Supporting Information

Regio and stereoselective synthesis of 1,4-enynes by iron-catalysed Suzuki–Miyaura coupling of propargyl electrophiles under ligand-free condition

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1. General Information

All reactions were carried out in dry vessels under a positive pressure of argon. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, Silica gel 60 F254). The TLC plates were visualized by exposure to ultraviolet light (254 nm) and colored by vaper iodine, or immersion in PMA or basic $KMnO_4$ solution followed by heating on a hot plate. Flash column chromatography was performed on Wakogel 60N (38–100 μm). Florisil 150–250 (60–100 mesh) was purchased from Wako Pure Chemical Industries, Ltd. (Wako).

Preparative recycling gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-9204 instrument equipped with JAIGEL-1H-20/JAIGEL-2H-20 columns, using $CHCl_3$ and toluene as the eluent. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a JEOL ECS-400NR NMR spectrometer. Chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane (TMS), $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively, and are referenced to TMS (δ 0.00), $CDCl_3$ (δ 77.16), $BF_3{\cdot}Et_2O$ (δ 0.00), and $CFCl_3$ (δ 0.00), respectively. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances). GC analysis was conducted on a Shimadzu GC-2010 instrument equipped with an FID detector and a capillary column, ZB-1MS (Phenomenex Inc., 10 m × 0.10 mm i.d., 0.10 μm film thickness). High-resolution mass spectra (HRMS) were obtained in fast atom bombardment (FAB) ionization or electron ionization (EI) mode on a JEOL JMS-700 mass spectrometer.

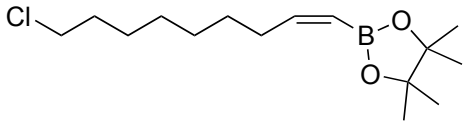
Metal salts were purchased from commercial suppliers and used without further purification: $FeCl_3$ (>99.99%, Aldrich Inc.); $CoCl_2$ (Nacalai Tesque Inc.); $MnCl_2$ (>99%, Aldrich Inc.); $NiCl_2$ (>99.99%, Aldrich Inc.); $PdCl_2$ (99%, Aldrich Inc.); CuCl (97%, Aldrich Inc.). Propargyl halides[1] and alkenylboronate[2,3] were synthesized according to the previous procedure. A solution of $MgBr_2$ in THF (0.2 M) was prepared from Mg and 1,2-dibromoethane. Other materials were purchased from Aldrich Inc., Tokyo Chemical Industry Co., Ltd. (TCI), Wako, and other commercial suppliers, and were used after appropriate purification unless otherwise noted. THF was purchased from Wako and distilled over sodium/benzophenone ketyl before use. Water content of the distilled THF

was determined with a Karl Fischer Moisture titrator (MKC-610, Kyoto Electronics Company) to be less than 15 ppm.

2. Experimental Procedures

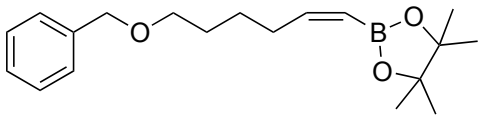
2.1 Procedures for Preparation of (*Z*)-Alkenylboronate

General procedure for Preparation of (*Z*)-Alkenylboronate: Synthesis of (*Z*)-(9-chlorononon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*1a*)



A solution of P(*i*-Pr)$_3$ in hexane (28.8 mg, 10 wt %, 0.018 mmol), [Rh(cod)Cl]$_2$ (1.27 mg, 0.0026 mmol), Et$_3$N (30.4 mg, 0.30 mmol) and catecholborane (36.0 mg, 0.30 mmol) were dissolved in cyclohexane (0.9 mL). After the mixture was stirred at room temperature for 30 min, an alkyne, 9-chlorononon-1-yne (57.1 mg, 0.36 mmol) was added to the reaction mixture. After the mixture was stirred at room temperature for 4 h, pinacol (53.2 mg, 0.45 mmol) was added. After the resulting mixture was stirred at room temperature for 12 h, aqueous NH_4Cl was added to the reaction mixture at 0 ºC. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were filtered and concentrated under the reduced pressure to give the crude product. The crude product was purified by silica gel column chromatography with 0.7 % ethyl acetate in hexane (R_f = 0.07) to give the title compound (69.0 mg, 80%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.27 (s, 12 H, -C*H*$_3$), 1.29–1.44 (m, 8 H, -C*H*$_2$-), 1.77 (quint, *J* = 7.5 Hz, 2 H, Cl-CH$_2$-C*H*$_2$-), 2.39 (td, *J* = 7.3, 6.7 Hz, 2 H, -CH$_2$-C*H*$_2$-CH=CH-), 3.53 (t, *J* = 6.7 Hz, 2 H, Cl-C*H*$_2$-), 5.33 (d, *J* = 13.3 Hz, 1 H, -CH$_2$-CH=C*H*-), 6.42 (dt, *J* = 13.7, 7.1 Hz, 1 H, -CH$_2$-C*H*=CH-); ^{13}C NMR (99 MHz, $CDCl_3$) δ 24.99 (4C), 26.97, 28.80, 28.96, 29.44, 32.24, 32.80, 45.31, 82.94, 155.18; ^{11}B NMR (96 MHz, $CDCl_3$) δ 29.6; IR (neat, cm^{-1}) 2979, 2927, 2856, 1741, 1627, 1422, 1371, 1318, 1258, 1144, 968, 878, 847, 758, 726, 651; HRMS (EI) *m*/*z* [M]$^+$ calcd for $C_{15}H_{28}ClO_2B$ 286.1871; found, 286.1871; Anal. calcd for $C_{15}H_{28}ClO_2B$ C, 62.85; H, 9.85, found C, 62.79; H, 9.81.

Synthesis of (*Z*)-2-(6-(benzyloxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-

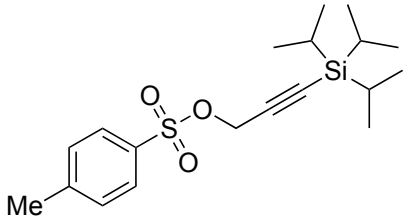


dioxaborolane (*1b*)

The reaction was carried out according to the general procedure on a 10.0 mmol scale. The crude product was purified by silica gel column chromatography using 9.1% ethyl acetate in hexane as the eluent (R_f = 0.23) to give the title compound (1.37 mg, 43%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.25 (s, 12 H, -CH_3), 1.48 (quint, J = 7.4 Hz, 2 H, $PhCH_2OCH_2$-CH_2-), 1.64 (quint, J = 7.1 Hz, 2 H, $PhCH_2OCH_2CH_2$-CH_2-), 2.39 (td, J = 7.3, 1.3 Hz, 2 H, -CH_2-CH_2-CH=CH-), 3.49 (t, J = 6.7 Hz, 2 H, $PhCH_2OCH_2$-), 5.33 (td, J = 13.3, 1.3 Hz, 1 H, -CH_2-CH=CH-), 6.42 (dt, J = 13.1, 7.6 Hz, 1H, -CH_2-CH=CH-), 7.26–7.36 (m, 5 H, ArH_5); ^{13}C NMR (99 MHz, $CDCl_3$) δ 24.99 (4C), 26.15, 29.28, 32.06, 70.49, 73.01, 82.95, 127.60, 127.73 (2C), 128.48 (2C), 138.88, 154.92; ^{11}B NMR (96 MHz, $CDCl_3$) δ 29.0; IR (neat, cm^{-1}) 3031, 2991, 2978, 2935, 2856, 2791, 1627, 1496, 1480, 1454, 1436, 1423, 1390, 1379, 1371, 1317, 1280, 1258, 1214, 1165, 1143, 1103, 1029, 1005, 967, 878, 847, 834, 732, 696; HRMS (EI) *m*/*z* [M+Na]$^+$ calcd for $C_{19}H_{29}O_3BNa$ 339.2111; found, 339.2112; Anal. calcd for $C_{19}H_{29}O_3B$ C, 72.16; H, 9.24, found C, 72.20; H, 9.35.

2.2 Procedures for Preparation of Propargyl Tosylate

Synthesis of 3-(triisopropylsilyl)prop-2-yn-1-yl 4-methylbenzenesulfonate (*2a_OTs*)

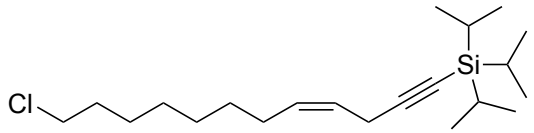


To a 15 mL of dichloromethane was added 3-(triisopropylsilyl)prop-2-yn-1-ol (1.06 g, 5.0 mmol) and pyridine (1.2 mL, 15.0 mmol, 0.98 g/mL). After the mixture was cool down to 0 ºC, tosyl chloride (1.15 g, 6.0 mmol) was added to the reaction mixture. After the mixture was stirred at room temperature overnight, water was added to the reaction mixture. The aqueous layer was extracted with dichloromethane three times. The combined organic layer was washed respectively with 1N HCl and brine, then dried over $MgSO_4$ and concentrated. The crude product was purified by silica gel column

chromatography using 9.1% ethyl acetate in hexane (R_f = 0.50) then GPC to give the title compound (261 mg, 14%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.98–1.10 (m, 21H, -SiCHCH_3, -SiCHCH_3), 2.44 (s, 3 H, -C_6H_4CH_3), 4.77 (s, 2 H, -O-CH_2-C≡C-), 7.33 (d, J = 8.5 Hz, 2H, ArH_2), 7.82 (d, J = 8.1 Hz, 2H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.11 (3C), 18.55 (6C), 21.78, 58.65, 91.66, 98.25, 128.19 (2C), 130.02 (2C), 133.49, 145.05; IR (neat, cm^{-1}) 2943, 2892, 2866, 2182, 1599, 1496, 1463, 1372, 1308, 1292, 1253, 1211, 1190, 1176, 1097, 1026, 997, 944, 882, 832, 813; HRMS (FAB) m/z [M+Na]$^+$ calcd for $C_{19}H_{30}O_3SSiNa$ 389.1587, found 389.1585; Anal. calcd for $C_{19}H_{30}O_3SSi$ C, 62.25; H, 8.25, found C, 62.51; H, 8.49.

2.3 Procedures for Synthesis of 1,4-Enynes

General procedure: Synthesis of (*Z*)-(12-chlorododec-4-en-1-yn-1-yl)triisopropylsilane (*3a*)

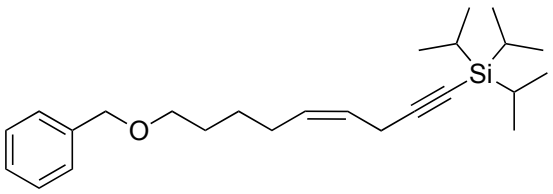


A solution of BuLi in THF (0.46 mL, 1.53 M, 0.70 mmol) was added to a solution of (*Z*)-(9-chlorononon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (217 mg, 0.76 mmol) in THF (2.0 mL) at –78 ºC. After the mixture was stirred at the same temperature for 30 min, the reaction mixture was warmed to 0 ºC and stirred for 30 min. The solvent was removed in vacuo at room temperature. A substrate, (3-bromoprop-1-yn-1-yl)triisopropylsilane (136 mg, 0.50 mmol), a solution of $MgBr_2$ in THF (0.5 mL, 0.2 M, 0.10 mmol), a solution of $FeCl_3$ (100 μL, 0.05 M, 0.005 mmol) and THF (0.65 mL) were added to the residual borate at –78 ºC. After stirring the reaction mixture at 0 ºC for 1 h, saturated aqueous ammonium chloride was added to the reaction mixture at 0 ºC. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was filtered through a pad of Florisil and concentrated under the reduced pressure to give the crude product. The product yield (95%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

The large-scale synthesis was also carried out on a 9.45 mmol scale. After the reaction was performed at 0 ºC for 1 h, saturated aqueous ammonium chloride was added to the

mixture at 0 ºC. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over $MgSO_4$, and filtered through a pad of Florisil. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.48) to give the title compound (2.92 g, 87%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.98–1.10 (m, 21H, -SiCHCH_3, -SiCHCH_3), 1.21–1.48 (m, 8H, -CH_2-), 1.77 (quint, J = 7.2 Hz, 2H, Cl-CH$_2$-CH_2-), 2.05 (td, J = 6.1, 5.5 Hz, 2H, -CH$_2$-CH_2-CH=CH-), 2.99 (d, J = 5.1 Hz, 2H, -CH=CH-CH_2-C≡C-), 3.53 (t, J = 6.7 Hz, 2H, Cl-CH_2-), 5.40–5.48 (m, 2H, -CH=CH-); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.45 (3C), 18.55, 18.77 (6C), 26.98, 27.30, 28.92, 29.19, 29.35, 32.78, 45.30, 79.99, 107.25, 124.57, 131.68; IR (neat, cm^{-1}) 2979, 2927, 2856, 1741, 1627, 1422, 1371, 1318, 1258, 1144, 968, 878, 847, 758, 726, 651; HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{21}H_{38}ClSi$ 353.2431, found 353.2428; Anal. calcd for $C_{21}H_{39}ClSi$ C, 71.04; H, 11.07, found C, 70.82; H, 10.97.

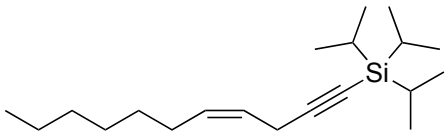
Synthesis of (*Z*)-(9-benzyloxy-non-4-en-1-yn-1-yl)triisopropylsilane (*3b*)



The reaction was carried out according to the general procedure on a 0.5 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (1 mol %) was used. The product yield (78%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 1.9% ethyl acetate in hexane (R_f = 0.29) as the eluent then GPC to give the title compound (131 mg, 68%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.97–1.10 (m, 21 H, -SiCHCH_3, -SiCHCH_3), 1.42–1.50 (quint, 2 H, -OCH$_2$-CH_2-CH$_2$-), 1.59–1.67 (quint, 2 H, -CH$_2$-CH_2-CH$_2$), 2.06 (td, J = 7.6, 5.4 Hz, 2 H, -CH$_2$-CH_2-CH=CH-), 2.98 (d, J = 4.9 Hz, 2 H, -CH=CH-CH_2-C≡C-), 3.47 (t, J = 6.5 Hz, 2 H, -O-CH_2-CH$_2$-), 4.50 (s, 2 H, -O-CH_2-Ph), 5.40–5.48 (m, 2 H, -CH=CH-), 7.27–7.37 (m, 5 H, ArH_5); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.44 (3C), 18.55, 18.76 (6C), 26.08, 27.11, 29.47, 70.35, 73.04, 80.02, 107.20, 124.78, 127.64, 127.78 (2C), 128.50 (2C), 131.43, 138.79; IR (neat, cm^{-1}) 3027, 2942, 2891, 2863, 2172, 1495, 1462, 1454, 1417, 1382, 1364, 1280, 1242, 1205, 1102, 1075, 1028, 1017, 995, 919, 906, 882, 733, 696, 676, 660, 634, 585; HRMS (FAB) m/z [M+Na]$^+$ calcd

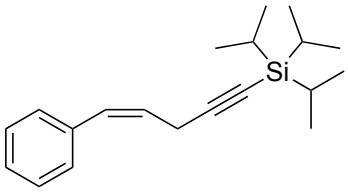
for $C_{25}H_{40}OSiNa$ 407.2746, found 407.2744; Anal. calcd for $C_{25}H_{40}OSi$ C, 78.06; H, 10.48, found C, 77.87; H, 10.66.

Synthesis of (*Z*)-triisopropyl(undec-4-en-1-yn-1-yl)silane (*3c*)



The reaction was carried out according to the general procedure on a 0.5 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (1 mol %) was used. The product yield (95%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.72) to give the title compound (142 mg, 93%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 6.7 Hz, CH_3-CH_2-), 0.98–1.11 (m, 21 H, -SiCHCH_3, -SiC$H$$CH_3$), 1.21–1.40 (m, 8 H, CH_3-(CH_2)$_4$-CH_2-), 2.04 (td, J = 7.1, 6.7 Hz, 2 H, -CH_2-CH_2-CH=CH-), 2.99 (d, J = 5.4 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.39–5.48 (m, 2 H, -CH=CH-); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.46 (3C), 14.24, 18.55, 18.76 (6C), 22.77, 27.37, 29.07, 29.45, 31.90, 79.94, 107.35, 124.41, 131.90; IR (neat, cm^{-1}) 3022, 2956, 2941, 2924, 2895, 2864, 2173, 1462, 1381, 1366, 1282, 1243, 1074, 1062, 1018, 995, 970, 919, 904, 882, 723, 676, 660; HRMS (EI) m/z $[M]^+$ calcd for $C_{20}H_{38}Si$ 306.2743, found 306.2742; Anal. calcd for $C_{20}H_{38}Si$ C, 78.35; H, 12.46, found C, 77.97; H, 12.51.

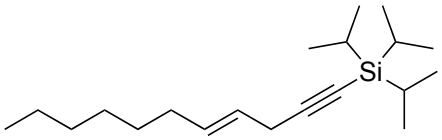
Synthesis of (*Z*)-triisopropyl(5-phenylpent-4-en-1-yn-1-yl)silane (*3d*)



The reaction was carried out according to the general procedure on a 0.5 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (5 mol %) was used. The product yield (>99%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using Hexane as the eluent (R_f = 0.64) to give the title compound (142 mg, 95%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.98–1.12 (m, 21 H, -SiCHCH_3, -SiC$H$$CH_3$), 3.22 (dd, J =

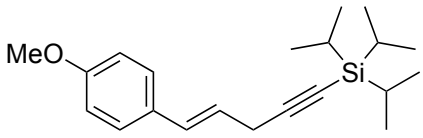
7.2, 1.8 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.77 (dt, J = 11.3, 7.4 Hz, 1 H, -CH=CH-CH$_2$-), 6.51 (d, J = 11.2 Hz, 1 H, Ph-CH=CH-), 7.22–7.27 (m, 1 H, ArH), 7.31–7.36 (m, 4 H, ArH_4); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.44 (3C), 18.76 (6C), 20.14, 80.90, 106.74, 126.80, 127.15, 128.40 (2C), 128.93 (2C), 130.58, 136.79; IR (neat, cm^{-1}) 3025, 2957, 2943, 2922, 2891, 2864, 2171, 1600, 1500, 1496, 1463, 1447, 1424, 1399, 1382, 1366, 1282, 1243, 1075, 1036, 1030, 1006, 996, 918, 902, 882, 806, 767, 699, 674, 658, 614; HRMS (EI) m/z [M]$^+$ calcd for $C_{20}H_{30}Si$ 298.2117, found 298.2115; Anal. calcd for $C_{20}H_{30}Si$ C, 80.46; H, 10.13, found C, 80.32; H, 10.24.

Synthesis of (*E*)-triisopropyl(undec-4-en-1-yn-1-yl)silane (*3e*)



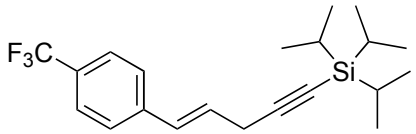
The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (90%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.74) to give the title compound (251 mg, 82%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, CH_3-CH$_2$-), 0.98–1.12 (m, 21 H, -SiCHCH_3, -SiCHCH$_3$), 1.21–1.40 (m, 8 H, CH$_3$-(CH_2)$_4$-CH$_2$-), 2.02 (tdd, J = 7.1, 7.1. 1.6 Hz, 2 H, -CH$_2$-CH_2-CH=CH-), 2.97 (dq, J = 5.4, 1.5 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.40 (dtt, J = 15.2, 5.2 Hz, J = 1.6 Hz, 1 H, -CH=CH-CH$_2$-C≡C-), 5.75 (dtt, J = 15.2, 6.7 Hz, J = 1.8 Hz, 1 H, -CH$_2$-CH=CH-CH$_2$-); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.47 (3C), 14.25, 18.78 (6C), 22.80, 23.16, 28.91, 29.46, 31.91, 32.37, 82.22, 106.37, 123.91, 132.42; IR (neat, cm^{-1}) 3035, 2958, 2942, 2926, 2890, 2864, 2173, 1462, 1418, 1382, 1366, 1072, 1062, 1011, 995, 965, 918, 882, 675, 660, 632, 602; HRMS (EI) m/z [M]$^+$ calcd for $C_{20}H_{38}Si$ 306.2743, found 306.2743; Anal. calcd for $C_{20}H_{38}Si$ C, 78.35; H, 12.49, found C, 78.13; H, 12.50.

Synthesis of (*E*)-triisopropyl(5-(4-methoxyphenyl)pent-4-en-1-yn-1-yl)silane (*3f*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (87%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 4.8% ethyl acetate in hexane (R_f = 0.50) as the eluent then GPC to give the title compound (258 mg, 78%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 1.02–1.16 (m, 21 H, -SiCHCH_3, -SiCHCH_3), 3.24 (dd, J = 5.4, 1.8 Hz, 2 H, -CH=CH-CH_2-C≡C-), 3.80 (s, 3 H, -OCH_3), 6.04 (dt, J = 15.7, 5.2 Hz, 1 H, -CH_2-CH=CH-CH_2-), 6.68 (dt, J = 15.7, 1.8 Hz, 1 H, -CH=CH-CH_2-C≡C-), 6.85 (d, J = 9.0 Hz, 2 H, ArH_2), 7.28 (d, J = 8.5 Hz, 2 H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.47 (3C), 18.81 (6C), 23.50, 55.44, 83.26, 105.40, 114.11 (2C), 122.20, 127.48 (2C), 130.22, 130.72, 159.11; IR (neat, cm^{-1}) 3034, 3033, 2941, 2890, 2865, 2835, 2171, 1608, 1578, 1510, 1463, 1441, 420, 1382, 1366, 1299, 1244, 1174, 1108, 1037, 1013, 994, 966, 920, 883, 834, 774, 676, 663; HRMS (EI) m/z $[M]^+$ calcd for $C_{21}H_{32}OSi$ 328.2222, found 328.2223; Anal. calcd for $C_{21}H_{32}OSi$ C, 76.77; H, 9.82, found 76.67; H, 9.91.

