

Supporting Information for

**Aryl Radicals Induced Desulfonylative *ipso*-Substitution of
Diaryliodonium Salts: An Efficient Route to Steric Hindered
Biarylamines**

Huangguan Chen^a, Limin Wang^a, and Jianwei Han^{a*}

^aKey Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center,
Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University
of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China

Email: jianweihan@ecust.edu.cn

Table of Contents

Part 1. General Information	3
Part 2. Synthesis and Characterization of Diaryliodonium Salts	4
Part 3. Optimization of Desulfonylative <i>ipso</i> -Substitution Cascade reaction	23
Part 4. Synthesis and Characterization of Products from Desulfonylative Cascade Reactions.....	24
Part 5. Radical Trapping Experiments, EPR Experiments and Deuteration Experiment.	41
Part 6. Derivatization of Products.....	44
Part 7. References	48
Part 8. ¹ H, ¹³ C, and ¹⁹ F NMR spectra of Products	49

Part 1. General Information

a. Methods:

NMR spectrum: ^1H , ^{13}C , and ^{19}F NMR spectra were recorded in CDCl_3 or DMSO-d_6 (with tetramethylsilane as an internal standard) on a Bruker AVANCE 400 spectrometer at ambient temperature, operating at 400 MHz, 100 MHz, and 376 MHz respectively. Data were reported as follows: Chemical shifts (δ) are reported in ppm, coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Mass spectroscopy: Mass spectra were in general recorded on a Waters LCT Premier XE spectrometer or EI Mass spectra were measured on HP HP5989A, Agilent HP5873 or Waters Micromass GCT mass spectrometer. ESI-MS analyses were performed in positive ionization mode on an Agilent 1100-MSD or Bruker Daltonics FTMS-7 mass spectrometer.

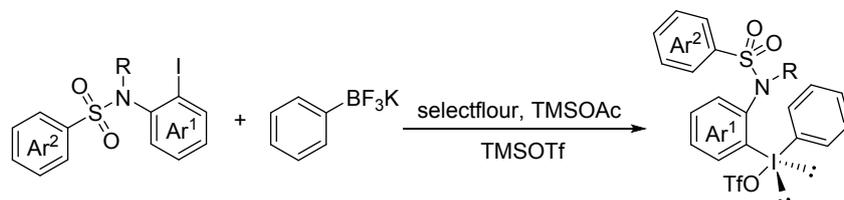
Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

b. Materials:

All solvents were purchased from Adamas-beta and dried and/or distilled by standard methods. All reagents were purchased from commercial sources (Adamas-beta; Sinopharma reagents; TCI; Acros) and used without further purification. Reactions were monitored by TLC (detection with UV light). *ortho*-iodo sulfonamides were synthesized following the literature procedures.¹⁻³ The preparation of all other materials is described in detail below.

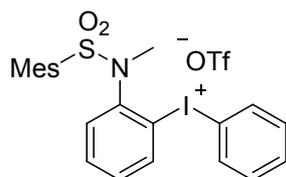
Part 2. Synthesis and Characterization of Diaryliodonium Salts

General Procedure:



Following the modified procedure of literature.⁴ Under an atmosphere of dry nitrogen, *ortho*-iodo sulfonamides (4.5 mmol), Selectfluor™ (2.07 g, 1.3 equiv.) and 15 mL of dry CH₃CN were introduced to an oven-dried Schlenk flask. TMSOAc (1.8 mL, 2.6 equiv.) was added by syringe dropwise with stirring. The mixture was stirred at 50 °C for 24 h. The reaction mixture was cooled to room temperature and solid potassium tetrakis(pentafluorophenyl)borate (1.0 equiv.) was added directly to the flask against a flow of nitrogen. Once the added solid was dissolved, TMSOTf (1.0 equiv.) was added dropwise by syringe and the mixture was allowed to stir at room temperature for 12 hours. The solvents were removed under reduced pressure and 100 mL of acetate buffer (NaOAc: HOAc = 0.5 M: 0.5 M, pH = 5) was added. The mixture was extracted with CH₂Cl₂ for 3 times. The combined organic extracts were dried with Na₂SO₄, filtered, and the solvent was removed by rotary evaporation. The residue was dissolved in CH₂Cl₂ and a solution of potassium trifluoromethanesulfonate (4.0 equiv.) in H₂O was added with stirring for 0.5 hour. The mixture was transferred to a separatory funnel and extracted with CH₂Cl₂. The combined organic extracts were dried with Na₂SO₄, filtered, and the solvent was removed by rotary evaporation. The residue was either triturated with diethyl ether or subjected to column chromatography directly on silica gel to afford pure diaryliodonium salts. The details for the specific scale, purification process of reactions, and characterization data of individual compounds are listed as following.

Phenyl(2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1a)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.31 g, 80 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 167-169 °C.

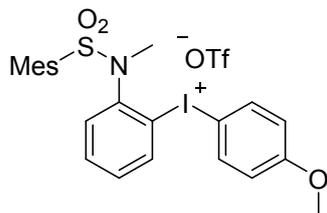
¹H NMR (400 MHz, DMSO) δ 8.24 (d, *J* = 7.5 Hz, 2H), 8.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.52 (td, *J* = 7.7, 1.6 Hz, 1H), 7.10 (s, 2H), 7.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 3.04 (s, 3H), 2.29 (s, 3H), 2.18 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 143.46, 141.27, 139.73, 136.66, 135.81, 133.45, 132.52, 132.37, 131.82, 131.73, 129.77, 129.10, 121.26, 120.69 (q, *J*_{C-F} = 323.7 Hz), 116.15, 39.10, 23.25, 20.46.

¹⁹F NMR (376 MHz, DMSO) δ -77.73.

HRMS *m/z* (ESI-TOF): calculated for C₂₂H₂₃NO₂SI⁺ [M-OTf]⁺ 492.0494, found 492.0494.

(4-Methoxyphenyl)(2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1b)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.33 g, 77 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 172-173 °C.

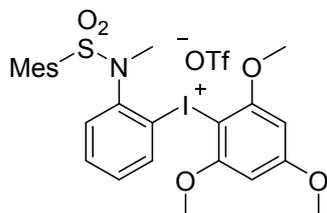
^1H NMR (400 MHz, DMSO) δ 8.19 (d, $J = 9.0$ Hz, 2H), 8.15 – 8.00 (m, 1H), 7.66 – 7.36 (m, 2H), 7.14 (d, $J = 9.0$ Hz, 2H), 7.11 (s, 2H), 7.09 – 7.04 (m, 1H), 3.83 (s, 3H), 3.11 (s, 3H), 2.29 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 162.29, 143.54, 141.03, 139.79, 138.06, 136.08, 133.26, 132.59, 131.75, 129.72, 128.98, 121.52, 120.71 (q, $J_{\text{C-F}} = 323.5$ Hz), 117.61, 104.72, 55.82, 39.31, 23.34, 20.52.

^{19}F NMR (376 MHz, DMSO) δ -77.77.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_3\text{SI}^+ [\text{M-OTf}]^+$ 522.0600, found 522.0608.

(2-((N,2,4,6-Tetramethylphenyl)sulfonamido)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate (1c)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.63 g, 80 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 180-182 °C.

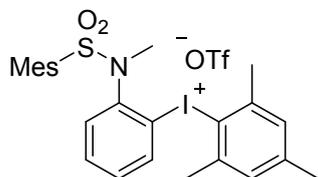
^1H NMR (400 MHz, DMSO) δ 7.83 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.53 (td, $J = 7.7, 1.4$ Hz, 1H), 7.45 (td, $J = 7.8, 1.4$ Hz, 1H), 7.10 (m, 3H), 6.51 (s, 2H), 3.93 (s, 6H), 3.89 (s, 3H), 3.17 (s, 3H), 2.29 (s, 3H), 2.18 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 166.70, 159.40, 143.57, 140.68, 139.77, 135.31, 133.07, 132.53, 131.86, 129.68, 128.76, 120.71 (q, $J_{\text{C-F}} = 323.5$ Hz), 120.67, 92.21, 86.23, 57.40, 56.30, 39.04, 23.20, 20.49.

^{19}F NMR (376 MHz, DMSO) δ -77.76.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{25}\text{H}_{29}\text{NO}_5\text{SI}^+ [\text{M-OTf}]^+$ 582.0811, found 582.0809.

Mesityl(2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1d)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.84 g, 60 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 182-184 °C.

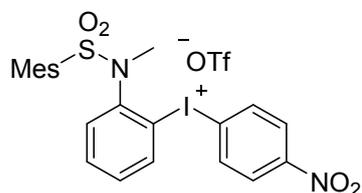
^1H NMR (400 MHz, DMSO) δ 7.75 (d, $J = 7.9$ Hz, 1H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.28 (s, 2H), 7.10 (m, 3H), 3.03 (s, 3H), 2.54 (s, 6H), 2.33 (s, 3H), 2.29 (s, 3H), 2.15 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.77, 143.67, 141.94, 140.94, 139.99, 135.13, 133.19, 132.61, 132.07, 130.08, 129.19, 129.02, 121.97, 120.69 (q, $J_{\text{C-F}} = 323.5$ Hz), 118.71, 38.90, 26.14, 23.25, 20.55, 20.50.

^{19}F NMR (376 MHz, DMSO) δ -77.76.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{25}\text{H}_{29}\text{NO}_2\text{Si}^+$ [M-OTf] $^+$ 534.0964, found 534.0968.

(4-Nitrophenyl)(2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1e)



Prepared according to the **general procedure** on 4.5 mmol scale and a light yellow powder (1.67 g, 54 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 187-189 °C.

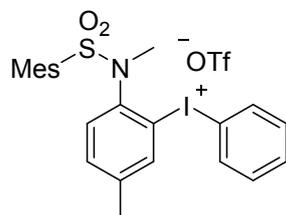
^1H NMR (400 MHz, DMSO) δ 8.45 – 8.29 (m, 5H), 7.68 – 7.51 (m, 2H), 7.13 – 7.04 (m, 3H), 2.93 (s, 3H), 2.28 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 149.39, 143.45, 141.68, 139.75, 137.68, 136.78, 133.89, 132.57, 131.79, 129.81, 129.26, 126.14, 122.77, 122.46, 120.70 (q, $J_{\text{C-F}} = 323.5$ Hz), 39.10, 23.38, 20.49.

^{19}F NMR (376 MHz, DMSO) δ -77.77.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Si}^+$ [M-OTf] $^+$ 537.0345, found 537.0337.

(5-Methyl-2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ab)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.15 g, 73 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 171-173 °C.

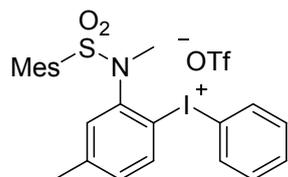
^1H NMR (400 MHz, DMSO) δ 8.21 (d, $J = 7.5$ Hz, 2H), 8.06 (d, $J = 1.2$ Hz, 1H), 7.71 (t, $J = 7.4$ Hz, 1H), 7.58 (dd, $J = 10.7, 4.8$ Hz, 2H), 7.40 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.10 (s, 2H), 6.94 (d, $J = 8.1$ Hz, 1H), 2.97 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 2.19 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.35, 142.06, 139.69, 138.79, 136.89, 135.73, 134.00, 132.50, 132.28, 131.79, 129.99, 128.59, 121.04, 120.68 (q, $J_{\text{C-F}} = 323.7$ Hz), 116.06, 39.17, 23.34, 20.48, 20.33.

^{19}F NMR (376 MHz, DMSO) δ -77.76.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{Si}^+$ [M-OTf] $^+$ 506.0651, found 506.0636.

(4-Methyl-2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ac)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.09 g, 71 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 169-171 °C.

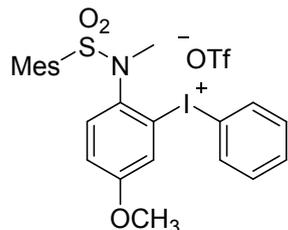
^1H NMR (400 MHz, DMSO) δ 8.19 (d, $J = 8.0$ Hz, 2H), 8.08 (d, $J = 8.3$ Hz, 1H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.57 (dd, $J = 10.8, 4.7$ Hz, 2H), 7.34 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.11 (s, 2H), 6.80 (d, $J = 1.4$ Hz, 1H), 2.97 (s, 3H), 2.30 (s, 3H), 2.18 (s, 6H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 144.23, 143.44, 141.25, 139.79, 136.54, 135.64, 132.42, 132.23, 131.75, 129.72, 129.69, 120.69 (q, $J_{\text{C-F}} = 323.6$ Hz), 117.58, 116.25, 39.20, 23.25, 20.47, 20.43.

^{19}F NMR (376 MHz, DMSO) δ -77.75.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{Si}^+$ [M-OTf] $^+$ 506.0651, found 506.0659.

(5-Methoxy-2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ad)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.48 g, 82 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 182-183 °C.

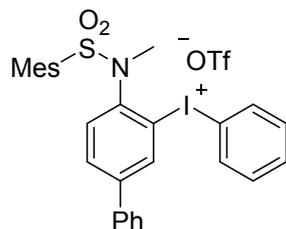
^1H NMR (400 MHz, DMSO) δ 8.24 (d, $J = 8.3$ Hz, 2H), 7.79 (d, $J = 2.8$ Hz, 1H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.58 (dd, $J = 10.8, 4.7$ Hz, 2H), 7.14 (dd, $J = 8.9, 2.8$ Hz, 1H), 7.09 (s, 2H), 6.97 (d, $J = 8.9$ Hz, 1H), 3.78 (s, 3H), 2.96 (s, 3H), 2.28 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 160.07, 143.30, 139.67, 135.75, 133.69, 132.50, 132.35, 131.80, 130.11, 129.48, 122.21, 121.65, 120.70 (q, $J_{\text{C-F}} = 323.6$ Hz), 118.32, 116.22, 56.35, 39.31, 23.34, 20.49.

^{19}F NMR (376 MHz, DMSO) δ -77.75.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_3\text{Si}^+$ [M-OTf] $^+$ 522.0600, found 522.0593.

Phenyl(4-((*N*,2,4,6-tetramethylphenyl)sulfonamido)-[1,1'-biphenyl]-3-yl)iodonium trifluoromethanesulfonate (1ae)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.77 g, 55 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 128-130 °C.

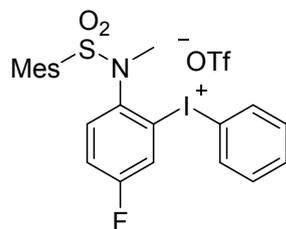
¹H NMR (400 MHz, DMSO) δ 8.58 (d, *J* = 2.1 Hz, 1H), 8.28 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.91 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.76 – 7.65 (m, 3H), 7.58 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.49 – 7.42 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.11 (s, 2H), 2.99 (s, 3H), 2.29 (s, 3H), 2.23 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 143.47, 142.83, 140.43, 139.78, 136.73, 135.77, 134.75, 132.59, 132.30, 131.80, 131.22, 129.92, 129.33, 129.16, 129.00, 126.95, 122.33, 120.72 (q, *J*_{C-F} = 326.0 Hz), 116.56, 39.05, 23.37, 20.53.

¹⁹F NMR (376 MHz, DMSO) δ -77.74.

HRMS *m/z* (ESI-TOF): calculated for C₂₈H₂₇NO₂SI⁺ [M-OTf]⁺ 568.0807, found 568.0803.

(5-Fluoro-2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1af)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.01 g, 68 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 190-192 °C.

