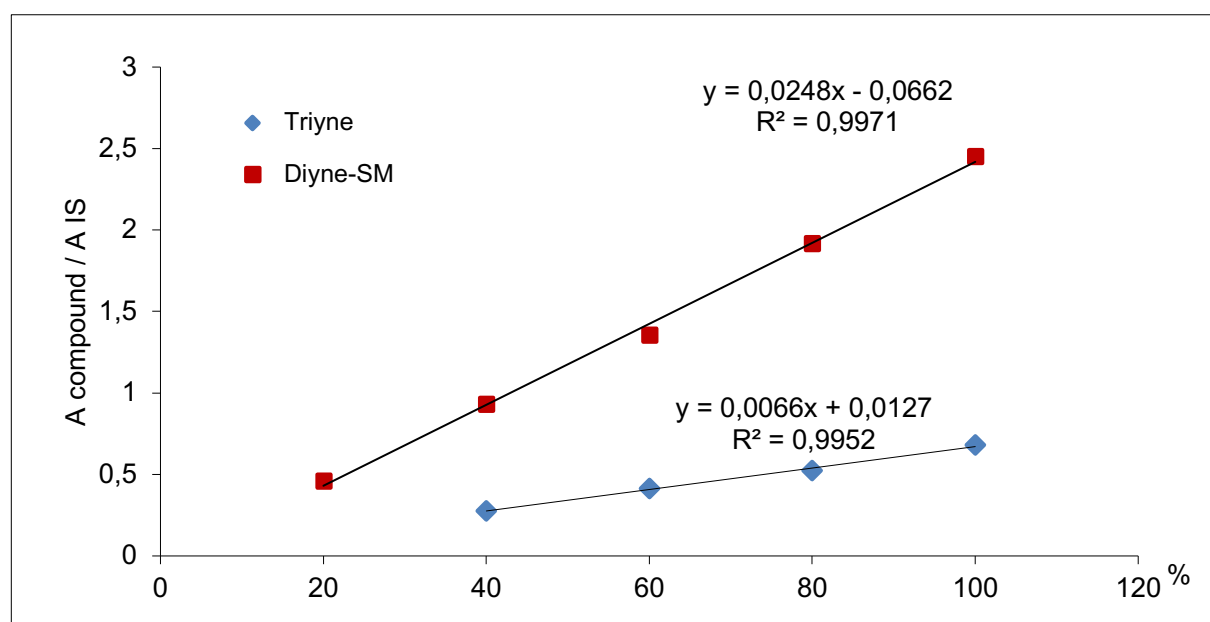
Description of GC-method:

Instrument:	Shimadzu GC-2014
Carrier gas:	Helium
Inlet temperature:	300 °C
Pressure:	143.4 kPa
Column flow:	1.79 mL / min; 40.6 cm / s
Split ratio:	20
Internal standard:	acetophenone (2.0 equiv)

Temperature protocol:



Determination of response factors:



- ◆ Area under Peak of triyne **14a** / area under peak of acetophenone
- Area under Peak of diyne starting material **13a** / area under Peak of acetophenone

Determination of GC conversion and yield:

$$\text{Triyne } \mathbf{14a} \text{ (\%)} = 151.5 * [(\text{Area of triyne } \mathbf{14a} / \text{area of acetophenone}) - 0,0127]$$

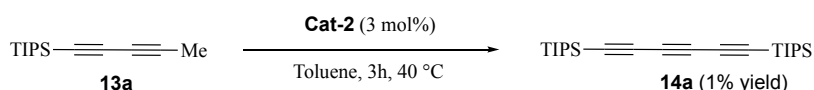
$$\text{Diyne } \mathbf{13a} \text{ (\%)} = 40.3 * [(\text{Area of diyne } \mathbf{13a} / \text{area of acetophenone}) + 0.0662]$$

entry	diynes	Cat-2 (mol%)	Conv. (%) ^a	Ratio 14:15 ^b	Yield 14 (%) ^a	Yield 15 (%) ^a
1 ^c	13a	3	50	nd	1	-
2	13a	3	96	86:14	86	-
3	13a	2	91	90:10	80	-
4 ^d	13a	2	89	90:10	74	-
5	13a	1	75	95:5	59	-
6 ^e	13a	3	96	81:19	63 ^f	-
7 ^g	13f	3	91	0:100	-	48
8	13b	3	>98	2:98	-	56
9 ^h	13c	3	95 ⁱ	40:60 ^j	12 ^{j,k}	13 ^{j,k}

Table S1 : Self-metathesis of TIPS-diynes **13a** catalyzed by Mo-complex **Cat-2**

^aDetermined by GC-analysis with acetophenone as internal standard. ^bDetermined by GC-analysis^cPerformed without MS 4Å/5Å. ^dPerformed at 20 °C. ^ePerformed at 0.55 mmol-scale. ^fIsolated yield after silica gel chromatography.^gPerformed at 20 °C over 1h. ^hPerformed at 0.26 mmol-scale. ⁱBased on the recovered starting material. ^jDetermined by quantitative ¹³C NMR spectroscopy. ^kEstimated yield from an isolated mixture of **14c** + **15c**.

Self-metathesis of TIPS-diyne **13a** (Table 1- Entries 1-6)



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TIPS-diyne **13a** (14.3 mg, 0.032 mmol, 2.0 equiv.) were added toluene (250 μL). Then 100 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00096 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box and acetophenone (14.9 μL , 0.128 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

- GC-trace of Table 1, entry 1 (13a without molecular sieves)

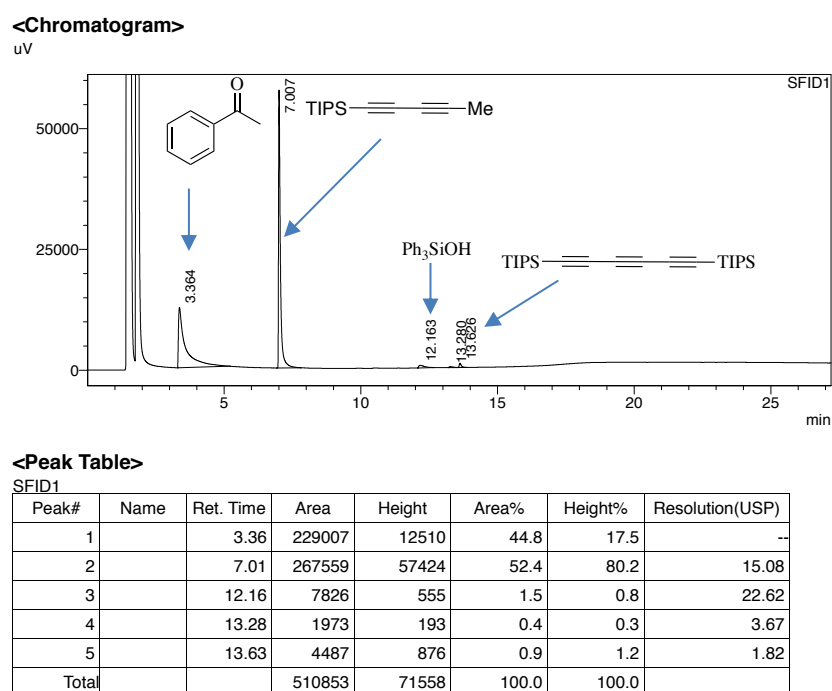


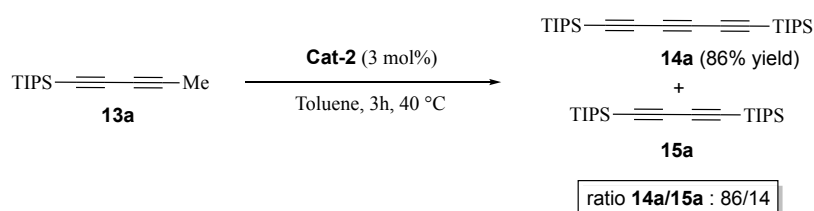
Figure S1: GC chromatogram of Table 1, entry 1

Calculation details:

Conversion of **13a** = $100 - [40.3 * [(267559 / 229007) + 0.0662]] = 50\%$

Yield of **14a** = $151.5 * [(4487 / 229007) - 0.0127] = 1\%$

Ratio **14a** / **15a** = 100 / 0



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TIPS-diyne **13a** (8.6 mg, 0.039 mmol, 2.0 equiv.) were added powdered molecular sieves 4 \AA (40 mg) and powdered molecular sieves 5 \AA (40 mg) in toluene (100 μL). Then 100 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00096 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 $^\circ\text{C}$. Then the microwave tube was removed from the glove box and acetophenone (9.1 μL , 0.078 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

- GC-trace of Table 1, entry 2 (**13a** with powdered molecular sieves 4 Å and 5 Å)

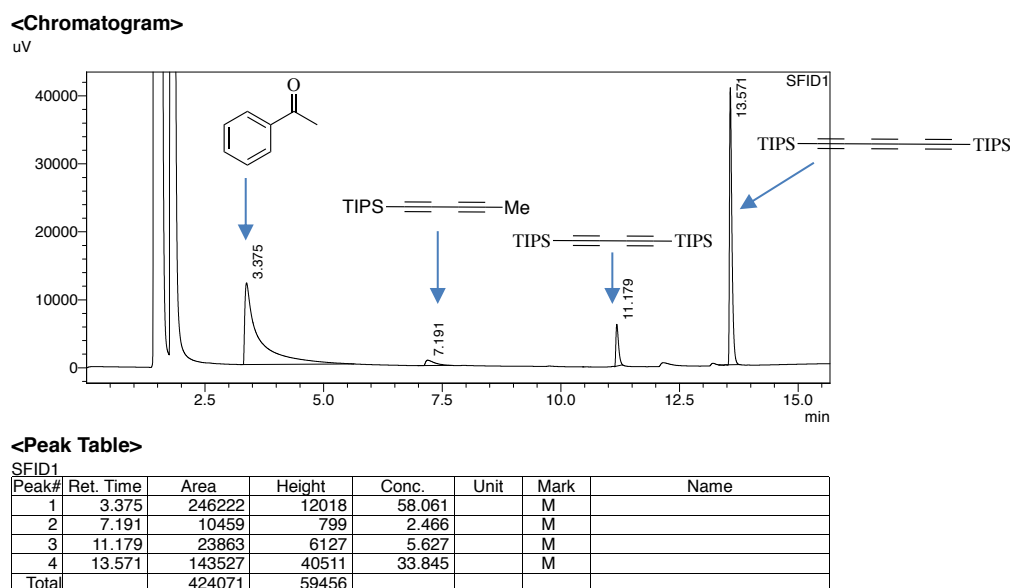


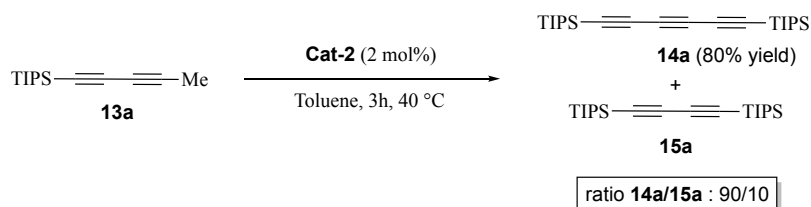
Figure S2: GC chromatogram of Table 1, entry 2

Calculation details:

Conversion of **13a** = $100 - [40.3 * [(10459 / 246222) + 0.0662]] = 96\%$

Yield of **14a** = $151.5 * [(143527 / 246222) - 0.0127] = 86\%$

Ratio **14a** / **15a** = $(143527 / 23863) = 6.01$ corresponding to a ratio of 86 / 14



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TIPS-diyne **13a** (8.7 mg, 0.039 mmol, 2.0 equiv.) were added powdered molecular sieves 4 Å (40 mg) and powdered molecular sieves 5 Å (40 mg) in toluene (134 μL). Then 66 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00063 mmol, 2 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box and acetophenone (9.1 μL , 0.078 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

- GC-trace of Table 1, entry 3 (13a with 2 mol% of Cat-2)

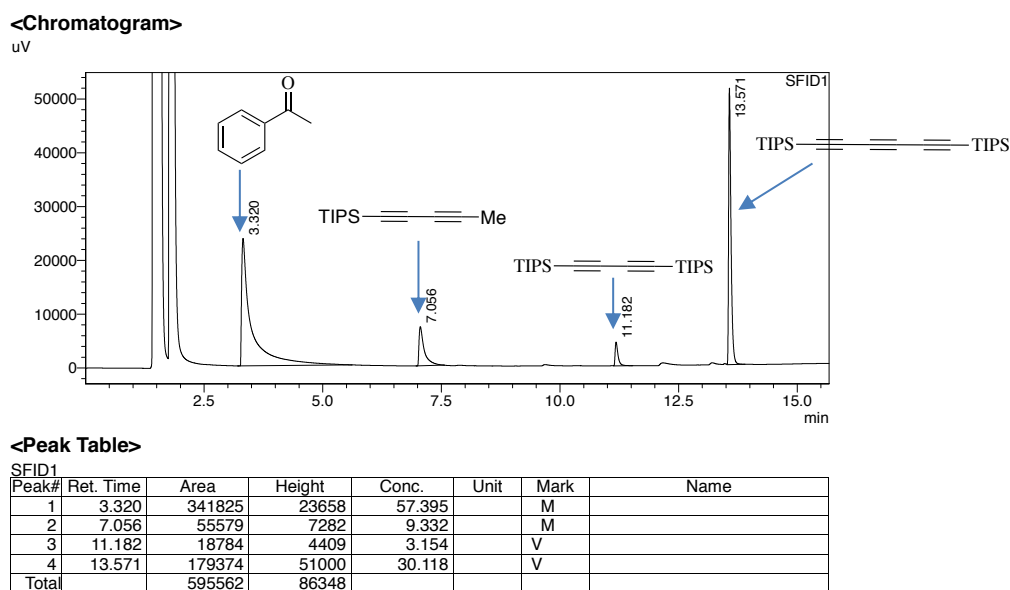


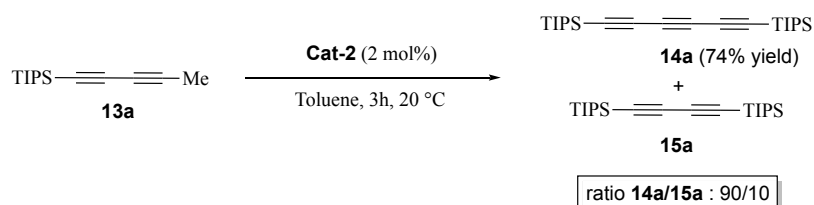
Figure S3: GC chromatogram of Table 1, entry 3

Calculation details:

Conversion of **13a** = $100 - [40.3 * [(55579 / 341825) + 0.0662]] = 91\%$

Yield of **14a** = $151.5 * [(179374 / 341825) - 0.0127] = 80\%$

Ratio **14a** / **15a** = $(179374 / 18784) = 9.55$ corresponding to a ratio of 90 / 10



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TIPS-diyne **13a** (8.8 mg, 0.040 mmol, 2.0 equiv.) were added powdered molecular sieves 4 \AA (40 mg) and powdered molecular sieves 5 \AA (40 mg) in toluene (134 μL). Then 66 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00063 mmol, 2 mol%) was added and the reaction was stirred for 3 hours at 20 $^\circ\text{C}$. Then the microwave tube was removed from the glove box and acetophenone (9.1 μL , 0.078 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

- GC-trace of Table 1, entry 4 (**13a** with 2 mol% of **Cat-2** at 20 °C)

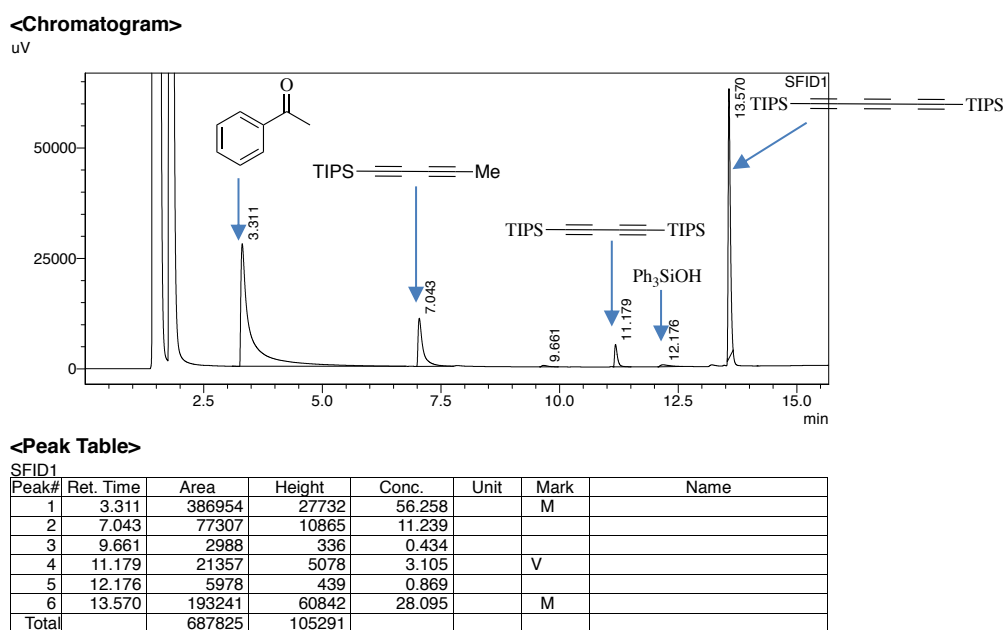


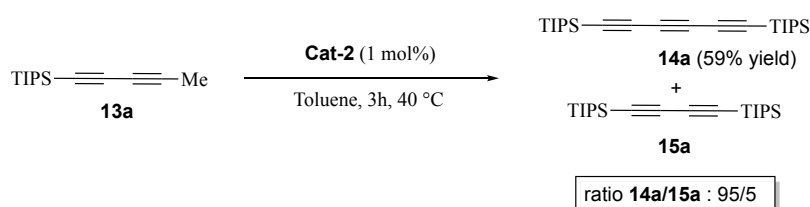
Figure S4: GC chromatogram of Table 1, entry 4

Calculation details:

Conversion of **13a** = $100 - [40.3 * [(77307 / 386954) + 0.0662]] = 89\%$

Yield of **14a** = $151.5 * [(193241 / 386954) - 0.0127] = 74\%$

Ratio **14a** / **15a** = $(193241 / 21357) = 9.05$ corresponding to a ratio of 90 / 10



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TIPS-diyne **13a** (8.8 mg, 0.040 mmol, 2.0 equiv.) were added powdered molecular sieves 4 Å (40 mg) and powdered molecular sieves 5 Å (40 mg) in toluene (167 μL). Then 33 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00032 mmol, 1 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box and acetophenone (9.1 μL , 0.078 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

- GC-trace of Table 1, entry 5 (**13a** with 1 mol% of **Cat-2**)

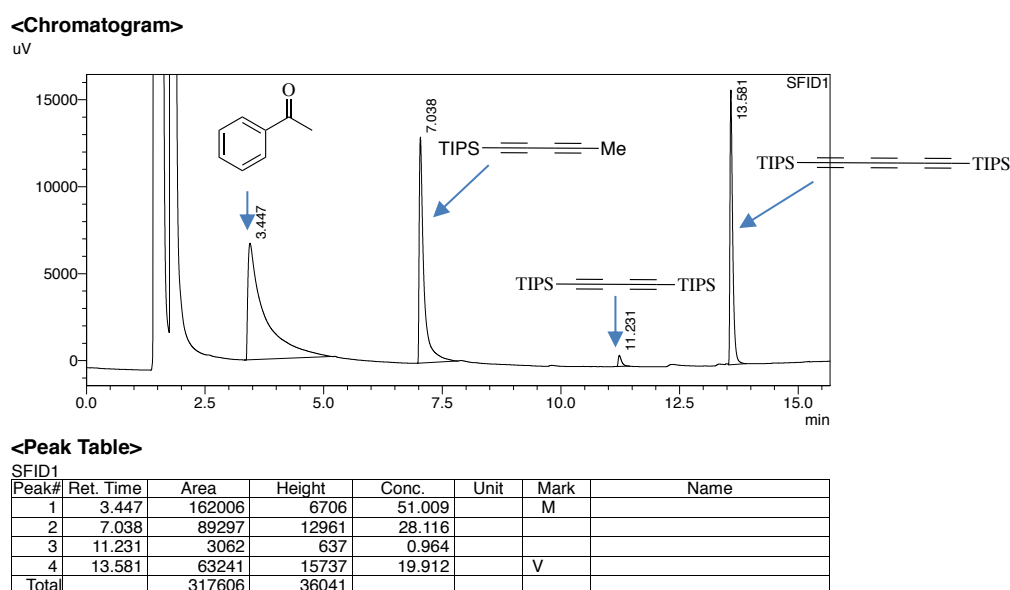


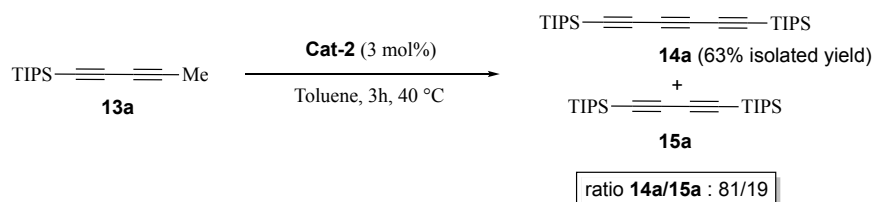
Figure S5: GC chromatogram of Table 1, entry 5

Calculation details:

Conversion of **13a** = $100 - [40.3 * [(89297 / 162006) + 0.0662]] = 75\%$

Yield of **14a** = $151.5 * [(63241 / 162006) - 0.0127] = 59\%$

Ratio **14a** / **15a** = $(63241 / 3062) = 20.65$ corresponding to a ratio of 95 / 5



To a microwave tube charged with TIPS-diyne **13a** (121.0 mg, 0.549 mmol, 2.0 equiv.) were added powdered molecular sieves 4 Å (500 mg) and powdered molecular sieves 5 Å (500 mg) in toluene (3 mL). Then catalyst **Cat-2** (8.6 mg, 0.0082 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box and the crude reaction mixture was filtered through a pad of silica, rinsed with dichloromethane and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:DCM 100:0 to 90:10) and the obtained solid was washed with pentane to give the triyne **14a** as white solid (66.6 mg, **63% yield**).