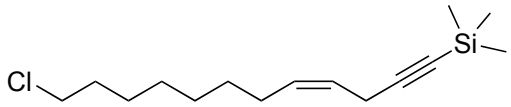
Synthesis of (*E*)-triisopropyl(5-(4-trifluoromethylphenyl)pent-4-en-1-yn-1-yl)silane (*3g*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (99%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.51) to give the title compound (313 mg, 86%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 1.04–1.14 (m, 21 H, -SiCHCH_3, -SiCHCH_3), 3.24 (dd, J = 4.9, 1.8 Hz, 2 H, -CH=CH-CH_2-C≡C-), 6.29 (dt, J = 15.7, 5.2 Hz, 1 H, -CH_2-CH=CH-CH_2-), 6.80 (dt, J = 15.7, 1.8 Hz, 1 H, -CH=CH-CH_2-C≡C-), 7.43 (d, J = 8.1 Hz, 2 H, ArH_2), 7.55 (d, J = 8.1 Hz, 2 H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.45 (3C), 18.81 (6C), 23.63, 84.11, 104.38, 124.39 (q, $J_{C–F}$ = 272.9 Hz), 125.67 (2C) (q, $J_{C–F}$ = 3.8 Hz), 126.53 (2C), 127.24, 129.26 (q, $J_{C–F}$ = 32.7 Hz), 130.26, 140.81;

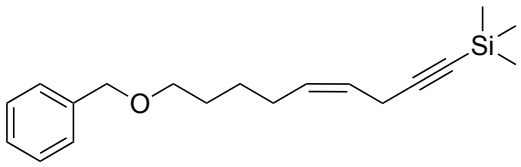
^{19}F NMR (368 MHz, $CDCl_3$) δ –62.4; IR (neat, cm^{-1}) 2943, 2891, 2865, 2175, 1655, 1616, 1578, 1464, 1415, 1383, 1367, 1324, 1256, 1165, 1124, 1109, 1068, 1017, 996, 968, 952, 921, 882, 845, 780, 694, 676, 659, 638, 621; HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{21}H_{29}F_3Si$ 366.1991, found 366.1991; Anal. calcd for $C_{21}H_{29}F_3Si$ C, 68.81; H, 7.98, found 68.67; H, 7.86.

Synthesis of (*Z*)-(12-chlorododec-4-en-1-yn-1-yl)trimethylsilane (*3h*)



The reaction was carried out according to the general procedure on a 0.5 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (1 mol %) was used. The product yields **3i** (85%) and **4i** (6%) were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.43) to give the title compound (111 mg, 82%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.15 (s, 9H, -SiC*H*$_3$), 1.25–1.46 (m, 8H, -C*H*$_2$-), 1.77 (quint, *J* = 7.2 Hz, 2H, Cl-CH$_2$-C*H*$_2$-), 2.04 (td, *J* = 6.7, 6.7 Hz, 2H, -CH$_2$-C*H*$_2$-CH=CH-), 2.97 (d, *J* = 5.8 Hz, 2H, -CH=CH-C*H*$_2$-C≡C-), 3.53 (t, *J* = 6.9 Hz, 2H, Cl-C*H*$_2$-), 5.38–5.50 (m, 2H, -C*H*=C*H*-); ^{13}C NMR (99 MHz, $CDCl_3$) δ 0.25 (3C), 18.51, 26.97, 27.26, 28.90, 29.19, 29.31, 32.75, 45.28, 84.22, 105.58, 124.06, 131.98; IR (neat, cm^{-1}) 3021, 2955, 2929, 2857, 2175, 1462, 1283, 1249, 1029, 838, 759, 723, 697, 650, 643; HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{15}H_{27}ClSi$ 270.1571, found 270.1570.

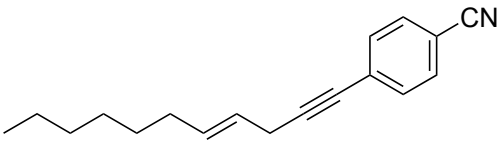
Synthesis of (*Z*)-(9-benzyloxynon-4-en-1-yn-1-yl)trimethylsilane (*3i*)



The reaction was carried out according to the general procedure on a 0.5 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (1 mol %) was used. The product yield (>99%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 4.8% ethyl

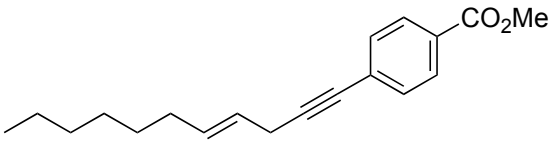
acetate in hexane (R_f = 0.44) as the eluent then GPC to give the title compound (121 mg, 81%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.14 (s, 9 H, -SiCH_3), 1.42–1.50 (quint, 2 H, -OCH$_2$-CH_2-CH$_2$-), 1.59–1.67 (quint, 2 H, -CH$_2$-CH_2-CH$_2$-), 2.06 (td, J = 7.3, 7.1 Hz, 2 H, -CH$_2$-CH_2-CH=CH-), 2.96 (d, J = 4.9 Hz, 2 H, -CH=CH-CH_2-C≡C-), 3.47 (t, J = 6.5 Hz, 2 H, -O-CH_2-CH$_2$), 4.50 (s, 2 H, -O-CH_2-Ph), 5.38–5.50 (m, 2 H, -CH=CH-), 7.26–7.30 (m, 1 H, ArH), 7.30–7.37 (m, 4 H, ArH_4); ^{13}C NMR (99 MHz, $CDCl_3$) δ 0.25 (3C), 18.52, 26.07, 27.11, 29.49, 70.34, 73.05, 84.26, 105.54, 124.27, 127.65, 127.78 (2C), 128.51 (2C), 131.74, 138.78; IR (neat, cm^{-1}) 3026, 2934, 2858, 2791, 2175, 1496, 1455, 1415, 1361, 1282, 1294, 1204, 1102, 1040, 1028, 840, 758, 732, 696, 642; HRMS (FAB) m/z [M+Na]$^+$ calcd for $C_{19}H_{28}OSiNa$ 323.1807, found 323.1807; Anal. calcd for $C_{19}H_{28}OSi$ C, 75.94; H, 9.39, found C, 75.84; H, 9.62.

Synthesis of (*E*)-4-(undec-4-en-1-yn-1-yl)benzonitrile (*3j*)



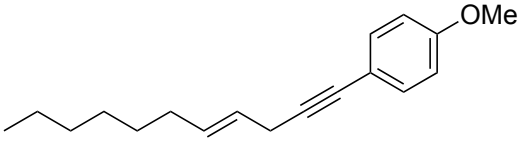
The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (83%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 4.8% ethyl acetate in hexane (R_f = 0.47) as the eluent then GPC to give the title compound (71.5 mg, 28%) as a colorless oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, CH_3-CH$_2$-), 1.21–1.46 (m, 8 H, CH$_3$-(CH_2)$_4$-CH$_2$-), 2.05 (tdd, J = 7.2, 6.9, 1.7 Hz, 2 H, -CH$_2$-CH_2-CH=CH-), 3.15 (dd, J = 5.4, 1.4 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.45 (dtt, J = 15.2, 5.8, 1.3 Hz, 1 H, -CH=CH-CH$_2$-C≡C-), 5.73 (dtt, J = 14.8, 6.7, 1.6 Hz, 1 H, -CH$_2$-CH=CH-CH$_2$-), 7.48 (d, J = 8.5 Hz, 2 H, ArH_2), 7.58 (d, J = 8.5 Hz, 2 H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.23, 22.77, 22.86, 29.01, 29.34, 31.86, 32.47, 80.94, 93.16, 111.13, 118.76, 123.03, 129.06, 132.07 (2C), 132.28 (2C), 133.31; IR (neat, cm^{-1}) 2955, 2926, 2871, 2853, 2227, 1605, 1501, 1465, 1418, 1406, 1378, 1271, 1177, 1105, 1019, 965, 836, 723, 554; HRMS (EI) m/z [M+H]$^+$ calcd for $C_{18}H_{22}N$ 252.1752 found, 252.1752.

Synthesis of methyl (*E*)-4-(undec-4-en-1-yn-1-yl)benzoate (*3k*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (60%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 4.8% ethyl acetate in hexane (R_f = 0.38) as the eluent then GPC to give the title compound (159 mg, 56%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, CH_3-CH_2-), 1.24–1.42 (m, 8 H, CH_3-(CH_2)$_4$-CH_2-), 2.05 (tdd, J = 7.3, 6.7, 1.2 Hz, 2 H, -CH_2-CH_2-CH=CH-), 3.15 (dd, J = 5.8, 1.3 Hz, 2 H, -CH=CH-CH_2-C≡C-), 3.91 (s, 3 H, OCH_3), 5.46 (dtt, J = 15.2, 5.6, 1.3 Hz, 1 H, -CH=CH-CH_2-C≡C-), 5.74 (dtt, J = 15.2, 6.7, 1.6 Hz, 1 H, -CH_2-CH=CH-CH_2-), 7.46 (d, J = 8.5 Hz, 2 H, ArH_2), 7.95 (d, J = 8.5 Hz, 2 H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.24, 22.78, 22.87, 29.02, 29.37, 31.87, 32.48, 52.30, 81.66, 91.46, 123.37, 128.83, 129.13, 129.54 (2C), 131.65 (2C), 133.07, 166.80; IR (neat, cm^{-1}) 3028, 2997, 2970, 2953, 2924, 2873, 2856, 1722, 1606, 1560, 1507, 1456, 1435, 1407, 1366, 1308, 1271, 1230, 1217, 1193, 1175, 1106, 1096, 1019, 964, 856, 826, 768, 723, 696; HRMS (EI) m/z $[M+H]^+$ calcd for $C_{19}H_{25}O_2$ 285.1855 found, 285.1856.

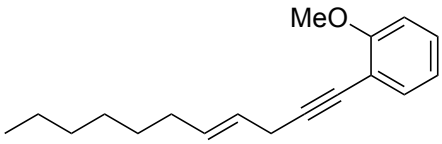
Synthesis of (*E*)-1-methoxy-4-(undec-4-en-1-yn-1-yl)benzene (*3l*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (57%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 4.8% ethyl acetate in hexane (R_f = 0.46) as the eluent then GPC to give the title compound (145 mg, 57%) as a yellow oil; ^1H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, CH_3-CH_2-), 1.24–1.40 (m, 8 H, CH_3-(CH_2)$_4$-CH_2-), 2.04 (tdd, J = 7.3, 6.7, 1.5 Hz, 2 H, -CH_2-CH_2-CH=CH-), 3.11 (dd, J = 5.4, 1.3 Hz, 2 H, -CH=CH-CH_2-C≡C-), 3.80 (s, 3 H, -OCH_3), 5.47 (dtt, J = 15.3, 5.4, 1.3 Hz, 1 H, -CH=CH-CH_2-C≡C-), 5.73 (dtt, J = 15.3, 6.7, 1.6 Hz,

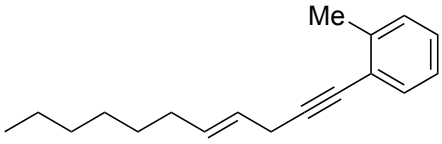
1 H, -CH_2-C*H*=CH-CH_2-), 6.81 (d, *J* = 9.0 Hz, 2 H, ArH_2), 7.35 (d, *J* = 8.5 Hz, 2 H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.25, 22.80 (2C), 29.04, 29.42, 31.89, 55.40, 81.95, 86.32, 113.95 (2C), 116.18, 124.09, 132.56, 133.06 (2C), 159.25; IR (neat, cm^{-1}) 3038, 3001, 2955, 2923, 2872, 2854, 2837, 1607, 1570, 1508, 1464, 1441, 1419, 1376, 1288, 1244, 1180, 1171, 1107, 1033, 965, 831, 807, 796, 724, 656, 642, 604, 534; HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{18}H_{24}O$ 256.1827 found, 256.1827.

Synthesis of (*E*)-1-methoxy-2-(undec-4-en-1-yn-1-yl)benzene (*3m*)



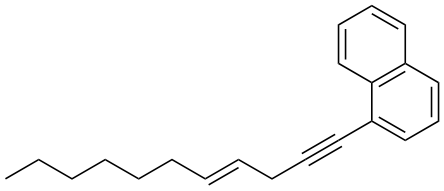
The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (53%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using 4.8% ethyl acetate in hexane (R_f = 0.44) as the eluent then GPC to give the title compound (134 mg, 52%) as a yellow oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, C*H*$_3$-CH_2-), 1.21–1.46 (m, 8 H, CH_3-(C*H*$_2$)$_4$-CH_2-), 2.05 (dtt, *J* = 7.2, 6.6, 1.2 Hz, 2 H, -CH_2-C*H*$_2$-CH=CH-), 3.11 (dd, *J* = 5.4, 1.8 Hz, 2 H, -CH=CH-C*H*$_2$-C≡C-), 3.88 (s, 3 H, -OC*H*$_3$), 5.49 (dtt, *J* = 15.3, 5.4, 1.4 Hz, 1 H, -CH=C*H*-CH_2-C≡C-), 5.79 (dtt, *J* = 15.2, 6.7, 1.6 Hz, 1 H, CH_2-C*H*=CH-CH_2-), 6.82–6.90 (m, 2 H, ArH_2), 7.24 (td, *J* = 7.9, 1.8 Hz, 1 H, Ar*H*), 7.40 (dd, *J* = 7.6, 1.8 Hz, 1 H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.25, 22.79, 23.15, 29.03, 29.44, 31.90, 32.51, 55.93, 78.39, 92.15, 110.67, 113.12, 120.53, 123.91, 129.17, 132.64, 133.81, 160.00; IR (neat, cm^{-1}) 3033, 2997, 2954, 2925, 2870, 2854, 1597, 1574, 1492, 1464, 1434, 1419, 1378, 1292, 1277, 1257, 1236, 1180, 1161, 1115, 1051, 1026, 964, 931, 792, 747; HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{18}H_{24}O$ 256.1827 found, 256.1827.

Synthesis of (*E*)-1-methyl-2-(undec-4-en-1-yn-1-yl)benzene (*3n*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h, $FeCl_3$ (10 mol %). The product yield (75%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. $FeCl_3$ (10 mol %) was used. The crude product was purified by silica gel column chromatography using Hexane as the eluent (R_f = 0.61) to give the title compound (145 mg, 60%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 6.7 Hz, CH_3-CH_2-), 1.21–1.42 (m, 8 H, CH_3-(CH_2)$_4$-CH_2-), 2.05 (tdd, J = 7.3, 6.9, 1.6 Hz, 2 H, -CH_2-CH_2-CH=CH-), 2.43 (s, 3 H, ArCH_3), 3.17 (dd, J = 5.4, 1.4 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.48 (dtt, J = 15.3, 5.4, 1.4 Hz, 1 H, -CH=CH-CH_2-C≡C-), 5.78 (dtt, J = 15.2, 6.7, 1.8 Hz, 1 H, -CH_2-CH=CH-CH_2-), 7.07–7.13 (m, 1 H, ArH), 7.14–7.19 (m, 2 H, ArH_2) 7.38 (d, J = 7.6 Hz, 1 H, ArH); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.24, 20.91, 22.79, 22.90, 29.01, 29.44, 31.89, 32.46, 81.19, 91.84, 123.80, 124.06, 125.54, 127.74, 129.44, 132.01, 132.58, 140.18; IR (neat, cm^{-1}) 3028, 2954, 2924, 2871, 2855, 2237, 1670, 1600, 1541, 1526, 1506, 1485, 1466, 1457, 1420, 1378, 1338, 1275, 1113, 1044, 964, 939, 754, 724, 715; HRMS (EI) m/z $[M]^+$ calcd for $C_{18}H_{24}$ 240.1878 found, 240.1877; Anal. calcd for $C_{18}H_{24}$ C, 89.94, H, 10.06, found C, 89.95; H, 10.15.

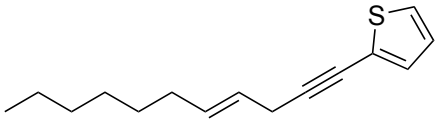
Synthesis of (*E*)-1-(undec-4-en-1-yn-1-yl)naphthalene (*3o*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h. $FeCl_3$ (10 mol %) was used. The product yield (74%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using Hexane as the eluent (R_f = 0.46) to give the title compound (198 mg, 72%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 6.7 Hz, CH_3-CH_2-), 1.24–1.44 (m, 8 H, CH_3-(CH_2)$_4$-CH_2-), 2.08 (tdd, J = 7.4, 7.1, 0.8 Hz, 2 H, -CH_2-CH_2-CH=CH-), 3.29 (dd, J = 5.8, 1.3 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.57 (dtt, J = 15.2, 5.4, 1.3 Hz, 1 H, -CH=CH-CH_2-C≡C-), 5.85 (dtt, J = 14.8, 7.2, 1.6 Hz, 1 H, -CH_2-CH=CH-CH_2-), 7.40 (dd, J = 7.8, 7.1 Hz, 1 H, ArH), 7.49 (td, J = 7.5, 1.2 Hz, 1 H, ArH), 7.55 (td, J = 7.3, 1.2 Hz, 1 H, ArH),

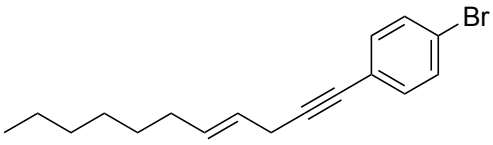
7.64 (dd, J = 7.2, 1.3 Hz, 1 H, Ar*H*), 7.78 (d, J = 8.5 Hz, 1 H, Ar*H*), 7.83 (d, J = 8.4 Hz, 1 H, Ar*H*), 8.35 (d, J = 8.5 Hz, 1 H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.25, 22.79, 23.10, 29.02, 29.44, 31.90, 32.51, 80.28, 93.00, 121.73, 123.94, 125.36, 126.37, 126.48, 126.64, 128.19, 128.33, 130.25, 132.87, 133.34, 133.64; IR (neat, cm^{-1}) 3057, 2954, 2923, 2871, 2853, 2230, 1670, 1585, 1577, 1507, 1466, 1460, 1438, 1417, 1395, 1377, 1332, 1283, 1240, 1216, 1206, 1175, 1155, 1141, 1100, 1063, 1016, 963, 907, 862, 797, 771, 732, 723, 673; HRMS (EI) m/z $[M]^+$ calcd for $C_{21}H_{24}$ 276.1878 found, 276.1878; Anal. calcd for $C_{21}H_{24}$ C, 91.25; H, 8.75, found 91.08; H, 8.90.

Synthesis of (*E*)-2-(undec-4-en-1-yn-1-yl)thiophene (*3p*)



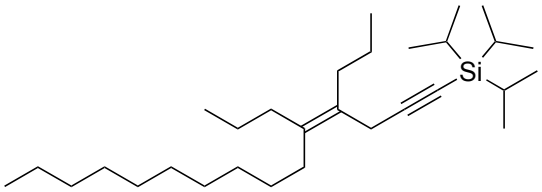
The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: Conditions: 0 ºC, 3 h. $FeCl_3$ (10 mol %) was used. The product yield (60%) was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.59) to give the title compound (135 mg, 56%) as a light yellow oil; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, C*H*$_3$-CH$_2$-), 1.21–1.42 (m, 8 H, CH$_3$-(C*H*$_2$)$_4$-CH$_2$-), 2.04 (tdd, J = 7.3, 6.9, 1.6 Hz, 2 H, -CH$_2$-C*H*$_2$-CH=CH-), 3.14 (dd, J = 5.4, 1.3 Hz, 2 H, -CH=CH-C*H*$_2$-C≡C-), 5.45 (dtt, J = 15.3, 5.6, 0.9 Hz, 1 H, -CH=C*H*-CH$_2$-C≡C-), 5.71 (dtt, J = 15.2, 6.7, 1.6 Hz, 1 H, -CH$_2$-C*H*=CH-CH$_2$-), 6.94 (dd, J = 5.4, 3.6 Hz, 1 H, Ar*H*), 7.13 (dd, J = 3.6, 0.9 Hz, 1 H, Ar*H*), 7.18 (dd, J = 5.4, 1.3 Hz, 1 H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.24, 22.78, 23.05, 29.02, 29.36, 31.87, 32.48, 75.28, 90.05, 123.41, 124.13, 126.20, 126.91, 131.27, 133.00; IR (neat, cm^{-1}) 3035, 2957, 2924, 2873, 2854, 2237, 1792, 1669, 1589, 1519, 1465, 1456, 1428, 1418, 1377, 1355, 1309, 1276, 1238, 1190, 1079, 1064, 1044, 964, 847, 827, 693; HRMS (EI) m/z $[M]^+$ calcd for $C_{15}H_{20}S$ 232.1286 found, 232.1285; Anal. calcd for $C_{15}H_{20}S$ C, 77.53; H, 8.68, found 77.37; H, 8.84.

