Advanced Synthesis & Catalysis

Accepted Article

Title: Decarboxylative Tribromination for the Selective Synthesis of Tribromomethyl Ketone and Tribromovinyl Derivatives

Authors: Aravindan Jayaraman, Eunjeong Cho, Jimin Kim, and Sunwoo Lee

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800851

Link to VoR: http://dx.doi.org/10.1002/adsc.201800851

10.1002/adsc.201800851

FULL PAPER

DOI: 10.1002/adsc.200((will be filled in by the editorial staff))

Decarboxylative Tribromination for the Selective Synthesis of Tribromomethyl Ketone and Tribromovinyl Derivatives

Aravindan Jayaraman,[a] Eunjeong Cho,[a] Jimin Kim,[a] and Sunwoo Lee*,[a]

[a] Department of Chemistry, Chonnam National University, Gwangju 61186, Republic of Korea
Fax: (+82) 62-530-3389; e-mail: sunwoo@chonnam.ac.kr

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200######.

Abstract. Tribromomethyl ketone and tribromovinyl derivatives were selectively prepared from the decarboxylative tribromination. The reaction between propiolic acid derivatives and dibromoisocyanuric acid (DBCA)/H_2O afforded predominantly a tribromomethyl ketone derivative in the presence of AgOAc (10 mol%). When the same reaction was conducted with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) instead of AgOAc, tribromovinyl derivatives were exclusively formed in good yields. It was found that ethynyl bromide is an intermediate.

Keywords: Decarboxylation; bromine; tribromomethyl ketone; tribromovinyl; dibromoisocyanuric acid; electrophilic addition

Introduction

The development of selective synthetic methods for preparing a series of valuable compounds from a single starting material has received significant attention in the field of organic synthesis.[1] In addition, much effort has been devoted to developing one-pot multi-bond forming reactions due to their advantages in the atom and step economy in the overall synthesis.[2]

Bromine-containing compounds are important building blocks in organic synthesis and are widely used in pharmaceuticals, agrochemicals and materials science.[3] However tribromomethyl ketone and tribromovinyl derivatives have been infrequently studied compared to other multi-halogenated compounds even though they have been used extensively as bioactive compounds,[4] because, to the best of our knowledge, few general synthetic methods for their synthesis are available. Tribromomethyl ketone is formed as a minor product in the reaction of methyl ketone and H_2O_2-HBr system or 1,3-dibromo-5,5-dimethylhydantoin (DBH).[5] A tribromovinyl derivative was synthesized when terminal alkyne was allowed to react with the excess amount of alumina supported $CuBr_2$.[6] It is known that tribromovinyl group can be prepared from the alkynyl tellurium and silane.[7] Recently, the synthesis of tribromomethyl ketone and tribromovinyl derivatives from the reaction of alkynylsilane with oxone-KBr was reported. However, it exhibited a very limited substrate scope because the selectivity is highly dependent on the electronic effects of the alkyne substituents.[8] Very recently, we reported the metal-free decarboxylative chlorination of propiolic acid for the synthesis of trichloromethyl ketones.[9] A variety of trichloromethyl ketone derivatives were successfully synthesized under mild reaction conditions. This result provided insight into the development of synthetic methods for the production of tribrominated compounds such as tribromomethyl ketone and tribromovinyl derivatives. We envisioned that the use of dibromoisocyanuric acid (DBCA), which is an analogue of trichloroisocyanuric acid (TCCA), in the reaction of propiolic acids might provide both products selectively. Dibromoisocyanuric acid is well known to the powerful reagent for the electrophilic bromination of aromatic compounds.[10] However, it has never been used for the synthesis of tribromomethyl ketone and tribromovinyl derivatives. Herein, we report the selective synthesis of tribromomethyl ketone and tribromo vinyl groups from the reaction of DBCA and propiolic acid derivatives.

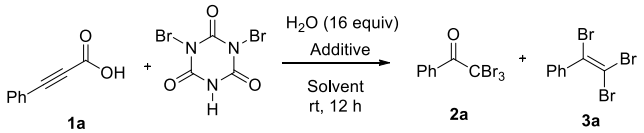
Results and Discussion

Phenyl propiolic acid was chosen as a standard substrate and reacted with DBCA in the presence of H_2O. The amount of H_2O used was 16 equiv which was the same amount as in the synthesis of trichloromethyl ketone. A number of solvents were first tested, as shown in Table 1. When the reaction was conducted in CH_3CN, **2a** was formed as a major

10.1002/adsc.201800851

product with minor amounts of **3a** (entry 1). The reaction in DMF showed similar results, but the selectivity decreased (entry 2). However, for the reactions in DMAc and DMSO, the major product was **3a** (entries 3 and 4). The addition of $Pd(OAc)_2$, $Cu(OTf)_2$ and $Ni(OAc)_2$ did not yield satisfactory results (entries 5 - 7). Interestingly, the reactions with Ag_2O and AgOAc afforded only **2a** with 76% and 79% yields, respectively (entries 8 and 9). No formation of **3a** was observed in these reaction mixtures. Surprisingly, when the reaction conducted in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), **3a** was exclusively formed (entry 10). From these results, the optimal conditions for the synthesis of tribromomethyl ketone and tribromovinyl groups were determined. When the reaction of propiolic acid and DBCA/H_2O was performed with AgOAc, the tribromomethyl ketone group was predominantly formed. When the same reaction was performed in the presence of TEMPO instead of AgOAc, the tribromovinyl group was exclusively formed.

Table 1. Optimization of the reaction conditions for the synthesis of **2a** and **3a**.[a]

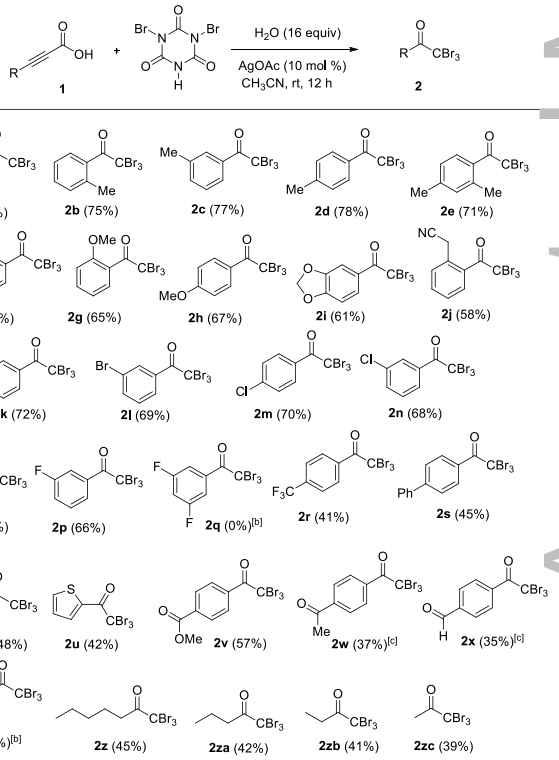


Entry	Solvent	Additive	Yield (%)[b] 2a/3a
1	CH_3CN	-	71/7
2	DMF	-	66/11
3	DMAc	-	8/57
4	DMSO	-	5/36
5	CH_3CN	$Pd(OAc)_2$[c]	40 / 27
6	CH_3CN	$Cu(OTf)_2$[c]	52 / 13
7	CH_3CN	$Ni(OAc)_2$[c]	64 / 8
8	CH_3CN	Ag_2O[c]	76 / -
9	CH_3CN	AgOAc[c]	79 / -
10	CH_3CN	TEMPO[d]	-/90

[a]Reaction conditions : **1a** (0.3 mmol), DBCA (0.45 mmol) and H_2O (4.8 mmol) were reacted in solvent (1.5 mL) at 25 °C for 12h. [b]Determined by ^1H and ^{13}C NMR with an internal standard. [c]0.03 mmol was used. [d]0.3 mmol was used.

To evaluate the selective synthesis of tribromomethyl ketone, a variety of aryl and alkyl-substituted propiolic acids were reacted with DBCA/H_2O in the presence of AgOAc and the results are summarized in Table 2. As expected, the phenyl propiolic acid was successfully converted to **2a** with 79% yield. The yields ranged from 70 to 78% for the formation of the alkyl-substituted 2,2,2-tribromoacetophenones such as **2b**, **2c**, **2d**, **2e,** and **2f**. Alkoxy-substituted aryl propiolic acids afforded the corresponding tribromomethyl ketones **2g**, **2h**, and **2i** with 65%, 67%, and 61% yields, respectively. In addition, 3-(2-cyanomethyl)phenyl propiolic acid (**1j**) afforded **2j** in 58% yield. Phenyl propiolic acids with halide groups such as bromide, chloride, and fluoride were afforded in good yields. However, **2q** was not obtained from the reaction of 3-(3,5-difluorophenyl)propiolic acid, but 3-(4-trifluoromethyl)phenyl, 1,1'-biphenyl-4-yl, naphthalene-2-yl, and thiophen-2-yl propiolic acids were transformed into their corresponding 2,2,2-tribromomethyl ketone derivatives (**2r**, **2s**, **2t** and **2u**) in 41-48% yields. Phenyl propiolic acids with electronic withdrawing substituents such as esters, ketones, and aldehyde groups afforded the desired products in moderate to low yields. For ketone and aldehyde substituents, the desired products **2w** and **2x** were not obtained from the reaction performed in CH_3CN, but in DMF the reaction proceeded. However, the 4-cyano-substituted phenyl propiolic acid failed to yield **2y** in either CH_3CN or DMF. Alkyl-substituted propiolic acids such as 2-octynoic, 2-hexynoic, 2-pentynoic and 2-butynoic acids afforded the corresponding tribromomethyl ketone derivatives **2z**, **2za**, **2zb**, and **2zc** with 39-45% yields.

