Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information of

Fluorescent and Phosphorescent Study of Germanium-Acetylene Polymers and Germa[*N*]pericyclynes

Hiroki Tanimoto,*[a] Tomohiko Nagao,[a] Taro Fujiwara,[a] Takahiro Kakuta,[b] Kazuo Tanaka,[b] Yoshiki Chujo,[b] and Kiyomi Kakiuchi*[a]

[a] Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayamacho, Ikoma, Nara 630-0192, Japan

[b] Department of Polymer Chemistry, Graduate School of Engineering Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

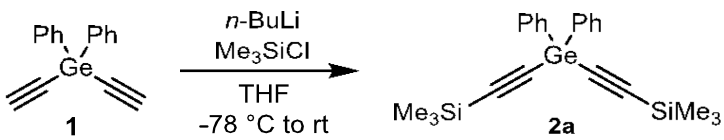
tanimoto@ms.naist.jp; kakiuchi@ms.naist.jp

• General information

^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak ($CDCl_3$, δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR) or tetramethylsilane (δ 0 for ^{1}H NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad peak), and m (complex multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a Jasco FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStaion [EI (70 eV), CI, FAB, and ESI], and Bruker Autoflex II (MALDI-TOF). UV-visble UV/visible spectra were recorded using Jasco V-630. Fluorescence spectra were collected using JASCO FP-6500. Low temperature fluorescence and phosphorescence emission spectra were recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. The cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing n-Bu_4NPF_6 as the supporting electrolyte at 298 K (100 mV s^{-1}). The glassy carbon working electrode was polished using BAS polishing alumina suspension and rinsed with water before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to Ag/$AgNO_3$ and normalized with respect to Fc/Fc^{+}. Flash column chromatography was performed using Merck Silica gel 60. The progress of the reactions was monitored by silica gel thin layer chromatography (TLC) (Merck TLC Silica gel 60 F_{254}). The further purifications of the crude materials were performed using a LC-908 recycling preparative high-performance liquid chromatography (HPLC) equipped with a JAIGEL 2H-40 column (chloroform elution) made by Japan Analytical Industry Co., Ltd. The number-average molecular weight (M_n) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of polymer were estimated by size-exclusion chromatography with a TOSOH G3000HXI system equipped with three consecutive polystyrene gel columns (TOSOH gels:α-4000,α-3000, α-2500) and ultraviolet detector, at 40 °C. The system was operated at a flow rate of 1.0 mL/min with chloroform as an eluent. Iodine on silica gel and Ethanol solutions of phosphomolybdic acid were used for the TLC stains, and TLC was also monitored with UV lamp. All the reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd, TCI (Tokyo Chemical Industry, Co. Ltd), Kanto Chemical Co. Inc., and Nakalai Tesque. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical, which was further dehydrated over activated molecular sieves 4A. Density Functional Theory (DFT) calculations were performed using the Gaussian09, and the geometries of the molecules were optimized by employing the B3LYP density functionals and the 6-31G(d,p) basis set in this series of calculations. For preparation procedures and characterizations of compounds which are not noted here, see our previous works.[1,2]

• Synthesis of germanium-acetylene materials

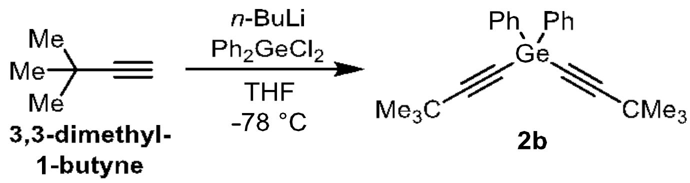
Diphenylbis((trimethylgermyl)ethynyl)germane (2a)



n-Butyllithium (1.63 M in hexane, 1.98 mL, 3.23 mmol) was added dropwise to a sttired solution of diethynyldiphenylgermane **1a** (406 mg, 1.47 mmol)[1] in THF (14 mL) at –78 °C under a nitrogen atmosphere. After 2 h, chlorotrimethylsilane (350 mg, 3.23 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature and was stirred for 71 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane to hexane/dichloromethane = 1/20) to afford diphenylbis((trimethylsilyl)ethynyl)germane **2a** (539 mg, 87%) as a white solid. Recrystallization (dichloromethane–hexane) was also performed to afford colorless crystal.

colorless crystal; R_f value 0.14 (hexane/dichloromethane = 20/1); m.p. 80.5–81.0 °C; IR (KBr, disc) ν_{max} 3068, 3053, 2962, 1484, 1431, 1249, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68–7.66 (m, 4H), 7.41–7.39 (m, 6H), 0.23 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.2, 133.7, 129.8, 128.4, 116.4, 104.8, –0.16; LRMS (ESI) *m*/*z* 444 $[M+Na]^+$.

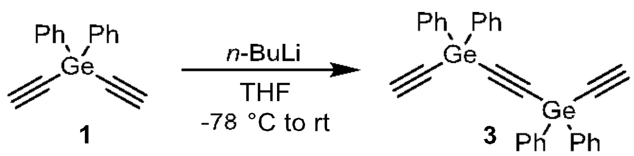
Bis(3,3-dimethylbut-1-yn-1-yl)diphenylgermane (2b)



n-Butyllithium (1.63 M in hexane, 4.53 mL, 7.39 mmol) was added dropwise to a stirred solution of 3,3-dimethyl-1-butyne (603 mg, 7.39 mmol) in THF (33 mL) at –78 °C under nitrogen atmosphere. After 2 h, dichlorodiphenylgermane (1.0 g, 3.36 mmol) was added at the same temperature, and the reaction mixture was stirred for 1 h. The reaction mixture was warmed up to ambient temperature and stirred for 13 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane to hexane/dichloromethane = 20/1) to afford bis(3,3-dimethylbut-1-yn-1-yl)diphenylgermane **2b** (1.39 g, quant.) as a white solid. Recrystallization (dichloromethane–hexane) was also performed to afford colorless crystal.

colorless crystal; R_f value 0.16 (hexane/dichloromethane = 20/1); m.p. 77.6–79.8 °C; IR (KBr, disc) ν_{max} 3069, 3056, 2972, 2180, 2147, 1484, 1431, 1250, 1093 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69–7.66 (m, 4H), 7.39–7.37 (m, 6H), 1.30 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 133.6, 129.4, 128.2, 117.6, 74.8, 30.9, 28.4; LRMS (ESI) *m*/*z* 413 $[M+Na]^+$.

1,2-Bis(ethynyldiphenylgermyl)ethyne (3)

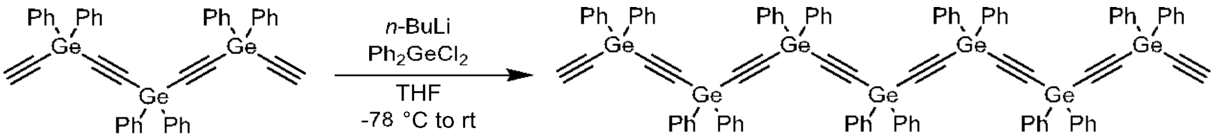


To a stirred solution of diethynyldiphenylgermane **1** (1.0 g, 3.61 mmol)[1] in THF (36 mL) was added *n*-butyllithium (1.6 M in hexane, 2.26 mL, 3.61 mmol) at -78 °C under nitrogen atmosphere. After 12 h, the reaction mixture was warmed up to room temperature and was stirred for 10 h. The reaction was quenched with saturated ammonium chloride aqueous solution at 0 °C. The mixture was extracted with ether and was washed with brine. The combined organic layers were dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 20/1) to afford dimer **3** (435 mg, 46%) as a white solid, and recovered starting material **1** (300 mg, 30%).

white crystal; R_f value = 0.35 (hexane/dichloromethane = 3/1) ; m.p. 137.8–139.1 °C; IR (KBr, disc) ν_{max} 3435, 3277, 3047, 2038, 1486, 1434, 1262, 1095 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72–7.70 (m, 8H), 7.46–7.39

(m, 12H), 2.61 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 133.1, 130.1, 128.6, 107.4, 95.2, 82.5; LRMS (ESI) *m*/*z* 551 $[M+Na]^+$.

3,3,6,6,9,9,12,12,15,15,18,18,21,21-Tetradecaphenyl-3,6,9,12,15,18,21-heptagermatricosa-1,4,7,10,13,16,19,22-octayne (5)

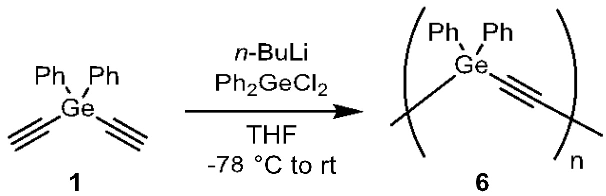


4 6

n-Butyllithium (1.63 M in hexane, 0.66 mL, 1.08 mmol) was added dropwise to a stirred solution of bis((ethynyldiphenylgermyl)ethynyl)diphenylgermane **4** (840 mg, 1.08 mmol)[2] in THF (11 mL) at -78 °C under nitrogen atmosphere. After 2 h, dichlorodiphenygermane (153 mg, 0.51 mmol) was added at the same temperature. Then the reaction mixture was warmed up to ambient temperature and stirred for 15 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with dichloromethane, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane/dichloromethane = 3/1 to 3/2) to afford diethynyldiphenylgermane-heptamer **5** (179 mg, 20%).

white solid; R_f value 0.16 (hexane/dichloromethane = 2/1); m.p. 157.1–159.4 °C; IR (KBr, disc) ν_{max} 3267, 3070, 3024, 2037, 1485, 1433, 1094, 736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.73–7.68 (m, 28H), 7.74–7.30 (m, 42H), 2.58 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8, 133.7, 133.42, 133.35, 133.1, 130.1, 130.0, 129.96, 128.6, 128.5, 107.9, 107.79, 107.75, 107.70, 107.6, 107.3, 95.3, 82.6 ; LRMS (ESI) *m*/*z* 1805 $[M+Na]^+$.

