Access to Cyclohexadiene and Benzofuran Derivatives via Catalytic Arene Cyclopropanation of α-Cyanodiazocarbonyl Compounds

Mei-Lin Chen, Chi-wen Chou, Jia-Liang Zhu* and Ming-Hsuan Tsai

Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan E-mail: jlzhu@gms.ndhu.edu.tw

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Supporting Information

1) General remarks

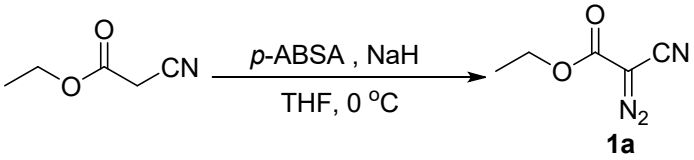
Dichloromethane, benzene, toluene and tetrahydrofuran were properly dried (CH_2Cl_2/benzene/toluene with CaH_2 and THF with Na) and freshly distilled before each use. Acetonitrile (HPLC-grade) was stored with 3Å molecular sieve in a dry box before usage. Other chemicals purchased from commercial sources were used as received without further purification. All reactions were carried out under a N_2 atmosphere, monitored by thin-layer chromatography on 0.25 mm silica plates (60F-254), and visualized with UV light, ethanolic solution of vanillin (5%) or aqueous KMnO4 solution (10%). Chromatographic separation was performed with 70-230 mesh silica gel or basic aluminum oxide. 7-Cyanonorcaradienyl esters **2a**-**d** or bis(cyclopropanated) adducts **3a**/**3a'**/**3c**-**j** were purified over Et_3N-deactivated silica gel by pre-eluting the silica gel column with 2% triethylamine in hexane (100 mL for 50 g of silica gel) followed by pure hexane (50 mL). The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or C_6D_6 at 300 K on a Bruker 400 or an Agilent Technologies 600 MHz Fourier transform spectrometer. The ^1H NMR data are reported as the chemical shift in parts per million (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m. multiplet), coupling constants (*J*) in Hertz, and number of protons. The resonances of infrared (IR) spectra are reported in wave numbers (cm^{-1}). Mass spectra were determined in electron impact (EI) ionization mode (70 eV) with magnetic sector analyzer. Crystal crystallographic data of compounds **3c**, **3f** and **3h** have been deposited in the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 2348559, 2348853 and 2348856.

2) Preparation of Diazo Substrates

Ethyl diazoacetate (**1d**) was purchased as a CH_2Cl_2 solution with the concentration calculated as 9.29 M. Substrates **1e-g** were synthesized according to the procedures in our previous report.[1]

i) Preparation and NMR Spectra of α-Cyanodiazoacetates 1a-c

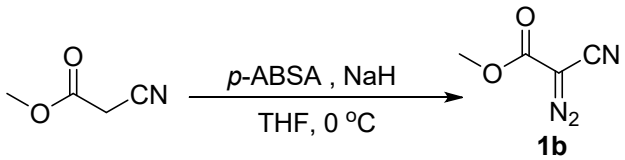
Ethyl 2-cyano-2-diazoacetate (**1a**)[2]



1a

A solution of ethyl cyanoacetate (300 mg, 98%, 0.29 mL, 2.65 mmol) in THF (20 mL, 0.1326 M) was stirred in an ice bath for 1 h followed by the addition of NaH (127.2 mg, 60%, 3.18 mmol) in one portion. After stirring for an additional 3 min, 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 1.95 g, 98%, 7.96 mmol) was introduced, and the mixture was continuously stirred in the ice bath for 15 min before quenched by slowly adding 2 mL of water. The resulting suspension was diluted with CH_2Cl_2 (300 mL) and successively washed with saturated NH_4Cl aqueous solution (70 mL), water (70 mL) and brine (70 mL). The organic layer was separated and concentrated under reduced pressure. The crude residue was subjected to chromatographic purification (silica gel; hexane/ethyl acetate = 6:1, 3:1) to give **1a** as a colorless oil (181 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4,33 (q, J = 7.1 Hz, 2 H), 1.32 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (C=O), 107.3 (C≡N), 63.4 (CH_2), 51.1 ($C=N_2$), 14.2 (CH_3) ppm.

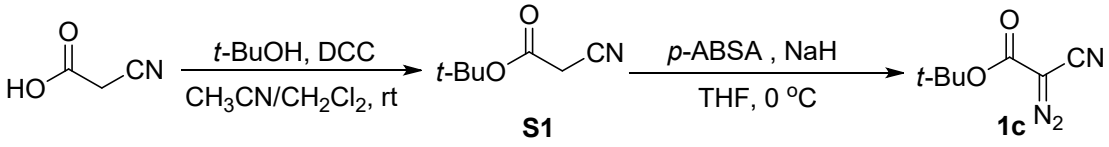
Methyl 2-cyano-2-diazoacetate (**1b**)[3]



1b

The titled compound was synthesized from methyl cyanoacetate following the procedure for the preparation of **1a**. Chromatographic purification (silica gel; hexane/ethyl acetate = 6:1) afforded **1b** as a yellow oil (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (C=O), 107.2 (C≡N), 53.8 (CH_3), 51.2 ($C=N_2$) ppm.

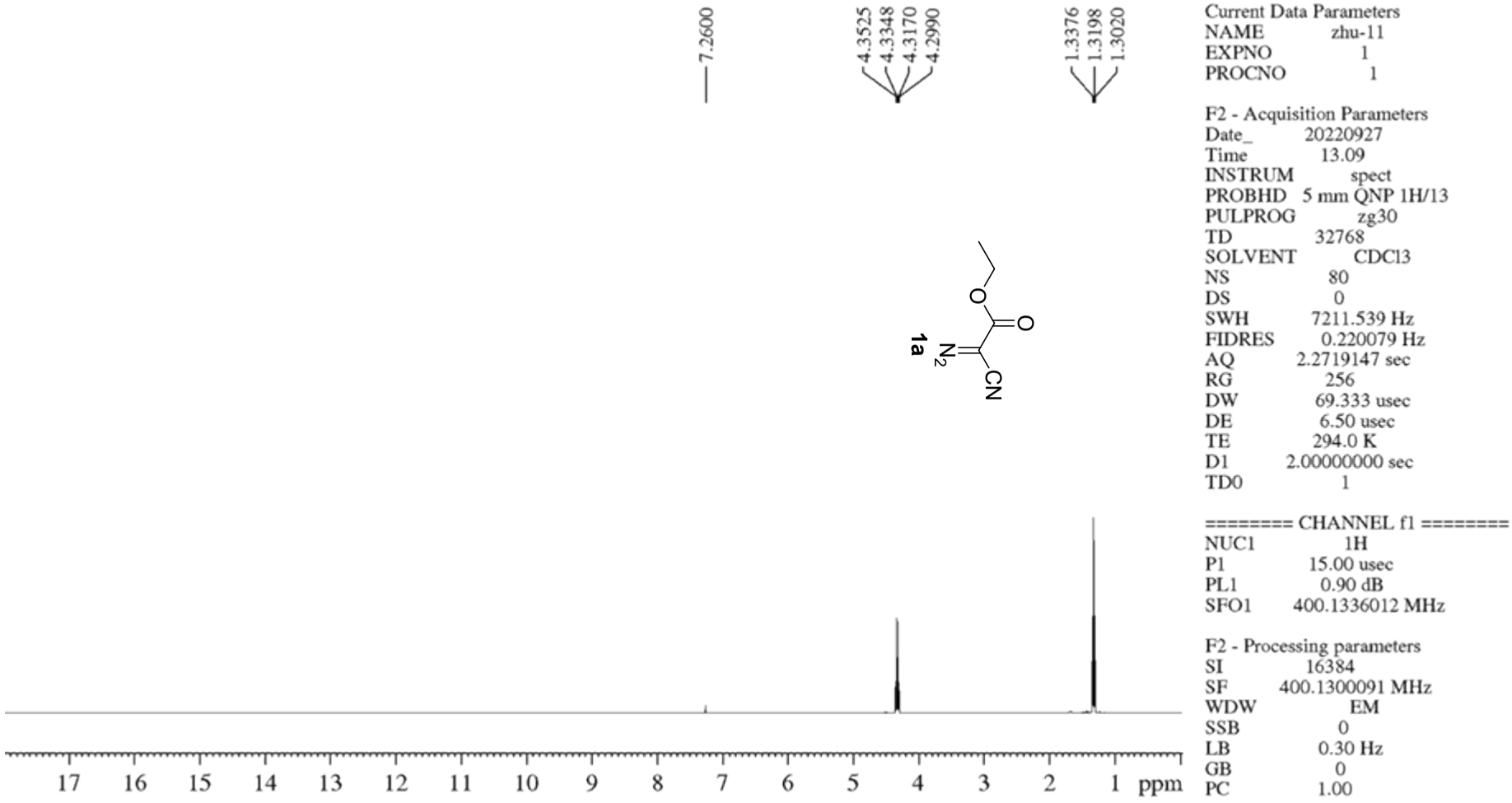
t-Butyl 2-cyano-2-diazoacetate (**1c**)[2]



S1 **1c**

To a stirred mixture of 2-cyanoacetic acid (500 mg, 5.88 mmol) and *t*-butyl alcohol (0.7 mL, 7.34 mmol) in CH_3CN (5.9 mL), a solution of *N*,*N*'-dicyclohexylcarbodiimide (1.35 g, 99%, 6.47 mmol) in CH_2Cl_2 (6.5 mL) was added via a syringe over 5 min. After stirring for an additional 40 min, the resulting white suspension was directly loaded on silica gel column and eluted with hexane-ethyl acetate (6:1, 3:1) to give *tert*-butyl 2-cyanoacetate[4] (**S1**) as a yellow oil (689.7 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 2 H), 1.48 (s, 9 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (C=O), 113.5 (C≡N), 84.3(C-O), 27.7 (CH_3), 25.8 (CH_2) ppm.

Compound **1c** was synthesized from **S1** following the procedure for the preparation of **1a**. Chromatographic purification (silica gel; hexane/ethyl acetate = 40:1, 35:1, 10:1) afforded **1c** as a yellow oil (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 9 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (C=O), 107.8 (C≡N), 85.5 (C-O), 51.2 ($C=N_2$), 28.0 (CH_3) ppm.



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DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
TD0 1

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PL1 0.90 dB
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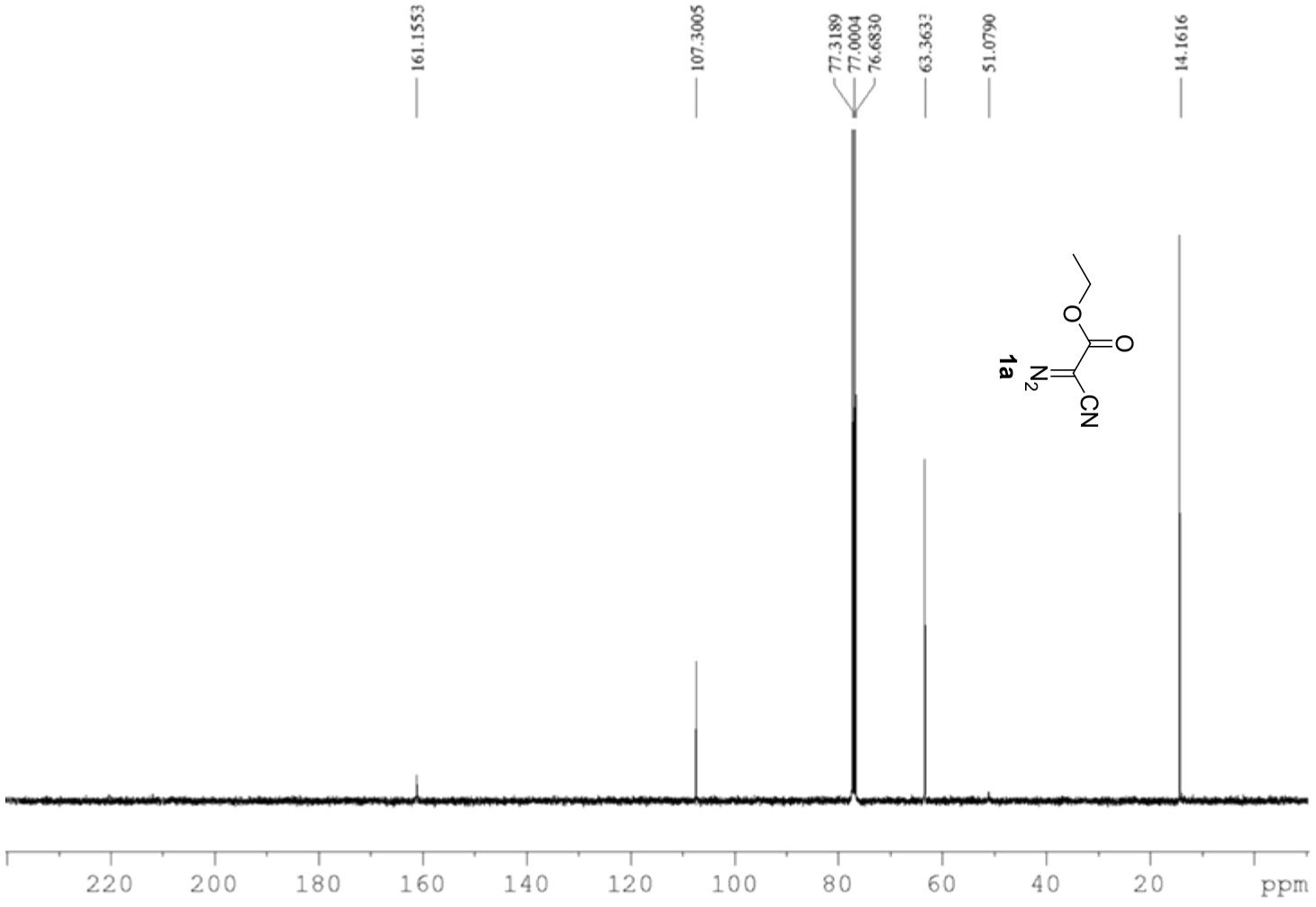

1a

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FIDRES 0.385323 Hz
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DE 6.50 usec
TE 294.2 K
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d11 0.03000000 sec
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TD0 1

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PL1 6.20 dB
SFO1 100.6243395 MHz

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NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
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SF 100.6127777 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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PROCNO 1
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PULPROG zg30
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SWH 7211.539 Hz
FIDRES 0.220079 Hz
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RG 406
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DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
TD0 1
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F2 - Processing parameters
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WDW EM
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CN
O
N2
1b
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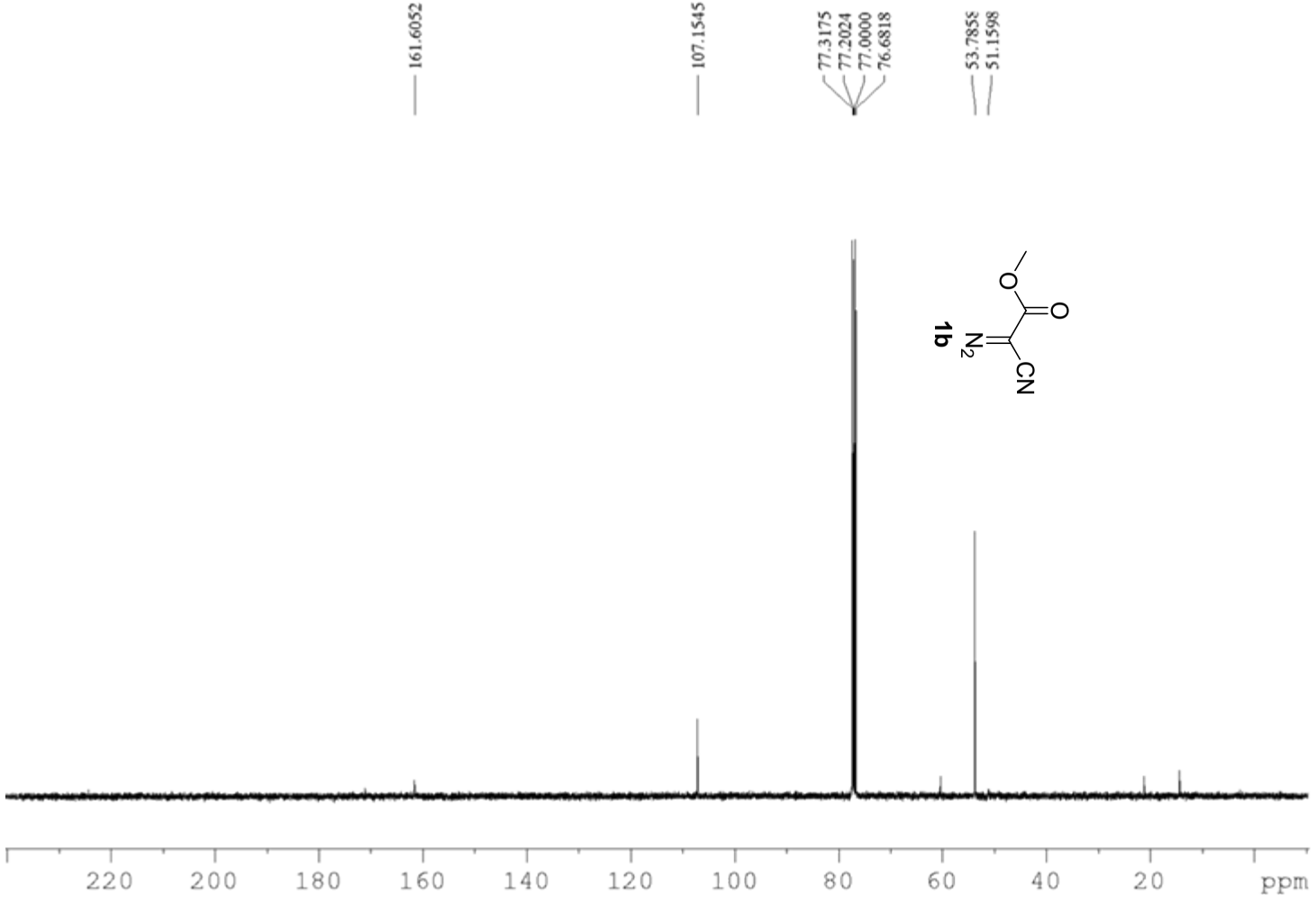
3.0000
ppm



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PROCNO 1

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FIDRES 0.385323 Hz
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RG 2050
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DE 6.50 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
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TD0 1

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SFO1 100.6243395 MHz

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PCPD2 90.00 usec
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PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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PROCNO 1
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SOLVENT CDCl3
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SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 101
DW 69.333 usec
DE 6.50 usec
TE 292.0 K
D1 2.00000000 sec
TD0 1
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SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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CN
t-BuO
S1
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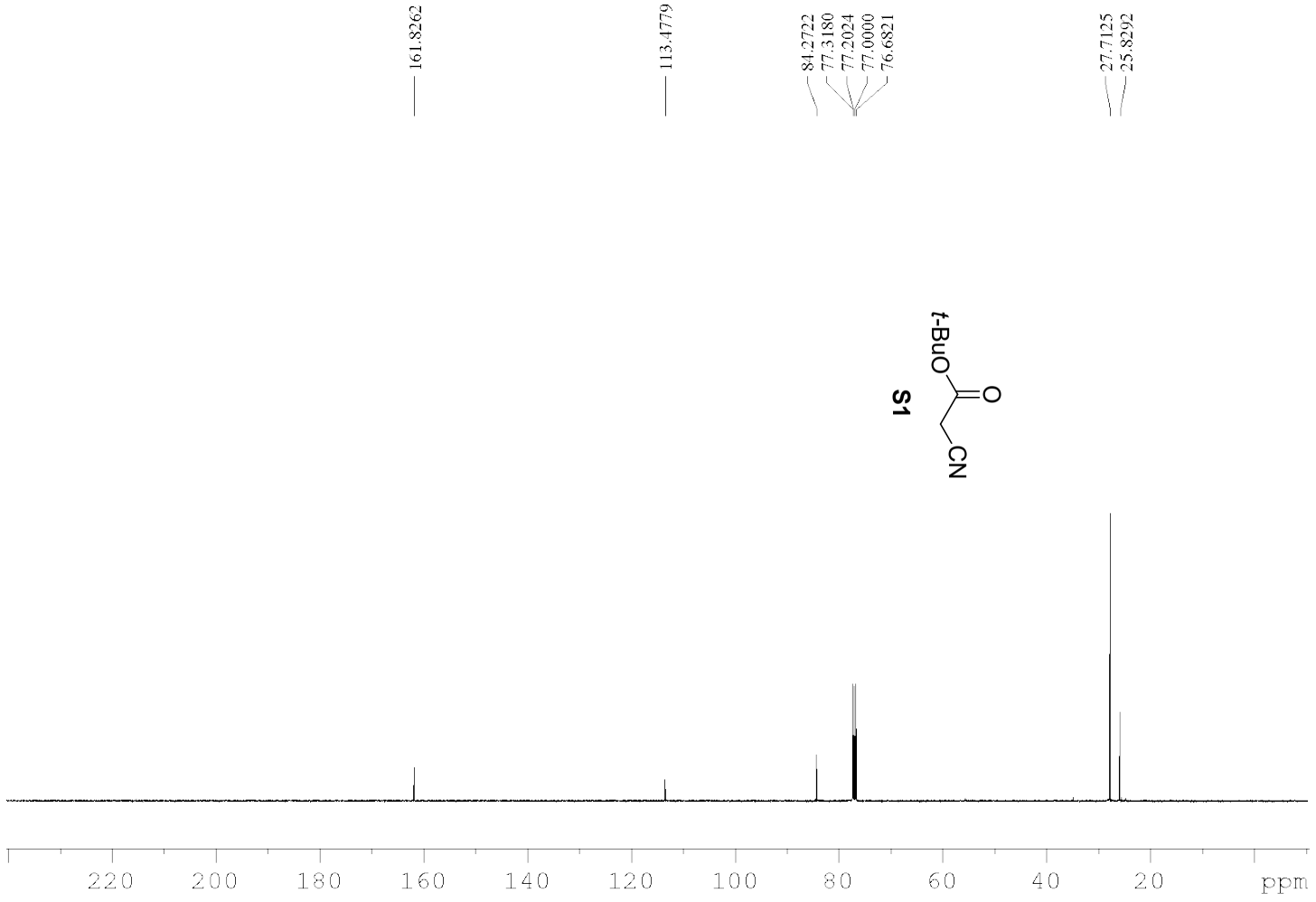

S1

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DE 6.50 usec
TE 292.1 K
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d11 0.03000000 sec
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TD0 1

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PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
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PL13 18.50 dB
SFO2 400.1316005 MHz

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LB 1.00 Hz
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EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 12.09
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 80
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SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 228
DW 69.333 usec
DE 6.50 usec
TE 292.4 K
D1 2.00000000 sec
TD0 1
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PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
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SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
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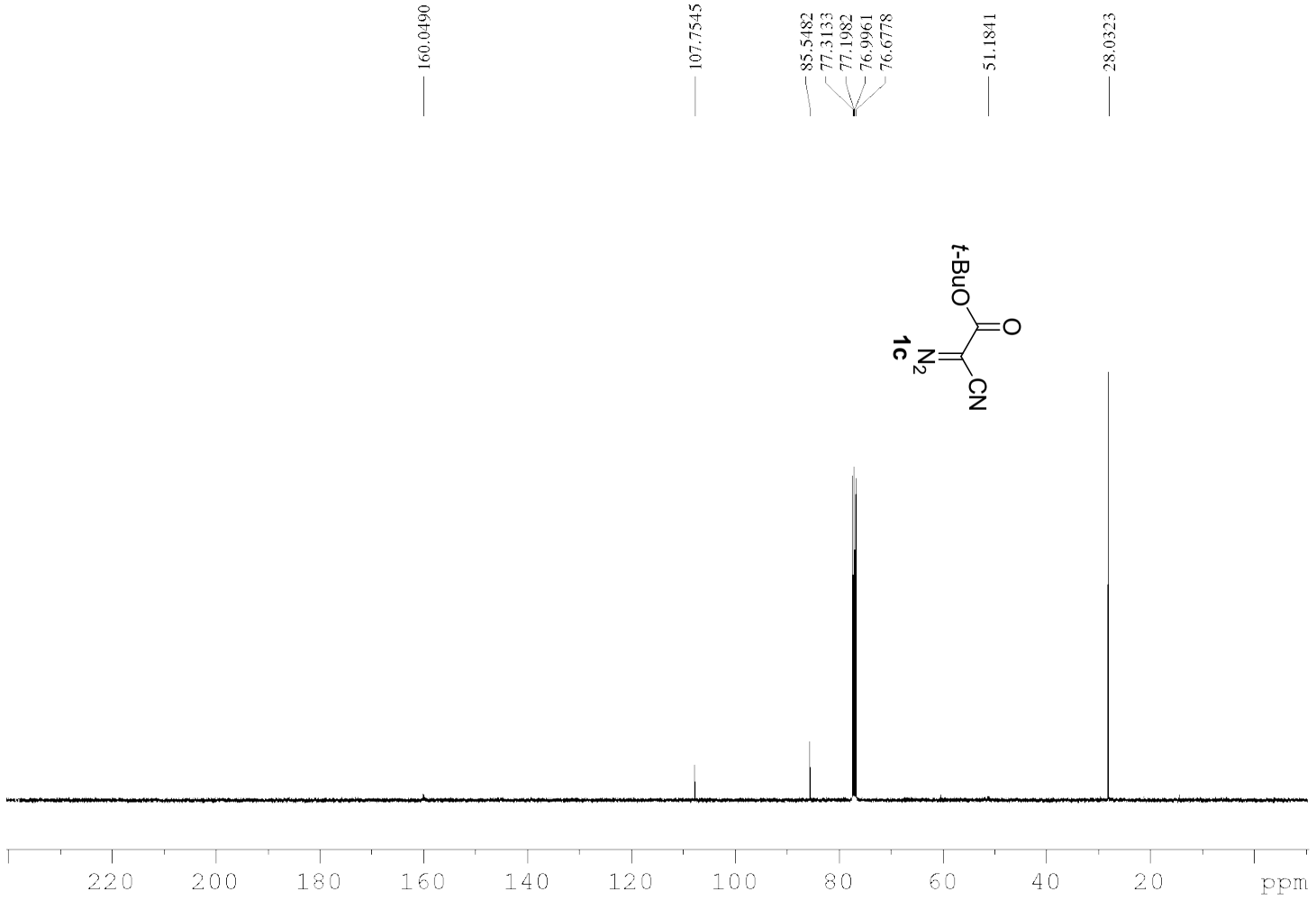
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm



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PROCNO 1

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FIDRES 0.385323 Hz
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DE 6.50 usec
TE 292.6 K
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d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

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PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
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PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
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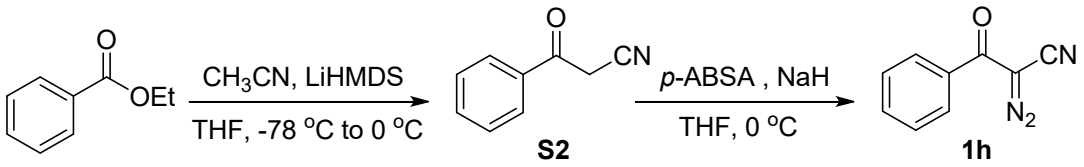
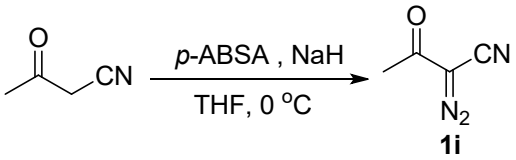
ii) Preparation and NMR Spectra of α-Diazo-β-ketonitriles 1h and 1i 2-Diazo-3-oxo-3-phenylpropanenitrile (**1h**)[2]



A flame-dried flask equipped with a stir bar was charged with THF (11 mL) and LiHMDS (1M in THF, 11.7 mL, 11.7 mmol). The solution was stirred at -78 ˚C for 40 min followed by the addition of CH_3CN (0.72 mL, 13.85 mmol) in one portion. After stirring for an additional 30 min, a solution of ethyl benzoate (800 mg, 5.33 mmol) in THF (33 mL) was dropwise added via a syringe pump over 10 min. The reaction mixture was allowed to warm to 0 ˚C in 1 h, then diluted by ethyl acetate (400 mL) and washed with saturated NH_4Cl aqueous solution (100 mL), water (100 mL) and brine (100 mL). The organic layer was separated and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel; hexane/ethyl acetate = 10:1, 3:1) to afford 3-oxo-3-phenylpropanenitrile[5] (**S2**) as a white solid (813 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2 H), 7.67 (t, *J* = 7.3 Hz, 1 H), 7.53 (t, *J* = 7.7 Hz, 2 H), 4.10 (s, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1 (C=O), 134.7, 134.2, 129.1, 128.4, 113.8 (C≡N), 29.4 (CH_2) ppm.

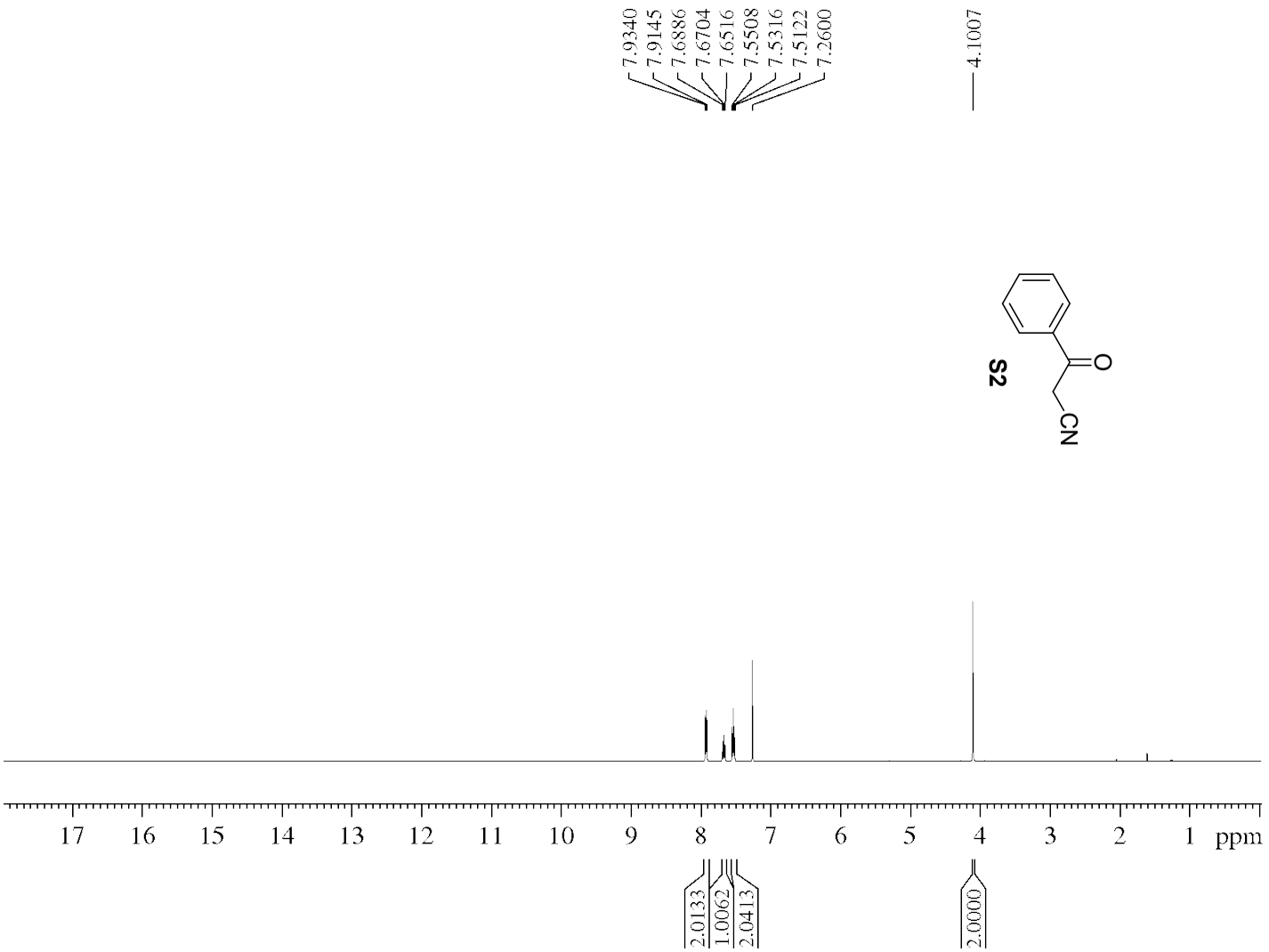
A solution of **S2** (567.4 mg, 3.91 mmol) in THF (29.2 mL, 0.1326 M) was stirred in an ice bath for 1 h followed by the introduction of *p*-ABSA (2.87 g, 98%, 11.73 mmol). After stirring for 5 min, NaH (187.6 mg, 60%, 4.69 mmol) was added in two portions at 5 min interval (first 100 mg then 87.6 mg). The reaction mixture was stirred in the ice bath for an additional 6 min before quenched by adding 5 mL of water. The resulting suspension was diluted by CH_2Cl_2 (400 mL) and washed with saturated NH_4Cl aqueous solution (80 mL), water (80 mL) and brine (80 mL). After concentration, the residue was subjected to chromatographic purification (silica gel; hexane/ethyl acetate = 5:1) to give **1h** as a yellow solid (231 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 1 H)), 7.50 (t, *J* = 7.9 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9 (C=O), 134.5, 133.8, 128.8, 128.0, 109.1 (C≡N), 58.9 (C=N_2) ppm.

2-Diazo-3-oxobutanenitrile (**1i**)[6]



The titled compound was synthesized from commercially available 3-oxobutanenitrile following the procedure for the preparation of **1h**. Chromatographic purification

(silica gel; hexane/ethyl acetate = 3:1) gave **1i** in 21% yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3 (C=O), 108.5 (C≡N), 57.9 ($C=N_2$), 26.6 (CH_3) ppm.



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D1 2.00000000 sec
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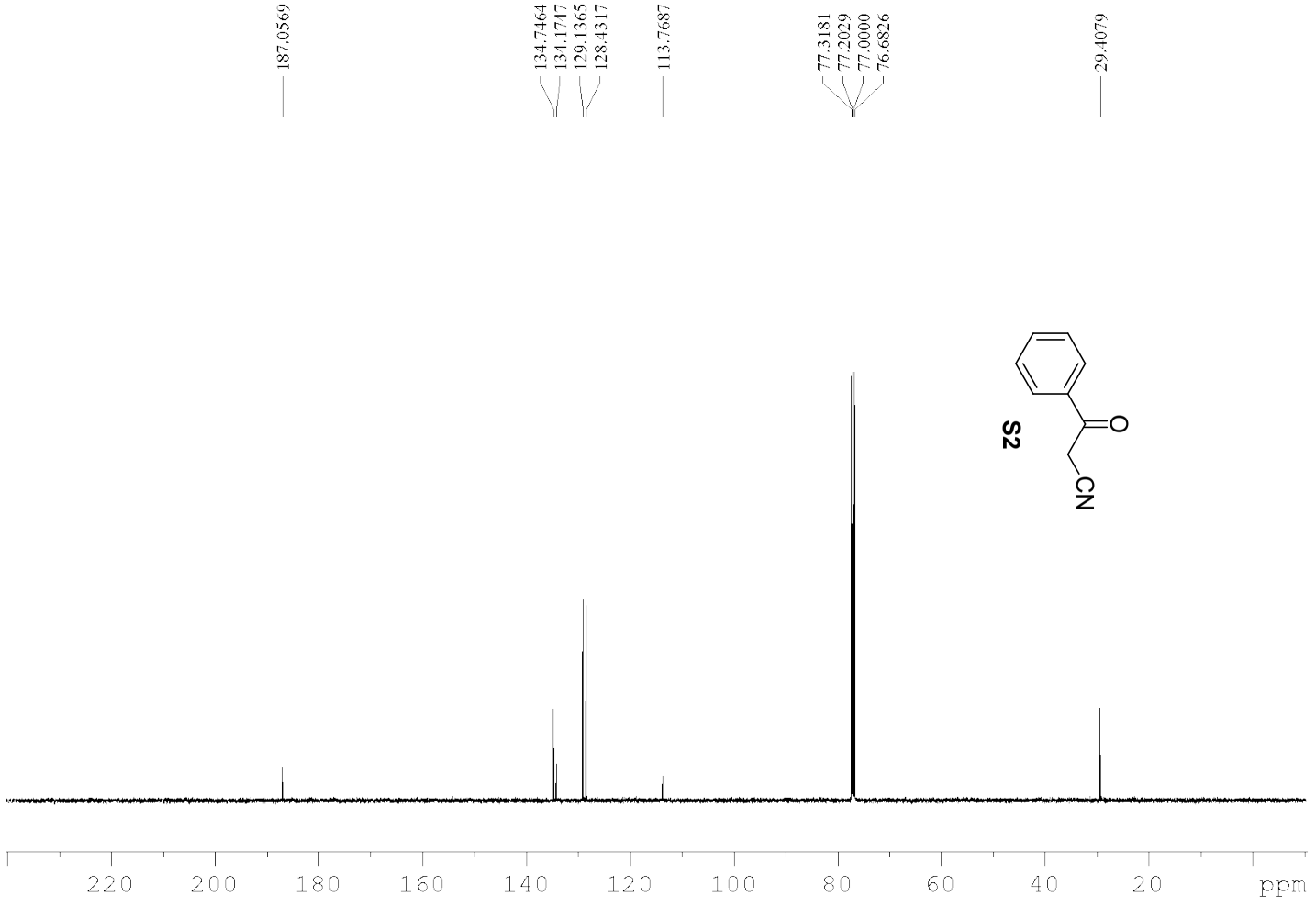

S2

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PROCNO 1

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DE 6.50 usec
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d11 0.03000000 sec
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PL12 15.80 dB
PL13 18.50 dB
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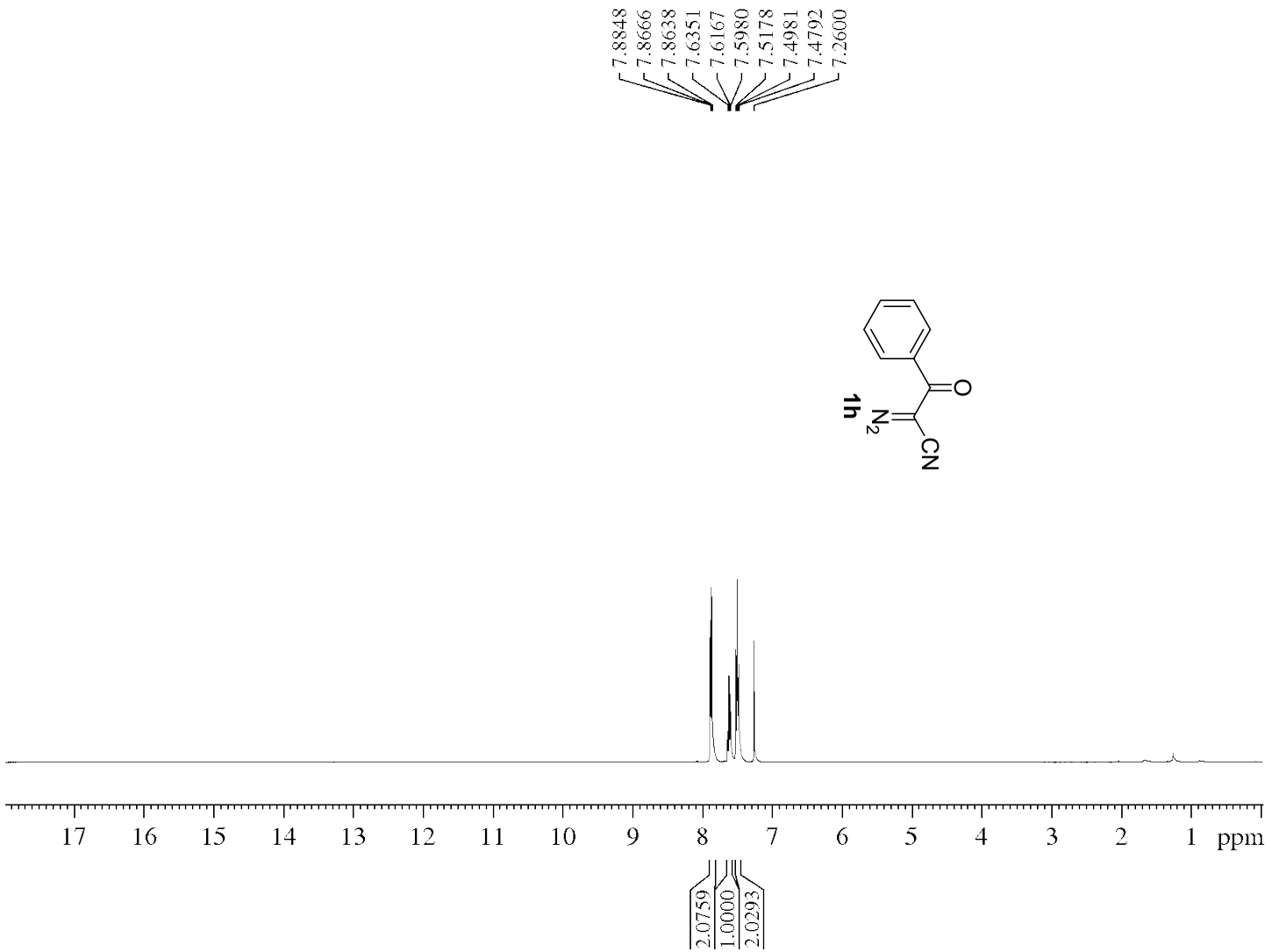

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RG 287
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DE 6.50 usec
TE 291.0 K
D1 2.00000000 sec
TD0 1

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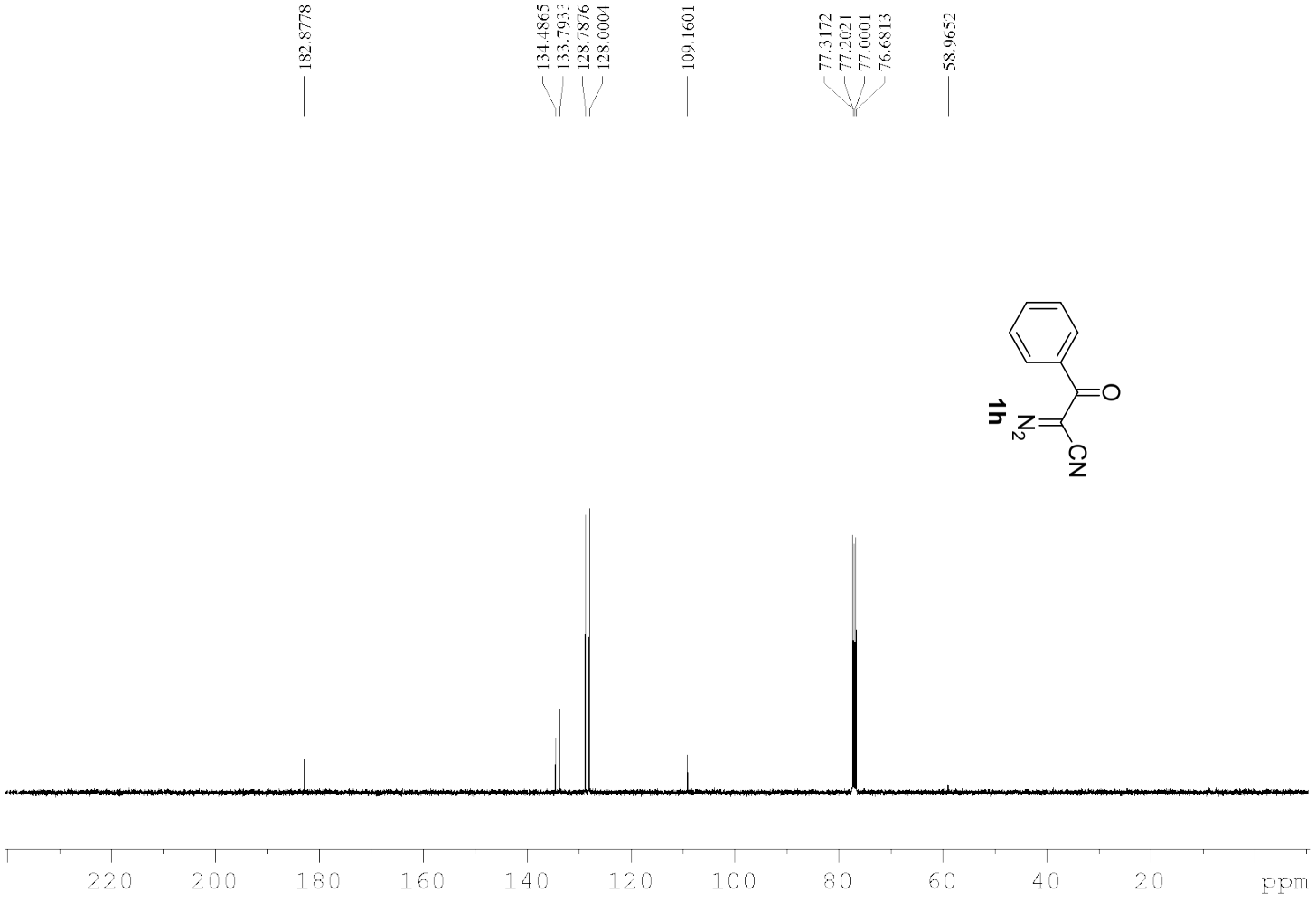

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PROCNO 1

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FIDRES 0.385323 Hz
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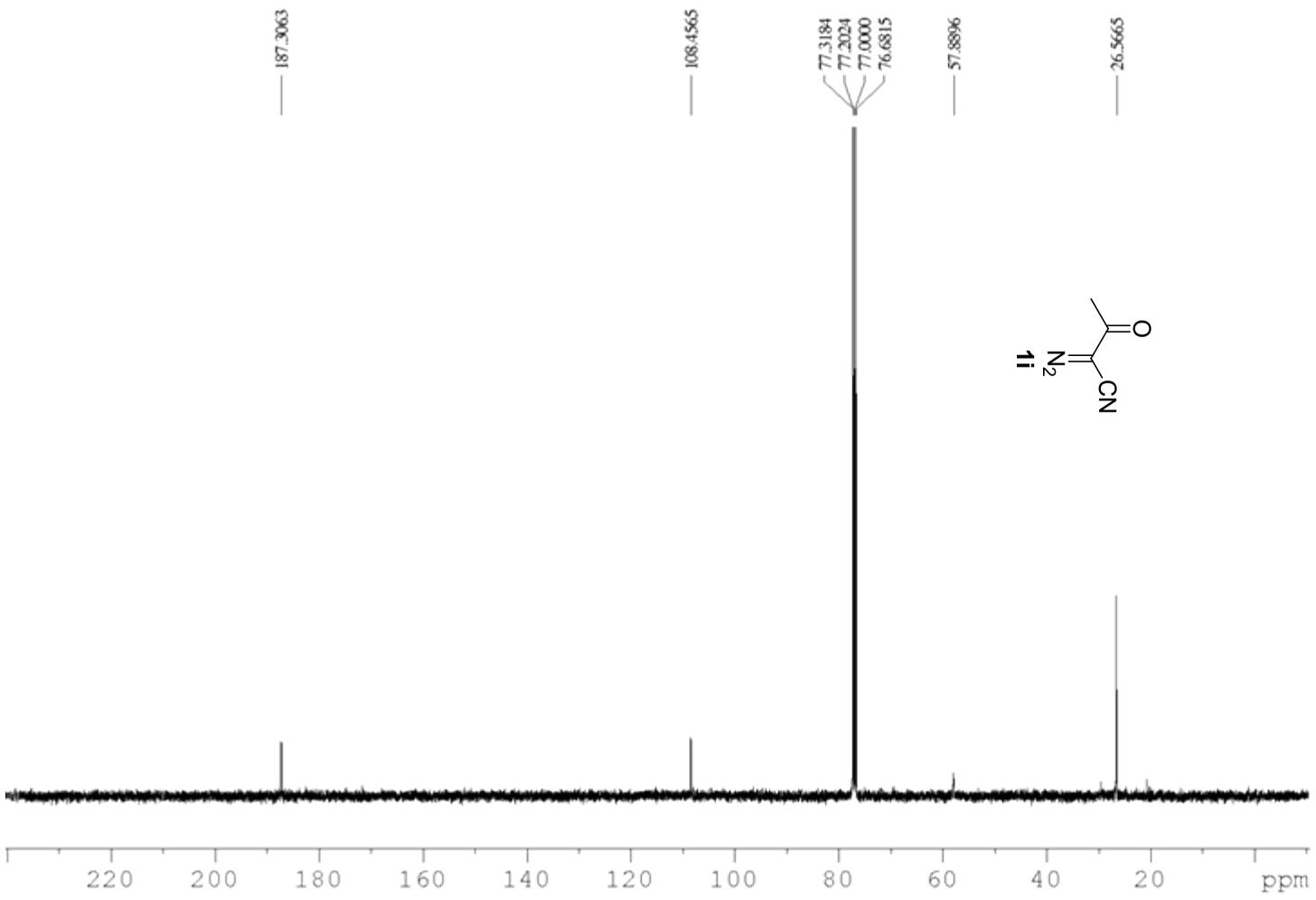
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 291.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127788 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Current Data Parameters
NAME zhu-22
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20221128
Time 12.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 41
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 228
DW 69.333 usec
DE 6.50 usec
TE 293.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.2600
2.3386
3.0000
O
CN
N2
1i
ppm



Current Data Parameters
NAME zhu-22
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221128
Time 12.25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 350
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

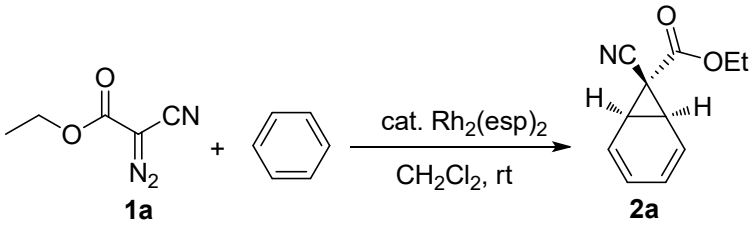
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127807 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

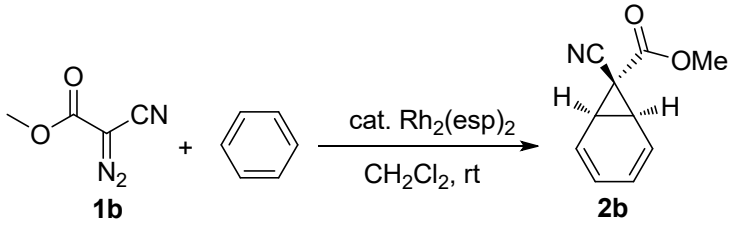
3) Preparation and NMR Spectra of Norcaradienes 2a-d

Typical Procedure: A solution of α-cyanodiazoaceates **1** (0.8376 mmol) in CH_2Cl_2 (4.3 mL) was added dropwise to a stirred mixture of benzene or toluene (50.20 mmol, 60 equiv) and $Rh_2(esp)_2$ (19.8 mg, 96%, 0.03 equiv relative to **1**) in CH_2Cl_2 (4 mL) *via* a syringe over 6 min. The reaction mixture was stirred for an additional 1 h followed by the concentration under reduced pressure. The crude residue was subjected to chromatographic purification on triethylamine-deactivated silica gel by eluting with hexane/ethyl acetate to furnish **2a-d**. (*1R**,*6S**,*7R**)-Ethyl-7-cyanobicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**2a**)[7]



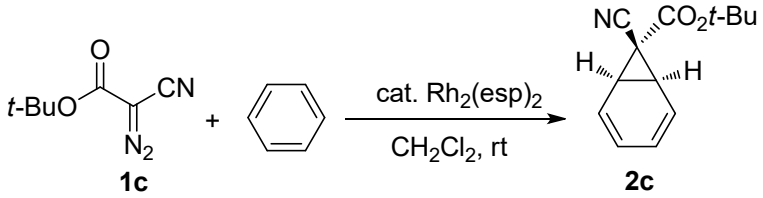
The titled compound was synthesized from **1a** and benzene by following the typical procedure. After chromatographic purification (triethylamine-deactivated silica gel; hexane/ethyl acetate = 6:1, 3:1), **2a** was obtained in 66% yield as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (dd, *J* = 7.4, 2.8 Hz, 2 H, =CH), 6.24-6.19 (m, 2 H, =CH), 4.31 (q, *J* = 7.1 Hz, 2 H, CH_3CH_2O), 3.24-3.22 (m, 2 H), 1.36 (t, *J* = 7.1 Hz, 3 H, CH_3CH_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (C=O), 127.2 (=CH), 122.1 (=CH), 112.4 (C≡N), 63.2 (CH_2O), 39.3 (CH), 14.1 (CH_3), 12.1 (C) ppm.

