

Supporting Information File 1

for

**Visible-light-induced, Ir-catalyzed reactions of *N*-methyl-*N*-((trimethylsilyl))methylaniline with cyclic  $\alpha,\beta$ -unsaturated carbonyl compounds**

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# 1. Experimental

**General:** Reactions containing moisture sensitive compounds were conducted in flame-dried glass vessels under argon atmosphere. Dry solvents (CH<sub>3</sub>CN, MeOH, DMF, toluene, 1,4-dioxane, DMSO, DMA) were purchased from *Sigma-Aldrich*, *Acros Organics*, *Fluka* or *Merck*. Dry CH<sub>2</sub>Cl<sub>2</sub> and THF were taken from a MB-SPS-800 apparatus (*M. Braun*). Common solvents for chromatography [pentane (P), EtOAc, CH<sub>2</sub>Cl<sub>2</sub>, MeOH] were distilled prior to use. IR spectra were recorded on a *JASCO* IR-4100 (ATR); MS and HRMS measurements were performed on a *Finnigan* MAT 8200 (EI), a *Finnigan* MAT 95-S (HR–EI), a *Finnigan* LCQ classic (ESI) and a Thermo *Finnigan* LTQ FT (HRMS–ESI). <sup>1</sup>H and <sup>13</sup>C NMR: Bruker AV-250, Bruker AV-360, Bruker AV-500, Bruker AV-500cr recorded at 303 K. Chemical shifts are reported relative to the used solvent (CHCl<sub>3</sub>). All coupling constants (*J*) are reported in Hertz (Hz). Melting points were measured on a *Kofler* melting point apparatus (*Reichert*) and are uncorrected.

Photoreactions were carried out in Pyrex phototubes (diameter = 1 cm) using 8 *Osram* cool white lamps (L 8W/640) [S1]. α,β-Unsaturated compounds **9**, **12** and **15** were purchased from *Alfa Aesar* and *Sigma-Aldrich*. Compounds **18a** [S2], **18b** [S2], and **20** [S3] were prepared according to literature known procedures. Amine **5** was synthesized from *N*-methylaniline [S4]. Photocatalysts [Ir(ppy)<sub>2</sub>(bpy)]BF<sub>4</sub> [S5], [Ir(ppy)<sub>2</sub>(dtbbpy)]BF<sub>4</sub> (**7**) [S5], [Ir((dF)(CF<sub>3</sub>)-ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> [S6], [Ir((dF)(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> [S6] were prepared by heating of the corresponding iridium dimer with the according ligand in ethylene glycol.

## General procedure for PET catalyzed reactions

In a flame-dried phototube, all compounds except the photocatalyst were dissolved in the corresponding solvent under an argon atmosphere. The solution was degassed three times via freeze–pump–thaw cycles prior to addition of the catalyst. Irradiation was followed by

addition of 10 mL saturated aqueous NaHCO<sub>3</sub> solution and 15 mL CH<sub>2</sub>Cl<sub>2</sub>. The layers were separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica.

### **5-Methyl-3a,4,5,9b-tetrahydrofuro[3,4-*c*]quinolin-1(3*H*)-one (10)**

According to the general procedure for PET reactions, 7.17 µL (8.58 mg, 100 µmol, 1.00 equiv) of **9** and 32.6 µL (29.0 mg, 150 µmol, 1.50 equiv) of **5** were irradiated for 5 h (MeOH) or 24 h (CH<sub>2</sub>Cl<sub>2</sub>) in 1 mL of the corresponding solvent. In CH<sub>2</sub>Cl<sub>2</sub> 1 mol % of catalyst **7** (856 µg) were used, in MeOH 2.5 mol % (2.14 mg). Column chromatography on silica (P/EtOAc 1:1) gave for the reaction in CH<sub>2</sub>Cl<sub>2</sub> 9.4 mg (46 µmol, 46%) for the reaction in MeOH 10.0 mg (49 µmol, 49%) of the title compound as a white solid.

$R_f$  = 0.50 (P/EtOAc 1:1) [UV, KMnO<sub>4</sub>].

