Advanced Synthesis of Dihydrofurans.

Effect of Formic Acid on the Mn(III)-Based Oxidation

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Supplementary Information

Measurements, materials, IR, ^1H and ^{13}C NMR spectra, DEPT and HRMS data including copies of ^1H and ^{13}C NMR spectra for **5ba**, **5bb**, **5bc**, **5bd**, **5da**, and **7-10**.

* Received in

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EXPERIMENTAL

Measurements

Melting points were taken using a Yanagimoto micromelting point apparatus and are uncorrected. The NMR spectra were recorded using a JNM ECX 500 or AL300 FT-NMR spectrometer at 500 or 300 MHz for ^1H and at 125 or 75 MHz for ^{13}C , with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants in Hz. The following abbreviations are used for the multiplicities; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet for the ^1H NMR spectrum. The IR spectra were measured in CHCl_3 or KBr using a Shimadzu 8400 FT IR spectrometer and expressed in cm^{-1} . The EI MS spectra were obtained by a Shimadzu QP-5050A gas chromatograph-mass spectrometer at the ionizing voltage of 70 eV. The high-resolution mass spectra and the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

Materials.

Manganese(II) acetate tetrahydrate, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, was prepared according to our modified method.^[12] Nitrilotris(ethane-2,1-diyl) tris(3-oxobutanoate) (**1**) was prepared by the imidazole-catalyzed reaction of 2,2',2''-nitrilotriethanol with diketene in dry tetrahydrofuran at room temperature. The diarylethenes **2a-d** were prepared by the Grignard reaction of the corresponding arylmagnesium bromides with acetophenones followed by acid-catalyzed dehydration. Imidazole, 2,2',2''-nitrilotriethanol, diketene, propyl 3-oxobutanoate (**4c**), and butyl 3-oxobutanoate (**4e**) were purchased from Tokyo Kasei Co., Ltd., and methyl 3-oxobutanoate (**4a**), ethyl 3-oxobutanoate (**4b**), isopropyl 3-oxobutanoate (**4d**), 2,4-pentanedione (**6a**), malonic acid (**6b**), and diethyl malonate (**6c**) were from Wako Pure Chemical Ind., Ltd., and used as received. Flash column chromatography was performed on silica gel 60N (40-50 μm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 (45 μm) from Wako Pure Chemical Ind., Ltd. The solvents were commercially available first grade and used as received.

The physical data of the known products **5ba**, **5bb**, **5bc**, **5bd**, **5da**, and **7-10** and references are listed below.

Ethyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**5ba**)^[13]

Light yellow oil; $R_f = 0.4$ (EtOAc–hexane, 2:8); IR (CHCl_3) ν 1690 ($\text{C}=\text{O}$); ^1H NMR (CDCl_3) δ 7.39–7.22 (10H, m, arom H), 4.15 (2H, q, $J = 7.2$ Hz, $\text{CH}_2\text{--CH}_3$), 3.60 (2H, s, CH_2), 2.35 (3H, s, CH_3), 1.26 (3H, t, $J = 7.2$ Hz, $\text{CH}_2\text{--CH}_3$); ^{13}C NMR (CDCl_3) δ 166.2 ($\text{C}=\text{O}$), 165.8 ($=\text{CO}-$), 145.1 (2C) (arom C), 128.3 (4C), 127.4 (2C), 125.6 (4C) (arom CH), 101.7 ($>\text{C}=\text{}$), 91.4 ($>\text{C}<$), 59.5 ($-\text{OCH}_2$), 44.1 ($-\text{CH}_2-$), 14.4 (CH_3), 14.2 (CH_3); FAB HRMS (acetone/NBA) calcd for $\text{C}_{20}\text{H}_{21}\text{O}_3$ 309.1491 (M+H). Found: 309.1510.

