Supplementary information

Organic amines-mediated free-radical carbocyclization reactions of 2,2,2-trihalogeno substituted N-(2-alkynylphenyl)acetamides

Tsung-Han Chuang and Che-Ping Chuang*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China.
Fax: +886-6-2740552; E-mail: cpchuang@mail.ncku.edu.tw

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Experimental Section

General considerations: Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. The multiplicity of the $^{13}$C NMR signals was determined by means of DEPT 135 experiments. Elemental analyses were performed with Heraeus ChN-Rapid Analyzer. Mass spectra were recorded on a Jeol JMS-SX 102A mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh).

1) Experimental details and characterization data of starting N-(2-alkynylphenyl)-2,2,2-trichloroacetamides 7.

Typical procedure for the preparation of N-(alkynylphenyl)-2,2,2-trichloroacetamides 7:

A solution of N-benzyl-2-(phenylethynyl)phenylamine (1.08 g, 3.81 mmol), 2,2,2-trichloroacetylchloride (1.06 g, 5.83 mmol), triethylamine (603 mg, 5.96 mmol) and DMAP (49 mg, 0.40 mmol) in chloroform (20 ml) was stirred in an ice-water bath for 15 min. The reaction mixture was then diluted with 100 ml of ethyl acetate washed with water (3 × 50 ml), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 1.20 ethyl acetate–hexanes) to give 1.41 g (86%) of 7a.

Based on $^1$H NMR spectra, trichloroacetamides 7a, 7b, 7d–p exist as a mixture of two rotamers, which do not interconvert easily at room temperature.

N-Benzyl-2,2,2-trichloro-N-[2-(phenylethynyl)phenyl]acetamide 7a. Colorless crystals; mp 123–124 °C (from ethyl acetate–hexanes); yield: 86 %; $^1$H NMR (400 MHz, CDCl$_3$): δ 4.30 (d, J = 12.4 Hz, 1H, NCH), 5.81 (d, J = 12.4 Hz, 1H, NCH), 6.97 (d, J = 7.9 Hz, 1H, ArH), 7.16 (td, J = 7.9, 1.3 Hz, 1H, ArH), 7.20–7.35 (m, 6H, ArH), 7.36–7.41 (m, 3H, ArH), 7.51–7.56 (m, 2H, ArH), 7.58 (dd, J = 7.9, 1.3 Hz, 1H, ArH); IR (KBr): 2950, 1670, 1590, 1450, 1245 cm$^{-1}$; HRMS(EI) calcld for C$_{18}$H$_{13}$Cl$_3$NO: m/z 427.0297 [M$^+$], found: m/z 427.0297.

2,2,2-Trichloro-N-ethyl-N-[2-(phenylethynyl)phenyl]acetamide 7b. Yellow oils; yield: 94%; $^1$H NMR (400 MHz, CDCl$_3$): δ 1.23 (t, J = 6.8 Hz, 3H, CH$_3$), 3.45 (bs, 1H, NCH), 4.37 (bs, 1H, NCH), 7.31–7.42 (m, 6H, ArH), 7.46–7.52 (m, 2H, ArH), 7.61 (brs, 1H, ArH); IR (neat): 2935, 1680, 1600, 1450, 1280 cm$^{-1}$; HRMS(EI) calcld for C$_{18}$H$_{13}$Cl$_3$NO: m/z 366.0213 [MH$^+$], found: m/z 366.0203.

2,2,2-Trichloro-N-[2-(phenylethynyl)phenyl]acetamide 7c. Colorless crystals; mp 104–105 °C (from ethyl acetate–hexanes); yield: 88%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.20 (t, J = 7.9 Hz, 1H, ArH), 7.35–7.46 (m, 4H, ArH), 7.51–7.55 (m, 2H, ArH), 7.57 (d, J = 7.9 Hz, 1H, ArH), 8.38 (d, J = 7.9 Hz, 1H, ArH), 9.45 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ 83.3 (s), 93.0 (s), 113.6 (s), 119.0 (d), 121.9 (s), 125.1 (d), 128.6 (2 × d), 129.2 (d), 129.9 (d), 131.5 (2 × d), 131.7 (d), 131.7 (s), 159.0 (s); IR (KBr): ν = 3360, 1720, 1580, 1450, 755 cm$^{-1}$; HRMS(EI) calcld for C$_{18}$H$_{13}$Cl$_3$NO: m/z 336.9828 [M$^+$], found: m/z 336.9828.

