Electronic Supplementary Material (ESI) for Dalton Transactions.
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Supporting Information

Synthesis and Characterization of Germa[*n*]pericyclynes

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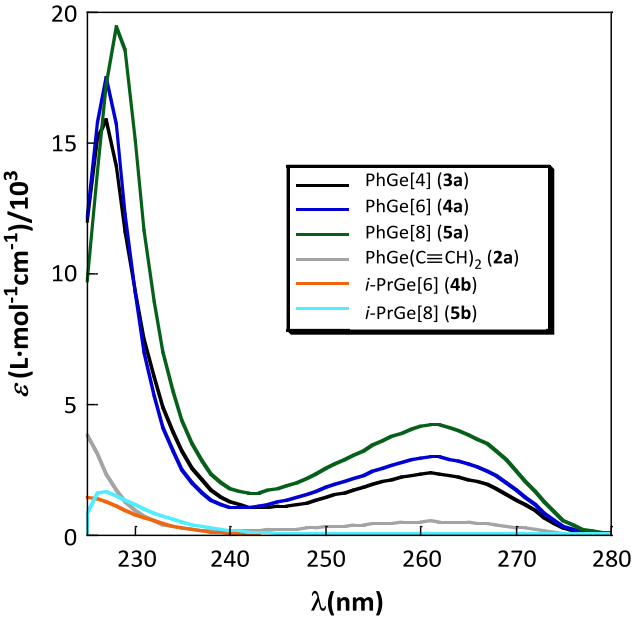
General information

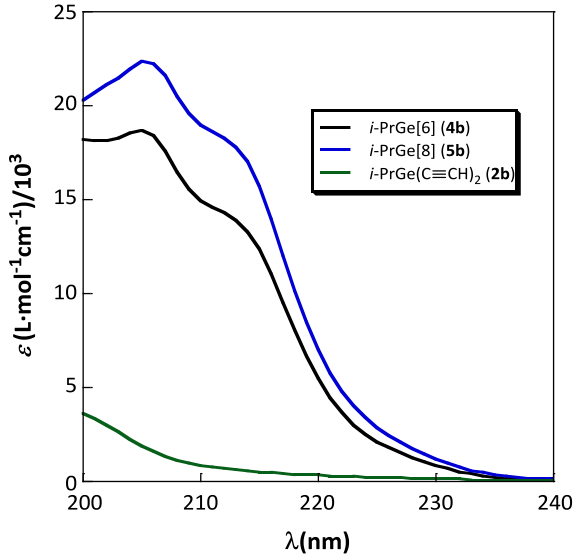
^{1}H and ^{13}C NMR spectra were recorded using a Jeol JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak ($CDCl_3$, δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR) or tetramethylsilane (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]. X-ray diffraction (XRD) analyses were performed using a Rigaku R-AXIS RAPID/S imaging plate diffractometer. UV/visible spectra were recorded using Jasco V-630. Fluorescence spectra were collected using Jasco FP-6500. Raman spectra were obtained using a Jasco laser Raman spectrophotometer, NRS-2100. 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 purification of the mixture of germapericyclynes was performed using a LC-908 recycling preparative high-performance liquid chromatography (HPLC) equipped with a JAIGEL 2H-40 column made by Japan Analytical Industry Co., Ltd. Ethanol solutions of phosphomolybdic acid and anisaldehyde-acetic acid-sulfuric acid were used as the TLC stains. 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. 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 6-311G* basis set in this series of calculations.

UV-visible and fluorescence emission spectra



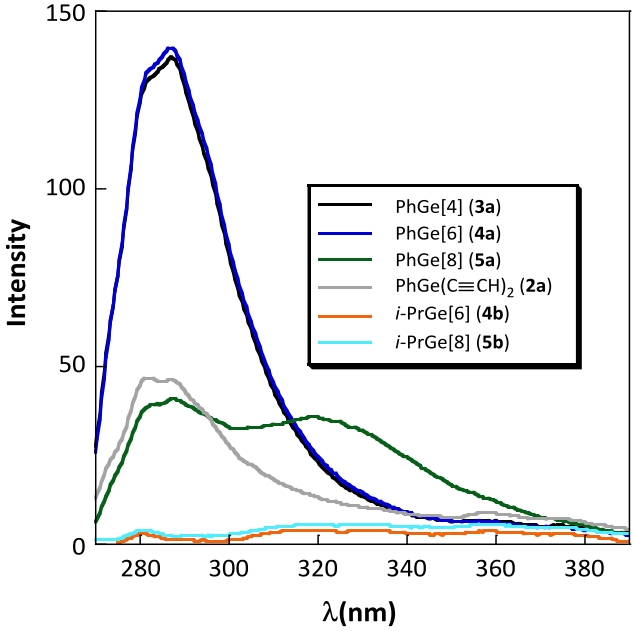
Compounds	Absorption maxima / nm (ε)
2a	225 (3840), 261 (531)
3a	227 (15900), 261 (2375)
4a	227 (17500), 261 (3010)
5a	228 (19440), 261 (4240)
4b	225 (1446)
5b	227 (1648)

Fig S1. UV-visible spectra of germa[*n*]pericyclynes (0.1 mM in CH_2Cl_2)



Compounds	Absorption maxima / nm (ε)
2b	—
4b	205 (18683), 213 (13919)
5b	205 (22377), 213 (17798)