Poly(diphenylgermylene)ethynylene (6)



To a stirred solution of diethynyldiphenylgermane **1** (1.02 g, 3.68 mmol) in THF (180 mL) was added *n*-butyllithium (1.63 M in hexane, 4.52 mL, 7.37 mmol) dropwise at -78 °C under nitrogen atmosphere. After 2 h, dichlorodiphenylgermane (1.09 g, 3.68 mmol) was added at the same temperature. Then the reaction mixture was warmed up to ambient temperature and stirred for 48 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with dichloromethane, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane/dichloromethane = 5/1 to dichloromethane elution) to afford Diethynyldiphenylgermane-polymer **6** (757 mg, 41%) as a light pink amorphous, which were transformed into light pink solid by reprecipitation (dichloromethane/hexane).

light pink solid; R_f value 0.23–0.10 (multispot) (hexane/ dichloromethane = 1/2); m.p. 70–86 °C (for amorphous), 109.9–127.8 °C (for reprecipitation solid); IR (KBr, disc) ν_{max} 3268, 3070, 3025, 2037, 1485, 1094, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85–7.67 (br, 85H), 7.49–7.23 (br, 123H), 2.63–2.59 (br, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8, 133.7, 133.5, 133.4, 130.1, 130.0, 128.5, 128.2, 107.9, 107.8, 107.3, 95.3, 82.6;

TOF-MS (MALDI) *m*/*z* 7334 (max) (M^+); Weight-average molecular weight M_w = 3420; Number-average molecular weight M_n = 2780; M_w/M_n = 1.2; Degree of polymerization DP = 10.9 estimated by number-average molecular weight.

• **UV-visible and fluorescence emission spectra**

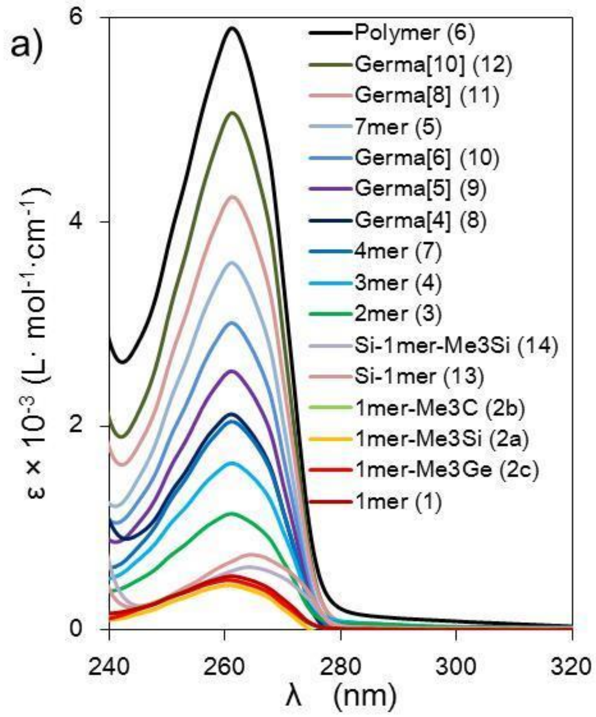


Fig SI 1. UV-vis absorption spectra (0.1 mM in CH_2Cl_2)

Compounds		Number of Ph rings	ε at 260 nm ($L \cdot mol^{-1} \cdot cm^{-1}$)
1mer	**1**[1]	2	520
1mer-Si	**2a**	2	440
1mer-C	**2b**	2	490
1mer-Ge	**2c**[2]	2	490
Si-1mer[a]	**13**	2	640
Si-1mer-Si[b]	**14**	2	560
2mer	**3**	4	1130
3mer	**4**	6	1610
4mer	**7**	8	2010
Ge[4]	**8**[1]	8	2100
Ge[5]	**9**[2]	10	2500
Ge[6]	**10**[1]	12	3000
7mer	**5**	14	3540
Ge[8]	**11**[1]	16	4170
Ge[10]	**12**[2]	20	4980
poly	**6**	≈22	5800

[a] λ_{max} = 264 nm (ε = 740), [b] λ_{max} = 264 nm (ε = 620)

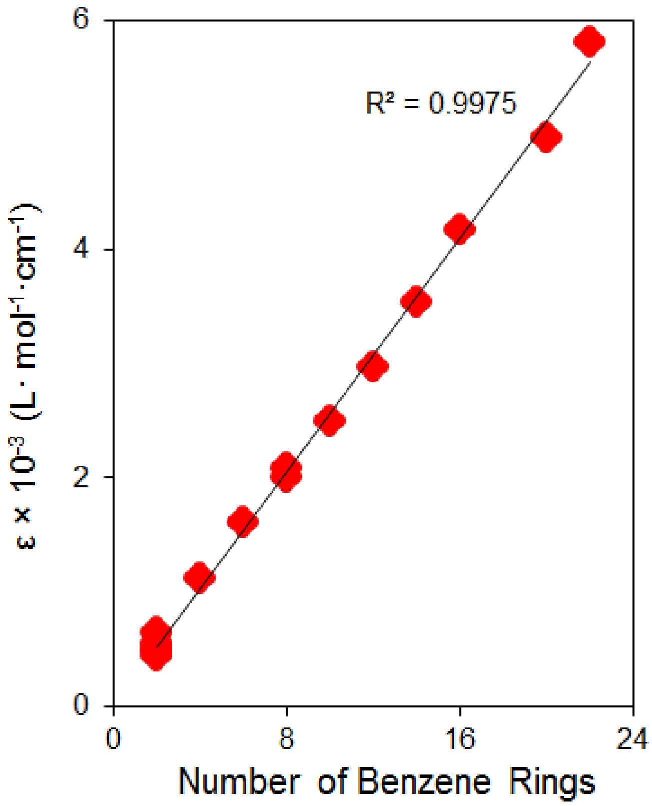


Fig SI 2. ε values at 260 nm versus number of benzene rings (0.1 mM in CH_2Cl_2)

ε values of **1**, **2c** and **8**–**12** are referred from our previous reports[1,2]

• **Fluorescence emission spectra**

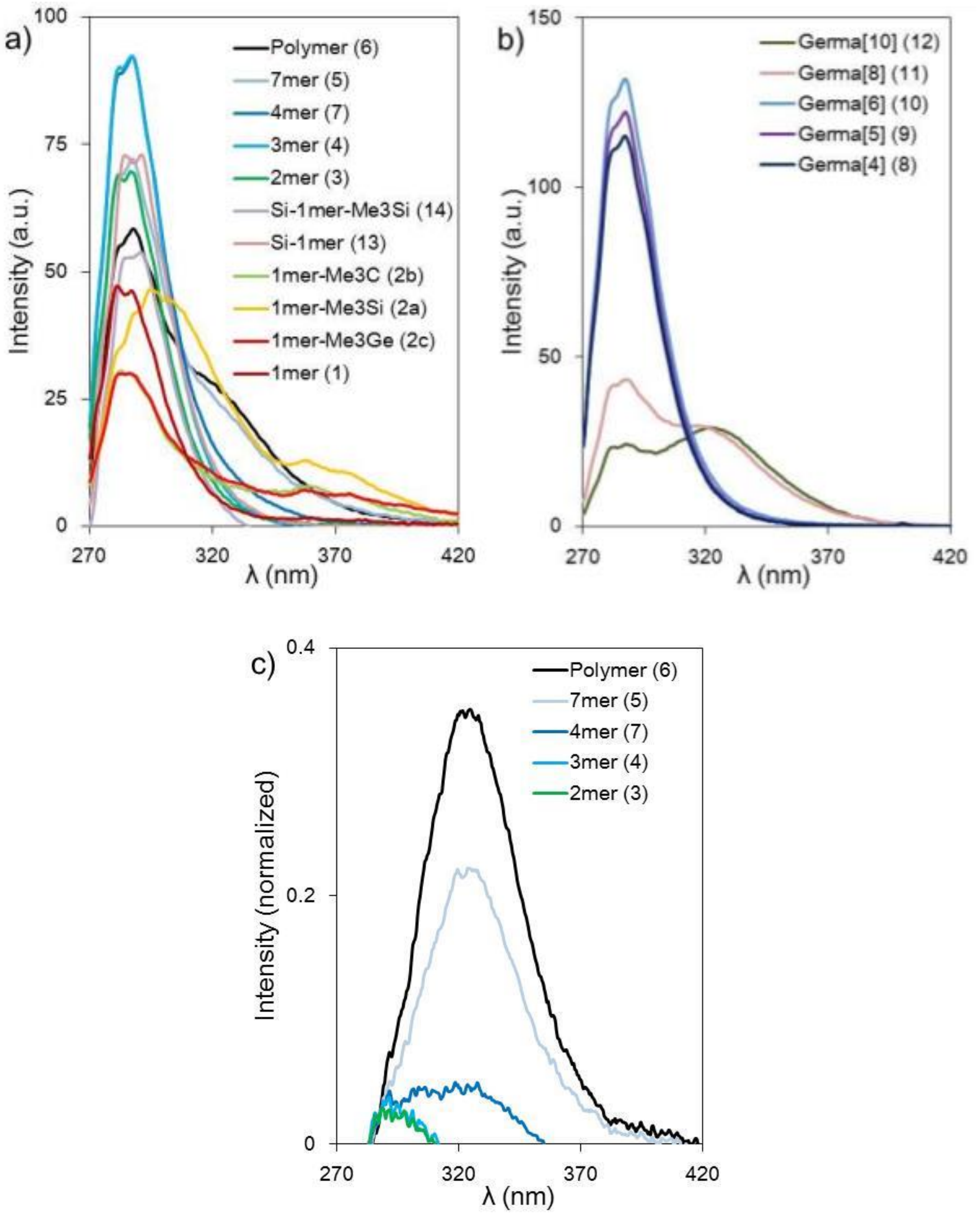


Fig SI 3. Fluorescence emission spectra [0.1 mM in CH_2Cl_2, a: polymers (λ_{ex} = 260 nm), b: pericyclynes (λ_{ex} = 260 nm) referred from previous work for comparison,[2] c: normalized differential spectra of polymers (λ_{ex} = 260 nm)]

