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Protonation and transformations of α-diazo-β-dicarbonyl compounds in superacids: generation of the strongest carbon-centered cationic electrophiles at the protonation of diazomalonates in Friedel–Crafts reactions

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ABSTRACT

Protonation of diazodiketones $N_2C(COR)_2$ in Brønsted superacids (TfOH, FSO_3H, TfOH–SbF_5) gives rise to stable and non-reactive O,O-diprotonated at carbonyl oxygens species $N_2C(C(=OH^+)R)_2$, which were studied by means of ^1H and ^{13}C NMR. Diazomalonates $N_2C(CO_2Alk)_2$, contrary to diazodiketones, react with TfOH or HF, releasing nitrogen and producing triflates of oxymalonates $TfOCH(CO_2Alk)_2$ or fluoromalonates $FCH(CO_2Alk)_2$, respectively. Diazoketoesters $N_2C(COR)(CO_2Alk)$ react in the same way only with TfOH, but not with HF. The reactions of diazomalonates with arenes ArH (benzene, toluene, xylenes) in TfOH solution yield corresponding Friedel–Crafts reaction products $ArCH(CO_2Alk)_2$. According to performed DFT calculations, trication $^+CH(C(=OH^+)OMe)_2$, a possible intermediate, which is derived from protonation of dimethyl diazomalonate, should be the strongest cationic carbon-centered electrophile known up to date.

1. Introduction

Diazocarbonyl compounds play an important role in organic synthesis. In general, reactions of these compounds are catalyzed by transition metal compounds and proceed via the formation of metal–carbene complexes as key intermediates leading to various functionalized derivatives of carbo- and heterocycles.[1] Apart from that, many reactions of diazocarbonyl compounds are promoted by Brønsted acids (see reviews 2a–c). The transformation of diazocompounds in Brønsted superacids still remains a poorly studied area of chemistry (see recent research papers 2d,e). At the same time, strong ability of protonation and extremely low nucleophilicity of superacids play a crucial role in the generation and stabilization of cationic species. The application of superacids in the chemistry of diazocompounds could provide new possibilities for organic synthesis.

This research is an expansion of our recent works on activation of organic compounds in superacids.[3] The main goal of the project was to investigate the protonation and subsequent transformations of diazodicarbonyl compounds in Brønsted superacids, including Friedel–Crafts reactions with arenes. Three types of diazodicarbonyl compounds, diazodiketones **1a**–**e**, diazoketoesters **1f**,**g**, and diazomalonates **1h**,**i**, were used in this study (Fig. 1).

2. Results and discussion

2.1. NMR study of protonation of diazocompounds 1a–i in Brønsted superacids. Reactions of diazocompounds 1f–i with TfOH and HF

First, the stability of diazocompounds **1a**–**i** was investigated in various Brønsted superacids. It was found that diazoketoesters **1f**,**g** and diazomalonates **1h**,**i** reacted with CF_3SO_3H (TfOH) (Hammet acidity function H_0 −14 [see Ref. 4]) or FSO_3H (H_0 −15) at room temperature releasing nitrogen (vide infra). Despite this fact, diazodiketones **1a**–**e** were stable not only in solutions of these acids, but even in much more stronger conjugate Brønsted–Lewis superacid TfOH–SbF_5 (H_0 ~−19) at room temperature. No evolution of nitrogen was observed with diazodiketones **1a**–**e** and they

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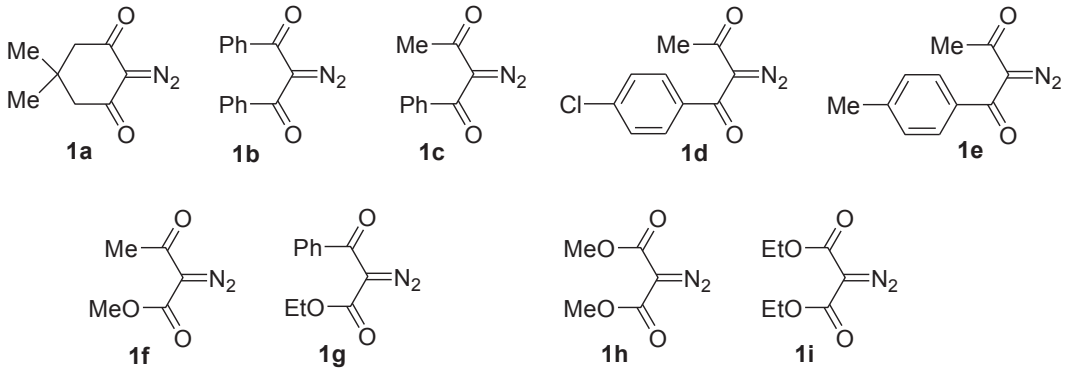
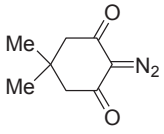
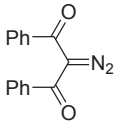
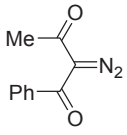
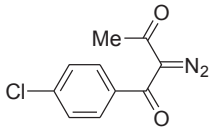
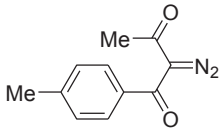


Fig. 1. Diazocompounds **1a**–**i** used in this study.

were quantitatively recovered after quenching of their superacid solutions with water.

Based on this extreme stability and non-reactivity of **1a**–**e** in superacids, we undertook a study on their protonation in TfOH and FSO_3H using NMR. Table 1 contains the data on ^{13}C NMR spectra of diazodiketones **1a**–**e** in $CDCl_3$ and their protonated forms in TfOH at room temperature (see spectral figures in Supplementary data). Principally, compounds **1a**–**e** in TfOH solutions may form protonated (specifically solvated) species on the carbonyl oxygen atoms and/or on the nitrogen atom of diazo group. However, taking

Table 1
Selected ^{13}C NMR data of starting diazodiketones **1a**–**e** ($CDCl_3$) and their protonated forms (TfOH)

