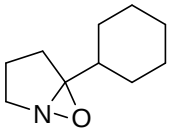
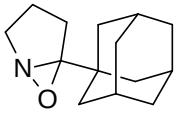
Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 29–30

Transformation of cyclic ketimines to oxaziridines and nitrones

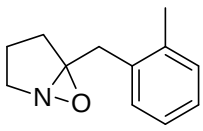
Natalia G. Voznesenskaia, Olga I. Shmatova and Valentine G. Nenajdenko



5-Cyclohexyl-6-oxa-1-azabicyclo[3.1.0]hexane **(2b)**, 87 %, yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00-1.22 (5H, m), 1.49-1.76 (9H, m), 2.10-2.15 (1H, m), 2.72-2.80 (1H, m), 3.28-3.33 (1H, m, CH_2-N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 25.6, 25.7, 25.8, 26.0, 27.8, 28.2, 40.4, 55.1 (**C**H_2-N), 92.7 (C_q). IR (ATR, ZnSe): 2928, 2853, 1450 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{18}NO^+$ $[M+H]^+$ 168.1383, found 168.1381.

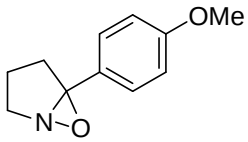


5-(Adamantan-1-yl)-6-oxa-1-azabicyclo[3.1.0]hexane **(2c)**, 96 %, yellowish liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50-1.66 (14H, m), 1.63-1.92 (4H, m), 2.08-2.13 (1H, m), 2.69-2.77 (1H, m), 3.30-3.36 (1H, m, CH_2-N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 23.8, 27.9, 34.1, 36.7, 37.6, 55.2 (**C**H_2-N), 94.8 (C_q). IR (ATR, ZnSe): 2905, 2848, 1454, 1354 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{22}NO^+$ $[M+H]^+$ 220.1696, found 220.1692.

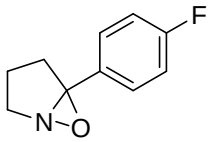


5-(2-Methylbenzyl)-6-oxa-1-azabicyclo[3.1.0]hexane **(2d)**, 82 %, brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54-1.79 (3H, m), 2.18 (1H, dd, $^{2}J_{H,H}$ = 14.0 Hz, $^{3}J_{H,H}$ = 7.5 Hz), 2.37 (3H, c), 2.87-2.95 (1H, m), 3.16 (1H, d, $^{2}J_{H,H}$ = 14.6 Hz, CH_2-Ar), 3.21 (1H, d, $^{2}J_{H,H}$ = 14.6 Hz, CH_2-Ar), 3.41-3.46 (1H, m, CH_2-N), 7.16-7.24 (4H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 19.9, 28.2, 36.3, 55.3 (**C**H_2-N), 90.3 (C_q), 125.8 (Ar), 128.9 (Ar), 130.2

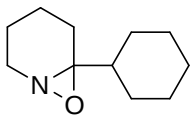
(Ar), 130.3 (Ar), 134.3 (C_q-Ar), 136.7 (C_q-Ar). IR (ATR, ZnSe): 2962, 1496, 1459, 1362, 743 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{16}NO+$ $[M+H]^+$ 190.1227, found 190.1225.



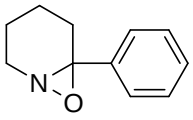
5-(4-Methoxyphenyl)-6-oxa-1-azabicyclo[3.1.0]hexane **(2f)**, 76 %, colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72-1.80 (2H, m), 2.27-2.35 (1H, m), 2.62 (1H, dd, $^2J_{H,H}$ = 14.3 Hz, $^3J_{H,H}$ = 7.6 Hz), 3.00-3.08 (1H, m), 3.48-3.53 (1H, m, CH_2-N), 3.78 (3H, s, OCH_3), 6.87-6.89 (2H, m, Ar-H), 7.41-7.44 (2H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 27.7, 55.1, 55.5, 87.6 (C_q), 113.5 (Ar), 127.1 (C_q-Ar), 128.5, 160.2 (C_q-Ar). IR (ATR, ZnSe): 2962, 1614, 1519, 1358, 1253,1175, 1031 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}NO_2^+$ $[M+H]^+$ 192.1020, found 192.1019.



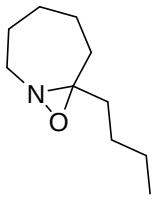
5-(4-Fluorophenyl)-6-oxa-1-azabicyclo[3.1.0]hexane **(2g)**, 93 %, pink liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-1.84 (2H, m), 2.27-2.35 (1H, m), 2.60-2.65 (1H, m), 3.04-3.10 (1H, m), 3.48-3.54 (1H, m, CH_2-N), 7.03 (2H, t, $^3J_{H,H}$ = 8.70 Hz, Ar-H), 7.46-7.49 (2H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 27.8, 55.6 (**C**H_2-N), 87.3 (C_q), 115.2 (d, $^2J_{C,F}$ = 21.8 Hz, Ar), 129.2 (d, $^3J_{C,F}$ = 8.5 Hz, Ar), 131.1 (d, $^4J_{C,F}$ = 3.3 Hz, C_q-Ar), 163.2 (d, $^1J_{C,F}$ = 248.4 Hz, Cq-F).^{19}F NMR (376 MHz, $CDCl_3$): δ -112.1-(-112.0) (Ar-F). IR (ATR, ZnSe): 2965, 1610, 1515, 1357, 1226, 1158, 845 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{11}FNO^+$ $[M+H]^+$ 180.0820, found 180.0819.



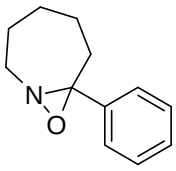
6-Cyclohexyl-7-oxa-1-azabicyclo[4.1.0]heptane **(2h)**, 77 %, yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97-1.24 (8H, m), 1.42-1.67 (7H, m), 1.87-2.00 (2H, m), 3.13-3.34 (2H, m, CH_2-N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.3, 19.1, 23.0, 25.6, 25.7, 26.2, 26.6, 27.3, 46.3, 51.2 (**C**H_2-N), 83.6 (C_q). IR (ATR, ZnSe): 2928, 2853, 1449 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{20}NO^+$ $[M+H]^+$ 182.1540, found 182.1539.



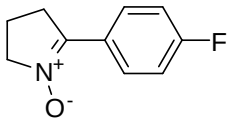
6-Phenyl-7-oxa-1-azabicyclo[4.1.0]heptane **(2i)**, 76 %, yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41-1.79 (4H, m), 2.46-2.58 (2H, m), 3.43-3.61 (2H, m, CH_2-N), 7.32-7.40 (3H, m, Ar-H), 7.49-7.51 (2H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.0, 19.4, 26.4, 50.9 (**C**H_2-N), 79.8 (C_q), 125.9 (Ph), 128.1 (Ph), 128.5 (Ph), 140.0 (C_q-Ar). IR (ATR, ZnSe): 2941, 1448, 1370, 758, 732, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}NO^+$ $[M+H]^+$ 176.1070, found 176.1068.



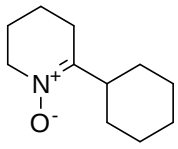
7-Butyl-8-oxa-1-azabicyclo[5.1.0]octane **(2j)**, 77 %, yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81-0.84 (3H, t, $^{3}J_{H,H}$ = 7.0 Hz, CH_3), 1.19-1.33 (5H, m), 1.42-1.52 (3H, m), 1.67-1.81 (5H, m), 2.13 (1H, dd, $^{2}J_{H,H}$ = 14.4 Hz, $^{3}J_{H,H}$ = 7.8 Hz), 2.64 (1H, t, $J_{H,H}$ = 11.5 Hz), 3.46 (1H, dd, $^{2}J_{H,H}$ = 11.6 Hz, $^{2}J_{H,H}$ = 7.1 Hz, CH_2-N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.7, 24.1, 24.6, 25.5, 29.8, 30.5, 36.0, 55.6 (**C**H_2-N), 85.1 (C_q). IR (ATR, ZnSe): 2930, 1455, 1385 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{20}NO^+$ $[M+H]^+$ 170.1540, found 170.1541.



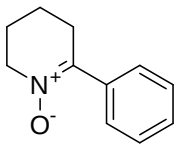
7-Phenyl-8-oxa-1-azabicyclo[5.1.0]octane **(2k)**, 85 %, yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39-1.48 (1H, m), 1.57-1.74 (2H, m), 1.86-1.90 (3H, m), 2.08-2.14 (1H, m), 2.76-2.92 (2H, m), 3.74 (1H, dd, $^{2}J_{H,H}$ = 11.6 Hz, $^{3}J_{H,H}$ = 6.8 Hz, CH_2-N) 7.32-7.40 (3H, m, Ar-H), 7.53-7.55 (2H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 24.7, 29.9, 30.6, 56.0 (**C**H_2-N), 83.4 (C_q), 126.9 (Ph), 128.0 (Ph), 128.3 (Ph), 139.1 (C_q-Ar). IR (ATR, ZnSe): 2928, 1447, 1329, 753, 694 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{16}NO^+$ $[M+H]^+$ 190.1227, found 190.1224.



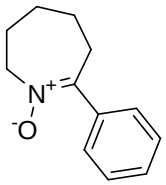
5-(4-Fluorophenyl)-3,4-dihydro-2H-pyrrole 1-oxide **(3g)**, 99 %, yellowish solid, m.p. 92-93ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03-2.11 (2H, m), 2.99-3.02 (2H, m), 4.08 (2H, t, $J_{H,H}$ = 8.0 Hz, CH_2-N), 6.95-7.00 (2H, m, Ar-H), 8.23-8.27 (2H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 30.5, 64.5 (**C**H_2-N), 115.0 (d, $^{2}J_{C,F}$ = 21.4 Hz, Ar), 125.4 (d, $^{4}J_{C,F}$ = 3.0 Hz, C_q-Ar), 129.1 (d, $^{3}J_{C,F}$ = 8.1 Hz, Ar), 138.9 (C=N^+), 162.8 (d, $^{1}J_{C,F}$ = 252.1 Hz, C_q-Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.6-(-108.5) (Ar-F). IR (ATR, ZnSe): 2959, 1560, 1500, 1373, 1211, 835 cm^{-1}. HRMS (ESI): calcd. for C10H11FNO^+ $[M+H]^+$ 180.0820, found 162.0819.



6-Cyclohexyl-2,3,4,5-tetrahydropyridine 1-oxide **(3h)**, 47 %, yellowish liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03-1.17 (3H, m), 1.27-1.37 (2H, m), 1.61-1.71 (7H, m), 2.27 (2H, t, ^{3}J = 6.3 Hz), 3.35 (1H, t, ^{2}J = 12.3 Hz), 3.72 (2H, t, $^{3}J_{H,H}$ = 6.2 Hz, CH_2-N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 22.6, 24.6, 25.6, 25.8, 27.6, 37.9, 58.0 (**C**H_2-N), 153.0 (C=N^+). IR (ATR, ZnSe): 3389 (bs), 2927, 2852, 1660, 1448, 1154 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{20}NO^+$ $[M+H]^+$ 182.1539, found 182.1539.

