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Supporting Information
for DOI: 10.1055/a-2404-2853

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# Supporting Information

## Formation of Carbon–carbon *Double* Bond between Cp Ligand and Alkenyl Carbon of Titanacyclopentenes.

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## Materials and Methods

General Information.

All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox under nitrogen or argon. $^{1}$H NMR (at 400 or 600 MHz) and $^{13}$C NMR (at 101 or 151 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane or given relative to the respective residual solvent peaks ($^{1}$H: $CHCl_3$ at 7.26, $C_6H_6$ at 7.16, $^{13}$C: $CHCl_3$ at 77.16, $C_6H_6$ at 128.06). NMR yields were determined by using dichloromethane or mesitylene as internal standard. Tetrahydrofuran (THF) and toluene were distilled from benzophenone-ketyl under nitrogen prior to use. All the other chemicals were obtained from commercial sources unless otherwise noted. All yields were calculated according to the alkynes used in the formation of titanacyclopentadiene or titanacyclopentene.

The following instruments were used for characterization of the compounds.

| | |
|---|---|
| NMR | JEOL JNM-ECX400 ($^{1}$H: 400 MHz, $^{13}$C: 101 MHz)<br>JEOL JNM-ECX600 ($^{1}$H: 600 MHz, $^{13}$C: 151 MHz) |
| GC | SHIMADZU GC-14B gas chromatograph<br>SHIMADZU CBP1-M25-025 fused capillary column<br>SHIMADZU CR-6A-Chromatopac integrator |
| GPC | Japan Analytical Industry LC-9201<br>JAIGEL column 2H, JAIGEL column H-P |

For the column chromatography, silica gel 60N (spherical, neutral, 100-210 μm) was used and the fraction was monitored by TLC (Merck TLC Silica gel 60 $F_{254}$).

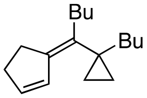
## Representative Procedures for Synthesis of 2.

A typical procedure is given for the synthesis of **2a**. To a solution of Cp$_2$TiCl$_2$ (156mg, 0.625 mmol) in THF (2.5 mL) was added EtMgBr (1.0 M in THF, 1.25 mL, 1.25 mmol) dropwise at –78 ºC, and the mixture was stirred for 1 h at the same temperature. After addition of 5-decyne (0.09 mL, 0.5 mmol) at –78 ºC, the mixture was warmed up to –30 ºC and stirred for 3 h to form bis（η$^5$-cyclopentadienyl)titanacyclopentene **1a**. To the deep red solution was added TEMPO (156.2 mg, 1.0 mmol) and the mixture was stirred for 30 min at the same temperature. After addition of BiI$_3$ (295 mg, 0.5 mmol) at –30 ºC, the mixture was heated to 50 ºC and stirred for 1 h. After the solution was cooled to –20 ºC, the reaction was quenched with 12 M aqueous HCl and extracted with hexane. The organic phase was washed with water, aqueous saturated NaHCO$_3$ and brine, dried over Na$_2$SO$_4$, filtered, then evaporated. The crude product was further purified by column chromatography using silica gel (eluent: hexane) and GPC, which gave **2a** as a colorless oil (36 mg, yield 31%). Product **2a** was obtained as a mixture of double-bond positional isomers in a ratio of 34:66.

## Synthesis of 2a

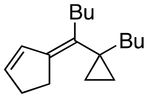
Product **2a** was obtained as a mixture of double-bond positional isomers in a ratio of 34:66.
NMR yield: 56%. Isolated yield: 31%.

**(Z)-3-(1-(1-butylcyclopropyl)pentylidene) cyclopent-1-ene (2a, minor isomer).**



$^1$H NMR (400MHz, C$_6$D$_6$): δ 0.48-0.50 (m, 2H), 0.68-0.71 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 1.22-1.40 (m, 8H), 1.47-1.55 (m, 2H), 2.16-2.21 (m, 2H), 2.31-2.33 (m, 2H), 2.38-2.41 (m, 2H), 5.92 (dt, *J* = 5.7 Hz, 2.8 Hz, 1H), 6.80 (dt, *J* = 5.8 Hz, 2.2 Hz, 1H) $^{13}$C{$^1$H} NMR(400MHz, C$_6$D$_6$): δ 13.7 (2C), 14.3, 14.4, 23.5, 23.9, 25.8, 28.0, 30.0, 31.8, 31.8, 35.0, 40.1, 131.0, 133.0, 135.5, 144.6. HRMS(EI) Calcd for C$_{17}$H$_{28}$: 232.2191. Found:232.2185.

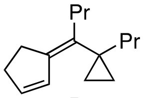
**(E)-3-(1-(1-butylcyclopropyl)pentylidene) cyclopent-1-ene (2a, major isomer).**



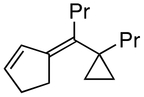
$^1$H NMR (400MHz, C$_6$D$_6$): δ 0.46-0.48 (m, 2H), 0.67-0.70 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H), 1.22-1.43 (m, 8H), 1.47-1.55 (m, 2H), 2.26-2.30 (m, 2H), 2.34-2.38 (m, 2H), 2.59-2.62 (m, 2H), 5.91 (dt, *J* = 5.7 Hz, 2.8 Hz, 1H), 6.45 (dt, *J* = 6.0 Hz, 2.2 Hz, 1H) $^{13}$C{$^1$H} NMR(400MHz, C$_6$D$_6$): δ 13.6 (2C), 14.3, 14.4, 23.6, 23.8, 26.3, 28.1, 30.0, 32.5, 34.1, 34.5, 39.3, 131.2, 132.8, 135.7, 144.5. HRMS(EI) Calcd for C$_{17}$H$_{28}$: 232.2191. Found:232.2183.

## Synthesis of 2b

Product **2b** was obtained as a mixture of double-bond positional isomers in a ratio of 35:65.
NMR yield: 47%. Isolated yield: 24%.



**(Z)-3-(1-(1-propylcyclopropyl)butylidene) cyclopent-1-ene**
**(2b, minor isomer).**

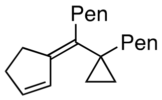


**(E)-3-(1-(1-propylcyclopropyl)butylidene) cyclopent-1-ene**
**(2b, major isomer).**

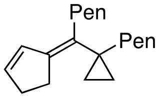
$^1$H NMR (400MHz, C$_6$D$_6$): δ 0.43-0.47 (m, major - 2H, minor - 2H), 0.62-0.67 (m, major - 2H, minor - 2H), 0.83-0.88 (m, major - 3H, minor - 3H), 0.89-0.96 (m, major - 3H, minor - 3H), 1.28-1.56 (m, major - 6H, minor - 6H), 2.11-2.15 (m, minor - 2H), 2.20-2.24 (m, major - 2H), 2.30-2.38 (m, major - 2H, minor - 4H), 2.54-2.58 (m, major – 2H), 5.9 (m, major - 1H, minor - 1H), 6.40 (dt, *J* = 5.7 Hz, 2.3 Hz, major - 1H), 6.71 (m, *J* = 5.7 Hz, 2.2 Hz, minor - 1H) $^{13}C\{^1H\}$ NMR (400MHz, $C_6D_6$): δ 13.5 (2C), 13.6 (2C), 14.8, 14.9, 15.0, 15.1, 21.0, 21.1, 22.8, 25.0, 25.8, 26.2, 28.0, 28.0, 31.8, 32.4, 37.0, 37.5, 42.0, 42.8, 130.9, 131.0, 132.8, 133.1, 135.5, 135.6, 144.6, 144.8. HRMS(EI) Calcd for $C_{15}H_{24}$: 204.1878. Found:204.1877.

**Synthesis of 2c**

Product **2c** was obtained as a mixture of double-bond positional isomers in a ratio of 34:66.
NMR yield: 57%. Isolated yield: 33%.



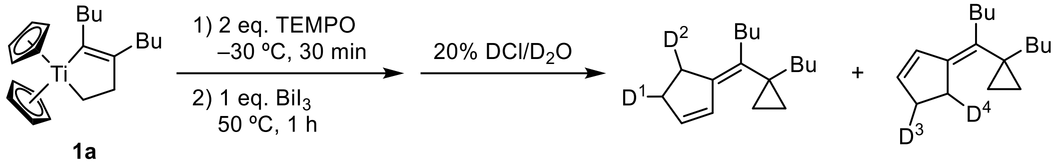
**(Z)-3-(1-(1-pentylcyclopropyl)hexylidene) cyclopent-1-ene (2c, minor isomer).**



**(E)-3-(1-(1-pentylcyclopropyl)hexylidene) cyclopent-1-ene (2c, major isomer).**

$^1H$ NMR (400MHz, $C_6D_6$): δ 0.48-0.52 (m, major - 2H, minor - 2H), 0.68-0.72 (m, major - 2H, minor - 2H), 0.86-0.95 (m, major - 6H, minor - 6H), 1.20-1.58 (m, major - 14H, minor - 14H), 2.17-2.22 (m, minor - 2H), 2.26-2.43 (m, major - 4H, major - 4H ), 2.60-2.63 (m, major – 2H), 5.92 (m, major - 1H, minor - 1H), 6.46 (dt, *J* = 6.0 Hz, 2.2 Hz, major - 1H), 6.81 (m, *J* = 6.0 Hz, 2.2 Hz, minor - 1H). $^{13}C\{^1H\}$ NMR (400MHz, $C_6D_6$): δ 13.6(2C), 13.7(2C), 14.4(4C), 23.0, 23.1, 23.1(2C), 25.9, 26.3, 27.6, 28.0, 28.1, 29.3, 31.6, 31.8, 32.5(2C), 32.7, 32.8, 32.9, 33.1, 34.8, 35.2, 39.6, 40.4, 131.1, 131.3, 132.8, 133.1, 135.5, 135.7, 144.5, 144.7. HRMS(EI) Calcd for $C_{19}H_{32}$: 260.2504. Found: 260.2507.

**Deuteriolysis of the reaction mixture prepared from 1a with 20% DCl/D$_2$O.**



**1a**

**2a-*d***, 34%[a] (34:66)
$D^1$ = 59%, $D^2$ = 67%
$D^3$ = 66%, $D^4$ = 60%

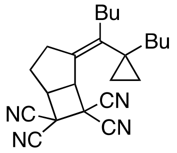
[a] combined NMR yields of double bond regioisomers

To know the source of the additional hydrogen atom at the coupled Cp ring in product **2**, we carried out a deuteration experiment. Deuteriolysis of the reaction mixture prepared from **1a** with 20% DCl/D$_2$O gave deuterated compounds **2a-*d*** as a mixture. The mixture of major isomers and the mixture of minor isomers were separated by column chromatography using silica gel (eluent: hexane) and GPC and then analyzed by HRMS and NMR (Figure S9-12).

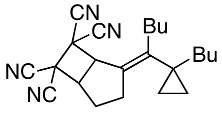
**deuterated compounds 2a-*d***
NMR yield: 34%.
**(2a-*d*, a mixture of major isomers)**
$^1$H NMR (396MHz, $C_6D_6$): δ 0.46-0.48 (m, 2H), 0.67-0.69 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.22-1.42 (m, 8H), 1.47-1.55 (m, 2H), 2.26-2.30 (m, 2H), 2.34-2.38 (m, 1.34H), 2.58-2.62 (m, 1.40H), 5.91 (m (overlapping), 1H), 6.44 (m (overlapping), 1H). $^{13}$C{$^1$H} NMR(400MHz, $C_6D_6$): δ 13.6 (2C), 14.3, 14.4, 23.6, 23.8, 26.3, 27.8, 28.0, 30.0, 32.1, 32.4, 34.1, 34.5, 39.3, 131.2, 131.2, 132.8, 132.8, 135.6, 135.7,144.4, 144.5.
HRMS(EI) Calcd for $C_{17}H_{27}D$: 233.2254. Found:233.2256.
**(2a-*d*, a mixture of minor isomers)**
$^1$H NMR (400MHz, $C_6D_6$): δ 0.48-0.50 (m, 2H), 0.68-0.71 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 1.22-1.40 (m, 8H), 1.47-1.55 (m, 2H), 2.16-2.21 (m, 2H), 2.30-2.32 (m, 1.41H), 2.38-2.40 (m, 1.33H), 5.92 (m (overlapping), 1H), 6.80 (m (overlapping), 1H) $^{13}$C{$^1$H} NMR(400MHz, $C_6D_6$): δ 13.7 (2C), 14.3, 14.4, 23.5, 23.9, 25.8, 27.6, 27.9, 30.0, 31.5, 31.7, 31.8, 34.9, 40.1, 131.0, 131.1, 133.1, 133.1, 135.5, 135.5, 144.6, 144.6.
HRMS(EI) Calcd for $C_{17}H_{27}D$: 233.2254. Found:233.2252.