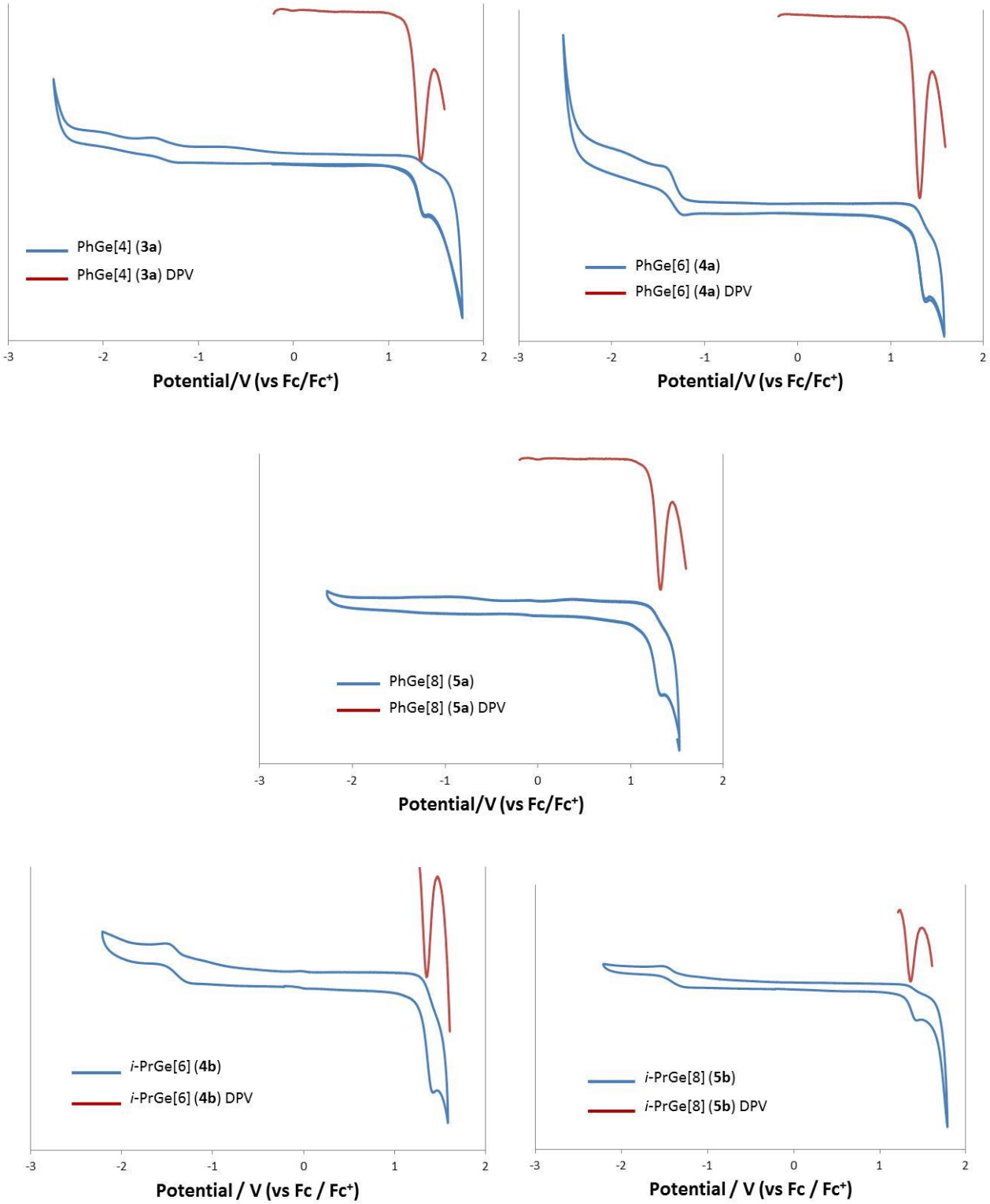
Fig S2. UV-visible spectra of isopropylgerma[*n*]pericyclynes (0.1 mM in hexane)



Compounds	Emission maxima / nm
2a	282, 288
3a	281, 288
4a	281, 288
5a	281, 288, 318
4b	—
5b	—

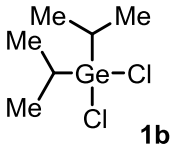
Fig S3. Fluorescence emission spectra of germa[*n*]pericyclynes (0.1 mM in CH_2Cl_2, λ_{EXT} = 260 nm)

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



Compounds	Oxidation potential from DPV / V
3a	1.336
4a	1.312
5a	1.320
4b	1.352
5b	1.356

Fig S3. Cyclic and differential pulse voltammograms of germa[*n*]pericyclynes (1.0 mM (3a, 4a, 4b, and 5b); 0.5 mM (5a) in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 solution; Scan rate = 0.1 V/s)



1b

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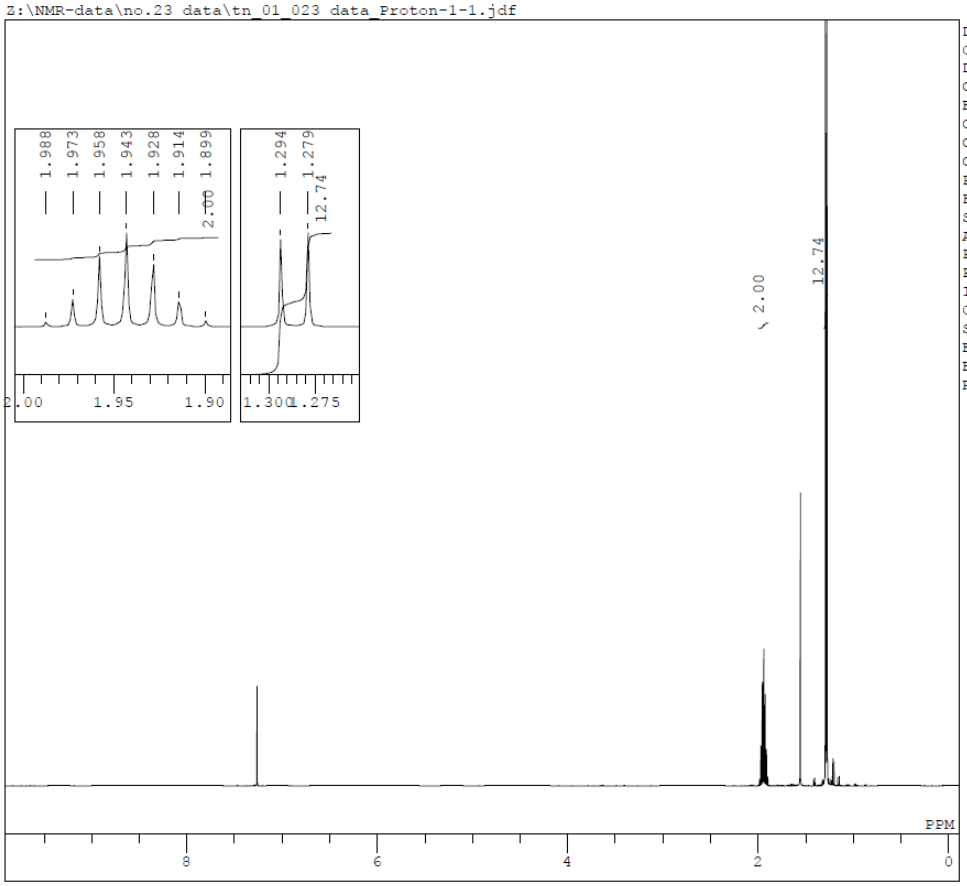


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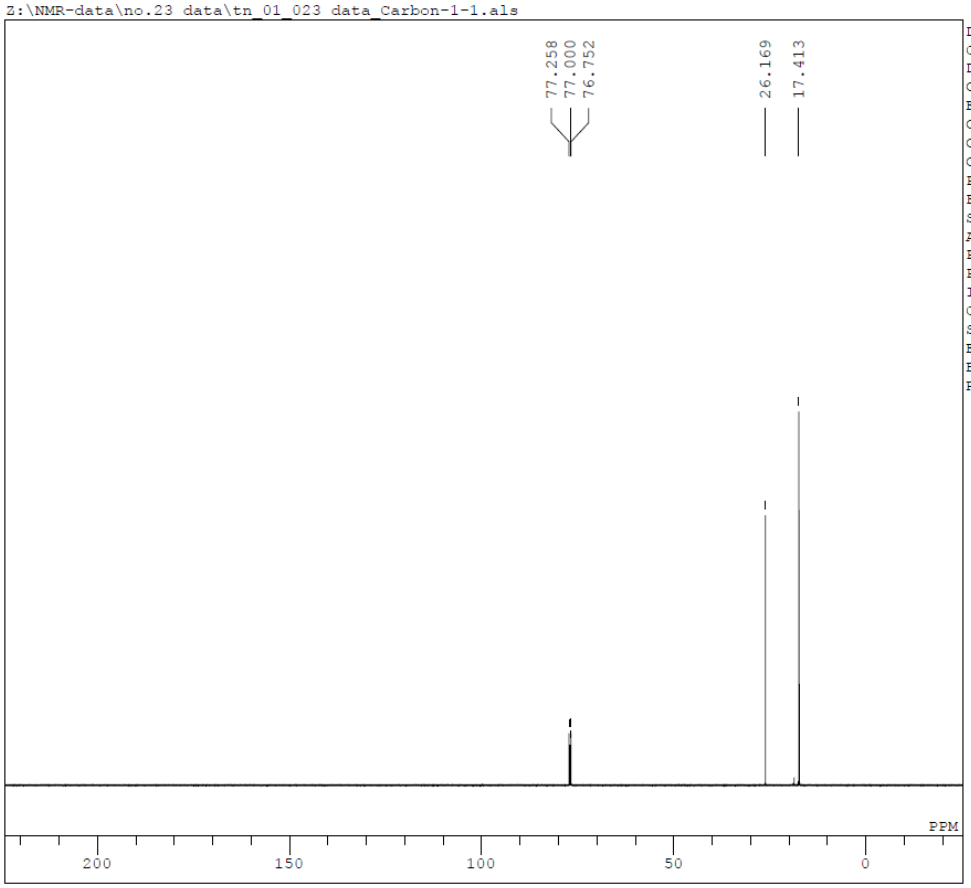


