Rhodium Fluoroapatite Catalyzed Conjugate Addition of Arylboronic Acids to *α*,*β*-Unsaturated Carbonyl Compounds

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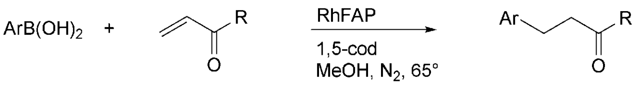
Rhodium fluoroapatite (RhFAP) is an efficient catalyst for conjugate addition of organoboron reagents to *α*,*β*-unsaturated carbonyl compounds. A variety of arylboronic acids and *α*,*β*-unsaturated carbonyl compounds were converted to the corresponding conjugate-addition products, demonstrating the versatility of the reaction. The reaction is highly selective. RhFAP was recovered quantitatively by simple filtration, and reused for four cycles.

Introduction. – Rhodium (Rh)-catalyzed conjugate addition of arylboronic acids to *α*,*β*-unsaturated carbonyl compounds has received considerable attention in the field of organic synthesis, ever since it was reported by *Miyaura* and co-workers in 1997 [1]. The discovery of such an important reaction has triggered much research activity in the area of C,C-bond formation catalyzed by Rh complexes [2]. *Zou et al.* reported the use of phosphinerhodium catalyst for selective *Heck*-type coupling and conjugate addition by synergistically tuning the supporting ligand, the boronic acid to olefin ratio, and other reaction conditions [3]. Despite the advantages of homogeneous metal complex catalysts, difficulties in recovering the expensive catalyst metals and ligands from the reaction mixture severely limit their industrial applications. Heterogeneous catalysis is particularly attractive as it allows production and ready separation of large quantities of products with the use of a small amount of catalyst. *Kaneda et al.* reported the 1,4-addition of organoboron reagents to *α*,*β*-unsaturated carbonyl compounds by using a highly efficient heterogeneous catalyst, Rh-grafted hydrotalcite [4].

Apatites are metal basic phosphates for which the chemical formula is $M_{10}(PO_4)_6(X)_2$ (M = divalent metal, X = monovalent anion), and the most typical apatite is calcium hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$ (CaHAP). Various kinds of cations and anions can be readily introduced into their framework due to their large ion-exchange ability, and such exchanged apatites are already in use in several organic transformations [5–7]. Previously, we reported the preparation of recyclable heterogeneous Cu-exchanged fluoroapatite and Cu-exchanged (*tert*-butoxy)apatite catalysts for *N*-arylation of imidazoles and other heterocycles with iodo-, bromo-, chloro-, and fluoroarenes (electron-withdrawing groups) with good to excellent yields. We also reported a PdFAP catalyst (fluoroapatite-supported Pd catalyst) for the *Suzuki*- and *Heck*-coupling reaction [8]. Very recently, we described the preparation of a recyclable heterogeneous rhodium fluoroapatite (RhFAP) catalyst by a simple ion-exchange technique by treatment of fluoroapatite with $RhCl_3$ in H_2O, which successfully promoted cross coupling of *Baylis–Hillman* adducts with arylboronic acids to yield trisubstituted olefins [9]. Thus, in continuation of our work with the RhFAP catalyst, we herein report the conjugate addition of organoboron reagents to α,β-unsaturated carbonyl compounds to yield conjugate-addition products (*Scheme*).

Scheme



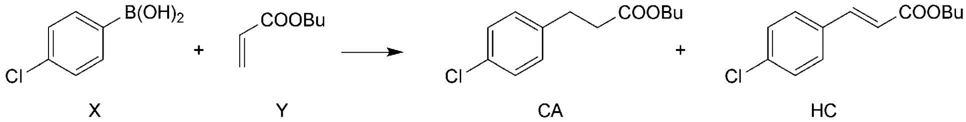
Ar = Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-MeC_6H_4, 2-FC_6H_4, 4-FC_6H_4,
1-naphthyl, 3-$CHOC_6H_4$, 3-$NO_2C_6H_4$, PhCH=CH, furan-3-yl, 3-thienyl

