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. *Supplementary Information*

A comparison between dithienosilole and dithienogermole Donor-Acceptor type Copolymers for Organic Bulk Heterojunction Photovoltaic Devices

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Experimental

Thin film transistors (TFTs) were fabricated by spin coating of homopolymers from a 1 wt% concentration in dichlorobenzene (DCB) with bottom-gate and bottom-contact configuration using heavily doped n-type Si wafers as the gate electrodes with a silicon dioxide and HMDS (hexamethyldisilazane) layer as the gate dielectric. The gold source and drain electrodes were deposited through a shadow mask.

Table S1. Thin film transistor (TFT) mobilities of polymers studied in this work.

	Saturation Mobility (cm^2/Vs)					
	As cast			**After annealing**		
	Average (E-06)	**Std. Dev. (E-06)**	**Max (E-06)**	**Average (E-06)**	**Std. Dev. (E-06)**	**Max (E-06)**
MeGeBT	16.7	10.9	26.6	69.8[a]	41.2[a]	97.1[a]
MeSiBT	7.84	2.67	10.7	17.7[b]	13.3[b]	39.5[b]
BuGeBT	9.99	2.79	12.8	8.57[b]	3.84[b]	15.0[b]
BuSiBT	2.19	0.07	2.26	0.57[a]	0.22[a]	0.86[a]

Annealing at [a]: 150^{o}C and [b]: 200^{o}C

Table S2. Summary of the Polymer:PC70BM blend OPV device performance.

Donor	Acceptor	Condition	J_{sc}	V_{oc}	FF	PCE
MeGeBT	PC70BM	Solvent (CB), Blend ratio (1:3), spin coating (900rpm, 60s), slow drying	6.51	0.94	0.43	2.61
		Solvent (CB), Blend ratio (1:3), spin coating (1000rpm, 90s)	6.27	0.93	0.42	2.46
		Solvent (CB), Blend ratio (1:3.5), spin coating (900rpm, 60s), slow drying	6.11	0.89	0.39	2.11
		Solvent (CB), Blend ratio (1:3.5), spin coating (1000rpm, 90s)	6.15	0.94	0.44	2.55
		Solvent (CB), Blend ratio (1:4), spin coating (900rpm, 60s), slow drying	6.20	0.91	0.37	2.08
		Solvent (CB), Blend ratio (1:4), spin coating (1000rpm, 90s)	7.04	0.91	0.43	2.73
		Solvent (CB), Blend ratio (1:4), spin coating (900rpm, 120s)	5.51	0.91	0.47	2.37
		Solvent (CB), Blend ratio (1:4), spin coating (1000rpm, 120s)	4.99	0.92	0.49	2.23
		Solvent (CB), Blend ratio (1:4), spin coating (1200rpm, 120s)	4.22	0.91	0.50	1.91
		Solvent (CB+OT), Blend ratio (1:3), spin coating (1000rpm, 120s)	1.17	0.55	0.33	0.22
		Solvent (CB+OT), Blend ratio (1:3.5), spin coating (1000rpm, 120s)	1.89	0.62	0.36	0.42
		Solvent (CB+OT), Blend ratio (1:4), spin coating (1000rpm, 120s)	1.43	0.45	0.31	0.19
		Solvent (CB+OT), Blend ratio (1:3), spin coating (1000rpm, 120s)_Thermal annealing (TA) at 120^{o}C	1.2	0.43	0.31	0.16
		Solvent (CB+OT), Blend ratio (1:3.5), spin coating (1000rpm, 120s)_TA 120^{o}C	1.00	0.38	0.33	0.13

