

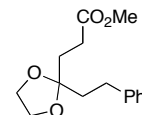
Supporting Information

DIASTEREO- AND ENANTIOSELECTIVE CONSTRUCTION OF 6,7-DIOXABICYCLO[2.2.1]HEPTANE DERIVATIVES BY A DIRHODIUM(II)-CATALYZED INTRAMOLECULAR C–H INSERTION REACTION

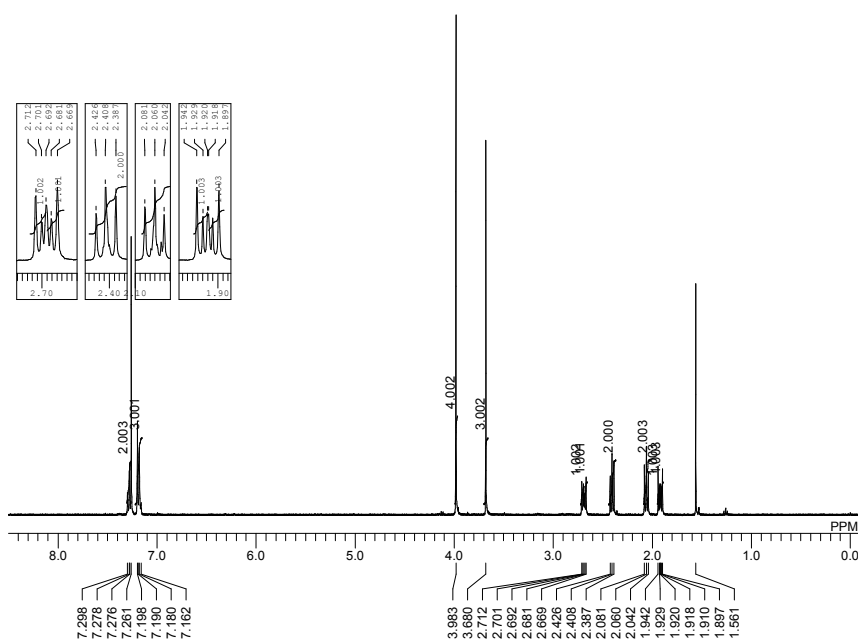
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Shigeki Matsunaga, and Shunichi Hashimoto*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan

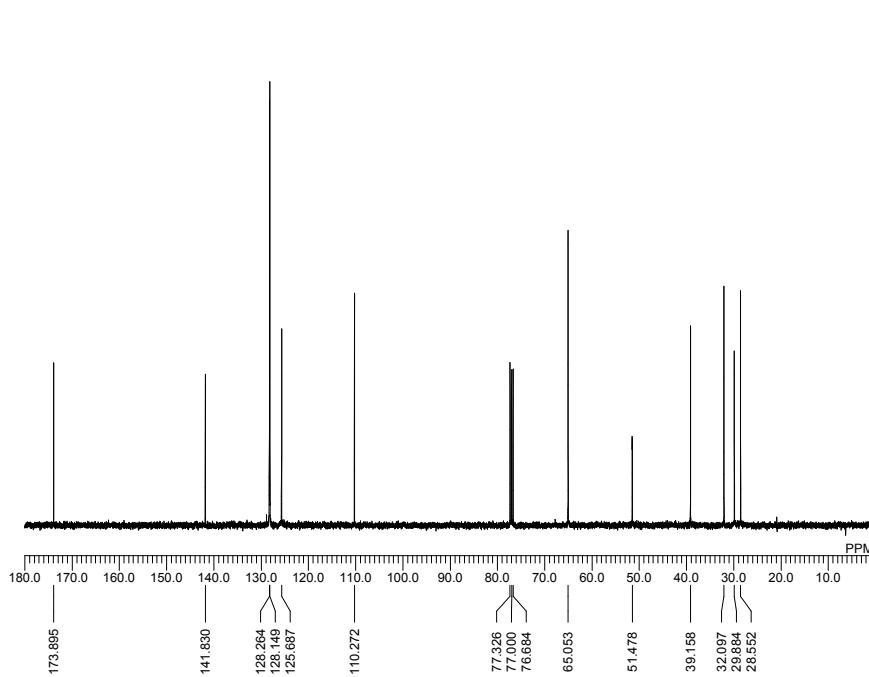
Methyl 3-[2-(2-phenylethyl)-1,3-dioxolan-2-yl]propanoate (17)



17

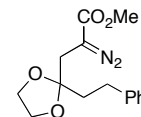


DFILE 12 methyl 3-[2-(2-phenylethyl
 COMNT 12 methyl 3-[2-(2-phenylethyl
 DATIM 2016-06-07 21:22:10
 1H
 EXMOD single_pulse.ex2
 OBFREQ 395.88 MHz
 OBSET 6.28 KHz
 OBFIN 0.87 Hz
 POINT 13107
 FREQU 5938.15 Hz
 SCANS 8
 ACQTM 2.2073 sec
 PD 3.0000 sec
 PW1 6.40 usec
 1H
 IRNUC 21.4 c
 CTEMP CDCL3
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 40

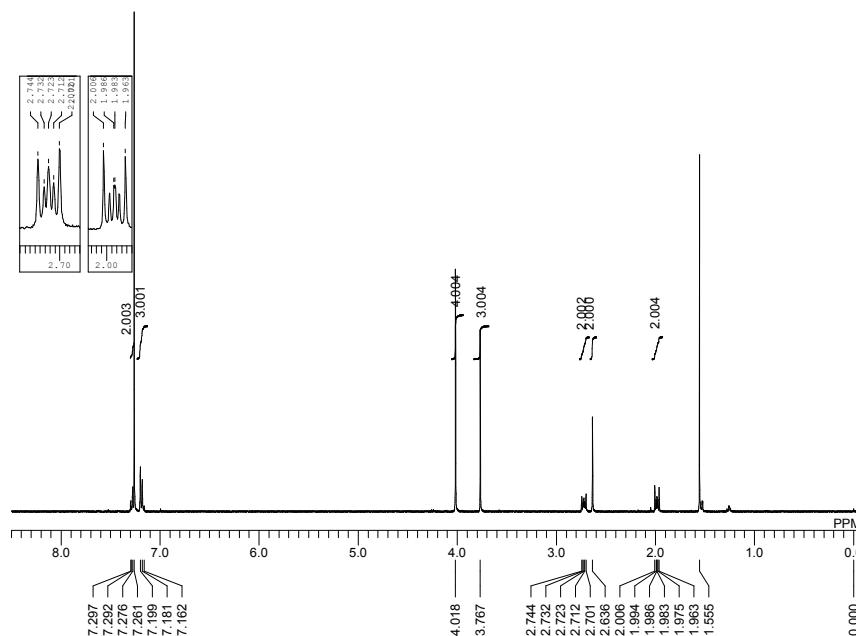


DFILE 12 methyl 3-[2-(2-phenylethyl
 COMNT 12 methyl 3-[2-(2-phenylethyl
 DATIM 2016-08-16 15:19:55
 13C
 EXMOD single_pulse_dec
 OBFREQ 99.55 MHz
 OBSET 5.13 KHz
 OBFIN 0.98 Hz
 POINT 26214
 FREQU 24999.62 Hz
 SCANS 54
 ACQTM 1.0486 sec
 PD 2.0000 sec
 PW1 3.33 usec
 1H
 IRNUC 21.5 c
 CTEMP CDCL3
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.00 Hz
 RGAIN 60

