An Efficient, High-Yield, One-Pot Preparation of Pyrrolo[2,3-*b*]pyridines by a Consecutive Aza Wittig Reaction–Electrocyclic Ring Closure–Intramolecular Amination Process

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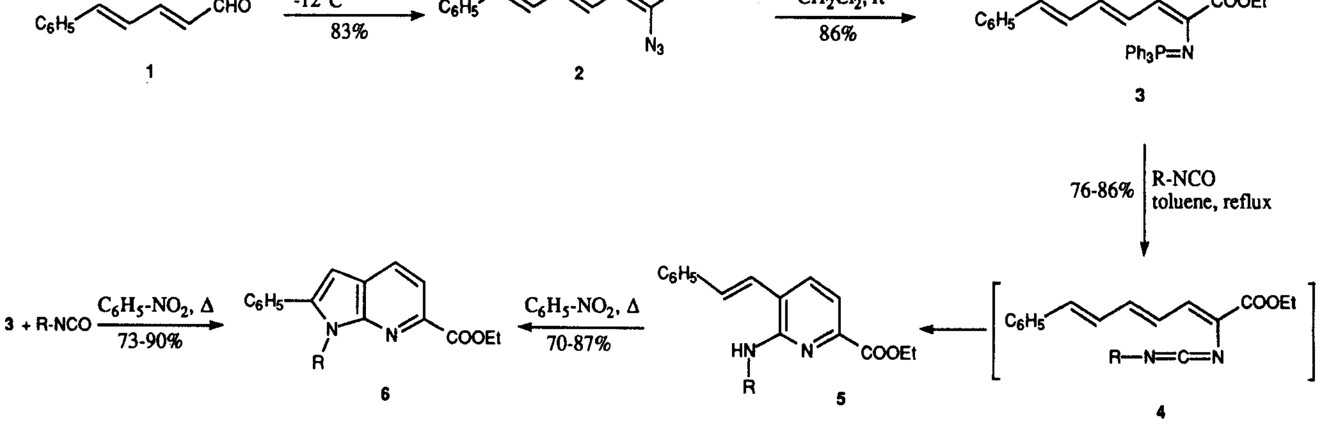
Aza Wittig reaction of iminophosphoranes derived from ethyl (*E,E,E*)-1-azido-7-phenyl-2,4,6-heptatrienoate with aromatic isocyanates in nitrobenzene at reflux temperature leads directly to pyrrolo[2,3-*b*]pyridines in good yields.

Pyrrolo[2,3-*b*]pyridines (7-azaindoles) have been the target of extensive synthetic studies as a consequence of their potent pharmacological activity.[1] The most general method for the construction of this ring system involves pyrrolo annelation into a preformed pyridine ring. However, available routes to pyrrolo[2,3-*b*]pyridines such as Madelung[2,3] or Fisher[4,5] type synthesis are often of limited synthetic interest, mainly due to their narrow scope. Recently, pyrrolo annelation has been achieved either from 2-fluoropyridine by metalation–$S_{RN}1$ substitution coupling methodology,[6] or from 3-picoline by metalation, subsequent reaction with nitriles and finally intramolecular Chichibabin type reaction.[7] A different approach is based on the simultaneous formation of the pyridine and the pyrrole ring. Thus, intramolecular inverse electron demand Diels–Alder cycloaddition of heterocyclic azadienes such as 1,2,4-triazines[8] or pyrimidines[9] carrying a dienophilic side chain tethered through a nitrogen atom to the appropriate position of the heterocyclic ring, has been shown to be an useful methodology for the formation of dihydropyrrolo[2,3-*b*]pyridines. In the course of our studies directed towards the iminophosphorane-mediated synthesis of fused heterocycles, we have developed a consecutive aza Wittig reaction–electrocyclic ring closure–intramolecular amination process for the synthesis of 1,9-diazaphenalene derivatives.[10,11] As a further extension of this methodology we would now like to report a new synthetic strategy to the preparation of pyrrolo[2,3-*b*]pyridines, which commences with a common iminophosphorane precursor and constructs both the pyridine and the pyrrole ring through the aforementioned consecutive process.

