JOC The Journal of Organic Chemistry

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Selective Synthesis of Functionalized Spiro[indoline-3,2′-pyridines] and Spiro[indoline-3,4′-pyridines] by Lewis Acid Catalyzed Reactions of Acetylenedicarboxylate, Arylamines, and Isatins

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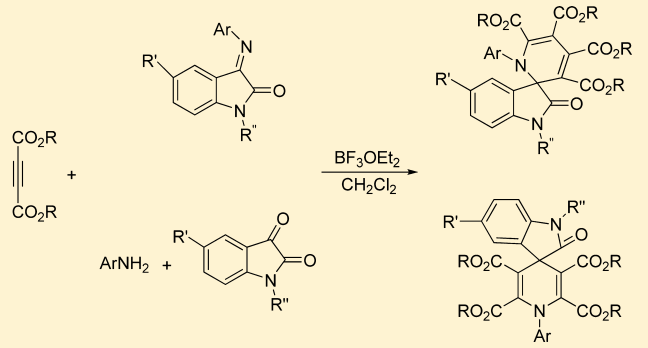
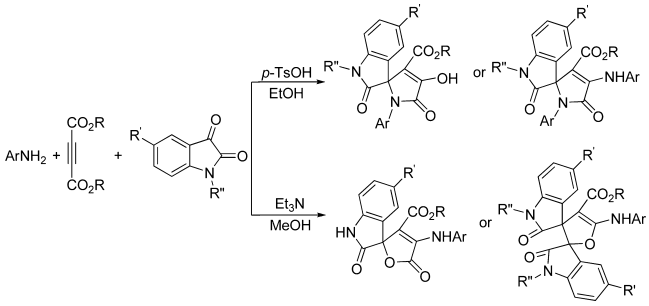
Supporting Information

ABSTRACT: The functionalized spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylates were efficiently synthesized by BF_3·OEt_2-catalyzed reactions of isatin-3-imines with acetylenedicarboxylates in methylene dichloride. Under similar conditions, the BF_3·OEt_2-catalyzed three-component reactions of acetylenedicarboxylates, arylamines, and isatins afforded functionalized spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylates in moderate yields.



In the past decades, multicomponent reactions have attracted particular attention because of their high efficiency in the construction of complex molecular framework in a single step from readily available reagents.[1] Compared to traditional stepwise reactions, multicomponent reactions not only have the advantages of atom economy, simpler procedures, lower costs, and high variability but also are often accompanied by significant increases in molecular diversity and impressive selectivity.[2] Thus, the development of new multicomponent reactions is one of the hottest research topics in organic synthetic chemistry.[3,4] In recent years, Huisgen 1,4-dipoles, which can be easily generated from the addition reaction of nitrogen heterocycles or amines to electron-deficient alkynes,[5] has been widely recognized as key component for design versatile multicomponent reactions for developing efficient synthetic procedures for many nitrogen-containing heterocyclic systems.[6−12] Practically, the three-component reaction of arylamine, isatin, and acetylenedicarboxylate showed very interesting molecular diversity. In the presence of *p*-toluenesulfonic acid as the catalyst or in the admicellar catalytic system, the three-component reaction afforded 3′-hydroxy- or 3′-*N*-arylaminospiro[indoline-3,5′-pyrrolines].[13,14] On the other hand, the three-component reaction resulted in the functionalized spirolactones and dispirodihydrofuranyl oxindoles when triethylamine was used as base catalyst (Scheme 1).[15] Very recently, we reported that the three-component reaction of acetylenedicarboxylates, arylamines, and aromatic aldehydes resulted in the polysubstituted 1,4-dihydropyridines in the acidic system.[16] We envisioned that the spiro[indoline-pyridine] derivatives could also be formed when isatin was used to replace aromatic aldehyde in above three-component reactions. In continuation of our efforts to explore the practical

Scheme 1. Synthesis of Various Spirooxindoles via Three-Component Reaction



applications of Huisgen 1,4-dipoles in multicomponent reactions, herein we report the selective synthesis of functionalized spiro[indoline-3,2′-pyridines] and spiro[indoline-3,4′-pyridines] by Lewis acid catalyzed reactions of acetylenedicarboxylate, arylamines, and isatins.

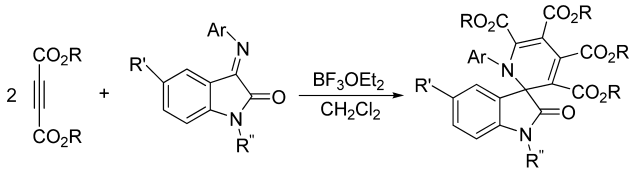
At first, the reaction of isatin-3-imine with dimethyl acetylenedicarboxylate was investigated. An equivalomolecular isatin-3-imine and dimethyl acetylenedicarboxylate in methylene dichloride in the presence of BF_3·OEt_2 was stirred at elevated temperature for 7 h. After workup, the expected spiro[indoline-3,2′-quinoline] was not obtained, which might be formed from the imine-Diels−Alder reaction.[17] Instead, spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate **1a** was obtained in 48% yield, in which two moieties of acetylenedicarboxylate to take part in to form the skeleton of 1,4-

Received: January 20, 2014
Published: April 2, 2014

   dx.doi.org/10.1021/jo500144z | J. Org. Chem. 2014, 79, 4131−4136

dihydropyridine. When 2 equiv of acetylenedicarboxylate was used, **1a** was obtained in 65% yield (Table 1, entry 1). The

Table 1. Synthesis of Spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylates[a]



