Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Control of Ziegler-Natta Catalyst Activity by Structural Design of Alkoxysilane-based External Donors

Vikas Khatri,[a] Usharani Sahoo,[b] Sukhdeep Kaur,[b] Rashmi Rani,[b] Gurmeet Singh,[b] Gurpreet Singh Kapur,[b] and Hemant K. Kashyap[a,]*

[a]*Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India*
[b]*Petrochemical & Polymer Department, R&D Center, IndianOil Corporation Ltd., Sector-13, Faridabad 121007, Haryana, India*
*Corresponding author, E-mail: hkashyap@chemistry.iitd.ac.in

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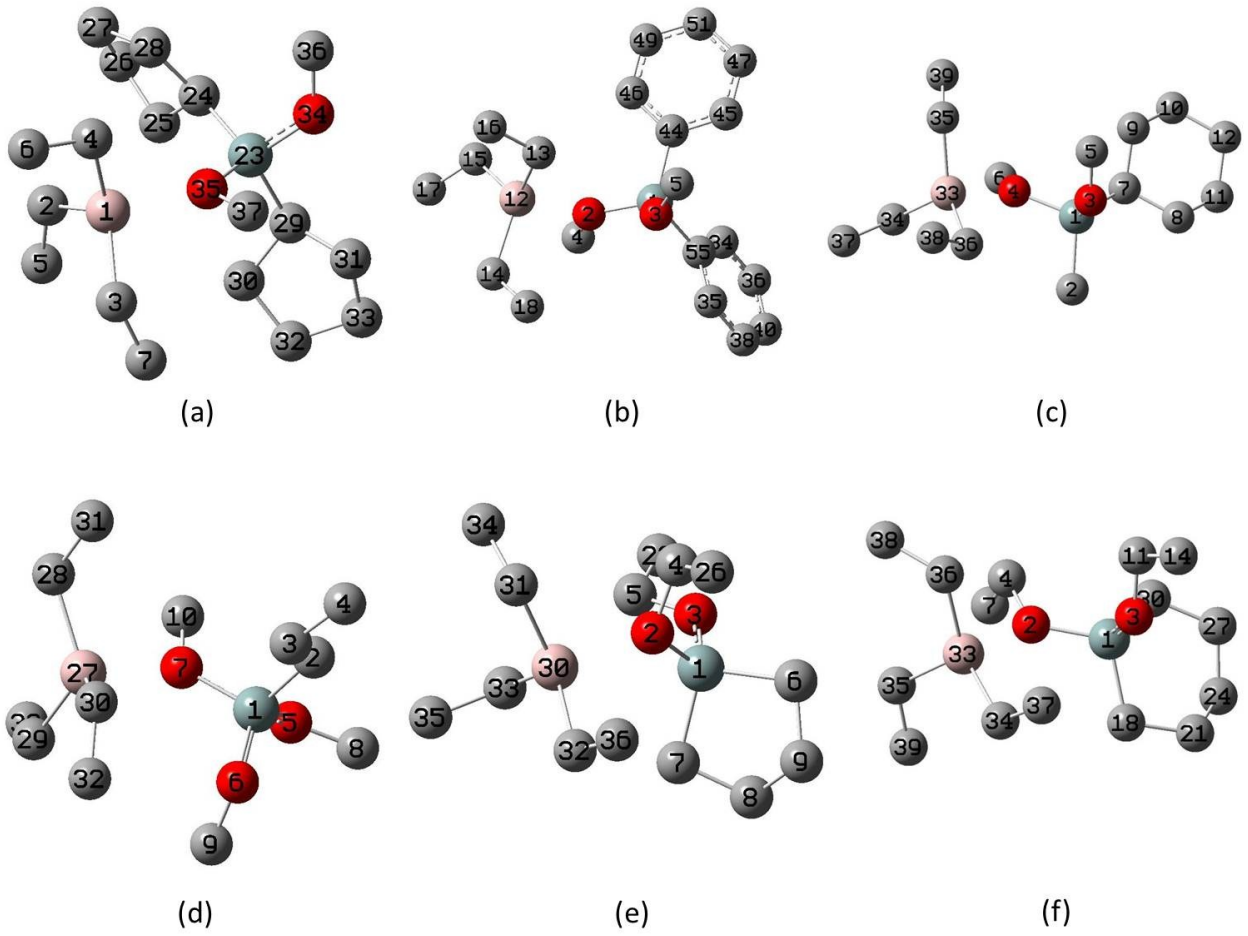