(1*R**,6*S**,7*R**)-Methyl-7-cyanobicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**2b**)[8]



The titled compound was synthesized from **1b** and benzene by following the typical procedure. After chromatographic purification (triethylamine-deactivated silica gel; hexane/ethyl acetate = 10:1, 6:1), **2b** was obtained in 71% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (dd, *J* = 7.4, 2.8 Hz, 2 H, =CH), 6.24-6.20 (m, 2 H, =CH), 3.87 (s, 3 H, CH_3O), 3.25 (br t, *J* = 3.1 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (C=O), 127.4 (=CH), 122.0 (=CH), 112.4 (C≡N), 53.9 (CH_3O), 39.4 (CH), 12.2 (C) ppm.

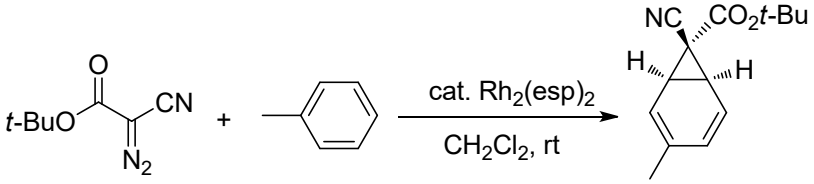
(1*R**,6*S**,7*R**)-*tert*-Butyl-7-cyanobicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**2c**)[9]



1c **2c**

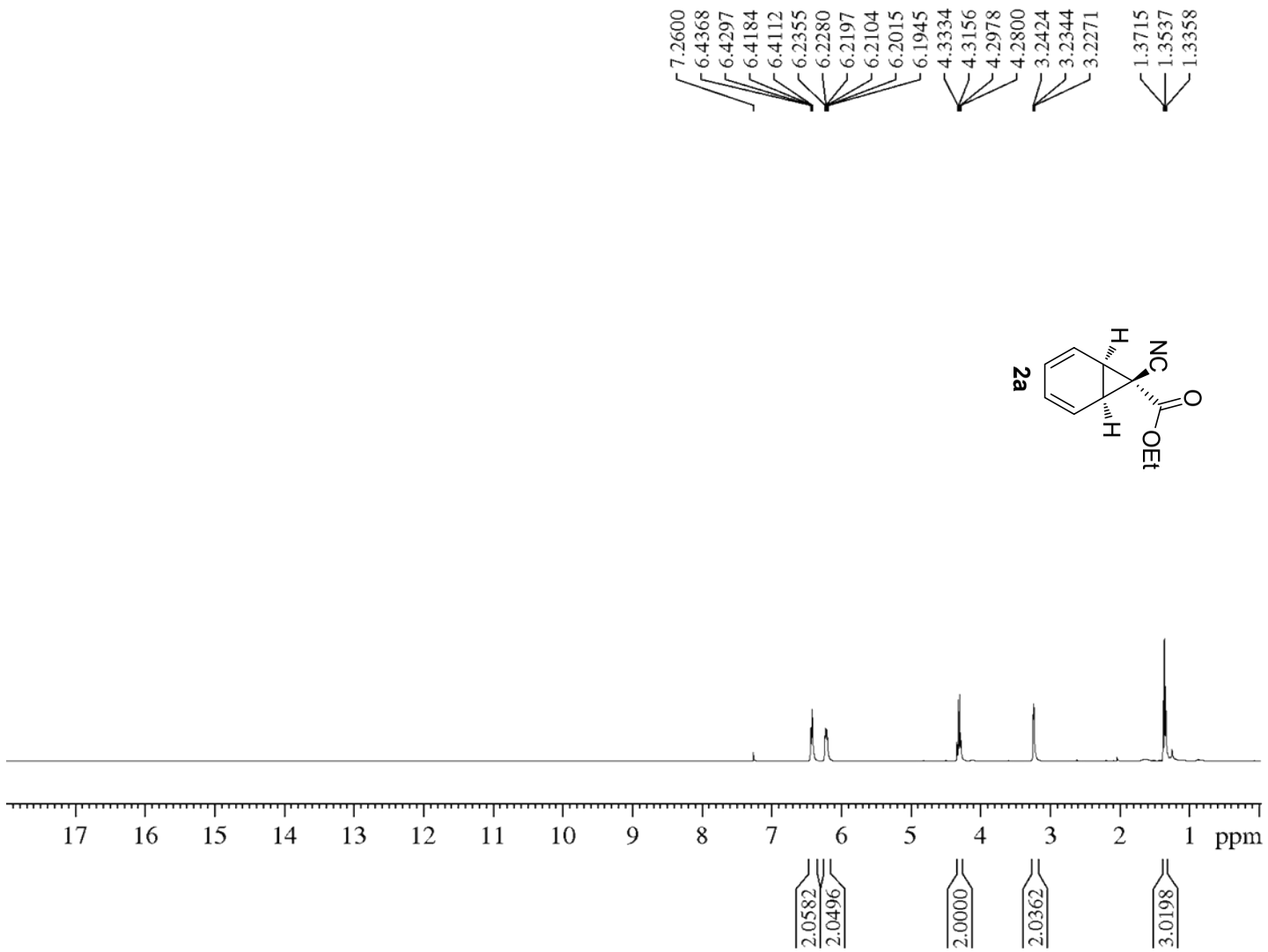
The titled compound was synthesized from **1c** and benzene by following the typical procedure. After chromatographic purification (triethylamine-deactivated silica gel; hexane/ethyl acetate = 12:1), **2c** was obtained in 54% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (dd, J = 7.4, 2.9 Hz, 2 H, =CH), 6.22-6.18 (m, 2 H, =CH), 3.15 (br t, J = 3.2 Hz, 2 H), 1.53 (s, 9 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (C=O), 127.1 (=CH), 122.2 (=CH), 112.7 (C≡N), 84.2 (C-O), 39.0 (CH), 27.9 (CH_3), 12.7 (C) ppm.

(1*R**,6*S**,7*R**)-*tert*-Butyl-7-cyano-3-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**2d**)[9]



1c **2d** (rr: 10/1)

The titled compound was synthesized from **1c** and toluene by following the typical procedure. Chromatographic purification (triethylamine-deactivated silica gel; hexane/ethyl acetate = 50:1, 10:1, 6:1) afforded 59% of **2d** as a mixture of two regioisomers (rr: 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 6.23 (br d, J = 9.5 Hz, 1 H, =CH), 6.16-6.13 (m, 1 H, =CH), 5.87 (m, 1 H, =CH), 3.07-3.02 (m, 2 H), 1.92 (s, 3 H, CH_3), 1.49 (s, 9 H, methyl of *tert*-Bu) ppm; minor isomer: δ 6.30 (dd, J = 9.3, 6.3 Hz, 1 H, =CH), 6.14-6.10 (m, 1 H, =CH), 6.01 (dd, J = 9.3, 5.4 Hz, 1 H, =CH), 2.94-2.92 (m, 2 H), 2.02 (s, 3 H, CH_3), 1.50 (s, 9 H, methyl of *tert*-Bu) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 168.7 (C=O), 135.6, 130.9, 112.1, 117.0, 112.9 (CN), 83.7 (C-O), 38.7 (CH), 37.3 (CH), 27.8 (methyl of *t*-Bu), 21.4 (CH_3), 13.5 (C) ppm; minor isomer: δ 168.9 (C=O), 132.0, 127.6, 122.4, 118.7, 112.6 (CN), 83.9 (C-O), 40.9 (C), 39.1 (C), 27.8 (methyl of *t*-Bu), 22.9 (CH_3), 13.5 (C) ppm.

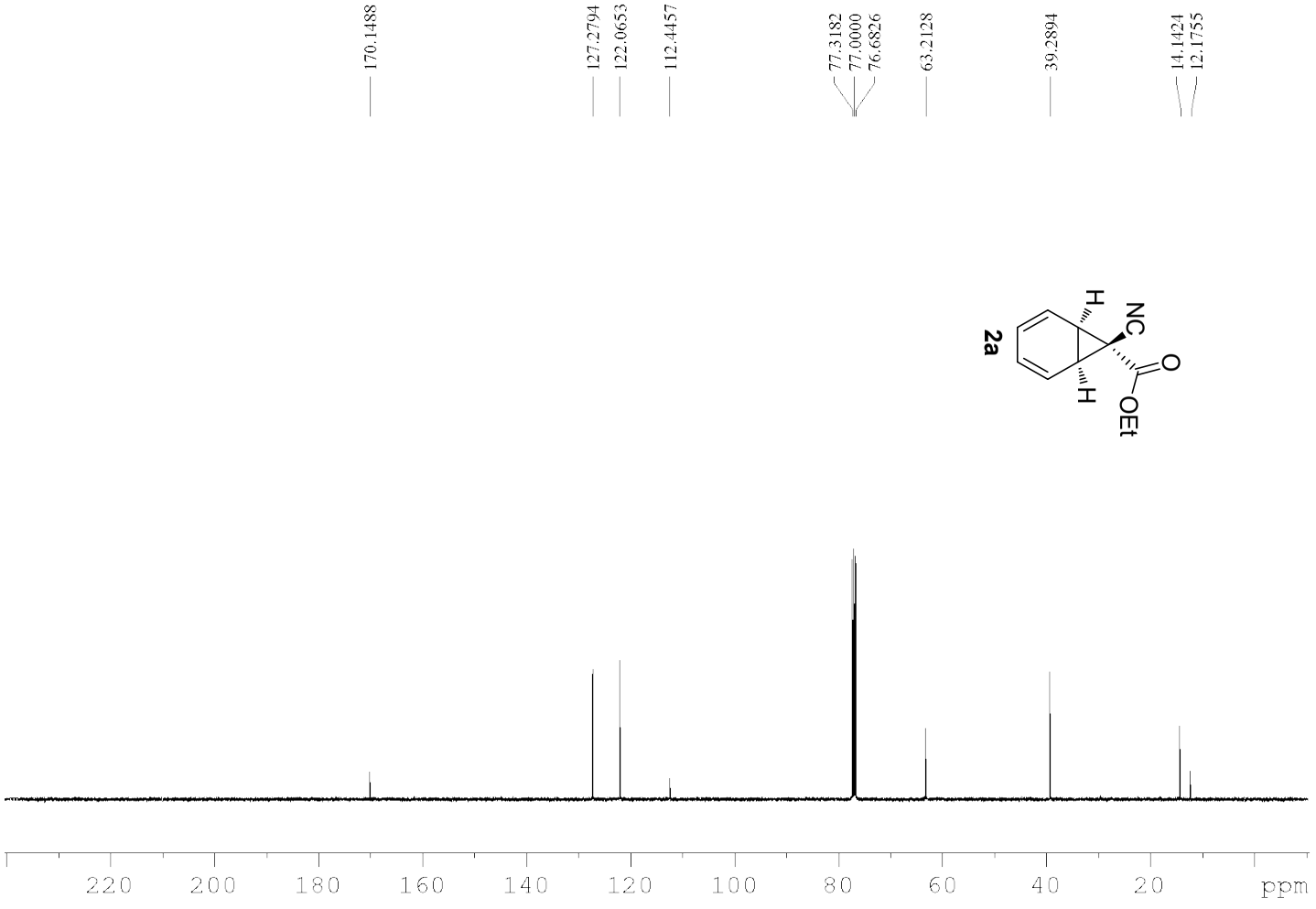


Current Data Parameters
NAME zhu-12-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221001
Time 14.25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 40
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 228
DW 69.333 usec
DE 6.50 usec
TE 293.9 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



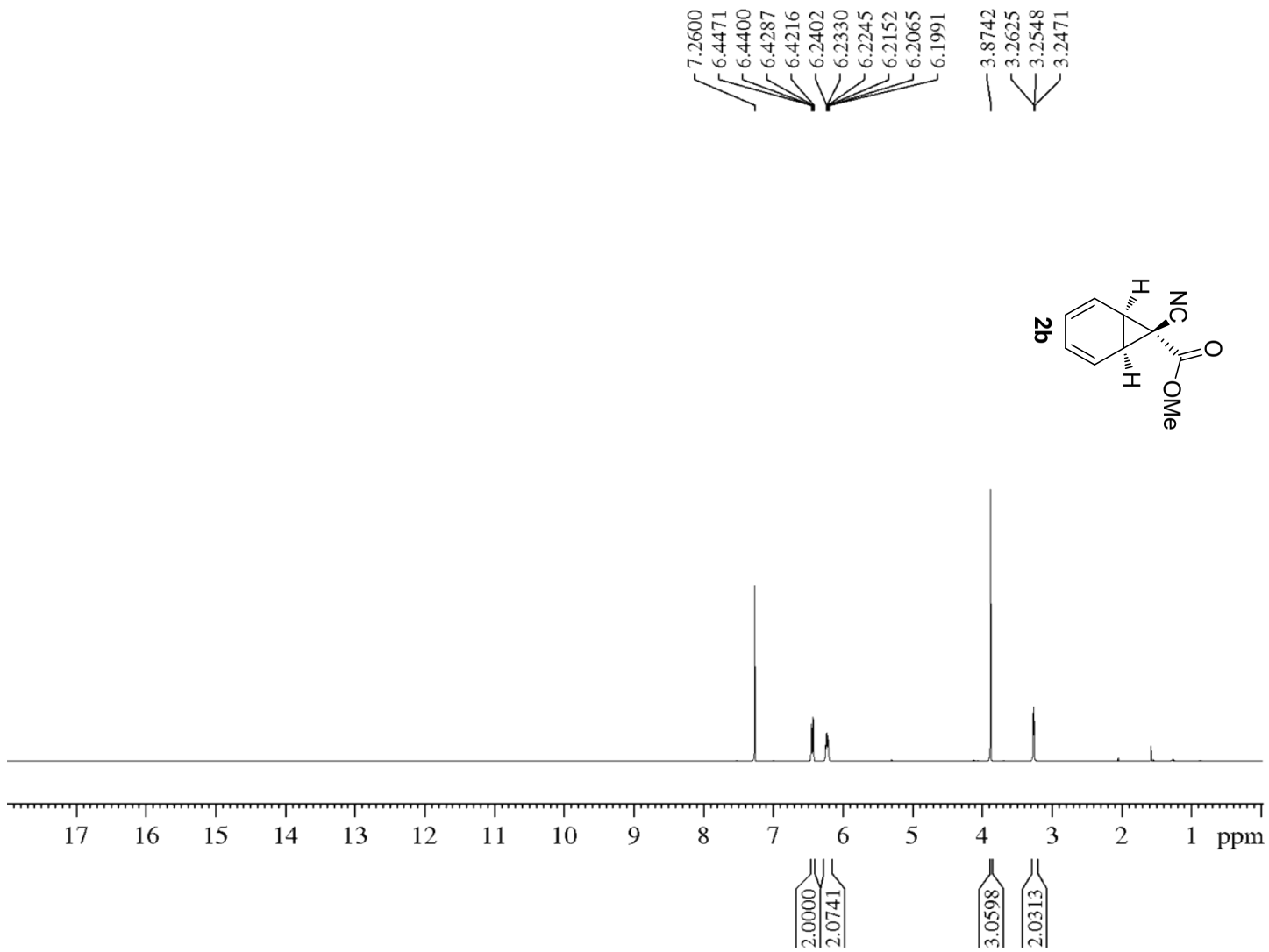
Current Data Parameters
NAME zhu-12-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221001
Time 14.32
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 601
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127755 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

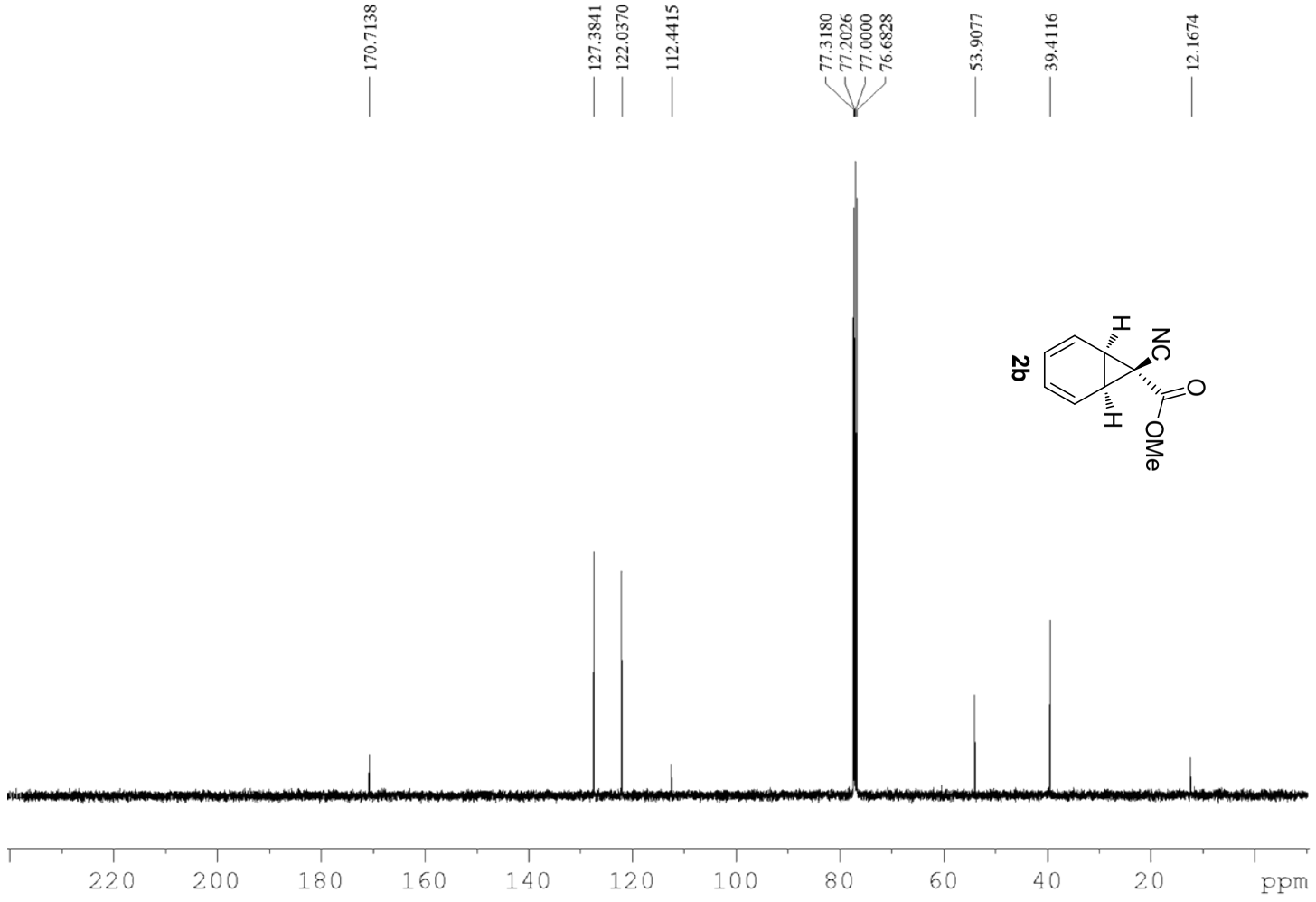


Current Data Parameters
NAME zhu-80
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230717
Time 16.34
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 456
DW 69.333 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



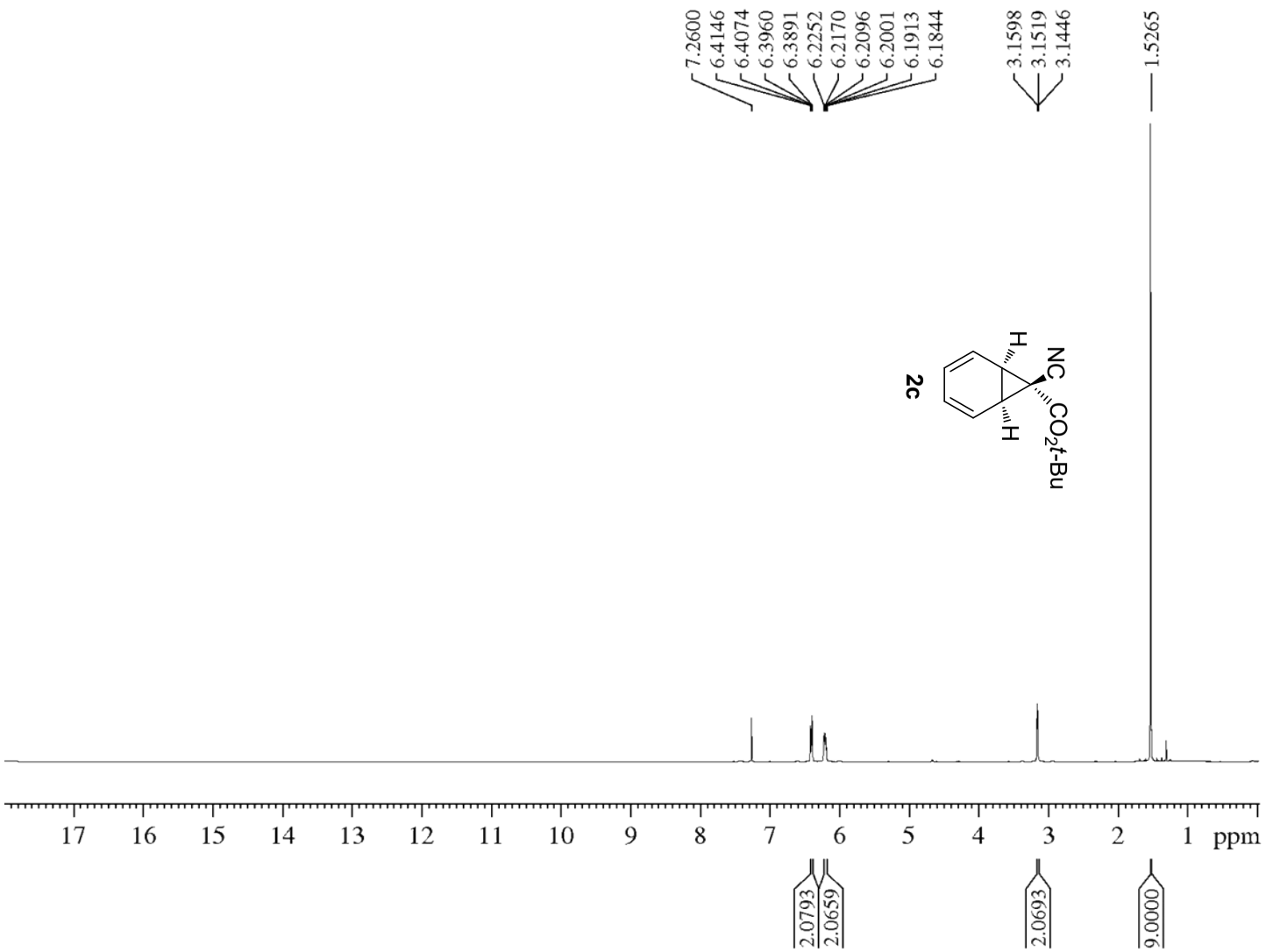
Current Data Parameters
NAME zhu-80
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230717
Time 16.41
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 252
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127730 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

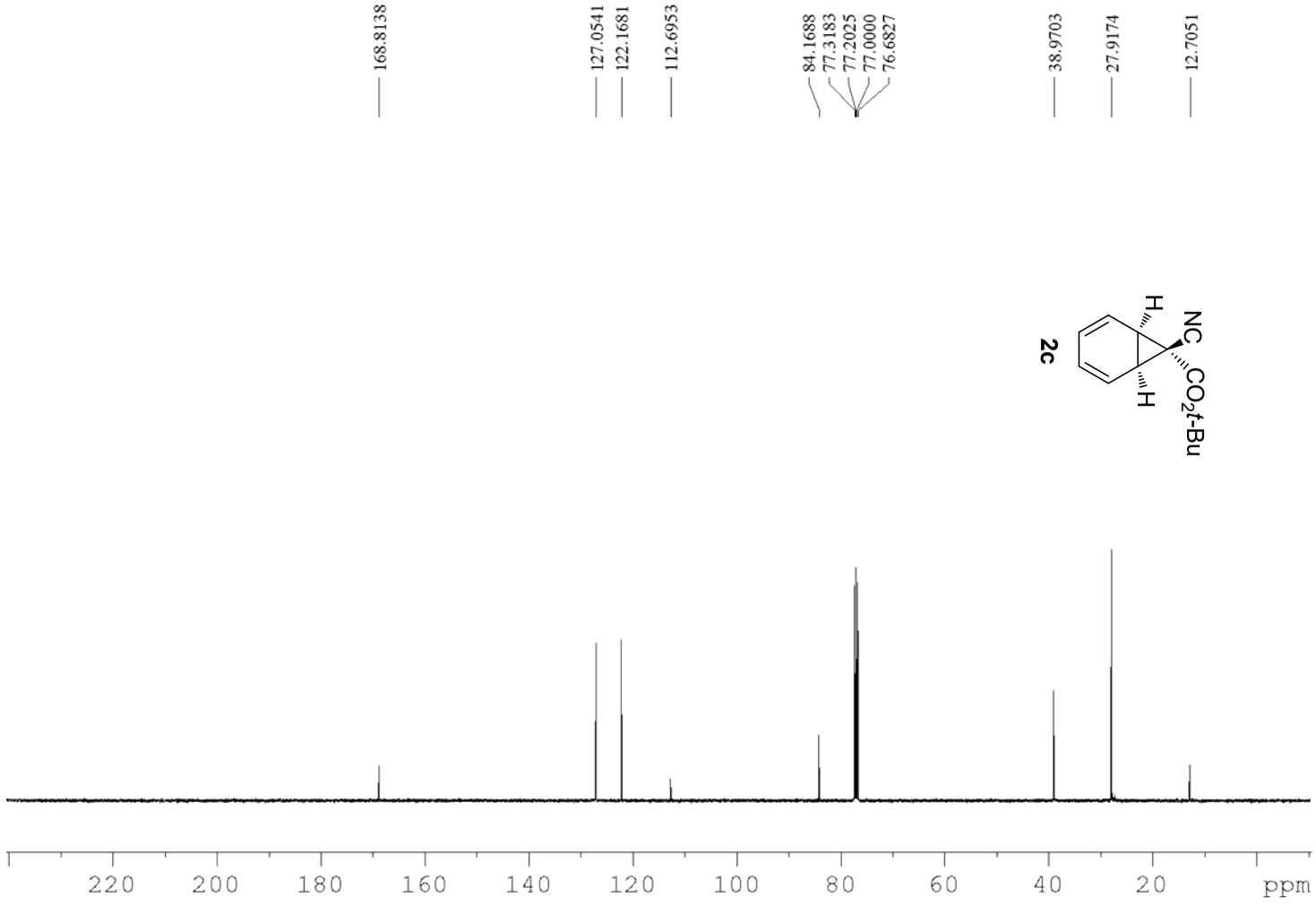


Current Data Parameters
NAME zhu-76
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230710
Time 13.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 203
DW 69.333 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



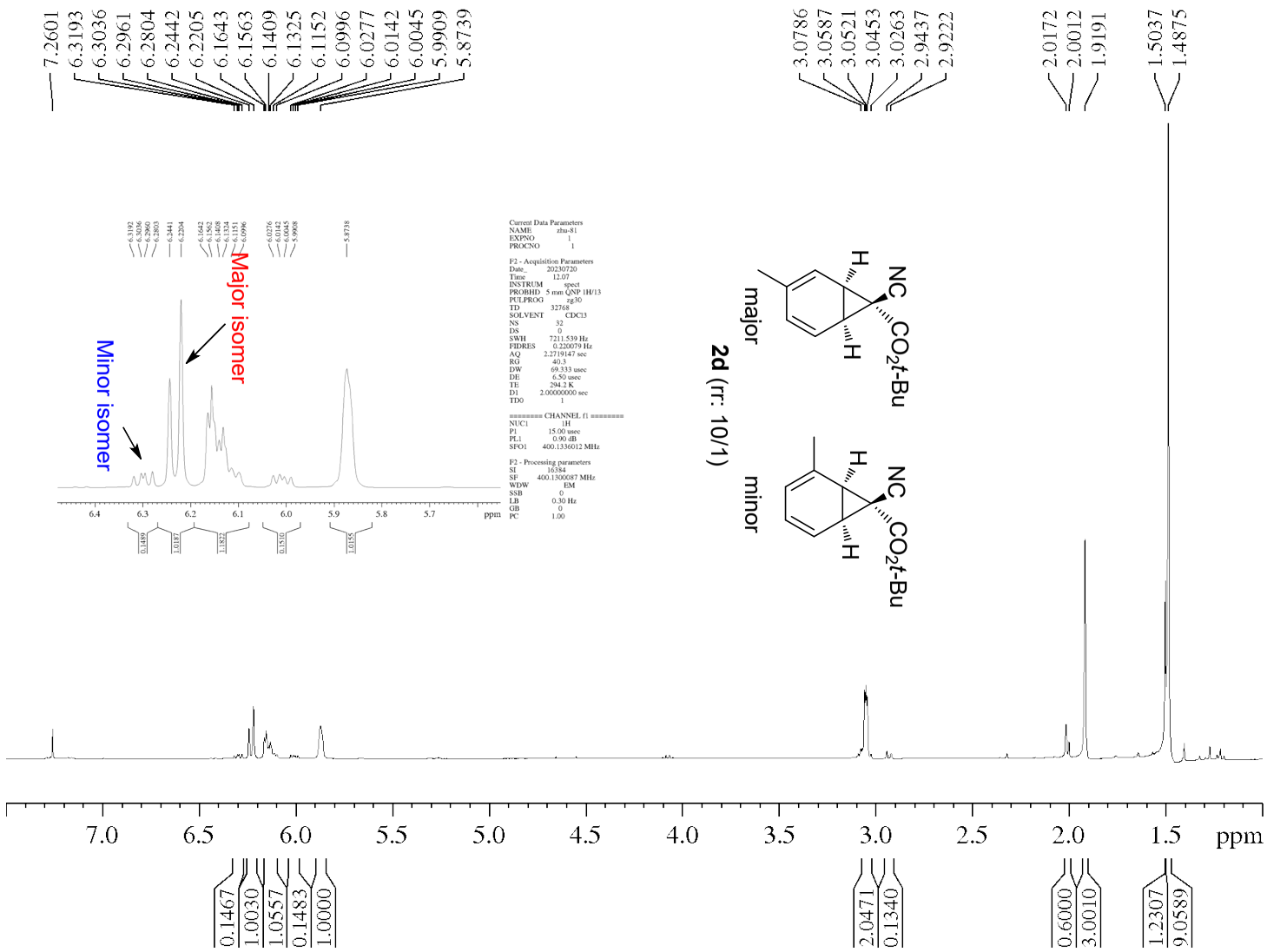
Current Data Parameters
NAME zhu-76
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230710
Time 13.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 361
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127761 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

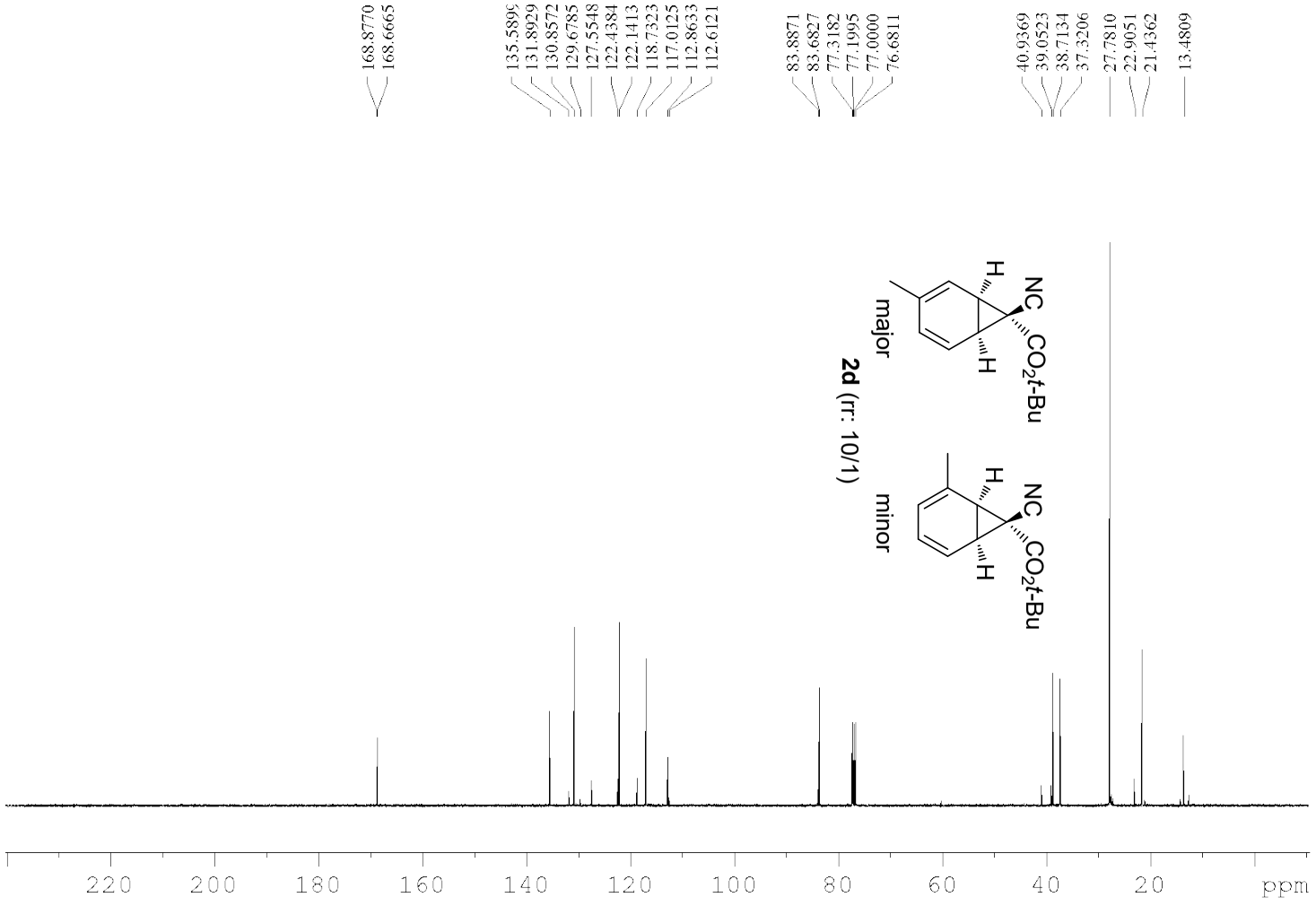


Current Data Parameters
NAME zhu-81
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230720
Time 12.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 40.3
DW 69.333 usec
DE 6.50 usec
TE 294.2 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-81
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230720
Time 12.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

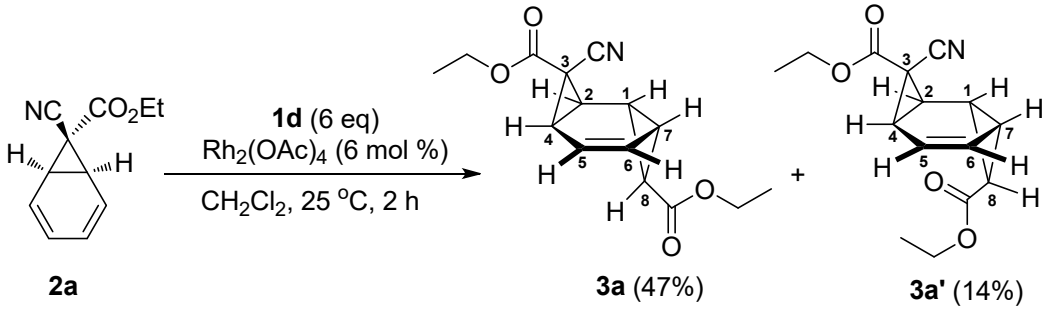
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127873 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4) Synthesis and ^{1}H-NMR ^{13}C-NMR, COSY, NOESY Spectra of 3a/3a' together with ^{1}H- and ^{13}C-NMR Spectra of (*E*)- and (*Z*)-Diethyl Fumarates

(1*R**,2*S**,3*S**,4*R**,7*R**,8*S**)-Diethyl-3-cyanotricyclo[5.1.0.0^{2,4}]oct-5-ene-3,8-dicarboxylate (**3a**) and (1*R**,2*S**,3*S**,4*R**,7*R**,8*R**)-Diethyl 3-cyanotricyclo[5.1.0.0^{2,4}]oct-5-ene-3,8-dicarboxylate (**3a'**)



2a **3a** (47%) **3a'** (14%)

A flame-dried flask equipped with a stir bar was successively charged with **2a** (42.2 mg, 0.223 mmol), DCM (0.5 mL) and $Rh_2(OAc)_4$ (6 mg, 99%, 0.0134 mmol, 0.06 equiv relative to **2a**). The flask was then connected to a dropping funnel containing a solution of **1d** (purchased as a 9.29 M solution in DCM, 0.144 mL, 1.34 mmol, 6.0 equiv relative to **2a)** in DCM (4 mL), which was slowly added to the vigorously stirred mixture over 1 h. After the addition was completed, the reaction mixture was stirred for an additional 1 h and concentrated under reduced pressure. The crude residue was subjected to chromatographic purification (Et_3N-deactivated silica gel; hexane/ethyl acetate = 12:1, 10:1, 3:1) to afford a mixture of **3a** and **3a'** (38 mg, **3a**/**3a'** = 78:22, **3a**: 47%; **3a'**: 14%) plus (*E*)- and (*Z*)-diethyl fumarates (44 and 54 mg). **3a** and **3a'** can be resolved by preparative TLC on silica gel plate (petroleum ether/acetone = 20:1).

IR (neat, mixed **3a**/**3a'**): 2921, 2243, 1723, 1245, 1184, 853, 712 cm^{-1}.

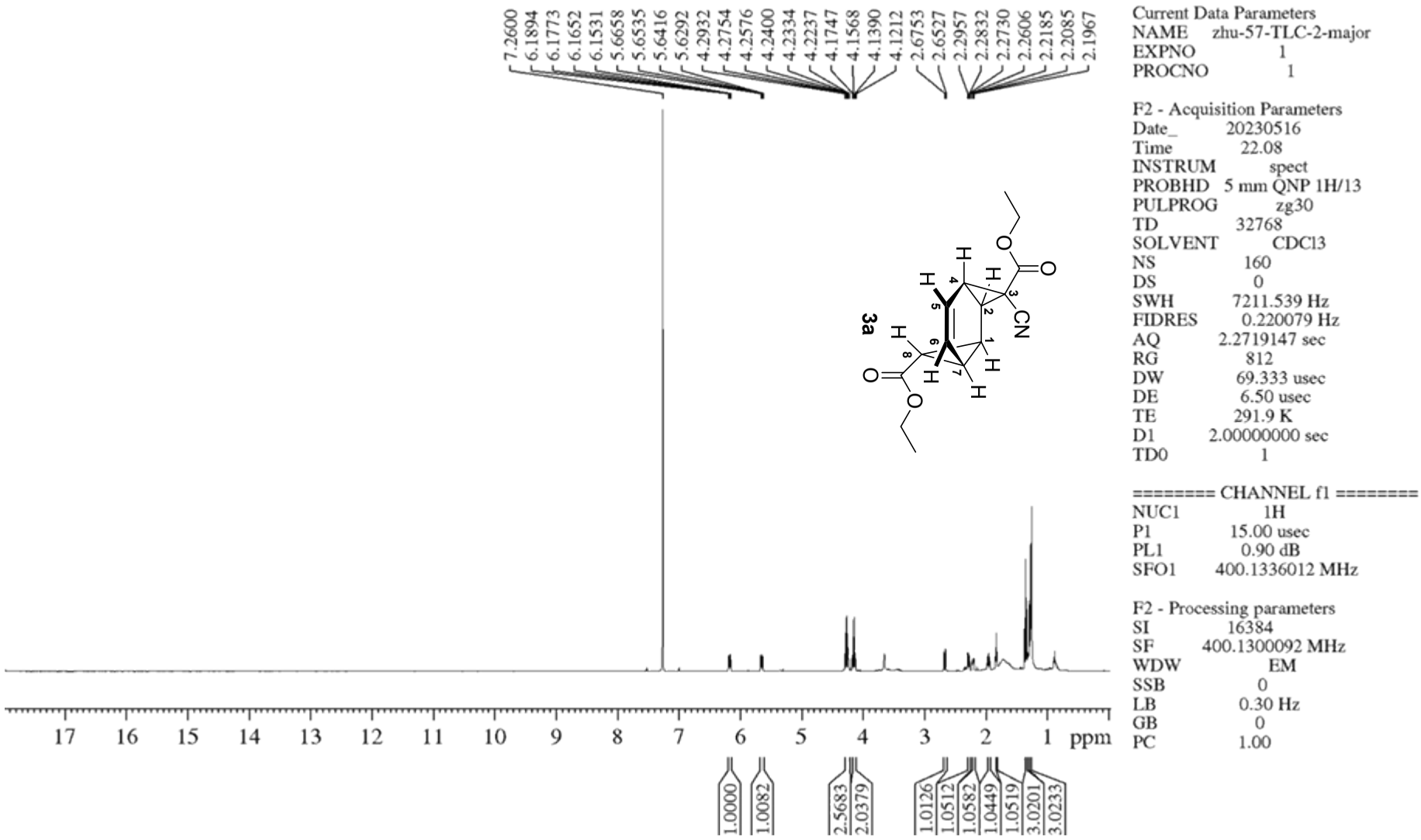
3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dd, $J_{6\text{-}5}$ = 9.7 Hz, $J_{6\text{-}7}$ = 4.8 Hz, **H-6**), 5.65 (dd, $J_{5\text{-}6}$ = 9.7 Hz, $J_{5\text{-}4}$ = 4.9 Hz, **H-5**), 4.27 (q, J = 7.1 Hz, OC**H**$_2$CH$_3$), 4.15 (q, J = 7.2 Hz, OC**H**$_2$CH$_3$), 2.67 (d, $J_{2\text{-}4}$ = 9.1 Hz, **H-2**), 2.23 (dd, $J_{4\text{-}2}$ = 9.1 Hz, $J_{4\text{-}5}$ = 4.9 Hz, **H-4**), 2.20 (dd, $J_{7\text{-}1}$ = 8.7 Hz, $J_{8\text{-}1}$ = 4.2 Hz, **H-1**), 1.95 (ddd, $J_{1\text{-}7}$ = 8.7 Hz, $J_{6\text{-}7}$ = 4.8 Hz, $J_{8\text{-}7}$ = 4.1 Hz, **H-7**), 1.83 (dd, $J_{1\text{-}8}$ = 4.2 Hz, $J_{7\text{-}8}$ = 4.1 Hz, **H-8**), 1.34 (t, J = 7.2 Hz, OCH$_2$C**H**$_3$), 1.29 (t, J = 7.1 Hz, OCH$_2$C**H**$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0 (C=O), 166.2 (C=O), 129.8 (=CH), 117.8 (=CH), 115.0 (CN), 63.0 (O**C**H$_2$CH$_3$), 61.0 (O**C**H$_2$CH$_3$), 30.8, 30.7, 30.1, 29.0, 21.4, 20.3, 14.2 (OCH$_2$**C**H$_3$), 14.1 (OCH$_2$**C**H$_3$) ppm; HRMS-EI: *m/z* [M]$^+$ calcd. for $C_{15}H_{17}NO_4$: 275.1158; found: 275.1143.

3a': ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (dd, $J_{6\text{-}5}$ = 10.0 Hz, $J_{6\text{-}7}$ = 3.8 Hz, **H-6**), 5.85 (dd, $J_{5\text{-}6}$ =10.0 Hz, $J_{5\text{-}4}$ = 4.6 Hz, **H-5**), 4.26 (q, J = 7.1 Hz, OC**H**$_2$CH$_3$), 4.17-4.07 (m, OC**H**$_2$CH$_3$), 2.62 (d, $J_{2\text{-}4}$ = 9.2 Hz, **H-2**), 2.46 (dd, $J_{4\text{-}2}$ = 9.2 Hz, $J_{4\text{-}5}$ = 4.6 Hz, **H-4**),

2.16 (dd, $J_{8\text{-}1}$ = 8.8 Hz, $J_{8\text{-}7}$ = 8.8 Hz, **H-8**), 1.95-1.89 (m, **H-1**), 1.95-1.89 (m, **H-7**), 1.34 (t, J = 7.1 Hz, $OCH_2C\mathbf{H}_3$), 1.26 (t, J = 7.2 Hz, $OCH_2C\mathbf{H}_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (C=O), 166.4 (C=O), 124.5 (=CH), 121.2 (=CH), 115.4 (CN), 62.8 ($O\mathbf{C}H_2CH_3$), 60.5 ($O\mathbf{C}H_2CH_3$), 31.5, 30.8, 29.1, 26.1, 18.8, 16.7, 14.3 ($OCH_2\mathbf{C}H_3$), 14.1 ($OCH_2\mathbf{C}H_3$) ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_{17}NO_4$: 275.1158; found: 275.1147.

(*E*)-Diethyl fumarates:[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2 H), 4.22 (q, J = 7.2 Hz, 4 H), 1.28 (t, J = 7.2 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 133.5, 61.2, 14.0 ppm.

(*Z*)-Diethyl fumarates:[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (s, 2 H), 4.25 (q, J = 7.1 Hz, 4 H), 1.31 (t, J = 7.1 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 129.8, 61.2, 14.0 ppm.