Table 2. Synthesis of tribromomethyl ketone derivatives[a]

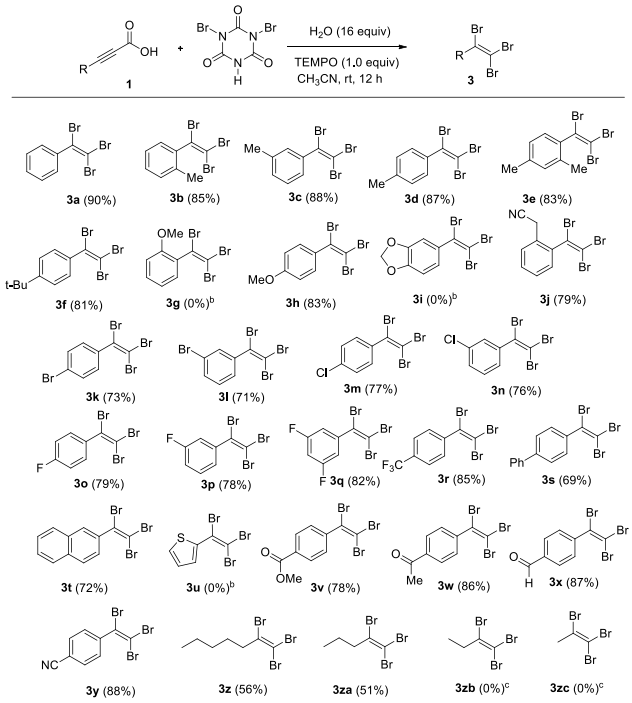


[a]Reaction conditions : **1** (2.0 mmol), DBCA (3.0 mmol), AgOAc (0.2 mmol) and H_2O (32.0 mmol) were reacted in CH_3CN (8.0 mL) at 25 °C for 12 h. [b]No product was formed in ether CH_3CN or DMF. [c]DMF was used as a solvent.

10.1002/adsc.201800851

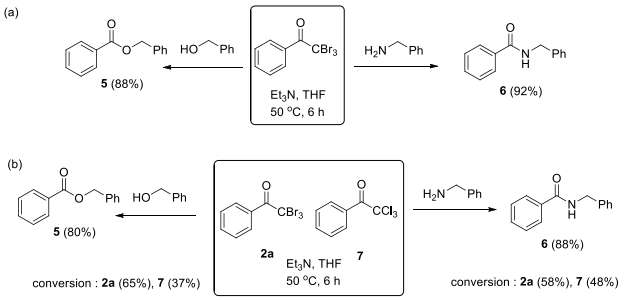
After successfully demonstrating the selective synthesis of tribromomethyl ketones in Table 2, we proceeded to evaluate the synthesis of tribromovinyl groups using the same starting materials. All propiolic acid derivatives were reacted with DBCA/H_2O in the presence of TEMPO. As shown in Table 3, in most cases the desired products bearing tribromo vinyl groups were successfully obtained with higher yields than those with tribromomethyl ketone. Especially, 1,2,2-tribromovinyl benzene derivatives bearing electron withdrawing groups, such as **3v**, **3w**, **3x** and **3y**, were obtained in 78%, 86%, 87%, and 88% yields, respectively. However, we failed to obtain **3g**, **3i**, and **3u** due to bromination of their aryl rings. In addition, we failed to isolate **3zb** and **3zc** due to their volatility, but they were detected in the GC MS analysis.

Table 3. Synthesis of tribromovinyl derivatives[a]



[a]Reaction conditions : **1** (2.0 mmol), DBCA (3.0 mmol), TEMPO (2.0 mmol) and H_2O (32.0 mmol) were reacted in CH_3CN (8.0 mL) at 25 °C for 12 h. [b]Failed to isolate the pure product. [c]~30% yield of the product was detected using ^1H NMR.

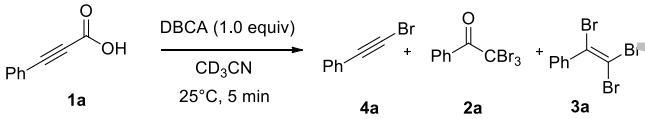
It was observed that 2,2,2,-tribromoacetophenone was successfully transformed into the corresponding ester and amide via acyl substitution reactions with benzyl alcohol and amine as shown in Scheme 1. When 2,2,2-tribromo- and 2,2,2-trichloroacetophenone were used in a competitive acyl substitution reaction with benzyl alcohol and benzyl amine, 2,2,2-tribromoacetophenone (**2a**) showed slightly higher reactivity than 2,2,2-trichloroacetophenone (**7**).



Scheme 1. Acyl substitution reactions

The intermediates of the reaction pathway were investigated to develop a plausible mechanism. To identify the intermediate, the initial reaction 5 min of phenyl propiolic acid and DBCA was monitored by ^1H and ^{13}C NMR spectroscopy and the results are summarized in Table 4. When the reaction was conducted in the absence of H_2O and TEMPO, phenylethynyl bromide (**4a**) and **3a** were found with 71% and 12% yields, respectively, but only trace amount of **2a** was obtained (entry 1). When the same reaction was conducted in the presence of TEMPO, the yield of **4a** decreased to 60% but remained as the major product (entry 2). The reaction with H_2O afforded **2a** as a major product and **4a** as a minor product in the absence of TEMPO (entry 3). However, **4a** was formed as a major product in the presence of TEMPO (entry 4). Based on these results, we propose that phenylethynyl bromide (**4a**) was an intermediate in the formation of both **2a** and **3a**.[11]

Table 4. Studies on the intermediate in the synthesis of **2a** and **3a**[a]



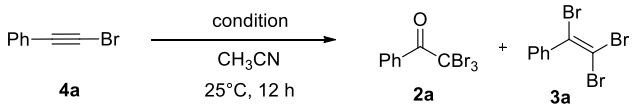
Entry	H_2O (equiv)	TEMPO (equiv)	Yield (%)		
			4a	**2a**	**3a**
1	0	0	71	trace	12
2	0	1.0	60	ND	20
3	16.0	0	11	51	trace
4	16.0	1.0	52	ND	29

[a]Reaction conditions : **1a** (0.3 mmol) and DBCA (0.3 mmol) were reacted in CD_3CN (1.5 mL) at 25 °C for 5 minute. [b]Determined by ^1H and ^{13}C NMR with internal standard. ND = not detected.

Next, we studied the reaction of **4a** as an intermediate to identify the reaction pathway, as shown in Table 5. The reaction with DBCA/H_2O in the absence of TEMPO afforded **2a** as a major product (entry 1), and the same reaction with AgOAc produced only **2a** in 90% yield (entry 2). When the reaction was conducted with TEMPO, only **3a** formed

with 91% yield (entry 3). These results are consistent with that the reaction of **1a**. When **4a** was reacted with Br_2 instead of DBCA, only **3a** was formed with 89% yield (entry 4), but the yield of **3a** decreased to 68% when using Br_2/H_2O (entry 5). When the reaction was performed with TEMPO, **3a** was formed with 40% yield (entry 6). These results suggest the following: 1) DBCA/H_2O might provide Br_2 and others; 2) Br_2 is a key reagent for the formation of **3a**, but not for **2a**; 3) the formation of Br_2 does not occur through a radical pathway.

Table 5. Results of the reaction pathway studies[a]

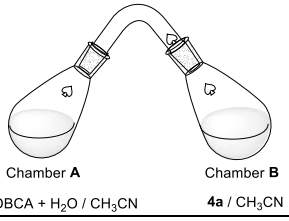


Entry	Reagents	Additive	Yield (%)	
			2a	**3a**
1	DBCA (1 equiv) / H_2O (16 equiv)	-	89	2
2	DBCA (1 equiv)/ H_2O (16 equiv)	AgOAc	90	0
3	DBCA (1 equiv) / H_2O (16 equiv)	TEMPO	0	91
4	Br_2 (1 equiv)	-	0	89
5	Br_2 (1 equiv) / H_2O (16 equiv)	-	0	68
6	Br_2 (1 equiv) / H_2O (16 equiv)	TEMPO	0	40

[a]Reaction conditions : **4a** (0.4 mmol) was used in CH_3CN (1.5 mL) at 25 °C for 12 h. [b]Determined by ^1H and ^{13}C NMR with internal standard.

