Single Isomer Iodochlorination of Alkynes and Chlorination of Alkenes Using Tetrabutylammonium Iodide and Dichloroethane

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General. Reactions were performed under nitrogen in oven-dried glassware equipped with a magnetic stirbar and a rubber septum unless otherwise indicated. Solvents were freshly distilled prior to use as follows: THF over sodium/benzophenone; dichloroethane, dichloromethane and DMF over calcium hydride. Triethylamine and diisopropylethylamine were freshly distilled over calcium hydride. All other were purchased and used without further purification unless otherwise indicated. Reactions were monitored by TLC analysis using glass plates precoated (250 µm thickness) with silica gel 60 F254. TLC plates were visualized using ultraviolet light and potassium permanganate stain. Flash chromatography was carried out on 230-400 mesh silica gel 60, or preparatory TLC glass plates precoated with silica gel (Si250F). NMR spectra
were acquired on 300 MHz, 400 MHz or 500 MHz spectrometers in the specified solvent. Infrared spectra were acquired on a FTIR spectrometer.

**Synthetic Methods**

**General procedure for the halogenation of alkenes and alkynes using Bu₄NI/DCE.**

*(E)-Methyl 3-chloro-2-iodoacrylate (9).*¹ A solution of methyl-2-propiolate 4 (250 mg, 2.98 mmol, 1.0 equiv) and tetrabutylammonium iodide (3.25 g, 8.95 mmol, 3.0 equiv) in dichloroethane (25 mL) was heated at reflux for 18 h. The reaction mixture was cooled, diluted with Et₂O and washed with NaHSO₃ (20 % wt solution), saturated NaHCO₃ and brine. The organic phase was then dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. The pure product was obtained by flash chromatography eluting with hexanes then 5 % EtOAc in hexanes to give the title product as a colorless oil (528 mg, 72 %). ¹H NMR (300 MHz, CDCl₃) δ 7.00 (s, 1H), 3.79 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 162.6 (C), 129.4 (CH), 84.3 (C), 53.2 (CH₃); IR (neat) 1728, 1567 cm⁻¹; MS (EI) 246 (M⁺); HRMS Calcd for C₄H₄ClIO₂ (M⁺) 245.8945, found 245.8926.

*(E)-Ethyl 4-(tert-butyldimethylsilyloxy)-3-chloro-2-iodobut-2-enoate (17).* Prepared from ethyl 4-(tert-butyldimethylsilyloxy)but-2-ynoate (100 mg, 0.41 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (152 mg, 92 %). ¹H NMR (400 MHz, CDCl₃) δ 4.53 (s, 2H), 4.31 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H), 0.93 (s, 9H), 0.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 164.6 (C), 137.1 (C), 80.1 (C), 68.6 (CH₂), 62.6 (CH₂), 25.8 (CH₃), 18.3 (C), 13.9 (CH₃); IR (neat) 2956, 1733, 1472 cm⁻¹; HRMS Calcd for C₈H₁₃ClIO₃Si

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¹ Ref. 1.
(M⁺ - t-Bu) 346.9367, found 346.9352; Calcd for C₁₁H₁₉ClIO₃Si (M⁺ - CH₃) 388.9837, found 388.9830.