The starting aldehyde[12] **1** was easily prepared from the commercially available (*E*)-*β*-bromostyrene by standard chemistry: reaction with methyl acrylate in the presence of anhydrous palladium acetate (47 %); reduction with DIBAL at room temperature (85 %) and oxidation with activated manganese dioxide (65 %). Condensation of **1** with ethyl azidoacetate in ethanol in the presence of sodium ethoxide at −12 °C leads to the azide **2** (83 %) which is converted into the key iminophosphorane **3** (83 %) by reaction with triphenylphosphine in dry dichloromethane at room temperature. Iminophosphorane **3** reacts with several aliphatic or aromatic isocyanates in toluene at reflux temperature to give pyridines **5** in good yields (76–86 %) (Table 1). The ^{1}H and ^{13}C NMR data of compounds **5** revealed that they have *E* configuration[13] (Table 2). All attempts to cyclize compounds **5** to



5	R
a	CH_3
b	i-C_3H_7
c	C_6H_5
d	4-$H_3CC_6H_4$
e	4-FC_6H_4
f	4-$H_3COC_6H_4$

6	R
a	C_6H_5
b	4-$H_3CC_6H_4$
c	4-FC_6H_4
d	4-$H_3COC_6H_4$

Scheme

Table 1. Compounds 5 and 6 Prepared[a]

Product	Yield[b] (%)	mp (°C) Solvent	MS (70 eV) m/z (%)
5a	86	107–108 Et_2O/hexane	282 (M^+, 13), 208 (100), 180 (10), 131 (23), 91 (21)
5b	84	121–122 Et_2O/hexane	310 (M^+, 26), 236 (93), 221 (60), 194 (100), 103 (17)
5c	76	109–111 Et_2O/hexane	344 (M^+, 30), 270 (50), 193 (100), 168 (41), 77 (99)
5d	85	112–114 Et_2O/hexane	358 (M^+, 25), 284 (41), 207, (33), 91 (99), 65 (100)
5e	83	122–124 Et_2O/hexane	362 (M^+, 6), 211 (25), 129 (22), 111 (20), 95 (43)
5f	81	114–116 Et_2O/hexane	374 (M^+, 69), 300 (100), 223 (53), 115 (46), 77 (78)
6a	90	169–170 CH_2Cl_2/hexane	342 (M^+, 48), 295 (39), 270 (100), 139 (33), 77 (33)
6b	76	179–180 CH_2Cl_2/hexane	356 (M^+, 63), 309 (56), 284 (100), 139 (35), 91 (28)
6c	80	188–189 CH_2Cl_2/hexane	360 (M^+, 61), 313 (35), 285 (48), 139 (31), 95 (36)
6d	73	173–174 CH_2Cl_2/hexane	372 (M^+, 100), 325 (93), 297 (58), 139 (26), 77 (16)

[a] Satisfactory microanalyses were obtained for compounds **2**, **3**, **5a–f**, **6a–d**: C, H, N ± 0.3%

[b] Yield of isolated pure product.

compounds **6** by heating a toluene soluion at 160 °C in a sealed tube failed. However, when compounds **5** were heated in nitrobenzene at reflux temperature the corresponding pyrrolo[2,3-*b*]pyridines **6** were isolated in yields higher than 70%, except for compounds **5a** and **5b** which were recovered unchanged. The ^{1}H NMR data of compounds **6** are in good agreement with the previously reported values for this kind of ring system[6–8] (Table 2).

Compounds **6** can also be prepared directly in one pot in good yields (73–90%) from the precursor iminophosphorane **3** and isocyanates, without isolation of the intermediate pyridine **5**, by heating in nitrobenzene at reflux temperature (Scheme).