	Solvent (DCB), Blend ratio (1:4), spin coating (1000rpm, 120s)	6.11	0.94	0.46	2.66
	Solvent (DCB), Blend ratio (1:4), spin coating (1000rpm, 120s)_TA 150°C	4.84	0.67	0.43	1.38
	Solvent (DCB+OT), Blend ratio (1:4), spin coating (1000rpm, 120s)	2.80	0.84	0.33	0.78
	Solvent (DCB+OT), Blend ratio (1:4), spin coating (1000rpm, 120s)_TA 150°C	1.75	0.59	0.29	0.30
ICBA	Solvent (CB), Blend ratio (1:4), spin coating (900rpm, 120s)	0.59	1.06	0.24	0.15
	Solvent (CB), Blend ratio (1:4), spin coating (900rpm, 120s)_TA 150°C	0.36	0.92	0.25	0.08
	Solvent (CB), Blend ratio (1:4), spin coating (1000rpm, 90s)	0.69	1.04	0.25	0.18
	Solvent (CB), Blend ratio (1:3), spin coating (1000rpm, 90s)	0.66	1.09	0.24	0.17
	Solvent (CB), Blend ratio (1:3), spin coating (900rpm, 120s)	0.51	0.85	0.26	0.11
	Solvent (CB), Blend ratio (1:3), spin coating (900rpm, 120s)_TA 150°C	0.27	0.85	0.24	0.06
	Solvent (CB), Blend ratio (1:1), spin coating (1100rpm, 90s)	0.19	1.06	0.21	0.04
	Solvent (CB), Blend ratio (1:1), spin coating (1000rpm, 90s)	0.16	1.05	0.22	0.04
	Solvent (CB), Blend ratio (1:1), spin coating (900rpm, 60s), slow drying	0.15	1.06	0.23	0.04
	Solvent (CB), Blend ratio (1:1), spin coating (900rpm, 120s)	0.10	0.76	0.27	0.02
	Solvent (CB), Blend ratio (1:1), spin coating (900rpm, 120s)_TA 150°C	0.07	0.75	0.24	0.01

MeSiBT	PC70BM	Solvent (DCB), Blend ratio (1:4), spin coating (900rpm, 120s)	4.80	0.91	0.44	1.92
		Solvent (DCB), Blend ratio (1:4), spin coating (1000rpm, 120s)	4.57	0.89	0.43	1.75
		Solvent (DCB), Blend ratio (1:4), spin coating (1200rpm, 120s)	4.29	0.94	0.45	1.84
BuGeBT	PC70BM	Solvent (DCB), Blend ratio (1:4), spin coating (1000rpm, 120s)	3.71	0.90	0.45	1.50
BuSiBT	PC70BM	Solvent (DCB), Blend ratio (1:3), spin coating (900rpm, 60s), slow drying	1.98	0.52	0.32	0.33
		Solvent (DCB), Blend ratio (1:3), spin coating (1000rpm, 90s)	2.18	0.76	0.36	0.60
		Solvent (DCB), Blend ratio (1:3.5), spin coating (900rpm, 60s), slow drying	1.53	0.75	0.36	0.41
		Solvent (DCB), Blend ratio (1:3.5), spin coating (1000rpm, 90s)	1.72	0.83	0.35	0.50
		Solvent (DCB), Blend ratio (1:4), spin coating (900rpm, 120s)	2.03	0.81	0.36	0.59
		Solvent (DCB), Blend ratio (1:4), spin coating (1000rpm, 90s)	1.76	0.64	0.36	0.41

Figure S1. Optimized molecular geometry with calculated bond length and torsion angle for MeGeBT (structure of donor-acceptor-donor (D-A-D) and acceptor-donor-acceptor (A-D-A)), MeSiBT (D-A-D and A-D-A), BuGeBT (D-A-D and A-D-A) and BuSiBT (D-A-D and A-D-A) molecules. Light blue: Si or Ge, S in yellow, N in blue, C in gray and H in white.

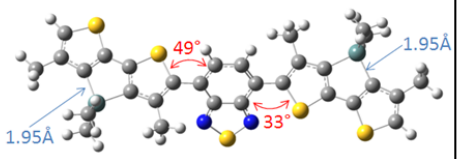
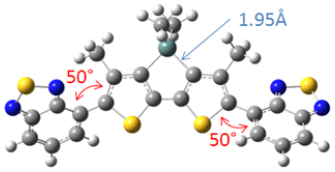
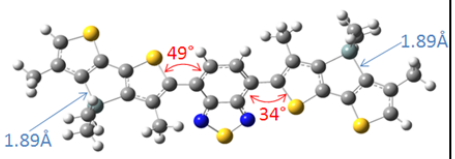
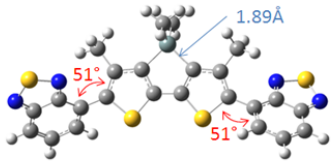
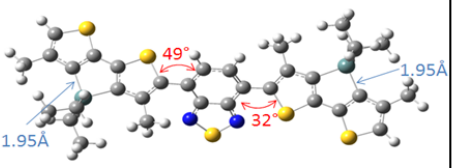
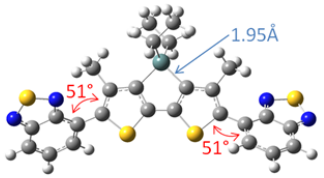
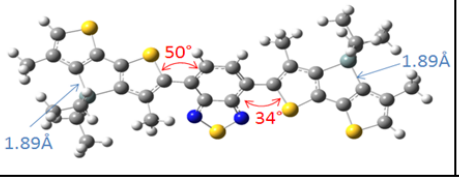
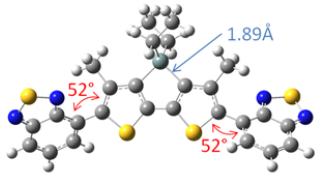
	Methyl-	Butyl-
Si DAD		
Si ADA		
Ge DAD		
Ge ADA		