### Synthesis of Diels-Alder adduct 3a and 4a

To a solution of **2a** (83.6 mg, 0.36 mmol) in toluene (5 mL) was added tetracyanoethylene (46 mg, 0.36 mmol) and the mixture was heated to 90 ºC. After stirring for overnight, the dark brown solution was cooled to room temperature and solvent was remove under reduced pressure. The crude product was purified by column chromatography using silica gel (eluent: hexane:ethyl acetate = 4:1). Tetracyanoethylene adduct **3a** and **4a** were obtained as a colorless solid (91.5 mg, yield 71%). Crystals suitable for X-ray analysis were obtained by slow diffusion of an ethyl acetate solution.



**(Z)-2-(1-(1-butylcyclopropyl)pentylidene)bicycle[3.2.0]heptane-6,6,7,7-tetracarbonitrile (4a). (minor product).**



**(*E*)-2-(1-(1-butylcyclopropyl)pentylidene)bicyclo[3.2.0]heptane-6,6,7,7-tetracarbonitrile (3a). (major product).**

$^1$H NMR (400MHz, CDCl$_3$): δ 0.54-0.76 (m, major - 4H, minor - 4H), 0.84-0.97 (m, major - 6H, minor - 6H), 1.18-1.59 m, major - 10H, minor - 10H), 1.98-2.30 (m, major - 4H, minor - 4H), 2.61-2.81 (m, major - 1H, minor - 2H), 2.90-2.97 (m, major - 1H), 3.67-3.76 (m, major - 1H, minor - 1H), 4.11-4.15 (d, *J* = 7.4 Hz, major - 1H), 4.51-4.53 (d, *J* = 8.0 Hz, minor - 1H). $^{13}$C{$^1$H} NMR (400MHz, C$_6$D$_6$): δ 11.2, 13.1, 13.7, 14.1, 14.1, 14.2, 14.3(2C), 23.3, 23.3, 23.6, 23.8, 26.3, 26.9, 28.9, 29.1, 29.4, 29.5, 29.6, 30.1, 32.2, 32.8, 35.6, 35.8, 37.5(2C), 38.4, 39.7, 40.5(2C), 47.2, 47.3, 49.6, 49.9, 108.7, 108.9, 108.9, 109.0, 111.3, 111.5, 111.6, 111.6, 132.8, 133.4, 147.8, 148.5. HRMS(EI) Calcd for C$_{23}$H$_{28}$N$_4$ 360.2314. Found:360.2303.

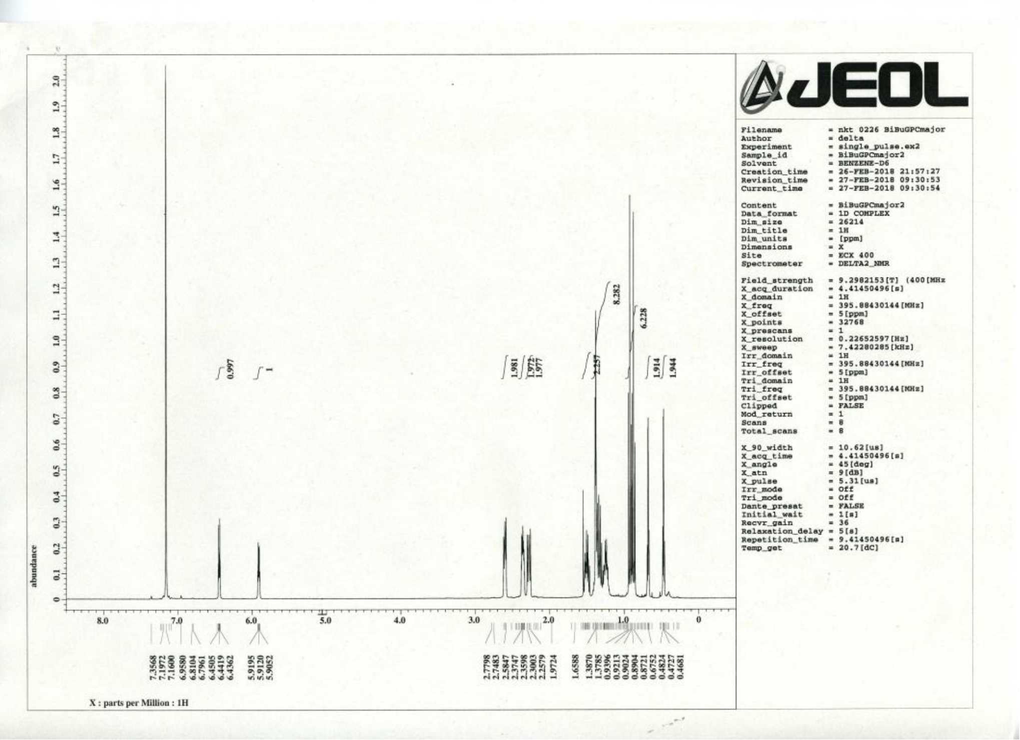


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**Fig. S1.** $^{1}$H NMR Spectrum of **2a** (major isomer)

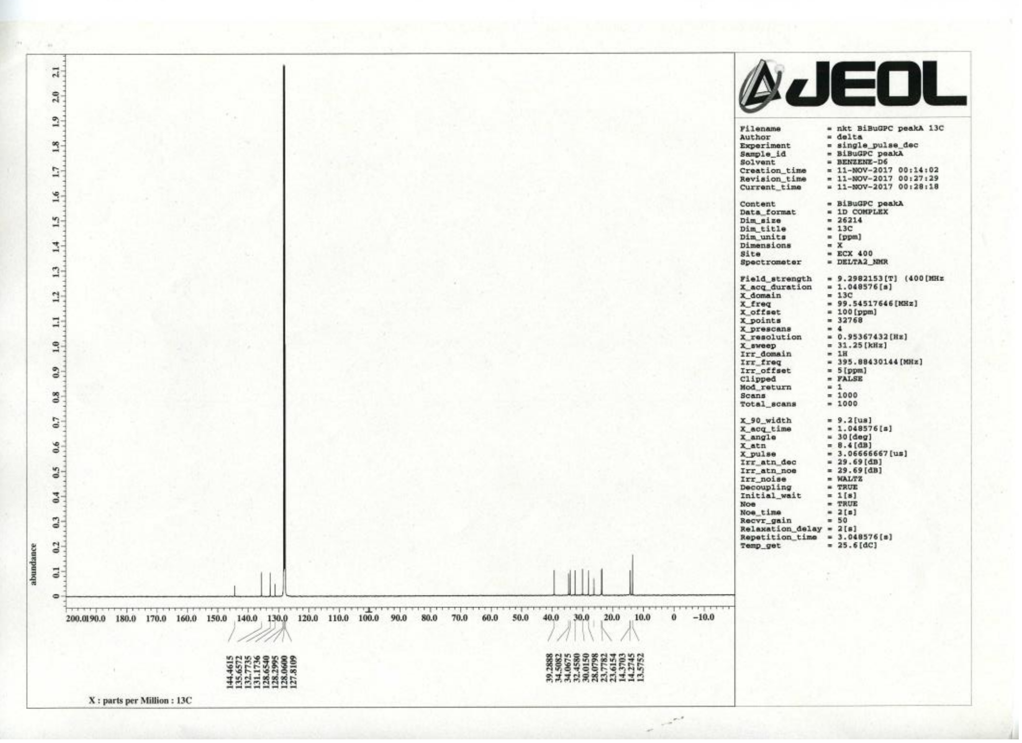

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**Fig. S2.** $^{13}$C NMR Spectrum of **2a** (major isomer)

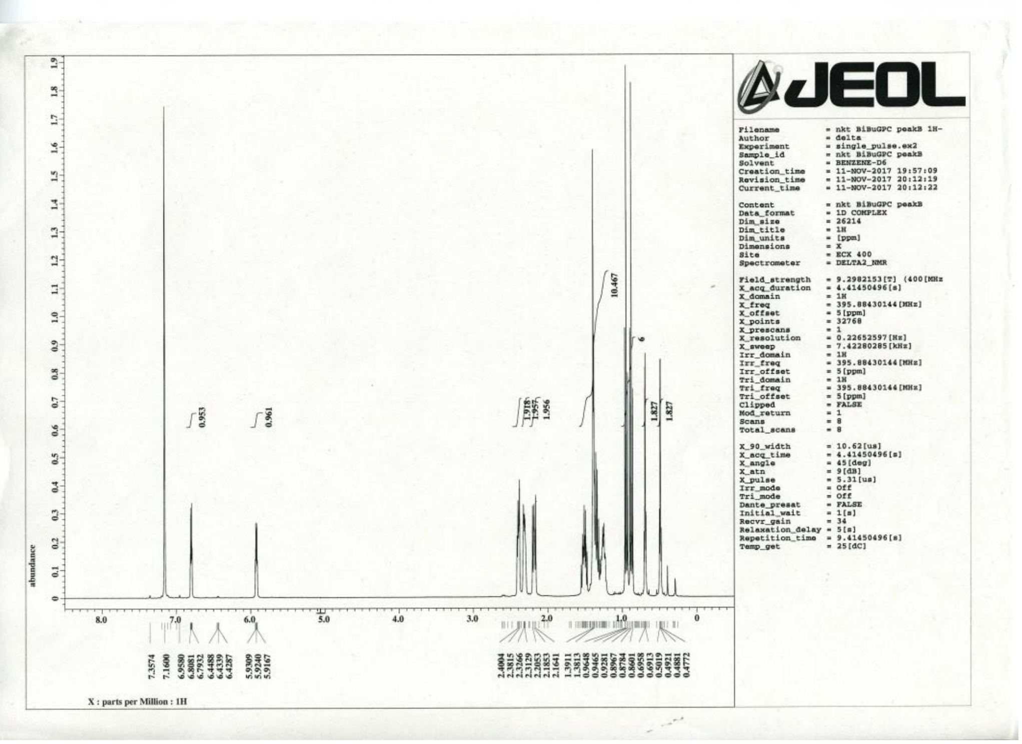

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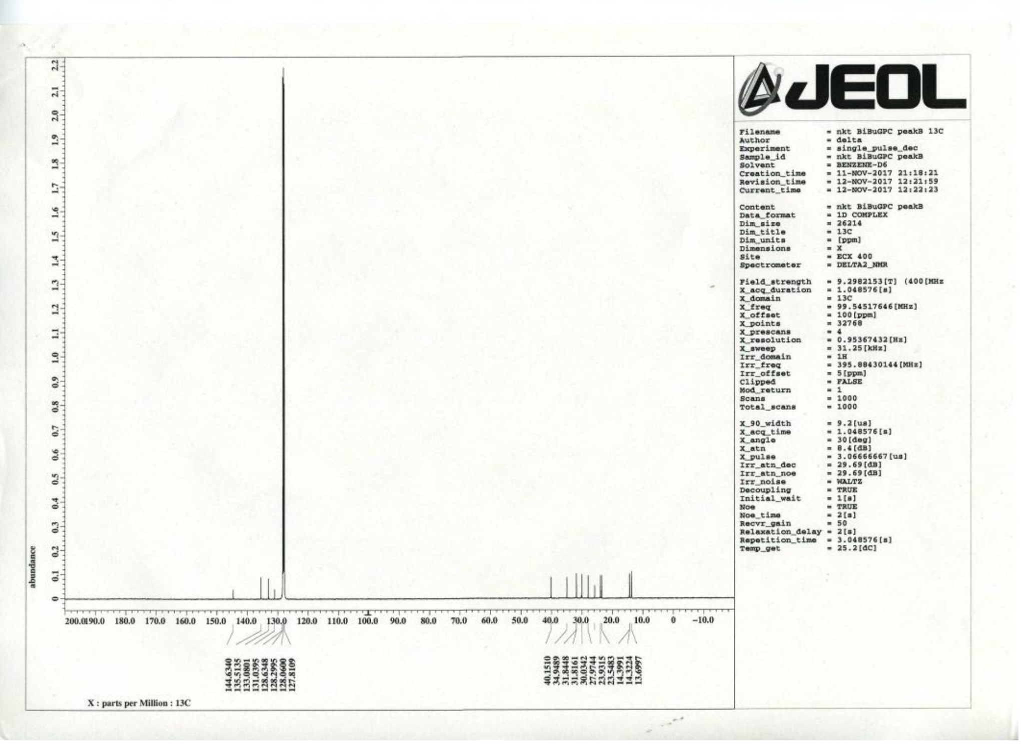
**Fig. S3.** $^{1}$H NMR Spectrum of **2a** (minor isomer)



