Synthesis A. Alizadeh et al. Paper

Intramolecular Diels–Alder and [3+2] Cycloaddition Reactions in the One-Pot Synthesis of Epoxypyrrolo[3,4-*g*]indazoles

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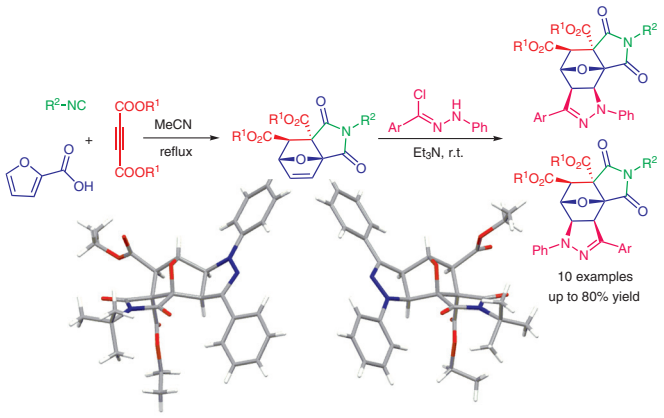

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Abstract A one-pot approach for the synthesis of epoxypyrrolo[3,4-*g*]indazoles is presented. The first step was initiated by a three-component reaction of an isocyanide, a dialkyl acetylenedicarboxylate, and 2-furancarboxylic acid, and led to 1,3-dioxoepoxyisoindole, followed by the addition of hydrazonoyl chloride through a [3+2]-cycloaddition reaction in the second step. The key step in the formation of final compound involves a bicyclization strategy through intramolecular Diels–Alder (IMDA) reaction.

Key words isocyanide, dialkyl acetylenedicarboxylate, 2-furancarboxylic acid, epoxypyrrolo[3,4-*g*]indazole, IMDA, [3+2] cycloaddition, oxabicyclo compounds

Oxabicyclo core is one of the current templates present in natural products[1] and plays a major role in the total synthesis. The ability of ring cleavage in this building block has made it one of the best candidates as starting material in the total synthesis of natural products.[2] For instance, estrone,[3] epoxyquinol A and B,[4] *trans*-kumausyne,[5] and peduncularine[6] are some of the natural products, where oxabicyclo compounds have been used in their synthetic routes. Not only the oxabicyclo template is used in the total synthesis of natural products as starting material, but it also appeared directly in the structure of multiple natural products (Figure 1). Prostaglandins, terpenoids, and carotenoids are some classes of these natural products.[7]

Researches revealed many biological and medicinal aspects of oxabicyclo containing compounds. For example, McCluskey and co-workers showed that some new class of cantharides can act as potential protein phosphatase.[8] In another study by Li et al., different oxabicyclo compounds exhibited the antiproliferative effect on breast cancer cells.[9]

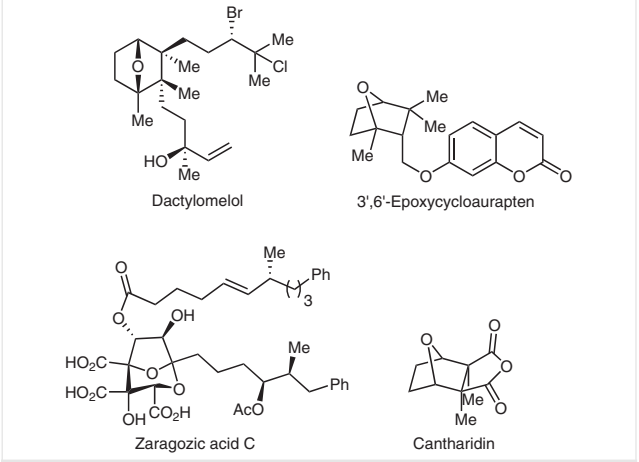
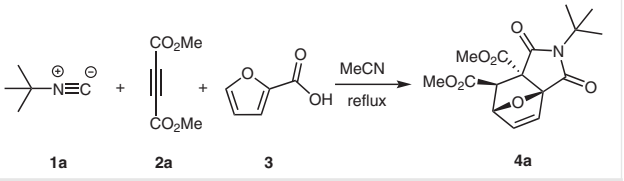


Figure 1 Structure of some natural products containing oxabicyclo skeleton

Due to the importance of structural and application of these compounds either as starting material or product, significant effort has been made in this area and Diels–Alder reaction is a dynamic tool for accessing these compounds. This reaction has become an integral part of synthetic chemistry owing to its stereospecific product, atom economy, and formation of two new bonds. Intramolecular reactions are faster, cleaner, and more selective compared with intermolecular reactions so the development of new substrates to perform intramolecular reactions – mostly intramolecular Diels–Alder reaction – found remarkable interests.[10] A literature survey showed that many chemists take

advantages of this powerful tool in total synthesis especially in the synthesis of oxabicyclic compounds.[11] Liu and co-workers reported the synthesis of the oxapentacyclic core of cortistatins through intramolecular Diels–Alder (IMDA) reaction.[12] The reaction consists of many intermediates but the key intermediate was synthesized through IMDA followed by Lewis acid mediated aromatization of oxabicyclic structure. Solanoeclepin A is another oxabicyclic natural product, which was synthesized through IMDA reaction.[13] Miyashita and co-workers reported the total synthesis of alkaloid norzoanthamine consisting of oxabicyclo core in its structure. An IMDA reaction lies in the middle of this method, which formed three stereogenic centers simultaneously.[14] Herein we describe a novel IMDA-based reaction for the synthesis of new classes of oxabicyclic compounds.

Recently, employment of IMDA reaction in acetylene-based isocyanide multicomponent reaction has been reported by Gao et al.[15] In continuation of our previous works in acetylene-based isocyanide multicomponent reaction with different carboxylic acids,[16] we were interested in the reaction of isocyanide **1a** with acetylene ester **2a** in the presence of 2-furancarboxylic acid (**3**). Based on our previous experience in IMCR, the reaction was performed in anhydrous DCM and THF at room temperature, which resulted in 20% and 25% yield, respectively. The best result was achieved in MeCN at 80 °C and the desired 1,3-dioxoepoxyisoindole **4a** was obtained in 86% yield (Scheme 1).



Scheme 1 Synthesis of 1,3-dioxoepoxyisoindole **4a**

The reaction was performed in different solvents at different temperature but the best results were obtained under reflux in acetonitrile (Table 1).

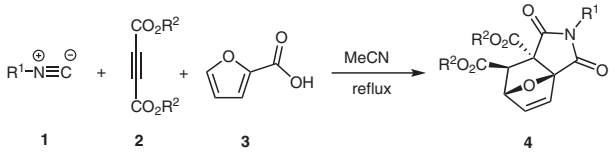
Table 1 Different Conditions for the Synthesis of **4a**

Entry	Solvent	Temp (°C)	Yield (%)
1	DCM	r.t	20
2	THF	r.t	25
3	THF	70	60
4	MeCN	80	86
5	toluene	80	55
6	EtOH	80	5
7	toluene	100	43
8	MeCN	100	72

The structure of **4a** was verified using IR spectrophotometry, mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy. The molecular ion peak of **4a** appeared at *m/z* 337 in mass spectrometry, which confirmed the proposed structure. ^{1}H NMR spectrum of **4a** displayed a singlet at 1.49 ppm, which was recognized as *tert*-butyl hydrogens. The next singlet signal at 3.25 ppm is related to a single hydrogen, connected to the ester group. Hydrogens of two methoxy groups of esters appeared at 3.64 and 3.68 ppm, respectively. The bridgehead hydrogen signal was identified at 5.33 ppm. The existence of 14 signals in ^{13}C NMR spectrum is in agreement with the suggested structure. In ^{13}C NMR spectrum, the *tert*-butyl group appeared in 27.52 ppm. Two signals at 51.95 ppm and 54.02 ppm are related to two methoxy groups. Four signals 165.75, 169.16, 170.30, and 170.71 ppm at the end of the spectrum are assigned to two ester and two amide groups.

The flexibility of the reaction toward different isocyanides and acetylenic esters was explored and the results are presented in Table 2. Unfortunately, when 2-thiophenecarboxylic acid was applied instead of 2-furancarboxylic acid the reaction did not provide the desired product even at higher temperatures and in different solvents.