Diazodiketones	^{13}C NMR data (500 MHz, room temperature)					
	Signal of C=O			Signal of C=N		
	Starting diazodiketone in $CDCl_3$, δ_{CDCl_3}, ppm	Protonated form in TfOH, δ_{TfOH}, ppm	Chemical shift difference $\Delta\delta_C = \delta_{TfOH} - \delta_{CDCl_3}$	Starting diazodiketone in $CDCl_3$, δ_{CDCl_3}, ppm	Protonated form in TfOH, δ_{TfOH}, ppm	Chemical shift difference $\Delta\delta_C = \delta_{TfOH} - \delta_{CDCl_3}$
 **1a**	189.0	199.4	10.4	82.6	95.2	12.6
 **1b**	186.0	196.4	10.4	83.9	87.7	3.8
 **1c**	190.6 [C=O(Me)] 184.9 [C=O(Ph)]	202.8 [C=O(Me)] 195.3 [C=O(Ph)]	12.2 [C=O(Me)] 10.4 [C=O(Ph)]	83.5	90.5	7.0
 **1d**	189.9 [C=O(Me)] 183.5 [C=O(Ar)]	203.4 [C=O(Me)] 193.90 [C=O(Ar)]	13.5 [C=O(Me)] 10.5 [C=O(Ar)]	83.3	90.5	7.2
 **1e**	190.7 [C=O(Me)] 184.6 [C=O(Ar)]	202.0 [C=O(Me)] 194.5 [C=O(Ar)]	11.3 [C=O(Me)] 9.9 [C=O(Ar)]	83.1	89.3	6.2

into account the higher basicity of the carbonyl oxygen ($pK_{BH^+} = -2.85$ to -5.55), one would expect that the predominant protonated forms of diazodiketones **1a**–**e** are O,O-diprotonated structures **Aa**–**e**. Further protonation of diazo group is unlikely. This is in agreement with the literature data on protonation of diazomonocarbonyl compounds, which produce in superacids only O-protonated cations.[1a,5]

In the ^{1}H NMR spectra of protonated forms of **1a**–**e** the signals of protons bonded to carbonyl oxygen were not registered due to the fast proton exchange in superacid TfOH at room temperature (see spectral figures in Supplementary data). Also, for compounds **1a**–**e** all signals of protons of aryl and alkyl groups in TfOH were down-field shifted relative to the same signals in $CDCl_3$. The difference of the chemical shifts of carbonyl groups in ^{13}C NMR spectra in TfOH and $CDCl_3$ solutions was around 9.9–13.5 ppm (see Table 1). This kind of down-field shift of these carbon signals indicates a substantial degree of protonation of carbonyl groups in TfOH. When compared to the carbon spectra in $CDCl_3$, the signals of carbon atoms of diazo group were down-field shifted for 3.8–12.6 ppm (see Table 1). This may point out to an induced shift due to the protonation of carbonyls. Protonation of carbon atom of diazo group in **1a**–**e** was not observed by ^{1}H and ^{13}C NMR, since no new signals corresponding to C–H fragment were registered in the spectra.

Three new signals of protons, which are attached to carbonyl oxygens, were observed in the region of 14–15.5 ppm in ^{1}H NMR spectrum of protonated form of diazodiketone **1e** in FSO_3H at low temperature −80 °C (Fig. 2). Proton exchange with superacidic medium is suppressed at −80 °C as compared to room temperature. The most probably that protonation of two carbonyl groups of **1e** leads to a dication, the structure of which may be presented as the mesomeric forms **I**, **II**, and **III** or as a general form **Ae** (Scheme 1). Moreover, at this low temperature dication **Ae** may exist as *E*,*Z*-conformers (Scheme 1) with hindered rotation around C(O)–C(N_2) bonds, analogous to *E*,*Z*-conformers of the initial diazodicarbonyl compounds.[6,7] An observation of several signals of non-equivalent methyl group of acetyl moiety in ^{1}H NMR (Fig. 2) may be an additional evidence for the existence of *E*,*Z*-conformers of **Ae**. Apart from that, in these conformers the protons, which are bonded to carbonyl oxygens may give several signals, as well. Due to exchange with superacidic media, the signals of these protons are broadened and so their integration is not quantitative. Also the signals of aromatic protons were broad and unresolved due to high viscosity of FSO_3H at −80 °C.

When reactions of compounds **1f**–**i** were carried out in neat TfOH, the evolution of nitrogen was observed. Diazomalonates **1h**,**i** reacted with TfOH at room temperature very fast leading easily to the formation of the corresponding triflates of oxymalonates **2c**,**d** in quantitative yields (Scheme 2). The same type of extrusion of nitrogen by the triflate group occured with diazoketoesters **1f**,**g**. Nevertheless, in this case formation of triflates **2a**,**b** took place harder and required increasing of reaction time up to 4 h (Scheme 2). It should be noted that these types of dicarbonyl triflates **2** are rare.[8]

Therefore, qualitative observation shows that diazodiketones **1a**–**e** are very stable and completely non-reactive in superacids (vide supra), while diazoketoesters **1f**,**g** react harder than diazomalonates **1h**,**i**. This range of the reactivity reflects a difference in an electron withdrawing character of the protonated keto and ester groups. According to the found range of basicity of these groups in the superacids PhC=O>MeC=O>CO_2Et,[3a] similar range should be assumed for the acceptor properties of the protonated groups PhC(=OH$^+$)>MeC(=OH$^+$)>C(=OH$^+$)OEt. It means that protonated keto and ester groups in the species **Af**–**i** (Scheme 3), which are derived from diazoketoesters **1f**,**g** and diazomalonates **1h**,**i**, are weaker acceptors relative to O-protonated keto groups in diazodiketones **1a**–**e**. Consequently, in superacids further protonation of carbon or nitrogen atoms of diazo group in the compounds **1g**–**i** (but not in **1a**–**e**) may occur leading to the formation of the species **Bf**–**i** or **Df**–**i**, respectively (Scheme 3). It is very likely that both of these species may eliminate nitrogen giving rise to intermediate species **Cf**–**i** or react with triflate ion producing triflates **2** (Scheme 2).

