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1 2	A Facile Iron-Catalyzed Dual C-C Bond Cleavage: An Approach towards NJ00149B Triaryl Methanes
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10	Abstract
11	A facile iron-catalyzed dual C-C bond cleaving reaction involving 1,3-dicarbonyl unit along
12	with electron-rich and sterically bulky arene as efficient carbon-based leaving groups has
13	been developed. The scope of the dual C-C bond breaking reaction was studied in detail using
14	a range of nucleophiles to produce symmetrical triaryl methanes in good to excellent yields.
15	We found success in isolating the intermediate of the reaction, formed via the initial $C_{sp3}$ - $C_{sp3}$
16	bond cleavage, and subsequently converted the intermediate to the final product via the $C_{sp3}$ -
17	C <sub>sp2</sub> bond cleavage. A notable difference in the leaving aptitudes of the two carbon-based
18	leaving groups perceived during the study enabled us to develop an application of the dual C-
19	C bond breaking reaction for the synthesis of unsymmetrical triaryl methanes in a stepwise
20	manner. To improve the synthetic utility, we have also fashioned a one-pot procedure to
21	generate unsymmetrical triaryl methanes via sequential C-C bond breaking reactions. In
22	addition to studying a novel dual C-C bond breaking reaction and providing a hint to the
23	mechanistic pathway, the application molded from the study for the synthesis of symmetrical
24	and especially unsymmetrical triaryl methanes may render value to the present work.
25	Keywords
26 27	Arene leaving group, 1,3-dicarbonyl leaving group, dual C-C bond cleavage, FeCl <sub>3</sub> catalyzed, triaryl methanes.

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#### 29 Introduction

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The utilization of carbon-based leaving groups that operates through C-C bond cleavage still lacks popularity in the realm of organic synthesis. The high bond dissociation energy of the C-C bonds, kinetic inaccessibility, and poor selectivity are among the major challenges to encounter before developing an efficient carbon-based leaving group.<sup>1,2</sup> Over the past years, several reports involving C-C bond cleavages have been published.<sup>3-10</sup> However, adapting the cleavage of a C-C bond to develop an efficient carbon-based leaving group has proved to be a significant challenge. In recent times, researchers have shown immense interest in developing new strategies that apply C-C bond cleavage in organic synthesis. In this regard, carbon-based leaving groups such as meldrum's acid,<sup>11,12</sup> dimedone,<sup>13-15</sup> barbituric acid,<sup>16</sup> and others,<sup>17,18</sup> have been developed. Li et al. also developed and popularized the use of 1,3-dicarbonyl compounds as efficient carbon-based leaving groups from diarylmethyl substituted 1,3-dicarbonyl derivatives 1 (Figure 1a).<sup>19,20</sup> High selectivity can be achieved when employing 1.3-dicarbonyl unit as a leaving group in a C-C bond cleaving variant of the classical Friedel-Crafts reaction.<sup>19</sup> Apart from 1,3-dicarbonyl moieties, relevant literature reveals that electron-rich and sterically bulky arenes also shows promise for use as a viable leaving group. Such arenes were observed on several occasions to leave through C-C bond cleavage causing unwanted side reactions thereby giving an account of their untapped potential as leaving groups.<sup>21-25</sup> Roy et al. in 2011 established the use of such electron-rich and sterically bulky arene as a leaving group from diaryl methanamines in presence of Lewis acidic heterobimetallic Ir<sup>III</sup>-SnCl<sub>3</sub> catalyst.<sup>26</sup> However, commercial unavailability and toxicity of the catalyst in addition to lack of mechanistic insight into the reaction have largely restrained the reported protocol. In this respect, we have recently developed FeCl<sub>3</sub> as a readily available catalyst for tandem C<sub>sp3</sub>-N and C<sub>sp3</sub>-C<sub>sp2</sub> bond cleaving reaction in diaryl methanamines involving electron-rich and sterically bulky arenes (such as 1,3,5-trimethoxybenzene and 3,5-dimethoxytoluene) as leaving groups (Figure 1b).<sup>27</sup> We have demonstrated that 1,3,5-trimethoxybenzene which is an electron-rich and sterically bulky arene perform exceedingly well as a leaving group in mild reaction conditions. It may be pointed out that while the leaving 1,3-dicarbonyl moiety results in the cleavage of a  $C_{sp3}$ - $C_{sp3}$ bond, the leaving electron-rich, and sterically bulky arene causes the cleavage of a  $C_{sp3}$ - $C_{sp2}$ bond. Herein, we have directed our efforts towards integrating the two unusual yet efficient carbon-based leaving groups (i.e. 1,3-dicarbonyl unit along with electron-rich and sterically bulky arene) in one substrate and successfully developed a novel method involving dual C-C 

