Supporting Information

o-Phenylene-Bridged Cp/Sulfonamido Titanium Complexes for Ethylene/1-Octene Copolymerization

*Dae June Joe,[a] Chun Ji Wu,[a] Taekki Bok,[a] Eun Jung Lee,[b] Choong Hoon Lee,[b] Won-Sik Han,[c] Sang Ook Kang,[c] and Bun Yeoul Lee**

[a]Department of Molecular Science and Technology, Ajou University, Suwon 443-749 Korea, [b]LG Chem Ltd. / Research Park, 104-1, Munji-dong, Yuseong-gu, Daejon 305-380, Korea and [c]Department of Chemistry, Korea University, 208 Seochang, Chochiwon, Chung-nam, 339-700, Korea; Email: bunyeoul@ajou.ac.kr; fax: 82-31-219-2394; Tel: 82-31-219-1844

Synthetic Details for Compounds 2-20

2-(Dihydroxyboryl)-3,4-dimethyl-2-cyclopenten-1-one (2). To a Schlenk flask containing 2-bromo-3-methyl-2-cyclopenten-1-one ethylene ketal[1] (44.8 g, 205 mmol) was added THF (240 ml). After the solution was cooled to -78 ^{o}C, n-BuLi (81.8 mL, 205 mmol) was added with syringe. The solution was stirred for 1 hour at -78 ^{o}C. B(O*i*Pr)$_3$ (42.3 g, 225 mmol) in THF (42 ml), which had been cooled to -78 ^{o}C, was added to the lithiated solution via cannula. After the solution was stirred for 1 hour at -78 ^{o}C, it was warmed to -30 ^{o}C slowly for 30 minutes. HCl solution (2 N, 150 mL) was added and the reaction mixture was transferred to a separatory funnel containing ethyl acetate (220 mL). Organic phase was collected and the aqueous phase was extracted with additional ethyl acetate (150 mL). After the combined organic phase was dried over anhydrous $MgSO_4$, solvent was removed with rotary evaporator to give a yellow residue, which was triturated in hexane to give a white solid (26.9 g, 94 %). M.p. 123 ^{o}C. IR (neat): 3317 (O-H), 1635 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 3H, CH_3), 2.51-2.49 (m, 2H, CH_2), 2.69-2.67 (m, 2H, CH_2), 6.75 (s, 2H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.42, 35.12, 35.73, 193.42, 217.35 ppm. Anal. Calc. ($C_6H_9BO_3$): C, 51.49; H, 6.48. Found: C, 51.38; H, 6.51%.

Compound 3. Compound **2** (4.00 g, 28.6 mmol), Na_2CO_3 (4.13 g, 39.0 mmol) and $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) were added into a Schlenk flask inside a glovebox. The flask was brought out and deoxygenated DME (80 mL), deoxygenated water (27 mL) and 2-bromoaniline (3.00 mL, 26.0 mmol) were added successively with syringe. The mixture was stirred for 12 hours at 95 ^oC. After the solution was cooled to room temperature, it was transferred to a separatory funnel containing ethyl acetate (200 mL). Water (100 ml) was added and the organic phase was collected. The water phase was extracted with additional ethyl acetate (100 mL × 2). The organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed with rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 1:1). A white solid was obtained (3.55 g, 73 %). M.p. 110 ^oC. IR (neat): 3440 and 3347 (N-H), 1681 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 3H, CH_3), 2.56–2.54 (m, 2H, CH_2), 2.71–2.68 (m, 2H, CH_2), 3.72 (br s, 2H, NH_2), 6.72 (dd, J = 7.6, 1.2 Hz, 1H, $H^{3 \text{ or } 6}$), 6.77 (td, J = 7.6, 1.2 Hz, 1H, $H^{4 \text{ or } 5}$), 6.89 (dd, J = 7.6, 1.6 Hz, 1H, $H^{3 \text{ or } 6}$), 7.12 (td, J = 7.6, 1.6 Hz, 1H, $H^{4 \text{ or } 5}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.56, 32.13, 34.74, 116.30, 117.84, 118.13, 128.73, 130.44, 139.42, 144.60, 174.84, 207.84 ppm. Anal. Calc. ($C_{12}H_{13}NO$): C, 76.98; H, 7.00; N, 7.48. Found: C, 76.85; H, 7.32; N, 7.22 %.