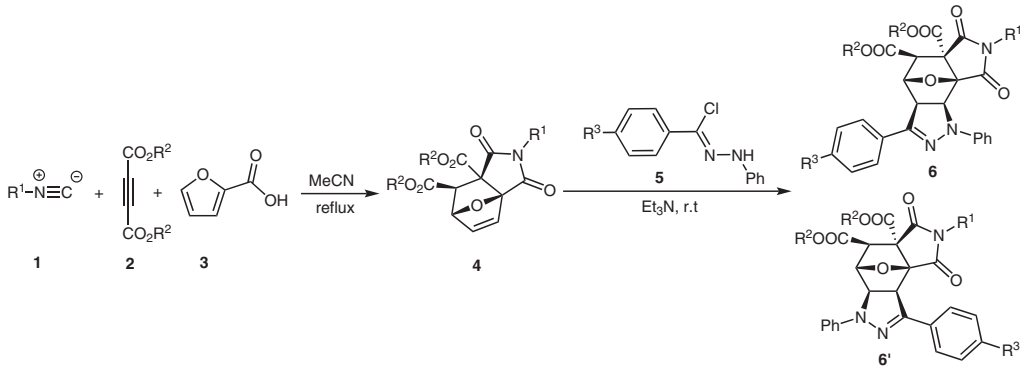
Table 2 Synthetic Pathway to 1,3-Dioxoepoxyisoindoles **4**



Entry	R^1	R^2	Product	Yield (%)
1	*t*-Bu	Me	**4a**	86
2	*t*-Bu	Et	**4b**	80
3	cyclohexyl	Me	**4c**	72
4	cyclohexyl	Et	**4d**	50
5	4-MeOC$_6$H$_4$	Me	**4e**	66
6	ethylmorpholine	Me	**4f**	54

In the sequel of our research, we noticed the double bond in the structure of 1,3-dioxoepoxyisoindoles. Therefore, we decided to investigate the reactivity of this bond toward [3+2] cycloaddition reaction. To achieve this goal, first 2-furancarboxylic acid (**3**) and isocyanide **1a** were introduced in the reaction pot followed by the addition of dimethyl acetylenedicarboxylate (**2a**). After 4–5 hours and formation of **4a**, which was confirmed by TLC, hydrazonoyl chloride **5a** with an equivalent amount of triethylamine were added to the reaction mixture. The reaction outcome was the predicted epoxypyrrolo[3,4-*g*]indazole in the form of two diastereomers. Different hydrazonoyl chloride was tried to develop the scope of the reaction and final products were obtained in good yields (Table 3). The structure of all

Table 3 Synthetic Approach to 6,8-Dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylates **6**



Entry	R^1	R^2	R^3	**6**:**6′**	Product	Yield (%)
1	*t*-Bu	Me	H	50:50	**6a**, **6′a**	80
2	*t*-Bu	Et	H	50:50	**6b**, **6′b**	75
3	cyclohexyl	Me	H	46:54	**6c**, **6′c**	68
4	*t*-Bu	Me	Cl	93:7	**6d**, **6′d**	83
5	cyclohexyl	Me	Cl	10:90	**6e**, **6′e**	66
6	*t*-Bu	Me	NO_2	4:96	**6f**, **6′f**	77
7	cyclohexyl	Me	NO_2	25:75	**6g**, **6′g**	70

the products **6a–j** were verified by mass, IR, ^{1}H NMR, ^{13}C NMR spectra and single-crystal X-ray probe of **6b**/**6′b**. The molecular ion peak of **6a** appeared at *m*/*z* = 531. IR spectrum displayed ester carbonyl stretching frequency at 1746 cm^{-1}. Signals at ^{1}H NMR and ^{13}C NMR are related to a mixture of two diastereomers, which go along with suggested structures.

Finally, single crystal of **6b** and **6′b** was analyzed by X-ray crystallography to obtain the exact structure of both regioisomers (Figure 2).

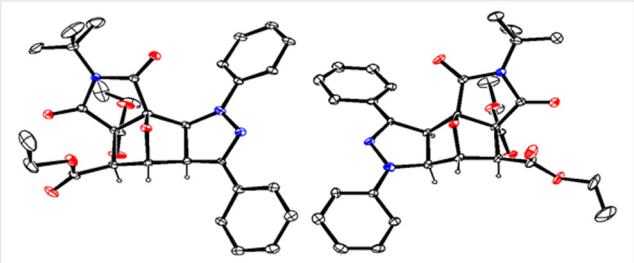


Figure 2 ORTEP diagram for regioisomers of **6b** and **6′b**[17]

We used ^{1}H NMR to relate each spectrum to the appropriate structure of each diastereomer. Bridgehead hydrogen chemical shift helped us to achieve this goal. Figure 3 illustrates a part of ^{1}H NMR of **6a** with its related diastereomeric structure.

In one diastereomer, bridgehead hydrogen is affected by the β-effect of the nitrogen atom (depicted by green). In the other diastereomer, the nitrogen atom is far from bridgehead hydrogen, so the hydrogen does not affect by nitrogen (depicted by red). Therefore, the hydrogen atom circled in green (**6′a**) is more deshielded compare to the hydrogen atom circled in red (**6a**). This pattern is repeated in the rest of the diastereomeric mixtures.

Based on reported publications on IMCR,[18] a proposed mechanism is indicated in Scheme 2. Reasonably, the addition of isocyanide to dialkyl acetylenedicarboxylate affords zwitterion **7**, which is hydrogenated by 2-furancarboxylic acid. Then a Passerini type addition of carboxylate to nitrilium generates intermediate **8**, which leads to intermediate **9** with a Mumm rearrangement. This intermediate produces the product **4** with an intramolecular Diels–Alder reaction. On the other hand, hydrazonoyl chloride converts to its 1,3-dipolar form in the presence of triethylamine. [3+2] Cycloaddition of hydrazonoyl to product **4** affords the final epoxypyrrolo[3,4-*g*]indazole **6**.

Briefly, we have expanded a reported method to synthesize new classes of 1,3-dioxoepoxyisoindoles and epoxypyrrolo[3,4-*g*]indazoles. All starting materials are present in the final products, which were synthesized with minimum use of additives. Catalyst and metal-free condition, one-pot reaction, and stereoselectivity in the first step are some of the advantages of this reaction.

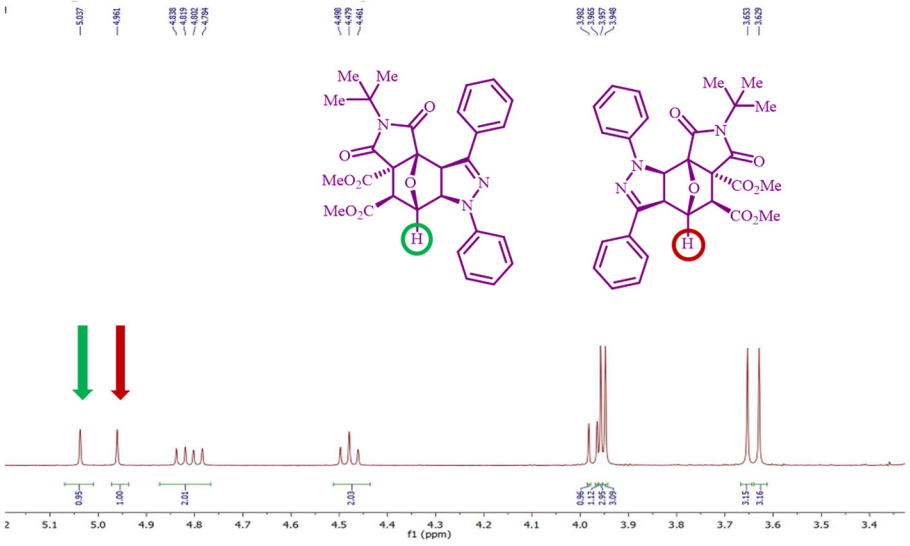
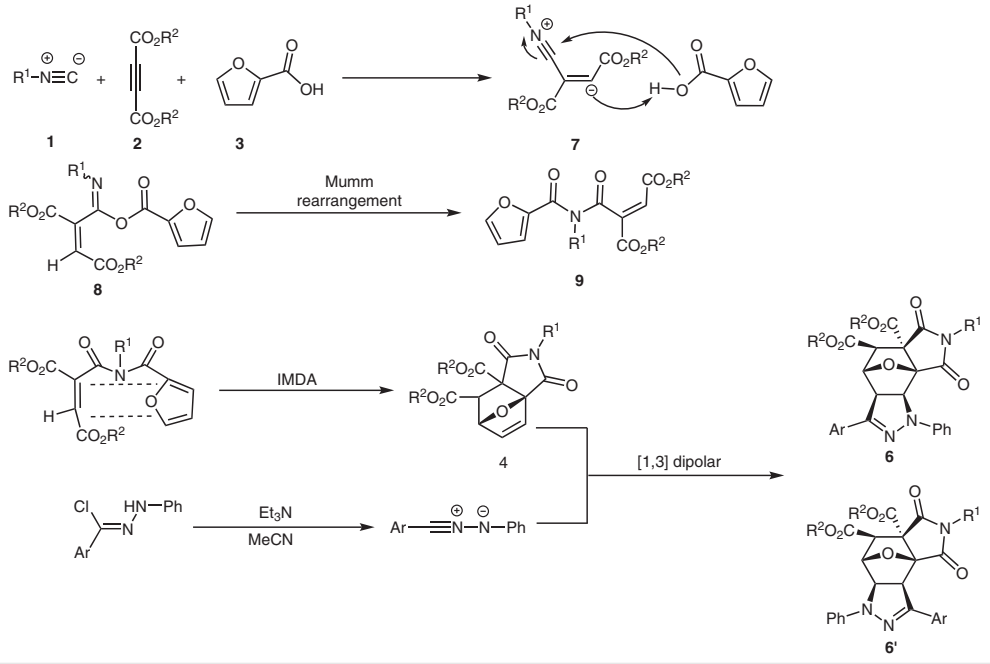


