Supporting Information

General Procedures. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. Dry triethylamine was obtained by passing it over anhydrous alumina using a solvent purification system from Anhydrous Engineering. CD_3CN, $CDCl_3$ and d_8-THF were vacuum transferred. d_8-Toluene was dried over potassium and d_7-DMF was dried over CaH_2. All air or moisture-sensitive reactions were run under an atmosphere of argon. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 precoated silica gel plates. Eluting solvents are reported as volume ratios or volume percentages. Visualization was performed with UV light (254 nm) or iodine stain. Flash column chromatography was conducted with silica gel 60 (230-400 mesh) from EM science.

The ^{1}H and ^{13}C NMR spectra were recorded on 400 or 500 MHz spectrometers in NMR laboratory, School of Chemical Science (SCS), University of Illinois. Chemical shifts are expressed in parts per million (δ) using the residual solvent protons as an internal standard. Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Low and high resolution EI were obtained through the Mass Spectrometry Facility, SCS, University of Illinois. Elemental analysis was performed by the Micro Analytical Service Laboratory, SCS, University of Illinois.

Trisamidomolybdenum(VI) propylidyne (5): All manipulations were performed in an inert argon atmosphere. To a solution of molybdenum triamide **1** (0.5053 g, 0.81 mmol) in THF (18 mL) was added $CH_3CH_2CHCl_2$ (160 μL, 1.6 mmol) resulting in a color change from red to dark amber within 5 min. Magnesium turnings (0.2412 g, 10.1 mmol)

were added and the resulting mixture was stirred for 1.5 h at room temperature. The solvent was removed *in vacuo* and the residue was redissolved in pentane (25 mL). The solid precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. The product was obtained as a light yellow powder in 91 % yield (492 mg). ^{1}H NMR (d_8-THF, 500 MHz, -80 ^{o}C): δ 6.72 (3H, s), 5.73 (6H, s), 3.53 (2H, q, J = 7.5Hz), 2.09 (18H, s), 1.46 (3H, t, J = 8.0Hz), 1.27 (27H, s); ^{13}C NMR (d_8-THF, 125 MHz): δ 302.6, 151.4, 137.5, 131.0, 128.0, 61.3, 45.7, 34.0, 21.7, 14.8 (coalesce of different isomers was observed when temperature gradually raised from –80 ^{o}C to room temperature); MS (EI): m/z (%): M^+ 665.4 (13), 610.3 (15), 552.2 (8), 490.2 (7), 162.1 (100), 121.1 (40); HR-MS (EI) ($C_{39}H_{59}MoN_3$): calcd 665.3607, found 665.3605; elemental analysis cald (%) for $C_{39}H_{59}MoN_3$ (665.83): C 70.35, H 8.93, N 6.31; found C 69.75, H 8.84, N 6.25.

***α,α,α*-Trifluoro-*p*-cresol molybdenum(VI) propylidyne**: To a solution of *α,α,α*-trifluoro-*p*-cresol (25.5 mg, 0.16 mmol) in THF (1 mL) was added molybdenum(VI) propylidyne **5** (35.0 mg, 0.053 mmol). The solution was stirred occasionally at room temperature for 5 min. Then the solvent was removed in vacuo and the residue was heated at 60 ^{o}C under vacuum (0.09 mm Hg) overnight to remove the side product *N*-(3,5-dimethylphenyl)-*t*-butylamine. A dark red tacky solid was obtained (31.1 mg, 96%). ^{1}H NMR (d_8-toluene, 500 MHz, -25°C): δ 7.18 (6H, d, J = 7.9 Hz), 6.54 (6H, d, J = 7.9 Hz), 3.22 (2H, q, J = 6.5 Hz), 0.91 (3H, t, J = 6.5 Hz); ^{19}F NMR (d_8-toluene, 470 MHz): δ –61.5; ^{13}C NMR (d_8-THF, 125 MHz): δ 311.1, 174.0, 127.6, 127.1 (q), 119.4, 116.4, 26.3, 14.2.

4-Methoxybenzyl amide (6): Application of the general procedure of the Negishi cross-coupling[1] as for the preparation of **8** [$ZnBr_2$ (0.901 g, 4.0 mmol), propynyllithium (0.202

g, 4.4 mmol), 4-iodophenylamide (0.804 g, 2.2 mmol) and $Pd(PPh_3)_4$ (0.254 g, 0.22 mmol) in THF (8 mL)] gave **6** as white crystals (0.53 g, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.06 (3H, s), 3.80 (3H, s), 4.55 (2H, d, *J* = 4.8 Hz), 6.38 (1H, s), 6.87 (2H, d, *J* = 8.8 Hz), 7.26 (2H, d, *J* = 8.7 Hz), 7.42 (2H, d, *J* = 8.7 Hz), 7.68 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 159.1, 133.1, 131.6, 130.1, 129.3, 127.4, 126.8, 114.1, 88.6, 79.1, 55.3, 43.6, 4.4; MS (EI): m/z (%): 279.3 (100), 143.2 (100), 115.2 (35), 89.1 (9), 65.1 (5); HR-MS ($C_{18}H_{17}NO_2$): calcd 279.1259, found 279.1259; TLC R_f = 0.23 (EtOAc/*n*-Hexane, 3/7).

4,4'-Dimethoxybenzylamidophenylethynylene (7): ^{1}H NMR (d_6-DMSO, 500 MHz): δ 3.72 (6H, s), 4.40 (4H, d, *J* = 4.7 Hz), 6.88 (2H, d, *J* = 8.8 Hz), 7.24 (2H, d, *J* = 8.7 Hz), 7.66 (2H, d, *J* = 8.7 Hz), 7.93 (2H, d, *J* = 8.8 Hz), 9.08 (2H, t, *J* = 4.8 Hz); ^{13}C NMR (d_6-DMSO, 125 MHz): δ 165.6, 158.3, 134.5, 131.5, 128.7, 127.7, 124.6, 113.7, 109.3, 90.6, 78.8, 55.1, 42.2; MS (EI): m/z (%): 504.3 (100), 368.2 (74), 230.1 (8), 204.1 (40), 176.1 (18), 121.1 (45), 77.1 (7); HR-MS ($C_{32}H_{28}N_2O_4$): calcd 504.2049, found 504.2055.

2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3-propynylbenzoate (8): To a solution of $ZnBr_2$ (1.72 g, 7.6 mmol) and propynyl lithium (0.374 g, 8.1 mmol) in THF (4 mL) was added the solution of 2-[2-(2-methoxyethoxy)ethoxy]ethyl 3-iodobenzoate (2.00 g, 5.1 mmol) in THF (4 mL), followed by addition of tetrakis(triphenylphosphine)palladium (0) (0.352 g, 0.30 mmol). The solution was stirred for 4 h at 60 ^{o}C. After cooling, the mixture was added to dilute hydrochloric acid (60 mL, 0.8 mol/L) and the product was extracted into ether (3 x 70 mL). After drying ($MgSO_4$), the ethereal solution was evaporated to a dark oil which was chromatographed on silica (EtOAc/*n*-Hexane, 3/7) to give pure product 2-[2-(2-methoxyethoxy)ethoxy]ethyl 3-propynylbenzoate (yellow oil, 1.43 g, 92%). ^{1}H

NMR ($CDCl_3$, 500 MHz): δ 8.07 (1H, t, *J* = 1.5 Hz), 7.95 (1H, dt, *J* = 1.5, 8.0 Hz), 7.56 (1H, dt, *J* = 1.5, 8.0 Hz), 7.35 (1H, t, *J* = 8.0 Hz), 4.46-4.48 (m, 2H), 3.82-3.84 (m, 2H), 3.71-3.72 (m, 2H), 3.64-3.69 (m, 4H), 3.52-3.54 (m, 2H), 3.37 (3H, s), 2.06 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 135.8, 132.7, 130.2, 128.7, 128.3, 124.4, 86.9, 78.8, 71.9, 70.7, 70.6, 70.5, 69.1, 64.2, 59.0, 4.3; MS (EI): m/z (%): 306 (21), 187 (94), 160 (18), 143 (100), 115 (42), 103 (11), 89 (15), 59 (38); HR-MS ($C_{17}H_{22}O_5$): calcd 306.1467, found 306.1467; TLC R_f= 0.18 (EtOAc/*n*-Hexane, 3/7).

4-Propynylbenzonitrile (9a): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.58 g, 7.0 mmol), propynyllithium (0.344 g, 7.5 mmol), 4-bromobenzonitrile (0.802 g, 4.4 mmol) and $Pd(PPh_3)_4$ (0.509 g, 0.44 mmol) in THF (8 mL)] gave **9a** as yellow crystals (0.53 g, 85%). ^1H NMR ($CDCl_3$, 500 MHz): δ 2.08 (s, 3H), 7.45 (d, 2H, *J* = 8.8 Hz), 7.56 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.1, 131.9, 129.1, 118.6, 110.9, 91.1, 78.6, 4.4; MS (EI): m/z (%): 141.1 (75), 114.0 (25), 91.1 (20), 77.0 (100); HR-MS ($C_{10}H_7N$): calcd 141.0578, found 141.0581; TLC R_f= 0.38 (EtOAc/*n*-Hexane, 1/19).

