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Regioselective Annulation of Nitrosopyridine with Alkynes: Straightforward Synthesis of *N*-Oxide-imidazopyridines

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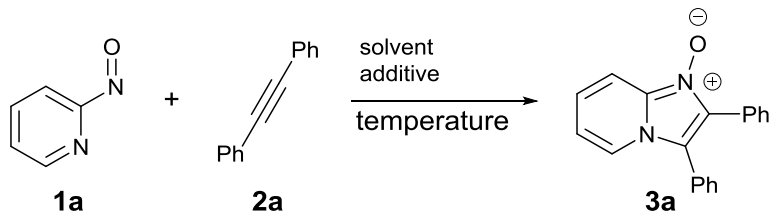
General information:

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade. Dry solvents were purified by the Solvent Purification System *M-BRAUN Glovebox Technology SPS-800*. Analytical thin layer chromatography (TLC) was performed on Merck silica gel *aluminium plates* with *F-254 indicator*, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR and ^{13}C-NMR were recorded on a *Bruker DRX400 (400 MHz), DRX500 (500 MHz)* and *DRX600* (600 MHz) spectrometer in $CDCl_3$ (δ = 7.26 ppm for ^{1}H, = 77.16 ppm for ^{13}C). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). High resolution mass spectra were recorded on a LTQ Orbitrap mass spectrometer coupled to an *Acceka HPLC-System* (HPLC column: *Hypersyl GOLD*, 50 mm × 1 mm, 1.9 μm). Fourier transform infrared spectroscopy (FT- IR) spectra were obtained with a Bruker Tensor 27 spectrometer (ATR, neat) and are reported in terms of frequency of absorption (cm^{-1}). Chemical yields refer to isolated pure substances. **N**itrosopyridine were prepared according to literature procedures and characteristic data are matching with reported products.[1]

[1] (a) F. Li, B. Yang, M. J. Miller, J. Zajicek, B. C. Noll, U. Möllmann, H.-M. Dahse and P. A. Miller; *Org. Lett.*, **2007**, *9*, 2923-2926; (b) E. C. Taylor, C.-P. Tseng, and J. B. Rampal; *J. Org. Chem.*, **1982**, *47*, 552-55.

Optimization of the reaction conditions[a]



1a **2a** **3a**

Entry	Solvent	Additive (equiv)	Time [h]	Yield [%][b]
1	CH_3CN	-	24	20
2	CH_2Cl_2	-	24	45
3	$CHCl_3$	-	12	65
4	H_2O	-	12	n.d.
5	MeOH	-	12	n.d.
6	CF_3CH_2OH	-	24	40
7	HFIP	-	12	86
8	EtOAc	-	12	n.d.
9	EtOH	-	12	n.d.
10	C_6H_6	-	12	n.d.
11	HFIP: CH_2Cl_2 (1:1)	CF_3CO_2H (2)	12	50
12	MeOH	CH_3CO_2H (2)	12	n.d.
13	$CHCl_3$	CF_3CO_2H (2)	12	20
14	$CHCl_3$	CF_3CO_2H (2)	12	15
15	HFIP	CF_3CO_2H (2)	12	54
16[c]	HFIP	-	12	70

[a] Reaction conditions: 1a (0.25 mmol), 2a (0.28 mmol) in solvent (1.0 mL) at 40°C for 12 h. [b] Isolated yields [c] Reaction was carried out at ambient temperature. n.d. = not determined. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

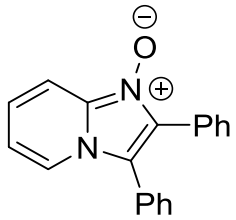
Initially, the reaction of 2-nitrosopyridine (**1a**) with diphenylacetylene (**2a**) was chosen as model reaction to investigate the possibility of cycloaddition in the absence of transition metal catalyst. At first, we tried to utilize the polarity of the solvent to polarize the nitroso-group (Table 1, entries 1-10). Hence, in the initial experiments, we stirred the substrates together in CH_2Cl_2 and CH_3CN at 40°C. We were absolutely delighted to obtain 45% and 20% of product **3a** in CH_2Cl_2 and CH_3CN respectively.

These results prompted us to further screen various solvents. Chloroform proved to be a better solvent compared to CH_2Cl_2 with a yield of 65%. However, no desired product could be detected in EtOAc and benzene. Further screening of polar protic solvents revealed 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) to be the best solvent with a yield of 86%. Other similar solvents like CF_3CH_2OH were less effective (40% yield). Surprisingly, MeOH and ethanol completely prevented the cycloaddition and only led to dimerization of **1a**. We also tried HFIP/CH_2Cl_2 mixture as solvent but the result was found to be inferior. At this stage, we tried some acid additives such as CF_3CO_2H and AcOH to further improve the efficiency of the reaction (entries 12-15). However, they were found to be not useful. When the reaction was carried out at ambient temperature, the yield of **3a** decreased to 70%. An increase in temperature to 60°C also had a deleterious effect on the yield (52%).

General procedure for the imidazo[1,2-*a*]pyridine 1-oxide synthesis:

To a screw cap reaction vial 2-nitrosopyridine derivatives (0.25 mmol, 1 equiv), alkyne (0.28 mmol, 1.1 equiv), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 1.0 mL) were added under air. The reaction mixture was stirred vigorously at RT-60 ^oC until completion. The crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system.

Analytical data



2,3-Diphenylimidazo[1,2-*a*]pyridine 1-oxide (3a)

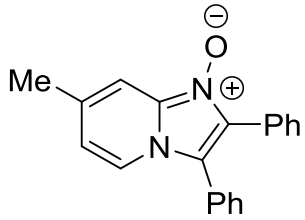
Prepared according to the general procedure and the product was obtained as light yellow solid in 86% yield (62 mg), mp 185-189 ^{o}C. This reaction was carried out in 4 mmol scale and the pure product was obtained in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.75 – 7.68 (m, 2H), 7.49 – 7.42 (m, 3H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 3H), 7.20 (ddd, *J* = 9.1, 6.7, 0.8 Hz, 1H), 6.78 ppm (td, *J* = 6.9, 1.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.97, 132.91, 130.51, 130.13, 129.75, 129.71, 128.98, 128.26, 126.72, 126.50, 124.92, 122.60, 117.28, 114.48, 112.87 ppm.

FT-IR: $\tilde{\nu}$ = 3015, 2926, 1630, 1506, 1514, 1450, 1423, 1371, 1279, 1113 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{15}N_2O$: 287.11789 found: 287.11743.



7-Methyl-2,3-diphenylimidazo[1,2-a]pyridine 1-oxide (3b)

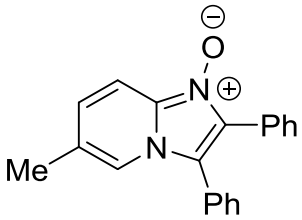
Prepared according to the general procedure and the product was obtained as light yellow solid in 67% yield (50 mg), mp 174-178 ^{o}C;

^{1}H NMR (400 MHz, $CDCl_3$) 7.87 (d, *J* = 7.1 Hz, 1H), 7.68-7.65 (m, 3H), 7.47 – 7.41 (m, 3H), 7.34 – 7.29 (m, 2H), 7.29 – 7.25 (m, 3H), 6.66 (dd, *J* = 7.1, 1.1 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.39, 134.35, 132.51, 130.43, 130.07, 129.66, 128.90, 128.20, 126.64, 126.45, 122.10, 117.37, 116.82, 110.70, 21.45 ppm.

FT-IR: $\tilde{\nu}$ = 2999, 1635, 1505, 1444, 1457, 1241, 1174, 1040 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{20}H_{17}N_2O$: 301.13354 found: 301.13354.



6-Methyl-2,3-diphenylimidazo[1,2-a]pyridine 1-oxide (3c)

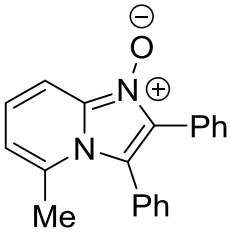
Prepared according to the general procedure and the product was obtained as light yellow solid in 82% yield (62 mg), mp 137-140 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.2 Hz, 1H), 7.73 (s, 1H), 7.66 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.33 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.10 (d, *J* = 9.2 Hz, 1H), 2.25 ppm (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.30, 132.50, 130.57, 130.07, 129.71, 128.89, 128.63, 128.21, 126.77, 126.49, 124.73, 119.97, 116.99, 112.05, 18.42 ppm.

FT-IR: $\tilde{\nu}$ = 3063, 2960, 1645, 1513, 1380, 1369, 1259, 1182, 1068 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{20}H_{17}N_2O$: 301.134354 found: 301.13439.



5-Methyl-2,3-diphenylimidazo[1,2-a]pyridine 1-oxide (3d)

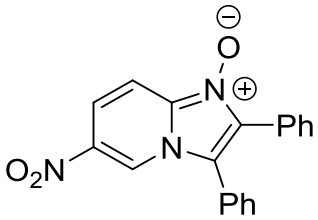
Prepared according to the general procedure and the product was obtained as light yellow solid in 87% yield (65 mg), mp 163-165 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.1 Hz, 1H), 7.56 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.50 – 7.30 (m, 5H), 7.28 – 7.14 (m, 4H), 6.57 (d, *J* = 6.8 Hz, 1H), 2.06 ppm (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.66, 135.45, 133.80, 133.01, 130.19, 130.00, 129.32, 128.82, 128.12, 128.02, 126.32, 125.60, 118.63, 115.95, 110.71, 21.60 ppm.

FT-IR: $\tilde{\nu}$ = 3064, 2955, 1633, 1517, 1393, 1336, 1221, 1106 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{20}H_{17}N_2O$: 301.13354 found: 301.13353.



6-Nitro-2,3-diphenylimidazo[1,2-*a*]pyridine 1-oxide (3e)

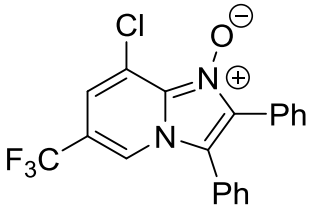
Prepared according to the general procedure using and the product was obtained as light yellow solid in 96% yield (80 mg), mp 204-209 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.00 (d, *J* = 10.0 Hz, 1H), 7.84 (dd, *J* = 10.0, 1.6 Hz, 1H), 7.72 (dd, *J* = 7.1, 2.1 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.42-7.34 ppm (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.84, 136.33, 133.33, 130.87, 130.42, 130.25, 130.06, 129.92, 128.52, 125.33, 125.08, 123.65, 120.32, 117.83, 113.28 ppm.

FT-IR: $\tilde{\nu}$ = 3060, 2996, 1726, 1605, 1503, 1369, 1325, 1126, 1075 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{14}N_3O_3$: 332.10297 found: 332.10374.



8-Chloro-2,3-diphenyl-6-(trifluoromethyl)imidazo[1,2-*a*]pyridine 1-oxide (3f)

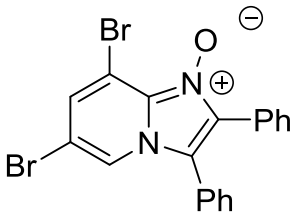
Prepared according to the general procedure and the product was obtained as light yellow solid in 64% yield (62 mg), mp 193-196 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.72 – 7.68 (m, 2H), 7.58 – 7.52 (m, 3H), 7.39 – 7.36 (m, 2H), 7.34 (dd, *J* = 5.7, 4.6 Hz, 3H), 7.15 ppm (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.44, 130.88, 130.52, 130.28, 130.24, 129.90, 129.79, 128.37, 125.29, 125.25, 123.46, 123.12, 122.38 (q, *J* = 272.52 Hz), 120.69, 120.62 (q, *J* = 5.9 Hz), 118.49, 118.21 ppm.

FT-IR: $\tilde{\nu}$ = 3050, 2940, 1636, 1531, 1416, 1309, 1231, 1121, 1074 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{21}H_{12}ClF_3N_2O$: 389.05903 found: 389.06982.



6,8-Dibromo-2,3-diphenylimidazo[1,2-*a*]pyridine 1-oxide (3g)

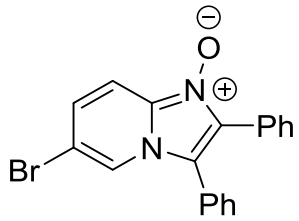
Prepared according to the general procedure and the product was obtained as light yellow solid in 81% yield (90 mg), mp 171-175 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.3 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.52 – 7.49 (m, 3H), 7.36 – 7.32 (m, 3H), 7.31 – 7.27 ppm (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.97, 130.99, 130.55, 130.48, 130.15, 130.03, 129.37, 129.00, 128.17, 125.70, 125.65, 121.75, 118.18, 108.12, 107.55 ppm.

FT-IR: $\tilde{\nu}$ = 3035, 2980, 1602, 1599, 1504, 1488, 1361, 1329, 1244, 1140, 1031 cm^{-1}.

HRMS: $C_{19}H_{13}{}^{79}Br_2N_2O$ $[M+H]^+$ calc.: 442.93891 found: 442.94002; $C_{19}H_{13}{}^{79}Br^{81}BrN_2O$ $[M+H]^+$ calc.: 444.94687 found: 444.93711, $C_{19}H_{13}{}^{81}Br_2N_2$ $[M+H]^+$ calc.: 446.93482found : 446.93442.



6-Bromo-2,3-diphenylimidazo[1,2-*a*]pyridine 1-oxide (3h)

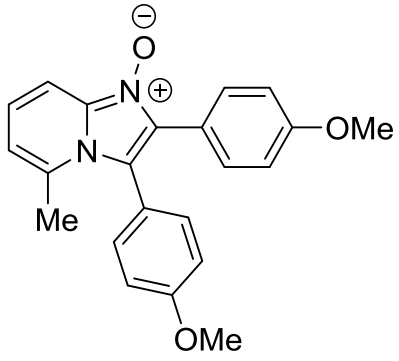
Prepared according to the general procedure and the product was obtained as light yellow solid in 95% yield (87 mg), mp 184-187 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.92 (d, *J* = 9.6 Hz, 1H), 7.70 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.51 (dd, *J* = 6.5, 3.6 Hz, 3H), 7.40 – 7.28 ppm (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.55, 132.85, 130.53, 130.32, 130.16, 130.01, 129.47, 128.73, 128.46, 126.01, 125.82, 122.51, 117.87, 113.75, 109.76 ppm.

FT-IR: $\tilde{\nu}$ = 3096, 3004, 1625, 1510, 1376, 1355, 1175, 1078 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{14}{}^{79}BrN_2O$: 365.03004 found: 365.02840. HRMS: calc. for $[M+H]^+$ $C_{19}H_{14}{}^{79}BrN_2O$: 367.02726 found: 367.02636.



2,3-Bis(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyridine 1-oxide (3i)

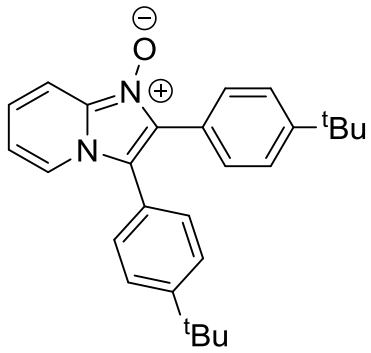
Prepared according to the general procedure and the product was obtained as light yellow solid in 87% yield (78 mg), mp 90-93 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.1 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.73 (t, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 6.8 Hz, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 2.04 ppm (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.62, 159.66, 136.43, 135.16, 134.22, 133.57, 131.38, 124.81, 121.42, 118.94, 117.75, 115.51, 113.49, 113.46, 110.55, 55.35, 55.15, 21.51 ppm.

FT-IR: $\tilde{\nu}$ = 2996, 2837, 1609, 1519, 1494, 1395, 1293, 1247, 1160, 1027 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{22}H_{21}N_2O_3$: 361.15467 found: 361.15525.



2,3-Bis(4-(*tert*-butyl)phenyl)imidazo[1,2-*a*]pyridine 1-oxide (3j)

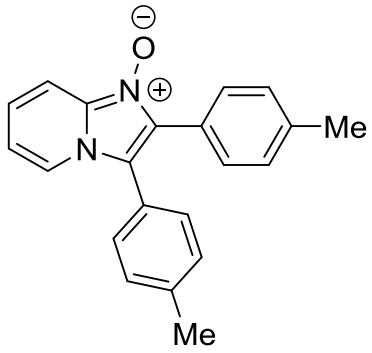
Prepared according to the general procedure and the product was obtained as light yellow solid in 95% yield (95 mg), mp 88-92 ^{o}C;

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01 – 7.87 (m, 2H), 7.76 – 7.64 (m, 2H), 7.54 – 7.45 (m, 2H), 7.39 – 7.28 (m, 4H), 7.20 (ddd, *J* = 9.4, 6.7, 0.9 Hz, 1H), 6.83 – 6.72 (m, 1H), 1.36 (s, 9H), 1.29 ppm(s, 9H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 152.92, 151.88, 133.92, 132.90, 130.29, 129.73, 126.64, 125.29, 124.69, 123.86, 123.67, 122.78, 117.19, 114.24, 112.82, 35.02, 34.85, 31.35, 31.33 ppm.

FT-IR: $\tilde{\nu}$ = 2962, 2915, 1605, 1492, 1363, 1283, 1177, 1089 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{27}H_{31}N_2O$: 399.24310 found: 399.24309.



2,3-Di-*p*-tolylimidazo[1,2-*a*]pyridine 1-oxide (3k)

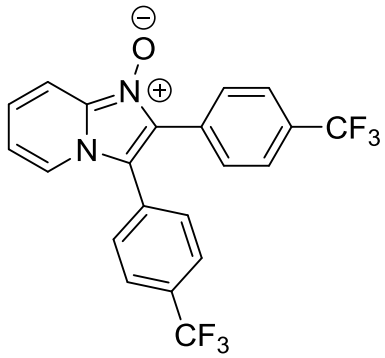
Prepared according to the general procedure and the product was obtained as light yellow solid in 88% yield (69 mg), mp 150-153 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7-317.28 (m, 4H), 7.26 – 7.21 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 6.86-8.81 (m, 6.9, 1H), 2.45 (s, 3H), 2.35 ppm(s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.84, 138.92, 133.83, 132.75, 130.36, 130.30, 129.89, 128.95, 124.97, 123.60, 123.50, 122.62, 117.19, 114.32, 112.59, 21.47, 21.44 ppm.

FT-IR: $\tilde{\nu}$ =2988, 2921, 1620, 157, 1407, 1360, 1232, 1110 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{21}H_{19}N_2O$: 315.14919 found: 315.15023.



2,3-Bis(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine 1-oxide (3l)

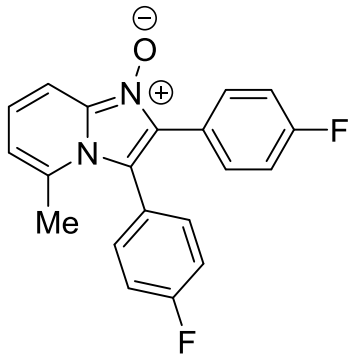
Prepared according to the general procedure at 60 °C and the product was obtained as light yellow solid in 77% yield (81 mg), mp 120-125 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 9.5, 6.8 Hz, 1H), 6.91 ppm (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 134.73, 132.33, 132.18, 131.89 (q, *J* =31.02 Hz), 131.41 (q, *J* =30.68 Hz), 130.97, 130.51, 130.03, 129.67, 127.02 (q, *J* = 3.6 Hz), 126.16, 125.53 (q, *J* =3.7 Hz), 122.12 (q, *J* =271.09 Hz), 121.82 (q, *J* =272.35 Hz), 116.30, 115.55, 113.31 ppm.

FT-IR: ṽ = 3158, 2950, 1620, 1413, 1320, 1159, 1008 cm-1.

HRMS: calc. for $[M+H]^+$ $C_{21}H_{13}N_2OF_6$: 423.09266 found: 423.09283.



2,3-Bis(4-fluorophenyl)-5-methylimidazo[1,2-*a*]pyridine 1-oxide (3m)

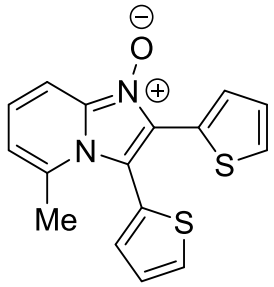
Prepared according to the general procedure at 60 °C and the product was obtained as light yellow solid in 91 % yield (77 mg), mp 117-120 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.1 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.42 – 7.36 (m, 2H), 7.19 – 7.13 (m, 1H), 7.09 (t, *J* = 8.5 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 6.8 Hz, 1H), 2.07 ppm (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) 163.63 (d, *J* = 251.80 Hz), 162.87 (d, *J* = 249.6 Hz), 136.28, 135.49, 134.87 (d, *J* = 8.4 Hz), 133.31, 132.17 (d, *J* = 8.4 Hz), 125.46 (d, J = 3.7 Hz),, 125.32, 122.47 (d, *J* = 3.3 Hz), 117.10, 115.58, 115.52 (d, *J* = 21.8 Hz), 115.30 (d, *J* = 21.7 Hz), 111.03ppm.

FT-IR: ṽ = 3093, 3051, 1637, 1595, 1517, 1493, 1377, 1222, 1158, 1070 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{20}H_{15}N_2OF_2$: 337.11470 found: 337.11470.



5-Methyl-2, 3-di (thiophen-2-yl)imidazo[1,2-*a*]pyridine 1-oxide (3n)

Prepared according to the general procedure and the product was obtained as light yellow solid in 92% yield (72 mg), mp 166-169 °C;

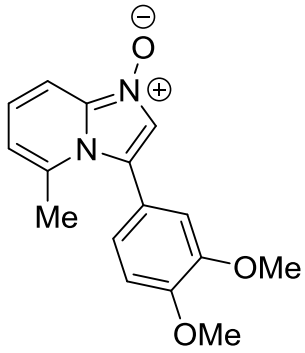
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.68 (dd, *J* = 5.3, 1.2 Hz, 1H), 7.38 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.22 (dd, *J* = 5.3, 3.5 Hz, 1H), 7.16 (dd, *J* = 9.0,

6.9 Hz, 1H), 7.11 (dd, *J* = 3.9, 1.0 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.56 (d, *J* = 6.8 Hz, 1H), 2.28 ppm(s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.85, 135.90, 134.89, 131.54, 130.97, 129.70, 128.55, 127.63, 127.41, 127.33, 126.25, 125.29, 116.28, 110.52, 106.36, 20.14 ppm.

FT-IR: $\tilde{\nu}$ = 3055, 2960, 1627, 1537, 1441, 1421, 1387, 1197, 1151, 1035 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{16}H_{13}N_2OS_2$: 313.04638 found: 313.04711.



3-(3,4-Dimethoxyphenyl)-5-methylimidazo[1,2-*a*]pyridine 1-oxide (3o)

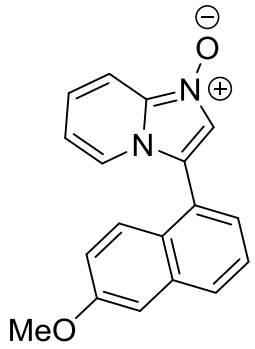
Prepared according to the general procedure and the product was obtained as light yellow solid in 74% yield (53 mg), mp 63-66 ^oC;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.1 Hz, 1H), 7.61 (s, 1H), 7.17 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.98 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.89 (m, 2H), 6.55 (d, *J* = 6.8 Hz, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 2.15 ppm (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.59, 148.25, 137.10, 135.59, 125.78, 125.21, 124.43, 121.35, 120.69, 115.51, 115.12, 110.60, 110.31, 56.22, 56.10, 21.10 ppm.

FT-IR: $\tilde{\nu}$ = 2954, 2931, 1640, 1582, 1461, 1250, 1233, 1130 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{16}H_{17}N_2O_3$: 285.12337 found: 285.12435.



3-(6-Methoxynaphthalen-1-yl)imidazo[1,2-*a*]pyridine 1-oxide (3p)

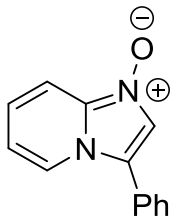
Prepared according to the general procedure and the product was obtained as light yellow solid in 87% yield (63 mg), mp 119-122 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.1 Hz, 1H), 7.91-7,84 (m, 3H), 7.82 – 7.73 (m, 2H), 7.48 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.25 – 7.13 (m, 3H), 6.84 (t, *J* = 6.8 Hz, 1H), 3.92 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.89, 134.92, 134.36, 129.71, 128.81, 128.34, 128.08, 126.00, 125.12, 123.20, 122.92, 121.05, 121.00, 120.28, 114.64, 112.89, 105.84, 55.51 ppm.

FT-IR: $\tilde{\nu}$ = 3042, 2929, 1628, 1607, 1416, 1394, 1113, 1035 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{18}H_{15}N_2O_2$: 291.11280 found: 291.11361.



3-Phenylimidazo[1,2-*a*]pyridine 1-oxide (3q)

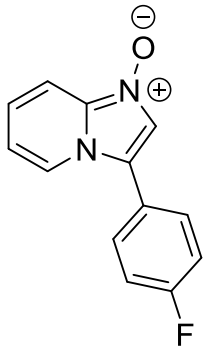
Prepared according to the general procedure and the products were formed in 2:1 regioisomeric ratio in 76% combined yield and the major product could be isolated as light yellow solid in 40% yield (21 mg) (mp 115-117 ^{o}C) in pure form which was fully characterized. The identity of the minor product in case of reaction with phenylacetylene has been confirmed by comparison of the NMR data of the corresponding deoxygenated product with the literature known data.;

^{1}H NMR (400 MHz, $CDCl_3$+ CD_3OD) δ 8.20 (d, *J* = 7.0 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.79 (s, 1H), 7.60 – 7.48 (m, 5H), 7.34 – 7.27 (m, 1H), 6.90 ppm (t, *J* = 7.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.67, 130.01, 129.80, 128.82, 126.06, 125.93, 123.25, 122.81, 121.12, 114.95, 112.93 ppm.

FT-IR: $\tilde{\nu}$ = 3052, 2954, 1641, 1474, 1416, 1327, 1147cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{13}H_{11}N_2O$: 211.08659 found: 211.08659.



3-(4-Fluorophenyl)imidazo[1,2-*a*]pyridine 1-oxide (3r)

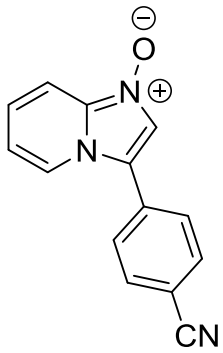
Prepared according to the general procedure and the products were formed in 4:1 regioisomeric ratio in 78% combined yield and the major product could be isolated as light yellow solid in 51% yield (29 mg) in pure form which was fully characterized, mp 117-121 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$+ CD_3OD) 8.18 (d, *J* = 7.1 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.78 (s, 1H), 7.60 – 7.50 (m, 2H), 7.42 (dd, *J* = 9.1, 6.9 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.00 (t, *J* = 6.9 Hz, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.61 (d, *J* = 251.7 Hz), 134.57, 131.06 (d, *J* = 8.6 Hz), 127.06, 123.22, 122.27, 121.68 (d, *J* = 3.5 Hz), 120.53, 117.04 (d, *J* = 22.1 Hz), 115.32, 112.34 ppm.

FT-IR: $\tilde{\nu}$ = 3037, 1719, 1495, 1413, 1335, 1225, 1088 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{13}H_{10}N_2OF$: 229.07717 found: 229.07791.



3-(4-Bromo)imidazo[1,2-*a*]pyridine 1-oxide (3s)

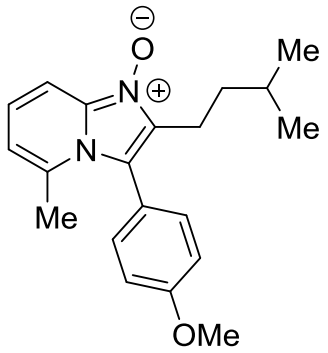
Prepared according to the general procedure using 2 equiv of alkyne and the products were formed in 3:1 regioisomeric ratio in 65% combined yield and the major product could be isolated as light yellow semi-solid in 43% yield (25 mg) in pure form which was fully characterized;

^{1}H NMR (500 MHz, DMSO) δ 8.49 (d, *J* = 7.0 Hz, 1H), 8.18 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 9.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 9.1, 6.7 Hz, 1H), 7.00 ppm(t, *J* = 6.8 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 133.90, 132.24, 130.26, 125.64, 125.30, 124.25, 122.81, 122.24, 118.79, 114.76, 111.87 ppm.

FT-IR: $\tilde{\nu}$ = 3090, 2935, 2229, 1684, 1495, 1395, 1173, 1123 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{14}H_{10}N_3O$: 236.08184 found: 236.08252.



2-Isopentyl-3-(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyridine 1-oxide (3t)

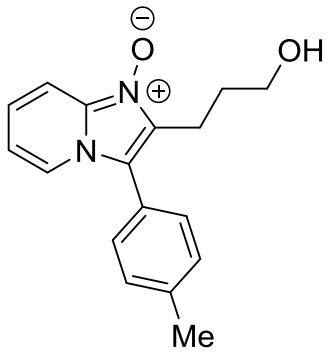
Prepared according to the general procedure and the product was obtained as light yellow solid in 83% yield (67 mg), mp 66-68 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 9.1 Hz, 1H), 7.33 – 7.22 (m, 2H), 7.07 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.98 – 6.81 (m, 2H), 6.45 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 2.69 – 2.56 (m, 2H), 2.03 (s, 3H), 1.51-1.46 (m, 3H), 0.76 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.71, 136.74, 136.33, 134.91, 133.73, 124.63, 121.26, 117.80, 114.96, 113.40, 110.08, 55.47, 36.91, 27.86, 22.30, 21.43, 20.61 ppm.

FT-IR: $\tilde{\nu}$ = 3056, 2949, 2866, 1638, 1580, 1505, 1310, 1247, 1142, 1033 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{20}H_{25}N_2O_2$: 325.19105 found: 325.19229.



2-(3-Hydroxypropyl)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridine 1-oxide (3u)

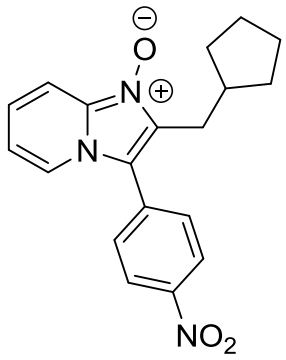
Prepared according to the general procedure and the product was obtained as light yellow solid in 53% yield (38 mg), mp 142-145 ^{o}C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.83 (t, *J* = 7 Hz, 1H), 3.69 – 3.57 (m, 2H), 3.11 – 2.96 (m, 2H), 2.46 (s, 3H), 1.95 – 1.77 ppm (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.34, 135.15, 133.56, 130.52, 129.94, 125.74, 123.07, 122.98, 118.06, 114.43, 112.23, 60.80, 32.91, 21.58, 19.17 ppm.

FT-IR: $\tilde{\nu}$ = 2920, 1738, 1543, 1391, 1108, 1056, 1011 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{17}H_{19}N_2O_2$: 383.14410 found: 283.14481.



2-(Cyclopentylmethyl)-3-(4-nitrophenyl)imidazo[1,2-*a*]pyridine 1-oxide (3v)

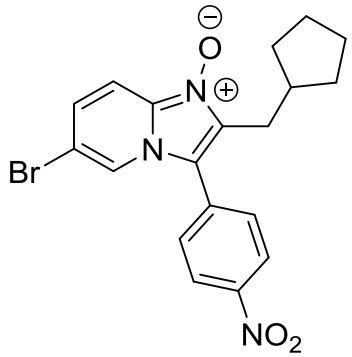
Prepared according to the general procedure and the product was obtained as light yellow solid in 82% yield (69 mg), mp 99-102 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.92 (dd, *J* = 9.2, 0.9 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.26 (m, 1H), 6.89 (td, *J* = 7, 1.1 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 2H), 2.49 – 2.40 (m, 1H), 1.66-1.59 (m , 2H), 1.50 (ddd, *J* = 7.9, 6.7, 5.1 Hz, 2H), 1.46 – 1.40 (m, 2H), 1.11 – 0.99 ppm (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.09, 136.52, 134.41, 133.56, 130.83, 125.70, 124.94, 122.37, 115.12, 115.00, 112.74, 38.42, 32.54, 28.23, 24.71 ppm.

FT-IR: $\tilde{\nu}$ = 3105, 2949, 2866, 1732, 1599, 1515, 1344, 1107 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{20}N_3O_3$: 338.14992 found: 338.15093.



6-Bromo-2-(cyclopentylmethyl)-3-(4-nitrophenyl)imidazo[1,2-*a*]pyridine 1-oxide (3w)

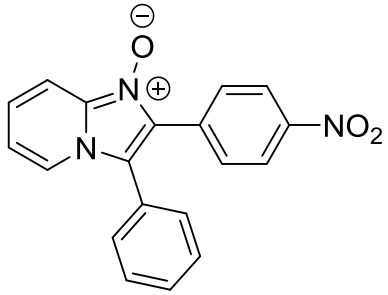
Prepared according to the general procedure and the product was obtained as light yellow solid in 76% yield (79 mg), mp 104-110 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.8 Hz, 2H), 8.01 (s, 1H), 7.81 (d, *J* = 9.6 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.24 (m, 1H), 2.90 (d, *J* = 7.5 Hz, 2H), 2.39 (dt, *J* = 15.5, 7.8 Hz, 1H), 1.60 (dt, *J* = 11.3, 6.5 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.41 (m, 2H), 1.01 ppm (m, Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.37, 137.07, 132.88, 131.89, 130.91, 128.59, 125.10, 122.11, 115.41, 113.44, 109.83, 38.29, 32.52, 28.23, 24.70 ppm.

FT-IR: $\tilde{\nu}$ = 3093, 2951, 2862, 1611, 1515, 1382, 1345, 1206, 1055 cm^{-1}.

HRMS: $[M+H]^+$ $C_{19}H_{19}{}^{79}BrN_3O_3$: 416.06043 found: 416.06132. HRMS: calc. for $[M+H]^+$ $C_{19}H_{19}{}^{81}BrN_3O_3$: 418.05838 found: 418.05834.



2-(4-Nitrophenyl)-3-phenylimidazo[1,2-*a*]pyridine 1-oxide (3x)

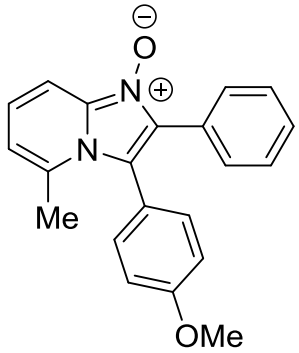
Prepared according to the general procedure and the product was obtained as light yellow solid in 84% yield (70 mg), mp 85-90 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 7.0 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.61 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.34 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.31 – 7.26 (m, 1H), 6.91 ppm (dd, *J* = 6.6, 1.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.87, 134.85, 134.21, 133.40, 131.09, 130.31, 129.69, 128.66, 125.97, 125.63, 124.85, 122.34, 115.52, 114.86, 113.31, ppm.

FT-IR: $\tilde{\nu}$ = 3025, 2929, 1597, 1514, 1443, 1383, 1345, 1104 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{14}N_3O_3$: 332.10297 found: 332.10432.



3-(4-Methoxyphenyl)-5-methyl-2-phenylimidazo[1,2-*a*]pyridine 1-oxide (3y)

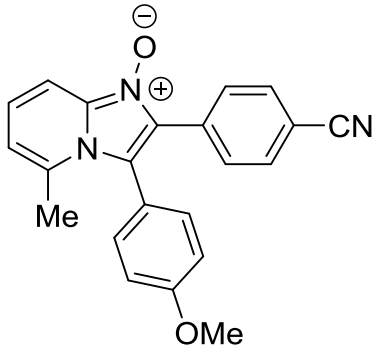
Prepared according to the general procedure and the product was obtained as light yellow solid in 85% yield (70 mg), mp 173-177 ^oC;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.1 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.22 (m, 3H), 7.11 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 2.05 ppm (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.65, 136.57, 135.25, 133.78, 130.14, 128.64, 127.96, 126.64, 125.10, 121.16, 118.38, 115.65, 113.45, 110.75, 55.36, 21.54 ppm.

FT-IR: $\tilde{\nu}$ = 2987, 2963, 1631, 1605, 1542, 1391, 1290, 1246, 1161, 1027 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{21}H_{19}N_2O_2$: 331.14410 found: 331.14496.



