

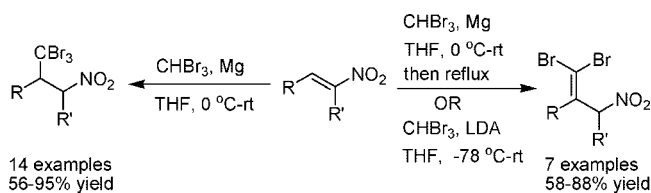
Facile Synthesis of β -Tribromomethyl and Dibromomethylenated Nitroalkanes via Conjugate Addition of Bromoform to Nitroalkenes

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Addition of bromoform to conjugated nitroalkenes in the presence of Mg provided β -tribromomethyl nitroalkanes in good to excellent yields and diastereoselectivity. These novel Michael adducts, formed under radical conditions, underwent elimination of HBr in the same pot under reflux to afford β -dibromomethylenated nitroalkanes in good yield. Alternatively, a one-pot high yielding synthesis of the dibromides was possible under anionic conditions via LDA mediated addition of bromoform to nitroalkenes.

Polyhalonitro compounds exhibit potential biological properties.¹ Such compounds are also attractive synthetic intermediates owing to the ability of both halo and nitro groups to undergo diverse transformations. For instance, a trihalomethyl group can be readily converted to carboxylic acids² and a dihalomethylidene functionality is amenable for transformation to acetylenes,³ crossed enediynes,⁴ carbo- and heterocycles,⁵ and amides

and carboxylic acids,⁶ to mention a few. Similarly, the versatility of nitroalkyl moiety to undergo transformations to a variety of functionalities such as carbonyls, oximes, hydroxylamines, amines, nitriles, and 1,3-dipoles such as nitrile oxides and silyl nitronates is well-documented in the literature.⁷

Haloform is a ready source of trihalomethyl and dihalomethylene and the reaction of haloform with alkenes under anionic⁸⁻¹² and radical¹³ conditions is well-established. The base mediated reaction, in the absence¹² and more often in the presence⁸⁻¹¹ of phase transfer catalysts (PTC), is the method of choice for the cyclopropanation of alkenes. While the formation of cyclopropane derivatives from unactivated alkenes presumably takes place via dibromocarbene addition, such product formation from activated alkenes appears to proceed via an initial Michael addition of the trihalomethyl carbanion followed by intramolecular cyclization pathway.^{9,10} In the case of activated alkenes, the Michael adducts and their β -elimination products, the alkyldiene dibromides, are also isolated.¹⁰

As part of our sustained interest in the chemistry of conjugated nitroalkenes,¹⁴ we surveyed the literature reports on the reactivity of haloform with nitroalkenes under different conditions. Makosza and Kwast reported one example of potassium *tert*-butoxide promoted addition of chloroform to β -nitrostyrene from which they isolated 1-(1,1-dichloro-3-nitroprop-1-en-2-yl)benzene in moderate yield.¹⁰ Cunico and Zhang investigated the CsF catalyzed reaction of trimethylsilyltrichloromethane (CCl₃SiMe₃) with β -nitroalkenes affording β -(trichloromethyl)nitroalkanes in low to moderate yields.¹⁵ However, the reaction of an α,β -disubstituted nitroethylene with bromoform mediated by aq NaOH/*n*-Bu₄N⁺Cl⁻ provided the cyclopropanation product (in low yield) rather than the Michael adduct.¹⁶ To our knowledge, there are no general and efficient methods for the synthesis of β -trihalomethyl and dihalomethylidene nitroalkanes.

Notably, when we reacted β -substituted nitroethylene **1a** with bromoform under the above PTC conditions,¹⁶ we isolated only polymeric material. However, we were delighted to isolate the tribromonitroalkane **2a** when **1a** was treated with bromoform in the presence of Mg in THF (Scheme 1).¹⁷ Our optimization studies revealed that an excess of magnesium (8 equiv) and

