Halide Anion Activated Reactions of Michael Acceptors with Tropylium Ion

Mohanad A. Hussein, Uyen P. N. Tran, Vien T. Huynh, Junming Ho, Mohan Bhadbhade, Herbert Mayr, **Thanh Vinh Nguyen**

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Tropylium bromide undergoes non-catalyzed, regioselective additions to a large variety of Michael acceptors. In this way, acrylic esters are converted into β -bromo- α -cycloheptatrienyl-propionic esters. The reactions are interpreted by nucleophilic attack of bromide ions at the electron-deficient olefins and trapping of the incipient carbanion by the tropylium ion. Quantum chemical calculations were performed to elucidate the analogy to the amine or phosphine-catalyzed Rauhut-Currier reactions. Subsequent synthetic transformations of the bromo-cycloheptatrienylated adducts are reported.

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Halide Anion Activated Reactions of Michael Acceptors with Tropylium Ion

Mohanad A. Hussein,^[a] Uyen P. N. Tran,^[a] Vien T. Huynh,^[b] Junming Ho,^[a] Mohan Bhadbhade,^[c] Herbert Mayr^[d] and Thanh V. Nguyen^{*[a]}

Abstract: Tropylium bromide undergoes non-catalyzed, regioselective additions to a large variety of Michael acceptors. In this way, acrylic esters are converted into β -bromo- α -cycloheptatrienyl-propionic esters. The reactions are interpreted by nucleophilic attack of bromide ions at the electron-deficient olefins and trapping of the incipient carbanion by the tropylium ion. Quantum chemical calculations were performed to elucidate the analogy to the amine or phosphine-catalyzed Rauhut-Currier reactions. Subsequent synthetic transformations of the bromo-cycloheptatrienylated adducts are reported.

Michael acceptors are versatile building blocks in organic synthesis.^[1] Their activation by tertiary amines and phosphines in Morita-Baylis-Hillman and Rauhut-Currier reactions is well-established (Scheme 1).^[1e,2] In recent years *N*-heterocyclic carbene-catalyzed reactions of Michael acceptors have become increasingly popular.^[1b-d,3] [4] To our knowledge, halide ions have so far not been used to initiate reactions of Michael acceptors because the Lewis basicity of Br⁻ and Cl⁻ towards C-centered Lewis acids is 4 - 10 orders of magnitude smaller than that of the commonly employed phosphines and amines.^[5] In this communication we will demonstrate, however, that halide ion addition to Michael acceptors is possible when the emerging carbanion is stabilized through ion pairing with a tropylium ion,^[6] which possibly represents a first example of a more general reaction principle for linking Michael acceptors with stabilized carbocations. The transformations reported in this communication provide an efficient access to a wide range of synthetically valuable^[7] substituted cycloheptatrienes.

While tropylium salts have been known to trigger polymerization reactions of electron-rich alkenes,^[8] we found that tropylium bromide (**2a**) reacted with electron-deficient alkenes such as methyl acrylate (**1a**) to give the bromocycloheptatrienylated adduct **4a** in a highly regioselective manner (Procedure A, Table 1). The resulting products correspond to those of the TiCl₄-induced Baylis-Hillman reactions^[9] and the tandem thiol-mediated Rauhut Currier reactions.^[10] One may consider these reactions as the nucleophilic counterparts of the Lewis acid catalyzed additions of alkyl halides to nucleophilic alkenes (Prins reaction)^[11] and as heterolytic variants of the Kharasch radical additions^[12] to olefins. This new chemical transformation thus

Scheme 1. Nucleophilic activation of Michael acceptors for reactions with electrophiles.

allows direct haloalkylation of electron-deficient olefins in a catalyst-free, metal-free and non-radical fashion.^[12b,13]

Optimization of the reaction with methyl acrylate (**1a**, see page S3 in the SI)^[14] showed that slightly better yields of **4a** were obtained when we used a combination of tropylium tetrafluoroborate (**2b**) and TMSBr in DCE (Procedure B, Table 1), which is a practical way to avoid handling of the hygroscopic tropylium bromide.^[15] Tropylium salt **2b** reacted with Me₃SiBr (TMSBr) *instantaneously* to give TMSF and a mixture of tropylium bromide and BF₃ (which coordinate to give tropylium bromotrifluoroborate,^[16] see page S5 in the SI for more details). This mixture renders the bromocycloheptatrienylation process in a similar way as tropylium bromide. Other bromide sources such as alkali- or tetrabutylammonium bromide in combination with tropylium tetrafluoroborate gave unsatisfactory results.^[14]

Under these optimized reaction conditions, we were able to carry out the bromocycloheptatrienylations of a series of monosubstituted Michael acceptors (Table 1) with electrophilicity parameters^[17] ranging from $-24 < E < -14$ in good yields. Some substrates were functionalized using both Procedures A and B (**4a**, **4b**, **4c**, **4d**, **4i**, **4j**, **4l**, **4n**, Table 1). Acrylates with bulky alkyl groups (**1e** and **1g**), reacted with cleavage of the esters to form the corresponding carboxylic acid **4e**. C-C multiple bonds without acceptor substituents (**1i** and **1j**) and amide groups (**1k**) tolerated the reaction conditions. However, vinyl sulfone and several 1,1- and 1,2-disubstituted Michael acceptors did not react under various conditions (see page S16 in the SI for more details on other non-reacting substrates).^[14] Replacement of TMSBr by either TMSCl or TMSI in Procedure B (Table 1) afforded comparable yields of the chloro- and iodocycloheptatrienylated adducts **4aCl** and **4aI**, respectively. Tropylium fluoride did not react, probably because of the covalent nature of this compound.

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Table 1. Halocycloheptatrienylation reactions of Michael acceptors.^[a]

 DCE, rt, 36 h [Procedure A]			 DCE, rt, 24 h [Procedure B]		
Substrate ^[b]	Product	Yield	Substrate ^[b]	Product	Yield
		67% [A] 75% [B]			73% [B]
		55% [B] with TMSCl as 3			82% [B]
		66% [B] with TMSI as 3			75% [B]
		70% [A] 73% [B]	Acrylate-PEG5-Acrylate 1h ^[c]		63% [B]
		59% [A] 68% [B]			70% [A] 77% [B]
		64% [A] 71% [B]			59% [A] 78% [B]
		91% [B]			77% [A] 79% [B]
		71% [B]			68% [A] 76% [B]
		67% [B] ^[c]			64% [B]

[a] Reaction conditions: **[A]** **1** (1.0 mmol) and **2a** (1.0 mmol) in DCE (10 mL), rt, 36 h; **[B]** **1** (1.0 mmol) and **2b** (1.0 mmol) in DCE (10 mL) then **3** (1 mmol), rt, 24 h. [b] When there is steric hindrance at the α -position of the electron-withdrawing group, the reaction did not work. A full list of non-reactive Michael acceptors we tested can be found page S16 in the SI. [c] With 2.0 equivalents of **2a** or **2b** and **3**, the mono-cycloheptatrienylation product was only formed in trace amounts.

Butenolide **1q** reacted differently and gave cycloheptatriene **4q** and γ -ketoacid **4q'**. Treatment of the crude mixture of **4q** and **4q'** with aqueous HCl solution resulted in the quantitative formation of **4q'** (Scheme 2). This reaction can be rationalized by the tautomerization of butenolide **1q** to 2-hydroxyfuran, which is subsequently attacked by the tropylium ion to produce **4q** (see pages S17-18 in the SI for a possible mechanistic pathway for the formation of **4q'**).

Scheme 2. Reaction with butenolide **1q**

Electron-deficient alkynes behaved similarly to their olefinic analogues. Thus propiolates **5a,b** and dimethyl acetylene dicarboxylate **5c** (Scheme 3) reacted smoothly with tropylium tetrafluoroborate and TMSBr to give *E/Z*-mixtures of the corresponding bromoalkenes **6a-c**, with the *Z*-isomers being major products.

Scheme 3. Halocycloheptatrienylation reactions of electron-deficient alkynes.

Figure 1. M06-2X/6-31+G(d,p) + SMD (dichloroethane) free energy profile. Distances are shown in Å. Energy levels are not to scale.