The conversion **3** → **6** can be rationalized in terms of an initial aza Wittig reaction to give the intermediate carbodiimide **4** (as evidenced by IR) which undergoes electrocyclic ring closure followed by [1,3] proton shift to give the pyridine **5**. This compound eventually undergoes an unusual thermal intramolecular amination followed by oxidative aromatization to provide the bicyclic compound **6**. Although intramolecular cyclization of a primary or secondary amino group onto a remote carbon–carbon double bond has been achieved by photolysis,[14,15] mediated by a transition metal catalyst (aminomercuration,[16,17,18] aminopalladation[19,20]), and by the action of a catalytic amount of butyllithium,[21] the thermal intramolecular cyclization is rare.[22]

This experimentally convenient sequence provides direct access to pyrrolo[2,3-*b*]pyridines in a one-pot process, and is competitive with previously reported syntheses of this ring system. Table 1 presents some pyrrolo[2,3-*b*]pyridines **6** made readily available via this methodology.

Melting points are uncorrected. IR spectra were recorded on a Nicolet FT 5DX spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AC-200 spectrometer. Mass spectra were recorded on a Hewlett-Packard 5993C instrument.

Ethyl (*E,E,E*)-2-Azido-7-phenyl-2,4,6-heptatrienoate (2):

To a well stirred solution containing Na (0.54 g, 22 mmol) in dry EtOH (20 mL), a solution of ethyl azidoacetate (3.25 g, 22 mmol) and (*E,E*)-5-phenyl-2,4-pentadienal (**1**) (1.0 g, 6.3 mmol) in dry EtOH (30 mL) was added dropwise at −12 °C under nitrogen. The reaction mixture was stirred for 6 h at the same temperature and then allowed to warm to r.t. After this it was poured into aq 30% NH_4Cl (50 mL) and the formed solid was separated by filtration, washed with H_2O (30 mL), air-dried and chromatographed on a silica gel column (40 cm × 3.5 cm, 70–230 mesh) eluting with CH_2Cl_2/hexane (1 : 1) to give **2**; yellow prisms; yield 1.41 g (83%); mp 72–73 °C.

IR (Nujol): ν = 2135 (N_3), 1709 (COOEt) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.35 (t, 3 H, J = 7.1 Hz, CH_3), 4.30 (q, 2 H, J = 7.1 Hz, CH_2O), 6.66 (m, 3 H), 6.87 (m, 1 H), 7.32 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 61.8 (CH_2O), 125.2 (C_α), 126.3, 126.6, 126.7 (C_o), 128.3 (C_p), 128.5, 128.7 (C_m), 136.2, 136.6 (C_i), 139.4, 163.1 (C=O).

MS: m/z (%) = 269 (M^+, 4), 168 (100).

Ethyl (*E,E,E*)-7-Phenyl-2-(triphenylphosphoranylidene)amino-2,4,6-heptatrienoate (3):

To a solution of Ph_3P (0.54 g, 2.1 mmol) in dry CH_2Cl_2 (15 mL), a solution of the azide **2** (0.56 g, 2.1 mmol) in the same solvent (10 mL) was added dropwise at r.t. and stirred for 2 h. The solvent was removed under reduced pressure at 35 °C and the residual material was chromatographed on a silica gel column (40 cm × 3.5 cm, 70–230 mesh) eluting with EtOAc/hexane (1 : 3) and then recrystallized from CH_2Cl_2/hexane (1 : 1) to give **3**; yellow prisms; yield 0.91 g (86%); mp 85–86 °C.

IR (Nujol): ν = 1696 (COOEt) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.00 (t, 3 H, J = 7.1 Hz, CH_3), 3.86 (q, 2 H, J = 7.1 Hz, CH_2O), 6.57 (m, 3 H), 6.96 (dd, 1 H, J = 15.3, 11.0 Hz), 7.28 (m, 15 H), 7.74 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 60.5 (CH_2O), 120.0 (d, $^3J_{P\text{-}C}$ = 19.7 Hz, C_β), 126.1, 126.8, 128.1 (d, $^3J_{P\text{-}C}$ = 12.2 Hz, C_mPhP), 128.5, 130.5, 130.6, 131.0 (d, $^4J_{P\text{-}C}$ = 2.8 Hz, C_pPhP), 131.2, 131.5, 132.3 (d, $^2J_{P\text{-}C}$ = 9.5 Hz, C_oPhP), 132.74 (d, $^1J_{P\text{-}C}$ = 103.1 Hz, C_iPhP), 137.4 (d, $^2J_{P\text{-}C}$ = 5.8 Hz, C_α), 137.9 (C_iPh), 167.2 (d, $^3J_{P\text{-}C}$ = 6.4 Hz, C=O).

