

General. All air sensitive materials were manipulated under nitrogen in a glove box or by standard high vacuum and Schlenk techniques. Hexane, pentane, THF, and diethyl ether were distilled from sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2 . 4-Ethynyltoluene was purchased from Lancaster. Unless stated otherwise, all other reagents were purchased from Aldrich.

^1H NMR spectra were obtained on a Bruker AC 250, AC 300, or Varian Unity 500 spectrometer. ^{13}C NMR spectra were obtained on a Varian Unity 500 spectrometer operating at 125 MHz. Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. Mass spectra were obtained on a Kratos MS-80 or Micromass AutoSpec spectrometer. Infrared spectra were obtained using an *in situ* internal reflectance FTIR reaction monitoring system (Applied Systems React IR 1000).

Procedure for Synthesis of Benzoyl and Toluoyl Manganese Complexes.

PhLi or TolLi (1 equiv) in hexane was added dropwise to a solution of $(\text{C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_3$ (1 equiv, 1 M) in diethyl ether at 0°C or at room temperature. The bright yellow solution quickly turned deep red, and after stirring for several h at room temperature, a bright orange powder precipitated. The supernatant was removed by cannula transfer. The orange solid was washed with 1:1 ether : pentane, dried *in vacuo*, and weighed and handled in a glove box.

Cp(CO)₂MnC(O)(C₆H₄-4-CH₃)Li·0.5Et₂O (5). Reaction of CpMn(CO)₃ (7.00 g, 34.30 mmol) with *p*-tolyllithium (46.7 mL, 0.75 M, ether, 35.0 mmol, prepared from Li dispersion and 4-bromotoluene in ether) led to the isolation of **5** (10.13 g, 78%). ^1H NMR (500 MHz, acetone- d_6) δ 7.167 (d, J = 6.5 Hz, 2H, H_{Ar}), 6.930 (d, J = 6.5 Hz, 2H,

H_{Ar}), 4.337 (s, Cp), 3.400 (q, $J = 6.5$ Hz, 2H, Et_2O), 2.229 (s, 3H, Me), 1.106 (t, $J = 7.0$ Hz, 3H, Et_2O). ^{13}C NMR (125 MHz, acetone- d_6) δ 311.97 (s, COAr), 238.04 (s, CO), 156.44 (s, C_{Ar}), 135.92 (s, C_{Ar}), 127.91 (d, $^1J_{\text{CH}} = 155$ Hz, C_{Ar}), 124.95 (d, $^1J_{\text{CH}} = 157$ Hz, C_{Ar}), 85.01 (d, $^1J_{\text{CH}} = 173$ Hz, Cp), 66.17 (t, $^1J_{\text{CH}} = 140$ Hz, Et_2O), 21.13 (q, $^1J_{\text{CH}} = 129$, Me), 15.64 (q, $^1J_{\text{CH}} = 129$ Hz, Et_2O). IR (CH_2Cl_2) 1902, 1798 cm^{-1} .

(C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-OCH₃)Li·Et₂O (14). Reaction of (C₅H₄Me)Mn(CO)₃ (3.81 mL, 24.1 mmol) with LiC₆H₄-2-OCH₃ [prepared from 2-bromoanisole (3.00 mL, 24.1 mmol), and BuLi (15.06 mL, 1.6 M, 24.1 mmol)] led to the isolation of **14** (5.06 g, 69%). ^1H NMR (500 MHz, acetone- d_6) spectrum was broad: δ 6.93 (2H, H_{Ar}), 6.81 (2H, H_{Ar}), 4.26 (2H, C₅H₄Me), 4.14 (2H, C₅H₄Me), 3.74 (OMe), 1.85 (C₅H₄Me). ^{13}C { ^1H } NMR (125 MHz, acetone- d_6) δ 236.49 (CO), 149.59 (2C, C_{Ar}), 125.25 (C_{Ar}), 125.05 (C_{Ar}), 119.93 (C_{Ar}), 111.69 (C_{Ar}), 111.69 (C_{Ar}), 99.07 (C₅H₄Me), 84.359 (C₅H₄Me), 84.11 (C₅H₄Me), 68.48 (OMe), 13.65 (C₅H₄Me). Acyl carbon not found above baseline noise. IR (CH_2Cl_2) 1919, 1830 cm^{-1} .

(C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-CH₃)Li·Et₂O (15). Reaction of (C₅H₄Me)Mn(CO)₃ (5.00 mL, 31.6 mmol) with LiC₆H₄-2-CH₃ [prepared from 2-bromotoluene (3.81 mL, 31.6 mmol), and BuLi (19.8 mL, 1.6 M, hexanes, 31.6 mmol)] led to the isolation of **15** (7.97 g, 80%). Solvent was evaporated and the residue was washed with hexanes/ ether in a glove box to give a bright yellow powder. ^1H NMR (500 MHz, acetone- d_6) δ 6.94 (t, $J = 7.0$ Hz, 1H, H_{Ar}), 6.88 (d, $J = 7.0$ Hz, 1H, H_{Ar}), 6.81 (t, $J = 6.5$ Hz, 1H, H_{Ar}), 6.74 (d, $J = 7.5$ Hz, 1H, H_{Ar}), 4.28 (s, 2H, C₅H₄Me), 4.15 (s, 2H, C₅H₄Me), 3.42 (q, $J = 7.0$ Hz, Et_2O), 2.15 (s, C₆H₄Me), 1.873 (s, C₅H₄Me), 1.117 (t, $J = 7.0$ Hz, Et_2O). ^{13}C NMR (125 MHz,

acetone- d_6) δ 317.09 (s, COAr), 236.58 (s, CO), 156.50 (s, C_{Ar}), 129.05 (d, $^1J_{CH} = 153$ Hz, C_{Ar}), 126.71 (s, C_{Ar}), 124.03 (dd, $^1J_{CH} = 156$ Hz, $^2J_{CH} = 7$ Hz, C_{Ar}), 123.32 (dd, $^1J_{CH} = 158$ Hz, $^2J_{CH} = 7$ Hz, C_{Ar}), 121.21 (dd, $^1J_{CH} = 154$ Hz, $^2J_{CH} = 7$ Hz, C_{Ar}), 98.91 (s, C₅H₄Me), 84.63 (dd, $^1J_{CH} = 173$ Hz, $^2J_{CH} = 7$ Hz, C₅H₄Me), 84.12 (d, $^1J_{CH} = 169$ Hz, C₅H₄Me), 65.10 (t, $^1J_{CH} = 126$ Hz, Et₂O), 18.12 (q, $^1J_{CH} = 126$ Hz, C₅H₄Me), 14.72 (q, $^1J_{CH} = 124$ Hz, Et₂O), 13.59 (q, $^1J_{CH} = 126$ Hz, C₅H₄Me). IR (CH₂Cl₂) 1919, 1812 cm⁻¹.

(C₅H₄Me)(CO)₂MnC(O)(C₆H₄-3-OCH₃)Li·Et₂O (16). Reaction of

(C₅H₄Me)Mn(CO)₃ (6.24 mL, 39.5 mmol) with LiC₆H₄-3-OCH₃ [prepared from 3-bromoanisole (5.00 mL, 39.5 mmol), and BuLi (24.7 mL, 1.6 M, 39.5 mmol)] led to the isolation of **16** (4.52 g, 34%). ¹H NMR (500 MHz, acetone- d_6) spectrum was broad: δ 7.04 (1H, H_{Ar}), 6.81 (2H, H_{Ar}), 6.62 (1H, H_{Ar}), 4.28 (2H, C₅H₄Me), 4.17 (2H, C₅H₄Me), 3.76 (3H, OMe), 1.85 (3H, C₅H₄Me). ¹³C {¹H} NMR (125 MHz, acetone- d_6) δ 311.47 (COAr), 238.26 (CO), 160.52 (C_{Ar}), 159.46 (C_{Ar}), 128.18 (C_{Ar}), 117.15 (C_{Ar}), 112.09 (C_{Ar}), 109.85 (C_{Ar}), 100.01 (C₅H₄Me), 85.59 (C₅H₄Me), 84.71 (C₅H₄Me), 69.30 (OMe), 14.56 (C₅H₄Me). IR (CH₂Cl₂) 1912, 1793 cm⁻¹.

(C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-F)Li·Et₂O (17). Reaction of (C₅H₄Me)Mn(CO)₃

(2.88 mL, 18.2 mmol) with LiC₆H₄-4-F [prepared from 4-bromofluorobenzene (2.00 mL, 18.2 mmol), and BuLi (11.4 mL, 1.6 M, 18.2 mmol)] led to the isolation of **17** (4.46 g, 62%). ¹H NMR (500 MHz, acetone- d_6 , broad peaks) δ 7.34 (2H, H_{Ar}), 6.97 (2H, H_{Ar}), 4.29 (2H, C₅H₄Me), 4.19 (2H, C₅H₄Me), 1.84 (C₅H₄Me). ¹³C {¹H} NMR (125 MHz, acetone- d_6) δ 310.00 (COAr), 238.21 (CO), 162.20 (d, $^1J_{CF} = 247$ Hz, C-F), 154.98 (C_{Ar}),

126.77 (C_{Ar}), 113.42 (d, $^2J_{CF} = 22$ Hz, C_{Ar}), 100.15 (s, C_5H_4Me), 85.65 (C_5H_4Me), 84.67 (C_5H_4Me), 14.38 (C_5H_4Me). IR (CH_2Cl_2) 1907, 1803 cm^{-1} .

