A Straightforward and Highly Efficient Catalyst-Free One-Pot Synthesis of Dithiocarbamates Under Solvent Free Conditions

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Experimental procedure:S2

Copy of ¹H and ¹³C NMRS3-S31

General

NMR spectra were recorded on a Bruker ACF 500 using $\text{CDCl}_3/\text{CCl}_4$ or $\text{CDCl}_3/\text{DMSO-d}^6$ as solvent. Column chromatography was performed on silica gel, Merck grade 60. Ethyl acetate, petroleum ether and water were distilled before use. Alkyl halides and amines and other chemical were purchased and used without further purification.

General procedure for one-pot synthesis of dithiocarbamates

A ice cold mixture of the organic halide (3 mmol) and carbon disulfide (6 mmol) in the test tube, amine (6 mmol) was added and stirred at 0 °C for 30 min, then warmed to room temperature and stirring was continued until the reaction was complete (reaction mixture solidified or monitored by TLC). The reaction was quenched by addition of water and was extracted with EtOAc, dried over anhyd. Na_2SO_4 , and evaporated to give NMR pure product. Further purification in some cases can be achieved by silica gel column chromatography eluted with petroleum ether and ethyl acetate or recrystallized to afford the pure dithiocarbamate.

Table 1, Entry 1

Current Data Parameters
 NAME Aryanasab
 EXPNO 100
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050610
 Time 11.30
 INSTRUM spect
 PROBHD 5 mm BB1 3H-BB
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 1
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305175 Hz
 AQ 1.6385000 sec
 RG 6.3
 DW 50.000 use
 DE 6.50 use
 TE 295.3 K
 D1 1.00000000 sec
 XPREST 0.00000000 sec
 XCHWK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.30 use
 PL1 2.00 dB
 SF01 500.1330865 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1330000 MHz
 MDW EV
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 10.79 cm
 F1P 12.210 ppm
 F1 6106.52 Hz
 F2P -0.354 ppm
 F2 -177.26 Hz
 PPMCM 0.69802 ppm
 HZCM 349.09909 Hz/

a-297 ¹³CNMR in CDCl₃ at 298 K 85/3/20

Table 1, Entry 3

Current Data Parameters
NAME Torkian
EXPNO 26
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060428
Time 10.11
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 4.5
RC 50.000 usec
DE 6.50 usec
TE 291.8 K
D1 2.00000000 sec
MDREST 0.00000000 sec
MCWRC 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

10 NMR plot parameters
CX 18.00 cm
CY 11.73 cm
FIP 11.086 ppm
F1 5544.65 Hz
F2P 0.037 ppm
F2 18.33 Hz
PPMCM 0.51388 ppm/cm
HZCM 307.01755 Hz/cm

Table 1, Entry 3

a-299 ¹H-NMR in CDCl₃ at 298 K 85/3/20

Table 1, Entry 4

Current Data Parameters
NAME Aryanasab
EXPNO 102
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060610
Time 11:37
INSTRUM spect
PROBHD 5 mm BBI 1H-88
PULPROG zg
TD 32768
SOLVENT CDCl₃
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 3.6
DW 50.000 usec
DE 6.50 usec
TE 296.4 K
D1 3.0000000 sec
MCHST 0.0000000 sec
MCWK 0.0150000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 7.21 cm
F1P 9.711 ppm
F1 -4856.53 Hz
F2P -0.452 ppm
F2 -75.91 Hz
PRCM 0.54791 ppm/
HZCM 274.02402 Hz/ci

a-299 ¹³CNMR in CDCl₃ at 298 K 05/3/20

Table 1, Entry 4

ppm

Table 1, Entry 6

a-303 ¹H NMR in CDCl₃ at 298 K 85/4/4

Current Data Parameters
 NAME Aryanasab
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060825
 Time 15:50
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDCl₃
 NS 4
 DS 0
 SWH 10330.578 Hz
 FIDRES 0.315264 Hz
 AQ 1.5860696 sec
 RG 16
 DW 48.400 usec
 DE 6.50 usec
 TE 297.9 K
 D1 3.00000000 sec
 MCHST 0.00000000 sec
 MCHPK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 11.08 cm
 F1P 9.532 ppm
 F1 4757.23 Hz
 F2P -0.256 ppm
 F2 -128.06 Hz
 PPMCM 0.54378 ppm/cm
 HZCM 271.96030 Hz/cm