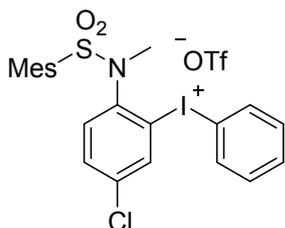
¹H NMR (400 MHz, DMSO) δ 8.29 – 8.16 (m, 3H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.59 (dd, *J* = 10.8, 4.7 Hz, 2H), 7.56 – 7.46 (m, 1H), 7.14 (dd, *J* = 9.0, 5.1 Hz, 1H), 7.11 (s, 2H), 2.95 (s, 3H), 2.29 (s, 3H), 2.20 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 161.22 (d, *J*_{C-F} = 255.4 Hz), 143.52, 139.73, 138.08 (d, *J*_{C-F} = 3.4 Hz), 135.79, 132.60, 132.45, 131.88, 130.42 (d, *J*_{C-F} = 9.1 Hz), 129.72, 124.00 (d, *J*_{C-F} = 26.1 Hz), 122.10 (d, *J*_{C-F} = 8.1 Hz), 120.70 (q, *J*_{C-F} = 323.6 Hz), 120.52 (d, *J*_{C-F} = 22.5 Hz), 116.68, 39.18, 23.33, 20.51.

¹⁹F NMR (376 MHz, DMSO) δ -77.76, -107.88.

HRMS *m/z* (ESI-TOF): calculated for C₂₂H₂₂NO₂FSI⁺ [M-OTf]⁺ 510.0400, found 510.0391.

(5-Chloro-2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ag)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.04 g, 67 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 206-207 °C.

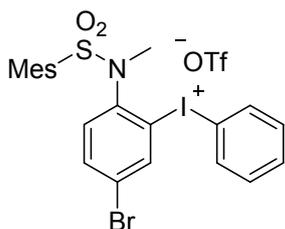
^1H NMR (400 MHz, DMSO) δ 8.39 (d, J = 2.4 Hz, 1H), 8.25 (d, J = 7.5 Hz, 2H), 7.71 (dt, J = 8.5, 4.9 Hz, 2H), 7.60 (t, J = 7.8 Hz, 2H), 7.11 (s, 2H), 7.10 (d, J = 8.7 Hz, 1H), 2.92 (s, 3H), 2.29 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.56, 140.55, 139.71, 136.24, 135.79, 134.84, 133.38, 132.61, 132.43, 131.85, 130.11, 129.65, 122.58, 120.69 (q, $J_{\text{C-F}}$ = 323.5 Hz), 116.75, 38.97, 23.35, 20.50.

^{19}F NMR (376 MHz, DMSO) δ -77.75.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{SClI}^+ [\text{M-OTf}]^+$ 526.0105, found 526.0103.

(5-Bromo-2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ah)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.20 g, 68 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 208-209 °C.

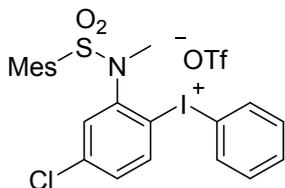
^1H NMR (400 MHz, DMSO) δ 8.49 (d, J = 2.2 Hz, 1H), 8.25 (d, J = 7.5 Hz, 2H), 7.81 (dd, J = 8.5, 2.2 Hz, 1H), 7.72 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.8 Hz, 2H), 7.12 (s, 2H), 7.02 (d, J = 8.6 Hz, 1H), 2.92 (s, 3H), 2.29 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.56, 140.90, 139.71, 138.92, 136.31, 135.79, 132.62, 132.42, 131.84, 130.47, 129.65, 123.22, 122.93, 120.69 (q, $J_{\text{C-F}}$ = 323.7 Hz), 116.76, 38.90, 23.35, 20.50.

^{19}F NMR (376 MHz, DMSO) δ -77.74.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{SBrI}^+ [\text{M-OTf}]^+$ 569.9599, found 569.9592.

(4-Chloro-2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ai)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.07 g, 68 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 197-198 °C.

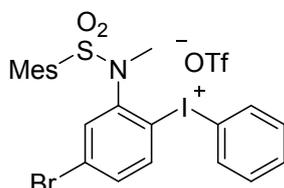
¹H NMR (400 MHz, DMSO) δ 8.23 (dd, *J* = 4.9, 3.9 Hz, 3H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.67 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.14 (s, 2H), 2.97 (s, 3H), 2.30 (s, 3H), 2.20 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 143.69, 142.83, 139.85, 138.05, 137.98, 135.77, 132.58, 132.42, 131.87, 131.55, 129.40, 129.37, 120.70 (q, *J*_{C-F} = 323.5 Hz), 119.80, 116.52, 38.90, 23.26, 20.50.

¹⁹F NMR (376 MHz, DMSO) δ -77.75.

HRMS *m/z* (ESI-TOF): calculated for C₂₂H₂₂NO₂SClI⁺ [M-OTf]⁺ 526.0105, found 526.0103.

(4-Bromo-2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1aj)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.17 g, 67 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 206-208 °C.

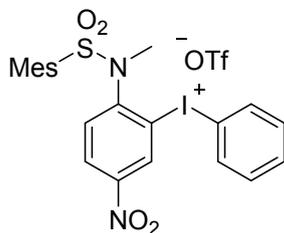
¹H NMR (400 MHz, DMSO) δ 8.26 – 8.17 (m, 2H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.78 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.14 (s, 2H), 2.97 (s, 3H), 2.30 (s, 3H), 2.20 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 143.67, 142.72, 139.85, 138.10, 135.78, 134.45, 132.57, 132.41, 132.20, 131.86, 129.34, 126.48, 120.70 (q, *J*_{C-F} = 323.4 Hz), 120.51, 116.49, 38.96, 23.26, 20.51.

¹⁹F NMR (376 MHz, DMSO) δ -77.74.

HRMS *m/z* (ESI-TOF): calculated for C₂₂H₂₂NO₂SBrI⁺ [M-OTf]⁺ 569.9599, found 569.9587.

(5-Nitro-2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ak)



Prepared according to the **general procedure** on 4.5 mmol scale and a light yellow powder (1.64 g, 53 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 206-208 °C.

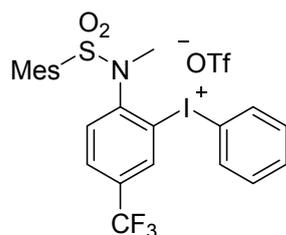
¹H NMR (400 MHz, DMSO) δ 9.08 (d, *J* = 2.5 Hz, 1H), 8.40 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.14 (s, 2H), 2.89 (s, 3H), 2.30 (s, 3H), 2.22 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 147.27, 147.20, 143.86, 139.82, 135.81, 132.76, 132.48, 132.08, 131.88, 129.57, 129.38, 128.17, 122.36, 120.69 (q, $J_{\text{C-F}} = 323.5$ Hz), 117.15, 38.63, 23.45, 20.53.

^{19}F NMR (376 MHz, DMSO) δ -77.76.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{SI}^+$ [M-OTf] $^+$ 537.0345, found 537.0331.

Phenyl(2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)-5-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (1a1)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.04 g, 64 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 191-193 °C.

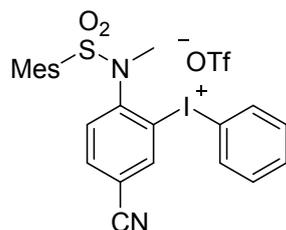
^1H NMR (400 MHz, DMSO) δ 8.70 (d, $J = 1.5$ Hz, 1H), 8.26 (d, $J = 8.2$ Hz, 2H), 8.03 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.14 (s, 2H), 2.91 (s, 3H), 2.30 (s, 3H), 2.20 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 145.53, 143.77, 139.76, 135.81, 134.20 (q, $J_{\text{C-F}} = 3.7$ Hz), 132.73, 132.51, 131.89, 130.57, 129.82, 129.45, 122.58 (q, $J_{\text{C-F}} = 274.4$ Hz), 122.32, 120.70 (q, $J_{\text{C-F}} = 323.7$ Hz), 116.72, 38.69, 23.33, 20.51.

^{19}F NMR (376 MHz, DMSO) δ -61.14, -77.78.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{22}\text{NO}_2\text{SF}_3\text{I}^+$ [M-OTf] $^+$ 560.0368, found 560.0367.

(5-Cyano-2-((*N*,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1am)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.89 g, 63 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 208-209 °C.

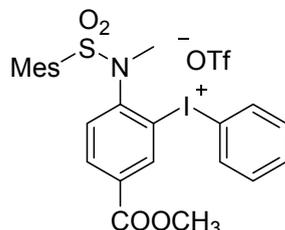
^1H NMR (400 MHz, DMSO) δ 8.83 (d, $J = 1.8$ Hz, 1H), 8.23 (d, $J = 7.5$ Hz, 2H), 8.12 (dd, $J = 8.3, 1.9$ Hz, 1H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.59 (dd, $J = 10.8, 4.8$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.12 (s, 2H), 2.91 (s, 3H), 2.29 (s, 3H), 2.19 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 145.87, 143.79, 140.79, 139.79, 137.30, 135.80, 132.72, 132.48, 131.90, 129.67, 129.42, 122.36, 120.70 (q, $J_{\text{C-F}} = 323.6$ Hz), 116.92, 116.41, 113.44, 38.62, 23.38, 20.53.

^{19}F NMR (376 MHz, DMSO) δ -77.76.

HRMS m/z (ESI-TOF): calculated for $C_{23}H_{22}N_2O_2Si^+$ [M-OTf]⁺ 517.0447, found 517.0442.

(5-(Methoxycarbonyl)-2-((N,2,4,6-tetramethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1an)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.17 g, 69 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 194-196 °C.

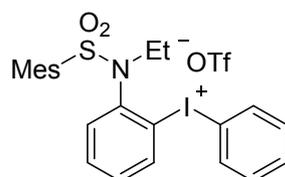
¹H NMR (400 MHz, DMSO) δ 8.74 (d, *J* = 1.9 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 2H), 8.08 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.12 (s, 2H), 3.88 (s, 3H), 2.91 (s, 3H), 2.29 (s, 3H), 2.19 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 163.91, 145.60, 143.74, 139.78, 137.51, 135.87, 133.76, 132.69, 132.46, 131.88, 131.67, 129.42, 129.15, 121.83, 120.70 (q, *J*_{C-F} = 323.5 Hz), 116.51, 52.99, 38.71, 23.40, 20.53.

¹⁹F NMR (376 MHz, DMSO) δ -77.77.

HRMS m/z (ESI-TOF): calculated for $C_{24}H_{25}NO_4Si^+$ [M-OTf]⁺ 550.0549, found 550.0544.

(2-((N-Ethyl-2,4,6-trimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ba)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.77 g, 60 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 168-170 °C.

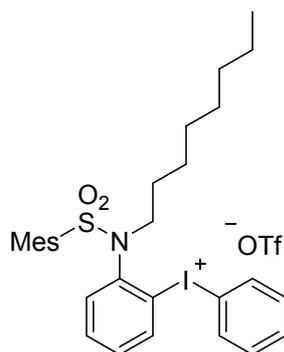
¹H NMR (400 MHz, DMSO) δ 8.26 (d, *J* = 7.5 Hz, 2H), 8.06 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.53 (td, *J* = 7.8, 1.5 Hz, 1H), 7.19 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.08 (s, 2H), 4.06 (m, 1H), 3.59 (m, 1H), 2.28 (s, 3H), 2.16 (s, 6H), 0.92 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, DMSO) δ 143.57, 139.60, 138.09, 135.95, 135.84, 133.33, 132.80, 132.53, 132.23, 132.07, 130.29, 130.18, 122.42, 120.69 (q, *J*_{C-F} = 323.6 Hz), 116.15, 45.91, 23.10, 20.46, 12.98.

¹⁹F NMR (376 MHz, DMSO) δ -77.74.

HRMS m/z (ESI-TOF): calculated for $C_{23}H_{25}NO_2Si^+$ [M-OTf]⁺ 506.0651, found 506.0642.

Phenyl(2-((2,4,6-trimethyl-N-octylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1ca)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.83 g, 55 %) was obtained through the procedure of column chromatography.

M. p.: 45-47 °C.

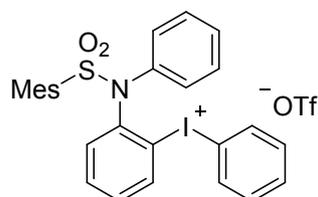
^1H NMR (400 MHz, CDCl_3) δ 8.04 – 7.91 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.57 (dd, J = 8.2, 1.2 Hz, 1H), 7.51 (m, 3H), 7.42 – 7.35 (m, 1H), 7.06 (dd, J = 8.0, 1.4 Hz, 1H), 6.95 (s, 2H), 4.14 (ddd, J = 12.6, 9.8, 6.3 Hz, 1H), 3.45 – 3.29 (m, 1H), 2.31 (s, 3H), 2.18 (s, 6H), 1.39 – 1.31 (m, 2H), 1.30 – 1.17 (m, 10H), 0.84 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.50, 140.45, 139.23, 136.25, 134.51, 133.41, 133.22, 133.03, 132.61, 132.49, 130.30, 130.04, 121.64, 120.48 (q, $J_{\text{C-F}}$ = 321.4 Hz), 114.61, 51.91, 31.79, 29.20, 28.54, 26.93, 23.73, 22.67, 21.12, 14.16.

^{19}F NMR (376 MHz, CDCl_3) δ -78.24.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{29}\text{H}_{37}\text{NO}_2\text{SI}^+$ [M-OTf] $^+$ 590.1590, found 590.1591.

Phenyl(2-((2,4,6-trimethyl-*N*-phenylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1da)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.80 g, 57 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 161-163 °C.

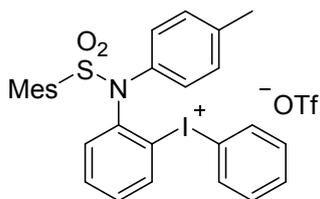
^1H NMR (400 MHz, DMSO) δ 8.47 (dd, J = 8.0, 1.2 Hz, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.71 (td, J = 7.7, 1.2 Hz, 1H), 7.57 (dt, J = 9.2, 4.3 Hz, 3H), 7.47 – 7.31 (m, 7H), 7.09 (s, 2H), 2.30 (s, 3H), 2.01 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.89, 140.17, 139.99, 139.40, 138.50, 134.75, 133.87, 132.42, 132.28, 132.12, 132.09, 131.91, 131.63, 129.53, 128.58, 128.21, 120.86, 120.71 (q, $J_{\text{C-F}}$ = 323.4 Hz), 116.18, 22.87, 20.55.

^{19}F NMR (376 MHz, DMSO) δ -77.74.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{SI}^+$ [M-OTf] $^+$ 554.0651, found 554.0642.

Phenyl(2-((2,4,6-trimethyl-*N*-(*p*-tolyl)phenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1ea)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.00 g, 62 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 138-140 °C.

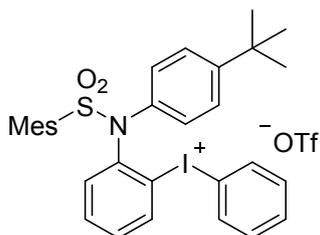
^1H NMR (400 MHz, DMSO) δ 8.43 (dd, J = 8.3, 1.3 Hz, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.75 – 7.65 (m, 1H), 7.65 – 7.52 (m, 3H), 7.41 (t, J = 7.9 Hz, 2H), 7.17 (m, 4H), 7.09 (s, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 2.03 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.83, 140.48, 139.99, 138.48, 137.95, 136.86, 134.63, 133.82, 132.38, 132.19, 132.06, 131.92, 131.67, 131.57, 129.95, 128.52, 120.72, 120.70 (q, $J_{\text{C-F}}$ = 323.7 Hz), 116.23, 22.93, 20.55, 20.51.

^{19}F NMR (376 MHz, DMSO) δ -77.74.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{SI}^+$ [M-OTf] $^+$ 568.0807, found 568.0813.

