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Ru^{III}-catalyzed double-conjugate 1,4-addition of indoles to symmetric enones

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Abstract

Double-conjugate 1,4-addition of indoles to dibenzylidenacetones using Ru^{III} as catalyst is reported. It was found that the system involving Ru^{III} catalyzes formation of two C–C bonds in one pot in good to high yields.

Keywords: Ruthenium; Indole; Symmetric enones; Michael addition

1. Introduction

The investigation of the chemistry of indoles has been, and continues to be, one of the most active areas of heterocyclic chemistry [1,2]. Various indole derivatives occur in many pharmacologically and biologically active compounds [3]. In particular, β-indolylketones have received much attention as important building blocks for the synthesis of many natural products and other biologically active compounds [4]. Over the past few years, many synthetic methods for preparation of these compounds have been reported [5–22]. Many of these procedures involved strong acidic conditions, expensive reagents, long reaction times, low yields of products and complex handling. However, relatively less attention has been paid to the double-conjugate 1,4-addition of indoles to symmetric enones leading to di(indol-3-yl) derivatives. On the other hand, Ru^{III} salts are well known to catalyze a variety of organic transformations, including aldol and Michael reactions [23–26], oxidation reactions of alkanes [27], oxidative cyanation of amines [28] and many others [29]. We found that ruthenium(III) chloride hydrate smoothly catalyzes the reaction of indoles and dibenzylidenacetones leading to two C–C bonds in one pot, affording the desired adducts in high yields (Scheme 1).

2. Results and discussion

Typical results of the ruthenium catalyzed double Michael addition of indoles to (1*E*,4*E*)-1,5-disubstituted-1,4-dien-3-ones are shown in Table 1. Treatment of indole (1 mmol) with dibenzylidenacetone (0.5 mmol) in the presence of $RuCl_3{\cdot}nH_2O$ catalyst (5 mol%) in methanol (2 mL) under reflux conditions for 180 min. gave the corresponding 1,5-di(3-indolyl)-1,5-diphenyl-pentan-3-one in 77% yield as a diastereomeric mixture (dr = 55:45). In the 500 MHz ^1H NMR spectra, the C_2–H and also NH protons of indole substituents showed two distinct signals with 1.1:0.9 integral ratio. The reaction seems to occur via a classic Friedel–Crafts alkylation pathway. The NH proton of indole does not play a significant role in the turnover of the catalytic cycle (entries 4 and 5). In the addition of 1-methylindole to dibenzylidenacetone, the reaction furnished an excellent yield with the same diastereoselectivity of 55:45 (entry 4) in a rather short time (monitored by TLC). This may be due to the fact that the product is insoluble in the reaction solvent. In this case, after cooling the reaction mixture to ambient temperature, the white solid precipitate was filtered, washed with methanol, dissolved in dry THF and then purified by using preparative TLC (10:3 petroleum ether:ethylacetate), which provided the desired product. With regard to the indole moiety, substituted and unsubstituted indoles can be utilized in the optimized procedure (Table 1). The present protocol is also tolerant toward the solvent system. In the case of entries 3 and 5, due to solubility problems, a 1:1 mixture of methanol and THF was selected,

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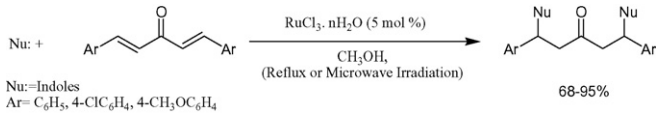
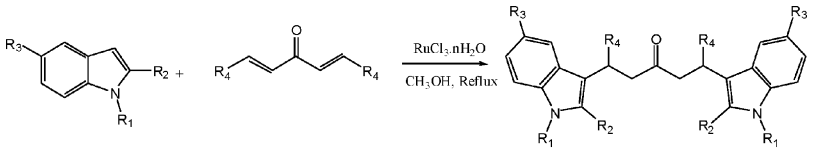


Scheme 1.