Compound 4. The compound was synthesized from **2** and 2-bromo-4,6-dimethylaniline using same conditions and procedures as for **3.** White solid was obtained (yield, 96 %). M.p. 110 ^oC. IR (neat): 3440 and 3363 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.58–2.60 (m, 2H, CH_2), 2.74–2.72 (m, 2H, CH_2), 3.49 (br s, 2H, NH_2), 6.60 (s, 1H, Ph-H), 6.88 (s, 1H, Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.89, 18.71, 20.48, 32.19, 34.93, 117.56, 123.00, 126.96, 128.58, 131.04, 139.97, 140.18, 174.68, 207.97 ppm. Anal. Calc. ($C_{14}H_{17}NO$): C, 78.10; H, 7.96; N, 6.51. Found: C, 78.41; H, 7.55; N, 6.23 %.

Compound 5. The compound was synthesized from **2** and 2-bromo-4,6-difluoroaniline using same conditions and procedures as for **3.** White solid was obtained (yield, 79 %). M.p. 115 ^oC. IR (neat): 3440 and 3347 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.07 (s, 3H, CH_3), 2.54-2.52 (m, 2H, CH_2), 2.71-2.69 (m, 2H, CH_2), 3.65 (br s, 2H, NH_2), 6.45 (ddd, J = 9.2, 2.8, 1.6 Hz, 1H, H^5), 6.74 (ddd,

J = 11.2, 7.6, 2.8 Hz, 1H, H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.50 (CH_3), 32.28 (CH_2), 34.66 (CH_2), 103.00 (dd, $^2J_{CF}$ = 25.3, $^2J_{CF}$ = 23.5 Hz, CH), 111.97 (dd, $^2J_{CF}$ = 22.0, $^4J_{CF}$ = 3.8 Hz, CH), 120.43 (dd, J = 9.1, 4.6 Hz), 129.65 (dd, J = 9.8, 3.1 Hz), 137.79 (=*C*-CO), 151.32 (dd, $^1J_{CF}$ = 239, $^3J_{CF}$ = 12.1 Hz, CF), 154.05 (dd, $^1J_{CF}$ = 237, $^3J_{CF}$ = 13.7 Hz, CF), 176.05 (=*C*CH_3), 207.05 (CO) ppm. Anal. Calc. ($C_{12}H_{11}F_2NO$): C, 64.57; H, 4.97; N, 6.27. Found: C, 64.89; H, 5.21; N, 6.15 %.

Compound 6. The compound was synthesized from **1** and 2-bromoaniline using same conditions and procedures as for **3**. Light yellow oil was obtained (Yield, 87 %). M.p. 58 ^oC. IR (neat): 3440 and 3363 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32 (d, J = 3.6 Hz, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.19 (dd, J = 18.4, 1.6 Hz, 1H, CH_2), 2.83 (dd, J = 18.4, 6.4 Hz, 1H, CH_2), 2.92-2.97 (m, 1H, CH), 3.72 (br s, 2H, NH_2), 6.77 (dd, J = 7.6, 1.6 Hz, 1H, $H^{3 \text{ or } 6}$), 6.81 (td, J = 7.6, 1.6 Hz, 1H, $H^{4 \text{ or } 5}$), 6.91 (dd, J = 7.6, 1.6 Hz, 1H, $H^{3 \text{ or } 6}$), 7.15 (td, J = 7.6, 1.6 Hz, 1H, $H^{4 \text{ or } 5}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.39, 19.39, 37.97, 43.51, 116.60, 117.01, 118.16, 118.55, 128.97, 130.67, 144.45, 178.93, 207.02 ppm. Anal. Calc. ($C_{13}H_{15}NO$): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.35; H, 7.55; N, 6.70 %.