Figure S1: Optimized geometries of (a) **TEAL-D1,** (b) **TEAL-D2**, (c) **TEAL-D3**, (d) **TEAL-D4**, (e) **TEAL-D5**, and (f) **TEAL-D6** complexes. Hydrogen atoms are omitted for the sake of clarity.

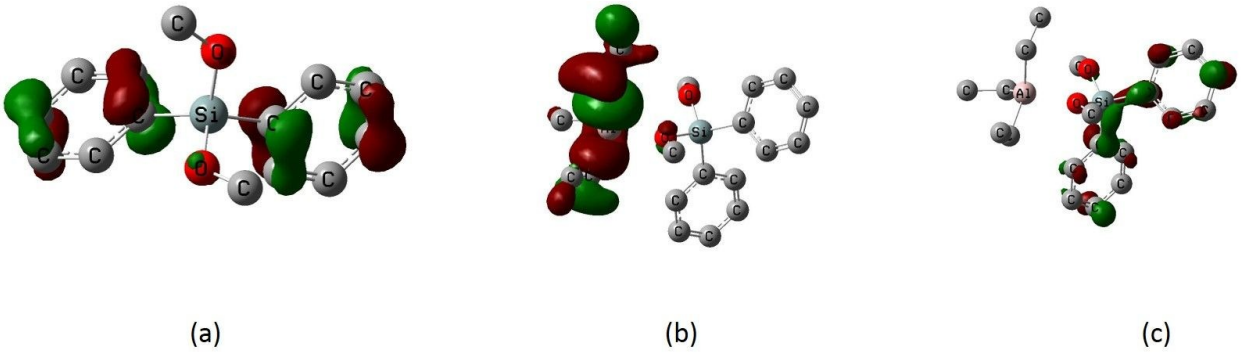
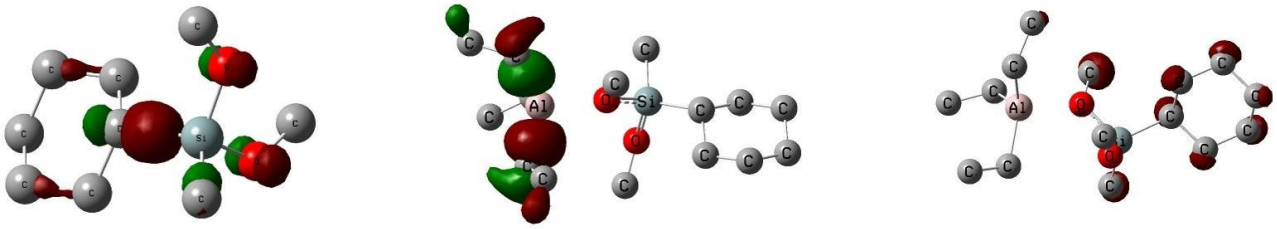
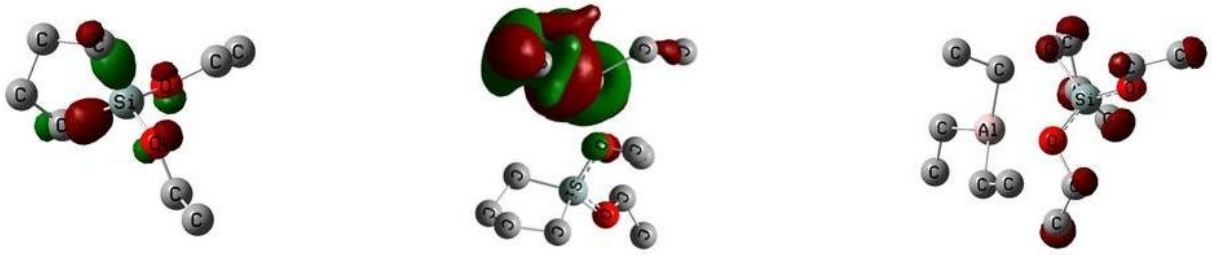