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bond cleavage in 1,3-dicarbonyl derivatives with diarylmethyl substituents at the as the as the as the as the as the as the substituents at the as the substituents at the substituents at the substituents at the substituent of the substituent methylene position, 1, to synthesize triaryl methanes (TRAMs) (Figure 1c). We have examined the effect of various substitutions made in substrate 1 of Figure 1c as well as studied the effect of a range of nucleophiles to test the scope of the reaction. We have also isolated the intermediate formed via  $C_{sp3}$ - $C_{sp3}$  bond cleavage and then subsequently converted the intermediate to the final product via C<sub>sp3</sub>-C<sub>sp2</sub> bond cleavage. Exploiting the different leaving aptitudes of the 1,3-dicarbonyl group and such arene in substrate 1, we have successfully synthesized unsymmetrical TRAMs by selectively breaking the C<sub>sp3</sub>-C<sub>sp3</sub> bond and C<sub>sp3</sub>-C<sub>sp2</sub> bond one after another in a stepwise manner. In a bid to further improve the synthetic utility of the C-C bond breaking reaction, we were able to fashion a one-pot procedure to synthesize unsymmetrical TRAMs in good yields. One may note that the TRAMs are an important class of organic compounds, present in several natural products, pharmaceuticals, dyes etc.<sup>28-30</sup> Several strategies are reported in recent times for the synthesis of symmetrical and unsymmetrical TRAMs.<sup>31-39</sup> However, synthesis of unsymmetrical TRAMs is commonly considered a challenging task<sup>40-44</sup> and as per our knowledge, this is the first ever method of synthesizing unsymmetrical TRAMs through dual C-C bond cleavage. In addition to studying a novel dual C-C bond breaking reaction and providing a hint to the mechanistic pathway, the application bloomed out of the study for the synthesis of symmetrical and especially unsymmetrical TRAMs may render value to the present work. 

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Figure 1: A correlation of the present work with the literature

#### 83 **Results and Discussion**

At the outset we considered 1,3-diphenyl-2-(phenyl(2,4,6-trimethoxyphenyl)methyl)propane-84 85 1,3-dione 1a and indole 2a as our model substrates to optimize the reaction conditions (Table 1). In this regard, we tested several reaction conditions and analyzed the results based on the 86 87 isolated yield of the desired bis-indolyl methane 3aa (formed via dual C-C bond cleavage) and the unsymmetrical TRAM 4a (formed via Csp3-Csp3 bond cleavage only). As previous 88 studies have suggested that FeCl3 is a potent catalyst for breaking Csp3-Csp3 bonds in 89 diarylmethyl substituted 1,3-dicarbonyl derivatives<sup>19</sup> as well as C<sub>sp3</sub>-C<sub>sp2</sub> bonds in N-90 protected diaryl methanamines,<sup>27</sup> we considered FeCl<sub>3</sub> as the catalyst for screening various 91 solvents. While MeNO2, DCE and toluene as solvents performed reasonably well for the 92 cleavage of both the  $C_{sp3}$ - $C_{sp3}$  and  $C_{sp3}$ - $C_{sp2}$  bonds, DMF and THF did not show any 93 promising results (Table 1, entries 1-5). Among all the screened solvents, we found that 94 MeCN serves as the best medium for the model reaction producing 88% yield of the desired 95 product 3aa in 1 h (Table 1, entry 6). Other inexpensive and readily available Lewis acids 96 that were studied for catalyzing the model reaction could not outclass the catalytic efficiency 97 of FeCl<sub>3</sub> (Table 1, entries 6-10). It is worth pointing out that ZnCl<sub>2</sub> as a catalyst could only 98 catalyze the cleavage of  $C_{sp3}$ - $C_{sp3}$  bond in **1a** giving rise to 58% of the unsymmetrical TRAM 99

4a (Table 1, entry 7). TsOH, which is a Brønsted acid, was also successful in catalyzing Hardicle Online dual C-C bond cleaving reaction producing a good yield of the desired product **3aa** (Table 1, entry 11). The reaction does not proceed in the absence of any catalyst (Table 1, entry 12). We have found that temperature plays a crucial role in the progress of the reaction as lowering the temperature from 80 °C to 50 °C proves detrimental to the yield of the desired product (Table 1, entry 13). Further lowering of the temperature from 50 °C to room temperature resulted in no reaction as starting materials were isolated quantitatively after 6 hours (Table 1, entry 14). As indicated in Table 1, 10 mol% loading of FeCl<sub>3</sub> catalyst was found to be optimum for the dual C-C bond cleaving reaction (entries 6, 15-16). It needs to be pointed out that the leaving 1,3-diphenylpropan-1,3-dione and 1,3,5-trimethoxybenzene were isolated in 96% and 91% yield, respectively, after the synthesis of 3aa in our optimized reaction conditions. 