(2-((N-(4-(tert-Butyl)phenyl)-2,4,6-trimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1fa)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.88 g, 55 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 165-167 °C.

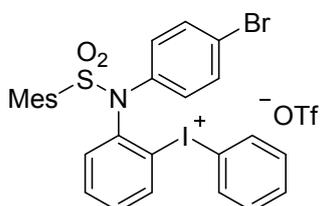
^1H NMR (400 MHz, DMSO) δ 8.45 (dd, J = 8.0, 1.3 Hz, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.72 (td, J = 7.7, 1.3 Hz, 1H), 7.64 – 7.49 (m, 3H), 7.39 (dd, J = 12.4, 5.4 Hz, 4H), 7.28 (d, J = 8.7 Hz, 2H), 7.08 (s, 2H), 2.30 (s, 3H), 2.01 (s, 6H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, DMSO) δ 150.94, 143.80, 140.34, 139.97, 138.45, 136.74, 134.66, 133.86, 132.37, 132.18, 132.09, 131.75, 131.60, 128.21, 126.23, 120.76, 120.70 (q, $J_{\text{C-F}}$ = 323.6 Hz), 116.11, 34.37, 30.97, 22.80, 20.54.

^{19}F NMR (376 MHz, DMSO) δ -77.72.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{31}\text{H}_{33}\text{NO}_2\text{SI}^+$ [M-OTf] $^+$ 610.1277, found 610.1254.

(2-((N-(4-Bromophenyl)-2,4,6-trimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ga)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.04 g, 58 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 178-180 °C.

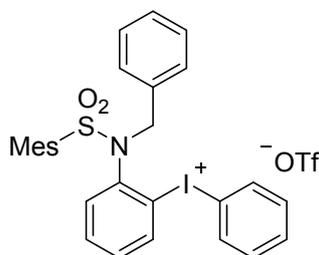
^1H NMR (400 MHz, DMSO) δ 8.54 (dd, J = 8.0, 1.3 Hz, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.72 (td, J = 7.7, 1.4 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.52 (t, J = 5.9 Hz, 2H), 7.46 (dd, J = 7.9, 1.4 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.26 (t, J = 5.9 Hz, 2H), 7.09 (s, 2H), 2.30 (s, 3H), 2.02 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 144.06, 139.99, 139.62, 139.10, 138.83, 134.49, 133.99, 132.48, 132.33, 132.03, 131.95, 131.81, 131.48, 130.13, 120.97, 120.78, 120.70 (q, $J_{\text{C-F}}$ = 323.7 Hz), 116.00, 22.86, 20.57.

^{19}F NMR (376 MHz, DMSO) δ -77.74.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{SBrI}^+$ [M-OTf] $^+$ 631.9756, found 631.9762.

(2-((*N*-Benzyl-2,4,6-trimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ha)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.97 g, 61 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 203-205 °C.

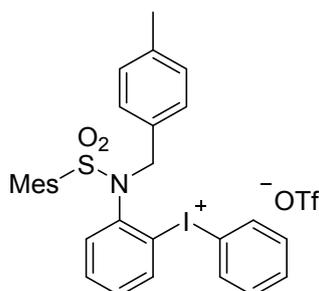
^1H NMR (400 MHz, DMSO) δ 7.74 – 7.64 (m, 2H), 7.57 – 7.49 (m, 4H), 7.50 – 7.45 (m, 2H), 7.43 – 7.35 (m, 4H), 7.35 – 7.29 (m, 2H), 7.12 (s, 2H), 5.44 (d, J = 13.0 Hz, 1H), 4.77 (d, J = 13.0 Hz, 1H), 2.30 (s, 3H), 2.20 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.87, 139.72, 137.55, 135.46, 134.86, 134.51, 132.95, 132.77, 132.64, 132.22, 131.95, 130.64, 130.15, 128.87, 128.57, 122.60, 120.70 (q, $J_{\text{C-F}}$ = 323.5 Hz), 116.37, 54.70, 23.08, 20.48.

^{19}F NMR (376 MHz, DMSO) δ -77.73.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{SI}^+$ [M-OTf] $^+$ 568.0807, found 568.0800.

Phenyl(2-((2,4,6-trimethyl-*N*-(4-methylbenzyl)phenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1ia)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.84 g, 56 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 195-196 °C.

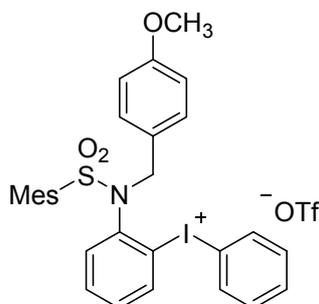
^1H NMR (400 MHz, DMSO) δ 7.71 (ddd, J = 14.3, 8.9, 6.0 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.52 – 7.44 (m, 5H), 7.44 – 7.35 (m, 1H), 7.23 – 7.15 (m, 4H), 7.12 (s, 2H), 5.41 (d, J = 13.0 Hz, 1H), 4.72 (d, J = 12.9 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 2.19 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 143.85, 139.69, 138.10, 137.56, 135.43, 134.90, 133.05, 132.89, 132.64, 132.29, 131.99, 131.43, 130.71, 130.22, 130.19, 129.38, 122.41, 120.70 (q, $J_{\text{C-F}}$ = 323.7 Hz), 116.19, 54.54, 23.09, 20.71, 20.51.

^{19}F NMR (376 MHz, DMSO) δ -77.75.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{29}\text{H}_{29}\text{NO}_2\text{SI}^+$ [M-OTf] $^+$ 582.0964, found 582.0958.

(2-((*N*-4-Methoxybenzyl)-2,4,6-trimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1ja)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.02 g, 60 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 175-177 °C.

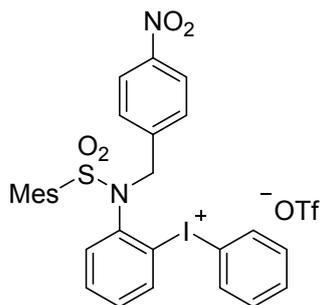
^1H NMR (400 MHz, DMSO) δ 7.72 (t, J = 7.4 Hz, 2H), 7.57 (m, 3H), 7.52 – 7.37 (m, 4H), 7.22 (d, J = 8.5 Hz, 2H), 7.12 (s, 2H), 6.91 (d, J = 8.5 Hz, 2H), 5.38 (d, J = 12.9 Hz, 1H), 4.71 (d, J = 13.0 Hz, 1H), 3.72 (s, 3H), 2.30 (s, 3H), 2.18 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 159.40, 143.85, 139.70, 137.59, 135.50, 134.95, 133.04, 132.94, 132.66, 132.28, 131.94, 131.57, 130.79, 130.24, 126.35, 122.61, 120.71 (q, $J_{\text{C-F}}$ = 323.5 Hz), 116.29, 114.16, 55.25, 54.24, 23.12, 20.53.

^{19}F NMR (376 MHz, DMSO) δ -77.77.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{29}\text{H}_{29}\text{NO}_3\text{SI}^+$ [M-OTf] $^+$ 598.0913, found 598.0926.

Phenyl(2-((2,4,6-trimethyl-*N*-(4-nitrobenzyl)phenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1ka)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.30 g, 67 %) was obtained through the procedure of column chromatography.

M. p.: 216-218 °C.

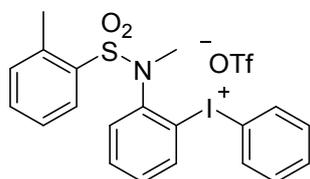
¹H NMR (400 MHz, DMSO) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.89 – 7.82 (m, 1H), 7.77 – 7.67 (m, 3H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.39 (m, 4H), 7.13 (s, 2H), 5.49 (d, *J* = 13.4 Hz, 1H), 4.96 (d, *J* = 13.4 Hz, 1H), 2.30 (s, 3H), 2.19 (s, 6H).

¹³C NMR (101 MHz, DMSO) δ 147.40, 144.14, 142.07, 139.91, 137.56, 135.48, 135.16, 133.22, 132.91, 132.75, 132.39, 131.99, 131.28, 130.47, 129.61, 123.91, 121.49, 120.70 (q, *J*_{C-F} = 323.6 Hz), 116.08, 53.46, 23.12, 20.52.

¹⁹F NMR (376 MHz, DMSO) δ -77.75.

HRMS *m/z* (ESI-TOF): calculated for C₂₈H₂₆N₂O₄SI⁺ [M-OTf]⁺ 613.0658, found 613.0655.

(2-((*N*,2-Dimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1f)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.74 g, 63 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 151-152 °C.

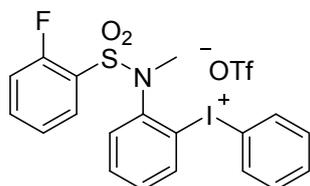
¹H NMR (400 MHz, DMSO) δ 8.33 – 8.17 (m, 3H), 7.72 (t, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.58 (m, 3H), 7.51 (m, 3H), 6.92 (dd, *J* = 7.7, 1.7 Hz, 1H), 2.93 (s, 3H), 2.12 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 141.30, 137.93, 137.05, 135.79, 134.18, 133.55, 133.37, 133.16, 132.29, 131.78, 131.70, 130.48, 128.35, 126.97, 121.80, 120.69 (q, *J*_{C-F} = 323.7 Hz), 116.30, 39.10, 20.70.

¹⁹F NMR (376 MHz, DMSO) δ -77.73.

HRMS *m/z* (ESI-TOF): calculated for C₂₀H₁₉NO₂SI⁺ [M-OTf]⁺ 464.0181, found 464.0168.

(2-((2-Fluoro-*N*-methylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1g)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.17 g, 78 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 126-127 °C.

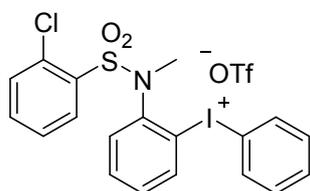
¹H NMR (400 MHz, DMSO) δ 8.37 (d, *J* = 7.9 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 2H), 7.87 (ddd, *J* = 8.2, 6.1, 1.6 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.66 – 7.49 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 2.96 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 158.35 (d, *J*_{C-F} = 256.9 Hz), 141.23, 137.56, 137.31 (d, *J*_{C-F} = 8.6 Hz), 135.78, 133.88, 132.28, 131.88, 131.78, 131.56, 128.43, 125.46 (d, *J*_{C-F} = 3.2 Hz), 122.88 (d, *J*_{C-F} = 14.0 Hz), 121.88, 120.71 (q, *J*_{C-F} = 323.6 Hz), 118.16 (d, *J*_{C-F} = 21.9 Hz), 116.24, 38.89.

¹⁹F NMR (376 MHz, DMSO) δ -77.74, -106.61.

HRMS *m/z* (ESI-TOF): calculated for C₁₉H₁₆NO₂FSI⁺ [M-OTf]⁺ 467.9931, found 467.9939.

(2-((2-Chloro-*N*-methylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1h)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.00 g, 70 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 143-145 °C.

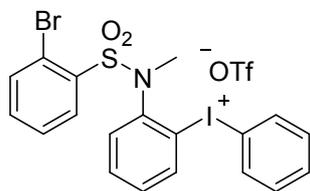
¹H NMR (400 MHz, DMSO) δ 8.33 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 2H), 7.82 – 7.74 (m, 3H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.64 – 7.56 (m, 4H), 7.53 (td, *J* = 7.8, 1.4 Hz, 1H), 7.12 (dd, *J* = 7.8, 1.3 Hz, 1H), 3.05 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 141.11, 137.42, 135.75, 133.81, 133.27, 132.92, 132.71, 132.32, 131.90, 131.81, 131.43, 129.16, 128.19, 121.48, 120.71 (q, *J*_{C-F} = 323.6 Hz), 116.28, 39.41.

¹⁹F NMR (376 MHz, DMSO) δ -77.74.

HRMS *m/z* (ESI-TOF): calculated for C₁₉H₁₆NO₂ClSI⁺ [M-OTf]⁺ 483.9635, found 483.9638.

(2-((2-Bromo-*N*-methylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1i)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.83 g, 60 %) was obtained through the procedure of column chromatography.

M. p.: 129-131 °C.

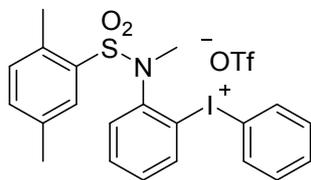
¹H NMR (400 MHz, DMSO) δ 8.31 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.26 – 8.20 (m, 2H), 7.94 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.80 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.61 – 7.56 (m, 3H), 7.53 (td, *J* = 7.7, 1.6 Hz, 1H), 7.10 (dd, *J* = 7.9, 1.5 Hz, 1H), 3.08 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 141.11, 137.34, 136.48, 135.71, 135.54, 135.04, 133.81, 132.78, 132.30, 131.90, 131.79, 129.26, 128.64, 121.34, 120.69 (q, *J*_{C-F} = 323.4 Hz), 119.82, 116.22, 40.00.

^{19}F NMR (376 MHz, DMSO) δ -77.73.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{BrSI}^+ [\text{M-OTf}]^+$ 527.9130, found 527.9133.

Phenyl(2-((*N*,2,5-trimethylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1j)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.64 g, 58 %) was obtained through the procedure of column chromatography.

M. p.: 153-154 °C.

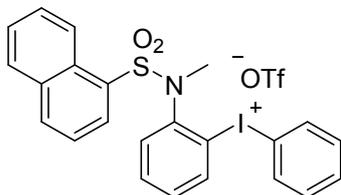
^1H NMR (400 MHz, DMSO) δ 8.25 (t, J = 7.6 Hz, 3H), 7.72 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.9 Hz, 3H), 7.51 (m, 3H), 7.32 (d, J = 7.7 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 2.92 (s, 3H), 2.35 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 141.35, 136.97, 136.52, 135.84, 134.85, 133.51, 133.26, 132.71, 132.36, 131.83, 131.71, 130.54, 128.35, 121.59, 120.70 (q, $J_{\text{C-F}}$ = 323.4 Hz), 116.14, 39.10, 20.36, 20.24.

^{19}F NMR (376 MHz, DMSO) δ -77.73.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{SI}^+ [\text{M-OTf}]^+$ 478.0338, found 478.0340.

(2-(*N*-Methylnaphthalene-1-sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1k)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.58 g, 54 %) was obtained through the procedure of column chromatography.

M. p.: 138-140 °C.

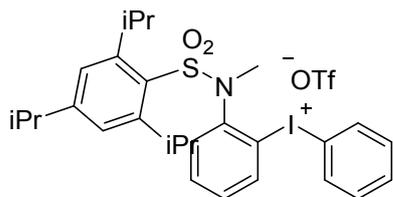
^1H NMR (400 MHz, DMSO) δ 8.40 (d, J = 8.2 Hz, 1H), 8.34 (dd, J = 8.1, 1.2 Hz, 1H), 8.26 (d, J = 7.5 Hz, 2H), 8.18 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 8.08 (dd, J = 7.5, 1.0 Hz, 1H), 7.73 (td, J = 7.7, 3.0 Hz, 2H), 7.69 – 7.54 (m, 3H), 7.53 – 7.43 (m, 2H), 7.34 (td, J = 7.8, 1.3 Hz, 1H), 6.70 (dd, J = 8.0, 1.3 Hz, 1H), 2.91 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 141.27, 137.28, 135.85, 135.81, 134.05, 133.37, 132.34, 131.84, 131.77, 131.68, 130.47, 129.21, 129.01, 128.48, 128.12, 127.13, 124.74, 124.53, 121.72, 120.71 (q, $J_{\text{C-F}}$ = 323.4 Hz), 116.13, 39.10.