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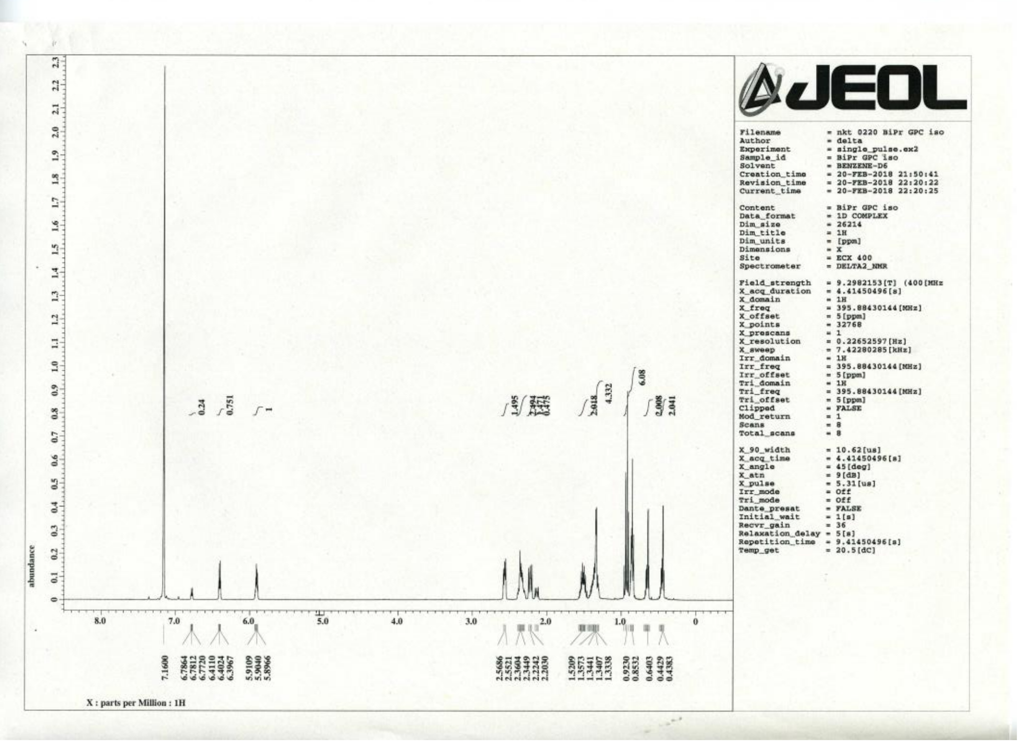
X_resolution      = 0.95367432[Hz]
X_sweep           = 31.25[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1000
Total_scans       = 1000

X_90_width        = 9.2[us]
X_acq_time        = 1.048576[s]
X_angle           = 30[deg]
X_atn             = 8.4[dB]
X_pulse           = 3.06666667[us]
Irr_atn_dec       = 29.69[dB]
Irr_atn_noe       = 29.69[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.048576[s]
Temp_get          = 25.2[dC]
```

**Fig. S4.** $^{13}$C NMR Spectrum of **2a** (minor isomer)



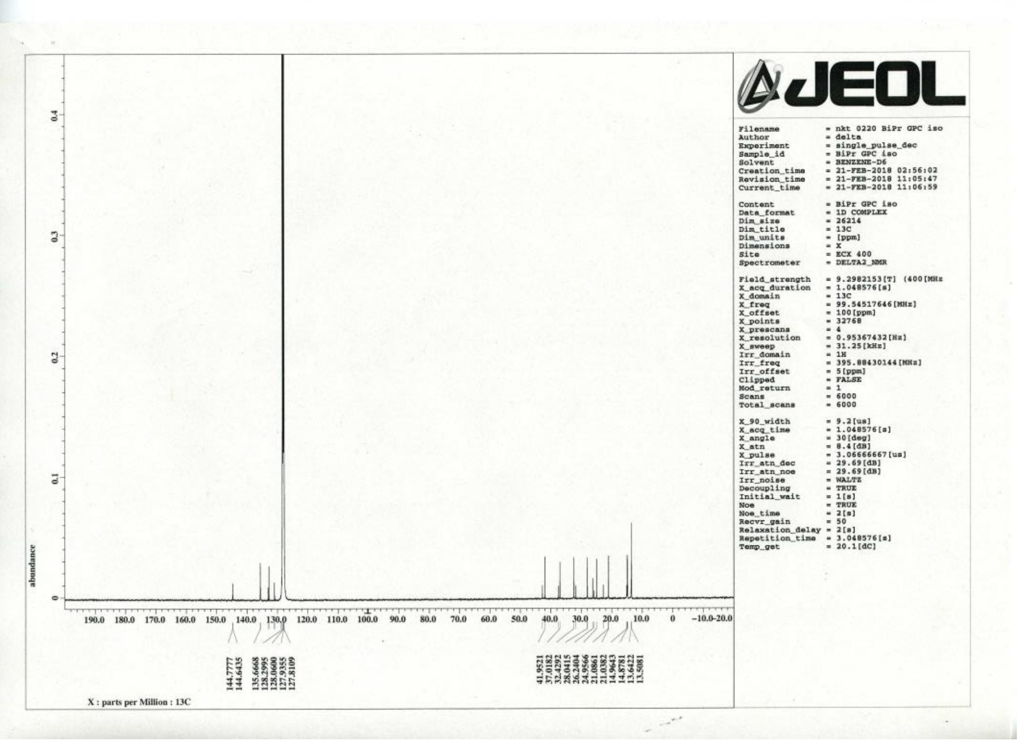
```
Filename          = nkt 0220 BiPr GPC iso
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = BiPr GPC iso
Solvent           = BENZENE-D6
Creation_time     = 20-FEB-2018 21:50:41
Revision_time     = 20-FEB-2018 22:20:22
Current_time      = 20-FEB-2018 22:20:25

Content           = BiPr GPC iso
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 4.41450496[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22652597[Hz]
X_sweep           = 7.42280285[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.62[us]
X_acq_time        = 4.41450496[s]
X_angle           = 45[deg]
X_atn             = 9[dB]
X_pulse           = 5.31[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 5[s]
Repetition_time   = 9.41450496[s]
Temp_get          = 20.5[dC]
```

**Fig. S5.** $^{1}$H NMR Spectrum of **2b** (a mixture of major isomer and minor isomer)



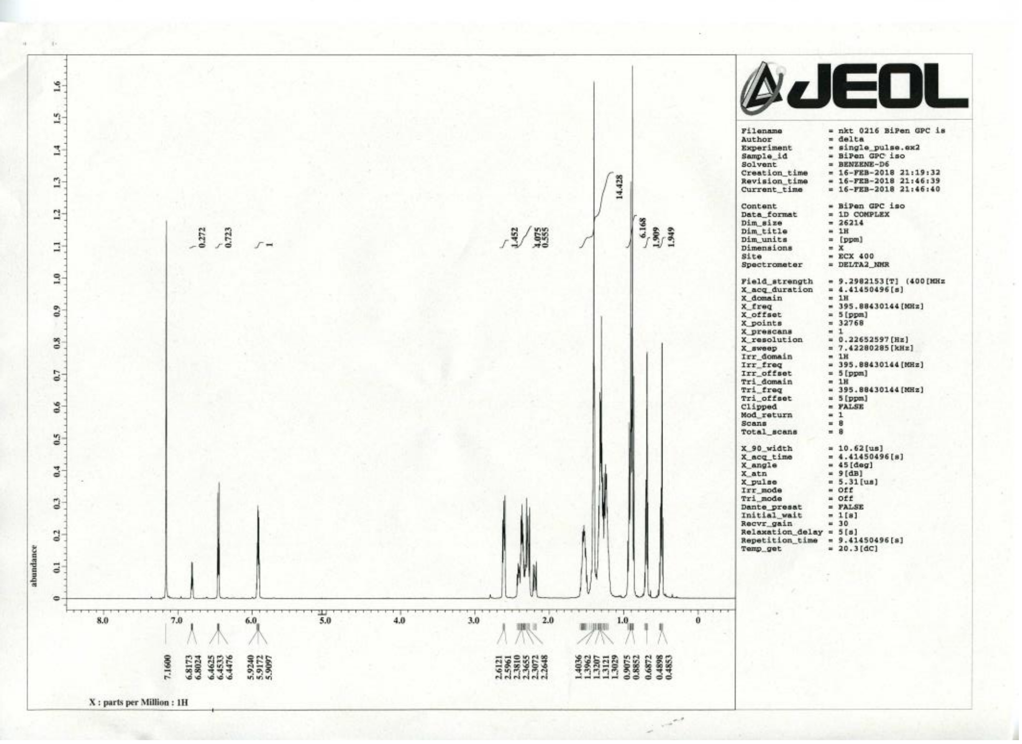
```
Filename          = nkt 0220 BiPr GPC iso
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = BiPr GPC iso
Solvent           = BENZENE-D6
Creation_time     = 21-FEB-2018 02:56:02
Revision_time     = 21-FEB-2018 11:05:47
Current_time      = 21-FEB-2018 11:06:59

Content           = BiPr GPC iso
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 1.048576[s]
X_domain          = 13C
X_freq            = 99.54517646[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95367432[Hz]
X_sweep           = 31.25[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 6000
Total_scans       = 6000

X_90_width        = 9.2[us]
X_acq_time        = 1.048576[s]
X_angle           = 30[deg]
X_atn             = 8.4[dB]
X_pulse           = 3.06666667[us]
Irr_atn_dec       = 29.69[dB]
Irr_atn_noe       = 29.69[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.048576[s]
Temp_get          = 20.1[dC]
```

**Fig. S6.** $^{13}$C NMR Spectrum of **2b** (a mixture of major isomer and minor isomer)



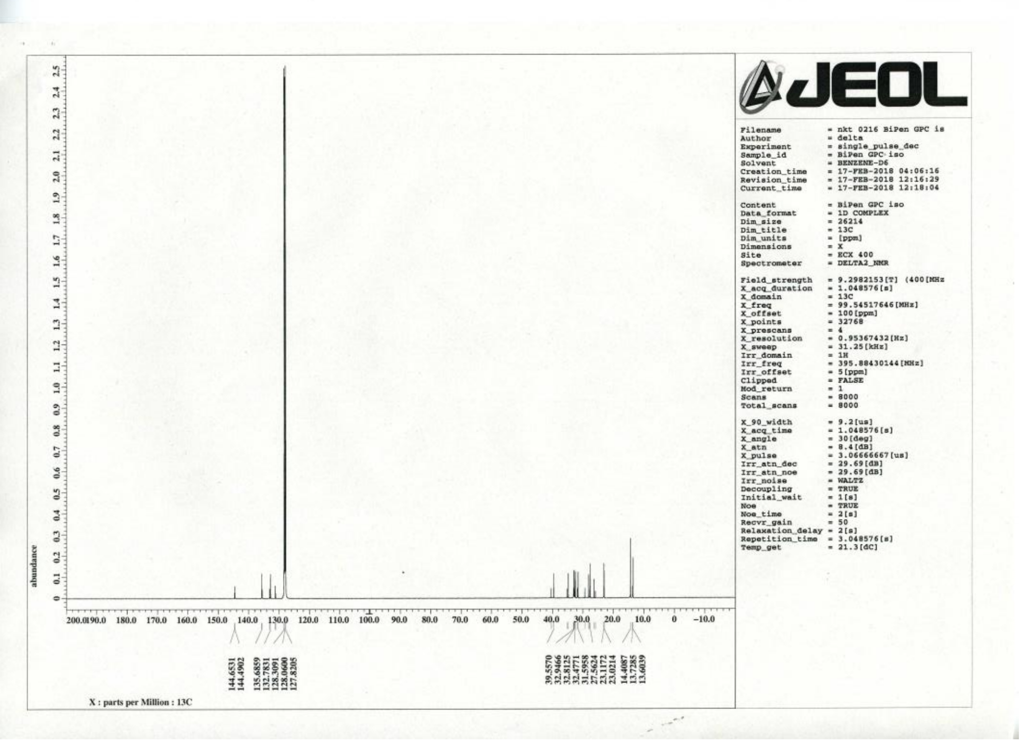
```
Filename          = nkt 0216 BiPen GPC is
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = BiPen GPC iso
Solvent           = BENZENE-D6
Creation_time     = 16-FEB-2018 21:19:32
Revision_time     = 16-FEB-2018 21:46:39
Current_time      = 16-FEB-2018 21:46:40

