Supporting Information for

Surfactant-Type Asymmetric Organocatalyst: Organocatalytic Asymmetric Michael Addition to Nitrostyrenes in Water

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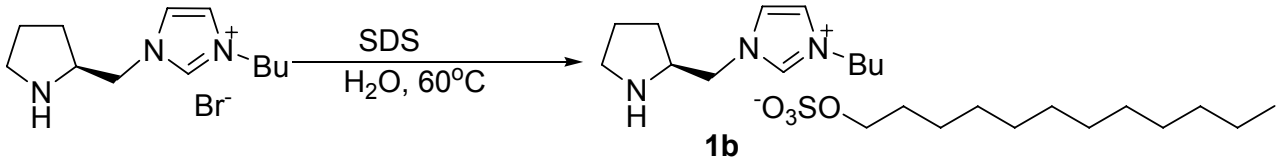
General Information: Commercial reagents were used as received, unless otherwise stated. ^{1}H and ^{13}C NMR were recorded on either a Bruker-DPX 300 or AV-400 sepectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d= doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Mass spectra were obtained using fast-atom bombard (FAB) spectrometer or electrospray ionization (ESI) mass spectrometer. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Perkin-Elmer 341 digital polarimeter and are reported as follows: $[\alpha]_D^{rt}$ (*c* in g per 100 mL of solvent). HPLC analysis was performed on Shimadzu CTO-10AS using ChiralPak columns purchased from Daicel Chemical Industries, LTD.

Dodecylbenzenesulfonic acid (>95% content for the alkylbenzesulfonic acids) was commercially available in the form of a mixture of linear alkyl (C_{11}-C_{13}) benzenesulfonic acids. Its molecular weight is regarded as 326.50.

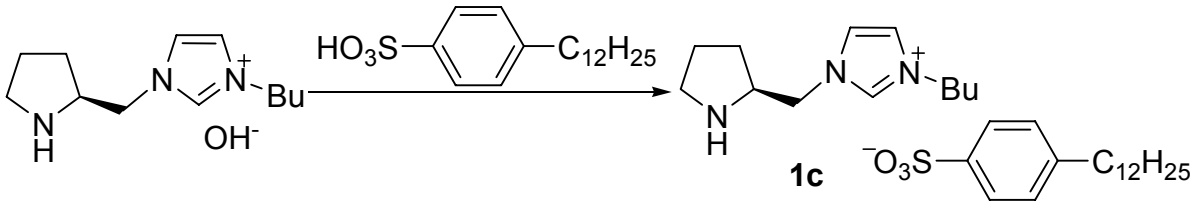
Synthesis of Surfactant-Type Asymmetric Organocatalyst by anion metathesis (Procedure a):



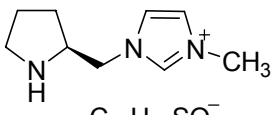
1b

Chiral ionic-liquid bromide (0.5 g, 1.73 mmol) and SDS (0.42 g, 1.45 mmol) were mixed in 10 mL of distilled water. The mixture was heated to ca. 60 ^{o}C till a clear solution was obtained. The solution was then concentrated under *vacuum* to dryness. The residue was dissolved in 100 mL of CH_2Cl_2 and the organic solution was filtered to remove the insoluble salts. The filtrate was washed with distilled water (10 mL×6). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford the desired product **1b** as pale yellow syrup (0.48 g, 70%). $[\alpha]_D^{20}$= +16.5^{o} (c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (3H, t, *J*= 6.6 Hz), 0.92 (3H, t, *J*= 7.2 Hz), 1.14-1.37 (20H, m br), 1.42-1.52 (1H, m), 1.56-1.66 (2H, m), 1.71-1.89 (3H, m), 1.98-2.09 (1H, m), 2.97 (2H, t, *J*= 6.6 Hz), 3.66 (2H, br s), 3.96 (2H, t, *J*= 6.9 Hz), 4.18-4.38 (3H, m), 4.39-4.43 (1H, m), 7.30 (1H, s), 7.61 (1H, s), 9.40 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.4, 13.1, 18.5, 21.7, 24.3, 24.9, 27.9, 28.3, 28.4, 28.5, 28.6, 28.7, 30.9, 31.0, 31.1, 45.5, 48.8, 52.2, 57.3, 66.8, 120.5, 122.3, 136.2; HRMS for $C_{12}H_{22}N_3^+$ (M^+), calcd. 208.1808, found 208.1807; HRMS for $C_{12}H_{25}O_4S^-$ (M^-), calcd. 265.1479, found 265.1478.

Synthesis of Surfactant-Type Asymmetric Organocatalyst by neutralization (Procedure b):



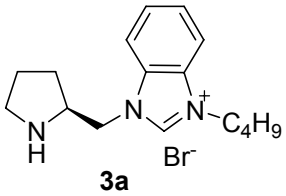
Chiral Ionic-liquid hydroxide was obtained by treatment of the corresponding bromide (0.5 g, 1.73 mmol) with strong basic anion-exchange resin. The hydroxide (100 mL solution in water) was treated with *p*-dodecyl benzenesulfonic acid (0.47 g, 1.44 mmol) and the solution was stirred overnight at room temperature. Water was removed under *vacuum* and the residue was dissolved in 100 mL of dichloromethane. The organic layer was washed with distilled water (10 mL×6) and was dried over anhydrous Na_2SO_4. Organic solvent was removed under vacuum to afford the desired product **1c** as pale yellow syrup (0.42 g, 55%). $[\alpha]_D^{20}$= +11.5° (c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ(for mixtures of C_{11}-C_{13} isomers) 0.78-0.92 (6H, m), 1.16-1.34 (20H, m), 1.43-1.58 (6H, m), 1.69-1.86 (4H, m), 1.94-2.04 (1H, m), 2.39-2.50 (1H, m), 2.95 (2H, t, *J*= 6.9 Hz), 3.72-3.82 (1H, m), 4.19 (2H, t, *J*= 7.5 Hz)), 4.29-4.47 (2H, m), 4.54 (1H, br), 7.10 (2H, d, *J*= 8.1 Hz), 7.21 (1H, s), 7.62 (1H, s), 7.76 (2H, d, *J*= 8.1 Hz), 9.81 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (for mixtures of C_{11}-C_{13} isomers) 12.4, 12.9, 13.1, 18.5, 21.5, 21.6, 21.7, 24.2, 26.5, 26.6, 27.8, 28.3, 28.7, 30.7, 30.8, 30.9, 31.0, 35.8, 35.9, 44.5, 44.8, 45.2, 48.8, 52.1, 57.2, 120.1, 122.2, 124.8, 124.9, 125.7, 126.4, 136.8, 142.6, 147.1; HRMS for $C_{12}H_{22}N_3^+$ (M^+), calcd. 208.1808, found 208.1806; HRMS for $C_{17\text{-}19}H_{27\text{-}31}O_4S^-$ (M^-), calcd. 311.1686, 325.1843, 339.1999, found 311.1682, 325.1837, 339.2013.



2

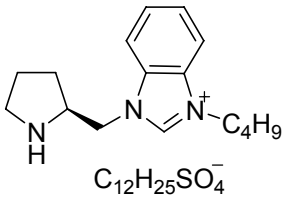
STAO 2 was synthesized following procedure **A**. $[\alpha]_D^{20}$= +14.6° (c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83-0.88 (3H, m), 1.20-1.30 (20H, br), 1.61-1.78 (4H, m), 2.94-2.98 (2H, m), 3.23 (1H, br), 3.68 (1H, br), 3.98 (3H, s), 4.01-4.13 (3H, m), 4.32-4.36 (1H, m), 7.31 (1H, s), 7.54 (1H, s), 9.43 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 14.2, 21.0, 22.6, 25.6, 25.9, 29.0, 29.3, 29.4, 29.6, 31.9, 36.5, 46.5, 53.8,

57.9, 60.3, 67.8, 122.7, 123.1, 137.9; HRMS for $C_9H_{16}N_3^+$ (M^+), calcd. 166.1339, found 166.1338; HRMS for $C_{12}H_{25}O_4S^-$ (M^-), calcd. 265.1479, found 265.1478.



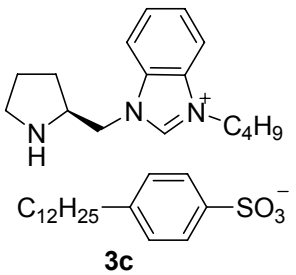
3a

3a was synthesized following published procedure.[1] $[\alpha]_D^{20}$= +25.7° (c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (3H, *J*= 7.2 Hz), 1.41-1.48 (3H, m), 1.70-1.84 (2H, m), 2.00-2.05 (4H, m), 2.91-2.96 (2H, m), 3.84-3.93 (1H, m), 4.46-4.49 (1H, m), 4.53-4.60 (3H, m), 7.60-7.80 (4H, m), 11.19 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ13.5, 19.8, 26.0, 29.6, 31.3, 46.6, 47.4, 51.5, 56.7, 112.8, 113.5, 126.9, 131.0, 131.9, 143.2; HRMS for $C_{16}H_{24}N_3^+$ (M^+), calcd. 258.1965, found 258.1964.



3b

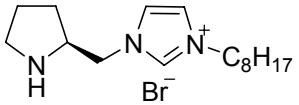
STAO 3b was synthesized following procedure **A**. $[\alpha]_D^{20}$= +14.9° (c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (3H, *J*= 6.6 Hz), 0.98 (3H, *J*= 7.2 Hz), 1.23 (18H, br), 1.41-1.56 (3H, m), 1.62-1.83 (4H, m), 1.97-2.13 (3H, m), 2.97 (3H, t, *J*= 6.6 Hz), 3.86 (1H, br), 4.01 (2H, t, *J*= 6.9 Hz), 4.48-4.58 (4H, m), 7.59-7.69 (3H, m), 7.79-7.81 (1H, m), 10.47 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.4, 14.1, 14.2, 19.7, 22.6, 25.6, 25.9, 29.3, 29.4, 29.5, 29.6, 31.2, 31.9, 46.4, 47.4, 51.2, 57.0, 60.3, 67.8, 112.8, 113.6, 126.8, 126.9, 131.1, 132.0, 143.4; HRMS for $C_{16}H_{24}N_3^+$ (M^+), calcd. 258.1965, found 258.1960; HRMS for $C_{12}H_{25}O_4S^-$ (M^-), calcd. 265.1479, found 265.1472.



