Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis, characterization, and catalytic application of dimeric alumatranes with a tricyclic five-membered ring

Yoseph Kim,[†,§] Kang Mun Lee,[‡,§] So Han Kim,[†,§] Jung Hee Moon,[†] and Youngjo Kim[†,*]

[†] *Department of Chemistry and BK21+ Program Research Team, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea*
[‡] *Department of Chemistry, Institute for Molecular Science and Fusion Technology, Kangwon National University, Chuncheon, Gangwon 24341, Republic of Korea*

Contents

1. NMR, IR and EI–MS spectra of **1**·····S2–S6
2. NMR, IR and EI–MS spectra of **2**·····S6–S12
3. NMR, IR and EI–MS spectra of **3**·····S13–S18
4. Literature References for Known Compounds ·····S19–S22
5. ^{1}H and ^{13}C NMR Spectra for Known Compounds·····S23–S42
6. The angles (φ_N) between unbridge side arms for alumatranes and titanatranes·····S43–S44
7. Cartesian coordinates of the ground state (S_0) fully optimized geometries ·····S45–S55

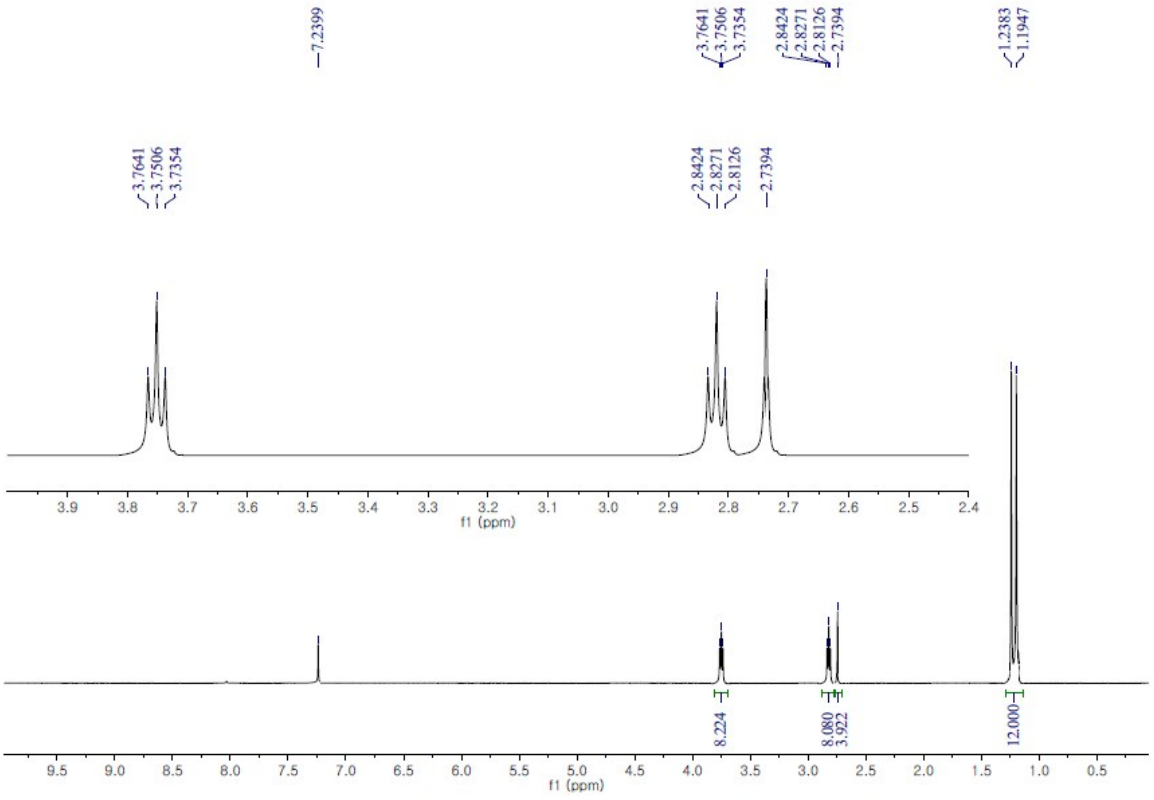


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$

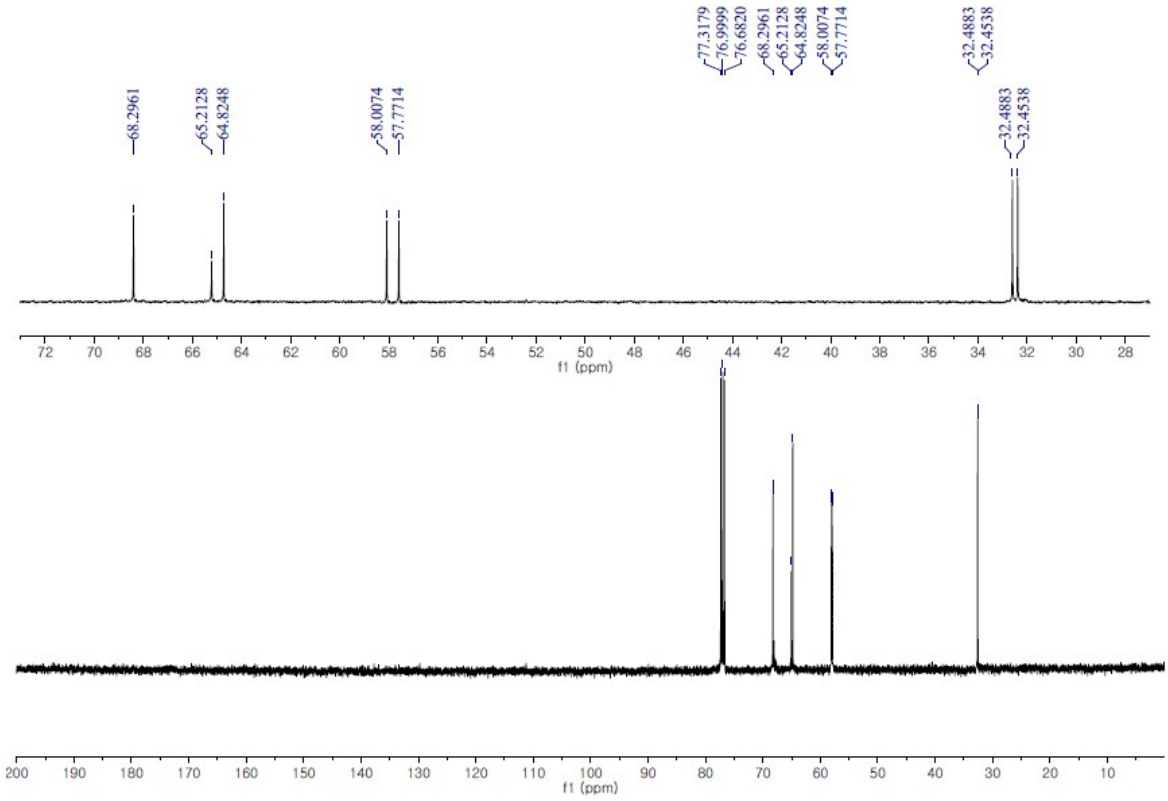


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$

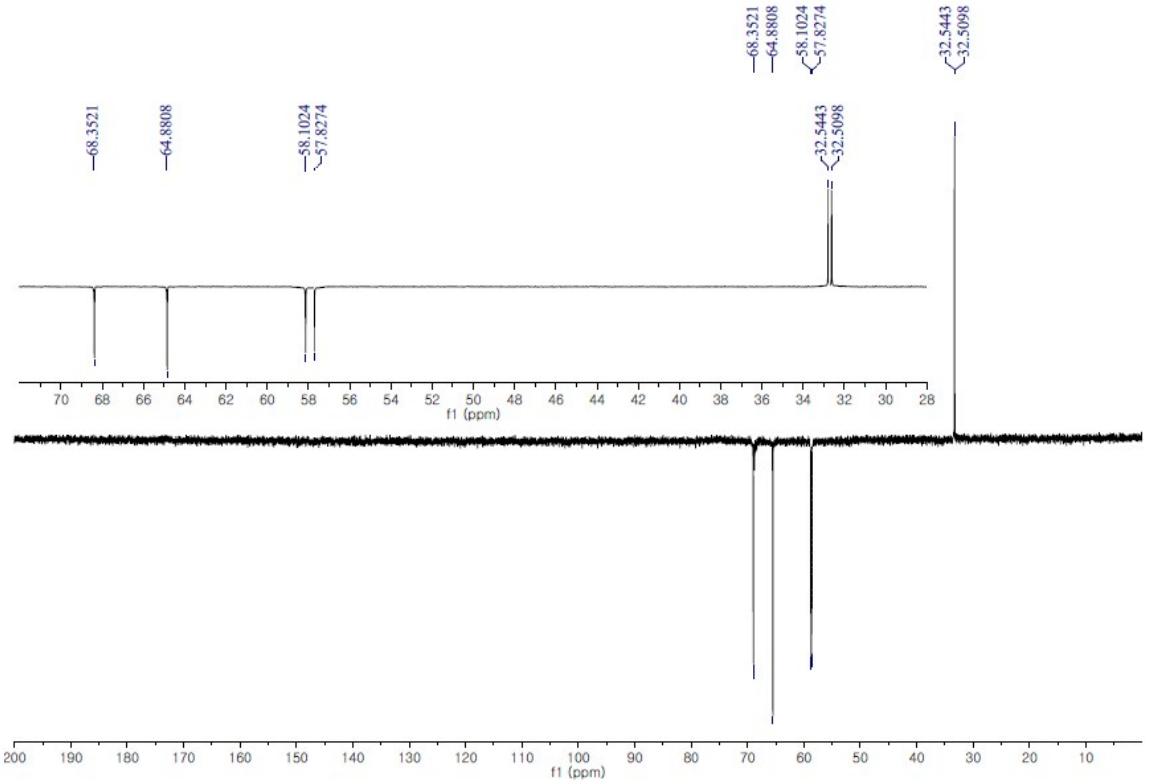


Figure S3. DEPT 135 NMR spectrum of **1** in $CDCl_3$

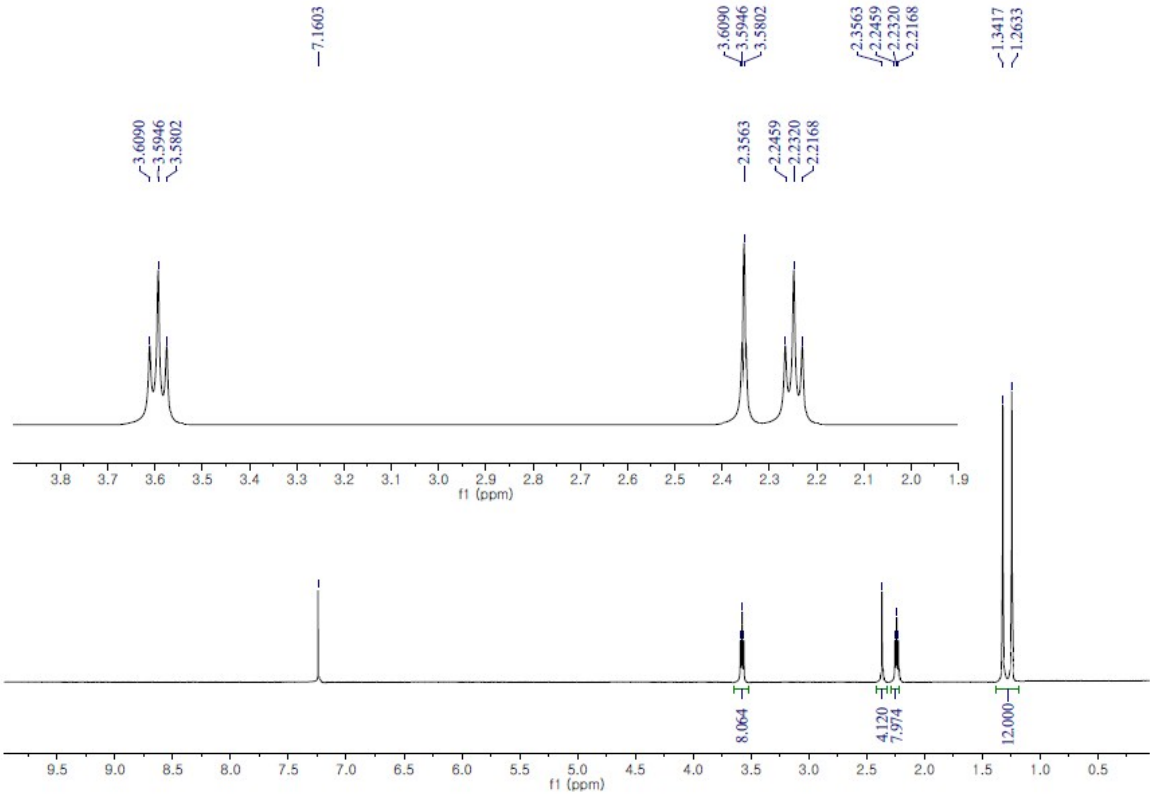


Figure S4. ^1H NMR spectrum of **1** in C_6D_6

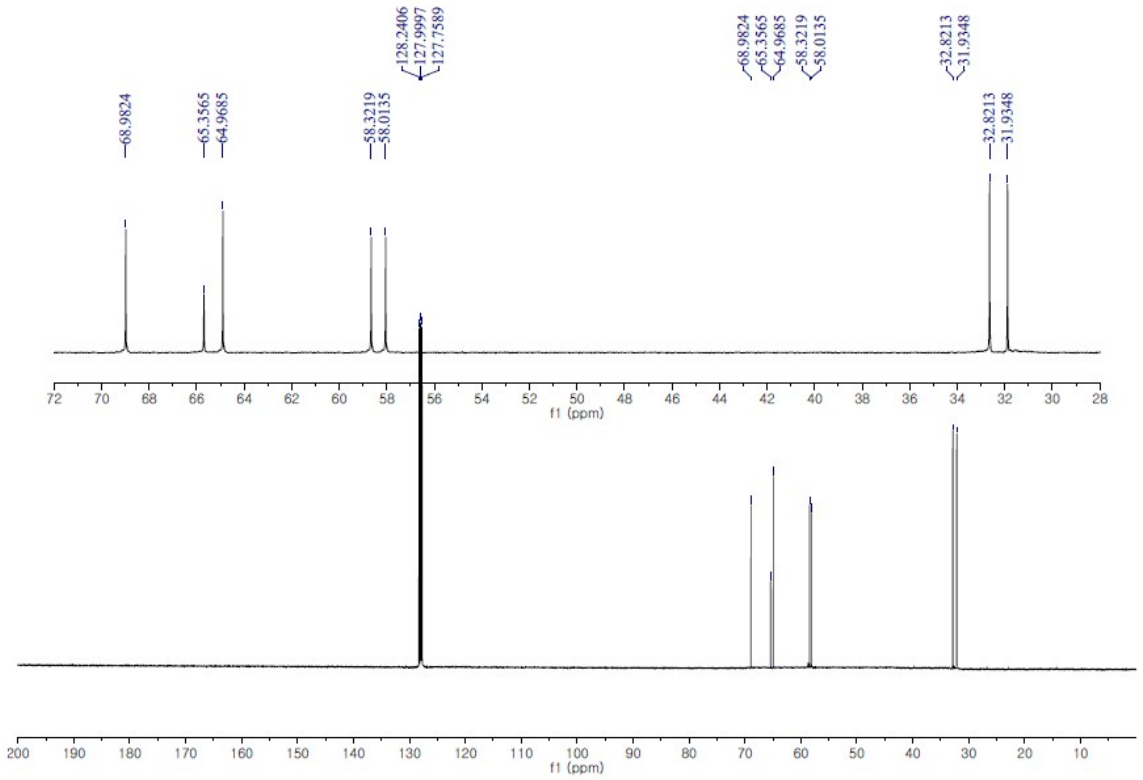


Figure S5. ^{13}C NMR spectrum of **1** in C_6D_6

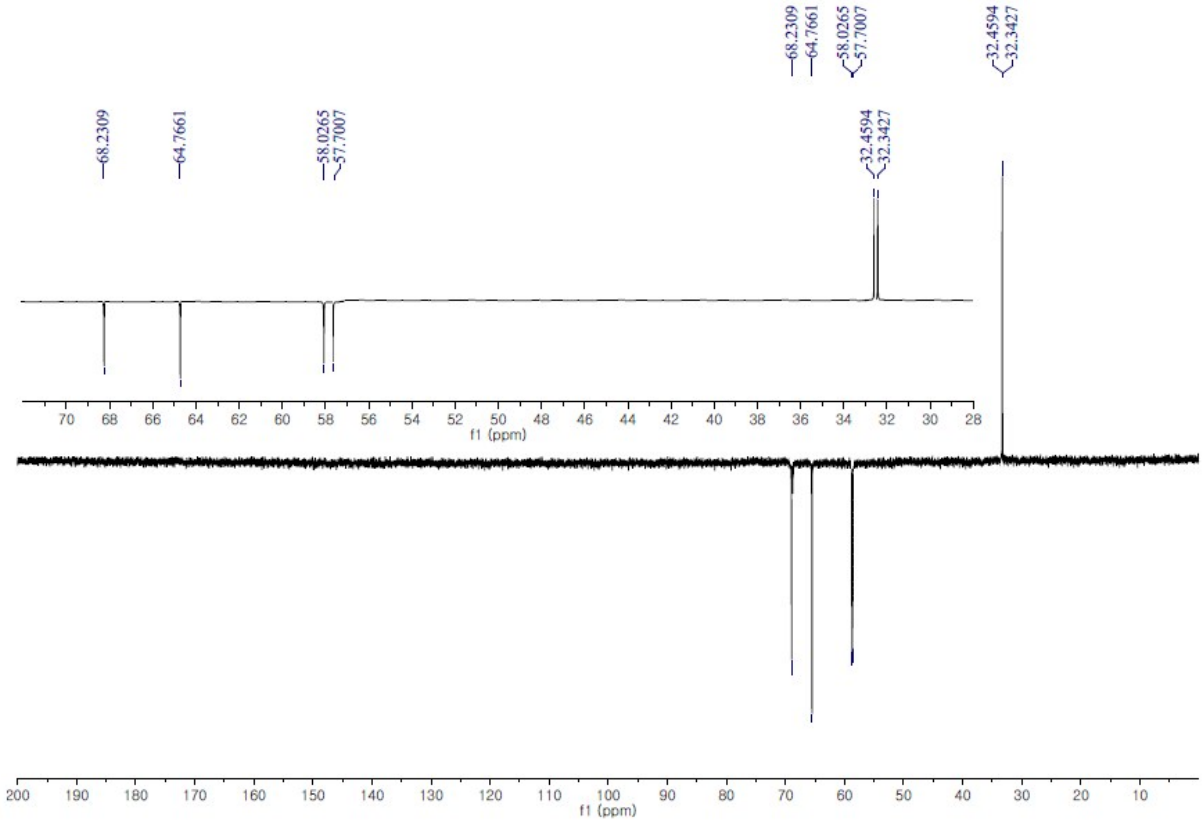


Figure S6. DEPT 135 NMR spectrum of **1** in C_6D_6

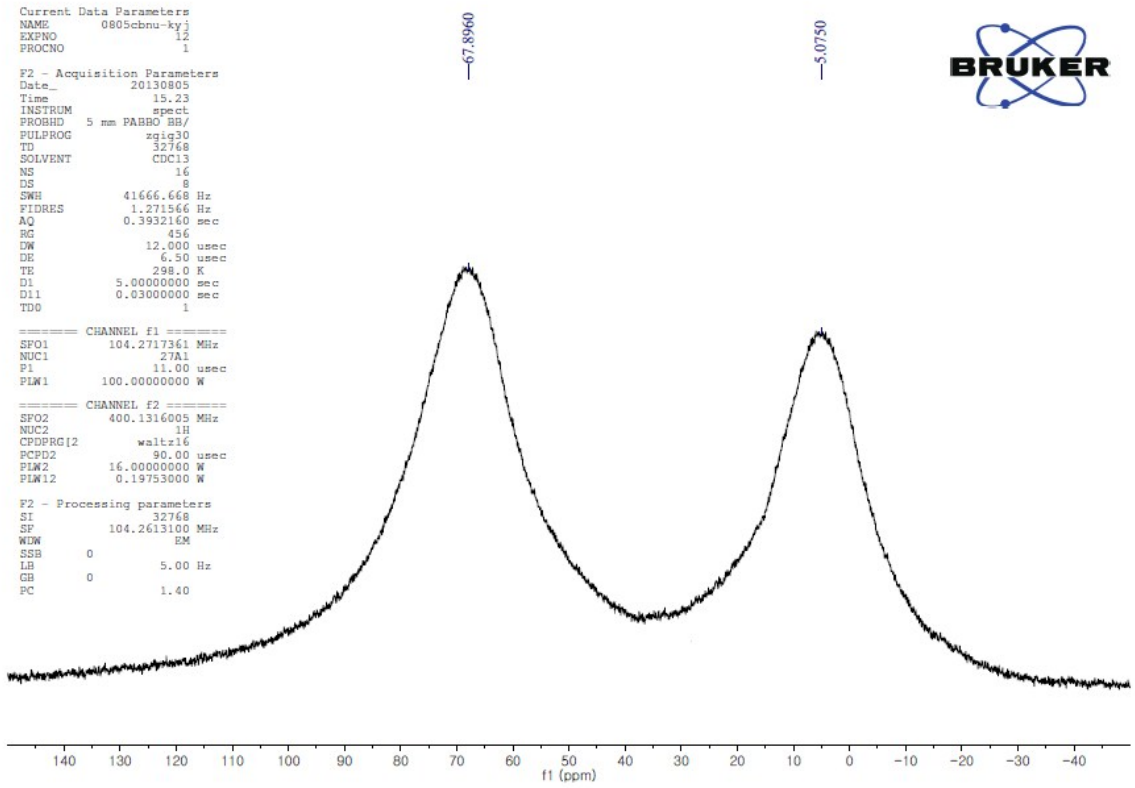


Figure S7. ^{27}Al NMR spectrum of **1** in $CDCl_3$

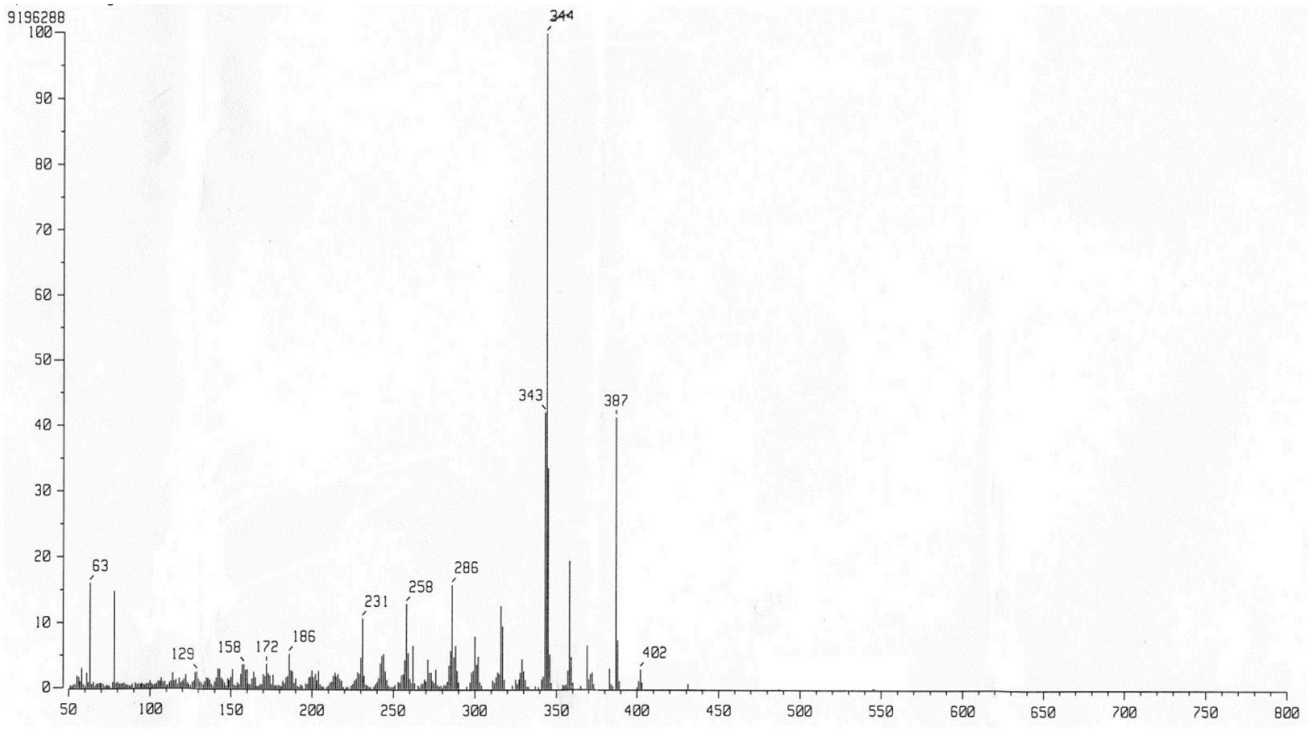
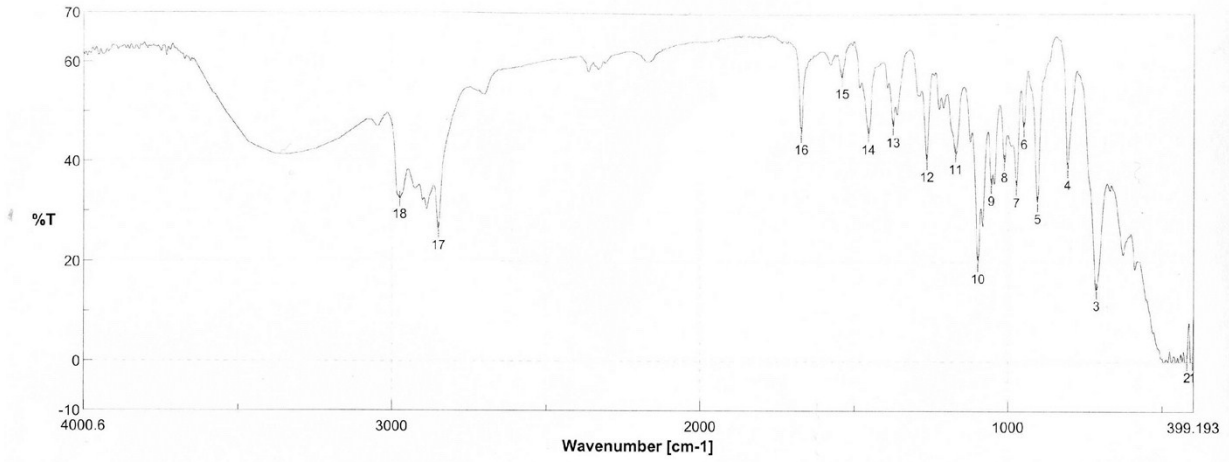


Figure S8. EI-MS spectrum of **1**



Date/Time 2010-10-05 3:13오후
Operator
File Name Memory#2
Sample Name FRS
Comment

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	403.05	-1.17549E-038	2	420.406	-1.17549E-038	3	714.497	14.3442	4	808.027	38.5151	5	905.415	31.6947
6	949.77	46.6814	7	973.876	34.9524	8	1013.41	40.048	9	1055.84	35.3082	10	1099.23	19.7201
11	1172.51	41.6392	12	1266.04	40.1136	13	1375.96	47.0024	14	1455.99	45.5509	15	1541.81	56.8317
16	1672.94	45.4988	17	2851.24	26.2659	18	2976.59	32.4518						

