

Supporting Information

**Curtius-Like Rearrangement of Iron-Nitrenoid Complex and
Application in Biomimetic Synthesis of Bisindolylmethanes**

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List of Supporting Information

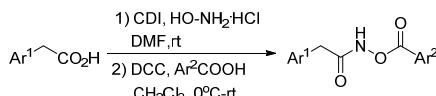
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1. General Information

All reactions were performed in oven-dried round-bottom flasks. CH_2Cl_2 was refluxed with CaH_2 . All reagents were used from commercial sources without further purifications, unless otherwise noted. The silica gel (200-300 meshes) was used for column chromatography. Thin layer chromatographies (TLC) were carried out on GF254 plates (0.25 mm layer thickness). Visualization of the developed chromatogram was performed by fluorescence quenching or by ceric ammonium molybdate stain. Yields reported were for isolated, spectroscopically pure compounds.

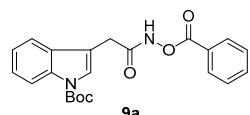
^1H NMR and ^{13}C NMR experiments were performed on Bruker AM-400 spectrometer at ambient temperature. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data were presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). Chemical shifts (δ) were given in ppm with reference to solvent signals [^1H NMR: CDCl_3 (7.26), Acetone-*d*6 (2.05); ^{13}C NMR: CDCl_3 (77.16), Acetone-*d*6 (29.84, 206.26)]. The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. HRMS (ESI) was taken on Agilent 6540 Q-TOF spectrometer.

2. Preparation of acyl hydroxamates



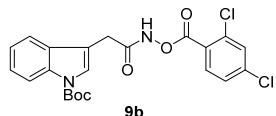
At room temperature, CDI (2 eq.) was added to a solution of carboxylic acids (1 eq.) in DMF (2 mL/mmol). The reaction mixture was stirred for 0.5 h and then $\text{HO-NH}_2\text{HCl}$ (4 eq.) was added. After being stirred for overnight at room temperature, H_2O was added and the reaction system was stirred for another 15 min, and then diluted with EtOAc and water. The aqueous phase was extracted with EtOAc three times and the combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo to afford the crude product hydroxamates.

To a solution of the obtained hydroxamates (1 eq.) and benzoic acids (1 eq.) in CH_2Cl_2 (10 mL/mmol), DCC (1 eq.) in CH_2Cl_2 (3 mL/mmol) was added dropwise at 0 °C. After being stirred for 1.0 h, the reaction mixture was diluted by Et_2O (15 mL/mmol). The byproduct precipitated out and was removed by filtration. CH_2Cl_2 was removed under vacuum and the residue was purified by silica gel flash column chromatography (petroleum ether / acetone = 6 : 1) to afford acyl hydroxamates.

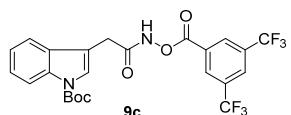


Compound 9a. White foam in 210 mg, 86% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.27 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.66-7.58 (m, 3H), 7.44 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 3.82 (s, 2H),

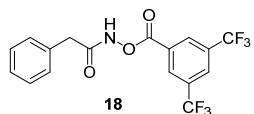
1.67 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 164.8, 149.6, 135.7, 134.4, 130.1, 129.7, 128.8, 126.6, 125.2, 125.1, 123.1, 119.2, 115.5, 112.1, 84.1, 30.8, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$, 417.1421, found 417.1425.



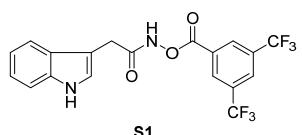
Compound 9b. White powder in 1.29 g, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.16 (br s, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.65 (s, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 1.2$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.31-7.26 (m, 2H), 3.82 (s, 2H), 1.67 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 162.8, 149.6, 140.1, 135.9, 135.7, 133.1, 131.4, 129.7, 127.4, 125.3, 125.2, 124.7, 123.2, 119.1, 115.6, 111.8, 84.2, 30.8, 28.3. $\text{C}_{22}\text{H}_{20}\text{C}_{12}\text{N}_2\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$, 485.0641, found 485.0642.



Compound 9c. White powder in 2.87 g, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.23 (br s, 1H), 8.46 (s, 2H), 8.14 (d, $J = 8.0$ Hz, 1H), 8.10 (s, 1H), 7.66 (s, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 3.84 (s, 2H), 1.67 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 162.5, 149.6, 135.7, 133.2, 132.9, 132.6, 132.2, 130.2, 130.2, 129.5, 128.9, 127.7, 127.7, 127.7, 127.6, 125.3, 125.3, 124.1, 123.3, 121.3, 119.1, 115.6, 111.7, 84.4, 30.7, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{24}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$, 553.1169, found 553.1172.

