Tetrahedron 67 (2011) 8800–8807

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Carbene adduct of cyclopalladated ferrocenylimine catalyzed α-arylation of ketones with aryl chlorides or bromides

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ARTICLE INFO

Article history:
Received 10 June 2011
Received in revised form 9 August 2011
Accepted 16 August 2011
Available online 22 August 2011

Keywords:
Cyclopalladated ferrocenylimine
N-Heterocyclic carbene
α-Arylation
Ketones
Aryl halides

ABSTRACT

Carbene adduct of cyclopalladated ferrocenylimine exhibited highly catalytic activity for the α-arylation of ketones with aryl halides. The corresponding products were obtained in moderate to excellent yields. Such protocol was applied to various ketones and a broad scope of aryl halides including aryl chlorides, bromides as well as unactivated and sterically hindered aryl halides.

1. Introduction

The α-aryl carbonyl functionality is an important component of many natural products, pharmaceutical candidates, synthetic intermediates, and precursors of emissive polymers.[1,9a] Over the last decades, great efforts[2–5] have been devoted to the transition metal-catalyzed α-arylations of ketones with aryl halides or pseudohalides to construct C_{sp2}—C_{sp3} bonds at the α-position of a carbonyl group. Of particular interest is palladium-catalyzed such transformation.[6–12] For most cases, a phosphine was required as a ligand, which often brought many practical drawbacks, such as high cost, air and moisture sensitivity, and pollution. On the other hand, *N*-heterocyclic carbene (NHC) recently emerged as an ancillary ligand with high strong σ-donating property and steric bulk,[13] and was applied in palladium-catalyzed α-arylation of ketones.[14–18] However, these procedures remain challenge associated with limitation of 'unactivated and sterically hindered' aryl chlorides as coupling partners.[19] Therefore, it is necessary to develop an efficient catalytic system for such substrates in the view of less cost and readily commercially available.

We have successfully applied cyclopalladated ferrocenylimine as catalysts in various coupling reactions[20] (Fig. 1). Herein, we disclose our ongoing research of carbene adduct of cyclopalladated ferrocenylimine as an efficient catalyst for α-arylation of ketones with unactivated and sterically hindered aryl chlorides or bromides.

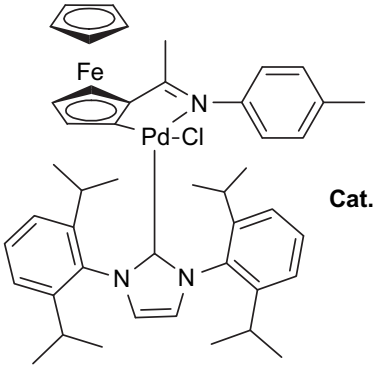

Fig. 1. Carbene adduct of cyclopalladated ferrocenylimine.

2. Results and discussions

Initially, we chose the α-arylation of acetophenone with 4-chlorotoluene in the presence of 1 mol % carbene adduct of cyclopalladated ferrocenylimine as a model reaction to screen the reaction conditions including bases and solvents. As shown in Table 1, it was found that the use of KO^{t}Bu and toluene give the best results (entry 4).

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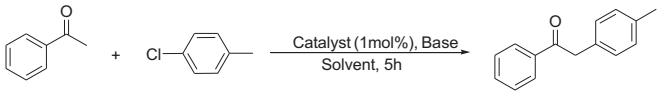
doi:10.1016/j.tet.2011.08.036

Table 1
Screening of bases and solvents for α-arylation of 4-chlorotoluene with acetophenone



Entry[a]	Catalyst	Base	Solvent	T (°C)	Yield[b] (%)
1	Cat.	NaO^tBu	Toluene	Reflux	61
2	Cat.	Cs_2CO_3	Toluene	Reflux	31
3	Cat.	NaH	Toluene	Reflux	57
4[c]	Cat.	KO^tBu	Toluene	Reflux	88
5	Cat.	K_2CO_3	Toluene	Reflux	19
6	Cat.	K_3PO_4	Toluene	Reflux	30
7	Cat.	KOAc	Toluene	Reflux	Trace
8	Cat.	KO^tBu	Dioxane	100	52
9	Cat.	KO^tBu	THF	70	46
10	Cat.	KO^tBu	DMF	130	37
11[c]	$PdCl_2$	KO^tBu	Toluene	Reflux	Trace
12[c]	$Pd(OAc)_2$	KO^tBu	Toluene	Reflux	Trace
13[c]	$Pd(PPh_3)Cl_2$	KO^tBu	Toluene	Reflux	Trace
14[c]	$Pd(PPh_3)_4$	KO^tBu	Toluene	Reflux	Trace
15[c]	$PdCl_2$+DPPF	KO^tBu	Toluene	Reflux	Trace