Ethyl 5,5-Bis(4-fluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (**5bb**)^[13]

Colorless liquid; $R_f = 0.5$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1697 ($\text{C}=\text{O}$); ^1H NMR (CDCl_3) δ 7.34–7.30 (4H, m, arom H), 7.04–6.99 (4H, m, arom H), 4.16 (2H, q, $J = 7.2$ Hz, $\text{CH}_2\text{--CH}_3$), 3.55 (2H, q, $J = 1.5$ Hz, CH_2), 2.34 (3H, t, $J = 1.5$ Hz, CH_3), 1.27 (3H, t, $J = 7.2$ Hz, $\text{CH}_2\text{--CH}_3$); ^{13}C NMR (CDCl_3) δ 166.0 ($\text{C}=\text{O}$), 165.6 ($=\text{CO}-$), 162.1 (2C) (arom C-F, $J = 245.6$ Hz) 140.8 (2C, $J = 2.4$ Hz, arom C-1'), 127.5 (4C, $J = 7.1$ Hz, arom C-2'), 115.2 (4C, $J = 21.4$ Hz, arom C-3'), 101.8 ($>\text{C}=\text{}$), 90.6 ($>\text{C}<$), 59.7 ($-\text{OCH}_2$), 44.3 ($-\text{CH}_2-$), 14.4 (CH_3), 14.2 (CH_3).

Ethyl 5,5-Bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (**5bc**)^[14]

Colorless amorphous; $R_f = 0.5$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1701 ($\text{C}=\text{O}$); ^1H NMR (CDCl_3) δ 7.32–7.26 (8H, m, arom H), 4.16 (2H, q, $J = 7.2$ Hz, $\text{CH}_2\text{--CH}_3$), 3.53 (2H, br. q, $J = 1.8$ Hz, CH_2), 2.33 (3H, t, $J = 1.8$ Hz, CH_3),

1.27 (3H, t, $J = 7.2$ Hz, $\text{CH}_2\text{-CH}_3$); ^{13}C NMR (CDCl_3) δ 165.9 (C=O), 165.5 (=CO-), 143.2 (2C) (arom C), 133.7 (2C) (arom C), 128.6 (4C), 127.0 (4C) (arom CH), 101.8 ($>\text{C=}$), 90.5 ($>\text{C}<$), 59.7 ($\text{-OCH}_2\text{-}$), 44.0 ($\text{-CH}_2\text{-}$), 14.4 (CH_3), 14.2 (CH_3); FAB HRMS (acetone/NBA) calcd for $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{O}_3$ 377.0711 (M+H); found: 377.0692.

Ethyl 5,5-Bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bd)^[13]

Light yellow oil; $R_f = 0.5$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1690 (C=O); ^1H NMR (CDCl_3) δ 7.26–7.25 (4H, m, arom H), 7.13–7.12 (4H, m, arom H), 4.15 (2H, q, $J = 7.2$ Hz, $\text{CH}_2\text{-CH}_3$), 3.60 (2H, q, $J = 1.5$ Hz, CH_2), 2.33 (3H, t, $J = 1.5$ Hz, CH_3), 2.32 (6H, s, $\text{CH}_3 \times 2$), 1.26 (3H, t, $J = 7.2$ Hz, $\text{CH}_2\text{-CH}_3$); ^{13}C NMR (CDCl_3) δ 166.3 (C=O), 165.9 (=CO-), 142.4 (2C) (arom C), 137.1 (2C) (arom CCH_3), 128.9 (4C), 125.6 (4C) (arom CH), 101.7 ($>\text{C=}$), 91.4 ($>\text{C}<$), 59.5 ($\text{-OCH}_2\text{-}$), 44.1 ($\text{-CH}_2\text{-}$), 21.0, 14.4, 14.2 (CH_3).