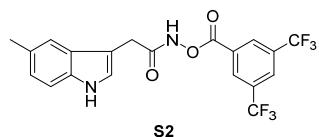


Compound 18. White powder in 1.15 g, 90% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.93 (br s, 1H), 8.50 (s, 2H), 8.13 (s, 1H), 7.42-7.34 (m, 5H), 3.75 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.6, 133.3, 133.0, 132.7, 132.6, 132.3, 130.2, 129.5, 129.4, 129.0, 128.1, 127.8, 127.8, 127.7, 124.1, 121.4, 41.0. HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_6\text{NO}_3 [\text{M}+\text{H}]^+$, 392.0716, found 392.0719.

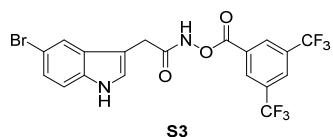


Compound S1. White powder in 2.99 g, 70 % yield. ^1H NMR (400 MHz, Acetone- d_6) δ 10.19 (br s, 1H), 8.57 (s, 2H), 8.43 (s, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.36 (s, 1H), 7.12 (t, $J = 8.0$ Hz, 1H), 7.05 (t, $J = 8.0$ Hz, 1H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 170.0, 163.1, 137.6, 133.5, 133.1, 132.8, 132.4, 131.1, 130.82, 130.78, 128.4, 128.4, 128.35, 128.3, 125.2, 125.0, 124.8, 122.5, 122.4,

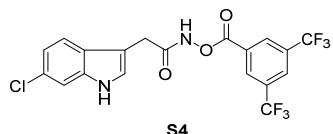
119.8, 119.6, 112.2, 112.1, 108.2, 30.4; HR-ESI-MS (*m/z*): calcd. for C₁₉H₁₃F₆N₂O₃ [M+H]⁺, 431.0825, found 431.0821.



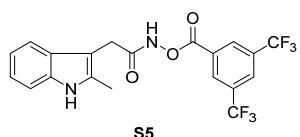
Compound S2. White powder in 1.09 g, 73 % yield. ¹H NMR (400 MHz, Acetone-*d*₆): δ 11.12 (br s, 1H), 10.06 (br s, 1H), 8.57 (s, 2H), 8.43 (s, 1H), 7.46 (s, 1H), 7.31-7.27 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, Acetone-*d*₆) δ 170.1, 163.1, 136.0, 133.5, 133.1, 132.8, 132.4, 131.1, 130.8, 130.8, 128.7, 128.6, 128.4, 125.3, 125.1, 124.9, 124.0, 122.5, 119.2, 111.9, 111.9, 107.7, 30.4, 21.7; HR-ESI-MS (*m/z*): calcd. for C₂₀H₁₅F₆N₂O₃ [M+H]⁺, 445.0981, found 445.0981.



Compound S3. White powder in 1.69 g, 86 % yield. ¹H NMR (400 MHz, Acetone-*d*₆) δ 11.22 (br s, 1H), 10.40 (br s, 1H), 8.57 (s, 2H), 8.43 (s, 1H), 7.87 (s, 1H), 7.42 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.84 (s, 2H); ¹³C NMR (100 MHz, Acetone-*d*₆) δ 169.7, 163.1, 136.2, 136.1, 133.5, 133.1, 132.8, 132.5, 131.0, 130.9, 130.8, 130.2, 128.42, 128.39, 128.35, 126.7, 126.5, 125.2, 125.0, 122.5, 122.3, 114.1, 114.0, 112.8, 108.2, 30.0; HR-ESI-MS (*m/z*): calcd. for C₁₉H₁₁BrF₆N₂O₃Na [M+Na]⁺, 530.9749, found 530.9747.