Figure S2. X-ray diffraction data of homo polymers (MeGeBT, MeSiBT, BuGeBT and BuSiBT).

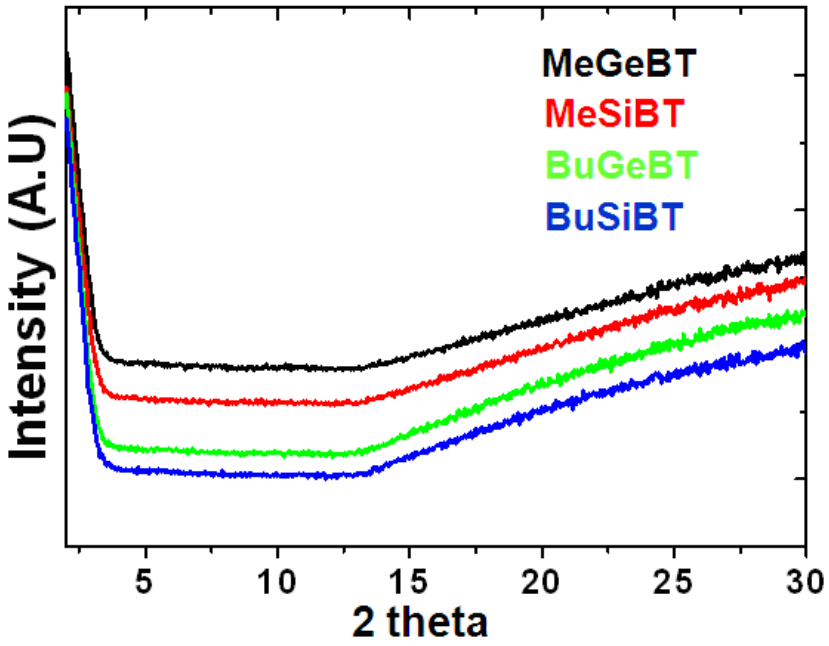


Figure S3. Potential energy curves for torsion angle dependency from 0-180 degrees. The lowest single point energy of each curve is set to zero for comparison. MeSiBT and MeGeBT have a similar tendency that means there is no significant difference in backbone stiffness.