3c

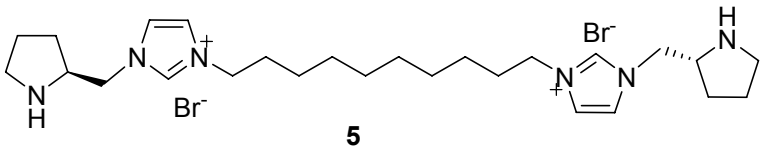
STAO 3c was synthesized following procedure **A** or **B**. $[\alpha]_D^{20}$= +12.9° (c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ(for mixtures of C_{11}-C_{13} isomers) 0.78-0.85 (6H, m), 0.94-1.18 (20H, m), 1.34-1.65 (6H, m), 1.86-2.14 (4H, m), 2.47 (1H, br), 2.96-3.01 (2H, m), 3.89-3.98 (1H, m), 4.19 (1H, br), 4.46-4.51 (2H, m), 4.65-4.68 (2H, m), 7.08 (2H, d, *J*= 8.1 Hz), 7.55-7.64 (3H, m), 7.75 (2H, d, *J*=8.1 Hz), 7.83-7.85 (1H, m), 10.54 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (for mixtures of C_{11}-C_{13} isomers) 13.4, 14.0, 19.7, 22.5, 22.6, 22.7, 25.2, 27.2, 27.5, 29.2, 29.3, 29.7, 31.1, 31.7, 31.8, 31.9, 36.6,

36.9, 45.5, 45.8, 46.3, 47.4, 50.4, 57.5, 112.7, 113.5, 125.9, 126.7, 126.8, 127.3, 131.2, 132.0, 143.4, 143.8, 148.0; HRMS for $C_{16}H_{24}N_3^+$ (M^+), calcd. 258.1965, found 258.1964; HRMS for $C_{17\text{-}19}H_{27\text{-}31}O_4S^-$ (M^-), calcd. 311.1686, 325.1843, 339.1999, found 311.1686, 325.1844, 339.2001.



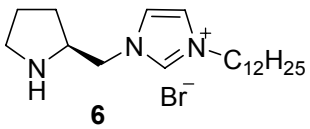
4

Chiral ionic liquid **4** was synthesized following our published procedure. [1] $[\alpha]_D^{20}$= +7.2° (c=1.0, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.71-0.75 (3H, m), 1.11-1.18 (12H, br m), 1.55-1.61 (2H, m), 1.79-1.86 (3H, m), 2.36 (1H, br), 2.74-2.81 (2H, m), 3.54 (1H, br), 4.06-4.34 (4H, m), 7.33 (1H, s), 7.64 (1H, s), 10.10 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 22.4, 25.8, 26.1, 28.8, 28.9, 29.1, 30.2, 31.5, 46.5, 49.9, 54.2, 57.4, 121.2, 123.3, 137.0; HRMS for $C_{16}H_{30}N_3^+$ (M^+), calcd. 264.2434, found 264.2435.



5

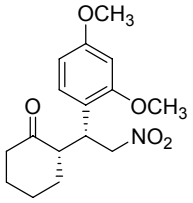
Chiral ionic liquid **5** was synthesized following our published procedure. [1] $[\alpha]_D^{20}$= -1.30° (c=1.0, EtOH); ^{1}H NMR (300 MHz, DMSO): δ 1.24 (14H, br), 1.56-1.60 (4H, m), 1.78-1.81 (6H, br), 2.64-2.83 (3H, br m), 2.95 (1H, br), 3.39-3.42 (2H, m), 3.93-4.00 (2H, m), 4.13-4.30 (7H, br m), 7.84 (4H, br), 9.33-9.59 (2H, br m); ^{13}C NMR (DMSO, 75 MHz): δ 23.9, 25.9, 28.7, 29.0, 29.2, 29.8, 46.3, 49.1, 53.8, 57.5, 122.3, 123.4, 136.8; HRMS for $C_{26}H_{46}N_6Br^+$ (M^{2+}+Br^-), calcd.521.2967 and 523.2947, found 521.2958 and 523.2927.



6

Chiral ionic liquid **6** was synthesized following our published procedure. [1] $[\alpha]_D^{20}$= +20.5° (as hydrochloride salt, c=1.0, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80-0.85 (3H, m), 1.20 (18H, br), 1.51-1.94 (5H, m), 2.84-3.12 (2H, m), 3.60 (1H, br), 4.06-4.54 (4H, m), 7.28 (1H, br), 7.37 (1H, s), 10.34 (1H, br); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.6, 23.5, 26.4, 28.1, 29.0, 29.3, 29.4, 29.5, 29.6, 29.8, 31.8, 45.4, 49.0, 50.2, 50.5, 60.2, 122.6, 123.7, 136.4; HRMS for $C_{20}H_{38}N_3^+$ (M^+), calcd. 320.3060, found 320.3061.

General procedure: To a solution of **3c** (29 mg, 0.05 mmol) in water (0.5 mL) in a vial, was added nitrostyrene (37 mg, 0.25 mmol) at room temperature. The mixture was stirred vigorously for 5 minutes, and then cyclohexanone was added (130 μL, 1.25 mmol). The reaction mixture was stirred for 12 h. The water was decanted after centrifuge at 6000rpm for 3 minutes. The residue was purified by Flash chromatograph on silica gel to afford the Michael adduct (58 mg, 93%) as white solid. In cases organic extraction is necessary; the aqueous layer was extracted with ether (1mL ×3). The organic extraction was concentrated and purified by flash chromatograph to afford the desired product. Products **7-13, 15-16** are known compounds. [1-4]



14

White solid. $[\alpha]_D^{rt}$= -32° (91% *ee*, c=1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17-1.29 (1H, m), 1.61-1.84 (4H, m), 2.02-2.13 (1H, m), 2.32-2.43 (2H, m), 2.90-2.95 (1H, m), 3.75 (3H, s), 3.78 (3H, s), 3.83-3.87 (1H, m), 4.73-4.82 (2H, m), 6.36-6.42 (2H, m), 6.95 (1H, d, *J*=8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.2, 28.6, 33.3, 40.9, 42.7, 50.7, 53.5, 55.4, 99.1, 104.4, 117.6, 131.5, 158.6, 160.4, 212.7. The enantiomeric excess was determined by HPLC with a AD-H column at 254 nm (2-propanol: hexane=10:90), 0.5 mL/min; t_R= 26.8 min (minor), 40.9 min (major).

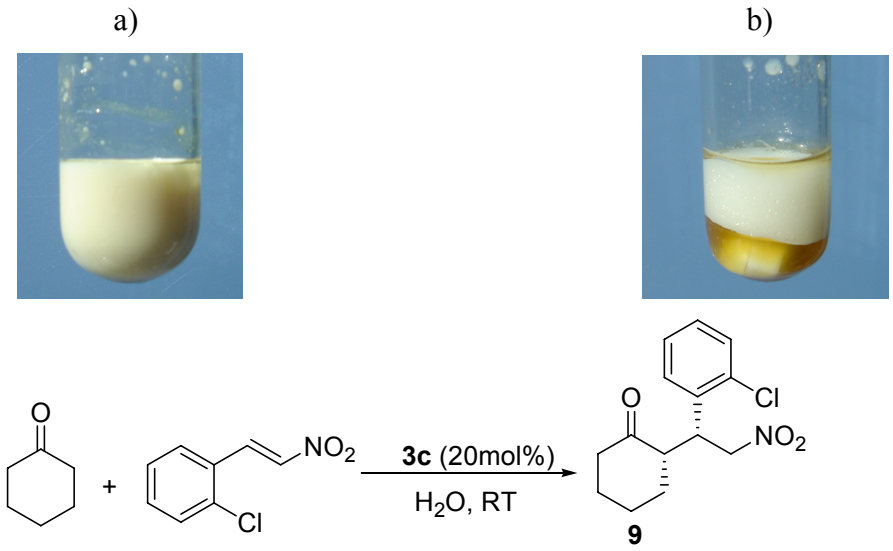


Figure Pictures showing **3c** catalyzed reaction of 2-chloro-nitrostyrene at the beginning (a) and in the end (b).

Reference:

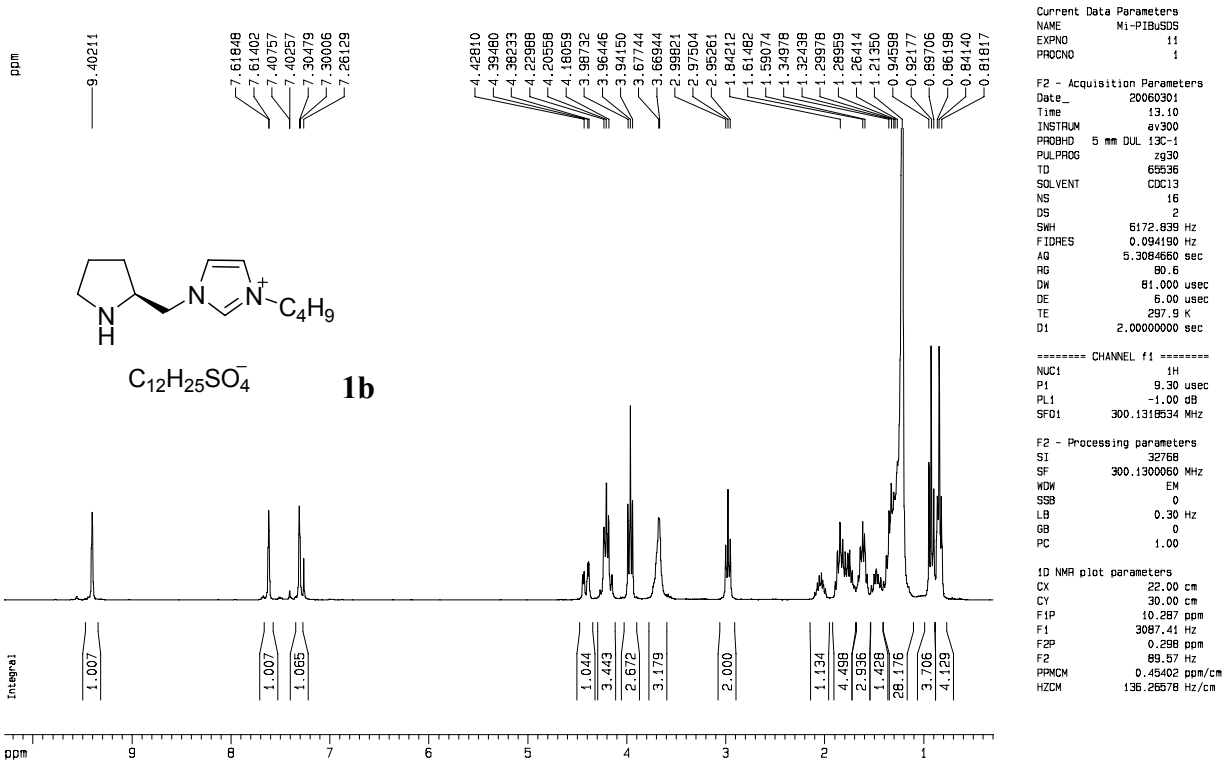
[1] S. Luo, X. Mi, L. Zhang, S. Liu, H. Xu, J.-P. Cheng, *Angew. Chem. Int. Ed.* 2006, 45, 3093。