Figure S2: Computed frontier highest occupied molecular orbitals of (a) **D2** and (b) **TEAL-D2** complex, and the lowest unoccupied molecular orbital of (c) **TEAL-D2**. In **D2**, the HOMOs are localized over phenyl rings. MOs of **TEAL-D2** complex indicate the donation of electron from the donor to **TEAL**.



(a) (b) (c)

Figure S3: Computed frontier highest occupied molecular orbitals of (a) **D3** and (b) **TEAL-D3** complex, and the lowest unoccupied molecular orbital of (c) **TEAL-D3**. In **D3**, the HOMOs are localized on oxygen atoms and the carbon atom directly bonded to Si atom. MOs of **TEAL-D3** complex indicate the donation of electron from the donor to **TEAL**.



(a) (b) (c)

Figure S4: Computed frontier highest occupied molecular orbitals of (a) **D5** and (b) **TEAL-D5** complex, and the lowest unoccupied molecular orbital of (c) **TEAL-D5**. In **D5**, the HOMOs are localized on oxygen atoms and the carbon atoms directly bonded to Si atom. MOs of **TEAL-D5** complex indicate the donation of electron from the donor to **TEAL**.

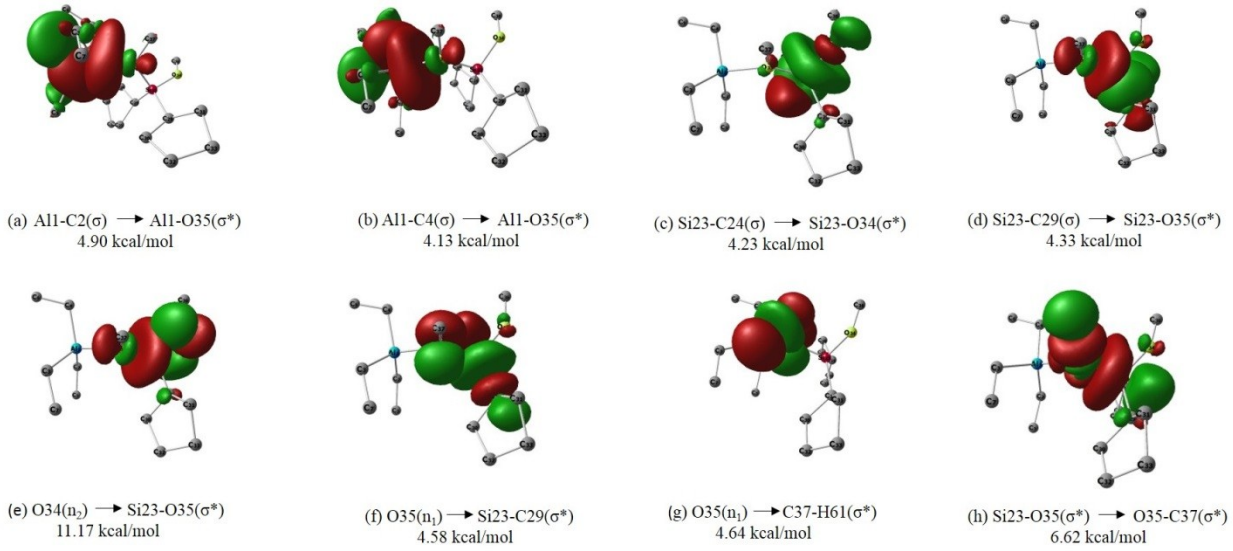


Figure S5: NBO diagrams of **TEAL-D1** complex showing donor-acceptor interaction for the stabilization of the complex. Hydrogen atoms are omitted for the sake of clarity.