#### **112 Table 1:** Optimization of reaction conditions<sup>*a*</sup>



Entry	Catalyst	Solvent	Time (h)	Yield of <b>3aa</b> (%) <sup>b</sup>	Yield of <b>4a</b> (%) <sup>b</sup>
1	FeCl <sub>3</sub>	MeNO <sub>2</sub>	1	72	10
2	FeCl <sub>3</sub>	DCE	1	75	15
4	FeCl <sub>3</sub>	Toluene	1	70	18
3	FeCl <sub>3</sub>	DMF	6	_	_
$5^c$	FeCl <sub>3</sub>	THF	1	12	trace
6	FeCl <sub>3</sub>	MeCN	1	88	9
7	ZnCl <sub>2</sub>	MeCN	1	trace	58
8	$SnCl_2.2H_2O$	MeCN	1	73	14
9	CoCl <sub>2</sub> .6H <sub>2</sub> O	MeCN	1	20	trace
10	BiCl <sub>3</sub>	MeCN	1	42	15
11	TsOH	MeCN	1	78	14
12	No catalyst	MeCN	1	_	_
13 <sup>d</sup>	FeCl <sub>3</sub>	MeCN	1	44	36
$14^e$	FeCl <sub>3</sub>	MeCN	6	_	_
15 <sup>f</sup>	FeCl <sub>3</sub>	MeCN	1	85	10
16 <sup>g</sup>	FeCl <sub>3</sub>	MeCN	1	70	12
<sup><i>a</i></sup> Reaction conditions: <b>1a</b> (1.0 mmol), <b>2a</b> (2.2 mmol), Catalyst (10 mol%),					

Solvent (5 mL), Temperature 80 °C; <sup>*b*</sup>Isolated Yield; <sup>*c*</sup>Temperature 60 °C; <sup>View Article Online <sup>d</sup>Temperature 50 °C; <sup>*e*</sup>Temperature 25 °C; <sup>*f*</sup>FeCl<sub>3</sub> (20 mol%); <sup>*g*</sup>FeCl<sub>3</sub> (5 mol%).</sup>

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After optimization of the reaction conditions, we evaluated the generality of the FeCl<sub>3</sub> catalyzed dual C-C bond cleaving reaction (Table 2). Initially, we decided to study the effect of different substituents present in the 1,3-dicarbonyl moiety of substrate 1 by varying  $R_1$  and  $R_2$  groups (Table 2, entries 1-6). Firstly, we fixed  $R_1$  as -Ph and substituted  $R_2$  with various substituents such as -Ph, -'Bu and -Me to study the effect on the yield of the product 3aa (Table 2, entries 1-3). We noted that the variations in yields of the product 3aa were dependent on the affinity of the various 1,3-dicarbonyl moiety to complex with the Lewis acidic FeCl<sub>3</sub>, which in turn depended on the combination of the steric and electronic influence of the substituents present at  $R_1$  and  $R_2$  of the 1,3-dicarbonyl moiety. The observations were found to be in good agreement with previously published results by Li et al.<sup>19</sup> When both R<sub>1</sub> and R<sub>2</sub> were substituted with -Me groups, the yield of **3aa** dropped to 41% (Table 2, entry 4). The yield of the desired product **3aa** plummets further when an -OEt group was present in the 1,3-dicarbonyl unit of substrate 1 (Table 2, entries 5-6). Since the 1,3-dicarbonyl group present in 1a, i.e.  $R_1 = R_2 = Ph$ , gives the highest yield of the product 3aa, we have chosen this 1,3-dicarbonyl moiety for further studies. Subsequently, we set out to test the substrate scope of the dual C-C bond breaking reaction by varying the aromatic group (-Ar) present in substrate 1 in Table 2. We also evaluated various nucleophiles 2 (Figure 2) based on their performance in the dual C-C bond breaking reaction. Initially, we varied the -Ar group by installing several electron-donating groups (EDG) and electron-withdrawing groups (EWG) at varying positions of the aromatic ring in substrate 1 and studied their effects on the reaction. We found that there is no significant change in the yield of the product 3 depending on the position of the EWG in the aromatic ring (Table 2, entries 7-9). It is apparent from the data presented in Table 2 that EDG at the aromatic ring produces a slightly lower yield of product 3 when compared with EWG (Table 2, entries 7-13). The reaction performed well when -Ar group was taken as a polycyclic aromatic entity viz. 1-naphthyl in 1n giving 82% of the product 3na (Table 2, entry 14). Heteroaromatic substituent viz. 2-thienyl in substrate 10 also gave the desired reaction yielding 76% of the corresponding product **30a** (Table 2, entry 15). We have then evaluated the performance of a list of nucleophiles 2 in the dual C-C bond breaking reaction. In this regard we have tested 