Current Data Parameters
NAME zhu-57-TLC-2-major
EXPNO 1
PROCNO 1

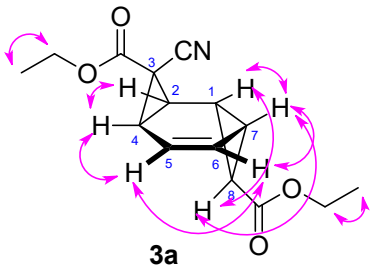
F2 - Acquisition Parameters
Date_ 20230516
Time 22.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 160
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 812
DW 69.333 usec
DE 6.50 usec
TE 291.9 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

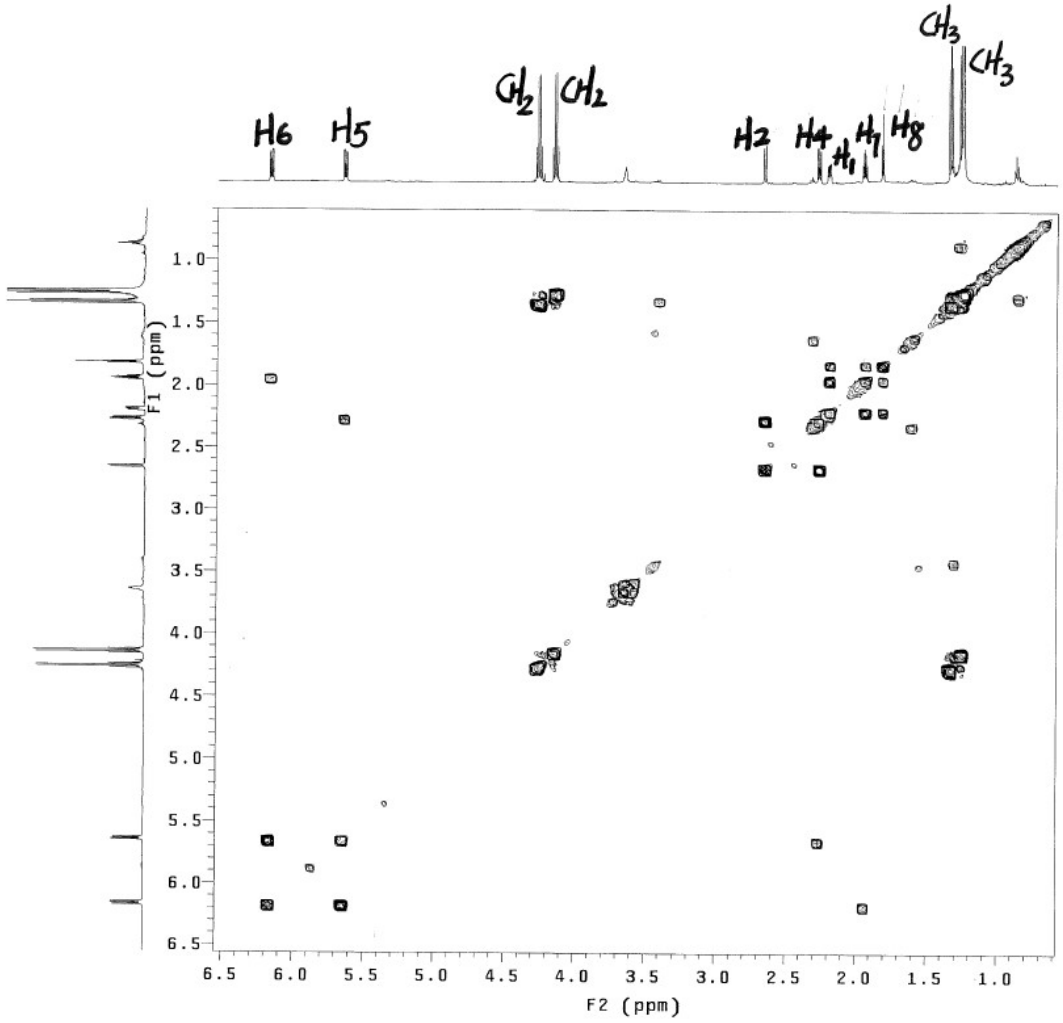
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME zhu-57-TLC-2-major
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230516
Time 22.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10892
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 1620
DW 19.800 usec
DE 6.50 usec
TE 292.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
14.0932
14.2079
20.2511
21.3828
29.0202
30.0848
30.7067
30.7935
61.0261
63.0206
76.6831
77.0000
77.2043
77.3181
114.9824
117.7595
129.8191
166.2131
171.0012
O
CN
H
O
3a
O
ppm
220
200
180
160
140
120
100
80
60
40
20

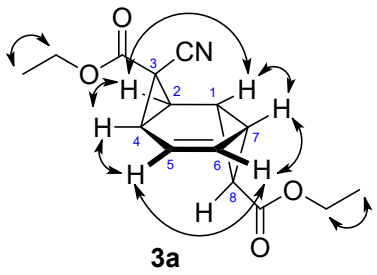
H-H COSY of **3a** (600 MHz):



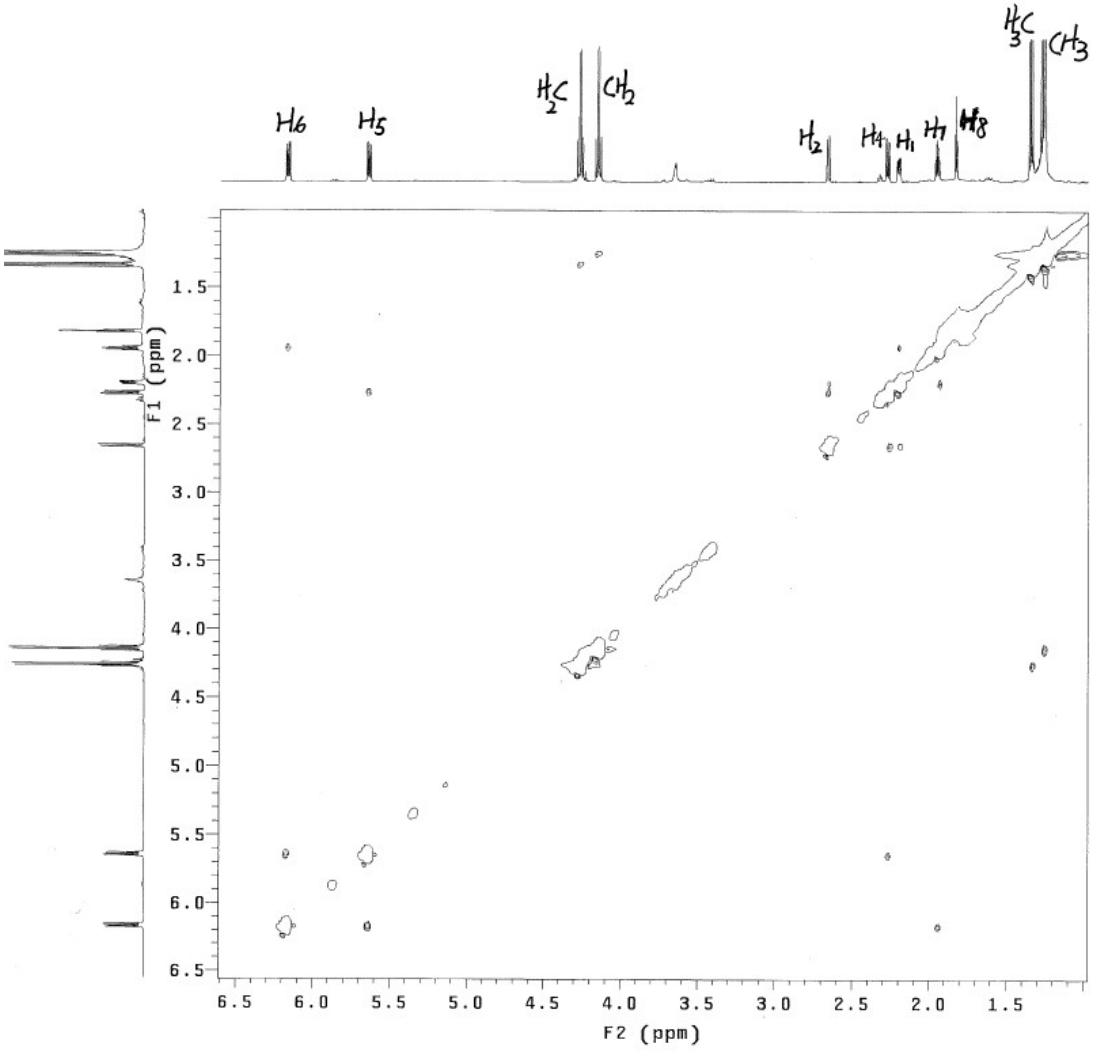
3a

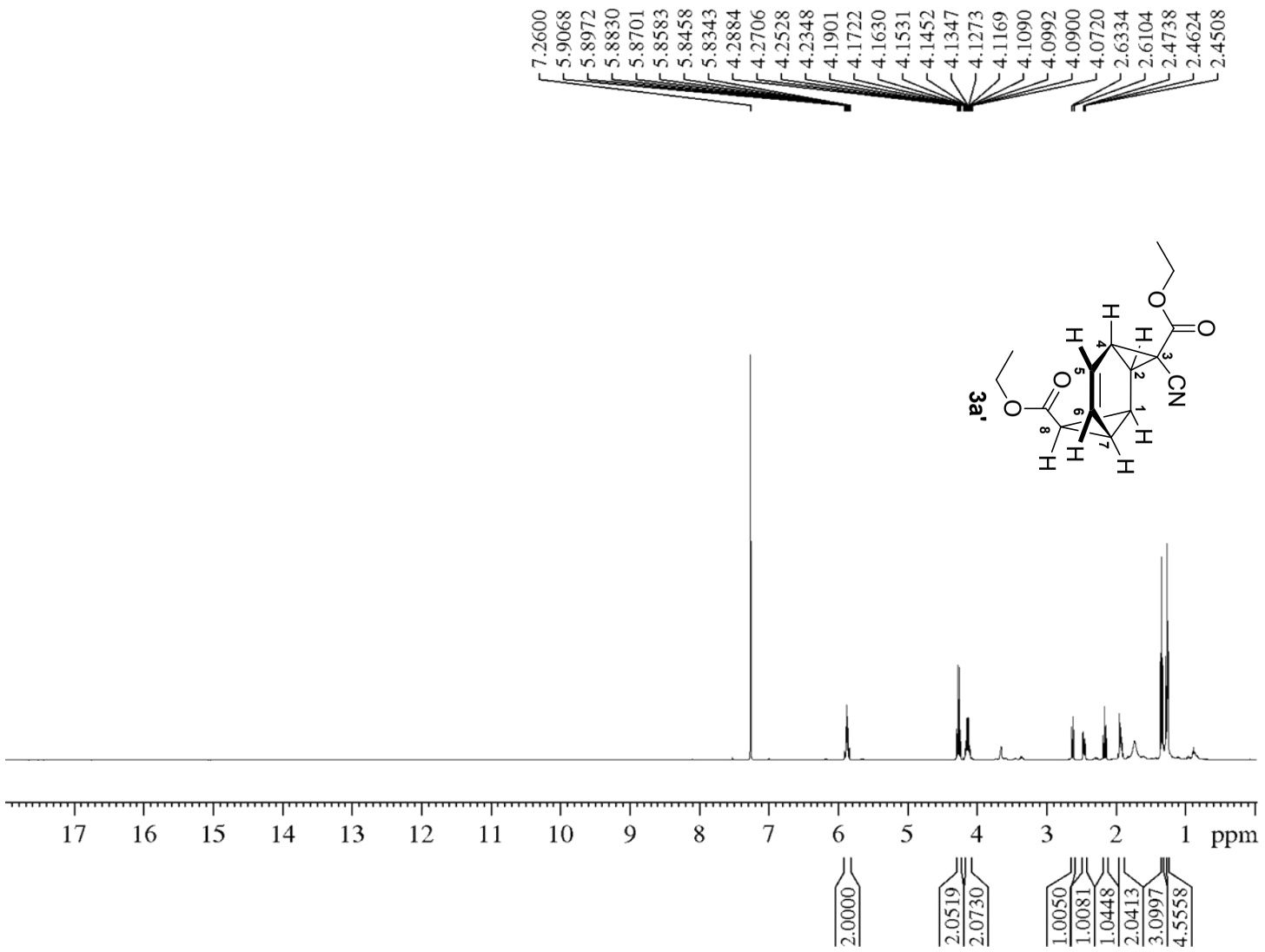


NOESY spectrum of **3a** (600 MHz)：



3a



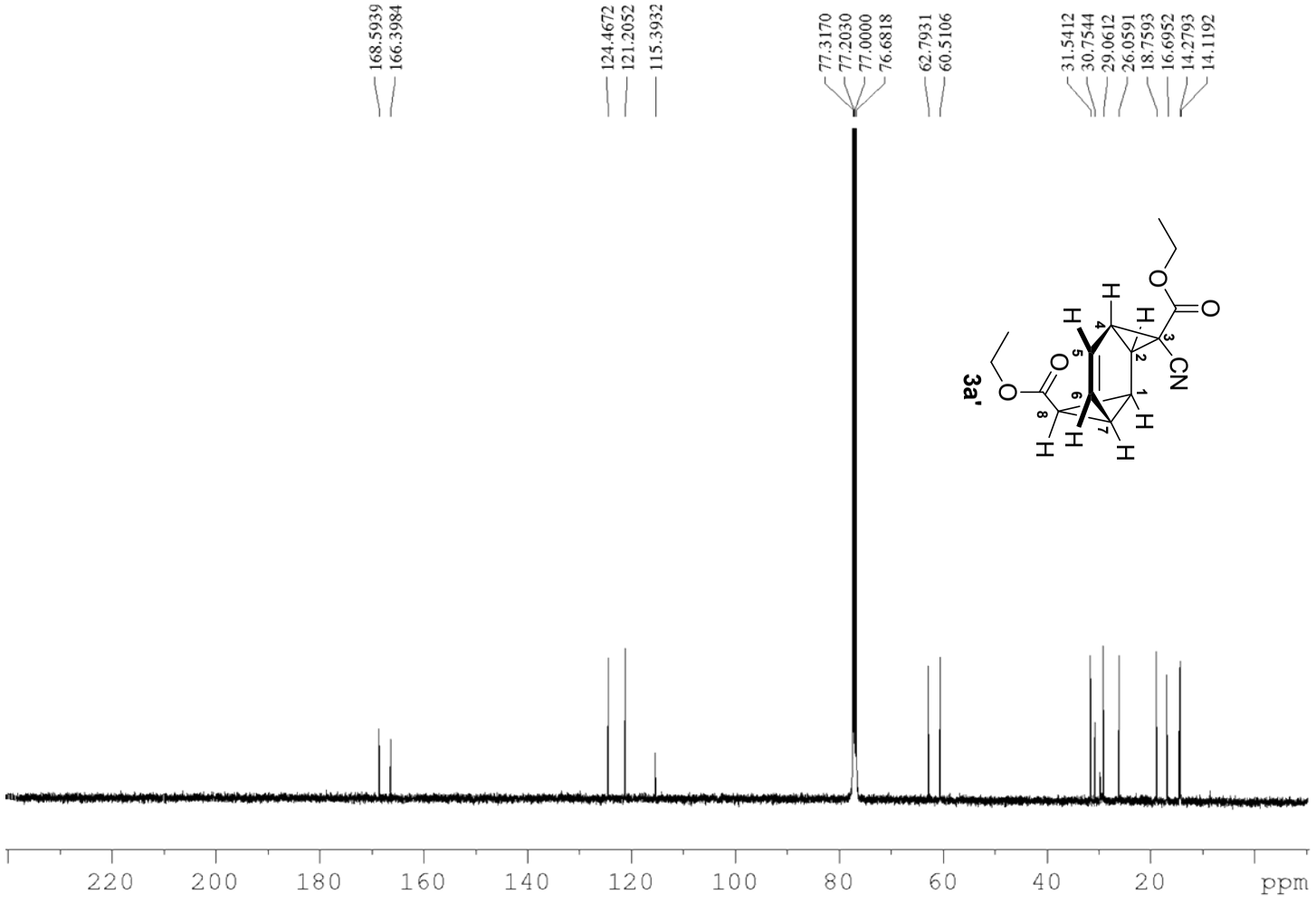


Current Data Parameters
NAME zhu-57-3-minor
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230518
Time 22.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 320
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 645
DW 69.333 usec
DE 6.50 usec
TE 292.4 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-57-3-minor
EXPNO 3
PROCNO 1

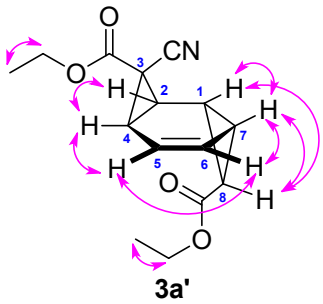
F2 - Acquisition Parameters
Date_ 20230518
Time 22.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10704
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 1620
DW 19.800 usec
DE 6.50 usec
TE 293.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

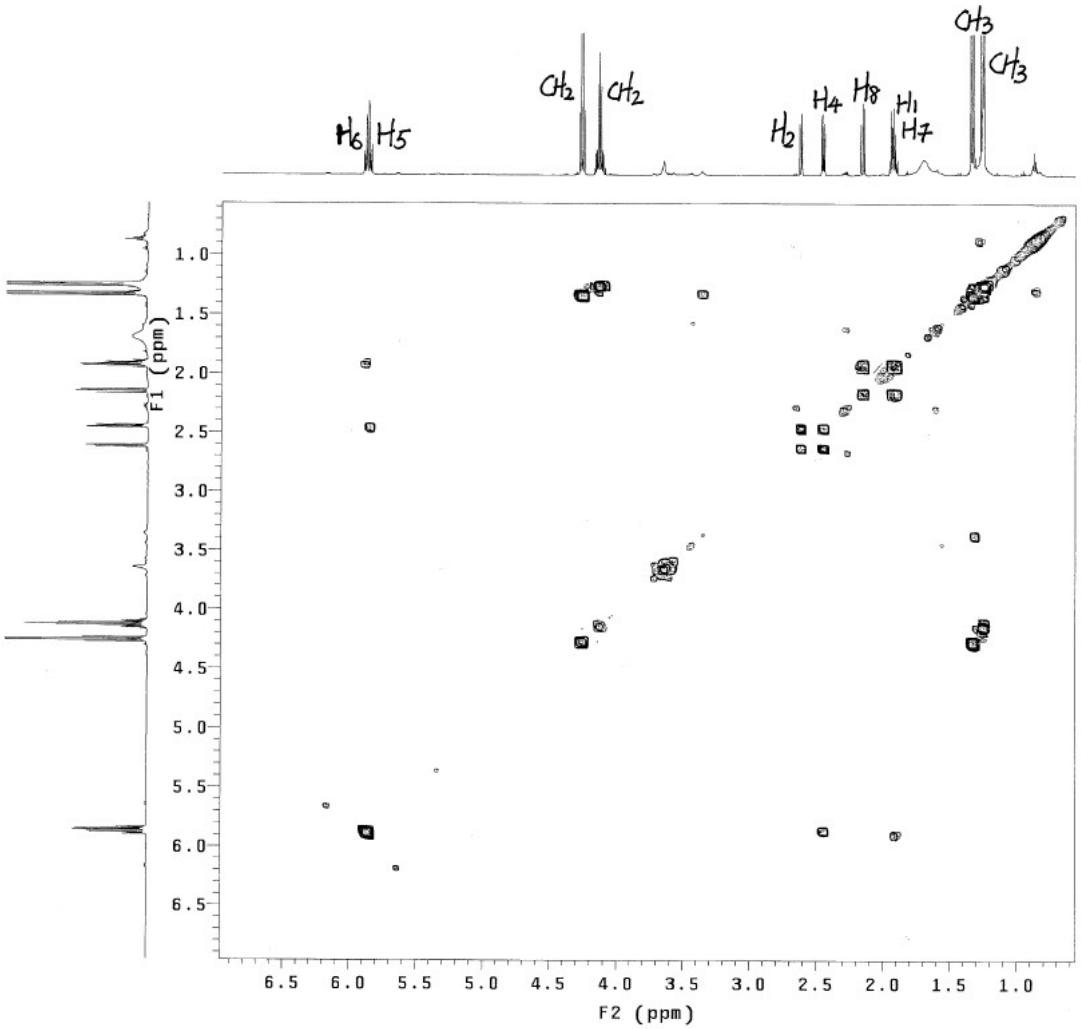
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

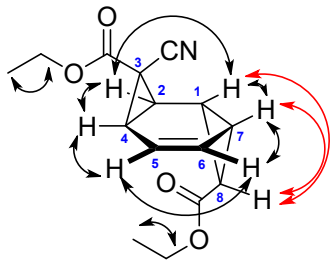
H-H COSY spectrum of **3a'** (600 MHz):



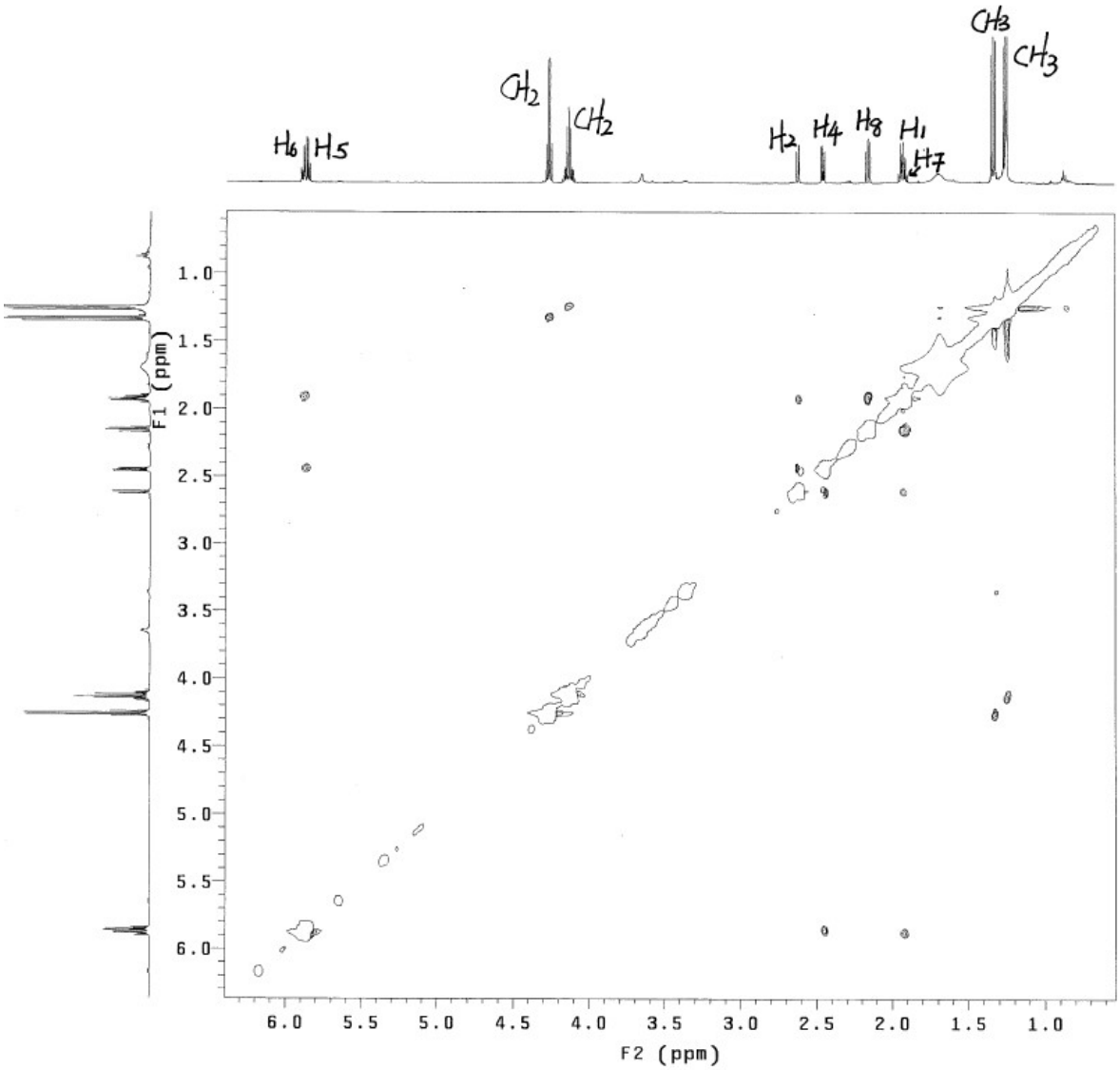
3a'



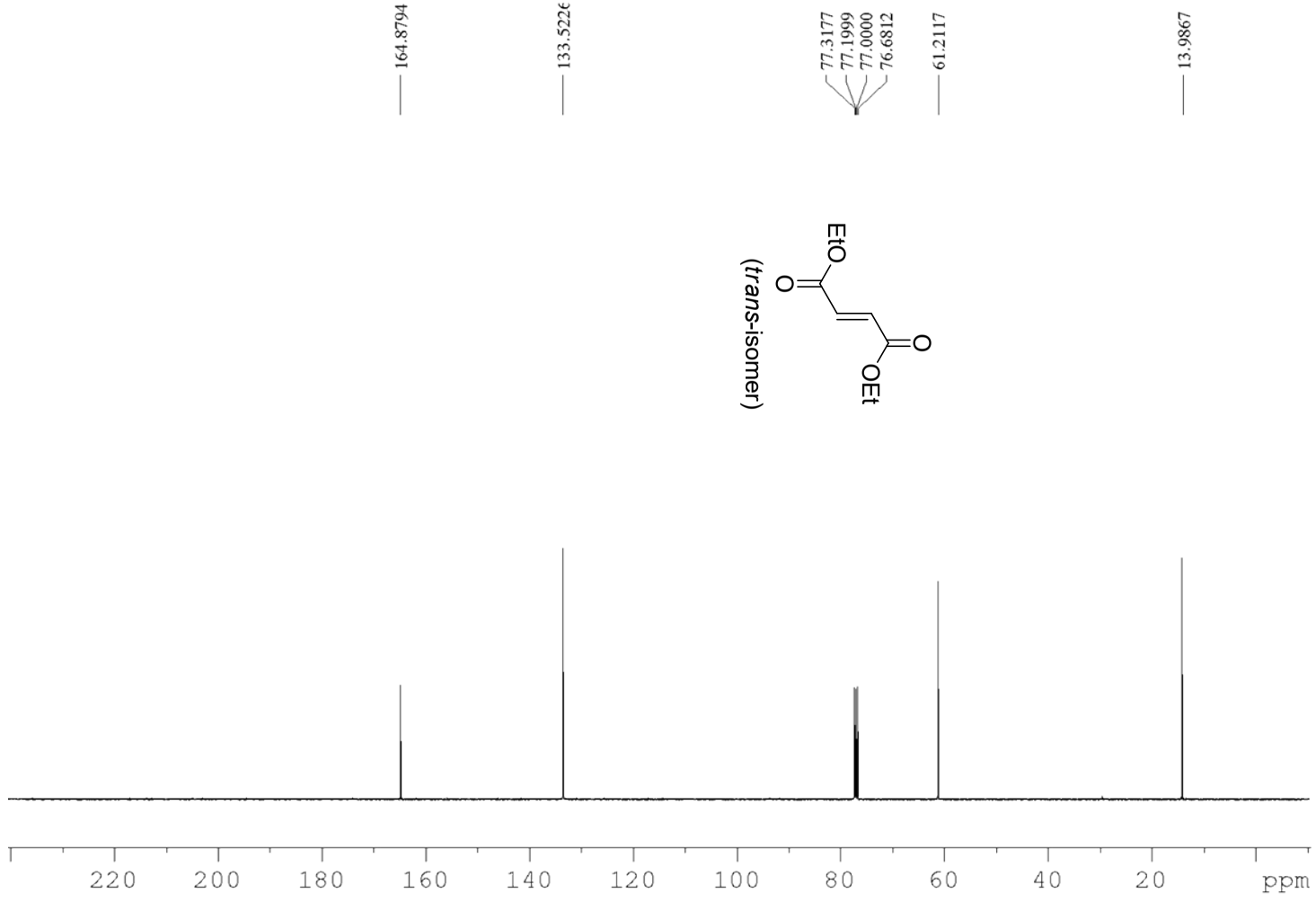
NOESY spectrum of **3a'** (600 MHz):



3a'



Current Data Parameters
NAME zhu-50-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230329
Time 13.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 57
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.27191147 sec
RG 64
DW 69.333 usec
DE 6.50 usec
TE 291.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.2579
1.2758
1.2937
4.1887
4.2066
4.2245
4.2423
6.8060
7.2600
EtO
OEt
O
O
(trans-isomer)
6.0299
4.0766
2.0000
ppm



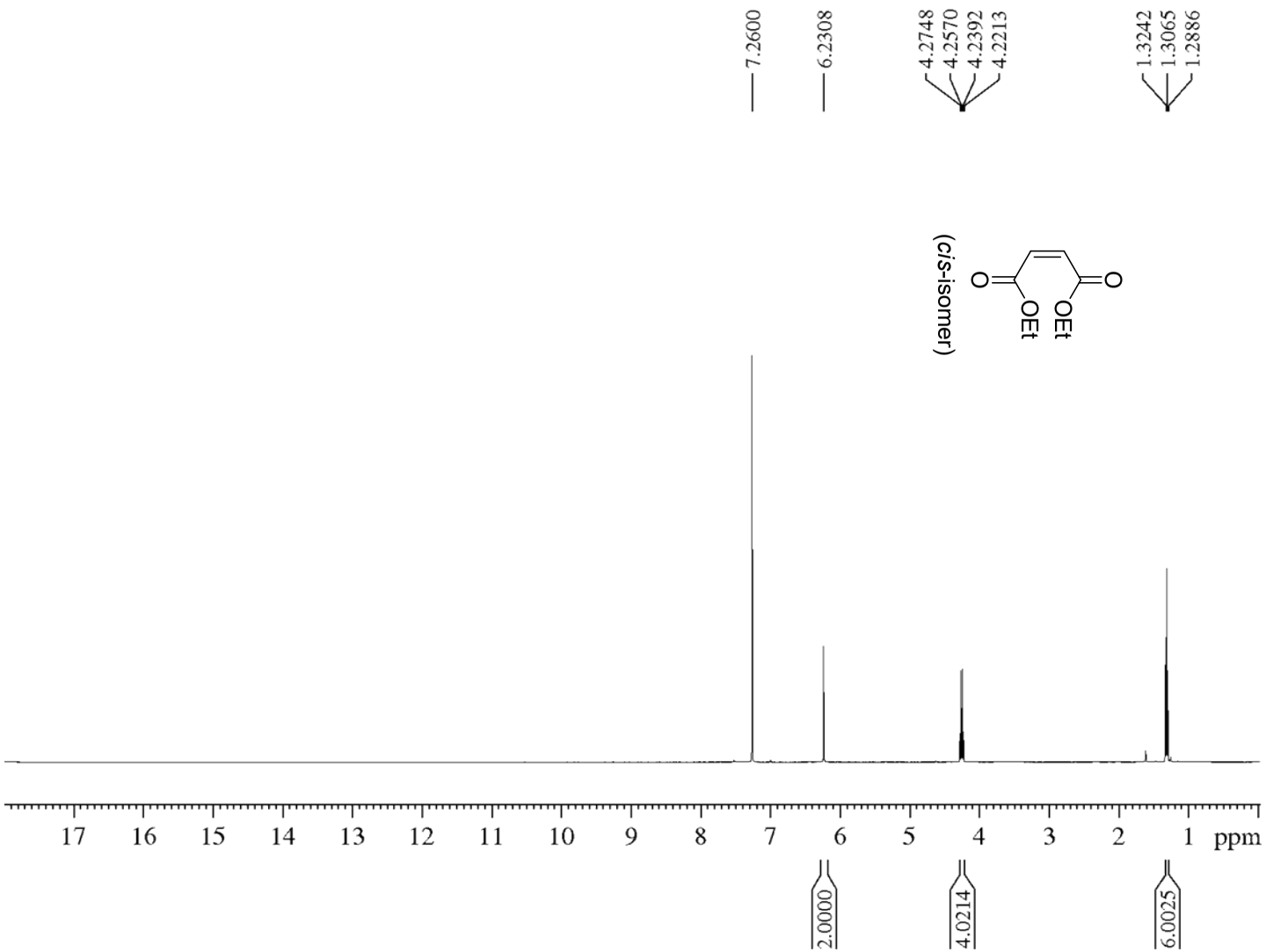
Current Data Parameters
NAME zhu-50-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230329
Time 13.55
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 291.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127774 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME zhu-50-2
EXPNO 3
PROCNO 1

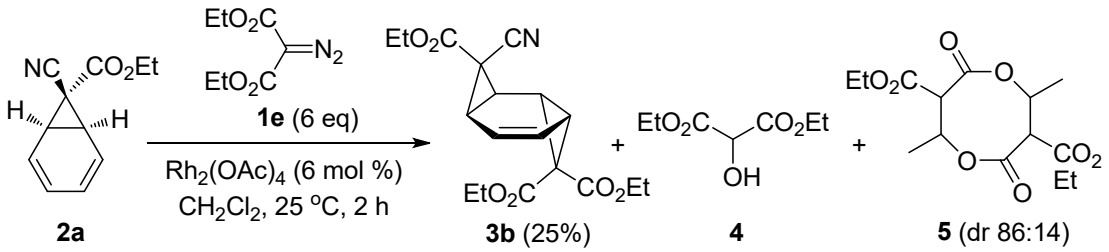
F2 - Acquisition Parameters
Date_ 20230406
Time 10.54
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 41
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 322
DW 69.333 usec
DE 6.50 usec
TE 292.8 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME zhu-50-2
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230406
Time 11.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127730 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13.9936
61.2419
76.6827
77.0000
77.2033
77.3177
129.7760
165.2698
O
OEt
OEt
O
(cis-isomer)
ppm
220
200
180
160
140
120
100
80
60
40
20

5) Formation and NMR Spectra of 3b/4/5



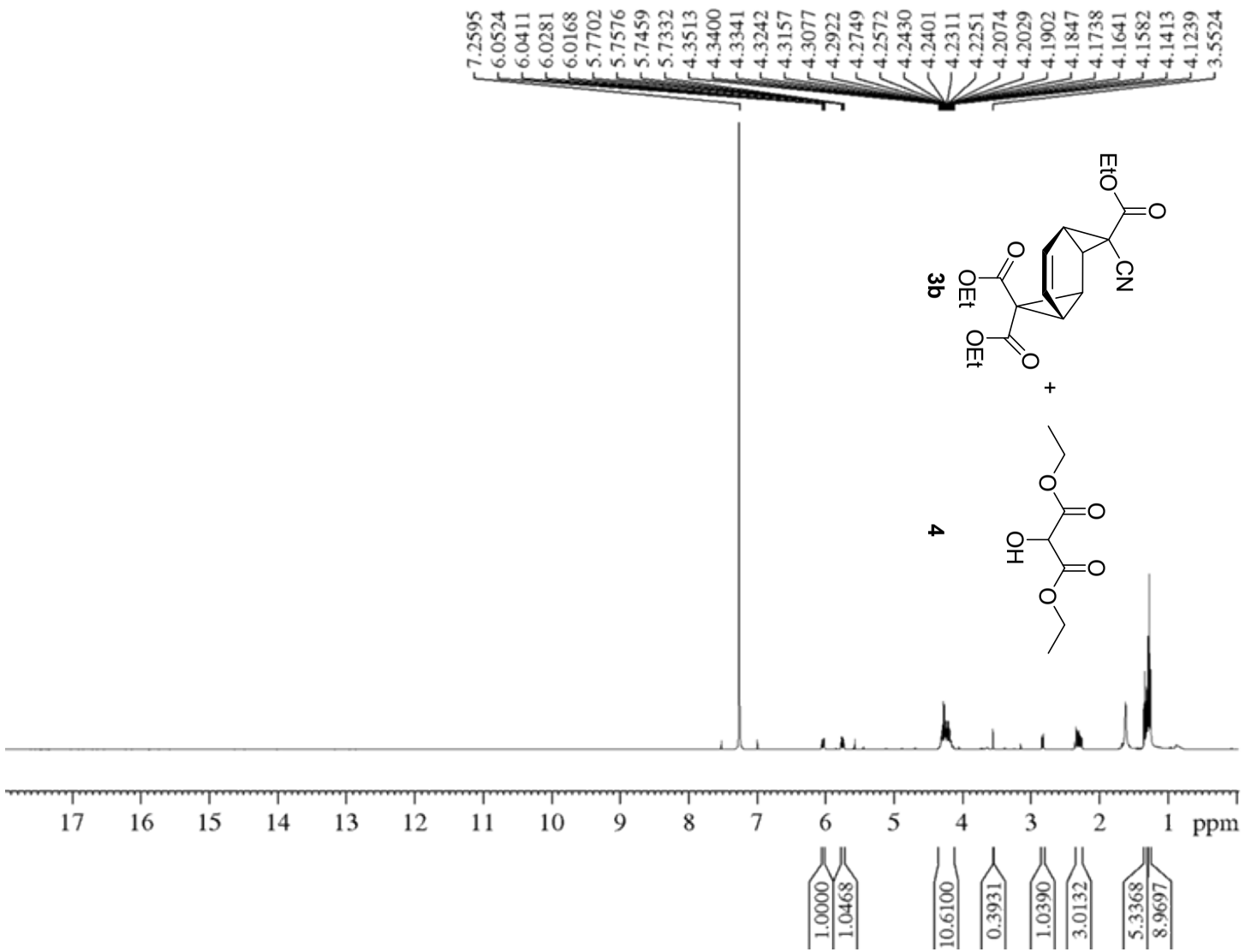
Following the same procedure described for the preparation of **3a/3a'**, the titled compounds were obtained from the reaction of **2a** (57 mg, 0.30 mmol) with **1e** (336.5 mg, 1.81 mmol, 6.0 equiv relative to **2a)** in the presence of $Rh_2(OAc)_4$ (8.1 mg, 99%, 0.018 mmol, 0.06 equiv relative to **2a**). After slow addition of **1e** over 1 h and stirring for an additional 1 h, the reaction mixture was concentrated under vacuo and subjected to flash column chromatography (silica gel; hexane/ethyl acetate = 10:1, 6:1) to give 39 mg of the mixed **3b** and **4** (**3b**: 26 mg, 25%; **4**: 13 mg; determined by integrals of the ^{1}H NMR resonances) along with **5** (191 mg, dr: 86:14).

(1*R**,2*S**,4*R**,7*R**,8*S**)-Triethyl-8-cyanotricyclo[5.1.0.02,4]oct-5-ene-3,3,8-tricarboxylate (**3b**) and Diethyl 2-hydroxymalonate (**4**)[12]

^{1}H NMR (400 MHz, $CDCl_3$) **3b**: δ 6.04 (dd, *J* = 9.7, 4.5 Hz, 1 H, =CH), 5.75 (dd, *J* = 9.7, 5,1 Hz, 1 H, =CH), 4.35-4.12 (m, 6 H, OCH_2), 2.34-2.26 (m, 4 H, CH), 1.29 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.27 (t, *J* = 7.2 Hz, 6 H, CH_3 x 2) ppm; **4**: δ 4.35-4.12 (m, 4 H, CH_2), 3.55 (s, 1 H, CH), 1.36 (t, *J* = 7.2 Hz, 6 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) **3b**: δ 168.1 (C=O), 166.0 (C=O), 165.2 (C=O), 126.2 (=C-H), 120.0 (=C-H), 114.8 (CN), 63.0 (CH_2), 62.2 (CH_2), 61.6 (CH_2), 41.2, 29.9, 29.6, 29.5, 24.6, 23.8, 14.1 (x 2, CH_3), 14.0 (CH_3) ppm; **4**: δ 165.6 (C=O), 72.2 (CH), 62.7 (CH_2), 13.9 (CH_3) ppm.

Diethyl 2,6-dimethyl-4,8-dioxo-1,5-dioxocane-3,7-dicarboxylate (**5**)[13]

^{1}H NMR (400 MHz, $CDCl_3$) major: δ 4.96 (qd, *J* = 6.2, 4.3, 2 H), 4.26 (q, *J* = 7.1 Hz, 4 H), 4.10 (d, *J* = 4.3 Hz, 2 H), 1.62 (d, *J* = 6.2 Hz, 6 H), 1.29 (t, *J* = 7.1 Hz, 6 H) ppm; minor δ 4.88 (dq, *J* = 7.0, 6.3 Hz , 2 H), 4.57 (d, *J* = 7.0 Hz, 2 H), 4.25 (q, *J* = 7.1 Hz, 4 H), 1.58 (d, *J* = 6.3 Hz, 6 H), 1.27 (t, *J* = 7.1 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 164.2 (C=O), 162.6 (C=O), 71.2 (CH), 62.4 (CH_2), 61.6 (CH), 19.7 (CH_3), 14.0 (CH_3) ppm; minor: δ 164.0 (C=O), 163.2 (C=O), 70.1 (CH), 62.1 (CH_2), 58.3 (CH), 16.5 (CH_3), 14.1 (CH_3) ppm.

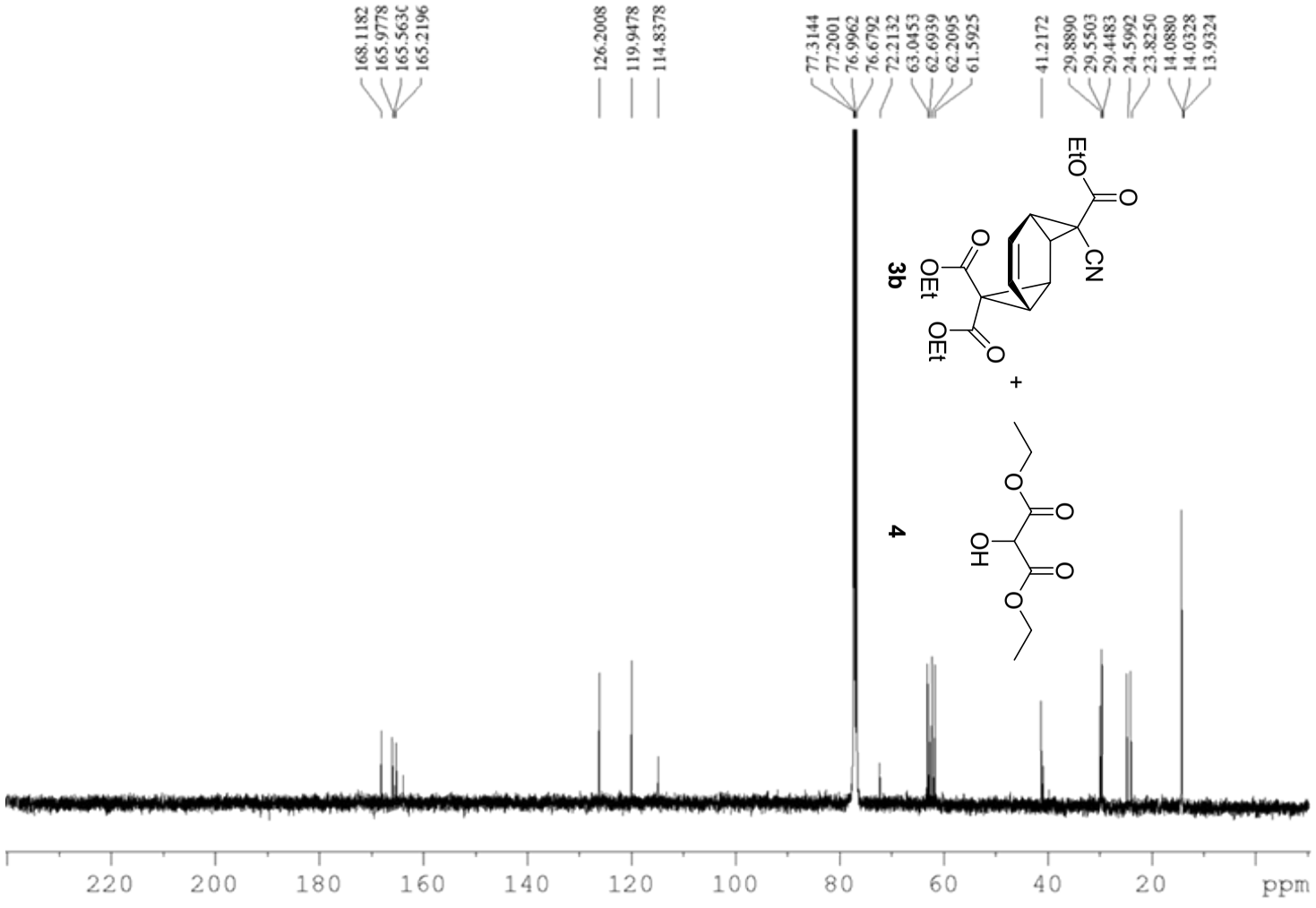


Current Data Parameters
NAME zhu-53-3-TLC
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230628
Time 22.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 162
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 575
DW 69.333 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-53-3-TLC
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230628
Time 22.40
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10469
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127724 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Current Data Parameters
NAME zhu-55-2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230424
Time 11.27
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 80
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 228
DW 69.333 usec
DE 6.50 usec
TE 291.7 K
D1 2.00000000 sec
TD0 1
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PL1 0.90 dB
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F2 - Processing parameters
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SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.2600
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4.9783
4.9672
4.9629
4.9519
4.9365
4.9128
4.8966
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4.8483
4.5861
4.5690
4.2904
4.2792
4.2726
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4.1035
4.0927
1.6382
1.6228
1.5908
EtO
OEt
5 (dr 86:14)
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3.0043
0.5099
3.1850
ppm

Current Data Parameters
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EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
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SWH 25252.525 Hz
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DE 6.50 usec
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PCPD2 90.00 usec
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PL12 15.80 dB
PL13 18.50 dB
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F2 - Processing parameters
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SF 100.6127743 MHz
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16.5398
19.6902
58.2675
61.6350
62.1442
62.4332
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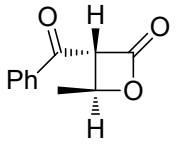
163.2081
164.0121
164.2295
EtO
OEt
O
ppm
220
200
180
160
140
120
100
80
60
40
20

5 (dr 86:14)

6) Formation and NMR Spectra of 6

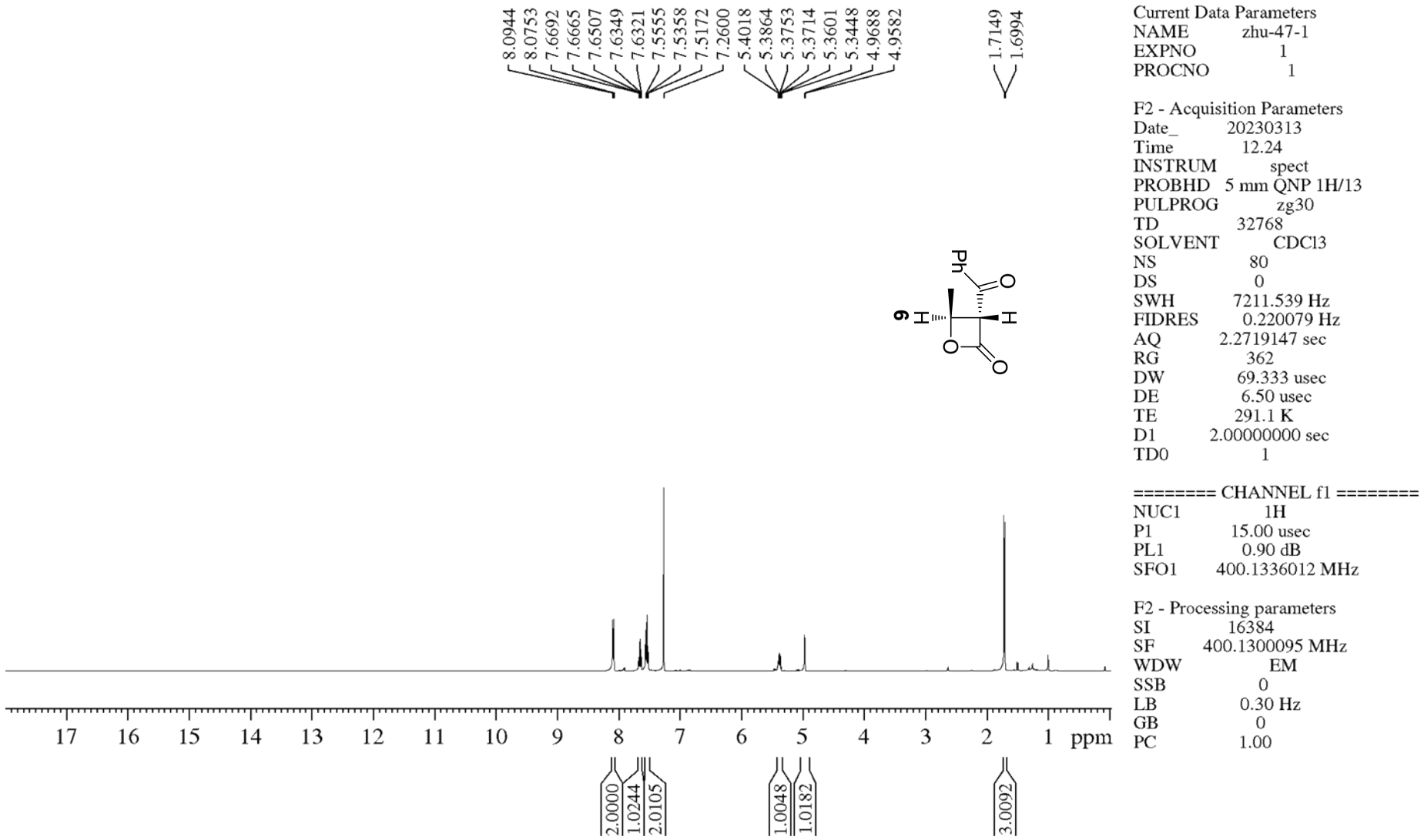
(3*R**,4*S**)-3-Benzoyl-4-methyloxetan-2-one (**6**)[14]



6

Following the procedure for the preparation of **3a**/**3a'**, the titled compound was obtained from the reaction of **2a** (54.7 mg, 0.289 mmol) with ethyl 2-diazo-3-oxo-3-phenylpropanoate (**1f**, 378.5 mg, 1.73 mmol) in the presence of $Rh_2(OAc)_4$ (7.74 mg, 99%, 0.017 mmol). After slow addition of **1f** over 30 min and stirring for an additional 1 h, the reaction mixture was concentrated and the crude residue was subjected to chromatography (silica gel; hexane/ethyl acetate = 12:1, 10:1, 8:1) to afford **6** (165 mg) as the only identifiable product plus an unidentifiable mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (br d, *J* = 7.4 Hz, 2 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.56-7.52 (m, 2 H), 5.37 (dq, *J* = 6.2, 4.3 Hz, 1 H), 4.97 (d, *J* = 4.3 Hz, 1 H), 1.71 (d, *J* = 6.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 163.6, 134.8, 134.5, 129.3, 128.9, 70.2, 66.4, 19.6 ppm.



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PROCNO 1

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RG 362
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TE 291.1 K
D1 2.00000000 sec
TD0 1

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F2 - Processing parameters
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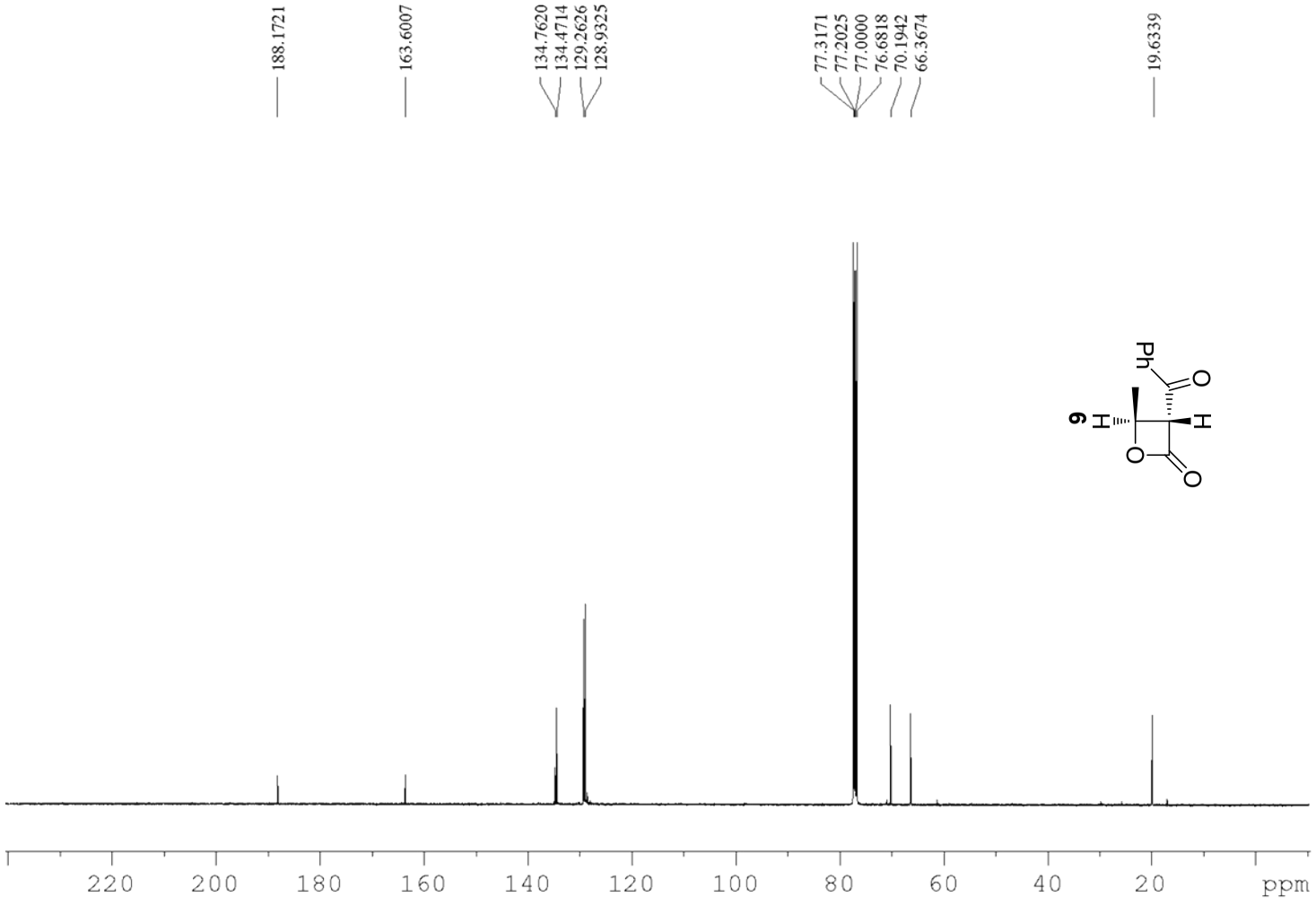

Current Data Parameters
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PROCNO 1

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FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 291.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
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P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
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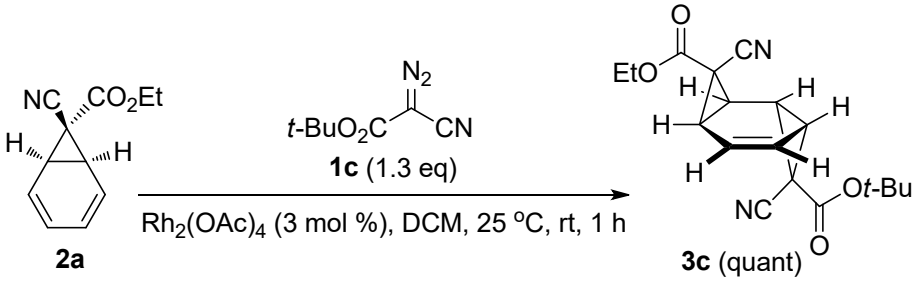
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127735 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

7) Preparation and NMR spectra of Bis(cyclopropanated) Adducts 3c-j

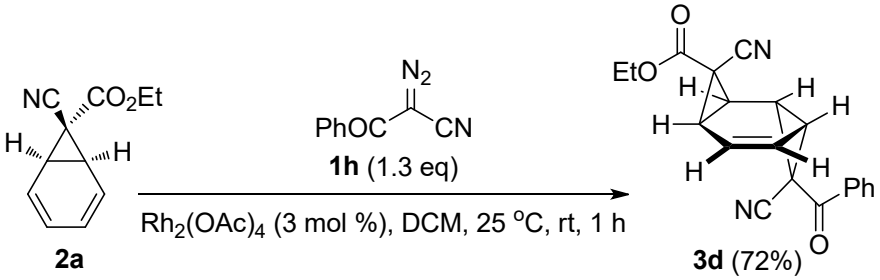
Typical Procedure: A flame-dried flask equipped with a stir bar was successively charged with 7-cyanonorcaradienyl esters **2** (0.3277 mmol), DCM (2 mL) and $Rh_2(OAc)_4$ (0.0098 mmol, 0.03 equiv). A solution of diazo compounds **1** (0.426 mmol, 1.3 equiv) in DCM (4.6 mL) was then added to the vigorously stirred mixture via a syringe over 40 min. After the addition was completed, the reaction mixture was stirred for an additional 1 h and concentrated under reduced pressure. The crude residue was purified by chromatography on triethylamine-deactivated silica gel by eluting with hexane/ethyl acetate to afford **3c-j**.