[2] (a)T. Ishii, S. Fujioka, Y. Sekiguchi, H. Kotsuki, *J. Am. Chem. Soc.* 2004, **126**, 9558-9559; (b) J. M. Betancort, K. Sakthivel, R. Thayumanavan, F. Tanaka, C. F. Barbas III, *Synthesis* 2004, 1509-1521. (c) B. List, P. Pojarliev, H. J. Martin, *Org. Lett.* 2001, **3**, 2423-2425.

[3] (a) A. J. A. Cobb, D. A. Longbottom, D. M. Shaw, S. V. Ley, *Chem. Commun.* 2004, 1808-1809; (b) A. J. A. Cobb, D. M. Shaw, D. A. Longbottom, J. B. Gold, S. V. Ley, *Org. Biomol. Chem.* 2005, **3**, 84-96; (c) C. E. T. Mitchell, A. J. A. Cobb, S. V. Ley, *Synlett* 2005, 611-614.

[4] (a) W. Wang, J. Wang, H. Li, *Angew. Chem. Int. Ed.* 2005, **44**, 1369; (b) Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem. Int. Ed*. 2005, **44**, 4212-4215.

NMR spectra for STAOs and new compounds

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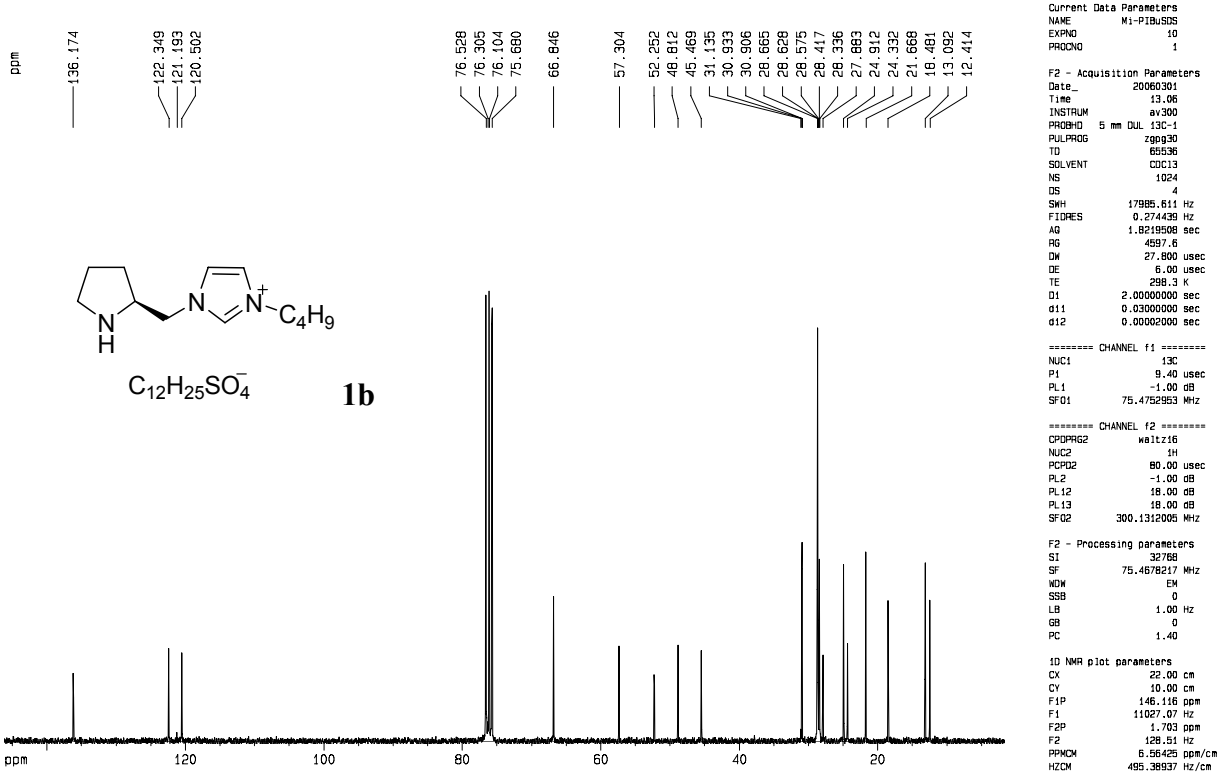


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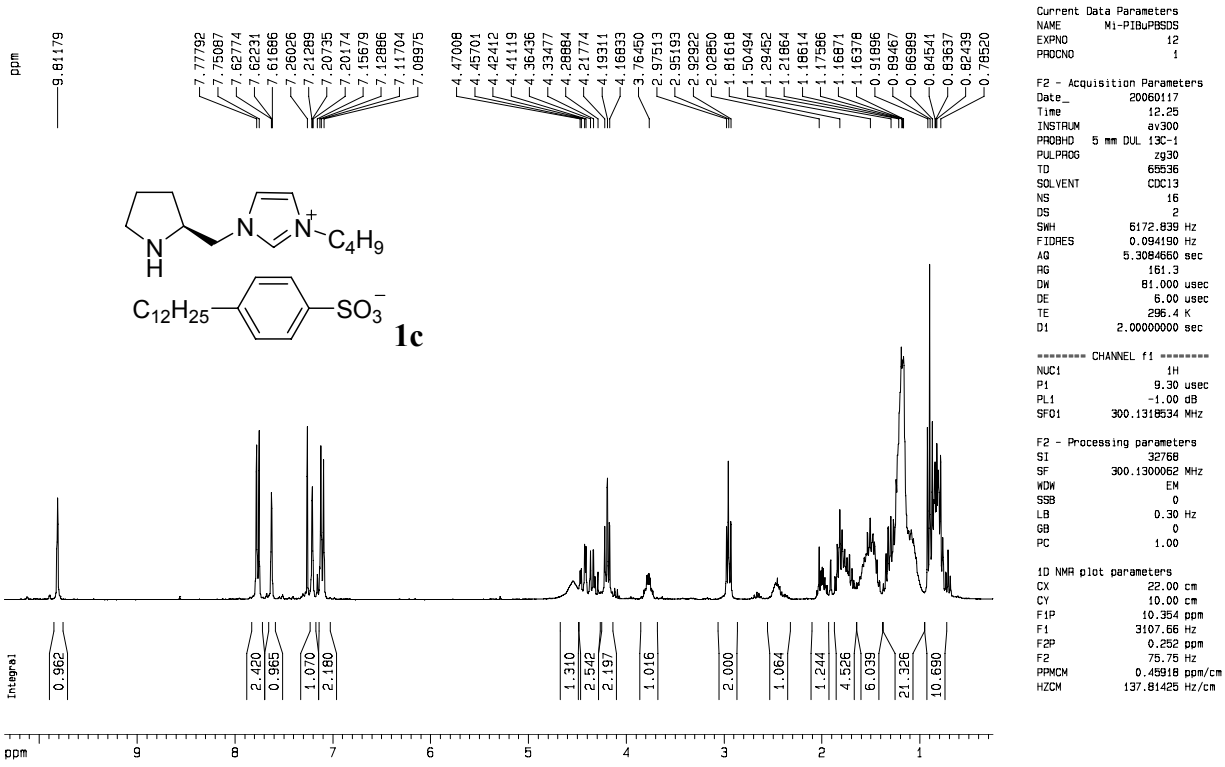


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PROCNO                 1

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D1           2.00000000 sec

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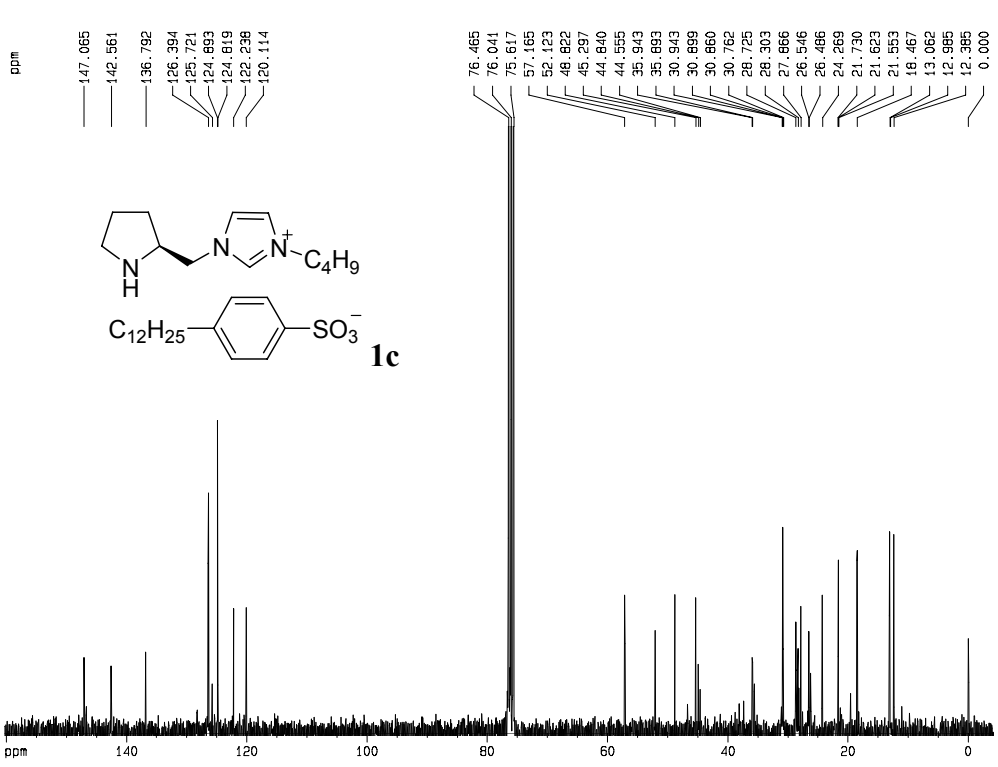
NUC1                   1H
P1                  9.30 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300062 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P               10.354 ppm
F1              3107.66 Hz
F2P                0.252 ppm
F2                75.75 Hz
PPMCM           0.45918 ppm/cm
HZCM          137.81425 Hz/cm
```



1c