Density functional theory (M06-2X/6-31+G(d,p)^[18] and SMD^[19]) calculations were carried out to investigate the mechanism of the reaction of methyl acrylate (**1a**) with tropylium bromide **2a**, which exists as ion-pair in DCE solution, 21.8 kJ mol⁻¹ more stable than the separate ions.^[20] In contrast to the mechanism of related Baylis-Hillman and Rauhut-Currier reactions, where DABCO was calculated to add to methyl acrylate (**1a**) with endergonic formation of a zwitterion ($\Delta G^0 = +65$ kJ mol⁻¹ in acetonitrile)^[21] the analogous covalent adduct of Br⁻ to **1a** was neither found as a local minimum in the gas phase nor in solution. This finding is not surprising in view of the fact that the DABCO-adduct is in a very shallow local minimum (barrier for decomposition 8 kJ mol⁻¹)^[21] and the Lewis basicity of Br⁻ toward C-centers is 36 kJ mol⁻¹ lower than that of DABCO.^[5]

However, when tropylium bromide (**2a**) instead of free Br⁻ was combined with methyl acrylate **1a** in DCE, the nucleophilic attack of Br⁻ at **1a** was electrophilically assisted by the tropylium ion as shown by **TS-11** in Figure 1 (pathway a). Though adduct **4a** is thus formed by a concerted pathway, the Wiberg bond indices (C-Br = 0.502, C-C = 0.187) show that the formation of the C-Br bond is considerably further advanced in **TS-11** than the formation of the new C-C bond. Foregoing nucleophilic attack by bromide supported by electrophilic attack of the tropylium ion can also be derived from the relative lengths of the two new σ -bonds in the transition state. Whereas the new C-Br bond (2.39 Å) has the 1.23-fold length of a covalent C-Br bond, the new C-C bond (2.48 Å) has the 1.63-fold length of the C-C bond in the product.

An alternative pathway for the reaction of tropylium bromide with **1a** may be initiated by electrophilic attack of the tropylium ion at the carbonyl oxygen of **1a** to give carboxonium ion **8** (Figure 1, pathway b). This intermediate may either undergo a retroaddition with regeneration of the reactants or combine with Br⁻ to give ketene acetal **10**, which might undergo a subsequent sigmatropic rearrangement (red arrows in structure **10**) to yield

4a. Though we were not able to identify a transition state for the last step, pathway (b) can already be ruled out due to the fact that the barrier for formation of **10** is higher than that for the direct formation of **4a** via pathway (a).

An *anti*-addition as shown in **TS-11** may also be preferred in reactions with acetylenic Michael acceptors. This could account for the predominant formation of the Z-isomers of **6a-c** (Scheme 3).

Cycloheptatriene derivatives are useful building blocks in organic synthesis, as demonstrated by the Echavarren group and others.^[7a,7b] To demonstrate the synthetic utility of our readily accessible bromocycloheptatriene products, some preliminary work on further functionalization of a representative compound, product **4a**, was carried out and reported in Scheme 4. Dehydrobromination reaction of product **4a** afforded 95% of cycloheptatrienyl acrylate **12**, potentially a useful monomer for redox active polymers. Compound **12** can be considered as a formal Morita-Baylis-Hillman-type product from methylacrylate **1a** and tropylium ion as the electrophile. However, such products cannot be formed directly by phosphine (Ph₃P) or tertiary amine (DABCO) mediated reactions, as the tropylium ion will coordinate to these nucleophilic catalysts and thus deactivate them.

On the other hand, because cycloheptatriene is a versatile moiety for cycloaddition reaction,^[22] we thus demonstrated this reactivity by a reaction between **4a** and maleimide, which resulted in the norcaradiene-type [4+2] cycloaddition adduct **13** as a mixture of two enantiomers. The structure of this compound was confirmed by X-ray crystallographic analysis (see X-ray crystal structure in page S30 in the SI),^[23] which revealed the exclusive *endo*-selectivity and the diastereoselectivity of the cycloaddition reaction.

Scheme 4. Further functionalizations of bromocycloheptatrienylated product.

Given that tropylium moiety (C7) can potentially be oxidative ring-contracted to give the phenyl ring (C6),^[24] we treated cycloheptatriene **4a** with nitrosonium tetrafluoroborate^[25] to generate the tropylium derivative *in situ* then directly oxidize it in the same reaction pot with hydrogen peroxide.^[26] Interestingly, the reaction worked as expected to give the ring-contracted product **14** in good yield. In another study, treatment of adduct **4a** with tellurium tetrachloride^[27] led to the rearrangement of the cycloheptatriene ring to the benzyl group in conjunction with the addition of one chlorine atom to afford product **15**, an interesting dihalogenated ester. All products **12–15** in Scheme 4 are novel compounds and accessible in 1–2 steps from methylacrylate **1a** using our newly developed chemical transformation.

In conclusion, we have developed a new method using halide ions to activate electron-deficient olefins for nucleophilic attack at tropylium ions. Since one can expect analogous reactions of Michael acceptors with other types of stabilized carbocations (including iminium ions), the generality of this approach for the difunctionalization of electron-deficient olefins in a catalyst-free, metal-free and non-radical fashion is presently investigated. The adducts produced by our protocol have enormous potential in organic synthesis as the cycloheptatriene moiety can be used as a building block to quickly access unprecedented structures.

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Supporting Information

Table of Contents

General Methods.....	2
Table S1. Optimization Studies	3
General procedures for the reactions of Michael acceptors with tropylium salts.....	4
Mechanistic studies.....	5
Characterization data of products in Table 1	7
Unreactive substrates	16
Characterization of products in Scheme 2	17
Characterization of products in Scheme 3	19
Characterization data of products in Scheme 4.....	21
References.....	23
Computational Studies	24
X-ray Crystallography:	30
Table S2. Crystallographic Experimental details	31
NMR Spectra.....	32

General Methods

Commercially available solvents and reagents were used as purchased unless otherwise noted. Tropylium bromide was prepared according to a literature procedure.¹ Analytical thin layer chromatography was performed using aluminium plates precoated with silica gel 60 F₂₅₄ (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using an Avance III HD 400 (400.1 MHz, ¹H; 100.6 MHz, ¹³C, 376.5 MHz, ¹⁹F) or an Avance III 300 (300 MHz, ¹H; 75 MHz, ¹³C; 282.5 MHz, ¹⁹F). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform, 5.27 ppm for dichloromethane) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J* in Hz) and integration (number of protons). ¹³C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform).

Infrared spectra were obtained on a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm⁻¹). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.

Table S1. Optimization Studies

Entry	Tropylium salt	Additive	Solvent	Ratio 1a : 2	Temp.	Yield (%)
1	Trop.Br 2a	-	MeCN	1 : 2	rt	43
2	Trop.Br 2a	-	DCE	1 : 2	rt	52
3	Trop.Br 2a	-	DCE	1 : 2	0 °C	45
4	Trop.Br 2a	-	DCE	1 : 2	50 °C	39
5	Trop.Br 2a	-	DCE	1 : 1.5	rt	59
6	Trop.Br 2a	-	DCE	1 : 1.05	rt	67
7	Trop.BF ₄ 2b	NaBr (2 equiv)	DCE	1 : 1.05	rt	traces
8	Trop.BF ₄ 2b	LiBr (2 equiv)	DCE	1 : 1.05	rt	traces
9	Trop.BF ₄ 2b	ⁿ Bu ₄ NBr (2 equiv)	DCE	1 : 1.05	rt	20
10	Trop.BF ₄ 2b	TMSBr (2 equiv)	DCE	1 : 1.05	rt	60
11	Trop.BF ₄ 2b	TMSBr (1.05 equiv)	DCE	1 : 1.05	rt	75

The reaction was optimized to obtain maximum yield of **4a** with the reaction time being when the reaction did not progress any further as monitored by TLC and ¹H NMR.

Procedure A follows the conditions in entry 6.

Procedure B follows the conditions in entry 11.

General procedures for the reactions of Michael acceptors with tropylium salts

Procedure A with tropylium bromide

To a solution of alkene (**1**, 1.00 mmol) in 1,2-dichloroethane (DCE, 10 mL) in a 25 mL round bottom flask was added tropylium bromide (**2a**, 1.05 mmol, 1.05 equiv.). The reaction mixture was stirred at room temperature for 36 h under N₂ atmosphere. The reaction mixture was subsequently concentrated under reduced pressure. The residues were purified by flash column chromatography (silica-gel, hexanes/EtOAc = 1 : 9) to obtain product **4**.