R = BuO, EtO, MeO, ^{t}BuO, Me

Results and Discussion. – In an effort to develop a better catalytic system, various reaction parameters were screened for the conjugate addition of (4-chlorophenyl)boronic acid to butyl acrylate (= butyl prop-2-enoate) to yield butyl 4-chlorobenzenepropanoate, and the results are presented in *Table 1*. The RhFAP catalyst, combined with cycloocta-1,5-diene (1,5-cod; 0.12 mmol), in MeOH at 65° exhibited the highest catalytic activity leading to the conjugate-addition (CA) product (*Table 1*, *Entry 4*), while the reaction conducted in the absence of 1,5-cod did not yield the CA product (*Table 1*, *Entry 3*). No reaction took place with homogeneous $RhCl_3$ catalyst in the presence and absence of 1,5-cod under similar conditions (*Table 1*, *Entries 1* and *2*), and there was no reaction with $RhCl_3$ impregnated on FAP support (RhFAP-impregnated) and Rh/SiO_2 (*Table 1*, *Entries 10* and *11*). The solvent had a pronounced effect in these reactions, both in terms of yield and selectivity of CA product. MeOH and EtOH were good solvents with good selectivity, whereas H_2O, toluene/H_2O 3 : 1, and THF/H_2O 2 : 1 provided moderate yields of CA product with poor selectivity (*Table 1*). The concentration of boronic acid, olefin, Rh, and 1,5-cod were tuned to get the conjugate addition product selectively, and these results are presented in *Table 2*. The CA product was obtained with 99% selectivity when the ratio of (4-chlorophenyl)boronic acid to olefin was 1.2 : 1, and Rh to 1,5-cod was 1 : 12.

The controlled reaction conducted under identical conditions devoid of RhFAP and 1,5-cod gave no CA product, despite prolonged reaction times. RhFAP was recovered quantitatively by simple centrifugation, and reused for four recycles with a minimal loss of activity (*Table 1*, *Entry 4*). The X-ray photoelectron spectrum (XPS) of the used RhFAP catalyst showed retention of the +3 oxidation state. To check the heterogeneity of the catalyst, a reaction between (4-chlorophenyl)boronic acid and butyl acrylate was terminated at 31% conversion (1 h), and the catalyst was separated by simple filtration. The reaction was continued for additional 6 h, and the conversion remained unchanged. These studies clearly demonstrate that no leaching of Rh had taken place from the catalyst, and throughout the reaction, Rh was bounded to the support.

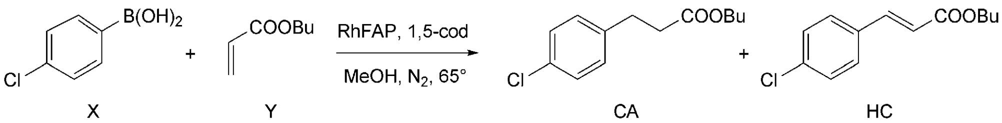
Table 1. *Screening of Reaction Parameters for the Synthesis of Butyl 4-Chlorobenzenepropanoate*[a])



Entry	Catalyst	Solvent	Yield[b]) [%]	Ratio CA/HC[c])
1[d])[e])	$RhCl_3$	MeOH	0	0
2[f])[e])	$RhCl_3$	MeOH	0	0
3[d])	RhFAP	MeOH	0	0
4[f])	RhFAP	MeOH	92, 90[g])	99 : 1
5[f])	RhFAP	H_2O	68	92 : 8
6[f])	RhFAP	1,4-dioxane	12	99 : 1
7[f])	RhFAP	toluene/H_2O 3 : 1	64	73 : 27
8[f])	RhFAP	THF/H_2O 2 : 1	79	82 : 18
9[f])	RhFAP	EtOH	91	96 : 4
10[f])	RhFAP (impregnated)	MeOH	0	0
11[f])	Rh/SiO_2	MeOH	0	0

[a]) X (1.2 mmol), Y (1 mmol), catalyst (100 mg), 1,5-cod (0.12 mmol), solvent (4 ml), reaction time (6 h), N_2, 65°. [b]) Yield of isolated products. [c]) Ratio of CA (conjugative addition) and HC (*Heck*-type coupling) product is based on GC analysis by comparison with authentic samples. [d]) Without any additive. [e]) 2 mol-% of $RhCl_3$ was used. [f]) 1,5-cod was used (0.12 mmol). [g]) Yield after fourth recycle.