(1*R**,2*R**,3*S**,4*R**,7*R**,8*S**)-3-*tert*-Butyl 8-ethyl 3,8-dicyanotricyclo[5.1.0.0^{2,4}]oct- -5-ene-3,8-dicarboxylate (**3c**)



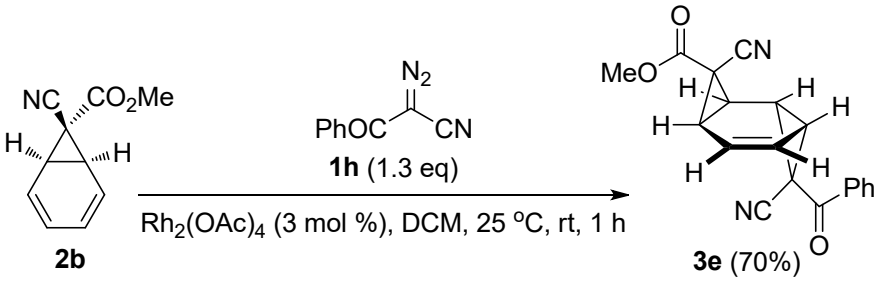
The titled compound was synthesized from **2a** and **1c** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 12:1, 5:1), **3c** was obtained quantitatively as a white solid. The isolated product was crystalized from CH_2Cl_2 to form colorless crystals that were suitable for X-ray crystallographic analysis. IR (neat): 3057, 2983, 2246, 1731, 1287, 1249, 1155, 839, 779 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (dd, *J* = 9.2, 4.6 Hz, 1 H, =CH), 6.05 (dd, *J* = 9.2, 4.6 Hz, 1 H, =CH), 4.26 (q, *J* = 7.2 Hz, 2 H, OC***H***$_2$CH$_3$), 2.67 (br d, *J* = 8.9 Hz, 1 H), 2.59 (br d, *J* = 8.9 Hz, 1 H), 2.48 (dd, *J* = 8.9, 4.6 Hz, 1 H), 2.41 (dd, *J* = 8.9, 4.6 Hz, 1 H), 1.49 (s, 9 H, *t*-Bu), 1.32 (t, *J* = 7.2 Hz, 3 H, OCH$_2$C***H***$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (C=O), 163.9 (C=O), 123.5 (=CH), 123.0 (=CH), 114.4 (CN), 114.2 (CN), 84.7 (C-O), 63.2 (O**C**H$_2$CH$_3$), 29.0, 28.9, 28.3, 28.2, 27.2 (methyl of *t*-Bu), 27.4, 26.7, 14.0 (OCH$_2$**C**H$_3$) ppm; HRMS-EI: *m/z* [M]$^+$ calcd. for $C_{18}H_{20}N_2O_4$: 328.1423; found: 328.1425.

(1*R**,2*S**,3*S**,4*R**,7*R**,8*S**)-Ethyl 8-benzoyl-3,8-dicyanotricyclo[5.1.0.0^{2,4}]oct-5- -ene-3-carboxylate (**3d**)



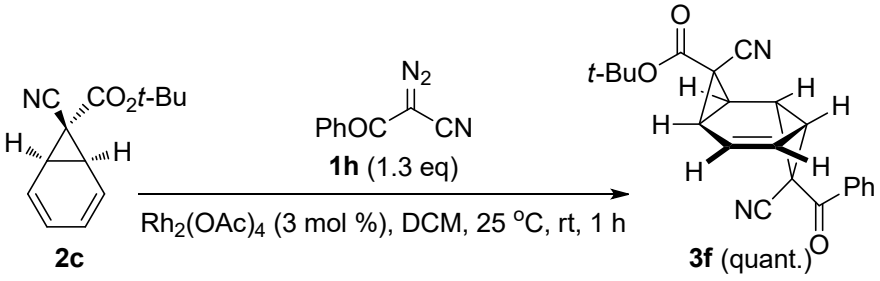
The titled compound was synthesized from **2a** and **1h** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 10:1, 5:1), **3d** was obtained in 72% yield as a white solid. IR (neat): 3057, 2920, 2243, 1735, 1699, 245, 782, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2 H, phenyl), 7.64 (t, *J* = 7.2 Hz, 1 H, phenyl), 7.52 (t, *J* = 7.5 Hz, 2 H, phenyl), 6.25-6.15 (m, 2 H, =CH), 4.30 (q, *J* = 7.1 Hz, 2 H, OC***H***$_2CH_3$), 2.99 (br d, *J* = 8.7 Hz, 1 H), 2.75 (br d, *J* = 8.8 Hz, 1 H), 2.62-2.57 (m, 2 H), 1.36 (t, *J* = 7.1 Hz, 3 H, OCH_2C***H***$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6 (C=O, benzoyl), 165.4 (C=O, ester), 135.2, 134.0, 128.8, 128.7, 124.0, 123.5, 116.4 (CN), 114.2 (CN), 63.4 (O***C***H_2CH_3), 33.2, 31.0, 29.1, 28.4, 27.6, 27.5, 14.0 (OCH_2C***H***$_3$) ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{20}H_{16}N_2O_3$: 332.1161; found: 332.1163.

(1*R**,2*S**,3*S**,4*R**,7*R**,8*S**)-Methyl 8-benzoyl-3,8-dicyanotricyclo[5.1.0.0^{2,4}]oct- -5-ene-3-carboxylate (**3e**)



The titled compound was synthesized from **2b** and **1h** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 10:1, 3:1), **3e** was obtained in 70% yield as a colorless oil. IR (neat): 3058, 2956, 2243, 1738, 1682, 1250, 780, 732, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2 H, phenyl), 7.64 (t, *J* = 7.4 Hz, 1 H, phenyl), 7.52 (t, *J* = 7.7 Hz, 2 H, phenyl), 6.22-6.16 (m, 2 H, =CH), 3.86 (s, 3 H, OCH_3), 2.98 (br d, *J* = 8.8 Hz, 1 H), 2.76 (br d, *J* = 8.9 Hz, 1 H), 2.62-2.57 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6 (C=O, benzoyl), 165.9 (C=O, ester), 135.2, 134.0, 128.7, 128.6, 123.8, 123.6, 116.3 (CN), 114.2 (CN), 53.9 (OCH_3), 33.1, 30.9, 29.3, 28.2, 27.8, 27.5 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{19}H_{14}N_2O_3$: 318.1004; found: 318.1010.

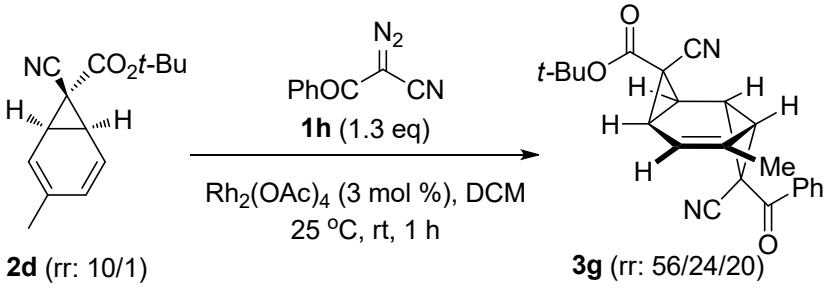
(1*R**,2*S**,3*S**,4*R**,7*R**,8*S**)-*tert*-Butyl 8-benzoyl-3,8-dicyanotricyclo[5.1.0.0^{2,4}]- -oct-5-ene-3-carboxylate (**3f**)



The titled compound was synthesized from **2c** and **1h** by following the typical

procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 12:1, 8:1), **3f** was obtained in quantitative yield as a yellow solid. The isolated product was crystalized from CH_2Cl_2-MeOH to form colorless crystals that were suitable for X-ray crystallographic analysis.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2 H, phenyl), 7.63 (t, *J* = 7.4 Hz, 1 H, phenyl), 7.51 (t, *J* = 7.6 Hz, 2 H, phenyl), 6.21-6.14 (m, 2 H, =CH), 2.97 (br d, *J* = 8.8 Hz, 1 H), 2.67 (br d, *J* = 8.8 Hz, 1 H), 2.60 (dd, *J* = 8.8, 4.4 Hz, 1 H), 2.49 (dd, *J* = 8.8, 4.3 Hz, 1 H), 1.52 (s, 9 H, *t*-Bu) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7 (C=O, benzoyl), 164.0 (C=O, ester), 135.2, 133.9, 128.7, 128.6, 124.2, 123.2, 116.4 (CN), 114.5 (CN), 84.8 (C-O), 33.2, 31.0, 29.1, 28.5, 27.8 (methyl of *t*-Bu), 27.1 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{22}H_{20}N_2O_3$: 360.1474; found: 360.1472.

(1*S**,2*S**,3*S**,4*R**,7*S**,8*R**)-*tert*-Butyl 8-benzoyl-3,8-dicyano-6-methyltricyclo-[5.1.0.0^{2,4}]-oct-5-ene-3-carboxylate (**3g**)

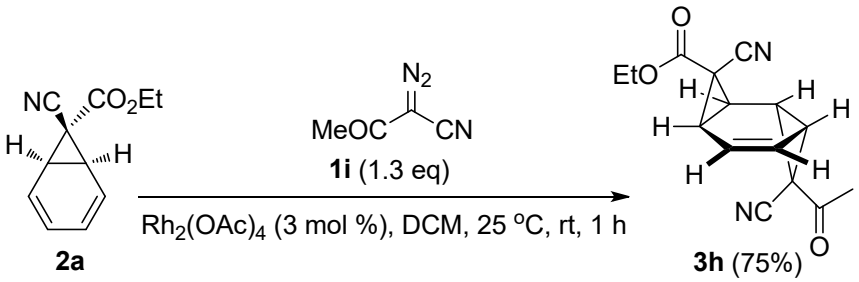


2d (rr: 10/1) **3g** (rr: 56/24/20)

The titled compound was synthesized from **2d** (rr: 10/1) and **1h** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 15:1, 10:1, 8:1), **3g** was obtained in 80% yield as an inseparable mixture of three regioisomers (rr: 56/24/20). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer (56%): δ 7.99 (d, *J* = 7.4 Hz, 2 H, Ph), 7.64 (t, *J* = 7.4 Hz, 1 H, Ph), 7.52 (t, *J* = 7.8 Hz, 2 H, Ph), 5.90-5.85 (m, 1 H, =CH), 2.99 (br d, *J* = 8.8 Hz, 1 H), 2.63 (br d, *J* = 8.9 Hz, 1 H), 2.49-2.43 (m, 1 H), 2.45 (d, *J* = 8.9 Hz, 1 H), 2.01 (s, 3 H, Me), 1.51 (s, 9 H, *t*-Bu) ppm; minor isomer-1 (24%): δ 7.96 (d, *J* = 7.2 Hz, 2 H, Ph), 7.68-7.60 (m, 1 H, Ph), 7.56-7.50 (m, 2 H, Ph), 5.90-5.85 (m, 1 H, =CH), 3.02-2.96 (m, 1 H), 2.73-2.49 (m, 3 H), 2.01 (s, 3 H, Me), 1.52 (s, 9 H, *t*-Bu) ppm; minor isomer-2 (20%): δ 7.89 (d, *J* = 7.4 Hz, 2 H, Ph), 7.66-7.61 (m, 1 H, Ph), 7.52-7.48 (m, 2 H, Ph), 6.21 (dd, *J* = 9.8, 5.2 Hz, 1 H, =CH), 6.08 (d, *J* = 9.8 Hz, 1 H, =CH), 2.94 (br s , 1 H), 2.73-2.49 (m, 1 H), 2.35 (d, *J* = 8.9 Hz, 1 H), 2.01 (s, 3 H, Me), 1.53 (s, 9 H, *t*-Bu) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1 (C=O, benzoyl, minor), 189.9 (C=O, benzoyl, major), 188.7 (C=O benzoyl, minor), 164.3 (x 2, C=O, ester), 164.1 (C=O, ester), 135.4, 135.3 (x 2), 134.3, 134.0 (x 2), 133.8, 133.5, 132.2, 129.0, 128.9, 128.7 (x 2), 128.6, 128.5, 123.7, 117.4 (x 2), 116.9 (CN, minor), 116.7 (CN, minor), 116.5 (CN, major) 116.3, (CN, major), 114.9 (CN, minor), 114.8 (CN, minor), 84.9 (C-O,

minor), 84.7 (C-O, minor), 84.6 (C-O, major), 37.1, 36.5, 35.2 (x 2), 32.9, 32.6, 32.6, 32.4 (x 2), 29.7, 29.5, 29.2, 28.7, 28.5, 28.2, 28.1, 27.9, 27.8 (x 2, methyl of *t*-Bu), 27.1, 26.5, 22.7, 22.6, 17.8 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{23}H_{22}N_2O_3$: 374.1630; found: 374.1627.

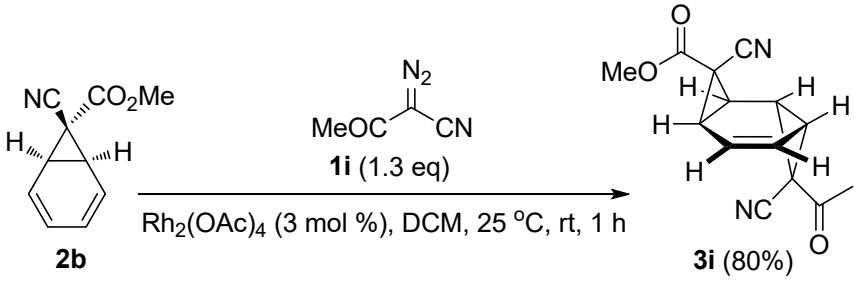
(1*R**,2*S**,3*S**,4*R**,7*R**,8*S**)-Ethyl 8-acetyl-3,8-dicyanotricyclo[5.1.0.0^{2,4}]oct- -5-ene-3-carboxylate (**3h**)



2a **3h** (75%)

The titled compound was synthesized from **2a** and **1i** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 12:1, 8:1, 4:1), **3h** was obtained in 75% yield as a colorless oil. The isolated product was crystalized from ethyl acetate to form colorless crystals that were suitable for X-ray crystallographic analysis. IR (neat): 3056, 2986, 2244, 1732, 1712, 1248, 855, 790 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (dd, *J* = 9.5, 4.6 Hz, 1 H, =CH), 6.07 (dd, *J* = 9.5, 4.4 Hz, 1 H, =CH), 4.27 (q, *J* = 7.1 Hz, 2 H, $OC\boldsymbol{H}_2CH_3$), 2.69 (br d, *J* = 8.8 Hz, 1 H), 2.65 (br d, *J* = 8.7 Hz, 1 H), 2.57 (s, 3 H, CH_3CO), 2.50 (dd, *J* = 8.8, 4.6 Hz, 1 H), 2.46 (dd, *J* = 8.7, 4.4 Hz, 1 H), 1.34 (t, *J* = 7.1 Hz, 3 H, $OCH_2C\boldsymbol{H}_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3 (C=O, acetyl), 165.4 (C=O, ester), 123.6 (=CH), 123.5 (=CH), 116.2 (CN), 114.0 (CN), 63.4 ($O\mathbf{C}H_2CH_3$), 35.0, 31.7, 29.6, 29.3, 28.9, 28.1, 27.7, 14.0 ($OCH_2\mathbf{C}H_3$) ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_{14}N_2O_3$: 270.1004; found: 270.0998.

(1*R**,2*S**,3*S**,4*R**,7*R**,8*S**)-Methyl 8-acetyl-3,8-dicyanotricyclo[5.1.0.0^{2,4}]oct- -5-ene-3-carboxylate (**3i**)

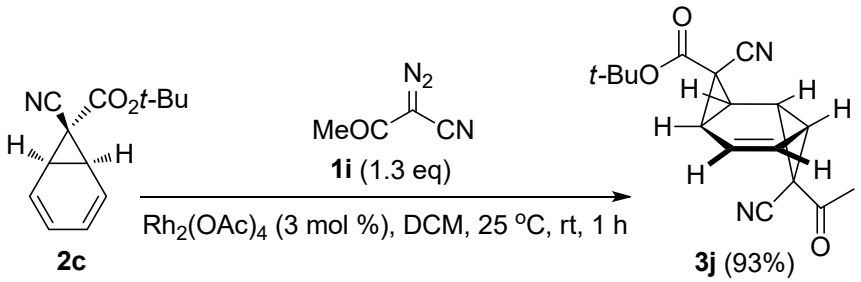


2b **3i** (80%)

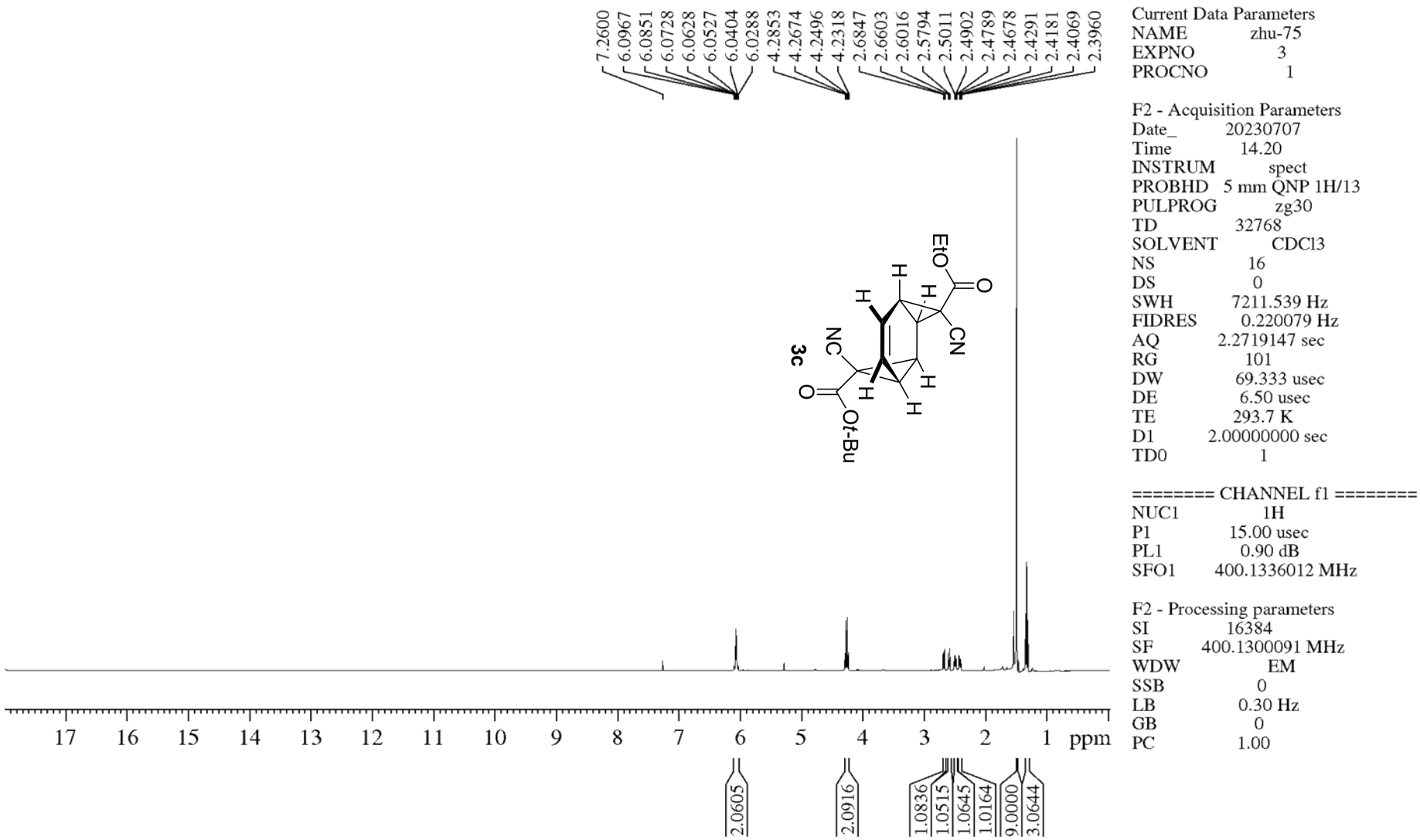
The titled compound was synthesized from **2b** and **1i** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 8:1, 5:1, 2:1), **3h** was obtained in 80% yield as a white solid. IR (neat): 3056, 2958, 2244, 1738, 1711, 1253, 862, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12-6.06 (m, 2 H, =CH), 3.84 (s, 3 H, OCH_3), 2.69 (br d, *J* = 8.8 Hz, 1 H), 2.67 (br d, *J* =

8.7 Hz, 1 H), 2.58 (s, 3 H, CH_3CO), 2.52 (dd, J = 8.8, 4.4 Hz, 1 H), 2.46 (dd, J = 8.7, 4.4 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3 (C=O, acetyl), 165.9 (C=O, ester), 123.7 (=CH), 123.4 (=CH), 116.1 (CN), 114.0 (CN), 53.9 (OCH_3), 34.9, 31.7, 29.6, 29.2, 29.1, 27.9, 27.2 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{14}H_{12}N_2O_3$: 256.0848; found: 256.0839.

(1*R*,*2*S*,*3*S*,*4*R*,*7*R*,*8*S**)-*tert*-Butyl 8-acetyl-3,8-dicyanotricyclo[5.1.0.02,4]oct- -5-ene-3-carboxylate (**3j**)



The titled compound was synthesized from **2c** and **1i** by following the typical procedure. After chromatography (triethylamine-deactivated silica gel; hexane/ethyl acetate = 8:1, 5:1, 3:1), **3j** was obtained in 93% yield as a white solid. IR (neat): 3057, 2982, 2240, 1726, 1712, 1224, 839, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.09 (dd, J = 9.8, 4.8 Hz, 1 H, =CH), 6.04 (dd, J = 9.8, 4.7 Hz, 1 H, =CH), 2.69 (br d, J = 8.8 Hz, 1 H), 2.56 (br d, J = 8.2 Hz, 1 H), 2.55 (s, 3 H, CH_3CO), 2.45 (dd, J = 8.8, 4.7 Hz, 1 H), 2.42 (dd, J = 8.2, 4.8 Hz, 1 H), 1.49 (s, 9 H, *t*-Bu) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3 (C=O, acetyl), 164.0 (C=O, ester), 123.7 (=CH), 123.3 (=CH), 116.2 (CN), 114.3 (CN), 84.7 (C-O), 35.0, 31.8, 29.5, 29.4, 28.8, 28.3, 27.7 (methyl of *t*-Bu), 27.0 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{18}N_2O_3$: 298.1317; found: 298.1323.



Current Data Parameters
NAME zhu-75
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230707
Time 14.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 101
DW 69.333 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
TD0 1

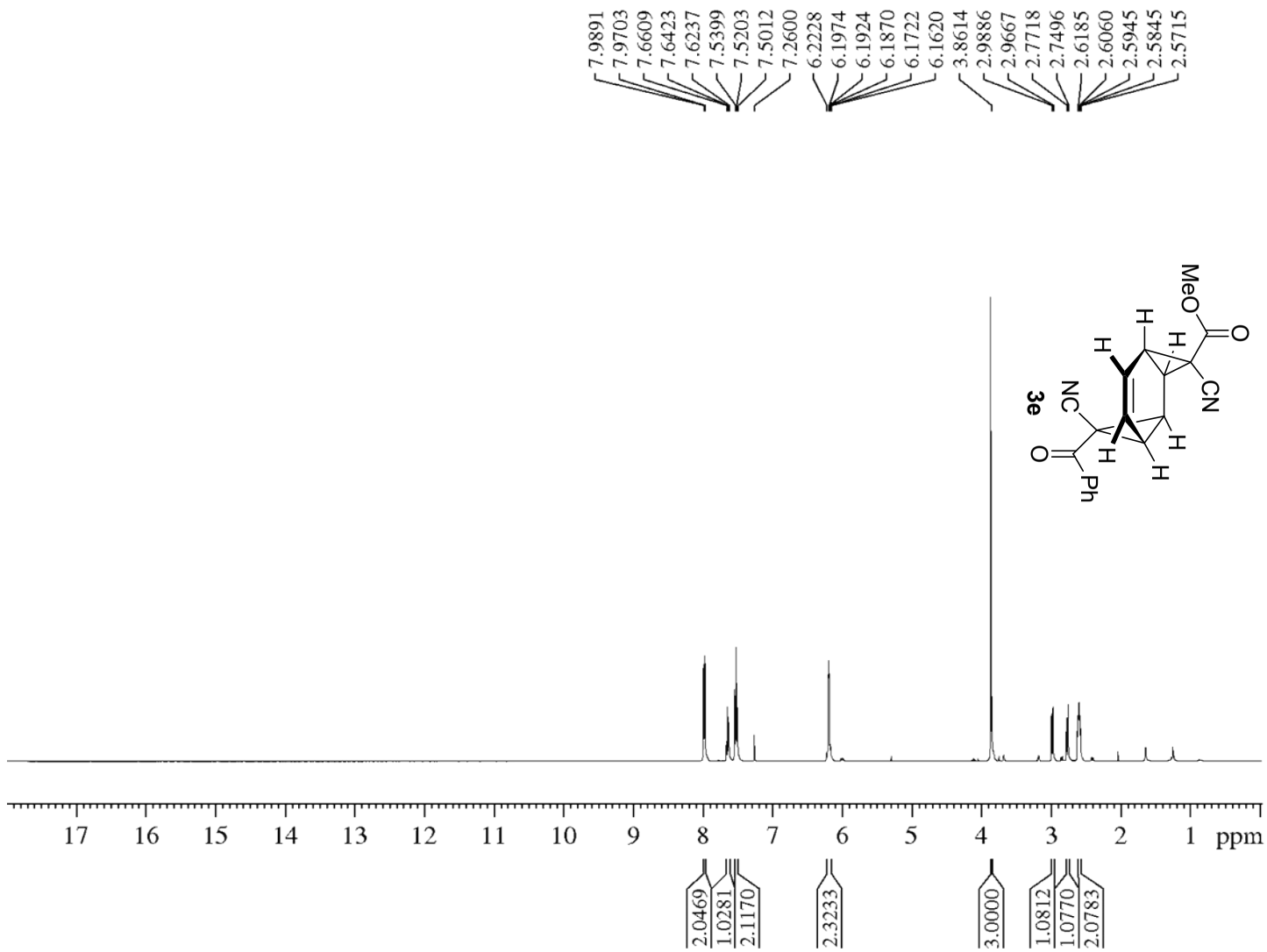
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME zhu-75
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230707
Time 14.30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127813 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13.9636
26.7329
27.3989
27.6289
27.7302
28.2254
28.2627
28.8774
28.9683
63.2612
76.6811
77.0000
77.3176
84.7325
114.1511
114.4099
122.9521
123.5178
163.9291
165.3168
O
CN
EtO
H
H
H
H
H
NC
Ot-Bu
O
3c
220
200
180
160
140
120
100
80
60
40
20
ppm

Current Data Parameters
NAME zhu-65
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230724
Time 12.29
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 256
DW 69.333 usec
DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.3440
1.3618
1.3795
2.5679
2.5934
2.6201
2.7401
2.7622
2.9743
2.9961
4.2771
4.2948
4.3126
4.3303
6.1966
7.2600
7.5051
7.5242
7.5430
7.6269
7.6450
7.6631
7.9741
7.9938
EtO
O
CN
H
H
H
H
H
H
NC
Ph
O
3d
3.0942
2.0445
1.0035
1.0172
2.0978
2.0000
2.0657
1.0536
2.0346
ppm

Current Data Parameters
NAME zhu-64-2
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230608
Time 12.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 420
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 812
DW 19.800 usec
DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127772 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CN
EtO
H
H
H
H
H
H
Ph
NC
O
3d
14.0347
27.5925
27.6295
28.3696
29.0884
30.9318
33.1604
63.4285
76.6820
77.0000
77.2023
77.3177
114.2186
116.3678
123.4940
123.9513
128.6978
128.7530
134.0057
135.1974
165.4171
189.6233
ppm
220
200
180
160
140
120
100
80
60
40
20

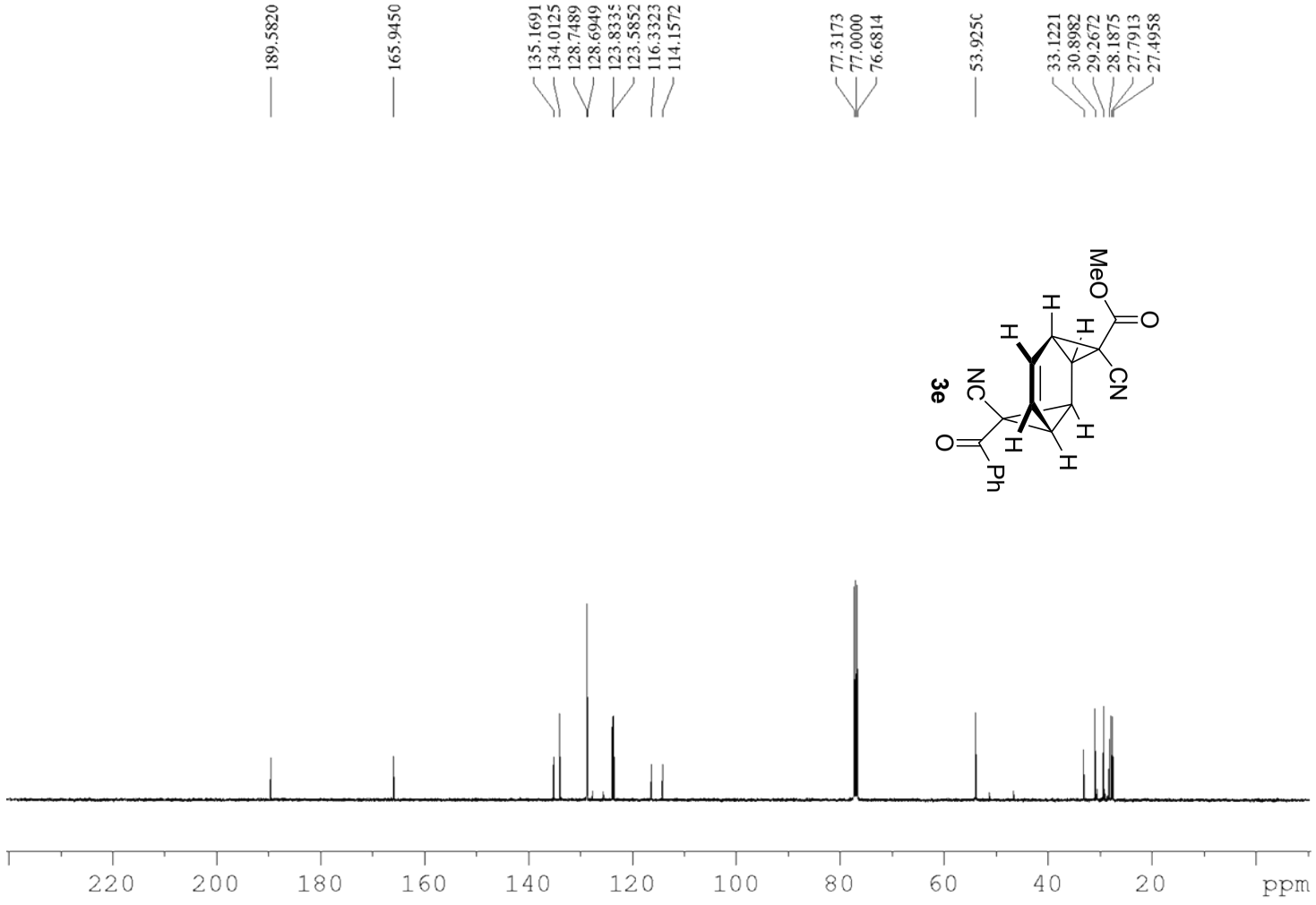


Current Data Parameters
NAME zhu-92
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231031
Time 12.13
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 80
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 228
DW 69.333 usec
DE 6.50 usec
TE 293.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



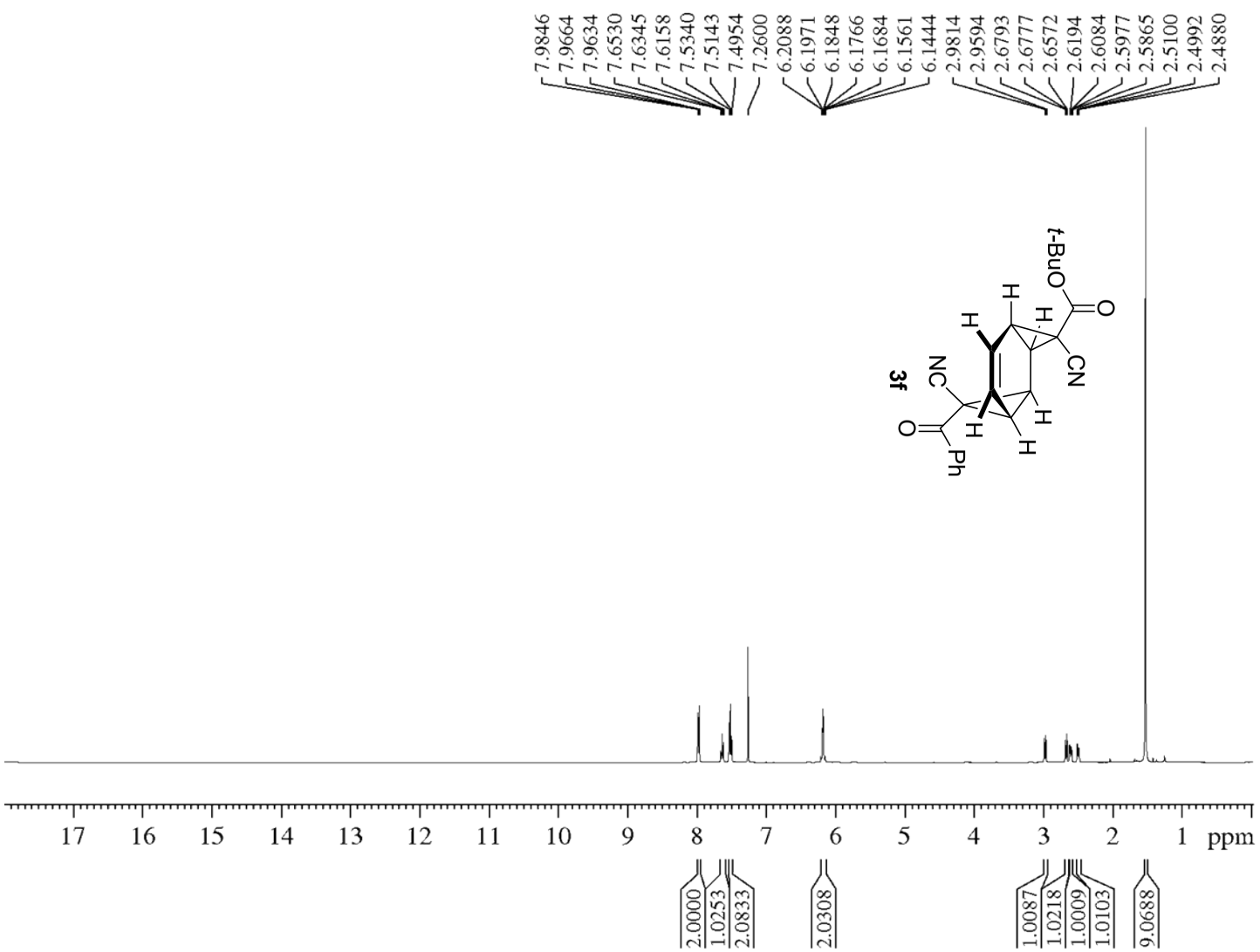
Current Data Parameters
NAME zhu-92
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231031
Time 12.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 695
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127782 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

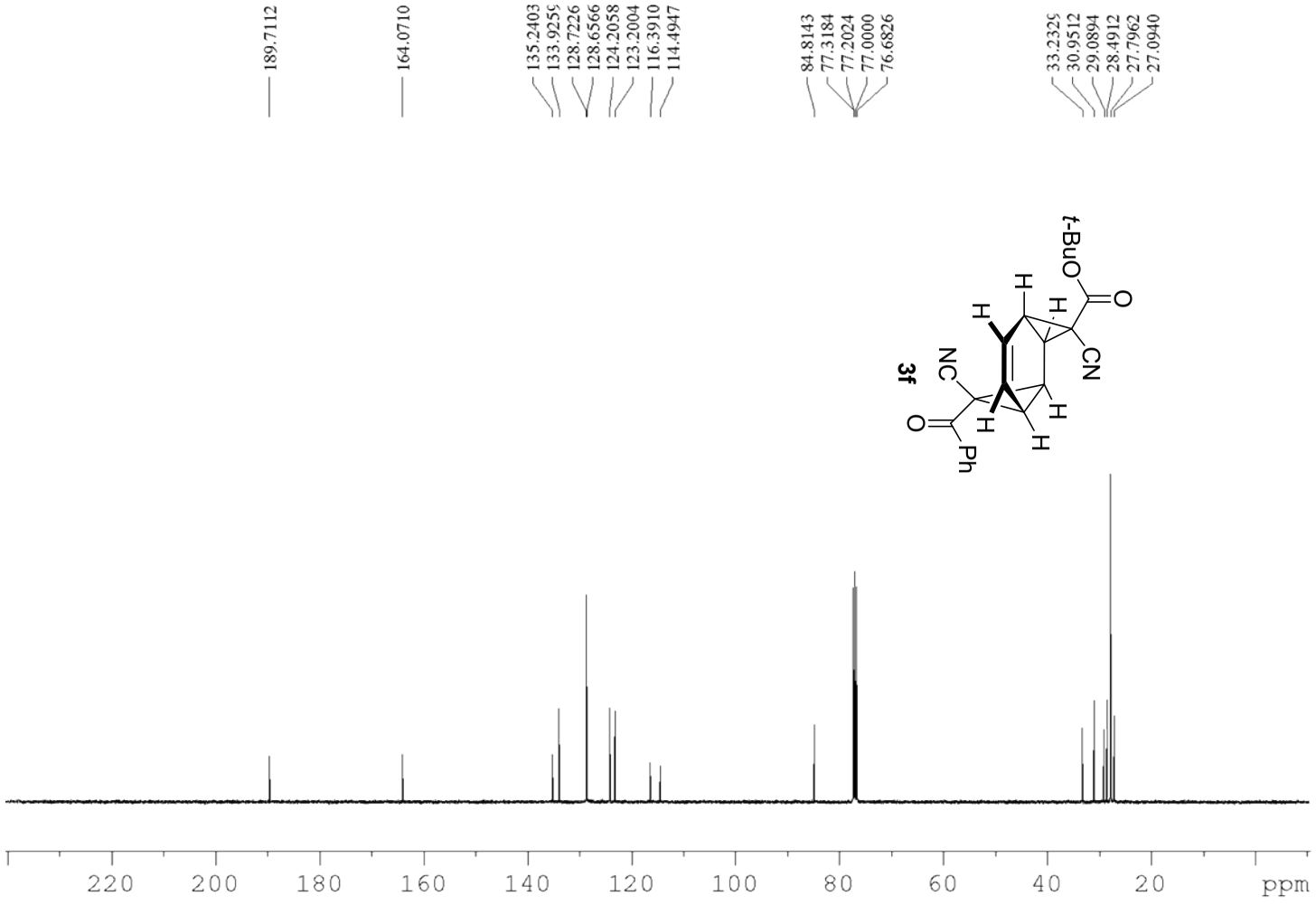


Current Data Parameters
NAME zhu-94
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231123
Time 16.12
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 40
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 101
DW 69.333 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



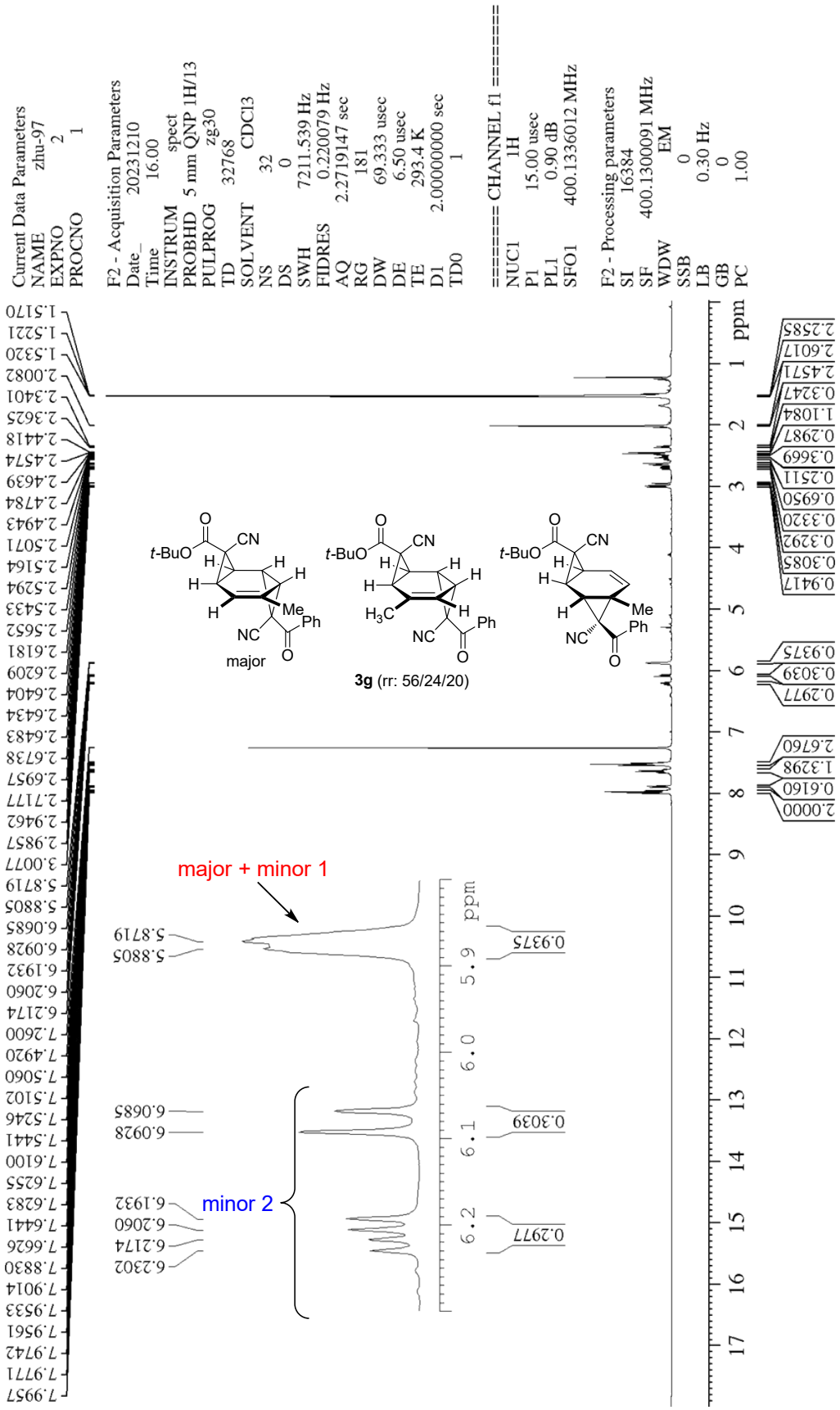
Current Data Parameters
NAME zhu-94
EXPNO 2
PROCNO 1

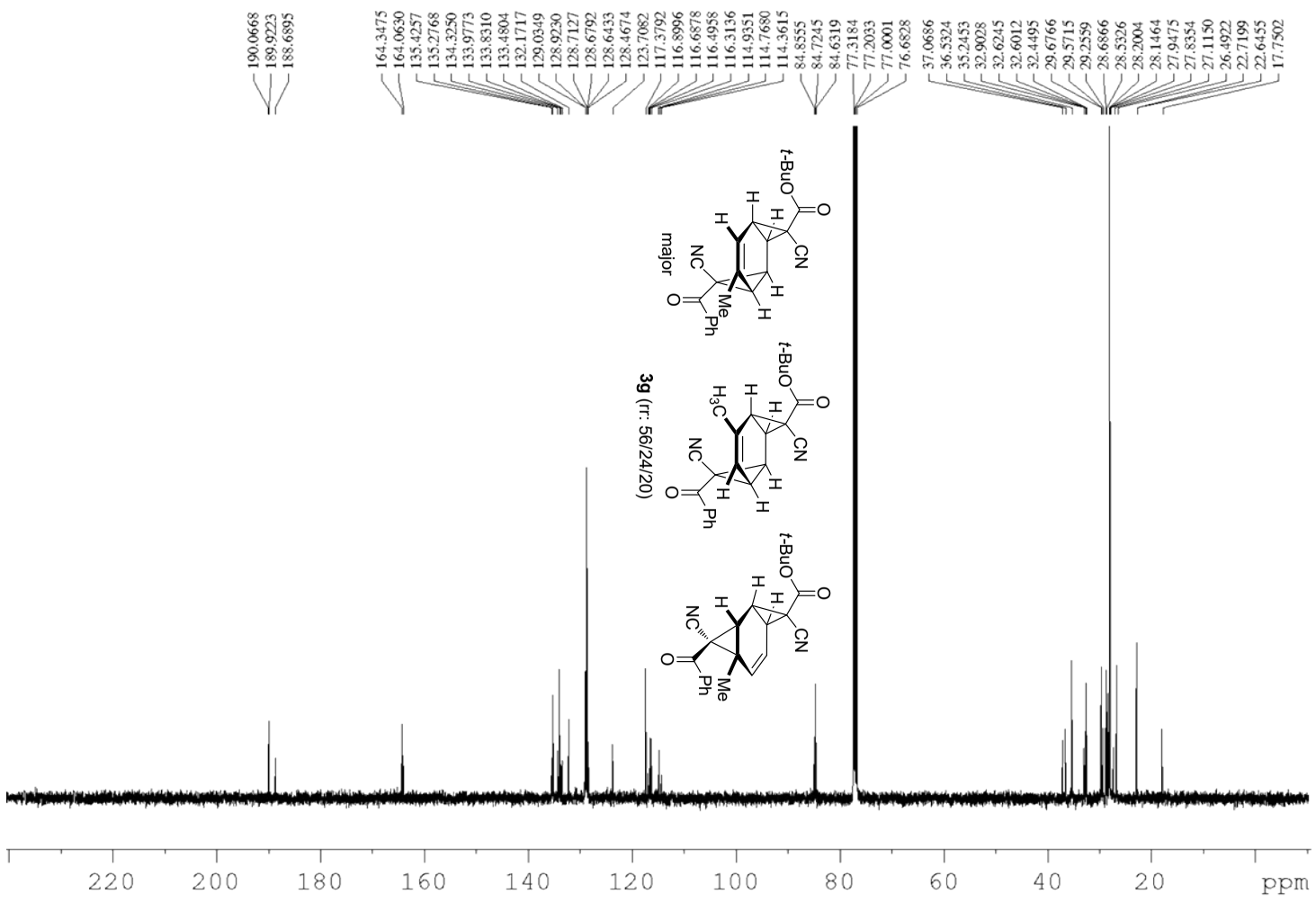
F2 - Acquisition Parameters
Date_ 20231123
Time 16.17
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127792 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


major + minor 1
minor 2
major
3g (rr: 56/24/20)
t-BuO
CN
NC
Me
Ph
ppm



Current Data Parameters
NAME zhu-97
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231210
Time 16.04
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

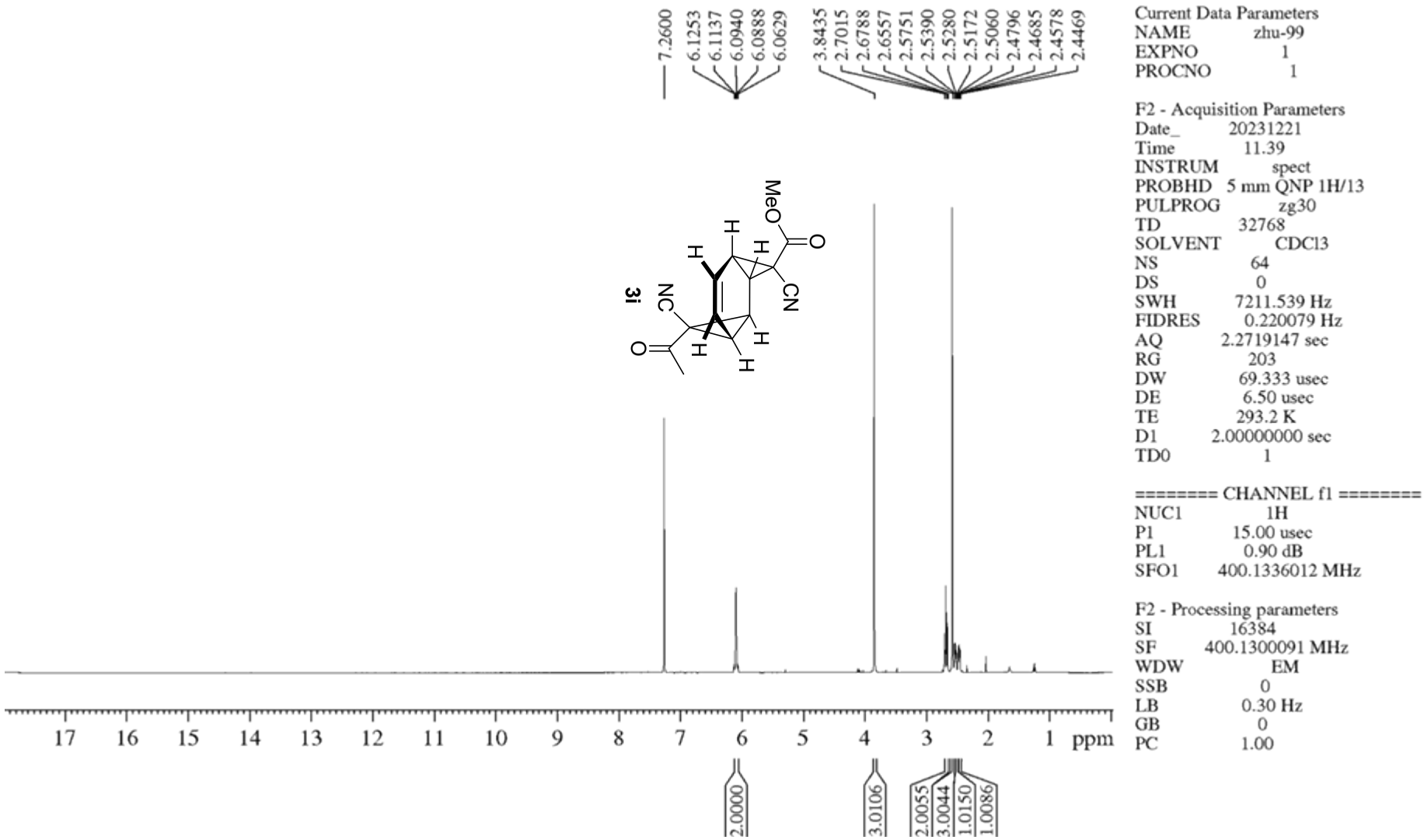
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127763 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Current Data Parameters
NAME zhu-74
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230705
Time 14.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 181
DW 69.333 usec
DE 6.50 usec
TE 293.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.2600
6.1243
6.1126
6.1003
6.0892
6.0785
6.0662
6.0545
4.2999
4.2821
4.2642
4.2463
2.7026
2.6807
2.6613
2.6389
2.5695
2.5211
2.5101
2.4990
2.4879
2.4772
2.4662
2.4552
EtO
O
CN
H
H
H
H
H
NC
O
3h
2.0000
2.0434
2.0356
3.0189
2.0603
3.0276
ppm

Current Data Parameters
NAME zhu-74
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230705
Time 14.56
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127783 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13.9923
27.4993
28.0930
28.8978
29.2958
29.5739
31.7310
34.9561
63.3932
76.6819
77.0000
77.2015
77.3180
114.0409
116.1769
123.4579
123.6289
165.3654
196.3123
O
EtO
CN
H
H
H
H
H
NC
O
3h
ppm
220
200
180
160
140
120
100
80
60
40
20



Current Data Parameters
NAME zhu-99
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231221
Time 11.39
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 203
DW 69.333 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME zhu-99
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20231221
Time 11.47
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 240
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
CHANNEL f2
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127777 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CN
MeO
H
H
H
H
H
NC
O
3i
27.6788
27.9361
29.0940
29.2247
29.5922
31.6983
34.9336
53.9203
76.6827
77.0000
77.2026
77.3185
113.9900
116.1457
123.3613
123.7346
165.9160
196.3042
ppm
220
200
180
160
140
120
100
80
60
40
20

Current Data Parameters
NAME zhu-103
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240130
Time 15.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 90.5
DW 69.333 usec
DE 6.50 usec
TE 293.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.2600
6.1137
6.1017
6.0895
6.0776
6.0603
6.0486
6.0363
6.0244
2.6977
2.6757
2.5736
2.5530
2.4619
2.4502
2.4398
2.4320
2.4289
2.4206
2.4102
2.3983
1.4883
O
CN
t-BuO
H
H
H
H
H
NC
O
3j
9.0000
2.0736
3.5273
0.5082
1.0173
2.0451
ppm

Current Data Parameters
NAME zhu-103
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240130
Time 15.23
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
CHANNEL f2
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127810 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CN
t-BuO
H
H
H
H
H
NC
O
3j
26.9578
27.7385
28.2815
28.7962
29.4566
29.5226
31.7766
35.0211
76.6820
77.0000
77.2020
77.3182
84.7671
114.3058
116.1970
123.3205
123.7063
163.9972
196.3305
ppm
220
200
180
160
140
120
100
80
60
40
20

8) Preparation of 7 via SmI_2-promoted Ring-opening of 3

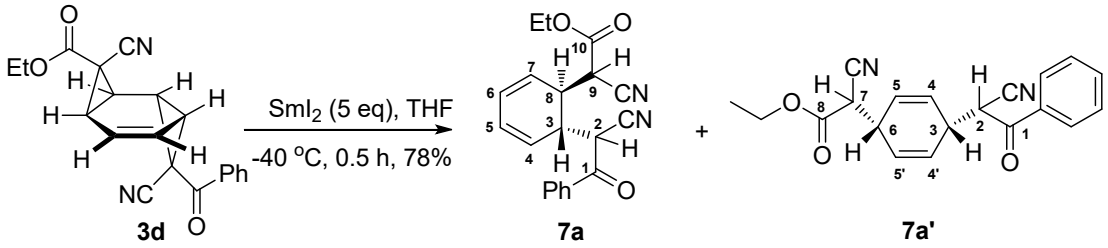
i) General Procedures

Procedure A: A solution of **3** (0.152 mmol) in THF (7.1 mL, 0.0214 M) was stirred at -40 ˚C for 50 min followed by the injection of SmI_2 reagent (purchased as a 0.1 M solution in THF, 7.6 mL, 0.76 mmol, 5 equiv) via a syringe in one portion. The resulting blue mixture was continued to stir at -40 ˚C for 0.5 h, then quenched by adding 10 mL of saturated $Na_2S_2O_3$ aqueous solution, and diluted with ethyl acetate (200 mL). The solution was washed with water (50 mL x 1) and brine (50 mL x 1), and concentrated in vacuo. The crude residue was purified by chromatography on silica gel to afford the mixtures of **7a/7a'** to **7f/7f'**.

