α-Arylation and Alkynylation of Cyclic α-Iodoenones Using Palladium-Catalyzed Cross-Coupling Reactions with Trifluoroborate Salts

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Abstract: An expeditious synthesis of α-aryl- and α-alkynylcyclohexenones is described and illustrated by palladium-catalyzed cross-coupling reaction of cyclic α-iodoenones with potassium aryltrifluoroborate salts. This procedure offers easy access to α-arylated and alkynylated cyclohexenones functionalized with electron-donor and -acceptor substituents in good yields.

Key words: cross-coupling reaction, cyclic α-iodoenones, α-substituted enones

The introduction of functional groups at the α-position of α,β-unsaturated enones is a challenging and important synthetic transformation in organic chemistry. α-Substituted functionalized α,β-enones are important synthetic intermediates for the synthesis of several biologically active scaffolds[1,2] and common structural motifs found in various natural products.[3] In the past two decades, some α-alkynylenones containing natural products have been isolated such as harveynone (**I**),[4] tricholomenyns A (**II**) and B (**III**).[5] In addition, both naturally occurring compounds harveynone and tricholomenyns have been identified as novel anticancer agents[6] in the past few years.

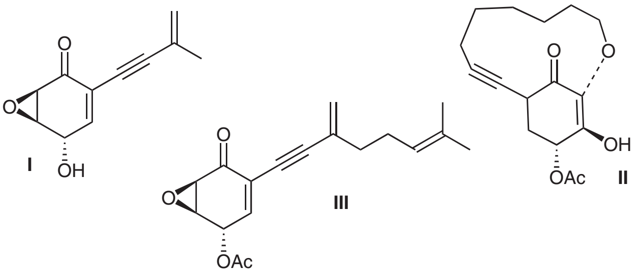

Figure 1 Structures of α-alkynylenones containing natural products

Most of the synthetic approaches for α-arylation, alkenylation, and alkynylation of α,β-enones at α-position are associated with transition-metal-catalyzed cross-coupling of α-organometallics with aryl halides or the complementary combination of α-halocarbonyl compound with aryl organometallics, although some other methodologies are also available.[7] In a few reports, the synthesis of α-arylated and alkynylated α,β-enones have been achieved by the palladium-catalyzed Stille cross-coupling reactions of α-iodoenones or α-tosylenones with corresponding tributyltin compounds.[8] Some of α-alkynylenones have been synthesized by palladium-catalyzed cross-coupling reaction of α-haloenones with terminal alkynes.[2,9] Recently, Krische and his research group have achieved the synthesis of α-arylated enones by phosphine-catalyzed nucleophilic reaction of cyclohex-2-enone with arylbismuth compounds.[10] Most of the synthetic approaches for the synthesis of α-substituted enones, specially α-arylenones are associated with the palladium-catalyzed cross-coupling reactions of α-haloenones with organoboronic acids or esters.[11] The organoboronic acids and esters are associated with some serious drawbacks such as expense, low stability, and high sensitivity to air and moisture. Thus, there is a need to develop an expedient route for the synthesis of these systems that could offer an economical route with the flexibility of introducing desirable functionalities into their molecular architecture.

In the past few years, potassium organotrifluoroborate salts (RBF_3K)[12] have received a great deal of attention with regard to their application in organic synthesis and have emerged as some of the most important organometallic reagents for Suzuki–Miyaura cross-coupling reactions. These compounds are crystalline solids, stable in air and moisture, and easily prepared by the addition of inexpensive KHF_2 to a variety of organoboron intermediates.[12] Recently, we have achieved several palladium-catalyzed cross-coupling and homocoupling reactions using potassium organotrifluoroborate salts.[13]

Herein, we report an alternative approach for the synthesis of α-arylenones by palladium-catalyzed cross-coupling reaction of 2-iodocyclohex-2-enone **2** with aryltrifluoroborates **3**. The strength of this coupling approach lies in the formation of C–C bond and introduction of electron-donor or -acceptor functionalities into their molecular structure.

