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Ionic Liquids Promoted the C-Acylation of Acetals in Solvent-free Conditions

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Abstract The synthesis of a series of fourteen 4-alkoxy-1,1,1-trihalo-3-alke\n-2-ones (**2,3**) [$CX_3COC(R^2)=C(R^1)$-OMe, where X = Cl, F; R^1/R^2 = Me/H, Bu/H, *i*-Bu/H, Ph/H, Thien-2-yl/H, $-(CH_2)_4-$, $-CH(CH_2)_4CH(CH_2)_2-$] from the acylation reactions of acetals (**1**) with trichloroacetyl chloride or trifluoroacetic anhydride in the presence of equimolar amounts of pyridine and imidazolium based ionic liquid ([BMIM][BF_4] or [BMIM][PF_6]) is reported. The reaction time, yields and IL recyclation are also investigated and this method showed advantages over the methods described in the literature.

Keywords Ionic liquids · Enones · Halogen compounds · C-Acylation

1 Introduction

Addition of an acyl group to enol ether compounds may be one of the most attractive and challenging issues involved in preparing α,β-unsaturated carbonyl compounds [1, 2], which are important synthetic intermediates of useful heterocycles [1, 2]. However, the synthetic utility of the acyl cation has been considerably limited because of its instability and difficulties in generation and treatment [3–5]. Furthermore, application of its chemical equivalents in organic synthesis generally requires troublesome and complicated procedures for their protection and deprotection [6]. Conventionally, enol ethers have been prepared from symmetrical ketone or aldehyde acetals [7, 8]. However, the isolation of these enol ethers, in some cases (e.g., those derived from unsymmetrical ketones), involves the mixture of kinetic and thermodynamic enol ethers. In addition, the presence of trace acids in the reaction leads to the polymerization or hydrolysis of enol ethers [7, 8]. At the same time, the direct acylation of vinyl ethers involves problems such as (1) the requirement of strong activation from acylating agents; (2) the employment of Friedel–Crafts catalysts is naturally limited to enol ethers with a negligible polymerization tendency [7]; (3) electronegative substituents such as trifluoro or trichloro methyl groups attached to the carbonyl carbon increase the reactivity of the acyl cation. Fischer [7] have already demonstrated how the course of the reaction depends on the electrophilic potential of the acyl function. Our research group has systematically studied this reaction for around 20 years and we have developed a classical method for the acylation of enol ethers with trihaloacetyl acylants to obtain a series of 4-alkoxy-1,1,1-trihalo-3-alken-2-ones in the presence of pyridine and in an anhydrous atmosphere, with dichloromethane as solvent [1, 8]. This procedure is tedious and the reaction time is relatively long (16–48 h) [8]. Recently, we reported an acylation method for enol ethers with trihaloacetyl acylants to obtain a series of 4-alkoxy-1,1,1-trihalo-3-alken-2-ones in the presence of pyridine, using ionic liquid in catalytic conditions [9]. This procedure has the advantages of faster reaction times, easier work up, easier purification of products and better yields than classical methods. On the other hand, we previously reported an alternative one-pot protocol to obtain 4-alkoxy-1,1,1-trihalo-3-alken-2-ones which had some benefits over the direct acylation of enol ethers [10–13]. In this procedure,

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enol ethers are generated in situ from the respective ketone acetal and then they are acylated to obtain 4-alkoxy-1,1,1-trihalo-3-alken-2-ones. This reaction was carried out with acetal and the acylant in a molar ratio of 1:2, respectively, in order to generate the enol ether in situ followed by its acylation. This method demonstrated the advantages of greater control of reaction conditions, for instance, polymerization of enol ethers; the one-pot procedure avoided long and difficult processes to obtain enol ethers from ketones; and it allowed for the attachment of many kinds of substituents (e.g., alkyl, aryl, heteroaryl) to 1,1,1-trihalo-3-alken-2-ones. However, the procedure continues to be tedious and demands a long reaction time (16–48 h) [10–13]. Considering that our research group has systematically utilized α,β-unsaturated trihalomethylated ketones to obtain trihalomethylated heterocycles, the development of faster and 'greener' synthetic methods with higher yields is primer. The lack of studies that aim to improve this route to obtain α,β-unsaturated trihalomethylated ketones shows that this reaction has not been well explored. Considering our results using ionic liquid in catalytic conditions in enol ether acylations [9] as well as the potential of ionic liquids as a 'green' solvent to substitute hazardous traditional organic solvents [14, 15]; their solvating ability and easy recyclability [16, 17]; and the fact that they can promote and catalyze organic transformations at room temperatures without the need of any added catalyst or ligand [18, 19], we report here the C-acylation of enol ethers from acetals (**1**) with trifluoroacetic anhydride or trichloroacetyl chlorides, promoted by ionic liquids, to give the corresponding 4-alkoxy-1,1,1-trihalo-3-alken-2-ones (**2,3**) in good yields.

