# Synthesis of New Pro-PYE Ligands as Co-Catalysts toward Pd-Catalyzed Heck-Mizoroki Cross Coupling Reactions

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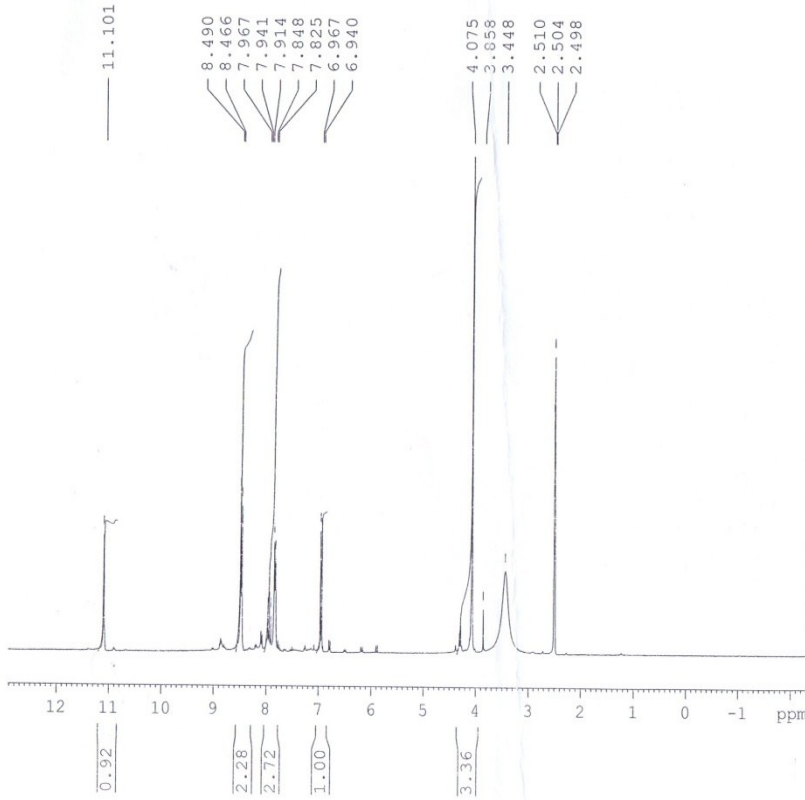[4]*Centre for Interdisciplinary Research in Basic Sciences (CIRBS), International Islamic University, Islamabad, Pakistan.*
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DR.NAVEED ZAFAR/NAIMA/NA-03_1HNMR_DMSO

DR.NAVEED ZAFAR/NAIMA/NA-03P_13CNMR_DMSO

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2324.69

1737.89

3296.04
3208.75
3080.15

1638.67  1581.09
1514.93  1547.21  1491.74
1436.71  1477.08  1365.07
1278.92
1225.04  1240.93  1199.93
1150.15
1025.52
802.76  837.41
735.34  758.19  714.25  669.14
682.55
632.31  572.56
505.63

Transmittance [%]

Wavenumber cm-1

Sample Name: NA 03P

**Figure S1:** $^1H$, $^{13}C$NMR, IR spectra of $[H_2L^1][OTf]_2$

9.110
8.182
8.159
7.935
7.912
7.215
7.208
7.191
6.750
6.742
6.727

3.809
3.713
3.693
3.357
2.510
2.505
1.937
1.898
1.755
1.729
1.527
1.496
1.458
1.405
1.374

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Current Data Parameters
NAME         PD-CY04_1HNMR_DMSO
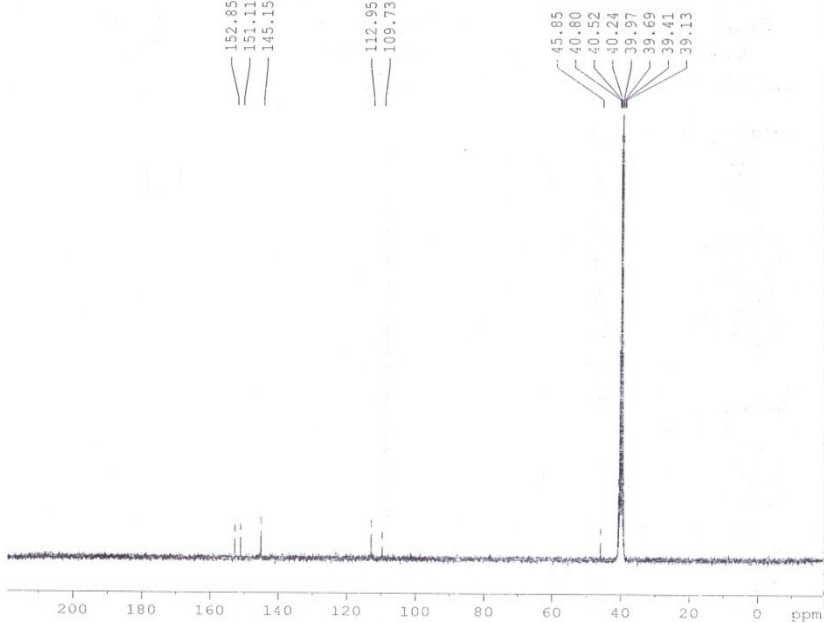EXPNO                        1
PROCNO                       1