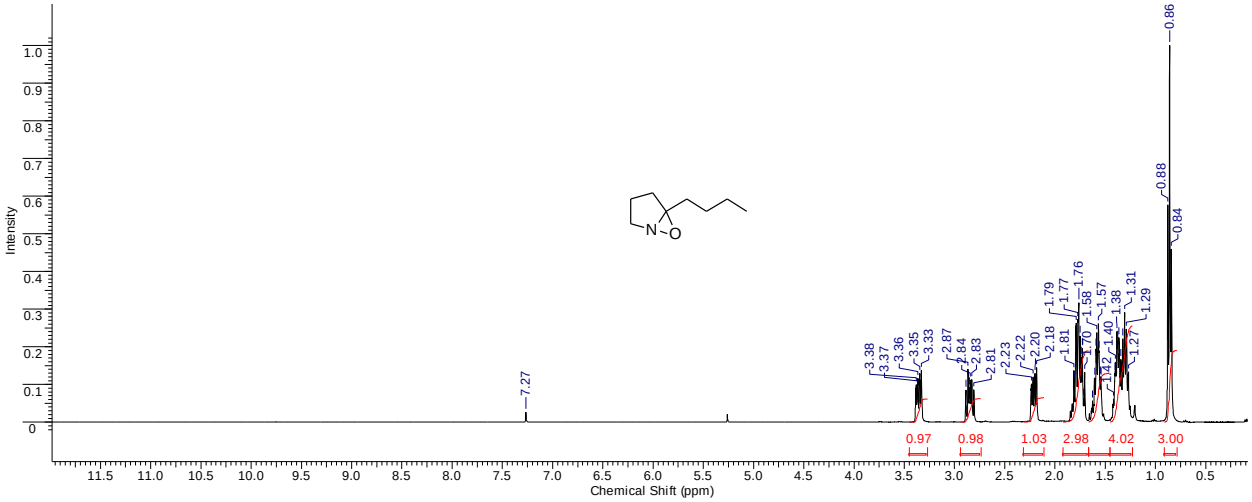


6-Phenyl-2,3,4,5-tetrahydropyridine 1-oxide **(3i)**, 99 %, colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.77 (2H, m), 1.87-1.93 (2H, m), 2.67 (2H, t, $J_{H,H}$ = 6.4 Hz), 3.88 (2H, t, $^{3}J_{H,H}$ = 6.2 Hz, CH_2-N), 7.22-7.32 (3H, Ar-H), 7.91-7.93 (2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 22.7, 28.8, 59.9 (**C**H_2-N), 127.5 (Ar), 127.6 (Ar), 128.9 (Ar), 133.5 (C_q-Ar), 141.8 (C=N^+). IR (ATR, ZnSe): 3387 (bs), 2947, 2866, 1681, 1576, 1441, 1194, 1165, 762, 693 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}NO^+$ $[M+H]^+$ 176.1070, found 1176.1069.



7-Phenyl-3,4,5,6-tetrahydro-2H-azepine 1-oxide **(3k)**, 99 %, yellow oil liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-1.97 (6H, m), 2.84-2.86 (2H, m), 4.29-4.32 (2H, m, CH_2-N), 7.30-7.41 (3H, m, Ar-H), 7.87-7.89 (2H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 25.1, 29.5, 32.5, 67.5 (**C**H_2-N), 127.9 (Ph), 128.2 (Ph), 128.9 (Ph), 134.6 (C_q-Ar), 144.8 (C=N^+). IR (ATR, ZnSe): 2929, 2855, 1738, 1545, 1442, 1181, 764, 694 cm^{-1}HRMS (ESI): calcd. for $C_{12}H_{16}NO^+$ $[M+H]^+$ 190.1227, found 190.1227.

2a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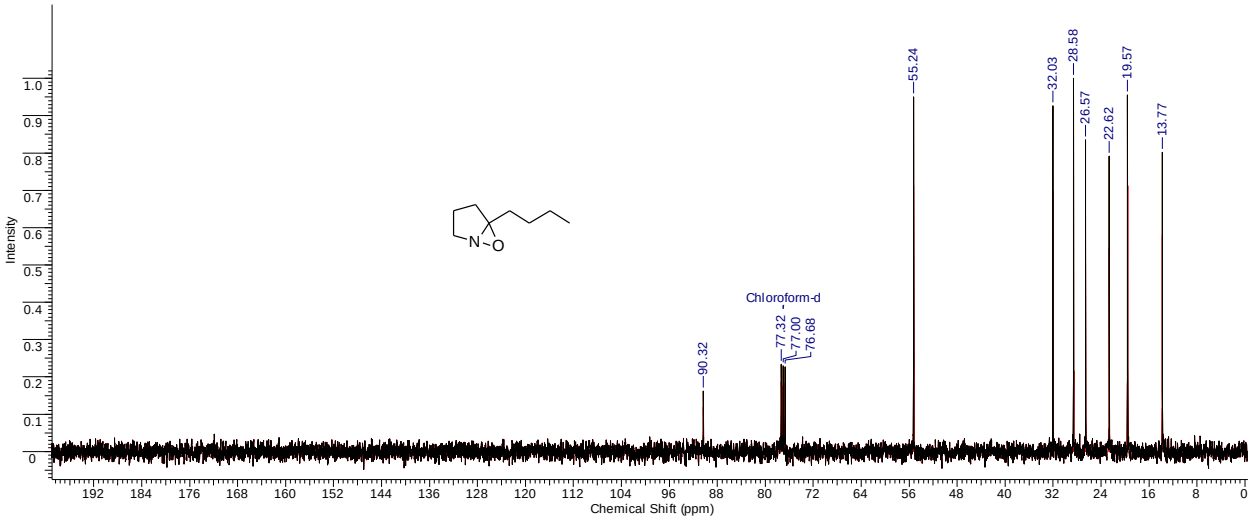
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Chemical Shift (ppm)
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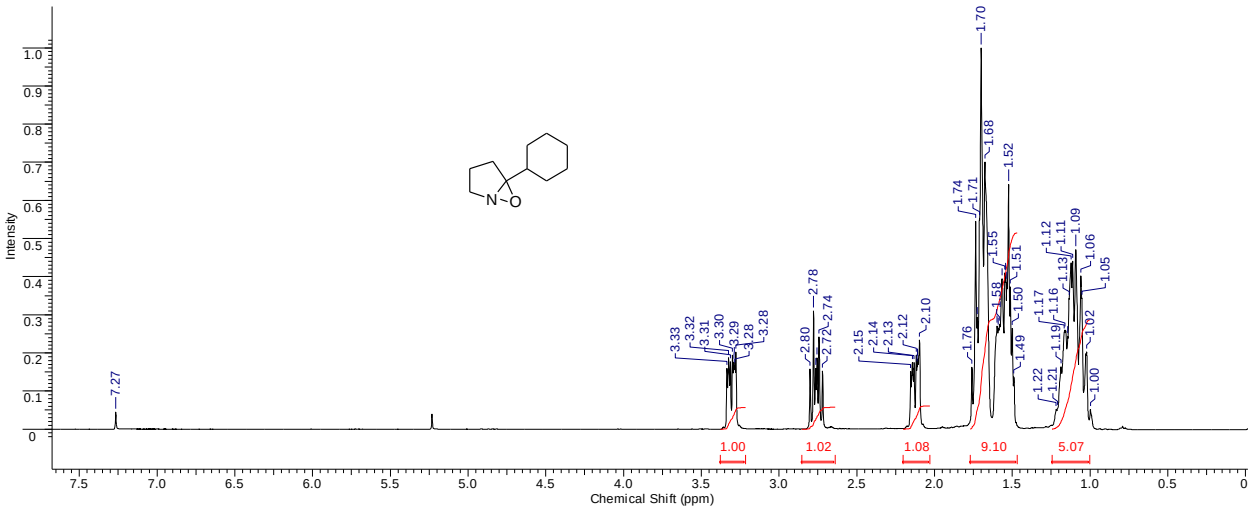
2b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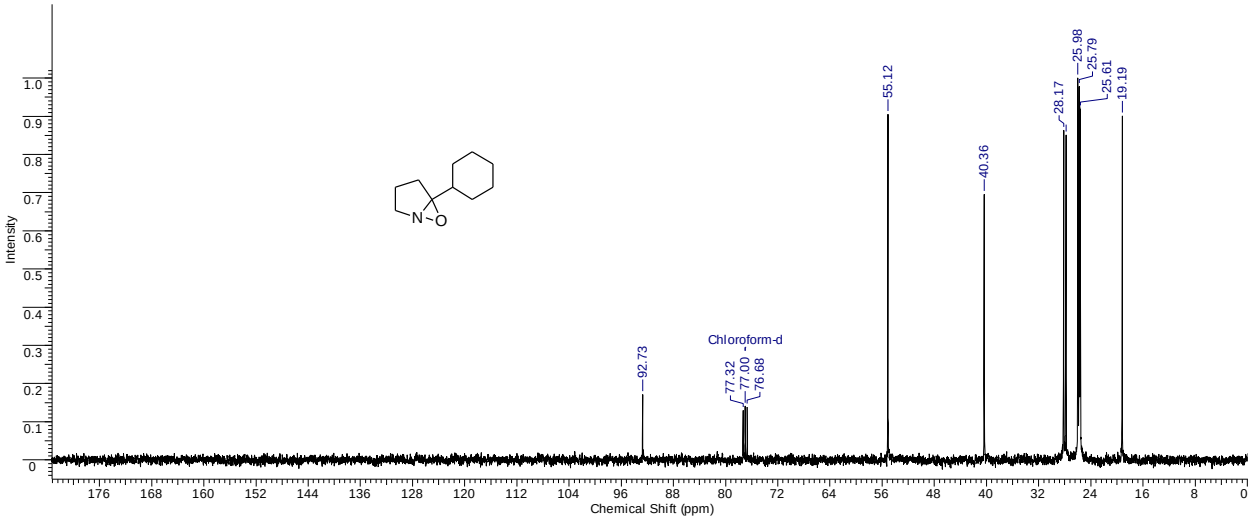
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Chloroform-d
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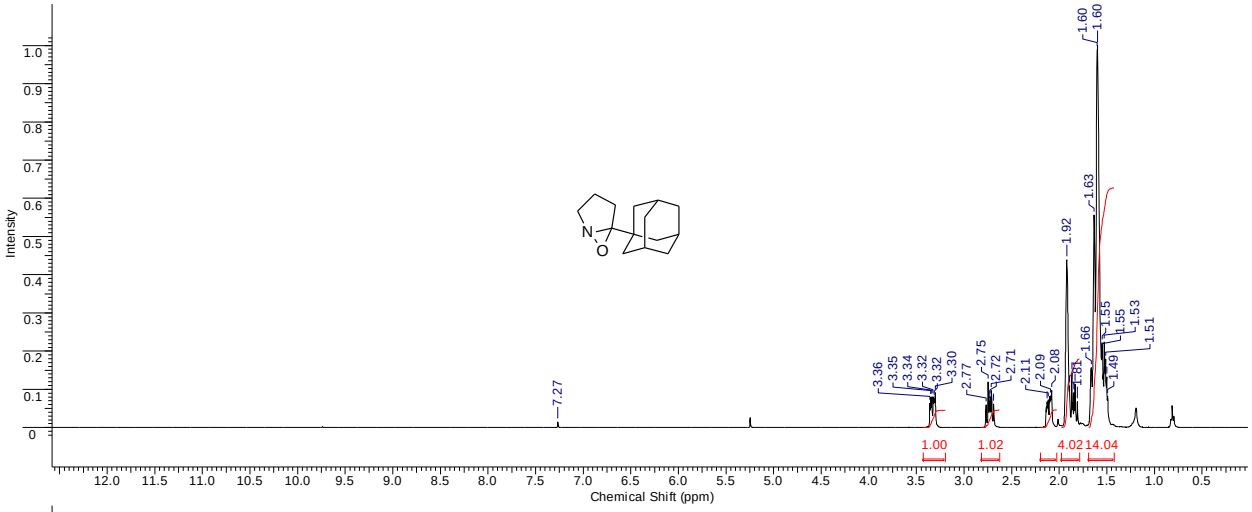
76.68