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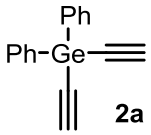

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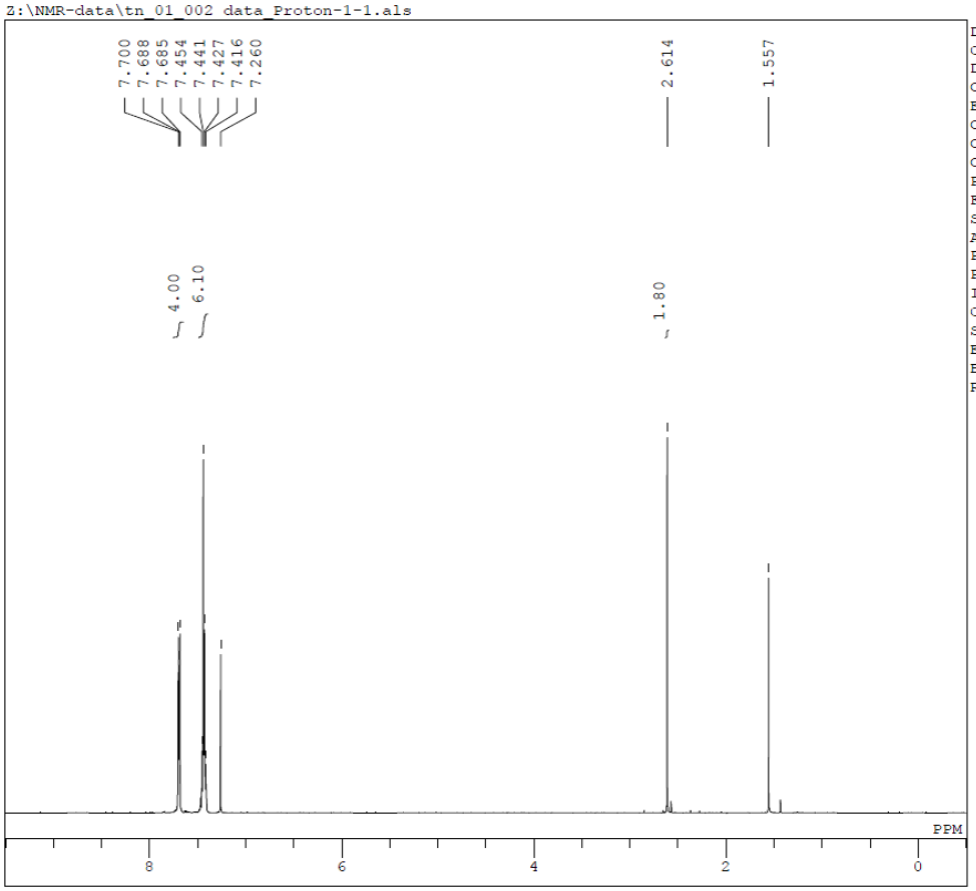


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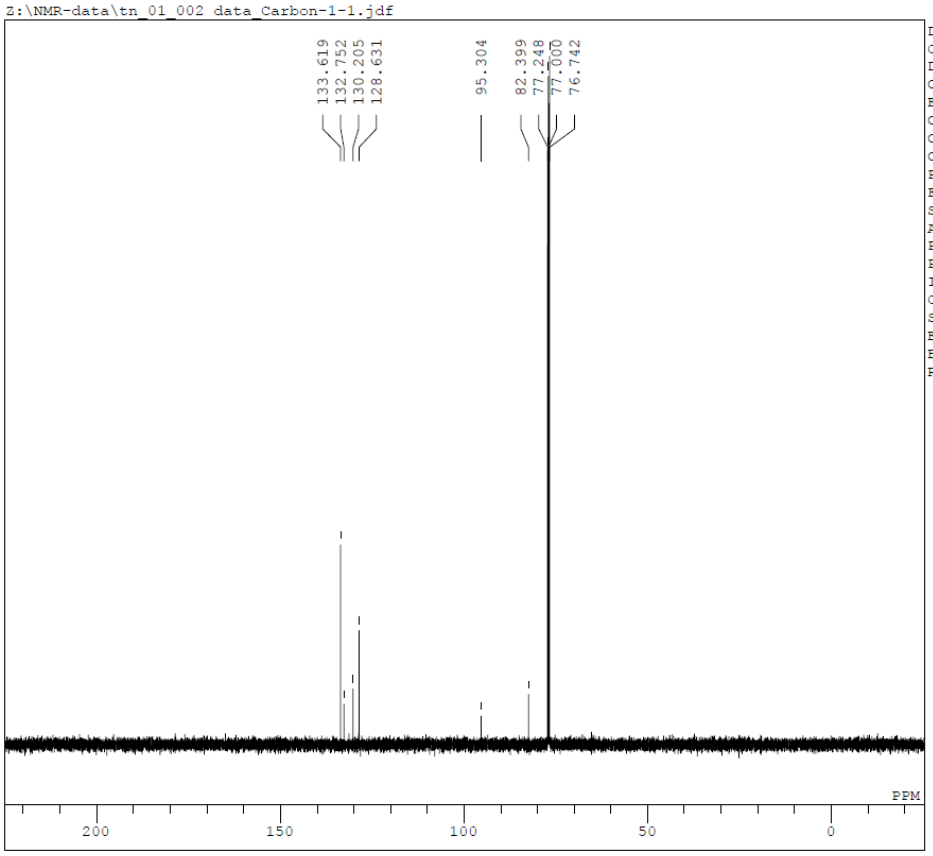


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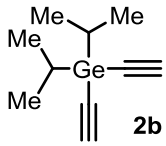