N-Benzyl-2,2,2-trichloro-N-[4-methyl-2-(phenylethynyl)phenyl]acetamide 7d. Colorless crystals; mp 74–75 °C (from ethyl acetate–hexanes); yield: 94%; $^1$H NMR (400 MHz, CDCl$_3$): δ 2.34 (s, 3H, CH$_3$), 4.26 (d, J = 14.0 Hz, 1H, NCH), 5.79 (d, J = 14.0 Hz, 1H, NCH), 6.84 (d, J = 8.2 Hz, 1H, ArH), 6.96 (dd, J = 8.2, 1.6 Hz, 1H, ArH), 7.20–7.30 (m, 5H, ArH), 7.34–7.42 (m, 4H, ArH), 7.49–7.56 (m, 2H, ArH); IR (KBr): ν = 2950, 1670, 1600, 1245, 835 cm$^{-1}$; HRMS(EI) calcld for C$_{21}$H$_{15}$Cl$_3$NO: m/z 441.0454 [M$^+$], found: m/z 441.0456.

N-Benzyl-2,2,2-trichloro-N-[4,5-dimethyl-2-(phenylethynyl)phenyl]acetamide 7e. Yellow oils; yield: 91%; $^1$H NMR (400 MHz, CDCl$_3$): δ 2.11 (s, 3H, CH$_3$), 2.25 (s, 3H, CH$_3$), 4.28 (d, J = 13.8 Hz, 1H, NCH), 5.74 (d, J = 13.8 Hz, 1H, NCH), 6.73 (s, 1H, ArH), 7.20–7.30 (m, 5H, ArH), 7.32–7.40 (m, 4H, ArH), 7.48–7.53 (m, 2H, ArH); IR (neat): 2920, 1680, 1595, 1455, 1245 cm$^{-1}$; HRMS(EI) calcld for C$_{21}$H$_{15}$Cl$_3$NO: m/z 455.0611 [M$^+$], found: m/z 455.0616.

N-Benzyl-2,2,2-trichloro-N-[4-chloro-2-(phenylethynyl)phenyl]acetamide 7f. Yellow oils; yield: 95%; $^1$H NMR (400 MHz, CDCl$_3$): δ 4.25 (brs, 1H, NCH), 5.81 (d, J = 14.4 Hz, 1H, NCH), 6.86 (d, J = 8.6 Hz, 1H, ArH), 7.11 (dd, J = 8.6, 2.4 Hz, 1H, ArH), 7.18–7.23 (m, 2H, ArH), 7.24–7.30 (m, 3H, ArH), 7.36–7.43 (m, 3H, ArH), 7.50–7.56 (m, 2H, ArH); IR (KBr): 2930, 1670, 1590, 1450, 1245 cm$^{-1}$; HRMS(EI) calcld for C$_{18}$H$_{13}$Cl$_3$NO: m/z 459.0457 [M$^+$], found: m/z 459.0457.
**N-Benzyloctyl-2-(hex-1-ynyl)phenylacetamide 7n.** Yellow oils; yield: 99%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.09 (t, \(J = 7.8\) Hz, 2H, CH\(_2\)), 1.49 (sextet, \(J = 7.8\) Hz, 2H, CH\(_2\)), 1.61 (quintet, \(J = 7.8\) Hz, 2H, CH\(_2\)), 2.46 (t, \(J = 7.8\) Hz, 2H, CH\(_2\)), 4.20 (d, \(J = 14.0\) Hz, 1H, NCH), 5.74 (d, \(J = 14.0\) Hz, 1H, NCH), 5.84 (d, \(J = 7.4\) Hz, 1H, ArH), 7.07 (t, \(J = 7.4\) Hz, 1H, ArH), 7.15–7.32 (m, 6H, ArH), 7.44 (dd, \(J = 7.4\), 0.8 Hz, 1H, ArH); IR (neat): 2935, 1680, 1455, 1235 cm\(^{-1}\); HRMS (EI) calcd for C\(_{23}\)H\(_{24}\)BrNO: m/z 457.0403 [M\(^+\)]; found: m/z 457.0399.

