## Supporting Information

# Palladium-Catalyzed Synthesis of 2-(Aminomethyl)indoles from Ethyl 3-(o-Trifluoroacetamidophenyl)-1-propargyl Carbonate 

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Melting points were determined with a Büchi B-545 apparatus and are uncorrected. All of the reagents, catalysts, and solvents are commercially available and were used as purchased, without further purification. Compounds $\mathbf{1 a}$ and $\mathbf{1 b}$ were purified on axially compressed columns, packed with $\mathrm{SiO}_{2} 25-40 \mu \mathrm{~m}$ (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with $n$-hexane/ethyl acetate mixtures. Reaction products were purified by flash chromatography, using basic $\mathrm{Al}_{2} \mathrm{O}_{3}$ Brockmann activity II (Fluka) as stationary phase, eluting with $n$-hexane/ethyl acetate mixtures. ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz ), ${ }^{13} \mathrm{C}$ NMR ( 100.6 MHz ) and ${ }^{19}$ F NMR ( 376.5 MHz ) spectra were recorded with a Bruker Avance 400 spectrometer. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), sp (septuplet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer.

Preparation of (1a): o-iodoaniline ( $1.50 \mathrm{~g}, 6.85 \mathrm{mmol}), \mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(0.072 \mathrm{~g}, 0.103 \mathrm{mmol})$ and $\mathrm{CuI}(0.020 \mathrm{~g}, 0.103 \mathrm{mmol})$ were added to 2.5 mL of DMF and 5.0 mL of $\mathrm{Et}_{2} \mathrm{NH}$ and the mixture was stirred under argon for 15 minutes. Then, tetrahydro-2-(2-propynyloxy)- $2 H$-pyran ( $1.15 \mathrm{~g}, 1.15$ $\mathrm{mL}, 8.22 \mathrm{mmol}$ ) was added dropwise in 5 minutes and the resulting reaction mixture was stirred at $60{ }^{\circ} \mathrm{C}$ for 12 h . After cooling, the reaction mixture was diluted with diethyl ether, washed twice with $\mathrm{NH}_{4} \mathrm{Cl}$ solution, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure.
The crude mixture was dissolved in 10 mL of THF containing $\mathrm{Et}_{3} \mathrm{~N}(6.85 \mathrm{mmol}, 0.95 \mathrm{~mL})$ and cooled at $0{ }^{\circ} \mathrm{C}$. Then, trifluoroacetic anhydride ( $13.7 \mathrm{mmol}, 1.93 \mathrm{~mL}$ ) was added dropwise in 10 minutes and the resultant solution was stirred at room temperature for 2 hours. After this time, the solution was diluted with diethyl ether, washed twice with a saturated $\mathrm{NaHCO}_{3}$ solution, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure.
The residue was dissolved in 12 mL of an acetone/water 1:1 solution and $p$-toluensulfonic acid hydrate ( $1.30 \mathrm{~g}, 6.85 \mathrm{mmol}$ ) was added. The resulting solution was heated at $40{ }^{\circ} \mathrm{C}$ and stirred for 6 hours. After cooling, the reaction mixture was diluted with diethyl ether, washed twice with $\mathrm{NaHCO}_{3}$ solution, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure.
The final crude mixture was dissolved in 7 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{Et}_{3} \mathrm{~N}(10.3 \mathrm{mmol}, 1.427 \mathrm{~mL})$ was added and ethyl chloroformate ( $8.22 \mathrm{mmol}, 0.78 \mathrm{~mL}$ ) was added dropwise at $0^{\circ} \mathrm{C}$. The resulting solution was stirred at room temperature for 2 hours. Then, the reaction mixture was diluted with diethyl ether, washed twice with a saturated NaCl solution, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure. The residue was purified by chromatography $\left(\mathrm{SiO}_{2}, 140 \mathrm{~g} ; n\right.$-hexane/ethylacetate $90 / 10 \mathrm{v} / \mathrm{v}$ ) to give 1.73 g ( $80 \%$ overall yield) of 1a: m.p.: $69-70^{\circ} \mathrm{C}$; IR ( KBr ): 3319, 2987, 1748, $1713,1379 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.73(\mathrm{bs}, 1 \mathrm{H}), 8.36(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.44(\mathrm{~m}, 2 \mathrm{H})$, $7.20(\mathrm{t}, J=7.6 \mathrm{~Hz} 1 \mathrm{H}), 5.01(\mathrm{~s}, 2 \mathrm{H}), 4.27(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.35(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 154.7(\mathrm{q}, J=37.6 \mathrm{~Hz}), 154.6,136.8,132.3,130.5,125.5,119.9,115.6(\mathrm{q}, J=288.8 \mathrm{~Hz})$ 112.2, 91.3, 81.1, 64.8, 55.4, 14.3; ${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta-75.8$ Anal calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{~F}_{3} \mathrm{NO}_{4}, \mathrm{C}$, $53.34 ;$ H, 3.84; N, 4.44. Found C, 53.21; H, 3.85; N, 4.40.

