Supporting Information

KO'iBu Mediated Efficient Approach for the Synthesis of fused heterocycles via Intramolecular O-/N-Arylations

Raju Singha, Atiur Ahmed, Yasin Nuree, Munmun Ghosh and Jayanta K. Ray*

Department of Chemistry, Indian Institute of Technology, Kharagpur721302, India

* Corresponding author. Tel.: +91 3222283326; fax: +91 3222282252.

E-mail address: jkray@chem.iitkgp.ernet.in (J. K. Ray).

Table of contents

<table>
<thead>
<tr>
<th></th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General</td>
<td>2</td>
</tr>
<tr>
<td>2. General procedures</td>
<td>2</td>
</tr>
<tr>
<td>2.1 General procedure for the synthesis 2'-bromo-biphenyl-2-carbaldehydes: GP-1</td>
<td>2</td>
</tr>
<tr>
<td>2.2 General procedure for the synthesis of 2'-bromo-biphenyl-2-methanols: GP-2</td>
<td>3</td>
</tr>
<tr>
<td>2.3 General procedure for the synthesis of 6H-benzo[c]chromenes: GP-3</td>
<td>3</td>
</tr>
<tr>
<td>2.4 General procedure for the synthesis of 2'-bromo-biphenyl-2-carboxylic acids: GP-4</td>
<td>4</td>
</tr>
<tr>
<td>2.5 General procedure for the synthesis of 6H-benzo[c]chromen-6-ones: GP-5</td>
<td>4</td>
</tr>
<tr>
<td>2.6 General procedure for the synthesis of 2'-bromo-biphenyl-2-amines: GP-6</td>
<td>5</td>
</tr>
<tr>
<td>2.7 General procedure for the synthesis of carbazoles: GP-7</td>
<td>5</td>
</tr>
<tr>
<td>2.8 General procedure for the synthesis of 2'-bromo-biphenyl-2-diacylamines: GP-8</td>
<td>6</td>
</tr>
<tr>
<td>2.9 General procedure for the synthesis of 2-(2-bromobenzyloxy)phenol: GP-9</td>
<td>6</td>
</tr>
<tr>
<td>3. Spectroscopic data</td>
<td>7</td>
</tr>
<tr>
<td>4. References</td>
<td>20</td>
</tr>
<tr>
<td>5. $^1$H and $^{13}$C NMR spectra</td>
<td>21</td>
</tr>
</tbody>
</table>
1. General methods:

High quality reagents were purchased from Sigma Aldrich. Analytical grade commercial reagents and solvents were purified by standard procedures prior to use. Chromatographic purification was done with 60-120 mesh silica gel (Merck). For reaction monitoring, pre-coated silica gel 60 F254 sheets (Merck) were used. $^1$H NMR (200 MHz) spectra were recorded on a BRUCKER-AC 200 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, bs = broad singlet), coupling constant (Hz). $^{13}$C NMR (50 MHz) spectra were recorded on a BRUKER-AC 200 MHz Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.23 ppm). HRMS (ESI) spectra were taken using Waters Xevo G2 QTof mass spectrometer.

2. General procedures

2.1 General procedure for the synthesis 2’-bromo-biphenyl-2-carbaldehydes: GP-1

The compounds were synthesized using our previously reported Suzuki-Miyaura cross coupling procedure.

The compound 2-bromobenzaldehyde (1.5 mmol), 2-bromophenylboronic acid (1.6 mmol), $\text{K}_2\text{CO}_3$ (1.5 mmol) and $\text{PPh}_3$ (0.25 equiv.) were taken in two-neck round bottomed flask and flashed with nitrogen gas. Then 3 mL of dry DMF was added and degassed with $\text{N}_2$ for 15 min. Then the catalyst Pd(OAc)$_2$ (5 mol%) was added and the reaction mixture was heated at 90 °C for 4h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and then diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$,
evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.

2.2 General procedure for the synthesis 2′-bromo-biphenyl-2-methanol: GP-2

The compounds were synthesized using the literature reported sodium borohydride reduction procedure:

The compound 2′-bromobiphenyl-2-carbaldehyde (0.5 mmol) and NaBH₄ (0.6 mmol) were taken in a two-neck round bottomed flask and then 3.0 mL of acetonitrile was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 3h. After completion of the reaction the reaction mixture was diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.

2.3 General procedure for the synthesis of 6H-benzo[c]chromens: GP-3

The compounds were synthesized using our optimized reaction condition:

The substrate 2′-bromobiphenyl-2-methanol (0.3 mmol) and potassium tert-butoxide (0.9 mmol) were taken in two-neck round bottomed flask. The flask was first evacuated and then filled with nitrogen gas. Then 3 mL of DMSO solvent was added and heated at 100 °C for 3h. After completion of the reaction, the reaction mixture was cooled to room temperature and then diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.
2.4 General procedure for the synthesis of 2'-bromo-biphenyl-2-carboxylic acids: **GP-4**

The compounds were synthesized using the Pinnick oxidation procedure:

![Chemical structure of 2'-bromo-biphenyl-2-carboxylic acid](image)

The solvent acetonitrile (3 mL) was added to the substrate 2'-bromobiphenyl-2-carbaldehyde (0.5 mmol) taken in round bottomed flask. The reaction mixture was cooled to 0 °C and then NaH₂PO₄ (0.5 mmol) dissolved in minimum amount of water was added. Then few drops of H₂O₂ and NaClO₂ (1.5 equiv.) in water were added and the reaction mixture was stirred at room temperature for 3h. After completion of the reaction the reaction mixture was diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.

2.5 General procedure for the synthesis of 6H-benzo[c]chromen-6-ones: **GP-5**

The compounds were synthesized using our modified reaction condition:

![Chemical structure of 6H-benzo[c]chromen-6-one](image)

The substrate 2'-bromobiphenyl-2-carboxylic acid (0.3 mmol) and potassium tert-butoxide (0.9 mmol) were taken in two-neck round bottomed flask. The flask was first evacuated and then filled with nitrogen gas. Then 3 mL of DMSO solvent was added and heated at 130 °C for 3h. After completion of the reaction, the reaction mixture was cooled to room temperature and then diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.
2.6 General procedure for the synthesis of 2'-bromo-biphenyl-2-amines: GP-6

The compounds were synthesized using the Suzuki-Miyaura cross coupling procedure.

\[
\text{NH}_2 \quad \text{Br} \quad \text{I} \quad \text{NH}_2 \\
\text{I} \quad \text{Br} \quad \text{Br} \quad \text{Br}
\]

\[
Pd(OAc)_2, PPh_3, K_2CO_3, DMF \quad 90 ^\circ C, 3h
\]

The compound 2-iodoaniline (1.0 mmol), 2-bromophenylboronic acid (1.1 mmol), K$_2$CO$_3$ (1.0 mmol) and PPh$_3$ (0.25 equiv.) were taken in two-neck round bottomed flask and flashed with nitrogen gas. Then 3 mL of dry DMF was added and degassed with N$_2$ for 15 min. Then the catalyst Pd(OAc)$_2$ (5 mol%) was added and the reaction mixture was heated at 90 °C for 3h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and then diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.