**N-Methoxy-N-methylnon-2-ynamide (25).** To a solution of 1-hexyne (2.6 mL, 17.7 mmol, 1.0 equiv) in hexanes (150 mL) at -78 °C was added a solution of butyllithium (2.26 M in THF, 8.63 mL, 19.5 mmol, 1.1 equiv). After 1 hour a solution of N-methoxy-N-methylcarbamoyl chloride\(^2\) (2.40 g, 19.4 mmol, 1.1 equiv) in THF (20 mL) was slowly added via canula. The reaction was stirred for 1 hour at -78 °C then allowed to warm to room temperature for 1 hour. The reaction was quenched by the dropwise addition of 10 % HCl and diluted with ether. The organic layer was washed sequentially with a saturated solution of sodium bicarbonate and brine, then dried over anhydrous MgSO₄, filtered and concentrated. The pure product was obtained by chromatography eluting with 5% EtOAc in hexanes then 20% EtOAc in hexanes to give the title product as a pale yellow oil (3.02 g, 77%). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 3.40 (s, 3H), 2.94 (s, 3H), 2.03 (t, \(J = 6.4\) Hz, 2H), 1.36 – 1.14 (m, 8H), 0.93 (t, \(J = 6.8\) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl₃) \(\delta\) 73.0 (CH₃), 61.8 (CH₃), 31.1 (CH₂), 30.8 (CH₂), 28.4 (CH₂), 27.6 (CH₂), 22.4 (CH₂), 18.8 (CH₂), 13.6 (CH₃); IR (neat) 2237, 1644 cm⁻¹; HRMS Calcd for C₁₁H₁₉NO₂ (M⁺) 197.1416, found 197.1405.

(\(E\))-3-Chloro-2-iodo-N-methoxy-N-methylnon-2-enamide (26). Prepared from N-methoxy-N-methylnon-2-ynamide (3.02 g, 15.3 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (5.05 g, 92 %). \(^1\)H NMR (400 MHz, C₆D₆) \(\delta\) 3.22 (s, 3H), 2.82 (s, 3H), 2.46 (br s, 2H), 1.48 – 1.45 (m, 2H), 1.19 – 1.14 (m, 6H), 0.84 (t, \(J = 6.8\) Hz, 3H); \(^1\)C NMR (100 MHz, C₆D₆) \(\delta\) 166.3 (C), 135.1 (C), 82.7 (C), 60.8 (CH₃), 40.4 (CH₂), 32.4 (CH₃), 31.8 (CH₂), 28.3
(CH₂), 27.1 (CH₂), 22.8 (CH₂), 14.1 (CH₃); IR (neat) 2954, 2930, 2858, 1654, 1459 cm⁻¹; HRMS Calcd for C₁₁H₁₀ClIO₂ (M⁺) 359.0149, found 359.0201.

(E)-5-Chloro-6-iododec-5-ene (28). Prepared from 5-decyne (0.13 mL, 0.76 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (210 mg, 92 %). ¹H NMR (400 MHz, acetone-d₆) δ 2.68 (t, J = 7.2 Hz, 4H), 1.60 – 1.48 (m, 4H), 1.39 – 1.32 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, acetone-d₆) δ 133.0 (C), 100.6 (C), 44.3 (CH₂), 43.2 (CH₂), 32.2 (CH₂), 30.9 (CH₂), 23.3 (CH₂), 23.0 (CH₂), 15.2 (CH₃), IR (neat) 2957, 2860, 1623, 1464 cm⁻¹; MS (EI) 300 (M⁺); HRMS Calcd for C₁₀H₁₈ClI (M⁺) 300.0142, found 300.0132.

(E)-(2-Chloro-3-iodobut-2-ene-1,4-diyl)bis(oxy)bis(methylene)dibenzene (30). Prepared from 1,4-bis(benzyloxy)but-2-yne³ (50 mg, 0.19 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (75 mg, 93 %). ¹H NMR (400 MHz, acetone-d₆) δ 7.42 – 7.29 (m, 10 H), 4.57 (s, 2H), 4.55 (s, 2H), 4.51 (s, 2H), 4.44 (s, 2H); ¹³C NMR (100 MHz, acetone-d₆) δ 139.9 (C), 139.8 (C), 132.7 (C), 130.03 (CH), 130.01 (CH), 129.63 (CH), 129.56 (CH), 129.41 (CH), 129.38 (CH), 102.6 (C), 77.9 (CH₂), 74.8 (CH₂), 73.5 (CH₂), 73.2 (CH₂); IR (nujol) 2957, 1640, 1458 cm⁻¹; MS (EI) 428 (M⁺); HRMS Calcd for C₁₈H₁₈ClIO₂ (M⁺) 428.0040, found 428.0043.