1a-1r

entry	compd	R	R′	R″	Ar	yield[b] (%)
1	**1a**	CH_3	CH_3	H	*p*-$CH_3CH_2OC_6H_4$	65
2	**1b**	CH_3	CH_3	H	*p*-$(CH_3)_2CHC_6H_4$	66
3	**1c**	CH_3	CH_3	H	*p*-$(CH_3)_3CC_6H_4$	62
4	**1d**	CH_3	Cl	H	*p*-$(CH_3)_3CC_6H_4$	60
5	**1e**	CH_3	H	Bn	*p*-$CH_3C_6H_4$	63
6	**1f**	CH_3	H	Bn	*p*-$(CH_3)_3CC_6H_4$	66
7	**1g**	CH_3	H	Bn	*p*-BrC_6H_4	60
8	**1h**	CH_3	CH_3	Bn	C_6H_5	70
9	**1i**	CH_3	CH_3	Bn	*p*-$CH_3C_6H_4$	63
10	**1j**	CH_3	CH_3	Bn	*p*-$CH_3OC_6H_4$	62
11	**1k**	CH_3	CH_3	Bn	*p*-$(CH_3)_3CC_6H_4$	68
12	**1l**	CH_3	CH_3	Bn	*p*-BrC_6H_4	58
13	**1m**	CH_3	CH_3	n-C_4H_9	*p*-$CH_3C_6H_4$	61
14	**1n**	CH_3	Cl	Bn	*p*-$CH_3C_6H_4$	65
15	**1o**	CH_3	Cl	Bn	*p*-$(CH_3)_3CC_6H_4$	60
16	**1p**	CH_3	Cl	Bn	*p*-ClC_6H_4	50
17	**1q**	CH_2CH_3	CH_3	Bn	C_6H_5	55
18	**1r**	CH_2CH_3	Cl	Bn	*p*-$CH_3C_6H_4$	72

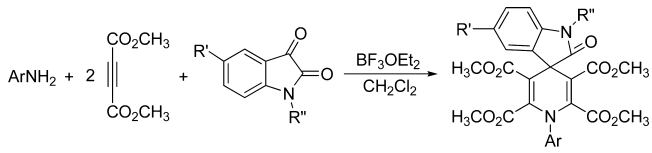
[a].Reaction conditions: acetylenedicarboxylate (2.0 mmol) and isatin-3-imine (1.0 mmol), $BF_3{\cdot}OEt_2$ (0.5 mmol) in CH_2Cl_2 (10.0 mL), reflux, 24 h. [b]Isolated yield.

yield of spiro compound **1a** could not be increased when excess dimethyl acetylenedicarboxylate was utilized in the reaction. Similarly, various isatin-3-imines were used in the reactions under the same conditions. The results are summarized in Table 1. Isatin itself and its 5-fluoro, 5-chloro, 5-methyl and 1-benzyl, 1-butyl derivatives showed similar reactivity and reacted efficiently to give the spiro products (Table 1, entries 1−16). It should be pointed out that arylamines with alkyl, alkoxy, and halo groups proceeded smoothly to afford the corresponding spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylates. Diethyl acetylenedicarboxylate also used in the reactions to give the corresponding tetraethyl spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylates **1q** and **1r** in good yields (Table 1, entries 17 and 18). The structures of the spiro[indoline-3,2′-pyridine]tetracarboxylates were characterized by ^1H and ^{13}C NMR, HRMS, and IR spectra. The structures of **1e** and **1k** were further confirmed by single-crystal X-ray diffraction method (Figures s1 and s2, Supporting Information).

A tentative mechanistic rationale portraying the probable sequence of events is briefly given in Scheme 2 on the basis of the previous reported reactions of electron-deficient alkynes with aldimines.[18] The first step is the addition of isatin-3-imine to the triple bond of acetylenedicarboxylate gives one 1,4-dipolar intermediate (**A**) under the catalysis of $BF_3{\cdot}OEt_2$. Second, the 1,4-dipolar intermediate (**A**) can react with second acetylenedicarboxylate to give a double addition intermediate (**B**). Third, the intramolecular coupling of the negative charge with the positive charge affords the spiro[indoline-3,2′-pyridine] **1** as the final product.

In the light of the operational simplicity and mild conditions of our spiro[indoline-3,2′-pyridine] synthesis, we intended to expand the above-described protocol to a three-component reaction. Thus, a mixture of arylamines, isatins, and two molecular dimethyl acetylenedicarboxylates in methylene dichloride in the presence of $BF_3{\cdot}OEt_2$ was refluxed for about 1 day. We were pleased to find that the isomeric spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylates **2a−e** were obtained in moderate yields (Table 2). The structures of the spiro-

Table 2. Synthesis of Spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylates[a]



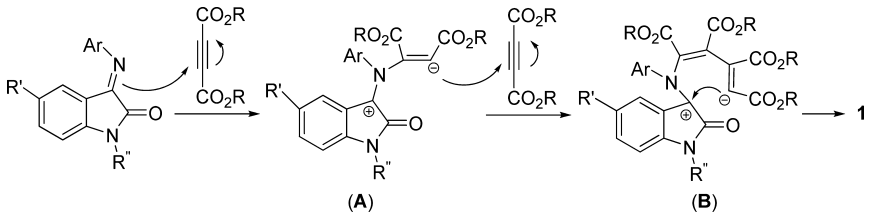
2a-2e

entry	compd	R	R′	R″	yield[b] (%)
1	**2a**	*p*-$CH_3C_6H_4$	H	H	45
2	**2b**	*p*-$CH_3OC_6H_4$	H	H	55
3	**2c**	*p*-$CH_3CH_2OC_6H_4$	H	H	55
4	**2d**	C_6H_5	CH_3	Bn	48
5	**2e**	*p*-$CH_3OC_6H_4$	CH_3	Bn	53

[a].Reaction condition: acetylenedicarboxylate (2.0 mmol), isatin (1.0 mmol), arylamine (1.0 mmol), $BF_3{\cdot}OEt_2$ (0.5 mmol) in CH_2Cl_2 (10.0 mL), reflux, 24 h. [b]Isolated yield.