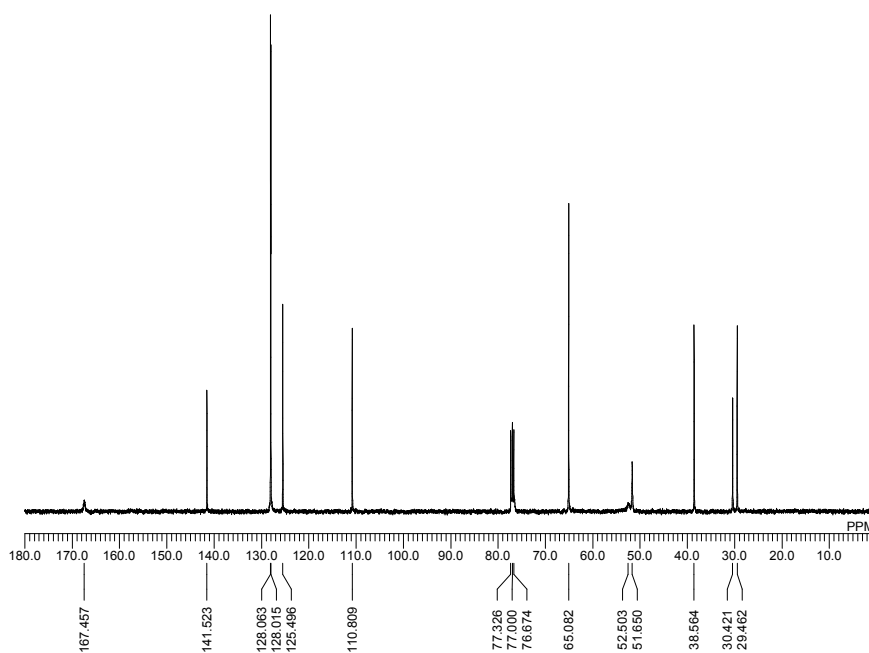
Methyl 2-diazo-3-[2-(2-phenylethyl)-1,3-dioxolan-2-yl]propanoate (13)



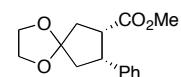
13



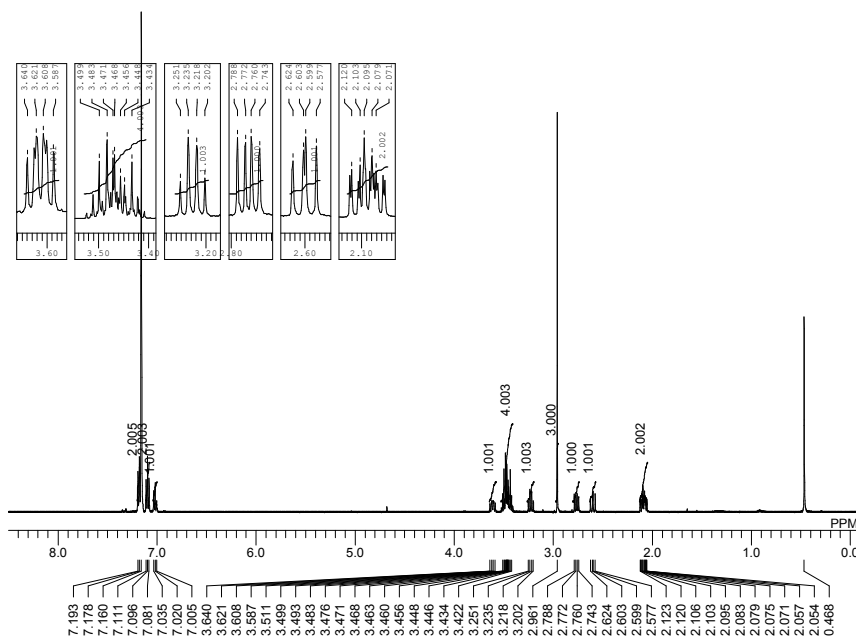
DFILE 13-1 methyl 2-diazo-3-[2-(2-pl
 COMNT 13 methyl 2-diazo-3-[2-(2-pl
 DATIM 2016-06-10 13:32:23
 1H
 EXMOD single_pulse.ex2
 OBFREQ 395.88 MHz
 OBSSET 6.28 KHz
 OBFIN 0.87 Hz
 POINT 13107
 FREQU 5938.15 Hz
 SCANS 8
 ACQTM 2.2073 sec
 PD 3.0000 sec
 PW1 6.40 usec
 1H
 IRNUC 21.0 c
 CTMP CDCL3
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 42



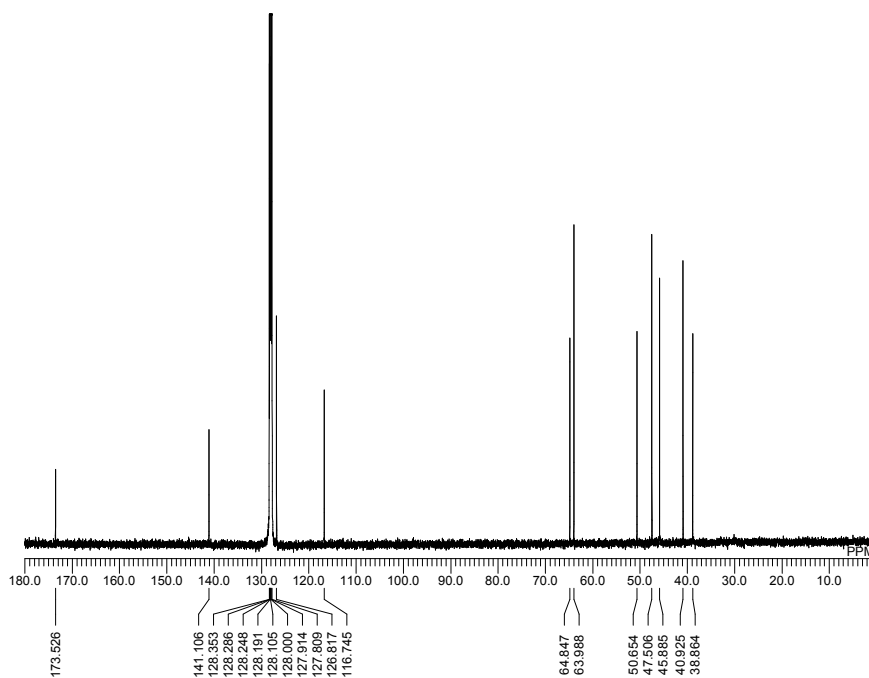
DFILE 13 methyl 2-diazo-3-[2-(2-pl
 COMNT 13 methyl 2-diazo-3-[2-(2-pl
 DATIM 2016-08-20 11:16:14
 13C
 EXMOD single_pulse_dec
 OBFREQ 99.55 MHz
 OBSSET 5.13 KHz
 OBFIN 0.98 Hz
 POINT 26214
 FREQU 24999.62 Hz
 SCANS 54
 ACQTM 1.0486 sec
 PD 5.0000 sec
 PW1 3.33 usec
 1H
 IRNUC 21.7 c
 CTMP CDCL3
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 60

(7*S*,8*R*)-Methyl *cis*-8-phenyl-1,4-dioxaspiro[4.4]nonane-7-carboxylate (14)

