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Convenient Synthesis of Ferrocenylethynyl Ketones via Carbonylative Coupling of Ferrocenylethyne with Aryl Iodides by Using Water as Solvent

**Chonglong Li · Xiaolong Li · Qianqian Zhu ·
Hongyun Cheng · Qianru Lv · Baohua Chen**

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Abstract Carbonylative coupling reaction of aryl iodides with ferrocenylethyne catalyzed by $PdCl_2$ was carried out using sodium dodecyl sulphonate (SDS) as surfactant and water as solvent. The reaction gave much better yields of aryl ferrocenylethynyl ketones, which proceeded for 6 h at room temperature under a balloon pressure of carbon monoxide with Et_3 N as base.

Keywords Ferrocenylethynyl ketones · Carbonylation · SDS · Carbon monoxide · Water · Sonogashira coupling · Palladium catalysis

1 Introduction

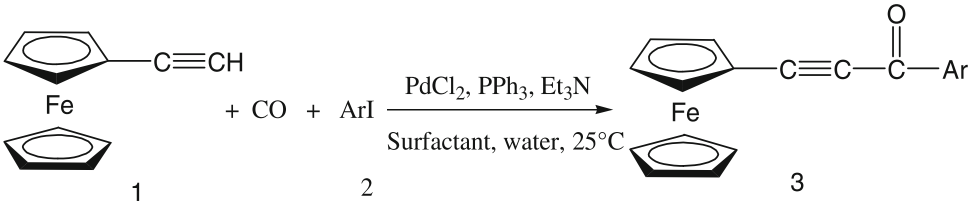
α, β-Alkynyl ketones have attracted considerable interest as useful intermediates for the synthesis of some biologically active molecules [1] and heterocyclic derivatives [2–4], such as pyrroles [5], furans [6, 7], furanones [8], triazoles [9], pyrazoles [10], 3,4,5-trisubstituted isoxazoles [11], indolizidinones [12], pyridinones [13], and quinolines [14]. They have also been used in the synthesis of natural products [15], such as chiral propargylic alcohols [16], conjugated dienones [17] and so on. It is well known that molecules possessing extensive conjugated π-electron systems exhibit large nonlinear optical properties [18, 19]. Molecules with π-donor–acceptor interactions, like ferrocenylethene and ferrocenylethyne derivatives, are examples of those structures which may offer a variety of potential applications, for example, photoactive semiconductors [20] and liquid crystals [21]. Considerable work has been done to synthesize new conjugated π-electron systems, such as ferrocenyl chalcones [22, 23]. Single compounds conjugated π-electron systems containing ferrocenylethynyl ketone have also been reported [24, 25].

At the same time,lots of general and versatile synthetic methodologies to α, β-alkynyl ketones are developed [26–29]. Usually they can be prepared by the Sonogashira coupling of acid chloride with terminal alkynes [27–29]. But these methodologies have great problems which maybe pollute environment by using organic solvents and carboxylic acid chloride. Thus, it is undoubted that 'green' interest has been devoted to the use of water as a cleaner green solvent for organic reactions [30–32]. Therefore, alkynyl ketones reaction by the palladium-catalyzed carbonylation of terminal alkynes with aryl iodides in water is considered to be a preferred method [33]. However, the use of water in organic reaction processes is rather limited because many reactive intermediates and catalysts do not dissolve and can be decomposed in it [34]. The general reaction yield may be very low.

In this paper we report that, by adding sodium dodecyl sulphonate (SDS) as surfactant, a facile carbonylative coupling reaction of aryl iodides with ferrocenylethyne using Et_3 N as base and water as solvent, resulted in excellent yields of aryl ferrocenylethynyl ketones. The reaction proceeded at room temperature for 6 h. The scheme of conducted reaction is depicted as the following (Scheme 1):

C. Li · X. Li · Q. Zhu · H. Cheng · Q. Lv · B. Chen (✉)
State Key Laboratory of Applied Organic Chemistry, Lanzhou University, 730000 Lanzhou, People's Republic of China
e-mail: chbh@lzu.edu.cn

Scheme 1 $PdCl_2$-catalyzed carbonylative coupling reaction of ferrocenylethyne with aryl iodides using SDS in water