[indoline-3,4′-pyridine] were established with the spectroscopic methods and confirmed by X-ray determination of single crystal **2b** (Figure s3, Supporting Information). Because there is no direct connection between the moieties of arylamine and oxindoles, it can be concluded that the isatin-3-imine did not form in this reaction and this three-component reaction must proceed with other reaction mechanisms.

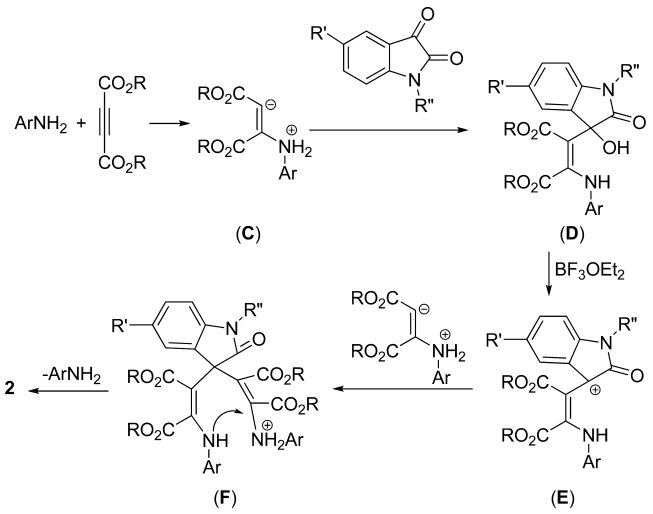
Scheme 2. Formation Mechanism of Spiro[indoline-3,2′-pyridine] 1



dx.doi.org/10.1021/jo500144z | J. Org. Chem. 2014, 79, 4131−4136

In order to explain the formation mechanism of spiro[indoline-3,4′-pyridine] **2**, a rational domino reaction mechanism is proposed in Scheme 3 based on the reported similar

Scheme 3. Formation Mechanism of Spiro[indoline-3,4′-pyridine] 2



reactions of electron-deficient alkynes with arylamines and aromatic aldehydes.[16,19,20] First, the addition of arylamine to acetylenedicarboxylate gives the expected 1,3-dipolar *β*-enamino ester (**C**). Then the nucleophilic addition of intermediate (**C**) to the 3-carbonyl group of isatin affords the intermediate (**D**). Third, in the presence of stronger Lewis acid $BF_3{\cdot}OEt_2$, the intermediate (**D**) was dehydrated to give a carbocation intermediate (**E**), which in turn reacts with second molecular *β*-enamino ester (**C**) to give the intermediate (**F**). Finally, the intermediate (**F**) transforms to spiro[indoline-3,4′-pyridine] **2** by splitting out of one arylamino group. The last step has been described in the similar formation of 1,4-dihydropyridine derivatives by $TiCl_4$-catalyzed trimerization of *β*-enamino ester and $Sc(OTf)_3$-catalyzed reaction of methyl propiolate with aromatic aldimines.[19,20]

In summary, we have found that the isomeric spiro[indoline-3,2′-pyridines] and spiro[indoline-3,4′-pyridines] can be selectively and efficiently prepared by the Lewis acid catalyzed reactions of acetylenedicarboxylates with isatin-3-imines and three-component reactions of acetylenedicarboxylates with isatin and arylamines. The rational formation mechanism for the two isomeric spirooxindoles was briefly discussed. This reaction has the advantages of the readily variable substrates, short reaction time, and easiness of handling. The potential uses of this reaction in synthetic and medicinal chemistry might be quite significant.

EXPERIMENTAL SECTION

1. General Procedure for the Preparation of Spiro[indoline-3,2′-pyridine]tetracarboxylates 1a−r from Reactions of Dimethyl Acetylenedicarboxylate with Isatin-3-imines. To a stirred solution of acetylenedicarboxylate (2.0 mmol) and isatin-3-imine (1.0 mmol) in methylene dichloride (10.0 mL) was added $BF_3{\cdot}OEt_2$ (0.5 mmol) at room temperature. Then the mixture was refluxed for about 1 day. The solvent was removed by evaporation, and the residue was subjected to preparative thin-layer chromatography (25 × 15 cm SiO_2 plate) with a mixture of light petroleum and ethyl acetate (V/V = 2:1) as developing reagent to give the pure products **1a−r** for analysis.

*Tetramethyl 1′-(4-ethoxyphenyl)-5-methyl-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1a**):* yellow solid, 0.366 g, 65%; mp 248−250 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.27 (s, 1H), 7.32 (s, 1H), 7.12−7.07 (m, 2H), 6.87 (d, J = 7.2 Hz, 1H), 6.60−6.55 (m, 2H), 6.20 (d, J = 7.2 Hz, 1H), 3.93 (d, J = 7.2 Hz, 2H), 3.76 (s, 3H), 3.60 (s, 3H), 3.43 (s, 3H), 3.32 (s, 3H), 2.31 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.4, 166.4, 162.9(2C), 161.9, 158.9, 152.4, 138.5, 138.4, 131.9, 131.7, 131.6, 131.0, 130.8, 128.8, 124.7, 113.7, 113.5, 111.9, 109.9, 93.8, 70.0, 63.3, 52.6, 52.3, 52.0, 51.8, 20.6, 14.4; IR (KBr) ν 3312, 2954, 1742, 1610, 1500, 1435, 1353, 1307, 1247, 1013, 837, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_2NaO_{10}$ ([M + Na]$^+$) 587.1636, found 587.1636.