To study the role of TEMPO and AgOAc in the subsequent reaction step, two chambers were prepared and connected, as shown in Table 6. Chamber **A** contained DBCA and H_2O reacted in CH_3CN at 45 °C and Chamber **B** contained **4a** dissolved in CH_3CN at 25 °C. We obtained **3a** in 56% yield in Chamber **B** (entry 1). The yield of **3a** showed 52% when TEMPO was added to Chamber **A** (entry 2). These results indicated that Br_2 is likely generated from the reaction of DBCA and H_2O and is vaporized to react with **4a** to afford **3a** without forming radicals. When either 10 mol% or an equal amount of AgOAc were added, the yields of products were 12% and 0%, respectively (entries 3 and 4). From these results, it can be concluded that AgOAc deactivates or blocks the formation of Br_2.

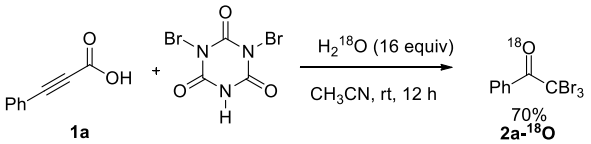
Table 6. Studies regarding the role of TEMPO and AgOAc[a]



Entry	Chamber **A**	Chamber **B**	
	Additive	Yield (%)	
		2a	**3a**
1	-	0	56
2	TEMPO	0	52
3	AgOAc	0	12
4	AgOAc	0	0

[a]Reaction conditions : Chamber **A** = DBCA (2.0 mmol) and H_2O (32.0 mmol) were reacted in CH_3CN (8.0 mL) at 45 °C, Chamber **B** = **4a** (1.0 mmol) was stirred in CH_3CN (3.0 mL) at 25 °C.

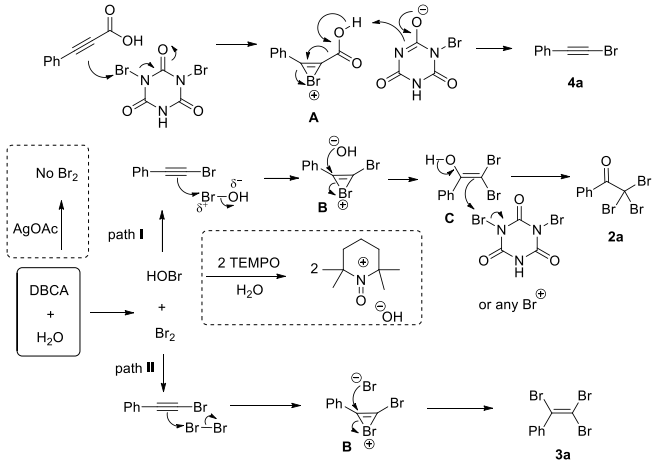
When isotopically labeled $H_2{}^{18}O$ was used in the reaction with **1a** and DBCA, the desired product **2a** bearing oxygen-18 was identified using high-resolution mass spectrometry (HRMS), with a molecular-mass of m/z = 356.7981 which corresponds to that of $C_8H_5Br_3{}^{18}O$ (m/z calculated for $[M+H]^+$: 356.8011). This suggests that the reaction pathway for tribromomethyl ketone is different from that of trichloromethyl ketone.



Scheme 2. Reaction with $H_2{}^{18}O$.

Based on the above-mentioned results, we proposed a reaction pathway as shown in Scheme 3. Phenylpropiolic acid was chosen as a representative alkynoic acids. Phenylpropiolic acid reacts with DBCA to form 2-carboxy-3-phenylbromiren-1-ium (**A**) followed by decarboxylation to afford **4a** as an intermediate through an ionic mechanism. It has been previously demonstrated that the reaction of DBCA and H_2O generates bromine and hypobromous acid.[12] In the presence of AgOAc, only HOBr can participate in path **I**. The reaction of **4a** and hypobromous acid provided intermediate **B** and, followed by the addition of hydroxide, afforded intermediate **C** and further bromination yielded **2a**. HOBr has been demonstrated to oxidize TEMPO.[13] In the presence of TEMPO, path **II** is predominant because HOBr can oxidize TEMPO, in contrast to path **I**. Bromine predominantly reacts with **4a** to form intermediate **B** and followed by the addition of bromide to afford **3a**.

Although path **I** was suggested as an ionic mechanism, we cannot rule out a radical mechanism.



Scheme 3. Proposed reaction pathways.

Conclusion

In summary, the selective synthesis of tribromomethyl ketone and tribromovinyl derivatives were developed using the reaction of propiolic acid derivatives and DBCA/H_2O. In the presence of AgOAc (10 mol%), tribromomethyl ketone derivatives were successfully obtained in good yields. When the reaction was conducted in the presence of TEMPO, tribromovinyl derivatives were exclusively formed in good yields. Alkynyl bromide was proposed to be formed as an intermediate through an ionic pathway. The formation of tribromomethyl ketone likely occur through the reaction with HOBr and the tribromovinyl group is likely produced via reaction with bromine.

Experimental Section

General experimental procedure for the synthesis of tribromomethyl ketones:

To a 20-mL screw cap vial added aryl propiolic acid (2.0 mmol, 1.0 equiv), silver acetate (23 mg, 0.2 mmol, 0.1 equiv) dibromoisocyanuric acid (861 mg, 3.0 mmol, 1.5 equiv) and water (576 mg, 32.0 mmol, 16.0 equiv) in acetonitrile (5.0 mL), closed tightly. The solution was stirred at 25 °C for 12 h. The resulting mixture charged to the separating funnel added water, 10% sodium thiosulphate extracted with EtOAc. The organic layer washed with water and dried over anhydrous $MgSO_4$. After removing the EtOAc under vacuum, the crude product was purified by column chromatography on a silica gel column with n-hexane/ethyl acetate as eluent to obtain the desired product.

2,2,2-Tribromo-1-phenylethanone (2a)[8]:

Phenylpropiolic acid (292 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-phenylethanone (**2a**) (564 mg, 1.58 mmol, 79% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.7 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 181.5, 133.9, 131.8, 128.2, 128.2, 42.0; FTIR (neat) υ 3053, 1696, 1214, 991, 803 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_5Br_3O$ [M]$^+$: 353.7891, found: 353.7892; Anal. calcd. for $C_8H_5Br_3O$: C, 26.93; H, 1.41. Found : C, 26.74; H, 1.67.

2,2,2-Tribromo-1-(o-tolyl)ethanone (2b)[14]:

3-(*o*-Tolyl)propiolic acid (320 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(*o*-tolyl)ethanone (**2b**) (556 mg, 1.5 mmol, 75% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 187.4, 137.9, 132.3, 131.8, 131.2, 128.3, 125.1, 43.7, 20.8; FTIR (neat) υ 3057, 1728, 1261, 967, 817 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3O$ [M]$^+$: 367.8047, found:.367.8047; Anal. calcd. for $C_9H_7Br_3O$: C, 29.15; H, 1.90. Found : C, 29.44; H, 1.73.

2,2,2-Tribromo-1-(*m*-tolyl)ethanone (2c):

3-(*m*-Tolyl)propiolic acid (320 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(*m*-tolyl)ethanone (**2c**) (571 mg, 1.54 mmol, 77% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.9 Hz, 1H), 8.09 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 181.8, 138.2, 134.7, 132.2, 128.9, 128.3, 127.9, 42.2, 21.4; FTIR (neat) υ 2920, 1694, 1165, 997, 808 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3O$ [M]$^+$: 367.8047, found: 367.8047; Anal. calcd. for $C_9H_7Br_3O$: C, 29.15; H, 1.90. Found : C, 29.42; H, 1.82.

2,2,2-Tribromo-1-(p-tolyl)ethanone (2d)[8]:

3-(*p*-Tolyl)propiolic acid (320 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(*p*-tolyl)ethanone (**2d**) (578 mg, 1.56 mmol, 78% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 181.0, 145.2, 132.0, 128.9, 125.3, 42.4, 21.7; FTIR (neat) υ 3034, 1691, 1183, 993, 832 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3O$ [M]$^+$: 367.8047, found: 367.8047; Anal. calcd. for $C_9H_7Br_3O$: C, 29.15; H, 1.90. Found : C, 29.33; H 1.75.

2,2,2-Tribromo-1-(2,4-dimethylphenyl)ethanone (2e):

3-(2,4-Dimethylphenyl)propiolic acid (348 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(2,4-dimethylphenyl)ethanone (**2e**) (547 mg, 1.42 mmol, 71% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 186.6, 142.1, 138.8, 132.2, 128.9, 128.6, 125.6, 44.2, 21.4, 20.9;

FTIR (neat) υ 2976, 1698, 1217, 979, 824 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_9Br_3O$ $[M]^+$: 381.8204, found: 381.8212; Anal. calcd. for $C_{10}H_9Br_3O$: C, 31.21; H, 2.36. Found : C, 30.97; H, 2.49.

