SUPPORTING INFORMATION

Diaryliodonium Salts as Efficient Lewis Acid Catalysts for Direct Three Component Mannich Reactions

Yanxia Zhang, Jianwei Han* and Zhen-Jiang Liu*

a. School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, P. R. China. Fax: (+86)-21- 60877231; Tel: (+86)-21- 60877227; E-mail: zjliu@sit.edu.cn

b. Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200237, P. R. China. Fax: (+86)-21- 54925383; Tel: (+86)-21- 54925551; E-mail: jianweihan@sioc.ac.cn

Table of Contents

Part 1. General Information........................................................................................................S2
   a. Methods
   b. Materials

Part 2. Experimental Section....................................................................................................S3-S4
   a. Typical procedure for three components Mannich reaction (Table 1)
   b. Screen solvents for three components Mannich reaction
   c. Screen catalyst dosage for three components Mannich reaction
   d. Synthesis of the Chiral Diaryliodonium Salt

Part 3. Characterization of the Products..................................................................................S4-S12

Part 4. References....................................................................................................................S12

Part 5. Copies of $^1$H-NMR, $^{13}$C-NMR and $^{19}$F-NMR Spectra............................................S13-S36
Part 1. General Information

a. Methods:

NMR spectrum: $^1$H and $^{13}$C, $^{19}$F NMR spectra were recorded on a Bruker AVANCE 300 spectrometer, operating at 300 MHz for $^1$H NMR; 75 MHz for $^{13}$C NMR; 282 MHz for $^{19}$F NMR. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC analyses were on an Thermo Scientific Ultimate 3000 series with DAICEL chiral columns. Mass spectra were recorded by the State Key Laboratory of Organometallic Chemistry of Shanghai Institute of Organic Chemistry.

Chromatography: Column chromatography was performed with silica gel (300-400 mesh ASTM; Huanghai).

b. Materials: All solvents were dried and/or distilled by standard methods. Aniline and benzaldehyde distilled by standard methods, other reagents were purchased from commercial sources (Adamas, Acros and Aldrich) and used without further purification. All the diaryliodonium salts were synthesized according to the literature procedures. Salts 2a, 2b, 2c, 2d, 2e were prepared from iodine and the corresponding arene in the presence of mCPBA and TfOH described by Olofsson and co-workers.$^1$ Salt 2f was synthesized by situ anion exchange described by Olofsson and co-workers.$^2$ Salt 2g was prepared from the corresponding arene with sodium metaperiodate as the coupling reagent in acidic media described by Skulski and co-workers.$^3$ Salt 2h was prepared from oxidation of an iodoarene with mCPBA in the presence of TsOH followed by reaction with an arene by Olofsson and co-workers.$^4$ Salt 2i were prepared from the corresponding Koser’s reagent and phenylacetylene described by Gerald F. Korse and co-workers.$^5$ Salt 2j was synthesized by Viktor V. Zhdankin and co-workers.$^6$
Part 2. Experimental Section

a. Typical procedure for three components Mannich reaction (Table 1)
PhCOCH₃ (9a, 1.0 mmol, 1.0 equiv.), PhCHO (10a, 1.0 mmol, 1.0 equiv.) and PhNH₂(11a, 1.0 mmol, 1.0 equiv) were added into hydrogenated tube under free-solvent, and then added catalyst. The mixture was stirred under at room temperature for 24 h, the solvents were removed via a rotary evaporator. The residue was purified with silica gel chromatography (ethyl acetate/petroleum ether=1:30) to provide pure products.

b. Screen solvents for three components Mannich reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>hexane</td>
<td>24</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>ethanol</td>
<td>24</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>ethyl acetate</td>
<td>24</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>chloroform</td>
<td>24</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>acetonitrile</td>
<td>24</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>methanol</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>water</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>Free-solvent</td>
<td>24</td>
<td>86</td>
</tr>
</tbody>
</table>

Unless otherwise specified, reaction conditions: 9a (1 mmol), 10a (1 mmol), 11a (1 mmol) in the presence of iodonium salt 8a (0.1 mmol) in solvent (1 mL) at room temperature for 24 hours. b Isolated yield.