*Tetramethyl 1′-(4-isopropylphenyl)-5-methyl-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1b**):* yellow solid, 0.371 g, 66%, mp 230−232 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.32 (s, 1H), 7.24−7.22 (m, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.09−7.07 (m, 1H), 6.97−6.96 (m, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.25−6.23 (m, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 3.43 (s, 3H), 3.25 (s, 3H), 2.84−2.79 (m, 1H), 2.31 (s, 3H), 1.12−1.10 (m, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.3, 166.4, 162.9(2C), 161.9, 152.2, 150.2, 138.3, 138.2, 134.2, 132.0, 131.8, 130.8, 130.0, 129.5, 126.2, 125.8, 124.6, 112.1, 110.0, 94.2, 69.7, 52.4, 52.3, 52.0, 51.9, 32.9, 23.5, 23.4, 20.6; IR (KBr) ν 3299, 2956, 1746, 1606, 1499, 1438, 1350, 1305, 1234, 1009, 826, 776 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{30}N_2NaO_9$ ([M + Na]) 585.1844, found 585.1850.

*Tetramethyl 1′-(4-tert-butylphenyl)-5-methyl-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1c**):* yellow solid, 0.357 g, 62%; mp 248−250 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.31 (s, 1H), 7.39−7.37 (m, 1H), 7.33 (s, 1H), 7.13−7.08 (m, 3H), 6.58 (d, J = 7.8 Hz, 1H), 6.26−6.24 (m, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 3.44 (s, 3H), 3.23 (s, 3H), 2.31 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.3, 166.4, 162.9(2C), 161.9, 152.5, 152.2, 138.3, 138.2, 134.0, 132.0, 131.8, 130.8, 129.8, 129.1, 125.3, 124.7, 124.6, 112.1, 110.0, 94.3, 69.7, 52.4, 52.3, 52.0, 51.9, 34.4, 30.8, 20.6; IR (KBr) ν 3289, 2958, 1745, 1711, 1677, 1604, 1498, 1438, 1352, 1306, 1240, 1160, 1127, 1013, 966, 855, 825, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{32}N_2NaO_9$ ([M + Na]$^+$) 599.2000, found 599.2000.

*Tetramethyl 1′-(4-tert-butylphenyl)-5-chloro-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1d**):* yellow solid, 0.358 g, 60%, mp >250 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.61 (s, 1H), 7.54 (s, 1H), 7.40−7.38 (m, 2H), 7.17 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 3.77(s, 3H), 3.61 (s, 3H), 3.46 (s, 3H), 3.25 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.0, 166.1, 162.8, 162.7, 161.8, 152.7, 152.0, 139.9, 138.6, 133.9, 132.2, 131.5, 129.7, 129.1, 126.4, 125.5, 124.9, 124.2, 111.8, 111.7, 94.8, 69.5, 52.5, 52.4, 52.2, 51.9, 34.5, 30.8; IR (KBr) ν 3268, 2957, 1749, 1710, 1678, 1606, 1502, 1438, 1354, 1309, 1240, 1146, 1048, 1014, 965, 887, 856, 827, 781 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{29}ClN_2NaO_9$ ([M + Na]$^+$) 619.1454, found 619.1460.

*Tetramethyl 1-benzyl-1′-(4-methylphenyl)-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1e**):* yellow solid, 0.384 g, 63%; mp 172−174 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.63 (s, 1H), 7.32 (s, 1H), 7.21−7.16 (m, 5H), 7.07 (s, 1H), 6.85 (s, 1H), 6.76 (s, 2H), 6.70 (s, 1H), 6.18 (s, 1H), 4.72 (d, J = 15.0 Hz, 1H), 4.45 (d, J = 15.0 Hz, 1H), 3.77(s, 3H), 3.62 (s, 3H), 3.37 (s, 3H), 3.30 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.1, 166.2, 162.8, 161.7, 152.4, 141.5, 139.8, 138.6, 135.1, 133.7, 131.5, 130.0, 129.8, 129.6, 129.4, 128.7, 128.2, 127.3, 127.1, 124.5, 123.8, 112.0, 109.7, 94.4, 69.4, 52.6, 52.4, 52.1, 51.9, 43.4, 20.8; IR (KBr) ν 3005, 2953, 1743, 1702, 1608, 1501, 1440, 1356, 1311, 1247, 1199, 1139, 1022, 995, 953, 904, 848, 815, 761 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{30}N_2NaO_9$ ([M + Na]$^+$) 633.1844, found 633.1859.

*Tetramethyl 1-benzyl-1′-(4-tert-butylphenyl)-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1f**):* yellow solid, 0.430 g, 66%; mp 90−92 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.63 (d, J = 3.6 Hz, 1H), 7.36 (d, J = 4.8 Hz, 1H), 7.20−7.17 (m, 4H), 7.11 (d, J = 4.8 Hz, 2H), 6.88 (s, 2H), 6.67 (d, J = 4.8 Hz, 1H),

dx.doi.org/10.1021/jo500144z | J. Org. Chem. 2014, 79, 4131−4136

6.27 (d, J = 4.8 Hz, 1H), 4.67 (d, J = 15.6 Hz, 1H), 4.44 (d, J = 15.6 Hz, 1H), 3.77(s, 3H), 3.61 (s, 3H), 3.36 (s, 3H), 3.24 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.1, 166.2, 162.8, 161.8, 152.7, 152.4, 141.5, 138.5, 135.2, 133.8, 131.5, 129.8, 129.4, 128.3, 127.3, 127.1, 125.6, 124.8, 124.4, 123.8, 112.1, 109.8, 94.5, 69.2, 52.4(2C), 52.1, 51.9, 43.6, 34.5, 30.8; IR (KBr) ν 2955, 1744, 1609, 1504, 1436, 1348, 1311, 1234, 1138, 1015, 958, 829, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{37}H_{36}N_2NaO_9$ ([M + Na]$^+$) 675.2313, found 675.2296.

