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$Rh_2(OAc)_4$ catalyzed substrate selective [4+2]/[2+2] cycloaddition of acylketenes: a highly chemo- and regioselective synthesis of spiro(oxindolyl)oxazinones and β-lactams

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ABSTRACT

A rhodium(II) catalyzed [4+2]/[2+2] cycloaddition reaction of *N*-protected isatin-3-arylimine with acylketene derived from α-diazocarbonyl compounds has been achieved for the first time for the preparation of a novel class of spiro(oxindolyl)oxazinone and spiro(oxindolyl)-β-lactam derivatives.

The transition metal catalyzed cycloaddition reactions have received significant interest in organic synthesis especially for the construction of carbocycles and heterocycles.[1] In particular, the ketene cycloaddition is one of the most popular methods for the synthesis of four-membered ring systems.[2,3] Ketenes are known to undergo preferentially [2+2] cycloaddition with unsaturated systems to give the four-membered ring compounds. However, the reactivity of acylketene is quite different from a simple ketene as it behaves exclusively as 1,3-oxadiene in inverse demand hetero-Diels–Alder reaction with a ketone or an aldehyde to give the 1,3-dioxinone derivatives.[4] Recently, microwave-assisted cycloaddition of aldimines with acylketenes, generated in situ from cyclic 2-diazo-1,3-diketone via the Wolff rearrangement has been reported. However, the scope of this method is limited to cyclic diazodiketones.[5] Though, aldehydes and aldimines have been successfully utilized in trapping acylketenes, the ketimines are notoriously absent.

The spirooxindoles,[6] oxazinones[7] and β-lactams[8] and related heterocycles are important components of many natural products and medicinally relevant compounds (Fig. 1).

The oxindole appended spirooxazinone or β-lactam may be attractive class of compounds in medicinal chemistry, since the concept of hybrid drugs is gaining popularity in medicine. In view of the relevance of such spirocyclic moiety and the difficulty of its synthesis necessitates the development of a novel and convenient strategy.

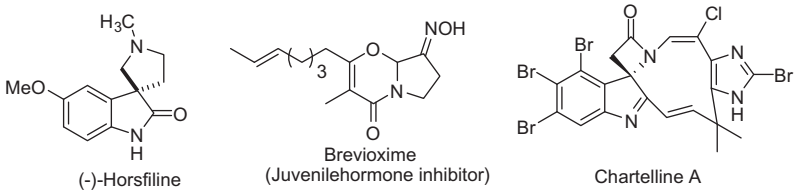

Figure 1. Representative examples of spirooxindole, oxazinones and spiro-β-lactam containing natural products.

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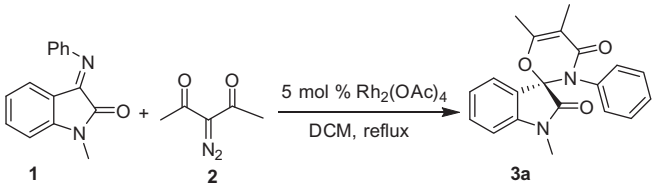


Scheme 1. Formation of spiro(oxindolyl)oxazinone **3a**.

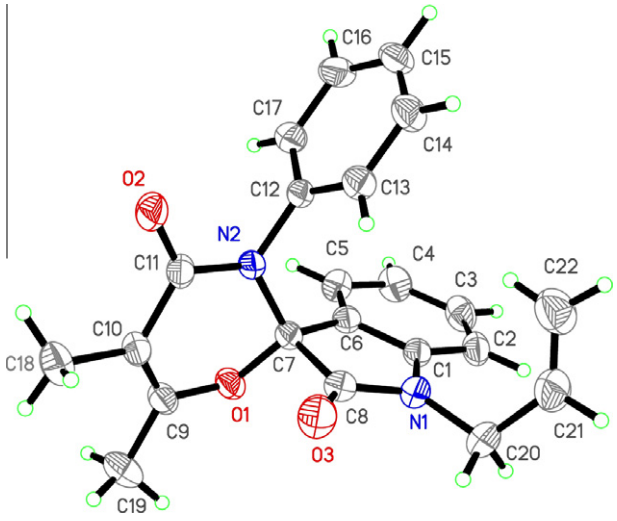
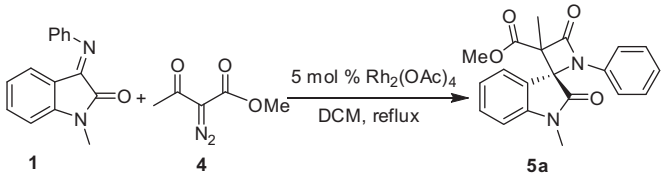


Figure 2. Crystal structure of compound **3e**.