***i*-Propyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5da)**^[3e]

Light yellow oil; $R_f = 0.5$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1684 (C=O); ^1H NMR (CDCl_3) δ 7.40–7.24 (10H, m, arom H), 5.04 (1H, sep, $J = 6.2$ Hz, $>\text{CH-}$), 3.59 (2H, q, $J = 1.5$ Hz, CH_2), 2.34 (3H, t, $J = 1.5$ Hz, CH_3), 1.24 (6H, d, $J = 6.2$ Hz, $\text{-CH(CH}_3)_2$); ^{13}C NMR (CDCl_3) δ 165.9 (C=O), 165.4 (=CO-), 145.3 (2C) (arom C), 128.3 (4C), 127.4 (2C), 125.7 (4C) (arom CH), 102.0 ($>\text{C=}$), 91.3 ($>\text{C}<$), 66.7 (-OCH-), 44.2 ($\text{-CH}_2\text{-}$), 22.1 ($\text{-CH(CH}_3)_2$), 14.2 (CH_3); FAB HRMS (acetone/NBA) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_3$ 323.1647 (M+H); found 323.1665.

3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (7)^[3a]

Light yellow oil; $R_f = 0.3$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1667 (C=O); ^1H NMR (CDCl_3) δ 7.39–7.25 (10H, m, arom H), 3.66 (2H, q, $J = 2.0$ Hz, CH_2), 2.38 (3H, t, $J = 2.0$ Hz, CH_3), 2.22 (3H, s, -COCH_3); ^{13}C NMR (CDCl_3) δ 194.1 (C=O), 165.9 (=CO-), 144.9 (2C) (arom C), 128.3 (4C), 127.6 (2C), 125.6 (4C) (arom CH), 112.2 ($>\text{C=}$), 91.5 ($>\text{C}<$), 44.8 ($\text{-CH}_2\text{-}$), 29.4 (-COCH_3), 15.2 (CH_3).

3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (8)^[15]

Colorless microcrystals (from CHCl_3 /hexane); mp 287–290 °C (lit, mp 284.5–285.0 °C); $R_f = 0.8$ (CHCl_3); IR (CHCl_3) ν 1798, 1667 (C=O); ^1H NMR (CDCl_3) δ 7.43–7.35 (6H, m, arom H), 7.31–7.23 (14H, m, arom H), 3.01 (2H, d, $J = 13.5$ Hz, $\text{-CH}_2\text{-}$), 2.61 (2H, d, $J = 13.5$ Hz, $\text{-CH}_2\text{-}$); ^{13}C NMR (CDCl_3) δ 173.5 ($\text{C=O} \times 2$), 142.1 (2C), 142.0 (2C) (arom C), 128.9 (4C), 128.6 (4C), 128.5 (2C), 128.3 (2C), 125.5 (4C), 125.4 (4C) (arom CH), 88.60 ($\text{Ph}_2\text{CO-} \times 2$), 53.9 ($>\text{C}<$), 45.6 ($\text{-CH}_2\text{-} \times 2$).

Ethyl 2-oxo-5,5-diphenyl-2,5-dihydrofuran-3-carboxylate (9)^[8e,9]

Colorless microcrystals (from EtOH); mp 105–108 °C (lit, mp 107.9–109.4 °C); $R_f = 0.2$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1780 (C=O), 1719 (C=O), 1267 (C-O-C); ^1H NMR (CDCl_3) δ 8.60 (1H, s, $>\text{CH-}$), 7.41–7.26 (10H, m, arom H), 4.36 (2H, q, $J = 7.0$ Hz, CH_2), 1.37 (3H, t, $J = 7.0$ Hz, $\text{-CH}_2\text{CH}_3$); ^{13}C NMR (CDCl_3) δ 166.5 (C=O), 164.5 (=C-), 160.1 (C=O), 138.1 (2C) (arom C), 129.0 (4C), 128.9 (2C), 126.6 (4C) (arom CH), 123.7 ($>\text{C=}$), 89.2 ($>\text{CPh}_2$), 61.89 ($\text{-CH}_2\text{CH}_3$), 14.1 ($\text{-CH}_2\text{CH}_3$).