Content           = BiPen GPC iso
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 4.41450496[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22652597[Hz]
X_sweep           = 7.42280285[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.62[us]
X_acq_time        = 4.41450496[s]
X_angle           = 45[deg]
X_atn             = 9[dB]
X_pulse           = 5.31[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 9.41450496[s]
Temp_get          = 20.3[dC]
```

**Fig. S7.** $^{1}$H NMR Spectrum of **2c** (a mixture of major isomer and minor isomer)



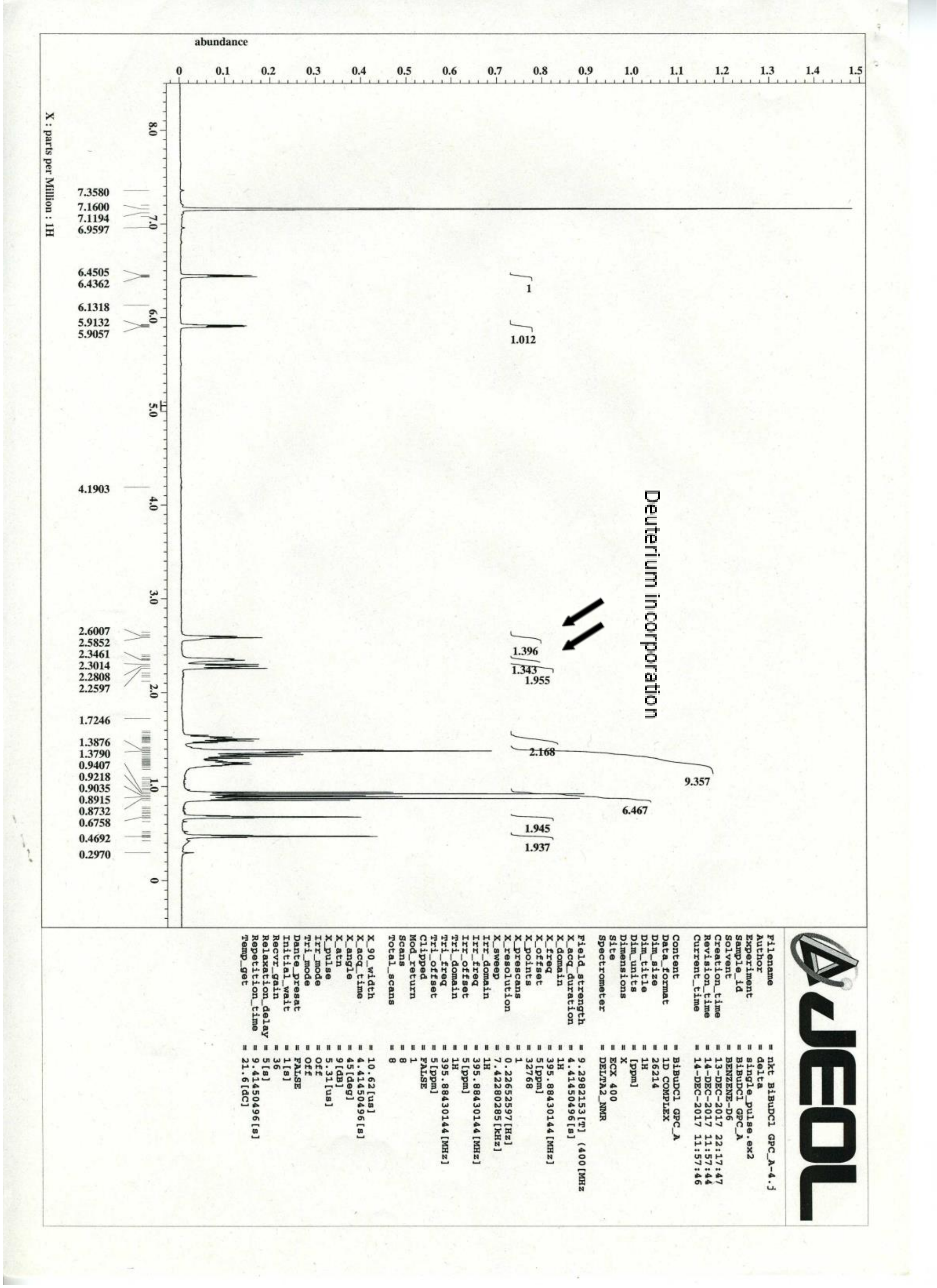
```
Filename          = nkt 0216 BiPen GPC is
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = BiPen GPC iso
Solvent           = BENZENE-D6
Creation_time     = 17-FEB-2018 04:06:16
Revision_time     = 17-FEB-2018 12:16:29
Current_time      = 17-FEB-2018 12:18:04

Content           = BiPen GPC iso
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 1.048576[s]
X_domain          = 13C
X_freq            = 99.54517646[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95367432[Hz]
X_sweep           = 31.25[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8000
Total_scans       = 8000

X_90_width        = 9.2[us]
X_acq_time        = 1.048576[s]
X_angle           = 30[deg]
X_atn             = 8.4[dB]
X_pulse           = 3.06666667[us]
Irr_atn_dec       = 29.69[dB]
Irr_atn_noe       = 29.69[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.048576[s]
Temp_get          = 21.3[dC]
```

**Fig. S8.** $^{13}$C NMR Spectrum of **2c** (a mixture of major isomer and minor isomer)



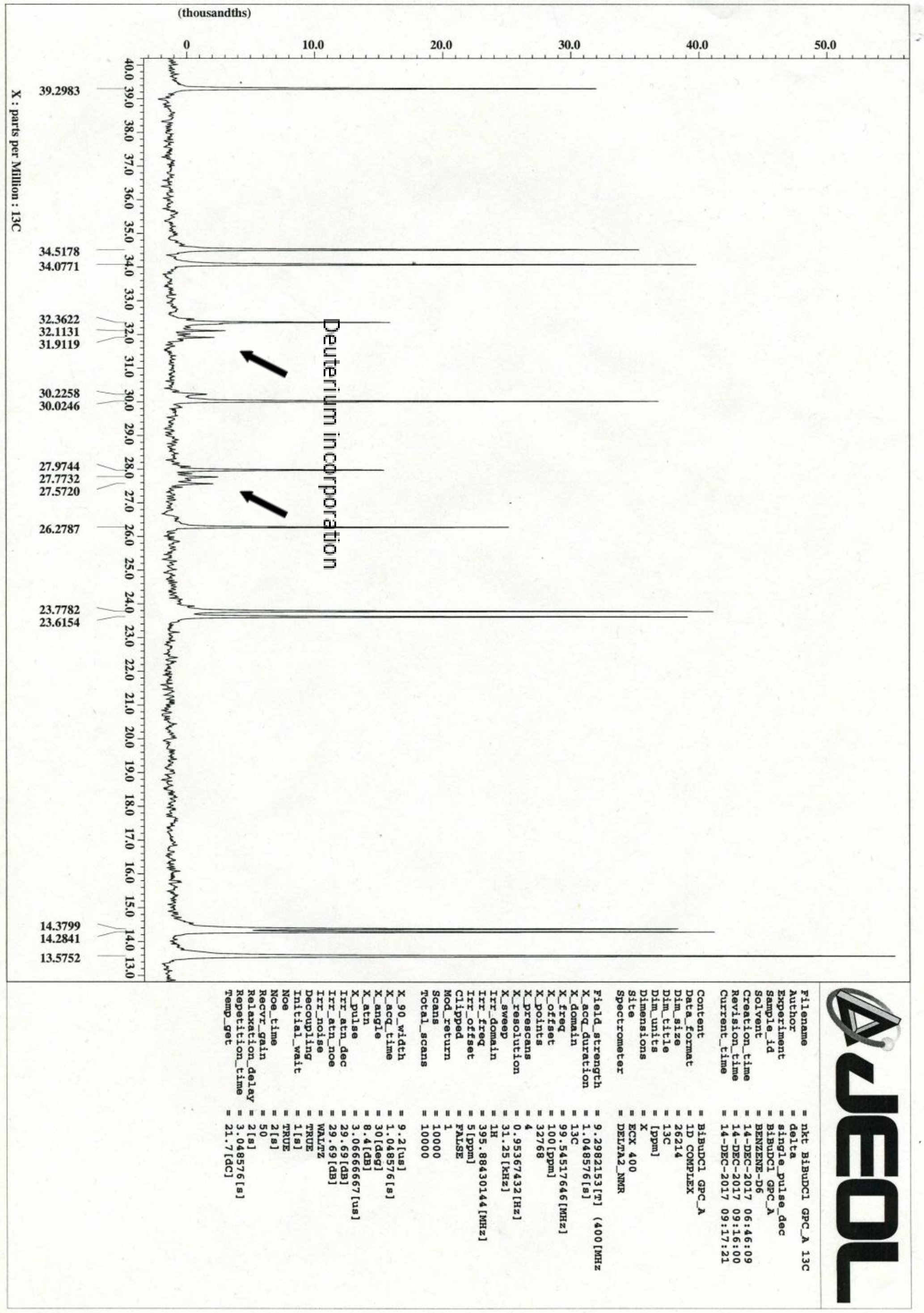
```
Filename          = nkt BiBuDCl GPC_A-4.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = BiBuDCl GPC_A
Solvent           = BENZENE-D6
Creation_time     = 13-DEC-2017 22:17:47
Revision_time     = 14-DEC-2017 11:57:44
Current_time      = 14-DEC-2017 11:57:46

Content           = BiBuDCl GPC_A
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 4.41450496[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22652597[Hz]
X_sweep           = 7.42280285[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.62[us]
X_acq_time        = 4.41450496[s]
X_angle           = 45[deg]
X_atn             = 9[dB]
X_pulse           = 5.31[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 5[s]
Repetition_time   = 9.41450496[s]
Temp_get          = 21.6[dC]
```

**Fig. S9.** $^{1}$H NMR Spectrum of **2a-*d*** (major isomers)



```
Filename          = nkt BiBuDCl GPC_A 13C
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = BiBuDCl GPC_A
Solvent           = BENZENE-D6
Creation_time     = 14-DEC-2017 06:46:09
Revision_time     = 14-DEC-2017 09:16:00
Current_time      = 14-DEC-2017 09:17:21

Content           = BiBuDCl GPC_A
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 1.048576[s]
X_domain          = 13C
X_freq            = 99.5451764 6[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95367432[Hz]
X_sweep           = 31.25[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 10000
Total_scans       = 10000

