Simple synthesis of pyrrolo[3,2-e]indole-1-carbonitriles

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Abstract
Alkylation of 5-nitroindol-4-ylacetonitriles with ethyl chloroacetate, α-halomethyl ketones, and chloroacetonitrile followed by a treatment of the products with chlorotrimethylsilane in the presence of DBU gives 1-cyanopyrrolo[3,2-e]indoles substituted in position 2 with electron-withdrawing groups.

Introduction
Indole and its analogues bearing condensed arene and heteroarene rings are privileged structures amongst biologically active compounds. The 1,2-dihydropyrrolo[3,2-e]indole fragment is present in anticancer agents, such as CC-1065 [1], duocarmycin [1], and yatakemycin [2]. Some pyrrolo[3,2-e]indole derivatives show antimicrobial activity [3]. One method of synthesis of the 1,2-dihydropyrrolo[2,3-e]indoles is reduction of pyrrolo[3,2-e]indoles with sodium cyanoborohydride [4]. On the other hand there are many methods of synthesis of pyrrolo[3,2-e]indoles such as the copper-catalyzed transformation of tetrahydroquinoline derivatives [4], photocatalytic cyclization of 1,2-bis(2-pyrrole)ethylenes [5], the Fischer indole synthesis from indol-5-ylhydrazones [3], or a palladium-catalyzed hydrogenation of 5-nitroindol-4-ylacetonitriles [6]. In the latter synthesis of pyrrolo[3,2-e]indole 3 the starting nitrile 2 was obtained by the vicarious nucleophilic substitution (VNS) [7-11] of hydrogen in 1-alkyl-5-nitroindole 1 with 4-chlorophenoxyacetonitrile [12] (Scheme 1).

In our previous papers [13-16] we have shown that α-nitroarylacetonitriles alkylated and alkenylated at the α-position to the cyano group can be converted into indoles under basic conditions in the presence of a silylating agent.

Results and Discussion
Here we report a simple two-step procedure for the transformation of 5-nitroindol-4-ylacetonitriles into pyrrolo[3,2-e]indole-1-carbonitriles 6 bearing an additional electron-withdrawing group.
substituent at position 2. In our approach the starting material was 1-benzyloxymethyl-4-cyanomethyl-2-methyl-5-nitroindole (4) obtained via the VNS of hydrogen in 1-benzyloxymethyl-2-methyl-5-nitroindole with 4-chlorophenoxyacetonitrile according to our earlier elaborated method [12]. Alkylation of the nitrile 4 with ethyl bromoacetate in the presence of K₂CO₃ led to the expected cyanoester 5a in 68% yield, but the product contained some contaminants difficult to separate by crystallization or column chromatography. Searching for more convenient reaction conditions, we have found that this reaction proceeds satisfactorily in almost quantitative yield when diazabicycloundecene (DBU) was used as the base. Analogous alkylation with α-halomethyl ketones, chloroacetanitriile, chloroacetamide and cinnamyl bromide provided the expected alkylation products 5b-g in good yields (Scheme 2 and Table 1).

To find optimal conditions for cyclization of the model compound 5a we screened various combinations of base and a reagent promoting the cyclization. With chlorotrimethylsilane–triethylamine the reaction proceeded slowly, and the starting material was completely consumed after 24 h, but the product 6a was isolated in moderate 30% yield. However, when we replaced triethylamine with a stronger base, such as DBU, the reaction was completed in 30 min, and the product was isolated in 90% yield. Similarly, with N,O-bis(trimethylsilyl)acetamide (BSA) the reaction was completed in 30 min giving 6a in 67% yield. With tributylchlorostannane combined with DBU the reaction proceeded slowly to form after 24 h product 6a in 72% yield. Methanesulfonyl and pivaloyl chlorides, in combination with DBU proved ineffective in this reaction giving a very low rate of conversion after 24 h. Thus, transformations of other nitriles 5b-g into pyrrolo[3,2-
Table 1: Alkylation products 5 and synthesized 1-cyano-3-hydroxy-pyrrolo[3,2-e]indoles 6.