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 2.89 (s, 3 H, *N*-CH<sub>3</sub>), 2.92 (dd, <sup>2</sup>*J* = 11.6 Hz, <sup>3</sup>*J* = 8.8 Hz, 1 H, C4-H), 3.08 (virt. tddd, <sup>3</sup>*J* ≅ 8.4 Hz, <sup>3</sup>*J* = 6.7 Hz, <sup>3</sup>*J* = 4.6 Hz, <sup>3</sup>*J* = 3.6 Hz, 1 H, C3a-H), 3.22 (ddd, <sup>2</sup>*J* = 11.6 Hz, <sup>3</sup>*J* = 4.6 Hz, <sup>4</sup>*J* = 0.8 Hz, 1 H, C4-H), 3.71 (d, <sup>3</sup>*J* = 8.4 Hz, 1 H, C9b-H), 4.21 (dd, <sup>2</sup>*J* = 9.2 Hz, <sup>3</sup>*J* = 3.6 Hz, 1 H, C3-H), 4.47 (dd, <sup>2</sup>*J* = 9.2 Hz, <sup>3</sup>*J* = 6.7 Hz, 1 H, C3-H), 6.71 (dd, <sup>3</sup>*J* = 8.4 Hz, <sup>4</sup>*J* = 1.0 Hz, 1 H, C6-H), 6.83 (td, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz, 1 H, C8-H), 7.19-7.22 (m, 1 H, C7-H), 7.47 (d, <sup>3</sup>*J* = 7.5 Hz, 1 H, C9-H).

<sup>13</sup>C-NMR (90.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 34.3 (C3a), 39.7 (CH<sub>3</sub>), 40.9 (C9b), 51.3 (C4), 69.6 (C3), 112.3 (C6), 116.9 (C9a), 118.5 (C8), 128.7 (C7), 130.7 (C9), 146.9 (C5a), 176.8 (C1).

The analytical data are in agreement with the previously reported data for this compound [S7].

**6-Methyl-3,4,4a,5,6,10b-hexahydro-1*H*-pyrano[4,3-*c*]quinolin-1-one (13) and 4-[[methyl(phenyl)amino]methyl]tetrahydro-2*H*-pyran-2-one (14)**

According to the general procedure for PET reactions, 22.7  $\mu\text{L}$  (25.8 mg, 250  $\mu\text{mol}$ , 1.00 equiv) of **12** and 81.3  $\mu\text{L}$  (72.4 mg, 375  $\mu\text{mol}$ , 1.50 equiv) of **5** were irradiated for 5 h (MeOH) or 24 h ( $\text{CH}_2\text{Cl}_2$ ) in 2.5 mL of the corresponding solvent. In  $\text{CH}_2\text{Cl}_2$  1 mol % of catalyst **7** (2.14 mg) were used, in MeOH 2.5 mol % (5.35 mg). Column chromatography on silica (P/EtOAc 2:1) yielded for the reaction in MeOH 27.6 mg product, for the reaction in  $\text{CH}_2\text{Cl}_2$  22.3 mg. The relative amounts of **13** and **14** were determined by  $^1\text{H}$  NMR integration (MeOH reaction **13/14** = 20:80,  $\text{CH}_2\text{Cl}_2$  reaction: **13/14** = 55:45).

$R_f$  = 0.39 (**14**), 0.34 (**13**) (P/EtOAc 1:1) [UV,  $\text{KMnO}_4$ ].

IR (ATR):  $\tilde{\nu}$  = 3061  $\text{cm}^{-1}$ , 3025, 2906, 2827, 1729, 1599, 1505, 1364, 1256, 1079, 992, 747.

