

Supporting Information

Phosphine mediated formal [5+1] aminobenzannulations of Morita-Baylis-Hillman carbonates with isocyanates

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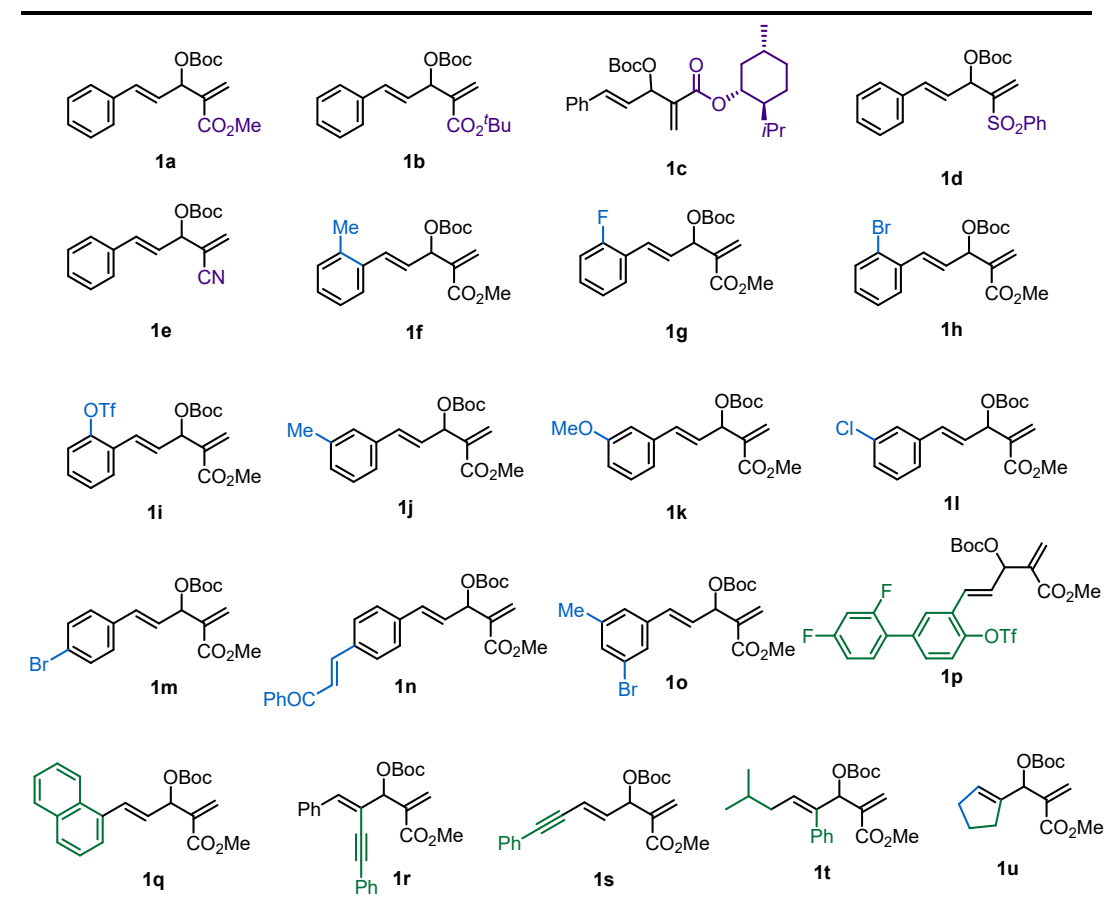
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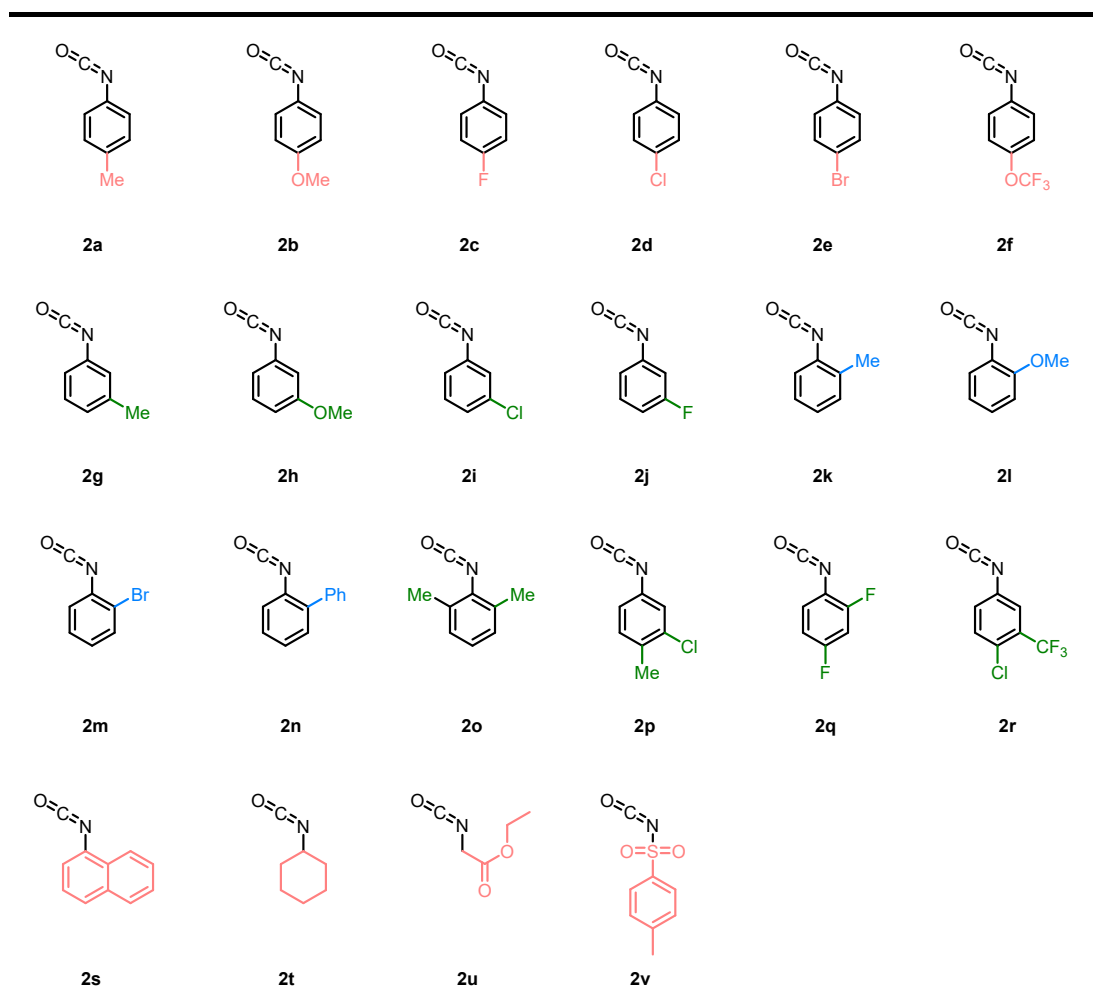
1. General Information

Commercial reagents and solvents were used as received without further purification, unless otherwise stated. Yields referred to isolated compounds through preparative TLC. ^1H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. Chemical shifts for protons are reported in ppm and are referenced to the tetramethylsilane (TMS) and NMR solvent peak (Chloroform-*d*: δ 7.26 ppm). Chemical shifts for carbons are reported in ppm and are referenced to the carbon resonances of the NMR solvent peak (Chloroform-*d*: δ 77.0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), h (heptet) and m (multiplet). High resolution mass spectrometry (HRMS) was obtained on Q Exactive Focus or Agilent 6520 Q-TOF LC/MS with ESI resource. Melting points were measured on a RY-I apparatus and reported uncorrected.

2. The Substrates Examined in This Report

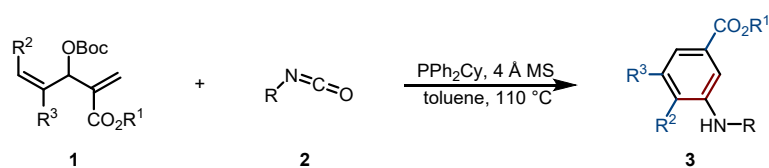
Table S1. The Substrates Examined in This Report





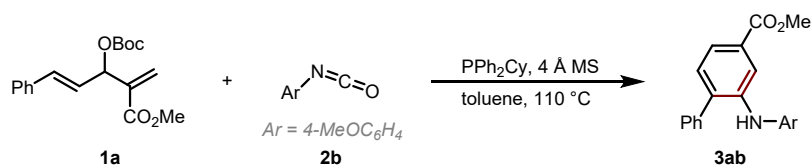
The MBH carbonate derivatives **1a–1u** were reported by our previous work^[1]. The isocyanates were commercially available.

3. General Procedure A for the Synthesis of arylamines **3**



To a 10 mL glass vial was added MBH carbonate **1** (0.10 mmol, 1.0 equiv), isocyanate **2** (0.12 mmol, 1.2 equiv), PPh₂Cy (0.11 mmol, 1.1 equiv), 4 Å MS (200 mg) and 1.0 mL of toluene. The resulting suspension was stirred at 110 °C until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and the residue was purified by silica gel flash column chromatography to afford corresponding products **3**.

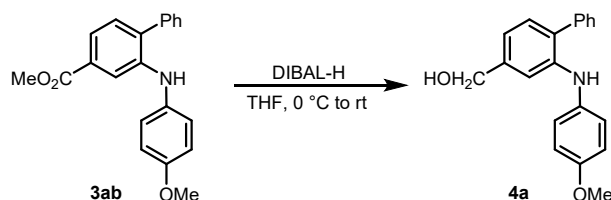
4. General Procedure for the Scale-Up Reaction of **3ab**



To an oven-dried 100 mL round-bottom flask was added MBH carbonate **1a** (3.77 mmol), isocyanate **2b** (5.65 mmol, 1.2 equiv), PPh₂Cy (4.15 mmol, 1.1 equiv), 4 Å MS (7.5 g) and toluene (16.0 mL). Then the reaction was warm up to 110 °C and stirred for 4 h. After the removal of the 4 Å MS and solvent, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 15:1) to afford product **3ab** as a yellow solid (742.6 mg, 59% yield).