Synthesis of (*E*)-1-bromo-4-(undec-4-en-1-yn-1-yl)benzene (*3q*)



The reaction was carried out according to the general procedure on a 1.0 mmol scale. Conditions: 0 ºC, 1 h, $FeCl_3$ (10 mol %). The product yield (87%) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. $FeCl_3$ (10 mol %) was used. The crude product was purified by silica gel column chromatography using hexane as the eluent (R_f = 0.62) to give the title compound (232 mg, 76%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, CH_3-CH_2-) 1.21–1.42 (m, 8 H, CH_3-(CH_2)$_4$-CH_2-), 2.04 (tdd, J = 7.3, 6.7, 1.6 Hz, 2 H, -CH_2-CH_2-CH=CH-), 3.11 (dd, J = 5.4, 1.3 Hz, 2 H, -CH=CH-CH_2-C≡C-), 5.45 (dtt, J = 15.2, 5.4, 1.4 Hz, 1 H, -CH=CH-CH_2-C≡C-), 5.72 (dtt, J = 15.3, 6.7, 1.6 Hz, 1 H, -CH_2-CH=CH-CH_2-), 7.27 (d, J = 8.1 Hz, 2 H, ArH_2), 7.41 (d, J = 8.5 Hz, 2 H, ArH_2); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.24, 22.78, 22.81, 29.02, 29.38, 31.87, 32.47, 32.47, 81.19, 89.29, 121.89, 122.99, 123.54, 131.56 (2C), 132.92, 133.20 (2C); IR (neat, cm^{-1}) 3032, 2954, 2924, 2871, 2854, 2240, 1898, 1669, 1643, 1587, 1485, 1466, 1459, 1417, 1394, 1377, 1338, 1278, 1176, 1110, 1095, 1070, 1011, 964, 821, 727, 703; HRMS (EI) m/z $[M]^+$ calcd for $C_{17}H_{21}Br$ 304.0827 found, 304.0827; Anal. calcd for $C_{17}H_{21}Br$ C, 66.89; H, 6.93, found C, 66.84; H, 7.07.

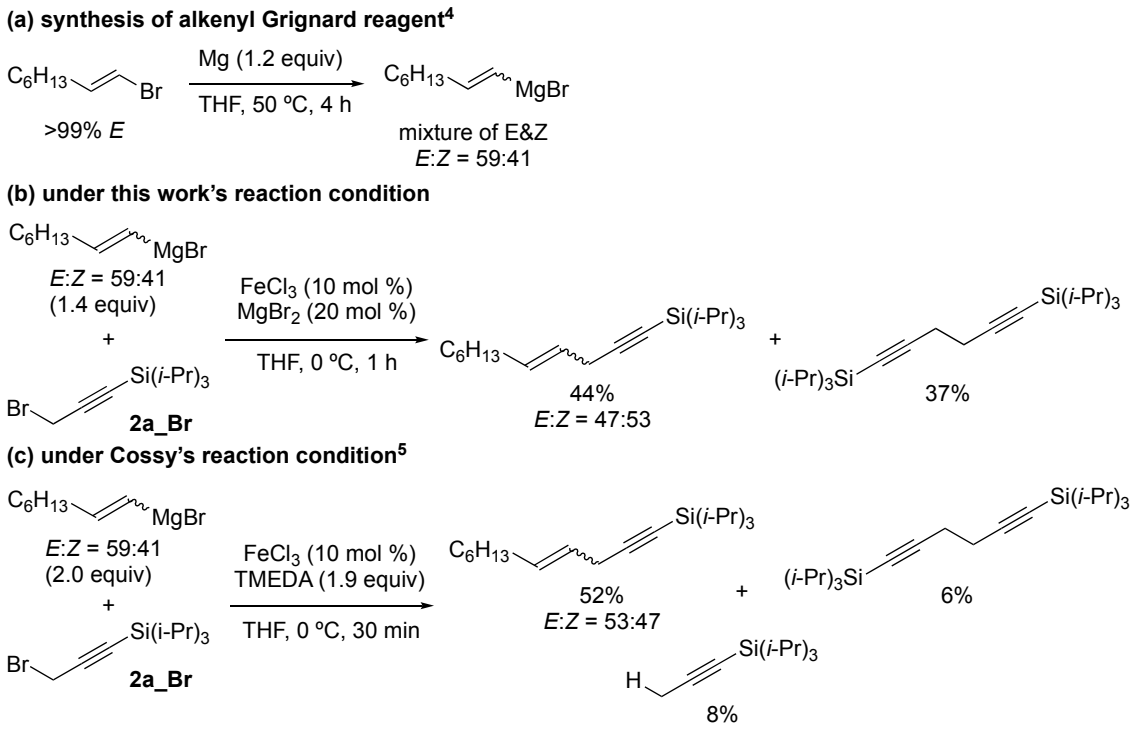
Synthesis of (*Z*)-(4,5-dipropylpentadec-4-en-1-yn-1-yl)triisopropylsilane (*3r*)



The reaction was carried out according to the general procedure on a 0.316 mmol scale. Conditions: 40 ºC, 1 h. $FeCl_3$ (5 mol %) was used. The crude product was purified by silica gel column chromatography using Hexane as the eluent (R_f = 0.79) to give the title compound (78.1 mg, 55%) as a colorless oil; ^1H NMR (392 MHz, $CDCl_3$) δ 0.85–0.92 (m, 9 H, CH_3-CH_2-), 0.96–1.10 (m, 21 H, -SiCHCH_3, -SiCHCH_3), 1.19–1.51 (m, 20 H, CH_3-(CH_2)$_8$-CH_2-, CH_3-CH_2-CH_2-), 1.95–2.04 (m, 4 H, -CH_2-CH_2-C=C- in Pr), 2.14 (t, J = 9.9 Hz, 2 H, -CH_2-CH_2-C=C- in $C_{10}H_{21}$), 2.97 (s, 2 H, -C=C-CH_2-C≡C-); ^{13}C NMR

(99 MHz, $CDCl_3$) δ 11.51 (3C), 14.27, 14.32, 14.41, 18.77 (6C), 22.01, 22.23, 22.84 (2C), 29.04, 29.50, 29.80, 29.82, 29.85, 30.18, 32.08, 32.47, 34.16, 34.39, 79.68, 108.26, 128.46, 135.79; IR (neat, cm^{-1}) 2957, 2924, 2894, 2864, 2168, 1464, 1378, 1366, 1071, 1017, 994, 919, 882, 740, 721, 675, 661; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{30}H_{58}Si$ 446.4308, found 446.4306; Anal. calcd for $C_{30}H_{58}Si$ C, 80.63; H, 13.08, found C, 80.69; H, 13.20.

3. Cross coupling using Alkenyl Grignard Reagent



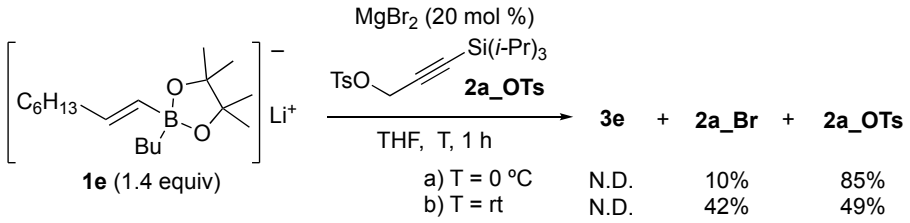
Preparation of alkenyl Grignard reagent: To a dry, three-necked 100 mL round-bottomed flask was added magnesium turnings (439 mg, 18.0 mmol) and strongly stirred for 1 h. After magnesium turnings were activated, 20 mL THF was added and alkenyl bromide was added dropwise. The reaction mixture was stirred under 50 °C until GC analysis showed that the starting material was completely consumed. The ratio of alkenyl Grignard reagent was determined by GC after quenched by I_2.

Procedure of reaction b: To a solution of propargyl bromide **2a_Br** (137.8 mg, 0.5 mmol) was added 0.5 mL $MgBr_2$ (0.2 M in THF), then a THF solution of the alkenyl Grignard reagent (0.296 M, 2.53 mL) and $FeCl_3$ (0.1M in THF, 0.5 mL) was added dropwise (at a rate of around 5 mL/h) using a syringe pump at 0 °C. The reaction mixture was further stirred for 1 h at 0 °C, the reaction mixture was quenched by adding an aqueous saturated NH_4Cl solution. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was filtered through a pad of Florisil and concentrated under the reduced pressure to give the crude product. The product yield and *E*:*Z* ratio (44%, *E:Z* = 47:53) were determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

Procedure of reaction c[5]: To a solution of propargyl bromide **2a_Br** (138.1 mg, 0.5 mmol) and $FeCl_3$ (8.1 mg, 0.05 mmol) in THF (0.5 mL), a solution of the alkenyl Grignard reagent (0.296 M in THF, 3.38 mL) and TMEDA (110.4 mg, 0.95 mmol) was added dropwise (at a rate of around 5 mL/h) using a syringe pump at 0 °C. The reaction mixture was further stirred for 30 min at 0 °C, the reaction mixture was quenched by adding an aqueous saturated NH_4Cl solution. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was filtered through a pad of Florisil and concentrated under the reduced pressure to give the crude product. The product yield (52%, *E:Z* = 53:47) was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

These reactions afforded a mixture of (*E*)- and (*Z*)-coupling products in low yields and a large amount of homo-coupling products.

4. Halogen Exchange of Propargyl Tosylate



The reaction was carried out according to the general procedure on a 0.50 mmol scale. Conditions: a) 0 ºC, 1 h; b) rt, 1 h. The yield of **3e**, **2a_Br** and the recovery of **2a_OTs** were determined by GC analysis using undecane as an internal standard.

The reaction clarifies that $MgBr_2$ facilitates the halogen exchange of propargyl tosylate **2a_OTs** to afford the corresponding propargyl bromide **2a_Br** under 0 °C. Elevating reaction temperature enhances the halogen exchange, resulting in the complete consumption of $MgBr_2$ to afford **2a_Br** quantitatively. Notably, cross-coupling product was not observed without iron catalyst.

5. Spectral Data

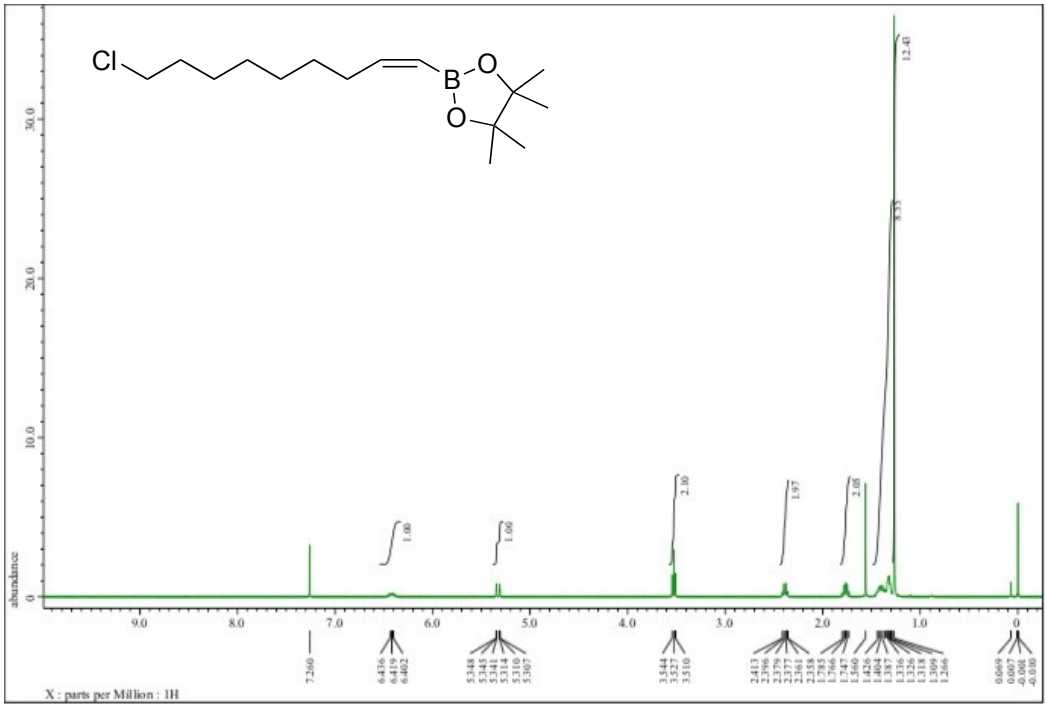


Figure S1. ^{1}H NMR spectrum of (*Z*)-(9-chlorononon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**).

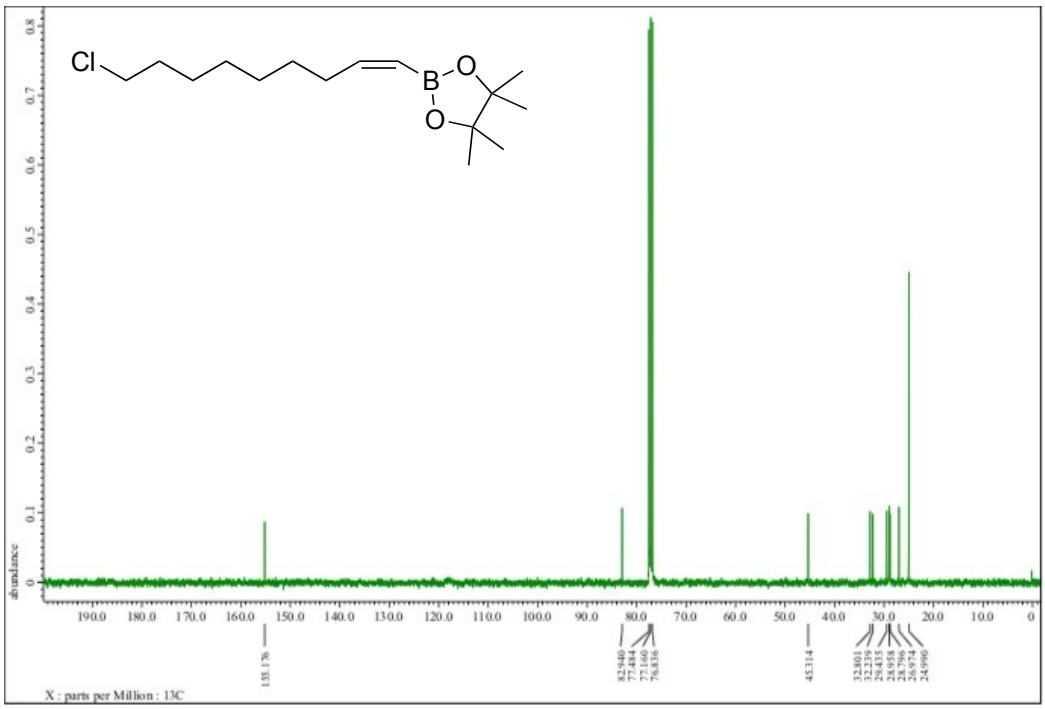


Figure S2. ^{13}C NMR spectrum of (*Z*)-(9-chlorononon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**).

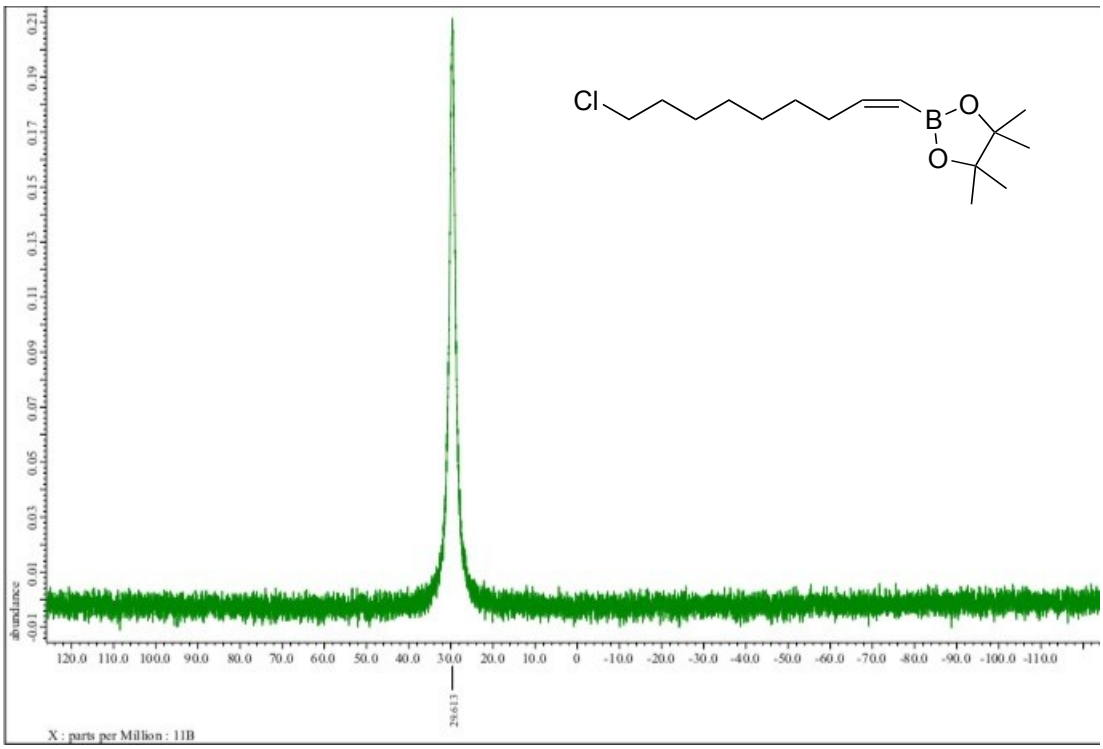


Figure S3. ^{11}B NMR spectrum of (*Z*)-(9-chloronon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**).

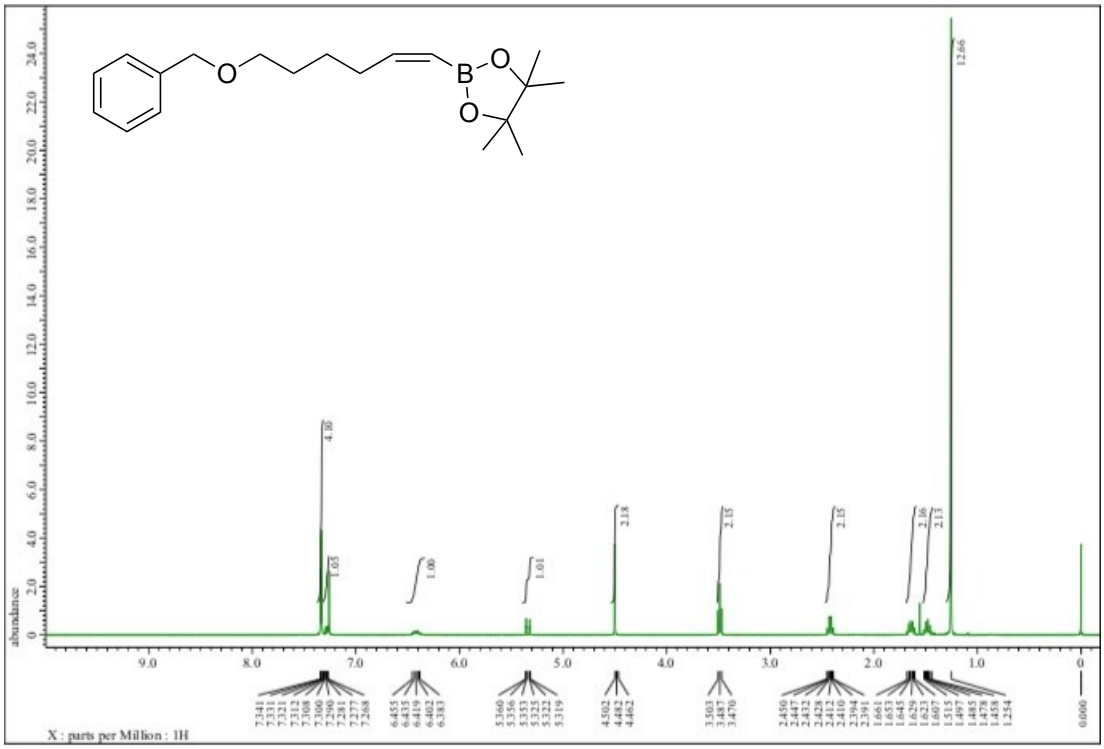


Figure S4. ^{1}H NMR spectrum of (*Z*)-2-(6-(benzyloxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1b**).

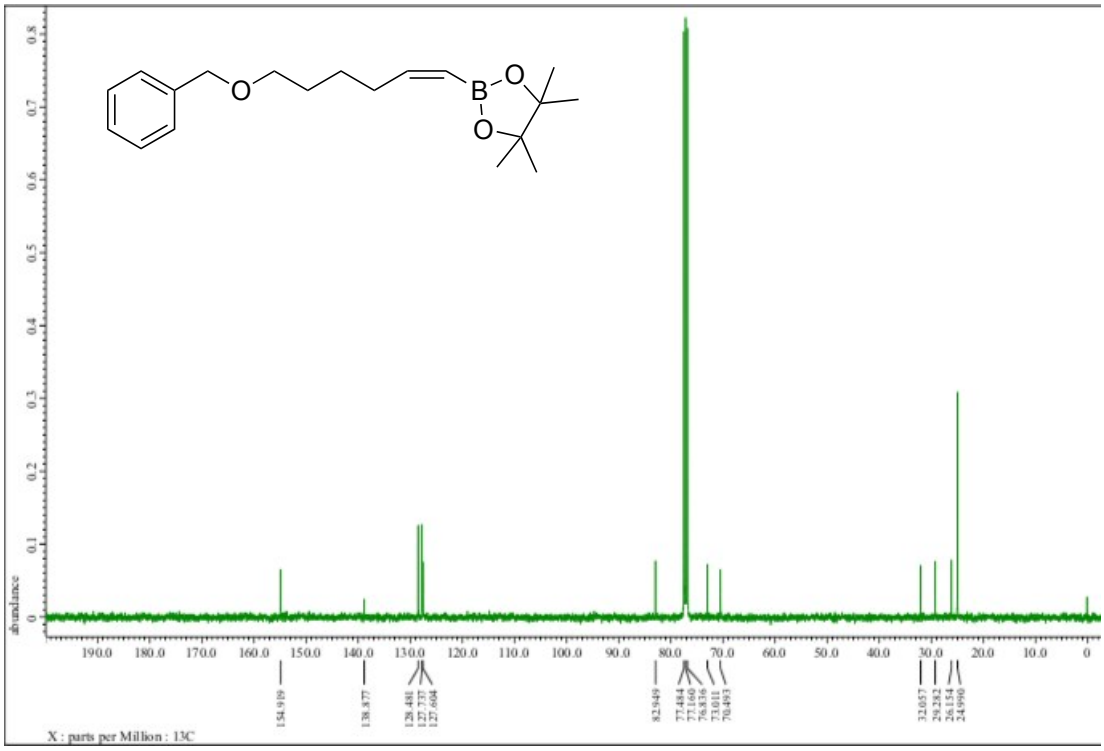


Figure S5. ^{13}C NMR spectrum of (*Z*)-2-(6-(benzyloxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1b**).