^{19}F NMR (376 MHz, DMSO) δ -77.71.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{SI}^+ [\text{M-OTf}]^+$ 500.0181, found 500.0180.

Phenyl(2-((2,4,6-triisopropyl-*N*-methylphenyl)sulfonamido)phenyl)iodonium trifluoromethanesulfonate (1l)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.73 g, 53 %) was obtained through the procedure of column chromatography.

M. p.: 183-185 °C.

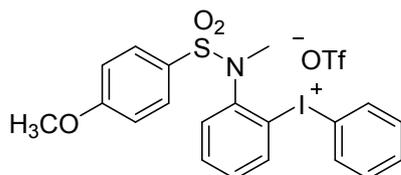
¹H NMR (400 MHz, CDCl₃) δ 8.20 – 8.08 (m, 2H), 7.74 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.38 – 7.30 (m, 1H), 7.15 (s, 2H), 7.07 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.38 (s, 3H), 3.37 – 3.30 (m, 2H), 2.89 (m, 1H), 1.25 (s, 3H), 1.23 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H), 0.97 (s, 3H), 0.96 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.55, 151.86, 141.58, 136.51, 135.15, 133.70, 133.13, 132.54, 132.10, 128.86, 128.61, 124.77, 120.48 (q, *J*_{C-F} = 321.6 Hz), 120.19, 114.79, 39.31, 34.24, 30.89, 25.42, 24.82, 23.54.

¹⁹F NMR (376 MHz, CDCl₃) δ -78.24.

HRMS *m/z* (ESI-TOF): calculated for C₂₈H₃₅NO₂SI⁺ [M-OTf]⁺ 576.1433, found 576.1434.

(2-((4-Methoxy-*N*-methylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1m)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.07 g, 73 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 144-145 °C.

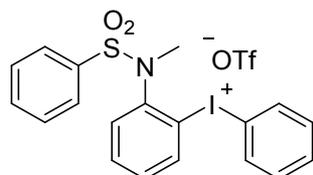
¹H NMR (400 MHz, DMSO) δ 8.31 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.43 (m, 6H), 7.20 (t, *J* = 5.9 Hz, 2H), 6.94 – 6.80 (m, 1H), 3.88 (s, 3H), 2.85 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 163.52, 141.89, 137.11, 135.79, 133.71, 132.22, 131.74, 131.58, 130.49, 127.88, 125.94, 122.28, 120.69 (q, *J*_{C-F} = 322.1 Hz), 116.18, 114.81, 55.87, 38.89.

¹⁹F NMR (376 MHz, DMSO) δ -77.73.

HRMS *m/z* (ESI-TOF): calculated for C₂₀H₁₉NO₃SI⁺ [M-OTf]⁺ 480.0130, found 480.0115.

(2-(*N*-Methylphenylsulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1n)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.48 g, 55 %) was obtained through the procedure of column chromatography.

M. p.: 177-179 °C.

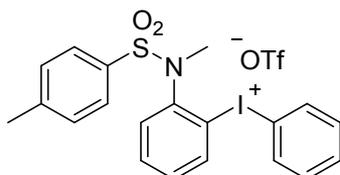
^1H NMR (400 MHz, DMSO) δ 8.35 (d, J = 7.8 Hz, 1H), 8.23 (d, J = 7.8 Hz, 2H), 7.83 (t, J = 7.1 Hz, 1H), 7.73 – 7.67 (m, 3H), 7.64 (d, J = 7.6 Hz, 2H), 7.61 – 7.48 (m, 4H), 6.82 (d, J = 7.9 Hz, 1H), 2.88 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 141.67, 137.33, 135.76, 134.59, 134.29, 133.75, 132.22, 131.73, 129.69, 129.45, 128.15, 127.92, 127.60, 122.24, 120.70 (q, $J_{\text{C-F}}$ = 323.7 Hz), 116.28, 39.04.

^{19}F NMR (376 MHz, DMSO) δ -77.72.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{19}\text{H}_{17}\text{NO}_2\text{Si}^+$ [M-OTf] $^+$ 450.0025, found 450.0026.

(2-((*N*,4-Dimethylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1o)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.23 g, 81 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 127-129 °C.

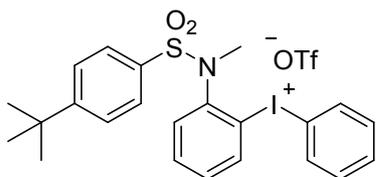
^1H NMR (400 MHz, DMSO) δ 8.33 (dd, J = 8.0, 1.0 Hz, 1H), 8.23 (d, J = 7.8 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.64 – 7.56 (m, 3H), 7.55 – 7.46 (m, 5H), 6.85 (dd, J = 7.9, 1.4 Hz, 1H), 2.86 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 144.89, 141.79, 137.25, 135.80, 133.78, 132.28, 131.77, 131.69, 131.67, 130.12, 128.23, 127.91, 122.06, 120.70 (q, $J_{\text{C-F}}$ = 323.5 Hz), 116.08, 38.95, 21.15.

^{19}F NMR (376 MHz, DMSO) δ -77.73.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{Si}^+$ [M-OTf] $^+$ 464.0181, found 464.0184.

(2-((4-(*tert*-Butyl)-*N*-methylphenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1p)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.80 g, 61 %) was obtained through the procedure of column chromatography.

M. p.: 78-80 °C.

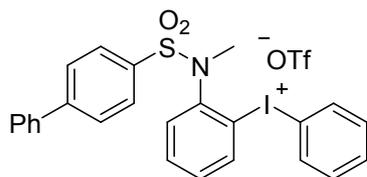
^1H NMR (400 MHz, CDCl_3) δ 8.12 (dd, J = 8.4, 0.9 Hz, 2H), 7.71 (dd, J = 8.2, 1.3 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.56 – 7.48 (m, 4H), 7.48 – 7.43 (m, 3H), 7.41 – 7.31 (m, 1H), 6.79 (dd, J = 8.0, 1.5 Hz, 1H), 3.21 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.73, 141.57, 136.56, 134.95, 133.47, 133.20, 132.58, 132.23, 130.52, 128.61, 127.56, 126.52, 120.48 (q, $J_{\text{C-F}}$ = 321.5 Hz), 119.97, 114.17, 39.22, 35.51, 31.10.

^{19}F NMR (376 MHz, CDCl_3) δ -78.21.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{Si}^+$ [M-OTf] $^+$ 506.0651, found 506.0656.

(2-(*N*-Methyl-[1,1'-biphenyl]-4-sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1q)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.76 g, 58 %) was obtained through the procedure of column chromatography.

M. p.: 147-149 °C.

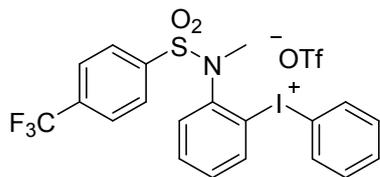
¹H NMR (400 MHz, DMSO) δ 8.37 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.85 – 7.75 (m, 2H), 7.72 (t, *J* = 7.4 Hz, 3H), 7.66 – 7.57 (m, 3H), 7.55 (ddd, *J* = 7.7, 3.4, 1.6 Hz, 3H), 7.50 – 7.44 (m, 1H), 6.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 2.91 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 145.44, 141.75, 137.97, 137.37, 135.79, 133.88, 133.32, 132.27, 131.78, 131.74, 129.24, 128.93, 128.91, 128.07, 127.68, 127.18, 122.13, 120.71 (q, *J*_{C-F} = 323.6 Hz), 116.15, 39.04.

¹⁹F NMR (376 MHz, DMSO) δ -77.72.

HRMS *m/z* (ESI-TOF): calculated for C₂₅H₂₁NO₂SI⁺ [M-OTf]⁺ 526.0338, found 526.0335.

(2-(*N*-Methyl-4-(trifluoromethyl)phenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1r)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (1.62 g, 54 %) was obtained through the procedure of column chromatography.

M. p.: 154-155 °C.

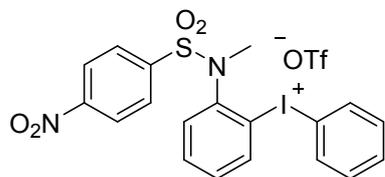
¹H NMR (400 MHz, DMSO) δ 8.41 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.66 – 7.50 (m, 4H), 6.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 2.92 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 141.40, 138.67, 137.64, 135.75, 134.06, 133.60 (q, *J*_{C-F} = 32.5 Hz), 132.28, 131.93, 131.77, 129.26, 128.23, 126.92 (q, *J*_{C-F} = 3.5 Hz), 123.38 (q, *J*_{C-F} = 274.3 Hz), 122.03, 120.70 (q, *J*_{C-F} = 323.6 Hz), 116.22, 39.10.

¹⁹F NMR (376 MHz, DMSO) δ -61.71, -77.76.

HRMS *m/z* (ESI-TOF): calculated for C₂₀H₁₆NO₂SF₃I⁺ [M-OTf]⁺ 517.9899, found 517.9899.

(2-(*N*-Methyl-4-nitrophenyl)sulfonamido)phenyl)(phenyl)iodonium trifluoromethanesulfonate (1s)



Prepared according to the **general procedure** on 4.5 mmol scale and a white powder (2.03 g, 70 %) was obtained through the procedure of trituration with diethyl ether.

M. p.: 165-166 °C.

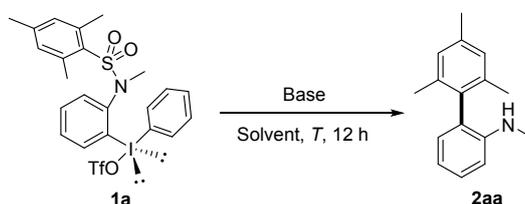
¹H NMR (400 MHz, DMSO) δ 8.47 (d, *J* = 8.9 Hz, 2H), 8.42 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 2H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.52 (m, 4H), 6.96 (dd, *J* = 7.7, 1.6 Hz, 1H), 2.93 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 150.56, 141.24, 140.04, 137.67, 135.69, 134.05, 132.21, 131.98, 131.72, 129.86, 129.13, 128.27, 124.92, 124.80, 122.16, 120.68 (q, *J*_{C-F} = 323.6 Hz), 116.41, 39.21.

¹⁹F NMR (376 MHz, DMSO) δ -77.74.

HRMS *m/z* (ESI-TOF): calculated for C₁₉H₁₆N₂O₄Si⁺ [M-OTf]⁺ 494.9876, found 494.9866.

Part 3. Optimization of Desulfonylative *ipso*-Substitution Cascade reaction ^[a]

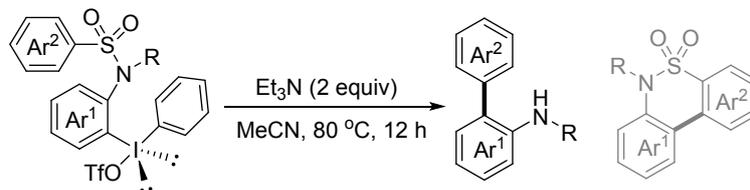


Entry	Base	Solvent	<i>T</i> [°C]	Yield [%] ^[b]
1	Morpholine	MeCN	50	11
2	4-Methylmorpholine	MeCN	50	6
3	DIPEA	MeCN	50	68
4	Et ₃ N	MeCN	50	70
5	1-Ethylpiperidine	MeCN	50	39
6	DBU	MeCN	50	Trace
7	DMAP	MeCN	50	n. r.
8	Pyridine	MeCN	50	n. r.
9	NH ₃ ·H ₂ O	MeCN	50	n. r.
10	Na ₂ CO ₃	MeCN	50	n. r.
11	Cs ₂ CO ₃	MeCN	50	Trace
12	KOH	MeCN	50	8
13	K ₃ PO ₄	MeCN	50	5
14	KOtBu	MeCN	50	6
15	Et ₃ N	Toluene	50	21
16	Et ₃ N	DCE	50	45
17	Et ₃ N	DMF	50	42
18	Et ₃ N	DMSO	50	39
19	Et ₃ N	THF	50	42
20	Et ₃ N	1,4-Dioxane	50	60
21	Et ₃ N	CHCl ₃	50	23
22	Et ₃ N	TFE	50	n. r.
23	Et ₃ N	MeOH	50	Trace
24	Et ₃ N	H ₂ O	50	n. r.
25	Et ₃ N	MeCN	80	86 (80 ^[c])

26	/	MeCN	80	n. r.
27 ^[d]	Et ₃ N	MeCN	80	34
28 ^[e]	Et ₃ N	MeCN	80	49

[a] Reaction conditions: **1a** (0.3 mmol), base (2 equiv.) in 5 mL solvent, temperature (see table). [b] Isolated yield. [c] 5.0 mmol scale. [d] 1.2 equiv. of base was used. [e] 1.5 equiv. of base was used. n. r. = no reaction. OTf = triflate. DCE = 1,2-dichloroethane, DMF = *N, N*-dimethylformamide, DMSO = dimethylsulfoxide, THF = tetrahydrofuran, TFE = 2,2,2-trifluoroethanol.

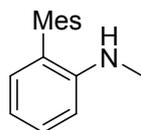
Part 4. Synthesis and Characterization of Products from Desulfonylative Cascade Reactions.



General procedure:

To a Schlenk tube was added iodonium salts (0.3 mmol, 1 equiv.) and the tube was degassed with argon for three times. Acetonitrile (5 mL) and Et_3N (0.6 mmol, 2.0 equiv.) was added via syringe, and the mixture was stirred at $80\text{ }^\circ\text{C}$ in an oil bath for 12 h. The solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford the desired products.

N,2',4',6'-Tetramethyl-[1,1'-biphenyl]-2-amine (2aa)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 86% (58 mg) as a white solid.

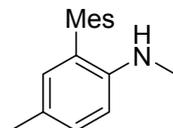
M. p.: $45\text{--}46\text{ }^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.26 (m, 1H), 6.99 (s, 2H), 6.90 (dd, $J = 7.3, 1.6$ Hz, 1H), 6.78 (td, $J = 7.3, 1.0$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 1H), 3.32 (br, 1H), 2.78 (s, 3H), 2.35 (s, 3H), 2.00 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.39, 137.48, 137.13, 134.94, 129.57, 128.58, 128.35, 125.99, 116.96, 109.59, 30.83, 21.22, 20.24.

HRMS m/z (EI-TOF): calculated for $\text{C}_{16}\text{H}_{19}\text{N}$ $[\text{M}]^+$ 225.1517, found 225.1519.

N,2',4',5,6'-Pentamethyl-[1,1'-biphenyl]-2-amine (2ab)



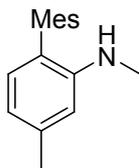
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 72% (52 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.10 (dd, $J = 8.2, 1.6$ Hz, 1H), 6.98 (s, 2H), 6.73 (d, $J = 2.0$ Hz, 1H), 6.64 (d, $J = 8.2$ Hz, 1H), 3.18 (br, 1H), 2.77 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H), 2.01 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.24, 137.38, 136.98, 135.11, 130.20, 128.66, 128.52, 126.15, 126.02, 109.86, 31.20, 21.20, 20.61, 20.29.

HRMS m/z (EI-TOF): calculated for $\text{C}_{17}\text{H}_{21}\text{N}$ $[\text{M}]^+$ 239.1674, found 239.1673.

***N*,2',4,4',6'-Pentamethyl-[1,1'-biphenyl]-2-amine (2ac)**



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 89% (64 mg) as a white solid.

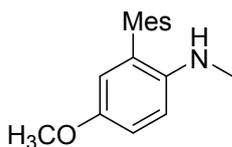
M. p.: 43-45 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.97 (s, 2H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 6.53 (s, 1H), 3.26 (br, 1H), 2.77 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H), 2.00 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 146.25, 138.00, 137.68, 136.99, 134.96, 129.39, 128.53, 123.20, 117.75, 110.53, 30.85, 21.97, 21.21, 20.31.