4-Propynylbenzotrifluoride (9b): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.49 g, 6.6 mmol), propynyllithium (0.338 g, 7.4 mmol), 4-iodobenzotrifluoride (1.00 g, 3.7 mmol) and $Pd(PPh_3)_4$ (0.425 g, 0.37 mmol) in THF (8 mL)] gave **9b** as a colorless oil (0.64 g, 94%). ^1H NMR ($CDCl_3$, 500 MHz): δ 2.07 (s, 3H), 7.47 (d, 2H, *J* = 8.8 Hz), 7.53 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.7, 129.4, 127.9, 125.1(q), 122.9, 88.7, 78.7, 4.3; MS (EI): m/z (%): 184.1 (71), 165.1 (12), 141.1 (12), 115.1 (100), 77.0 (16), 63.0 (11); HR-MS ($C_{10}H_7F_3$): calcd 184.0500, found 141.0501; TLC R_f= 0.50 (*n*-Hexane).

4-Propynylbenzaldehyde (9c): To a sealed tube fitted with a magnetic stir bar was added 4-bromobenzaldehyde (1.01 g, 5.4 mmol), $Pd_2(dba)_3$ (0.151 g, 0.16 mmol), CuI (65 mg, 0.34 mmol), PPh_3 (0.355 g, 1.4 mmol) and dry triethylamine (25 mL). The mixture was evacuated and back-filled with nitrogen three times, after which propyne gas was bubbled through the solution. The tube was then sealed and stirred at 80 ^{o}C for 24 h. The reaction mixture was sparged with propyne gas every a few hours, during which time a white precipitate formed. After cooling, the solution was diluted with EtOAc (100 mL), filtered to remove the precipitate and concentrated in vacuo leaving a red oil. The residue was purified by silica gel column chromatography (EtOAc/n-Hexane, 1/19) to give **9c** as yellow crystals (0.75 g, 97%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.09 (s, 3H), 7.52 (d, 2H, *J* = 8.7 Hz), 7.80 (d, 2H, *J* = 8.7 Hz), 9.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 191.5, 135.0, 132.0, 130.5, 129.5, 90.7, 79.2, 4.5; MS (EI): m/z (%): 144.0 (53), 115.0 (40), 82.9 (100), 73.0 (5), 63.0 (10); HR-MS ($C_{10}H_8O$): calcd 144.0575, found 144.0572; TLC R_f= 0.45 (EtOAc/*n*-Hexane, 1/19).

4-Propynylanisole (9d): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.54 g, 6.8 mmol), propynyllithium (0.334 g, 7.3 mmol), 4-iodoanisole (1.00 g, 4.3 mmol) and $Pd(PPh_3)_4$ (0.493 g, 0.43 mmol) in THF (8 mL)] gave **9d** as a yellow oil (0.60 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.03 (s, 3H), 3.80 (s, 3H), 6.81 (d, 2H, *J* = 9.0 Hz), 7.32 (d, 2H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 132.8, 116.1, 113.8, 84.1, 79.4, 55.2, 4.3; MS (EI): m/z (%): 146.1 (96), 131.1 (29), 115.1 (16), 103.1 (44), 77.0 (47); HR-MS ($C_{10}H_{10}O$): calcd 146.0718, found 146.0716; TLC R_f= 0.17 (*n*-Hexane).

4-Propynyl-*N*,*N*-dimethylaniline (9e): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.37 g, 6.1 mmol), propynyllithium (0.298 g, 6.5 mmol), 4-iodo-N,N-dimethylaniline (1.00 g, 4.1 mmol) and $Pd(PPh_3)_4$ (0.281 g, 0.24 mmol) in THF (8 mL)] gave **9e** as yellow crystals (0.38 g, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.03 (s, 3H), 2.96 (s, 6H), 6.63 (d, 2H, *J* = 8.9 Hz), 7.28 (d, 2H, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.7, 132.4, 111.9, 111.1, 83.0, 80.2, 40.3, 4.4; MS (EI): m/z (%): 159.1 (100), 143.1 (16), 115.1 (22), 89.0 (5), 63.0 (6); HR-MS ($C_{11}H_{13}N$): calcd 159.1048, found 159.1048; TLC R_f = 0.44 (EtOAc/*n*-Hexane, 1/19).

2-Propynylthiophene (9f): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.04 g, 4.6 mmol), propynyllithium (0.226 g, 4.9 mmol), 2-bromothiophene (0.50 g, 3.1 mmol) and $Pd(PPh_3)_4$ (78 mg, 0.15 mmol) in THF (8 mL)] gave **9f** as a colorless oil (0.20 g, 54%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.08 (s, 3H), 6.94 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.12 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.17 (dd, 1H, *J* = 5.1, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.1, 127.0, 126.1, 124.4, 90.2, 73.1, 4.8. The spectroscopic data are in agreement with those reported in the literature.[2]

4-Propynylbenzoic acid *N*-methoxyethyl amide (9g): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (0.932 g, 4.1 mmol), propynyllithium (0.212 g, 4.6 mmol), 4-iodophenylamide (0.70 g, 2.3 mmol) and $Pd(PPh_3)_4$ (0.266 g, 0.23 mmol) in THF (8 mL)] gave **9g** as yellow crystals (0.43 g, 87%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.06 (3H, s), 3.38 (3H, s), 3.55 (2H, m), 3.64 (2H, m), 6.51 (1H, br s), 7.42 (2H, d, *J* = 8.4 Hz), 7.70 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 133.2, 131.6, 127.4, 126.9, 88.6, 79.1, 71.1, 58.8, 39.7, 4.4; MS (EI):

m/z (%): 217.2 (8), 185.1 (25), 159.1 (16), 143.1 (100), 115.1 (26), 89.1 (7), 63.0 (4); HR-MS ($C_{13}H_{15}NO_2$): calcd 217.1103, found 217.1097; TLC R_f = 0.09 (EtOAc/*n*-Hexane, 3/7).

4,4'-Dicyanophenylethynylene (10a): To a solution of 4-propynylbenzonitrile (17 mg, 0.12 mmol) in 1,2,4-trichlorobenzene (1 mL) was added a solution of molybdenum triamide **5** (8.0 mg, 0.012 mmol) and α, α, α-trifluoro-*o*-cresol (5.8 mg, 0.036 mmol) in 1,2,4-trichlorobenzene (1 mL). The resulting mixture was stirred for 22 h at 30 ^{o}C under vacuum (5 mm Hg). The solvent was removed by distillation under high vacuum (0.2 mm Hg) at 40 ^{o}C and the residue was chromatographed on silica (EtOAc/*n*-Hexane, 3/17) to give pure product **10a** as white crystals (5.1 mg, 37%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (4H, d, *J* = 8.2 Hz), 7.68 (4H, d, *J* = 8.2Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.3, 132.2, 127.1, 118.3, 112.4, 91.5; MS (EI): m/z (%): 228.0 (100), 201.0 (10), 175.0 (6), 151.0 (6), 121.0 (7), 100.3 (6), 75.0 (5), 57.0 (5); HR-MS ($C_{16}H_8N_2$): calcd 228.0687, found 228.0681; TLC R_f= 0.20 (EtOAc/*n*-Hexane, 1/9).

4,4'-Ditrifluoromethylphenylethynylene (10b): Application of the general procedure of alkyne homodimerization as for the preparation of **10a** [4-propynylbenzotrifluoride (22.1 mg, 0.12 mmol), molybdenum triamide **5** (8.0 mg, 0.012 mmol) and α, α, α-trifluoro-*o*-cresol (5.8 mg, 0.036 mmol) in 1,2,4-trichlorobenzene (2 mL)] gave **10b** as white crystals (9.6 mg, 51%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (8H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.0, 130.4, 126.4, 125.4 (q, *J* = 3.3 Hz), 122.8, 90.1; ^{19}F NMR ($CDCl_3$, 470 MHz): δ -63.3 Hz (6F, s); MS (EI): m/z (%): 314.0 (100), 295.0 (23), 264.0 (13), 225.0 (9), 157.1 (6), 132.1 (7), 107.1 (9); HR-MS ($C_{16}H_8F_6$): calcd 314.0543, found 314.0537; TLC R_f= 0.44 (*n*-Hexane).

Diphenylacetylene-4,4'-dicarbaldehyde (10c): Application of the general procedure of alkyne homodimerization as for the preparation of **10a** [4-propynylbenzaldehyde (17.3 mg, 0.12 mmol), molybdenum triamide **5** (8.0 mg, 0.012 mmol) and α, α, α-trifluoro-*o*-cresol (5.8 mg, 0.036 mmol) in 1,2,4-trichlorobenzene (2 mL)] gave **10c** as white crystals (6.6 mg, 47%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (4H, d, J = 8.0 Hz), 7.90 (4H, d, J = 8.0 Hz), 10.04 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.5, 135.9, 132.4, 129.7, 128.7, 91.7; MS (EI): m/z (%): 234.1 (100), 205.1 (14), 176.1 (42), 151.1 (17), 102.2 (7), 75.0 (6); HR-MS ($C_{16}H_{10}O_2$): calcd 234.0681, found 234.0687; TLC R_f = 0.23 (EtOAc/*n*-Hexane, 1/9).

4,4'-Dimethoxyphenylethynylene (10d): Application of the general procedure of alkyne homodimerization as for the preparation of **10a** [4-propynylanisole (17.5 mg, 0.12 mmol), molybdenum triamide **5** (8.0 mg, 0.012 mmol) and α, α, α-trifluoro-*o*-cresol (5.8 mg, 0.036 mmol) in 1,2,4-trichlorobenzene (2 mL)] gave **10d** as white crystals (11.9 mg, 83%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.82 (6H, s), 6.87 (4H, d, J = 8.7 Hz), 7.45 (4H, d, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.4, 132.9, 115.7, 114.0, 87.9, 55.3; MS (EI): m/z (%): 238.1 (87), 223.1 (68), 195.1 (22), 180.0 (12), 162.1 (17), 152.1 (23), 121.1 (100), 65.0 (11); HR-MS ($C_{16}H_{14}O_2$): calcd 238.0994, found 238.0994; TLC R_f = 0.41 (EtOAc/*n*-Hexane, 1/9).