Our approach to synthesize α-arylenones **2a**–**m** was based on palladium-catalyzed cross-coupling of α-iodoenone with potassium aryltrifluoroborate salts **3a**–**m**. The parent precursor α-iodoenone **2** was conveniently prepared by direct iodination of cyclohex-2-enone **1** with iodine in CCl_4–pyridine (1:1) at 0 °C under nitrogen atmosphere (Scheme 1).[8]

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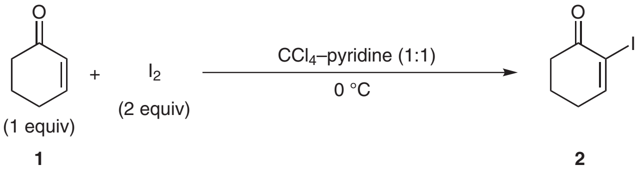
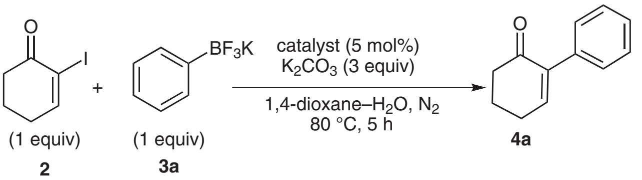


Scheme 1

Initially, we paid our attention to develop an optimum set of reaction conditions for the palladium-catalyzed cross-coupling reaction of 2-iodocyclohex-2-enone (**2**) with potassium aryltrifluoroborates **3**. In order to screen this coupling reaction, we selected 2-iodo-cyclohex-2-enone (**2**) and potassium phenyltrifluoroborate salt **3a** as coupling partners. To get the best catalyst, we attempted few reactions with some palladium (Table 1, entry 2–5) and non-palladium (Table 1, entry 6 and 7) catalysts while the reaction was working successfully only with palladium catalysts. The reactions were carried out using 3 equivalents of sodium carbonate as base and 1,4-dioxane–water as solvent while the reaction was stirred for five hours at 80 °C. When the reaction was performed in the absence of Pd catalyst no product was formed, indicating that the Pd catalyst is essential to initiate the reaction. The best result was obtained with $PdCl_2$ (Table 1, entry 2).

Table 1 Study of Catalyst Effect on Cross-Coupling of α-Iodoenone **2** with Phenyltrifluoroborate Salt **3a**



Entry	Catalyst[a]	Yield (%)[b]
1	–	n.r.
2	$PdCl_2$	86
3	$Pd(OAc)_2$	56
4	$PdCl_2(PhCN)_2$	75
5	$Pd(PPh_3)_4$	59
6	CuI	n.r.
7	$NiCl_2·6H_2O$	n.r.

[a] The amount of 5 mol% of catalyst was used.

[b] The yields were determined by GC.

After getting the best catalyst, a variety of bases like Et_3N, i-Pr_2NEt (Hünig's base), K_2CO_3, Cs_2CO_3, and NaOH were tested. The reaction with organic bases Et_3N and $(i$-$Pr)_2NH$ was not working nicely and the desired product observed in 15% and 23% yields, respectively (Table 2, entry 1 and 2). On the other hand, when inorganic bases were used, we observed slight increase in yield to 35% with NaOH (Table 2, entry 3), to 40% with Cs_2CO_3 (Table 2, entry 4), while a remarkable improvement (86%) was observed with K_2CO_3 (Table 2, entry 5).

Table 2 Study of Base Effect on Cross-Coupling of α-Iodoenone **2** with Phenyltrifluoroborate Salt **3a**

Entry	Base	Yield (%)[a]
1	Et_3N	15
2	$(i$-$Pr)_2NH$	23
3	NaOH	35
4	Cs_2CO_3	40
5	K_2CO_3	86

[a] The yields were determined by GC analysis.