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indoles (2a-g), furans (2h-i), 1,3-dimethoxybenzene 2j and 4-methoxythiophenol 2k<sup>View</sup> Article Online nucleophiles and observed that the desired product 3 was formed via the cleavage of two C-C bonds (Table 2, entries 16-25). In presence of indole derivatives 2b-g, the symmetrical bis-indolyl methanes 3 were isolated in good yields via the dual C-C bond cleavage (Table 2, entries 16-21). Furans (2h-i) and 1,3-dimethoxybenzene 2j also reacted smoothly with 1a to generate the respective products 3 (Table 2, entries 22-24). Interestingly, two C-S bonds were formed at the cost of two C-C bonds when 4-methoxythiophenol 2k was employed as the nucleophile in the reaction with 1a (Table 2, entry 25). 



Figure 2: List of nucleophiles 2





Entry	Ar, R <sub>1</sub> , R <sub>2</sub> ; <b>1</b>	Nu-H, <b>2</b>	Time (h)	Yield of $3$ (%) <sup>b</sup>
1	Ph, Ph, Ph; <b>1a</b>	2a	1	<b>3aa</b> (88)
2	Ph, Ph, <sup><i>t</i></sup> Bu; <b>1b</b>	2a	6	<b>3aa</b> (65)
3	Ph, Ph, Me; <b>1c</b>	2a	6	<b>3aa</b> (58)
4	Ph, Me, Me; <b>1d</b>	2a	6	<b>3aa</b> (41)
5	Ph, Ph, OEt; 1e	2a	6	<b>3aa</b> (23)
6	Ph, Me, OEt; 1f	2a	6	<b>3aa</b> (15)
7	4-ClC <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1g</b>	2a	1	<b>3ga</b> (84)
8	3-ClC <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1h</b>	2a	1	<b>3ha</b> (85)
9	2-ClC <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1i</b>	2a	1	<b>3ia</b> (85)
10	4-BrC <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1j</b>	2a	1	<b>3ja</b> (83)
11	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1</b> k	2a	1	<b>3ka</b> (72)
12	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1</b> I	2a	1	<b>3la</b> (72)
13	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> , Ph, Ph; <b>1m</b>	2a	1	<b>3ma</b> (70)
14	1-Naphthyl, Ph, Ph; <b>1n</b>	2a	1	<b>3na</b> (82)
15	2-Thienyl, Ph, Ph; 10	2a	1	<b>30a</b> (76)
16	1a	2b	1	<b>3ab</b> (78)
17	1a	2c	1	<b>3ac</b> (87)

18	<b>1</b> a	2d	1	View Article Onlin 3ad (79) DOI: 10.1039/C9NJ00149I
19	<b>1</b> a	2e	1	<b>3ae</b> (72)
20	<b>1</b> a	2f	1	<b>3af</b> (75)
21	<b>1</b> a	2g	1	<b>3ag</b> (70)
22	<b>1</b> a	2h	1	<b>3ah</b> (83)
23	<b>1</b> a	2i	1	<b>3ai</b> (82)
24	<b>1</b> a	2j	6	<b>3aj</b> (70)
25	<b>1</b> a	2k	1	<b>3ak</b> (82)
aRead	ction condit	ons: 1 (1.0 mmol), 2 (2.2 mmo	ol), FeCl <sub>3</sub> (1	0 mol%), MeCN (5
mL),	Temperatu	e 80 °C; <sup>b</sup> Isolated yield.		