2 Experimental

2.1 Materials and Methods

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) in 5 mm sample tubes at 298 K (digital resolution ± 0.01 ppm) in $CDCl_3$/TMS solutions. The physical and the ^{1}H and ^{13}C NMR data of compounds **2,3** are in accordance with the literature data presented in the references [10–13].

2.2 Synthesis of Ionic Liquids [BMIM][BF_4] and [BMIM][PF_6]

The ionic liquids were synthesized as described in the literature [20].

2.3 Synthesis of 4-Alkoxy-1,1,1-trihalo-3-alken-2-one (**2,3**)

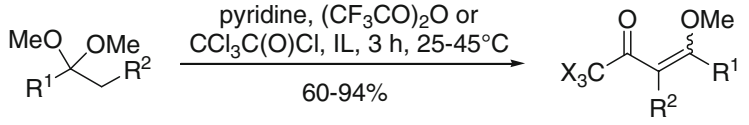
General procedure for the synthesis of 4-alkoxy-1,1,1-trihalo-3-alken-2-one: all glassware must be meticulously dried for this procedure. A mixture of acetal (5 mmol) and pyridine (10 mmol) was slowly (drop-by-drop) added to a round-bottomed flask containing trichloroacetyl chloride (10 mmol) or trifluoroacetic anhydride (10 mmol), and IL (10 mmol) in an ice-bath or ice/salt mixture, under magnetic stirring. After the addition, the ice-bath was removed and the reaction took place during 3–3.5 h at 40 °C. The reaction mixture was extracted with diethyl ether (3 × 10 mL), and then the solvent was evaporated in a rotary evaporator, and traces of solvent were removed under vacuum (10 mbar) for 1 h, and the product was obtained without further purification. The IL was completely recovered by addition of CH_2Cl_2 and filtration of the precipitate, then the solvent was evaporated in a rotary evaporator, and the ionic liquid was purified under vacuum (10 mbar) for 8 h.

3 Results and Discussion

As a result of the straightforward procedure, simple equipment, high potential for large scale preparation, and mild reaction conditions, this reaction seems to be one of the most promising methods for compound synthesis from the acylation reaction of acetals. The reaction was very successful for a range of ketone acetals (**1**) as shown in Table 1. The ketone acetals (**1**) were prepared from the reaction of ketones with trimethyl orthoformate, containing a catalytic amount of *p*-toluenesulfonic acid [21]. The reactions were performed by slowly adding the mixture of pyridine and **1** to the mixture of acylant and IL in an ice bath. Two equivalents of acylating agent per acetal were required to obtain the 4-alkoxy-1,1,1-trihalo-3-alken-2-ones (**2,3**) since one molecule of the acylant promotes the formation of the enol ether by trapping the alkoxide group released by the acetal and the second molecule of the acylant promotes acylation [10–13]. The *E*-isomer was the only acyclic product observed [13]. Products **2,3** were extracted from the reaction media with diethyl ether and were obtained without further purification. The IL was completely recovered by addition of CH_2Cl_2, filtration of the precipitate and evaporation of the solvent. The compound structures were determined by ^{1}H and ^{13}C NMR spectroscopy and compared with those from literature data [10–13].

In the present study, the Lewis Acid was not employed in the acetal acylation reaction, however, the reactant/IL ratio is critical for thorough conversion to the desired

Table 1 Yields of enones **2,3** obtained from acetal acylation in the presence of ionic liquids