(2,3-Dichloropropoxy)benzene (33).⁴ Prepared from allyloxybenzene (100 mg, 0.75 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (151 mg, 99 %). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.05 – 6.94 (m, 3H), 4.41 – 4.35 (m, 1H), 4.30 (dd, J = 6.4, 1.2 Hz, 2H),

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4.02 – 3.89 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.9 (C), 129.6 (CH), 121.6 (CH), 114.7 (CH), 68.1 (CH$_2$), 57.3 (CH), 45.0 (CH$_2$); IR (neat) 2959, 2933, 1599, 1496 cm$^{-1}$; MS (EI) 204 (M$^+$); HRMS Calcd for C$_9$H$_{10}$Cl$_2$O (M$^+$) 204.0109, found 204.0105.

4,5-Dichloropentyl benzoate (36). Prepared from pent-4-enyl benzoate$^5$ (100 mg, 0.53 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (118 mg, 99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (dd, $J$ = 6.4, 1.2 Hz, 2H), 7.55 – 7.54 (m, 1H), 7.44 (dd, $J$ = 8.0, 1.6 Hz, 2H), 4.38 – 4.35 (m, 2H), 4.13 – 4.10 (m, 1H), 3.79 (dd, $J$ = 11.0, 5.0 Hz, 1H), 3.66 (dd, $J$ = 11.4, 7.8 Hz, 1H), 2.22 – 1.84 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.4 (C), 132.9 (CH), 130.0 (C), 129.5 (CH), 128.3 (CH), 63.9 (CH$_2$), 60.4 (CH), 47.9 (CH$_2$), 31.7 (CH$_2$), 25.2 (CH$_2$); IR (neat) 2956, 2849, 1718, 1451 cm$^{-1}$; MS (EI) 260 (M$^+$); HRMS Calcd for C$_{12}$H$_{14}$ClO$_2$ (M$^+$ - Cl) 225.0682, found 225.0700.

2-(2,3-Dichloropropyl)phenol (39). Prepared from 2-allylphenol$^6$ (100 mg, 0.74 mmol) using a procedure similar to that described above for compound 9 that provided the title compound as a colorless oil (135 mg, 89%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 – 7.16 (m, 2H), 6.94 (dd, $J$ = 7.4, 7.4 Hz, 1H), 6.79 (d, $J$ = 8.0 Hz, 1H), 5.42 (br s, 1H), 4.53 – 4.66 (m, 1H), 3.78 (dd, $J$ = 11.7, 5.5 Hz, 1H), 3.76 (dd, $J$= 11.7, 5.36 Hz, 1H), 3.35 (dd, $J$ = 14.0, 6.0 Hz, 1H), 3.09 (dd, $J$ = 14.0, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.6 (C), 131.8 (CH), 128.6 (CH), 123.1 (C), 120.9 (CH), 115.5 (CH), 60.3 (CH), 48.4 (CH$_2$), 36.5 (CH$_2$); IR (neat) 3540, 2951, 1609, 1502 cm$^{-1}$; MS (EI) 204 (M$^+$); HRMS Calcd for C$_9$H$_{10}$Cl$_2$O (M$^+$) 204.0109, found 204.0121.

Butyl 2,3-dichloropropanoate$^7$ (48): Prepared from $n$-butyl acrylate (50 mg, 0.39 mmol) using a procedure similar to that described above for compound 9 that provided
the title compound as a colorless oil (15.5 mg, 20%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.42 (dd, $J = 8.7$, 5.2 Hz, 1H), 4.24 (t, $J = 6.8$ Hz, 2H), 3.96 (dd, $J = 11.1$, 8.7 Hz, 1H), 3.80 (dd, $J = 11.1$, 5.2 Hz, 1H), 1.71 – 1.64 (m, 2H), 1.44 – 1.39 (m, 2H), 0.95 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1 (C), 66.5 (CH$_2$), 55.1 (CH), 43.9 (CH$_2$), 30.4 (CH$_2$), 18.9 (CH$_2$), 13.6 (CH$_3$); IR (neat) 2936, 1750 cm$^{-1}$.

