A Mild and Regioselective Method for α -Bromination of β -Keto Esters and 1,3-Diketones Using Bromodimethylsulfonium Bromide (BDMS)

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Experimental

General: All reactions were carried out at room temperature without any inert atmosphere. Elemental analyses were carried out in an automatic carbon, hydrogen, nitrogen and sulfur. Starting materials were purchased from commercial sources and used without further purification; some of the starting materials were prepared using standard literature procedure. Column chromatographic separations were done on silica gel (60-120 mesh). IR spectra were recorded in KBr or neat on a FTIR spectrophotometer. ^1H - and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in CDCl_3 using TMS as an internal reference.

Compound 1b:

SAMPLE
date Jun 15 2006 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 pw90 14.600
at 1.998 alfa 20.000
np 25528
fb not used i1 n
bs 4 in n
d1 1.000 dp y
nt 32 hs nn
ct 20
TRANSMITTER lb 0.10
tn H1 fn 65536
sfrq 399.853 DISPLAY
tof 362.8 sp -795.8
tpwr 60 wp 6389.8
pw 7.300 rfi 795.8
DECOUPLER C13 rfp 0
dn C13 rp 73.0
dof 0 lp -90.0
dm nnn
dmm c wc 250
dpwr 50 sc 0
dmf 17100 vs 73
nm cdc ph 20

SAMPLE
date Jun 15 2006 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25125.6 pw90 21.000
at 1.199 alfa 20.000
np 60270
fb 13800 i1 n
bs 16 in n
d1 1.000 dp y
nt 2000 hs nn
ct 808
TRANSMITTER C13 lb 2.00
tn C13 fn 65536
sfrq 100.554 DISPLAY
tof 1536.3 sp -1517.9
tpwr 61 wp 25125.6
pw 10.500 rfi 9282.8
DECOUPLER H1 rfp 7764.9
dn H1 rp -61.5
dof 0 lp -285.8
dm yyy
dmm w wc 250
dpwr 43 sc 0
dmf 8900 vs 22
nm no ph 5

Compound 2b:

```

SAMPLE
date Jun 8 2006 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 pw90 14.600
at 1.988 a1fa 20.000
np 25528
fb not used i1 n
bs 4 in n
d1 1.000 dp y
nt 32 hs nn
ct 28
TRANSMITTER lb 0.10
tn H1 fn 65536
sfrq 399.853 sp DISPLAY -803.2
tof 362.8 wp 6389.8
tpwr 60 rfl 803.2
pw 7.300 rfp 0
DECOUPLER C13 rp 73.1
dn 0 lp -89.8
dm mn
dmm c wc 250
dpwr 50 sc 0
dmf 17100 vs 29
nm cdc ph 4

```

```

SAMPLE
date Jun 19 2006 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25125.6 pw90 21.000
at 1.199 a1fa 20.000
np 80270
fb 13800 i1 n
bs 16 in n
d1 1.000 dp y
nt 2000 hs mn
ct 224
TRANSMITTER C13 lb 2.00
tn H1 fn 65536
sfrq 100.624 sp DISPLAY -1522.5
tof 1536.3 wp 25125.6
tpwr 61 rfl 3287.4
pw 10.500 rfp 7764.9
DECOUPLER H1 rp -48.0
dn 0 lp -236.3
dm yyv wc 250
dmm 43 sc 0
dpwr 8900 vs 27
dmf nm no ph 5

```

Compound 3b:

Compound 4b:

SAMPLE
date Jun 21 2006
solvent CDC13
file ACQUISITION
sw 6389.8
at 1.398
np 25528
fb not used
bs 1.000
d1 32
nt 32
ct 32
TRANSMITTER
tn 399.853
sfrq 362.8
tpwr 7.300
pw DECOUPLER
dn C13
dm nnn
dmm 50
dpwr 17100
dmf 17100