*Tetramethyl 1-benzyl-1′-(4-bromophenyl)-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1g**):* yellow solid, 0.403 g, 60%; mp 182−184 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.43−7.42 (m, 1H), 7.30−7.28 (m, 1H), 7.25−7.22 (m, 4H), 7.13 (t, J = 7.8 Hz, 1H), 7.07−7.06 (m, 1H), 6.69 (d, J = 7.2 Hz, 2H), 6.51 (d, J = 7.8 Hz, 1H), 6.19−6.17 (m, 1H), 4.86 (d, J = 16.2 Hz, 1H), 4.27 (d, J = 16.2 Hz, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.50 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 167.0, 163.6, 163.3, 162.4, 152.2, 141.6, 139.4, 135.9, 134.8, 133.0, 132.2, 132.1, 131.5, 131.4, 130.3, 128.7, 127.7, 127.1, 125.1, 124.3, 124.0, 112.3, 109.2, 95.7, 69.9, 52.6, 52.5, 52.3, 52.1, 44.5; IR (KBr) ν 3029, 2951, 2845, 1740, 1704, 1605, 1513, 1483, 1436, 1343, 1299, 1179, 1134, 1070, 1008, 954, 867, 823, 784 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{33}H_{27}BrN_2NaO_9$ ([M + Na]$^+$) 697.0792, found 697.0799.

*Tetramethyl 1-benzyl-1′-phenyl-5-methyl-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1h**):* yellow solid, 0.427 g, 70%; mp 88−90 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.45−7.41 (m, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.2 Hz, 2H), 7.17−7.12 (m, 3H), 7.08 (d, J = 7.2 Hz, 1H), 6.66 (d, J = 7.2 Hz, 2H), 6.54 (d, J = 7.8 Hz, 1H), 6.32 (d, J = 7.8 Hz, 1H), 4.65 (d, J = 16.2 Hz, 1H), 4.40 (d, J = 16.2 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 3.36 (s, 3H), 3.28 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.0, 166.2, 162.9, 162.8, 161.7, 152.2, 139.2, 138.6, 136.2, 135.2, 133.1, 131.8, 130.3, 130.1, 130.0, 129.9, 128.9, 128.4, 128.3(2C), 127.2, 126.9, 124.8, 112.0, 109.6, 94.2, 69.5, 52.6, 52.4, 52.1, 52.0, 43.3, 20.6; IR (KBr) ν 3006, 2951, 2852, 1744, 1606, 1495, 1437, 1345, 1313, 1238, 1151, 999, 820, 769 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{30}N_2NaO_9$ ([M + Na]$^+$) 633.1844, found 633.1853.

*Tetramethyl 1-benzyl-1′-(4-methylphenyl)-5-methyl-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1i**):* yellow solid, 0.393 g, 63%; mp 182−184 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.30−7.28 (m, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.2 Hz, 2H), 7.09 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.67 (d, J = 7.2 Hz, 2H), 6.33 (d, J = 7.8 Hz, 1H), 6.23−6.21 (m, 1H), 4.76 (d, J = 15.6 Hz, 1H), 4.24 (d, J = 15.6 Hz, 1H), 3.89 (s, 3H), 3.71 (s, 3H), 3.48 (s, 3H), 3.37 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7, 167.4, 163.4, 162.7, 153.0, 139.9, 139.7, 139.3, 135.1, 134.3, 133.6, 131.6, 131.0, 130.8, 130.3, 129.4, 128.6, 127.3, 127.1, 125.7, 111.6, 109.1, 94.7, 70.2, 52.5, 52.2, 52.0, 44.4, 21.4, 21.1; IR (KBr) ν 3058, 2989, 2949, 1725, 1608, 1502, 1439, 1350, 1305, 1243, 1198, 1149, 1007, 963, 900, 813 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{35}H_{32}N_2NaO_9$ ([M + Na]$^+$) 647.2000, found 647.2004.

*Tetramethyl 1-benzyl-1′-(4-methoxyphenyl)-5-methyl-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1j**):* yellow solid, 0.397 g, 62%; mp 198−200 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.43 (s, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.14−7.11 (m, 4H), 6.89 (d, J = 7.2 Hz, 1H), 6.67 (d, J = 7.2 Hz, 2H), 6.61−6.56 (m, 2H), 6.19 (d, J = 7.2 Hz, 1H), 4.73 (d, J = 15.6 Hz, 1H), 4.39 (d, J = 15.6 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.62 (s, 3H), 3.38 (s, 3H), 3.32 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.1, 166.3, 162.8, 161.8, 160.0, 152.8, 139.2, 138.7, 135.2, 133.0, 131.8, 131.7, 131.3, 130.0, 128.7, 128.1, 127.2, 126.9, 124.7, 113.7, 111.7, 109.6, 93.9, 69.7, 55.3, 52.6, 52.3, 52.1, 51.9, 43.3, 20.6; IR (KBr) ν 3003, 2950, 2840, 1724, 1608, 1501, 1437, 1350, 1437, 1350, 1306, 1245, 1200, 1151, 1030, 1007, 961, 825 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{35}H_{32}N_2NaO_{10}$ ([M + Na]$^+$) 663.1949, found 663.1941.