2b

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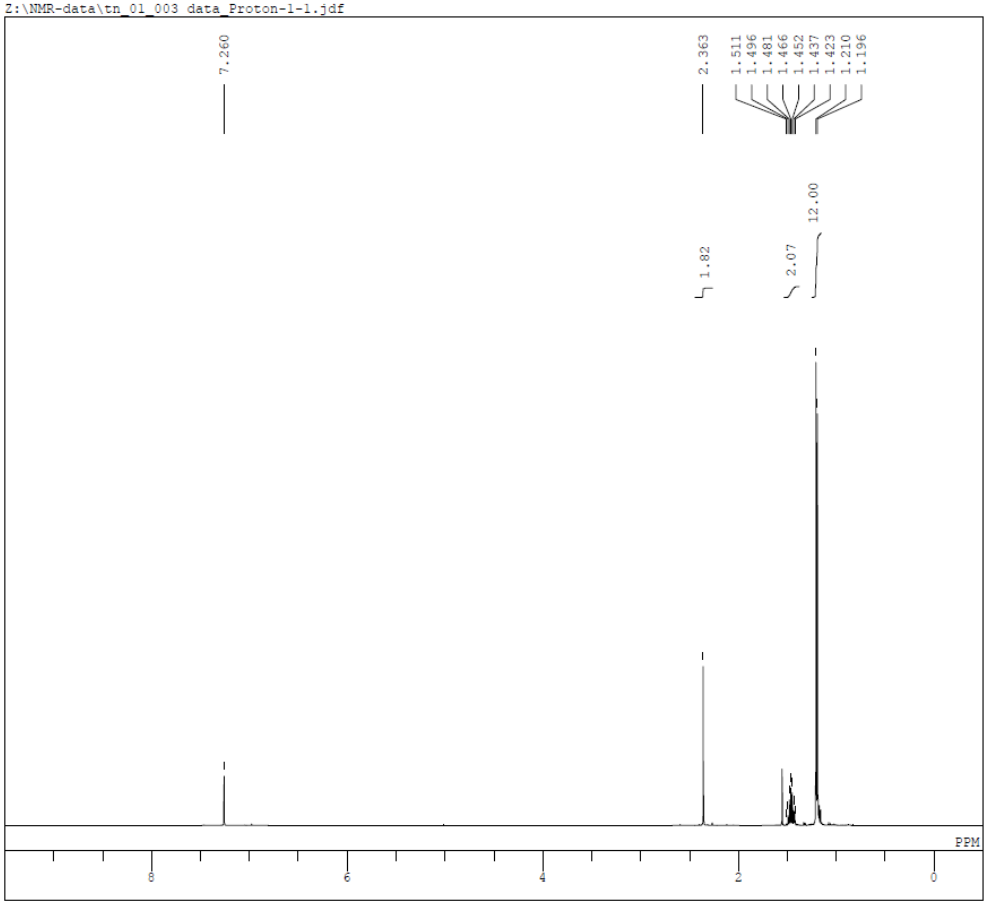


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CTEMP          19.1 c
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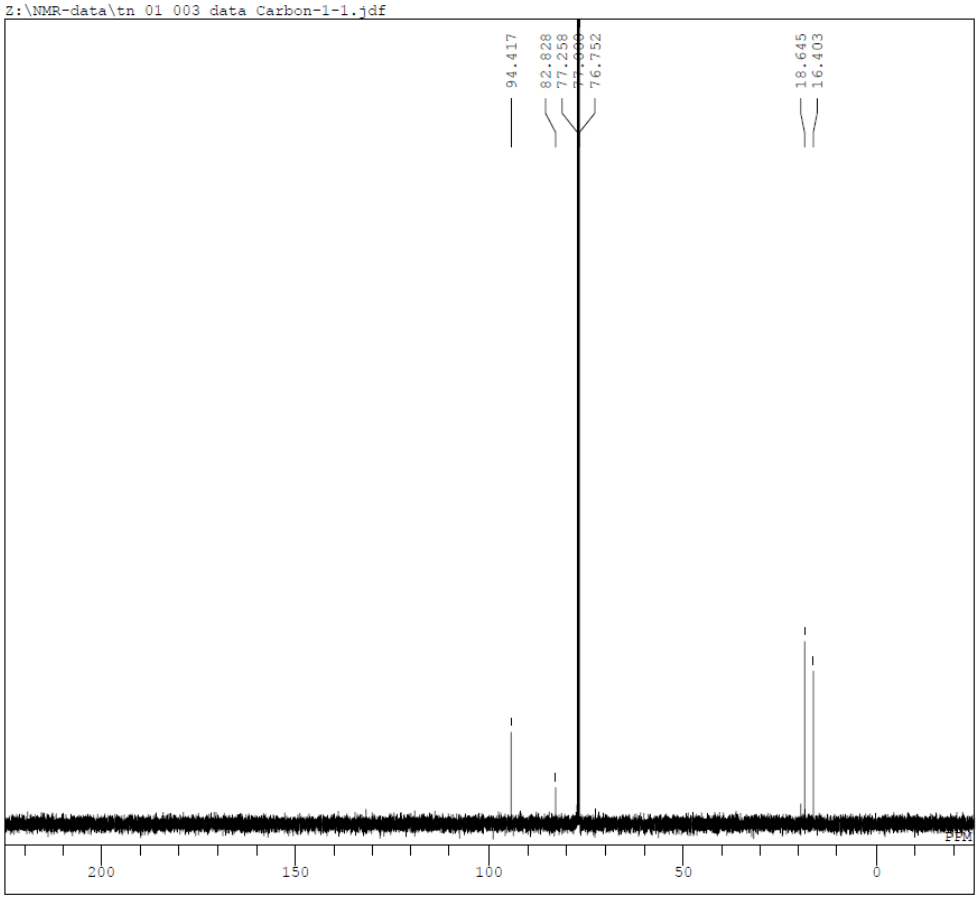


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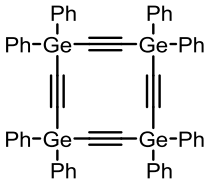
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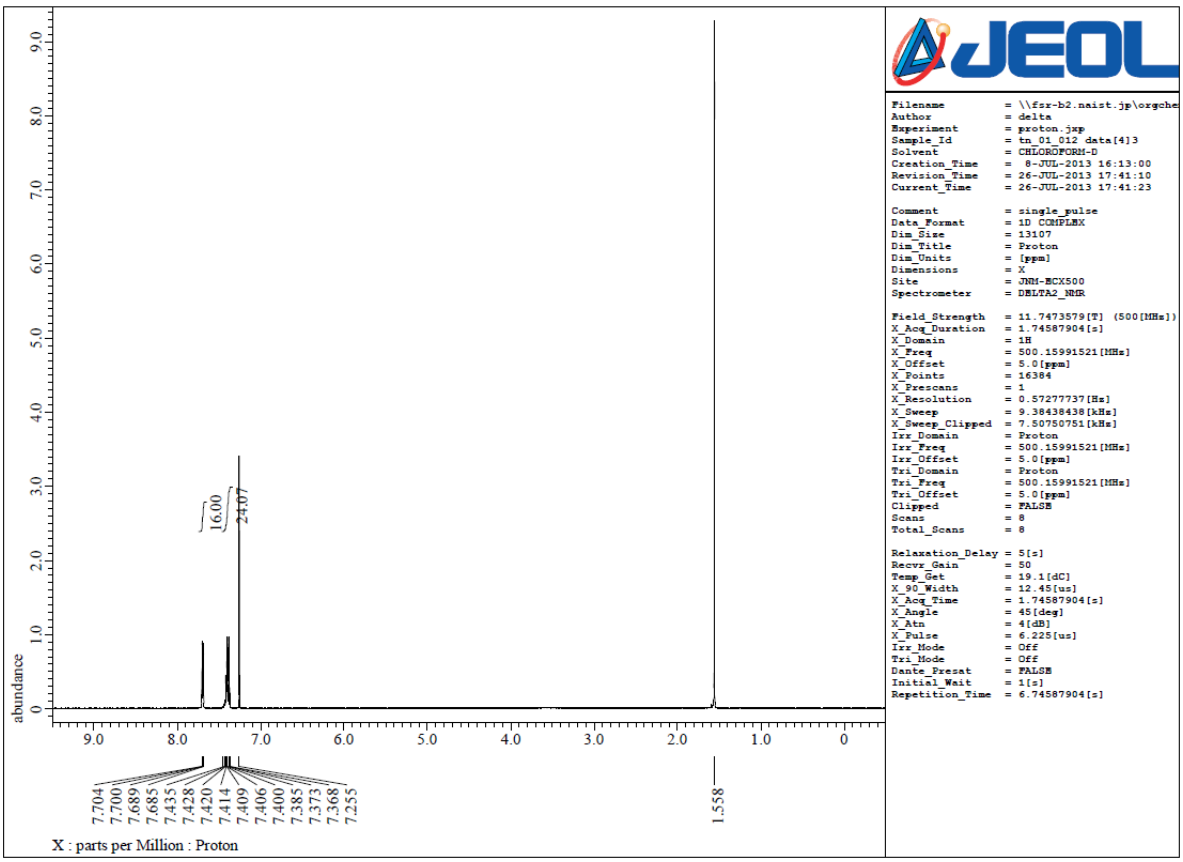
Ph
Ph-Ge
Ge-Ph
Ph-Ge
Ge-Ph
Ph
Ph