(C_5H_4Me)(CO)₂MnC(O)(C_6H_4 -4-Cl)Li·Et₂O (18). Reaction of (C_5H_4Me)Mn(CO)₃ (7.59 mL, 48.0 mmol) with LiC₆H₄-4-Cl [prepared from 4-bromochlorobenzene (9.19 g, 48.0 mmol), and BuLi (30.0 mL, 1.6 M, 48.0 mmol)] led to the isolation of **18** (14.47 g, 73%). 1H NMR was too broad for accurate assignments. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d₆) δ 310.84 (COAr), 238.07 (CO), 156.96 (C_{Ar}), 131.48 (C_{Ar}), 127.27 (HC_{Ar}), 126.10 (HC_{Ar}), 100.25 (C_5H_4Me), 85.75 (C_5H_4Me), 84.85 (C_5H_4Me), 66.06 (Et₂O), 15.59 (Et₂O), 14.38 (C_5H_4Me). IR (CH_2Cl_2) 1910, 1804 cm^{-1} .

(C_5H_4Me)(CO)₂MnC(O)(C_6H_4 -4-CF₃)Li·Et₂O (19). Reaction of (C_5H_4Me)Mn(CO)₃ (5.92 mL, 37.5 mmol) with LiC₆H₄-4-CF₃ [prepared from *p*-chlorobenzotrifluoride (5.00 mL, 37.5 mmol), and BuLi (23.4 mL, 1.6 M, 37.5 mmol)] led to the isolation of **19** (4.75 g, 29%). No precipitate formed, so the solvent was evaporated, and the residue was extracted into hexanes. Large crystals formed over several weeks. 1H NMR (500 MHz, acetone-d₆) δ 7.46 (br, 2H, H_{Tol}), 7.21 (br, 2H, H_{Tol}), 4.33 (br, 2H, C_5H_4Me), 4.22 (br, 2H, C_5H_4Me), 3.65 (br, 4H, Et₂O), 1.87 (s, C_5H_4Me), 1.80 (6H, Et₂O). ^{13}C NMR (125 MHz, acetone-d₆) δ 311.02 (s, COAr), 237.00 (s, CO), 160.87 (s, C_{Ar}), 126.19 (s, C_{Ar}), 123.94 (d, $^1J_{CH} = 160$ Hz, C_{Ar}), 123.07 (d, $^1J_{CH} = 160$ Hz, C_{Ar}), 99.62 (s, C_5H_4Me), 84.98 (d, $^1J_{CH} = 176$ Hz, C_5H_4Me), 84.35 (d, $^1J_{CH} = 173$ Hz, C_5H_4Me), 67.37 (t, $^1J_{CH} = 144$ Hz, Et₂O), 25.37 (q, $^1J_{CH} = 131$ Hz, Et₂O), 13.59 (q, $^1J_{CH} = 126$ Hz, C_5H_4Me). CF₃ carbon not observed. IR (CH_2Cl_2) 1914, 1809 cm^{-1} .

(C₅H₄Me)(CO)₂MnC(O)[C₆H₃-2,6-(OMe)₂]Li·nEt₂O (20). Reaction of

(C₅H₄Me)Mn(CO)₃ (4.82 mL, 30.5 mmol) with LiC₆H₃-2,6-(OMe)₂ [prepared from 1,3-dimethoxybenzene (4.00 mL, 30.5 mmol), TMEDA (0.2 mL) and BuLi (19.08 mL, 1.6 M, 30.5 mmol in ether (35 mL) at 0 °C] led to the isolation of **20** (8.36 g, 76%). Solvent was evaporated and the residue was washed with hexanes/ether in a glove box to give a bright yellow powder. ¹H NMR (500 MHz, acetone-*d*₆) δ 6.93 (br, 1H, Ar), 6.53 (br, 2H, Ar), 4.26 (br, 2H, C₅H₄Me), 4.11 (br, 2H, C₅H₄Me), 3.75 (br, OMe), 1.89 (br, C₅H₄Me). ¹³C {¹H} NMR (125 MHz, acetone-*d*₆) δ 237.13 (CO), 152.61 (C_{Ar}), 138.91 (C_{Ar}), 125.43 (C_{Ar}), 105.47 (C_{Ar}), 99.82 (C_{Ar}), 85.07 (C_{Ar}), 84.73 (C_{Ar}), 69.29 (OMe), 14.53 (C₅H₄Me), COAr carbon not observed. IR (CH₂Cl₂) 1923, 1821 cm⁻¹.

(2-Me-C₆H₄)C≡CC(CH₂CH₂CH₂)=CC≡C(C₆H₄-2-Me) (22). Addition of trifluoroacetic anhydride (130 μL, 0.92 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-Me)Li·Et₂O (**15**) (264 mg, 0.84 mmol) was followed by addition of CuBr (43 mg), LiI (50 mg), NEt(*i*-Pr₂) (130 μL), and 1,6-heptadiyne (38 μL, 0.33 mmol) in CH₂Cl₂ (12 mL).

The solution was poured into 50 mL 10% ether/hexanes and photolyzed.

Chromatography gave **22** (69 mg, 70% based on diyne) as a slightly yellow oil. ¹H NMR (250 MHz, CDCl₃) δ 7.50 (d, *J* = 7 Hz, 2H, H_{Ar}), 7.28-7.24 (m, 4H, H_{Ar}), 7.22-7.17 (m, 2H, H_{Ar}), 2.779 (t, *J* = 7.5 Hz, 2H, C=CCH₂), 2.538 (s, Me), 2.091 (p, *J* = 7.5 Hz, 4H, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 140.16 (s, CMe), 131.82 (d, ¹J_{CH} = 160 Hz, C_{Ar}), 129.93 (s, C=C), 129.36 (d, ¹J_{CH} = 158 Hz, C_{Ar}), 128.26 (dd, ¹J_{CH} = 160 Hz, ²J_{CH} = 8 Hz, C_{Ar}), 125.48 (d, ¹J_{CH} = 158 Hz, C_{Ar}), 123.18 (s, C_{ipso}), 95.38 (s, C≡CAr), 90.29 (s, C≡CAr), 37.19 (t, ¹J_{CH} = 132 Hz, C=CCH₂), 23.19 (t, ¹J_{CH} = 131 Hz, C=CCH₂CH₂), 20.79

(q, $^1J_{\text{CH}} = 125.6$ Hz, Me). HRMS(EI) m/z calcd for $\text{C}_{23}\text{H}_{20}$ (M^+) 296.1566; found, 296.1564.

(4-Cl-C₆H₄)C=CC(CH₂CH₂CH₂)=CC=C(C₆H₄-4-Cl) (23). Addition of trifluoroacetic anhydride (353 μL , 2.50 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Cl)Li·Et₂O (**18**) (801 mg, 2.38 mmol) was followed by addition of CuBr (48 mg), LiI (47 mg), NEt(*i*-Pr₂) (370 μL), and 1,6-heptadiyne (114 μL , 0.996 mmol) in CH₂Cl₂ (200 mL). The solution was poured into 100 mL 10% ether/hexanes and photolyzed. Chromatography gave **23** (345 mg, 93% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, $J = 8$ Hz, 4H, H_{Ar}), 7.31 (d, $J = 8$ Hz, 4H, H_{Ar}), 2.698 (t, $J = 8.0$ Hz, C=CCH₂CH₂), 2.028 (p, $J = 8.0$ Hz, 2 H, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 134.28 (s, CCl), 132.67 (dd, $^1J_{\text{CH}} = 164$ Hz, $^2J_{\text{CH}} = 7$ Hz, C_{Ar}), 130.40 (s, C=C), 128.61 (dd, $^1J_{\text{CH}} = 166$ Hz, $^2J_{\text{CH}} = 5$ Hz, C_{Ar}), 121.77 (t, $^2J_{\text{CH}} = 8$ Hz, C_{ipso}), 95.56 (s, C≡CAr), 87.11 (s, C≡CAr), 36.90 (t, $^1J_{\text{CH}} = 132$ Hz, C=CCH₂CH₂), 23.09 (t, $^1J_{\text{CH}} = 132$ Hz, C=CCH₂CH₂). HRMS(EI) m/z calcd for C₂₁H₁₄³⁵Cl₂ (M^+) 336.0472; found, 336.0471.