HRMS *m/z* (EI-TOF): calculated for C₁₇H₂₁N [M]⁺ 239.1674, found 239.1678.

5-Methoxy-*N*,2',4,6'-tetramethyl-[1,1'-biphenyl]-2-amine (2ad)



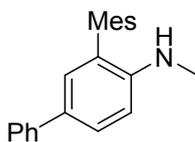
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 83% (63 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.97 (s, 2H), 6.87 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 3H), 3.02 (br, 1H), 2.75 (s, 3H), 2.34 (s, 3H), 2.00 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 151.76, 140.96, 137.29, 137.24, 134.81, 128.57, 127.34, 115.80, 113.29, 110.89, 55.88, 31.71, 21.19, 20.21.

HRMS *m/z* (EI-TOF): calculated for C₁₇H₂₁NO [M]⁺ 255.1623, found 255.1622.

***N*,2'',4'',6''-Tetramethyl-[1,1':3',1''-terphenyl]-4'-amine (2ae)**



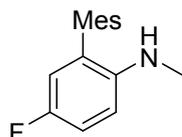
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 74% (67 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.53 (m, 3H), 7.45 – 7.33 (m, 2H), 7.25 (m, 2H), 7.00 (s, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 3.41 (br, 1H), 2.82 (s, 3H), 2.36 (s, 3H), 2.04 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.90, 141.40, 137.53, 137.30, 134.78, 129.64, 128.77, 128.65, 128.16, 126.84, 126.32, 126.22, 125.99, 109.88, 30.83, 21.23, 20.33.

HRMS *m/z* (EI-TOF): calculated for C₂₂H₂₃N [M]⁺ 301.1830, found 301.1829.

5-Fluoro-*N*,2',4',6'-tetramethyl-[1,1'-biphenyl]-2-amine (2af)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 41% (30 mg) as a white solid.

M. p.: 67-69 °C.

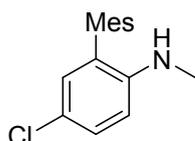
¹H NMR (400 MHz, CDCl₃) δ 7.03 – 6.90 (m, 3H), 6.67 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.60 (dd, *J* = 8.9, 4.7 Hz, 1H), 3.16 (br, 1H), 2.75 (s, 3H), 2.34 (s, 3H), 1.99 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 155.60 (d, *J*_{C-F} = 235.4 Hz), 142.93 (d, *J*_{C-F} = 1.5 Hz), 137.54, 137.22, 133.89, 128.69, 127.11 (d, *J*_{C-F} = 7.3 Hz), 116.31 (d, *J*_{C-F} = 22.0 Hz), 114.31 (d, *J*_{C-F} = 21.8 Hz), 110.21 (d, *J*_{C-F} = 7.9 Hz), 31.36, 21.21, 20.12.

¹⁹F NMR (376 MHz, CDCl₃) δ -129.12.

HRMS *m/z* (EI-TOF): calculated for C₁₆H₁₈NF [M]⁺ 243.1423, found 243.1424.

5-Chloro-*N*,2',4',6'-tetramethyl-[1,1'-biphenyl]-2-amine (2ag)



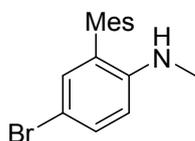
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 99% (77 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.98 (s, 2H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.61 (d, *J* = 8.7 Hz, 1H), 3.32 (d, *J* = 3.9 Hz, 1H), 2.76 (d, *J* = 5.0 Hz, 3H), 2.34 (s, 3H), 2.00 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.09, 137.59, 137.26, 133.56, 129.21, 128.71, 128.07, 127.44, 121.41, 110.58, 30.83, 29.85, 21.21, 20.15.

HRMS *m/z* (EI-TOF): calculated for C₁₆H₁₈NCl [M]⁺ 259.1128, found 259.1129.

5-Bromo-*N*,2',4',6'-tetramethyl-[1,1'-biphenyl]-2-amine (2ah)



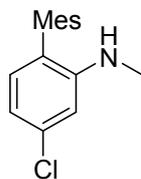
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 88% (80 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.35 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.97 (s, 2H), 6.56 (d, *J* = 8.7 Hz, 1H), 3.34 (d, *J* = 4.0 Hz, 1H), 2.75 (d, *J* = 5.0 Hz, 3H), 2.34 (s, 3H), 1.99 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.50, 137.61, 137.27, 133.46, 131.92, 130.97, 128.70, 127.92, 111.09, 108.50, 30.74, 29.85, 21.21, 20.17.

HRMS *m/z* (EI-TOF): calculated for C₁₆H₁₈NBr [M]⁺ 303.0623, found 303.0621.

4-Chloro-*N*,2',4',6'-tetramethyl-[1,1'-biphenyl]-2-amine (2ai)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 78% (61 mg) as a white solid.

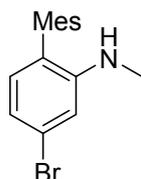
M. p.: 67-69 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.97 (s, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.74 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 2.76 (s, 3H), 2.34 (s, 3H), 1.97 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 147.32, 137.53, 137.48, 134.06, 133.70, 130.50, 128.71, 124.37, 116.79, 109.71, 30.63, 21.21, 20.17.

HRMS *m/z* (EI-TOF): calculated for C₁₆H₁₈NCl [M]⁺ 259.1128, found 259.1129.

4-Bromo-*N*,2',4',6'-tetramethyl-[1,1'-biphenyl]-2-amine (2aj)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 77% (70 mg) as a white solid.

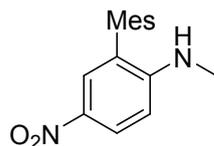
M. p.: 54-56 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.97 (s, 2H), 6.88 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.80 (d, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 3.40 (d, *J* = 4.7 Hz, 1H), 2.76 (d, *J* = 5.2 Hz, 3H), 2.34 (s, 3H), 1.98 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 147.60, 137.52, 137.39, 133.71, 130.82, 128.70, 124.74, 122.29, 119.61, 112.40, 30.54, 21.20, 20.16.

HRMS *m/z* (EI-TOF): calculated for C₁₆H₁₈NBr [M]⁺ 303.0623, found 303.0620.

N,2',4',6'-Tetramethyl-5-nitro-[1,1'-biphenyl]-2-amine (2ak)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 53% (43 mg) as a yellow solid.

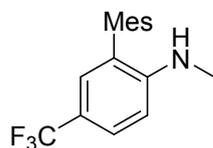
M. p.: 171-173 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.85 (d, *J* = 2.7 Hz, 1H), 6.99 (s, 2H), 6.62 (d, *J* = 9.1 Hz, 1H), 4.17 (br, 1H), 2.87 (s, 3H), 2.34 (s, 3H), 1.97 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.69, 138.36, 137.99, 137.31, 131.93, 129.04, 126.21, 126.02, 125.27, 107.77, 30.29, 21.22, 20.08.

HRMS m/z (EI-TOF): calculated for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 270.1368, found 270.1369.

***N*,2',4',6'-Tetramethyl-5-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (2al)**



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 74% (65 mg) as a white solid.

M. p.: 82-84 °C.

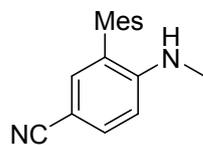
^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.14 (d, $J = 2.0$ Hz, 1H), 6.99 (s, 2H), 6.69 (d, $J = 8.5$ Hz, 1H), 3.67 (d, $J = 4.5$ Hz, 1H), 2.81 (d, $J = 5.2$ Hz, 3H), 2.35 (s, 3H), 1.98 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.84, 137.80, 137.39, 133.36, 128.82, 126.66 (q, $J_{\text{C-F}} = 3.7$ Hz), 125.89 (q, $J_{\text{C-F}} = 3.8$ Hz), 125.52, 125.35 (q, $J_{\text{C-F}} = 271.3$ Hz), 118.44 (q, $J_{\text{C-F}} = 32.5$ Hz), 108.56, 30.37, 21.19, 20.12.

^{19}F NMR (376 MHz, CDCl_3) δ -60.63.

HRMS m/z (EI-TOF): calculated for $\text{C}_{17}\text{H}_{18}\text{NF}_3$ $[\text{M}]^+$ 293.1391, found 293.1390.

2',4',6'-Trimethyl-6-(methylamino)-[1,1'-biphenyl]-3-carbonitrile (2am)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 80% (60 mg) as a white solid.

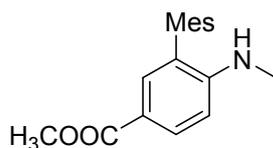
M. p.: 102-104 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.14 (d, $J = 2.0$ Hz, 1H), 6.98 (s, 2H), 6.64 (d, $J = 8.5$ Hz, 1H), 2.81 (s, 3H), 2.33 (s, 3H), 1.95 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.63, 138.13, 137.27, 133.39, 133.26, 132.23, 128.94, 126.15, 109.00, 98.51, 30.09, 21.20, 20.04.

HRMS m/z (EI-TOF): calculated for $\text{C}_{17}\text{H}_{18}\text{N}_2$ $[\text{M}]^+$ 250.1470, found 250.1469.

Methyl 2',4',6'-trimethyl-6-(methylamino)-[1,1'-biphenyl]-3-carboxylate (2an)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 70% (59 mg) as a white solid.

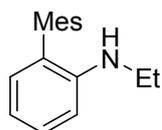
M. p.: 157-159 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.60 (d, $J = 2.1$ Hz, 1H), 6.97 (s, 2H), 6.65 (d, $J = 8.6$ Hz, 1H), 3.84 (s, 3H), 2.82 (d, $J = 5.2$ Hz, 3H), 2.33 (s, 3H), 1.97 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.73, 150.16, 137.58, 137.44, 133.54, 131.45, 131.02, 128.73, 125.05, 118.01, 108.24, 51.60, 30.24, 21.19, 20.13.

HRMS m/z (EI-TOF): calculated for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ $[\text{M}]^+$ 283.1572, found 283.1571.

***N*-Ethyl-2',4',6'-trimethyl-[1,1'-biphenyl]-2-amine (2ba)**



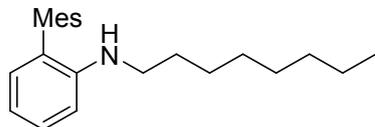
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 68% (49 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.20 (m, 1H), 6.98 (s, 2H), 6.89 (dd, $J = 7.3, 1.6$ Hz, 1H), 6.80 – 6.67 (m, 2H), 3.23 (br, 1H), 3.15 (d, $J = 6.7$ Hz, 2H), 2.35 (s, 3H), 2.00 (s, 6H), 1.11 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.36, 137.41, 137.07, 134.95, 129.78, 128.58, 128.26, 126.10, 116.86, 110.22, 38.33, 21.23, 20.22, 15.00.

HRMS m/z (EI-TOF): calculated for $\text{C}_{17}\text{H}_{21}\text{N}$ $[\text{M}]^+$ 239.1674, found 239.1675.

2',4',6'-Trimethyl-*N*-octyl-[1,1'-biphenyl]-2-amine (2ca)



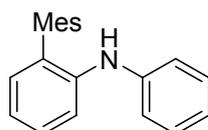
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 75% (73 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.20 (m, 1H), 6.98 (s, 2H), 6.89 (dd, $J = 7.3, 1.6$ Hz, 1H), 6.74 (ddd, $J = 10.8, 8.5, 4.6$ Hz, 2H), 3.29 (br, 1H), 3.08 (m, 2H), 2.35 (s, 3H), 2.00 (s, 6H), 1.53 – 1.41 (m, 2H), 1.35 – 1.16 (m, 10H), 0.89 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.47, 137.44, 137.06, 134.95, 129.74, 128.58, 128.25, 126.01, 116.69, 110.09, 43.87, 31.91, 29.50, 29.43, 29.38, 27.17, 22.79, 21.23, 20.24, 14.25.

HRMS m/z (EI-TOF): calculated for $\text{C}_{23}\text{H}_{33}\text{N}$ $[\text{M}]^+$ 323.2613, found 323.2614.

2',4',6'-Trimethyl-*N*-phenyl-[1,1'-biphenyl]-2-amine (2da)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 56% (48 mg) as a white solid.

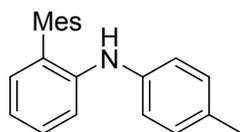
M. p.: 97-99 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 8.2 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.10 – 7.02 (m, 3H), 7.02 – 6.88 (m, 4H), 5.20 (br, 1H), 2.36 (s, 3H), 2.05 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.01, 140.92, 137.40, 137.32, 134.52, 130.52, 129.35, 129.02, 128.74, 127.88, 121.52, 120.44, 119.09, 115.44, 21.23, 20.40.

HRMS m/z (EI-TOF): calculated for $\text{C}_{21}\text{H}_{21}\text{N}$ $[\text{M}]^+$ 287.1674, found 287.1677.

2',4',6'-Trimethyl-*N*-(*p*-tolyl)-[1,1'-biphenyl]-2-amine (2ea)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 61% (55 mg) as a white solid.

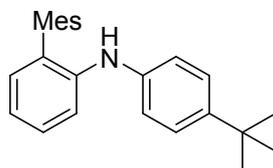
M. p.: 92-93 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 1H), 7.26 – 7.19 (m, 1H), 7.06 (d, J = 8.3 Hz, 2H), 7.03 – 6.95 (m, 5H), 6.92 (td, J = 7.3, 1.2 Hz, 1H), 5.11 (br, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 2.05 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.64, 140.30, 137.39, 137.35, 134.60, 131.40, 130.41, 129.87, 128.72, 128.40, 127.89, 120.06, 119.83, 114.72, 21.22, 20.84, 20.40.

HRMS m/z (EI-TOF): calculated for $\text{C}_{22}\text{H}_{23}\text{N}$ $[\text{M}]^+$ 301.1830, found 301.1829.

N-(4-(*tert*-Butyl)phenyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-amine (2fa)



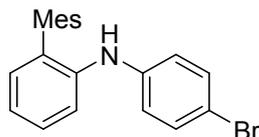
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 65% (67 mg) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.30 (m, 1H), 7.27 – 7.18 (m, 3H), 7.04 – 6.95 (m, 5H), 6.91 (td, J = 7.4, 1.1 Hz, 1H), 5.12 (br, 1H), 2.33 (s, 3H), 2.03 (s, 6H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.66, 141.44, 140.23, 137.37, 137.34, 134.60, 130.40, 128.72, 128.45, 127.86, 126.13, 119.85, 119.38, 114.79, 34.31, 31.58, 21.22, 20.42.

HRMS m/z (EI-TOF): calculated for $\text{C}_{25}\text{H}_{29}\text{N}$ $[\text{M}]^+$ 343.2300, found 343.2298.

N-(4-Bromophenyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-amine (2ga)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 74% (81 mg) as a white solid.

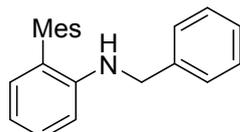
M. p.: 96-98 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.29 (m, 3H), 7.27 (m, 1H), 7.05 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.00 (m, 3H), 6.96 – 6.88 (m, 2H), 5.16 (br, 1H), 2.35 (s, 3H), 2.02 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 142.28, 140.25, 137.61, 137.52, 137.22, 134.28, 132.22, 130.68, 129.56, 128.78, 127.97, 121.15, 120.17, 116.01, 113.20, 21.22, 20.40.

HRMS *m/z* (EI-TOF): calculated for C₂₁H₂₀NBr [M]⁺ 365.0779, found 365.0782.