[a] Reaction conditions: acetophenone (1.1 mmol), 4-chlorotoluene (1 mmol), base (1.5 mmol), solvent (1.5 mL).
[b] Isolated yields.
[c] Reaction time: 3 h.

Under the optimized reaction conditions, the scope of the substrates including ketones and aryl chlorides was investigated. As shown in Table 2, the reaction was drastically influenced by electronic effect from aryl chlorides. When the electron-rich aryl chlorides were employed, moderate to excellent yields were obtained (Table 2, entries 1–6). As for the electron-deficient aryl chlorides, such catalytic system was suitable for limited substrates. For example, the reaction of 2-trifluoromethyl chlorobenzene with acetophenone could give 67% yield after refluxing for 12 h in toluene (Table 2, entry 7). While, trace amount of α-arylation products was obtained for 4-nitrochlorobenzene and 3-chloropyridine (Table 2, entries 8 and 9). To our delight, carbene adduct of cyclopalladated ferrocenylimine was highly efficient for the coupling of unactivated and sterically hindered aryl chlorides with acetophenone under the optimized conditions (Table 2, entries 10 and 11). Inspired by above results, we subsequently investigated the coupling of various ketones with unactivated and sterically hindered aryl chloride, such as 2-chlorotoluene or 2-chloro-*m*-xylene under the optimized reaction conditions. This protocol was applied to both aromatic and aliphatic ketones, such as *o*-methylacetophenone, *p*-methoxyacetophenone, cyclopentanone, 1-ferrocene ethanone, and 1-acetonaphthone. Various sterically hindered α-arylated ketones were obtained in 59–96% yields (Table 2, entries 12–20). These results indicate that the electronic and steric effects in ketone molecules have no significant influence on the reaction. Notably, the aliphatic ketone, such as cyclopentanone was also performed successfully, affording 65% yield[11a] (Table 2, entry 21).

This catalytic system was also applied to the coupling of sterically hindered aryl bromides, such as 2-bromotoluene, 2-bromo-*m*-xylene or 2-bromo-1,3,5-triisopropylbenzene with various ketones. The results were shown in Table 3. As expected, sterically hindered aryl bromides were proved to be suitable substrates under the optimized conditions, and could undergo α-arylation with electron-rich, electron-neutral, electron-deficient, or sterically hindered ketones in excellent yields within shorter reaction time, compared to analogous of aryl chlorides with 0.5 mol % catalyst loading.

3. Conclusion

In summary, a new catalytic system for the construction of α-arylated ketones with various aryl chlorides or bromides has been developed using carbene adduct of cyclopalladated ferrocenylimine as catalyst. Such protocol was successfully applied to various ketones and a broad scope of aryl chlorides or bromides, in particular for unactivated and sterically hindered aryl chlorides or bromides.

4. Experimental section

4.1. General

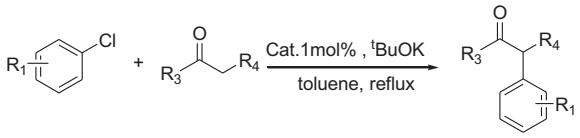
Melting points were measured on an XT-5 microscopic apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. High-resolution mass spectra were measured on a Waters Q-Tof Micro spectrometer. Preparative TLC was performed on dry silica gel plates developed with petroleum/EtOAc.

All reactions were carried out in glassware that was flame-dried under vacuum, and cooled under nitrogen. All solvents were purified by the standard methods. The carbene adduct of cyclopalladated ferrocenylimine[21] was prepared according to the reported procedures. Ketones except 1-ferrocene ethanone and aryl halides were purchased from commercial sources and generally used without further purification.

