Supplementary Material (ESI) for Dalton Transactions

Supporting Information

to the paper

Synthesis and characterization of the titanium complexes bearing two β-enaminoketonato ligands with electron withdrawing groups/modified phenyls and their behaviors for ethylene (co-) polymerization

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Additional experimental details

Compounds 1c-t were prepared via a procedure similar to that for 1b and the ^{1}H NMR of these obtained compounds are as followes :

PhN=C(CF_3)CHC(*m*-FPh)OH (1c). yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.27 (s, 1H, O-H), 7.67-7.15 (m, 9H, Ar), 6.30 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.76, 163.00, 149.08, 140.83, 137.55, 130.23, 129.08, 127.32, 126.04, 123.12, 120.15, 119.22, 114.37, 91.44. Anal. Calcd. for $C_{16}H_{11}F_4NO$: C, 62.14; H, 3.59; N, 4.53. Found: C, 62.10; H, 3.55; N, 4.47.

PhN=C(CF_3)CHC(*p*-FPh)OH (1d). yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.31 (s, 1H, O-H), 8.00 (m, 2H, Ar), 7.39-7.14 (m, 7H, Ar), 6.39 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.80, 165.41, 148.73, 137.71, 134.92, 129.99, 129.07, 127.21, 126.04, 120.15, 115.71, 91.43. Anal. Calcd. for $C_{16}H_{11}F_4NO$: C, 62.14; H, 3.59; N, 4.53; Found: C, 62.25; H, 3.64; N, 4.56.

PhN=C(CF_3)CHC(*p*-ClPh)OH (1e). yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.34 (s, 1H, O-H), 7.90 (d, 2H, Ar), 7.51-7.13 (m, 7H, Ar), 6.37 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.85, 148.90, 138.70, 137.62, 136.94, 129.08, 128.91, 127.26, 126.02, 120.10, 91.42. Anal. Calcd. for $C_{16}H_{11}ClF_3NO$: C, 59.00; H, 3.40; N, 4.30. Found: C, 58.85; H, 3.35; N, 4.27.

PhN=C(CF_3)CHC(*p*-OMePh)OH (1f). yield 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.20 (s, 1H, O-H), 7.90-7.87 (dd, 2H, Ar), 7.32-7.16 (m, 5H, Ph), 6.92-6.88 (dd, 2H, Ar), 6.33 (s, 1H, =CH), 3.82 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ190.14, 163.15, 147.88, 138.05, 131.40, 129.67, 129.01, 126.88, 125.91, 120.32, 113.87, 91.82, 55.43. Anal. Calcd. for $C_{17}H_{14}F_3NO_2$: C, 63.55; H, 4.39; N, 4.36; Found: C, 63.52; H, 4.37; N, 4.33.

PhN=C(CF_3)CHC(*p*-CF_3Ph)OH (1g). yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.40 (s, 1H, O-H), 7.88 (dd, 4H, Ar-H), 7.38-7.24 (m, 5H, Ar-H), 6.39 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.87, 149.45, 141.55, 137.38, 133.63, 129.10, 127.78, 127.45, 126.05, 125.66, 123.78, 119.97, 91.46. Anal. Calcd. for $C_{17}H_{11}F_6NO$: C, 56.83; H, 3.09; N, 3.90. Found: C, 56.75; H, 3.12; N, 3.85.

PhN=C(CF_3)CHC(*m*-CF_3Ph)OH (1h). yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.40 (s, 1H, O-H), 8.20 (s, 1H, Ar), 8.12 (d, 1H, Ar), 7.79 (d, 1H, Ar), 7.62 (t, 1H, Ar), 7.43-7.26 (m, 5H, Ar), 6.40 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.55, 149.48, 139.24, 137.41, 131.25, 130.58,

129.22, 129.10, 128.65, 127.43, 126.03, 124.36, 123.86, 119.99, 91.16. Anal. Calcd. for $C_{17}H_{11}F_6NO$: C, 56.83; H, 3.09; N, 3.90. Found: C, 56.74; H, 3.14; N, 3.92.