Table 2. *Screening of Molar Parameters for the Selective Formation of the Conjugate-Addition Product*

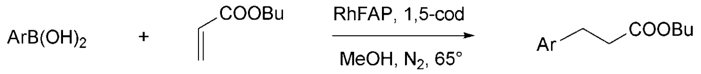


X [mmol]	Y [mmol]	Rh [mmol][a])	1,5-Cod [mmol]	Ration CA/HC[b])
0.5	1.0	0.005	0.06	89 : 11
0.5	1.0	0.005	0.12	88 : 12
0.6	1.0	0.01	0.12	90 : 10
1.0	1.5	0.01	0.12	98 : 2
1.2	1.0	0.01	0.12	99 : 1

[a]) Amount of Rh in the RhFAP catalyst. [b]) Ratio of CA (conjugate addition) and HC (*Heck*-type coupling) product is based on GC by comparison with authentic samples.

To understand the scope and limitations of RhFAP-catalyzed conjugate-addition reactions, various structurally different arylboronic acids possessing a wide range of functional groups were treated with butyl acrylate to give the corresponding conjugate-addition products, and the results are summarized in *Table 3*. Phenylboronic acids with a substituent at *ortho*-position (*Table 3*, *Entries 6* and *7*) afforded lower yields compared with the phenylboronic acids having a substituent at *para*-position (*Table 3*, *Entries 4* and *8*), which might be due to an *ortho* steric effect. Heteroaromatic boronic

Table 3. *Conjugate Addition of Organoboron Reagents X to Butyl Acrylate* (Y) *Catalyzed by RhFAP*[a])



X Y CA

Entry	Ar	Time [h]	Yield[b]) [%]
1	Ph	7	86
2	4-ClC_6H_4	6	92, 90[c])
3	4-BrC_6H_4	6	90
4	4-MeC_6H_4	8	93
5	4-$MeOC_6H_4$	12	82
6	2-MeC_6H_4	12	78
7	2-FC_6H_4	8	79
8	4-FC_6H_4	8	89
9	1-naphthyl	8	81
10	3-$CHOC_6H_4$	8	82
11	3-$NO_2C_6H_4$	8	84
12	PhCH=CH	10	76
13	furan-3-yl	8	84
14	3-thienyl	8	81

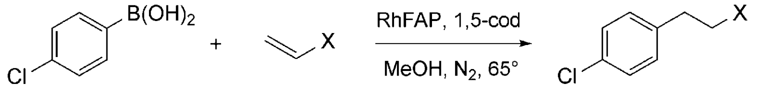
[a]) X (1.2 mmol), Y (1 mmol), catalyst (100 mg), cycloocta-1,5-diene (0.12 mmol), MeOH (4 ml), N_2, 65°. [b]) Yield of isolated CA product. [c]) Yield of CA after the 4th recycle.

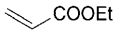
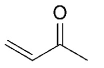
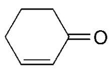
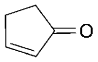
acids such as furan-3-ylboronic acid and 3-thienylboronic acid (*Table 1*, *Entries 13* and *14*) gave good yields of the corresponding conjugate-addition products. Aliphatic boronic acids such as vinylboronic acids gave lower yields of the desired product after a long reaction time (*Table 3*, *Entry 12*). To expand the scope of the method, a variety of α,β-unsaturated carbonyl compounds were successfully treated with (4-chlorophenyl)-boronic acid, and the results are summarized in *Table 4*. The cyclic enones such as cyclohex-2-en-1-one and cyclopent-2-en-1-one reacted slowly with good yields compared to other α,β-unsaturated carbonyl compounds. Selectivity of all the products was determined by both GC and ^{1}H-NMR, the selectivity of all the CA products being $> 96\%$.

Conclusions. – We developed a simple and efficient method for the conjugate addition of organoboron reagents to α,β-unsaturated carbonyl compounds to yield conjugate-addition products by using the RhFAP catalyst. A variety of arylboronic acids and α,β-unsaturated carbonyl compounds were converted to the corresponding conjugate-addition products, demonstrating the versatility of the reaction. The catalyst can be readily recovered and reused. The process is highly selective towards conjugate-addition products. We believe that this methodology will find widespread use in organic synthesis for the preparation of conjugate-addition products.

We wish to thank *CSIR* and *UGC*, New Delhi, for financial support.

Table 4. *Conjugate Addition of 4-(Chlorophenyl)boronic Acid to α,β-Unsaturated Carbonyl Compounds Catalyzed by RhFAP*[a])



Entry	Olefin	Time [h]	Yield[b]) [%]
1		8	86
2		8	84
3		8	85
4		8	89
5		9	90
6		9	88

[a]) Boronic acid (1.2 mmol), olefin (1 mmol), catalyst (100 mg), MeOH (4 ml), cycloocta-1,5-diene (0.12 mmol), N_2, 65°. [b]) Yield of isolated product.