14

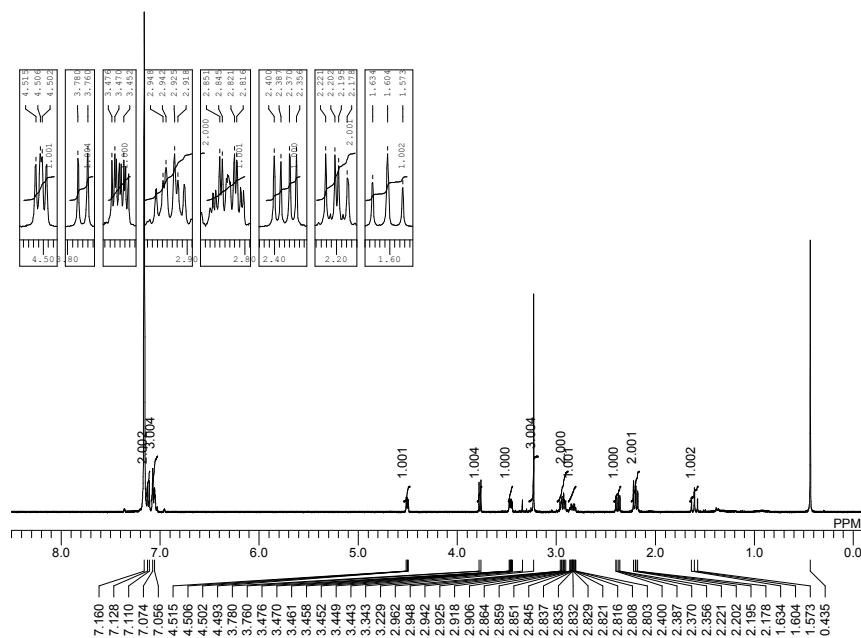
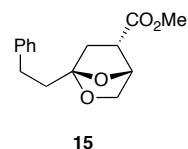


DFILE 14 (7*S*, 8*R*) methyl *cis*-8-ph
 COMNT TM03131 pro2, *cypentane* ()
 DATIM 2016-08-22 23:59:49
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 7.0000 sec
 PW1 6.35 usec
 IRNUC 1H
 CTEMP 24.3 c
 SLVNT CDCl₃
 EXREF 7.16 ppm
 BF 0.12 Hz
 RGAIN 48

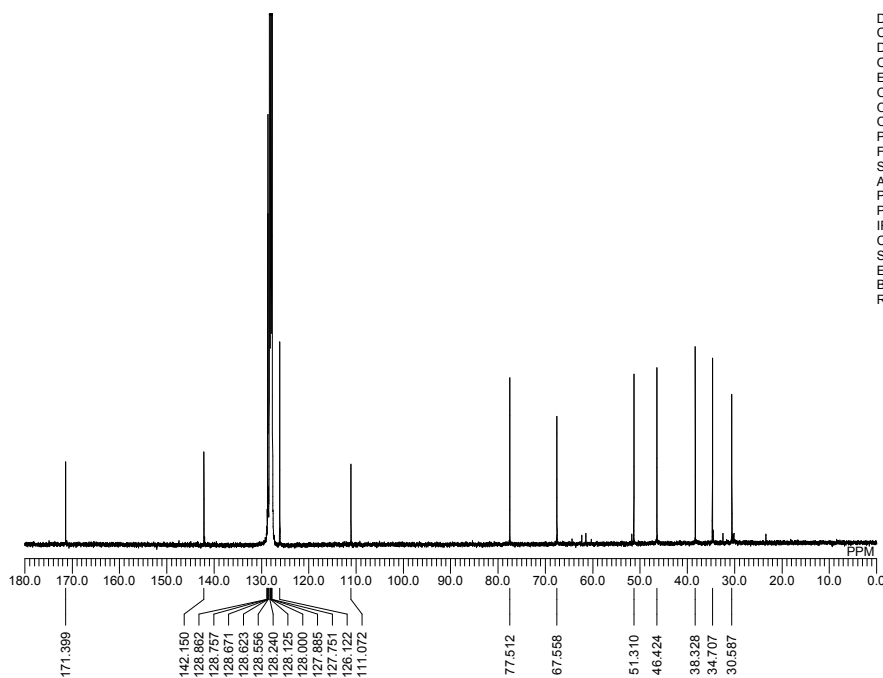


DFILE 14 (7*S*, 8*R*) methyl *cis*-8-ph
 COMNT 14 (7*S*, 8*R*) methyl *cis*-8-ph
 DATIM 2016-06-22 12:32:48
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 2340
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.57 usec
 IRNUC 1H
 CTEMP 22.7 c
 SLVNT CDCl₃
 EXREF 128.00 ppm
 BF 1.00 Hz
 RGAIN 60

(1*S*,3*S*,4*R*)-methyl 1-(2-phenylethyl)-6,7-dioxabicyclo[2.2.1]heptane-3-carboxylate (15)

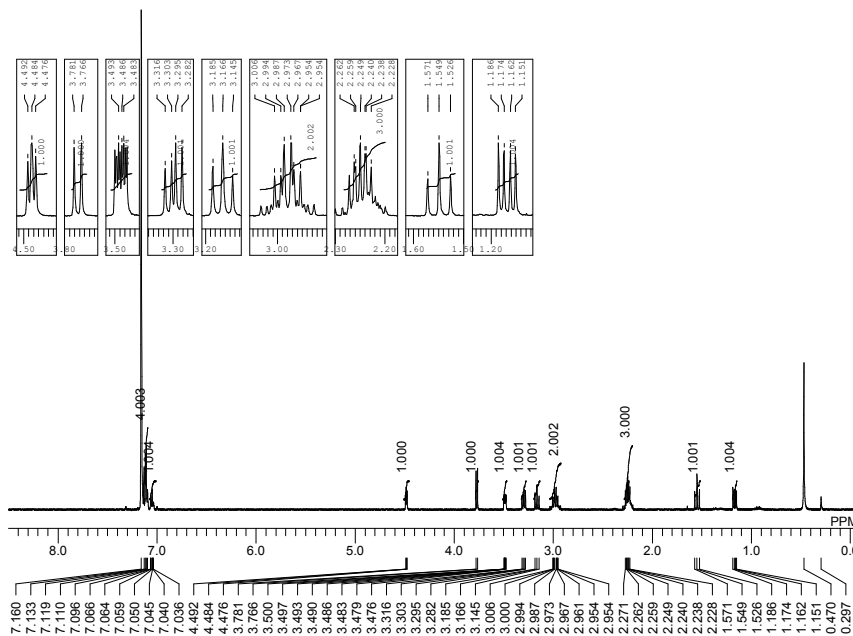
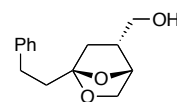


DFILE 15 (1*S*, 3*S*, 4*R*)-methyl 1-2
 COMNT 15 (1*S*, 3*S*, 4*R*)-methyl 1-2
 DATIM 2016-09-02 09:23:51
 OBNUC 1H
 EXMOD 1H.ex2
 OBFREQ 391.78 MHz
 OBSSET 8.51 KHz
 OBFIN 3.34 Hz
 POINT 16384
 FREQU 7352.94 Hz
 SCANS 8
 ACQTM 2.2282 sec
 PD 3.0000 sec
 PW1 5.80 usec
 IRNUC 1H
 CTEMP 19.2 c
 SLVNT C6D6
 EXREF 7.16 ppm
 BF 0.12 Hz
 RGAIN 46