MS: m/z (%) = 503 (M^+, 5), 183 (100).

Ethyl 6-Alkyl(aryl)amino-5-styrylpyridine-2-carboxylates 5; General Procedure:

A solution of iminophosphorane **3** (0.25 g, 0.49 mmol) and the appropriate isocyanate (0.49 mmol) in dry toluene (15 mL) was stirred at r.t. for 2 h, and then heated at reflux for 48 h. After cooling, the solvent was removed under reduced pressure at 35 °C and the residual material was chromatographed on a silica gel column (40 cm × 3.5 cm, 70–230 mesh) eluting with EtOAc/hexane (1 : 3) to give **5** which was isolated as a crystalline solid after recrystallization from Et_2O/hexane (1 : 1) (Table 1).

Ethyl 1-Aryl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine-6-carboxylates 6; General Procedure:

Method A. A solution of pyridine **5** (1 mmol) in nitrobenzene (5 mL) was heated at reflux for 12 h. After cooling, the solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column (40 cm × 3.5 cm, 70–230 mesh) eluting with CH_2Cl_2 to give **6** which was isolated as a yellow crystalline solid after recrystallization from CH_2Cl_2/hexane (1 : 1).

Method B. A mixture of iminophosphorane **3** (0.5 g, 0.99 mmol) and the corresponding isocyanate (0.99 mmol) in nitrobenzene (5 mL) was stirred at r.t. for 1 h and then heated at reflux for 12 h. Workup was similar to that described in method A (Table 1).

Table 2. Spectral Data of Compounds **5** and **6**.