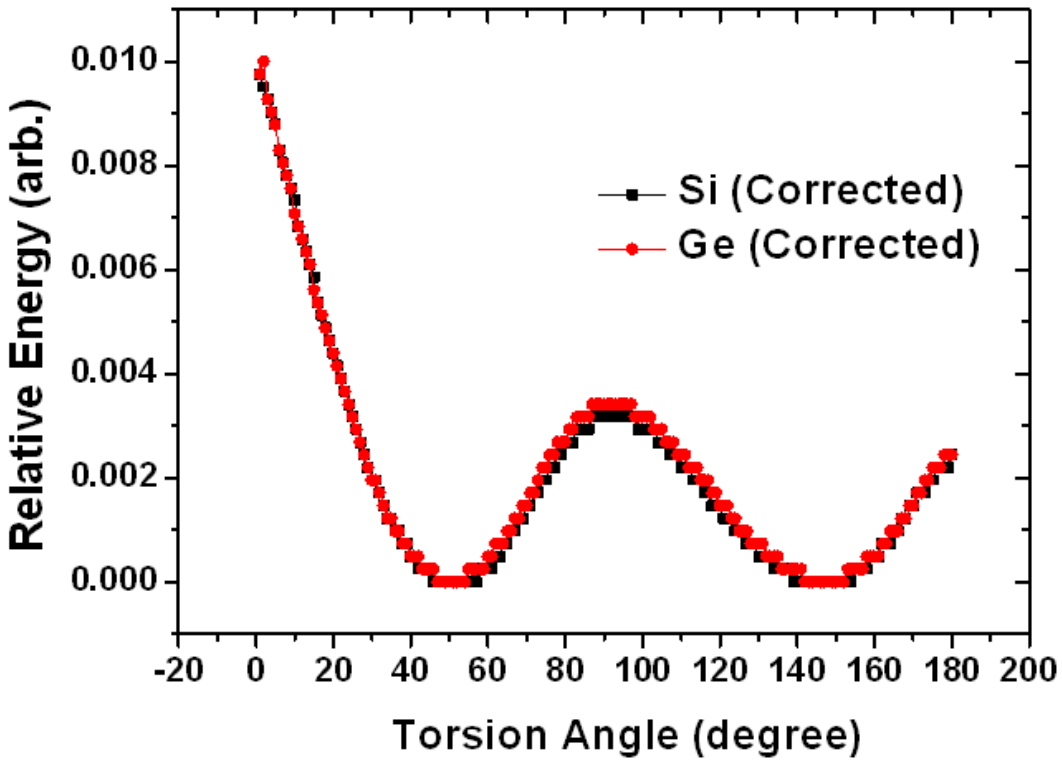


Figure S4. HOMO and LUMO energy levels of the MeSiBT (D-A-D and A-D-A) and BuSiBT (D-A-D and A-D-A) molecules calculated using the Gaussian09 package; density functional theory (DFT) at the B3LYP level of theory with a basis set of 6-31G(d).

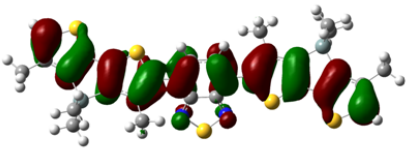
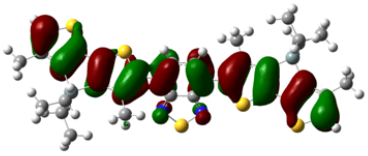
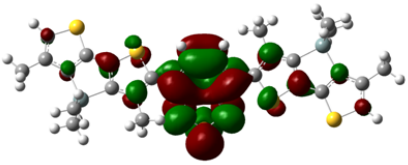
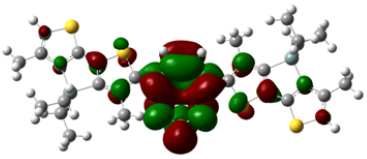
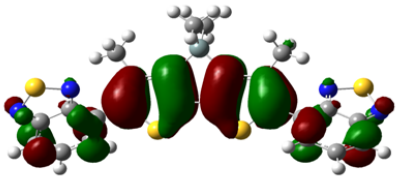
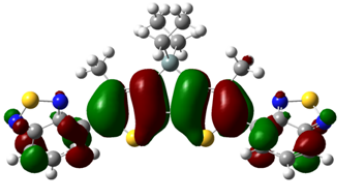
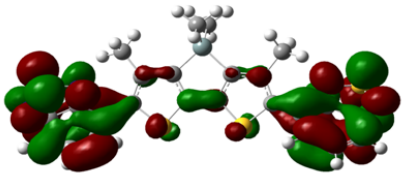
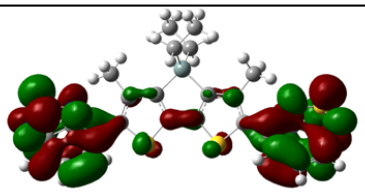
	Methyl-	Butyl-
Si DAD HOMO		
Si DAD LUMO		
Si ADA HOMO		
Si ADA LUMO		

Figure S5. HOMO and LUMO energy levels of the MeGeBT (D-A-D and A-D-A) and BuGeBT (D-A-D and A-D-A) molecules calculated using the Gaussian09 package; density functional theory (DFT) at the B3LYP level of theory with a basis set of 6-31G(d).

