

Supporting Information
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Facile CuI-Catalyzed Arylation of Azoles and Amides by Using Simple Enaminone as Efficient Ligands

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General: The NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometry using CDCl₃ or DMSO-d₆ as solvent and TMS as the internal standard. Melting points of new products were determined using Yanaco MP-500 apparatus and were not corrected. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. Mass spectra were performed on a Bruker Esquire 3000 mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer.

General procedure for preparation of L1-L5:

Dimethylformamide dimethylacetal (DMFDMA) (0.01 mol) was added to ketone (0.01 mol) in xylem (50 ml). The reaction mixture was refluxed for 6-9 h. Removal of solvent under reduced pressure yielded the crude product, which was crystallized from ethanol. Compounds (**L1-L5**) were obtained as yellow crystals with physical characteristics identical with those reported in literature.¹⁻³

General procedure for preparation of L7 and L8:

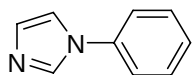
A solution of **L1** or **L5** (0.01 mol) in ethanol (30 ml) was treated with aniline (0.01 mol) and the reaction mixture was then refluxed for 3 h. Solvent was then evaporated in vacuum. The resulting products were triturated with H₂O and acidified with HCl. The solid products, so formed, were collected by filtration and crystallized from ethanol. **L7** and **L8** were formed as yellow crystals.¹

General procedure for preparation of L9 and L10:

A mixture of acetylacetic ether (5 mmol), amine (5 mmol) and InBr₃ (0.05 mmol) was stirred at room temperature for appropriate time. After completion of the reaction as indicated by TLC, the reaction mixture was extracted with ethyl acetate (3x10 ml), washed with water (3x10 ml), and dried over Na₂SO₄. After the solvent was removed, the crude mixture was purified by silica gel column chromatography to provide the desired product (**L9** and **L10**).⁴

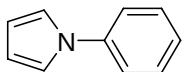
References:

- (1) Al-Saleh, B.; El-Asasery, M. A.; Abdel-Aziz, R. S.; Elnagdi, M. H. *J. Heterocyclic Chem.* **2005**, *42*, 563.
- (2) Kantevari, S.; Chary, M. V.; Vuppalapati, S. V. N. *Tetrahedron*. **2007**, *63*, 13024.
- (3) Vasselin, D. A.; Westwell, A. D.; Matthews, C. S.; Bradshaw, T. D.; Stevens, M. F. G. *J. Med. Chem.* **2006**, *49*, 3973.
- (4) Zhang, Z.; Yin, L.; Wang, Y. *Adv. Synth. Catal.* **2006**, *348*, 184.



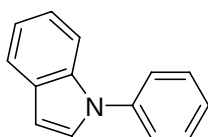
2a: ^1H NMR (CDCl_3 , 500MHz): δ =7.82 (s, 1H), 7.45 (t, J = 8.14 Hz, 2H), 7.31-7.35 (m, 3H), 7.25 (s, 1H), 7.16 (s, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ =137.4, 135.6, 130.4, 129.9, 127.6, 121.5, 118.4.

ESI-MS: 145 $[\text{M}+\text{H}]^+$.



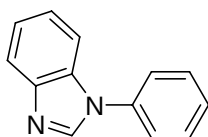
2b: ^1H NMR (CDCl_3 , 500MHz): δ =7.43-7.48 (m, 4H), 7.27-7.30 (m, 1H), 7.14 (t, J = 4.08 Hz, 2H), 6.41 (t, J = 2.09 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ =141.0, 129.8, 125.8, 120.8, 119.5, 110.5.

APCI-MS (EI, 20eV): 144 $[\text{M}+\text{H}]^+$.



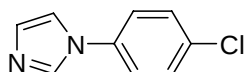
2c: ^1H NMR (CDCl_3 , 500MHz): δ =7.74 (d, J = 7.76 Hz, 1H), 7.62 (d, J = 8.11 Hz, 1H), 7.55 (t, J = 3.86 Hz, 4H), 7.37-7.39 (m, 2H), 7.20-7.28 (m, 2H), 6.73 (d, J = 3.17 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ =140.1, 136.1, 129.8, 129.5, 128.2, 126.7, 124.6, 122.6, 121.4, 120.6, 110.7, 103.8.