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SCHEME 1

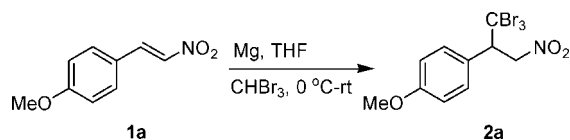


TABLE 1. Mg Mediated Addition of Bromoform to Nitroalkenes **1a**^a

entry	1	R	2	% yield ^b of 2
1	1a	4-OMe-Ph	2a	93
2	1b	2,4-(MeO) ₂ -Ph	2b	56
3	1c	2,5-(MeO) ₂ -Ph	2c	74
4	1d	3,4-(MeO) ₂ -Ph	2d	55
5	1e	3,4-(−OCH ₂ O−)Ph	2e	58
6	1f	3-MeO-4-OH-Ph	2f	50 ^c
7	1g	4-NMe ₂ -Ph	2g	63
8	1h	4-NO ₂ -Ph	2h	89
9	1i	4-F-Ph	2i	75
10	1j	2-(O-allyloxy)phenyl	2j	52
11	1k	3-furyl	2k	72
12	1l	3-thienyl	2l	95

^a THF:CHBr₃ (10:1 v/v, 4 M). ^b Isolated yield after purification by silica gel column chromatography. ^c Excess magnesium and bromoform were used.

bromoform (16 equiv) would be desirable to ensure complete consumption of the starting nitroalkene **1a**. Finally, the best yield of the Michael adduct **2a** (93%) was obtained by employing further excess of bromoform (22 equiv) while maintaining a THF:bromoform ratio of 10:1 and an overall concentration of 4 M for the reaction mixture (see Tables S1–S4, Supporting Information).

Having fully optimized the conditions for the conjugated addition of bromoform to *p*-methoxynitrostyrene **1a**, we subjected a variety of nitroalkenes, viz. β -aryl **1a–j** (entries 1–10) and β -heteroaryl **1k–l** (entries 11 and 12) nitroethylenes to the above reaction conditions and were pleased to isolate the Michael adducts **2a–l** in good to excellent yield (Table 1).

The structure of tribromides **2** was confirmed from their spectral characteristics.¹⁸ Later, unequivocal structural assignment was made via single crystal X-ray analysis of a representative tribromide **2c** (see the Experimental Section).

Subsequently, the diastereoselectivity in the Mg mediated addition of bromoform was investigated by using nitroalkenes **3a–c** (Table 2). While the formation of adducts **4a,b** from cyclic nitroalkenes **3a,b** took place in good yield (60% and 72%, respectively) and 100% diastereoselectivity (Table 2, entries 1 and 2), similar adduct **4c** from open chain nitroalkene **3c** proceeded in lower yield (56%) and selectivity (75:25, entry 3).

(18) Appearance of CBr₃ carbon in the range of δ 39–45 in ¹³C NMR and four peaks for the molecular ion (e.g., M⁺, [M + 2]⁺, [M + 4]⁺, and [M + 6]⁺) in ca. 1:3:3:1 ratio in the mass spectrum.

(19) The diaxial coupling between the two methine protons in ¹H NMR (8.4 Hz in **4a** and 7.6 Hz in **4b**) was confirmed by ¹H–¹H COSY experiment. NOE is also observed between the two vicinal protons. The structure was further unambiguously established by single crystal X-ray analysis (see the Supporting Information).

(20) A coupling of 9.2 Hz between the benzylic proton and the proton α to nitro group in ¹H NMR of **4c** confirmed that the two are anti to each other. The absence of any NOE between Ar and CH₃ confirmed the trans relationship between them and between CBr₃ and NO₂ (see the Supporting Information).

TABLE 2. Mg Mediated Diastereoselective Addition of Bromoform to Nitroalkenes **3a**

entry	3	R, R'	% yield ^b of 4	dr ^c
1	3a	(CH ₂) ₄	60	100:0 ^d
2	3b	O(CH ₂) ₃	72	100:0 ^d
3	3c	3,4-(OCH ₂ O)Ph, Me	56	75:25 ^e

^a THF:CHBr₃ (10:1 v/v, 4 M). ^b Isolated yield after purification by silica gel column chromatography. ^c Trans/cis or anti/syn. ^d CBr₃ and NO₂ are trans e.e., see ref 19. ^e CBr₃ and NO₂ are anti in the major isomer, see ref 20.

TABLE 3. One-Pot Synthesis of Alkylidene Dibromides **5** from Nitroalkenes **1** and Bromoform under Mg Mediated Conditions^a

entry	1	R	5	% yield ^b of 5
1	1a	4-OMe-Ph	5a	58
2	1d	3,4-(MeO) ₂ -Ph	5d	51
3	1e	3,4-(−OCH ₂ O−)Ph	5e	65
4	1g	4-NMe ₂ -Ph	5g	72
5	1h	4-NO ₂ -Ph	5h	62
6	1k	3-furyl	5k	60
7	1l	3-thienyl	5l	58

^a Method A. ^b Isolated yield after purification by silica gel column chromatography.