4.2. General procedure for ketone α-arylations reaction

An oven-dried, resealable Schlenk tube containing a stirbar was charged with aryl halide (1.0 mmol), ketone (1.1 mmol), potassium *tert*-butoxide (1.5 mmol), and 1 mol % catalyst, and backfilled with nitrogen. Toluene (1.5 mL) was sequentially injected, and the mixture was stirred in an oil bath at reflux temperature for the time specified. After the reaction was completed, the reaction mixture was filtered by chromatographed on silica gel and washed with EtOAc. The filtrate was dried over $MgSO_4$ and filtered before the solvent was removed on a rotary evaporator. The pure product was obtained by preparative TLC and the yield was calculated based on ArX (the purified products were identified by comparison of melting points with the literature data or by ^1H NMR and ^{13}C NMR spectra. New compounds were determined by HRMS spectra).

Table 2
α-Arylation of ketones with aryl chlorides



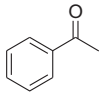
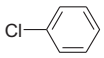
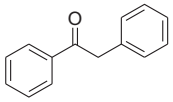
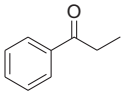
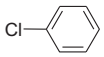
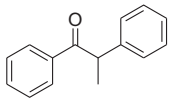
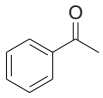
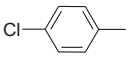
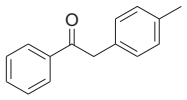
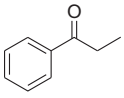
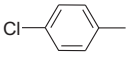
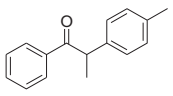
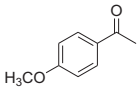
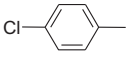
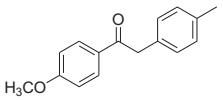
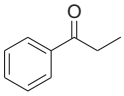
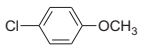
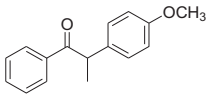
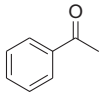
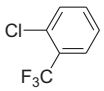
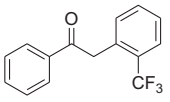
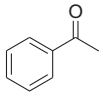
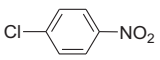
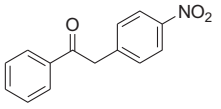
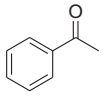
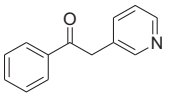
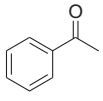
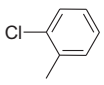
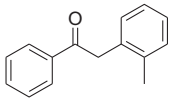
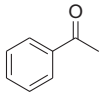
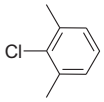
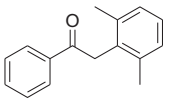
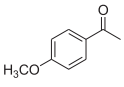
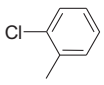
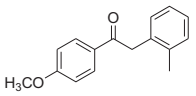
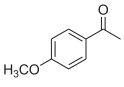
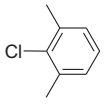
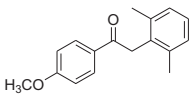
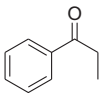
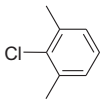
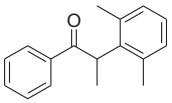
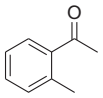
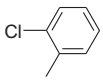
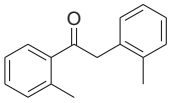
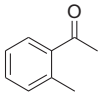
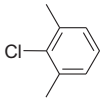
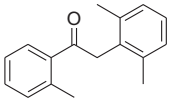
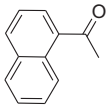
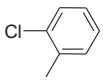
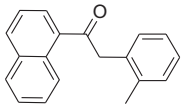
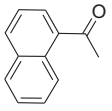
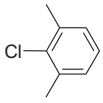
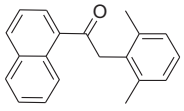
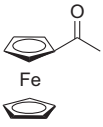
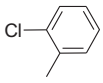
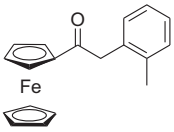
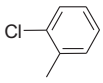
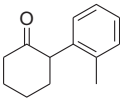
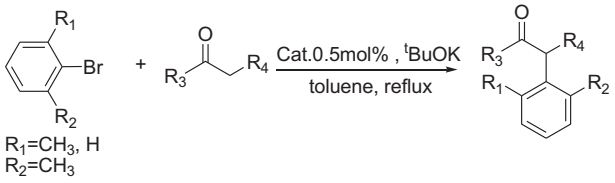
Entry[a]	Ketone	Aryl halide	Product	Time (h)	Yield[b] (%)
1				5	78
2[d]				7	75
3				3	88
4[d]				5	89
5				5	80
6[d]				5	90
7				12	67
8				12	Trace
9				12	Trace
10				2	96
11				1	97
12				2	91
13				2	96
14[d]				2	91