a-303 13CNMR in CDCl3 at 298 K 85/4/4

Table 1, Entry 6

Table 1, Entry 7

a-283 ¹H NMR in CDCl₃ at 298K 85/2/12

Current Data Parameters
NAME Anyasab
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060503
Time 9.59
INSTRUM spect
PROBHD 5 mm BB1 1H-BB
PULPROG zg
TO 32768
SOLVENT CDCl₃
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 7.1
DN 50.000 usec
DE 6.50 usec
TE 292.6 K
D1 3.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1330000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 7.21 cm
F1P 11.151 ppm
F1 5577.04 Hz
F2P -0.245 ppm
F2 -122.50 Hz
PPMCM 0.63312 ppm/cm
HZCM 316.64117 Hz/cm

a-283 13CNMR in CDCl3 at 298K 85/2/12

Table 1, Entry 7

Current Data Parameters:
NAME: Aryanash
EXPNO: 91
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20060503
Time: 10.01
INSTRUM: spect
PROBHD: 5 mm BBI 1H-8B
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 160
DS: 4
SWH: 30030.029 Hz
FIDRES: 0.458222 Hz
AQ: 1.0912410 sec
RG: 3251
CW: 16.650 usec
DE: 6.50 usec
TE: 293.7 K
D1: 9.00000000 sec
DELTA: 0.03000000 sec
MCREST: 0.00000000 sec
MCMRG: 0.01500000 sec
===== CHANNEL f1 =====
NUC1: 13C
P1: 10.50 usec
PL1: 0.00 dB
SFO1: 125.7703643 MHz
===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 79.00 usec
PL2: 3.00 dB
PL12: 23.00 dB
PL13: 23.00 dB
SFO2: 500.1320005 MHz
F2 - Processing parameters
SI: 32768
SF: 125.757350 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
1D NMR plot parameters
CX: 20.00 cm
CY: 12.50 cm
FIP: 255.932 ppm
F1: 28400.54 Hz
F2: -2.024 ppm
FZ: -254.55 Hz
FRCM: 10.59760 ppm/cm
HZCN: 1332.75476 Hz/cm

Table 1, Entry 8

Table 1, Entry 8

a-276 ¹HNMR in CDCl₃ at 298 K 85/2/5

Table 1, Entry 9

Current Data Parameters
 NAME Aryanasab
 EXPNO 80
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060428
 Time 9.54
 INSTRUM spect
 PROBHD 5 mm BBI 1H-BB
 PULPROG zg30
 TO 32768
 SOLVENT CDCl₃
 NS 4
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6385000 sec
 RG 4
 DW 50.000 usec
 DE 6.50 usec
 TE 291.8 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCWRRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 ¹H
 P1 10.30 usec
 PL1 2.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 S1 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 7.21 cm
 FIP 11.437 ppm
 F1 5720.09 Hz
 F2P -0.753 ppm
 F2 -376.41 Hz
 PPMCM 0.67721 ppm/cm
 HZCM 338.69400 Hz/cm

Table 1, Entry 9

a-276 ^{13}C NMR in CDCl_3 at 298 K 85/2/5

279 1HNMR in CDCl3 at 300 K 84/6/22

ppm

Table 1, Entry 10

Current Data Parameters
NAME Aryanasab
EXPNO 86
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080503
Time 9.47
INSTRUM spect
PROBHD 5 mm BB1 1H-BB
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305175 Hz
AQ 1.6385000 sec
RG 7.1
DM 50.000 usec
DE 6.50 usec
TE 292.7 K
O1 3.00000000 sec
MCHST 0.00000000 sec
MCWPK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1330000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 7.21 cm
FIP 10.876 ppm
F1 5439.42 Hz
F2 -0.107 ppm
F2 -53.69 Hz
PPMCM 0.61019 ppm/cm
HZCM 305.17331 Hz/cm

279 ¹³CNMR in CDCl₃ at 298K 85/2/12

Table 1, Entry 10

Table 1, Entry 11

B-B ¹H NMR in CDCl₃ at 298 K 84/12/2

a-282 ¹H-NMR in CDCl₃ at 298K 85/2/12

281

a-281 1HNMR in CDCl₃ at 298K 85/2/12

Table 1, Entry 13

Current Data Parameters
 NAME Anyanasab
 EXPNO 84
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060503
 Time 9.35
 INSTRUM spect
 PROBHD 5 mm BBI 1H-8B
 PULPROG zg
 TD 32768
 SOLVENT CDCl₃
 NS 1
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305175 Hz
 AQ 1.6385000 sec
 RG 7.1
 DW 50.000 usec
 DE 6.50 usec
 TE 292.7 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.30 usec
 PL1 2.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 MDK EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 7.21 cm
 F1p 11.151 ppm
 F1 5577.04 Hz
 F2p -0.656 ppm
 F2 -328.32 Hz
 PPMCM 0.85605 ppm/cm
 HZCM 328.10910 Hz/cm