2-(4-Cyanophenyl)-3-(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyridine 1-oxide (3z)

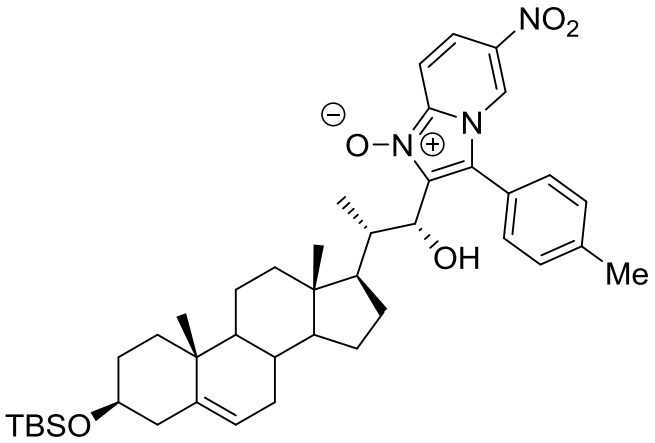
Prepared according to the general procedure and the product was obtained as light yellow solid in 85% yield (76 mg), mp 98-102 ^oC;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.16 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 2.08 ppm (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.16, 136.96, 135.80, 134.16, 131.79, 131.48, 130.52, 126.12, 124.69, 120.35, 119.30, 118.68, 116.33, 113.94, 112.15, 110.91, 55.51, 21.58 ppm.

FT-IR: $\tilde{\nu}$ = 3006, 2967, 2839, 1912, 1609, 1546, 1333, 1291, 1253, 1180, 1071 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{22}H_{18}N_3O_2$: 356.13935 found: 356.14013.



2-((1*R*,2*S*)-2-((8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-1-hydroxypropyl)-6-nitro-3-(p-tolyl)imidazo[1,2-*a*]pyridine 1-oxide (3aa)

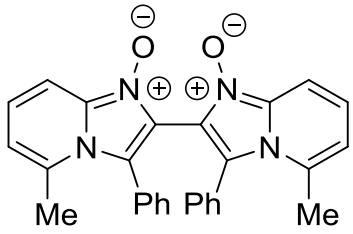
Prepared according to the general procedure using 2 equiv of nitroso compound with 1 equiv of alkyne (0.1 mmol scale) and the product was obtained as light yellow solid in 85% yield (61 mg), mp 228-231 ^oC;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 1.0 Hz, 1H), 7.93 (s, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 5.29 (dd, *J* = 2.9, 2.1 Hz, 1H), 4.90 (d, *J* = 4.9 Hz, 1H), 3.47 – 3.42 (m, 1H), 2.49 (s, 3H), 2.23 (dd, *J* = 17.8, 6.7 Hz, 1H), 2.17 – 2.10 (m, 2H), 1.91 (dt, *J* = 24.0, 8.6 Hz, 2H), 1.78 – 1.73 (m, 1H), 1.68 (d, *J* = 12.4 Hz, 1H), 1.54 – 1.47 (m, 1H), 1.41 (ddd, *J* = 14.5, 12.7, 6.9 Hz, 3H), 1.38 – 1.31 (m, 2H), 1.26 – 1.18 (m, 2H), 1.10 – 1.04 (m, 1H), 0.98 (dd, *J* = 11.6, 5.4 Hz, 5H), 0.94 (s, 3H), 0.87 (s, 8H), 0.69 (dd, *J* = 11.3, 4.1 Hz, 1H), 0.63 (s, 3H), 0.04 ppm (s, 6H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 141.89, 141.77, 138.92, 136.43, 133.01, 130.96, 130.79, 123.91, 121.17, 121.04, 120.58, 118.82, 112.24, 72.73, 72.06, 56.72, 53.26, 50.31, 45.56, 43.08, 42.89, 39.85, 37.48, 36.61, 32.15, 31.97, 31.83, 28.23, 26.04, 24.61, 21.67, 21.06, 19.49, 18.37, 15.10, 11.66, -4.48 ppm.

FT-IR: $\tilde{\nu}$ = 2928, 2855, 1525, 1509, 1515, 1460, 1332, 1249, 1195, 1078 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{42}H_{60}N_2O_5Si$: 714.42967 found: 714.43019.



5,5'-Dimethyl-3,3'-diphenyl-[2,2'-biimidazo[1,2-*a*]pyridine] 1,1'-dioxide (3ab)

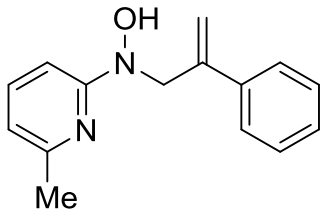
Prepared according to the general procedure using 1 equiv alkyne, 2 equiv 6-methyl-2-nitrosopyridine and the products were formed in 73% combined yield and the major product could be isolated as light yellow solid in 65 % yield (72.00 mg), mp 72-76 ^oC;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.58 – 7.49 (m, 4H), 7.33 – 7.23 (m, 8H), 6.74 (d, *J* = 6.9 Hz, 2H), 2.09 ppm (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.69, 137.33, 135.68, 130.11, 128.98, 128.78, 126.99, 125.58, 117.79, 111.77, 104.13, 18.90 ppm.

FT-IR: $\tilde{\nu}$ = 3063, 2926, 2915, 1634, 1546, 1444, 1406, 1209, 1114 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{28}H_{23}N_4O_2$: 447.18155 found: 447.18190.



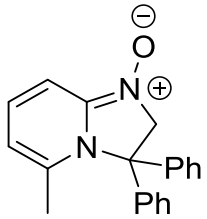
N-(6-methylpyridin-2-yl)-N-(2-phenylallyl)hydroxylamine (4a)

To a screw cap reaction vial 6-methyl-2-nitrosopyridine (0.25 mmol, 1 equiv), α-methyl-styrene (0.5 mmol, 2 equiv), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 1.0 mL) were added under air. The reaction mixture was stirred vigorously at RT for 3 h. The crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using ethylacetate/petroleum ether as an eluent system. The product was obtained as light yellow liquid in 93% yield (53 mg);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.34-7.26 (m, 3H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 7.2 Hz, 1H), 5.55 (s, 1H), 5.37 (s, 1H), 4.67 (s, 2H), 2.45 ppm (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.52, 155.98, 143.65, 139.38, 138.13, 128.41, 127.84, 126.45, 115.45, 115.40, 106.18, 59.12, 24.25 ppm.

FT-IR: $\tilde{\nu}$ = 3058, 2925, 2854, 1632, 1589, 1449, 1333, 1263, 1195, 1029 cm^{-1}.



5-Methyl-3,3-diphenyl-2,3-dihydroimidazo[1,2-a]pyridine 1-oxide (4b)

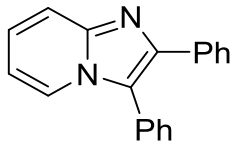
To a screw cap reaction vial 6-methyl-2-nitrosopyridine (0.25 mmol, 1 equiv), alpha-phenyl-styrene (0.5 mmol, 2 equiv), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 1.0 mL) were added under air. The reaction mixture was stirred vigorously at RT for 12 h. The crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system. The product was obtained as light yellow solid in 85% yield (61 mg), mp 133-136 ^{o}C;

1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 6H), 7.27 – 7.23 (m, 4H), 6.61 (d, J = 6.4 Hz, 2H), 5.77 – 5.69 (m, 1H), 4.65 (s, 2H), 2.14ppm (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.39, 147.04, 140.63, 132.52, 129.25, 129.14, 127.53, 109.00, 107.75, 73.45, 70.00, 21.97 ppm.

FT-IR: $\tilde{\nu}$ = 3059, 2955, 1655, 1538, 1493, 1446, 1356, 1130, 1081 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{17}N_2O$: 289.13354 found: 289.13333.



2,3-Diphenylimidazo[1,2-a]pyridine (5a)

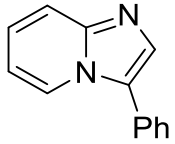
To a screw cap reaction vial 2,3-diphenylimidazo[1,2-a]pyridine 1-oxide (**2a**, 0.25 mmol) and acetonitrile (2.0 mL) were added under air. The reaction mixture was stirred vigorously at 125-130 ^{o}C for 3 h. After completion the crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system. The product was obtained as brown solid in 95% yield (64 mg), mp 138-141 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.8, 1.0 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.62-7.57 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.42 (m, 1H), 7.41 – 7.37 (m, 2H), 7.24 – 7.19 (m, 3H), 7.18 – 7.14 (m, 1H), 6.70 ppm (dd, *J* = 6.8, 1.0 Hz, 1H);

^{13}C NMR (126 MHz, CDC_3) δ 144.60, 133.73, 130.90, 129.75, 129.19, 128.47, 128.26, 127.82, 125.32, 123.49, 121.24, 117.50, 112.76 ppm.

FT-IR: $\tilde{\nu}$ = 3058, 2925, 1666, 1600, 1505, 1442, 1344, 1212, 1027 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{15}N_2$: 271.12298 found: 271.12367.



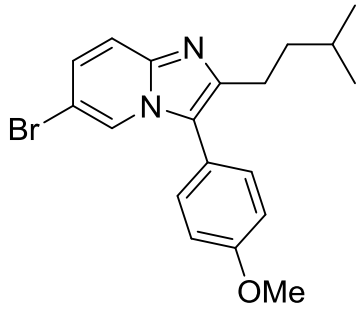
3-Phenylimidazo[1,2-*a*]pyridine (5b)

To a screw cap sealed reaction tube 3-phenylimidazo[1,2-*a*]pyridine 1-oxide (**3q**, 0.25 mmol) and acetonitrile (2.0 mL) were added under air. The reaction mixture was stirred vigorously at 140 ^oC for 12 h. After completion the crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system. The product was obtained as brown oil in 86% yield (42 mg);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.31 (m, 1H), 7.72-7.70 (m, 2H), 7.58 – 7.54 (m, 2H), 7.54 – 7.50 (m, 2H), 7.45 – 7.40 (m, 1H), 7.23 (s, 1H), 6.83 ppm (dd, *J* = 6.8, 1.0 Hz, 1H); ^{13}C **NMR (126 MHz, $CDCl_3$)** δ 146.01, 132.11, 129.42, 129.26, 128.46, 128.26, 124.72, 123.55, 118.26, 112.89 ppm;

FT-IR: $\tilde{\nu}$ = 3055, 2936, 2851, 1643, 1499, 1353, 1297, 1148, 1010 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{13}H_{11}N_2O$: 195.09167 found: 195.0912.



6-Bromo-2-isopentyl-3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (5c)

To a screw cap sealed reaction tube 6-bromo-2-isopentyl-3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine 1-oxide (0.15 mmol) and propionitrile (2.0 mL) were added under air. The reaction mixture was stirred vigorously at 150 ^oC for 12 h. After completion the crude reaction mixture

was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system. The product was obtained as black amorphous solid in 65% yield (62 mg);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.0 Hz, 1H), 7.56 (d, *J* = 9.4 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.24 (dd, *J* = 9.4, 1.6 Hz, 1H), 7.11 – 7.06 (m, 2H), 3.90 (s, 3H), 2.78 – 2.69 (m, 2H), 1.69 – 1.61 (m, 2H), 1.56 (td, *J* = 13.2, 6.6 Hz, 1H), 0.87 ppm (d, *J* = 6.5 Hz, 6H);

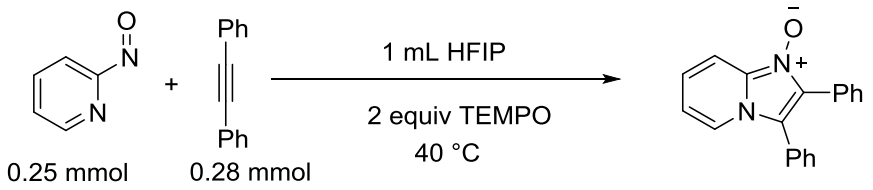
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.03, 142.10, 131.20, 127.88, 124.56, 123.25, 120.11, 117.28, 114.88, 107.12, 55.38, 38.82, 27.92, 25.34, 22.33;

FT-IR: $\tilde{\nu}$ = 3060, 2966, 1656, 1538, 1493, 1446, 1355, 1278, 1130 cm^{-1}.

HRMS: calc. for $[M+H]^+$ $C_{19}H_{22}{}^{79}BrN_2O$: 373.09100 found: 373.09266. HRMS: calc. for $[M+H]^+$ $C_{19}H_{22}{}^{81}BrN_2O$: 375.08896 found: 375.08997.

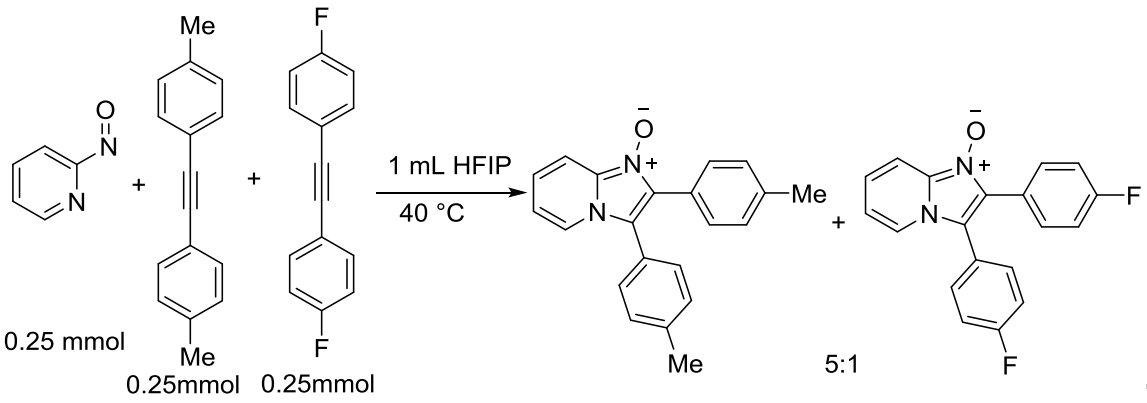
Reaction Mechanism Studies:

(1) Radical trapping

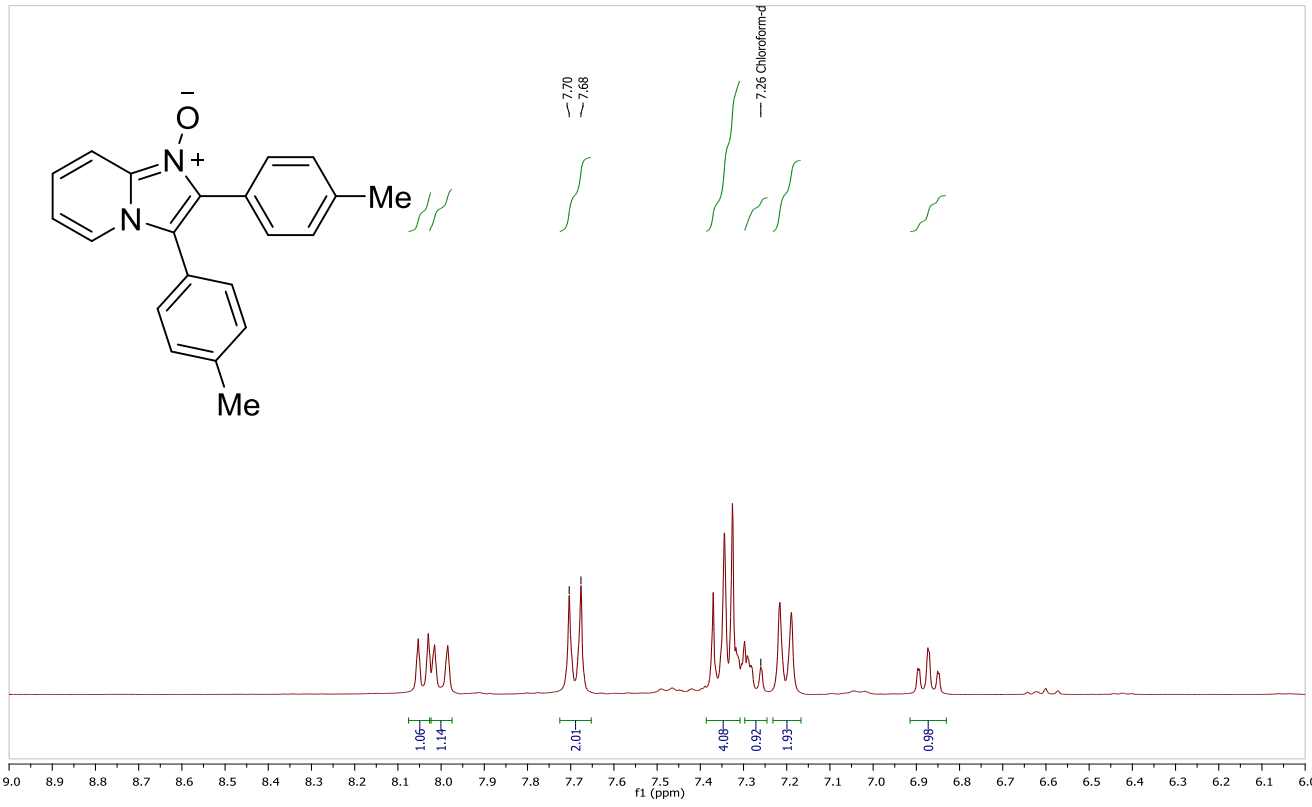


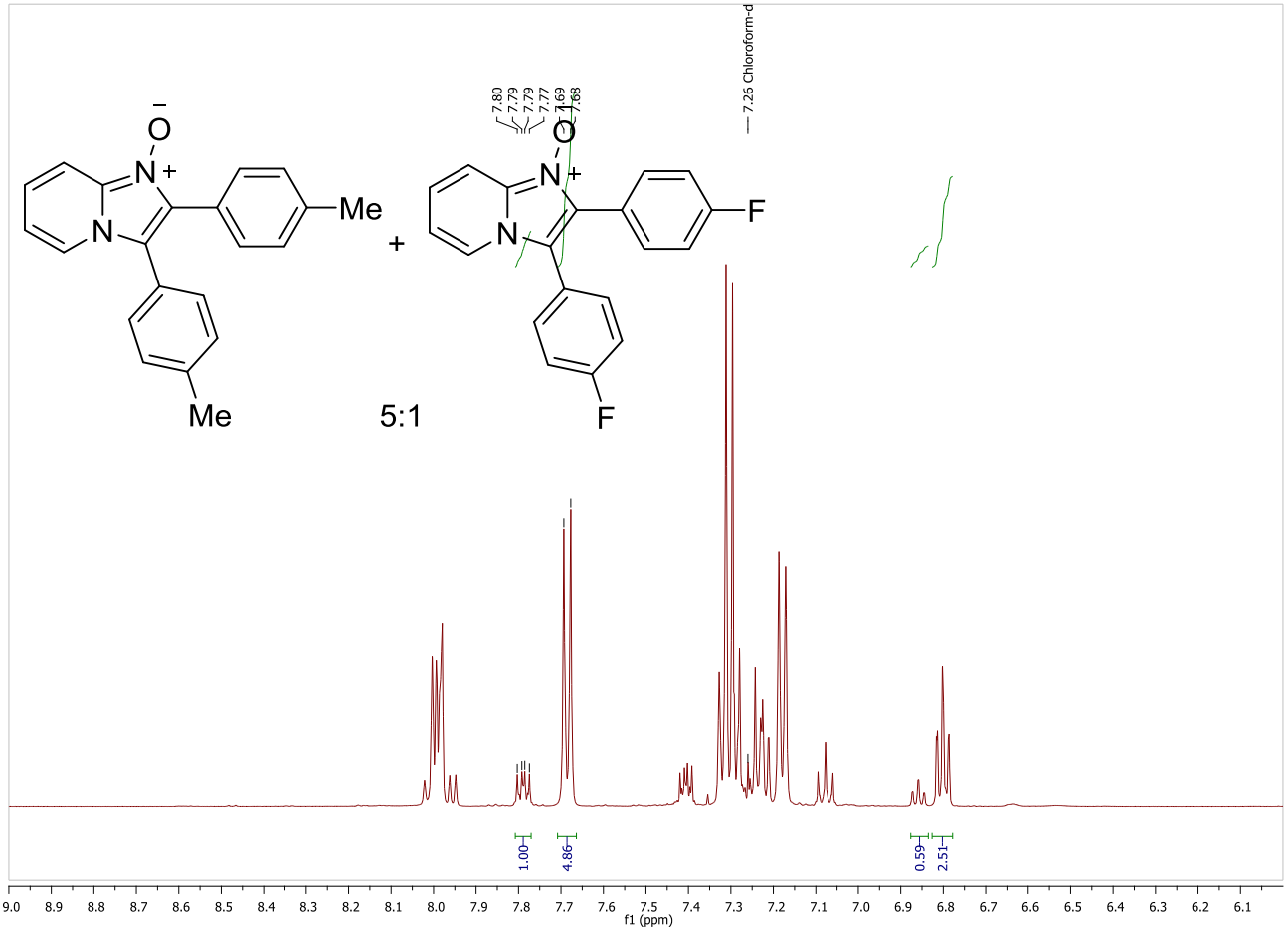
To a screw cap reaction vial 2-nitrosopyridine (0.25 mmol, 1 equiv), diphenylacetylene (0.28 mmol, 1.1 equiv), TEMPO (2 equiv) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP1.0 mL) were added. The reaction mixture was heated to 40 ^{o}C for 12 h. The crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system and isolated yield was 40%.

(2) Competition study

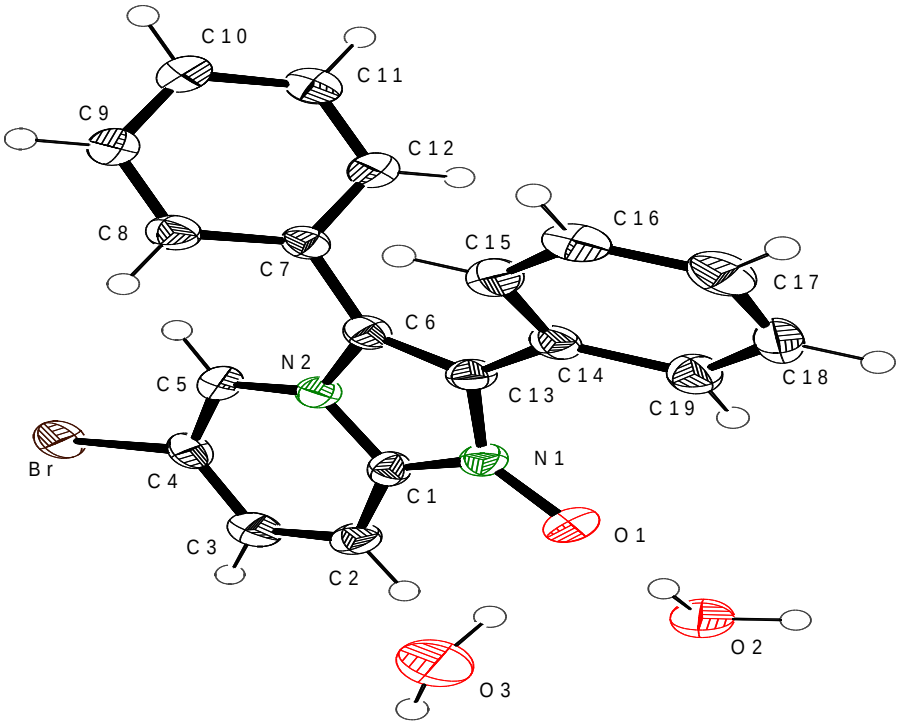


To a screw cap reaction vial, 2-aminosopyridine derivatives (0.25 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.24 mmol, 1.0 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.24 mmol, 1.0 equiv),, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP1.0 mL) were added. The reaction mixture was heated to 40 ^{o}C for 6 h. The crude reaction mixture was concentrated under reduced pressure and subsequently purified by flash column chromatography over silica gel using dichloromethane/methanol as an eluent system. The ratio of the product was checked by ^{1}H NMR analysis and it was 5:1.


7.70
7.68
7.26 Chloroform-d
Me
Me
1.06
1.14
2.01
4.08
0.92
1.93
0.98
f1 (ppm)


7.80
7.79
7.79
7.79
7.77
7.69
7.68
7.26 Chloroform-d
Me
Me
5:1
F
F
1.00
4.86
0.59
2.51
f1 (ppm)

Crystallographic data for the compound 3h:



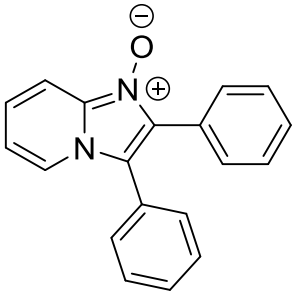
Crystal structure of the N-oxide product. ORTEP of (**3h**) Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 1018375.

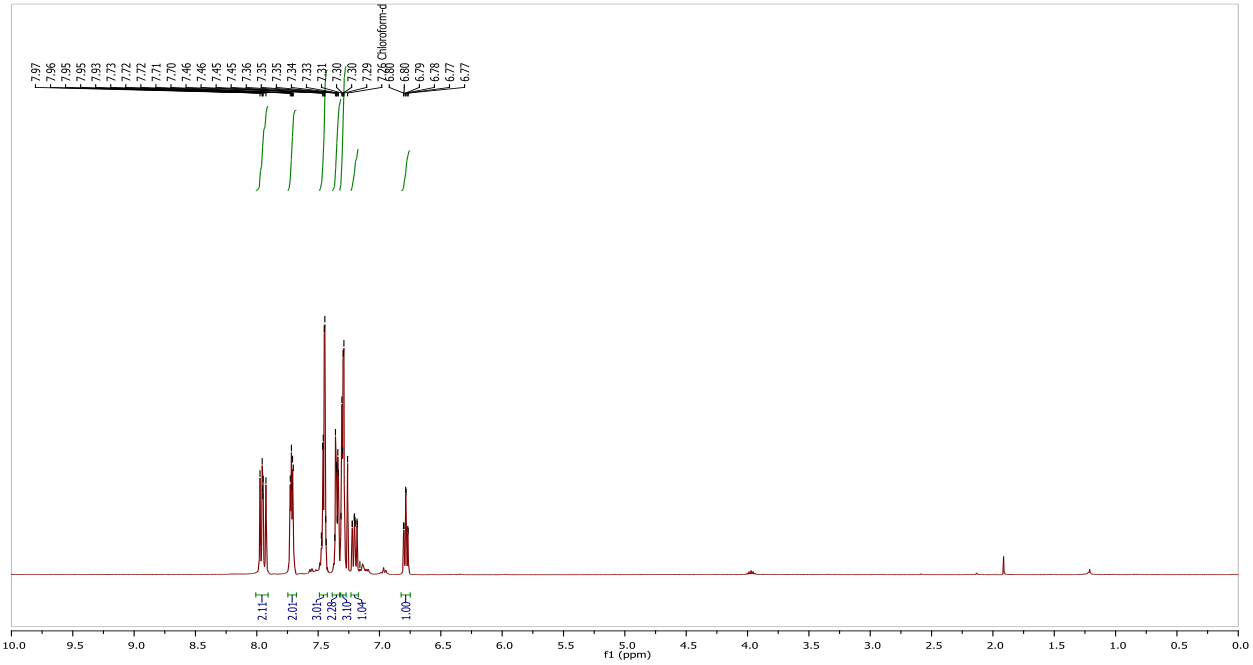
Table 1. Crystal data and structure refinement for **3g**.

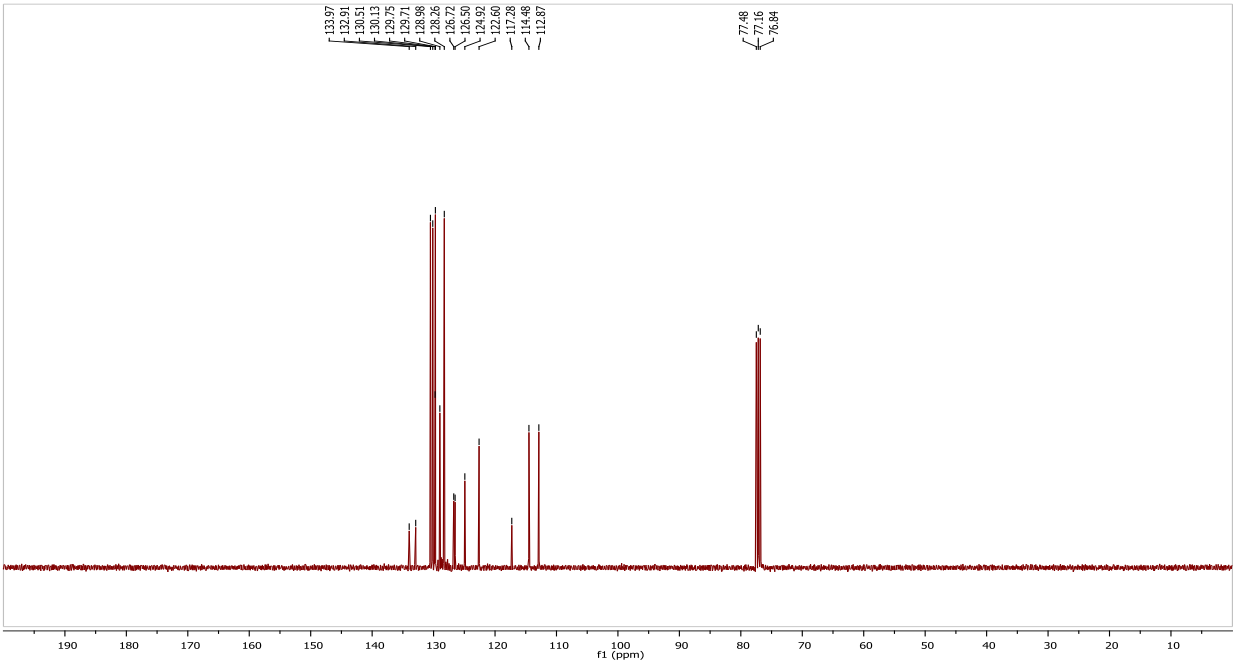
Identification code	CCDC 1018375	
Empirical formula	C_{19} H_{17} Br N_2 O_3	
Formula weight	401.25	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.6130(4) Å	a= 90°.
	b = 16.0480(14) Å	b= 90°.
	c = 18.9931(15) Å	g = 90°.
Volume	1710.8(2) $Å^3$	

Z	4
Density (calculated)	1.558 Mg/m^3
Absorption coefficient	2.424 mm^{-1}
F(000)	816
Crystal size	0.401 x 0.043 x 0.023 mm^3
Theta range for data collection	2.492 to 25.997°.
Index ranges	-6<=h<=6, -19<=k<=19, -23<=l<=23
Reflections collected	54577
Independent reflections	3355 [R(int) = 0.1113]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3355 / 4 / 242
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0688
R indices (all data)	R1 = 0.0542, wR2 = 0.0753
Absolute structure parameter	-0.026(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.336 and -0.235 $e.Å^{-3}$

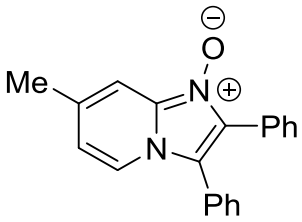
(3a)



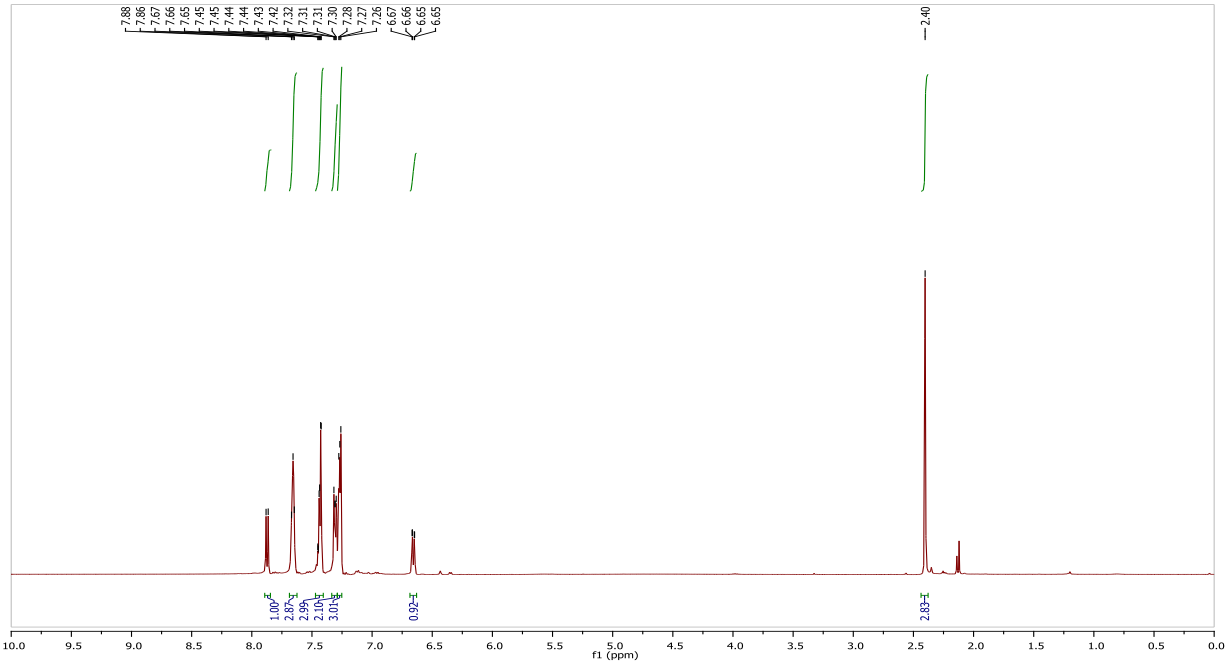

7.97
7.96
7.95
7.95
7.93
7.73
7.72
7.72
7.71
7.70
7.46
7.46
7.45
7.45
7.36
7.35
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.26 Chloroform-d
6.80
6.79
6.78
6.77
6.77
2.11
2.01
3.01
2.28
3.10
1.04
1.00
f1 (ppm)

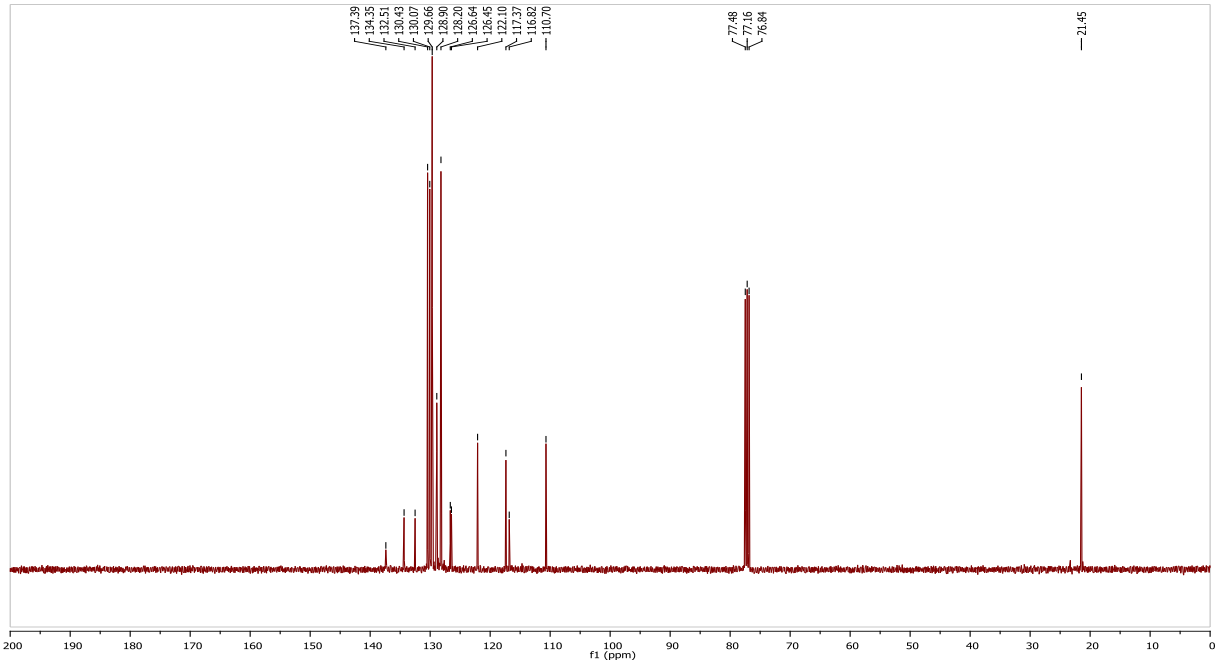

133.97
132.91
130.51
130.13
129.75
129.71
128.98
128.26
126.72
126.50
124.92
122.60
117.28
114.48
112.87
77.48
77.16
76.84
f1 (ppm)

(3b)