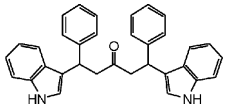
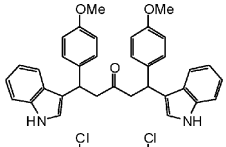
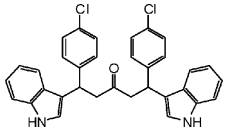
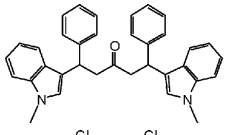
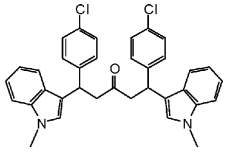
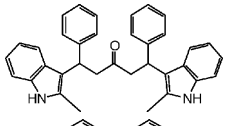
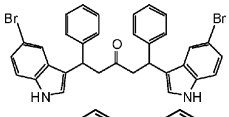
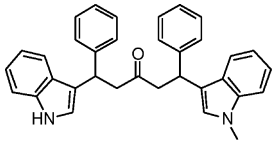
furnishing the desired products in good yields (dr = 62:38 and 50:50, respectively). In contrast to the previous reported methods for conjugate addition of indoles to simple α,β-unsaturated ketones, the catalytic system using Ru^{III} has the advantage of using methanol instead of non-environment-friendly solvents such as acetonitrile, chlorinated solvents and toluene [4,5,7]. Sequential conjugate addition of different indole moieties in one-pot furnished product **3aba** in 55% isolated yield (dr = 60:40, entry 8).

Table 1
Ru^{III}-catalyzed double Michael addition of indoles to symmetric enones



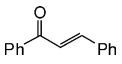
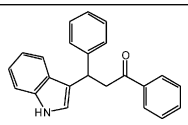
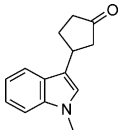
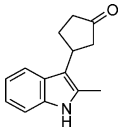
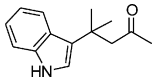
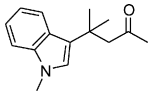
1a: R_1=R_2=R_3= H
1b: R_1=Me, R_2=R_3= H
1c: R_1=R_3= H, R_2=Me
1d: R_1= R_2= H, R_3=Br

2a: R_4= C_6H_5
2b: R_4= 4-$MeOC_6H_4$
2c: R_4= 4-ClC_6H_4

Entry[a]	Indole	Enone	Product	Time (min)	Yield[b] (%)
1	**1a**	**2a**	 **3aa**	180	77
2	**1a**	**2b**	 **3ab**	180	80
3	**1a**	**2c**	 **3ac**	180	68[c]
4	**1b**	**2a**	 **3ba**	15	95
5	**1b**	**2c**	 **3bc**	180	73[c,d]
6	**1c**	**2a**	 **3ca**	120	80[e]
7	**1d**	**2a**	 **3da**	120	71
8	**1a**, **1b**	**2a**	 **3aba**	180	55

[a] All products were characterized by ^{1}H NMR, ^{13}C NMR and IR data.
[b] Isolated yields.
[c] Methanol:THF (1:1) as solvent system.
[d] In addition to the main product, single adduct **3′bc** was also obtained in 19.5% yield.
[e] Identified by comparison with authentic samples [5].

Table 2
Ru^{III}-catalyzed Michael addition of indoles to α,β-unsaturated compounds

Entry[a]	Indole	Enone	Product	Time (min)	Yield[b] (%)
1	**1a**			180	80[c]
2	**1b**			10	75[c]
3	**1c**			15	85[c]
4	**1a**			60	80
5	**1b**			60	85

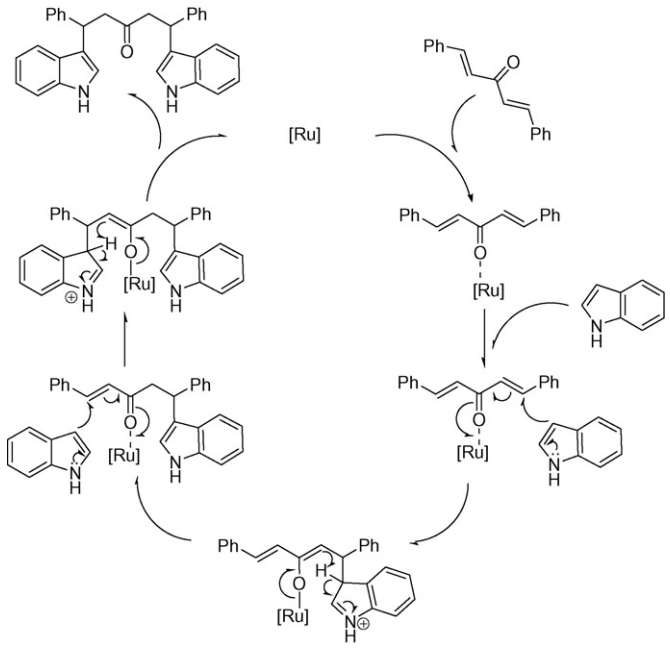
[a] All products were characterized by ^{1}H NMR, ^{13}C NMR and IR data.
[b] Isolated yields.
[c] Identified by comparison with authentic samples [5].