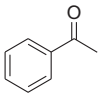
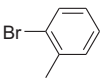
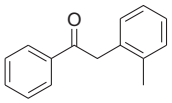
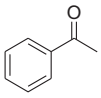
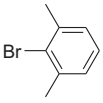
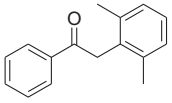
Table 2 (*continued*)

Entry[a]	Ketone	Aryl halide	Product	Time (h)	Yield[b] (%)
15[d]				2	92
16				2	81
17				2	83
18				3	77
19				2	75
20[c]				5	59
21				3	65

[a] Reaction conditions: ketone (1.1 mmol), aryl chlorides (1 mmol), KO^{t}Bu (1.5 mmol), cat. 0.01 mmol, toluene (1.5 mL).
[b] Isolated yields.
[c] Ketone (0.55 mmol), aryl chlorides (0.5 mmol), KO^{t}Bu (0.75 mmol), cat. 0.005 mmol, toluene (2 mL).
[d] Propiophenone (1.2 mmol).

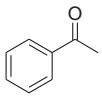
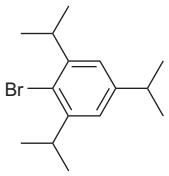
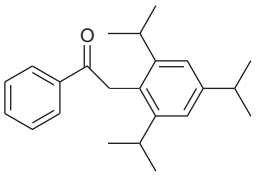
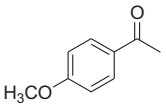
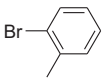
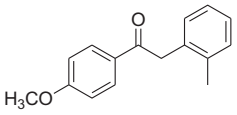
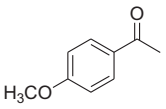
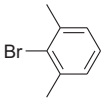
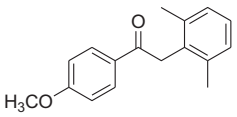
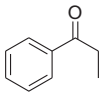
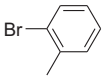
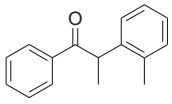
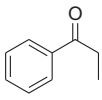
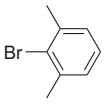
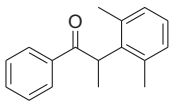
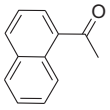
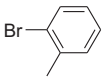
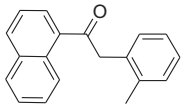
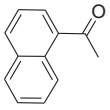
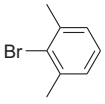
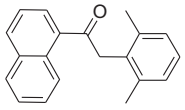
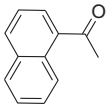
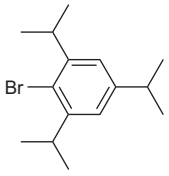
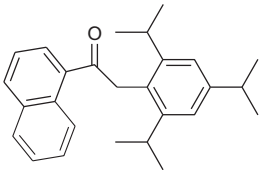
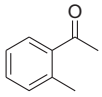
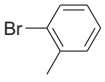
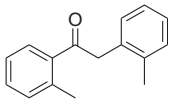
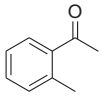
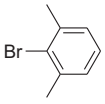
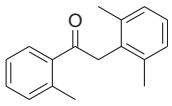
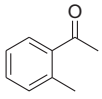
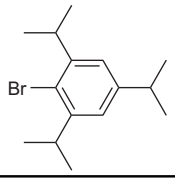
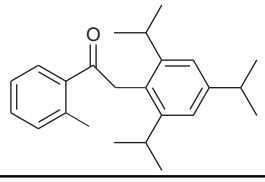
Table 3
α-Arylation of ketones with sterically hindered arylbromides