1 **2,3**

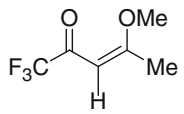
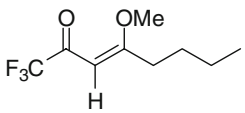
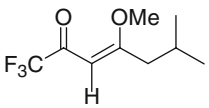
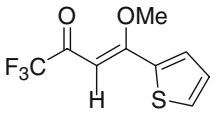
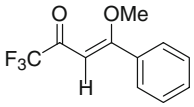
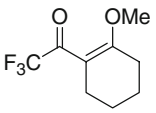
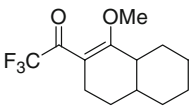
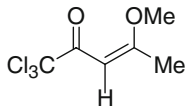
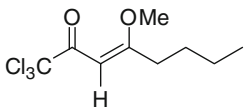
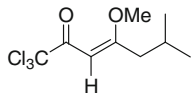
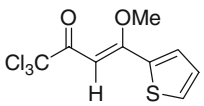
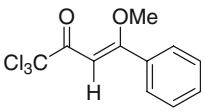
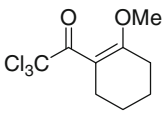
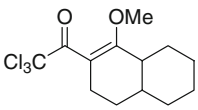
Entry	X	R^1	R^2	Product	Isolated yield (%)		
					Conventional method[6]	[BMIM] [BF_4]	[BMIM] [PF_6]
1	F	Me	H		–	69	65
2	F	Bu	H		–	76	72
3	F	*i*-Bu	H		86[6]	80	81
4	F	Thien-2-yl	H		82[6]	61	60
5	F	Ph	H		92[6]	69	66
6	F	$-(CH_2)_4-$			75[6]	91	90
7	F	$-(CH_2)_2CH(CH_2)_4CH-$			–	69	71

Table 1 continued

Entry	X	R^1	R^2	Product	Isolated yield (%)		
					Conventional method[6]	[BMIM] [BF_4]	[BMIM] [PF_6]
8	Cl	Me	H		–	70	72
9	Cl	Bu	H		90[6]	78	75
10	Cl	*i*-Bu	H		–	70	69
11	Cl	Thien-2-yl	H		86[6]	63	65
12	Cl	Ph	H		88[6]	91	86
13	Cl	$-(CH_2)_4-$			70[6]	70	73
14	Cl	$-(CH_2)_2CH(CH_2)_4CH-$			–	89	86

products. The acetal acylation in equimolar amounts of ILs allowed the formation of 4-alkoxy-1,1,1-trihalo-3-alken-2-ones (**2,3**) with similar yields to those obtained by the conventional method, however in a shorter time. The results from the present study in regard to the reactant/IL ratio differ from those published by us for enol ether acylation [9], where less than an equimolar proportion of the ionic liquid was sufficient to obtain optimum results beyond which there was no further increase of conversion. Conversely, data from the literature [22, 23] have demonstrated that in the Friedel–Crafts acylation in ionic liquids in the presence of a Lewis Acid, the rate of acylation depends on the Acid Lewis/IL molar ratio and that almost no reaction occurs if this ratio is ≤ 0.5. In addition, the main contribution of ILs to the improvement of Friedel–Crafts acylation is with regard to regioselectivity [22, 23]. It has been suggested that the presence of IL in this medium, in equimolar amounts with the acylant,

Table 2 Results obtained using recycled ionic liquid

Entry	Yield (%)[a]			
	[BMIM][BF_4]		[BMIM][PF_6]	
	1° cycle	2° cycle	1° cycle	2° cycle
1	69	68	65	60
2	76	77	72	71
9	70	70	72	71
10	78	80	75	78

[a] Yield of isolated product

affords a strong stabilization of the acyl cation; then, the enhanced rate of the reactions is due to the decrease of activation energy of the slow reaction step [24]. This behavior is in accordance with the general IL effect that can be expected for reactions involving highly polar or charged intermediates, such as carbocations or carbanions, and activated complexes which could become more stable and long-lived in IL media [24].

The advantage of using ILs as novel media for this acylation reaction is that they can be easily recovered and reused. To support this, we investigated the reusability and efficiency of the ionic liquids [BMIM][BF_4] and [BMIM][PF_6]. After the first reaction, the IL was recovered from the extraction product by filtration of the pyridine salt since the products were not soluble in the ionic liquid phase. Products **2,3** were easily separated by simple extraction with ethyl ether followed by evaporation under vacuum. The same yields were presented when a second run was performed with the recovered IL. The results showed that the ionic liquids could be recovered quantitatively without loss of activity (Table 2).

4 Conclusion

In summary, the method proposed in this study allows a mild and efficient *green* protocol for the acylation of enol ethers, generated in situ from acetals. This reaction furnishes α,β-unsaturated trihalomethylated ketones an important chemical intermediate for heterocyclic synthesis [1] and for enaminone synthesis [25].