(2-Me-C₆H₄)C=CC(CH₂OCH₂)=CC=C(C₆H₄-2-Me) (24). Addition of trifluoroacetic anhydride (43 μL , 0.30 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-CH₃)Li·Et₂O (**15**) (87 mg, 0.28 mmol) was followed by addition of CuBr (31 mg), LiI (25 mg), NEt(*i*-Pr₂) (43 μL), and dipropargyl ether (11 μL , 0.107 mmol) in CH₂Cl₂ (10 mL). The solution was poured into 50 mL 10% ether/hexanes and photolyzed. Chromatography gave **24** (22.9 mg, 72% based on diyne) as a slightly yellow oil. ¹H NMR (250 MHz, CDCl₃) δ 7.476 (d, $J = 7.5$ Hz, 2H, H_{Ar}), 7.30-7.24 (m, 4H, H_{Ar}), 7.192 (t, $J = 7.5$ Hz, 2H, H_{Ar}), 4.886 (s, CH₂), 2.509 (s, Me). ¹³C NMR (125 MHz, CDCl₃) δ 140.36 (s, CMe), 131.98 (dd, $^1J_{\text{CH}} = 161$

Hz, $^2J_{\text{CH}} = 6.3$ Hz, C_{Ar}), 129.50 (d, $^1J_{\text{CH}} = 158$ Hz, C_{Ar}), 128.89 (dd, $^1J_{\text{CH}} = 160$ Hz, $^2J_{\text{CH}} = 8$ Hz, C_{Ar}), 125.62 (dd, $^1J_{\text{CH}} = 161$ Hz, $^2J_{\text{CH}} = 7$ Hz, C_{Ar}), 125.41 (s, C=C), 122.40 (s, C_{ipso}), 97.84 (s, C=CAr), 85.25 (s, C=CAr), 77.51 (t, $^1J_{\text{CH}} = 149$ Hz, CH₂), 20.73 (q, $^1J_{\text{CH}} = 126$ Hz, Me). HRMS(EI) *m/z* calcd for C₂₂H₁₈O (M⁺) 298.1358; found, 298.1365.

(3-MeO-C₆H₄)C=CC(CH₂OCH₂)=CC=C(OC₆H₄-3-OMe) (25). Addition of trifluoroacetic anhydride (183 μL , 1.30 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-3-OMe)Li (16) (415 mg, 1.25 mmol) was followed by addition of CuBr (22 mg), LiI (16 mg), NEt(*i*-Pr)₂ (216 μL), and dipropargyl ether (54 μL , 0.52 mmol) in CH₂Cl₂ (80 mL) at 20 °C. The solution was poured into 100 mL 20% ether/hexanes and photolyzed. Chromatography gave 25 (139 mg, 80% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.258 (t, $J = 8$ Hz, 1H, H_{Ar}), 7.118 (br d, $J = 7.5$ Hz, 1H, H_{Ar}), 7.040 (dd, $J = 2.5$, 1.5 Hz, 1H, H_{Ar}), 6.918 (ddd, $J = 8$, 2.5, 1.5 Hz, 1H, H_{Ar}), 4.839 (s, CH₂), 3.811 (s, OMe). ¹³C NMR (125 MHz, CDCl₃) δ 159.32 (s, COMe), 129.46 (d, $^1J_{\text{CH}} = 162$ Hz, C_{Ar}), 125.79 (s, C=C), 124.28 (dt, $^1J_{\text{CH}} = 165$, $^2J_{\text{CH}} = 6$ Hz, C_{Ar}), 123.53 (s, C_{ipso}), 116.44 (d, $^1J_{\text{CH}} = 161$ Hz, C_{Ar}), 115.51 (d, $^1J_{\text{CH}} = 161$ Hz, C_{Ar}), 99.04 (s, C=CAr), 81.14 (s, C=CAr), 77.38 (t, $^1J_{\text{CH}} = 150$ Hz, CH₂), 55.25 (q, $^1J_{\text{CH}} = 142$ Hz, OMe). HRMS(EI) *m/z* calcd for C₂₂H₁₈O₃ (M⁺) 330.1256; found, 330.1267.

(4-F-C₆H₄)C=CC(CH₂OCH₂)=CC=C(C₆H₄-4-F) (26). Addition of trifluoroacetic anhydride (217 μL , 1.53 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-F)Li•Et₂O (17) (582 mg, 1.48 mmol) was followed by addition of CuBr (16 mg), LiI (17 mg), NEt(*i*-Pr)₂ (255 μL), and dipropargyl ether (64 μL , 0.620 mmol) in CH₂Cl₂ (80 mL) at 20 °C. The solution was poured into 100 mL 20% ether/hexanes and photolyzed. Chromatography gave 26

(176 mg, 93% based on diyne) as a slightly yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.487 (dd, $J_{\text{HH}} = 8.0$ Hz, $J_{\text{HF}} = 5.5$ Hz, 2H, H_{Ar}), 7.053 (t $J_{\text{HH}} = J_{\text{HF}} = 8.5$ Hz, 2H, H_{Ar}), 4.841 (s, CH_2). ^{13}C NMR (125 MHz, CDCl_3) δ 165.57 (d, $^1J_{\text{CF}} = 249$ Hz, C-F), 133.67 (ddd $^1J_{\text{CH}} = 165$, $^3J_{\text{CF}} = 22$ $J_{\text{CH}} = 4.4$ Hz, C_{Ar}), 115.80 (ddd $^1J_{\text{CH}} = 164$ Hz, $^3J_{\text{CF}} = J_{\text{CH}} = 8$ Hz, C_{Ar}), 125.50 (s, C=C), 118.68 (s, C_{ipso}), 97.93 (s, C≡CAr), 80.99 (s, C≡CAr), 77.42 (t, $^1J_{\text{CH}} = 149$ Hz, CH_2). HRMS(EI) *m/z* calcd for $\text{C}_{20}\text{H}_{12}\text{F}_2\text{O}$ (M^+) 306.0856; found, 306.0867.

(4-CF₃-C₆H₄)C=CC(CH₂OCH₂)=CC=C(C₆H₄-4-CF₃) (27). Addition of trifluoroacetic anhydride (81 μL , 0.57 mmol) to $(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnC(O)(C}_6\text{H}_4\text{-4-CF}_3\text{)Li}\cdot\text{Et}_2\text{O}$ (**19**) (231 mg, 0.52 mmol) was followed by addition of CuBr (34 mg), LiI (40 mg), NEt(*i*-Pr)₂ (81 μL), and dipropargyl ether (22.5 μL , 0.218 mmol) in CH_2Cl_2 (12 mL). The solution was poured into 50 mL 10% ether/hexanes and photolyzed.

Chromatography gave **27** (43.7 mg, 49% based on diyne) as a slightly yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.70-7.60 (m, 8H, H_{Ar}), 4.891 (s, CH_2). ^{13}C NMR (125 MHz, CDCl_3) δ 131.96 (d, $^1J_{\text{CH}} = 165$ Hz, C_{Ar}), 126.44 (s, C=C), 125.40 (d, $^1J_{\text{CH}} = 154$ Hz, C_{Ar}), 97.83 (s, C≡CAr), 83.22 (s, C≡CAr), 77.40 (t, $^1J_{\text{CH}} = 150$ Hz, CH_2), some quaternary carbons were not observed. HRMS(EI) *m/z* calcd for $\text{C}_{22}\text{H}_{12}\text{F}_6\text{O}$ (M^+) 406.0793; found, 406.0781.

[2,6-(MeO)₂-C₆H₃]C=CC(CH₂OCH₂)=CC=C[C₆H₃-2,6-(MeO)₂] (28). Addition of trifluoroacetic anhydride (192 μL , 1.36 mmol) to $(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnC(O)[C}_6\text{H}_3\text{-2,6-(OMe)}_2\text{]Li}$ (**20**) (447 mg, 1.23 mmol) was followed by addition of CuBr (21 mg), LiI (27 mg), NEt(*i*-Pr)₂ (213 μL), and dipropargyl ether (53 μL , 0.52 mmol) in CH_2Cl_2 (100 mL) at

-40 °C. The solution was poured into 100 mL methanol and photolyzed.

Chromatography gave **28** (145 mg, 72% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.229 (t, J = 8.5 Hz, 2H, H_{Ar}), 6.521 (d, J = 8 Hz, 4H, H_{Ar}), 4.875 (s, CH₂), 3.822 (s, OMe). ¹³C NMR (125 MHz, CDCl₃) δ 161.48 (s, COMe), 130.15 (d, ¹J_{CH} = 160 Hz, C_{Ar}), 125.29 (s, C=C), 103.61 (dd, ¹J_{CH} = 161 Hz, ²J_{CH} = 8 Hz, C_{Ar}), 91.17 (s, C≡CAr), 89.73 (s, C≡CAr), 77.73 (t, ¹J_{CH} = 149 Hz, CH₂), 56.07 (q, ¹J_{CH} = 143 Hz, OMe), C_{ipso} not observed. HRMS(EI) m/z calcd for C₂₄H₂₂O₅ (M⁺) 390.1468; found, 390.1483.