4,4'-Bis(*N,N*-dimethylaminophenyl)ethynylene (10e): Application of the general procedure of alkyne homodimerization as for the preparation of **10a** [4-propynyl-*N,N*-dimethylaniline (19.1 mg, 0.12 mmol), molybdenum triamide **5** (8.0 mg, 0.012 mmol) and α, α, α-trifluoro-*o*-cresol (5.8 mg, 0.036 mmol) in 1,2,4-trichlorobenzene (2 mL)] gave **10e** as white crystals (12.1 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.98 (12H, s),

6.65 (4H, d, J = 8.9 Hz), 7.38 (4H, d, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.6, 132.4, 111.9, 111.1, 88.1, 40.3; MS (EI): m/z (%): 264.1 (17), 251.8 (27), 241.1 (15), 162.1 (26), 121.1 (100), 77.0 (11), 63.0 (17); HR-MS ($C_{18}H_{20}N_2$): calcd 264.1626, found 264.1627; TLC R_f= 0.21 (EtOAc/*n*-Hexane, 1/19).

2,2'-Dithiophenylethynylene (10f): Application of the general procedure of alkyne homodimerization as preparation of **10a** [2-butynylthiophene (16.3 mg, 0.12 mmol), molybdenum triamide **5** (8.0 mg, 0.012 mmol) and *α, α, α*-trifluoro-*o*-cresol (5.8 mg, 0.036 mmol) in 1,2,4-trichlorobenzene (2 mL)] gave **10f** as white crystals (7.9 mg, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.01 (dd, 2H, J = 5.1, 3.6 Hz), 7.28 (dd, 1H, J = 3.6, 1.2 Hz), 7.31 (dd, 1H, J = 5.1, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.1, 127.6, 127.1, 122.9, 86.2; MS (EI): m/z (%): 190.0 (100), 158.0 (8), 145.0 (15), 132.0 (7), 114.1 (8), 102.1 (6), 95.0 (8), 58.0 (7); HR-MS ($C_{10}H_6S_2$): calcd 189.9911, found 189.9909; TLC R_f= 0.32 (*n*-Hexane).

4,4'-Diamidophenylethynylene (10g): Application of the general procedure of alkyne homodimerization as for the preparation of **10a** [4-propynylbenzoamide **9g** (19.5 mg, 0.090 mmol), molybdenum triamide **5** (15 mg, 0.023 mmol) and *α, α, α*-trifluoro-*o*-cresol (10.9 mg, 0.068 mmol) in 1,2,4-trichlorobenzene (2 mL)] gave **10g** as a white solid (16.9 mg, 99%). ^{1}H NMR (d_6-DMSO, 500 MHz): δ 3.26 (s, 6H), 3.40-3.47 (m, 8H), 7.66 (d, 4H, J = 8.2 Hz), 7.90 (d, 4H, J = 8.2 Hz), 8.64 (t, 2H, J = 5.5 Hz); ^{13}C NMR (d_6-DMSO, 125MHz): δ 165.5, 134.4, 131.4, 127.7, 124.6, 90.6, 70.4, 57.9, 39.1; MS (EI): m/z (%): 380.3 (18), 322.2 (17), 306.2 (100), 264.2 (45), 248.1 (37), 204.1 (42), 176.1 (24), 150.1 (6); HR-MS ($C_{22}H_{24}N_2O_4$): calcd 380.1736, found 380.1739.

4-Butynylbenzonitrile (11b): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.19 g, 5.3 mmol), 1-butynyllithium (0.343 g, 5.7 mmol), 4-bromobenzonitrile (0.80 g, 4.4 mmol) and $Pd(PPh_3)_4$ (0.305 g, 0.26 mmol) in THF (8 mL)] gave **11b** as yellow crystals (0.63 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.24 (3H, t, *J* = 7.3 Hz), 2.44 (2H, q, *J* = 7.3 Hz), 7.45 (2H, d, *J* = 8.4 Hz), 7.56 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.1, 131.9, 129.1, 118.7, 110.8, 96.8, 78.7, 13.6, 13.2; MS (EI): m/z (%): 155.1 (83), 140.0 (100), 127.0 (36), 115.0 (21), 101.0 (6), 87.0 (7), 76.2 (13), 63.0 (18); HR-MS ($C_{11}H_9N$): calcd 155.0735, found 155.0734; TLC R_f= 0.50 (EtOAc/*n*-Hexane, 1/9).

4-(3-Methybutynyl)benzonitrile (11c): Application of the general procedure of Sonogashira cross-coupling[3] as for the preparation of **9c** [4-bromobenzonitrile (1.0 g, 5.5 mmol), 3-methyl-1-butyne (1.70 mL, 16.6 mmol), $Pd_2(dba)_3$ (0.152 g, 0.17 mmol), CuI (0.0665 g, 0.35 mmol), PPh_3 (0.362 g, 1.37 mmol) in dry triethylamine (25 mL)] gave **11c** as a yellow oil (0.87 g, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26 (6H, d, *J* = 6.7 Hz), 2.79 (1H, m), 7.45 (2H, d, *J* = 8.4 Hz), 7.56 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.1, 131.9, 129.1, 118.7, 110.8, 100.8, 78.6, 22.7, 21.2; MS (EI): m/z (%): 169.1 (37), 154.0 (100), 140.0 (7), 127.0 (38), 101.0 (5), 83.1 (6), 63.1 (7); HR-MS ($C_{12}H_{11}N$): calcd 169.0891, found 169.0896; TLC R_f= 0.56 (EtOAc/*n*-Hexane, 1/19).

4-(3,3-Dimethylbutynyl)benzonitrile (11d): Application of the general procedure of Sonogashira cross-coupling as for the preparation of **9c** [4-bromobenzonitrile (1.0 g, 5.5 mmol), 3,3-dimethyl-1-butyne (2.05 mL, 16.7 mmol), $Pd_2(dba)_3$ (0.152 g, 0.17 mmol), CuI (0.0665 g, 0.35 mmol), PPh_3 (0.362 g, 1.37 mmol) in dry triethylamine (25 mL)] gave **11d** as white crystals (0.76 g, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.32 (9H, s),

7.45 (2H, d, J = 8.5 Hz), 7.56 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.1, 131.8, 129.1, 118.7, 110.7, 103.5, 78.0, 30.7, 28.1; MS (EI): m/z (%): 183.0 (100), 168.1 (62), 153.1 (20), 140.1 (12), 127.1 (5), 102.0 (83), 75.0 (33), 63.0 (10); HR-MS ($C_{13}H_{13}N$): calcd 183.1048, found 183.1051; TLC R_f= 0.49 (EtOAc/*n*-Hexane, 1/19).

4-Butynylbenzotrifluoride (12b): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (0.994 g, 4.4 mmol), 1-butynyllithium (0.287 g, 4.8 mmol), 4-iodobenzotrifluoride (1.0 g, 3.7 mmol) and $Pd(PPh_3)_4$ (0.212 g, 0.18 mmol) in THF (8 mL)] gave **12b** as a colorless oil (0.67 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (3H, t, J = 7.6 Hz), 2.44 (2H, q, J = 7.6 Hz), 7.48 (2H, d, J = 8.0 Hz), 7.54 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 131.8, 129.4, 129.1, 127.9, 125.1 (q), 94.5, 78.8, 13.7, 13.1; MS (EI): m/z (%): 198.1 (100), 183.1 (77), 151.1 (11), 129.1 (94), 86.0 (6), 74.0 (9), 63.0 (10); HR-MS ($C_{11}H_9F_3$): calcd 198.0656, found 198.0653; TLC R_f= 0.61 (*n*-Hexane).

4-Butynylbenzaldehyde (12c): Application of the general procedure of Sonogashira cross-coupling as for the preparation of **9c** [4-bromobenzaldehyde (1.0 g, 5.4 mmol), 1-butyne (250 mL, 11.2 mmol), $Pd_2(dba)_3$ (0.151 g, 0.16 mmol), CuI (0.0649 g, 0.34 mmol), PPh_3 (0.355 g, 1.35 mmol) in dry triethylamine (25 mL)] gave **12c** as a yellow oil (0.83 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (3H, t, J = 7.2 Hz), 2.46 (2H, q, J = 7.2 Hz), 7.53 (2H, d, J = 8.0 Hz), 7.80 (2H, d, J = 8.0 Hz), 9.98 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5, 134.9, 132.1, 130.5, 129.5, 96.4, 79.4, 13.6, 13.2; MS (EI): m/z (%): 158.1 (100), 143.1 (12), 129.1 (65), 115.1 (52), 102.1 (6), 89.0 (5), 77.0 (11), 63.0 (12); HR-MS ($C_{11}H_{10}O$): calcd 158.0732, found 158.0732; TLC R_f= 0.41 (EtOAc/*n*-Hexane, 1/19).