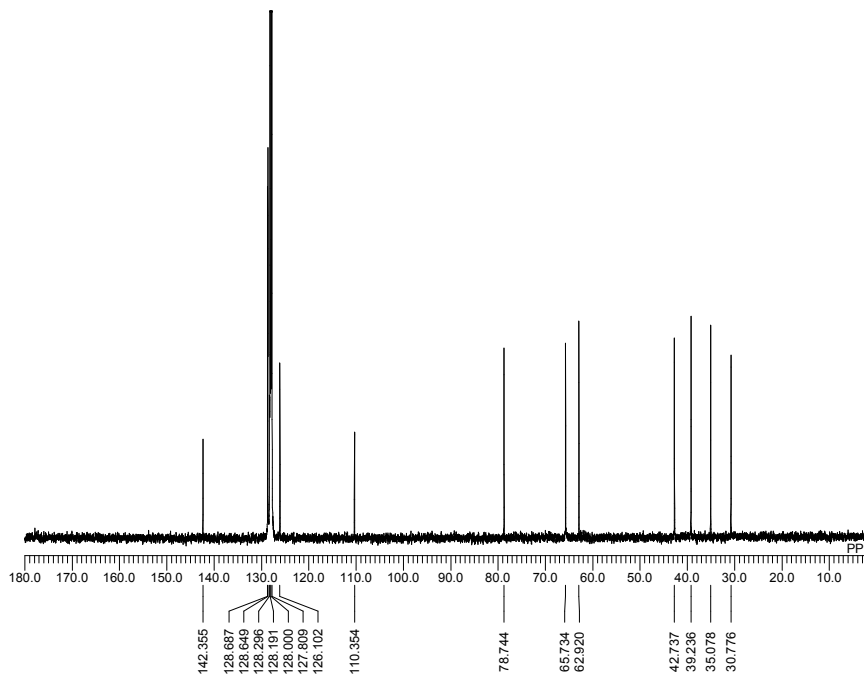


DFILE 15 (1*S*, 3*S*, 4*R*)-methyl 1-2
 COMNT 15 (1*S*, 3*S*, 4*R*)-methyl 1-2
 DATIM 2016-09-06 07:24:08
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 99.55 MHz
 OBSSET 5.13 KHz
 OBFIN 0.98 Hz
 POINT 32768
 FREQU 31250.00 Hz
 SCANS 12705
 ACQTM 1.0486 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 21.9 c
 SLVNT C6D6
 EXREF 128.00 ppm
 BF 1.00 Hz
 RGAIN 60

**[(1*S*,3*R*,4*R*)-1-(2-phenylethyl)-6,7-dioxabicyclo[2.2.1]heptan-3-yl]
methanol**

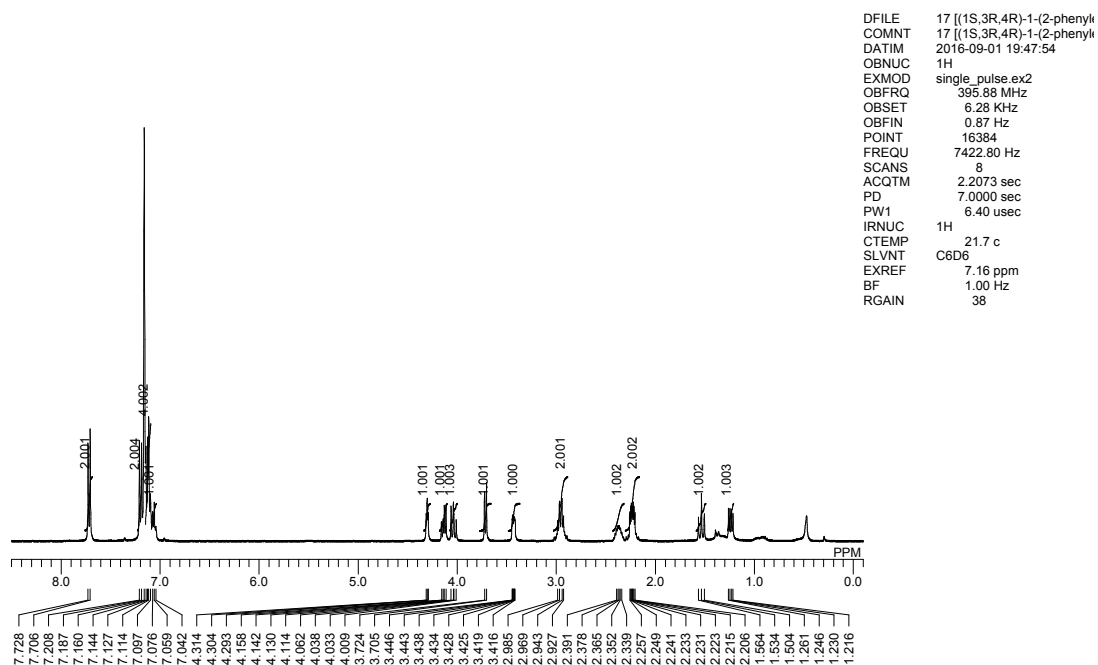
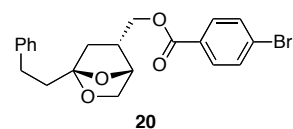


DFILE 17-1 [(1*S*,3*R*,4*R*)-1-(2-phen
COMNT 17-1 [(1*S*,3*R*,4*R*)-1-(2-phen
DATIM 2016-08-24 19:20:10
OBNUC 1H
EXMOD single_pulse.ex2
OBFREQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 7.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 423.7 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.12 Hz
RGAIN 48

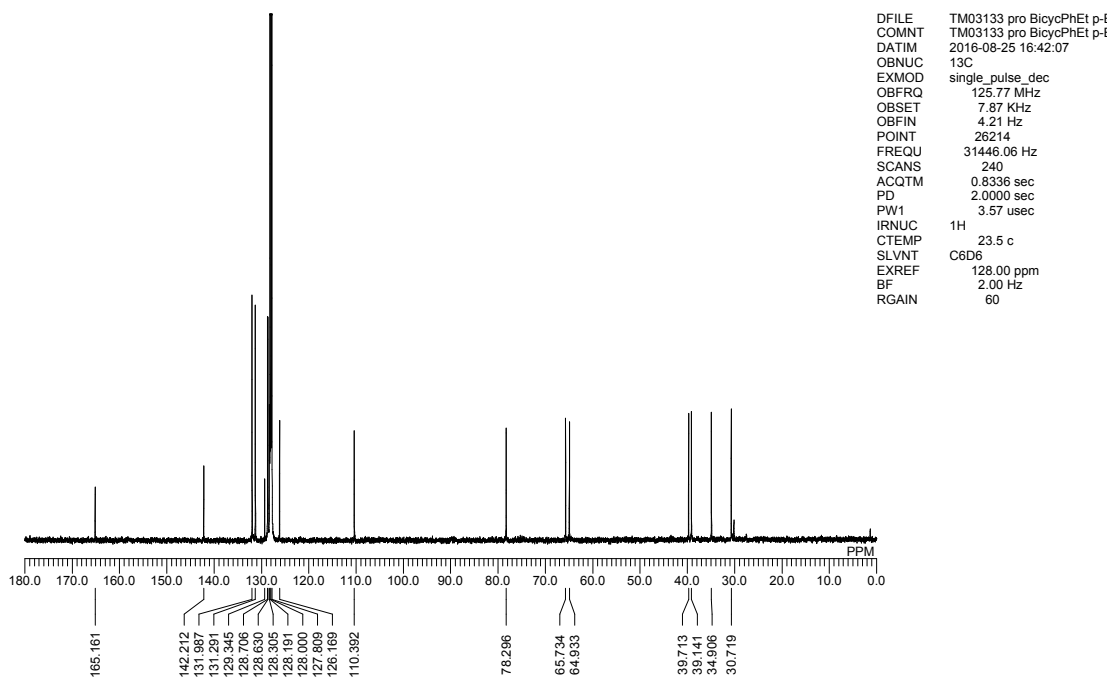


DFILE 17-1 [(1*S*,3*R*,4*R*)-1-(2-phen
COMNT 17-1 [(1*S*,3*R*,4*R*)-1-(2-phen
DATIM 2016-08-24 19:35:44
OBNUC 13C
EXMOD single_pulse_dec
OBFREQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 199
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 387.8 c
SLVNT C6D6
EXREF 128.00 ppm
BF 2.00 Hz
RGAIN 60

[(1*S*,3*R*,4*R*)-1-(2-phenylethyl)-6,7-dioxabicyclo[2.2.1]heptan-3-yl]methyl 4-bromobenzoate (20)