Figure S9. IR spectrum of **1**

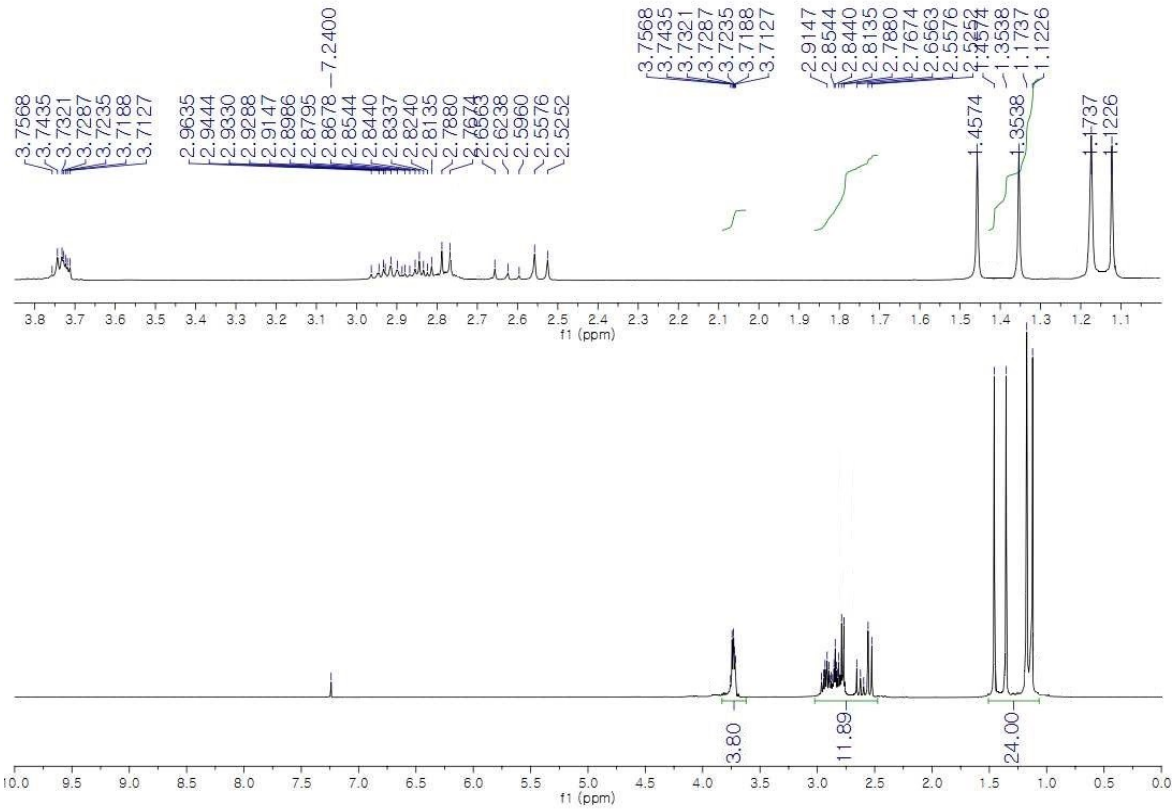


Figure S10. ^{1}H NMR spectrum of **2** in $CDCl_3$

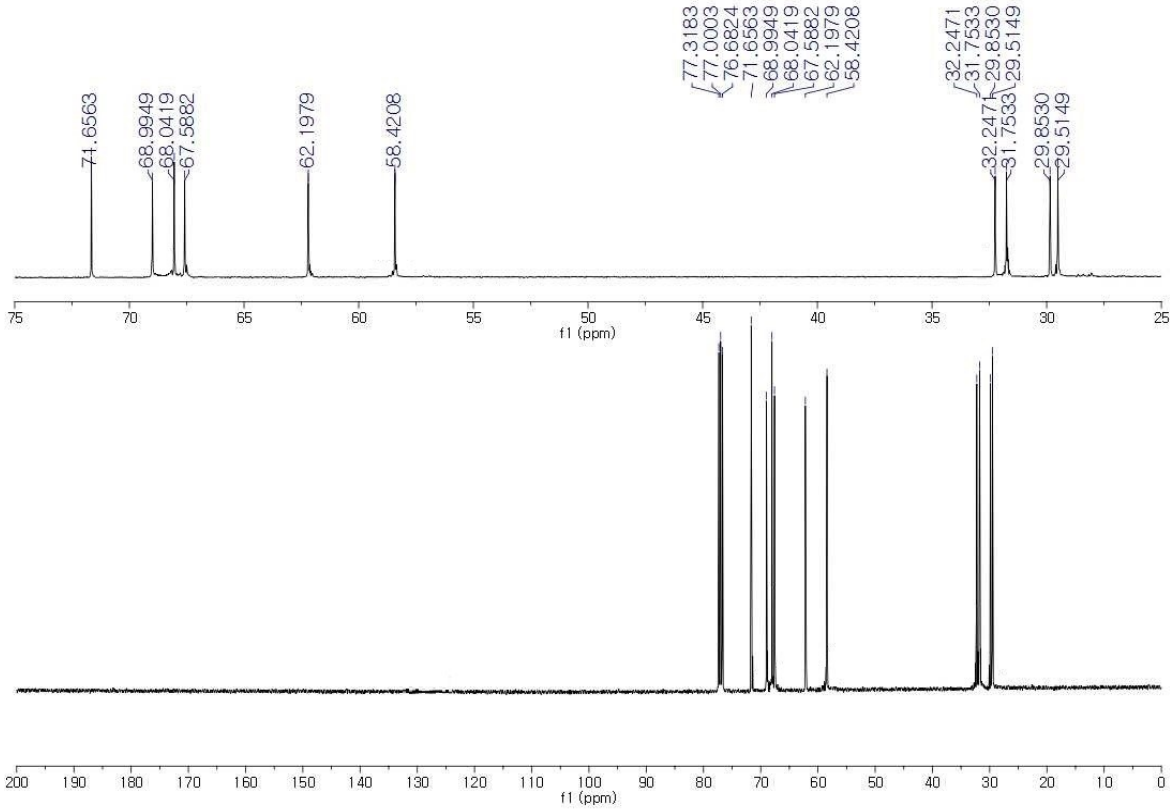


Figure S11. ^{13}C NMR spectrum of **2** in $CDCl_3$

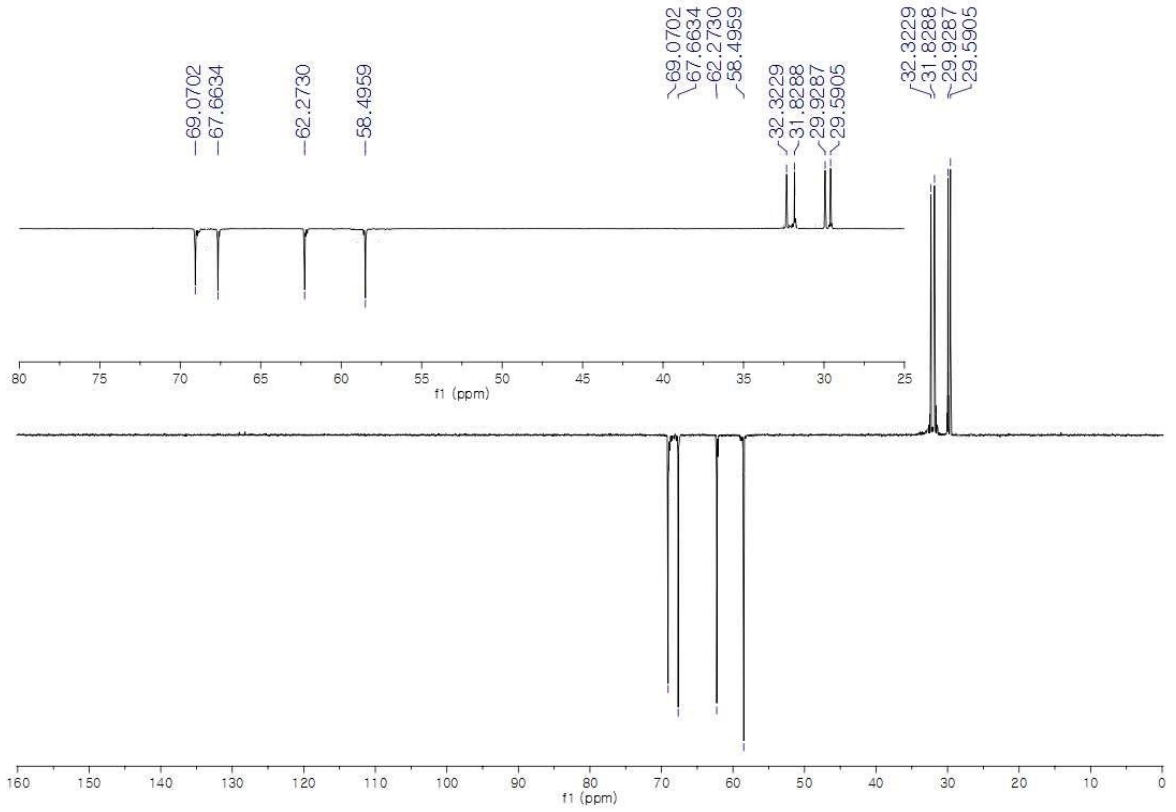


Figure S12. DEPT 135 NMR spectrum of **2** in $CDCl_3$

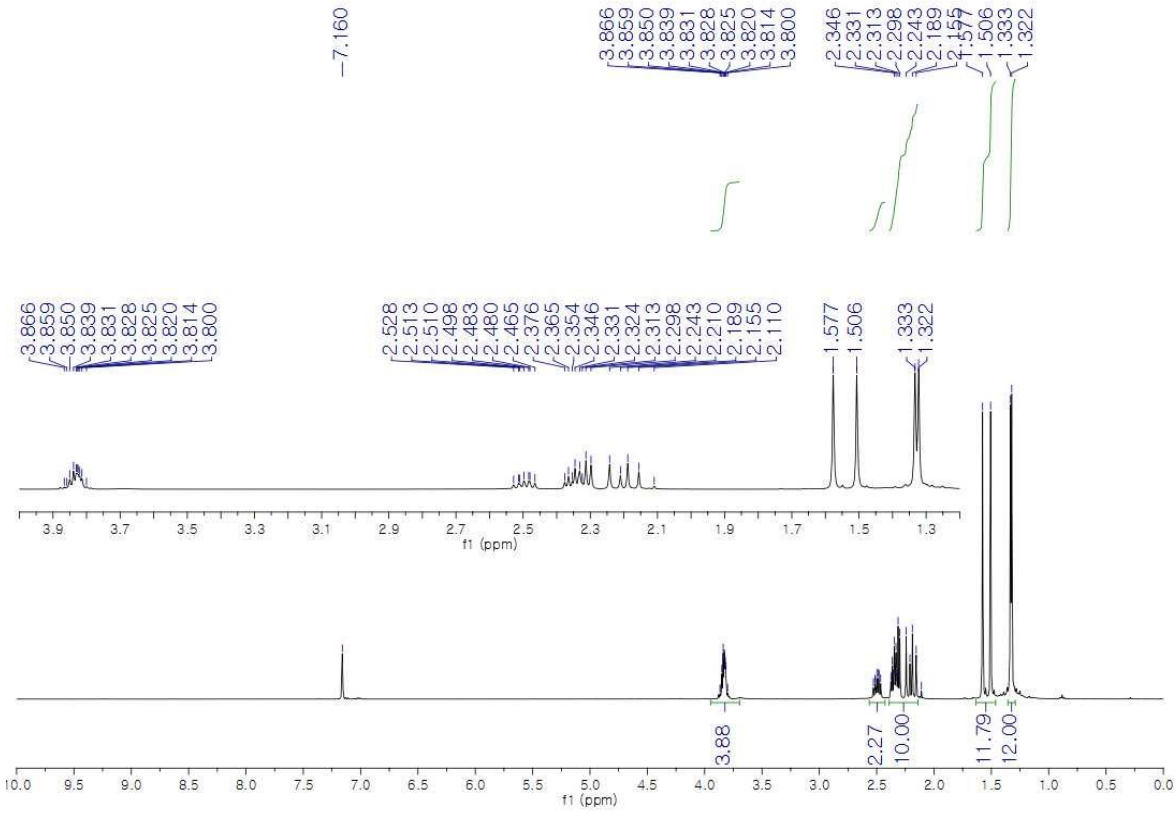


Figure S13. ^1H NMR spectrum of **2** in C_6D_6

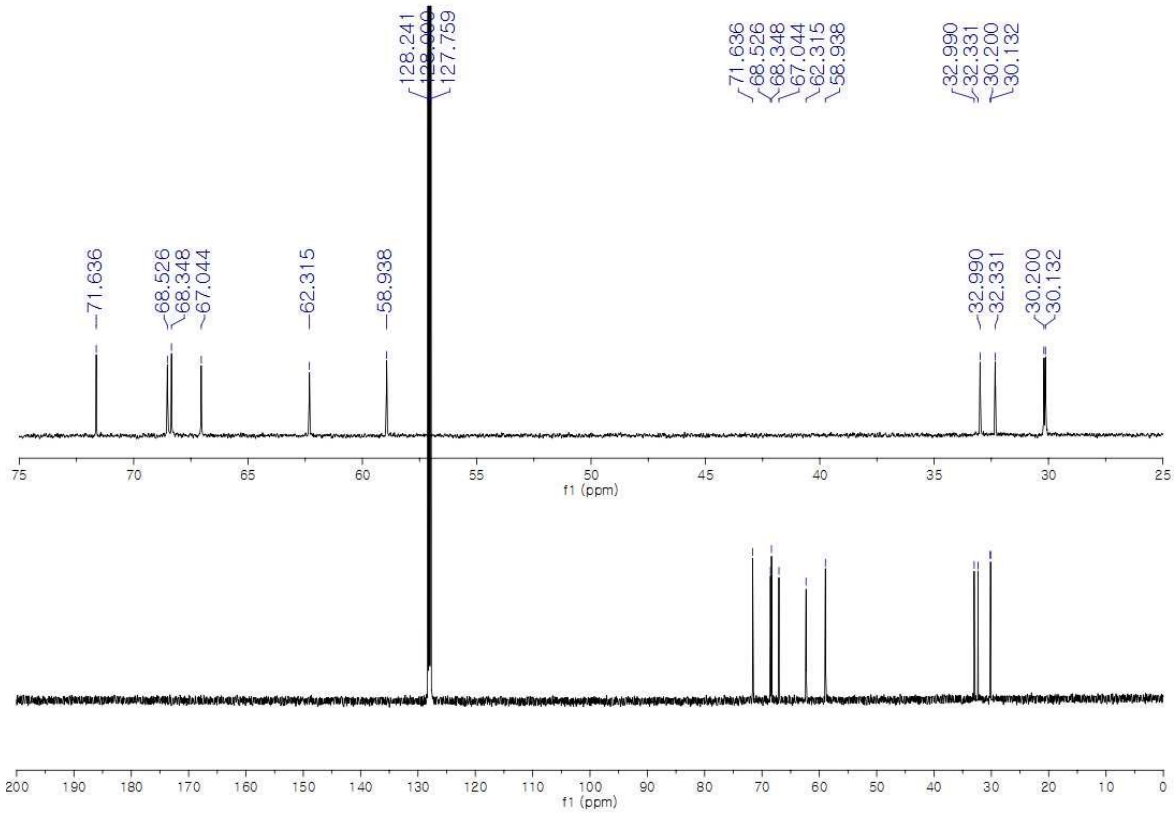


Figure S14. ^{13}C NMR spectrum of **2** in C_6D_6

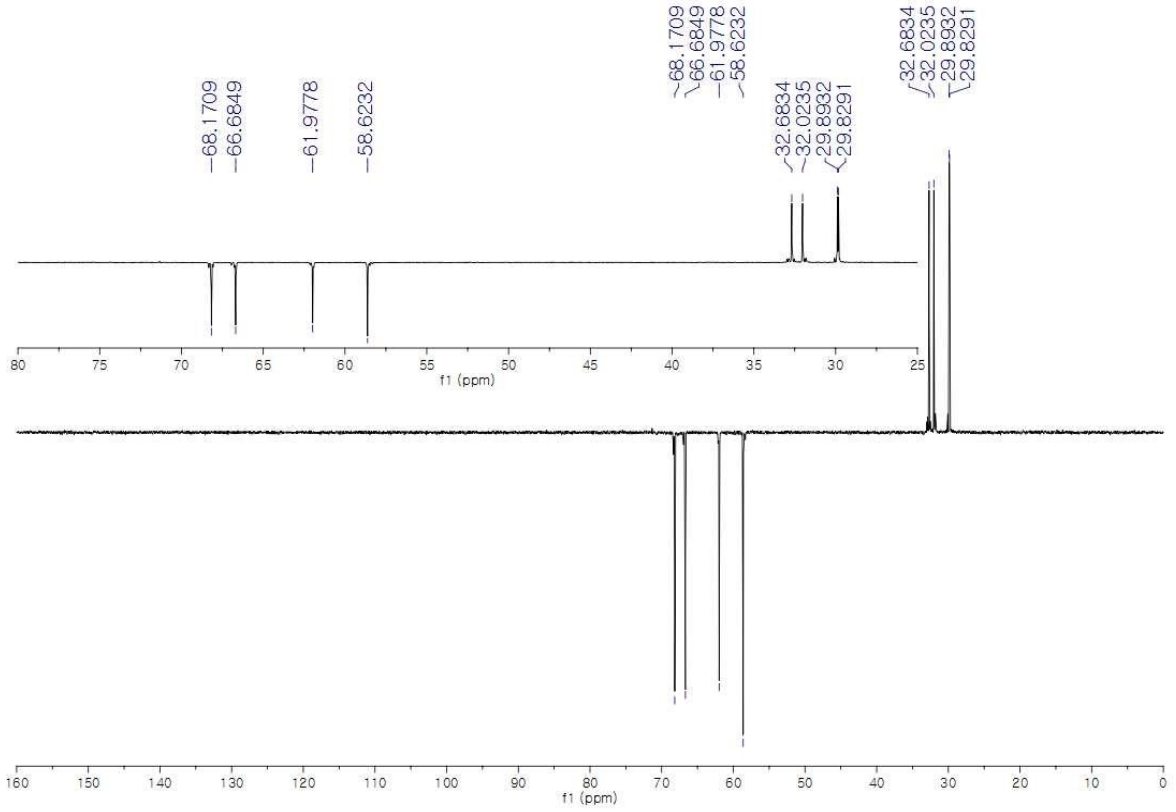


Figure S15. DEPT 135 NMR spectrum of **2** in C_6D_6

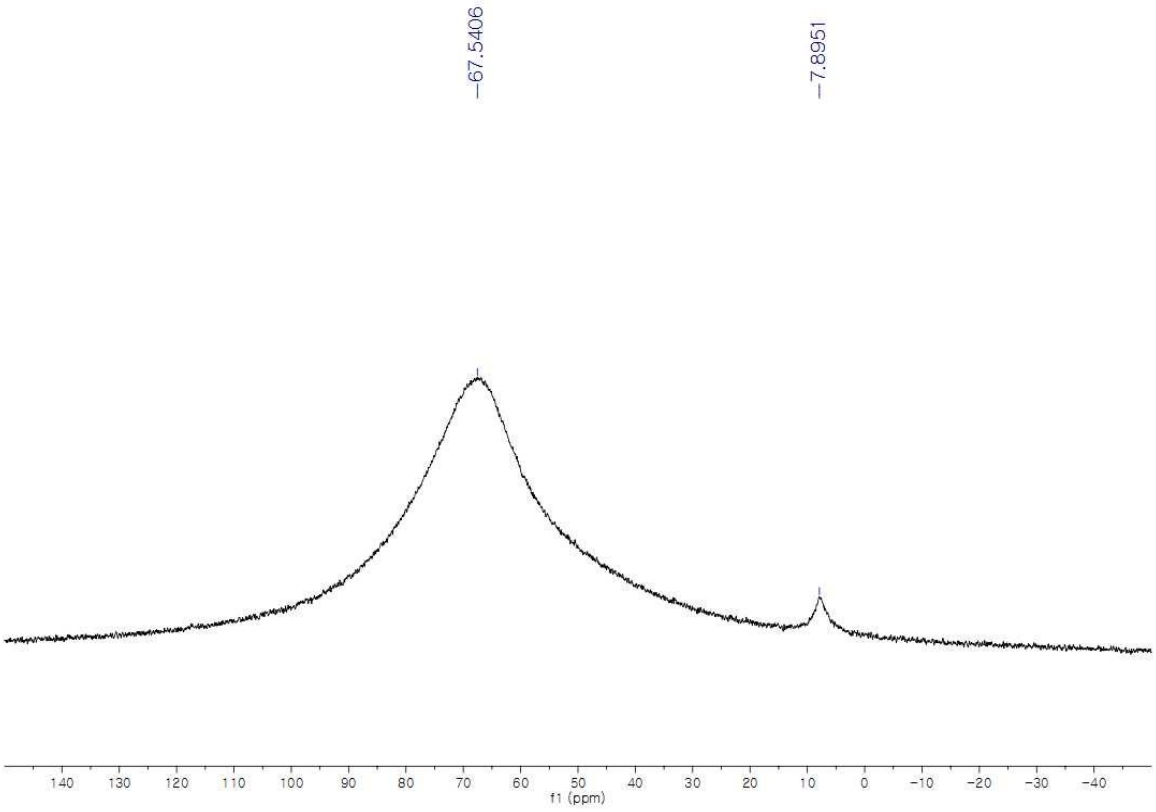


Figure S16. ^{27}Al NMR spectrum of **2** in $CDCl_3$

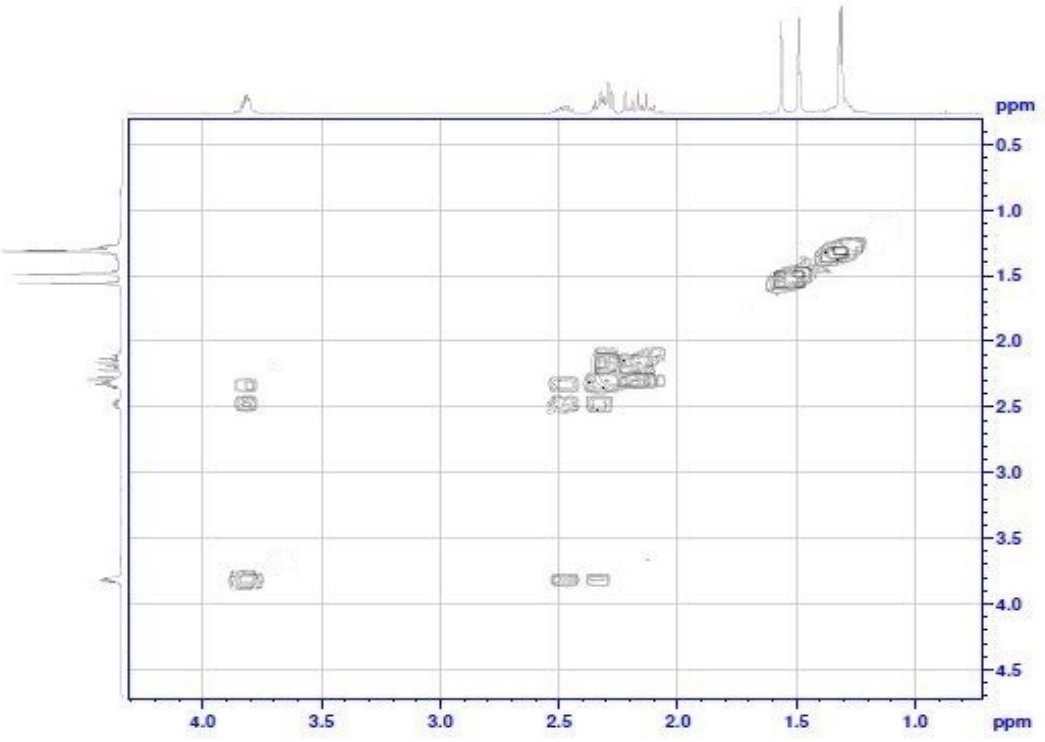


Figure S17. COSY(2D NMR spectrum) of **2** in C_6D_6

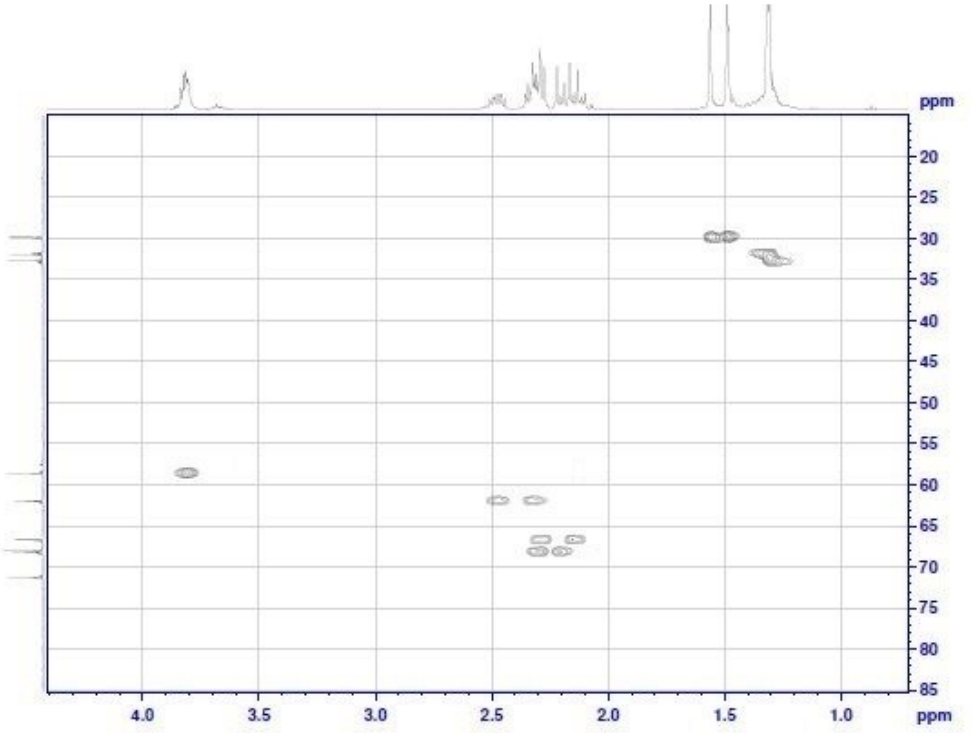


Figure S18. HSQC (2D NMR spectrum) of **2** in C_6D_6

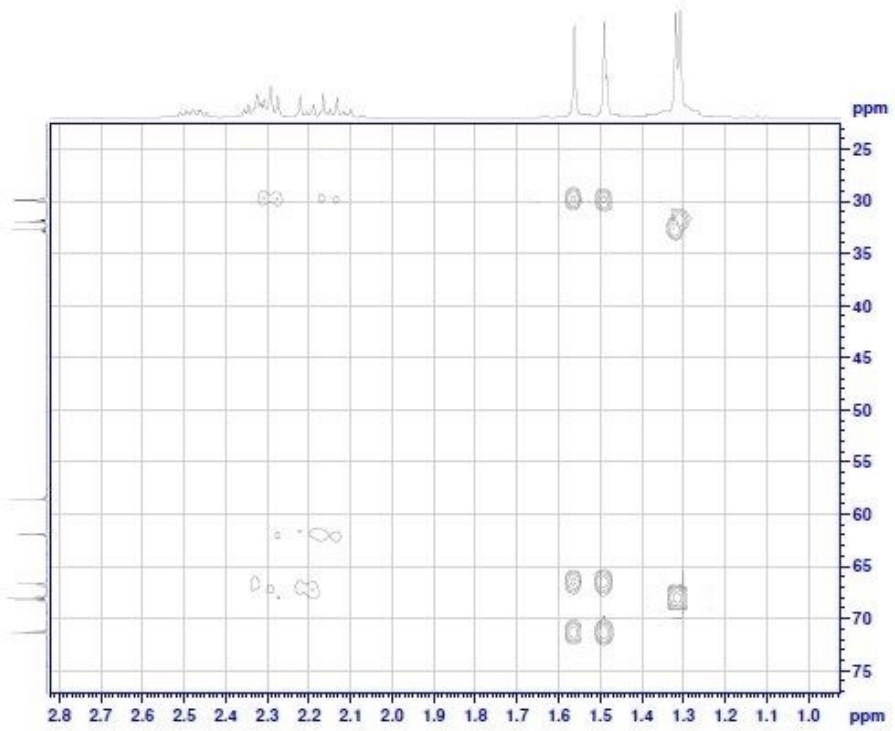


Figure S19. HMBC(2D NMR spectrum) of **2** in C_6D_6

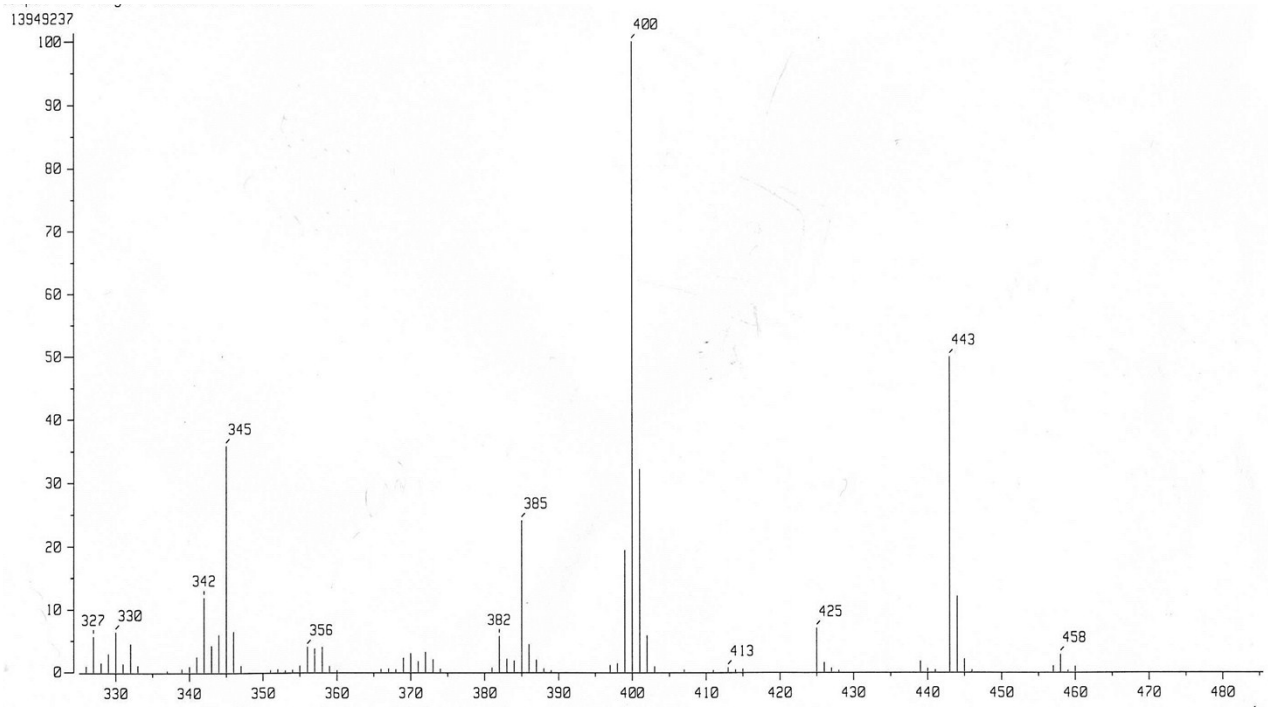
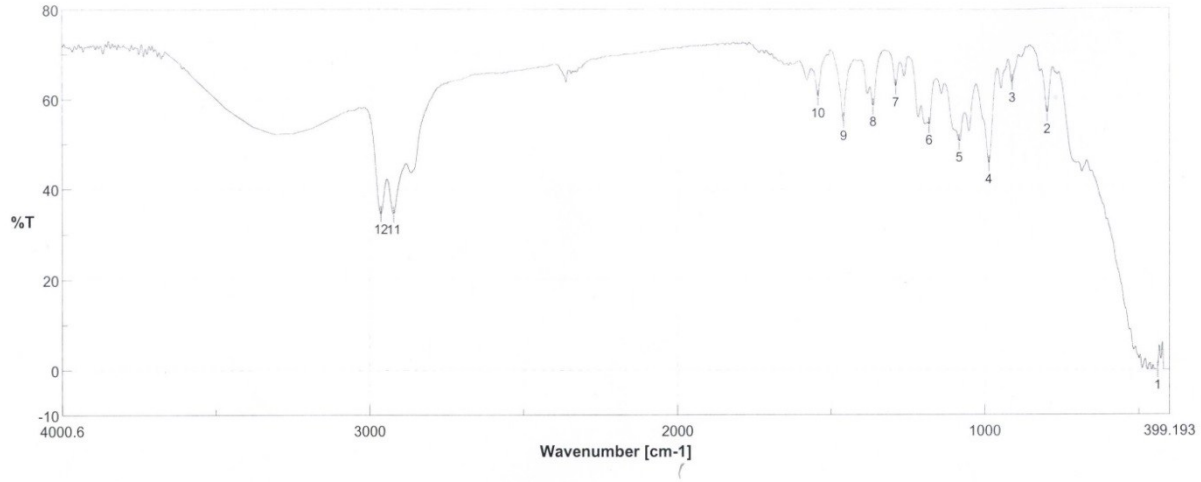


Figure S20. EI-MS spectrum of **2**



Date/Time 2010-10-05 3:32오후
Operator
File Name Memory#4
Sample Name FRS
Comment

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	437.762	-1.17549E-038	2	798.385	56.5879	3	911.2	63.6164	4	986.411	45.4826	5	1081.87	50.3701
6	1180.22	54.2012	7	1288.22	62.6488	8	1362.46	58.2501	9	1458.88	55.1176	10	1541.81	60.1402
11	2922.59	34.5629	12	2964.05	34.6154									