Compound 7. The compound was synthesized from **1** and 2-bromo-4,6-dimethylaniline using using same conditions and procedures as for **3**. White solid was obtained (yield, 74 %). M.p. 113 ^oC. IR (neat): 3440 and 3363 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32 (d, J = 3.6 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.20 (1H, CH_2), 2.24 (s, 3H, CH_3), 2.82 (dd, J = 18.4, 6.4 Hz, 1H, CH_2), 2.92-2.96 (m, 1H, CH), 3.48 (br s, 2H, NH_2), 6.60 (s, 1H, Ph-H), 6.88 (s, 1H, Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.19, 17.76, 19.32, 20.37, 37.67, 43.45, 117.42, 122.79, 126.74, 128.44, 130.88 (two Cs), 140.02, 178.58, 206.85 ppm. Anal. Calc. ($C_{15}H_{19}NO$): C, 78.56; H, 8.35; N, 6.11. Found: C, 78.27; H, 8.20; N, 6.52 %.

Compound 8. The compound was synthesized from **1** and 2-bromo-4,6-difluoroaniline using same conditions and procedures as for **3**. White solid was obtained (yield, 76 %). M.p. 70 ^oC. IR (neat): 3440 and 3363 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.29 (d, J = 3.6 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.15 (dd, J = 18.8, 2.0 Hz, 1H, CH_2), 2.79 (dd, J = 18.8, 14.4 Hz, 1H, CH_2), 2.93 (br quintet, J = 6.4 Hz, 1H, CH), 3.65 (br s, 2H, NH_2), 6.47 (ddd, J = 8.8, 2.8, 2.0 Hz, 1H, H^5), 6.76 (ddd, J = 10.8, 8.4,

5.2 Hz, 1H, H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.25 (CH_3), 19.10 (CH_3), 38.01 (CH_2), 43.27 (CH_2), 103.08 (dd, $^2J_{CF}$ = 26.6, $^2J_{CF}$ = 23.5 Hz, CH), 112.04 (dd, $^2J_{CF}$ = 22.0, $^4J_{CF}$ = 3.8 Hz, CH), 120.51 (dd, *J* = 9.0, 4.6 Hz), 129.74 (dd, *J* = 16.7, 15.9 Hz), 137.36 (=*C*-CO), 151.30 (dd, $^1J_{CF}$ = 239, $^3J_{CF}$ = 12.2 Hz, CF), 154.09 (dd, $^1J_{CF}$ = 237, $^3J_{CF}$ = 12.1 Hz, CF), 179.93 (=*C*CH_3), 206.09 (CO) ppm. Anal. Calc. ($C_{13}H_{13}F_2NO$): C, 65.81; H, 5.52; N, 5.90 %. Found: C, 65.97; H, 5.16; N, 5.95 %.

Compound 9. Anhydrous $CeCl_3$ (3.68 g, 14.9 mmol) and THF (35 ml) were added into a Schlenk flask inside a glovebox. The flask was brought out and the solution was cooled to -78 °C. MeLi (8.34 mL, 13.3 mmol, 1.6 M solution in diethyl ether) was added with syringe. The mixture was stirred for 1 hour at -78 °C. Compound **3** (1.00 g, 5.34 mmol) was added as a solid under a weak N_2 flow. After the mixture was stirred for 2 hours at -78 °C, it was transferred to a separatory funnel containing H_2O (30 ml) and ethyl acetate (30 mL). The organic phase was collected and the water phase was extracted further with additional ethyl acetate (10 mL × 2). The combined organic phase was shaken vigorously with aqueous HCl (2 N, 15 mL) for 2 minutes. Aqueous saturated $NaHCO_3$ (20 mL) was added carefully to neutralize the solution. After the collected organic phase was dried over anhydrous $MgSO_4$, the solvent was removed with rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). White oil was obtained (0.634 g, 64 %). IR (neat): 3455 and 3363 (N-H) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.82 (q, *J* = 1.6 Hz, 3H, CH_3), 1.92 (s, 3H, CH_3), 3.01-3.02 (m, 2H, CH_2), 3.80 (br s, 2H, NH_2), 5.99 (q, *J* = 1.6 Hz, 1H, =CH), 6.78 (dd, *J* = 7.6, 1.6 Hz, 1H, $H^{3\text{ or }6}$), 6.79 (td, *J* = 7.6, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 6.97 (dd, *J* = 7.6, 1.6 Hz, 1H, $H^{3\text{ or }6}$), 7.14 (td, *J* = 7.6, 1.6 Hz, 1H, $H^{4\text{ or }5}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.68, 14.77, 44.39, 114.70, 117.79, 122.17, 124.26, 127.86, 130.19, 139.18, 141.38, 143.63, 144.24 ppm. Anal. Calc. ($C_{13}H_{15}N$): C, 84.28; H, 8.16; N, 7.56 %. Found: C, 84.52; H, 8.44; N, 7.35 %.