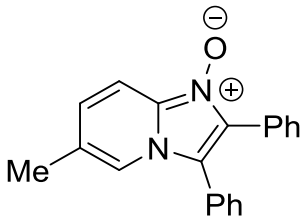

Me
O
N
Ph
N
Ph

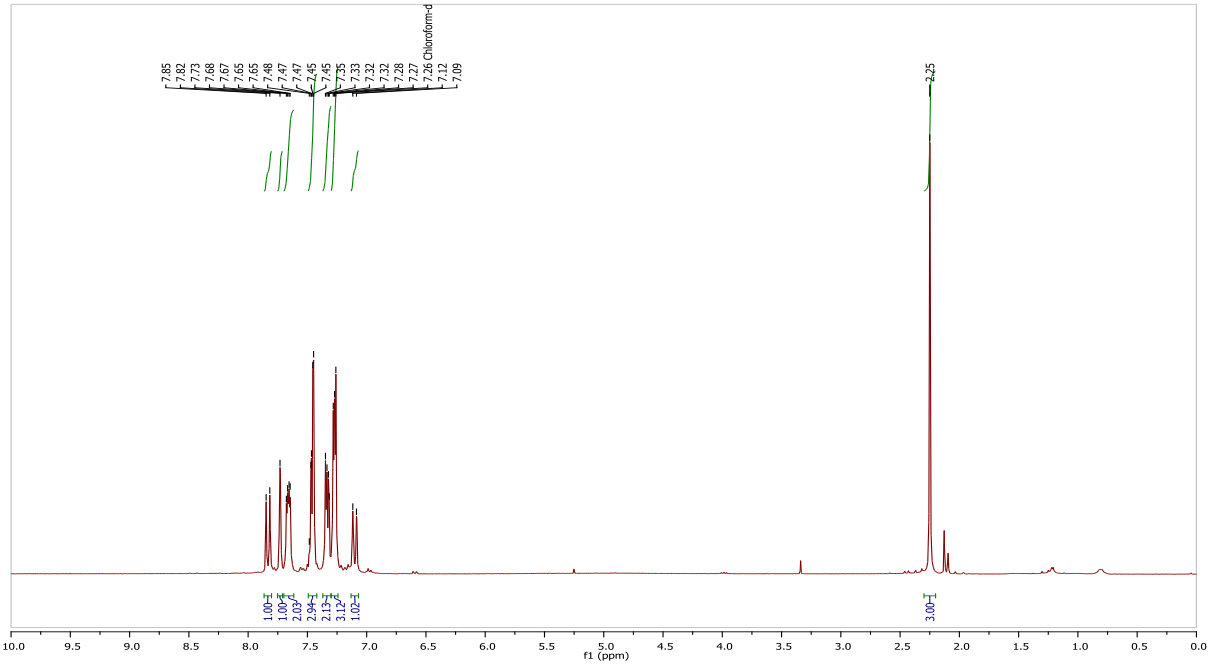
(3


7.88
7.86
7.67
7.66
7.65
7.45
7.45
7.44
7.44
7.43
7.42
7.32
7.31
7.31
7.30
7.28
7.27
7.26
6.67
6.66
6.65
6.65
2.40
1.00
2.87
2.99
2.10
3.01
0.92
2.83
f1 (ppm)


137.39
134.35
132.51
130.43
130.07
129.66
128.90
128.20
126.64
126.45
122.10
117.37
116.82
110.70
77.48
77.16
76.84
21.45
f1 (ppm)

(3c)


O
N
Ph
N
Me
Ph


7.85
7.82
7.73
7.68
7.67
7.65
7.48
7.47
7.47
7.45
7.45
7.35
7.33
7.32
7.32
7.28
7.27
7.26 Chloroform-d
7.12
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1.00
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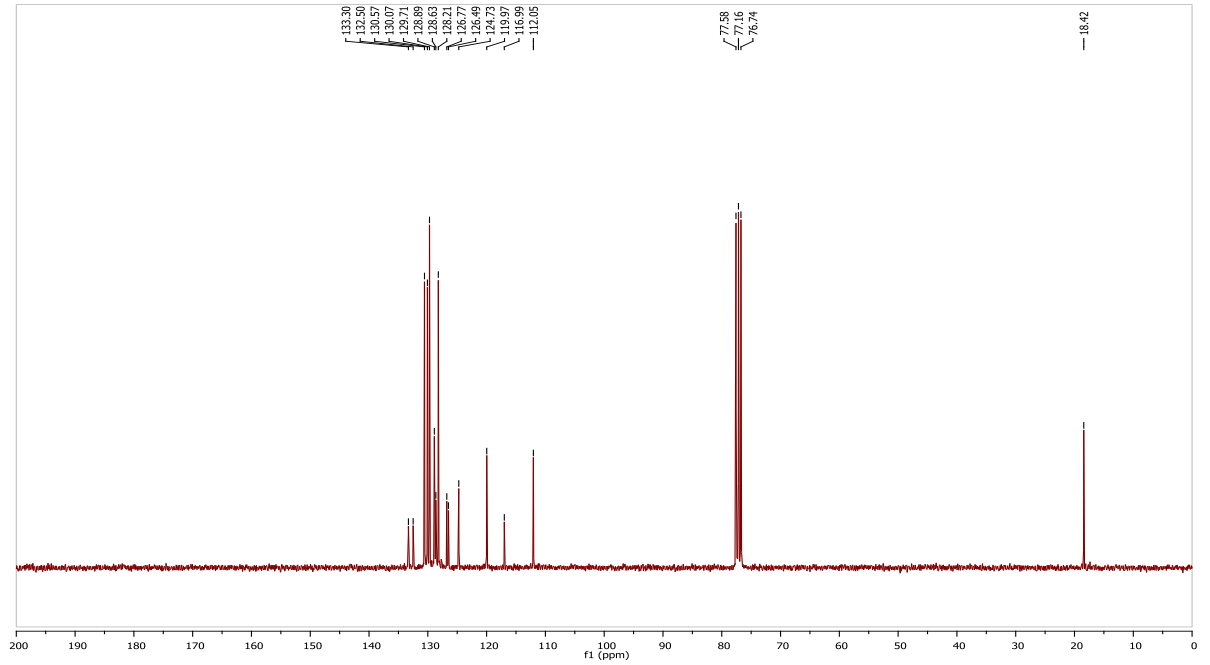
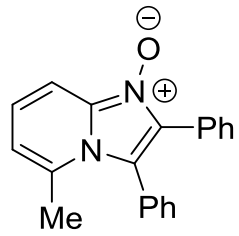
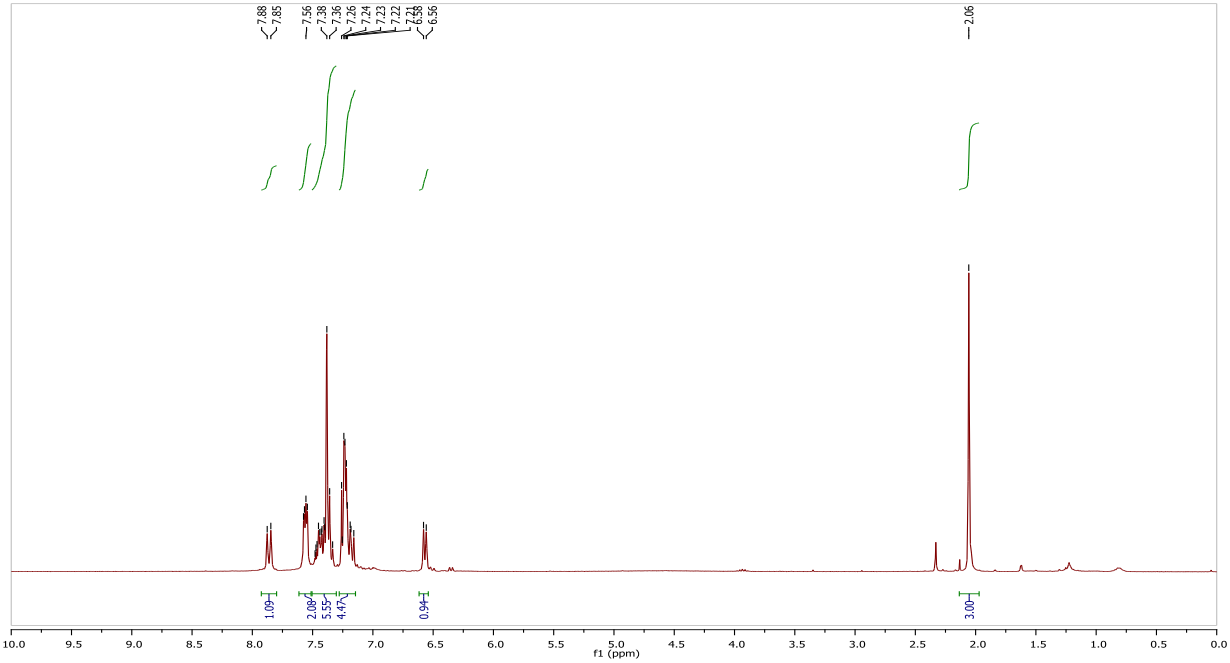
2.03
2.94
2.13
3.12
1.02
3.00
f1 (ppm)


133.30
132.50
130.57
130.07
129.71
128.89
128.63
128.21
126.77
126.49
124.73
119.97
116.99
112.05
77.58
77.16
76.74
18.42
f1 (ppm)

(3d)


O
N
Ph
N
Me
Ph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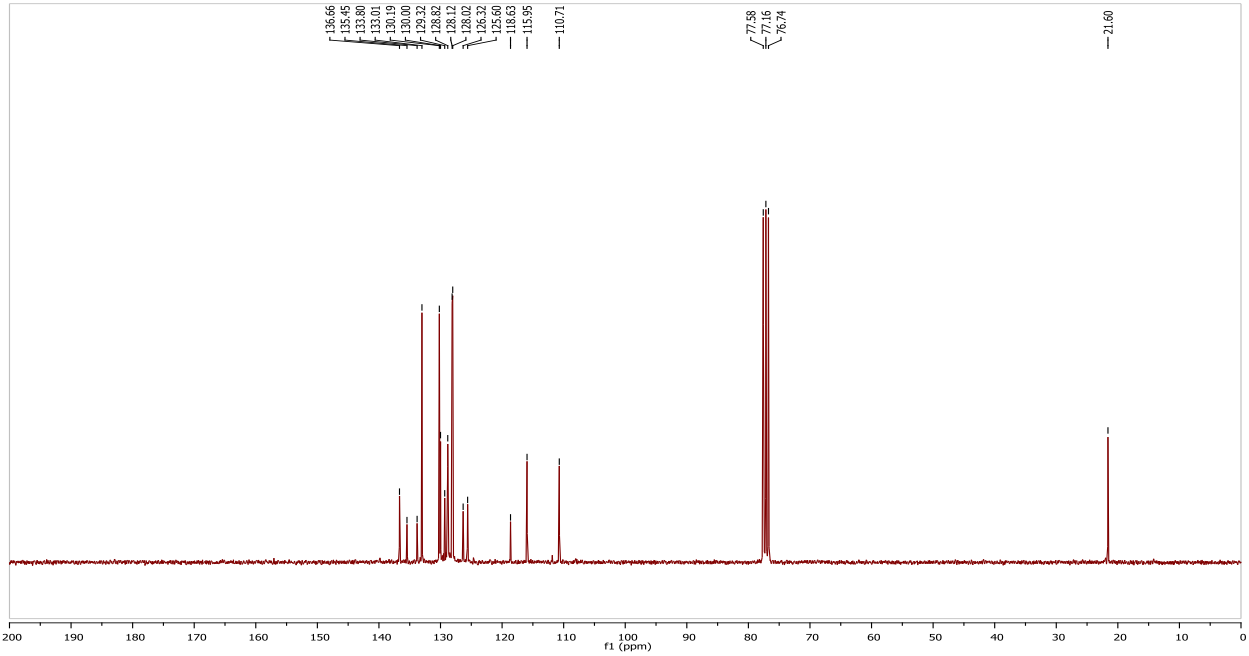
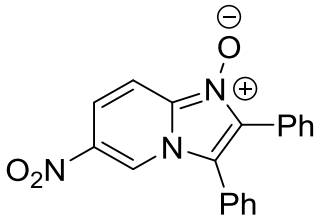
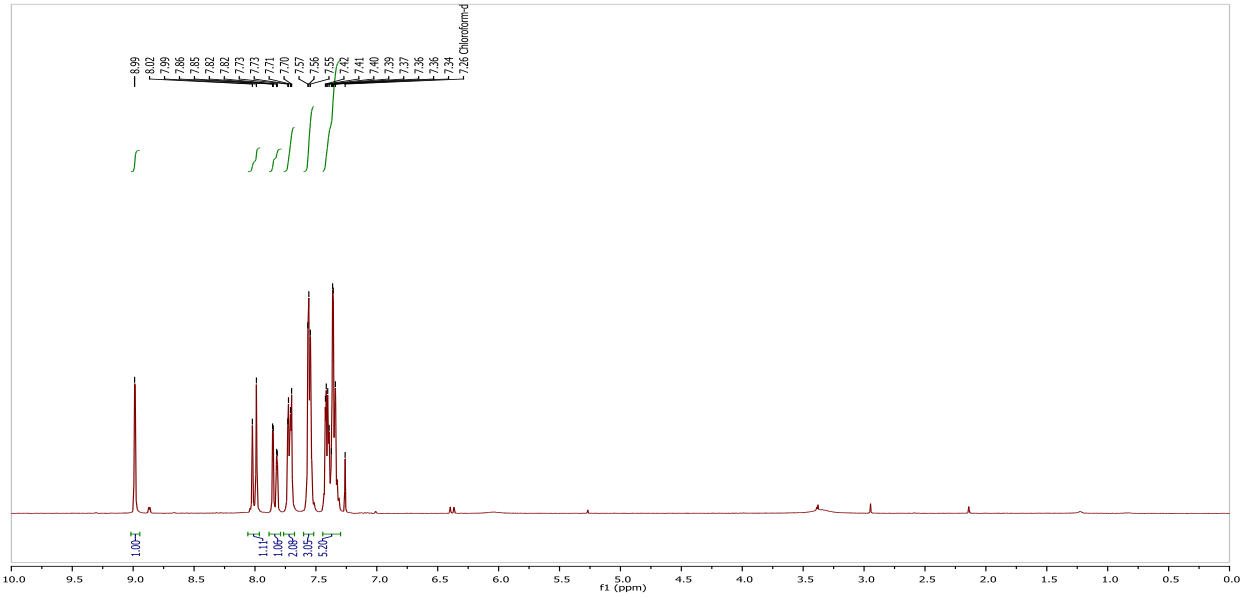
7.85
7.56
7.38
7.36
7.26
7.24
7.23
7.22
6.58
6.56
2.06
1.09
2.08
5.55
4.47
0.94
3.00
f1 (ppm)


136.66
135.45
133.80
133.01
130.19
130.00
129.32
128.82
128.12
128.02
126.32
125.60
118.63
115.95
110.71
77.58
77.16
76.74
21.60
f1 (ppm)

(3e)


O
N
Ph
N
O2N
Ph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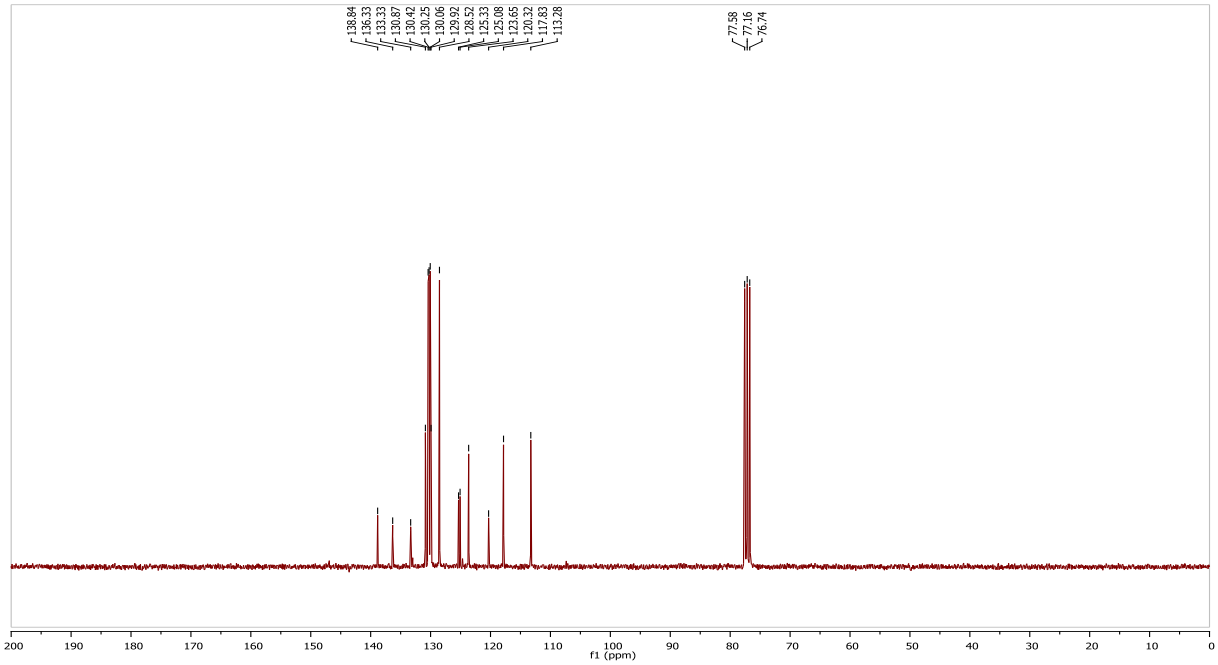
8.02
7.99
7.86
7.85
7.82
7.82
7.73
7.73
7.71
7.70
7.57
7.56
7.55
7.42
7.41
7.40
7.39
7.37
7.36
7.36
7.34
7.26 Chloroform-d
1.00
1.11
1.09
2.08
3.05
5.20
f1 (ppm)


138.84
136.33
133.33
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130.42
130.25
130.06
129.92
128.52
125.33
125.08
123.65
120.32
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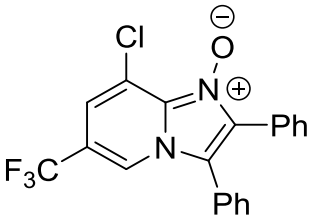
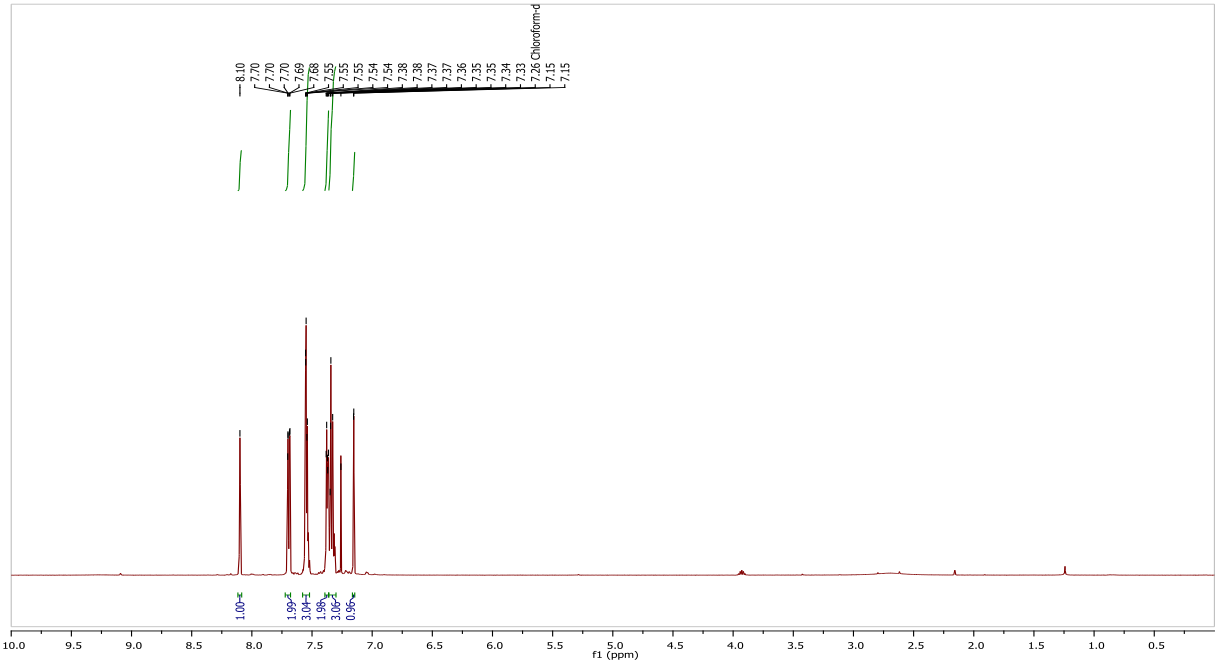
113.28
77.58
77.16
76.74
f1 (ppm)

(3f)


Cl
O
N
Ph
N
F3C
Ph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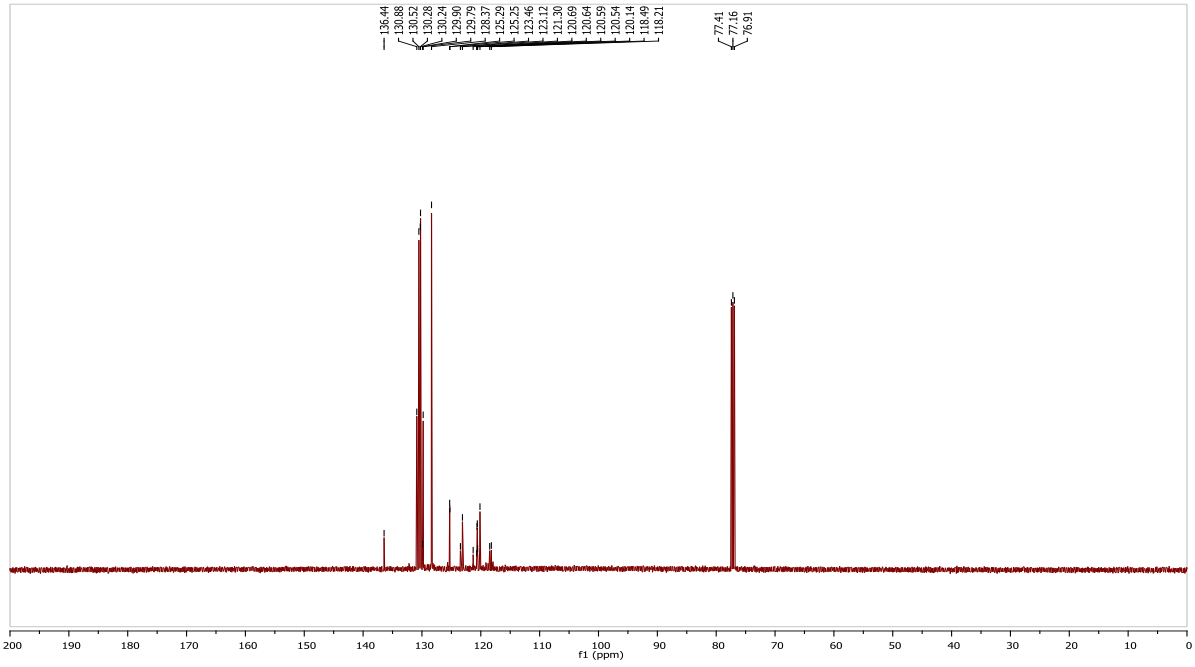
7.70
7.70
7.69
7.68
7.55
7.55
7.55
7.54
7.54
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.26 Chloroform-d
7.15
7.15
1.00
1.99
3.04
1.98
3.06
0.96
f1 (ppm)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130.88
130.52
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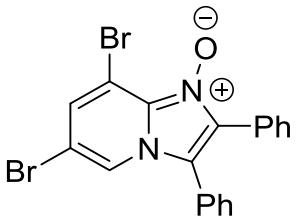
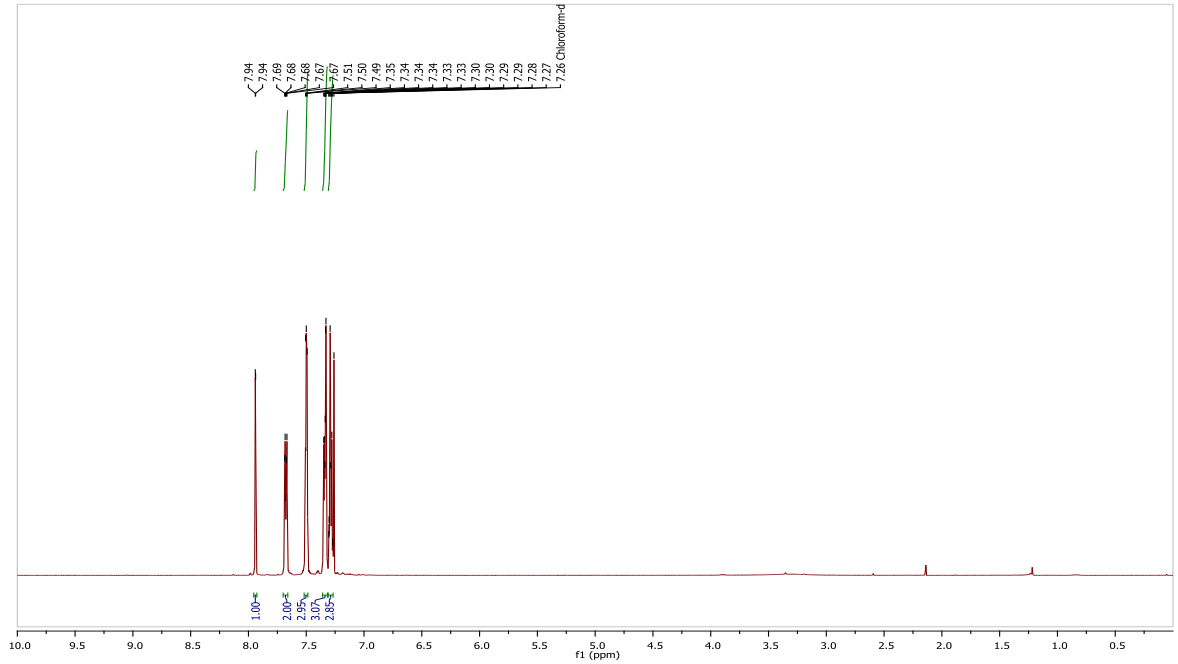
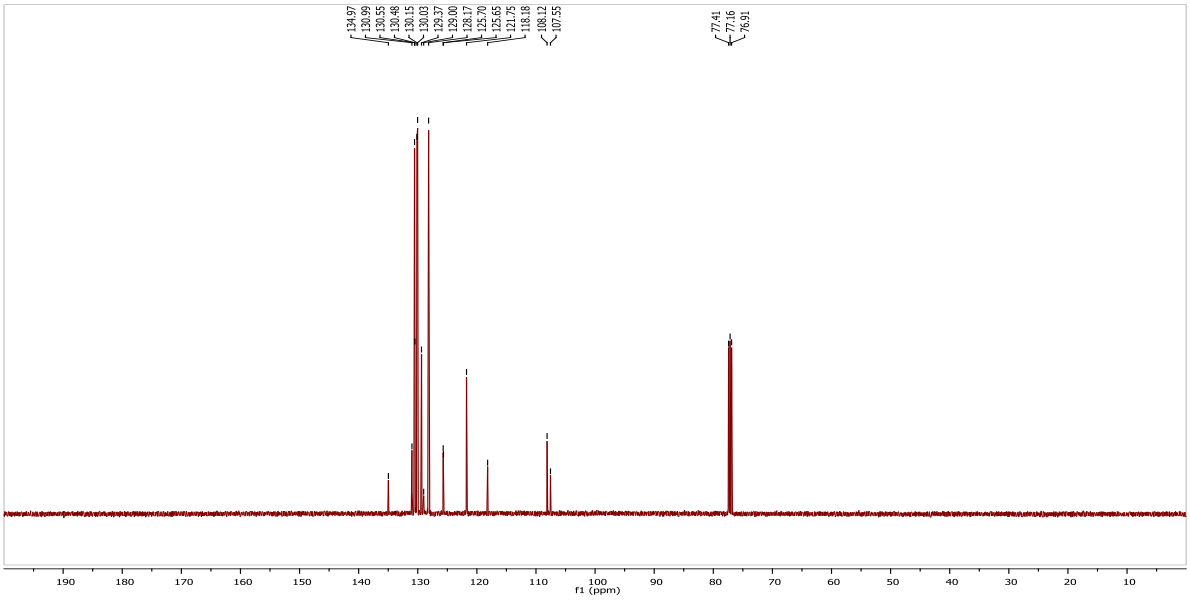
130.24
129.90
129.79
128.37
125.29
125.25
123.46
123.12
121.30
120.69
120.64
120.59
120.54
120.14
118.49
118.21
77.41
77.16
76.91
f1 (ppm)

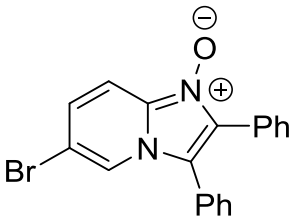
(3g)

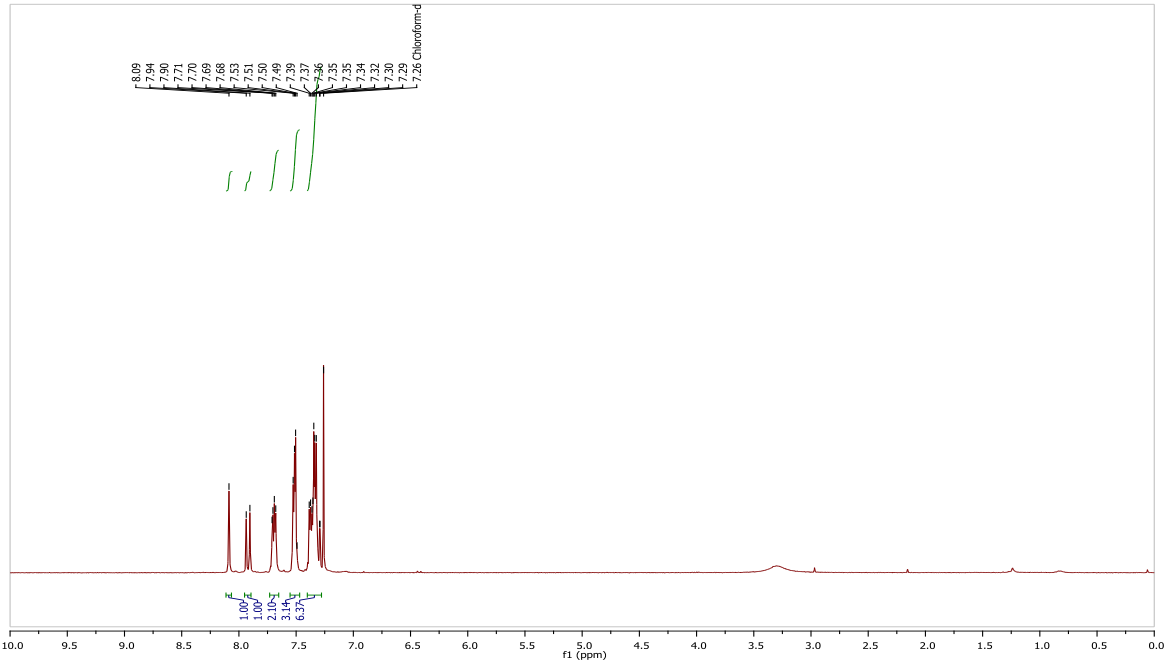

Br
O
N
Ph
N
Br
Ph


7.94
7.94
7.69
7.68
7.68
7.67
7.67
7.51
7.50
7.49
7.35
7.34
7.34
7.34
7.33
7.33
7.30
7.30
7.29
7.29
7.28
7.27
7.26 Chloroform-d
1.00
2.00
2.55
3.07
2.85
f1 (ppm)


134.97
130.99
130.55
130.48
130.15
130.03
129.37
129.00
128.17
125.70
125.65
121.75
118.18
108.12
107.55
77.41
77.16
76.91
f1 (ppm)

(3h)


O
N
Ph
N
Br
Ph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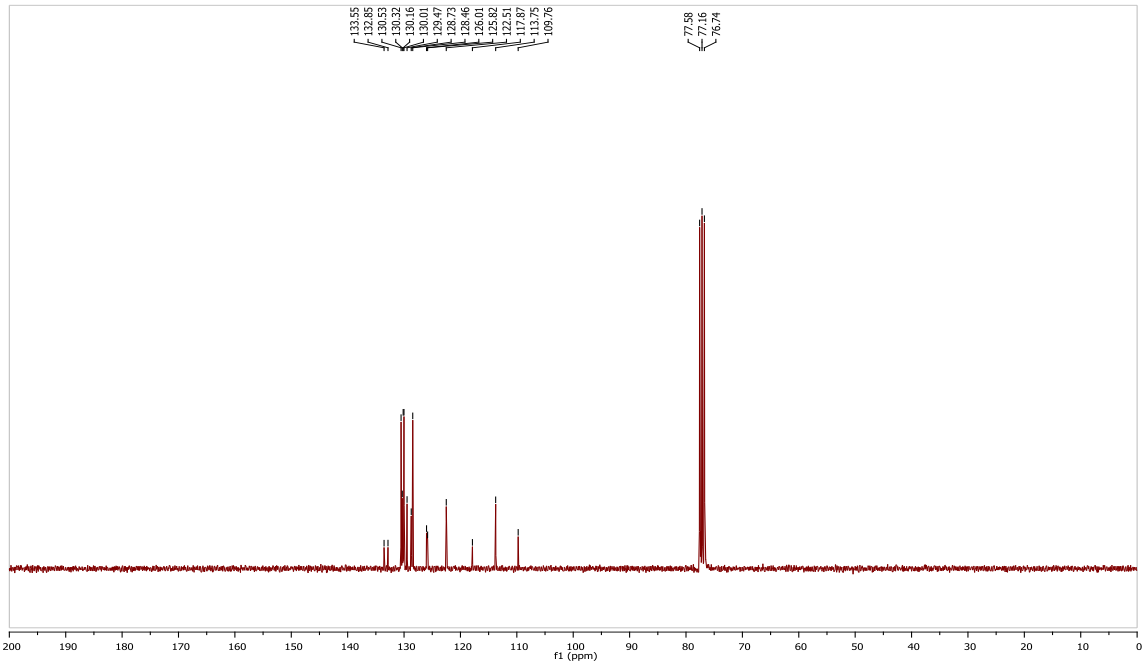
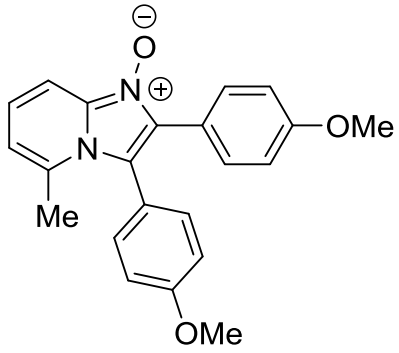
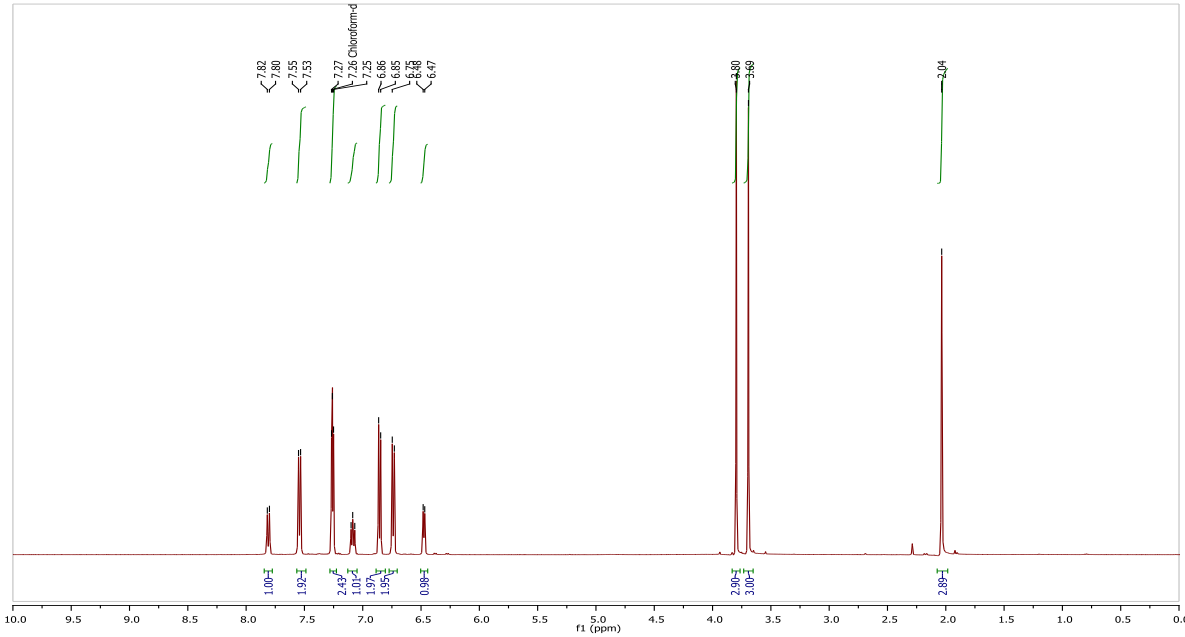
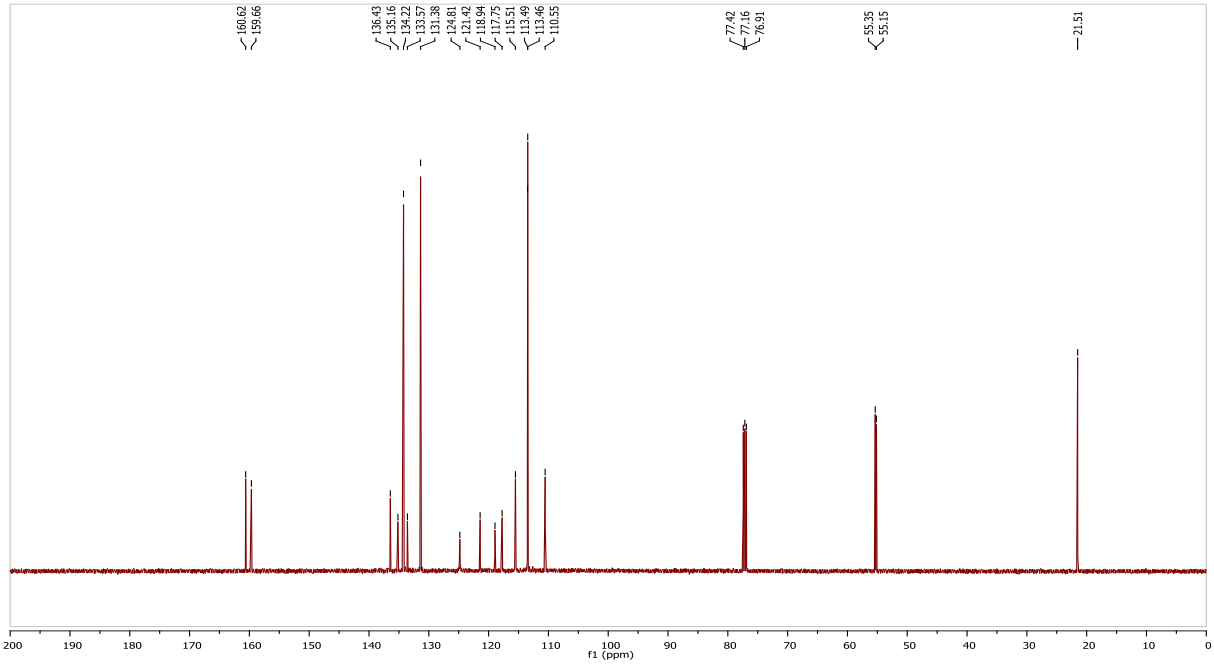
7.94
7.90
7.71
7.70
7.69
7.68
7.53
7.51
7.50
7.49
7.39
7.37
7.36
7.35
7.35
7.34
7.32
7.30
7.29
7.26 Chloroform-d
1.00
1.00
2.10
3.14
6.37
f1 (ppm)