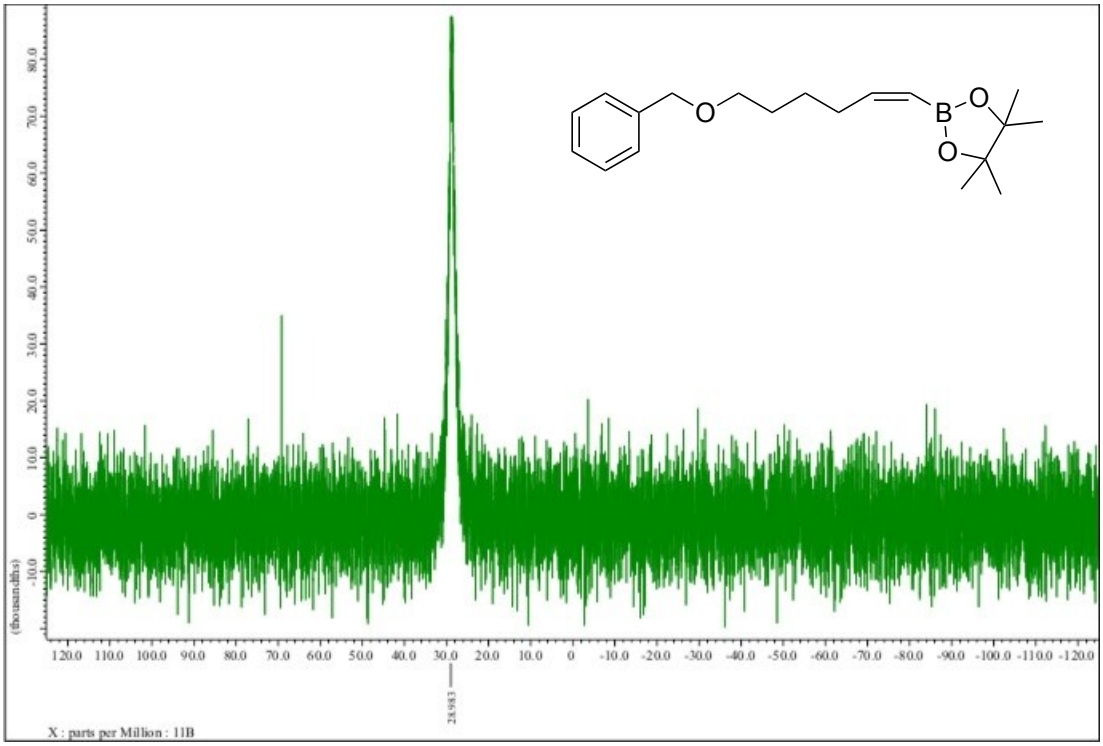


Figure S6. ^{11}B NMR spectrum of (*Z*)-2-(6-(benzyloxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1b**).

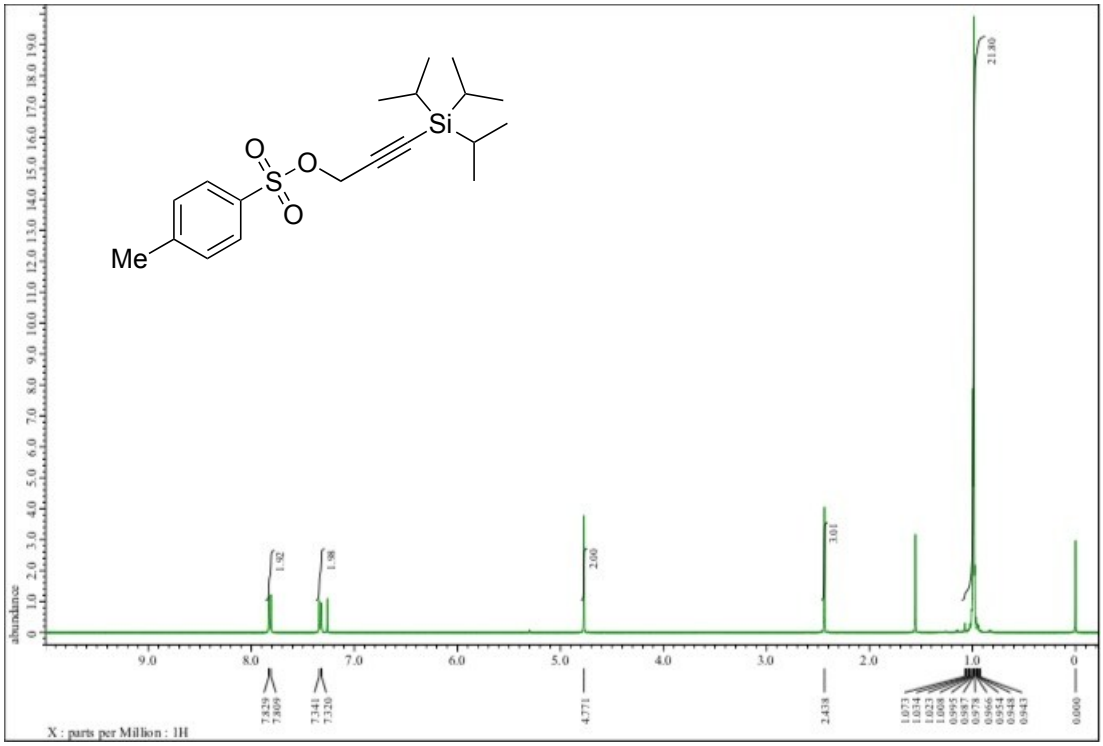


Figure S7. ^{1}H NMR spectrum of 3-(triisopropylsilyl)prop-2-yn-1-yl 4-methylbenzenesulfonate (**2a_OTs**)

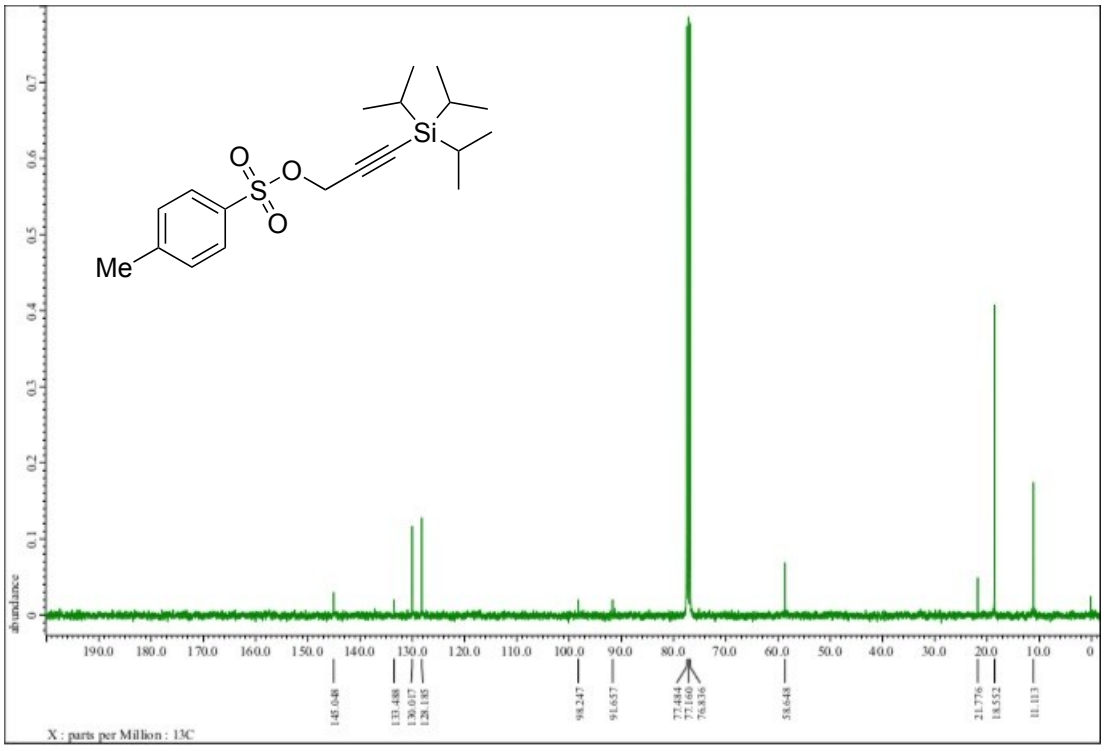


Figure S8. ^{13}C NMR spectrum of 3-(triisopropylsilyl)prop-2-yn-1-yl 4-methylbenzenesulfonate (**2a_OTs**).

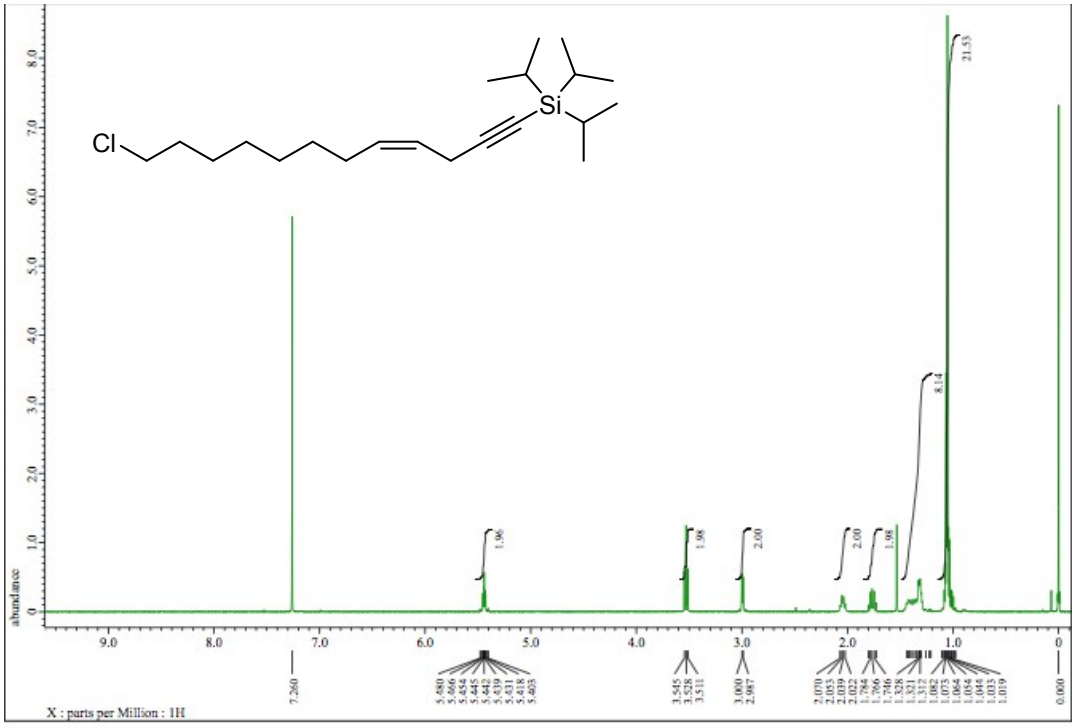


Figure S9. ^{1}H NMR spectrum of (*Z*)-(12-chlorododec-4-en-1-yn-1-yl)triisopropylsilane (**3a**).

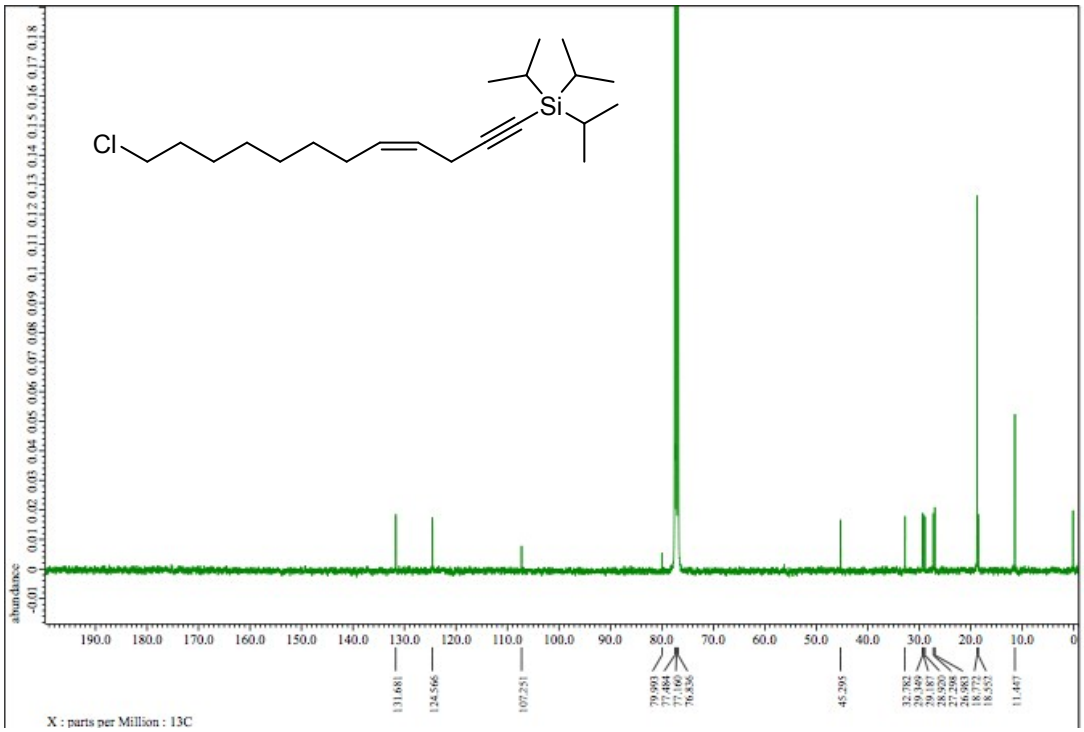


Figure S10. ^{13}C NMR spectrum of (*Z*)-(12-chlorododec-4-en-1-yn-1-yl)triisopropyl - silane (**3a**).

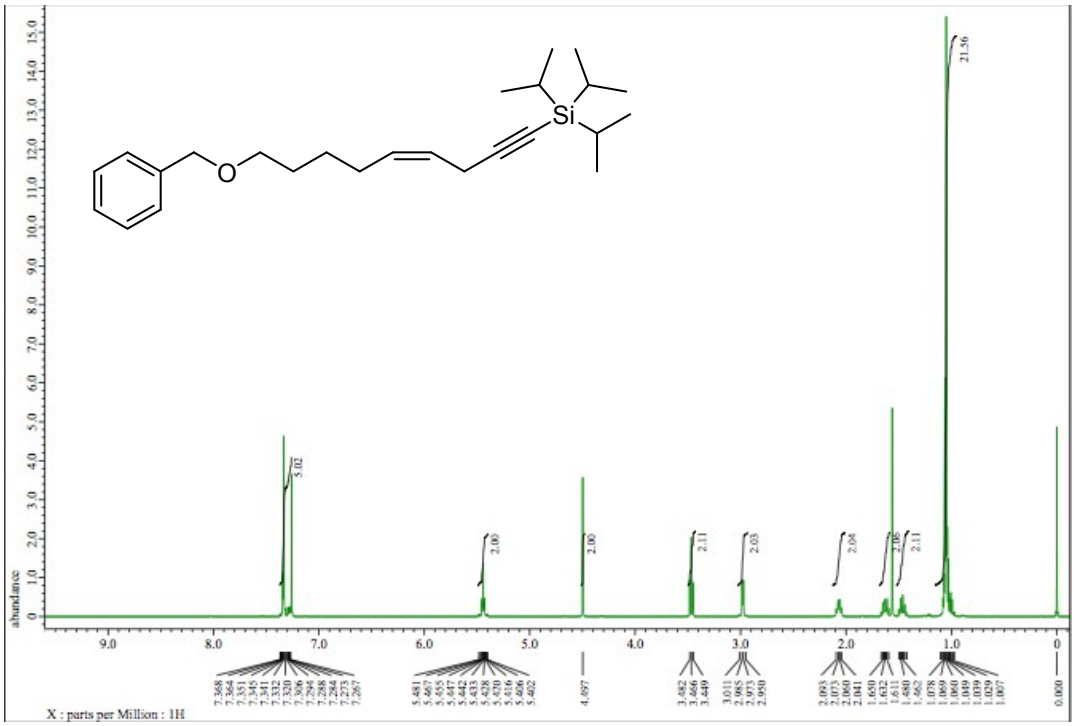


Figure S11. ^{1}H NMR spectrum of (*Z*)-(9-benzyloxy-non-4-en-1-yn-1-yl)triisopropyl - silane (**3b**).

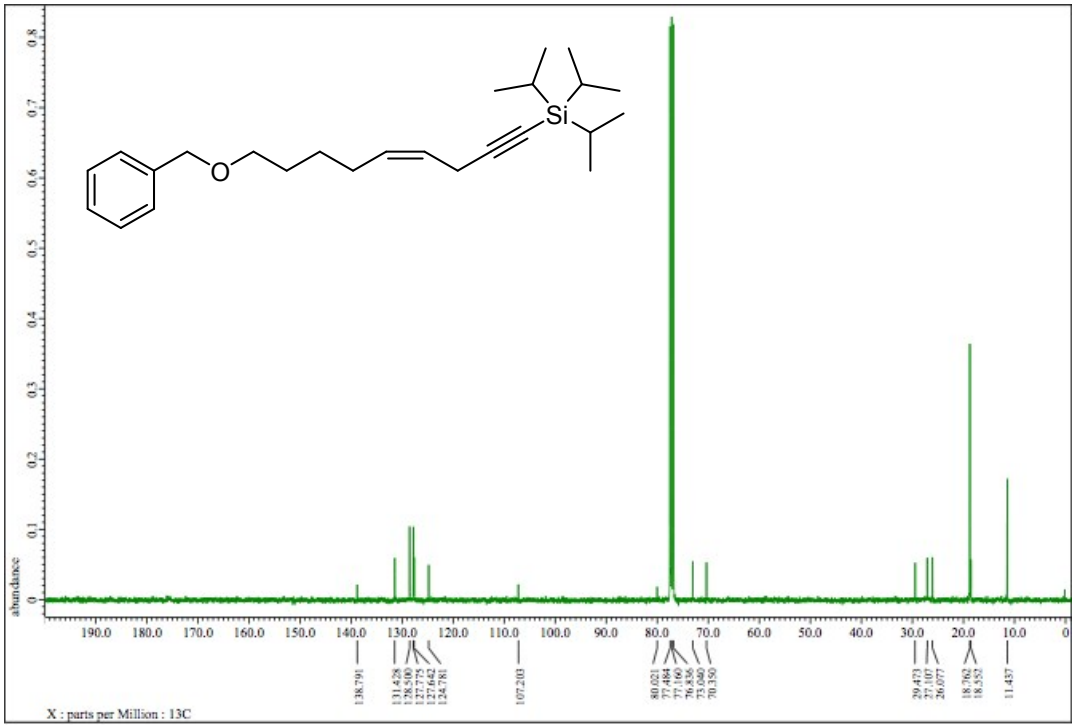


Figure S12. ^{13}C NMR spectrum of (*Z*)-(9-benzyloxy-non-4-en-1-yn-1-yl)triisopropyl - silane (**3b**).

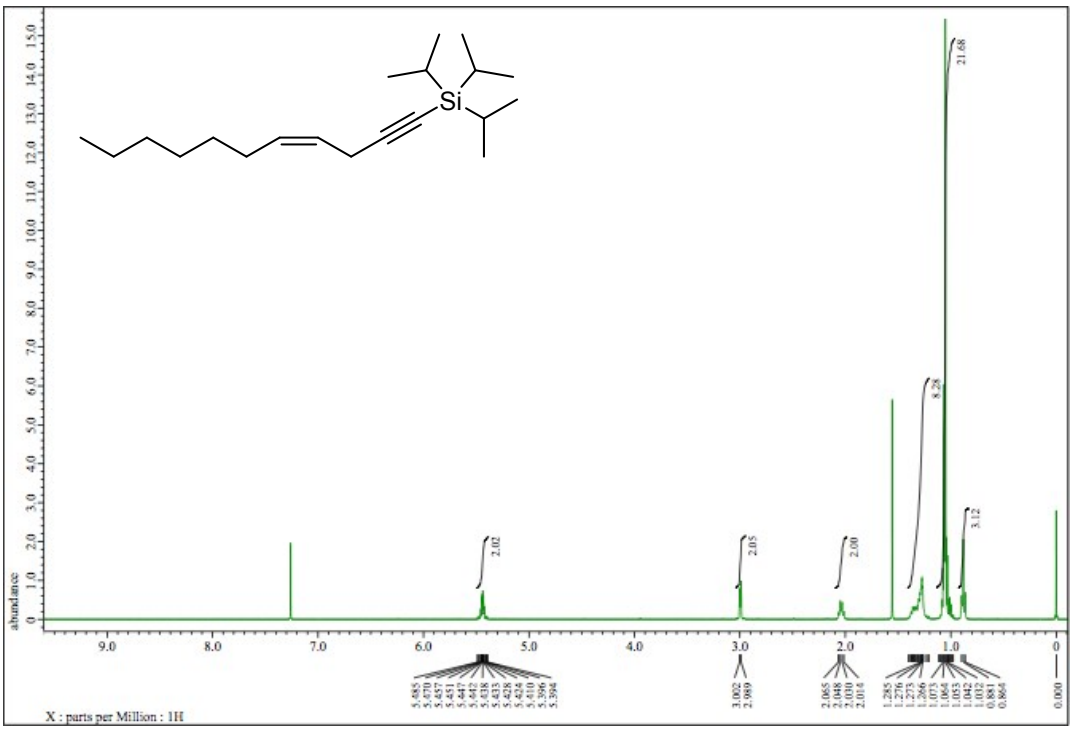


Figure S13. ^{1}H NMR spectrum of (*Z*)-triisopropyl(undec-4-en-1-yn-1-yl)silane (**3c**).