| Entry | X–CH₂–Z      | Indole 5 | Yield (%) | Pyrrolo[3,2-e]indole 6 | Yield (%) |
|-------|---------------|----------|-----------|------------------------|-----------|
| 1     | Br–CH₂CO₂Et   | ![Indole 5a](image) | 99        | ![Pyrrolo[3,2-e]indole 6a](image) | 90        |
| 2     | Cl–CH₂COMe    | ![Indole 5b](image) | 88        | ![Pyrrolo[3,2-e]indole 6d](image) | 61        |
| 3     | Cl–CH₂COCMe₃  | ![Indole 5c](image) | 82        | ![Pyrrolo[3,2-e]indole 6c](image) | 55        |
| 4     | Br–CH₂COPh    | ![Indole 5d](image) | 98        | ![Pyrrolo[3,2-e]indole 6d](image) | 30        |
| 5     | Cl–CH₂CN      | ![Indole 5e](image) | 86        | ![Pyrrolo[3,2-e]indole 6e](image) | 30        |
| 6     | Cl–CH₂CONMe₂  | ![Indole 5f](image) | 95        | ![Pyrrolo[3,2-e]indole 6f](image) | 44        |
| 7     | Br–CH₂CH=CH₂Ph| ![Indole 5g](image) | 50        | ![Pyrrolo[3,2-e]indole 6g](image) | 25        |
The removal of the benzyloxymethyl group from 1-(benzyloxymethyl)pyrrolo[3,2-\(e\)]indoles by catalytic hydrogenation has been described by Macor [6]. The hydroxy group from the \(N\)-hydroxyppyrole fragment can be removed by a procedure elaborated by us [18] employing \(\alpha\)-bromoacetophenone in the presence of triethylamine as exemplified for pyrroloindoles \(6a\) and \(6d\) that were transformed under these conditions into the corresponding derivatives \(8a\) and \(8d\) (Scheme 2). The crude 3-hydroxy-pyrrolo[3,2-\(e\)]indole \(6d\) without isolation and purification was subjected to dehydroxylation giving compound \(8d\) in 47\% yield.

A plausible route to the formation of 3-hydroxy-1-cyano-pyrrolo[3,2-\(e\)]indoles is exemplified by the synthesis of 1,2-dicyano derivative \(6e\) from the dinitrile \(5e\) (Scheme 3). In the first step the \(o\)-nitrobenzylic carbanion is silylated with trimethylchlorosilane to form trimethylsilylnitronate \(A\). Then a consecutive deprotonation forms another carbanion \(B\) at the \(\beta\)-position to the ring. The attack of this carbanion on the trimethylsilylnitronate results in the substitution of trimethoxysiloxyl and formation of \(C\) in that the five-membered ring finally isomerizes to the \(N\)-hydroxyppyrole fragment of \(6e\).

To remove the benzyloxymethyl group from the compound \(8a\) we adopted the procedure proposed by Macor [6]. Heating \(8a\) with ammonium formate and 10\% palladium on carbon as a catalyst in isopropanol in a sealed tube (95 °C) led to a mixture of the expected product \(9a\) and the product \(10a\) in that the cyano group was reduced to a methyl substituent (Scheme 4). There is a literature precedence [19] for similar transformations of cyanoarenes into corresponding methyl derivatives upon transfer hydrogenation with ammonium formate in the presence of palladium on a carbon catalyst.

**Conclusion**

In conclusion, the approach presented herein can be useful for the synthesis of variously substituted pyrrolo[3,2-\(e\)]indoles. The method does not require reductive conditions for the formation of the pyrrole ring and, thus, can be applicable for derivatives bearing sensitive substituents.
Experimental

Melting points (mp) are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 500 or Varian vnmr s500 (both 500 MHz for $^1$H and 125 MHz for $^{13}$C spectra) instruments at 298 K. Chemical shifts $\delta$ are expressed in parts per million referenced to TMS; coupling constants $J$ in hertz. IR spectra were recorded in KBr on a Perkin Elmer PE Spectrum 2000 spectrometer. Electron impact mass spectra (EI, 70 eV) were obtained on AMD-604 and AutoSpec Premier spectrometer. Electrospray mass spectra (ESI) were obtained on 4000 Q-TRAP and SYNAPT G2-S HDMS. Silica gel (Merck 60, 230–400 mesh) was used for column chromatography (CC). All reagents and solvents were of reagent grade or purified according to standard methods before use. 1-Benzoxymethyl-4-(cyanomethyl)-2-methyl-5-nitroindole (4) was obtained by VNS of hydrogen in 1-benzoxymethyl-2-methyl-5-nitroindole with 4-chlorophenoxacyanitronitrile following our previously elaborated method [12].