Diethyl 2-(2,2-diphenylethenyl)malonate (10)^[9,16]

Colorless liquid; $R_f = 0.3$ (EtOAc–hexane, 1:9); IR (CHCl_3) ν 1734 (C=O); ^1H NMR (CDCl_3) δ 7.41–7.34 (3H, m, arom H), 7.29 (5H, s, arom H), 7.23–7.201 (2H, m, arom H), 6.33 (1H, d, $J = 11.0$ Hz, -CH=Ph_2), 4.21 (4H, q, $J = 7.0$ Hz, $\text{-CH}_2\text{CH}_3 \times 2$), 4.19 (1H, d, $J = 11.0$ Hz, $>\text{CH-CO}_2\text{Et}$), 1.27 (6H, t, $J = 7.0$ Hz, $\text{-CHCH}_3 \times 2$); ^{13}C NMR (CDCl_3) δ 168.3 ($\text{C=O} \times 2$), 141.3 (2C) (arom C), 138.5 (-CH=CPh_2), 129.8 (2C), 128.4 (2C), 128.1 (2C), 127.8 (2C), 127.6 (2C) (arom CH), 119.7 (-CH=CPh_2), 61.5 ($\text{-CH}_2\text{CH}_3 \times 2$), 53.0 ($>\text{CH-}$), 14.0 ($\text{-CH}_2\text{CH}_3 \times 2$).

REFERENCES

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[Mass Spectrum]
 Date : 08-Aug-2013 11:35
 Sample: N-dihydrofurun/Matsumoto
 Note : Acetone+NBA
 Inlet : Direct
 Ion Mode : FAB+
 Spectrum Type : Normal Ion [MF-Linear]
 RT : 0.53 min Scan# : (3,6)
 BP : m/z 154.1109 Int. : 35.89
 Output m/z range : 50.0000 to 1120.4749
 Cut Level : 0.00 %

0.000

1.622

2.349

2.352

2.356

3.600

3.604

3.689

7.241

7.248

7.256

7.267

7.270

7.309

7.321

7.325

7.335

7.340

7.372

7.382

7.386

7.389

ppm

0

2

4

6

8

0

 $J=18$ $J=2 \text{ Hz}$

3.00

1.97

3.01

10.34

5aa

Me NOH

Me BCM

5aa

14.181

44.016

50.836

128.288
127.486
125.598

PPM

25

50

75

100

125

150

175

200

5aa

Me DEPT

[Mass Spectrum]
Date : 24-Jul-2014 16:03
Data : nishino2355
Sample: rm-Me/Matsumoto
Note : Acetone+NBR
Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
Scan# : (4,7)
RT : 0.78 min
BP : m/z 262.1921 Int. : 110.86
Output m/z range : 50.0000 to 515.3561
Cut Level : 0.00 %
4649516

5aa

4000.0 3500.0 3000.0 2500.0 2000.0 1750.0 1500.0 1250.0 1000.0 750.0 1/cm
 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
 %T
 17:52:11 2014/07/24 時刻: 10 積算回数: 10
 SHIMADZU 検出器: standard
 %T 3998.16 波数範囲: 4000 4.0
 192868 分解能: 2.8(low)
 auto ミニ速度:

Et NON

Et DEPT

[Mass Spectrum]

Date : 23-May-2014 14:53

Data : nishino2319

Sample: rm-381/Matsumoto

Note : Acetone+NBA

Inlet : Direct Ion Mode : FIB+

Spectrum Type : Normal Ion [MF-Linear]

RT : 0.52 min Scan# : (3,5)