Preparation of (1b): compound 1b was prepared as $\mathbf{1 a}$ with the exception of the last step that was carried out as follow: the crude mixture derived from the acid-catalyzed hydrolysis of the tetrahydropyranyl intermediate was dissolved in 5 mL of pyridine. Then, acetic anhydride ( 34.2 $\mathrm{mmol}, 3.2 \mathrm{~mL}$ ) was added dropwise at $0^{\circ} \mathrm{C}$. The resulting solution was stirred at room temperature for 2 hours. After this time, the reaction mixture was diluted with diethyl ether, washed ( HCl 2 N , saturated $\mathrm{NaHCO}_{3}$ solution, saturated NaCl solution), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure. The residue was purified by chromatography $\left(\mathrm{SiO}_{2}, 140 \mathrm{~g} ; n\right.$-hexane/ethylacetate $90 / 10 \mathrm{v} / \mathrm{v}$ ) to give $1.44 \mathrm{~g}\left(78 \%\right.$ yield) of 1b: m.p.: $89-91^{\circ} \mathrm{C}$; IR ( KBr ): $3319,2987,1748,1713$, $1379 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.69(\mathrm{bs}, 1 \mathrm{H}), 8.35(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.50-7.40(\mathrm{~m}, 2 \mathrm{H}), 7.19(\mathrm{t}, J$ $=7.6 \mathrm{~Hz} \mathrm{1H}), 4.96(\mathrm{~s}, 2 \mathrm{H}), 2.15(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 170.1,154.6(\mathrm{q}, J=37.7 \mathrm{~Hz}), 136.7$, $132.1,130.4,125.5,119.9,113.3(\mathrm{q}, J=288.8 \mathrm{~Hz}), 112.4,91.9,80.5,52.3,20.6 ;{ }^{19} \mathrm{~F} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right)$ $\delta$-75.8; Anal calcd for $\mathrm{C}_{13} \mathrm{H}_{10} \mathrm{~F}_{3} \mathrm{NO}_{3}, \mathrm{C}, 54.74 ; \mathrm{H}, 3.53 ; \mathrm{N}, 4.91$; Found C, $54.59 ; \mathrm{H}, 3.51 ; \mathrm{N}, 4.88$.

Typical procedure for the preparation of 2-(aminomethyl)indoles: a Carousel Tube Reactor (Radley Discovery), equipped with a magnetic stirrer, was charged with $\mathbf{1 a}(0.050 \mathrm{~g}, 0.159 \mathrm{mmol})$, $N$-ethyl piperazine $(0.055 \mathrm{~g}, 0.477 \mathrm{mmol})$, and $\operatorname{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(0.009 \mathrm{~g}, 0.00795 \mathrm{mmol})$ in 1.0 mL of dry THF under argon. The mixture was warmed at $80^{\circ} \mathrm{C}$ and stirred for 1.5 h . After cooling, the reaction mixture was dried under reduced pressure and the residue was purified by flash chromatography $\left(\mathrm{Al}_{2} \mathrm{O}_{3}, 50 \mathrm{~g}\right.$; $n$-hexane/ethylacetate $70 / 30 \mathrm{v} / \mathrm{v}$ ) to give 0.035 g of $\mathbf{6 a}(90 \%$ yield): oil; IR (neat): $3404,2935,2816,1454 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.64(\mathrm{bs}, 1 \mathrm{H}), 7.56(\mathrm{~d}, J=8.3 \mathrm{~Hz}$, $1 \mathrm{H}), 7.33(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.16-7.07(\mathrm{~m}, 2 \mathrm{H}), 6.37(\mathrm{~s}, 1 \mathrm{H}), 3.67(\mathrm{~s}, 2 \mathrm{H}), 2.54-2.41(\mathrm{~m}, 10 \mathrm{H})$, $1.09(\mathrm{t}, J=8.3 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 136.2,135.8,128.4,121.6,120.2,119.6,110.7,101.7$, 55.9, 53.3, 52.8, 52.3, 12.0; Anal calcd for $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{~N}_{3}, \mathrm{C}, 74.03$; H, 8.70; N, 17.27. Found C, 74.01; H, 8.68; N, 17.25.