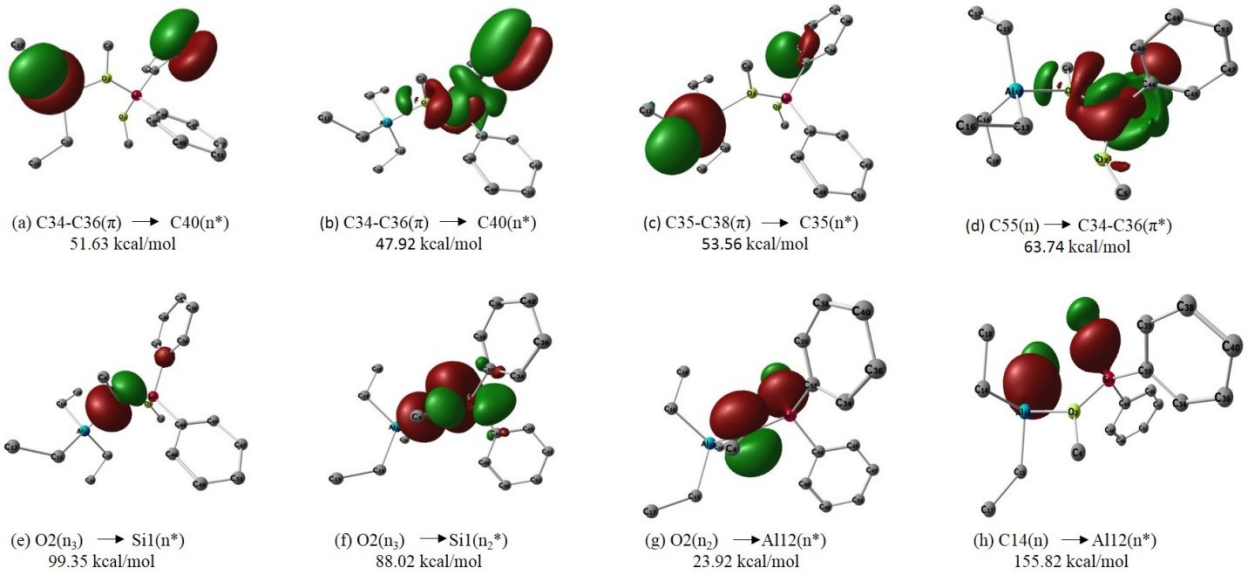


Figure S6: NBO diagrams of **TEAL-D2** complex showing donor-acceptor interaction for the stabilization of the complex. Hydrogen atoms are omitted for the sake of clarity.