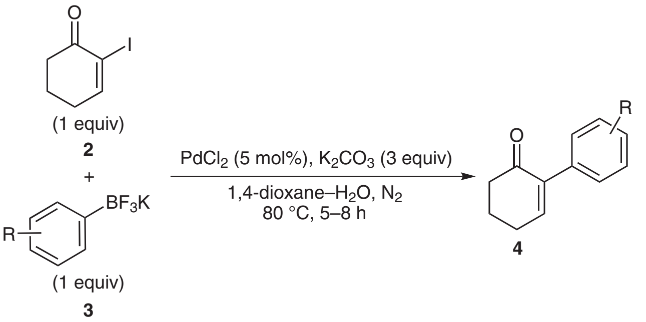
After determined the optimal catalyst and base, we performed the reaction using different solvent systems (MeOH, EtOH, *i*-PrOH, THF, DME, and 1,4-dioxane), both under anhydrous and aqueous conditions. The solvent mixture 1,4-dioxane–H_2O proved to be ideal, giving the desired product in 86% yield. The outcome of the reaction was further improved by a decrease in the catalyst loading from 10 mol% to 5 mol%, which increased the reaction yield from 86% to 93%.

Encouraged by the establishment of the optimum reaction conditions, we tested a series of substituted potassium aryltrifluoroborate salts **3a**–**n** with α-iodoenone **2** under our standard Suzuki–Miyaura cross-coupling conditions using 5 mol% of $PdCl_2$, 3 equivalents of K_2CO_3 in 1,4-dioxane–water (5:1) at 80 °C. The corresponding α-arylcyclohex-2-enone derivatives **4a**–**n** were isolated in moderate to good yields (26–97%).[14]

Almost all the reactions of electron-withdrawing aryl trifluoroborate salts with 2-iodo-cyclohex-2-enone proceeded successfully (Table 3, **3b**–**g**). We can discern that chloro, bromo, fluoro, and trifluoromethyl substituents at *meta* or *para* positions of the aromatic ring exert a moderate to strong influence upon the Suzuki–Miyaura cross-coupling reaction. The only substituent that was not tolerated was a cyano group at the *para* position of the aromatic ring (Table 3, **3g**). 3-Thiophenetrifluoroborate salt (**3h**) also provided the cross-coupling product in low yield (Table 3, **3h**).

The Suzuki–Miyaura cross-coupling reactions of aryltrifluoroborate salts **3** bearing electron-rich functional groups such as methyl and methoxy at the *ortho*, *meta*, and *para* positions furnished moderate to high yields of the desired products (Table 3, **3i** and **3k**). The presence of a hydroxy group at the *meta* position and a protected amino group at the *para* position of the aromatic ring afforded 11% and 42% yields, respectively (Table 3, **3j** and **3l**). Probably due to steric hindrance, the salt **3m** was not reactive under our reaction conditions. An interesting product resulting from a double cross-coupling reaction of two equivalents of 2-iodocyclohex-2-enone (**2**) with dipotassium phenylene-1,4-bistrifluoroborate salt (**3n**) was obtained in low yield (26%) (Table 3). The success of the reaction was observed to be dependent on the presence of water as a co-solvent. One possible explanation is the better solubility of the potassium aryltrifluoroborate salts in aqueous medium.[15]

Table 3 Suzuki–Miyaura Cross-Coupling Reaction of Aryltrifluoroborates and 2-Iodocyclohex-2-enone