The catalytic activity toward simple α,β-unsaturated ketones led to acceptable yields (Table 2). It is noteworthy that reaction of different indoles with isomeric mixtures of mesityloxide (4-methylpent-3-en-2-one) and 4-methylpent-4-en-2-one selectively furnished 1,4-addition to α,β-unsaturated isomer and provided the desired product class (entries 4 and 5).

A proposed mechanistic pathway for the reaction of indole with dibenzylidenacetone conducted in the presence of Ru^{III} is presented in Scheme 2.

Encouraged by these results, we decided to overcome the problem of somehow prolonged reaction times using microwave irradiation. A mixture of indole (1 mmol), dibenzylidenacetone (0.5 mmol) and 5 mol% of catalyst was dissolved in the minimum amount of methanol required and irradiated in a 450 W microwave oven in an open vessel at 50 °C for 5 min until the disappearance of the starting enone was confirmed by TLC. The crude mixture was purified by preparative TLC (10:4, petroleum ether:ethyl acetate) and provided **3aa** in 75% yield. The results are summarized in Table 3.

These results reveal the potential application of microwave irradiation in promotion of the catalyzed reaction. Generally, the products are limited to Michael adducts without formation of *N*-alkylation products. This result provided a remarkable contrast to similar reactions under palladium catalysis, where *N*-alkylation was predominant [30]. In contrast to the reflux method, higher conversions of the starting enone was obtained; however, the yield of desired double-conjugate adduct decreased in some cases (entries 1 and 2) along with the formation of single adducts as side products.



Scheme 2. Proposed mechanism for the Ru^{III}-catalyzed double-conjugate 1,4-addition.

Table 3
Ru^{III}-catalyzed double Michael addition of indoles to symmetric enones under microwave irradiation

Entry[a]	Indole	Enone	Product	Yield[b] (%)	Time (min)
1	**1a**	**2a**	**3aa**	75	5
2	**1a**	**2c**	**3ac**	65[c]	10
3	**1c**	**2a**	**3ca**	80.1[d]	3
4	**1d**	**2a**	**3da**	77	3
5	**1b**	**2a**	**3ba**	95	3

[a] All products were characterized by ^{1}H NMR, ^{13}C NMR and IR data.
[b] Isolated yields.
[c] Methanol:THF (1:1) as solvent system.
[d] Identified by comparison with authentic samples [5].

3. Conclusion

We have developed a convenient method for the double-conjugate 1,4-addition of indoles to symmetric enones. To the best of our knowledge this is the first report on the double Michael additions using Ru^{III} as catalyst. The advantages of the present protocol are ease of work up and little waste. However, diastereoselectivity toward one diastereoisomer remains a challenging object. This may be achieved using chiral ruthenium complexes. Further works in this context is currently underway in our laboratory.

4. Experimental

4.1. General

IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. ^{1}H NMR spectra were obtained on a Bruker DRX-500 Avance spectrometer and ^{13}C NMR spectra were obtained on a Bruker DRX-125 Avance spectrometer. Chemical shifts of ^{1}H

and ^{13}C NMR spectra were expressed in ppm downfield from tetramethylsilane. Melting points were measured on a Büchi Melting Point B-540 instrument and are uncorrected. Elemental analyses were made by a Carlo-Erba EA1110 CNNO-S analyzer and agreed with the calculated values.

4.2. Materials

HPLC grade methanol was used as solvent, dibenzylidenacetones were synthesized by using the reported procedure [31] and all other materials were purchased from Merck and used without further purification.