• **Phosphorescence emission spectra**

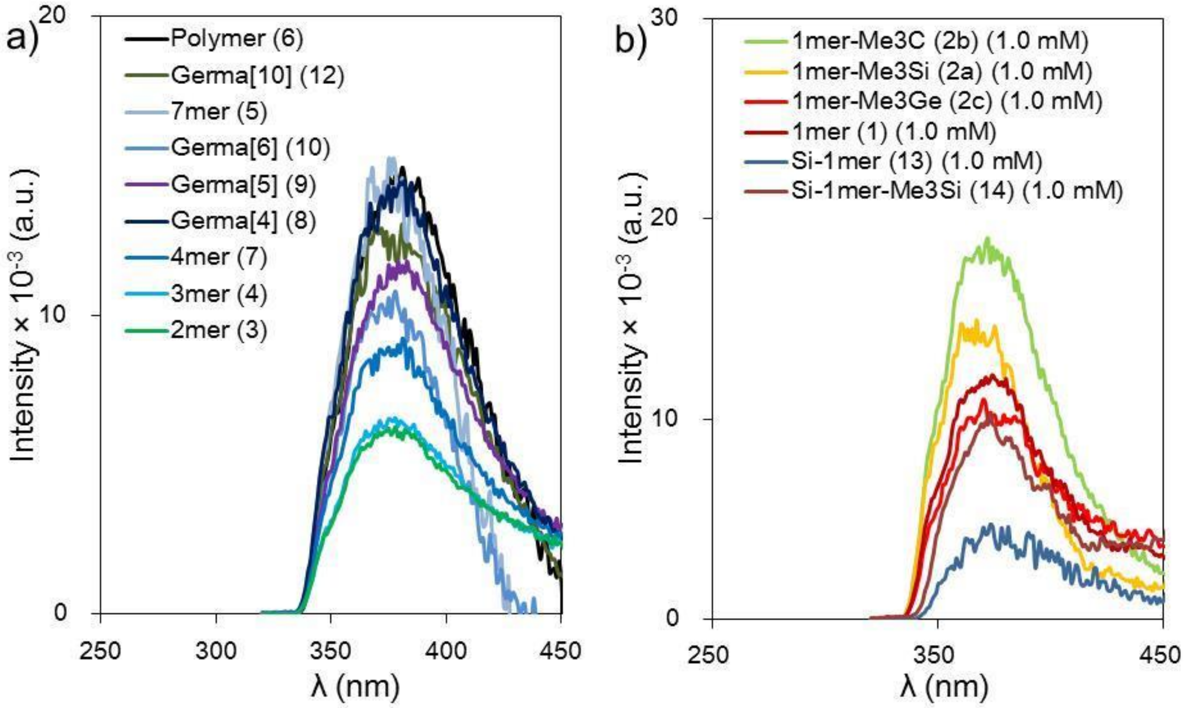


Fig SI 4. Phosphorescence emission spectra

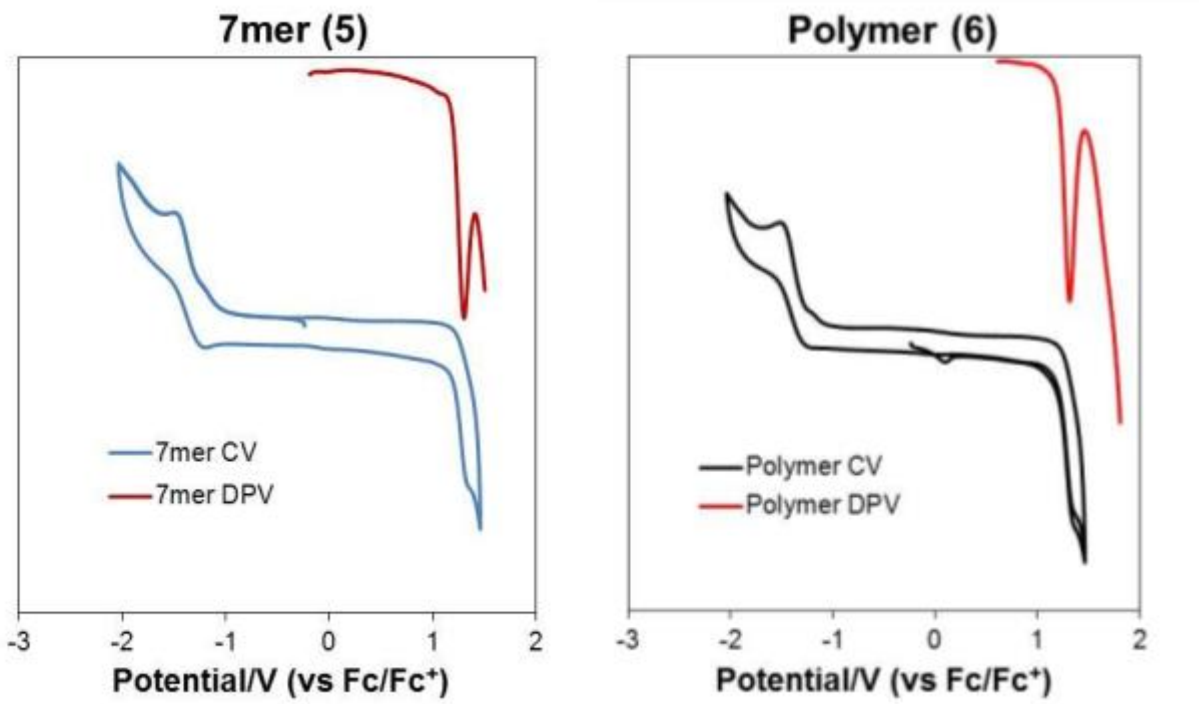
(77K in 2-methyltetrahydrofuran, λ_{ex} = 260 nm, background cut off; a: 0.1 mM, b) 1.0 mM)

Table SI. Phosphorescence maxima, intensity, and lifetime of compounds sorted by the number of phenyl rings[a]

Compounds	Number of Ph rings	Emission maxima (nm)	τ_P (μs)
1mer **1** (1.0 mM)	2	380	13.4
1mer-GeMe$_3$ **2a** (1.0 mM)	2	387	14.5
1mer- SiMe$_3$ **2b** (1.0 mM)	2	375	13.4
1mer-CMe$_3$ **2c** (1.0 mM)	4	381	15.4
2mer **3**	4	382	14.7
3mer **4**	6	386	15.5
4mer **5**	8	381	15.5
Ge[4] **8**	8	382	18.2
Ge[5] **9**	10	383	14.0
Ge[6] **10**	12	389	17.9
7mer **5**	14	377	15.3
Ge[8] **11**	16	Insoluble	
Ge[10]**12**	20	388	14.7
Polymer **6**	≈22	388	18.2
Si-1mer **13** (1.0 mM)	2	390	11.2
Si-1mer-SiMe$_3$ **14** (1.0 mM)	2	382	13.4

[a] Measured at 77 K as 0.1 mM solution of 2-methyltetrahydrofuran unless otherwise noted.

• **Cyclic voltammetry (CV) and differential pulse voltammetry (DPV)**



Compounds	Oxidation potential from DPV / V
7mer (**5**)	1.31
Polymer (**6**)	1.31

Fig S5. Cyclic and differential pulse voltammograms of germa[5], and [10]pericyclynes (1.0 mM in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 solution; Scan rate = 0.1 V/s for **5**, 0.05 V/s for **6**)

• GPC analysis results

¥Documents and Settings¥gamess¥My Documents¥システム３¥yamane.mdb 20141031-aza-konica-rep7times0005 Ph-polymer 20141106
Thursday, Nov 6 2014

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<表題部>

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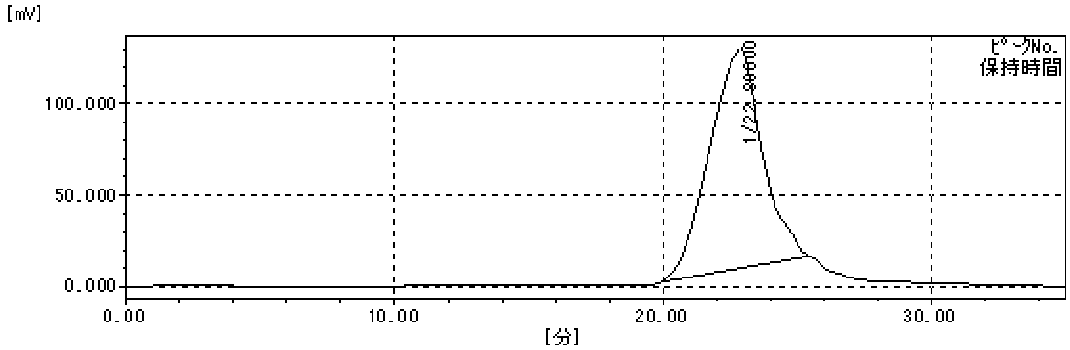

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	[分]	[mV]	[MOL]
ﾋﾟｰｸｽﾀｰﾄ :	19.92	2.450	12,108
ﾋﾟｰｸﾄｯﾌﾟ :	22.88	130.578	2,905
ﾋﾟｰｸｴﾝﾄﾞ :	25.47	16.738	607
面積[mV･秒]		16,353.827	
面積比[%]		100.000	
高さ[mV]		120.502	
[η]		3,420.14904	