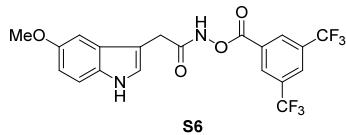


Compound S4. White powder in 1.46 g, 80 % yield. ¹H NMR (400 MHz, Acetone-*d*₆) δ 11.23 (br s, 1H), 10.34 (br s, 1H), 8.57 (s, 2H), 8.43 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 1.3 Hz, 1H), 7.40 (s, 1H), 7.07-7.05 (m, 1H), 3.84 (s, 2H); ¹³C NMR (100 MHz, Acetone-*d*₆) δ 169.8, 163.1, 137.9, 133.5, 133.1, 132.8, 132.5, 131.0, 130.8, 130.8, 128.8, 127.9, 127.2, 126.1, 126.0, 125.2, 122.5, 121.0, 120.2, 112.02, 111.97, 108.7, 30.2; HR-ESI-MS (*m/z*): calcd. for C₁₉H₁₂ClF₆N₂O₃ [M+H]⁺, 465.0435, found 465.0437.



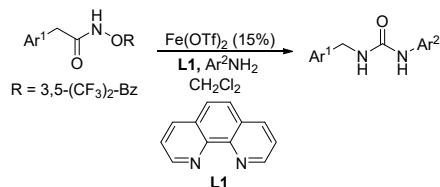
Compound S5. White powder in 0.996 g, 76% yield. ¹H NMR (400 MHz, Acetone-*d*₆)

δ 11.02 (br s, 1H), 10.04 (br s, 1H), 8.54 (s, 2H), 8.41 (s, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 3.79 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 170.1, 163.1, 136.5, 134.7, 133.4, 133.1, 132.8, 132.4, 131.0, 130.8, 130.7, 129.6, 128.4, 128.3, 128.3, 127.9, 125.2, 122.5, 121.5, 119.7, 118.7, 111.2, 103.9, 29.3, 11.7; HR-ESI-MS (m/z): calcd. for $\text{C}_{20}\text{H}_{15}\text{F}_6\text{N}_2\text{O}_3$ [M+H] $^+$, 445.0981, found 445.0982.

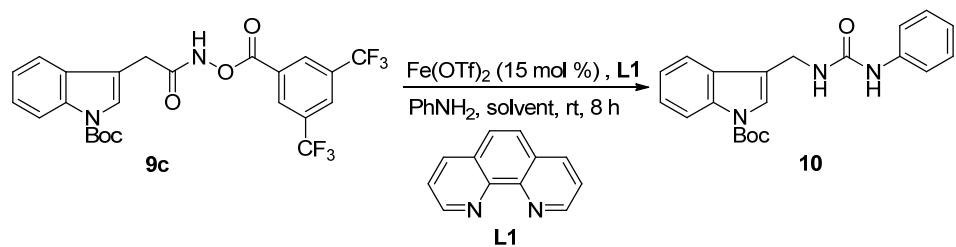


Compound S6. White powder in 0.71 g, 71% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 11.11 (br s, 1H), 10.04 (br s, 1H), 8.57 (s, 2H), 8.43 (s, 1H), 7.31-7.28 (m, 2H), 7.21 (s, 1H), 6.78 (dd, J = 8.0, 2.2 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 2H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 163.1, 155.0, 133.5, 133.1, 132.8, 132.5, 131.1, 130.8, 130.8, 128.79, 128.75, 128.39, 128.36, 128.32, 125.6, 125.5, 125.2, 122.5, 112.9, 112.8, 112.7, 107.9, 101.3, 55.9, 30.4; HR-ESI-MS (m/z): calcd. for $\text{C}_{20}\text{H}_{15}\text{F}_6\text{N}_2\text{O}_4$ [M+H] $^+$, 461.0931, found 461.0931.

3. Iron(II)-Catalyzed Curtius-like Rearrangement



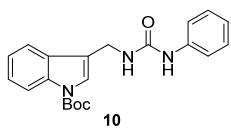
A solution of $\text{Fe}(\text{OTf})_2$ (0.015 mmol) and **L1** (0.03 mmol) in CH_2Cl_2 (2 mL) was stirred for 0.5 h, after which time the resulting catalyst system was added to a solution of acyl hydroxamates (0.1 mmol) and anilines (0.2 mmol) in CH_2Cl_2 (2 mL) at room temperature. After being stirred for 8-20 h when all the starting material acyl hydroxamates was fully consumed, the reaction was quenched with saturated NaHCO_3 aqueous solution, and the aqueous phase was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether / acetone = 6 : 1) to give ureas .