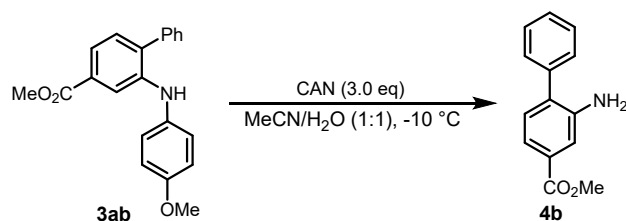
5. Synthetic Transformations

Scheme S1. The reduction reaction



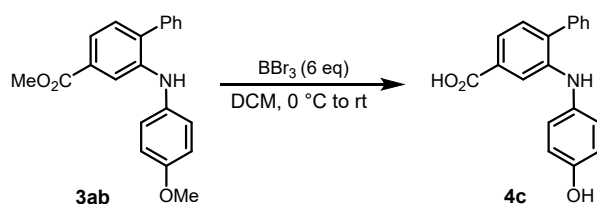
To a stirred solution of **3ab** (0.1 mmol, 1.0 eq.) in 1 mL anhydrous THF was added DIBAL-H (0.3 mmol, 3.0 eq.) at 0 °C under the protection of N₂. The mixture was stirred at room temperature and extracted with ethyl acetate (1 mL×3). The organic phases were combined, washed with 5% ammonia aqueous solution (2 mL) and saturated NaCl aqueous solution (2 mL) in turn, dried with Na₂SO₄ and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to provide the desired product **4a** as a yellow solid (30.3 mg, 99% yield, mp: 130-132 °C).

Scheme S2. The deprotection of *p*-methoxyphenyl group.



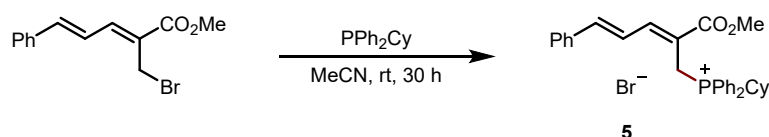
To a stirred solution of **3ab** (33.4 mg, 0.1 mmol, 1.0 eq.) in acetonitrile (1 mL) was added H₂O (1 mL) solution of CAN (164.5 mg, 0.3 mmol, 3.0 eq.) at 0 °C under the protection of N₂. And the mixture was stirred for 10 min and then extracted with ethyl acetate (1 mL×3). The organic phases were combined, washed with 5% NaHSO₃ aqueous solution (2 mL) and saturated NaCl aqueous solution (2 mL) in turn, dried with Na₂SO₄ and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 3:1) to provide the desired product **4b** as a white solid (10.0 mg, 44% yield, mp: 46-48 °C).

Scheme S3. The deprotection of methyl group.

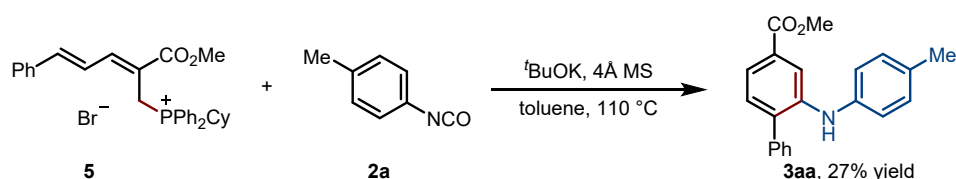


To a stirred solution of **3ab** (0.1 mmol, 1.0 eq.) in 1 mL anhydrous DCM was added BBr_3 (0.6 mmol, 6.0 eq.) at 0°C under the protection of N_2 . The mixture was stirred 1 h at room temperature. The organic phases washed with H_2O (2 mL) and saturated NaCl aqueous solution (2 mL) in turn, dried with Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 1:1) to provide the desired product **4c** as a yellow solid (29.0 mg, 95% yield, mp: $46\text{--}48^\circ\text{C}$).

6. Mechanism verification experiment



MBH bromide (3.2 mmol) and PPh_2Cy (3.2 mmol, 1.0 equiv) were dissolved in 10 mL MeCN and stirred for 30 h. Then the mixture was concentrated in vacuo. The crude product was recrystallized to provide the desired phosphonium salt **5** as a white solid (1.23 g, 70% yield).



To a 10 mL glass vial was added phosphonium salt **5** (0.1 mmol, 1.0 equiv), isocyanate **2a** (0.12 mmol, 1.2 equiv), $t\text{BuOK}$ (12.3 mg, 0.11 mmol, 1.1 eq), 4 Å MS (100 mg) and 1.0 mL of toluene. The resulting suspension was stirred at 110°C until the complete consumption of the starting materials monitored by TLC. After filtration and evaporation, the residue was purified by silica gel flash column chromatography (petroleum ether: ethyl acetate = 5:1) to afford corresponding product **3aa** (8.6 mg, 27% yield).

7. X-Ray Crystallography Data of 3ag

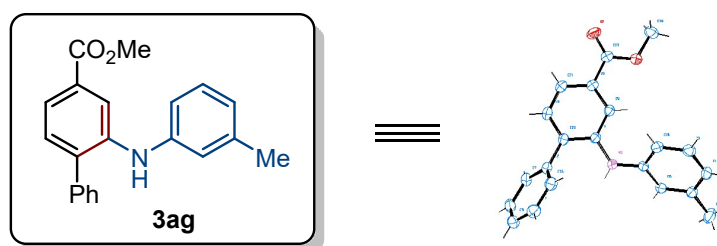


Figure S1. ORTEP diagram of **3ag** (CCDC: 2260766). Thermal ellipsoids are shown at the 50% probability level. A colorless stick-shaped crystal of **3ag** for X-ray diffraction was obtained by slowly

volatilizing a saturated solution of **3ag** in hexane/dichloromethane (10:1).

Table S2. Crystal data and structure refinement for **3ag**.

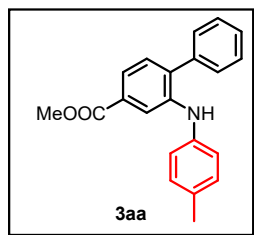
Identification code	3ag
Empirical formula	C ₂₁ H ₁₉ NO ₂
Formula weight	317.37
Temperature/K	298.30
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.7871(6)
b/Å	15.5197(10)
c/Å	24.4352(17)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	3332.3(4)
Z	8
ρ calc/g/cm ³	1.265
μ /mm ⁻¹	0.081
F(000)	1344.0
Crystal size/mm ³	0.200 × 0.180 × 0.120
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.25 to 52.766
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 19, -29 ≤ l ≤ 30
Reflections collected	33641
Independent reflections	3394 [Rint = 0.0621, Rsigma = 0.0347]
Data/restraints/parameters	3394/0/220
Goodness-of-fit on F ²	1.054
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0402, wR2 = 0.0986
Final R indexes [all data]	R1 = 0.0632, wR2 = 0.1108
Largest diff. peak/hole / e Å ⁻³	0.18/-0.20

8. References

- [1] Cai, W.; Huang, Y. Metal Free Dötz-Type Aminobenzannulation Reaction via 1,1-Dipoles Cross-Coupling. *Angew. Chem., Int. Ed.* **2023**, *62*, e202310133.

9. Characterization Data

Methyl 2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3aa**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3aa** as yellow solid (19.3 mg, 61% yield, mp: 110-112 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1).

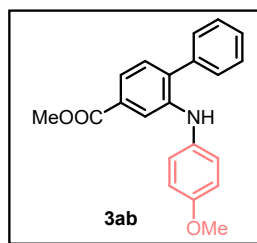
¹H-NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, $J = 1.7$ Hz, 1H), 7.59 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.46 (d, $J = 4.4$ Hz, 4H), 7.39 (q, $J = 4.4$ Hz, 1H), 7.25 (s, 1H), 7.10 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 8.3$ Hz, 2H), 5.61 (s, 1H), 3.88 (s, 3H), 2.31 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 134.5, 131.6, 130.6, 129.9, 128.9, 127.8, 120.9, 119.6, 116.5, 51.9, 20.6.

HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_2$ $[M + H]^+$: 318.1494; Found: 318.1498.

IR (KBr): 3032, 3020, 2985, 2898, 1717, 1650, 1542, 1520, 762, 755 cm^{-1} .

Methyl 2-((4-methoxyphenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ab**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2b** (0.1 mmol, 1.2 equiv) to give **3ab** as white solid (20.3 mg, 61% yield, mp: 115-116 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

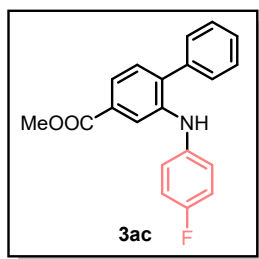
¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.74$ (d, $J=1.8$, 1H), 7.40 (q, $J=7.2, 5.4$, 6H), 7.25 (d, $J=3.1$, 1H), 7.10 – 6.97 (m, 2H), 6.87 (d, $J=8.5$, 2H), 5.58 (s, 1H), 3.87 (s, 3H), 3.80 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 167.2, 155.9, 142.7, 138.3, 135.0, 133.6, 130.7, 130.2, 129.2, 129.1, 128.0, 123.3, 120.3, 115.1, 114.9, 55.6, 52.1.

HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_3$ $[M + H]^+$: 334.1443; Found: 334.1447.

IR (KBr): 3500, 3030, 2890, 2880, 1716, 1646, 1567, 1299, 749 cm^{-1} .

Methyl 2-((4-fluorophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ac**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0equiv) and **2c** (0.12 mmol, 1.2 equiv) to give **3ac** as white solid (18.7 mg, 58% yield, mp: 77-79 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.83$ (d, $J=1.7$, 1H), 7.60 (dd, $J=7.9$, 1.7, 1H), 7.52 – 7.37 (m, 6H), 7.27 (d, $J=12.0$, 2H), 7.09 – 6.89 (m, 5H), 5.60 (s, 1H), 3.89 (s, 3H).

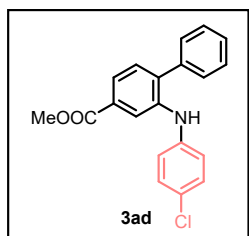
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 167.1$, 158.6 (d, $J=241.1$), 141.4, 138.3 (d, $J=2.8$), 138.0, 134.6, 130.8, 130.2, 129.1, 129.0, 128.1, 121.8 (d, $J=7.7$), 121.3, 116.2 (d, $J=2.2$), 116.0, 52.1.

$^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) $\delta = -120.68$.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{FNO}_2$ $[\text{M} + \text{H}]^+$: 322.1243; Found: 322.1248.