Mn	:	2,778
Mw	:	3,420
Mz	:	4,110
Mz+1	:	4,839
Mv	:	3,420
Mp	:	2,961
Mz/Mw	:	1.202
Mw/Mn	:	1.231
Mz+1/Mw	:	1.415

<Ch1 分子量計算結果>
全体

	[分]	[mV]	[MOL]
ﾋﾟｰｸｽﾀｰﾄ :	19.92	2.450	12,108
ﾋﾟｰｸﾄｯﾌﾟ :	22.88	130.578	2,905
ﾋﾟｰｸｴﾝﾄﾞ :	25.47	16.738	607
面積[mV･秒]		16,353.827	
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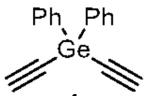
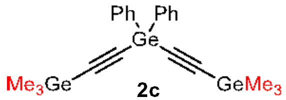
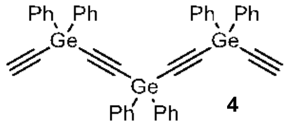
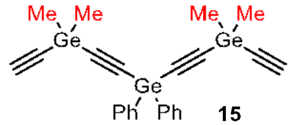
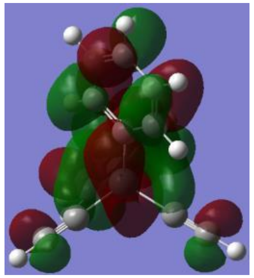
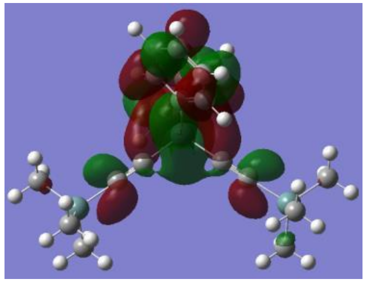
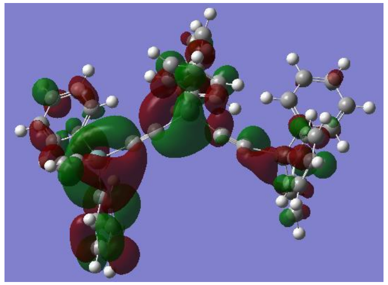
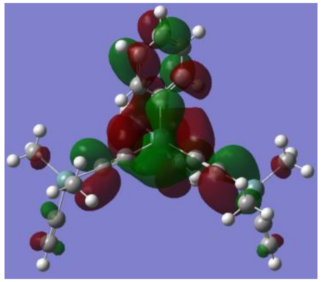
高さ[mV]		120.502	
[η]		3,420.14904	

Mn	:	2,778
Mw	:	3,420
Mz	:	4,110
Mz+1	:	4,839
Mv	:	3,420
Mp	:	2,961
Mz/Mw	:	1.202
Mw/Mn	:	1.231
Mz+1/Mw	:	1.415

• HOMO/LUMO orbitals and energy levels estimated by DFT calculation (Table SI 2)

[Gaussian 09, DFT- B3LYP6-31G(d,p); Calculations of **8** and **10** are based on obtained cif file conformation.

The results of germa[5]pericyclyne **9** is referred from our reported data for comparison.[2] Compound **15** was calculated as a model compound]

	 **1**	 **2c**	 **4**	 **15**
LUMO+1				
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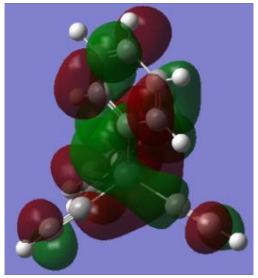
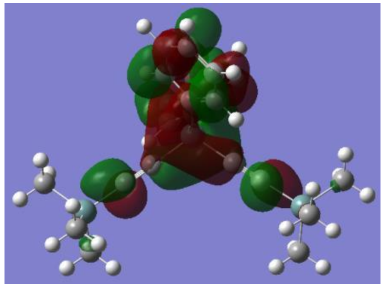
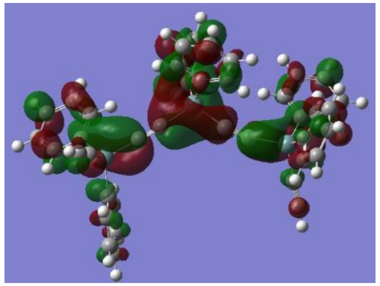
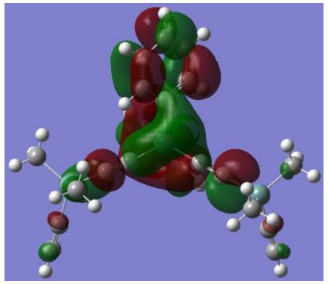
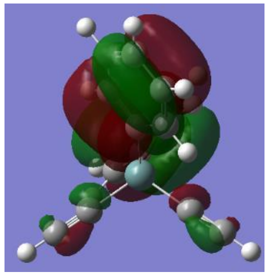
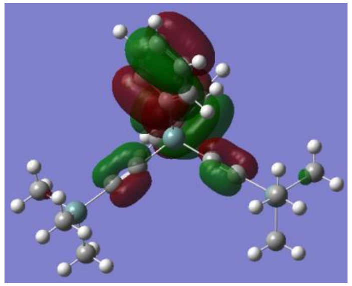
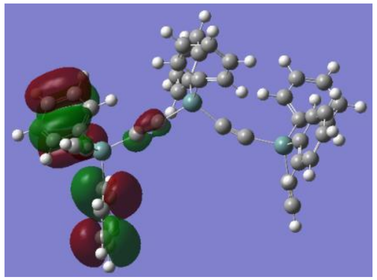
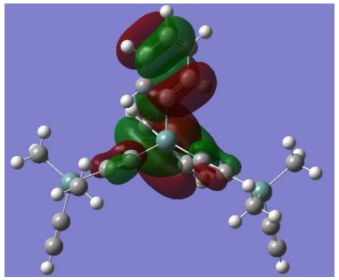
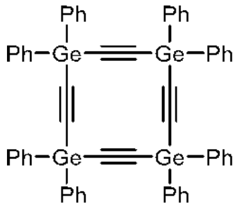
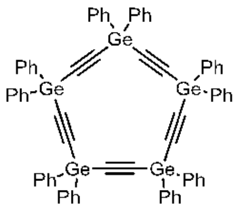
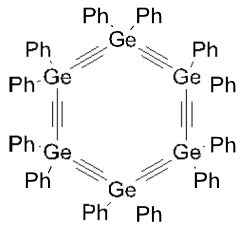
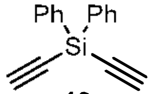
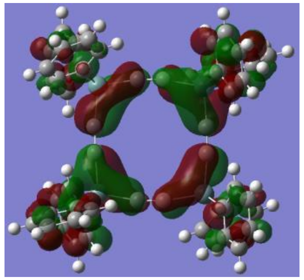
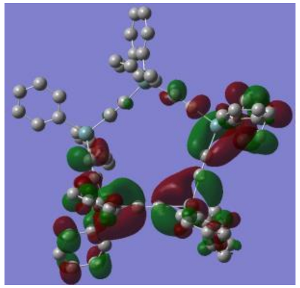
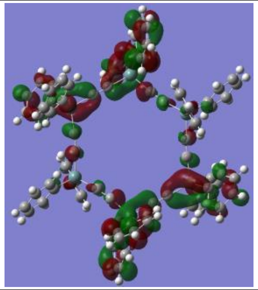
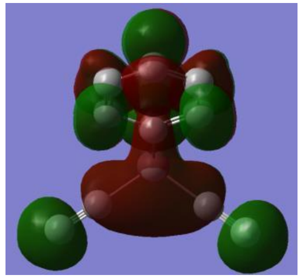
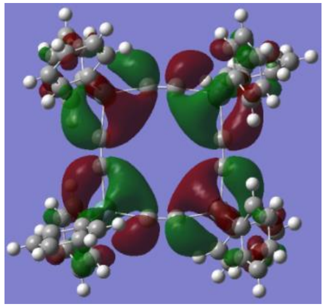
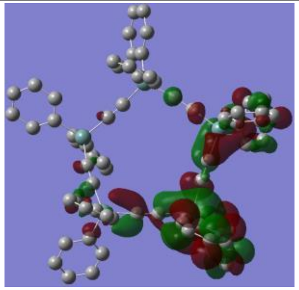
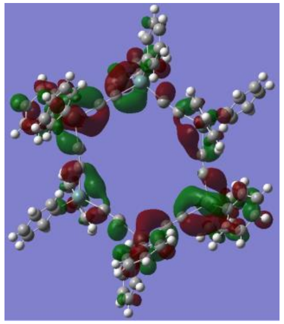
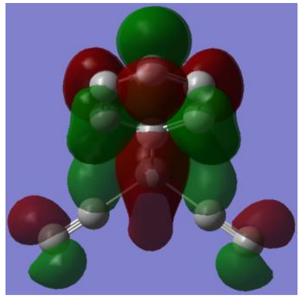
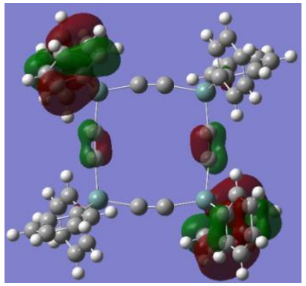
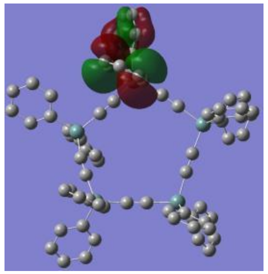
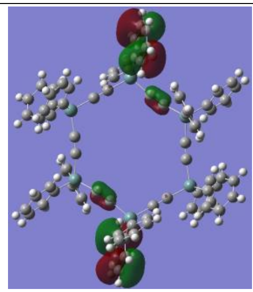
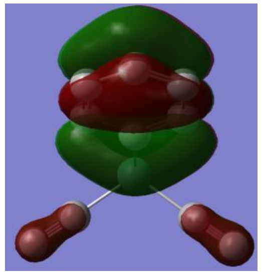
LUMO				
	-0.543 eV	-0.401 eV	-0.644 eV	-0.542 eV
HOMO				
	-6.74 eV	-6.56 eV	-6.68 eV	-6.65 eV