SPECIAL
temp not used
gain not used
spin not used
hs 0.008
pw90 14.600
alpha 20.000
FLAGS
i1 n
in n
dp y
hs nn
PROCESSING
lb 0.10
fn 65536
sp -803.0
wp 6389.8
rf1 803.0
rfp 0
lp -99.2
wc 250
sc 0
vs 121
th 4
nm cdc ph

SAMPLE
date Jun 22 2006
solvent CDC13
file ACQUISITION
sw 25125.6
at 1.199
np 60270
fb 13800
bs 16
d1 1.000
nt 2000
ct 1440
TRANSMITTER
tn C13
sfrq 100.554
tpwr 1536.3
pw 10.500
DECOUPLER
dn H1
dm yyy
dmm 43
dpwr 8900
dmf 8900

SPECIAL
temp not used
gain not used
spin not used
hs 0.008
pw90 21.000
alpha 20.000
FLAGS
i1 n
in n
dp y
hs nn
PROCESSING
lb 2.00
fn 65536
sp -1514.9
wp 25125.6
rf1 8275.6
rfp 7764.9
lp -45.1
wc 250
sc 79
vs 4
th 4
nm no ph

Compound 5b:

S7

Compound 6b:

S8

Compound 7b:

SAMPLE
 date Jun 23 2006 temp not used
 solvent CDC13 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
 sw 6389.8 pw90 14.600
 at 1.998 a1fa 20.000
 np 25525
 fb not used l1 n
 bs 4 in n
 d1 1.000 dp y
 nt 32 hs
 ct 24
 TRANSMITTER lb 0.10
 tn H1 fn 65536
 sfrq 399.853 DISPLAY
 tof 362.8 sp -799.7
 tpr 60 wp 6389.8
 pw 7.300 rf1 799.7
 DECOUPLER rfp 0
 dn C13 rp 80.4
 dof 0 lp -140.9
 dm nnn
 dmm c wc 250
 dpwr 50 sc 0
 dmf 17100 vs 68
 nm cdc ph 5

SAMPLE
 date Jun 25 2006 temp not used
 solvent CDC13 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
 sw 25125.6 pw90 21.000
 at 1.199 a1fa 20.000
 np 60270
 fb 13800 l1 n
 bs 4 in n
 d1 5.000 dp y
 nt 2000 hs
 ct 80
 TRANSMITTER lb 2.00
 tn C13 fn 65536
 sfrq 100.554 DISPLAY
 tof 1536.3 sp -1517.9
 tpr 61 wp 25125.6
 pw 10.500 rf1 9282.8
 DECOUPLER rfp 7764.3
 dn H1 rp -53.3
 dof 9 lp -308.4
 dm yyy
 dmm w wc 250
 dpwr 43 sc 0
 dmf 8900 vs 24
 nm no ph 3

Compound 8b:

SAMPLE
date Jun 22 2006 temp SPECIAL
solvent CDCl3 gain not used
file ACQUISITION exp spin not used
sw 6389.8 pw90 14.000
at 1.998 a1fa 20.000
np not used 11 FLAGS n
fb not used 4 in n
bs 1.000 dp y
d1 32 hs nn
nt 24
ct
TRANSMITTER 1b PROCESSING 0.10
tn H1 fn 65536
sfrq 399.853 DISPLAY -802.6
tof 362.8 sp -802.6
tpwr 6.0 wp 6389.8
pw 7.300 rf1 802.6
DECOUPLER rf2 0
dn C13 rp 51.8
dof 0 tp -40.2
dm nnn PLOT 250
dmm c wc 0
dpwr 50 sc 0
dmf 17100 vs 34
nm cdc ph 5

SAMPLE
date Jun 23 2006 temp SPECIAL
solvent CDCl3 gain not used
file ACQUISITION exp spin not used
sw 25125.6 pw90 21.000
at 1.189 a1fa 20.000
np 60270 11 FLAGS n
fb 13800 4 in n
bs 38 1n n
d1 1.000 dp y
nt 2000 hs nn
ct
TRANSMITTER 1b PROCESSING 2.00
tn C13 fn 65536
sfrq 100.554 DISPLAY -1515.6
tof 1536.3 sp -1515.6
tpwr 6.1 wp 25125.6
pw 10.500 rf1 9280.5
DECOUPLER rf2 776.8
dn H1 rp -77.4
dof 0 tp -244.7
dm yvv PLOT 250
dmm v wc 0
dpwr 43 sc 0
dmf 8900 vs 67
nm no ph 4