2 Experiments

2.1 Typical Procedure for the Preparation of 3-Ferrocenyl-1-(4-methoxyphenyl) prop-2-yn-1-one (3a)

To a 25 mL of Schlenk tube equipped with a magnetic stirring bar were added ferrocenylethyne (252 mg, 1.2 mmol), $PdCl_2$ (8.8 mg, 0.05 mmol), PPh_3 (26.2 mg, 0.1 mmol), 4-iodoanisole (234 mg, 1.0 mmol), sodium dodecyl sulphonate (45 mg, 0.16 mmol). The mixture was degassed with CO three times, and H_2O (2.5 mL) was injected into the tube. Then the mixture was stirred for 5 min and Et_3 N (0.42 mL, 3.0 mmol) was added to the tube by a syringe. After that, the mixture was continually stirred for 6 h at room temperature under a balloon pressure of CO. When the reaction was completed, the mixture was extracted with ethyl acetate (3 × 5 mL), and the combined organic layer was washed with water and brine, then dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography [silica gel (200–300 mesh), hexanes–EtOAc] to give product 3a.

The materials ferrocenylethyne [35] and aryl iodides [36, 37] were prepared according to literature methods. All manipulations were completed under CO atmosphere. ^1H NMR spectra was collected on a Mercury 4 N-PEG-300 (1 H: 300 MHz; 13 C: 75 MHz), using $CDCl_3$ as solvent and TMS as the internal standard. Mass Spectra was obtained by using fast atom bombardment (FAB). Elemental analysis was carried out on an Elementary Vario EL analyzer. IR spectra were recorded on a Nicolet 670 FT-IR spectrophotometer as KBr pellets. In the reported results, the melting points were uncorrected.

3 Results and Discussion

In preliminary experiments, we attempted to perform the carbonylative coupling reaction using $PdCl_2(PPh_3)_2$ in water with 4-iodoanisole and ferrocenylethyne as substrates. However, the palladium precipitate was formed very rapidly under the reductive reaction conditions (CO, H_2O).

At the same time, we tried to use Et_3 N as base and $PdCl_2$ as catalyst to perform the reaction with the presence of Ph_3P in water, a very low yield (only 15%) was obtained. In order to improve reaction yields, we attempted to perform the coupling reaction under different surfactants conditions. We prepared for surfactants such as cetyl trimethyl ammonium bromide (CTAB), sodium dodecylbenzene sulphonate (SDBS), tetrabutyl ammonium bromide (TBAB), sodium dodecyl sulphonate (SDS), and then these surfactants were evaluated in the above carbonylative coupling reaction. Fortunately, yields were improved in the presence of a small amount of surfactant. The corresponding yields were listed in the Table 1.

From the results in Table 1, when we used CTAB, SDBS and TBAB as surfactants, the yields were moderate (entries 2–4). However, when we used SDS as surfactant, high yield (up to 83%) was obtained (entry 5). We also used different bases in this system. It can be seen from Table 1 that the effect of the base in the coupling reaction was significant. In general, Et_3 N led yield superior to those led by KOBu-t and K_2CO_3 (entries 6–7).

It is obvious that the reaction is carried out easily with the presence of SDS in water, to produce the alkynyl ketones in high yield at room temperature. Without surfactant, the yield dropped to 15%, which probably indicates that SDS helped distribute the organic substrates into water. So always using SDS as surfactant, we further conducted the experiments of the carbonylative coupling of ferrocenylethyne with various aryl iodides at room temperature under a balloon pressure of carbon monoxide for 6 h. The results were listed in the following Table 2.

Table 1 $PdCl_2$-catalyzed carbonylative reaction with different surfactant

Entry	Surfactant	Base	Yield (%)[a]
1	None	Et_3 N	15
2	Cetyl trimethyl ammonium bromide	Et_3 N	25
3	Sodium dodecylbenzene sulphonate	Et_3 N	32
4	Tetrabutyl ammonium bromide	Et_3 N	47
5	Sodium dodecyl sulphonate	Et_3 N	83
6	Sodium dodecyl sulphonate	KOBu-t	66
7	Sodium dodecyl sulphonate	K_2CO_3	52

[a] Isolated yield based on aryl iodide

Table 2 $PdCl_2$-catalyzed carbonylative coupling reactions of aryl iodides with ferrocenylethyne in water