Figure 3 ^{1}H NMR of the mixture of two regioisomers **6a** and **6′a**



Scheme 2 The probable mechanism for generation of **6**

Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded as KBr pellets on a Nicolet FTIR 100 spectrophotometer. ^{1}H NMR (500 MHz, 300 MHz) and ^{13}C NMR (125 MHz, 75 MHz) spectra were obtained using Bruker DRX-500 Avance and Bruker DRX-300 Avance spectrometers. All NMR spectra were recorded at r.t. in DMSO-d_6. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Coupling constants (*J* values) are reported in hertz (Hz), and standard abbreviations were used to indicate spin multiplicities. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a Finnigan-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. CH_2Cl_2 was dried over P_2O_5. THF and toluene were dried using Na as a drying agent. 4-Methoxyphenyl isocyanide was prepared according to the reported procedure. All other chemicals and solvents were purchased from Merck or Aldrich and were used without further purification.

Compounds 4a–f; General Procedure

To a magnetically stirred solution of 2-furancarboxylic acid (112 mg, 1 mmol) and isocyanide **1** (1 mmol) in anhyd MeCN was added dropwise a solution of dialkyl acetylenedicarboxylate **2** (1 mmol) in MeCN (2 mL) at r.t. Then the reaction mixture was refluxed for 4–5 h until the starting materials were consumed. The solvent was removed under reduced pressure and the residue was subjected to column chromatography using EtOAc/hexane (1:5 to 1:3) as eluent to obtain **4a–f**.

Dimethyl (3a*S*,6*R*,7*S*,7a*S*)-2-*tert*-Butyl-1,3-dioxo-2,3,6,7-tetrahydro-3a,6-epoxyisoindole-7,7a(1*H*)-dicarboxylate (4a)

Yield: 288 mg (86%); colorless crystals; mp 109–111 °C.

IR (KBr): 1789 and 1700 (CO–N–CO), 1745 (CO_2Me), 1307 and 1267 (C–O of ester), 1174 and 1125 cm^{-1} (C–O of ether).

^1H NMR (300 MHz, DMSO-d_6): δ = 1.49 (9 H, s, *t*-C_4H_9), 3.25 (1 H, s, CH^7), 3.64 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 5.33 (1 H, d, $^3J_{HH}$ = 1.3 Hz, CH^6), 6.72 (1 H, d, $^3J_{HH}$ = 5.9 Hz, CH^4), 6.74 (1 H, dd, $^3J_{HH}$ = 5.9 Hz, $^3J_{HH}$ = 1.4 Hz, CH^5).

^{13}C NMR (75.46 MHz, DMSO-d_6): δ = 27.5 [C(CH_3)$_3$], 49.1 (CH^7), 51.9 (OCH_3), 54.0 (OCH_3), 58.6 (CMe_3), 68.0 (C^{7a}), 84.57 (CH^6), 90.6 (C^{3a}), 130.2 (CH^5), 140.4 (CH^4), 165.7 (CO_2Me), 169.2 (NCO), 170.3 (CO_2Me), 170.7 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 337 (M^+, 5), 322 (16), 305 (23), 282 (15), 278 (40), 250 (43), 249 (18), 233 (24), 222 (36), 206 (30), 183 (13), 171 (100), 179 (67), 172 (19), 166 (68), 151 (50), 135 (7), 119 (9), 95 (72), 77 (14), 59 (37), 57 (60), 56 (16), 53 (15).

Anal. Calcd for $C_{16}H_{19}NO_7$ (337.33): C, 56.97; H, 5.68; N, 4.15. Found: C, 56.93; H, 5.70; N, 4.11.

Diethyl (3a*S*,6*R*,7*S*,7a*S*)-2-*tert*-Butyl-1,3-dioxo-2,3,6,7-tetrahydro-3a,6-epoxyisoindole-7,7a(1*H*)-dicarboxylate (4b)

Yield: 290 mg (80%); colorless crystals; mp 129–131 °C.

IR (KBr): 1724 (CO_2Me), 1309 and1389 (C–O of ester), 1219 cm^{-1} (C–O of ether).

^1H NMR (300 MHz, DMSO-d_6): δ = 1.14 (3 H, t, $^3J_{HH}$ = 7.00 Hz, OCH_2CH_3), 1.20 (3 H, t, $^3J_{HH}$ = 7.00 Hz, OCH_2CH_3), 1.50 (9 H, s, *t*-C_4H_9), 3.22 (1 H, s, CH^7), 4.07–4.15 (4 H, m, 2 × OCH_2CH_3) 5.31 (1 H, s, CH^6), 6.72 (2 H, s, CH^4 and CH^5).

^{13}C NMR (75.46 MHz, DMSO-d_6): δ = 13.6 (OCH_2CH_3), 13.9 (OCH_2CH_3), 27.5 [C(CH_3)$_3$], 49.1 (CH^7), 58.5 (CMe_3), 60.7 (OCH_2CH_3), 62.9 (OCH_2CH_3), 68.0 (C^{7a}), 84.7 (CH^6), 90.4 (C^{3a}), 130.2 (CH^5), 140.3 (CH^9), 165.0 (CO_2Et), 169.3 (NCO), 169.6 (CO_2Et), 170.6 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 365 (M^+, 8), 319 (18), 292 (47), 264 (63), 263 (23), 247 (21), 236 (44), 220 (34), 211 (12), 199 (51), 193 (89), 190 (18), 171 (60), 166 (100), 165 (80), 143 (64), 137 (19), 125 (15), 121 (10), 95 (75), 57 (45).

Anal. Calcd for $C_{18}H_{23}NO_7$ (365.38): C, 59.17; H, 6.34; N, 3.83. Found: C, 59.09; H, 6.34; N, 3.85.

Dimethyl (3a*S*,6*R*,7*S*,7a*S*)-2-Cyclohexyl-1,3-dioxo-2,3,6,7-tetrahydro-3a,6-epoxyisoindole-7,7a(1*H*)-dicarboxylate (4c)

Yield: 260 mg (72%); colorless crystals; mp 122–124 °C.

IR (KBr): 1720 (CO_2Me), 1364 and 1334 (C–O of ester), 1220 and 1182 cm^{-1} (C–O of ether).

^1H NMR (300 MHz, DMSO-d_6): δ = 1.09–2.49 (10 H, m, 5 × CH_2 of cyclohexyl), 3.29 (1 H, s, CH^7), 3.65 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 3.89 (1 H, tt, $^3J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 3.4 Hz, NCH), 5.36 (1 H, s, CH^6), 6.77 (2 H, s, CH^4 and CH^5).