S10

Compound 9b:

Compound 10b:

Compound 11b:

SAMPLE
date Aug 2 2005 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 pw90 14.600
at 1.998 alfa 20.000
np 25528
fb not used ll n
bs 4 in n
d1 1.000 dp y
nt 100 hs nn
ct 36
TRANSMITTER lb 0.10
tn H1 fn 65536
sfrq 399.853 DISPLAY
tof 362.8 sp -801.3
tpwr 60 wp 6389.8
pw 7.300 rfl 801.3
DECOUPLER C13 rfp 0
dn 0 rp -87.2
dof 0 lp -103.5
dm mn WC 250
dmm 50 SC 0
dpwr 17100 vs 139
def th -2
nm cdc ph

SAMPLE
date May 29 2006 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25125.6 pw90 21.000
at 1.199 alfa 20.000
np 60270
fb 13800 ll n
bs 16 in n
d1 1.000 dp y
nt 5000 hs nn
ct 2720
TRANSMITTER lb 2.00
tn C13 fn 65536
sfrq 100.554 DISPLAY
tof 1536.3 sp -1511.0
tpwr 61 wp 25125.6
pw 10.500 rfl 9275.9
DECOUPLER H1 rfp -50.1
dn 0 lp -333.7
dm VVY WC 250
dmm 43 SC 0
dpwr 8900 vs 54
def th 4
nm no ph

Compound 12b:

```

SAMPLE
date Aug 23 2006 temp SPECIAL
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 pw90 14.000
at 1.888 alfa 20.000
np 25528
fb not used i1 n
bs 4 in n
d1 1.000 dp y
nt 32 hs
ct 32 hs
TRANSMITTER H1 lb 0.10
tn 389.853 fn 65536
sfrq 382.8 sp DISPLAY -802.3
tof 60 wp 6389.8
tpwr 7.300 rfl 802.3
pw DECOUPLER C13 rfp 0
dn 0 lp 88.6
dof 0 lp -95.3
dm nnn
dmm c PLOT 250
dpwr 50 sc 0
dmf 17100 vs 144
nm cdc ph 7

```

```

SAMPLE
date Jun 14 2006 temp SPECIAL
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25125.6 pw90 21.000
at 1.199 alfa 20.000
np 60270
fb 13800 i1 n
bs 16 in n
d1 1.000 dp y
nt 2000 hs
ct 960 hs
TRANSMITTER C13 lb 2.00
tn 100.554 fn 65536
sfrq 1536.3 sp DISPLAY -1517.2
tof 61 wp 25125.6
tpwr 10.500 rfl 9282.1
pw DECOUPLER H1 rfp 7764.9
dn 0 lp -57.1
dof 0 lp -313.6
dm yyy PLOT 250
dmm w wc 0
dpwr 43 sc 38
dmf 8900 vs 2
nm no ph

```

S14

Compound 13b:

SAMPLE
 date Jun 13 2006 temp not used
 solvent CDCl3 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
 sw 6389.8 pw90 14.600
 at 1.199 alfa 20.000
 np 25528
 fb not used
 bs 4
 dl 1.000
 nt 32
 ct 32
 TRANSMITTER H1
 tn 389.853
 tof 382.8
 tpwr 60
 pw 7.300
 DECOUPLER C13
 dn C13
 dof 0
 dm nnn
 dmm 50
 dpwr 17100
 dmf 17100
 SPECIAL
 temp not used
 gain not used
 spin not used
 hst 0.008
 pw90 14.600
 alfa 20.000
 FLAGS
 n
 n
 n
 y
 nn
 0.10
 65536
 DISPLAY
 -795.8
 6389.8
 795.8
 0
 74.4
 -91.3
 PLOT
 250
 0
 57
 20
 nm cdc ph

