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Efficient one-pot catalyst-free synthesis of novel coumarin- spiro[indoline-3,4′-pyran] conjugates via three-component domino reaction in aqueous medium

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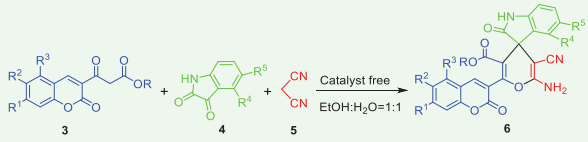
ABSTRACT

A simple, efficient, eco-friendly and catalyst-free procedure was developed for the construction of novel coumarin-spiro[indoline-3,4′-pyran] conjugates via three-component reactions of various synthetic beta-ketoesters with isatins and malononitrile in aqueous medium. In addition to operational simplicity and absence of tedious separation procedures, being catalyst–free is the prominent advantage of this method.



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KEYWORDS
Coumarins; spiro-indoline; pyran; one-pot synthesis; catalyst-free

Introduction

Coumarins constitute a major class of widely distributed *O*-heterocyclic natural products which are isolated from fruits, vegetables, spices and herbs (*1*). Natural and synthetic coumarins have been found to exhibit versatile pharmacological activities, acting as antineoplastics (*2*), anticoagulant (*3*), antidepressants (*4*), anti-inflammatories (*5*), antifungals (*6*), antihypertensives (*7*), antiasthmatics (*8*). On the other hand, the intrinsic photophysical characteristics of coumarins and derivatives enable their use as fluorescent brightening agents (*9*), organic light emitting diodes (*10*), optical sensors (*9*), light harvesting materials (*11*), non-linear optical materials (*12*) and fluorogenic probe in biological imaging (*13*).

Among heterocyclic scaffolds, pyran is a valuable intermediates in modern organic synthesis (*14*). It also possesses wide range of pharmacological activities and act as vasodilator (*15*), antineoplastic (*16*), antibacterial (*17*), antimicrobial (*18*) and anti-inflammatory (*19*) agents. The heterocyclic spirooxindole ring system is a kind of frequently encountered structural motif in numerous natural alkaloids (*20*). A number of spirooxindole scaffolds deliver important pharmacological activity such as antimalarial (*21*), antimicrobial (*22*), analgesic (*23*) and antipyretic (*24*) activities.

One of the desirable goals in organic synthesis is the assembly of simple and readily available precursor molecules into chemically complex products. Multicomponent reactions (MCRs), in which three or more starting materials are brought together in an efficiently convergent way to construct molecular structure and complexity, have been enthralling considerable attention over the past decades (*25–29*).

As far as we know coumarins have already been used as starting materials in MCRs (*30–32*), and it is noteworthy that coumarins fused with other heterocyclic scaffolds have arresting properties. Studies have revealed that numerous biologically important properties of the coumarins fused with other heterocycles are dependent upon structural features of other heterocycles (*33*). Chemical modification of other heterocycles offers a way to alter the functional groups, sizes, and stereochemistry of the coumarin derivatives, and many structure–activity relationships have been built up by such synthetic alterations (*34–36*). Due to the distinctive biological and pharmacological properties of the coumarin, pyran and spiro-oxindole scaffolds, the research on developing synthetic methods to enable facile access to heterocyclic compounds of this sort is being interesting. To the best of our knowledge, however, no protocol access to fluorescent coumarin-spiro[indoline-3,4′-pyran] conjugates has been reported yet. Accordingly, the aim of this work is to set up a protocol for achieving a novel

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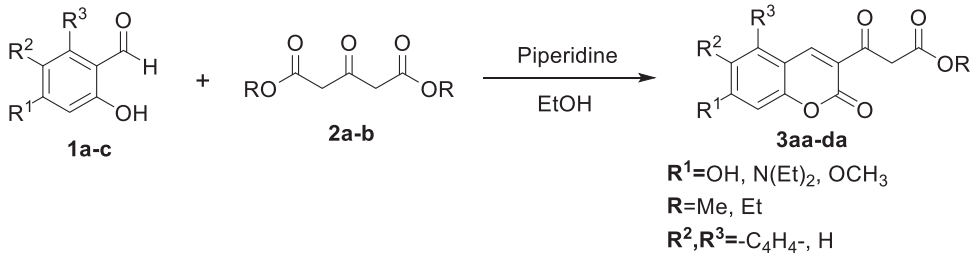
collection of coumarin-spiro[indoline-3,4′-pyran] conjugates from synthetic coumarin beta-ketoester derivatives in efficient way.

Results and discussion

Encouraged by previous reports (*37*), our initial work was focused on preparing various coumarin beta-ketoester derivatives. These coumarin beta-ketoester derivatives were synthesized successfully by using 2,4-dihydroxybenzaldehyde **1a**, 4-Diethylaminosalicylaldehyde **1b**, 2-Hydroxy-4-methoxybenzaldehyde **1c** or 2-Hydroxy-1-naphthaldehyde **1d** and dimethyl 3-oxopentanedioate **2a** or diethyl 3-oxopentanedioate **2b** (Scheme 1) according to literature method (*37*).