Experimental Part

General. All reactants were commercially available and used without purification. NMR Spectra: *Avance-300* and *Gemini-200* spectrometer; δ in ppm rel. to Me_4Si as internal standard, J in Hz. GC Analyses: *Shimadzu GC 2010*, with *ZB-5* capillary column.

Conjugate-Addition Product: General Procedure. RhFAP (100 mg, *i.e.*, 0.01 mmol of Rh) was added to a mixture of arylboronic acid (1.2 mmol), olefin (1.0 mmol), and 1,5-cod (0.12 mmol) in MeOH (4 ml) under N_2 at 65°, and the mixture was stirred for 6–12 h. On completion of the reaction (TLC monitoring), the mixture was centrifuged, and the centrifugate was concentrated under reduced pressure to give the crude product. The latter was purified by column chromatography (silica gel) to afford the corresponding conjugate-addition product. The recovered catalyst was washed with MeOH, dried, and reused for the next cycle. The conjugate-addition products were characterized by ^{1}H-NMR spectroscopy and MS.

Butyl Benzenepropanoate (*Table 3*, *Entry 1*) [10a]: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.28–7.20 (*m*, 2 H); 7.18–7.05 (*m*, 3 H); 4.03 (*t*, J = 6.8, 2 H); 2.92 (*t*, J = 7.9, 2 H); 2.57 (*t*, J = 7.9, 2 H); 1.62–1.50 (*m*, 2 H); 1.38–1.28 (*m*, 2 H); 0.92 (*t*, J = 7.2, 3 H). ESI-MS: 229 ($[M+Na]^+$).

Butyl 4-Chlorobenzenepropanoate (*Table 3*, *Entry 2*) [10a]: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.22 (*d*, J = 8.3, 2 H); 7.11 (*d*, J = 8.3, 2 H); 4.03 (*t*, J = 6.8, 2 H); 2.90 (*t*, J = 7.5, 2 H); 2.56 (*t*, J = 7.5, 2 H); 1.62–1.50 (*m*, 2 H); 1.40–1.25 (*m*, 2 H); 0.92 (*t*, J = 7.2, 3 H). EI-MS: 240 (100, $M^{+\bullet}$), 184 (77), 167 (36), 138 (86), 125 (85), 103 (69), 89 (32), 77 (55), 57 (62), 41 (69).

Butyl 4-Bromobenzenepropanoate (*Table 3*, *Entry 3*) [10b]: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.20 (*d*, J = 8.2, 2 H); 7.08 (*d*, J = 8.2, 2 H); 4.03 (*t*, J = 6.8, 2 H); 2.89 (*t*, J = 7.5, 2 H); 2.54 (*t*, J = 7.5, 2 H); 1.64–1.48 (*m*, 2 H); 1.38–1.23 (*m*, 2 H); 0.93 (*t*, J = 7.15, 3 H). ESI-MS: 308 ($[M+Na]^+$).

Butyl 4-Methylbenzenepropanoate (*Table 3*, *Entry 4*) [10a]: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.12–6.97 (*m*, 4 H); 4.06 (*t*, J = 6.52, 2 H); 2.89 (*t*, J = 7.56, 2 H); 2.57 (*t*, J = 7.56, 2 H); 2.32 (*s*, 3 H); 1.67–1.50 (*m*, 2 H); 1.40–1.25 (*m*, 2 H); 0.92 (*t*, J = 7.2, 3 H). ESI-MS: 243 ($[M+Na]^+$).

Butyl 4-Methoxybenzenepropanoate (*Table 3*, *Entry 5*) [10a]: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.06 (*d*, $J = 8.3$, 2 H); 6.75 (*d*, $J = 8.3$, 2 H); 4.03 (*t*, $J = 6.8$, 2 H); 3.75 (*s*, 3 H); 2.86 (*t*, $J = 7.9$, 2 H); 2.54 (*t*, $J = 7.9$, 2 H); 1.65 – 1.50 (*m*, 2 H); 1.40 – 1.27 (*m*, 2 H); 0.92 (*t*, $J = 7.2$, 3 H). EI-MS: 236 (21, $M^{+\bullet}$), 134 (67), 121 (100), 103 (24), 91 (34), 77 (44), 41 (56).