c. Screen catalyst loading for Mannich reaction of three components

<table>
<thead>
<tr>
<th>entry</th>
<th>Catalyst Loading ( mol%)</th>
<th>Time(h)</th>
<th>Yield(%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>24</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>24</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>24</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>12.5</td>
<td>24</td>
<td>80</td>
</tr>
</tbody>
</table>

 Unless otherwise specified, reaction conditions: 9a (1 mmol), 10a (1 mmol), 11a (1 mmol) in the presence of iodonium salt 8a at room temperature for 24 hours. b Isolated yield.

d. Synthesis of the Chiral Diaryliodonium Salt

1.
A solution of diphenyliodonium triflate (1.00 g, 2.3mmol) in dichloromethane (75 ml) was treated with a solution of sodium (1D)-camphor-10-sulfonate (2.87g, 11.3mmol) in water (10 ml) at room temperature. After separation of the phases, the aqueous phase was extracted thrice with dichloromethane(10 ml X 3). The combined organic extracts were concentrated to dryness. The material obtained was dissolved in dichloromethane(10 ml) and the procedure outlined repeated. After a total of three such treatments, complete anion exchange was accomplished (as determined by $^1$H NMR). The crude material was triturated with diethyl ether, to yield the salt (0.94 g, 79%) as an off-white solid after isolation by filtration and several washes with diethyl ether.

2.

A solution of mesityl(perfluorophenyl)iodonium salts (0.16 g, 0.28 mmol) in dichloromethane (10 ml) was treated with a solution of sodium (R)-(−)-1,1′-binaphthyl-2,2′-diylhydrogenphosphate (0.11g, 0.28mmol) in water(10ml) at room temperature. After separation of the phases, the aqueous phase was extracted thrice with dichloromethane(10 ml X 3). The combined organic extracts were concentrated to dryness. The material obtained was dissolved in dichloromethane (10 ml) and the procedure outlined repeated. After a total of three such treatments, complete anion exchange was accomplished (as determined by $^1$H NMR). The crude material was triturated with diethyl ether, to yield the salt (0.17g, 80%) as an off-white solid after isolation by filtration and several washes with diethyl ether.

Part 3. Characterization of the Products

1,3-diphenyl-3-(phenylamino)propan-1-one(12a)
The product (93% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^7\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.96-7.89 (d, 2H), 7.60-7.53 (t, 1H), 7.50-7.40 (m, 4H), 7.35-7.30 (t, 2H), 7.25-7.20 (t, 1H), 7.15-7.06 (t, 2H), 6.73-6.64 (t, 1H), 6.61-6.55 (d, 2H), 5.00(t, 1H) 3.60-3.40(m, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 198.49, 147.14, 143.16, 136.84, 133.69, 129.34, 129.06, 128.94, 128.44, 127.59, 126.59, 118.00, 102.99, 54.99, 46.54.

3-phenyl-3-(phenylamino)-1-(pyridine-2-yl)propan-1-one (12b)

The product (83% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^8\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.80-8.72 (d, 1H), 8.10-8.02 (d, 1H), 7.89-7.80 (t, 1H), 7.55-7.47 (d, 3H), 7.40-7.30 (t, 2H), 7.30-7.20 (t, 1H), 7.05-7.02 (t, 2H), 6.68-6.60 (t, 1H), 6.56-6.50 (d, 2H), 5.10-5.00(m, 1H), 3.85-3.52 (m, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 200.06, 153.45, 149.14, 147.23, 143.41, 137.38, 129.28, 128.94, 127.63, 127.42, 126.63, 122.55, 117.55, 113.66, 55.56, 46.11.