ESI-MS: 194 $[\text{M}+\text{H}]^+$.



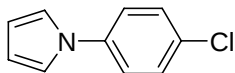
2d: ^1H NMR (CDCl_3 , 500MHz): δ =8.13 (s, 1H), 7.89-7.90 (m, 1H), 7.35-7.59 (m, 6H), 7.31-7.35 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ =144.2, 142.5, 136.5, 133.9, 130.3, 128.2, 124.2, 123.9, 123.0, 120.8, 110.7.

ESI-MS: 195 $[\text{M}+\text{H}]^+$.



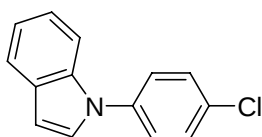
2e: ^1H NMR (CDCl_3 , 500MHz): δ =7.81 (s, 1H), 7.42-7.44 (t, J = 7.01 Hz, 2H), 7.19-7.32 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ =136.0, 135.7, 133.3, 130.9, 130.1, 122.8, 118.3.

ESI-MS: 179 $[\text{M}+\text{H}]^+$.



2f: ^1H NMR (CDCl_3 , 500MHz): δ =7.40-7.43 (m, 2H), 7.34-7.36 (m, 2H), 7.09 (t, J = 2.17 Hz, 2H), 6.41(t, J = 2.15 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ =139.5, 131.2, 129.8, 121.8, 119.5, 111.0.

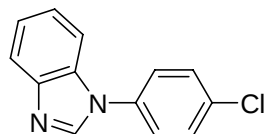
APCI-MS: 178 $[\text{M}+\text{H}]^+$.



2g: ^1H NMR (CDCl_3 , 500MHz): δ = 7.79 (d, J = 7.78 Hz, 1H), 7.48-7.60 (m, 5H), 7.27-7.35 (m,

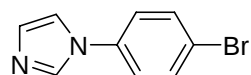
3H), 6.78 (d, $J = 3.20$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 138.5, 135.9, 132.1, 129.9, 129.6, 127.9, 125.7, 122.8, 121.5, 120.8, 110.5, 104.3$.

ESI-MS: 228 $[\text{M}+\text{H}]^+$.



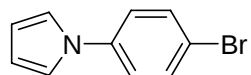
2h: ^1H NMR (CDCl_3 , 500MHz): $\delta = 8.09$ (s, 1H), 7.88-7.90 (m, 1H), 7.55-7.56 (m, 2H), 7.45-7.50 (m, 3H), 7.34-7.36 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 144.2, 142.2, 135.0, 134.0, 133.7, 130.5, 125.5, 124.2, 123.2, 120.9, 110.4$.

ESI-MS: 229 $[\text{M}+\text{H}]^+$.



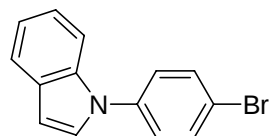
2i: ^1H NMR (CDCl_3 , 500MHz): $\delta = 7.83$ (s, 1H), 7.62 (t, $J = 8.67$ Hz, 2H), 7.21-7.29 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 136.6, 135.7, 133.2, 130.9, 123.2, 121.1, 118.3$.

ESI-MS: 223 $[\text{M}+\text{H}]^+$.



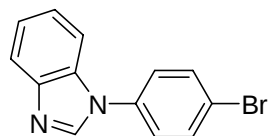
2j: ^1H NMR (CDCl_3 , 500MHz): $\delta = 7.56$ -7.58 (m, 2H), 7.29-7.31 (m, 2H), 7.09 (t, $J = 2.02$ Hz, 2H), 6.41 (t, $J = 2.07$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 139.9, 132.8, 122.0, 119.4, 118.9, 111.1$.

APCI-MS: 222 $[\text{M}+\text{H}]^+$.



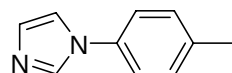
2k: ^1H NMR (CDCl_3 , 500MHz): $\delta = 7.75$ (d, $J = 7.79$ Hz, 1H), 7.66-7.69 (m, 2H), 7.58 (d, $J = 8.18$ Hz, 1H), 7.41-7.43 (m, 2H), 7.22-7.33 (m, 3H), 6.75 (d, $J = 3.10$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 139.1, 135.9, 132.9, 129.6, 127.8, 125.9, 122.9, 121.5, 120.9, 119.9, 110.5, 104.4$.