**6-Methyl-3,4,4a,5,6,10b-hexahydro-1*H*-pyrano[4,3-*c*]quinolin-1-one (13)**

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.59-1.67 (m, 1 H, C4-H), 1.71-1.79 (m, 1 H, C4-H), 2.76-2.84 (m, 1 H, C4a-H), 2.93 (s, 3 H,  $\text{CH}_3$ ), 2.98 (dd,  $^2J$  = 11.6 Hz,  $^3J$  = 8.5 Hz, 1 H, C5-H), 3.23 (ddd,  $^2J$  = 11.6 Hz,  $^3J$  = 3.5 Hz,  $J$  = 0.8 Hz, 1 H, C5-H), 3.95 (d,  $^3J$  = 7.3 Hz, 1 H, C10b-H), 4.27 (ddd,  $^2J$  = 11.4 Hz,  $^3J$  = 7.3 Hz,  $J$  = 0.8 Hz, 1 H, C3-H), 4.35 (ddd,  $^2J$  = 11.4 Hz,  $^3J$  = 8.8 Hz,  $^3J$  = 4.3 Hz, 1 H, C3-H), 6.68-6.74 (m, 2 H, C8-H, C10-H), 7.18 (d,  $^3J$  = 7.6 Hz, 1 H, C7-H), 7.21 (td,  $^3J$  = 8.3 Hz,  $^4J$  = 1.4 Hz, 1 H, C9-H).

$^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 26.3 (C4), 29.1 (C4a), 39.6 ( $\text{CH}_3$ ), 43.0 (C10b), 55.2 (C5), 66.3 (C3), 112.1 (C6), 116.5 (s. C10a), 117.6 (C8), 128.9 (C7), 130.4 (C9), 146.4 (C6a), 173.0 (C1).

MS (EI):  $m/z$  (%) = 217 [ $\text{M}^+$ ] (9), 158 (1), 145 (3), 120 (100), 106 (6), 91 (2), 76 (8).

HRMS (EI): calc. for  $\text{C}_{13}\text{H}_{15}\text{NO}_2$  = 217.1097, found: 217.1095.

#### 4-[[Methyl(phenyl)amino]methyl]tetrahydro-2H-pyran-2-one (14)

IR (ATR):  $\tilde{\nu}$  = 3061  $\text{cm}^{-1}$ , 3025, 2906, 2827, 1729, 1599, 1505, 1364, 1256, 1079, 992, 747.

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.58-1.67 (m, 1 H, C5-H), 1.99-2.05 (m, 1 H, C5-H), 2.26 (dd,  $^2J$  = 17.2 Hz,  $^3J$  = 10.1 Hz, 1 H, C3-H), 2.45-2.55 (m, 1 H, C4-H), 2.72 (ddd,  $^2J$  = 17.2 Hz,  $^3J$  = 6.1 Hz,  $^4J$  = 1.5 Hz, 1 H, C3-H), 3.01 (s, 3 H,  $\text{CH}_3$ ), 3.24-3.33 (m, 2 H,  $N\text{-CH}_2$ ), 4.26 (td,  $^2J$  = 11.3 Hz,  $^3J$  = 3.7 Hz, 1 H, C6-H), 4.46 (ddd,  $^2J$  = 11.3 Hz,  $^3J$  = 4.9 Hz,  $^3J$  = 3.7 Hz, 1 H, C6-H), 6.72 (dd,  $^3J$  = 8.7 Hz,  $^4J$  = 0.8 Hz, 2 H,  $\text{C}_{\text{ortho}}\text{-H}$ ), 6.76 (tt,  $^3J$  = 7.3 Hz,  $^4J$  = 0.8 Hz, 1 H,  $\text{C}_{\text{para}}\text{-H}$ ), 7.25-7.29 (m, 2 H,  $\text{C}_{\text{meta}}\text{-H}$ ).

$^{13}\text{C}$ -NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 27.3 (C5), 31.0 (C4), 34.4 (C3), 40.0 ( $\text{CH}_3$ ), 58.2 ( $N\text{-CH}_2$ ), 68.6 (C6), 112.5 ( $2 \times \text{C}_{\text{ortho}}$ ), 117.2 ( $\text{C}_{\text{para}}$ ), 129.5 ( $2 \times \text{C}_{\text{meta}}$ ), 149.3 ( $\text{C}_{\text{ar}}\text{-N}$ ), 170.9 (C2).