2,2,2-Tribromo-1-(4-(*tert*-butyl)phenyl)ethanone (2f)[14]**:**
3-(4-(*tert*-Butyl)phenyl)propiolic acid (404 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(4-(*tert*-butyl)phenyl)ethanone (**2f**) (578 mg, 1.4 mmol, 70% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 1.36 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 181.0, 158.1, 132.0, 125.2, 125.2, 42.5, 35.3, 31.0; FTIR (neat) υ 2963, 1693, 1224, 991, 850 cm^{-1}; HRMS (FD) m/z cacld. for $C_{12}H_{13}Br_3O$ $[M]^+$: 409.8517, found: 409.8517; Anal. calcd. for $C_{12}H_{13}Br_3O$: C, 34.90; H, 3.17. Found : C, 35.22; H, 3.39.

2,2,2-Tribromo-1-(2-methoxyphenyl)ethanone (2g):
3-(2-Methoxyphenyl)propiolic acid (352 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(2-methoxyphenyl)ethanone (**2g**) (503 mg, 1.3 mmol, 65% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.67 (m, 1H), 7.47 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.02 – 6.97 (m, 2H), 3.87 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 187.1, 156.9, 132.5, 129.3, 122.8, 120.1, 111.8, 55.7, 43.6; FTIR (neat) υ 2923, 1650, 1485, 879, 747 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3O_2$ $[M]^+$: 383.7996, found: 383.7996; Anal. calcd. for $C_9H_7Br_3O_2$: C, 27.94; H, 1.82. Found : C, 28.05; H, 1.63.

2,2,2-Tribromo-1-(4-methoxyphenyl)ethanone (2h)[8]**:**
3-(4-Methoxyphenyl)propiolic acid (352 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(4-methoxyphenyl)ethanone (**2h**) (518 mg, 1.34 mmol, 67% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 9.1 Hz, 2H), 6.94 (d, *J* = 9.1 Hz, 2H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 180.0, 164.0, 134.6, 120.1, 113.5, 55.6, 42.8; FTIR (neat) υ 2970, 1682, 1594, 1171, 843 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3O_2$ $[M]^+$: 383.7996, found: 383.7995; Anal. calcd. for $C_9H_7Br_3O_2$: C, 27.94, H 1.82. Found : C, 28.22; H, 1.66.

1-(Benzo[d][1,3]dioxol-5-yl)-2,2,2-tribromoethanone (2i):
3-(Benzo[d][1,3]dioxol-5-yl)propiolic acid (380 mg, 2.0 mmol) afforded 1-(benzo[d][1,3]dioxol-5-yl)-2,2,2-tribromoethanone (**2i**) (489 mg, 1.22 mmol, 61% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.09 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 179.7, 152.5, 147.5, 129.1, 121.6, 111.7, 107.8, 102.2, 42.2; FTIR (neat) υ 2888, 1682, 1484, 1439, 1247 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_5Br_3O_3$ $[M]^+$: 397.7789, found: 397.7788; Anal. calcd. for $C_9H_5Br_3O_3$: C, 26.97; H, 1.26. Found : C, 27.01; H, 1.19.

2-(2-(2,2,2-Tribromoacetyl)phenyl)acetonitrile (2j):
3-(2-(Cyanomethyl)phenyl)propiolic acid (370 mg, 2.0 mmol) afforded 2-(2-(2,2,2-tribromoacetyl)phenyl)acetonitrile (**2j**) (459 mg, 1.16 mmol, 58% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 185.3, 133.0, 131.3, 130.4, 130.1, 127.6, 117.1, 41.5, 22.9; FTIR (neat) υ 3069, 2260, 1700, 1221, 792 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_6Br_3NO$ $[M]^+$: 392.8000, found: 392.8002. Anal. calcd. for $C_{10}H_6Br_3NO$: C, 30.34; H, 1.53; N, 3.54. Found : C, 30.75; H, 1.66; N, 3.27.

2,2,2-Tribromo-1-(4-bromophenyl)ethanone (2k)[14]**:**
3-(4-Bromophenyl)propiolic acid (450 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(4-bromophenyl)ethanone (**2k**) (627 mg, 1.44 mmol, 72% yield); brown oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 180.7, 133.3, 131.7, 129.5, 127, 41.2; FTIR (neat) υ 2664, 1696, 1580, 1213, 737 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_4O$ $[M]^+$: 431.6996, found: 431.6996; Anal. calcd. for $C_8H_4Br_4O$: C, 22.05; H, 0.93. Found : C, 22.17; H, 1.18.

2,2,2-Tribromo-1-(3-bromophenyl)ethanone (2l):
3-(3-Bromophenyl)propiolic acid (450 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(3-bromophenyl)ethanone (**2l**) (601 mg, 1.38 mmol, 69% yield); brown oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 180.3, 136.73, 134.4, 130.2, 130.8, 129.6, 122.3, 40.7; FTIR (neat) υ 3066, 1691, 1206, 750, 672 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_4O$ $[M]^+$: 431.6996, found: 431.6996; Anal. calcd. for $C_8H_4Br_4O$: C, 22.05; H, 0.93. Found : C, 22.24; H, 1.26.

2,2,2-Tribromo-1-(4-chlorophenyl)ethanone (2m)[14]**:**
3-(4-Chlorophenyl)propiolic acid (361 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(4-chlorophenyl)ethanone (**2m**) (548 mg, 1.4 mmol, 70% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 180.4, 140.6, 133.2, 128.6, 126.5, 41.2; FTIR (neat) υ 2879, 1697, 1585, 1214, 748 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3ClO$ $[M]^+$: 387.7501, found: 387.7504; Anal. calcd. for $C_8H_4Br_3ClO$: C, 24.56; H, 1.03. Found : C, 24.44; H, 1.24.

2,2,2-Tribromo-1-(3-chlorophenyl)ethanone (2n):

3-(3-Chlorophenyl)propiolic acid (361 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(3-chlorophenyl)ethanone (**2n**) (532 mg, 1.36 mmol, 68% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (t, *J* = 1.9 Hz, 1H), 8.23 (ddd, *J* = 8.0, 1.8, 1.0 Hz, 1H), 7.58 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.5, 134.8, 133.9, 131.6, 130.0, 129.8, 129.5, 40.8; FTIR (neat) υ 3071, 1678, 1274, 1207, 750 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3ClO$ [M]$^+$: 387.7501, found: 387.7504; Anal. calcd. for $C_8H_4Br_3ClO$: C, 24.56; H, 1.03. Found : C, 24.22; H, 0.87.

2,2,2-Tribromo-1-(4-fluorophenyl)ethanone (2o)[14]**:**
3-(4-Fluorophenyl)propiolic acid (328 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(4-fluorophenyl)ethanone (**2o**) (502 mg, 1.34 mmol, 67% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (m, 2H), 7.15 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.0, 165.9 (d, *J* = 258.1 Hz), 134.8 (d, *J* = 9.5 Hz), 124.3 (d, *J* = 3.3 Hz), 115.6 (d, *J* = 22.0 Hz), 41.5; FTIR (neat) υ 3079, 1682, 1506, 1231, 1155 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3FO$ [M]$^+$: 371.7796, found: 371.7799; Anal. calcd. for $C_8H_4Br_3FO$: C, 25.63; H, 1.08. Found : C, 25.41; H, 0.94.

2,2,2-Tribromo-1-(3-fluorophenyl)ethanone (2p):
3-(3-Fluorophenyl)propiolic acid (328 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(3-fluorophenyl)ethanone (**2p**) (495 mg, 1.32 mmol, 66% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (ddd, *J* = 7.9, 1.7, 1.0 Hz, 1H), 8.01 (ddd, *J* = 9.8, 2.4, 1.9 Hz, 1H), 7.49-7.45 (m, 1H), 7.32 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.4 (d, *J* = 2.5 Hz), 161.9 (d, *J* = 248.0 Hz), 130.2 (d, *J* = 7.0 Hz), 129.9 (d, *J* = 7.7 Hz), 127.6 (d, *J* = 3.2 Hz), 121.1 (d, *J* = 21.3 Hz), 118.7 (d, *J* = 24.1 Hz), 40.9; FTIR (neat) υ 2987, 1733, 1264, 1045, 733 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3FO$ [M]$^+$: 371.7796, found: 371.7799; Anal. calcd. for $C_8H_4Br_3FO$: C, 25.63; H 1.08. Found : C, 25.77; H, 0.95.