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PROBHD    5 mm BBO BB-1H
PULPROG                   zg30
TD                       65536
SOLVENT                   DMSO
NS                           8
DS                           0
SWH               6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                         512
DW               81.000 usec
DE                 6.00 usec
TE                   294.9 K
D1          1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                   9.00 usec
PL1                  2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                       32768
SF          300.1300000 MHz
WDW                         EM
SSB                          0
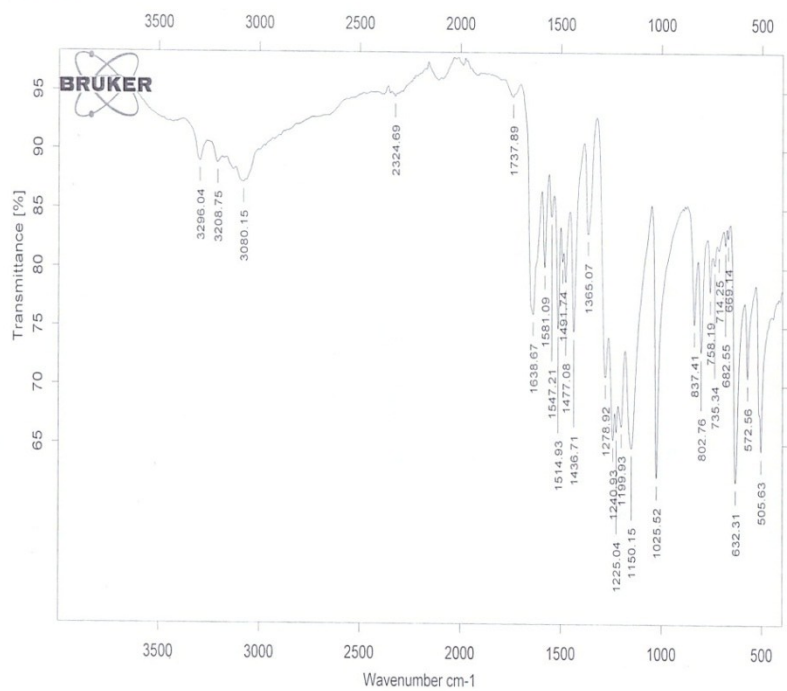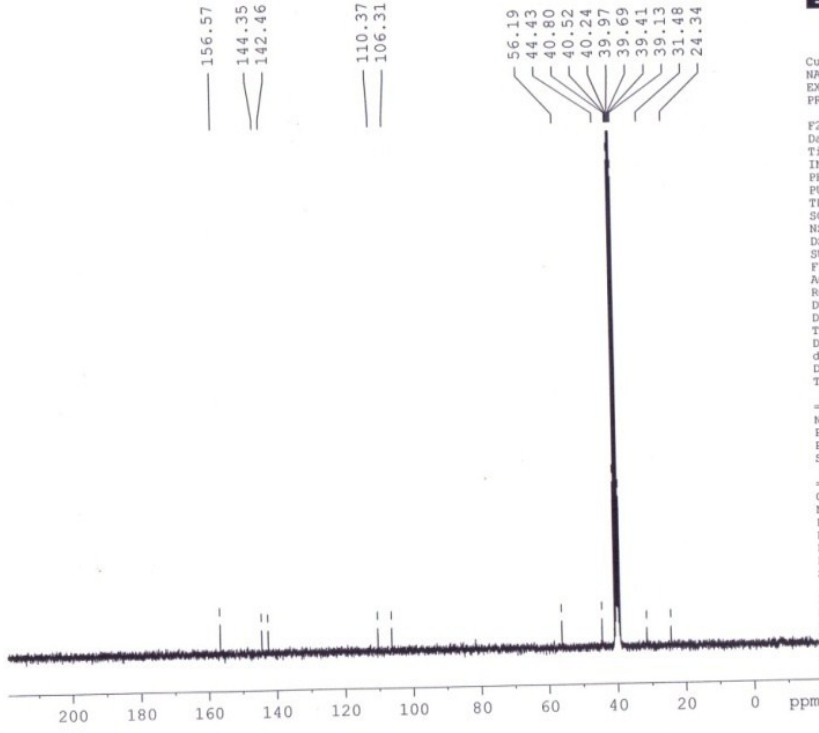LB                   0.30 Hz
GB                           0
PC                        1.00

12  11  10  9  8  7  6  5  4  3  2  1  0  -1  ppm

1.00   1.11 1.03 1.03 1.02      3.17 1.07   1.11 1.15 2.33

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156.57
144.35
142.46
110.37
106.31
56.19
44.43
40.80
40.52
40.24
39.97
39.69
39.41
39.13
31.48
24.34

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200   180   160   140   120   100   80   60   40   20   0   ppm
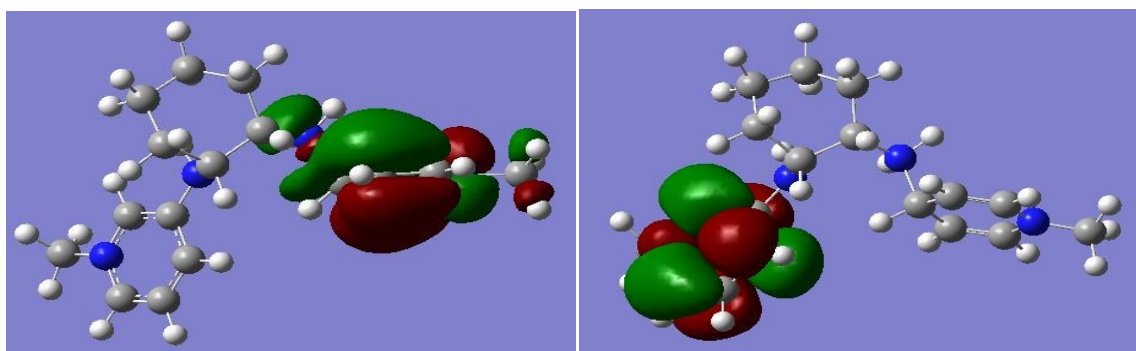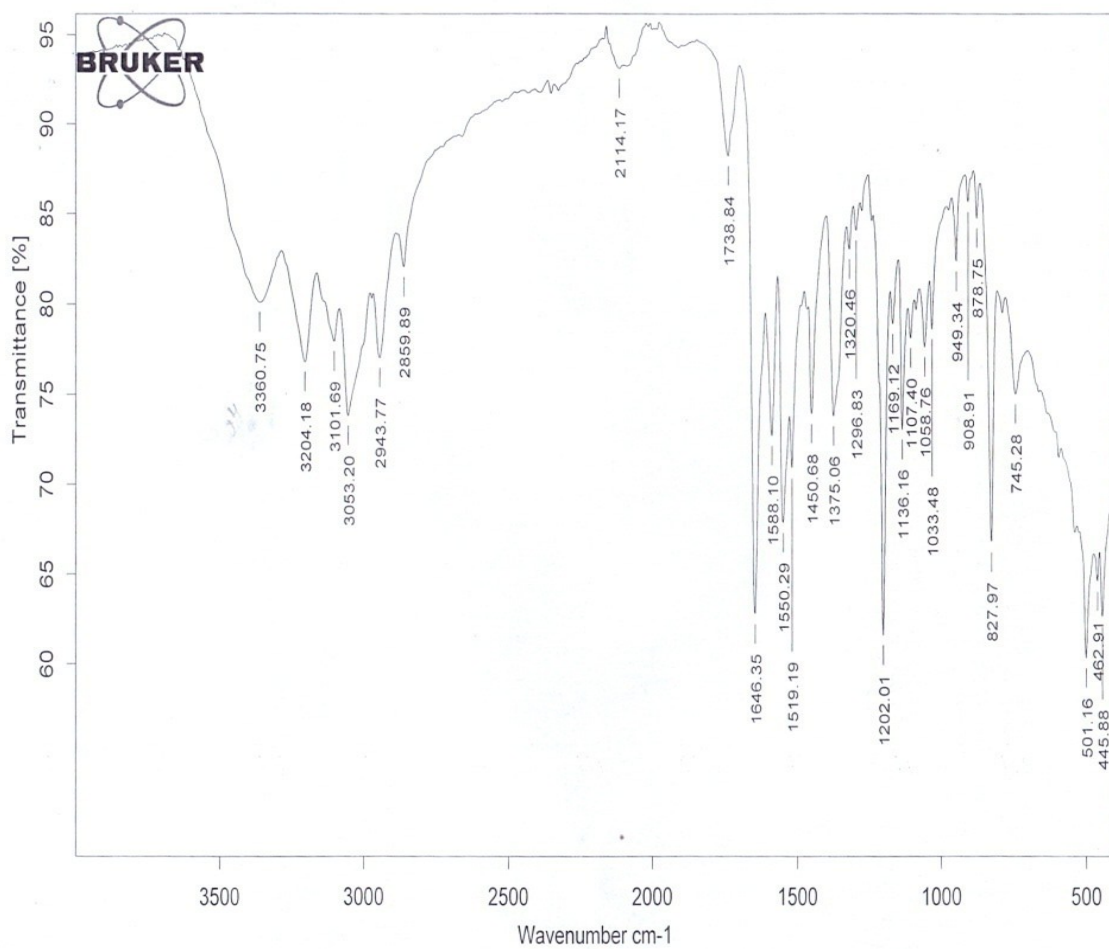
**HOMO (Gaussian)**                    **LUMO (Gaussian)**