X_90_width        = 9.2[us]
X_acq_time        = 1.048576[s]
X_angle           = 30[deg]
X_atn             = 8.4[dB]
X_pulse           = 3.06666667[us]
Irr_atn_dec       = 29.69[dB]
Irr_atn_noe       = 29.69[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.048576[s]
Temp_get          = 21.7[dC]
```

**Fig. S10.** An Enlarged $^{13}$C NMR Spectrum of **2a-*d*** (major isomers)

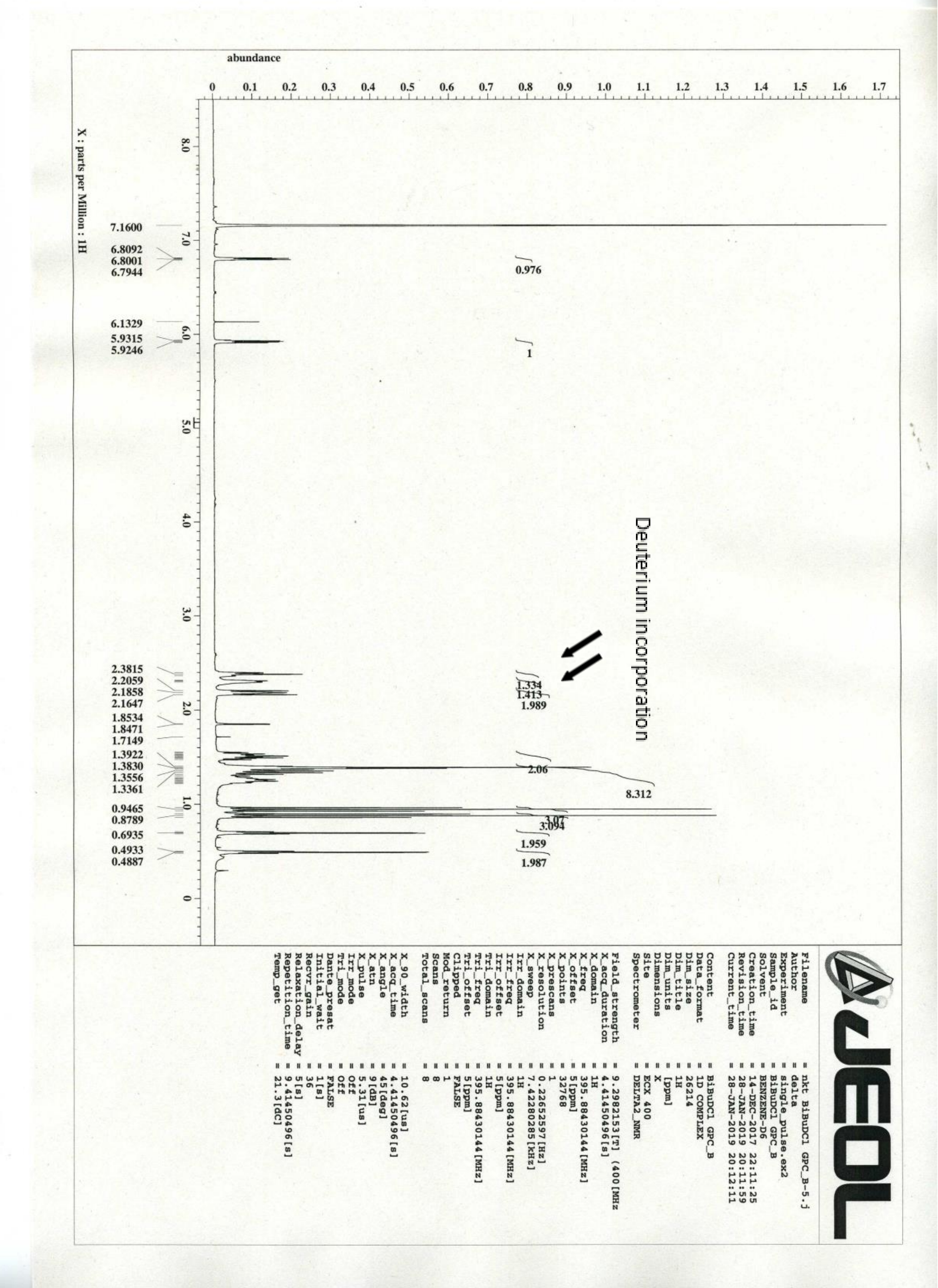
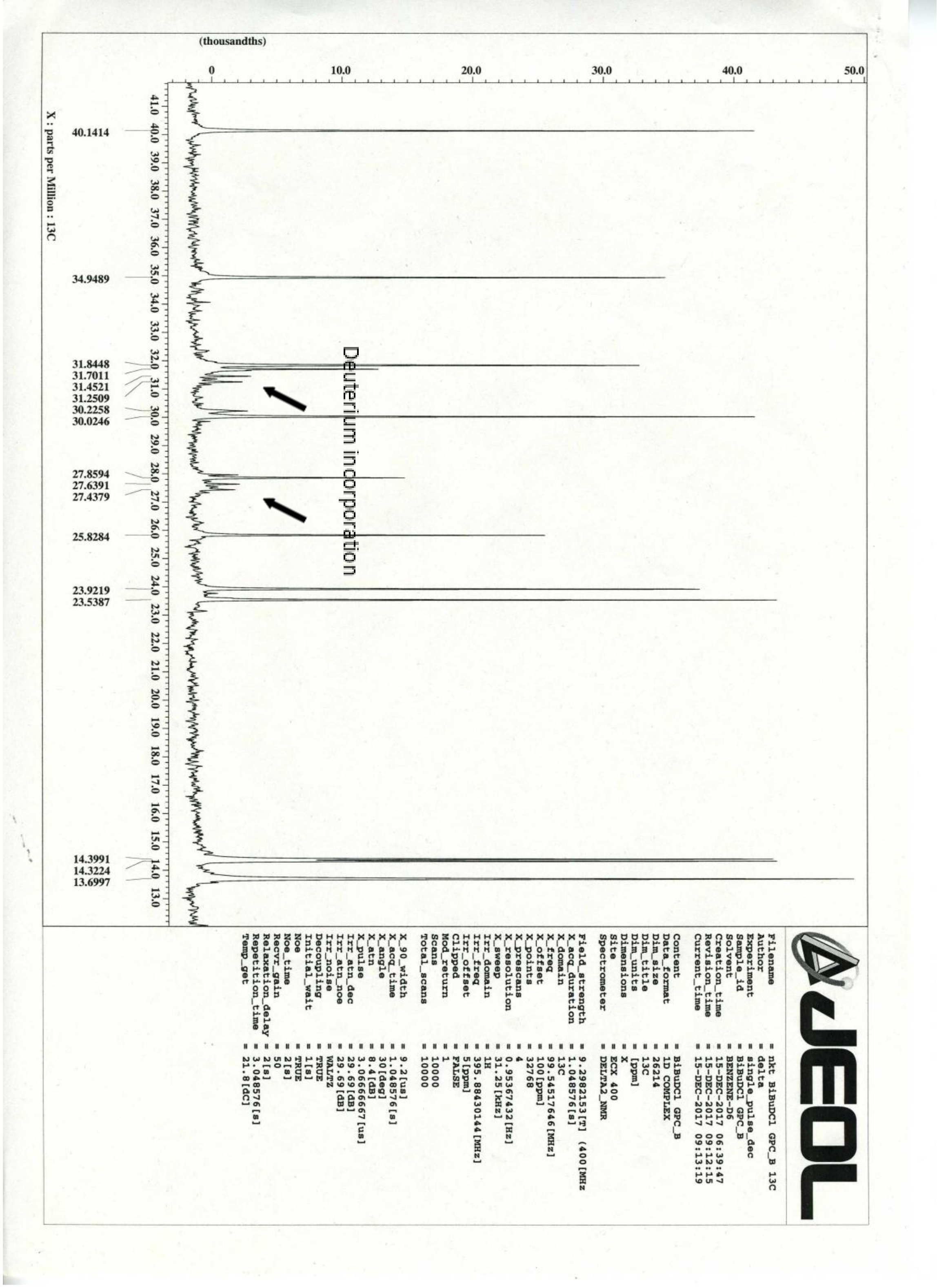


**Fig. S11.** $^1$H NMR Spectrum of **2a-*d*** (minor isomers)



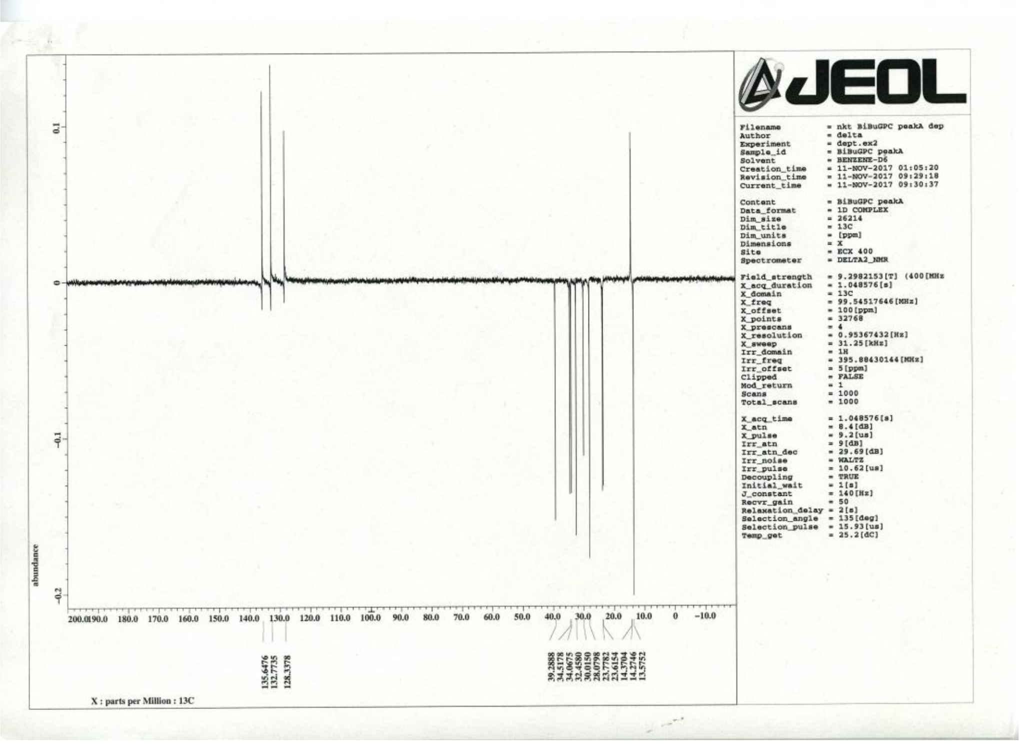
```
Filename           = nkt BiBuDCl GPC_B 13C
Author             = delta
Experiment         = single_pulse_dec
Sample_id          = BiBuDCl GPC_B
Solvent            = BENZENE-D6
Creation_time      = 15-DEC-2017 06:39:47
Revision_time      = 15-DEC-2017 09:12:15
Current_time       = 15-DEC-2017 09:13:19

Content            = BiBuDCl GPC_B
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 13C
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.2982153[T] (400[MHz
X_acq_duration     = 1.048576[s]
X_domain           = 13C
X_freq             = 99.54517646[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.95367432[Hz]
X_sweep            = 31.25[kHz]
Irr_domain         = 1H
Irr_freq           = 395.88430144[MHz]
Irr_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 10000
Total_scans        = 10000

X_90_width         = 9.2[us]
X_acq_time         = 1.048576[s]
X_angle            = 30[deg]
X_atn              = 8.4[dB]
X_pulse            = 3.06666667[us]
Irr_atn_dec        = 29.69[dB]
Irr_atn_noe        = 29.69[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Recvr_gain         = 50
Relaxation_delay   = 2[s]
Repetition_time    = 3.048576[s]
Temp_get           = 21.8[dC]
```

**Fig. S12.** An Enlarged $^{13}$C NMR Spectrum of **2a-*d*** (minor isomers)



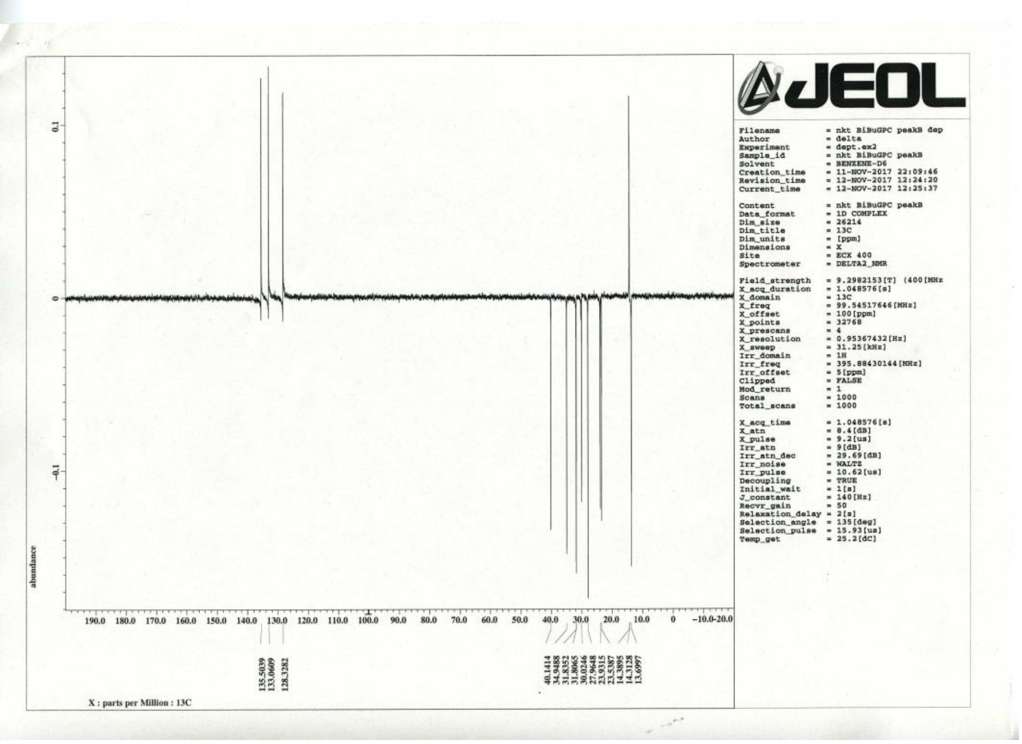
```
Filename           = nkt BiBuGPC peakA dep
Author             = delta
Experiment         = dept.ex2
Sample_id          = BiBuGPC peakA
Solvent            = BENZENE-D6
Creation_time      = 11-NOV-2017 01:05:20
Revision_time      = 11-NOV-2017 09:29:18
Current_time       = 11-NOV-2017 09:30:37