2.7 General procedure for the synthesis of carbazoles: GP-7

The compounds were synthesized using our modified reaction condition:

\[
\text{Br} \quad \text{NH}_2 \quad \text{DMSO, KO}^t\text{Bu} \quad \text{H}
\]

\[
130 ^\circ C, 12h
\]

The substrate 2’-bromobiphenyl-2-amine (0.3 mmol) and potassium tert-butoxide (0.9 mmol) were taken in two-neck round bottomed flask. The flask was first evacuated and then filled with nitrogen gas. Then 3 mL of DMSO solvent was added and heated at 130 °C for 12h. After completion of the reaction, the reaction mixture was cooled to room temperature and then diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.
2.8 General procedure for the synthesis of 2’-bromo-biphenyl-2-diacylamines: **GP-8**

The compound was synthesized by acylation of 2’-bromobiphenyl-2-amine.

\[
\text{BrNH}_2 + \text{CH}_3\text{COCl} \rightarrow \text{AcNH} \quad 0 \, ^\circ \text{C} - \text{rt}, 30 \, \text{min}
\]

The substrate 2’-bromobiphenyl-2-amine (0.5 mmol) in DCM (5 mL) was cooled to 0 °C and then acetyl chloride (1.2 mmol) was added slowly through a syringe. The reaction mixture was then stirred at room temperature for 30 minutes. After completion of the reaction the reaction mixture was diluted with water and extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.

2.9 General procedure for the synthesis of 2-(2-bromobenzyloxy)phenol: **GP-9**

\[
\text{Catechol (1mmol) and K}_2\text{CO}_3 (1\text{eqv.}) \quad \text{i) } \text{K}_2\text{CO}_3, \text{DMF, 60 } ^\circ \text{C}, 1\text{h} \quad \text{ii) } \text{Br, 60 } ^\circ \text{C, 3h}
\]

Catechol (1mmol) and K\textsubscript{2}CO\textsubscript{3} (1eqv.) were taken in a two-neck round bottomed flask and it was filled with nitrogen gas. Then DMF(5 mL) was added and the reaction mixture was stirred at 60 °C for 1h. Then 1 mmol of 2-bromobenzylbromide in 2 mL of DMF was added and the reaction mixture was stirred at 60 °C for another 3h. After completion of the reaction, the reaction mixture was cooled to room temperature and then diluted with water and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, evaporated under reduced pressure. Then the crude product was purified by column chromatography using silica gel (60-120 mesh) and hexane/EtOAc as eluent.
2'-bromobiphenyl-2-methanol (1a):

According to the GP-2 the substrate 2'-bromobiphenyl-2-carbaldehyde afforded 2'-bromobiphenyl-2-methanol (1a) as a white solid; \( ^1\text{H NMR} \) (CDCl\(_3\), 200 MHz) \( \delta \): 2.48 (1H, bs), \( \delta_A = 4.43, \delta_B = 4.48 \) (2H, AB, \( J = 10.2 \) Hz), 7.18-7.51 (6H, m), 7.60-7.74 (2H, m); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 50 MHz) \( \delta \): 62.8, 123.7, 127.3 (2 x CH), 127.6, 128.4, 129.2, 129.6, 131.1, 132.6, 138.6, 139.8, 141.4.

2'-bromo-4-methoxy-biphenyl-2-methanol (1b):

According to the GP-2 the substrate 2'-bromo-4-methoxybiphenyl-2-carbaldehyde afforded 2'-bromo-4-methoxybiphenyl-2-methanol (1b) as a white solid; \( ^1\text{H NMR} \) (CDCl\(_3\), 200 MHz) \( \delta \): 2.29 (1H, bs), 3.89 (3H, s), \( \delta_A = 4.41, \delta_B = 4.46 \) (2H, AB, \( J = 10.0 \) Hz), 6.92 (1H, dd, \( J = 8.4, 2.4 \) Hz), 7.10 (1H, d, \( J = 8.4 \) Hz), 7.18-7.41 (4H, m), 7.68 (1H, d, \( J = 7.6 \) Hz); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 50 MHz) \( \delta \): 55.4, 62.9, 112.6, 112.9, 124.4, 127.4, 129.1, 130.8, 131.6, 132.2, 132.6, 140.2, 141.2, 159.6.

2'-bromo-4,5-dimethoxybiphenyl-2-methanol (1c):

According to the GP-2 the substrate 2'-bromo-4,5-dimethoxybiphenyl-2-carbaldehyde afforded 2'-bromo-4,5-dimethoxybiphenyl-2-methanol (1c) as a yellow solid; \( ^1\text{H NMR} \) (CDCl\(_3\), 200 MHz) \( \delta \): 2.49 (1H, bs), 3.84 (3H, s), 3.90 (3H, s), \( \delta_A = 4.32, \delta_B = 4.38 \) (2H, AB, \( J = 11.0 \) Hz), 6.65 (1H, s), 7.10 (1H, s), 7.16-7.36 (3H, m), 7.63 (1H, d, \( J = 8.0 \) Hz); \( ^{13}\text{C NMR} \) (CDCl\(_3\), 50 MHz) \( \delta \): 55.9, 56.0, 62.5, 110.8, 112.6, 124.1, 127.2, 129.0, 131.0, 131.5, 132.1, 132.6, 141.1, 147.7, 148.8.

2'-bromo-4,5,6-trimethoxybiphenyl-2-methanol (1d):

According to the GP-2 the substrate 2'-bromo-4,5,6-trimethoxybiphenyl-2-carbaldehyde afforded 2'-bromo-4,5,6-trimethoxybiphenyl-2-methanol (1d) as a white solid; \( ^1\text{H NMR} \) (CDCl\(_3\), 200 MHz) \( \delta \): 2.80-2.90 (1H, m), 3.70 (3H, s), 3.92 (3H, s), 3.95 (3H, s), \( \delta_A = 4.29, \delta_B = 4.32 \) (2H, AB, \( J = 6.4 \) Hz), 6.96 (1H, s), 7.21-7.43 (3H, m), 7.68
(1H, d, J = 7.8 Hz); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 56.1, 61.0 (2 x CH$_3$), 62.8, 106.6, 124.9, 126.7, 127.4, 129.3, 131.9, 132.6, 134.5, 137.5, 141.4, 151.0, 153.6.