Scheme 2. Formation of spiro(oxindolyl)-β-lactam **5a**.

Herein, we wish to report a rhodium(II) catalyzed [4+2] cycloaddition of *N*-protected isatin-3-arylimine with 2-diazoacetylacetone. This protocol is extended to explore the acylketene for a rare [2+2] cycloaddition. Initially, we attempted the cycloaddition of *N*-methylisatin-3-phenylimine and 2-diazoacetylacetone as model reaction using rhodium(II) acetate (5 mol %) as a catalyst. The reaction proceeded through a [4+2] cycloaddition to give the spiro(oxindolyl)oxazinone in 79% yield (Scheme 1).[9]

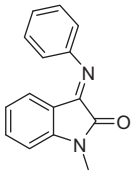
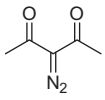
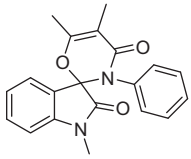
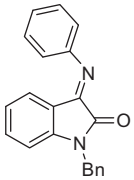
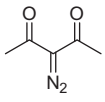
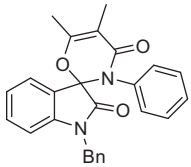
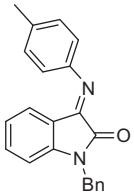
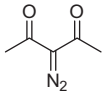
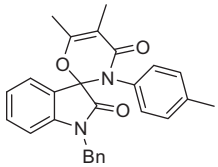
The structure of **3a**, was established by various spectroscopic methods such as NMR, IR and mass spectrometry. The characteristic absorption bands at 1728 and 1674 cm^{-1} correspond to amide carbonyls in IR spectroscopy and the chemical shifts at δ 164.1 and 170.0 (amide carbonyls) in ^{13}C NMR spectroscopy provided the required evidences for the proposed structure. Further evidence for the proposed structure comes from HRMS. To confirm the structure of spiro(oxindolyl)oxazinone, derivative **3e** was selected as a representative example and was characterized by X-ray crystallography (CCDC 837878, Fig. 2).

Upon screening of various solvents to find out the best choice, it was found that the reaction proceeds effectively in aprotic solvents like dichloromethane and benzene. There seems to be no difference between these solvents as they are equally effective in terms of conversion. A catalytic loading of 5 mol % was found to be optimal as reaction progressed well when compared to either higher (10 mol %) or lower (2 mol %) catalyst loading. Next, we extended our study to investigate the substrate scope and limitations. Thus various isatin-3-arylimines treated with 2-diazoacetylacetone for its efficiency under optimized conditions. Interestingly, a high level of chemoselectivity was achieved with *N*-allylisatinimine. No evidence for a possible cyclobutanone formation was observed from *N*-allylisatinimine.[3]

We next attempted the cycloaddition of isatin-3-arylimine with other diazo compounds such as diazoketoesters. To our surprise, a four-membered β-lactam was formed when isatin-3-arylimine reacts with diazoketoester.