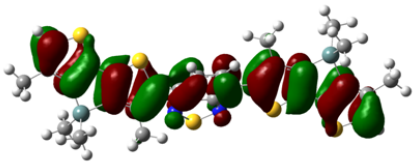
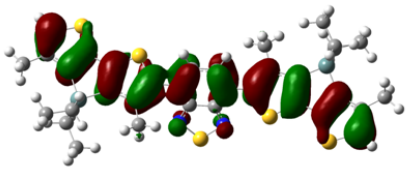
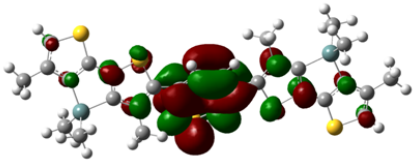
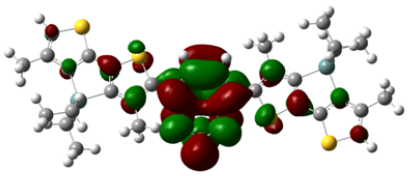
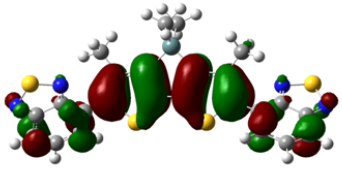
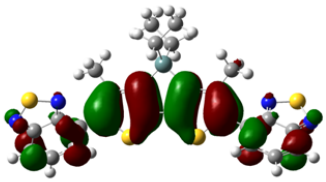
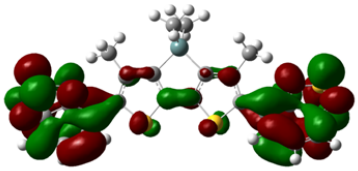
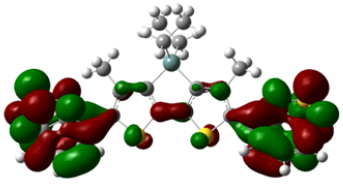
	Methyl-	Butyl-
Ge DAD HOMO		
Ge DAD LUMO		
Ge ADA HOMO		
Ge ADA LUMO		

Figure S6. ^{1}NMR spectrum of **BuSiBT** in $CDCl_3$.

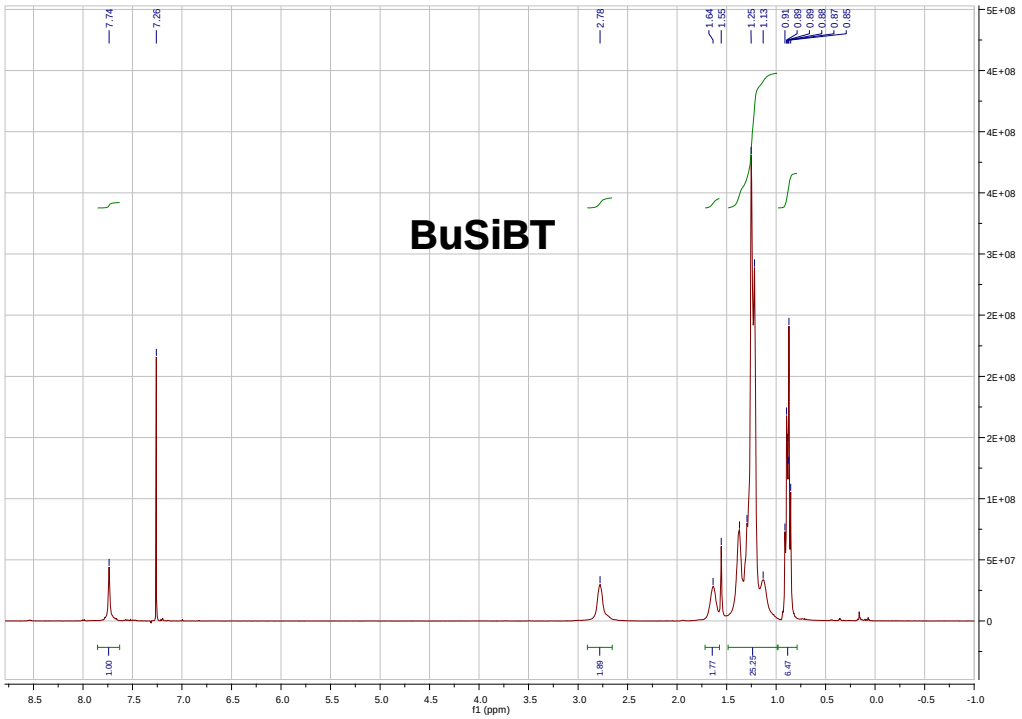


Figure S7. ^{1}NMR spectrum of **BuSiBT** in $CDCl_3$.