ESI-MS: 272 $[\text{M}+\text{H}]^+$.



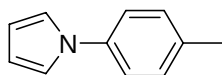
2l: ^1H NMR (CDCl_3 , 500MHz): $\delta = 8.09$ (s, 1H), 7.88-7.89 (m, 1H), 7.69-7.71 (m, 2H), 7.49-7.50 (m, 1H), 7.39-7.41 (m, 2H), 7.34-7.36 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 144.2, 142.2, 135.6, 133.6, 133.4, 125.7, 124.1, 123.2, 121.8, 120.9, 110.4$.

ESI-MS: 273 $[\text{M}+\text{H}]^+$.



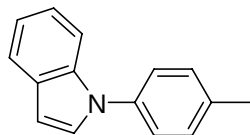
2m: ^1H NMR (CDCl_3 , 500MHz): $\delta = 7.85$ (s, 1H), 7.28 (d, $J = 7.00$ Hz, 5H), 7.22 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 138.3, 136.0, 135.8, 131.1, 130.8, 122.2, 119.2, 21.0$.

ESI-MS: 159 $[\text{M}+\text{H}]^+$.



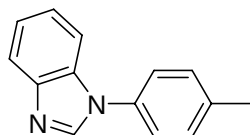
2n: ^1H NMR (CDCl_3 , 500MHz): δ = 7.22-7.31 (m, 5H), 7.07 (t, J = 2.00 Hz, 2H), 6.35 (t, J = 2.09 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ = 138.7, 135.6, 130.2, 120.8, 119.6, 110.3, 21.1.

APCI-MS (EI, 20eV): 158 $[\text{M}+\text{H}]^+$.



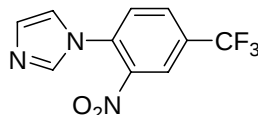
2o: ^1H NMR (CDCl_3 , 500MHz): δ = 7.80 (d, J = 7.74 Hz, 1H), 7.65 (d, J = 8.16 Hz, 1H), 7.49 (d, J = 8.20 Hz, 2H), 7.41 (t, J = 3.53 Hz, 3H), 7.26-7.33 (m, 2H), 6.78 (d, J = 3.10 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ = 137.5, 136.5, 136.2, 130.4, 129.4, 128.3, 124.5, 122.4, 121.3, 120.4, 110.7, 103.4, 21.3.

ESI-MS: 208 $[\text{M}+\text{H}]^+$.



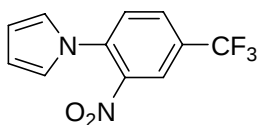
2p: ^1H NMR (CDCl_3 , 500MHz): δ = 8.10 (s, 1H), 7.89 (d, J = 7.97 Hz, 1H), 7.54 (t, J = 6.54 Hz, 1H), 7.27-7.42 (m, 6H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ = 144.2, 142.8, 138.4, 134.1, 134.0, 130.8, 124.3, 123.8, 122.9, 120.8, 110.7, 21.4.

ESI-MS: 209 $[\text{M}+\text{H}]^+$.



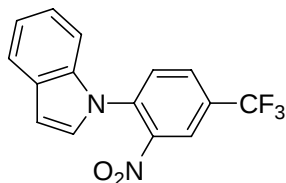
2q: ^1H NMR (CDCl_3 , 500MHz): δ =8.29 (s, 1H), 8.03 (d, J = 8.38 Hz, 1H), 7.71 (s, 1H), 7.67 (d, J = 8.32 Hz, 1H), 7.23 (s, 1H), 7.10 (s, 1H); ^{13}C NMR (CDCl_3 , 125MHz): δ = 145.2, 137.3, 133.5, 132.6(d, J = 34.6 Hz), 130.8, 129.6, 123.5(d, J = 30 Hz), 120.3.

ESI-MS: 258 $[\text{M}+\text{H}]^+$.