Content            = BiBuGPC peakA
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 13C
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.2982153[T] (400[MHz
X_acq_duration     = 1.048576[s]
X_domain           = 13C
X_freq             = 99.54517646[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.95367432[Hz]
X_sweep            = 31.25[kHz]
Irr_domain         = 1H
Irr_freq           = 395.88430144[MHz]
Irr_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 1000
Total_scans        = 1000

X_acq_time         = 1.048576[s]
X_atn              = 8.4[dB]
X_pulse            = 9.2[us]
Irr_atn            = 9[dB]
Irr_atn_dec        = 29.69[dB]
Irr_noise          = WALTZ
Irr_pulse          = 10.62[us]
Decoupling         = TRUE
Initial_wait       = 1[s]
J_constant         = 140[Hz]
Recvr_gain         = 50
Relaxation_delay = 2[s]
Selection_angle    = 135[deg]
Selection_pulse    = 15.93[us]
Temp_get           = 25.2[dC]
```

**Fig. S13.** DEPT Spectrum of **2a** (major isomer, selection angle 135 degree)



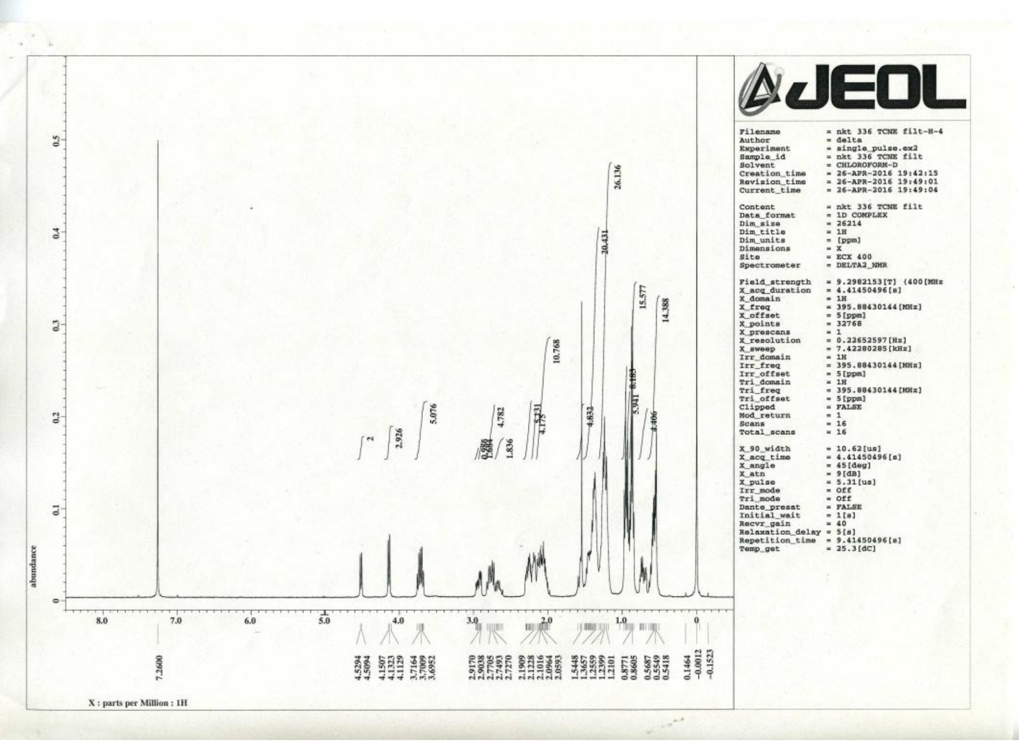
```
Filename           = nkt BiBuGPC peakB dep
Author             = delta
Experiment         = dept.ex2
Sample_id          = nkt BiBuGPC peakB
Solvent            = BENZENE-D6
Creation_time      = 11-NOV-2017 22:09:46
Revision_time      = 12-NOV-2017 12:24:20
Current_time       = 12-NOV-2017 12:25:37

Content            = nkt BiBuGPC peakB
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 13C
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.2982153[T] (400[MHz
X_acq_duration     = 1.048576[s]
X_domain           = 13C
X_freq             = 99.54517646[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.95367432[Hz]
X_sweep            = 31.25[kHz]
Irr_domain         = 1H
Irr_freq           = 395.88430144[MHz]
Irr_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 1000
Total_scans        = 1000

X_acq_time         = 1.048576[s]
X_atn              = 8.4[dB]
X_pulse            = 9.2[us]
Irr_atn            = 9[dB]
Irr_atn_dec        = 29.69[dB]
Irr_noise          = WALTZ
Irr_pulse          = 10.62[us]
Decoupling         = TRUE
Initial_wait       = 1[s]
J_constant         = 140[Hz]
Recvr_gain         = 50
Relaxation_delay = 2[s]
Selection_angle    = 135[deg]
Selection_pulse    = 15.93[us]
Temp_get           = 25.2[dC]
```

**Fig. S14.** DEPT Spectrum of **2a** (minor isomer, selection angle 135 degree)



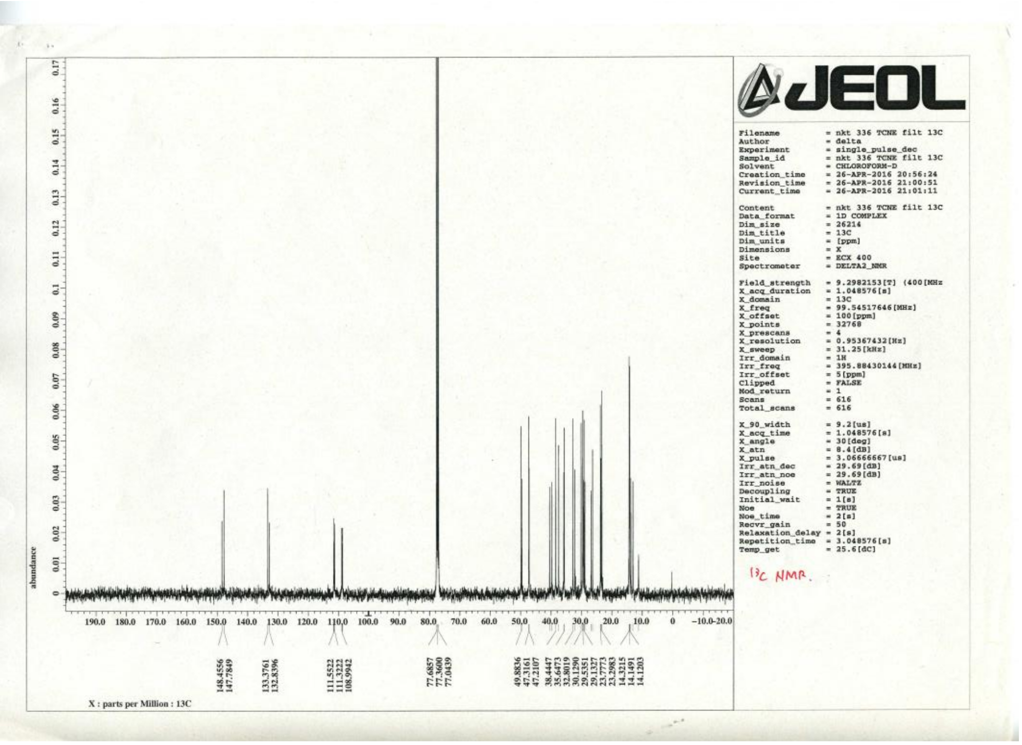
```
Filename           = nkt 336 TCNE filt-H-4
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = nkt 336 TCNE filt
Solvent            = CHLOROFORM-D
Creation_time      = 26-APR-2016 19:42:15
Revision_time      = 26-APR-2016 19:49:01
Current_time       = 26-APR-2016 19:49:04

Content            = nkt 336 TCNE filt
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.2982153[T] (400[MHz
X_acq_duration     = 4.41450496[s]
X_domain           = 1H
X_freq             = 395.88430144[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22652597[Hz]
X_sweep            = 7.42280285[kHz]
Irr_domain         = 1H
Irr_freq           = 395.88430144[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 395.88430144[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 16
Total_scans        = 16

X_90_width         = 10.62[us]
X_acq_time         = 4.41450496[s]
X_angle            = 45[deg]
X_atn              = 9[dB]
X_pulse            = 5.31[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 40
Relaxation_delay = 5[s]
Repetition_time    = 9.41450496[s]
Temp_get           = 25.3[dC]
```

**Fig. S15.** $^{1}$H NMR Spectrum of **3a** and **4a**.



```
Filename           = nkt 336 TCNE filt 13C
Author             = delta
Experiment         = single_pulse_dec
Sample_id          = nkt 336 TCNE filt 13C
Solvent            = CHLOROFORM-D
Creation_time      = 26-APR-2016 20:56:24
Revision_time      = 26-APR-2016 21:00:51
Current_time       = 26-APR-2016 21:01:11