Since the tribromides **2** and **4** were synthesized and isolated under mild reaction conditions, we felt that further elimination of HBr to afford synthetically useful alkylidene dibromide **5** would take place under forcing conditions. To this end, the reaction mixture was refluxed for 24 h, which resulted in the formation of dibromides **5** in good to high yield (Table 3). It may be noted that the one-pot transformation of nitroalkenes **1** to alkylidene dibromides **5** has been demonstrated for selected aromatic nitroalkenes with electron donating groups (**1a**, **1d**, **1e**, and **1g**, entries 1–4) and electron withdrawing groups (**1h**, entry 5) as well as for heteroaromatic nitroalkenes **1k** and **1l** (entries 6 and 7, Table 3).

As in the case of **2** and **4**, spectral characteristics enabled us to assign the structure of dibromides **5**.²¹ Further, the structure of dibromide **5** was unambiguously confirmed as in the case of **2** via single crystal X-ray analysis of a representative compound **5a** (see the Experimental Section).

Requirement of an excess of Mg and bromoform in the above procedure for the synthesis of tribromides **2** and **4** and dibromides **5** prompted us to further explore the role of strong bases in promoting the generation of the tribromomethyl carbanion and its addition to nitroalkenes (see Tables S5 and S6, Supporting Information).²² Thus, while the reaction of nitroalkene **1a** with bromoform mediated by bases such as NaOMe, *t*-BuOK, and NaH in THF provided the desired dibromide **5a** in low to moderate yield, excess LDA (6 equiv) provided **5a** in high yield (74%). Quite remarkably, unlike in

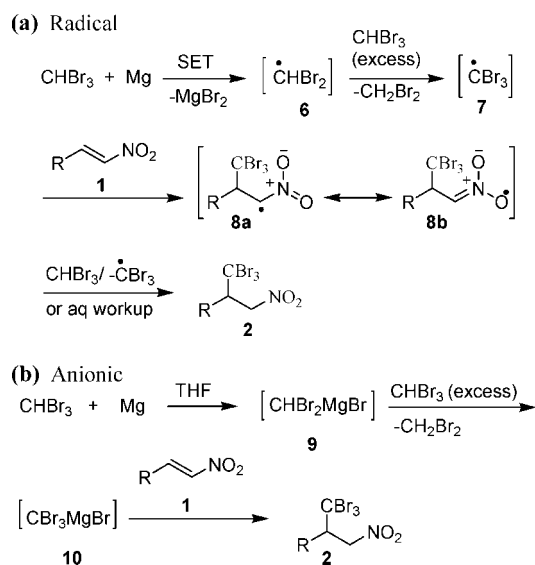
(21) Appearance of CBr₂ carbon in the range of δ 99–105 in ¹³C NMR and three peaks for the molecular ion (e.g., M⁺, [M + 2]⁺, and [M + 4]⁺) in ca. 1:2:1 ratio in the mass spectrum.

(22) The pK_a reported for bromoform is 11.8: Scharlin, P. *Acta Chem. Scand. Ser. A: Phys. Inorg. Chem.* **1987**, *A41*, 480.

TABLE 4. One-Pot Synthesis of Alkylidene Dibromides **5** from Nitroalkenes **1** and Bromoform under LDA Mediated Conditions^a

entry	1	R	5	% yield ^a of 5
1	1a	4-OMe-Ph	5a	74
2	1d	3,4-(MeO) ₂ -Ph, H	5d	66
3	1e	3,4-(−OCH ₂ O−)Ph	5e	72
4	1g	4-NMe ₂ -Ph	5g	77
5	1h	4-NO ₂ -Ph	5h	76
6	1k	3-furyl	5k	88
7	1l	3-thienyl	5l	77

^a Method B. ^b Isolated yield after purification by silica gel column chromatography.

SCHEME 2. Mechanistic Pathways Considered for the Mg Mediated Addition of Bromoform to Nitroalkenes **2a**

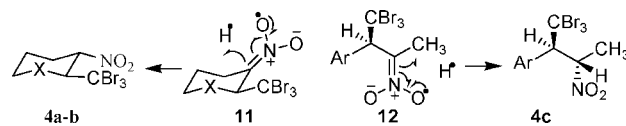
the case of Mg mediated reaction, this reaction required only 1.1 equiv of bromoform.