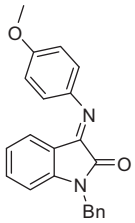
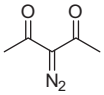
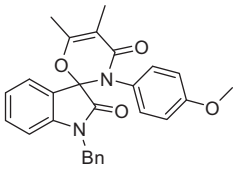
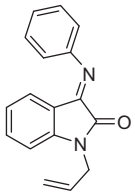
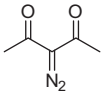
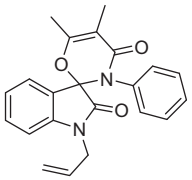
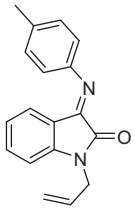
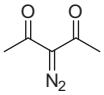
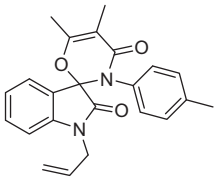
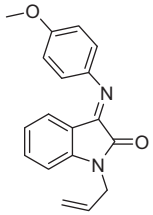
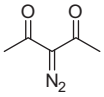
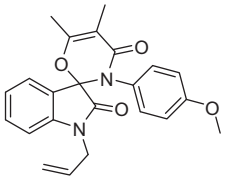
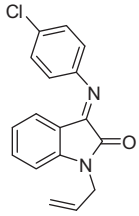
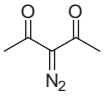
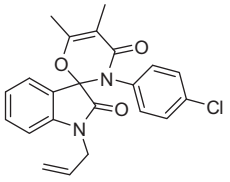
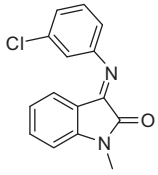
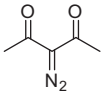
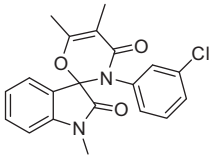
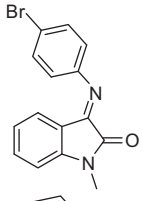
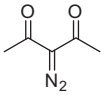
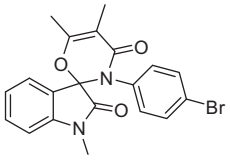
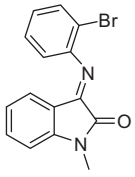
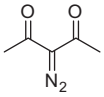
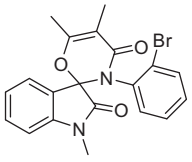
We assume that acylketene generated from 2-diazoalkylacetoacetate undergoes a rare [2+2] cycloaddition to produce the spiro(oxindolyl)-β-lactam **5a** (Scheme 2, Table 2).

Table 1
[4+2] Cycloaddition between isatin-3-arylimines and 2-diazo-1,3-diketones[a]

Entry	Imine (**1**)	Diazo (**2**)	Product (**3**)[b]	Time (min)	Yield[c] (%)
a				30	79
b				30	83
c				30	83

(*continued on next page*)

Table 1 (*continued*)

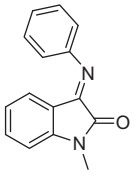
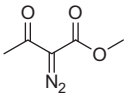
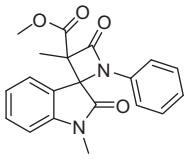
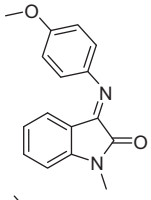
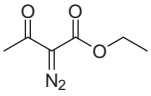
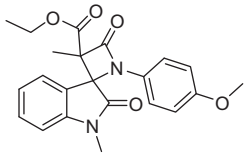
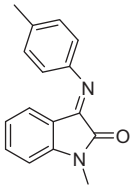
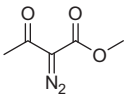
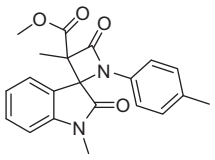
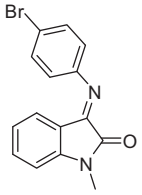
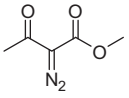
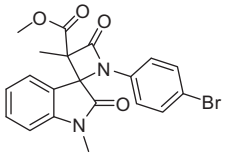
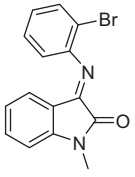
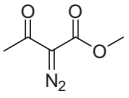
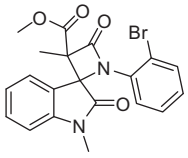
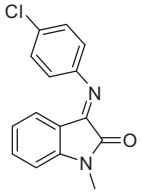
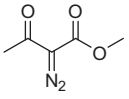
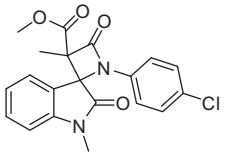
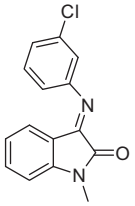
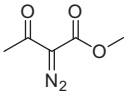
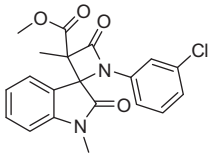
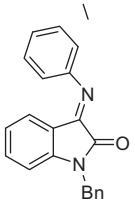
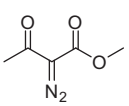
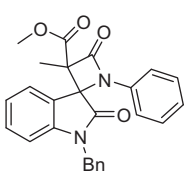
Entry	Imine (**1**)	Diazo (**2**)	Product (**3**)[b]	Time (min)	Yield[c] (%)
d				30	84
e				30	81
f				30	83
g				30	82
h				30	84
i				30	78
j				30	84
k				30	70

[a] The reactions were carried out under reflux conditions for 30 min.
[b] All products were characterized by ^{1}H & ^{13}C NMR, IR spectroscopy.
[c] Yield refers to pure products after chromatography.