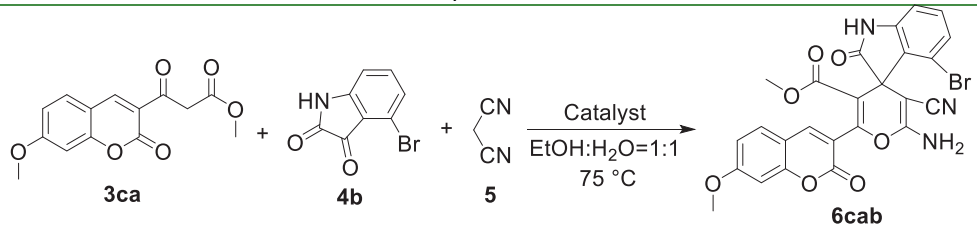
The coumarin beta-ketoesters **3** were confirmed by analysis of ^{1}H NMR. With the coumarin beta-ketoesters in hand, to seek out the best synthesis condition for the titled compounds **6** we chose coumarin beta-ketoester **3ca** (0.4 mmol), 4-Bromoisatin **4b** (0.4 mmol) and malononitrile **5** (0.4 mmol) as model substrates. Ethanol is coincidently a better solvent from an environmental perspective, however, studies indicate that ethanol–water mixtures are more environmentally favorable compared to pure alcohol (*38*, *39*). Using aqueous medium as a solvent in organic reaction is not only inexpensive and environmentally benign, but also offers advantages over those occurring in organic solvents (*40*, *41*).Thus, the model reaction was performed without any catalysts in a mixture of ethanol-water (EtOH/H_2O = 1:1) at 75°C, we were pleased to see that excellent yield of product was afforded after 9 h (Table 1, entry 1). With this fascinating result of the model reaction, we examined other catalysts to shorten the reaction time as well as increase the yield further.

Therefore, various catalysts such as L-proline, CTAB, DABCO, TEBA, BHDC were tested in the same condition of the model reaction. However, using these catalysts neither increased the yield of product nor shortened the reaction time significantly. The results were



Scheme 1. Preparation of coumarin beta-ketoester moieties.

Table 1. Optimization of reaction conditions for the multicomponent reactions[a].



Entry	Catalyst	Time(h)	Yield(%)[b]
1	Catalyst free	9	86
2	CTAB (20 mol %)[c]	10	88
3	DABCO (20 mol %)[d]	10	78
4	TEBA (20 mol %)[e]	10	87
5	L-proline (10 mol %)	9	80
6	L-proline (20 mol %)	10	89
7	L-proline (30 mol %)	9	90
8	BHDC (20 mol %)[f]	9	90
9	BHDC (30 mol %)	8	87

[a]Coumarin beta-ketoester **3ca** (0.4 mmol), 4-Bromoisatin **4b** (0.4 mmol) and malononitrile **5** (0.4 mmol) H_2O/EtOH = 1:1 (5 mL), 75°C.
[b]Isolated yield.
[c]Hexadecyltrimethylammonium bromide.
[d]1,4-Diazabicyclo[2.2.2]octane.
[e]Triethylbenzylammonium chloride.
[f]Benzylhexadecyldimethylammonium chloride.

summarized in Table 1. Among them, 30 mol % amount of L-proline and 20 mol % amount of BHDC showed the highest yield (Table 1, entries 7 and 8).Afterwards, when the amount of BHDC was increased to 30 mol %, except the slight decreasing of yield, not any improvement was observed. Having optimized the reaction parameters, we generalized the applicability of this method for synthesis of a series of coumarin-spiro[indoline-3,4′-pyran] conjugates starting from various substituted coumarin β-ketoesters and isatins(Table 2). The work-up procedure of the reaction is very convenient, after completion the reaction(monitored by TLC), the product was isolated from the reaction mixture simply by filtration and pure target compounds were obtained in considerably high yields after further recrystallization.

The coumarin-spiro[indoline-3,4′-pyran] conjugates **6** structural assignments have been made on the basis of IR, ^{1}H NMR, ^{13}C NMR and mass spectra. The ^{1}H NMR spectra of compounds **6** reveal typical singlet at δ7.27–7.52 for two protons of amino hydrogens (N-CH_2) which confirms the formation of pyran ring. In addition, a singlet of NH which originated from the isatin moiety appears in the region of δ10.48–11.29 could also be identified easily.

We suggest Scheme 2 as a working mechanism. In the first step, isatin **4** undergoes Knoevenagel condensation with malononitrile **5** to give intermediate product **A**, which acts as a Michael acceptor. The carbanion of coumarin β-ketoester is generated by the abstraction of a proton from the active methylene group, which is stabilized by resonance. Then it attacks at the Knoevenagel adduct intermediate **A** in Michael addition manner to produce an acyclic intermediate **B** which might undergo intramolecular cyclization followed by tautomerization to form the desired coumarin-spiro[indoline-3,4′-pyran] conjugate.

Conclusion

In conclusion, we have developed a completely eco-friendly, efficient, facile, one-pot, three-component, catalyst-free protocol for the synthesis of fluorescent coumarin-spiro[indoline-3,4′-pyran] conjugates in aqueous ethanol. No chromatography, no toxic organic solvents, and good to excellent product yields are some of the obvious achievements of this protocol.

Experimental

General information

Reagents and solvents were from Aladdin, Acros or Energy Chemical. Melting points were determined in capillary tubes using Buchi B-540 digital melting point apparatus; they are uncorrected. The progress of the reaction was monitored by TLC using analytical-grade silica gel plates (GF254). All target compounds were characterized from their ^{1}H NMR, ^{13}C NMR, IR, and MS spectra. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were run on a Bruker Inova-400 instrument using DMSO-d_6 as solvent. Chemical shifts are given in ppm relative to TMS as an internal standard, and J values are given in Hz. IR spectra were recorded on a Bruker Vertex70 spectrophotometer using samples as KBr pellets. HRMS data were obtained using Thermo Scientific LTQ Orbitrap XL spectrometer.