¹H NMR (400 MHz, CDCl₃): δ 1.12-1.09 (m, 42 H). ¹³C NMR (101 MHz, CDCl₃): δ 90.0, 84.9, 61.5, 18.7, 11.4. Spectral data were consistent with those previously reported.^[9]

Conversion of **13a** = 96%

- GC-trace of Table 1, entry 6 (**13a** with 3 mol% of **Cat-2** performed at 0.27 mmol-scale)

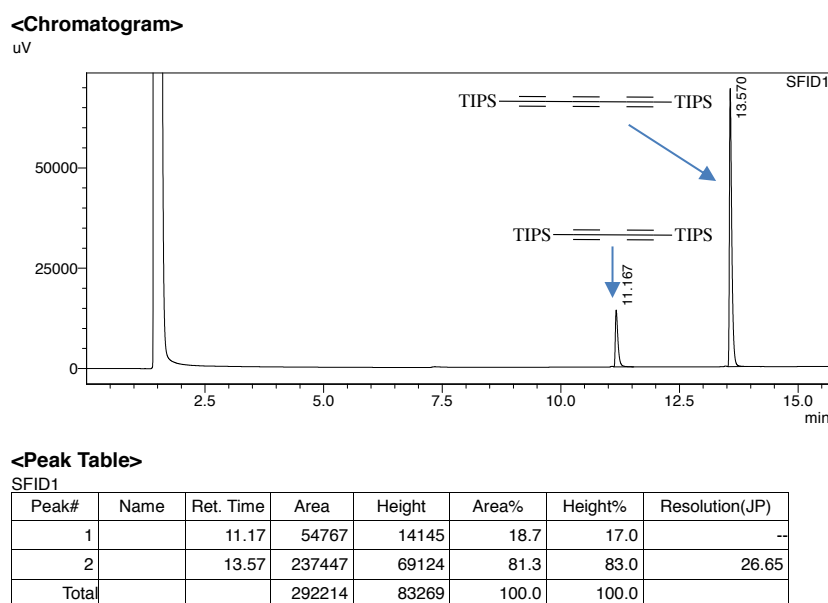
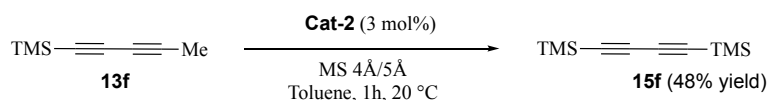


Figure S6: GC chromatogram of Table 1, entry 6

Self-metathesis of TMS-diyne **13f** (Table 1- Entry 7)



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TMS-diyne **13f** (8.9 mg, 0.065 mmol, 2.0 equiv.) were added powdered molecular sieves 4 \AA (60 mg) and powdered molecular sieves 5 \AA (60 mg) in toluene (250 μL). Then 100 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00096 mmol, 3 mol%) was added and the reaction was stirred for 1 hour at 20 $^\circ\text{C}$. Then the microwave tube was removed from the glove box and *n*-dodecane (29.8 μL , 0.132 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

Note: Commercial 1,4-bis(trimethylsilyl)buta-1,3-diyne **15f** was used to establish the GC-method.

- GC-analysis:**

Description of GC-method:

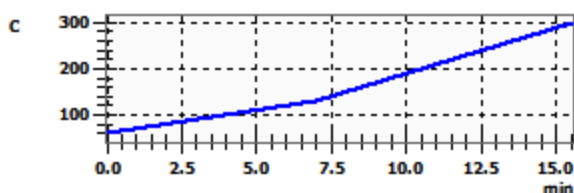
Instrument: Shimadzu GC-2014
 Carrier gas: Helium
 Inlet temperature: 280 °C
 Pressure: 137.7 kPa
 Column flow: 1.86 mL / min; 40.0 cm / s
 Split ratio: 20
 Internal standard: *n*-dodecane (2.0 equiv.)

Temperature protocol:

Temperature: C
 Equilibration Time: min

Column Information (TR-5)

Column ID:
 Installation Date: 05/04/01
 Column Max Temp.: 340 C
 Length: 30.0 m
 Inner Diameter: 0.25 mm ID
 Film Thickness: 0.25 µm
 Column No.:
 Comment:

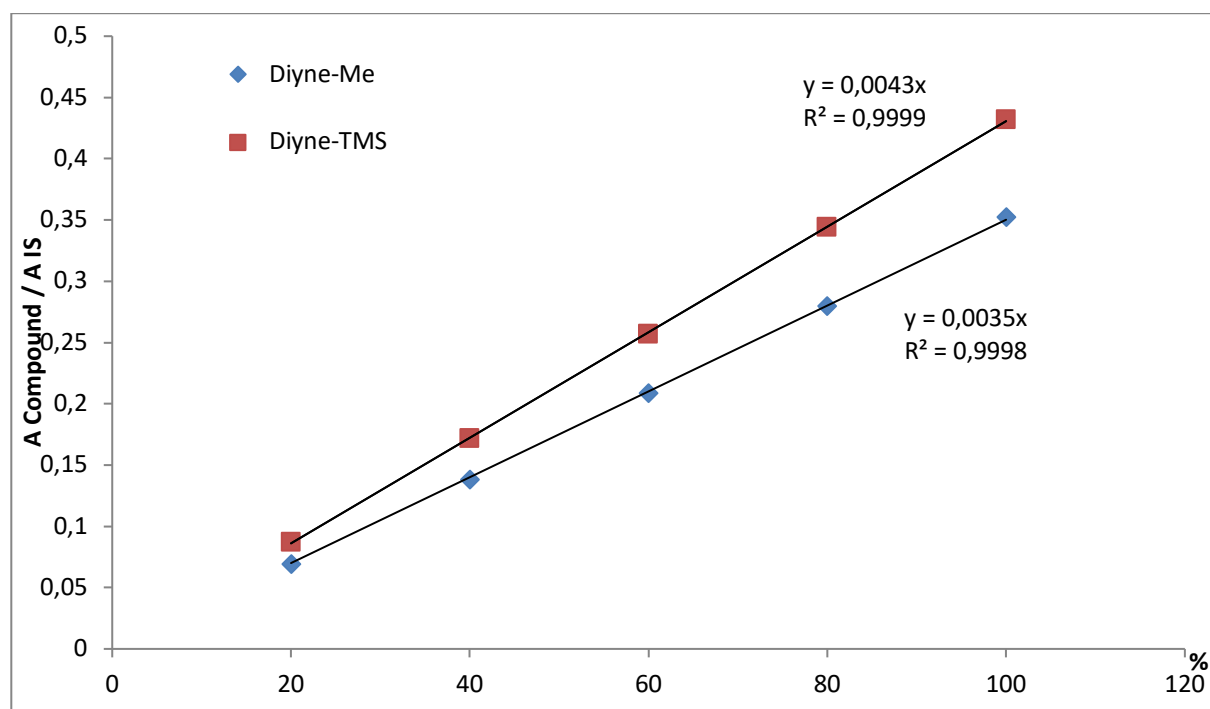


Column Oven Temperature Program

	Rate	Temperature	Hold Time
0	-	60.0	0.00
1	10.00	130.0	0.00
2	20.00	300.0	0.00
3	0.00	0.0	0.00

Total Program Time : 15.50 min

Determination of response factors:



- ◆ Area under Peak of diyne product **15f** / area under peak of *n*-dodecane
- Area under Peak of diyne-Me (starting material) **13f** / area under Peak of *n*-dodecane

Determination of GC conversion and yield:

Diyne-Me 13f (%)	= 285.7 * (Area of diyne-Me 13f / area of <i>n</i> -dodecane)
Diyne 15f (%)	= 232.6 * (Area of diyne 15f / area of <i>n</i> -dodecane)

- GC-trace of Table 1, entry 7 (**13f** with 3 mol% of **Cat-2**)

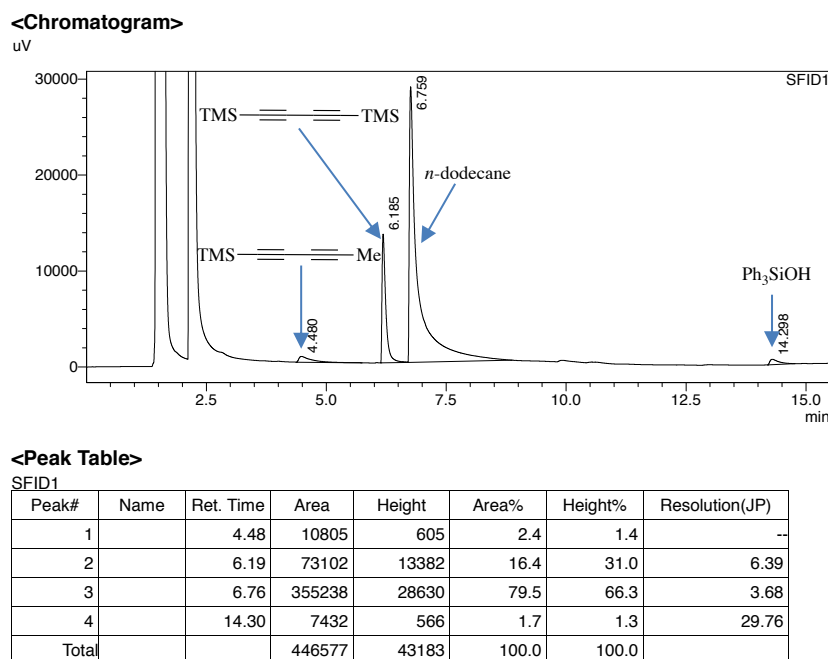


Figure S7: GC chromatogram of Table 1, entry 7

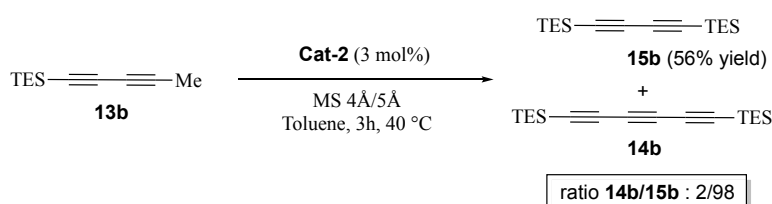
Calculation details:

Conversion of **13f** = $100 - [285.7 * (10805 / 355238)] = 91\%$

Yield of **15f** = $232.6 * (73102 / 355238) = 48\%$

Ratio **14** / **15** = 0 / 100

Self-metathesis of TES-diyne 13b (Table 1- Entry 8)



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μL) was prepared in the glove-box. To a microwave tube charged with TES-diyne **13b** (11.7 mg, 0.066 mmol, 2.0 equiv.) were added powdered molecular sieves 4 \AA (60 mg) and powdered molecular sieves 5 \AA (60 mg) in toluene (250 μL). Then a freshly prepared stock solution of catalyst **Cat-2** (100 μL , 0.00096 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 $^\circ\text{C}$. Then the microwave tube was removed from the glove box and *n*-dodecane (14.9 μL , 0.132 mmol, 2.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2

µm, 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

Note: All reactions were carried out in a glove-box with degassed solvents. Powdered molecular sieves 4 Å (CAS: 70955-01-0; Ref. No. 11424553 Alfa Aesar™) and 5 Å (CAS : 69912-79-4; Ref. No. 10296980 Acros Organics™) were heated with a heatgun (~ 300 °C for 10 min at 1 mbar) prior introduction into the glove box.

- **GC-analysis:**

Description of GC-method:

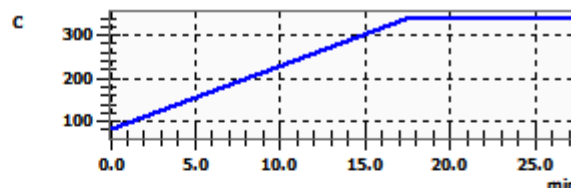
Instrument: Shimadzu GC-2014
Carrier gas: Helium
Inlet temperature: 280 °C
Pressure: 143.4 kPa
Column flow: 1.79 mL / min; 40.0 cm / s
Split ratio: 20
Internal standard: acetophenone (2.0 equiv.)

Temperature protocol:

Temperature: C
Equilibration Time: min

Column Information (TR-5)

Column ID:
Installation Date: 05/04/01
Column Max Temp.: 340 C
Length: 30.0 m
Inner Diameter: 0.25 mm ID
Film Thickness: 0.25 µm
Column No.: 10
Comment:

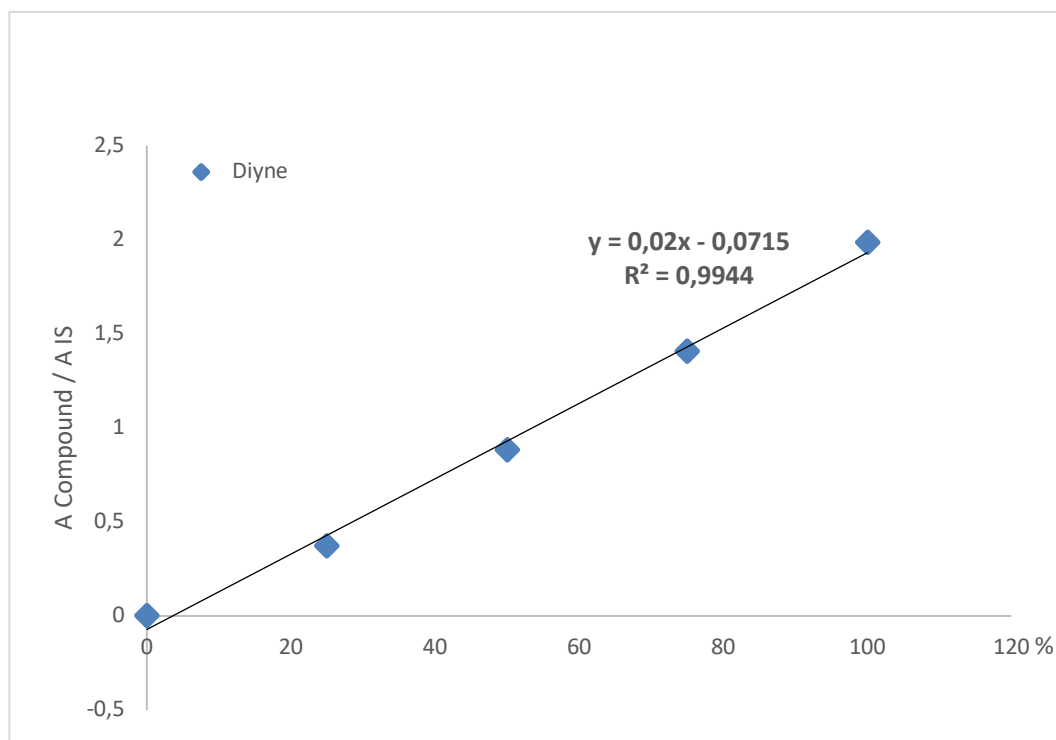


Column Oven Temperature Program

	Rate	Temperature	Hold Time	
0	-	80.0	0.00	
1	15.00	340.0	10.00	
2	0.00	0.0	0.00	
3	0.00	0.0	0.00	

Total Program Time : 27.33 min

Determination of response factors:

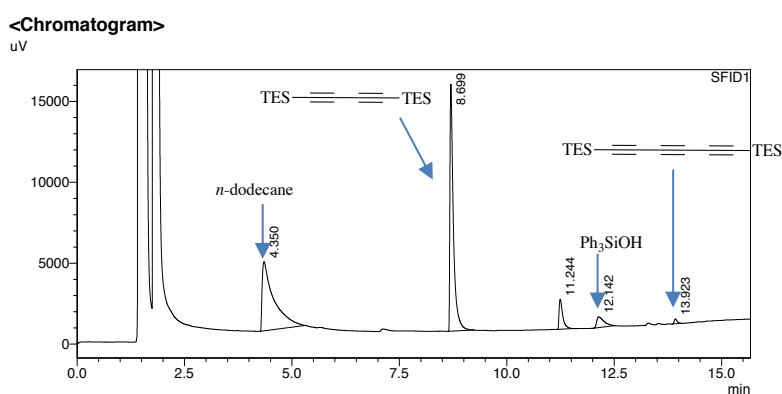


- ◆ Area under Peak of diene **15b** / area under peak of acetophenone

Determination of GC conversion and yield:

$$\text{Diene } \mathbf{15b} \text{ (\%)} = 50 * [(\text{Area of diene } \mathbf{15b} / \text{area of } n\text{-dodecane}) + 0,0715]$$

- GC-trace of Table 1, entry 8 (**13b** with 3 mol% of **Cat-2**)



<Peak Table>

SFID1

Peak#	Name	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1		4.35	81463	4276	43.5	19.2	--
2		8.70	85595	15209	45.7	68.2	16.32
3		11.24	10930	1855	5.8	8.3	18.72
4		12.14	7928	665	4.2	3.0	4.02
5		13.92	1310	288	0.7	1.3	8.43
Total			187226	22293	100.0	100.0	

Figure S8: GC chromatogram of Table 1, entry 8

Calculation details:

Yield of **15b** = $50 * [(85595 / 81463) + 0.0715] = 56\%$

Ratio **14** / **15** = $1310 / 85595 = 0.015$ corresponding to a ratio of 2 / 98

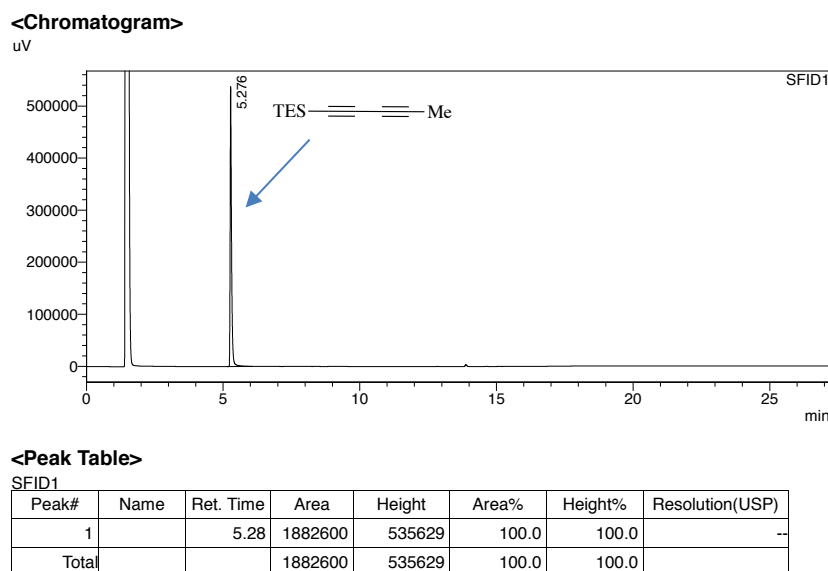
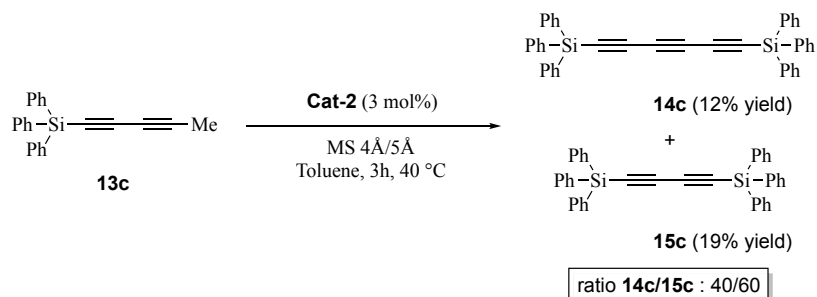


Figure S9: GC chromatogram of Starting Material TES-diyne **13b**

Self-metathesis of Ph₃Si-diyne **13c** (Table 1, Entry 9)



To a microwave tube charged with Ph₃Si-diyne **13c** (83.1 mg, 0.258 mmol, 2.0 equiv.) were added powdered molecular sieves 4 Å (240 mg) and powdered molecular sieves 5 Å (240 mg) in toluene (1.4 mL). Then catalyst **Cat-2** (4.2 mg, 0.0040 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box and the crude reaction mixture was filtered through a pad of silica, rinsed with dichloromethane and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:DCM 100:0 to 95:5) and the obtained solid was washed with pentane to give the mixture of triyne **14c** and diyne **15c** as a pale yellow solid (22.8 mg). Ratio 40:60

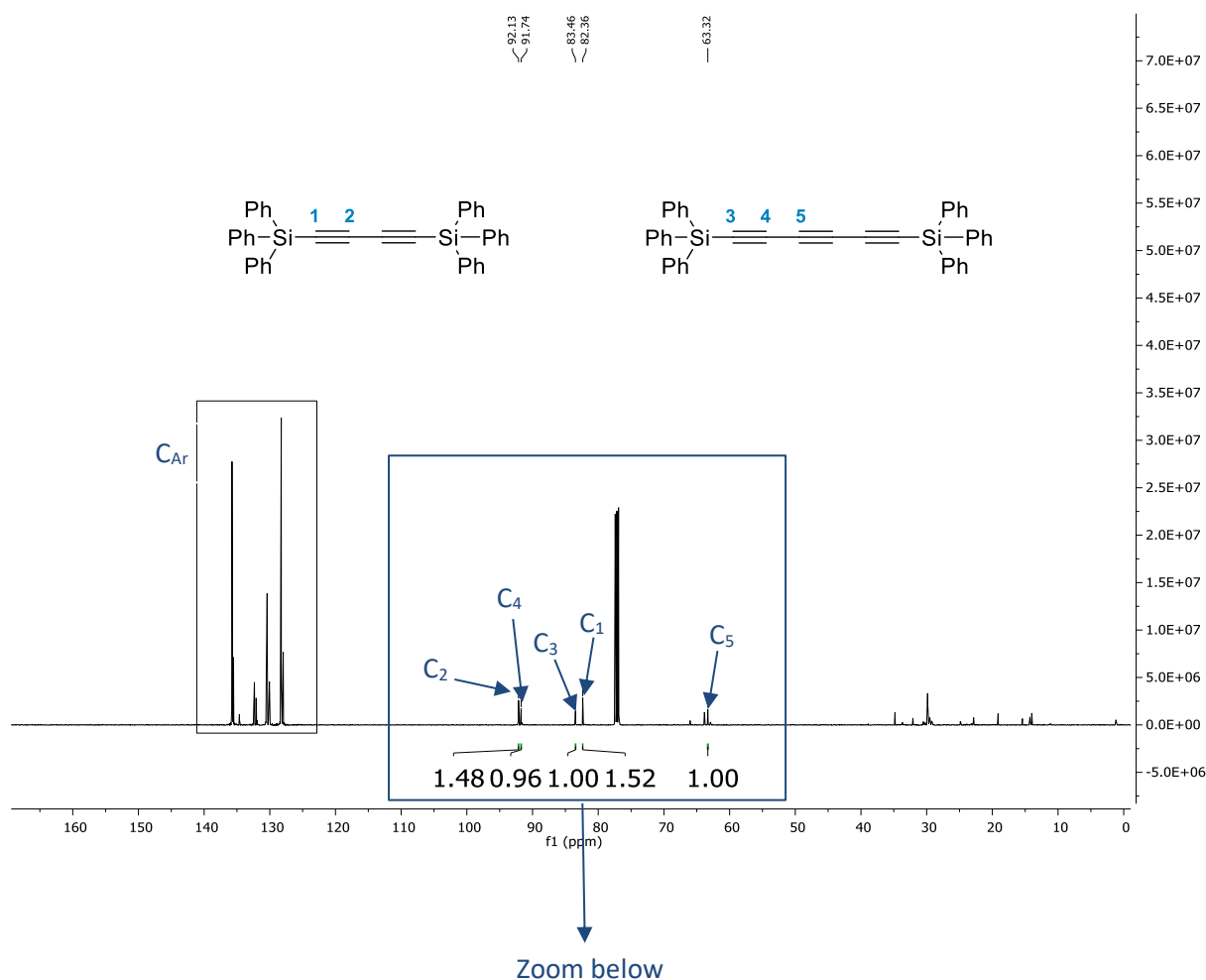
determined by quantitative ^{13}C NMR spectroscopy (Estimated yield: 19% of diyne **15c** and 12% of triyne **14c** products were formed). Conversion >95%

Note: HRMS analysis could not performed but X-Ray structure was obtained for **14c** (CCDC 1966970)

NMR description of the mixture of **15c** and **14c** :

^1H NMR (400 MHz, CDCl_3): δ 7.65-7.63 (m, 12 H), 7.45-7.37 (m, 18 H). ^{13}C NMR (101 MHz, CDCl_3): δ 135.8 (C_{Ar}), 135.7 (C_{Ar}), 135.5 (C_{Ar}), 132.3 (C_{Ar}), 130.5 (C_{Ar}), 130.4 (C_{Ar}), 130.0 (C_{Ar}), 128.3 (C_{Ar}), 128.2 (C_{Ar}), 128.0 (C_{Ar}), 92.1 (C_2), 91.7 (C_4), 83.4 (C_3), 83.2 (C_1), 63.3 (C_5).