IR (KBr): 3501, 2995, 2952, 1718, 1646, 1567, 1217, 830, 750 cm^{-1} .

Methyl 2-((4-chlorophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ad**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2d** (0.12 mmol, 1.2 equiv) to give **3ad** as white solid (14.4 mg, 43% yield, mp: 44-46 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

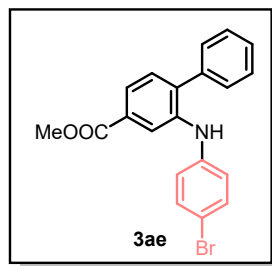
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.95$ (d, $J=1.6$, 1H), 7.66 (dd, $J=7.9$, 1.7, 1H), 7.49 – 7.37 (m, 5H), 7.31 (d, $J=7.8$, 1H), 7.28 – 7.19 (m, 2H), 6.97 (d, $J=8.8$, 2H), 5.62 (s, 1H), 3.90 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.9$, 141.4, 140.2, 137.9, 135.8, 131.0, 130.2, 129.5, 129.1, 129.0, 128.2, 126.5, 122.3, 119.8, 118.0, 52.2.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{ClNO}_2$, $[\text{M} + \text{H}]^+$: 338.0948; Found: 338.0951.

IR (KBr): 3547, 3027, 2951, 2890, 1717, 1670, 1586, 1276, 749 cm^{-1} .

Methyl 2-((4-bromophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ae**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2e** (0.12 mmol, 1.2 equiv) to give **3ae** as white solid (19.7 mg, 52% yield, mp: 61-63 °C). $R_f = 0.7$ (petroleum ether/ethyl acetate = 3:1).

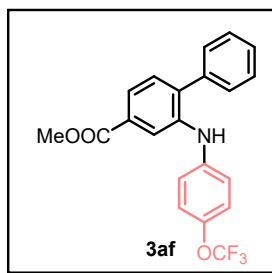
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.97$ (d, $J=2.8$, 1H), 7.71 – 7.63 (m, 1H), 7.46 – 7.39 (m, 4H), 7.33 (ddd, $J=18.8$, 8.4, 3.0, 4H), 6.91 (dd, $J=8.9$, 3.0, 2H), 5.61 (s, 1H), 3.90 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.9$, 142.0, 139.9, 137.9, 136.0, 132.4, 131.0, 130.2, 129.1, 129.0, 128.2, 122.5, 119.9, 118.3, 52.2.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_2$, $[\text{M} + \text{H}]^+$: 382.0443; Found: 382.0444.

IR (KBr): 3502, 3030, 2991, 2890, 1716, 1646, 1557, 1299, 748 cm^{-1} .

Methyl 2-((4-(trifluoromethoxy)phenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3af**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2f** (0.12 mmol, 1.2 equiv) to give **3af** as white solid (17.9 mg, 46% yield, mp: 86-88 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.99$ (s, 1H), 7.68 (d, $J=7.9$, 1H), 7.44 (dq, $J=13.1$, 7.0, 6.3, 5H), 7.32 (d, $J=7.9$, 1H), 7.13 (d, $J=8.5$, 2H), 7.03 (d, $J=8.6$, 2H), 5.66 (s, 1H), 3.91 (s, 3H).

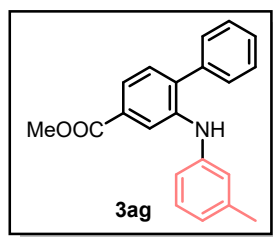
$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.9$, 143.4, 141.9, 140.1, 137.9, 131.1, 130.2, 129.1, 129.0, 128.2, 122.5, 122.5, 120.6 (q, $J=256.2$, 255.7), 119.1, 118.1, 52.2.

$^{19}\text{F-NMR}$ (376 MHz, Chloroform-*d*) $\delta = -58.22$.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_3\text{NO}_3$, $[\text{M} + \text{H}]^+$: 388.1161; Found: 388.1165.

IR (KBr): 3501, 3030, 2990, 2888, 1715, 1646, 1592, 1279, 749 cm^{-1} .

Methyl 2-(*m*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ag**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2g** (0.2 mmol, 2.0 equiv) to give **3ag** as white solid (19.0 mg, 60% yield, mp: 60-62 °C). $R_f = 0.7$ (petroleum ether/ethyl acetate = 3:1).

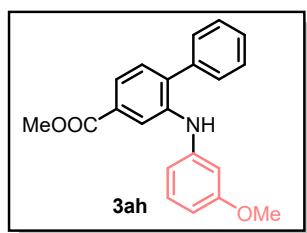
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 8.02$ (d, $J=1.6$, 1H), 7.63 (dd, $J=7.9$, 1.7, 1H), 7.45 (d, $J=3.8$, 4H), 7.41 – 7.36 (m, 1H), 7.29 (d, $J=7.9$, 1H), 7.17 (t, $J=7.7$, 1H), 6.90 (dd, $J=8.0$, 2.3, 1H), 6.85 (d, $J=2.6$, 1H), 6.80 (d, $J=7.5$, 1H), 5.63 (s, 1H), 3.89 (s, 3H), 2.30 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 167.1, 142.5, 140.7, 139.4, 138.2, 135.3, 130.9, 130.1, 129.3, 129.1, 128.1, 122.7, 121.7, 119.6, 117.8, 115.8, 52.1, 21.5.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$, $[\text{M} + \text{H}]^+$: 318.1494; Found: 318.1499.

IR (KBr): 3458, 3029, 2919, 2849, 1717, 1600, 1565, 756, 701 cm^{-1} .

Methyl 2-((3-methoxyphenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ah**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2h** (0.2 mmol, 2.0 equiv) to give **3ah** as white solid (15.4 mg, 46% yield, mp: 50-52 °C). $R_f = 0.7$ (petroleum ether/ethyl acetate = 3:1).

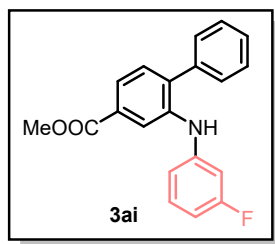
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 8.07$ (s, 1H), 7.65 (d, $J=7.9$, 1H), 7.51 – 7.37 (m, 5H), 7.31 (d, $J=7.9$, 1H), 7.18 (t, $J=8.2$, 1H), 6.68 – 6.56 (m, 2H), 6.52 (d, $J=8.3$, 1H), 5.65 (s, 1H), 3.90 (s, 3H), 3.77 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 167.0, 160.8, 144.1, 140.3, 138.1, 135.8, 130.9, 130.3, 130.1, 129.1, 129.1, 128.1, 122.1, 118.6, 110.9, 107.2, 104.1, 55.3, 52.2.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_3$, $[\text{M} + \text{H}]^+$: 334.1443; Found: 334.1448.

IR (KBr): 3363, 2950, 2889, 1718, 1662, 1518, 1218, 818, 750 cm^{-1} .

Methyl 2-((3-fluorophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ai**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2i** (0.12 mmol, 1.2 equiv) to give **3ai** as white oil (16.2 mg, 42% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 8.05$ (d, $J=1.7$, 1H), 7.71 (dd, $J=7.9$, 1.6, 1H), 7.50 – 7.39 (m, 5H), 7.33 (d, $J=7.9$, 1H), 7.19 (td, $J=8.1$, 6.6, 1H), 6.79 – 6.70 (m, 2H), 6.62 (td, $J=8.3$, 2.4, 1H), 5.67 (s, 1H), 3.92 (s, 3H).

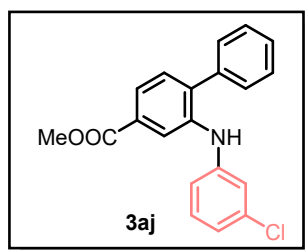
$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.8$, 163.8 (d, $J=244.9$), 144.9 (d, $J=10.3$), 139.4, 137.8, 136.6, 131.0, 130.6 (d, $J=10.0$), 130.2, 129.1, 129.0, 128.2, 122.9, 119.4, 113.2 (d, $J=2.7$), 107.9 (d, $J=21.4$), 104.5 (d, $J=24.9$), 52.2.

$^{19}\text{F-NMR}$ (376 MHz, Chloroform-*d*) $\delta = -111.80$.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{FNO}_2$, $[\text{M} + \text{H}]^+$: 322.1243; Found: 322.1248.

IR (KBr): 3490, 3001, 2990, 2890, 1716, 1593, 1550, 1275, 763, 750 cm^{-1} .

Methyl 2-((3-chlorophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3aj**)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2j** (0.12 mmol, 1.2 equiv) to give **3aj** as yellow oil (16.2 mg, 48% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

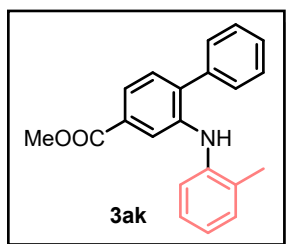
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 8.02$ (d, $J=1.7$, 1H), 7.71 (dd, $J=7.9$, 1.7, 1H), 7.48 – 7.39 (m, 5H), 7.33 (d, $J=7.9$, 1H), 7.17 (t, $J=8.0$, 1H), 6.97 (t, $J=2.1$, 1H), 6.91 (ddd, $J=7.7$, 5.2, 2.1, 2H), 5.63 (s, 1H), 3.91 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.8$, 144.4, 139.5, 137.8, 136.6, 135.2, 131.1, 130.5, 130.3, 129.1, 129.0, 128.2, 123.0, 121.3, 119.3, 117.8, 115.8, 52.2.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{ClNO}_2$, $[\text{M} + \text{H}]^+$: 338.0948; Found: 338.0953.

IR (KBr): 3476, 3011, 2990, 2890, 1716, 1644, 1259, 751 cm^{-1} .

Mmethyl 2-(*o*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (3ak)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2k** (0.12 mmol, 1.2 equiv) to give **3ak** as white oil (18.4 mg, 58% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 3:1).