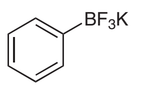
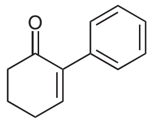
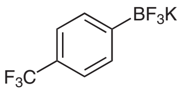
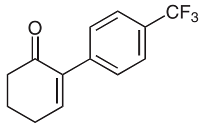
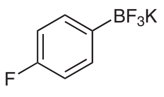
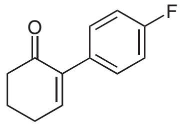
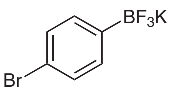
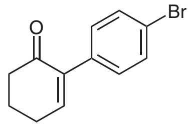
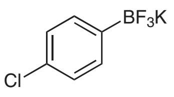
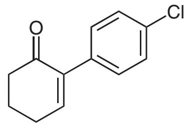
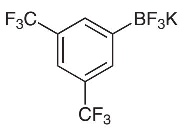
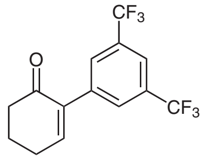
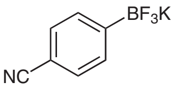
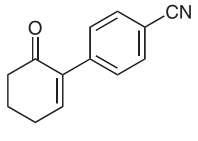
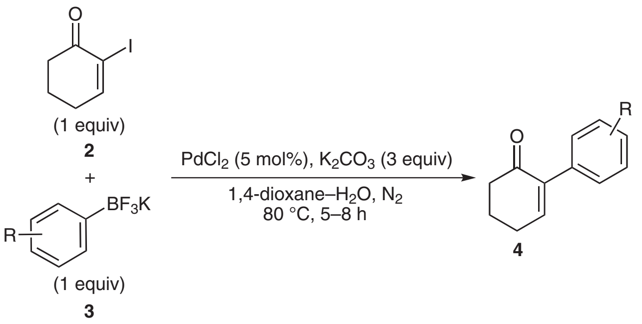
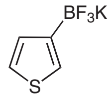
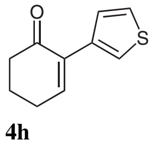
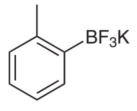
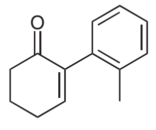
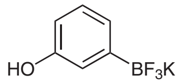
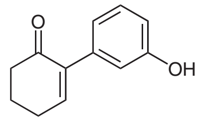
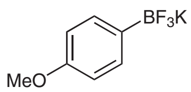
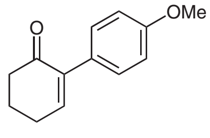
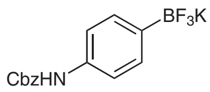
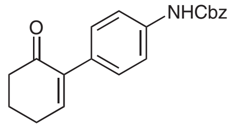
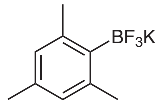
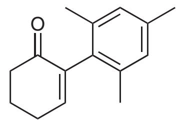
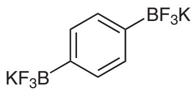
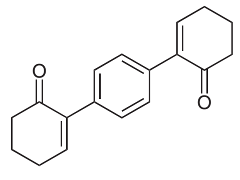
Entry	Aryltrifluoroborate **3**	Product **4**	Yield (%)[a]
1	 **3a**	 **4a**	85
2	 **3b**	 **4b**	72
3	 **3c**	 **4c**	69
4	 **3d**	 **4d**	47
5	 **3e**	 **4e**	46
6	 **3f**	 **4f**	26
7	 **3g**	 **4g**	n.r.

Table 3 Suzuki–Miyaura Cross-Coupling Reaction of Aryltrifluoroborates and 2-Iodocyclohex-2-enone (continued)

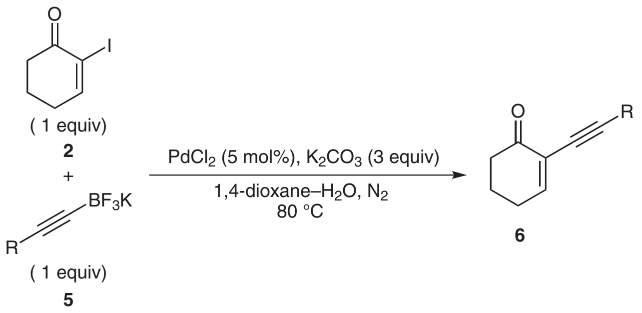


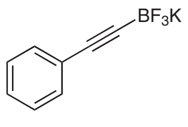
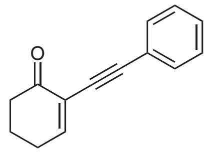
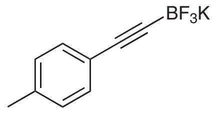
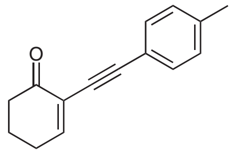
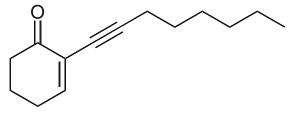
Entry	Aryltrifluoroborate **3**	Product **4**	Yield (%)[a]
8	 **3h**	 **4h**	46
9	 **3i**	 **4i**	97
10	 **3j**	 **4j**	11
11	 **3k**	 **4k**	74
12	 **3l**	 **4l**	42
13	 **3m**	 **4m**	n.r.
14	 **3n**	 **4n**	26

[a] Isolated yields.