Table S1. Solvents Optimization

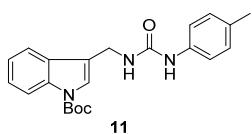
entry	solvent	conversion (%)	yield (%)
1	toluene	100	33
2	CH₂Cl₂	100	85
3	THF	100	57
4	dioxane	100	41
5	MeCN	100	57
6	TFE	100	69
7	HFIP	100	69
8	DMF	100	65
9	DMSO	100	65

Table S2. Catalysts Optimization

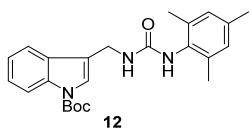
entry	Catalyst	conversion (%)	yield (%)
1	-	0	0
2	Fe(OTf)₂	100	85
3	FeCl ₂	100	61
4	FeBr ₂	100	51
5	Fe(OAc) ₂	100	53
6	FeSO ₄	60	51
7	K ₄ Fe(CN) ₆	<1	trace
8	Fe(NTf ₂) ₂	5	4
9	Zn(OTf) ₂	0	0
10	Sc(OTf) ₃	0	0



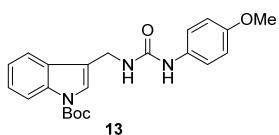
Compound 10. Reaction time: 8 h. White powder in 30.9 mg, 85% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.47 (s, 1H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.24-7.18 (m, 5H), 7.06-7.03 (m, 1H), 6.81 (s, 1H), 5.25 (t, $J = 4.0$ Hz, 1H), 4.50 (d, $J = 4.0$ Hz, 2H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 149.7, 138.4, 135.8, 129.4, 129.3, 124.8, 124.2, 124.0, 122.9, 121.5, 119.3, 118.0, 115.4, 84.0, 35.7, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}]^+$, 366.1812, found 366.1815.



Compound 11. Reaction time: 8 h. White powder in 32.0 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.44 (s, 1H), 7.28 (t, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.84 (s, 1H), 5.35 (t, $J = 4.0$ Hz, 1H), 4.45 (d, $J = 4.0$ Hz, 2H), 2.25 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 149.7, 135.8, 135.7, 134.0, 129.9, 129.4, 124.8, 123.9, 122.9, 122.0, 119.3, 118.2, 115.4, 83.9, 35.7, 28.3, 20.9. HR-ESI-MS (m/z): calcd. for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_3\text{Na}$ [$\text{M}+\text{Na}]^+$, 402.1788, found 402.1782.

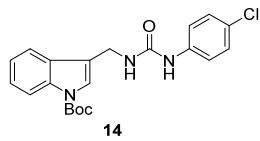


Compound 12. Reaction time: 8 h. White powder in 31.8 mg, 78% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.41 (s, 1H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 6.86 (s, 2H), 5.90 (s, 1H), 4.52 (s, 3H), 2.23 (s, 3H), 2.18 (s, 6H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.0, 149.7, 137.9, 137.2, 135.8, 131.1, 129.6, 129.3, 124.8, 123.7, 122.8, 119.5, 118.6, 115.3, 83.7, 35.7, 28.3, 21.0, 18.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{24}\text{H}_{30}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}]^+$, 408.2282, found 408.2287.

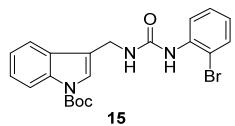


Compound 13. Reaction time: 8 h. White powder in 34.2 mg, 87% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.47 (s, 1H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.79 (d, $J =$

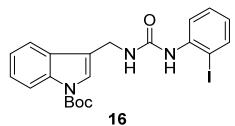
8.0 Hz, 2H), 6.39 (s, 1H), 5.00 (br s, 1 H), 4.51 (d, $J = 5.3$ Hz, 2H), 3.75 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.3, 156.6, 149.7, 135.8, 130.7, 129.4, 125.2, 124.8, 124.0, 122.9, 119.4, 118.3, 115.4, 114.8, 83.9, 55.6, 35.8, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}_4$ [$\text{M}+\text{H}]^+$, 396.1918, found 396.1922.



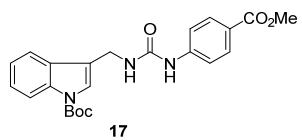
Compound 14. Reaction time: 8 h. White powder in 32.2 mg, 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.41 (s, 1H), 7.27 (t, $J = 8.0$ Hz, 1H), 7.15 (t, $J = 8.0$ Hz, 1H), 7.10 (s, 4H), 6.87 (s, 1H), 5.31 (t, $J = 4.0$ Hz, 1H), 4.37 (d, $J = 4.0$ Hz, 2H), 1.62 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.0, 149.7, 137.2, 135.7, 129.2, 128.7, 124.9, 123.9, 122.9, 121.8, 119.1, 117.8, 115.5, 84.1, 35.7, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{21}\text{H}_{22}\text{ClN}_3\text{O}_3\text{Na}$ [$\text{M}+\text{Na}]^+$, 422.1242, found 422.1243.