Butyl 2-Methylbenzenepropanoate (*Table 3*, *Entry 6*) [10c]: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.18 – 6.96 (*m*, 4 H); 4.06 (*t*, $J = 6.8$, 2 H); 2.91 (*t*, $J = 7.9$, 2 H); 2.54 (*t*, $J = 7.9$, 2 H); 2.33 (*s*, 3 H); 1.65 – 1.50 (*m*, 2 H); 1.40 – 1.27 (*m*, 2 H); 0.92 (*t*, $J = 7.2$, 3 H). ESI-MS: 243 ($[M + \mathrm{Na}]^+$).

Butyl 2-Fluorobenzenepropanoate (*Table 3*, *Entry 7*): ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 7.30 – 7.10 (*m*, 2 H); 7.10 – 6.92 (*m*, 2 H); 4.06 (*t*, $J = 6.9$, 2 H); 2.97 (*t*, $J = 7.63$, 2 H); 2.60 (*t*, $J = 7.63$, 2 H); 1.69 – 1.46 (*m*, 2 H); 1.46 – 1.22 (*m*, 2 H); 0.93 (*t*, $J = 7.2$, 3 H). ESI-MS: 247 ($[M + \mathrm{Na}]^+$).

Butyl 4-Fluorobenzenepropanoate (*Table 3*, *Entry 8*): ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.13 (*d*, $J = 8.1$, 2 H); 6.90 (*d*, $J = 8.1$, 2 H); 4.03 (*t*, $J = 6.8$, 2 H); 2.90 (*t*, $J = 7.9$, 2 H); 2.55 (*t*, $J = 7.9$, 2 H); 1.65 – 1.44 (*m*, 2 H); 1.42 – 1.23 (*m*, 2 H); 0.92 (*t*, $J = 6.9$, 3 H). ESI-MS: 247 ($[M + \mathrm{Na}]^+$).

Butyl Naphthalene-1-propanoate (*Table 3*, *Entry 9*): ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 7.99 (*d*, $J = 8.08$, 1 H); 7.88 – 7.73 (*m*, 2 H); 7.67 (*d*, $J = 8.08$, 1 H); 7.55 – 7.37 (*m*, 3 H); 4.06 (*t*, $J = 6.6$, 2 H); 3.38 (*t*, $J = 7.7$, 2 H); 2.71 (*t*, $J = 7.7$, 2 H); 1.65 – 1.50 (*m*, 2 H); 1.41 – 1.23 (*m*, 2 H); 0.92 (*t*, $J = 7.3$, 3 H). EI-MS: 256 (56, $M^{+\bullet}$), 200 (19), 183 (15), 154 (92), 141 (100), 129 (28), 115 (45), 41 (39).

Butyl 3-Formylbenzenepropanoate (*Table 3*, *Entry 10*): ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 9.98 (*s*, 1 H); 7.95 (*s*, 1 H); 7.71 (*s*, 1 H); 7.50 – 7.41 (*m*, 2 H); 4.03 (*t*, $J = 6.8$, 2 H); 3.02 (*t*, $J = 7.55$, 2 H); 2.64 (*t*, $J = 7.55$, 2 H); 1.63 – 1.50 (*m*, 2 H); 1.40 – 1.25 (*m*, 2 H); 0.92 (*t*, $J = 7.2$, 3 H). ESI-MS: 257 ($[M + \mathrm{Na}]^+$).

Butyl 3-Nitrobenzenepropanoate (*Table 3*, *Entry 11*): ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 8.14 – 8.01 (*m*, 2 H); 7.60 – 7.38 (*m*, 2 H); 4.03 (*t*, $J = 6.87$, 2 H); 3.06 (*t*, $J = 7.56$, 2 H); 2.65 (*t*, $J = 7.56$, 2 H); 1.67 – 1.47 (*m*, 2 H); 1.40 – 1.23 (*m*, 2 H); 0.92 (*t*, $J = 7.2$, 3 H). ESI-MS: 252 ($[M + \mathrm{H}]^+$).

Butyl 5-Phenylpent-4-enoate (*Table 3*, *Entry 12*): ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 7.30 – 7.20 (*m*, 5 H); 6.42 (*d*, $J = 14.7$, 1 H); 6.23 – 6.12 (*m*, 1 H); 4.05 (*t*, $J = 6.8$, 2 H); 2.48 – 2.54 (*m*, 4 H); 1.62 – 1.51 (*m*, 2 H); 1.39 – 1.29 (*m*, 2 H); 0.93 (*t*, $J = 7.2$, 3 H). ESI-MS: 255 ($[M + \mathrm{Na}$).