BP : m/z 262.2130 Int. : 32.81

Output m/z range : 50.0000 to 495.4392

Cut Level : 0.00 %

0.000

1.259

1.273

1.287

1.609

2.334

2.337

3.547

3.549

4.142

4.157

4.171

4.186

6.994

7.001

7.004

7.018

7.030

7.035

7.041

7.259

7.301

7.307

7.311

7.318

7.321

7.325

7.331

7.335

7.342

PPM

0

2

4

6

8

0

$$(1.287 - 1.259) \div 2 \times 500 = 71.0 \text{ Hz}$$

$$= 0.515$$

$$(1.337 - 2.334) \div 2 \times 500 = 500$$

3.00

$$(3.549 - 3.547) \times 500 = 1$$

2.04

2.00

$$(4.186 - 4.142) \div 3 \times 500 = 731 \text{ Hz}$$

3.92

3.93

5bb

- F Not

-F BcH

-F DEPT

4000.0 3500.0 3000.0 2500.0 2000.0 1750.0 1500.0 1250.0 1000.0 750.0 1/cm

DEFAULT: IRS: cm Phf
 日付: 2014/10/02
 時刻: 17:02
 機種: HYPER IR
 波数範囲: 4000.0 ~ 100.0
 分解能: 4.0
 ミラー速度: 2.8 (low)

22:36:48
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 検出器: 検出器
 波数範囲: 4000.0 ~ 100.0
 分解能: 4.0
 ミラー速度: 2.8 (low)

22:36:48
 SHIMADZU
 検出器: 検出器
 波数範囲: 4000.0 ~ 100.0
 分解能: 4.0
 ミラー速度: 2.8 (low)

C:\Users\CEAC\Z@NMR-p\Desktop\NMR\H26 M2ffHf^\1/4-{-\alpha^1\phcl non-1.jdf

DFILE	phcl non-1.jdf
COMNT	single_pulse
DATIM	2014-10-01 20:44:29
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16384
FREQU	9384.38 Hz
SCANS	4
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.25 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	50

128 BC1

14.352
14.123

43.959

59.697

128.545
126.990

-cd DEPT

4000.0
 DEFAULT IRS: m Phcl
 日付: 2014/10/02
 時刻: 22:27:57
 測定機: SHIMADZU
 検出器: 検出器: None
 波数範囲: 4000
 分解能: 4.0
 ミラー速度: 2.8(low)

-H₂ NOH

-Me DEPT

4000.0
 DEFAULT: ohms
 日付: 2015/02/26
 機種: HYPER IR
 測定波数: 601.75
 最小波数: 1762
 測定範囲: 1.92868
 分解能: auto
 積分: auto
 3500.0
 時刻: ユーザー
 機種: SHIMADZU
 測定波数: 3998.16
 最小波数: 1.92868
 測定範囲: 1.92868
 分解能: auto
 積分: auto
 3000.0
 積算回数: 10
 検出器: standard
 フォトダイオード: None
 波数範囲: 1/cm
 分解能: 4.0
 ミラー速度: 2.8(low)

NR Non

10.55

2.98

2.92

2.12

2.03

2.00

$(0.963-0.933) \div 2 \times 500$
 $\delta = 7.5$

$(4.072-4.046) \div 2 \times 500$
 $\delta = 1.5$

$J = 1.9$

$J = 1.5$

$J = 6.6$

PPM

0.000

0.933

0.948

0.963

1.615

1.625

1.639

1.653

1.667

1.681

2.352

2.356

3.604

3.607

4.046

4.060

4.072

7.241

7.244

7.256

7.270

7.311

7.326

7.337

7.341

7.380

7.394

7.397

nPr BCM

5ca

*ν*Pr DEPT

5ca

[Mass Spectrum]
Date : 24-Jul-2014 16:27
Data : nishino2357
Sample: rm-nPr/Matsumoto
Note : Acetone-NBR
Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion (MF-Linear)
Scan# : (4,7)
RT : 0.78 min
BP : m/z 262.1862 Int. : 86.98
Output m/z range : 50.0000 to 768.8427
Cut Level : 0.00 %
3648240

5ca

4000.0
 DEFAULT: IRS: cm-1
 3500.0
 3000.0
 2500.0
 2000.0
 1750.0
 1500.0
 1250.0
 1000.0
 750.0
 667.3
 1/cm

18.0446
 SHIMADZU
 2014/07/24
 HYPER IR
 1/cm
 601.75
 1.92868
 auto
 10
 standard
 10
 3998.16
 1/cm
 4.0
 2.8(low)

2879.5
 2399.3
 2972.1
 1490.9
 1448.4
 1380.9
 1330.8
 1208.3
 1137.9
 1099.3
 1078.1
 974.0
 910.3
 826.8
 731.0
 702.0
 667.3