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 However, in the case of nucleophiles **2l-n**, the reaction only causes the exclusive  $C_{sp3}-C_{sp3}$ bond cleavage generating corresponding products **4b-d** even after prolonged reaction times and a large excess of the nucleophiles (Scheme 1). These results indicate that the  $C_{sp3}-C_{sp3}$ bond is easier to cleave in comparison to  $C_{sp3}-C_{sp2}$  bond in substrate **1a** during the dual C-C bond breaking reaction which is a reflection of the differences in their bond strengths.<sup>45</sup>



 Scheme 1: Instances of C<sub>sp3</sub>-C<sub>sp3</sub> bond cleavage

Above results encouraged us to track the intermediate formed during the dual C-C bond cleaving reaction. In this regard, we treated **1a** with 1.0 equivalent of the nucleophile **2a** in slightly milder reaction conditions anticipating the formation of **4a** through the  $C_{sp3}$ - $C_{sp3}$  bond cleavage (Scheme 2). The reaction proceeded as anticipated to give **4a** as the major product (62%) while 15% of **3aa** was also isolated along with a small amount of the unreacted substrate **1a**. When the isolated intermediate **4a** was treated with 1.0 equivalent more of **2a** under the optimized reaction conditions, we noticed the formation of **3aa** in excellent yield

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 (93%). This observation not only establishes the intermediate formed during the reaction of the section of the sectio



Scheme 2: Isolation of intermediate 4a and its conversion to 3aa.

We also wanted to study the effect of substitutions made at the sterically bulky and electron-rich aromatic leaving group (-Ar') present in substrate 1 (Table 3). In this regard, we took several substrates 1 with varying -Ar' group and reacted with indole 2a under the optimized reaction conditions. We found that 2,4,6-trimethoxyphenyl group as the sterically bulky and electron-rich aromatic substituent in **1a** produced an excellent yield of the product **3aa** through the dual C-C bond cleavage while a minor amount of the intermediate 4a was also observed (Table 3, entry 1). Lowering the electron richness of the aromatic substituent (-Ar') by replacing one of the -OMe groups with a -Me group in substrate 1p resulted in lower yield of 3aa even after longer reaction times (Table 3, entry 2).<sup>27</sup> We observed that the intermediate 4e formed in a minor quantity (16%) while a significant amount of the starting substrates remained unreacted (Table 3, entry 2). It is worth pointing out that the steric bulkiness at the benzylic reaction center is not changing when the substrate is changed from 1a to 1p. This significant decrease in the leaving aptitude may have been caused by the diminished electron-richness of the aromatic leaving group (-Ar'). When the electron-richness of -Ar' was lowered further, the reaction ceased to produce any isolable amount of 3aa (Table 3, entries 3-4). In these cases, the starting substrates (1q and 2a; 1r and 2a) were isolated almost quantitatively after 6 h of reaction in the optimized conditions. 

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**Table 3:** Effect of electron richness on the aromatic leaving group<sup>*a*</sup>





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Based on the above experimental observations and the knowledge of relevant literature, we propose the plausible mechanism for the FeCl<sub>3</sub> catalyzed dual C-C bond cleaving reaction in Scheme 3. The reaction could be initiated by the coordination of the FeCl<sub>3</sub> catalyst with the 1,3-dicarbonyl moiety of 1a which may lead to the formation of an ion pair A.<sup>19,46</sup> The carbocation is then trapped by the nucleophile 2a to generate 4a and successively release 1,3-diphenylpropan-1,3-dione. TRAMs such as 4a are known to be activated by Lewis acids by interacting with the *ipso* position to yield species **B**.<sup>21,47</sup> Electron donating assistance from the indolyl group of species **B** may be an important factor that promotes the formation of ion pair C. This explains why less electron-rich groups in substrate 4 fail to cause the  $C_{sp3}$ - $C_{sp2}$  bond cleavage (Scheme 1). A second molecule of the nucleophilic indole 2a then reacts with the electrophilic center involved in C to yield the desired product 3aa and consequently release the 1,3,5-trimethoxybenzene leaving group. 