The fluorination of diazomalonates **1h**,**i** with neat HF gave rise to fluoromalonates **3a**,**b**, respectively (Scheme 4). Ketoesters **1f**,**g** did not react with HF, due to its reduced acidity as compared to TfOH. Diazomalonates **1h**,**i** did not lead to formation of corresponding compounds **3a**,**b** in less acidic system HF–pyridine,

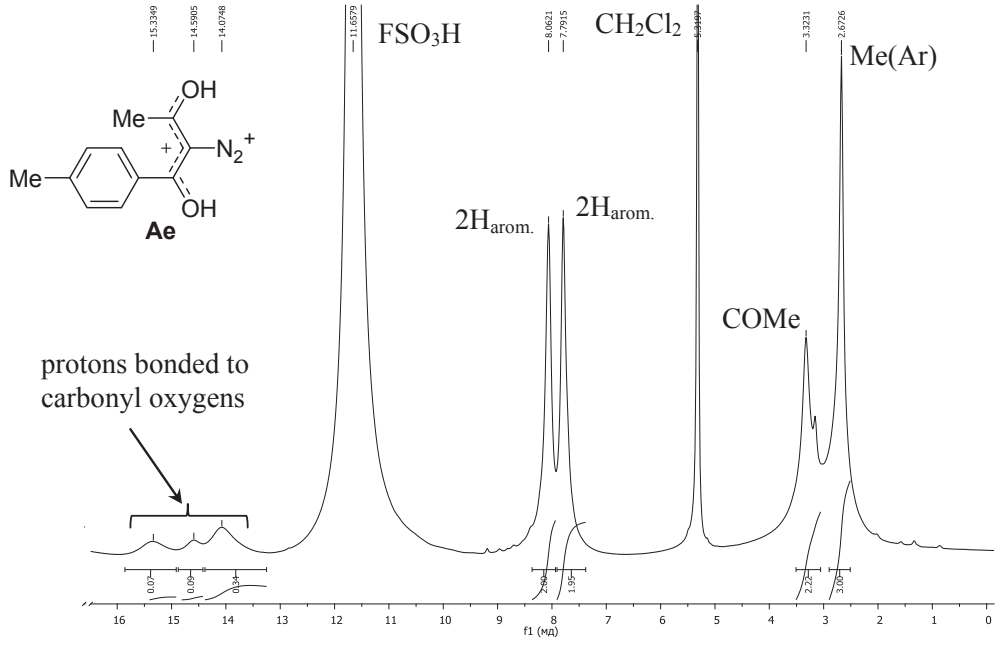
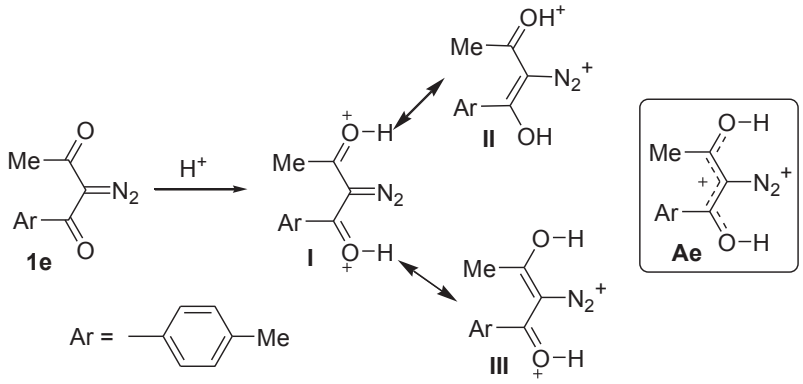
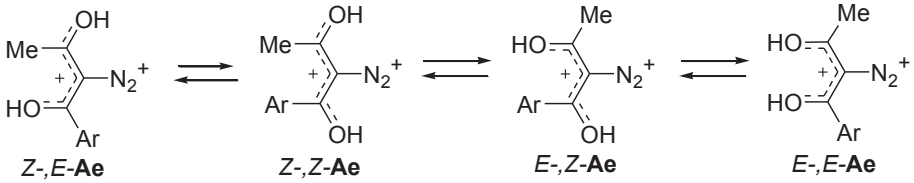
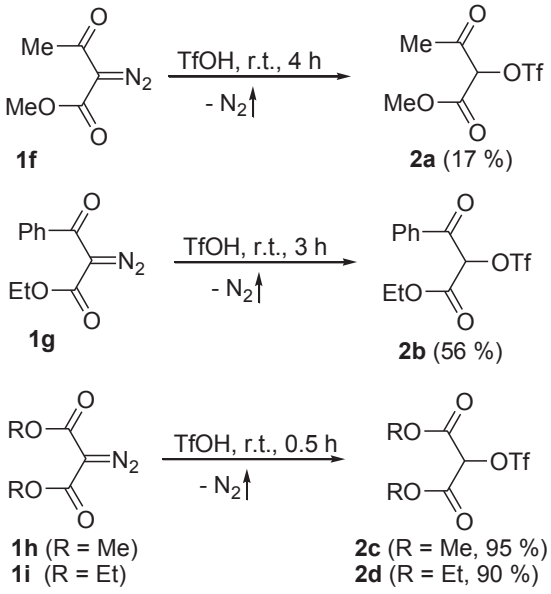


Fig. 2. ^{1}H NMR spectrum of protonated form **Ae** of diazodiketone **1e** in FSO_3H at 80 °C (500 MHz, CH_2Cl_2 was added as internal standard).



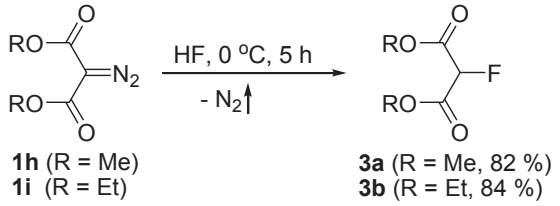


Scheme 1. Possible structures of protonated forms of diazodiketone **1e**.



Scheme 2. Formation of triflates **2a**–**d** from diazodicarbonyl compounds **1f**–**i** in TfOH (yield of **2a** was low (17%) due to incomplete conversion of starting compound **1f**).

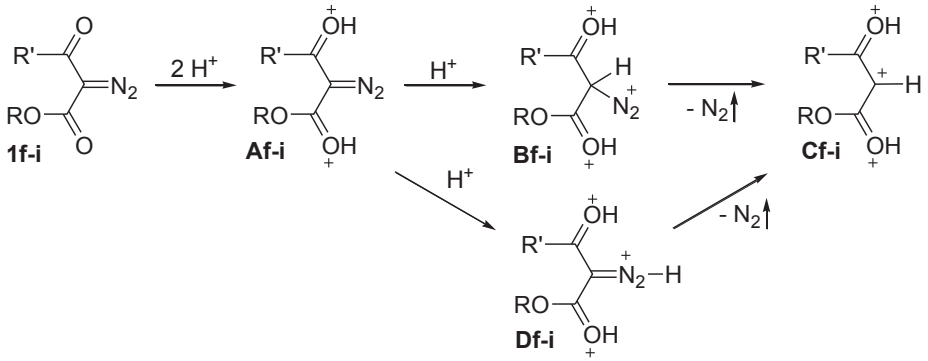
which was previously used for fluorination of diazomonocarbonyl derivatives.[9] This synthesis of fluoromalonates **3a**,**b** is one of a number of ways to diazocompounds using various fluorine sources.[10]



Scheme 4. Formation of fluoromalonates **3a**,**b** from diazomalonates **1h**,**i** in neat HF.