2'-Bromo-5-methylbiphenyl-2-methanol (1e):

According to the GP-2 the substrate 2'-bromo-5-methylbiphenyl-2-carbaldehyde afforded 2'-bromo-5-methylbiphenyl-2-methanol (1e) as a white solid; $^1$H NMR (CDCl$_3$, 200 MHz) δ: 2.45 (Me + OH = 4H, bs), δ$_A$ = 4.41, δ$_B$ = 4.46 (2H, AB, J = 10.0 Hz), 7.04 (1H, s), 7.25-7.44 (4H, m), 7.50 (1H, d, J = 7.8 Hz), 7.71 (1H, d, J = 7.8 Hz); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 21.2, 62.7, 123.7, 127.3, 127.9, 129.1, 129.2, 130.3, 131.2, 132.6, 135.7, 137.1, 139.9, 141.6.

2'-bromo-4-fluorobiphenyl-2-methanol (1f):

According to the GP-2 the substrate 2'-bromo-4-fluorobiphenyl-2-carbaldehyde afforded 2'-bromo-4-fluorobiphenyl-2-methanol (1f) as a white solid; $^1$H NMR (CDCl$_3$, 200 MHz) δ: 2.84 (1H, bs), δ$_A$ = 4.37, δ$_B$ = 4.43, (2H, AB, J = 10.8 Hz), 7.01-7.43 (6H, m), 7.66-7.71 (1H, m); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 62.2, 113.9 (CH, d, J = 22.5 Hz), 114.0 (CH, d, J = 21.0 Hz), 123.8, 127.5, 129.4, 131.1 (CH, d, J = 5.5 Hz), 131.3, 132.7, 135.2 (C, d, J = 3.0 Hz), 140.4, 141.3 (C, d, J = 7.0 Hz), 162.8 (CF, d, J = 145.0 Hz).

2'-bromo-5-nitrobiphenyl-2-methanol (1g):

According to the GP-2 the substrate 2'-bromo-5-nitrobiphenyl-2-carbaldehyde afforded 2'-bromo-5-nitrobiphenyl-2-methanol (1g) as a white solid; $^1$H NMR (CDCl$_3$, 200 MHz) δ: 2.48 (1H, bs), δ$_A$ = 4.50, δ$_B$ = 4.56 (2H, AB, J = 10.8 Hz), 7.21-7.47 (4H, m), 7.71 (1H, d, J = 7.6 Hz), 8.20 (1H, dd, J = 8.2, 2.4 Hz), 8.51 (1H, s); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 62.0, 122.2 (2 x CH), 122.6, 127.8, 130.2, 130.4, 130.8, 133.1, 139.3, 141.2, 145.7, 148.1.

2'-Fluorobiphenyl-2-methanol (1aF):

According to the GP-2 the substrate 2'-fluorobiphenyl-2-carbaldehyde afforded 2'-fluorobiphenyl-2-methanol (1aF) as a colourless liquid; $^1$H NMR (CDCl$_3$, 200 MHz) δ: 1.96 (1H, bs), 4.55 (2H, s), 7.11-7.63 (8H, m); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 63.2 (d, J = 3.0 Hz), 115.7 (d, J = 22.5 Hz),
124.3 (d, J = 3.5 Hz), 127.7, 128.1 (d, J = 16.5 Hz), 128.2, 128.6, 129.6 (d, J = 8.0 Hz), 130.5, 131.8 (d, J = 3.0 Hz), 134.6, 139.4, 159.7 (d, J = 243.0 Hz).

2'-Chlorobiphenyl-2-methanol (1aCl):

According to the GP-2 the substrate 2'-chlorobiphenyl-2-carbaldeyde afforded 2'-chlorobiphenyl-2-methanol (1aCl) as a white solid; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$: 2.19 (1H, bs), $\delta_A = 4.42$, $\delta_B = 4.47$ (2H, AB, J = 13.0 Hz), 7.18-7.61 (8H, m); $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$: 62.9, 126.8, 127.5, 127.8, 128.5, 129.1, 129.5, 129.8, 131.3, 133.3, 138.1, 138.9, 139.4.

2'-Iodobiphenyl-2-methanol (1aI):

According to the GP-2 the substrate 2'-iodobiphenyl-2-carbaldehyde afforded 2'-iodobiphenyl-2-methanol (1aI) as a white solid; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$: 1.79 (1H, bs), $\delta_A = 4.41$, $\delta_B = 4.45$ (2H, AB, J = 8.0 Hz), 7.03-7.61 (7H, m), 7.95 (1H, d, J = 8.0 Hz); $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$: 63.3, 100.2, 127.6, 127.9, 128.3, 128.6, 129.3, 129.8, 130.1, 138.3, 139.1, 143.3, 145.6.

6H-benzo[c]chromene (2a):

According to GP-3 the substrate 2'-bromobiphenyl-2-methanol afforded 6H-benzo[c]chromene as a colourless oil; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$: 5.19 (2H, s), 7.06-7.23 (3H, m), 7.28-7.48 (3H, m), 7.75-7.83 (2H, m); $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$: 68.6, 117.6, 122.2, 122.3, 123.1, 123.5, 124.8, 127.8, 128.6, 129.6, 130.3, 131.6, 155.0. HRMS (ESI) calculated for C$_{13}$H$_{11}$O [M + H]$^+$: 183.0804; found: 183.0801; Spectral data are in well agreement with the literature reported data.$^1$

8-methoxy-6H-benzo[c]chromene (2b):

According to GP-3 the substrate 2'-bromo-4-methoxybiphenyl-2-methanol afforded 8-methoxy-6H-benzo[c]chromene as a white solid; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$: 3.88 (3H, s), 5.14 (2H, s), 6.74 (1H, d, J = 2.0 Hz), 6.95-7.13 (3H, m), 7.28 (1H, d, J = 7.2 Hz), 7.65-7.73 (2H, m); $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$: 55.4, 68.6, 110.2, 114.2, 117.4, 122.3, 122.8, 123.1, 123.2, 123.6, 128.6,
133.2, 154.2, 159.6; **HRMS** (ESI) calculated for C\textsubscript{14}H\textsubscript{13}O\textsubscript{2} [M + H]\textsuperscript{+}: 213.0910; found: 213.0915. The spectral data are in well agreement with the literature reported data.\textsuperscript{2}

**8,9-dimethoxy-6\textsubscript{H}-benzo[c]chromene (2c):**

According to **GP-3** the substrate 2'-bromo-4,5-dimethoxybiphenyl-2-methanol afforded 8,9-dimethoxy-6\textsubscript{H}-benzo[c]chromene as a white solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) δ: 3.92 (3H, s), 3.98 (3H, s), 5.01 (2H, s), 6.67 (1H, s), 6.99-7.27 (4H, m), 7.66 (1H, dd, J = 7.6, 1.4 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50 MHz) δ: 56.1, 56.2, 68.2, 105.6, 108.0, 117.3, 122.1, 122.6, 122.9, 123.1, 124.1, 128.6, 149.1, 149.3, 154.2. **HRMS** (ESI) calculated for C\textsubscript{15}H\textsubscript{15}O\textsubscript{3} [M + H]\textsuperscript{+}: 243.1016; found: 243.1019.