**Figure S2:** ^{1}H, ^{13}CNMR, IR spectra and HOMO-LUMO of $[H_2L^2][OTf]_2$

HOMO (Gaussian)  LUMO (Gaussian)

## Bond angles

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|---|---|---|---|---|---|
| C1-N1-C2 | 123.0 | 124.9 | O1-S1-O3 | 114.8 | 113.2 |
| N1-C2-C3 | 123.6 | 122.9 | O2-S1-O1 | 114.3 | 113.8 |
| C2-C3-C4 | 120.6 | 121.4 | O3-S1-O2 | 115.3 | 105.1 |
| C3-C4-C5 | 119.8 | 119.5 | O1-S1-C8 | 103.7 | 106.2 |
| C4-C5-C6 | 119.0 | 118.7 | O3-S1-C8 | 103.8 | 106.5 |
| C5-C6-N2 | 121.7 | 122.0 | O2-S1-C8 | 102.7 | 106.4 |
| C6-N2-C7 | 119.4 | 117.2 | F3-C8-F1 | 107.1 | 110.1 |
| C6-N2-C2 | 120.8 | 121.5 | F2-C8-F3 | 106.0 | 111.3 |
| N2-C2-C3 | 118.0 | 117.0 | F1-C8-F2 | 105.1 | 109.5 |
| C7-N2-C2 | 119.7 | 121.2 | F2-C8-S1 | 112.0 | 106.0 |
| N2-C2-N1 | 118.4 | 120.1 | F3-C8-S1 | 111.8 | 108.5 |

**Figure S3:** $^1H$, $^{13}C$NMR, IR spectra, HOMO-LUMO and bond angles of $[H_2L^3][OTf]_2$

Sample Name: SRM 2B

HOMO (Gaussian)                                    LUMO (Gaussian)

**Bond angles**

| Atom no's | Experimental | Calculated | Atom no's | Experimental | Calculated |
|-----------|--------------|------------|-----------|--------------|------------|
| C1-N1 | 1.46 | 1.49 | O1-S1 | 1.43 | 1.47 |
| N1-C2 | 1.34 | 1.39 | O2-S1 | 1.43 | 1.39 |
| C2-C3 | 1.40 | 1.41 | S1-C8 | 1.82 | 1.82 |
| C3-C4 | 1.36 | 1.39 | F3-C8 | 1.31 | 1.37 |
| C4-C5 | 1.39 | 1.38 | F1-C8 | 1.33 | 1.36 |
| C5-C6 | 1.34 | 1.38 | F2-C8 | 1.32 | 1.36 |
| C6-N2 | 1.36 | 1.35 | C1-C1 | 1.51 | 2.19 |
| N2-C7 | 1.46 | 1.48 | N2-C2 | 1.36 | 1.38 |
| N2-C2 | 1.36 | 1.38 | O3-SI | 1.42 | 1.47 |
| O3-SI | 1.42 | 1.47 | O1-S1 | 1.43 | 1.47 |

**Figure S4:** $^1H$, $^{13}CNMR$, IR spectra, HOMO-LUMO & bond angles of $[H_2L^4][OTf]_2$
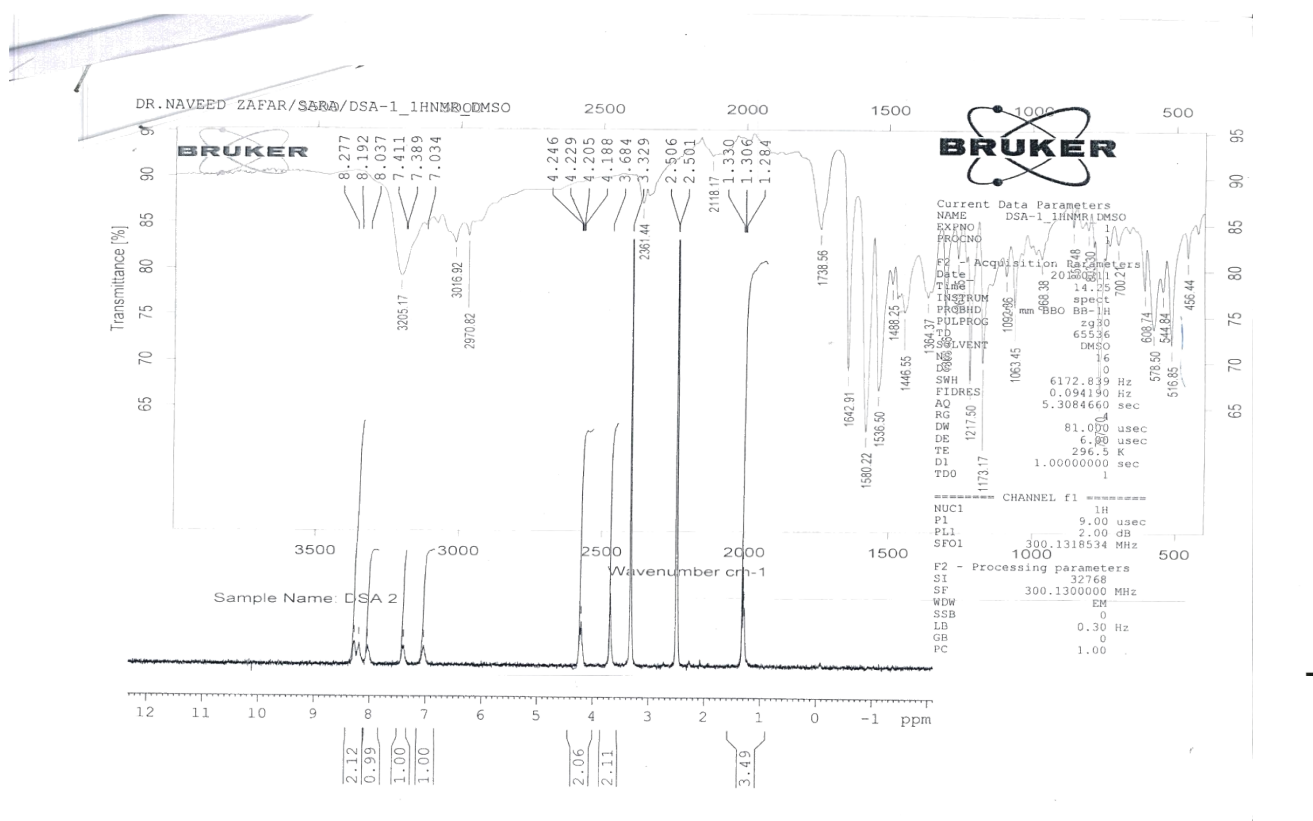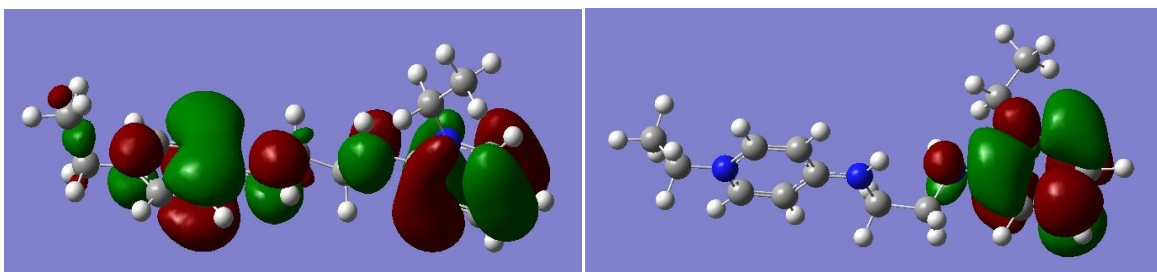
HOMO (Gaussian)                                              LUMO (Gaussian)