**N-Benzyloctyl-2-(2-phenylethynyl)phenylacetamide 7o.** Colorless crystals; mp 79–81 °C (from ethyl acetate–hexanes); yield: 83%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.28 (d, \(J = 12.2\) Hz, 1H, NCH), 5.78 (d, \(J = 12.2\) Hz, 1H, NCH), 6.96 (d, \(J = 7.4\) Hz, 1H, ArH), 7.15 (td, \(J = 7.4\), 1.2 Hz, 1H, ArH), 7.18–7.35 (m, 8H, ArH), 7.56 (d, \(J = 7.4\) Hz, 1H, ArH), 7.57 (s, 1H, ArH); IR (KBr): 2950, 1670, 1595, 1455, 1245 cm\(^{-1}\); HRMS (EI) calcd for C\(_{23}\)H\(_{22}\)Cl\(_2\)NO: m/z 432.9862 [M\(^+\)]; found: m/z 432.9861.
Typical procedure for the preparation of N-(alkynylyphenyl)-2,2,2-tribromoacetamides 9:
A solution of 2,2,2-tribromocarboxylic acid (1.19 g, 3.74 mmol) and phosphorus oxychloride (751 mg, 3.74 mmol) in toluene (20 mL) was stirred in an ice-water bath. After stirred for 1 h, N-benzyl-2-(phenylethynyl)phenylamine (703 mg, 2.48 mmol) and triethylamine (525 mg, 5.19 mmol) was added. The resulting solution was stirred in an ice-water bath for another 5 h. The reaction mixture was then diluted with 100 mL of ethyl acetate, washed with water (3 × 50 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 1:20 ethyl acetate–hexanes) to give 1.28 g (92%) of 9a.

Based on ¹H NMR spectra, tribromoacetamides 9a–i exist as a mixture of two rotamers, which do not interconvert easily at room temperature.

**N-Benzyl-2,2,2-tribromo-N-[2-(phenylethynyl)phenyl]acetamide 9a.** White solids; mp 91–92 °C (from ethyl acetate–hexanes); yield: 92%; "H NMR (400 MHz, CDCl₃): δ = 4.32 (brs, 1H, NCH), 5.85 (d, J = 14.4 Hz, 1H, NCH), 7.10 (brs, 1H, ArH), 7.17 (td, J = 7.7, 1.2 Hz, 1H, ArH), 7.21–7.33 (m, 6H, ArH), 7.34–7.42 (m, 3H, ArH), 7.52–7.62 (m, 3H, ArH); IR (KBr): ν = 3060, 1650, 1450, 1240, 760 cm⁻¹; HRMS (ESI) calcd for C₂₃H₁₉Br₃NO: m/z 593.8465 [MH⁺], found: m/z 593.8460.

**N-Benzyl-2,2,2-tribromo-N-[4-methyl-2-(phenylethynyl)phenyl]acetamide 9b.** Colorless oils; yield: 88%; "H NMR (400 MHz, CDCl₃): δ = 2.34 (s, 3H, CH₃), 4.28 (brs, 1H, NCH), 5.84 (d, J = 14.4 Hz, 1H, NCH), 6.89–7.05 (m, 2H, ArH), 7.22–7.32 (m, 5H, ArH), 7.35–7.43 (m, 4H, ArH), 7.52–7.60 (m, 2H, ArH); IR (neat): 2920, 1670, 1400, 1240 cm⁻¹; HRMS (ESI) calcd for C₂₃H₂₁Br₃NO: m/z 573.9011 [MH⁺], found: m/z 573.9014.

**N-Benzyl-2,2,2-tribromo-N-[4-chloro-2-(phenylethynyl)phenyl]acetamide 9c.** Yellow oils; yield: 94%; "H NMR (400 MHz, CDCl₃): δ = 4.31 (brs, 1H, NCH), 5.85 (d, J = 14.4 Hz, 1H, NCH), 6.99 (brs, 1H, ArH), 7.12 (dd, J = 8.4, 2.4 Hz, 1H, ArH), 7.20–7.33 (m, 5H, ArH), 7.36–7.41 (m, 3H, ArH), 7.52–7.58 (m, 3H, ArH); IR (neat): 2950, 1670, 1600, 1495, 1235 cm⁻¹; HRMS (ESI) calcd for C₂₂H₁₉Br₃ClNO: m/z 593.8465 [MH⁺], found: m/z 593.8466.