Procedure B with tropylium tetrafluoroborate and TMSHal

To a solution of alkene (**1**, 1.00 mmol) in DCE (10 mL) in a 25 mL round bottom flask was added tropylium tetrafluoroborate (**2b**, 1.05 mmol, 1.05 equiv.) followed by TMSHal (**3**, 1.05 mmol, 1.05 eq.). The reaction mixture was stirred at room temperature for 24 h under N₂ atmosphere. The reaction mixture was subsequently concentrated under reduced pressure. The residues were purified by flash column chromatography (silica-gel, hexanes/EtOAc = 1 : 9) to obtain product **4**.

Mechanistic studies

NMR samples were prepared by dissolving 0.05 mmol of tropylium tetrafluoroborate or TMSBr or a mixture of tropylium tetrafluoroborate and TMSBr (1 : 1 ratio on 0.05 mmol scale) in CD₃CN (1 mL). CD₃CN was used instead of DCE for better shimming and locking in NMR experiments. ¹H and ¹⁹F NMR spectra were recorded immediately after sample preparation. They indicated that TMSF formation occurred instantaneously.

Figure S1a. Mechanistic ¹H NMR studies

^{19}F in CD_3CN , 376 MHz, 25 °C

Figure S1b. Mechanistic ^1H NMR studies

From these studies, it can be concluded that tropylium tetrafluoroborate reacted with TMSBr to give a mixture of TMSF , tropylium ion and a mixture of BF_3 , Br^- and BF_3Br^-

Characterization data of products in Table 1

Methyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound 4a) Prepared by procedure B from (methyl acrylate **1a**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give compound **4a** as a colorless oil (192 mg, 75% yield).

4a

¹H NMR (400 MHz, CDCl₃) δ 6.67-6.65 (m, 2H), 6.29-6.21 (m, 2H), 5.35 (dd, J = 9.6, 6.5 Hz, 1H), 5.29 (dd, J = 9.6, 6.5 Hz, 1H), 3.75 (s, 3H), 3.65-3.56 (m, 2H), 3.10 (ddd, J = 9.7, 8.0, 4.9 Hz, 1H), 2.28 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.5, 131.3, 130.9, 126.3, 126.0, 122.0, 121.4, 52.1, 49.0, 40.5, 31.0 ppm;

IR (KBr) 3016, 2950, 1734, 1435 cm⁻¹;

HRMS (ESI+) m/z : [M+Na]⁺ Calcd. for C₁₁H₁₃BrO₂+Na 278.9997 (100%), 280.9976 (97.3%); Found 278.9992 (100%), 280.9967 (97.3%).

Methyl 3-chloro-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound number 4aCl): Prepared using the general procedure B from (methyl acrylate **1a**), tropylium tetrafluoroborate **2b** and TMSCl **3Cl** as anion source to give the title compound as a colorless oil (117 mg, 55% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.67-6.65 (m, 2H), 6.30-6.2 (m, 2H), 5.35 (dd, J = 9.4, 6.6 Hz, 1H), 5.29 (dd, J = 9.4, 6.6 Hz, 1H), 3.76 (s, 3H), 3.42-3.33 (m, 2H), 3.00 (td, J = 9.1, 4.3 Hz, 1H), 2.23 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.9, 131.4, 131.0, 126.4, 126.1, 122.3, 121.5, 52.3, 49.3, 42.2, 3.1 ppm.

IR (KBr) 3012, 2356, 2119, 1709, 1402 cm⁻¹;

HRMS (ESI+) m/z : [M+Na]⁺ Calcd. for C₁₁H₁₃ClO₂+Na 235.0502; Found 235.0498.

Methyl 2-(cyclohepta-2,4,6-trien-1-yl)-3-iodopropanoate (compound number 4aI): Prepared using the general procedure B from (methyl acrylate **1a**), tropylium tetrafluoroborate **2b** and TMSI **3I** as anion source to give the title compound as a colorless oil (200 mg, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.76-6.61 (m, 2H), 6.36-6.17 (m, 2H), 5.37 (dd, J = 9.5, 6.5 Hz, 1H), 5.31 (dd, J = 9.5, 6.5 Hz, 1H), 3.76 (s, 3H), 3.42-3.33 (m, 2H), 3.03 (td, J = 9.1, 4.4 Hz, 1H), 2.25 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.8, 131.3, 130.9, 126.3, 126.0, 122.2, 121.4, 52.1, 49.1, 42.1, 3.0 ppm.

IR (KBr) 3014, 2949, 2848, 1731, 1434 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₁H₁₃I₁O₂+Na 326.9858; Found 326.9854.

Ethyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound 4b) and (compound 4b-H): Prepared using the general procedure B from (ethyl acrylate **1b**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (198 mg, 73% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.75-6.61 (m, 2H), 6.36-6.17 (m, 2H), 5.39 (dd, J = 9.6, 6.4 Hz, 1H), 5.33 (dd, J = 9.6, 6.4 Hz, 2H), 4.26 (qd, J = 7.1, 0.9 Hz, 2H), 3.72-3.55 (m, 2H), 3.10 (ddd, J = 9.4, 8.4, 4.7 Hz, 1H), 2.30 (m, 1H), 1.31 (t, J = 7.0 Hz, 3H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.2, 131.5, 131.0, 126.3, 126.4, 122.2, 121.6, 61.2, 49.2, 40.7, 31.2, 14.5 ppm.

IR (KBr) 3015, 2979, 1729, 1426 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₂H₁₅Br₁O₂+Na 293.0153 (100%), 295.0133 (97.3%); Found 293.0145 (100%), 294.0127 (97.3%).

***n*-Butyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound 4c):** Prepared using the general procedure B from (*n*-butyl acrylate **1c**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (202 mg, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.76-6.61 (m, 2H), 6.36-6.16 (m, 2H), 5.38 (dd, J = 9.6, 6.4 Hz, 1H), 5.32 (dd, J = 9.6, 6.4 Hz, 1H), 4.22-4.12 (m, 2H), 3.65-3.56 (m, 2H), 3.07 (ddd, J = 9.5, 8.1, 4.9 Hz, 1H), 2.26 (m, 1H), 1.68-1.60 (m, 2H), 1.44-1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 131.5, 131.0, 126.4, 126.1, 122.3, 121.6, 65.1, 49.3, 40.7, 31.2, 30.8, 19.3, 13.8 ppm.

IR (KBr) 3017, 2958, 2871, 1730, 1617, 1461, 1427 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₄H₁₉BrO₂+Na 321.0466 (100%), 323.0440 (97.3%); Found 321.0462 (100%), 323.0446 (97.3%).

***Isobutyl* 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound 4d):** Prepared using the general procedure B from (*isobutyl* acrylate **1d**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (211 mg, 71% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.76-6.6 (m, 2H), 6.34-6.16 (m, 2H), 5.43-5.25 (m, 2H), 4.04-3.86 (m, 2H), 3.7-3.57 (m, 2H), 3.09 (ddd, J = 9.5, 7.9, 5.0 Hz, 1H), 2.27 (m, 1H), 1.97 (dp, J = 13.4, 6.7 Hz, 1H) 0.95 (d, J = 6.7 Hz, 6H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 131.4, 131.0, 126.4, 126.1, 122.3, 121.6, 71.3, 49.3, 40.7, 31.2, 27.9, 19.3 ppm.

IR (KBr) 2955, 2921, 2852, 2359, 2341, 1734, 1456 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₄H₁₉BrO₂+Na 321.0466 (100%), 323.0440 (97.3%); Found 321.0459 (100%), 321.0438 (97.3%)

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoic acid (compound 4e/4g): Prepared using the general procedure B from (*t*-butyl acrylate **1e** or isobornyl acrylate **1g**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (178 mg, 73% yield with **1e** or 183 mg, 75% with **1g**).

¹H NMR (400 MHz, CDCl₃) δ 6.77 – 6.63 (m, 2H), 6.38 – 6.25 (m, 2H), 5.45 (dd, J = 9.6, 6.5 Hz, 1H), 5.36 (dd, J = 9.5, 6.7 Hz, 1H), 3.65 (m, 2H), 3.13 (dt, J = 9.4, 6.2 Hz, 1H), 2.42 (m, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 177.4, 131.3, 131.0, 126.7, 126.3, 122.2, 48.4, 40.3, 30.6 ppm.

IR (KBr) 3015, 2926, 2656, 1704, 1433, 1401 cm⁻¹;

HRMS (ESI+) m/z : [M+Na]⁺ Calcd. for C₁₀H₁₁BrO₂+Na 264.9840 (100%), 266.9812 (97.3%); Found 264.9833 (100%), 266.9820 (97.3%).