PhN=C(CF_3)CHC(*o*-CF_3Ph)OH (1i). yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.04 (s, 1H, O-H), 7.74 (d, 1H, Ph-H), 7.62-7.56 (m, 3H, Ph-H), 7.42-7.25 (m, 5H, Ph-H), 6.00 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.95, 148.76, 140.25, 137.28, 131.79, 129.97, 129.07, 128.20, 127.51, 127.27, 126.74, 126.15, 123.78, 119.84, 95.05. Anal. Calc. for $C_{17}H_{11}F_6NO$: C, 56.83; H, 3.09; N, 3.90; Found: C, 56.70; H, 3.14; N, 8.93.

PhN=C(CF_3)CHC(*o*-ClPh)OH (1j). yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.12 (s, 1H, O-H), 7.55-7.25 (m, 8H, Ar), 6.18 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.57, 147.28, 138.55, 136.40, 130.84, 130.34, 130.12, 128.45, 126.27, 125.85, 125.22, 124.97, 118.93, 94.87. Anal. Calc. for $C_{16}H_{11}ClF_3NO$: C, 59.00; H, 3.40; N, 4.30; Found: C, 58.89; H, 3.45; N, 4.27.

PhN=C(CF_3)CHC(*o*-BrPh)OH (1k). yield 68%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.08 (s, 1H, O-H),7.62 (d, 1H, Ar), 7.52 (d, 1H, Ar), 7.41-6.84 (m, 7H, Ar), 6.13 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.48, 147.31, 140.58, 136.37, 132.71, 130.34, 128.27, 128.00, 126.39, 126.30, 122.24, 118.90, 118.40, 94.65. Anal. Calc. for $C_{16}H_{11}BrF_3NO$: C, 51.92; H, 3.00; N, 3.78; Found: C, 51.90; H, 3.04; N, 3.81.

PhN=C(CF_3)CHC(*o*-IPh)OH (1l). yield 43%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.07 (s, 1H, O-H), 7.94 (d, 1H, Ar), 7.47-7.13 (m, 7H, Ar), 7.12 (t, 1H, Ar), 6.07 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.24, 149.00, 145.27, 140.92, 137.79, 131.80, 129.46, 128.95, 128.53, 127.79, 126.49, 120.30, 95.48, 92.58. Anal. Calc. for $C_{16}H_{11}F_3INO$: C, 46.07; H, 2.66; N, 3.36; Found: C, 46.19; H, 2.71; N, 3.40.

PhN=C(CF_3)CHC(2,4-F_2Ph)OH (1m). yield 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.22 (s, 1H, O-H), 7.85(q, 1H, Ar), 7.83-7.18 (m, 5H, Ar), 6.92-6.75 (m, 2H, Ar) 6.32 (s, 1H, =CH). Anal. Calc. for $C_{16}H_{10}F_5NO$: C, 58.72; H, 3.08; N, 4.28; Found: C, 58.54; H, 3.11; N, 4.30.

PhN=C(CF_3)CHC(2,6-F_2Ph)OH (1n). yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.04 (s, 1H, O-H), 7.35-7.11 (m, 5H, Ar), 6.91-6.78 (m, 3H, Ar), 5.98 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.27, 160.05, 148.68, 137.22, 131.92, 129.07, 127.52, 126.13, 122.60, 118.55, 112.09, 97.14. Anal. Calc. for $C_{16}H_{10}F_5NO$: C, 58.72; H, 3.08; N, 4.28; Found: C, 58.68; H, 3.13; N, 4.33.

PhN=C(CF_3)CHC(3,4-F_2Ph)OH (1o). yield 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.23 (s, 1H, O-H), 7.73-7.63 (m, 2H, Ar), 7.35-7.15 (m, 6H, Ar), 6.25(s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.46, 153.49, 150.13, 149.26, 137.45, 135.71, 129.10, 127.41, 126.07, 124.17, 120.01,117.45, 116.86, 90.92. Anal. Calc. for $C_{16}H_{10}F_5NO$: C, 58.72; H, 3.08; N, 4.28. Found: C, 58.96; H, 3.13; N, 4.26.