2r: ^1H NMR (CDCl_3 , 500MHz): δ =8.12 (d, J = 1.50 Hz, 1H), 7.91 (m, 1H), 7.63 (d, J = 8.00 Hz, 1H), 6.82 (t, J = 2.07 Hz, 2H), 6.42 (t, J = 2.15 Hz, 2H); ^{13}C NMR (CDCl_3 , 125MHz): δ = 144.8, 137.1, 133.2, 130.2, 128.4, 123.3(d, J = 50 Hz), 121.3, 112.5.

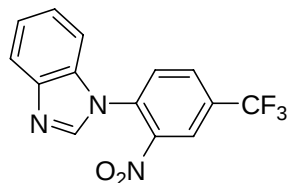
APCI-MS: 257 $[\text{M}+\text{H}]^+$.



2s: ^1H NMR (CDCl_3 , 500MHz): δ =8.35 (s, 1H), 7.99-8.01 (m, 1H), 7.72-7.77 (m, 2H), 7.16-7.29

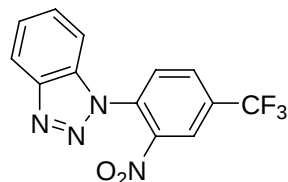
(m, 4H), 6.81 (d, $J = 3.30$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125MHz): $\delta = 145.6$, 136.(d, $J = 23.6$ Hz), 130.6 (d, $J = 3.25$ Hz), 130.5, 130.3, 129.5, 127.6, 123.7(d, $J = 23.3$ Hz), 123.4, 121.9(d, $J = 4.1$ Hz), 109.5, 106.6.

ESI-MS: 307 $[\text{M}+\text{H}]^+$.



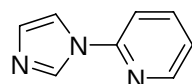
2t: ^1H NMR (CDCl_3 , 500MHz): $\delta = 8.41$ (d, $J = 1.35$ Hz, 1H), 7.99-8.07 (m, 2H), 7.86 (d, $J = 7.75$ Hz, 1H), 7.74 (d, $J = 8.25$ Hz, 1H), 7.29-7.36 (m, 2H), 7.12 (s, 1H); ^{13}C NMR (CDCl_3 , 125MHz): $\delta = 145.5$, 143.6, 142.1, 134.1, 133.9, 132.6(t, $J = 28.9$ Hz), 131.2 (d, $J = 2.12$ Hz), 130.6, 128.3, 124.8(d, $J = 122.4$ Hz), 123.7, 121.1, 118.3, 118.1, 109.4.

ESI-MS: 308 $[\text{M}+\text{H}]^+$



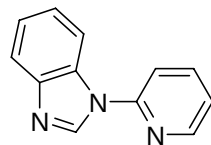
2u: ^1H NMR (CDCl_3 , 500MHz): $\delta = 8.45$ (s, 1H), 8.21 (d, $J = 8.30$ Hz, 1H), 8.14 (d, $J = 8.26$ Hz, 1H), 7.97 (d, $J = 8.28$ Hz, 1H), 7.64 (t, $J = 7.38$ Hz, 1H), 7.53 (t, $J = 7.88$ Hz, 1H), 7.46 (d, $J = 7.45$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125MHz): $\delta = 146.3$, 133.0, 132.7, 131.1, 129.7, 128.9, 125.4, 123.9(d, $J = 3.6$ Hz), 121.2, 109.2.

ESI-MS: 309 $[\text{M}+\text{H}]^+$



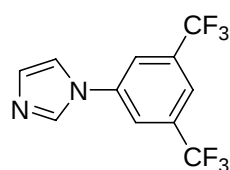
2v: ^1H NMR (CDCl_3 , 500MHz): $\delta = 8.50$ (t, $J = 3.54$ Hz, 2H), 7.82-7.86 (m, 2H), 7.38 (d, $J = 8.16$ Hz, 2H), 7.27 (m, 1H); ^{13}C NMR (CDCl_3 , 125MHz): $\delta = 149.5$, 139.3, 135.0, 130.5, 122.5, 116.7, 112.7.

ESI-MS: 146 $[\text{M}+\text{H}]^+$.