	 8	 9 (ref 2)	 10	 13
LUMO+1				
	-0.525 eV	-0.485 eV	-0.446 eV	-0.442 eV
LUMO				
	-0.801 eV	-0.559 eV	-0.492 eV	-0.696 eV
HOMO				
	-6.55 eV	-6.48 eV	-6.45 eV	-6.61 eV

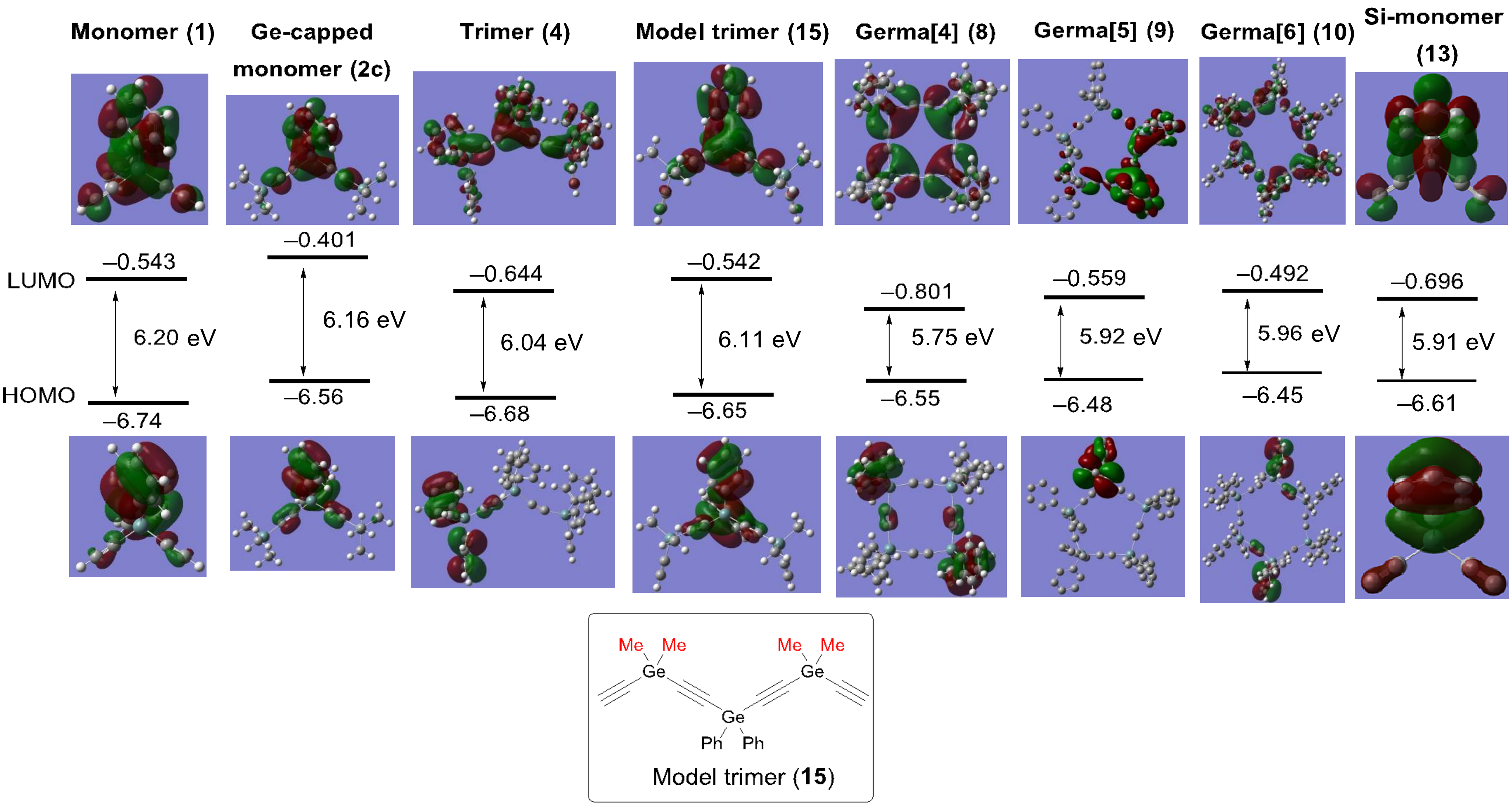
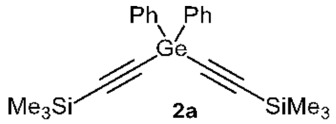
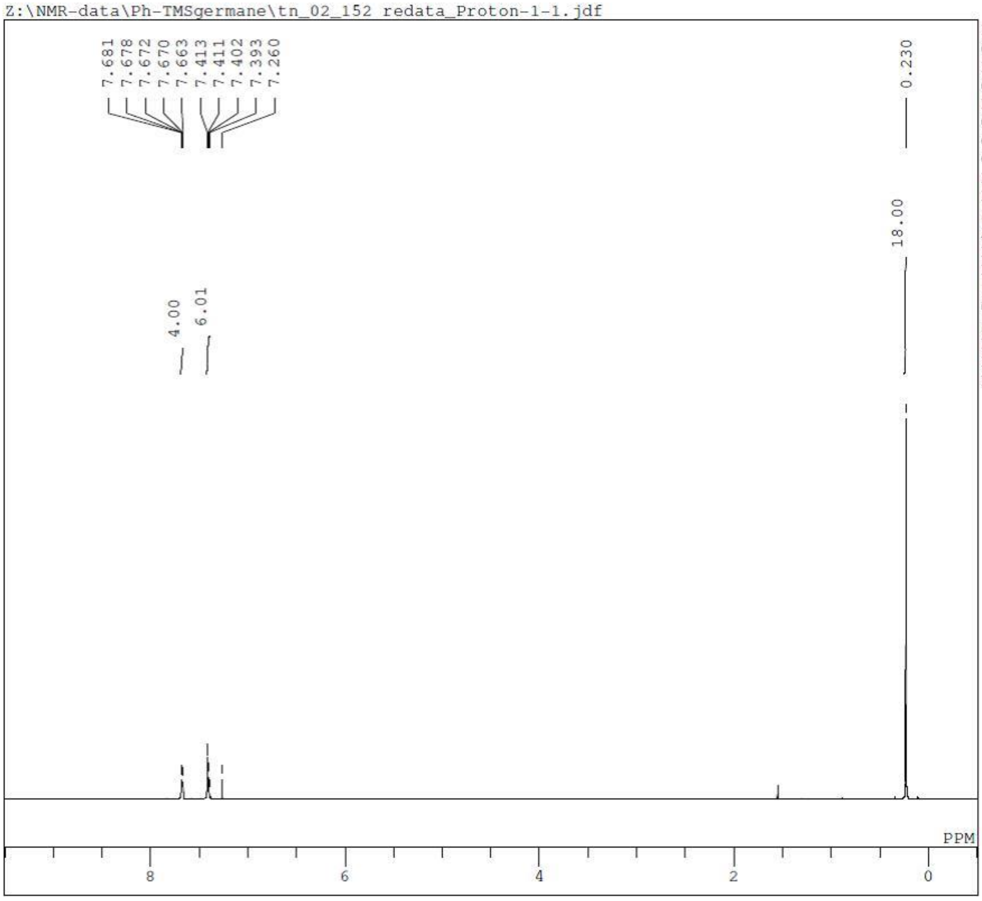


Fig SI 5. HOMO-LUMO orbitals and levels of acyclic/cyclic germylene-ethynylene materials



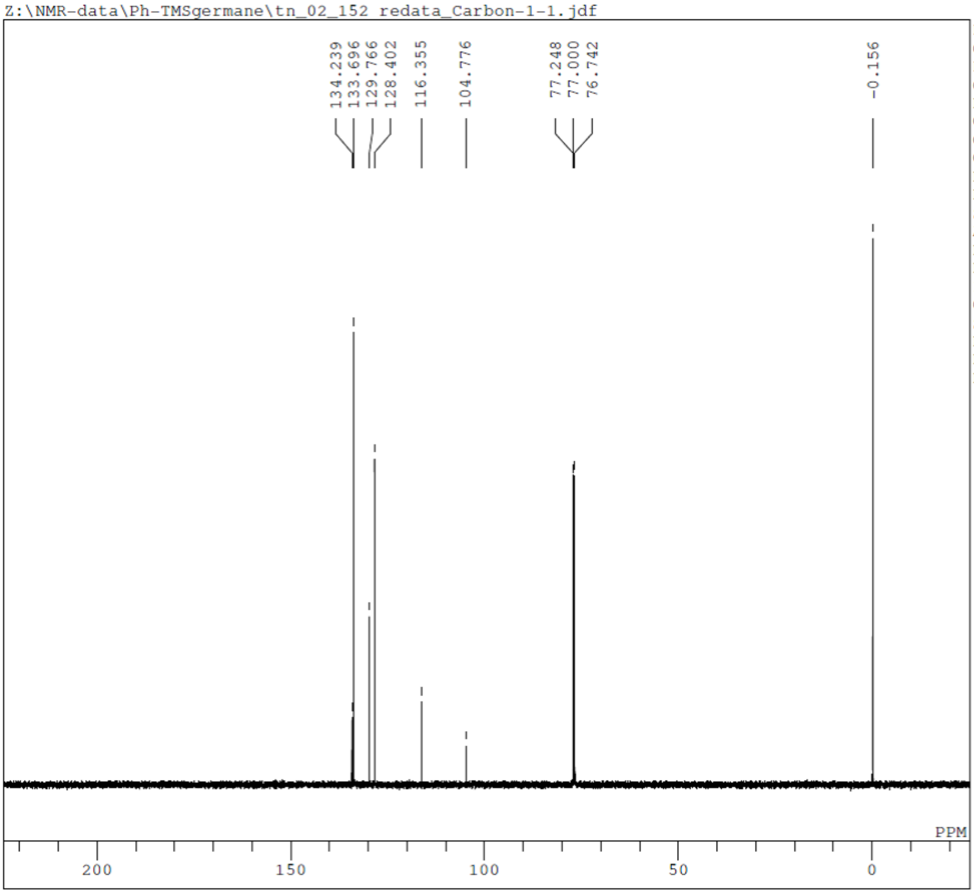
2a

Z:\NMR-data\Ph-TMSgermane\tn_02_152 redata_Proton-1-1.jdf

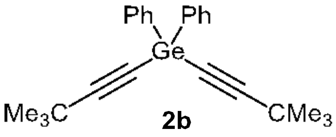


DFILE	tn_02_152 redata_Proton-1-1.jdf
COMNT	single_pulse
DATIM	2014-11-12 14:12:03
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16384
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.22 usec
IRNUC	1H
CTEMP	16.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	40