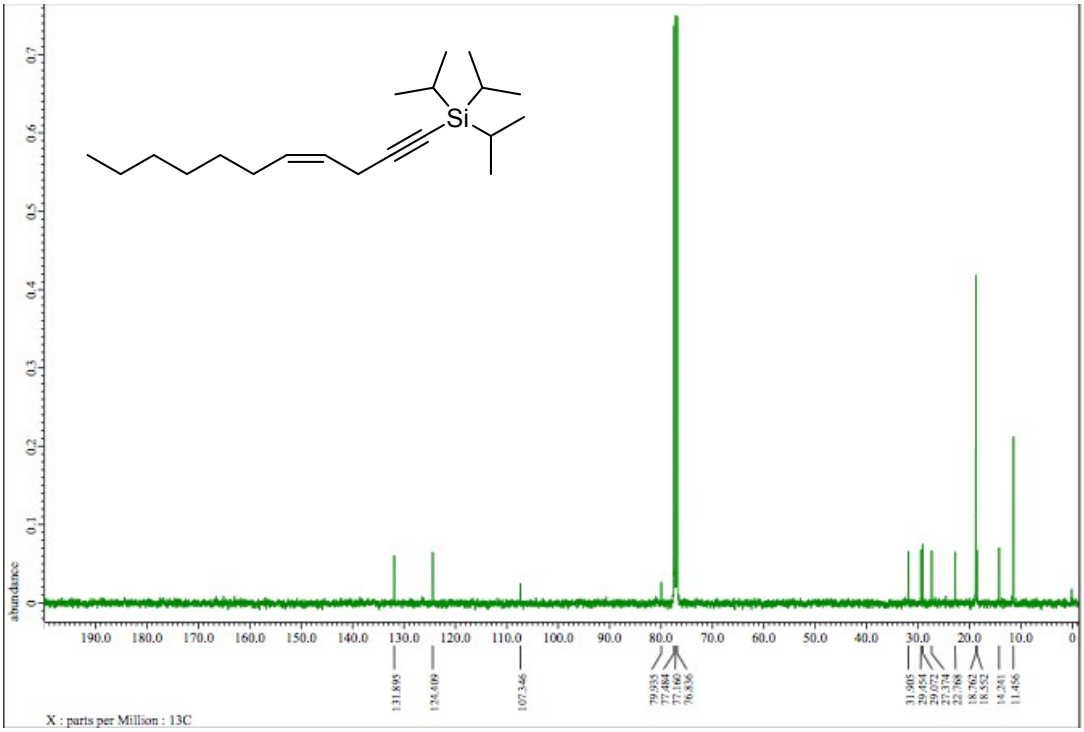


Figure S14. ^{13}C NMR spectrum of (*Z*)-triisopropyl(undec-4-en-1-yn-1-yl)silane (**3c**).

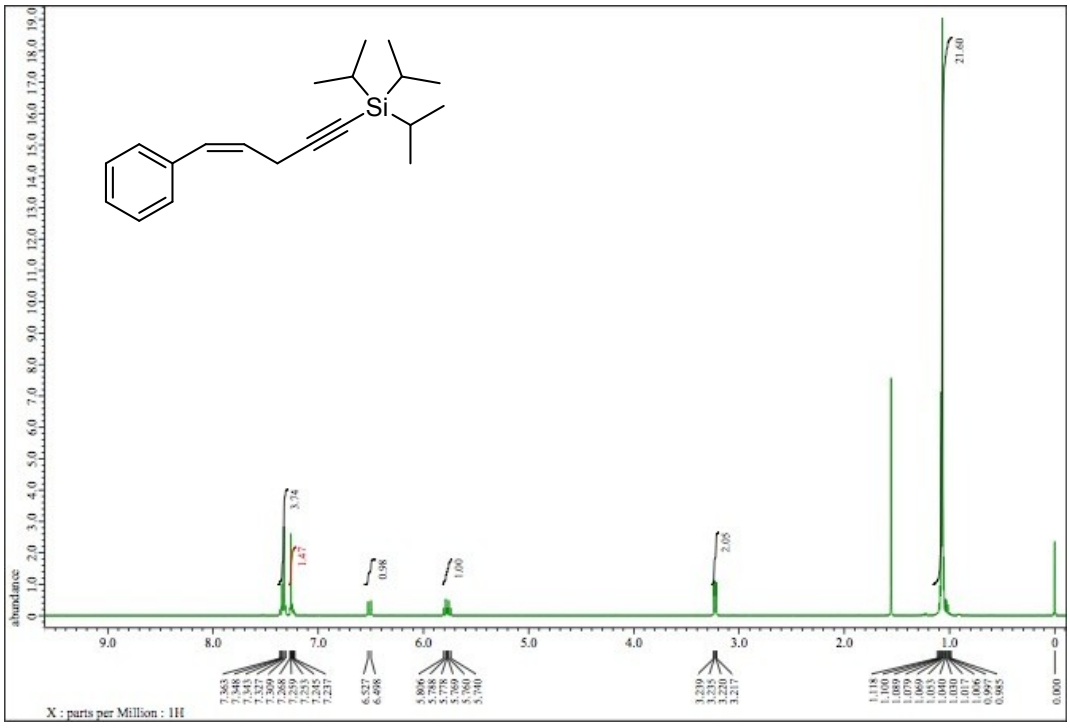


Figure S15. ^{1}H NMR spectrum of (*Z*)-triisopropyl(5-phenylpent-4-en-1-yn-1-yl)silane (**3d**).

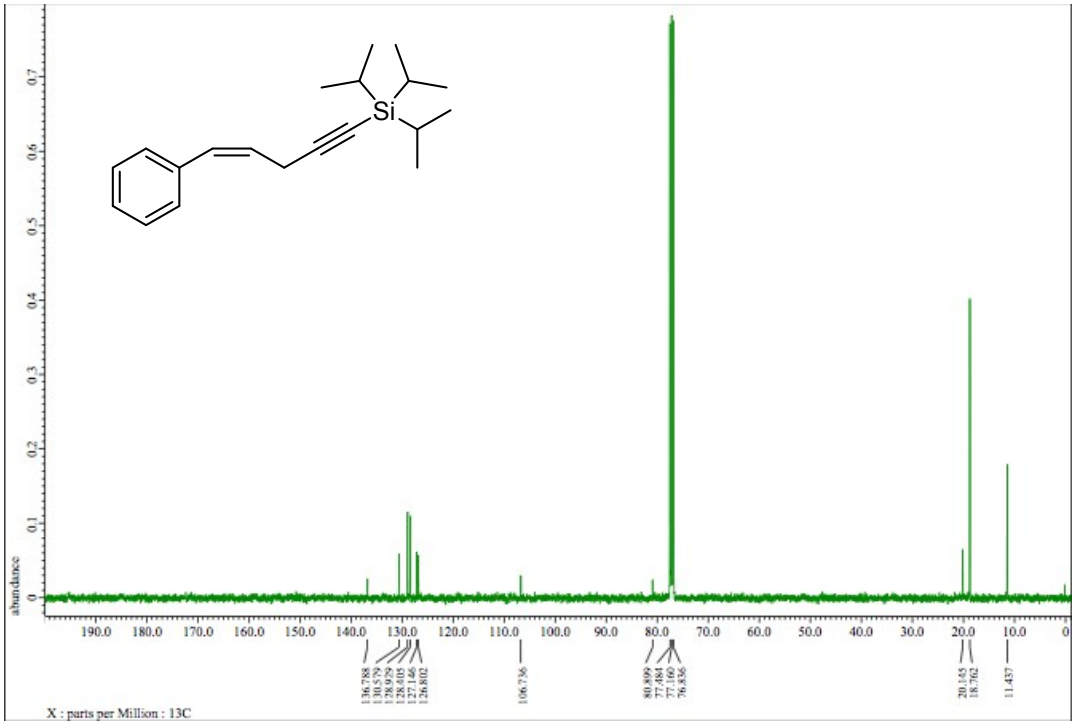


Figure S16. ^{13}C NMR spectrum of (*Z*)-triisopropyl(5-phenylpent-4-en-1-yn-1-yl)silane (**3d**).

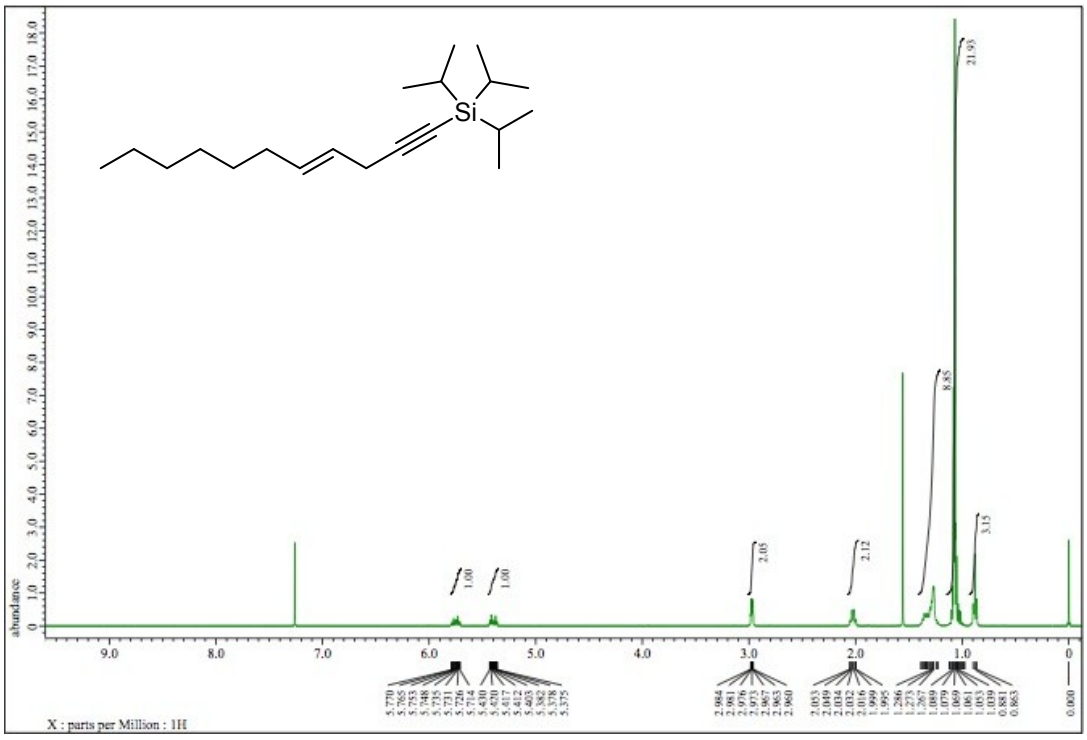


Figure S17. ^{1}H NMR spectrum of (*E*)-triisopropyl(undec-4-en-1-yn-1-yl)silane (**3e**).

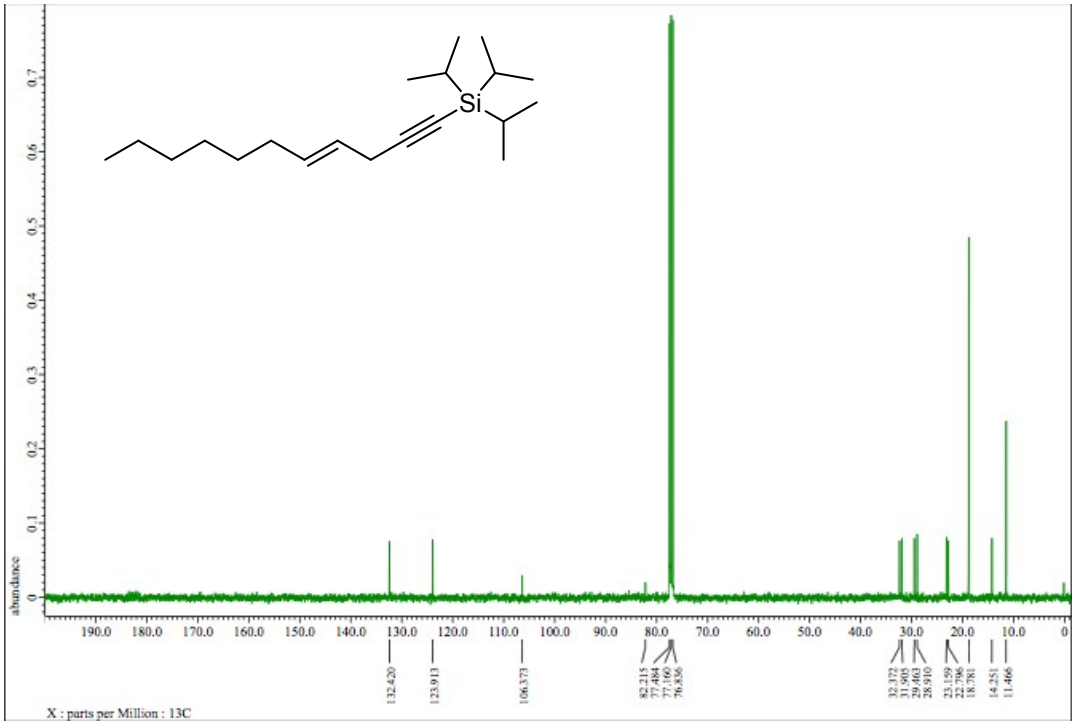


Figure S18. ^{13}C NMR spectrum of (*E*)-triisopropyl(undec-4-en-1-yn-1-yl)silane (**3e**).

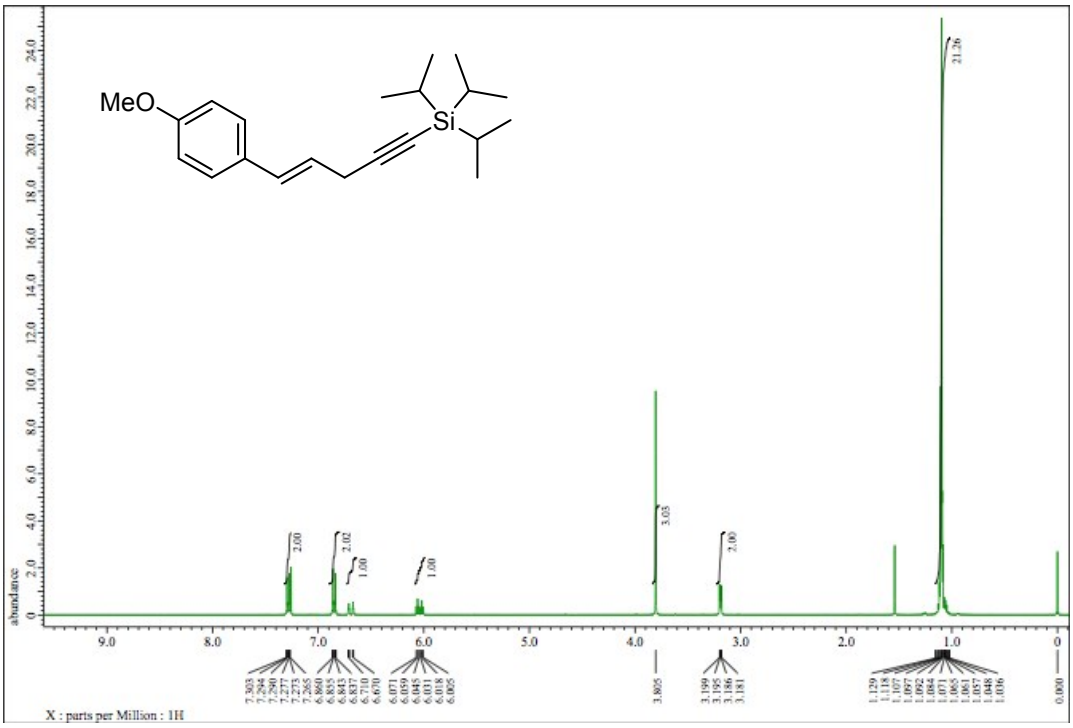


Figure S19. ^{1}H NMR spectrum of (*E*)-triisopropyl(5-(4-methoxyphenyl)pent-4-en-1 -yn-1-yl)silane (**3f**).

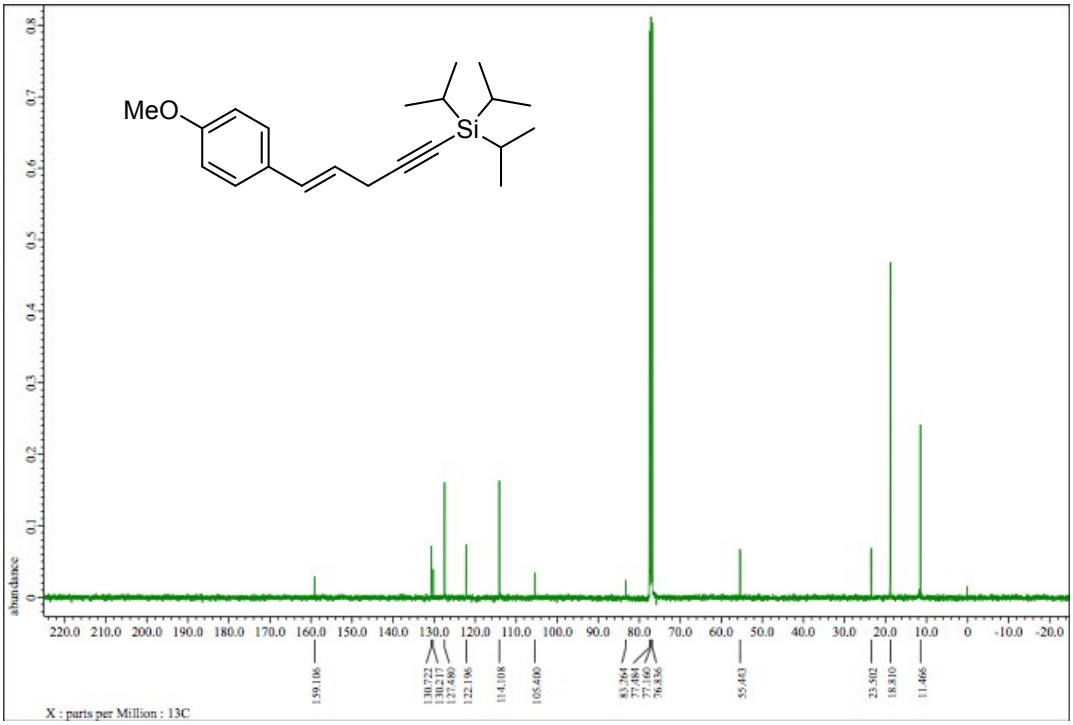


Figure S20. ^{13}C NMR spectrum of (*E*)-triisopropyl(5-(4-methoxyphenyl)pent-4-en-1 -yn-1-yl)silane (**3f**).

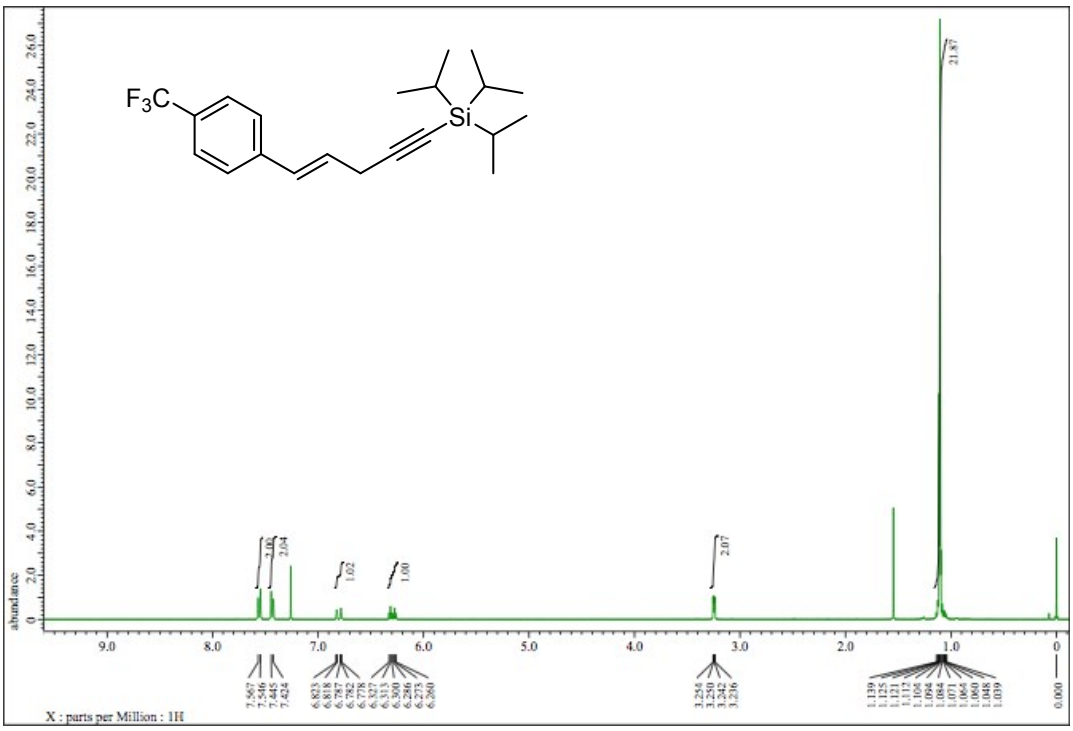


Figure S21. ^{1}H NMR spectrum of (*E*)-triisopropyl(5-(4-trifluoromethylphenyl)pent-4-en-1-yn-1-yl)silane (**3g**).