Figure S21. IR spectrum of **2**

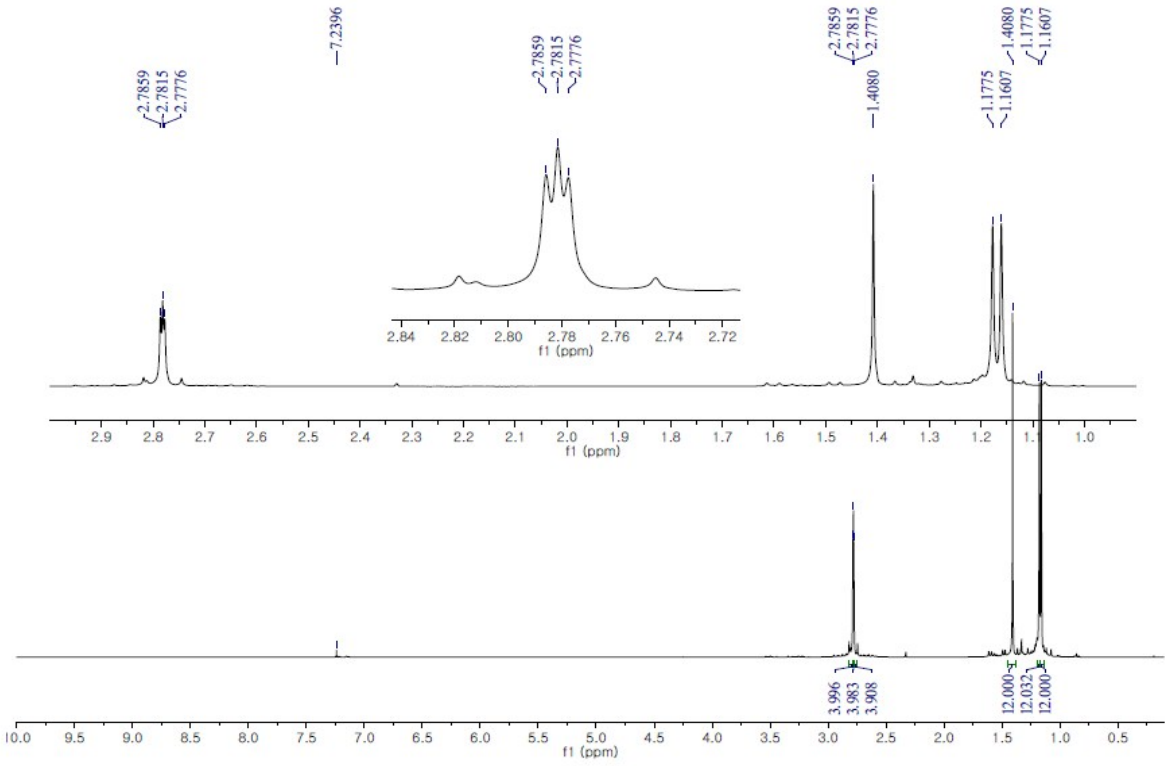


Figure S22. ^{1}H NMR spectrum of **3** in $CDCl_3$

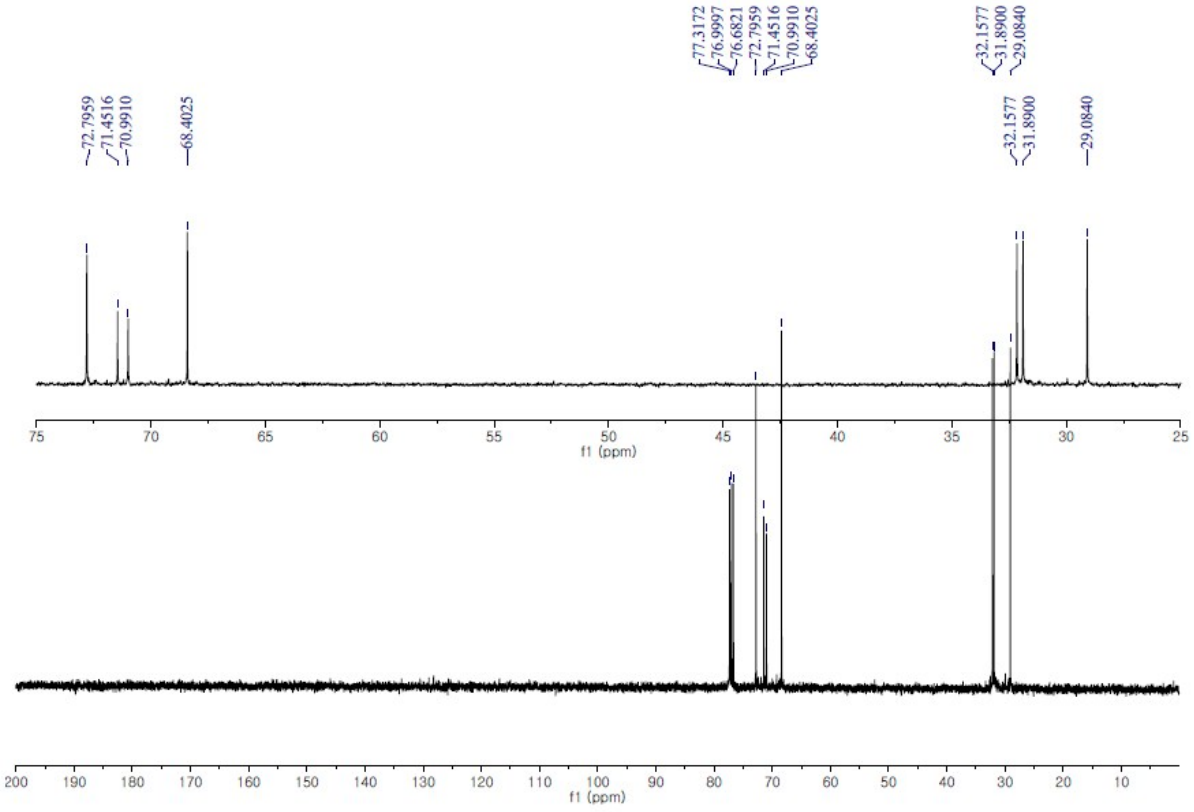


Figure S23. ^{13}C NMR spectrum of **3** in $CDCl_3$

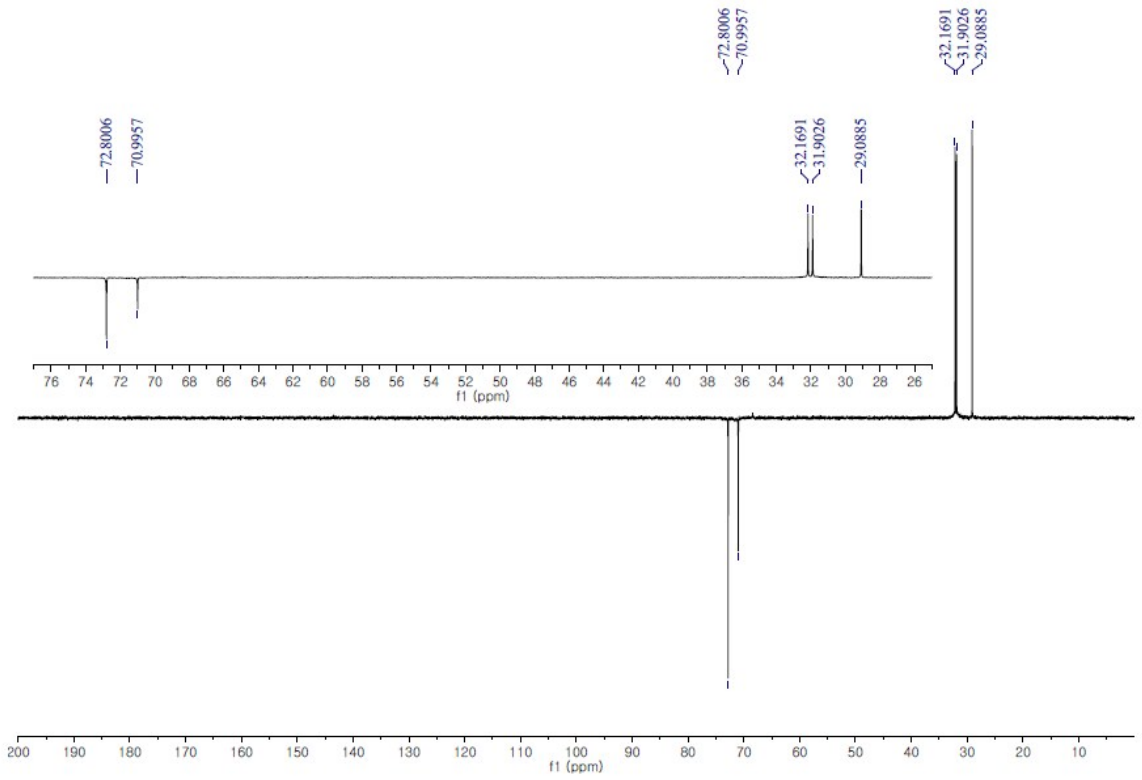


Figure S24. DEPT 135 NMR spectrum of **3** in $CDCl_3$

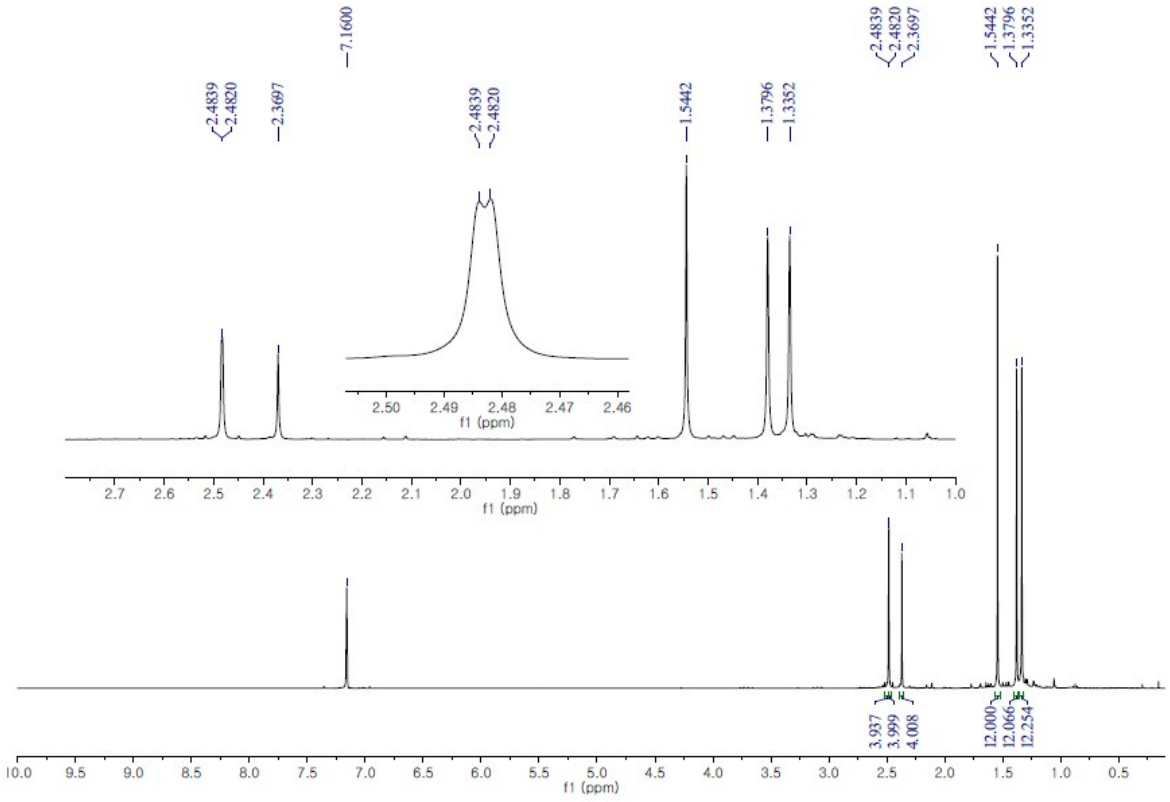


Figure S25. ^1H NMR spectrum of **3** in C_6D_6

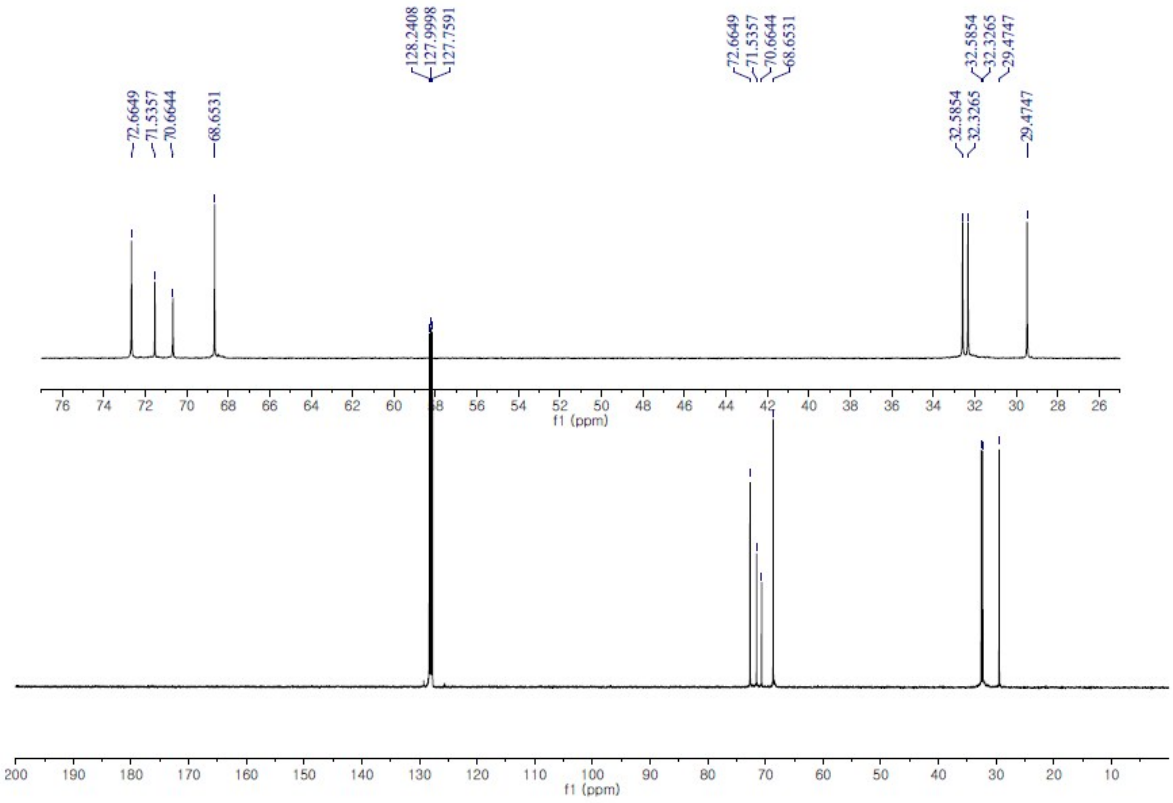


Figure S26. ^{13}C NMR spectrum of **3** in C_6D_6

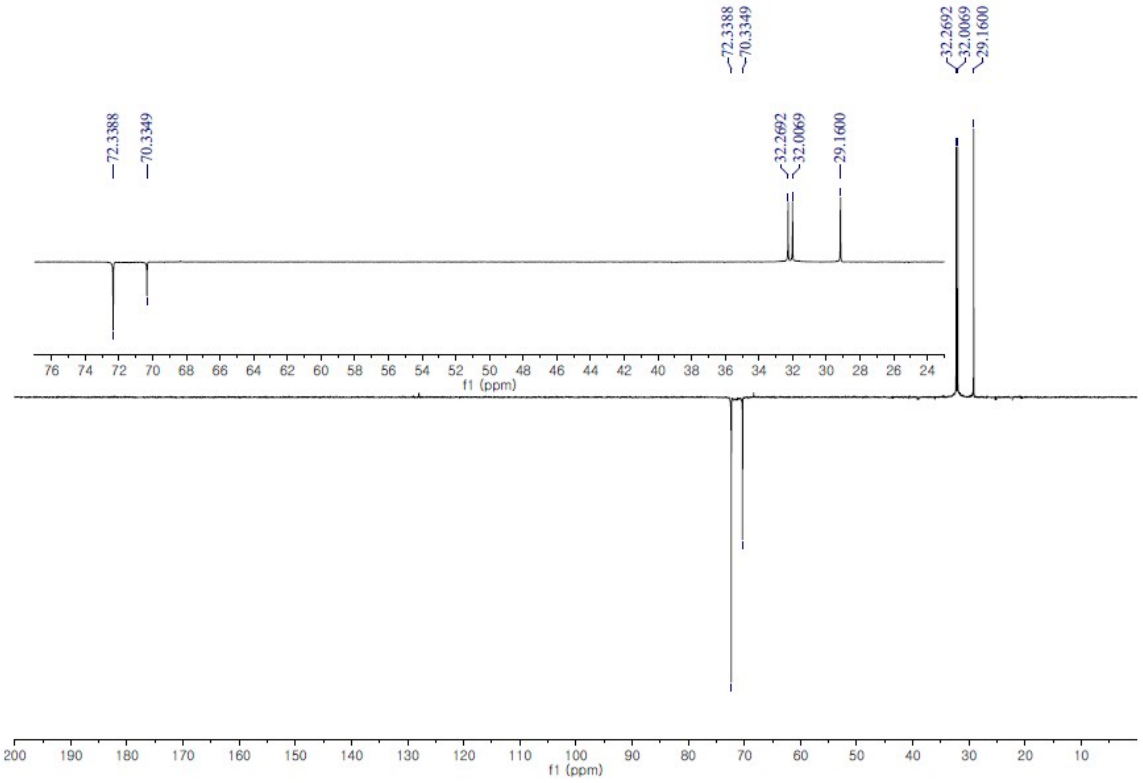


Figure S27. DEPT 135 NMR spectrum of **3** in C_6D_6

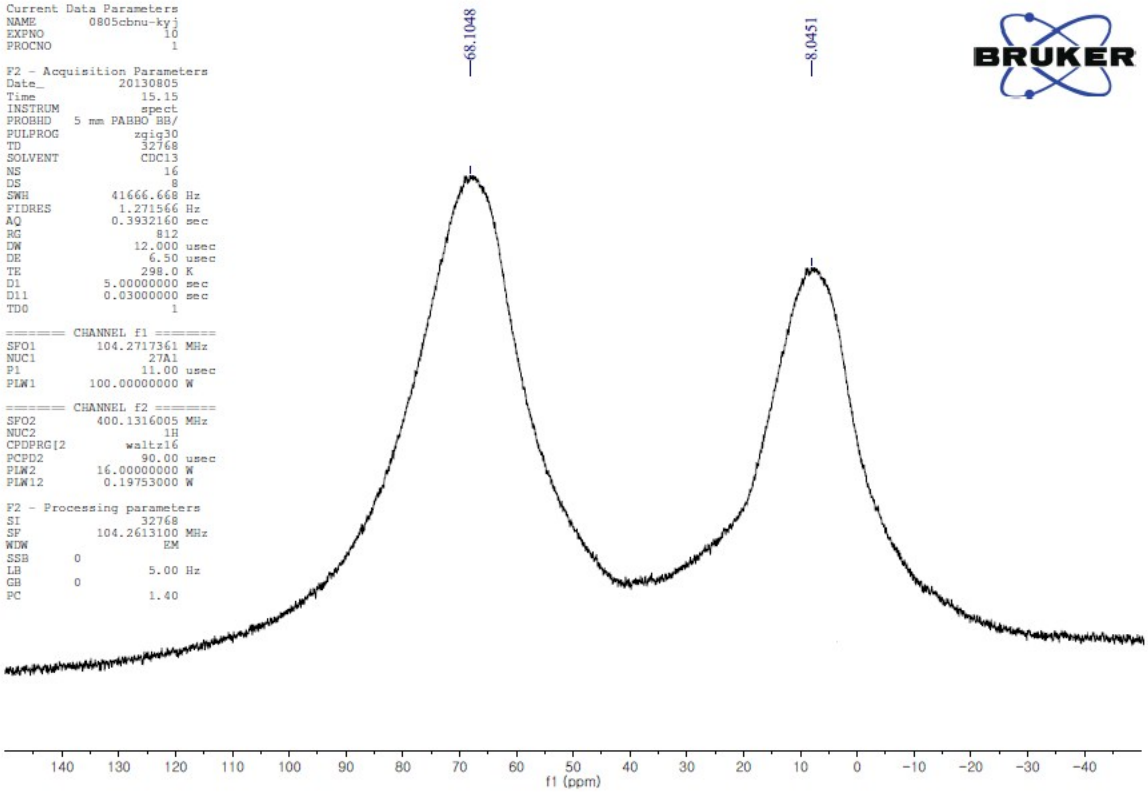


Figure S28. ^{27}Al NMR spectrum of **3** in $CDCl_3$

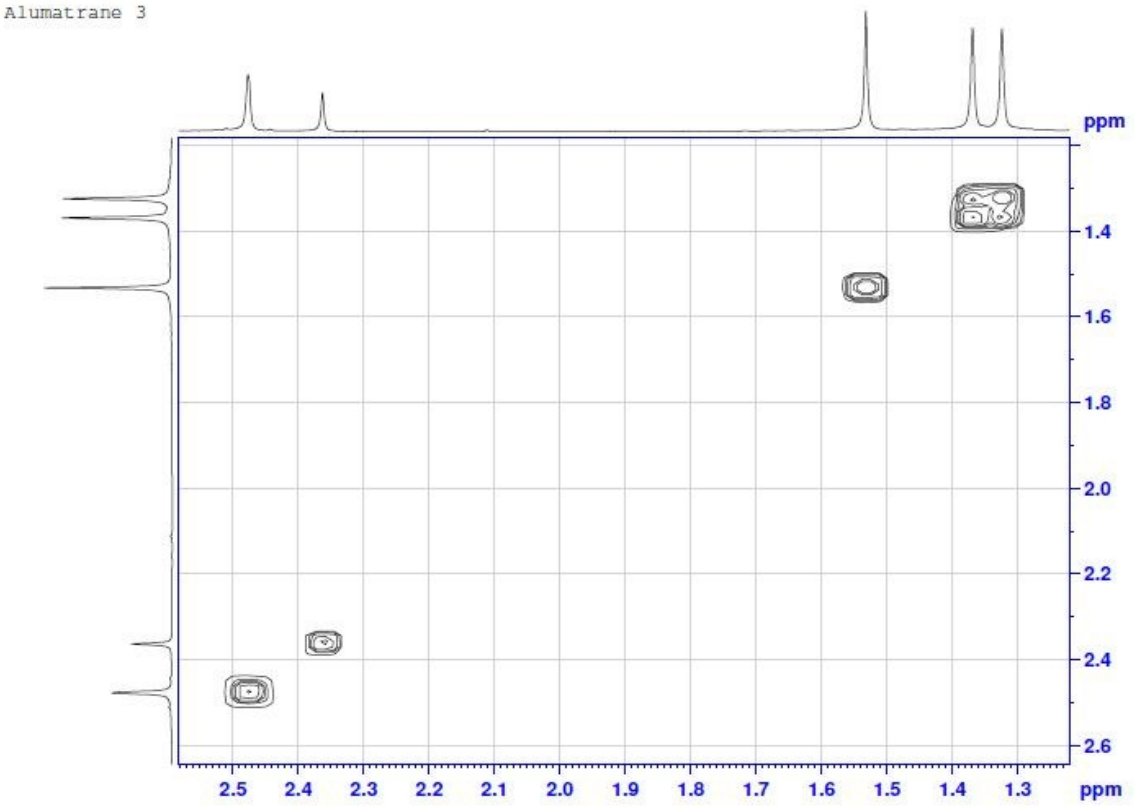


Figure S29. COSY(2D NMR spectrum) of **3** in C_6D_6

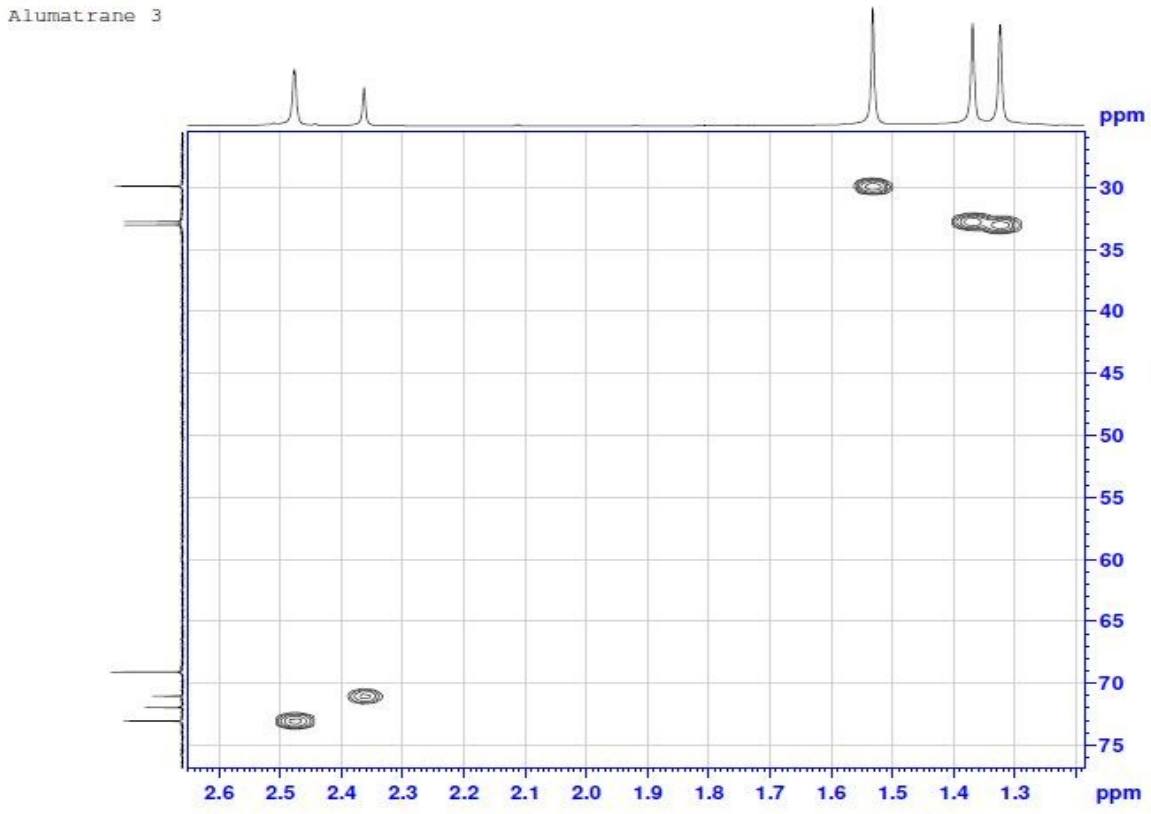


Figure S30. HSQC(2D NMR spectrum) of **3** in C_6D_6

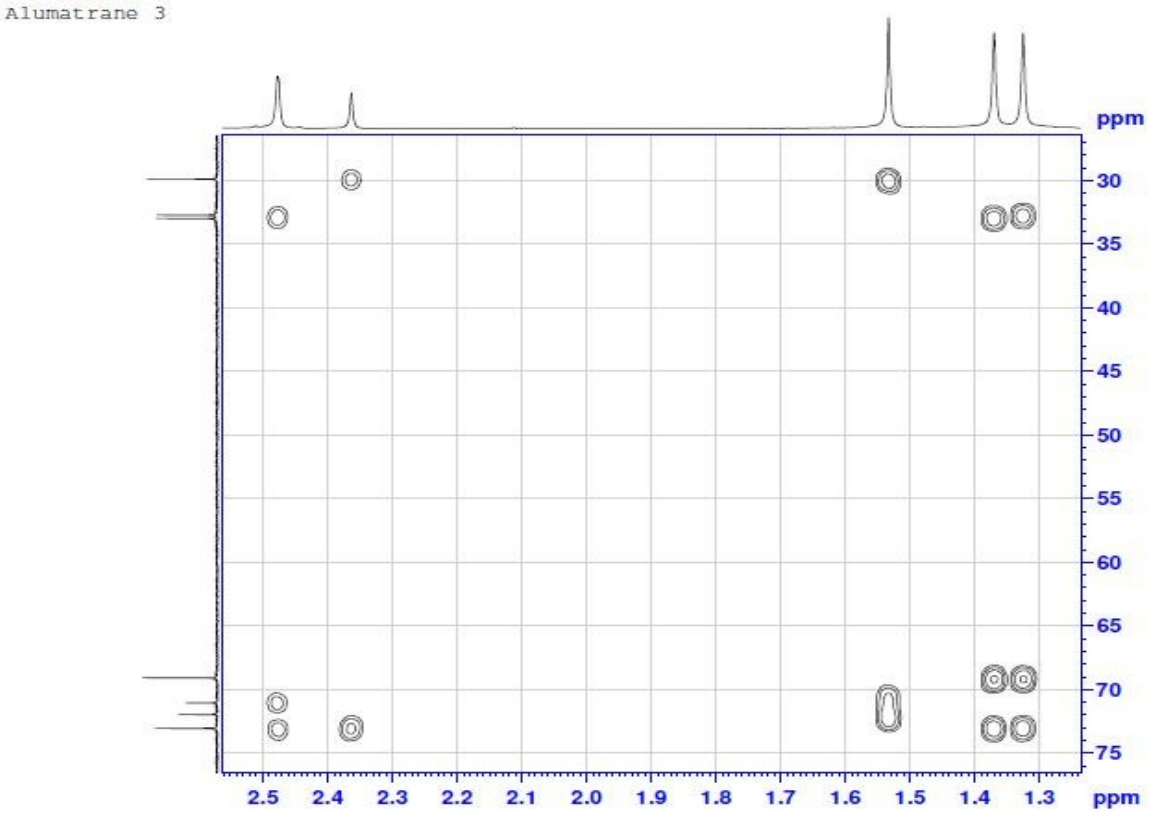


Figure S31. HMBC(2D NMR spectrum) of **3** in C_6D_6

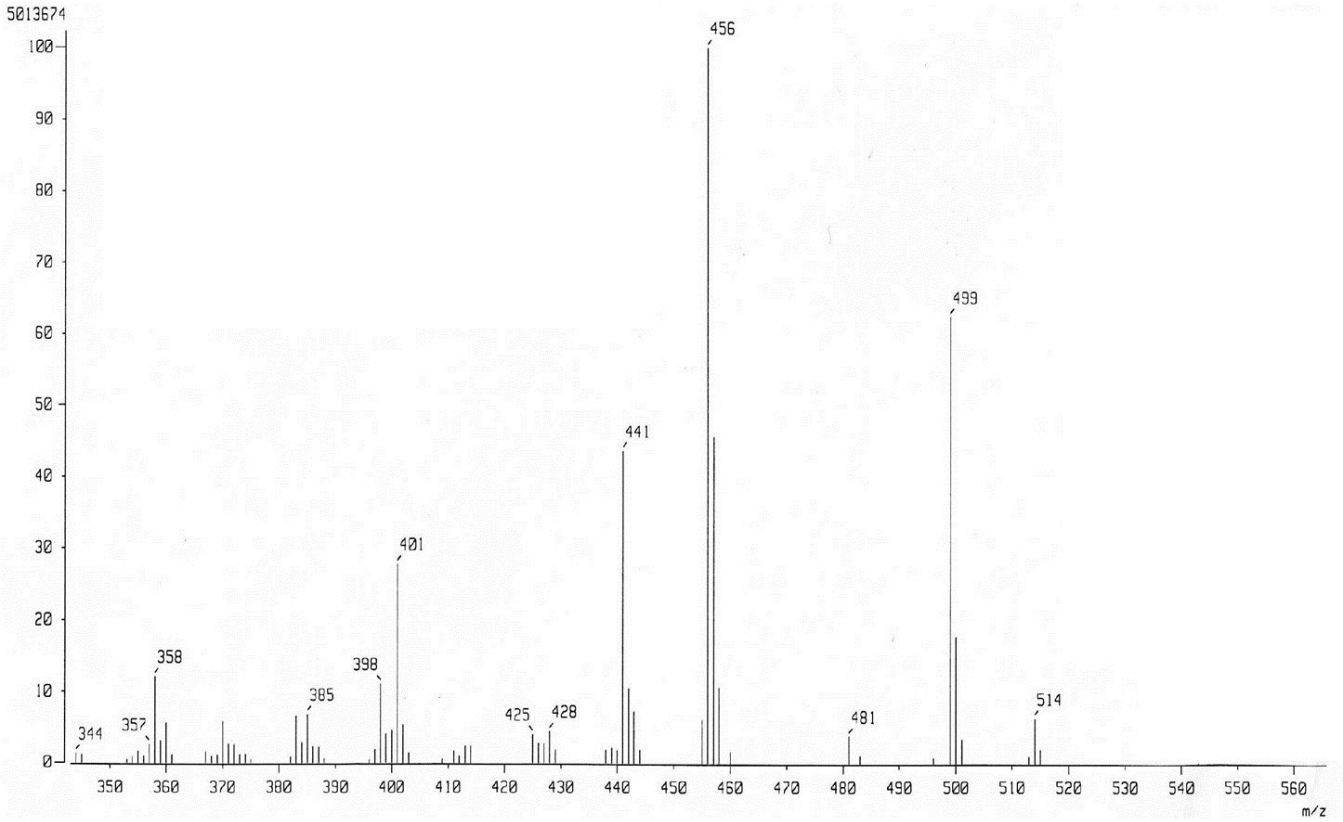
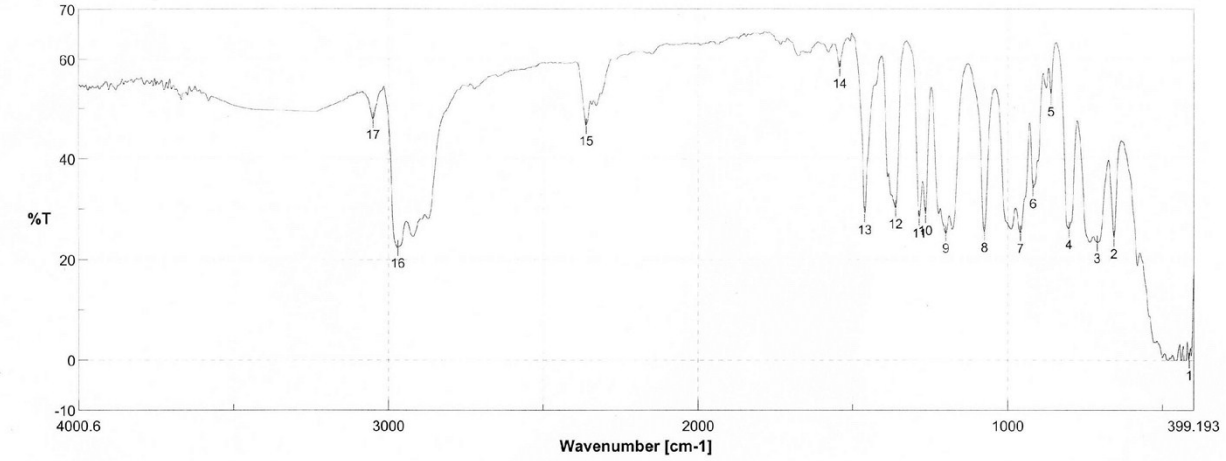


Figure S32. EI-MS spectrum of **3**

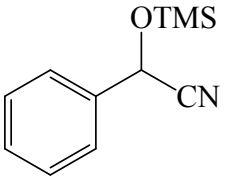


Date/Time	2010-10-05 0:00오전
Operator	
File Name	Memory#3
Sample Name	FRS
Comment	

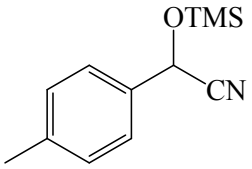
No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	413.656	-1.17549E-038	2	657.607	24.1588	3	711.604	23.2991	4	803.206	26.0183	5	862.025	52.4391
6	919.878	34.1373	7	960.376	25.2677	8	1076.08	25.4666	9	1200.47	25.259	10	1266.04	28.7725
11	1285.32	28.2234	12	1361.5	30.0471	13	1461.78	28.8946	14	1542.77	58.0692	15	2362.37	46.5513
16	2970.8	22.2644	17	3051.8	47.8565									

Figure S33. IR spectrum of **3**

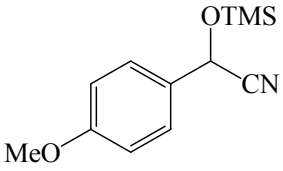
Literature References for Known Compounds



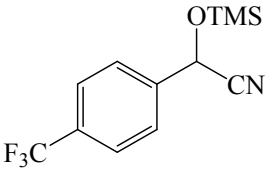
(**Table 2, entries 1–16, & Table 3, entry 1**): North, M.; Omedes-Pujol, M.; Williamson, C. *Chem. Eur. J.* **2010**, *16*, 11367.