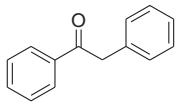
Entry[a]	Ketone	Aryl halide	Product	Time (h)	Yield[b] (%)
1				2	93
2				2	96

(*continued on next page*)

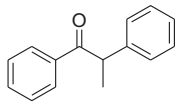
Table 3 (*continued*)

Entry[a]	Ketone	Aryl halide	Product	Time (h)	Yield[b] (%)
3				3	81
4				2	81
5				2	95
6[c]				2	90
7[c]				2	87
8				2	75
9				2	78
10				3	65
11				2	90
12				2	84
13				3	85

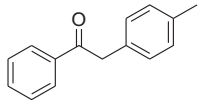
[a] Reaction conditions: ketone (1.1 mmol), aryl bromides (1 mmol), KO^{t}Bu (1.5 mmol), cat. 0.01 mmol, toluene (1.5 mL).
[b] Isolated yields.
[c] Propiophenone (1.2 mmol).



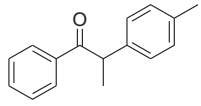
4.2.1. 1,2-Diphenyl ethanone[7,22] *(Table 2, entry 1).* White solid; mp: 48–50 °C, lit.:[15c] 50.2–52.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J=7.8 Hz, 2H), 7.47 (d, J=7.4 Hz, 2H), 7.40–7.37 (m, 2H), 7.28–7.24 (m, 2H), 7.20–7.18 (m, 3H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 136.5, 134.5, 133.1, 129.4, 128.6, 128.6, 128.6, 126.9, 45.5.



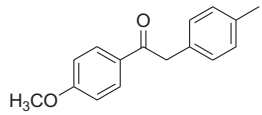
4.2.2. 1,2-Diphenyl-1-propanone[12a] *(Table 2, entry 2).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J=7.8 Hz, 2H), 7.45 (d, J=7.4 Hz, 1H) 7.39–7.35 (m, 2H), 7.3–7.2 (m, 5H), 4.71–4.66 (m, 1H), 1.53 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 136.4, 132.7, 128.9, 128.9, 128.8, 128.7, 128.5, 128.4, 127.7, 126.8, 47.8, 19.5.



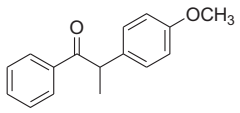
4.2.3. 2-(4-Methylphenyl)-1-phenyl ethanone (Table 2, entry 3). Slight yellow solid, mp: 90–92 °C, lit.:[22] 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.99 (m, 2H), 7.55–7.43 (m, 3H), 7.16–7.11 (m, 4H), 4.23 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 136.7, 136.5, 133.1, 131.5, 129.4, 129.3, 129.2, 128.6, 128.5, 128.4, 128.2, 126.2, 45.1, 21.1.



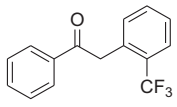
4.2.4. 2-(4-Methylphenyl)-1-phenyl-1-propanone[12a,b] *(Table 2, entry 4).* Slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.39–7.35 (m, 3H), 7.27–7.23 (m, 1H), 7.16–7.08 (m, 3H), 4.84–4.79 (m, J=6.8 Hz, 1H), 2.54 (s, 3H), 1.54–1.52 (m, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 140.2, 136.7, 134.6, 132.7, 131.0, 128.5, 127.0, 127.0, 126.8, 44.6, 19.6, 18.1.



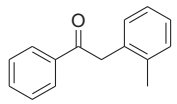
4.2.5. 1-(4-Methoxyphenyl)-2-(4-methylphenyl) ethanone (Table 2, entry 5). Slight yellow solid; mp: 91–93 °C, lit.:[23] 90–90.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J=8.4 Hz, 2H), 7.09–7.03 (m, 4H), 6.87–6.83 (m, 2H), 4.11 (s, 2H) 3.79–3.74 (m, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 163.4, 13.3, 131.9, 130.6, 129.6, 129.4, 129.2, 128.9, 113.7, 113.7, 113.7, 55.5, 44.9, 21.1.