**8,9,10-trimethoxy-6\textsubscript{H}-benzo[c]chromene (2d):**

According to **GP-3** the substrate 2'-bromo-4,5,6-trimethoxybiphenyl-2-methanol afforded 8,9,10-trimethoxy-6\textsubscript{H}-benzo[c]chromene as a white solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) δ: 3.84 (3H, s), 3.89 (3H, s), 3.92 (3H, s), 4.94 (2H, s), 6.52 (1H, s), 6.97-7.23 (3H, m), 8.32 (1H, dd, J = 7.8, 1.4 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50 MHz) δ: 56.3, 60.5, 61.2, 69.0, 104.5, 116.7, 117.1, 122.1, 122.4, 127.3, 128.4, 129.0, 142.9, 151.8, 153.1, 154.6. **HRMS** (ESI) calculated for C\textsubscript{16}H\textsubscript{17}O\textsubscript{4} [M + H]\textsuperscript{+}: 273.1121; found: 273.1128.

**9-Methyl-6\textsubscript{H}-benzo[c]chromene (2e):**

According to **GP-3** the substrate 2'-bromo-5-methylbiphenyl-2-methanol afforded 9-methyl-6\textsubscript{H}-benzo[c]chromene as a white solid; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) δ: 2.51 (3H, s), 5.19 (2H, s), 7.10-7.38 (5H, m), 7.62 (1H, s), 7.84 (1H, d, J = 7.6 Hz); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) δ: 21.6, 68.5,
117.5, 122.2, 122.8, 123.2, 123.3, 124.7, 128.5, 128.7, 129.4, 130.0, 138.1, 155.0; HRMS (ESI) calculated for C_{14}H_{13}O [M + H]^+ : 197.0961; found: 197.0964. The spectral data are in well agreement with the literature reported data.\(^1\)

8-fluoro-6H-benzo[c]chromene (2f):

According to \textit{GP-3} the substrate 2'-bromo-4-fluorobiphenyl-2-methanol afforded 8-fluoro-6H-benzo[c]chromene as a colourless oil; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 4.97 (2H, s), 6.76 (1H, dd, \(J = 8.4, 2.6\) Hz), 6.87-7.01 (3H, m), 7.09-7.18 (1H, m), 7.51-7.55 (2H, m); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 68.2, 111.9 (d, \(J = 22.0\) Hz), 115.5 (d, \(J = 22.0\) Hz), 117.6, 122.4, 122.5, 123.2, 124.1 (d, \(J = 8.0\) Hz), 126.5, (d, \(J = 2.5\) Hz), 129.5, 133.7 (d, \(J = 7.5\) Hz), 154.4, 162.5 (d, \(J = 246.0\) Hz); HRMS (ESI) calculated for C_{13}H_{10}FO [M + H]^+ : 201.0710; found: 201.0717. The spectral data are in well agreement with the literature reported data.\(^1\)

9-nitro-6H-benzo[c]chromene (2g):

According to \textit{GP-3} the substrate 2'-bromo-5-nitrobiphenyl-2-methanol afforded 9-nitro-6H-benzo[c]chromene as a yellow solid; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 5.24 (2H, s), 7.02-7.14 (2H, m), 7.33 (1H, d, \(J = 7.4\) Hz), 7.75-7.88 (3H, m), 7.99 (1H, d, \(J = 8.4\) Hz); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 68.6, 117.8, 118.4, 122.5, 122.6, 123.1, 124.0, 124.6, 130.6, 132.5, 133.1, 152.1, 155.3. HRMS (ESI) calculated for C_{13}H_{10}NO_3 [M + H]^+ : 228.0655; found: 228.0652; Spectral data are in well agreement with the literature reported data.\(^1\)

3-methyl-6H-benzo[c]chromen (2h):
According to **GP-3** the substrate 2’-bromo-4’-methylbiphenyl-2-methanol afforded 3-methyl-6\(H\)-benzo[c]chromene as a Colourless liquid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 2.39 (3H, s), 5.14 (2H, s), 6.87-6.93 (2H, m), 7.17 (1H, \(d\), \(J = 7.2\) Hz), 7.25-7.43 (2H, m), 7.64-7.72 (2H, m); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\):21.5, 68.7, 117.9, 120.4, 121.8, 123.2, 123.3, 124.8, 127.4, 128.5, 130.5, 131.2, 140.0, 154.9. Spectral data are in well agreement with the literature reported data.

**3-Chloro-6\(H\)-benzo[c]chromen (2i):**

According to **GP-3** the substrate 2’-bromo-4’-chlorobiphenyl-2-methanol afforded 3-chloro-6\(H\)-benzo[c]chromene as a Colourless liquid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 5.13 (2H, s), 7.03-7.07 (2H, m), 7.15 (1H, \(d\), \(J = 7.2\) Hz), 7.27-7.43 (2H, m), 7.62-7.66 (2H, m); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\): 68.8, 117.9, 121.7, 122.0, 122.5, 124.3, 124.9, 128.1, 128.7, 129.4, 131.0, 134.6, 155.5. Spectral data are in well agreement with the literature reported data.

**2’-bromobiphenyl-2-carboxylic acid (3a):**

According to **GP-4** the substrate 2’-bromobiphenyl-2-carbaldehyde afforded 2’-bromobiphenyl-2-carboxylic acid as a white solid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 7.25-7.67 (7H, m), 8.14 (1H, \(d\), \(J = 7.6\) Hz), 10.97 (1H, bs); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\): 123.1, 127.2, 128.1, 128.9, 129.1, 130.2, 131.1, 131.5, 132.4, 132.8, 142.5, 143.0, 172.2.