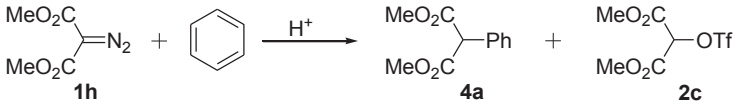
2.2. Reactions of diazocompounds 1f–i with arenes in TfOH

The main results on reactions of dimethyl diazomalonate **1h** with benzene under the action of TfOH are presented in Table 2. Diazoester **1h** produces Friedel–Crafts alkylation product **4a** along with triflate **2c** in TfOH (entries 1–3). Other Brønsted acids FSO_3H (H_0=−15, 40 equiv, −35 °C, 1 h), and Tf_2NH (30 equiv, 80 °C, 1 h) or



Scheme 3. The assumed mechanism of protonation of diazoketoesters **1f**,**g** and diazomalonates **1h**,**i** in superacids.

Table 2
Reactions of dimethyl diazomalonate **1h** with benzene in TfOH



Entry	Reaction conditions			Reaction products			
	Acid[a]	Temperature, °C	Time, h	Yield, %		Total yield of **4a** and **2c**, %	Ratio of **4a**/**2c**
				4a	**2c**		
1	TfOH (H_0=−14) (40 equiv)	rt	0.5	34	50	84	1:1.5
2	TfOH (H_0=−14) (40 equiv)	rt	24	33	19	52	1.8:1
3	TfOH (H_0=−14) (40 equiv)	60	0.25	80	5	85	16:1
4	TfOH–SbF_5 (H_0=−19) (40 equiv)	rt	0.25	—[b]	Traces	—	—

[a] Hammet acidity function values H_0 are from Ref. 4.
[b] Complete conversion of **2a** with formation of unidentified compounds.

methyltriflate MeOTf (30 equiv, 80 °C, 1 h) did not yield **4a**. In these cases quantitative recovery of unreacted starting compound **1h** took place. Apart from that, reactions of **1h** under the action of FSO_3H (40 equiv, rt, 1 h), TfOH–SbF_5 (H_0=−19, 40 equiv, rt, 0.25 h), H_2SO_4 (100 equiv, rt, 1 h), or $AlCl_3$ (5 equiv, rt, 1 h, CH_2Cl_2 as co-solvent) resulted in the formation of complex mixtures of unidentified compounds. So, TfOH seems to be the best media to conduct Friedel–Crafts reactions of diazomalonates with arenes.

The formation of both dimethyl phenylmalonate **4a** and triflate **2c**, which were formed in concurrent reactions, evidenced on the high reactivity of intermediate cationic species (see Scheme 3), which were derived from **1h** in the superacid TfOH. A higher reaction temperature 60 °C allowed to increase the yield of **4a** (entry 3), indicating that activation barrier is higher for Friedel–Crafts process, than for triflate formation.

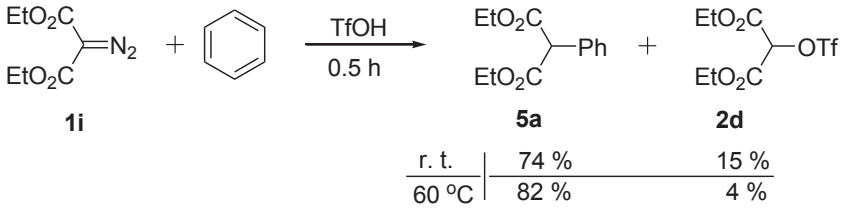
The same trends were observed for reaction of diazomalonate **1i** with benzene, resulting in the formation of malonate **5a** and triflate **2d** (Scheme 5). Contrary to compounds **1h**,**i**, diazoketoesters **1f**,**g** did not give the products of benzene (and other arenes) alkylation, forming only corresponding triflates **2a**,**b** (see Scheme 2). It could be explained by a higher electrophilicity and reactivity (and result, lower selectivity) of intermediate cationic species, generated from **1f**,**g**, as compared to the same species from **1h**,**i**. The reason for this is likely due to the stronger electron withdrawing properties of protonated keto group in **1f**,**g**, relative to protonated ester group in **1h**,**i** (vide supra).

formed. The same reactivity was observed with anisol and veratrol, apparently due to a proto-solvation of methoxy groups in superacids,[4] that make these arenes slightly deactivated for electrophilic substitution.

Both the formation of triflates **2c**,**d** and low regioselectivity in reactions with arenes evidence on the extremely high reactivity of intermediate cations, which were derived from **1h**,**i** in TfOH. Thus, reaction with toluene affords *ortho*-, *meta*- and *para*-isomers **4b**–**d** (entries 1 and 2, Table 3) and **5b**–**d** (entry 1, Table 4) in approximately equal amounts. The same situation is observed with reactions with *o*-xylene (entries 3 and 4, Table 3; entry 2, Table 4), and *m*-xylene (entries 5 and 6, Table 3; entry 3, Table 4). Furthermore, the migration of methyl group in aromatic ring is observed under the formation of compounds **4h** (entries 5 and 6, Table 3), **4g** (entries 7 and8, Table 3), **5h** (entry 3, Table 4), **5g** (entry 4, Table 4) that is akin to the behavior of polymethylated arenes in superacidic media.[4] Increasing the reaction temperature up to 60 °C do not lead to substantial increase of amount of Friedel–Crafts reaction products **4** (compare pairs of experiments at rt and 60 °C in Table 4).