Scheme 3: Plausible mechanism of the FeCl<sub>3</sub> catalyzed dual C-C bond cleaving reaction

We sought to develop an application of the method for the synthesis of unsymmetrical TRAMs (Table 4). As the previous observations showed that the 1,3-dicarbonyl group has different leaving aptitude with respect to the electron-rich and sterically bulky aromatic group, we directed our efforts towards developing reaction conditions that selectively activates one of the leaving groups while keeping the other leaving group dormant. Crafting such control would enable us to use two different nucleophiles to selectively substitute the two carbon-based leaving groups sequentially. In this regard, we realized that ZnCl<sub>2</sub> as a catalyst exclusively generated product 4a (Table 1, entry 7) through Csp3-Csp3 bond cleavage although the yield was low. We revised the reaction conditions to improve the yield without compromising on the selectivity of substituting the 1,3-dicarbonyl group exclusively by 1 nucleophile Nu<sup>1</sup>-H as depicted in Table 4. Once the substitution of the 1,3-dicarbonyl group by Nu<sup>1</sup>-H was complete, we isolated the product 4 and treated it with another nucleophile Nu<sup>2</sup>-H to substitute the electron-rich and sterically bulky aromatic leaving group in presence of the proven FeCl<sub>3</sub> catalyst. The reaction progressed effectively to generate unsymmetrical TRAMs comprising of both the nucleophiles Nu<sup>1</sup>-H and Nu<sup>2</sup>-H (Table 4). We have also confirmed that the nucleophile plays a very inconsequential role in determining the selectivity of the C<sub>sp3</sub>-C<sub>sp3</sub> and C<sub>sp3</sub>-C<sub>sp2</sub> bond cleaving reaction (Table 4, entries 2-3). Irrespective of the nucleophile (Nu<sup>1</sup>-H or Nu<sup>2</sup>-H), the presence of ZnCl<sub>2</sub> catalyst exclusively caused the cleavage of C<sub>sp3</sub>-C<sub>sp3</sub> bond (product 4 formed after Step 1) while the addition of FeCl<sub>3</sub> ensured the subsequent activation of the electron-rich and sterically bulky aromatic leaving group. Furthermore, to demonstrate the generality of the method, we have successfully tested

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several pairs of nucleophiles to produce unsymmetrical TRAMs in good yields (Table Online entries 1-5, 7-9). The sequential cleavage of C<sub>sp3</sub>-C<sub>sp3</sub> and C<sub>sp3</sub>-C<sub>sp2</sub> bond can also be achieved by nucleophile 4-methoxythiophenol 2k (Nu<sup>1</sup>-H) and 5-bromoindole 2f (Nu<sup>2</sup>-H) under standard reaction conditions to generate 5e (Table 4, entry 6). Substitutions made in the parent substrate 1 were well-tolerated in the reaction medium as evident from the yields of the corresponding products (Table 4, entries 7-9). In our attempt to boost the synthetic utility of the dual C-C bond breaking method, we were able to fashion a one-pot procedure for the generation of unsymmetrical TRAMs 5. In this respect, we have treated substrate 1 with nucleophile Nu<sup>1</sup>-H in the presence of ZnCl<sub>2</sub> and monitored the progress of the reaction. After complete consumption of Nu<sup>1</sup>-H, we have added Nu<sup>2</sup>-H and FeCl<sub>3</sub> in the same reaction vessel and allowed the reaction to proceed (See the experimental section for details). We were pleased to obtain comparable yields of the unsymmetrical TRAMs using the one-pot protocol in all the cases as mentioned in Table 4. The one-pot method presented here offers an expedient route for the generation of unsymmetrical TRAMs in mild reaction conditions. 





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<sup>*b*</sup>Reaction conditions for the one-pot procedure: (i) **1** (1.0 mmol), Nu<sup>1</sup>-H **2** (1.0 mmol), Zuget Article Online (10 mol%), MeCN (5 mL), Temperature 80 °C, Time 12 h; (ii) Nu<sup>2</sup>-H **2** (1.0 mmol), FeCl<sub>3</sub> (10 mol%), Temperature 80 °C, Time 1 h; <sup>*c*</sup>Isolated yield via stepwise procedure. <sup>*d*</sup>Isolated yield via one-pot procedure; <sup>*e*</sup>Time 6 h, Temperature 60 °C.