**Bond angles**

| Concerned Atoms | Experimental | Calculated |
|:---:|:---:|:---:|
| C1-N1-C2 | 123.7 | 122.9 |
| N1-C2-C3 | 123.5 | 121.7 |
| C2-C3-C4 | 121.2 | 121.4 |
| C3-C4-C5 | 119.6 | 119.3 |
| C4-C5-C6 | 119.0 | 118.8 |
| C5-C6-N2 | 122.7 | 122.1 |
| C6-N2-C2 | 120.0 | 121.2 |
| N2-C2-C3 | 117.4 | 117.3 |
| N2-C2-N1 | 119.1 | 121.0 |
| C6-N2-C7 | 120.1 | 116.9 |
| N2-C7-C8 | 110.0 | 109.5 |

**Figure S5:** $^1$H, $^{13}$CNMR, IR spectra, HOMO-LUMO and bond angles of $[H_2L^5][I]_2$
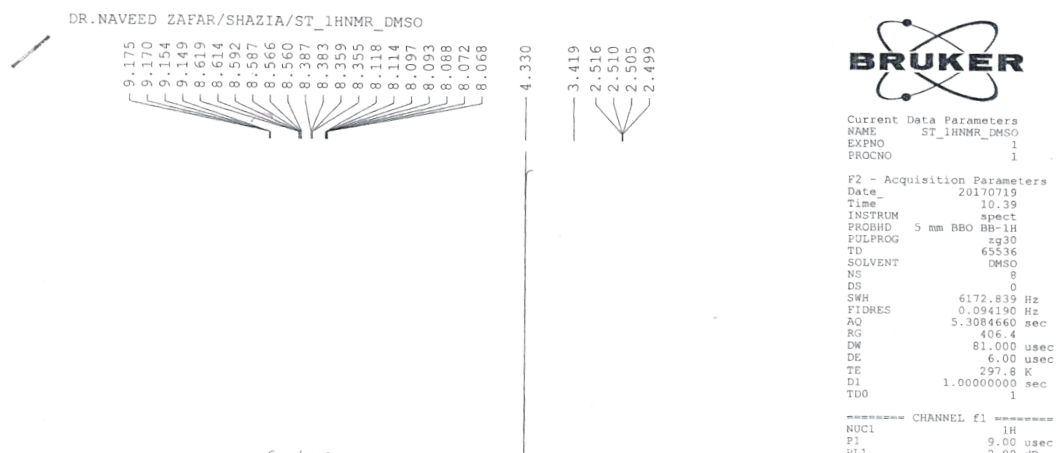
DR.NAVEED ZAFAR/SHAZIA/ST_1HNMR_DMSO

9.175
9.170
9.154
9.149
8.619
8.614
8.592
8.587
8.566
8.560
8.387
8.383
8.359
8.355
8.118
8.114
8.097
8.093
8.088
8.072
8.068

4.330

3.419

2.516
2.510
2.505
2.499

BRUKER

Current Data Parameters
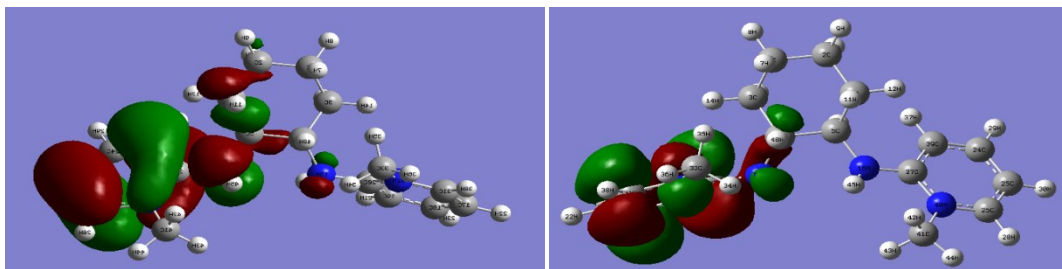NAME          ST_1HNMR_DMSO
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PROCNO                    1

F2 - Acquisition Parameters
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Time                  10.39
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                        8
DS                        0
SWH             6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                    406.4
DW              81.000 usec
DE               6.00 usec
TE                  297.8 K
D1          1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1               9.00 usec