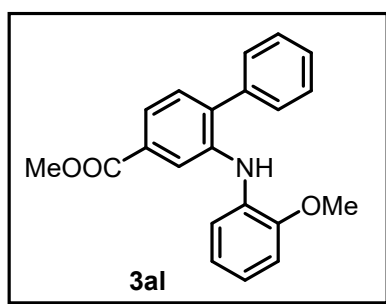
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.71$ (d, $J=1.7$, 1H), 7.60 (dd, $J=7.9$, 1.7, 1H), 7.50 – 7.42 (m, 4H), 7.39 (dq, $J=5.9$, 2.7, 1H), 7.29 (d, $J=7.8$, 1H), 7.25 (d, $J=2.0$, 1H), 7.18 (d, $J=7.5$, 2H), 7.02 – 6.93 (m, 1H), 5.50 (s, 1H), 3.87 (s, 3H), 2.09 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 167.2, 141.5, 140.5, 138.2, 134.6, 131.1, 130.7, 130.2, 129.7, 129.1, 129.0, 128.1, 127.0, 123.0, 121.0, 119.9, 116.8, 52.1, 17.9.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$, $[\text{M} + \text{H}]^+$: 318.1494; Found: 318.1499.

IR (KBr): 3479, 3030, 2900, 2890, 1717, 1508, 1235, 750, 703 cm^{-1} .

Methyl 2-(1,3-bis(2-methoxyphenyl)ureido)-[1,1'-biphenyl]-4-carboxylate (3al)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2l** (0.12 mmol, 1.2 equiv) to give **3al** as yellow solid (24.2 mg, 50% yield, mp: 120-121 $^{\circ}\text{C}$). $R_f = 0.4$ (petroleum ether/ethyl acetate = 3:1).

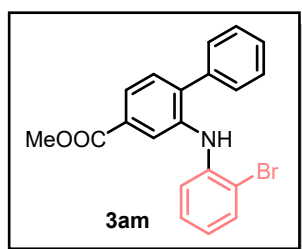
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 8.09$ (s, 1H), 7.65 (dt, $J=7.9$, 1.6, 1H), 7.49 – 7.42 (m, 4H), 7.41 – 7.34 (m, 2H), 7.31 (dd, $J=7.9$, 1.4, 1H), 6.97 – 6.83 (m, 3H), 6.13 (s, 1H), 3.90 (s, 3H), 3.74 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 166.1, 148.1, 139.3, 137.2, 135.2, 131.3, 129.9, 129.0, 128.0, 127.8, 126.9, 120.9, 120.0, 119.9, 117.2, 114.8, 109.8, 54.6, 51.1.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3$, $[\text{M} + \text{H}]^+$: 334.1443; Found: 334.1447.

IR (KBr): 3574, 3000, 2980, 2889, 1716, 1651, 1291, 1105, 747, 702cm⁻¹.

Methyl 2-((2-bromophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (3am)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2m** (0.12 mmol, 1.2 equiv) to give **3am** as white solid (16.2 mg, 42% yield, mp: 60-62 °C). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1).

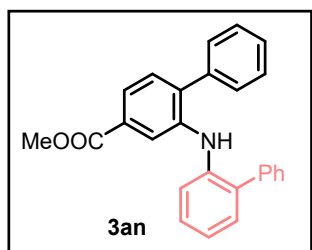
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 8.03$ (s, 1H), 7.73 (d, $J=8.0$, 1H), 7.51 – 7.43 (m, 5H), 7.35 (dd, $J=18.8$, 8.0, 3H), 7.21 (t, $J=7.7$, 1H), 6.78 (t, $J=7.7$, 1H), 6.12 (s, 1H), 3.91 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 166.9, 140.6, 139.2, 137.8, 137.2, 133.1, 131.0, 130.1, 129.0, 128.9, 128.3, 128.2, 123.1, 121.9, 119.5, 116.8, 113.5, 52.2.

HRMS (ESI) m/z calcd for C₂₀H₁₆BrNO₂, [M + H]⁺: 382.0443; Found: 382.0446.

IR (KBr): 3309, 3000, 2923, 2890, 1719, 1646, 1260, 763, 749 cm⁻¹.

Methyl 2-([1,1'-biphenyl]-2-ylamino)-[1,1'-biphenyl]-4-carboxylate (3an)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2n** (0.12 mmol, 1.2equiv) to give **3an** as colorless solid (14.0 mg, 37% yield, mp: 90-92 °C). $R_f = 0.7$ (petroleum ether/ethyl acetate = 5:1).

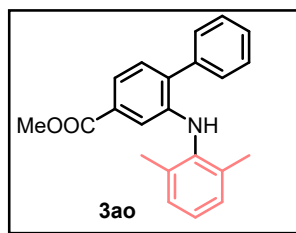
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 8.04$ (s, 1H), 7.60 (d, $J=7.9$, 1H), 7.43 (d, $J=8.1$, 1H), 7.33 – 7.27 (m, 6H), 7.25 – 7.15 (m, 7H), 7.02 (t, $J=7.4$, 1H), 5.82 (s, 1H), 3.90 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.1, 140.6, 139.4, 138.8, 138.0, 135.8, 132.8, 130.8, 130.7, 130.1, 129.0, 128.9, 128.7, 128.7, 128.4, 127.8, 127.3, 121.7, 121.5, 117.9, 117.0, 52.1.

HRMS (ESI) m/z calcd for C₂₆H₂₁NO₂, [M + H]⁺: 380.1651; Found: 380.1655.

IR (KBr): 3461, 3000, 2987, 2887, 1716, 1636, 1579, 1259, 749, 719 cm⁻¹.

Methyl 2-((2,6-dimethylphenyl)amino)-[1,1'-biphenyl]-4-carboxylate (3ao)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2o** (0.12 mmol, 1.2 equiv) to give **3ao** as white solid (13.6 mg, 41% yield, mp: 106-108 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

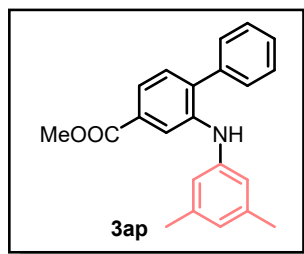
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.51$ (dt, $J=24.4, 8.1$, 5H), 7.42 (d, $J=7.2$, 1H), 7.22 (d, $J=7.8$, 1H), 7.10 (d, $J=2.8$, 3H), 6.87 – 6.81 (m, 1H), 5.33 (s, 1H), 3.81 (s, 3H), 2.16 (s, 6H).

¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 167.4, 143.3, 138.6, 137.5, 136.1, 131.8, 130.4, 130.3, 129.2, 129.1, 128.7, 128.0, 126.3, 119.0, 112.1, 52.0, 18.4$.

HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_2$, $[M + H]^+$: 332.1651; Found: 332.1654.

IR (KBr) : 3473, 3030, 2998, 2889, 1716, 1637, 1242, 750 cm^{-1} .

Methyl 2-((3,5-dimethylphenyl)amino)-[1,1'-biphenyl]-4-carboxylate (3ap)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2p** (0.12 mmol, 1.2 equiv) to give **3ap** as yellow solid (10.1 mg, 30% yield, mp: 108-110 °C). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1).

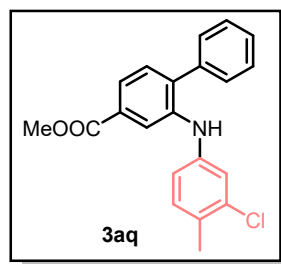
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 8.02$ (s, 1H), 7.62 (d, $J=8.0$, 1H), 7.44 (d, $J=4.2$, 4H), 7.41 – 7.36 (m, 1H), 7.28 (d, $J=8.0$, 1H), 6.66 (d, $J=24.8$, 3H), 5.58 (s, 1H), 3.89 (s, 3H), 2.27 (s, 6H).

¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 167.4, 143.3, 138.6, 137.5, 136.1, 131.8, 130.4, 130.3, 129.2, 129.1, 128.7, 128.0, 126.3, 119.0, 112.1, 52.0, 18.4$.

HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_2$, $[M + H]^+$: 332.1651; Found: 332.1654.

IR (KBr): 3320, 3122, 2900, 2890, 1718, 1665, 1552, 1299, 749 cm^{-1} .

Methyl 2-((3-chloro-4-methylphenyl)amino)-[1,1'-biphenyl]-4-carboxylate (3aq)



The reaction was performed according to **General Procedure** with **1a** (0.1 mmol, 1.0 equiv) and **2q** (0.12 mmol, 1.2 equiv) to give **3aq** as yellow solid (17.5 mg, 50% yield, mp: 110-112 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

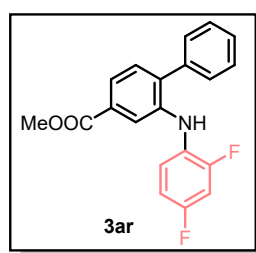
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.94$ (s, 1H), 7.65 (d, $J=7.8$, 1H), 7.45 – 7.36 (m, 4H), 7.30 (d, $J=8.0$, 1H), 7.11 (d, $J=8.1$, 1H), 7.02 (s, 1H), 6.89 (d, $J=8.3$, 1H), 5.58 (s, 1H), 3.90 (s, 3H), 2.31 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 166.9$, 141.7, 140.3, 138.0, 135.6, 135.0, 131.5, 130.9, 130.2, 129.2, 129.1, 129.0, 128.2, 122.1, 119.4, 118.0, 117.2, 52.2, 19.3.

HRMS (ESI) m/z calcd for $C_{21}H_{18}ClNO_2$, $[M + H]^+$: 352.1104; Found: 352.1109.

IR (KBr): 3512, 3073, 2922, 2890, 1715, 1579, 1258, 750, 701 cm^{-1} .

Methyl 2-((2,4-difluorophenyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3ar**)



The reaction was performed according to **General Procedure** with **1a** (0.1 mmol, 1.0 equiv) and **3r** (0.12 mmol, 1.2 equiv) to give **3ar** as white solid (16.8 mg, 50% yield, mp: 110-112 °C). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1).

¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.75$ (s, 1H), 7.64 (d, $J=7.9$, 1H), 7.47 (d, $J=5.6$, 4H), 7.43 – 7.38 (m, 1H), 7.30 (d, $J=8.1$, 2H), 6.84 (q, $J=9.3$, 8.7, 2H), 5.58 (s, 1H), 3.89 (s, 3H).

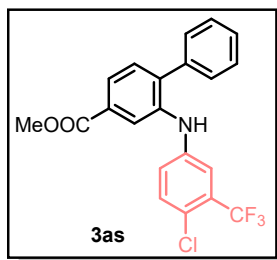
¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 166.9$, 157.9 (dd, $J=244.0$, 11.1), 154.6 (dd, $J=246.6$, 11.8), 140.7, 137.9, 135.2, 130.9, 130.2, 129.2, 128.9, 128.2, 126.7 (dd, $J=11.7$, 3.5), 121.9, 121.9 (d, $J=3.8$), 116.4, 111.3 (dd, $J=22.1$, 3.9), 104.6 (dd, $J=26.4$, 23.6), 52.2.