#### 249 Conclusion

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In conclusion, we have developed a facile FeCl<sub>3</sub> catalyzed dual C-C bond cleaving reaction 250 involving 1,3-dicarbonyl units along with electron-rich and sterically bulky arenes as carbon-251 based leaving groups. We have tested several 1,3-dicarbonyl units and electron-rich arenes to 252 select the best performing leaving group of each kind. With the two carbon-based leaving 253 groups integrated into one substrate, we examined the substrate scope of the dual C-C bond 254 cleaving reaction. We observed that indoles, furans, 1,3-dimethoxybenzene, 4-255 256 methoxythiophenol were all compatible nucleophiles in the dual C-C bond breaking reaction. We were also able to isolate the intermediate formed in the reaction through the initial  $C_{sp3}$ -257  $C_{sp3}$  bond cleavage and subsequently converted it to the final product through the eventual 258  $C_{sp3}$ - $C_{sp2}$  bond cleavage. By varying the reaction conditions, we controlled the leaving 259 260 aptitudes of the 1,3-dicarbonyl group and the arene and successfully applied this controlled activation of the leaving groups to synthesize unsymmetrical TRAMs in a stepwise manner as 261 well as in one-pot. Furthermore, the 1,3-dicarbonyl compound and the electron-rich arene can 262 263 be recovered and reused. Apart from developing a novel dual C-C bond breaking reaction and giving insight into the mechanistic pathway, the results presented here demonstrate the first 264 ever synthesis of TRAMs through dual C-C bond cleavage. Further investigation on the 265 scope, mechanism, and synthetic applications of the dual C-C bond cleaving reaction are on-266 going in our laboratory. 267

#### 268 Experimental

#### 269 General remarks

All reagents and solvents are of AR grade and were procured from Sigma Aldrich, Alfa Aesar, Spectrochem and Sisco Research Laboratories Pvt. Ltd. and used without further purification. All the reactions were done in oven-dried glass apparatus in an air atmosphere unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60  $F_{254}$  using UV light and *p*-anisaldehyde stain as visualizing agents. Organic products were purified by dry column vacuum chromatography<sup>48</sup> using silica gel G as the stationary phase and petroleum ether 60-80 °C/ethyl acetate as the eluent. <sup>1</sup>H and <sup>13</sup>C NMR Page 15 of 20

spectra were measured on a Bruker Avance II (<sup>1</sup>H NMR: 400 MHz and <sup>13</sup>C NMR: 100 MHz and <sup></sup> spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard (unless otherwise mentioned, chloroform:  $\delta$  7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, dd=double doublet, m=multiplet), coupling constant (in Hz), integration. <sup>13</sup>C NMR spectra were recorded at 100 MHz with proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (unless otherwise mentioned, chloroform:  $\delta$  77.0 ppm). Elemental analyses were carried out using a CHNS Analyzer Perkin Elmer 2400 Series II instrument. The starting substrates 1 were prepared from reported procedures<sup>49,50</sup> after minor modifications. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the synthesized starting substrates 1 were satisfactory and in good agreement with reported data. 

#### Typical procedure for the synthesis of symmetrical TRAM 3aa

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with 1a (1.0 mmol), 2a (2.2 mmol), MeCN (5 mL) and FeCl<sub>3</sub> (10 mol%) in an air atmosphere. The flask was placed in a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **3aa** in 88% yield. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.71 (br, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.27-7.12 (m, 7H), 7.08 (t, J = 7.6 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 6.50 (d, J = 2.4 Hz, 2H), 5.79 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 144.0, 136.7, 128.7, 128.2, 127.0, 126.2, 123.7, 121.9, 119.9, 119.6, 119.2, 111.1, 40.2. 

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Physical and spectral data are in good agreement with the reported literature.<sup>21</sup> 

#### Typical procedure for the synthesis of 4a from substrate 1a via ZnCl<sub>2</sub> catalyzed C<sub>sn3</sub>-C<sub>sn3</sub> bond cleavage

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with 1a (1.0 mmol), 2a (1.0 mmol), MeCN (5 mL) and ZnCl<sub>2</sub> (10 mol%) in air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product 

**4a** in 86% yield. Light pink solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 7.84 (sol 1H)  $\frac{1}{10039}$  (Sol 1H)  $\frac{1}{200149B}$ 

310 (d, J = 6.7, 4H), 7.25-7.18 (m, 5H), 6.86 (d, J = 2.6, 1H), 6.28 (s, 1H), 6.15 (s, 2H), 3.79 (s,

311 3H), 3.57 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 159.7, 159.0, 144.6, 136.0, 128.2,

126.9, 124.9, 121.8, 121.4, 119.1, 118.9, 117.9, 114.3, 110.8, 91.7, 55.7, 55.2, 53.4, 36.3.