SAMPLE
 date Jun 30 2006 temp not used
 solvent CDCl3 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
 sw 25125.6 pw90 21.000
 at 1.199 alfa 20.000
 np 60270
 fb 13800
 bs 16
 dl 1.000
 nt 2000
 ct 1152
 TRANSMITTER C13
 tn 100.554
 tof 1536.3
 tpwr 61
 pw 10.500
 DECOUPLER H1
 dn H1
 dof 0
 dm yyy
 dmm w
 dpwr 43
 dmf 8900
 SPECIAL
 temp not used
 gain not used
 spin not used
 hst 0.008
 pw90 21.000
 alfa 20.000
 FLAGS
 n
 n
 n
 y
 nn
 2.00
 65536
 DISPLAY
 -1521.0
 25125.6
 9285.9
 7764.9
 -47.1
 -320.8
 PLOT
 250
 0
 67
 4
 nm no ph

Compound 14b:

```

date Feb 13 2006 temp not used
solvent CDCl3 gain not used
file ACQUISITION exp spin not used
sw 6389.8 pw90 14.600
at 1.998 a1fa 20.000
np 25528 FLAGS
fb not used il n
bs 1 in n
d1 1.000 dp n
nt 16 hs nm
ct
TRANSMITTER 16 lb fn 0.10
tn H1 fn 65536
sfrq 399.853 sp DISPLAY
tof 362.3 sp -797.8
tpwr 60 wp 6389.8
pw 7.300 rfp 797.8
DECOUPLER C13 rfp 0
dn 0 tp -59.5
dm nnn PLOT 250
dmm c wc 0
dpwr 50 sc 91
dmf 17100 vs th 6
nm cdc ph

```

```

SAMPLE
date Feb 22 2006 temp not used
solvent CDCl3 gain not used
file ACQUISITION exp spin not used
sw 25125.6 pw90 21.000
at 1.199 a1fa 20.000
np 60270 FLAGS
fb 13800 il n
bs 16 in n
d1 1.000 dp y
nt 5000 hs nm
ct
TRANSMITTER 1280 lb fn 2.00
tn C13 fn 65536
sfrq 100.554 sp DISPLAY
tof 1536.3 sp -1549.5
tpwr 61 wp 25125.6
pw 10.500 rfp 9291.3
DECOUPLER H1 rfp 741.6
dn 0 tp -42.0
dm 0 PLOT 250
dmm vvy wc 58
dpwr 43 sc 0
dmf 8900 vs th 5
nm no ph

```

Compound 15b:

SAMPLE		SPECIAL	
date	Mar 6 2006	temp	not used
solvent	CDC13	gain	not used
file		spin	not used
ACQUISITION			
sw	6389.8	hst	0.008
at	1.998	pw90	14.500
np	25526	alpha	20.000
rb	not used	il	n
bs	6	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	16		
TRANSMITTER		PROCESSING	
tn	H1	lb	0.10
sfreq	399.853	fn	65536
tof	382.8	sp	-805.0
tpwr	60	wp	6389.8
pw	7.300	rf1	805.0
DECOUPLER			
dn	C13	rfp	0
dof	0	lp	-87.1
dm	nnn		
dmm	c	wc	250
dpwr	50	sc	0
dmf	17100	vs	64
		th	4
	nm	cdc	ph

SAMPLE		SPECIAL	
date	Jun 14 2005	temp	not used
solvent	CDC13	gain	not used
file		spin	not used
ACQUISITION			
sw	25125.6	hst	0.008
at	1.199	pw90	21.000
np	60279	alpha	20.000
rb	13600	il	n
bs	64	in	n
d1	1.000	dp	y
nt	2000	hs	nn
ct	1024		
TRANSMITTER		PROCESSING	
tn	C13	lb	2.00
sfreq	100.554	fn	65536
tof	1536.3	sp	675.3
tpwr	61	wp	21525.3
pw	10.500	rf1	1503.1
DECOUPLER			
dn	H1	rfp	0
dof	0	lp	-41.3
dm	yyy		-301.4
dmm	w	wc	250
dpwr	43	sc	0
dmf	8900	vs	105
		th	6
	nm	no	ph