```
Current Data Parameters
NAME        Mi-PIBuPBSDS
EXPNO               13
PROCNO               1

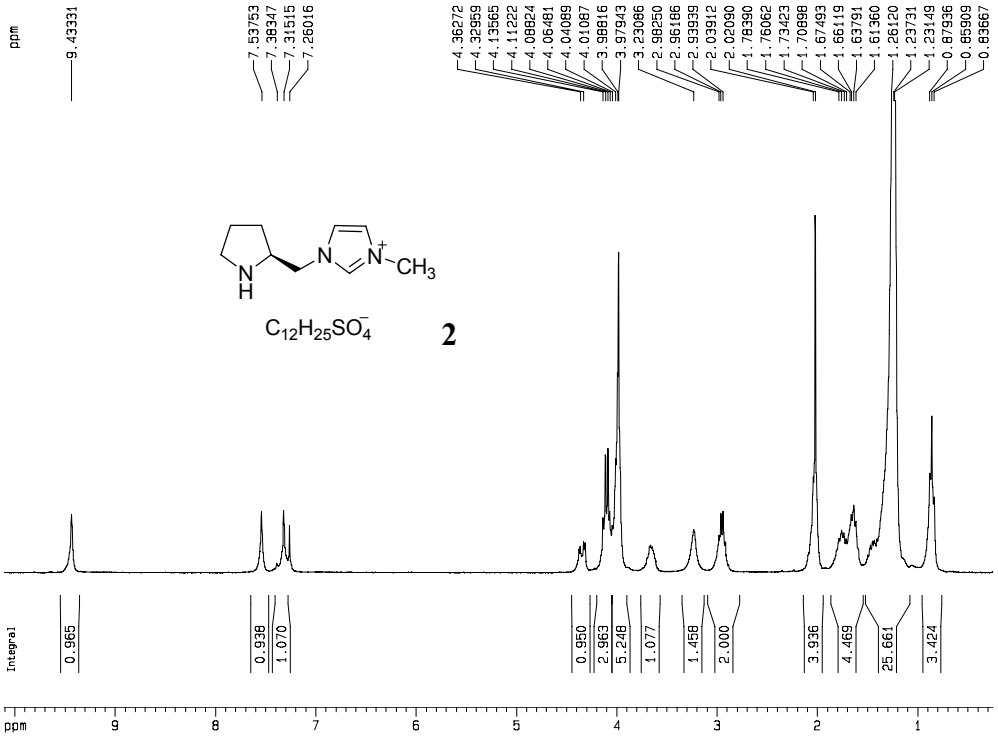
F2 - Acquisition Parameters
Date_          20060117
Time              12.28
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 510
DS                   4
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                6502
DW               27.800 usec
DE                6.00 usec
TE               296.8 K
D1          2.00000000 sec
d11         0.03000000 sec
d12         0.00002000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                9.40 usec
PL1               -1.00 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL2               -1.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4678236 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX               22.00 cm
CY               30.00 cm
F1P             160.295 ppm
F1            12097.15 Hz
F2P              -4.110 ppm
F2             -310.15 Hz
PPMCM          7.47296 ppm/cm
HZCM         563.96790 Hz/cm
```



2

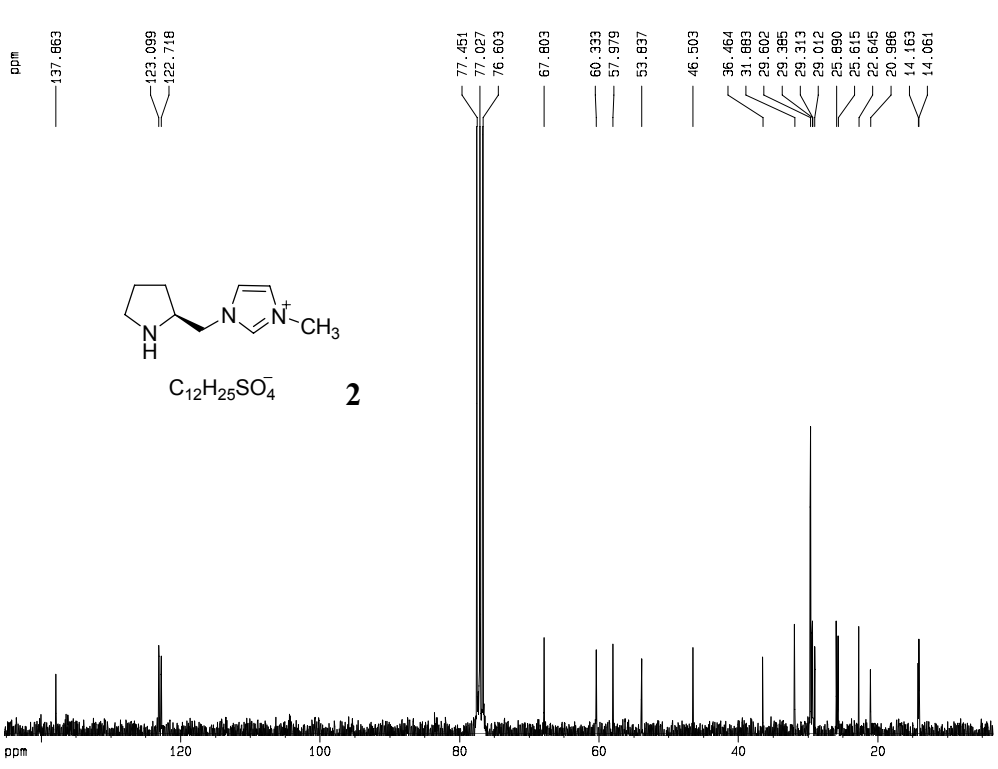
```
Current Data Parameters
NAME          Mi-PIMeSDS
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20060108
Time              12.45
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                 181
DW               81.000 usec
DE                6.00 usec
TE               299.7 K
D1          2.00000000 sec

======== CHANNEL f1 ========
NUC1               1H
P1                9.30 usec
PL1               -1.00 dB
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                EM
SSB                 0
LB                0.30 Hz
GB                  0
PC                1.00