Procedure B: The procedure is similar to that described for *Procedure A*, except for conducting the reaction at ambient temperature After the introduction of SmI_2 to a THF solution of **3** at 25 ˚C, the resulting blue mixture was stirred until the starting material had disappeared (TLC). The reaction was then quenched by adding $Na_2S_2O_3$ aqueous solution, diluted with ethyl acetate, washed with water and brine, and concentrated under vacuum. The crude residue was subjected to the chromatographic purification on silica gel to afford the mixtures of **7g/7g'** and **7h/7h'**.

ii) Preparation of 7a/7a' and ^{1}H-NMR ^{13}C-NMR, DEPT, NOESY spectra

Trans-Ethyl 2-cyano-2-[6-(1-cyano-2-oxo-2-phenylethyl)cyclohexa-2,4-dien-1-yl] acetate (**7a**) and *Cis*-Ethyl 2-cyano-2-[4-(1-cyano-2-oxo-2-phenylethyl)cyclohexa-2,5-dien-1-yl]acetate (**7a'**)



The titled compounds were synthesized from **3d** by following *Procedure A*. After chromatography (silica gel; hexane/ethyl acetate = 5:1, 2:1), a mixture of **7a**/**7a'** was obtained in 78% yield as a yellow solid (rr: 50/50). (**7a** and **7a'** each contains two diastereomeric pairs deriving from the configurations at C-2/C-9 and C-2/C-7).

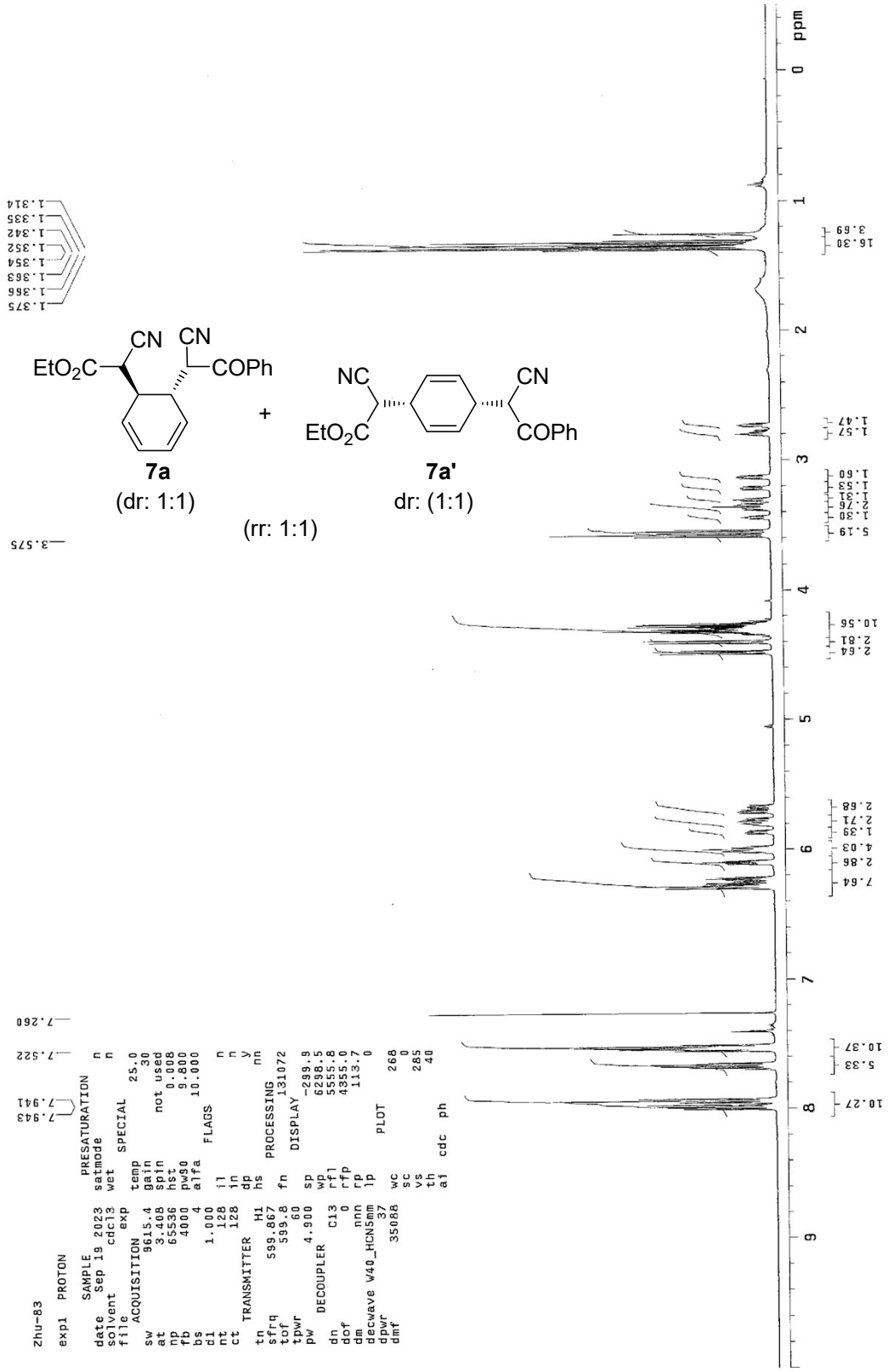
IR (neat): 3054, 2982, 2249, 2205, 1739, 1694, 1682, 1260, 1026, 800, 692 cm^{-1}.

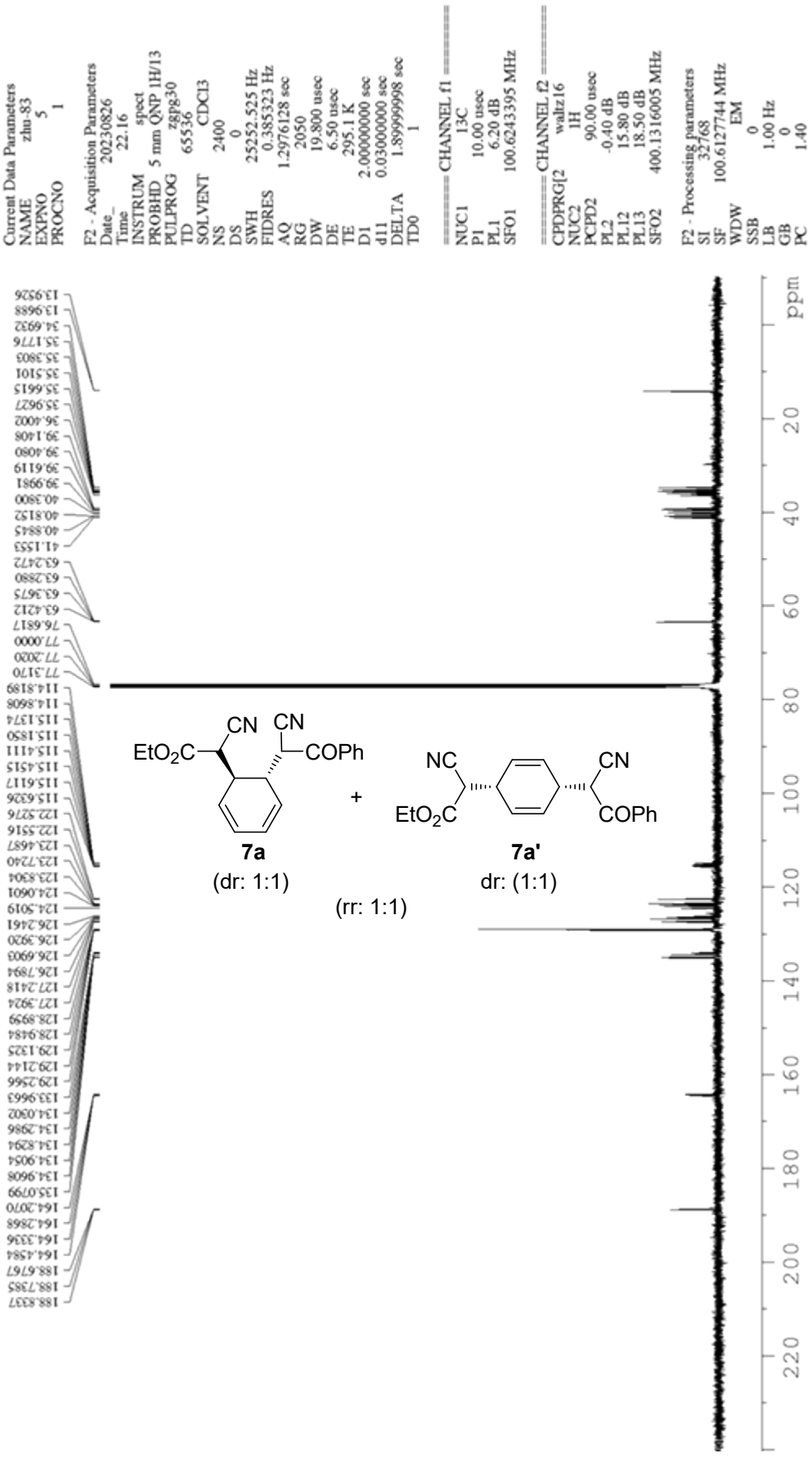
^{1}H NMR (600 MHz, $CDCl_3$) Phenyl protons of **7a**/**7a'**: δ 8.01-7.93 (m, 2 H), 7.70-7.65 (m, 1 H), 7.56-7.50 (m, 2 H); Olefinic protons of **7a**/**7a'**: δ 6.30-6.26 (m, 1 H), 6.25-6.21 (m, 0.5 H), 6.12-6.09 (m, 0.5 H), 6.03-5.98 (m. 0.75 H), 5.87 (dd, *J* = 9.0, 6.6 Hz, 0.25 H, $H_4/H_{4'}$ or $H_5/H_{5'}$ of **7a'**, deduced from the NOESY), 5.82-5.76 (m, 0.5 H, C=CH), 5.71 (dd, *J* = 9.6, 6.0 Hz, 0.25 H, C=CH), 5.67 (dd, *J* = 9.0, 6.0 Hz, 0.25 H, C=CH, $H_4/H_{4'}$ or $H_5/H_{5'}$ of **7a'**, deduced from the NOESY); H-2 of **7a**/**7a'**: δ 4.49 (d, *J*

= 9.0 Hz, 0.25 H, PhCO-C*H*-CN), 4.48 (d, *J* = 8.4 Hz, 0.25 H, PhCO-C*H*-CN), 4.40 (d, *J* = 9.6 Hz, 0.25 H, PhCO-C*H*-CN), 4.39 (d, *J* = 9.0 Hz, 0.25 H, PhCO-C*H*-CN); Methylene protons of EtO: δ 4.33-4.26 (m, 2 H); H-9 of **7a** and H-7 of **7a'**: δ 3.58 (d, *J* = 9.0 Hz, 0.5 H, EtOCO-C*H*-CN), 3.56 (d, *J* = 9.0 Hz, 0.25 H, EtOCO-C*H*-CN), 3.54 (d, *J* = 7.2 Hz, 0.25 H, EtOCO-C*H*-CN); H-3 and H-8 of **7a**/H-3 and H-6 of **7a'** (the signals showing the NOESY correlations are marked in the same color): δ 3.44 (br t, *J* = 6.6 Hz, 0.25 H), 3.37 (dd, *J* = 9.0, 6.6 Hz, 0.25 H), 3.36-3.34 (m, 0.25 H, from **7a**, deduced from the NOESY), 3.31 (br t, *J* = 7.2 Hz, 0.25 H, from **7a'**, deduced from the NOESY), 3.22 (ddd, *J* = 9.0, 6.0, 1.1 Hz, 0.25 H, allylic C-H), 3.13 (dd, *J* = 9.0, 6.0 Hz, 0.25 H, allylic C-H), 2.80 (br t, *J* = 7.2 Hz, 0.25 H, allylic C-H, from **7a'**), 2.73 (ddd, *J* = 9.0, 6.0, 1.0 Hz, 0.25 H, from **7a**, deduced from the NOESY); Methyl protons of EtO: δ 1.37 (t, *J* = 7.2 Hz, 0.75 H, C*H*$_3$CH$_2$O), 1.35 (t, *J* = 7.2 Hz, 0.75 H, C*H*$_3$CH$_2$O), 1.34 (t, *J* = 7.2 Hz, 0.75 H, C*H*$_3$CH$_2$O), 1.31 (t, *J* = 7.2 Hz, 0.75 H, C*H*$_3$CH$_2$O) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8 (x 2, Ph*C*O), 188.7 (Ph*C*O), 188.6 (Ph*C*O), 164.5 (EtO*C*O), 164.3 (EtO*C*O), 164.3 (EtO*C*O), 164.2 (EtO*C*O), 135.1 (CH), 135.0 (CH), 134.9 (CH), 134.8 (CH), 134.3 (C x 2), 134.0 (C), 133.9 (C), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.9 (CH x 2), 128.8 (CH), 127.4 (CH), 127.2 (CH), 126.8 (CH x 2), 126.7 (CH), 126.4 (CH), 126.2 (CH), 124.5 (CH), 124.0 (CH), 123.8 (CH), 123.7 (CH), 123.5 (CH), 122.6 (CH), 122.5 (CH), 115.6 (CN), 115.6 (CN), 115.5 (CN), 115.4 (CN), 115.2 (CN), 115.1 (CN), 114.9 (CN), 114.8 (CN), 63.4 (CH_2O), 63.4 (CH_2O), 63.3 (CH_2O), 63.2 (CH_2O), 41.2 (CH), 40.9 (CH), 40.8 (CH), 40.4 (CH), 40.0 (CH), 39.6 (CH), 39.4 (CH), 39.1 (CH), 36.4 (CH), 36.0 (CH), 35.7 (CH), 35.5 (CH), 35.4 (CH), 35.2 (CH), 34.7 (CH x 2), 14.0 (CH_3), 13.9 (CH_3), 13.9 (CH_3), 13.8 (CH_3) ppm.

HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{20}H_{18}N_2O_3$: 334.1317; found: 334.1317.


CN
CN
EtO2C
COPh
+
NC
CN
EtO2C
COPh
7a
(dr: 1:1)
7a'
dr: (1:1)
(rr: 1:1)
ppm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EXPNO 5
PROCNO 1
P2 - Acquisition Parameters
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Time 22.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
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NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127744 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13.9526
13.9688
34.6932
35.1776
35.3803
35.5101
35.6615
35.9627
36.4002
39.1408
39.4080
39.6119
39.9981
40.3800
40.8152
40.8845
41.1553
63.2472
63.2880
63.3675
63.4212
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77.0000
77.2020
77.3170
114.8189
114.8608
115.1374
115.1850
115.4111
115.4515
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115.6326
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122.5516
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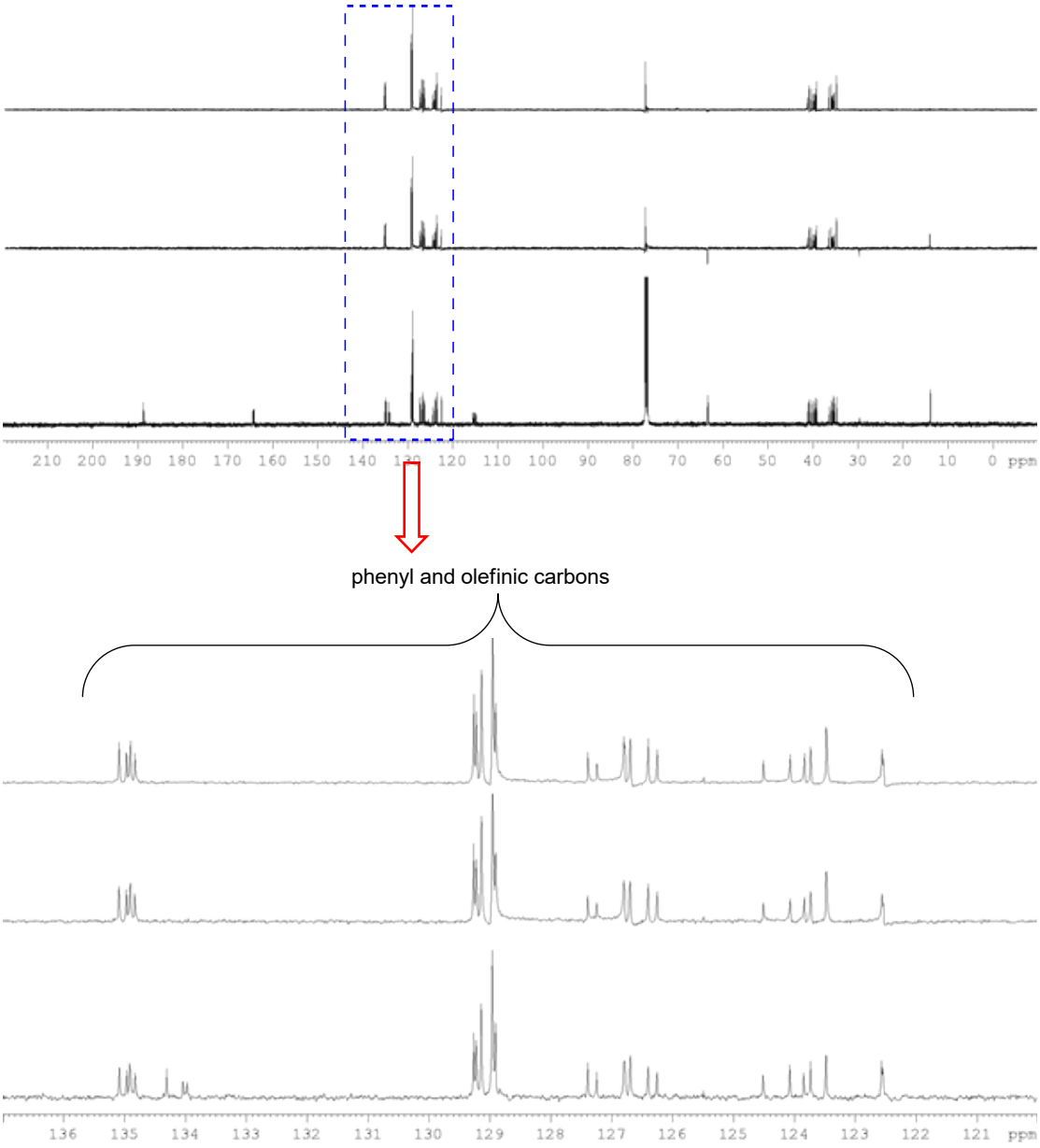
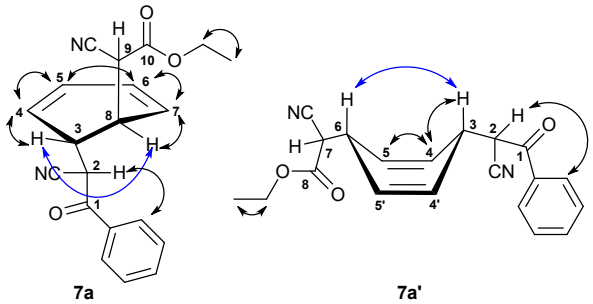
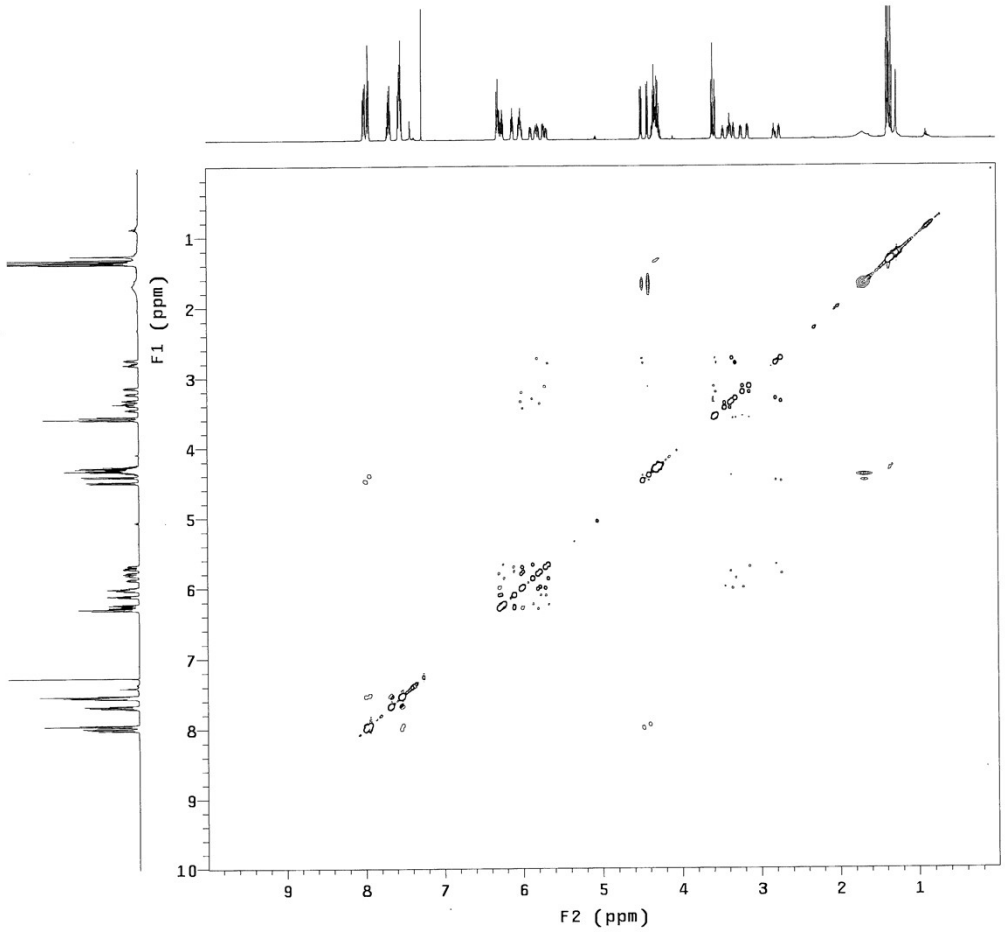
123.8304
124.0601
124.5019
126.2461
126.3920
126.6903
126.7894
127.2418
127.3924
128.8999
128.9484
129.1325
129.2144
129.2566
133.9663
134.0902
134.2986
134.8294
134.9054
134.9608
135.0799
164.2070
164.2868
164.3336
164.4584
188.6767
188.7385
188.8337
CN
CN
EtO2C
COPh
7a
(dr: 1:1)
+
NC
CN
EtO2C
COPh
7a'
dr: (1:1)
(rr: 1:1)
ppm
220
200
180
160
140
120
100
80
60
40
20

DEPT 90, 135 and ^{13}C NMR spectra (100 MHz):

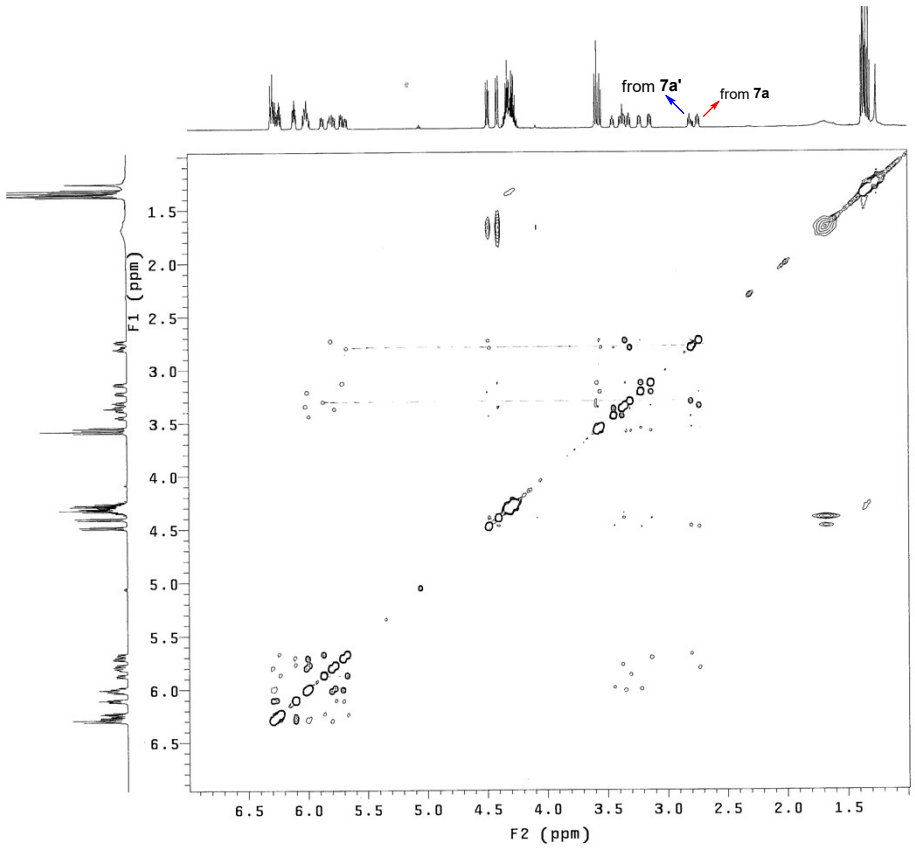


NOESY spectrum (600 MHz):

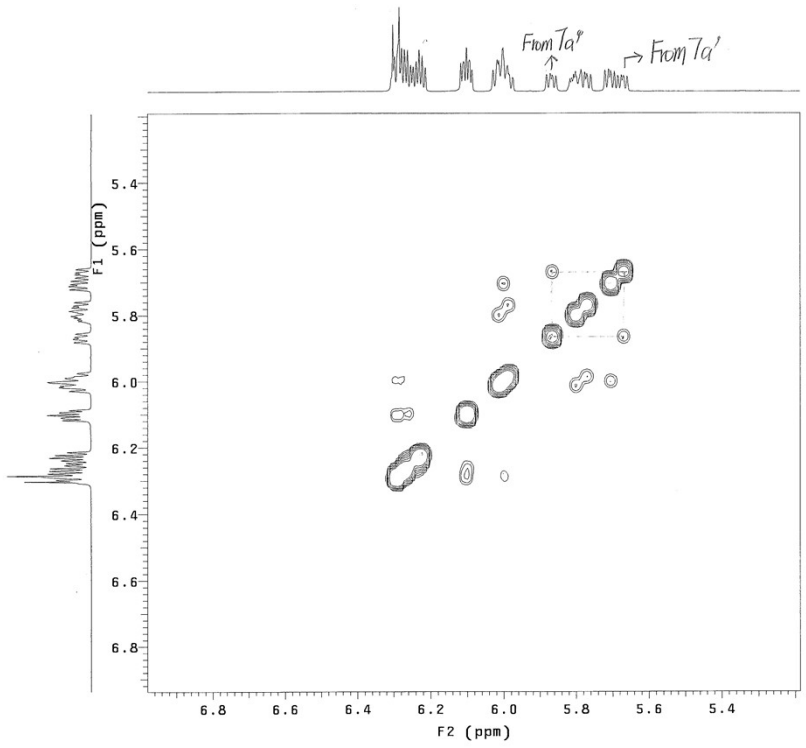




(Expansion-1):



(Expansion-2):



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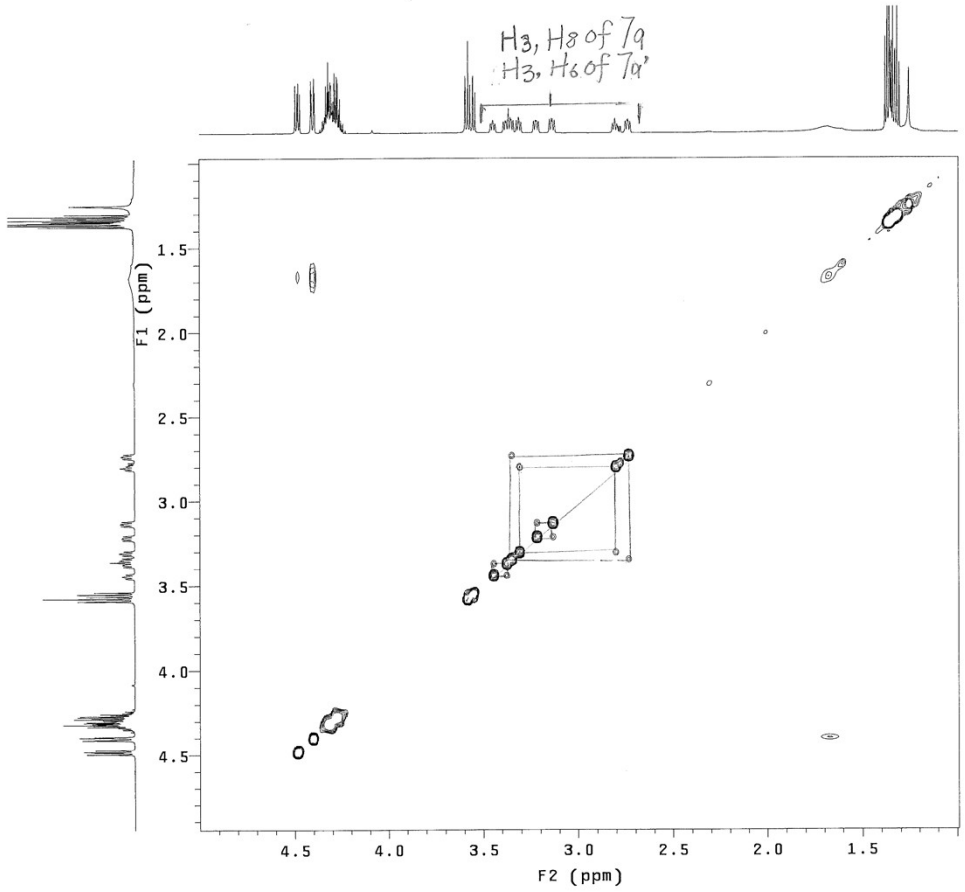
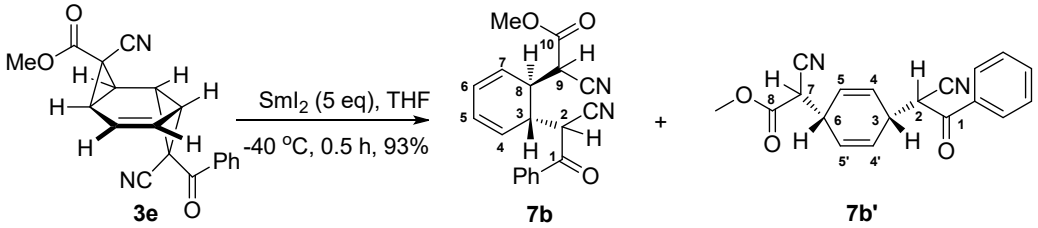

H3, H8 of 7a
H3, H6 of 7a'
F1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
F2 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5

iii) Preparation of 7b/7b' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-Methyl 2-cyano-2-[6-(-1-cyano-2-oxo-2-phenylethyl)cyclohexa-2,4-dien-1-yl] acetate (**7b**) and *Cis*-Methyl 2-cyano-2-[4-(1-cyano-2-oxo-2-phenylethyl)cyclohexa-2,5-dien-1-yl]acetate (**7b'**)



The titled compounds were synthesized from **3e** by following *Procedure A*. After chromatography (silica gel; hexane/ethyl acetate = 6:1, 3:1 2:1), a mixture of **7b**/**7b'** was obtained in 93% yield as a colorless oil (rr: 50/50). (**7b** and **7b'** each includes two diastereomeric pairs deriving from the configurations at C-2/C-9 and C-2/C-7).

IR (neat): 3049, 2956, 2247, 1746, 1694, 1261, 690, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Phenyl protons of **7b**/**7b'**: δ 8.00-7.92 (m, 2 H), 7.71-7.64 (m, 1 H), 7.56-7.50 (m, 2 H); Olefinic protons of **7a**/**7a'**: δ 6.30-6.21 (m, 1.5 H), 6.13-6.08 (m, 0.5 H), 6.00-5.97 (m, 0.75 H), 5.86 (dd, *J* = 9.3, 5.9 Hz, 0.25 H), 5.80-5.64 (m, 1 H); H-2 of **7b**/**7b'**: δ 4.48 (d, *J* = 9.6 Hz, 0.25 H, PhCO-C*H*-CN), 4.47 (d, *J* = 8.5 Hz, 0.25 H, PhCO-C*H*-CN), 4.40 (d, *J* = 9.2 Hz, 0.5 H, PhCO-C*H*-CN); CH_3O of **7b**/**7b'**: δ 3.87 (s, 0.75 H), 3.85 (s, 0.75 H), 3.82 (s, 0.75 H), 3.81 (s, 0.75 H);

H-9 of **7b** and H-7 of **7b'**: δ 3.62 (d, *J* = 8.8 Hz, 0.25 H, EtOCO-C*H*-CN), 3.60 (d, *J* = 7.7 Hz, 0.25 H, EtOCO-C*H*-CN), 3.58 (d, *J* = 8.8 Hz, 0.25 H, EtOCO-C*H*-CN), 3.57 (d, *J* = 7.7 Hz, 0.25 H, EtOCO-C*H*-CN); H-3 and H-8 of **7b**/H-3 and H-6 of **7b'**: δ 3.44 (br t, *J* = 7.3 Hz, 0.25 H), 3.36 (dd, *J* = 8.8, 6.2 Hz, 0.25 H), 3.37-3.27 (m, 0.5 H), 3.21 (br t, *J* = 7.7 Hz, 0.25 H), 3.13 (dd, *J* = 8.8 Hz, 0.25 H), 2.79 (br t, *J* = 7.1 Hz, 0.25 H, from **7b'**), 2.72 (ddd, *J* = 8.8, 6.0, 1.0 Hz, 0.25 H, from **7b**) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8 (x 2, Ph*C*O), 188.7 (Ph*C*O), 188.6 (Ph*C*O), 164.9 (MeO*C*O), 164.8 (MeO*C*O), 164.8 (MeO*C*O), 164.7 (MeO*C*O), 135.1 (CH), 135.0 (CH), 134.9 (CH), 134.8 (CH), 134.2 (x 2, C), 134.0 (C), 133.9 (C), 129.2 (CH), 129.2 (CH), 129.1 (CH), 128.9 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.4 (CH), 126.2 (CH), 124.4 (CH), 123.9 (CH), 123.8 (CH), 123.6 (CH), 123.4 (CH), 123.3 (CH), 122.4 (CH), 122.3 (CH), 115.6 (CN), 115.5 (CN), 115.4 (CN), 115.4 (CN), 115.0 (CN), 114.9 (CN), 114.7 (CN), 114.6 (CN), 53.8 (CH_3O x 2), 53.8 (CH_3O), 53.7 (CH_3O), 41.2 (CH), 41.0 (CH), 40.8 (CH), 40.2 (CH), 39.8 (CH), 39.6 (CH), 39.3 (CH), 39.1 (CH), 36.4 (CH), 36.0 (CH), 35.5 (CH), 35.4 (CH), 35.2 (CH), 34.6 (CH), 34.5 (CH x 2) ppm.

HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{19}H_{16}N_2O_3$: 320.1161; found: 320.1163.

Current Data Parameters
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PROCNO 1
F2 - Acquisition Parameters
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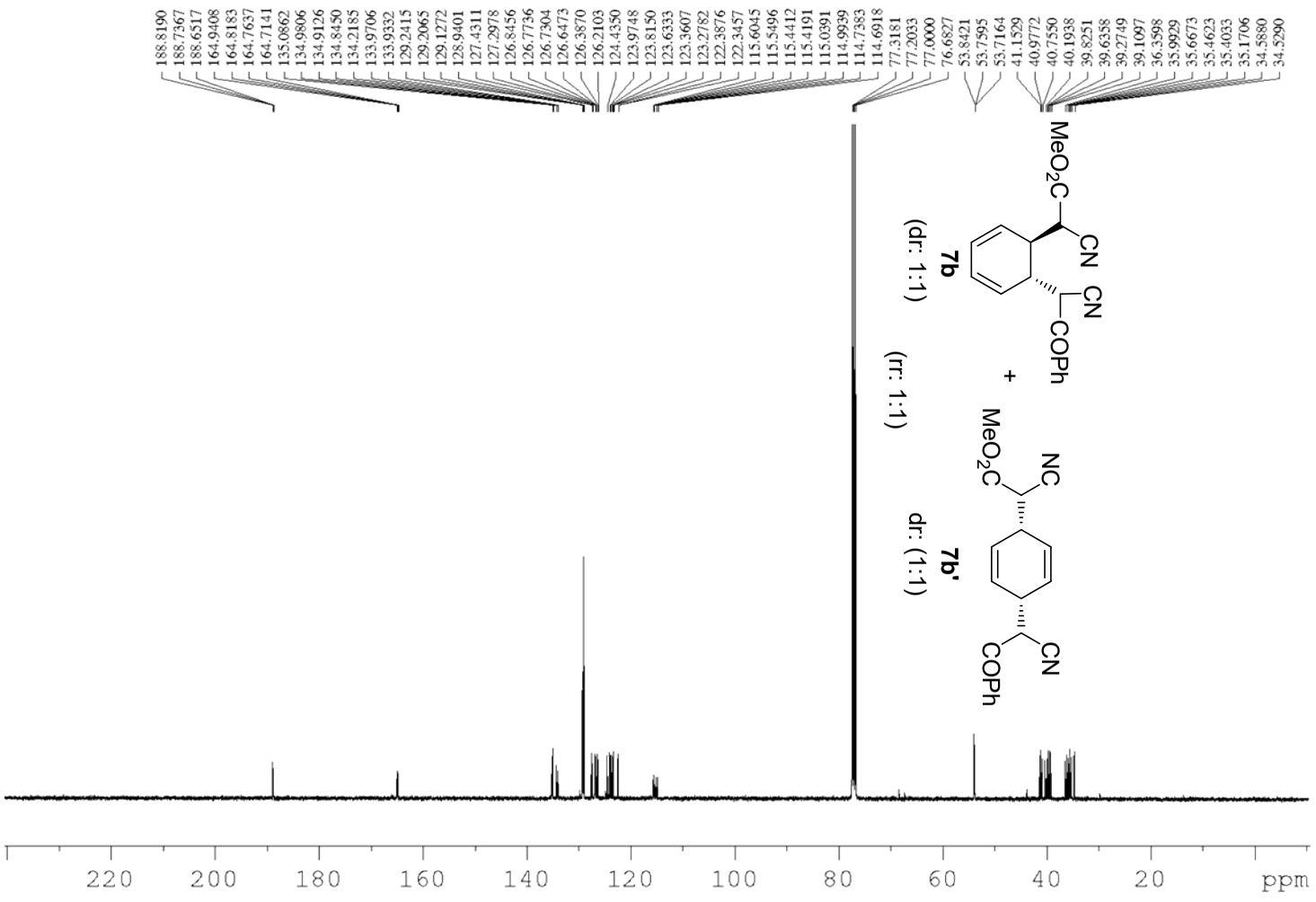
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 160
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 256
DW 69.333 usec
DE 6.50 usec
TE 292.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CN
CN
MeO2C
COPh
7b
(dr: 1:1)
+
NC
CN
MeO2C
COPh
7b'
dr: (1:1)
(rr: 1:1)
ppm



Current Data Parameters
NAME zhu-93
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
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Time 22.24
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
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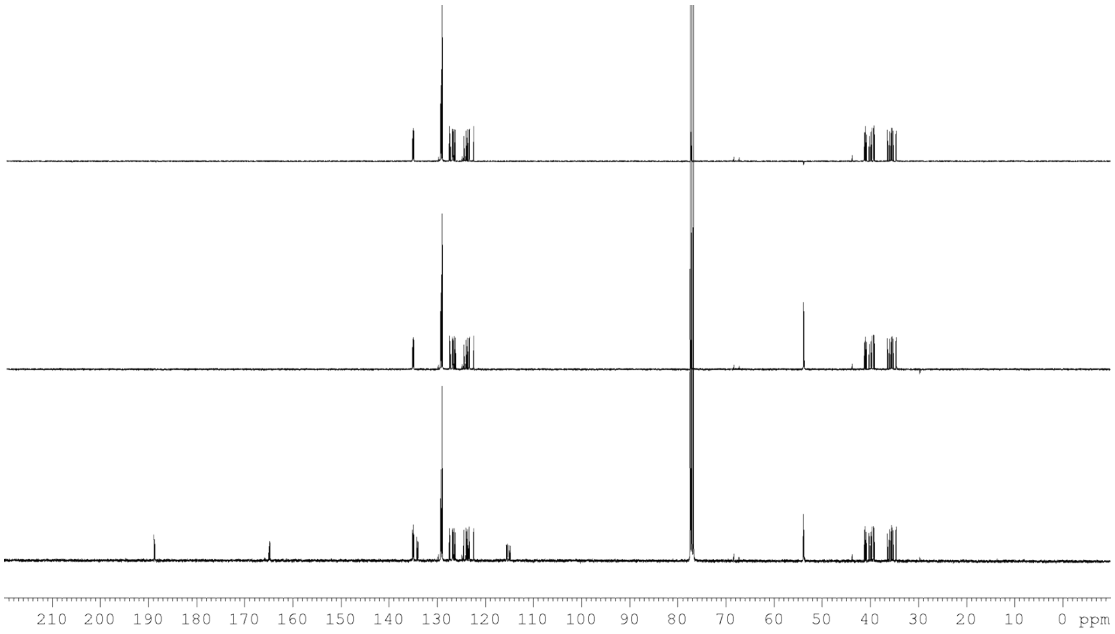
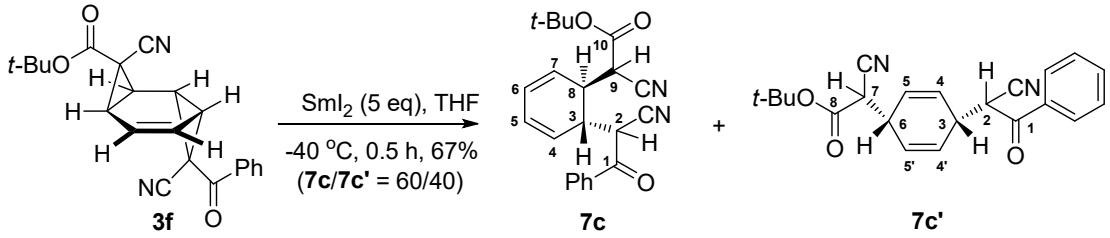
SF 100.6127757 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DEPT 90, 135 and ^{13}C-NMR spectra (100 MHz):



iv) Preparation of 7c/7c' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-tert-Butyl 2-cyano-2-[6-(1-cyano-2-oxo-2-phenylethyl)cyclohexa-2,4-dien-1-yl] acetate (**7c**) and *Cis-tert*-Butyl 2-cyano-2-[4-(1-cyano-2-oxo-2-phenylethyl)cyclohexa-2,5-dien-1-yl]acetate (**7c'**)



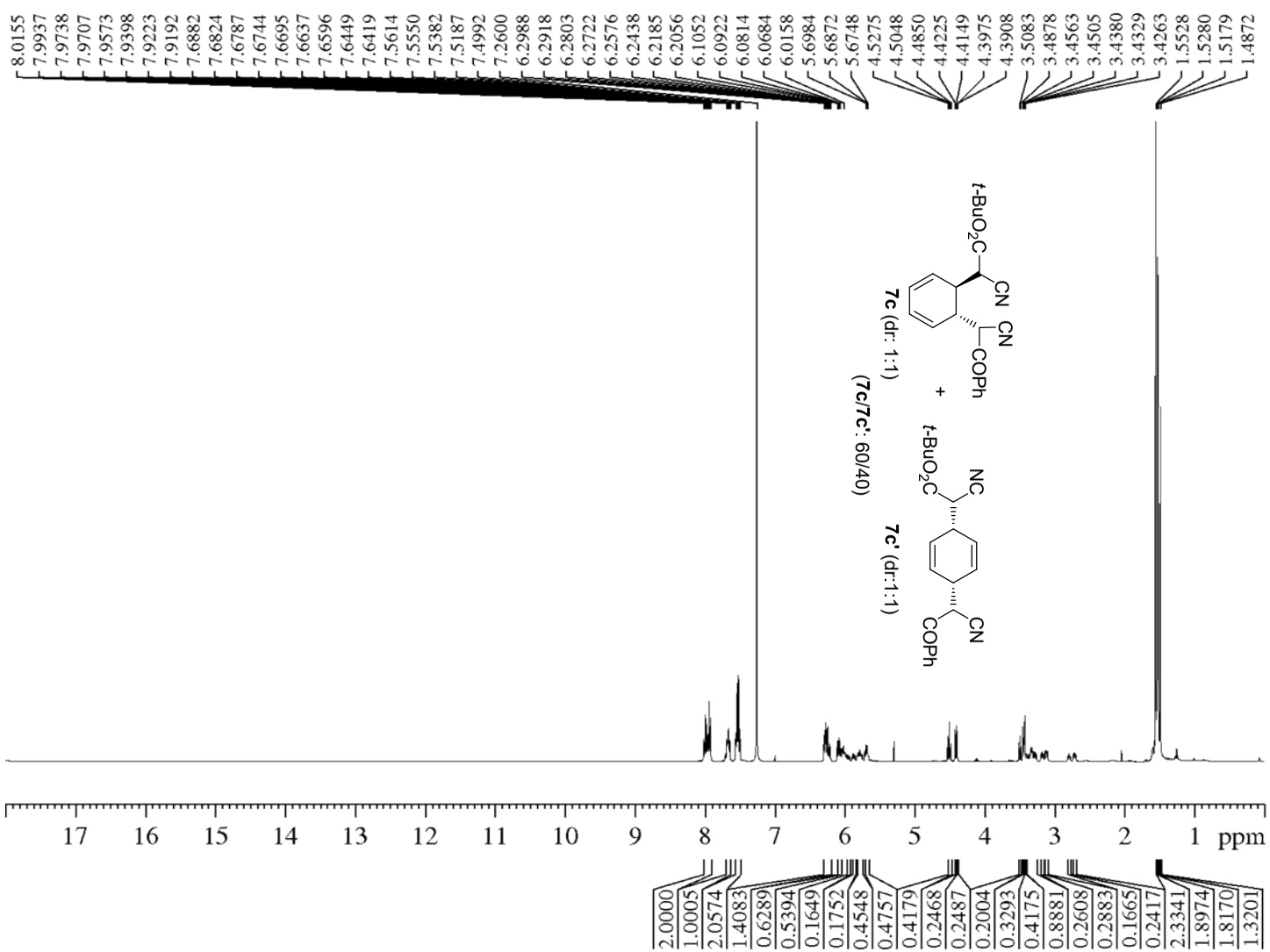
The titled compounds were synthesized from **3f** by following *Procedure A*. After chromatography (silica gel; hexane/ethyl acetate = 10:1, 5:1), a mixture of **7c**/**7c'** was obtained in 67% yield as a yellow oil (**7c**/**7c'** = 60/40). (**7c** and **7c'** each includes two diastereomeric pairs deriving from the configurations at C-2/C-9 and C-2/C-7).