***N*-Benzyl-2',4',6'-trimethyl-[1,1'-biphenyl]-2-amine (2ha)**



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 66% (59 mg) as a white solid.

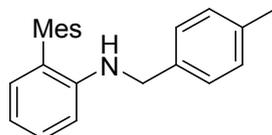
M. p.: 57-59 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.18 (m, 5H), 7.18 – 7.10 (m, 1H), 6.95 (s, 2H), 6.88 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.73 (td, *J* = 7.4, 0.8 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 4.28 (d, *J* = 5.6 Hz, 2H), 3.81 (br, 1H), 2.30 (s, 3H), 2.02 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.03, 140.02, 137.45, 137.19, 134.81, 129.78, 128.65, 128.61, 128.26, 127.00, 126.10, 117.27, 110.48, 47.85, 21.20, 20.31.

HRMS *m/z* (EI-TOF): calculated for C₂₂H₂₃N [M]⁺ 301.1830, found 301.1832.

2',4',6'-Trimethyl-*N*-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (2ia)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 64% (60 mg) as a white solid.

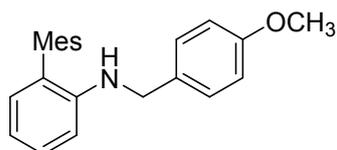
M. p.: 100-102 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.18 (m, 1H), 7.14 (m, 4H), 6.99 (s, 2H), 6.92 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.77 (td, *J* = 7.4, 1.1 Hz, 1H), 6.72 – 6.63 (m, 1H), 4.29 (d, *J* = 5.6 Hz, 2H), 3.81 (br, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.05 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.13, 137.46, 137.17, 136.92, 136.61, 134.85, 129.77, 129.30, 128.64, 128.26, 127.03, 126.08, 117.18, 110.47, 47.64, 21.20, 20.32.

HRMS *m/z* (EI-TOF): calculated for C₂₃H₂₅N [M]⁺ 315.1987, found 315.1989.

***N*-(4-Methoxybenzyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-amine (2ja)**



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 40% (40 mg) as a white solid.

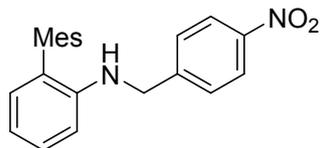
M. p.: 58-59 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.13 (m, 3H), 6.97 (s, 2H), 6.90 (dd, J = 7.4, 1.6 Hz, 1H), 6.87 – 6.79 (m, 2H), 6.76 (td, J = 7.4, 1.0 Hz, 1H), 6.67 (d, J = 8.1 Hz, 1H), 4.25 (d, J = 4.9 Hz, 2H), 3.78 (s, 3H), 3.76 (br, 1H), 2.33 (s, 3H), 2.03 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.69, 145.09, 137.44, 137.17, 134.82, 131.96, 129.78, 128.63, 128.25, 126.10, 117.20, 114.00, 110.48, 55.38, 47.34, 21.22, 20.32.

HRMS m/z (EI-TOF): calculated for $\text{C}_{23}\text{H}_{25}\text{NO}$ $[\text{M}]^+$ 331.1936, found 331.1935.

2',4',6'-Trimethyl-*N*-(4-nitrobenzyl)-[1,1'-biphenyl]-2-amine (2ka)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 46% (48 mg) as a yellow solid.

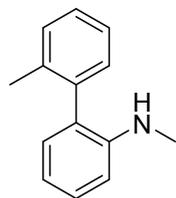
M. p.: 155-156 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.28 – 8.01 (m, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.14 (td, J = 8.1, 1.6 Hz, 1H), 7.00 (s, 2H), 6.94 (dd, J = 7.4, 1.6 Hz, 1H), 6.79 (td, J = 7.4, 1.0 Hz, 1H), 6.55 – 6.38 (m, 1H), 4.42 (d, J = 5.6 Hz, 2H), 3.97 (br, 1H), 2.34 (s, 3H), 2.04 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.12, 147.19, 144.21, 137.49, 137.41, 134.48, 130.05, 128.76, 128.33, 127.43, 126.36, 123.98, 118.04, 110.32, 47.33, 21.22, 20.35.

HRMS m/z (EI-TOF): calculated for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 346.1681, found 346.1680.

N,2'-Dimethyl-[1,1'-biphenyl]-2-amine (2f)



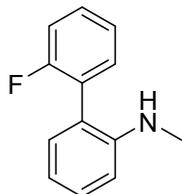
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 68% (40 mg) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.22 (m, 4H), 7.21 – 7.14 (m, 1H), 6.98 (dd, J = 7.4, 1.6 Hz, 1H), 6.76 (td, J = 7.4, 1.0 Hz, 1H), 6.68 (d, J = 8.1 Hz, 1H), 3.42 (br, 1H), 2.77 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.43, 138.68, 137.39, 130.50, 130.41, 129.70, 128.68, 127.82, 127.32, 126.37, 116.62, 109.56, 30.80, 19.79.

HRMS m/z (EI-TOF): calculated for $\text{C}_{14}\text{H}_{15}\text{N}$ $[\text{M}]^+$ 197.1204, found 197.1205.

2'-Fluoro-N-methyl-[1,1'-biphenyl]-2-amine (2g)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 70% (42 mg) as a white solid.

M. p.: 33-35 °C.

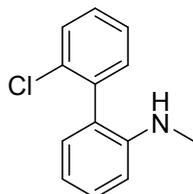
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.28 (m, 3H), 7.26 – 7.21 (m, 1H), 7.18 (dd, $J = 9.8, 8.5$ Hz, 1H), 7.11 (dd, $J = 7.4, 1.4$ Hz, 1H), 6.80 (td, $J = 7.4, 0.9$ Hz, 1H), 6.74 (d, $J = 8.2$ Hz, 1H), 2.83 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.16 (d, $J_{\text{C-F}} = 247.6$ Hz), 146.78, 132.37 (d, $J_{\text{C-F}} = 3.6$ Hz), 130.71, 129.57, 129.55 (d, $J_{\text{C-F}} = 7.9$ Hz), 126.62 (d, $J_{\text{C-F}} = 16.7$ Hz), 124.70 (d, $J_{\text{C-F}} = 3.7$ Hz), 121.28, 116.81, 116.25 (d, $J_{\text{C-F}} = 22.4$ Hz), 110.13, 30.94.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -114.05.

HRMS m/z (EI-TOF): calculated for $\text{C}_{13}\text{H}_{12}\text{NF}$ $[\text{M}]^+$ 201.0954, found 201.0955.

2'-Chloro-N-methyl-[1,1'-biphenyl]-2-amine (2h)



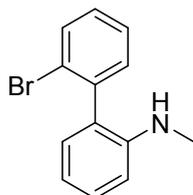
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 66% (43 mg) as a colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 1H), 7.40 – 7.29 (m, 4H), 7.04 (dd, $J = 7.4, 1.6$ Hz, 1H), 6.80 (td, $J = 7.4, 1.0$ Hz, 1H), 6.74 (d, $J = 8.1$ Hz, 1H), 3.47 (br, 1H), 2.82 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.49, 137.98, 134.31, 132.29, 130.07, 129.47, 129.17, 127.41, 125.08, 116.67, 110.01, 30.92.

HRMS m/z (EI-TOF): calculated for $\text{C}_{13}\text{H}_{12}\text{NCl}$ $[\text{M}]^+$ 217.0658, found 217.0659.

2'-Bromo-N-methyl-[1,1'-biphenyl]-2-amine (2i)



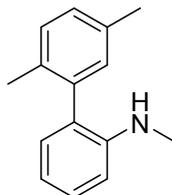
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 63% (49 mg) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.40 (td, $J = 7.5, 1.2$ Hz, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.15 (m, 1H), 7.01 (dd, $J = 7.4, 1.6$ Hz, 1H), 6.79 (td, $J = 7.4, 1.1$ Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 3.42 (br, 1H), 2.82 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.33, 140.08, 133.28, 132.21, 129.92, 129.46, 129.35, 128.05, 126.92, 124.74, 116.66, 110.04, 30.93.

HRMS m/z (EI-TOF): calculated for $\text{C}_{13}\text{H}_{12}\text{NBr}$ $[\text{M}]^+$ 261.0153, found 261.0152.

***N*-, 2',5'-Trimethyl-[1,1'-biphenyl]-2-amine (2j)**



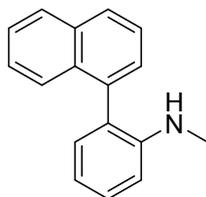
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 65% (41 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.23 (m, 1H), 7.19 (d, $J = 7.7$ Hz, 1H), 7.10 (d, $J = 7.7$ Hz, 1H), 7.02 (s, 1H), 6.99 (d, $J = 7.3$ Hz, 1H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 8.1$ Hz, 1H), 3.46 (br, 1H), 2.79 (s, 3H), 2.35 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.44, 138.52, 135.81, 134.08, 131.12, 130.28, 129.66, 128.59, 128.51, 127.51, 116.61, 109.52, 30.81, 21.04, 19.26.

HRMS m/z (EI-TOF): calculated for $\text{C}_{15}\text{H}_{17}\text{N}$ $[\text{M}]^+$ 211.1361, found 211.1362.

***N*-Methyl-2-(naphthalen-1-yl)aniline (2k)**



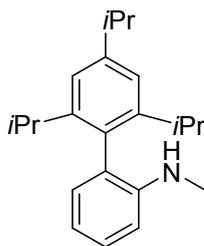
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 56% (39 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.91 (t, $J = 8.8$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 1H), 7.56 (dd, $J = 8.2, 7.1$ Hz, 1H), 7.51 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.47 – 7.34 (m, 3H), 7.14 (dd, $J = 7.4, 1.6$ Hz, 1H), 6.85 (td, $J = 7.4, 1.1$ Hz, 1H), 6.82 – 6.72 (m, 1H), 3.45 (br, 1H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.15, 137.04, 133.99, 132.09, 130.91, 129.13, 128.41, 128.13, 127.98, 126.36, 126.21, 126.16, 126.03, 125.75, 116.74, 109.84, 30.82.

HRMS m/z (EI-TOF): calculated for $\text{C}_{17}\text{H}_{15}\text{N}$ $[\text{M}]^+$ 233.1204, found 233.1203.

2',4',6'-Triisopropyl-*N*-methyl-[1,1'-biphenyl]-2-amine (2l)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 94% (87 mg) as a white solid.

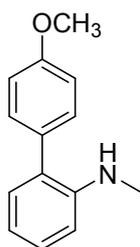
M. p.: 73-75 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.29 (td, $J = 8.0, 1.5$ Hz, 1H), 7.09 (s, 2H), 6.93 (dd, $J = 7.3, 1.5$ Hz, 1H), 6.75 (dd, $J = 10.6, 4.0$ Hz, 1H), 6.68 (d, $J = 8.1$ Hz, 1H), 3.31 (d, $J = 4.8$ Hz, 1H), 2.95 (m, 1H), 2.77 (d, $J = 5.1$ Hz, 3H), 2.68 – 2.51 (m, 2H), 1.33 (s, 3H), 1.31 (s, 3H), 1.10 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.46, 147.91, 147.38, 132.59, 130.36, 128.20, 125.52, 121.28, 116.38, 109.24, 34.39, 30.70, 30.40, 24.77, 24.22, 24.11.

HRMS m/z (EI-TOF): calculated for $\text{C}_{22}\text{H}_{31}\text{N}$ $[M]^+$ 309.2457, found 309.2458.

4'-Methoxy-N-methyl-[1,1'-biphenyl]-2-amine (2m)



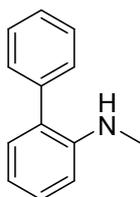
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 69% (44 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.22 (m, 1H), 7.08 (dd, $J = 7.4, 1.6$ Hz, 1H), 7.02 – 6.93 (m, 2H), 6.77 (td, $J = 7.4, 1.1$ Hz, 1H), 6.69 (d, $J = 8.1$ Hz, 1H), 3.96 (br, 1H), 3.86 (s, 3H), 2.80 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.89, 146.52, 131.76, 130.64, 130.19, 128.62, 127.39, 116.89, 114.38, 109.81, 55.45, 30.95.

HRMS m/z (EI-TOF): calculated for $\text{C}_{14}\text{H}_{15}\text{NO}$ $[M]^+$ 213.1154, found 213.1155.

N-Methyl-[1,1'-biphenyl]-2-amine (2n)



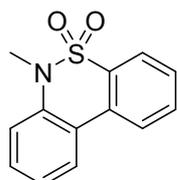
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 44% (24 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.41 (m, 4H), 7.39 – 7.33 (m, 1H), 7.29 (td, J = 8.1, 1.6 Hz, 1H), 7.11 (dd, J = 7.4, 1.6 Hz, 1H), 6.79 (td, J = 7.4, 1.0 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 3.98 (br, 1H), 2.81 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.30, 139.63, 130.15, 129.54, 128.99, 128.90, 127.70, 127.31, 116.92, 109.92, 30.90.

HRMS m/z (EI-TOF): calculated for $\text{C}_{13}\text{H}_{13}\text{N}$ $[\text{M}]^+$ 183.1048, found 183.1047.

6-Methyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2n')



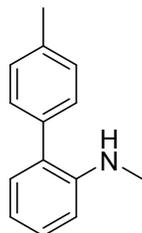
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 31% (23 mg) as a brown oil.

^1H NMR (400 MHz, CDCl_3) δ 8.01 (dd, J = 7.9, 1.2 Hz, 2H), 7.96 (d, J = 8.0 Hz, 1H), 7.71 (td, J = 7.8, 1.4 Hz, 1H), 7.57 (td, J = 7.7, 1.0 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.38 – 7.28 (m, 2H), 3.45 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.57, 134.31, 132.56, 132.51, 130.56, 128.35, 125.63, 125.55, 124.80, 124.07, 122.58, 119.51, 32.87.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 246.0589, found 246.0587.

N,4'-Dimethyl-[1,1'-biphenyl]-2-amine (2o)



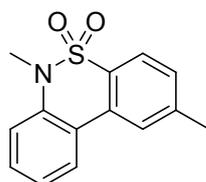
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 66% (39 mg) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 7.09 (dd, J = 7.4, 1.6 Hz, 1H), 6.78 (td, J = 7.4, 1.1 Hz, 1H), 6.70 (d, J = 8.1 Hz, 1H), 3.99 (br, 1H), 2.80 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.40, 137.00, 136.58, 130.15, 129.68, 129.39, 128.72, 127.67, 116.89, 109.84, 30.91, 21.32.

HRMS m/z (EI-TOF): calculated for $\text{C}_{14}\text{H}_{15}\text{N}$ $[\text{M}]^+$ 197.1204, found 197.1205.

2,6-Dimethyl-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2o')



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 26% (20 mg) as a white solid.

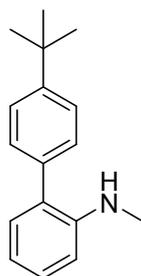
M. p.: 109-111 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.00 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.76 (s, 1H), 7.49 (td, $J = 8.1, 1.5$ Hz, 1H), 7.37 (dd, $J = 8.0, 0.7$ Hz, 1H), 7.31 (ddd, $J = 15.6, 7.9, 1.0$ Hz, 2H), 3.43 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.15, 139.73, 132.43, 131.75, 130.41, 129.17, 125.89, 125.57, 124.70, 124.10, 122.64, 119.50, 32.77, 22.07.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 282.0565, found 282.0566.