2-Phenoxyethyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound number 4f) Prepared using the general procedure B from (ethylene glycol phenyl ether acrylate **1f**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (297 mg, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 3H), 7.03 – 6.89 (m, 3H), 6.70 – 6.62 (m, 2H), 6.31 – 6.24 (m, 1H), 6.22 – 6.14 (m, 1H), 5.39 (dd, J = 9.5, 6.5 Hz, 1H), 5.32 (dd, J = 9.5, 6.5 Hz, 1H), 4.63 – 4.49 (m, 2H), 4.28 – 4.16 (m, 2H), 3.71 – 3.57 (m, 2H), 3.16 (ddd, J = 9.5, 8.2, 4.8 Hz, 1H), 2.31 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 172.2, 131.5, 131.0, 126.4, 129.7, 126.5, 126.2, 122.1, 121.5, 114.8, 65.8, 63.4, 49.0, 40.7, 31.0 ppm.

IR (KBr) 2925, 1734, 2871, 1598, 1587, 1495, 1455, 1404 cm⁻¹;

HRMS (ESI+) m/z : [M+Na]⁺ Calcd. for C₁₈H₁₉BrO₃+Na 385.0408 (100%), 387.0406 (97.3%); Found 385.0418 (100%), 387.0395 (97.3%).

((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl)bis(3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate) (compound number **4h**): Prepared using the general procedure B from (tetra(ethylene glycol) diacrylate **1h**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a yellow oil (405 mg, 63% yield).

¹H-NMR (300 MHz CDCl₃) δ 6.69 – 6.62 (m, 2H), 6.31 – 6.18 (m, 2H), 5.42 – 5.26 (m, 3H), 4.37 – 4.29 (m, 2H), 3.74 – 3.56 (m, 4H), 3.64 (s, 4H), 3.12 (ddd, J = 9.4, 8.1, 4.8 Hz, 1H), 2.28 (m, 1H) ppm.

¹³C-NMR (75 MHz CDCl₃) δ 172.0, 131.3, 130.9, 126.3, 126.0, 122.1, 121.4, 70.7, 70.6, 69.1, 64.0, 48.9, 40.5, 31.1 ppm.

IR (KBr): 2870, 1720, 1635, 1522, 1406 cm⁻¹;

HRMS (ESI⁺) m/z [M+Na]⁺ Calcd. for C₂₈H₃₆Br₂O₇+Na 667.0705 (100%), 665.0724 (97.3%); Found 667.0700 (100%), 665.0725 (97.3%).

Vinyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound number **4i**): Prepared using the general procedure B from (vinyl acrylate **1i**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (206 mg, 77% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.32 (dd, J = 13.9, 6.3 Hz, 1H), 6.73 – 6.66 (m, 2H), 6.37 – 6.23 (m, 2H), 5.41 (dd, J = 9.6, 6.7 Hz, 1H), 5.35 (dd, J = 9.6, 6.7 Hz, 1H), 4.98 (dd, J = 13.9, 1.8 Hz, 1H), 4.67 (dd, J = 6.3, 1.8 Hz, 1H), 3.71 – 3.57 (m, 2H), 3.16 (ddd, J = 9.5, 7.6, 5.0 Hz, 1H), 2.45 (m, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 169.4, 141.1, 131.5, 131.0, 126.7, 126.4, 122.0, 121.2, 98.8, 48.5, 40.4, 30.5 ppm.

IR (KBr) 3018, 1746, 1645, 1357, 1254, 1142 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₂H₁₃BrO₂+Na 290.9997 (100%), 292.9976 (97.3%); Found 290.9994 (100%), 292.9972 (97.3%).

Prop-2-yn-1-yl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (compound 4j): Prepared using the general procedure B from (propargyl acrylate **1j**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a colorless oil (218 mg, 78% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.75 – 6.63 (m, 2H), 6.35 – 6.22 (m, 2H), 5.41 (dd, J = 9.5, 6.6 Hz, 1H), 5.33 (dd, J = 9.5, 6.6 Hz, 1H), 4.79 (d, J = 2.5 Hz, 1H), 4.77 (d, J = 2.5 Hz, 1H), 3.70 – 3.58 (m, 2H), 3.15 (ddd, J = 9.5, 7.9, 4.9 Hz, 1H), 2.52 (t, J = 2.5 Hz, 1H), 2.39 (m, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 171.5, 131.5, 126.6, 122.1, 121.3, 75.4, 52.6, 48.6, 40.6, 30.8 ppm.

IR (KBr) 3292, 3017, 1739, 1432 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₃H₁₃BrO₂+Na 302.9997 (100%), 304.9970 (97.3%); Found 302.9993 (100%), 304.9976 (97.3%).

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanamide (compound 4k): Prepared using the general procedure B from (acrylamide **1k**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a white solid (220 mg, 91% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.72 – 6.65 (m, 2H), 6.36 – 6.24 (m, 2H), 6.02 (bs, 1H), 5.76 (bs, 1H), 5.42 (dd, J = 9.6, 6.7 Hz, 1H), 5.33 (dd, J = 9.6, 6.7 Hz, 1H), 3.69 – 3.56 (m, 2H), 2.82 (td, J = 9.8, 3.8 Hz, 1H), 2.39 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 174.2, 131.2, 131.1, 126.7, 126.3, 122.5, 121.6, 49.6, 41.0, 31.5 ppm.

IR (KBr) 3382, 3187, 3009, 2915, 1654, 1434 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₀H₁₂BrN₁O₁+Na 264.0000 (100%), 265.9979 (97.3%); Found 263.9997 (100%), 265.9973 (97.3%).

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)-*N,N*-dimethylpropanamide (compound 4l) and 3-Bromo-*N,N*-dimethylpropanamide² (compound 4l-H): Prepared using the general procedure B from (*N,N*-dimethylacrylamide **1l**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a yellowish oil (214 mg, 79% yield) and compound **4l-H** as a yellowish oil (36 mg, 20% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.70 – 6.63 (m, 2H), 6.33 (m, 1H), 6.23 (m, 1H), 5.41 (dd, J = 9.7, 7.2 Hz, 1H), 5.33 (dd, J = 9.7, 7.2 Hz, 1H), 3.67 (dd, J = 10.9, 9.4 Hz, 1H), 3.54 (dd, J = 9.4, 3.4 Hz, 1H), 3.36 (td, J = 10.5, 3.4 Hz, 1H), 3.04 (s, 3H), 3.03 (s, 3H), 2.72 (m, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 172.6, 131.0, 130.8, 126.9, 126.5, 123.2, 122.9, 43.3, 41.9, 37.9, 36.1, 32.7 ppm.

IR (KBr) 3454, 2931, 2359, 1629, 1496 cm⁻¹;

HRMS (ESI+) m/z : [M+Na]⁺ Calcd. for C₁₂H₁₆BrN₁O₁+Na 292.0313 (100%), 294.0292 (97.3%); Found 292.0307 (100%), 294.0286 (97.3%).

4l-H

¹H NMR (400 MHz, CDCl₃) δ 3.67 (t, J = 7.2 Hz, 2H), 3.04 (s, 3H), 2.99 (s, 3H), 2.93 (t, J = 7.2 Hz, 2H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 170.2, 37.3, 36.8, 35.6, 27.5 ppm.

IR (KBr) 3015, 2924, 2359, 1715, 1636, 1493, 1420 cm⁻¹;

HRMS (ESI+) m/z : [M+Na]⁺ Calcd. for C₅H₁₀BrN₁O₁+Na 201.9838 (100%), 203.9818 (97.3%); Found 201.9843 (100%), 201.9823 (97.3%).

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)-1-morpholinopropan-1-one (compound 4m): Prepared using the general procedure B from (4-acryloylmorpholine **1m**), tropylium

tetrafluoroborate **2a** and TMSBr **3** as anion source to give the title compound as a colorless oil (220 mg, 71% yield).

¹H-NMR (300 MHz CDCl₃) δ 6.67 – 6.56 (m, 2H), 6.30 (ddd, *J* = 9.8, 4.8, 1.5 Hz, 1H), 6.22 (ddd, *J* = 9.8, 4.8, 1.5 Hz, 1H), 5.39 (dd, *J* = 9.7, 7.4 Hz, 1H), 5.30 (dd, *J* = 9.7, 7.4 Hz, 1H), 3.86 – 3.75 (m, 1H), 3.72 – 3.42 (m, 8H), 3.40 – 3.29 (m, 1H), 3.23 (td, *J* = 10.6, 3.3 Hz, 1H), 2.83 (m, 1H) ppm;

¹³C-NMR (75 MHz CDCl₃) δ 171.1, 131.1, 130.6, 127.1, 126.6, 123.1, 122.8, 67.1, 66.8, 46.6, 42.5, 42.1, 41.8, 32.5 ppm.