4a: oil; IR (neat): 3401, 2924, 2855, $1455 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 9.03(\mathrm{bs}, 1 \mathrm{H}), 7.57$ (d, $J=8.3$ $\mathrm{Hz}, 1 \mathrm{H}), 7.35(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.18-7.07(\mathrm{~m}, 2 \mathrm{H}), 6.37(\mathrm{~s}, 1 \mathrm{H}), 3.67(\mathrm{~s}, 2 \mathrm{H}), 2.51-2.41(\mathrm{~m}, 4 \mathrm{H})$, $1.62(\mathrm{t}, J=5.3 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 136.3,135.7,128.3,121.5,120.1,119.5,110.9,101.8$, 56.5, 54.6, 25.8, 24.2; Anal calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{~N}_{2}, \mathrm{C}, 78.46 ; \mathrm{H}, 8.47$; N; 13.07. Found C, 78.39; H, 8.46; N; 13.04.

4b: oil; IR (neat): $3400,2923,2885,1455,1114 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.61(\mathrm{bs}, 1 \mathrm{H}), 7.59\left(\mathrm{~d}, J_{1}\right.$ $=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.35\left(\mathrm{dd}, J_{1}=7.7 \mathrm{~Hz}, J_{2}=0.8 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.20-7.10(\mathrm{~m}, 2 \mathrm{H}), 6.41(\mathrm{~s}, 1 \mathrm{H}), 3.75(\mathrm{t}, J=$ $4.7 \mathrm{~Hz}, 4 \mathrm{H}), 3.68(\mathrm{~s}, 2 \mathrm{H}), 2.51(\mathrm{t}, J=4.4 \mathrm{~Hz}, 4 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 136.2,135.2,128.3,121.7$, 120.2, 119.7, 110.7, 101.9, 66.9, 56.2, 53.7; Anal calcd for $\mathrm{C}_{13} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}, \mathrm{C}, 72.19 ; \mathrm{H}, 7.46$; $\mathrm{N}, 12.95$. Found C, 72.10; H, 7.44; N, 12.96.

4c: oil; IR (neat): $3401,2924,2855,1455,1060 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.72(\mathrm{bs}, 1 \mathrm{H}), 7.55(\mathrm{~d}, J$ $=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.17-7.05(\mathrm{~m}, 2 \mathrm{H}), 6.35(\mathrm{~s}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 2 \mathrm{H}), 2.58(\mathrm{q}, J=$ $7.1 \mathrm{~Hz}, 4 \mathrm{H}), 1.06(\mathrm{t}, J=7.1 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}^{\left(\mathrm{CDCl}_{3}\right)} \delta 137.3,136.0,128.7,121.4,120.1,119.6$, 110.8, 100.9, 51.0, 46.9, 11.7; Anal calcd for $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{~N}_{2}, \mathrm{C}, 77.18$; H, 8.97; N, 13.85. Found C, 77.02; H, 8.95; N, 13.80.

4d: oil; IR (neat): 3401, 2938, 2825, 1445, $1065 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.49$ (bs, 1H), 7.51 (d, $J$ $=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.32(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.17-7.05(\mathrm{~m}, 2 \mathrm{H}), 6.38(\mathrm{~s}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 2 \mathrm{H}), 3.10(\mathrm{sp}, J=$ $6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.07(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 12 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 137.2,136.0,128.7,121.4,120.1$, 119.6, 110.8, 100.9, 48.5, 40.5, 20.8; Anal calcd for $\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{~N}_{2}, \mathrm{C}, 78.21 ; \mathrm{H}, 9.63 ; \mathrm{N}, 12.16$. Found C, 78.05; H, 9.64; N, 12.11.