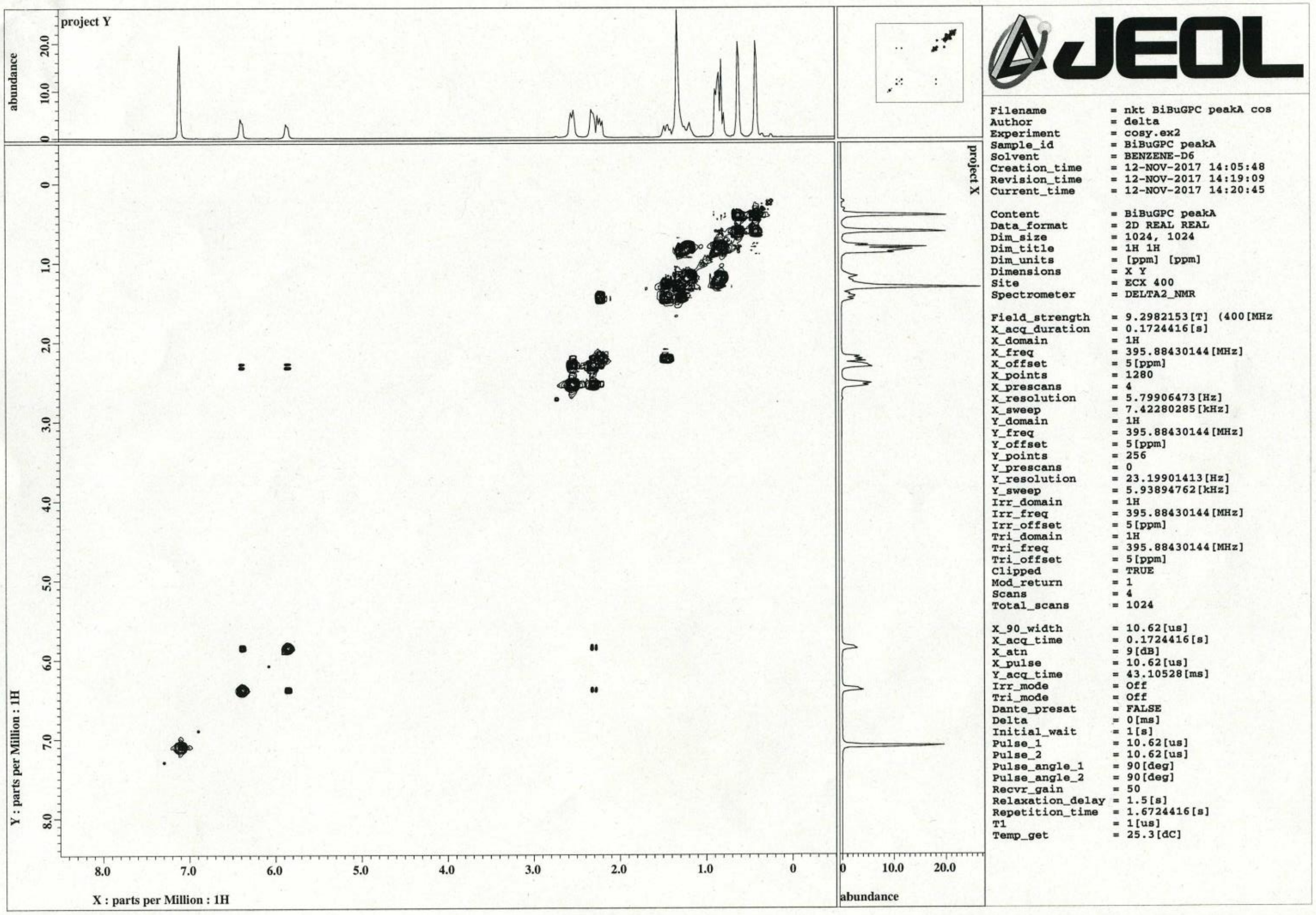
Content            = nkt 336 TCNE filt 13C
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 13C
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.2982153[T] (400[MHz
X_acq_duration     = 1.048576[s]
X_domain           = 13C
X_freq             = 99.54517646[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.95367432[Hz]
X_sweep            = 31.25[kHz]
Irr_domain         = 1H
Irr_freq           = 395.88430144[MHz]
Irr_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 616
Total_scans        = 616

X_90_width         = 9.2[us]
X_acq_time         = 1.048576[s]
X_angle            = 30[deg]
X_atn              = 8.4[dB]
X_pulse            = 3.06666667[us]
Irr_atn_dec        = 29.69[dB]
Irr_atn_noe        = 29.69[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Recvr_gain         = 50
Relaxation_delay = 2[s]
Repetition_time    = 3.048576[s]
Temp_get           = 25.6[dC]
```

$^{13}$C NMR.

**Fig. S16.** $^{13}$C NMR Spectrum of **3a** and **4a**.



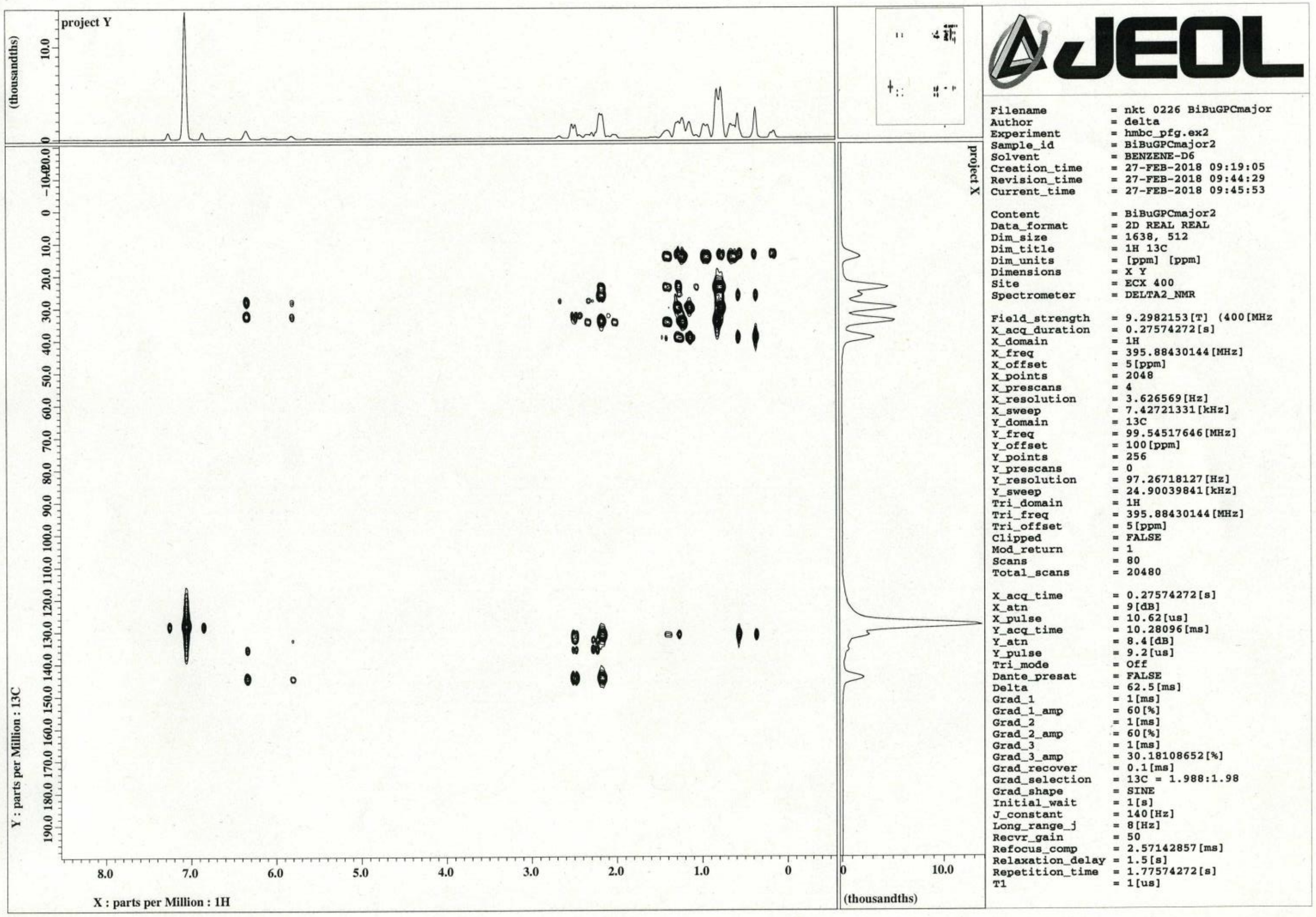
```
Filename          = nkt BiBuGPC peakA cos
Author            = delta
Experiment        = cosy.ex2
Sample_id         = BiBuGPC peakA
Solvent           = BENZENE-D6
Creation_time     = 12-NOV-2017 14:05:48
Revision_time     = 12-NOV-2017 14:19:09
Current_time      = 12-NOV-2017 14:20:45

Content           = BiBuGPC peakA
Data_format       = 2D REAL REAL
Dim_size          = 1024, 1024
Dim_title         = 1H 1H
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 0.1724416[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 1280
X_prescans        = 4
X_resolution      = 5.79906473[Hz]
X_sweep           = 7.42280285[kHz]
Y_domain          = 1H
Y_freq            = 395.88430144[MHz]
Y_offset          = 5[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 23.19901413[Hz]
Y_sweep           = 5.93894762[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 4
Total_scans       = 1024

X_90_width        = 10.62[us]
X_acq_time        = 0.1724416[s]
X_atn             = 9[dB]
X_pulse           = 10.62[us]
Y_acq_time        = 43.10528[ms]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Delta             = 0[ms]
Initial_wait      = 1[s]
Pulse_1           = 10.62[us]
Pulse_2           = 10.62[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 50
Relaxation_delay  = 1.5[s]
Repetition_time   = 1.6724416[s]
T1                = 1[us]
Temp_get          = 25.3[dC]
```

**Fig. S17.** H-HCOSY Spectrum of **2a** (major isomer)



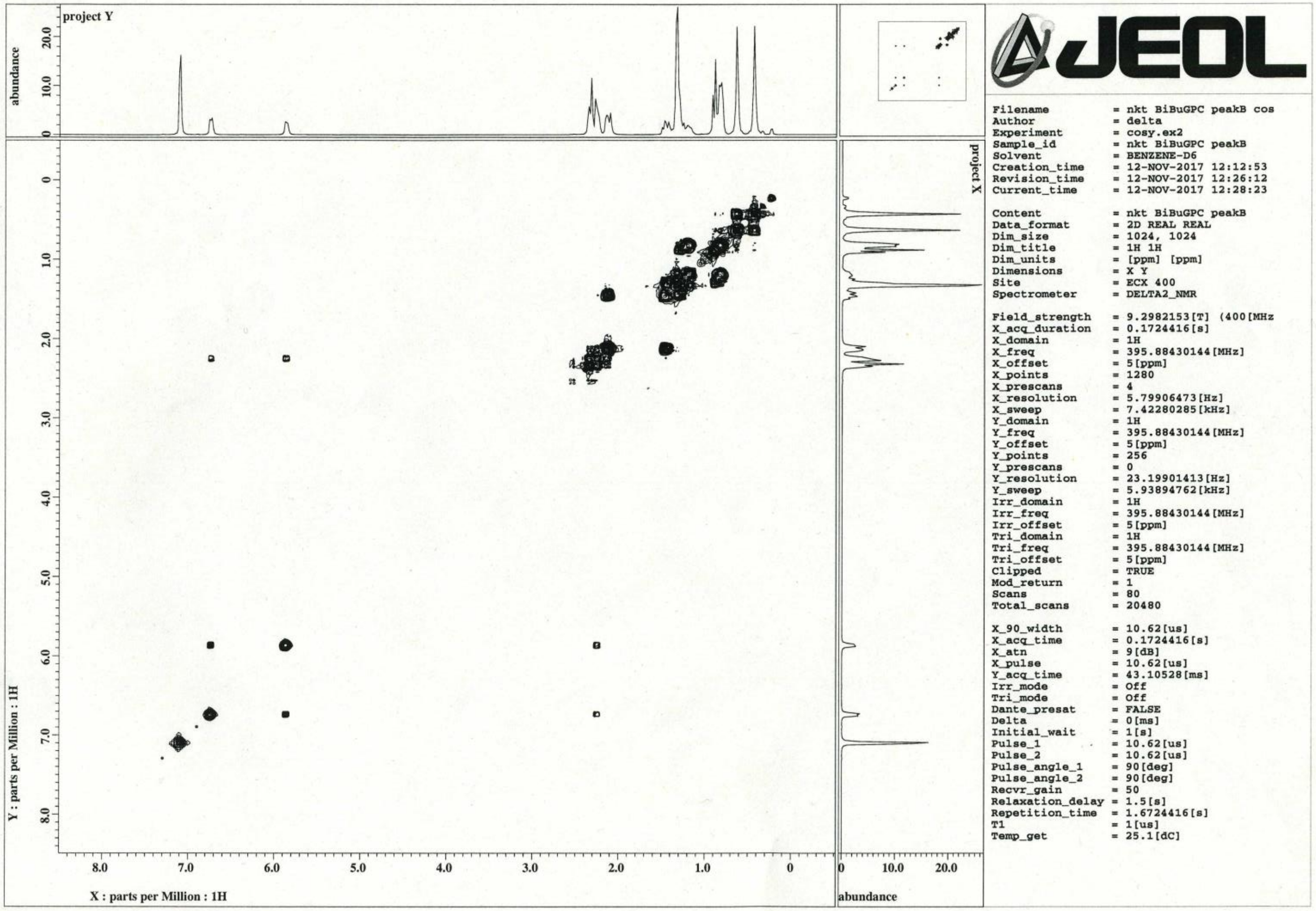
```
Filename          = nkt 0226 BiBuGPCmajor
Author            = delta
Experiment        = hmbc_pfg.ex2
Sample_id         = BiBuGPCmajor2
Solvent           = BENZENE-D6
Creation_time     = 27-FEB-2018 09:19:05
Revision_time     = 27-FEB-2018 09:44:29
Current_time      = 27-FEB-2018 09:45:53