The ratio between **14c** and **15c** was determined by quantitative ^{13}C analysis. (zig sequence from Bruker library was used, Acquisition time was set to 0.52s and D1 fixed to 12s for better relaxation)



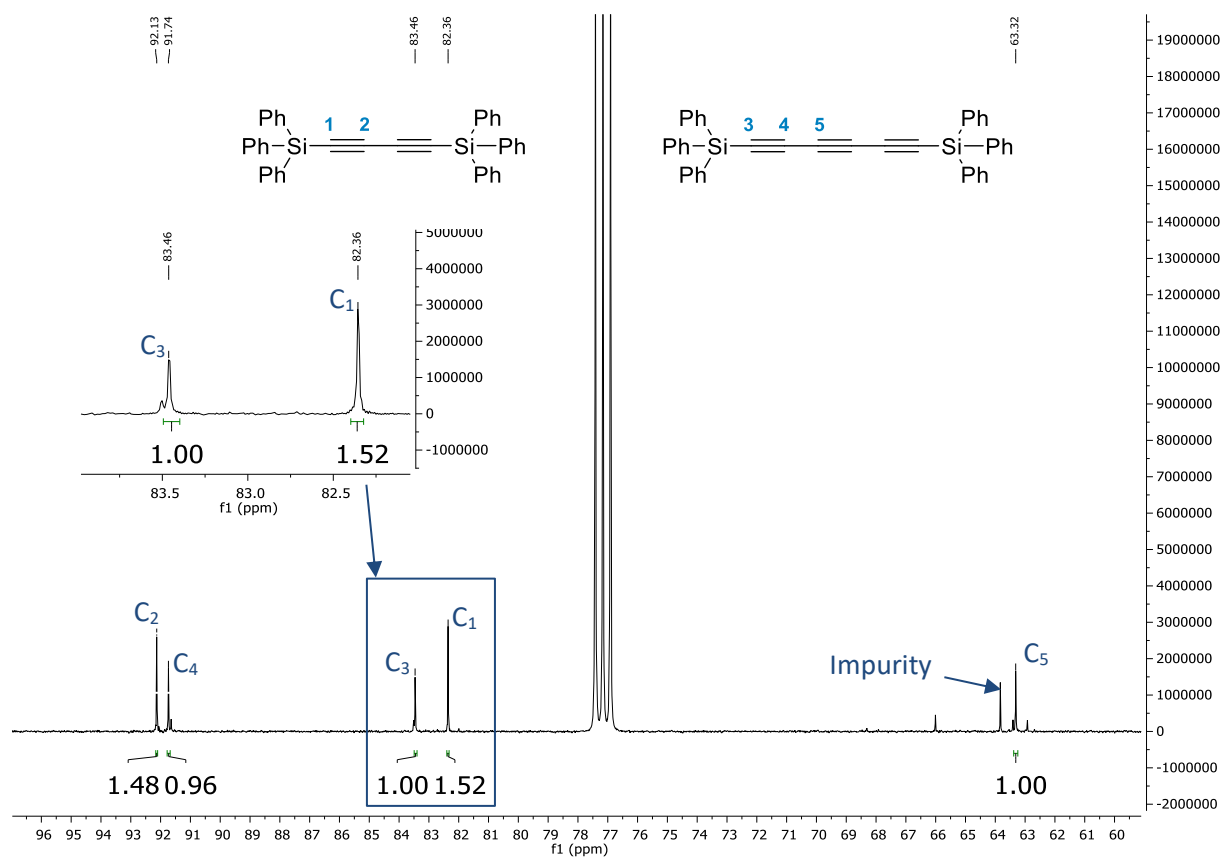


Figure S10: Quantitative ^{13}C NMR spectra of Table 1, entry 9

Calculation details:

Relaxation time for C_1 and C_3 were considered identical due to their similar chemical environment and **14c/15c** ratio was determined on their corresponding signals.

Ratio **14c** / **15c** = 1.00 / 1.52 corresponding to a ratio of 40 / 60

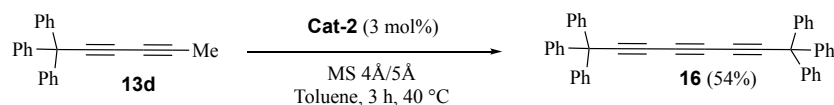
Yield of **15c** : $[(m_{\text{sample}} * \mathbf{15c}(\%)) / M_{\mathbf{15c}}] / n_{\text{total}} * 100$

Yield of **15c** = $[(22.8 * 0.60) / 566.85] / 0.128 * 100 = 19\%$

Yield of **14c** : $[(m_{\text{sample}} * \mathbf{14c}(\%)) / M_{\mathbf{14c}}] / n_{\text{total}} * 100$

Yield of **14c** = $[(22.8 * 0.40) / 590.87] / 0.128 * 100 = 12\%$

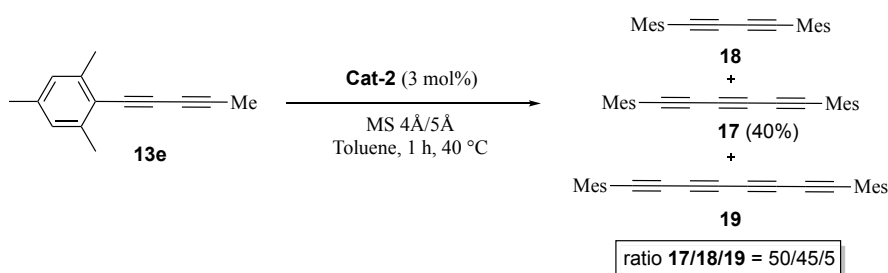
Synthesis of 1,1,1,8,8,8-hexaphenylocta-2,4,6-triyne (**16**) (Scheme 2, a)



In the glove-box, to a microwave tube charged with Trityl-diyne **13d** (78.7 mg, 0.257 mmol, 2.0 equiv.) were added powdered molecular sieves 4 Å (240 mg) and powdered molecular sieves 5 Å (240 mg) in toluene (1.4 mL). Then catalyst **Cat-2** (4.1 mg, 0.0039 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box. The crude reaction mixture was filtered through a pad of silica and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:DCM 100:0 to 90:10) and the obtained solid was washed with pentane to give the desired triyne **16** as white solid (38.5 mg, 0.069 mmol, **54% yield**). $R_f = 0.30$ (*n*-pentane). m.p. 280-282 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.32-7.20 (m, 30 H). **¹³C NMR** (101 MHz, CDCl₃): δ 144.0, 129.2, 128.3, 127.4, 84.3, 70.2, 63.3, 56.6. **HRMS** (ESI) *m/z* calcd. for C₄₄H₃₁ [M+H]⁺ 558.2342, found 558.2338.

Synthesis of 1,6-dimesitylhexa-1,3,5-triyne (17) (Scheme 2, b)



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 μ L) was prepared in the glove-box. To a microwave tube charged with Mes-diyne **13e** (11.8 mg, 0.065 mmol, 2.0 equiv.) were added powdered molecular sieves 4 Å (60 mg) and powdered molecular sieves 5 Å (60 mg) in toluene (250 μ L). Then 100 μ L of the previously prepared stock solution of catalyst **Cat-2** (0.00096 mmol, 3 mol%) was added and the reaction was stirred for 1 hour at 40 °C. Then the microwave tube was removed from the glove box and acetophenone (9.1 μ L, 0.078 mmol, 4.0 equiv.) was added. Approximately 100 μ L of this solution was removed, filtered through syringe filter (0.2 μ m, 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC and GS-MS.

- **GC-MS analysis:**

Description of GC-method:

Instrument:	GC-MS Shimadzu QP2010SE
Carrier gas:	Helium
Inlet temperature:	300 °C
Pressure :	79.5 kPa
Column flow:	40 cm / s
Split ratio:	20
External standard:	<i>n</i> -dodecane (2.0 equiv)

Temperature protocol:

Inj. Port : SPL1 Inj. Heat Port : INJ1

Column Oven Temp. : 80.0 °C

Injection Temp. : 300.0 °C

Injection Mode : Split

Sampling Time : 1.00 min

Carrier Gas : He Prim. Press. : 500-900

Flow Control Mode : Linear Velocity

Pressure : 79.5 kPa

Total Flow : 27.8 mL/min

Column Flow : 1.18 mL/min

Linear Velocity : 40.0 cm/sec

Purge Flow : 3.0 mL/min

Split Ratio : 20.0

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	80.0	0.00
1	15.00	330.0	20.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 36.67 min

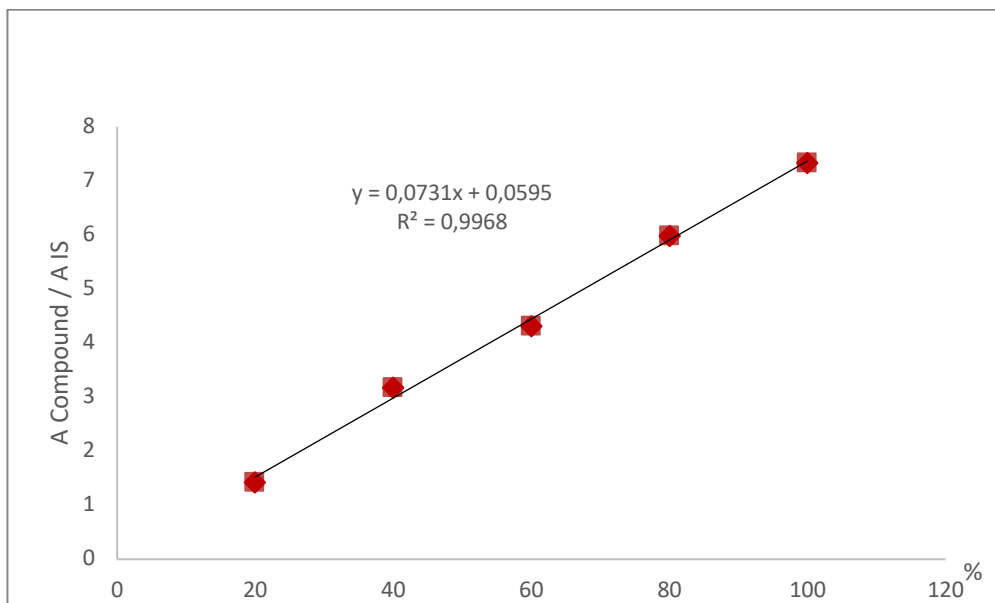
Column

Name SH-Fxi-5ms Thickness : 0.25 um

Length : 30.0 m Diameter : 0.25 mm

High Press. Injection Carrier Gas Saver

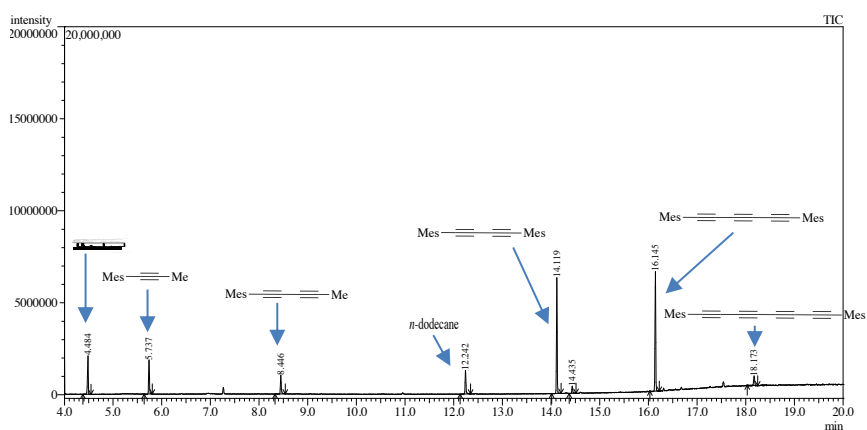
Determination of response factors:



■ Area under Peak of triyne 17 / area under Peak of *n*-dodecane

Determination of GC yield:

Triyne 17 (%)	= 13.7 * [(Area of triyne 17 / area of <i>n</i> -dodecane) – 0.0595]
---------------	--



Peak#	R.Time	E.Time	Area	Area%	Height
1	4.484	4.547	2403677	10.76	2089280
2	5.737	5.807	2239055	10.02	1849696
3	8.446	8.540	1321476	5.91	1021796
4	12.242	12.347	1588951	7.11	1282338
5	14.119	14.207	6465990	28.94	6294562
6	14.435	14.513	484196	2.17	390322
7	16.145	16.227	7175170	32.11	6502187
8	18.173	18.247	667307	2.99	525039
			22345822	100.00	19955220

Figure S11: GC-MS chromatogram obtained for the self-metathesis of **13e**

Calculation details:

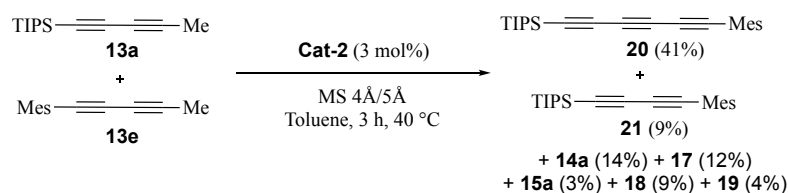
Yield of **17** = $13.7 * [(7175170 / 2403677) - 0.0595] = 40\%$

Ratio **17** / **18** / **19** = 0.015 corresponding to a ratio of 50 / 45 / 5

V- Mo-catalyzed cross-metathesis of diynes

Note: All reactions were carried out in a glove-box with degassed solvents. The powdered molecular sieves 4 Å (CAS: 70955-01-0; Ref. No. 11424553 Alfa Aesar™) and 5 Å (CAS: 69912-79-4; Ref. No. 10296980 Acros Organics™) were heated with a heatgun (~ 300 °C for 10 min at 1 mbar) prior to introduction into the glove box.

Cross metathesis of triisopropyl(penta-1,3-diyne-1-yl)silane (**13a**) and 1,3,5-trimethyl-2-(penta-1,3-diyne-1-yl)benzene (**13e**) (Scheme 3, c)



A stock solution of catalyst **Cat-2** (5.0 mg) in toluene (500 µL) was prepared in the glove-box. To a microwave tube charged with TIPS-diyne **13a** (7.1 mg, 0.032 mmol, 1.0 equiv.) and Mes-diyne **13e** (5.6 mg, 0.031 mmol, 1.0 equiv.) were added powdered molecular sieves 4 Å (60 mg) and powdered molecular sieves 5 Å (60 mg) in toluene (250 µL). Then 100 µL of the previously prepared stock solution of catalyst **Cat-2** (0.00096 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box and acetophenone (9.1 µL, 0.078 mmol, 4.0 equiv.) was added. Approximately 100 µL of this solution was removed, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC and GS-MS. All products were identified and results are available in Table S3.

• GC-MS analysis:

Description of GC-method:

Instrument:	GC-MS Shimadzu QP2010SE
Carrier gas:	Helium
Inlet temperature:	300 °C
Pressure :	79.5 kPa
Column flow:	40 cm / s
Split ratio:	20
External standard:	<i>n</i> -dodecane (2.0 equiv)

Temperature protocol:

Inj. Port : SPL1 Inj. Heat Port : INJ1

Column Oven Temp. : 80.0 °C

Injection Temp. : 300.0 °C

Injection Mode : Split

Sampling Time : 1.00 min

Carrier Gas : He Prim. Press. : 500-900

Flow Control Mode : Linear Velocity

Pressure : 79.5 kPa

Total Flow : 27.8 mL/min

Column Flow : 1.18 mL/min

Linear Velocity : 40.0 cm/sec

Purge Flow : 3.0 mL/min

Split Ratio : 20.0

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	80.0	0.00
1	15.00	330.0	20.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 36.67 min

Column

Name SH-Rxi-5ms Thickness : 0.25 um

Length : 30.0 m Diameter : 0.25 mm

High Press. Injection Carrier Gas Saver

Product	w%
TIPS — — — — TIPS	3%
Mes — — — — Mes	9%
TIPS — — — — Mes	9%
TIPS — — — — TIPS	14%
Mes — — — — Mes	12%
TIPS — — — — Mes	41%
TIPS — — — — TIPS	3%
Mes — — — — Mes	4%
TIPS — — — — Mes	1%

Table S3: GC-MS distribution obtained for the cross-metathesis of **13a** and **13c**

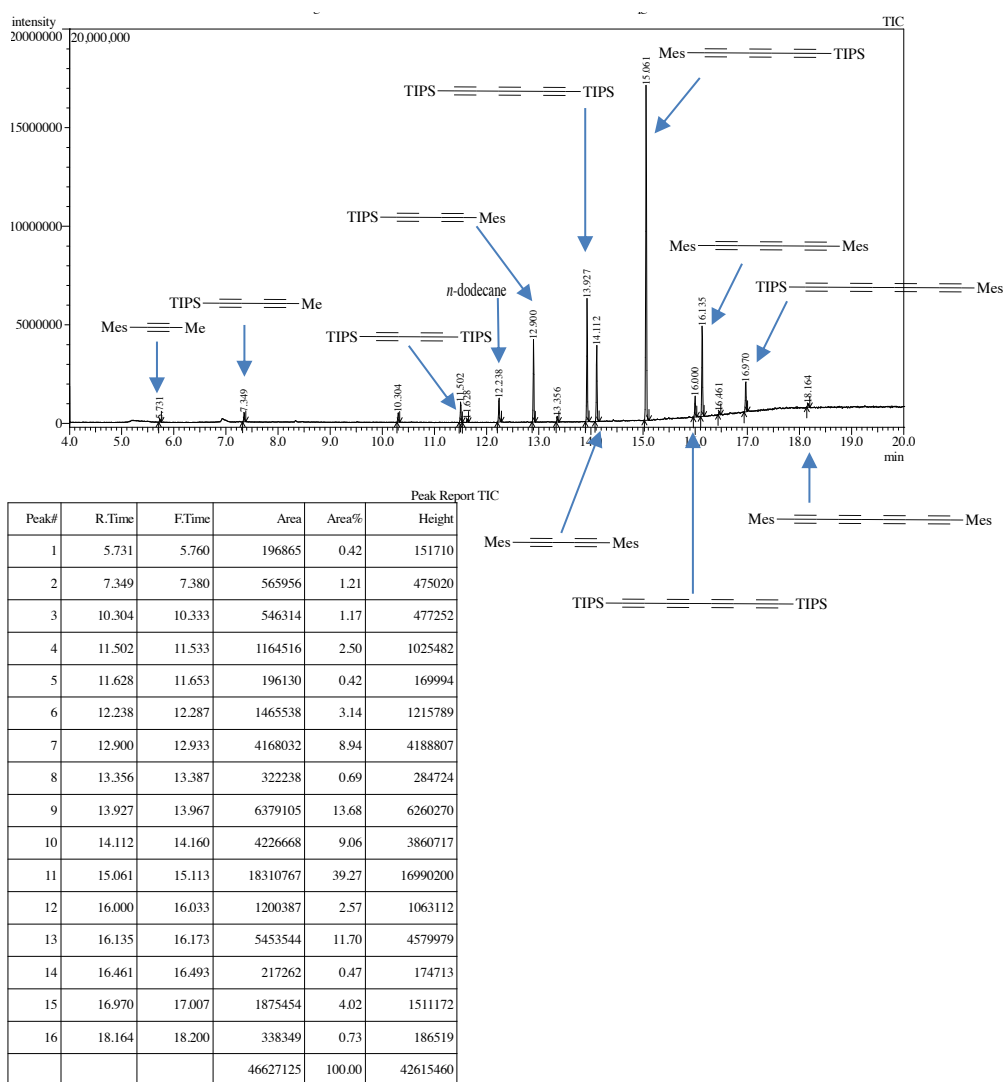
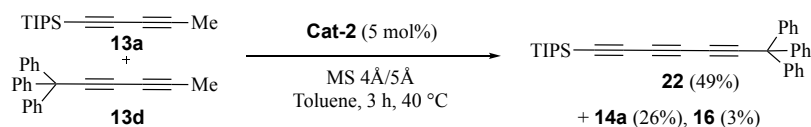


Figure S12: GC-MS chromatogram obtained for the cross-metathesis of **13a** and **13e**

Cross metathesis of triisopropyl(penta-1,3-diyne-1-yl)silane (13a**) and hexa-2,4-diyne-1,1,1-triyltribenzene (**13d**) (Scheme 3, d)**



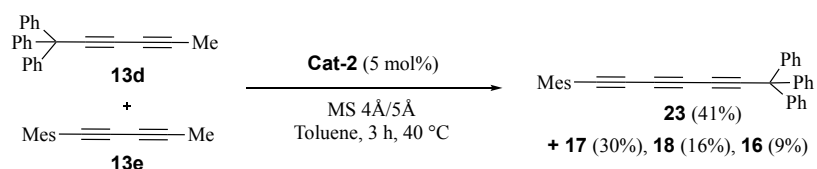
In the glove-box, to a microwave tube charged with TIPS-diyne **13a** (42.6 mg, 0.193 mmol, 1.0 equiv.) and trityl-diyne **13d** (58.7 mg, 0.192 mmol, 1.0 equiv.) were added powdered molecular sieves 4 Å (380 mg) and powdered molecular sieves 5 Å (380 mg) in toluene (2.1 mL). Then catalyst **Cat-2** (10.0 mg, 0.0096 mmol, 5 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box. The crude reaction

mixture was filtered through a pad of silica and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:DCM 100:0 to 90:10) and the obtained solid was washed with pentane to give the desired triyne **22** as white solid (44.0 mg, 0.093 mmol, **49% yield**). $R_f = 0.30$ (*n*-pentane). m.p. 280-282 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36-7.27 (m, 9 H), 7.24-7.18 (m, 6 H), 1.10 (s, 21 H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 129.2, 128.3, 127.4, 18.7, 11.4. **HRMS** (ESI) m/z calcd. for $\text{C}_{34}\text{H}_{37}\text{Si}$ $[\text{M}+\text{H}]^+$ 472.2581, found 472.2582.