Entry	Ar	Product	Yield (%)[a]
1	4-$MeOC_6H_4$	3a	83
2	2-$MeOC_6H_4$	3b	68
3	Ph	3c	58
4	3,4-$Me_2C_6H_3$	3d	80
5	4-$EtOC_6H_4$	3e	84
6	4-MeC_6H_4	3f	79
7	2-naphthyl	3g	52
8	4-$Me_2NC_6H_3$	3h	82
9	2-MeC_6H_4	3i	48
10	2-$O_2NC_6H_4$	3j	74
11	4-$Et_2NC_6H_4$	3k	83
12	2-$H_2NC_6H_4$	3l	40
13	2-H_2N-5-$H_3CC_6H_3$	3m	42
14	4-$MeHNC_6H_4$	3n	50
15	4-ClC_6H_4	3o	10
16	2-Pyridyl	–	–
17	2-$HO_2CC_6H_4$	–	–
18	4-$O_2NC_6H_4$	–	–

[a] Isolated yield based on aryl iodide

According to Table 2, we found that most of the reactions produce moderate to excellent yields of carbonylative coupling products (entries 1–14). It seems that the substituted iodides having electron-donating group (entries 1–2, 4–6, 8, 11) give better yields than those having electron-withdrawing group (entries 10, 15–18). The results also indicated that the stronger electron-donating group, the higher the yield. However, only a trace amount of carbonylation products were observed for aryl iodides containing 2-carbonyl or 4-nitro or 2-pyridyl substrates (entries 15–18).

When *O*-aminophenyl iodide participated in the reaction, a low yield could be obtained, along with noncarbonylative coupling product (Table 2, entry 12). Presumably because the key for selective carbonylative coupling would be the competition between transmetalation and CO insertion, the alkyne reacts too rapidly with the palladium complex derived from the oxidative addition of aryl iodide to palladium without insertion of CO [26].

4 Conclusion

Carbonylative coupling reactions of aryl iodides with ferrocenylethyne proceeded efficiently to give aryl ferrocenylethynyl ketones in good yields for 6 h at room temperature under a balloon pressure of carbon monoxide, when using SDS as surfactant, $PdCl_2$ as catalyst, and Et_3 N as base.

5 Spectral Data

5.1 3-Ferrocenyl-1-(4-methoxyphenyl)prop-2-yn-1-one (3a)

Orange–red solid; Mp 110–112 °C. IR (KBr): 2194 ($C{\equiv}C$), 1626 cm^{-1} (C=O).

^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.89$ (s, 3 H), 4.27 (s, 5 H), 4.39–4.40 (t, $J = 1.8$ Hz, 2 H), 4.66–4.67 (t, $J = 1.8$ Hz, 2 H), 6.96–7.00 (d, $J = 8.7$ Hz, 2 H), 8.13–8.16 (d, $J = 8.7$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.5$, 60.5, 70.4, 70.6, 73.0, 85.3, 95.5, 113.7, 130.4, 131.7, 164.1, 176.4.

MS (FAB): m/z (%) = 344 [M^+].

Anal. Calcd for $C_{20}H_{16}FeO_2$: C, 69.79; H, 4.69. Found: C, 69.71; H, 4.75.

5.2 3-Ferrocenyl-1-(2-Methoxyphenyl)prop-2-yn-1-one (3b)

Orange–red solid; Mp 110–112 °C. IR (KBr): 2180 ($C{\equiv}C$), 1632 cm^{-1} (C=O).

^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.96$ (s, 3 H), 4.26 (s, 5 H), 4.38 (s, 2 H), 4.62 (s, 2 H), 6.99–7.07 (q, $J = 8.1$ Hz, $J = 7.5$ Hz, 2 H), 7.49–7.55 (t, $J = 8.1$ Hz, $J = 7.8$ Hz, 1 H), 8.01–8.04 (d, $J = 7.5$ Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$, 60.9, 70.3, 70.6, 73.0, 87.7, 94.9, 112.2, 120.2, 127.1, 132.3, 134.5, 159.5, 176.5.

MS (FAB): m/z (%) = 344 [M^+].

Anal. Calcd for $C_{20}H_{16}FeO_2$: C, 69.79; H, 4.69. Found: C, 69.74; H, 4.82.