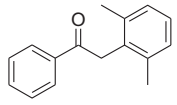
4.2.6. 2-(4-Methoxyphenyl)-1-phenyl-1-propanone[12a,24] *(Table 2, entry 6).* Slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=7.8 Hz, 2H), 7.49–7.36 (m, 3H), 7.27–7.21 (m, 2H), 6.85–6.81(m, 2H), 4.69–4.64 (m, J=6.8 Hz, 1H), 3.75 (s, 3H), 1.53 (d, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 158.5, 136.6, 133.5, 132.7, 128.8, 128.7, 128.5, 114.4, 55.2, 47.0, 19.5.



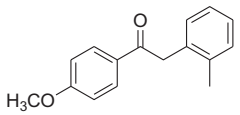
4.2.7. 1-Phenyl-2-[2-(trifluoromethyl)phenyl] ethanone[24] *(Table 2, entry 7).* Slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J=8.3 Hz, 2H), 7.70 (d, J=8.2 Hz, 1H), 7.63–7.49 (m, 4H), 7.42 (m, 1H), 7.31 (m, 1H), 4.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 136.4, 133.3, 133.1, 132.8, 131.8, 128.7, 128.2, 127.2, 126.1 (q, J=6.1 Hz), 121.6 (q, J=272.0 Hz), 42.4.



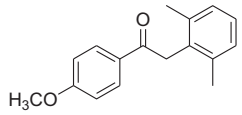
4.2.8. 2-(2-Methylphenyl)-1-phenyl ethanone[12a] *(Table 2, entry 10 and Table 3, entry 1).* Slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.8 Hz, 2H), 7.52-7.47 (m, 1H), 7.42-7.37(m, 2H), 7.16-7.06 (m, 4H), 4.23 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 137.0, 137.0, 133.7, 133.3, 130.5, 128.8, 128.4, 127.3, 126.2, 43.6, 19.9.



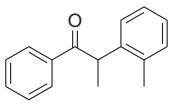
4.2.9. 2-(2,6-Dimethylphenyl)-1-phenyl ethanone[25] *(Table 2, entry 11 and Table 3, entry 2).* White solid; mp: 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J=7.8 Hz, 2H), 7.63–7.58 (m, 1H), 7.53–7.48 (m, 2H), 7.12–7.06 (m, 3H), 4.38 (s, 2H, CH_2(CO)), 2.22 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 197.6, 137.0, 133.7, 133.3, 130.5, 128.8, 128.4, 127.3, 126.2, 43.6, 19.9.



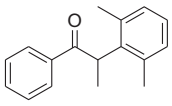
4.2.10. 1-(4-Methoxyphenyl)-2-(2-methylphenyl) ethanone (Table 2, entry 12 and Table 3, entry 4). Slight yellow solid, mp: 77–79 °C, lit.:[26] 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J=8.8 Hz, 2H), 7.18–7.06 (m, 4H), 6.88 (d, J=8.8 Hz, 2H), 4.18 (s, 2H, CH_2(CO)), 3.80 (s, 3H, OCH_3), 2.20 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 163.5, 136.8, 133.8, 130.6, 130.3, 130.2, 130.0, 127.0, 126.0, 55.4, 43.1, 19.8.



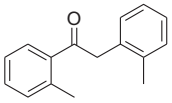
4.2.11. 2-(2,6-Dimethylphenyl)-1-(4-methoxyphenyl) ethanone[25] *(Table 2, entry 13 and Table 3, entry 5).* Slight brown solid, mp: 91–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ 8.01 (d, J=8.7 Hz, 2H), 7.05–6.99 (m, 3H), 6.92 (d, J=8.7 Hz, 2H), 4.26 (s, 2H, CH_2(CO)), 3.82 (s, 3H, OCH_3), 2.16 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.5, 136.9, 132.7, 130.3, 127.9, 126.7, 113.7, 55.5, 39.2, 20.3.*



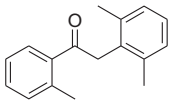
4.2.12. 2-(2-Methylphenyl)-1-phenyl-1-propanone[12a] *(Table 2, entry 14 and Table 3, entry 6).* Slight yellow oil; ^{1}*H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=6.8 Hz, 2H), 7.55 (d, J=7.2 Hz, 1H), 7.49–7.46 (m, 2H), 7.40–7.11 (m, 4H), 4.71–4.66 (m, J=6.8 Hz, 1H), 2.30 (s, 3H), 1.55 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 138.5, 136.6, 136.5, 132.9, 132.7, 128.8, 128.6, 128.5, 128.0, 127.7, 47.5, 21.0, 19.5.*