4-Butynylanisole (12d): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.15 g, 5.1 mmol), 1-butynyllithium (0.333 g, 5.6 mmol), 4-iodoanisole (1.0 g, 4.3 mmol) and $Pd(PPh_3)_4$ (0.296 g, 0.26 mmol) in THF (8 mL)] gave **12d** as a yellow oil (0.64 g, 94%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22 (3H, t, *J* = 7.5 Hz), 2.40 (2H, q, *J* = 7.5 Hz), 3.79 (3H, s), 6.81 (2H, d, *J* = 8.7 Hz), 7.33 (2H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.9, 132.8, 116.1, 113.8, 90.0, 79.5, 55.2, 14.0, 13.1; MS (EI): m/z (%): 160.1 (100), 145.0 (71), 129.0 (8), 117.0 (21), 91.0 (10), 75.0 (4), 63.0 (7); HR-MS ($C_{11}H_{12}O$): calcd 160.0888, found 160.0893; TLC R_f = 0.55 (EtOAc/*n*-Hexane, 1/19).

4-Butynyl-*N,N*-dimethylaniline (12e): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.35 g, 6.0 mmol), 1-butynyllithium (0.39 g, 6.5 mmol), 4-iodo-*N,N*-dimethylaniline (1.24 g, 5.0 mmol) and $Pd(PPh_3)_4$ (0.347 g, 0.30 mmol) in THF (8 mL)] gave **12e** as yellow crystals (0.66 g, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.23 (3H, t, *J* = 7.1 Hz), 2.41 (2H, q, *J* = 7.1 Hz), 2.95 (6H, s), 6.62 (2H, d, *J* = 8.8 Hz), 7.28 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.7, 132.5, 111.9, 111.1, 89.0, 80.3, 40.3, 14.2, 13.1; MS (EI): m/z (%): 173.1 (100), 158.1 (66), 129.1 (7), 118.1 (21), 104.1 (10), 91.1 (5), 77.0 (15), 63.0 (11); HR-MS ($C_{12}H_{15}N$): calcd 173.1204, found 173.1200; TLC R_f= 0.46 (EtOAc/*n*-Hexane, 1/19).

2-Butynylthiophene (12f): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (1.33 g, 5.9 mmol), 1-butynyllithium (0.38 g, 6.4 mmol), 2-bromothiophene (0.80 g, 4.9 mmol) and $Pd(PPh_3)_4$ (0.34 g, 0.29 mmol) in THF (8 mL)] gave **12f** as a yellow oil (0.64 g, 95%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.23 (3H, t, *J* = 7.2 Hz), 2.44 (2H, q, *J* = 7.2), 6.93 (1H, dd, *J* = 5.1, 3.5 Hz), 7.11 (1H, dd, *J* =

3.5, 1.0 Hz), 7.17 (1H, dd, J = 5.1, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 130.9, 126.7, 125.9, 124.2, 95.7, 73.0, 13.6, 13.3; MS (EI): m/z (%): 136.0 (100), 121.0 (67), 103.1 (7), 91.1 (27), 77.0 (18), 63.0 (13); HR-MS (C_8H_8S): calcd 136.0347, found 136.0344; TLC R_f = 0.46 (*n*-Hexane).

2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3-butynylbenzoate (13): Application of the general procedure of the Negishi cross-coupling as for the preparation of **8** [$ZnBr_2$ (0.82 g, 3.7 mmol), 1-butynyllithium (0.24 g, 4.0 mmol), 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-iodobenzoate (1.2 g, 3.0 mmol) and $Pd(PPh_3)_4$ (0.18 g, 0.15 mmol) in THF (8 mL)] gave **13** as a yellow oil (0.75 g, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07 (1H, t, J = 1.5 Hz), 7.94 (1H, dt, J = 1.5, 8.0 Hz), 7.56 (1H, dt, J = 1.5, 8.0 Hz), 7.35 (1H, t, J = 8.0 Hz), 4.46-4.48 (m, 2H), 3.82-3.84 (m, 2H), 3.71-3.72 (m, 2H), 3.64-3.69 (m, 4H), 3.52-3.54 (m, 2H), 3.37 (3H, s), 2.42 (2H, q, J = 7.1 Hz), 1.24 (3H, t, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 135.8, 132.8, 130.2, 128.7, 128.3, 124.4, 92.7, 79.0, 71.9, 70.7, 70.6, 70.5, 69.2, 64.2, 59.0, 13.8, 13.0; MS (EI): m/z (%): 320.2 (3), 201.1 (60), 157.1 (84), 128.1 (23), 103.1 (8), 84.0 (100), 59.1 (53); HR-MS ($C_{18}H_{24}O_5$): calcd 320.1637, found 320.1631; TLC R_f = 0.19 (EtOAc/*n*-Hexane, 3/7).

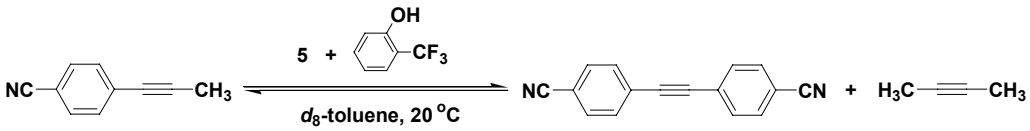
Reference

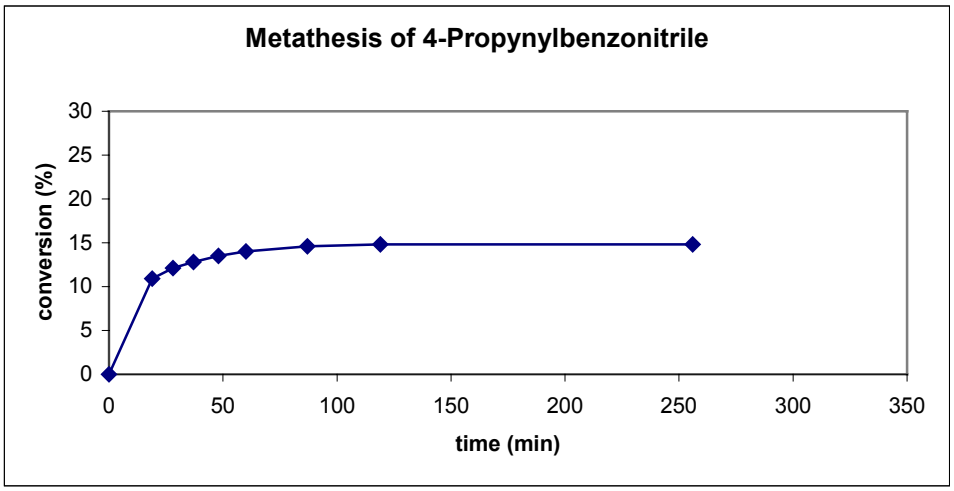
1. (a) King, A. O.; Okukado, N,; Negishi, E. *J. Chem. Soc. Chem. Commun*. **1977**, 683-684. (b) King, A. O.; Negishi, E.; Villani, F. J. Jr.; Silveira, A. Jr. *J. Org. Chem*. **1978**, *43*, 358-360.
2. Pschirer, N. G.; Bunz, U. H. F. *Tetrahedron Lett*. **1999**, *40*, 2481.

3. (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett*. **1975**, 4467-4470. (b) Sonogashira, K.; Yatake, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. *J. Chem. Soc. Chem. Commun*. **1977**, 291-292.

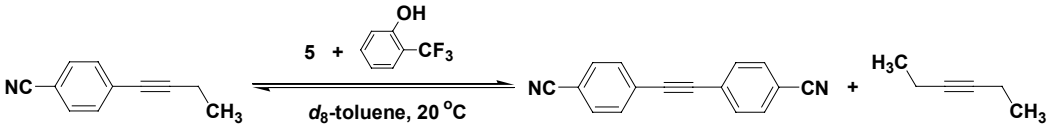
General procedure for kinetic studies: To a solution of molybdenum(VI) propylidyne **5** (0.012 mmol) and phenol/alcohol (0.036 mmol) in d_8-toluene (0.6 mL) was added the substrate (0.12 mmol). The metathesis reactions were run in sealed NMR tubes at 20 ^{o}C and monitored by ^{1}H NMR (d1 = 40 s) until the ratio of product dimer to monomer stayed constant. Ferrocene was used as internal standard and in all cases the mass balance was higher than 95%. Conversion was calculated from the integration ratio of product to initial starting material.