MS (EI):  $m/z$  (%) = 219 [ $\text{M}^+$ ] (13), 174 [ $\text{M}^+ - \text{CO}_2$ ] (5), 135 (19), 120 (100), 106 (31), 93 (20), 85 (41), 83 (63).

HRMS (EI): calc. for  $\text{C}_{13}\text{H}_{17}\text{NO}_2$  = 219.1254, found: 219.1254.

**5-Methyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[*c*]quinolin-1-one (16) and 3-  
{[methyl(phenyl)amino]methyl}cyclopentan-1-one (17)**

According to the general procedure for PET reactions, 21.4  $\mu\text{L}$  (20.9 mg, 250  $\mu\text{mol}$ , 1.00 equiv) of **15** and 81.3  $\mu\text{L}$  (72.4 mg, 375  $\mu\text{mol}$ , 1.50 equiv) of **5** were irradiated for 4.5 h (MeOH) or 24 h ( $\text{CH}_2\text{Cl}_2$ ) in 2.5 mL of the corresponding solvent. In  $\text{CH}_2\text{Cl}_2$  1 mol % of catalyst **7** (2.14 mg) were used, in MeOH 2.5 mol % (5.35 mg). Column chromatography on silica (P/EtOAc 15:1  $\rightarrow$  10:1) yielded 34.1 mg product for the reaction in MeOH and 23.0 mg for  $\text{CH}_2\text{Cl}_2$ . Relative amounts of **16** and **17** were determined by  $^1\text{H}$  NMR integration. (MeOH reaction **16/17** = 19:81,  $\text{CH}_2\text{Cl}_2$  reaction: **16/17** = 39:61)

$R_f$  = 0.56 (**16**), 0.57 (**17**) (P/EtOAc 1:1) [UV,  $\text{KMnO}_4$ ].

IR (ATR):  $\tilde{\nu}$  = 3094  $\text{cm}^{-1}$ , 3061, 3025, 2952, 2935, 2898, 2877, 1739, 1599, 1505, 1360, 1155, 992, 747.

**5-Methyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[*c*]quinolin-1-one (16)**

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.97-2.03 (m, 1 H, C3-H), 2.11-2.16 (m, 1 H, C3-H), 2.31-2.37 (m, 2 H, C2-H), 2.82-2.87 (m, 2 H, C3a-H, C4-H), 2.99 (s, 3 H,  $\text{CH}_3$ ), 3.20 (*virt.* q,  $^3J \cong 8.5$  Hz, 1 H, C4-H), 3.31 (d,  $^3J = 7.0$  Hz, 1 H, C9b-H), 6.67 (d,  $^3J = 8.4$  Hz, 1 H, C6-H), 6.77 (td,  $^3J = 7.5$  Hz,  $^4J = 0.8$  Hz, 1 H, C8-H), 7.13-7.17 (m, 1 H, C7-H), 7.34 (d,  $^3J = 7.5$  Hz, 1 H, C9-H).

$^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 24.1 (C3), 34.7 (C3a), 34.8 (C2), 39.8 ( $\text{CH}_3$ ), 50.0 (C9b), 52.9 (C4), 111.9 (C6), 117.8 (C8), 117.8 (C9a), 128.0 (C7), 130.7 (C9), 146.4 (C5a), 217.1 (C1).

MS (ESI):  $m/z$  (%) = 202 [ $\text{M}^+ + \text{H}$ ] (100), 184 [ $\text{M}^+ - \text{OH}$ ] (15), 158 (4), 111 (21), 78 (1).

HRMS (ESI): calc. for  $\text{C}_{13}\text{H}_{16}\text{NO}$  = 202.12264, found: 202.12269.