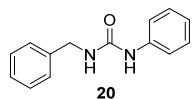
Compound 15. Reaction time: 8 h. White powder in 35.7 mg, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 1H), 8.01 (dd, $J = 8.0, 0.9$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.55 (s, 1H), 7.48 (dd, $J = 8.0, 0.9$ Hz, 1H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.27-7.22 (m, 2H), 6.93-6.89 (m, 1H), 6.79 (s, 1H), 5.21 (br s, 1H), 4.57 (d, $J = 4.0$ Hz, 2H), 1.65 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 149.7, 136.6, 135.9, 132.6, 129.3, 128.5, 124.9, 124.8, 124.3, 123.0, 122.7, 119.3, 117.6, 115.5, 114.6, 84.0, 36.1, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{21}\text{H}_{23}\text{BrN}_3\text{O}_3$ [$\text{M}+\text{H}]^+$, 444.0917, found 444.0921.



Compound 16. Reaction time: 8 h. White powder in 37.5 mg, 77% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.53 (s, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.27-7.20 (m, 2H), 6.78-6.76 (m, 2H), 5.41 (br s, 1H), 4.54 (d, $J = 4.0$ Hz, 2H), 1.65 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 149.7, 139.3, 139.2, 135.8, 129.4, 129.3, 125.7, 124.9, 124.2, 123.3, 122.9, 119.4, 117.8, 115.5, 92.1, 84.0, 36.0, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{21}\text{H}_{23}\text{IN}_3\text{O}_3$ [$\text{M}+\text{H}]^+$, 492.0779, found 492.0779.

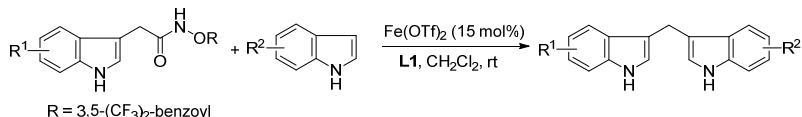


Compound 17. Reaction time: 8 h. White powder in 33.0 mg, 79% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.51 (s, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.41 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.27-7.23 (m, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 5.72 (t, $J = 4.0$ Hz, 1H), 4.41 (d, $J = 4.0$ Hz, 2H), 3.81 (s, 3H), 1.61 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 155.3, 149.7, 143.6, 135.7, 131.0, 129.2, 124.9, 124.0, 122.9, 119.1, 118.2, 117.7, 115.4, 84.1, 52.1, 35.6, 28.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{23}\text{H}_{26}\text{N}_3\text{O}_5$ [$\text{M}+\text{H}]^+$, 424.1867, found 424.1872.

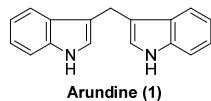


Compound 20. Reaction time: 20 h. White powder in 11.6 mg, 51% yield. ^1H NMR (400 MHz, Acetone-*d*6) δ 8.00 (s, 1H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.36-7.29 (m, 4H), 7.24-7.19 (m, 3H), 6.91 (t, $J = 8.0$ Hz, 1H), 6.21 (br s, 1H), 4.41 (d, $J = 4.0$ Hz, 2H). ^{13}C NMR (100 MHz, Acetone-*d*6) δ 156.1, 141.6, 141.4, 129.4, 129.2, 128.2, 127.6, 122.2, 118.9, 118.8, 44.1. HR-ESI-MS (m/z): calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}$ [$\text{M}+\text{H}]^+$, 227.1179, found 227.1185.

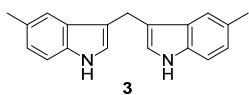
4. Biomimetic Synthesis of Bisindolylmethanes



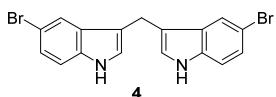
A solution of $\text{Fe}(\text{OTf})_2$ (0.015 mmol) and **L1** (0.03 mmol) in CH_2Cl_2 (2 mL) was stirred for 0.5 h, after which time the resulting catalyst system solution was added to a solution of acyl hydroxamates (0.1 mmol) and indoles (0.2 mmol) in CH_2Cl_2 (2 mL) at room temperature. After being stirred for 5 h when all the starting material acyl hydroxamates was fully consumed. the reaction was quenched with saturated NaHCO_3 aqueous solution, and the aqueous phase was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether / EtOAc = 6 : 1) to give bisindolylmethanes.