**2’-bromo-4-fluorobiphenyl-2-carboxylic acid (3b):**

According to **GP-4** the substrate 2’-bromo-4-fluorobiphenyl-2-carbaldehyde afforded 2’-bromo-4-fluorobiphenyl-2-carboxylic acid as a white solid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 7.22-7.43 (5H, m), 7.65 (1H, \(d\), \(J = 7.8\) Hz), 7.83 (1H, \(dd\), \(J = 9.2, 2.6\) Hz), 11.64 (1H, bs); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\): 117.9 (CH, \(d\), \(J = 24.0\) Hz), 119.9 (CH, \(d\), \(J = 21.0\) Hz), 123.3, 127.3, 129.1, 130.3, 130.8 (C, \(d\), \(J = 7.5\) Hz), 132.4, 133.3 (CH, \(d\), \(J = 7.5\) Hz), 139.1 (C, \(d\), \(J = 4.0\) Hz), 141.4, 161.9 (CF, \(d\), \(J = 246.5\) Hz), 171.3.
2'-bromo-4-methoxybiphenyl-2-carboxylic acid (3c):

According to GP-4 the substrate 2'-bromo-4-methoxybiphenyl-2-carbaldehyde afforded 2'-bromo-4-methoxybiphenyl-2-carboxylic acid as a white solid; \(^1H\) NMR (CDCl\(_3\), 200 MHz) \(\delta\): 3.76 (3H, s), 6.91-7.23 (5H, m), 7.43-7.53 (2H, m), 9.09 (1H, bs); \(^13C\) NMR (CDCl\(_3\), 50 MHz) \(\delta\): 55.2, 114.6, 117.2, 123.3, 126.7, 128.1, 130.4, 131.7, 131.9 (C + CH), 134.2, 142.6, 158.6, 168.1.

2'-bromo-4,5-dimethoxybiphenyl-2-carboxylic acid (3d):

According to GP-4 the substrate 2'-bromo-4,5-dimethoxybiphenyl-2-carbaldehyde afforded 2'-bromo-4,5-dimethoxybiphenyl-2-carboxylic acid as a white solid; \(^1H\) NMR (CDCl\(_3\), 200 MHz) \(\delta\): 3.94 (3H, s), 3.99 (3H, s), 6.71 (1H, s), 7.19-7.40 (3H, m), 7.61-7.65 (2H, m), 10.25 (1H, bs); \(^13C\) NMR (CDCl\(_3\), 50 MHz) \(\delta\): 56.2, 56.3, 113.4, 113.9, 120.7, 123.4, 127.1, 128.7, 130.3, 132.3, 137.7, 142.7, 148.1, 152.3, 171.6.

2'-bromo-4,5,6-trimethoxybiphenyl-2-carboxylic acid (3e):

According to GP-4 the substrate 2'-bromo-4,5,6-trimethoxybiphenyl-2-carbaldehyde afforded 2'-bromo-4,5,6-trimethoxybiphenyl-2-carboxylic acid as a white solid; \(^1H\) NMR (CDCl\(_3\), 200 MHz) \(\delta\): 3.66 (3H, s), 3.97 (3H, s), 4.00 (3H, s), 7.19-7.39 (3H, m), 7.48 (1H, s), 7.64 (1H, d, \(J = 8.0\) Hz), 9.05 (1H, bs); \(^13C\) NMR (CDCl\(_3\), 50 MHz) \(\delta\): 56.3, 61.1 (2 x CH\(_3\)), 110.1, 123.9, 124.2, 126.8, 128.7, 130.9, 131.3, 131.8, 132.1, 138.2, 146.7, 151.5, 152.8, 171.1.

2'-bromo-5-methylbiphenyl-2-carboxylic acid (3f):

According to GP-4 the substrate 2'-bromo-5-methylbiphenyl-2-carbaldehyde afforded 2'-bromo-5-methylbiphenyl-2-carboxylic acid as a white solid; \(^1H\) NMR (CDCl\(_3\), 200 MHz) \(\delta\): 2.48 (3H, s), 7.11 (1H, s), 7.18-7.42 (4H, m), 7.65 (1H, d, \(J = 8.0\) Hz), 8.06 (1H, d, \(J = 8.0\) Hz), 11.07 (1H, bs); \(^13C\) NMR (CDCl\(_3\), 50 MHz) \(\delta\): 21.7, 123.1, 126.2, 127.1, 128.7, 128.8, 130.1, 131.3, 132.1, 132.2, 142.7, 143.1, 143.6, 172.3.

6H-benzoc[chromen-6-one (4a):
According to the **GP-5** with 2'-bromobiphenyl-2-carboxylic acid (3a) afforded 6H-benzo[c]chromen-6-one (4a) as a white solid; ¹H NMR (CDCl₃, 200 MHz) δ: 7.30-7.39 (2H, m), 7.45-7.63 (2H, m), 7.79-7.87 (1H, m), 8.04-8.14 (2H, m), 8.40 (1H, d, J = 8 Hz); ¹³C NMR (CDCl₃, 50 MHz) δ: 117.9, 118.2, 121.4, 121.9, 122.9, 124.7, 129.1, 130.6, 130.8, 134.9, 135.0, 151.5, 161.4. HRMS (ESI) for C₁₃H₈O₂: Calculated 197.0603 (M⁺+H); Found: 197.0609. The spectral data are in well agreement with our previously reported data.³

8-Fluoro-6H-benzo[c]chromen-6-one (4b):

According to the **GP-5** with 2'-bromo-4-fluoro-biphenyl-2-carboxylic acid (3b) afforded 8-fluoro-6H-benzo[c]chromen-6-one (4b) as a white solid; ¹H NMR (CDCl₃, 200 MHz) δ: 7.31-7.40 (2H, m), 7.45-7.60 (2H, m), 7.99-8.17 (3H, m); ¹³C NMR (CDCl₃, 50 MHz) δ: 116.4 (d, J = 23 Hz), 117.6, 118.1, 122.8, 123.2 (d, J = 9 Hz), 123.5, 124.5 (d, J = 7.5 Hz), 125.0, 130.6, 131.5, 151.1, 160.3 (d, J = 13.5 Hz), 165.2. HRMS (ESI) for C₁₃H₈FO₂: Calculated 215.0503 (M⁺+H); Found: 215.0508. The spectral data are in well agreement with our previously reported data.³

8-Methoxy-6H-benzo[c]chromen-6-one (4c):

According to the **GP-5** with 2'-bromo-4-methoxy-biphenyl-2-carboxylic acid (3c) afforded 8-methoxy-6H-benzo[c]chromen-6-one (4c) as a white solid; ¹H NMR (CDCl₃, 200 MHz) δ: 3.92 (3H, s), 7.27-7.46 (4H, m), 7.78 (1H, d, J = 2.8 Hz), 7.94-8.03 (2H, m); ¹³C NMR (CDCl₃, 50 MHz) δ: 55.9, 111.4, 117.7, 118.3, 122.3, 122.6, 123.6, 124.4, 124.7, 128.3, 129.5, 150.6, 160.2, 161.4; HRMS (ESI) for C₁₄H₁₁O₃: Calculated 227.0703 (M⁺+H); Found: 227.0701. The spectral data are in well agreement with the literature reported data.⁴