Compound 16b:

SAMPLE		SPECIAL	
date	Jun 6 2006	temp	not used
solvent	CDC13	gain	not used
file		spin	not used
ACQUISITION		exp	hst
sw	6389.8	pw90	0.008
at	1.998	alpha	14.800
np	25528	alpha	20.000
fb	not used	l1	n
bs	4	ln	n
d1	1.000	dp	y
nt	32	hs	nm
ct	32		
TRANSMITTER		l1	0.10
tn	H1	fn	65536
sfrq	399.853	sp	-799.9
tof	362.8	wp	6389.8
tpwr	60	rf1	799.9
pw	7.300	rfl	0
DECOUPLER		rfp	67.7
dn	C13	rp	-106.6
dof	0	lp	
dm	nnn	vc	250
dmm	c	sc	0
dpwr	50	vs	54
dmf	17100	th	20
	nm	cdc	ph

SAMPLE		SPECIAL	
date	Jun 9 2006	temp	not used
solvent	CDC13	gain	not used
file		spin	not used
ACQUISITION		exp	hst
sw	25125.6	pw90	0.008
at	1.199	alpha	20.000
np	86270	alpha	20.000
fb	13600	l1	n
bs	16	ln	n
d1	1.000	dp	y
nt	2000	hs	nm
ct	2000		
TRANSMITTER		l1	2.00
tn	C13	fn	65536
sfrq	100.554	sp	-1514.1
tof	1536.2	wp	25125.6
tpwr	61	rf1	3279.0
pw	10.500	rfl	7764.9
DECOUPLER		rfp	-43.4
dn	H1	rp	-375.7
dof	0	lp	
dm	yyy	vc	250
dmm	w	sc	0
dpwr	43	vs	34
dmf	8900	th	2
	nm	no	ph

Compound 17b:

SPECIAL
temp not used
gain not used
spin not used
hst 0.008
fid pw90 14.600
alpha 20.000

ACQUISITION
sw 6389.8
at 1.998
np 25528
fb not used
bs 4
dl 1.000
nt 16
ct 16

TRANSMITTER
tn H1
sfrq 399.853
tof 362.8
tpwr 60
pw 7.300
DECOUPLER C13

PROCESSING
0.10
65536

DISPLAY
-802.5
6389.8
802.5
0
71.9
-92.6

PLOT
250
0
43
17

nm cdc ph

exp1 s2pu1
SAMPLE

SPECIAL
temp not used
gain not used
spin not used
hst 0.008
fid pw90 21.000
alpha 20.000

ACQUISITION
sw 25125.6
at 1.189
np 60270
fb 13900
bs 16
dl 1.000
nt 2000
ct 768

TRANSMITTER
tn C13
sfrq 100.553
tof 1536.3
tpwr 61
pw 10.500
DECOUPLER H1

PROCESSING
2.00
65536

DISPLAY
-1543.4
25125.6
5285.1
7741.8
-26.8
-301.2

PLOT
250
0
131
4

nm no ph

Compound 18b:

CDCl₃ + CD₃OD

Compound 19b:

exp1 s2pu1

SAMPLE		SPECIAL	
date	Aug 18 2006	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	
sw	6389.8	hst	0.008
at	1.998	pw90	14.600
np	25528	alpha	20.000
fb	not used	l1	FLAGS
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	24	PROCESSING	
tn	TRANSMITTER	lb	0.10
sfrq	H1	fn	65536
tof	399.853	DISPLAY	
tpwr	362.8	sp	-802.0
pw	60	wp	6389.8
DECOUPLER	7.300	rfl	802.0
dn	C13	rffp	0
dof	0	rp	77.2
dm	nnn	lp	-91.7
dnn	C	PLOT	
dpwr	50	wc	250
dmf	17100	sc	0
		vs	94
		th	5
		nm	cdc ph

Compound 1b : Liquid

Yield 85%. IR (Neat) ν : 1751, 1716 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 2.45 (s, 3H), 3.84 (s, 3H), 4.77 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 26.7, 48.9, 54.0, 165.6, 196.1 ppm. Analysis: $\text{C}_5\text{H}_7\text{BrO}_3$ (195.01) requires C: 30.80, H: 3.62 found C: 30.55, H: 3.53%.