### 3-[[Methyl(phenyl)amino]methyl]cyclopentan-1-one (17)

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.61-1.72 (m, 1 H, C4-H), 1.95 (ddd,  $^2J = 18.4$  Hz,  $^3J = 10.1$  Hz,  $^4J = 1.2$  Hz, 1 H, C2-H), 2.13-2.21 (m, 2 H, C4-H, C5-H), 2.30-2.36 (m, 1 H, C5-H), 2.38 (dd,  $^2J = 18.4$  Hz,  $^3J = 7.3$  Hz, 1 H, C2-H), 2.61-2.71 (m, 1 H, C3-H), 2.98 (s, 3 H,  $\text{CH}_3$ ), 3.40 (d,  $^3J = 7.1$  Hz, 2 H,  $N\text{-CH}_2$ ), 6.71-6.73 (m, 3 H,  $\text{C}_{\text{para}}\text{-H}$ ,  $\text{C}_{\text{ortho}}\text{-H}$ ), 7.23-7.26 (m, 2 H,  $\text{C}_{\text{meta}}\text{-H}$ ).

$^{13}\text{C}$ -NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 27.8 (C4), 36.2 (C3), 38.3 (C5), 39.6 ( $\text{CH}_3$ ), 43.6 (C2), 57.5 ( $N\text{-CH}_2$ ), 112.4 ( $2 \times \text{C}_{\text{ortho}}$ ), 116.8 ( $\text{C}_{\text{para}}$ ), 129.5 ( $2 \times \text{C}_{\text{meta}}$ ), 149.4 ( $\text{C}_{\text{ar}}\text{-N}$ ), 218.7 (C1).

MS (ESI):  $m/z$  (%) = 204 [ $\text{M}^+ + \text{H}$ ] (57), 184 (4), 120 (5), 111 (100).

HRMS (ESI): calc. for  $\text{C}_{13}\text{H}_{18}\text{NO}$  = 204.13829, found: 204.13836.

***tert*-Butyl 5-methyl-1-oxo-1,3,3a,4,5,9b-hexahydro-2*H*-pyrrolo[3,4-*c*]quinoline-2-carboxylate (19a)**

According to the general procedure for PET reactions, 45.8 mg (250  $\mu$ mol, 1.00 equiv) of **18a** and 81.3  $\mu$ L (72.4 mg, 375  $\mu$ mol, 1.50 equiv) of **5** were irradiated for 6 h in 2.5 mL of MeOH using 2.5 mol % (5.35 mg) of catalyst **7**. Column chromatography on silica (P/EtOAc 5:1  $\rightarrow$  3:1) yielded 22.7 mg (75.0  $\mu$ mol, 30%) of **19a** as pale yellow oil.  $R_f$  = 0.54 (P/EtOAc 1:1) [UV, KMnO<sub>4</sub>].

IR (ATR):  $\tilde{\nu}$  = 3068 cm<sup>-1</sup>, 3032, 2978, 2931, 2902, 2811, 1779, 1747, 1710, 1602, 1501, 1368, 1151.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 1.51 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.82-2.87 (m, 1 H, C3a-H), 2.88 (s, 3 H, *N*-CH<sub>3</sub>), 2.90-2.94 (m, 1 H, C3-H), 3.18 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 3.6 Hz, 1 H, C3-H), 3.66 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 3.9 Hz, 1 H, C4-H), 3.70 (d, <sup>3</sup>*J* = 8.1 Hz, 1 H, C9b-H), 3.88 (dd, <sup>2</sup>*J* = 11.0 Hz, <sup>3</sup>*J* = 7.1 Hz, 1 H, C4-H), 6.68 (dd, <sup>3</sup>*J* = 8.3 Hz, <sup>4</sup>*J* = 1.0 Hz, 1 H, C6-H), 6.80 (td, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz, 1 H, C8-H), 7.17 (ddd, <sup>3</sup>*J* = 8.3 Hz, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 0.8 Hz, 1 H, C7-H), 7.47 (d, <sup>3</sup>*J* = 7.5 Hz, 1 H, C9-H).