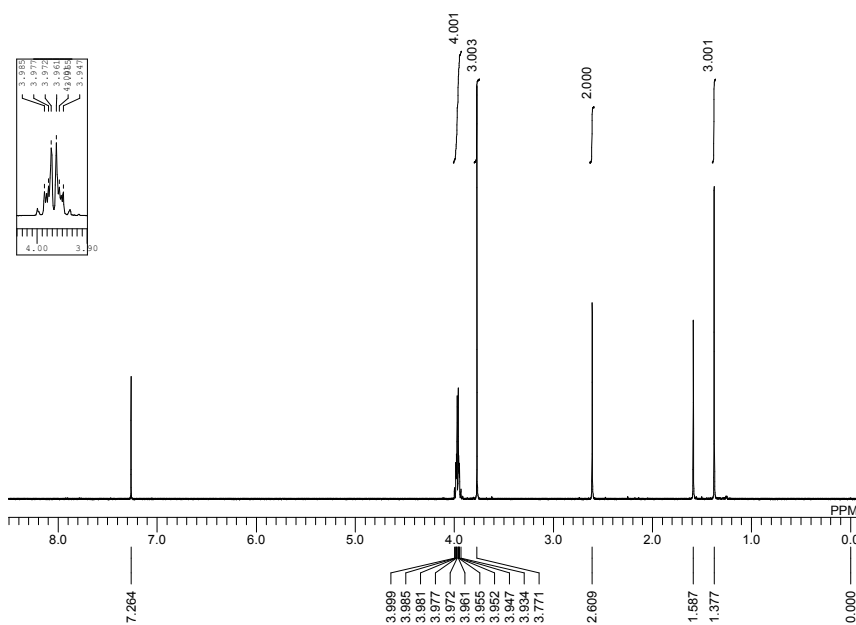
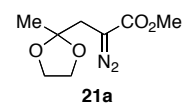


DFILE 17 [(1*S*,3*R*,4*R*)-1-(2-phenyl
COMNT 17 [(1*S*,3*R*,4*R*)-1-(2-phenyl
DATIM 2016-09-01 19:47:54
OBNUC 1H
EXMOD single_pulse.ex2
OBFREQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 16384
FREQU 7422.80 Hz
SCANS 8
ACQTM 2.2073 sec
PD 7.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCl₃
EXREF 7.16 ppm
BF 1.00 Hz
RGAIN 38

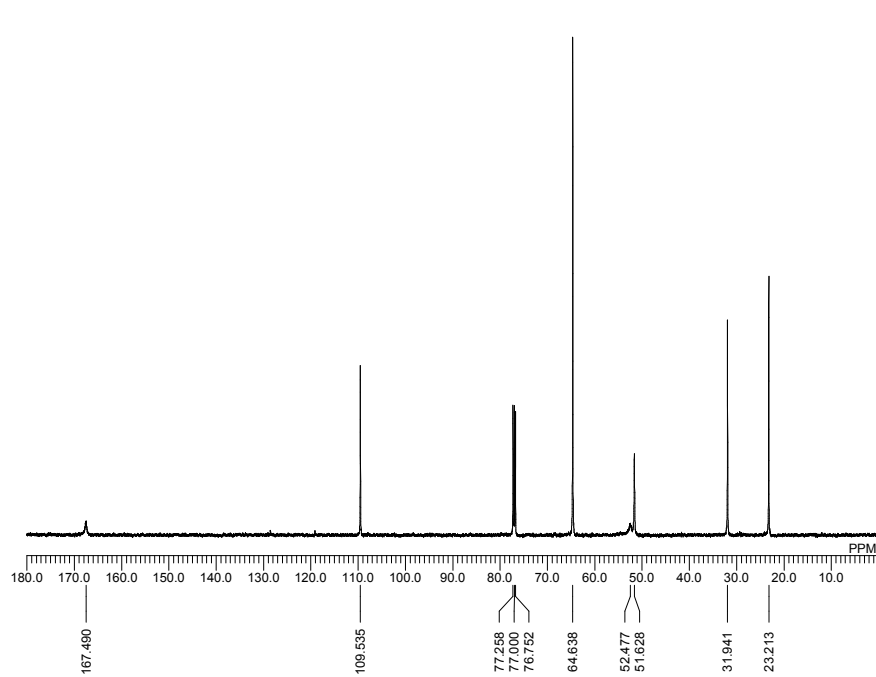


DFILE TM03133 pro BicycPhEt p-t
COMNT TM03133 pro BicycPhEt p-t
DATIM 2016-08-25 16:42:07
OBNUC 13C
EXMOD single_pulse_dec
OBFREQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 240
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCl₃
EXREF 128.00 ppm
BF 2.00 Hz
RGAIN 60

Methyl 2-diazo-3-(2-methyl-1,3-dioxolan-2-yl)propanoate (21a)

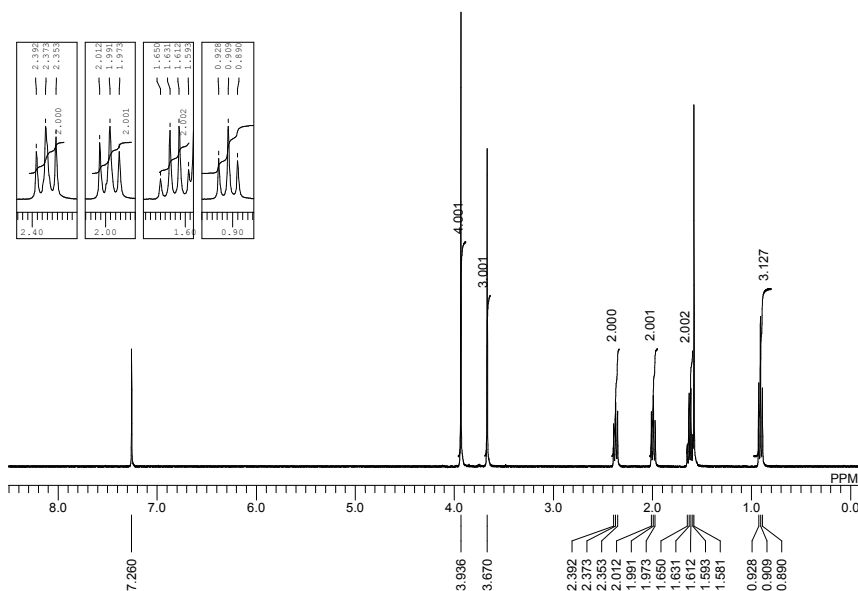
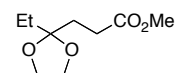


DFILE 13-2 methyl 2-diazo-3-(2-m
 COMNT 13-2 methyl 2-diazo-3-(2-m
 DATIM 2016-08-12 22:12:27
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFREQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 3.0000 sec
 PW1 6.35 usec
 IRNUC 1H
 CTEMP 22.7 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 50

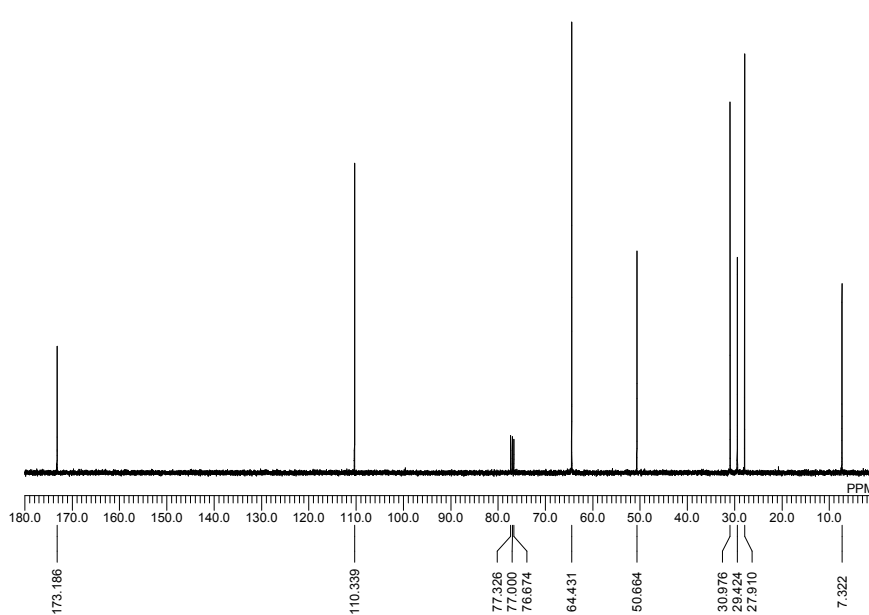


DFILE 13-2 methyl 2-diazo-3-(2-m
 COMNT 13-2 methyl 2-diazo-3-(2-m
 DATIM 2016-08-12 22:31:37
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 128
 ACQTM 0.8336 sec
 PD 5.0000 sec
 PW1 3.57 usec
 IRNUC 1H
 CTEMP 23.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 5.00 Hz
 RGAIN 60

