

# Synthesis and styrene copolymerization of novel bromo, chloro, and fluoro ring-disubstituted tert-butyl phenylcyanoacrylates

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## Abstract

Novel ring-disubstituted tert-butyl phenylcyanoacrylates,  $RPhCH=C(CN)CO_2C(CH_3)_3$ , where R is 3,5-dibromo, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluoro, were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and tert-butyl cyanoacetate, and characterized by CHN analysis, IR,  $^1H$  and  $^{13}C$  NMR. All the acrylates were copolymerized with styrene in solution with radical initiation at 70°C. The compositions of the copolymers were calculated from nitrogen analysis.

## Introduction

3,5-Dibromophenyl ethyl phenylcyanoacrylates (PCA) is reported in potassium-functionalized graphitic carbon nitride catalyzed Knoevenagel condensation [1], and in synthesis of ethyl 3-amino-1-aryl-1H-benzo[f]chromene-2-carboxylates [2], whereas its propyl ester in its synthesis and styrene copolymerization [3]. 3-Bromophenyl ring-substituted 1-methylethyl PCA is used styrene radical copolymerization [4]; in metallic ytterbium-mediated reductive dimerization cyclization of arylmethylenecyanoacetates [5], and in cyclodimerization of arylidenecyanoacetate promoted by samarium diiodide [6]. (2*E*)-2,4-Dichlorophenyl 1,1-dimethylethyl PCA is mentioned in bifunctional phosphine-catalyzed cross-Rauhut-Currier/Michael/aldol condensation triple domino reaction leading to functionalized cyclohexenes [7]. 2,6-Dichlorophenyl 1,1-dimethylethyl PCA is reported in Knoevenagel condensation [8, 9], whereas (2*E*)-3,4-Dichlorophenyl 1,1-dimethylethyl PCA is used in development of two-pore domain potassium channel TWIK-related K<sup>+</sup> channel 1-selective agonist possessing in vivo antinociceptive activity [10]. 3,4-Dichlorophenyl 1,1-diethylpropyl PCA is reported in copper-catalyzed 1,4-addition of organoboronates to alkylidene cyanoacetates [11]. 3,5-Difluorophenyl ethyl PCA is mentioned in condensation catalyzed by ionic liquid covalently modified magnesium-aluminum hydrotalcite [12]; in preparation of bicyclic pyridine derivatives as fatty acid binding protein inhibitors [13], and in synthesis and styrene copolymerization [14]. (2*E*)-3,5-Difluorophenyl ethyl PCA is used in rhodium-catalyzed conjugate addition/cyclization cascade for the asymmetric synthesis of 2-

amino-4H-chromenes [15]; in condensation catalyzed by hydroxide anchored ionic liquids [16]. 3,4-Difluorophenyl 1-methylethyl [17] and 2,3-difluorophenyl [18] PCAs are prepared and copolymerized.

In this work we have prepared tert-butyl ring-disubstituted phenylcyanoacrylates,  $RPhCH=C(CN)CO_2C(CH_3)_3$ , where R is 3,5-dibromo, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluoro, and explored the feasibility of their copolymerization with styrene. To the best of our knowledge, except 2,6-dichloro [8, 9] and 3,4-dichloro [10], there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [19].

## 2. Experimental

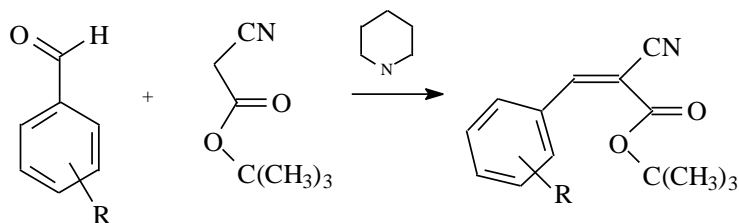
3,5-Dibromo, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluorobenzaldehyde, tert-butyl cyanoacetate ( $\geq 98.0\%$ ), piperidine (99%), styrene ( $\geq 99\%$ ), 1,1'-azobis(cyclohexanecarbonitrile) (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received.

Instrumentation was reported in [20].

## 3. Results and discussion

### 3.1. Synthesis and characterization of tert-butyl phenylcyanoacrylates

All tert-butyl phenylcyanoacrylates (TBCA) compounds were synthesized by Knoevenagel condensation [21] of appropriate benzaldehydes with tert-butyl cyanoacetate, catalyzed piperidine (Scheme 1).