<sup>13</sup>C-NMR (90.6 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 28.3 (3  $\times$  CH<sub>3</sub>), 29.8 (C3a), 39.7 (*N*-CH<sub>3</sub>), 45.1 (C9b), 48.1 (C4), 51.9 (C3), 83.3 (C(CH<sub>3</sub>)<sub>3</sub>), 112.0 (C6), 117.5 (C9a), 118.2 (C8), 128.5 (C7), 130.9 (C9), 146.9 (C5a), 151.0 (NCOO), 173.0 (C1).

MS (ESI):  $m/z$  (%) = 303 [ $M^+$  + H] (67), 247 (100), 203 (58).

HRMS (ESI): calc. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> = 303.1709, found: 303.1707.



### 5-Methyl-2-tosyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (19b)

According to the general procedure for PET reactions, 47.4 mg (200  $\mu\text{mol}$ , 1.00 equiv) of **19a** and 65.1  $\mu\text{L}$  (57.9 mg, 300  $\mu\text{mol}$ , 1.50 equiv) of **5** were irradiated for 5 h in 2 mL of MeOH using 2.5 mol % (4.28 mg) of catalyst **7**. Column chromatography on silica (P/EtOAc 7:3) yielded 34.9 mg (98.0  $\mu\text{mol}$ , 49%) of **19b** as off white solid.  $R_f$  = 0.22 (P/EtOAc 7:3) [UV,  $\text{KMnO}_4$ ]; mp: 155  $^{\circ}\text{C}$ .

IR (ATR):  $\tilde{\nu}$  = 3036  $\text{cm}^{-1}$ , 2992, 2949, 2924, 2873, 2808, 2757, 1728, 1678, 1602, 1509, 1201, 952.

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.41 (s, 3 H,  $\text{CH}_3$ ), 2.75-2.80 (m, 1 H, C3-H), 2.84 (s, 3 H, *N*- $\text{CH}_3$ ), 2.89 (qdd,  $^3J$  = 8.0 Hz,  $^3J$  = 4.5 Hz,  $^3J$  = 2.9 Hz, 1 H, C3a-H), 3.15 (ddd,  $^2J$  = 11.5 Hz,  $^3J$  = 4.5 Hz,  $^4J$  = 0.7 Hz, 1 H, C3-H), 3.63 (d,  $^3J$  = 8.0 Hz, 1 H, C9b-H), 3.77 (dd,  $^2J$  = 10.3 Hz,  $^3J$  = 2.9 Hz, 1 H, C4-H), 4.05 (dd,  $^2J$  = 10.3 Hz,  $^3J$  = 6.9 Hz, 1 H, C4-H), 6.65 (d,  $^3J$  = 8.2 Hz, 1 H, C6-H), 6.74 (td,  $^3J$  = 7.3 Hz,  $^4J$  = 0.7 Hz, 1 H, C8-H), 7.15 (ddd,  $^3J$  = 8.2 Hz,  $^3J$  = 7.3 Hz,  $^4J$  = 1.6 Hz, 1 H, C7-H), 7.28-7.31 (m, 3 H, C9-H,  $\text{C}_{\text{meta}}$ -H), 7.88 (d,  $^3J$  = 8.2 Hz, 2 H,  $\text{C}_{\text{ortho}}$ -H).

$^{13}\text{C}$ -NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 21.9 ( $\text{CH}_3$ ), 30.4 (C3a), 39.6 (*N*- $\text{CH}_3$ ), 44.5 (C9b), 48.9 (C4), 51.7 (C3), 112.1 (C6), 116.3 (C9a), 118.2 (C8), 128.3 ( $2 \times \text{C}_{\text{ortho}}$ ), 128.7 (C7), 129.9 ( $2 \times \text{C}_{\text{meta}}$ ), 130.8 (C9), 135.2 (C-S), 145.4 ( $\underline{\text{C}}\text{-CH}_3$ ), 146.7 (C5a), 172.4 (C1).

MS (EI):  $m/z$  (%) = 356 [ $\text{M}^+$ ] (3), 279 (4), 234 (58), 171 (19), 135 (54), 106 (60), 57 (100).

HRMS (EI): calc. for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$  = 356.1189, found: 356.1187.