Methyl 3-(2-ethyl-1,3-dioxolan-2-yl)propanoate

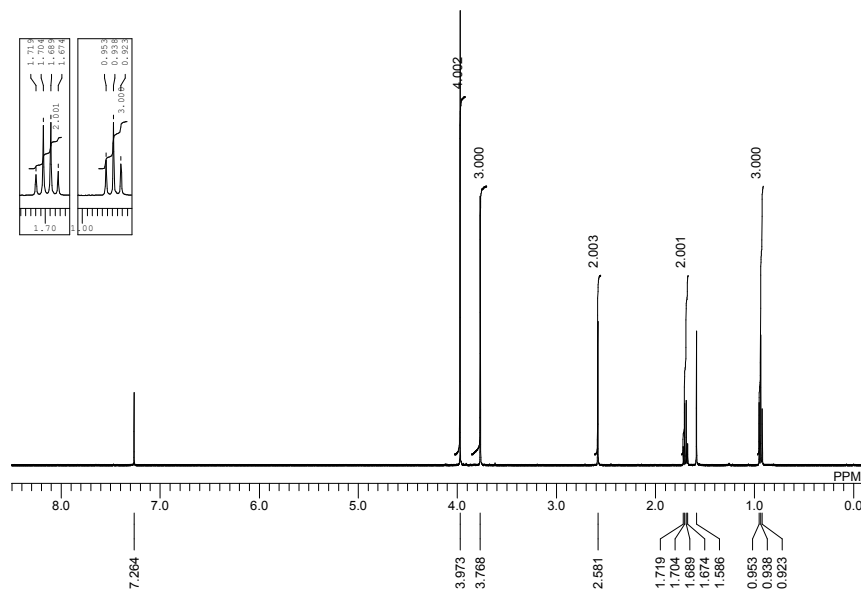
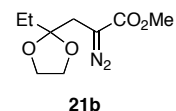


DFILE 12-3 methyl 3-(2-ethyl-1,3-d
 COMNT 12-3 methyl 3-(2-ethyl-1,3-d
 DATIM 2016-08-31 00:37:21
 1H
 EXMOD single_pulse.ex2
 OBFREQ 395.88 MHz
 OBSSET 6.28 KHz
 OBFIN 0.87 Hz
 POINT 13107
 FREQU 5938.15 Hz
 SCANS 8
 ACQTM 2.2073 sec
 PD 3.0000 sec
 PW1 6.40 usec
 1H
 CTEMP 21.6 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 40

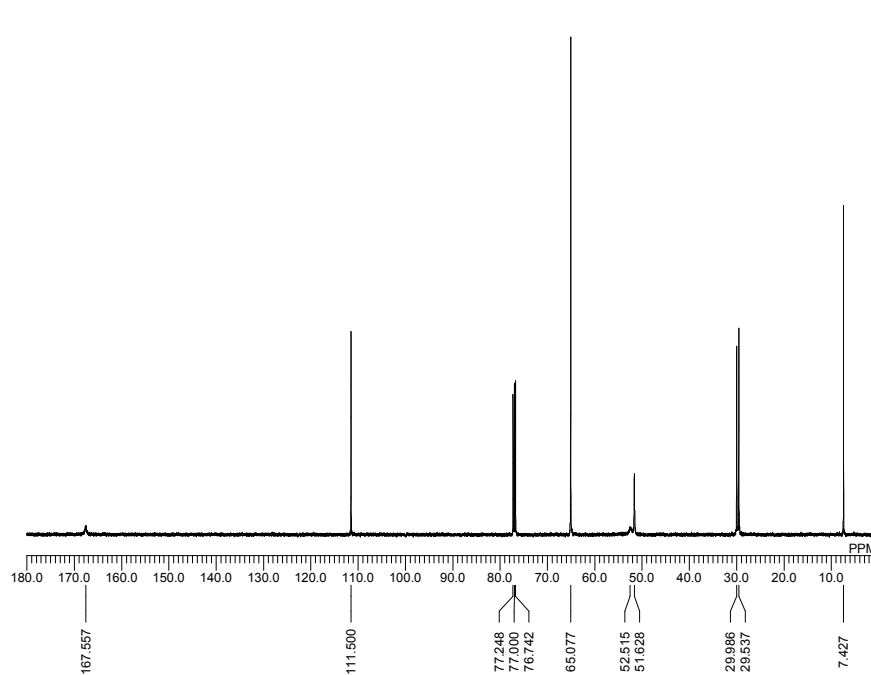


DFILE 12-3 methyl 3-(2-ethyl-1,3-d
 COMNT 12-3 methyl 3-(2-ethyl-1,3-d
 DATIM 2016-08-31 00:43:11
 13C
 EXMOD single_pulse_dec
 OBFREQ 99.55 MHz
 OBSSET 5.13 KHz
 OBFIN 0.98 Hz
 POINT 26214
 FREQU 24999.62 Hz
 SCANS 18
 ACQTM 1.0486 sec
 PD 2.0000 sec
 PW1 3.33 usec
 1H
 CTEMP 21.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

Methyl 2-diazo-3-(2-ethyl-1,3-dioxolan-2-yl)propanoate (21b)

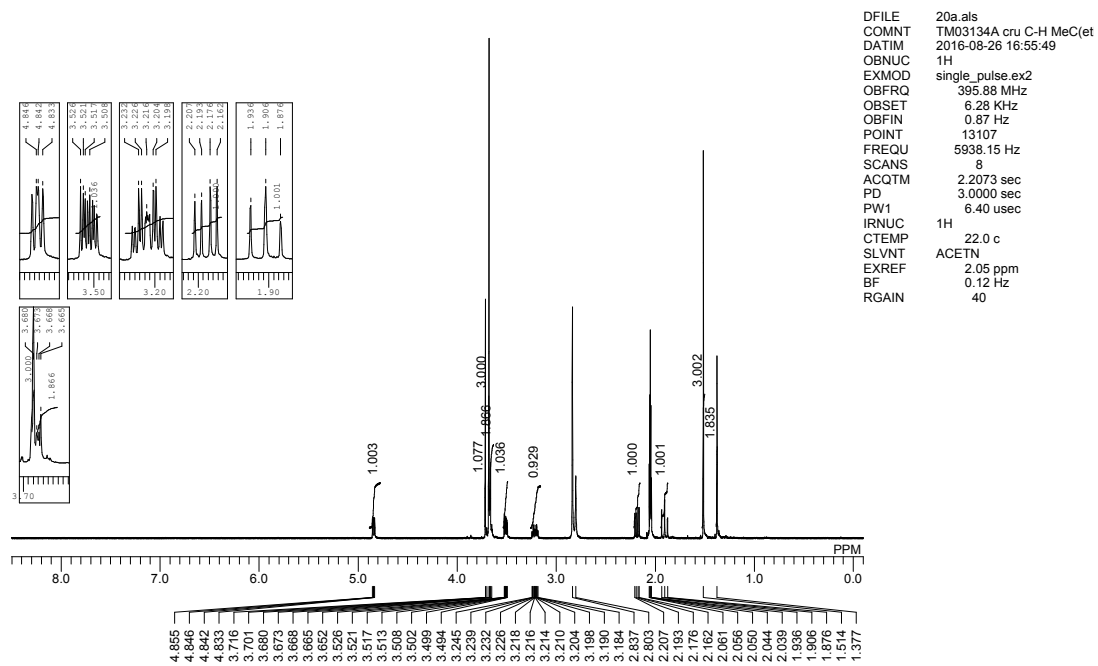
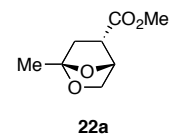