**N-Benzyl-2,2,2-tribromo-N-[4-bromo-2-(phenylethynyl)phenyl]acetamide 9d.** Yellow oils; yield: 92%; "H NMR (400 MHz, CDCl₃): δ = 4.35 (brs, 1H, NCH), 5.84 (d, J = 14.4 Hz, 1H, NCH), 6.91 (d, J = 7.6 Hz, 1H, ArH), 7.22–7.30 (m, 6H, ArH), 7.34–7.42 (m, 3H, ArH), 7.52–7.58 (m, 2H, ArH), 7.71 (d, J = 2.0 Hz, 1H, ArH); IR (neat): 3030, 1670, 1600, 1495, 1235 cm⁻¹; HRMS (ESI) calcd for C₂₃H₁₈Br₃NO: m/z 637.7960 [MH⁺], found: m/z 637.7952.

**N-Benzyl-2,2,2-tribromo-N-[4-methoxy carbonyl-2-(phenylethynyl)phenyl]acetamide 9e.** Colorless oils; yield: 84%; "H NMR (400 MHz, CDCl₃): δ = 3.33 (s, 3H, OCH₃), 4.46 (brs, 1H, NCH), 5.86 (d, J = 14.0 Hz, 1H, NCH), 7.14 (d, J = 7.8 Hz, 1H, ArH), 7.21–7.29 (m, 5H, ArH), 7.36–7.43 (m, 3H, ArH), 7.54–7.61 (m, 2H, ArH), 7.81 (dd, J = 7.8, 1.9 Hz, 1H, ArH), 8.25 (d, J = 1.9 Hz, 1H, ArH); IR (neat): 2950, 1725, 1670, 1600, 1255 cm⁻¹; HRMS(ESI) calcd for C₂₃H₁₈Br₃NO: m/z 617.8909 [MH⁺], found: m/z 617.8898.

**N-Benzyl-2,2,2-tribromo-N-[2-(4-methoxyphenyl)ethyl]acetamide 9f.** Colorless oils; yield: 92%; "H NMR (400 MHz, CDCl₃): δ = 2.39 (s, 3H, CH₃), 4.34 (brs, 1H, NCH), 5.85 (d, J = 14.4 Hz, 1H, NCH), 7.09 (brs, 1H, ArH), 7.15 (t, J = 7.4 Hz, 1H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 7.22–7.33 (m, 6H, ArH), 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.56 (d, J = 7.4 Hz, 1H, ArH); IR (neat): 2920, 1670, 1450, 1240, 815 cm⁻¹; HRMS (ESI) calcd for C₂₄H₂₀Br₂NO: m/z 593.9011 [MH⁺], found: m/z 593.9005.

**N-Benzyl-2,2,2-tribromo-N-[2-(4-methoxyphenyl)ethyl]acetamide 9g.** Colorless oils; yield: 80%; "H NMR (400 MHz, CDCl₃): δ = 3.83 (s, 3H, OCH₃), 4.34 (brs, 1H, NCH), 5.84 (d, J = 14.0 Hz, 1H, NCH), 6.90 (d, J = 8.8 Hz, 2H, ArH), 7.08 (brs, 1H, ArH), 7.13 (t, J = 7.6 Hz, 1H, ArH), 7.19–7.30 (m, 6H, ArH), 7.50 (d, J = 8.8 Hz, 2H, ArH), 7.54 (d, J = 7.6 Hz, 1H, ArH); IR (neat): 2935, 1660, 1605, 1455, 1255 cm⁻¹; HRMS (ESI) calcd for C₂₃H₁₈Br₂NO: m/z 589.8960 [MH⁺], found: m/z 589.8944.