133.55
132.85
130.53
130.32
130.16
130.01
129.47
128.73
128.46
126.01
125.82
122.51
117.87
113.75
109.76
77.58
77.16
76.74
f1 (ppm)

(3i)


O
N
N
OMe
Me
OMe


7.82
7.80
7.55
7.53
7.27
7.26 Chloroform-d
7.25
6.86
6.85
6.48
6.47
3.80
3.69
2.04
1.00
1.92
2.49
1.07
1.97
1.95
0.98
2.90
3.00
2.89
f1 (ppm)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159.66
136.43
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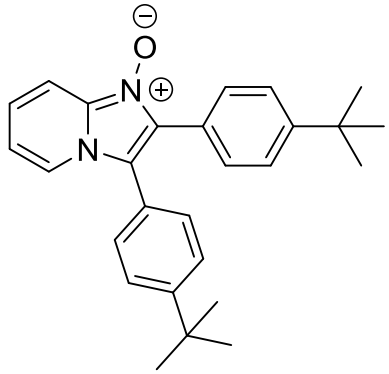
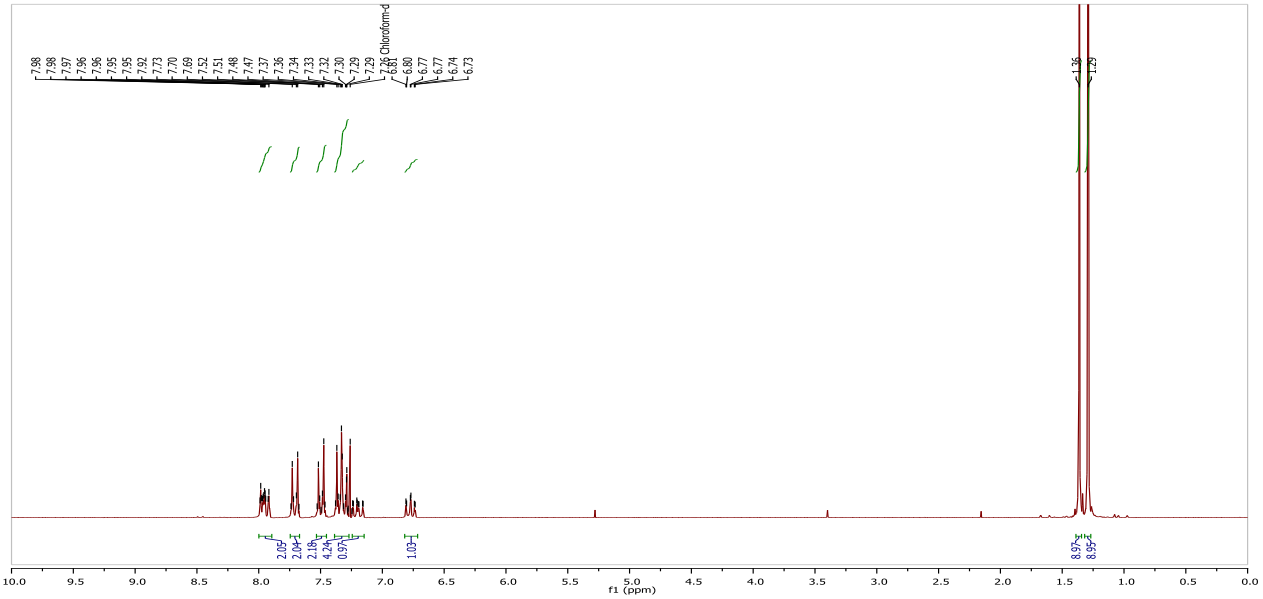
134.22
133.57
131.38
124.81
121.42
118.94
117.75
115.51
113.49
113.46
110.55
77.42
77.16
76.91
55.35
55.15
21.51
f1 (ppm)

(3j)

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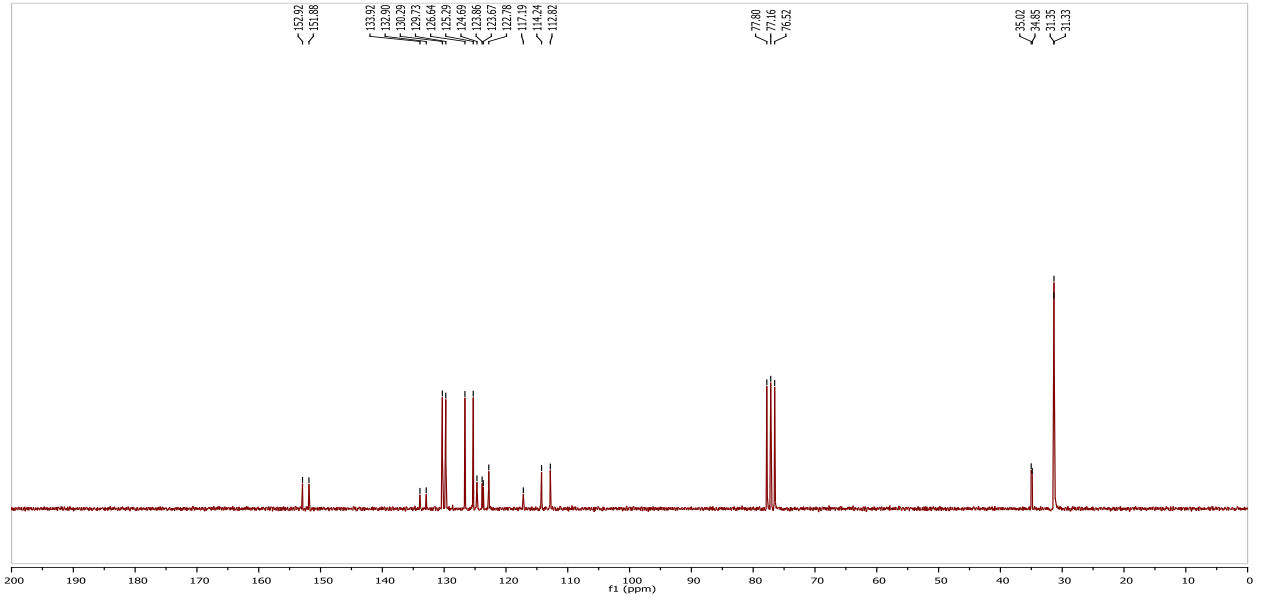
7.98
7.97
7.96
7.96
7.95
7.95
7.92
7.73
7.70
7.69
7.52
7.51
7.48
7.47
7.37
7.36
7.34
7.33
7.32
7.30
7.29
7.28 Chloroform-d
6.81
6.80
6.77
6.77
6.74
6.73
1.36
1.29
2.00
2.04
2.16
4.24
0.91
1.03
8.97
8.95
f1 (ppm)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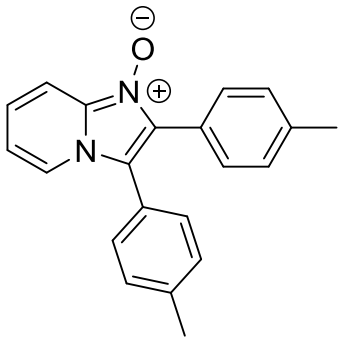
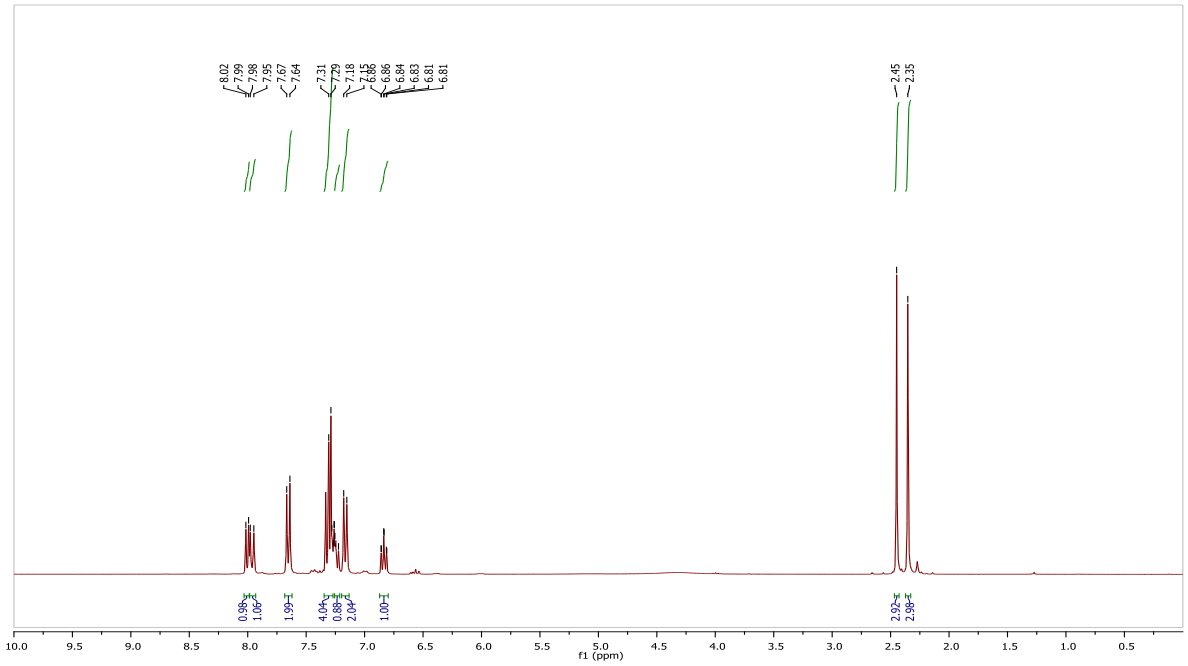
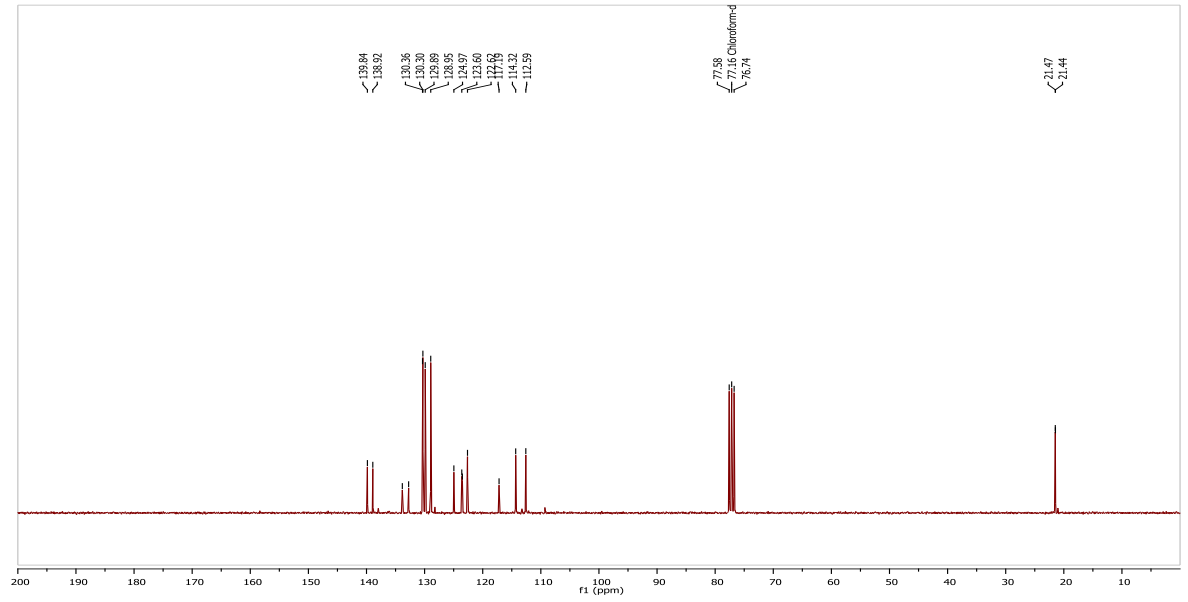
151.88
133.92
132.90
130.29
129.73
126.64
125.29
124.69
123.86
123.67
122.78
117.19
114.24
112.82
77.80
77.16
76.52
35.02
34.85
31.35
31.33
f1 (ppm)

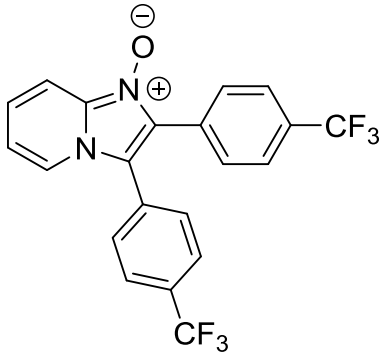
(3k)

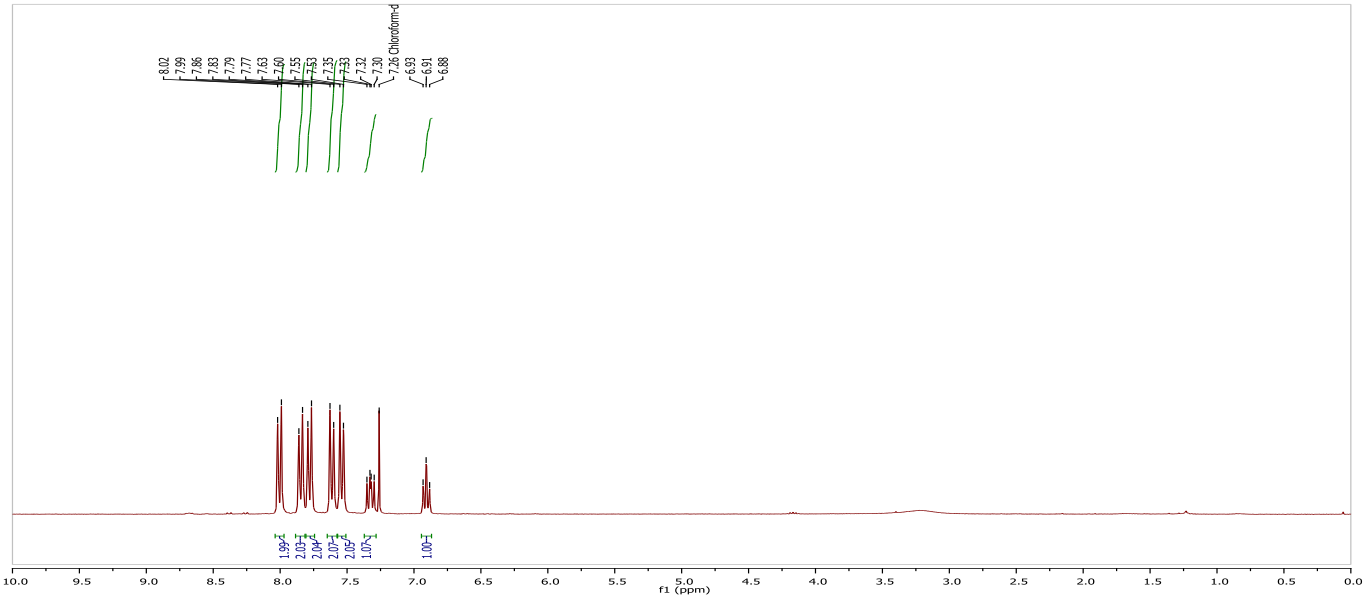


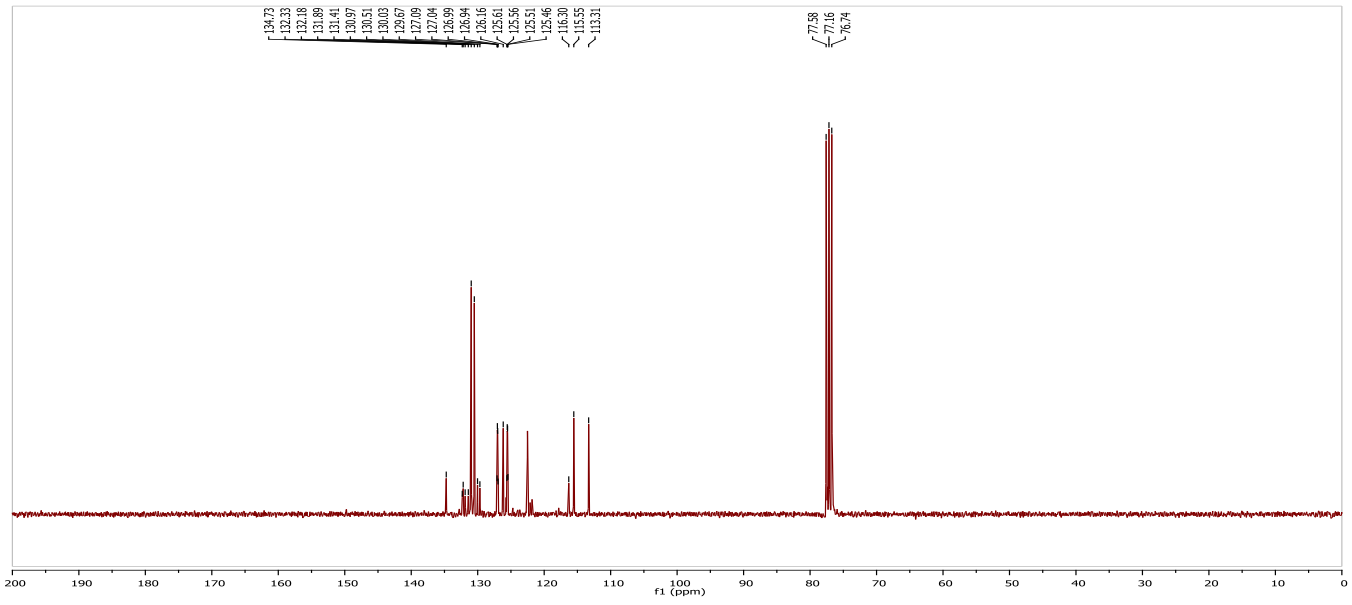

8.02
7.99
7.98
7.95
7.67
7.64
7.31
7.29
7.18
7.15
6.86
6.84
6.83
6.81
6.81
2.45
2.35
0.98
1.06
1.99
4.04
0.88
2.04
1.00
2.92
2.98
f1 (ppm)


139.84
138.92
130.36
130.30
129.89
128.95
124.97
123.60
114.32
112.99
77.58
77.16 Chloroform-d
76.74
21.47
21.44
f1 (ppm)

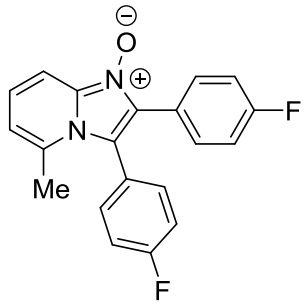
(3l)

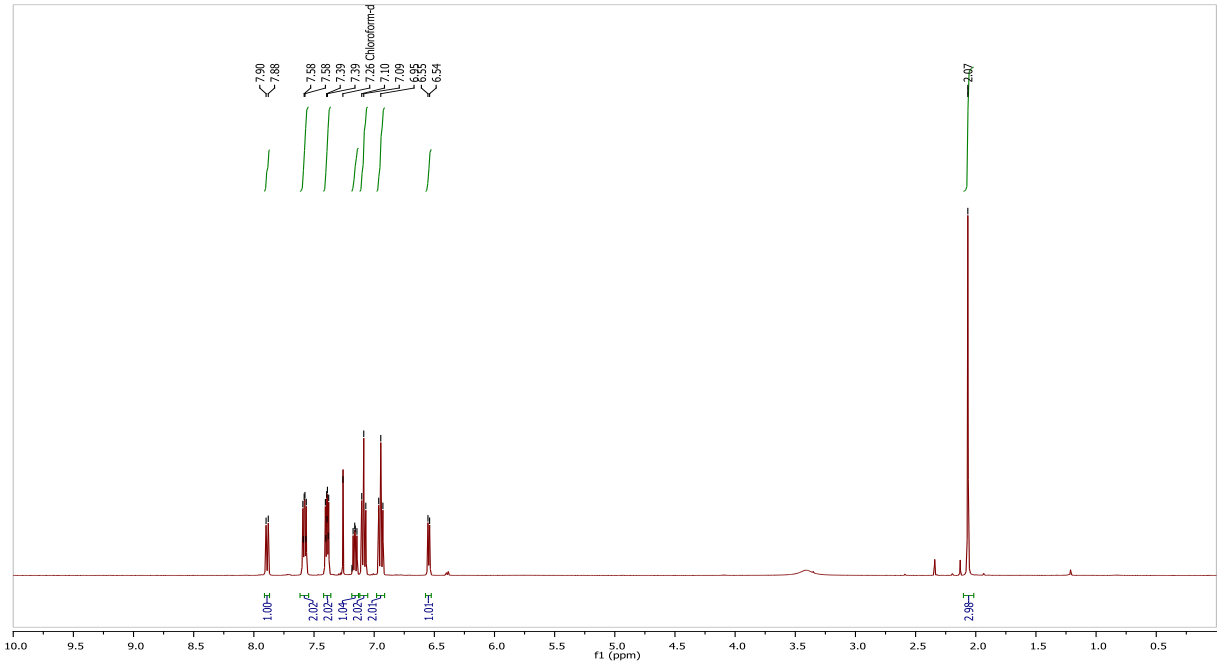

O
N
N
CF3
CF3

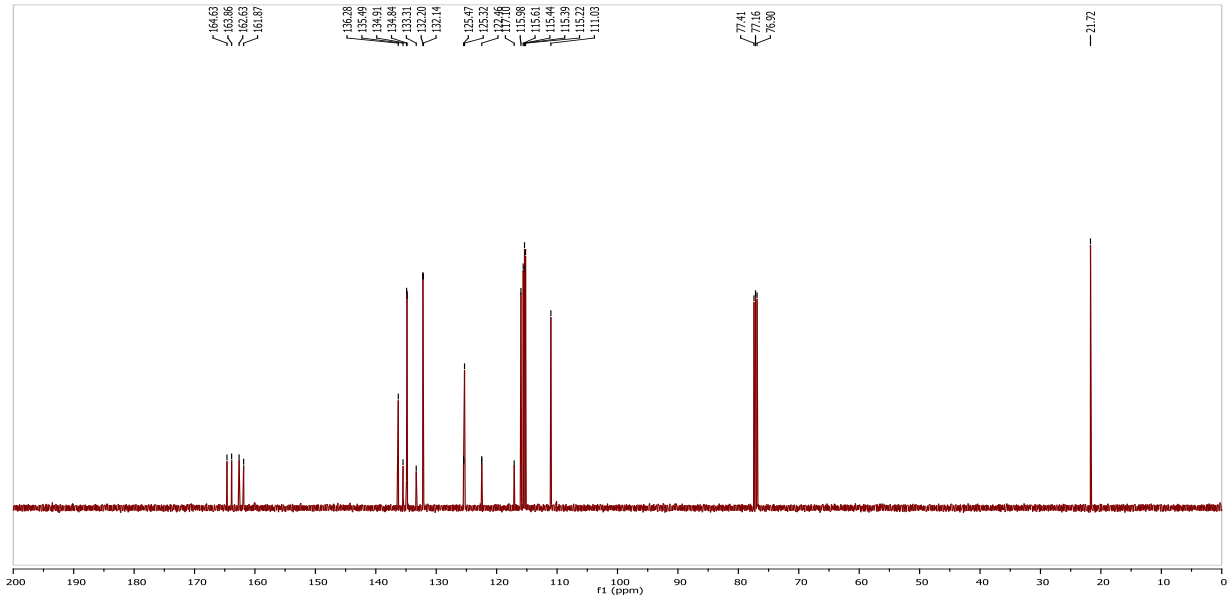

8.02
7.99
7.86
7.83
7.79
7.77
7.63
7.60
7.55
7.53
7.35
7.33
7.32
7.30
7.26 Chloroform-d
6.93
6.91
6.88
1.99
2.03
2.04
2.07
2.05
1.07
1.00
f1 (ppm)


134.73
132.33
132.18
131.89
131.41
130.97
130.51
130.03
129.67
127.09
127.04
126.99
126.94
126.16
125.61
125.56
125.51
125.46
116.30
115.55
113.31
77.58
77.16
76.74
f1 (ppm)

(3m)


O
N
N
F
Me
F


7.90
7.88
7.58
7.58
7.39
7.39
7.26 Chloroform-d
7.10
7.09
6.55
6.55
6.54
2.07
1.00
2.02
2.02
1.04
2.02
2.01
1.01
2.98
f1 (ppm)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162.63
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135.49
134.91
134.84
133.31
132.20
132.14
125.47
125.32
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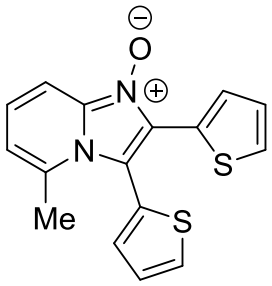
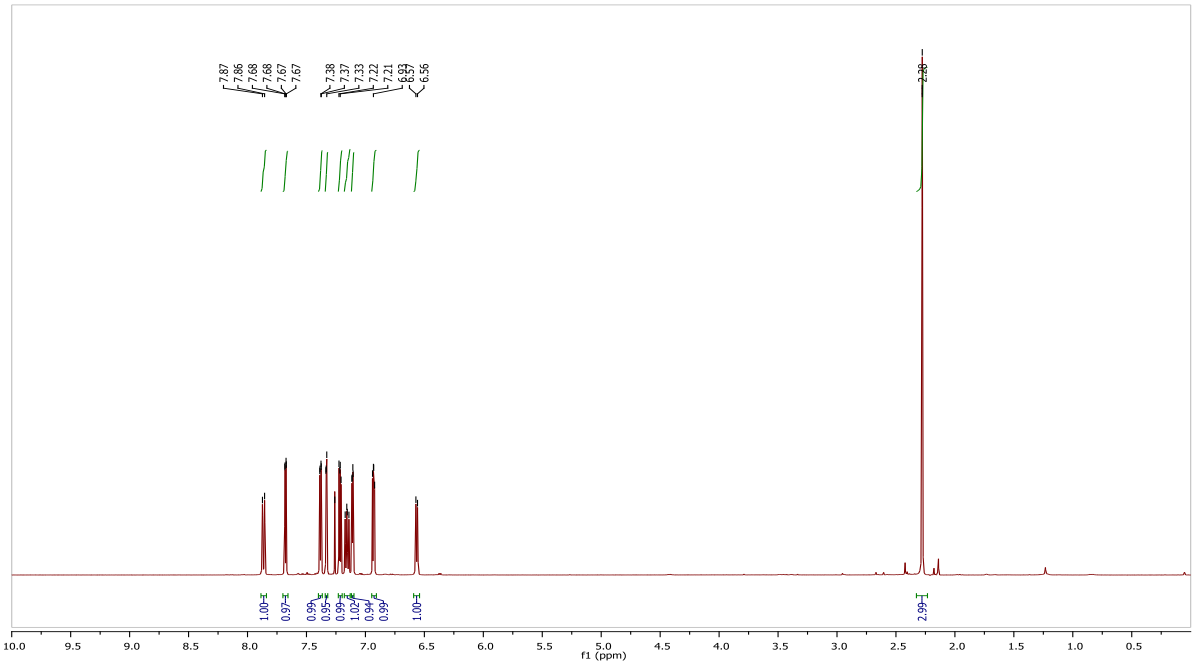
77.16
76.90
21.72
f1 (ppm)

(3n)


O
N
N
S
Me
S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7.86
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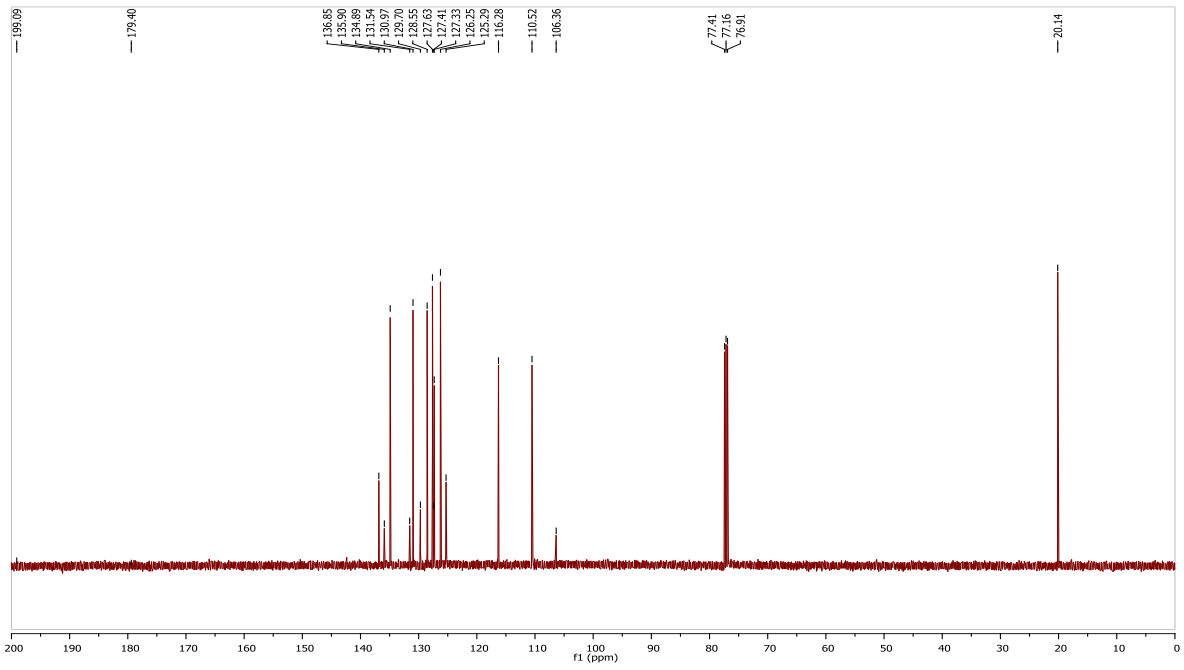
7.68
7.67
7.67
7.38
7.37
7.33
7.22
7.21
6.57
6.56
2.30
1.00
0.97
0.95
0.99
1.02
0.94
0.99
1.00
2.99
f1 (ppm)


199.09
179.40
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135.90
134.89
131.54
130.97
129.70
128.55
127.63
127.41
127.33
126.25
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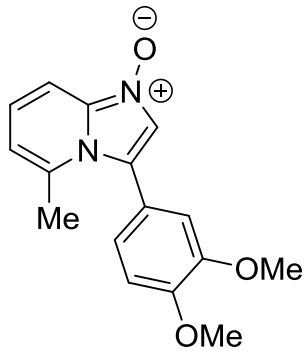
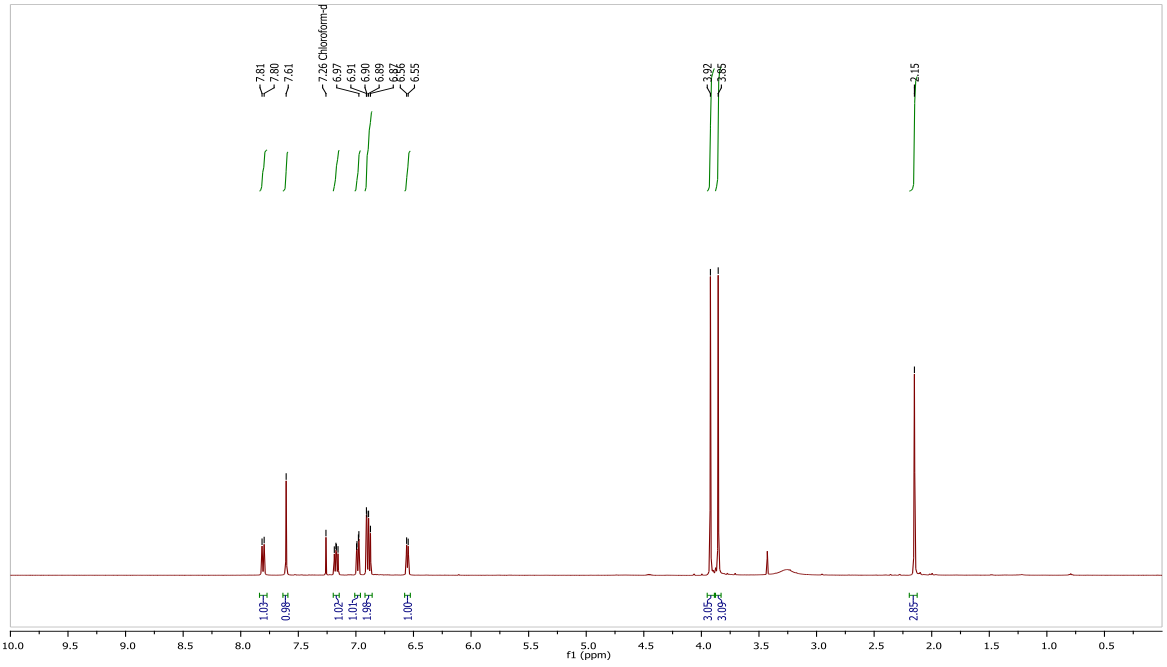
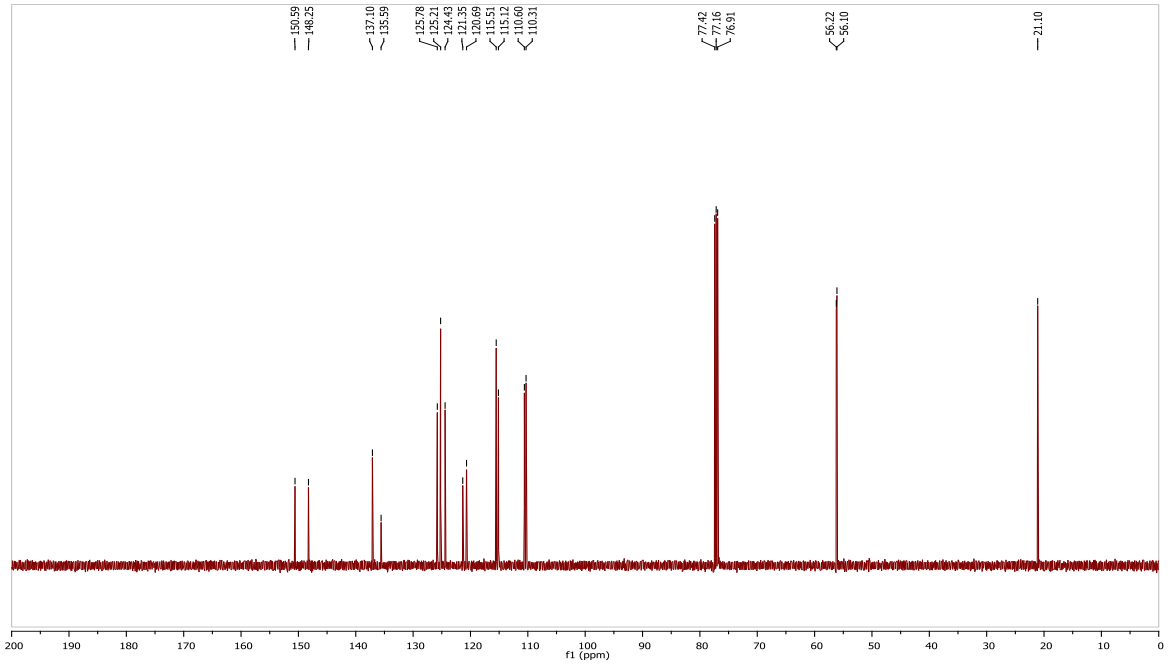
106.36
77.41
77.16
76.91
20.14
f1 (ppm)