(2-Me-C₆H₄)C≡C-C[CH₂C(CO₂Me)₂CH₂]=CC≡C(C₆H₄-2-Me) (29). Addition of trifluoroacetic anhydride (413 μL, 2.92 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-Me)Li (**15**) (840 mg, 2.66 mmol) was followed by addition of CuBr (31 mg), LiI (32 mg), NEt(i-Pr)₂ (414 μL), and dimethyl dipropargylmalonate (235 mg, 1.13 mmol) in CH₂Cl₂ (180 mL). The solution was poured into 100 mL methanol and photolyzed. Chromatography gave **29** (388 mg, 83% based on diyne) as a slightly yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, J = 7.5 Hz, 2H, H_{Ar}), 7.25-7.21 (m, 4H, H_{Ar}), 7.16 (td, J = 7.5, 2.0 Hz, 2H, H_{Ar}), 3.806 (s, CO₂CH₃), 3.419 (s, CH₂), 2.498 (s, Me). ¹³C NMR (125 MHz, CDCl₃) δ 171.27 (s, CO₂Me), 140.16 (CMe), 131.79 (dd, ¹J_{CH} = 159, ²J_{CH} = 6 Hz, C_{Ar}), 129.31 (d, ¹J_{CH} = 157 Hz, C_{Ar}), 128.51 (dd, ¹J_{CH} = 160, ²J_{CH} = 9 Hz, C_{Ar}), 126.08 (s, C=C), 125.43 (dd, ¹J_{CH} = 159 Hz, ²J_{CH} = 5 Hz, C_{Ar}), 122.55 (s, C_{ipso}), 95.68 (s, C≡CAr), 88.75 (s, C≡CAr), 57.94 (s, C(CO₂Me)₂), 52.96 (q, ¹J_{CH} = 147 Hz, CO₂Me), 43.78 (t, ¹J_{CH} = 136 Hz, CH₂), 20.60 (q, ¹J_{CH} = 127 Hz, Me). HRMS(ESI) m/z calcd for C₂₇H₂₄O₄Na (M⁺) 435.1572; found, 435.1576.

(2-MeO-C₆H₄)C=C-C[CH₂C(CO₂Me)₂CH₂]=CC=C(C₆H₄-2-OMe) (30). Addition of trifluoroacetic anhydride (235 μ L, 1.66 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-OMe)Li (15) (503 mg, 1.51 mmol) was followed by addition of CuBr (26 mg), LiI (25 mg), NEt(*i*-Pr)₂ (235 μ L), and dimethyl dipropargylmalonate (130 mg, 0.62 mmol) in CH₂Cl₂ (100 mL) at -50 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave **30** (140 mg, 51% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.48 (dd, *J* = 7.5, 1.5 Hz, 2H, H_{Ar}), 7.28 (td, *J* = 8.0, 2.0 Hz, 2H, H_{Ar}), 6.90 (td, *J* = 7.5, 1.0 Hz, 2H, H_{Ar}), 6.87 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 3.83 (s, CO₂Me), 3.77 (s, OMe), 3.38 (s, CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 171.39 (s, CO₂Me), 159.89 (s, COMe), 133.78 (dd, ¹*J*_{CH} = 161 Hz, ²*J*_{CH} = 9 Hz, C_{Ar}), 130.29 (dd, ¹*J*_{CH} = 159 Hz, ²*J*_{CH} = 9 Hz, C_{Ar}), 126.48 (s, C=C), 121.24 (dd, ¹*J*_{CH} = 161 Hz, ²*J*_{CH} = 8 Hz, C_{Ar}), 112.33 (s, C_{ipso}), 110.75 (dd, ¹*J*_{CH} = 158 Hz, ²*J*_{CH} = 8 Hz, C_{Ar}), 93.25 (s, C≡CAr), 88.98 (s, C≡CAr), 58.04 (s, C(CO₂Me)₂), 55.72 (q, ¹*J*_{CH} = 143 Hz, CO₂Me), 52.98 (q, ¹*J*_{CH} = 148 Hz, OMe), 43.66 (t, ¹*J*_{CH} = 136 Hz, CH₂). HRMS(ESI) *m/z* calcd for C₂₇H₂₄O₆Na (M⁺) 467.1471; found, 467.1492.

(4-F-C₆H₄)C=CC[CH₂C(CO₂Me)₂CH₂]=CC=C(C₆H₄-4-F) (31). Addition of trifluoroacetic anhydride (246 μ L, 1.74 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-F)Li-Et₂O (17) (661 mg, 1.68 mmol) was followed by addition of CuBr (20 mg), LiI (23 mg), NEt(*i*-Pr)₂ (290 μ L), and dimethyl dipropargylmalonate (148 mg, 0.71 mmol) in CH₂Cl₂ (80 mL). The solution was poured into 100 mL 10% ether/hexanes and photolyzed. Chromatography gave **31** (224 mg, 75% based on diyne) as a slightly yellow oil. A white solid was obtained after repeated chromatography and thorough

drying. ^1H NMR (500 MHz, CDCl_3) δ 7.46 (dd, $J_{\text{HH}} = 8.5$ Hz, $J_{\text{HF}} = 5.5$ Hz, 4H, H_{Ar}), 7.03 (t, $J_{\text{HH}} = J_{\text{HF}} = 8.5$ Hz, 4H, H_{Ar}), 3.80 (s, CO_2Me), 3.35 (s, 4H, CH_2). ^{13}C NMR (125 MHz, CDCl_3) δ 171.35 (s, CO_2Me), 163.70 (d, $^1J_{\text{CF}} = 254$ Hz, C-F), 133.57 (ddd, $^1J_{\text{CH}} = 163$ Hz, $^3J_{\text{CF}} = J = 8$ Hz, C_{Ar}), 126.45 (s, C=C), 118.98 (s, C_{ipso}), 115.73 (dd, $^1J_{\text{CH}} = 163$ Hz, $^2J_{\text{CF}} = 22$ Hz, C_{Ar}), 95.89 (s, C=CAr), 84.50 (s, C=CAr), 58.07 (s, CO_2Me), 53.17 (q, $^1J_{\text{CH}} = 147$ Hz, CO_2Me), 43.67 (t, $^1J_{\text{CH}} = 136$ Hz, CH_2). HRMS(EI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{F}_2\text{O}_4$ (M^+) 420.1173; found, 420.1156.

(4-Cl-C₆H₄)C=CC[CH₂C(CO₂Me)₂CH₂]=CC=C(C₆H₄-4-Cl) (32). Addition of trifluoroacetic anhydride (300 μL , 2.12 mmol) to $(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnC(O)(C}_6\text{H}_4\text{-4-Cl) Li}\cdot\text{Et}_2\text{O}$ (18) (812 mg, 0.21 mmol) was followed by addition of CuBr (29 mg), LiI (31 mg), NEt(*i*-Pr)₂ (354 μL), and dimethyl dipropargylmalonate (179 mg, 0.86 mmol) in CH_2Cl_2 (80 mL). The solution was poured into 100 mL 10% ether/hexanes and photolyzed. Repeated chromatography gave **32** (126 mg, 32% based on diyne) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, $J = 9$ Hz, 4H, H_{Ar}), 7.31 (d, $J = 9$ Hz, 4H, H_{Ar}), 3.78 (s, CO_2Me), 3.33 (s, CH_2). ^{13}C NMR (125 MHz, CDCl_3) δ 171.25 (s, CO_2Me), 134.74 (s, C_{Ar}), 132.80 (d, $^1J_{\text{CH}} = 164$ Hz, C_{Ar}), 128.74 (d, $^1J_{\text{CH}} = 166$ Hz, C_{Ar}), 126.74 (s, C=C), 121.28 (s, C_{ipso}), 95.96 (s, C=CAr), 85.65 (s, C=CAr), 58.07 (s, $\text{C}(\text{CO}_2\text{Me})_2$), 53.17 (q, $^1J_{\text{CH}} = 147$ Hz, CO_2Me), 43.64 (t, $^1J_{\text{CH}} = 137$ Hz, CH_2). MS(ESI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{Cl}_2\text{O}_4\text{Na}$ ($\text{M}+\text{Na}^+$) 475.0; found, 475.0.

[2,6-(MeO)₂C₆H₃]C=CC[CH₂C(CO₂Me)₂CH₂]=CC=C[C₆H₃-2,6-(OMe)₂] (33).