5.3 3-Ferrocenyl-1-phenylprop-2-yn-1-one (3c)

Orange–red solid; Mp 121–123 °C. IR (KBr): 2176 ($C{\equiv}C$), 1622 cm^{-1} (C=O).

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.30$ (s, 5 H), 4.43 (s, 2 H), 4.70 (s, 2 H), 7.50–7.55 (t, $J = 7.5$ Hz, 2 H), 7.61–7.63 (d, $J = 7.5$ Hz, 1 H), 8.18–8.21 (d, $J = 7.5$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.2$, 70.4, 70.8, 73.1, 85.5, 96.6, 128.5, 129.3, 133.7, 137.1, 177.5.

MS (FAB): m/z (%) = 314 [M^+].

Anal. Calcd for $C_{19}H_{14}FeO$: C, 72.64; H, 4.49. Found: C, 72.57; H, 4.44.

5.4 3-Ferrocenyl-1-(3, 4-dimethylphenyl)prop-2-yn-1-one (3d)

Orange–red solid; Mp 154–155 °C. IR (KBr): 2191 ($C{\equiv}C$), 1630 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.35$ (s, 6 H), 4.27–4.28 (d, $J = 2.1$ Hz, 5 H), 4.40–4.41 (d, $J = 1.8$ Hz, 2 H), 4.67–4.68 (t, $J = 1.8$ Hz, 2 H), 7.25–7.28 (d, $J = 6.6$ Hz, 1 H), 7.91 (d, $J = 6.6$ Hz, 1 H), 7.94 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.8$, 20.2, 60.6, 70.4, 70.6, 73.0, 85.5, 95.7, 127.4, 129.8, 130.1, 135.2, 136.9, 143.5, 177.6.

MS (FAB): m/z (%) = 342 [M^+].

Anal. Calcd for $C_{21}H_{18}FeO$: C, 73.70; H, 5.30. Found: C, 73.80; H, 5.36.

5.5 3-Ferrocenyl-1-(4-ethoxyphenyl)prop-2-yn-1-one (3e)

Orange–red solid, Mp 106–108 °C. IR (KBr): 2179 (C≡C), 1627 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$–1.47 (t, $J = 6.9$ Hz, 3 H), 4.08–4.15 (q, $J = 7.2$ Hz, 2 H, $J = 6.9$ Hz), 4.27(s, 5 H), 4.38–4.40 (t, $J = 1.8$ Hz, 2 H), 4.65–4.66 (t, $J = 1.8$ Hz, 2 H), 6.94–6.97 (d, $J = 8.7$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.6$, 60.6, 63.8, 70.3, 70.6, 72.9, 85.3, 95.3, 114.1, 130.3, 131.7, 163.5, 176.3.

MS (FAB): m/z (%) = 358 (M^+).

Anal. Calcd for $C_{21}H_{18}FeO_2$: C, 70.41; H, 5.06. Found: C, 70.50; H, 5.11.

5.6 3-Ferrocenyl-1-(4-methylphenyl)prop-2-yn-1-one (3f)

Orange–red solid; Mp 153–155 °C. IR (KBr): 2192 (C≡C), 1630 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.44$ (s, 3 H), 4.28 (t, 5 H), 4.41–4.42 (t, $J = 1.8$ Hz, 2 H), 4.67–4.68 (d, $J = 1.2$ Hz, 2 H), 7.29–7.32 (d, $J = 7.8$ Hz, 2 H), 8.06–8.09 (d, $J = 7.8$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.8$, 60.4, 70.4, 70.7, 73.0, 85.5, 95.9, 129.2, 129.5, 134.8, 144.7, 177.3.

MS (FAB): m/z (%) = 328 [M^+].

Anal. Calcd for $C_{20}H_{16}FeO$: C, 73.19; H, 4.91. Found: C, 73.27; H, 4.86.