Note: Along the purification over SiO_2 , triyne **14a** was obtained as a white solid (19.6 mg, 0.051 mmol, **26% yield**). Triyne **16** was also obtained as a white solid (2.8 mg, 0.005 mmol, **3% yield**).

Cross metathesis of 1,3,5-trimethyl-2-(penta-1,3-diyne-1-yl)benzene (**13e**) and hexa-2,4-diyne-1,1,1-triyltribenzene (**13d**) (Scheme 3, e)



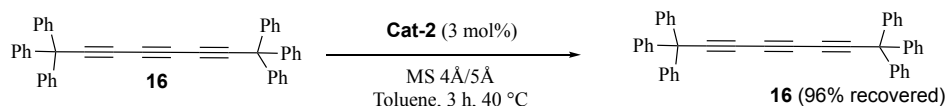
In the glove-box, to a microwave tube charged with TIPS-diyne **13e** (26.0 mg, 0.140 mmol, 1.0 equiv.) and trityl-diyne **13d** (43.0 mg, 0.140 mmol, 1.0 equiv.) were added powdered molecular sieves 4 Å (260 mg) and powdered molecular sieves 5 Å (260 mg) in toluene (1.5 mL). Then catalyst **Cat-2** (7.5 mg, 0.0072 mmol, 5 mol%) was added and the reaction was stirred for 3 hours at 40 °C. Then the microwave tube was removed from the glove box. The crude reaction mixture was filtered through a pad of silica and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:DCM 100:0 to 90:10) and the obtained solid was washed with pentane to give the triyne **23** as a pale yellow solid (25.1 mg, **41% yield**).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.35-7.25 (m, 15 H), 6.88 (s, 2 H), 2.42 (s, 6 H), 2.31 (s, 3 H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.7, 144.1, 142.8, 139.5, 129.2, 128.3, 128.0, 127.3, 117.9, 86.5, 81.4, 75.4, 70.4, 68.0, 63.2, 56.7, 21.6, 21.0. **HRMS** (ESI) m/z calcd. for $\text{C}_{34}\text{H}_{27}$ $[\text{M}+\text{H}]^+$ 435.21073, found 435.2107.

Note: Along the purification over SiO_2 , triyne **17** and diyne **18** were obtained as an inseparable isolated mixture with a **17/18** ratio of 55/45. (19.8 mg, corresponding to an estimated yield of **30%** for **17** and **16%** for **18**). Triyne **16** was also obtained as a white solid (6.8 mg, 0.012 mmol, **9% yield**).

VI- Stability study of **16** and **14a** toward the Mo-benzylidyne catalyst **Cat-2**

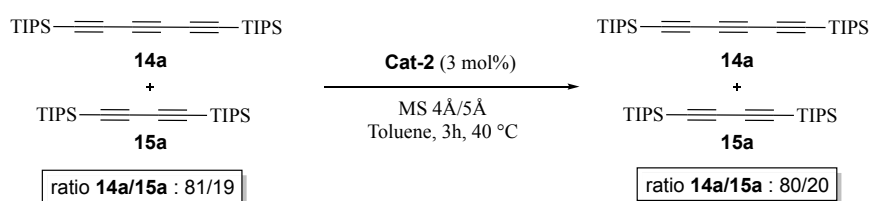
Stability study of **16**



A stock solution of catalyst **Cat-2** (4.1 mg) in toluene (410 μL) was prepared in the glove-box. In the glove-box, to a microwave tube charged with a trityl-triynes **16** (20.4 mg, 0.037 mmol, 1.0 equiv.) were added powdered molecular sieves 4 \AA (70 mg) and powdered molecular sieves 5 \AA (70 mg) in toluene (0.4 mL). Then 110 μL of the previously prepared stock solution of catalyst **Cat-2** (0.00106 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 $^\circ\text{C}$. Then the microwave tube was removed from the glove box. The crude reaction mixture was filtered through a pad of silica and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:DCM 100:0 to 90:10) and the obtained solid was washed with pentane to give the desired triynes **16** as white solid (19.8 mg, 0.035 mmol, **96% yield**).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32-7.20 (m, 30 H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.0, 129.2, 128.3, 127.4, 84.3, 70.2, 63.3, 56.6.

Stability study of **14a**



A stock solution of catalyst **Cat-2** (4.1 mg) in toluene (410 μL) was prepared in the glove-box. To a microwave tube charged with a mixture of TIPS-triynes **14a** and TIPS-diynes **15a** (81:19) (5.7 mg, 0.013 mmol, 1.0 equiv.) were added toluene (140 μL). Then a freshly prepared stock solution of catalyst **Cat-2** (40 μL , 0.00038 mmol, 3 mol%) was added and the reaction was stirred for 3 hours at 40 $^\circ\text{C}$. Then the microwave tube was removed from the glove box and acetophenone (6 μL , 0.051 mmol, 4.0 equiv.) was added. Approximately 100 μL of this solution was removed, filtered through syringe filter (0.2 μm , 25 mm) and rinsed with 1.5 mL of diethyl ether. The resulting solution was analyzed by GC.

- GC-trace of stability study of **14a** (with 3 mol% of **Cat-2** at 40 °C)

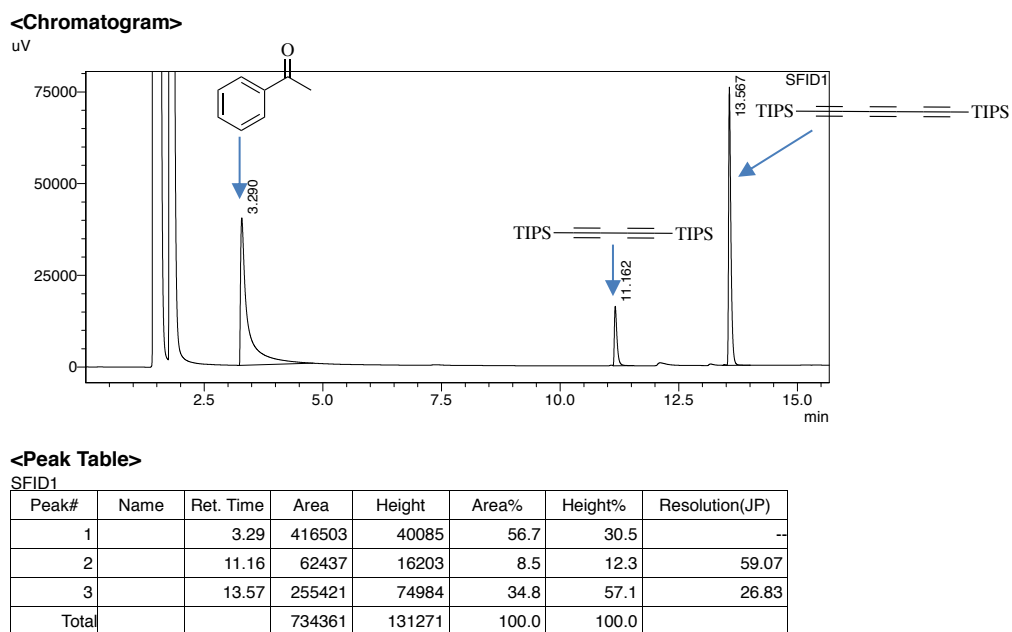


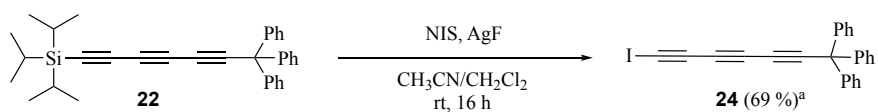
Figure S14: GC chromatogram

Calculation details:

$$\text{Yield of } \mathbf{14a} = 151.5 * [(255421 / 416503) - 0.0127] = 91\%$$

$$\text{Ratio } \mathbf{14a} / \mathbf{15a} = (255421 / 62437) = 4.09 \text{ corresponding to a ratio of } 80 / 20$$

VII- Post-functionalization of dissymmetrical triyne **22**



Compound **22** (36.1 mg, 0.076 mmol, 1.0 equiv.) was placed in a round bottom flask under an argon atmosphere and dissolved in acetonitrile:DCM (1:1) (1 mL). The flask was protected from light and N-iodosuccinimide (21.7 mg, 0.097 mmol, 1.3 equiv.) and silver fluoride (11.2 mg, 0.088 mmol, 1.2 equiv.) were added. After 16 h, 10 mL of CH₂Cl₂ were added and the solution was filtered through a pad of silica and volatiles were evaporated. The crude mixture was purified by column chromatography (Pentane:Et₂O 100:0 to 98:2) and the obtained solid was washed with pentane to give the desired triyne **24** as yellow solid (23.2 mg, 0.052 mmol, **69% yield**).

¹H NMR (400 MHz, CDCl₃): δ 7.33-7.28 (m, 9H), 7.24-7.21 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 143.9, 129.2, 128.4, 127.4, 83.5, 79.1, 69.6, 64.1, 59.2, 56.5. **HRMS** (ESI) *m/z* calcd. for C₂₅H₁₅I [M]⁺ 442.0234, found 442.1220.

VIII- NMR spectra

(*E*)-(4-chlorobut-3-en-1-yn-1-yl)-triisopropylsilane (**12a**)

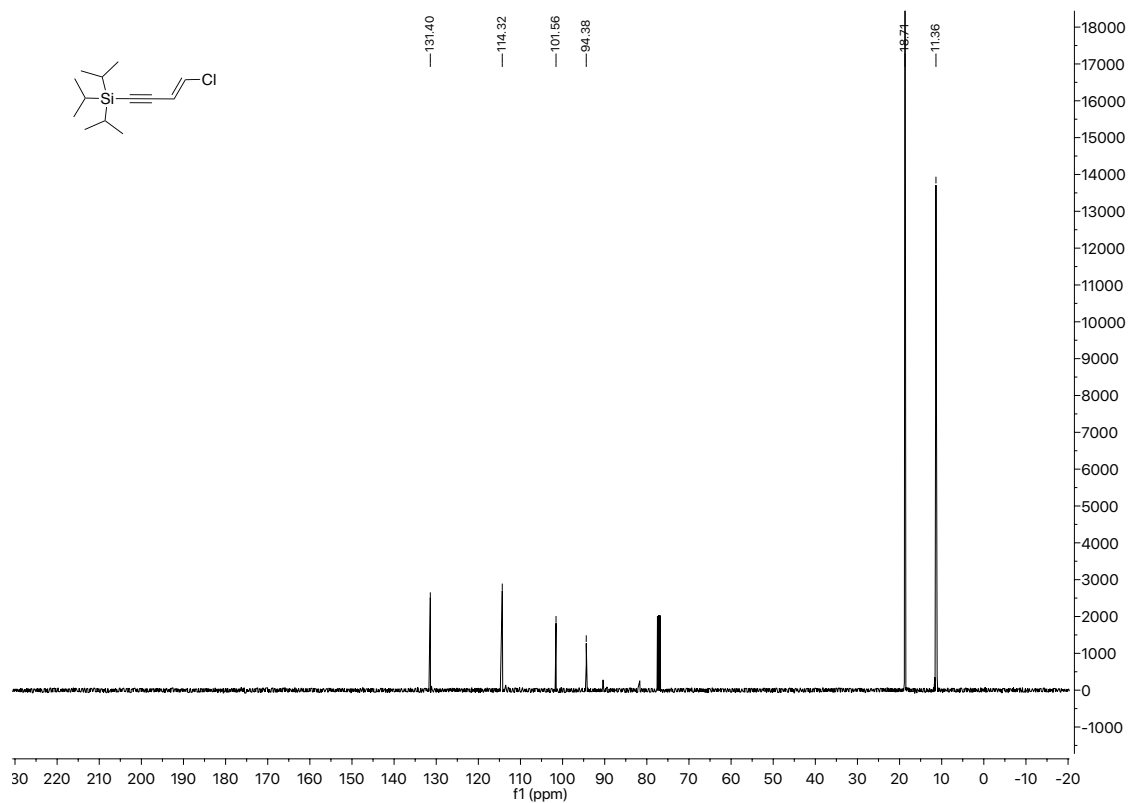
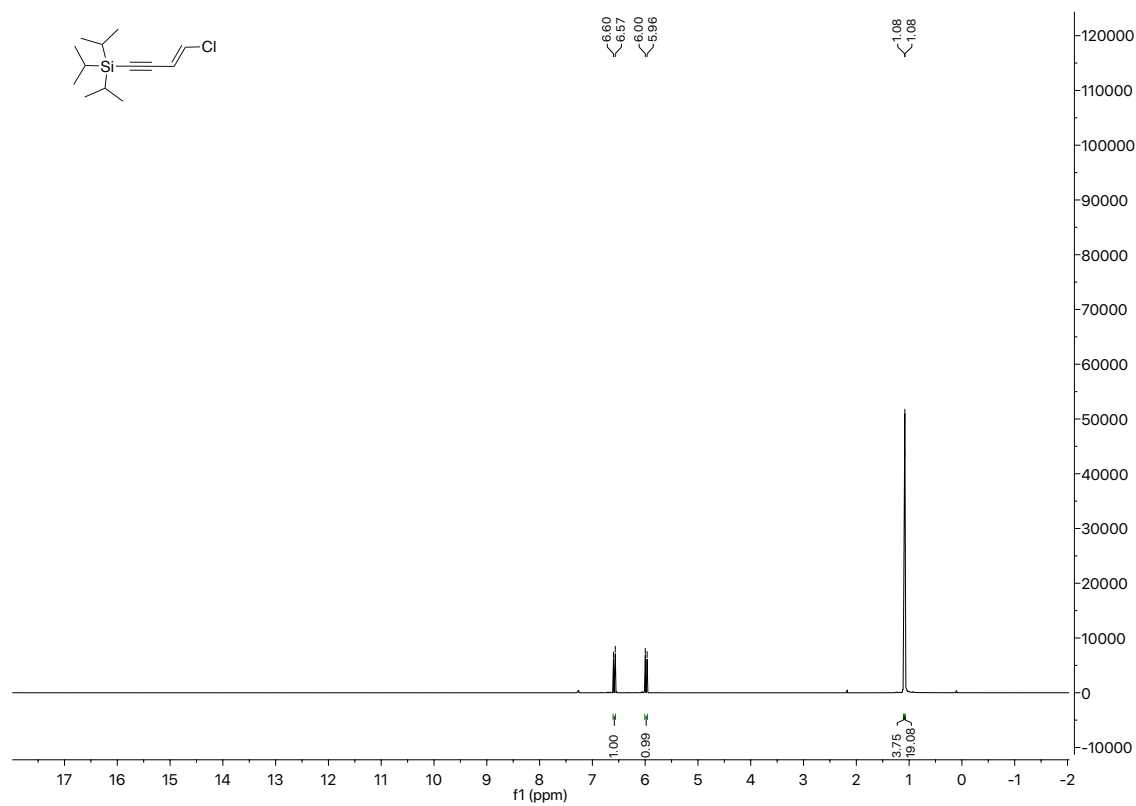


Figure S15: ¹H and ¹³C NMR spectra of **12a** in CDCl₃

Triisopropyl(penta-1,3-diynyl)silane (13a)

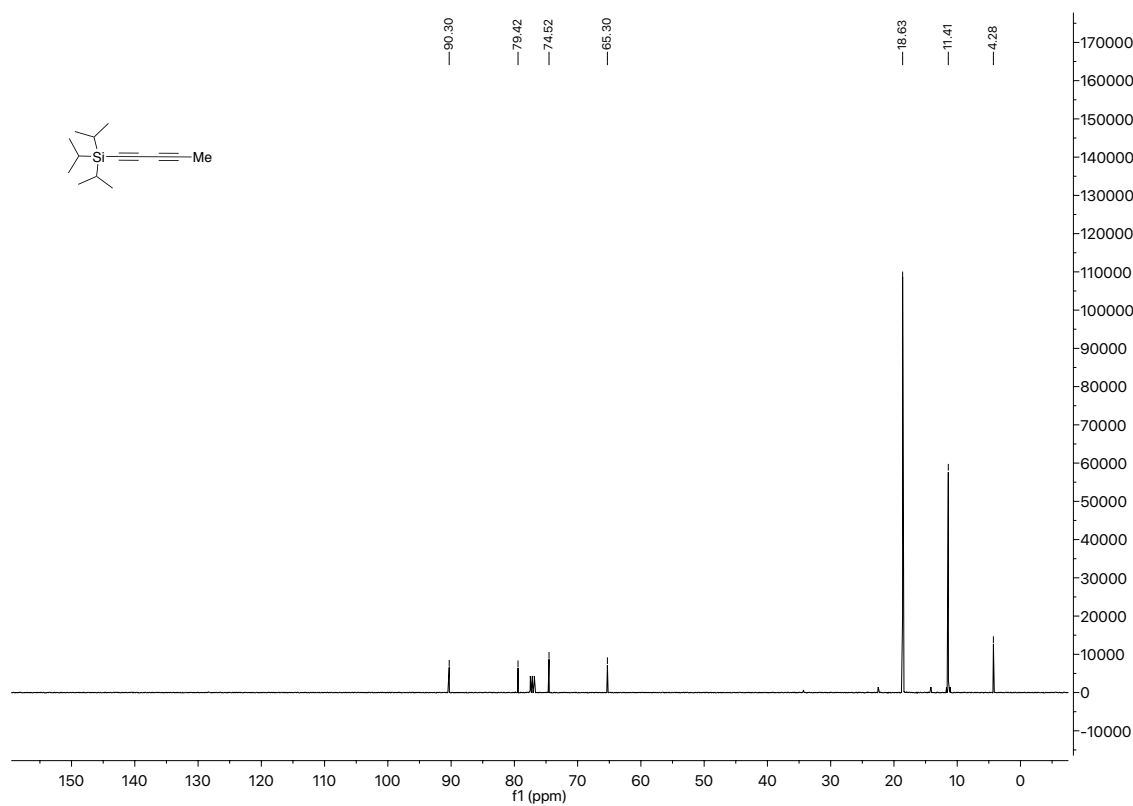
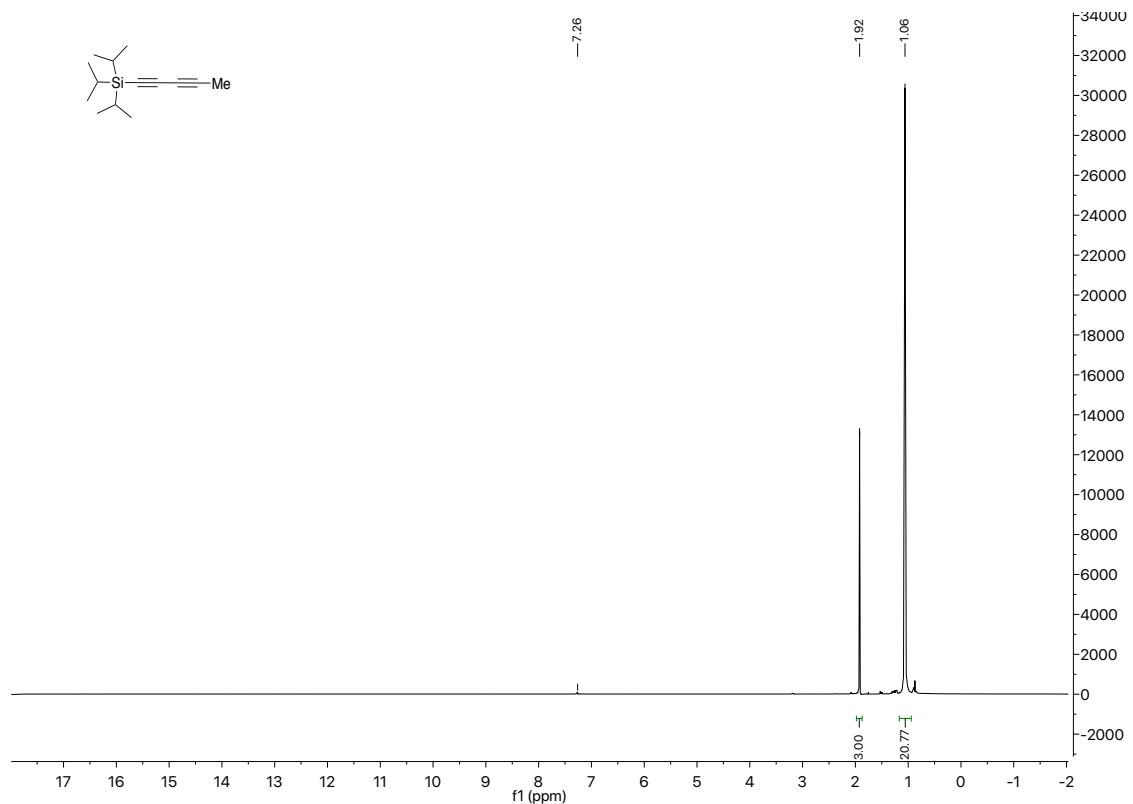


Figure S16: ^1H and ^{13}C NMR spectra of **13a** in CDCl_3

(E)-(4-chlorobut-3-en-1-yn-1-yl)triethylsilane (12b)