3a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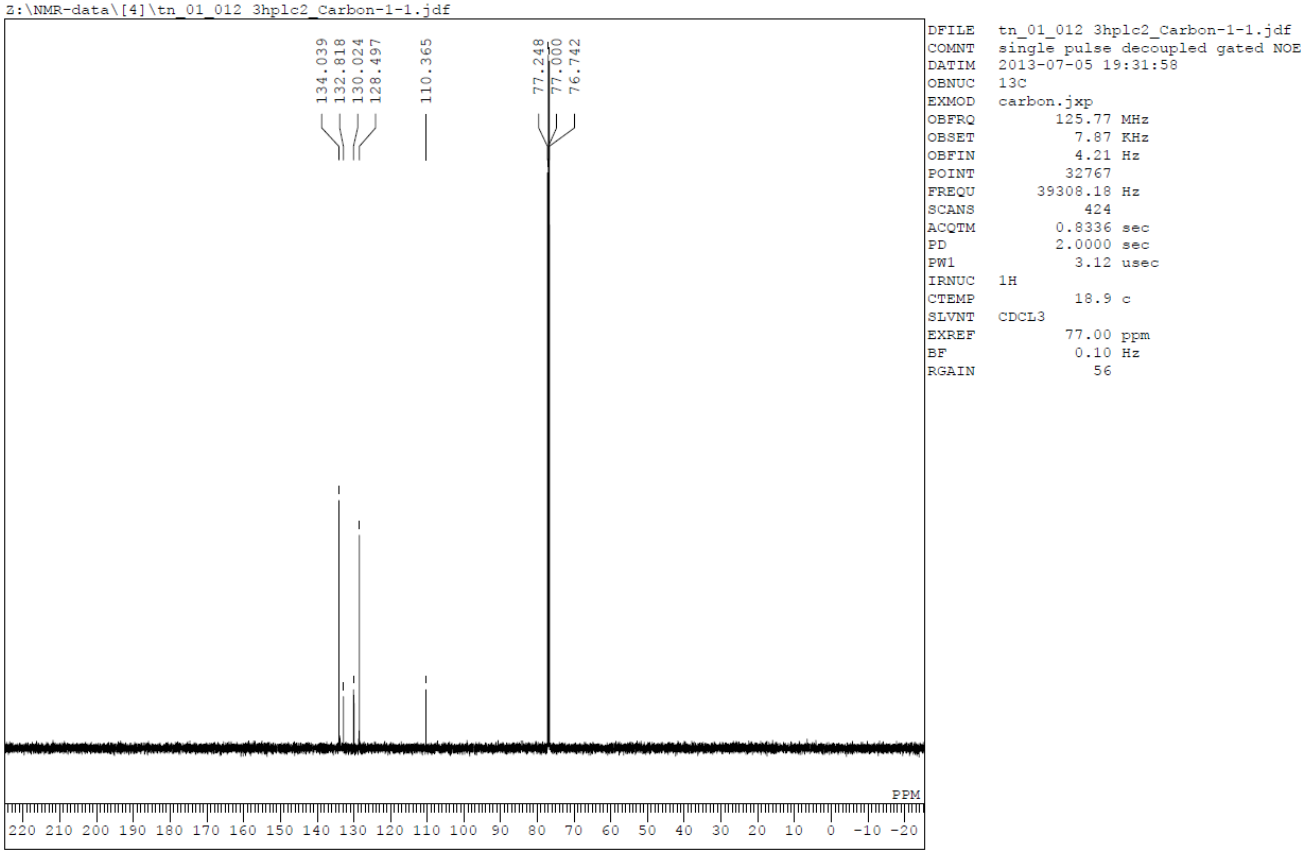
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77.000
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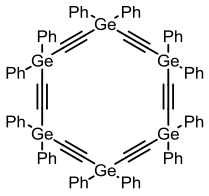
RGAIN 56