DFILE 13-3 methyl 2-diazo-3-(2-ethyl
 COMNT 13-3 methyl 2-diazo-3-(2-ethyl
 DATIM 2016-08-12 20:37:11
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFREQ 500.16 MHz
 OBSETE 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 3.0000 sec
 PW1 6.35 usec
 IRNUC 1H
 CTEMP 248.7 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 48

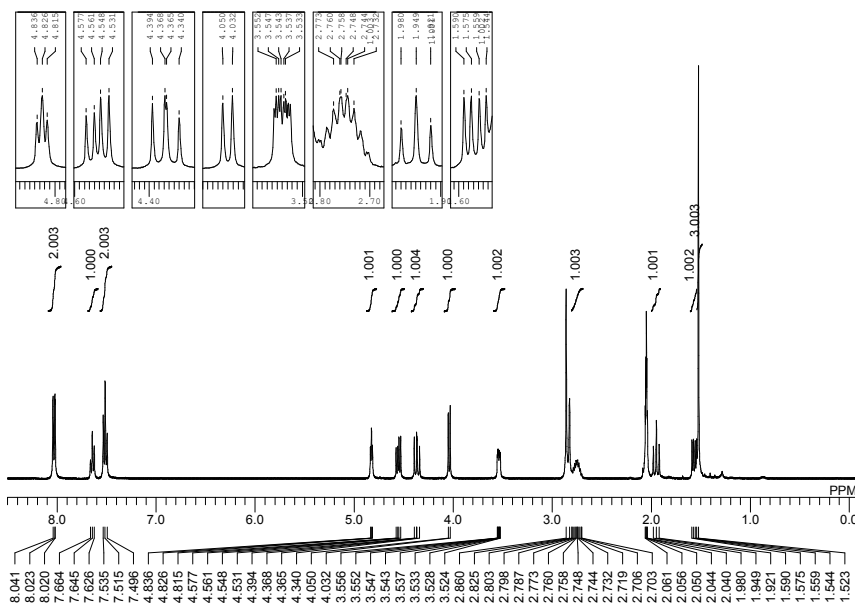
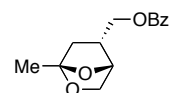


DFILE 13-3 methyl 2-diazo-3-(2-ethyl
 COMNT 13-3 methyl 2-diazo-3-(2-ethyl
 DATIM 2016-08-12 20:56:33
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSETE 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 131
 ACQTM 0.8336 sec
 PD 5.0000 sec
 PW1 3.57 usec
 IRNUC 1H
 CTEMP 23.8 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 60

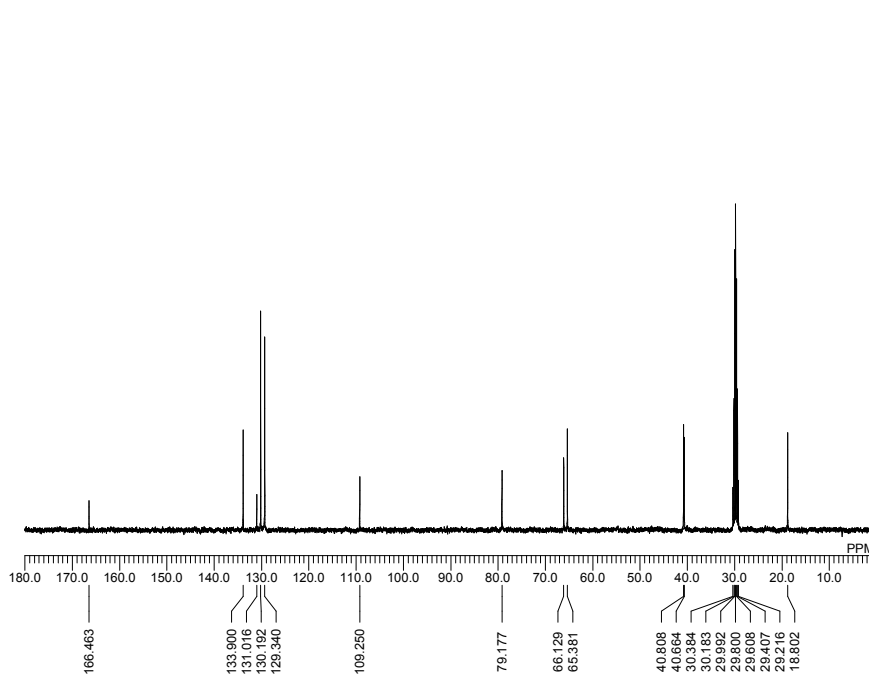
(1*S,3*S**,4*R**)-methyl 1-methyl-6,7-dioxabicyclo[2.2.1]heptane-3-carboxylate (22a)**
 (contaminated with an unidentified impurity)



[(1*S,3*R**,4*R**)-1-methyl-6,7-dioxa-bicyclo[2.2.1]heptan-3-yl]methyl benzoate**

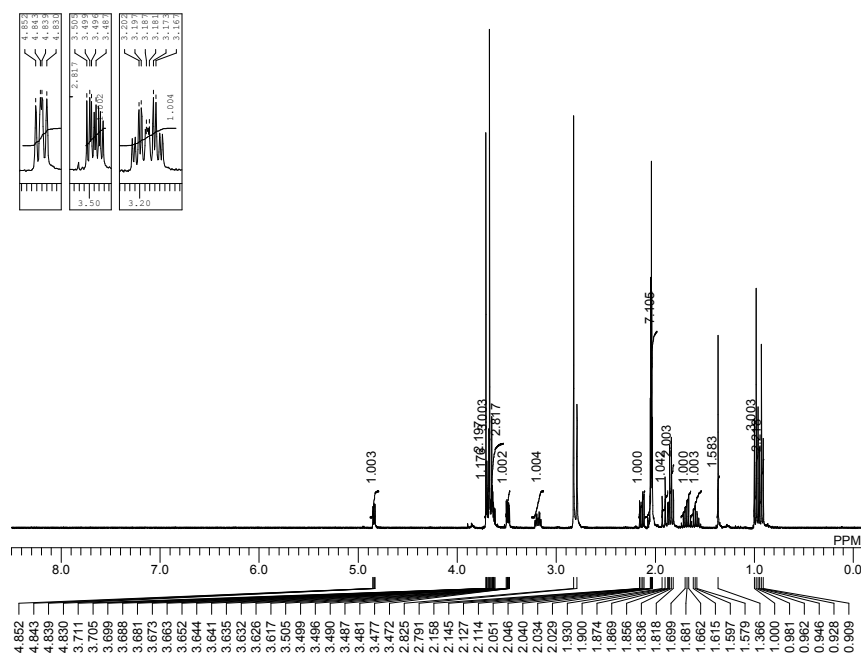
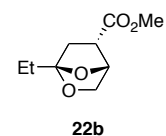