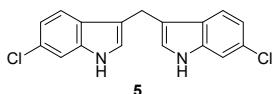
Arundine (1). Slightly red powder in 17.8 mg, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (br s, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.20 (t, $J = 8.0$ Hz, 2H), 7.10 (t, $J = 8.0$ Hz, 2H), 6.94 (s, 2H), 4.25 (s, 2H); ^{13}C NMR (100 MHz, Acetone-*d*6) δ 137.9, 128.7, 123.5, 121.9, 119.7, 119.2, 115.8, 112.0, 21.9; HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{K}$ [$\text{M}+\text{K}]^+$, 285.0789, found 285.0799.



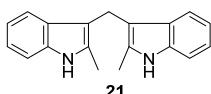
Compound 3. Slightly red powder in 19.3 mg, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (br s, 2H), 7.41 (s, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.86 (s, 2H), 4.17 (s, 2H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.9, 128.5, 127.9, 123.6, 122.6, 119.0, 115.3, 110.8, 21.6, 21.3; HR-ESI-MS (m/z): calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{K}[\text{M}+\text{K}]^+$, 313.1102, found 313.1101.



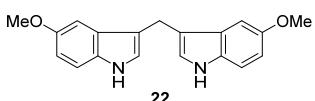
Compound 4. Slightly red powder in 29.6 mg, 73% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (br s, 2H), 7.74 (s, 2H), 7.32-7.28 (m, 4H), 6.99 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.2, 129.3, 125.0, 123.6, 121.9, 115.0, 112.7, 21.2. HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{11}\text{Br}_2\text{N}_2[\text{M}-\text{H}]^-$, 400.9294, found 400.9292.



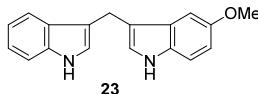
Compound 5. Slightly red powder in 23.7 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (br s, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 1.4$ Hz, 2H), 7.05 (dd, $J = 8.0, 1.6$ Hz, 2H), 6.92 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 128.1, 126.2, 122.9, 120.2, 115.7, 111.2, 21.3; HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{11}\text{Cl}_2\text{N}_2[\text{M}-\text{H}]^-$, 313.0305, found 313.0307.



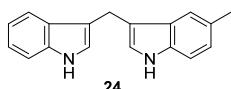
Compound 21. Slightly red powder in 18.1 mg, 66% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 9.75 (br s, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.93 (t, $J = 8.0$ Hz, 2H), 6.83 (t, $J = 7.4$ Hz, 2H), 4.09 (s, 2H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 136.6, 131.9, 130.1, 120.9, 119.0, 118.96, 111.2, 111.0, 19.9, 11.9; HR-ESI-MS (m/z): calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{K}[\text{M}+\text{K}]^+$, 313.1102, found 313.1102.



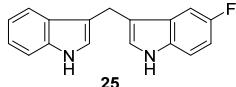
Compound 22. Slightly red powder in 20.7 mg, 68% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (br s, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 2.1$ Hz, 2H), 6.93 (s, 2H), 6.88 (dd, $J = 8.0, 2.3$ Hz, 2H), 4.19 (s, 2H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 131.8, 128.1, 123.2, 115.5, 112.2, 111.9, 101.2, 56.1, 21.4; HR-ESI-MS (m/z): calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{K}[\text{M}+\text{K}]^+$, 345.1000, found 345.0999.



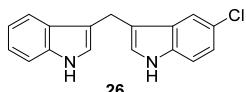
Compound 23. Slightly red powder in 19.7 mg, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (br s, 1H), 7.82 (br s, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.28 (s, 1H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 2.2$ Hz, 1H), 6.95 (br s, 2H), 6.88 (dd, $J = 8.0, 2.3$ Hz, 1H), 4.24 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 136.6, 131.7, 128.1, 127.7, 123.2, 122.3, 122.1, 119.4, 119.3, 115.8, 115.5, 112.2, 111.9, 111.2, 101.2, 56.1, 21.4; HR-ESI-MS (m/z): calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{OK} [\text{M}+\text{K}]^+$, 315.0894, found 315.0895.



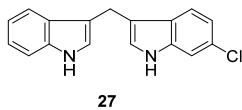
Compound 24. Slightly red powder in 19.3 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (br s, 1H), 7.80 (br s, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.44 (s, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.28 (s, 1H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 8.0, 2$ Hz), 4.27-4.21 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 134.9, 128.5, 127.9, 127.7, 123.6, 122.5, 122.3, 122.0, 119.4, 119.3, 119.0, 115.9, 115.2, 111.2, 110.8, 21.6, 21.3; HR-ESI-MS (m/z): calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{K} [\text{M}+\text{K}]^+$, 299.0945, found 299.0945.