PhN=C(CF_3)CHC(3,5-F_2Ph)OH (1p). yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.35 (s, 1H, O-H), 7.47-7.25 (m, 7H, Ar), 6.96 (m, 1H, Ar), 6.30 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.19, 162.74, 149.66, 141.75, 137.30, 129.10, 127.51, 126.06, 119.91, 110.41,107.39, 90.99. Anal. Calc. for $C_{16}H_{10}F_5NO$: C, 58.72; H, 3.08; N, 4.28. Found: C, 58.64; H, 3.13; N, 4.25.

PhN=C(CF_3)CHC(2,3,4,5,6-F_5Ph)OH (1q). yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.10 (s, 1H, O-H), 7.44-7.20 (m, 5H, Ar), 5.96 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.25, 149.96, 144.27, 142.33, 137.68, 136.67, 129.15, 127.97, 126.18, 119.49, 115.63, 96.15. Anal. Calc. for $C_{16}H_7F_8NO$: C, 50.41; H, 1.85; N, 3.67; Found: C, 50.37; H, 1.90; N, 3.63.

PhN=C(CF_3)CHC(2,3,4,6-F_4,4-OMePh)OH (1r). yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.10 (s, 1H, O-H), 7.43-7.25 (m, 5H, Ar), 6.00 (s, 1H, =CH), 4.16 (t, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.69, 149.79, 145.05, 141.04, 140.52, 137.34, 129.46, 128.09, 126.51, 120.04, 113.93, 96.99, 62.37. ^{19}F NMR ($CDCl_3$): δ -162.5, -192.2, -206.6. Anal. Calc. for $C_{17}H_{10}F_7NO_2$: C, 51.92; H, 2.56; N, 3.56; Found: C, 52.01; H, 2.61; N, 3.50.

PhN=C(CF_3)CHC(2,6-Cl_2Ph)OH (1s). yield 77%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.96 (s, 1H, O-H), 7.40-7.23 (m, 8H, Ar), 5.87 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.23, 149.07, 139.35, 137.23, 131.67, 130.45, 129.12, 128.25, 127.62, 126.20, 119.82, 96.22. Anal. Calc. for $C_{16}H_{10}Cl_2F_3NO$: C, 53.36; H, 2.80; N, 3.89; Found: C, 53.32; H, 2.75; N, 3.85.

PhN=C(CF_3)CHC(2,5-Cl_2Ph)OH (1t). yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.12 (s, 1H, O-H), 7.55-7.27 (m, 8H, Ar), 6.13 (s, 1H, =CH). ^{13}C NMR (75MHz, $CDCl_3$): δ 190.94, 148.99, 140.75, 137.20, 133.05, 131.74, 131.26, 129.45, 129.44, 129.11, 127.58, 126.11, 119.83, 95.40. Anal. Calc. for $C_{16}H_{10}Cl_2F_3NO$: C, 53.36; H, 2.80; N, 3.89; Found: C, 53.32; H, 2.84; N, 3.93.

Complexes 2c-2t were prepared via a procedure similar to that for 2b , the ^{1}H NMR and the ^{13}C NMR **of these obtained complexes are as followes :**

[PhN=C(CF_3)CHC(*m*-FPh)O]$_2$$TiCl_2$ (2c). yield 49%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.43

(m, 2H, Ar-H), 7.38-7.33 (m, 4H, Ar-H), 7.38-7.33 (m, 4H, Ar-H), 7.29-7.21 (m, 4H, Ar-H), 7.10-7.00 (m, 4H, Ar-H), 6.87-6.82 (m, 2H, Ar-H), 6.78 (d, 2H, Ar-H), 6.49 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.05, 162.94, 158.01, 147.94, 135.19, 130.59, 128.60, 128.13, 126.96, 126.82, 123.94, 122.07, 120.25, 119.34, 115.15, 99.81. Anal. Calcd. for $C_{32}H_{20}Cl_2F_8N_2O_2Ti$: C, 52.27; H, 2.74; N, 3.81; Found: C, 52.24; H, 2.69; N, 3.76.