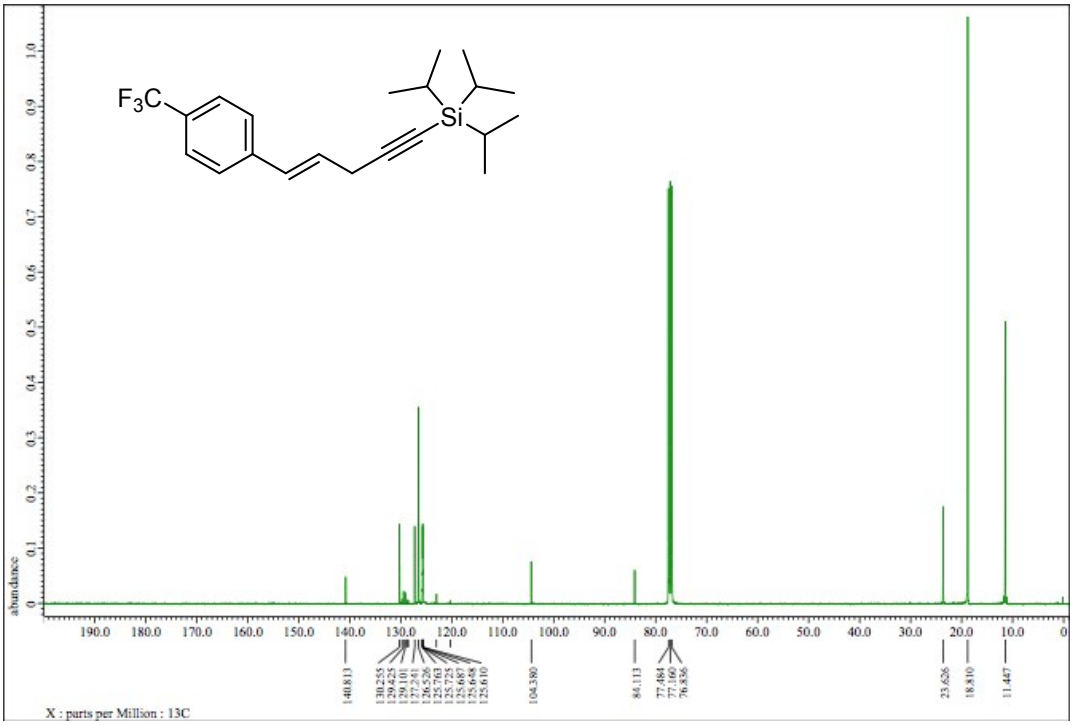


Figure S22. ^{13}C NMR spectrum of (*E*)-triisopropyl(5-(4-trifluoromethylphenyl)pent-4-en-1-yn-1-yl)silane (**3g**).

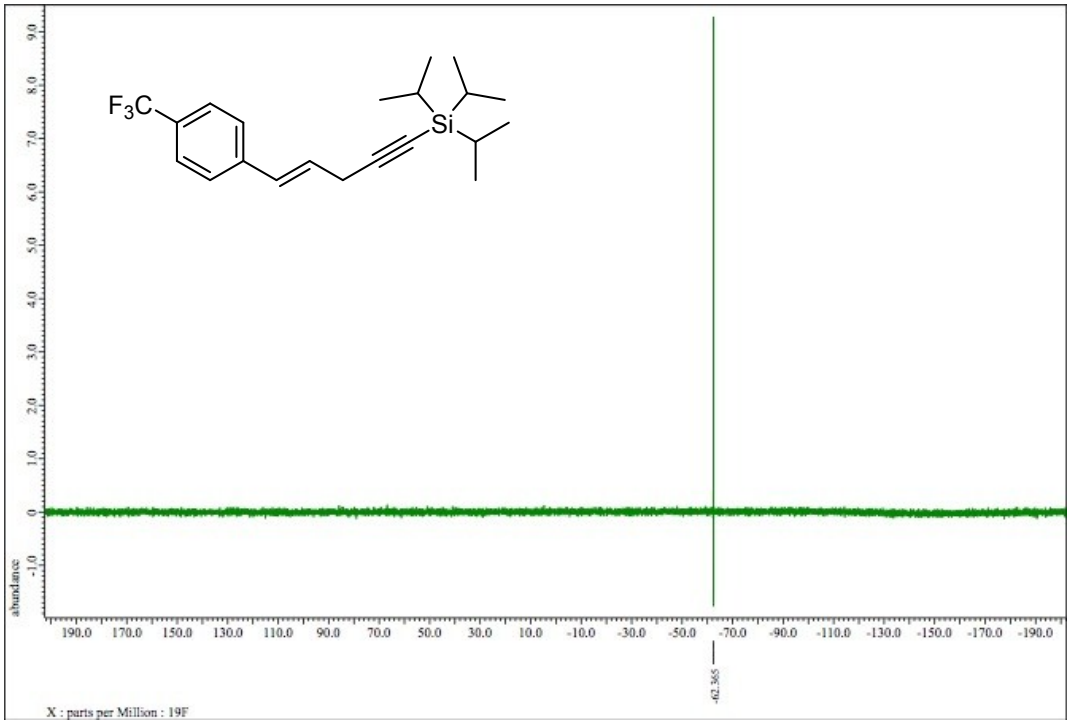


Figure S23. ^{13}F NMR spectrum of (*E*)-triisopropyl(5-(4-trifluoromethylphenyl)pent-4-en-1-yn-1-yl)silane (**3g**).

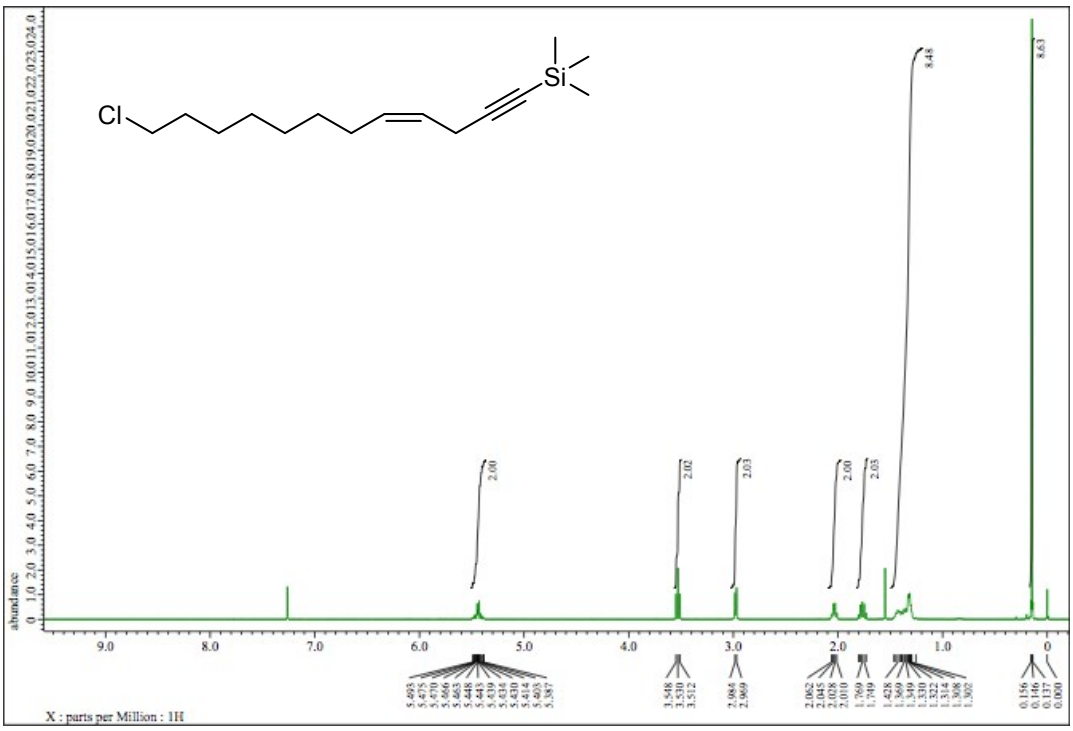


Figure S24. ^{1}H NMR spectrum of (*Z*)-(12-chlorododec-4-en-1-yn-1-yl)trimethylsilane (**3h**).

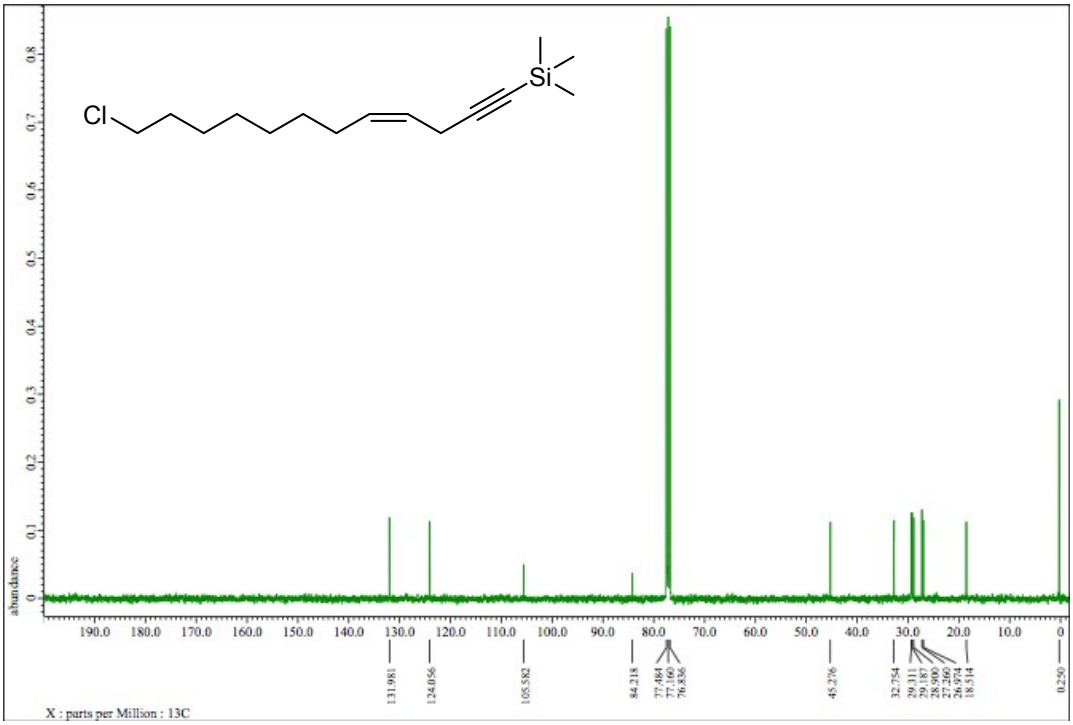


Figure S25. ^{13}C NMR spectrum of (*Z*)-(12-chlorododec-4-en-1-yn-1-yl)trimethylsilane (**3h**).

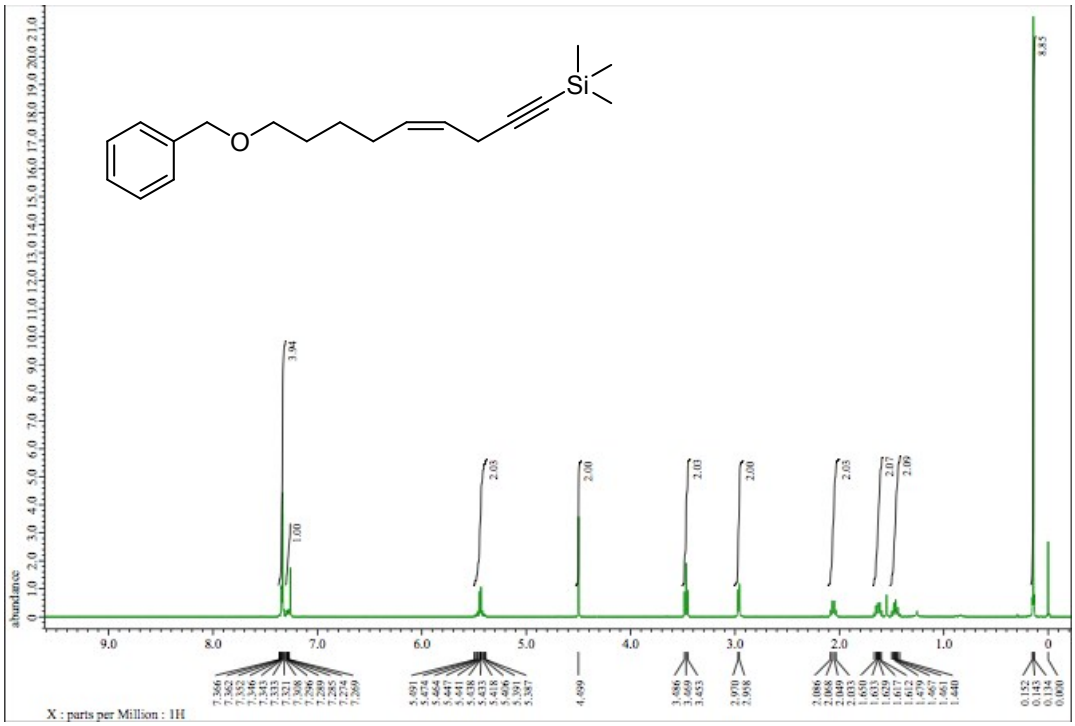


Figure S26. ^{1}H NMR spectrum of (*Z*)-(9-benzyloxynon-4-en-1-yn-1-yl)trimethylsilane (**3i**).

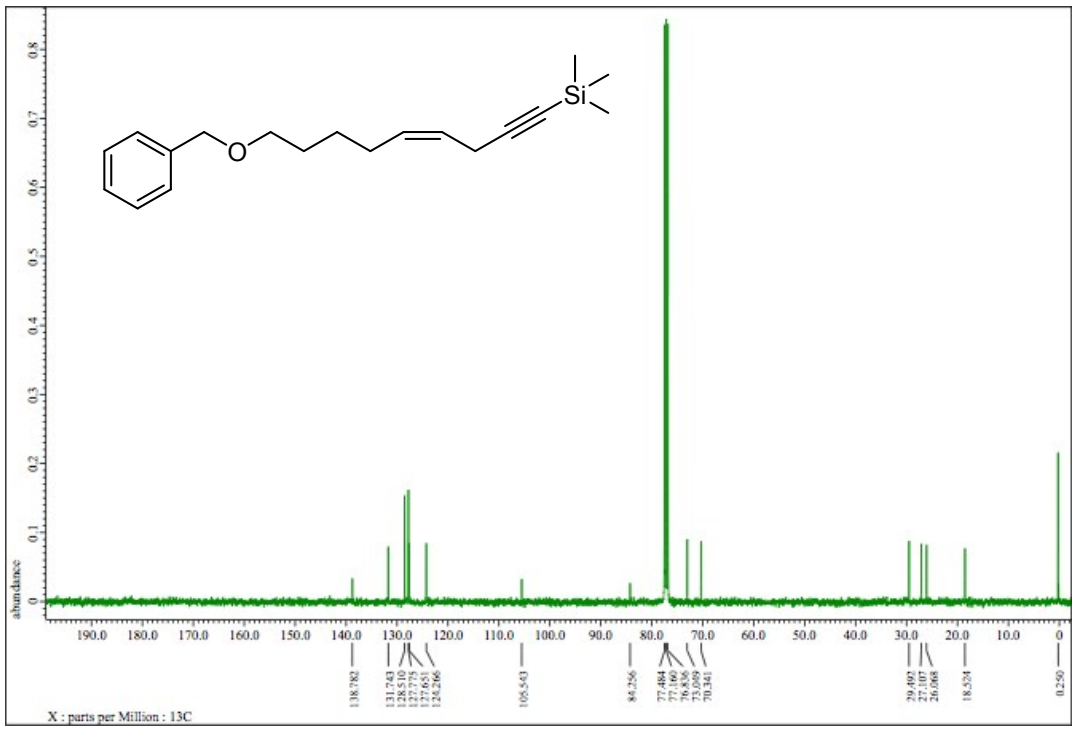


Figure S27. ^{13}C NMR spectrum of (*Z*)-(9-benzyloxynon-4-en-1-yn-1-yl)trimethylsilane (**3i**).

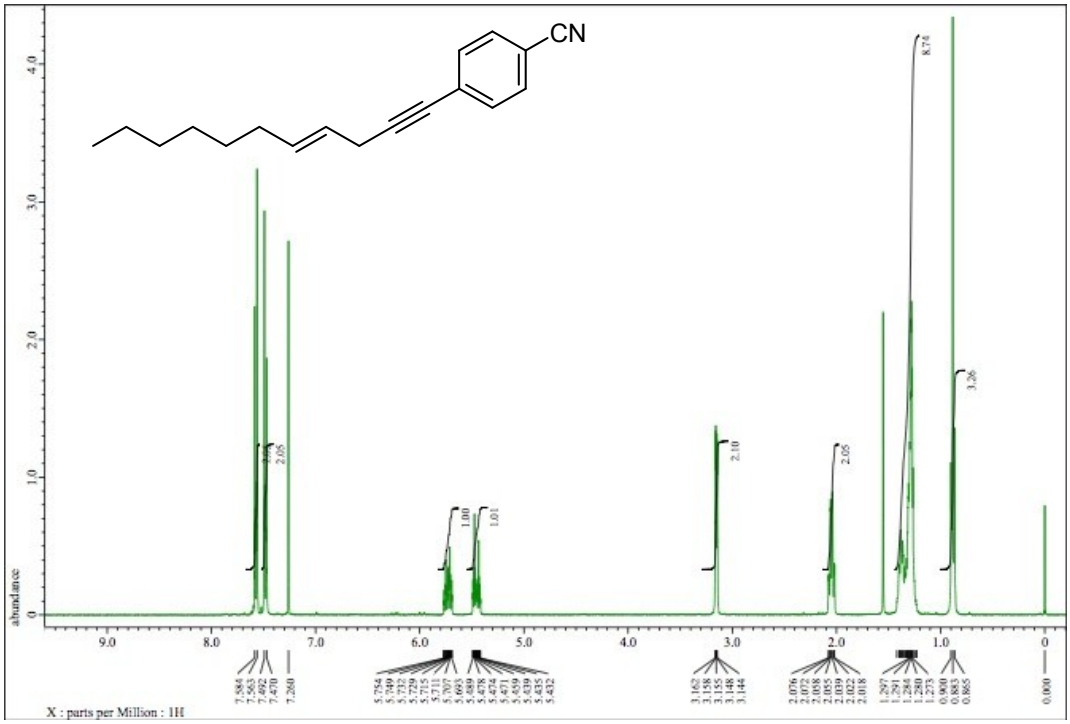


Figure S28. ^{1}H NMR spectrum of (*E*)-4-(undec-4-en-1-yn-1-yl)benzonitrile (**3j**).

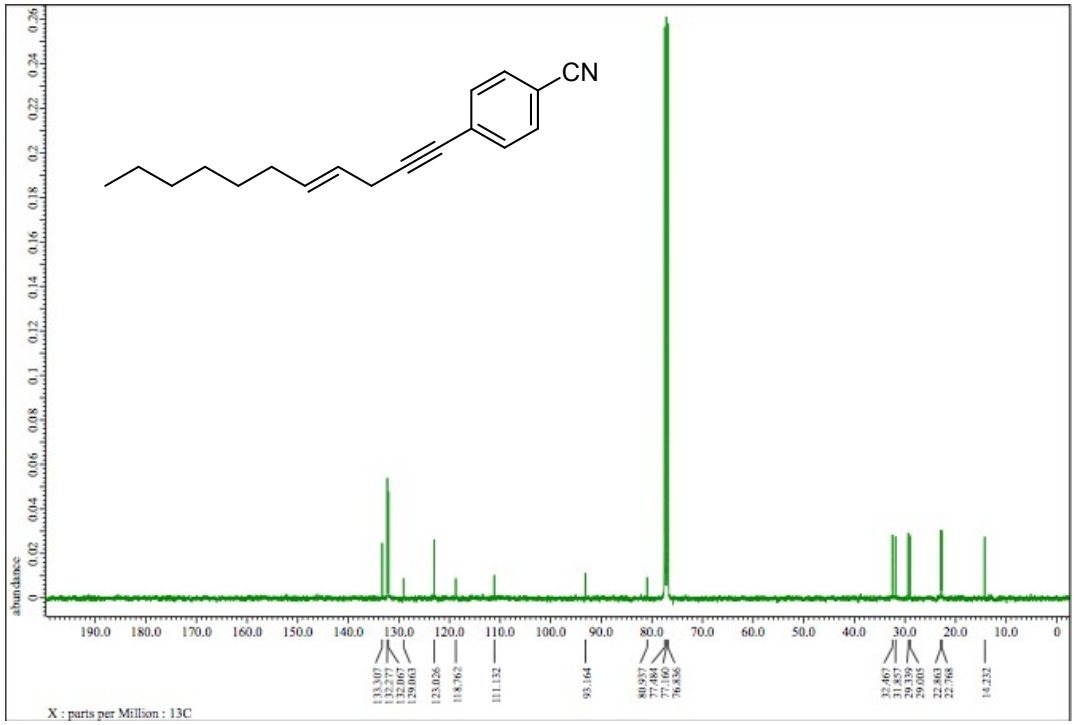


Figure S29. ^{13}C NMR spectrum of (*E*)-4-(undec-4-en-1-yn-1-yl)benzonitrile (**3j**).