General procedure for compounds 6aaa–dbc

A mixture of beta-ketoester coumarin compound **3** (0.4 mmol), the corresponding isatin **4** (0.4 mmol) and malononitrile **5** (0.4 mmol) in EtOH-H_2O (1:1, 5 mL) was taken in a round-bottomed flask connected to a reflux condenser, and the mixture was stirred in an oil-bath (75°C). The progress of the reaction was monitored by TLC using acetone–chloroform(1: 5) as the eluent. After completion of the reaction, the reaction mixture was cooled to room temperature. Then the precipitate product was filtered and washed with ethanol and pure product was obtained after further recrystallization from ethanol.

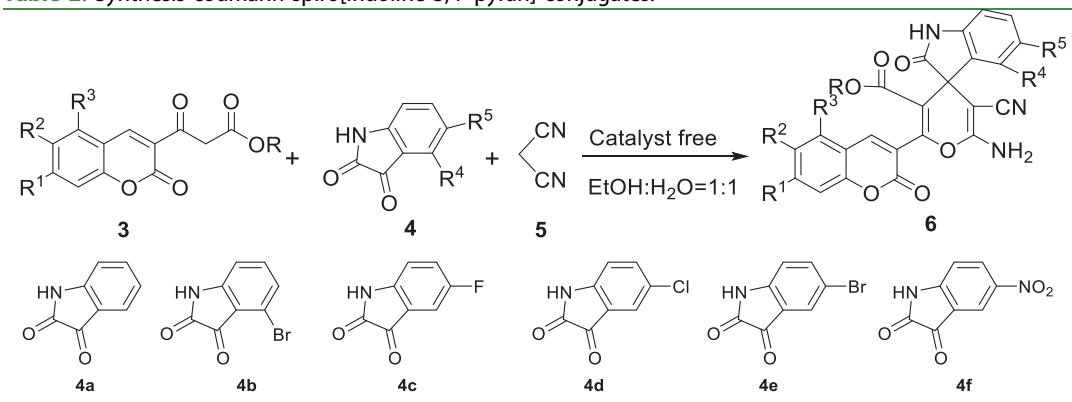
*Methyl 2′-amino-3′-cyano-6′-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6aaa**)*

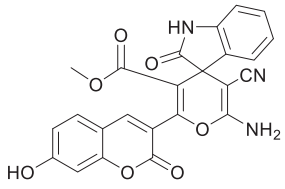
Yield: 65%; mp 275–277°C; IR (KBr, cm^{-1}) 3432, 3286, 3168, 3068, 2955, 2194, 1724, 1698, 1612, 1567, 1503, 1468, 1410, 1375, 1327; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (s, 1H), 10.51 (s, 1H), 8.28 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.30 (s, 2H), 7.21 (td, J = 7.7, 1.3 Hz, 1H), 7.11 (d, J = 6.8 Hz, 1H), 6.98 (td, J = 7.5, 1.0 Hz, 1H), 6.88–6.78 (m, 3H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.96, 164.47, 163.00, 159.79, 158.09, 155.78, 151.03, 144.19, 142.06, 134.22, 131.05, 129.03, 123.78, 122.22, 117.52, 116.52, 114.21, 110.67, 109.66, 108.70, 102.31, 56.77, 51.67, 49.72; HRMS (ESI) m/z calcd for $C_{24}H_{16}N_3O_7^+$ $(M+H)^+$ 458.09828, found 458.09836.

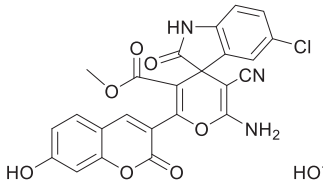
*Methyl 2′-amino-5-chloro-3′-cyano-6′-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6aad**)*

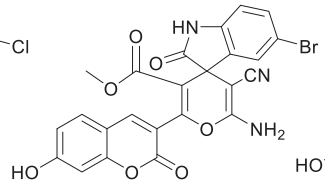
Yield: 80%; mp 282–284°C; IR (KBr, cm^{-1}) 3358, 3150, 2963, 2197, 1733, 1678, 1514, 1474, 1436, 1370,1323; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.94 (s, 1H), 10.67 (s, 1H), 8.30 (d, J = 0.7 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.39 (s, 2H), 7.30–7.19 (m, 2H), 6.91–6.81 (m, 2H), 6.79 (d, J = 2.2 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.74, 164.39, 163.02, 159.75, 158.08, 155.79, 151.70, 144.34, 140.98, 136.42, 131.04, 128.98, 126.05, 123.86,

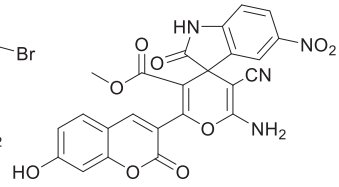
Table 2. Synthesis coumarin-spiro[indoline-3,4′-pyran] conjugates.