Compound 10. The compound was synthesized from **4** using same conditions and procedures as for **9**. Brown oil was obtained (yield, 70 %). IR (neat): 3455 and 3363 (N-H) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.83 (d, *J* = 1.6 Hz, 3H, CH_3), 1.93 (s, 3H, CH_3), 2.22 (s, 3H, Ph-CH_3), 2.28 (s, 3H, Ph-CH_3), 3.02 (q, *J* = 1.6 Hz, 2H, CH_2), 3.50 (br s, 2H, NH_2), 5.99 (s, 1H, CH), 6.68 (s, 1H, Ph-H), 6.88 (s, 1H, Ph-H) ppm.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.72, 14.80, 17.94, 20.58, 44.34, 121.88, 122.03, 124.17, 126.33, 128.22, 129.76, 139.65, 139.89, 141.03, 143.75 ppm. Anal. Calc. ($C_{15}H_{19}N$): C, 84.46; H, 8.98; N, 6.57 %. Found: C, 84.21; H, 9.27; N, 6.32 %.

Compound 11. The compound was synthesized from **5** using same conditions and procedures as for **9**. Light brown oil was obtained (yield, 60 %). IR (neat): 3471 and 3378 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.71 (d, J = 1.6 Hz, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.90-2.92 (m, 2H, CH_2), 3.43 (br s, 2H, NH_2), 5.89 (d, J = 1.6 Hz, ,1H, CH), 6.44 (ddd, J = 8.8, 2.4, 1.2 Hz, 1H, H^5), 6.66 (ddd, J = 10.8, 8.8, 2.8 Hz, 1H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.46 (CH_3), 14.65 (CH_3), 44.48 (CH_2), 102.19 (t, $^{2}J_{CF}$ = 25.8 Hz, CH), 111.64 (dd, $^{2}J_{CF}$ = 21.2, $^{4}J_{CF}$ = 4.0 Hz, CH), 124.55 (dd, J = 9.0, 5.0 Hz), 124.84 (=CH), 128.98 (dd, J = 12.1, 5.0 Hz), 137.37 (=C-C_6), 142.50 (=*C*CH_3), 142.70 (=*C*CH_3), 150.59 (dd, $^{1}J_{CF}$ = 239, $^{3}J_{CF}$ = 12.1 Hz, CF), 153.94 (dd, $^{1}J_{CF}$ = 235, $^{3}J_{CF}$ = 12.1 Hz, CF) ppm. Anal. Calc. ($C_{13}H_{13}F_2N$): C, 70.57; H, 5.92; N, 6.33 %. Found: C, 70.48; H, 6.15; N, 6.48 %.

Compound 12. The compound was synthesized from **6** using same conditions and procedures as for **9**. Light brown solid was obtained (yield, 89 %). M.p. 45 ^{o}C. IR (neat): 3455 and 3378 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.82 (s, 2H, CH_2), 3.55 (br s, 2H, NH_2), 6.62 (dd, J = 7.6, 1.6 Hz, 1H, $H^{3\text{ or }6}$), 6.65 (td, J = 7.6, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 6.82 (dd, J = 7.6, 1.6 Hz, 1H, $H^{3\text{ or }6}$), 6.99 (td, J = 7.6, 1.6 Hz, 1H, $H^{4\text{ or }5}$) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 11.67, 13.63, 14.35, 48.80, 114.67, 117.76, 122.79, 127.69, 130.13, 133.14, 135.54, 136.73, 139.61, 144.14 ppm. Anal. Calc. ($C_{14}H_{17}N$): C, 84.37; H, 8.60; N, 7.03 %. Found: C, 84.18; H, 8.59; N, 7.19 %.