1D NMR plot parameters
CX               22.00 cm
CY               20.00 cm
F1P             10.105 ppm
F1            3032.91 Hz
F2P              0.253 ppm
F2              75.94 Hz
PPMCM          0.44783 ppm/cm
HZCM         134.40761 Hz/cm
```



$C_{12}H_{25}SO_4^-$ **2**

Current Data Parameters
NAME Mi-PIMeSOS
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060108
Time 12.49
INSTRUM av300
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 395
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 5160.6
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

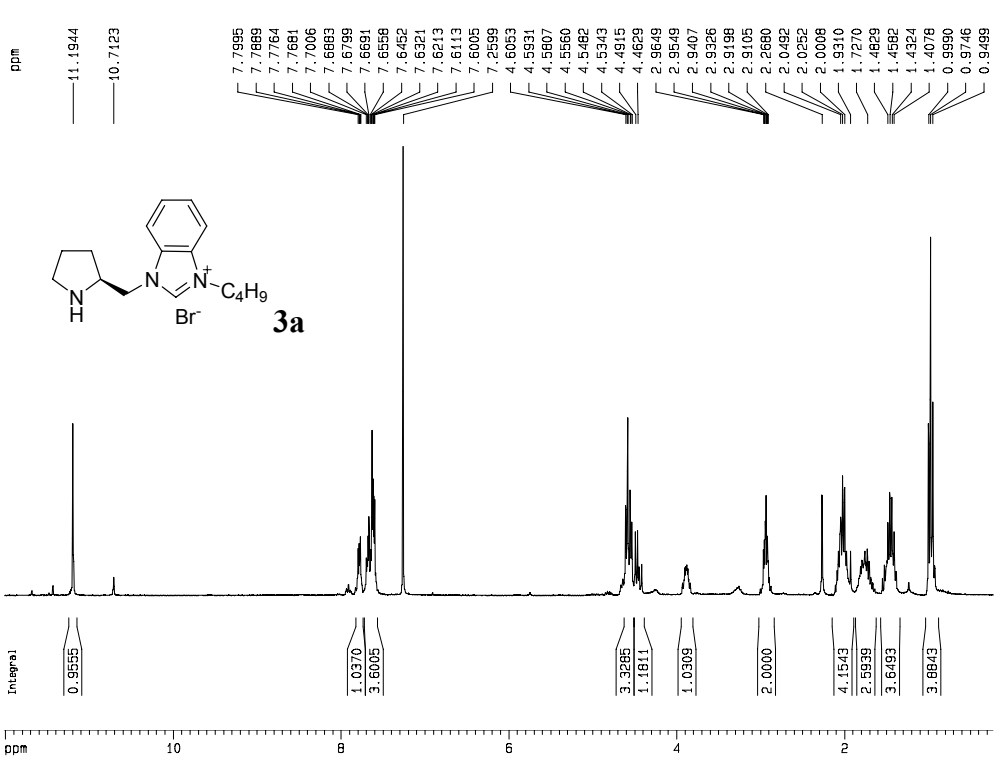
======== CHANNEL f1 ========
NUC1 13C
P1 9.40 usec
PL1 -1.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 145.238 ppm
F1 10960.79 Hz
F2P 3.455 ppm
F2 260.74 Hz
PPMCM 6.44468 ppm/cm
HZCM 486.36588 Hz/cm

2b



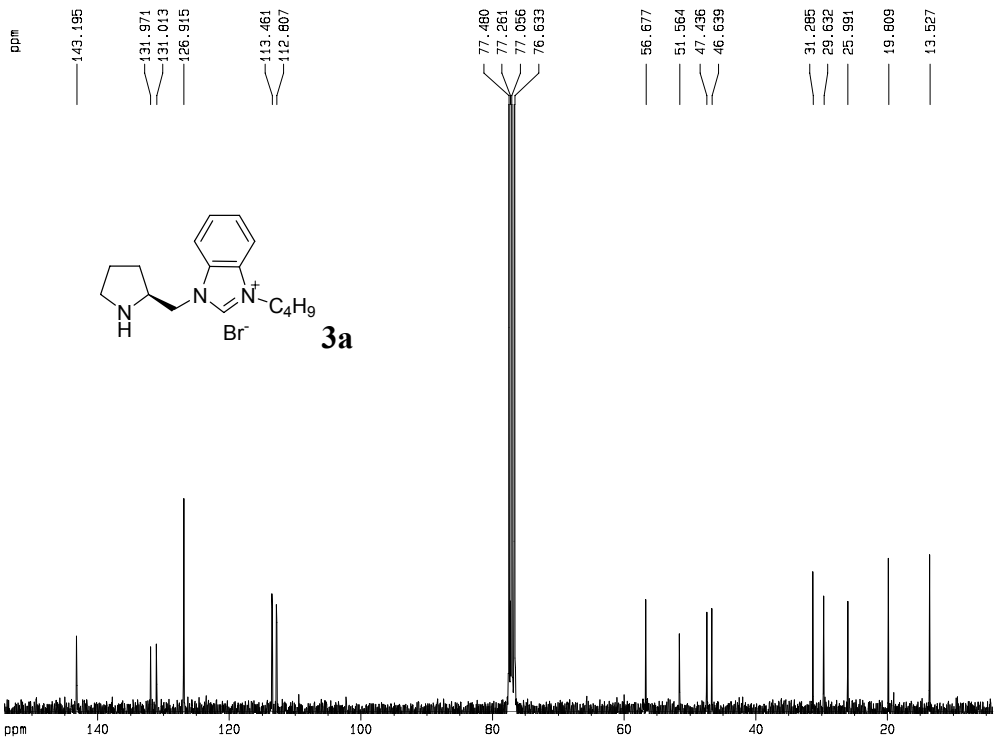

```
Current Data Parameters
NAME          Liu-PBIBuBr
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20051201
Time               12.11
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                 287.4
DW                81.000 usec
DE                 6.00 usec
TE                296.2 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1               -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300066 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00

1D NMR plot parameters
CX                22.00 cm
CY                10.00 cm
F1P              12.010 ppm
F1             3604.66 Hz
F2P               0.228 ppm
F2               68.56 Hz
PPMCM          0.53554 ppm/cm
HZCM          160.73169 Hz/cm
```




```
Current Data Parameters
NAME          Liu-PBIBuBr
EXPNO                  11
PROCNO                  1

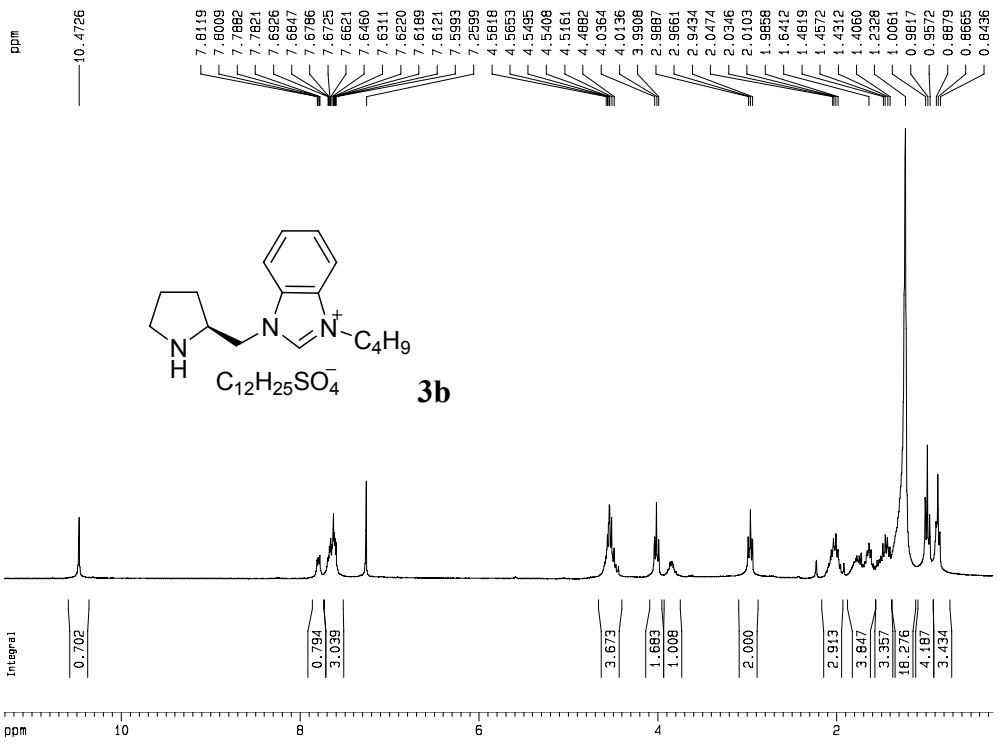
F2 - Acquisition Parameters
Date_           20051201
Time               12.38
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   926
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                  6502
DW                27.800 usec
DE                 6.00 usec
TE                296.7 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.40 usec
PL1               -1.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                22.00 cm
CY                30.00 cm
F1P             154.182 ppm
F1            11635.74 Hz
F2P               3.981 ppm
F2              300.44 Hz
PPMCM          6.82730 ppm/cm
HZCM          515.24103 Hz/cm
```



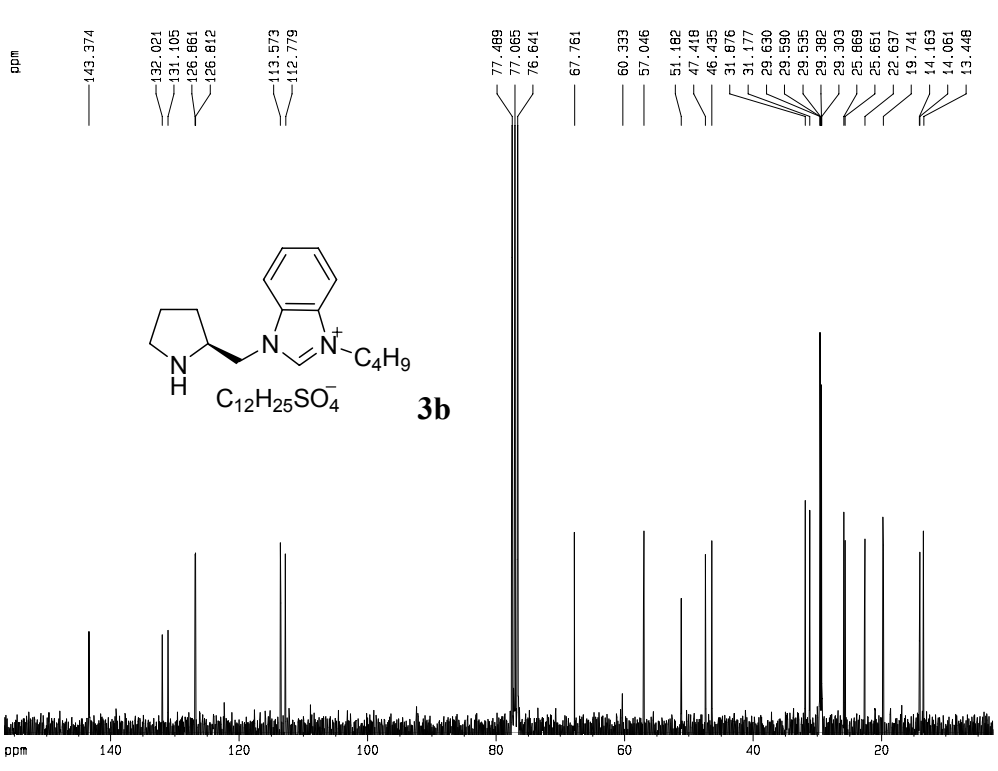

```
Current Data Parameters
NAME        Mi-PBImBuSDS
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060302
Time               13.50
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                   256
DW                81.000 usec
DE                 6.00 usec
TE                296.8 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300058 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P               11.309 ppm
F1              3394.20 Hz
F2P                0.254 ppm
F2                76.13 Hz
PPMCM           0.50252 ppm/cm
HZCM          150.82144 Hz/cm
```




```
Current Data Parameters
NAME        Mi-PBImBuSDS
EXPNO                 11
PROCNO                 1