Table 1, Entry 12

a-282 ¹³CNMR in CDCl₃ at 298K 85/2/12

221

a-281 13CNMR in COCl₃ at 298K 85/2/12

Table 1, Entry 13

Current Data Parameters
 NAME Aryanash
 EXPNO 85
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060503
 Time_ 9.37
 INSTRUM spect
 PROBHD 5 mm BBI 1H-BB
 PULPROG zgpg30
 TO 65536
 SOLVENT COCl₃
 NS 66
 DS 4
 SWH 30030.029 Hz
 FIDRES 0.458022 Hz
 AQ 1.0912410 sec
 RG 3251
 DM 16.650 usec
 DE 6.50 usec
 TE 292.8 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MDELTA 0.00000000 sec
 MCKRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.50 usec
 PL1 0.00 dB
 SF01 125.7703643 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 79.00 usec
 PL2 2.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SF02 500.1326005 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7577390 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

10 NMR plot parameters
 IX 20.00 cm
 CY 12.50 cm
 F1P 210.479 mm
 F1 28469.42 Hz
 F2P 6.132 mm
 F2 -771.12 Hz
 PPMCM 10.83056 mm/cm
 MZCM 1362.02710 Hz/cm

Table 1, Entry 28

Current Data Parameters
NAME Bagheri
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060218
Time 9.19
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 8
DS 1
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 20.2
DE 50.000 usei
TE 298.0 K
D1 3.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usei
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 8.94 cm
F1P 10.183 ppm
F1 5093.01 Hz
F2P 0.028 ppm
F2 14.18 Hz
PPMCM 0.56417 ppm
HZCM 282.15714 Hz/

Table 1, Entry 30

a-301 1HNMR in CDCl₃ at 298 K 85/3/20

Current Data Parameters
 NAME Arvanasu
 EXPNO 106
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060610
 Time 11.51
 INSTRUM spect
 PROBHD 5 mm BBI 1H-BB
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl₃
 NS 4
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6385000 sec
 RG 5.7
 DW 50.000 usec
 DE 6.50 usec
 TE 296.4 K
 D1 3.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.30 usec
 PL1 2.00 dB
 SF01 500.1300865 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 7.21 cm
 F1P 11.715 ppm
 F1 5858.78 Hz
 F2P -0.062 ppm
 F2 -30.86 Hz
 PPMCM 0.65423 ppm/cm
 HZCM 327.20218 Hz/cm

Table 1, Entry 30

a-301 ¹³CNMR in CDCl₃ at 298 K 65/3/20

8-295 1H-NMR in CDCl₃ at 298 K 85/3/20

Table 1, Entry 34

Current Data Parameters
 NAME Aryanasab
 EXPNO 104
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080610
 Time 11.47
 INSTRUM spect
 PROBHD 5 mm BBI 1H-BB
 PULPROG zg
 TD 32768
 SOLVENT CDCl₃
 NS 4
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6385000 sec
 RG 3.6
 DW 50.000 usec
 DE 6.50 usec
 TE 295.3 K
 D1 3.00000000 sec
 MCOREST 0.00000000 sec
 MCWRR 0.01500000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 10.30 usec
 PL1 2.00 dB
 SFO1 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 7.21 cm
 F1P 8.697 ppm
 F1 4349.77 Hz
 F2P 0.051 ppm
 F2 25.44 Hz
 PPMCM 0.48036 ppm/cm
 HZCM 240.24023 Hz/cm

Table 1, Entry 34

a-295 13CNMR in CDCl3 at 298 K 85/3/20

Scheme 3, 3e

a-285 1H-NMR in CDCl₃ at 298 K 85/2/25

Current Data Parameters
 NAME Aryanasab
 EXPNO 92
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060515
 Time 10.36
 INSTRUM spect
 PROBHD 5 mm BBI 1H-09
 PULPROG zg
 TD 32768
 SOLVENT CDCl₃
 NS 4
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6385000 sec
 RG 16
 DW 50.000 usec
 DE 6.50 usec
 TE 298.1 K
 D1 3.00000000 sec
 MCREST 0.00000000 sec
 MCRPK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 ¹H
 P1 10.30 usec
 PL1 2.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 16.98 cm
 F1P 10.853 ppm
 F1 5427.96 Hz
 F2P -0.153 ppm
 F2 -76.63 Hz
 PPMCM 0.61146 ppm/cm
 HZCM 305.81039 Hz/cm

Scheme 3, 3e

a-265 ¹³CNMR in CDCl₃ at 298 K 05/2/25