Next we examined the Suzuki-Miyaura cross-coupling reaction of 2-iodocyclohex-2-enone (**2**) with alkynyltrifluoroborate salts (**5**) as summarized in Table 4.[16] The cross-coupling reactions of phenyl- and *p*-methylphenyl-

Table 4 Suzuki–Miyaura Cross-Coupling Reaction of Alkynyltrifluoroborates **5** and α-Iodocyclohexen-2-enone



Entry	Alkynyl trifluoroborate **5**	Product **6**	Time (h)	Yield (%)
1	 **5a**	 **6a**	7	73
2	 **5b**	 **6b**	20	61
3	 **5c**	 **6c**		n.r.

ethynyltrifluoroborate salts (**5a** and **5b**) proceeded smoothly, and the products were obtained in good yields [73% (**6a**) and 61% (**6b**), respectively; Table 4, entries 1 and 2]. However, no reaction was observed when alkylethynyltrifluoroborate salt **5c** was treated with 2-iodocyclohex-2-enone (**2**, Table 4, entry 3).

To further investigate the scope and limitations of this methodology, we carried out the cross-coupling of two different α-iodoenones (**7a** and **7b**), as summarized in Table 5.[17] Both compounds (**8a** and **8b**) were obtained in moderate yields.

In summary, we have developed an alternative synthetic route for the synthesis of α-arylated and α-alkynylated enones through the Suzuki–Miyaura coupling reaction of aryltrifluoroborate salts with α-iodocyclohex-2-enone catalyzed by palladium. Gratifyingly, almost all substrates tested during our studies gave cross-coupled products in moderate to good yields, with a variety of substitution patterns being tolerated.

Acknowledgment

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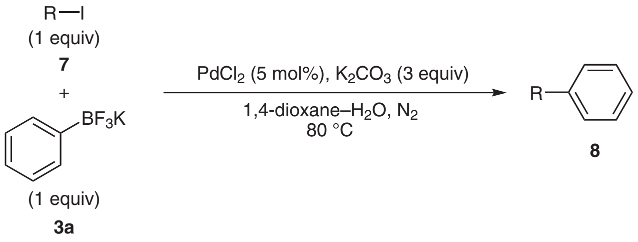
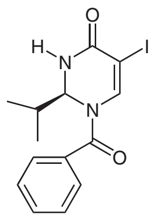
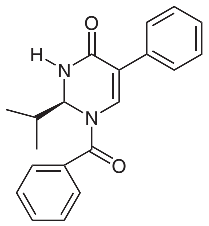
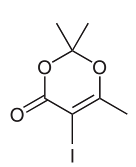
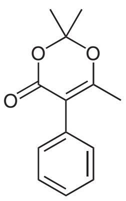
Table 5 Suzuki–Miyaura Cross-Coupling of Phenyltrifluoroborates **3a** and 2-Iodo-2-enones **7**



Entry	α-Iodoenone **7**	Product **8**	Time (h)	Yield (%)
1			2	65
2			1	50

References and Notes

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(14) **General Procedure for the Cross-Coupling Reaction of Aryltrifluoroborate Salts with 2-Iodocyclohex-2-enone (Table 3, Entry 1)**
To a round-bottomed flask containing phenyltrifluoroborate salt (0.5 mmol), 2-iodocyclohex-2-enone (0.5 mmol), K_2CO_3 (1.5 mmol), and $PdCl_2$ (5 mol%) was added a mixture of 1,4-dioxane (4 mL) and degassed H_2O (1.0 mL). The reaction mixture was allowed to stir at 80 °C for 5 h. After this time, the mixture was cooled to r.t., diluted with EtOAc (10 mL), and washed with sat. aq NH_4Cl (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane–EtOAc (8:2) as the eluent.
Selected Spectral and Analytical Data for 2-Phenylcyclohex-2-enone (4a)
Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.40 (m, 5 H), 7.06 (t, 1 H, *J* = 4.1 Hz), 2.53–2.64 (m, 4 H), 2.09–2.17 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.9, 147.9, 140.3, 136.5, 128.5, 127.9, 127.5, 39.0, 26.5, 22.9. LRMS: *m/z* (%) = 172 (100) [M$^+$], 144 (64), 130 (26), 115 (82), 103 (16), 71 (12), 63 (14), 51 (15). IR (KBr): ν = 1662, 2933, 3016 cm^{-1}. Mp 93–94 °C (lit.[13] 92–93 °C).