2c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2.08
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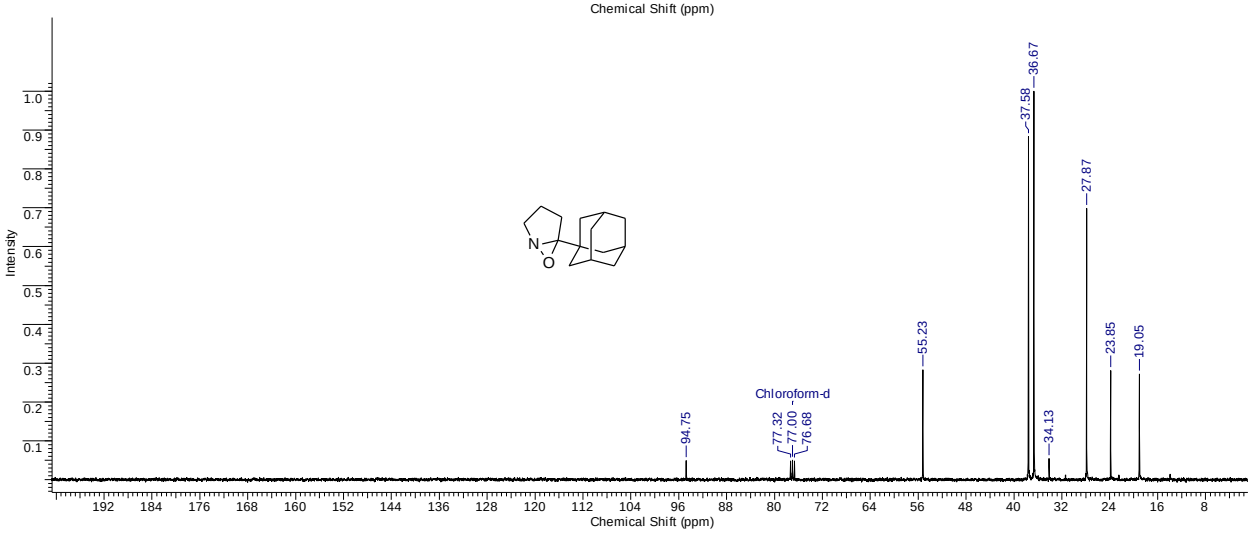
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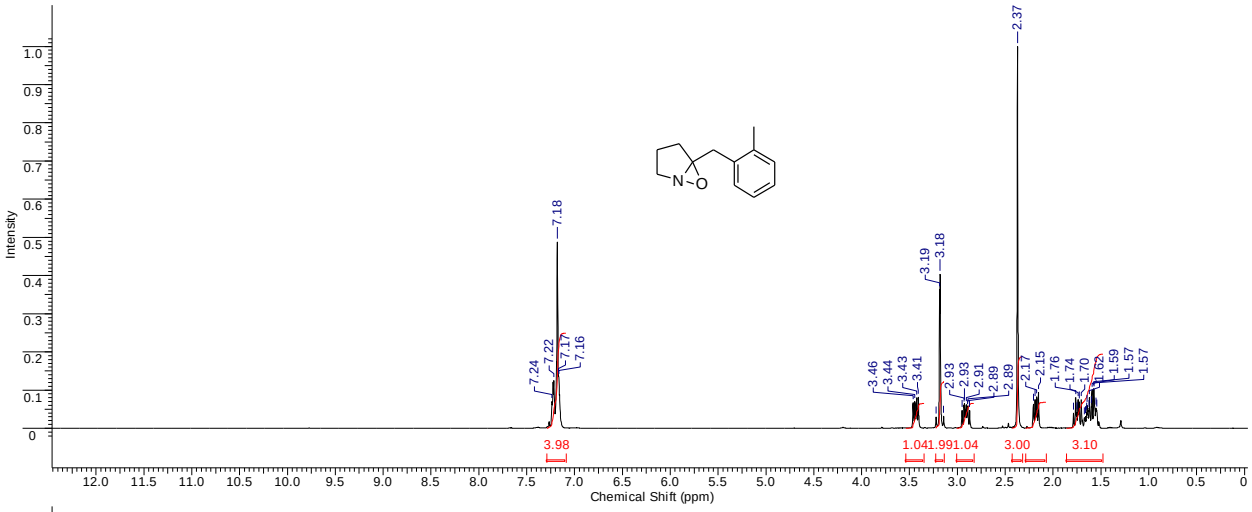
2d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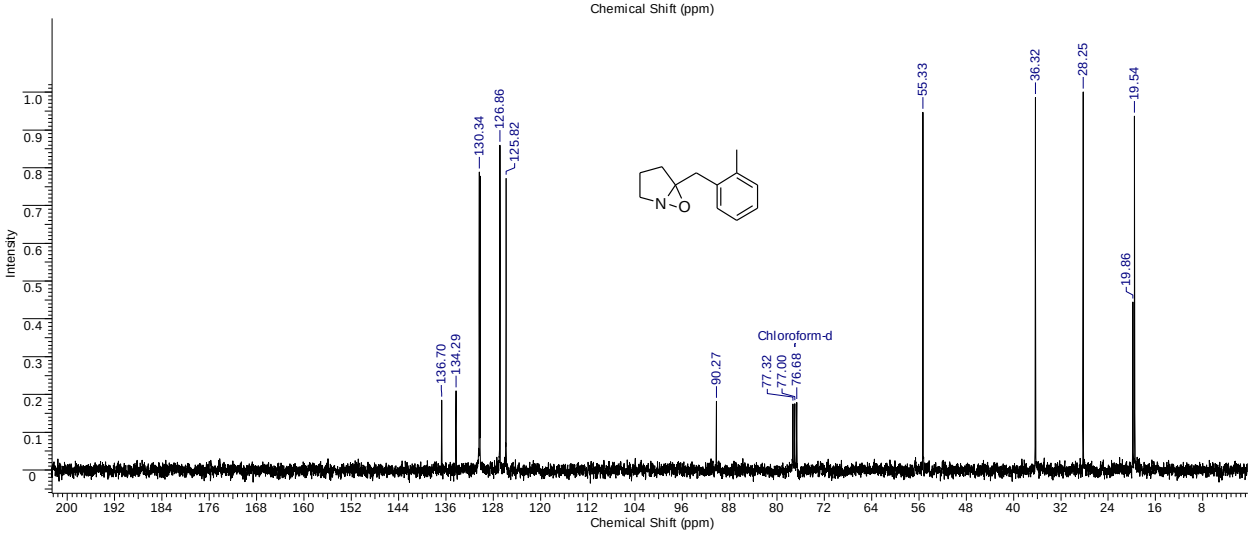
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Chemical Shift (ppm)
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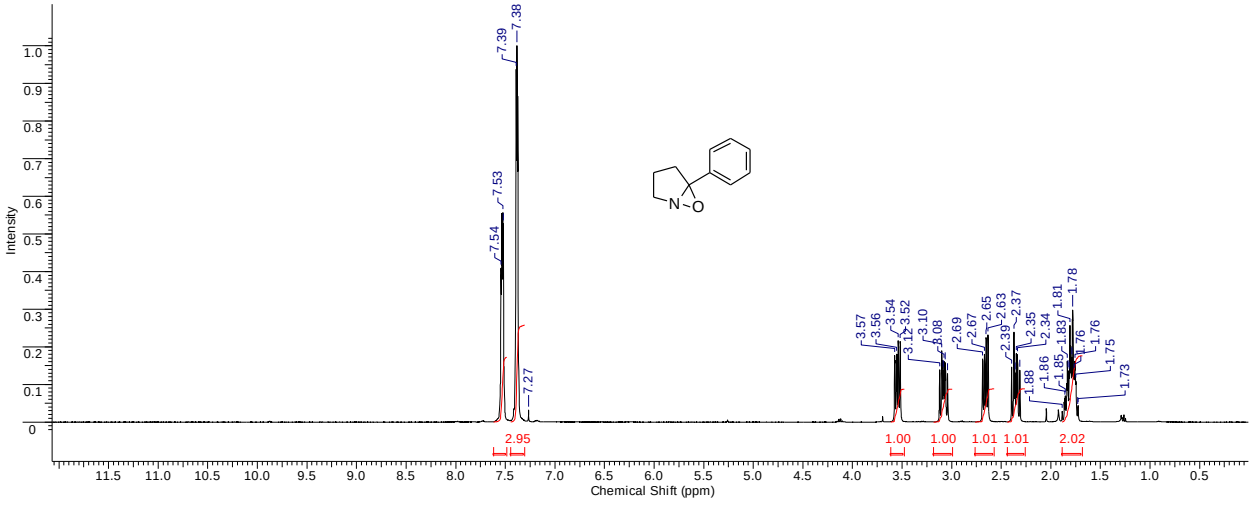
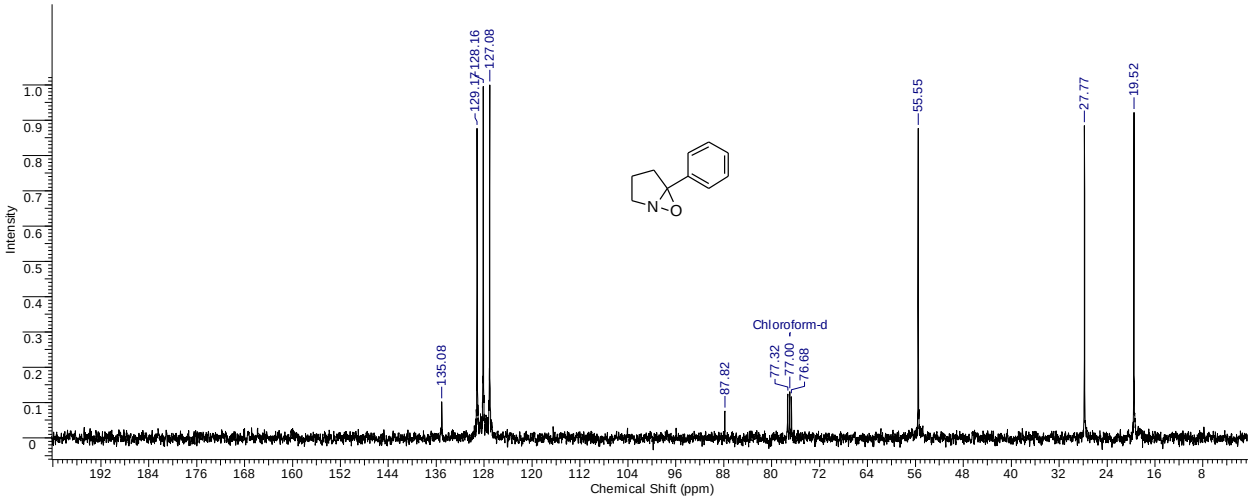
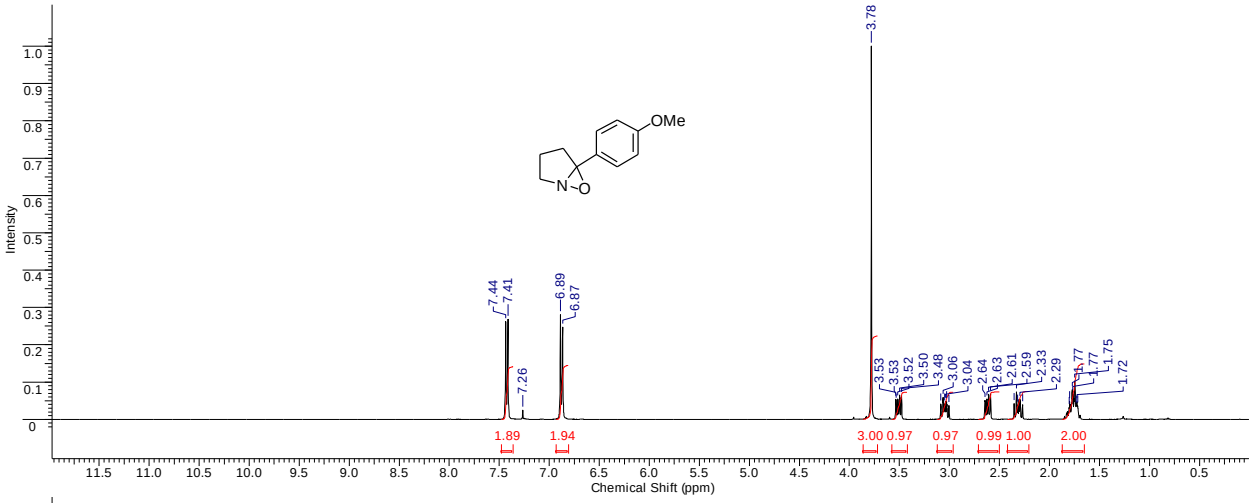
Chloroform-d
55.33
36.32
28.25
19.86
19.54