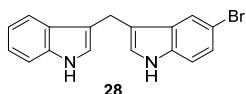
Compound 25. Slightly red powder in 19.0 mg, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (m, 2H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.25-7.22 (m, 2H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.99 (s, 1H), 6.95 (s, 1H), 6.91 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 156.6, 136.6, 133.1, 127.6, 124.1, 122.3, 122.1, 119.4, 119.3, 115.4, 111.8, 111.7, 111.2, 110.5, 110.3, 104.4, 104.2, 21.4; HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{12}\text{FN}_2 [\text{M}-\text{H}]^-$, 263.0990, found 263.0990.



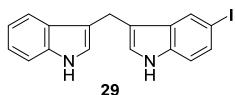
Compound 26. Slightly red powder in 20.0 mg, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (br s, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 3.4$ Hz, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.14-7.07 (m, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 134.9, 128.8, 127.6, 125.1, 123.7, 122.4, 122.3, 122.2, 119.4, 119.3, 118.9, 115.7, 115.4, 112.2, 111.2, 21.3; HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{13}\text{ClN}_2\text{K} [\text{M}+\text{K}]^+$, 319.0399, found 319.0405.



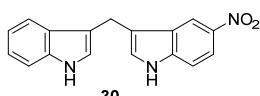
Compound 27. Slightly red powder in 24.0 mg, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (m, 2H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 1.4$ Hz, 1H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.10 (t, $J = 8.0$ Hz, 1H), 7.05 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.93 (s, 2H), 4.22 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 136.6, 128.0, 127.6, 126.3, 123.0, 122.3, 122.2, 120.3, 120.1, 119.4, 119.3, 116.0, 115.5, 111.2, 111.1, 21.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{13}\text{ClN}_2\text{K} [\text{M}+\text{K}]^+$, 319.0399, found 319.0396.



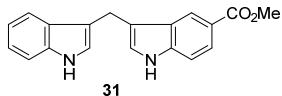
Compound 28. Slightly red powder in 23.0 mg, 77% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (br s, 2H), 7.77 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.31-7.21 (m, 3H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.97 (br s, 2H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 135.2, 129.5, 127.6, 124.9, 123.6, 122.3, 122.2, 122.0, 119.4, 119.3, 115.6, 115.3, 112.7, 112.6, 111.3, 21.3. HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{13}\text{BrN}_2\text{K} [\text{M}+\text{K}]^+$, 362.9894, found 362.9893.



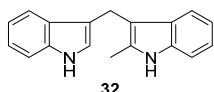
Compound 29. Slightly red powder in 25.2 mg, 68% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 10.16 (br s, 1H), 9.96 (br s, 1H), 7.94 (d, $J = 0.6$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.38-7.33 (m, 2H), 7.25 (d, $J = 8.5$ Hz, 1H), 7.15-7.12 (m, 2H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.96 (t, $J = 8.0$ Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 137.9, 136.9, 131.4, 130.1, 128.6, 128.5, 124.8, 123.5, 122.0, 119.7, 119.3, 115.4, 114.5, 112.1, 82.2, 21.7. HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{13}\text{IN}_2\text{K} [\text{M}+\text{K}]^+$, 410.9755, found 410.9755.



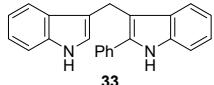
Compound 30. Slightly red powder in 14.4 mg, 50% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 10.68 (br s, 1H), 10.02 (br s, 1H), 8.57 (d, $J = 2.0$ Hz, 1H), 8.01 (dd, $J = 8.0, 2.2$ Hz, 1H), 7.56 (t, $J = 8.0$ Hz, 2H), 7.40 (s, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.21 (s, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.96 (t, $J = 8.0$ Hz, 1H), 4.33 (s, 2H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 141.8, 140.9, 137.9, 128.5, 127.9, 127.3, 123.6, 122.1, 119.6, 119.4, 118.9, 117.4, 116.9, 115.0, 112.4, 112.2, 21.7; HR-ESI-MS (m/z): calcd. for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2\text{K} [\text{M}+\text{K}]^+$, 330.0639, found 330.0639.