4'-(*tert*-Butyl)-*N*-methyl-[1,1'-biphenyl]-2-amine (2p)



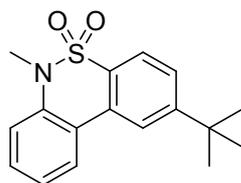
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 56% (40 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 7.7$ Hz, 2H), 7.37 (d, $J = 7.5$ Hz, 2H), 7.27 (dd, $J = 11.7, 3.9$ Hz, 1H), 7.12 (d, $J = 7.4$ Hz, 1H), 6.79 (t, $J = 7.3$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 1H), 4.04 (br, 1H), 2.81 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.16, 146.46, 136.56, 130.18, 129.13, 128.69, 127.65, 125.90, 116.88, 109.84, 34.72, 31.52, 30.91.

HRMS m/z (EI-TOF): calculated for $\text{C}_{17}\text{H}_{21}\text{N}$ $[\text{M}]^+$ 239.1674, found 239.1675.

2-(*tert*-Butyl)-6-methyl-6*H*-dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (2p')



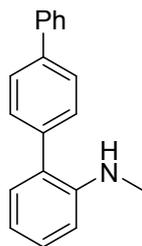
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 22% (20 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.9$ Hz, 1H), 7.96 (s, 1H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.61 (d, $J = 8.3$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 1H), 3.44 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.22, 139.74, 132.13, 131.75, 130.37, 125.81, 125.55, 124.71, 124.50, 122.46, 122.34, 119.51, 35.58, 32.77, 31.32.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 302.1215, found 302.1217.

N-Methyl-[1,1':4',1''-terphenyl]-2-amine (2q)



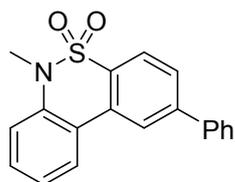
Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 52% (40 mg) as a colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (m, 4H), 7.51 (m, 4H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.17 (d, $J = 7.3$ Hz, 1H), 6.83 (t, $J = 7.3$ Hz, 1H), 6.75 (d, $J = 8.1$ Hz, 1H), 4.06 (br, 1H), 2.85 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.38, 140.86, 140.15, 138.60, 130.15, 129.93, 128.97, 127.70, 127.50, 127.26, 127.18, 117.00, 109.99, 30.92.

HRMS m/z (EI-TOF): calculated for $\text{C}_{19}\text{H}_{17}\text{N}$ $[\text{M}]^+$ 259.1361, found 259.1360.

6-Methyl-2-phenyl-6H-dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (2q')



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 19% (18 mg) as a white solid.

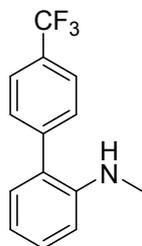
M. p.: 165-167 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 (s, 1H), 8.08 (t, $J = 8.9$ Hz, 2H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 2H), 7.51 (m, 3H), 7.48 – 7.41 (m, 1H), 7.35 (dd, $J = 13.0, 7.7$ Hz, 2H), 3.47 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.78, 139.85, 139.81, 133.01, 132.95, 130.68, 129.25, 128.67, 127.61, 127.23, 125.69, 124.85, 124.32, 124.19, 123.21, 119.62, 32.91.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 322.0902, found 322.0903.

N-Methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (2r)

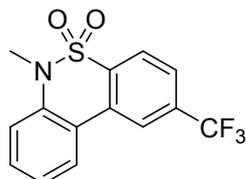


Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 45% (34 mg) as a colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.35 – 7.29 (m, 1H), 7.09 (dd, $J = 7.4, 1.6$ Hz, 1H), 6.81 (td, $J = 7.4, 1.0$ Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 3.86 (br, 1H), 2.82 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.10, 143.51, 130.10, 129.94, 129.63, 129.47 (q, $J_{\text{C-F}} = 32.6$ Hz), 126.15, 125.95 (q, $J_{\text{C-F}} = 3.7$ Hz), 124.35 (q, $J_{\text{C-F}} = 273.1$ Hz), 117.16, 110.24, 30.84.
 ^{19}F NMR (376 MHz, CDCl_3) δ -62.47.
HRMS m/z (EI-TOF): calculated for $\text{C}_{14}\text{H}_{12}\text{NF}_3$ $[\text{M}]^+$ 251.0922, found 251.0923.

6-Methyl-2-(trifluoromethyl)-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2r')



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 21% (20 mg) as a brown oil.

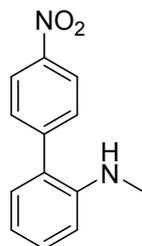
^1H NMR (400 MHz, CDCl_3) δ 8.22 (s, 1H), 8.13 (d, $J = 8.2$ Hz, 1H), 8.06 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.82 (dd, $J = 8.2, 0.9$ Hz, 1H), 7.57 (td, $J = 8.2, 1.4$ Hz, 1H), 7.39 (td, $J = 7.9, 1.1$ Hz, 1H), 7.35 (dd, $J = 8.2, 0.8$ Hz, 1H), 3.48 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.67, 136.97, 134.46 (q, $J_{\text{C-F}} = 33.1$ Hz), 133.44, 131.52, 125.82, 125.19, 124.97 (q, $J_{\text{C-F}} = 3.6$ Hz), 123.57, 123.42 (q, $J_{\text{C-F}} = 274.2$ Hz), 123.25, 122.85 (q, $J_{\text{C-F}} = 3.8$ Hz), 119.75, 33.13.

^{19}F NMR (376 MHz, CDCl_3) δ -62.96.

HRMS m/z (ESI-TOF): calculated for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{SF}_3$ $[\text{M}+\text{H}]^+$ 314.0463, found 314.0465.

N-Methyl-4'-nitro-[1,1'-biphenyl]-2-amine (2s)



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 64% (44 mg) as a yellow solid.

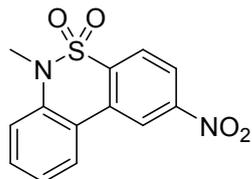
M. p.: 153-155 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.36 – 8.21 (m, 2H), 7.70 – 7.53 (m, 2H), 7.33 (td, $J = 8.3, 1.6$ Hz, 1H), 7.09 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.82 (td, $J = 7.4, 0.9$ Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 3.85 (br, 1H), 2.82 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.99, 146.86, 145.95, 130.39, 130.21, 130.10, 125.17, 124.29, 117.37, 110.52, 30.85.

HRMS m/z (EI-TOF): calculated for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 228.0899, found 228.0900.

6-Methyl-2-nitro-6H-dibenzo[c,e][1,2]thiazine 5,5-dioxide (2s')



Prepared according to the general procedure on 0.3 mmol scale and obtained an isolated yield of 9% (8 mg) as a yellow solid.

M. p.: 160-162 °C.

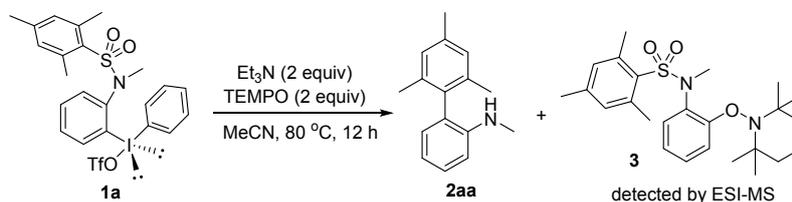
^1H NMR (400 MHz, CDCl_3) δ 8.84 (d, $J = 2.1$ Hz, 1H), 8.40 (dd, $J = 8.6, 2.1$ Hz, 1H), 8.18 (d, $J = 8.6$ Hz, 1H), 8.12 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.67 – 7.56 (m, 1H), 7.44 (td, $J = 7.9, 1.1$ Hz, 1H), 7.38 (dd, $J = 8.2, 0.9$ Hz, 1H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.17, 139.69, 138.58, 134.41, 132.05, 126.05, 125.42, 124.42, 122.90, 122.81, 121.06, 119.79, 33.26.

HRMS m/z (EI-TOF): calculated for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4\text{S}$ $[\text{M}]^+$ 290.0361, found 290.0360.

Part 5. Radical Trapping Experiments, EPR Experiments and Deuteration Experiment.

Radical trapping experiment:



To a Schlenk tube was added iodonium salts **1a** (0.3 mmol, 1 equiv.) and TEMPO (0.6 mmol, 2.0 equiv.). The tube was degassed with argon for three times. Acetonitrile (5 mL) and Et_3N (2 equiv) was added via syringe, and the mixture was stirred at $80\text{ }^\circ\text{C}$ in an oil bath for 12 h. After cooling to room temperature, a drop of the reaction mixture was delivered to ESI-MS analysis, and the remaining solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford the desired products **2aa** (37%).

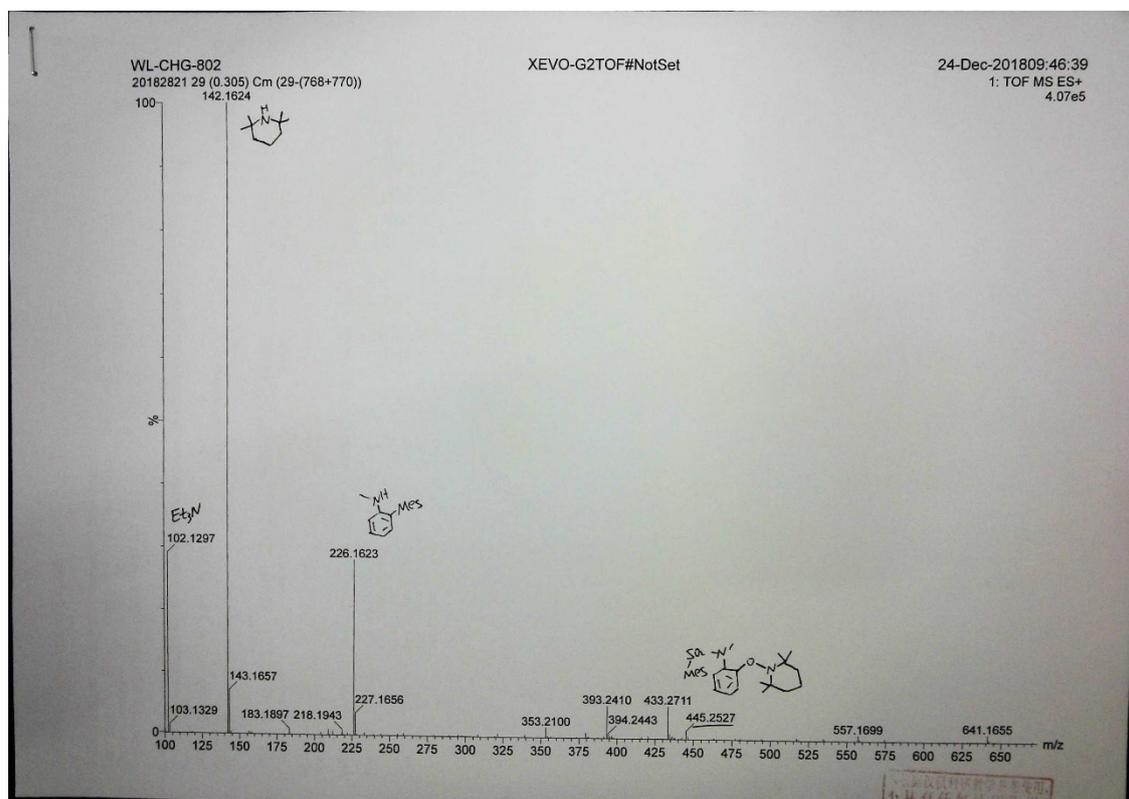


Figure 1. ESI-MS spectra of crude reaction mixture.

EPR experiment:

Line 1a: A 25 mL Schlenk tube equipped magnetic stir bar was charged with **1a** (0.1 mmol, 1.0 equiv), Et_3N (0.2 mmol, 2.0 equiv), PBN (0.2 mmol, 2.0 equiv), and MeCN (5 mL). EPR spectrum was recorded by Bruker EMX-8/2.7 EPR spectrometer immediately.

Line 1b: A 25 mL Schlenk tube equipped magnetic stir bar was charged with **1b** (0.1 mmol, 1.0 equiv), Et₃N (0.2 mmol, 2.0 equiv), PBN (0.2 mmol, 2.0 equiv), and MeCN (5 mL). EPR spectrum was recorded by Bruker EMX-8/2.7 EPR spectrometer immediately.

Line 1c: A 25 mL Schlenk tube equipped magnetic stir bar was charged with **1c** (0.1 mmol, 1.0 equiv), Et₃N (0.2 mmol, 2.0 equiv), PBN (0.2 mmol, 2.0 equiv), and MeCN (5 mL). EPR spectrum was recorded by Bruker EMX-8/2.7 EPR spectrometer immediately.

Line 1d: A 25 mL Schlenk tube equipped magnetic stir bar was charged with **1d** (0.1 mmol, 1.0 equiv), Et₃N (0.2 mmol, 2.0 equiv), PBN (0.2 mmol, 2.0 equiv), and MeCN (5 mL). EPR spectrum was recorded by Bruker EMX-8/2.7 EPR spectrometer immediately.

Line 1e: A 25 mL Schlenk tube equipped magnetic stir bar was charged with **1e** (0.1 mmol, 1.0 equiv), Et₃N (0.2 mmol, 2.0 equiv), PBN (0.2 mmol, 2.0 equiv), and MeCN (5 mL). EPR spectrum was recorded by Bruker EMX-8/2.7 EPR spectrometer immediately.

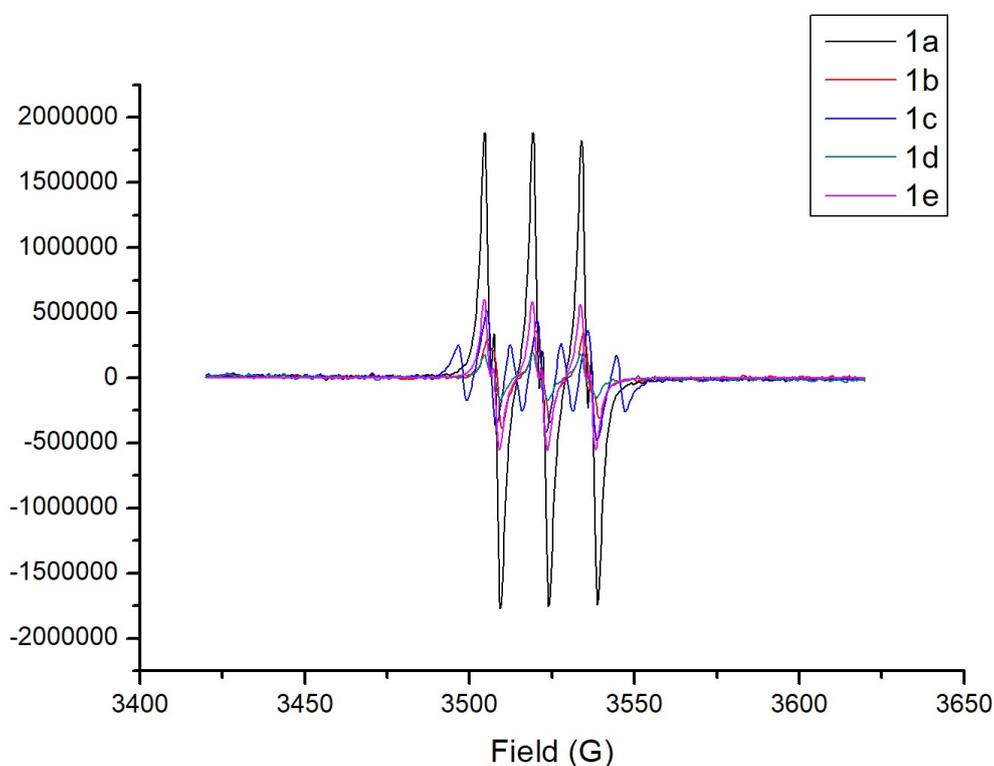


Figure 2. EPR Spectra of spin adducts generated in MeCN (5 mL) in the presence of iodonium salts **1** (0.1 mmol), Et₃N (0.2 mmol), and PBN (0.2 mmol) at room temperature. PBN = *α*-phenyl-*N-tert*-butylnitron.