5 Spectroscopic Data of Compounds 2,3 (Table 1)

5.1 (*Z*)-1,1,1-Trifluoro-4-methoxy-3-penten-2-one 2a (Entry 1)

$C_6H_7F_3O_2$ (mw 168.11). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 2.41 (s, 3H, H6), 3.80 (s 3H, H5), 5.70 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 26.3 (C6) 61.8 (C5) 116.5 (q, $^1J_{C\text{-}F} = 290$, C1), 120.7 (C3) 184.5 (C4) 187.0 (C2).

5.2 (*Z*)-1,1,1-Trifluoro-4-methoxy-3-octen-2-one 2b (Entry 2)

$C_9H_{13}F_3O_2$ (mw 210.19). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 0.92 (t, 2H, H9), 1.40 (m, 2H, H8), 1.55 (m, 2H, H7), 2.80 (t, 2H, H6), 3.80 (s, 3H, H5), 5.39 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 14.1 (C8), 23.5 (C7), 26.3 (C6), 37.6 (C5), 51.4 (OMe), 89.8 (C3), 117.7 (q, $^1J_{C\text{-}F} = 290$, C1), 174.7 (C4), 176.5 (q, $^2J_{C\text{-}F} = 33$, C2).

5.3 (*Z*)-1,1,1-Trifluoro-4-methoxy-7-methyl-3-octen-2-one 2c (Entry 3)

$C_{10}H_{15}F_3O_2$ (mw 224.22). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 0.87 (s, 3H, H11), 0.90 (s, 3H, H10), 1.41 (t, 3H, H6), 1.45 (m, 2H, H8), 1.48 (m, 1H, H9), 2.44 (t, 2H, H7), 4.43 (q, 2H, H5), 5.30 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 22.0 (C7) (C8), 27.8 (C6), 46.0 (C5), 56.5 (OMe), 91.5 (C3), 116.8 (q, $^1J_{C\text{-}F} = 292$, C1), 178.4 (q, $^2J_{C\text{-}F} = 33$, C2), 184.6 (C4).

5.4 (*Z*)-1,1,1-Trifluoro-4-methoxy-4-(thien-2-yl)-3-buten-2-one 2d (Entry 4)

$C_8H_5F_3O_2S$ (mw 236.21). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 3.95 (s, 3H, OMe), 6.2 (s,1H, H3); Tn: 7.12 (t, 1H, H4), 7.57 (d, 1H, H3), 8.28 (d, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 117.7 (q, $^1J_{C\text{-}F} = 278$, C1), 178.2 (q, $^2J_{C\text{-}F} = 36$, C2), 89.6 (q, $^2J_{C\text{-}F} = 2.5$, C3), 168.6 (C4), 56.9 (OMe), Tn: 134.9 (C2), 131.5 (C3), 127.3 (C4), 133.8 (C5).

5.5 (*Z*)-1,1,1-Trifluoro-4-methoxy-4-phenyl-3-buten-2-one 2e (Entry 5)

$C_{11}H_9F_3O_2$ (mw 230.18). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 3.92 (s, 3H, H5), 6.56 (s, 1H, H3), 7.38–7.61 (m, 5H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 31.0 (C9), 57.2 (C5), 91.7 (C3), 116.6 (q, $^1J_{C\text{-}F} = 292$, C1), 127.9 (C7, C7′), 128.7 (C8, C8′), 133.6 (C6), 177.3 (q, $^2J_{C\text{-}F} = 36$, C2), 178.0 (C4).

5.6 (*Z*)-2,2,2-Trifluoro-1-(2-methoxy-1-cyclohexenyl)ethanone 2f (Entry 6)

$C_9H_{11}F_3O_2$ (mw 208.18). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 1.73–1.89 (m, 6H, $3CH_2$), 2.38 (m, 2H, H9), 3.93 (s, 3H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 21.7

(C6, C7), 23.9 (C5), 25.7 (C8), 54.2 (OMe), 110.2 (C3), 116.7 (q, $^{1}J_{C\text{-}F} = 289$), 170.1 (C4), 181.2 (q, $^{2}J_{C\text{-}F} = 36$, C2).

5.7 (*Z*)-2,2,2-Trifluoro-1-(1-methoxy3,4,4a,5,6,7,8,8a-octahydro-2-naphthalenyl)ethanone 2g (Entry 7)

$C_{13}H_{17}F_3O_2$ (mw 262.27). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 1.40–1.73 (m, 11H, H7-H12), 2.45–2.47 (m, 1H, H6), 2.81 (m, 2H, H13), 4.30 (s, 3H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 25.4 (C8, C9), 25.6 (C12), 30.0 (C7, C10), 32.1 (C13), 43.0 (C11), 45.1 (C6), 58.9 (C5), 114.1 (C3), 116.76 (q, $^{1}J_{C\text{-}F} = 289$, C1), 180.0 (C4), 190.7 (q, $^{2}J_{C\text{-}F} = 36$, C2).