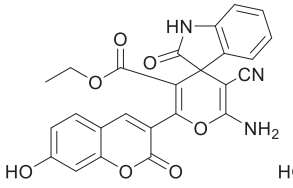


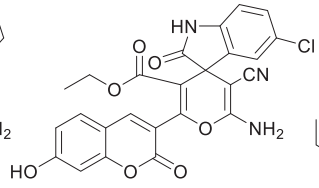

6aaa, 65%, 12h

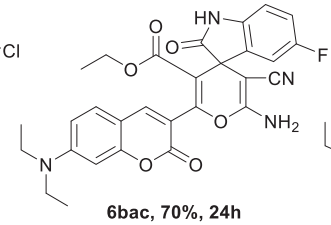

6aad, 80%, 20h

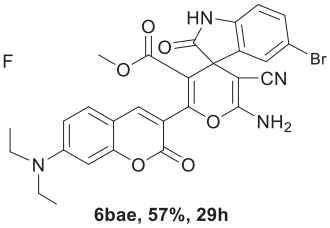

6aae, 55%, 19h

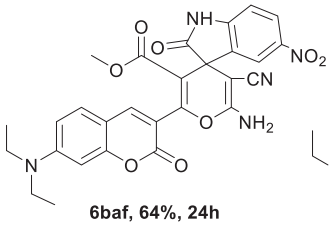

6aaf, 59%, 15h

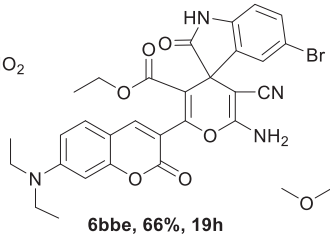

6aba, 62%, 14h

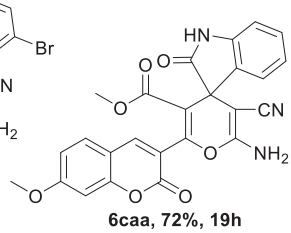

6abd, 60%, 20h

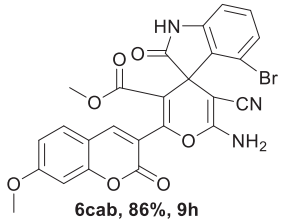

6bac, 70%, 24h

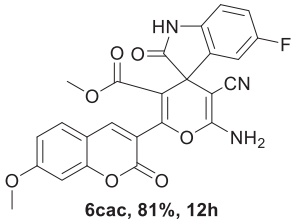

6bae, 57%, 29h

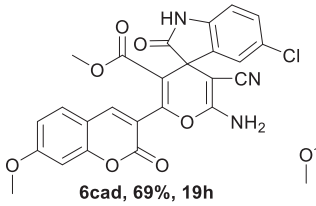

6baf, 64%, 24h

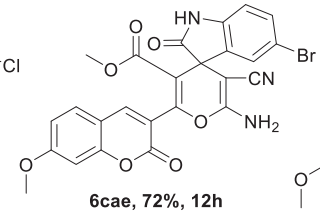

6bbe, 66%, 19h

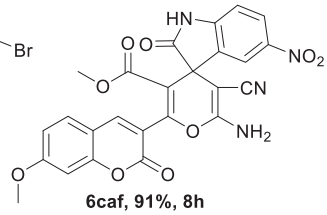

6caa, 72%, 19h

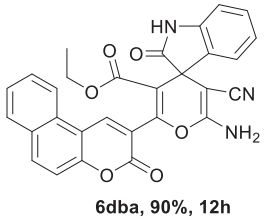

6cab, 86%, 9h

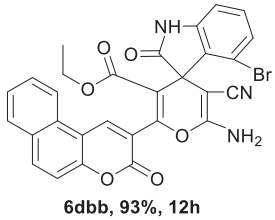

6cac, 81%, 12h

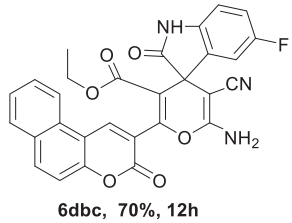

6cad, 69%, 19h

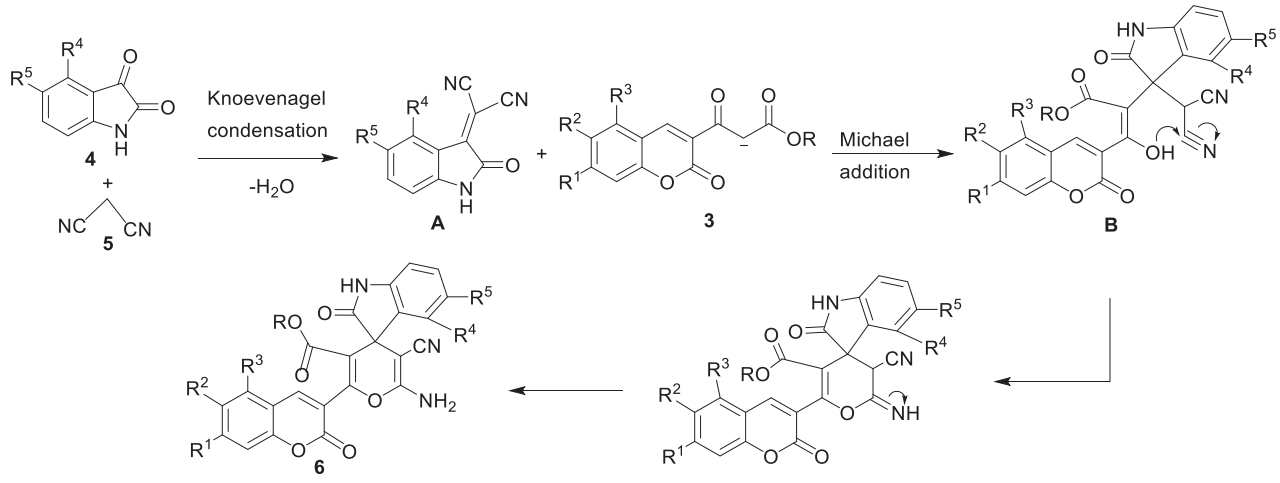

6cae, 72%, 12h


6caf, 91%, 8h


6dba, 90%, 12h


6dbb, 93%, 12h


6dbc, 70%, 12h



Scheme 2. Plausible reaction mechanism for the formation of the coumarin-spiro [indoline-3,4′-pyran] conjugates.