Butyl Furan-3-propanoate (*Table 3*, *Entry 13*): ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.30 (*s*, 1 H); 7.20 (*s*, 1 H); 6.21 (*s*, 1 H); 4.04 (*t*, $J = 6.4$, 2 H); 2.74 (*t*, $J = 7.55$, 2 H); 2.52 (*t*, $J = 7.2$, 2 H); 1.71 – 1.51 (*m*, 2 H); 1.51 – 1.30 (*m*, 2 H); 0.93 (*t*, $J = 7.2$, 3 H). EI-MS: 196 (36, $M^{+\bullet}$), 167 (41), 138 (29), 111 (24), 96 (31), 55 (65), 41 (100).

Butyl Thiophene-3-propanoate (*Table 3*, *Entry 14*) [10a]: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.23 – 7.17 (*m*, 1 H); 6.95 – 6.86 (*m*, 2 H); 4.05 (*t*, $J = 6.8$, 2 H); 2.95 (*t*, $J = 7.5$, 2 H); 2.59 (*t*, $J = 7.5$, 2 H); 1.65 – 1.51 (*m*, 2 H); 1.41 – 1.30 (*m*, 2 H); 0.93 (*t*, $J = 7.2$, 3 H). EI-MS: 212 (67, $M^{+\bullet}$), 156 (31), 139 (29), 113 (100), 97 (29), 41 (60).

Ethyl 4-Chlorobenzenepropanoate (*Table 4*, *Entry 1*) [11a]: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.22 – 7.02 (*m*, 4 H); 4.2 (*t*, $J = 7.05$, 2 H); 2.93 (*t*, $J = 7.9$, 2 H); 2.56 (*t*, $J = 7.9$, 2 H); 1.2 (*t*, $J = 7.2$, 3 H). ESI-MS: 235 ($[M + \mathrm{Na}]^+$).

Methyl 4-Chlorobenzenepropanoate (*Table 4*, *Entry 2*) [11b]: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.22 (*d*, $J = 8.3$, 2 H); 7.10 (*d*, $J = 8.3$, 2 H); 3.67 (*s*, 3 H); 2.93 (*t*, $J = 7.9$, 2 H); 2.62 (*t*, $J = 7.9$, 2 H). ESI-MS: 221 ($[M + \mathrm{Na}]^+$).

tert-*Butyl 4-Chlorobenzenepropanoate* (*Table 4*, *Entry 3*): ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.22 (*d*, $J = 8.31$, 2 H); 7.10 (*d*, $J = 8.31$, 2 H); 2.85 (*t*, $J = 7.55$, 2 H); 2.48 (*t*, $J = 7.55$, 2 H); 1.40 (*s*, 3 H). ESI-MS: 263 ($[M + \mathrm{Na}]^+$).

4-(4-Chlorophenyl)butan-2-one (*Table 4*, *Entry 4*) [11c]: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.26 – 7.05 (*m*, 4 H); 2.90 (*t*, $J = 6.8$, 2 H); 2.75 (*t*, $J = 7.2$, 2 H); 2.15 (*s*, 3 H). ESI-MS: 205 ($[M + \mathrm{Na}]^+$).

3-(4-Chlorophenyl)cyclohexanone (*Table 4*, *Entry 5*): ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): 7.27 (*d*, $J = 8.6$, 2 H); 7.12 (*d*, $J = 8.6$, 2 H); 3.08 – 2.88 (*m*, 1 H); 2.61 – 2.23 (*m*, 4 H); 2.22 – 1.96 (*m*, 2 H); 1.92 – 1.67 (*m*, 2 H). EI-MS: 208 (26, $M^{+\bullet}$), 165 (24), 151 (56), 138 (49), 115 (58), 101 (58), 77 (41), 42 (100).

3-(4-Chlorophenyl)cyclopentanone (*Table 4*, *Entry 6*): ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$): 7.29 – 7.14 (*m*, 4 H); 3.42 – 3.36 (*m*, 1 H); 2.67 – 2.23 (*m*, 5 H); 2.02 – 1.96 (*m*, 1 H). ESI-MS: 217 ($[M + \mathrm{Na}]^+$).

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