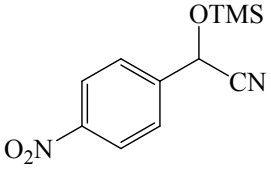
(Table 3, entry 2): North, M.; Omedes-Pujol, M.; Williamson, C. *Chem. Eur. J.* **2010**, *16*, 11367.



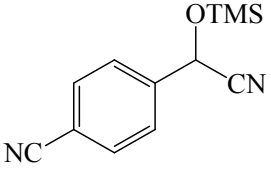
(Table 3, entry 3): Strappaveccia, G.; Lanari, D.; Gelman, D.; Pizzo, F.; Rosati, O.; Curini, M.; Vaccaro, L. J. *Green. Chem.* **2013**, *15*, 199.



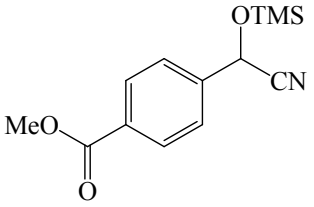
(Table 3, entry 4): North, M.; Omedes-Pujol, M.; Williamson, C. *Chem. Eur. J.* **2010**, *16*, 11367.



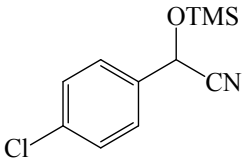
(Table 3, entry 5): Strappaveccia, G.; Lanari, D.; Gelman, D.; Pizzo, F.; Rosati, O.; Curini, M.; Vaccaro, L. J. *Green. Chem.* **2013**, *15*, 199.



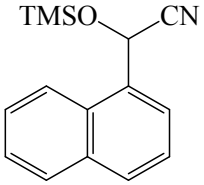
(Table 3, entry 6): Strappaveccia, G.; Lanari, D.; Gelman, D.; Pizzo, F.; Rosati, O.; Curini, M.; Vaccaro, L. J. *Green. Chem.* **2013**, *15*, 199.



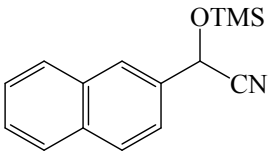
(Table 3, entry 7): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



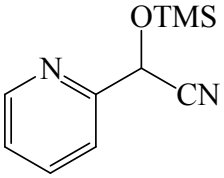
(Table 3, entry 8): Strappaveccia, G.; Lanari, D.; Gelman, D.; Pizzo, F.; Rosati, O.; Curini, M.; Vaccaro, L. J. *Green. Chem.* **2013**, *15*, 199.



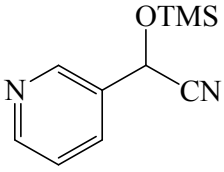
(Table 3, entry 9): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



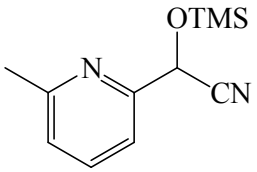
(Table 3, entry 10): Kurono, N.; Yamaguchi, M.; Suzuki, K.; Ohkuma, T. *J. Org. Chem.* **2005**, *70*, 6530.



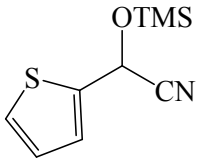
(Table 4, entry 1): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



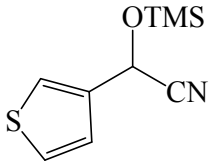
(Table 4, entry 2): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



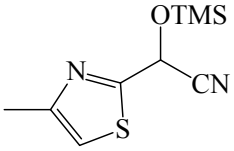
(Table 4, entry 3): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



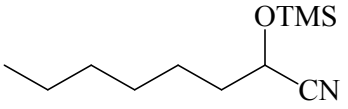
(Table 4, entry 4): Raders, S. M.; Verkade, J. G. *Tetrahedron Letters* **2009**, *50*, 5317.



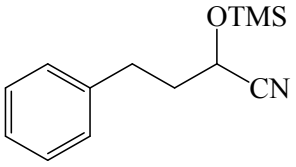
(Table 4, entry 5): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



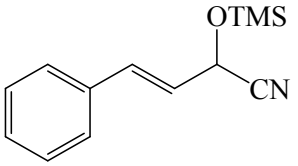
(Table 4, entry 6): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



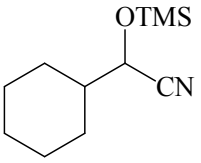
(Table 4, entry 7): Raders, S. M.; Verkade, J. G. *Tetrahedron Lett.* **2009**, *50*, 5317.



(Table 4, entry 8): Qin, Y.-C.; Liu, L.; Pu, L. *Org. Lett.* **2005**, 7, 2381.



(Table 4, entry 9): Qin, Y.-C.; Liu, L.; Pu, L. *Org. Lett.* **2005**, 7, 2381.



(Table 4, entry 10): Strappaveccia, G.; Lanari, D.; Gelman, D.; Pizzo, F.; Rosati, O.; Curini, M.; Vaccaro, L. J. *Green. Chem.* **2013**, *15*, 199.

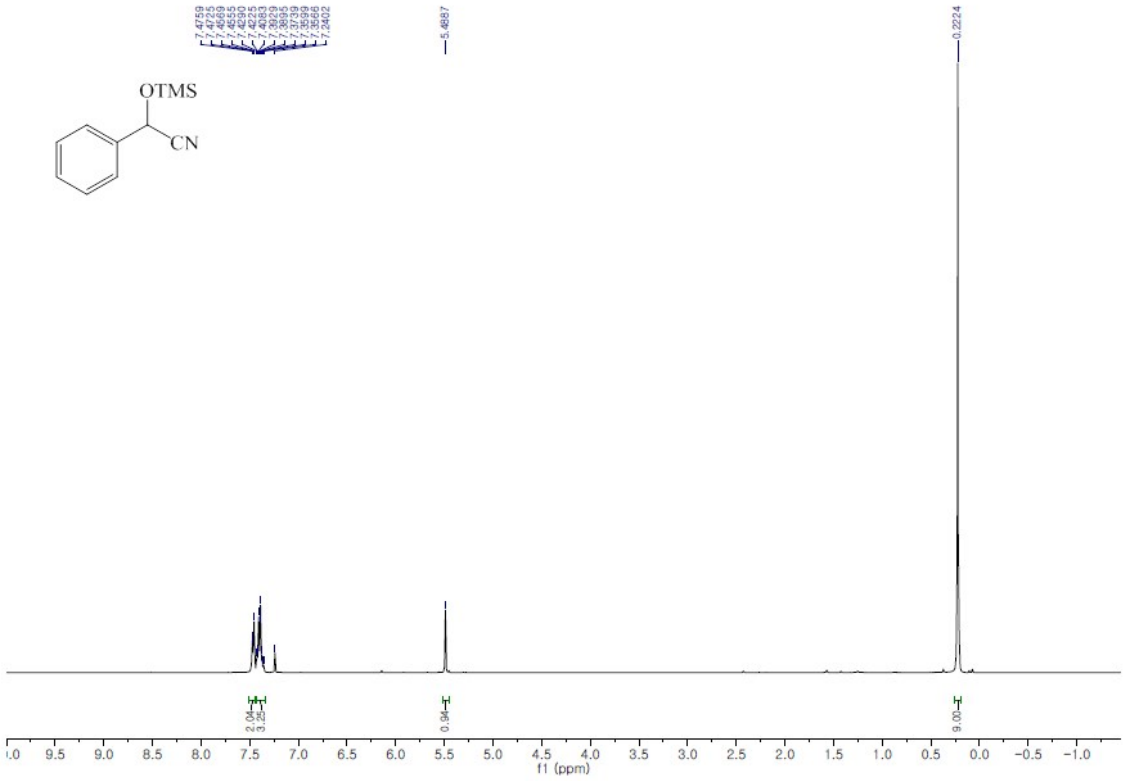


Figure S34. ^{1}H NMR spectrum of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 2, entries 1 – 16 & Table 3, entry 1)

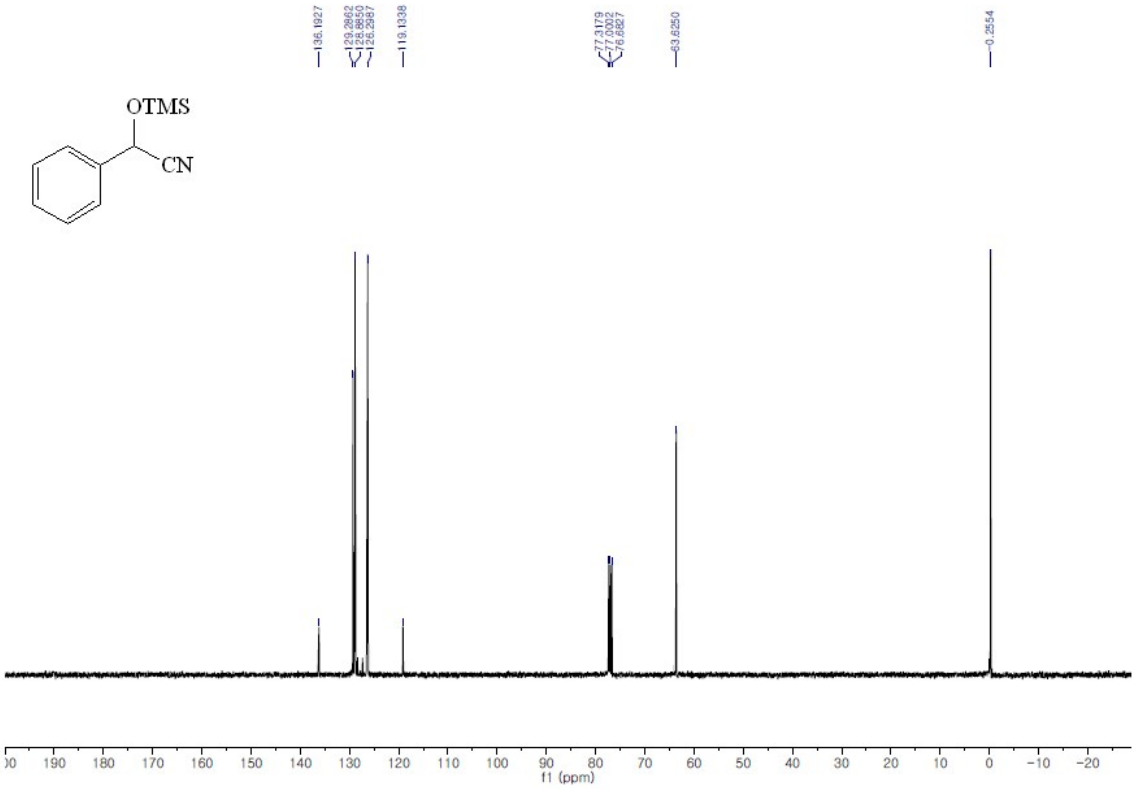


Figure S35. ^{13}C NMR spectrum of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 1, entries 4 – 14 & Table 3, entry 1)

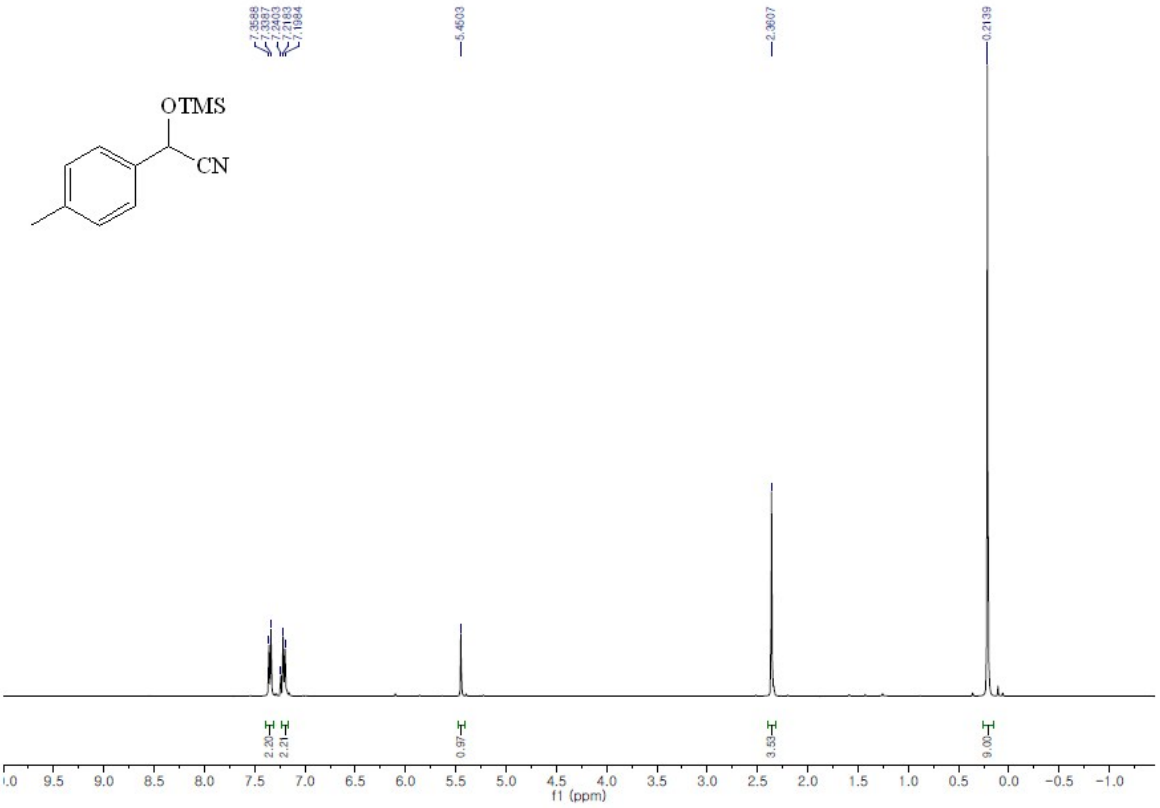


Figure S36. ^{1}H NMR spectrum of 2-(*p*-tolyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 2)

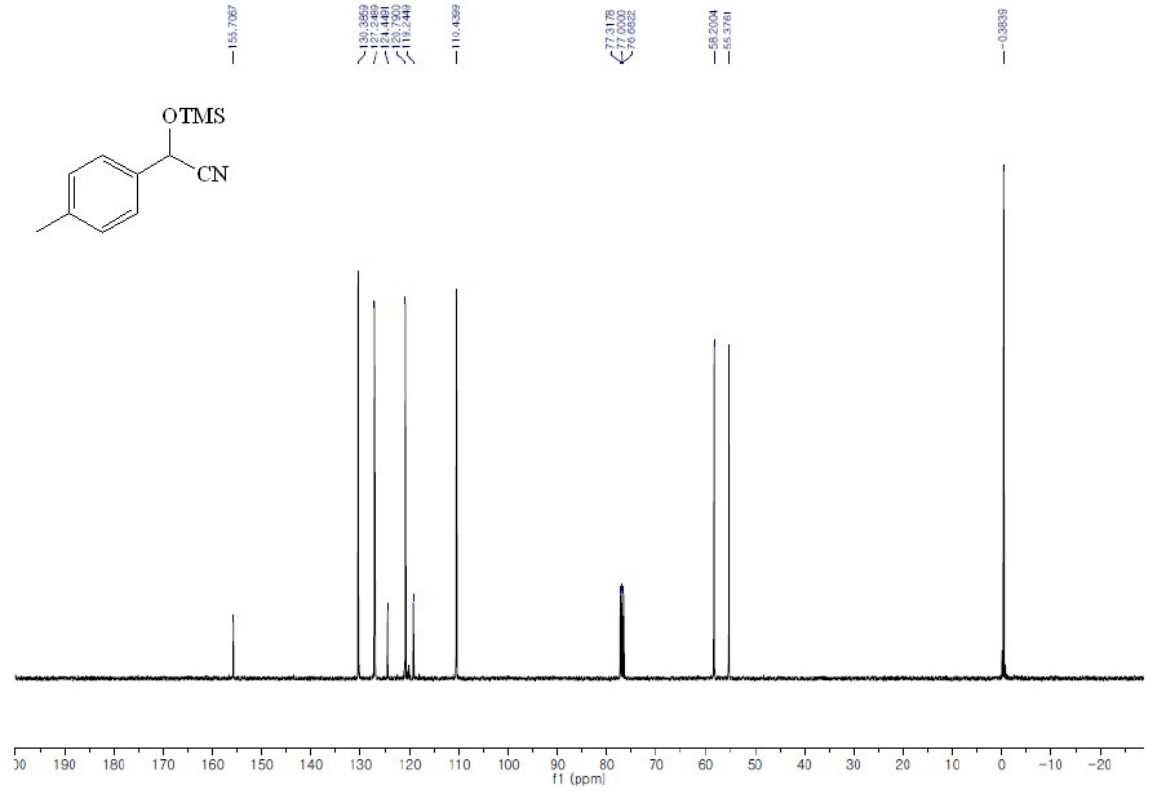


Figure S37. ^{13}C NMR spectrum of 2-(*p*-tolyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 2)

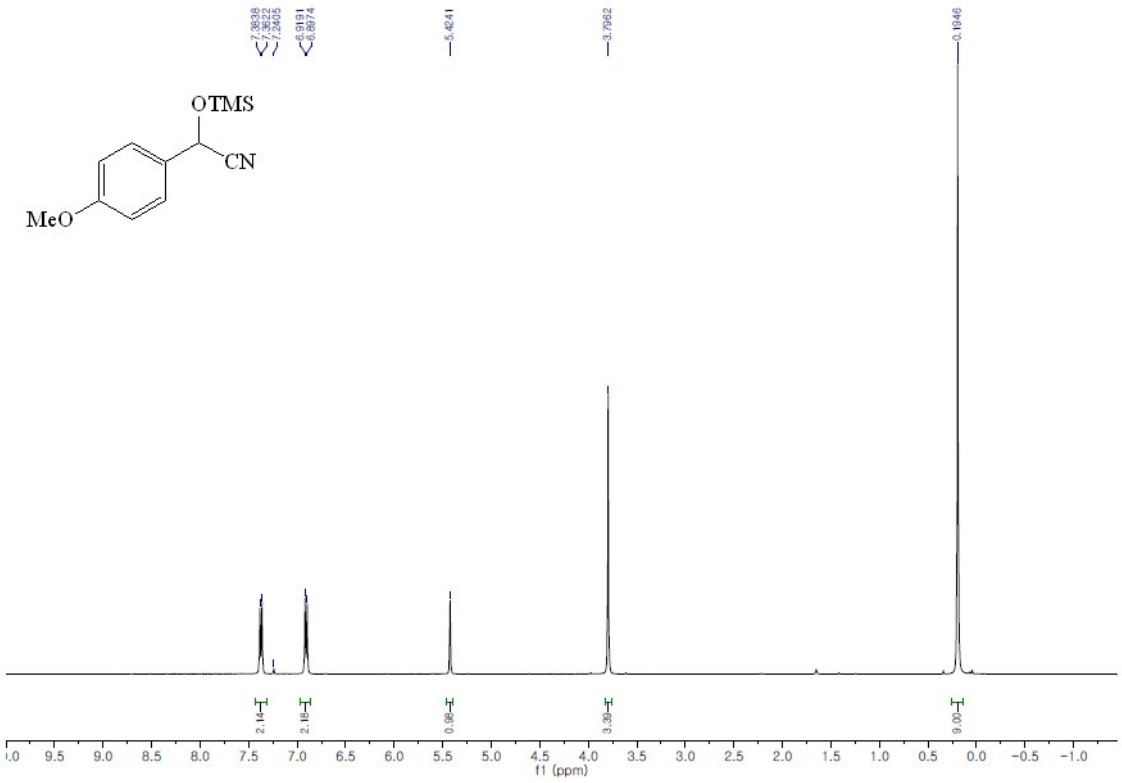


Figure S38. ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 3)

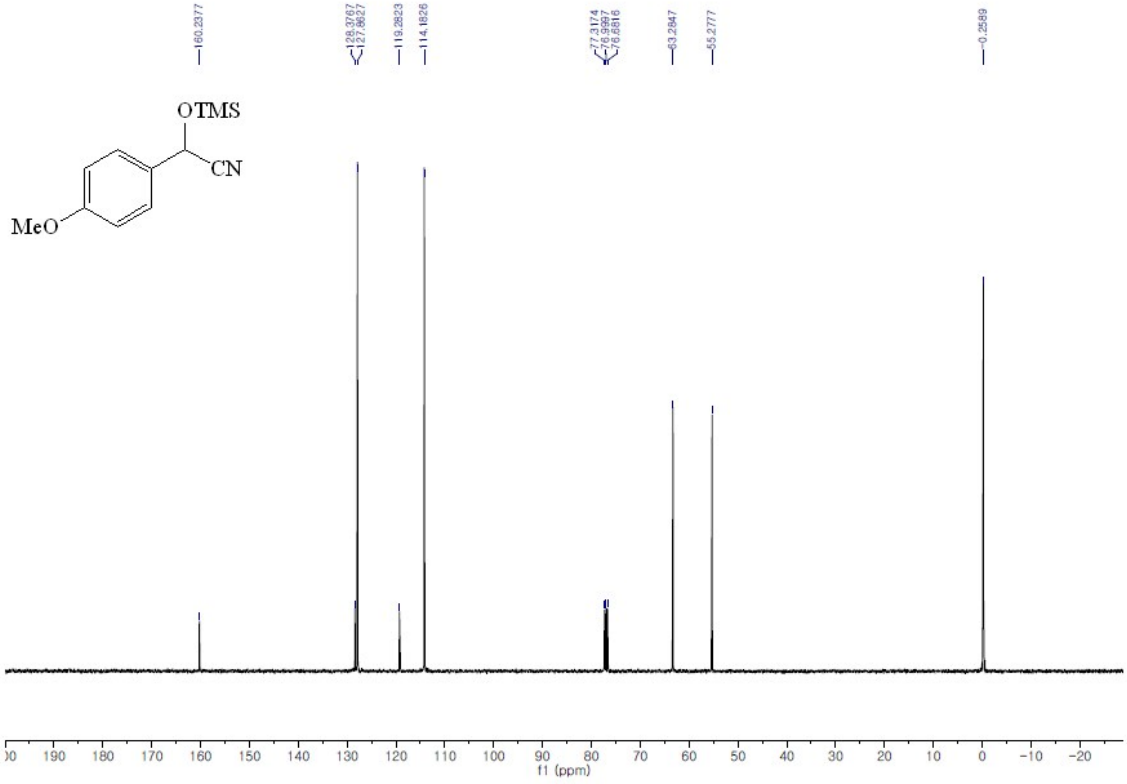


Figure S39. ^{13}C NMR spectrum of 2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 3)

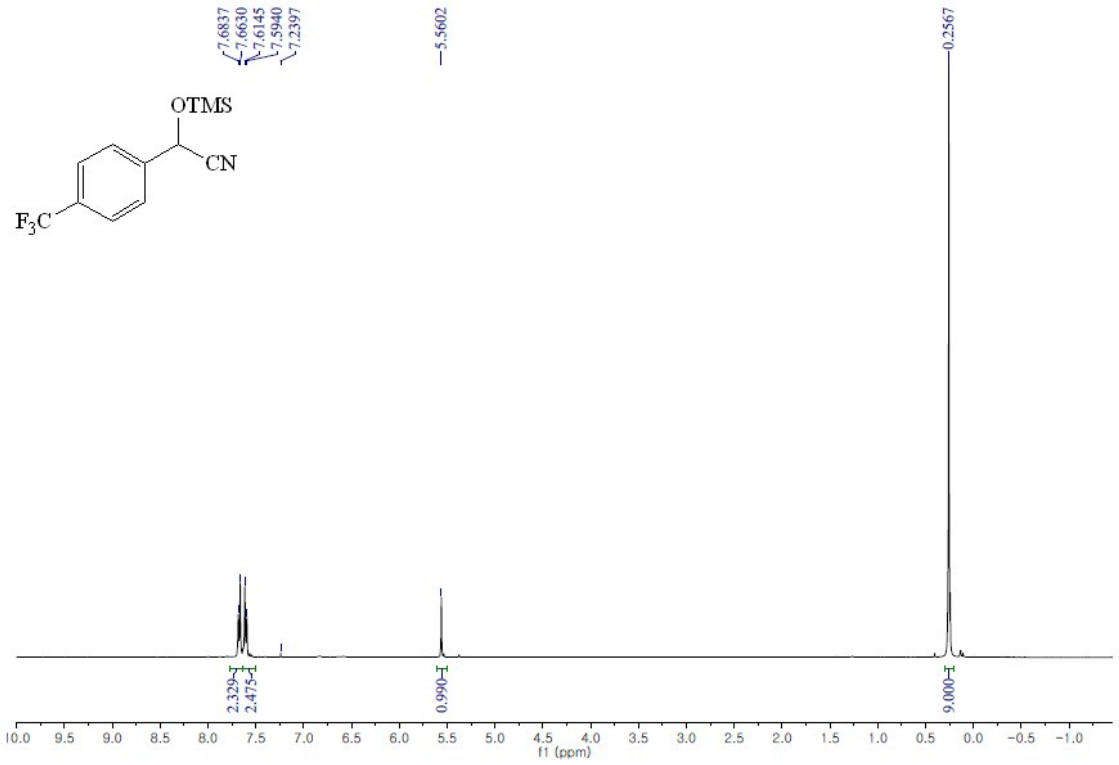


Figure S40. ^{1}H NMR spectrum of 2-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 4)

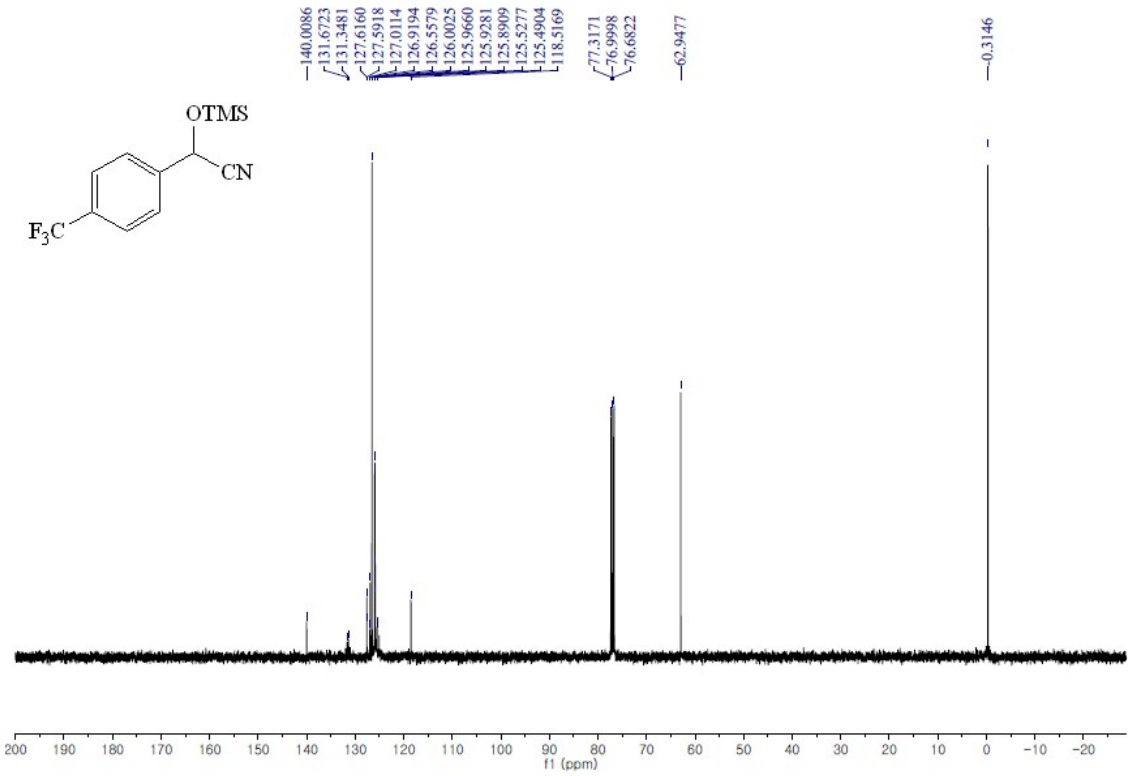


Figure S41. ^{13}C NMR spectrum of 2-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 4)

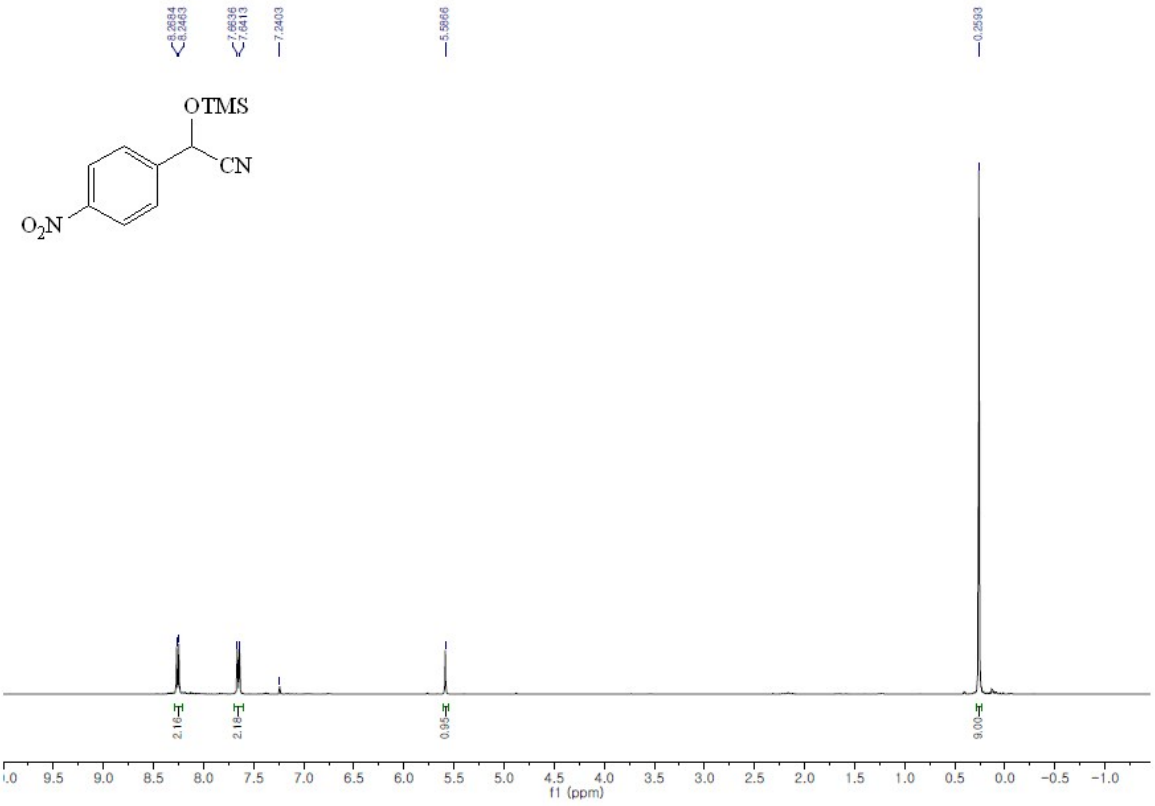


Figure S42. ^{1}H NMR spectrum of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 5)