Addition of trifluoroacetic anhydride (314 μL , 2.22 mmol) to $(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnC(O)[C}_6\text{H}_3\text{-2,6-(OMe)}_2\text{]Li}$ (20) (766 mg, 2.12 mmol) was followed by

addition of CuBr (30 mg), LiI (29 mg), NEt(*i*-Pr)₂ (366 μ L), and dimethyl dipropargylmalonate (188 mg, 0.90 mmol) in CH₂Cl₂ (170 mL) at -35 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave **33** (180 mg, 40% based on diyne) as an off-white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.188 (t, J = 8 Hz, 2H, H_{Ar}), 6.941 (d, J = 8 Hz, 4H, H_{Ar}), 3.774 (s, OMe), 3.759 (s, CO₂Me), 3.404 (s, CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 171.57 (s, CO₂Me), 161.40 (s, COMe), 129.77 (d, $^1J_{CH}$ = 160 Hz, C_{Ar}), 126.06 (s, C=C), 103.58 (d, $^1J_{CH}$ = 160 Hz, C_{Ar}), 93.27 (s, C≡CAr), 88.90 (s, C≡CAr), 57.92 (s, C(CO₂Me)), 55.98 (q, $^1J_{CH}$ = 144 Hz, OMe), 52.93 (q, $^1J_{CH}$ = 147 Hz, CO₂Me), 43.98 (t, $^1J_{CH}$ = 136 Hz, CH₂). C_{ipso} not observed. MS(ESI) *m/z* calcd for C₂₉H₂₈O₈ (M+Na⁺) 527.1; found, 527.1.

(4-Me-C₆H₄)C=CC[CH₂N(SO₂C₆H₄-4-CH₃)CH₂]=CC=C(C₆H₄-4-Me) (**34**). Addition of trifluoroacetic anhydride (78 μ L, 2.22 mmol) to (C₅H₄Me)(CO)₂MnC(O)[C₆H₄-4-Me]Li•Et₂O¹ (196 mg, 0.51 mmol) was followed by addition of CuBr (29 mg), LiI (14 mg), NEt(*i*-Pr)₂ (87 μ L), and *N*-(toluenesulfonyl) dipropargyl amine (62 mg, 0.25 mmol) in CH₂Cl₂ (70 mL) at -45 °C. The solution was poured into 200 mL methanol and photolyzed. Chromatography gave **34** (66 mg, 58% based on diyne) as a beige solid. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, J = 7.5 Hz, 2H, H_{Tol}), 7.73 (d, J = 8.0 Hz, 6H, H_{Tol}), 7.16 (d, J = 8.0 Hz, 4H, H_{Tol}), 4.32 (s, 4H, CH₂), 2.46 (s, 3H, SO₂CH₃), 2.38 (s, 6H, Me). ¹³C NMR (125 MHz, CDCl₃) δ 143.93 (s, TsO C_{ipso}), 139.40 (2C, s, Tol CMe), 133.41 (s, Tos CMe), 131.62 (4C, dd, $^1J_{CH}$ = 161 Hz, $^2J_{CH}$ = 6 Hz, C_{Tol}), 129.95 (2C, d, $^1J_{CH}$ = 160 Hz, Tos), 129.20 (4C, d, $^1J_{CH}$ = 158 Hz, C_{Tol}), 127.55 (2C, dd, $^1J_{CH}$ = 164 Hz, $^2J_{CH}$ = 5.1 Hz, Tos), 123.52 (2C, s, C=C), 119.13 (2C, t, $^2J_{CH}$ = 5 Hz, C_{ipso}), 98.80 (2C, s, C≡CAr),

81.45 (2C, s, C≡CAr), 56.68 (2C, t, $^1J_{CH} = 147$ Hz, CH₂), 21.55 (3C, q, $^1J_{CH} = 126$ Hz, Me). MS(ESI) *m/z* calcd for C₂₉H₂₅NO₂SNa (M+Na⁺) 474.1; found, 474.1.

(2-Me-C₆H₄)C=CC(CH₂CH₂CH₂CH₂)=CC=C(C₆H₄-2-Me) (35). Addition of trifluoroacetic anhydride (110 μ L, 0.78 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-Me)Li (15) (223 mg, 0.71 mmol) was followed by addition of CuBr (34 mg), LiI (32 mg), NEt(*i*-Pr)₂ (110 μ L), and 1,7-octadiyne (37.5 μ L, 0.28 mmol) in CH₂Cl₂ (10 mL) at -5 °C. The solution was poured into 100 mL 10% ether/hexanes and photolyzed. Chromatography gave **35** (82 mg, 94% based on diyne) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.825 (d, *J* = 7.5 Hz, 2H, H_{Ar}), 7.25-7.21 (m, 4H, H_{Ar}), 7.20-7.14 (m, 2H, H_{Ar}), 2.499 (s, Me), 2.50-2.44 (m, 4H, C=CCH₂), 1.80-1.74 (m, 4H, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 140.12 (s, C-Me), 131.79 (dd, $^1J_{CH} = 160$ Hz, $^2J_{CH} = 5$ Hz, C_{Ar}), 129.29 (d, $^1J_{CH} = 157$ Hz, C_{Ar}), 128.03 (dd, $^1J_{CH} = 160$ Hz, $^2J_{CH} = 8$ Hz, C_{Ar}), 125.96 (s, C=C), 125.40 (d, $^1J_{CH} = 157$ Hz, C_{Ar}), 123.37 (s, C_{ipso}), 94.42 (s, C≡CAr), 92.53 (s, C≡CAr), 30.43 (t, $^1J_{CH} = 128$ Hz, C=CCH₂CH₂), 21.93 (t, $^1J_{CH} = 128$ Hz, C=CCH₂CH₂), 20.77 (q, $^1J_{CH} = 126$ Hz, Me). HRMS(EI) *m/z* calcd for C₂₄H₂₂ (M⁺) 310.1723; found, 310.1724.

(3-MeO-C₆H₄)C=CC(CH₂CH₂CH₂CH₂)=CC=C(OC₆H₄-3-OMe) (36). Addition of trifluoroacetic anhydride (169 μ L, 1.19 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-3-OMe)Li (16) (384 mg, 1.15 mmol) was followed by addition of CuBr (16 mg), LiI (21 mg), NEt(*i*-Pr)₂ (200 μ L), and 1,7-octadiyne (64 μ L, 0.48 mmol) in CH₂Cl₂ (80 mL) at 20 °C. The solution was poured into 100 mL 20% ether/hexanes and photolyzed. Chromatography gave **36** (138 mg, 83% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.223 (t, *J* = 8.0 Hz, 2H, H_{Ar}), 7.104 (d, *J* = 7.5 Hz, 2H, H_{Ar}), 7.03 (br s, 2H,

H_{Ar}), 6.873 (dd, $J = 7.5, 1.5$ Hz, 2H, H_{Ar}), 3.764 (s, OMe), 2.400 (br s, C=CCH₂), 1.732 (br s, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 159.26 (s, COMe), 129.30 (d, $^1J_{CH} = 160$ Hz, C_{Ar}), 126.67 (s, C=C), 124.62 (s, C_{ipso}), 124.03 (d, $^1J_{CH} = 163$ Hz, C_{Ar}), 116.06 (d, $^1J_{CH} = 160$ Hz, C_{Ar}), 114.92 (d, $^1J_{CH} = 158$ Hz, C_{Ar}), 93.61 (s, C≡CAr), 90.28 (s, C≡CAr), 55.15 (q, $^1J_{CH} = 143$ Hz, OMe), 29.95 (t, $^1J_{CH} = 127$ Hz, C=CCH₂), 21.83 (t, $^1J_{CH} = 126$ Hz, C=CCH₂CH₂). HRMS(EI) *m/z* calcd for C₂₄H₂₂O₂ (M⁺) 342.1620; found, 342.1629.

(4-Cl-C₆H₄)C=CC(CH₂CH₂CH₂CH₂)=CC=C(C₆H₄-4-Cl) (37). Addition of trifluoroacetic anhydride (274 μL, 1.94 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Cl)Li·Et₂O (18) (741 mg, 1.87 mmol) was followed by addition of CuBr (27 mg), LiI (25 mg), NEt(*i*-Pr₂) (323 μL), and 1,7-octadiyne (104 μL, 0.784 mmol) in CH₂Cl₂ (150 mL) at 20 °C. The solution was poured into 100 mL methanol and photolyzed.

Chromatography gave **37** (171 mg, 62% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, $J = 8.5$ Hz, 4H, H_{Ar}), 7.30 (d, $J = 8.0$ Hz, 4H, H_{Ar}), 2.38 (br s, C=CCH₂), 1.720 (br s, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 134.13 (s, C_{Ar}), 132.59 (d, $^1J_{CH} = 164$ Hz, C_{Ar}), 128.66 (d, $^1J_{CH} = 165$ Hz, C_{Ar}), 126.66 (s, C=C), 122.05 (s, C_{ipso}), 92.62 (s, C≡CAr), 91.26 (s, C≡CAr), 29.96 (t, $^1J_{CH} = 128$ Hz, C=CCH₂CH₂), 21.78 (t, $^1J_{CH} = 128$ Hz, C=CCH₂CH₂). HRMS(EI) *m/z* calcd for C₂₂H₁₆³⁵Cl₂ (M⁺) 350.0629; found, 350.0633.