¹⁹F NMR (376 MHz, Chloroform-*d*) $\delta = -117.36$ (d, $J=4.2$), -123.83 (d, $J=4.0$).

HRMS (ESI) m/z calcd for $C_{20}H_{15}F_2NO_2$, $[M + H]^+$: 340.1149; Found: 340.1154.

IR (KBr): 3616, 3019, 2980, 2775, 1718, 1567, 1260, 848, 749 cm^{-1} .

Methyl 2-((4-chloro-3-(trifluoromethyl)phenyl)amino)-[1,1'-biphenyl]-4-carboxylate (3as)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2s** (0.12 mmol, 1.2 equiv) to give **3as** as white solid (17.5 mg, 43% yield, mp: 114-116 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.97$ (s, 1H), 7.75 (d, $J=7.8$, 1H), 7.45 (d, $J=7.1$, 2H), 7.42–7.32 (m, 5H), 7.22 (d, $J=2.7$, 1H), 7.14 (dd, $J=8.6, 2.8$, 1H), 5.71 (s, 1H), 3.92 (s, 3H).

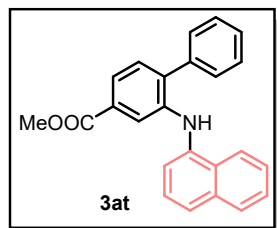
¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 166.6, 142.0, 138.8, 137.6, 137.1, 132.3, 131.2, 130.3, 129.1, 128.9, 128.3, 123.6, 120.1$ (d, $J=131.3$), 116.6 (q, $J=5.4$), 52.2.

¹⁹F-NMR (376 MHz, Chloroform-*d*) $\delta = -62.86$.

HRMS (ESI) m/z calcd for $C_{21}H_{15}ClF_3NO_2$, $[M + H]^+$: 406.0822; Found: 406.0819.

IR (KBr): 3202, 3001, 2998, 2890, 1718, 1546, 1199, 749 cm^{-1} .

Methyl 2-(naphthalen-1-ylamino)-[1,1'-biphenyl]-4-carboxylate (3at)



The reaction was performed according to *General Procedure* with **1a** (0.1 mmol, 1.0 equiv) and **2t** (0.2 mmol, 2.0 equiv) to give **3at** as white oil (14.7 mg, 42% yield). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1).

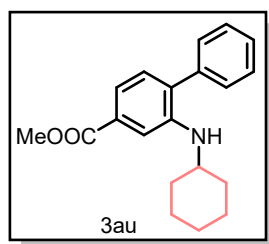
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.87$ –7.80 (m, 2H), 7.73 (d, $J=1.7$, 1H), 7.65–7.53 (m, 4H), 7.52–7.43 (m, 4H), 7.46–7.35 (m, 5H), 7.34 (d, $J=7.9$, 1H), 5.99 (s, 1H), 3.82 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 167.1, 142.3, 138.3, 138.2, 134.8, 134.7, 130.8, 130.3, 129.3, 129.0, 128.6, 128.3, 128.2, 126.2, 126.1, 125.9, 123.8, 121.6, 121.2, 117.3, 117.2, 52.1$.

HRMS (ESI) m/z calcd for $C_{24}H_{19}NO_2$, $[M + H]^+$: 354.1489; Found: 354.1477.

IR (KBr): 3323, 3003, 2998, 2880, 1712, 1646, 1239, 749 cm^{-1} .

Methyl 2-(cyclohexylamino)-[1,1'-biphenyl]-4-carboxylate (**3au**)



The reaction was performed according to **General Procedure** with **1a** (0.1 mmol, 1.0 equiv) and **2u** (0.12 mmol, 1.2 equiv) to give **3au** as white oil (9.2 mg, 30% yield). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1).

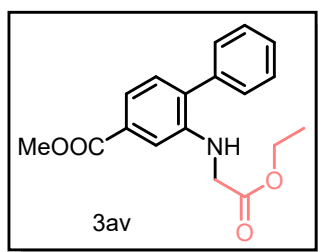
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ 7.45 (t, $J = 7.5$ Hz, 2H), 7.42 – 7.33 (m, 5H), 7.10 (d, $J = 7.7$ Hz, 1H), 4.03 – 3.80 (m, 4H), 3.38 (tt, $J = 9.8, 3.7$ Hz, 1H), 1.99 (dd, $J = 13.0, 4.2$ Hz, 2H), 1.63 (ddt, $J = 20.2, 8.0, 4.2$ Hz, 3H), 1.45 – 1.30 (m, 2H), 1.23 – 1.02 (m, 2H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 167.6, 144.2, 138.7, 131.9, 130.2, 130.2, 129.0, 127.6, 117.5, 111.6, 52.0, 51.3, 33.0, 25.8, 24.7.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_2$, $[\text{M} + \text{H}]^+$: 310.1802; Found: 310.1798.

IR (KBr): 3400, 3030, 2887, 2790, 1715, 1650, 1546, 1299, 749 cm^{-1} .

Methyl 2-((2-ethoxy-2-oxoethyl)amino)-[1,1'-biphenyl]-4-carboxylate (**3av**)



The reaction was performed according to **General Procedure** with **1a** (0.1 mmol, 1.0 equiv) and **S4-1** (0.12 mmol, 1.2equiv) to give **3av** as colorless oil (15.0 mg, 48% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 15:1).

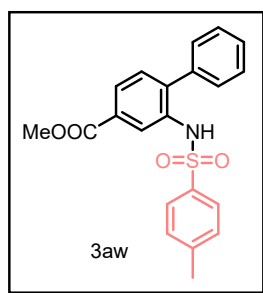
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ = 7.48 (h, $J=7.1, 6.2, 5\text{H}$), 7.41–7.34 (m, 1H), 7.21 (dd, $J=26.0, 9.3, 2\text{H}$), 4.69 (s, 1H), 4.20 (q, $J=7.2, 2\text{H}$), 3.95 (s, 2H), 3.92 (s, 3H), 1.27 (t, $J=7.1, 3\text{H}$).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 177.1, 170.8, 167.4, 144.0, 138.2, 132.6, 130.3, 129.1, 129.0, 128.0, 119.1, 111.1, 61.4, 52.1, 45.7, 14.2.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$, $[\text{M} + \text{H}]^+$: 314.1392; Found: 314.1397.

IR (KBr): 3490, 3011, 2990, 2890, 1717, 1715, 1660, 1546, 1236, 1055, 751 cm^{-1} .

Methyl 2-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate (**3aw**)



The reaction was performed according to **General Procedure** with **1a** (0.1 mmol, 1.0 equiv) and **2w** (0.12 mmol, 1.2 equiv) to give **3aw** as white solid (13.3mg, 35% yield, mp: 92-94 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

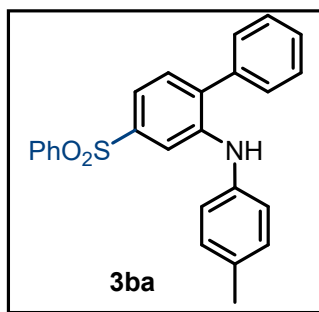
¹H-NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, $J = 1.6$ Hz, 1H), 7.39 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.35 – 7.29 (m, 2H), 7.12 – 7.03 (m, 2H), 3.92 (s, 4H), 2.37 (s, 3H), 1.34 (s, 9H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 166.4, 144.1, 138.1, 136.3, 136.0, 134.1, 130.6, 130.4, 129.7, 129.3, 128.7, 128.6, 127.3, 125.9, 122.1, 52.4, 21.6.

HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_4S$, $[M + Na]^+$: 404.0932; Found: 404.0934.

IR (KBr): 3516, 3043, 2951, 2920, 1717, 1654, 1338, 1229, 1058, 812, 759 cm^{-1}

4-(Phenylsulfonyl)-*N*-(*p*-tolyl)-[1,1'-biphenyl]-2-amine (**3ba**)



The reaction was performed according to **General Procedure** with **1b** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ba** as colorless oil (22.7 mg, 57% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

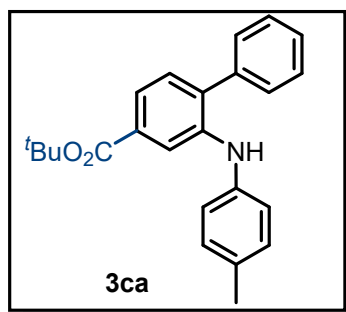
¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.94 (dd, $J=7.0, 1.8$, 2H), 7.77 (d, $J=1.8$, 1H), 7.58 – 7.50 (m, 3H), 7.45 (d, $J=6.6$, 2H), 7.42 – 7.37 (m, 4H), 7.25 (d, $J=1.5$, 1H), 7.11 (d, $J=7.9$, 2H), 6.96 – 6.90 (m, 2H), 5.73 (s, 1H), 2.33 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.6, 141.9, 141.3, 138.5, 137.4, 134.1, 133.1, 133.0, 131.5, 130.2, 129.3, 129.2, 129.0, 128.4, 127.7, 120.7, 118.1, 113.2, 20.8.

HRMS (ESI) m/z calcd for $C_{25}H_{21}NO_2S$, $[M + Na]^+$: 422.1191; Found: 422.1190.

IR (KBr): 3400, 3000, 2998, 2890, 1716, 1589, 1100, 763, 753, 749 cm^{-1}

Tert-butyl 2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (3ca)



The reaction was performed according to *General Procedure* with **1c** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ca** as yellow oil (15.0 mg, 42% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

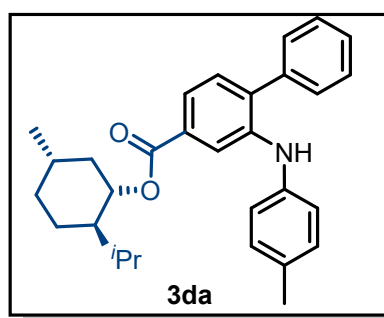
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.92$ (d, $J=1.7$, 1H), 7.45 (d, $J=4.3$, 4H), 7.38 (ddd, $J=8.7$, 5.2, 3.6, 1H), 7.24 (d, $J=7.4$, 2H), 7.09 (d, $J=8.1$, 2H), 7.01 – 6.95 (m, 2H), 5.61 (s, 1H), 2.30 (s, 3H), 1.57 (s, 9H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $^{13}\text{C NMR } \delta = 165.8, 141.2, 139.8, 138.4, 134.2, 132.1, 131.6, 130.6, 130.0, 129.1, 129.1, 127.9, 120.9, 119.6, 116.5, 80.9, 28.2, 20.7.$

HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2$, $[\text{M} + \text{H}]^+$: 360.1964; Found: 360.1967.