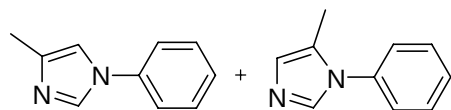


2w: ^1H NMR (CDCl_3 , 500MHz): $\delta = 8.56$ (s, 2H), 8.04 (t, $J = 7.29$ Hz, 1H), 7.82-7.86 (m, 2H), 7.52 (d, $J = 8.10$ Hz, 1H), 7.32-7.36 (m, 2H), 7.23-7.28 (m, 1H); ^{13}C NMR (CDCl_3 , 125MHz): $\delta = 150.6$, 150.1, 145.3, 142.1, 139.7, 132.8, 124.9, 124.0, 122.6, 121.3, 115.0, 113.4.

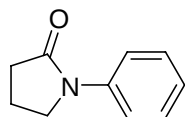
ESI-MS: 196 $[\text{M}+\text{H}]^+$.



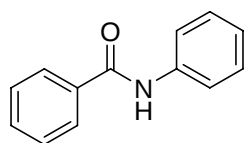
2x: ^1H NMR (CDCl_3 , 500MHz): δ = 7.99 (s, 1H), 8.89 (s, 1H), 7.86 (s, 1H), 7.40 (s, 1H), 7.32 (s, 1H); ^{13}C NMR (CDCl_3 , 125MHz): δ = 138.9, 134.4(m, J = 33.9 Hz), 132.1, 126.1, 123.9, 121.7, 121.3 (t, J = 2.9 Hz), 119.6.
ESI-MS: 281 $[\text{M}+\text{H}]^+$.



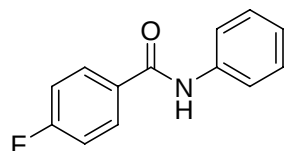
2y-1 + 2y-2: The ratio of **2y-1** and **2y-2** was 6.5: 1. ^1H NMR (CDCl_3 , 500 MHz): δ = 7.76 (s, 1H), 7.45-7.50 (m, 2H), 7.27-7.37 (m, 3H), 7.01 (s, 1H), 2.30 (s, major regioisomer), 2.17 (s, minor regioisomer). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 139.7, 137.7, 134.8, 130.0, 128.5, 127.3, 125.8, 121.3, 114.8, 13.8.
ESI-MS: 159 $[\text{M}+\text{H}]^+$.



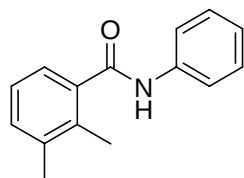
3a: ^1H NMR (CDCl_3 , 500MHz): δ = 7.59-7.62 (m, 2H), 7.35-7.38 (m, 2H), 7.12-7.16 (m, 1H), 3.86 (t, J = 6.97 Hz, 2H), 3.62 (t, J = 8.03 Hz, 2H), 2.11-2.18 (m, 2H); ^{13}C NMR (CDCl_3 , 125MHz): δ = 174.4, 139.6, 128.9, 124.6, 120.1, 48.9, 32.9, 18.2.
ESI-MS: 162 $[\text{M}+\text{H}]^+$.



3b: ^1H NMR (DMSO-d_6 , 500MHz): δ = 10.24 (s, 1H), 7.96 (t, J = 7.30 Hz, 2H), 7.79 (t, J = 8.25 Hz, 2H), 7.51-7.61 (m, 3H), 7.37 (t, J = 7.95 Hz, 2H), 7.12 (t, J = 7.40 Hz, 1H); ^{13}C NMR (DMSO-d_6 , 125MHz): δ = 166.5, 140.1, 134.9, 132.5, 129.6, 129.6, 129.4, 124.6, 121.3.
ESI-MS: 196 $[\text{M}-\text{H}]^-$.

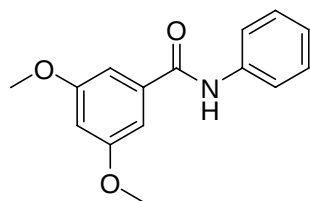


3c: ^1H NMR (DMSO-d_6 , 500MHz): δ = 10.26 (s, 1H), 8.02-8.05 (m, 2H), 7.78 (d, J = 8.00 Hz, 2H), 7.34-7.38 (m, 4H), 7.12 (t, J = 7.30 Hz, 1H); ^{13}C NMR (DMSO-d_6 , 125MHz): δ = 166.2, 165.6, 164.3, 140.3, 132.6, 131.6, 129.8, 124.9, 121.6, 116.6, 116.4.
ESI-MS: 214 $[\text{M}-\text{H}]^-$.