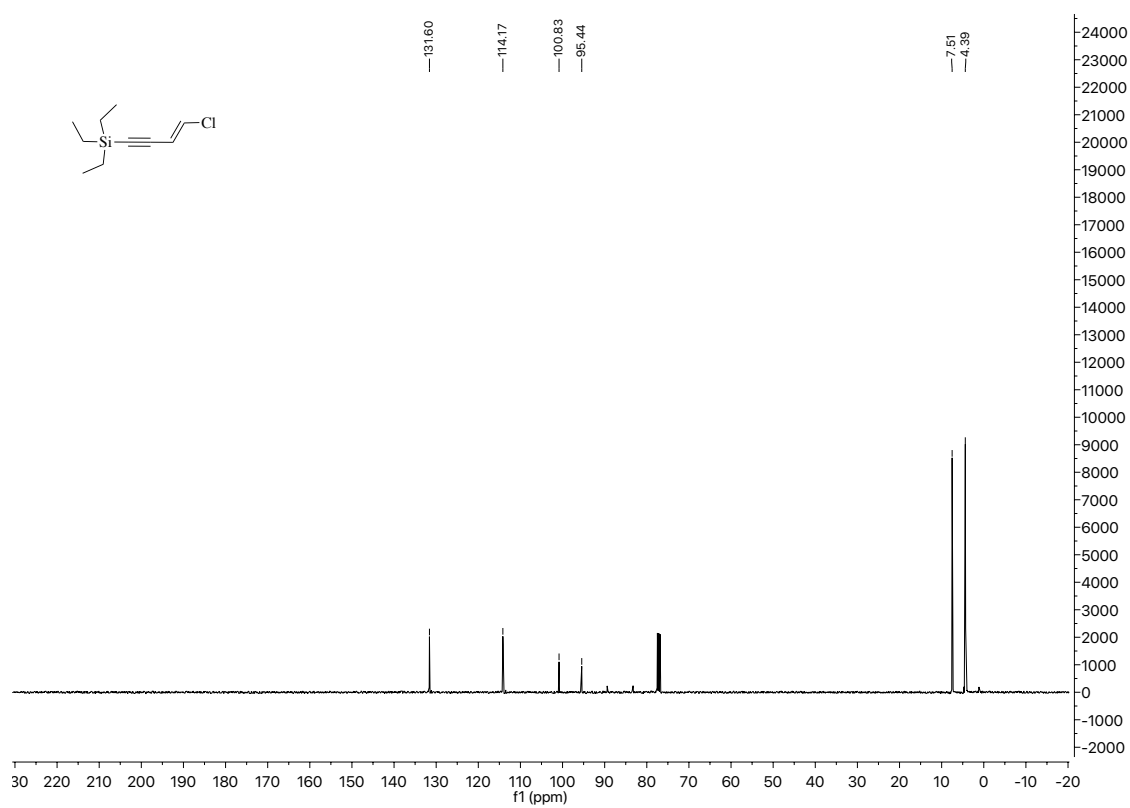
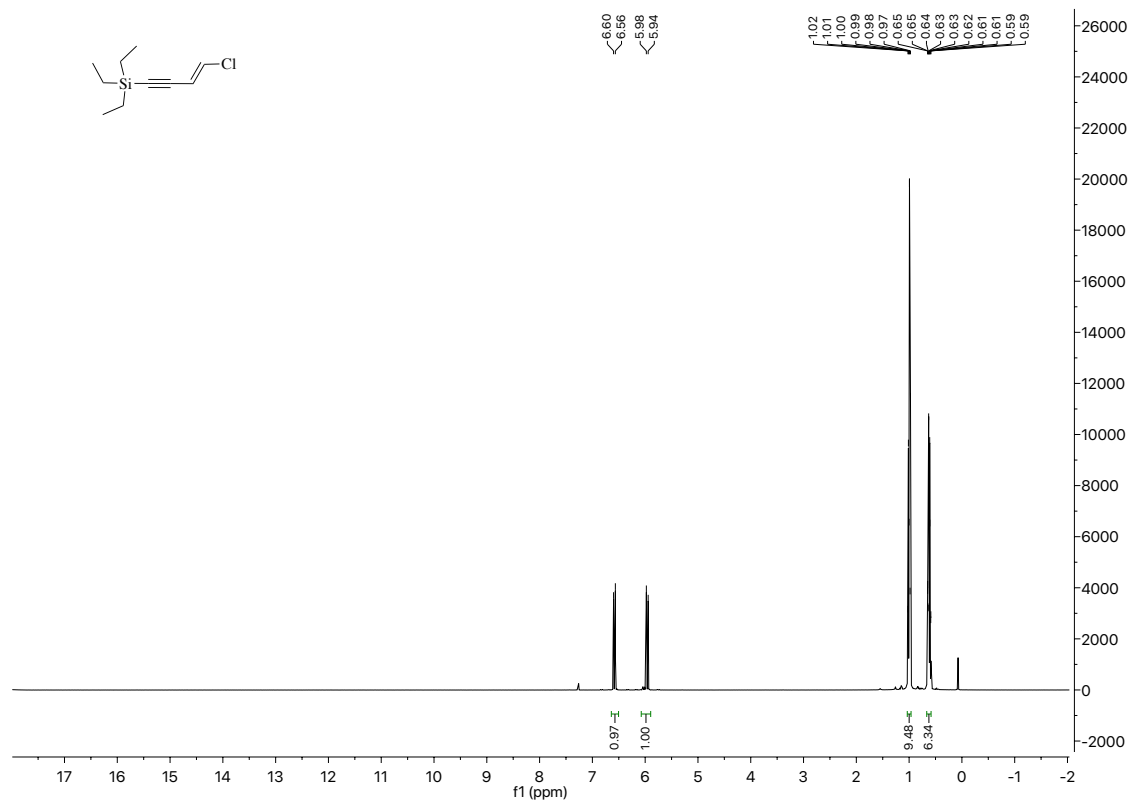


Figure S17: ^1H and ^{13}C NMR spectra of **12b** in CDCl_3

Triethyl(penta-1,3-diyn-1-yl)silane (13b)

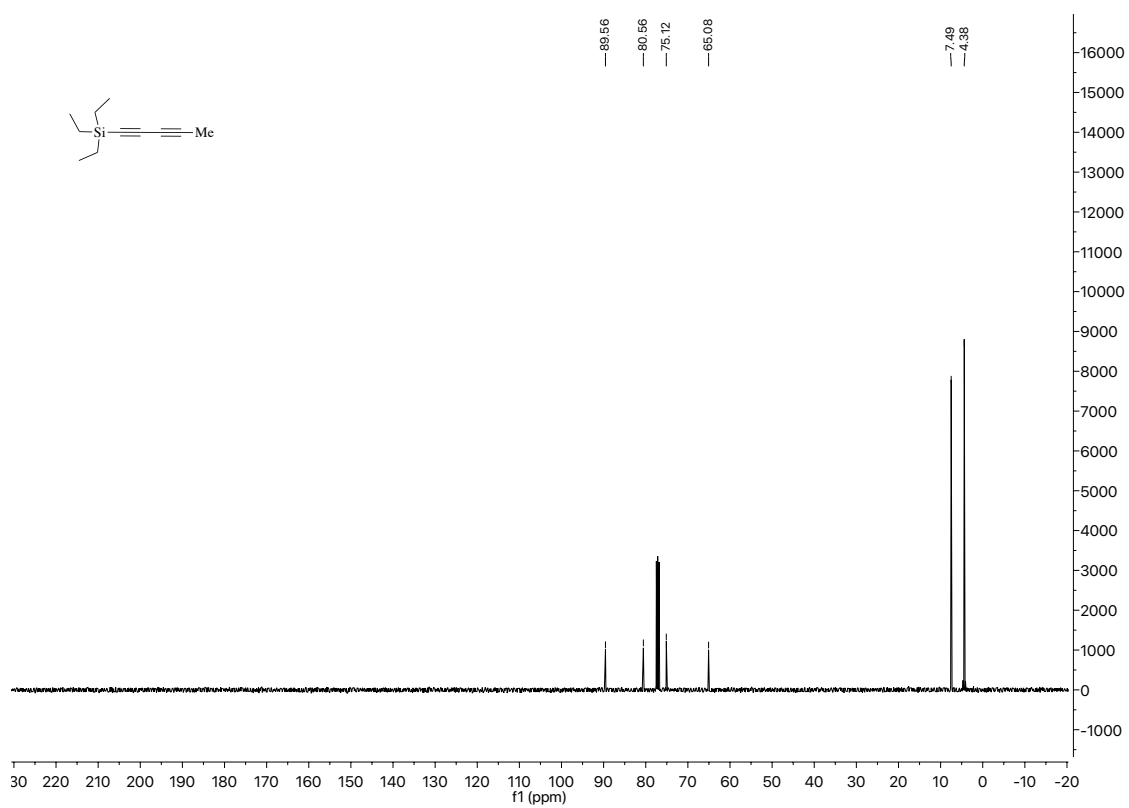
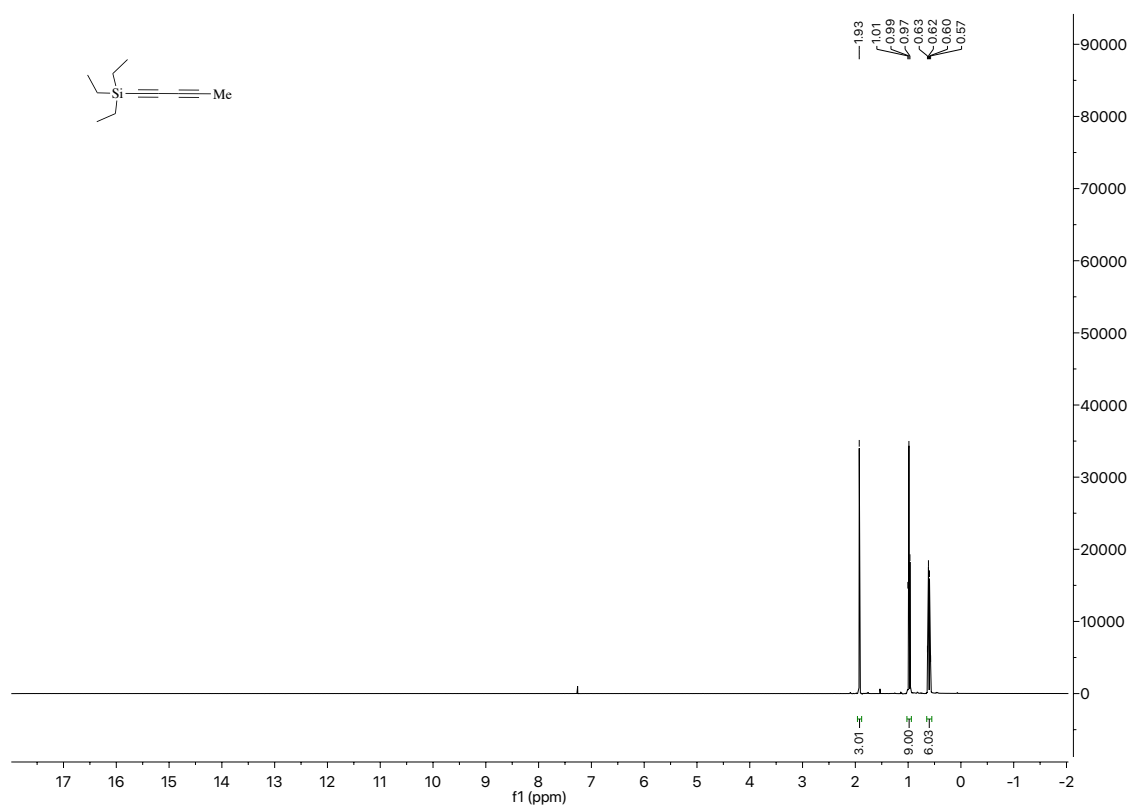


Figure S18: ^1H and ^{13}C NMR spectra of **13b** in CDCl_3

(E)-(4-chlorobut-3-en-1-yn-1-yl)triphenylsilane (12c)

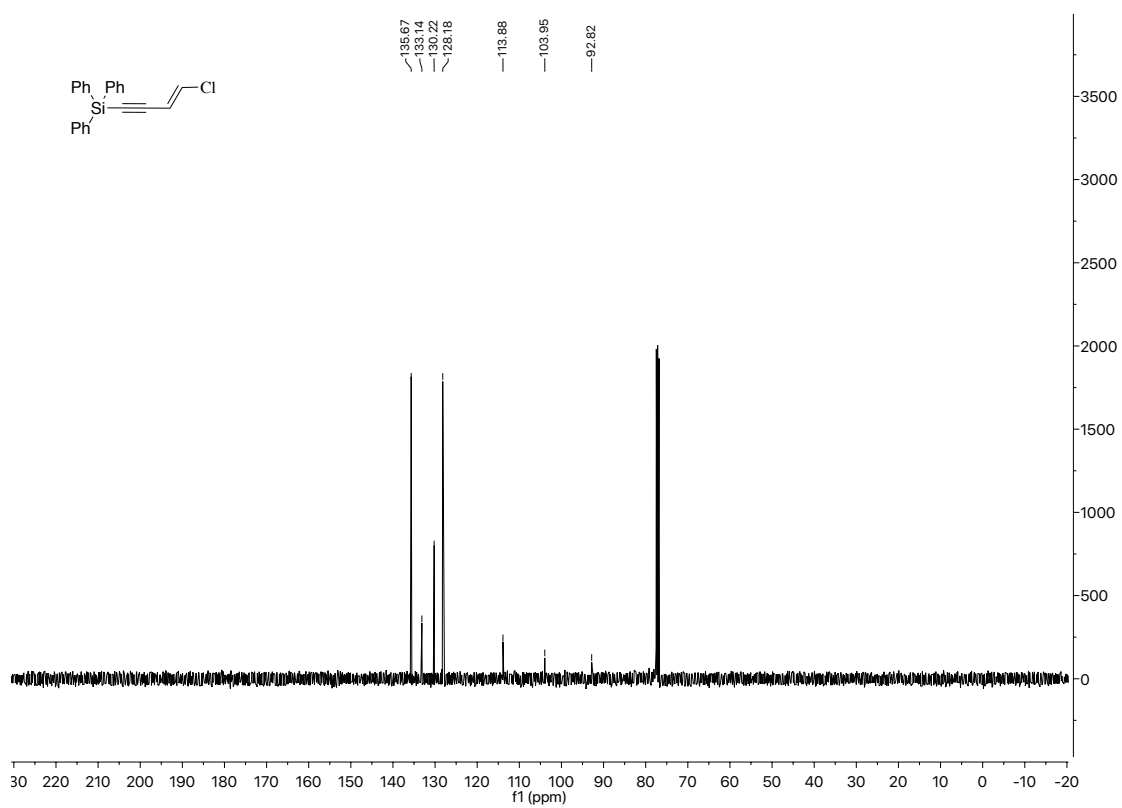
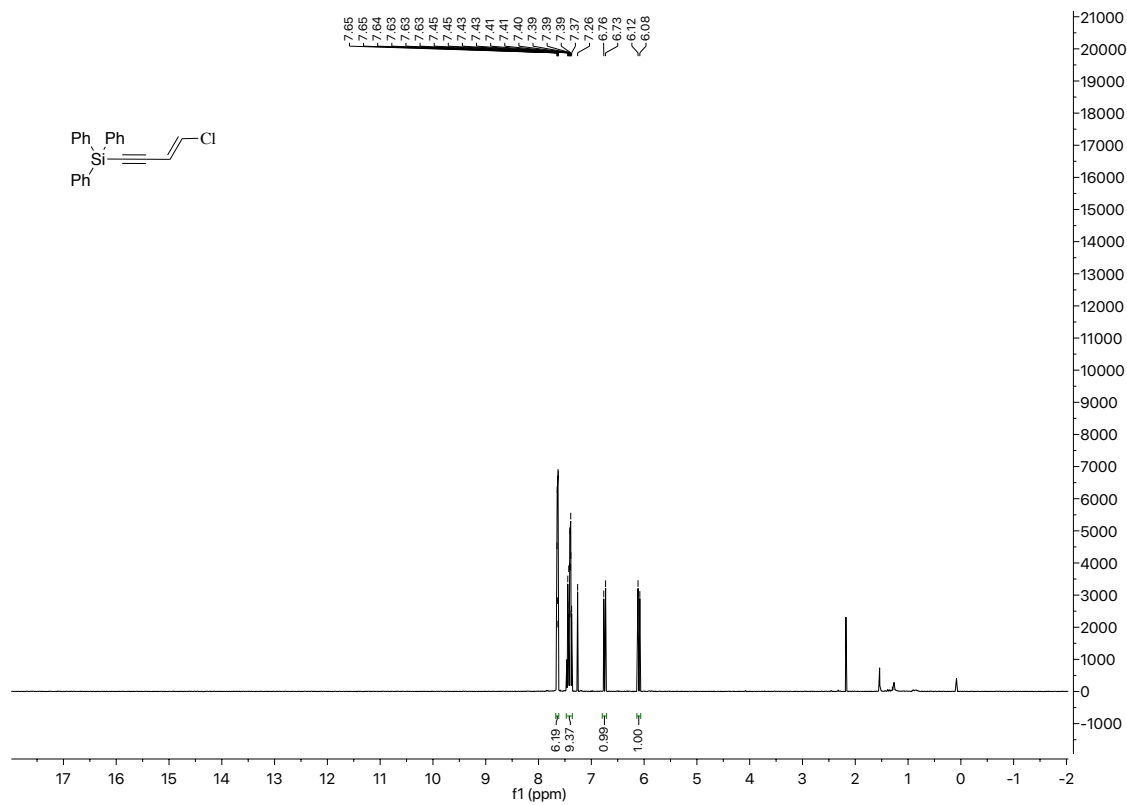


Figure S19: ¹H and ¹³C NMR spectra of **12c** in CDCl₃

(penta-1,3-diyne-1-yl)triphenylsilane (13c)

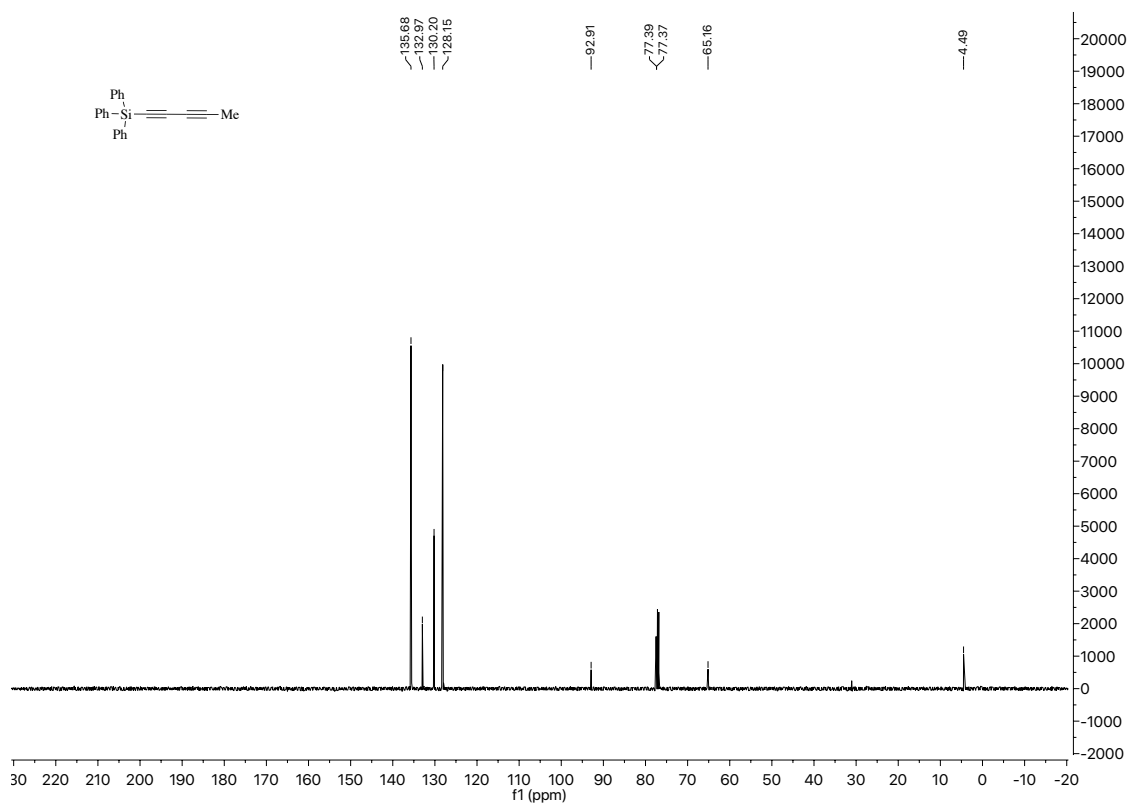
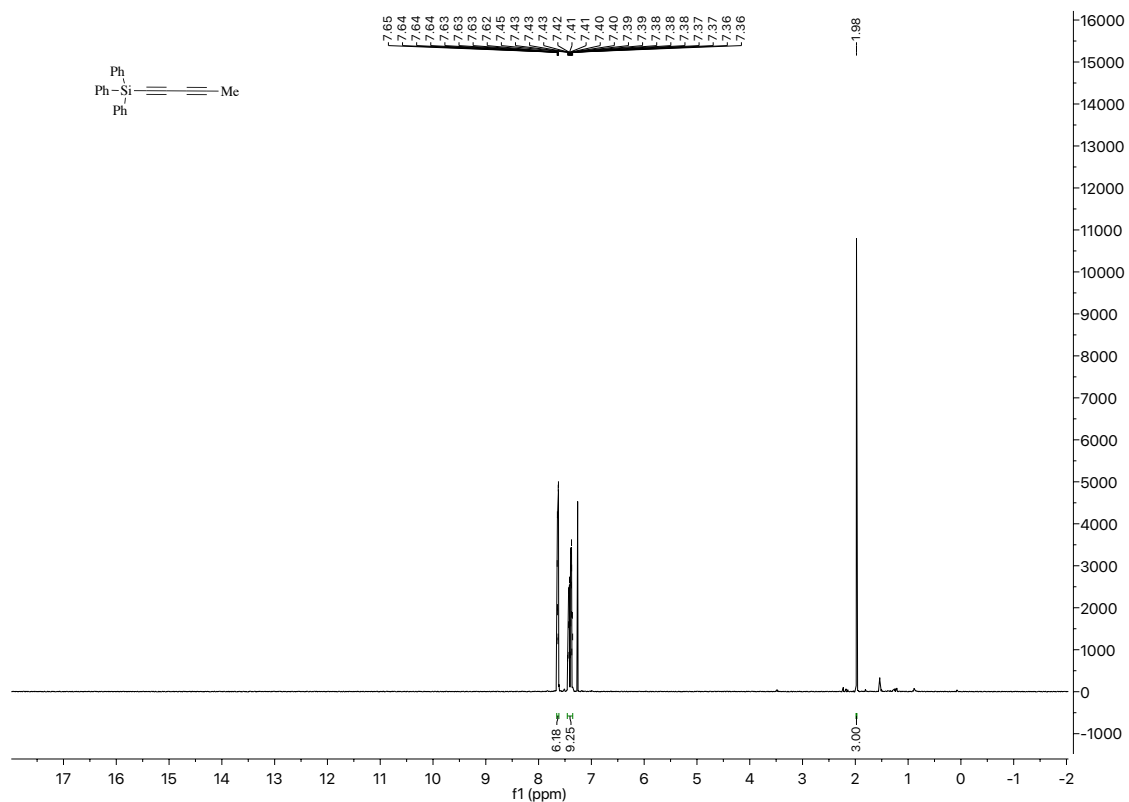


Figure S20: ¹H and ¹³C NMR spectra of 13c in CDCl₃

(E)-(3-chloroprop-2-ene-1,1,1-triyl)tribenzene (12d)