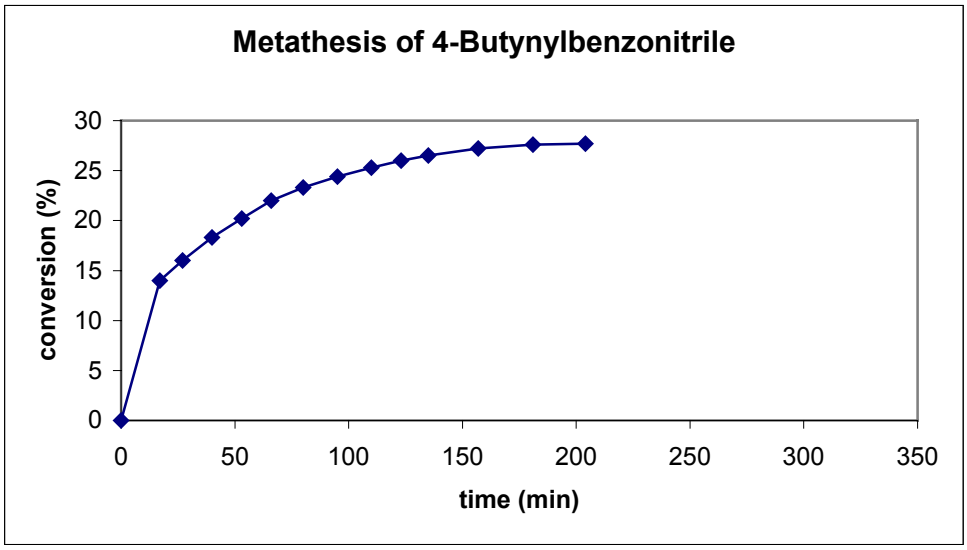
I. Kinetic studies on substituent effect on metathesis reaction:
Metathesis reaction conversion vs reaction time (time scale is **350** min)



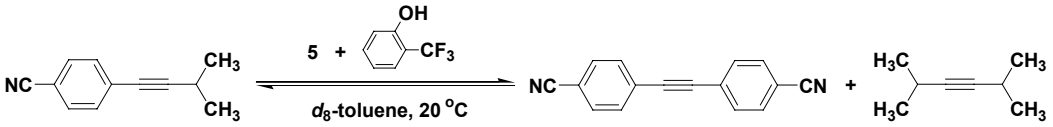


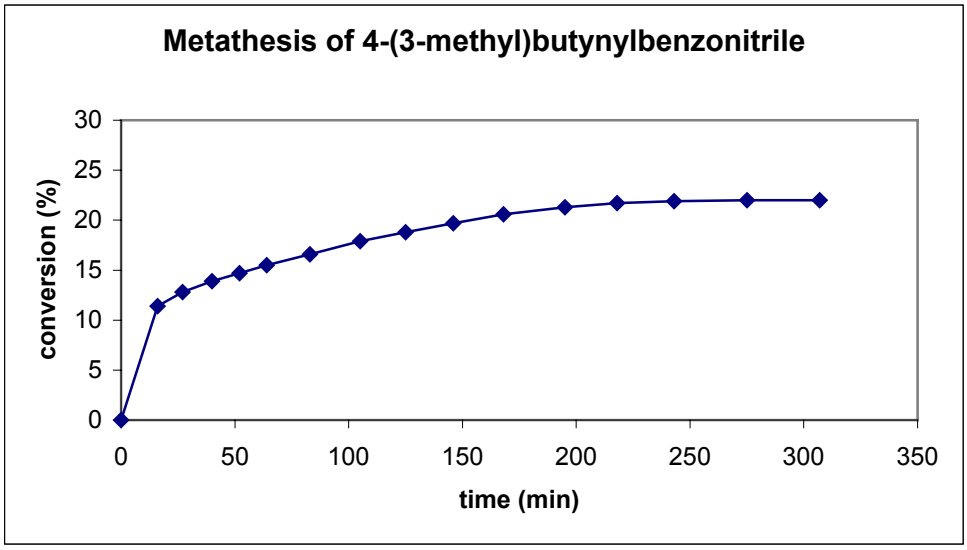
Time (min)	Conversion (%)
0	0
19	10.9
28	12.1
37	12.8
48	13.5
60	14
87	14.6
119	14.8
256	14.8



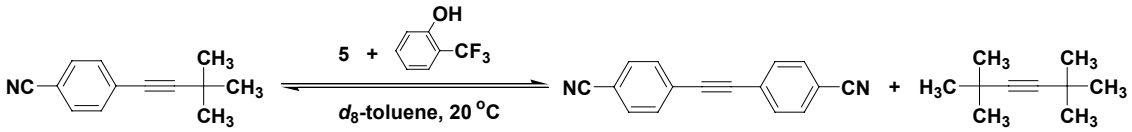


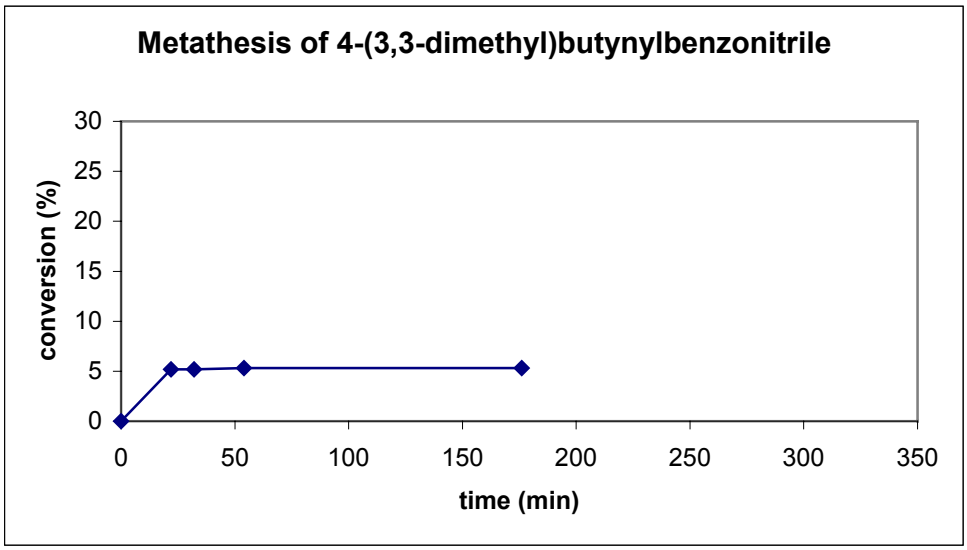
Time (min)	Conversion (%)
0	0
17	14
27	16
40	18.3
53	20.2
66	22
80	23.3
95	24.4
110	25.3
123	26
135	26.5
157	27.2
181	27.6
204	27.7





Time (min)	Conversion (%)
0	0
16	11.4
27	12.8
40	13.9
52	14.7
64	15.5
83	16.6
105	17.9
125	18.8
146	19.7
168	20.6
195	21.3
218	21.7
243	21.9
275	22
307	22



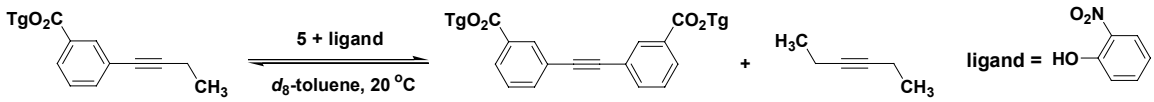


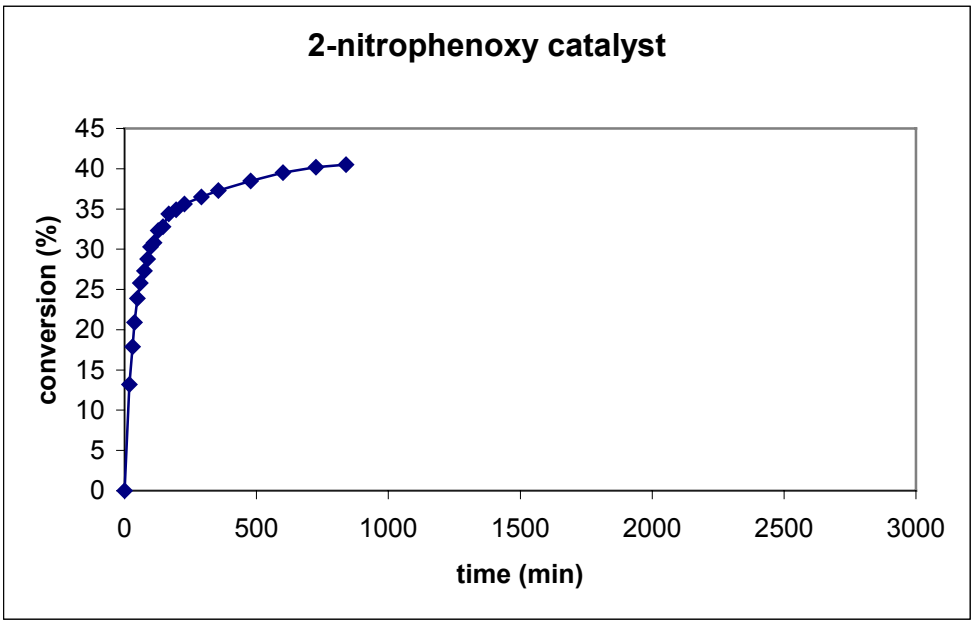
Time (min)	Conversion (%)
0	0
22	5.2
32	5.2
54	5.3
176	5.3

The observed 5% of starting material is presumably converted to Mo(VI) *t*-pentylidyne complex, which has low reactivity for further alkyne metathesis due to the large steric hindrance of *t*-butyl group.