*Tetramethyl 1-benzyl-1′-(4-tert-butylphenyl)-5-methyl-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1k**):* yellow solid, 0.453g, 68%; mp 164−166 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.43 (s, 1H), 7.36 (d, J = 4.8 Hz, 1H), 7.18 (s, 3H), 7.12 (s, 3H), 6.85 (s, 2H), 6.53 (d, J = 5.4 Hz, 1H), 6.28 (d, J = 4.8 Hz, 1H), 4.63 (d, J = 15.6 Hz, 1H), 4.38 (d, J = 15.6 Hz, 1H), 3.77(s, 3H), 3.61 (s, 3H), 3.35 (s, 3H), 3.23 (s, 3H), 2.32 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.2, 166.4, 162.9, 162.8, 161.8, 152.8, 152.4, 139.2, 138.6, 135.2, 133.7, 133.1, 131.8, 130.0, 129.9, 129.6, 128.3, 127.3, 126.9, 125.6, 124.8, 124.7, 111.9, 109.6, 94.1, 69.4, 52.4(2C), 52.2, 51.9, 43.6, 34.5, 30.8, 20.5; IR (KBr) ν 2956, 1744, 1701, 1602, 1500, 1436, 1344, 1309, 1238, 1201, 1152, 998, 955, 824 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{38}H_{38}N_2NaO_9$ ([M + Na]$^+$) 689.2470, found 689.2480.

*Tetramethyl 1-benzyl-1′-(4-bromophenyl)-5-methyl-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1l**):* yellow solid, 0.399 g, 58%; mp 220−222 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42−7.41 (m, 1H), 7.29−7.27 (m, 1H), 7.25−7.22 (m, 1H), 7.08−7.03 (m, 2H), 6.96 (d, J = 5.4 Hz, 2H), 6.40−6.39 (m, 1H), 6.20−6.19 (m, 1H), 4.81 (d, J = 15.6 Hz, 1H), 4.24 (d, J = 15.6 Hz, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.50 (s, 3H), 3.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 167.1, 163.6, 163.3, 162.5, 152.1, 139.4, 139.3, 135.9, 134.9, 133.8, 133.0, 132.2, 132.1, 131.8, 131.3, 130.4, 128.6, 127.6, 127.1, 125.7, 124.3, 112.3, 109.2, 95.6, 70.1, 52.6, 52.4, 52.2, 52.0, 44.5, 21.1; IR (KBr) ν 3057, 2990, 2946, 1727, 1609, 1523, 1491, 1438, 1408, 1350, 1243, 1198, 1151, 1074, 1008, 960, 898, 818 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{29}BrN_2NaO_9$ ([M + Na]$^+$) 711.0949, found 711.0953.

*Tetramethyl 1-n-butyl-1′-(4-methylphenyl)-5-methyl-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1m**):* yellow solid, 0.360 g, 61%; mp 156−158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 6.15 (d, J = 7.8 Hz, 1H), 3.88 (s, 3H), 3.70 (s, 3H), 3.50 (s, 3H), 3.45−3.40 (m, 1H), 3.37 (s, 3H), 3.08−3.03 (m, 1H), 2.38 (s, 3H), 2.24 (s, 3H), 1.06−0.98 (m, 3H), 0.88−0.85 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 167.4, 163.8, 163.4, 162.7, 152.9, 139.9, 139.8, 139.5, 134.2, 133.2, 131.6, 131.0, 129.9, 129.1, 128.3, 125.8, 111.4, 108.0, 94.6, 70.0, 52.4, 52.1, 51.9, 39.9, 29.0, 21.1, 20.1, 13.8; IR (KBr) ν 2953, 2872, 1718, 1602, 1501, 1437, 1337, 1209, 1155, 1108, 1010, 878, 823, 763 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{32}H_{34}N_2NaO_9$ ([M + Na]$^+$) 613.2157, found 613.2165.

*Tetramethyl 1-benzyl-1′-(4-methylphenyl)-5-chloro-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1n**):* yellow solid, 0.419 g, 65%; mp 190−192 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.8 Hz, 2H), 7.14 (t, J = 7.2 Hz, 2H), 7.10 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz, 2H), 6.36 (d, J = 8.4 Hz, 1H), 6.28 (d, J = 7.8 Hz, 1H), 4.79 (d, J = 15.6 Hz, 1H), 4.26 (d, J = 15.6 Hz, 1H), 3.89 (s, 3H), 3.71 (s, 3H), 3.52 (s, 3H), 3.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 167.0, 163.6, 163.3, 162.4, 152.9, 140.4, 140.2, 140.1, 134.5, 134.1, 132.0, 131.2, 131.0, 130.1, 129.6, 129.0, 128.8, 128.5, 127.5, 127.1, 125.4, 111.2, 110.5, 94.9, 70.0, 52.5(2C), 52.4, 52.1, 44.5, 21.4; IR (KBr) ν 3070, 3004, 2951, 2850, 1745, 1706, 1608, 1450, 1438, 1349, 1315, 1246, 1201, 1143, 1022, 995, 952, 883, 817, 787 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{29}ClN_2NaO_9$ ([M + Na]$^+$) 667.1454, found 667.1453.