^{13}C NMR (75.46 MHz, DMSO-d_6): δ = 24.7, 25.0, 25.1, 27.6, 28.3 (5 × CH_2 of cyclohexyl), 48.6 (CH^7), 51.6 (NCH), 52.0 (OCH_3), 54.0 (OCH_3), 67.8 (C^{7a}), 84.7 (C^6), 90.7 (CH^{3a}), 130.2 (CH^5), 140.5 (CH^4), 165.6 (CO_2Me), 168.3 (NCO), 169.9 (CO_2Me), 170.1 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 363 (M^+, 3), 304 (11), 283 (19), 282 (83), 250 (39), 222 (29), 206 (33), 192 (16), 182 (10), 179 (64), 172 (23), 171 (100), 151 (32), 95 (78), 77 (9), 59 (21), 55 (18).

Anal. Calcd for $C_{18}H_{21}NO_7$ (363.36): C, 59.50; H, 5.83; N, 3.85. Found: C, 59.48; H, 5.85; N, 3.85.

Diethyl (3a*S*,6*R*,7*S*,7a*S*)-2-Cyclohexyl-1,3-dioxo-2,3,6,7-tetrahydro-3a,6-epoxyisoindole-7,7a(1*H*)-dicarboxylate (4d)

Yield: 194 mg (50%); colorless crystals; mp 126–128 °C.

IR (KBr): 1741 (CO_2Me), 1307 and 1224 (C–O of ester), 1190 and 1116 cm^{-1} (C-O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.10 (3 H, t, $^3J_{HH}$ = 7.00 Hz, OCH_2CH_3), 1.17 (3 H, t, $^3J_{HH}$ = 7.00 Hz, OCH_2CH_3), 1.13–2.03 (10 H, m, 5 × CH_2 of cyclohexyl), 3.75 (1 H, d, $^3J_{HH}$ = 4.0 Hz, CH^7), 3.91 (1 H, tt, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 3.7 Hz, NCH), 4.01–4.07 (4 H, m, 2 × OCH_2CH_3), 5.45 (1 H, dd, $^3J_{HH}$ = 4.0 Hz, $^4J_{HH}$ = 1.6 Hz, CH^6), 6.75 (1 H, d, $^3J_{HH}$ = 5.8 Hz, CH^4), 6.81 (1 H, dd, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 1.6 Hz, CH^5).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.0 (OCH_2CH_3), 14.3 (OCH_2CH_3), 25.1, 25.5, 25.6, 28.0, 29.0 (5 × CH_2 of cyclohexyl), 51.1 (CH^7), 52.1 (NCH), 61.1 (OCH_2CH_3), 63.1 (OCH_2CH_3), 68.7 (C^{7a}), 83.8 (CH^6), 92.7 (C^{3a}), 129.5 (CH^5), 139.9 (CH^4), 164.9 (CO_2Et), 168.6 (NCO), 168.7 (CO_2Et), 172.0 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 391 (M^+, 3), 318 (19), 264 (18), 238 (13), 236 (21), 220 (71), 199 (21), 193 (100), 192 (21), 171 (19), 165 (63), 143 (28), 137 (19), 125 (12), 95 (93), 81 (17), 69 (14), 55 (21).

Anal. Calcd for $C_{20}H_{25}NO_7$ (391.42): C, 61.37; H, 6.44; N, 3.58. Found: C, 61.22; H, 6.39; N, 3.59.

Dimethyl (3a*S*,6*R*,7*S*,7a*S*)-2-(4-Methoxyphenyl)-1,3-dioxo-2,3,6,7-tetrahydro-3a,6-epoxyisoindole-7,7a(1*H*)-dicarboxylate (4e)

Yield: 255 mg (66%); colorless crystals; mp 117–119 °C.

IR (KBr): 1789 and 1700 (CO–N–CO), 1745 (CO_2Me), 1307 and 1267 (C–O of ester), 1174 and 1125 cm^{-1} (C–O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 3.62 (3 H, s, OCH_3), 3.67 (3 H, s, OCH_3), 3.68 (1 H, s, CH^7) 3.81 (3 H, s, OCH_3), 5.60 (1 H, d, $^3J_{HH}$ = 1.3 Hz CH^6), 6.67 (1 H, d, $^3J_{HH}$ = 5.8 Hz CH^4), 6.74 (1 H, dd, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 1.6 Hz CH^5), 7.01 (2 H, d, $^3J_{HH}$ = 8.4 Hz, 2 × CH of Ar), 7.16 (2 H, d, $^3J_{HH}$ = 8.4 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.9 (CH^7), 52.0 (OCH_3), 53.9 (OCH_3), 55.3 (OCH_3), 68.3 (C^{7a}), 85.2 (CH^6), 90.7 (C^{3a}), 114.3 (2 × CH of Ar), 126.8 (2 × CH of Ar), 129.8 (C_i-N), 131.7 (CH^5), 140.9 (CH^4), 161.2 (C_i-OMe), 166.9 (CO_2Me), 169.4 (NCO), 169.8 (CO_2Me), 171.0 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 387 (M^+, 2), 223 (29), 195 (59), 179 (67), 166 (7), 96 (8), 95 (100), 69 (19).

Anal. Calcd for $C_{19}H_{17}NO_8$ (387.34): C, 58.92; H, 4.42; N, 3.62. Found: C, 58.89; H, 4.43; N, 3.61.

Dimethyl (3a*S*,6*R*,7*S*,7a*S*)-2-(2-Morpholin-4-ylethyl)-1,3-dioxo-2,3,6,7-tetrahydro-3a,6-epoxyisoindole-7,7a(1*H*)-dicarboxylate (4f)

Yield: 210 mg (54%); colorless crystals; mp 104–106 °C.

IR (KBr): 1720 (CO_2Me), 1335 (C–O of ester), 1221 and 1181 cm^{-1} (C-O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.40–2.42 (4 H, m, 2 × NCH_2), 2.80–2.85 (2 H, m, NCH_2), 3.51–3.54 (4 H, m, 2 × OCH_2), 3.59 (1 H, s, CH^7), 3.62 (3 H, s, OCH_3), 3.69 (3 H, s, OCH_3), 3.86–3.90 (2 H, m, NCH_2), 5.62 (1 H, s, CH^6), 6.64 (1 H, d, $^3J_{HH}$ = 5.85 Hz, CH^4), 6.78 (1 H, d, $^3J_{HH}$ = 5.85 Hz, CH^5).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 37.8 (NCH_2), 51.1 (CH^7), 51.9 (OCH_3), 53.6 (2 × NCH_2), 54.1 (OCH_3), 55.1 (NCH_2), 66.5 (2 × OCH_2), 68.2 (C^{7a}), 84.8 (CH^6), 90.6 (C^{3a}), 134.1 (CH^5), 141.0 (CH^4), 167.3 (CO_2Me), 169.4 (NCO), 170.1 (CO_2Me), 171.7 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 394 (M^+, 1), 223 (22), 195 (100), 136 (46), 119 (39), 95 (91), 91 (36), 82 (84), 69 (21).

Anal. Calcd for $C_{18}H_{22}N_2O_8$ (394.38): C, 54.82; H, 5.62; N, 7.10. Found: C, 54.84; H, 5.61; N, 7.06.

Compounds 6a–j; General Procedure

To a magnetically stirred solution of 2-furancarboxylic acid (**3**; 112 mg, 1 mmol) and isocyanide **1** (1 mmol) in anhyd MeCN was added dropwise a solution of dialkyl acetylenedicarboxylate **2** (1 mmol) in MeCN (2 mL) at r.t. Then, the reaction mixture was refluxed for 4–5 h until the starting materials were consumed. Then, hydrazonoyl chloride **5** (1 mmol) was added to the reaction mixture followed by the dropwise addition of Et_3N (1.05 mmol). The reaction mixture was left at r.t. until the consumption of hydrazonoyl chloride. The solvent was evaporated under reduced pressure and the residue was washed with H_2O and EtOH and recrystallized from EtOH to obtain the final product.

Dimethyl (3a*S*,4*R*,5*S*,5a*S*,8a*R*,8b*S*)-7-*tert*-Butyl-6,8-dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-1*H*-4,8a-epoxypyrrolo[3,4-*g*]indazole-5,5a(6*H*)-dicarboxylate (6a)

Yield: 425 mg (80%): pale yellow powder; mp 216–218 °C.