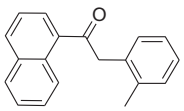
4.2.13. 2-(2,6-Dimethylphenyl)-1-phenyl-1-propanone[25] *(Table 2, entry 15 and Table 3, entry 7).* White solid, mp: 100–102 °C; ^{1}*H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J=7.6 Hz, 2H), 7.43–7.39 (m, 1H), 7.31–7.27 (m, 2H), 7.05–6.99 (m, 3H), 4.79–4.71 (m, J=6.8 Hz, 1H), 2.54 (s, 6H), 1.54–1.52 (m, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 140.0, 136.9, 135.6, 129.6, 128.3, 128.2, 126.8, 46.2, 20.6, 14.9.*



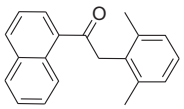
4.2.14. 1,2-Di-(2-methylphenyl) ethanone[27] *(Table 2, entry 16 and Table 3, entry 11).* Colorless oil; ^{1}*H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J=7.6 Hz, 1H), 7.36–7.34 (m, 1H), 7.28–7.22 (m, 2H), 7.18–7.10 (m, 4H), 4.22 (s, 2H), 2.45 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 138.3, 137.8, 136.9, 133.4, 132.0, 131.3, 130.5, 130.3, 128.4, 127.2, 126.1, 125.7, 46.3, 21.3, 19.8.*



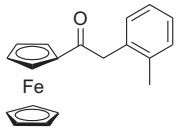
4.2.15. 2-(2,6-Dimethylphenyl)-1-(2-methylphenyl) ethanone (Table 2, entry 17 and Table 3, entry 12). Pale yellow solid, mp: 47–49 °C; ^{1}*H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=7.7 Hz, 1H), 7.30 (d, J=7.6 Hz, 1H), 7.28–7.25 (m, 1H), 7.11–7.04 (m, 3H), 4.28 (s, 2H), 2.46 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 138.3, 138.0, 137.0, 132.5, 132.1, 131.4, 128.1, 127.0, 125.8, 42.7, 21.2, 20.5; HRMS (positive ESI) calcd for $C_{17}H_{18}NaO$ (MNa^+): 261.1255; found: 261.1254.*



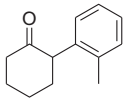
4.2.16. 2-(2-Methylphenyl)-1-(1-naphthalenyl) ethanone (Table 2, entry 18 and Table 3, entry 8). Slight yellow solid, mp: 74–78 °C; ^{1}*H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J=8.5 Hz, 1H) 7.90–7.88 (dd, J=7.1, 1.4 Hz, 2H), 7.79 (d, J=7.9 Hz, 1H), 7.51–7.39 (m, 3H), 7.16–7.13 (m, 4H), 4.32 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 137.0. 135.7, 134.0, 133.6, 132.8, 130.6, 130.5, 130.3, 128.5, 128.1, 127.7, 127.4, 126.5, 126.2, 125.8, 124.4, 47.0, 20.0; HRMS (positive ESI) calcd for $C_{19}H_{18}O$ (MH^+): 261.1279; found: 261.1344.*



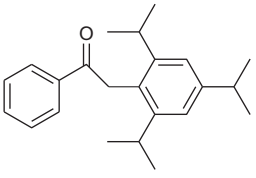
4.2.17. 2-(2,6-Dimethylphenyl)-1-(1-naphthalenyl) ethanone[25] *(Table 2, entry 19 and Table 3, entry 9).* Slight yellow solid, mp: 84–86 °C; ^{1}*H NMR (400 MHz, $CDCl_3$) δ: 8.59 (d, J=8.3 Hz, 1H, ArH), 8.10–8.06 (m, 2H, ArH), 7.92–7.90 (m, 1H, ArH), 7.59–7.54 (m, 3H, ArH), 7.17–7.12 (m, 3H, ArH), 4.48 (s, 2H, CH_2(CO)), 2.33 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 201.3, 137.1, 136.2, 134.0, 132.7, 132.6, 130.1, 128.5, 128.1, 128.1, 127.2, 127.1, 126.6, 125.7, 124.4, 43.3, 20.6.*