Alkylation of indolyacetonitrile 4 with ethyl bromoacetate. Synthesis of 3-(1-benzoxymethyl-2-methyl-5-nitro-1H-indol-4-yl)-3-cyanopropionic acid ethyl ester (5a) – Typical procedure

A solution of 1-benzoxymethyl-2-methyl-5-nitro-1H-indol-4-yl)acetonitrile (4, 0.335 g, 1 mmol) and ethyl bromoacetate (0.25 g, 1.5 mmol) were stirred in DMF (5 mL) and DBU (0.30 g, 2 mmol) at 60 °C until the starting material 4 disappeared (usually 24 h, TLC control). Then the reaction mixture was poured into diluted HCl and the product was purified with EtOAc (3 × 30 mL) and dried with Na$_2$SO$_4$. After evaporation of the solvent the residue was purified by column chromatography (SiO$_2$, hexane–EtOAc, 2:1). Yellow crystals; mp 92–94 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.15 (s, 3H), 2.53 (d, $J = 0.8$ Hz, 3H), 3.14 (dd, $J = 17.9, 4.9$ Hz, 1H), 3.57 (dd, $J = 17.9, 9.1$ Hz, 1H), 4.47 (s, 2H), 5.32 (dd, $J = 9.1, 4.9$ Hz, 1H), 5.55 (s, 2H), 6.78 (br s, 1H), 7.24–7.37 (m, 6H), 7.83 (d, $J = 9.0$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 12.84, 26.11, 26.91, 40.21, 44.06, 70.05, 71.92, 102.10, 109.66, 118.83, 119.42, 121.47, 127.10, 127.65, 128.26, 128.62, 136.40, 139.37, 141.18, 142.21, 210.44; IR (KBr, cm$^{-1}$): 2969, 2244, 1707, 1606, 1652, 1517, 1477, 1340, 1071, 1029, 818, 757, 740; EIMS (70 eV) m/z (% relative intensity): 433 (3) [M]$^+$, 399 (6), 92 (8), 91 (100); HRMS–EI (70 eV, m/z): [M]$^+$ calcd for C$_{22}$H$_{22}$N$_3$O$_4$, 391.1532; found, 391.1540.

2-(1-Benzoxymethyl-2-methyl-5-nitro-1H-indol-4-yl)-4,5-dimethyl-4-oxo-4-oxopentanenitrile (5b). Yellow crystals; mp 123–125 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.52 (d, $J = 1.0$ Hz, 3H), 3.68 (dd, $J = 18.0, 5.1$ Hz, 1H), 4.05 (dd, $J = 18.0, 8.7$ Hz, 1H), 4.47 (s, 2H), 5.55 (s, 2H), 5.58 (dd, $J = 8.7, 5.1$ Hz, 1H), 6.83 (m, 1H), 7.25 (s, 1H), 7.26 (s, 1H), 7.30–7.37 (m, 4H), 7.44–7.48 (m, 2H), 7.56–7.60 (m, 1H), 7.85 (d, $J = 9.0$ Hz, 1H), 7.93–7.96 (m, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 12.86, 26.64, 42.01, 70.09, 71.96, 102.14, 109.78, 118.89, 119.46, 121.36, 127.15, 127.67, 128.17, 128.78, 138.55, 135.57, 136.44, 139.45, 141.27, 142.37, 194.46; IR (KBr, cm$^{-1}$) v: 2921, 2246, 1690, 1559, 1518, 1447, 1343, 1213, 1086, 1071, 803, 751, 689; EIMS (70 eV) m/z (% relative intensity): 453 (2) [M]$^+$, 419 (9), 105 (35), 92 (8), 91 (100), 77 (13); HRMS–EI (70 eV, m/z): [M]$^+$ calcd for C$_{22}$H$_{22}$N$_3$O$_4$, 453.1689; found, 453.1671.