Compound	IR (Nujol) υ ($\mathrm{cm^{-1}}$)	^{1}H NMR (200 MHz) (solvent/TMS)[a] δ, J(Hz)	^{13}C NMR (50 MHz) (solvent/TMS)[a] δ
5a	3428, 1717	1.38 (t, 3 H, $J = 7.2$, $\mathrm{C}H_3\mathrm{CH_2}$), 3.08 (s, 3 H, $\mathrm{NCH_3}$), 4.38 (q, 2 H, $J = 7.2$, $\mathrm{CH_3C}H_2$), 4.87 (s, 1 H, NH), 6.99 (d, 1 H, $J = 15.9$, H_α), 6.99 (d, 1 H, $J = 15.9$, H_β), 7.28, t, 1 H, $J = 6.9$, $\mathrm{H}_p\mathrm{Ph}$), 7.33 (t, 2 H, $J = 6.9$, $\mathrm{H_mPh}$), 7.41 (d, 1 H, $J = 7.6$, H-3), 7.47 (d, 2 H, $J = 7.2$, $\mathrm{H}_o\mathrm{Ph}$), 7.57 (d, 1 H, $J = 7.6$, H-4)	14.13 ($C\mathrm{H_3CH_2}$), 28.46 ($\mathrm{NCH_3}$), 61.3 ($\mathrm{CH_3}C\mathrm{H_2}$), 114.52 (C-3), 121.89 (C_α), 122.31 (C-5), 126.52 ($\mathrm{C}_o\mathrm{Ph}$), 128.13 ($\mathrm{C}_p\mathrm{Ph}$), 128.59 ($\mathrm{C}_m\mathrm{Ph}$), 133.34 (C_β), 133.71 (C-4), 136.51 ($\mathrm{C}_i\mathrm{Ph}$), 145.09 (C-2), 156.05 (C-6), 165.76 (C=O)
5b	3405, 1717	1.26 [d, 6 H, $J = 5.8$, $(\mathrm{C}H_3)_2\mathrm{CH}$], 1.39 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 4.38 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 4.45 [m, 2 H, NH, $(\mathrm{CH_3})_2\mathrm{C}H$], 6.94 (d, 1 H, $J = 16.0$, H_α), 7.01 (d, 1 H, $J = 16.0$, H_β), 7.33 (m, 4 H), 7.51 (d, 2 H, $J = 7.4$, $\mathrm{H}_o\mathrm{Ph}$), 7.58 (d, 1 H, $J = 7.6$, H-4)	14.19 ($C\mathrm{H_3CH_2}$), 22.98 [$(C\mathrm{H_3})_2\mathrm{CH}$], 42.68 [$(C\mathrm{H_3})_2C\mathrm{H}$], 61.04 ($\mathrm{CH_3}C\mathrm{H_2}$), 114.33 (C-3), 121.98 (C-5), 122.17 (C_α), 126.62 ($\mathrm{C}_o\mathrm{Ph}$), 128.23 ($\mathrm{C}_p\mathrm{Ph}$), 128.70 ($\mathrm{C}_m\mathrm{Ph}$), 133.43 (C_β), 134.13 (C-4), 136.67 ($\mathrm{C}_i\mathrm{Ph}$), 145.34 (C-2), 154.89 (C-6), 165.78 (C=O)
5c	3412, 1715	1.40 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 4.37 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.66 (s, 1 H, NH), 6.86 (t, 1 H, $J = 7.4$, $\mathrm{H}_o\mathrm{Ph}$), 6.91 (d, 1 H, $J = 16.2$, H_α), 6.91 (d, 1 H, $J = 16.2$, H_β), 7.18 (m, 5 H), 7.31 (d, 2 H, $J = 7.5$), 7.49 (d, 1 H, $J = 7.8$, H-3), 7.57 (m, 3 H, H-4, $\mathrm{H}_o\mathrm{Ph}$)	14.08 $C\mathrm{H_3CH_2}$), 61.26 ($\mathrm{CH_3}C\mathrm{H_2}$), 117.08 (C-3), 118.73, 121.65, 121.84 (C_α), 124.00 (C-5), 126.65 ($\mathrm{C}_o\mathrm{Ph}$), 128.40 ($\mathrm{C}_p\mathrm{Ph}$), 128.63, 128.66 ($\mathrm{C}_m\mathrm{Ph}$), 134.32 (C_β), 135.14 (C-4), 136.21 ($\mathrm{C}_i\mathrm{Ph}$), 140.53 (q), 144.60 (C-2), 151.83 (C-6), 165.26 (C=O)