2.3. DFT calculations of cationic species derived from protonation of diazomalonate 1h

Based on the obtained data on transformations of diazomalonates **1h**,**i** in TfOH (Scheme 2) or HF (Scheme 4), and their re-



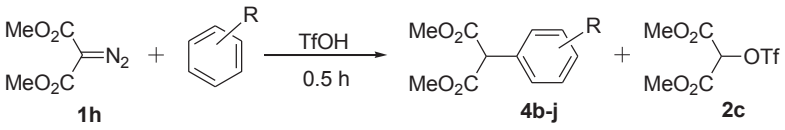
Scheme 5. Reaction of diazomalonate **1i** with benzene in neat TfOH (40 equiv) at various temperatures for 0.5 h.

The results of reactions of diazomalonates **1h**,**i** with donating arenes (toluene, isomeric xylenes) in TfOH are presented in Tables 3 and 4. These reactions produced mixtures of Friedel–Crafts alkylation products **4b**–**j**, **5b**–**j** and triflates **2c**,**d**. The structures of dialkyl arylmalonates **4b**–**j**, **5b**–**j** were determined by means of ^{1}H NMR and GC–MS, along with comparison with literature spectral data for these compounds (see Experimental part).

Reactions of **1h**,**i** with electron deficient arenes, chlorobenzene, bromobenzene, 1,2-dichlorobenzenes, did not lead to Friedel–Crafts products at all. In these cases triflates **2c**,**d** were solely

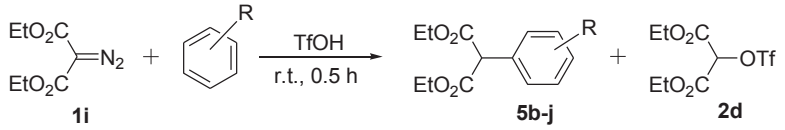
actions with arenes in TfOH (Tables 2–4, Scheme 5), one may assume the formation of several intermediate cationic species **B**, **C**, **D** (see Scheme 3), which are able to take part in the considered reactions in superacids. To estimate electronic and electrophilic properties of such species the DFT study of cations **Bh**, **Dh**, **Ch**, derived from diazomalonate **1h**, was undertaken (Table 5). For this purpose charge distribution, contribution of atomic orbital into LUMO, and global electrophilicity indices ω[11] were calculated. As it is evident from the obtained data, among three species, **Bh**, **Dh**, **Ch**, the trication **Ch** has the highest value of electrophilicity 24.0 eV that

Table 3
Reactions of dimethyl diazomalonate **1h** with arenes in neat TfOH (40 equiv) for 0.5 h at various temperatures



Entry	Arene, R	Reaction temperature, °C	Reaction products					
			Dimethyl arylmalonate **4**			Yield of **2c**, %	Total yield of **4** and **2c**, %	Ratio of **4**/**2c**
			No.	R	Yield, %			
1	Me	rt	**4b**	2-Me	9	56	84	(**4b**+**4c**+**4d**)/**2c**
			4c	3-Me	9			1:2
			4d	4-Me	10			
2	Me	60	**4b**	2-Me	17	17	67	(**4b**+**4c**+**4d**)/**2c**
			4c	3-Me	16			3:1
			4d	4-Me	17			
3	1,2-Me_2	rt	**4e**	2,3-Me_2	10	48	73	(**4e**+**4f**)/**2c**
			4f	3,4-Me_2	15			1:2
4	1,2-Me_2	60	**4e**	2,3-Me_2	7	25	37	(**4e**+**4f**)/**2c**
			4f	3,4-Me_2	5			1:2
5	1,3-Me_2	rt	**4g**	2,4-Me_2	15	57	82	(**4g**+**4h**+**4i**)/**2c**
			4h	3,5-Me_2	5			1:2
			4i	2,6-Me_2	5			
6	1,3-Me_2	60	**4g**	2,4-Me_2	10	47	64	(**4g**+**4h**+**4i**)/**2c**
			4h	3,5-Me_2	4			1:2.8
			4i	2,6-Me_2	3			
7	1,4-Me_2	rt	**4j**	2,5-Me_2	25	60	90	(**4j**+**4g**)/**2c**
			4g	2,4-Me_2	5			1:2
8	1,4-Me_2	60	**4j**	2,5-Me_2	24	19	49	(**4j**+**4g**)/**2c**
			4g	2,4-Me_2	6			1.5:1

Table 4
Reactions of diethyl diazomalonate **1i** with arenes in neat TfOH (40 equiv) at room temperature for 0.5 h



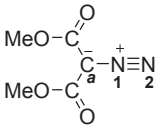
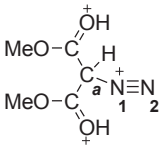
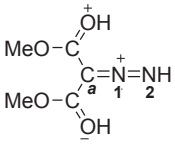
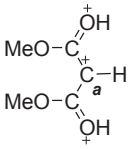
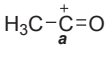
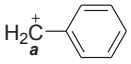
Entry	Arene, R	Reaction products					
		Diethyl arylmalonate **5**			Yield of **2d**, %	Total yield of **5** and **2d**, %	Ratio of **5**/**2d**
		No.	R	Yield, %			
1	Me	**5b**	2-Me	13	31	70	(**5b**+**5c**+**5d**)/**2d**
		5c	3-Me	26 (**5c**+**5d**)			1.2:1
		5d	4-Me				
2	1,2-Me_2	**5e**	2,3-Me_2	18	30	75	(**5e**+**5f**)/**2d**
		5f	3,4-Me_2	27			1.5:1
3	1,3-Me_2	**5g**	2,4-Me_2	24	35	75	(**5g**+**5h**+**5i**)/**2d**
		5h	3,5-Me_2	8			1.1:1
		5i	2,6-Me_2	8			
4	1,4-Me_2	**5j**	2,5-Me_2	30	35	70	(**5j**+**5g**)/**2d**
		5g	2,4-Me_2	5			1:1

allows it to be considered as a 'superelectrophile'.[12] Apart from that, **Ch** bears the biggest positive charge on the carbon C^a, and possesses the highest contribution of this carbon into its LUMO, as compared to cations **Bh** and **Dh** that shows a coincidence of charge and orbital control in the reactivity of the atom C^a in **Ch**.

In our opinion, the participation of the N-protonated cation **Dh** in these reactions is unlikely, because in order to achieve target products the proton migration should occur to the carbon of diazo group that may considerably increase activation barrier for transformations of **Dh**. More probable is formation of species **Bh** and **Ch**, which can both operate as reactive intermediates: the former reacts in S_N2 way, the latter in S_N1 one. Of course, it is difficult to distinguish between these two, **Bh** and **Ch**, in the studied processes. But, taking into account extremely high reactivity of trication **Ch**, namely this species may be the most probable reactive intermediate generated while protonation of diazomalonates in superacid.