## Bond angles

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|---|---|---|---|---|---|
| $Cl_1$-$C_1$-$N_1$ | 117.5 | 117.4 | H6B-C6-H6C | 109.5 | 109.5 |
| $C_6$-$N_1$-$C_5$ | 118.7 | 118.8 | H6B-C6-H6A | 109.5 | 109.5 |
| $C_1$-$N_1$-$C_5$ | 119.3 | 120.3 | H6A-C6-H6C | 109.5 | 109.5 |
| $C_1$-$N_1$-$C_6$ | 121.9 | 120.6 | H6C-C6-N1 | 109.5 | 109.5 |
| $C_4$-$C_5$-$N_1$ | 121.3 | 121.3 | H6B-C6-N1 | 109.5 | 109.5 |
| $N_1$-$C_1$-$C_2$ | 121.2 | 119.6 | H6A-C6-N1 | 109.5 | 109.5 |
| $C_5$-$C_4$-$C_3$ | 119.4 | 119.0 | F1-C7-S1 | 112.0 | 111.9 |
| $C_4$-$C_3$-$C_2$ | 119.7 | 119.5 | F3-C7-S1 | 111.4 | 111.6 |
| $C_3$-$C_2$-$C_1$ | 119.0 | 119.0 | O2-S1-O1 | 114.0 | 113.9 |



Sample Name: P2 20H
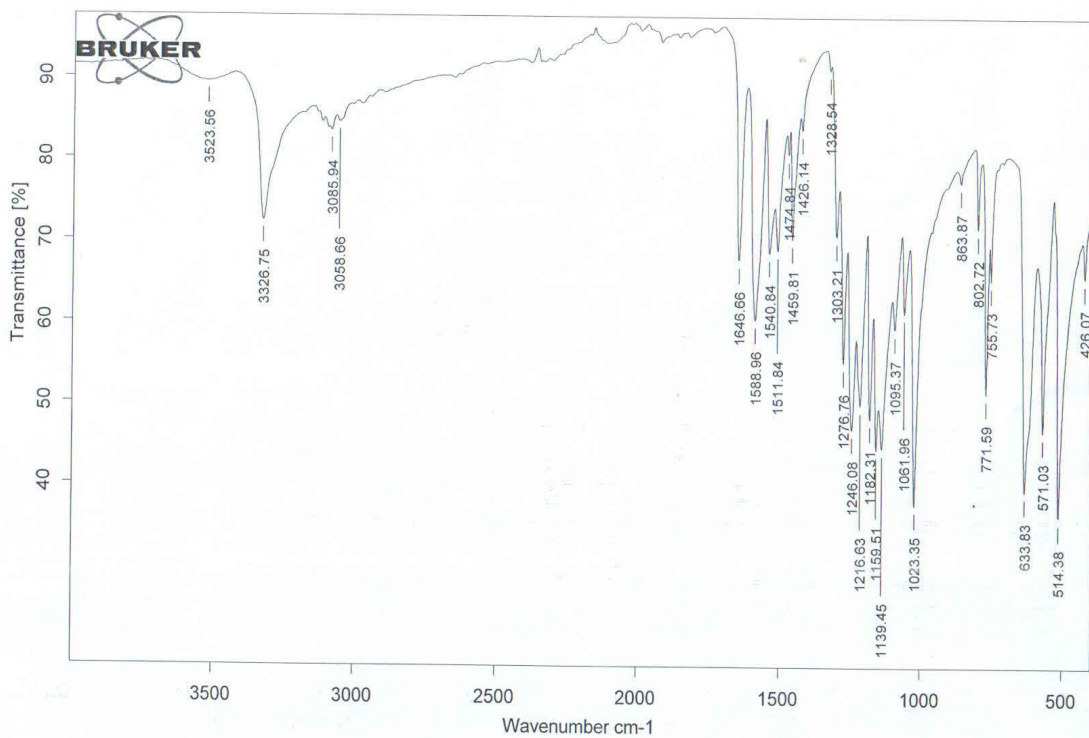
| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|---|---|---|---|---|---|
| Cl1-C1-C2 | 121.3 | 118.1 | O3-S1-O1 | 115.1 | 115.0 |
| C7-S1-O2 | 103.3 | 106.4 | N1-C5-H5 | 119.4 | 119.2 |
| C7-S1-O3 | 103.4 | 106.5 | H5-C5-C4 | 119.3 | 119.1 |
| C7-S1-O1 | 103.1 | 106.4 | H2-C2-C3 | 120.5 | 120.4 |
| F1-C7-F3 | 108.4 | 112.5 | H2-C2-C1 | 120.5 | 120.4 |
| F3-C7-F2 | 109.6 | 113.4 | C2-C3-H3 | 120.2 | 120.1 |
| F1-C7-F2 | 106.5 | 105.7 | H3-C3-C4 | 120.1 | 120.1 |
| F2-C7-S1 | 112.6 | 107.6 | C5-C4-H4 | 120.3 | 120.4 |
| O2-S1-O3 | 115.6 | 114.5 | C3-C4-H4 | 120.3 | 120.4 |