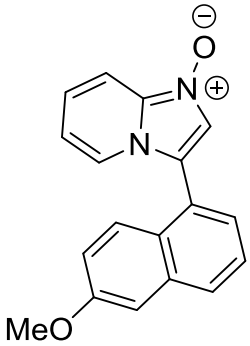
(3o)

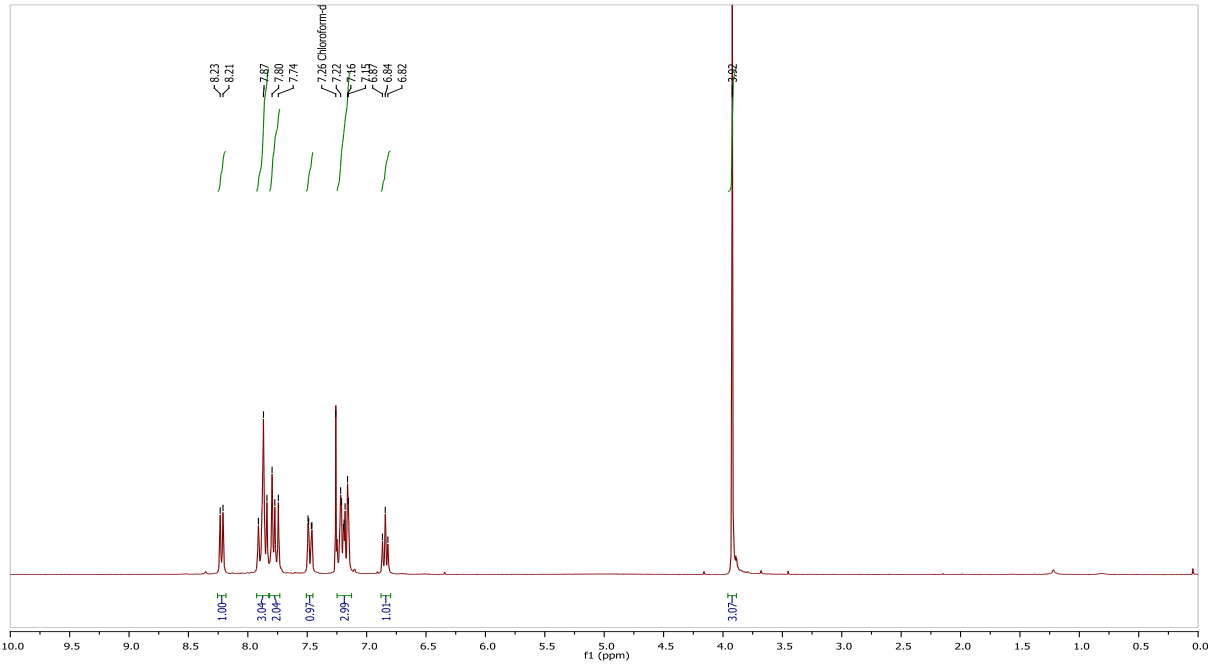

O
N
N
Me
OMe
OMe

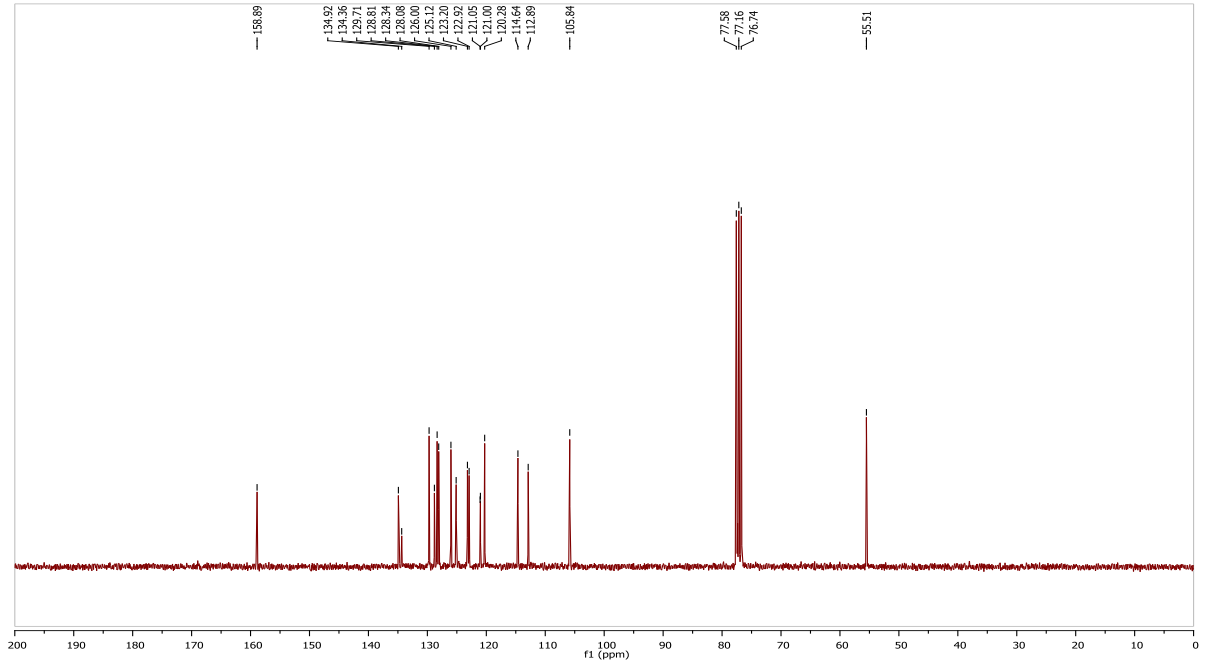

7.81
7.80
7.61
7.26 Chloroform-d
6.97
6.91
6.90
6.89
6.87
6.56
6.55
3.92
3.85
2.15
1.03
0.98
1.02
1.01
1.98
1.00
3.05
3.09
2.85
f1 (ppm)


150.59
148.25
137.10
135.59
125.78
125.21
124.43
121.35
120.69
115.51
115.12
110.60
110.31
77.42
77.16
76.91
56.22
56.10
21.10
f1 (ppm)

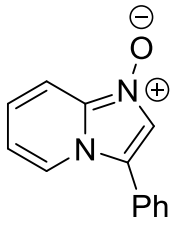
(3p)

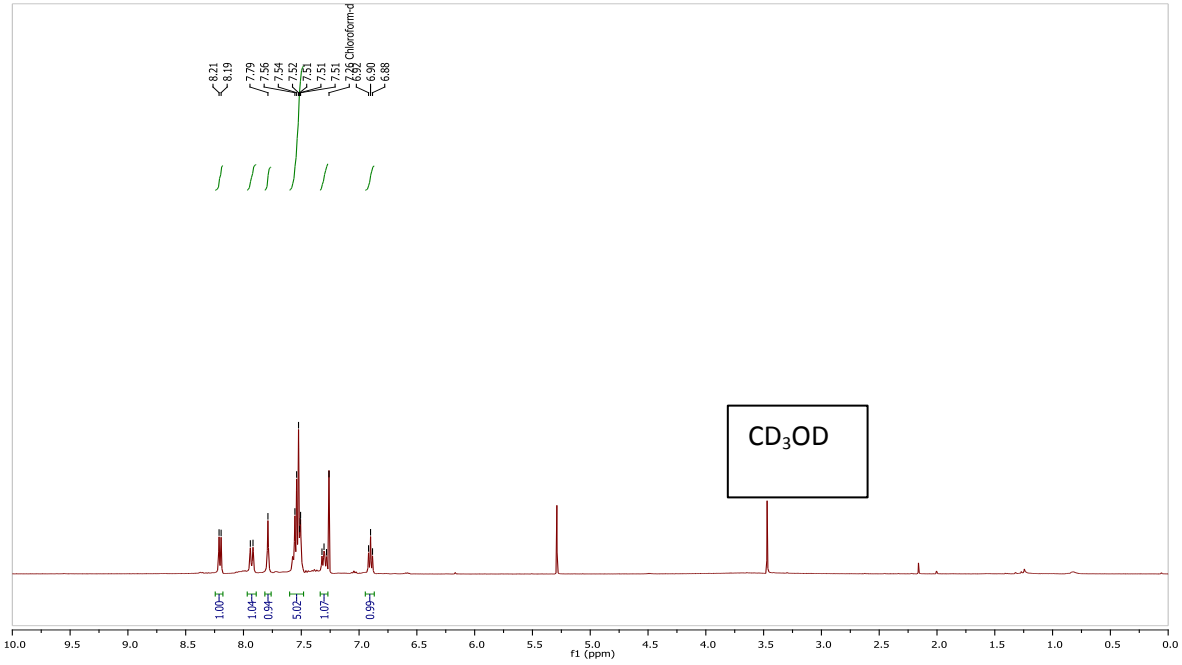

O
N
N
MeO

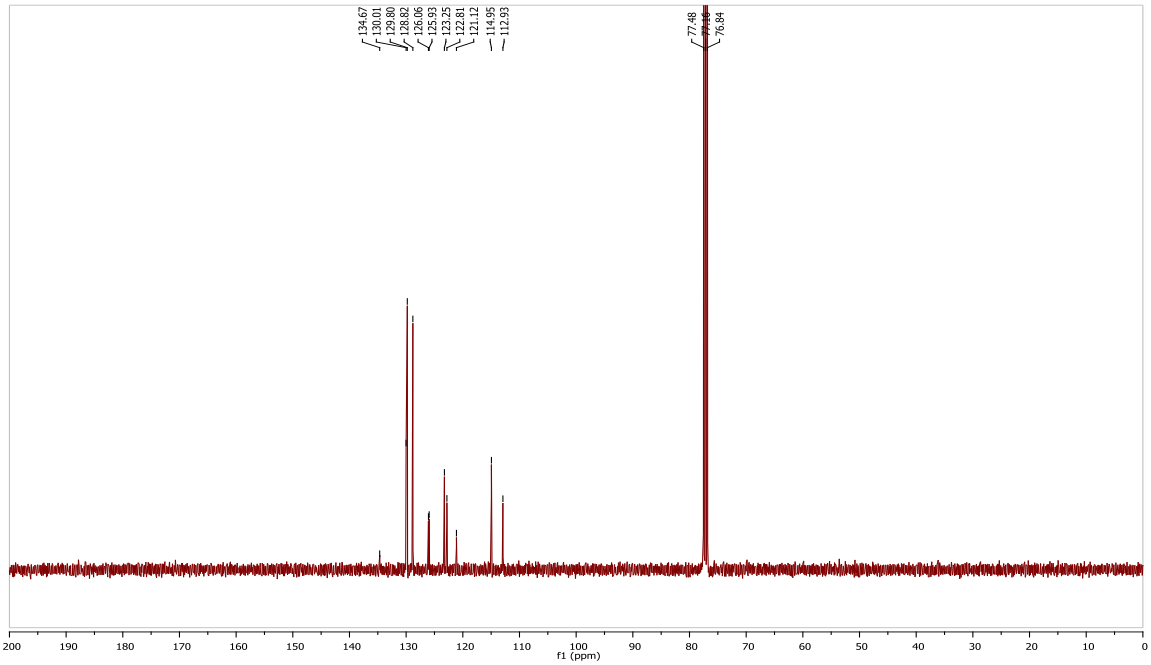

8.23
8.21
7.87
7.80
7.74
7.26 Chloroform-d
7.22
7.16
6.87
6.84
6.82
3.92
1.00
3.04
2.04
0.97
2.99
1.01
3.07
f1 (ppm)


158.89
134.92
134.36
129.71
128.81
128.34
128.08
126.00
125.12
123.20
122.92
121.05
121.00
120.28
114.64
112.89
105.84
77.58
77.16
76.74
55.51
f1 (ppm)

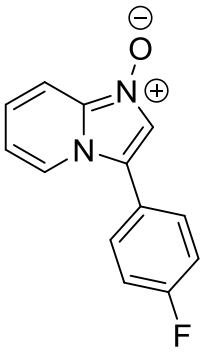
(3q)

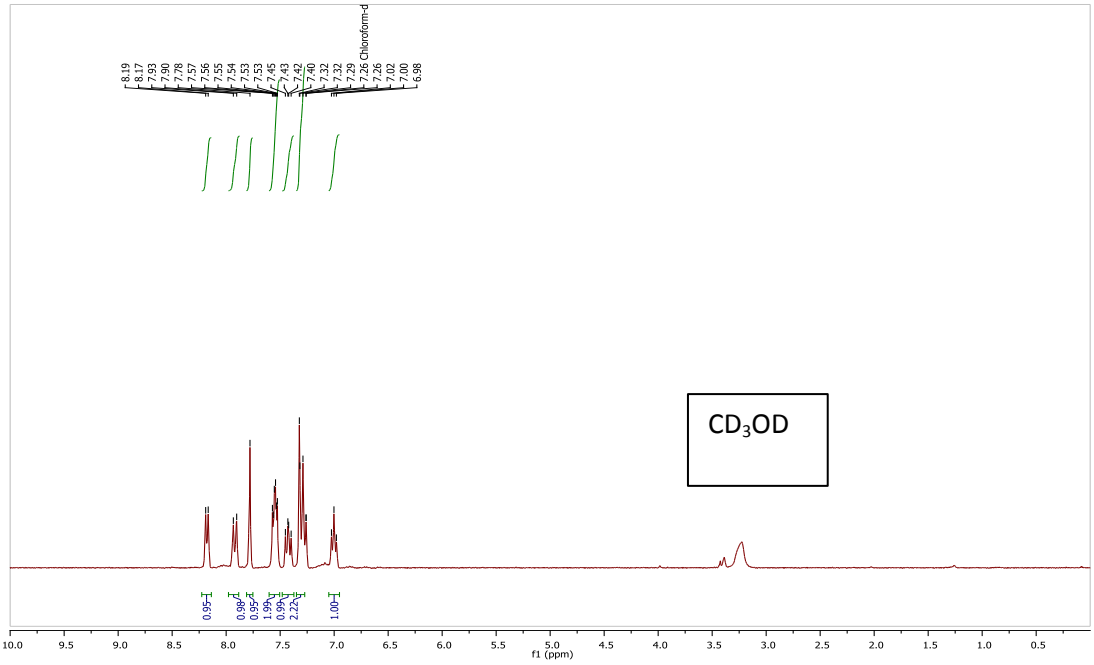

O
N
N
Ph

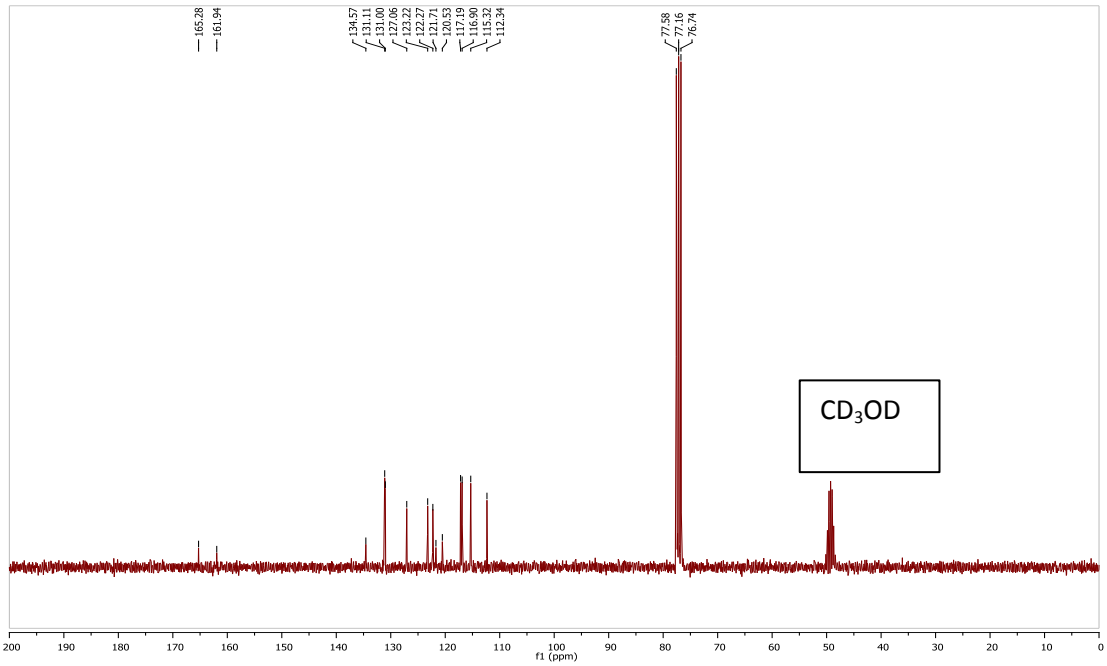

8.21
8.19
7.79
7.56
7.54
7.52
7.51
7.51
7.51
7.26 Chloroform-d
6.92
6.90
6.88
CD3OD
1.00
1.04
0.94
5.02
1.07
0.99
f1 (ppm)


134.67
130.01
129.80
128.82
126.06
125.93
123.25
122.81
121.12
114.95
112.93
77.48
77.16
76.84
f1 (ppm)

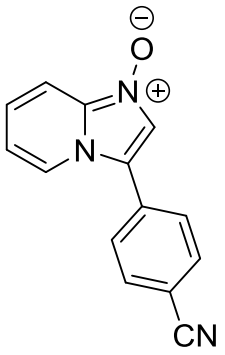
(3r)

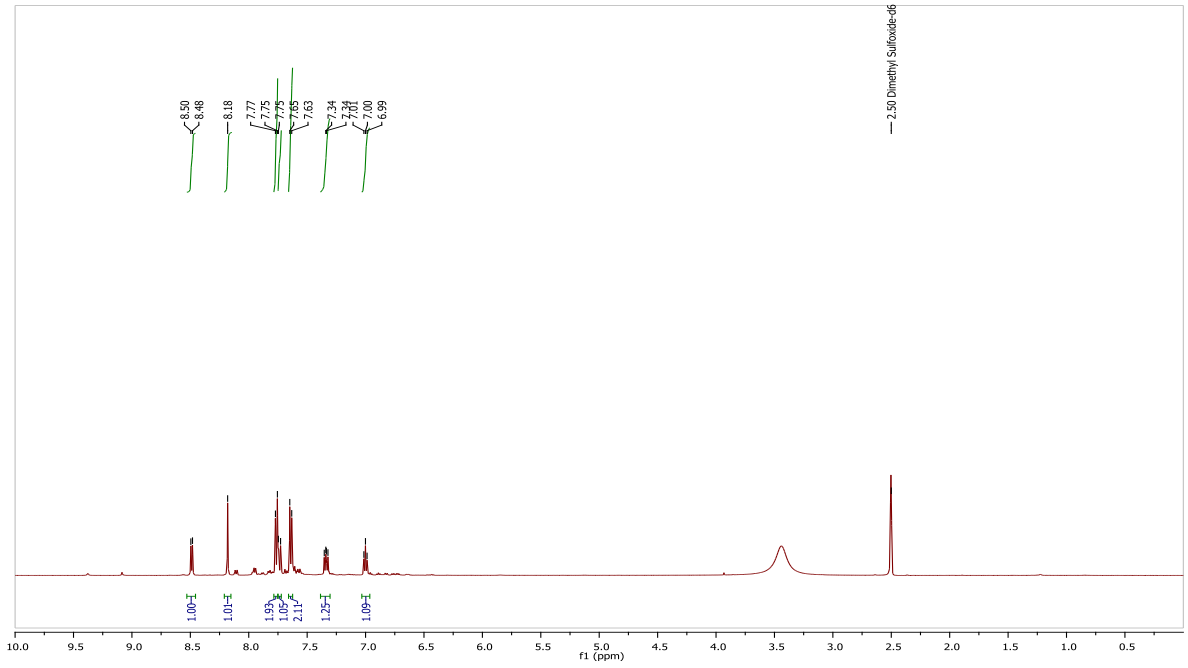

O
N
N
F

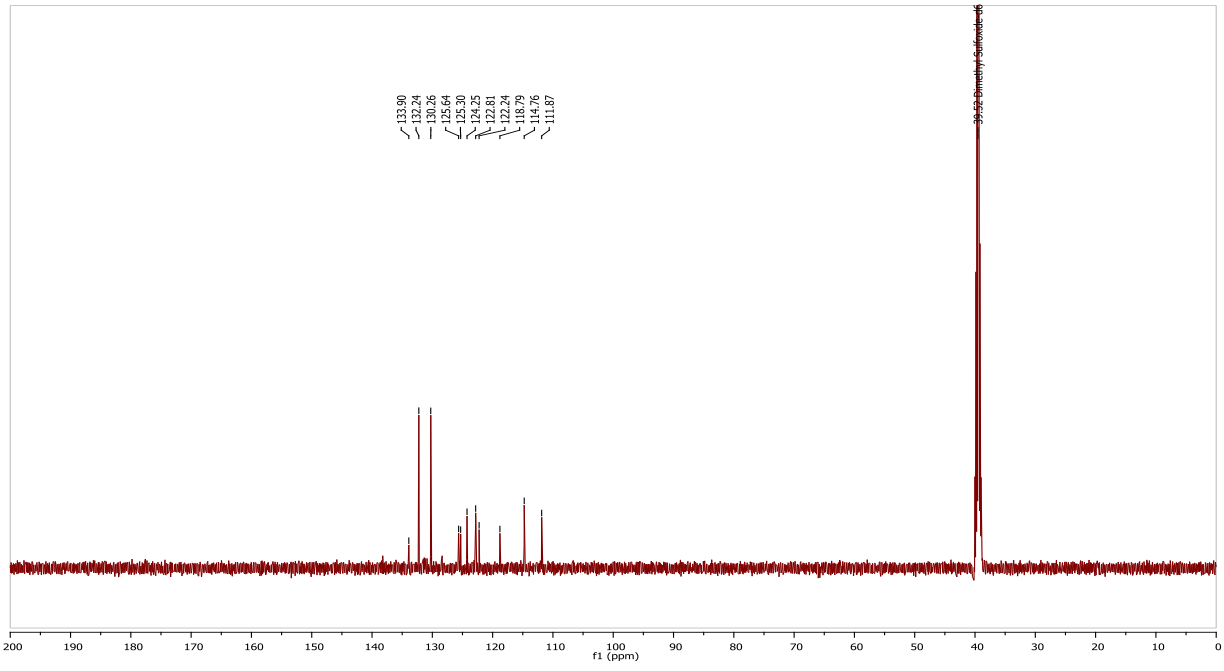

8.19
8.17
7.93
7.90
7.78
7.57
7.56
7.55
7.54
7.53
7.53
7.45
7.43
7.42
7.40
7.32
7.29
Chloroform-d
7.26
7.26
7.02
7.00
6.98
CD3OD
0.95
0.98
0.95
1.99
0.99
2.22
1.00
f1 (ppm)


165.28
161.94
134.57
131.11
131.00
127.06
123.22
122.27
121.71
120.53
117.19
116.90
115.32
112.34
77.58
77.16
76.74
CD3OD
f1 (ppm)

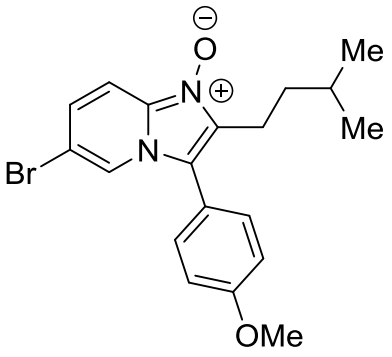
(3s)

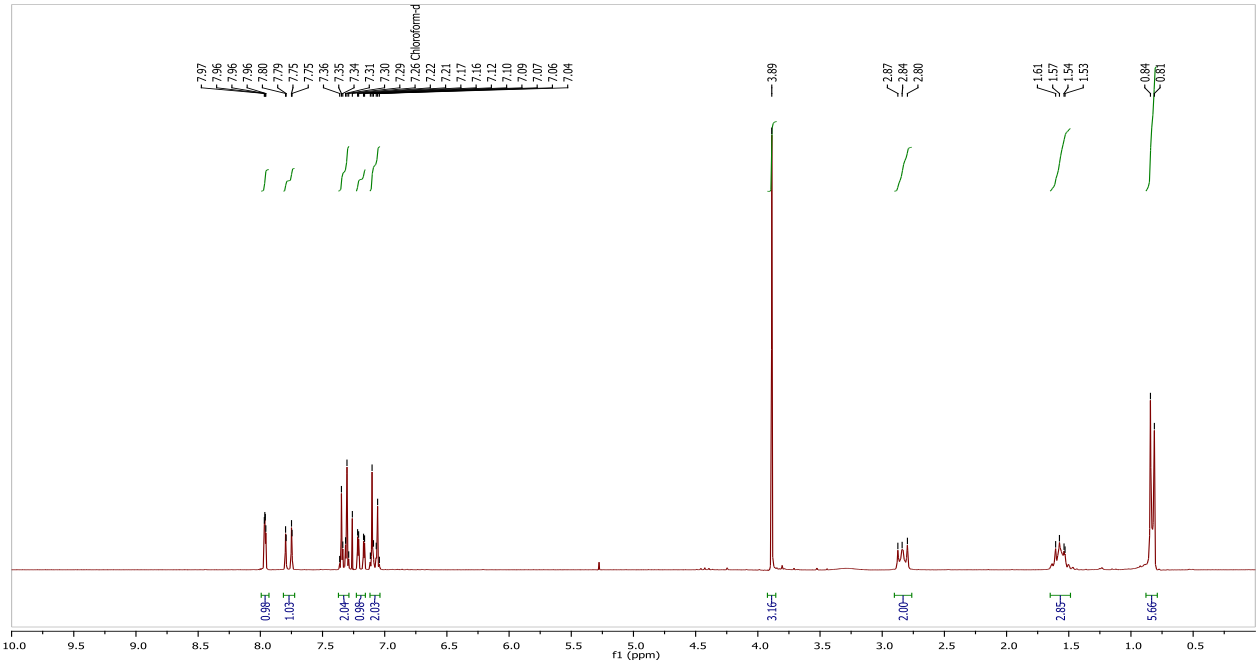

O
N
N
CN

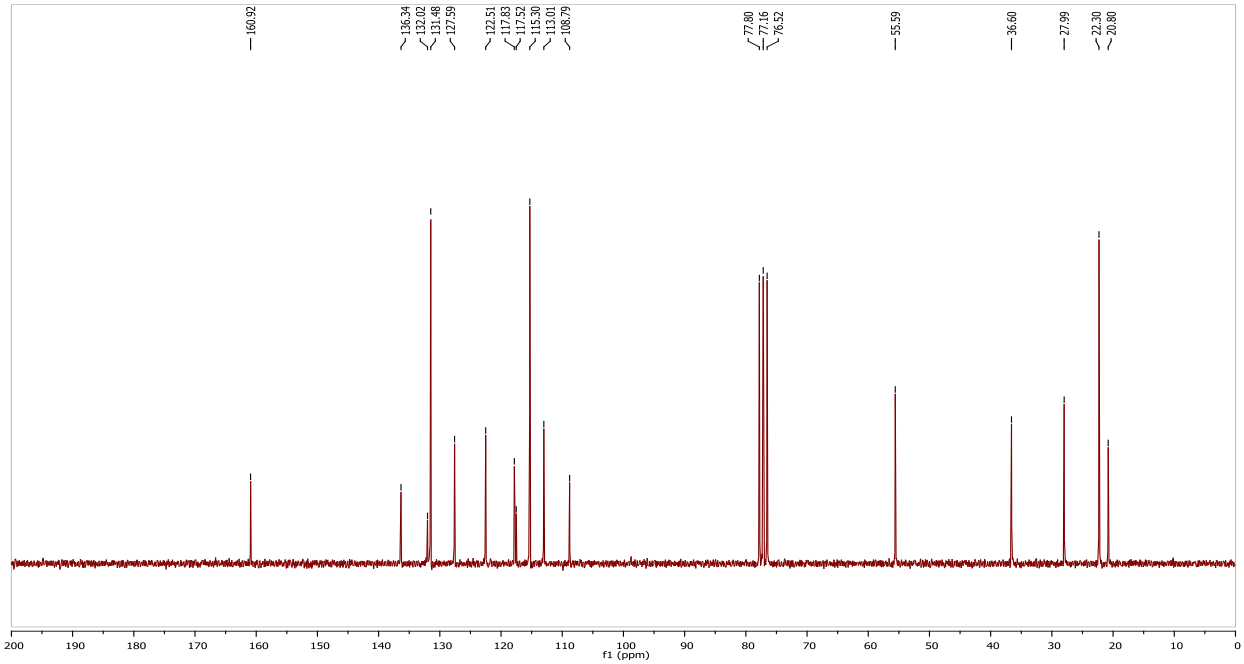

8.50
8.48
8.18
7.77
7.75
7.75
7.65
7.63
7.34
7.31
7.00
6.99
2.50 Dimethyl Sulfoxide-d6
1.00
1.01
1.93
1.05
2.11
1.25
1.09
f1 (ppm)


133.90
132.24
130.26
125.64
125.30
124.25
122.81
122.24
118.79
114.76
111.87
39.52 Dimethyl Sulfoxide-d6
f1 (ppm)

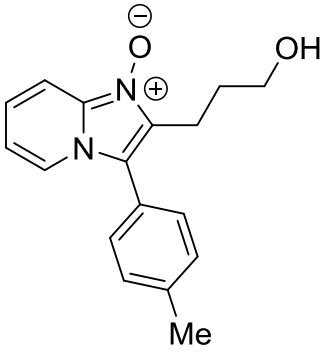
(3t)

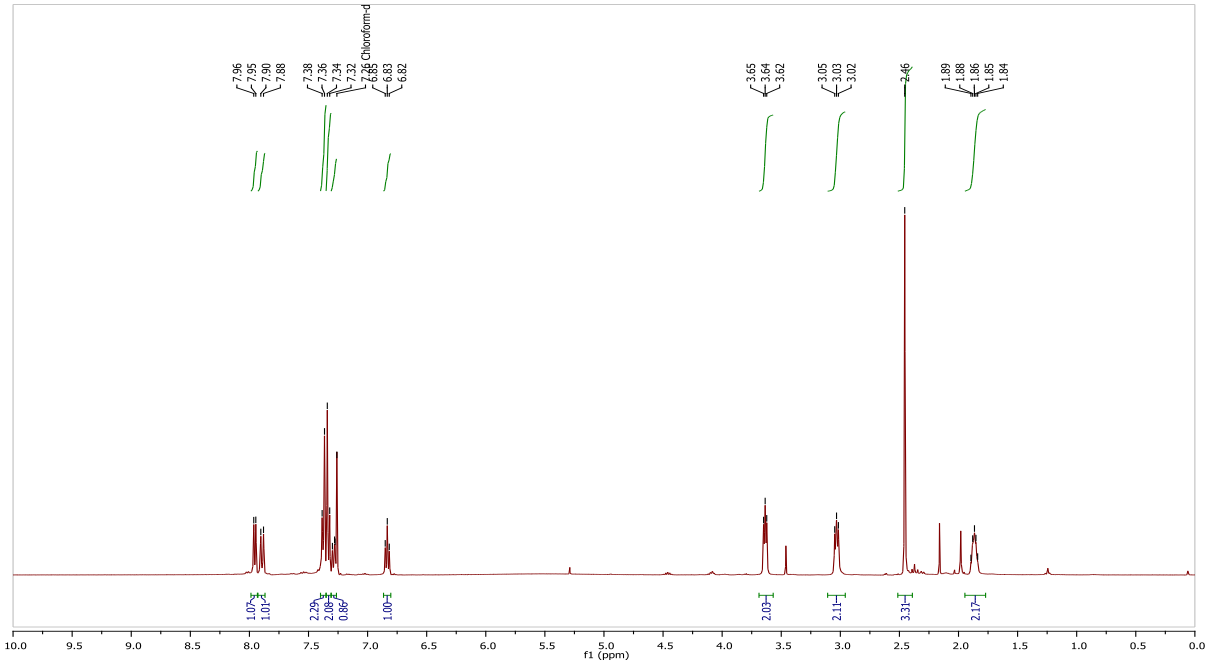

O
N
Me
Me
N
Br
OMe

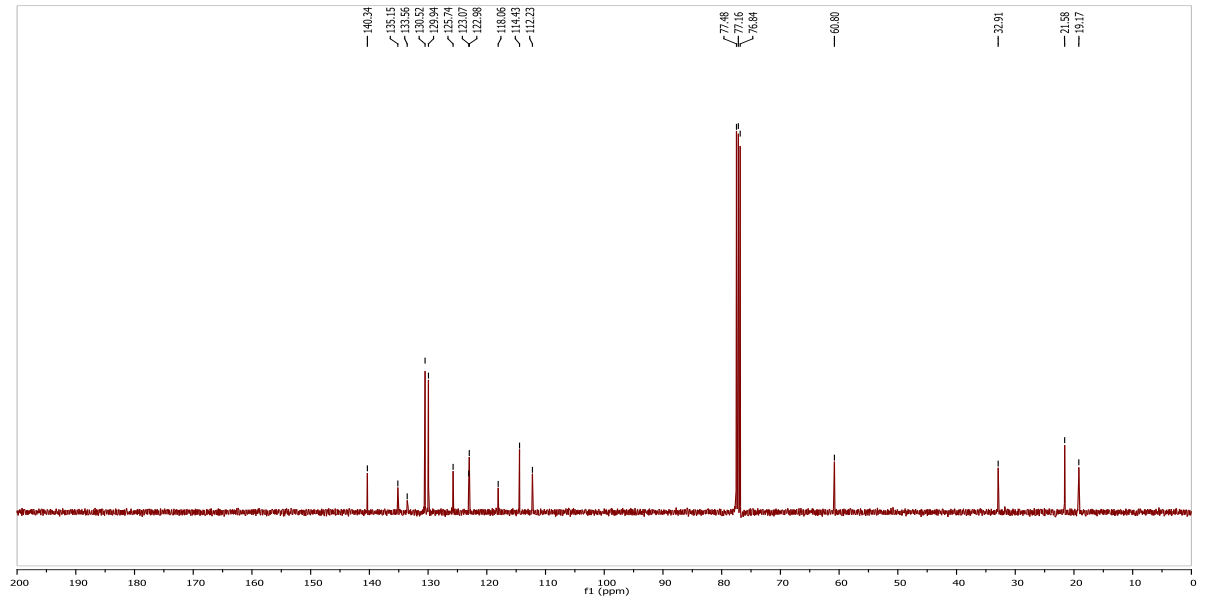

7.97
7.96
7.96
7.96
7.80
7.79
7.75
7.75
7.36
7.35
7.34
7.31
7.30
7.29
7.26 Chloroform-d
7.22
7.21
7.17
7.16
7.12
7.10
7.09
7.07
7.06
7.04
3.89
2.87
2.84
2.80
1.61
1.57
1.54
1.53
0.84
0.81
0.98
1.03
2.04
0.98
2.03
3.16
2.00
2.85
5.66
f1 (ppm)