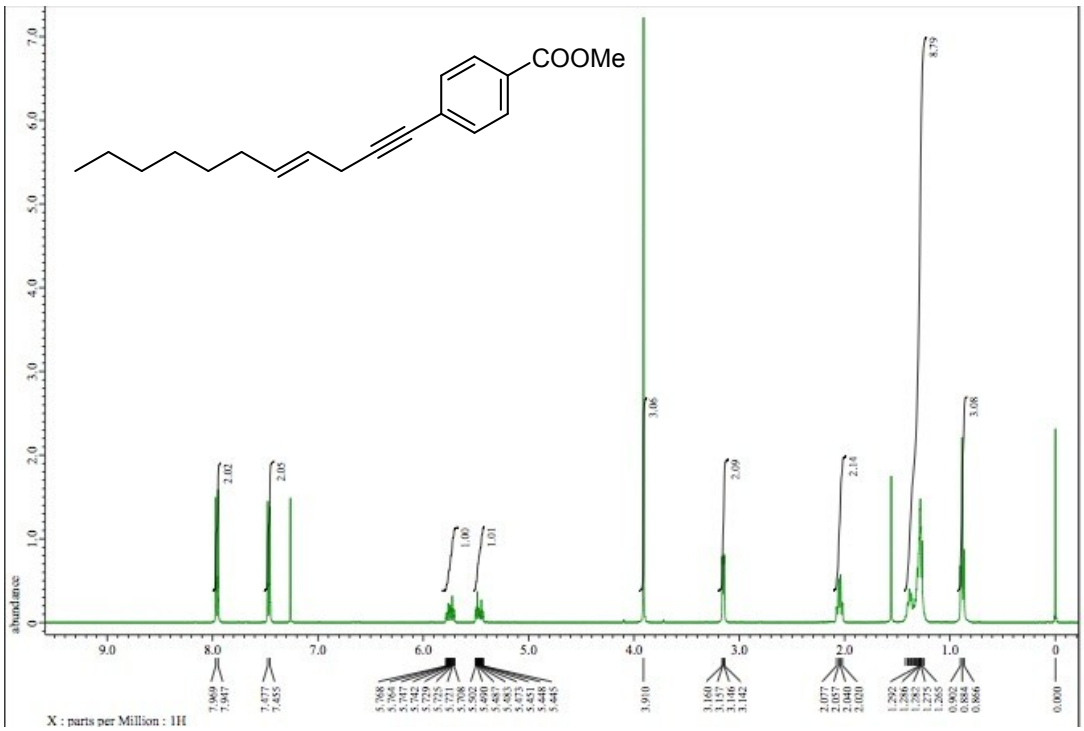


Figure S30. ^{1}H NMR spectrum of methyl (*E*)-4-(undec-4-en-1-yn-1-yl)benzoate (**3k**).

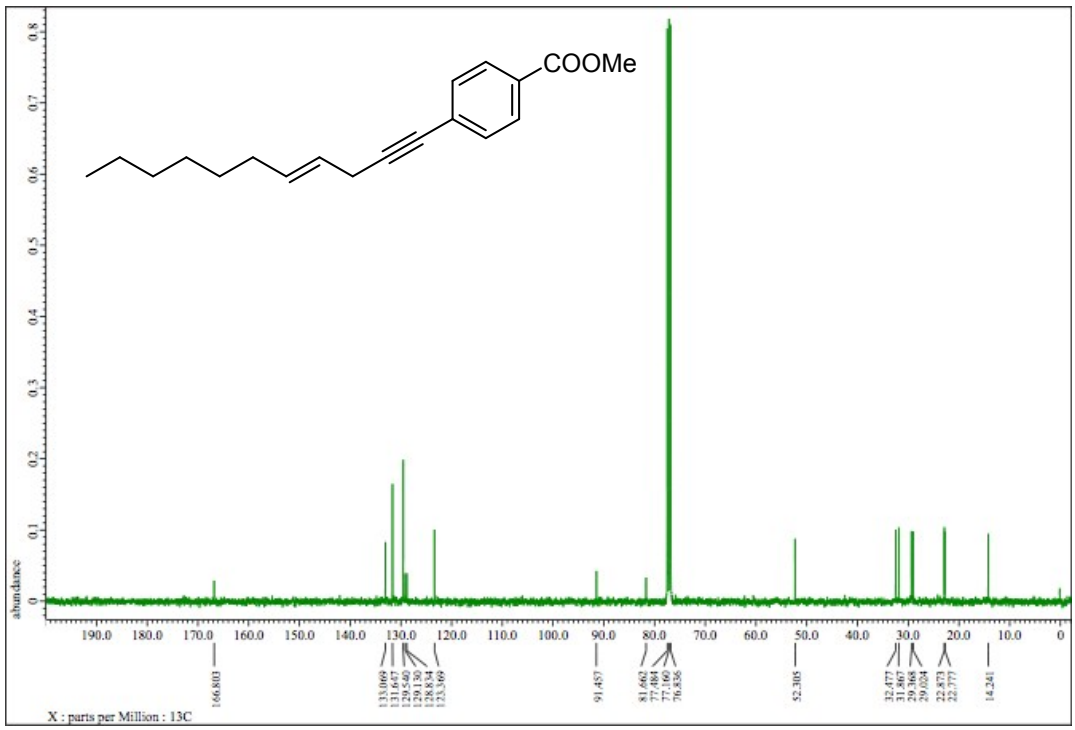


Figure S31. ^{13}C NMR spectrum of methyl (*E*)-4-(undec-4-en-1-yn-1-yl)benzoate (**3k**).

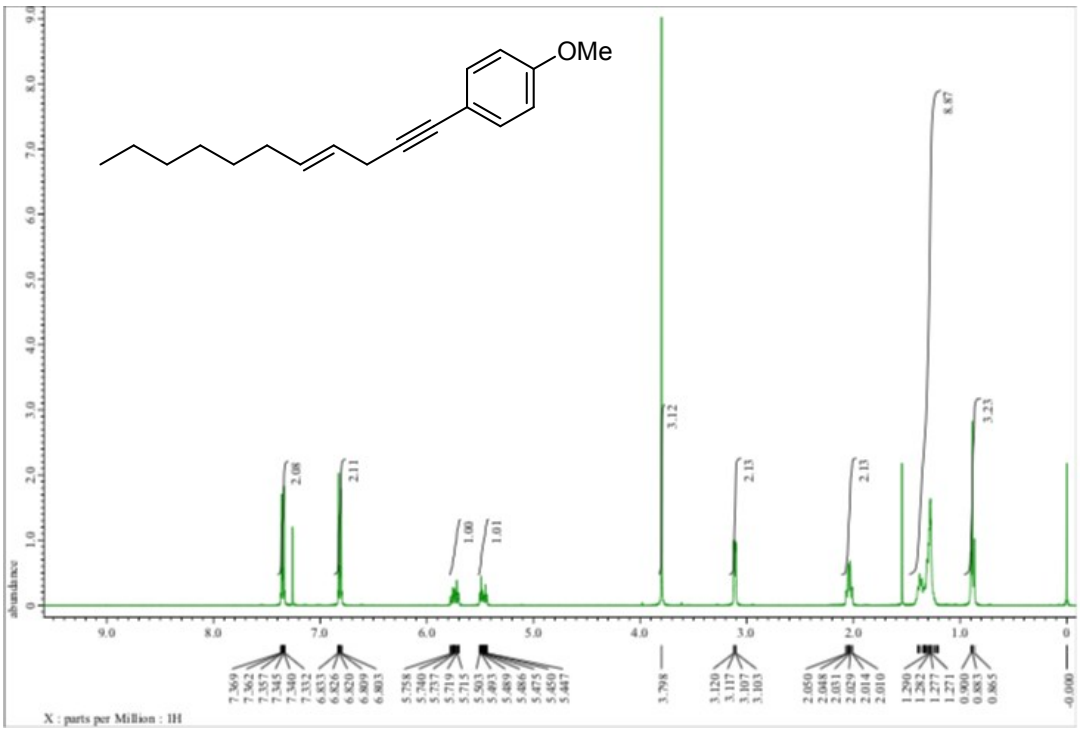


Figure S32. ^{1}H NMR spectrum of (*E*)-1-methoxy-4-(undec-4-en-1-yn-1-yl)benzene (**3l**).

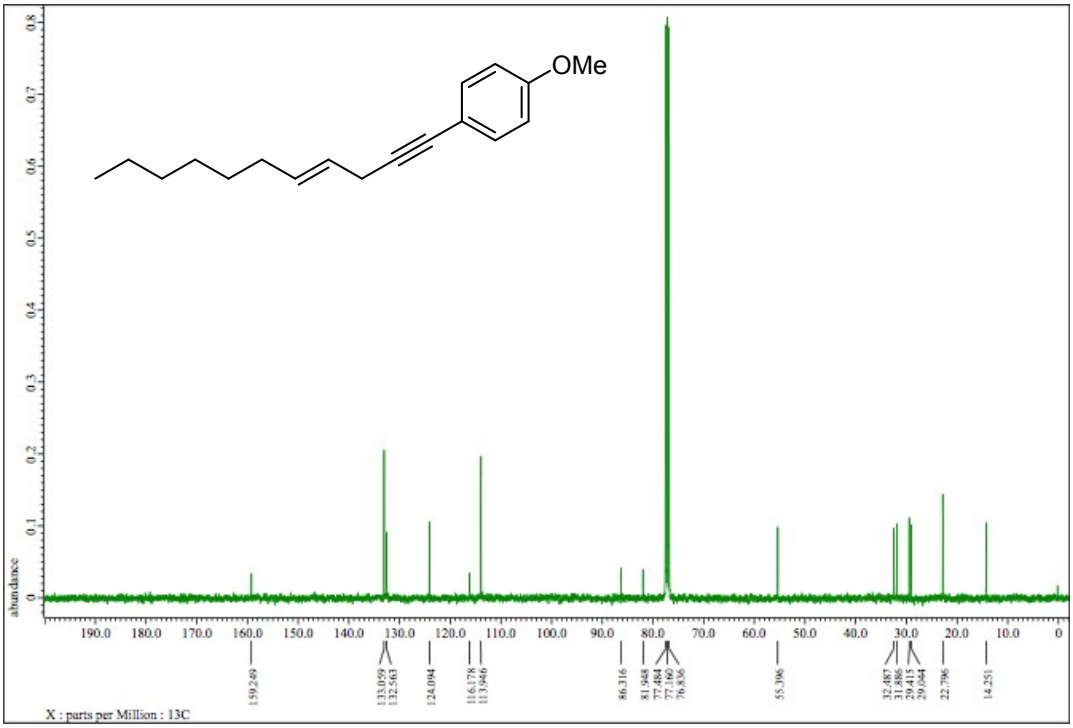


Figure S33. ^{13}C NMR spectrum of (*E*)-1-methoxy-4-(undec-4-en-1-yn-1-yl)benzene (**3l**).

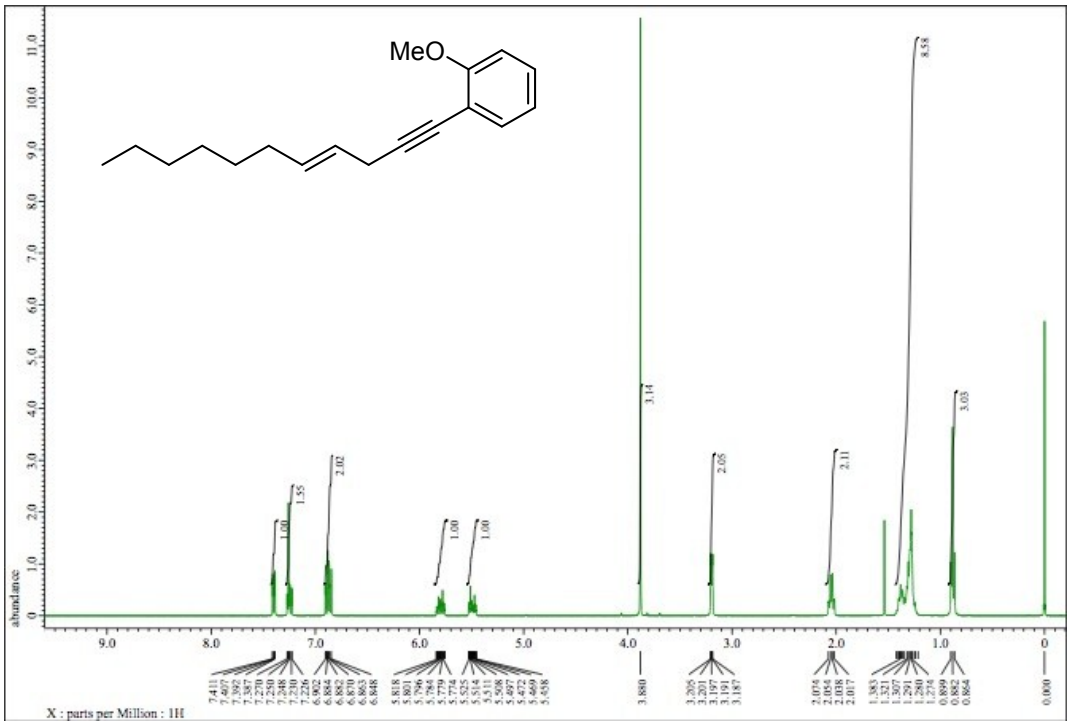


Figure S34. ^{1}H NMR spectrum of (*E*)-1-methoxy-2-(undec-4-en-1-yn-1-yl)benzene (**3m**).

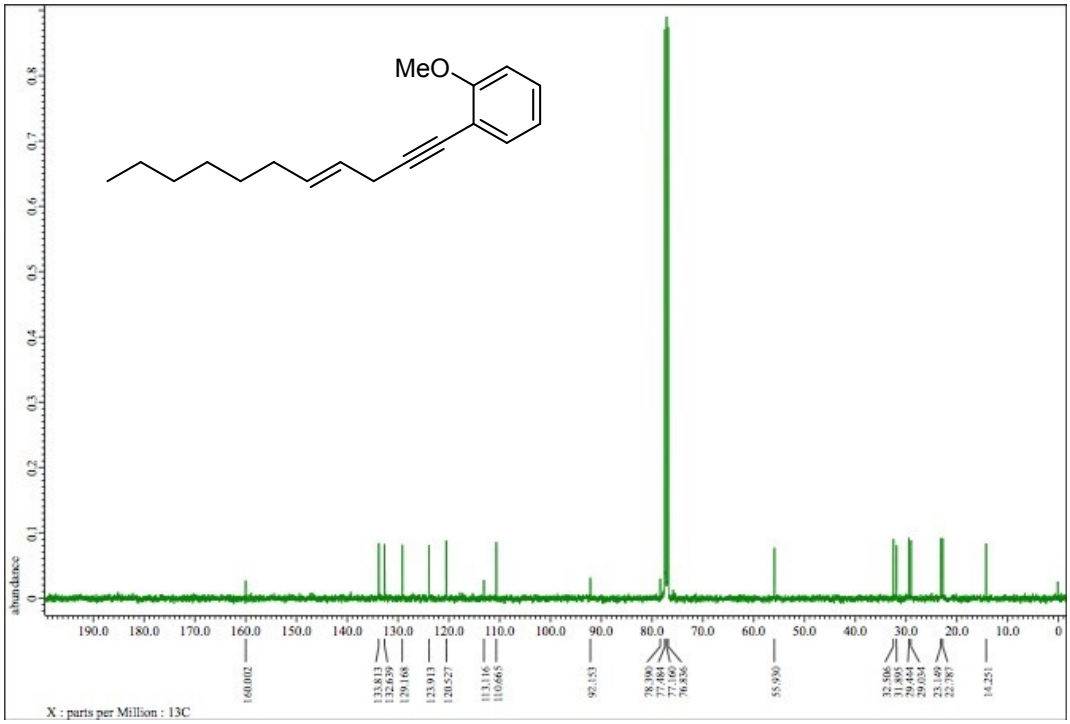


Figure S35. ^{13}C NMR spectrum of (*E*)-1-methoxy-2-(undec-4-en-1-yn-1-yl)benzene (**3m**).

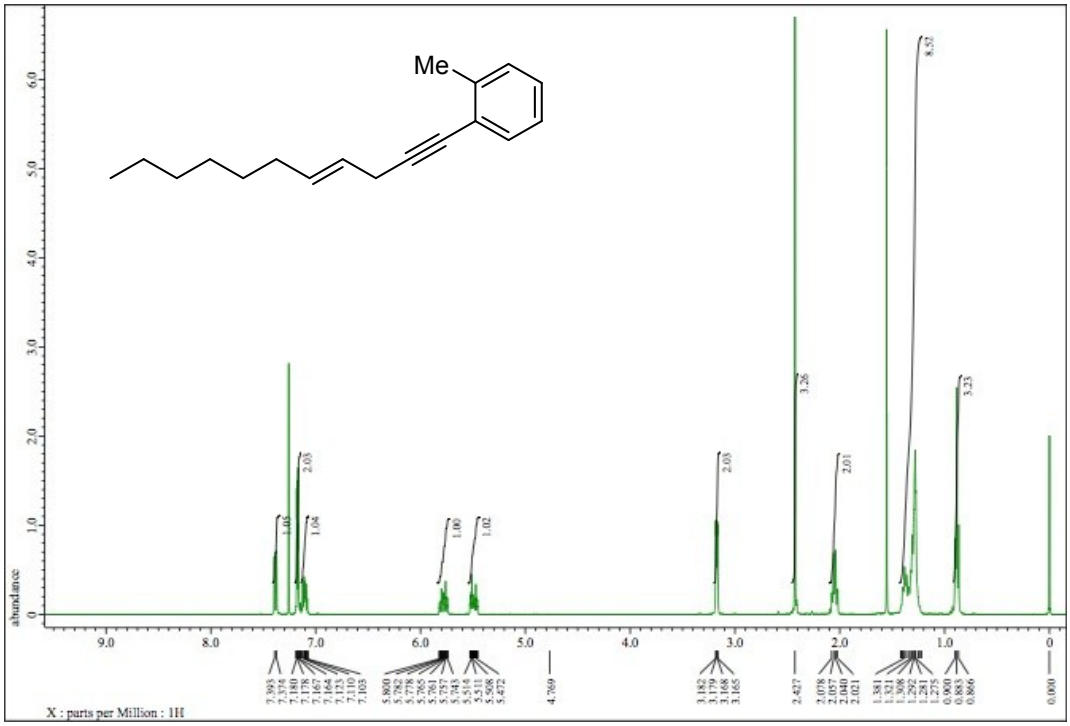


Figure S36. ^{1}H NMR spectrum of (*E*)-1-methyl-2-(undec-4-en-1-yn-1-yl)benzene (**3n**).

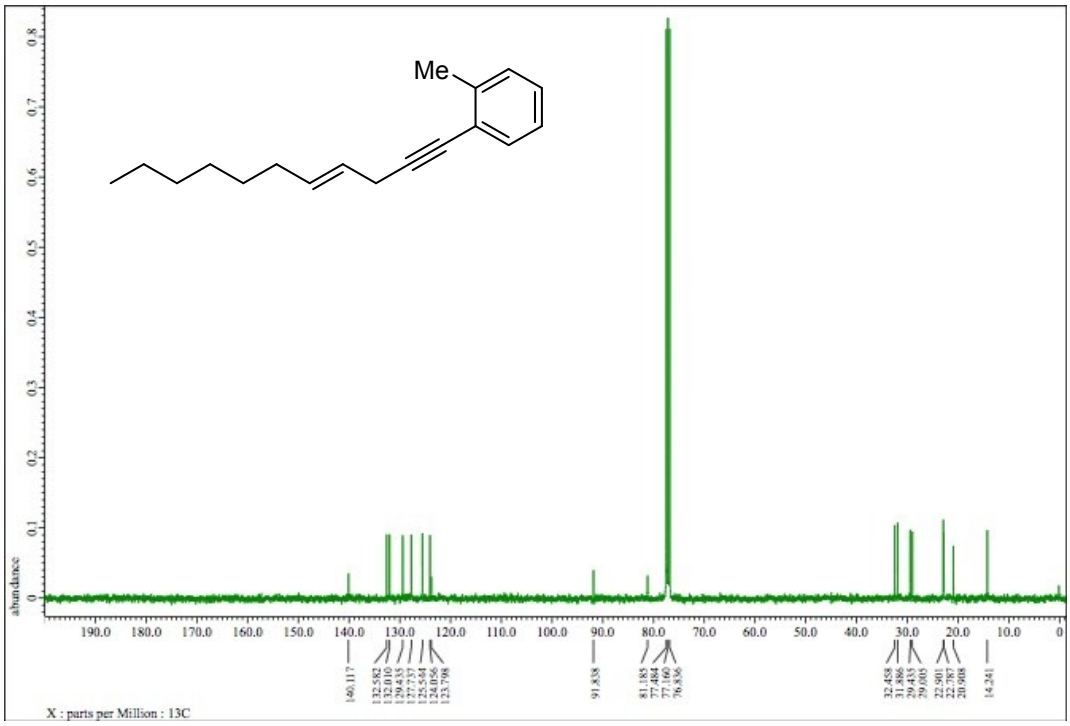


Figure S37. ^{13}C NMR spectrum of (*E*)-1-methyl-2-(undec-4-en-1-yn-1-yl)benzene (**3n**).