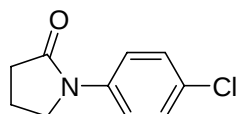
3d: mp 97-99 °C. ^1H NMR (DMSO-d_6 , 500MHz): δ = 10.29 (s, 1H), 7.76 (d, J = 8.00 Hz, 2H), 7.35 (t, J = 7.75 Hz, 2H), 7.24-7.28 (m, 2H), 7.20 (t, J = 7.45 Hz, 1H), 7.09 (t, J = 7.30 Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (DMSO-d_6 , 125MHz): δ = 169.7, 140.5, 139.3, 138.3, 134.4, 131.8, 129.9, 126.5, 125.8, 124.7, 120.7.

ESI-MS: 224 $[M-H]^-$. HRMS (ESI): $([M+Na]^+)$: Calcd for $C_{15}H_{15}NONa$: 248.1046; Found: 248.1051.



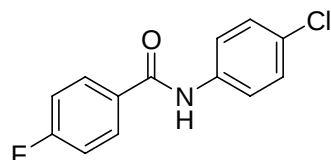
3e: 1H NMR (DMSO- d_6 , 500MHz): δ = 10.17 (s, 1H), 7.77 (d, J = 7.85 Hz, 2H), 7.37 (t, J = 7.80 Hz, 2H), 7.10 (s, 2H), 6.72 (s, 1H), 3.82 (s, 6H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 166.2, 161.6, 140.2, 138.2, 129.8, 124.9, 121.7, 106.8, 104.5, 56.7.

ESI-MS: 256 $[M-H]^-$.



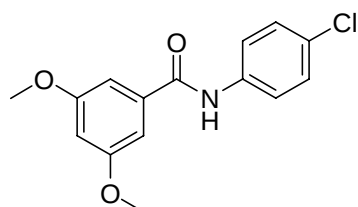
3f: 1H NMR (DMSO- d_6 , 500MHz): δ = 7.70 (d, J = 6.46 Hz, 2H), 7.42 (s, J = 6.50 Hz, 2H), 3.80 (s, 2H), 2.49 (s, 2H), 2.05 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 175.1, 139.6, 129.6, 128.7, 121.9, 49.1, 33.4, 18.4.

ESI-MS: 196 $[M+H]^+$.



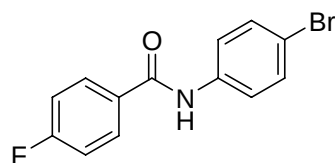
3g: 1H NMR (DMSO- d_6 , 500MHz): δ = 10.38 (s, 1H), 8.02-8.05 (m, 2H), 7.82 (d, J = 8.80 Hz, 2H), 7.35-7.41 (m, 4H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 166.3, 165.7, 164.3, 139.3, 132.3, 131.7, 131.6, 129.7, 128.5, 123.1, 116.6, 116.5.

ESI-MS: 248 $[M-H]^-$.



3h: mp 135-137 $^{\circ}C$. 1H NMR (DMSO- d_6 , 500MHz): δ = 10.29 (s, 1H), 7.81 (d, J = 8.70 Hz, 2H), 7.42 (d, J = 8.70 Hz, 2H), 7.09 (d, J = 8.70 Hz, 2H), 6.72 (s, 1H), 3.82 (s, 6H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 166.3, 161.6, 139.2, 137.9, 129.7, 128.5, 123.1, 106.8, 104.6, 56.7.

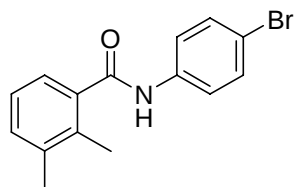
ESI-MS: 290 $[M-H]^-$. HRMS (ESI): $([M+Na]^+)$: Calcd for $C_{15}H_{14}NO_3ClNa$: 314.0554; Found: 314.0557.