*Tetramethyl 1-benzyl-1′-(4-tert-butylphenyl)-5-chloro-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1o**):* yellow solid, 0.412 g, 60%; mp 106−108 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.68 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.23−7.17 (m, 4H), 7.10 (d, J = 7.2 Hz, 1H), 6.88 (d, J = 7.2 Hz, 2H), 6.71 (d, J = 8.4 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 4.68 (d, J = 15.6 Hz, 1H), 4.46 (d, J = 15.6 Hz, 1H), 3.78(s, 3H), 3.62 (s, 3H), 3.38 (s, 3H), 3.25 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 166.9, 163.5, 163.3, 162.3, 153.4, 152.9, 140.5, 140.1, 134.7, 134.1, 132.2, 131.1, 130.9, 129.9, 129.0, 128.7, 127.6, 127.1, 125.8, 125.3, 124.7, 111.2, 110.6, 95.2, 70.0, 52.4, 52.3(2C), 52.0, 44.8, 34.8, 31.2; IR (KBr) ν 2955, 1746, 1701, 1608, 1504, 1435, 1344, 1312, 1234, 1141, 1018, 956, 878, 823, 787 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{37}H_{35}ClN_2NaO_9$ ([M + Na]$^+$) 709.1923, found 709.1909.

dx.doi.org/10.1021/jo500144z | J. Org. Chem. 2014, 79, 4131−4136

*Tetramethyl 1-benzyl-1′-(4-chlorophenyl)-5-chloro-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1p**):* yellow solid, 0.332 g, 50%; mp 146−148 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.29 (s, 1H), 7.23−7.22 (m, 4H), 6.96 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 4.2 Hz, 2H), 6.43 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 8.4 Hz, 1H), 4.84 (d, J = 15.6 Hz, 1H), 4.25 (d, J = 15.6 Hz, 1H), 3.89 (s, 3H), 3.72 (s, 3H), 3.54 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 166.8, 163.4, 163.2, 162.2, 152.2, 140.3, 139.8, 136.3, 135.1, 134.3, 132.8, 131.8, 131.6, 131.5, 129.4, 129.2, 128.7, 128.5, 127.8, 127.0, 125.4, 111.7, 110.6, 95.7, 69.9, 52.8, 52.6, 52.5, 52.2, 44.6; IR (KBr) ν 3005, 2952, 2849, 1744, 1701, 1606, 1513, 1484, 1435, 1348, 1297, 1246, 1138, 1092, 1014, 956, 888, 821, 787 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{33}H_{26}Cl_2N_2NaO_9$ ([M + Na]$^+$) 687.0909, found 687.0917.

*Tetraethyl 1-benzyl-1′-phenyl-5-methyl-2-oxo-1′H-spiro-[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1q**:).* yellow solid, 0.366 g, 55%; mp 64−66 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.31−7.28 (m, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.11 (t, J = 7.2 Hz, 2H), 7.00 (d, J = 7.8 Hz, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 7.8 Hz, 2H), 6.37 (d, J = 7.2 Hz, 1H), 6.29 (d, J = 8.4 Hz, 1H), 4.77 (d, J = 15.6 Hz, 1H), 4.38−4.31 (m, 2H), 4.24−4.16 (m, 3H), 4.07−4.01 (m, 1H), 3.95−3.90 (m, 1H), 3.82−3.74 (m, 2H), 2.36 (s, 3H), 1.38 (s, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.8, 166.7, 163.4, 163.1, 162.2, 152.3, 139.6, 137.1, 135.1, 133.4, 131.7, 131.4, 131.0(2C), 129.6, 128.7, 128.5, 127.9, 127.3, 127.0, 125.8, 112.2, 109.0, 95.3, 70.4, 61.9, 61.4, 61.1, 60.7, 44.4, 21.1, 14.0, 13.9, 13.7, 13.3; IR (KBr) ν 2983, 1739, 1606 1495, 1410, 1372, 1334, 1303, 1232, 1195, 1026, 857, 806, 769 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{38}H_{38}N_2NaO_9$ ([M + Na]$^+$) 689.2470, found 689.2477.

*Tetraethyl 1-benzyl-1′-(4-methylphenyl)-5-chloro-2-oxo-1′H-spiro[indoline-3,2′-pyridine]-3′,4′,5′,6′-tetracarboxylate (**1r**):* yellow solid, 0.503 g, 72%; mp 80−82 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.31−7.29 (m, 1H), 7.20−7.17 (m, 2H), 7.13 (t, J = 7.2 Hz, 2H), 7.08 (d, J = 8.4 Hz, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.61 (d, J = 7.2 Hz, 2H), 6.33 (d, J = 8.4 Hz, 1H), 6.30−6.29 (m, 1H), 4.85 (d, J = 16.2 Hz, 1H), 4.37−4.30 (m, 2H), 4.24−4.16 (m, 3H), 4.08−4.03 (m, 1H), 3.98−3.93 (m, 1H), 3.83−3.77 (m, 2H), 2.31 (s, 3H), 1.38 (s, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6, 166.4, 163.2, 163.0, 161.9, 152.5, 140.5, 140.1, 140.0, 134.6, 134.3, 132.4, 131.3, 131.0, 130.5, 129.4, 128.8, 128.6, 128.4, 127.5, 127.1, 125.5, 111.5, 110.3, 95.3, 70.2, 62.0, 61.5, 61.3, 60.8, 44.6, 21.3, 14.0, 13.9, 13.7, 13.3; IR (KBr) ν 2983, 1741, 1701, 1607, 1502, 1410, 1372, 1334, 1303, 1229, 1192, 1140, 1025, 859, 815, 785 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{38}H_{37}ClN_2NaO_9$ ([M + Na]$^+$) 723.2080, found 723.2078.

2. General Procedure for the Preparation of Spiro[indoline-3,4′-pyridine]tetracarboxylates 2a−e from One-Pot Reactions of Arylamine, Dimethyl Acetylenedicarboxylate, and Isatins. To a stirred solution of arylamine (1.0 mmol), dimethyl acetylenedicarboxylate (2.0 mmol), and isatin (1.0 mmol) in methylene dichloride (10.0 mL), BF_3·OEt_2 (0.5 mmol) was added at room temperature. Then the mixture was refluxed for about 1 day. Then the solvent was removed by evaporation and the residue was subjected to preparative thin-layer chromatography (25 × 15 cm SiO_2 plate) with a mixture of light petroleum and ethyl acetate (V/V = 1:1) as developing reagent to give the pure products **2a−e** for analysis.