IR (KBr): 3607, 2977, 2924, 1713, 1518, 1299, 763, 702 cm^{-1}

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (3da)



The reaction was performed according to *General Procedure* with **1d** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3da** as yellow solid (12.0 mg, 27% yield, mp: 70-72 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.97$ (d, $J=1.6$, 1H), 7.60 (dd, $J=7.9$, 1.7, 1H), 7.46 (d, $J=4.3$, 3H), 7.41 – 7.36 (m, 1H), 7.26 (d, $J=1.8$, 1H), 7.09 (d, $J=8.0$, 2H), 7.02 – 6.94 (m, 2H), 5.63 (s, 1H), 4.88 (td, $J=10.8$, 4.3, 1H), 2.31 (s, 3H), 2.12 (s, 1H), 1.99 – 1.92 (m, 1H), 1.75 – 1.67 (m, 2H), 1.54 – 1.44 (m, 2H), 1.34 – 1.28 (m, 1H), 1.19 – 1.00 (m, 3H), 0.91 (dd, $J=6.8$, 4.0, 6H), 0.80 (d, $J=6.9$, 3H).

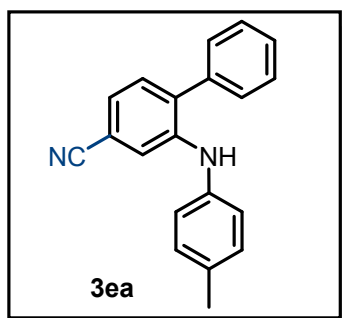
$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.1, 141.3, 139.8, 138.3, 134.5, 131.7, 130.8, 130.7, 130.0,$

129.1, 128.0, 121.0, 119.6, 116.7, 74.9, 47.2, 40.9, 34.3, 31.4, 26.7, 23.8, 22.1, 20.7, 16.8.

HRMS (ESI) m/z calcd for $C_{30}H_{35}NO_2$, $[M + H]^+$: 442.2746; Found: 442.2749.

IR (KBr): 3479, 3029, 2954, 2890, 1709, 1518, 1275, 750, 701 cm^{-1}

Methyl 2'-cyano-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (3ea)



The reaction was performed according to *General Procedure* with **1e** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ea** as yellow solid (6.4 mg, 23% yield, mp: 88-90 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

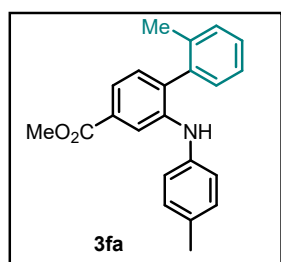
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.54 - 7.36$ (m, 7H), 7.23 (d, $J=2.5$, 1H), 7.15 - 7.12 (m, 2H), 7.02 - 6.95 (m, 2H), 5.69 (s, 1H), 2.33 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 142.8, 138.2, 137.4, 133.6, 133.5, 131.3, 130.3, 129.3, 129.0, 128.5, 122.6, 121.7, 119.3, 117.0, 111.9, 20.8.

HRMS (ESI) m/z calcd for $C_{22}H_{18}N_2O_2$, $[M + H]^+$: 343.1447; Found: 343.1440.

IR (KBr): 3307, 3104, 2917, 2850, 2231, 1683, 1557, 1515, 815, 763, 743 cm^{-1} .

Methyl 2'-methyl-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (3fa)



The reaction was performed according to *General Procedure* with **1f** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3fa** as yellow solid (17.9 mg, 54% yield, mp: 60-62 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

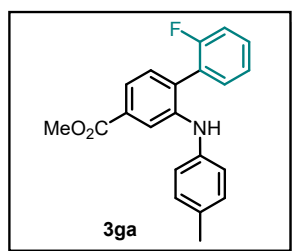
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.92$ (d, $J=1.7$, 1H), 7.56 (dd, $J=7.8$, 1.6, 1H), 7.30 (d, $J=6.3$, 3H), 7.22 (d, $J=6.2$, 1H), 7.16 (d, $J=7.8$, 1H), 7.09 (d, $J=8.0$, 2H), 6.97 (d, $J=8.0$, 2H), 5.25 (s, 1H), 3.88 (s, 3H), 2.30 (s, 3H), 2.16 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.3, 142.0, 139.3, 137.4, 136.9, 134.0, 132.1, 130.6, 130.5, 130.1, 130.0, 129.9, 128.4, 126.5, 120.5, 120.3, 115.1, 52.1, 20.8, 19.7.

HRMS (ESI) m/z calcd for C₂₂H₂₁NO₂, [M + H]⁺: 332.1651; Found: 332.1655.

IR (KBr): 3527, 2950, 2887, 1717, 1654, 1519, 1275, 766, 750 cm⁻¹.

Methyl 2'-fluoro-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ga**)



The reaction was performed according to **General Procedure** with **1g** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ga** as yellow solid (20.0 mg, 60% yield, mp: 97-99 °C). R_f = 0.5 (petroleum ether/ethyl acetate = 5:1).

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.93 (s, 1H), 7.59 (d, $J=7.9$, 1H), 7.39 (q, $J=7.0$, 2H), 7.27 – 7.15 (m, 3H), 7.09 (d, $J=7.9$, 2H), 6.97 (d, $J=7.9$, 2H), 5.46 (s, 1H), 3.88 (s, 3H), 2.30 (s, 3H).

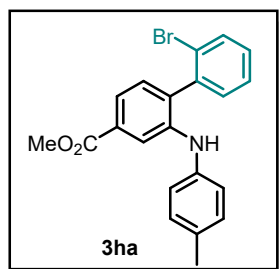
¹³C-NMR (101 MHz, Chloroform-*d*) δ = 167.0, 159.8 (d, $J=247.6$), 142.3, 139.6, 131.9, 131.7 (d, $J=3.2$), 131.4, 130.1 (d, $J=8.2$), 130.0, 128.7, 125.5 (d, $J=16.0$), 124.8 (d, $J=3.8$), 120.8, 120.1, 116.8, 116.4, 116.2, 52.1, 20.7.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.64.

HRMS (ESI) m/z calcd for C₂₁H₁₈FNO₂, [M + H]⁺: 336.1400; Found: 336.1402.

IR (KBr): 3321, 3020, 2930, 2870, 1715, 1579, 1292, 749 cm⁻¹.

Methyl 2'-bromo-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ha**)



The reaction was performed according to **General Procedure** with **1h** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ha** as white solid (24.8 mg, 63% yield, mp: 83-85 °C). R_f = 0.5 (petroleum ether/ethyl acetate = 5:1).

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.90 (d, $J=1.5$, 1H), 7.71 (d, $J=8.0$, 1H), 7.58 (dd, $J=7.9$, 1.7,

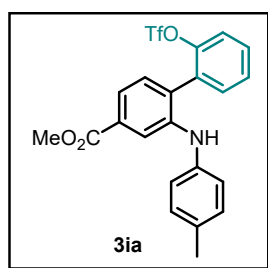
1H), 7.41 (t, $J=7.4$, 1H), 7.33 (dd, $J=7.7$, 1.8, 1H), 7.28 (dd, $J=7.7$, 1.9, 1H), 7.17 (d, $J=7.9$, 1H), 7.09 (d, $J=7.9$, 2H), 7.00 (d, $J=8.0$, 2H), 5.23 (s, 1H), 3.88 (s, 3H), 2.30 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform- d) δ 167.1, 142.1, 139.3, 138.9, 133.4, 133.3, 132.3, 131.6, 130.8, 130.7, 130.0, 129.8, 128.1, 124.0, 120.6, 120.4, 115.9, 52.1, 20.8.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{BrNO}_2$, $[\text{M} + \text{H}]^+$: 396.0599; Found: 396.0599.

IR (KBr): 3534, 3080, 2900, 2887, 1716, 1617, 1275, 750 cm^{-1} .

Methyl 2-(*p*-tolylamino)-2'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-carboxylate (**3ia**)



The reaction was performed according to **General Procedure** with **1i** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ia** as yellow solid (31.7 mg, 68% yield, mp: 80-82 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

$^1\text{H-NMR}$ (400 MHz, Chloroform- d) δ = 7.92 (d, $J=1.7$, 1H), 7.60 (dd, $J=7.9$, 1.7, 1H), 7.49 (d, $J=4.2$, 3H), 7.41 (d, $J=6.9$, 1H), 7.23 (s, 1H), 7.10 (d, $J=7.9$, 2H), 6.96 (d, $J=7.9$, 2H), 5.28 (s, 1H), 3.87 (s, 3H), 2.31 (s, 3H).

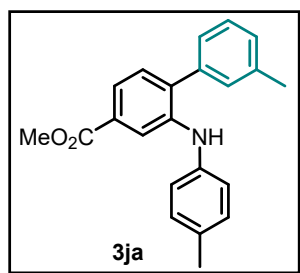
$^{13}\text{C-NMR}$ (101 MHz, Chloroform- d) δ = 166.9, 147.3, 142.7, 139.2, 132.5, 132.3, 132.2, 131.4 (d, $J=5.0$), 130.2, 130.0, 129.0, 127.7, 122.4, 120.7, 120.5, 116.7, 52.1, 20.7.

$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -73.91.

HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{18}\text{F}_3\text{NO}_5\text{S}$, $[\text{M} + \text{Na}]^+$: 488.0755; Found: 488.0757.

IR (KBr): 3296, 3016, 2917, 2850, 1715, 1697, 1557, 1220, 1061, 764, 749 cm^{-1} .

Methyl 3'-methyl-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ja**)



The reaction was performed according to **General Procedure** with **1j** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ja** as yellow solid (15.5 mg, 47% yield, mp: 120-121 °C). $R_f = 0.5$ (petroleum

ether/ethyl acetate = 5:1).