2-(1-Benzoxymethyl-2-methyl-5-nitro-1H-indol-4-yl)-sucinonitrile (5e). Brown oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.54 (d, $J = 1.0$ Hz, 3H), 3.25, 3.31, 5.34 (ABX, $J = 17.0, 8.0, 6.8$ Hz, 3H), 4.48 (s, 2H), 5.56 (s, 2H), 6.87 (br s, 1H), 7.24–7.27 (m, 2H), 7.31–7.37 (m, 3H), 7.41 (d, $J = 8.9$ Hz, 1H), 7.93 (d, $J = 8.9$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 12.88, 22.04, 28.75, 70.20, 71.98, 102.00, 110.78, 115.41, 117.06, 121.08, 127.03, 127.64, 128.03, 128.62, 136.39, 139.40, 141.21, 142.19, 202.77; IR (KBr, cm$^{-1}$) v: 2915, 2250, 2240, 1714, 1607, 1559, 1517, 1504, 1451, 1400, 1330, 1257, 1238, 1170, 1081, 1060, 1006, 948, 817, 733; EIMS (70 eV) m/z (% relative intensity): 391 (3) [M]$^+$, 357 (11), 92 (8), 91 (100); HRMS–EI (70 eV, m/z): [M]$^+$ calcd for C$_{22}$H$_{22}$N$_3$O$_4$, 391.1532; found, 391.1540.
3-(1-Benzoxymethyl-2-methyl-5-nitro-1H-indol-4-yl)-3-cyano-N,N-dimethylpropionamide (5f). Orange oil; 1H NMR (500 MHz, CDCl₃) δ 2.52 (s, 3H), 2.97 (br s, 1H), 2.96 (s, 3H), 2.98 (s, 3H), 3.40 (dd, J = 16.4, 8.8 Hz, 1H), 4.47 (s, 2H), 5.44 (dd, J = 8.8, 5.4 Hz, 1H), 5.54 (s, 2H), 6.81 (m, 1H), 7.25–7.30 (m, 2H), 7.31–7.37 (m, 4H), 7.83 (d, J = 9.0 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 12.83, 28.10, 35.69, 36.93, 36.99, 70.07, 71.94, 102.26, 109.66, 118.88, 119.58, 121.67, 127.32, 127.66, 128.26, 128.64, 134.45, 141.10, 142.39, 167.99; IR (KBr, cm⁻¹): 2932, 2244, 1651, 1561, 1519, 1400, 1340, 1267, 1241, 1150, 1070, 822, 737, 700; EIMS (70 eV) m/z (% relative intensity): 420 (2) [M]+, 375 (6), 374 (16), 195 (8), 108 (8), 107 (6), 92 (12), 49 (49); HRMS–EI (70 eV, m/z); [M]+ calecd for C₂₃H₂₄N₂O₄, 420.1798; found, 420.1796.

6-Benzoxymethyl-1-cyano-3-hydroxy-7-methyl-3,6-di-hydroxypropyrolo[3,2-ε]indole-1-carbonitrite (6a). Yellow crystals; mp 119–121 °C; 1H NMR (500 MHz, DMSO-d₆) δ 1.37 (t, J = 7.1 Hz, 3H), 2.58 (s, 3H), 4.41 (q, J = 7.1 Hz, 2H), 4.48 (s, 2H), 5.77 (s, 2H), 6.84 (s, 1H), 7.23–7.36 (m, 5H), 7.73 (d, J = 9.1 Hz, 1H), 11.22 (br s, 1H); 13C NMR (125 MHz, CD₂SOCD₃) δ 12.64, 14.44, 62.30, 70.32, 73.18, 85.95, 100.46, 104.26, 112.46, 116.13, 115.69, 119.80, 126.68, 128.37, 128.41, 128.45, 129.12, 131.11, 134.06, 138.27, 138.73, 159.36; IR (KBr, cm⁻¹): 2987, 2212, 1753, 1682, 1618, 1597, 1499, 1453, 1430, 1368, 1333, 1321, 1265, 1136, 1062, 1028, 775; EIMS (70 eV) m/z (% relative intensity): 403 (38) [M]+, 387 (13), 311 (11), 297 (14), 283 (13), 281 (6), 192 (5), 92 (8), 91 (100); HRMS–EI (70 eV, m/z); [M]+ calecd for C₂₃H₂₃N₂O₄, 403.1532; found, 403.1519.