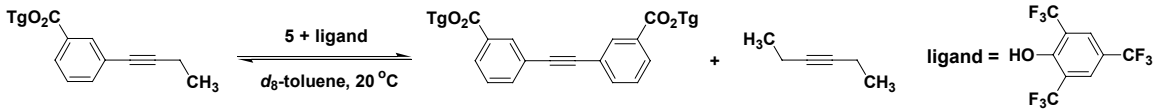
II. Kinetic studies on screening for highly active catalyst ligands:

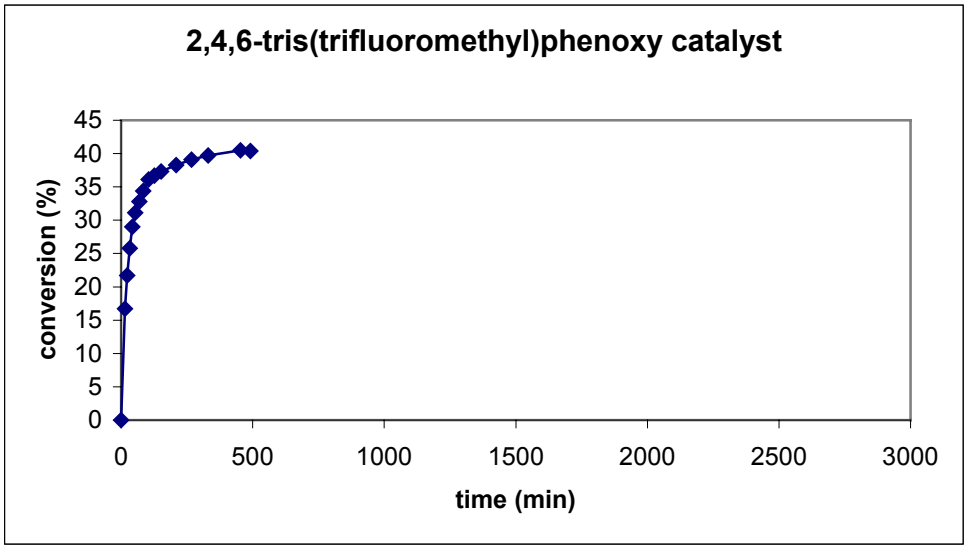
Metathesis reaction conversion vs reaction time (time scale is **3000** min)



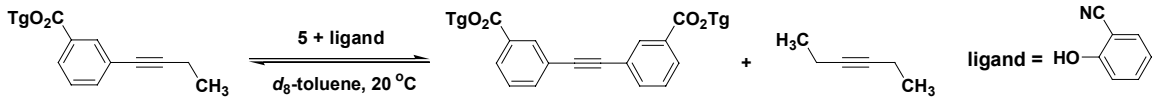


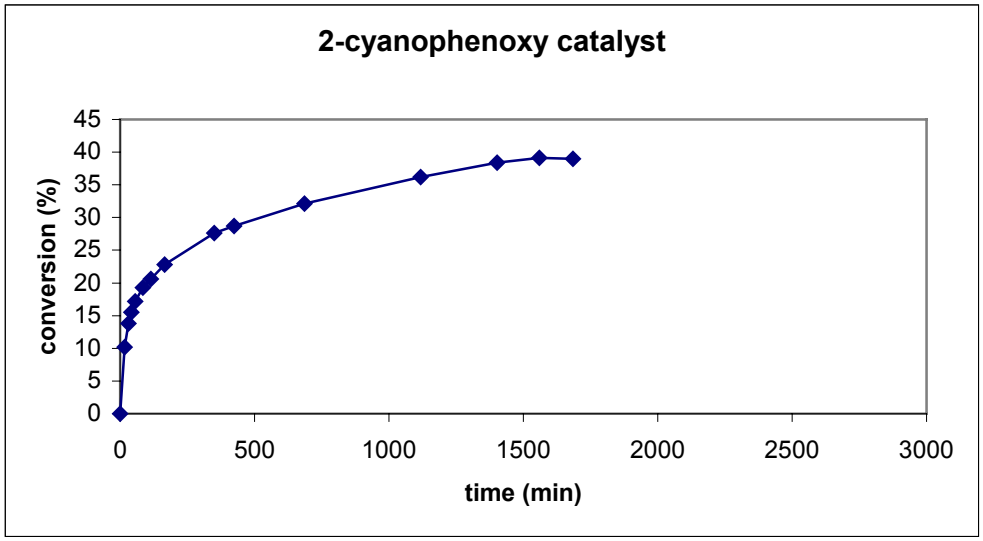
Time (min)	Conversion (%)
0	0
18	13.2
30	17.9
38	20.9
49	23.9
60	25.8
75	27.3
87	28.8
98	30.3
111	30.8
127	32.3
145	32.8
167	34.4
195	34.9
227	35.6
291	36.5
355	37.3
478	38.5
601	39.5
725	40.2
840	40.5



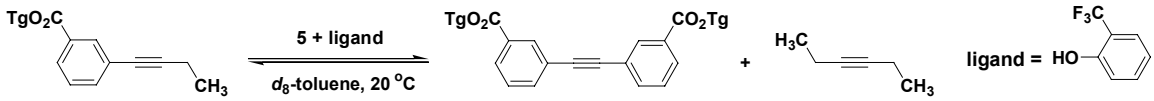


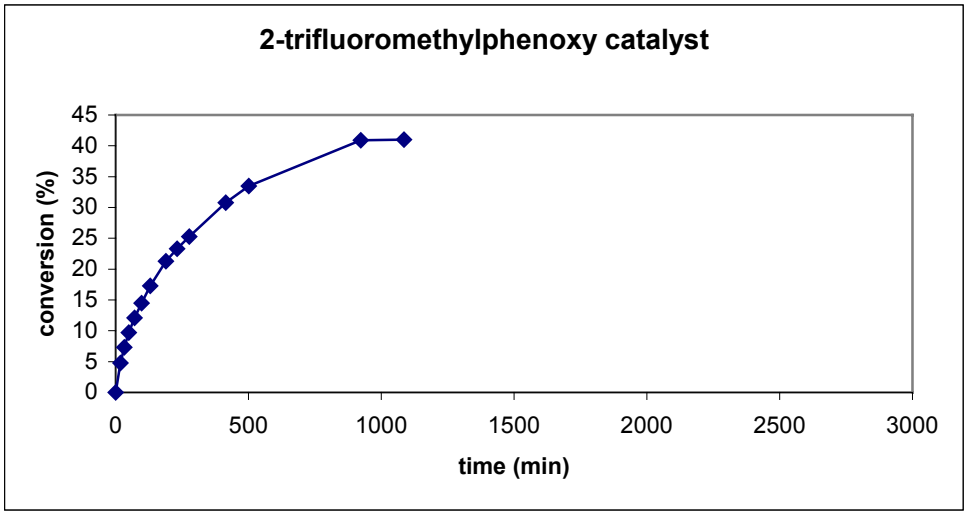
Time (min)	Conversion (%)
0	0
14	16.7
23	21.7
33	25.8
43	29
54	31.1
69	32.8
84	34.4
105	36.1
126	36.7
152	37.3
209	38.3
268	39.1
331	39.7
454	40.5
491	40.4



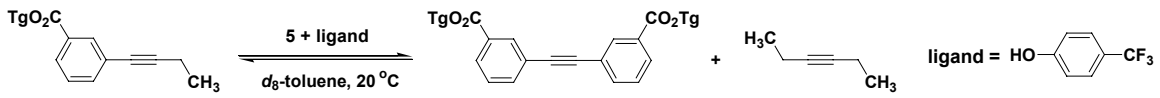


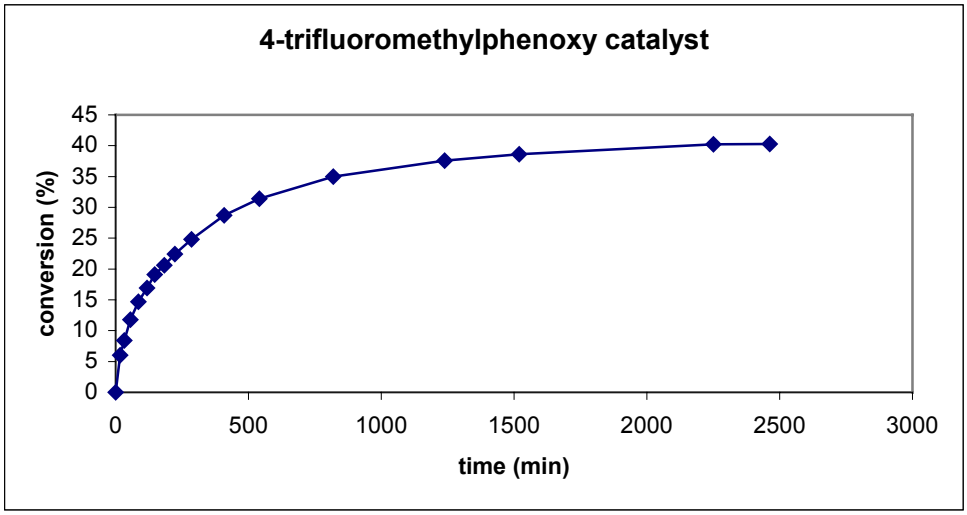
Time (min)	Conversion (%)
0	0
17	10.2
31	13.8
42	15.5
56	17.2
85	19.3
114	20.6
166	22.8
350	27.6
424	28.7
686	32.1
1118	36.2
1402	38.4
1560	39.1
1684	39