2,2,2-Tribromo-1-(4-(trifluoromethyl)phenyl)ethanone (2r):
3-(4-(Trifluoromethyl)phenyl)propiolic acid (428 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(4-(trifluoromethyl)phenyl)ethanone (**2r**) (348 mg, 0.82 mmol, 41% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.8, 134.9 (q, *J* = 33.1 Hz), 132.0, 131.7, 123.2 (q, *J* = 273.5 Hz), 125.2 (q, *J* = 3.7 Hz), 40.5; FTIR (neat) υ 3055, 1699, 1325, 1264, 733 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_4Br_3F_3O$ [M]$^+$: 421.7764, found: 421.7766; Anal. calcd. for $C_9H_4Br_3F_3O$: C, 25.44; H, 0.95. Found : C, 25.67; H, 1.15.

1-([1,1'-Biphenyl]-4-yl)-2,2,2-tribromoethanone (2s)[8]**:**
3-([1,1'-Biphenyl]-4-yl)propiolic acid (444 mg, 2.0 mmol) afforded 1-([1,1'-biphenyl]-4-yl)-2,2,2-tribromoethanone (**2s**) (390 mg, 0.9 mmol, 45% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.41 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 181.1, 146.7, 139.3, 132.6, 129.1, 128.7, 127.3, 126.8, 126.7, 42.2; FTIR (neat) υ 3031, 1690, 1599, 1191, 690 cm^{-1}; HRMS (FD) m/z cacld. for $C_{14}H_9Br_3O$ [M]$^+$: 429.8204, found: 429.8204; Anal. calcd. for $C_{14}H_9Br_3O$: C, 38.84; H, 2.10. Found : C, 38.99; H, 2.11.

2,2,2-Tribromo-1-(naphthalen-2-yl)ethanone (2t):
3-(Naphthalen-2-yl)propiolic acid (392 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(naphthalen-2-yl)ethanone (**2t**) (391 mg, 0.96 mmol, 48% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.31 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 181.5, 135.6, 134.2, 131.9, 129.9, 129.4, 127.9, 127.7, 127.1, 126.7, 125.4, 42.2; FTIR (neat) υ 2985, 1737, 1373, 1236, 1044 cm^{-1}; HRMS (FD) m/z cacld. for $C_{12}H_7Br_3O$ [M]$^+$: 403.8047, found: 403.8051; Anal. calcd. for $C_{12}H_7Br_3O$: C, 35.42; H, 1.73. Found : C, 35.55; H, 1.51.

2,2,2-Tribromo-1-(thiophen-2-yl)ethanone (2u)[14]**:**
3-(Thiophen-2-yl)propiolic acid (304 mg, 2.0 mmol) afforded 2,2,2-tribromo-1-(thiophen-2-yl)ethanone (**2u**) (305 mg, 0.84 mmol, 42% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 4.0 Hz, 1H), 7.74 (d, *J* = 5.0 Hz, 1H), 7.17 (t, *J* = 4.7 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.4, 137.4, 136.5, 132.6, 128.1, 40.9; FTIR (neat) υ 3103, 1666, 1404, 1241, 723 cm^{-1}; HRMS (FD) m/z cacld. for $C_6H_3Br_3OS$ [M]$^+$: 359.7455, found: 359.7457; Anal. calcd. for $C_6H_3Br_3OS$: C, 19.86; H, 0.83. Found : C, 20.04; H, 1.03.

Methyl 4-(2,2,2-tribromoacetyl)benzoate (2v):
3-(4-(Methoxycarbonyl)phenyl)propiolic acid (408 mg, 2.0 mmol) afforded methyl 4-(2,2,2-tribromoacetyl)benzoate (**2v**) (473 mg, 1.14 mmol, 57% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 3.97 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 181.3, 165.8, 134.4, 132.2, 131.6, 129.3 52.6, 40.9; FTIR (neat) υ 2952, 1724, 1702, 1278, 749 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_7Br_3O_3$ [M]$^+$: 411.7945, found: 411.7945; Anal. calcd. for $C_{10}H_7Br_3O_3$: C, 28.95; H, 1.70. Found : C, 28.99; H, 1.92.

1-(4-Acetylphenyl)-2,2,2-tribromoethanone (2w):
3-(4-Acetylphenyl)propiolic acid (376 mg, 2.0 mmol) afforded 1-(4-acetylphenyl)-2,2,2-tribromoethanone (**2w**) (295 mg, 0.74 mmol, 37% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 2.66 (s, 3H); ^{13}C{^{1}H}

NMR (126 MHz, $CDCl_3$) δ 197.1, 181.3, 140.5, 132.3, 131.9, 127.9, 40.9, 26.9; FTIR (neat) υ 2930, 1695, 1687, 1273, 749 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_7Br_3O_2$ $[M]^+$: 395.7996, found: 395.7996; Anal. calcd. for $C_{10}H_7Br_3O_2$: C, 30.11; H, 1.77. Found : C, 29.87; H, 1.49.

4-(2,2,2-Tribromoacetyl)benzaldehyde (2x):
3-(4-Formylphenyl)propiolic acid (348 mg, 2.0 mmol) afforded 4-(2,2,2-tribromoacetyl)benzaldehyde (**2x**) (269 mg, 0.7 mmol, 35% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 10.13 (s, 1H), 8.46 (d, *J* = 8.3 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.1, 181.8, 139.2, 133.5, 132.2, 129.1, 40.6; FTIR (neat) υ 2986, 1721, 1707, 1241, 735 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_5Br_3O_2$ $[M]^+$: 381.7840, found: 381.7840; Anal. calcd. for $C_9H_5Br_3O_2$: C, 28.09; H, 1.31. Found : C, 28.11; H, 1.42.

1,1,1-Tribromoheptan-2-one (2z):
Oct-2-ynoic acid (280 mg, 2.0 mmol) afforded 1,1,1-tribromoheptan-2-one (**2z**) (316 mg, 0.9 mmol, 45% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 3.18 (t, *J* = 7.4 Hz, 2H), 7.19 (pentet, *J* = 7.9 Hz, 2H), 1.36-1.40 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H),; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 190.9, 46.8, 32.9, 31.0, 25.4, 22.3, 13.9; FTIR (neat) υ 2957, 1736, 1121, 1059, 751, cm^{-1}; HRMS (FD) m/z cacld. for $C_7H_{11}Br_3O$ $[M]^+$: 347.8360, found: 347.8366; Anal. calcd. for $C_7H_{11}Br_3O$: C, 23.96; H, 3.16. Found : C, 24.01; H, 3.28.

1,1,1-Tribromopentan-2-one (2za):
Hex-2-ynoic acid (224 mg, 2.0 mmol) afforded 1,1,1-tribromopentan-2-one (**2za**) (271 mg, 0.84 mmol, 42% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 3.17 (t, *J* = 7.3 Hz, 2H), 1.82 (sextet, *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 190.7, 46.8, 34.7, 19.2, 13.4; FTIR (neat) υ 2968, 1735, 1264, 1120, 729 cm^{-1}; HRMS (FD) m/z cacld. for $C_5H_7Br_3O$ $[M]^+$: 319.8047, found: 319.8055; Anal. calcd. for $C_5H_7Br_3O$: C, 18.60; H, 2.19. Found : C, 18.88; H, 2.00.

1,1,1-Tribromobutan-2-one (2zb):
Pent-2-ynoic acid (184 mg, 2.0 mmol) afforded 1,1,1-tribromobutan-2-one (**2zb**) (253 mg, 0.82 mmol, 41% yield); brown oil; ^1H NMR (500 MHz, $CDCl_3$): δ 3.22 (q, *J* = 7.3 Hz, 3H), 1.30 (t, *J* = 7.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.8, 46.1, 26.5, 10.2; FTIR (neat) υ 2982, 1736, 1458, 1045, 735 cm^{-1}; HRMS (FD) m/z cacld. for $C_4H_5Br_3O$ $[M]^+$: 305.7891, found: 305.7898; Anal. calcd. for $C_4H_5Br_3O$: C, 15.56; H, 1.63. Found : C, 15.67; H, 1.77.

1,1,1-Tribromopropan-2-one (2zc):
But-2-ynoic acid (168 mg, 2.0 mmol) afforded 1,1,1-tribromopropan-2-one (**2zc**) (230 mg, 0.78 mmol, 39% yield); brown oil; ^1H NMR (500 MHz, $CDCl_3$): δ 2.79 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 187.9, 45.9, 20.4; FTIR (neat) υ 2919, 1737, 1421, 1210, 821 cm^{-1}; HRMS (FD) m/z cacld. for $C_3H_3Br_3O$ $[M]^+$: 291.7734, found: 291.7738; Anal. calcd. for $C_3H_3Br_3O$: C, 12.22; H, 1.03. Found : C, 12.59; H, 0.97.

General experimental procedure for the synthesis of tribromovinyl derivatives:
To a 20-mL screw cap vial added aryl propiolic acid (2.0 mmol, 1.0 equiv), acetonitrile, water (576 mg, 32.0 mmol, 16.0 equiv), TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl) (312.4 mg, 2.0 mmol, 1.0 equiv) dibromoisocyanuric acid (861 mg, 3.0 mmol, 1.5 equiv). The solution was stirred at 25 °C for 12 h. The resulting mixture charged to the separating funnel added water, 10% sodium thiosulphate extracted with EtOAc. The organic layer washed with water and dried over anhydrous $MgSO_4$. After removing the EtOAc under vacuum, the crude product was purified by column chromatography on a silica gel column with n-hexane/ethyl acetate as eluent to obtain the desired product.