*Tetramethyl 2-oxo-1′-(4-methylpheny)-1′H-spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylate (**2a**):* yellow solid, 0.234 g, 45%; mp 228−230 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.05 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 3.44 (s, 6H), 3.42 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.8, 164.5, 162.9, 143.2, 140.8, 140.3, 135.8, 134.4, 130.0, 129.5, 129.1, 124.8, 122.7, 108.8, 105.6, 52.5, 51.9, 50.2, 21.3; IR (KBr) ν 3204, 3094, 2952, 1752, 1718, 1617, 1582, 1507, 1472, 1439, 1328, 1291, 1234, 1195, 1149, 981, 861 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{24}N_2NaO_9$ ([M + Na]$^+$) 543.1374, found 543.1368.

*Tetramethyl 2-oxo-1′-(4-methoxyphenyl)-1′H-spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylate (**2b**):* yellow solid, 0.295 g, 55%; mp 243−245 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.46 (s, 1H), 7.29 (d, J = 9.0 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 9.0 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 3.79 (s, 3H), 3.39 (s, 6H), 3.35 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.9, 163.8, 162.3, 159.9, 142.4(2C), 135.3, 131.1, 129.1, 129.0, 123.8, 121.7, 114.1, 108.9, 106.3, 55.5, 52.6, 51.8, 49.6; IR (KBr) ν 3195, 3089, 3035, 2956, 2901, 2846, 1716, 1621, 1582, 1511, 1469, 1440, 1330, 1294, 1290, 1152, 1084, 1020, 986, 947, 900, 867, 833 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{24}N_2NaO_{10}$ ([M + Na]$^+$) 559.1323, found 559.1316.

*Tetramethyl 2-oxo-1′-(4-ethoxyphenyl)-1′H-spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylate (**2c**):* yellow solid, 0.303 g, 55%; mp 228−230 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.34−7.30 (m, 3H), 7.21 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.86−6.82 (m, 3H), 4.05−4.01 (m, 2H), 3.44 (s, 12H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.1, 164.5, 162.9, 159.8, 143.4, 141.1, 135.9, 131.7, 129.3, 129.0, 124.6, 122.5, 114.3, 109.0, 105.7, 63.8, 52.5, 51.8, 50.3, 14.6; IR (KBr) ν 3214, 3094, 3035, 2954, 2886, 2845, 1716, 1618, 1584, 1510, 1473, 1439, 1394, 1330, 1294, 1240, 1192, 1151, 1084, 1040, 986, 935, 900, 867, 834 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{28}H_{26}N_2NaO_{10}$ ([M + Na]$^+$) 573.1480, found 573.1493.

*Tetramethyl 1-benzyl-5-methyl-2-oxo-1′-phenyl-1′H-spiro-[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylate (**2d**):* yellow solid, 0.293 g, 48%; mp 86−88 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.41 (s, 2H), 7.35 (t, J = 7.2 Hz, 3H), 7.28(s, 1H), 7.15 (s, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 4.92 (s, 2H), 3.40 (s, 6H), 3.20 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 164.6, 163.0, 143.0, 141.2, 136.5, 135.3, 132.2, 130.4, 130.0, 129.2, 128.9, 128.7, 128.6, 128.5, 128.2, 127.6, 125.3, 114.1, 108.3, 107.6, 106.3, 52.5, 51.8, 49.8, 45.1, 21.1; IR (KBr) ν 3025, 2952, 1717, 1591, 1494, 1438, 1325, 1288, 1232, 1194, 1145, 1086, 982, 853, 814 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{30}N_2NaO_9$ ([M + Na]$^+$) 633.1844, found 633.1836.

*Tetramethyl 1-benzyl-5-methyl-2-oxo-1′-(4-methoxyphenyl)-1′H-spiro[indoline-3,4′-pyridine]-2′,3′,5′,6′-tetracarboxylate (**2e**:).* yellow solid, 0.340 g, 53%; mp 228−230 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 2H), 7.36−7.33 (m, 4H), 7.27 (d, J = 7.8 Hz, 1H), 7.13 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.86 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 7.8 Hz, 1H), 4.91 (s, 2H), 3.81 (s, 3H), 3.44 (s, 6H), 3.20 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 164.6, 163.1, 160.3, 143.4, 141.3, 136.6, 135.4, 132.1, 131.8, 129.7, 129.2, 128.6, 128.5, 127.6, 125.3, 113.9, 107.6, 106.2, 55.5, 52.5, 51.8, 49.8, 45.1, 21.1; IR (KBr) ν 3007, 2949, 2843, 1748, 1715, 1641, 1583, 1502, 1439, 1363, 1329, 1290, 1239, 1193, 1142, 1088, 1020, 982, 954, 898, 859, 801 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{35}H_{32}N_2NaO_{10}$ ([M + Na]$^+$) 663.1949, found 663.1938.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org/. Crystallographic data for **1e** (CCDC 979514), **1k** (CCDC 979515), and **2b** (CCDC 979516) been deposited at the Cambridge Crystallographic Database Centre. These data can be obtained free of charge via www.ccdc.ac.ck./data_request/cif.

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Notes

The authors declare no competing financial interest.

dx.doi.org/10.1021/jo500144z | J. Org. Chem. 2014, 79, 4131−4136

■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant No. 21272200) and the Priority Academic Program Development of Jiangsu Higher Education Institutions. We also thank the Analysis and Test Center of Yangzhou University providing instruments for analysis.

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