IR (KBr): 3013, 2961, 2918, 2853, 1632, 1437 cm⁻¹;

HRMS (ESI+) m/z [M+Na]⁺ Calcd. for C₁₄H₁₈BrO₂+Na 334.0419 (100%), 336.0398 (97.3%); Found 334.0412 (100%), 336.0393 (97.3%).

(3*R*,4*S*) and (3*S*,4*R*)-3-bromo-4-(cyclohepta-2,4,6-trien-1-yl)-1-methylpyrrolidine-2,5-dione (compound **4n):** Prepared using the general procedure B from (1-methyl-1*H*-pyrrole-2,5-dione **1n**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a yellowish oil (214 mg, 76% yield). The small H-H coupling constant of (3*H*,4*H*) indicated that the compounds was formed with exclusive *anti*-selectivity to give a mixture of (3*R*,4*S*) and (3*S*,4*R*) diastereoisomers.

¹H-NMR (300 MHz CDCl₃) δ 6.74-6.70 (m, 2H), 6.37-6.28 (m, 2H), 5.52-5.27 (m, 2H), 4.49 (d, *J* = 3.7 Hz, 1H), 3.47-3.40 (dd, *J* = 7.5, 3.7 Hz, 1H), 3.07 (s, 3H), 2.15-2.07 (m, 1H) ppm;

¹³C-NMR (75 MHz CDCl₃) δ 175.7, 173.3, 132.3, 131.8, 127.8, 126.9, 122.2, 120.3, 53.2, 41.2, 40.4, 26.3 ppm;

IR (KBr): 3015, 2940, 1703, 1431 cm⁻¹;

HRMS (ESI+) m/z [M+Na]⁺ Calcd. for C₁₂H₁₂BrNO₂+Na 303.9949 (100%), 305.9929 (97.3%); Found 303.9941(100%), 305.9922 (97.3%).

(3*R*,4*S*) and (3*S*,4*R*)-3-bromo-1,4-di(cyclohepta-2,4,6-trien-1-yl)pyrrolidine-2,5-dione (compound 4o): Prepared using the general procedure B from (maleimide 1o), tropylium tetrafluoroborate 2b (2 equiv) and TMSBr 3 (2 equiv) as anion source to give the title compound as white crystals (240 mg, 67% yield). The small H-H coupling constant of (3H,4H) indicated that the compounds was formed with exclusive *anti*-selectivity to give a mixture of (3*R*,4*S*) and (3*S*,4*R*) diastereoisomers.

¹H NMR (400 MHz, CDCl₃) δ 6.77-6.66 (m, 4H), 6.37-6.19 (m, 4H), 5.51-5.32 (m, 4H), 4.55 (d, *J* = 3.4 Hz, 1H), 4.17 (tt, *J* = 3.4, 1.5 Hz, 1H), 3.49 (dd, *J* = 8.2, 3.4 Hz, 1H), 2.20-2.14 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 174.8, 172.5, 131.9, 131.7, 131.6, 131.4, 127.5, 126.6, 124.8, 124.7, 121.9, 121.7, 119.8, 52.6, 51.2, 40.9, 40.0 ppm.

IR (KBr) 3015, 2925, 2854, 1785, 1711, 1439 cm⁻¹;

HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd. for C₁₈H₁₆BrN₁O₂+Na 380.0262 (100%), 382.0242 (97.3%); Found 380.0258 (100%), 382.0239 (97.3%).

1-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)pentan-3-one (compound 4p): Prepared using the general procedure B from (1-penten-3-one 1p), tropylium tetrafluoroborate 2b and TMSBr 3 as anion source to give the title compound as a colorless oil (164 mg, 64% yield).

¹H-NMR (300 MHz CDCl₃) δ 6.69 – 6.61 (m, 2H), 6.33 – 6.18 (m, 2H), 5.33 – 5.21 (m, 2H), 3.61 – 3.48 (m, 2H), 3.21 (m, 1H), 2.62 – 2.40 (m, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm;

¹³C-NMR (75 MHz CDCl₃) δ 211.5, 131.2, 131.1, 126.8, 126.5, 122.5, 121.6, 53.5, 40.9, 38.1, 31.0, 7.3 ppm

IR (KBr): 3010, 2945, 2923, 2853, 2359, 1714, 1617, 1456 cm⁻¹;

HRMS (ESI⁺) m/z [M+Na]⁺ Calcd. for C₁₂H₁₅BrO₁+Na 277.0204 (100%), 277.0199 (97.3%); Found 277.0199 (100%), 277.0177 (97.3%).

Unreactive substrates

2-Hydroxyethyl 3-bromopropanoate (compound number 4r): Prepared using the general procedure B from (2-hydroxyethyl acrylate **1r**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give the title compound as a (151 mg, 77% yield).

¹H NMR (400 MHz, CDCl₃) δ 4.46 (t, J = 6.2 Hz, 2H), 3.59 (t, J = 6.8 Hz, 2H), 3.52 (t, J = 6.2 Hz, 2H), 2.97 (t, J = 6.8 Hz, 2H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 170.2, 64.3, 37.7, 28.5, 25.7 ppm.

IR (KBr) 2969, 1735, 1511, 1384, 1345 cm⁻¹;

HRMS (ESI⁺) m/z [M+Na]⁺ Calcd. for C₅H₉BrO₃+Na 218.9633 (100%), 220.9608 (97.3%); Found 218.9629 (100%), 220.9612 (97.3%).

Characterization of products in Scheme 2

5-(cyclohepta-2,4,6-trien-1-yl)furan-2(5H)-one (compound **4q**) and **4-oxo-5-phenylpentanoic acid**³ (compound **4q'**) Prepared using the general procedure B from 2(5H)-Furanone **1q**, tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give **4q** as a colorless oil (104 mg, 60% yield) and **4q'** as a white solid (74 mg, 38% yield).

4q

¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, J = 5.7, 1.8 Hz, 1H), 6.74 – 6.64 (m, 2H), 6.36 – 6.27 (m, 2H), 6.25 (dd, J = 5.7, 1.8 Hz, 1H), 5.37 – 5.24 (m, 3H), 2.23 – 2.09 (m, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 172.9, 154.9, 131.4, 131.1, 126.8, 126.3, 122.8, 120.2, 119.9, 82.9, 41.9 ppm.

IR (KBr): 3023, 2923, 1751, 1602, 1326, 1243, 1160, 1096, 894, 816, 752 cm⁻¹;

HRMS (ESI+) m/z [M+Na]: calc. for C₁₁H₁₀O₂+Na: 197.0578; found: 197.0572.

4q'

¹H NMR (400 MHz, CDCl₃) δ 7.41-7.20 (m, 5H), 3.76 (s, 2H), 2.81-2.74 (m, 2H), 2.65-2.58 (m, 2H) ppm. NMR data corresponded to that reported in literature.³

¹³C NMR (100 MHz, CDCl₃) δ 206.5, 178.6, 133.9, 129.5, 128.8, 127.2, 50.0, 36.2, 27.9 ppm. NMR data corresponded to that reported in literature.³

A possible explanation for the formation of **4q** and **4q'** is depicted below:

Hydrolysis of **4q** led to the formation of **4q'** in quantitative yield.

Characterization of products in Scheme 3

Methyl (*E* or *Z*)-3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)acrylate (compound number **6a**):

Prepared using the general procedure B from (methyl propiolate **5a**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give an inseparable mixture of the *E*- and the *Z*-isomers as a colorless oil (244 mg, 96% total yield, *E* : *Z* (determined by ^1H NMR of the crude product) = 1 : 4.5). After several re-columning attempts, we were able to separate some fractions with enriched *Z*-isomer for ^1H and ^{13}C NMR analysis.

***Z*-isomer (contaminated with ~ 10% *E*-isomer):** ^1H NMR (400 MHz, CDCl_3) δ 6.68 – 6.60 (m, 2H), 6.55 (d, J = 1.3 Hz, 1H), 6.29-6.19 (m, 2H), 5.40-5.35 (m, 2H), 3.81 (s, 3H), 2.92 (m, 1H) ppm;

^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 138.6, 131.1, 125.8, 124.7, 124.6, 124.4, 122.5, 110.7, 52.5, 44.0, 41.5 ppm.