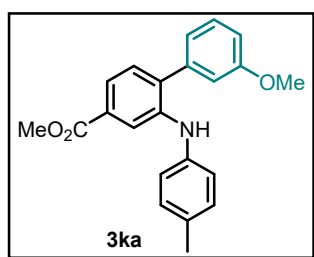
¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.92 (s, 1H), 7.60 – 7.54 (m, 1H), 7.34 (t, $J=7.6$, 1H), 7.25 – 7.17 (m, 3H), 7.10 (d, $J=8.0$, 2H), 6.99 (d, $J=7.9$, 2H), 5.66 (s, 1H), 3.88 (s, 3H), 2.39 (s, 3H), 2.31 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.2, 141.5, 139.7, 138.9, 138.2, 134.7, 131.8, 130.7, 130.0, 130.0, 129.8, 129.0, 128.8, 126.1, 120.9, 120.0, 116.3, 52.1, 21.5, 20.8.

HRMS (ESI) m/z calcd for C₂₂H₂₁NO₂, [M + H]⁺: 332.1651; Found: 332.1653.

IR (KBr): 3320, 3030, 2998, 2880, 1710, 1640, 1239, 749 cm⁻¹.

Methyl 3'-methoxy-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ka**)



The reaction was performed according to *General Procedure* with **1k** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ka** as white solid (20.4 mg, 59% yield, mp: 128-130 °C). R_f = 0.5 (petroleum ether/ethyl acetate = 5:1).

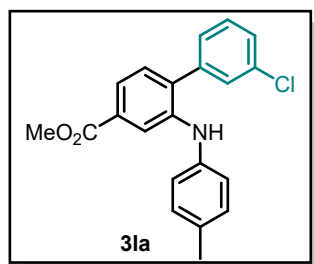
¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.92 (t, $J=1.7$, 1H), 7.57 (dt, $J=7.9$, 1.5, 1H), 7.37 (t, $J=7.9$, 1H), 7.27 (d, $J=8.3$, 1H), 7.10 (d, $J=8.0$, 2H), 7.06 – 6.90 (m, 5H), 5.69 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.31 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.1, 160.1, 141.5, 139.7, 139.6, 134.4, 131.9, 130.6, 130.2, 130.0, 121.3, 120.9, 120.0, 116.4, 114.6, 113.6, 55.3, 52.1, 20.7.

HRMS (ESI) m/z calcd for C₂₂H₂₁NO₃, [M + H]⁺: 348.1600; Found: 348.1603.

IR (KBr): 3490, 3029, 2998, 2890, 1716, 1565, 1299, 750 cm⁻¹

Methyl 3'-chloro-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3la**)



The reaction was performed according to *General Procedure* with **1l** (0.1 mmol, 1.0 equiv) and **2a** (0.12

mmol, 1.2 equiv) to give **3la** as yellow solid (24.0 mg, 68% yield, mp: 76-78 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

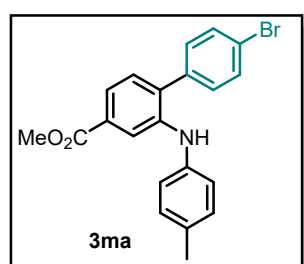
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.91$ (s, 1H), 7.57 (d, $J=7.5$, 1H), 7.45 (s, 1H), 7.36 (s, 3H), 7.24 (s, 1H), 7.11 (d, $J=7.9$, 2H), 6.98 (d, $J=7.9$, 2H), 5.53 (s, 1H), 3.88 (s, 3H), 2.31 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 167.0, 141.5, 140.1, 139.4, 135.0, 133.0, 132.2, 130.7, 130.6, 130.3, 130.1, 129.3, 128.2, 127.3, 121.1, 120.2, 116.6, 52.1, 20.8.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_2$, $[\text{M} + \text{H}]^+$: 352.1104; Found: 352.1107.

IR (KBr): 3502, 3041, 2998, 2890, 1715, 1556, 1276, 751 cm^{-1}

Methyl 4'-bromo-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ma**)



The reaction was performed according to *General Procedure* with **1m** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ma** as yellow solid (23.0 mg, 58% yield, mp: 114-116 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

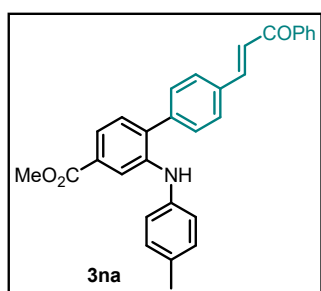
$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.93$ (d, $J=1.7$, 1H), 7.58 (dd, $J=8.2$, 1.9, 3H), 7.37 – 7.30 (m, 2H), 7.23 (d, $J=7.9$, 1H), 7.13 – 7.08 (m, 2H), 6.99 – 6.95 (m, 2H), 5.49 (s, 1H), 3.88 (s, 3H), 2.31 (s, 3H).

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ 167.0, 141.3, 139.5, 137.1, 133.4, 132.3, 132.0, 130.8, 130.6, 130.5, 130.1, 122.3, 121.3, 119.7, 117.0, 52.2, 20.8.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{BrNO}_2$, $[\text{M} + \text{H}]^+$: 396.0599; Found: 396.0597.

IR (KBr): 3464, 3001, 2995, 2990, 1716, 1637, 1299, 763, 751 cm^{-1}

Methyl (*E*)-4'-(3-oxo-3-phenylprop-1-en-1-yl)-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3na**)



The reaction was performed according to *General Procedure* with **1n** (0.1 mmol, 1.0 equiv) and **2a** (0.12

mmol, 1.2 equiv) to give **3na** as yellow solid (26.6 mg, 59% yield, mp: 118-119 °C). $R_f = 0.3$ (petroleum ether/ethyl acetate = 5:1).

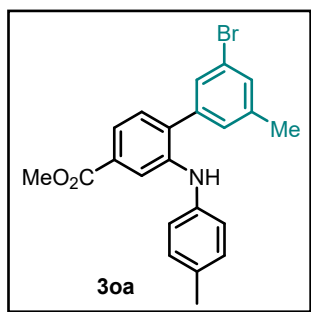
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 8.16$ (d, $J=12.5$, 2H), 8.01 (d, $J=7.7$, 2H), 7.93 – 7.87 (m, 2H), 7.85 – 7.77 (m, 2H), 7.58 (dd, $J=15.2$, 11.3, 2H), 7.48 (t, $J=7.6$, 2H), 7.13 (d, $J=7.9$, 2H), 7.04 (d, $J=7.9$, 2H), 6.19 (s, 1H), 3.91 (s, 3H), 2.33 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 190.3, 167.1, 144.5, 141.2, 140.4, 138.1, 134.7, 133.9, 132.9, 131.8, 130.7, 130.2, 129.1, 128.7, 128.5, 128.4, 124.5, 124.2, 123.5, 122.8, 119.6, 112.4, 52.3, 20.8.

HRMS (ESI) m/z calcd for $C_{30}H_{25}NO_3$, $[M + H]^+$: 448.1913; Found: 448.1911.

IR (KBr): 3501, 2955, 2917, 1725, 1715, 1662, 1656 cm^{-1}

Methyl 3'-bromo-5'-methyl-2-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3oa**)



The reaction was performed according to *General Procedure* with **1o** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3oa** as white solid (26.1 mg, 64% yield, mp: 108-110 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

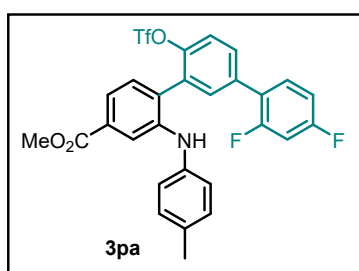
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.90$ (s, 1H), 7.55 (d, $J=7.9$, 1H), 7.38 (d, $J=17.4$, 2H), 7.20 (d, $J=8.1$, 2H), 7.12 (d, $J=7.9$, 2H), 7.00 (d, $J=7.9$, 2H), 5.56 (s, 1H), 3.87 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.0, 141.6, 140.9, 140.1, 139.3, 132.9, 132.2, 131.7, 130.7, 130.5, 130.1, 129.1, 128.5, 122.9, 120.8, 120.4, 116.1, 52.1, 21.2, 20.8.

HRMS (ESI) m/z calcd for $C_{22}H_{20}BrNO_2$, $[M + H]^+$: 410.0756; Found: 410.0753.

IR (KBr): 3295, 3020, 2949, 2919, 1716, 1570, 1517, 1107, 1004, 764 cm^{-1}

Methyl 5'-argio-2-(*p*-tolylamino)-2'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-carboxylate (**3pa**)



The reaction was performed according to **General Procedure** with **1p** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3pa** as white solid (14.8 mg, 51% yield, mp: 84-86 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1).

¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.92$ (s, 1H), 7.61 (d, $J=6.8$, 3H), 7.47 (d, $J=9.2$, 1H), 7.37 (q, $J=8.3$, 1H), 7.28 (d, $J=8.1$, 1H), 7.10 (d, $J=7.9$, 2H), 6.95 (dd, $J=19.3, 9.5$, 4H), 5.37 (s, 1H), 3.88 (s, 3H), 2.31 (s, 3H).

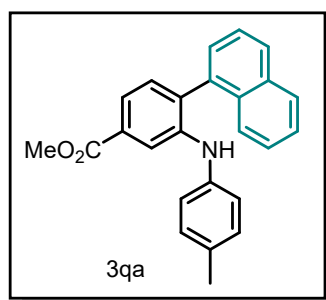
¹³C-NMR (101 MHz, Chloroform-*d*) $\delta = 166.8, 162.9$ (dd, $J=251.1, 12.0$), 159.7 (dd, $J=251.7, 11.8$), 146.6, 142.8, 139.1, 135.9, 132.8 (d, $J=2.9$), 132.4 (d, $J=2.4$), 131.5, 131.5, 131.3 (dd, $J=9.7, 4.4$), 130.5 (d, $J=3.1$), 130.0, 127.4, 123.1 – 122.8 (m), 122.5, 120.8, 120.7, 116.8, 112.0 (dd, $J=21.4, 3.8$), 104.7 (t, $J=25.9$), 52.2, 20.7.

¹⁹F NMR (376 MHz, Chloroform-*d*) $\delta -73.81, -109.16 - -109.39$ (m), -113.10 (q, $J = 9.2$ Hz).

HRMS (ESI) m/z calcd for $C_{28}H_{20}F_5NO_5S$, $[M + H]^+$: 578.1055; Found: 578.1039.

IR (KBr): 3404, 3002, 2998, 2890, 1718, 1546, 1289, 755 cm^{-1}

Methyl 4-(naphthalen-1-yl)-3-(*p*-tolylamino)benzoate (**3qa**)



The reaction was performed according to **General Procedure** with **1q** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3qa** as white oil (13.4 mg, 36% yield). $R_f = 0.4$ (petroleum ether/ethyl acetate = 4:1).