160.92
136.34
132.02
131.48
127.59
122.51
117.83
117.52
115.30
113.01
108.79
77.80
77.16
76.52
55.59
36.60
27.99
22.30
20.80
f1 (ppm)

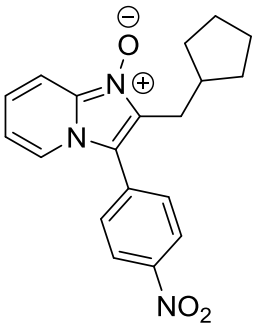
(3u)

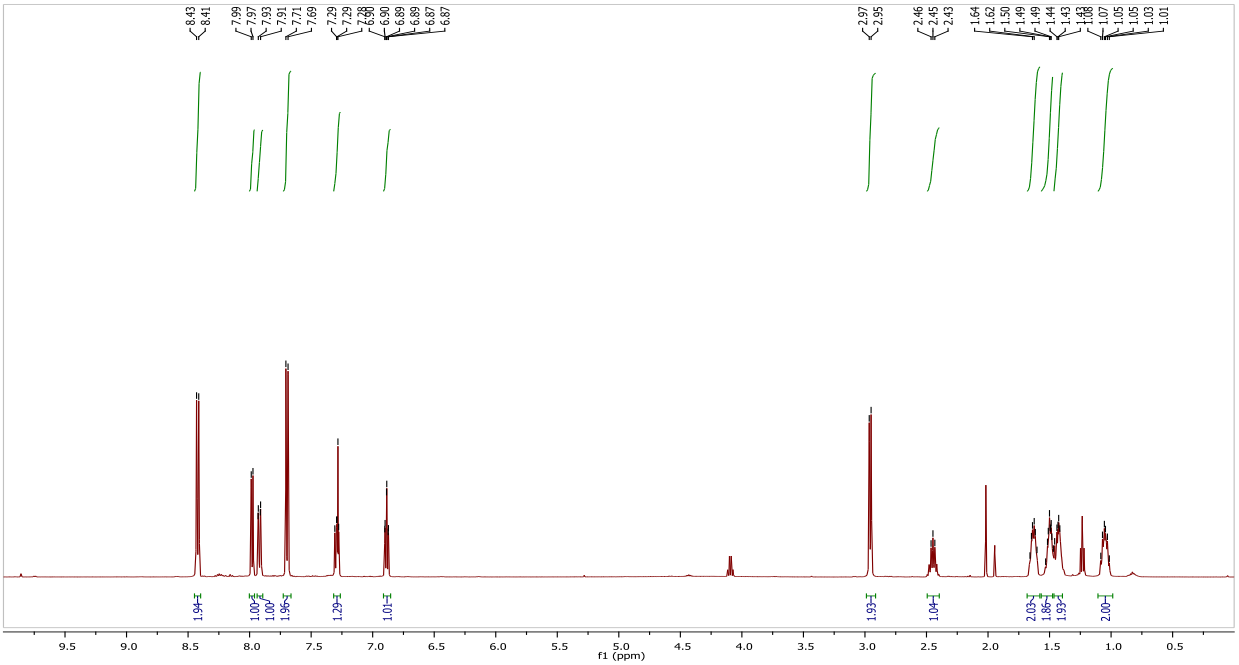

O
N
N
OH
Me

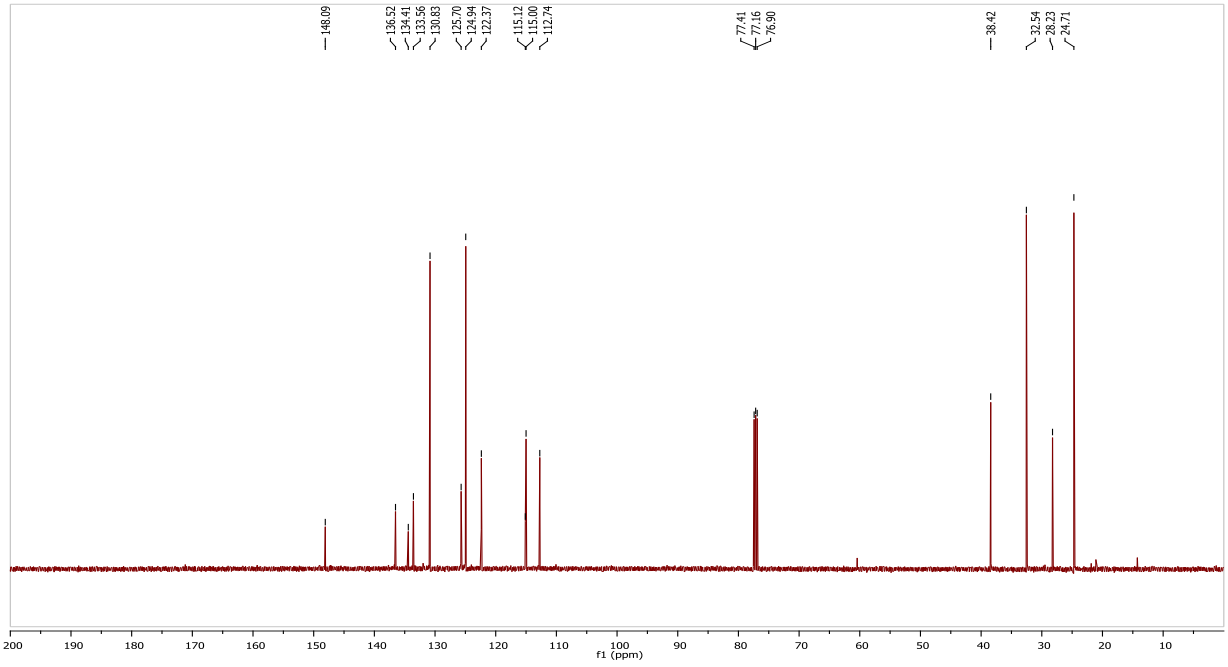

7.96
7.95
7.90
7.88
7.38
7.36
7.34
7.32
7.26
Chloroform-d
6.83
6.82
3.65
3.64
3.62
3.05
3.03
3.02
2.46
1.89
1.88
1.86
1.85
1.84
1.07
1.01
2.29
2.08
0.86
1.00
2.03
2.11
3.31
2.17
f1 (ppm)


140.34
135.15
133.56
130.52
129.94
125.74
122.07
122.98
118.06
114.43
112.23
77.48
77.16
76.84
60.80
32.91
21.58
19.17
f1 (ppm)

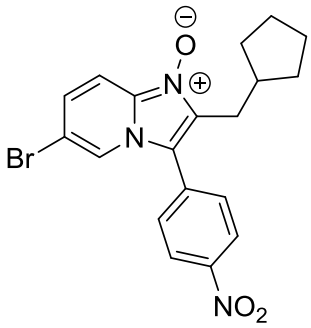
(3v)

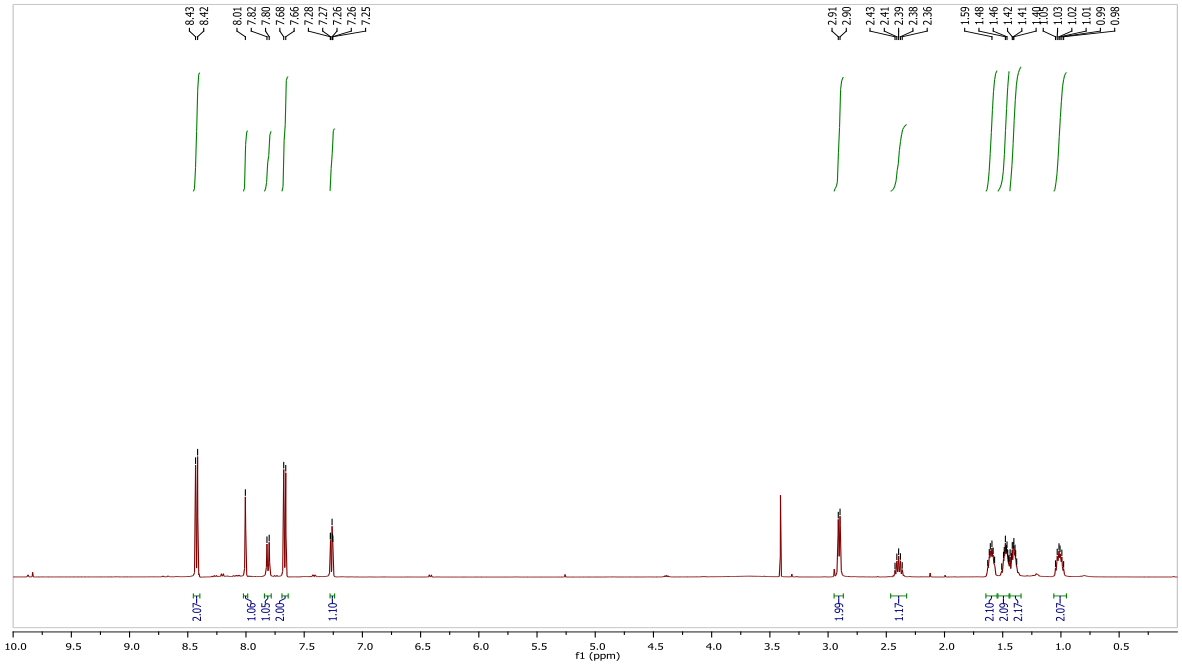

O
N
N
NO2

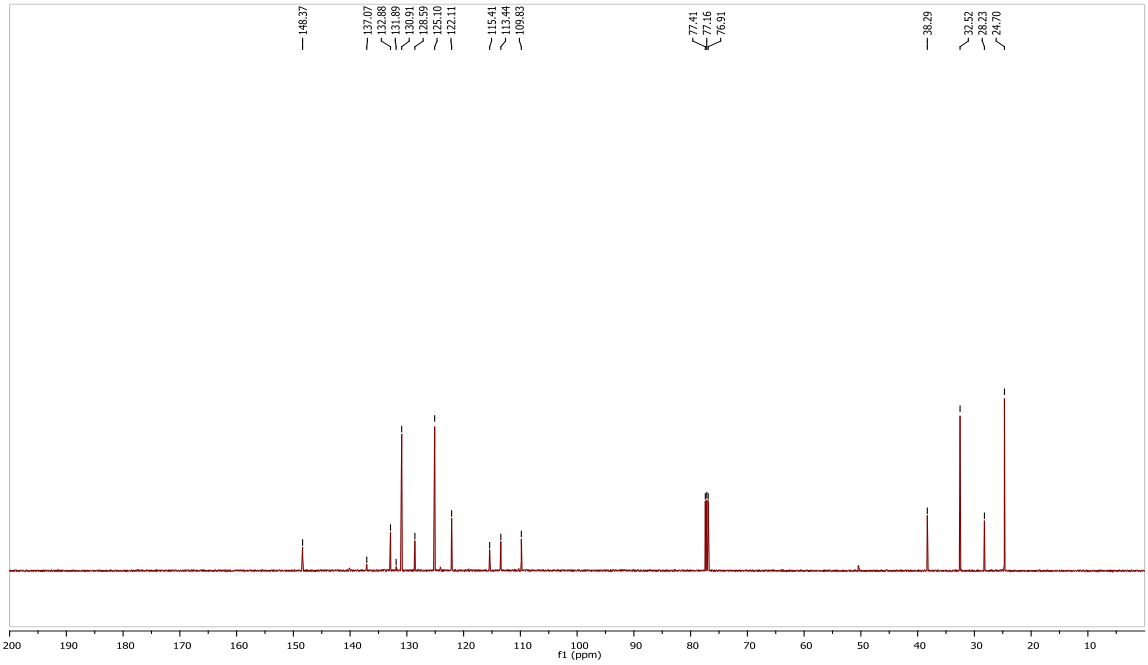

8.43
8.41
7.99
7.97
7.93
7.91
7.71
7.69
7.29
7.29
6.90
6.89
6.89
6.87
6.87
2.97
2.95
2.46
2.45
2.43
1.64
1.62
1.50
1.49
1.49
1.44
1.43
1.08
1.07
1.05
1.05
1.03
1.01
1.94
1.00
1.00
1.96
1.29
1.01
1.93
1.04
2.03
1.86
1.93
2.00
f1 (ppm)


148.09
136.52
134.41
133.56
130.83
125.70
124.94
122.37
115.12
115.00
112.74
77.41
77.16
76.90
38.42
32.54
28.23
24.71
f1 (ppm)

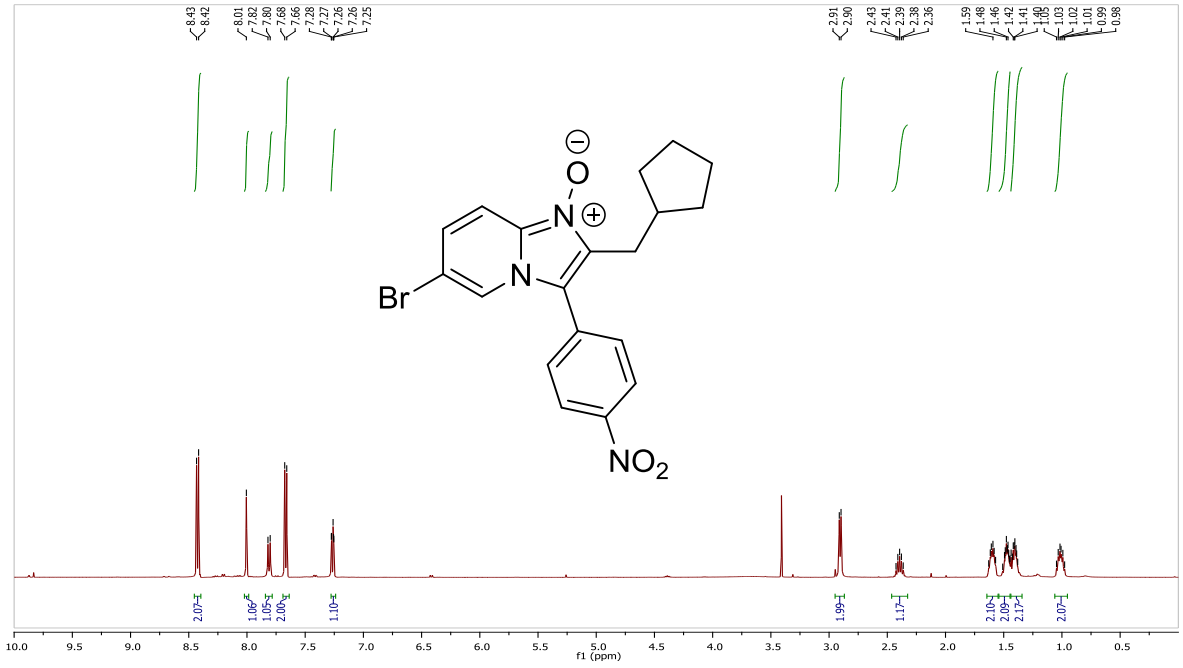
(3w)

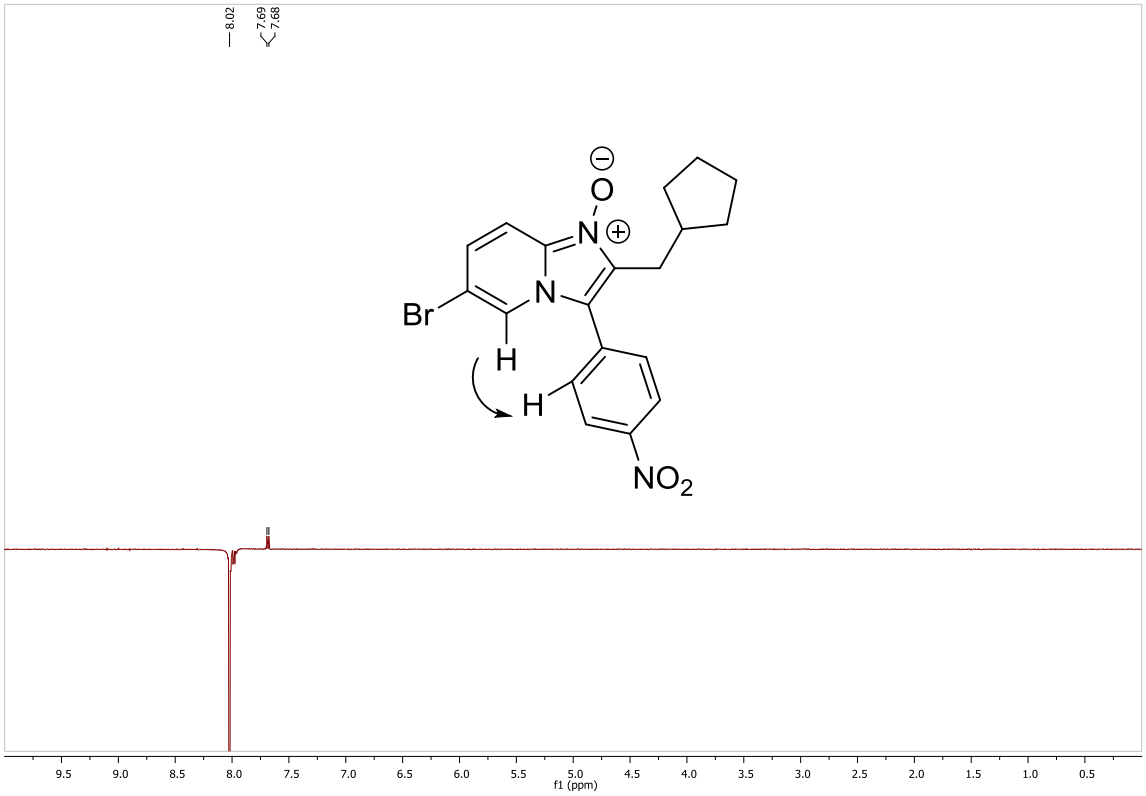

O
N
N
Br
NO2

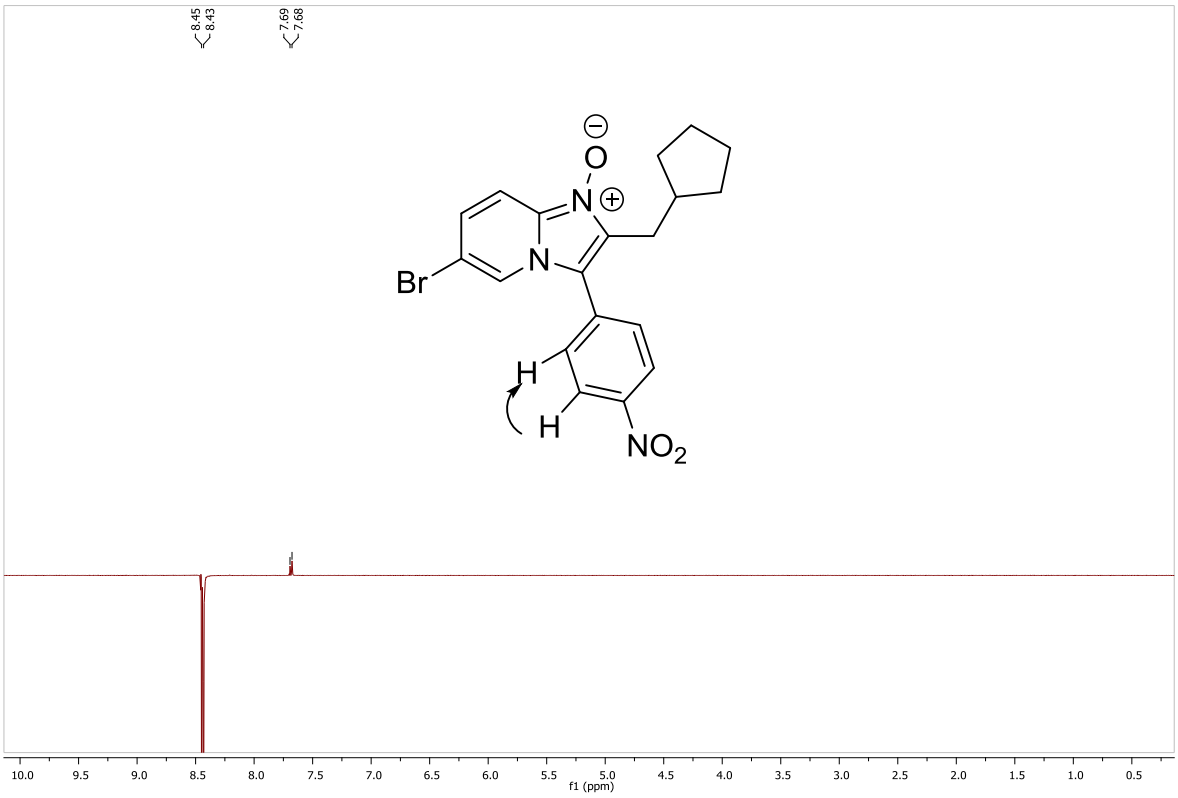

8.43
8.42
8.01
7.82
7.80
7.68
7.66
7.28
7.27
7.26
7.26
7.25
2.91
2.90
2.43
2.41
2.39
2.38
2.36
1.59
1.48
1.46
1.42
1.41
1.40
1.05
1.03
1.02
1.01
0.99
0.98
2.07
1.06
1.05
2.00
1.10
1.99
1.17
2.10
2.09
2.17
2.07
f1 (ppm)

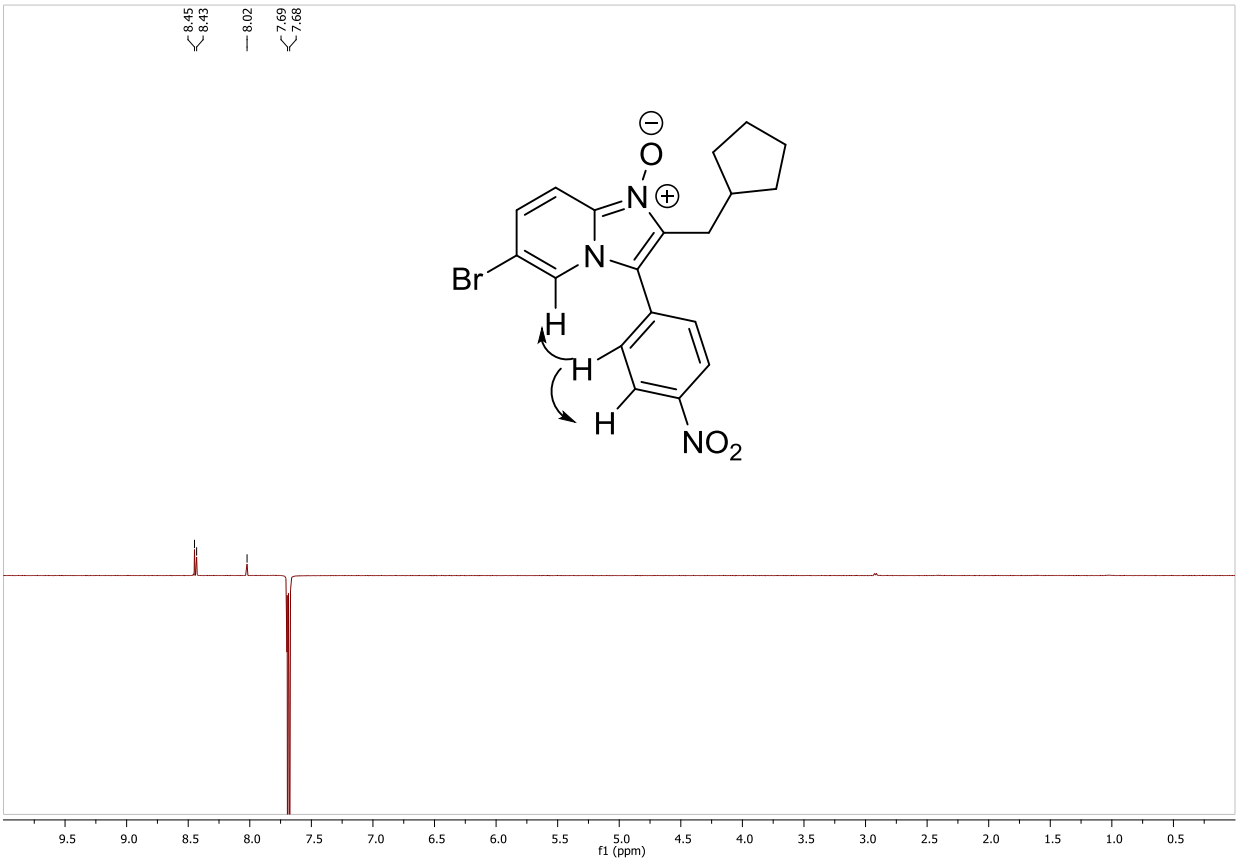

148.37
137.07
132.88
131.89
130.91
128.59
125.10
122.11
115.41
113.44
109.83
77.41
77.16
76.91
38.29
32.52
28.23
24.70
f1 (ppm)

NOE of 3w

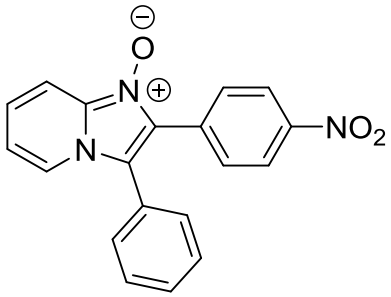

8.43
8.42
8.01
7.82
7.80
7.68
7.66
7.28
7.27
7.26
7.26
7.25
2.91
2.90
2.43
2.41
2.39
2.38
2.36
1.59
1.48
1.46
1.42
1.41
1.05
1.03
1.02
1.01
0.99
0.98
O
N
N
Br
NO2
2.07
1.06
1.05
2.00
1.10
1.99
1.17
2.10
2.09
2.17
2.07
f1 (ppm)

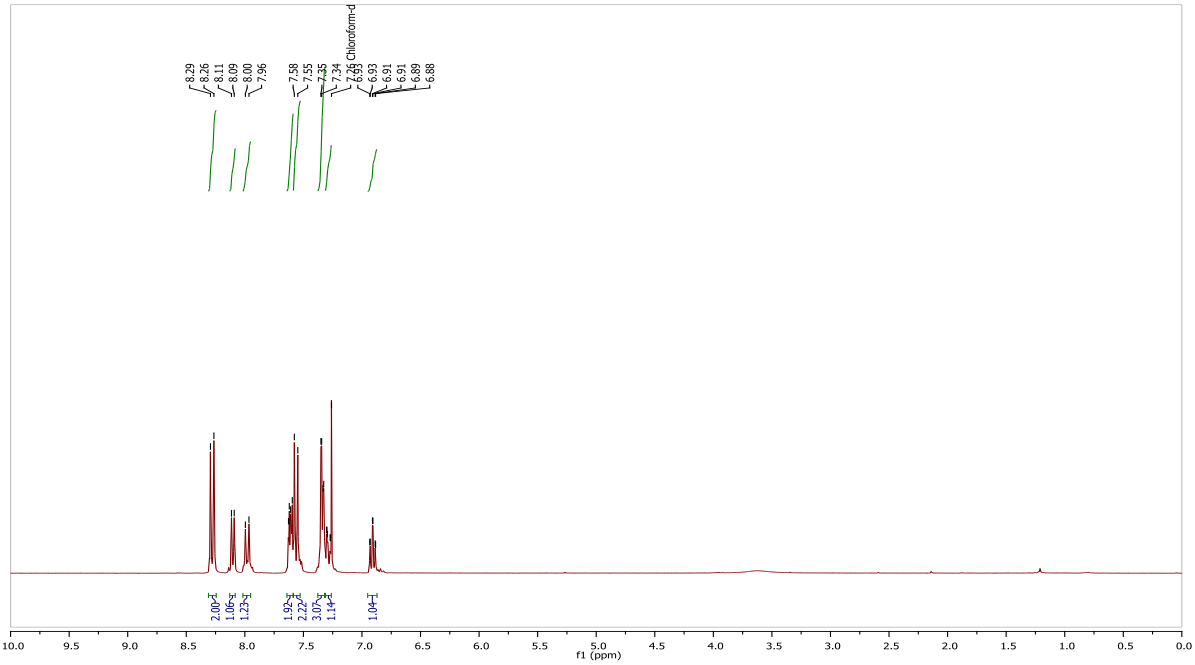

8.02
7.69
7.68
O
N
N
Br
H
H
NO2
f1 (ppm)

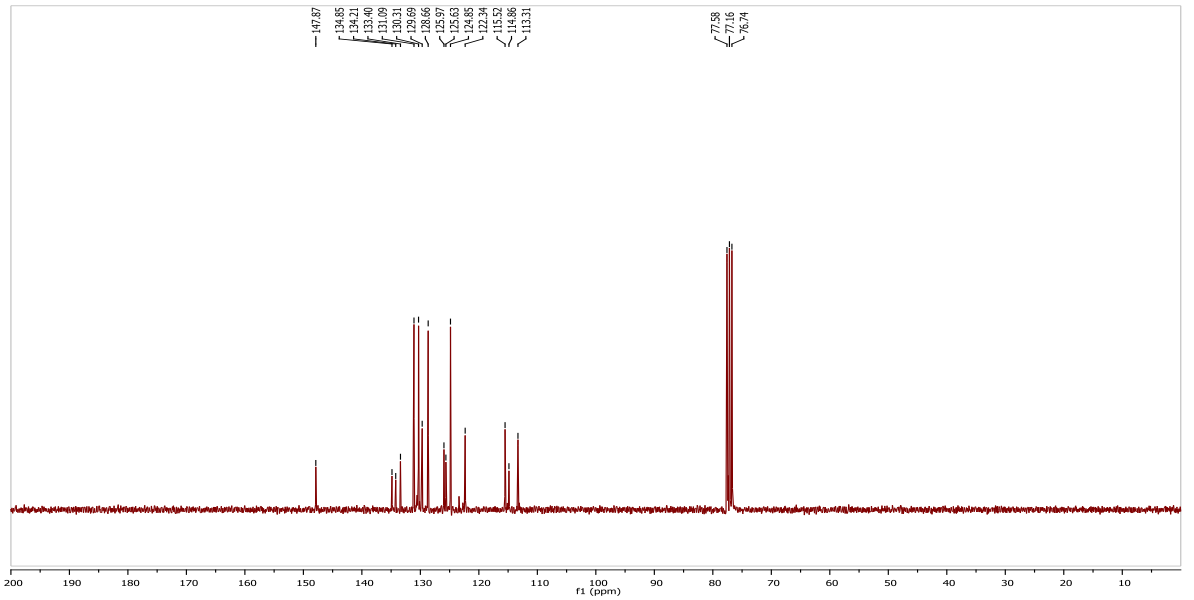

8.45
8.43
7.69
7.68
O
N
N
Br
H
H
NO2
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


8.45
8.43
8.02
7.69
7.68
O
N
N
Br
H
H
H
NO2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

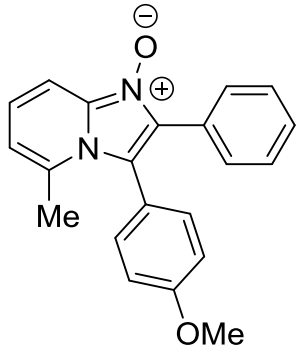
(3x)

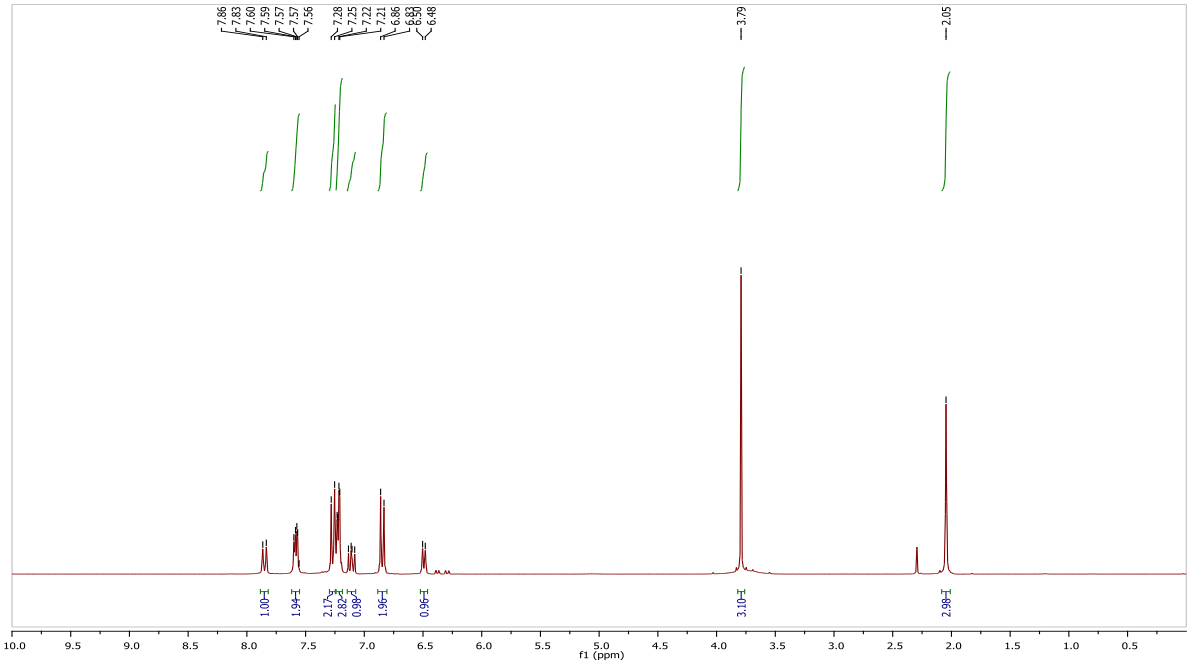

O
N
N
NO2

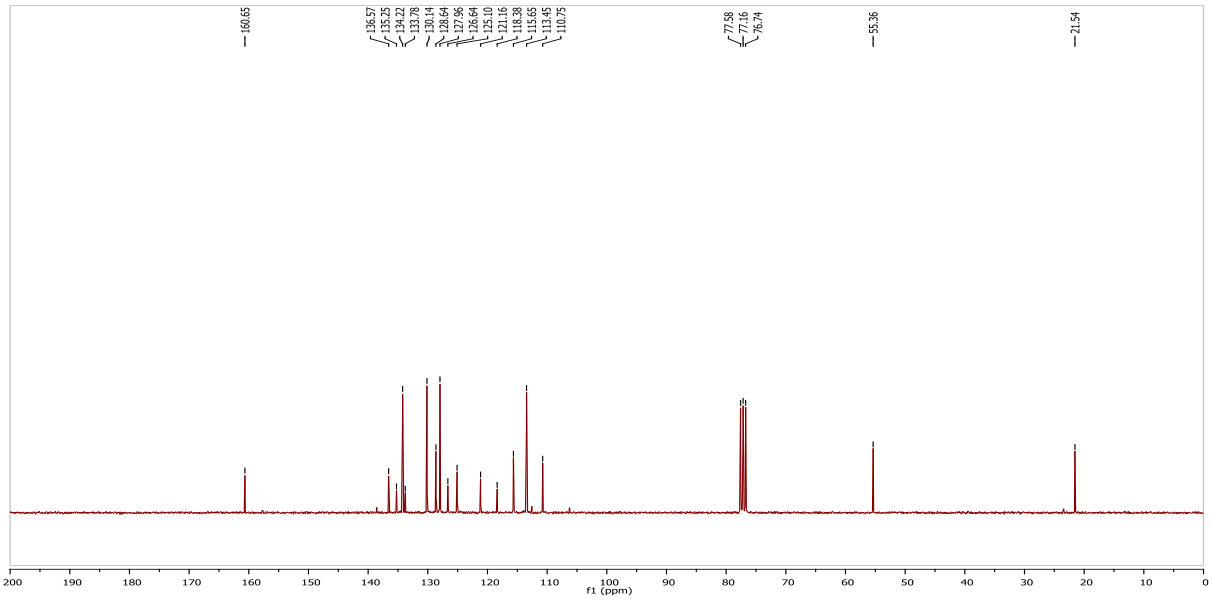

8.29
8.26
8.11
8.09
8.00
7.96
7.58
7.55
7.35
7.34
7.26 Chloroform-d
6.93
6.91
6.91
6.89
6.88
2.00
1.06
1.23
1.92
2.22
3.07
1.14
1.04
f1 (ppm)


147.87
134.85
134.21
133.40
131.09
130.31
129.69
128.66
125.97
125.63
124.85
122.34
115.52
114.86
113.31
77.58
77.16
76.74
f1 (ppm)