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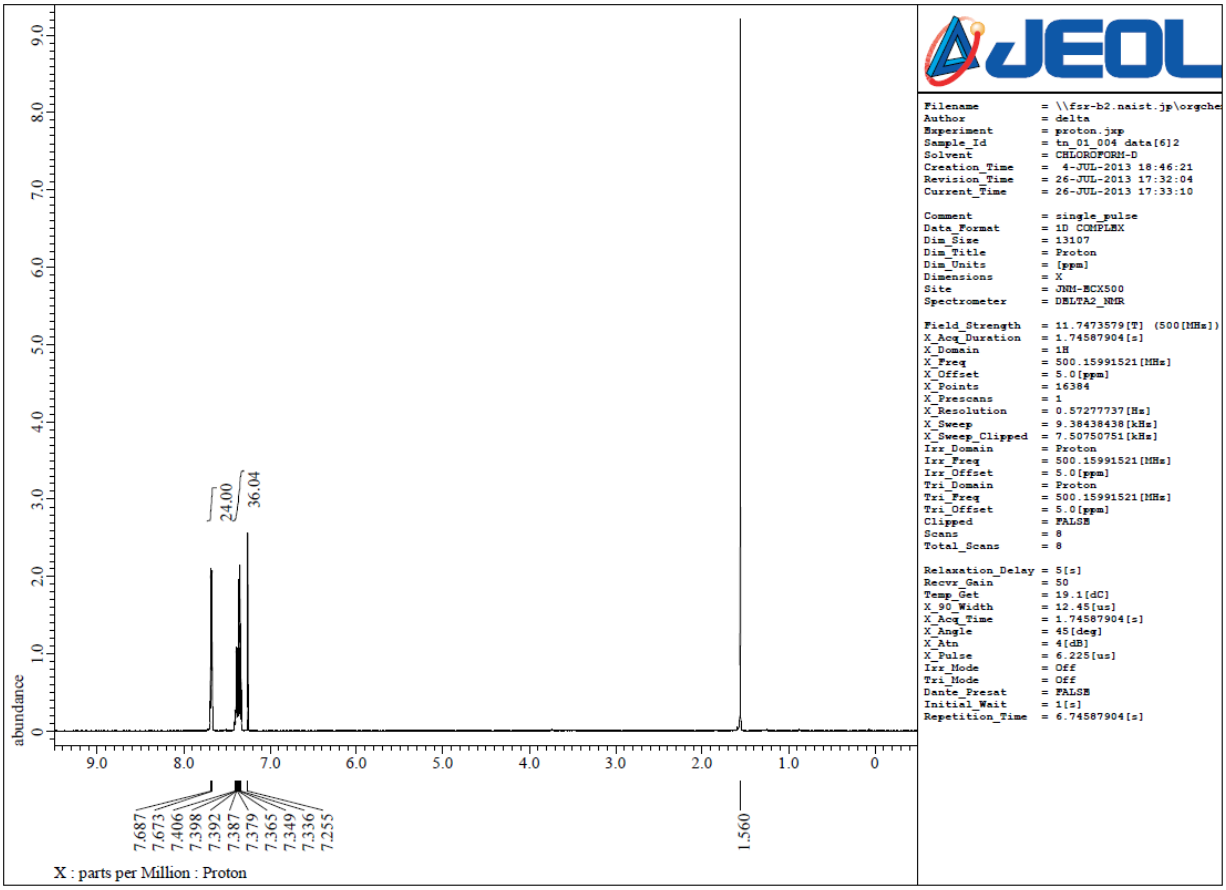


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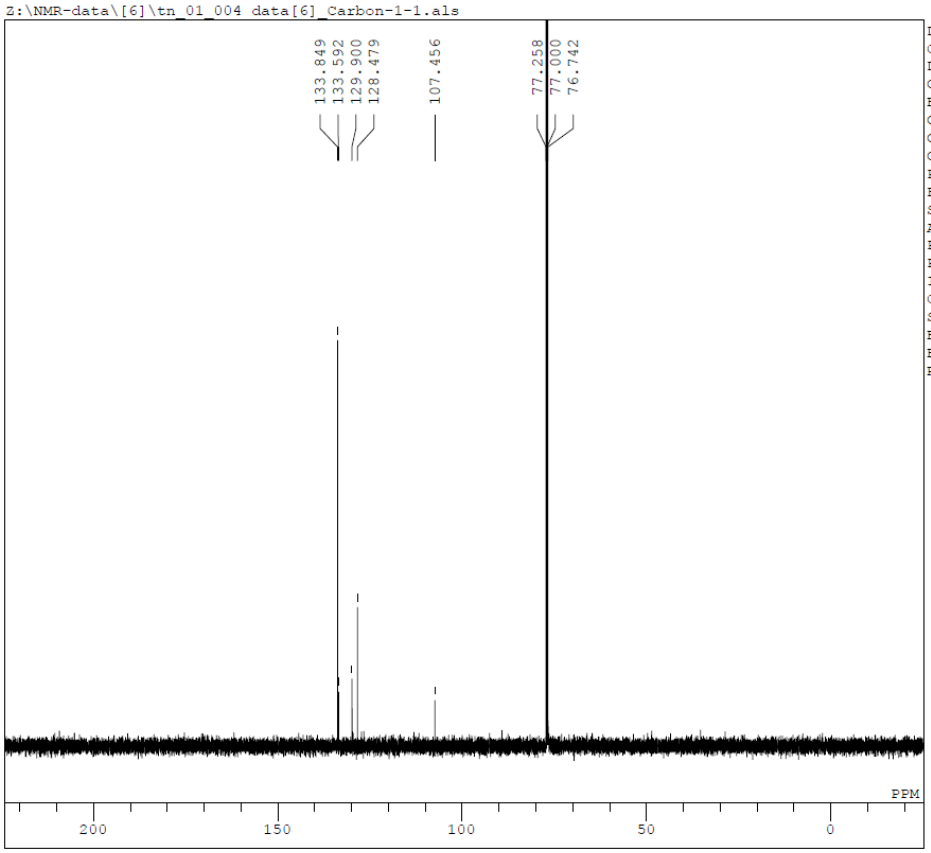


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RGAIN           58
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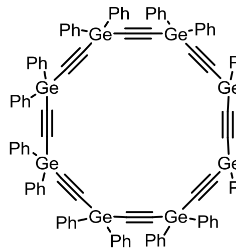

5a

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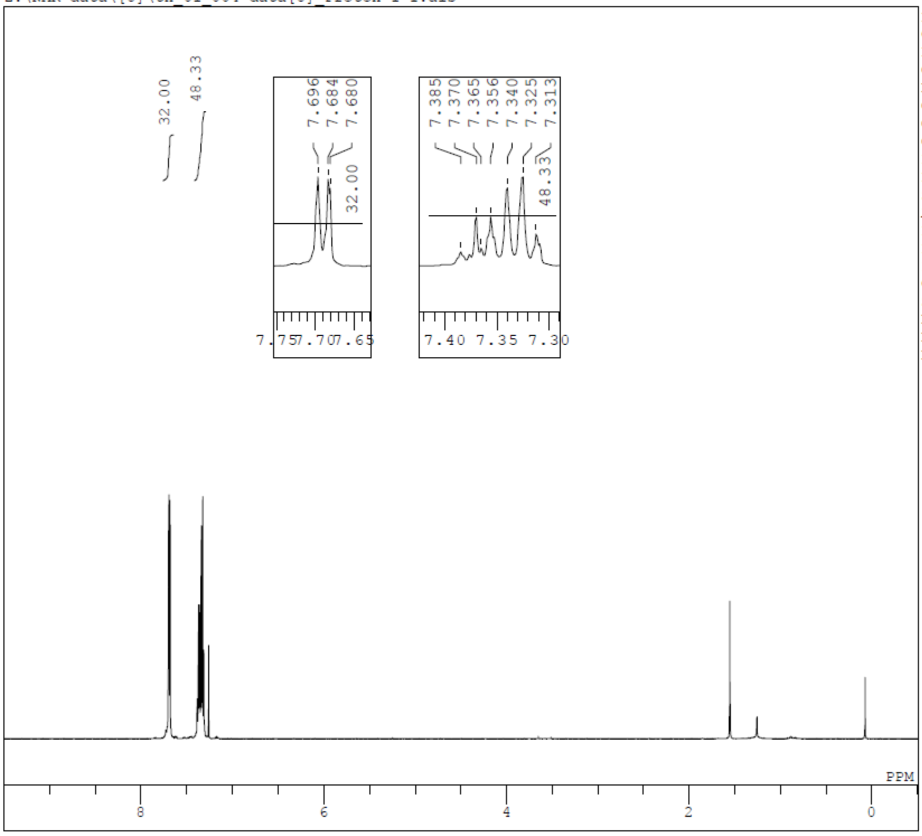