Under the above optimized conditions, i.e., bromoform (1.1 equiv) and LDA (6 equiv) in THF at $-78\text{ }^{\circ}\text{C}$ to rt, representative β -arylated nitroethylenes with electron donating (**1a**, **1d**, **1e**, and **1g**, entries 1–4) and electron withdrawing (**1h**, entry 5) groups as well as β -heteroarylated nitroethylenes (**1k**, **l**, entries 6 and 7) have been transformed to dibromides **5** in excellent yield (Table 4). A comparison of Tables 3 and 4 shows that the LDA mediated reaction is superior to the Mg mediated reaction both in terms of the product yields and the requirement of bromoform.

While the LDA mediated reaction presumably proceeds via anionic mechanism, an alternative radical mechanism is also a probability under Mg mediated conditions. For instance, single electron transfer (SET) from Mg could generate dibromomethyl radical **6**,²³ which could abstract H radical from bromoform to generate tribromomethyl radical **7** (Scheme 2a). Conjugate addition of radical **7** to nitroalkene **1** could provide tribromide **2** via resonance stabilized nitroalkyl radical **8**.^{24,25}

An alternative mechanism outlined in Scheme 2b envisages initial formation of dibromomethylmagnesium bromide **9** from

(23) In bromoform a carbon–halogen bond is broken in the initiation step: Weizmann, M.; Israeleshvili, S.; Halevy, A.; Bergmann, F. *J. Am. Chem. Soc.* **1947**, *69*, 2569.

SCHEME 3

bromoform and Mg and its abstraction of proton from excess bromoform in the medium to generate tribromomethylmagnesium bromide **10** (Scheme 2b). Conjugate addition of **10** to nitroalkene **1** provides tribromide **2**.

Although the absence of any cyclized product when nitroalkene **1j**²⁶ was subjected to Mg mediated reaction (entry 10, Table 1, and in the Supporting Information, Scheme S1) prompted us to rule out the radical mechanism,²⁷ further confirmation of the mechanism was sought by reacting a nitroalkene with a radical trap such as 1,4-cyclohexadiene. Thus, the Mg mediated reaction of nitroalkene **1a** with bromoform in the presence of 3 equiv of 1,4-cyclohexadiene provided **2a** in marginally lower yield (80%). Although GC and NMR analysis of the crude product did not indicate the formation of benzene, the radical mechanism could not be ruled out because a viscous liquid isolated, besides **2a**, whose spectral characteristics indicated it to be an oligomeric/polymeric material arising from 1,4-cyclohexadiene.²⁸

Subsequently, the EPR analysis of the reaction mixture was carried out at 0, 5, 10, 15, 20, 25, 30, 35, and 45 min time intervals and finally after 5 h. While no EPR signals were observed up to 15 min, the analysis after 20 min showed the appearance of two EPR signals with *g* values 2.16 and 2.09 attributable to two separate radical species, presumably the nitroalkyl radical **8**²⁹ and the CBr₃ radical **7**.³⁰ The intensity of these peaks remained high during subsequent measurements (25, 30, 35, and 45 min). After 5 h, the intensity of the signals decreased drastically indicating the decay of the radicals.

The trans/anti stereochemistry of products **4a–c**^{19,20} arises from addition of hydrogen radical from the cis/syn side of the CBr₃ group, i.e., *Re* face of the nitronate radical, as in **11–12** (Scheme 3, Table 2).

Finally, a simple and convenient synthesis of β,γ,γ -triaryl nitroalkenes, e.g., **13**, via Suzuki coupling of dibromide **5a** with phenyl boronic acid is shown in Scheme 4 (see the Supporting Information for experimental details).

In conclusion, a convenient methodology has been developed for the one-pot synthesis of β -dibromomethylenated nitroalkanes

(24) (a) For addition of bromoform to fluoroethylene in the presence of radical initiator: see ref 13. (b) A radical mechanism was proposed for the reaction of cyclohexene with bromoform in the presence of Mg to form the cyclopropanation product: see ref 17.

(25) For evaluation of the capacity of an α -nitroalkyl radical for hydrogen abstraction see: Bolsman, T. A. B. M.; Verhoeven, J. W.; de Boer, T. J. *Tetrahedron* **1975**, *31*, 1015.