IR (KBr): 1746 (COO), 1592 and 1493 (Ar), 1328 and 1278 (C–O of ester), 1130 and 1209 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.38 (9 H, s, *t*-C_4H_9), 3.62 (3 H, s, OCH_3), 3.94 (3 H, s, OCH_3), 3.96 (1 H, s, CH^5), 4.46 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 4.79 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.96 (1 H, s, CH^4), 6.83 (1 H, t, $^3J_{HH}$ = 8.0 Hz, CH_p of Ph), 7.02 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.26 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.27 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.38 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH_m of Ph), 7.57 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH_o of Ph).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 27.9 [$C(CH_3)_3$], 52.3 (CH^5), 52.4 (OCH_3), 55.1 (OCH_3), 57.7 (CH^{3a}), 59.4 (CMe_3), 65.1 (CH^{8b}), 68.4 (C^{5a}), 85.6 (CH^4), 90.6 (C^{8a}), 113.2 (2 × CH_o of Ph), 119.8 (CH_p of Ph), 126.7 (2 × CH_o of Ph), 128.4 (2 × CH_m of Ph), 129.2 (2 × CH_m of Ph), 129.6 (CH_p of Ph), 133.1 (C_i-C=N), 145.1 (C_i-N), 146.2 (C=N), 166.0 (CO_2Me), 168.0 (NCO) 170.1 (CO_2Me), 170.7 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 531 (M^+, 100), 384 (16), 343 (8), 245 (77), 342 (34), 315 (9), 314 (29), 273 (10), 260 (7), 246 (15), 245 (77), 233 (53), 221 (19), 220 (21), 219 (16).

Anal. Calcd for $C_{29}H_{29}N_3O_7$ (531.20): C, 65.53; H, 5.50; N, 7.91. Found: C, 65.49; H, 5.51; N, 7.95.

Dimethyl (3a*R*,4*S*,5*S*,5a*S*,8a*S*,8b*R*)-7-*tert*-Butyl-6,8-dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6′a)

Yield: 425 mg (80%); pale yellow powder; mp 216–218 °C.

IR (KBr): 1746 (COO), 1592 and 1493 (Ar), 1328 and 1278 (C–O of ester), 1130 and 1209 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.44 (9 H, s, *t*-C_4H_9), 3.65 (3 H, s, OCH_3), 3.95 (3 H, s, OCH_3), 3.98 (1 H, s, CH^5), 4.48 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.82 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 5.03 (1 H, s, CH^4), 6.83 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH_p of Ph), 7.27 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH_o of Ph), 7.31 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.37 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH_m of Ph), 7.44 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH_m of Ph), 7.88 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH_o of Ph).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 27.9 [$C(CH_3)_3$], 50.1 (CH^5), 51.4 (CH^{8b}), 52.7 (OCH_3), 55.0 (OCH_3), 59.3 (CMe_3), 69.7 (C^{5a}), 70.1 (CH^{3a}), 84.7 (CH^4), 90.7 (C^{8a}), 114.2 (2 CH_o of Ph), 119.9 (CH_p of Ph), 126.3 (2 × CH_o of Ph), 128.6 (2 × CH_m of Ph), 128.9 (2 × CH_m of Ar), 129.5 (CH_p of Ph), 131.1 (C_i-C=N), 143.8 (C_i-N), 148.5 (C=N), 166.1 (CO_2Me), 168.4 (NCO) 170.2 (CO_2Me), 170.8 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 531 (M^+, 100), 384 (16), 343 (8), 245 (77), 342 (34), 315 (9), 314 (29), 273 (10), 260 (7), 246 (15), 245 (77), 233 (53), 221 (19), 220 (21), 219 (16).

Anal. Calcd for $C_{29}H_{29}N_3O_7$ (531.20): C, 65.53; H, 5.50; N, 7.91. Found: C, 65.49; H, 5.51; N, 7.95.

Diethyl (3a*S*,4*R*,5*S*,5a*S*,8a*R*,8b*S*)-7-(*tert*-Butyl)-6,8-dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-1*H*-4,8a-epoxypyrrolo[3,4-*g*]indazole-5,5a(6*H*)-dicarboxylate (6b)

Yield: 419 mg (75%); pale yellow powder; mp 223–224 °C.

IR (KBr): 1729 (COO), 1496 and 1527 (Ar), 1336 and 1280 (C–O of ester), 1207 and 1126 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.23 (3 H, dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 7.4 Hz, OCH_2CH_3), 1.35 (3 H, dd, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =7.0 Hz, OCH_2CH_3), 1.48 (9 H, s, *t*-C_4H_9), 4.0 (1 H, s, CH^5), 4.35–4.42 (4 H, m, 2 × OCH_2CH_3), 4.47 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 4.78 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.97 (1 H, s, CH^4), 6.85 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.06 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.28 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.33 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.38 (1 H, t, $^3J_{HH}$ = 8.0 Hz, CH_p of Ph), 7.61 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH_o of Ph).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.18 (OCH_2CH_3), 14.31 (OCH_2CH_3), 27.91 [$C(CH_3)_3$], 52.85 (CH^5), 57.65 (CH^{3a}), 59.34 (CMe_3), 61.16 (OCH_2CH_3), 64.33 (OCH_2CH_3), 65.24 (CH^{8b}), 68.50 (C^{5a}), 84.79 (CH^4), 90.45 (C^{8a}), 113.25 (2 × CH_o of Ph), 119.94 (CH_p of Ph), 126.76 (2 × CH_o of Ph), 128.62 (2 × CH_m of Ph), 129.21 (2 × CH_m of Ar), 129.53 (CH_p of Ph), 133.08 (C_i-C=N), 145.09 (C_i-N), 146.16 (C=N), 165.17 (CO_2Et), 168.56 (NCO) 169.61 (CO_2Me), 170.62 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 559 (M^+, 66), 384 (13), 342 (16), 314 (17), 273 (13), 246 (22), 245 (100), 233 (45), 221 (19), 220 (20), 219 (15), 234 (8).

Anal. Calcd for $C_{31}H_{33}N_3O_7$ (559.23): C, 66.53; H, 5.94; N, 7.51. Found: C, 66.58; H, 5.92; N, 7.50.

Crystal Data for 6b

$C_{31}H_{33}N_3O_7{\cdot}C_{31}H_{33}N_3O_7{\cdot}2(C_2H_6O_1S_1)$: M_W = 637.42, triclinic, P-1, *a* = 11.351(2) Å, *b* = 17.285(3) Å, *c* = 19.727(4) Å, α = 65.15(3), β = 82.29(3), γ = 73.42(3), *V* = 3365.6(14) Å^3, *Z* = 4, *Dc* = 1.258 mg/m^3, F (000) = 1352, radiation, Mo Kα (λ = 0.71073 Å), 1.872 ≤ 2θ ≤ 23.255, intensity data were collected at 293(2) K with a Bruker APEX area-detector diffractometer, and employing ω/2θ scanning technique, in the range of −12 ≤ *h* ≤ 12, −19 ≤ *k* ≤ 19, −21 ≤ *l* ≤ 21. The structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 9536 observed reflections with *R* (into) = 0.1605 by a full-matrix least-squares technique converged to *R* = 0.0879 and *wR*2 = 0.2535 [*I*>2σ(*I*)].

Diethyl (3a*R*,4*S*,5*S*,5a*S*,8a*S*,8b*R*)-7-*tert*-Butyl-6,8-dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6′b)

Yield: 419 mg (75%); pale yellow powder; mp 223–224 °C.

IR (KBr): 1729 (COO), 1496 and 1527 (Ar), 1336 and 1280 (C–O of ester), 1207 and 1126 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.23 (3 H, dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 7.4 Hz, OCH_2CH_3), 1.35 (3 H, dd, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.42 (9 H, s, *t*-C_4H_9), 3.98 (1 H, s, CH^5), 4.09–4.13 (4 H, m, 2 × OCH_2CH_3), 4.50 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.85 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 5.05 (1 H, s, CH^4), 6.85 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.27 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.30 (1 H, t, $^3J_{HH}$ = 8.0 Hz, CH_p of Ph), 7.37 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.45 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH_m of Ph), 7.91 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH_o of Ph).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.18 (OCH_2CH_3), 14.33 (OCH_2CH_3), 27.87 [$C(CH_3)_3$], 50.24 (CH^5), 51.49 (CH^{8b}), 59.25 (CMe_3), 61.16 (OCH_2CH_3), 64.29 (OCH_2CH_3), 69.65 (C^{5a}), 70.15 (CH^{3a}), 85.57 (CH^4), 90.45 (C^{8a}), 114.21 (2 × CH_o of Ph), 119.79 (CH_p of Ph), 126.27 (2 × CH_o of Ph), 128.29 (2 × CH_m of Ph), 128.83 (2 × CH_m of Ar), 129.58 (CH_p of Ph), 131.07 (C_i-C=N), 143.77 (C_i-N), 148.57 (C=N), 165.26 (CO_2Et), 168.19 (NCO) 169.55 (CO_2Me), 170.69 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 559 (M^+, 66), 384 (13), 342 (16), 314 (17), 273 (13), 246 (22), 245 (100), 233 (45), 221 (19), 220 (20), 219 (15), 234 (8).