[PhN=C(CF$_3$)CHC(*p*-FPh)O]$_2$TiCl$_2$ (2d). yield 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69-7.63 (m, 4H, Ph-H), 7.33 (d, 2H, Ph-H), 7.10-7.04 (m, 4H, Ph-H), 6.99 (dt, 2H, Ph-H), 6.83-6.78 (m, 4H, Ph-H), 6.46 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.57, 166.14, 157.59, 148.12, 131.03, 129.22, 128.48, 128.09, 126.83, 126.38, 122.33, 119.46, 116.20, 99.18. Anal. Calcd. for $C_{32}H_{20}Cl_2F_8N_2O_2Ti$: C, 52.27; H, 2.74; N, 3.81; Found: C, 52.29; H, 2.69; N, 3.77.

[PhN=C(CF$_3$)CHC(*p*-ClPh)O]$_2$TiCl$_2$ (2e). yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (dd, 8H, Ar-H), 7.31 (d, 2H, Ar-H), 7.10-6.97 (td, 4H, Ar-H), 6.85-6.76 (m, 4H, Ar-H), 6.48 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.37, 157.86, 148.02, 139.89, 131.36, 129.65, 129.28, 128.57, 128.10, 126.94, 126.82, 122.21, 119.52, 99.45. Anal. Calcd. for $C_{32}H_{20}Cl_4F_6N_2O_2Ti$: C, 50.03; H, 2.62; N, 3.65; Found: C, 50.32; H, 2.57; N, 3.69.

[PhN=C(CF$_3$)CHC(*p*-OMePh)O]$_2$TiCl$_2$ (2f). yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (dd, 4H, Ar-H), 7.35 (d, 2H, Ar-H), 7.07-6.96 (m, 4H, Ar-H), 6.87-6.77 (m, 8H, Ar-H), 6.44 (s, 2H, =CH), 3.89 (s, 6H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.85, 164.37, 156.86, 148.48, 130.93, 128.32, 127.93, 127.11, 126.53, 125.49, 122.74, 120.28, 114.38, 98.53, 55.99. Anal. Calcd. for $C_{34}H_{26}Cl_2F_6N_2O_4Ti$: C, 53.78; H, 3.45; N, 3.69; Found: C, 53.85; H, 3.49; N, 3.67.

[PhN=C(CF$_3$)CHC(*p*-CF$_3$Ph)O]$_2$TiCl$_2$ (2g). yield 49%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, 8H, Ar-H), 7.30 (d, 2H, Ar-H), 7.10-6.99 (m, 4H, Ar-H), 6.84-6.75 (m, 4H, Ar-H), 6.52 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.30, 157.90, 147.84, 136.17, 134.24, 129.44, 128.29, 128.01, 127.10, 126.70, 126.45, 125.89, 122.15, 121.19, 100.20. Anal. Calcd. for $C_{34}H_{20}Cl_2F_{12}N_2O_2Ti$: C, 48.89; H, 2.41; N, 3.35; Found: C,49.12; H, 2.36; N, 3.39.

[PhN=C(CF$_3$)CHC(*m*-CF$_3$Ph)O]$_2$TiCl$_2$ (2h). yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, 2H, Ar-H), 7.76 (br d, 4H, Ar-H), 7.54 (t, 2H, Ar-H), 7.35 (d, 2H, Ar-H), 7.09 (td, 2H, Ar-H), 7.02 (td, 2H, Ar-H), 6.80 (t, 2H, Ar-H), 6.54 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.65, 157.85, 147.90, 133.82, 132.16, 131.73, 131.34, 129.61, 128.63, 128.19, 127.01, 126.75, 125.74,

124.98, 121.98, 119.27, 99.79. Anal. Calcd. for $C_{34}H_{20}Cl_2F_{12}N_2O_2Ti$: C, 48.89; H, 2.41; N, 3.35; Found: C,48.95; H, 2.43; N, 3.31.

[PhN=C(CF$_3$)CHC(*o*-CF$_3$Ph)O]$_2$TiCl$_2$ (2i).