The structure of **5a** was established by spectroscopic methods such as ^{13}C NMR, IR and mass spectrometry. The structure of β-lactam was characterized by infrared spectral data in which the characteristic amide absorption peaks were identified at 1767 and 1722 cm^{-1}. Further support for the formation of β-lactam comes from the ^{13}C NMR spectrum in which the characteristic carbonyl peaks were appeared at δ 163.2, 170.1, and 172.0.

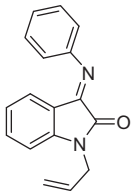
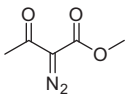
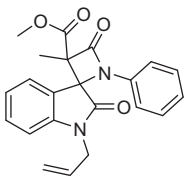
The product selectivity in both 2-diazo-1,3-diketones and 2-diazo alkylacetoacetate are found to be excellent. No formation of possible side products such as spiro(oxindolyl)aziridine or

Table 2
[2+2] Cycloaddition between isatin-3-arylimines and alkyl diazoacetoacetates[a]

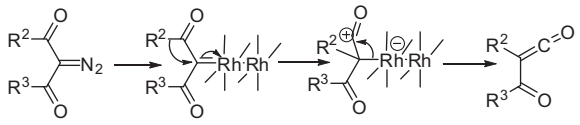
Entry	Imine (**1**)	Diazoketoester (**4**)	Product (**5**)[b]	Time (min)	Yield[c] (%)
a				30	78
b				30	80
c				30	82
d				30	84
e				30	68
f				30	80
g				30	72
h				30	78

(*continued on next page*)

Table 2 (*continued*)

Entry	Imine (**1**)	Diazoketoester (**4**)	Product (**5**)[b]	Time (min)	Yield[c] (%)
i				30	78

[a] The reactions were carried out under reflux conditions for 30 min.
[b] All products were characterized by ^{1}H & ^{13}C NMR, IR spectroscopy.
[c] Yield refers to pure products after chromatography.



Scheme 3. A plausible mechanism of ketene generation through rhodium carbenoid.

spiro(oxindolyl)oxazoline was observed in both reaction pathways. The formation of ketene intermediate from 2-diazo-1,3-diketone and its monoester counterpart is shown in Scheme 3.

Mechanistically, the acylketene is generated from the rhodium carbenoid through a Wolf rearrangement.

Thus formed acylketene may undergo either [4+2] or [2+2] cycloaddition depending on the diazodicarbonyl compound used. The reaction between 2-diazo-1,3-diketone and isatin-3-arylimine afforded the spiro(oxindolyl)oxazinone via [4+2] cycloaddition whereas 2-diazoalkylacetoacetate (alkyl = methyl and ethyl) gave the spiro(oxindolyl)-β-lactam through [2+2] cycloaddition (Scheme 4). The regioselectivity of the reaction depends on the nature of acylketene intermediate. The exclusive formation of two different products from different diazo compounds may be explained on the basis of reactivity as depicted in Scheme 4. The difference in reactivity may be explained by the presence of tautomerism in acylketene derived from 2-diazo-1,3-diketone, which is lacking in acylketene generated from 2-diazoketoester.

In conclusion, we have demonstrated the rhodium(II) acetate catalyzed cycloaddition of cyclic ketimines with acylketenes generated in situ from diazo compounds for the synthesis of a novel class of spiro(oxindolyl)oxazinone and spiro(oxindolyl)-β-lactam derivatives. The acylketene derived from 2-diazo-1,3-diketone was successfully trapped with N-protected isatin-3-arylimine to produce a six-membered spiro(oxindolyl)oxazinone through [4+2] cycloaddition. The spiro(oxindolyl)-β-lactam was formed by the [2+2] cycloaddition of isatin-3-arylimine with acylketene derived from 2-diazoalkylacetoacetate.