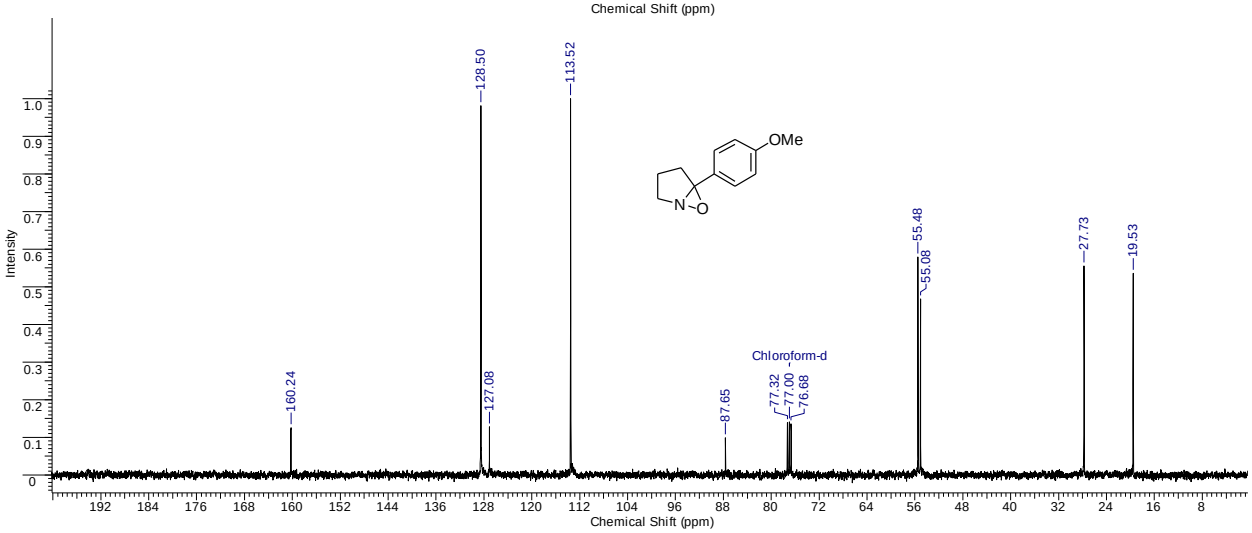
2e


Intensity
Chemical Shift (ppm)
7.39
7.38
7.53
7.54
7.27
3.57
3.56
3.54
3.52
3.10
3.08
2.69
2.67
2.65
2.63
2.39
2.37
2.35
2.34
1.88
1.86
1.85
1.83
1.81
1.78
1.76
1.76
1.75
1.73
2.95
1.00
1.00
1.01
1.01
2.02

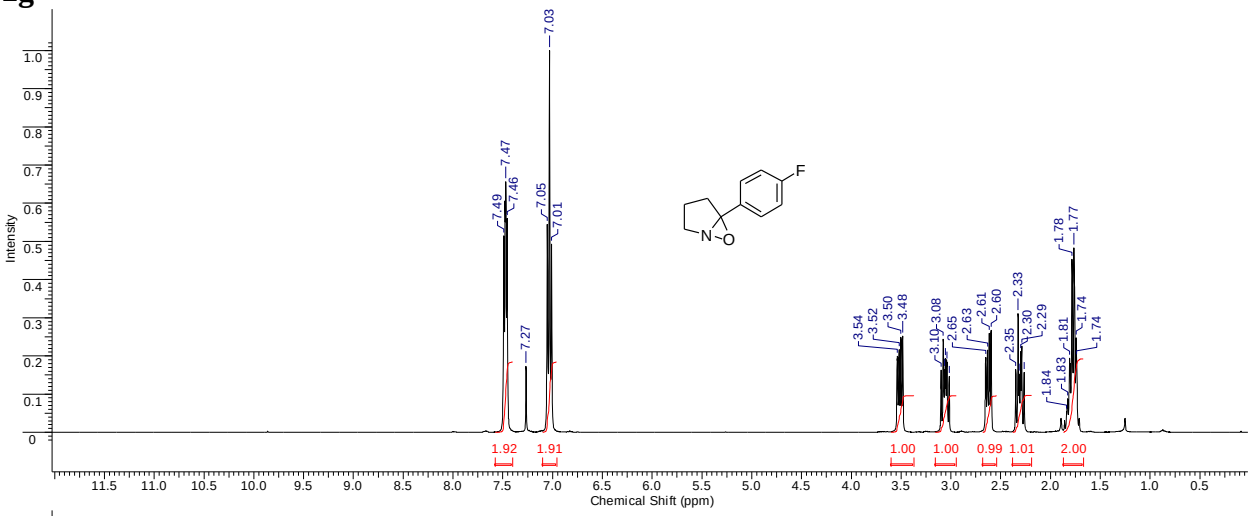

Intensity
Chemical Shift (ppm)
135.08
129.17
128.16
127.08
87.82
Chloroform-d
77.32
77.00
76.68
55.55
27.77
19.52

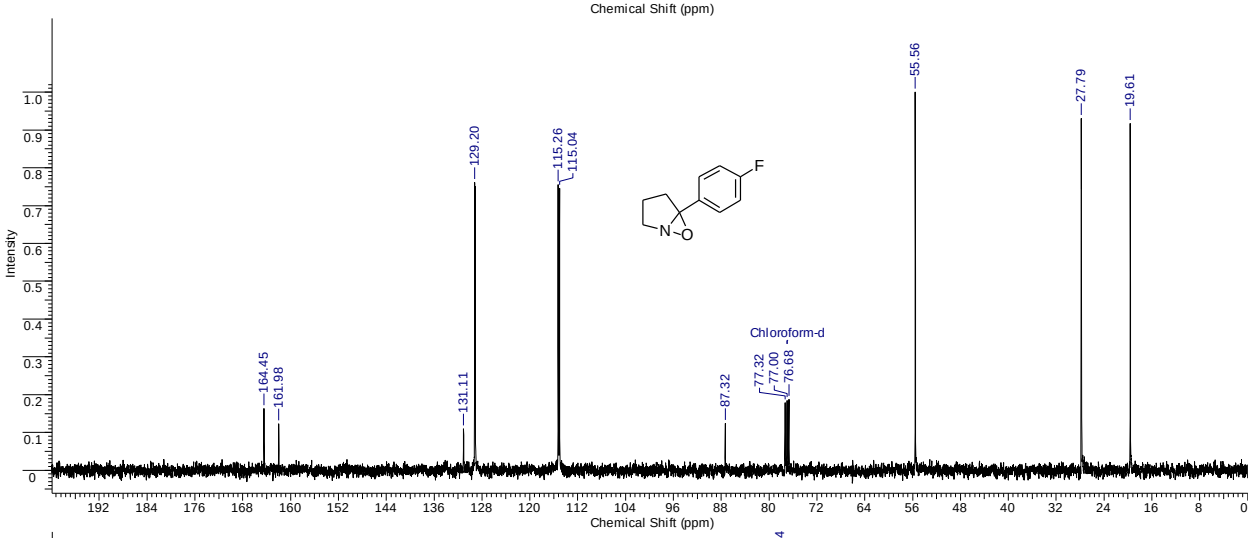
2f

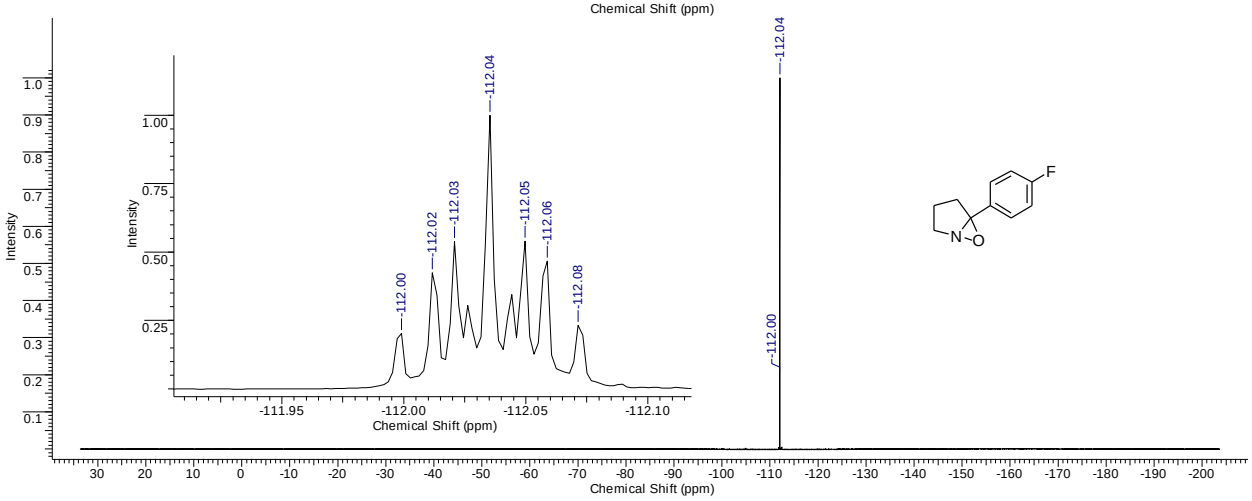

Intensity
Chemical Shift (ppm)
OMe
3.78
7.44
7.41
7.26
6.89
6.87
3.53
3.53
3.52
3.50
3.48
3.06
3.04
2.64
2.63
2.61
2.59
2.33
2.29
1.77
1.77
1.75
1.72
1.89
1.94
3.00
0.97
0.97
0.99
1.00
2.00


Intensity
Chemical Shift (ppm)
OMe
128.50
113.52
160.24
127.08
87.65
Chloroform-d
77.32
77.00
76.68
55.48
55.08
27.73
19.53