117.36, 116.53, 114.24, 111.16, 110.63, 107.80, 102.35, 56.19, 51.83, 50.05; HRMS (ESI) m/z calcd for $C_{24}H_{15}ClN_3O_7^+$ $(M+H)^+$ 492.05930, found 492.05930.

*Methyl 2′-amino-5-bromo-3′-cyano-6′-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6aae**)*

Yield: 55%; mp 291–293°C; IR (KBr, cm^{-1}) 3342, 3195, 3050, 2975, 2890, 2200, 1708, 1676, 1642, 1612, 1473, 1451, 1411, 1379, 1330; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (s, 1H), 10.67 (s, 1H), 8.30 (d, J = 0.7 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.40–7.38 (m, 3H), 7.32 (d, J = 2.1 Hz, 1H), 6.87 (dd, J = 8.6, 2.3 Hz, 1H), 6.76 (s, 2H),3.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.62, 164.41, 163.04, 159.74, 158.10, 155.80, 151.73, 144.36, 141.40, 136.83, 131.85, 131.05, 126.56, 117.39, 116.55, 114.25, 113.73, 111.71, 110.64, 107.77, 102.36, 51.84, 49.99; HRMS (ESI) m/z calcd for $C_{24}H_{15}BrN_3O_7^+$ $(M+H)^+$ 536.00879, found 536.00897.

*Methyl 2′-amino-3′-cyano-6′-(7-hydroxy-2-oxo-2H-chromen-3-yl)-5-nitro-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6aaf**)*

Yield: 59%; mp > 300°C; IR (KBr, cm^{-1}) 3645, 3541, 3451, 3370, 3320, 3199, 2200, 1711, 1659, 1619, 1563, 1564, 1523, 1504, 1481, 1453, 1420, 1368, 1344, 1327; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (s, 1H), 10.96 (s, 1H), 8.35 (s, 1H), 8.21 (dd, J = 8.6, 2.4 Hz, 1H), 8.07 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.52 (s, 2H), 7.06 (d, J = 8.6 Hz, 1H), 6.88 (dd, J = 8.5, 2.3 Hz, 1H), 6.80 (d, J = 2.2 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.50, 164.38, 163.10, 159.86, 158.10, 155.83, 152.24, 148.60, 144.57, 142.71, 135.47, 131.10, 126.58, 119.43, 117.21, 116.43, 114.29, 110.61, 110.01, 107.10, 102.38, 55.43, 51.99, 49.93, 40.61; HRMS (ESI) m/z calcd for $C_{24}H_{15}N_4O_9^+$ $(M+H)^+$ 503.08335, found 503.08331.

*Ethyl 2′-amino-3′-cyano-6′-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6aba**)*

Yield: 62%; mp 281–283°C; IR (KBr, cm^{-1}) 3472, 3416, 3311, 3141, 2999, 2201, 1707, 1664, 1619, 1569, 1503, 1470,1409, 1369, 1323; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (s, 1H), 10.50 (s, 1H), 8.25 (s, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.29 (s, 2H), 7.21 (td, J = 7.7, 1.3 Hz, 1H), 7.12 (dd, J = 7.5, 1.2 Hz, 1H), 6.97 (td, J = 7.5, 1.0 Hz, 1H), 6.90–6.76 (m, 3H), 3.67 (qd, J = 7.1, 5.2 Hz, 2H), 0.68 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.97, 163.73, 162.84, 159.71, 158.07, 155.70, 151.43, 143.97, 142.18, 134.30, 130.91, 128.92, 123.74, 122.12, 117.45, 116.83, 114.12, 110.64, 109.59, 108.71, 102.23, 60.51, 56.16, 49.62, 13.05; HRMS (ESI) m/z calcd for $C_{25}H_{18}N_3O_7^+$ $(M+H)^+$ 472.11393, found 472.11407.

*Ethyl 2′-amino-5-chloro-3′-cyano-6′-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6abd**)*

Yield: 60%; mp 286–288°C; IR (KBr, cm^{-1}) 3375, 3308, 3189, 2980, 2930, 2202, 1719, 1661, 1618, 1570, 1505, 1476, 1417, 1370; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.92 (s, 1H), 10.66 (s, 1H), 8.28 (s, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.38 (s, 2H), 7.31–7.20 (m, 2H), 6.91–6.81 (m, 2H), 6.79 (d, J = 2.2 Hz, 1H), 3.71 (qd, J = 7.1, 2.3 Hz, 2H), 0.71 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.79, 163.67, 162.90, 159.70, 158.12, 155.73, 152.09, 144.19, 141.11, 136.52, 130.95, 128.92, 126.02, 123.87, 117.38, 116.82, 114.20, 111.13, 110.62, 107.79, 102.29, 60.76, 56.20, 56.18, 49.95, 18.74, 13.12; HRMS (ESI) m/z calcd for $C_{25}H_{17}ClN_3O_7^+$ $(M+H)^+$ 506.07495, found 506.07516.