Z:\NMR-data\Ph-TMSgermane\tn_02_152 redata_Carbon-1-1.jdf

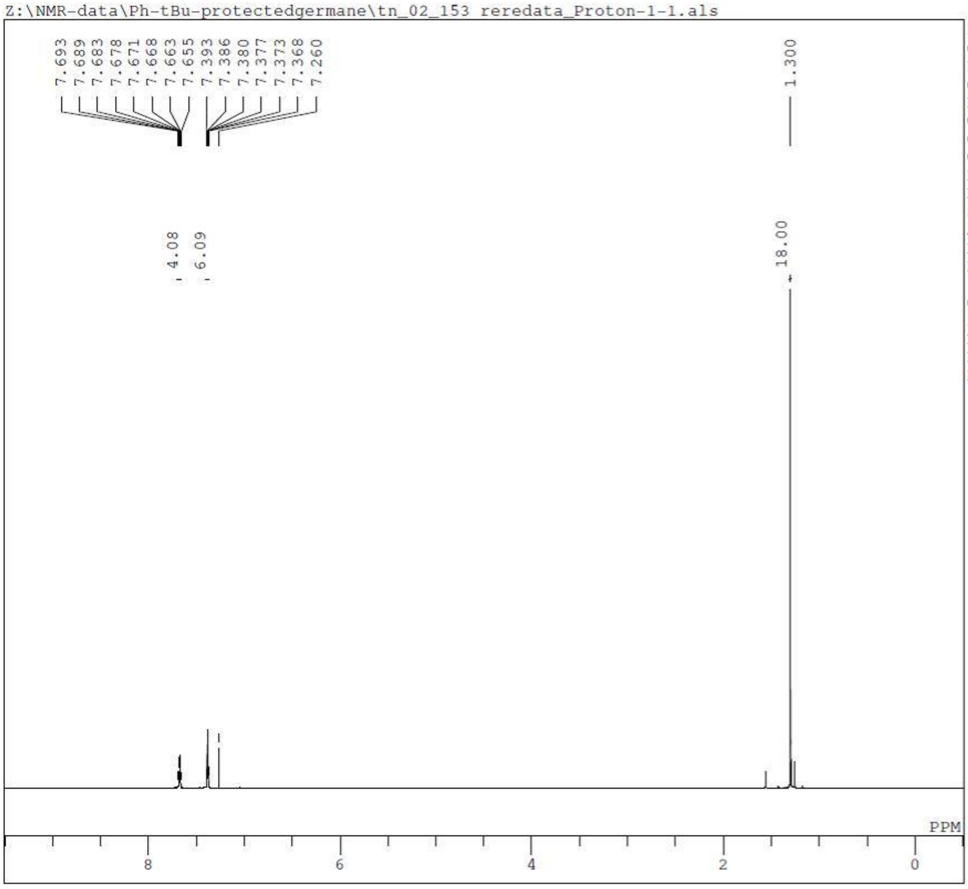


DFILE	tn_02_152 redata_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2014-11-12 13:34:23
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32767
FREQU	39308.18 Hz
SCANS	545
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	16.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



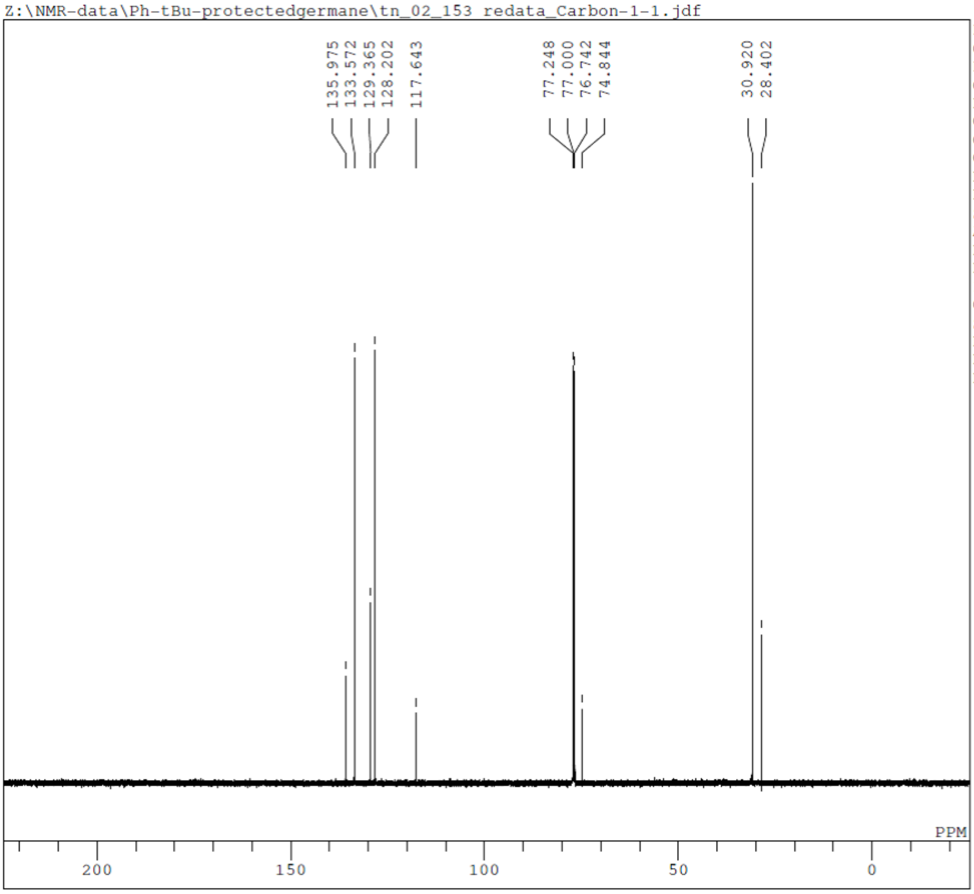
2b

Z:\NMR-data\Ph-tBu-protectedgermane\tn_02_153 reredata_Proton-1-1.als




```
DFILE  tn_02_153 reredata_Proton-1-1.als
COMNT  single_pulse
DATIM  2014-11-17 20:14:25
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT        13107
FREQU       7507.51 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          14.8 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            44
```