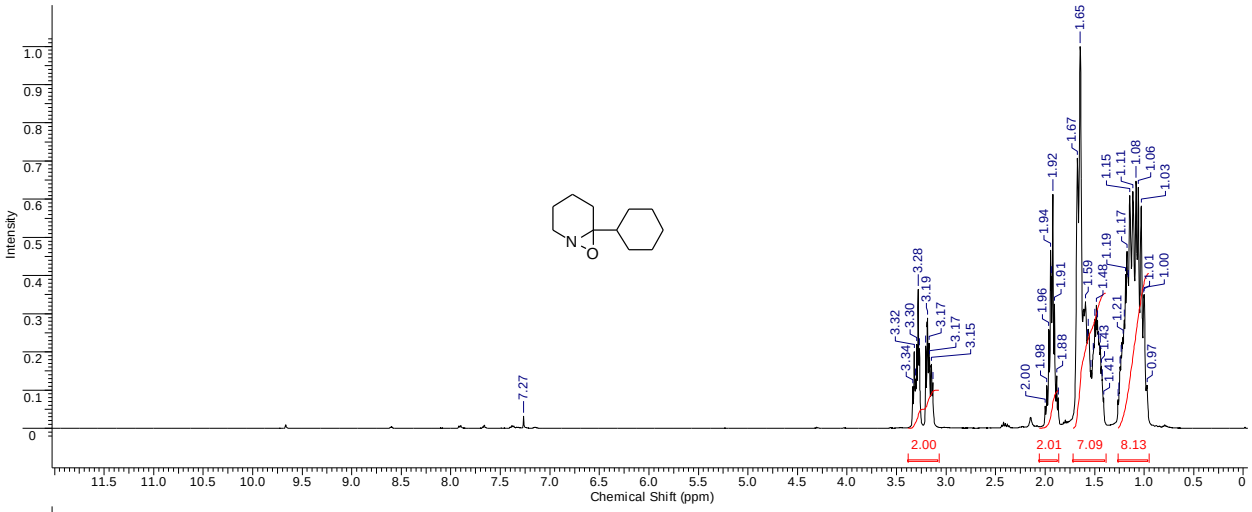
2g

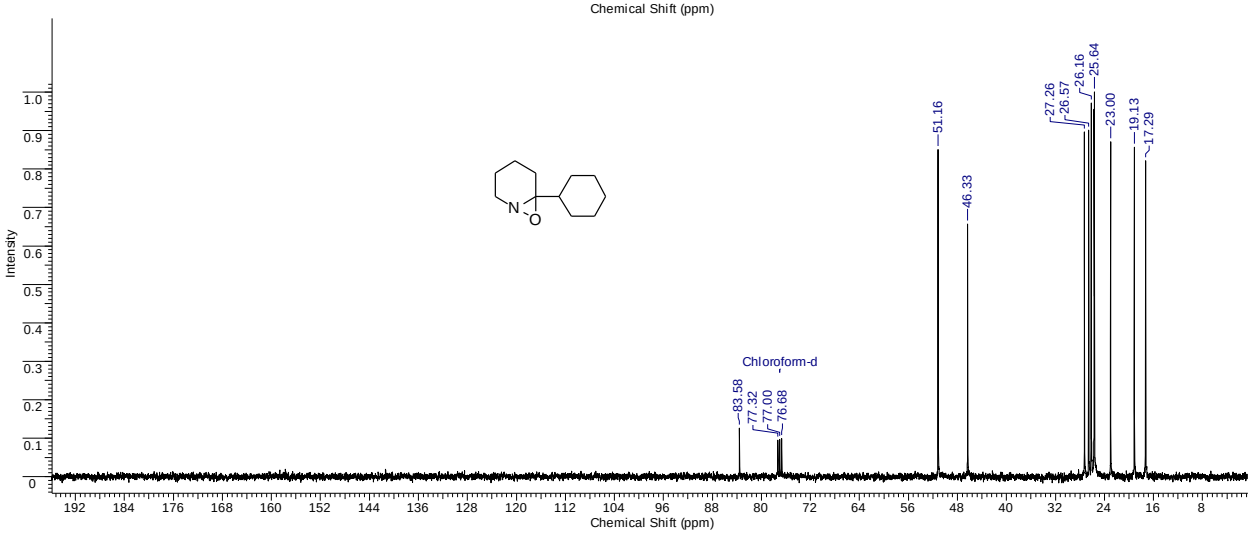

7.49
7.47
7.46
7.27
7.05
7.03
7.01
3.54
3.52
3.50
3.48
3.10
3.08
2.65
2.63
2.61
2.60
2.35
2.33
2.30
2.29
1.84
1.83
1.81
1.78
1.77
1.74
1.74
F
N
O
1.92
1.91
1.00
1.00
0.99
1.01
2.00
Intensity
Chemical Shift (ppm)


164.45
161.98
131.11
129.20
115.26
115.04
87.32
77.32
77.00
76.68
Chloroform-d
55.56
27.79
19.61
F
N
O
Intensity
Chemical Shift (ppm)

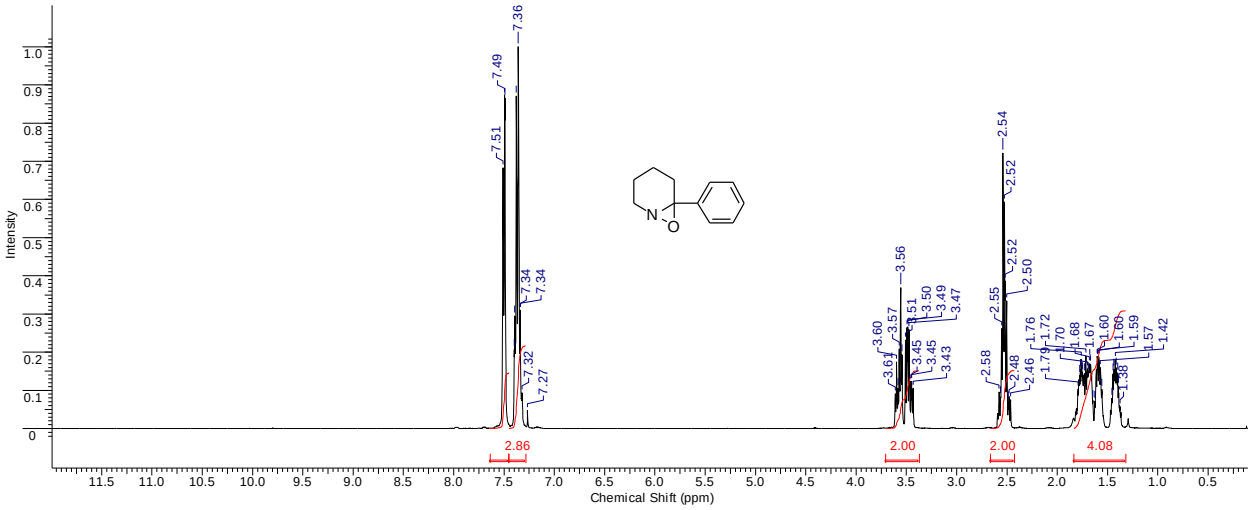

112.00
112.02
112.03
112.04
112.05
112.06
112.08
112.04
112.00
F
N
O
Intensity
Chemical Shift (ppm)

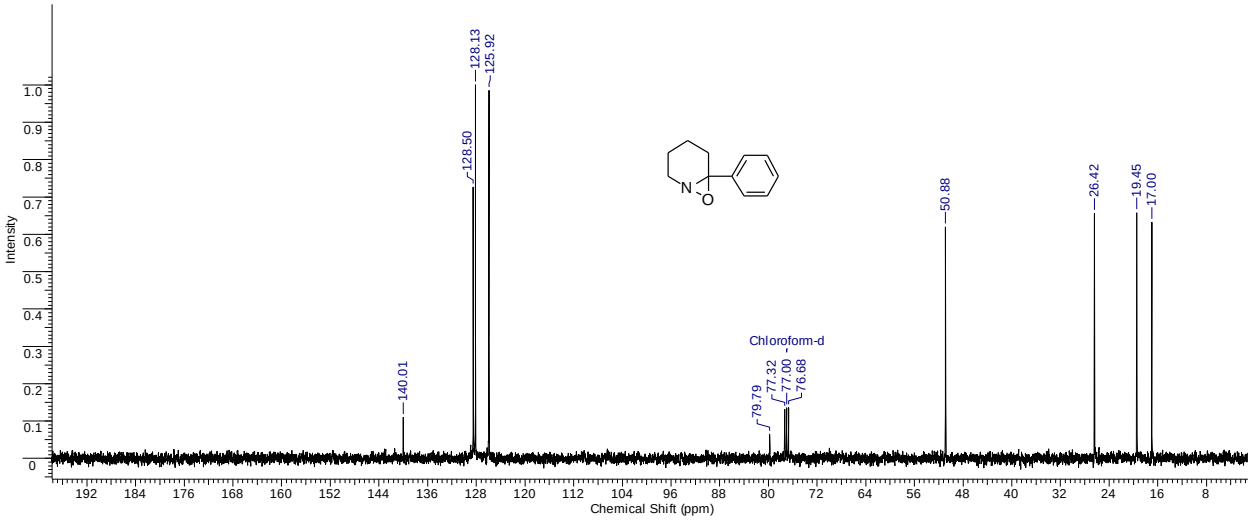
2h


Intensity
Chemical Shift (ppm)
7.27
3.34
3.32
3.30
3.28
3.19
3.17
3.15
2.00
1.98
1.96
1.94
1.92
1.91
1.88
1.67
1.65
1.59
1.48
1.43
1.41
1.21
1.19
1.17
1.15
1.11
1.08
1.06
1.03
1.01
1.00
0.97
2.00
2.01
7.09
8.13

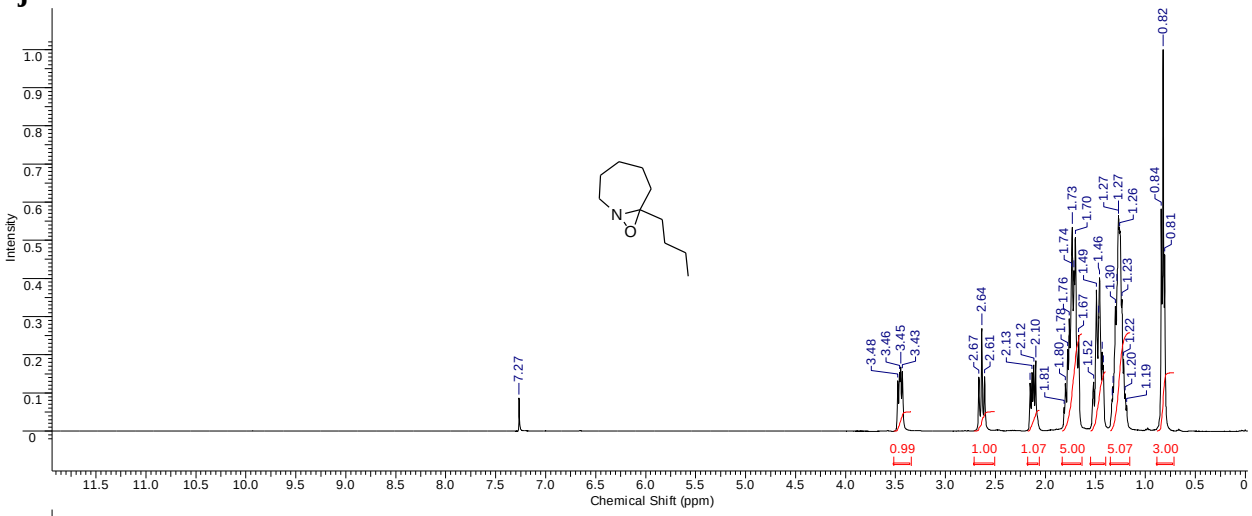

Intensity
Chemical Shift (ppm)
Chloroform-d
83.58
77.32
77.00
76.68
51.16
46.33
27.26
26.57
26.16
25.64
23.00
19.13
17.29

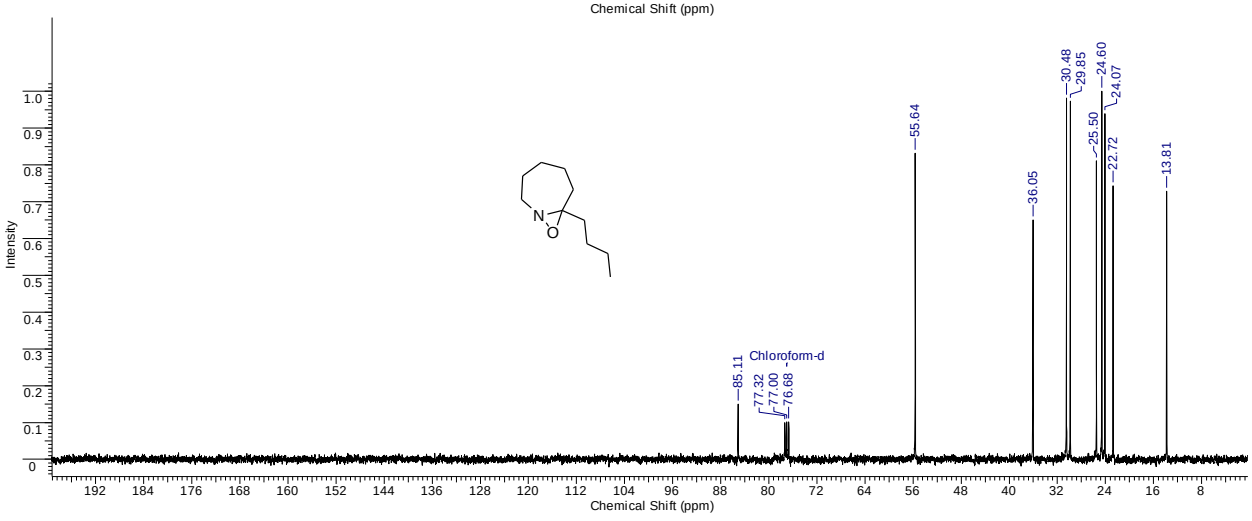
2i


Intensity
Chemical Shift (ppm)
7.49
7.36
7.51
7.34
7.34
7.32
7.27
3.61
3.60
3.57
3.56
3.51
3.50
3.49
3.47
3.45
3.43
2.58
2.55
2.54
2.52
2.52
2.50
2.48
2.46
1.79
1.76
1.72
1.70
1.68
1.67
1.66
1.60
1.59
1.57
1.42
1.38
2.86
2.00
2.00
4.08