*Ethyl 2′-amino-3′-cyano-6′-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-5-fluoro-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6bac**)*

Yield: 70%; mp 283–285°C; IR (KBr, cm^{-1}) 3327, 3271, 3179, 2976, 2934, 2903, 2712, 2637, 2202, 1739, 1711, 1660, 1614, 1584, 1512, 1488, 1459, 1413, 1352, 1319; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.10 (s, 1H), 7.52 (d, J = 8.9 Hz, 1H), 7.28 (s, 2H), 7.03 (ddt, J = 10.7, 7.7, 2.8 Hz, 2H), 6.79 (ddd, J = 16.9, 8.7, 3.4 Hz, 2H), 6.59 (d, J = 2.3 Hz, 1H), 3.76–3.64 (m, 2H), 3.46 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.0 Hz, 6H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.15, 163.97, 159.88, 159.50, 157.61(d, $^1J_{CF}$ = 192.1 Hz), 157.14, 156.63, 152.06, 151.84, 143.96, 138.39, 136.16 (d, $^3J_{CF}$ = 7.6 Hz), 130.52, 117.47, 115.28, 115.05, 112.80, 111.60, 111.36, 110.40, 110.5 (d, $^2J_{CF}$ = 24 Hz), 107.32, 106.99, 96.39, 60.48, 56.30, 50.27, 44.35, 39.15, 13.21, 12.48; HRMS (ESI) m/z calcd for $C_{29}H_{26}FN_4O_6^+$ $(M+H)^+$ 545.18309, found 545.18335.

*Methyl 2′-amino-5-bromo-3′-cyano-6′-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6bae**)*

Yield: 57%; mp 260–262°C; IR (KBr, cm^{-1}) 3347, 3295, 3177, 3040, 2973, 2898, 2204, 1717, 1665, 1611, 1582, 1510, 1472, 1453, 1415, 1346, 1329; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 8.14 (s, 1H), 7.53 (d, J = 8.9 Hz, 1H), 7.38 (dd, J = 8.2, 2.1 Hz, 1H), 7.33 (s, 2H), 7.28 (d, J = 2.1 Hz, 1H), 6.83–6.74 (m, 2H), 6.60 (d, J = 2.4 Hz, 1H), 3.45 (dq, J = 11.0, 7.1 Hz, 4H), 3.26 (s, 3H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.73, 164.72, 159.88, 158.56, 156.69, 151.94, 151.89, 144.12, 141.38, 136.93, 131.72, 130.62, 126.48, 117.47, 113.65, 112.48, 111.64, 109.83, 107.03, 106.99, 96.45, 56.19, 51.66, 50.12, 44.39, 12.50; HRMS (ESI) m/z calcd for $C_{28}H_{24}B_rN_4O_6^+$ $(M+H)^+$ 591.08737, found 591.08826.

*Methyl 2′-amino-3′-cyano-6′-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-5-nitro-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6baf**)*

Yield: 64%; mp > 300°C; IR (KBr, cm^{-1}) 3338, 3260, 3184, 3083, 2976, 2716, 2634, 2199, 1720, 1660, 1614, 1581, 1511, 1459, 1412, 1342; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 8.25–8.14 (m, 2H), 8.02 (d, J = 2.4 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.46 (s, 2H), 7.06 (d, J = 8.6 Hz, 1H), 6.78 (dd, J = 9.0, 2.5 Hz, 1H), 6.60 (d, J = 2.3 Hz, 1H), 3.46 (dt, J = 12.8, 6.9 Hz, 4H), 3.26(s, 3H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.62, 164.74, 160.00, 158.57, 156.74, 152.43, 152.01, 148.61, 144.33, 142.64, 135.59, 130.67, 126.47, 119.30, 117.29, 112.31, 109.95, 109.88, 107.01, 106.30, 96.47, 56.19, 55.40, 51.80, 50.05, 44.40, 39.59, 18.73, 12.51; HRMS (ESI) m/z calcd for $C_{28}H_{24}N_5O_8^+$ $(M+H)^+$ 558.16194, found 558.16229.

*Ethyl 2′-amino-5-bromo-3′-cyano-6′-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6bbe**)*

Yield: 66%; mp 286–288°C; IR (KBr, cm^{-1}) 3340, 3283, 3186, 3072, 2973, 2930, 2900, 2715, 2639, 2200, 1892, 1739, 1659, 1614, 1584, 1512, 1474, 1413, 1351, 1320; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.11 (s, 1H), 7.53 (d, J = 8.9 Hz, 1H), 7.39 (dd, J = 8.2, 2.1 Hz, 1H), 7.33 (s, 2H), 7.29 (d, J = 2.0 Hz, 1H), 6.78 (dd, J = 12.2, 8.8 Hz, 2H), 6.59 (d, J = 2.4 Hz, 1H), 3.72 (q, J = 7.1 Hz, 2H), 3.46 (p, J = 6.3, 5.4 Hz, 4H), 1.10 (dt, J = 33.2, 7.0 Hz, 6H), 0.75 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.77, 163.99, 159.86, 158.59, 156.65, 152.24, 151.85,144.02, 141.52, 136.99, 131.68, 130.54, 126.50, 117.49, 113.62, 112.82, 111.62, 109.77, 107.09, 106.99, 96.39, 60.57, 56.18, 50.03, 44.37, 39.35, 13.22, 12.49; HRMS (ESI) m/z calcd for $C_{29}H_{26}B_rN_4O_6^+$ $(M+H)^+$ 605.10302, found 605.10315.