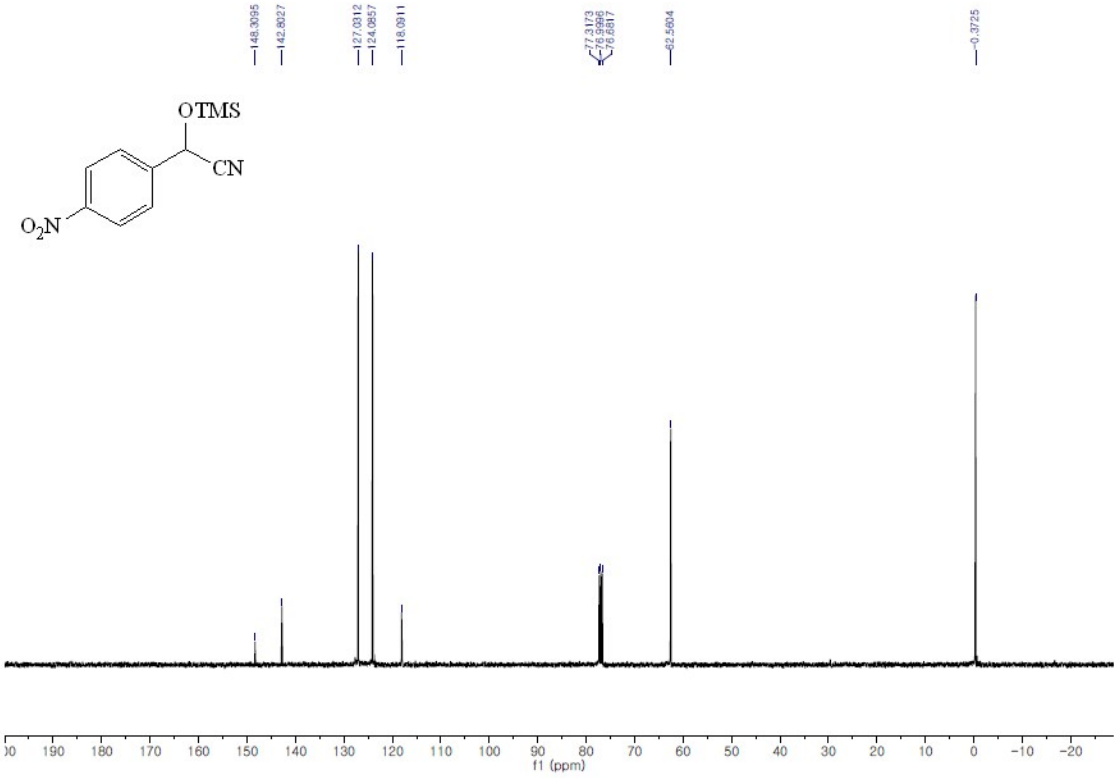


Figure S43. ^{13}C NMR spectrum of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 5)

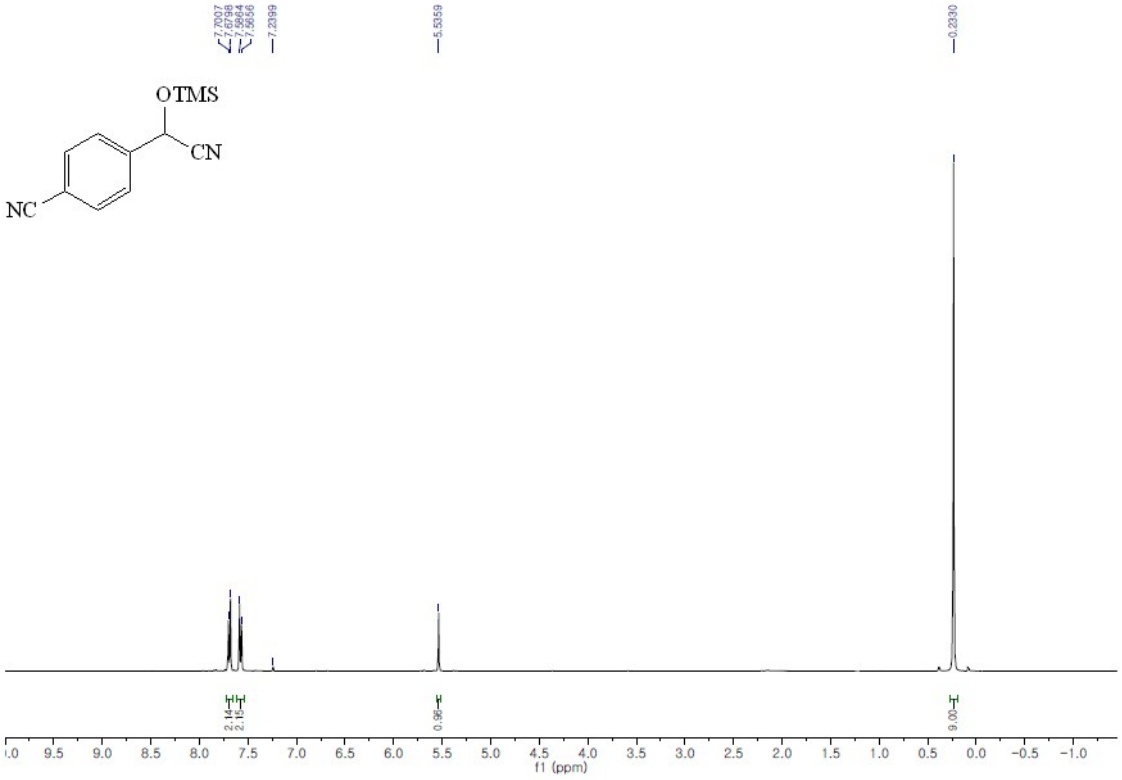


Figure S44. ^{1}H NMR spectrum of 4-(cyano((trimethylsilyl)oxy)methyl)benzonitrile in $CDCl_3$ (Table 3, entry 6)

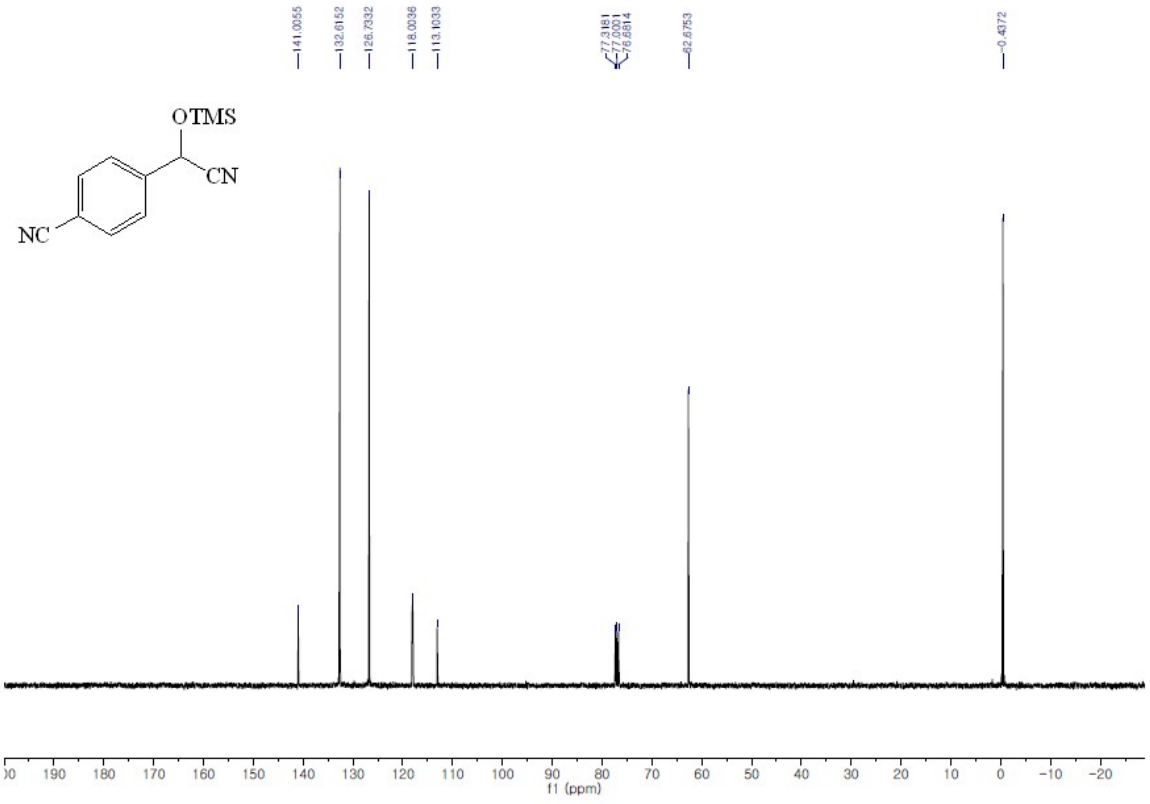


Figure S45. ^{13}C NMR spectrum of 4-(cyano((trimethylsilyl)oxy)methyl)benzonitrile in $CDCl_3$ (Table 3, entry 6)

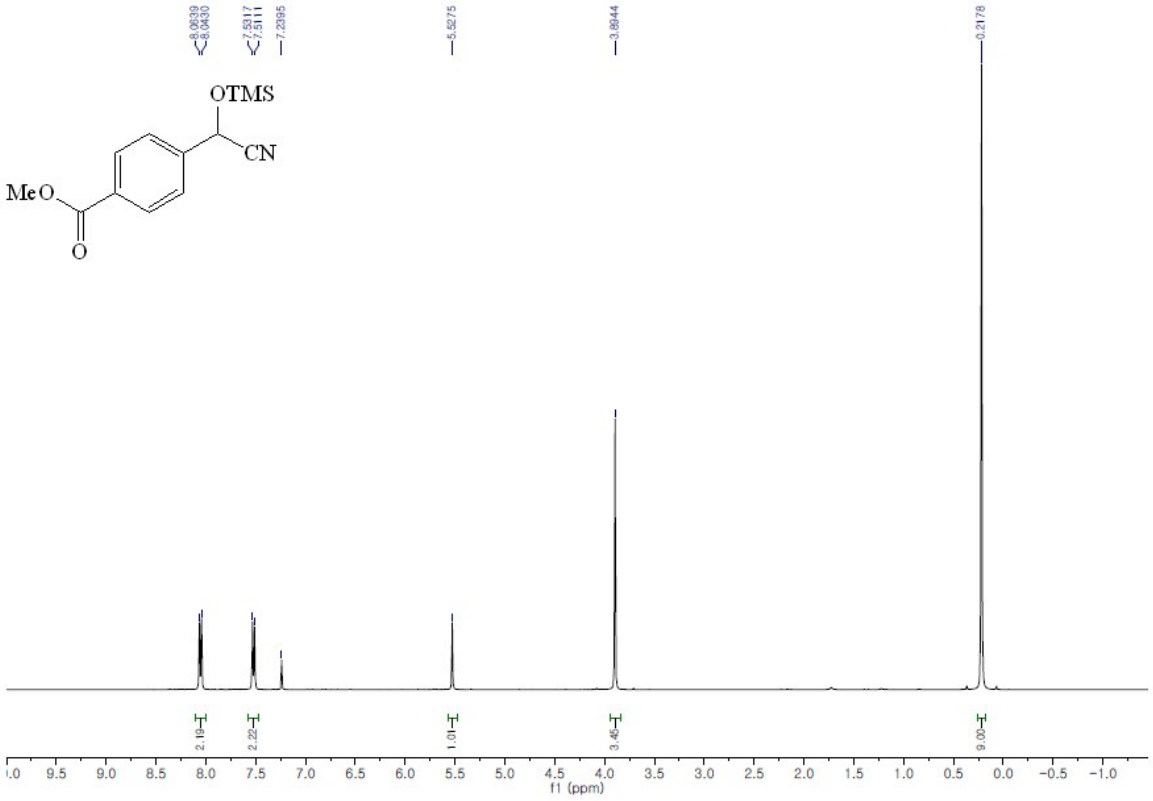


Figure S46. ^{1}H NMR spectrum of methyl 4-(cyano((trimethylsilyl)oxy)methyl)benzoate in $CDCl_3$ (Table 3, entry 7)

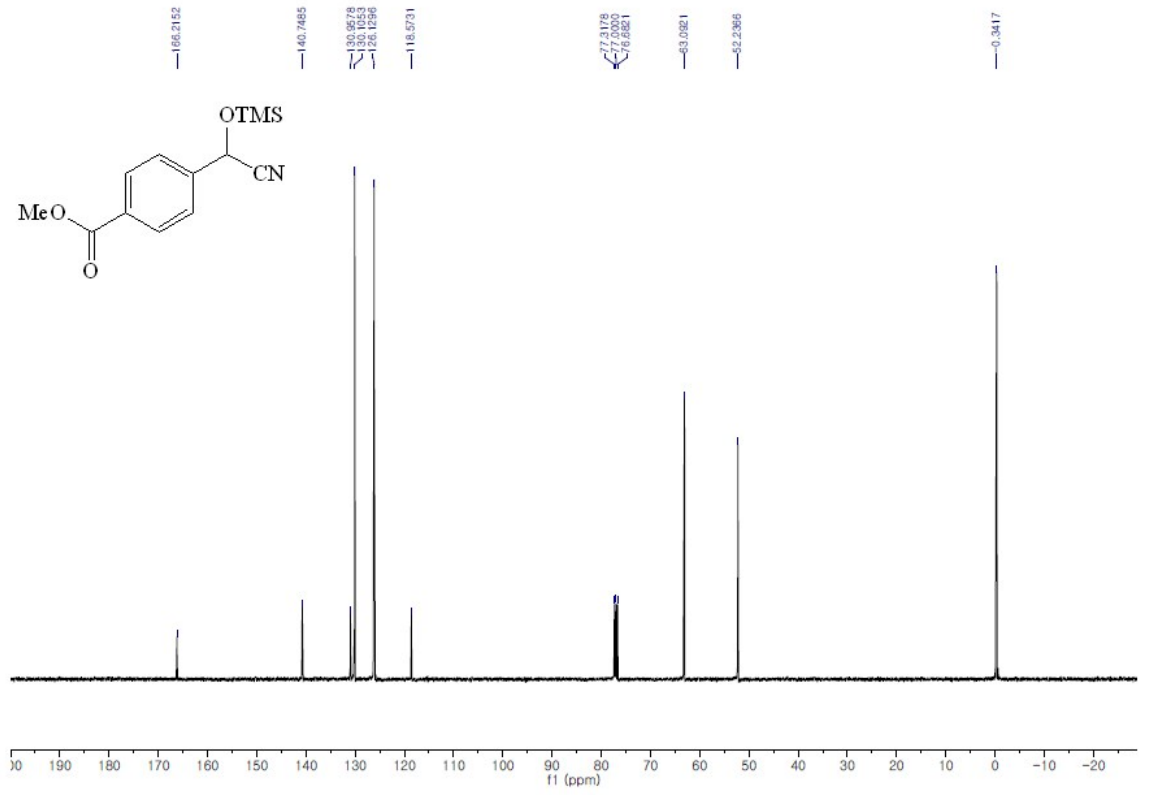


Figure S47. ^{13}C NMR spectrum of methyl 4-(cyano((trimethylsilyl)oxy)methyl)benzoate in $CDCl_3$ (Table 3, entry 7)

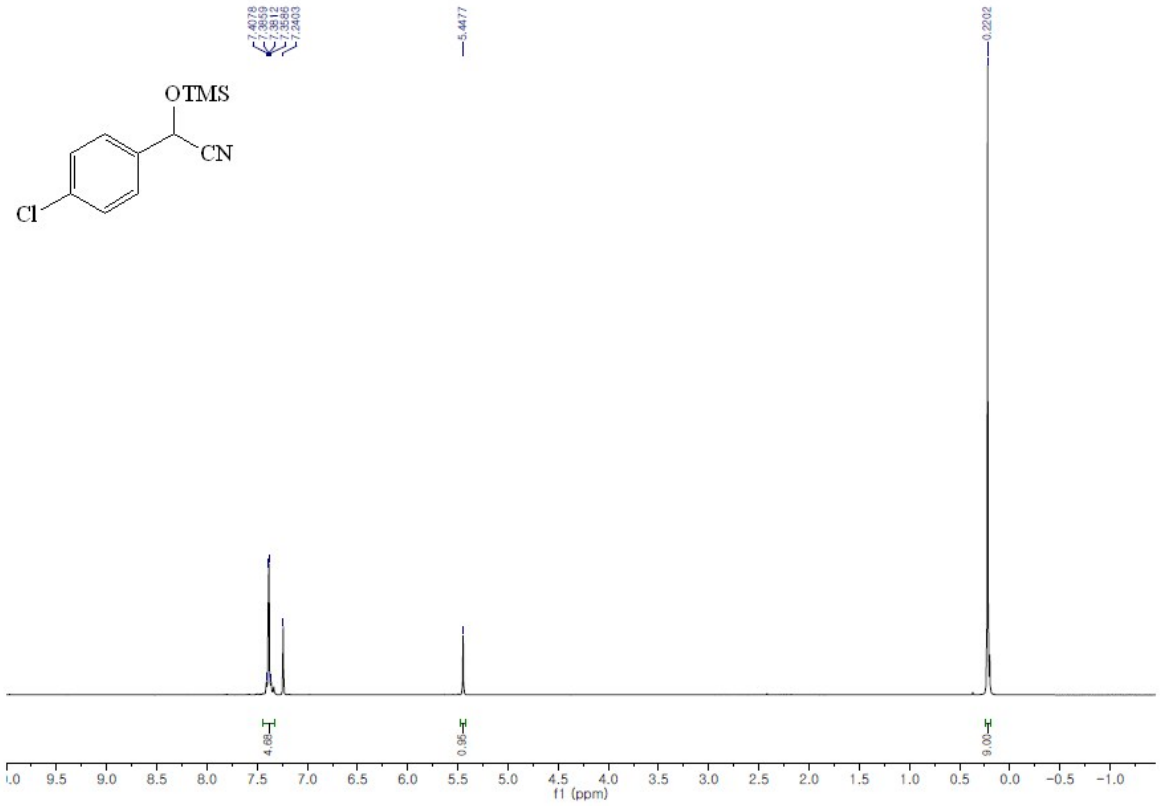


Figure S48. ^{1}H NMR spectrum of 2-(4-chlorophenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 8)

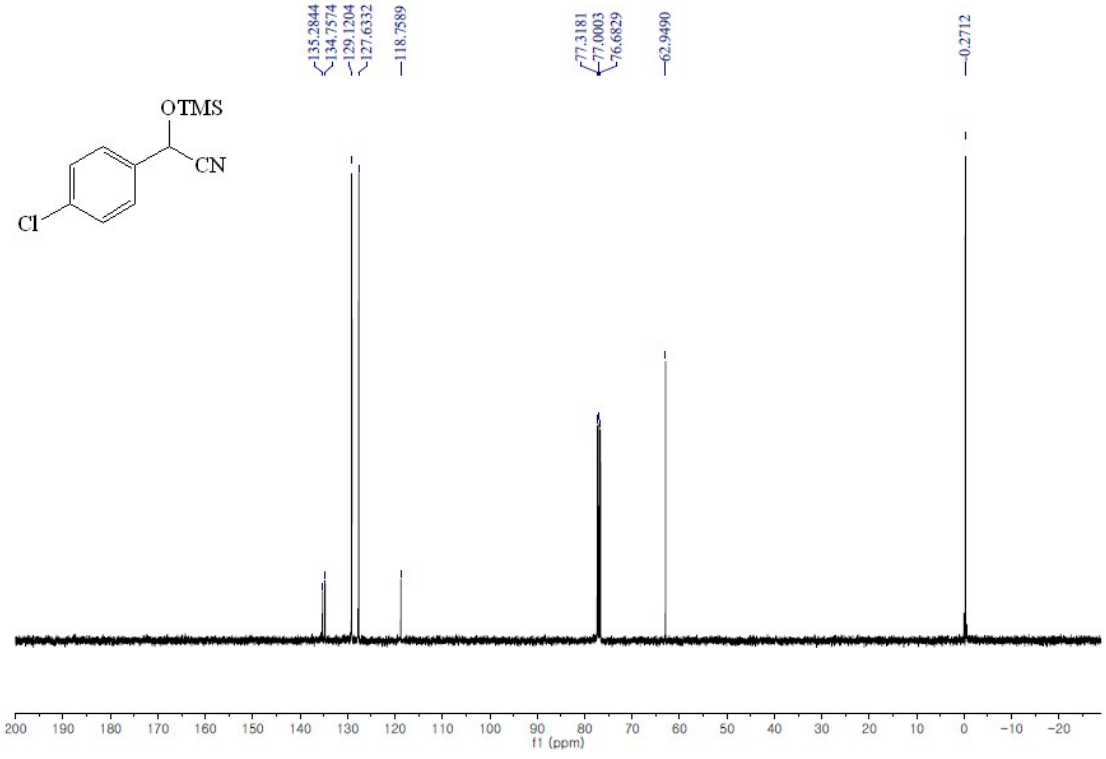


Figure S49. ^{13}C NMR spectrum of 2-(4-chlorophenyl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 8)

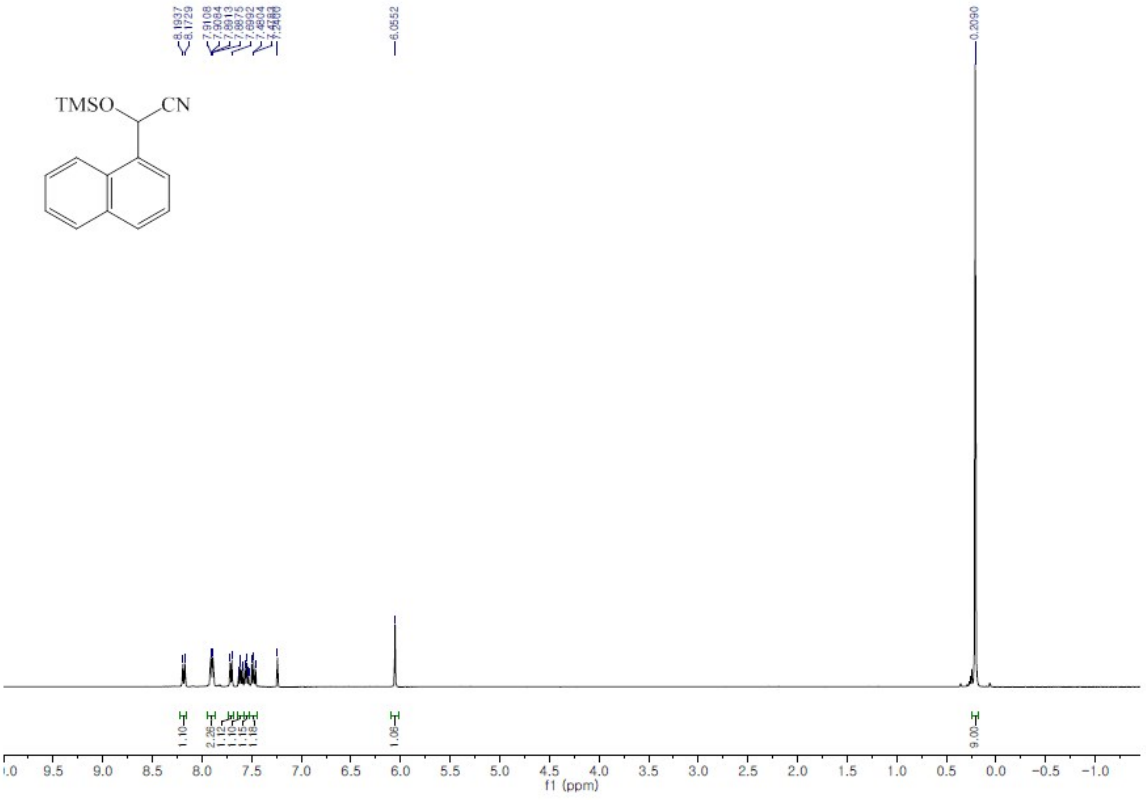


Figure S50. ^{1}H NMR spectrum of 2-(naphthalen-1-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 9)

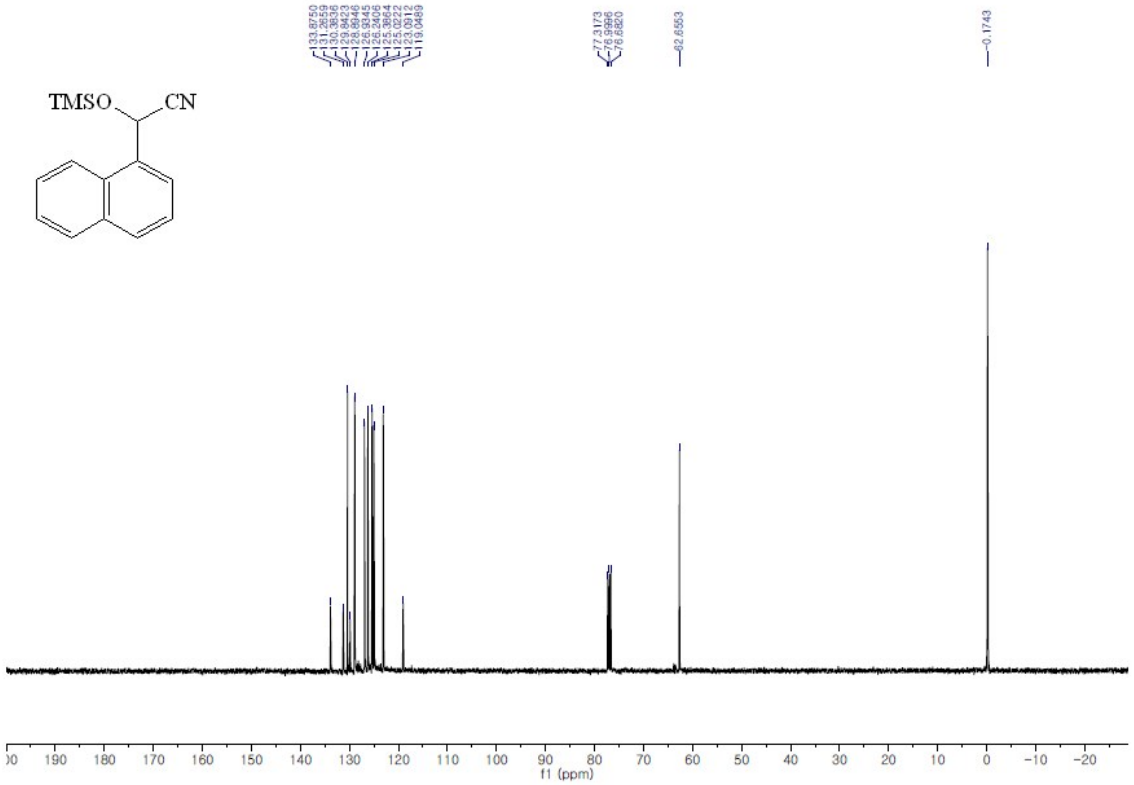


Figure S51. ^{13}C NMR spectrum of 2-(naphthalen-1-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 9)

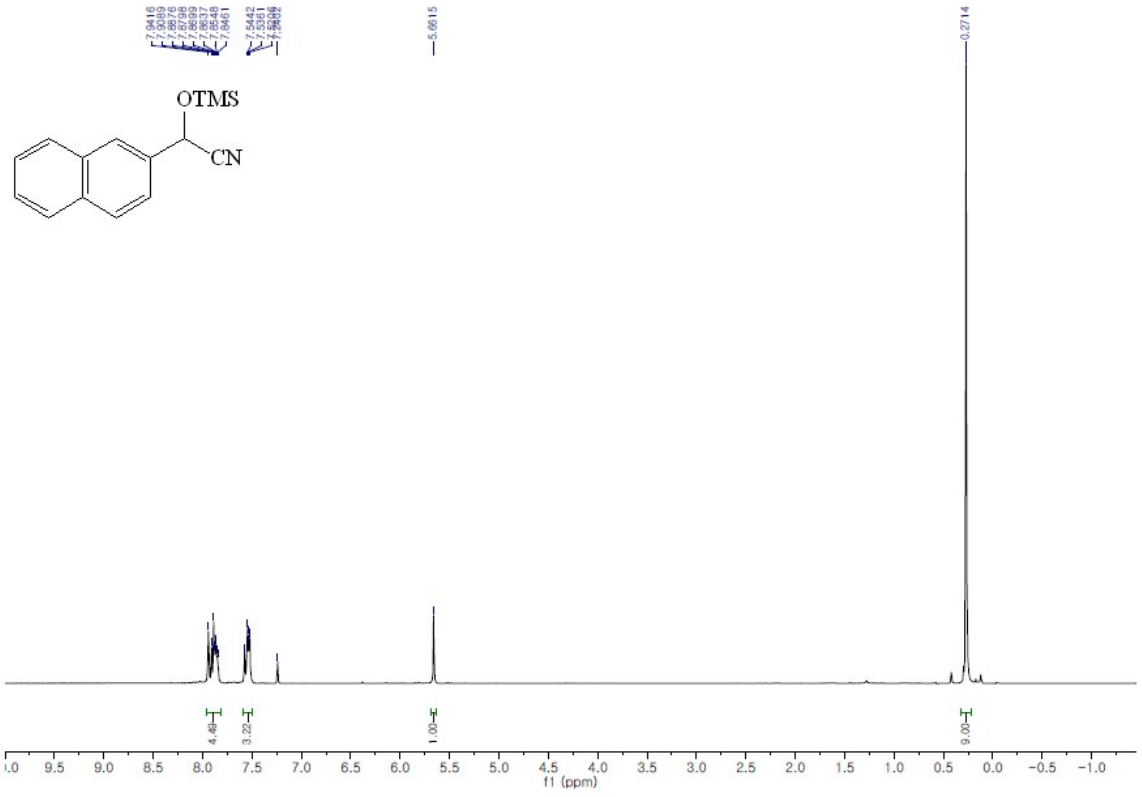


Figure S52. ^{1}H NMR spectrum of 2-(naphthalen-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 10)

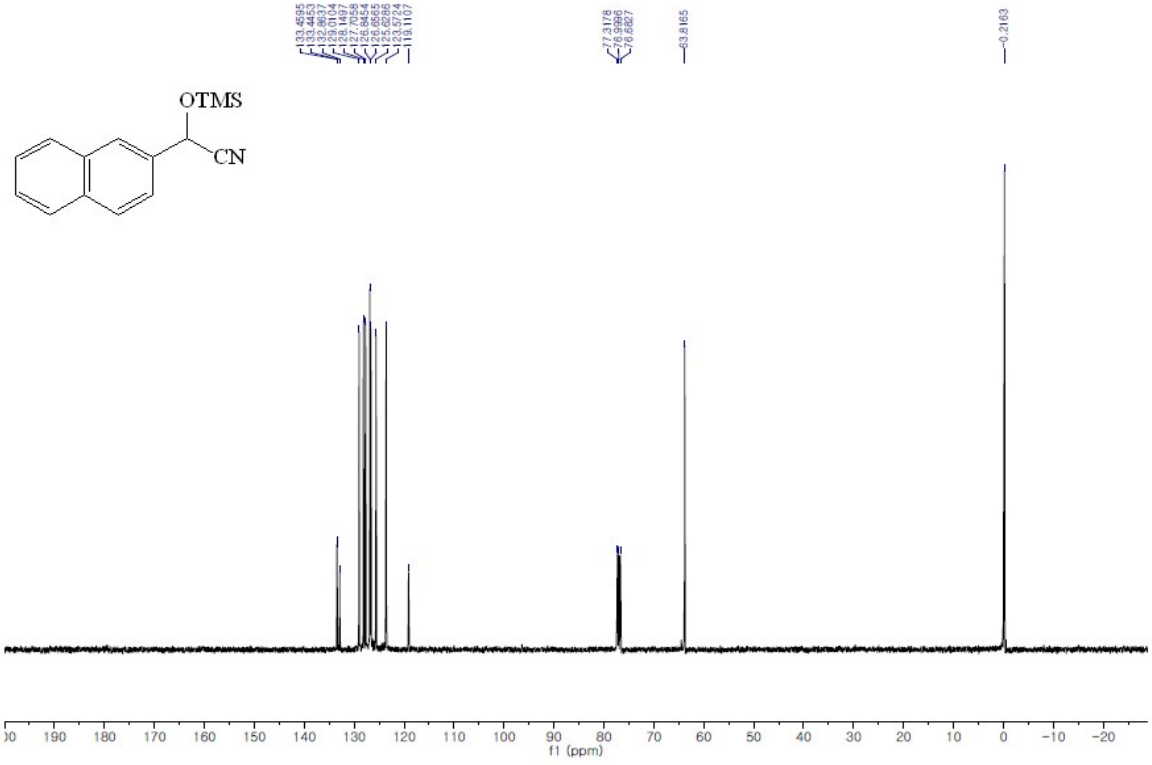


Figure S53. ^{13}C NMR spectrum of 2-(naphthalen-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 3, entry 10)