(4-CF₃-C₆H₄)C=CC(CH₂CH₂CH₂CH₂)=CC=C(C₆H₄-4-CF₃) (38). Addition of trifluoroacetic anhydride (194 μL, 1.37 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-CF₃)Li·Et₂O (19) (555 mg, 1.25 mmol) was followed by addition of CuBr (18 mg), LiI (20 mg), NEt(*i*-Pr₂) (194 μL), and 1,7-octadiyne (66 μL, 0.497 mmol) in CH₂Cl₂ (90 mL) at

70 °C. The solution was poured into 100 mL methanol and photolyzed.

Chromatography gave **38** (145 mg, 70% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.61 (br s, 8H, H_{Ar}), 2.44 (br s, C=CCH₂CH₂), 1.77 (br s, C=CCH₂). ¹³C NMR (125 MHz, CDCl₃) δ 131.59 (d, ¹J_{CH} = 165 Hz, C_{Ar}), 127.23 (s, C=C), 125.26 (d, ¹J_{CH} = 163 Hz, C_{Ar}), 122.83 (s, C_{ipso}), 92.50 (s, C≡CAr), 92.44 (s, C≡CAr), 29.95 (t, ¹J_{CH} = 129 Hz, CH₂), 21.67 (t, ¹J_{CH} = 128 Hz, CH₂). CCF₃ carbons not observed. HRMS(EI) *m/z* calcd for C₂₄H₁₆F₆ (M⁺) 418.1157; found, 418.1150.

(4-Cl-C₆H₄)C=CC(CH₂CH₂OCH₂)=CC=C(C₆H₄-4-Cl) (**39**). Addition of trifluoroacetic anhydride (476 μL, 3.36 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Cl)Li•Et₂O (**18**) (1.286 g, 3.24 mmol) was followed by addition of CuBr (46 mg), LiI (47 mg), NEt(*i*-Pr₂) (561 μL), and HC≡CCH₂CH₂OCH₂C≡CH (186 μL, 81% solution in toluene, 1.36 mmol) in CH₂Cl₂ (100 mL) at 20 °C. The solution was poured into 100 mL 20% ether/hexanes and photolyzed. Chromatography gave **39** (451 mg, 93% based on diyne) as a light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 7.39 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 7.31 (d, *J* = 8.0 Hz, 4H, H_{Ar}), 4.31 (s, C=CCH₂O), 3.86 (t, *J* = 5.5 Hz, C=CCH₂CH₂O), 2.50-2.44 (m, C=CCH₂CH₂O). ¹³C NMR (125 MHz, CDCl₃) δ 134.62 (s, C_{Ar}), 134.55 (s, C_{Ar}), 132.67 (4C, d, ¹J_{CH} = 165 Hz, C_{Ar}), 128.74 (4C, d, ¹J_{CH} = 170 Hz, C_{Ar}), 125.45 (s, C=C), 123.99 (s, C=C), 121.52 (s, C_{ipso}), 121.36 (s, C_{ipso}), 95.31 (s, C≡CAr), 93.70 (s, C≡CAr), 89.41 (s, C≡CAr), 86.77 (s, C≡CAr), 67.58 (t, ¹J_{CH} = 147 Hz, C=CCH₂O), 63.76 (t, 145 Hz, C=CCH₂CH₂O), 29.09 (t, ¹J_{CH} = 130 Hz, C=CCH₂CH₂O). HRMS(EI) *m/z* calcd for C₂₁H₁₄³⁵Cl₂O (M⁺) 352.0422; found, 352.0420.

(4-MeO-C₆H₄)C=CC(CH₂CH₂OCH₂)=CC=C(C₆H₄-4-OMe) (40). Addition of trifluoroacetic anhydride (221 μ L, 1.56 mmol) to Cp(CO)₂MnC(O)(C₆H₄-4-OMe)]Li·Et₂O (592 mg, 1.51 mmol) was followed by addition of CuBr (20 mg), LiI (25 mg), NEt(*i*-Pr)₂ (261 μ L), and HC≡CCH₂CH₂OCH₂C≡CH (86 μ L, 81% solution in toluene, 0.63 mmol) in CH₂Cl₂ (70 mL) at 0 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave **40** (133 mg, 61% based on diyne) as a light brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.42 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 6.86 (d, *J* = 8.5 Hz, 4H, H_{Ar}), 4.31 (br s, C≡CCH₂O), 3.85 (t, *J* = 5.5 Hz, C≡CCH₂CH₂), 3.83 (s, OMe), 2.49-2.50 (m, C≡CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 159.64 (2C, s, COMe), 132.90 (4C, d, ¹*J*_{CH} = 161 Hz, C_{Ar}), 124.50 (s, C≡C), 123.04 (s, C≡C), 115.25 (s, C_{ipso}), 115.08 (s, C_{ipso}), 113.93 (4C, d, ¹*J*_{CH} = 159 Hz, C_{Ar}), 96.15 (s, C≡CAr), 94.57 (s, C≡CAr), 87.60 (s, C≡CAr), 84.89 (s, C≡CAr), 67.65 (t, ¹*J*_{CH} = 148 Hz, C≡CCH₂O), 63.80 (t, ¹*J*_{CH} = 144 Hz, C≡CCH₂CH₂), 55.15 (q, ¹*J*_{CH} = 143 Hz, COMe), 29.14 (t, ¹*J*_{CH} = 130 Hz, C≡CCH₂CH₂). HRMS(EI) *m/z* calcd for C₂₃H₂₀O₃ (M⁺) 344.1412; found, 344.1423.

(2-Me-C₆H₄)C=CC(CH₂CH₂CH₂OCH₂)=CC=C(C₆H₄-2-Me) (41). Addition of trifluoroacetic anhydride (434 μ L, 3.07 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-2-Me)]Li (15) (844 mg, 2.80 mmol) was followed by addition of CuBr (34 mg), LiI (27 mg), NEt(*i*-Pr)₂ (434 μ L), and HC≡CCH₂CH₂CH₂OCH₂C≡CH (137 μ L, 1.12 mmol) in CH₂Cl₂ (180 mL) at 0 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave **41** (226 mg, 62% based on diyne) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.484 (d, *J* = 7.5 Hz, 1H, H_{Ar}), 7.468 (d, *J* = 8.0 Hz, 1H, H_{Ar}),

7.27-7.21 (m, 4H, H_{Ar}), 7.19-7.13 (m, 2H, H_{Ar}), 4.489 (s, C=CCH₂O), 3.955 (t, J = 5.5 Hz, CH₂CH₂O), 2.85-2.79 (m, C=CCH₂CH₂), 2.496 (s, Me), 2.480 (s, Me), 2.012 (p, J = 6.0 Hz, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 140.14 (s, CMe), 140.03 (s, CMe), 131.79 (d, ¹J_{CH} = 160 Hz, C_{Ar}), 131.74 (d, ¹J_{CH} = 160 Hz, C_{Ar}), 131.48 (s, C=C), 129.31 (d, ¹J_{CH} = 156 Hz, C_{Ar}), 129.19 (s, C=C), 128.27 (dd, ¹J_{CH} = 159 Hz, ²J_{CH} = 7 Hz, C_{Ar}), 128.22 (dd, ¹J_{CH} = 159 Hz, ²J_{CH} = 6.8 Hz, C_{Ar}), 125.40 (dd, ¹J_{CH} = 158 Hz, ²J_{CH} = 6 Hz, C_{Ar}), 123.07 (2C, s, C_{ipso}), 95.36 (s, C≡CAr), 95.00 (s, C≡CAr), 94.49 (s, C≡CAr), 93.13 (s, C≡CAr), 72.53 (t, ¹J_{CH} = 142 Hz, C=CCH₂O), 71.99 (t, ¹J_{CH} = 144 Hz, CH₂CH₂O), 31.16 (t, ¹J_{CH} = 128 Hz, CH₂CH₂O), 26.84 (t, ¹J_{CH} = 125 Hz, C=CCH₂CH₂), 20.71 (q, ¹J_{CH} = 126 Hz, Me). HRMS(EI) m/z calcd for C₂₄H₂₂O (M⁺) 326.1671; found, 326.1683.