## Bond lengths

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|---|---|---|---|---|---|
| Cl1-C1 | 1.69 | 1.70 | S1-O3 | 1.42 | 1.39 |
| C1-C2 | 1.37 | 1.39 | S1-O2 | 1.43 | 1.40 |
| C2-C3 | 1.37 | 1.39 | S1-O1 | 1.43 | 1.40 |
| C3-C4 | 1.37 | 1.37 | N1-C1 | 1.34 | 1.33 |
| C4-C5 | 1.36 | 1.36 | C5-H5 | 0.93 | 0.95 |
| N1-C5 | 1.35 | 1.35 | C2-H2 | 0.93 | 0.95 |
| C6-N1 | 1.48 | 1.47 | C3-H3 | 0.93 | 0.95 |
| C7-S1 | 1.80 | 1.76 | C4-H4 | 0.93 | 0.95 |
| C7-F2 | 1.32 | 1.30 | C6-H6B | 0.96 | 1.00 |
| C7-F3 | 1.32 | 1.31 | C6-H6A | 0.96 | 1.00 |
| C7-F1 | 1.32 | 1.33 | C6-H6C | 0.96 | 1.00 |
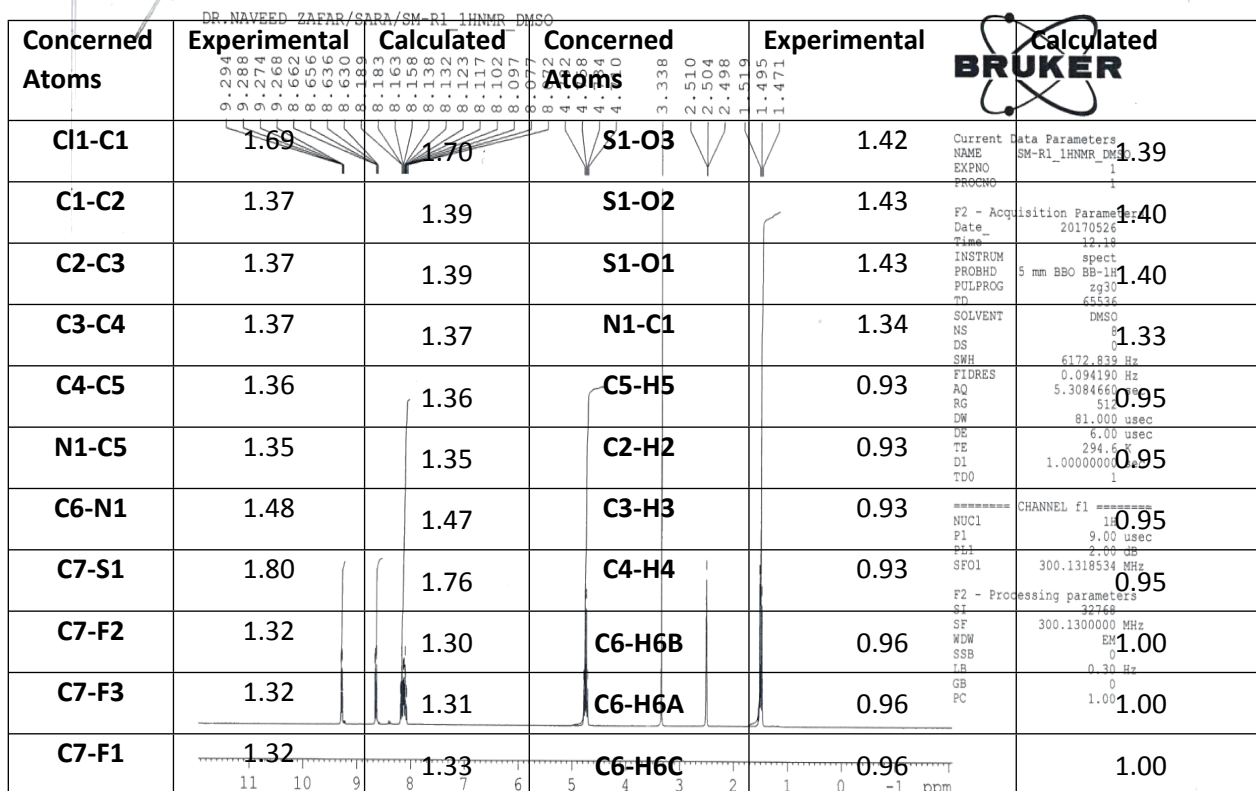
**Figure S6:** $^1$H, $^{13}$CNMR, IR, bond lengths and bond angles of $[P^2{}_{Me}][CF_3SO_3{}^-]$

DR.NAVEED ZAFAR/SARA/SRM-1_13CNMR_DMSO

147.86
147.36
145.14

128.86
123.26
121.91
118.99

48.53
40.82
40.54
40.26
39.99
39.71
39.43
39.15



148   146   144   142      ppm

Transmittance [%]

200  180  160  140  120  100  80  60  40  20  0   ppm

3500   3000   2500   2000   1500   1000   500

Wavenumber cm-1

Sample Name: SRE 1

HOMO (Gaussian)                    LUMO (Gaussian)

**Bond angles**

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|---|---|---|---|---|---|
| C5-C4-C3 | 114.5 | 119.2 | C4-C5-H5 | 114.2 | 114.1 |
| C4-C3-C2 | 113.7 | 119.2 | N1-C6-H6A | 110.0 | 109.1 |
| C3-C2-C1 | 130.6 | 120.3 | N1-C6-H6B | 109.9 | 108.7 |
| I1-C1-N1 | 117.7 | 125.5 | N1-C6-C7 | 109.1 | 108.3 |
| N1-C5-C4 | 131.5 | 121.6 | H6A-C6-H6B | 108.2 | 107.8 |
| I1-C1-C2 | 127.7 | 115.1 | H6A-C6-C7 | 109.9 | 108.9 |
| N1-C6-C7 | 109.1 | 109.8 | H6B-C6-C7 | 109.8 | 108.9 |
| C1-N1-C6 | 114.7 | 115.4 | C6-C7-H7A | 109.5 | 108.7 |
| C5-N1-C6 | 130.1 | 131.0 | C6-C7-H7B | 109.5 | 108.7 |

| | | | | | |
|---|---|---|---|---|---|
| C1-I1-I2 | 177.5 | 178.4 | C6-C7-H7C | 109.5 | 108.7 |
| C1-C2-H2 | 114.6 | 114.5 | H7A-C7-H7B | 109.5 | 108.7 |
| H2-C2-C3 | 114.8 | 113.9 | N1-C1-C2 | 114.6 | 114.4 |
| C2-C3-H3 | 123.1 | 122.4 | H7A-C7-H7C | 109.5 | 108.9 |
| H3-C3-C4 | 123.2 | 122.5 | H7B-C7-H7C | 109.4 | 108.9 |

**Bond lengths**

| Concerned Atoms | Experimental values | Computed values | Concerned Atoms | Experimental values | Computed values |
|---|---|---|---|---|---|
| N1-C1 | 1.09 | 1.10 | C1-I1 | 2.02 | 2.12 |
| C1-C2 | 1.31 | 1.36 | C2-H | 0.93 | 1.00 |
| C2-C3 | 1.33 | 1.35 | C3-H | 0.93 | 1.00 |
| C3-C4 | 1.12 | 1.23 | C4-H | 0.93 | 1.00 |
| C4-C5 | 1.31 | 1.35 | C5-H | 0.93 | 1.00 |
| N1-C6 | 1.43 | 1.43 | C6-H | 0.97 | 1.02 |
| C6-C7 | 1.24 | 1.25 | C6-H | 0.97 | 1.01 |
| N1- C5 | 1.29 | 1.34 | C7-H | 0.96 | 1.00 |
| I1-I2 | 3.24 | 3.36 | C7-H | 0.96 | 1.00 |

**Figure S7:** $^1$H, $^{13}$CNMR, IR spectra, HOMO LUMO, bond lengths and bond angles of $[P^3_{Et}][I^-]$

**Table 1:** Crystal structure Data of S3

Table 1: Crystal data and structure refinement for a.