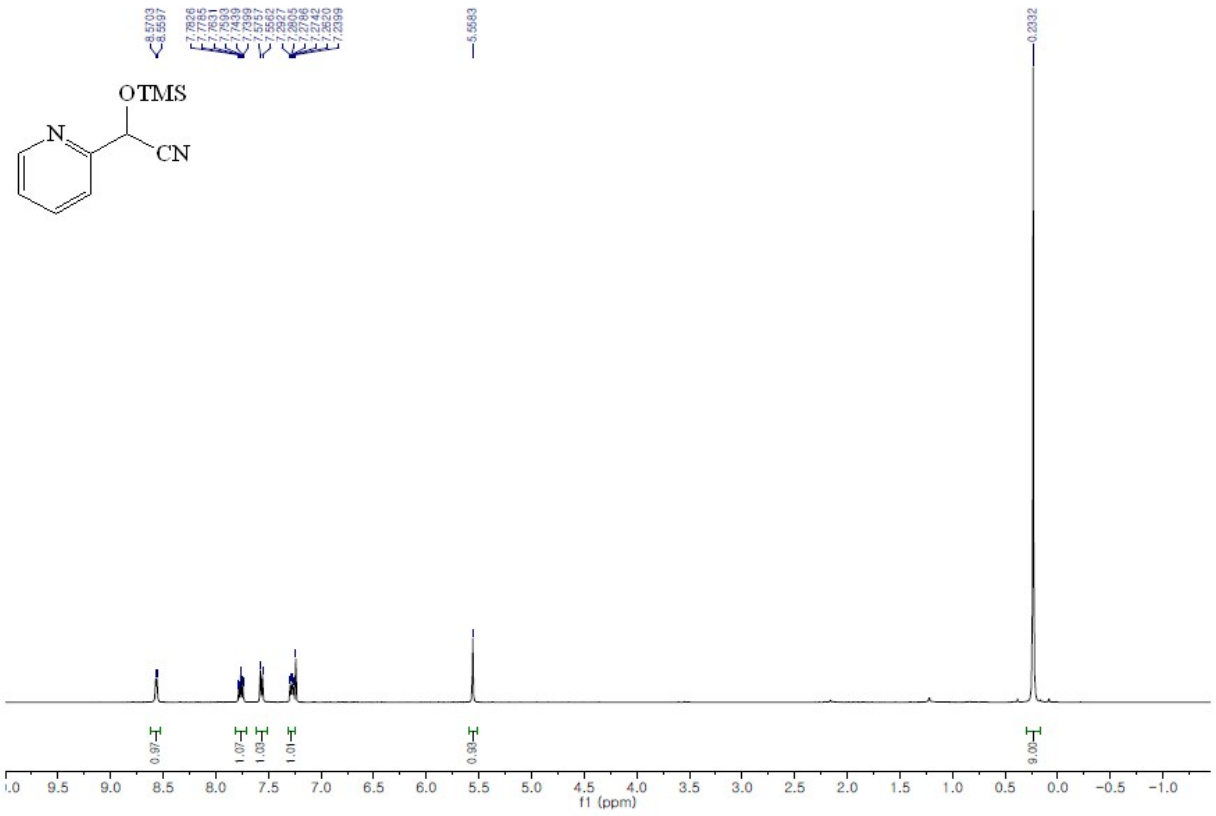


Figure S54. ^{1}H NMR spectrum of 2-(pyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 1)

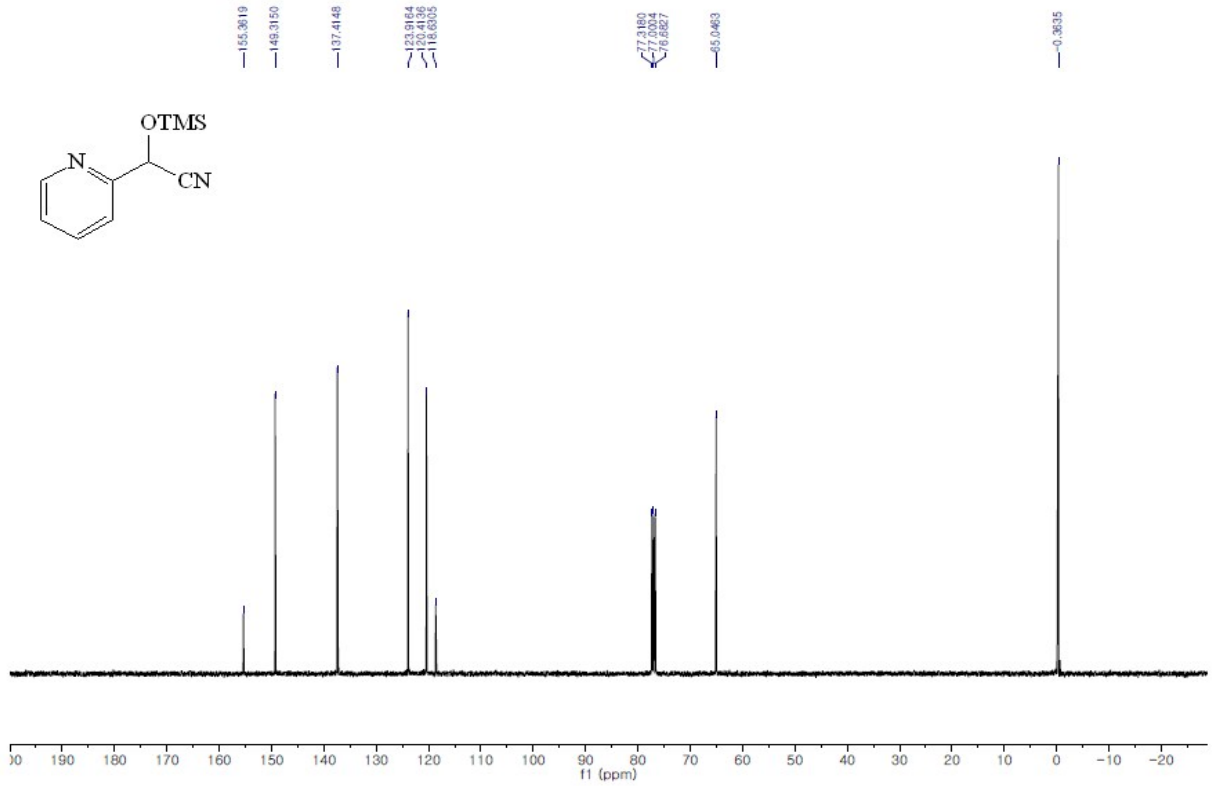


Figure S55. ^{13}C NMR spectrum of 2-(pyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 1)

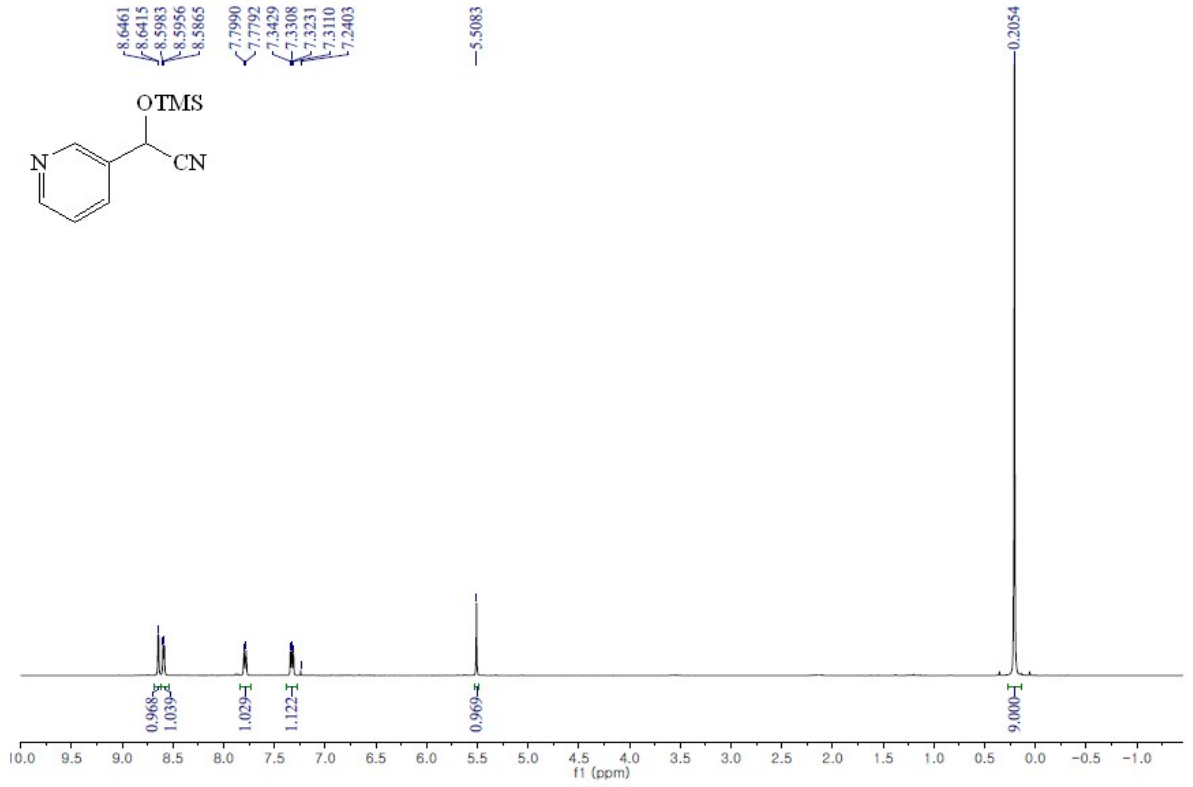


Figure S56. ^{1}H NMR spectrum of 2-(pyridin-3-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 2)

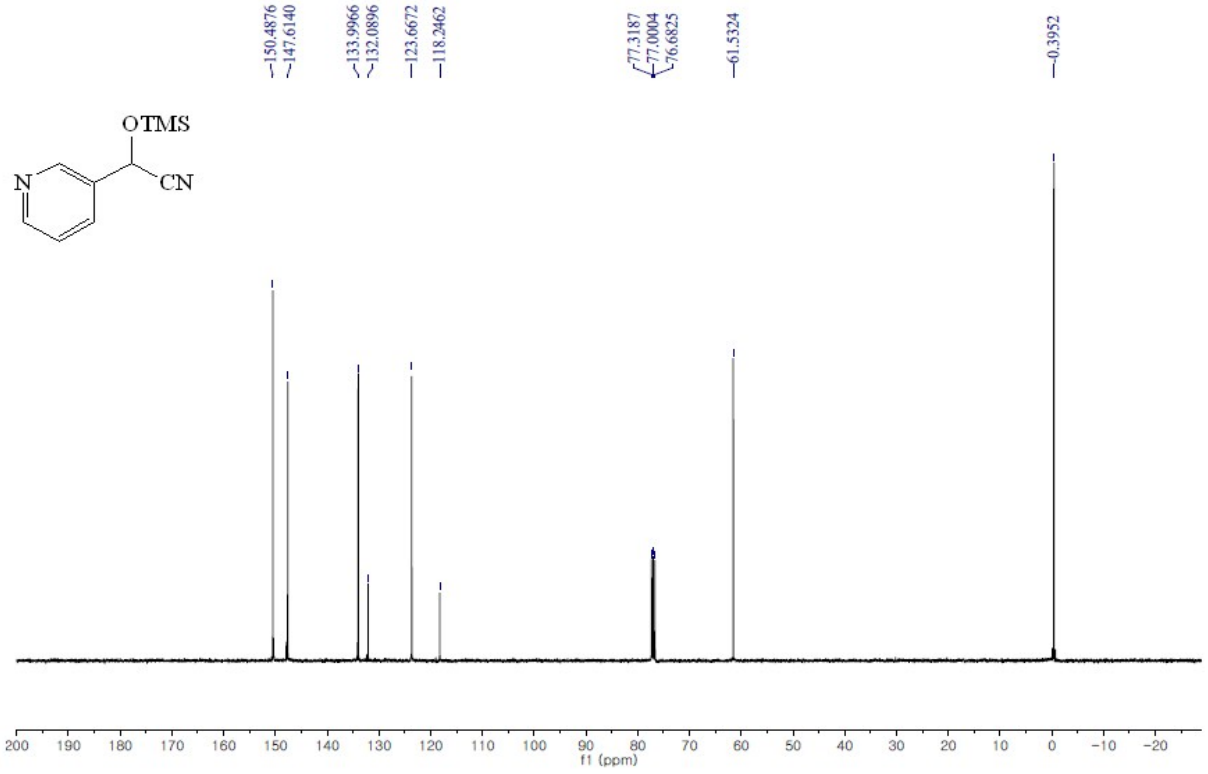


Figure S57. ^{13}C NMR spectrum of 2-(pyridin-3-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 2)

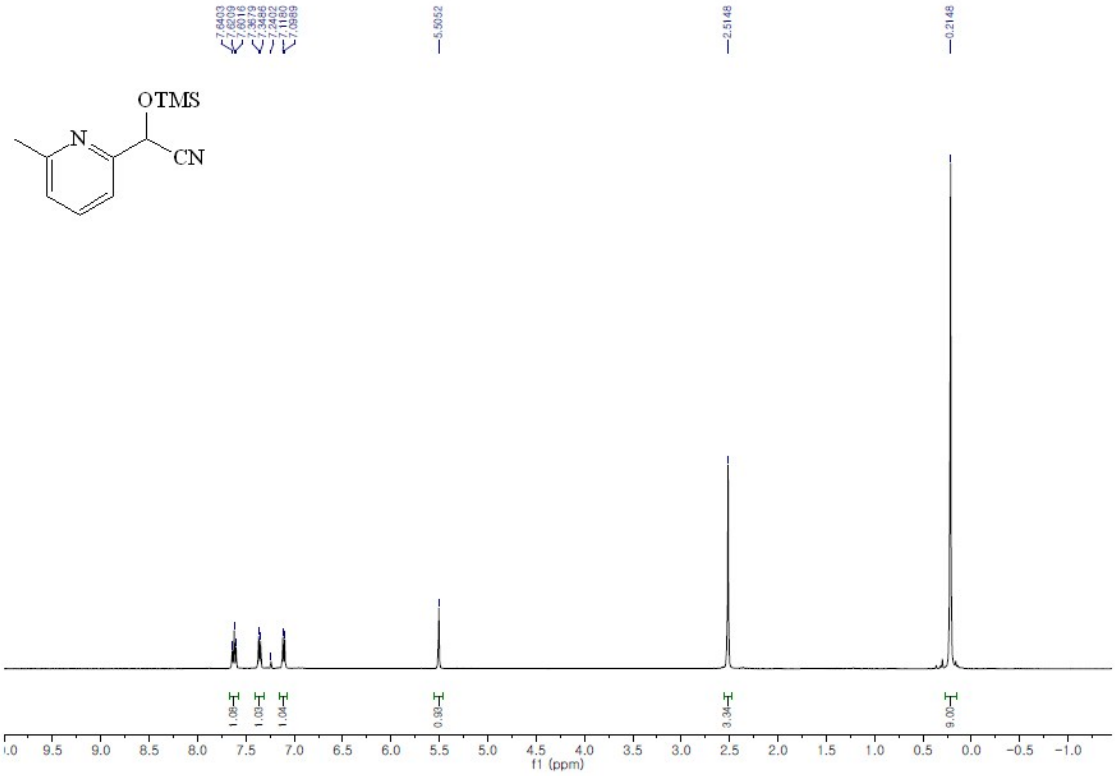


Figure S58. ^{1}H NMR spectrum of 2-(6-methylpyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 3)

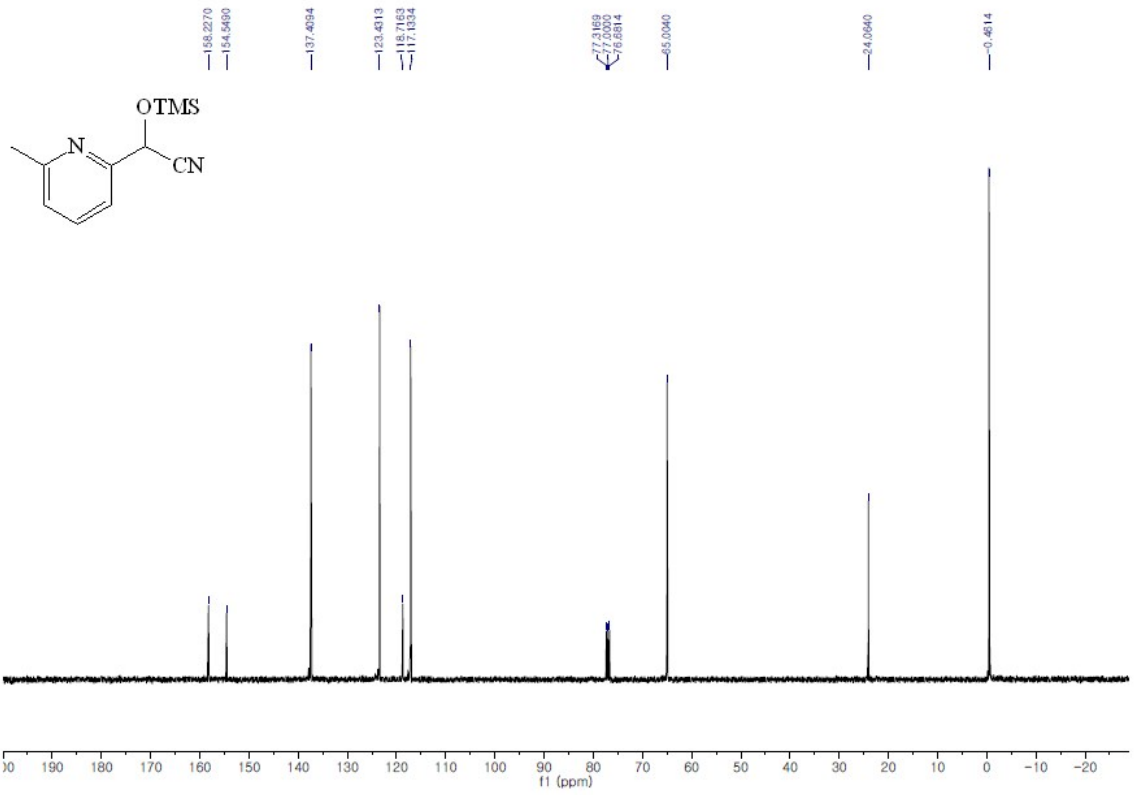


Figure S59. ^{13}C NMR spectrum of 2-(6-methylpyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 3)

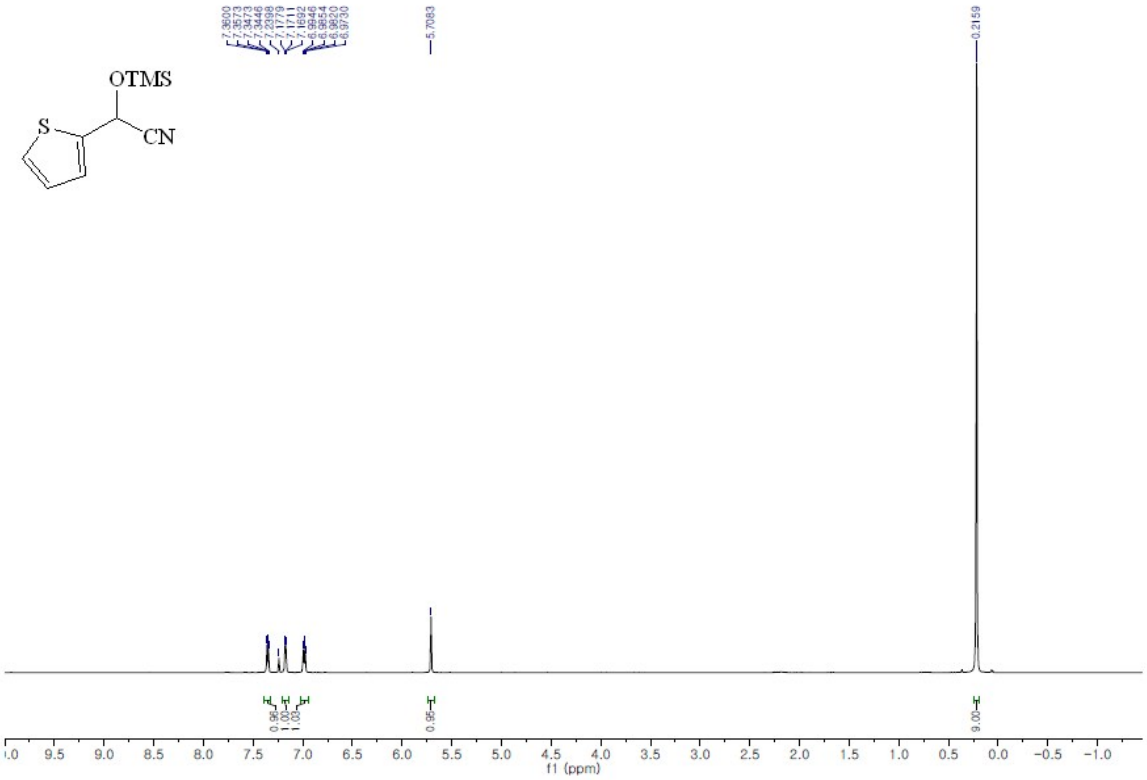


Figure S60. ^{1}H NMR spectrum of 2-(thiophen-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 4)

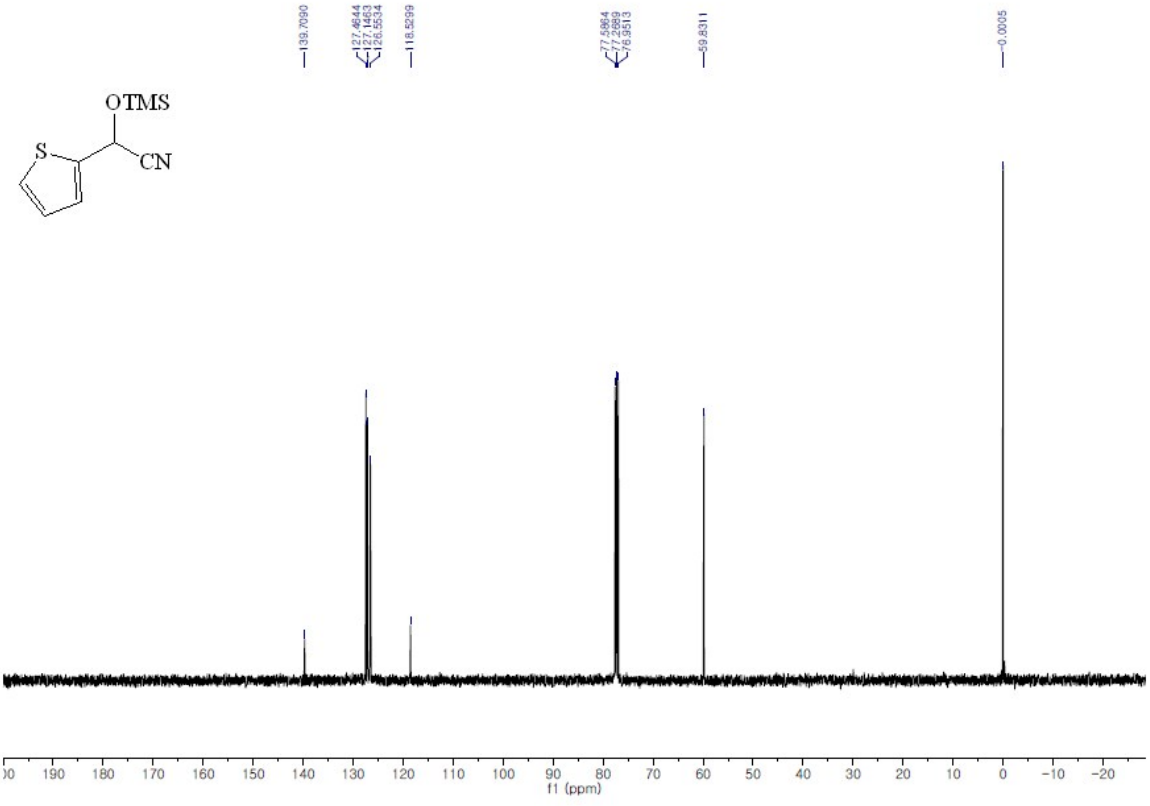


Figure S61. ^{13}C NMR spectrum of 2-(thiophen-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 4)

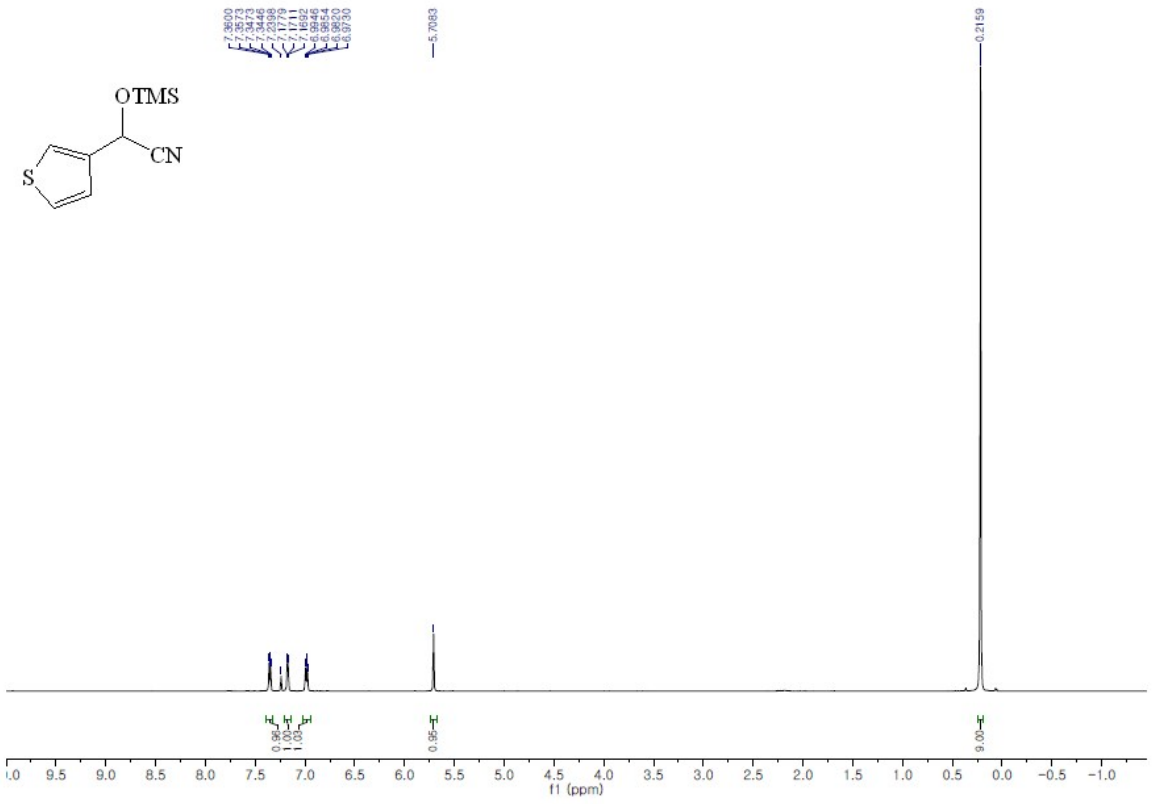


Figure S62. ^{1}H NMR spectrum of 2-(thiophen-3-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 5)

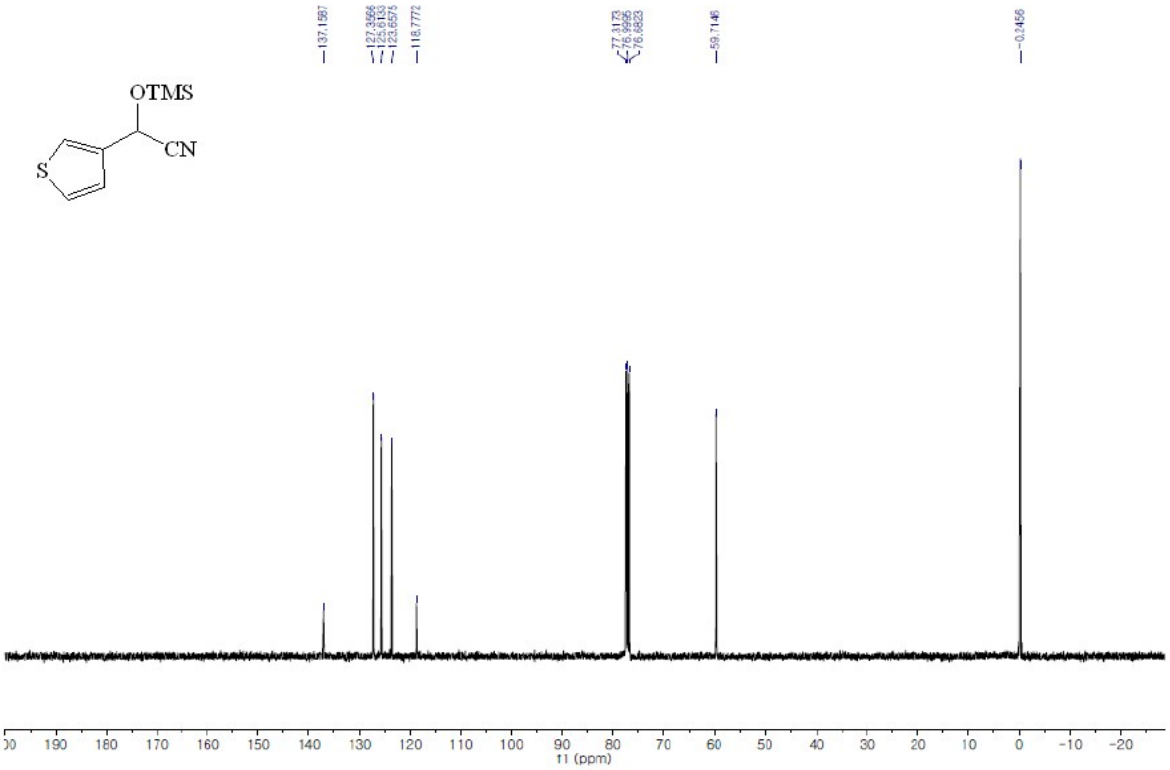


Figure S63. ^{13}C NMR spectrum of 2-(thiophen-3-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 5)

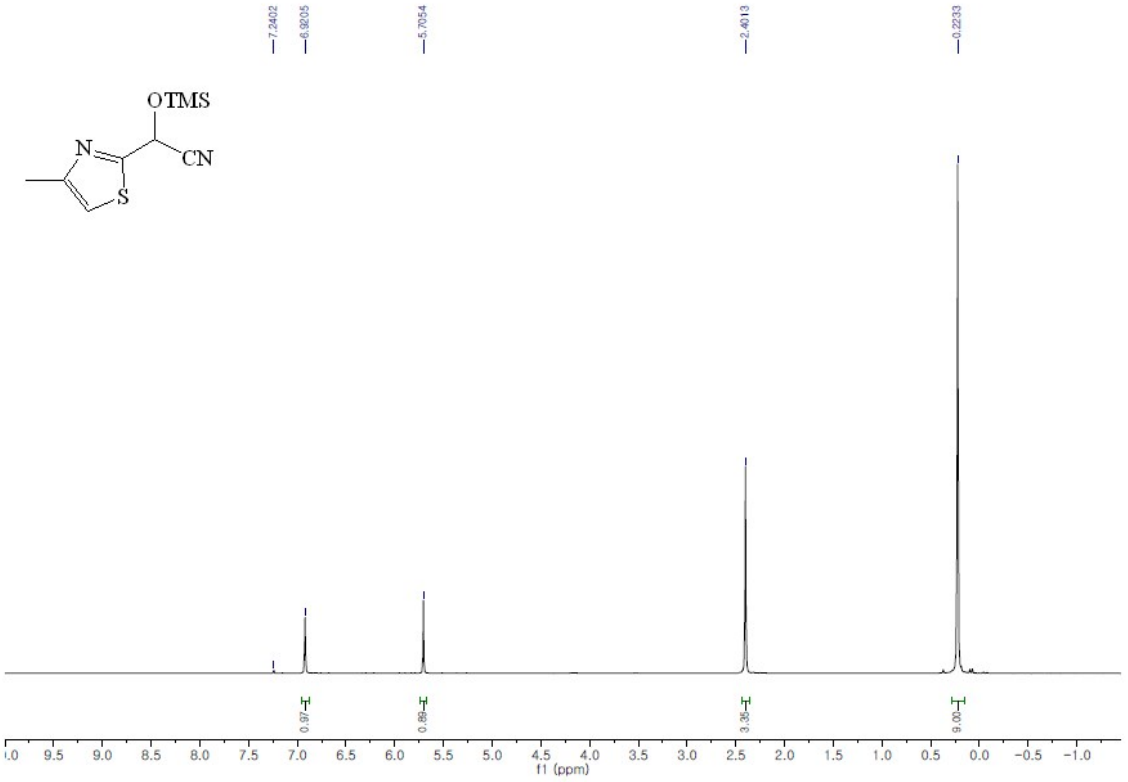


Figure S64. ^{1}H NMR spectrum of 2-(4-methylthiazol-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 6)