5ca

0.000

1.235
1.247

2.343

3.588
3.5915.000
5.012
5.025
5.038
5.050
5.063
5.0747.241
7.249
7.255
7.270
7.311
7.327
7.342
7.382
7.397

PPM

$$(1.247 - 1.235) \times 500$$

$$= 6.1 \text{ Hz}$$

6.03

 $\delta = 5$

2.93

 $\delta = 1.5$

2.00

$$(5.074 - 5.000) \approx 6 \times 300$$

$$= 6.2 \text{ Hz}$$

500

0.93

10.53

5da

2 Ph NOH

14.238
22.107
44.245
66.718
76.742
77.000
77.248
91.288
102.057
125.655
127.448
128.288
145.275
165.382
165.859

ppm

5da

28.86CM

14.209

22.078

44.217

66.689

125.626

127.420

128.259

PPM

0

25

50

75

100

125

150

175

200

5da

2P1 DEPT

[Mass Spectrum]
Data : nishino2359
Sample: rm-IPr/Matsumoto
Note : Acetone+NBR
Inlet : Direct
Spectrum Type : Normal Ion [MF-Linear]
Scan# : (3.5)
RT : 0.52 min
BP : m/z 262.2220 Int. : 178.04
Output m/z range : 50.0000 to 787.7596

Date : 25-Jul-2014 15:58

Ion Mode : FAB+

Cut Level : 0.00 %

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 2014/10/15
 HYPER IR
 1/cm
 601.75
 1762
 auto
 16:27:07
 SHIMADZU
 %T
 3998.16
 1.92868
 auto
 10
 standard
 None
 1/cm
 4.0
 28(low)
 ミラー速度

uBu NDN

5ea

11.19

ppm

- 7.397
- 7.393
- 7.390
- 7.382
- 7.380
- 7.377
- 7.373
- 7.342
- 7.338
- 7.328
- 7.325
- 7.315
- 7.312
- 7.307
- 7.274
- 7.272
- 7.269
- 7.262
- 7.257
- 7.252
- 7.249
- 7.246
- 7.242
- 7.240

- 4.115
- 4.101
- 4.087
- 3.599

- 2.352
- 2.349
- 2.345
- 1.649
- 1.635
- 1.622
- 1.606
- 1.592
- 1.427
- 1.412
- 1.397
- 1.382
- 1.367
- 1.352
- 0.946
- 0.931
- 0.916
- 0.000

nBu BOM

nBu DEPT

5ea

[Mass Spectrum]
 Date : 25-Jul-2014 16:19
 Data : nishino2361
 Sample: rm-rNbvMatsumoto
 Note : Acetone+NBA
 Inlet : Direct
 Ion Mode : FAB+
 Spectrum Type : Normal Ion [MF-Linear]
 Scan# : (5,10)
 RT : 1.12 min
 Int. : 66.59
 BP : m/z 262.2026
 Output m/z range : 50.0000 to 749.9258
 Cut Level : 0.00 %
 4189664

0.000

1.713

2.223

2.381

2.383

2.387

3.661

3.665

7.250

7.259

7.264

7.269

7.275

7.279

7.281

7.317

7.320

7.329

7.333

7.343

7.346

7.368

7.373

7.375

7.385

7.389

7.392

ppm

9

8

0

2.96

2.90

$\delta = 2.2 \times 10^{-5}$
(18.8°C - 19.4°C)

2.00

$\delta = 2.0 \times 10^{-5}$
(19.2°C - 19.9°C)

2.13

3.88

1.81

7

476-477 NON

476.477 Bcm

7

476-477 DEPT

7

DFILE No.481 TLC2-1 end.als
 COMNT single_pulse
 DATIM 2014-08-08 14:25:27
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 10
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.25 µsec
 IRNUC 1H
 CTEMP 23.1 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 46