5.7 3-Ferrocenyl-1-(2-naphthyl)prop-2-yn-1-one (3g)

Orange–red solid; Mp 90–92 °C. IR (KBr): 2189 (C≡C), 1620 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.32$ (s, 5 H), 4.45–4.46 (t, $J = 1.8$ Hz, 2 H), 4.74–4.75 (t, $J = 1.8$ Hz, 2 H), 7.59–7.64 (t, $J = 7.5$ Hz, $J = 9.0$ Hz, 2 H), 7.90–7.95 (t, $J = 8.1$ Hz, $J = 7.5$ Hz, 2 H), 8.03–8.06 (d, $J = 7.8$ Hz, 1 H), 8.20–8.23 (d, $J = 7.8$ Hz, 1 H), 8.75 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.4$, 70.5, 70.8, 73.1, 85.6, 96.5, 124.1, 126.8, 127.9, 128.4, 129.8, 132.1, 132.4, 134.7, 135.9.

MS (FAB): m/z (%) = 364 [M^+].

Anal. Calcd for $C_{23}H_{16}FeO$: C, 75.85; H, 4.43. Found: C, 75.69; H, 4.46.

5.8 3-Ferrocenyl-1-[4-(dimethylamino)phenyl]prop-2-yn-1-one (3h)

Orange–red solid; Mp 176–178 °C. IR (KBr): 2182 (C≡C), 1611 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.10$ (s, 6 H), 4.27 (s, 5 H), 4.37 (s, 2 H), 4.65 (s, 2 H), 6.68–6.71 (d, $J = 9.0$ Hz, 2 H), 8.06–8.09 (d, $J = 8.7$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.1$, 61.4, 65.4, 70.3, 72.8, 85.5, 109.8, 110.6, 125.8, 131.8, 153.9, 196.1.

MS (FAB): m/z (%) = 357 [M^+].

Anal. Calcd for $C_{21}H_{19}FeNO$: C, 70.61; H, 5.36; N, 3.92. Found: C, 70.68; H, 5.31; N, 3.96.

5.9 3-Ferrocenyl-1-(2-methylphenyl)prop-2-yn-1-one (3i)

Orange–red solid; Mp 81–83 °C. IR (KBr): 2178 (C≡C), 1629 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.67$ (s, 3 H), 4.28 (s, 5 H), 4.40 (s, 2 H), 4.63 (s, 2 H), 7.26–7.28 (t, $J = 6.9$ Hz, $J = 7.8$ Hz, 1 H), 7.33–7.38 (t, $J = 7.5$ Hz, $J = 7.8$ Hz, 1 H), 7.43–7.48 (t, $J = 6.9$ Hz, $J = 7.8$ Hz, 1 H), 8.03–8.06 (d, $J = 7.5$ Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.9$, 60.6, 70.4, 70.6, 73.0, 87.0, 95.1, 125.8, 132.1, 132.5, 132.7, 136.1, 140.1, 179.5.

MS (FAB): m/z (%) = 328 [M^+].

Anal. Calcd for $C_{20}H_{16}FeO$: C, 73.19; H, 4.91. Found: C, 73.22; H, 4.97.

5.10 3-Ferrocenyl-1-(2-nitrophenyl)prop-2-yn-1-one (3j)

Orange–red solid; Mp 101–102 °C. IR (KBr): 2207 (C≡C), 1606 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.30$ (d, $J = 1.2$ Hz, 5 H), 4.33 (s, 2 H), 4.56–4.57 (d, $J = 1.8$ Hz, 2 H), 7.38–7.44 (t, $J = 7.8$ Hz, 1 H), 7.52–7.57 (t, $J = 7.5$ Hz, 1 H), 7.64–7.66 (d, $J = 7.5$ Hz, 1 H), 8.03–8.06 (d, $J = 7.8$ Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 63.8$, 69.5, 70.2, 71.8, 81.2, 97.6, 119.4, 124.6, 127.7, 132.7, 134.4, 149.4, 175.7.

MS (FAB): m/z (%) = 359 [M^+].

Anal. Calcd for $C_{19}H_{13}FeNO_3$: C, 63.54; H, 3.65; N, 3.90. Found: C, 63.61; H, 3.71; N, 3.94.

5.11 3-Ferrocenyl-1-[4-(diethylamino)phenyl]prop-2-yn-1-one (3k)

Orange–red solid; Mp 142–144 °C. IR (KBr): 2184 (C≡C), 1616 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J = 6.9$ Hz, 3 H), 3.24–3.26 (m, $J = 6.9$ Hz, 2 H), 4.26 (s, 5 H), 4.36 (s, 2 H), 4.63 (s, 2 H), 6.57–6.60 (d, $J = 8.1$ Hz, 2H), 8.02–8.04 (d, $J = 8.1$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$, 37.8, 61.2, 70.3, 72.8, 85.4, 93.8, 111.2, 126.7, 132.1, 152.9, 175.9.