Identification code                        8A

Empirical formula                        C10 H13 F3 N2 O3 S

Formula weight                        298.28

Temperature                        100(2) K

Wavelength                        1.54178 Å

| Crystal system | Orthorhombic | |
| --- | --- | --- |
| Space group | Pbcn | |
| Unit cell dimensions | a = 15.5634(3) Å | $\alpha$= 90°. |
| | b = 12.4382(2) Å | $\beta$= 90°. |
| | c = 12.8282(3) Å | $\gamma$ = 90°. |
| Volume | 2483.29(9) Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.596 Mg/m$^3$ | |
| Absorption coefficient | 2.780 mm$^{-1}$ | |
| F(000) | 1232 | |
| Crystal size | 0.170 x 0.050 x 0.040 mm$^3$ | |
| Theta range for data collection | 4.551 to 68.305°. | |
| Index ranges | -18<=h<=18, -14<=k<=14, -15<=l<=15 | |
| Reflections collected | 36806 | |
| Independent reflections | 2282 [R(int) = 0.0771] | |
| Completeness to theta = 67.679° | 100.0 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2282 / 0 / 177 | |
| Goodness-of-fit on F$^2$ | 1.049 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0580, wR2 = 0.1377 | |
| R indices (all data) | R1 = 0.0684, wR2 = 0.1446 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.159 and -0.746 e.Å$^{-3}$ | |

**Atomic coordinates ( x 10$^4$) and equivalent isotropic displacement parameters (Å$^2$x 10$^3$)**

**for a. U(eq) is defined as one third of the trace of the orthogonalized U$^{ij}$ tensor.**

|        | x        | y        | z        | U(eq)    |
|--------|----------|----------|----------|----------|
| S(1)   | 2443(1)  | 6040(1)  | 5767(1)  | 17(1)    |
| F(1)   | 894(2)   | 5291(2)  | 5554(4)  | 104(2)   |
| F(2)   | 1788(1)  | 4081(2)  | 5875(2)  | 32(1)    |
| F(3)   | 1746(3)  | 4798(3)  | 4369(2)  | 99(2)    |
| O(1)   | 2345(2)  | 6101(2)  | 6870(2)  | 50(1)    |
| O(2)   | 3253(2)  | 5576(2)  | 5474(3)  | 46(1)    |
| O(3)   | 2196(2)  | 6945(2)  | 5156(2)  | 32(1)    |
| N(1)   | 4128(2)  | 4665(2)  | 2998(2)  | 14(1)    |
| N(2)   | 3768(2)  | 6459(2)  | 3240(2)  | 16(1)    |
| C(1)   | 3932(2)  | 7474(3)  | 3596(3)  | 23(1)    |
| C(2)   | 4672(2)  | 7707(3)  | 4100(3)  | 27(1)    |
| C(3)   | 5262(2)  | 6879(3)  | 4275(2)  | 21(1)    |
| C(4)   | 5089(2)  | 5857(3)  | 3949(2)  | 16(1)    |
| C(5)   | 4325(2)  | 5635(2)  | 3398(2)  | 13(1)    |
| C(6)   | 2971(2)  | 6281(3)  | 2649(3)  | 22(1)    |
| C(7)   | 4699(2)  | 3727(2)  | 2979(2)  | 13(1)    |
| C(8)   | 4142(2)  | 2714(2)  | 2962(3)  | 17(1)    |
| C(9)   | 4689(2)  | 1693(3)  | 2960(3)  | 21(1)    |
| C(10)  | 1688(2)  | 4992(3)  | 5367(3)  | 28(1)    |

**Bond lengths [Å] and angles [A°] for a**.

_____

S(1)-O(3)                1.425(3)

| | |
|---|---|
| S(1)-O(1) | 1.426(3) |
| S(1)-O(2) | 1.437(3) |
| S(1)-C(10) | 1.828(4) |
| F(1)-C(10) | 1.313(5) |
| F(2)-C(10) | 1.315(4) |
| F(3)-C(10) | 1.306(5) |
| N(1)-C(5) | 1.346(4) |
| N(1)-C(7) | 1.468(4) |
| N(1)-H(5) | 0.84(4) |
| N(2)-C(5) | 1.358(4) |
| N(2)-C(1) | 1.367(4) |
| N(2)-C(6) | 1.470(4) |
| C(1)-C(2) | 1.352(5) |
| C(1)-H(1) | 0.9500 |
| C(2)-C(3) | 1.398(5) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.366(5) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.412(4) |
| C(4)-H(4) | 0.9500 |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-C(8) | 1.529(4) |
| C(7)-C(7)#1 | 1.546(6) |

| | |
|---|---|
| C(7)-H(7) | 1.0000 |
| C(8)-C(9) | 1.528(4) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(9)#1 | 1.526(7) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |

| | |
|---|---|
| O(3)-S(1)-O(1) | 118.35(19) |
| O(3)-S(1)-O(2) | 114.25(18) |
| O(1)-S(1)-O(2) | 112.0(2) |
| O(3)-S(1)-C(10) | 103.68(16) |
| O(1)-S(1)-C(10) | 104.37(18) |
| O(2)-S(1)-C(10) | 101.78(18) |
| C(5)-N(1)-C(7) | 125.5(3) |
| C(5)-N(1)-H(5) | 121(3) |
| C(7)-N(1)-H(5) | 113(3) |
| C(5)-N(2)-C(1) | 121.9(3) |
| C(5)-N(2)-C(6) | 120.1(3) |
| C(1)-N(2)-C(6) | 118.0(3) |
| C(2)-C(1)-N(2) | 121.2(3) |
| C(2)-C(1)-H(1) | 119.4 |
| N(2)-C(1)-H(1) | 119.4 |
| C(1)-C(2)-C(3) | 118.6(3) |
| C(1)-C(2)-H(2) | 120.7 |

| | |
|---|---|
| C(3)-C(2)-H(2) | 120.7 |
| C(4)-C(3)-C(2) | 120.5(3) |
| C(4)-C(3)-H(3) | 119.8 |
| C(2)-C(3)-H(3) | 119.8 |
| C(3)-C(4)-C(5) | 120.1(3) |
| C(3)-C(4)-H(4) | 119.9 |
| C(5)-C(4)-H(4) | 119.9 |
| N(1)-C(5)-N(2) | 118.3(3) |
| N(1)-C(5)-C(4) | 123.9(3) |
| N(2)-C(5)-C(4) | 117.7(3) |
| N(2)-C(6)-H(6A) | 109.5 |
| N(2)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| N(2)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| N(1)-C(7)-C(8) | 108.2(2) |
| N(1)-C(7)-C(7)#1 | 112.4(2) |
| C(8)-C(7)-C(7)#1 | 109.4(2) |
| N(1)-C(7)-H(7) | 109.0 |
| C(8)-C(7)-H(7) | 109.0 |
| C(7)#1-C(7)-H(7) | 109.0 |
| C(9)-C(8)-C(7) | 111.7(3) |
| C(9)-C(8)-H(8A) | 109.3 |
| C(7)-C(8)-H(8A) | 109.3 |

| | |
|---|---|
| C(9)-C(8)-H(8B) | 109.3 |
| C(7)-C(8)-H(8B) | 109.3 |
| H(8A)-C(8)-H(8B) | 107.9 |
| C(9)#1-C(9)-C(8) | 110.8(2) |
| C(9)#1-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9A) | 109.5 |
| C(9)#1-C(9)-H(9B) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 108.1 |
| F(3)-C(10)-F(1) | 107.2(4) |
| F(3)-C(10)-F(2) | 108.6(3) |
| F(1)-C(10)-F(2) | 105.4(3) |
| F(3)-C(10)-S(1) | 111.3(3) |
| F(1)-C(10)-S(1) | 110.6(3) |
| F(2)-C(10)-S(1) | 113.5(2) |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

**Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for a. The anisotropic**

**displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$**

_____

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 16(1) | 15(1) | 21(1) | 0(1) | -3(1) | -1(1) |
| F(1) | 19(1) | 34(2) | 257(6) | 23(2) | -33(2) | -4(1) |

| | | | | | | |
|------|---------|--------|--------|---------|---------|---------|
| F(2) | 33(1) | 20(1) | 42(1) | 9(1) | -14(1) | -6(1) |
| F(3) | 201(4) | 65(2) | 32(2) | 2(1) | -28(2) | -83(3) |
| O(1) | 89(3) | 32(2) | 27(2) | -11(1) | 11(2) | -22(2) |
| O(2) | 19(1) | 33(2) | 84(2) | 18(2) | 5(1) | 6(1) |
| O(3) | 25(1) | 18(1) | 51(2) | 11(1) | -14(1) | -1(1) |
| N(1) | 10(1) | 14(1) | 17(1) | -1(1) | -2(1) | 2(1) |
| N(2) | 16(1) | 16(1) | 17(1) | -2(1) | -1(1) | 2(1) |
| C(1) | 28(2) | 14(2) | 27(2) | -6(1) | -1(2) | 5(1) |
| C(2) | 32(2) | 19(2) | 30(2) | -10(2) | -2(2) | -2(2) |
| C(3) | 21(2) | 26(2) | 15(2) | -4(1) | -1(1) | -6(1) |
| C(4) | 16(2) | 19(2) | 12(1) | 0(1) | 2(1) | 0(1) |
| C(5) | 13(1) | 15(2) | 10(1) | 0(1) | 4(1) | 0(1) |
| C(6) | 15(2) | 19(2) | 31(2) | -4(1) | -6(1) | 5(1) |
| C(7) | 10(1) | 12(2) | 16(2) | 0(1) | -1(1) | 2(1) |
| C(8) | 15(2) | 16(2) | 20(2) | 2(1) | 1(1) | -3(1) |
| C(9) | 23(2) | 13(2) | 26(2) | 3(1) | -2(2) | -2(1) |
| C(10) | 29(2) | 20(2) | 36(2) | 7(2) | -17(2) | -6(2) |

**Hydrogen coordinates ( x 10$^4$) and isotropic  displacement parameters (Å$^2$x 10$^3$)**

**for a**.

| | x | y | z | U(eq) |
|------|------|------|------|-------|
| H(1) | 3519 | 8025 | 3488 | 28 |
| H(2) | 4788 | 8419 | 4330 | 32 |

| | | | | |
|---|---|---|---|---|
| H(3) | 5787 | 7029 | 4623 | 25 |
| H(4) | 5484 | 5294 | 4094 | 19 |
| H(6A) | 3111 | 6002 | 1955 | 32 |
| H(6B) | 2660 | 6962 | 2580 | 32 |
| H(6C) | 2611 | 5759 | 3019 | 32 |
| H(7) | 5056 | 3725 | 3628 | 15 |
| H(8A) | 3762 | 2710 | 3581 | 20 |
| H(8B) | 3774 | 2723 | 2333 | 20 |
| H(9A) | 5016 | 1646 | 3620 | 25 |
| H(9B) | 4309 | 1056 | 2915 | 25 |
| H(5) | 3670(30) | 4570(30) | 2660(30) | 24(10) |

**Torsion angles [A°] for a.**

| | |
|---|---|
| C(5)-N(2)-C(1)-C(2) | 1.8(5) |
| C(6)-N(2)-C(1)-C(2) | -176.7(3) |
| N(2)-C(1)-C(2)-C(3) | -1.6(5) |
| C(1)-C(2)-C(3)-C(4) | -0.5(5) |
| C(2)-C(3)-C(4)-C(5) | 2.3(5) |
| C(7)-N(1)-C(5)-N(2) | 171.9(3) |
| C(7)-N(1)-C(5)-C(4) | -6.3(5) |
| C(1)-N(2)-C(5)-N(1) | -178.2(3) |
| C(6)-N(2)-C(5)-N(1) | 0.3(4) |
| C(1)-N(2)-C(5)-C(4) | 0.0(4) |
| C(6)-N(2)-C(5)-C(4) | 178.6(3) |
| C(3)-C(4)-C(5)-N(1) | 176.1(3) |

| | |
|---|---|
| C(3)-C(4)-C(5)-N(2) | -2.1(4) |
| C(5)-N(1)-C(7)-C(8) | 153.4(3) |
| C(5)-N(1)-C(7)-C(7)#1 | -85.7(4) |
| N(1)-C(7)-C(8)-C(9) | -179.1(3) |
| C(7)#1-C(7)-C(8)-C(9) | 58.3(4) |
| C(7)-C(8)-C(9)-C(9)#1 | -56.5(4) |
| O(3)-S(1)-C(10)-F(3) | 59.4(4) |
| O(1)-S(1)-C(10)-F(3) | -176.1(3) |
| O(2)-S(1)-C(10)-F(3) | -59.5(4) |
| O(3)-S(1)-C(10)-F(1) | -59.6(4) |
| O(1)-S(1)-C(10)-F(1) | 64.9(4) |
| O(2)-S(1)-C(10)-F(1) | -178.4(3) |
| O(3)-S(1)-C(10)-F(2) | -177.8(3) |
| O(1)-S(1)-C(10)-F(2) | -53.2(3) |
| O(2)-S(1)-C(10)-F(2) | 63.4(3) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

**Hydrogen bonds for a [Å and °].**

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(1)-H(1)...F(3)#2 | 0.95 | 2.51 | 3.233(4) | 132.7 |
| C(2)-H(2)...F(1)#3 | 0.95 | 2.36 | 3.165(5) | 142.4 |
| C(4)-H(4)...O(2)#4 | 0.95 | 2.31 | 3.221(4) | 160.4 |

| | | | | |
|---|---|---|---|---|
| C(6)-H(6B)...O(1)#5 | 0.98 | 2.58 | 3.442(5) | 147.4 |
| C(6)-H(6C)...F(3) | 0.98 | 2.50 | 3.450(5) | 163.9 |
| N(1)-H(5)...O(1)#6 | 0.84(4) | 2.45(4) | 3.271(5) | 167(4) |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2    #2 -x+1/2,y+1/2,z    #3 x+1/2,-y+3/2,-z+1

#4 -x+1,-y+1,-z+1    #5 -x+1/2,-y+3/2,z-1/2    #6 x,-y+1,z-1/2