Z:\NMR-data\Ph-tBu-protectedgermane\tn_02_153 redata_Carbon-1-1.jdf

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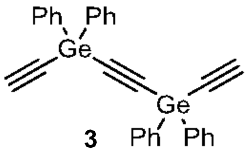
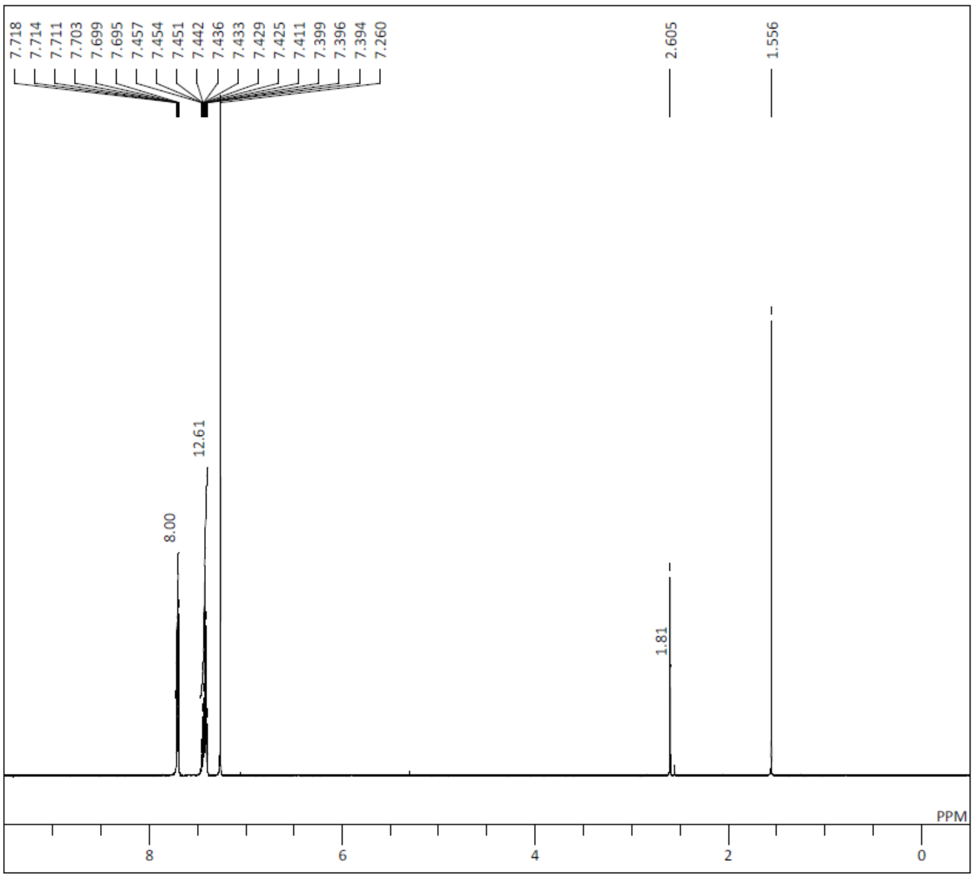
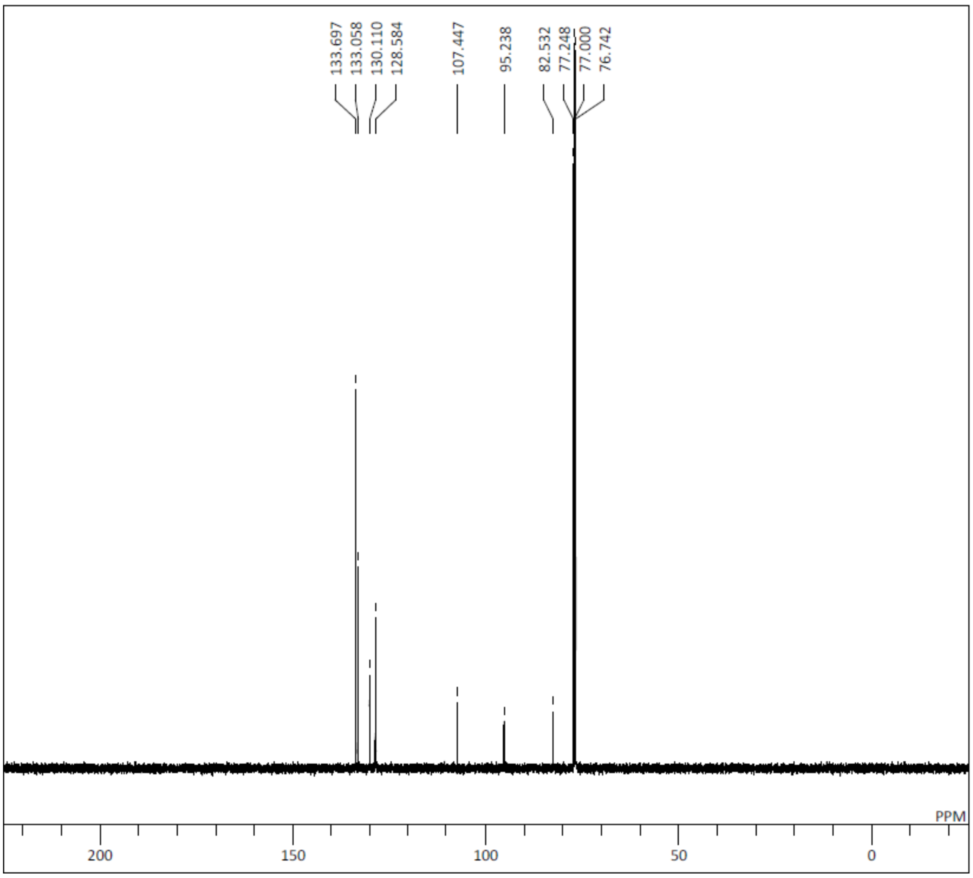
DFILE  tn_02_153 redata_Carbon-1-1.jdf
COMNT  single pulse decoupled gated NOE
DATIM  2014-11-14 17:58:09
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT        32767
FREQU      39308.18 Hz
SCANS         1024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          18.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            60
```



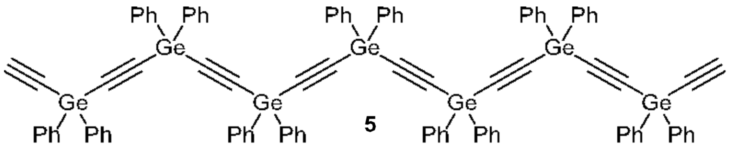
3



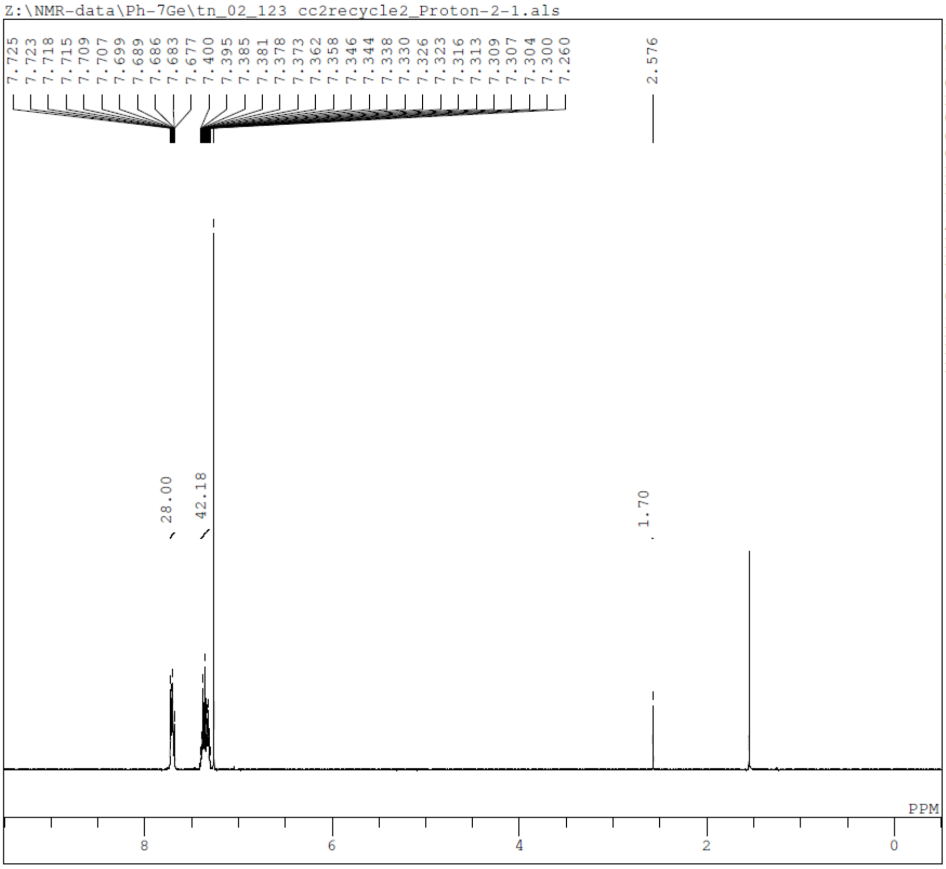
DFILE	Ph-Ge Dimer data_Proton-1-1.als
COMNT	single_pulse
DATIM	2014-12-17 21:14:38
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.22 usec
IRNUC	1H
CTEMP	15.3 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	48



DFILE	Dimer3_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2015-03-18 15:46:30
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	16.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	50

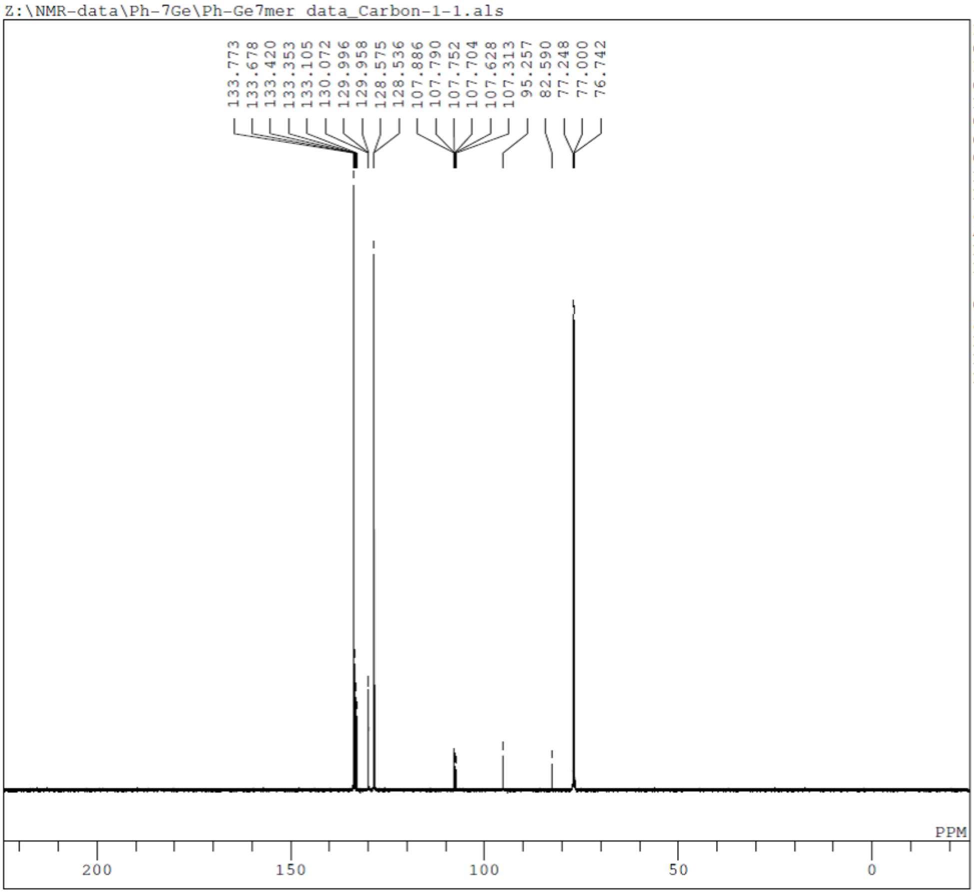


Z:\NMR-data\Ph-7Ge\tn_02_123 cc2recycle2_Proton-2-1.als

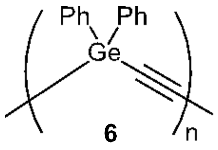


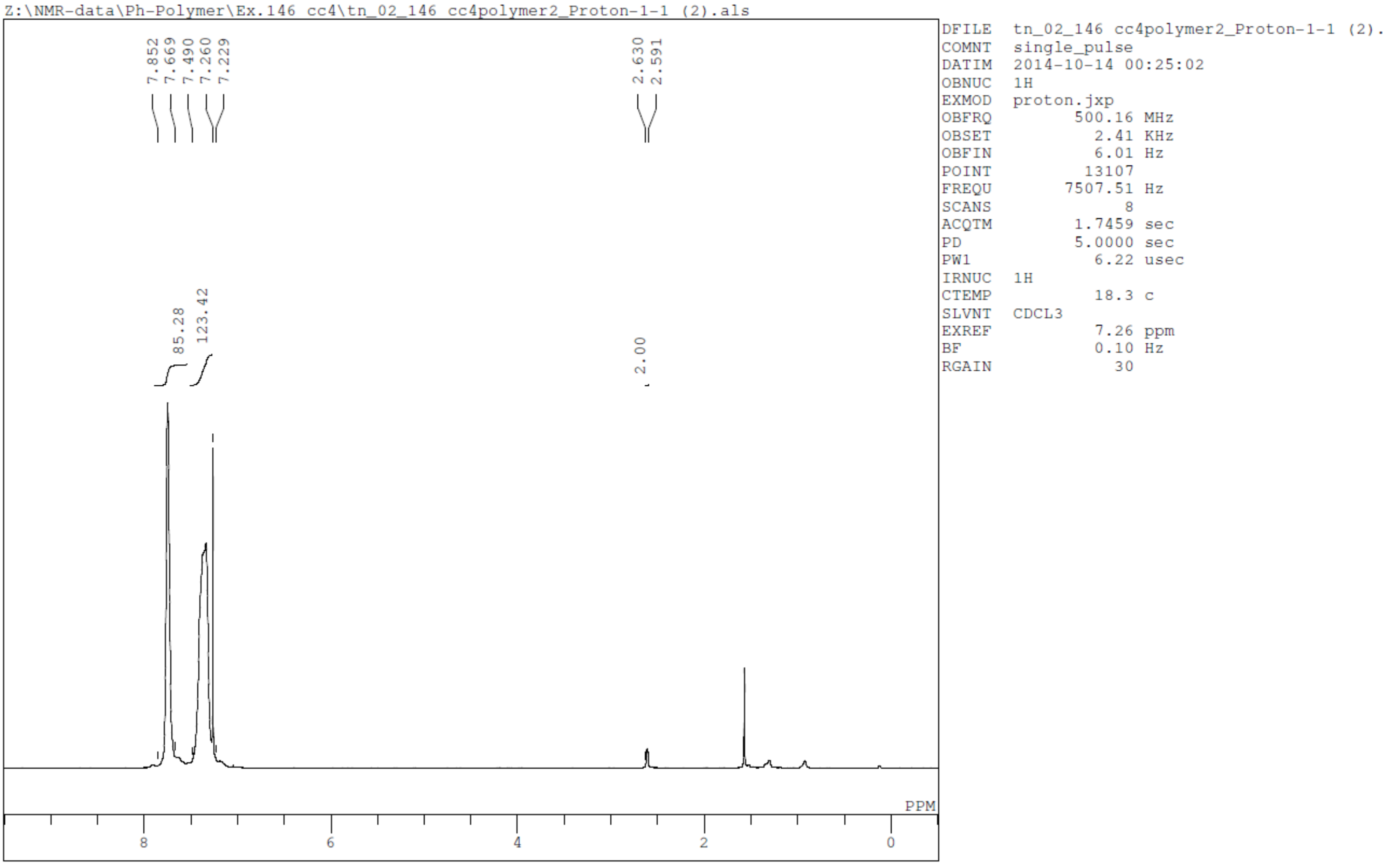