8,9-Dimethoxy-6H-benzo[c]chromen-6-one (4d):
According to the **GP-5** with 2′-bromo-4,5-dimethoxybiphenyl-2-carboxylic acid (3d) afforded 8,9-dimethoxy-6H-benzo[\(c\)]chromen-6-one (4d) as a white solid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 4.01 (3H, s), 4.11 (3H, s), 7.30-7.49 (4H, m), 7.72 (1H, s), 7.94 (1H, d, \(J = 7.6\) Hz); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\): 56.4, 56.5, 102.8, 110.6, 114.6, 117.8, 118.2, 122.3, 124.5, 129.7, 130.0, 150.3, 151.1, 155.2, 161.2; **HRMS** (ESI) for C\(_{15}\)H\(_{13}\)O\(_4\): Calculated 257.0808 (M\(^++H\)); Found: 257.0812. The spectral data are in well agreement with our previously reported data.\(^3\)

### 8,9,10-Trimethoxy-6H-benzo[\(c\)]chromen-6-one (4e):

According to the **GP-5** with 2′-bromo-4,5,6-trimethoxybiphenyl-2-carboxylic acid (3e) afforded 8,9,10-trimethoxy-6H-benzo[\(c\)]chromen-6-one (4e) as a white solid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 3.98 (3H, s), 4.00 (3H, s), 4.04 (3H, s), 7.27-7.44 (3H, m), 7.76 (1H, s), 8.85 (1H, d, \(J = 8.2\) Hz); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\): 56.5, 60.8, 61.4, 108.4, 117.6, 117.7, 117.8, 123.0, 124.9, 126.8, 129.4, 149.3, 150.6, 151.5, 154.0, 161.3; **HRMS** (ESI) for C\(_{16}\)H\(_{15}\)O\(_5\): Calculated 287.0914 (M\(^++H\)); Found: 287.0916. Spectral data are in well agreement with the literature reported data.\(^3\)

### 9-Methyl-6H-benzo[\(c\)]chromen-6-one (4f):

According to the **GP-5** with 2′-bromo-5-methylbiphenyl-2-carboxylic acid (3f) afforded 9-methyl-6H-benzo[\(c\)]chromen-6-one (4f) as a white solid; **\(^1\)H NMR** (CDCl\(_3\), 200 MHz) \(\delta\): 2.55 (3H, s), 7.27-7.46 (4H, m), 7.89 (1H, s), 8.03 (1H, d, \(J = 8.2\) Hz), 8.27 (1H, d, \(J = 8.2\) Hz); **\(^{13}\)C NMR** (CDCl\(_3\), 50 MHz) \(\delta\): 22.5, 117.9, 118.3, 119.0, 122.0, 122.9, 124.6, 130.3, 130.5, 130.7, 134.9, 146.1, 151.6, 161.5; **HRMS** (ESI) for C\(_{14}\)H\(_{11}\)O\(_2\): Calculated 211.0754 (M\(^++H\)); Found: 211.0755. The spectral data are in well agreement with the literature reported data.\(^3\)

### 3-Methyl-6H-benzo[\(c\)]chromen-6-one (4g):

---

3-Methyl-6H-benzo[\(c\)]chromen-6-one (4g):
According to the **GP-5** with 2'-bromo-4'-methylbiphenyl-2-carboxylic acid afforded 3-methyl-6H-benzo[c]chromen-6-one as a white solid; **1H NMR** (CDCl3, 200 MHz) δ: 2.45 (3H, s), 7.13-7.16 (2H, m), 7.54 (1H, t, J = 7.6 Hz), 7.80 (1H, t, J = 7.6 Hz), 7.92 (1H, d, J = 8.0 Hz), 8.07 (1H, d, J = 8.0 Hz), 8.38 (1H, d, J = 7.8 Hz); **13C NMR** (CDCl3, 50 MHz) δ: 21.6, 115.6, 118.1, 121.1, 121.6, 122.7, 125.9, 128.6, 130.7, 135.0, 135.2, 141.5, 151.5, 161.7. Spectral data are in well agreement with the literature reported data.

3-Chloro-6H-benzo[c]chromen-6-one (4h):

According to the **GP-5** with 2'-bromo-4'-chlorobiphenyl-2-carboxylic acid afforded 3-chloro-6H-benzo[c]chromen-6-one as a white solid; **1H NMR** (CDCl3, 200 MHz) δ: 7.28-7.37 (2H, m), 7.55-7.63 (1H, m), 7.83 (1H, ddd, J = 8.6, 7.4, 1.4 Hz), 7.95-8.08 (2H, m), 8.38 (1H, dd, J = 8.0, 1.2 Hz); **13C NMR** (CDCl3, 50 MHz) δ: 116.9, 118.2, 121.1, 121.9, 124.0, 125.2, 129.4, 130.9, 134.2, 135.3, 136.1, 151.7, 160.7. The spectral data are in well agreement with the literature reported data.

2'-bromo-5-methylbiphenyl-2-amine (5a):

According to the **GP-6** with 2-iodo-4-methylaniline and 2-bromophenylboronic acid afforded 2'-bromo-5-methylbiphenyl-2-amine as a yellow liquid; **1H NMR** (CDCl3, 200 MHz) δ: 2.36 (3H, s), 3.50 (2H, bs), 6.77 (1H, d, J = 8.2 Hz), 6.93 (1H, d, J = 1.4 Hz), 7.10 (1H, dd, J = 8.0, 1.8 Hz), 7.25-7.49 (3H, m), 7.76 (1H, dd, J = 8.0, 0.6 Hz); **13C NMR** (CDCl3, 50 MHz) δ: 20.6, 115.8, 124.3, 127.4, 127.6, 127.9, 129.2, 129.8, 130.7, 131.9, 133.1, 140.4, 141.2.

2'-bromo-5-chlorobiphenyl-2-amine (5b):

According to the **GP-6** with 2-iodo-4-chloroaniline and 2-bromophenylboronic acid afforded 2'-bromo-5-chlorobiphenyl-2-amine as a brown liquid; **1H NMR** (CDCl3, 200 MHz) δ: 3.62 (2H, s), 6.74 (1H, d, J = 8.4 Hz), 7.09 (1H, d, J = 2.2 Hz), 7.19-7.49 (4H, m),
7.75 (1H, d, J = 8.0 Hz); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 116.7, 122.6, 123.9, 128.0, 128.2, 128.9, 129.7, 129.8, 131.7, 133.2, 138.7, 142.3.

2'-bromo-3,5-dimethylbiphenyl-2-amine (5c):

According to the GP-6 with 2-iodo-2,4-dimethylaniline and 2-bromophenylboronic acid afforded 2'-bromo-3,5-dimethylbiphenyl-2-amine as a brown solid; $^1$H NMR (CDCl$_3$, 200 MHz) δ: 2.31 (3H, s), 2.38 (3H, s), 3.44 (2H, s), 6.85 (1H, s), 7.06 (1H, s), 7.27-7.56 (3H, m), 7.79 (1H, d, J = 8.0 Hz); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 17.9, 20.5, 122.7, 124.4, 127.0, 127.1, 127.9, 128.4, 129.2, 131.1, 132.0, 133.1, 139.2, 140.6.