7.430
 7.427
 7.423
 7.414
 7.409
 7.401
 7.398
 7.393
 7.386
 7.383
 7.381
 7.374
 7.369
 7.354
 7.309
 7.305
 7.301
 7.298
 7.291
 7.283
 7.281
 7.275
 7.270
 7.256
 7.250
 7.247
 7.242
 7.232
 7.227

45.562

128.822
128.516
128.412
128.249
125.436
125.388

4000.0 3500.0 3000.0 2500.0 2000.0 1750.0 1500.0 1250.0 1000.0 750.0 1/cm
 DEFAULT:IR: m malonic acid
 日付: 2014/10/02 時刻: 22:17:58
 デバイス: HYPER IR 検出器: SHIMADZU
 検出器: 1/cm 検出器: 10
 検出器: 601.75 検出器: 3998.16
 データ点数: 1762 検出器: 1.92868
 デバイス: auto 検出器: auto
 デバイス: 検出器: 2.8(low)

C:\Users\CEZ\Z@NMR...p\Desktop\NMRff\H26 M2ff\Hf\¼-{-α¹ diethyl malonate non-1,jdf

D:\FILE diethyl malonate non-1.jdf

COMNT single_pulse

DATIM 2014-10-01 20:35:03

OBNUC 1H

EXMOD single_pulse.ex2

OBFRQ	500.16 MHz
-------	------------

OBSET	2.41 KHZ
-------	----------

OBFIN	6.01 Hz
-------	---------

POINT 16384

FREOU 9384.38 Hz

SCANS 9

ACOTM 1.7459 sec

PD	5.0000 sec
ACQIM	1.7133 sec

PW1	6.25 μ sec
PW2	3.0000 sec

IRNIC 1H

ИННУС	III
СТЕМР	2110

INITIALS DATE

[illegible]

Label	Frequency
EAKRF	0.00 ppm
RE	0.10 Hz

BF	0.10 Hz
PCAIN	18

KGAIN 48

9

14.085

61.882

129.012
128.898
126.590

164.495

ppm

0 25 50 75 100 125 150 175 200

9

ACEAGEIRS: m. acetylacetone
 4000.0 3500.0 3000.0 2500.0 2000.0 1750.0 1500.0 1250.0 1000.0 750.0 1/cm
 日付: 2014/10/02 時刻: 22:42:32 積算回数: 10
 テーブル: HYPER IR SHIMADZU 検出器: standard
 検出器: 7本タイム 関数: None
 検出器: 3998.16 波数範囲: 1/cm
 テーブル: 1.92868 分解能: 4.0
 テーブル: auto ミラー速度: 2.8(low)

DFILE alkene addition non-1.jdf

COMNT single pulse

DATIM 2014-10-03 18:40:33

OBNUC 1H

EXMOD single_pulse.ex2

OBFREQ 500.16 MHz

OBSSET 2.41 KHz

OBFIN 6.01 Hz

POINT 16384

FREQ 9384.38 Hz

SCANS 13

ACQTM 1.7459 sec

PD 5.0000 sec

PW1 6.25 usec

IRNUC 1H

CTEMP 21.1 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 36

10

7.22

5.70

3.82
4.91

1.97

1.00

DFILE alkene addition bcm-1.jdf
 COMNT single pulse decoupled gated NOE
 DATIM 2014-10-03 18:43:55
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 32768
 FREQU 39308.18 Hz
 SCANS 48
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 21.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 58

alkene addition dept-1.jdf

COMPT DEPT with decoupling

DATIM 2014-10-03 18:45:46

OBNUC 13C

EXMOD deptex2

OBFRQ 125.77 MHz

OBSET 7.87 KHz

OBFIN 4.21 Hz

POINT 32768

FREQU 39308.18 Hz

SCANS 18

ACQTM 0.8336 sec

PD 2.0000 sec

PW1 10.00 usec

IRNUC 1H

CTEMP 21.3 c

SLVNT CDCL3

EXREF 77.00 ppm

BF 0.12 Hz

RGAIN 56

10