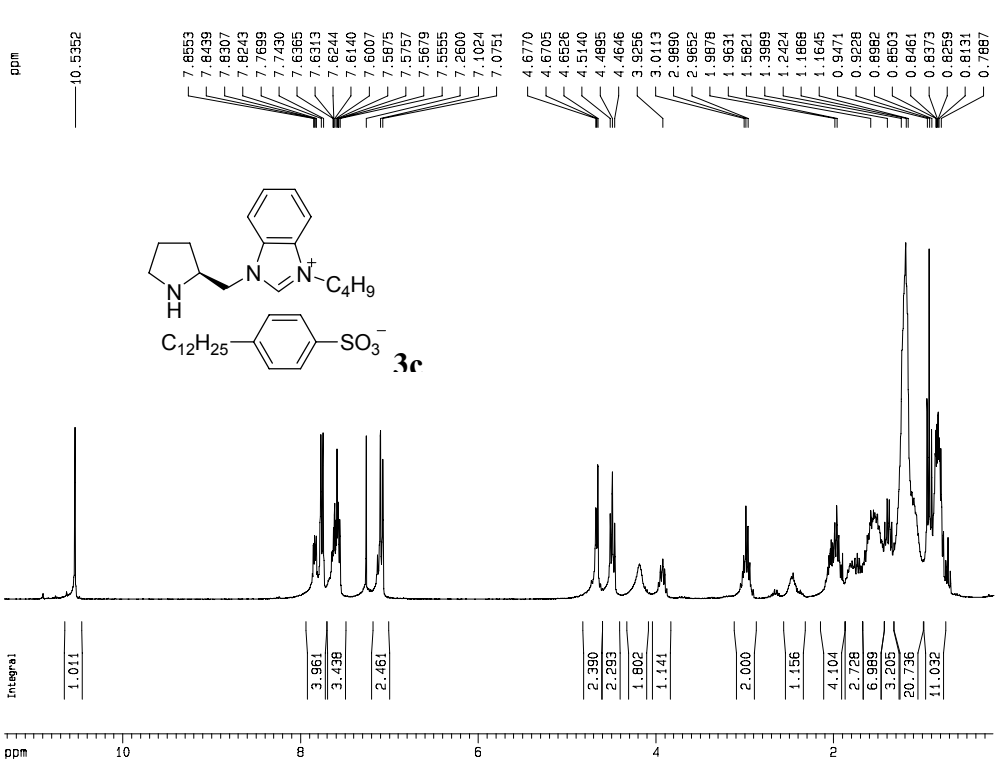
F2 - Acquisition Parameters
Date_           20060118
Time               13.21
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   153
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                5792.6
DW                27.800 usec
DE                 6.00 usec
TE                298.8 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.40 usec
PL1                -1.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 22.00 cm
CY                 20.00 cm
F1P              156.549 ppm
F1             11814.41 Hz
F2P                2.666 ppm
F2               201.18 Hz
PPMCM           6.99470 ppm/cm
HZCM          527.87396 Hz/cm
```



3c

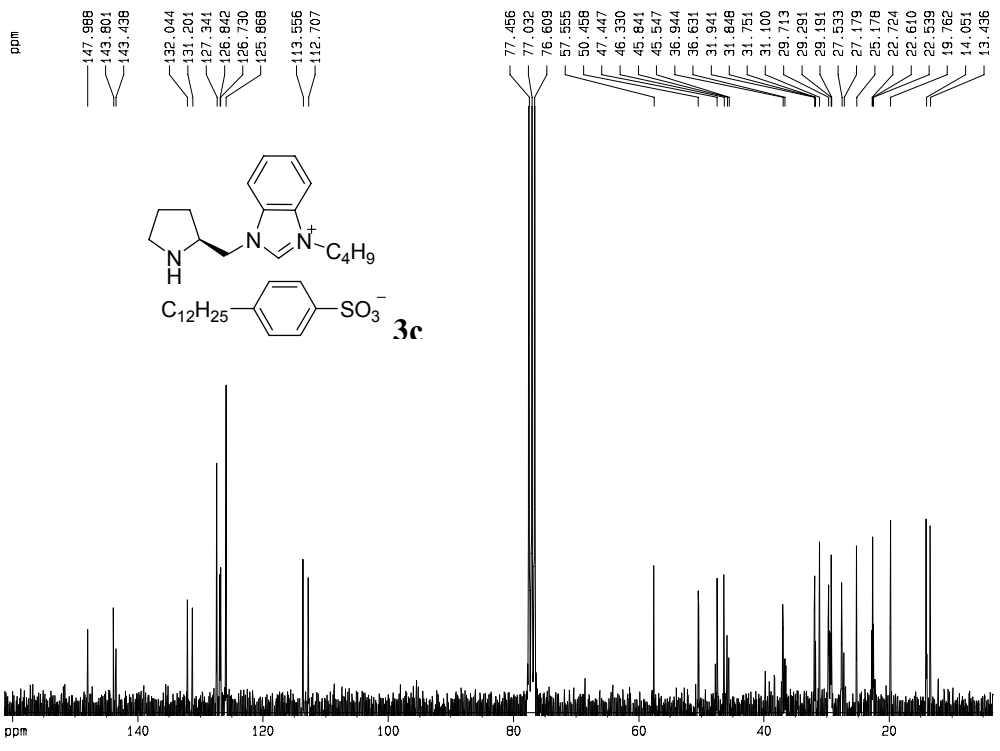
```
Current Data Parameters
NAME      Mi-PBImBuPBSDS
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060118
Time               12.22
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                 143.7
DW                81.000 usec
DE                 6.00 usec
TE                298.5 K
D1              2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1                -1.00 dB
SFO1         300.1318634 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P               11.331 ppm
F1              3400.82 Hz
F2P                0.208 ppm
F2                62.31 Hz
PPMCM          0.50562 ppm/cm
HZCM          151.75053 Hz/cm
```



3c

```
Current Data Parameters
NAME      Mi-PBImBuPBSDS
EXPNO                 11
PROCNO                 1

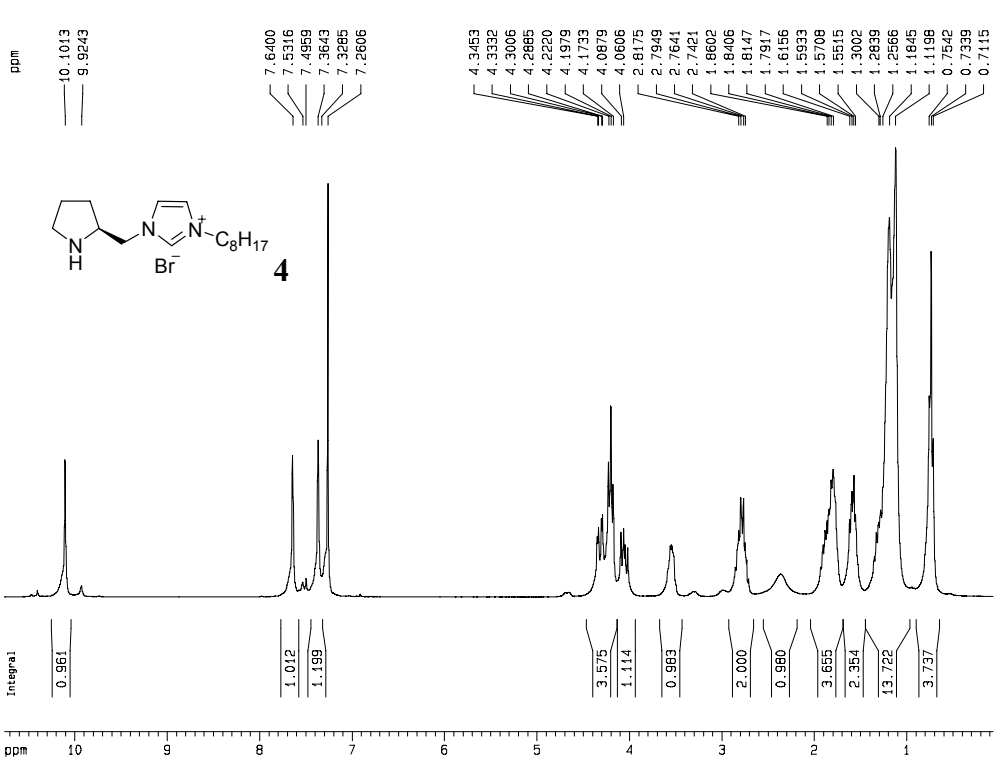
F2 - Acquisition Parameters
Date_           20060118
Time               12.25
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   337
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 3649.1
DW                27.800 usec
DE                 6.00 usec
TE                298.9 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.40 usec
PL1                -1.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 22.00 cm
CY                 30.00 cm
F1P              161.284 ppm
F1             12171.74 Hz
F2P                3.455 ppm
F2               260.74 Hz
PPMCM          7.17405 ppm/cm
HZCM          541.40912 Hz/cm
```



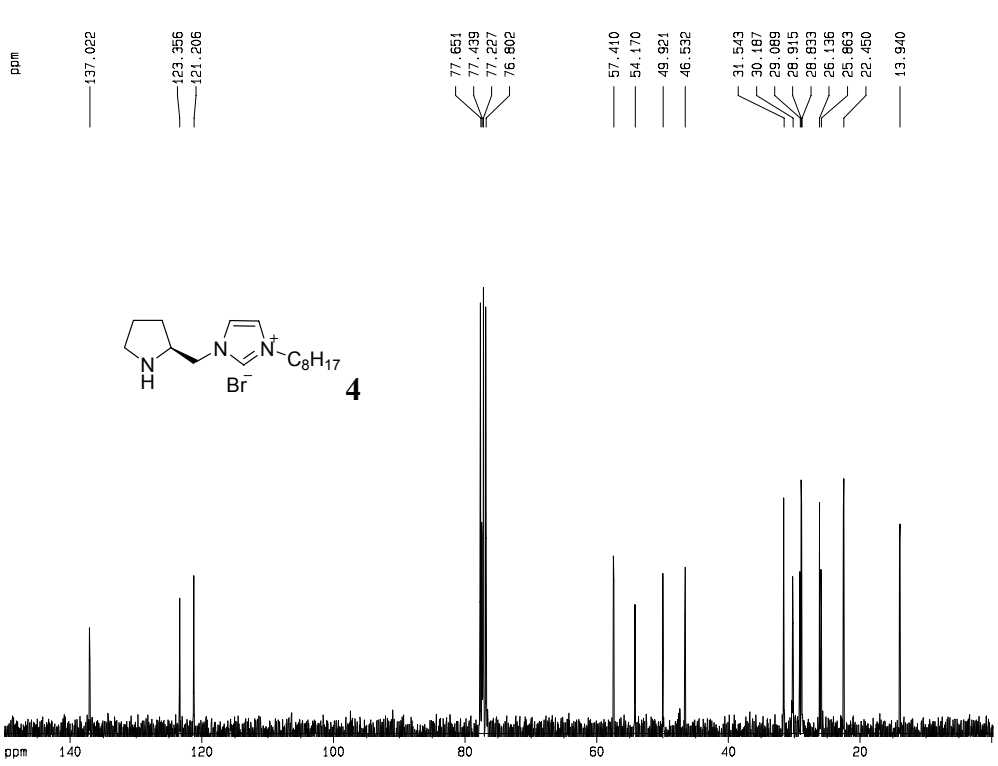