Complex **2i** was prepared via a procedure similar to that for **2b** as the red powder in 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, 2H, Ar-H), 7.56-7.48 (m, 4H, Ar-H), 7.30-7.22 (m, 4H, Ar-H), 7.09-7.07 (m, 6H, Ar-H), 6.83 (d, 2H, Ar-H), 6.26 (s, 2H, =CH). Anal. Calcd. for $C_{34}H_{20}Cl_2F_{12}N_2O_2Ti$: C, 48.89; H, 2.41; N, 3.35; Found: C,48.79; H, 2.39; N, 3.38.

[PhN=C(CF$_3$)CHC(*o*-ClPh)O]$_2$TiCl$_2$ (2j). yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.50 (dd, 2H, Ar), 7.41-7.37 (m, 4H, Ar-H), 7.32-7.22 (m, 6H, Ar-H), 6.98-6.93 (m, 4H, Ar-H), 6.87 (s, 2H, =CH), 6.83 (d, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ173.41, 158.50, 147.94, 133.23, 132.93, 132.61, 132.37, 131.53, 129.43, 128.31, 127.18, 127.04, 126.70, 121.82, 118.85, 104.78. Anal. Calcd. for $C_{32}H_{20}Cl_4F_6N_2O_2Ti$: C, 50.03; H, 2.62; N, 3.65; Found: C, 50.05; H, 2.67; N, 3.60.

[PhN=C(CF$_3$)CHC(*o*-BrPh)O]$_2$TiCl$_2$ (2k). yield 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (m, 2H, Ar-H), 7.35-7.25 (m, 10H, Ar-H), 7.01-6.97 (m,4H, Ar-H), 6.85 (d, 2H, Ar-H), 6.76 (s, 2H, =CH). Anal. Calc. for $C_{32}H_{20}Br_2Cl_2F_6N_2O_2Ti$: C, 51.92; H, 3.00; N, 3.78; Found: C, 51.85; H, 3.04; N, 3.82.

[PhN=C(CF$_3$)CHC(*o*-IPh)O]$_2$TiCl$_2$ (2l). yield 64%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, 2H, Ar-H), 7.38-7.28 (m, 6H, Ar-H), 7.13-6.96 (m, 8H, Ar-H), 6.85 (d, 2H, Ar-H), 6.55 (s, 2H, =CH). Anal. Calc. for $C_{32}H_{20}Cl_2F_6I_2N_2O_2Ti$: C, 40.41; H, 2.12; N, 2.95; Found: C, 40.69; H, 2.16; N, 3.01.

[PhN=C(CF$_3$)CHC(2,4-F$_2$Ph)O]$_2$TiCl$_2$ (2m). yield.68% ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (q, 2H, Ar-H), 7.28 (d, 2H, Ar-H), 7.13 (td, 2H, Ar-H), 6.99-6.92 (m, 6H, Ar-H and =CH), 6.74 (d, 2H, Ar-H). Anal. Calc. for $C_{32}H_{18}Cl_2F_{10}N_2O_2Ti$: C, 49.83; H, 2.35; N, 3.63; Found: C, 49.79; H, 2.29; N, 3.59.

[PhN=C(CF$_3$)CHC(2,6-F$_2$Ph)O]$_2$TiCl$_2$ (2n). yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7. 40 (m, 2H, Ph-H), 7.28-7.24 (m, 4H, Ph-H), 6.95-6.89 (m, 8H, Ph-H), 6.82 (d, 2H, Ph-H), 6.37 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.00, 161.33, 157.59, 147.85, 133.53, 129.44, 128.23, 127.94, 126.77, 126.52, 121.56, 119.20, 112.59, 106.09. Anal. Calc. for $C_{32}H_{18}Cl_2F_{10}N_2O_2Ti$: C, 49.83; H, 2.35; N, 3.63; Found: C, 49.69; H, 2.30; N, 3.58.