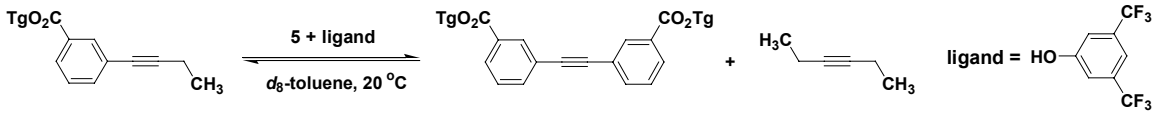


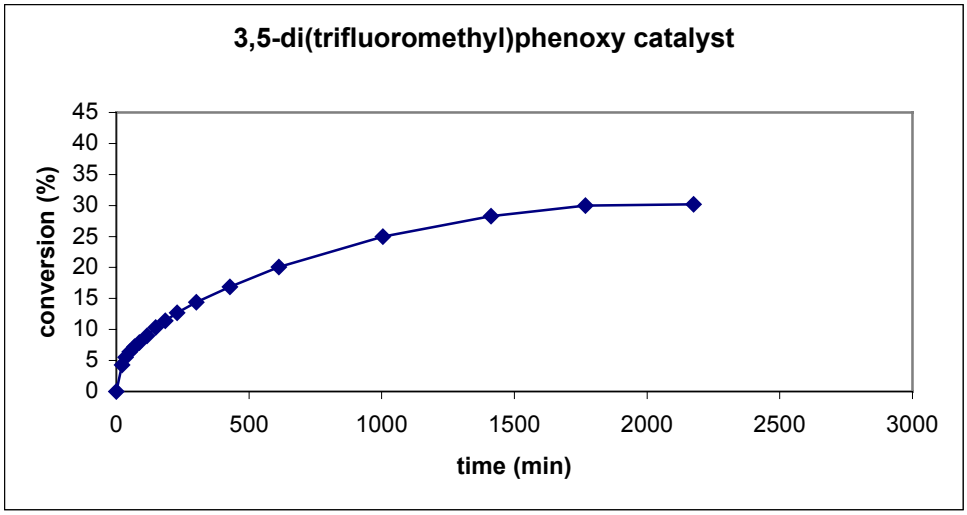
Time (min)	Conversion (%)
0	0
18	4.8
33	7.3
49	9.7
71	12.1
98	14.5
130	17.3
189	21.3
231	23.3
277	25.3
415	30.8
501	33.5
923	40.9
1085	41





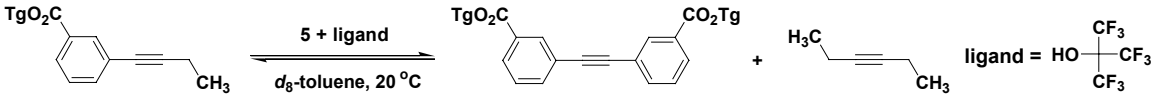
Time (min)	Conversion (%)
0	0
17	6
32	8.4
56	11.8
86	14.7
118	16.9
147	19.1
183	20.6
223	22.4
285	24.8
408	28.7
541	31.4
819	35
1238	37.6
1519	38.6
2250	40.2
2463	40.3

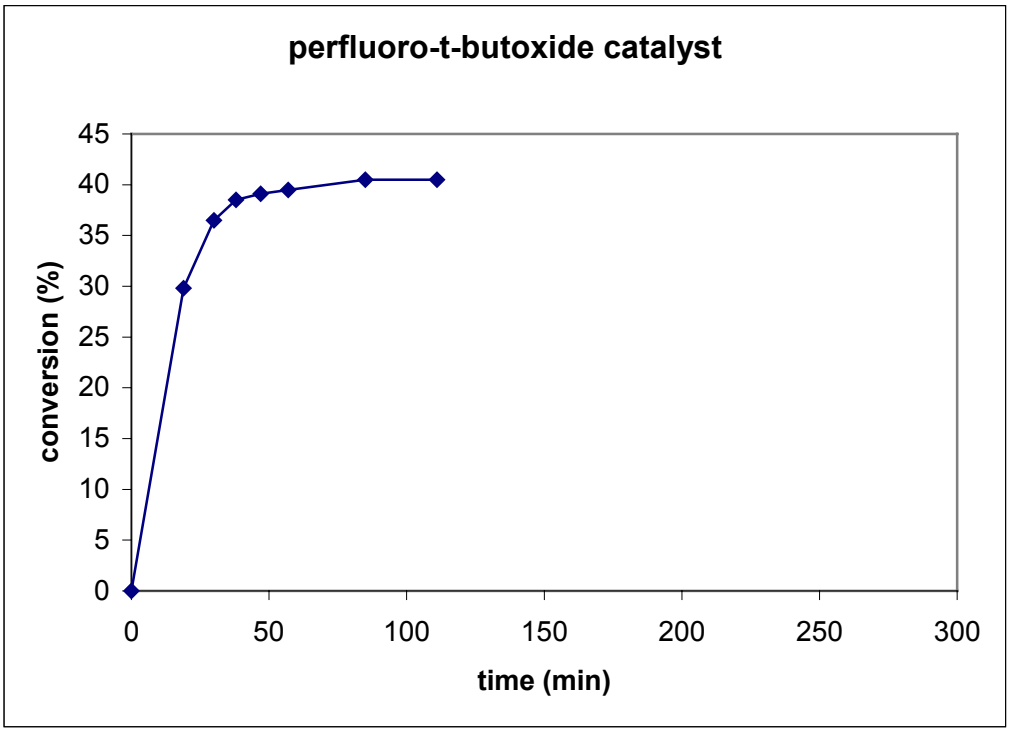




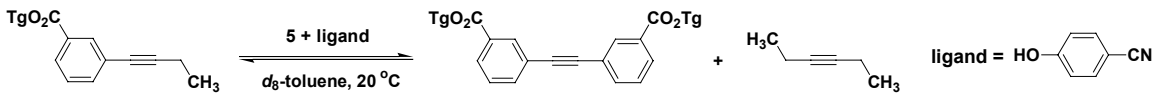
Time (min)	Conversion (%)
0	0
22	4.3
35	5.5
51	6.4
69	7.2
87	7.9
116	9
148	10.3
185	11.4
229	12.7
302	14.4
428	16.9
613	20.1
1005	25
1412	28.3
1768	30
2175	30.2

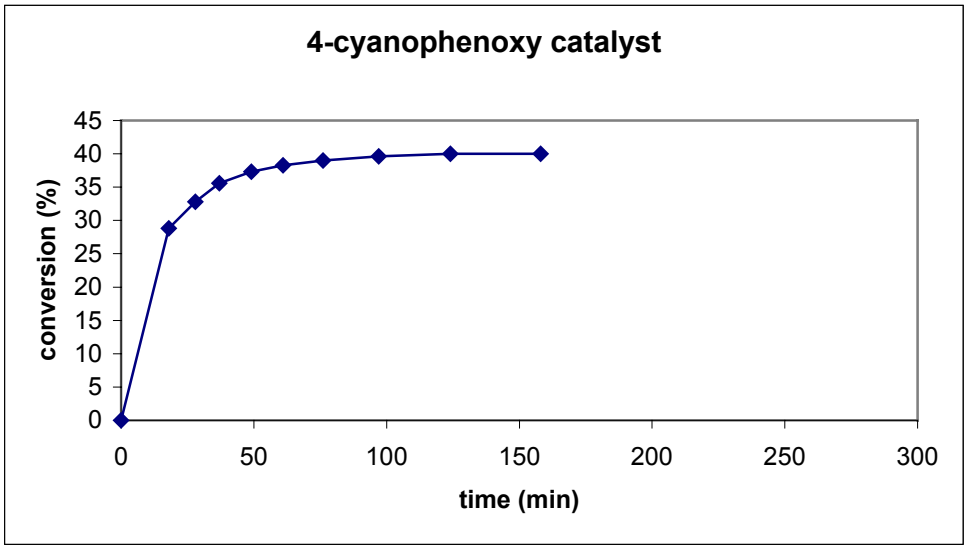
Metathesis reaction conversion vs reaction time (time scale is **300** min)



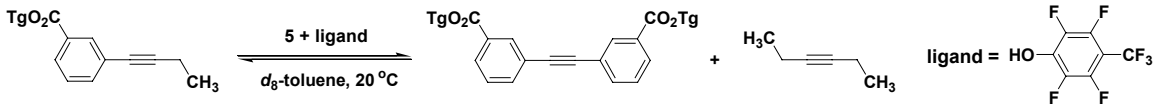


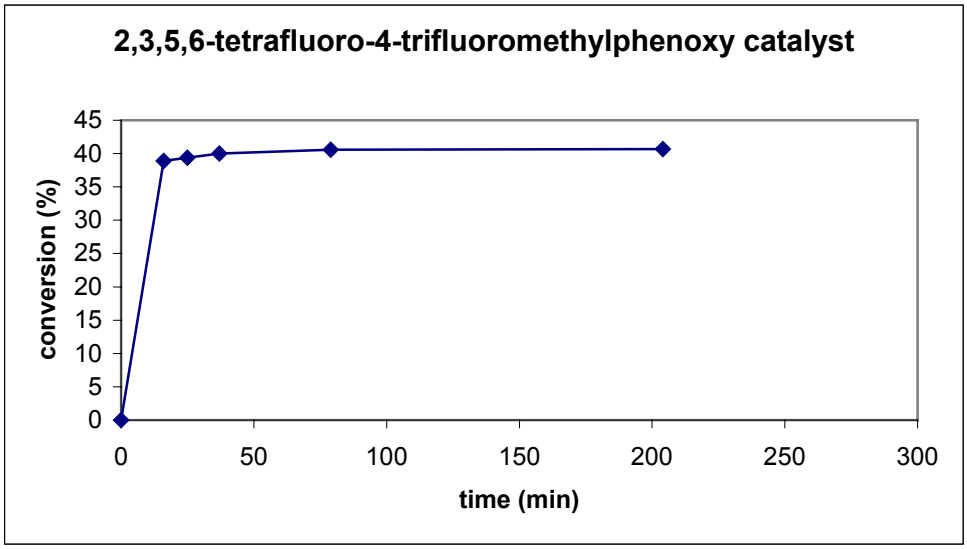
Time (min)	Conversion (%)
0	0
19	29.8
30	36.5
38	38.5
47	39.1
57	39.5
85	40.5
111	40.5