2'-bromobiphenyl-2-amine (5d):

According to the GP-6 with 2-iodoaniline and 2-bromophenylboronic acid afforded 2'-bromobiphenyl-2-amine as a yellow liquid; $^1$H NMR (CDCl$_3$, 200 MHz) δ: 3.66 (2H, s), 6.84-6.97 (2H, m), 7.14 (1H, d, J = 7.4 Hz), 7.22-7.53 (4H, m), 7.79 (1H, d, J = 7.8 Hz); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 115.6, 118.3, 124.3, 127.1, 127.9, 129.2, 130.3, 131.9, 133.1, 140.0, 143.6.

3-Methyl-9H-carbazole (6a):

According to the GP-7 with 2'-bromo-5-methylbiphenyl-2-amine afforded 3-methyl-9H-carbazole as a gray solid; $^1$H NMR (d$_6$-DMSO, 200 MHz) δ: 2.49 (3H, s), 7.11-7.25 (2H, m), 7.34-7.52 (3H, m), 7.92 (1H, s), 8.08 (1H, d, J = 7.8 Hz), 11.1 (1H, s); $^{13}$C NMR (d$_6$-DMSO, 50 MHz) δ: 21.6, 111.1, 111.3, 118.7, 120.4, 120.5, 122.7, 123.0, 125.8, 127.3, 127.5, 138.6, 140.5; HRMS (ESI) for C$_{13}$H$_{12}$N: Calculated 182.0964 (M$^+$+H) ; Found: 182.0962. Spectral data are in well agreement with the literature reported data.$^5$

3-Chloro-9H-carbazole (6b):

According to the GP-7 with 2'-bromo-5-chlorobiphenyl-2-amine afforded 3-methyl-9H-carbazole as a brown solid; $^1$H NMR (d$_6$-DMSO, 200 MHz) δ: 7.13-7.20 (1H, m), 7.35-7.53 (4H, m), 8.13-8.21 (2H, m); $^{13}$C NMR (d$_6$-DMSO, 50 MHz) δ: 111.2, 112.4, 118.9, 119.8, 120.7, 121.6, 122.9, 123.7, 125.3, 126.3, 138.1, 140.3; HRMS (ESI) for C$_{12}$H$_9$ClN:
Calculated 202.0418 (M+H) ; Found: 202.0419. Spectral data are in well agreement with the literature reported data.5

1,3-Dimethyl-9H-carbazole (6c):

According to the GP-7 with 2’-bromo-3,5-dimethylbiphenyl-2-amine afforded 1,3-dimethyl-9H-carbazole as a brown solid; \(^1\text{H} \text{NMR} \left(\text{d}_6-\text{DMSO}, 200 \text{ MHz}\right) \delta: 2.45 \ (3\text{H}, \text{s}), 2.55 \ (3\text{H}, \text{s}), 7.04 \ (1\text{H}, \text{s}), 7.10-7.18 \ (1\text{H}, \text{m}), 7.31-7.54 \ (2\text{H}, \text{m}), 7.73 \ (1\text{H}, \text{s}), 8.05 \ (1\text{H}, \text{d}, \text{J} = 7.6 \text{ Hz}), 11.07 \ (1\text{H}, \text{s}); \ ^{13}\text{C} \text{NMR} \left(\text{d}_6-\text{DMSO}, 50 \text{ MHz}\right) \delta: 17.4, 21.5, 111.5, 117.8, 118.7, 120.2, 120.5, 122.6, 123.1, 125.6, 127.7, 128.0, 137.8, 140.6; \text{HRMS} \ (\text{ESI}) \text{ for C}_{14}\text{H}_{14}\text{N}: \text{Calculated 196.1121 (M}^+\text{+H}) \text{; Found: 196.1124. Spectral data are in well agreement with the literature reported data.6}

9H-carbazole (6d):

According to the GP-7 with 2’-bromobiphenyl-2-amine afforded 9H-carbazole as a gray solid; \(^1\text{H} \text{NMR} \left(\text{d}_6-\text{DMSO}, 200 \text{ MHz}\right) \delta: 7.11-7.20 \ (2\text{H}, \text{m}), 7.34-7.43 \ (2\text{H}, \text{m}), 7.50-7.54 \ (2\text{H}, \text{m}), 8.09-8.13 \ (2\text{H}, \text{m}), 11.28 \ (1\text{H}, \text{bs}); \ ^{13}\text{C} \text{NMR} \left(\text{d}_6-\text{DMSO}, 50 \text{ MHz}\right) \delta: 110.9 \ (2 \times \text{CH}), 118.5 \ (2 \times \text{CH}), 120.1 \ (2 \times \text{CH}), 122.4 \ (2 \times \text{C}), 125.5 \ (2 \times \text{CH}), 139.7 \ (2 \times \text{C}); \text{HRMS} \ (\text{ESI}) \text{ for C}_{12}\text{H}_{10}\text{N}: \text{Calculated 168.0808 (M}^+\text{+H}) \text{; Found: 168.0803. Spectral data are in well agreement with the literature reported data.5}

2’-Bromo-5-methylbiphenyl-2-(diacyl)amine (7):

According to the GP-8 with 2’-bromo-5-methylbiphenyl-2-amine afforded 2’-Bromo-5-methylbiphenyl-2-(diacyl)amine as a brown liquid; \(^1\text{H} \text{NMR} \left(\text{CDCl}_3, 200 \text{ MHz}\right) \delta: 2.04 \ (3\text{H}, \text{s}), 2.44 \ (3\text{H}, \text{s}), 2.46 \ (3\text{H}, \text{s}), 7.13-7.35 \ (6\text{H}, \text{m}), 7.65-7.70 \ (2\text{H}, \text{m}); \ ^{13}\text{C} \text{NMR} \left(\text{CDCl}_3, 50 \text{ MHz}\right) \delta: 21.2, 26.4, 27.2, 122.8, 127.2, 129.5, 129.7, 130.2, 130.8, 133.3, 133.4, 134.7, 138.2, 138.6 \ (2 \times \text{C}), 172.7, 174.5.

2’-Bromobiphenylacetate(8):
According to the **GP-1** the substrates 2-iodophenylacetate and 2-bromophenylboronic acid afforded 2'-bromobiphenylacetate as a colourless liquid. \(^1\)H NMR (CDCl\(_3\), 200 MHz) \(\delta\): 2.00 (3H, s), 7.20-7.50 (9H, m), 7.65 (1H, d, \(J = 8.2\) Hz); \(^1^3\)C NMR (CDCl\(_3\), 50 MHz) \(\delta\): 20.8, 122.6, 123.8, 126.0, 127.2 (2 x CH), 129.4, 131.3, 131.6, 132.8, 134.3, 138.6, 148.1, 169.3.