Compound 13. The compound was synthesized from **7** using same conditions and procedures as for **9**. Yellow solid was obtained (yield, 75 %). M.p. 54 ^{o}C. IR (neat): 3270 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.74 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.26 (s, 3H, Ph-CH_3), 2.33 (s, 3H, Ph-CH_3), 3.00 (s, 2H, CH_2), 3.47 (br s, 2H, NH_2), 6.72 (s, 1H, Ph-H), 6.91 (s, 1H, Ph-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 11.72, 13.61, 14.40, 17.88, 20.55, 48.78, 121.78, 122.61, 126.21, 128.20, 129.60, 133.00, 135.66, 136.41, 139.85, 140.07 ppm. Anal. Calc. ($C_{16}H_{21}N$): C, 84.53; H, 9.31; N, 6.16 %. Found: C, 84.39; H, 9.58; N, 6.26 %.

Compound 14. The compound was synthesized from **8** using same conditions and procedures as for **9**. Light yellow oil was obtained (yield, 70 %). IR (neat): 3471 and 3378 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.67 (br s, CH_3), 1.87 (br s, CH_3), 1.97 (br s, 3H, CH_3), 2.96 (br s, 2H, CH_2), 3.53 (br s, 2H, NH_2), 5.89 (d, J = 1.6 Hz, CH_2), 6.53 (br d, J = 8.8 Hz, 1H, H^5), 6.76 (br t, J = 8.8 Hz, 1H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 11.58 (CH_3), 13.60 (CH_3), 14.35 (CH_3), 48.95 (CH_2), 102.08 (dd, $^{2}J_{CF}$ = 25.8, 22.8 Hz, CH), 111.65 (d, $^{2}J_{CF}$ = 12 Hz, CH), 125.26 (dd, J = 8.3, 4.5 Hz), 128.98 (d, J = 11.3 Hz), 133.85 (=*C*CH_3), 134.76 (=*C*CH_3), 137.83 (=C-C_6), 137.96 (=*C*CH_3), 150.72 (dd, $^{1}J_{CF}$ = 239, $^{3}J_{CF}$ = 12.9 Hz, CF), 154.08 (dd, $^{1}J_{CF}$ = 236, $^{3}J_{CF}$ = 12.1 Hz, CF) ppm. Anal. Calc. ($C_{14}H_{15}F_2N$): C, 71.47; H, 6.43; N, 5.95 %. Found: C, 71.41; H, 6.25; N, 6.15 %.

Compound 15. To a flask containing compound **9** (0.815 g, 4.40 mmol) in methylene chloride (8 mL) was added pyridine (0.418 g, 5.28 mmol) and *p*-TsCl (0.839 g, 4.40 mmol). The solution was stirred for 12 hours at room temperature. The solution was transferred to a separatory funnel containing aqueous HCl (2 N, 10 mL). The organic phase was collected and washed with aqueous saturated $NaHCO_3$ (10 mL). After the organic phase was dried over $MgSO_4$, solvent was removed with rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1). White solid was obtained (1.33 g, 89 %). M.p. 136 ^{o}C. IR (neat): 3266 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.91 (AB, J = 23.2 Hz, 1H, CH_2), 3.03 (AB, J = 23.2 Hz, 1H, CH_2), 5.93 (s, 1H, =CH), 6.64 (s, 1H, NH), 6.90 (d, J = 7.6 Hz, 1H, C_6H_4-C*H*), 7.02 (t, J = 7.6 Hz, 1H, C_6H_4-C*H*), 7.15 (d, J = 7.6 Hz, 2H, Ts-H), 7.21 (t, J = 7.6 Hz, 1H, C_6H_4-C*H*), 7.59 (d, J = 7.6 Hz, 2H, Ts-H), 7.66 (d, J = 7.6 Hz, 1H, C_6H_4-C*H*) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.05, 14.37, 21.46, 44.50, 118.11, 123.59, 125.38, 126.95, 127.95, 129.12, 129.32, 129.90, 134.55, 134.07, 137.32, 142.16, 143.00, 143.57 ppm. Anal. Calc. ($C_{20}H_{21}NO_2S$): C, 70.77; H, 6.24; N, 4.13 %. Found: C, 70.77; H, 6.24; N, 4.13 %.