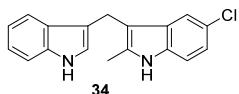
Compound 31. Slightly red powder in 20.0 mg, 66% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 10.33 (br s, 1H), 9.96 (br s, 1H), 8.36 (s, 1H), 7.79 (dd, J = 8.0, 1.5 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.11 (s, 1H), 7.08 (t, J = 8.0 Hz, 1H), 6.97 (t, J = 8.0 Hz, 1H), 4.28 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, Acetone- d_6) δ , 168.4, 140.4, 137.9, 128.6, 128.2, 125.3, 123.5, 123.3, 122.6, 122.0, 121.6, 119.7, 119.3, 117.4, 115.5, 112.1, 111.9, 51.8, 21.8; HR-ESI-MS (m/z): calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2\text{K} [\text{M}+\text{K}]^+$, 343.0843, found 343.0845.



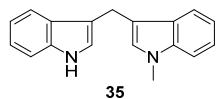
Compound 32. Slightly red powder in 14.0 mg, 54% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.32-7.24(m, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.13-7.07 (m, 2H), 7.01 (t, J = 8.0 Hz, 1H), 6.68 (s, 1H), 4.15 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 135.4, 131.4, 129.2, 127.6, 122.2, 122.0, 121.0, 119.3, 119.2, 119.0, 118.7, 116.4, 111.2, 110.5, 110.2, 20.1, 11.9. HR-ESI-MS (m/z): calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{K} [\text{M}+\text{K}]^+$, 299.0945, found 299.0945.



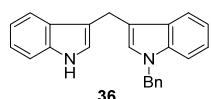
Compound 33. Slightly red powder in 23.0 mg, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (br s, 1H), 7.76 (br s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.54-7.50 (m, 3H), 7.40-7.29 (m, 5H), 7.23-7.18 (m, 2H), 7.14 (t, J = 8.0 Hz, 1H), 7.06 (t, J = 8.0Hz, 1H), 6.63 (s, 1H), 4.32 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.7, 136.2, 135.0, 133.1, 129.8, 129.1, 127.79, 127.75, 127.5, 122.6, 122.5, 122.1, 119.9, 119.8, 119.3, 119.1, 116.4, 111.6, 111.2, 110.9, 20.8. HR-ESI-MS (m/z): calcd. for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{K} [\text{M}+\text{K}]^+$, 361.1102, found 361.1104.



Compound 34. Slightly red powder in 20.0 mg, 68 % yield. ^1H NMR (400 MHz, Acetone- d_6) δ 10.04 (br s, 1H), 9.88 (br s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 1.4 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.98-6.94 (m, 3H), 4.14 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, Acetone- d_6) δ 137.9, 135.1, 134.5, 131.2, 128.5, 124.4, 123.3, 122.0, 120.9, 119.5, 119.3, 118.3, 115.9, 112.4, 112.1, 110.9, 20.6, 11.8; HR-ESI-MS (m/z): calcd. for $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{K} [\text{M}+\text{K}]^+$, 333.0555, found 333.0559.



Compound 35. Slightly red powder in 19.5 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (br s, 1H), 7.64 (dd, $J = 8.0, 4.5$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.25-7.18 (m, 2H), 7.13-7.08 (m, 2H), 6.95 (s, 1H), 6.79 (s, 1H), 4.25 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 136.6, 128.1, 127.7, 127.1, 122.3, 122.0, 121.6, 119.42, 119.40, 119.3, 118.7, 116.1, 114.3, 111.2, 109.2, 32.7, 21.2. HR-ESI-MS (m/z): calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{K}$ $[\text{M}+\text{K}]^+$, 299.0945, found 299.0946.



Compound 36. Slightly red powder in 24.5 mg, 73 % yield. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (br s, 1H), 7.54 (dd, $J = 8.0, 4.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 1H), 7.20-7.16 (m, 4H), 7.09 (dd, $J = 8.0$ Hz, 2H), 7.02-6.98 (m, 4H), 6.83 (d, $J = 8.0$ Hz, 2H), 5.15 (s, 2H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 137.0, 136.6, 128.8, 128.4, 127.7, 127.6, 126.8, 126.7, 122.3, 122.0, 121.8, 119.6, 119.4, 119.3, 119.0, 115.9, 114.9, 111.2, 109.8, 50.0, 21.4; HR-ESI-MS (m/z): calcd. for $\text{C}_{24}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$, 337.1699, found 337.1701.

5. Copies of ^1H NMR and ^{13}C NMR spectra.