Note: the multiple peaks in the case of **1c** may be ascribed to the existence of a considerable amount of stable 2,4,6-trimethoxyphenyl radicals.

Deuteration experiment:

To a Schlenk tube was added iodonium salts **1a** (0.3 mmol, 1 equiv.) and the tube was degassed with argon for three times. MeCN-*d*₃ (5 mL) and Et₃N (2 equiv) was added via syringe, and the mixture was stirred at 80 °C in

an oil bath for 12 h. After cooling to room temperature, the crude reaction mixture was directly delivered to ^1H NMR.

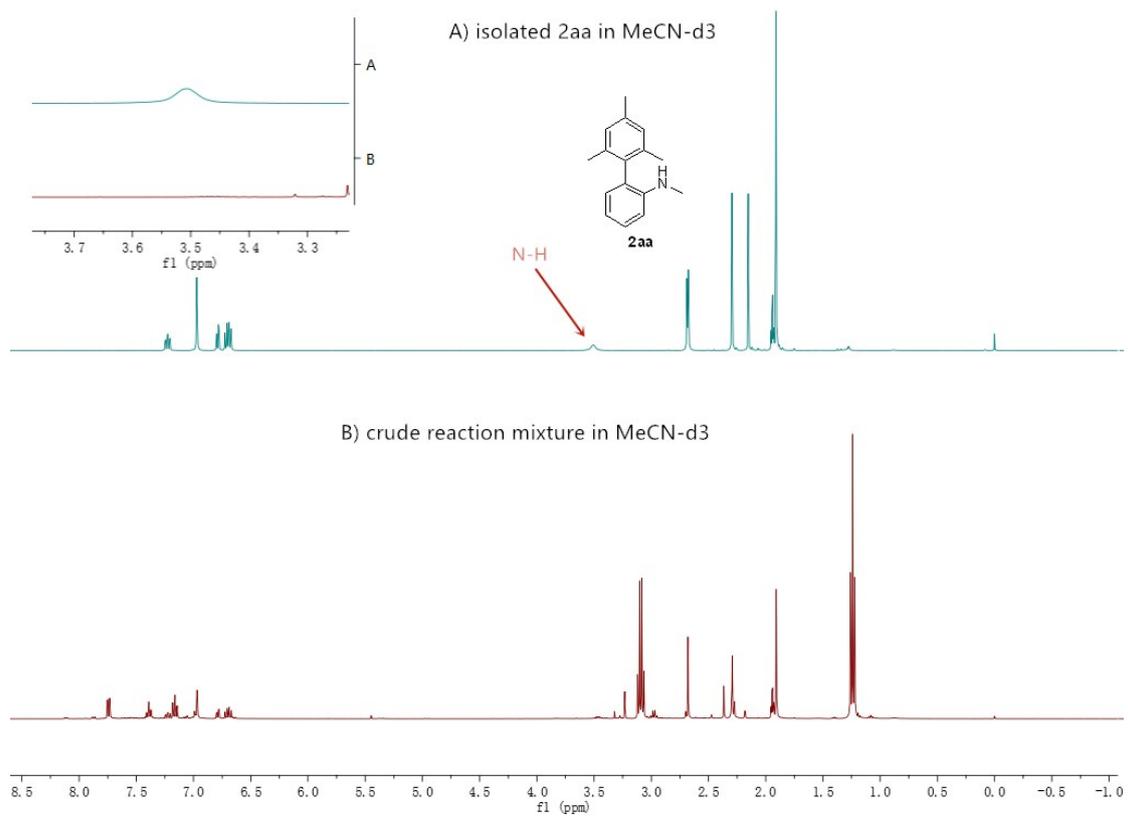
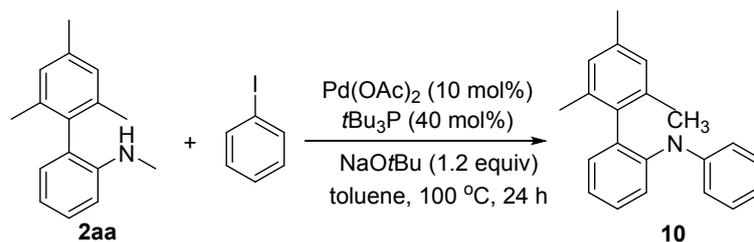


Figure 3. ^1H -NMR spectra of isolated product and crude reaction mixture .

Part 6. Derivatization of Products

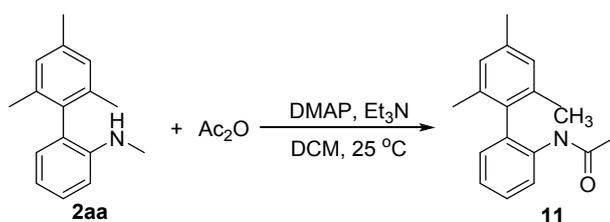


Following the modified procedure described by Bushby et al.⁵ An oven-dried screw cap test tube was charged with a magnetic stir bar, Pd(OAc)₂ (11 mg, 0.1 equiv.), NaOtBu (1.2 equiv.), and **2aa** (0.5 mmol, 1.0 equiv.). The tube was then evacuated and back-filled with argon. The evacuation/backfill sequence was repeated two additional times. Anhydrous toluene (2 mL) was added volumetrically followed by iodobenzene (2.0 equiv.) and tri-*tert*-butylphosphine (1M in toluene, 0.2 mL, 0.4 equiv.). The contents were heated at 100 °C for 24 h. The contents were allowed to cool and were treated with dilute (2 M) ammonium chloride and washed with a saturated solution of brine. The organic layer was separated and the aqueous extracted with ethyl acetate (3 x 25 mL). The organics were combined and dried with MgSO₄, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel. White solid, 105 mg, 70%. M. p.: 62-63 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.37 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.23 (td, *J* = 7.3, 1.4 Hz, 1H), 7.15 (ddd, *J* = 13.7, 7.0, 1.8 Hz, 3H), 6.87 (s, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 2.75 (s, 3H), 2.29 (s, 3H), 2.02 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 148.86, 147.55, 137.67, 136.68, 136.48, 136.43, 132.67, 128.70, 128.38, 127.98, 127.45, 125.09, 118.05, 115.02, 38.74, 21.15, 20.98.

HRMS *m/z* (EI-TOF): calculated for C₂₂H₂₃N [M]⁺ 301.1830, found 301.1832.



Amine **2aa** (0.5 mmol, 1.0 equiv) was dissolved in dichloromethane (5 mL) at 25 °C, followed by the addition of DMAP (0.2 equiv.) and Et₃N (1.5 equiv.). Ac₂O (1.5 equiv.) was added dropwise and the mixture was stirred for 24 h. The reaction was quenched with dilute hydrochloric acid (2M, 50 mL) and the mixture was extracted with CH₂Cl₂ for 3 times. The combined organic extracts were dried with Na₂SO₄, filtered, and the solvent was removed by rotary evaporation. Purification of the crude product by flash chromatography on silica gel afforded the *N*-acetyl amine **11** as a white solid (132 mg, 99% yield).

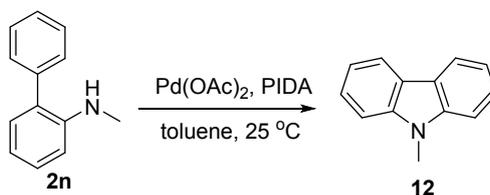
M. p.: 111-112 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.32 (m, 2H), 7.24 – 7.12 (m, 2H), 6.91 (d, *J* = 6.7 Hz, 2H), 2.83 (s, 0.29H), 2.75 (s, 2.75H), 2.32 (s, 0.37H), 2.30 (s, 2.58H), 2.06 (s, 0.30H), 2.01 (s, 2.67H), 1.99 (s, 0.71H), 1.97 (s, 5.32H).

¹³C NMR (101 MHz, CDCl₃) δ 170.73, 142.60, 138.31, 137.40, 135.90, 135.86, 135.03, 132.37, 128.86, 128.65, 128.58, 128.18, 127.85, 35.32, 22.59, 21.08, 20.44.

Note: two rotamers are visible due to restricted rotation of the amide bond.

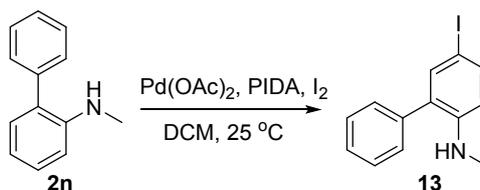
HRMS m/z (EI-TOF): calculated for C₁₈H₂₁NO [M]⁺ 267.1623, found 267.1625.



Following the modified procedure described by Gaunt et al.⁶ The biarylamine **2n** (0.5 mmol, 1.0 equiv) and Pd(OAc)₂ (10 mol%) were stirred in toluene (5 mL) under Ar atmosphere at 25 °C for 1 h. Phenylidonium diacetate (PIDA, 1.2 equiv) was then added and the reaction mixture was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel. White solid, 64 mg, 71%. Spectral data is consistent with that of previously reported.⁶

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.50 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.26 (td, *J* = 7.8, 0.9 Hz, 2H), 3.86 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 141.11, 125.79, 122.89, 120.42, 118.95, 108.54, 29.16.

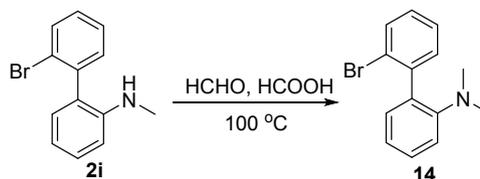


The biarylamine **2n** (0.5 mmol, 1.0 equiv), Pd(OAc)₂ (10 mol%), PIDA (1.0 equiv), and I₂ (1.0 equiv) were stirred in DCM (5 mL) under air atmosphere at 25 °C for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel. Light yellow oil, 100 mg, 65%.

¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.45 (dd, *J* = 10.4, 4.3 Hz, 2H), 7.36 (ddd, *J* = 6.6, 4.6, 2.0 Hz, 4H), 6.45 (d, *J* = 8.6 Hz, 1H), 3.99 (br, 1H), 2.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.97, 138.09, 138.03, 137.32, 130.03, 129.32, 129.14, 127.81, 112.09, 77.61, 30.71.

HRMS m/z (EI-TOF): calculated for C₁₃H₁₂I₂N [M]⁺ 309.0014, found 309.0013.



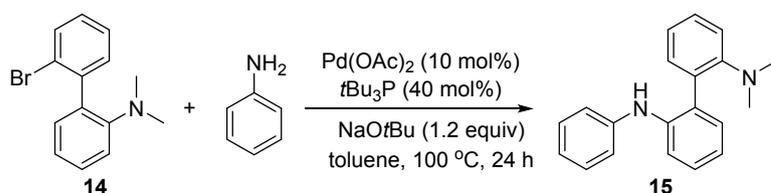
HCOOH (2.5 mL) was added to a stirred solution of **2i** (0.5 mmol) in HCHO (37%, 1.75 mL), and the mixture was kept at reflux overnight, cooled, neutralized with a saturated solution of NaHCO₃, and extracted with EtOAc. The combined organic extracts were dried with Na₂SO₄, filtered, and the solvent was removed by rotary evaporation. Purification of the crude product by flash chromatography on silica gel afforded **14** as a white solid (125 mg, 91% yield).

M. p.: 59-61 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.21 – 7.11 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 2.54 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 151.62, 142.66, 133.84, 133.09, 132.02, 131.96, 128.84, 128.30, 127.28, 124.03, 121.00, 118.02, 43.35.

HRMS *m/z* (EI-TOF): calculated for C₁₄H₁₄BrN [M]⁺ 275.0310, found 275.0310.



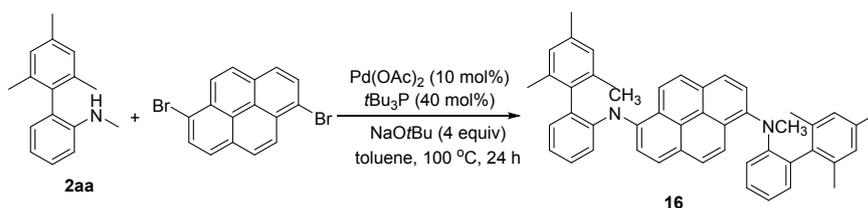
An oven-dried screw cap test tube was charged with a magnetic stir bar, Pd(OAc)₂ (11 mg, 0.1 equiv.), NaOtBu (1.2 equiv.), and **14** (0.5 mmol, 1.0 equiv.). The tube was then evacuated and back-filled with argon. The evacuation/backfill sequence was repeated two additional times. Anhydrous toluene (2 mL) was added volumetrically followed by aniline (5.0 equiv.) and tri-*tert*-butylphosphine (1M in toluene, 0.2 mL, 0.4 equiv.). The contents were heated at 100 °C for 24 h. The contents were allowed to cool and were treated with dilute (2 M) ammonium chloride and washed with a saturated solution of brine. The organic layer was separated and the aqueous extracted with ethyl acetate (3 x 25 mL). The organics were combined and dried with MgSO₄, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel. White solid, 130 mg, 90%.

M. p.: 106-108 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.64 (br, 1H), 7.44 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.34 – 7.25 (m, 3H), 7.25 – 7.19 (m, 1H), 7.19 – 7.11 (m, 2H), 7.10 – 7.00 (m, 2H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.90 (dd, *J* = 8.5, 0.9 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 2.65 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 150.58, 144.11, 141.04, 133.95, 133.48, 132.66, 131.70, 129.28, 128.43, 127.85, 122.51, 121.30, 119.76, 117.54, 117.46, 117.32, 43.30, 43.26.

HRMS *m/z* (EI-TOF): calculated for C₂₀H₂₀N₂ [M]⁺ 288.1626, found 288.1625.



Following the modified procedure described by Bushby et al.⁵ An oven-dried screw cap test tube was charged with a magnetic stir bar, Pd(OAc)₂ (11 mg, 0.1 equiv.), NaOtBu (4 equiv.), **2aa** (2 equiv.), and 1,6-dibromopyrene (0.5 mmol, 1.0 equiv.). The tube was then evacuated and back-filled with argon. The evacuation/backfill sequence was repeated two additional times. Anhydrous toluene (2 mL) was added volumetrically followed by tri-*tert*-butylphosphine (1M in toluene, 0.2 mL, 0.4 equiv.). The contents were heated at 100 °C for 24 h. The contents were allowed to cool and were treated with dilute (2 M) ammonium chloride and washed with a saturated solution of brine. The organic layer was separated and the aqueous extracted with ethyl acetate (3 x 25 mL). The organics were combined and dried with MgSO₄, and the solvent was removed under reduced

pressure. The crude product was purified by column chromatography on silica gel. Green solid, 260 mg, 80%.

M. p.: 278-280 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 9.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 9.2 Hz, 2H), 7.54 (d, J = 7.7 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.13 (t, J = 6.9 Hz, 2H), 6.98 (dd, J = 7.4, 1.4 Hz, 2H), 6.21 (s, 4H), 3.34 (s, 6H), 1.69 (s, 6H), 1.63 (s, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.31, 145.74, 136.87, 135.94, 135.54, 135.21, 131.85, 128.37, 127.79, 127.63, 127.20, 126.10, 125.33, 124.45, 124.26, 122.39, 122.11, 119.95, 43.75, 20.62, 20.31.

HRMS m/z (EI-TOF): calculated for $\text{C}_{48}\text{H}_{44}\text{N}_2$ $[\text{M}]^+$ 648.3504, found 648.3503.

Part 7. References

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Part 8. ^1H , ^{13}C , and ^{19}F NMR spectra of Products