Compound 16. The compound was synthesized from **10** using same conditions and procedures as for **15**. White solid was obtained (91 %). M.p. 132-134 ^{o}C. IR (neat): 3280 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.61 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.52 (AB,

J = 23.2 Hz, 1H, CH_2), 2.72 (AB, *J* = 23.2 Hz, 1H, CH_2), 5.74 (s, 1H, =CH), 6.45 (s, 1H, NH), 6.71 (s, 1H, C_6H_2-C*H*), 7.02 (s, 1H, C_6H_2-C*H*), 7.13 (d, *J* = 8.0 Hz, 2H, Ts-H), 7.52 (d, *J* = 8.0 Hz, 2H, Ts-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.62, 19.47, 20.77, 20.80, 21.29, 43.76, 124.03, 126.14, 128.60, 128.74, 128.88, 130.53, 134.81, 136.35, 137.17, 137.98, 139.55, 139.64, 142.25, 142.36 ppm. Anal. Calc. ($C_{22}H_{25}NO_2S$): C, 71.90; H, 6.86; N, 3.81 %. Found: C, 71.76; H, 6.92; N, 3.85 %.

Compound 17. The compound was synthesized from **11** using same conditions and procedures as for **15**. White solid was obtained (85 %). M.p. 126-127 ^oC. IR (neat): 3290 (N-H) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.72 (d, *J* = 2 Hz, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.75 (AB, *J* = 23.6 Hz, 1H, CH_2), 2.86 (AB, *J* = 23.6 Hz, 1H, CH_2), 5.87 (d, *J* = 1.6 Hz, 1H, =CH), 6.45 (s, 1H, NH), 6.64 (ddd, $^3J_{HF}$ = 8.4 Hz, $^4J_{HH}$ = 2.8 Hz, $^5J_{HF}$ = 1.2 Hz, 1H, $C_6H_2F_2$-H), 6.78 (t, ddd, $^3J_{HF}$ = 10.8 Hz, $^3J_{HF}$ = 8.0 Hz, $^4J_{HF}$ = 2.8 Hz, 1H, $C_6H_2F_2$-H), 7.20 (d, *J* = 8.0 Hz, 2H, Ts-H), 7.62 (d, *J* = 8.0 Hz, 2H, Ts-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.44, 14.69, 21.45, 44.30, 103.09 (t, $^2J_{CF}$ = 25.8 Hz, $C_6H_2F_2$-*C*H), 112.73 (dd, $^2J_{CF}$ = 21.2, $^4J_{CF}$ = 3.8 Hz, $C_6H_2F_2$-*C*H), 118.93 (dd, *J* = 12.9, 3.8 Hz, $C_6H_2F_2$-*C*N), 124.79 (=CH), 126.64 (Ts-*C*H), 128.93 (Ts-*C*H), 137.07, 137.36 , 137.66, 137.67, 141.84, 142,65, 143.05, 158.04 (dd, $^1J_{CF}$ = 247, $^3J_{CF}$ = 12.1 Hz, CF), 160.13 (dd, $^1J_{CF}$ = 247, $^3J_{CF}$ = 12.1 Hz, CF) ppm. Anal. Calc. ($C_{20}H_{19}F_2NO_2S$): C, 63.98; H, 5.10; N, 3.73 %. Found: C, 63.79; H, 4.98; N, 3.82 %.