Compound 2b: Liquid

Yield 84%. IR (Neat) ν : 1742, 1721 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.31 (t, $J = 7.2$ Hz, 3H), 2.44 (s, 3H), 4.28 (q, $J = 7.2$ Hz, 2H), 4.74 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 14.1, 26.6, 49.3, 63.3, 165.0, 196.1 ppm. Analysis: $\text{C}_6\text{H}_9\text{BrO}_3$ (209.04) requires C: 34.48, H: 4.34 found C: 34.29, H: 4.26%.

Compound 3b: Liquid

Yield 91%. IR (Neat) ν : 1745, 1726 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.49 (s, 9H), 2.42 (s, 3H), 4.67 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 26.2, 27.5 (3C), 50.6, 84.1, 163.5, 195.9 ppm. Analysis: $\text{C}_8\text{H}_{13}\text{BrO}_3$ (237.09) requires C: 40.53, H: 5.53 found C: 40.60, H: 5.59%.

Compound 4b: Liquid

Yield 95%. IR (Neat) ν : 1743, 1718 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 0.87 (t, $J = 6.8$ Hz, 3H), 1.26 (bs, 14 H), 1.66 (quin, $J = 6.8$ Hz, 2H), 2.43 (s, 3H), 4.20 (t, $J = 6.8$ Hz, 2H), 4.74 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 14.4, 23.0, 26.0, 26.7, 28.6, 29.4, 29.6, 29.8 (2C), 32.2, 49.4, 67.5, 165.2, 196.2 ppm. Analysis: $\text{C}_{14}\text{H}_{25}\text{BrO}_3$ (321.25) requires C: 52.34, H: 7.84 found C: 52.11, H: 7.89%.

Compound 5b: Liquid

Yield 95%. IR (Neat) ν : 1742, 1716 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 0.88 (t, J = 7.2 Hz, 3H), 1.26 (bs, 26H), 1.67 (quin, J = 6.8 Hz, 2H), 2.44 (s, 3H), 4.21 (t, J = 6.8 Hz, 2H), 4.74 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 14.5, 23.0, 26.0, 26.7, 28.6, 29.4, 29.7 (2C), 29.8 (2C), 29.9 (2C), 30.0 (3C), 32.2, 49.3, 67.5, 165.2, 196.2 ppm. Analysis: $\text{C}_{20}\text{H}_{37}\text{BrO}_3$ (405.41) requires C: 59.25, H: 9.20 found C: 59.01, H: 9.15%.

Compound 6b: Liquid (mixture of diastereomer)

Yield 93%. IR (Neat) ν : 1742, 1716 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 0.77 (d, J = 7.6 Hz, 3H), 0.78 (d, J = 7.6 Hz, 3H), 0.83-0.93 (m, 12H), 1.00-1.10 (m, 2H), 1.40-1.51 (m, 4H), 1.65-1.75 (m, 4H), 1.70-1.80 (m, 4H), 2.00-2.20 (m, 4H), 2.42 (s, 6H), 4.72 (s, 1H), 4.73 (s, 1H), 4.74-4.78 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 16.3, 16.4, 21.0 (2C), 22.2 (2C), 23.5, 23.6, 26.3, 26.4, 26.7 (2C), 31.7 (2C), 34.3 (2C), 40.5 (2C), 47.1, 47.1, 49.8, 49.9, 77.8 (2C), 164.7 (2C), 196.2 (2C) ppm. Analysis: $\text{C}_{14}\text{H}_{23}\text{BrO}_3$ (319.24) requires C: 52.67, H: 7.26 found C: 52.47, H: 7.35%.