Anal. Calcd for $C_{31}H_{33}N_3O_7$ (559.23): C, 66.53; H, 5.94; N, 7.51. Found: C, 66.58; H, 5.92; N, 7.50.

Crystal Data for 6′b

$C_{31}H_{33}N_3O_7$,$C_{31}H_{33}N_3O_7$,2($C_2H_6O_1S_1$): M_W = 637.42, triclinic, *P*-1, *a* = 11.351(2) Å, *b* = 17.285(3) Å, *c* = 19.727(4) Å, α = 65.15(3), β = 82.29(3), γ = 73.42(3), *V* = 3365.6(14) Å^3, *Z* = 4, *Dc* = 1.258 mg/m^3, *F*(000) = 1352, radiation, Mo Kα (λ = 0.71073 Å), 1.872 ≤ 2θ ≤ 23.255, intensity data were collected at 293(2) K with a Bruker APEX area-detector diffractometer, and employing ω/2θ scanning technique, in the range of −12 ≤ *h* ≤12, −19 ≤ *k* ≤ 19, −21 ≤ *l* ≤ 21; the structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 9536 observed reflections with *R* (into) = 0.1605 by a full-matrix least-squares technique converged to *R* = 0.0879 and *wR*2 = 0.2535 [*I*>2σ(*I*)].

Dimethyl (3a*S*,4*R*,5*R*,5a*R*,8a*R*,8b*S*)-7-Cyclohexyl-6,8-dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6c)

Yield: 378 mg (68%); pale yellow powder; mp 184–186 °C.

IR (KBr): 1730 (COO), 1595 and 1497 (Ar), 1357 and 1277 (C–O of ester), 1221 and 1116 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.17–1.30 (2 H, m, CH_2 of cyclohexyl), 1.43–1.58 (4 H, m, 2 × CH_2 of cyclohexyl), 1.69–1.93 (4 H, m, 2 × CH_2 of cyclohexyl), 3.63 (3 H, s, OCH_3), 3.74–3.82 (1 H, m, NCH of cyclohexyl), 3.93 (3 H, s, OCH_3), 4.02 (1 H, s, CH^5), 4.50 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 4.84 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.99 (1 H, s, CH^4), 6.83 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH_p of Ph), 7.27 (2 H, d, $^3J_{HH}$ = 6.0 Hz, 2 × CH_o of Ph), 7.32 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.43 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.57 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH_m of Ph), 7.89 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH_o of Ph).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.0, 25.1, 25.5, 28.7, 28.7 (5 × CH_2 of cyclohexyl), 49.9 (NCH of cyclohexyl), 52.3 (CH^5), 52.4 (OCH_3), 55.1 (OCH_3), 57.6 (CH^{3a}), 65.2 (CH^{8b}), 68.2 (C^{5a}), 85.1 (CH^4), 91.0 (C^{8a}), 114.0 (2 × CH_o of Ph), 119.9 (CH_p of Ph), 126.7 (2 × CH_o of Ph), 128.6 (2 × CH_m of Ph), 129.0 (2 × CH_m of Ph), 129.5 (CH_p of Ph), 131.1 (C_i-C=N), 143.8 (C_i-N), 146.0 (C=N), 165.9 (CO_2Me), 167.6 (CON) 169.96 (CO_2Me), 170.0 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 557 (M^+, 100), 495 (10), 481 (12), 466 (20), 424 (25), 396 (16), 343 (9), 342 (38), 314 (14), 273 (9), 246 (15), 245 (72), 233 (39), 221 (15), 220 (20), 219 (16), 77 (17).

Dimethyl (3a*S*,4*R*,5*S*,5a*S*,8a*R*,8b*S*)-7-Cyclohexyl-6,8-dioxo-1,3-diphenyl-3a,4,5,7,8,8b-hexahydro-1*H*-4,8a-epoxypyrrolo[3,4-*g*]indazole-5,5a(6*H*)-dicarboxylate (6′c)

Yield: 378 mg (68%); white powder; mp 184–186 °C.

IR (KBr): 1730 (COO), 1595 and 1497 (Ar), 1357 and 1277 (C–O of ester), 1221 and 1116 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.17–1.30 (2 H, m, CH_2 of cyclohexyl), 1.43–1.58 (4 H, m, 2 × CH_2 of cyclohexyl), 1.69–1.93 (4 H, m, 2 × CH_2 of cyclohexyl), 3.65 (3 H, s, OCH_3), 3.74–3.82 (1 H, m, NCH of cyclohexyl), 3.94 (3 H, s, OCH_3), 4.00 (1 H, s, CH^5), 4.54 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.84 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 5.06 (1 H, s, CH^4), 6.83 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH_p of Ph), 7.02 (2 H, d, $^3J_{HH}$ = 9.0 Hz, 2 × CH_o of Ph), 7.26 (2 H, t, $^3J_{HH}$ = 7.0 Hz, 2 × CH_m of Ph), 7.27 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH_p of Ph), 7.37 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH_m of Ph), 7.57 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.5, 25.4, 25.5, 27.9, 28.0 (5 × CH_2 of cyclohexyl), 51.5 (CH of cyclohexyl), 52.2 (CH^5), 52.4 (OCH_3), 55.2 (OCH_3), 56.5 (CH^{8b}), 69.5 (C^{5a}), 69.9 (CH^{3a}), 85.9 (CH^4), 90.8 (C^{8a}), 113.2 (2 × CH_o of Ph), 119.8 (CH_p of Ph), 126.2 (2 × CH_o of Ph), 128.5 (2 × CH_m of Ph), 129.2 (2 × CH_m of Ph), 129.6 (CH_p of Ph), 133.0 (C_i-C=N), 145.0 (C_i-N), 148.4 (C=N), 166.0 (CO_2Me), 167.2 (NCO) 169.98 (CO_2Me), 170.0 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 557 (M^+, 100), 495 (10), 481 (12), 466 (20), 424 (25), 396 (16), 343 (9), 342 (38), 314 (14), 273 (9), 246 (15), 245 (72), 233 (39), 221 (15), 220 (20), 219 (16), 77 (17).

Anal. Calcd for $C_{31}H_{31}N_3O_7$ (557.22): C, 66.78; H, 5.60; N, 7.54. Found: C, 66.75; H, 5.62; N, 7.55.

Dimethyl (3a*S*,4*R*,5*R*,5a*R*,8a*R*,8b*S*)-7-*tert*-Butyl-1-(4-chlorophenyl)-6,8-dioxo-3-phenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6d)

Yield: 468 mg (83%); pale yellow powder; mp 189–190 °C.

IR (KBr): 1720 (COO), 1598 and 1492 (Ar), 1335 and 1280 (C–O of ester), 1216 and 1126 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.44 (9 H, s, *t*-C_4H_9), 3.63 (3 H, s, OCH_3), 3.94 (3 H, s, OCH_3), 3.97 (1 H, s, CH^5), 4.47 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 4.82 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.96 (1 H, s, CH^4), 6.85 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.02 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.26 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.48 (2 H, d, $^3J_{HH}$ = 8.5 Hz, 2 × CH of Ar), 7.91 (2 H, d, $^3J_{HH}$ = 8.5 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 27.9 [$C(CH_3)_3$], 52.3 (OCH_3), 52.6 (CH^5), 55.1 (OCH_3), 57.6 (CH^{3a}), 59.4 (CMe_3), 65.2 (CH^{8b}), 68.4 (C^{5a}), 84.7 (CH^4), 90.7 (C^{8b}), 114.2 (2 × CH_o of Ph), 120.1 (CH_p of Ph), 128.4 (2 × CH of Ar), 129.0 (2 × CH_m of Ph), 129.2 (2 × CH of Ar), 130.0 (C_i-C=N), 134.0 (C_i-Cl), 145.9 (C_i-N), 147.4 (C=N), 166.0 (CO_2Me), 168.3 (NCO) 170.1 (CO_2Me), 170.6 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 565 (M^+, 82), 566 (M^+ + 1, 25), 567 (M^+ + 2, 30), 416 (11), 414 (26), 338 (15), 307 (16), 281 (34), 280 (23), 279 (100), 269 (27), 267 (82), 257 (9), 255 (29), 254 (25), 246 (30), 218 (17), 204 (10), 202 (14), 164 (11), 152 (12), 87 (11), 77 (25).