```
DFILE   tn_02_123 cc2recycle2_Proton-2-1.als
COMNT   single_pulse
DATIM   2014-10-27 19:51:40
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS              8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           16.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             50
```

Z:\NMR-data\Ph-7Ge\Ph-Ge7mer data_Carbon-1-1.als




```
DFILE   Ph-Ge7mer data_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2014-10-30 02:16:02
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS           4000
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           16.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             60
```


Ph
Ph
Ge
6
n


Z:\NMR-data\Ph-Polymer\Ex.146 cc4\tn_02_146 cc4polymer2_Proton-1-1 (2).als
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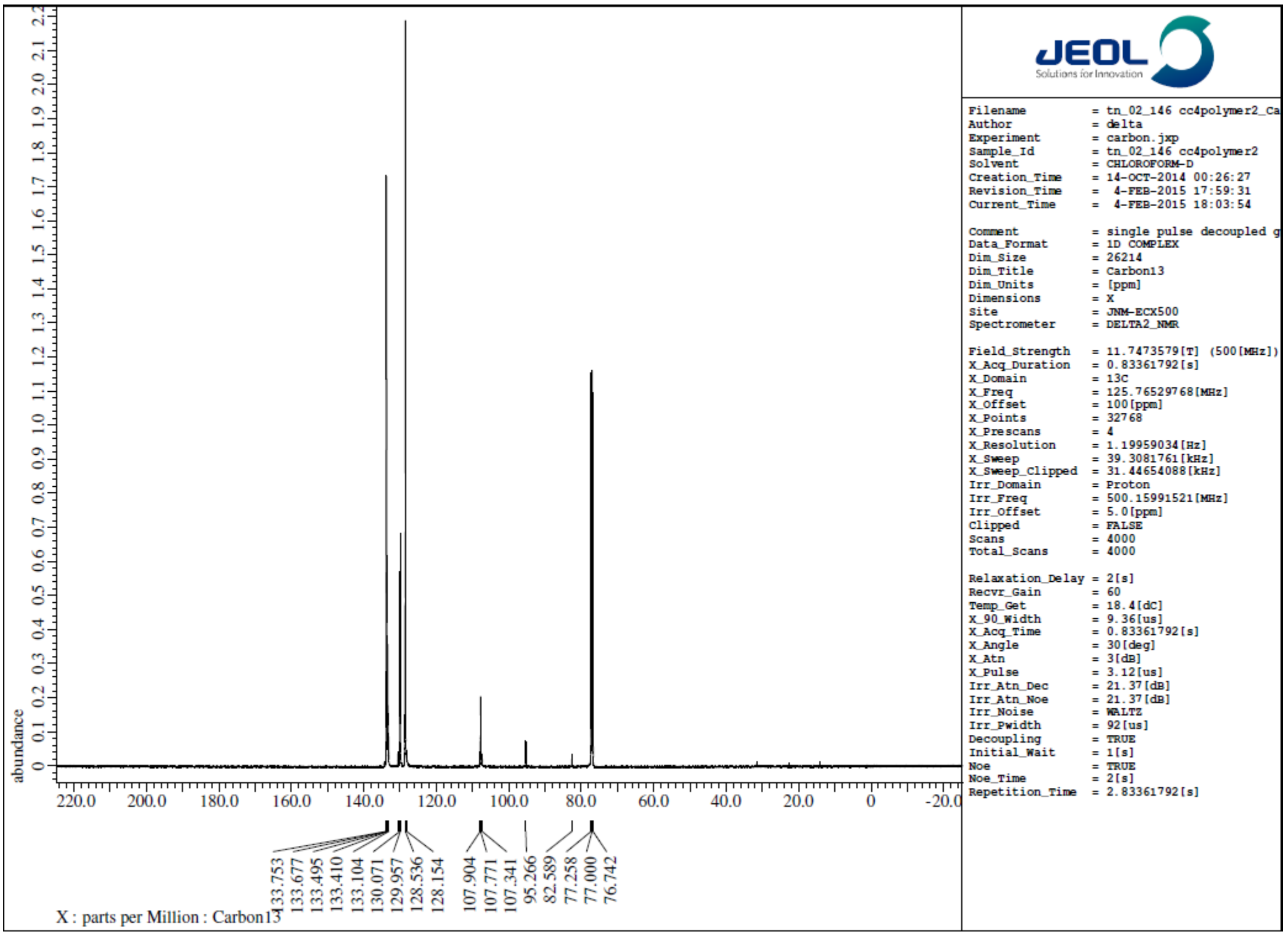
7.669
7.490
7.260
7.229
2.630
2.591
85.28
123.42
2.00
PPM
8
6
4
2
0
DFILE tn_02_146 cc4polymer2_Proton-1-1 (2).
COMNT single_pulse
DATIM 2014-10-14 00:25:02
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.22 usec
IRNUC 1H
CTEMP 18.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 30


abundance
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220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0
133.753
133.677
133.495
133.410
133.104
130.071
129.957
128.536
128.154
107.904
107.771
107.341
95.266
82.589
77.258
77.000
76.742
X : parts per Million : Carbon13
JEOL
Solutions for Innovation
Filename = tn_02_146 cc4polymer2_Ca
Author = delta
Experiment = carbon.jxp
Sample_Id = tn_02_146 cc4polymer2
Solvent = CHLOROFORM-D
Creation_Time = 14-OCT-2014 00:26:27
Revision_Time = 4-FEB-2015 17:59:31
Current_Time = 4-FEB-2015 18:03:54
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Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
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Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 4000
Total_Scans = 4000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 18.4[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 21.37[dB]
Irr_Atn_Noe = 21.37[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

•References

1) H. Tanimoto, T. Nagao, Y. Nishiyama, T. Morimoto, F. Iseda, Y. Nagato, T. Suzuka, K. Tsutsumi and K. Kakiuchi, *Dalton Trans*. 2014, **43**, 8338–8343.

2) H. Tanimoto, T. Nagao, T. Fujiwara, Y. Nishiyama, T. Morimoto, T. Suzuka, K. Tsutsumi and K. Kakiuchi, *Dalton Trans.* 2015, **44**, 11811–11818