**Dibenzofuran(9)**

According to the **GP-7** with 2'-bromobiphenylacetate afforded dibenzofuran as a white solid. \(^1\)H NMR (CDCl\(_3\), 200 MHz) \(\delta\): 7.32-7.62 (6H, m), 7.98 (2H, d, \(J = 7.6\) Hz); \(^1^3\)C NMR (CDCl\(_3\), 50 MHz) \(\delta\): 111.9 (2 x CH), 120.8 (2 x CH), 122.9 (2 x CH), 124.4 (2 x c), 127.3 (2 x CH), 156.4 (2 x c).

HRMS (ESI) for C\(_{12}\)H\(_9\)O: Calculated 169.0648 (M\(^+\)+H); Found: 169.0643. Spectral data are in well agreement with the literature reported data.\(^7\)

**3',5'-dichlorobiphenyl-2-methanol (10):**

According to **GP-2** the substrate 3',5'-dichlorobiphenyl-2-carbaldehyde afforded the compound 10 as a white solid; \(^1\)H NMR (CDCl\(_3\), 200 MHz) \(\delta\): 4.52 (2H, s), 7.20-7.55 (7H, m); \(^1^3\)C NMR (CDCl\(_3\), 50 MHz) \(\delta\): 62.7, 112.8, 115.2, 120.3, 122.3, 123.1, 127.8, 129.8, 134.8 (2 x C), 137.8, 138.7, 143.7.

**2-(2-bromobenzyloxy)phenol (11):**

According to the **GP-9** the substrates catechol and 2-bromobenzylbromide afforded 2-(2-bromobenzyloxy)phenol as a colourless liquid. \(^1\)H NMR (CDCl\(_3\), 200 MHz) \(\delta\): 5.22 (2H, s), 5.90 (1H, bs), 6.85-7.09 (4H, m), 7.22-7.40 (2H, m), 7.50 (1H, d, \(J = 7.6\) Hz), 7.66 (1H, d, \(J = 7.8\) Hz); \(^1^3\)C NMR (CDCl\(_3\), 50 MHz)\(\delta\): 70.8, 112.8, 115.2, 120.3, 122.3, 123.1, 127.8, 129.6, 129.9, 133.0, 135.7, 145.5, 146.1.

**5H-dibenzooxepin (12):**
According to the **GP-3** the substrate 2-(2-bromobenzyloxy)phenol afforded 5H-dibenzooxepin as a colourless liquid. $^1$H NMR (CDCl$_3$, 200 MHz) δ: 5.27 (2H, s), 6.86-7.01 (3H, m), 7.07-7.38 (5H, m); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 70.2, 120.2, 121.1, 122.2, 122.5, 124.1, 124.2, 129.0, 129.3, 130.3, 146.0, 148.7, 158.4. **HRMS** (ESI) for C$_{13}$H$_{11}$O$_2$: Calculated 199.0754 (M$^+$+H); Found: 199.0758.

**References:**


$^1$H NMR of compound 1a
$^{13}$C NMR of compound 1a

$^1$H NMR of compound 1b
$^{13}$C NMR of compound 1b

$^1$H NMR of compound 1c
$^{13}$C NMR of compound 1c

$^1$H NMR of compound 1d
$^{13}\text{C NMR of compound 1d}$

$^{1}\text{H NMR of compound 1e}$
$^{13}$C NMR of compound 1e

$^1$H NMR of compound 1f
$^{13}$C NMR of compound 1f

$^1$H NMR of compound 1g
$^{13}$C NMR of compound 1g

$^1$H NMR of compound 1aF
$^{13}$C NMR of compound 1aF

$^1$H NMR of compound 1aCl
$^{13}$C NMR of compound 1aCl

$^{1}$H NMR of compound 1aI
$^{13}\text{C}$ NMR of compound 1aI

$^1\text{H}$ NMR of compound 2a
$^{13}$C NMR of compound 2a

$^{1}$H NMR of compound 2b
$^{13}$C NMR of compound 2b

$^1$H NMR of compound 2c
$^{13}$C NMR of compound 2c

$^1$H NMR of compound 2d
$^{13}$C NMR of compound 2d

$^1$H NMR of compound 2e
$^{13}$C NMR of compound 2e

$^1$H NMR of compound 2f
$^{13}$C NMR of compound 2f

$^1$H NMR of compound 2g
$^{13}$C NMR of compound 2g

$^1$H NMR of compound 2h
13C NMR of compound 2h

1H NMR of compound 2i
$^{13}$C NMR of compound 2i

$^1$H NMR of compound 3a
$^{13}$C NMR of compound 3a

$^1$H NMR of compound 3b
$^{13}\text{C NMR of compound 3b}$

$^1\text{H NMR of compound 3c}$
$^{13}$C NMR of compound 3c

$^1$H NMR of compound 3d
$^{13}$C NMR of compound 3d

$^1$H NMR of compound 3e
$^{13}$C NMR of compound 3e

$^1$H NMR of compound 3f
$^{13}$C NMR of compound 3f

$^1$H NMR of compound 4a
$^{13}$C NMR of compound 4a

$^1$H NMR of compound 4b
$^{13}$C NMR of compound 4b

$^1$H NMR of compound 4c
$^{13}$C NMR of compound 4c

$^1$H NMR of compound 4d
$^{13}$C NMR of compound 4d

$^1$H NMR of compound 4e
$^{13}$C NMR of compound 4e

$^1$H NMR of compound 4f
$^{13}$C NMR of compound 4f

$^1$H NMR of compound 4g
$^{13}$C NMR of compound 4g
$^1$H NMR of compound 4h

$^{13}$C NMR of compound 4h
$^1$H NMR of compound 5a

$^{13}$C NMR of compound 5a
$^1$H NMR of compound 5b

$^{13}$C NMR of compound 5b
$^1$H NMR of compound 5c

$^{13}$C NMR of compound 5c
\(^1\)H NMR of compound 5d

\(^{13}\)C NMR of compound 5d
\(^1\)H NMR of compound 6a

\(^{13}\)C NMR of compound 6a
$^1$H NMR of compound 6b

$^{13}$C NMR of compound 6b
$^1$H NMR of compound 6c

$^{13}$C NMR of compound 6c
$^1$H NMR of compound 6d

$^{13}$C NMR of compound 6d
$^1$H NMR of compound 7

$^{13}$C NMR of compound 7
$^1$H NMR of compound 8

$^{13}$C NMR of compound 8
$^1$H NMR of compound 9

$^{13}$C NMR of compound 9
$^1$H NMR of compound 10

$^{13}$C NMR of compound 10
$^1$H NMR of compound 11

$^{13}$C NMR of compound 11
$^1$H NMR of compound 12

$^{13}$C NMR of compound 12