IR (KBr) 2870, 1720, 1635, 1522, 1406 cm^{-1} ;

HRMS (ESI+) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{11}\text{H}_{11}\text{BrO}_2+\text{Na}$ 276.9840 (100%), 278.9820 (97.3%); Found 276.9838 (100%), 278.9814 (97.3%).

Ethyl (*Z*)-3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)acrylate (compound number **6b**):

Prepared using the general procedure B from (ethyl propiolate **5b**), tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give an inseparable mixture of the *E*- and the *Z*-isomers as a colorless oil (265 mg, 99% total yield, *E* : *Z* (determined by ^1H NMR of the crude product) = 1 : 4.2). After several re-columning attempts, we were able to separate some fractions with enriched *Z*-isomer for ^1H and ^{13}C NMR analysis.

***Z*-isomer:** ^1H NMR (400 MHz, CDCl_3) δ 6.68 – 6.61 (m, 2H), 6.51 (d, J = 1.3 Hz, 1H), 6.29 – 6.19 (m, 2H), 5.44 – 5.34 (m, 2H), 4.31 (q, J = 7.1 Hz, 2H), 2.89 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H) ppm

^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 138.5, 131.1, 125.8, 122.4, 110.0, 61.5, 44.1, 14.3 ppm.

IR (KBr) 2980, 1716, 1604, 1463, 1393 cm^{-1} ;

HRMS (ESI+) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{12}\text{H}_{13}\text{BrO}_2+\text{Na}$ 290.9997 (100%), 292.9976 (97.3%); Found 290.9993 (100%), 292.9970 (97.3%).

Dimethyl 2-bromo-3-(cyclohepta-2,4,6-trien-1-yl)but-2-enedioate (compound **6c**) Prepared using the general procedure B from dimethyl acetylenedicarboxylate **5c**, tropylium tetrafluoroborate **2b** and TMSBr **3** as anion source to give a mixture of the *E*- and the *Z*-isomers as a colorless oil (159 mg, 51% total yield, *E* : *Z* (determined by ^1H NMR) = 1 : 2). After several re-columning attempts, we were able to separate some fractions with enriched *Z*- or *E*-isomer for ^1H and ^{13}C NMR analysis.

***E*-isomer:** ^1H NMR (400 MHz, CDCl_3) δ 6.74 – 6.67 (m, 2H), 6.28 – 6.19 (m, 2H), 5.37 – 5.27 (m, 2H), 3.92 (s, 3H), 3.78 (s, 3H), 3.16 (tt, J = 5.5, 1.4 Hz, 1H) ppm;

^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 163.1, 146.2, 131.1, 125.0, 119.9, 112.2, 53.3, 52.6, 42.3 ppm;

***Z*-isomer:** ^1H NMR (400 MHz, CDCl_3) δ 6.76 – 6.69 (m, 2H), 6.33 – 6.24 (m, 2H), 5.29 – 5.20 (m, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 2.98 (tt, J = 5.4, 1.5 Hz, 1H) ppm;

^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 163.2, 145.9, 131.0, 125.5, 119.0, 118.8, 53.7, 52.9, 44.5 ppm;

IR (KBr) 3015, 2956, 1725, 1609, 1425, 1252 cm^{-1} ;

HRMS (ESI+) m/z : Calc. for $\text{C}_{13}\text{H}_{13}\text{BrO}_4+\text{Na}$: 334.9895 (100%), 336.9874 (97.3%); Found 334.9891 (100%), 336.9869 (97.3%).

Characterization data of products in Scheme 4

Methyl 2-(cyclohepta-2,4,6-trien-1-yl)acrylate (compound 12): Prepared using the general procedure A from methyl acrylate **1b** and tropylium bromide **2a**, followed by quenching with aq. NH₃ and stirring for another 24 h to give the title compound as a colorless oil (113 mg, 64% yield over two steps, or 95% yield for dehydrobromination step).

¹H NMR (400 MHz, CDCl₃) δ 6.68 – 6.61 (m, 2H), 6.34 (s, 1H), 6.27 – 6.18 (m, 2H), 5.76 (s, 1H), 5.37 – 5.28 (m, 2H), 3.77 (s, 3H), 2.90 (td, J = 6.1, 1.2 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 167.3, 140.4, 130.8, 125.1, 124.9, 124.5, 52.0, 41.0 ppm.

IR (KBr) 2878, 1726, 1637, 1520, 1412 cm⁻¹;

HRMS (ESI+) m/z [M+Na]: Calc. for C₁₁H₁₂O₂+Na 199.0730; Found: 199.0730.

Methyl-3-bromo-2-(1,3-dioxodecahydro-4,6-ethanocyclopropa[f]isoindol-5-yl)propanoate (compound number 13): To a solution of **4a** (0.5 mmol) in DCE (5 mL) was added maleimide (0.5 mmol, 1 equiv.). After stirring for 24 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel, hexanes/EtOAc) to obtain the title compound as a bright white crystals (166 mg, 94% yield). X-ray crystal structure revealed that it is a racemic mixture of the two enantiomers below. See page S30 for more details.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (bs, 1H), 5.85 (dd, J = 4.8, 3.6 Hz, 2H), 3.74 (s, 3H), 3.56 (t, J = 9.8, 1H), 3.48-3.41 (m, 3H), 2.96 (dd, J = 1.6, 1.8 Hz, 2H), 2.28-2.23 (m, 1H), 1.22 (m, 1H), 1.07 (m, 1H), 0.82 (dt, J = 9.8, 3.0 Hz, 1H) ppm;

^{13}C NMR (100 MHz, CDCl_3) δ 178.1, 178.0, 172.6, 129.0, 128.5, 52.4, 50.1, 32.9, 32.9, 31.4, 19.9, 17.4, 16.0 ppm.

IR (KBr) 3017, 2950, 2851, 1718, 1628, 1435, 1406 cm^{-1} ;

HRMS (ESI+) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{18}\text{Br}_1\text{NO}_4+\text{Na}$ 376.0160 (100%), 378.0135 (97.3%); Found 376.0157 (100%), 378.0132 (97.3%).

Methyl 2-bromo-2-phenyl-3-hydroxypropanoate (compound 14): To a solution of **4a** (0.5 mmol) in MeCN (5 mL) was added nitrosonium tetrafluoroborate (1.0 mmol, 2 equiv.). After stirring for 1 h at room temperature, hydrogen peroxide (30% w/w aq. solution, 5 equiv.) was added and the reaction mixture was stirred for another 12 h. The reaction was quenched by 10% w/w aq. sodium metabisulfite solution. The organic products were extracted by DCM (2 x 15 mL), dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel, hexanes/EtOAc) to obtain the title compound as a colorless oil (83 mg, 63% yield). It should be noted that, apart from the oxidative ring-contraction, the reaction conditions also led to the oxidation of the side-chain and the rearrangement of the bromo functional group.

^1H NMR (400 MHz, CDCl_3) δ 7.50-7.47 (m, 2H), 7.39-7.32 (m, 3H), 4.19 (s, 2H), 3.86 (s, 3H) ppm;

^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 136.7, 129.1, 128.7, 127.6, 70.2, 67.9, 53.8 ppm.

IR (KBr) 3439, 2951, 1723, 1494, 1444 cm^{-1} ;

HRMS (ESI+) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{10}\text{H}_{11}\text{Br}_1\text{O}_3+\text{Na}$ 280.9789 (100%), 282.9769 (97.3%); Found 280.9785 (100%), 282.9763 (97.3%)

Methyl 2-(bromomethyl)-3-chloro-3-phenyl-3-propanoate (compound 15): Compound **4a** (0.5 mmol) was dissolved by 5 mL of DCM in a 21 mL vial charged a stirrer bar. The solution was cooled down to 0 °C and TeCl_4 was added in portion. The reaction mixture was warmed up to room temperature and stirred overnight. After completion, the mixture was filtered through a plug of celite, washed by 15 mL of DCM and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel, hexanes/EtOAc) to

obtain an inseparable mixture of two diastereoisomers (1 : 1.1, ratio by NMR analysis) as a colorless oil (119 mg, 82%).

¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.31 (m, 10.5H), 5.09 (d, *J* = 10.1 Hz, 1H), 5.08 (d, *J* = 9.8 Hz, 1.1H), 3.97-3.70 (m, 6.4H), 3.58-3.43 (m, 4.9H), 3.32-3.12 (m, 2.1H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 170.9, 170.1, 138.5, 137.6, 129.4, 129.1, 129.0, 128.7, 128.6, 127.5, 127.4, 62.3, 61.0, 56.5, 56.4, 52.5, 52.2, 30.3, 29.3 ppm.