Content           = BiBuGPCmajor2
Data_format       = 2D REAL REAL
Dim_size          = 1638, 512
Dim_title         = 1H 13C
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 0.27574272[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 2048
X_prescans        = 4
X_resolution      = 3.626569[Hz]
X_sweep           = 7.42721331[kHz]
Y_domain          = 13C
Y_freq            = 99.54517646[MHz]
Y_offset          = 100[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 97.26718127[Hz]
Y_sweep           = 24.90039841[kHz]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 80
Total_scans       = 20480

X_acq_time        = 0.27574272[s]
X_atn             = 9[dB]
X_pulse           = 10.62[us]
Y_acq_time        = 10.28096[ms]
Y_atn             = 8.4[dB]
Y_pulse           = 9.2[us]
Tri_mode          = Off
Dante_presat      = FALSE
Delta             = 62.5[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 60[%]
Grad_2            = 1[ms]
Grad_2_amp        = 60[%]
Grad_3            = 1[ms]
Grad_3_amp        = 30.18108652[%]
Grad_recover      = 0.1[ms]
Grad_selection    = 13C = 1.988:1.98
Grad_shape        = SINE
Initial_wait      = 1[s]
J_constant        = 140[Hz]
Long_range_j      = 8[Hz]
Recvr_gain        = 50
Refocus_comp      = 2.57142857[ms]
Relaxation_delay  = 1.5[s]
Repetition_time   = 1.77574272[s]
T1                = 1[us]
```

**Fig. S18.** HMBC Spectrum of **2a** (major isomer)



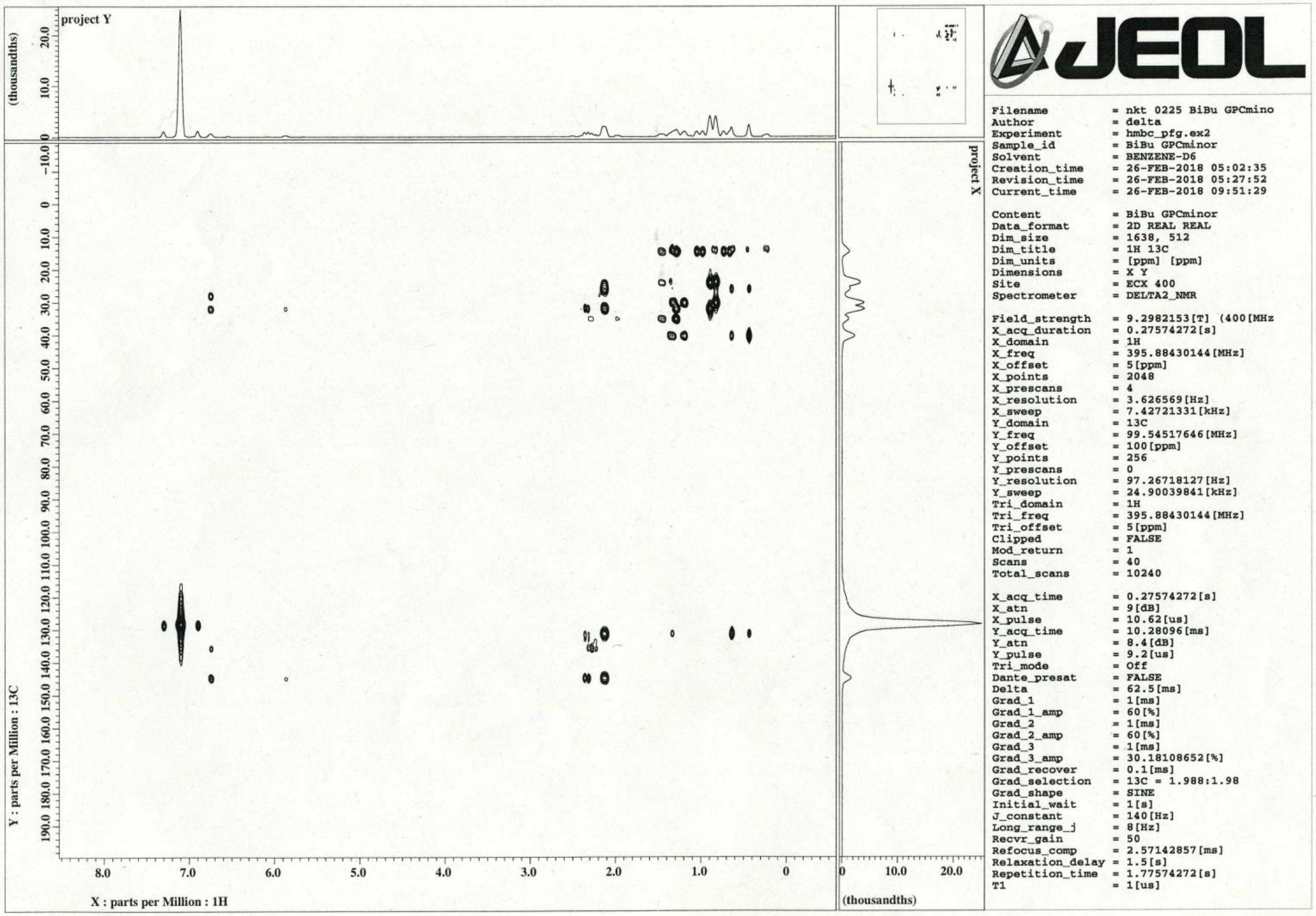
```
Filename            = nkt BiBuGPC peakB cos
Author              = delta
Experiment          = cosy.ex2
Sample_id           = nkt BiBuGPC peakB
Solvent             = BENZENE-D6
Creation_time       = 12-NOV-2017 12:12:53
Revision_time       = 12-NOV-2017 12:26:12
Current_time        = 12-NOV-2017 12:28:23

Content             = nkt BiBuGPC peakB
Data_format         = 2D REAL REAL
Dim_size            = 1024, 1024
Dim_title           = 1H 1H
Dim_units           = [ppm] [ppm]
Dimensions          = X Y
Site                = ECX 400
Spectrometer        = DELTA2_NMR

Field_strength      = 9.2982153[T] (400[MHz
X_acq_duration      = 0.1724416[s]
X_domain            = 1H
X_freq              = 395.88430144[MHz]
X_offset            = 5[ppm]
X_points            = 1280
X_prescans          = 4
X_resolution        = 5.79906473[Hz]
X_sweep             = 7.42280285[kHz]
Y_domain            = 1H
Y_freq              = 395.88430144[MHz]
Y_offset            = 5[ppm]
Y_points            = 256
Y_prescans          = 0
Y_resolution        = 23.19901413[Hz]
Y_sweep             = 5.93894762[kHz]
Irr_domain          = 1H
Irr_freq            = 395.88430144[MHz]
Irr_offset          = 5[ppm]
Tri_domain          = 1H
Tri_freq            = 395.88430144[MHz]
Tri_offset          = 5[ppm]
Clipped             = TRUE
Mod_return          = 1
Scans               = 80
Total_scans         = 20480

X_90_width          = 10.62[us]
X_acq_time          = 0.1724416[s]
X_atn               = 9[dB]
X_pulse             = 10.62[us]
Y_acq_time          = 43.10528[ms]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Delta               = 0[ms]
Initial_wait        = 1[s]
Pulse_1             = 10.62[us]
Pulse_2             = 10.62[us]
Pulse_angle_1       = 90[deg]
Pulse_angle_2       = 90[deg]
Recvr_gain          = 50
Relaxation_delay    = 1.5[s]
Repetition_time     = 1.6724416[s]
T1                  = 1[us]
Temp_get            = 25.1[dC]
```

**Fig. S19.** H-HCOSY Spectrum of **2a** (minor isomer)



```
Filename          = nkt 0225 BiBu GPCmino
Author            = delta
Experiment        = hmbc_pfg.ex2
Sample_id         = BiBu GPCminor
Solvent           = BENZENE-D6
Creation_time     = 26-FEB-2018 05:02:35
Revision_time     = 26-FEB-2018 05:27:52
Current_time      = 26-FEB-2018 09:51:29

Content           = BiBu GPCminor
Data_format       = 2D REAL REAL
Dim_size          = 1638, 512
Dim_title         = 1H 13C
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 0.27574272[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 2048
X_prescans        = 4
X_resolution      = 3.626569[Hz]
X_sweep           = 7.42721331[kHz]
Y_domain          = 13C
Y_freq            = 99.54517646[MHz]
Y_offset          = 100[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 97.26718127[Hz]
Y_sweep           = 24.90039841[kHz]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 40
Total_scans       = 10240

X_acq_time        = 0.27574272[s]
X_atn             = 9[dB]
X_pulse           = 10.62[us]
Y_acq_time        = 10.28096[ms]
Y_atn             = 8.4[dB]
Y_pulse           = 9.2[us]
Tri_mode          = Off
Dante_presat      = FALSE
Delta             = 62.5[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 60[%]
Grad_2            = 1[ms]
Grad_2_amp        = 60[%]
Grad_3            = 1[ms]
Grad_3_amp        = 30.18108652[%]
Grad_recover      = 0.1[ms]
Grad_selection    = 13C = 1.988:1.98
Grad_shape        = SINE
Initial_wait      = 1[s]
J_constant        = 140[Hz]
Long_range_j      = 8[Hz]
Recvr_gain        = 50
Refocus_comp      = 2.57142857[ms]
Relaxation_delay  = 1.5[s]
Repetition_time   = 1.77574272[s]
T1                = 1[us]
```

**Fig. S20.** HMBC Spectrum of **2a** (minor isomer)

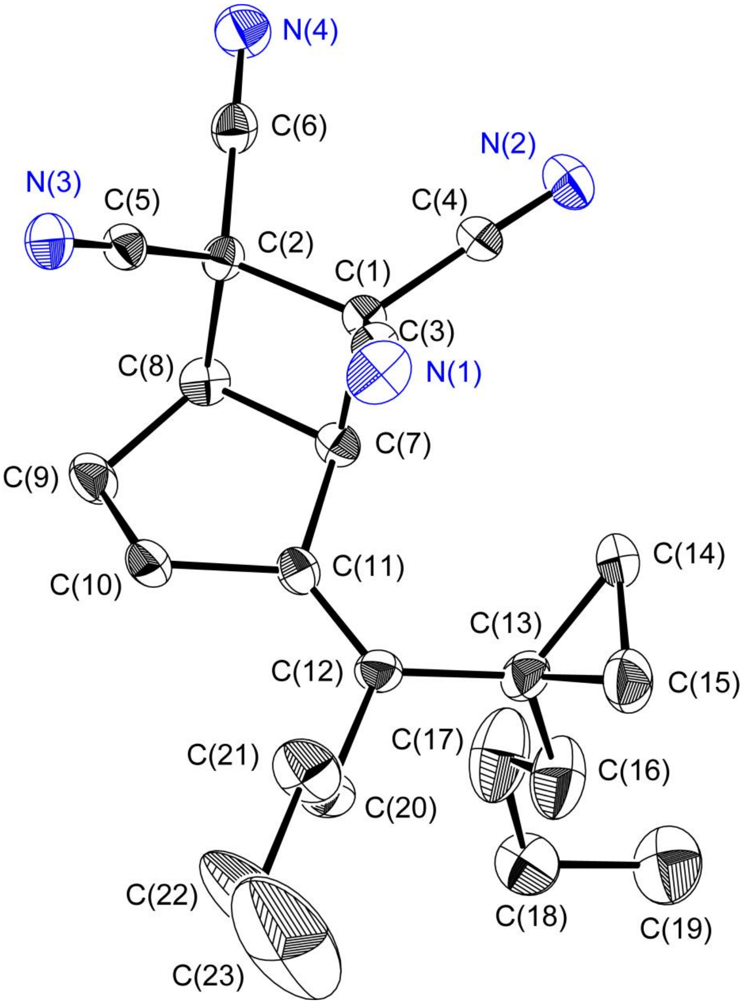


**Fig. S21.** X-ray Structure of compound **4a**. All hydrogen atoms are omitted for clarity.

## A Possible Reaction Mechanism