Compound 7b: Liquid

Yield 93%. IR (Neat) ν : 1740, 1726 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.30-1.50 (bs, 18H), 1.52-1.60 (m, 2H), 1.70-1.80 (m, 2H), 2.43 (s, 3H), 4.72 (s, 1H), 5.07-5.10 (m, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 21.1 (2C), 23.4 (2C), 23.6 (2C), 24.1, 24.3 (2C), 26.7, 29.1 (2C), 49.8, 76.1, 164.8, 196.3 ppm. Analysis: $\text{C}_{16}\text{H}_{27}\text{BrO}_3$ (347.29) requires C: 55.34, H: 7.84 found C: 55.10, H: 7.75%.

Compound 8b: Liquid

Yield 97%. IR (Neat) ν : 1747, 1727 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.33 (bs, 8H), 1.67 (quin, J = 6.4 Hz, 4H), 2.44 (s, 6H), 4.21 (t, J = 6.8 Hz, 4H), 4.75 (s, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 25.8 (2C), 26.8 (2C), 28.5 (2C), 29.2 (2C), 49.3 (2C), 67.3 (2C), 165.2 (2C), 196.3 (2C) ppm. Analysis: $\text{C}_{16}\text{H}_{24}\text{Br}_2\text{O}_6$ (472.17) requires C: 40.70, H: 5.12 found C: 40.48, H: 5.19%.

Compound 9b: Liquid

Yield 94%. IR (Neat) ν : 1746, 1725 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 2.39 (s, 3H), 4.78 (s, 1H), 5.23 (s, 2H), 7.31-7.35 (bs, 5H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 26.7, 49.3, 68.8, 128.4 (2C), 128.7 (2C), 128.8, 134.5, 164.9, 196.0 ppm. Analysis: $\text{C}_{11}\text{H}_{11}\text{BrO}_3$ (271.11) requires C: 48.73, H: 4.09 found C: 48.79, H: 4.15%.

Compound 10b: Liquid

Yield 94%. IR (Neat) ν : 1752, 1690 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.25 (t, J = 7.2 Hz, 3H), 4.27 (q, J = 7.2 Hz, 2H), 5.64 (s, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.97 (d, J = 8 Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 13.8, 46.3, 63.0, 128.6 (2C), 128.8 (2C), 133.0, 133.9, 164.7, 187.7 ppm. Analysis: $\text{C}_{11}\text{H}_{11}\text{BrO}_3$ (271.11) requires C: 48.73, H: 4.09 found C: 48.46, H: 4.02%.

Compound 11b: Liquid

Yield 89 %. IR (Neat) ν : 1747, 1716 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.01 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 2.22-2.27 (m, 2H), 2.34 (s, 3H), 4.27 (q, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 10.2, 14.3, 26.6, 30.9, 63.3, 70.9, 167.5, 197.6 ppm. Analysis: $\text{C}_8\text{H}_{13}\text{BrO}_3$ (237.09) requires C: 40.53, H: 5.53 found C: 40.59, H: 5.48%.

Compound 12b: Liquid

Yield 96 %. IR (Neat) ν : 1743, 1721 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.41 (s, 9H), 2.34 (s, 3H), 3.49 (d, J = 14.4 Hz, 1H), 3.59 (d, J = 14.8 Hz, 1H), 7.20-7.41 (bs, 5H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 27.2, 27.9 (3C), 42.7, 70.3, 84.7, 127.2, 128.2 (2C), 129.6 (2C), 135.0, 165.7, 198.0 ppm. Analysis: $\text{C}_{15}\text{H}_{19}\text{BrO}_3$ (327.22) requires C: 55.06, H: 5.85 found C: 54.85, H: 5.77%.