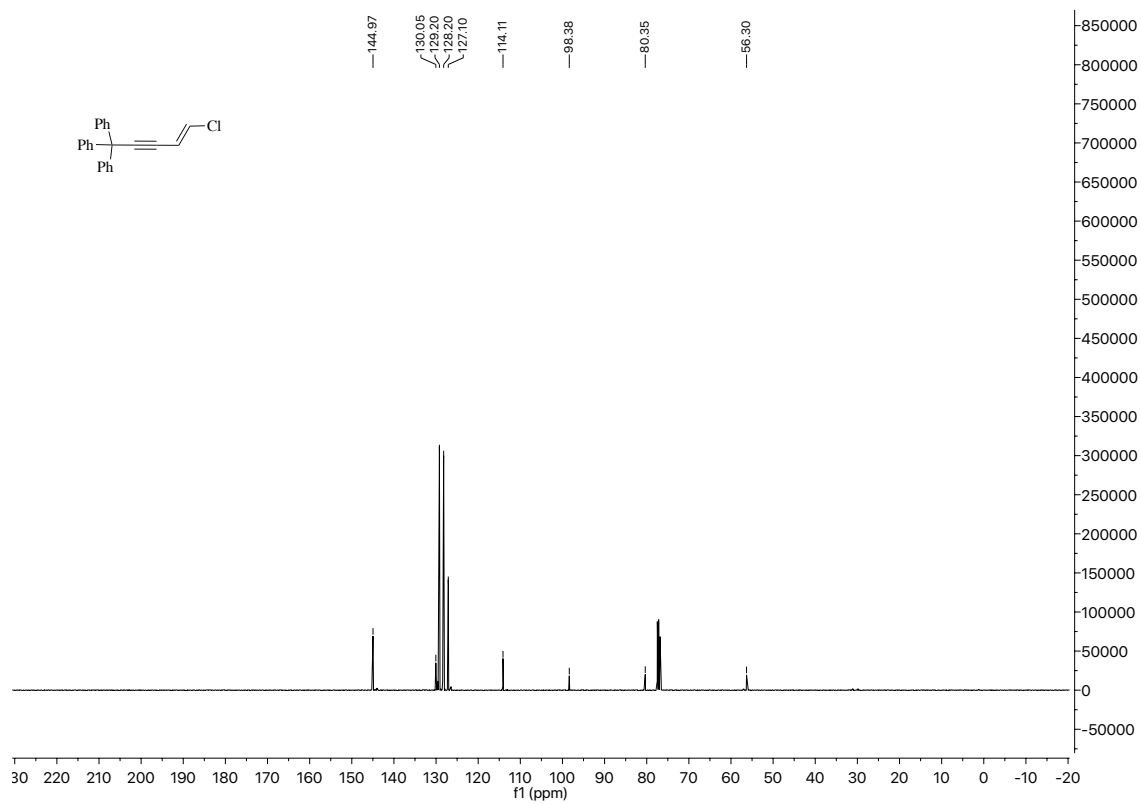
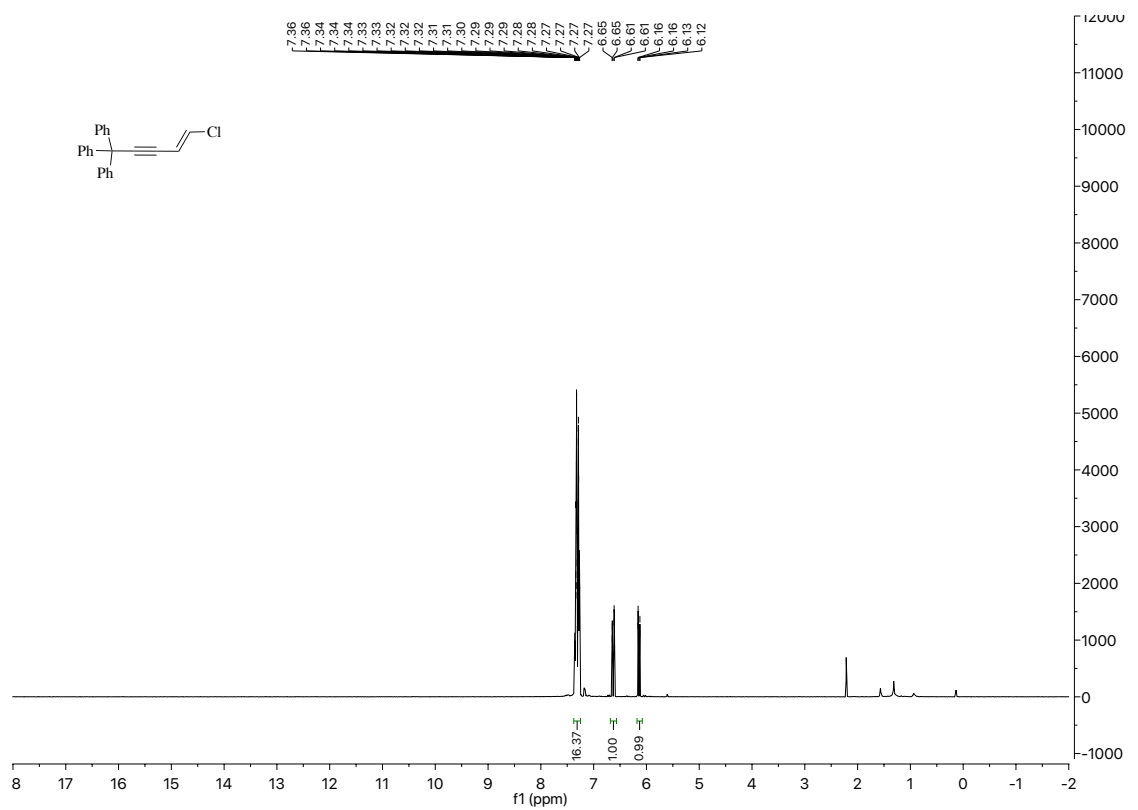


Figure S21: ¹H and ¹³C NMR spectra of **12d** in CDCl₃

Hexa-2,4-diyne-1,1,1-triyltribenzene (13d)

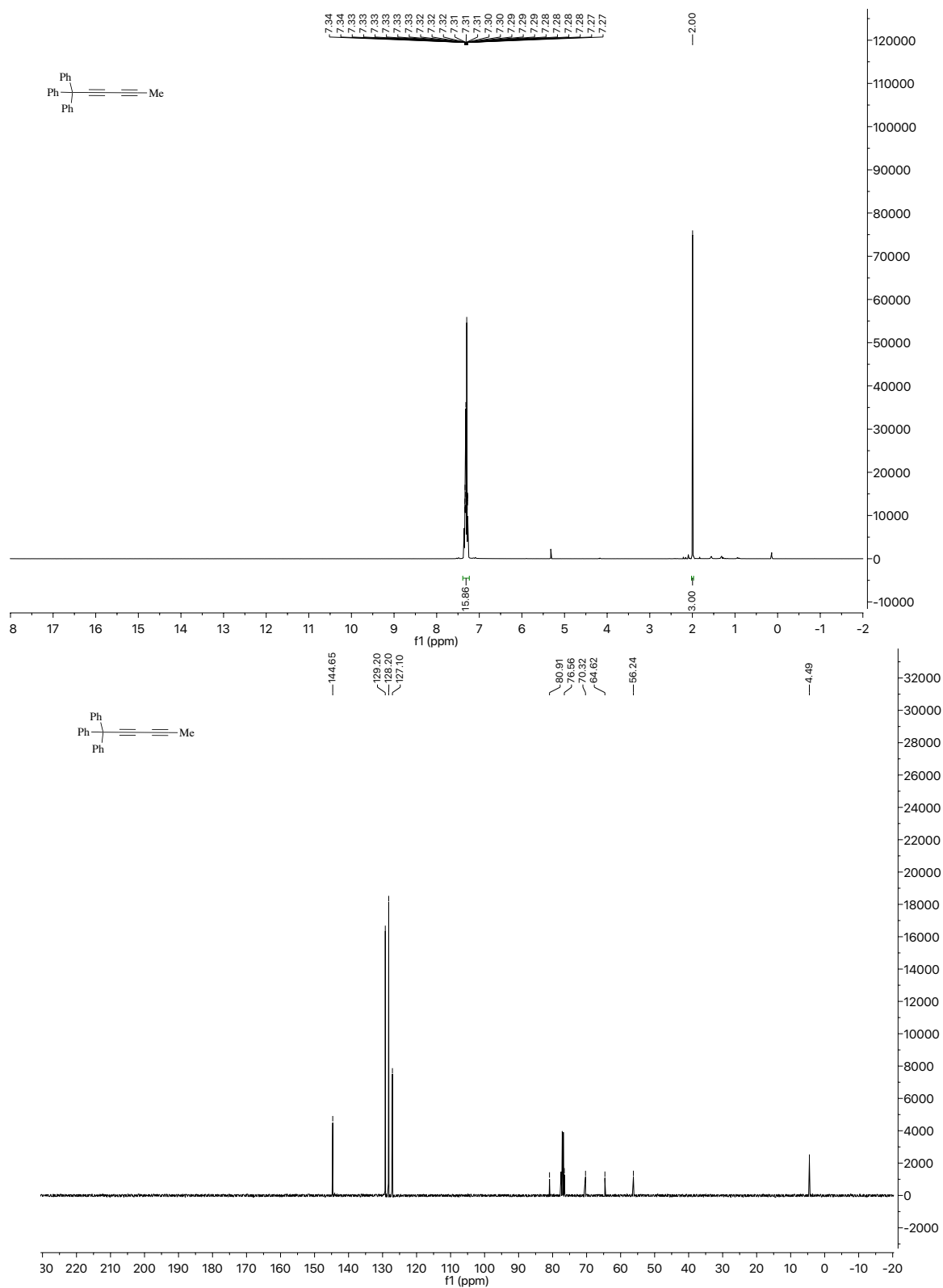


Figure S22: ¹H and ¹³C NMR spectra of **13d** in CDCl₃

(E)-(4-chlorobut-3-en-1-yn-1-yl)- 1,3,5-trimethylbenzene (12e)

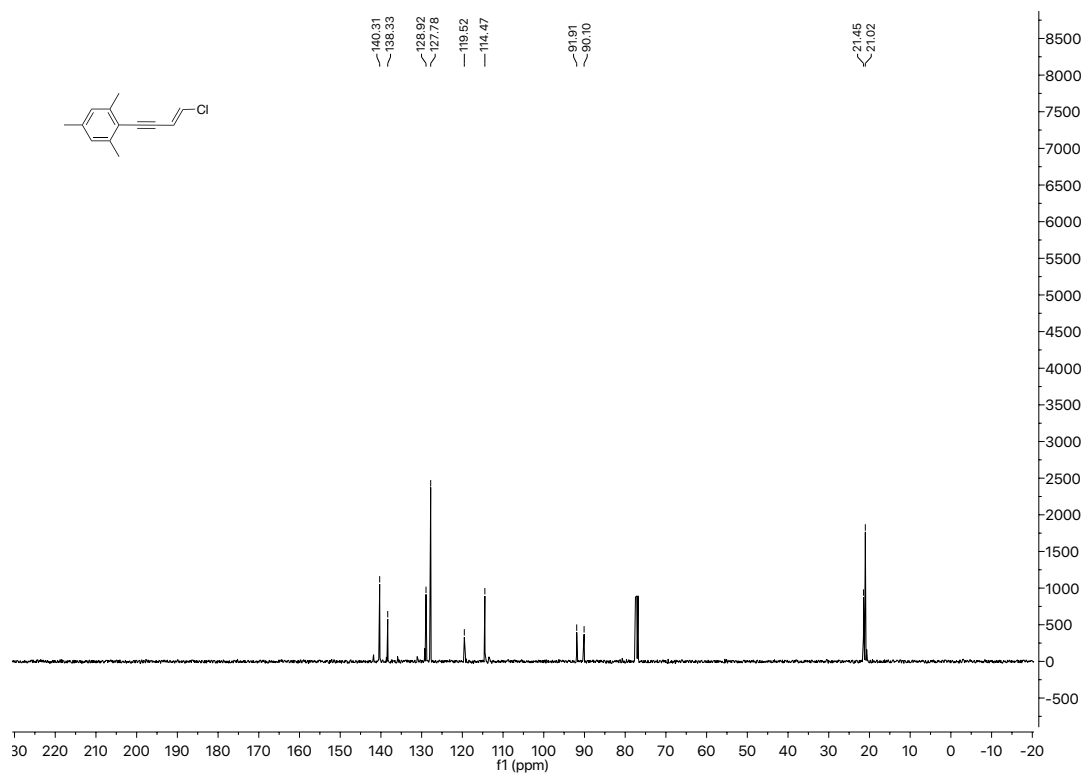
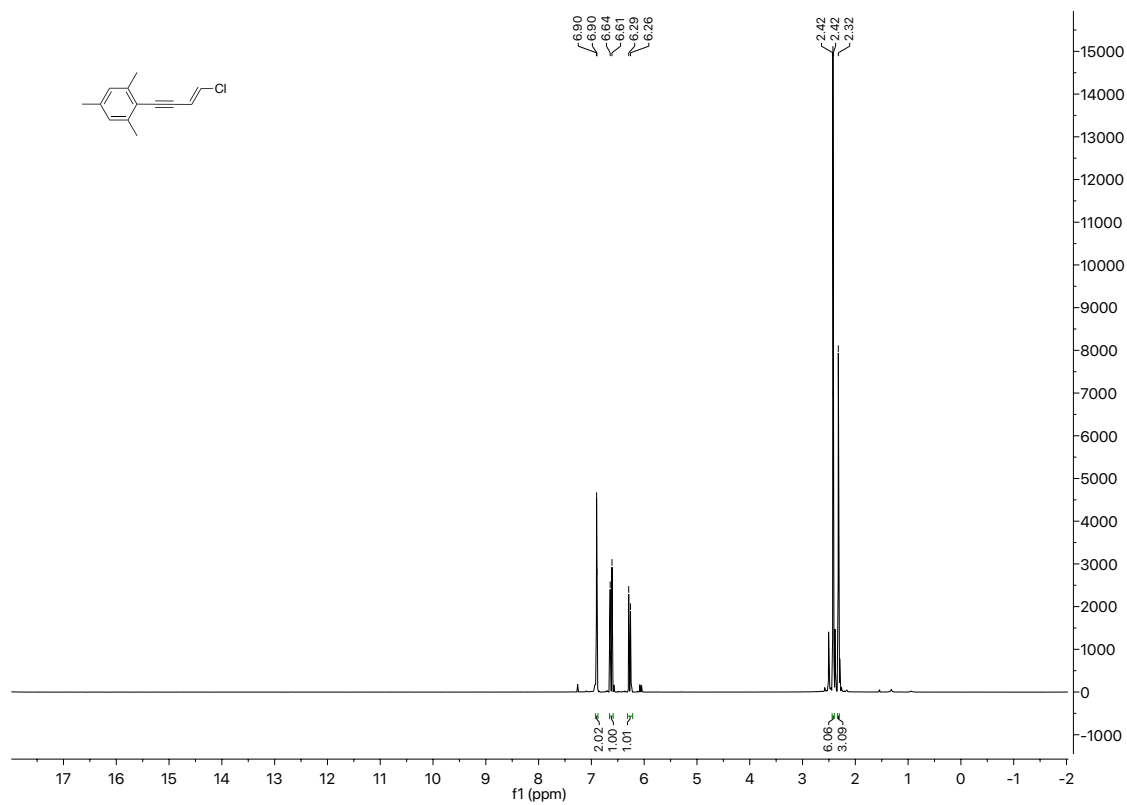


Figure S23: ^1H and ^{13}C NMR spectra of **12e** in CDCl_3

1,3,5-trimethyl-2-(penta-1,3-diyne-1-yl)benzene (13e)

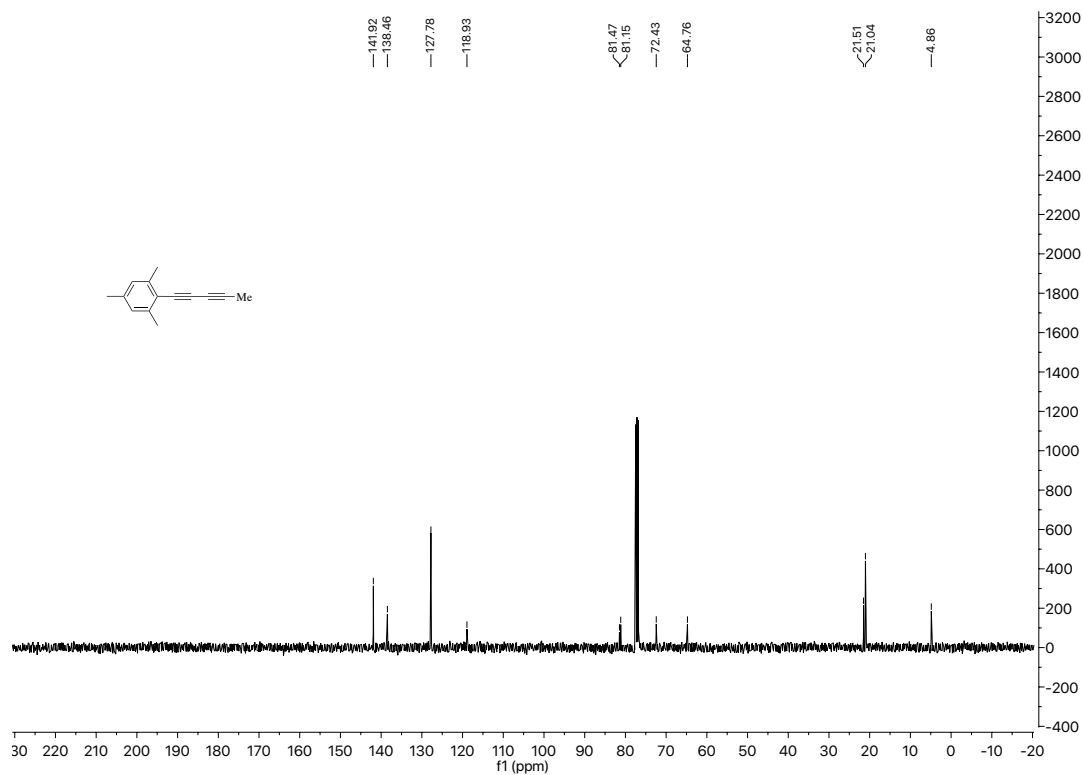
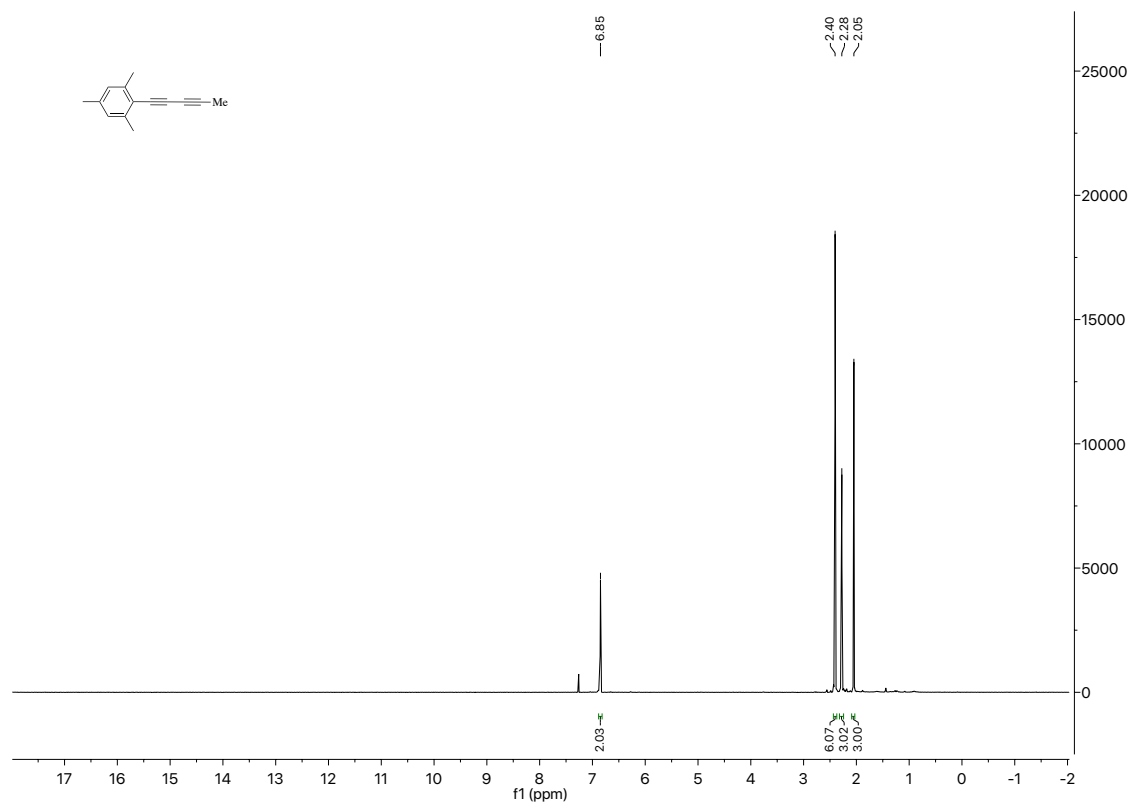


Figure S24: ^1H and ^{13}C NMR spectra of **13e** in CDCl_3

Bis-triisopropylsilylhexatriyne (14a)