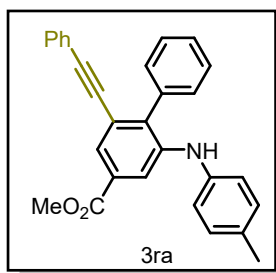
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.98$ (d, $J=1.6$, 1H), 7.92 (d, $J=8.2$, 2H), 7.66 – 7.56 (m, 3H), 7.48 (td, $J=16.1, 15.6, 7.5$, 3H), 7.29 (d, $J=7.8$, 1H), 7.04 (d, $J=7.9$, 2H), 6.90 (d, $J=8.0$, 2H), 5.27 (s, 1H), 3.91 (s, 3H), 2.27 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) $\delta 167.3, 142.8, 139.2, 135.6, 133.9, 132.3, 132.2, 131.6, 131.4, 130.5, 129.9, 128.7, 128.5, 127.6, 126.7, 126.3, 125.9, 125.6, 120.7, 120.3, 115.1, 52.1, 20.8$.

HRMS (ESI) m/z calcd for $C_{25}H_{21}NO_2$, $[M + H]^+$: 368.1651; Found: 368.1651.

IR (KBr): 3585, 3081, 2997, 2890, 1716, 1652, 1275, 761, 749 cm^{-1}

Methyl 2-(phenylethynyl)-6-(*p*-tolylamino)-[1,1'-biphenyl]-4-carboxylate (**3ra**)



The reaction was performed according to **General Procedure** with **1r** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ra** as yellow solid (8.5 mg, 20% yield, mp: 80-81 °C). $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1).

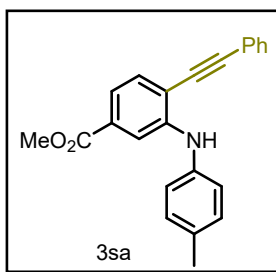
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.86$ (d, $J=1.5$, 1H), 7.80 (d, $J=1.6$, 1H), 7.49 (dd, $J=19.7$, 7.3, 5H), 7.25 – 7.22 (m, 3H), 7.13 – 7.09 (m, 4H), 6.98 (d, $J=8.1$, 2H), 5.46 (s, 1H), 3.90 (s, 3H), 2.31 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 166.6, 142.4, 139.2, 136.3, 135.8, 132.5, 131.4, 130.1, 130.1, 130.0, 128.9, 128.3, 128.2, 124.3, 124.1, 123.1, 120.7, 115.3, 93.1, 88.6, 52.2, 29.7, 20.8.

HRMS (ESI) m/z calcd for $C_{29}H_{23}NO_2$, $[M + H]^+$: 418.1807; Found: 418.1805.

IR (KBr): 3565, 3030, 2918, 1717, 1542, 1275, 761, 730 cm^{-1}

Methyl 4-(phenylethynyl)-3-(*p*-tolylamino)benzoate (**3sa**)



The reaction was performed according to **General Procedure** with **1s** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3sa** as colorless solid (11.7 mg, 34% yield, mp: 90-92 °C). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1)

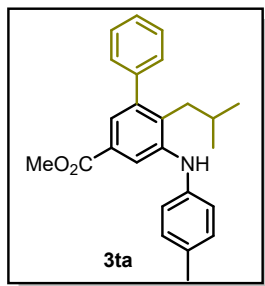
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.80$ (s, 1H), 7.56 – 7.48 (m, 3H), 7.43 (d, $J=8.0$, 1H), 7.40 – 7.34 (m, 3H), 7.16 (q, $J=8.3$, 4H), 6.49 (s, 1H), 3.86 (s, 3H), 2.35 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 166.9, 145.7, 138.2, 133.2, 132.4, 131.6, 130.8, 130.2, 128.9, 128.5, 122.6, 121.6, 119.4, 113.6, 113.3, 97.9, 85.1, 52.2, 20.9.

HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_2$, $[M + H]^+$: 342.1494; Found: 342.1494.

IR (KBr): 3456, 3350, 3020, 2980, 2870, 1636, 1560, 749 cm^{-1}

Methyl 6-isobutyl-5-(*p*-tolylamino)-[1,1'-biphenyl]-3-carboxylate(**3ta**)



The reaction was performed according to *General Procedure* with **1t** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ta** as colorless oil (11.4 mg, 31% yield). $R_f = 0.6$ (petroleum ether/ethyl acetate = 5:1)

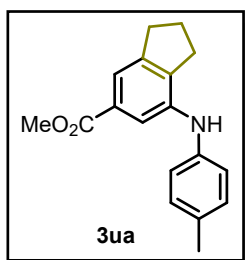
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.85$ (d, $J=1.8$, 1H), 7.49 (d, $J=1.8$, 1H), 7.42 – 7.34 (m, 3H), 7.28 (dd, $J=6.8$, 1.8, 2H), 7.12 (d, $J=8.1$, 2H), 6.96 (d, $J=8.3$, 2H), 5.48 (s, 1H), 3.84 (s, 3H), 2.57 (d, $J=7.2$, 2H), 2.32 (s, 3H), 1.77 (dq, $J=13.5$, 6.8, 1H), 1.58 (s, 1H), 1.51 (s, 1H), 0.70 (s, 3H), 0.68 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.2, 144.3, 142.7, 141.9, 140.9, 134.0, 131.0, 130.1, 129.8, 129.7, 129.5, 129.5, 128.0, 128.0, 127.0, 124.3, 118.8, 118.0, 52.0, 36.8, 28.4, 22.7, 20.7.

HRMS (ESI) m/z calcd for $C_{17}H_{21}NO_2$, $[M + H]^+$: 374.2042; Found: 374.2101

IR (KBr): 3500, 3031, 2986, 2890, 1716, 1646, 1299, 749 cm^{-1}

Methyl 7-(*p*-tolylamino)-2,3-dihydro-1*H*-indene-5-carboxylate(**3ua**)



The reaction was performed according to *General Procedure* with **1u** (0.1 mmol, 1.0 equiv) and **2a** (0.12 mmol, 1.2 equiv) to give **3ua** as yellow oil (10.8 mg, 44% yield). $R_f = 0.5$ (petroleum ether/ethyl acetate = 15:1).

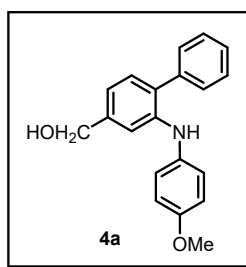
¹H-NMR (400 MHz, Chloroform-*d*) $\delta = 7.65$ (s, 1H), 7.47 (s, 1H), 7.11 (d, $J=8.0$, 2H), 7.01 – 6.95 (m, 2H), 5.39 (s, 1H), 3.85 (s, 3H), 2.97 (t, $J=7.5$, 2H), 2.79 (t, $J=7.4$, 2H), 2.32 (s, 3H), 2.15 (p, $J=7.5$, 2H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.6, 145.9, 140.1, 139.8, 137.0, 131.4, 130.0, 129.6, 119.4, 117.7, 114.0, 51.9, 33.1, 30.2, 24.8, 20.7.

HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_2$, $[M + H]^+$: 282.1494; Found: 282.1498.

IR (KBr): 3371, 3032, 2951, 2923, 1716, 1518, 1276, 813, 765 cm^{-1}

(2-((4-methoxyphenyl)amino)-[1,1'-biphenyl]-4-yl)methanol (**4a**)



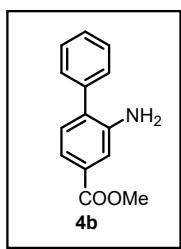
¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.44 (d, *J*=7.5, 4H), 7.35 (t, *J*=6.8, 1H), 7.17 (d, *J*=7.7, 1H), 7.08 (s, 1H), 7.03 (d, *J*=8.3, 2H), 6.85 (dd, *J*=14.1, 8.0, 3H), 5.54 (s, 1H), 4.58 (s, 2H), 3.77 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 155.6, 142.7, 141.4, 139.0, 135.5, 131.0, 129.4, 129.0, 128.8, 127.5, 123.3, 117.9, 114.8, 112.9, 65.4, 55.6.

HRMS (ESI) *m/z* calcd for C₂₀H₁₉NO₂, [M + H]⁺: 306.1489; Found: 306.1489.

IR (KBr): 3521, 3482, 2925, 2832, 1644, 1635, 1508, 1423, 820, 750, 762 cm⁻¹

Methyl 2-amino-[1,1'-biphenyl]-4-carboxylate (**4b**)



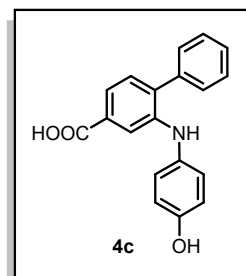
¹H-NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J*=1.7, 1H), 7.46 (d, *J*=3.6, 4H), 7.44 (d, *J*=1.6, 1H), 7.41 – 7.36 (m, 1H), 7.18 (d, *J*=7.8, 1H), 3.91 (s, 3H).

¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.2, 143.6, 138.6, 131.9, 130.5, 130.1, 129.0, 128.8, 127.8, 119.7, 116.4, 52.1.

HRMS (ESI) *m/z* calcd for C₁₄H₁₃NO₂, [M + H]⁺: 228.1019; Found: 228.1014.

IR (KBr): 3504, 3448, 2956, 2923, 1733, 1654, 1541, 767, 707 cm⁻¹

2-((4-hydroxyphenyl)amino)-[1,1'-biphenyl]-4-carboxylic acid (**4c**)



¹H-NMR (400 MHz, Dimethyl sulfoxide-*d*₆) δ 12.70 (s, 1H), 9.04 (s, 1H), 7.83 – 7.12 (m, 8H), 6.98 – 6.52 (m, 5H).

¹³C-NMR (101 MHz, Dimethyl sulfoxide-d₆) δ 167.8, 153.2, 143.7, 139.0, 134.8, 134.2, 131.5, 130.9, 129.2, 128.0, 123.2, 120.6, 116.8, 116.2.

HRMS (ESI) m/z calcd for C₁₉H₁₅NO₃, [M + H]⁺: 306.1125; Found: 306.1123.

IR (KBr): 3708, 3656, 3201, 3041, 2955, 2925, 1716, 1654, 1538, 1510, 1296, 759, 703 cm⁻¹

10. NMR Spectra