Additionally we compared electrophilic properties of various carbo-centered cations, H_3C^+, F_3C^+, $H_3C(O{=})C^+$, PhH_2C^+, which have been postulated as intermediate species in miscellaneous Friedel–Crafts reactions. As a result, trication **Ch** is characterized by the highest electrophilic properties relative to all other species

Table 5
Selected electronic characteristics (DFT calculations) of starting diazomalonate **1h**, cations **Bh**, **Dh**, **Ch**, derived from protonation of **1h** (see Scheme 3), and characteristics of other carbon-centered cationic electrophiles

Species	E_{HOMO}, eV	E_{LUMO}, eV	ω,[a] eV	$q(C^a)$,[b] e	$q(N^1)$,[b] e	$q(N^2)$,[b] e	$k(C^a)_{LUMO}$,[c] %	$k(N^1)_{LUMO}$,[c] %	$k(N^2)_{LUMO}$,[c] %
 **1h**	−7.44	−2.45	2.45	−0.21	0.13	0.11	18.6	15.5	16.1
 **Bh**	−12.25	−5.42	5.45	−0.20	0.16	0.48	0.1	36.5	46.2
 **Dh**	−11.59	−6.45	7.92	0.06	0.25	0.12	11.7	31.5	26.3
 **Ch**	−12.47	−9.87	*24.0*	*0.38*	—	—	*55.0*	—	—
	−15.23	−6.96	7.45	0.38	—	—	99.4	—	—
	−15.76	−5.13	5.13	1.45	—	—	65.2	—	—
	−13.51	−3.23	3.41	1.00	—	—	57.8	—	—
	−8.57	−4.85	6.05	0.04	—	—	45.0	—	—

[a] Global electrophilicity index $\omega=(E_{HOMO}+E_{LUMO})^2/8(E_{LUMO}-E_{HOMO})$.
[b] Natural charges.
[c] Contribution of atomic orbital into the molecular orbital.

from Table 5. This trication may be considered as the strongest carbon-centered electrophile.

3. Conclusions

Protonation and transformations of diazodicarbonyl compounds in Brønsted superacids (TfOH, FSO_3H, TfOH–SbF_5) have been studied for the first time. Diazodiketones in these superacids give rise to the stable and non-reactive O,O-diprotonated on carbonyl oxygens cations. Diazomalonates react with TfOH and HF, releasing nitrogen, with the formation of triflates of oxymalonates or fluoromalonates, respectively. Diazoketoesters have intermediate reactivity between diazodiketones and diazomalonates. Diazomalonates in TfOH behave with arenes as alkylating agent in Friedel–Crafts reactions. According to DFT calculations, intermediate tricationic species, which are derived from diazomalonates in superacids, are the strongest carbon-centered electrophiles.

4. Experimental part

4.1. General

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker-400 spectrometer at 25 °C (at 400, 101, and 376 MHz for ^1H, ^{13}C, and ^{19}F NMR spectra, respectively). The residual proton-solvent peak of $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra, the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra, and the signal of $CFCl_3$ (δ 0.0 ppm) for ^{19}F NMR spectra were used as references. NMR experiments in the superacids TfOH at 25 °C or in FSO_3H at −80 °C were performed on a Bruker AM-500 spectrometer (at 500, and 125 MHz for ^1H, and ^{13}C NMR spectra, respectively). NMR spectra in superacids were referenced to the signal of CH_2Cl_2 added as internal standard: δ 5.32 ppm for ^1H NMR spectra, and δ 53.84 ppm for ^{13}C NMR spectra. HRMS was carried out at instruments Bruker maXis HRMS-ESI-QTOF. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/

UV-254), using UV light for detection. Preparative column chromatography was performed on silica gel 60 Merck.

DFT calculations. All computations were carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) by using GAUSSIAN 2003 program packages.[13] The geometry optimization was performed using the 6-311+G(2d,2p) basis set (standard 6-311 basis set added with polarization (d,p) and diffuse functions). Optimizations were performed on all degrees of freedom and solvent-phase optimized structures were verified as true minima with no imaginary frequencies. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima and to estimate the thermodynamic parameters. Solvent-phase calculations used the Polarizable Continuum Model (PCM) with water as a solvent.

Synthesis and properties of starting diazodicarbonyl compounds **1a**–**i** are given in works.[1c,14]

4.2. General procedure for reaction of diazocompounds 1f–i in TfOH. Characterization of compounds 2a–d

Diazo compound (1.5 mmol) was added dropwise to a stirred portion of TfOH (3 mL) at room temperature. The reaction mixture was stirred for 0.5 h (for **1h**,**i**), 3 h (for **1g**) or 4 h (for **1f**), then poured into water (100 mL) and extracted with dichloromethane (3×30 mL). The combined organic layers were consequently washed with water (2×30 mL), saturated aqueous solution of $NaHCO_3$ (1×30 mL), water (2×30 mL), and dried over Na_2SO_4. Solvent was removed under reduced pressure. Crude material was purified by flash chromatography (silica gel; eluent: hexane/acetone; linear gradient: 0–5% of acetone) to afford compounds **2a**–**d**.

4.2.1. Methyl 3-oxo-2-(trifluoromethylsulfonyloxy)butanoate ***2a***. Yield 17% as a yellowish oil; δ_H (400 MHz, $CDCl_3$) 5.48 (1H, s, CH), 3.88 (3H, s, MeO), 2.37 (3H, s, Me); δ_C (101 MHz, $CDCl_3$) 193.3, 162.3, 118.4 (q, *J* 320 Hz), 84.1, 54.0, 26.5; δ_F (376 MHz, $CDCl_3$) −74.50; HRMS (ESI): MH^+, found 264.9994, $[C_6H_8F_3O_6S]^+$ requires 264.9988.