Anal. Calcd for $C_{29}H_{28}ClN_3O_7$ (565.16): C, 61.54; H, 4.99; N, 7.42. Found: C, 61.55; H, 5.01; N, 7.40.

Dimethyl (3a*R*,4*S*,5*R*,5a*R*,8a*S*,8b*R*)-3-(4-Chlorophenyl)-7-cyclohexyl-6,8-dioxo-1-phenyl-3a,4,5,7,8,8b-hexahydro-1*H*-4,8a-epoxypyrrolo[3,4-*g*]indazole-5,5a(6*H*)-dicarboxylate (6′e)

Yield: 390 mg (66%); pale yellow powder; mp 204–206 °C.

IR (KBr): 1727 (COO), 1601 and 1495 (Ar), 1372 and 1281 (C–O of ester), 1221 and 1129 cm^{-1} (C–O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.16–1.25 (2 H, m, CH_2 of cyclohexyl), 1.42–1.55 (4 H, m, 2 × CH_2 of cyclohexyl), 1.68–1.97 (4 H, m, 2 × CH_2 of cyclohexyl), 3.65 (3 H, s, OCH_3), 3.73–3.80 (1 H, m, NCH of cyclohexyl), 3.94 (3 H, s, OCH_3), 4.00 (1 H, s, CH^5), 4.56 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.87 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 5.05 (1 H, s, CH^4), 6.85 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH_p of Ph), 7.26–7.28 (4 H, m, 4 × CH of Ph), 7.46 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 × CH of Ar), 7.55 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.0, 25.4, 25.5, 27.9, 28.7 (5 × CH_2 of cyclohexyl), 49.9 (CH^5), 51.4 (NCH of cyclohexyl), 52.3 (CH^{8b}), 52.4 (OCH_3), 55.3 (OCH_3), 69.6 (C^{5a}), 69.9 (CH^{3a}), 85.9 (CH^4), 90.7 (C^{8a}), 113.3 (2 × CH_o of Ph), 120.0 (CH_p of Ph), 127.8 (2 × CH of Ar), 128.6 (2 × CH_m of Ph), 129.6 (2 × CH of Ar), 132.0 (C_i-C=N), 133.0 (C_i-Cl), 143.5 (C_i-N), 144.0 (C=N), 165.9 (CO_2Me), 167.3 (NCO), 169.9 (CO_2Me), 170.0 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 593 (M^+, 100), 594 (M^+ + 1, 38), 595 (M^+ + 2, 41), 420 (23), 419 (16), 418 (51), 390 (17), 378 (21), 376 (58), 350 (26), 348 (56), 281 (35), 279 (90), 267 (32), 255 (50), 254 (57), 70 (35), 57 (45).

Anal. Calcd for $C_{31}H_{30}ClN_3O_7$ (593.05): C, 62.89; H, 5.11; N, 7.1. Found: C, 62.86; H, 5.12; N, 7.2.

Dimethyl (3a*R*,4*S*,5*R*,5a*R*,8a*S*,8b*R*)-7-*tert*-Butyl-3-(4-nitrophenyl)-6,8-dioxo-1-phenyl-3a,4,5,7,8,8b-hexahydro-1*H*-4,8a-epoxypyrrolo[3,4-*g*]indazole-5,5a(6*H*)-dicarboxylate (6′f)

Yield: 443 mg (77%); orange powder; mp 239–240 °C.

IR (KBr): 1750 (COO), 1593 and 1498 (Ar), 1550 and 1389 (NO_2), 1331 and 1275 (C–O of ester), 1218 and 1143 cm^{-1} (C–O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.37 (9 H, s, *t*-C_4H_9), 3.65 (3 H, s, OCH_3), 3.98 (3 H, s, OCH_3), 3.99 (1 H, s, CH^5), 4.58 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.99 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 5.07 (1 H, s, CH^4), 6.91 (1 H, t, $^3J_{HH}$ = 7.0 Hz, CH_p of Ph), 7.30 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.35 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.76 (2 H, t, $^3J_{HH}$ = 9.0 Hz, 2 × CH of Ar), 8.26 (2 H, d, $^3J_{HH}$ = 9.0 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 27.8 [C(CH_3)$_3$], 50.8 (CH^5), 52.4 (OCH_3), 55.2 (OCH_3), 56.5 (CH^{8b}), 59.5 (CMe_3), 70.0 (C^{5a}), 70.1 (CH^{3a}), 85.5 (CH^4), 90.6 (CH^{8a}), 113.7 (2 × CH_o of Ph), 120.9 (CH_p of Ph), 123.8 (2 × CH of Ar), 126.8 (2 × CH of Ar), 129.7 (2 × CH_m of Ph), 139.7 (C_i-C=N), 142.7 (C_i-NO_2), 143.1 (C_i-N), 146.7 (C=N), 165.9 (CO_2Me), 168.3 (NCO), 170.0 (CO_2Me), 170.7 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 576 (M^+, 100), 443 (17), 429 (57), 418 (29), 401 (19), 400 (20), 388 (20), 387 (79), 359 (63), 341 (20), 313 (29), 266 (72), 265 (37) 251 (22), 164 (21), 153 (20), 105 (35), 81 (67), 77 (64), 57 (42).

Anal. Calcd for $C_{29}H_{28}N_4O_9$ (576.19): C, 60.41; H, 4.90; N, 9.72. Found: C, 60.40; H, 4.94; N, 9.71.

Dimethyl (3a*R*,4*S*,5*R*,5a*R*,8a*S*,8b*R*)-7-Cyclohexyl-3-(4-nitrophenyl)-6,8-dioxo-1-phenyl-3a,4,5,7,8,8b-hexahydro-1*H*-4,8a-epoxypyrrolo[3,4-*g*]indazole-5,5a(6*H*)-dicarboxylate (6′g)

Yield: 421 mg (70%); orange powder; mp 252–254 °C.

IR (KBr): 1737 (COO), 1595 and 1441 (NO_2), 1341 (C–O of ester), 1218 cm^{-1} (C–O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.22–1.26 (2 H, m, CH_2 of cyclohexyl), 1.45–1.56 (4 H, m, 2 × CH_2 of cyclohexyl), 1.7–1.9 (4 H, m, 2 × CH_2 of cyclohexyl), 3.67 (3 H, s, OCH_3), 3.74–3.78 (1 H, m, NCH of cyclohexyl), 3.99 (3 H, s, OCH_3), 4.05 (1 H, s, CH^5), 4.67 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 5.04 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 5.11 (1 H, s, CH^4), 6.93 (1 H, t, $^3J_{HH}$ = 7.4 Hz, CH_p of Ph), 7.32 (2 H, t, $^3J_{HH}$ = 7.0 Hz, 2 × CH_m of Ph), 7.37 (2 H, d, $^3J_{HH}$ = 9.0 Hz, 2 × CH_o of Ph), 7.77 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH of Ar), 8.26 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.0, 25.4, 25.4, 27.9, 28.7 (5 × CH_2 of cyclohexyl), 51.0 (NCH of cyclohexyl), 52.3 (CH^5), 52.5 (OCH_3), 55.4 (OCH_3), 60.2 (CH^{8b}), 69.8 (C^{5a}), 70.0 (CH^{3a}), 85.9 (CH^4), 90.8 (C^{8b}), 113.7 (2 CH_o of Ph), 120.9 (CH_p of Ph), 123.9 (2 × CH of Ar), 126.8 (2 CH of Ar), 129.7 (2 × CH_m of Ph), 139.6 (C_i-C=N), 142.6 (C_i-NO_2), 143.0 (C_i-N), 146.7 (C=N), 165.7 (CO_2Me), 167.5 (NCO), 169.9 (CO_2Me), 169.9 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 602 (M^+, 100), 511 (35), 469 (60), 411 (20), 387 (43), 341 (22), 290 (92), 278 (34), 266 (32), 265 (41), 244 (38), 219 (22), 218 (21), 164 (29), 153 (39), 81 (22), 77 (68), 67 (42), 59 (34), 55 (52).