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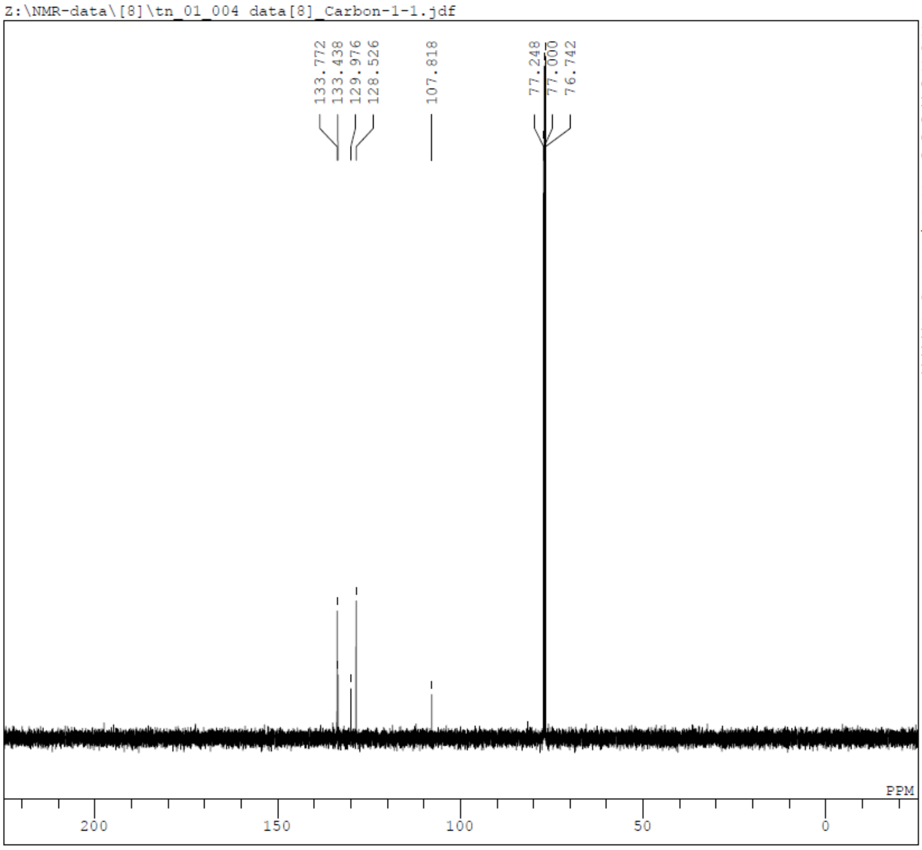

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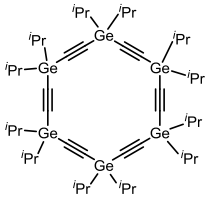
RGAIN 58



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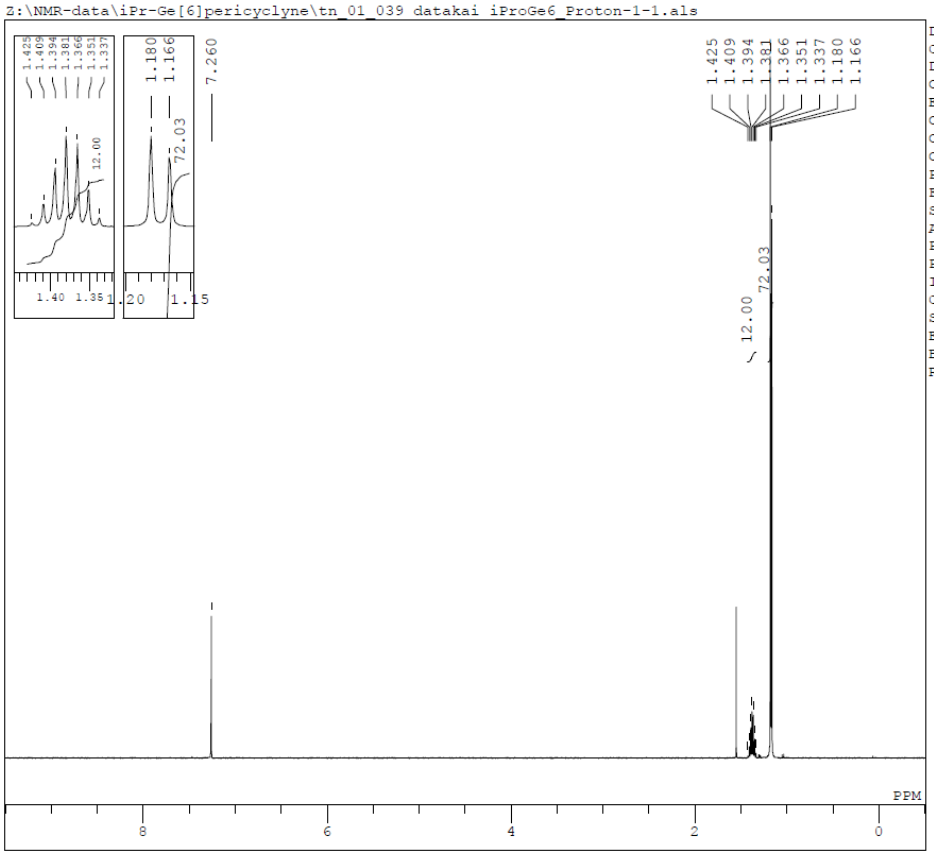