4.2.2. Ethyl 3-oxo-3-phenyl-2-(trifluoromethylsulfonyloxy)propanoate ***2b***. Yield 56% as a yellowish oil; δ_H (400 MHz, $CDCl_3$) 7.99 (2H, d, *J* 7.5 Hz, 2Harom.), 7.68 (1H, t, *J* 7.5 Hz, 1Harom.), 7.54 (2H, t, *J* 7.5 Hz, 2Harom.), 6.19 (1H, s, CH), 4.31 (2H, q, *J* 7.1 Hz, CH_2), 1.24 (3H, t, *J* 7.1 Hz, Me); δ_C (101 MHz, $CDCl_3$) 185.7, 162.5, 135.0, 132.9, 129.4, 129.1, 118.4 (q, *J* 320 Hz), 81.8, 63.8, 13.7; δ_F (376 MHz, $CDCl_3$) −74.27; HRMS (ESI): MNa^+, found 363.0124, $[C_{12}H_{11}F_3O_6SNa]^+$ requires 363.0126.

4.2.3. Dimethyl 2-(trifluoromethylsulfonyloxy)malonate ***2c***. Yield 95% as a yellowish oil; δ_H (400 MHz, $CDCl_3$) 5.52 (1H, s, CH), 3.91(6H, s, 2MeO); δ_C (101 MHz, $CDCl_3$) 162.2, 118.5 (q, *J* 320 Hz), 78.1, 54.3; δ_F (376 MHz, $CDCl_3$) −74.26; HRMS (ESI): MNa^+, found 302.9755, $[C_6H_7F_3O_7SNa]^+$ 302.9757.

4.2.4. Dimethyl 2-(trifluoromethylsulfonyloxy)malonate ***2d***. Yield 90% as a yellowish oil; δ_H (400 MHz, $CDCl_3$) 5.47 (1H, s, CH), 4.36 (4H, dq, *J* 7.1, 3.6 Hz, $2CH_2$), 1.34 (6H, t, *J* 7.1 Hz, 2Me); δ_C (101 MHz, $CDCl_3$) 161.7, 118.5 (q, *J* 320 Hz), 78.4, 63.9, 14.0; δ_F (376 MHz, $CDCl_3$) −74.30; HRMS (ESI): MNa^+, found 331.0068, $[C_8H_{11}F_3O_7SNa]^+$ requires 331.0070.

4.3. General procedure for reaction of diazomalonates 1h,i with HF. Characterization of compounds 3a,b

Anhydrous liquid hydrogen fluoride (5 mL, 0.25 mmol) was placed into polypropylene flask at 0 °C under nitrogen atmosphere. Diazomalonate (0.5 mmol) was added dropwise into the stirred reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 5 h. Then, reaction mixture was poured into ice-water (100 mL). The obtained mixture was neutralized with solid $NaHCO_3$, and extracted with dichloromethane (3×25 mL). The combined organic layers were washed with water (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Crude material was purified by column chromatography (silica gel; hexane/EtOAc; linear gradient: 0–2% EtOAc).

4.3.1. Dimethyl 2-fluoromalonate ***3a***.[15] Yield 82% as a colorless oil; δ_H (400 MHz, $CDCl_3$) 5.33 (1H, d, *J* 48 Hz, CH), 3.89 (6H, s, 2Me); δ_C (101 MHz, $CDCl_3$) 164.2 (d, *J* 24.2 Hz), 85.1 (d, *J* 198 Hz), 53.3; δ_F (376 MHz, $CDCl_3$) −195.24 (d, *J* 48 Hz); HRMS (ESI): MNa^+, found 201.0534, $[C_7H_{11}FO_4Na]^+$ requires 201.0539.

4.3.2. Diethyl 2-fluoromalonate ***3b***.[16] Yield 84% as a colorless oil; δ_H (400 MHz, $CDCl_3$) 5.28 (1H, d, *J* 48.2 Hz, CH), 4.34 (4H, qd, *J* 7.2, 2.7 Hz, $2CH_2$), 1.34 (6 H, t, *J* 7.2 Hz, 2Me); δ_C (101 MHz, $CDCl_3$) δ 163.9 (d, *J* 24.2 Hz), 85.3 (d, *J* 197 Hz), 62.7, 13.9; δ_F (376 MHz, $CDCl_3$) −195.09 (d, *J*=48.2 Hz); HRMS (ESI): MNa^+, found 173.0221, $[C_5H_7FO_4Na]^+$ requires 173.0226.

4.4. General procedure for reaction of diazomalonates 1h,i with arenes in TfOH. Characterization of compounds 4a–j, 5a–j

Mixture of TfOH (2 mL) and arene (0.5 mL for benzene; 1 mmol for other arenes) was stirred at room temperature or 60 °C (see Tables 2–4, Scheme 5), and diazo compound (0.6 mmol) was added dropwise The reaction mixture was stirred for 30 min, then poured into water (50 mL), and extracted with dichloromethane (3×30 mL). The combined organic layers were consequently washed with water (2×30 mL), saturated aqueous solution of $NaHCO_3$ (30 mL), water (2×30 mL), and dried over Na_2SO_4. Solvent was removed under reduced pressure. Crude material was purified by flash chromatography (silica gel; eluent: hexane/EtOAc; linear gradient: 0–20% of EtOAc). Yields of the obtained compounds **4a**–**j**, **5a**–**j** are given in Tables 2–4, and Scheme 5.

4.4.1. Dimethyl 2-phenylmalonate ***4a***.[17] Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.75 (s, 6H), 4.66 (s, 1H), 7.34–7.42 (m, 5H); δ_C (101 MHz, $CDCl_3$) 168.7, 132.7, 129.4, 128.8, 128.4, 57.7, 52.3; GC–MS (EI): 208 [M^+].

4.4.2. Dimethyl 2-(2-methylphenyl)malonate ***4b***.[18] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.37–7.40 (1H, m, 1Harom.), 7.16–7.29 (3H, m, 3Harom.), 4.91 (1H, s, CH), 3.76 (6H, s, 2MeO), 2.34 (3H, s, Me); GC–MS (EI): 222 [M^+].

4.4.3. Dimethyl 2-(3-methylphenyl)malonate ***4c***.[19] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.16–7.29 (4H, m, 4Harom.), 4.61 (1H, s, CH), 3.75 (6H, s, 2MeO), 2.36 (3H, s, Me); GC–MS (EI): 222 [M^+].

4.4.4. Dimethyl 2-(4-methylphenyl)malonate ***4d***.[20] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.16–7.29 (4H, m, 4Harom.), 4.61 (1H, s, CH), 3.75 (6H, s, 2MeO), 2.34 (3H, s, Me); GC–MS (EI): 222 [M^+].