3i: 1H NMR (DMSO- d_6 , 500MHz): δ = 10.37 (s, 1H), 8.02-8.04 (m, 2H), 7.76 (d, J = 8.80 Hz, 2H), 7.54 (d, J = 8.75 Hz, 2H), 7.39 (t, J = 8.75 Hz, 2H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 166.3,

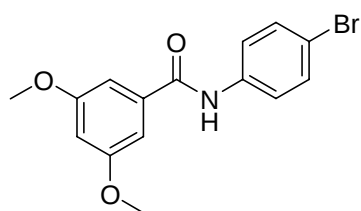
165.7, 164.3, 140.4, 139.7, 134.7, 132.6, 131.7, 131.6, 123.4, 116.6, 116.5.

ESI-MS: 292 [M-H]⁻.



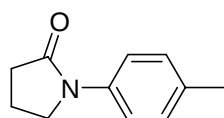
3j: mp 140-142 °C. ¹H NMR (DMSO-d₆, 500MHz): δ= 10.42 (s, 1H), 7.73 (d, J = 8.75 Hz, 2H), 7.53 (d, J = 8.75 Hz, 2H), 7.17-7.29 (m, 3H), 2.29 (s, 3H), 2.34 (s, 3H); ¹³C NMR (DMSO-d₆, 125MHz): δ= 169.7, 139.8, 138.9, 138.4, 134.4, 132.7, 131.9, 126.6, 125.8, 122.6, 116.3, 20.9, 17.2.

ESI-MS: 302 [M-H]⁻. HRMS (ESI): ([M+Na]⁺): Calcd for C₁₅H₁₄NOBrNa: 326.0151; Found: 326.0154.



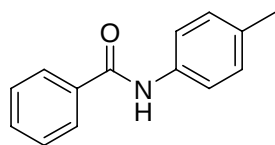
3k: mp 131-133 °C. ¹H NMR (DMSO-d₆, 500MHz): δ= 10.28 (s, 1H), 7.76 (d, J = 8.75 Hz, 2H), 7.54 (d, J = 8.70 Hz, 2H), 7.09 (d, J = 1.90 Hz, 2H), 6.72 (s, 1H), 2.49 (s, 6H); ¹³C NMR (DMSO-d₆, 125MHz): δ= 166.3, 161.6, 139.6, 137.9, 135.4, 132.6, 126.7, 126.1, 123.5, 106.8, 104.6, 56.7.

ESI-MS: 334 [M-H]⁻. HRMS (ESI): ([M+Na]⁺): Calcd for C₁₅H₁₄NO₃BrNa: 358.0049; Found: 358.0053.



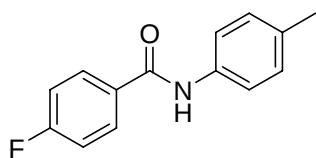
3l: ¹H NMR (DMSO-d₆, 500MHz): δ= 7.53 (d, J = 8.15 Hz, 2H), 7.17 (d, J = 8.10 Hz, 2H), 3.79 (t, J = 7.03 Hz, 2H), 2.49 (m, 2H), 2.27 (s, 3H), 2.06 (t, J = 7.44 Hz, 2H); ¹³C NMR (DMSO-d₆, 125MHz): δ= 174.7, 138.4, 134.0, 130.2, 120.5, 49.3, 33.5, 21.6, 18.6.

ESI-MS: 176 [M+H]⁺.

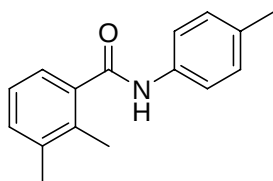


3m: ¹H NMR (DMSO-d₆, 500MHz): δ= 10.17 (s, 1H), 7.96 (t, J = 7.05 Hz, 2H), 7.67 (d, J = 8.35 Hz, 2H), 7.43-7.59 (m, 3H), 7.16 (d, J = 8.25 Hz, 2H), 2.28 (s, 3H); ¹³C NMR (DMSO-d₆, 125MHz): δ= 166.5, 137.8, 136.2, 133.7, 132.6, 130.2, 129.5, 128.8, 121.6, 21.7.

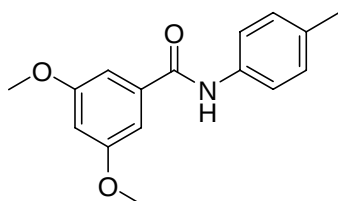
ESI-MS: 210 [M-H]⁻.