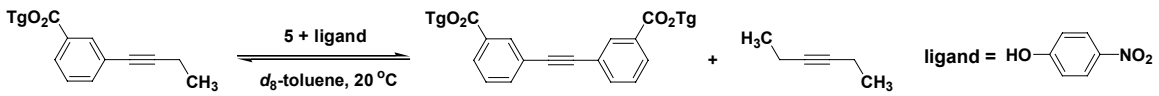


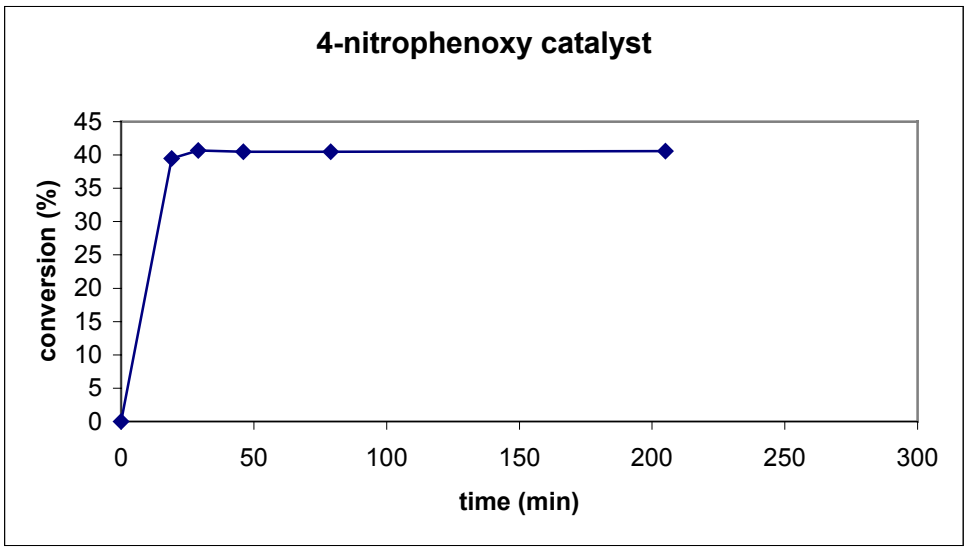
Time (min)	Conversion (%)
0	0
18	28.8
28	32.8
37	35.6
49	37.3
61	38.3
76	39
97	39.6
124	40
158	40





time (min)	Conversion (%)
0	0
16	38.9
25	39.4
37	40
79	40.6
204	40.7

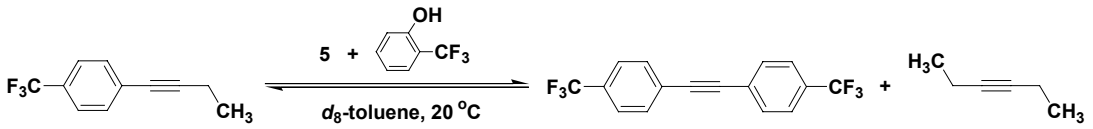


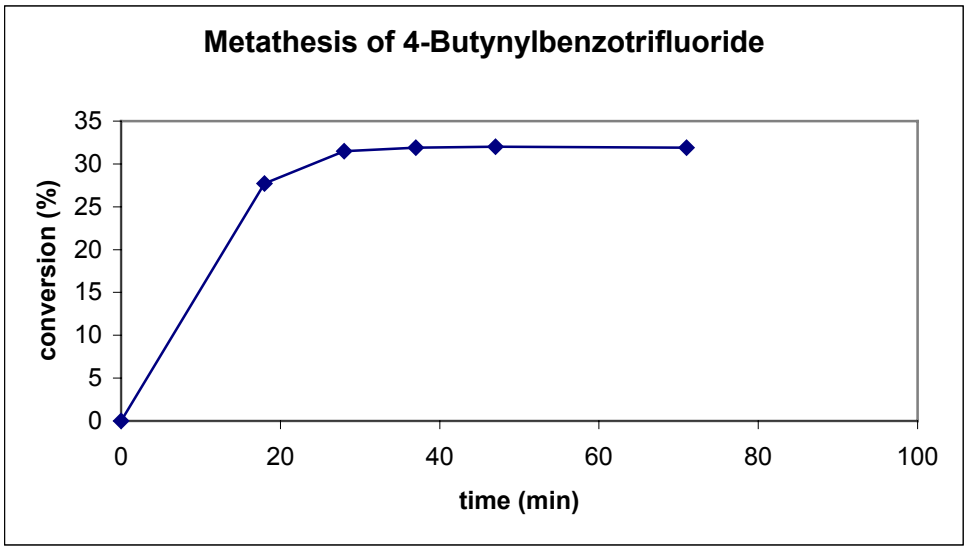


Time (min)	Conversion (%)
0	0
19	39.5
29	40.7
46	40.5
79	40.5
205	40.6

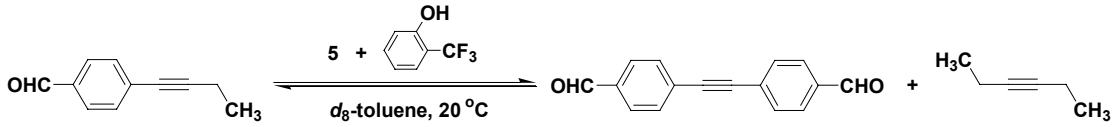
III. Kinetic studies on metathesis reactions catalyzed by *α,α,α*-trifluoro-*o*-cresol catalyst :

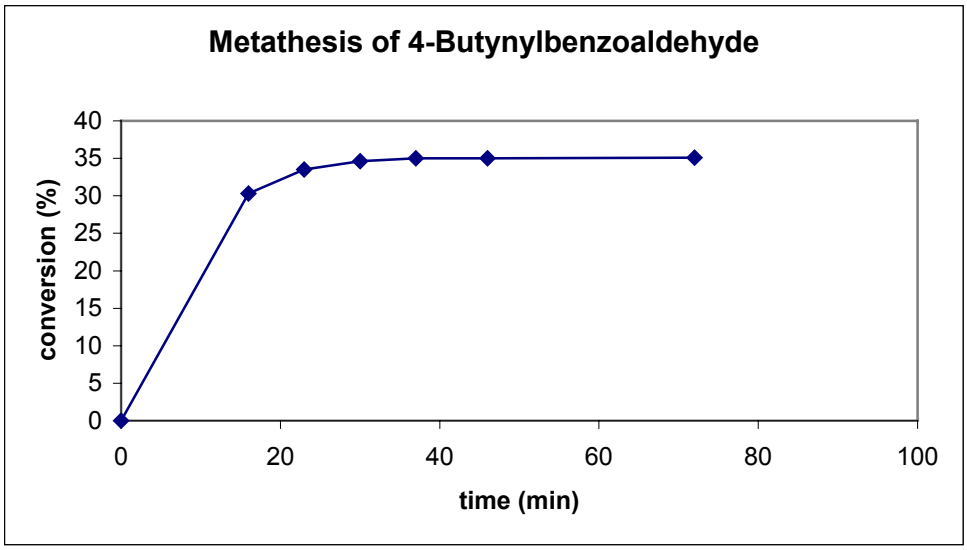
Metathesis reaction conversion vs reaction time (time scale is **100** min)



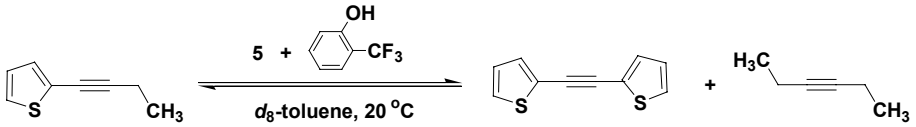


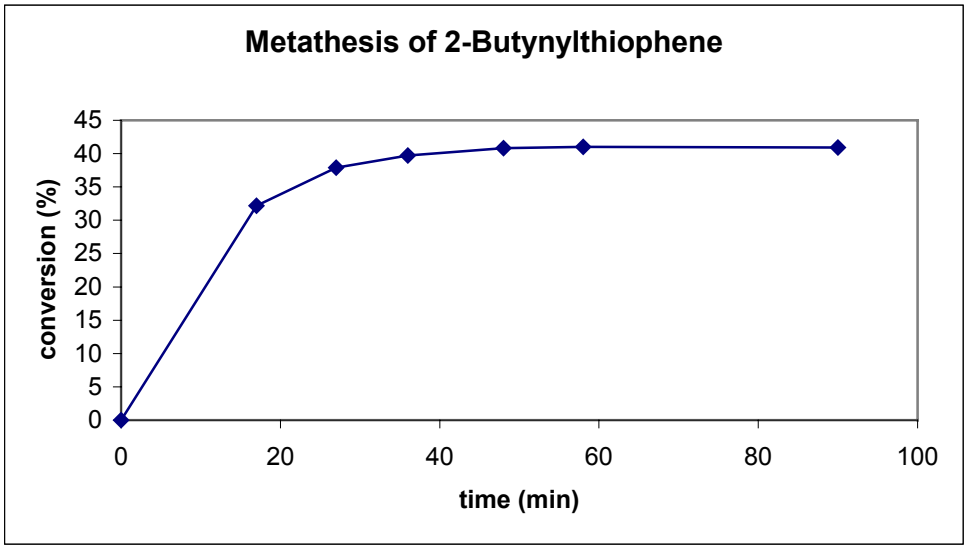
Time (min)	Conversion (%)
0	0
18	27.7
28	31.5
37	31.9
47	32
71	31.9





Time (min)	Conversion (%)
0	0
16	30.3
23	33.5
30	34.6
37	35
46	35
72	35.1





Time (min)	Conversion (%)
0	0
17	32.2
27	37.9
36	39.7
48	40.8
58	41
90	40.9