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(16) **General Procedure for the Cross-Coupling Reaction of Alkynyltrifluoroborate Salts with 2-Iodocyclohex-2-enone (Table 4, Entry 1)**
To a round-bottomed flask containing phenylethynyltrifluoroborate salt (0.5 mmol), 2-iodocyclohex-2-enone (0.5 mmol), K_2CO_3 (1.5 mmol), and $PdCl_2$ (5 mol%) was added a mixture of 1,4-dioxane (4 mL) and degassed H_2O (1.0 mL). The reaction mixture was allowed to stir at 80 °C for 7 h. After this time, the mixture was cooled to r.t, diluted with EtOAc (10 mL), and washed with sat. aq NH_4Cl (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane–EtOAc (8:2) as the eluent.
Selected Spectral and Analytical Data for 2-(Phenylethynyl)cyclohex-2-enone (6a)
Yield 73%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.64 (m, 2 H), 7.24–7.38 (m, 3 H), 6.47 (t, *J* = 1.89 Hz, 1 H), 2.48–2.57 (m, 2 H), 2.34–2.44 (m, 2 H), 1.89–1.98 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5, 153.3, 150.7, 131.4, 128.6 (2 C), 127.2, 123.7 (2 C), 122.4, 105.6, 62.4, 32.5, 23.0, 21.0. LRMS: *m/z* (%) = 196 (100) [M$^+$], 167 (44), 152 (17), 118 (19), 95 (22), 83 (27), 77 (16).

(17) **General Procedure for the Cross-Coupling Reaction of Phenyltrifluoroborate Salt with 2-Iodoen-2-ones (Table 5, Entry 1)**

To a round-bottomed flask containing phenyltrifluoroborate salt (0.5 mmol), (*S*)-1-benzoyl-5-iodo-2-isopropyl-2,3-dihydropyrimidin-4 (1*H*)-one (0.5 mmol), K_2CO_3 (1.5 mmol), and $PdCl_2$ (5 mol%) was added a mixture of 1,4-dioxane (4 mL) and degassed H_2O (1.0 mL). The reaction mixture was allowed to stir at 80 °C for 2 h. After this time, the mixture was cooled to r.t., diluted with EtOAc (10 mL), and washed with sat. aq NH_4Cl (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane–EtOAc (8:2) as the eluent.

Selected Spectral and Analytical Data for (*S*)-1-Benzoyl-2-isopropyl-5-phenyl-2,3-dihydropyrimidin-4 (1*H*)-one (8a)

Yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.59 (m, 6 H), 7.42 (dd, *J* = 7.5, 1.3 Hz, 2 H), 7.27–7.34 (m, 3 H), 6.66 (d, *J* = 4.4 Hz, 1 H), 5.67 (s, 1 H), 2.36–2.43 (m, 1 H), 1.09 (d, *J* = 6.7 Hz, 3 H), 1.01 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4, 163.4, 134.3, 133.4, 132.9, 131.4, 128.6 (2 C), 128.2 (2 C), 128.1 (2 C), 128.0, 127.5 (2 C), 116.6, 68.9, 32.8, 18.2, 17.4. LRMS: *m/z* (%) = 320 (1) [M$^+$], 277 (14), 105 (100), 89 (2), 77 (28), 51 (4), 43 (2). IR: ν = 3396, 3053, 2992, 2859, 1652, 1607 cm^{-1}. Mp 173.2–174.8 °C.