IR (KBr): 3034, 2324, 1739, 1437, 1347 cm⁻¹;

HRMS (ESI+): *m/z* [M+Na] Calc. for C₁₁H₁₂BrClO₂+Na 312.9607 (100%), 314.9586; (97.3%); Found: 312.9604 (100%), 314.9579 (97.3%).

References

- [1] W. Von E.Doering, L. H. Knox, *J. Am. Chem. Soc.* **1954**, 76, 3203-3206
- [2] X. Li, S. M. Singh, F. Labrie, *Synth. Commun.* **1994**, 24, 733-743.
- [3] A. C. Boye, D. Meyer, C. K. Ingison, A. N. French, T. Wirth, *Org. Lett.* **2003**, 5, 2157-2159.

Computational Studies

Density functional theory (M06-2X/6-31+G(d,p) and SMD) calculations were carried out to investigate the mechanism of the reaction. The calculations indicate that tropylium bromide exists as an ion-pair in dichloroethane solution ($-21.8 \text{ kJ mol}^{-1}$ relative to separate ions). This ion-pair may in turn mediate the bromocycloheptrienylation of **1a** through two possible pathways (a) CO addition to tropylium followed by addition of bromide to form intermediate **10**, which can undergo sigmatropic rearrangement (red arrows in structure **10**) to form the product **4a**. (b) direct addition of tropylium and bromide to the olefin to form **4a**.

Figure S2. M06-2X/6-31+G(d,p) + SMD (dichloroethane) free energy profile.

As shown in Figure S2, the first two steps of pathway (a) are associated with a relatively high Gibbs free energy barrier (**TS-7** and **TS-9**) of 120 and 128 kJ mol⁻¹ respectively. Inspection of the geometries of **TS-7** and **8** indicates that there is a significant shortening (*ca.* 0.04 Å) of both the C-OMe and C-C(O) bonds relative to **1a**; the structure of intermediate **8** depicted in Figure S2 represents one of the resonance forms. Attempts to locate the transition state for the sigmatropic rearrangement of **10** to form **4a** were unsuccessful and pathway (a) was deemed an unproductive pathway. On the other hand, the direct addition of tropylium and bromide across the olefin double bond is associated with a significantly lower barrier of 114 kJ mol⁻¹ to transition state **TS-11**. This pathway (b) leads directly to product **4a**, which is predicted to be an exergonic process ($\Delta G_{\text{rxn}} -35 \text{ kJ mol}^{-1}$).

Computational Details

All electronic structure calculations were carried using the Gaussian16 program.¹ Geometries and harmonic frequency calculations were performed at the M06-2X/6-31+G(d,p)² level directly within the SMD implicit solvent model³ (DCE solvent).⁴ Systematic conformer searches were carried out to locate the lowest energy conformers of each species in Figure S2. Frequency calculations confirm that all reactant and intermediates are true minimum energy structures and that all transition states are true first-order saddle points. Intrinsic reaction coordinate⁵ calculations were also carried out to ascertain that the transition states connected the correct reactants and products. Bond order calculations were carried out using the Wiberg scheme.⁶ Standard state corrections were applied so that all reported solution phase free energies correspond to a standard state of 1 mol L⁻¹.

Cartesian coordinates of M06-2X/6-31+G(d,p)/SMD(dichloroethane) optimized geometries.

1a

```
1\1\GINC-R3879\FOpt\RM062X\Gen\C4H6O2\ROOT\20-May-2019\0\#\#m062X/gen 6
D OPT Freq=Noraman INT(grid=ultrafine) SCRF=(SMD,Solvent=dichloroethane)
\vinylester.smd\0,1\O,-0.2763531994,-0.1645432708,0.\C,-1.61005949
32,-0.2787681622,0.\C,-2.0296560912,-1.7033415094,0.\C,0.2384104397,1.
1731344304,0.\O,-2.359623973,0.676651045,0.\C,-3.3220285399,-2.0267404
97,0.\H,-1.2407174465,-2.4488008199,0.\H,1.322362504,1.0716504767,0.\H
,-0.0944498845,1.7063971995,0.893057012\H,-0.0944498845,1.7063971995,-
0.893057012\H,-4.0879561691,-1.2555786925,0.\H,-3.6418782538,-3.063857
4072,0.\Version=ES64L-G16RevA.03\State=1-A'\HF=-306.3566243\RMSD=5.45
2e-09\RMSF=4.235e-05\Dipole=0.5558433,-0.5443501,0.\Quadrupole=1.04302
66,1.487114,-2.5301406,5.8974151,0.,0.\PG=CS [SG(C4H4O2),X(H2)]\@
```

Tropylium cation

```
1\1\GINC-R44\FOpt\RM062X\Gen\C7H7(1+)\ROOT\27-May-2019\0\#\#m062X/gen 6
D INT(grid=ultrafine) OPT Freq=noraman SCRF=(SMD,Solvent=dichloroethane)
\trop-cation.freq\1,1\C,-2.7912842413,1.7249249771,1.1663661029\C,
-4.1765511529,1.6346978294,1.027237556\C,-5.1566950487,2.5038934335,1.
5066988138\C,-4.993301823,3.676901047,2.2439602116\C,-3.8103097204,4.2
708655692,2.6845701815\C,-2.4972589542,3.8380648046,2.4961955533\C,-2.
0439574822,2.7048105926,1.8205236546\H,-4.5397275231,0.7743713351,0.47
21680423\H,-6.1827707924,2.2313832525,1.2755373285\H,-5.9093477486,4.1
963390368,2.511079105\H,-3.9266023888,5.1916777931,3.2494306856\H,-1.7
262677119,4.4664132952,2.933371635\H,-0.9664050526,2.5675125848,1.8012
185019\H,-2.21839036,0.925184449,0.704472628\Version=ES64L-G16RevA.03
\State=1-A'\HF=-270.6366223\RMSD=4.750e-09\RMSF=1.211e-04\Dipole=-0.000
4847,-0.001364,-0.0002266\Quadrupole=4.9150984,0.8336515,-5.7487498,-0
.3985817,0.6526003,6.6436249\PG=C01 [X(C7H7)]\@
```

Tropylium-bromide ion pair

```
1\1\GINC-R63\FOpt\RM062X\Gen\C7H7Br1\ROOT\27-May-2019\0\#\#m062X/gen 6D
INT(grid=ultrafine) OPT Freq=noraman SCRF=(SMD,Solvent=dichloroethane)
```

```
)\\trop-bromide.freq\\0,1\\Br,-4.6901813437,0.0596262954,-2.4005751586\\
C,-4.4476605393,-1.1127215815,0.98000394\\C,-4.6647316654,-0.9875301006
,2.3520398849\\C,-4.311383943,-1.8733146113,3.3704142667\\C,-3.655473762
2,-3.1002713955,3.2661648683\\C,-3.1899492703,-3.7469200834,2.120907326
6\\C,-3.2653246946,-3.32475065,0.7932537051\\C,-3.8251875938,-2.15199654
66,0.2868356031\\H,-4.8022301063,-0.3038992585,0.34169136\\H,-5.17544404
46,-0.0823638402,2.6697649236\\H,-4.5823698651,-1.5684057617,4.37775932
38\\H,-3.4841051266,-3.6228329382,4.2035417592\\H,-2.7048651151,-4.70539
77121,2.2857164584\\H,-2.8310992873,-3.9976055844,0.0585324022\\H,-3.784
113643,-2.0033862314,-0.7918606633\\Version=ES64L-G16RevA.03\\State=1-A
\\HF=-2844.7036191\\RMSD=6.852e-09\\RMSF=4.724e-06\\Dipole=1.3979445,-4.27
06084,7.6581651\\Quadrupole=-1.9488805,3.180028,-1.2311474,-4.7839539,-
3.1812431,5.3092961\\PG=C01 [X(C7H7Br1)]\\@
```