6b: oil; IR (neat): 3399, 2939, 2825, 1447, $752 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.48(\mathrm{bs}, 1 \mathrm{H}), 7.58(\mathrm{~d}, J=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.36(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.11(\mathrm{t}, J=$ $7.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{~d}, J=2.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.74\left(\mathrm{dd}, J_{1}=8.0 \mathrm{~Hz}, J_{2}=2.7 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.40(\mathrm{~s}, 1 \mathrm{H}), 3.73(\mathrm{~s}$, $2 \mathrm{H}), 3.18(\mathrm{t}, J=4.5 \mathrm{~Hz}, 4 \mathrm{H}), 2.63(\mathrm{t}, J=4.7 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 150.7,136.2,135.4$, $132.9,130.5,128.4,122.3,121.8,120.3,119.8,117.3,115.4,110.8,101.9,55.8,52.9,48.8$; Anal calcd for $\mathrm{C}_{19} \mathrm{H}_{19} \mathrm{Cl}_{2} \mathrm{~N}_{3}, \mathrm{C}, 63.34 ; \mathrm{H}, 5.32 ; \mathrm{N}, 11.66$. Found C, 67,$15 ; \mathrm{H}, 5,19 ; \mathrm{N}, 11.63$.

6c: wax; IR (neat): 3401, 2938, 2825, 1445, $751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.47$ (bs, 1H), 7.57 (d, $J$ $=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.44-7.30(\mathrm{~m}, 3 \mathrm{H}), 7.21-7.07(\mathrm{~m}, 3 \mathrm{H}), 6.37(\mathrm{~s}, 1 \mathrm{H}), 3.68(\mathrm{~s}, 2 \mathrm{H}), 3.47(\mathrm{~s}, 2 \mathrm{H}), 2.52-$ $2.42(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 138.8,136.2,135.8,132.4,131.0,130.8,130.3,128.4,128.3$, 121.6, 120.3, 119.7, 110.7, 101.7, 61.8, 55.8, 53.3, 53.1; Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{Cl}_{2} \mathrm{~N}_{3}, \mathrm{C}, 64.18 ; \mathrm{H}$, 5.65; N, 11.23. Found C, 64.28; H, 5.64; N, 11.22.

6d: wax; IR (neat): $3398,2940,2825,2218,1447,751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.50(\mathrm{bs}, 1 \mathrm{H})$, $7.61-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.50(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.36(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{t}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.11$ $(\mathrm{t}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.05-6.98(\mathrm{~m}, 2 \mathrm{H}), 6.42(\mathrm{~s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 2 \mathrm{H}), 3.26(\mathrm{t}, J=4.5 \mathrm{~Hz}, 4 \mathrm{H}), 2.73(\mathrm{t}, J$ $=4.6 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 155.5,136.2,135.3,134.3,133.8,128.4,121.8,121.6,120.3$, 119.7, 118.7, 118.4, 110.7, 106.0, 101.9, 55.7, 53.1, 51.5; Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{20} \mathrm{~N}_{4}, \mathrm{C}, 75.92 ; \mathrm{H}$, 6.37; N, 17.71. Found C, 75.75; H, 6.55; N, 17.75.

6e: m.p.: 139.7-141.8 ${ }^{\circ} \mathrm{C}$; IR (KBr): 3405, 2938, 2825, 1500, $752 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 8.55$ (bs, 1H), $7.60(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.37(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.20-7.11(\mathrm{~m}, 2 \mathrm{H}), 7.02-6.87(\mathrm{~m}, 4 \mathrm{H})$, $6.42(\mathrm{~s}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 2 \mathrm{H}), 3.15(\mathrm{t}, J=4.8 \mathrm{~Hz}, 4 \mathrm{H}), 2.67(\mathrm{t}, J=4.9 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta$ 156.7 (d, $J=238.9 \mathrm{~Hz}$ ), 147.4 (d, $J=2.1 \mathrm{~Hz}$ ), 135.7, 135.0, 127.9, 121.2, 119.8, 119.2, 117.3, (d, $J$ $=7.6 \mathrm{~Hz}), 115.0(\mathrm{~d}, J=21.9 \mathrm{~Hz}), 110.2,101.3,55.3,52.8,49.7$; ${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta-124.4$; Anal calcd for $\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{FN}_{3}, \mathrm{C}, 73.76 ; \mathrm{H}, 6.52$; N, 13.58. Found C, 73.68; H, 6.50; N, 13.55.