6-Benzoxymethyl-2-(2,2-dimethylpropionyl)-3-hydroxy-7-methyl-3,6-di-hydroxypropyrolo[3,2-ε]indole-1-carbonitrite (6c). Brown solid; mp 155–157 °C; 1H NMR (500 MHz, DMSO-d₆) δ 1.32 (s, 9H), 2.52 (d, J = 0.8 Hz, 3H), 4.47 (s, 2H), 5.73 (s, 2H), 6.68 (br s, 1H), 7.24–7.35 (m, 6H), 7.67 (d, J = 9.0 Hz, 1H), 12.50 (br s, 1H); 13C NMR (125 MHz, DMSO-d₆) δ 12.27, 26.00, 44.68, 69.08, 72.21, 78.41, 98.67, 103.69, 106.69, 114.83, 116.34, 118.20, 127.43, 127.59, 128.09, 128.28, 132.87, 137.25, 137.30, 137.58, 202.17; IR (KBr, cm⁻¹): 2969, 2244, 1707, 1562, 1519, 1477, 1398, 1340, 1071, 1029; EIMS (70 eV) m/z (% relative intensity): 415 (9) [M]+, 400 (15), 399 (59), 369 (6), 342 (7), 313 (5), 312 (17), 294 (5), 293 (19), 292 (8), 285 (7), 284 (8), 236 (8), 208 (5), 194 (6), 193 (5), 108 (6), 92 (8), 91 (100); HRMS–EI (70 eV, m/z); [M]+ calecd for C₂₃H₂₅N₃O₃, 415.1896; found, 415.1878.

7.29–7.39 (m, 4H), 7.53 (d, J = 9.1 Hz, 1H), 7.58–7.63 (m, 2H), 7.69–7.75 (m, 1H), 7.97–8.02 (m, 2H), 12.56 (br s, 1H); 13C NMR (125 MHz, CDCl3) δ 12.67, 69.59, 72.04, 85.65, 101.26, 103.34, 113.27, 115.64, 116.67, 119.00, 126.39, 127.74, 128.08, 128.56, 128.69, 128.97, 132.94, 134.15, 135.87, 136.85, 137.15, 189.1; IR (KBr, cm−1) v: 2921, 2215, 1639, 1599, 1569, 1496, 1479, 1424, 1367, 1329, 1216, 1085, 1072, 778, 732, 693; ESIMS (MeOH/CH2Cl2 m/z): 436 [M + H]+, 458 [M + Na]+; HRMS–ESI (m/z): [M + Na]+ calcd for C23H22N3O2Na, 456.1688; found, 456.1685.

6-Benzoxymethyl-1-cyano-7-methyl-3,6-dihydropyrrolo[3,2-e]indole-2-carboxylic acid ethyl ester (8a). Pale creamy crystals; mp 215–217 °C; 1H NMR (500 MHz, DMSO-d6) δ 1.06 (t, J = 7.1 Hz, 3H), 2.52 (s, 3H), 4.44 (q, J = 7.1 Hz, 2H), 4.47 (s, 2H), 5.71 (s, 2H), 6.74 (br s, 1H), 7.24–7.35 (m, 6H), 12.99 (br s, 1H); 13C NMR (125 MHz, DMSO-d6) δ 12.21, 29.26, 58.28, 127.41, 128.81, 131.00, 131.16, 136.84, 136.96, 137.54; IR (KBr, cm−1) v: 3256, 2219, 1689, 1527, 1455, 1434, 1362, 1315, 1261, 1064, 1055, 1025, 743; EIMS (70 eV) m/z (% relative intensity): 387 (60) [M]+, 312 (8), 311 (37), 281 (14), 280 (5), 266 (5), 235 (6), 220 (12), 206 (5), 192 (6), 165 (5), 92 (8), 91 (10); HRMS–ESI (m/z): [M]+ calcd for C23H23N3O2Na, 387.1583; found, 387.1587.