```
Current Data Parameters
NAME          Liu-PIm8Br
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060112
Time               12.22
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                    64
DW               81.000 usec
DE                6.00 usec
TE                297.5 K
D1           2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1               -1.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300072 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P               10.760 ppm
F1              3229.36 Hz
F2P                0.068 ppm
F2                20.30 Hz
PPMCM             0.48601 ppm/cm
HZCM            145.86632 Hz/cm
```




```
Current Data Parameters
NAME          Liu-PIm8Br
EXPNO                 11
PROCNO                 1

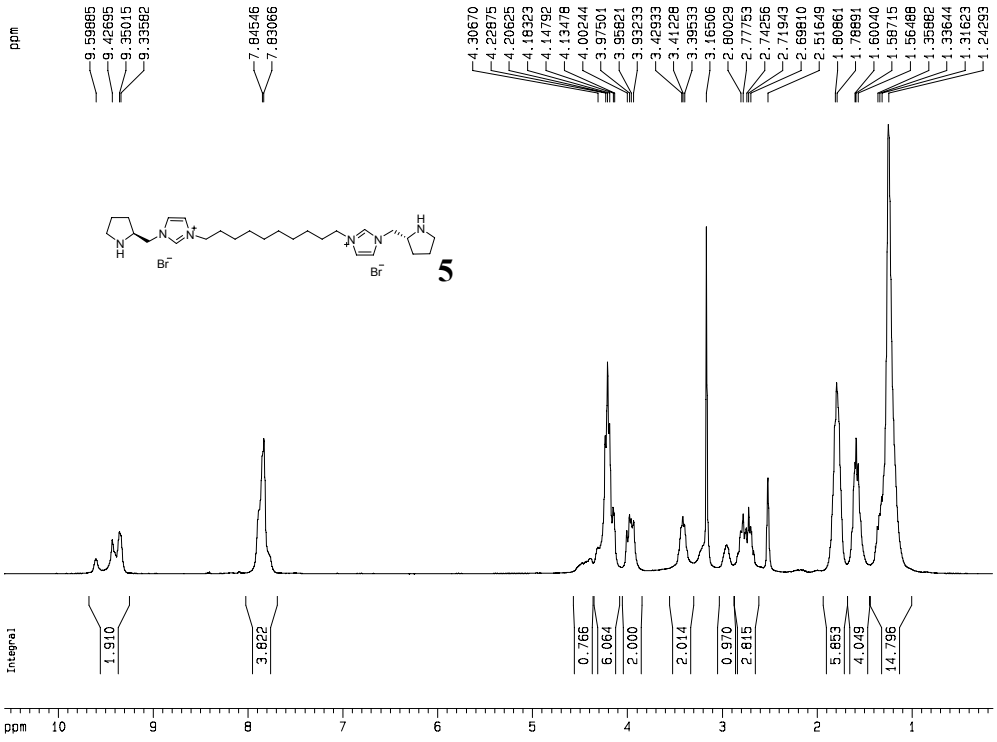
F2 - Acquisition Parameters
Date_           20060112
Time               12.25
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    88
DS                     4
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                5792.6
DW               27.800 usec
DE                6.00 usec
TE                297.7 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.40 usec
PL1               -1.00 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2               -1.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P              149.973 ppm
F1             11318.12 Hz
F2P               -0.228 ppm
F2                -17.19 Hz
PPMCM             6.82730 ppm/cm
HZCM            515.24103 Hz/cm
```



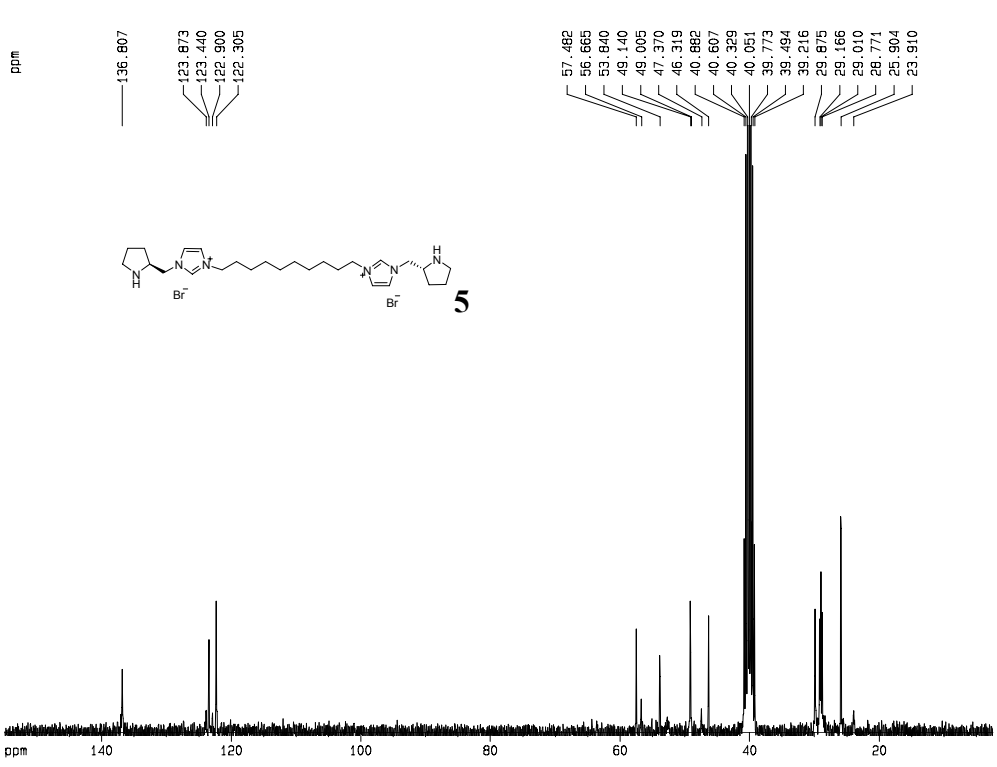

```
Current Data Parameters
NAME      Liu-PIdeca-diBr
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20060111
Time               12.27
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                  90.5
DW                 81.000 usec
DE                  6.00 usec
TE                 297.0 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  9.30 usec
PL1                -1.00 dB
SFO1         300.1318634 MHz

F2 - Processing parameters
SI                 32768
SF           300.1299965 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P               10.569 ppm
F1              3171.93 Hz
F2P                0.149 ppm
F2                44.63 Hz
PPMCM          0.47363 ppm/cm
HZCM          142.14998 Hz/cm
```




```
Current Data Parameters
NAME      Liu-PIdeca-diBr
EXPNO                  11
PROCNO                  1

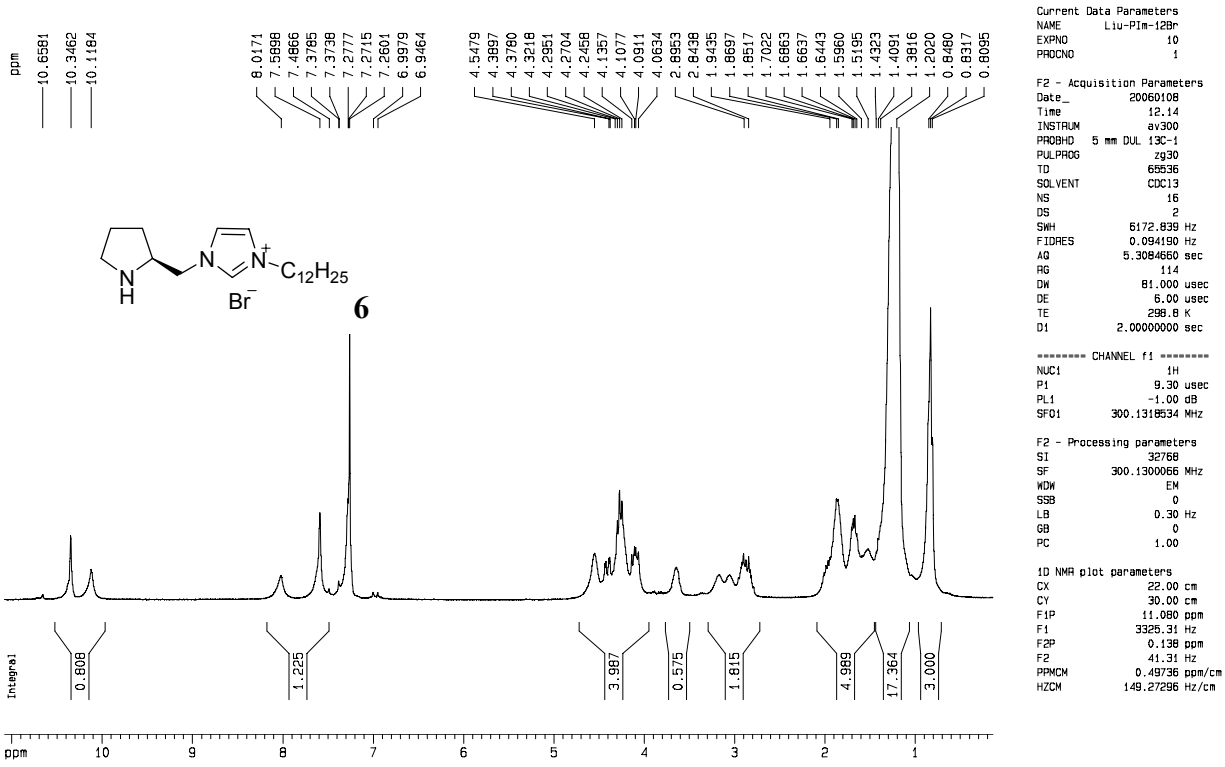
F2 - Acquisition Parameters
Date_           20060111
Time               12.33
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                   525
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 812.7
DW                27.800 usec
DE                 6.00 usec
TE                 297.8 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.40 usec
PL1                -1.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 22.00 cm
CY                 30.00 cm
F1P              154.971 ppm
F1             11695.30 Hz
F2P                2.403 ppm
F2               181.33 Hz
PPMCM          6.93491 ppm/cm
HZCM          523.36218 Hz/cm
```



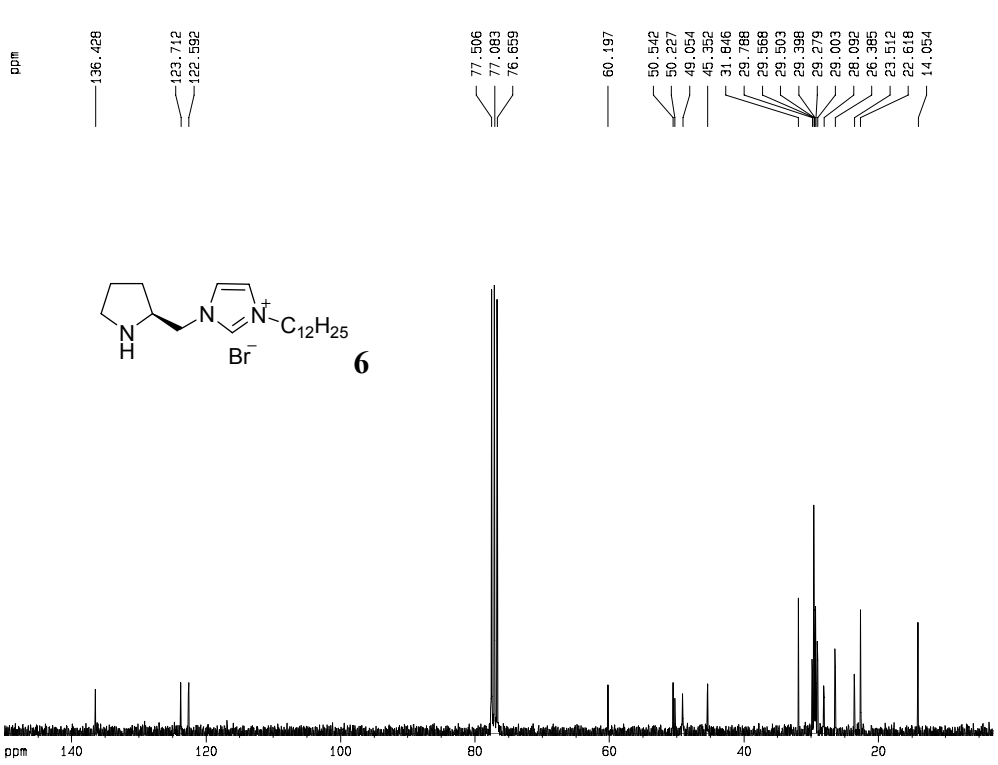