1-(4-bromophenyl)-3-phenyl-3-(phenylamino)propan-1-one (12c)

The product (90% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^9\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.80-7.72 (d, 2H), 7.63-7.55 (d, 2H), 7.47-7.40 (d, 2H), 7.38-7.30 (t, 2H), 7.30-7.27 (d, 1H), 7.17-7.07 (t, 2H), 6.74-6.65 (t, 1H), 6.63-6.53 (t, 2H), 5.08-5.00 (t, 1H), 3.52-3.38 (m, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 197.51, 147.05, 142.93, 135.60, 132.23, 129.93, 129.11, 127.71, 126.57, 118.13, 114.03, 54.90, 46.39.
1-(2-methoxyphenyl)-3-phenyl-3-(phenylamino)propan-1-one (12d)

\[
\text{O} \quad \text{N} \quad \text{O} \quad \text{Me}
\]

The product (85% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^8\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.67-7.62 (m, 1H), 7.53-7.42 (m, 3H), 7.37-7.30 (t, 2H), 7.25-7.21 (d, 1H), 7.13-7.05 (t, 2H), 7.03-6.95 (t, 2H), 6.70-6.63 (t, 1H), 6.57-6.50 (d, 2H), 5.02-4.95 (dd, 1H), 3.95 (s, 3H), 3.60-3.32 (m, 2H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 200.85, 158.67, 147.43, 143.61, 134.12, 130.84, 129.25, 128.89, 127.30, 126.60, 121.14, 117.64, 113.87, 111.72, 55.78, 55.21, 51.71.

2-(phenyl(phenylamino)methyl)cyclohexanone (12e)

\[
\text{O} \quad \text{N} \quad \text{H}
\]

The product (99% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^7\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.45-7.36 (t, 2H), 7.36-7.28 (m, 2H), 7.28-7.20 (m, 1H), 7.14-7.05 (m, 2H), 6.72-6.63 (m, 1H), 6.63-6.53 (t, 2H), 4.88-4.60 (m, 1H), 2.90-2.70 (m, 1H), 2.50-2.25 (m, 2H), 2.10-1.60 (m, 6H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 213.36, 211.60, 147.44, 141.93, 129.30, 129.25, 128.71, 128.61, 127.75, 127.50, 127.41, 127.24, 121.12, 117.90, 117.73, 114.29, 113.82, 58.18, 57.73, 57.44, 56.87, 42.66, 42.25, 42.02, 31.55, 28.89, 28.16, 27.28, 25.10, 23.89.

3-(4-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12f)

\[
\text{N} \quad \text{O} \quad \text{N} \quad \text{O}
\]

The product (67% yield) as a yellow solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^10\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.05-7.95 (m, 3H), 7.87-7.80 (d, 1H), 7.63-7.53 (m, 2H), 7.53-7.44 (m, 2H), 7.44-7.35 (t, 1H), 7.12-7.02 (t, 2H), 6.71-6.62 (t, 1H), 6.50-6.42 (d, 2H), 5.62-5.53 (m, 1H), 3.85-3.72 (m, 1H), 3.45-3.33 (m, 1H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.46, 148.93, 146.29, 138.54, 134.06, 133.98, 129.46, 129.31, 129.03, 128.63, 128.55, 125.21, 118.45, 113.65, 51.06, 44.99.

3-(3-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12g)

![Structure of 3-(3-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one](image)

The product (76% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^{11}$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.37-8.32 (s, 1H), 8.14-8.07 (d, 1H), 7.95-7.90 (d, 2H), 7.87-7.80 (d, 1H), 7.65-7.55 (t, 1H), 7.55-7.43 (q, 3H), 7.17-7.07 (t, 2H), 6.78-6.68 (t, 1H), 6.60-6.50 (d, 2H), 5.17-5.10 (t, 1H), 3.58-3.51 (d, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 197.54, 148.89, 146.51, 145.69, 136.50, 134.04, 133.24, 130.01, 129.51, 129.08, 128.39, 122.74, 121.70, 118.66, 114.05, 54.25, 46.07.