(4-MeO-C₆H₄)C=CC[CH₂C(CO₂Me)₂CH₂]=CC=CC₆H₅ (43). Addition of trifluoroacetic anhydride (310 μL, 2.19 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-OMe)Li (11) (333 mg, 1.00 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₅)Li·Et₂O (7)² (376 mg, 1.00 mmol) was followed by addition of CuBr (50 mg), LiI (44 mg), NEt(i-Pr)₂ (346 μL), and dimethyl dipropargylmalonate (206 mg, 0.989 mmol) in CH₂Cl₂ (150 mL) at -80 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave 43 (145 mg, 35% based on diyne) as a slightly yellow oil in the middle fraction. ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.49 (m, 2H, H_{Ph}), 7.45 (d, J = 8.5 Hz, 2H, H_{Ar}), 7.36-7.32 (m, 3H, H_{Ph}), 6.88 (d, J = 8.5 Hz, 2H, H_{Ar}), 3.83 (s, OMe), 3.80 (s, CO₂Me), 3.36 (s, 4H, CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 171.38 (s, CO₂Me), 159.86 (s, COMe), 133.13 (dd, ¹J_{CH} = 162 Hz, ²J_{CH} = 7 Hz, C_{Ph}), 131.58 (d, ¹J_{CH} = 161 Hz, C_{Ar}), 128.47 (dt, ¹J_{CH} = 168 Hz, ²J_{CH} = 7 Hz, C_{Ph}), 128.38 (d, ¹J_{CH} = 157 Hz, C_{Ph}), 126.87 (t, ²J_{CH} = 5 Hz, C=C),

125.48 (s, C=C), 122.95 (s, C_{ipso}), 114.93 (t, $^2J_{\text{CH}} = 8$ Hz, C_{ipso}), 113.98 (dd, $^1J_{\text{CH}} = 160$ Hz, $^2J_{\text{CH}} = 4$ Hz, C_{Ar}), 97.22 (s, C≡CAr), 96.63 (s, C≡CAr), 85.00 (s, C≡CAr), 83.73 (s, C≡CAr), 58.04 (s, C(CO₂Me)₂), 55.21 (q, $^1J_{\text{CH}} = 143$ Hz, OMe), 53.06 (q, $^1J_{\text{CH}} = 146$ Hz, CO₂Me), 43.96 (t, $^1J_{\text{CH}} = 136$ Hz, CH₂), 43.56 (t, $^1J_{\text{CH}} = 137$ Hz, CH₂). HRMS(EI) *m/z* calcd for C₂₆H₂₂O₅ (M⁺) 414.1468; found, 414.1470.

(4-MeO-C₆H₄)C≡CC[CH₂C(CO₂Me)₂CH₂]=CC=C(C₆H₄-4-Me) (44). Addition of trifluoroacetic anhydride (155 μL, 1.10 mmol) to (C₅H₄Me)(CO)₂MnC(O)[C₆H₄-4-OMe]Li (11) (165 mg, 0.50 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Me)Li·Et₂O¹ (193 mg, 0.49 mmol) was followed by addition of CuBr (19 mg), LiI (20 mg), NEt(*i*-Pr₂) (173 μL), and dimethyl dipropargylmalonate (103 mg, 0.495 mmol) in CH₂Cl₂ (100 mL) at -50 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave 44 (39 mg, 18% based on diyne) as a slightly yellow oil in the middle fraction. The first and third fractions were isolated in 19 and 15% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, $J = 8.0$ Hz, 2H, H_{Ar}), 7.41 (d, $J = 6.5$ Hz, 2H, H_{Tol}), 7.16 (d, $J = 7.5$ Hz, 2H, H_{Tol}), 6.88 (d, $J = 7.0$ Hz 2H, H_{Ar}), 3.84 (s, OMe), 3.81 (s, CO₂Me), 3.36 (s, 4H, CH₂), 2.39 (s, Me). ¹³C NMR (125 MHz, CDCl₃) δ 171.43 (s, CO₂Me), 160.05 (s, COMe), 138.68 (s, CMe), 133.18 (dd, $^1J_{\text{CH}} = 161$ Hz, $^2J_{\text{CH}} = 7$ Hz, C_{Ar}), 131.54 (d, $^1J_{\text{CH}} = 161$ Hz, C_{Tol}), 129.10 (d, $^1J_{\text{CH}} = 157$ Hz, C_{Tol}), 119.97 (s, C_{ipso}), 115.09 (s, C_{ipso}), 114.00 (d, $^1J_{\text{CH}} = 164$ Hz, C_{Ar}), 97.06 (2C, s, C≡CAr), 84.46 (s, C≡CAr), 83.86 (s, C≡CAr), 58.09 (s, C(CO₂Me)₂), 55.26 (q, $^1J_{\text{CH}} = 142$ Hz, CO₂Me), 53.35 (q, $^1J_{\text{CH}} = 147$ Hz, OMe), 53.09 (q, $^1J_{\text{CH}} = 146$ Hz, OMe), 43.70 (t, $^1J_{\text{CH}} = 130$ Hz, CH₂), 21.51 (q, $^1J_{\text{CH}} = 126$ Hz, Me). HRMS(EI) *m/z* calcd for C₂₇H₂₄O₅ (M⁺) 428.1624; found, 428.1621.

(2-MeO-C₆H₄)C=CC(CH₂OCH₂)=CC=C(C₆H₄-4-Me) (45). Addition of trifluoroacetic anhydride (155 μ L, 1.10 mmol) to (C₅H₄Me)(CO)₂MnC(O)[C₆H₄-2-OMe]Li (14) (168 mg, 0.51 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Me)Li-Et₂O¹ (195 mg, 0.50 mmol) was followed by addition of CuBr (27 mg), LiI (15 mg), NEt(*i*-Pr₂) (173 μ L), and dipropargyl ether (46 μ L, 0.45 mmol) in CH₂Cl₂ (100 mL) at -30 °C. The solution was poured into 100 mL methanol and photolyzed. Chromatography gave 45 (37 mg, 26% based on diyne) as a slightly yellow oil in the middle fraction. The first and third fractions were isolated in 22 and 31% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.48 (dd, *J* = 7.5, 2.0 Hz, 1H, H_{Ar}), 7.42 (d, *J* = 8.0 Hz, 2H, H_{Tol}), 7.325 (ddd, *J* = 9.5, 7.5, 2 Hz, 1H, H_{Ar}), 7.152 (d, *J* = 7.5 Hz, 2H, H_{Tol}), 6.938 (td, *J* = 7.5, 1.0 Hz, 1H, H_{Ar}), 6.899 (d, *J* = 8.5 Hz, 1H, H_{Ar}), 4.76-4.70 (m, 4H, CH₂), 3.756 (s, OMe), 2.257 (s, Me). ¹³C NMR (125 MHz, CDCl₃) δ 160.04 (s, COMe), 139.01 (s, CMe), 133.65 (dd, ¹J_{CH} = 162 Hz, ²J_{CH} = 8 Hz, C_{Ar}), 131.68 (dd, ¹J_{CH} = 161 Hz, ²J_{CH} = 6 Hz, C_{Tol}), 130.35 (d, ¹J_{CH} = 166 Hz, C_{Ar}), 129.10 (d, ¹J_{CH} = 161 Hz, C_{Tol}), 125.59 (s, C=C), 125.49 (s, C=C), 120.48 (dd, ¹J_{CH} = 162 Hz, ²J_{CH} = 8 Hz, C_{Ar}), 119.70 (s, C_{ipso}), 110.76 (dd, ¹J_{CH} = 159 Hz, ²J_{CH} = 7 Hz, C_{Ar}), 111.94 (s, C_{ipso}), 99.19 (s, C≡CAr), 95.36 (s, C≡CAr), 85.38 (s, C≡CAr), 81.01 (s, C≡CAr), 73.38 (2C, t, ¹J_{CH} = 150 Hz, OCH₂), 55.82 (q, ¹J_{CH} = 144 Hz, OMe), 21.52 (q, ¹J_{CH} = 126 Hz, Me). HRMS(El) *m/z* calcd for C₂₂H₁₈O₂ (M⁺) 314.1307; found, 314.1310.