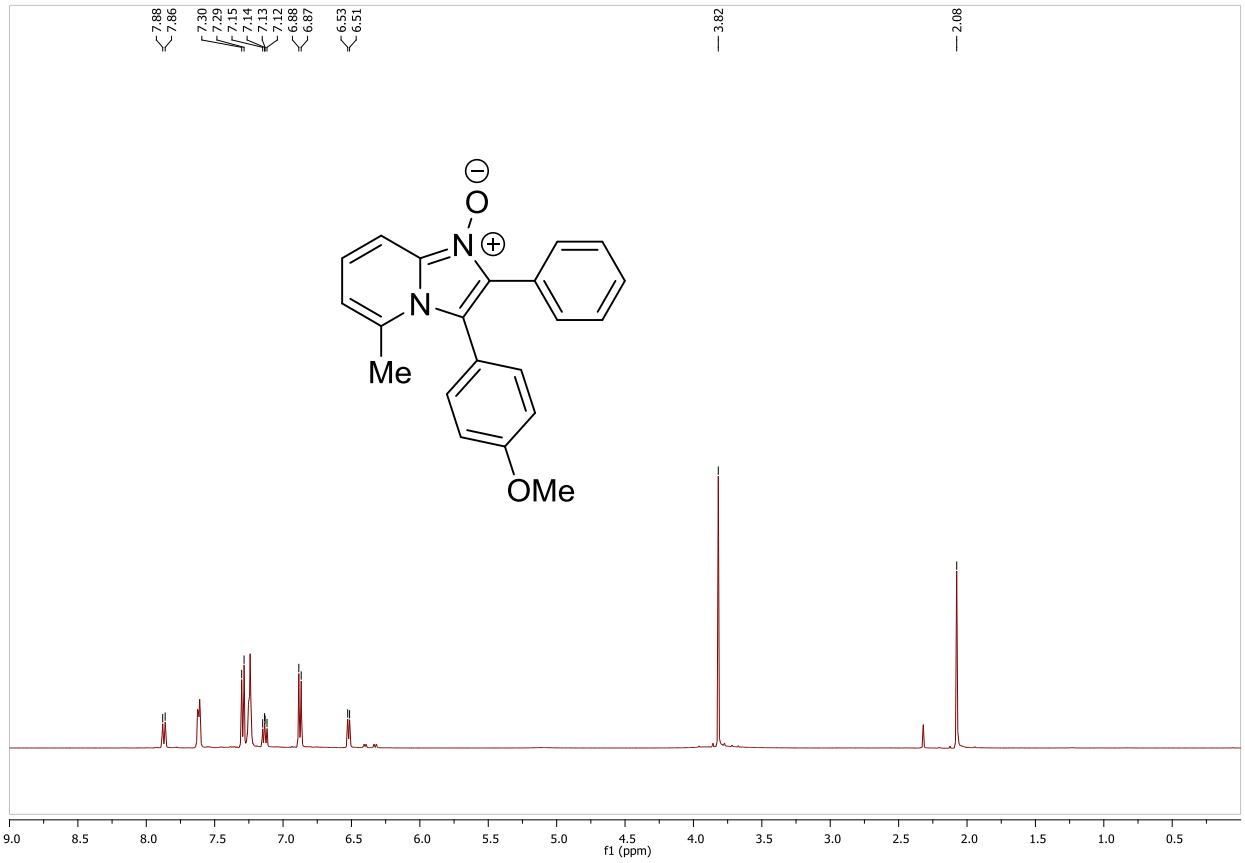
(3y)

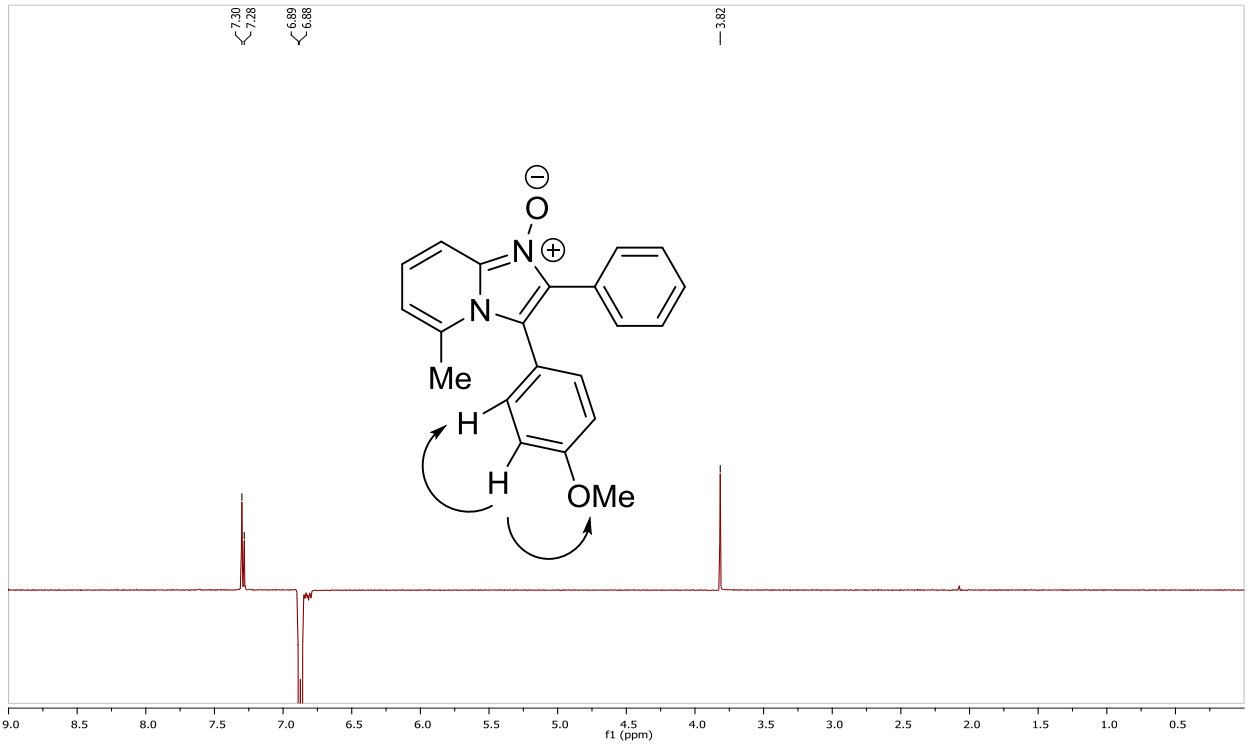

O
N
N
Me
OMe

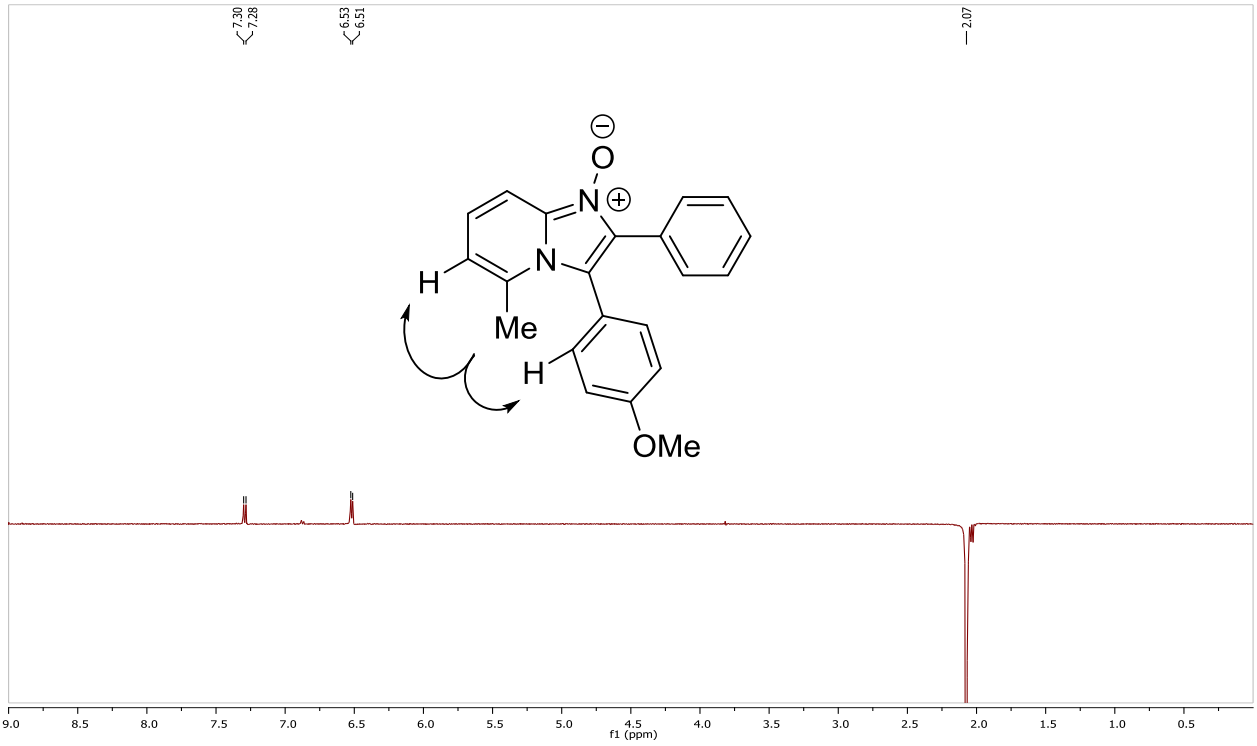

7.86
7.83
7.60
7.59
7.57
7.57
7.56
7.28
7.25
7.22
7.21
6.86
6.83
6.50
6.48
3.79
2.05
1.00
1.94
2.17
2.82
0.98
1.96
0.96
3.10
2.98
f1 (ppm)

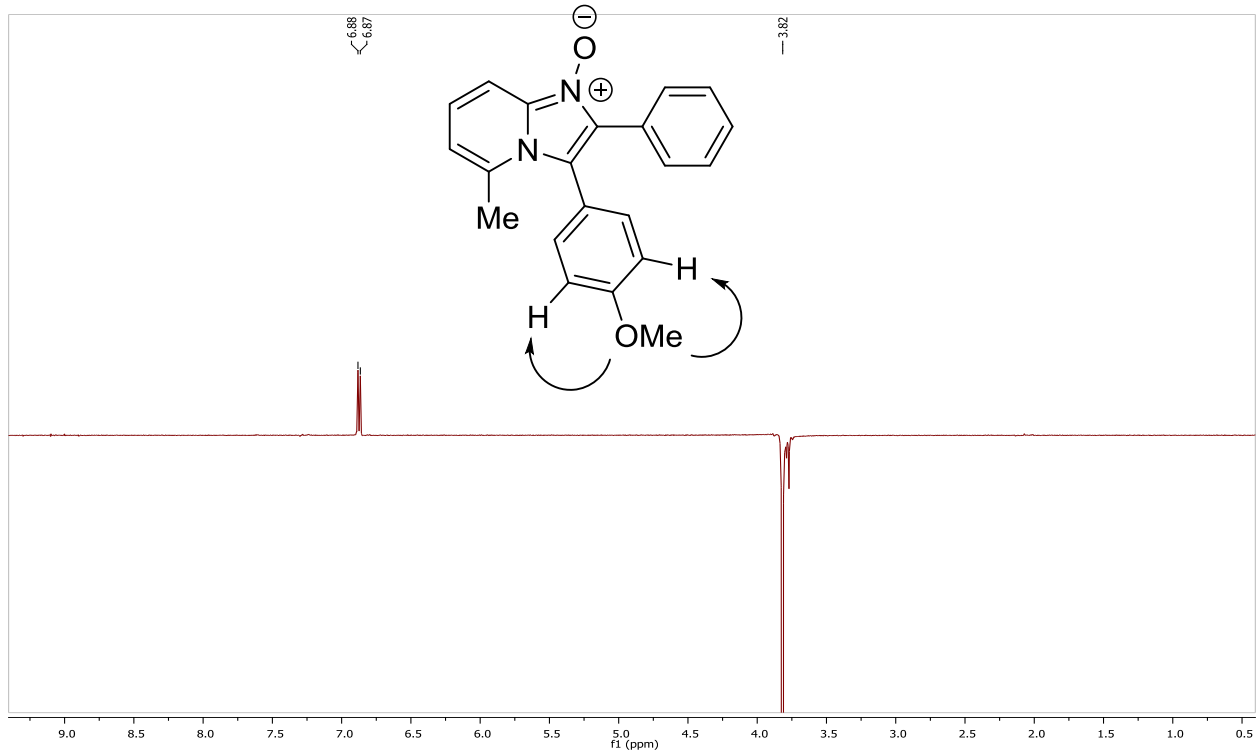

160.65
136.57
135.25
134.22
133.78
130.14
128.64
127.96
126.64
125.10
121.16
118.38
115.65
113.45
110.75
77.58
77.16
76.74
55.36
21.54
f1 (ppm)

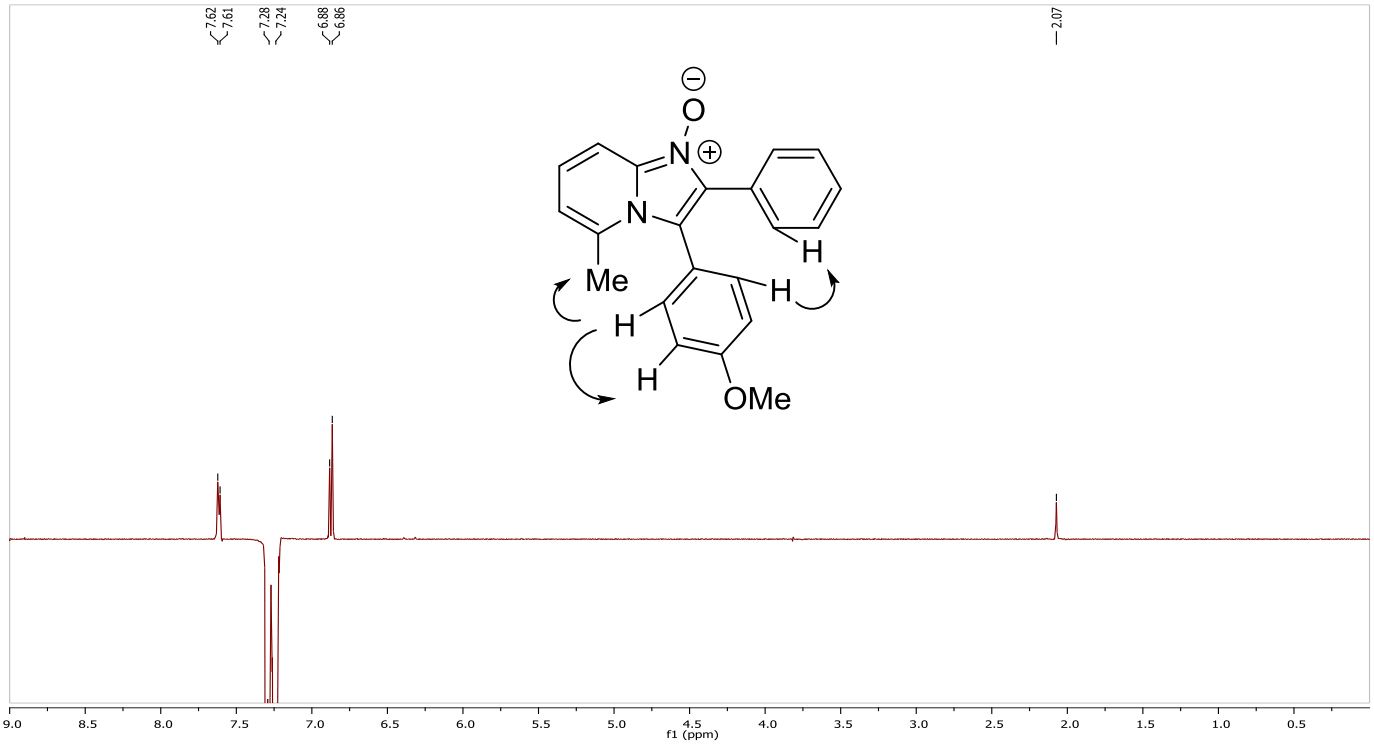
NOE of 3y


7.88
7.86
7.30
7.29
7.15
7.14
7.13
7.12
6.88
6.87
6.53
6.51
3.82
2.08
O
N
N
Me
OMe
f1 (ppm)

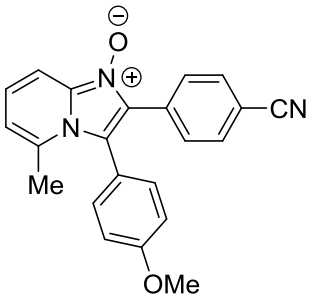

7.30
7.28
6.89
6.88
3.82
O
N
N
Me
H
H
OMe
f1 (ppm)

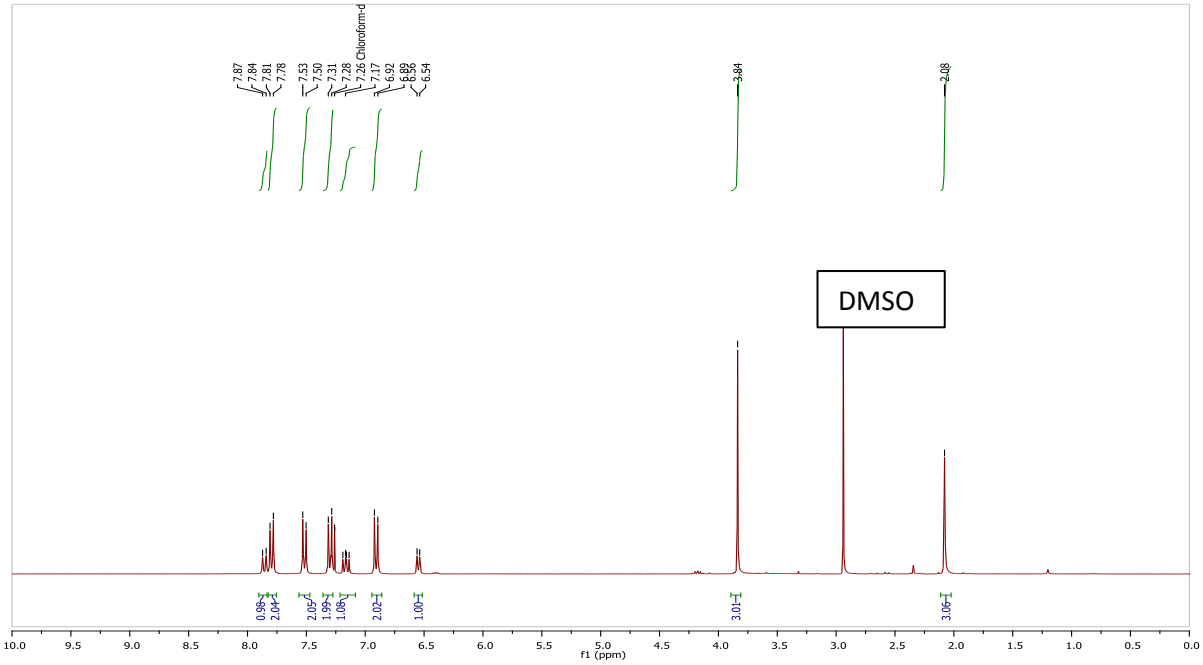

7.30
7.28
6.53
6.51
2.07
O
N
N
H
Me
H
OMe
f1 (ppm)

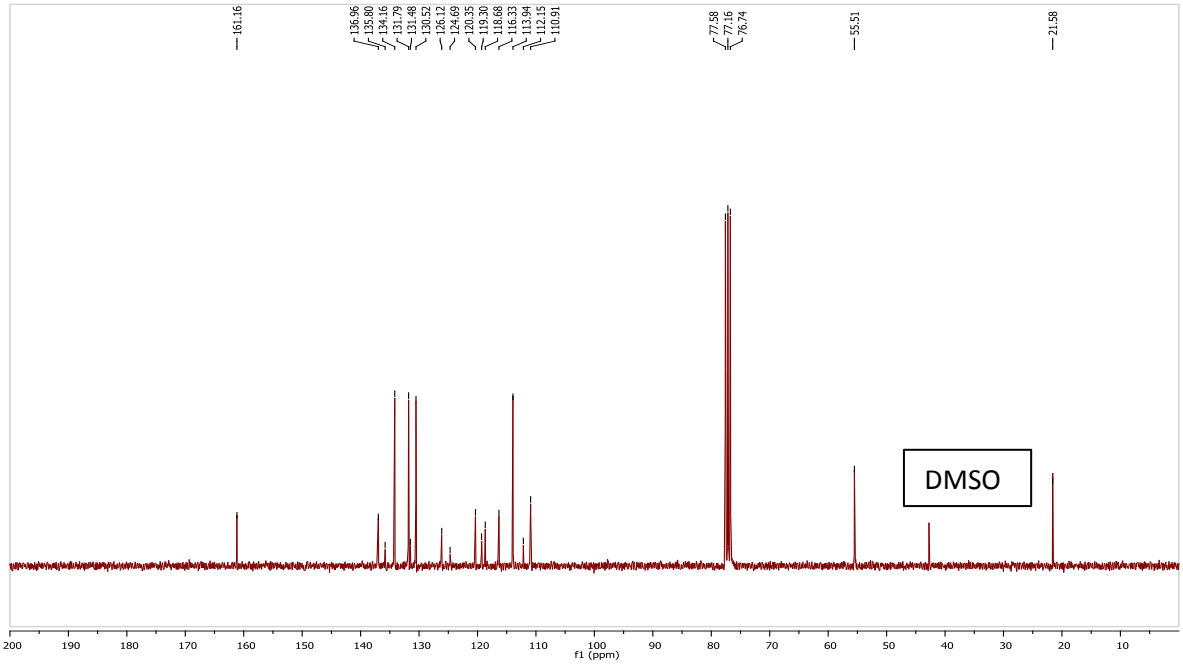

6.88
6.87
3.82
O
N
N
Me
H
H
OMe
f1 (ppm)


7.62
7.61
7.28
7.24
6.88
6.86
2.07
O
N
N
Me
H
H
H
H
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

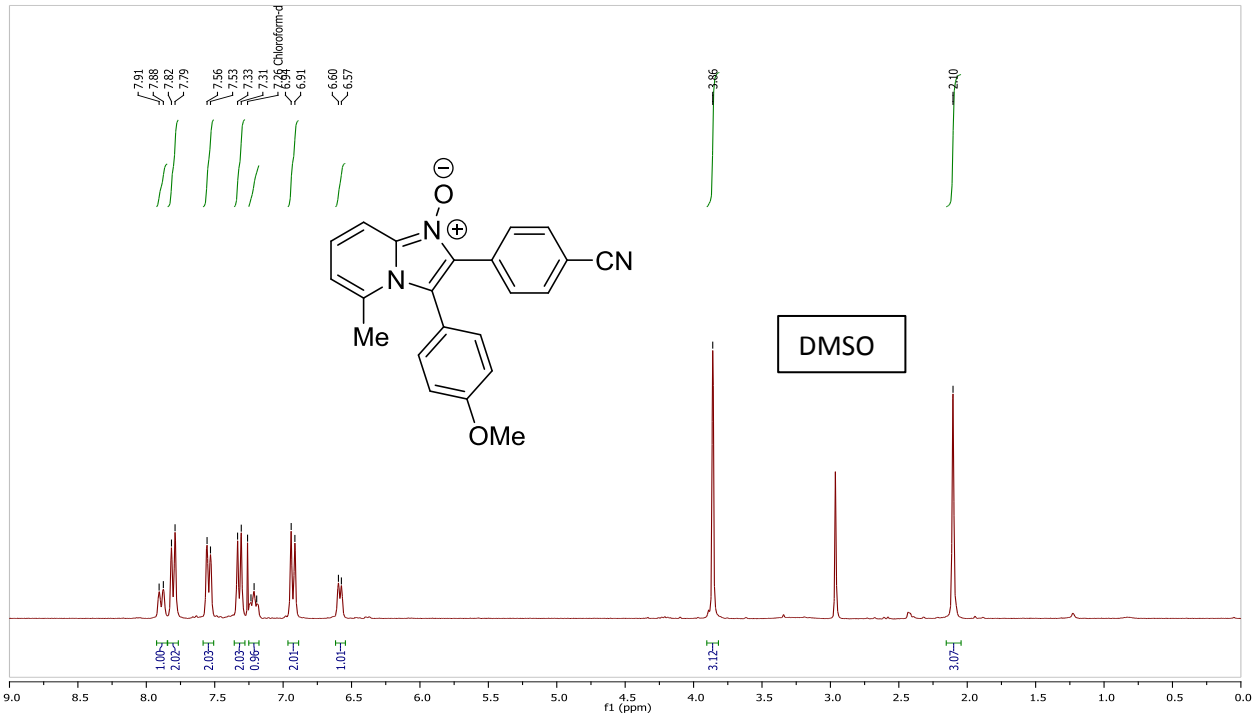
(3z)

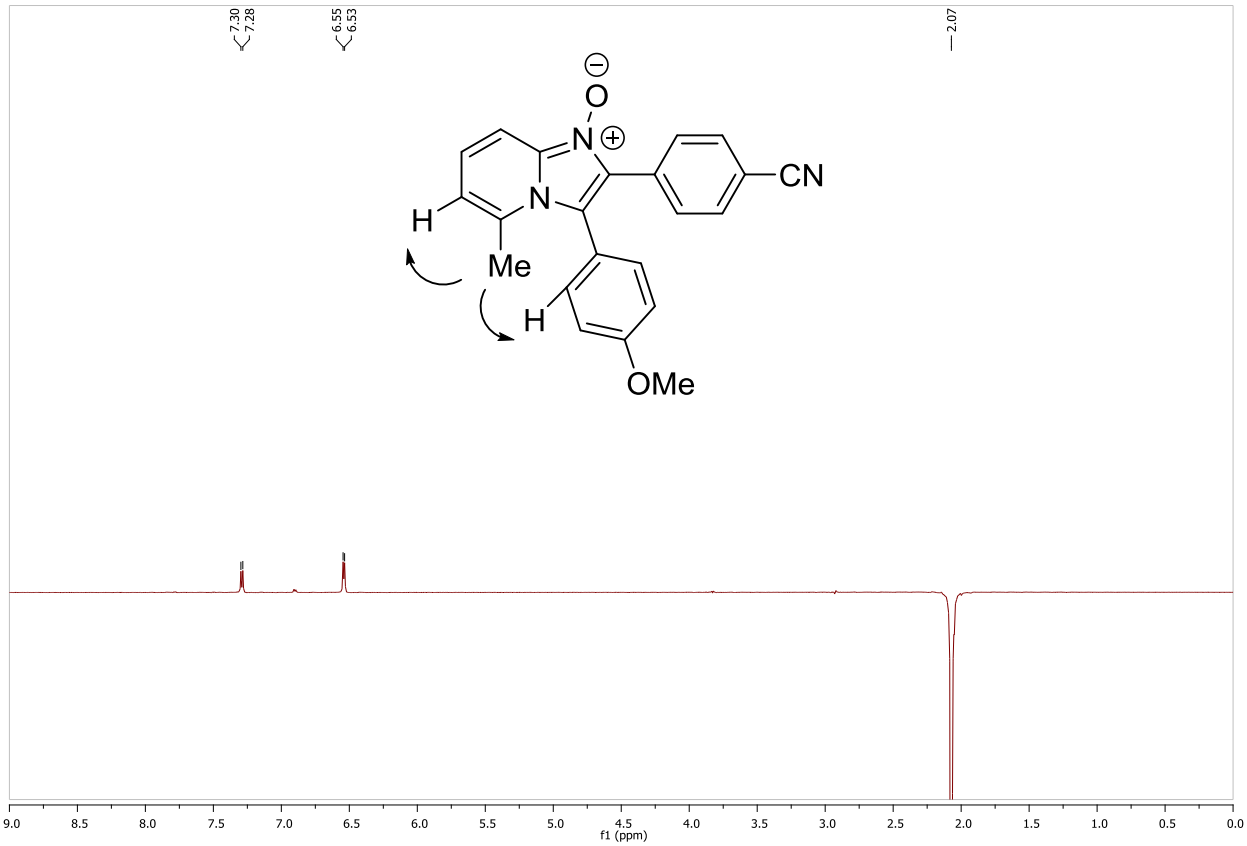

O
N
N
CN
Me
OMe

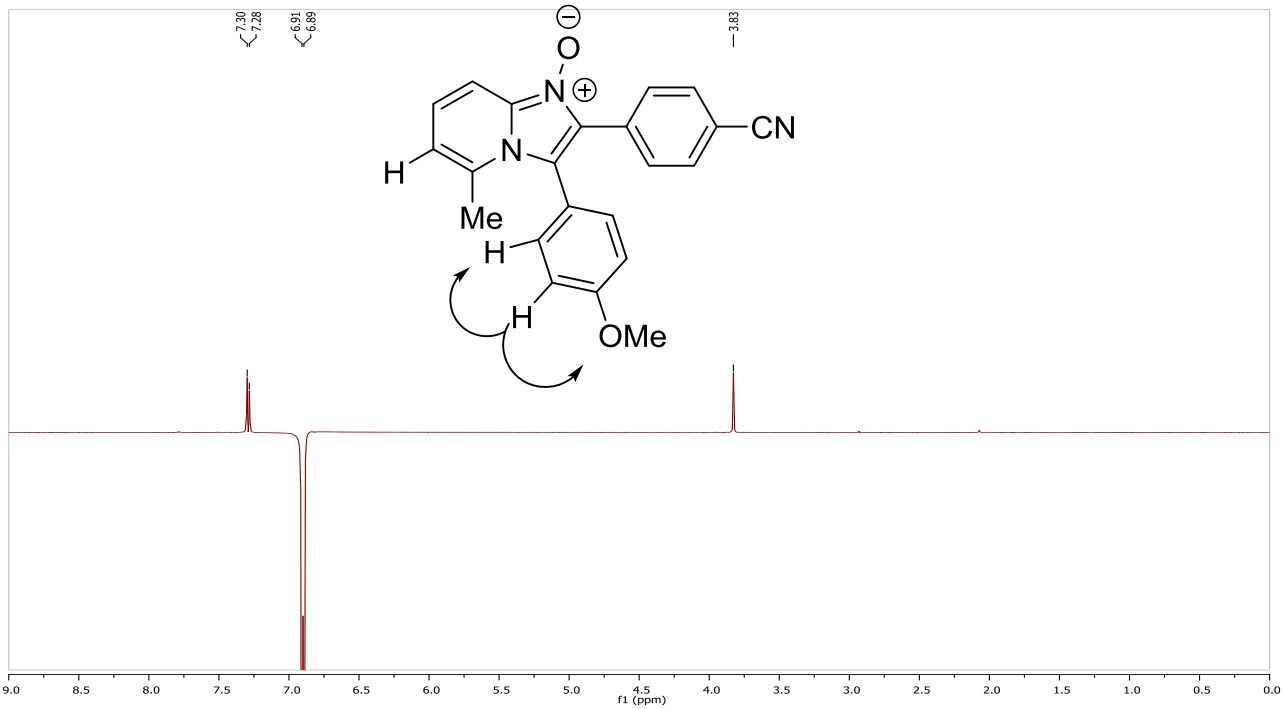

7.87
7.84
7.81
7.78
7.53
7.50
7.31
7.28
Chloroform-d
7.26
7.17
6.92
6.89
6.55
6.54
3.84
2.08
DMSO
0.98
2.04
2.05
1.99
1.08
2.02
1.00
3.01
3.06
f1 (ppm)

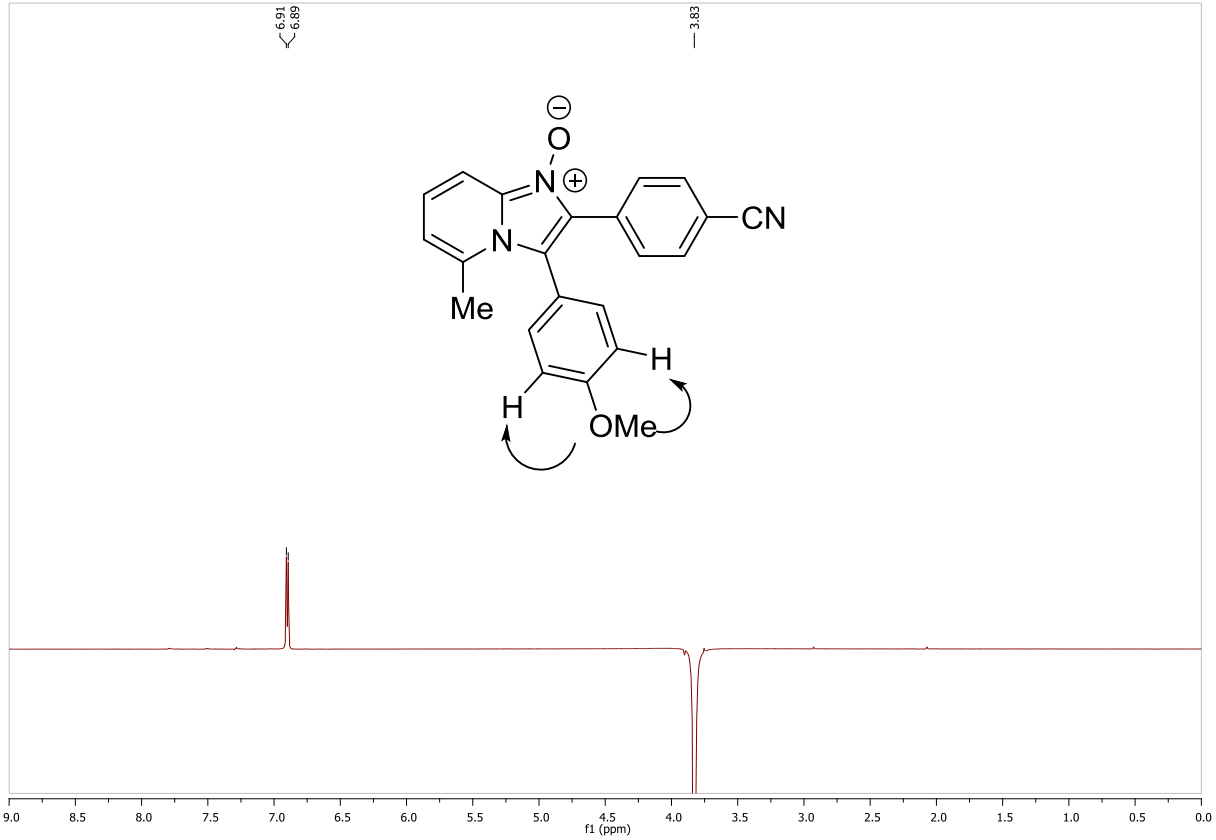

161.16
136.96
135.80
134.16
131.79
131.48
130.52
126.12
124.69
120.35
119.30
118.68
116.33
113.94
112.15
110.91
77.58
77.16
76.74
55.51
21.58
DMSO
f1 (ppm)

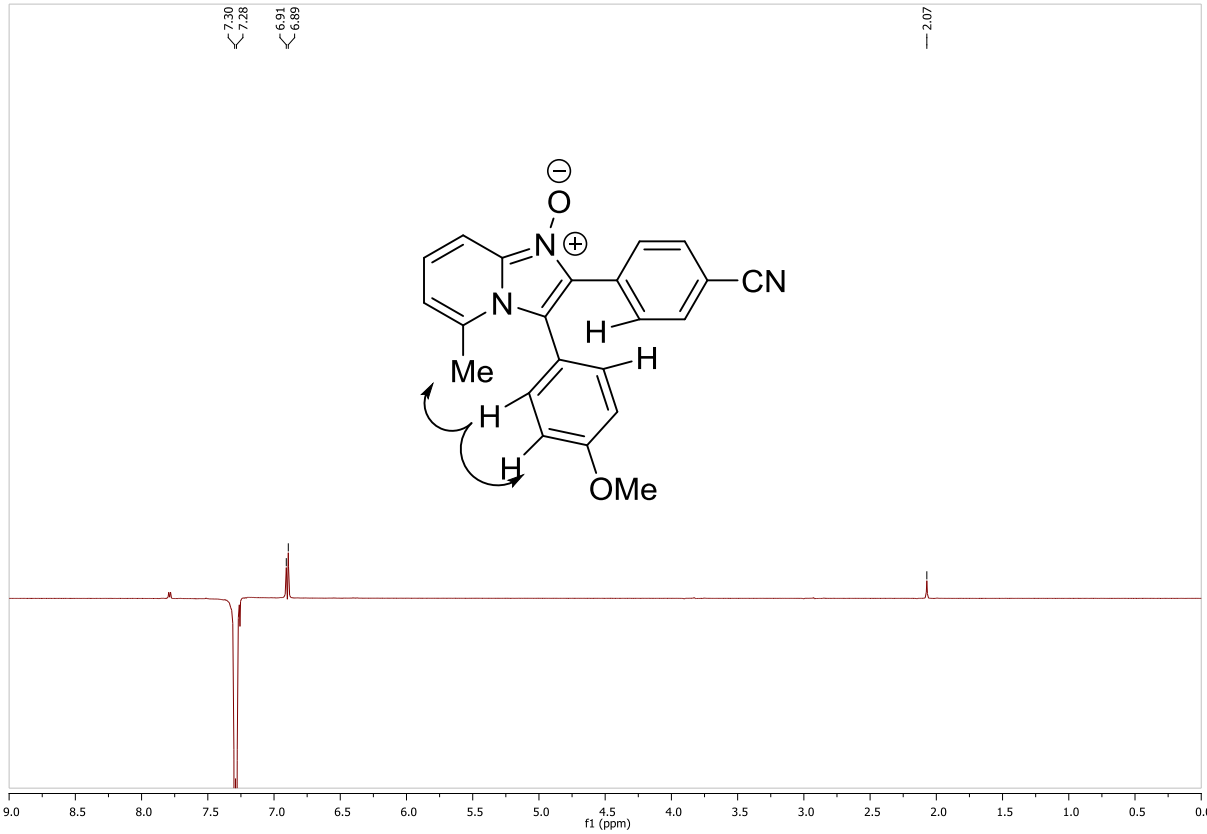
NOE of 3z


7.91
7.88
7.82
7.79
7.56
7.53
7.33
7.31
7.26 Chloroform-d
6.94
6.91
6.60
6.57
3.86
2.10
O
N
N
CN
Me
OMe
DMSO
1.00
2.02
2.03
2.03
0.96
2.01
1.01
3.12
3.07
f1 (ppm)