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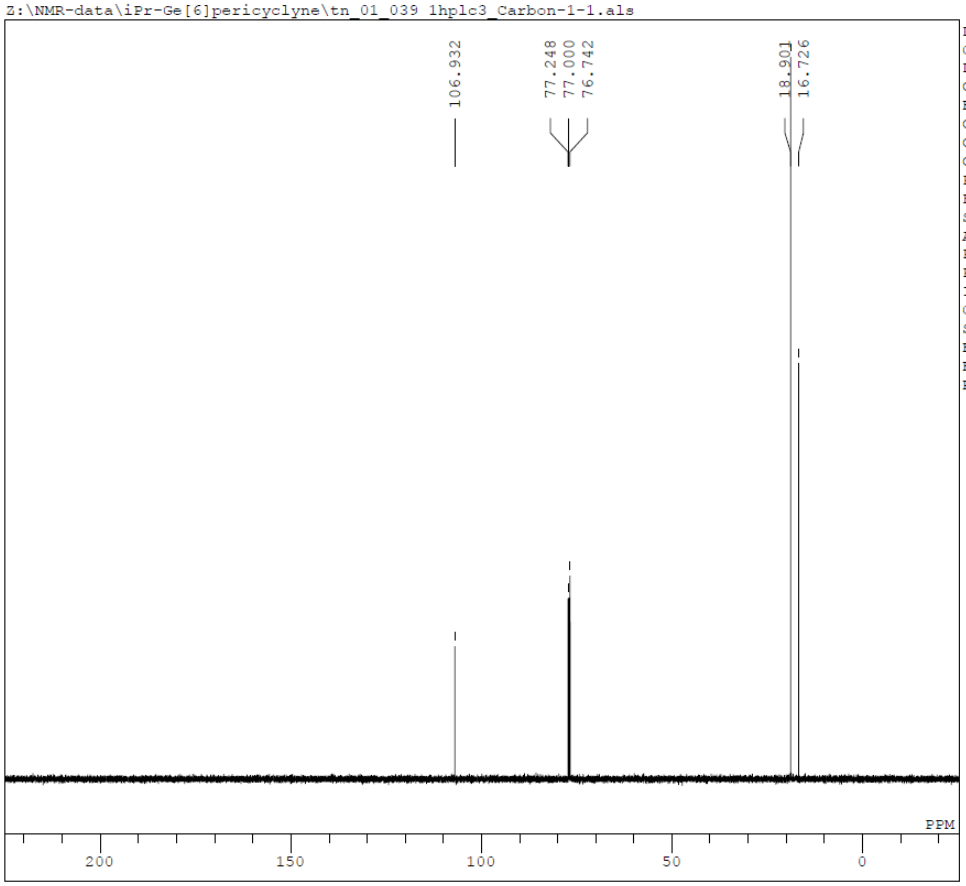
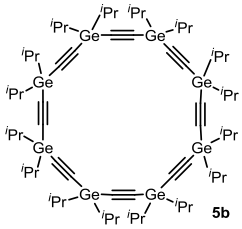
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           16.6 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             50
```

Z:\NMR-data\iPr-Ge[6]pericyclyne\tn_01_039 1hplc3_Carbon-1-1.als

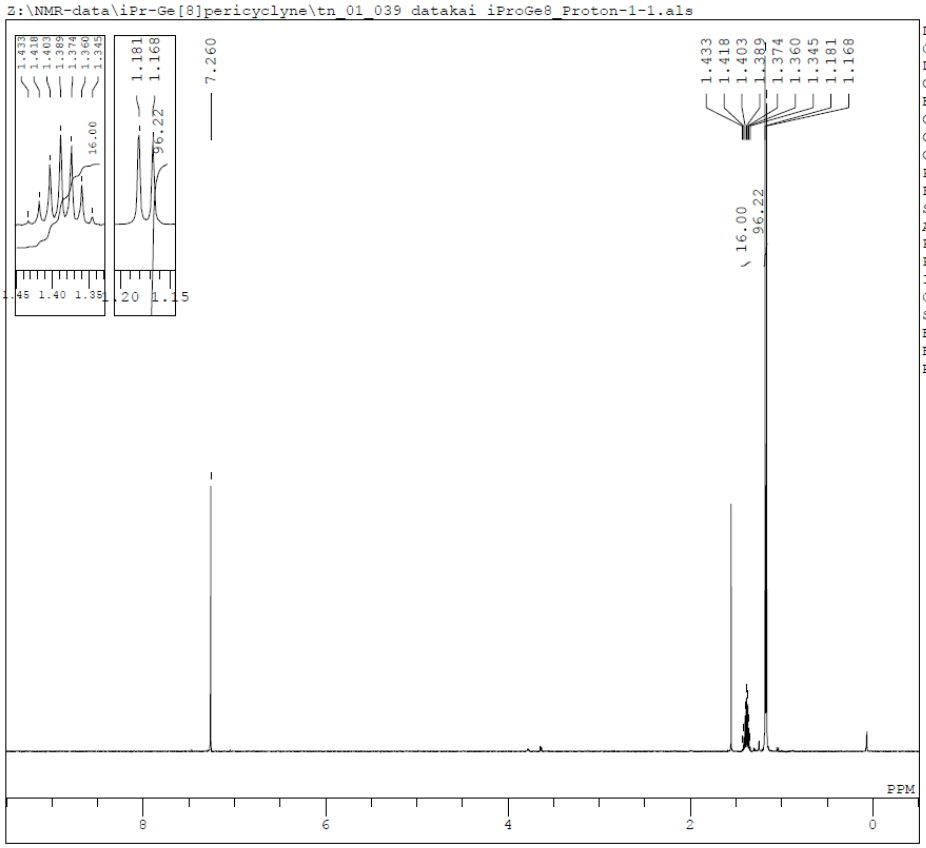



```
DFILE   tn_01_039 1hplc3_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2013-11-09 04:42:20
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS             52
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           16.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             56
```



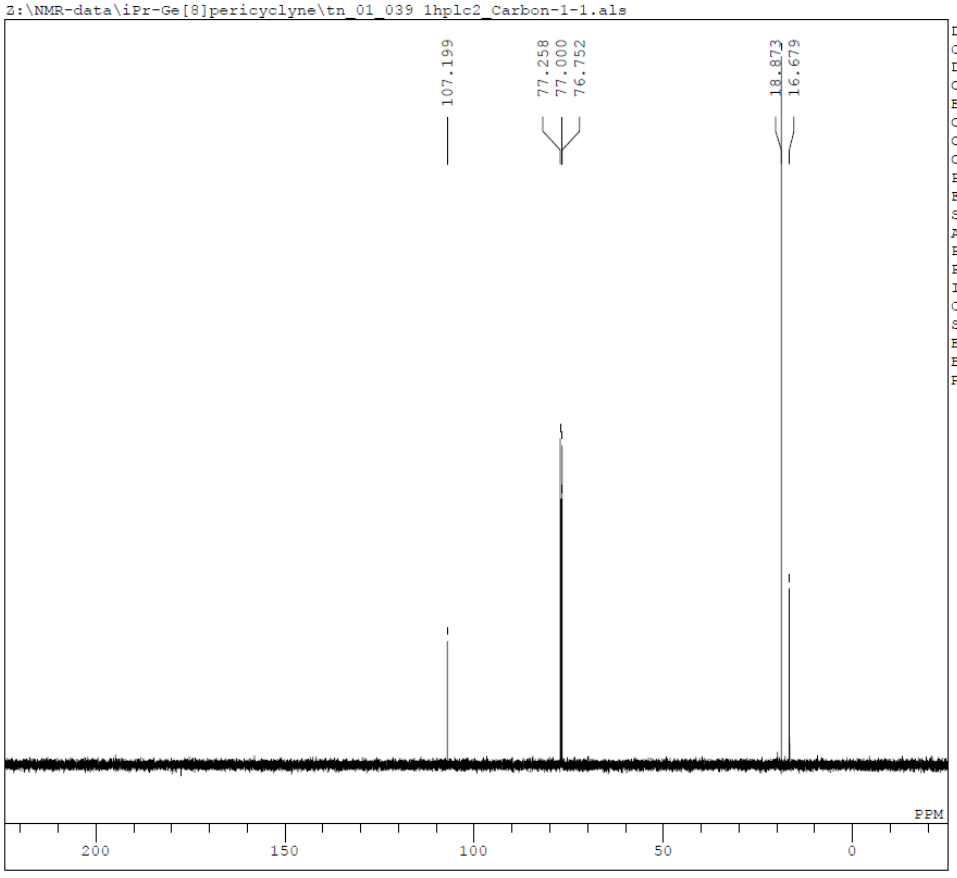
5b

Z:\NMR-data\iPr-Ge[8]pericyclyne\tn_01_039 datakai iProGe8_Proton-1-1.als




```
DFILE   tn_01_039 datakai iProGe8_Proton-1-1.a
COMNT   single_pulse
DATIM   2013-11-14 19:24:09
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           16.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             50
```

Z:\NMR-data\iPr-Ge[8]pericyclyne\tn_01_039 1hplc2_Carbon-1-1.als




```
DFILE   tn_01_039 1hplc2_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2013-11-09 04:31:55
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU        31446.54 Hz
SCANS              45
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             56
```