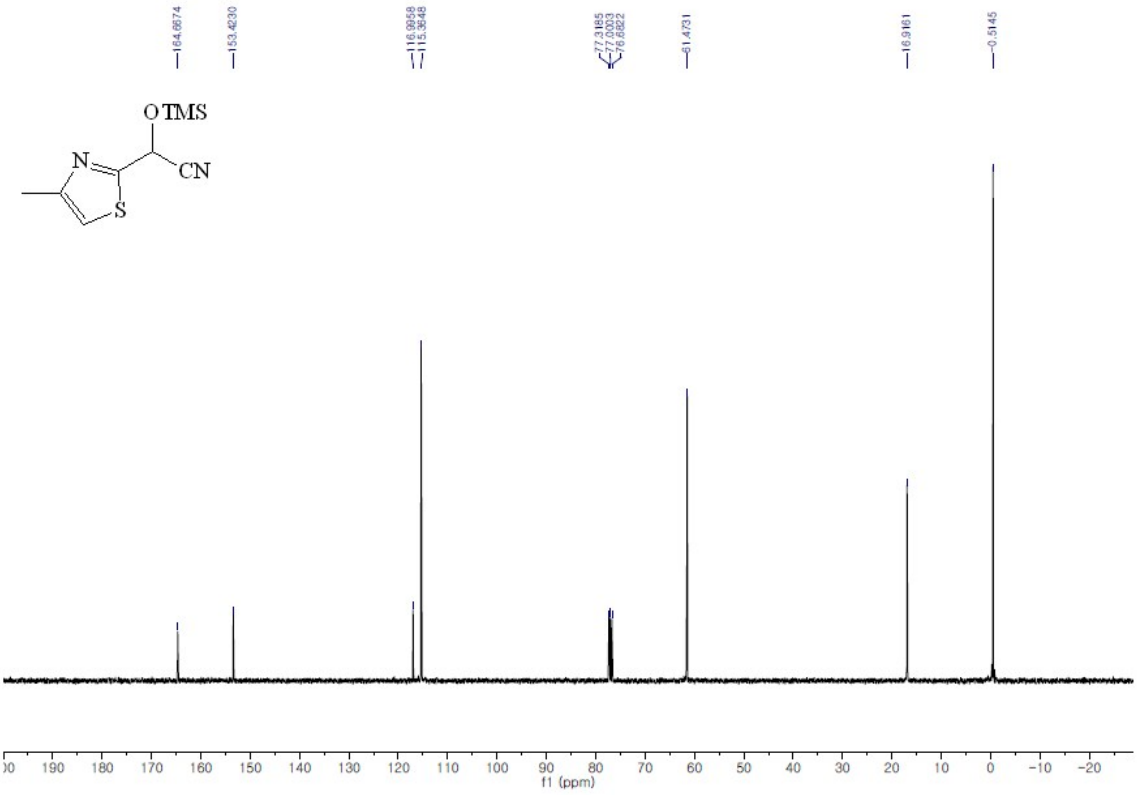


Figure S65. ^{13}C NMR spectrum of 2-(4-methylthiazol-2-yl)-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 6)

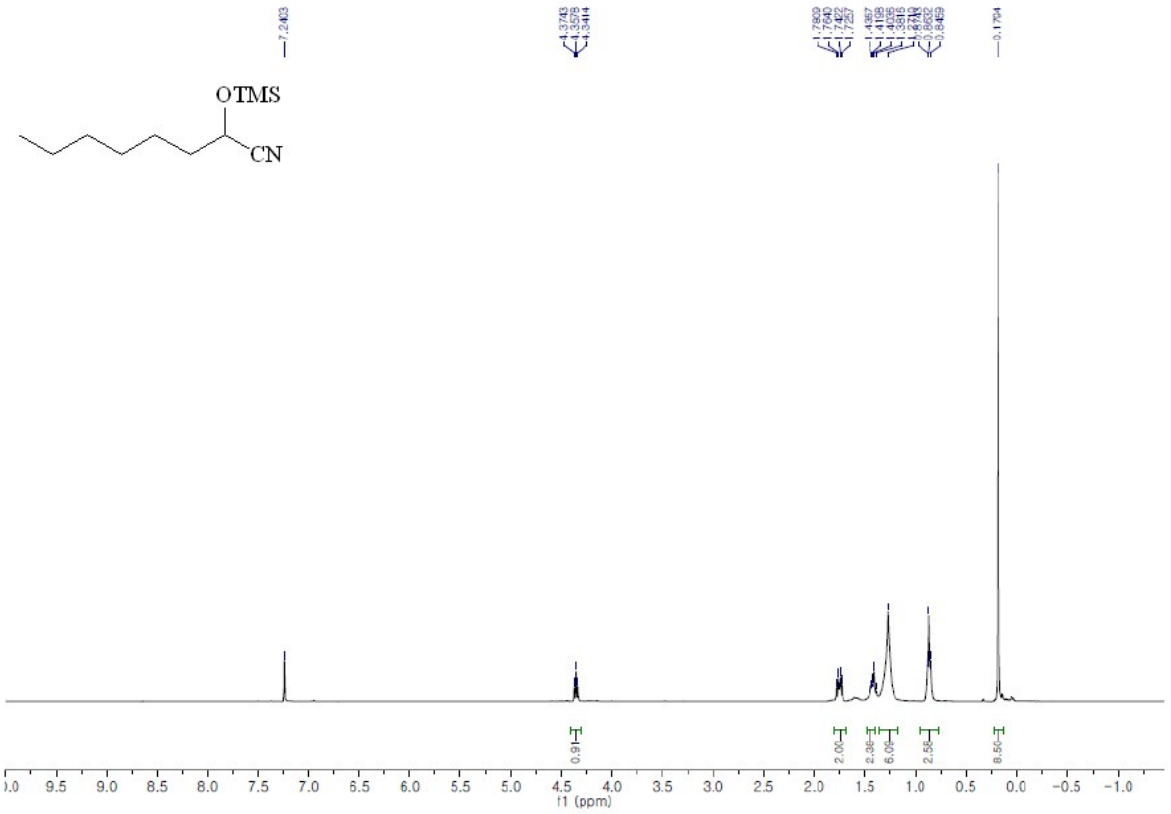


Figure S66. ^{1}H NMR spectrum of 2-((trimethylsilyl)oxy)octanenitrile in $CDCl_3$ (Table 4, entry 7)

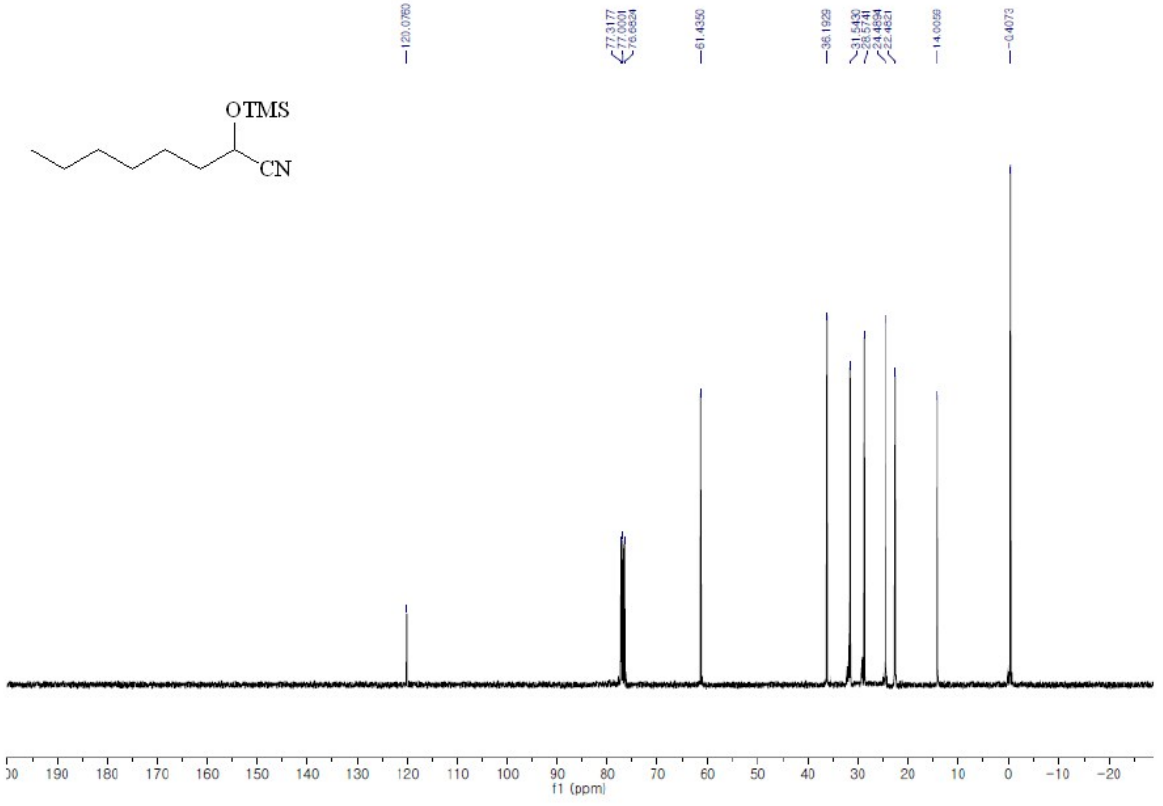


Figure S67. ^{13}C NMR spectrum of 2-((trimethylsilyl)oxy)octanenitrile in $CDCl_3$ (Table 4, entry 7)

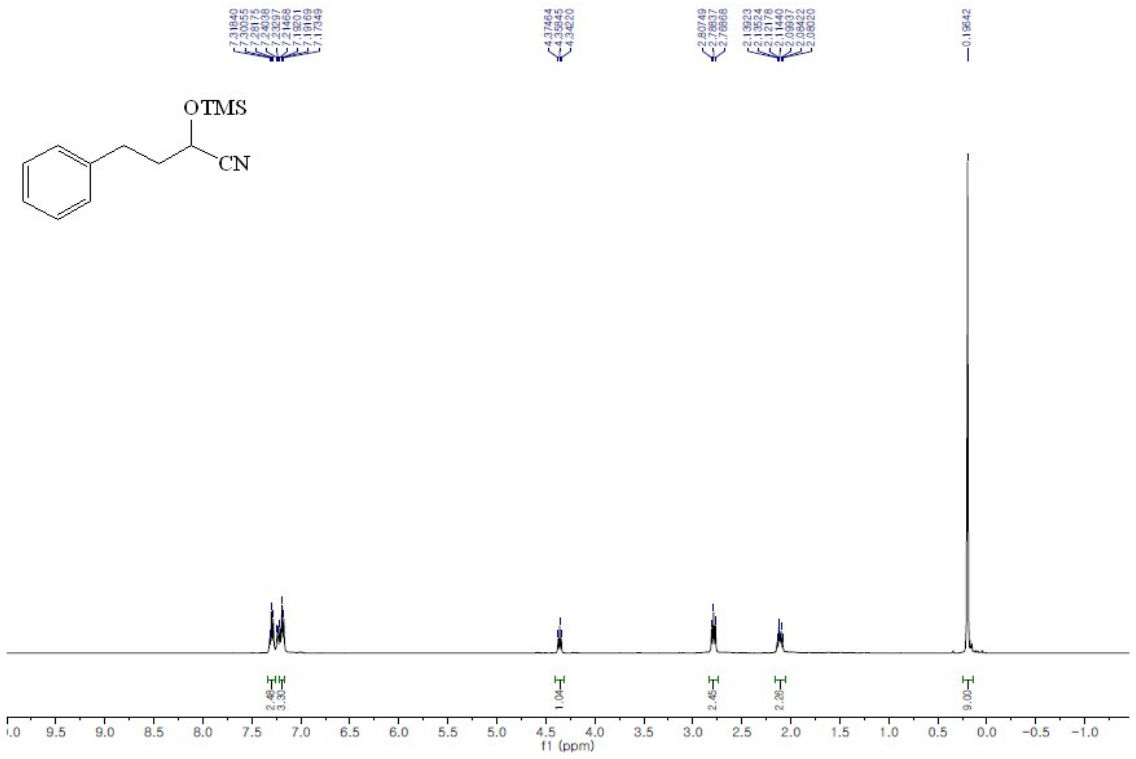


Figure S68. ^{1}H NMR spectrum of 4-phenyl-2-((trimethylsilyl)oxy)butanenitrile in $CDCl_3$ (Table 4, entry 8)

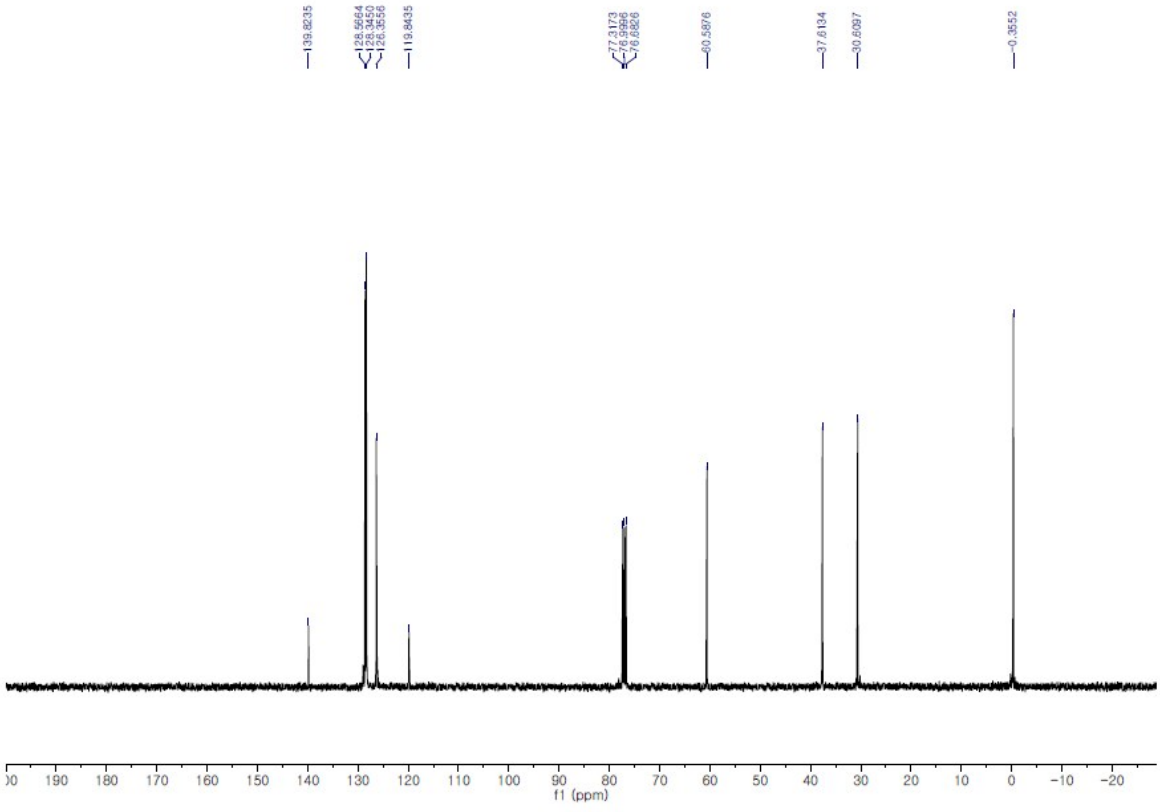


Figure S69. ^{13}C NMR spectrum of 4-phenyl-2-((trimethylsilyl)oxy)butanenitrile in $CDCl_3$ (Table 4, entry 8)

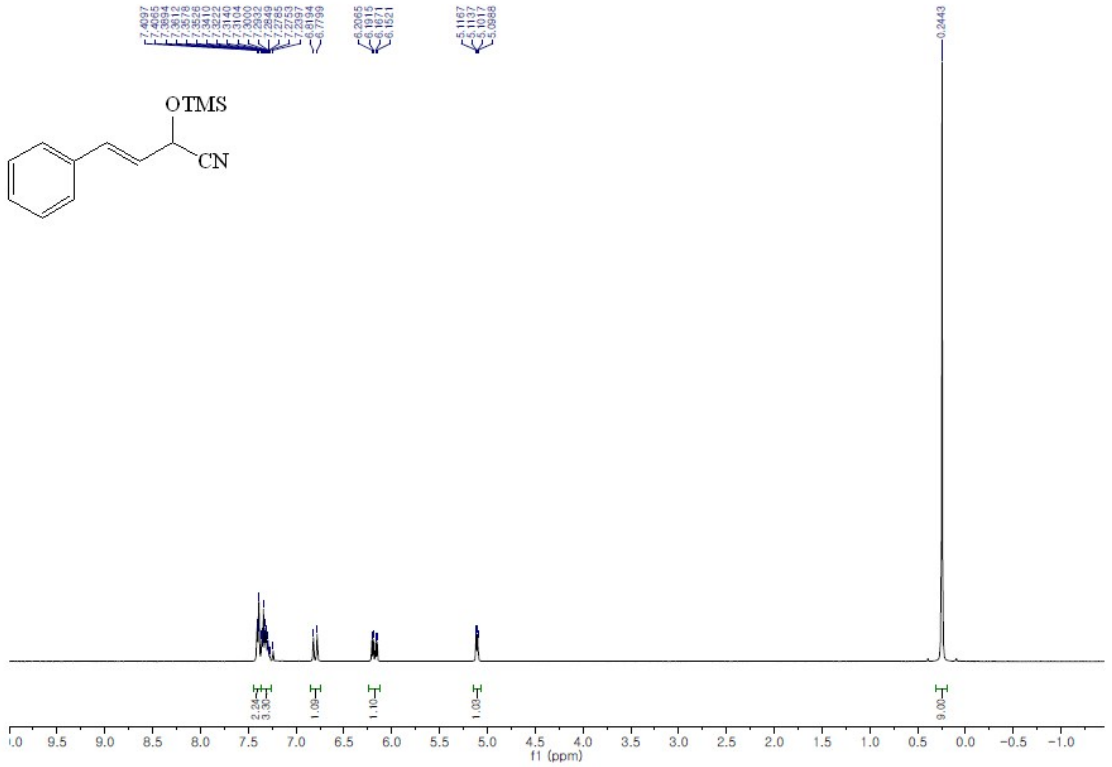


Figure S70. ^{1}H NMR spectrum of (*E*)-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile in $CDCl_3$ (Table 4, entry 9)

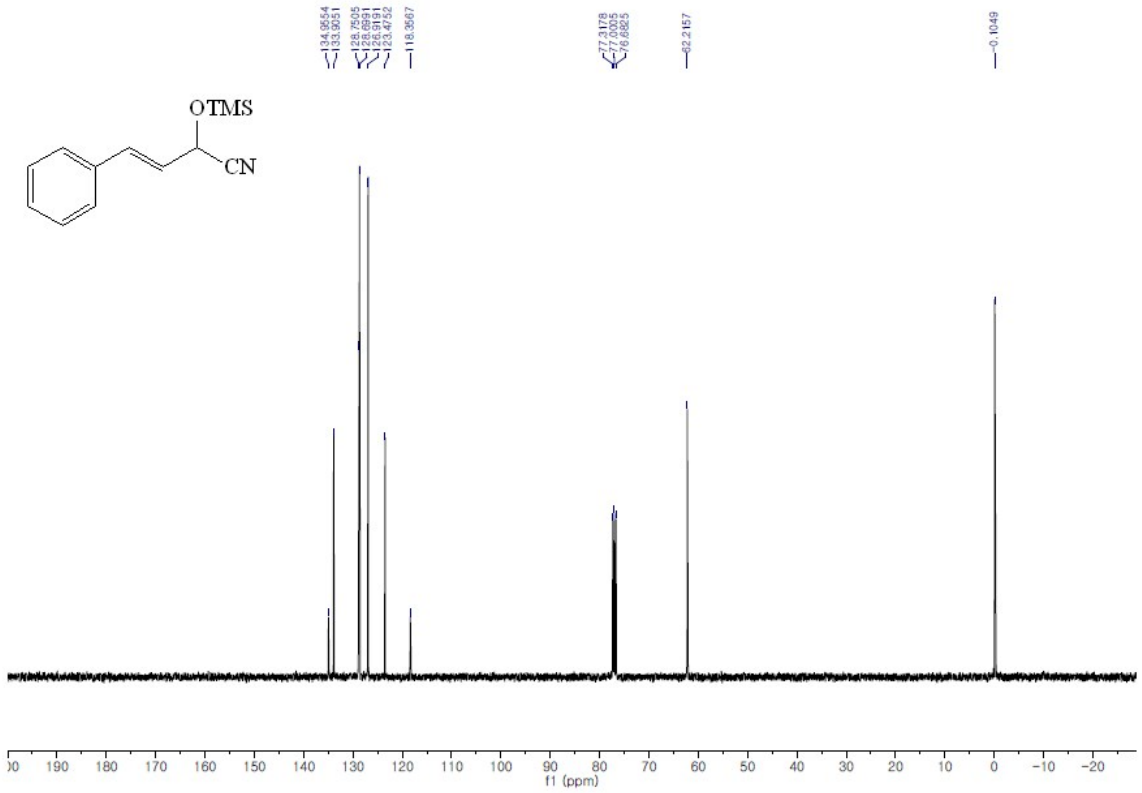


Figure S71. ^{13}C NMR spectrum of (*E*)-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile in $CDCl_3$ (Table 4, entry 9)

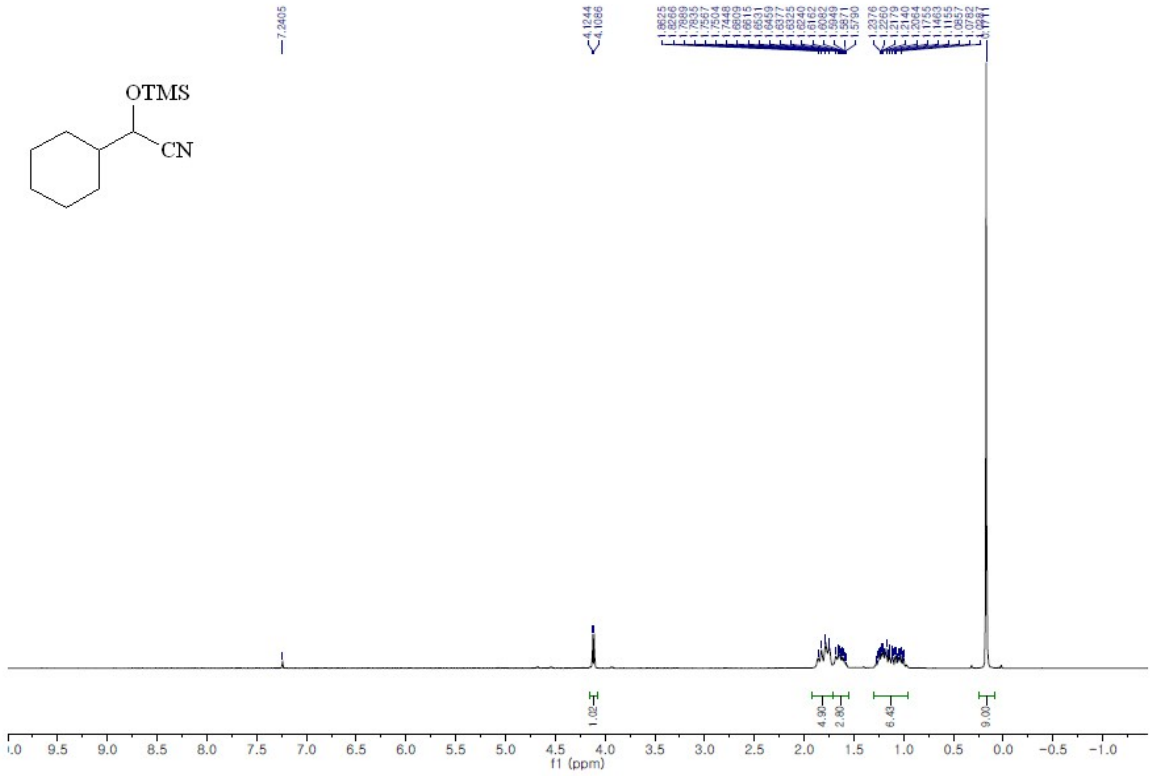


Figure S72. ^{1}H NMR spectrum of 2-cyclohexyl-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 10)

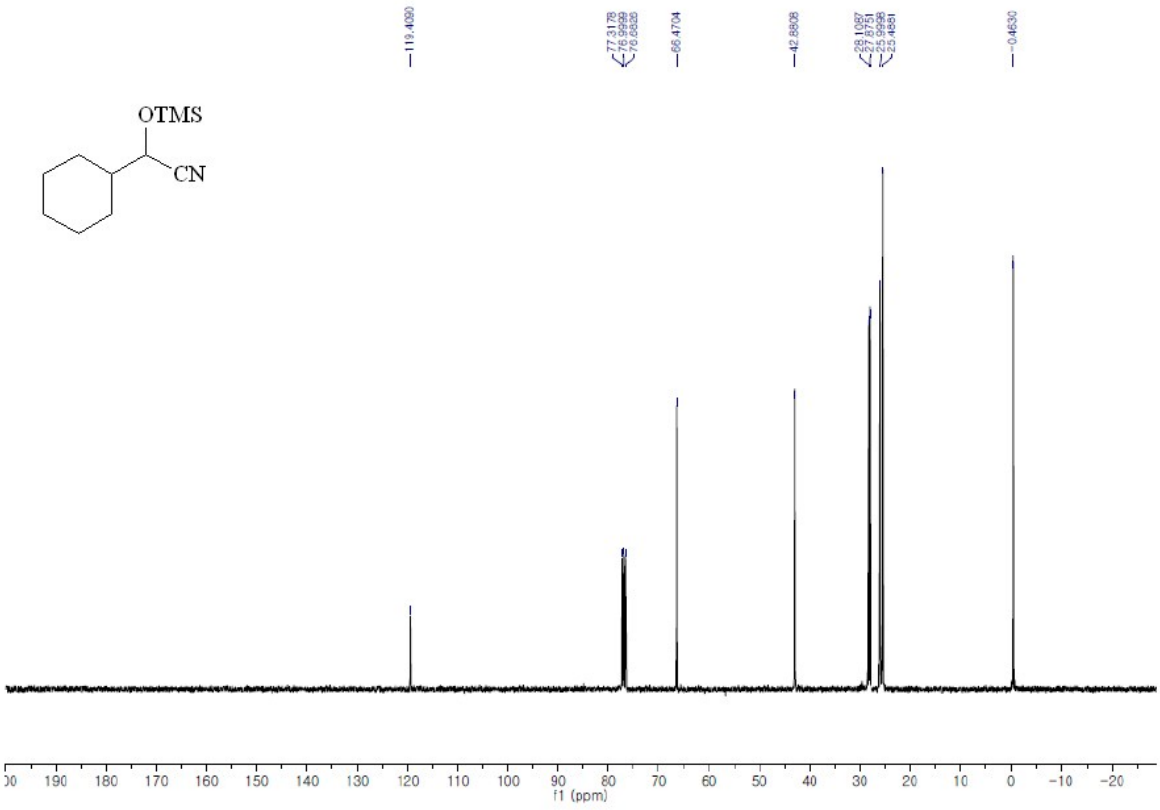
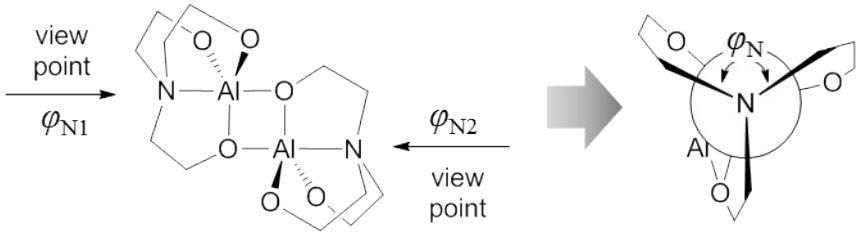


Figure S73. ^{13}C NMR spectrum of 2-cyclohexyl-2-((trimethylsilyl)oxy)acetonitrile in $CDCl_3$ (Table 4, entry 10)

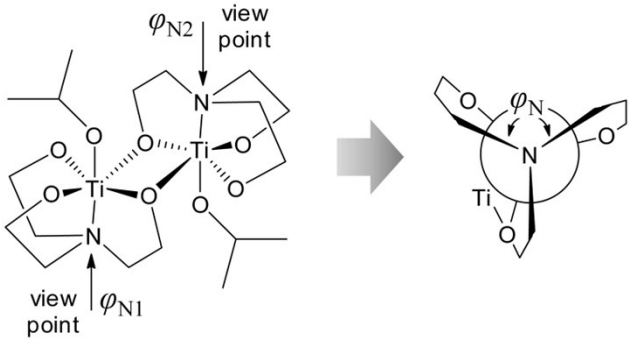
Table S1. The angles (φ_N/°) between unbridge side arms for alumatranes and their isomers in theoretical geometries



framework for alumatrane

	1	**1a**	**1b**	**1c**
φ_{N1}	113.86	113.90	115.99	116.08
φ_{N2}	113.82	116.07	116.05	116.05
	2	**2a**	**2b**	**2c**
φ_{N1}	115.84	115.79	116.01	118.32
φ_{N2}	115.80	115.82	118.52	118.44

Table S2. The angles (φ_N /°) between unbridged side arms for titanatranes from *Polyhedron* **2010**, *29*, 379–383 in theoretical geometries (ground-state optimized structures) and these relative free energy (ΔG /kcal·mol^{-1}) when ΔG of **Ti3** was assigned to zero.