3-(4-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12h)

![Structure of 3-(4-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one](image)

The product (96% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^8$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.95-7.90 (d, 2H), 7.63-7.55 (t, 1H), 7.50-7.37 (m, 4H), 7.34-7.25 (t, 2H), 7.15-7.07 (t, 2H), 6.75-6.67 (t, 1H), 6.60-6.50 (d, 2H), 5.05-4.95 (t, 1H), 3.58-3.41 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.09, 146.57, 141.48, 136.69, 133.85, 133.23, 129.40, 129.20, 129.00, 128.41, 128.13, 118.55, 114.31, 54.61, 46.23.

3-(4-bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12i)

![Structure of 3-(4-bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one](image)

The product (96% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^8$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.95-7.87 (d, 2H), 7.65-7.55 (t, 1H), 7.52-7.42 (t, 4H), 7.40-7.30 (d, 2H), 7.15-7.07 (t, 2H), 6.75-6.65 (t, 1H), 6.60-6.50 (d, 2H), 5.05-4.90 (t, 1H), 3.55-3.35 (m, 2H).
\( ^{13} \text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 198.09, 146.86, 142.27, 136.70, 133.85, 132.14, 129.39, 129.00, 128.43, 128.41, 121.26, 118.30, 114.06, 54.42, 46.30. \)

**3-(3-methoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one** (12j)

The product (88% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^8\)

\( ^1 \text{H NMR} (300 \text{ MHz, CDCl}_3) \delta 8.00-7.87 (d, 2H), 7.64-7.54 (t, 1H), 7.52-7.43 (t, 2H), 7.34-7.23 (t, 1H), 7.17-6.98 (m, 4H), 6.85-6.76 (d, 1H), 6.75-6.65 (t, 1H), 6.65-6.55 (d, 2H), 5.05-4.96 (t, 1H), 3.79 (s, 3H), 3.60-3.35 (m, 2H). \)

\( ^{13} \text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 198.47, 160.21, 147.25, 145.12, 136.89, 133.71, 130.13, 129.35, 128.96, 128.47, 118.87, 118.03, 114.05, 112.74, 112.42, 55.45, 55.04, 46.56. \)

**3-(2-bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one** (12k)

The product (69% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

\( ^1 \text{H NMR} (300 \text{ MHz, CDCl}_3) \delta 8.05-7.95 (d, 2H), 7.64-7.52 (q, 3H), 7.51-7.41 (t, 2H), 7.25-7.19 (m, 1H), 7.15-7.05 (q, 3H), 6.72-6.61 (t, 1H), 6.52-6.43 (d, 2H), 5.31-5.20 (dd, 1H), 3.70-3.57 (q, 1H), 3.35-3.21 (q, 1H). \)

\( ^{13} \text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 198.76, 146.64, 141.21, 133.83, 133.32, 129.33, 129.15, 128.94, 128.65, 128.50, 128.32, 122.82, 118.08, 113.85, 54.46, 44.04. \)

**1-phenyl-3-(phenylamino)-3-(p-tolyl)propan-1-one** (12l)

The product (94% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.\(^7\)

\( ^1 \text{H NMR} (300 \text{ MHz, CDCl}_3) \delta 7.97-7.90 (d, 2H), 7.65-7.55 (q, 1H), 7.50-7.41 (t, 2H), 7.40-7.32 (d, 2H), 7.20-7.05 (q, 4H), 6.74-6.66 (t, 1H), 6.64-6.56 (d, 2H), 5.05-4.95 (t, 1H), 3.60-3.40 (m, 2H), 2.36-
2.30 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 198.53, 146.92, 139.90, 137.25, 136.86, 133.66, 129.74, 129.34, 128.98, 128.45, 126.57, 118.22, 114.28, 54.96, 46.47, 21.34.

3-(3-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12m)

![Chemical structure of 3-(3-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12m)]

The product (87% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^{12}$

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.97-7.87 (d, 2H), 7.64-7.55 (t, 1H), 7.53-7.43 (t, 3H), 7.40-7.33 (d, 1H), 7.33-7.20 (m, 2H), 7.17-7.07 (t, 2H), 6.75-6.66 (t, 1H), 6.60-6.53 (d, 2H), 5.05-4.92 (t, 1H), 3.58-3.37 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.98, 146.89, 145.55, 136.69, 134.92, 133.84, 130.36, 129.40, 129.00, 128.42, 127.82, 126.77, 124.89, 118.32, 114.05, 54.60, 46.38.