IR (neat): 3050, 2981, 2247, 2204, 1738, 1694, 1260, 1151, 692, 672 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Phenyl protons of **7c**/**7c'**: δ 8.01-7.92 (m, 2 H), 7.71-7.64 (m, 1 H), 7.56-7.49 (m, 2 H); Olefinic protons of **7c**/**7c'**: δ 6.30-6.20 (m, 1.5 H), 6.10-6.05 (m, 0.75 H), 6.04-5.98 (m, 0.5 H), 5.95 (dd, *J* = 9.4, 6.0 Hz, 0.1 H), 5.87 (dd, *J* = 9.3, 6.4 Hz, 0.15 H), 5.82-5.74 (m, 0.5 H), 5.71-5.66 (m, 0.5 H); H-2 of **7c**/**7c'**: δ 4.52 (d, *J* = 9.1 Hz 0.15 H, PhCO-C*H*-CN), 4.49 (d, *J* = 7.9 Hz, 0.1 H, PhCO-C*H*-CN), 4.41 (d, *J* = 9.9 Hz, 0.15 H, PhCO-C*H*-CN), 4.40 (d, *J* = 9.6 Hz, 0.10 H, PhCO-C*H*-CN); H-9 of **7c** and H-7 of **7c'**: δ 3.50 (d, *J* = 8.2 Hz, 0.1 H, EtOCO-C*H*-CN), 3.44 (d, *J* = 9.9 Hz, 0.1 H, EtOCO-C*H*-CN), 3.44 (d, *J* = 9.0 Hz, 0.8 H, EtOCO-C*H*-CN); H-3 and H-8 of **7c**/H-3 and H-6 of **7c'**: δ 3.39-3.32 (m, 0.4 H, from **7c'**), 3.35-3.31 (m, 0.3 H, from **7c**), 3.27 (br t, *J* = 7.5 Hz, 0.2 H, from **7c'**), 3.18 (ddd, *J* = 9.9, 6.0, 1.1 Hz, 0.3 H, from **7c**), 3.12 (dd, *J* = 9.9, 6.0 Hz, 0.3 H, from **7c**), 2.79 (br t, *J* = 7.0 Hz, 0.2 H, from **7c'**), 2.71 (ddd, *J* = 9.0, 6.0. 1.0 Hz, 0.3 H, from **7c**); *tert*-Butyl protons of **7c**/**7c'**: δ 1.55 (s, 2.7 H, from **7c**), 1.53 (s, 2.7 H, from **7c**), 1.52 (s, 1.8 H, from **7c'**), 1.49 (s, 1.8 H, from **7c'**) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0 (Ph*C*O), 188.9 (Ph*C*O), 188.8 (Ph*C*O), 188.7 (Ph*C*O),163.3 (*t*-BuO*C*O), 163.2 (*t*-BuO*C*O), 163.2 (*t*-BuO*C*O), 163.2 (*t*-BuO*C*O), 135.0 (CH), 134.9 (CH x 2), 134.8 (CH), 134.4 (C x 2), 134.1 (C), 134.0 (C), 129.3 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 126.8 (CH), 126.6 (CH), 126.6 (CH), 126.4 (CH), 126.3 (CH), 124.6 (CH), 124.1 (CH), 123.8 (CH), 123.8 (CH), 123.7 (CH), 123.0 (CH), 122.9 (CH), 115.8 (CN x 2), 115.6 (CN), 115.5 (CN), 115.4 (CN x 2), 115.2 (CN x 2), 85.1 (C-O), 85.0 (C-O), 84.9 (C-O), 84.8 (C-O), 41.4 (CH), 41.3 (CH), 41.1 (CH), 41.0 (CH), 40.5 (CH), 40.4 (CH), 40.0 (CH), 39.7 (CH), 36.4 (CH), 35.9 (CH), 35.7 (CH), 35.6

(CH), 35.3 (CH), 35.2 (CH), 35.1 (CH), 35.0 (CH), 27.7 (methyl of *t*-Bu), 27.7 (methyl of *t*-Bu x 2), 27.6 (methyl of *t*-Bu) ppm.
HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{22}H_{22}N_2O_3$: 362.1630; found: 362.1637.

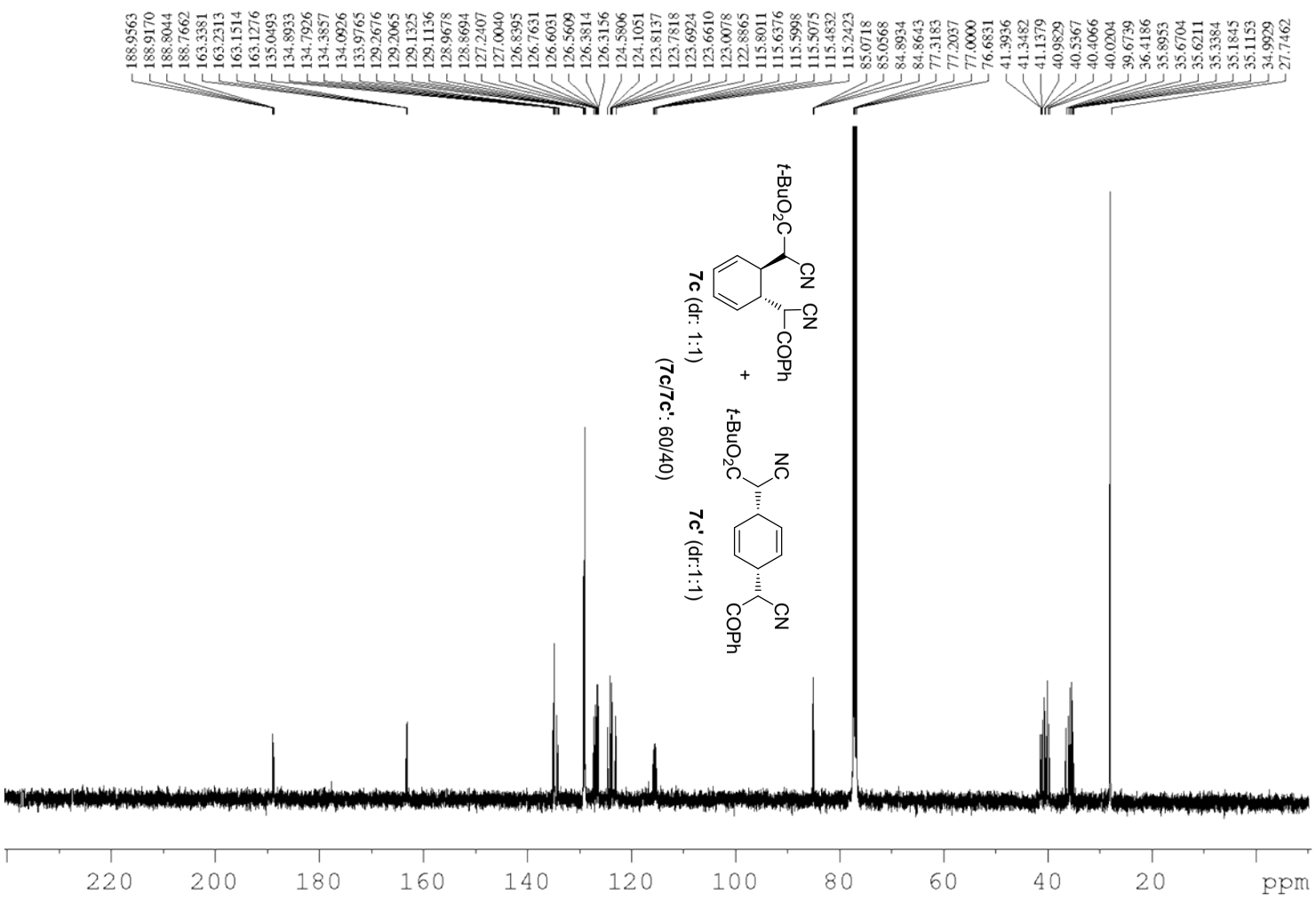


Current Data Parameters
NAME zhu-96
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231128
Time 21.58
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 60
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 287
DW 69.333 usec
DE 6.50 usec
TE 293.8 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters

NAME	zhu-96
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

Date_	20231128
Time	22.06
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2400
DS	0
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976128 sec
RG	2050
DW	19.800 usec
DE	6.50 usec
TE	294.0 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	10.00 usec
PL1	6.20 dB
SFO1	100.6243395 MHz

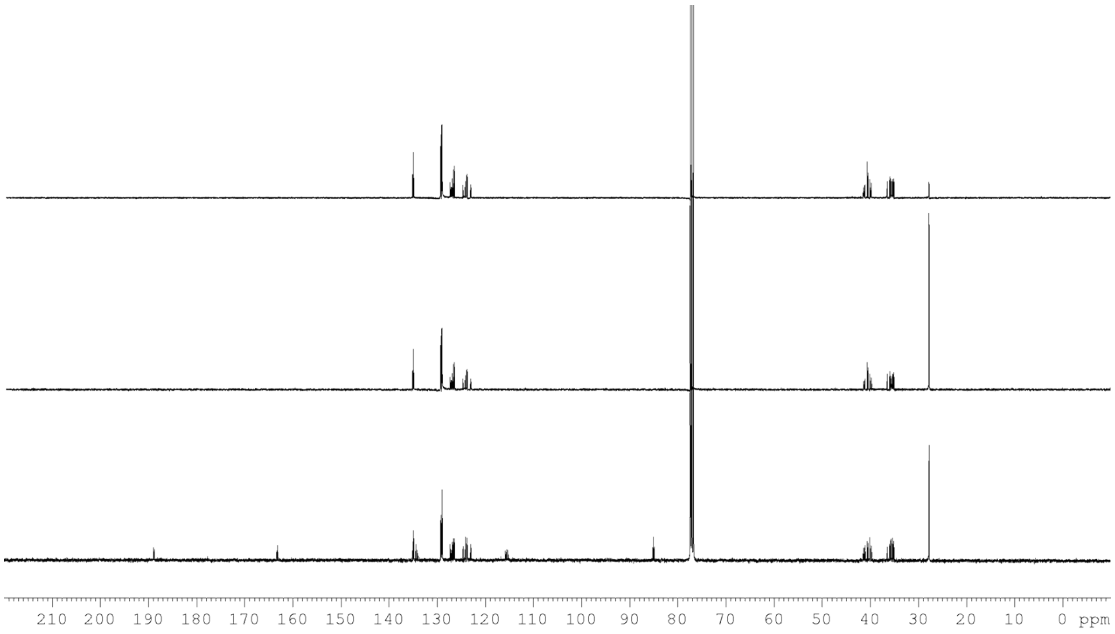
======== CHANNEL f2 ========

CPDPRG[2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-0.40 dB
PL12	15.80 dB
PL13	18.50 dB
SFO2	400.1316005 MHz

F2 - Processing parameters

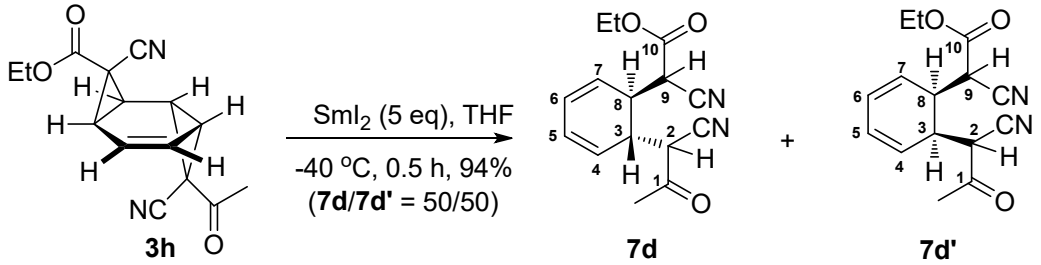
SI	32768
SF	100.6127735 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

DEPT 90, 135 and ^{13}C-NMR spectra (100 MHz):



v) Preparation of 7d/7d' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-Ethyl 2-cyano-2-[6-(1-cyano-2-oxopropyl)cyclohexa-2,4-dien-1-yl]acetate (**7d**) and *Cis*-Ethyl 2-cyano-2-[6-(1-cyano-2-oxopropyl)cyclohexa-2,4-dien-1-yl]acetate (**7d'**)



The titled compounds were synthesized from **3h** by following *Procedure A*. After chromatography (silica gel; hexane/ethyl acetate = 5:1, 2:1), a mixture of **7d**/**7d'** was obtained in 94% yield as a colorless oil (**7d**/**7d'**: 50/50). **(7d** and **7d'** each includes two diastereomeric pairs deriving from the configurations at C-2/C-9).

IR (neat): 3055, 2986, 2248, 2204, 1741, 1266, 737, 704 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Olefinic protons of **7d**/**7d'**: δ 6.26-6.14 (m, 2 H), 5.92-5.69 (m, 2 H); Methylene protons of EtO: δ 4.34-4.24 (m, 2 H); H-2/H-9 of **7d**/**7d'**: δ 3.54-3.49 (m, 2 H); H-3 and H-8 of **7c** and **7c'**: δ 3.18 (br t, *J* = 6.44 Hz, 0.25 H), 3.16-3.06 (m, 0.75 H), 2.99 (br t, *J* = 6.6 Hz, 0.25 H), 2.93 (br t, *J* = 6.5 Hz, 0.25 H), 2.82 (br t, *J* = 6.9 Hz, 0.5 H); MeCO of **7d**/**7d'**: δ 2.43 (s, 0.75 H), 2.41 (s, 0.75 H), 2.40 (s, 0.75 H), 2.39 (s, 0.75H); Methyl protons of EtO: δ 1.34 (t, *J* = 7.1 Hz, 1.5 H), 1.32 (t, *J* = 7.2 Hz, 1.5 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1 (Me*C*O), 197.0 (Me*C*O), 196.7 (Me*C*O), 196.6 (Me*C*O), 164.4 (EtO*C*O), 164.3 (EtO*C*O), 164.3 (EtO*C*O), 164.2 (EtO*C*O), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.4 (CH), 126.3 (CH), 123.8 (CH), 123.4 (CH), 123.2 (CH), 123.1 (CH), 123.0 (CH), 122.8 (CH), 122.6 (CH), 122.5 (CH), 115.9 (CN), 115.8 (CN), 115.5 (CN), 115.4 (CN), 115.1 (CN), 114.9 (CN), 114.8 (CN x 2), 63.4 (CH_3*C*H_2O), 63.4 (CH_3*C*H_2O), 63.3 (CH_3*C*H_2O), 63.2 (CH_3*C*H_2O), 47.0 (CH), 46.8 (CH), 46.7 (CH), 46.0 (CH), 40.2 (CH x 2), 39.5 (CH), 39.2 (CH), 36.0 (CH), 35.7 (CH x 2), 35.5 (CH), 34.6 (CH), 34.4 (CH), 34.2 (CH), 34.1 (CH), 29.5 (*C*H_3CO), 29.4 (*C*H_3CO), 28.5 (*C*H_3CO), 28.4 (*C*H_3CO), 13.9 (*C*H_3CH$_2$O x 4) ppm.

HRMS-EI: *m/z* [M]$^{+}$ calcd. for $C_{15}H_{16}N_2O_3$: 272.1161; found: 272.1164.

Current Data Parameters
NAME zhu-91
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20231022
Time 12.30
INSTRUM spect
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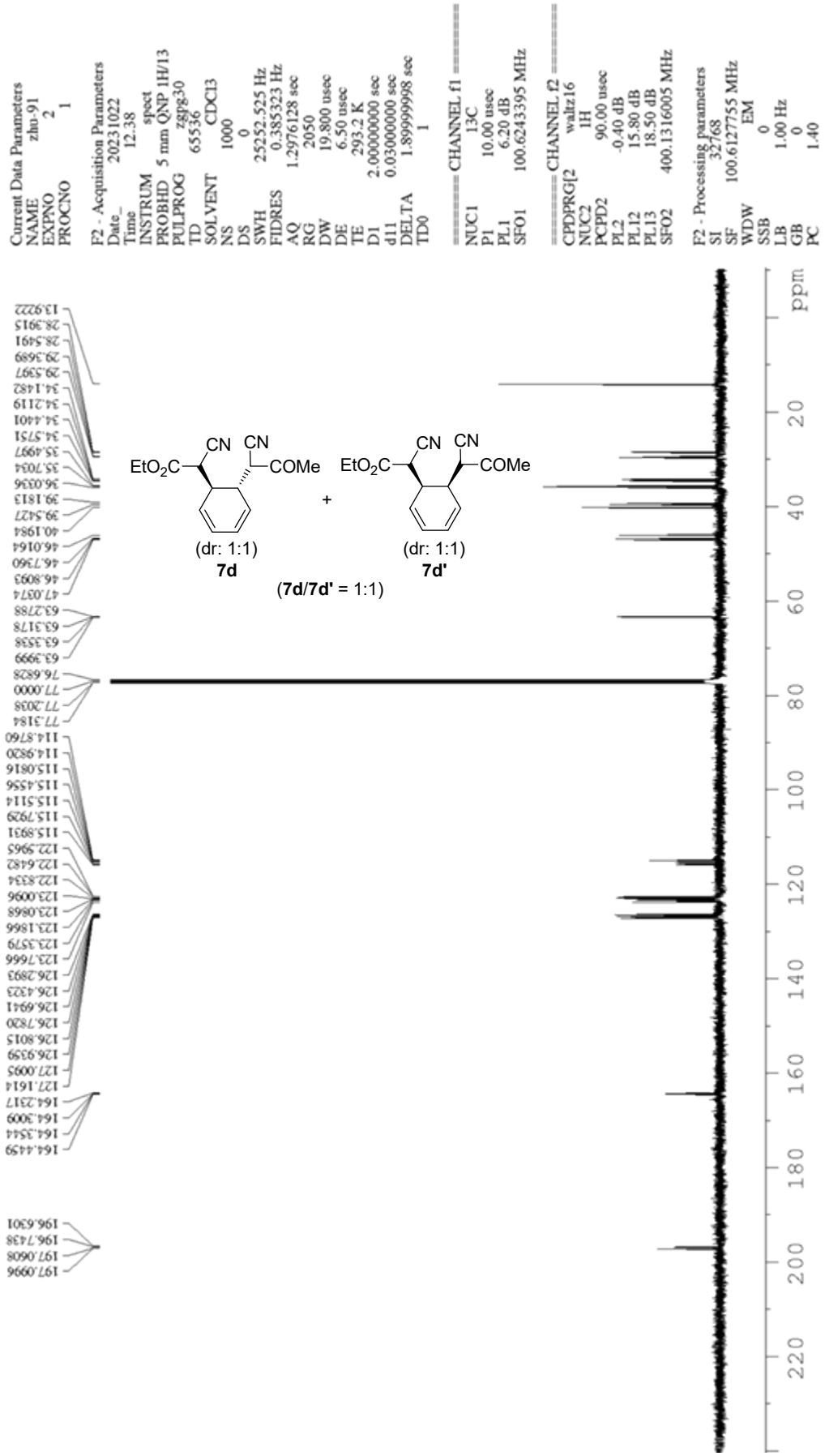
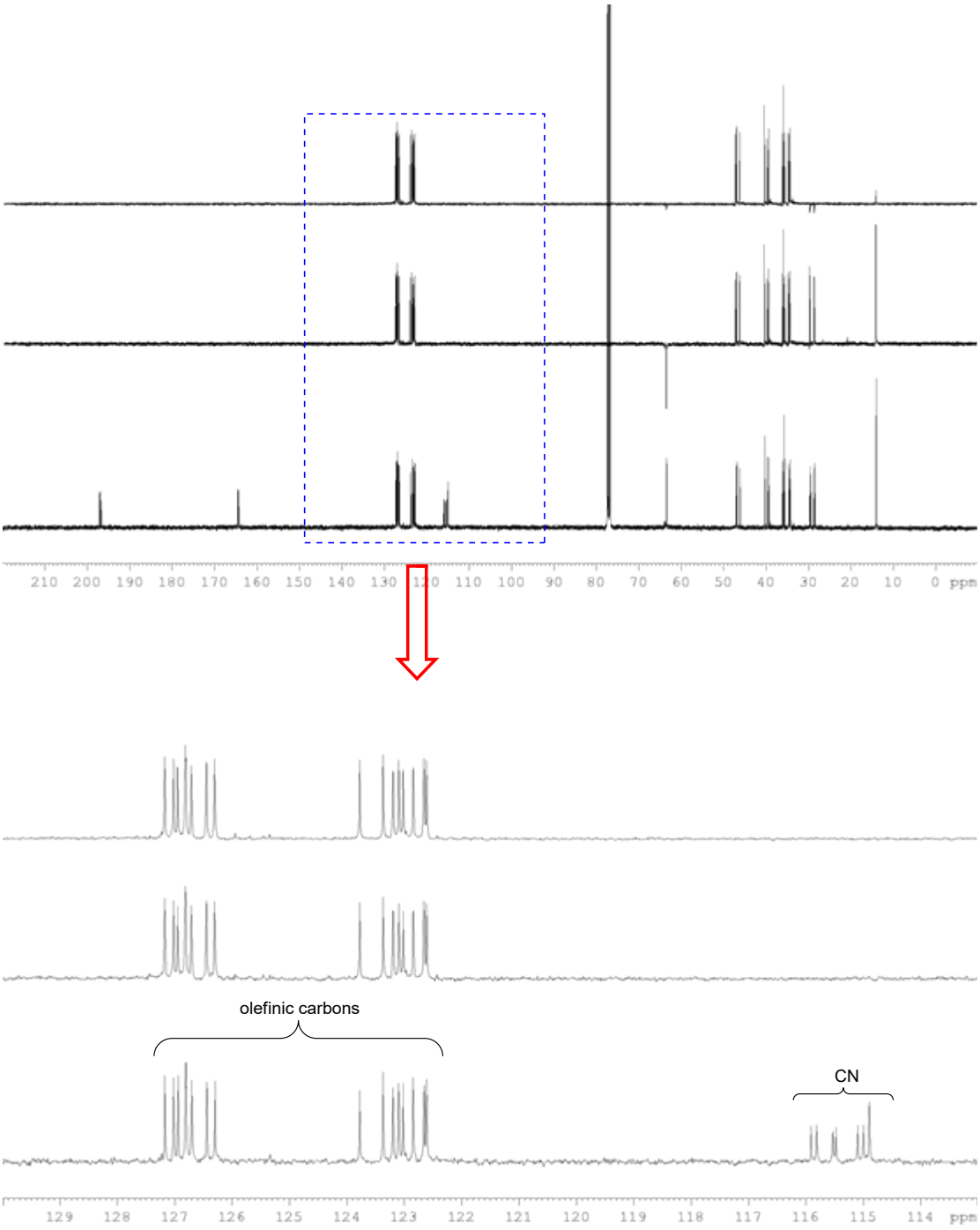
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 40
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 256
DW 69.333 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CN
CN
EtO2C
COMe
(dr: 1:1)
7d
+
CN
CN
EtO2C
COMe
(dr: 1:1)
7d'
(7d/7d' = 1:1)
ppm

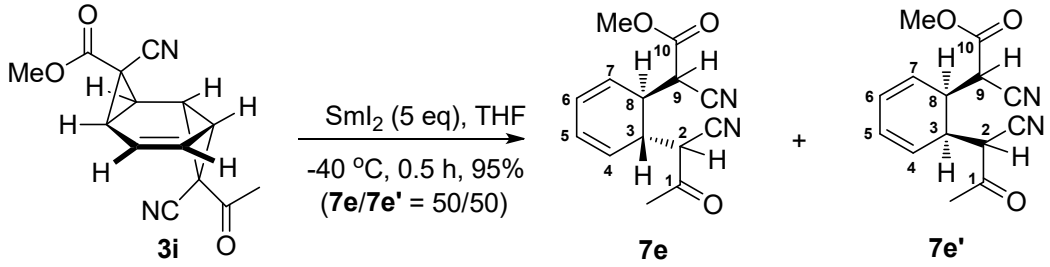

Current Data Parameters
NAME zhu-91
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20231022
Time 12.38
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127755 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
CN
CN
EtO2C
COMe
(dr: 1:1)
7d
+
(dr: 1:1)
7d'
(7d/7d' = 1:1)
ppm

DEPT 90, 135 and ^{13}C-NMR spectra (100 MHz):



vi) Preparation of 7e/7e' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-Methyl 2-cyano-2-[6-(1-cyano-2-oxopropyl)cyclohexa-2,4-dien-1-yl]acetate (**7e**) and *Cis*-Methyl 2-cyano-2-[6-(1-cyano-2-oxopropyl)cyclohexa-2,4-dien-1-yl]acetate (**7e'**)



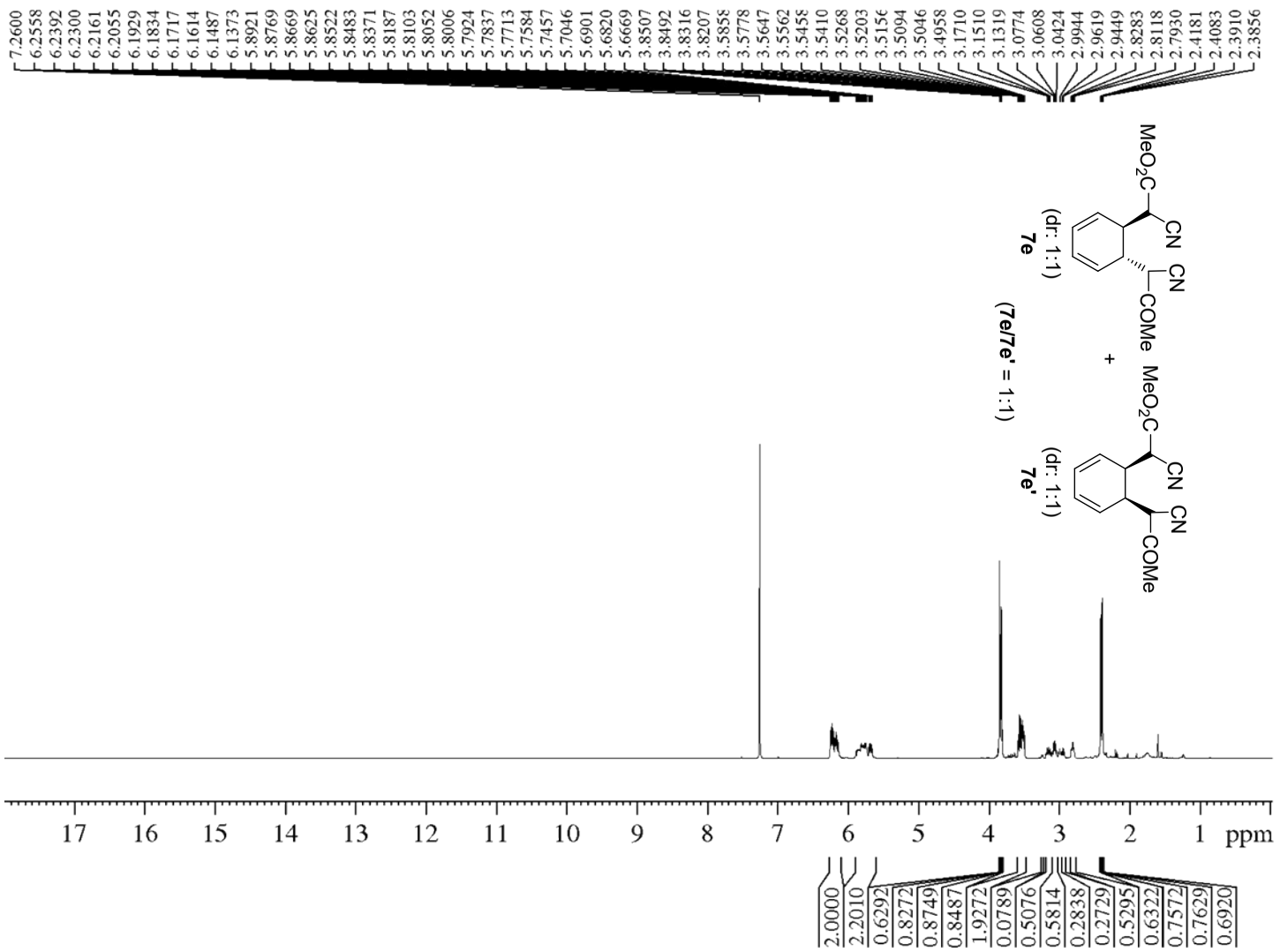
The titled compounds were synthesized from **3i** by following *Procedure A*. After chromatography (silica gel; hexane/ethyl acetate = 10:1, 5:1, 2:1), a mixture of **7e**/**7e'** was obtained in 95% yield as a colorless oil (**7e**/**7e'**: 50/50). (7**e** and **7e'** each includes two diastereomeric pairs deriving from the configurations at C-2/C-9).

IR (neat): 3046, 2957, 2247, 2202, 1745, 1651, 1260, 743, 713 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Olefinic protons of **7e**/**7e'**: δ 6.35-6.15 (m, 2 H), 5.89-5.67 (m, 2 H); MeO: δ 3.85 (s, 1.5 H), 3.83 (s, 0.75 H), 3.82 (s, 0.75 H); H-2/H-9 of **7e**/**7e'**: δ 3.58-3.49 (m, 2 H); H-3 and H-8 of **7e** and **7e'**: δ 3.18-3.04 (m, 1 H), 2.99 (br t, *J* = 6.5 Hz, 0.25 H), 2.94 (br t, *J* = 6.5 H, 0.25 H), 2.81 (br t, *J* = 6.5 H, 0.5 H); MeC=O: δ 2.42 (s, 0.75 H), 2.41 (s, 0.75 H), 2.39 (s, 0.75 H), 2.38 (s, 0.75 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1 (Me*C*O), 197.0 (Me*C*O), 196.8 (Me*C*O), 196.6 (Me*C*O), 164.9 (MeO*C*O), 164.8 (MeO*C*O), 164.8 (MeO*C*O), 164.7 (MeO*C*O), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH x 2), 126.4 (CH), 126.2 (CH), 123.7 (CH), 123.3 (CH), 123.0 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 122.5 (CH), 122.4 (CH), 115.8 (CN), 115.7 (CN), 115.5 (CN), 115.4 (CN), 114.9 (CN), 114.8 (CN), 114.7 (CN x 2), 53.8 (CH_3O), 53.8 (CH_3O), 53.8 (CH_3O), 53.7 (CH_3O), 47.0 (CH), 46.9 (CH), 46.6 (CH), 46.0 (CH), 40.1 (CH), 40.0 (CH), 39.5 (CH), 39.1 (CH), 36.0 (CH), 35.7 (CH), 35.7 (CH), 35.5 (CH), 34.5 (CH), 34.4 (CH), 34.1 (CH), 34.0 (CH), 29.5 (*C*H_3CO), 29.4 (*C*H_3CO), 28.5 (*C*H_3CO), 28.4 (*C*H_3CO) ppm.

HRMS-EI: *m/z* [M]$^{+}$ calcd. for $C_{14}H_{14}N_2O_3$: 258.1004; found: 258.0984.



Current Data Parameters
NAME zhu-100-TLC
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
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Time 22.01
INSTRUM spect
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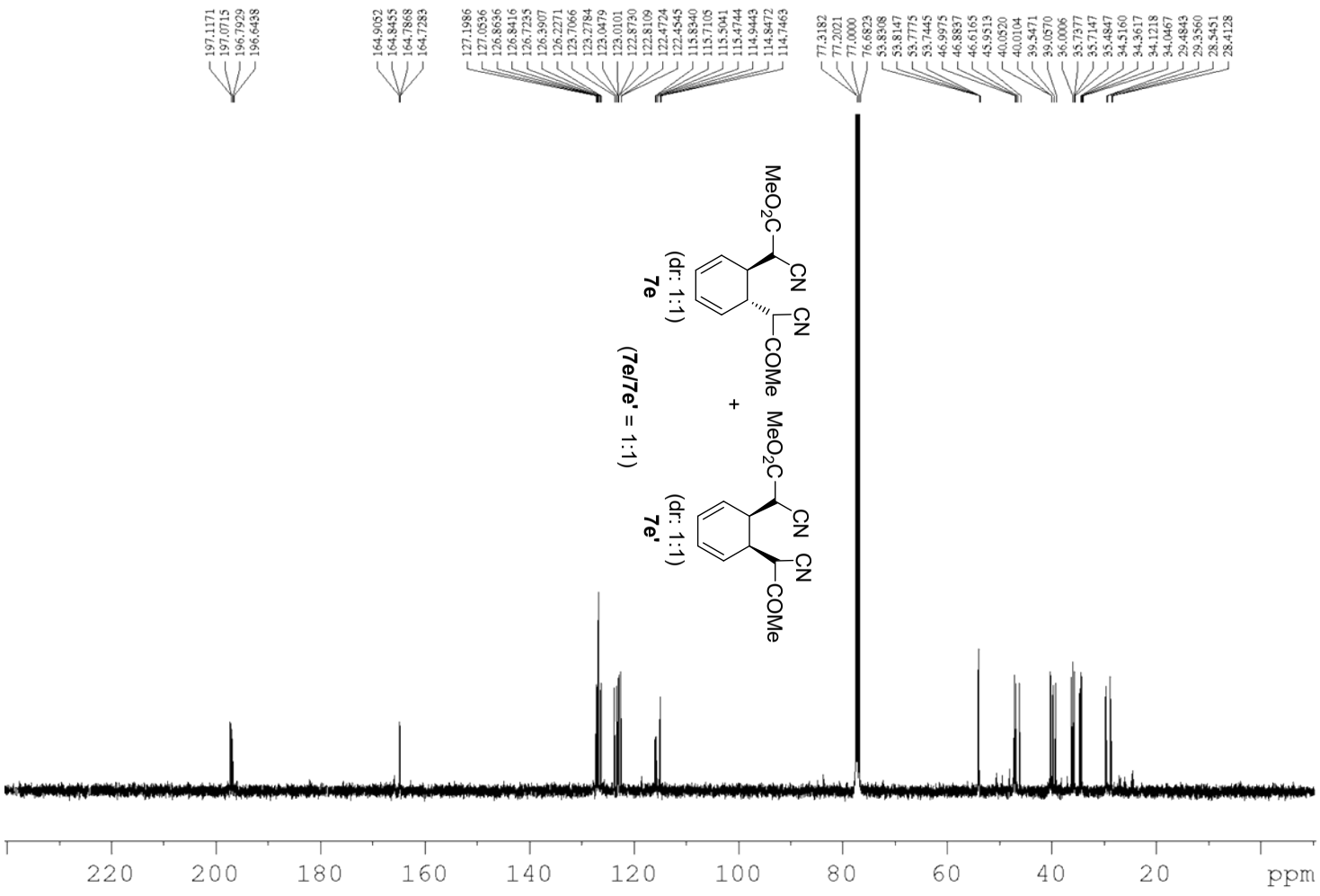
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 100
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 181
DW 69.333 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-100-TLC
EXPNO 2
PROCNO 1

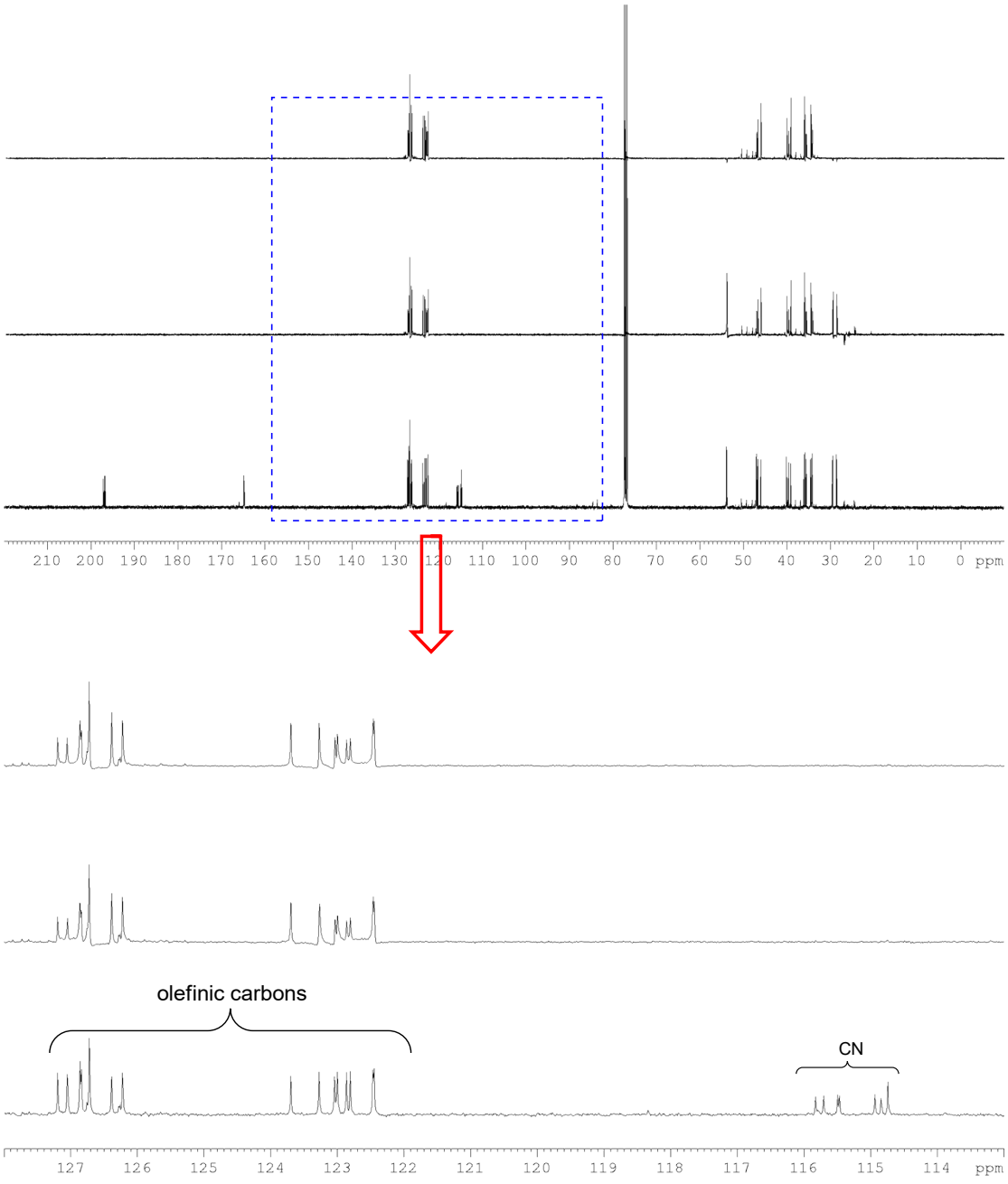
F2 - Acquisition Parameters
Date_ 20231231
Time 15.52
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

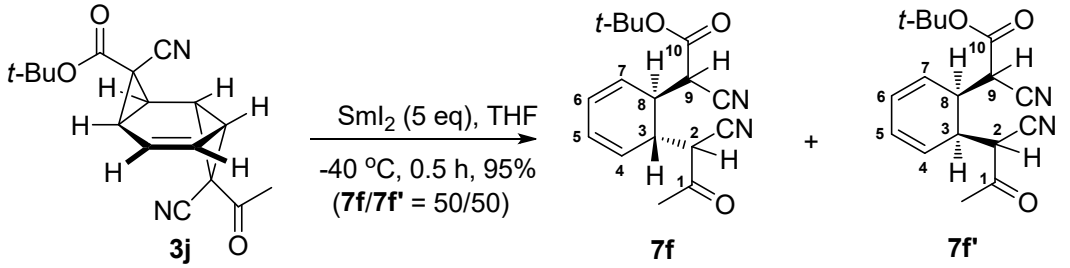
F2 - Processing parameters
SI 32768
SF 100.6127784 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DEPT 90, 135 and ^{13}C-NMR spectra (100 MHz):



vii) Preparation of 7f/7f' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-tert-Butyl 2-cyano-2-[6-(1-cyano-2-oxopropyl)cyclohexa-2,4-dien-1-yl]acetate (**7f**) and *Cis-tert*-Butyl 2-cyano-2-[6-(1-cyano-2-oxopropyl)cyclohexa-2,4-dien-1-yl]acetate (**7f'**)



The titled compounds were synthesized from **3j** by following *Procedure A*. After chromatography (silica gel; hexane/ethyl acetate = 10:1, 3:1), a mixture of **7f**/**7f'** was obtained in 95% yield as a colorless oil (**7f**/**7f'**: 50/50). (**7f** and **7f'** each includes two diastereomeric pairs deriving from the configurations at C-2/C-9).

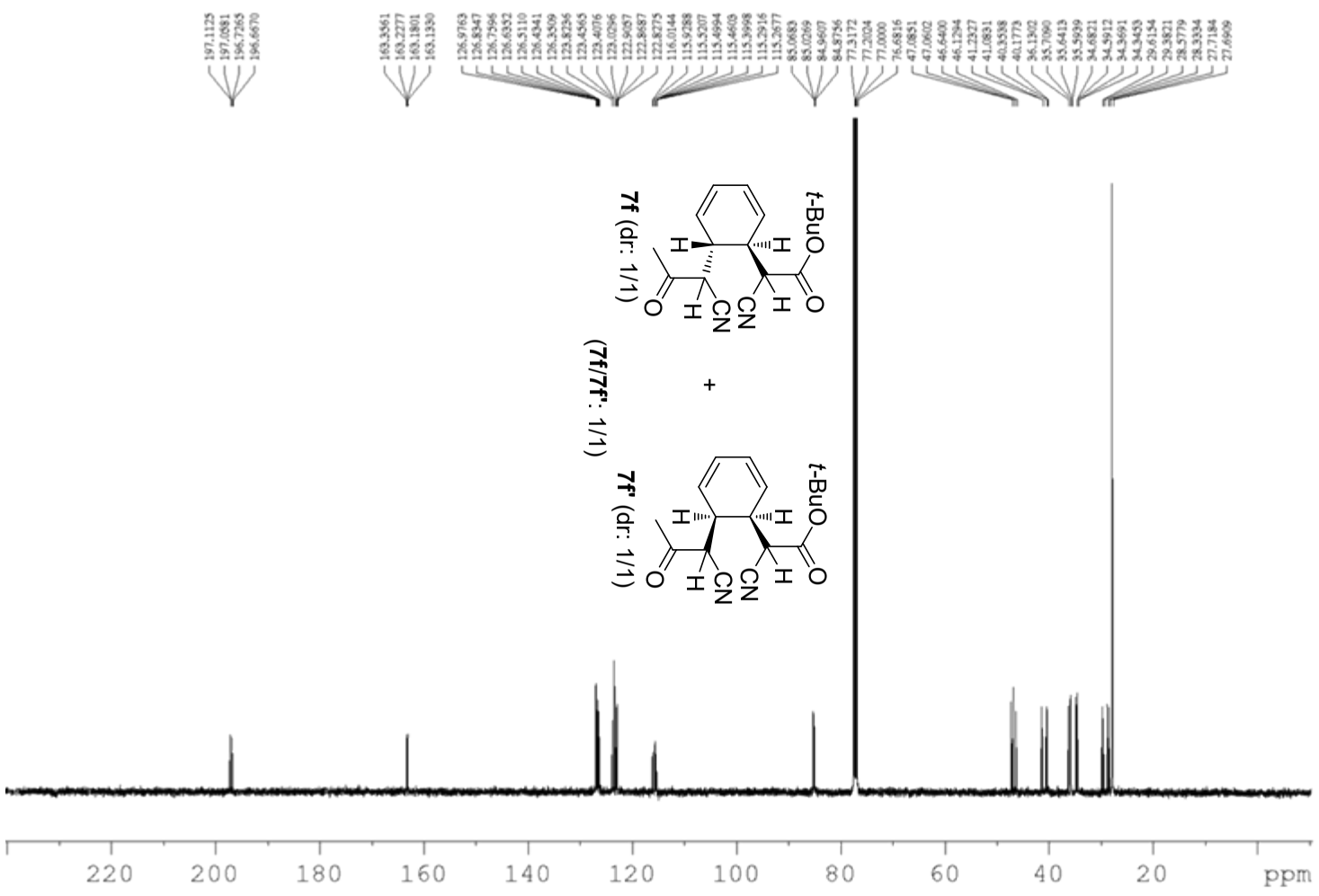
IR (neat): 3047, 2982, 2248, 2203, 1737, 1732, 1152, 743, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Olefinic protons of **7f**/**7f'**: δ 6.25-6.14 (m, 2 H), 5.92 (dd, *J* = 9.4, 6.1 Hz, 0.5 H), 5.86-5.75 (m, 1 H), 5.70 (dd, *J* = 9.4, 6.0 Hz, 0.5 H); H-2/H-9 of **7f**/**7f'**: δ 3.52 (d, *J* = 8.9 Hz, 0.5 H), 3.51-3.43 (m, 1 H), 3.40 (d, *J* = 8.9 Hz, 0.5 H); H-3 and H-8 of **7f**/**7f'**: δ 3.15 (br t, *J* = 6.6 Hz, 0.25 H), 3.13-3.01 (m, 0.75 H), 2.97 (br t, *J* = 6.2 Hz, 0.25 H), 2.89 (br t, *J* = 6.3 Hz, 0.25 H), 2.82-2.76 (m, 0.5 H); MeC=O: δ 2.43 (s, 0.75 H), 2.41 (s, 0.75 H), 2.39 (s, 0.75 H), 2.38 (s, 0.75 H); Methyl of *t*-Bu: δ 1.53 (s, 2.25 H), 1.52 (s, 2.25 H), 1.50 (s, 2.25 H), 1.49 (s, 2.25 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1 (Me*C*O), 197.0 (Me*C*O), 196.7 (Me*C*O), 196.6 (Me*C*O), 163.4 (*t*-BuO*C*O), 163.2 (*t*-BuO*C*O), 163.2 (*t*-BuO*C*O), 163.1 (*t*-BuO*C*O), 127.0 (CH x 2), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 126.3 (CH), 123.8 (CH), 123.5 (CH), 123.4 (CH x 2), 123.0 (CH), 122.9 (CH), 122.9 (CH), 122.8 (CH), 116.0 (CN), 115.9 (CN), 115.5 (CN), 115.5 (CN), 115.4 (CN), 115.3 (CN), 115.3 (CN), 115.2 (CN), 85.1 (C-O), 85.0 (C-O), 84.9 (C-O), 84.8 (C-O), 47.1 (CH), 47.0 (CH), 46.6 (CH), 46.1 (CH), 41.2 (CH), 41.1 (CH), 40.3 (CH), 40.2 (CH), 36.1 (CH), 35.7 (CH), 35.6 (CH), 35.5 (CH), 34.7 (CH), 34.6 (CH), 34.4 (CH), 34.3 (CH), 29.6 (*C*H_3CO), 29.4 (*C*H_3CO), 28.6 (*C*H_3CO), 28.3 (*C*H_3CO), 27.7 (methyl of *t*-Bu), 27.6 (methyl of *t*-Bu x 3) ppm

HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{20}N_2O_3$: 300.1474; found: 300.1464.

Current Data Parameters
NAME zhu-104
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240203
Time 22.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 203
DW 69.333 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
t-BuO
O
H
H
CN
CN
H
H
O
7f (dr: 1/1)
+
t-BuO
O
H
H
CN
CN
H
H
O
7f' (dr: 1/1)
(7f/7f': 1/1)
ppm



Current Data Parameters
NAME zhu-104
EXPNO 4
PROCNO 1

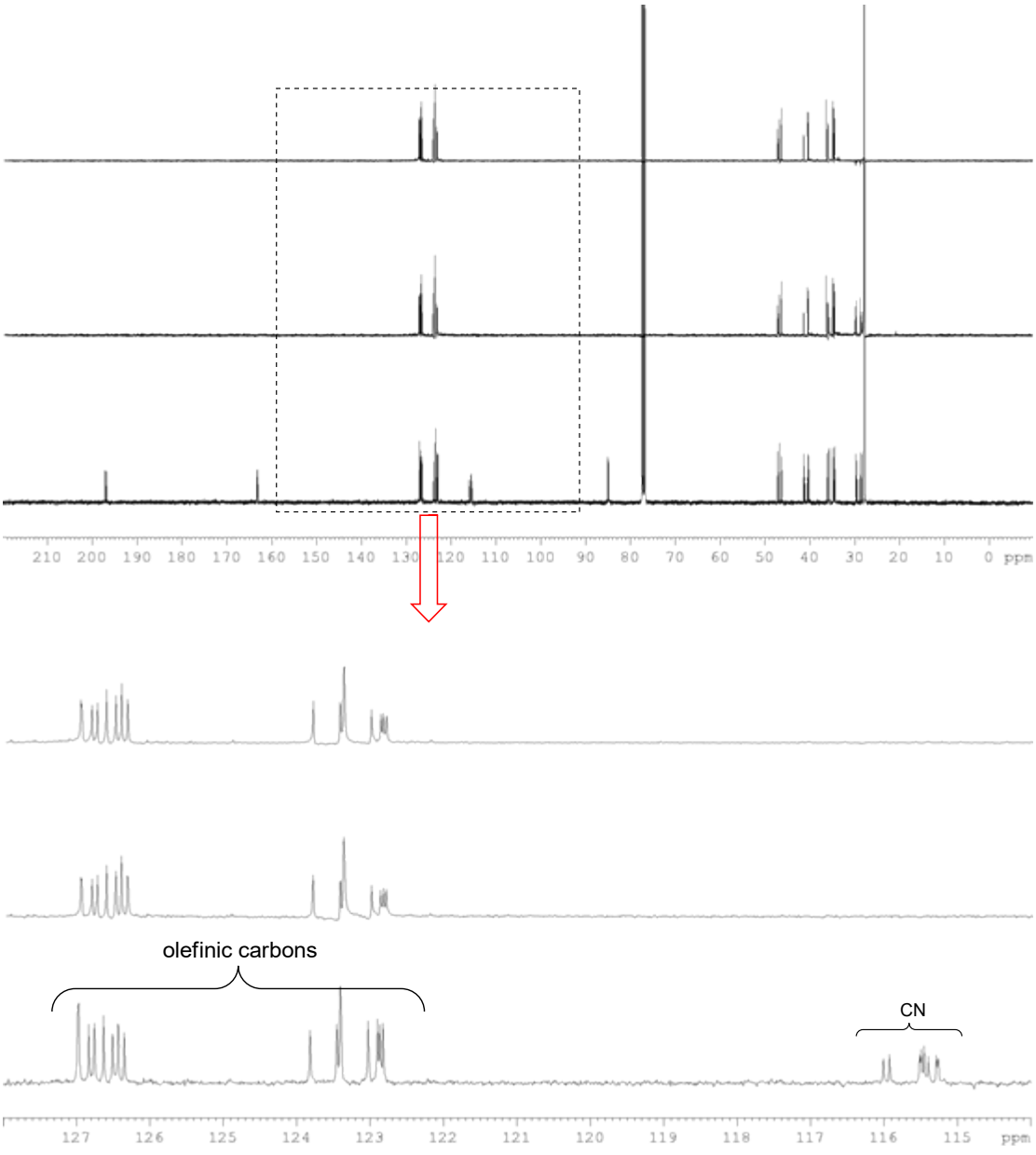
F2 - Acquisition Parameters
Date_ 20240203
Time 22.19
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

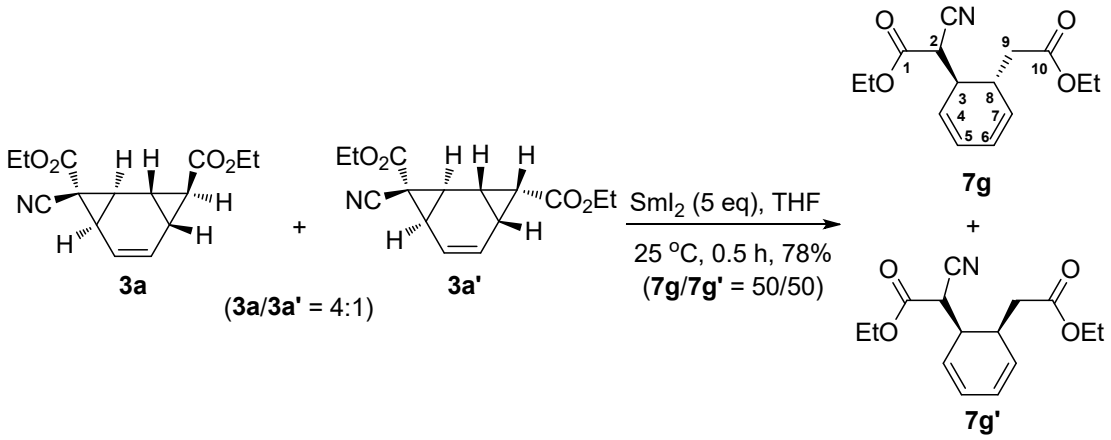
F2 - Processing parameters
SI 32768
SF 100.6127750 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DEPT 90, 135 and ^{13}C-NMR spectra (100 MHz):



viii) Preparation of 7g/7g' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-Ethyl 2-cyano-2-[6-(2-ethoxy-2-oxoethyl)cyclohexa-2,4-dien-1-yl]acetate (**7g**) and *Cis*-Ethyl 2-cyano-2-[6-(2-ethoxy-2-oxoethyl)cyclohexa-2,4-dien-1-yl]acetate (**7g'**)



The titled compounds were synthesized from **3a**/**3a'** by following *Procedure B*. The reaction was performed at ambient temperature for 30 min. After work-up and chromatography (silica gel; hexane/ethyl acetate = 10:1), a mixture of **7g**/**7g'** was obtained in 78% yield as a colorless oil (**7g**/**7g'**: 50/50).