4.4.5. Dimethyl 2-(2,3-dimethylphenyl)malonate ***4e***.[21] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.13–7.99 (3H, m, 3Harom.), 4.97 (1H, s, CH), 3.76 (6H, s, 2MeO), 2.31 (3H, s, Me), 2.23 (3H, s, Me); GC–MS (EI): 236 [M^+].

4.4.6. Dimethyl 2-(3,4-dimethylphenyl)malonate ***4f***.[21] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.13–7.19 (3H, m, 3Harom.), 4.59 (1H, s, CH), 3.75 (6H, s, 2MeO), 2.26 (3H, s, Me), 2.25 (3H, s, Me); GC–MS (EI): 236 [M^+].

4.4.7. Dimethyl 2-(2,4-dimethylphenyl)malonate ***4g***.[21] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.25–7.28 (1H, m, 1Harom.), 6.99–7.06 (2H, m,

2Harom.), 4.87 (1H, s, 1Harom.), 3.75 (6H, s, 2MeO), 2.30 (6H, s, 2Me); GC–MS (EI): 236 [M^+].

4.4.8. Dimethyl 2-(2,6-dimethylphenyl)malonate ***4h***.[21] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.00–7.05 (3H, m, 3Harom.), 5.07 (1H, s, CH), 3.76 (6H, s, 2MeO), 2.31 (6H, s, 2Me); GC–MS (EI): 236 [M^+].

4.4.9. Dimethyl 2-(3,5-dimethylphenyl)malonate ***4i***.[22] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.00–7.05 (3H, m, 3Harom.), 4.58 (1H, s, CH), 3.76 (6H, s, 2MeO), 2.35 (6H, s, 2Me); GC–MS (EI): 236 [M^+].

4.4.10. Dimethyl 2-(3,5-dimethylphenyl)malonate ***4j***.[21,23] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.19 (1H, m, 1Harom.), 7.03–7.09 (2H, m, 2Harom.), 4.88 (1H, s, 1Harom.), 3.77 (6H, s, 2MeO), 2.32 (3H, s, Me), 2.29 (3H, s, Me); GC–MS (EI): 236 [M^+].

4.4.11. Diethyl 2-phenylmalonate ***5a***.[17] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.34–7.42 (5H, m, 5Harom.), 4.61 (1H, s, CH), 4.17–4.26 (4H, m, $2CH_2$), 1.26 (6H, t, *J* 7.1 Hz, 2Me); δ_C (101 MHz, $CDCl_3$) 168.3, 132.9, 129.4, 128.7, 128.3, 61.9, 58.1, 14.1; GC–MS (EI): 236 [M^+].

4.4.12. Diethyl 2-(2-methylphenyl)malonate ***5b***.[24] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.39–7.41 (1H, m, 1Harom.), 7.13–7.29 (3H, m, 3Harom.), 4.87 (1H, s, CH), 4.20–4.24 (4H, m, $2CH_2$), 2.36 (3H, s, Me), 1.24–1.29 (6H, m, 2Me); GC–MS (EI): 250 [M^+].

4.4.13. Diethyl 2-(3-methylphenyl)malonate ***5c***.[24,25] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.13–7.29 (4H, m, 4Harom.), 4.57 (1H, s, CH), 4.20–4.24 (4H, m, $2CH_2$), 2.34 (3H, s, Me), 1.24–1.29 (6H, m, 2Me), GC–MS (EI): 250 [M^+].

4.4.14. Diethyl 2-(4-methylphenyl)malonate ***5d***.[24] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.13–7.23 (4H, m, 4Harom.), 4.57 (1H, s, 1Harom.), 4.20–4.24 (4H, m, $2CH_2$), 2.34 (3H, s, Me), 1.24–1.29 (6H, m, 2Me); GC–MS (EI): 250 [M^+].

4.4.15. Diethyl 2-(2,3-dimethylphenyl)malonate ***5e***.[26] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.10–7.24 (3H, m, 3Harom.), 4.93 (1H, s, CH), 4.16–4.26 (4H, m, $2CH_2$), 2.30 (3H, s, Me), 2.23 (3H, s, Me), 1.25–1.29 (6H, m, 2Me); GC–MS (EI): 264 [M^+].

4.4.16. Diethyl 2-(3,4-dimethylphenyl)malonate ***5f***.[26] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.10–7.24 (3H, m, 3Harom.), 4.54 (1H, s, CH), 4.16–4.26 (4H, m, $2CH_2$), 2.26 (3H, s, Me), 2.25 (3H, s, Me), 1.25–1.29 (6H, m, 2Me); GC–MS (EI): 264 [M^+].

4.4.17. Diethyl 2-(2,4-dimethylphenyl)malonate ***5g***.[26] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.27–7.29 (1H, m, 1Harom.), 7.00–7.19 (2H, m, 2Harom.), 4.83 (1H, s, CH), 4.19–4.25 (4H, m, $2CH_2$), 2.30 (6H, s, 2Me), 1.25–1.28 (6H, m, 2Me); GC–MS (EI): 264 [M^+].

4.4.18. Diethyl 2-(3,5-dimethylphenyl)malonate ***5h***.[17] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.00–7.19 (3H, m, 3Harom.), 4.53 (1H, s, CH), 4.19–4.25 (4H, m, $2CH_2$), 2.30 (6H, s, 2Me), 1.25–1.28 (6H, m, 2Me); GC–MS (EI): 264 [M^+].

4.4.19. Diethyl 2-(2,6-dimethylphenyl)malonate ***5i***.[24] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.00–7.19 (3H, m, 3Harom.), 5.03 (1H, s, CH), 4.19–4.25 (4H, m, $2CH_2$), 2.30 (6H, s, 2Me), 1.25–1.28 (6H, m, 2Me); GC–MS (EI): 264 [M^+].

4.4.20. Diethyl 2-(2,5-dimethylphenyl)malonate ***5j***.[27] Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.19 (1H, s, 1Harom.), 7.01–7.10 (2H, m, 2Harom.), 4.83 (1H, s, CH), 4.20–4.25 (4H, m, $2CH_2$), 2.31 (3H, s, Me), 2.29 (3H, s, Me), 1.25–1.29 (6H, m, 2Me); GC–MS (EI): 264 [M^+].

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Supplementary data

These data includes copies of ^1H, ^{13}C and ^{19}F NMR spectra of the obtained compounds and details of DFT calculations. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2016.06.051.

References and notes

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