6f: oil; IR (neat): 3405, 2938, 2825, 1500, $752 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.56(\mathrm{bs}, 1 \mathrm{H}), 7.57$ (d, $J=$ $7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.39-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.18-7.03(\mathrm{~m}, 4 \mathrm{H}), 6.37(\mathrm{~s}, 1 \mathrm{H}), 3.68-3.63(\mathrm{~m}, 4 \mathrm{H}), 2.81-2.22(\mathrm{~m}$, $8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 161.5(\mathrm{~d}, J=246.1 \mathrm{~Hz}), 136.3,135.5,131.7(\mathrm{~d}, J=4.5 \mathrm{~Hz}), 128.9(\mathrm{~d}, J=$ $8.2 \mathrm{~Hz}), 128.4,124.5(\mathrm{~d}, J=14.8 \mathrm{~Hz}), 123.9(\mathrm{~d}, J=3.5 \mathrm{~Hz}), 121.6,120.2,119.7,115.3(\mathrm{~d}, J=22.3$ $\mathrm{Hz}), 110.8,101.8,55.8,55.2,53.2,52.7 ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta-117.7$; Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{22} \mathrm{FN} 3, \mathrm{C}$, 74.28; H, 6.86; N, 12.99. Found C, 74.20; H, 6.87; N, 12.96.

6g: oil; IR (neat): 3406, 2938, 2824, 1500, $750 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.59(\mathrm{bs}, 1 \mathrm{H}), 7.59(\mathrm{~d}, J=$ $7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.36(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.22-7.06(\mathrm{~m}, 4 \mathrm{H}), 7.00-6.95(\mathrm{~m}, 2 \mathrm{H}), 6.43(\mathrm{~s}, 1 \mathrm{H}), 3.76(\mathrm{~s}$, 2 H ), 3.16-3.14 (m, 4H), 2.71-2.69 (m, 4H); ${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 155.8(\mathrm{~d}, J=245.9 \mathrm{~Hz}), 140.1(\mathrm{~d}, J$ $=8.7 \mathrm{~Hz}), 136.2,135.6,128.4,124.5(\mathrm{~d}, J=3.5 \mathrm{~Hz}), 122.5(\mathrm{~d}, J=7.9 \mathrm{~Hz}), 121.7,120.3,119.7$, $119.0(\mathrm{~d}, J=3 \mathrm{~Hz}), 116.2(\mathrm{~d}, J=20.8 \mathrm{~Hz}), 110.7,101.8,55.9,53.4,50.6 ;{ }^{19} \mathrm{~F} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-$ 122.6; Anal calcd for $\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{FN}_{3}, \mathrm{C}, 73.76 ; \mathrm{H}, 6.52$; N, 13.58. Found C, 73.67; H, 6.50; N, 13.54.

6h: mp: $145.6^{\circ} \mathrm{C}$; IR (KBr): 3401, 2938, 2825, 1445, $751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 8.49(\mathrm{bs}, 1 \mathrm{H})$, $7.55(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.35-7.24(\mathrm{~m}, 5 \mathrm{H}), 7.17-7.06(\mathrm{~m}, 2 \mathrm{H}), 6.36(\mathrm{~s}, 1 \mathrm{H}), 3.67(\mathrm{~s}, 2 \mathrm{H}), 3.49$, (s, $2 \mathrm{H}), 2.51-2.39(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 136.7,136.1,135.9,132.8,130.4,128.5,128.4$, 121.6, 120.2, 119.6, 110.7, 101.5, 62.2, 55.8, 53.3, 53.1; Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{22} \mathrm{ClN}_{3}, \mathrm{C}, 70.68 ; \mathrm{H}$, 6.52 ; N, 12.36. Found C, 70.60; H, 6.52; N, 12.32
.6i: mp: 159.8-161.7 ${ }^{\circ} \mathrm{C}$; IR (KBr): $3401,2938,2825,1445,751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 8.50$ (bs, $1 \mathrm{H}), 7.56(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.45(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.22-7.09(\mathrm{~m}, 4 \mathrm{H})$, $6.37(\mathrm{~s}, 1 \mathrm{H}), 3.67(\mathrm{~s}, 2 \mathrm{H}), 3.48(\mathrm{~s}, 2 \mathrm{H}), 2.52-2.40(\mathrm{~m}, 8 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 137.3,136.1,135.9$, $131.4,130.8,128.5,121.6,120.9,120.2,119.6,110.7,101.6,62.3,55.8,53.3,53.1$; Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{22} \mathrm{BrN}_{3}, \mathrm{C}, 62.50 ; \mathrm{H}, 5.77$; N, 10.93. Found C, $62.42 ; \mathrm{H}, 5,76 ; \mathrm{N}, 10.92$.