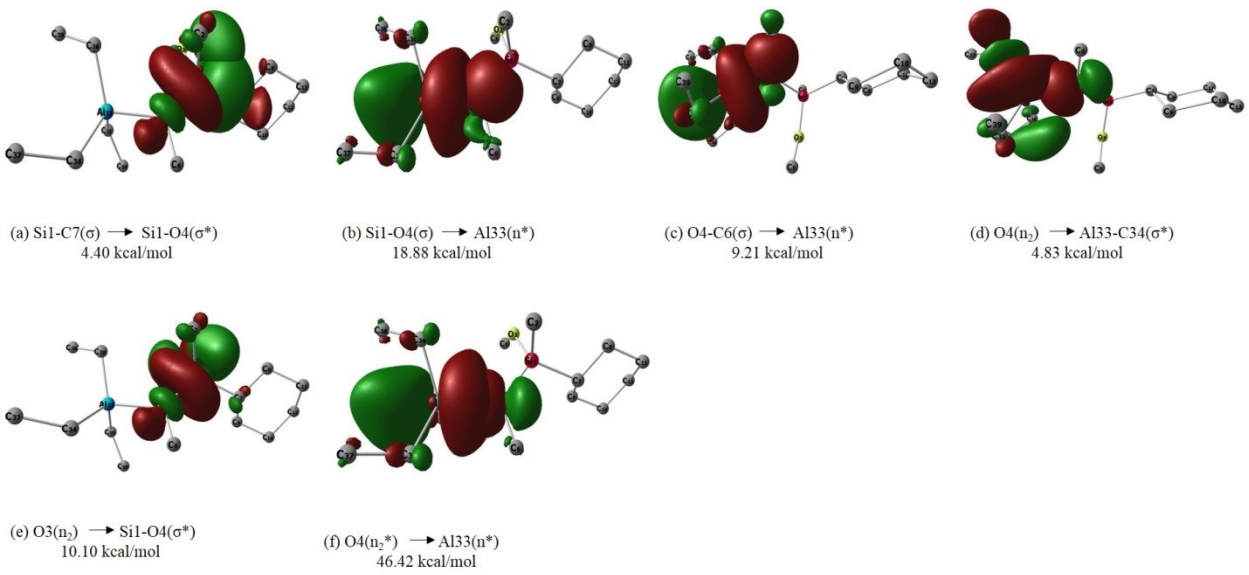


Figure S7: NBO diagrams of **TEAL-D3** complex showing donor-acceptor interaction for the stabilization of the complex. Hydrogen atoms are omitted for the sake of clarity.

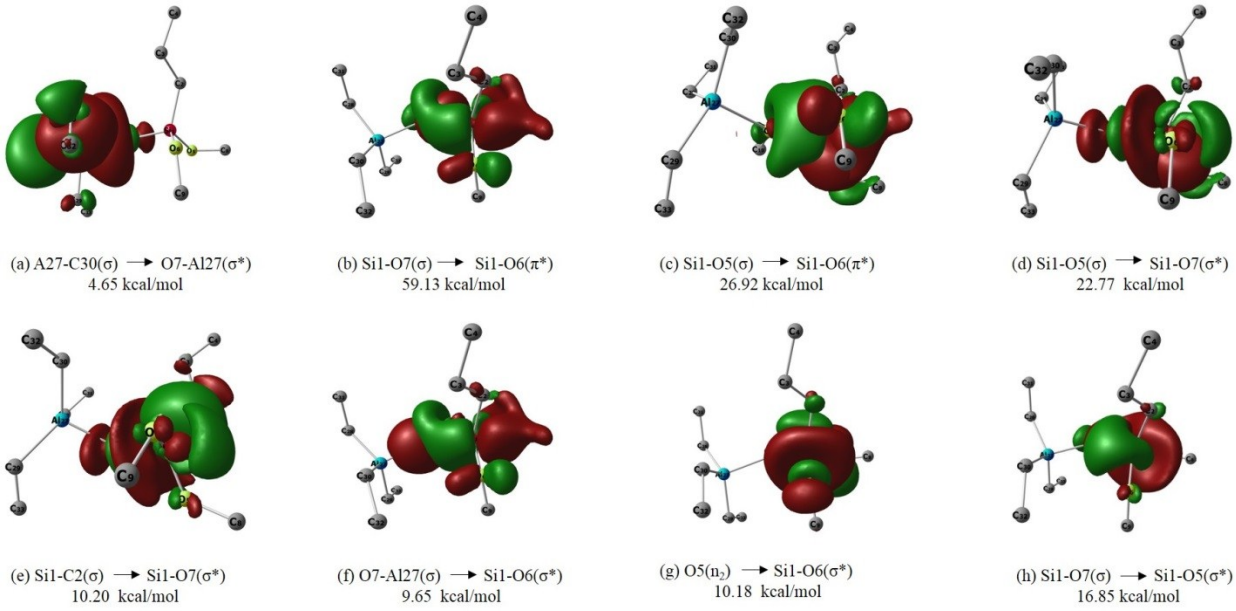


Figure S8: NBO diagrams of **TEAL-D4** complex donor-acceptor interaction for the stabilization of the complex. Hydrogen atoms are omitted for the sake of clarity.