*Methyl 2′-amino-3′-cyano-6′-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate (**6caa**)*

Yield: 72%; mp 233–235°C; IR (KBr, cm^{-1}) 3417, 3335, 3158, 3022, 2999, 2950, 2845, 2623, 2196, 1711, 1670, 1617, 1599, 1506, 1469, 1443, 1412, 1376, 1312; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.34 (s, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.27 (s, 2H), 7.21 (td, J = 7.7, 1.3 Hz, 1H), 7.15–7.07 (m, 2H), 7.07–6.93 (m, 2H), 6.83 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ177.93, 164.41, 163.93, 159.76, 158.00, 155.70, 150.94, 143.96, 142.06, 134.19, 130.68, 129.06, 123.78, 122.22, 117.65, 117.49, 113.57, 111.70, 109.68, 108.89, 100.87, 56.79, 56.36, 51.71, 49.71; HRMS (ESI) m/z calcd for $C_{25}H_{18}N_3O_7^+$ $(M+H)^+$ 472.11393, found 472.11398.

*Methyl 2′-amino-4-bromo-3′-cyano-6′-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6cab**)*

Yield: 86%; mp 260–262°C; IR (KBr, cm^{-1}) 3277, 3180, 3011, 2962, 2195, 1710, 1608, 1504, 1443, 1406, 1377, 1355, 1318; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (s, 1H), 8.30 (s, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.39 (s, 2H), 7.24–7.07 (m, 3H), 7.03 (dd, J = 8.7, 2.4 Hz, 1H), 6.85 (dd, J = 7.4, 1.2 Hz, 1H), 3.89 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.21, 164.34, 163.91, 160.40, 157.69, 155.70, 152.03, 144.24, 143.61, 130.93, 130.71, 125.62, 119.01, 117.86, 117.27, 113.50, 111.68, 109.16, 106.64, 100.82, 56.34, 54.06, 51.82, 51.56, 39.38; HRMS (ESI) m/z calcd for $C_{25}H_{17}BrN_3O_7^+$ $(M+H)^+$ 550.02444, found 550.02509.

*Methyl 2′-amino-3′-cyano-5-fluoro-6′-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6cac**)*

Yield: 81%; mp 241–243°C; IR (KBr, cm^{-1}) 3413, 3348, 3295, 3167, 3007, 2952, 2844, 2628, 2556, 2196, 1714, 1674, 1602, 1564, 1507, 1483, 1454, 1414, 1378, 1354,

1319; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.56 (s, 1H), 8.35 (s, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.39 (s, 2H), 7.11 (d, J = 2.4 Hz, 1H), 7.10–7.00 (m, 3H), 6.87–6.79 (m, 1H), 3.89 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.94, 164.31, 163.94, 159.53, 159.25 (d, $^1J_{CF}$ = 256 Hz), 157.17, 155.69, 151.39, 144.06, 138.26, 138.25, 135.96, 135.89, 130.65, 117.60, 117.34, 115.38 (d, $^2J_{CF}$ = 23.5 Hz), 113.58, 111.65, 111.40, 110.49 (d, $^3J_{CF}$ = 8.3 Hz),, 108.19, 100.88, 56.35, 56.29, 51.80, 50.22, 39.36; HRMS (ESI) m/z calcd for $C_{25}H_{17}FN_3O_7^+$ $(M+H)^+$ 490.10450, found 490.10483.

*Methyl 2′-amino-5-chloro-3′-cyano-6′-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6cad**)*

Yield: 69%; mp 254–256°C; IR (KBr, cm^{-1}) 3375, 3341, 3303, 3176, 2950, 2846, 2203, 1717, 1660, 1614, 1560, 1507, 1475, 1435, 1412, 1374, 1310; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.67 (s, 1H), 8.36 (s, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.40 (s, 2H), 7.31–7.20 (m, 2H), 7.14–7.09 (m, 1H), 7.04 (dd, J = 8.7, 2.4 Hz, 1H), 6.85 (dd, J = 8.2, 0.5 Hz, 1H), 3.89 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.66, 164.28, 163.93, 159.68, 157.95, 155.68, 151.57, 144.07, 140.97, 136.36, 130.63, 128.97, 126.03, 123.84, 117.62, 117.29, 113.56, 111.64, 111.14, 107.96, 100.88, 56.34, 56.19, 51.83, 50.01, 39.38, 39.16, 18.72; HRMS (ESI) m/z calcd for $C_{25}H_{17}ClN_3O_7^+$ $(M+H)^+$ 506.07495, found 506.07544.

*Methyl 2′-amino-5-bromo-3′-cyano-6′-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6cae**)*

Yield: 72%; mp 263–265°C; IR (KBr, cm^{-1}) 3403, 3338, 3230, 3089, 3040, 2959, 2933, 2837, 2191, 1726, 1676, 1642, 1610, 1556, 1504, 1472, 1441, 1408, 1378, 1325; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.69 (s, 1H), 8.36 (s, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.44–7.31 (m, 4H), 7.11 (d, J = 2.4 Hz, 1H), 7.04 (dd, J = 8.7, 2.4 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 3.89 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.52, 164.28, 163.93, 159.68, 157.95, 155.68, 151.60, 144.06, 141.37, 136.75, 131.81, 130.62, 126.51, 117.64, 117.27, 113.68, 113.53, 111.67, 111.63, 107.96, 100.88, 56.32, 56.26, 51.81, 49.96; HRMS (ESI) m/z calcd for $C_{25}H_{17}BrN_3O_7^+$ $(M+H)^+$ 550.02444, found 550.02441.