Acknowledgments

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References and notes

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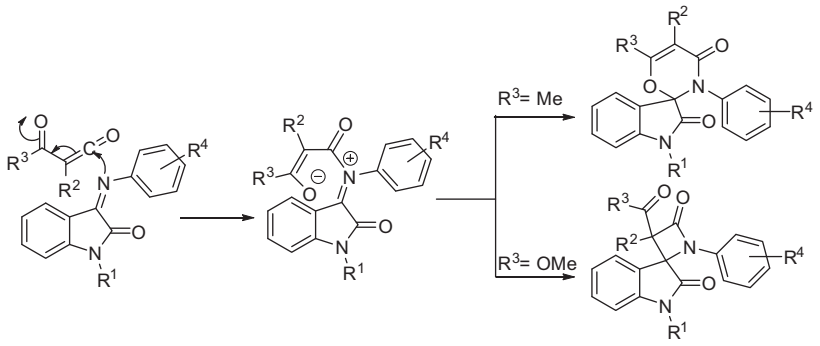

Scheme 4. A plausible mechanism for [4+2] and [2+2] cycloaddition.

8. (a) Palomo, C.; Aizpurua, J. M.; Ganboa, I.; Oiarbide, M. *Eur. J. Org. Chem.* **1999**, 3223; (b) Dürkheimer, W.; Blumbach, J.; Lattrell, R.; Scheunemann, K. H. *Angew. Chem., Int. Ed.* **1985**, *24*, 180; (c) Morin, R. B.; Gorman, M. In *Chemistry and Biology of β-Lactam Antibiotics*; Academic Press: New York, 1982; Vol. 123,; (d) Southgate, R; Branch, C.; Coulton, S.; Hunt, E. In *Recent Progress in the Chemical Synthesis of Antibiotics and Related Microbial Products*; Lukacs, G., Ed.; Springer-Verlag: Berlin, 1993; Vol. 2, p 621.

9. General procedure: A mixture of isatin-3-arylimine (1 mmol) and rhodium(II) acetate (5 mol %) was stirred in dry dichloromethane (10 mL). A solution of diazo compound (1.2 mmol) in dry dichloromethane (2 mL) was added drop wise over 15 min. The resulting mixture was stirred under reflux for a specified time (Table 1). After completion, as indicated by TLC, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel using *n*-hexanes/EtOAc (8/2) as eluent to afford the product **3**. In case of β-lactam synthesis, the product was eluted with *n*-hexanes/EtOAc (3/1). All the products were characterized by IR, NMR and mass spectral data.

The spectral data of the selected products: *1,5′,6′-trimethyl-3′-phenylspiro[indoline-3,2′-[1,3]oxazine]-2,4′(3′H)-dione* (***3a***): Colourless solid, mp 189–192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 3H), 2.03 (s, 3H), 3.04 (s, 3H), 6.73 (d, J = 8.0 Hz, 1H), 6.94 (m, 2H), 7.17 (m, 3H), 7.35 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.3, 17.5, 26.2, 89.5, 105.1, 109.0, 123.5, 125.0, 125.8, 128.0, 128.9, 128.9, 131.7, 136.8, 142.9, 158.7, 164.1, 170.0; IR (KBr): ν_{max} 2932, 1728, 1674, 1610, 1471, 1392, 1347, 1245, 1178, 1086, 762, 692 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{19}N_2O_3$ [M+H]: 335.1395, found: 336.1388.

1-Benzyl-5′,6′-dimethyl-3′-phenylspiro[indoline-3,2′-[1,3]oxazine]-2,4′(3′H)-dione (***3b***): Colourless solid, mp 179–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H), 2.07 (s, 3H), 4.45 (d, J = 16.0 Hz, 1H), 5.05 (d, J = 16.0 Hz, 1H), 6.59 (m, 1H), 6.80 (m, 2H), 7.00 (m, 1H), 7.28 (m, 7H), 7.65 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.3, 17.6, 43.8, 89.7, 105.1, 110.2, 123.6, 124.8, 126.2, 126.9, 127.6, 128.2, 128.77, 129.17, 129.7, 131.7, 134.4, 136.5, 142.0, 158.9, 164.0, 169.8; IR (KBr): ν_{max} 2926, 1724, 1666, 1608, 1462, 1396, 1356, 1288, 1182, 744, 692 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{23}N_2O_3$ [M+H]: 411.1708, found: 411.1727.