Scheme 1. Synthesis of tert-butyl phenylcyanoacrylates where R is 3,5-dibromo, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluoro.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of tert-butyl cyanoacetate and an appropriate benzaldehyde were mixed in equimolar ratio in a 20 mL vial. A few drops of piperidine were added with stirring. The product of the reaction was isolated by filtration and purified by crystallization from 2-propanol. The compounds were characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and elemental analysis. No stereochemical analysis of the novel compounds was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

### 3.1.1. *Tert-butyl 3,5-dibromophenylcyanoacrylate*

Yield 89%; mp 185°C;  $^1\text{H}$  NMR  $\delta$  8.0 (s, 1H, CH=), 7.9-6.3 (m, 3H, Ph), 1.5 (s, 9H, CH<sub>3</sub>);  $^{13}\text{C}$  NMR  $\delta$  166 (C=O), 150 (HC=), 147, 138, 135, 133, 132, 124 (Ph), 116 (CN), 103 (C=), 87 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2980 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1612 (s, C=C), 1155 (s, C-O-CH<sub>3</sub>), 786 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>Br<sub>2</sub>NO<sub>2</sub>: C, 43.44; H, 3.39; N, 3.62; Found: C, 44.73; H, 4.06; N, 4.13.

**3.1.2. Tert-butyl 2,4-dichlorophenylcyanoacrylate**

Yield 89%; mp 185°C;  $^1\text{H NMR}$   $\delta$  8.0 (s, 1H, CH=), 7.9-6.3 (m, 3H, Ph), 1.5 (s, 9H, CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  166 (C=O), 150 (HC=), 147, 138, 135, 133, 132, 124 (Ph), 116 (CN), 103 (C=), 87 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2980 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1612 (s, C=C), 1155 (s, C-O-CH<sub>3</sub>), 786 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 56.40; H, 4.39; N, 4.70; Found: C, 56.37; H, 4.06; N, 4.74.

**3.1.3. Tert-butyl 2,6-dichlorophenylcyanoacrylate**

Yield 94%; mp 111.6°C;  $^1\text{H NMR}$   $\delta$  8.2 (s, 1H, CH=), 7.5-7.2 (m, 3H, Ph), 1.6 (s, 9H, CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  159 (C=O), 150 (HC=), 134, 135, 131, 130, 128 (Ph), 116 (CN), 113 (C=), 85 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2980 (m, C-H), 2233 (m, CN), 1728 (s, C=O), 1630 (s, C=C), 1219 (s, C-O-CH<sub>3</sub>), 789 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 56.40; H, 4.39; N, 4.70; Found: C, 55.46; H, 4.67; N, 4.90.

**3.1.4. Tert-butyl 3,4-dichlorophenylcyanoacrylate**

Yield 48%; mp 108.9°C;  $^1\text{H NMR}$   $\delta$  8.1 (s, 1H, CH=), 8.0-7.5 (m, 3H, Ph), 1.6 (s, 9H, CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  161 (C=O), 151 (HC=), 137, 134, 133, 131, 129 (Ph), 115 (CN), 107 (C=), 84 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2984 (m, C-H), 2220 (m, CN), 1722 (s, C=O), 1609 (s, C=C), 1288 (s, C-O-CH<sub>3</sub>), 824 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 56.40; H, 4.39; N, 4.70; Found: C, 55.60; H, 4.64; N, 4.86.

**3.1.5. Tert-butyl 2,4-difluorophenylcyanoacrylate**

Yield 93%;  $^1\text{H NMR}$   $\delta$  8.4 (s, 1H, CH=), 8.0-6.7 (m, 3H, Ph), 1.6 (s, 9H, CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  163 (C=O), 160 (HC=), 143, 130, 131, 119, 115, 114, 113 (Ph), 116 (CN), 103 (C=), 86

(OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2984 (m, C-H), 2224 (m, CN), 1745 (s, C=O), 1612 (s, C=C), 1227 (s, C-O-CH<sub>3</sub>), 836 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>F<sub>2</sub>NO<sub>2</sub>: C, 63.39; H, 4.94; N, 5.28; Found: C, 62.70; H, 5.42; N, 5.81.

### **3.1.6. *Tert-butyl 2,5-difluorophenylcyanoacrylate***

Yield 97%; mp 91.4°C; <sup>1</sup>H NMR δ 8.2 (s, 1H, CH=), 7.5-7.0 (m, 3H, Ph), 1.6 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR δ 160 (C=O), 157 (HC=), 144, 122, 121, 119, 118, 115, 108 (Ph), 117 (CN), 107 (C=), 84 (OC), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2982 (m, C-H), 2224 (m, CN), 1705 (s, C=O), 1609 (s, C=C), 1250 (s, C-O-CH<sub>3</sub>), 833 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>F<sub>2</sub>NO<sub>2</sub>: C, 63.39; H, 4.94; N, 5.28; Found: C, 60.17; H, 4.86; N, 5.13.

### **3.1.7 *Tert-butyl 2,6-difluorophenylcyanoacrylate***

Yield 64%; mp 88.9°C; <sup>1</sup>H NMR δ 8.4 (s, 1H, CH=), 8.0-6.5 (m, 3H, Ph), 1.5 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR δ 162 (C=O), 160 (HC=), 142, 134, 131, 114, 112 (Ph), 116 (CN), 103 (C=), 85 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2984 (m, C-H), 2231 (m, CN), 1713 (s, C=O), 1626 (s, C=C), 1151 (s, C-O-CH<sub>3</sub>), 825 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>F<sub>2</sub>NO<sub>2</sub>: C, 63.39; H, 4.94; N, 5.28; Found: C, 62.70; H, 5.61; N, 5.80.