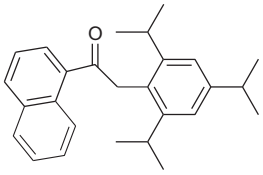
4.2.18. 2-(2-Methylphenyl)-1-ferrocene ethanone (Table 2, entry 20). Red solid, mp: 117–119 °C; ^{1}*H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 4H), 4.84–4.83 (m, 2H), 4.52–4.51 (m, 2H), 4.21 (s, 5H), 4.04 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 136.9, 133.7, 130.3, 130.1, 127.1, 126.0, 80.0, 72.2, 69.8, 69.6, 69.3, 44.6, 20.0; HRMS (positive ESI) calcd for $C_{19}H_{20}FeO$ (MH^+): 319.0785; found: 319.0839.*



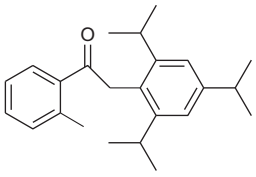
4.2.19. 2-(2-Methyl)phenyl cyclohexanone (Table 2, entry 21). White solid, mp: 52–54 °C, lit.:[28] *mp 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.12 (m, 4H), 3.80–3.76 (m, 1H), 2.55–2.50 (m, 2H), 2.26–2.26 (m, 1H), 2.21–2.03 (m, 6H), 1.84–1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 137.3, 136.1, 130.0, 127.6, 126.8, 125.9, 42.5, 34.1, 27.7, 25.8, 19.7.*



4.2.20. 1-Phenyl-2-[2,4,6-tris(1-methylethyl)phenyl] ethanone (Table 3, entry 3). Light yellow solid; mp: 113–115 °C, lit.:[29] *mp 113.5–114.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J=7.6 Hz, 2H), 7.60–7.58 (m, 1H), 7.52–7.48 (m, 2H), 7.03 (s, 1H), 4.44 (s, 2H, CH_2(CO)), 2.93–2.83 (m, 3H, CH(CH_3)$_2$), 1.27–1.17 (m, 18H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 197.7, 147.4, 147.1, 137.2, 133.1, 128.7, 128.1, 126.5, 121.0, 37.7, 34.2, 30.3, 24.1, 24.0.*



4.2.21. 1-(1-Naphthalenyl)-2-[2,4,6-tris(1-methylethyl)phenyl] ethanone (Table 3, entry 10). Slight yellow oil; *^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J=8.3 Hz, 1H, ArH), 8.06 (d, J=7.1 Hz, 1H, ArH), 7.98 (d, J=8.2 Hz, 1H, ArH), 7.85 (d, J=7.9 Hz, 1H, ArH), 7.55–7.12 (m, 3H, ArH), 7.09(s, 2H, ArH), 4.56 (s, 2H, CH_2(CO)), 3.04–2.90 (m, 3H, CH(CH_3)$_2$), 1.30–1.21 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ 201.8, 147.5, 147.2, 136.1, 134.0, 132.6, 130.2, 128.4, 128.0, 127.1, 126.6, 126.5, 125.7, 124.3, 121.0, 41.2, 34.2, 30.4, 24.1, 24.0. HRMS (positive ESI) calcd for $C_{27}H_{32}NaO$ (MNa^+): 395.2351; found: 395.2349.*



4.2.22. 1-(2-Methylphenyl)-2-[2,4,6-tris(1-methylethyl)phenyl] ethanone (Table 3, entry 13). Yellow oil; *^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J=7.6 Hz, 1H, ArH), 7.43–7.29 (m, 3H, ArH), 7.04 (s, 2H, ArH), 4.38 (s, 2H, CH_2(CO)), 2.94–2.87 (m, 3H, CH(CH_3)$_2$), 2.48 (s, 3H, CH_3), 1.28–1.20 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ 201.8, 147.4, 147.1, 138.3, 138.2, 132.1, 131.3, 128.1, 126.6, 125.7, 121.0, 40.7, 34.2, 30.3, 24.0, 21.2; HRMS (positive ESI) calcd for $C_{24}H_{32}NaO$ (MNa^+): 359.2351; found: 359.2355.*

Acknowledgements

We are grateful to the National Science Foundation of China (Project 20772114) and the Innovation Fund for Outstanding Scholar of Henan Province (Project 0621001100) for the financial support given to this research.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.036.

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