```
Current Data Parameters
NAME        Liu-PIm-12Br
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060108
Time               12.14
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                   114
DW                81.000 usec
DE                 6.00 usec
TE                298.8 K
D1           2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1               -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300066 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00

1D NMR plot parameters
CX                22.00 cm
CY                30.00 cm
F1P              11.080 ppm
F1               3325.31 Hz
F2P               0.138 ppm
F2                41.31 Hz
PPMCM          0.49736 ppm/cm
HZCM          149.27296 Hz/cm
```



6

```
Current Data Parameters
NAME      Liu-PIm-12Br-HC
EXPNO              11
PROCNO              1

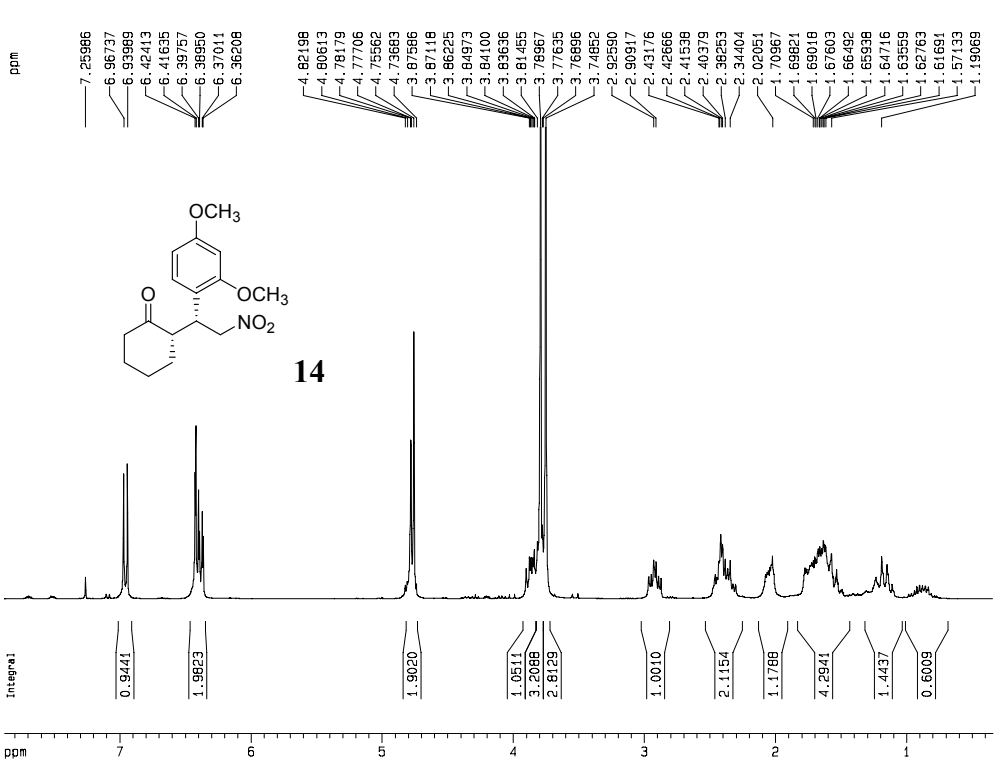
F2 - Acquisition Parameters
Date_          20060106
Time              12.43
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 171
DS                   4
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG               4597.6
DW              27.800 usec
DE               6.00 usec
TE               299.2 K
D1          2.00000000 sec
d11         0.03000000 sec
d12         0.00002000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                9.40 usec
PL1              -1.00 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             18.00 dB
PL13             18.00 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677490 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX               22.00 cm
CY               10.00 cm
F1P            149.973 ppm
F1           11318.12 Hz
F2P              2.929 ppm
F2             221.03 Hz
PPMCM          6.68382 ppm/cm
HZCM         504.41287 Hz/cm
```



14

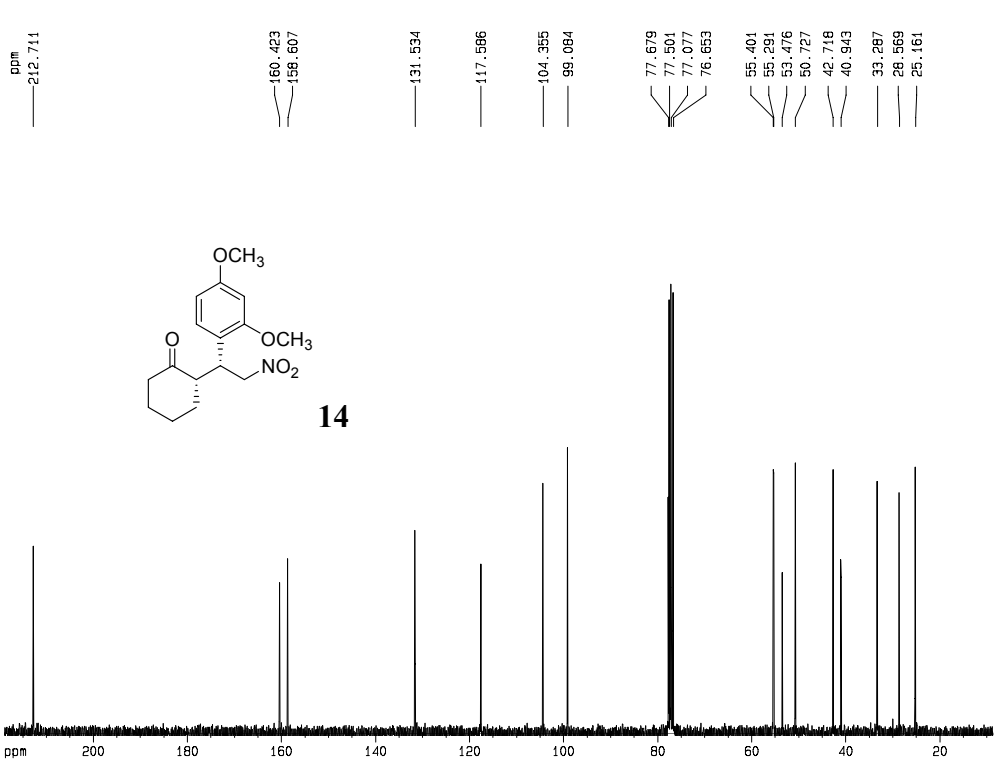
```
Current Data Parameters
NAME         Mi-DMONS-Br
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20051122
Time              13.11
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          6172.839 Hz
FIDRES       0.094190 Hz
AQ           5.3084660 sec
RG                  64
DW              81.000 usec
DE               6.00 usec
TE               296.8 K
D1          2.00000000 sec

======== CHANNEL f1 ========
NUC1               1H
P1                9.30 usec
PL1              -1.00 dB
SFO1       300.1318634 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC                1.00

1D NMR plot parameters
CX               22.00 cm
CY               20.00 cm
F1P             7.881 ppm
F1            2365.20 Hz
F2P              0.344 ppm
F2             103.19 Hz
PPMCM          0.34256 ppm/cm
HZCM         102.81873 Hz/cm
```

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Current Data Parameters
NAME              Mi-DMONS
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20051129
Time                12.51
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    198
DS                      4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 4597.6
DW                27.800 usec
DE                 6.00 usec
TE                 297.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PL1                -1.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P              218.892 ppm
F1             16519.25 Hz
F2P                8.716 ppm
F2               657.77 Hz
PPMCM            9.55344 ppm/cm
HZCM           720.97656 Hz/cm
```