3-(polyfluorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12n)

![Chemical structure of 3-(polyfluorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12n)]

The product (45% yield) as a yellow solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.00-7.92 (d, 2H), 7.67-7.57 (t, 1H), 7.55-7.45 (t, 2H), 7.24-7.14 (t, 2H), 6.83-6.67 (m, 3H), 5.71-5.57 (t, 1H), 3.85-3.65 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.37, 145.78, 136.31, 134.00, 129.77, 129.07, 128.29, 119.45, 113.93, 45.50, 43.78.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ -161.80 (td, $J_F = 24.0$, 9.0 Hz, 2F), -155.40 (t, $J_F = 21.0$ Hz, 1F), -144.05 (dd, $J_F = 21.0$, 6.0 Hz, 2F).

3-(4-bromophenyl)-3-(phenylamino)-1-(pyridine-2-yl)propan-1-one (12o)

![Chemical structure of 3-(4-bromophenyl)-3-(phenylamino)-1-(pyridine-2-yl)propan-1-one (12o)]

The product (94% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^8$
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.80-8.70 (d, 1H), 8.10-7.97 (d, 1H), 7.93-7.78 (t, 1H), 7.60-7.30 (m, 5H), 7.13-7.00 (t, 2H), 6.70-6.60 (t, 1H), 6.53-6.38 (d, 2H), 5.10-4.88 (m, 1H), 3.80-3.45 (m, 2H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 199.70, 153.31, 149.14, 146.87, 142.50, 137.42, 132.01, 129.31, 128.44, 127.72, 122.57, 121.12, 117.85, 113.68, 54.99, 45.86.

3-((4-methoxyphenyl)amino)-1,3-diphenylpropan-1-one (12p)

The product (90% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^{13}$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.95-7.87 (d, 2H), 7.60-7.53 (m, 1H), 7.50-7.42 (m, 4H), 7.37-7.30 (t, 2H), 7.25-7.22 (d, 1H), 6.72-6.67 (d, 2H), 6.60-6.53 (d, 2H), 4.98-4.91 (dd, 1H), 3.70 (s, 3H), 3.55-3.40 (m, 2H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.55, 152.76, 143.14, 140.95, 136.90, 133.63, 129.02, 128.91, 128.81, 128.42, 127.60, 126.74, 115.87, 114.91, 56.20, 55.90, 46.52.

4-bromo-2,3,5,6-tetrafluoro-1,1'-biphenyl (12q)

The product (86% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^7$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97-7.87 (d, 2H), 7.65-7.55 (t, 1H), 7.50-7.42 (m, 4H), 7.37-7.30 (t, 2H), 7.25-7.20 (m, 1H), 7.07-7.00 (d, 2H), 6.55-6.42 (d, 2H), 5.00-4.90 (t, 1H), 3.57-3.35 (m, 2H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.37, 145.67, 142.62, 136.74, 133.79, 129.14, 128.97, 128.42, 127.75, 126.52, 115.23, 55.16, 46.42.

3-((3-chlorophenyl)amino)-1,3-diphenylpropan-1-one (12r)

The product (89% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.$^{14}$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97-7.87 (d, 2H), 7.64-7.55 (t, 1H), 7.52-7.40 (q, 4H), 7.37-7.30 (t, 2H), 7.25-7.20 (m, 1H), 7.05-6.95 (t, 1H), 6.70-6.60 (d, 1H), 6.60-6.52 (s, 1H), 6.47-6.40 (dd, 1H), 5.08-4.95 (t, 1H), 3.60-3.35 (m, 2H).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.28, 148.39, 142.56, 136.76, 135.01, 133.81, 130.34, 129.17, 128.99,
128.44, 127.79, 126.51, 117.90, 113.81, 112.17, 54.83, 46.35.