[2,6-(MeO)₂-C₆H₃]C=CC(CH₂OCH₂)=CC=C(C₆H₄-4-F) (46). Addition of trifluoroacetic anhydride (155 μ L, 1.10 mmol) to (C₅H₄Me)(CO)₂MnC(O)[C₆H₃-2,6-(OCH₃)₂]Li (20) (191 mg, 0.53 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-F)Li-Et₂O (17) (196 mg, 0.50 mmol) was followed by addition of CuBr (20 mg), LiI (21 mg), NEt(*i*-Pr₂)

(173 μL), and dipropargyl ether (52 μL , 0.51 mmol) in CH_2Cl_2 (60 mL) at -80°C . The solution was poured into 200 mL methanol and photolyzed. Chromatography gave **46** (63 mg, 36% based on diyne) as a slightly yellow oil in the middle fraction. ^1H NMR (500 MHz, CDCl_3) δ 7.52 (dd, $J_{\text{CH}} = 7.5$ Hz, $J_{\text{HF}} = 5.5$ Hz, 2H, H_{Ar}), 7.27 (t, $J = 8.3$ Hz, 1H, $\text{H}_{\text{Ar}''}$), 7.04 (t, $J_{\text{HH}} = J_{\text{HF}} = 7.5$ Hz, 2H, H_{Ar}), 6.55 (d, $J = 8.5$ Hz, 2H, $\text{H}_{\text{Ar}''}$), 4.90-4.87 (m, 2H, CH_2), 4.85-4.81 (m, 2H, CH_2), 3.850 (s, 6H, OMe). ^{13}C NMR (125 MHz, CDCl_3) δ 162.62 (d, $^1J_{\text{CF}} = 251$ Hz, CF), 161.43 (s, COMe), 133.69 (ddd, $^1J_{\text{CH}} = 164$ Hz, $^2J_{\text{CH}} = 3J_{\text{CF}} = 8$ Hz, C_{Ar}), 130.51 (d, $^1J_{\text{CH}} = 160$ Hz, $\text{C}_{\text{Ar}''}$), 126.82 (s, C=C), 124.45 (s, C=C), 119.10 (s, C_{ipso}), 115.57 (dd, $^1J_{\text{CH}} = 163$ Hz, $^2J_{\text{CF}} = 21.6$ Hz, C_{Ar}), 103.46 (dd, $^1J_{\text{CH}} = 161$ Hz, $^2J_{\text{CH}} = 7$ Hz, $\text{C}_{\text{Ar}''}$), 97.42 (s, C=CAr), 91.91 (s, C=CAr), 89.47 (s, C=CAr), 81.62 (s, C=CAr), 77.44 (t, $^1J_{\text{CH}} = 149$ Hz, CH_2), 77.19 (t, $^1J_{\text{CH}} = 150$ Hz, CH_2), 56.07 (q, $^1J_{\text{CH}} = 143$ Hz, OMe). One C_{ipso} not observed. HRMS(EI) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{FO}_3$ (M^+) 348.1162; found, 346.1164.

[2,6-(MeO)₂C₆H₃]C=CC(CH₂OCH₂)=CC=C(C₆H₄-4-Me) (47). Addition of trifluoroacetic anhydride (155 μL , 1.10 mmol) to (C₅H₄Me)(CO)₂MnC(O)[C₆H₃-2,6-(OMe)₂]Li (**20**) (183 mg, 0.51 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Me)Li \cdot Et₂O¹ (192 mg, 0.49 mmol) was followed by addition of CuBr (15 mg), LiI (17 mg), NEt(*i*-Pr)₂ (173 μL), and dipropargyl ether (52 μL , 0.500 mmol) in CH_2Cl_2 (100 mL) at -60°C . The solution was poured into 100 mL methanol and photolyzed. Chromatography gave **47** (43 mg, 25% based on diyne) as a slightly yellow oil in the middle fraction. The first and third fractions were isolated in 25 and 11% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 8.0$ Hz, 2H, H_{Tol}), 7.27 (t, $J = 8.5$ Hz, 1H, H_{Ar}), 7.15 (d, $J = 8.0$ Hz, 2H, H_{Tol}), 6.56 (d,

$J = 8.5$ Hz, 2H, H_{Ar}), 4.86-4.84 (m, 2H, CH₂), 4.83-4.81 (m, 2H, CH₂), 3.87 (s, OMe); 2.38 (s, Me). ¹³C NMR (125 MHz, CDCl₃) δ 161.47 (s, COMe), 138.81 (s, CMe), 131.73 (d, ¹J_{CH} = 169 Hz, C_{Tol}), 130.41 (d, ¹J_{CH} = 161 Hz, C_{Ar}), 129.02 (d, ¹J_{CH} = 157 Hz, C_{Tol}) 126.11 (s, C=C), 124.91 (s, C=C), 121.59 (s, C_{ipso}), 119.91 (s, C_{ipso}), 103.47 (dd, ¹J_{CH} = 161 Hz, ²J_{CH} = 8 Hz, C_{Ar}), 98.92 (s, C≡CAr), 91.65 (s, C≡CAr), 89.67 (s, C≡CAr), 81.28 (s, C≡CAr), 77.46 (t, ¹J_{CH} = 150 Hz, CH₂), 77.35 (t, ¹J_{CH} = 149 Hz, CH₂), 56.12 (q, ¹J_{CH} = 143 Hz, OMe), 21.52 (q, ¹J_{CH} = 126 Hz, Me). HRMS(EI) *m/z* calcd for C₂₃H₂₀O₃ (M⁺) 344.1412; found, 344.1399.

(4-MeO-C₆H₄)C≡CC(CH₂CH₂CH₂CH₂)=CC≡C(C₆H₅) (**48**). Addition of trifluoroacetic anhydride (155 μL, 1.10 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-OMe)Li (**11**) (165 mg, 0.50 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₅)Li·Et₂O (**7**)² (187 mg, 0.50 mmol) was followed by addition of CuBr (15 mg), LiI (19 mg), NEt(*i*-Pr)₂ (173 μL), and 1,7-octadiyne (60 μL, 0.45 mmol) in CH₂Cl₂ (100 mL) at -80 °C. The solution was poured into 200 mL methanol and photolyzed. Chromatography gave **48** (26 mg, 18% based on diyne) as a slightly yellow oil in the middle fraction. The first and third fractions were isolated in 14 and 16% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.46 (m, 2H, H_{Ph}), 7.42 (d, $J = 9.0$ Hz, 2H, H_{Ar}), 7.34-7.28 (m, 3H, H_{Ph}), 6.84 (d, $J = 9$ Hz, 2H, H_{Ar}), 3.81 (s, OMe), 2.38 (br s, C=CCH₂), 1.70 (br s, C=CCH₂CH₂). ¹³C NMR (125 MHz, CDCl₃) δ 159.44 (s, COMe), 132.91 (dd, ¹J_{CH} = 161 Hz, ²J_{CH} = 8 Hz, C_{Ar}), 131.44 (d, ¹J_{CH} = 161 Hz, C_{Ph}), 128.44 (d, ¹J_{CH} = 163 Hz, C_{Ph}), 127.96 (dt, ¹J_{CH} = 160 Hz, ²J_{CH} = 8 Hz, C_{Ph}), 126.73 (s, C=C), 125.52 (s, C=C), 123.68 (s, C_{ipso}), 115.72 (t, ²J_{CH} = 7 Hz, C_{ipso}), 113.90 (dd, ¹J_{CH} = 159 Hz, ²J_{CH} = 4.9 Hz, C_{Ar}), 93.72 (s, C≡CAr), 93.36 (s, C≡CAr), 90.57

(s, C≡CAr), 89.17 (s, C≡CAr), 55.25 (q, $^1J_{CH} = 143$ Hz, OMe), 30.10 (t, $^1J_{CH} = 127$ Hz, C=CCH₂), 29.97 (t, $^1J_{CH} = 128$ Hz, C=CCH₂), 21.87 (2C, t, $^1J_{CH} = 128$ Hz, C=CCH₂CH₂). HRMS(EI) *m/z* calcd for C₂₃H₂₀O (M⁺) 312.1515; found, 312.1520.

(4-MeO-C₆H₄)C=CC(CH₂CH₂CH₂CH₂)=CC=C(C₆H₄-4-Me) (49). Addition of trifluoroacetic anhydride (155 μ L, 1.10 mmol) to (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-OMe)Li (11) (168 mg, 0.51 mmol) and (C₅H₄Me)(CO)₂MnC(O)(C₆H₄-4-Me)Li·Et₂O¹ (194 mg, 0.50 mmol) was followed by addition of CuBr (23 mg), LiI (26 mg), NEt(*i*-Pr₂) (173 μ L), and 1,7-octadiyne (60 μ L, 0.45 mmol) in CH₂Cl₂ (100 mL) at -80 °C. The solution was poured into 200 mL methanol and photolyzed. Chromatography gave 49 (41 mg, 28% based on diyne) as a slightly yellow oil in the middle fraction. The first and third fractions were isolated in 17 and 29% yield. ¹H NMR (500 MHz, CDCl₃, broad spectrum) δ 7.42 (4H, H_{Ar}), 7.13 (2H, H_{Ar}), 6.86 (2H, H_{Ar}), 3.83 (3H, OMe), 2.38 (7H, Me, CH₂), 1.71 (4H, CH₂). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 159.44 (COMe), 138.06 (CMe), 132.90 (HC_{Ar}), 131.33 (HC_{Ar}), 129.01 (HC_{Ar}), 126.27 (C=C), 125.72 (C=C), 120.64 (C_{ipso}), 115.85 (C_{ipso}), 113.90 (HC_{Ar}), 93.60 (2C, C≡CAr), 89.96 (s, C≡CAr), 89.29 (s, C≡CAr), 55.23 (OMe), 30.07 (CH₂), 21.91 (CH₂), 21.45 (Me). HRMS(EI) *m/z* calcd for C₂₄H₂₂O (M⁺) 326.1672; found, 326.1672.

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