DFILE 21a-1 [(1*S*,3*R*,4*R*)-1-methyl
 COMNT 21a-1 [(1*S*,3*R*,4*R*)-1-methyl
 DATIM 2016-08-29 19:41:48
 1H
 EXMOD 1H.ex2
 OBFREQ 391.78 MHz
 OBSET 8.51 KHz
 OBFIN 3.34 Hz
 POINT 13107
 FREQU 5882.26 Hz
 SCANS 8
 ACQTM 2.2282 sec
 PD 7.0000 sec
 PW1 5.80 usec
 1H
 IRNUC 19.0 c
 CTEMP ACETN
 SLVNT ACETN
 EXREF 2.05 ppm
 BF 0.12 Hz
 RGAIN 44



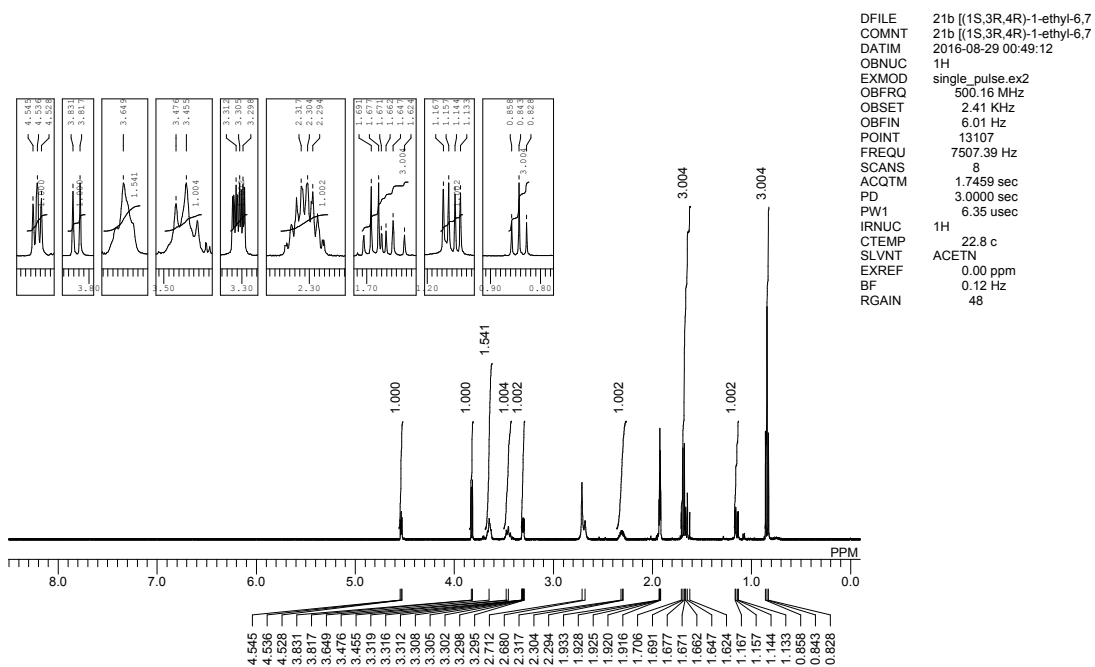
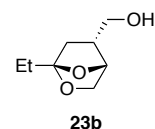
DFILE 21a-1 [(1*S*,3*R*,4*R*)-1-methyl
 COMNT 21a-1 [(1*S*,3*R*,4*R*)-1-methyl
 DATIM 2016-08-29 19:40:35
 13C
 EXMOD single_pulse_dec
 OBFREQ 99.55 MHz
 OBSET 5.13 KHz
 OBFIN 0.98 Hz
 POINT 26214
 FREQU 24999.62 Hz
 SCANS 84
 ACQTM 1.0486 sec
 PD 2.0000 sec
 PW1 3.33 usec
 1H
 IRNUC 21.8 c
 CTEMP ACETN
 SLVNT ACETN
 EXREF 29.80 ppm
 BF 2.00 Hz
 RGAIN 58

(1*S,3*S**,4*R**)-methyl 1-ethyl-6,7-dioxabicyclo[2.2.1]heptane-3-carboxylate**
(22b) (contaminated with an unidentified impurity)

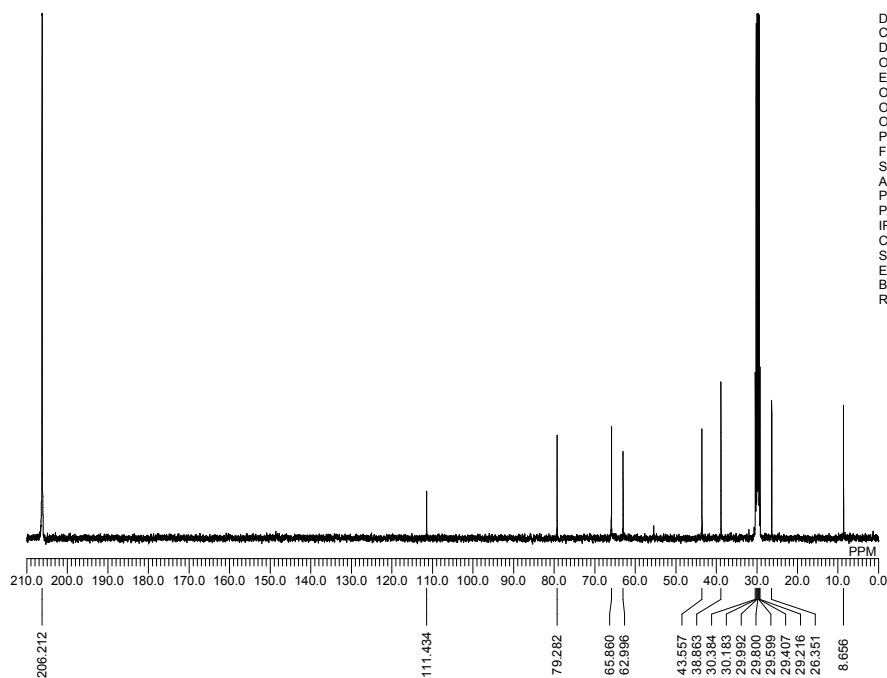


DFILE 20b.als
 COMNT 20b
 DATIM 2016-08-26 17:01:41
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRO 395.88 MHz
 OBSET 6.28 KHz
 OBFIN 0.87 Hz
 POINT 13107
 FREQU 5938.15 Hz
 SCANS 8
 ACQTM 2.2073 sec
 PD 3.0000 sec
 PW1 6.40 usec
 IRNUC 1H
 CTEMP 21.9 c
 SLVNT ACETN
 EXREF 2.04 ppm
 BF 0.12 Hz
 RGAIN 40

[(1*S**,3*R**,4*R**)-1-ethyl-6,7-dioxabicyclo[2.2.1]heptan-3-yl]methanol (23b)



DFILE 21b [(1*S*,3*R*,4*R*)-1-ethyl-6,7
 COMNT 21b [(1*S*,3*R*,4*R*)-1-ethyl-6,7
 DATIM 2016-08-29 00:49:12
 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 3.0000 sec
 PW1 6.35 usec
 1H
 CTEMP 22.8 c
 SLVNT ACETN
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 48



DFILE 21b [(1*S*,3*R*,4*R*)-1-ethyl-6,7
 COMNT 21b [(1*S*,3*R*,4*R*)-1-ethyl-6,7
 DATIM 2016-08-20 15:24:58
 13C
 EXMOD single_pulse_dec
 OBFRQ 99.55 MHz
 OBSET 5.13 KHz
 OBFIN 0.98 Hz
 POINT 26214
 FREQU 24999.62 Hz
 SCANS 501
 ACQTM 1.0486 sec
 PD 2.0000 sec
 PW1 3.33 usec
 1H
 CTEMP 21.6 c
 SLVNT ACETN
 EXREF 29.80 ppm
 BF 2.00 Hz
 RGAIN 60