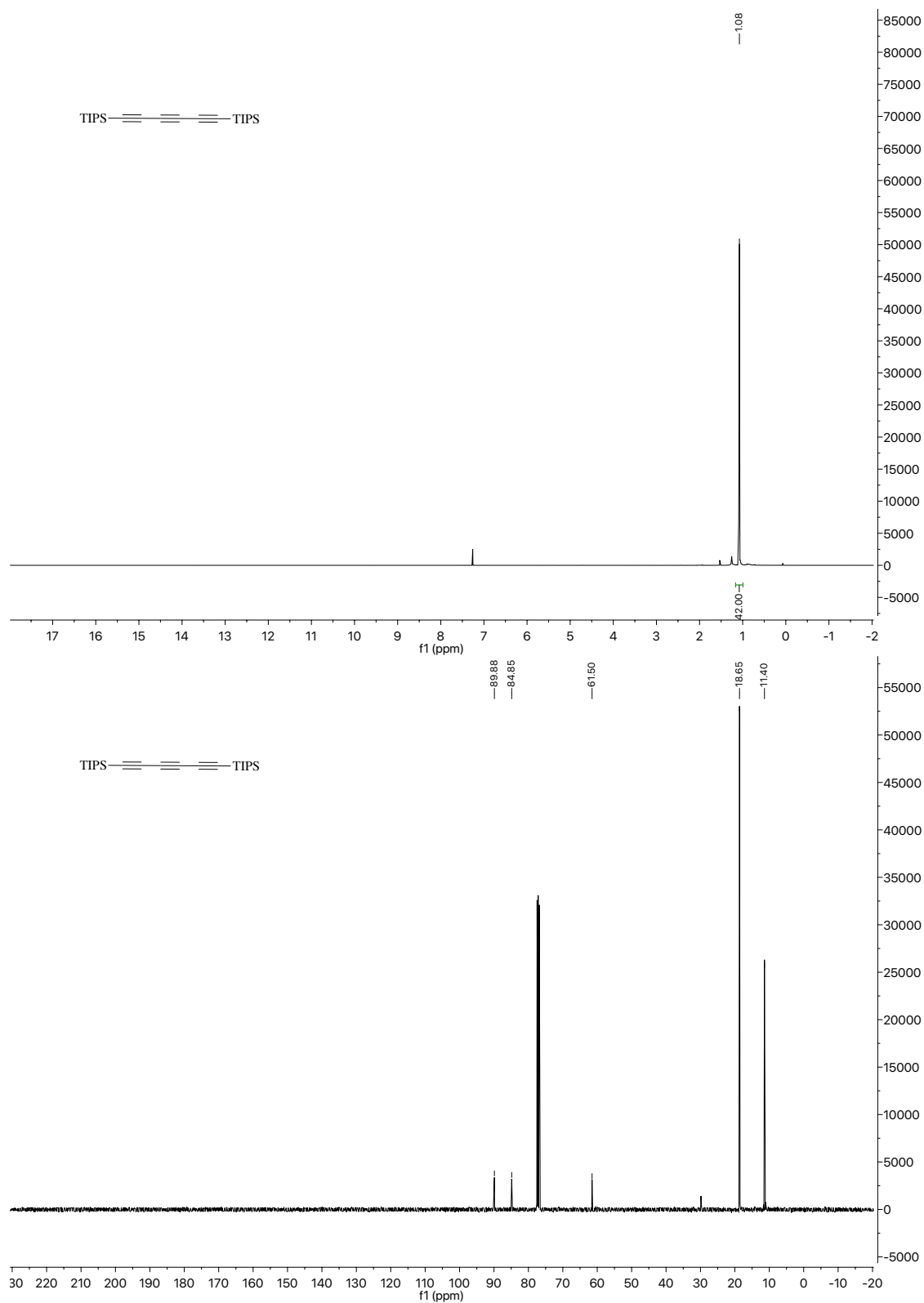


Figure S25: ¹H and ¹³C NMR spectra of 14a in CDCl₃

1,1,1,8,8,8-hexaphenylocta-2,4,6-triyn (16)

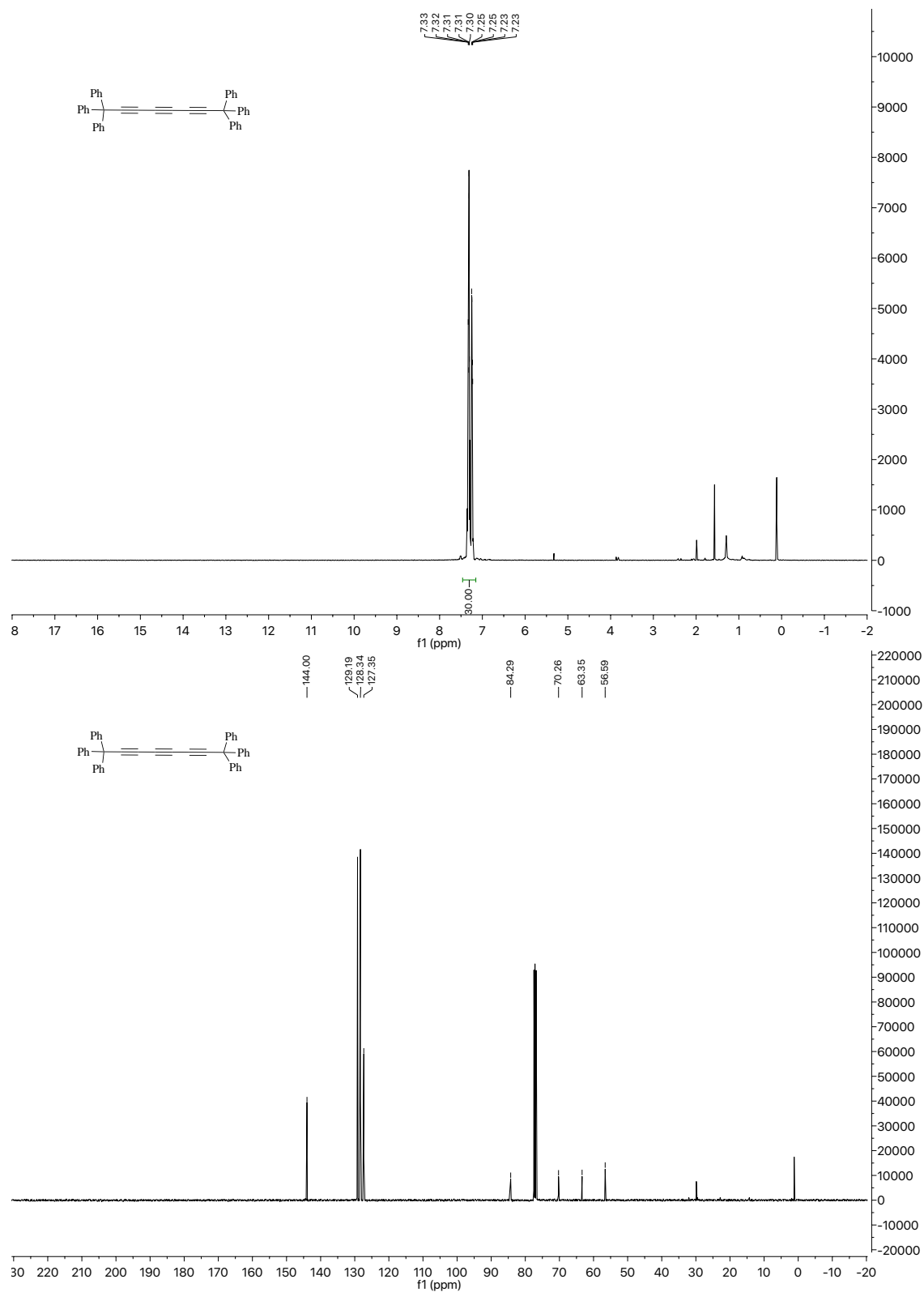


Figure S26: ¹H and ¹³C NMR spectra of 16 in CDCl₃

Triisopropyl(7,7,7-triphenylhepta-1,3,5-triyn-1-yl)silane (22)

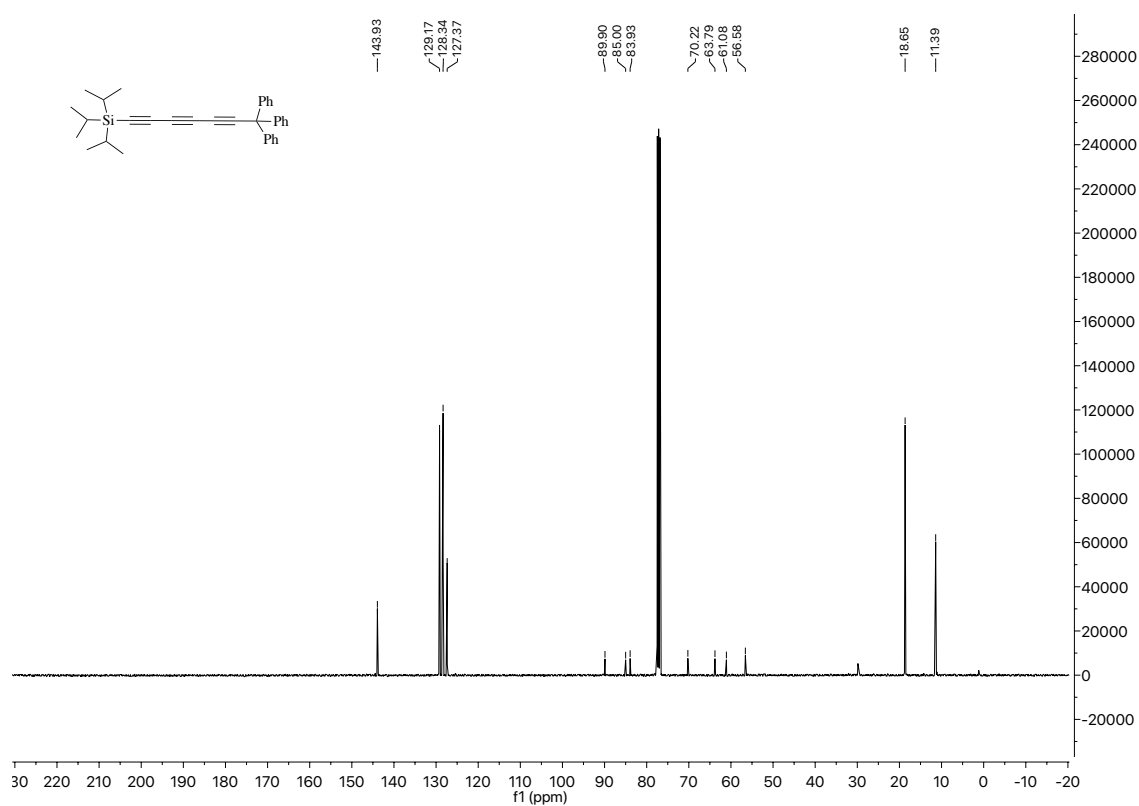
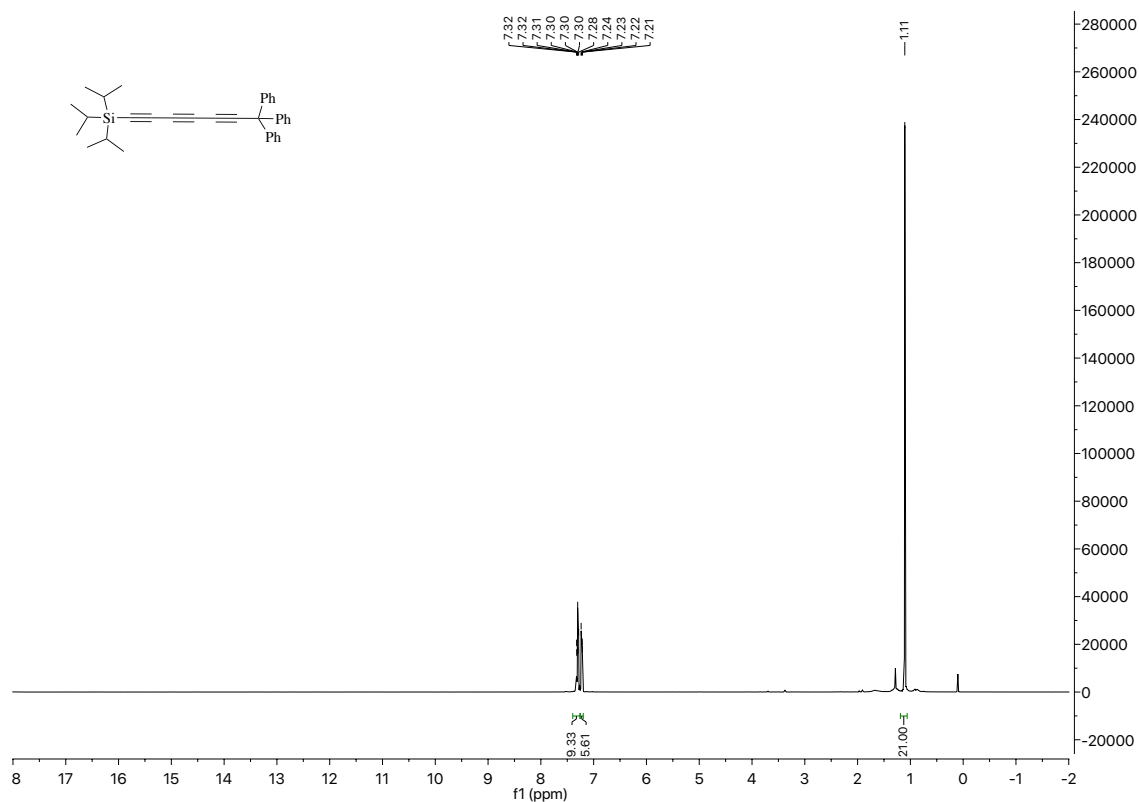


Figure S27: ¹H and ¹³C NMR spectra of 22 in CDCl₃

(7-mesitylhepta-2,4,6-triyn-1,1,1-triyl)tribenzene (23)

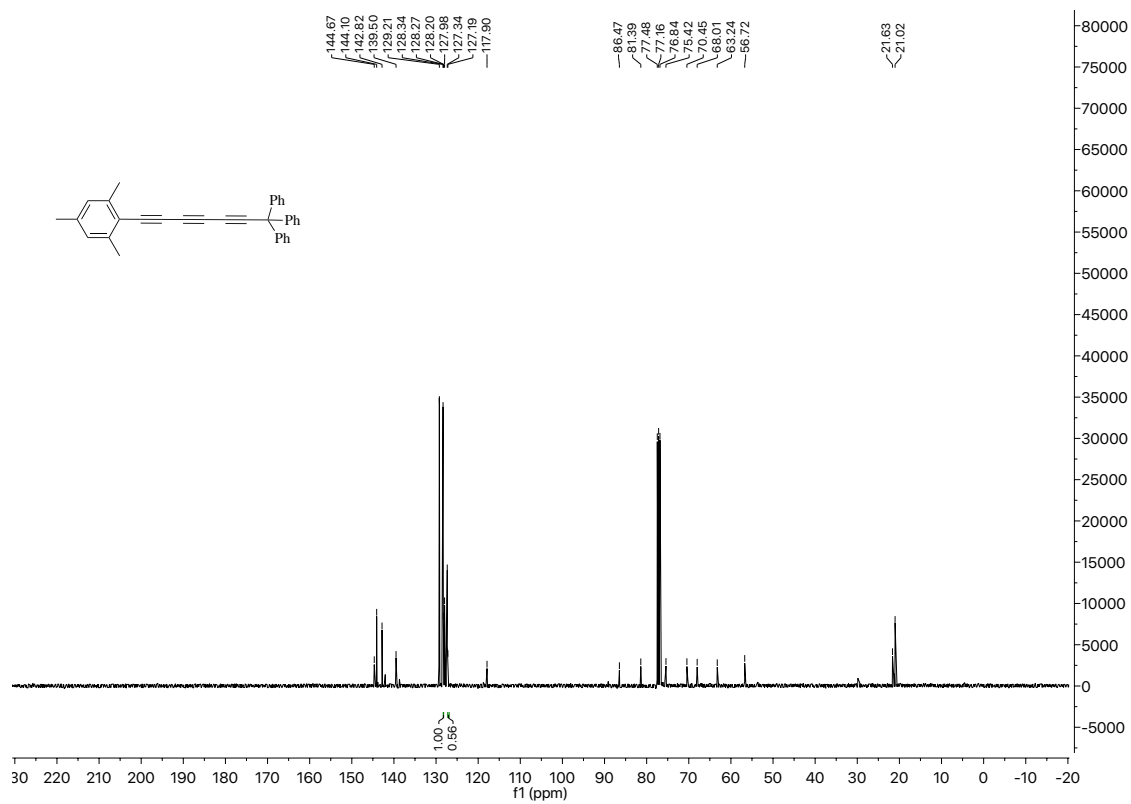
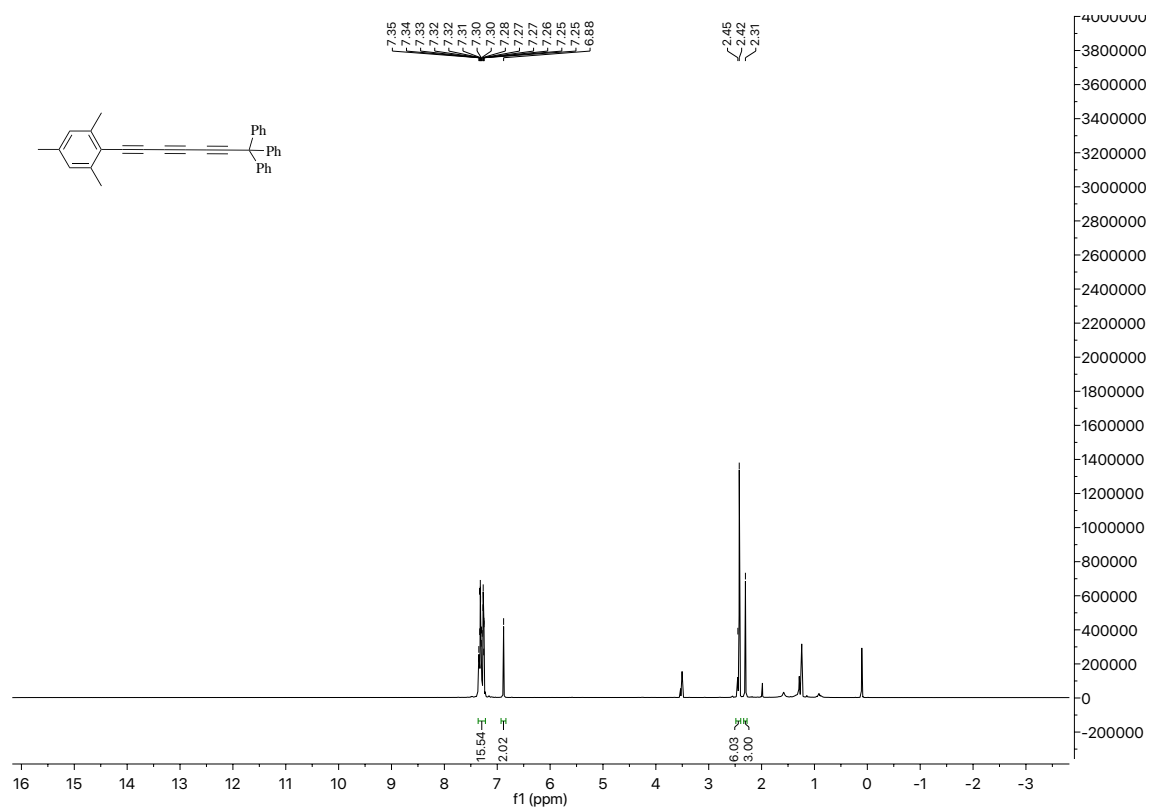


Figure S28: ¹H and ¹³C NMR spectra of 23 in CDCl₃

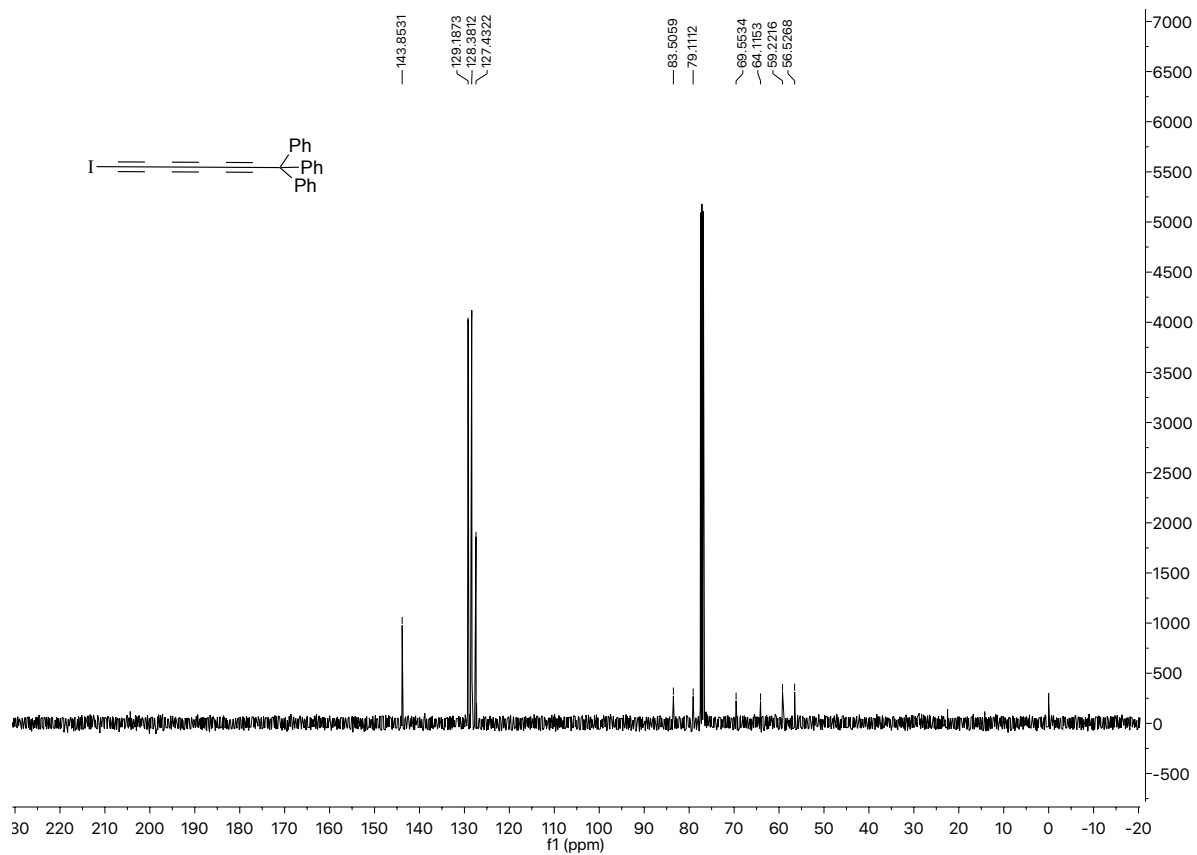
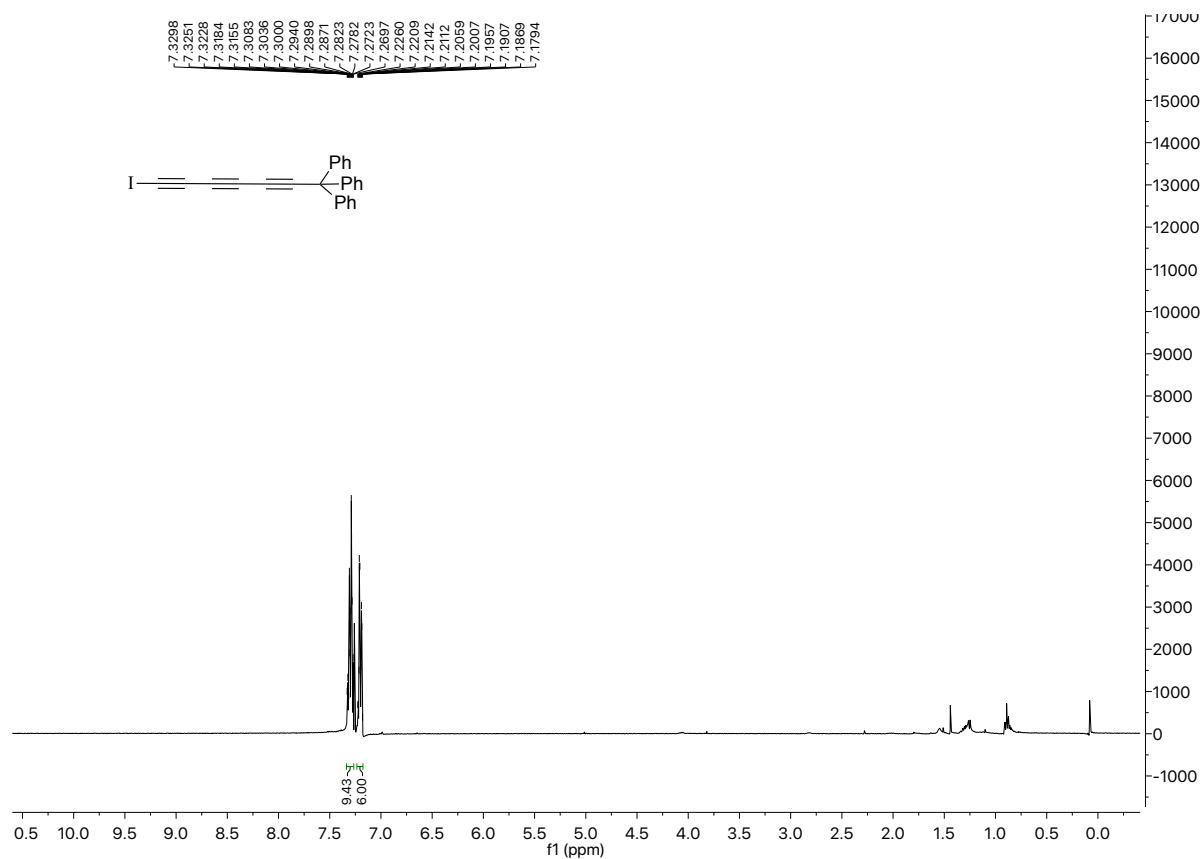