4.3. Ruthenium catalyzed double Michael addition of indoles to (1E,4E)-1,5-disubstituted-1,4-dien-3-ones

A 20 mL flask equipped with a magnetic stirring bar was charged with methanol (2 mL), dibenzylidenacetone (117.15 mg, 0.5 mmol), and indole (117.15 mg, 1 mmol). $RuCl_3{\cdot}nH_2O$ (5.35 mg, 0.025 mmol) was added into the flask and the reaction mixture was refluxed. After 3 h, the reaction mixture was purified by preparative TLC (petroleum ether:ethyl acetate = 10:4), providing a pure product (180.3 mg, 77%). The same procedure was also used for the other products listed in Table 1. For Table 3, irradiation in an open vessel in a 450 W microwave oven at 50 °C was conducted instead of refluxing.

4.3.1. 1,5-Di(3-indolyl)-1,5-diphenyl-pentan-3-one (**3aa**)

Solid, m.p. 74–76 °C, IR (KBr): υ (cm^{-1}): 580, 700, 742, 1010, 1097, 1336, 1417, 1456, 1492, 1704, 2887, 2921, 3026, 3056, 3413 (NH). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.11 (dd, J = 7.3, 16.4 Hz, 1H), 3.18 (dd, J = 7.4, 17 Hz, 2H), 3.27 (dd, J = 7.7, 16.4 Hz, 1H), 4.84 (t, J = 7.4 Hz, 2H), 6.72 (d, J = 1.7 Hz, 1H), 6.77 (d, J = 1.7 Hz, 1H), 7.04 (m, 2H), 7.16–7.41 (m, 16H), 7.86 (br, 1H, NH), 7.88 (br, 1H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 38.45, 38.51, 50.14, 50.30, 111.46, 111.51, 119.11, 119.18, 119.83, 119.85, 119.90, 119.95, 121.85, 122.00, 122.53, 126.63, 126.70, 126.93, 128.07, 128.20, 128.81, 128.88, 136.94, 136.98, 144.30, 144.50, 208.18, 208.30 ppm. Anal. calcd. for $C_{33}H_{28}N_2O$: C, 84.58; H, 6.02; N, 5.98; found: C, 84.63; H, 6.07; N, 6.00.

4.3.2. 1,5-Di(3-indolyl)-1,5-di(4-methoxyphenyl) pentan-3-one (**3ab**)

Solid, m.p. 107–109 °C, IR (KBr): υ (cm^{-1}): 547, 744, 756, 831, 921, 925, 989, 1033, 1072, 1097, 1174, 1249, 1423, 1454, 1512, 1598, 1720, 2887, 2954, 3062, 3404. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 3.08 (m, 4H), 3.73 (s, 6H), 4.73 (t, J = 7.5 Hz, 2H), 6.67–7.43 (m, 18H), 7.84 (br, 2H, NH) ppm. Anal. calcd. for $C_{35}H_{32}N_2O_3$: C, 79.52; H, 6.10; N, 5.30; found: C, 79.55; H, 6.12; N, 5.33.

4.3.3. 1,5-Di(4-chlorophenyl)-1,5-di(3-indolyl) pentan-3-one (**3ac**)

Solid, m.p. 87–89 °C, IR (KBr): υ (cm^{-1}): 474, 528, 580, 742, 765, 817, 1012, 1091, 1224, 1247, 1338, 1355, 1409, 1456, 1488, 1708, 2889, 2923, 3056, 3406 (NH). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.07 (dd, J = 7.9, 16.5 Hz, 1H), 3.11 (dd, J = 8.0, 16.7 Hz, 1H), 3.20 (dd, J = 6.9, 16.7 Hz, 1H), 3.23 (dd, J = 7.1, 16.5 Hz, 1H), 4.78–4.81 (m, 2H), 6.74 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 7.03–7.11 (m, 5H), 7.16–7.26 (m, 7H), 7.32–7.38 (m, 4H), 7.91 (br, 2H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 37.80, 37.84, 49.90, 50.10, 111.65, 111.69, 118.58, 118.61, 119.71, 120.03, 121.78, 121.93, 122.77, 126.68, 128.92, 128.99, 129.43, 129.57, 132.35, 132.38, 136.99, 142.71, 142.95, 207.61, 207.80 ppm. Anal. calcd. for $C_{33}H_{26}Cl_2N_2O$: C, 73.74; H, 4.88; N, 5.21; found: C, 73.81; H, 4.84; N, 5.25.