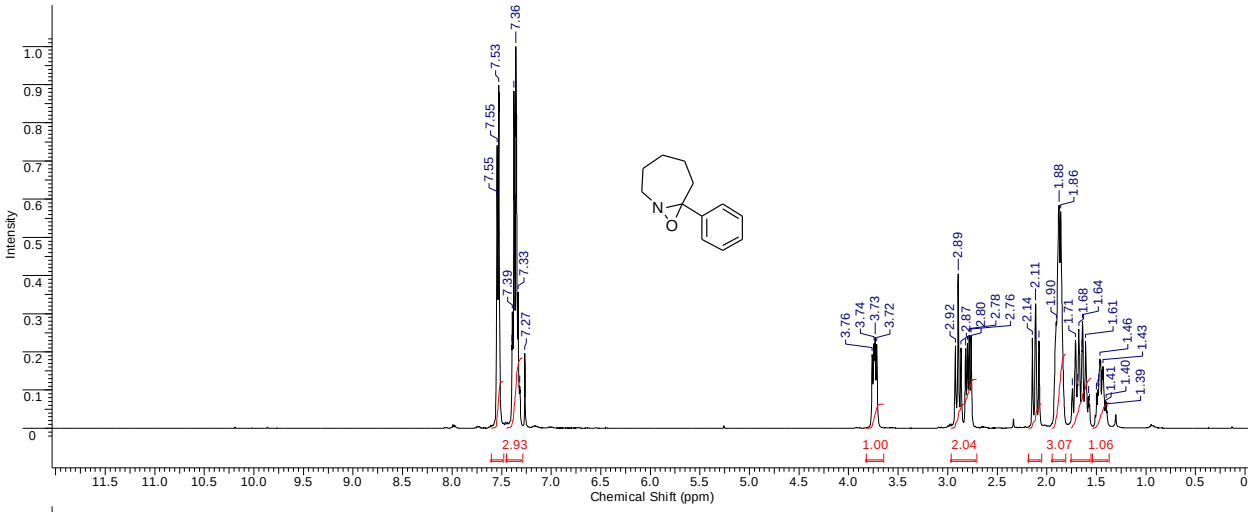

128.13
125.92
128.50
140.01
Chloroform-d
79.79
77.32
77.00
76.68
50.88
26.42
19.45
17.00
Intensity
Chemical Shift (ppm)

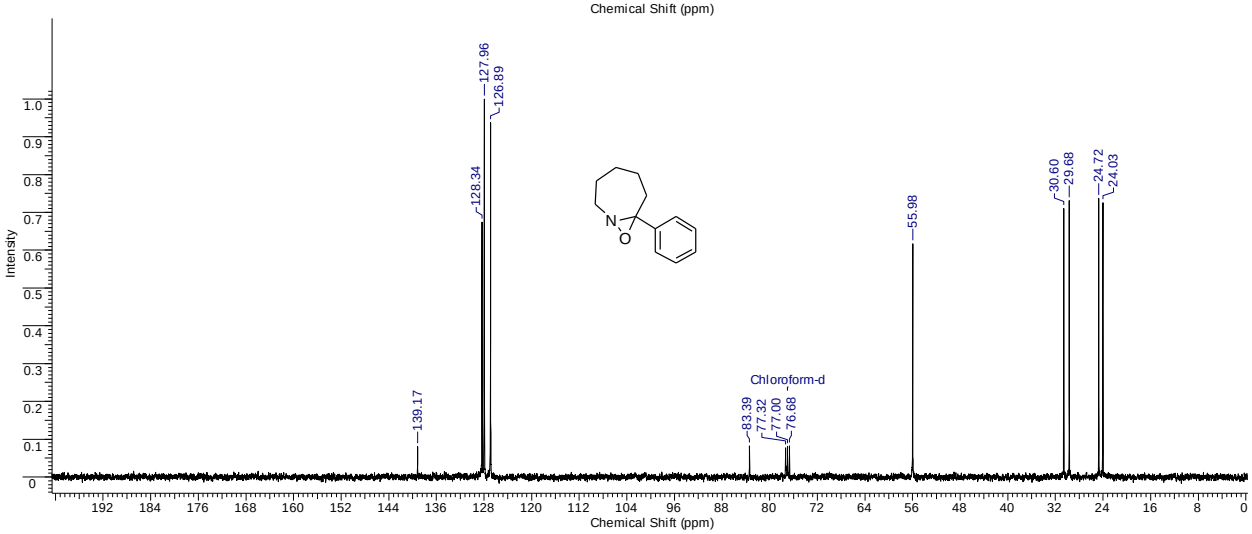
2j


0.82
0.84
0.81
7.27
3.48
3.46
3.45
3.43
2.67
2.64
2.61
2.13
2.12
2.10
1.81
1.80
1.78
1.76
1.74
1.73
1.70
1.67
1.52
1.49
1.46
1.30
1.27
1.27
1.26
1.23
1.22
1.20
1.19
0.99
1.00
1.07
5.00
5.07
3.00
Intensity
Chemical Shift (ppm)

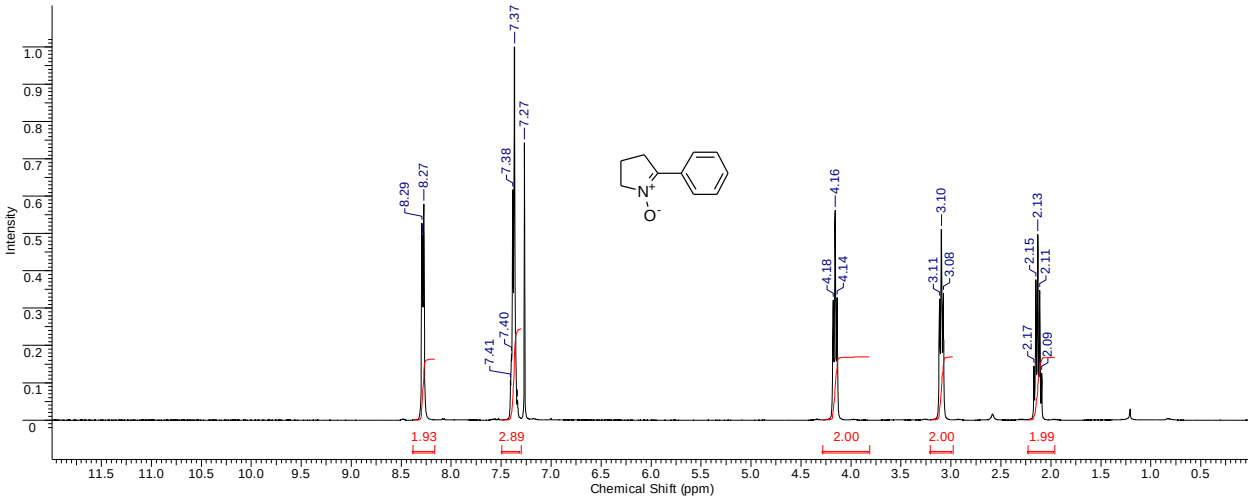

55.64
30.48
29.85
25.50
24.60
24.07
22.72
36.05
13.81
85.11
Chloroform-d
77.32
77.00
76.68
Intensity
Chemical Shift (ppm)

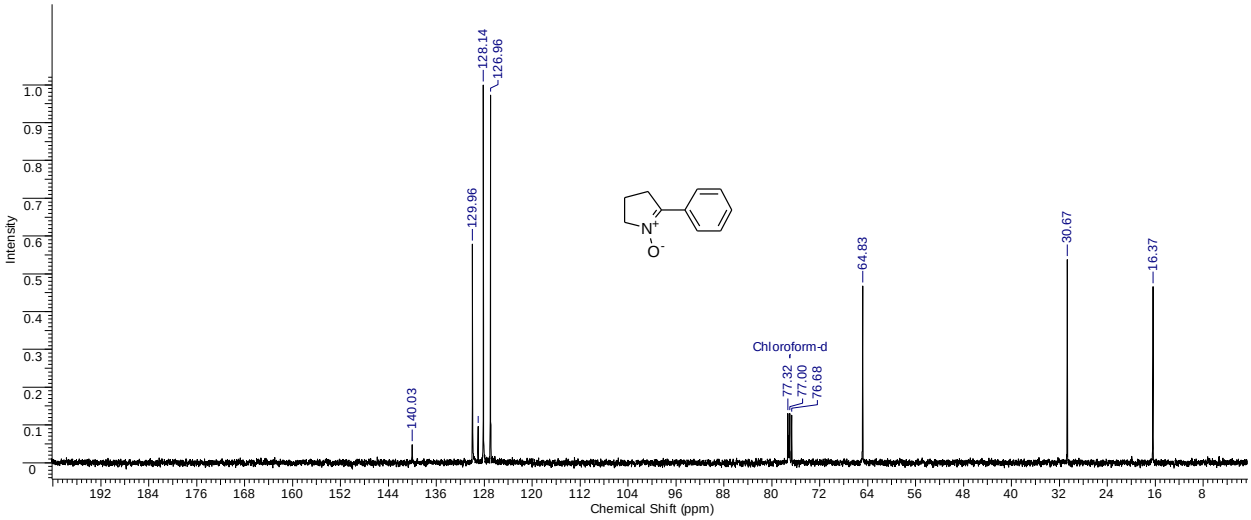
2k


Intensity
Chemical Shift (ppm)
7.53
7.55
7.55
7.36
7.39
7.33
7.27
3.76
3.74
3.73
3.72
2.92
2.87
2.80
2.78
2.76
2.89
2.14
2.11
1.90
1.88
1.86
1.71
1.68
1.64
1.61
1.46
1.43
1.41
1.40
1.39
2.93
1.00
2.04
3.07
1.06

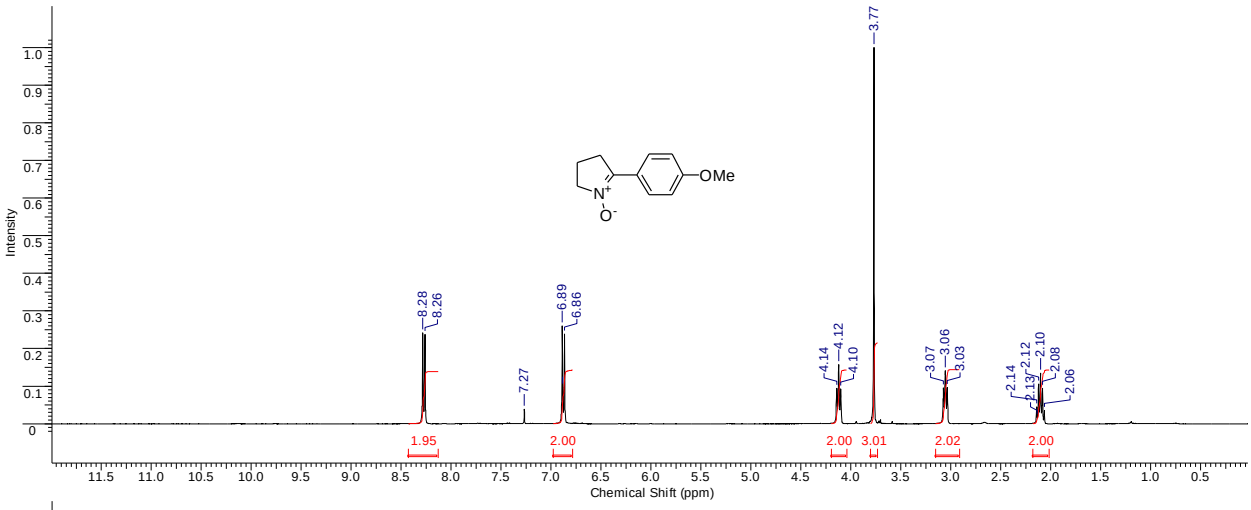

Intensity
Chemical Shift (ppm)
127.96
126.89
128.34
139.17
Chloroform-d
83.39
77.32
77.00
76.68
55.98
30.60
29.68
24.72
24.03