[PhN=C(CF_3)CHC(3,4-F_2Ph)O]$_2$TiCl$_2$ (2o). yield 59%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.40 (m, 4H, Ar-H), 7.33 (d, 2H, Ar-H), 7.19 (t, 2H, Ar), 7.16-7.03 (m, 4H, Ar-H), 6.87 (t, 2H, Ar-H), 6.77 (d, 2H, Ar-H), 6.25(s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.98, 158.04, 160.06, 150.56, 147.92, 130.06, 128.57, 128.20, 127.00, 126.80, 125.07, 122.11, 118.50, 118.00, 117.50, 99.33. Anal. Calc. for $C_{32}H_{18}Cl_2F_{10}N_2O_2Ti$: C, 49.83; H, 2.35; N, 3.63; Found: C, 49.78; H, 2.37; N, 3.65.

[PhN=C(CF_3)CHC(3,5-F_2Ph)O]$_2$TiCl$_2$ (2p). yield 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, 2H, Ph-H), 7.14-7.07 (m, 8H, Ph-H), 6.99-6.88 (m, 4H, Ar),6.75 (d, 2H, Ph-H), 6.42 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.97, 161.76, 156.91, 146.35, 134.70, 127.30, 126.87, 125.75, 125.32, 120.48, 117.78, 109.82, 107.01, 98.58. Anal. Calc. for $C_{32}H_{18}Cl_2F_{10}N_2O_2Ti$: C, 49.83; H, 2.35; N, 3.63; Found: C, 49.79; H, 2.38; N, 3.59.

[PhN=C(CF_3)CHC(2,3,4,5,6-F_5Ph)O]$_2$TiCl$_2$ (2q). yield 59%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.28 (m, 4H, Ph-H), 7.14-6.79 (m, 4H, Ph-H), 6.81 (d, 2H, Ph-H), 6.32 (s, 1H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.73, 165.82, 157.75, 147.67, 129.48, 128.36, 128.09, 126.80, 126.45, 121.56, 119.05, 107.50, 105.60, 97.15. Anal. Calc. for $C_{32}H_{12}Cl_2F_{16}N_2O_2Ti$: C, 43.72; H, 1.38; N, 3.19; Found: C, 43.59; H, 1.33; N, 3.23.

[PhN=C(CF_3)CHC(2,3,4,6-F_4,4-OMePh)O]$_2$TiCl$_2$ (2r). yield 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.23 (m, 4H, Ar), 7.09-6.99 (m, 4H, Ar), 6.80 (d, 2H, Ar), 6.29 (s, 2H, =CH), 4.21 (t, 6H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.73, 165.82, 157.93, 146.62, 143.29, 129.49, 128.36, 128.09, 126.80, 126.45, 121.56, 119.05, 107.50, 97.15, 62.43. Anal. Calc. for $C_{34}H_{18}Cl_2F_{14}N_2O_4Ti$: C, 45.21; H, 2.01; N, 3.10; Found: C, 45.54; H, 2.05; N, 3.08.

[PhN=C(CF_3)CHC(2,6-Cl_2Ph)O]$_2$TiCl$_2$ (2s). yield 89%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.22 (m, 16H, Ar), 5.89 (s, 2H, =CH). Anal. Calc. for $C_{32}H_{18}Cl_6F_6N_2O_2Ti$: C, 45.92; H, 2.17; N, 3.35; Found: C, 45.96; H, 2.23; N, 3.40.

[PhN=C(CF_3)CHC(2,5-Cl_2Ph)O]$_2$TiCl$_2$ (2t). yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (d, 4H, Ph-H), 7.29-7.24 (m, 4H, Ph-H), 7.18-6.90 (m, 6H, Ph-H), 6.82 (d, 2H, Ph-H), 6.74 (s, 2H, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.28, 158.35, 147.82, 133.86, 133.38, 132.59, 131.92, 131.71, 129.99, 129.46, 128.65, 128.44, 127.37, 121.68, 119.21, 104.66. Anal. Calc. for $C_{32}H_{18}Cl_6F_6N_2O_2Ti$: C, 45.92; H, 2.17; N, 3.35; Found: C, 45.87; H, 2.13; N, 3.30.