5d	3449, 1710	1.43 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 2.29 (s, 3 H, $\mathrm{CH_3Ar}$), 4.40 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.63 (s, 1 H, NH), 7.01 (d, 1 H, $J = 16.0$, H_α), 7.06 (d, 1 H, $J = 16.0$, H_β), 7.10 (d, 2 H, $J = 8.4$), 7.32 (t, 1 H, $J = 6.9$, $\mathrm{H}_p\mathrm{Ph}$), 7.36 (t, 2 H, $J = 7.2$, $\mathrm{H}_m\mathrm{Ph}$), 7.45 (d, 2 H, $J = 7.2$, $\mathrm{H}_o\mathrm{Ph}$), 7.55 (d, 2 H, $J = 8.4$), 7.60 (d, 1 H, $J = 7.8$, H-3), 7.72 (d, 1 H, $J = 7.8$, H-4)	14.21 ($C\mathrm{H_3CH_2}$), 20.68 ($\mathrm{CH_3Ar}$), 61.34 ($\mathrm{CH_3}C\mathrm{H}$), 116.89 (C-3), 119.12, 121.95 (C_α), 123.86 (C-5), 126.75 ($\mathrm{C}_o\mathrm{Ph}$), 128.52 ($\mathrm{C}_p\mathrm{Ph}$), 128.77 ($\mathrm{C}_m\mathrm{Ph}$), 129.30, 131.53 (q), 134.38 (C_β), 135.28 (C-4), 136.41 $\mathrm{C}_i\mathrm{Ph}$), 138.04 (q), 144.87 (C-2), 152.22 (C-6), 165.41 (C=O)
5e	3324, 1750	1.35 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 4.31 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 7.13 (dd, 2 H, $J = 8.3$), 7.46 (m, 7 H), 7.74 (d, 2 H, $J = 7.2$, $\mathrm{H}_o\mathrm{Ph}$), 7.93 (dd, 2 H, $J = 7.8, 4.7$), 8.10 (d, 1 H, $J = 7.4$, H-4)	14.14 ($C\mathrm{H_3CH_2}$), 60.85 ($\mathrm{CH_3CH_2}$), 114.65 (d, $^2J_\mathrm{F} = 21.7$), 116.35 (C-3), 121.50 (d, $^3J_\mathrm{F} = 7.1$), 121.75 (C_α), 123.10 (C-5), 127.24 ($\mathrm{C}_o\mathrm{Ph}$), 128.32 ($\mathrm{C}_p\mathrm{Ph}$), 128.68 ($\mathrm{C}_m\mathrm{Ph}$), 133.22 (C_β), 134.37 (C-4), 136.88 (q), 137.62 ($\mathrm{C}_i\mathrm{Ph}$), 143.68 (C-2), 151.93 (C-6), 157.20 (q, d, $^1J_F = 238.9$), 164.61 (C=O)
5f	3447, 1718	1.41 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 3.76 (s, 3 H, $\mathrm{CH_3OAr}$), 4.38 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.60 (s, 1 H, NH), 6.85 (d, 2 H, $J = 8.7$), 7.01 (d, 1 H, $J = 16.5$, H_α), 7.04 (d, 1 H, $J = 16.5$, H_β), 7.31 (t, 1 H, $J = 6.9$, $\mathrm{H}_p\mathrm{Ph}$), 7.35 (t, 2 H, $J = 7.1$, $\mathrm{H}_m\mathrm{Ph}$), 7.45 (d, 2 H, $J = 6.9$, $\mathrm{H}_o\mathrm{Ph}$), 7.58 (m, 3 H), 7.70 (d, 1 H, $J = 7.8$, H-4)	14.17 ($CH_3\mathrm{CH_2}$), 55.43 ($\mathrm{CH_3OAr}$), 61.28 ($\mathrm{CH_3}C\mathrm{H_2}$), 114.02. 116.62 (C-3), 120.89, 121.90 (C_α), 123.53 (C-5), 126.71 ($\mathrm{C}_o\mathrm{Ph}$), 128.45 ($\mathrm{C}_p\mathrm{Ph}$), 128.72 ($\mathrm{C}_m\mathrm{Ph}$), 133.91 (q), 134.23 (C_β), 135.15 (C-4), 136.39 ($\mathrm{C}_i\mathrm{Ph}$), 144.81 (C-2), 152.41 (C-6), 154.98 (q), 165.40 (C=O)