1,2,2-Tribromovinyl)benzene (3a):
Phenylpropiolic acid (292 mg, 2.0 mmol) afforded (1,2,2-tribromovinyl)benzene (**3a**) (613 mg, 1.8 mmol, 90% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34-7.41 (m, 5H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.4, 129.3, 128.7, 128.5, 124.6, 89.8; FTIR (neat) υ 3056, 1491, 1442, 783, 694 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_5Br_3$ $[M]^+$: 337.7941, found: 337.7941; Anal. calcd. for $C_8H_5Br_3$: C, 28.19; H, 1.48. Found : C, 28.43; H, 1.55.

1-Methyl-2-(1,2,2-tribromovinyl)benzene (3b)[7]**:**
3-(*o*-Tolyl)propiolic acid (320 mg, 2.0 mmol) afforded 1-methyl-2-(1,2,2-tribromovinyl)benzene (**3b**) (603 mg, 1.7 mmol, 85% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31-7.28 (m, 1H), 7.24 (t, *J* = 5.8 Hz, 2H), 7.21-7.19 (m, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.1, 135.6, 130.6, 129.6, 128.2, 126.3, 124.4, 90.8, 19.2; FTIR (neat) υ 2921, 1596, 1454, 822, 759 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3$ $[M]^+$: 351.8098, found: 351.8098; Anal. calcd. for $C_9H_7Br_3$: C, 30.46; H, 1.99. Found : C, 30.42; H, 2.22.

1-Methyl-3-(1,2,2-tribromovinyl)benzene (3c):
3-(*m*-Tolyl)propiolic acid (320 mg, 2.0 mmol) afforded 1-methyl-3-(1,2,2-tribromovinyl)benzene (**3c**) (625 mg, 1.76 mmol, 88% yield); colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.6 Hz, 1H), 7.23-7.18 (m, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.3, 138.6, 130.1, 129.1, 128.3, 125.7, 124.7, 89.6, 21.3; FTIR (neat) υ 2919, 1481, 1250, 752 701 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3$ $[M]^+$: 351.8098, found: 351.8098; Anal. calcd. for $C_9H_7Br_3$: C, 30.46; H, 1.99. Found : C, 30.57; H, 2.14.

1-Methyl-4-(1,2,2-tribromovinyl)benzene (3d):
3-(*p*-Tolyl)propiolic acid (320 mg, 2.0 mmol)

afforded 1-methyl-4-(1,2,2-tribromovinyl)benzene (**3d**) (617 mg, 1.74 mmol, 87% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.5, 136.6, 129.2, 128.7, 124.9, 89.5, 21.5; FTIR (neat) υ 3027, 1504, 1263, 907 735 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3$ $[M]^+$: 351.8098, found: 351.8098; Anal. calcd. for $C_9H_7Br_3$: C, 30.46; H, 1.99. Found : C, 30.55; H, 2.08.

2,4-Dimethyl-1-(1,2,2-tribromovinyl)benzene (**3e**)**:** 3-(2,4-Dimethylphenyl)propiolic acid (348 mg, 2.0 mmol) afforded 2,4-dimethyl-1-(1,2,2-tribromovinyl)benzene (**3e**) (612 mg, 1.66 mmol, 83% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 – 7.11 (m, 1H), 7.05 – 7.07 (m, 2H), 2.36 (s, 3H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.7, 136.3, 135.4, 131.3, 128.1, 127.1, 124.7, 90.7, 21.4, 19.2; FTIR (neat) υ 2918, 1510, 1444, 814, 776 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_9Br_3$ $[M]^+$: 365.8254, found: 365.8254; Anal. calcd. for $C_{10}H_9Br_3$: C, 32.56; H, 2.46. Found : C, 32.55; H, 2.47.

1-(*tert*-Butyl)-4-(1,2,2-tribromovinyl)benzene (**3f**)**:** 3-(4-(*tert*-butyl)phenyl)propiolic acid (404 mg, 2.0 mmol) afforded 1-(*tert*-butyl)-4-(1,2,2-tribromovinyl)benzene (**3f**) (643 mg, 1.62 mmol, 81% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 152.6, 136.4, 128.5, 125.4, 125.0, 89.3, 34.9, 31.2; FTIR (neat) υ 2961, 1604, 1470, 831, 703 cm^{-1}; HRMS (FD) m/z cacld. for $C_{12}H_{13}Br_3$ $[M]^+$: 393.8567, found: 393.8571; Anal. calcd. for $C_{12}H_{13}Br_3$: C, 36.31; H, 3.30. Found : C, 36.47; H, 3.16.

1-Methoxy-4-(1,2,2-tribromovinyl)benzene (**3h**)**:**

3-(4-Methoxyphenyl)propiolic acid (352 mg, 2.0 mmol) afforded 1-methoxy-4-(1,2,2-tribromovinyl)benzene (**3h**) (616 mg, 1.66 mmol, 83% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.1, 131.6, 130.7, 124.9, 113.8, 89.2, 55.9; FTIR (neat) υ 2957, 1604, 1503, 1249, 1173 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_7Br_3O$ $[M]^+$: 367.8047, found: 367.80442; Anal. calcd. for $C_9H_7Br_3O$: C, 29.15; H, 1.90. Found : C, 29.41; H, 1.84.

2-(2-(1,2,2-Tribromovinyl)phenyl)acetonitrile (**3j**)**:** 3-(2-(Cyanomethyl)phenyl)propiolic acid (370 mg, 2.0 mmol) afforded 2-(2-(1,2,2-tribromovinyl)phenyl)acetonitrile (**3j**) (600 mg, 1.58 mmol, 79% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 1H), 7.45 (td, *J* = 7.6, 1.6 Hz, 1H), 7.40 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.75 (d, *J* = 3.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.5, 130.5, 129.1, 129.0, 128.9, 127.5, 121.8, 116.9, 93.2, 21.3; FTIR (neat) υ 3065, 2250, 1482, 1411, 733 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_6Br_3N$ $[M]^+$: 376.8050, found: 376.8048; Anal. calcd. for $C_{10}H_6Br_3N$: C, 31.62; H, 1.59; N, 3.69. Found : C, 31.66; H, 1.68; N, 3.77.

1-Bromo-4-(1,2,2-tribromovinyl)benzene (**3k**)**:** 3-(4-Bromophenyl)propiolic acid (450 mg, 2.0 mmol) afforded 1-bromo-4-(1,2,2-tribromovinyl)benzene (**3k**) (613 mg, 1.46 mmol, 73% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.3, 131.8, 130.3, 123.6, 123.3, 90.6; FTIR (neat) υ 2555, 1481, 1391, 1072, 792 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_4$ $[M]^+$: 415.7047, found: 415.7045; Anal. calcd. for $C_8H_4Br_4$: C, 22.89; H, 0.96. Found : C, 22.99; H, 1.16.

1-Bromo-3-(1,2,2-tribromovinyl)benzene (**3l**)**:** 3-(3-Bromophenyl)propiolic acid (450 mg, 2.0 mmol) afforded 1-bromo-3-(1,2,2-tribromovinyl)benzene (**3l**) (596 mg, 1.42 mmol, 71% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (t, *J* = 2.0 Hz, 1H), 7.50 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.33 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 141.2, 132.4, 131.6, 130.0, 127.4, 122.6, 122.2, 91.1; FTIR (neat) υ 2872, 1559, 1465, 1260, 749 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_4$ $[M]^+$: 415.7047, found: 415.7045. Anal. calcd. for $C_8H_4Br_4$: C, 22.89; H, 0.96. Found : C, 22.95; H, 1.14.

1-Chloro-4-(1,2,2-tribromovinyl)benzene (**3m**)**:** 3-(4-Chlorophenyl)propiolic acid (361 mg, 2.0 mmol) afforded 1-chloro-4-(1,2,2-tribromovinyl)benzene (**3m**) (578 mg, 1.54 mmol, 77% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 9.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.8, 135.4, 130.2, 128.8, 123.3, 90.6; FTIR (neat) υ 3089, 1484, 1095, 827, 795 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3Cl$ $[M]^+$: 371.7552, found: 371.7549; Anal. calcd. for $C_8H_4Br_3Cl$: C, 25.60; H, 1.07. Found : C, 25.66; H, 0.98.