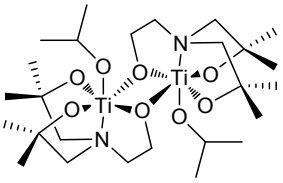
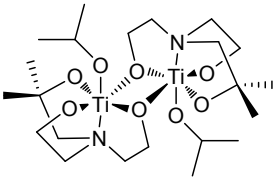
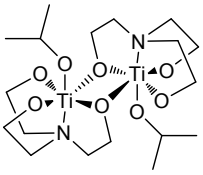
	Ti1	**Ti2**	**Ti3**
			
φ_{N1} /°	106.2	105.1	104.6
φ_{N2} /°	106.2	105.2	104.7
ΔG /kcal·mol^{-1}	0.48	0.22	0

Table S3. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **1** from B3LYP calculations (in Å)

Atom	x	y	z
Al	-1.23039	-0.69782	0.04005
O	0.61927	-0.99302	0.00441
O	-0.57947	1.04911	0.18564
Al	1.27012	0.75652	0.17211
O	-1.82026	-1.20994	-1.55403
N	-3.14324	0.33829	0.24624
N	3.16473	-0.24755	0.02954
C	2.90529	-1.70098	0.15394
H	2.99602	-1.94940	1.21528
H	3.66378	-2.28456	-0.38607
C	1.47019	-2.10932	-0.30782
C	-2.83764	1.77649	0.46202
H	-3.61182	2.41953	0.02174
H	-2.83913	1.95243	1.54020
C	-1.43104	2.18043	-0.07350
C	-3.21369	-1.19965	-1.71856
H	-3.47046	-1.17712	-2.78899
H	-3.66901	-2.11510	-1.30464
C	-3.82971	0.05046	-1.04528
H	-3.67649	0.91277	-1.69677
H	-4.91314	-0.06440	-0.89135
O	1.79218	1.67025	-1.25874
O	1.77490	1.24669	1.79903
O	-1.75916	-1.68244	1.41604
C	3.91173	0.31481	1.18928
H	4.72105	-0.36055	1.50619
H	4.36514	1.25354	0.85762
C	2.91372	0.62253	2.32199
H	3.40845	1.27225	3.06033
H	2.64220	-0.30856	2.85213
C	3.71041	0.19843	-1.27830
H	3.35812	-0.49720	-2.04187
H	4.81109	0.17450	-1.27913
C	3.15594	1.60780	-1.58135
H	3.30756	1.82448	-2.64953
H	3.72813	2.36701	-1.01931
C	-3.14626	-1.73999	1.61201
H	-3.37464	-2.08218	2.63316
H	-3.61782	-2.46246	0.92390
C	-3.76079	-0.33723	1.42422
H	-3.51580	0.25638	2.30844
H	-4.85648	-0.37422	1.33021
C	-1.40804	2.49336	-1.57826
H	-2.09705	3.31526	-1.81175
H	-0.39529	2.78383	-1.87222
H	-1.68055	1.61983	-2.17684
C	-0.92657	3.38736	0.72538
H	-0.81751	3.13286	1.78460
H	0.04854	3.71440	0.34996
H	-1.62580	4.22816	0.63201
C	1.36949	-2.40773	-1.81255
H	0.34363	-2.69595	-2.06052
H	1.61085	-1.53225	-2.42167
H	2.04475	-3.22710	-2.08972
C	1.02927	-3.33712	0.49839
H	0.04044	-3.67780	0.17753
H	1.74065	-4.16080	0.35509
H	0.97030	-3.09890	1.56490

Table S4. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **1a** from B3LYP calculations (in Å)

Atom	x	y	z
Al	-1.06366	0.05431	-0.48961
O	0.72886	0.61360	-0.51168
O	-0.19315	-1.43011	0.24693
Al	1.58282	-0.86306	0.27678
O	-1.84953	1.15792	0.64559
N	-2.81008	-1.20610	-0.20383
N	3.31529	0.37868	0.06297
C	2.92929	1.52394	-0.79489
H	3.15036	1.23500	-1.82647
H	3.53558	2.41090	-0.56431
C	1.40699	1.86504	-0.71278
C	-2.26882	-2.56363	0.08152
H	-3.00031	-3.19142	0.61209
H	-2.04458	-3.03460	-0.87860
C	-0.95886	-2.44693	0.86766
H	-1.12722	-2.18570	1.92101
H	-0.41950	-3.40052	0.83650
C	-3.13261	0.90865	1.17262
C	-3.49116	-0.60714	0.97453
H	-3.14081	-1.15435	1.85470
H	-4.57791	-0.75795	0.90982
O	1.93584	-0.85237	2.01362
O	2.38213	-1.99222	-0.83009
O	-1.53449	0.08424	-2.19328
C	4.29008	-0.54005	-0.58955
H	5.06475	0.02300	-1.13212
H	4.78014	-1.10951	0.20576
C	3.52008	-1.52053	-1.49521
H	4.18865	-2.35368	-1.76136
H	3.24203	-1.02291	-2.44232
C	3.69045	0.71841	1.46126
H	3.16957	1.63798	1.73289
H	4.77205	0.90460	1.54690
C	3.21944	-0.42779	2.38510
H	3.21853	-0.06472	3.42401
H	3.93938	-1.26449	2.34286
C	-2.90629	-0.05429	-2.43766
H	-3.07361	-0.36830	-3.47921
H	-3.42372	0.91115	-2.31417
C	-3.54644	-1.12235	-1.50016
H	-3.48843	-2.10197	-1.98269
H	-4.60803	-0.90894	-1.32190
C	-3.11391	1.20428	2.68324
H	-2.91673	2.26843	2.85312
H	-4.07193	0.95190	3.15791
H	-2.31768	0.63056	3.17083
C	-4.17117	1.82577	0.49760
H	-5.16395	1.70775	0.95183
H	-3.86110	2.87008	0.61252
H	-4.25894	1.62171	-0.57372
C	1.05465	2.81901	0.44026
H	-0.01650	3.03924	0.42159
H	1.26894	2.37442	1.41588
H	1.61218	3.75971	0.34804
C	0.97029	2.47484	-2.05034
H	-0.08857	2.74946	-2.02250
H	1.55374	3.37885	-2.26785
H	1.10880	1.75815	-2.86599

Table S5. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **1b** from B3LYP calculations (in Å)

Atom	x	y	z
Al	-1.39206	-0.55764	-0.25856
O	0.32717	-0.81286	-0.93583
O	-0.32446	-0.02073	1.19224
Al	1.39636	-0.23537	0.49686
O	-2.02988	0.76697	-1.23045
N	-2.99643	-0.09922	1.13118
N	2.98028	-0.55825	-0.97196
C	2.31205	-0.97513	-2.23488
H	2.94194	-1.66718	-2.81206
H	2.15579	-0.07876	-2.83956
C	0.93572	-1.59764	-1.94700
H	1.01420	-2.63841	-1.60936
H	0.32322	-1.58265	-2.85563
C	-2.32627	0.13387	2.44248
H	-2.93863	0.76116	3.10669
H	-2.18729	-0.83856	2.92083
C	-0.94031	0.74536	2.21328
H	-0.99529	1.79753	1.90314
H	-0.35007	0.69368	3.13514
C	-3.24028	1.41335	-0.91985
C	-3.61355	1.14337	0.58638
H	-3.23207	1.97602	1.18508
H	-4.70237	1.11670	0.72801
O	2.04499	1.39533	0.65280
O	2.10298	-1.59677	1.38022
O	-2.10667	-2.17013	-0.36492
C	3.80587	-1.62894	-0.34279
H	4.25948	-2.27243	-1.11165
H	4.61656	-1.13932	0.20002
C	2.95382	-2.44332	0.65842
H	3.63501	-2.97558	1.34027
H	2.37755	-3.21852	0.12406
C	3.65550	0.76858	-1.04327
H	3.23595	1.29751	-1.90255
H	4.73388	0.65199	-1.21988
C	3.36840	1.64398	0.22680
C	-3.48040	-2.23525	-0.09498
H	-3.76867	-3.26675	0.15866
H	-4.06916	-1.95453	-0.98316
C	-3.85287	-1.32259	1.10568
H	-3.66630	-1.87458	2.03049
H	-4.91699	-1.05093	1.09018
C	-3.05123	2.93031	-1.10335
H	-2.83278	3.15383	-2.15322
H	-3.95015	3.49020	-0.81110
H	-2.20638	3.28217	-0.50035
C	-4.35529	0.93321	-1.86930
H	-5.29198	1.48016	-1.69741
H	-4.04297	1.09892	-2.90601
H	-4.55634	-0.13578	-1.75039
C	3.48814	3.12071	-0.18418
H	3.30743	3.76324	0.68438
H	4.48574	3.35173	-0.58160
H	2.74003	3.36414	-0.94698
C	4.35049	1.35957	1.38240
H	5.39483	1.50639	1.07519
H	4.13725	2.04624	2.20929
H	4.23396	0.34282	1.76942

Table S6. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **1c** from B3LYP calculations (in Å)

Atom	x	y	z
Al	-1.30823	-0.25957	-0.46204
O	0.37280	0.28711	-1.07113
O	-0.33350	-0.19108	1.14040
Al	1.35264	0.32869	0.53610
O	-2.35786	1.12005	-0.77154
N	-2.87665	-0.95200	0.86738
N	2.91013	0.97867	-0.80938
C	2.42976	0.79476	-2.20772
H	3.19378	0.29602	-2.81628
H	2.26279	1.78468	-2.64090
C	1.10458	-0.00241	-2.25219
H	1.27876	-1.08217	-2.31468
H	0.52246	0.29476	-3.13185
C	-2.19960	-1.22877	2.16546
H	-2.90544	-1.19510	3.00855
H	-1.77952	-2.23593	2.10960
C	-1.03984	-0.24636	2.36685
H	-1.38889	0.75969	2.63535
H	-0.38272	-0.60242	3.16836
C	-3.66280	1.20344	-0.25057
C	-3.81348	0.20302	0.95344
H	-3.57009	0.74119	1.87456
H	-4.84831	-0.15275	1.05134
O	1.61550	1.83713	1.41864
O	2.36562	-1.08607	0.82022
O	-1.54795	-1.77771	-1.33477
C	4.07453	0.14353	-0.40669
H	4.74964	-0.01144	-1.25976
H	4.62662	0.71636	0.34368
C	3.64206	-1.22204	0.24048
C	3.06915	2.41048	-0.41390
H	2.31549	2.98173	-0.96268
H	4.06427	2.79519	-0.68590
C	2.77414	2.55392	1.09092
H	2.64375	3.62299	1.31810
H	3.63681	2.20734	1.68771
C	-2.83969	-2.31312	-1.24688
H	-2.82569	-3.38195	-1.50906
H	-3.51548	-1.82198	-1.96529
C	-3.40599	-2.17773	0.19639
H	-3.08396	-3.04242	0.78286
H	-4.50383	-2.17084	0.19510
C	-3.89326	2.63088	0.27799
H	-3.83900	3.34698	-0.54918
H	-4.87562	2.73307	0.75918
H	-3.11631	2.89519	1.00430
C	-4.69520	0.91012	-1.35700
H	-5.72183	1.05580	-0.99535
H	-4.52496	1.59009	-2.19864
H	-4.60776	-0.11327	-1.73455
C	4.65928	-1.57835	1.33940
H	4.40512	-2.54810	1.78096
H	5.68232	-1.63715	0.94332
H	4.63432	-0.82606	2.13609
C	3.61742	-2.35625	-0.80276
H	3.26242	-3.27693	-0.32776
H	2.93897	-2.13225	-1.63178
H	4.61694	-2.54157	-1.21814

Table S7. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **2** from B3LYP calculations (in Å)

Atom	x	y	z
Al	1.32683	0.37755	-0.43628
O	-0.36139	1.13241	-0.10603
O	0.36140	-1.13240	0.10602
Al	-1.32682	-0.37754	0.43628
O	1.52203	0.61210	-2.18695
N	2.93351	-1.04606	-0.59411
N	-2.93351	1.04607	0.59412
C	-2.32767	2.38634	0.38401
H	-2.04388	2.76335	1.37099
H	-3.05960	3.08757	-0.04011
C	-1.03728	2.34208	-0.48673
C	2.32768	-2.38633	-0.38400
H	2.04390	-2.76334	-1.37098
H	3.05961	-3.08756	0.04012
C	1.03726	-2.34208	0.48671
C	2.24748	-0.37729	-2.86518
C	3.42051	-0.85922	-1.99141
H	3.88139	-1.78182	-2.37586
H	4.18961	-0.08529	-1.97020
O	-2.34600	-1.19606	-0.75362
O	-1.52200	-0.61210	2.18694
O	2.34600	1.19607	0.75362
C	-3.42050	0.85920	1.99142
H	-3.88140	1.78178	2.37588
H	-4.18959	0.08526	1.97020
C	-2.24746	0.37728	2.86518
C	-3.91619	0.63071	-0.44212
H	-3.74973	1.25815	-1.31973
H	-4.94222	0.82136	-0.09734
C	-3.71410	-0.87166	-0.85856
C	3.71410	0.87166	0.85856
C	3.91619	-0.63069	0.44212
H	3.74973	-1.25813	1.31973
H	4.94223	-0.82135	0.09734
C	4.15391	1.02361	2.32509
H	5.20322	0.73009	2.46493
H	4.04351	2.06689	2.64009
H	3.52767	0.40633	2.97893
C	4.54335	1.83949	-0.01233
H	4.41047	2.86027	0.36316
H	5.61482	1.59950	0.01622
H	4.20827	1.83238	-1.05415
C	-4.15391	-1.02363	-2.32508
H	-4.04350	-2.06692	-2.64006
H	-5.20322	-0.73011	-2.46492
H	-3.52767	-0.40636	-2.97894
C	-4.54334	-1.83946	0.01236
H	-5.61481	-1.59948	-0.01620
H	-4.41045	-2.86025	-0.36308
H	-4.20826	-1.83229	1.05418
H	-2.64870	-0.01694	3.81136
H	-1.59475	1.22986	3.12710
H	1.59475	-1.22987	-3.12710
H	2.64872	0.01692	-3.81137
C	0.16023	-3.54776	0.12896
H	-0.74763	-3.55610	0.74057
H	-0.14093	-3.50896	-0.92277
H	0.70227	-4.48461	0.31098
C	1.31020	-2.31791	1.99903
H	0.36082	-2.32512	2.54176
H	1.90105	-3.19228	2.30047
H	1.83964	-1.40940	2.29778
C	-1.31025	2.31787	-1.99903
H	-1.90099	3.19229	-2.30052
H	-0.36087	2.32492	-2.54177
H	-1.83981	1.40940	-2.29772
C	-0.16026	3.54777	-0.12899
H	0.14093	3.50894	0.92273
H	0.74758	3.55618	-0.74064
H	-0.70235	4.48461	-0.31094

Table S8. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **2a** from B3LYP calculations (in Å)

Atom	x	y	z
Al	1.38778	-0.40808	-0.54450
O	-0.39641	-0.93592	-0.78950
O	0.47412	1.12715	0.02348
Al	-1.31098	0.58559	-0.19417
O	1.98004	-1.53762	0.68122
N	3.10641	0.79946	-0.05711
N	-3.04147	-0.61002	-0.65253
C	-2.53900	-1.81696	-1.35789
H	-2.54508	-1.58225	-2.42628
H	-3.21151	-2.67205	-1.20302
C	-1.07649	-2.18937	-0.97150
C	2.61374	2.04366	0.58386
H	2.63894	1.88420	1.66372
H	3.28035	2.88873	0.36234
C	1.14639	2.38904	0.17770
C	3.01926	-1.15707	1.55392
C	3.90589	-0.08203	0.83949
H	4.48466	0.51690	1.55673
H	4.62227	-0.61024	0.20342
O	-1.91465	0.58879	1.46695
O	-1.91077	1.70852	-1.43303
O	2.05343	-0.47906	-2.18701
C	-3.84489	0.27166	-1.54704
H	-4.47497	-0.32307	-2.22580
H	-4.50635	0.86661	-0.91486
C	-2.88977	1.21334	-2.30555
C	-3.68178	-0.87072	0.66431
H	-3.35448	-1.85774	0.99620
H	-4.77535	-0.90873	0.56004
C	-3.23823	0.18654	1.73958
C	3.41835	-0.17719	-2.29575
C	3.76717	1.01033	-1.37669
H	3.36247	1.92670	-1.80901
H	4.85308	1.14417	-1.25675
C	-3.28223	-0.49095	3.12016
H	-2.99457	0.22699	3.89583
H	-4.28733	-0.86731	3.35443
H	-2.57716	-1.32885	3.15866
C	-4.15913	1.42490	1.76197
H	-5.20957	1.15157	1.93032
H	-3.84341	2.09006	2.57346
H	-4.08660	1.99494	0.83070
H	-3.47614	2.03852	-2.73787
H	-2.42318	0.67815	-3.15234
C	0.49268	3.17839	1.31851
H	-0.53036	3.46323	1.05274
H	0.45006	2.57770	2.23247
H	1.05897	4.09619	1.52280
C	1.04097	3.18264	-1.13509
H	-0.00786	3.41711	-1.33721
H	1.60994	4.11881	-1.06780
H	1.40689	2.60571	-1.98876
C	-0.96902	-3.01934	0.31748
H	-1.54821	-3.94741	0.22915
H	0.07865	-3.27049	0.50460
H	-1.32281	-2.46126	1.18823
C	-0.43948	-2.94944	-2.14114
H	-0.39899	-2.31982	-3.03560
H	0.58377	-3.24905	-1.89419
H	-1.01523	-3.85583	-2.36880
C	2.41516	-0.63811	2.87560
H	1.84551	-1.44428	3.35059
H	3.19272	-0.30573	3.57678
H	1.71805	0.18757	2.70384
C	3.90136	-2.38151	1.85117
H	4.75916	-2.12096	2.48599
H	3.31260	-3.14710	2.36821
H	4.27539	-2.81551	0.91678
H	4.03972	-1.05215	-2.03196
H	3.67127	0.09076	-3.33290

Table S9. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **2b** from B3LYP calculations (in Å)

Atom	x	y	z
Al	-1.23556	-0.03381	0.21220
O	0.47357	-0.33872	0.93791
O	-0.19671	-0.25014	-1.33223
Al	1.51344	-0.46760	-0.61633
O	-2.20263	-1.38179	0.81489
N	-2.80053	0.22996	-1.25305
N	3.12389	-0.72584	0.78918
C	2.47781	-0.87011	2.12591
H	3.13997	-0.51180	2.92612
H	2.31444	-1.93762	2.28594
C	1.08429	-0.17900	2.22744
C	-2.21825	-0.11835	-2.57623
H	-2.36022	-1.18934	-2.72954
H	-2.73374	0.40972	-3.39184
C	-0.71470	0.18931	-2.57595
H	-0.22033	-0.34084	-3.39813
H	-0.51751	1.26316	-2.69586
C	-3.29986	-1.86594	0.07375
C	-3.87306	-0.70216	-0.81137
H	-4.43001	-1.08786	-1.67692
H	-4.57485	-0.12202	-0.20925
O	1.97039	-2.04899	-1.26449
O	2.36201	0.98830	-1.14462
O	-1.57321	1.63057	0.70421
C	3.93933	0.51838	0.65312
H	3.67411	1.16729	1.48957
H	5.00662	0.28031	0.75564
C	3.65927	1.29237	-0.68922
C	3.80694	-1.97913	0.33131
H	3.56251	-2.77024	1.04402
H	4.89676	-1.84741	0.34704
C	3.30757	-2.41216	-1.07514
H	3.42037	-3.50473	-1.15322
H	3.94894	-1.97688	-1.85856
C	-2.75445	2.26252	0.26313
C	-3.14196	1.67393	-1.13725
H	-2.54778	2.20040	-1.89075
H	-4.20140	1.84311	-1.37681
C	-2.47959	3.76567	0.08372
H	-3.35589	4.29355	-0.31645
H	-2.22069	4.21415	1.04898
H	-1.63496	3.91883	-0.59736
C	-3.86735	2.07986	1.31640
H	-4.69363	-1.49451	1.70635
H	-4.03832	-3.14044	1.66696
C	-4.40508	-2.31796	1.04338
H	-4.03157	1.02426	1.55175
H	-4.81774	2.52232	0.98892
H	-5.29824	-2.66470	0.50611
C	-2.84837	-3.07755	-0.76987
H	-3.66305	-3.46717	-1.39526
H	-1.99743	-2.82945	-1.41204
H	-2.51726	-3.87727	-0.09846
C	4.69893	0.93753	-1.77071
H	4.44077	1.45375	-2.70173
H	5.70951	1.24654	-1.47169
H	4.71818	-0.13562	-1.98091
C	3.74649	2.80369	-0.40659
H	2.95813	3.10987	0.28945
H	4.71977	3.08115	0.02060
H	3.60851	3.36358	-1.33808
C	0.25257	-0.92216	3.28087
H	-0.72669	-0.44831	3.40184
H	0.08909	-1.96201	2.98097
H	0.76133	-0.90708	4.25330
C	1.15431	1.31596	2.57573
H	1.66470	1.88958	1.79866
H	0.14195	1.72173	2.65590
H	1.67591	1.46607	3.52963
H	-3.56264	2.57357	2.24596

Table S10. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **2c** from B3LYP calculations (in Å)

Atom	x	y	z
Al	-1.40528	0.04033	0.37306
O	0.29836	0.06548	1.14409
O	-0.29836	-0.06578	-1.14410
Al	1.40529	-0.04052	-0.37307
O	-2.12999	-1.42842	1.03446
N	-2.94997	-0.03423	-1.11731
N	2.94996	0.03436	1.11731
C	2.28682	0.32810	2.41635
H	2.23164	1.41255	2.52468
H	2.87070	-0.06613	3.26079
C	0.86155	-0.24282	2.40711
H	0.26757	0.21251	3.20789
H	0.85706	-1.33100	2.55681
C	-2.28687	-0.32786	-2.41641
H	-2.23186	-1.41230	-2.52491
H	-2.87069	0.06660	-3.26077
C	-0.86151	0.24284	-2.40707
H	-0.26761	-0.21245	-3.20794
H	-0.85685	1.33104	-2.55658
C	-3.11120	-2.12720	0.30031
C	-3.85526	-1.11895	-0.64747
H	-4.31925	-1.63237	-1.50137
H	-4.65800	-0.64416	-0.08020
O	2.00897	-1.65256	-0.76778
O	2.12981	1.42828	-1.03457
O	-2.00875	1.65244	0.76788
C	3.85516	1.11909	0.64732
H	4.31915	1.63264	1.50115
H	4.65791	0.64431	0.08006
C	3.11098	2.12720	-0.30052
C	3.54163	-1.33275	1.07361
H	3.03959	-1.91953	1.84926
H	4.61084	-1.30019	1.32618
C	3.27955	-2.04356	-0.29843
C	-3.27933	2.04358	0.29864
C	-3.54154	1.33291	-1.07344
H	-3.03949	1.91973	-1.84907
H	-4.61076	1.30046	-1.32597
C	-3.27673	3.56214	0.05339
H	-4.23086	3.90709	-0.36781
H	-3.10740	4.08967	0.99826
H	-2.46889	3.83515	-0.63489
C	-4.35210	1.70867	1.35591
H	-4.14444	2.28010	2.26736
H	-5.36250	1.96600	1.01040
H	-4.33124	0.64939	1.62794
C	-4.14554	-2.71910	1.27301
H	-3.65897	-3.44096	1.93777
H	-4.58316	-1.92944	1.89416
H	-4.95548	-3.23413	0.73878
C	-2.44022	-3.27778	-0.47864
H	-1.99371	-3.98032	0.23348
H	-3.16174	-3.82716	-1.09849
H	-1.62892	-2.91427	-1.11693
C	3.27708	-3.56209	-0.05305
H	3.10784	-4.08973	-0.99788
H	4.23121	-3.90692	0.36824
H	2.46921	-3.83512	0.63520
C	4.35236	-1.70864	-1.35566
H	5.36275	-1.96593	-1.01010
H	4.14477	-2.28010	-2.26710
H	4.33148	-0.64936	-1.62772
C	2.43992	3.27777	0.47838
H	1.62871	2.91423	1.11676
H	3.16142	3.82730	1.09813
H	1.99327	3.98020	-0.23377
C	4.14524	2.71912	-1.27330
H	3.65857	3.44087	-1.93811
H	4.95513	3.23428	-0.73914
H	4.58292	1.92945	-1.89439

Table S11. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **Ti1** from B3LYP calculations (in Å)

Atom	x	y	z
Ti	1.650439	0.377345	0.212213
N	2.374111	-1.758338	-0.586360
O	3.025437	0.737128	-1.000718
C	4.091751	-0.086386	-1.428725
C	4.265275	0.053655	-2.952589
H	3.392680	-0.319368	-3.497962
H	5.143636	-0.507768	-3.295416
H	4.407059	1.107954	-3.214971
C	5.383477	0.379625	-0.731365
H	5.635259	1.399819	-1.042337
H	6.228131	-0.274875	-0.983901
H	5.249951	0.372782	0.355683
C	3.780794	-1.566166	-1.012733
H	4.022316	-2.258145	-1.831578
H	4.419771	-1.837976	-0.173691
O	2.444081	-0.452037	1.663333
C	2.566469	-1.841667	1.931273
C	3.977503	-2.111851	2.486014
H	4.763354	-1.793792	1.795006
H	4.115005	-3.179764	2.696238
H	4.114179	-1.558184	3.421617
C	1.529742	-2.241850	2.997251
H	1.736210	-1.722456	3.939846
H	1.562445	-3.322768	3.186952
H	0.522599	-1.973781	2.664130
C	2.253106	-2.628078	0.607529
H	2.887377	-3.523460	0.522106
H	1.215269	-2.964804	0.647385
O	0.297900	-0.127055	-1.148933
C	0.744347	-0.899460	-2.250236
H	1.404451	-0.283654	-2.870025
H	0.114205	-1.209056	-2.858673
C	1.461773	-2.138642	-1.701818
H	0.697803	-2.807740	-1.306225
H	2.008551	-2.667551	-2.495316
O	1.578913	2.156104	0.665388
C	2.468927	3.258617	0.573955
H	3.229869	3.002845	-0.178659
C	3.158368	3.482172	1.923624
H	2.421525	3.733167	2.697298
H	3.881375	4.305264	1.857073
H	3.691913	2.578524	2.237977
C	1.705125	4.499797	0.103470
H	1.215790	4.309616	-0.858504
H	2.389941	5.347971	-0.022418
H	0.937359	4.786361	0.833459
Ti	1.650167	-0.377345	-0.211775
N	2.374229	1.758628	0.586064
O	3.025198	-0.736899	1.001094
C	4.091659	0.086529	1.428820
C	5.383201	-0.379573	0.731158
H	5.249459	-0.372616	-0.355867
H	6.227968	0.274825	0.983580
H	5.634942	-1.399815	1.041999
C	4.265490	-0.053534	2.952652
H	4.407336	-1.107836	3.214988
H	5.143903	0.507904	3.295323
H	3.392980	0.319478	3.498179
C	3.780751	1.566396	1.012976
H	4.420102	1.838483	0.174297
H	4.021870	2.258184	1.832095
O	0.297810	0.127645	1.149297
C	0.744423	0.900485	2.250203
C	1.461598	2.139475	1.701090
H	2.008061	2.669125	2.494317
H	0.697464	2.808017	1.304867
O	2.444065	0.451343	-1.663136
C	2.567072	1.840806	-1.931575
C	2.253698	2.627867	-0.608222
H	1.215976	2.964905	-0.648433
H	2.888194	3.523122	-0.523082
O	1.577974	-2.156258	-0.664347
C	2.468273	-3.258626	-0.573544
H	3.228678	-3.003422	0.179808
C	1.704496	-4.500483	-0.104805
H	0.937239	-4.786468	-0.835555
H	2.389446	-5.348614	0.020620
H	1.214534	-4.311418	0.857069
C	3.158623	-3.480623	-1.922998
H	3.692101	-2.576512	-2.236119
H	3.881817	-4.303580	-1.856812
H	2.422335	-3.731062	-2.697382
H	0.114012	1.210291	2.858698
H	1.404718	0.284994	2.870111
C	1.530721	2.241036	-2.997911
H	1.737160	1.721329	-3.940338
H	1.563842	3.321891	-3.187898
H	0.523425	1.973430	-2.664871
C	3.978355	2.110188	-2.486046
H	4.115080	1.555916	-3.421283
H	4.763914	1.792299	-1.794626
H	4.116274	3.177937	-2.696853

Table S12. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **Ti2** from B3LYP calculations (in Å)

Atom	x	y	z
Ti	1.793649	0.355150	-0.125218
N	2.299208	-1.920500	-0.620311
O	3.159543	0.449936	-1.421368
C	3.881711	-0.622275	-1.971967
C	3.703140	-1.855759	-1.082815
H	3.995106	-2.783693	-1.599868
H	4.338085	-1.744829	-0.204948
O	2.527077	-0.347833	1.421720
C	2.536326	-1.692817	1.877600
C	2.151480	-2.625153	0.672311
H	2.737618	-3.556709	0.690473
H	1.097605	-2.895492	0.764567
O	0.366643	-0.226788	-1.384982
C	0.709729	-1.179453	-2.376681
H	1.380180	-0.712828	-3.107395
H	-0.195827	-1.502465	-2.904956
C	1.363811	-2.384813	-1.681561
H	0.572053	-2.965661	-1.208480
H	1.880050	-3.030186	-2.406989
O	1.940764	2.169316	0.090943
C	2.950269	3.139769	-0.148262
H	3.638117	2.714861	-0.894500
C	3.724466	3.412275	1.145001
H	3.063053	3.837046	1.910984
H	4.541390	4.122507	0.963747
H	4.153852	2.484132	1.537578
C	2.315387	4.409055	-0.722555
H	1.759103	4.180940	-1.638901
H	3.088395	5.148897	-0.966192
H	1.624585	4.862017	0.000081
Ti	-1.555444	-0.195364	-0.381451
N	-2.081881	2.102779	-0.065814
O	-2.952851	-0.168588	0.858620
C	-3.931272	0.825409	1.095713
C	-3.505833	2.130165	0.338199
H	-4.106438	2.215240	-0.569639
H	-3.712747	3.022661	0.944806
O	-0.144003	0.482228	0.839875
C	-0.497883	1.511678	1.747734
C	-1.144461	2.652746	0.949350
H	-1.655934	3.364283	1.612196
H	-0.348804	3.185663	0.426949
O	-2.326153	0.331293	-1.989332
C	-2.483062	1.654304	-2.444642
C	-1.865910	2.635045	-1.431337
H	-0.784951	2.683299	-1.586906
H	-2.275282	3.650688	-1.557113
O	-1.592312	-2.027440	-0.424529
C	-2.551478	-3.027733	-0.108605
H	-3.304638	-2.562255	0.544530
C	-1.873030	-4.169909	0.652493
H	-1.115649	-4.659810	0.027353
H	-2.611806	-4.925283	0.948481
H	-1.385594	-3.793444	1.558710
C	-3.235676	-3.513304	-1.390296
H	-3.703962	-2.675656	-1.918382
H	-4.012434	-4.252370	-1.156152
H	-2.507545	-3.982022	-2.064528
H	0.399932	1.881114	2.256729
H	-1.179678	1.100509	2.499654
C	3.924090	-2.005573	2.467587
H	3.963010	-3.036842	2.839738
H	4.125135	-1.330292	3.306540
H	4.727284	-1.876355	1.735923
C	1.478662	-1.851923	2.985532
H	1.418544	-2.895574	3.320951
H	0.495815	-1.543360	2.616685
H	1.738165	-1.228907	3.848928
H	4.950505	-0.367268	-2.035014
H	3.540109	-0.817501	-3.000287
H	-1.991322	1.783743	-3.420102
H	-3.554614	1.855247	-2.596694
C	-5.279384	0.332930	0.537060
H	-5.607794	-0.563425	1.074891
H	-6.055687	1.101970	0.644296
H	-5.181353	0.083952	-0.525420
C	-4.069957	1.058333	2.611388
H	-4.296129	0.110838	3.112944
H	-3.152405	1.464440	3.047898
H	-4.885321	1.761953	2.821360

Table S13. Cartesian coordinates of the ground state (S_0) fully optimized geometry in gas phase of **Ti3** from B3LYP calculations (in Å)

Atom	x	y	z
Ti	1.672521	-0.244159	0.140848
N	1.440861	-2.615065	-0.164138
O	2.988137	-0.703859	-1.122276
C	3.331529	-1.983874	-1.588283
C	2.780376	-3.039156	-0.622109
H	2.747037	-4.038656	-1.082981
H	3.435889	-3.095430	0.249792
O	2.171326	-0.987938	1.765894
C	1.996977	-2.314956	2.201550
C	1.118654	-3.084437	1.199869
H	1.247275	-4.173571	1.310718
H	0.067016	-2.846856	1.380747
O	0.109000	-0.478748	-1.071758
C	0.115309	-1.572301	-1.974183
H	0.886334	-1.405408	-2.735326
H	-0.854600	-1.637170	-2.481938
C	0.371576	-2.854392	-1.167197
H	-0.546521	-3.102164	-0.633435
H	0.628579	-3.697110	-1.824942
O	2.376014	1.444202	0.195915
C	3.621012	2.043620	-0.135827
H	4.173525	1.323157	-0.756978
C	4.418057	2.319536	1.142738
H	3.884289	3.030640	1.786030
H	5.399889	2.745481	0.899932
H	4.573479	1.394201	1.708045
C	3.375718	3.315688	-0.952102
H	2.790532	3.089397	-1.850657
H	4.328422	3.760395	-1.266166
H	2.829582	4.061103	-0.359947
Ti	-1.684912	0.250377	-0.125350
N	-1.477760	2.624327	-0.004924
O	-2.985678	0.778892	1.126701
C	-3.337296	2.086352	1.501265
C	-2.811332	3.072903	0.450539
H	-3.484513	3.063844	-0.409349
H	-2.774253	4.102895	0.837811
O	-0.112448	0.570495	1.053588
C	-0.118748	1.734772	1.862151
C	-0.387913	2.943493	0.953104
H	-0.627634	3.842151	1.539890
H	0.520139	3.138808	0.381623
O	-2.272930	0.859325	-1.780728
C	-2.097472	2.144993	-2.326276
C	-1.193227	2.989279	-1.409128
H	-0.146080	2.739836	-1.600765
H	-1.327291	4.066734	-1.598944
O	-2.316402	-1.462354	-0.028519
C	-3.524016	-2.084782	0.390851
H	-4.071451	-1.350822	1.000339
C	-3.199108	-3.305059	1.256521
H	-2.656828	-4.062876	0.676699
H	-4.121609	-3.761864	1.636454
H	-2.581952	-3.015469	2.114501
C	-4.368714	-2.450673	-0.833052
H	-4.581844	-1.560453	-1.434612
H	-5.322860	-2.895560	-0.523124
H	-3.840269	-3.175677	-1.465067
H	0.855124	1.850574	2.351707
H	-0.883210	1.627441	2.640117
H	4.425513	-2.080280	-1.655686
H	2.934771	-2.131805	-2.604404
H	-4.431246	2.177111	1.576979
H	-2.928175	2.313950	2.497473
H	-1.639442	2.076127	-3.323902
H	-3.083451	2.616511	-2.458452
H	2.984115	-2.788473	2.315731
H	1.518152	-2.328489	3.191461