**General procedure for the halogenation of alkenes and alkynes using ICl.**

**Reaction of methyl-2-propiolate with ICl.** To a solution of methyl-2-propiolate 4 (50 mg, 0.60 mmol, 1.0 equiv) in dichloroethane (25 mL) was added iodine monochloride (1.0 M solution in DCM, 0.60 mL, 0.60 mmol, 1 equiv) and the resulting mixture was stirred for 2 h. The reaction was diluted with Et$_2$O and washed sequentially with NaHSO$_3$ (20 % wt solution), saturated NaHCO$_3$ and brine. The organic phase was then dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo. The pure product was obtained by flash chromatography eluting with hexanes then 5 % EtOAc in hexanes to give an inseparable mixture of compounds 9, 10, 6, and 7 as a pale yellow oil (100 mg, 68 %).

(10) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (s, 1H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.4 (C), 142.6 (CH), 87.7 (C), 53.9 (CH$_3$). (6/7) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (s, 1H), 3.849 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9 (C), 128.3 (C), 85.5 (CH), 53.4 (CH$_3$); (6/7) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (s, 1H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.0 (C), 97.5 (C), 87.4 (CH), 53.4 (CH$_3$); IR (neat) 1725, 1563 cm$^{-1}$; MS (EI) 246 (M$^+$).
**Reaction of ethyl 2-butynoate with ICl.** Prepared from ethyl 2-butynoate (50 mg, 0.45 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of 12, 13, 14, and 15 as a yellow oil (110 mg, 90%).

(13) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.27 (q, $J = 7.2$ Hz, 2H), 2.54 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.1 (C), 128.3 (C), 84.9 (C), 62.6 (CH$_2$), 38.3 (CH$_3$), 13.9 (CH$_3$). (14/15) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.36 (q, $J = 7.2$ Hz, 2H), 2.66 (s, 3H), 1.35, (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.2 (C), 96.9 (C), 64.6 (C), 60.9 (CH$_2$), 25.2 (CH$_3$), 13.7 (CH$_3$). (14/15) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.18 (t, $J = 7.2$ Hz, 2H), 2.48, (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H); IR (neat) 1728, 1627 cm$^{-1}$; MS (EI) 274 (M$^+$).

**Reaction of 3-cyclohexylpropiolate with ICl.** Prepared from ethyl 3-cyclohexylpropiolate (50 mg, 0.28 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of 20 and 21 as a yellow oil (95 mg, 99%). (21) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.29 (q, $J = 7.2$ Hz, 2H), 2.96 (tt, $J = 11.1$, 3.3 Hz, 1H), 2.20 – 1.16 (m, 10H), 1.33 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.6 (C), 143.0 (C), 68.5 (C), 62.9 (CH$_2$), 52.0 (CH), 32.8 (CH$_2$), 26.4 (CH$_2$), 23.2 (CH$_2$), 14.3 (CH$_3$); IR (neat) 1732, 1611 cm$^{-1}$; MS (EI) 342 (M$^+$).

**Reaction of ethyl phenylpropiolate with ICl.** Prepared from ethyl phenylpropiolate (50 mg, 0.29 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of 23 and 24 as a yellow oil (89 mg, 93%). (24) $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 – 7.26 (m, 5H), 3.99 (q, $J = 7.0$ Hz, 2H), 0.94 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.6 (C), 149.0 (C), 138.6 (C), 134.7 (CH),
129.8 (CH), 127.9 (CH), 81.2 (C), 62.5 (CH₂), 13.4 (CH₃); IR (neat) 1728, 1615 cm⁻¹; MS (EI) 336 (M⁺).