***tert*-Butyl 4-[[methyl(phenyl)amino]methyl]-2-oxopiperidine-1-carboxylate (**22**)**

According to the general procedure for PET reactions, 54.3  $\mu\text{L}$  (48.3 mg, 250  $\mu\text{mol}$ , 1.00 equiv) of **5** and 69.1  $\mu\text{L}$  (73.9 mg, 375  $\mu\text{mol}$ , 1.50 equiv) of **20** were irradiated for 24 h in 2.5 mL of  $\text{CH}_2\text{Cl}_2$  using 1 mol % of catalyst **7** (2.14 mg). Column chromatography on silica (P/EtOAc 4:1) yielded 60.0 mg (188  $\mu\text{mol}$ , 75%) of **22** as pale yellow oil.  $R_f = 0.15$  (P/EtOAc 4:1) [UV,  $\text{KMnO}_4$ ].

IR (ATR):  $\tilde{\nu} = 2978\text{ cm}^{-1}$ , 2931, 2826, 1768, 1707, 1598, 1505, 1476, 1451, 1393, 1368.

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.46-1.51 (m, 1 H, C5-H), 1.52 (s, 9 H,  $\text{C}(\text{CH}_3)_3$ ), 1.99-2.05 (m, 1 H, C5-H), 2.21 (dd,  $^2J = 16.7\text{ Hz}$ ,  $^3J = 10.8\text{ Hz}$ , 1 H, C3-H), 2.30-2.43 (m, 1 H, C4-H), 2.63 (ddd,  $^2J = 16.7\text{ Hz}$ ,  $^3J = 5.3\text{ Hz}$ ,  $J = 2.3\text{ Hz}$ , 1 H, C3-H), 2.97 (s, 3 H,  $N\text{-CH}_3$ ), 3.24 (dd,  $^3J = 7.1\text{ Hz}$ ,  $J = 2.3\text{ Hz}$ , 2 H,  $N\text{-CH}_2$ ), 3.48 (ddd,  $^2J = 12.9\text{ Hz}$ ,  $^3J = 11.5\text{ Hz}$ ,  $^3J = 4.4\text{ Hz}$ , 1 H, C6-H), 3.85 (ddd,  $^2J = 12.9\text{ Hz}$ ,  $^3J = 5.1\text{ Hz}$ ,  $^3J = 3.9\text{ Hz}$ , 1 H, C6-H), 6.68 (ddd,  $^3J = 6.8\text{ Hz}$ ,  $^3J = 2.1\text{ Hz}$ ,  $^4J = 1.0\text{ Hz}$ , 2 H,  $\text{C}_{\text{ortho}}\text{-H}$ ), 6.71 (tt,  $^3J = 7.3\text{ Hz}$ ,  $^4J = 1.0\text{ Hz}$ , 1 H,  $\text{C}_{\text{para}}\text{-H}$ ), 7.21-7.25 (m, 2 H,  $\text{C}_{\text{meta}}\text{-H}$ ).

$^{13}\text{C}$ -NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 27.4 (C5), 28.2 ( $3 \times \text{CH}_3$ ), 32.1 (C4), 39.4 (C3), 40.0 ( $N\text{-CH}_3$ ), 45.6 (C6), 58.1 ( $N\text{-CH}_2$ ), 83.2 ( $\text{C}(\text{CH}_3)_3$ ), 112.4 ( $2 \times \text{C}_{\text{ortho}}$ ), 116.9 ( $\text{C}_{\text{para}}$ ), 129.5 ( $2 \times \text{C}_{\text{meta}}$ ), 149.3 ( $\text{C}_{\text{ar}}N$ ), 152.7 ( $N\text{C}\text{OO}$ ), 170.6 (C2).

MS (EI):  $m/z$  (%) = 318 [ $\text{M}^+$ ] (2), 218 (7), 120 (100), 97 (6), 77 (6), 68 (7), 56 (11).

HRMS (EI): calc. for  $\text{C}_{17}^{13}\text{C}_1\text{H}_{20}\text{N}_2\text{O}_3 = 319.1971$ , found: 319.1965.

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