### **3.1.8. *Tert-butyl 3,4-difluorophenylcyanoacrylate***

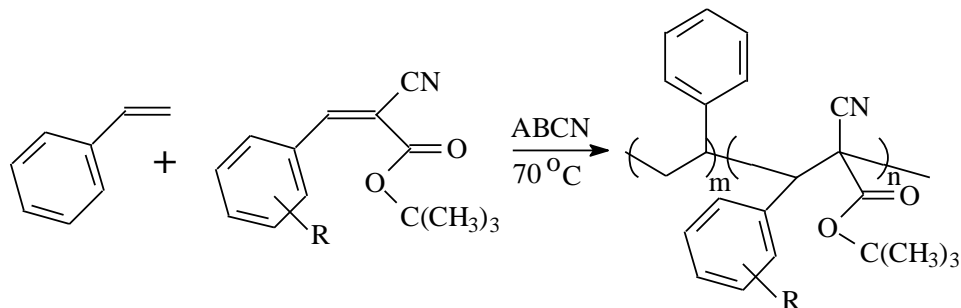
Yield 91%; mp 67.0°C; <sup>1</sup>H NMR δ 8.1 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 1.6 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR δ 161 (C=O), 154 (HC=), 151, 129, 128, 119, 118, 108 (Ph), 117 (CN), 106 (C=), 84 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2978 (m, C-H), 2226 (m, CN), 1720 (s, C=O), 1587 (s, C=C), 1275 (s, C-O-CH<sub>3</sub>), 835 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>F<sub>2</sub>NO<sub>2</sub>: C, 63.39; H, 4.94; N, 5.28; Found: C, 61.17; H, 4.88; N, 5.11.

### 3.1.9 *Tert-butyl 3,5-difluorophenylcyanoacrylate*

Yield 98%; mp 94°C;  $^1\text{H NMR}$   $\delta$  8.1 (s, 1H, CH=), 7.6-6.3 (m, 3H, Ph), 1.6 (s, 9H, CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  160 (C=O), 151 (HC=), 146, 134, 114, 112 (Ph), 116 (CN), 108 (C=), 85 (OC), 28 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 2984 (m, C-H), 2231 (m, CN), 1713 (s, C=O), 1626 (s, C=C), 1151 (s, C-O-CH<sub>3</sub>), 825 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>F<sub>2</sub>NO<sub>2</sub>: C, 63.39; H, 4.94; N, 5.28; Found: C, 61.50; H, 5.77; N, 6.19.

### 3.3. *Synthesis and characterization of styrene – TBCA copolymers*

Copolymers of the ST and the TBCA compounds, P(ST-co-TBCA) were prepared in 25-mL glass screw cap vials at ST/ TBCA = 3 (mol) the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 70°C. After a predetermined time, the mixture was cooled to room temperature, and precipitated dropwise in methanol. The composition of the copolymers was determined based on the nitrogen content (cyano group in TBCA). The novel synthesized TBCA compounds copolymerized readily with ST under free-radical conditions (Scheme 2) forming white flaky precipitates when their solutions were poured into methanol. The conversion of the copolymers was kept between 10 and 20% to minimize compositional drift (Table 1).



**Scheme 2.** Copolymerization of ST and the tert-butyl phenylcyanoacrylates, where R is 3,5-dibromo, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluoro.

**Table 1.** Copolymerization of styrene and tert-butyl phenylcyanoacrylates.

R	Yield <sup>a</sup> (wt%)	N (wt%)	ST in copol. (mol%)	TBCA in copol. (mol%)
3,5-Dibromo	12.1	2.29	68.3	31.7
2,4-Dichloro	12.8	2.51	71.4	28.6
2,6-Dichloro	14.2	1.5	85.9	14.1
3,4-Dichloro	11.7	2.21	76.3	23.7
2,4-Difluoro	15.2	1.88	82.2	17.8
2,5-Difluoro	14.2	2.57	72.9	27.1
2,6-Difluoro	16.4	1.25	89.2	10.8
3,4-Difluoro	13.1	2.56	73.0	27.0
3,5-Difluoro	14.2	1.63	85.1	14.9

Nitrogen elemental analysis showed that between 10.8 and 31.7 mol% of TBCA is present in the copolymers prepared at ST/ TBCA = 3 (mol), which is indicative of relatively high reactivity of the TBCA monomers towards ST radical which is typical of alkoxy ring-substituted TBCA. Since TBCA monomers do not homopolymerize, the most



likely structure of the copolymers would be isolated TBCA monomer units alternating with short ST sequences (Scheme 2).

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and  $\text{CHCl}_3$  and insoluble in methanol, ethyl ether, and petroleum ether.

#### 4 Conclusions

Novel trisubstituted ethylenes, tert-butyl phenylcyanoacrylates,  $\text{RPhCH}=\text{C}(\text{CN})\text{CO}_2\text{C}(\text{CH}_3)_3$  (where R is 3,5-dibromo, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluoro) were prepared and copolymerized with styrene.

#### Acknowledgments

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