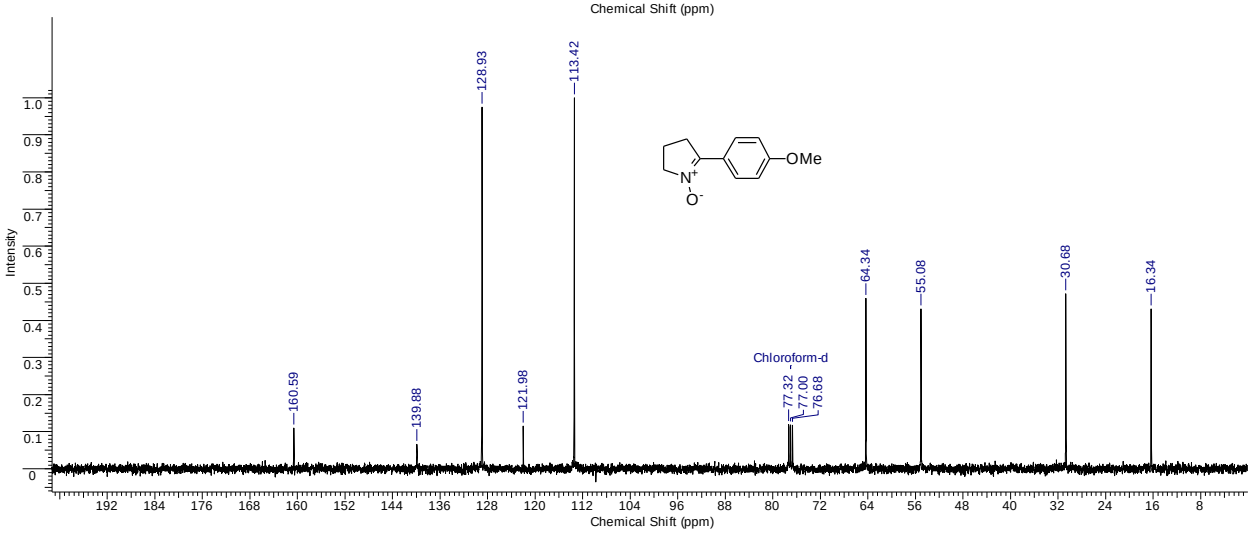
3e


Intensity
Chemical Shift (ppm)
7.37
7.27
7.38
8.29
8.27
7.41
7.40
4.16
4.18
4.14
3.10
3.11
3.08
2.13
2.15
2.11
2.17
2.09
1.93
2.89
2.00
2.00
1.99

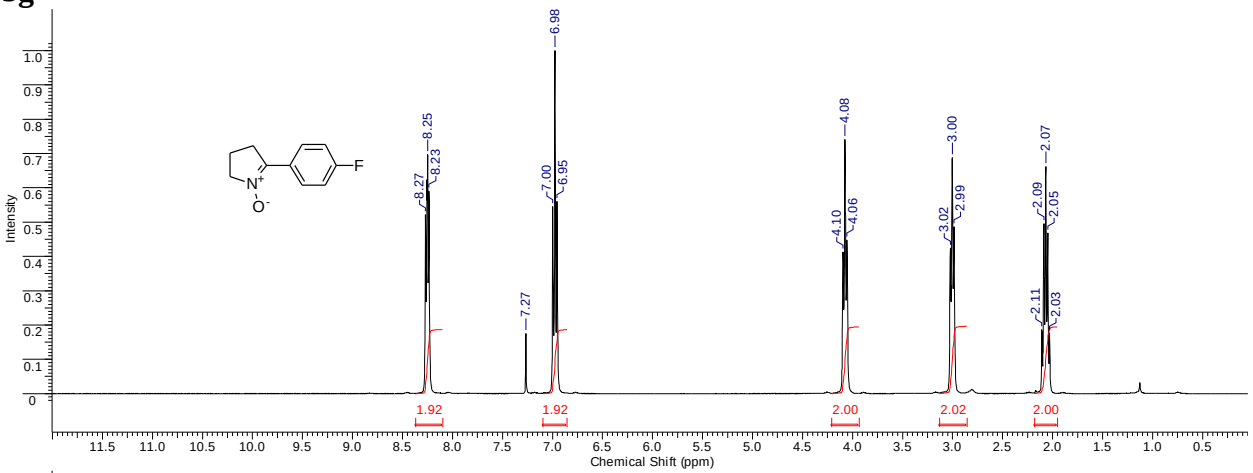

128.14
126.96
129.96
140.03
Chloroform-d
77.32 - 77.00 - 76.68
64.83
30.67
16.37
Intensity
Chemical Shift (ppm)

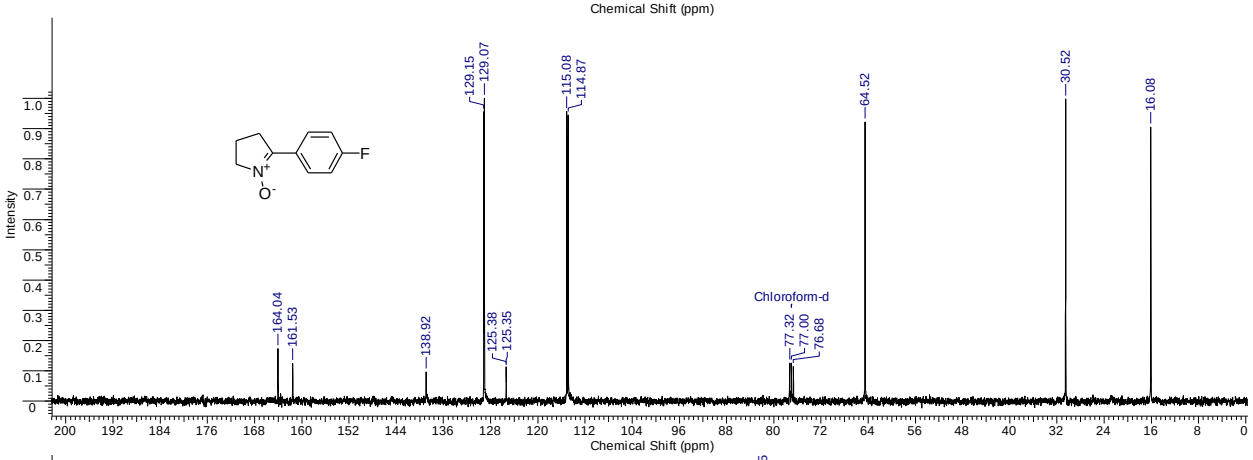
3f

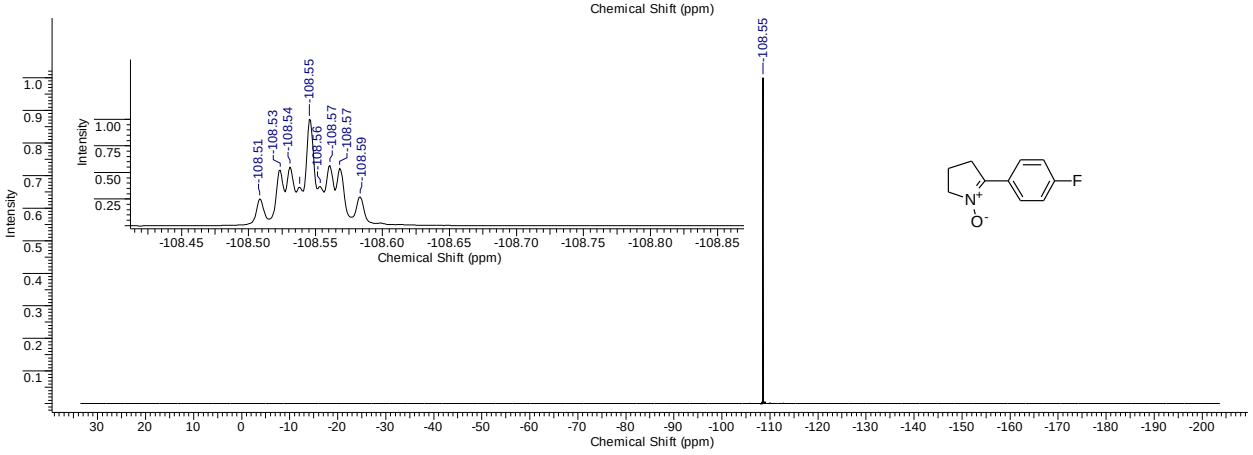

OMe
3.77
8.28
8.26
6.89
6.86
7.27
4.14
4.12
4.10
3.07
3.06
3.03
2.14
2.12
2.10
2.08
2.06
1.95
2.00
2.00
3.01
2.02
2.00
Intensity
Chemical Shift (ppm)


OMe
128.93
113.42
160.59
139.88
121.98
Chloroform-d
77.32 - 77.00 - 76.68
64.34
55.08
30.68
16.34
Intensity
Chemical Shift (ppm)

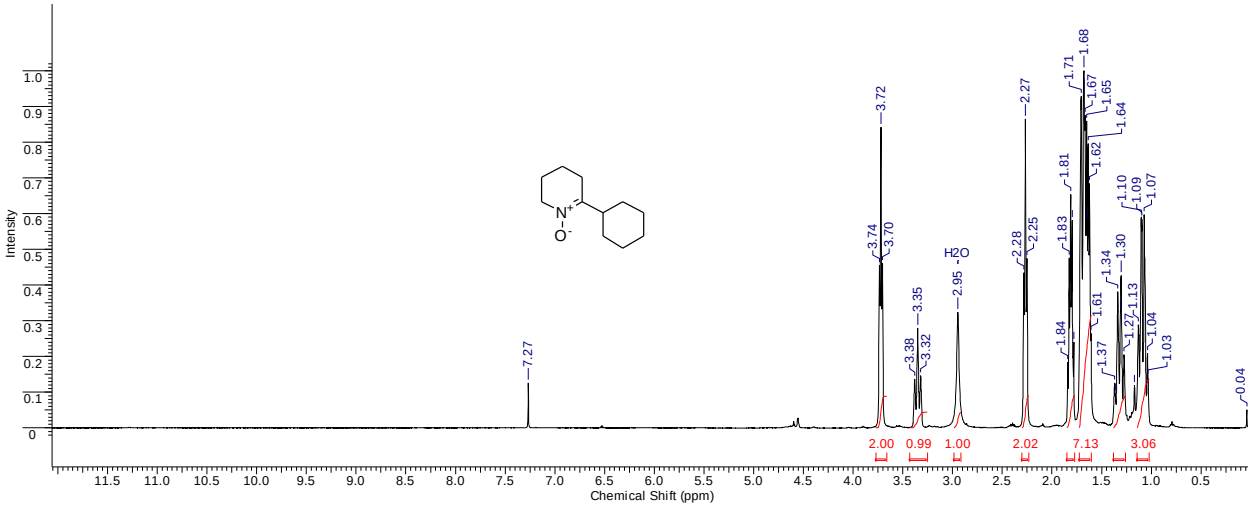
3g

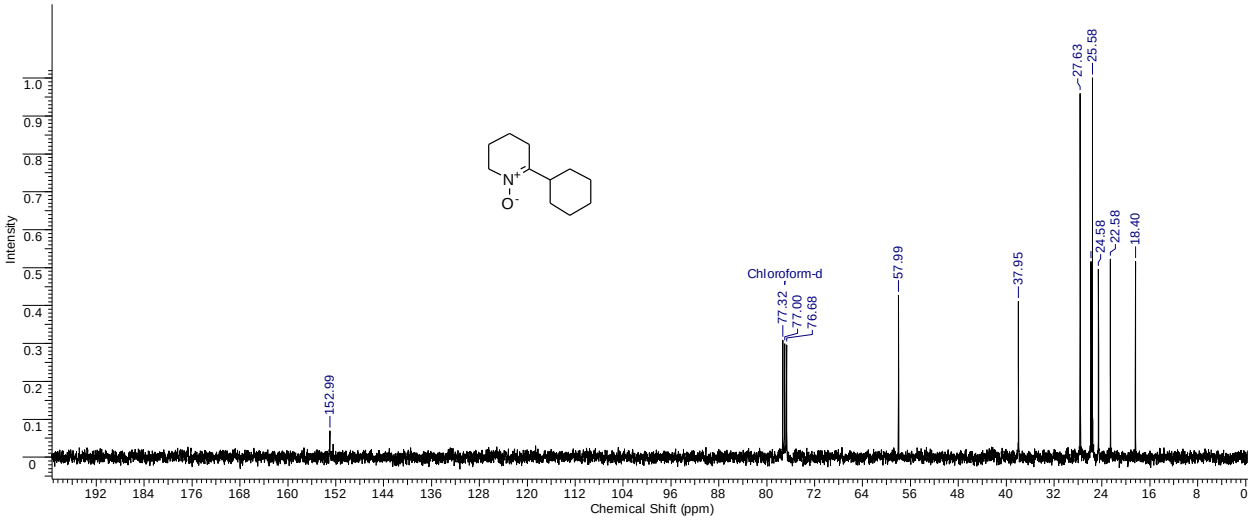

8.27
8.25
8.23
7.27
7.00
6.98
6.95
4.10
4.08
4.06
3.02
3.00
2.99
2.11
2.09
2.07
2.05
2.03
1.92
1.92
2.00
2.02
2.00
Intensity
Chemical Shift (ppm)