1-Chloro-3-(1,2,2-tribromovinyl)benzene (**3n**)**:** 3-(3-Chlorophenyl)propiolic acid (361 mg, 2.0 mmol) afforded 1-chloro-3-(1,2,2-tribromovinyl)benzene (**3n**) (570 mg, 1.52 mmol, 76% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (t, *J* = 1.8 Hz, 1H), 7.34 - 7.32 (m, 2H), 7.29 - 7.27 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 141.0, 134.3, 129.8, 129.5, 128.8, 126.9, 122.7, 91.0; FTIR (neat) υ 3063, 1564, 1467, 1210, 712, cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3Cl$ $[M]^+$: 371.7552, found: 371.7549; Anal. calcd. for $C_8H_4Br_3Cl$: C, 25.60; H, 1.07. Found : C, 25.64; H, 1.00.

1-Fluoro-4-(1,2,2-tribromovinyl)benzene (**3o**)**:** 3-(4-Fluorophenyl)propiolic acid (328 mg, 2.0 mmol) afforded 1-fluoro-4-(1,2,2-tribromovinyl)benzene (**3o**) (567 mg, 1.58 mmol, 79% yield); colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 - 7.37 (m, 2H), 7.10 - 7.05 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.8 (d, *J* = 250.6 Hz), 135.5 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.6 Hz), 123.6, 115.7 (d, *J* = 22.1 Hz), 90.5; FTIR (neat) υ 3068, 1585, 1476, 1257, 757 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3F$ $[M]^+$: 355.7847, found: 355.7851; Anal. calcd. for $C_8H_4Br_3F$: C, 26.78; H, 1.12. Found : C, 26.88; H, 1.09.

1-Fluoro-3-(1,2,2-tribromovinyl)benzene (**3p**)**:**
3-(3-Fluorophenyl)propiolic acid (328 mg, 2.0 mmol) afforded 1-fluoro-3-(1,2,2-tribromovinyl)benzene (**3p**) (560 mg, 1.56 mmol, 78% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (td, *J* = 8.0, 5.8 Hz, 1H), 7.19 (ddd, *J* = 7.7, 1.5, 1.0 Hz, 1H), 7.14 - 7.04 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 248.0 Hz), 141.3 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 8.4 Hz), 124.6 (d, *J* = 3.2 Hz), 122.9 (d, *J* = 2.4 Hz), 116.5 (d, *J* = 21.0 Hz), 116.0 (d, *J* = 23.0 Hz), 90.9; FTIR (neat) υ 3058, 1585, 1433, 1267, 767 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_4Br_3F$ $[M]^+$: 355.7847, found: 355.7851; Anal. calcd. for $C_8H_4Br_3F$: C, 26.78; H, 1.12. Found : C, 26.88; H, 1.14.

1,3-Difluoro-5-(1,2,2-tribromovinyl)benzene (**3q**)**:**
3-(3,5-Difluorophenyl)propiolic acid (364 mg, 2.0 mmol) afforded 1,3-difluoro-5-(1,2,2-tribromovinyl)benzene (**3q**) (618 mg, 1.64 mmol, 82% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 – 6.91 (m, 2H), 6.83 (tt, *J* = 8.8, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.6 (dd, *J* = 250.5, 12.9 Hz), 142.0 (t, *J* = 10.3 Hz), 121.4 (t, *J* = 2.9 Hz), 112.1 (dd, *J* = 20.3, 6.6 Hz), 105.0 (t, *J* = 25.1 Hz), 91.8; FTIR (neat) υ 2928, 1594, 1321, 1122, 725 cm^{-1}; HRMS (FD) m/z cacld. for $C_8H_3Br_3F_2$ $[M]^+$: 373.7753, found: 373.7753; Anal. calcd. for $C_8H_3Br_3F_2$: C, 25.50; H, 0.80. Found : C, 25.51; H, 0.77.

1-(1,2,2-Tribromovinyl)-4-(trifluoromethyl)benzene (**3r**)**:**
3-(4-(Trifluoromethyl)phenyl)propiolic acid (428 mg, 2.0 mmol) afforded 1-(1,2,2-tribromovinyl)-4-(trifluoromethyl)benzene (**3r**) (695 mg, 1.7 mmol, 85% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 7.66 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.9, 131.2 (q, *J* = 32.9 Hz), 129.2, 125.6 (q, *J* = 3.6 Hz), 122.6, 123.6 (q, *J* = 272.4 Hz), 91.3; FTIR (neat) υ 3058, 1322, 1168, 1130, 752 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_4Br_3F_3$ $[M]^+$: 405.7815, found: 405.7815; Anal. calcd. for $C_9H_4Br_3F_3$: C, 26.44; H, 0.99. Found : C, 26.12; H, 1.11.

4-(1,2,2-Tribromovinyl)-1,1'-biphenyl (**3s**)**:**
3-([1,1'-Biphenyl]-4-yl)propiolic acid (444 mg, 2.0 mmol) afforded 4-(1,2,2-tribromovinyl)-1,1'-biphenyl (**3s**) (575 mg, 1.38 mmol, 69% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 7.59 - 7.56 (m, 4H), 7.50 - 7.44 (m, 5H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 140.8, 138.9, 138.6, 132.0, 129.3, 128.7, 126.9, 124.1, 122.2, 90.0; FTIR (neat) υ 3028, 1477, 1276, 816, 744 cm^{-1}; HRMS (FD) m/z cacld. for $C_{14}H_9Br_3$ $[M]^+$: 413.8254, found: 413.8254; Anal. calcd. for $C_{14}H_9Br_3$: C, 40.33; H, 2.18. Found : C, 39.99; H, 2.09.

2-(1,2,2-Tribromovinyl)naphthalene (**3t**)**:**
3-(Naphthalen-2-yl)propiolic acid (392 mg, 2.0 mmol) afforded 2-(1,2,2-tribromovinyl)naphthalene (**3t**) (563 mg, 1.44 mmol, 72% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 7.91 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 3H), 7.53 (t, *J* = 6.4 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.7, 133.3, 132.7, 128.6, 128.4, 128.4, 127.8, 127.3, 126.8, 125.7, 124.8, 90.1; FTIR (neat) υ 3056, 1503, 1272, 814, 748 cm^{-1}; HRMS (FD) m/z cacld. for $C_{12}H_7Br_3$ $[M]^+$: 387.8098, found: 387.8098; Anal. calcd. for $C_{12}H_7Br_3$: C, 36.87; H, 1.80. Found : C, 36.88; H, 1.69.

Methyl 4-(1,2,2-tribromovinyl)benzoate (**3v**)**:**
3-(4-(Methoxycarbonyl)phenyl)propiolic acid (408 mg, 2.0 mmol) afforded methyl 4-(1,2,2-tribromovinyl)benzoate (**3v**) (622 mg, 1.56 mmol, 78% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 8.05 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.9, 142.3, 129.4, 128.4, 127.5, 121.8, 89.5, 51.0; FTIR (neat) υ 2878, 1725, 1277, 748, 709 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_7Br_3O_2$ $[M]^+$: 395.7996, found: 395.7997; Anal. calcd. for $C_{10}H_7Br_3O_2$: C, 30.11; H, 1.77. Found : C, 29.92; H, 1.65.

1-(4-(1,2,2-Tribromovinyl)phenyl)ethanone (**3w**)**:**
3-(4-Acetylphenyl)propiolic acid (376 mg, 2.0 mmol) afforded 1-(4-(1,2,2-tribromovinyl)phenyl)ethanone (**3w**) (659 mg, 1.72 mmol, 86% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 7.96 (d, *J* = 8.6 Hz, 2H) 7.49 (d, *J* = 8.6 Hz, 2H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 197.1, 143.7, 137.2, 129.0, 128.4, 123.0, 90.9, 26.7; FTIR (neat) υ 3003, 1682, 1601, 1261, 716 cm^{-1}; HRMS (FD) m/z cacld. for $C_{10}H_7Br_3O$ $[M]^+$: 379.8047, found: 379.8047; Anal. calcd. for $C_{10}H_7Br_3O$: C, 31.37; H, 1.84. Found : C, 31.58; H, 1.77.

4-(1,2,2-Tribromovinyl)benzaldehyde (**3x**)**:**
3-(4-Formylphenyl)propiolic acid (348 mg, 2.0 mmol) afforded 4-(1,2,2-tribromovinyl)benzaldehyde (**3x**) (642 mg, 1.74 mmol, 87% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 10.0 (s, 1H), 7.9 (d, *J* = 8.5 Hz, 2H), 7.6 (d, *J* = 8.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.2, 145.0, 136.4, 129.8, 129.5, 122.7, 91.3; FTIR (neat) υ 3086, 1686, 1599, 1205, 776 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_5Br_3O$ $[M]^+$: 365.7891, found: 365.7891; Anal. calcd. for $C_9H_5Br_3O$: C, 29.31; H, 1.37. Found : C, 19.68; H, 1.30.