6a	1740, 1589	1.38 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 4.39 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.75 (s, 1 H, H-3), 7.26 (m, 5 H), 7.33 (m, 5 H), 8.00 (d, 1 H, $J = 8.0$, H-5), 8.00 (d, 1 H, $J = 8.0$, H-4)	14.17 ($C\mathrm{H_3CH_2}$), 61.20 ($\mathrm{CH_3}C\mathrm{H_2}$), 101.64 (C-3), 118.60 (C-5), 123.55 (C-3a), 127.21, 128.02 ($\mathrm{C}_p\mathrm{Ph}$), 128.13 (C-4), 128.22 ($\mathrm{C}_o\mathrm{Ph}$), 128.22, 128.71, 128.91 ($\mathrm{C}_m\mathrm{Ph}$), 131.59 (C-2), 136.26 (q), 141.43 ($\mathrm{C}_i\mathrm{Ph}$), 144.44 (C-6), 149.11 (C-7a), 165.98 (C=O)
6b	1734, 1595	1.27 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 2.23 (s, 3 H, $\mathrm{CH_3Ar}$), 4.28 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.62 (s, 1 H, H-3), 7.10 (m, 9 H), 7.87 (d, 1 H, $J = 7.9$, H-5), 7.87 (d, 1 H, $J = 7.9$, H-4)	14.18 ($C\mathrm{H_3CH_2}$), 21.00 ($\mathrm{CH_3Ar}$), 61.14 ($\mathrm{CH_3}C\mathrm{H_2}$), 101.38 (C-3), 118.47 (C-5), 123.49 (C-3a), 127.92, 127.92 ($\mathrm{C}_p\mathrm{Ph}$), 128.13 (C-4), 128.20 ($\mathrm{C}_o\mathrm{Ph}$), 128.89 ($\mathrm{C}_m\mathrm{Ph}$), 129.37, 131.69 (C-2) 133.67 (q), 136.96 (q), 141.39 ($\mathrm{C}_i\mathrm{Ph}$), 144.43 (C-6), 149.18 (C-7a), 165.70 (C=O)
6c	1713, 1516	1.31 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 4.31 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.67 (s, 1 H, H-3), 6.99 (dd, 2 H, $J = 8.6$), 7.20 (m, 7 H), 7.92 (d, 1 H, $J = 7.9$, H-5), 7.92 (d, 1 H, $J = 7.9$, H-4)	14.22 ($C\mathrm{H_3CH_2}$), 61.31 ($\mathrm{CH_3}C\mathrm{H_2}$), 101.74 (C-3), 115.74 (d, $^1J_F = 22.8$), 118.75 (C-5), 123.53 (C-3a), 128.22 (C-4), 128.46 ($\mathrm{C}_p\mathrm{Ph}$), 128.46 ($\mathrm{C}_o\mathrm{Ph}$), 129.04 ($\mathrm{C}_m\mathrm{Ph}$), 129.85 (d, $^3J_F = 8.5$), 131.41 (C-2), 132.29 (q, d, $^4J_F = 2.9$), 136.96 (q), 141.57 ($\mathrm{C}_i\mathrm{Ph}$), 144.34 (C-6), 149.11 (C-7a), 161.50 (q, d, $^1J_F = 246.9$) 165.93 (C=O)
6d	1713, 1518	1.29 (t, 3 H, $J = 7.1$, $\mathrm{C}H_3\mathrm{CH_2}$), 3.70 (s, 3 H, $\mathrm{CH_3OAr}$), 4.29 (q, 2 H, $J = 7.1$, $\mathrm{CH_3C}H_2$), 6.64 (s, 1 H, H-3), 6.80 (d, 2 H, $J = 8.8$), 7.18 (m, 7 H), 7.89 (d, 1 H, $J = 7.8$, H-5), 7.89 (d, 1 H, $J = 7.8$, H-4)	14.20 ($C\mathrm{H_3CH_2}$), 55.31 ($\mathrm{CH_3OAr}$), 61.16 ($\mathrm{CH_3}C\mathrm{H_2}$) 101.15 (C-3), 114.06, 118.44 (C-5), 123.41 (C-3a) 127.90 ($\mathrm{C}_p\mathrm{Ph}$), 128.15 (C-4), 128.24 ($\mathrm{C}_o\mathrm{Ph}$), 128.93 ($\mathrm{C}_m\mathrm{Ph}$), 129.17 (q), 129.24, 131.67 (C-2), 141.40 ($\mathrm{C}_i\mathrm{Ph}$), 144.49 (C-6), 149.26 (C-7a), 158.53 (q) 166.01 (C=O)

[a] Solvent: $\mathrm{CDCl_3}$ for **5a–d**, **5f**, **6a–d**; DMSO-d_6 for **5e**.

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