Prepared from 1,4-bis(benzyloxy)but-2-yne (50 mg, 0.19 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of compounds 30 and 31 as a yellow oil (81 mg, 99 %). (31) ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.29 (m, 10H), 4.57 (s, 2H), 4.54 (s, 2H), 4.51 (s, 2H), 4.47 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.3 (C), 128.6 (C), 128.5 (C), 128.4 (CH), 127.92 (CH), 127.88 (CH), 100.8 (C), 81.5 (CH₂), 76.3 (CH₂), 73.1 (CH₂), 71.9 (CH₂); IR (neat) 1461, 1376 cm⁻¹; MS (EI) 393 (M⁺ - Cl), 301 (M⁺ - I).

**Reaction of alloxybenzene with ICl.** Prepared from allyloxybenzene (50 mg, 0.37 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of compounds 33 and 34 as a yellow oil (89.8 mg, 82%). (34) ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.33 (m, 2H), 7.06 – 7.02 (m, 1H), 6.99 – 6.96 (m, 2H), 4.54 – 4.29 (m, 1H), 4.07 (d, J = 6.8 Hz, 2H), 3.74 (dd, J = 10.7, 6.4 Hz, 1H), 3.67 (dd, J = 10.7, 4.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.8 (C), 129.3 (CH), 121.6 (CH), 114.7 (CH), 70.2 (CH₂), 54.1 (CH), 6.7 (CH₂); IR (neat) 1594, 1500 cm⁻¹; MS (EI) 296 (M⁺).

**Reaction of pent-4-enyl benzoate with ICl.** Prepared from pent-4-enyl benzoate (50 mg, 0.26 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of compounds 36 and 37 as a colorless oil (85 mg, 92%). (37) ¹H NMR (400 MHz, acetone-d₆) δ 8.06 (d, J = 10.4 Hz, 2H), 7.57 (dd, J = 10.0, 10.0 Hz), 7.44 (dd, J = 10.4, 10.4 Hz), 4.37 (t, J = 8.0 Hz, 2H), 4.35 – 4.23 (m, 1H), 4.09 – 3.86 (dd, J = 17.2, 5.6 Hz, 1H), 3.83 (dd, J = 14.4, 14.4 Hz, 1H), 2.33 – 1.86 (m, 4H); ¹³C
NMR (100 MHz, acetone-d₆) δ 166.5 (C), 133.0 (CH), 130.1 (C), 129.5 (CH), 128.4 (CH), 63.7 (CH₂), 33.9 (CH), 33.1 (CH₂), 28.2 (CH₂), 10.3 (CH₂); IR (neat) 1718, 1615 cm⁻¹; MS (EI) 225 (M⁺ - I), 317 (M⁺ - Cl).

2-(2-chloro-3-iodopropyl)phenol (40). Prepared from 2-allylphenol⁶ (50 mg, 0.37 mmol) using a procedure similar to that described above for compound 10 that provided compound 40 as a yellow oil (109 mg, 99%). ¹H NMR (400 MHz, CDCl₃) δ 7.17 – 7.11 (m, 2H), 6.87 (ddd, J = 8.0, 7.6, 0.8 Hz, 1H), 6.78 (d, J = 8.0 Hz), 4.92 – 4.85 (m, 1H), 3.45 (dd, Jₐₐ = 8.8, Jₐₓ = 5.1 Hz, 1H), 3.34 (dd, Jₐₐ = 8.8, Jₐₓ = 6.1 Hz, 1H), 3.40 (dd, J = 15.7, 8.9 Hz, 1H), 3.05 (dd, J = 15.7, 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 159.1 (C), 128.2 (CH), 125.7 (C), 125.0 (CH), 120.8 (CH), 109.6 (CH), 81.6 (CH), 36.1 (CH₂), 8.9 (CH₂); IR (neat) 1506, 1479 cm⁻¹; HRMS calc’d for C₉H₁₀ClIO (M⁺) 205.8965, found 205.8967.