4-(1,2,2-Tribromovinyl)benzonitrile (**3y**)[8]**:**

3-(4-Cyanophenyl)propiolic acid (342 mg, 2.0 mmol) afforded 4-(1,2,2-tribromovinyl)benzonitrile (**3y**) (644 mg, 1.76 mmol, 88% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 7.69 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.7, 132.4, 129.6, 122.0, 118.1, 113.1, 91.9; FTIR (neat) υ 3089, 2229, 1603, 1401, 744 cm^{-1}; HRMS (FD) m/z cacld. for $C_9H_4Br_3N$ $[M]^+$: 362.7894, found: 362.78865; Anal. calcd. for $C_9H_4Br_3N$: C, 29.55; H, 1.10; N, 3.83. Found : C, 29.65; H, 1.33; N, 3.64.

1,1,2-Tribromohept-1-ene (**3z**)**:**
Oct-2-ynoic acid (280 mg, 2.0 mmol) afforded 1,1,2-tribromohept-1-ene (**3z**) (375 mg, 1.12 mmol, 56% yield); ^{1}H NMR (500 MHz, $CDCl_3$): colorless oil; 2.66 (t, *J* = 7.5 Hz, 2H), 1.62 (pent, *J* = 7.6 Hz, 2H), 1.36 – 1.30 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 129.8, 86.8, 40.9, 30.6, 27.3, 22.4, 14.0; FTIR (neat) υ 2956, 1455, 1205, 813, 728 cm^{-1}; HRMS (FD) m/z cacld. for $C_7H_{11}Br_3$ $[M]^+$: 331.8411, found: 331.8418; Anal. calcd. for $C_7H_{11}Br_3$: C, 25.11; H, 3.31. Found : C, 25.21; H, 3.52.

1,1,2-Tribromopent-1-ene (**3za**)**:**
Hex-2-ynoic acid (224 mg, 2.0 mmol) afforded 1,1,2-tribromopent-1-ene (**3za**) (310 mg, 1.02 mmol, 51% yield); ^{1}H NMR (500 MHz, $CDCl_3$): colorless oil; 2.66 (t, *J* = 7.4 Hz, 2H), 1.65 (sextet, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 129.6, 87.0, 42.6, 21.0, 13.0; FTIR (neat) υ 2963, 1459, 1325, 1116, 742 cm^{-1}; HRMS (FD) m/z cacld. for $C_5H_7Br_3$ $[M]^+$: 303.8098, found: 303.8108; Anal. calcd. for $C_5H_7Br_3$: C, 19.57; H, 2.30. Found : C, 19.67; H, 2.64.

General experimental procedure for acyl substitution reactions:
To a 20-mL screw cap vial added 2,2,2-tribromo-1-phenylethanone (**2a**) (2 mmol, 1.0 equiv), amine or alcohol (2 mmol, 1.0 equiv), Et_3N (4 mmol, 2.0 equiv), in THF (5.0 mL). The solution was stirred at 50 °C for 6 h. The resulting mixture charged to the separating funnel added water, extracted with EtOAc. The organic layer washed with water and dried over anhydrous $MgSO_4$. After removing the EtOAc under vacuum, the crude product was purified by column chromatography on a silica gel column with n-hexane/ethyl acetate as eluent to give the desired product.

Benzyl benzoate (**5**)[9]**:**
2,2,2-Tribromo-1-phenylethanone (**2a**) (714 mg, 2.0 mmol) afforded benzyl benzoate (**5**) (373 mg, 1.76 mmol, 88% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 8.13 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.35 (m, 7H), 5.41 (s, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.3, 135.9, 132.9, 130.0, 129.6, 128.5, 128.3, 128.1, 128.1, 66.6; FTIR (neat) 3033, 1715, 1266, 1105, 707 cm^{-1}; HRMS (FD) m/z cacld. for $C_{14}H_{12}O_2$ $[M]^+$: 212.0837, found: 212.0837; Anal. calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found : C, 79.19; H, 5.69.

***N*-Benzylbenzamide** (**6**)[9]**:**
2,2,2-Tribromo-1-phenylethanone (**2a**) (714 mg, 2.0 mmol) afforded *N*-benzylbenzamide (**6**) (388 mg, 1.84 mmol, 92% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): 7.79 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.27 (m, 5H), 6.63 (s, 1H), 4.63 (d, J = 5.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.3, 138.2, 134.3, 131.5, 128.7, 128.5, 127.8, 127.5, 126.9, 44.0; FTIR (neat) 3311, 3060, 1637, 1538, 1308, 692 cm^{-1}; HRMS (FD) m/z cacld. for $C_{14}H_{14}NO$ $[M]^+$: 211.0997, found: 211.0997. Anal. calcd. for $C_{14}H_{14}NO$: C, 79.59; H, 6.20; N, 6.63. Found : C, 79.89; H, 6.10; N, 6.53.

Acknowledgements

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (NRF-2015R1A4A1041036, NRF-2017R1A2B2002929). The spectral and HRMS data were obtained from the Korea Basic Science Institute, Gwangju center and Daegu center.

References

[1] a) J. A. Calderone, W. L. Santos, *Angew. Chem., Int. Ed.* **2014**, 53, 4154; b) S. Li, H. Ji, L. Cai, G. Li, *Chem. Sci.* **2015**, *6*, 5595; c) A. M. Martinez, J. Echavarren, I. Alonso, N. Rodriguez, R. Gomez Arrayas, J. C. Carretero, *Chem. Sci.* **2015**, *6*, 5802; d) W. Su, T.-J. Gong, Q. Zhang, Q. Zhang, B. Xiao, Y. Fu, *ACS Catal.* **2016**, *6*, 6417.

[2] a) T. Zarganes-Tzitzikas, A. Domling, *Org. Chem. Front.* **2014**, *1*, 834; b) R. C. Cioc, E. Ruijter, R. V. A. Orru, *Green Chem.* **2014**, *16*, 2958; c) Y. Zhang, Y. Zhang, C. Zhong, F. Xiao, *Sci. Rep.* **2016**, *6*, 34578; d) Y. Hayashi, *Chem. Sci.* **2016**, *7*, 866.

[3] I. Saikia, A. J. Borah, P. Phukan, *Chem. Rev.* **2016**, *116*, 6837

[4] a) B. Sosnowska, B. Huras, B. Bukowska, *Pestic. Biochem. Phys.* **2015**, *118*, 43; b) B. Sosnowska, B. Huras, A. Krokosz, B. Bukowska, *Int. J. Biol. Macromol.* **2013**, *57*, 38; c) J. J. Parlow, M. D. Mahoney, *Pestic. Sci.* **1995**, 44, 137.

[5] a) A. O. Terent'ev, S. V. Khodvkin, I. B. Krylov, Y. N. Ogibin, G. I. Nikishin, *Synthesis*, **2006**, 1087; b) P. Wu, S. Xu, H. Xu, H. Hu, W. Zhang, *Tetrahedron Lett.* **2017**, *58*, 618.

[6] M. Kodomari, H. Satoh, S. Yoshitomi, *Chem. Soc. Jap.* **1986**, 1813.

10.1002/adsc.201800851

[7] M. J. Dabdoub, J. V. Comaseto, S. M. Barros, F. Moussa, *Synth. Commun.* **1990**, *20*, 2181.
[8] V. Sriramoju, R. Jillella, S. Kurva, S. Madabhushi, *Chem. Lett.* **2017**, *46*, 560.
[9] A. Jayaraman, E. Cho, F. M. Irudayanathan, J. Kim, S. Lee, *Adv. Synth. Catal.* **2018**, *360*, 130.
[10] a) W. Gottardi, *Monatsh. Chem.* **1969**, *100*, 42; b) S. Gronowitz, S.; K. Stenhammar, L. Syensson, *Heterocycles* **1981**, *15*, 947; c) A. A. Kogon, D. E. Bochkariov, B. P. Baskrunov, A. V. Cheprakov, *Liebigs Ann. Chem.* **1992**, 879.
[11] It was reported that **4a** was formed from the decarboxylative reaction of propiolic acid. See, a) S. J. Ehrlich, E. Berliner, *J. Am. Chem. Soc.* **1978**, *100*, 1525; b) F. Homsi, G. Rousseau, *Tetrahedron Lett.* **1999**, *40*, 1495; c) D. Naskar, S. Roy, *J. Org. Chem.* **1999**, *64*, 6896; d) K.-J. Lee, K. W. Lim, D. Y. Chi, *Bull. Korean Chem. Soc.* **2001**, *22*, 549.
[12] K. Niknam, M. A. Zolfigol, E. Madrakian, E. Ghaemi, *S. Afr. J. Chem.* **2007**, *60*, 109.
[13] A. E. J. de Nooy, A. C. Besemer, *Tetrahedron* **1995**, *51*, 8023.
[14] B. Hasimujiang, J. Zen, Z. Yanhui, A. A. Rexit, *Synth. Commun.* **2018**, *48*, 887.

10.1002/adsc.201800851

FULL PAPER

Decarboxylative Tribromination for the Selective Synthesis of Tribromomethyl Ketone and Tribromovinyl Derivatives

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Aravindan Jayaraman, Eunjeong Cho, Jimin Kim, and Sunwoo Lee*