4.3.4. 1,5-Di(1-methyl-3-indolyl)-1,5-diphenyl-pentan-3-one (**3ba**)

Solid, m.p. 69–71 °C, IR (KBr): υ (cm^{-1}): 565, 700, 738, 1012, 1155, 1244, 1326, 1373, 1452, 1473, 1483, 1544, 1600, 1612, 1710, 2821, 2881, 2931, 3026, 3055. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.17 (dd, J = 7.7, 16.5 Hz, 1H), 3.22 (dd, J = 8.5, 15.9 Hz, 2H), 3.30 (dd, J = 7.4, 16.4 Hz, 1H), 3.69 (s, 3H), 3.71 (s, 3H), 4.89 (t, J = 7.5 Hz, 2H), 6.67 (s, 1H), 6.71 (s, 1H), 7.05–7.11 (m, 2H), 7.21–7.33 (m, 14 H), 7.41 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 33.09, 33.11, 38.55, 38.59, 50.31, 50.47, 109.70, 109.75, 117.75, 117.86, 119.39, 119.41, 120.03, 120.07, 122.19, 122.21, 126.68, 126.70, 126.79, 127.42, 127.45, 128.19, 128.25, 128.91, 128.98, 137.80, 144.61, 144.84, 208.23, 208.32 ppm. Anal. calcd. for $C_{35}H_{32}N_2O$: C, 84.64; H, 6.49; N, 5.64; found: C, 84.59; H, 6.52; N, 5.65.

4.3.5. 1,5-Di(4-chlorophenyl)-1,5-di (1-methyl-3-indolyl)pentan-3-one (**3bc**)

Solid, m.p. 95–97 °C, IR (KBr): υ (cm^{-1}): 522, 740, 817, 1012, 1089, 1328, 1373, 1407, 1475, 1488, 1544, 1714, 2881, 2929, 3049. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.08 (dd, J = 6.9, 8.4 Hz, 1H), 3.10 (dd, J = 8.1, 16.8 Hz, 1H), 3.19 (dd, J = 6.9, 17.3 Hz, 1H), 3.21 (dd, J = 6.9, 16.8 Hz, 1H), 3.70 (s, 3H), 3.71 (s, 3H), 4.79 (t, J = 7.4 Hz, 2H), 6.63 (s, 1H), 6.67 (s, 1H), 7.03–7.11 (m, 4H), 7.15–7.32 (m, 11H), 7.36 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 33.07, 37.77, 37.83, 49.93, 50.16, 109.72, 109.76, 117.13, 117.16, 119.46, 119.69, 119.79, 122.28, 122.31, 126.53, 126.62, 127.07, 128.87, 128.96, 129.42, 129.50, 132.27, 132.33, 137.73, 142.86, 143.13, 207.46, 207.63 ppm. Anal. calcd. for $C_{35}H_{30}Cl_2N_2O$: C, 74.33; H, 5.35; N, 4.95; found: C, 74.37; H, 5.37; N, 4.90.

4.3.6. (E)-1,5-Di(4-chlorophenyl)-5-(1-methyl-3-indolyl) pent-1-en-3-one (**3′bc**)

Solid, m.p. 188–190 °C, IR (KBr): υ (cm^{-1}): 524, 715, 746, 765, 819, 977, 1012, 1066, 1089, 1178, 1247, 1404, 1487, 1589, 1610, 1654, 1685, 2877, 2933, 3047. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.40 (dd, J = 8.1, 16.1 Hz, 1H), 3.53 (dd, J = 6.7, 16.1 Hz, 1H), 3.78 (s, 3H), 4.97 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 16.1 Hz, 1H), 6.89 (s, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.23–7.45 (m, 11H), 7.47 (d, J = 16.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 33.17, 38.23, 47.96, 109.77, 117.48, 119.46, 119.90, 122.31, 126.69, 126.82, 127.18, 128.99, 129.61, 129.65, 129.85, 132.41, 133.32, 136.88, 137.82, 141.77,

143.16, 198.44 ppm. Anal. calcd. for $C_{26}H_{21}Cl_2NO$: C, 71.89; H, 4.87; N, 3.22; found: C, 71.88; H, 4.89; N, 3.21.