**N-Benzyl-2,2,2-tribromo-N-[2-(4-chlorophenyl)ethyl]acetamide 9h.** Brown oils; yield: 93%; "H NMR (400 MHz, CDCl₃): δ = 4.36 (brs, 1H, NCH), 5.80 (d, J = 14.0 Hz, 1H, NCH), 7.09 (brs, 1H, ArH), 7.17 (td, J = 7.5, 1.1 Hz, 1H, ArH), 7.21–7.31 (m, 6H, ArH), 7.34 (d, J = 8.4 Hz, 2H, ArH), 7.48 (d, J = 8.4 Hz, 2H, ArH), 7.55 (d, J = 7.5 Hz, 1H, ArH); IR (neat): ν = 3030, 1670, 1595, 1450, 1240 cm⁻¹; HRMS (ESI) calcd for C₂₃H₁₈Br₂ClNO: m/z 593.8465 [MH⁺], found: m/z 593.8460.
A-BenzyI-2,2,2-tribromo-N-(2-[(4-bromophenyl)ethynyl]phenyl)acetamide 9i. Brown oils; yield: 86%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.32 (brs, 1H, NCH), 5.81 (d, $J = 14.0$ Hz, 1H, NCH), 7.10 (brs, 1H, ArH), 7.19 (t, $J = 7.5$ Hz, 1H, ArH), 7.22–7.34 (m, 6H, ArH), 7.41 (d, $J = 8.4$ Hz, 2H, ArH), 7.52 (d, $J = 8.4$ Hz, 2H, ArH), 7.56 (d, $J = 7.5$ Hz, 1H, ArH); IR (neat): 3030, 1670, 1595, 1495, 1240 cm$^{-1}$; HRMS(ESI) calcd for C$_{23}$H$_{16}$Br$_4$NO: m/z 637.7960 [MH$^+$], found: m/z 637.7949.

3) Copies of $^1$H and $^{13}$C NMR spectra for the starting $N$-(2-alkynylphenyl) trichloroacetamides 7 $N$-(2-alkynylphenyl) tribromoacetamides 9.
$^1$ H NMR spectra of 7a

$^1$ H NMR spectra of 7b
\(^1\)H & \(^{13}\)C NMR spectra of 7c
$^1{}$H NMR spectra of 7d

$^1{}$H NMR spectra of 7e
$^1$H NMR spectra of 7f

$^1$H NMR spectra of 7g
$^1$H NMR spectra of 7h

$^1$H NMR spectra of 7i
$^1$H NMR spectra of 7j

$^1$H NMR spectra of 7k
$^1$H NMR spectra of 7l

$^1$H NMR spectra of 7m
$^1$H NMR spectra of 7n

$^1$H NMR spectra of 7o
$^1$H NMR spectra of $7p$

$^1$H NMR spectra of $9a$
$^1$H NMR spectra of 9b

$^1$H NMR spectra of 9c
$^1$H NMR spectra of 9d

$^1$H NMR spectra of 9e
$^{1}$H NMR spectra of 9f

![H NMR spectrum of 9f](image)

$^{1}$H NMR spectra of 9g

![H NMR spectrum of 9g](image)
$^1$H NMR spectra of 9h

$^1$H NMR spectra of 9i
4) Copies of $^1$H and $^{13}$C NMR spectra for 4-benzoylquinolin-2(1H)-ones 8 and 10.
$^1$H & $^{13}$C NMR spectra of 8b
$^1$H & $^{13}$C NMR spectra of 8d
$^1$H & $^{13}$C NMR spectra of 8e

![NMR Spectra Image]
$^1$H & $^{13}$C NMR spectra of 8f
$^1$H & $^{13}$C NMR spectra of 8g
$^1$H & $^{13}$C NMR spectra of 8h
$^1$H & $^{13}$C NMR spectra of 8i
$^1$H & $^{13}$C NMR spectra of 8j
$^1$H & $^{13}$C NMR spectra of 8k
$^1$H & $^{13}$C NMR spectra of 8I
$^1$H & $^{13}$C NMR spectra of $8m$
$^1$H & $^{13}$C NMR spectra of 8n
$^1$H & $^{13}$C NMR spectra of 8o
$^1$H & $^{13}$C NMR spectra of 8p
$^1$H & $^{13}$C NMR spectra of 10a
$^1$H & $^{13}$C NMR spectra of 10b
$^1$H & $^{13}$C NMR spectra of 10c
$^1$H & $^{13}$C NMR spectra of 10d
$^1$H & $^{13}$C NMR spectra of 10e
$^1$H & $^{13}$C NMR spectra of 10f
$^1$H & $^{13}$C NMR spectra of 10g
$^1$H & $^{13}$C NMR spectra of 10h
$^1$H & $^{13}$C NMR spectra of 10i