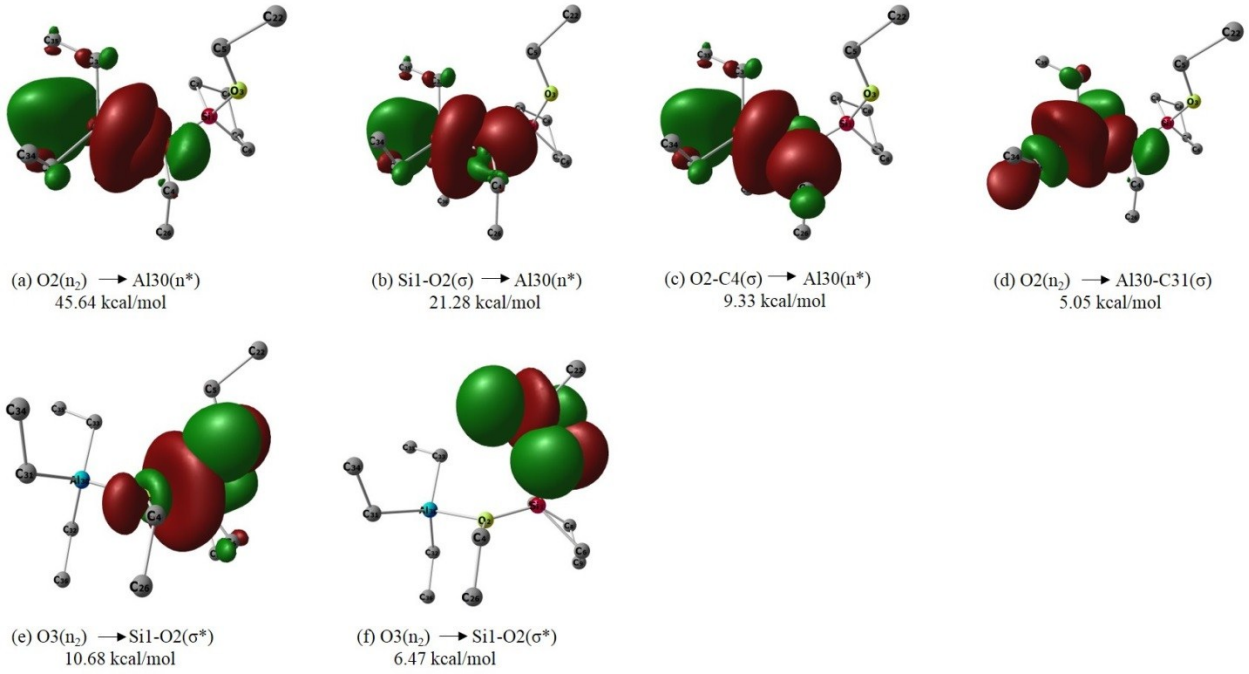


Figure S9: NBO diagrams of **TEAL-D5** complex showing donor-acceptor interaction for the stabilization of the complex. Hydrogen atoms are omitted for the sake of clarity.