Anal. Calcd for $C_{29}H_{28}N_4O_9$ (602.20): C, 61.79; H, 5.02; N, 9.30. Found: C, 61.80; H, 5.04; N, 9.32.

Dimethyl (3a*S*,4*R*,5*R*,5a*R*,8a*R*,8b*S*)-7-*tert*-Butyl-1-(4-*tert*-butylphenyl)-6,8-dioxo-3-phenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6h)

Yield: 363 mg (62%), white powder; mp 211–212 °C.

IR (KBr): 1724 (COO), 1599 and 1496 (Ar), 1340 and 1276 (C–O of ester), 1221 and 1124 cm^{-1} (C–O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.29 (9 H, s, *t*-C_4H_9), 1.45 (9 H, s, *t*-C_4H_9), 3.62 (3 H, s, OCH_3), 3.94 (3 H, s, OCH_3), 3.97 (1 H, s, CH^5), 4.48 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 4.76 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.95 (1 H, s, CH^4), 6.83 (1 H, t, $^3J_{HH}$ = 8.0 Hz, CH_p of Ph), 7.01 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.25 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.44 (2 H, t, $^3J_{HH}$ = 8.4 Hz, 2 × CH of Ar), 7.80 (2 H, d, $^3J_{HH}$ = 8.4 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 27.9 [C(CH_3)$_3$], 31.4 [C(CH_3)$_3$], 34.9 (CMe_3), 52.3 (OCH_3), 52.6 (CH^5), 55.0 (OCH_3), 57.8 (CH^{3a}), 60.0 (CMe_3), 65.0 (CH^{8b}), 68.5 (C^{5a}), 84.8 (CH^4), 90.7 (C^{8a}), 114.1 (2 × CH_o of Ph), 119.8 (CH_p of Ph), 126.0 (2 × CH of Ar), 126.6 (2 × CH of Ar), 128.3 (C_i-C=N), 128.9 (2 × CH_m of Ph), 146.4 (C_i-N), 148.5 (C=N), 152.2 (C_i-CMe_3), 166.0 (CO_2Me), 168.4 (NCO), 170.1 (CO_2Me), 170.7 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 587 (M^+, 60), 360 (14), 346 (13), 345 (52), 313 (16), 301 (12), 290 (23), 289 (100), 277 (17), 261 (38), 245 (30), 233 (24), 161 (16), 57 (34).

Anal. Calcd for $C_{33}H_{37}N_3O_7$ (587.67): C, 67.45; H, 6.35; N, 7.15. Found: C, 67.49; H, 6.31; N, 7.13.

Dimethyl (3a*S*,4*R*,5*R*,5a*R*,8a*R*,8b*S*)-1-(4-*tert*-Butylphenyl)-7-cyclohexyl-6,8-dioxo-3-phenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6i)

Yield: 361 mg (59%); white powder; mp 214–216 °C.

IR (KBr): 1745 (COO), 1598 and 1502 (Ar), 1328 (C–O of ester), 1208 cm^{-1} (C–O of ether).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.23–1.28 (2 H, m, CH_2 of cyclohexyl), 1.3 (9 H, s, *t*-C_4H_9), 1.38–1.60 (4 H, m, 2 × CH_2 of cyclohexyl), 1.74–1.95 (4 H, m, 2 × CH_2 of cyclohexyl), 3.64 (3 H, s, OCH_3), 3.73–3.80 (1 H, m, NCH of cyclohexyl), 3.94 (3 H, s, OCH_3), 4.03 (1 H, s, CH^5), 4.51 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{3a}), 4.83 (1 H, d, $^3J_{HH}$ = 9.0 Hz, CH^{8b}), 4.99 (1 H, s,

CH[4]), 6.85 (1 H, t, $^3J_{HH}$ = 8.0 Hz, CH_p of Ph), 7.02 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH_o of Ph), 7.26 (2 H, t, $^3J_{HH}$ = 8.0 Hz, 2 × CH_m of Ph), 7.45 (2 H, t, $^3J_{HH}$ = 7.5 Hz, 2 × CH of Ar), 7.82 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.0, 25.5, 25.5, 28.0, 28.7 (5 × CH_2 of cyclohexyl), 31.4 [C(CH_3)$_3$], 34.9 (CMe_3), 52.3 (NCH of cyclohexyl), 52.36 (CH[5]), 52.38 (OCH_3), 55.1 (OCH_3), 57.6 (CH[3a]), 65.1 (CH[8b]), 68.3 (C[5a]), 85.1 (CH[4]), 91.0 (C[8a]), 114.0 (2 × CH_o of Ph), 119.8 (CH_p of Ph), 126.0 (2 × CH of Ar), 126.6 (2 × CH_m of Ph), 128.3 (C_i-C=N), 129.0 (2 × CH of Ar), 152.3 (C_i-CMe_3), 146.2 (C_i-N), 148.5 (C=N), 165.9 (CO_2Me), 167.6 (NCO), 169.8 (CO_2Me), 170.0 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 613 (M$^+$, 6), 551 (9.8), 392 (10), 377 (24), 345 (9), 304 (41), 290 (23), 289 (100), 276 (14), 261 (37), 245 (9), 161 (20), 152 (12), 130 (9), 116 (11), 91 (12), 77 (30), 55 (8).

Anal. Calcd for $C_{35}H_{39}N_3O_7$ (613.28): C, 68.50; H, 6.41; N, 6.85. Found: C, 68.49; H, 6.43; N, 6.87.

Dimethyl (3a*S*,4*R*,5*R*,5a*R*,8a*R*,8b*S*)-7-*tert*-Butyl-1-(4-fluorophenyl)-6,8-dioxo-3-phenyl-3a,4,5,7,8,8b-hexahydro-3*H*-4,8a-epoxypyrrolo[3,4-*e*]indazole-5,5a(6*H*)-dicarboxylate (6j)

Yield: 292 mg (53%); pale yellow powder; mp 205–206 °C.

IR (KBr): 1738 (COO), 1366 (C–O of ester), 1217 cm^{-1} (C–O of ether).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.44 (9 H, s, *t*-C_4H_9), 3.63 (3 H, s, OCH_3), 3.94 (3 H, s, OCH_3), 3.97 (1 H, s, CH[5]), 4.48 (1 H, m, CH[3a]), 4.81 (1 H, d, $^3J_{HH}$ = 8.6 Hz, CH[8b]), 4.95 (1 H, s, CH[4]), 6.85 (1 H, dd, $^3J_{HF}$ = 12.4 Hz, $^3J_{HH}$ = 7.2 Hz, CH of Ar), 7.02 (2 H, dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HF}$ = 3.1 Hz, 2 × CH of Ar), 7.24–7.29 (3 H, m, 2 × CH_m of Ph and CH_p of Ph), 7.48 (1 H, d, $^3J_{HH}$ = 8.6 Hz, CH_o of Ph), 7.91 (2 H, d, $^3J_{HH}$ = 8.6 Hz, CH_o of Ph), 7.95 (1 H, dd, $^3J_{HF}$ = 12.4 Hz, $^3J_{HH}$ = 7.2 Hz, CH of Ar).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 27.9 [C(CH_3)$_3$], 52.3 (OCH_3), 52.7 (CH[5]), 55.0 (OCH_3), 57.6 (CH[3a]), 59.4 (CMe_3), 65.2 (CH[8b]), 68.4 (C[5a]), 84.7 (CH[4]), 90.7 (C[8a]), 114.19 (2 × CH_o of Ph), 120.08 (CH_p of Ph), 128.38 (2 × CH of Ar), 129.0 (2 × CH_m of Ph), 129.2 (2 × CH of Ar), 130.0 (C_i-C=N), 134.0 (C_i-F), 145.9 (C_i-N), 147.5 (C=N), 166.0 (CO_2Me), 168.3 (NCO), 170.1 (CO_2Me), 170.7 (NCO).

MS (EI, 70 eV): *m*/*z* (%) = 549 (M$^+$, 61), 402 (13), 360 (27), 332 (20), 323 (13), 291 (16), 281 (15), 279 (31), 267 (29), 266 (34), 263 (95), 251 (100), 239 (30), 238 (36), 153 (20), 95 (19), 81 (41).

Anal. Calcd for $C_{29}H_{28}FN_3O_7$ (549.56): C, 63.38; H, 5.14; N, 7.65. Found: C, 63.42; H, 5.13; N, 7.67.

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1612426.

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