164.04
161.53
138.92
129.15
129.07
125.38
125.35
115.08
114.87
Chloroform-d
77.32
77.00
76.68
64.52
30.52
16.08
Intensity
Chemical Shift (ppm)

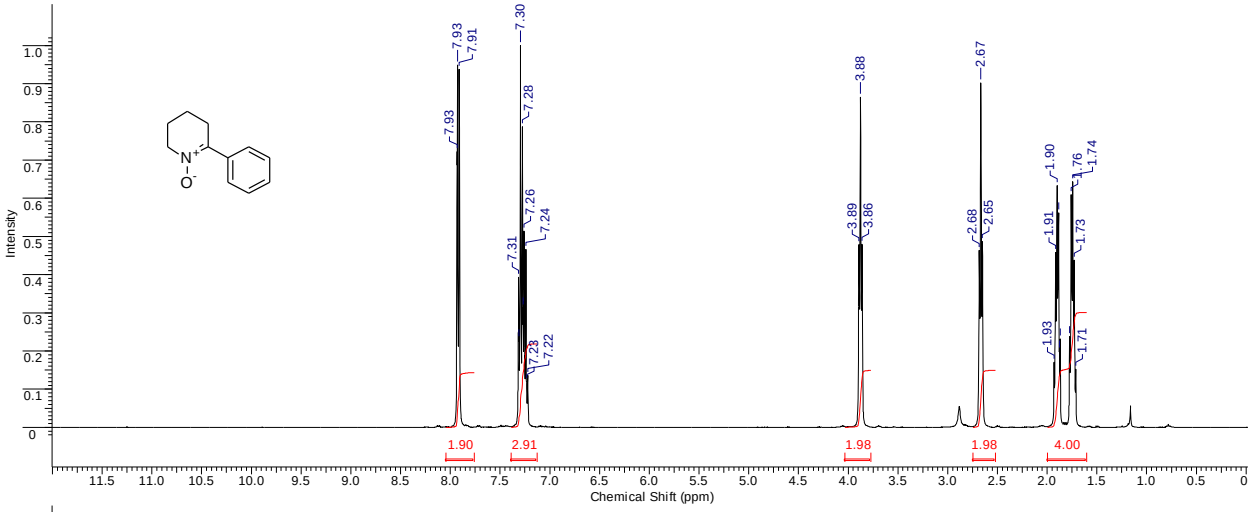

108.51
108.53
108.54
108.55
108.56
108.57
108.57
108.59
108.55
Intensity
Chemical Shift (ppm)

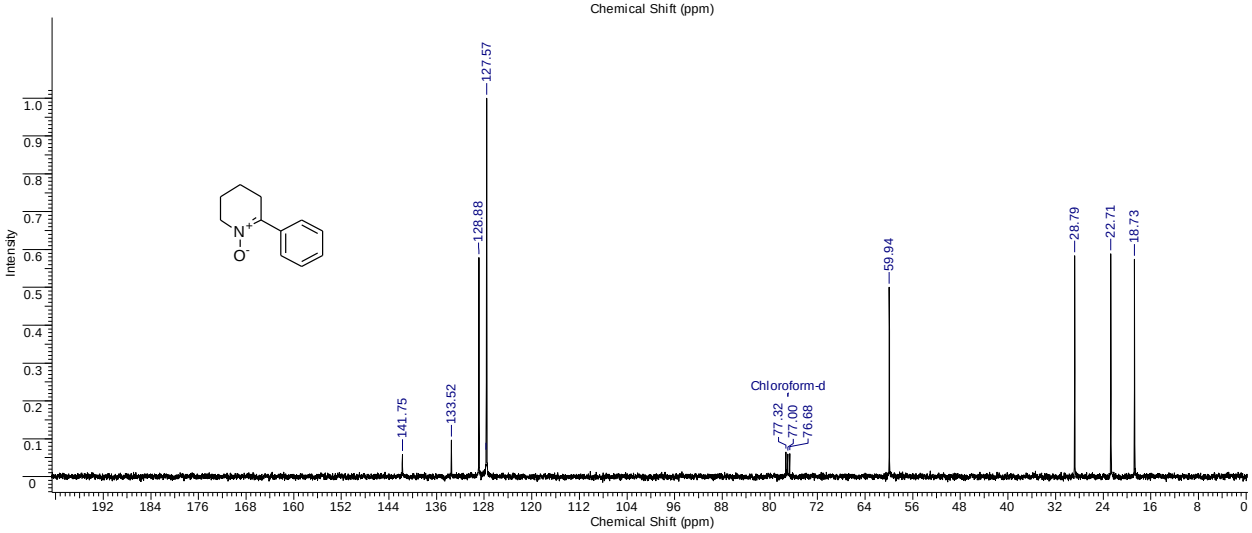
3h


7.27
3.74
3.72
3.70
3.38
3.35
3.32
2.95
H2O
2.28
2.27
2.25
1.84
1.83
1.81
1.71
1.68
1.67
1.65
1.64
1.62
1.61
1.37
1.34
1.30
1.27
1.13
1.10
1.09
1.07
1.04
1.03
0.04
2.00
0.99
1.00
2.02
7.13
3.06
Intensity
Chemical Shift (ppm)

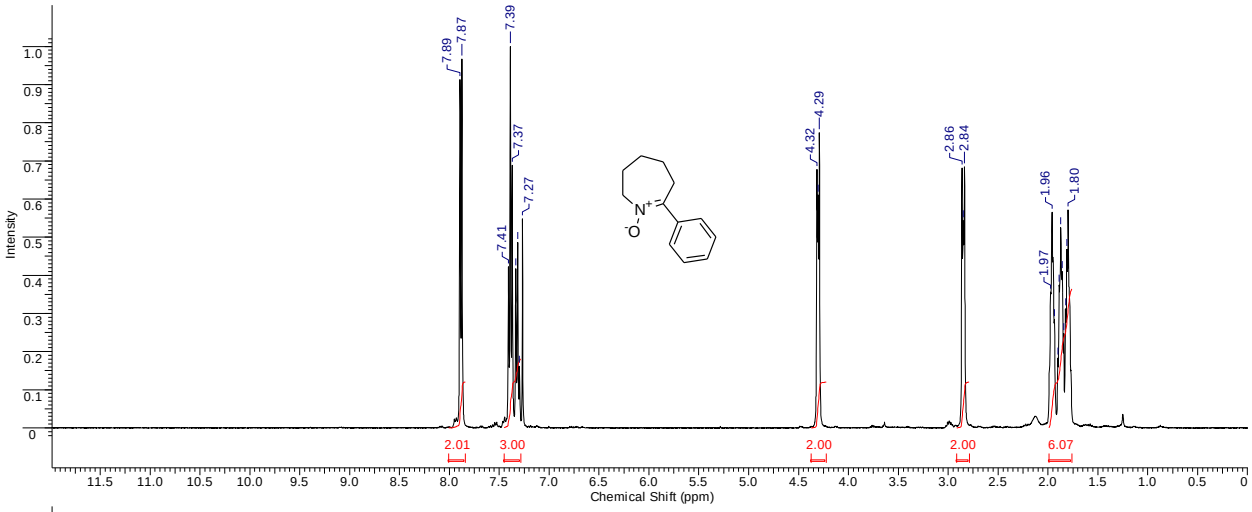

Intensity
Chemical Shift (ppm)
152.99
77.32
77.00
76.68
Chloroform-d
57.99
37.95
27.63
25.58
24.58
22.58
18.40

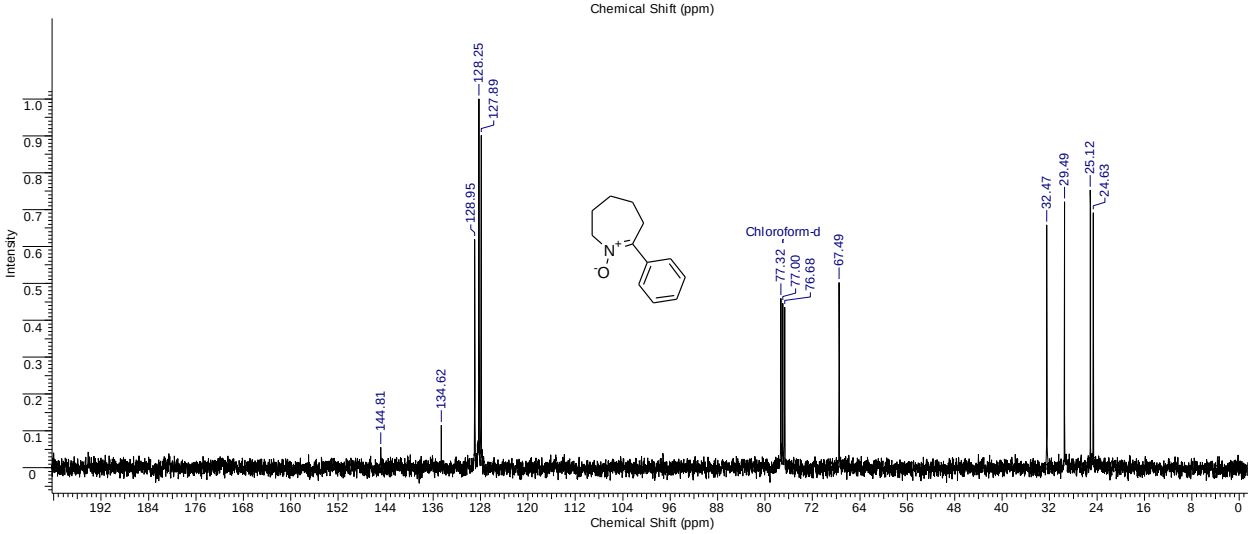
3i


Intensity
Chemical Shift (ppm)
7.93
7.91
7.30
7.28
7.26
7.24
7.31
7.23
7.22
3.88
3.89
3.86
2.67
2.68
2.65
1.90
1.91
1.93
1.76
1.74
1.73
1.71
1.90
2.91
1.98
1.98
4.00


Intensity
Chemical Shift (ppm)
127.57
128.88
141.75
133.52
77.32
77.00
76.68
Chloroform-d
59.94
28.79
22.71
18.73

3k


7.89
7.87
7.39
7.37
7.41
7.27
4.32
4.29
2.86
2.84
1.96
1.80
1.97
2.01
3.00
2.00
2.00
6.07
Intensity
Chemical Shift (ppm)


128.25
127.89
128.95
144.81
134.62
Chloroform-d
77.32
77.00
76.68
67.49
32.47
29.49
25.12
24.63
Intensity
Chemical Shift (ppm)