MS (FAB): m/z (%) = 385 [M^+].

Anal. Calcd for $C_{23}H_{23}FeNO$: C, 71.70; H, 6.02; N, 3.64. Found: C, 71.77; H, 6.08; N, 3.69.

5.12 3-Ferrocenyl-1-(2-aminophenyl)prop-2-yn-1-one (3 1)

Orange–red solid; Mp 124–126 °C. IR (KBr): 2183 (C≡C), 1619 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.28$ (s, 5 H), 4.38 (s, 2 H), 4.66 (s, 2 H), 6.37 (s, 2 H), 6.65–6.68 (d, $J = 8.7$ Hz, 1 H), 6.71–6.76 (t, $J = 7.2$ Hz, $J = 7.5$ Hz, 1 H), 7.26–7.33 (q, $J = 7.5$ Hz, $J = 8.7$ Hz, 1 H), 8.11–8.14 (d, $J = 7.2$ Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.9$, 70.3, 70.4, 72.8, 85.3, 95.0, 116.0, 116.7, 119.0, 134.3, 134.9, 150.9, 179.3.

MS (FAB): m/z (%) = 329 [M^+].

Anal. Calcd for $C_{19}H_{15}FeNO$: C, 69.33; H, 4.59; N, 4.26. Found: C, 69.24; H, 4.53; N, 4.27.

5.13 3-Ferrocenyl-1-(2-amino-5-methylphenyl)prop-2-yn-1-one (3m)

Orange–red solid; Mp 113–115 °C. IR (KBr): 2196 (C≡C), 1629 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.32$ (s, 3 H), 4.28 (s, 5 H), 4.38 (s, 2 H), 4.66 (s, 2 H), 6.23 (s, 2 H), 6.58–6.61 (d, $J = 8.4$ Hz, 1 H), 7.13–7.15 (t, $J = 8.4$ Hz, 1 H), 7.90 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.4$, 61.0, 70.3, 75.7, 84.6, 94.7, 116.8, 118.8, 124.9, 133.6, 136.2, 148.9, 179.2.

MS (FAB): m/z (%) = 343 [M^+].

Anal. Calcd for $C_{20}H_{17}FeNO$: C, 69.99; H, 4.99; N, 4.08. Found: C, 69.94; H, 4.93; N, 4.12.

5.14 3-Ferrocenyl-1-[4-(methylamino)phenyl]prop-2-yn-1-one (3n)

Orange–red solid; Mp 123–124 °C. IR (KBr): 2195 (C≡C), 1617 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.92$ (s, 3 H), 4.27 (s, 5 H), 4.37 (s, 2 H), 4.56 (s, 1 H), 4.64 (s, 2 H), 6.59–6.62 (d, $J = 8.7$ Hz, 2 H), 8.03–8.07 (d, $J = 8.7$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 30.0$, 61.2, 70.3, 72.8, 85.4, 93.8, 111.0, 126.8, 132.0, 153.8, 176.0

MS (FAB): m/z (%) = 343 [M^+].

Anal. Calcd for $C_{20}H_{17}FeNO$: C, 69.99; H, 4.99; N, 4.08. Found: C, 69.91; H, 4.91; N, 4.14.

5.15 3-Ferrocenyl-1-(4-chlorophenyl)prop-2-yn-1-one (3o)

Orange–red solid; Mp 123–125 °C. IR (KBr): 2181 (C≡C), 1624 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.28$ (s, 5 H), 4.40 (s, 2 H), 4.68 (s, 2 H), 7.47–7.50 (d, $J = 8.4$ Hz, 2 H), 8.10–8.12 (d, $J = 8.4$ Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.0$, 70.5, 70.9, 73.2, 85.3, 97.4, 128.9, 130.7, 135.6, 140.2, 176.2.

MS (FAB): m/z (%) = 348 [M^+].

Anal. Calcd for $C_{19}H_{13}ClFeO$: C, 65.46; H, 3.76. Found: C, 65.54; H, 3.71.

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