*Methyl 2′-amino-3′-cyano-6′-(7-methoxy-2-oxo-2H-chromen-3-yl)-5-nitro-2-oxospiro [indoline-3,4′-pyran]-5′-carboxylate (**6caf**)*

Yield: 91%; mp 280–282°C; IR (KBr, cm^{-1}) 3339, 3258, 3183, 2952, 2843, 2200, 1723, 1660, 1615, 1554, 1524, 1482, 1449, 1416, 1344, 1314; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (s, 1H), 8.41 (s, 1H), 8.22 (dd, J = 8.8, 2.3 Hz, 1H), 8.08 (d, J = 2.2 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.51 (s, 2H), 7.14–7.01 (m, 3H), 3.90 (s,3H), 3.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.46, 164.30, 164.00, 159.82, 158.00, 155.74, 152.13, 148.59, 144.32, 142.72, 135.43, 130.70, 126.57, 119.44, 117.55, 117.17, 113.62, 111.63, 110.00, 107.28, 100.91, 56.36, 56.20, 55.44, 52.01, 49.91, 30.86, 18.73; HRMS (ESI) m/z calcd for $C_{25}H_{17}N_4O_9^+$ $(M+H)^+$ 517.09900, found 517.09961.

*Ethyl 2′-amino-3′-cyano-2-oxo-6′-(3-oxo-3H-benzo[f]chromen-2-yl)spiro[indoline-3,4′-pyran]-5′-carboxylate (**6dba**)*

Yield: 90%; mp 262–264°C; IR (KBr, cm^{-1}) 3379, 3159, 2977, 2200, 1720, 1666, 1617, 1567, 1517, 1471, 1408, 1392, 1365; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 9.24 (s, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.30 (d, J = 9.1 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.81 (ddd, J = 8.5, 7.0, 1.3 Hz, 1H), 7.74–7.62 (m, 2H), 7.33 (s, 2H), 7.27–7.18 (m, 2H), 7.00 (td, J = 7.5, 1.1 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.48–3.41 (m, 2H), 0.68 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.95, 163.67, 159.77, 157.77, 153.66, 151.04, 142.14, 139.75, 135.04, 134.49, 130.22, 129.21, 129.05, 128.98, 128.89, 126.68, 123.87, 122.69, 122.17, 120.93, 117.52, 116.70, 112.50, 109.63, 109.08, 60.65, 56.19, 13.06; HRMS (ESI) m/z calcd for $C_{29}H_{20}N_3O_6^+$ $(M+H)^+$ 506.13466, found 506.13486.

*Ethyl 2′-amino-4-bromo-3′-cyano-2-oxo-6′-(3-oxo-3H-benzo[f]chromen-2-yl)spiro[indoline-3,4′-pyran]-5′-carboxylate (**6dbb**)*

Yield: 93%; mp 278–280°C; IR (KBr, cm^{-1}) 3584, 3501, 3358, 3281, 3162, 2979, 2198, 1911, 1865, 1726, 1661, 1611, 1585, 1564, 1515, 1467, 1446, 1414, 1392, 1365; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 9.10 (s, 1H), 8.74–8.66 (m, 1H), 8.31 (d, J = 9.0 Hz, 1H), 8.15–8.07 (m, 1H), 7.80 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.73–7.62 (m, 2H), 7.43 (s, 2H), 7.23–7.10 (m, 2H), 6.86 (dd, J = 7.4, 1.2 Hz, 1H),, 3.44 (q, J = 7.0 Hz, 2H), 0.73 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.20, 163.65, 160.51, 157.38, 153.67, 151.76, 144.27, 139.19, 135.10, 130.88, 130.80, 130.17, 129.15, 128.95, 128.83, 126.64, 125.59, 122.72, 121.00, 119.19, 117.28, 116.63, 112.35, 109.04, 107.03, 60.72, 54.29, 51.53, 13.09; HRMS (ESI) m/z calcd for $C_{29}H_{19}BrN_3O_6^+$ $(M+H)^+$ 584.04517, found 584.04596.

*Ethyl 2′-amino-3′-cyano-5-fluoro-2-oxo-6′-(3-oxo-3H-benzo[f]chromen-2-yl)spiro[indoline-3,4′-pyran]-5′-carboxylate (**6dbc**)*

Yield: 70%; mp 270–272°C; IR (KBr, cm^{-1}) 3421, 3278, 3081, 2989, 2198, 1720, 1665, 1626, 1598, 1564, 1515, 1488, 1393, 1366, 1348, 1302; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.56 (s, 1H), 9.26 (s, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 9.0 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.82 (ddd, J = 8.3, 7.0, 1.4 Hz, 1H), 7.73–7.63 (m, 2H), 7.42 (s, 2H), 7.15–7.02 (m, 2H), 6.89–6.80 (m, 1H), 3.72 (tdd, J = 7.2, 5.6, 1.7 Hz, 2H), 0.70 (td, J = 7.1, 1.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.02, 163.58, 159.59, 158.69 (d, $^1J_{CF}$ = 2175 Hz), 157.23, 153.71, 151.64, 139.93, 138.36, 136.30, 136.28 (d, $^3J_{CF}$ = 7.5 Hz), 135.11,

130.25, 129.17 (d, $^{2}J_{CF} = 22.8$ Hz), 128.97, 126.73, 122.58, 120.92, 117.39, 116.74, 115.46, 115.23, 112.48, 111.74, 111.49, 110.54, 110.46, 108.39, 60.83, 56.52, 50.18, 13.10; HRMS (ESI) m/z calcd for $C_{29}H_{19}FN_3O_6^+$ $(M+H)^+$ 524.12524, found 524.12512.

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