2-Benzoyl-1-benzoxymethyl-7-methyl-3,6-dihydropyrrolo[3,2-e]indole-1-carboxitrile (8d). Yellow crystals; mp 180–182 °C; 1H NMR (500 MHz, DMSO-d6) δ 2.53 (s, 3H), 4.47 (s, 2H), 5.74 (s, 2H), 6.75 (s, 1H), 7.23–7.38 (m, 3H), 7.60–7.78 (m, 2H), 7.89–7.94 (m, 2H), 8.47 (s, 1H), 8.86 (s, 1H), 12.96 (br s, 1H); 13C NMR (125 MHz, DMSO-d6) δ 12.21, 13.38, 37.24, 68.92, 72.06, 98.73, 104.84, 107.15, 115.29, 117.24, 117.99, 127.35, 127.49, 127.93, 128.22, 132.58, 135.89, 136.64 (3 peaks not visible); IR (KBr, cm−1) v: 3265, 2217, 1710, 1540, 1510, 1408, 1329, 1254, 1062, 778, 738, 698, 478 (EIMS 70 eV) m/z (% relative intensity): 402 (10) [M]+, 387 (7), 386 (27), 311 (6), 111 (17), 280 (5), 265 (6), 221 (5), 220 (6), 213 (6), 193 (6), 192 (5), 165 (14), 135 (7), 108 (39), 107 (10), 105 (7), 92 (10), 91 (100); HRMS–ESI (70 eV, m/z): [M]+ calcd for C23H23N3O2Na, 402.1629; found, 402.1684.

Debenzoxymethylation of compound 8a

Compound 8a (100 mg, 0.26 mmol), ammonium formate (0.16 g, 10 mmol) and 10% palladium on charcoal (90 mg) were suspended in isopropanol (5 mL), flushed with argon for 5 min and then heated in a sealed tube at 95 °C overnight. Then the reaction mixture was passed through Celite, washed with dichloromethane–methanol, 1:1 (15 mL). After evaporation the residue was purified by column chromatography on silica gel with hexane–ethyl acetate (gradient 4:1:1). The following compounds were obtained:

1-Cyano-7-methyl-3,6-dihydropyrrolo[3,2-e]indole-2-carboxylic acid ethyl ester (9a). Yield 22%; mp > 280 °C; 1H NMR (500 MHz, DMSO-d6) δ 1.39 (t, J = 7.1 Hz, 3H), 2.45 (s, 3H), 4.42 (q, J = 7.1 Hz, 2H), 5.65 (s, 1H), 7.19 (d, J = 8.8 Hz, 1H), 7.40 (d, J = 8.8 Hz, 1H), 11.33 (s, 1H), 12.85 (s, 1H);
$^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 13.27, 14.07, 61.19, 87.56, 97.30, 105.78, 112.34, 116.06, 118.75, 120.01, 128.49, 131.03, 131.09, 135.00, 159.14; IR (film, cm$^{-1}$) ν: 3265, 2256, 1690, 1549, 1526, 1439, 1363, 1254, 1115, 1073, 1016; EIMS (70 eV) m/z (% relative intensity): 267 (75) [M]+, 222 (26), 221 (100), 194 (25), 193 (55), 167 (17).

1,7-Dimethyl-3,6-dihydropyrrolo[3,2-$e$]indole-2-carboxylic acid ethyl ester (10a). Yield 34%; mp 225–227 °C dec; $^1$H NMR (500 MHz, DMSO-$d_6$) δ 1.35 (t, $J = 7.0$ Hz, 3H), 2.42 (s, 3H), 2.72 (s, 3H), 4.32 (q, $J = 7.0$ Hz, 2H), 6.46 (s, 1H), 7.04 (d, $J = 8.8$ Hz, 1H), 7.23 (d, $J = 8.8$ Hz, 1H), 10.97 (s, 1H), 11.21 (s, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 11.57, 13.27, 13.35, 14.40, 59.47, 98.24, 105.38, 110.99, 118.48, 119.62, 120.46, 120.54, 129.65, 131.77, 133.23, 162.01; IR (KBr, cm$^{-1}$): 14.40, 59.47, 98.24, 105.38, 110.99, 118.48, 119.62, 120.46, 120.54, 129.65, 131.77, 133.23, 162.01; IR (KBr, cm$^{-1}$): 3265, 2256, 1690, 1549, 1526, 1439, 1363, 1254, 1115, 1073, 1016; EIMS (70 eV) m/z (% relative intensity): 267 (75) [M]+, 222 (26), 221 (100), 194 (25), 193 (55), 167 (17).

Supporting Information
Supporting Information File 1
$^1$H and $^{13}$C NMR, IR and mass spectra for compounds 4, 5a–g, 6a–g, 8a, 8d, 9a and 10a. [http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-9-107-S1.pdf]

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