1-Allyl-5′,6′-dimethyl-3′-(p-tolyl)spiro[indoline-3,2′-[1,3]oxazine]-2,4′(3′H)-dione (***3f***): Colourless solid, mp 131–133 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (s, 3H), 2.02 (s, 3H), 2.23 (s, 3H), 3.97 (dd, J = 5.1, 11.3 Hz, 1H), 4.31 (dd, J = 4.7, 11.8 Hz, 1H), 4.78 (d, J = 17.1 Hz, 1H), 5.04 (d, J = 10.3 Hz, 1H), 5.52 (m, 1H), 6.52 (d, J = 7.7 Hz, 1H), 6.78 (m, 2H), 6.98 (m, 3H), 7.24 (m, 1H), 7.55 (d, J = 7.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.3, 17.5, 21.0, 42.1, 89.6, 105.0, 109.9, 117.4, 123.4, 124.9, 126.1, 129.2, 129.6, 130.0, 131.6, 133.8, 138.0, 142.1, 158.7, 164.01, 169.7; IR (KBr): ν_{max} 2919, 1742, 1659, 1607, 1469, 1394, 1355, 1270, 1186, 1120, 762 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_3$ [M+H]: 375.1708, found: 375.1723.

Methyl-1′,3-dimethyl-2′,4-dioxo-1-(p-tolyl)spiro[azetidine-2,3′-indoline]-3-carboxylate (***5c***): Colourless solid, mp 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H), 2.24 (s, 3H), 3.35 (s, 3H), 3.60 (s, 3H), 7.01 (m, 6H), 7.26 (m, 1H), 7.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 20.8, 26.9, 52.3, 66.8, 68.9, 109.1, 117.1, 122.2, 123.0, 124.1, 129.7, 131.1, 133.2, 134.5, 143.7, 162.9, 168.8, 171.6; IR (KBr): ν_{max} 2978, 2936, 1767, 1722, 1613, 1513, 1465, 1390, 1249, 1135, 1087, 1023, 826, 759 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_2O_4Na$: 387.1320, found: 387.1317.

Methyl-1′-allyl-3-methyl-2′,4-dioxo-1-phenylspiro[azetidine-2,3′-indoline]-3-carboxylate (***5e***): Colourless solid, mp 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (s, 3H), 3.59 (s, 3H), 4.35 (dd, J = 4.0, 12.0 Hz, 1H), 4.57 (dd, J = 4.0, 12.0 Hz, 1H), 5.27 (m, 2H), 5.89 (m, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.09 (m, 4H), 7.26 (m, 3H), 7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 45.6, 52.4, 66.8, 69.0, 110.0, 117.1, 117.9, 122.1, 122.9, 124.1, 124.7, 129.2, 130.6, 131.0, 136.2, 142.8, 163.1, 168.6, 171.2; IR (KBr): ν_{max} 2930, 1768, 1731, 1605, 1499, 1380, 1277, 1188, 1137, 946, 751, 687 cm^{-1}; HRMS(ESI) calcd for $C_{22}H_{20}N_2O_4Na$: 399.1320, found: 399.1338.

Methyl-1′-allyl-3-methyl-2′,4-dioxo-1-(p-tolyl)spiro[azetidine-2,3′-indoline]-3-carboxylate (***5f***): Colourless solid, mp 130–133 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71 (s, 3H), 2.23 (s, 3H), 3.56 (s, 3H), 4.32 (dd, J = 4.9, 11.5 Hz, 1H), 4.53 (dd, J = 5.1, 11.3 Hz, 1H), 5.27 (m, 2H), 5.88 (m, 1H), 6.88 (m, 3H), 6.99 (m, 3H), 7.23 (m, 1H), 7.34 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 20.8, 42.7, 52.4, 66.8, 68.9, 110.0, 117.1, 117.9, 122.2, 122.9, 124.0, 129.6, 130.6, 131.0, 133.7, 134.5, 142.8, 162.9, 168.7, 171.3; IR (KBr): ν_{max} 2929, 1769, 1728, 1611, 1515, 1377, 1275, 1175, 1133, 754, 701 cm^{-1}; HRMS(ESI) calcd for $C_{23}H_{22}N_2O_4Na$: 413.1477, found: 413.1497.