Compound 18. The compound was synthesized from **12** using same conditions and procedures as for **15**. White solid was obtained (85 %). M.p. 119 ^oC. IR (neat): 3270 (N-H) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.31 (d, *J* = 1.2 Hz, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.89 (AB, *J* = 22.8 Hz, 1H, CH_2), 3.00 (AB, *J* = 22.8 Hz, 1H, CH_2), 6.67 (s, 1H, NH), 6.92 (dd, *J* = 7.6, 1.6 Hz, 1H, C_6H_4-C*H*), 7.05 (td, *J* = 7.6, 1.6 Hz, 1H, C_6H_4-C*H*), 7.15 (d, *J* = 8.0 Hz, 2H, Ts-H), 7.24 (td, *J* = 7.6, 1.6 Hz, 1H, C_6H_4-C*H*), 7.62 (d, *J* = 8.0 Hz, 2H, Ts-H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H, C_6H_4-C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.62, 13.72, 14.28, 21.26, 49.02, 119.15, 124.00, 127.59, 127.89, 128.35, 129.58, 130.31, 134.65, 134.68, 135.86, 137.61, 138.45, 138.75, 143.30 ppm. Anal. Calc. ($C_{21}H_{23}NO_2S$): C, 71.36; H, 6.56; N, 3.96 %. Found: C, 71.45; H, 6.39; N, 4.10 %.

Compound 19. The compound was synthesized from **13** using same conditions and procedures as for **15**. White solid was obtained (86 %). M.p. 128-129 ^{o}C. IR (neat): 3266 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.30 (AB, *J* = 22.0 Hz, 1H, CH_2), 2.31 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.54 (AB, *J* = 22.0 Hz, 1H, CH_2), 6.09 (s, 1H, NH), 6.54 (s, 1H, C_6H_2-C*H*), 6.93 (s, 1H, C_6H_2-C*H*), 7.02 (d, *J* = 8.0 Hz, 2H, Ts-H), 7.36 (d, *J* = 8.0 Hz, 2H, Ts-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.87, 13.50, 14.50, 19.86, 21.02, 21.56, 48.36, 126.40, 128.60, 128.62, 128.79, 129.63, 130.73, 133.12, 134.56, 134.76, 135.28, 136.53, 137.41, 137.90, 142.34 ppm. Anal. Calc. ($C_{23}H_{27}NO_2S$): C, 72.40; H, 7.13; N, 3.67 %. Found: C, 72.26; H, 7.31; N, 3.49 %.

Compound 20. The compound was synthesized from **14** using same conditions and procedures as for **15**. White solid was obtained (68 %). M.p. 112-113 ^{o}C. IR (neat): 3290 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.53 (d, *J* = 1.2Hz, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.66 (AB, *J* = 22.4 Hz, 1H, CH_2), 2.77 (AB, *J* = 22.4 Hz, 1H, CH_2), 6.26 (s, 1H, NH), 6.61 (ddd, $^{3}J_{HF}$ = 8.4 Hz, $^{4}J_{HH}$ = 2.8 Hz, $^{5}J_{HF}$ = 1.2 Hz, 1H, $C_6H_2F_2$-H), 6.80 (t, ddd, $^{3}J_{HF}$ = 10.8 Hz, $^{3}J_{HF}$ = 8.0 Hz, $^{4}J_{HF}$ = 2.8 Hz, 1H, $C_6H_2F_2$-H), 7.21 (d, *J* = 8.4Hz, 2H, Ts-H), 7.62 (d, *J* = 8.4Hz, 2H, Ts-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.66, 13.48, 14.46, 21.61, 48.78, 103.19 (t, $^{2}J_{CF}$ = 25.8 Hz, $C_6H_2F_2$-*C*H), 112.70 (dd, $^{2}J_{CF}$ = 22.0, $^{4}J_{CF}$ = 3.8 Hz, $C_6H_2F_2$-*C*H), 118.98 (dd, *J* = 12.9, 3.8 Hz, $C_6H_2F_2$-*C*N), 126.74 (Ts-*C*H), 128.94 (Ts-*C*H), 129.06, 133.91, 133.98, 137.40, 137.48, 138.36, 143.06, 158.22 (dd, $^{1}J_{CF}$ = 247, $^{3}J_{CF}$ = 12.9 Hz, CF), 160.08 (dd, $^{1}J_{CF}$ = 247, $^{3}J_{CF}$ = 12.9 Hz, CF) ppm. Anal. Calc. ($C_{21}H_{21}F_2NO_2S$): C, 64.76; H, 5.43; N, 3.60 %. Found: C, 64.82; H, 5.29; N, 3.61 %.

Reference

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