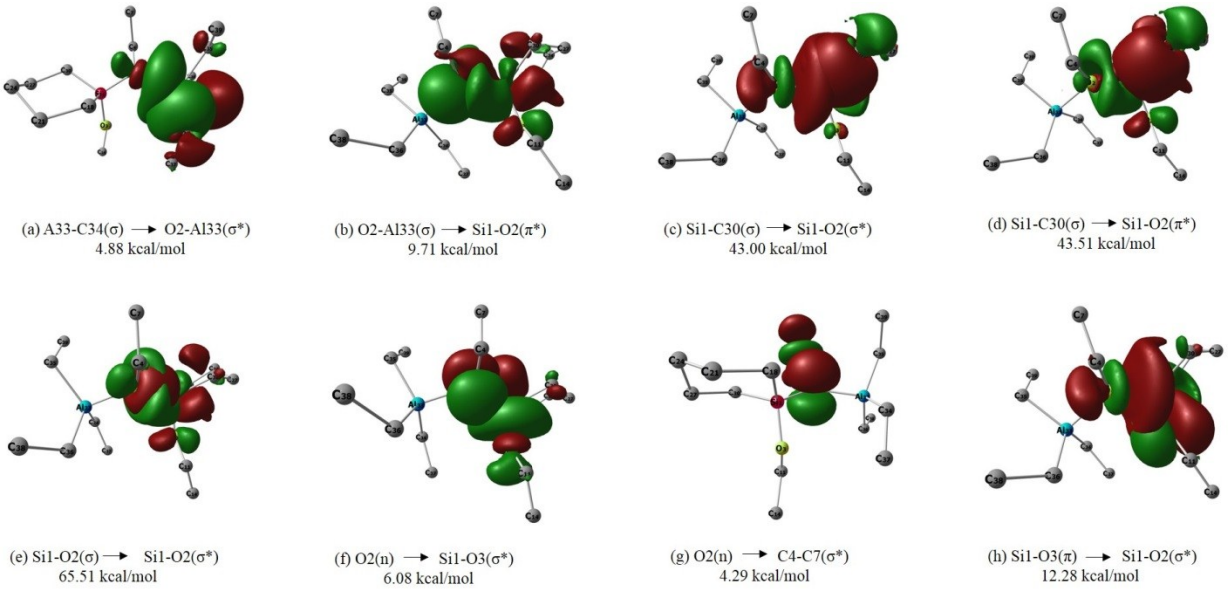


Figure S10: NBO diagrams of **TEAL-D6** complex showing donor-acceptor interaction for the stabilization of the complex. Hydrogen atoms are omitted for the sake of clarity.

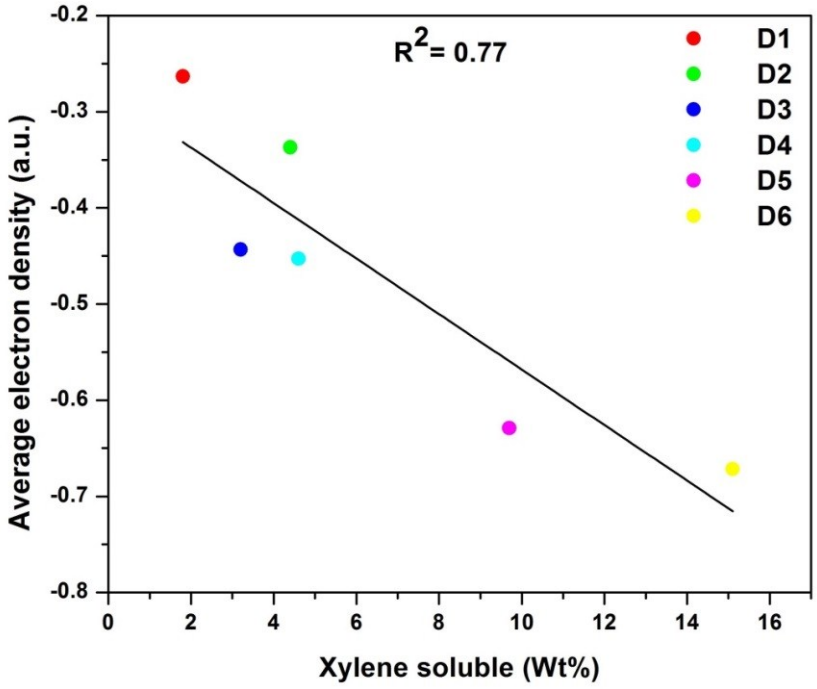


Figure S11: Correlation of average electron densities on the complexes formed between alkoxysilanes and **TEAL** with the xylene soluble (isotacticity) of polypropylene.