6j: oil; IR (neat): 3400, 2940, 2825, 1447, $742 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.51$ (bs, 1H), 7.52 (d, $J=$ $7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.49(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.39-7.20(\mathrm{~m}, 5 \mathrm{H}), 7.17-7.03(\mathrm{~m}, 2 \mathrm{H}), 6.29(\mathrm{~s}, 1 \mathrm{H}), 3.89(\mathrm{~s}$, $2 \mathrm{H}), 3.47\left(\mathrm{dd}, J_{1}=7.7 \mathrm{~Hz}, J_{2}=2.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.10-3.01(\mathrm{~m}, 2 \mathrm{H}), 2.86-2.76(\mathrm{~m}, 2 \mathrm{H}), 2.29(\mathrm{~s}, 3 \mathrm{H})$, 2.15-2.09 (m, 1H), $1.97(\mathrm{t}, J=10.0 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 141.4,136.2,135.8,128.6,128.4$, $128.3,121.2,119.9,119.4,110.5,101.2,67.3,63.7,55.2,52.2,52.0,45.7$; Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{~N}_{3}$, C, 78.65; H, 7.59; N, 13.76. Found C, 78.58; H, 7.60; N, 13.74.

6k: mp: $150.7^{\circ} \mathrm{C}$; IR (KBr): 3400, 2940, 2825, 1447, $749 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.66(\mathrm{bs}, 1 \mathrm{H})$, $7.62(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.26-7.11(\mathrm{~m}, 6 \mathrm{H}), 6.41(\mathrm{~s}, 1 \mathrm{H}), 3.70(\mathrm{~s}, 2 \mathrm{H})$, $3.55(\mathrm{~s}, 2 \mathrm{H}), 2.58-2.46(\mathrm{~m}, 8 \mathrm{H}), 2.40(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 136.7,136.1,135.9,134.9$, $129.2,128.9,128.4,121.5,120.2,119.6,110.7,101.5,62.7,55.8,53.3,53.0,21.1$; Anal calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{3}, \mathrm{C}, 78.96 ; \mathrm{H}, 7.89$; N, 13.15. Found C, 78.85; H, 7.87; N, 13.14.

61: wax; IR (neat): $3401,2938,2825,1445,751 ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 8.51$ (bs, 1H), $7.55(\mathrm{~d}, J=7.2$ $\mathrm{Hz}, 1 \mathrm{H}), 7.33\left(\mathrm{dd}, J_{I}=7.2 \mathrm{~Hz}, J_{2}=0.8 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.23-6.98(\mathrm{~m}, 5 \mathrm{H}), 6.35(\mathrm{~s}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 2 \mathrm{H}), 3.65$ (s, 2H), 2.63-2.49 (m, 8H); ${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 161.7$, (d, $J=249 \mathrm{~Hz}$ ), $136.2(\mathrm{~d}, J=5.9 \mathrm{~Hz}$ ), 135.6, 135.4, 128.6 (d, $J=9.7 \mathrm{~Hz}$ ), 127.9, $124.9(\mathrm{~d}, J=1.3 \mathrm{~Hz}), 123.3(\mathrm{~d}, J=18.3 \mathrm{~Hz}), 121.0$, 119.7, 119.1, $113.4(\mathrm{~d}, J=23.5 \mathrm{~Hz}), 110.2,101.0,55.3,52.8,52.2,51.8 ;{ }^{19} \mathrm{~F} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-$ 111.7 Anal calcd for $\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{ClFN}_{3}, \mathrm{C}, 67.13 ; \mathrm{H}, 5.91 ; \mathrm{N}, 11.74$. Found C, 67,$22 ; \mathrm{H}, 5,90 ; \mathrm{N}, 11.71$.