Compound 13b: Liquid

Yield 95 %. IR (Neat) ν : 1751, 1722 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.08 (t, J = 7.2 Hz, 6H), 2.41-2.48 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.53 (t, J = 6.4 Hz, 1H), 7.98 (d, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 9.7, 14.0, 32.2, 63.3, 68.4, 128.4 (2C), 129.4 (2C), 133.2, 133.9, 168.0, 189.1 ppm. Analysis: $\text{C}_{13}\text{H}_{15}\text{BrO}_3$ (299.16) requires C: 52.19, H: 5.05 found C: 52.01, H: 5.11%.

Compound 14b: Liquid

Yield 99 %. IR (Neat) ν : 1752, 1716 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.33 (t, J = 6.8 Hz, 3H), 1.71-1.92 (m, 4H), 2.20-2.22 (m, 1H), 2.42-2.50 (m, 1H), 2.85-2.96 (m, 2H), 4.29 (q, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 13.8, 23.1, 26.7, 30.8, 40.5, 62.8, 67.4, 167.1, 198.6 ppm. Analysis: $\text{C}_9\text{H}_{13}\text{BrO}_3$ (249.10) requires C: 43.40, H: 5.26 found C: 43.15, H: 5.20%.

Compound 15b: Liquid

Yield 97 %. IR (Neat) ν : 1731, 1680 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 2.45 (s, 3H), 5.60 (s, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.62 (t, $J = 6.8$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 27.5, 53.3, 129.2 (2C), 129.4 (2C), 133.9, 134.6, 190.0, 198.2 ppm. Analysis: $\text{C}_{10}\text{H}_9\text{BrO}_2$ (241.08) requires C: 49.82, H: 3.76 found C: 49.59, H: 3.69%.

Compound 16b: Viscous Liquid

Yield 86 %. IR (Neat) ν : 1715, 1688 1530, 1348 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 2.51 (s, 3H), 5.54 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 2H), 8.32 (d, $J = 8.4$ Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 27.7, 52.3, 124.1 (2C), 130.4 (2C), 138.2, 150.8, 188.8, 197.6 ppm. Analysis: $\text{C}_{10}\text{H}_8\text{BrNO}_4$ (286.08) requires C: 41.98, H: 2.82, N: 4.90 found C: 41.79, H: 2.85, N: 4.78%.

Compound 17b: Solid, mp 89 $^{\circ}\text{C}$.

Yield 98 %. IR (KBr) ν : 1689 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 6.54 (s, 1H), 7.45 (t, $J = 7.6$ Hz, 4H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.96 (d, $J = 7.2$ Hz, 4H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 52.6, 128.8 (4C), 129.0 (4C), 133.6 (2C), 134.1 (2C), 188.9 (2C) ppm. Analysis: $\text{C}_{15}\text{H}_{11}\text{BrO}_2$ (303.15) requires C: 59.43, H: 3.66 found C: 59.18, H: 3.58%.

Compound 18b: Solid, mp 156 °C.

Yield 98 %. IR (KBr) ν : 1636, 1574, 1370, 1323 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 1.12 (s, 6H), 2.48 (s, 4H) ppm. ^{13}C NMR ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 100 MHz): 27.9 (2C), 32.1, 47.3 (2C), 98.4, 182.0 (2C) ppm. Analysis: $\text{C}_8\text{H}_{11}\text{BrO}_2$ (219.08) requires C: 43.86, H: 5.06 found C: 43.92, H: 5.09%

Compound 19b: Viscous Liquid

Yield 81 %. IR (Neat) ν : 1738, 1718, 1650, 1491, 1425, 1359, 1273, 1224, 1143 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): 2.44(s, 3H), 4.69 (dd, $J = 1.2$ Hz, $J = 5.6$ Hz, 2H), 4.78 (s, 1H), 5.30 (dd, $J = 1.2$ Hz, $J = 10.4$ Hz, 1H), 5.37 (dd, $J = 1.2$ Hz, $J = 16.0$ Hz, 1H), 5.90 (m, 1H) ppm. Analysis: $\text{C}_7\text{H}_9\text{BrO}_3$ (221.05) requires C: 38.04, H: 4.10 found C: 37.78, H: 4.06 %.