(26) (a) Carter, M. E.; Nash, J. L., Jr.; Druke, E. W., Jr.; Schwietert, J. W.; Butler, G. B. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 937. See also: (b) Deb, I.; John, S.; Nambhothiri, I. N. N. *Tetrahedron* **2007**, *63*, 11991.

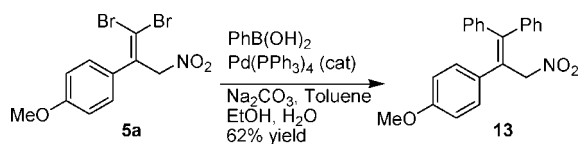
(27) Formation of cyclic products as an evidence for SET mechanism when the substrate has suitably located double bonds: (a) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414. (b) Ashby, E. C.; Pham, T. N.; Amrollah-Madjabadi, A. J. *Org. Chem.* **1991**, *56*, 1596.

(28) The absence of benzene may be due to the inability of the highly resonance stabilized nitroalkyl radical to abstract H radical from 1,4-cyclohexadiene (the product **2a** could be formed during aqueous workup) or polymerization rather than aromatization of the 1,4-cyclohexadienyl radical.

(29) For characterization of an α -nitroalkyl radical by EPR via spin trapping experiment with 2-methyl-2-nitrosopropane: Bolsman, T. A. B. M.; de Boer, T. J. *Tetrahedron* **1975**, *31*, 1019.

(30) EPR investigation of CBr₃ radical remains obscure: (a) Stoesser, R.; Proesch, U. *Z. Chem.* **1983**, *23*, 382. (b) Chen, S.; Ge, M.; Guo, S.; Xu, L.; Tao, F. *Youji Huaxue* **1990**, *10*, 74; *Chem. Abstr.* **1990**, *113*, 39784. (c) Karasev, A. L.; Petrova, A. A.; Zver'kov, V. A.; Vannikov, A. V. *Khimiya Vysokikh Energii* **1991**, *25*, 71; *Chem. Abstr.* **1991**, *114*, 196168.

SCHEME 4



via conjugate addition of bromoform to nitroalkenes in the presence of Mg or LDA. The intermediate β -tribromomethyl nitroalkanes, including those formed in a diastereoselective fashion, were also isolated under controlled Mg mediated conditions. Although excess reagent is necessary to obtain high yields of these synthetically and biologically relevant products, the relatively inexpensive nature of the reagent, Mg or LDA, and easily adaptable reaction conditions render this methodology an attractive one. In the Mg mediated reaction, an anionic mechanism has been ruled out and a radical mechanism has been confirmed by chemical and spectroscopic methods. Detailed studies on the mechanism, the asymmetric version of this conjugate addition, and various applications of the products will be reported in due course.

Experimental Section

General Procedure for Mg Mediated Addition of Bromoform to Nitroalkenes 1. To a stirred solution of magnesium (96 mg, 8 mmol) and nitroalkene **1** (0.5 mmol) in THF (10 mL) was added bromoform (2.7 g, 1 mL, 11 mmol) dropwise over a period of 10 min at 0 °C. The reaction mixture was gradually brought to room temperature over a period of 0.5 h during which the solution turned dark brown. The reaction mixture was subsequently quenched with saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with ethyl acetate (5×10 mL) and the combined organic layers were washed with H_2O (3×10 mL), dried (anhyd Na_2SO_4), and concentrated in vacuo to afford the crude product, which was subjected to silica gel column chromatography (ethyl acetate/hexane mixture, gradient elution) to afford pure 1,4-adduct **2**. Representative experimental data: **2-(1,1,1-Tribromo-3-nitroprop-2-yl)-1,4-dimethoxy-benzene (2c)**: colorless solid; yield 178 mg, 74%; mp 109 °C; IR (KBr, cm^{-1}) 2998 (m), 2965 (m), 2934 (w), 2835 (w), 1552 (vs), 1504 (s), 1429 (m), 1375 (m), 1292 (s), 1222 (s), 1053 (m), 1024 (m), 815 (m), 781 (m), 687 (m), 533 (s); ^1H NMR (CDCl_3 , 400 MHz) δ 3.78 (s, 3H), 3.86 (s, 3H), 5.00–5.06 (br m, 1H), 5.33 (dd, $J = 13.2, 3.5$ Hz, 1H), 5.50–5.60 (br m, 1H), 6.90 (ABq, $J = 15.5$ Hz, the lower half is further split into d, $J = 8.8$ Hz, 2H), 7.26 (br m, 1H); ^{13}C NMR (CDCl_3 , 400 MHz) δ 42.3, 54.5, 55.7, 56.5, 78.0, 112.6, 113.7, 114.6, 124.0, 152.4, 153.1; MS (ES-, Ar) m/z (rel intensity) 486 ($[\text{MNa} + 4]^+$, 2), 484 ($[\text{MNa} + 2]^+$, 10), 482 (MNa^+ , 10), 480 ($[\text{MNa} - 2]^+$, 2), 363 (10), 361 (15), 253 (94), 251 (96), 212 (100); HRMS (ES-, Ar) calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_4\text{Br}_3\text{Na}$ (MNa^+) 481.8214, found 481.8191. For X-ray data, see the Supporting Information.