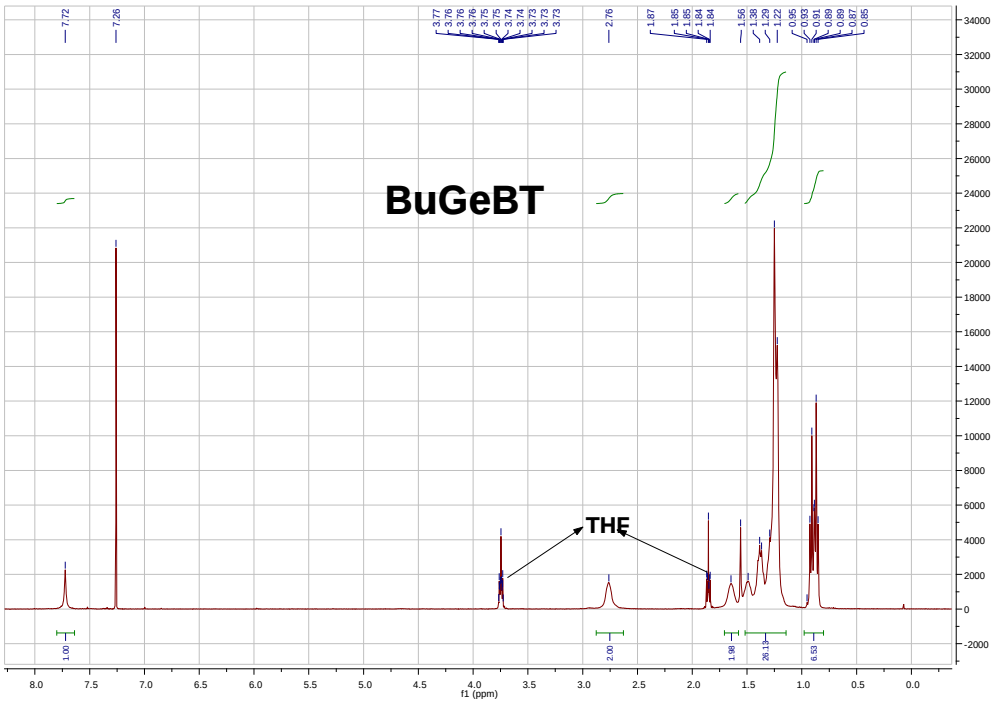


Figure S8. ^{1}NMR spectrum of **MeGeBT** in $CDCl_3$.

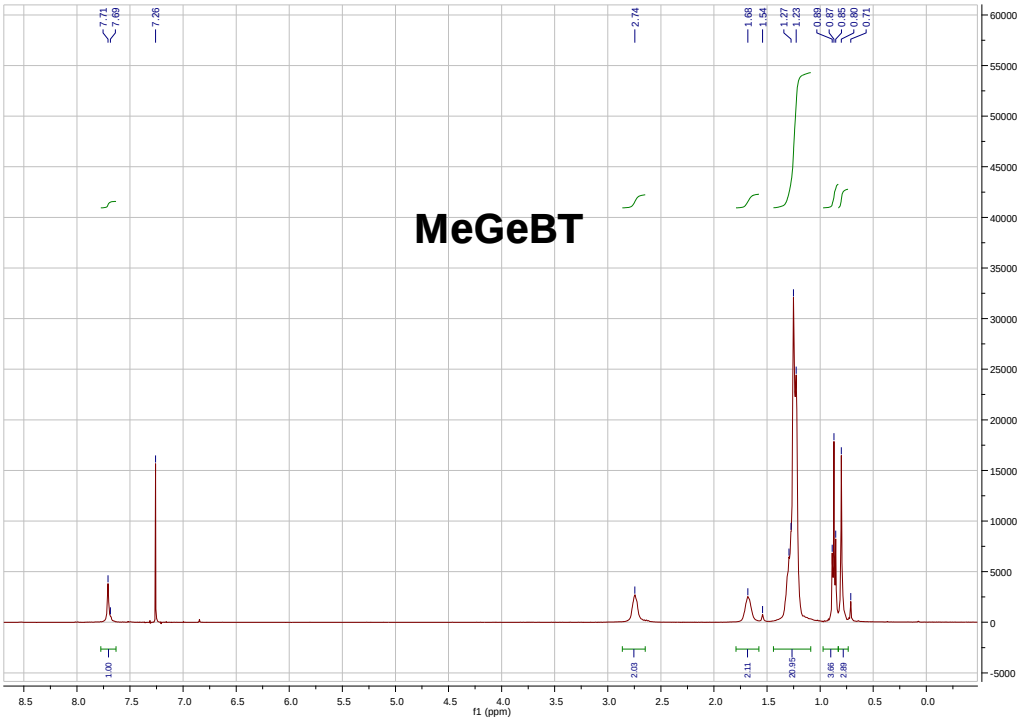


Figure S9. ^{1}NMR spectrum of **MeSiBT** in $CDCl_3$.