Figure S29: ¹H and ¹³C NMR spectra of **24** in CDCl₃

IX- X-Ray Crystallographic data

X-ray structure of triyne 16 (CCDC-1908075)

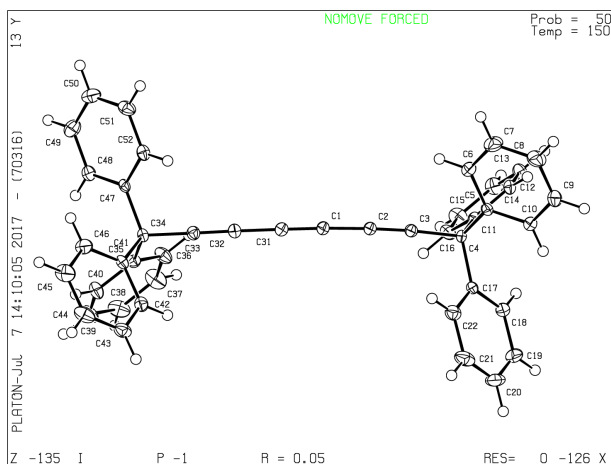


Table S4: Crystal data and structure refinement for **16**

Empirical formula	C ₄₄ H ₃₀	
Formula weight	558.68 g/mol	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, P -1	
Unit cell dimensions	a = 9.9378(9) Å,	α = 93.791(3) °
	b = 9.9882(8) Å,	β = 94.905(3) °
	c = 17.7699(15) Å,	γ = 98.931(3) °
Volume	1730.4(3) Å ³	
Z, Calculated density	2, 1.072 g.cm ⁻³	
Absorption coefficient	0.061 mm ⁻¹	
F(000)	588	
Crystal size	0.420 x 0.250 x 0.140 mm	
Crystal color	colourless	
Theta range for data collection	2.914 to 27.484 °	
h _{min} , h _{max}	-12, 12	
k _{min} , k _{max}	-12, 12	
l _{min} , l _{max}	-23, 23	
Reflections collected / unique	41529 / 7909 [R(int) = 0.0434]	
Reflections [I > 2σ(I)]	6557	
Completeness to theta _{max}	0.999	
Absorption correction type	multi-scan	
Max. and min. transmission	0.991, 0.000	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7909 / 0 / 397	
Goodness-of-fit	1.051	
Final R indices [I > 2σ(I)]	R1 = 0.0457, wR2 = 0.1170	
R indices (all data)	R1 = 0.0571, wR2 = 0.1244	
Largest diff. peak and hole	0.342 and -0.342 e.Å ⁻³	

X-ray structure of diyne 13d (CCDC-1908076)

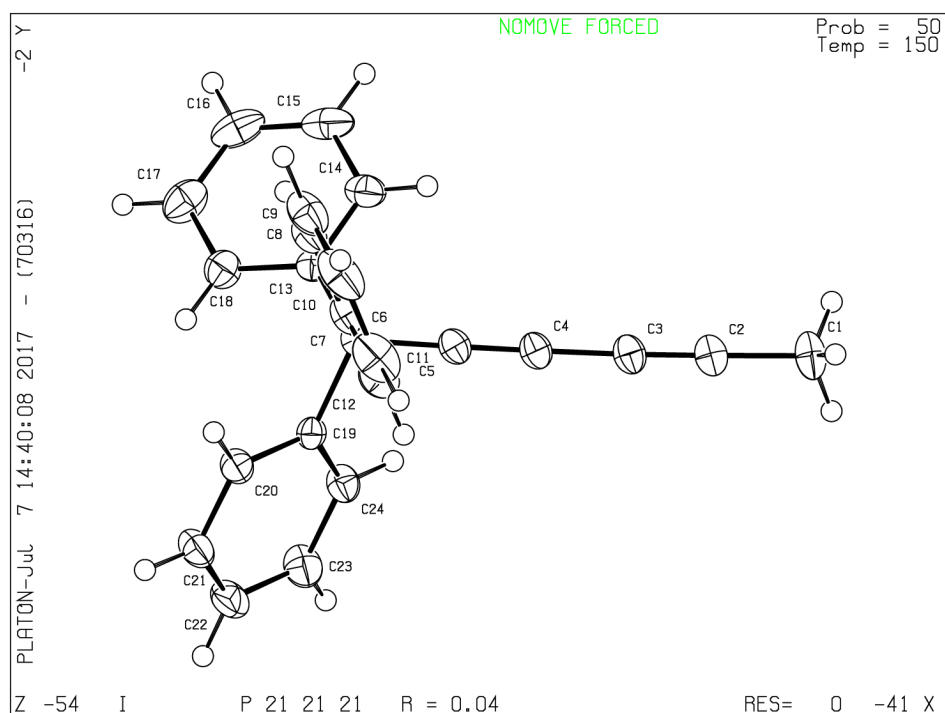


Table S5: Crystal data and structure refinement for **13d**.

Empirical formula	C ₁₆ H ₁₂
Formula weight	204.26 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, P 21 21 21
Unit cell dimensions	a = 9.3055(16) Å, $\alpha = 90^\circ$ b = 10.3538(15) Å, $\beta = 90^\circ$ c = 18.151(3) Å, $\gamma = 90^\circ$
Volume	1748.8(5) Å ³
Z, Calculated density	6, 1.164 g·cm ⁻³
Absorption coefficient	0.066 mm ⁻¹
F(000)	648
Crystal size	0.800 x 0.580 x 0.450 mm
Crystal color	colourless
Theta range for data collection	2.943 to 27.470 °
h _{min} , h _{max}	-12, 12
k _{min} , k _{max}	-13, 13
l _{min} , l _{max}	-19, 23
Reflections collected / unique	10436 / 3996 [R(int) = 0.0274]
Reflections [I > 2σ(I)]	3603
Completeness to theta _{max}	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.971, 0.000
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3996 / 0 / 219
Goodness-of-fit	1.029
Final R indices [I > 2σ(I)]	R1 = 0.0359, wR2 = 0.0870
R indices (all data)	R1 = 0.0433, wR2 = 0.0924
Largest diff. peak and hole	0.190 and -0.176 e·Å ⁻³

X-ray structure of diyne 13e (CCDC-1908077)

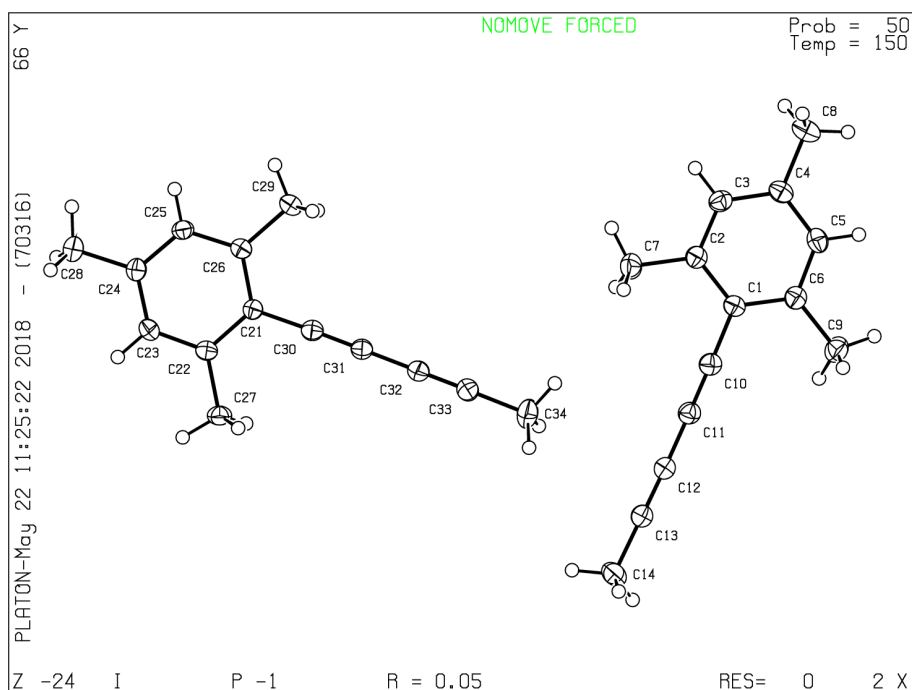


Table S6: Crystal data and structure refinement for **13e**.

Empirical formula	C ₁₄ H ₁₄	
Formula weight	182.25 g/mol	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, P -1	
Unit cell dimensions	a = 7.5855(9) Å,	α = 90.902(5) °
	b = 8.3989(11) Å,	β = 91.564(5) °
	c = 17.377(2) Å,	γ = 91.339(4) °
Volume	1106.2(2) Å ³	
Z, Calculated density	4, 1.094 g.cm ⁻³	
Absorption coefficient	0.061 mm ⁻¹	
F(000)	392	
Crystal size	0.490 x 0.410 x 0.270 mm	
Crystal color	colourless	
Theta range for data collection	3.347 to 27.480 °	
h_min, h_max	-9, 9	
k_min, k_max	-10, 10	
l_min, l_max	-22, 22	
Reflections collected / unique	21175 / 4978 [R(int) = 0.0363]	
Reflections [I > 2σ(I)]	4166	
Completeness to theta_max	0.982	
Absorption correction type	multi-scan	
Max. and min. transmission	0.984, 0.897	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4978 / 0 / 261	
Goodness-of-fit	1.049	
Final R indices [I > 2σ(I)]	R1 = 0.0506, wR2 = 0.1353	
R indices (all data)	R1 = 0.0605, wR2 = 0.1420	
Largest diff. peak and hole	0.307 and -0.265 e.Å ⁻³	

X-ray structure of triyne 14c (CCDC-1966970)

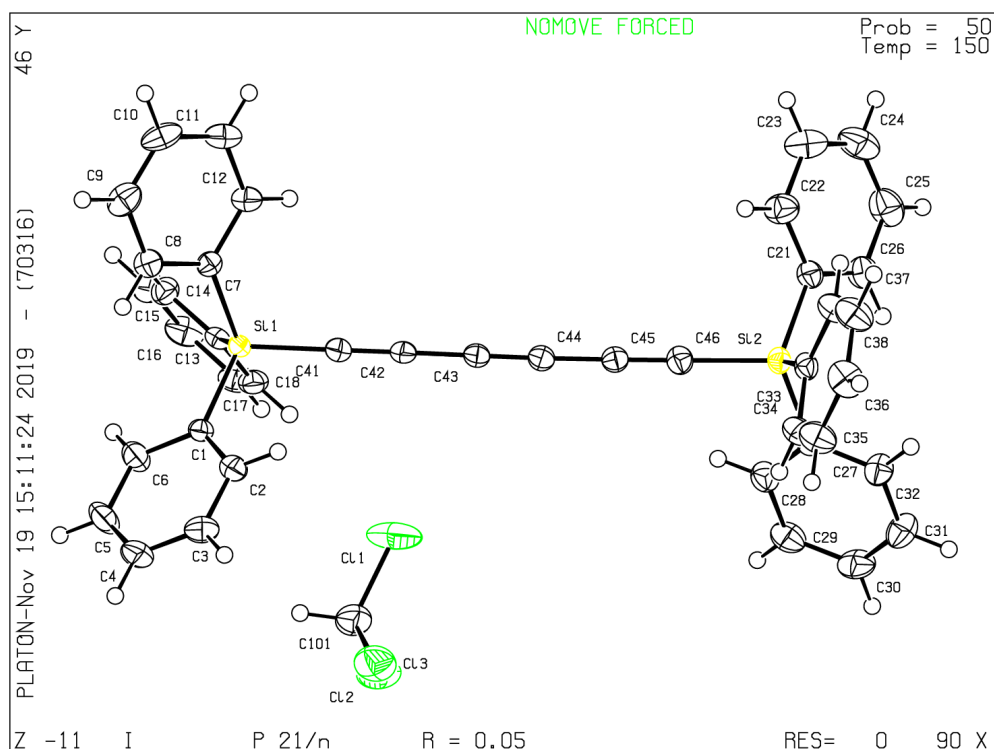


Table S7: Crystal data and structure refinement for **14c**

Empirical formula	$C_{43}H_{31}Cl_3Si_2$	
Formula weight	710.21 g/mol	
Temperature	150 K	
Wavelength	0.71073 \approx	
Crystal system, space group	monoclinic, P 21/n	
Unit cell dimensions	a = 10.4193(6) \approx , b = 21.2154(12) \approx , c = 17.2115(8) \approx ,	alpha = 90 ∞ beta = 99.801(2) ∞ gamma = 90 ∞
Volume	3749.1(3) \approx 3	
Z, Calculated density	4, 1.258 g.cm ⁻³	
Absorption coefficient	0.338 mm ⁻¹	
F(000)	1472	
Crystal size	0.390 x 0.280 x 0.130 mm	
Crystal color	colourless	
Crystal description	prism	
Theta range for data collection	2.137 to 27.581 ∞	
h_min, h_max	-13, 13	
k_min, k_max	-27, 24	
l_min, l_max	-22, 22	
Reflections collected / unique	34871 / 8525 [R(int) = 0.0558]	
Reflections [I > 2sigma(I)]	6305	
Completeness to theta_max	0.982	
Absorption correction type	multi-scan	
Max. and min. transmission	0.957, 0.774	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8525 / 0 / 433	
Goodness-of-fit	1.030	
Final R indices [I > 2sigma(I)]	R1 = 0.0491, wR2 = 0.1189	
R indices (all data)	R1 = 0.0765, wR2 = 0.1333	
Largest diff. peak and hole	0.358 and -0.619 e. ⁻³	

X-ray structure of triyne 22 (CCDC-1915266)

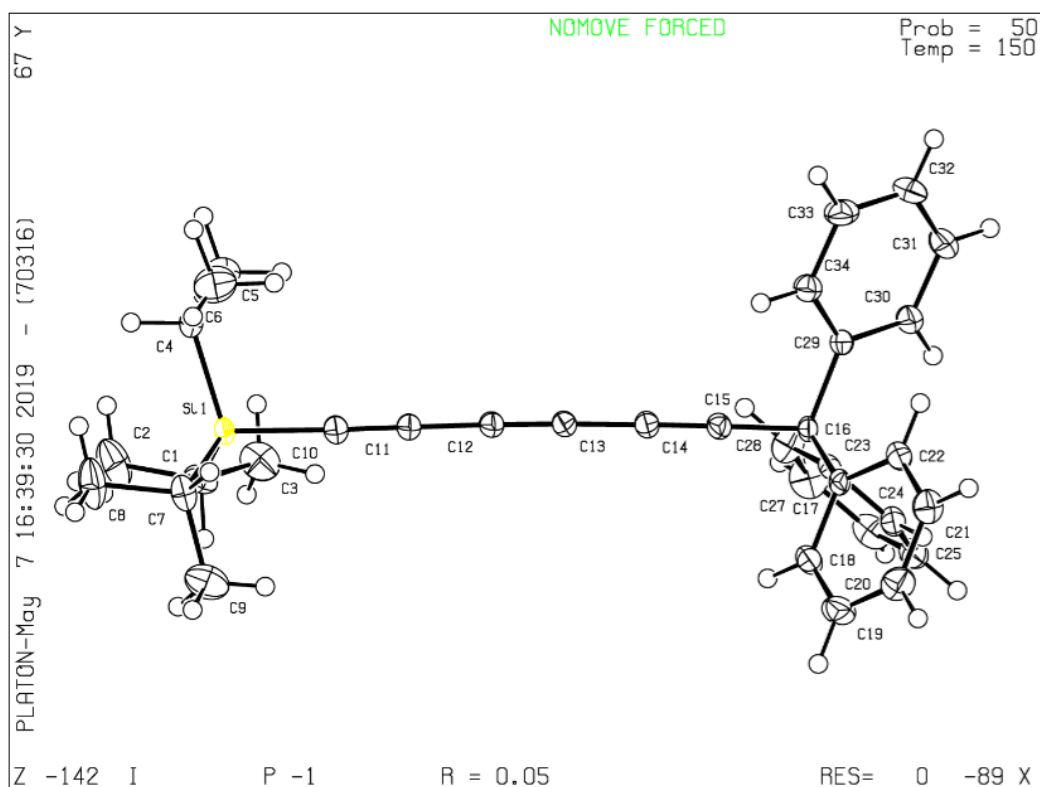


Table S8: Crystal data and structure refinement for **22**.

Empirical formula	C ₃₄ H ₃₆ Si	
Formula weight	472.72 g/mol	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, P -1	
Unit cell dimensions	a = 8.5423(11) Å,	α = 76.313(5) °
	b = 10.4335(14) Å,	β = 77.803(5) °
	c = 16.821(2) Å,	γ = 83.761(5) °
Volume	1421.0(3) Å ³	
Z, Calculated density	2, 1.105 g.cm ⁻³	
Absorption coefficient	0.102 mm ⁻¹	
F(000)	508	
Crystal size	0.420 x 0.280 x 0.090 mm	
Crystal color	colourless	
Theta range for data collection	2.444 to 27.582 °	
h _{min} , h _{max}	-10, 11	
k _{min} , k _{max}	-13, 13	
l _{min} , l _{max}	-21, 21	
Reflections collected / unique	26302 / 6444 [R(int) = 0.0702]	
Reflections [I > 2σ(I)]	5125	
Completeness to theta _{max}	0.978	
Absorption correction type	multi-scan	
Max. and min. transmission	0.991, 0.827	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6444 / 0 / 322	
Goodness-of-fit	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0477, wR2 = 0.1191	
R indices (all data)	R1 = 0.0648, wR2 = 0.1301	
Largest diff. peak and hole	0.453 and -0.368 e.Å ⁻³	

X-ray structure of triyne **23** (CCDC-1920652)

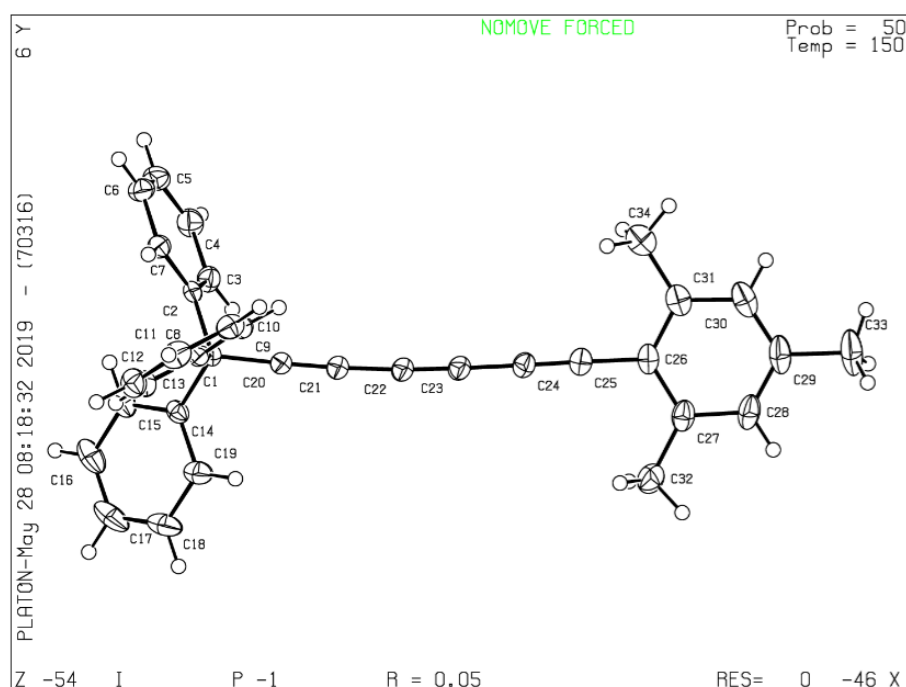


Table S9: Crystal data and structure refinement for **23**.

Empirical formula	C ₃₄ H ₂₆
Formula weight	434.55 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 8.5611(8) Å, α = 94.453(3) °, b = 10.3957(10) Å, β = 104.612(3) °, c = 14.5334(13) Å, γ = 98.456(3) °
Volume	1229.1(2) Å ³
Z, Calculated density	2, 1.174 g.cm ⁻³
Absorption coefficient	0.066 mm ⁻¹
F(000)	460
Crystal size	0.350 x 0.240 x 0.060 mm
Crystal color	colourless
Theta range for data collection	2.914 to 27.482 °
h_min, h_max	-11, 11
k_min, k_max	-13, 13
l_min, l_max	-17, 18
Reflections collected / unique	22961 / 5570 [R(int) = 0.0414]
Reflections [I > 2σ(I)]	4477
Completeness to theta_max	0.987
Absorption correction type	multi-scan
Max. and min. transmission	0.996, 0.874
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5570 / 0 / 310
Goodness-of-fit	0.034
Final R indices [I > 2σ(I)]	R1 = 0.0479, wR2 = 0.1201
R indices (all data)	R1 = 0.0628, wR2 = 0.1302
Largest diff. peak and hole	0.321 and -0.215 e.Å ⁻³

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