General Procedure for the Preparation of Alkylidene Dibromides 5 from Nitroalkenes 1. Method A: Magnesium

Mediated Reaction of Bromoform with Nitroalkenes 1. To a stirred solution of magnesium (96 mg, 4 mmol) and nitroalkene **1** (0.5 mmol) in THF (10 mL) was added bromoform (2.7 g, 1 mL, 11 mmol) dropwise over a period of 10 min at 0 °C. The reaction mixture was gradually brought to room temperature over a period of 0.5 h during which the solution turned dark brown. After the nitroalkene was fully consumed (monitored by TLC), the reaction mixture was refluxed for 24 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with ethyl acetate (5×10 mL) and the combined organic layers were washed with H_2O (3×10 mL) and dried (anhyd Na_2SO_4). The solvent was concentrated in vacuo and the crude residue was subjected to silica gel column chromatography (ethyl acetate/hexane mixture, gradient elution) to obtain pure alkylidene dibromide **5**.

Method B: LDA Mediated Reaction of Bromoform with Nitroalkenes 1. To a stirred solution of nitroalkene **1** (0.5 mmol) and bromoform (0.139 g, 0.55 mmol) in THF (10 mL) was added LDA (3 mmol, generated from 3 mmol of *n*-BuLi and 3.3 mmol of diisopropylamine in THF (5 mL) at 0 °C) dropwise over a period of 10 min at -78 °C. Low temperature was maintained for another 3 h and then the reaction mixture was gradually brought to ambient temperature. The resulting dark brown mixture was stirred at room temperature overnight then quenched by saturated aqueous NH_4Cl (5 mL), and the aqueous layer was extracted with ether (5×10 mL). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated in vacuo to obtain crude alkylidene dibromide **5**, which was then subjected to silica gel column chromatography (ethyl acetate/hexane mixture, gradient elution) to afford pure **5**. Representative experimental data: **1-(1,1-Dibromo-3-nitroprop-1-en-2-yl)-4-methoxybenzene (5a)**: yellow solid; yield from method A 108 mg, 62%, and from method B 129 mg, 74%, mp 88 °C; IR (KBr, cm^{-1}) 3019 (s), 2966 (m), 1607 (m), 1560 (m), 1510 (m), 1367 (m), 1295 (m), 1216 (s), 1069 (w), 1031 (m), 773 (vs), 669 (s); ^1H NMR (CDCl_3 , 300 MHz) δ 3.82 (s, 3H), 5.39 (s, 2H), 6.92 (dt, $J = 6.7, 2.2$ Hz, 2H), 7.21 (dd, $J = 6.7, 2.2$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.2, 80.2, 100.8, 114.2, 129.4, 129.6, 135.9, 159.9; MS (ES-, Ar) m/e (rel intensity) 352 ($[\text{M} + 3]^+$, 35), 350 ($[\text{M} + 1]^+$, 100), 348 ($[\text{M} - 1]^+$, 35); HRMS (ES-, Ar) calcd for $\text{C}_{10}\text{H}_8\text{NO}_3\text{Br}_2$ ($[\text{M} - 1]^+$) 347.8871, found 347.8886; for X-ray data, see the Supporting Information.

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Supporting Information Available: Optimization tables, X-ray data tables, ORTEP diagrams, complete experimental procedures, characterization data, and copies of NMR and ESR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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