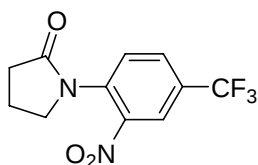
3n: ^1H NMR (DMSO- d_6 , 500MHz): δ = 10.18 (s, 1H), 8.02-8.05 (m, 2H), 7.65 (d, J = 8.25 Hz, 2H), 7.37(t, J = 8.80 Hz, 2H), 7.15 (d, J = 8.20 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 166.2, 165.4, 164.2, 137.7, 133.8, 132.6, 131.5 (d), 130.2, 121.6, 116.5, 116.4, 21.6.
ESI-MS: 228 $[\text{M-H}]^-$.



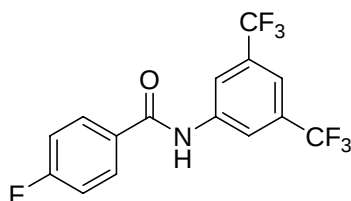
3o: ^1H NMR (DMSO- d_6 , 500MHz): δ = 10.18 (s, 1H), 7.63 (d, J = 8.10 Hz, 2H), 7.12-7.27 (m, 5H), 2.28 (d, J = 7.75 Hz, 6H), 2.24 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 169.2, 139.2, 138.1, 137.8, 134.2, 133.3, 131.5, 130.0, 126.3, 125.6, 120.5, 21.5, 20.8, 17.0.
ESI-MS: 238 $[\text{M-H}]^-$.



3p: ^1H NMR (DMSO- d_6 , 500MHz): δ = 10.08 (s, 1H), 7.64 (d, J = 8.20 Hz, 2H), 7.16 (d, J = 8.00 Hz, 2H), 7.09 (s, 2H), 3.82 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 166.0, 161.5, 137.7, 135.5, 133.9, 130.2, 121.7, 106.7, 104.4, 56.7, 21.7.
ESI-MS: 270 $[\text{M-H}]^-$.



3q: ^1H NMR (DMSO- d_6 , 500MHz): δ = 8.29 (d, J = 1.04 Hz, 1H), 8.16 (m, 1H), 7.82 (d, J = 8.45 Hz, 1H), 4.00 (t, J = 6.90 Hz, 2H), 2.47 (t, J = 7.93 Hz, 2H), 2.19 (m, 2H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 175.2, 145.4, 135.9, 131.7(d, J = 3 Hz), 127.7, 127.4, 123.7, 123.6, 49.9, 32.0, 19.6.
ESI-MS: 275 $[\text{M+H}]^+$.



3r: ^1H NMR (DMSO- d_6 , 500MHz): δ = 10.45 (s, 1H), 8.22 (s, 1H), 7.48 (m, 3H), 6.98 (d, J = 5.60 Hz, 3H); ^{13}C NMR (DMSO- d_6 , 125MHz): δ = 165.3, 162.3, 138.8, 134.8, 134.3, 131.6, 124.9, 120.3, 117.8, 117.1(d, J = 150 Hz)
ESI-MS: 350 $[\text{M-H}]^-$.

References:

- (1) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575
- (2) Wan, J.; Chai, Y.; Wu, J.; Pan, Y. *Synlett.* **2008**, *19*, 3068.
- (3) Zhu, L.; Cheng, L.; Zhang, Y.; Xie, R.; You, J. *J. Org. Chem.* **2007**, *72*, 2737
- (4) Lee, C. K.; Jun, J. H. Yu, J. S. *J. Heterocyclic. Chem.* **2000**, *37*, 15
- (5) Zhang, Z.; Yu, Y.; Liebeskind, L. S. *Org. Lett.* **2008**, *10*, 3005
- (6) Li, J.; Xu, F.; Zhang, Y.; Shen, Q. *J. Org. Chem.* **2009**, *74*, 2575
- (7) Lakshmi Kantam, M.; Venkanna, G. T.; Sreedhar, B.; Choudary, B. M. *J. Org. Chem.* **2006**, *71*, 9522
- (8) Ramalingan, C.; Park, Y. *J. Org. Chem.* **2007**, *72*, 4536
- (9) Zhu, L.; Guo, P.; Li, G.; Lan, J.; Xie, R.; You, J. *J. Org. Chem.* **2007**, *72*, 8535