5.8 (*Z*)-1,1,1-Trichloro-4-methoxy-3-penten-2-one 3a (Entry 8)

$C_6H_7Cl_3O_2$ (mw 217.48). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 1.32 (t, 3H, H6), 3.81 (s, 3H, H5), 6.01 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 16.5 (C5), 52.5 (C6), 98.8 (C1), 100.0 (C3), 170.0 (C4), 186.2 (C2).

5.9 (*Z*)-1,1,1-Trichloro-4-methoxy-3-octen-2-one 3b (Entry 9)

$C_9H_{13}Cl_3O_2$ (mw 259.56). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 0.92 (t, 2H, H9), 1.40 (m, 2H, H8), 1.55 (m, 2H, H7), 2.80 (t, 2H, H6), 3.80 (s, 3H, H5), 5.39 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 14.1 (C9), 23.5 (C8), 26.3 (C7), 37.6 (C6), 51.4 (C5), 89.8 (C3), 108.9 (C1), 174.7 (C4), 176.5 (C2).

5.10 (*Z*)-1,1,1-Trichloro-4-methoxy-7-methyl-3-octen-2-one 3c (Entry 10)

$C_{10}H_{15}Cl_3O_2$ (mw 273.58). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 1.41 (t, 3H, H9), 1.45 (m, 2H, H8), 1.48 (m, 1H, H7), 2.44 (t, 2H, H6), 4.43 (q, 3H, H5), 5.30 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 23.6 (C8, C9), 26.8 (C7), 39.3 (C6), 57.0 (C5), 97.3 (C1), 101.4 (C3), 176.5 (C4), 189.9 (C2).

5.11 (*Z*)-1,1,1-Trichloro-4-methoxy-4-(thien-2-yl)-3-buten-2-one 3d (Entry 11)

$C_8H_5Cl_3O_2S$ (mw 285.58). Oil.^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 3.95 (s, 3H, OMe), 5.8 (s, 1H,H3); Tn: 7.13 (t, 1H, H4), 7.6 (d, 1H, H3), 8.5 (d, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 98.2 (C1), 176.2 (C2), 90.0 (C3), 169.2 (C4) 56.9 (OMe), Tn: 135.0 (C2), 132.3 (C3), 127.4 (C4), 134.3 (C5).

5.12 (*Z*)-1,1,1-Trichloro-4-methoxy-4-phenyl-3-buten-2-one 3e (Entry 12)

$C_{11}H_9Cl_3O_2$ (mw 279.55). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 3.92 (s, 3H, H5), 6.56 (s, 1H, H3), 7.38–7.61 (m, 5H, H7, H7′, H8, H8′, H9). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 56.1 (C5), 97.1 (C1), 104.7 (C3), 128.2 (C7, C7′), 128.4 (C8, C8′), 131.1 (C9), 136.4 (C6), 178.0 (C4), 188.8 (C2).

5.13 (*Z*)-2,2,2-Trichloro-1-(2-methoxy-1-cyclohexenyl)ethanone 3f (Entry 13)

$C_9H_{11}Cl_3O_2$ (mw 257.54). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 1.73–1.89 (m, 6H, $3CH_2$), 2.38 (m, 2H, H9), 3.89 (s, 3H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 23.5 (C7), 24.3 (C8), 25.5 (C6, C9), 55.0 (C5), 96.6 (C1), 114.5 (C3), 181.1 (C4), 190.8 (C2).

5.14 (*Z*)-2,2,2-Trichloro-1-(1-methoxy-3,4,4a,5,6,7,8,8a-octahydro-2-naphthalenyl)ethanone 3 g (Entry 14)

$C_{13}H_{17}Cl_3O_2$ (mw 311.63). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ($J_{H\text{-}H}$, Hz) 1.40–1.73 (m, 11H, H7-H12), 2.45-2.47 (m, 1H, H6), 2.81 (m, 2H, H13), 4.00 (s, 3H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ ($J_{C\text{-}F}$, Hz) 25.4 (C8, C9), 25.6 (C12), 30.0 (C7, C10), 32.1 (C13), 43.0 (C11), 45.1 (C6), 58.9 (C5), 96.6 (C1), 114.1 (C3), 180.0 (C4), 190.7 (C2).

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