1,3-diphenyl-3-((3-(trifluoromethyl)phenyl)amino)propan-1-one (12s)

The product (76% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97-7.87 (d, 2H), 7.65-7.55 (t, 1H), 7.53-7.41 (t, 4H), 7.40-7.32 (t, 2H), 7.30-7.22 (m, 1H), 7.22-7.13 (t, 1H), 6.95-6.87 (d, 1H), 6.85-6.77 (s, 1H), 6.73-6.65 (d, 1H), 5.10-5.00 (t, 1H), 3.60-3.40 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.30, 147.32, 142.38, 136.56, 133.86, 129.77, 129.20, 129.00, 128.44, 127.85, 126.47, 116.61, 114.37, 110.55, 54.86, 46.35.

3-((4-bromophenyl)amino)-1,3-diphenylpropan-1-one (12t)

The product (98% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96-7.87 (d, 2H), 7.63-7.55 (t, 1H), 7.50-7.38 (q, 4H), 7.37-7.30 (t, 2H), 7.26-7.23 (m, 1H), 7.20-7.13 (d, 2H), 6.50-6.42 (d, 2H), 5.00-4.90 (t, 1H), 3.58-3.40 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.36, 149.87, 142.26, 136.72, 133.80, 132.04, 129.14, 128.97, 128.42, 127.82, 126.58, 115.99, 55.36, 46.25.

3-(4-bromo-2-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12u)

The product (83% yield) as a yellow liquid was purified with silica gel chromatography (ethyl acetate/petroleum ether).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.15-8.07 (s, 1H), 8.01-7.94 (d, 2H), 7.80-7.72 (d, 1H), 7.68-7.55 (q, 2H), 7.53-7.43 (t, 2H), 7.15-7.05 (t, 2H), 6.75-6.65 (t, 1H), 6.51-6.41 (d, 2H), 5.60-5.50 (dd, 1H), 3.83-3.70 (m, 1H), 3.48-3.33 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.13, 149.29, 146.01, 137.69, 137.10, 136.36, 134.12, 131.13, 129.55, 129.09, 128.58, 128.04, 121.60, 118.74, 115.35, 113.88, 50.80, 44.65.
The product (93% yield) as an off-white solid after isolation by filtration and several washes with diethyl ether. The analytical data is corresponding to those described in the literature.\textsuperscript{15}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 8.10-8.00 (d, 4H), 7.58-7.48 (t, 2H), 7.47-7.35 (t, 4H), 3.15-3.05 (d, 1H), 2.57-2.47 (d, 1H), 2.47-2.40 (m, 1H), 2.30-2.18 (m, 1H), 1.98-1.75 (m, 3H), 1.50-1.36 (m, 1H), 1.27-1.18 (m, 1H), 0.95-0.90 (s, 3H), 0.73-0.67 (s, 3H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 217.04, 135.22, 131.54, 123.52, 115.60, 58.40, 47.72, 47.01, 42.80, 42.47, 26.93, 24.20, 19.90, 19.69.

The product (80% yield) as an off-white solid after isolation by filtration and several washes with diethyl ether.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.92-7.75 (t, 4H), 7.45-7.31 (m, 4H), 7.30-7.15 (m, 4H), 6.76-6.64 (s, 2H), 2.67-2.45 (s, 6H), 2.15-2.05 (s, 3H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 148.64, 148.51, 142.58, 141.43, 132.33, 131.00, 129.98, 129.22, 128.08, 126.97, 125.87, 124.67, 124.67, 121.75, 121.72, 121.39, 121.35, 26.51, 20.86.

\textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) -157.57 (m, 2F), -146.80 (m, 1F), -122.45 (m, 2F).

HRMS(ESI): calcd for C\textsubscript{15}H\textsubscript{11}F\textsubscript{5}I\textsuperscript{+}([M-anion]+):412.9820, found 412.9819

Part 4. References

4. Tue B. Petersen, Rehan Khan, and Berit Olofsson*, \textit{Org. Lett.}, 2011, 13, 3462-3465
Part 5. Copies of $^1$H-NMR, $^{13}$C-NMR and $^{19}$F-NMR Spectra