313 Physical and spectral data are in good agreement with the reported literature.<sup>51</sup>

### Typical procedure for the synthesis of unsymmetrical TRAM 5a from intermediate 4a via FeCl<sub>3</sub> catalyzed C<sub>sp3</sub>-C<sub>sp2</sub> bond cleavage

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser was charged with 4a (0.5 mmol), 2d (0.5 mmol), MeCN (3 mL) and FeCl<sub>3</sub> (10 mol%) in air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **5a** in 82% yield. Light pink solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 7.89 (s, 1H), 7.43-7.17 (m, 12H), 7.13 (dd, J = 14.8, 7.9, 2H), 7.04-6.94 (m, 4H), 6.64 (d, J = 4.5, 2H), 5.91 (s, 1H), 5.20 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 144.05, 137.90, 137.01, 136.68, 132.51, 128.74, 128.66, 128.25, 127.95, 127.78, 127.38, 127.20, 127.07, 126.43, 126.13, 123.62, 121.92, 121.69, 120.12, 120.02, 119.80, 119.21, 118.96, 118.72, 111.03, 109.73, 49.92, 40.21. Anal. Cacld (%) for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>: C 87.35; H 5.86; Found: C 87.31; H 5.90. 

## 329 Typical procedure for the one-pot synthesis of unsymmetrical TRAM 5a from substrate 330 1a

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser was charged with 1a (1.0 mmol), Nu<sup>1</sup>-H 2a (1.0 mmol), MeCN (5 mL) and ZnCl<sub>2</sub> (10 mol%) in air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the full consumption of the starting materials, 1.0 mmol of the Nu<sup>2</sup>-H 2d as well as FeCl<sub>3</sub> (10 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir for 1 h at 80 °C. The progress of the reaction was monitored by TLC. On completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product 5a in 79% yield. 

**Supporting Information Summary** 

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Additional experimental details, characterization data as well as <sup>1</sup>H and <sup>13</sup>C NMR spectra of 342 the products 3, 4 and 5 are given in supporting information. 343 344 Acknowledgments Scientific and Engineering Research Board (SERB) is gratefully acknowledged for financial 345 support to P.N.C (sanction order no. SB/FT/CS-115/2014; dated 24/08/2015). We thank NIT 346 Meghalaya (for financial support to D.P.). P. N. C. thanks Dr. S. Pan, IIT Guwahati for useful 347 discussions and many help. IIT Guwahati and SAIF, NEHU are also acknowledged for 348 analytical facilities. 349 **Conflict of Interest** 350 The authors declare no conflict of interest. 351 References 352 1. B. Rybtchinski and D. Milstein, Angew. Chem. Int. Ed., 1999, 38, 870-883. 353 M. Tobisu and N. Chatani, Chem. Soc. Rev., 2008, 37, 300-307. 2. 354 3. E. Fillion, E. Beaton, Y. Nguyen, A. Wilsily, G. Bondarenko and J. Jacq, Adv. Synth. 355 Catal., 2016, 358, 3422-3434. 356 4. N. Zhang and J. Vozzolo, J. Org. Chem., 2002, 67, 1703-1704. 357 D. Nečas, M. Turský, I. Tišlerová, and M. Kotora, New J. Chem., 2006, 30, 671-674. 358 5. D. Nečas and M. Kotora, Org. Lett., 2008, 10, 5261-5263. 359 6. D. Necas, M. Turský, and M. Kotora, J. Am. Chem. Soc., 2004, 126, 10222-10223. 360 7. 8. Y. J. Park, J. -W. Park and C. -H. Jun, Acc. Chem. Res., 2008, 41, 222-234. 361 C. He, S. Guo, L. Huang, and A. Lei, J. Am. Chem. Soc., 2010, 132, 8273-8275. 362 9. C. Sen and S. C. Ghosh, Adv. Synth. Catal., 2018, 360, 905-910. 10. 363 S. J. Mahoney, T. Lou, G. Bondarenko, and E. Fillion, Org. Lett., 2012, 14, 3474-3477. 364 11. E. L. Armstrong, H. K. Grover, and M. A. Kerr, J. Org. Chem., 2013, 78, 10534-10540. 12. 365 M. Saha and A. K. Pal, Tetrahedron Lett., 2011, 52, 4872-4877. 366 13. 14. M. Li, A. Taheri, M. Liu, S. Sun and Y. Gu, Adv. Synth. Catal., 2014, 356, 537-556. 367 M. Li and Y. Gu, Adv. Synth. Catal., 2012, 354, 2484-2494. 368 15. P. Bhuyan and M. Deb, Synthesis, 2008, 2891-2898. 369 16.

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An efficient iron-catalyzed dual C-C bond cleavage reaction has been developed for the synthesis of triaryl methanes.