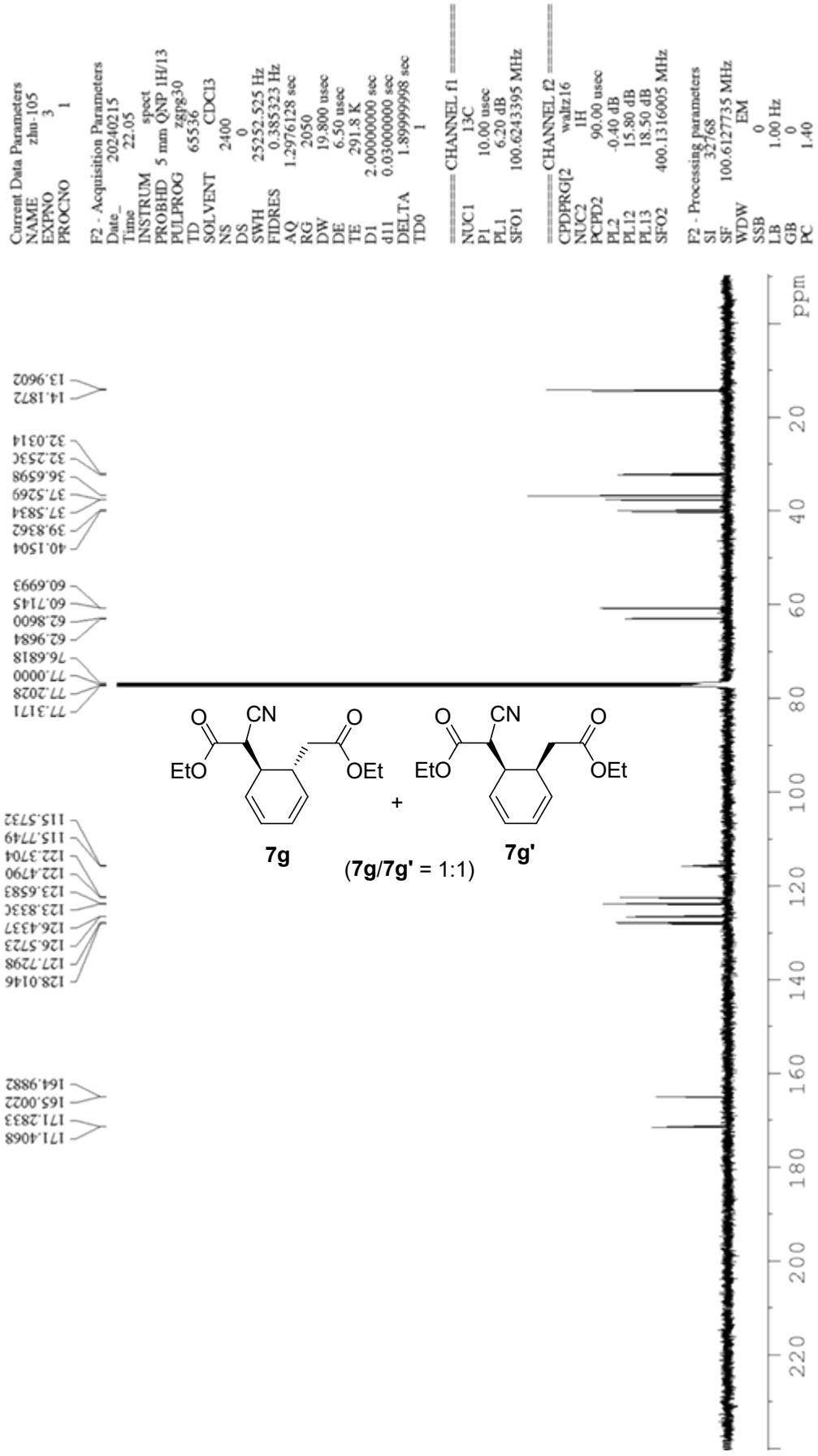
IR (neat): 3043, 2980, 2920, 2245, 1730, 1732, 1153, 851, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Olefinic protons of **7g**/**7g'**: δ 6.15 (dd, *J* = 9.6, 5.0 Hz, 0.5 H), 6.09 (dd, *J* = 9.6, 5.2 Hz, 0.5 H), 6.02-5.97 (m, 1 H), 5.85 (dd, *J* = 9.5, 5.8 Hz, 0.5 H), 5.81-5.77 (m, 1 H), 5.54 (dd, *J* = 9.5, 5.8 Hz, 0.5 H); Methylene protons of EtO groups: δ 4.31-4.22 (m, 2 H), 4.18-4.11 (m, 2 H); H-2 protons of **7g**/**7g'**: δ 3.53 (d, *J* = 8.6 Hz, 1 H), 3.50 (d, *J* = 9.1 Hz, 1 H); H-3 and H-8 of **7f**/**7f'**: δ 2.99-2.94 (m, 0.5 H), 2.86-2.79 (m, 1 H), 2.72-2.67 (m, 0.5 H); Methylene protons at C-9: 2.47-2.33 (m, 2 H); Methyl protons of EtO groups: δ 1.33 (t, *J* = 7.2 Hz, 1.5 H), 1.32 (t, *J* = 7.3 Hz, 1.5 H), 1.27 (t, *J* = 7.1 Hz, 1.5 H), 1.26 (t, *J* = 7.0 Hz, 1.5 H) ppm.

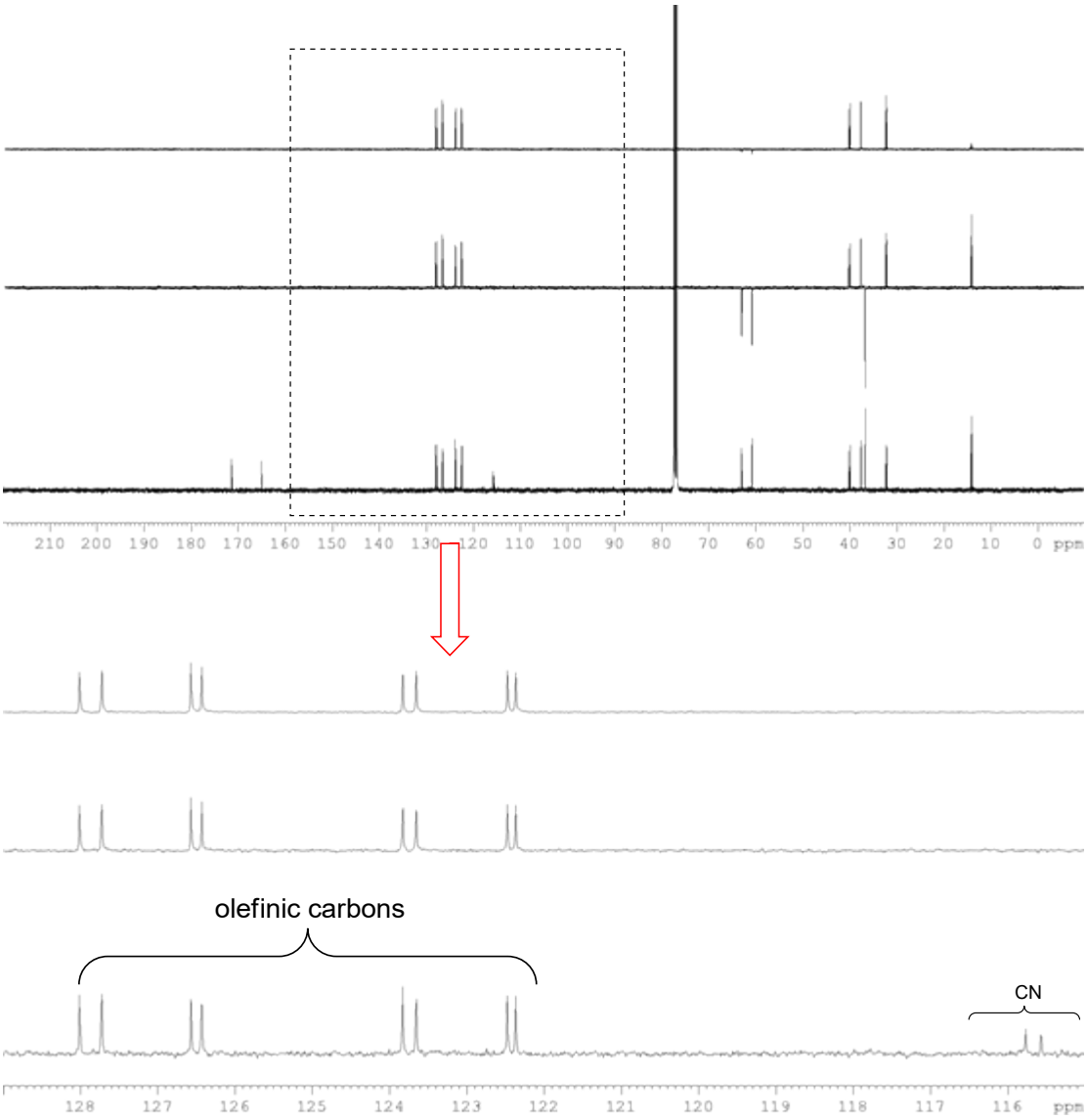
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4 (EtO*C*O), 171.3 (EtO*C*O), 165.0 (EtO*C*O), 164.9 (EtO*C*O), 128.0 (=CH), 127.7 (=CH), 126.6 (=CH), 126.4 (=CH), 123.8 (=CH), 123.7 (=CH), 122.5 (=CH), 122.4 (=CH), 115.8 (CN), 115.6 (CN), 63.0 (CH_2O), 62.9 (CH_2O), 60.7 (CH_2O), 60.6 (CH_2O), 40.2 (CH), 39.8 (CH), 37.6 (CH), 37.5 (CH), 36.7 (CH_2 x 2; C-9), 32.3 (CH), 32.0 (CH), 14.2 (CH_3 x 2), 14.0 (CH_3 x 2) ppm.

HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_{19}NO_4$: 277.1314; found: 277.1315.

Current Data Parameters
NAME zhu-105
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240215
Time 21.57
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 80
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 456
DW 69.333 usec
DE 6.50 usec
TE 291.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 16384
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
CN
O
EtO
OEt
7g
+
O
CN
O
EtO
OEt
7g'
(7g/7g' = 1:1)
ppm

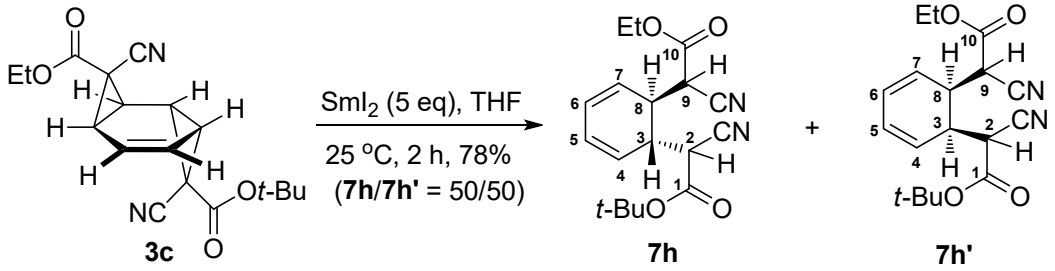

Current Data Parameters
NAME zhu-105
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240215
Time 22.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 291.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz
CHANNEL f2
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127735 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13.9602
14.1872
32.0314
32.2536
36.6598
37.5269
37.5834
39.8362
40.1504
60.6993
60.7145
62.8600
62.9684
76.6818
77.0000
77.2028
77.3171
115.5732
115.7749
122.3704
122.4790
123.6583
123.8336
126.4337
126.5723
127.7298
128.0146
164.9882
165.0022
171.2833
171.4068
ppm
O
CN
O
EtO
OEt
7g
+
O
CN
O
EtO
OEt
7g'
(7g/7g' = 1:1)

DEPT 90, 135 and ^{13}C NMR spectra (100 MHz)



ix) Preparation of 7h/7h' and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Trans-tert-Butyl-2-cyano-2-[6-(1-cyano-2-ethoxy-2-oxoethyl)cyclohexa-2,4-dien-1-yl] acetate (**7h**) and *Cis-tert*-Butyl-2-cyano-2-[6-(1-cyano-2-ethoxy-2-oxoethyl)cyclohexa-2,4-dien-1-yl]
acetate (**7h'**)



The titled compounds were synthesized from **3c** by following *Procedure B*. The reaction was performed at ambient temperature for 2 h. After work-up and chromatography (silica gel; hexane/ethyl acetate = 7:1), a mixture of **7h**/**7h'** was obtained in 90% yield as a pale yellow oil (**7h**/**7h'**: 50/50). (**7h** and **7h'** each includes two diastereomeric pairs deriving from the configurations at C-2/C-9).

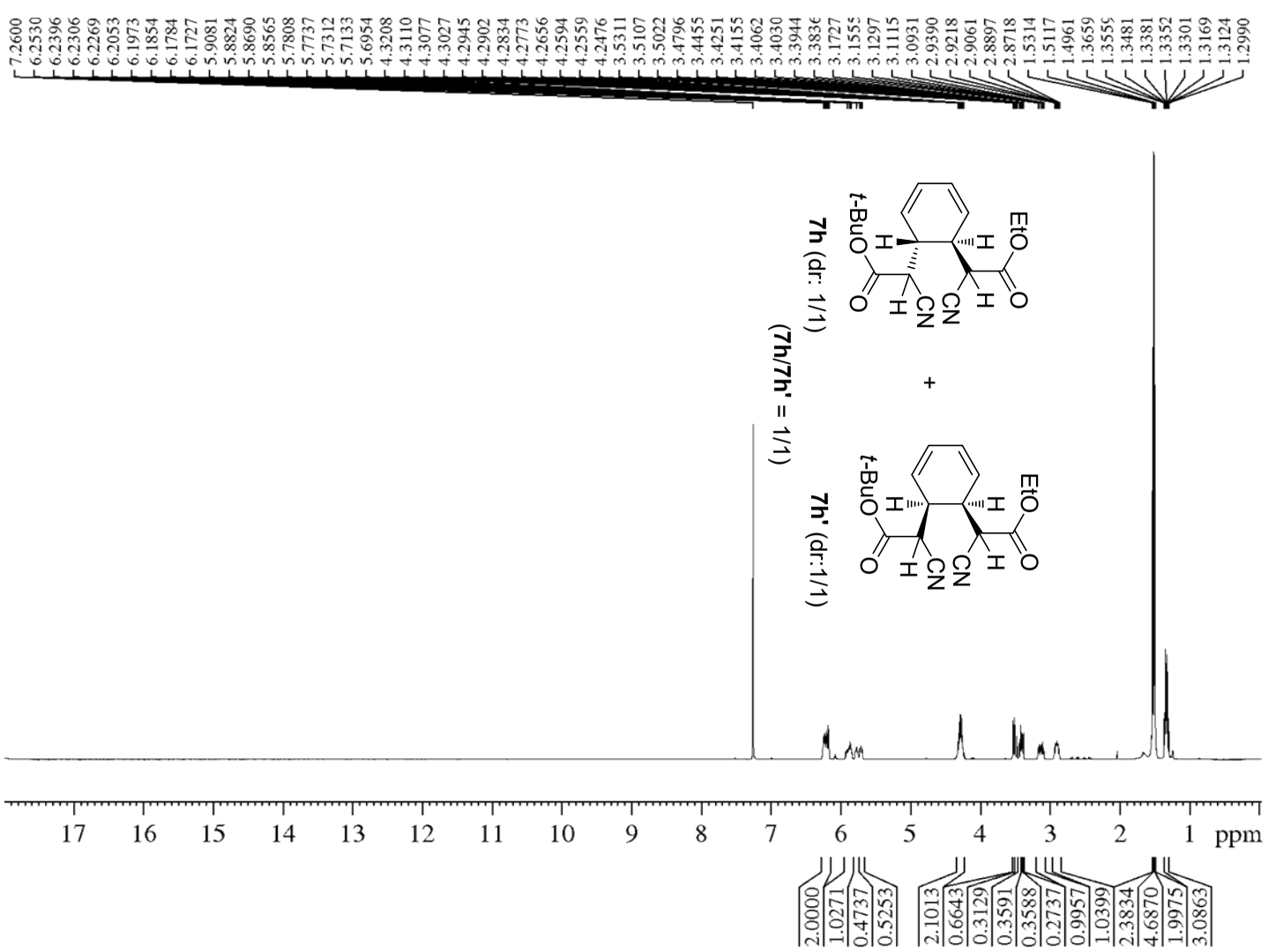
IR (neat): 3049, 2983, 2936, 2249, 1738, 1732, 1151, 1150, 837, 703 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) Olefinic protons of **7h**/**7h'**: δ 6.25-6.17 (m, 2 H), 5.93-5.84 (m, 1 H), 5.79-5.76 (m, 0.5 H), 5.71 (br t, *J* = 7.2 Hz, 0.5 H); Methylene protons of EtO: δ 4.35-4.23 (m, 2 H); H-2/H-9 of **7h**/**7h'**: δ 3.52 (d, *J* = 8.2 Hz, 0.75 H), 3.49 (d, *J* = 9.0 Hz, 0.25 H), 3.44 (d, *J* = 8.2 Hz, 0.25 H), 3.43-3.38 (m, 0.75 H); H-3 and H-8 of **7h**/**7h'**: δ 3.17-3.09 (m, 1 H), 2.94-2.87 (m, 1 H); Methyl of *t*-Bu: δ 1.53 (s, 2.25 H), 1.51 (s, 4.5 H), 1.50 (s, 2.25 H); Methyl protons of EtO: δ 1.35 (t, *J* = 7.1 Hz, 0.75 H), 1.34 (t, *J* = 7.1 Hz, 0.75 H), 1.33 (t, *J* = 7.1 Hz, 0.75 H), 1.31 (t, *J* = 7.1 Hz, 0.75 H) ppm.

^{13}C NMR (100 MHz) In $CDCl_3$: δ 164.4 (RO*C*O), 164.3 (RO*C*O), 164.3 (RO*C*O), 164.2 (RO*C*O), 163.2 (RO*C*O x 2), 163.1 (RO*C*O), 163.1 (RO*C*O), 127.0 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 123.3 (CH x 2), 123.1 (CH), 123.0 (CH), 122.9 (CH), 122.7 (CH), 122.6 (CH), 115.4 (CN x 2), 115.2 (CN), 115.2 (CN), 115.1 (CN), 115.0 (CN), 114.9 (CN x 2), 85.1 (C-O), 85.0 (C-O), 84.9 (C-O x 2), 63.3 (CH_3*C*H_2O), 63.3 (CH_3*C*H_2O), 63.2 (CH_3*C*H_2O), 63.2 (CH_3*C*H_2O), 41.3 (CH), 41.1 (CH), 40.5 (CH), 40.4 (CH), 40.3 (CH), 40.0 (CH), 39.9 (CH), 36.0 (CH), 35.9 (CH), 35.8 (CH), 35.7 (CH), 35.6 (CH), 35.6 (CH), 35.5 (CH x 3), 27.7 (methyl of *t*-Bu) 27.47 (methyl of *t*-Bu), 27.6 (methyl of *t*-Bu x 2), 13.9 (*C*H_3CH_2O x 2), 13.9 (*C*H_3CH_2O x 2) ppm; In C_6D_6: δ 164.6 (RO*C*O), 164.6 (RO*C*O), 164.5 (RO*C*O), 164.4 (RO*C*O), 163.7 (RO*C*O), 163.7 (RO*C*O), 163.6 (RO*C*O), 163.6 (RO*C*O), 126.7 (CH), 126.6 (CH), 126.5 (CH x 2), 126.4 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 123.5 (CH), 123.2 (CH), 123.2 (CH), 123.1 (CH), 123.1 (CH), 122.9 (CH),

122.8(CH), 122.7 (CH), 115.5 (CN), 115.4 (CN), 115.3 (CN), 115.2 (CN), 115.1 (CN x 3), 115.0 (CN), 84.4 (C-O), 84.2 (C-O), 84.2 (C-O), 84.1 (C-O), 62.9 (CH_3CH_2O), 62.9 (CH_3CH_2O), 62.8 (CH_3CH_2O), 62.7 (CH_3CH_2O), 41.8 (CH), 41.4 (CH), 41.0 (CH), 40.9 (CH), 40.8 (CH), 40.4 (CH), 40.2 (CH), 39.8 (CH), 36.5 (CH), 36.3 (CH), 36.2 (CH x 2), 35.1 (CH x 2), 36.0 (CH), 35.9 (CH), 27.5 (methyl of *t*-Bu) 27.4 (methyl of *t*-Bu), 27.4 (methyl of *t*-Bu x 2), 13.7 (CH_3CH_2O), 13.7 (CH_3CH_2O), 13.6 (CH_3CH_2O), 13.6 (CH_3CH_2O) ppm.

HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{18}H_{22}N_2O_4$: 330.1580; found: 330.1587.

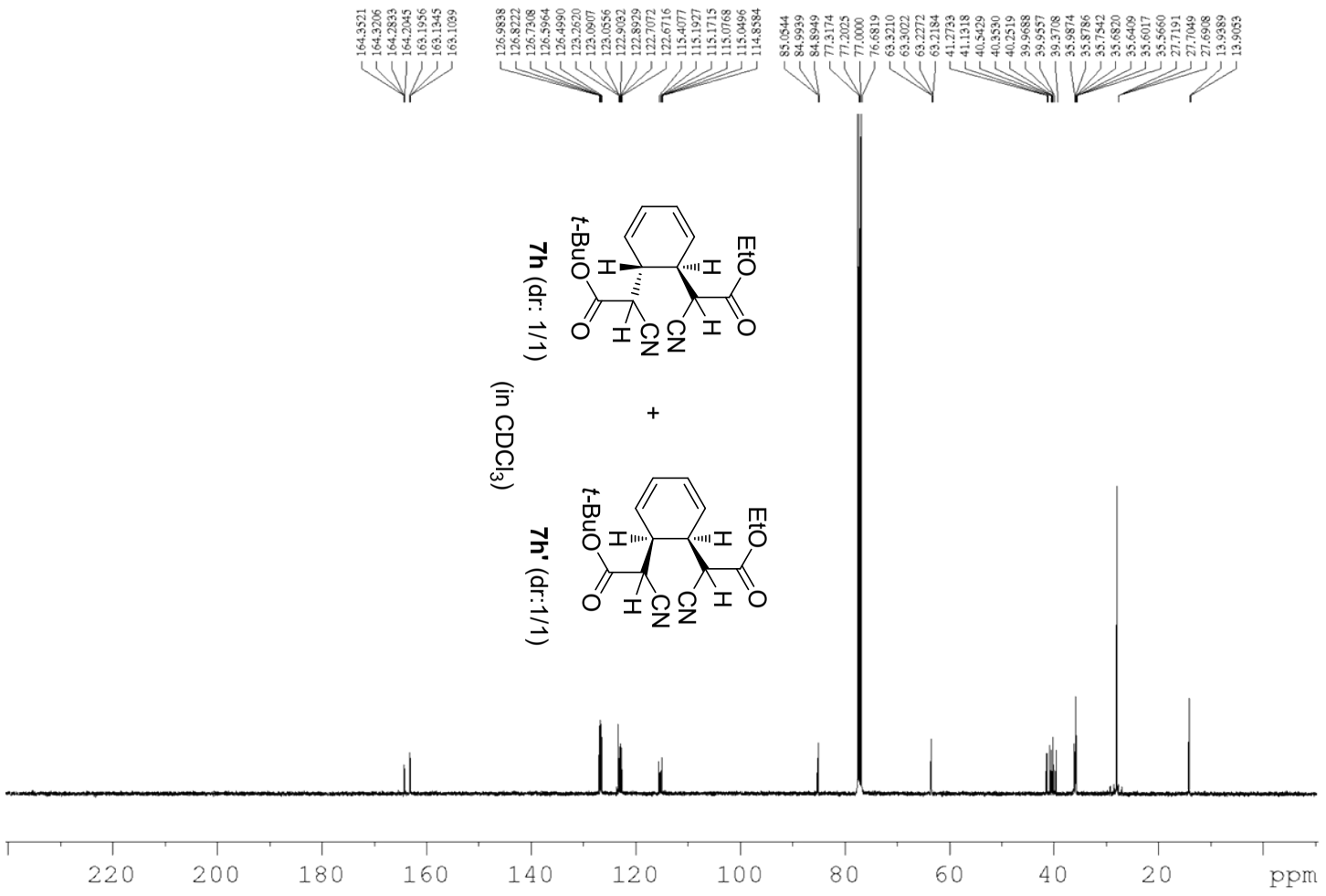


Current Data Parameters
NAME zhu-106 repeat
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240305
Time 22.12
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 80
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 228
DW 69.333 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-106 repeat
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
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Time 22.33
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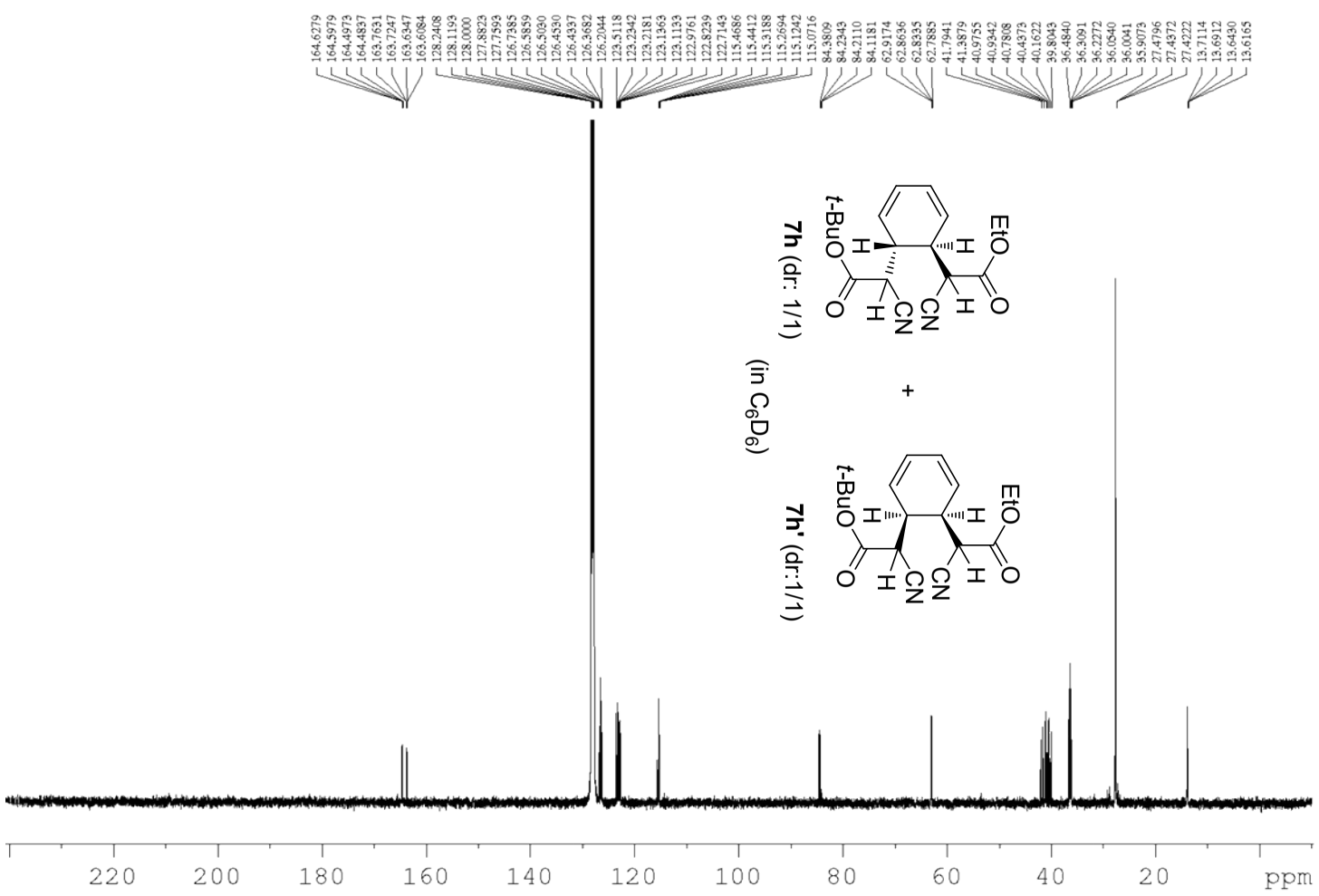
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127749 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters

NAME	zhu-106 c6d6
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

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TD	65536
SOLVENT	C6D6
NS	2400
DS	0
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976128 sec
RG	2050
DW	19.800 usec
DE	6.50 usec
TE	292.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	10.00 usec
PL1	6.20 dB
SFO1	100.6243395 MHz

======== CHANNEL f2 ========

CPDPRG[2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-0.40 dB
PL12	15.80 dB
PL13	18.50 dB
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127510 MHz
WDW	EM
SSB	0
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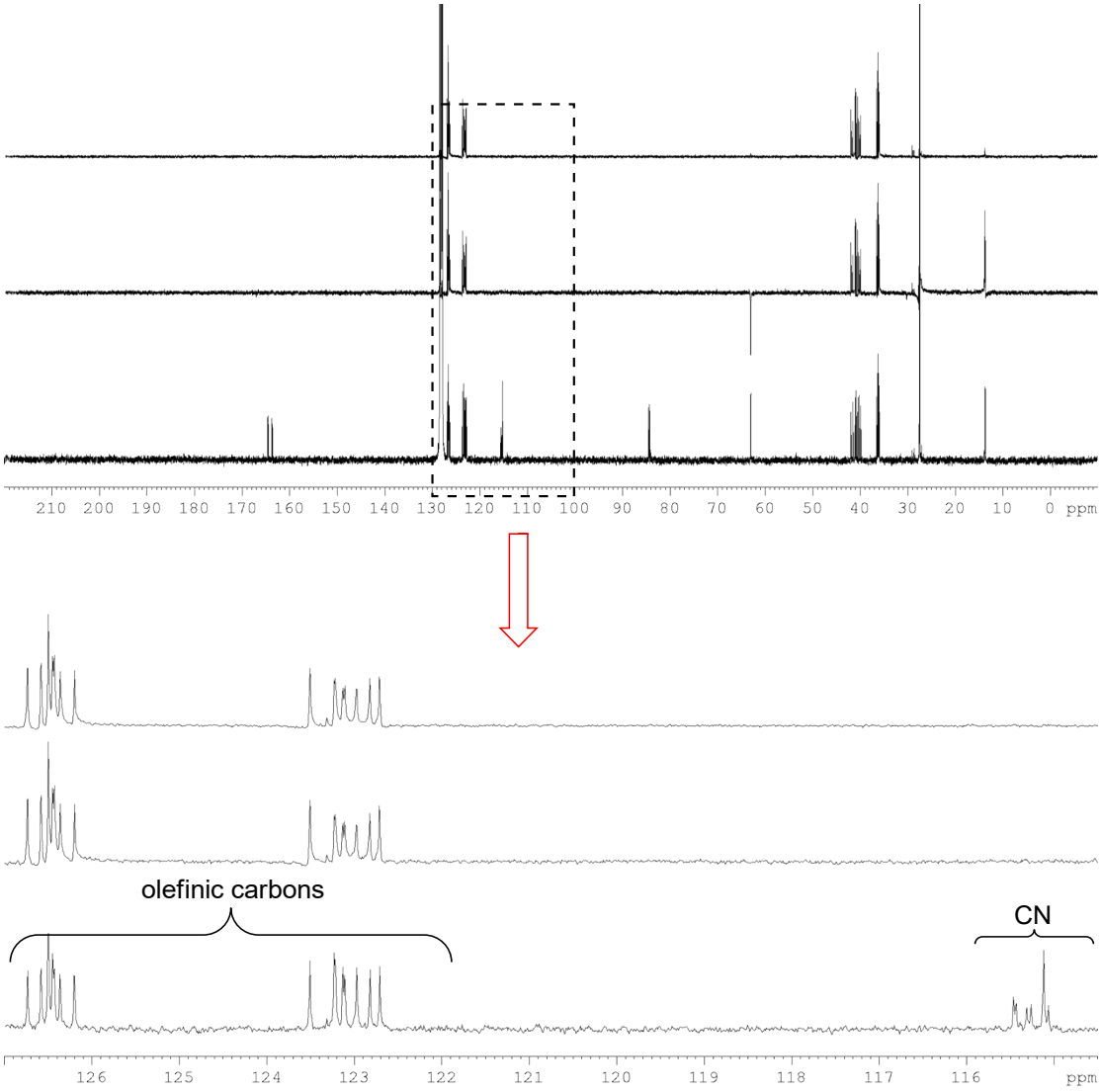
GB	0
PC	1.40

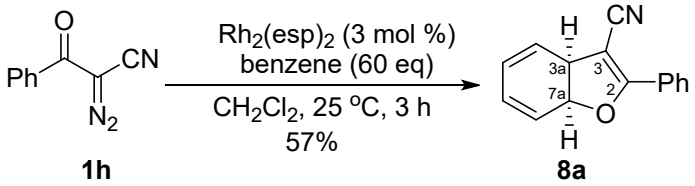
DEPT 90, 135 and ^{13}C NMR spectra (100 MHz in C_6D_6)



9) Formation of Dihydrobenzofurans 8a-c

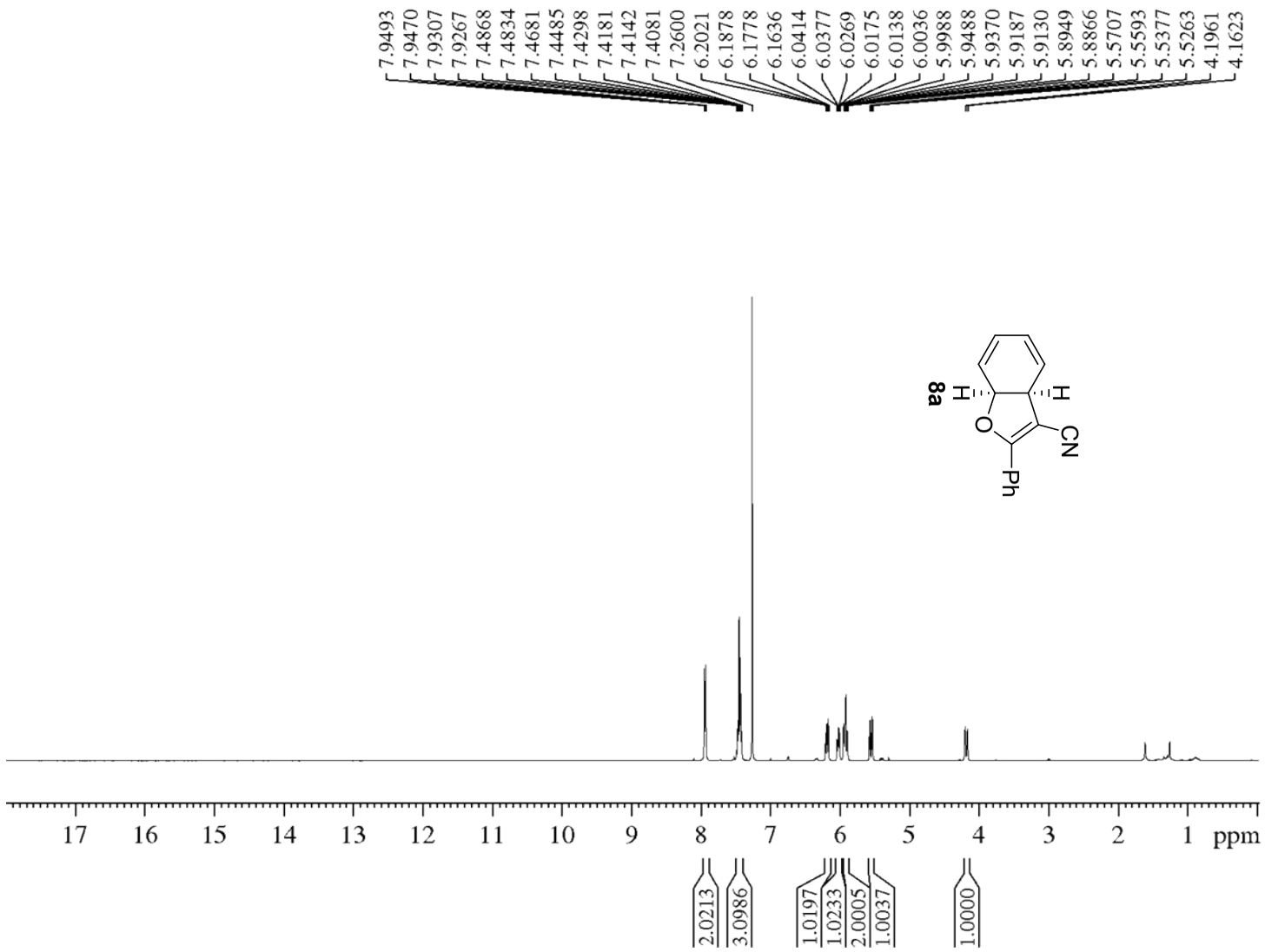
i) Formation of 8a and ^{1}H-NMR ^{13}C-NMR, DEPT, NOESY Spectra

Cis-2-Phenyl-3a,7a-dihydrobenzofuran-3-carbonitrile (**8a**)



1h **8a**

A solution of **1 h** (62.6 mg, 0.3657 mmol) in CH_2Cl_2 (4.1 mL, 0.09 M) was slowly added to a stirred suspension of $Rh_2(esp)_2$ (8.7 mg, 96%, 0.03 equiv relative to **1h**) in benzene (1.96 mL, 60 equiv, 21.94 mmol) via a syringe over 10 min. The mixture was stirred at rt for 3 h until TLC showed the complete conversion of initially formed norcaradiene (R_f = 0.35; hexane/ethyl acetate = 20:1) into **8a** (R_f = 0.5). After concentration, the crude residue was loaded on a basic Al_2O_3 column and eluted with hexane/ethyl acetate (50:1) to give **8a** as a yellow solid (46.1 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 6.9, 1.2 Hz, 2 H, Ph), 7.49-7.42 (m, 3 H, Ph), 6.18 (dd, *J* = 9.6, 5.4 Hz, 1 H), 6.04-6.00 (m, 1 H), 5.94-5.89 (m, 2 H), 5.55 (dd, *J* = 13.2, 4.8 Hz, 1 H, H-7a), 4.17 (dm, *J* = 13.2 Hz, 1 H, H-3a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4 (C-2), 131.5, 128.6, 127.7, 127.3, 127.2, 125.1, 121.5 119.7, 117.5 (CN), 82.7 (C-3), 78.6 (C-7a), 42.3 (C-3a) ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_{11}NO$: 221.0841; found: 221.0831.



Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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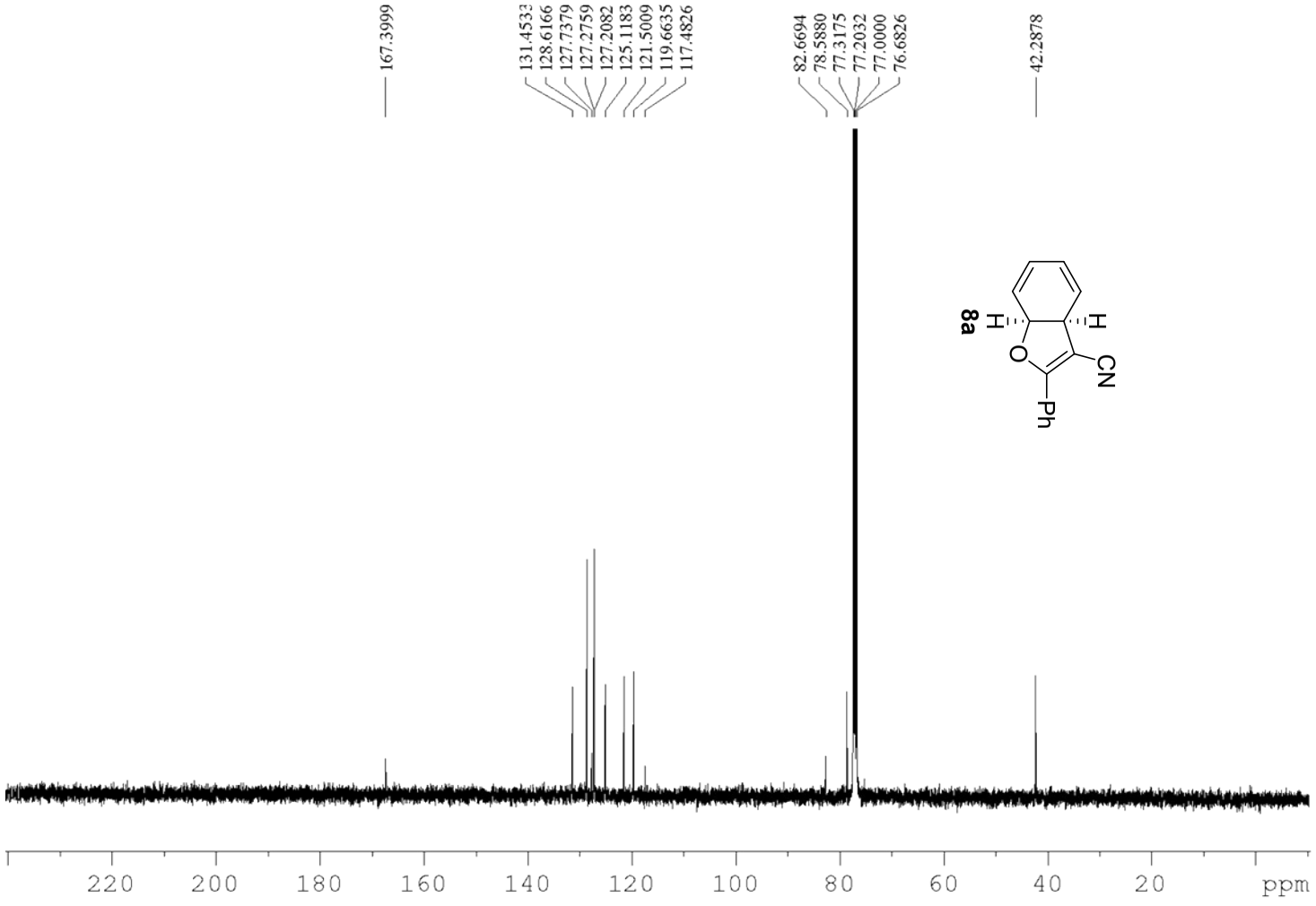
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 322
DW 69.333 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time 13.50
INSTRUM spect
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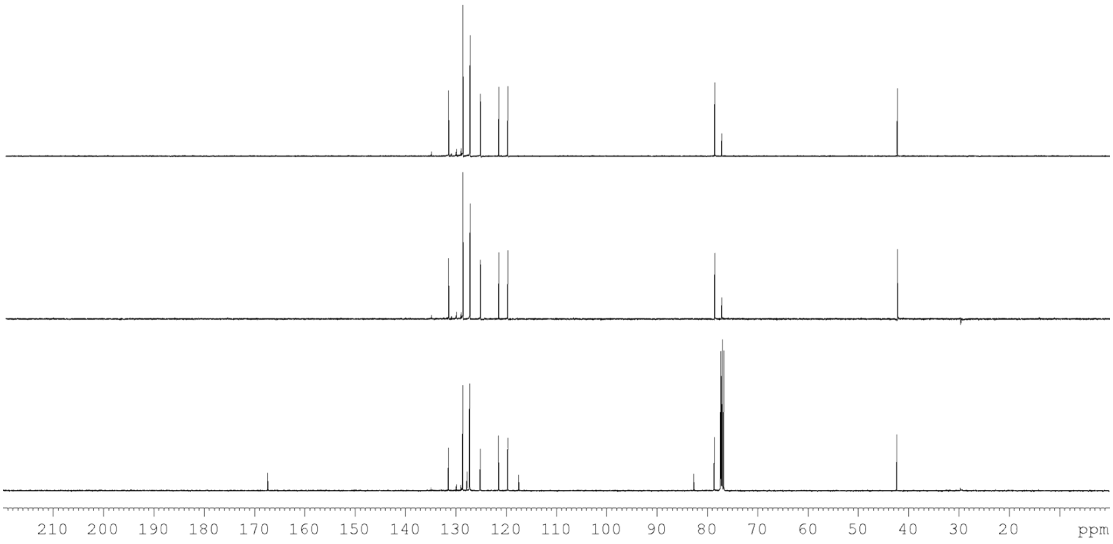
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 450
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 1030
DW 19.800 usec
DE 6.50 usec
TE 292.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

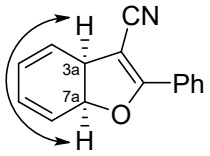
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

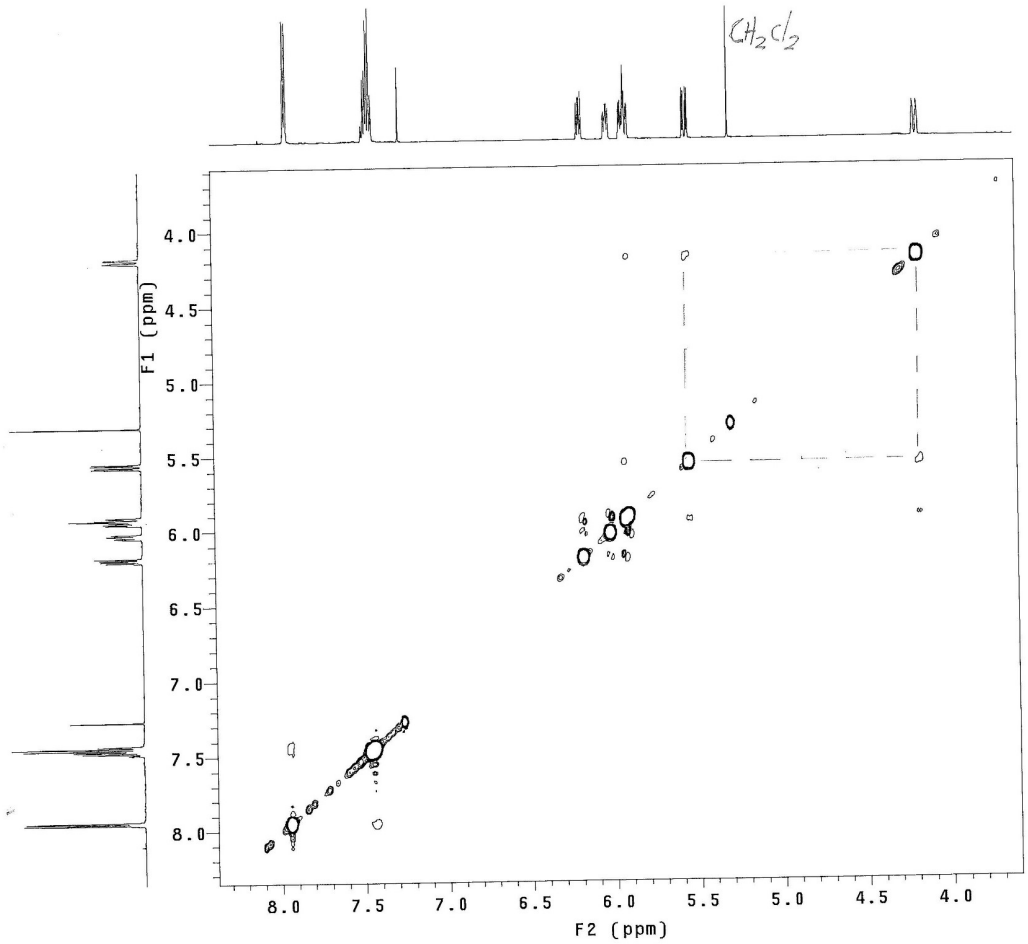
F2 - Processing parameters
SI 32768
SF 100.6127734 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DEPT 90, 135 and ^{13}C NMR spectra (100 MHz in $CDCl_3$):



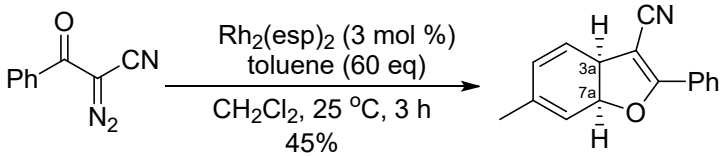
NOESY spectrum (600 MHz in $CDCl_3$):





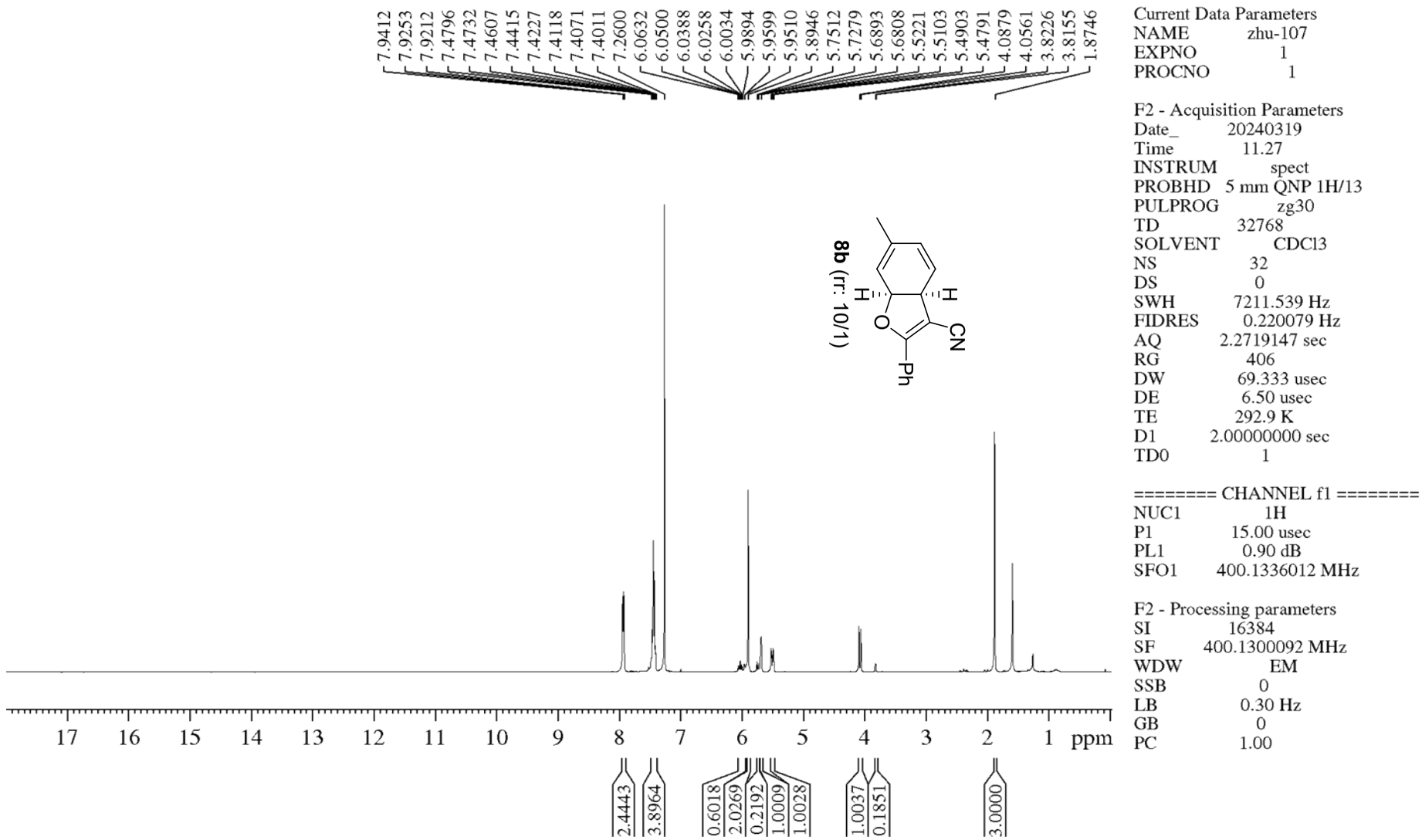
ii) Formation of 8b and ^{1}H-NMR, ^{13}C-NMR spectra

Cis-6-Methyl-2-phenyl-3a,7a-dihydrobenzofuran-3-carbonitrile (**8b**)



1h **8b** (rr: 10:1)

The titled compound was synthesized from **1h** (R_f = 0.4; hexane/ethyl acetate = 20:1) and toluene following the procedure for the preparation of **8a**. The reaction mixture was stirred at ambient temperature for 3 h until TLC showed the complete conversion of initially formed norcaradiene (R_f = 0.45; hexane/ethyl acetate = 20:1) to **8b** (R_f = 0.6). After concentration, the crude residue was subjected to chromatography (basic aluminium oxide; hexane/ethyl acetate = 60:1) to provide **8b** as a yellow solid (45%; rr = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 7.92 (br d, J = 6.9 Hz, 2 H, Ph), 7.47-7.40 (m, 3 H, Ph), 5.95-5.89 (m, 2 H), 5.75-5.68 (m, 1 H), 5.49 (dd, J = 13.1, 4.6 Hz, 1 H, H-7a), 4.09 (br d, J = 13.1 Hz, 1 H, H-3a), 1.87 (s, 3 H, CH_3) ppm; minor isomer: δ 7.94-7.80 (m, 2 H, Ph), 7.47-7.40 (m, 3 H, Ph), 6.05-5.70 (m, 3 H), 5.60-5.42 (m, 1 H, H-7a), 3.82 (m, 1 H, H-3a), 1.87 (s, 3 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 167.6 (C-2), 136.2, 131.4, 128.6, 127.8, 127.2 125.6, 125.3, 117.4, 114.5 (CN), 82.4 (C-3), 79.7 (C-7a), 41.9 (C-3a), 22.1 (Me) ppm; major isomer: δ 124.8, 124.5, 121.3, 48.9, 28.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{13}NO$: 235.0997; found: 235.1001.