TS-7

```
1\\1\\GINC-R4152\\FTS\\RM062X\\Gen\\C11H13Br1O2\\ROOT\\23-May-2019\\0\\#m062X/g
en 6D INT(grid=ultrafine) OPT=(TS,calcf,oeigentest) Freq=norman SCR
F=(SMD,Solvent=dichloroethane)\\TS.freq\\0,1\\O,1.949351828,2.844258564
9,0.0689979838\\C,1.0032840934,1.9653798941,-0.128009672\\C,-0.328612177
8,2.5418456352,-0.2686596434\\C,3.3021221204,2.3637951704,0.2422976672\\
O,1.308255938,0.7474956414,-0.2006290739\\C,-1.2719473919,1.9392953742,
-1.0027519925\\H,-0.4762454156,3.5137986061,0.1895095614\\H,3.8909971947
,3.2542840117,0.4489087458\\H,3.6396921856,1.8788363249,-0.674483381\\H,
3.3406442583,1.6668844584,1.0805763824\\Br,-3.304604156,-0.3138239393,0
.2565715024\\H,-2.2431666206,2.3987431719,-1.1447475626\\H,-1.0944411119
,1.0026103906,-1.5210036723\\C,0.2681717243,-0.5618746268,0.3230000728\\
C,1.0127154466,-1.0989070345,1.450103357\\C,2.1444337262,-1.8517715137,
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8

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4192609\\C,3.5099268875,2.1569477753,0.1483321975\\O,1.4522884709,0.6257
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9118906\\H,3.803542788,1.4970815523,-0.6687062016\\H,3.5091518845,1.6222
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2121118\\H,4.0690366992,-2.3142559815,0.3768802589\\H,3.2459224579,-2.42
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TS-9

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6\O,1.4482853422,0.602021628,-0.099530944\C,-1.1520091387,1.7262114479
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10

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TS-11

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4a

1\1\GINC-R60\FOpt\RM062X\Gen\C11H13Br1O2\ROOT\26-Jun-2019\0\#m062X/gen 6D OPT Freq=Noraman INT(grid=ultrafine) SCRF=(SMD,Solvent=dichloroethane)\product.smd\0,1\O,-0.786013652,0.3620787496,1.0153735165\C,-1.3964216761,-0.503234838,0.20378529\C,-2.9005858585,-0.2963359267,0.1726271411\O,-0.8114872235,-1.3654234729,-0.4164315552\C,-3.4263414094,-0.484658602,-1.2399700394\H,-3.1155887199,0.7179804925,0.5208512042\H,-3.1094752698,-1.4322017242,-1.6737373763\H,-4.5116718804,-0.3973873056,-1.2688880635\Br,-2.7376955194,0.9053173711,-2.4431509393\C,-3.6169098986,-1.2797621825,1.1289596469\C,-3.2289930346,-1.088780294,2.572995808\C,-3.9721490577,-1.6207798607,3.5648170133\C,-5.0783023215,-2.5386679052,3.3705298579\C,-5.172372096,-3.464532383,2.3755618325\C,-4.1801687377,-3.6913619587,1.3423692729\C,-3.3930573281,-2.7359082703,0.8066979355\H,-4.6953259568,-1.0758948841,1.0427579642\H,-2.3513032914,-0.48984508,2.8095312052\H,-3.7247684639,-1.3689113709,4.5942948748\H,-5.8229979485,-2.578649055,4.1628686462\H,-5.9857428021,-4.1846090204,2.4381244335\H,-4.0564380549,-4.7187679232,1.0051573248\H,-2.5909744452,-3.0089564554,0.1238987365\C,0.635750043,0.2039404217,1.1455338029\H,0.9560340135,0.9866527781,1.8308002035\H,1.1172317265,0.3255516515,0.1733319612\H,0.8682518629,-0.781734952,1.5539303024\Version=ES64L-G16RevA.03\State=1-A\HF=-3151.0982313\RMSD=4.031e-09\RMSF=3.014e-06\Dipole=-0.347073,-0.1207965,1.3204931\Quadrupole=5.1724787,-2.1983563,-2.9741224,6.0499058,2.5399079,2.5884049\PG=C01 [X(C11H13Br1O2)]\@

References

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X-ray Crystallography:

Suitable single crystal of adduct **13** was selected under the polarizing microscope (Leica M165Z), mounted on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker D8 Quest Single Crystal diffractometer with Photon II detector at 100 K by using I μ S 3.0 Microfocus Source with Mo-K α radiation (λ = 0.710723 Å). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream 800 attachment. Symmetry related absorption corrections using the program SADABS^[1] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX3 software.^[1] The structure was solved by ShelxT (intrinsic phasing)^[2] and the full-matrix least-square refinement was carried out using Shelxl^[3] in Olex2^[4]. The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using program Olex2.^[4]

Atomic coordinates, bond lengths and angles and displacement parameters for compound **13** have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 1922409). This data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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A complete structure solution, refinement and analysis program (2009). *J. Appl. Cryst.*, 42, 339-341.

Table S2. Crystallographic Experimental details

	Structure of 13
Crystal data	
Chemical formula	C ₁₅ H ₁₆ BrNO ₄
M_r	354.20
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	9.0366 (6), 13.2505 (8), 12.5159 (9)
β (°)	103.546 (3)
V (Å ³)	1456.96 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.84
Crystal size (mm)	0.22 × 0.07 × 0.04
Data collection	
Diffractometer	Bruker D8Quest
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. $wR2(int)$ was 0.1547 before and 0.1024 after correction. The Ratio of minimum to maximum transmission is 0.5697. The $\lambda/2$ correction factor is Not present.
T_{min}, T_{max}	0.425, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	45974, 3358, 2923
R_{int}	0.093
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.125, 1.09
No. of reflections	3358
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.87, -0.80

Computer programs: *SAINT* V8.38A (?, 2016), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

NMR Spectra

Methyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (**4a**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Chemical structure: COC(=O)C(Cl)c1ccccc1

¹H NMR (400 MHz, CDCl₃):

- 7.25-7.35 (m, 5H, aromatic protons)
- 5.30 (d, 1H, CH)
- 3.70 (s, 3H, OCH₃)
- 3.10 (s, 3H, CH₃)

¹³C NMR (100 MHz, CDCl₃):

- 172.90 (s, C=O)
- 131.42, 131.01, 126.42, 126.12, 121.53 (aromatic carbons)
- 52.25, 40.27 (methine and methoxy carbons)
- 3.11 (methyl carbon)

Methyl 2-(cyclohepta-2,4,6-trien-1-yl)-3-iodopropanoate (**4aI**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Ethyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (**4b**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Butyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (**4c**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Isobutyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (**4d**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoic acid (**4e/4g**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

2-Phenoxyethyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (**4f**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl)bis(3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate) (**4h**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Vinyl 3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanoate (**4i**); ¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃).

Prop-2-yn-1-yl (Z)-2-(bromomethyl)-3-methylhepta-4,6-dienoate (**4j**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)propanamide (**4k**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

3-Bromo-N,N-dimethylpropanamide (**4l-H**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

3-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)-1-morpholinopropan-1-one (**4m**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

3-Bromo-4-(cyclohepta-2,4,6-trien-1-yl)-1-methylpyrrolidine-2,5-dione(**4n**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

4-Bromo-3-(cyclohepta-2,4,6-trien-1-yl)-5-(cyclohepta-2,4,6-trien-1-yloxy)-3,4-dihydro-2H-pyrrol-2-one (**4o**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

1-Bromo-2-(cyclohepta-2,4,6-trien-1-yl)pentan-3-one (**4p**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

5-(cyclohepta-2,4,6-trien-1-yl)furan-2(5H)-one (**4q**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

4-oxo-5-phenylpentanoic acid (**4q'**): ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

2-Hydroxyethyl 3-bromopropanoate (**4r**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Methyl (*E*)-3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)acrylate (**6a**: *Z* and *E* mixture ~ 9 : 1 ratio); ¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃).

Ethyl (Z)-3-bromo-2-(cyclohepta-2,4,6-trien-1-yl)acrylate (**6b**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Dimethyl 2-bromo-3-(cyclohepta-2,4,6-trien-1-yl)but-2-enedioate (**6c**) **two isomers**; ¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃).

Methyl 2-(cyclohepta-2,4,6-trien-1-yl)acrylate (**12**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Methyl 3-bromo-2-(1,3-dioxodecahydro-4,6-ethanocyclopropa[f]isoindol-5-yl) propanoate
(13); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Methyl 2-bromo-2-phenyl-3-hydroxypropanoate (**14**); ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3).

Methyl 2-(bromomethyl)-3-chloro-3-phenyl-3-propanoate (**15**, mixture of diastereoisomers); ^1H NMR (300 MHz, CDCl_3), ^{13}C NMR (75 MHz, CDCl_3).

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