Reaction of 5-decene with ICl.⁹ Prepared from 5-decene (0.135 mL, 0.71 mmol) using a procedure similar to that described above for compound 7 that provided compound 43 as an inseparable mixture of 5,6-dichlorodecane (42) and 5-chloro-6-iododecane (43) as a colorless oil (142 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 4.26 – 4.21 (m, 1H), 3.93 – 3.88 (m, 1H), 2.11 – 2.03 (m, 1H), 1.98 – 1.80 (m, 3H), 1.62 – 1.52 (m, 2H), 1.46 – 1.27 (m, 6H), 0.93 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, acetone-d₆) δ 66.9 (CH), 42.5 (CH), 37.5 (CH₂), 36.8 (CH), 31.3 (CH₂), 28.2 (CH₂), 22.1 (CH₂), 21.9 (CH₂), 13.9 (CH₃); IR (neat) 2957, 2931, 1465 cm⁻¹; MS (EI) 302 (M⁺); HRMS calc’d for C₁₀H₂₀ClI (M⁺) 302.0298, found 302.0218.

Reaction of ((3-methylbut-3-enyloxy)methyl)benzene with ICl. Prepared from ((3-methylbut-3-enyloxy)methyl)benzene¹⁰ (50 mg, 0.28 mmol) using a procedure similar to
that described above for compound 10 that provided an inseparable mixture of compounds 45 and 46 as a colorless oil (12 mg, 14%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\Delta$ 7.36 – 7.36 (m, 5H), 4.51 (s, 2H), 3.81 – 3.60 (m, 4H), 2.29 – 2.15 (m, 2H), 1.66 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\Delta$ 138.1 (C), 128.4 (CH), 127.6 (CH), 127.5 (CH), 73.1 (CH$_2$), 70.2 (C), 66.7 (CH$_2$), 41.2 (CH$_2$), 28.6 (CH$_3$), 18.9 (CH$_2$); IR (neat) 2925, 1273 cm$^{-1}$; MS (EI) 338 (M$^+$).

**Reaction of n-butyl acrylate with ICl.** Prepared from n-butyl acrylate (50 mg, 0.39 mmol) using a procedure similar to that described above for compound 10 that provided an inseparable mixture of compounds 48 and 49 as a yellow oil (67 mg, 61%).

**Summary of variable Bu$_4$NI amount control reactions:**

**General procedure:** To a solution of alkyne 11 (50 mg, 0.45 mmol, 1 equiv) in DCE (4.0 mL) was added Bu$_4$NI (41 mg, 0.11 mmol, 0.25 equiv). To this was added ICl (1 M solution in DCM, 0.44 mL, 0.44 mmol, 0.98 equiv). The reaction was stirred for 2 hours, upon which time the solution was diluted with Et$_2$O and washed sequentially with NaHSO$_3$ (20 % solution), a saturated solution of NaHCO$_3$ and brine. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated to give a mixture of compounds 12:13 (28 mg, 23 % combined yield).

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<td>1:1</td>
</tr>
<tr>
<td>0.50</td>
<td>rt</td>
<td>5 h</td>
<td>DCE</td>
<td>11</td>
<td>1.2:1</td>
</tr>
<tr>
<td>1.05</td>
<td>rt</td>
<td>5 h</td>
<td>DCE</td>
<td>6</td>
<td>1:1</td>
</tr>
<tr>
<td>3.00</td>
<td>reflux</td>
<td>18 h</td>
<td>DCE</td>
<td>trace</td>
<td>1:1</td>
</tr>
<tr>
<td>3.00</td>
<td>reflux</td>
<td>18 h</td>
<td>benzene</td>
<td>9</td>
<td>33 exclusively</td>
</tr>
</tbody>
</table>

Bu₄NI (3 equiv)  
DCE, reflux, 18 h  

33  
Cl  

43 %  
19 %

Figure 1. Comparison of the crude products obtained from the reaction of 11 with ICl (1a) and with Bu₄NI/DCE (1b).
NMR Spectra