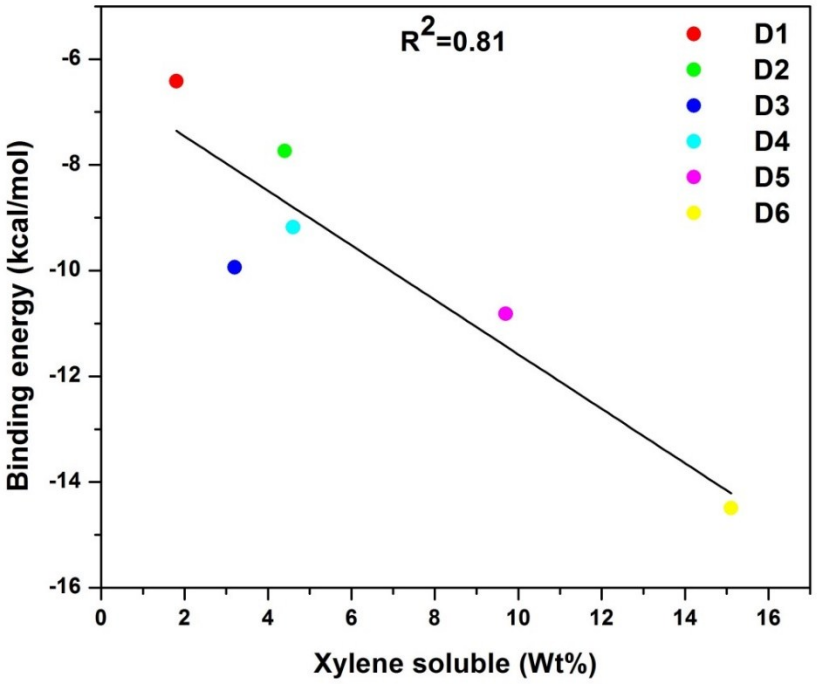


Figure S12: Correlation of binding energies of the complexes formed between alkoxysilanes and **TEAL** with the xylene soluble (isotacticity) of polypropylene.

Table S1: NPA charges (in a.u.) of relevant atoms of **TEAL**, external donors **D1-D6,** and complexes of **TEAL** and external donor.

	Si	Al	O(1)	O(2)	O(3)
TEAL	-	1.78	-	-	-
D1	2.16	-	-0.92	-0.92	-
TEAL-D1	2.20	1.77	-0.93	-0.95	-
D2	2.11	-	-0.91	-0.91	-
TEAL-D2	2.17	1.77	-0.94	-0.92	-
D3	2.13	-	-0.92	-0.92	-
TEAL-D3	2.16	1.78	-0.92	-0.94	-
D4	2.27	-	-0.92	-0.92	-0.92
TEAL-D4	2.31	1.74	-0.57	-0.93	-0.92
D5	2.08	-	-0.92	-0.92	-
TEAL-D5	2.12	1.78	-0.96	-0.93	-
D6	2.09	-	-0.92	-0.92	-
TEAL-D6	2.15	1.75	-0.96	-0.93	-

Table S2: ESP charges (in a.u.) of relevant atoms of **TEAL**, external donors **D1-D6,** and complexes of **TEAL** and external donor.

	Si	Al	O(1)	O(2)	O(3)
TEAL	-	0.874	-	-	-
D1	0.035	-	-0.293	-0.234	-
TEAL-D1	0.329	0.610	-0.396	-0.131	-
D2	0.689	-	-0.336	-0.338	-
TEAL-D2	0.928	0.650	-0.344	-0.419	-
D3	0.878	-	-0.525	-0.362	-
TEAL-D3	0.624	0.613	-0.365	-0.249	-
D4	1.076	-	-0.399	-0.496	-0.464
TEAL-D4	0.920	0.581	-0.370	-0.440	-0.311
D5	0.864	-	-0.629	-0.629	-
TEAL-D5	0.960	0.495	-0.512	-0.663	-
D6	1.165	-	-0.649	-0.694	-

TEAL-D6	1.040	0.600	-0.550	-0.540	-

Table S3: Wiberg bond index (WBI) of relevant atoms of **TEAL**, external donors **D1**-**D6,** and complexes of **TEAL** and external donor.

	Si	**Al**	**O(1)**	**O(2)**	**O(3)**
TEAL	-	1.87	-	-	-
D1	2.78	-	1.69	1.69	-
TEAL-D1	2.71	1.98	1.68	1.70	-
D2	2.86	-	1.70	1.70	-
TEAL-D2	2.77	1.97	1.70	1.71	-
D3	2.80	-	1.69	1.68	-
TEAL-D3	2.75	1.96	1.70	1.71	-
D4	2.69	-	1.68	1.69	1.69
TEAL-D4	2.64	2.01	1.68	1.71	1.71
D5	2.86	-	1.70	1.70	-
TEAL-D5	2.80	1.96	1.71	1.69	-
D6	2.85	-	1.70	1.70	-
TEAL-D6	2.77	2.00	1.71	1.70	-