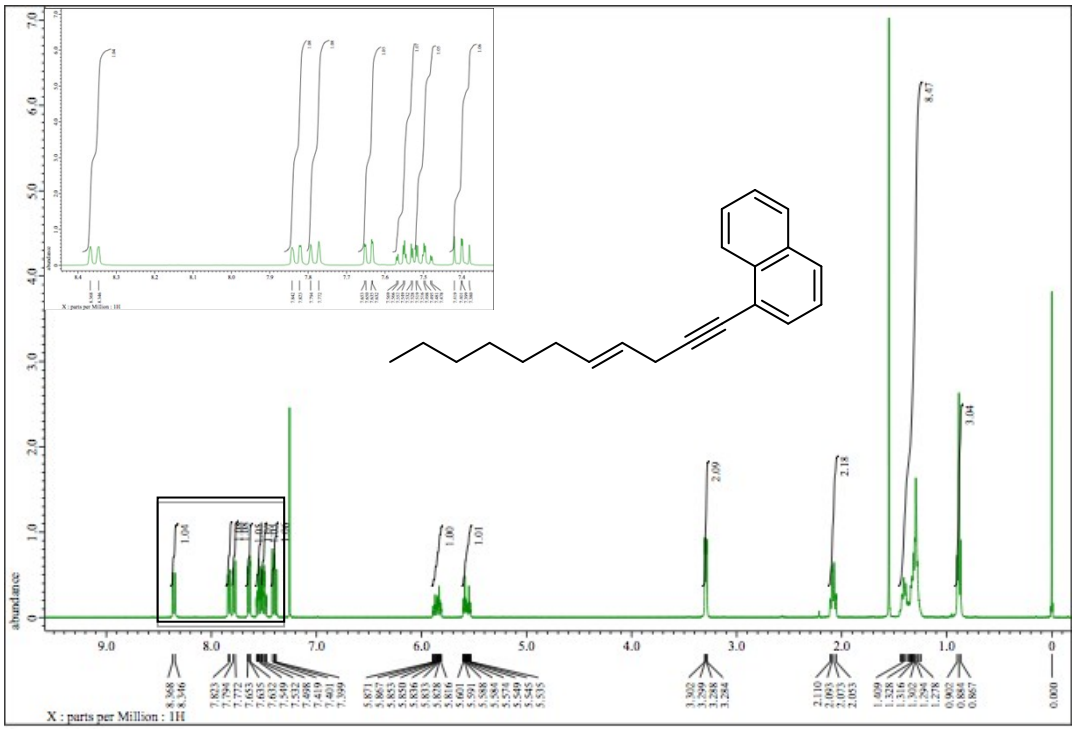


Figure S38. ^{1}H NMR spectrum of (*E*)-1-(undec-4-en-1-yn-1-yl)naphthalene (**3o**).

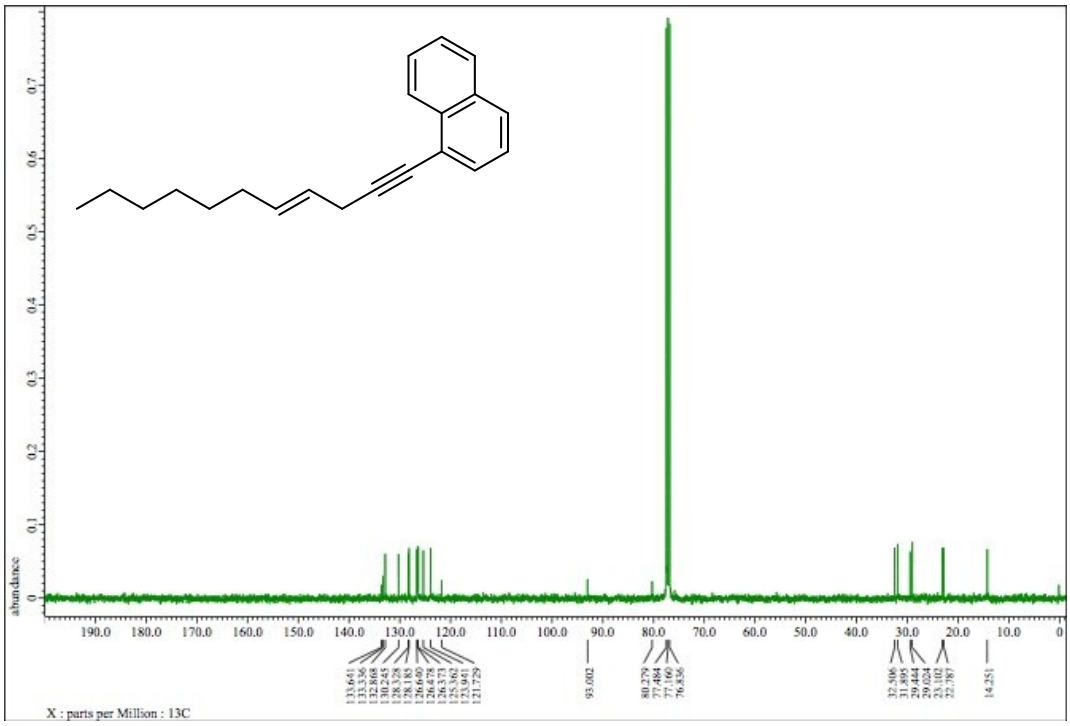


Figure S39. ^{13}C NMR spectrum of (*E*)-1-(undec-4-en-1-yn-1-yl)naphthalene (**3o**).

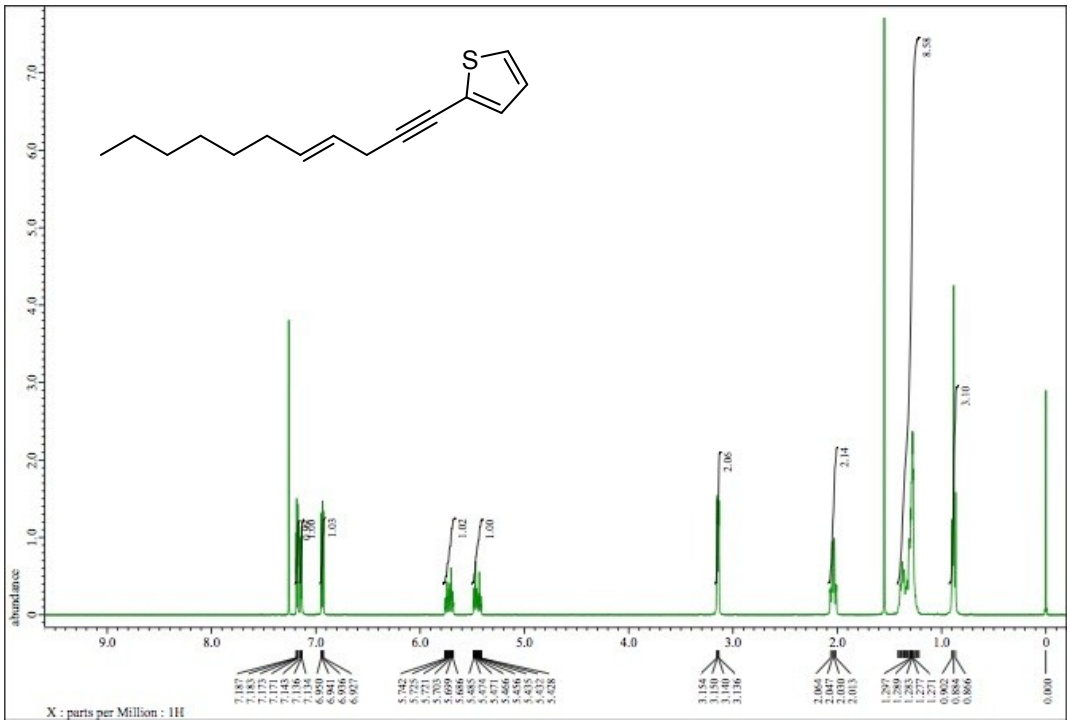


Figure S40. ^{1}H NMR spectrum of (*E*)-2-(undec-4-en-1-yn-1-yl)thiophene (**3p**).

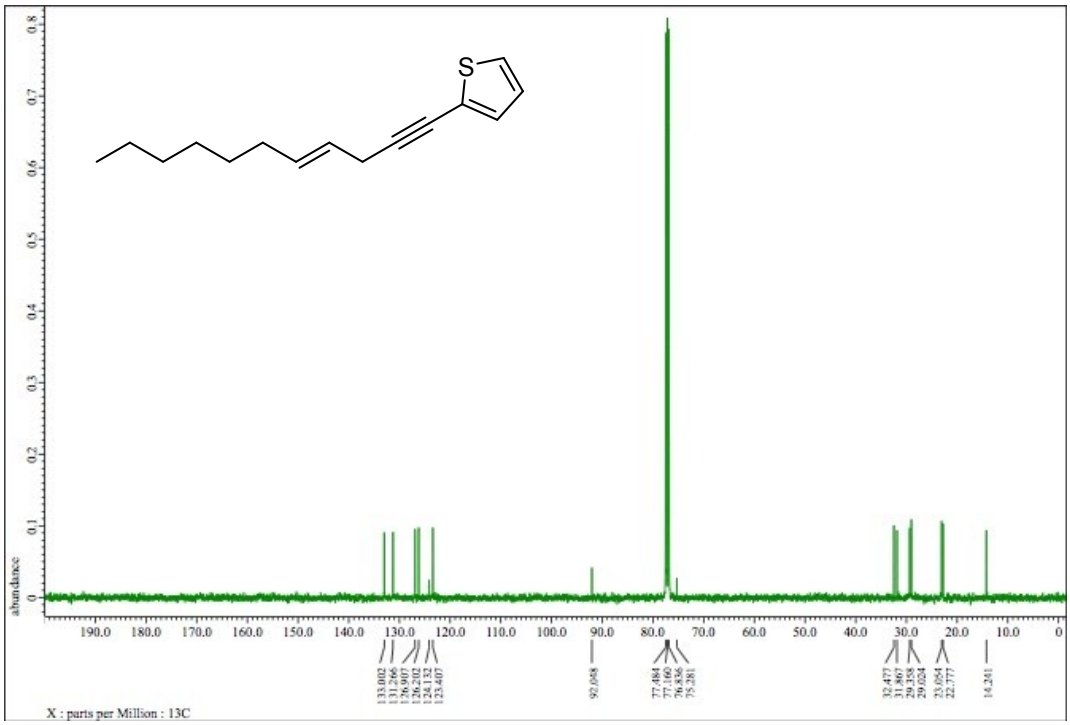


Figure S41. ^{13}C NMR spectrum of (*E*)-2-(undec-4-en-1-yn-1-yl)thiophene (**3p**).

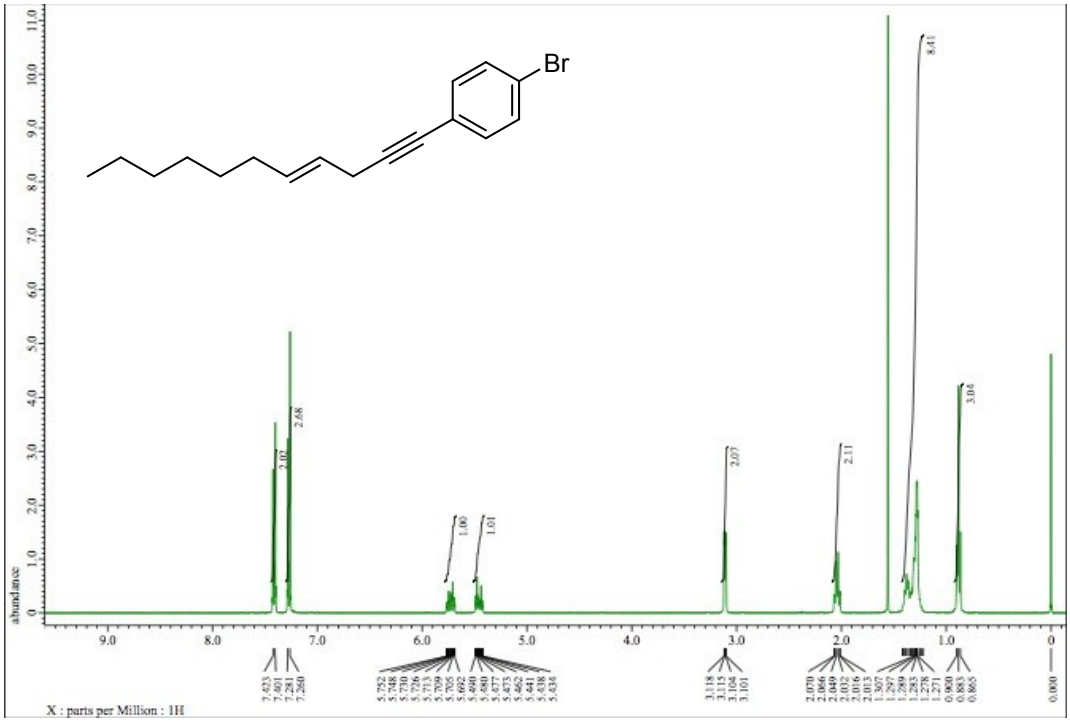


Figure S42. ^{1}H NMR spectrum of (*E*)-1-bromo-4-(undec-4-en-1-yn-1-yl)benzene (**3q**).

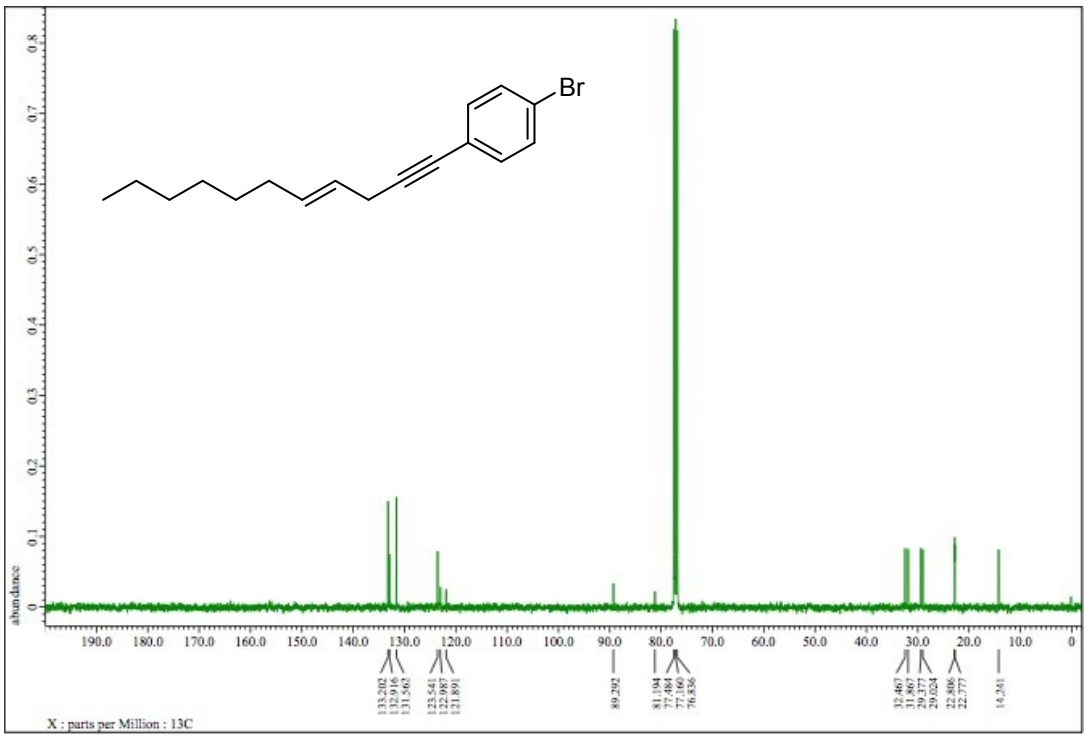


Figure S43. ^{13}C NMR spectrum of (*E*)-1-bromo-4-(undec-4-en-1-yn-1-yl)benzene (**3q**).

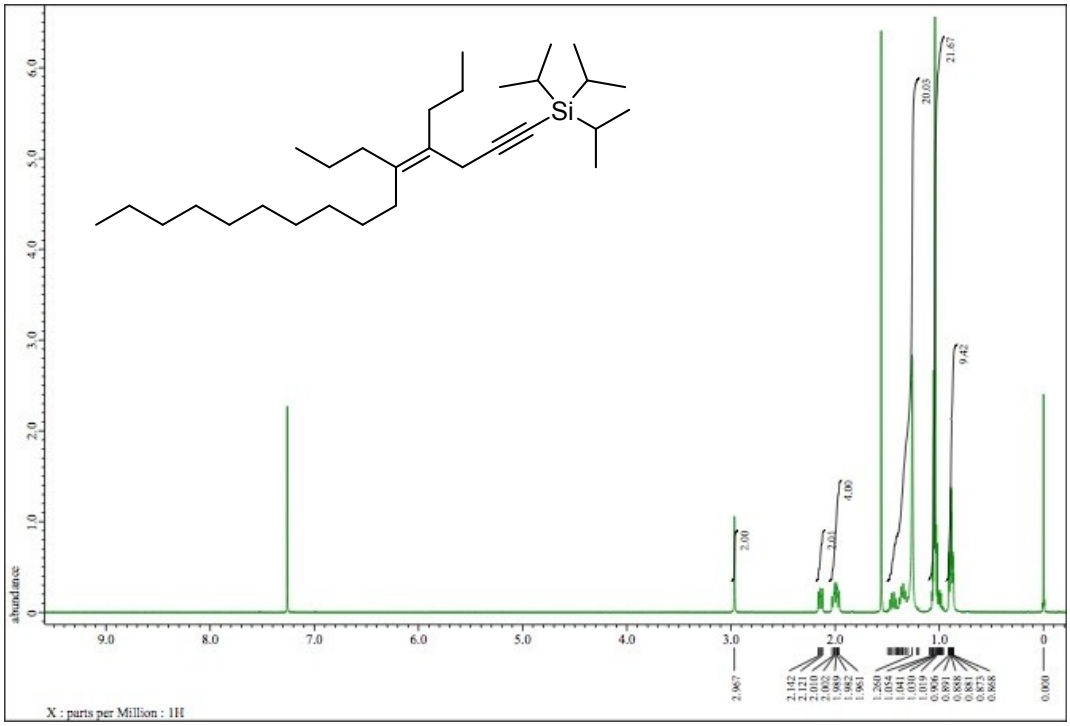


Figure S44. ^{1}H NMR spectrum of (*Z*)-(4,5-dipropylpentadec-4-en-1-yn-1-yl)triisopropylsilane (**3r**).

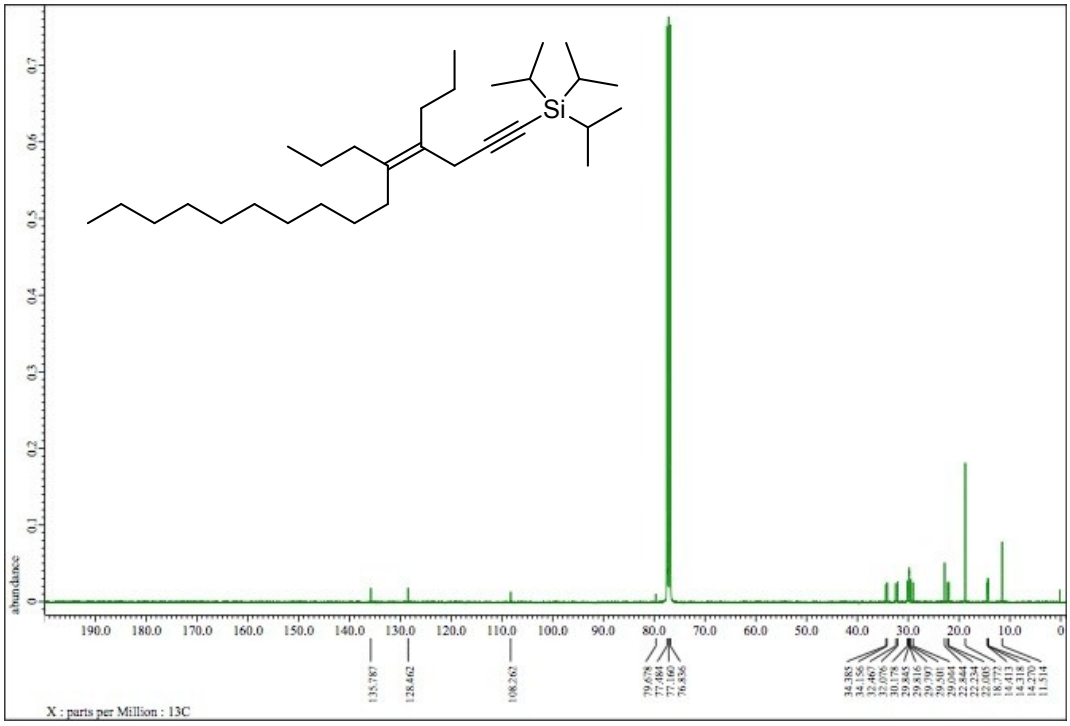


Figure S45. ^{13}C NMR spectrum of (*Z*)-(4,5-dipropylpentadec-4-en-1-yn-1-yl)triisopropylsilane (**3r**).

6. References

1. S. Thorand, and N. Krause, *J. Org. Chem.*, 1998, **63**, 8551.
2. For *Z*-selective hydroboration of terminal alkynes, see: T. Ohmura, Y. Yamamoto and N. Miyaura, *J. Am. Chem. Soc.*, 2000, **122**, 4990.
3. For *E*-selective hydroboration of terminal alkynes, see: (a) S. Chen, L. Yang, D. Yi, Q. Fu, Z. Zhang, W. Liang, Q. Zhang, J. Ji and W. Wei, *RSC Adv.*, 2017, **7**, 26070. (b) S. Liu, X. Zeng, G. B. Hammond and B. Xu, *Adv. Synth. Catal.*, 2018, **360**, 3667.
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