6m: mp: $151.6^{\circ} \mathrm{C}$; IR (KBr): 3404, 2914, 2815, 1456, 1290, 1251, $751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta$ $8.50(\mathrm{bs}, 1 \mathrm{H}), 7.55(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.34\left(\mathrm{dd}, J_{l}=8.0 \mathrm{~Hz}, J_{2}=0.75 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.25-7.21(\mathrm{~m}, 2 \mathrm{H})$, 7.17-7.06 (m, 2H), $6.86(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.35(\mathrm{~s}, 1 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 3.67(\mathrm{~s}, 2 \mathrm{H}), 3.48(\mathrm{~s}, 2 \mathrm{H})$, 2.59-2.49 (m, 8H); ${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta \quad 158.3,135.6,135.4,129.9,129.5,127.9,121.0,119.7$, $119.1,113.1,110.2,101.0,61.9,55.3,54.8,52.8,52.4$; Anal calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{3} \mathrm{O}, \mathrm{C}, 75.19$; H , 7.51 ; N, 12.53. Found C, 67,15; H, 5,19; N, 12.49.

6n: oil; IR (neat): 3401, 2938, 2825, 1445, $751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.57$ (bs, 1 H ), 7.57 (d, $J=$ $7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.36(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.19-7.10(\mathrm{~m}, 2 \mathrm{H}), 6.86(\mathrm{~s}, 2 \mathrm{H}), 6.36(\mathrm{~s}, 1 \mathrm{H}), 3.66(\mathrm{~s}, 2 \mathrm{H})$, $3.49(\mathrm{~s}, 2 \mathrm{H}), 2.52-2.42(\mathrm{~m}, 8 \mathrm{H}), 2.38(\mathrm{~s}, 6 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 137.6,135.8,135.6$, $135.5,131.3,128.4,127.9,121.0,119.7,119.1,110.2,100.9,55.36,55.32,53.1,52.2,20.4,19.6 ;$ Anal calcd for $\mathrm{C}_{23} \mathrm{H}_{29} \mathrm{~N}_{3}, \mathrm{C}, 79.50 ; \mathrm{H}, 8.41 ; \mathrm{N}, 12.09$. Found C, 79.43; H, 8.42; N, 12.06.

60: oil; IR (neat): 3401, 2938, 2825, 1445, $751 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 8.47(\mathrm{bs}, 1 \mathrm{H}), 7.54$ (d, $J=$ $7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.37-7.07(\mathrm{~m}, 12 \mathrm{H}), 6.34(\mathrm{~s}, 1 \mathrm{H}), 4.24(\mathrm{~s}, 1 \mathrm{H}), 3.67(\mathrm{~s}, 2 \mathrm{H}), 2.56-2.34(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 142.0,141.2,136.2,135.6,132.6,129.2,128.7,128.6,128.4,127.9,127.2,121.6$, 120.2, 119.6, 110.7, 101.7, 75.4, 55.8, 53.5, 51.7; Anal calcd for $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{ClN}_{3}, \mathrm{C}, 75.07$; H, 6.30; N, 10.10 . Found C, 74.98 ; H, 6.29 ; N, 10.06.

6p: oil; IR (neat): 3400, 2940, 2825, 1748, 1713, $1447 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}^{\mathrm{NMR}}\left(\mathrm{CDCl}_{3}\right) \delta 8.52(\mathrm{bs}, 1 \mathrm{H}), 7.57$ $(\mathrm{d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.35(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.20-7.07(\mathrm{~m}, 2 \mathrm{H}), 6.38(\mathrm{~s}, 1 \mathrm{H}), 4.16(\mathrm{q}, J=7.1 \mathrm{~Hz}$, $2 \mathrm{H}), 3.68(\mathrm{~s}, 2 \mathrm{H}), 3.54-3.46(\mathrm{~m}, 4 \mathrm{H}), 2.49-2.41(\mathrm{~m}, 4 \mathrm{H}), 1.28(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 155.6,136.2,135.4,128.4,121.7,120.3,119.8,110.8,101.9,61.5,55.9,52.9,43.8,14.7$; Anal calcd for $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{~N}_{2}, \mathrm{C}, 77.18 ; \mathrm{H}, 8.97$; N, 13.85. Found C, 77.02; H, 8.95; N, 13.80.