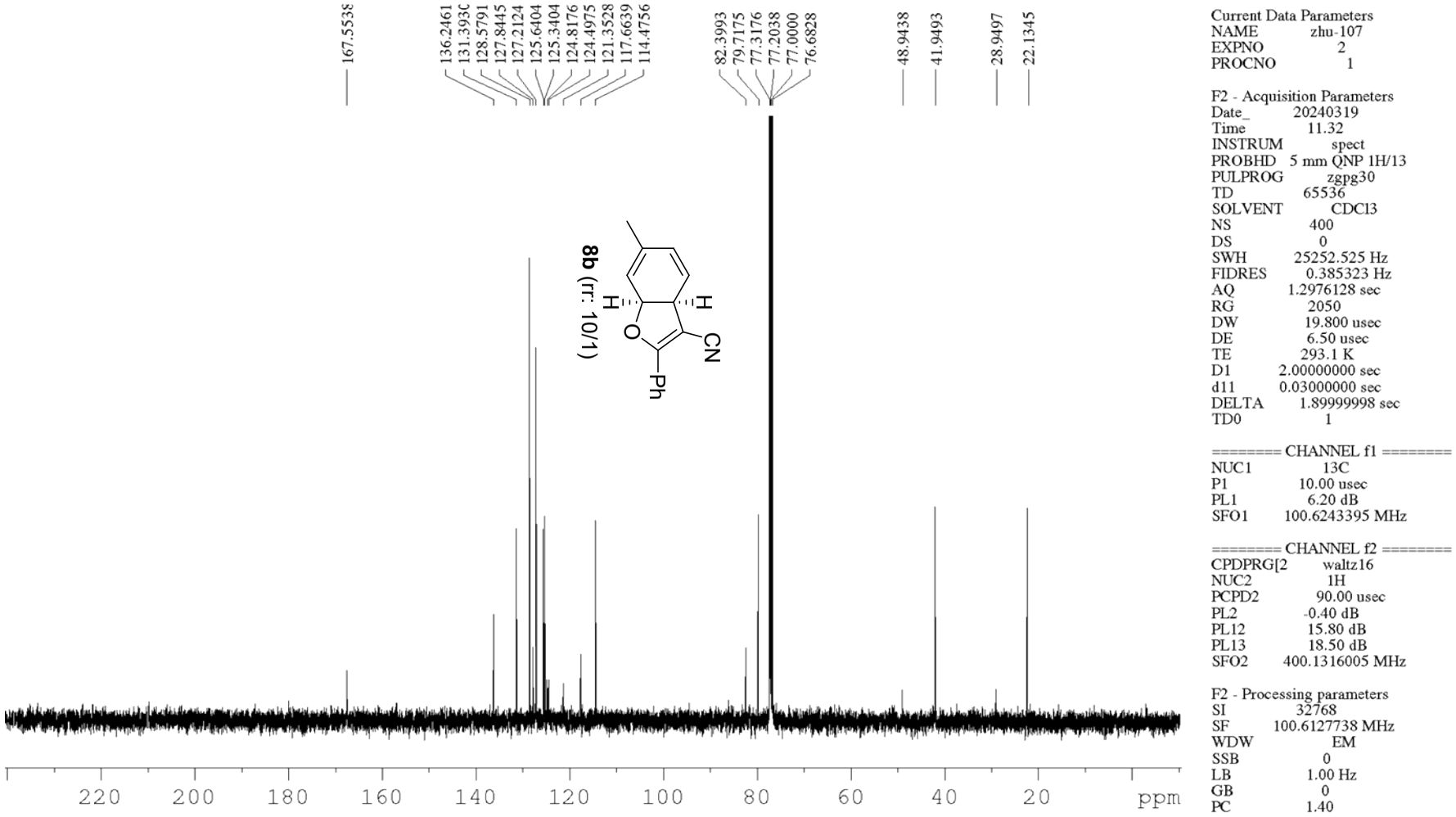


Current Data Parameters
NAME zhu-107
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240319
Time 11.27
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 406
DW 69.333 usec
DE 6.50 usec
TE 292.9 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-107
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240319
Time 11.32
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
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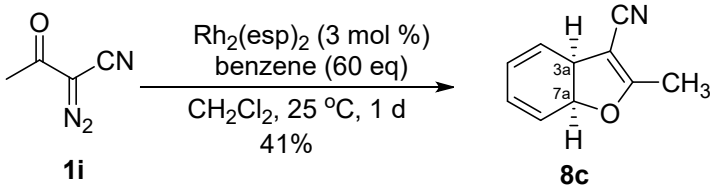
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127738 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

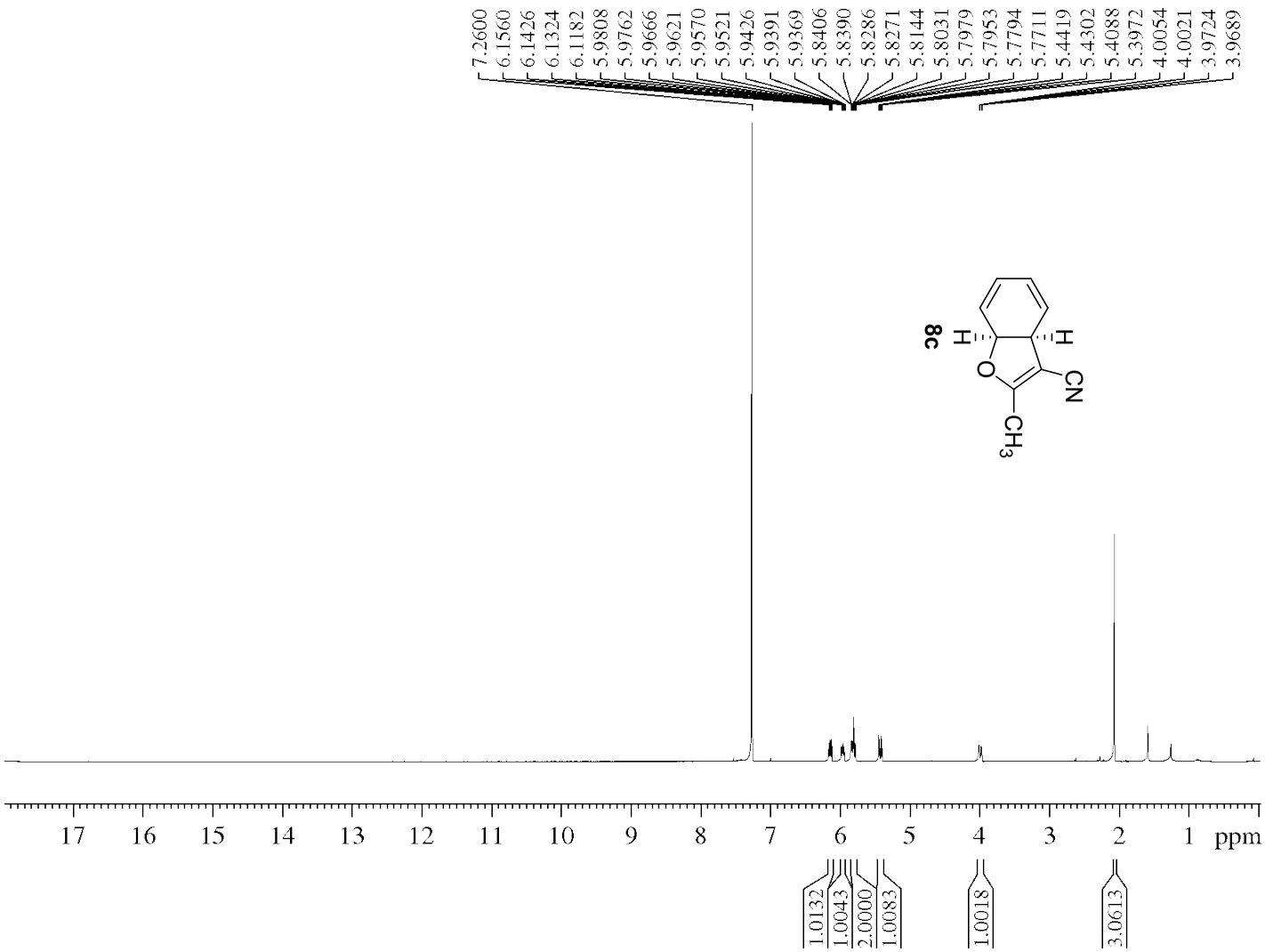
iii) Formation of 8c and ^{1}H-NMR ^{13}C-NMR, DEPT spectra

Cis-2-Methyl-3a,7a-dihydrobenzofuran-3-carbonitrile (**8c**)



1i **8c**

The titled compound was synthesized from **1i** (R_f = 0.3; hexane/ethyl acetate = 20:1) and benzene following the procedure for the preparation of **8a**. The reaction mixture was stirred at ambient temperature for 24 h until TLC showed the complete conversion of initially formed norcaradiene (R_f = 0.32; hexane/ethyl acetate = 20:1) into **8c** (R_f = 0.45). After concentration, the crude residue was subjected to chromatography (basic aluminium oxide; hexane/ethyl acetate = 40:1) to provide **8c** as a colorless oil in 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (dd, J = 9.5, 5.1 Hz, 1 H), 5.98-5.93 (m, 1 H), 5.84-5.79 (m, 2 H), 5.42 (dd, J = 13.2, 4.7 Hz, 1 H, H-7a), 4.00 (dm, J = 13.2 Hz, 1 H, H-3a), 2.07 (s, 3 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (C-2), 127.2, 125.4, 121.0, 119.5, 116.6 (CN), 85.4 (C-3), 79.6 (C-7a), 41.0 (C-3a), 13.6 (CH_3) ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{10}H_9NO$: 159.0684; found: 159.0681.



Current Data Parameters
NAME zhu-48-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230316
Time 13.41
INSTRUM spect
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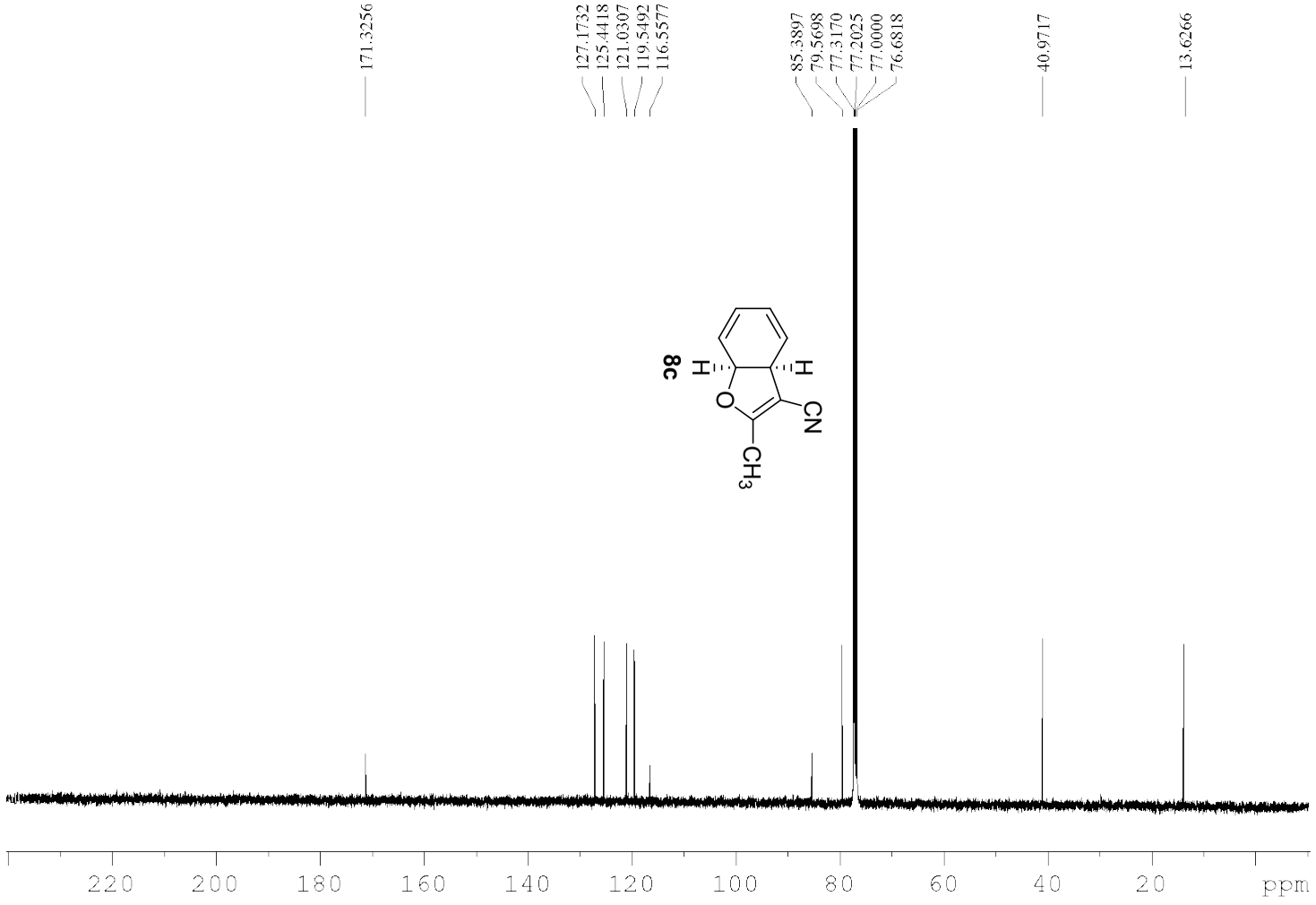
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 160
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 512
DW 69.333 usec
DE 6.50 usec
TE 292.3 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-48-1
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
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Time 22.28
INSTRUM spect
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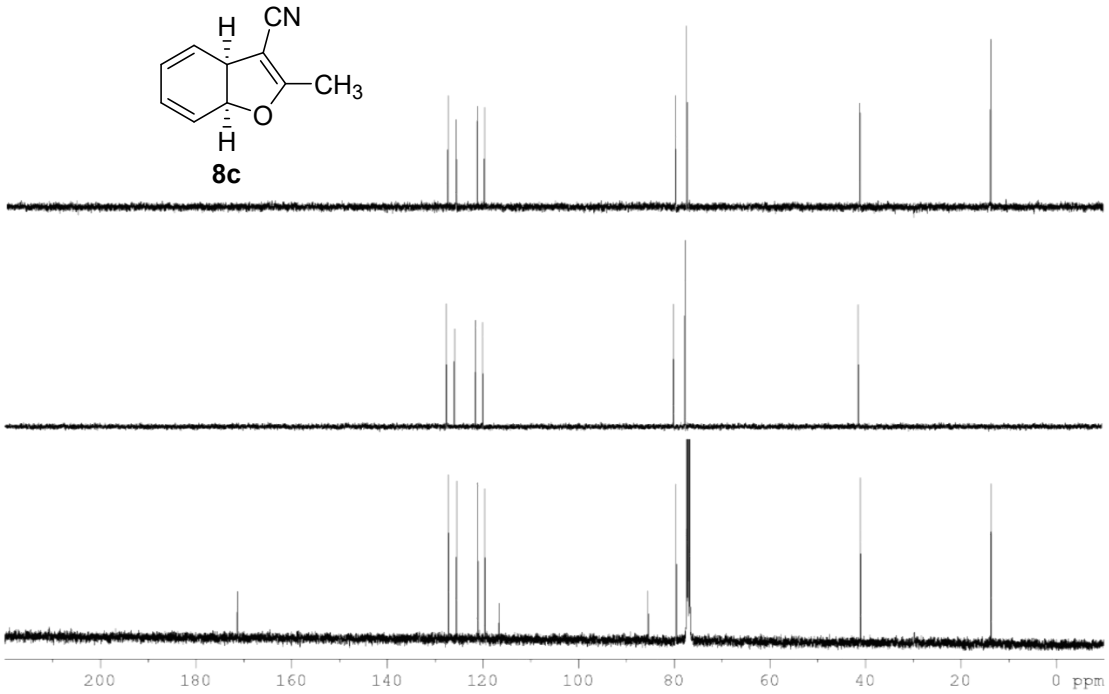
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 1820
DW 19.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

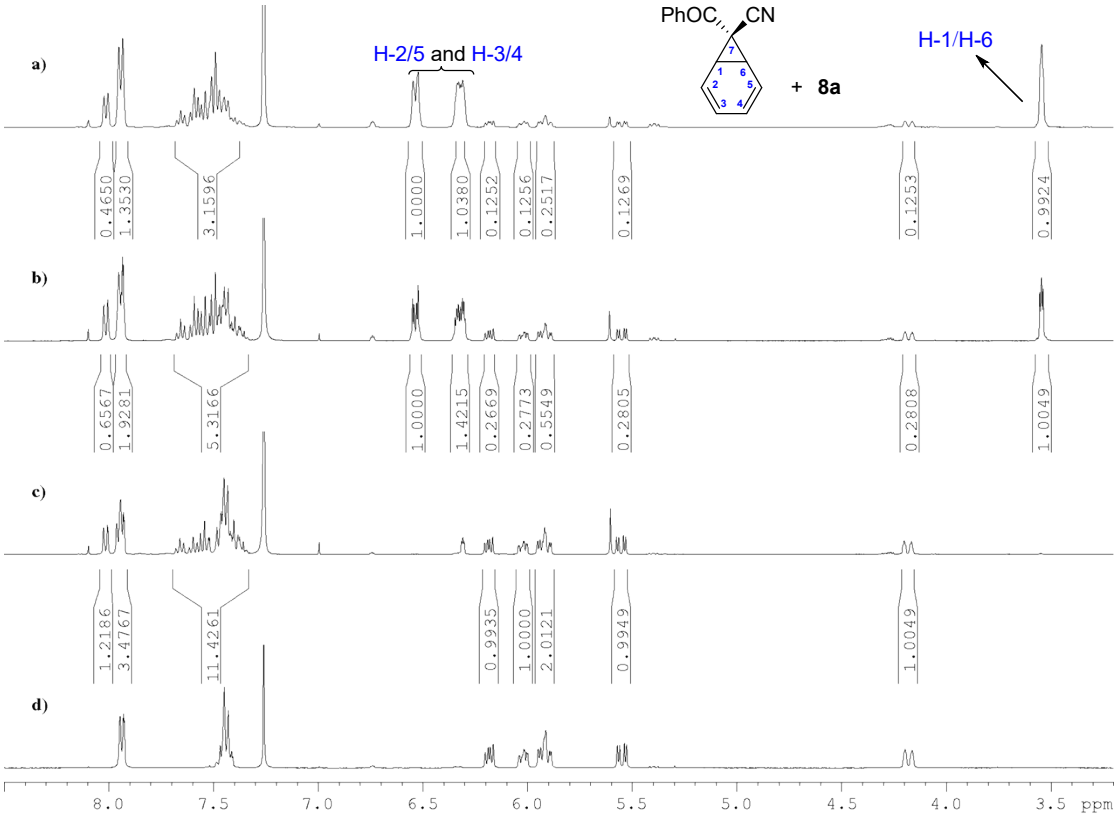
F2 - Processing parameters
SI 32768
SF 100.6127727 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DEPT 135, 90 and ^{13}C NMR spectra (100 MHz in $CDCl_3$):



8c

10) ^{1}H NMR Analysis of the Reaction of 1h with Benzene



^{1}H NMR analysis ($CDCl_3$, 400 MHz) to indicate the spontaneous conversion of norcaradiene intermediate to **8a** in the absence of the catalyst:

a) Reaction mixture after proceeding for 15 min followed by filtration over a Al_2O_3 pad to remove $Rh_2(esp)_2$ catalyst (norcaradiene /**8a** = 80/20).

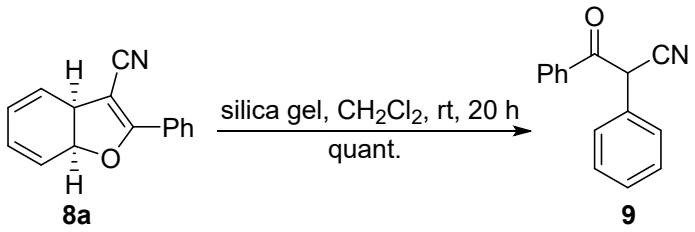
b) After stirring the mixture from **a**) in DCM for 10 h (norcaradiene /**8a** = 65/35).

c) After stirring the mixture from **a**) in DCM for 20 h (norcaradiene /**8a** = 0/100).

d) ^{1}H NMR spectrum of **8a**.

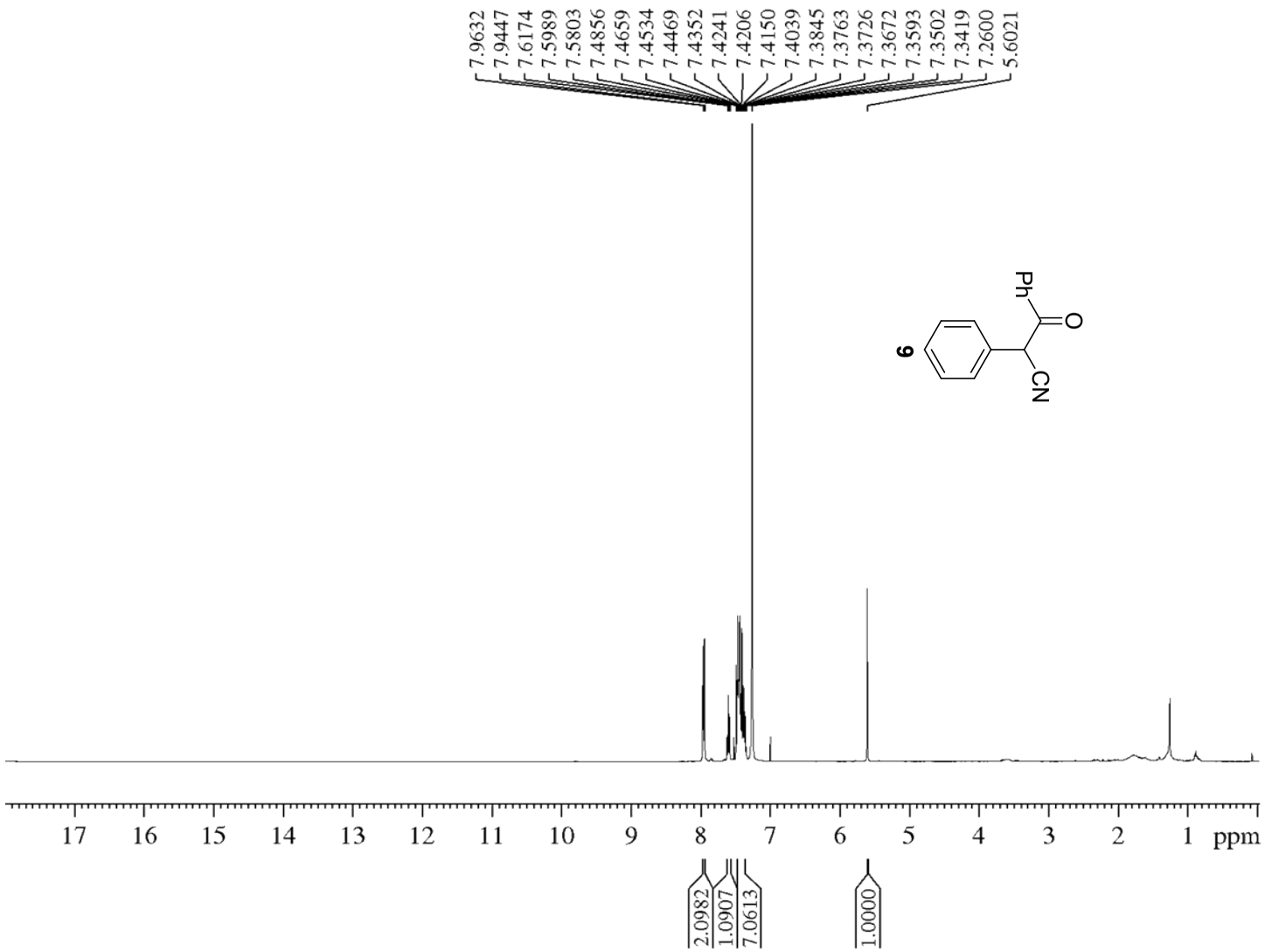
11) Conversion of 8a into 9 and ^{1}H-NMR, ^{13}C-NMR spectra

3-Oxo-2,3-diphenylpropanenitrile (**9**)[15]



8a **9**

To a solution of **8a** (41 mg, 0.185 mmol) in CH_2Cl_2 (4 ml), 40 mg of silica gel (70-230 mesh) was added. The suspension was stirred at ambient temperature for 20 h, then filtrated through a cotton pad and concentrated in vacuo to give 40 mg of **9** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br d, J = 7.4 Hz, 2 H), 7.60 (br t, J = 7.4 Hz, 1 H), 7.58-7.34 (m, 7 H), 5.60 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8 (C=O), 134.4, 133.6, 130.3, 129.7, 129.3, 129.1, 129.0, 128.2, 116.5 (CN), 46.7 ppm.



Current Data Parameters
NAME Zhu-56 TLC overnight
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230502
Time 23.39
INSTRUM spect
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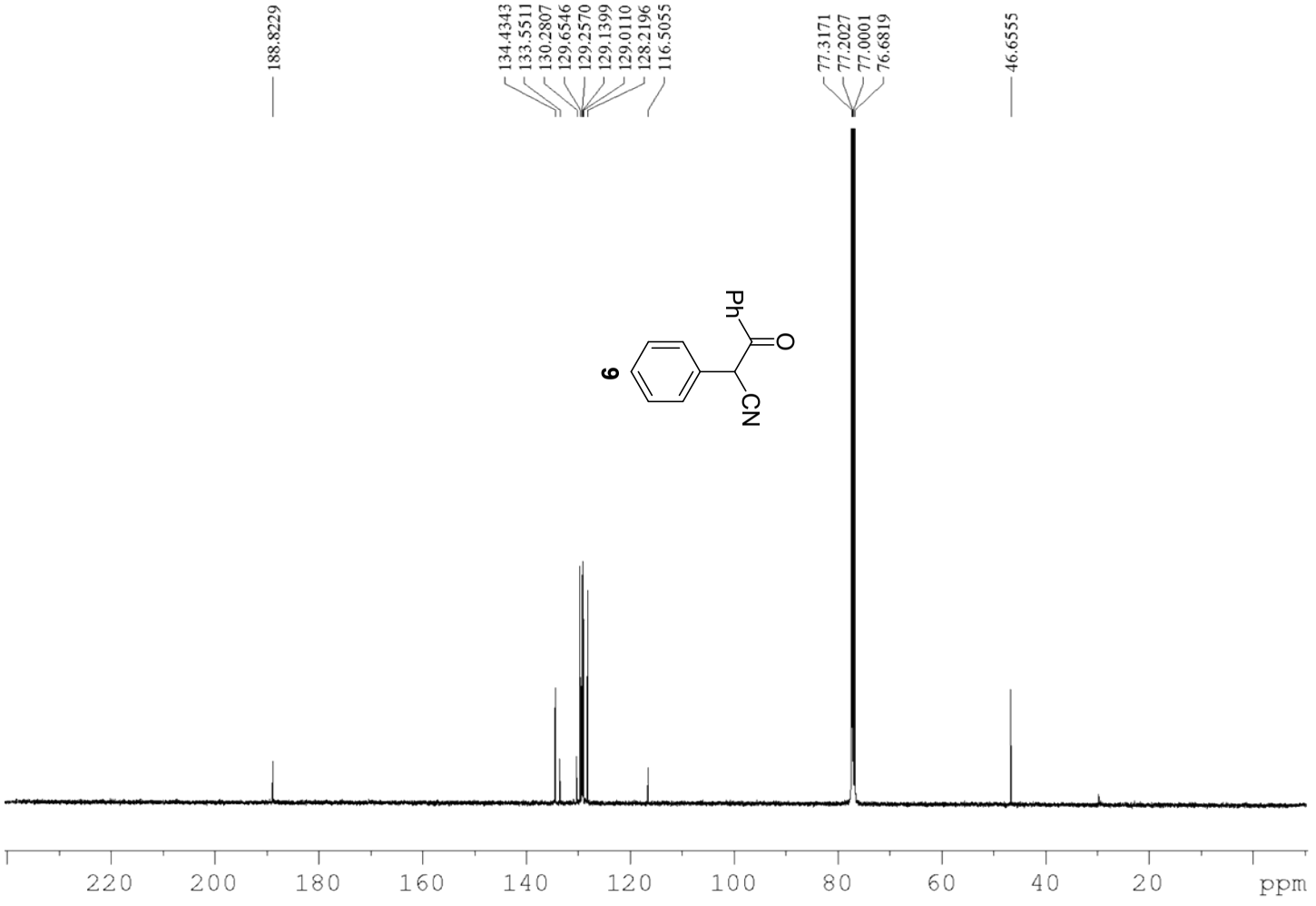
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 160
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 406
DW 69.333 usec
DE 6.50 usec
TE 292.5 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME Zhu-56 TLC overnight
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230502
Time 23.56
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 9140
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 292.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

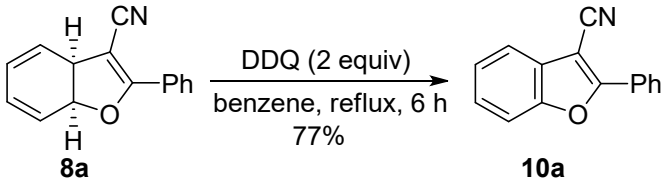
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127735 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

12) Oxidation of 8a/8b into 10a/10b and ^{1}H-NMR, ^{13}C-NMR spectra

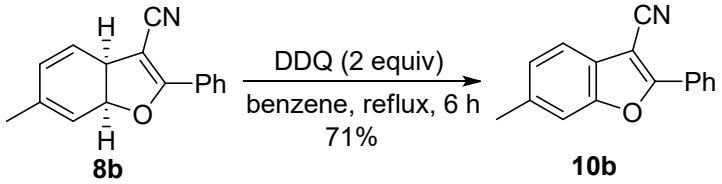
2-Phenylbenzofuran-3-carbonitrile (**10a**)[16]



8a **10a**

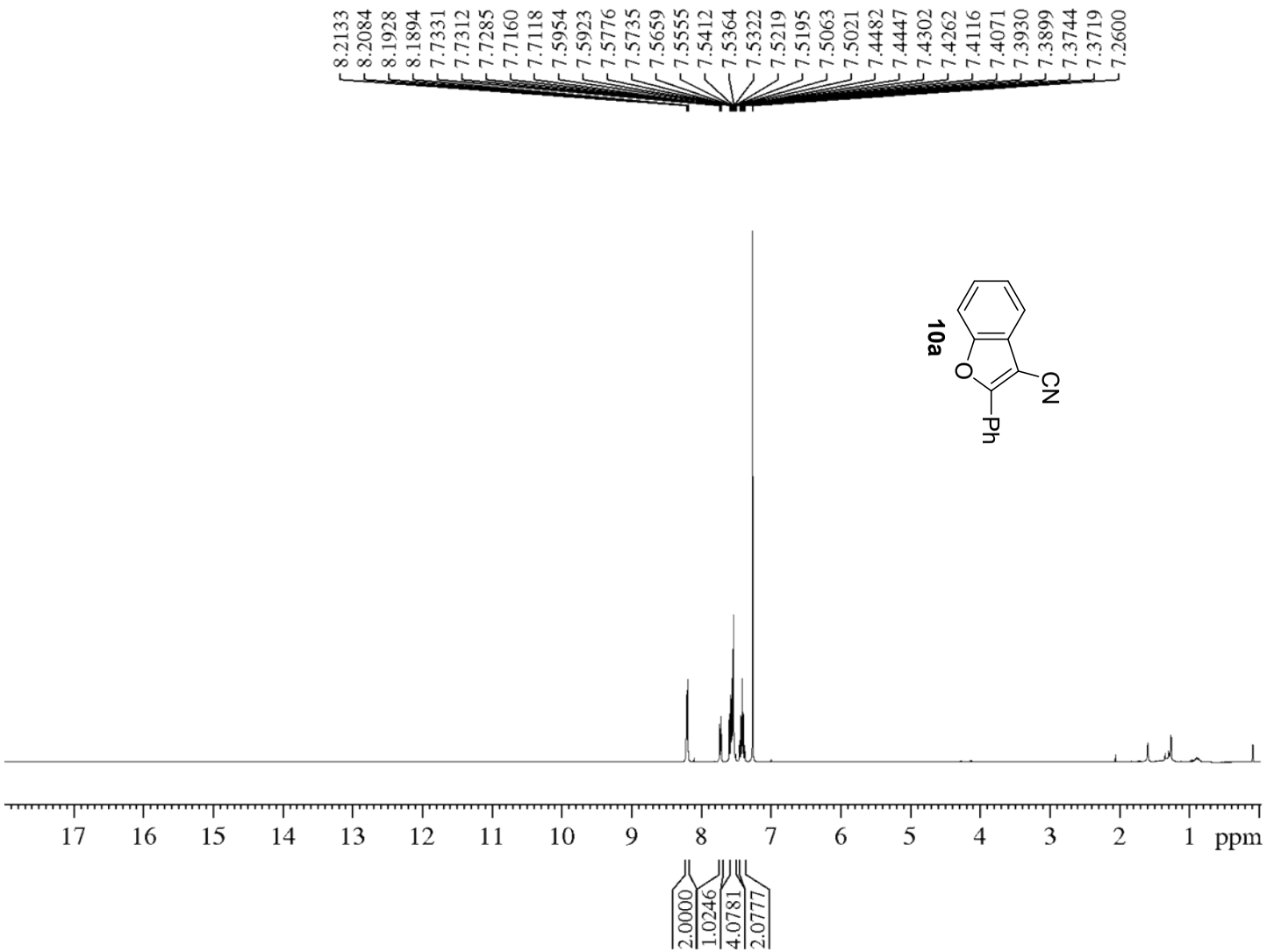
DDQ (63.6 mg, 0.28 mmol) was added to a flask containing a solution of **8a** (31 mg, 0.14 mmol) in benzene (5 mL). The mixture was stirred and refluxed in an oil bath (90 °C) for 6 h before cooling to room temperature and concentration under reduced pressure. The crude residue was purified by chromatography (silica gel; hexane/ethyl acetate = 60:1) to give **10a** as a white solid (23.6 mg, 77%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 6.9, 1.9 Hz, 2 H), 7.73-7.71 (m, 1 H), 7.59-7.54 (m, 4 H), 7.50-7.37 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 153.3, 131.2, 129.2, 127.8, 127.2, 126.5, 126.4, 124.7, 119.9, 114.3, 111.7, 88.1 ppm.

6-Methyl-2-phenylbenzofuran-3-carbonitrile (**10b**)[16]



8b **10b**

The titled compound was synthesized from **8b** following the procedure for the preparation of **10a**. **8b** was used as a 10:1 regioisomeric mixture, while only **10b** derived from the major isomer was obtained in 71% yield after chromatographic purification (silica gel; hexane/ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (br d, *J* = 6.8 Hz, 2 H), 7.60-7.56 (m, 4 H), 7.49 (br s, 1 H), 7.26-7.20 (m, 1 H), 2.52 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 153.8, 137.1, 131.0, 129.2, 128.0, 126.4, 126.1, 124.7, 119.4, 114.6, 111.9, 88.0, 21.8 ppm.



Current Data Parameters
NAME zhu-88
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PROCNO 1

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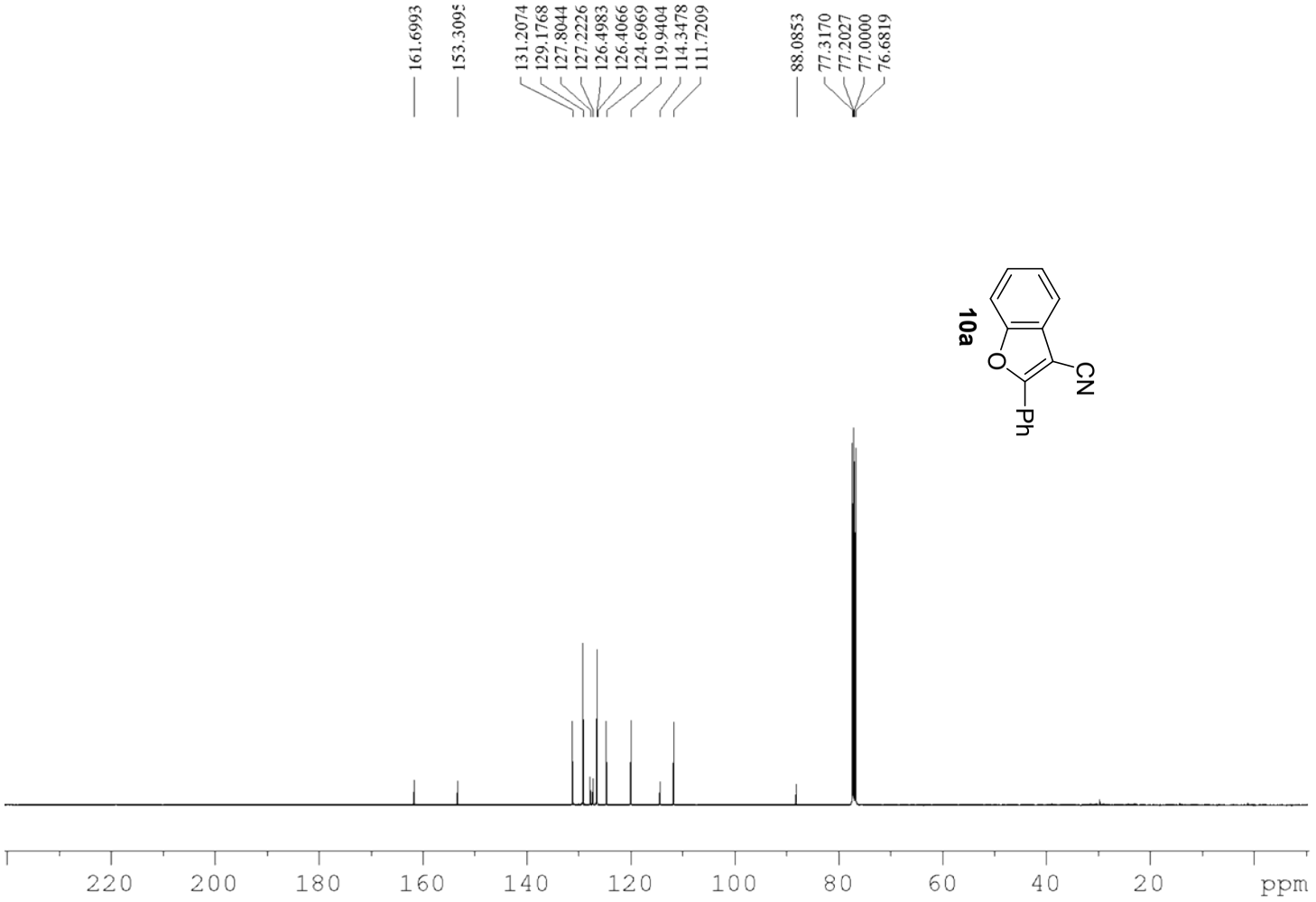
TD 32768
SOLVENT CDCl3
NS 160
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 322
DW 69.333 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



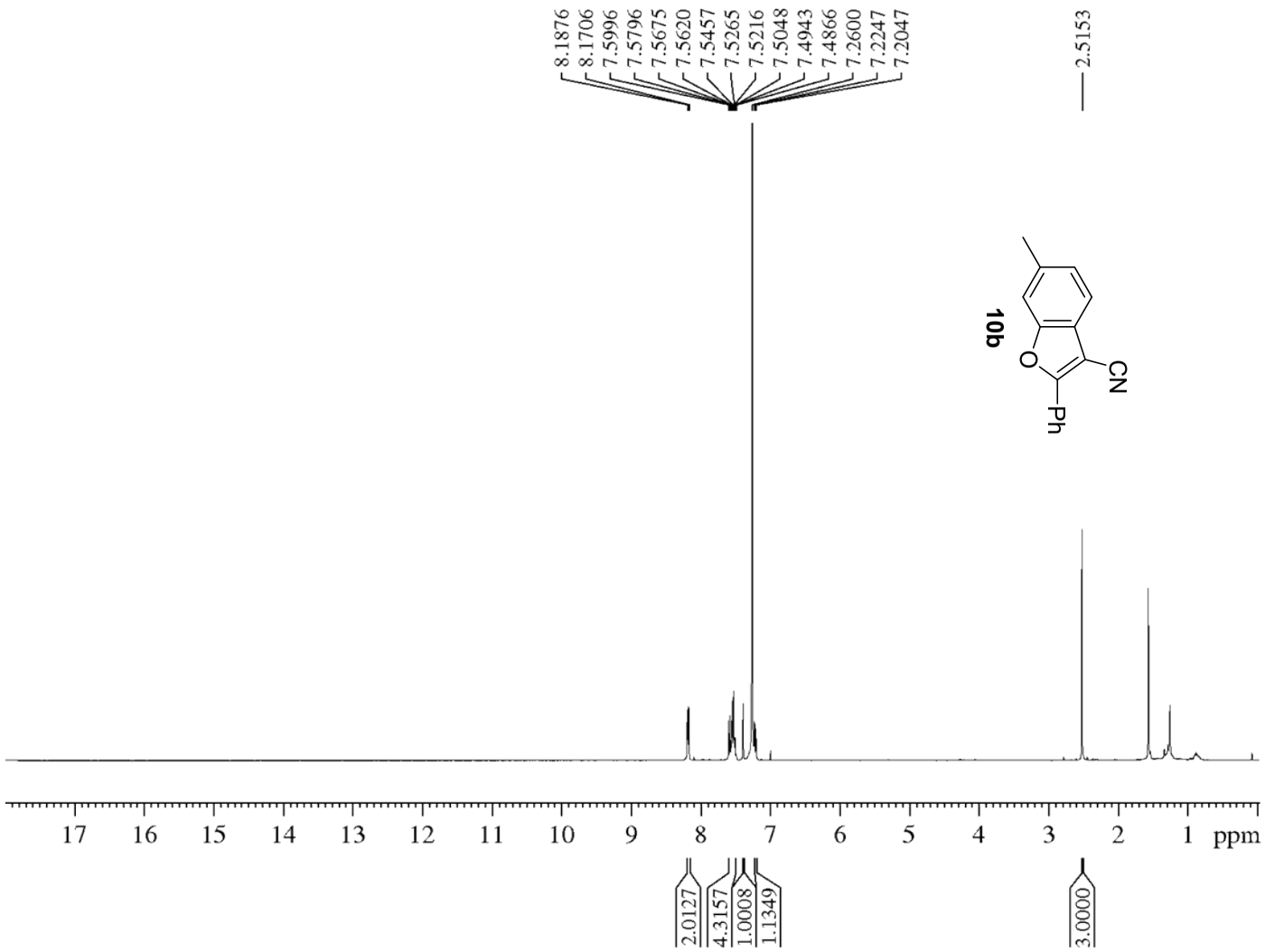
Current Data Parameters
NAME zhu-88
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230912
Time 22.32
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10522
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127744 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME zhu-108 overnght
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 22.04
INSTRUM spect
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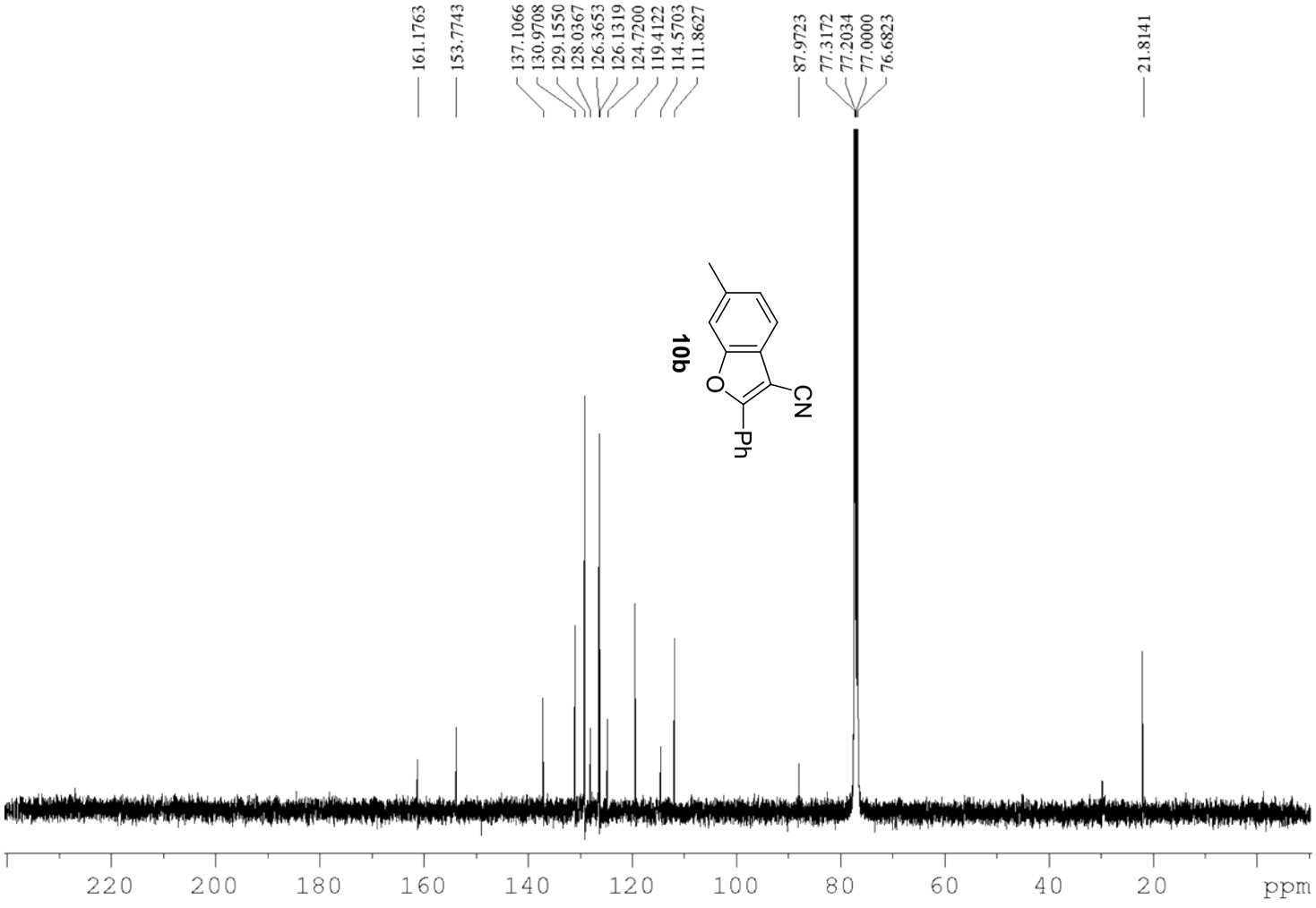
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 160
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 724
DW 69.333 usec
DE 6.50 usec
TE 292.6 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 0.90 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME zhu-108 overnght
EXPNO 2
PROCNO 1

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Time 22.18
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SOLVENT CDCl3
NS 10564
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 292.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 6.20 dB
SFO1 100.6243395 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.40 dB
PL12 15.80 dB
PL13 18.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127721 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

References

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