*4.3.7. 1,5-Di(5-bromo-3-indolyl)-1,5-diphenyl-pentan-3-one (**3da**)*

Solid, m.p. 90–92 °C, IR (KBr): υ (cm^{-1}): 582, 700, 750, 796, 883, 1045, 1101, 1247, 1415, 1460, 1492, 1704, 2889, 2923, 3025, 3058, 3423 (NH). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.07–3.21 (m, 4H), 4.75 (dt, J = 3.1, 7.4 Hz, 2H), 6.70 (d, J = 2.1 Hz, 1H), 6.78 (d, J = 2.1 Hz, 1H), 7.16–7.32 (m, 14H), 7.48 (d, J = 1.2 Hz, 1H), 7.52 (d, J = 1.2 Hz, 1H), 7.92 (br, 1H, NH), 7.98 (br, 1H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 39.66, 39.71, 51.50, 51.70, 114.43, 114.50, 114.62, 120.13, 120.26, 123.78, 124.50, 124.66, 126.93, 128.34, 128.41, 129.39, 129.48, 130.07, 130.12, 130.43, 130.49, 136.96, 137.01, 145.18, 145.43, 209.29, 209.37 ppm. Anal. calcd. for $C_{33}H_{26}Br_2N_2O$: C, 63.28; H, 4.18; N, 4.47; found: C, 63.25; H, 4.20; N, 4.48.

*4.3.8. 1-(3-Indolyl)-5-(1-methyl-3-indolyl)-1,5-diphenyl-pentan-3-one (**3aba**)*

Solid, IR (KBr): υ (cm^{-1}): 426, 700, 736, 1012, 1043, 1095, 1155, 1244, 1330, 1371, 1419, 1454, 1473, 1544, 1600, 1708, 2883, 2931, 3026, 3056, 3409 (NH). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.11–3.30 (m, 4H), 3.65 (s, 1.2H, CH_3), 3.68 (s, 1.8H, CH_3), 4.87 (t, J = 7.5 Hz, 2H), 6.63 (s, 0.4H), 6.69 (s, 0.6H), 6.72 (d, J = 2.0 Hz, 0.4H), 6.76 (d, J = 2.0 Hz, 0.6H), 7.03–7.08 (m, 2H), 7.19–7.45 (m, 16H), 7.89 (br, 1H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 33.00, 33.03, 38.42, 38.47, 38.52, 38.58, 50.32, 50.38, 60.87, 109.59, 109.64, 111.53, 111.58, 117.65, 117.71, 119.06, 119.20, 119.30, 119.33, 119.84, 119.88, 120.02, 121.94, 121.97, 122.10, 122.54, 126.58, 126.62, 126.66, 126.69, 127.35, 128.08, 128.11, 128.17, 128.21, 128.82, 128.85, 136.97, 137.00, 137.71, 137.73, 144.52, 144.54, 208.26, 208.36 ppm. Anal. calcd. for $C_{34}H_{30}N_2O$: C, 84.61; H, 6.27; N, 5.80; found: C, 84.68; H, 6.30; N, 5.82.

4.3.9. 4-(3-Indolyl)-4-methylpentan-2-one

Yellow liquid, IR (liquid film): υ (cm^{-1}): 505, 584, 742, 765, 1012, 1101, 1244, 1336, 1357, 1417, 1458, 1618, 1695, 2869, 2927, 2964, 3055, 3415 (NH). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.62 (s, 6H, CH_3), 1.81 (s, 3H, CH_3), 3.03 (s, 2H), 6.94 (s, 1H), 7.15 (t, J = 7.1 Hz, 1H), 7.2 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.12 (br, 1H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 29.31, 30.45, 32.22, 55.60, 111.57, 119.05, 121.06, 121.70, 122.13, 125.85, 126.78, 137.58, 209.97 ppm. Anal. calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51; found: C, 78.05; H, 8.00; N, 6.51.

4.3.10. 4-Methyl-4-(1-methyl-3-indolyl)-pentan-2-one

Yellow liquid, IR (liquid film): υ (cm^{-1}): 572, 740, 760, 1018, 1107, 1153, 1238, 1328, 1359, 1465, 1483, 1544, 1614, 1703, 2877, 2929, 2962, 3051. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.60 (s, 6H, CH_3), 1.80 (s, 3H, CH_3), 3.00 (s, 2H), 3.79 (s, 3H, CH_3), 6.86 (s, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 29.38, 32.30, 33.07, 34.88, 55.63, 110.06, 119.06, 121.27, 121.72, 122.66, 125.85, 126.38, 138.27, 209.57 ppm. Anal. calcd. for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11; found: C, 78.50; H, 8.30; N, 6.09.

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