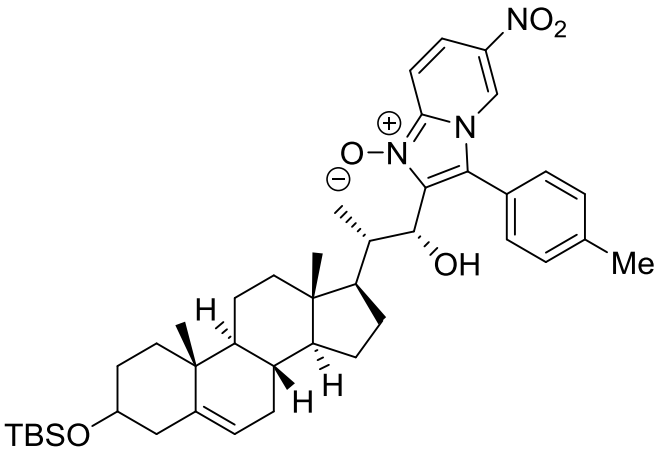

7.30
7.28
6.55
6.53
2.07
O
N
N
CN
H
Me
H
OMe
f1 (ppm)

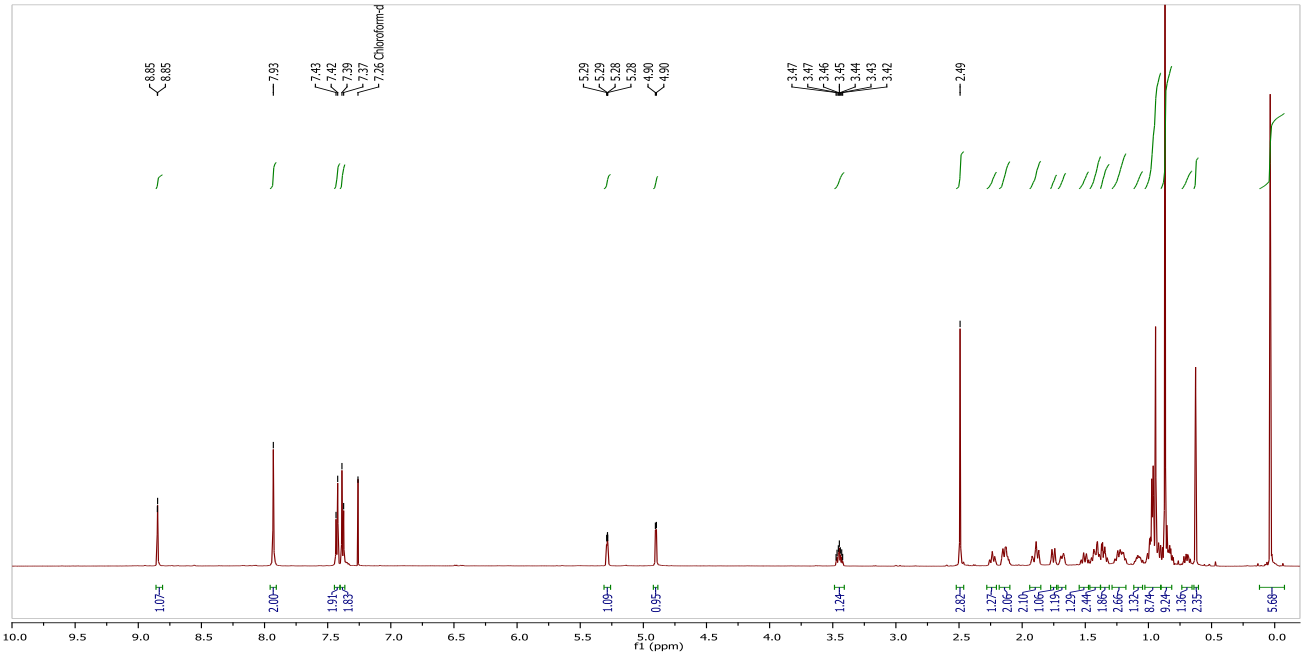

7.30
7.28
6.91
6.89
3.83
O
N
N
CN
H
Me
H
H
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

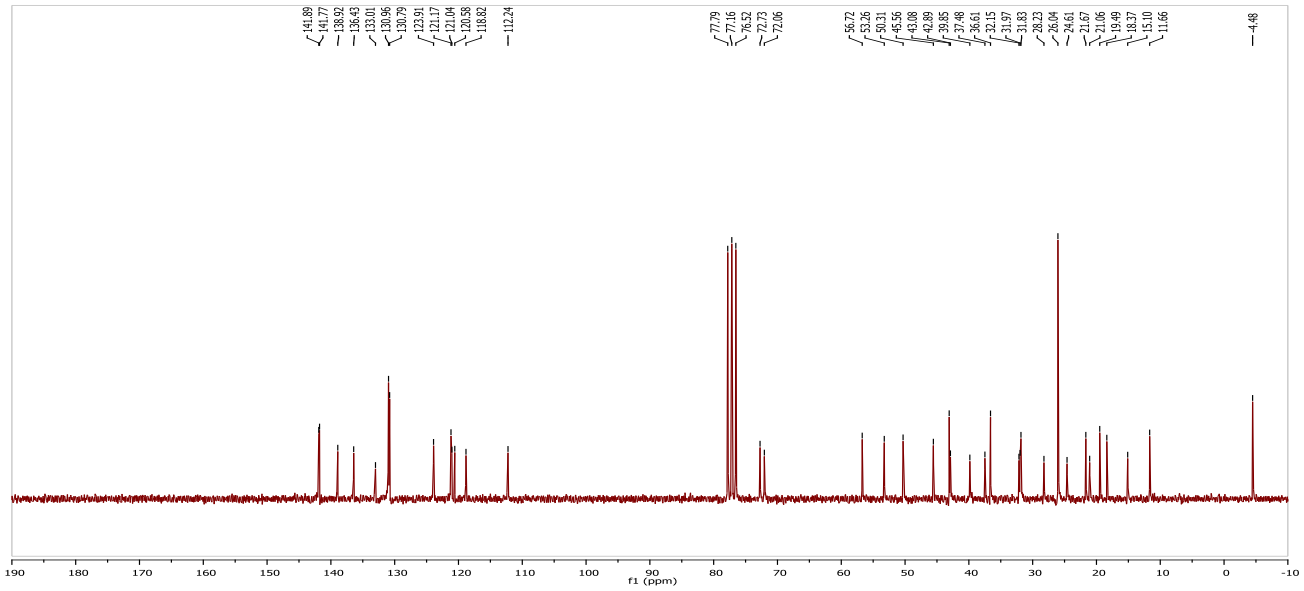

6.91
6.89
3.83
O
N
N
CN
Me
H
H
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.30
7.28
6.91
6.89
2.07
O
N
N
CN
H
H
Me
H
H
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

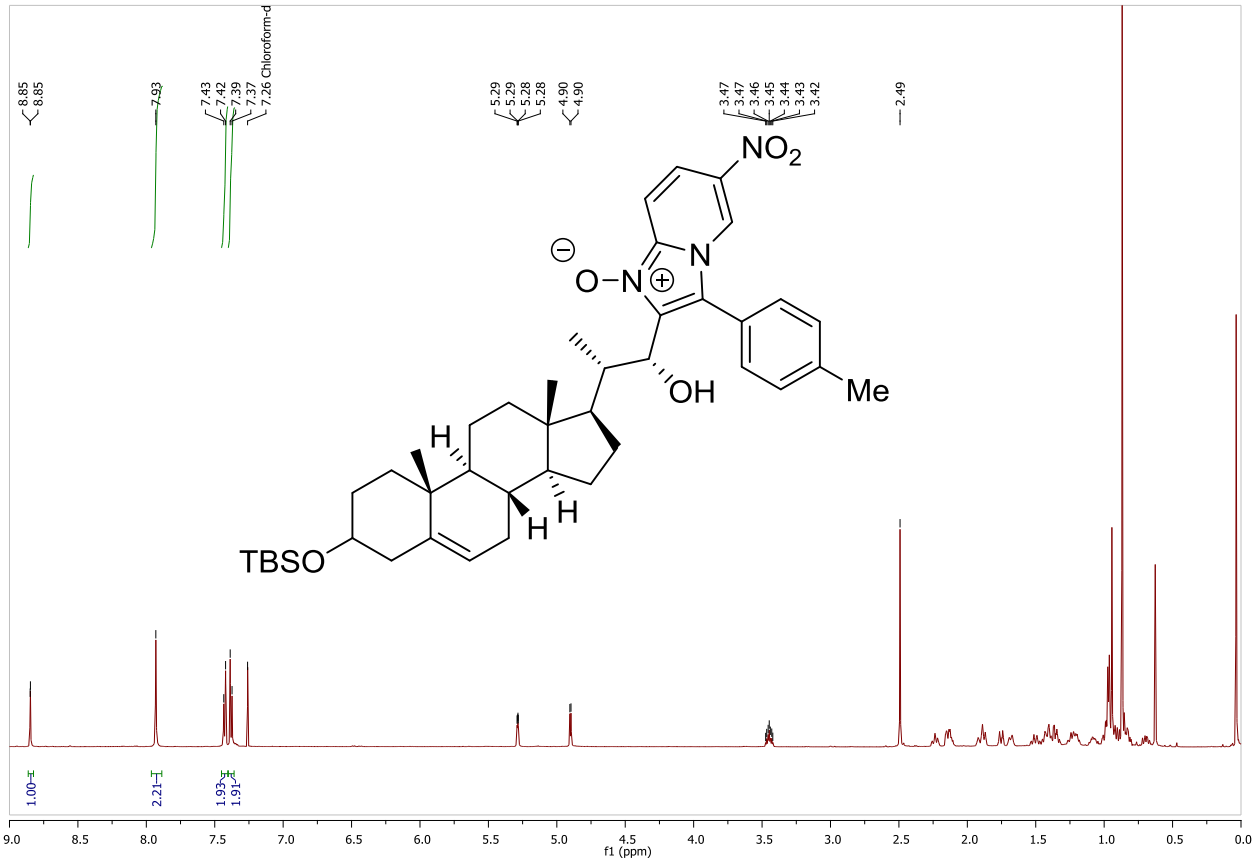
(3aa)

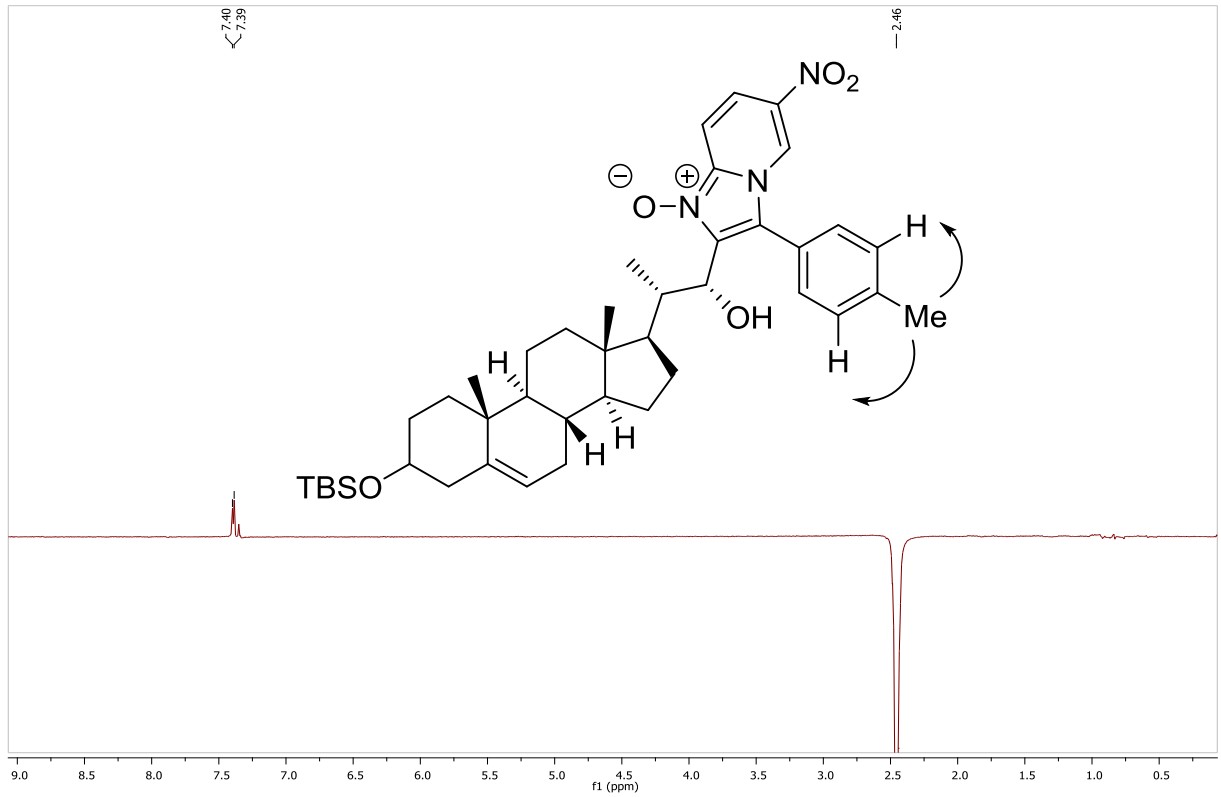

NO2
N
O−N
OH
Me
H
H
H
TBSO

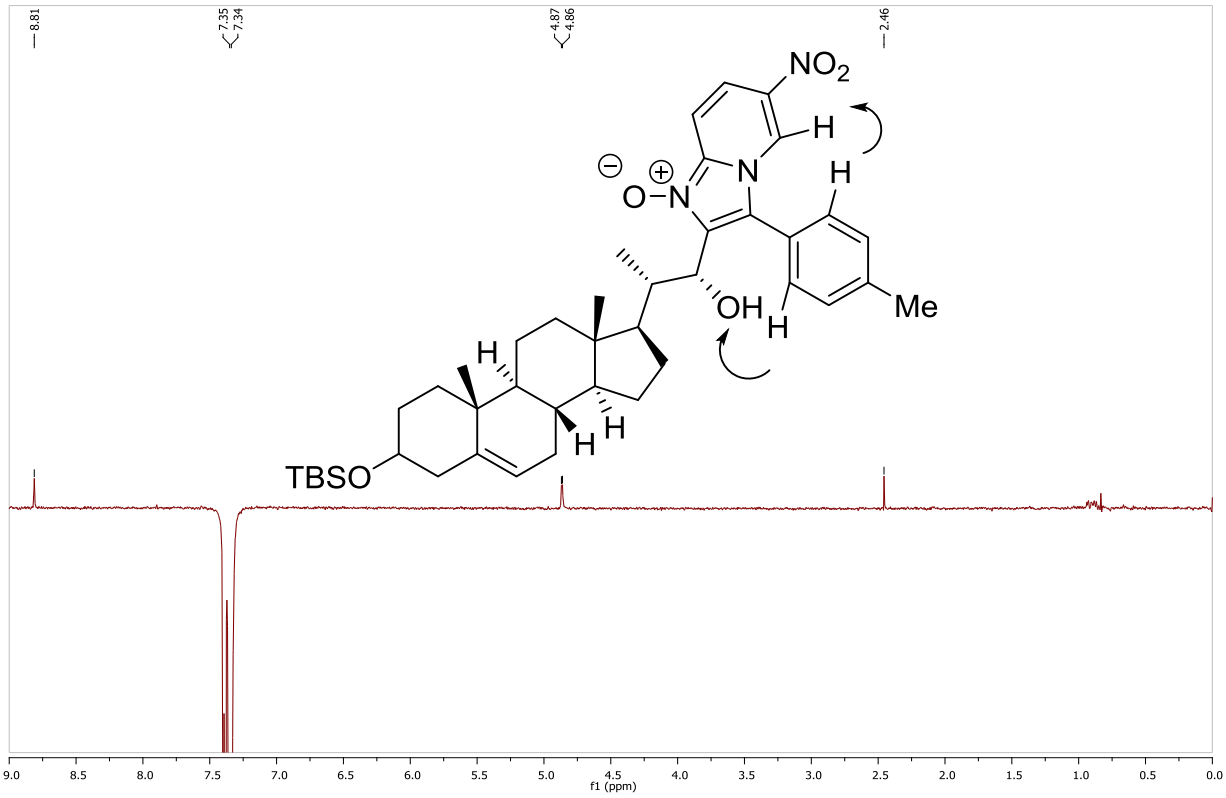

8.85
8.85
7.93
7.43
7.42
7.39
7.37
7.26 Chloroform-d
5.29
5.29
5.28
5.28
4.90
4.90
3.47
3.47
3.46
3.45
3.44
3.43
3.42
2.49
1.07
2.00
1.91
1.83
1.09
0.95
1.24
2.82
1.27
2.06
2.10
1.06
1.19
1.29
2.44
1.86
2.66
1.32
8.74
9.24
1.36
2.35
5.68
f1 (ppm)

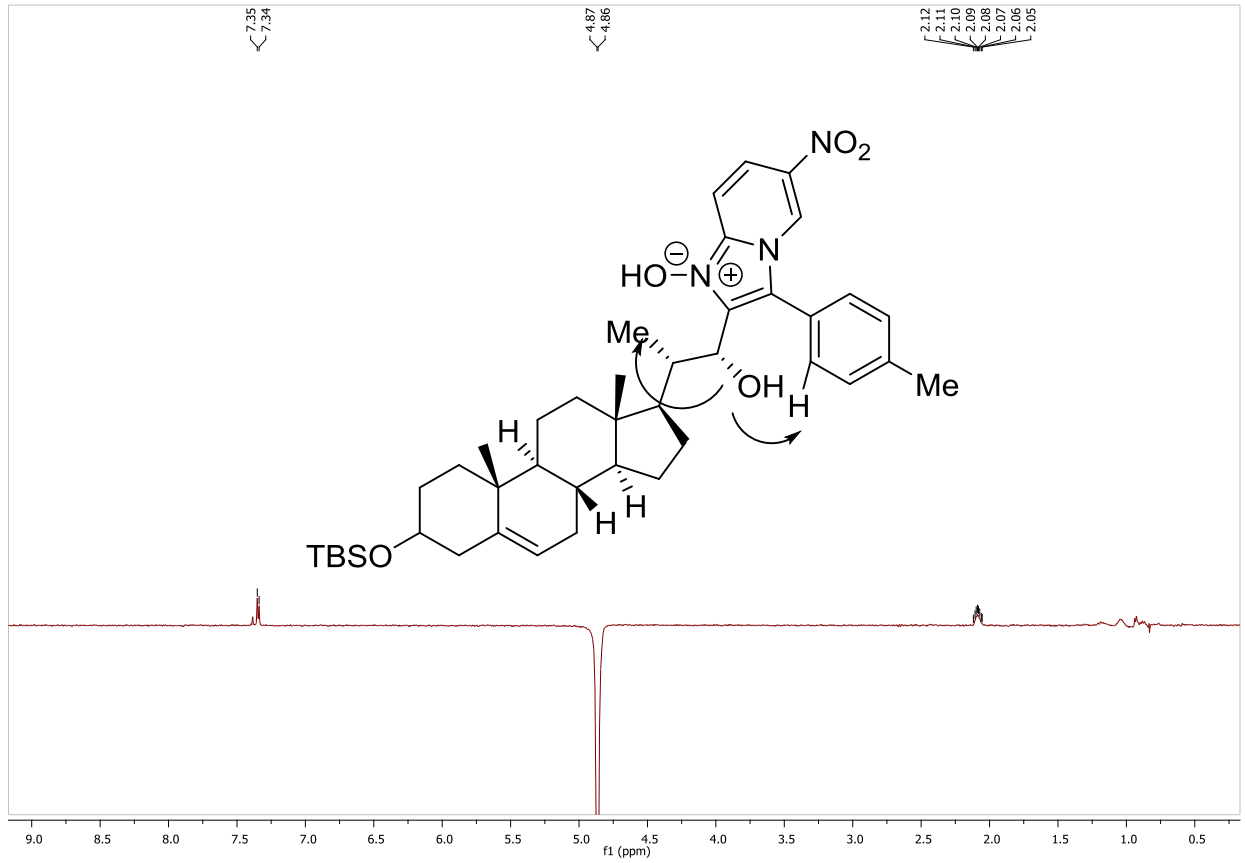

141.89
141.77
138.92
136.43
133.01
130.96
130.79
123.91
121.17
121.04
120.58
118.62
112.24
77.79
77.16
76.52
72.73
72.06
56.72
53.26
50.31
45.56
43.88
42.89
39.85
37.48
36.61
32.15
31.97
31.83
28.23
26.04
24.61
21.67
21.06
19.49
18.37
15.10
11.66
-4.48
f1 (ppm)

NOE of 3aa

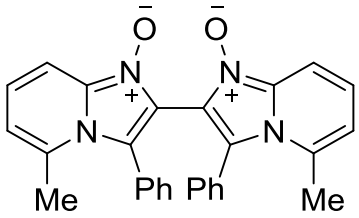

8.85
8.85
7.93
7.43
7.42
7.39
7.37
7.26 Chloroform-d
5.29
5.29
5.28
5.28
4.90
4.90
3.47
3.47
3.46
3.45
3.44
3.43
3.42
2.49
NO2
N
O−N
OH
Me
H
H
H
TBSO
1.00
2.21
1.93
1.91
f1 (ppm)

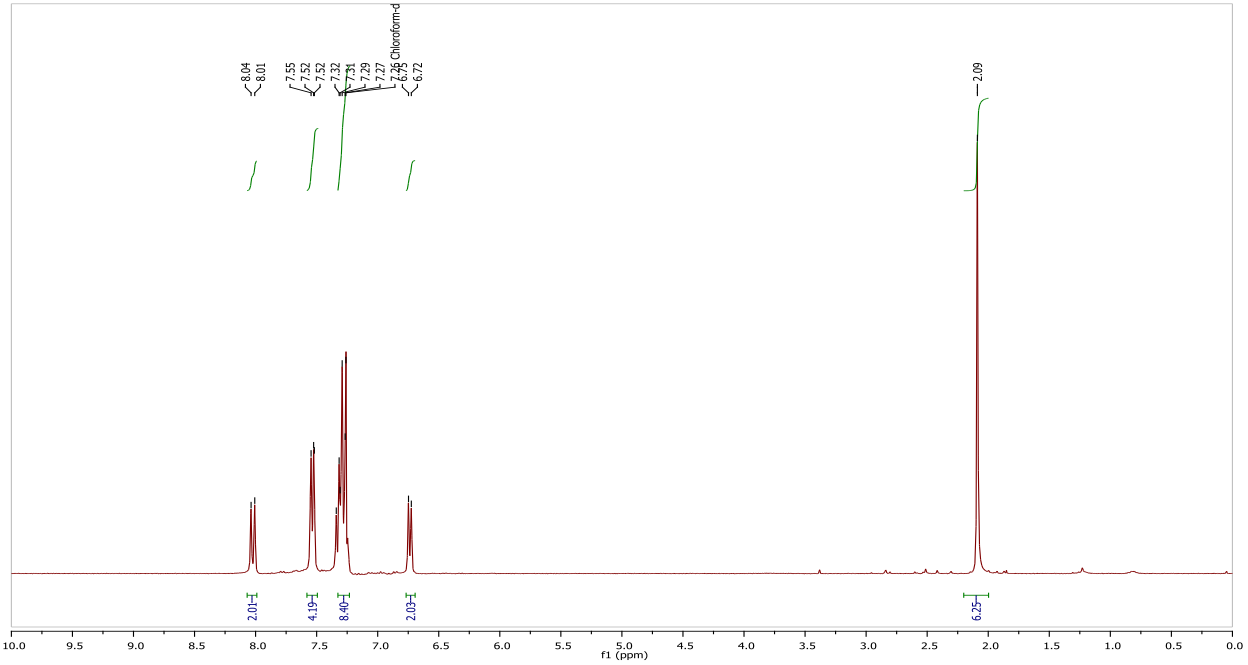

7.40
7.39
2.46
NO2
N
O−N
OH
H
Me
H
H
H
H
TBSO
f1 (ppm)

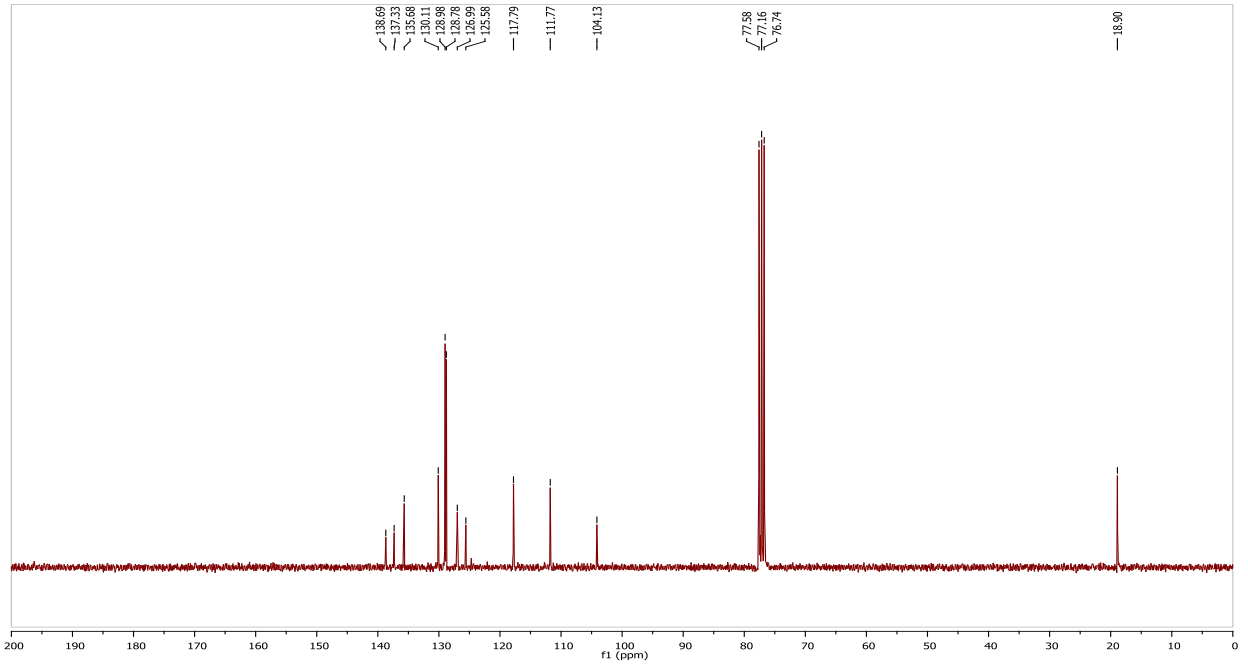

8.81
7.35
7.34
4.87
4.86
2.46
NO2
H
H
N
O−N
OH
H
Me
H
H
H
TBSO
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.35
7.34
4.87
4.86
2.12
2.11
2.10
2.09
2.08
2.07
2.06
2.05
NO2
N
HO−N
Me
OH
H
Me
H
H
H
TBSO
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

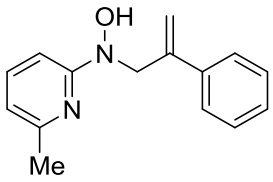
(3ab)

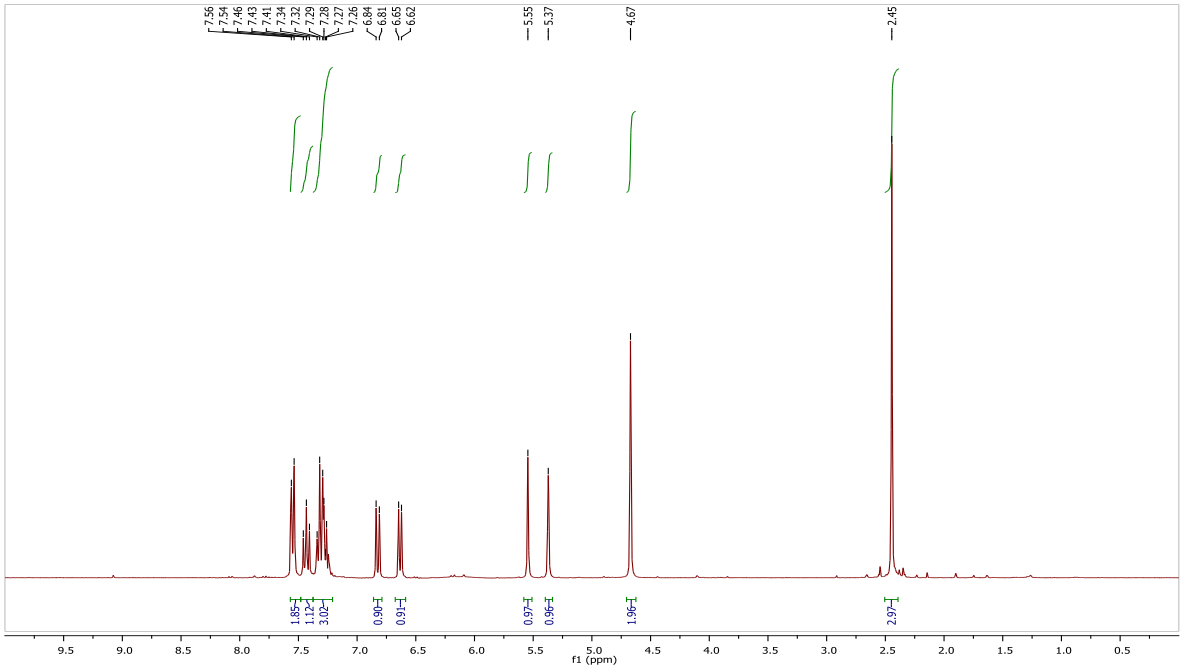

O
O
N
N
N
N
Me
Ph
Ph
Me

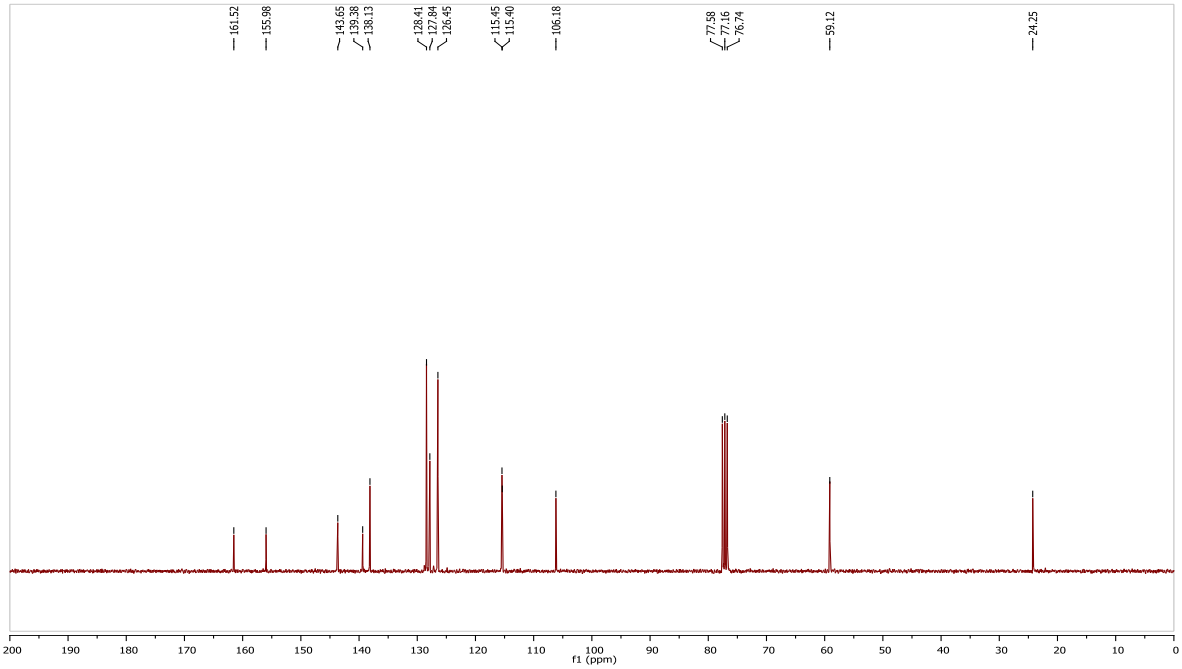

8.04
8.01
7.55
7.52
7.52
7.32
7.31
7.29
7.27
7.26 Chloroform-d
6.75
6.72
2.09
2.01
4.19
8.40
2.09
6.25
f1 (ppm)


138.69
137.33
135.68
130.11
128.98
128.78
126.99
125.58
117.79
111.77
104.13
77.58
77.16
76.74
18.90
f1 (ppm)

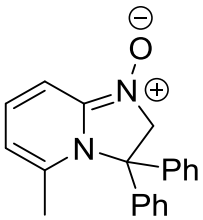
(4a)

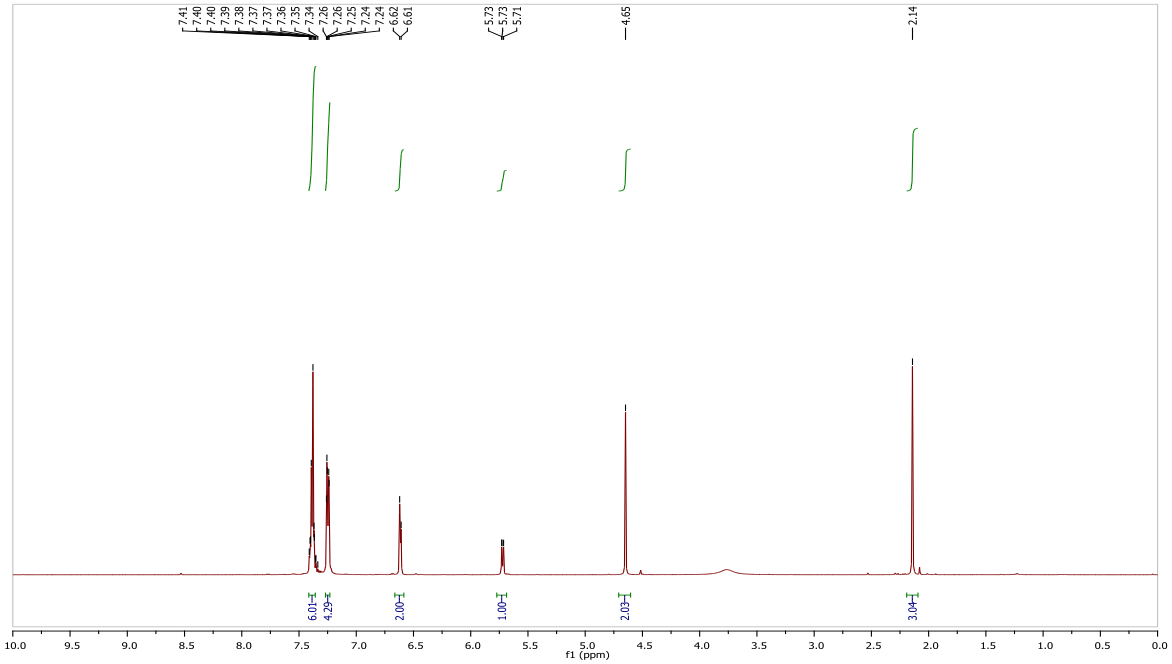

OH
N
N
Me

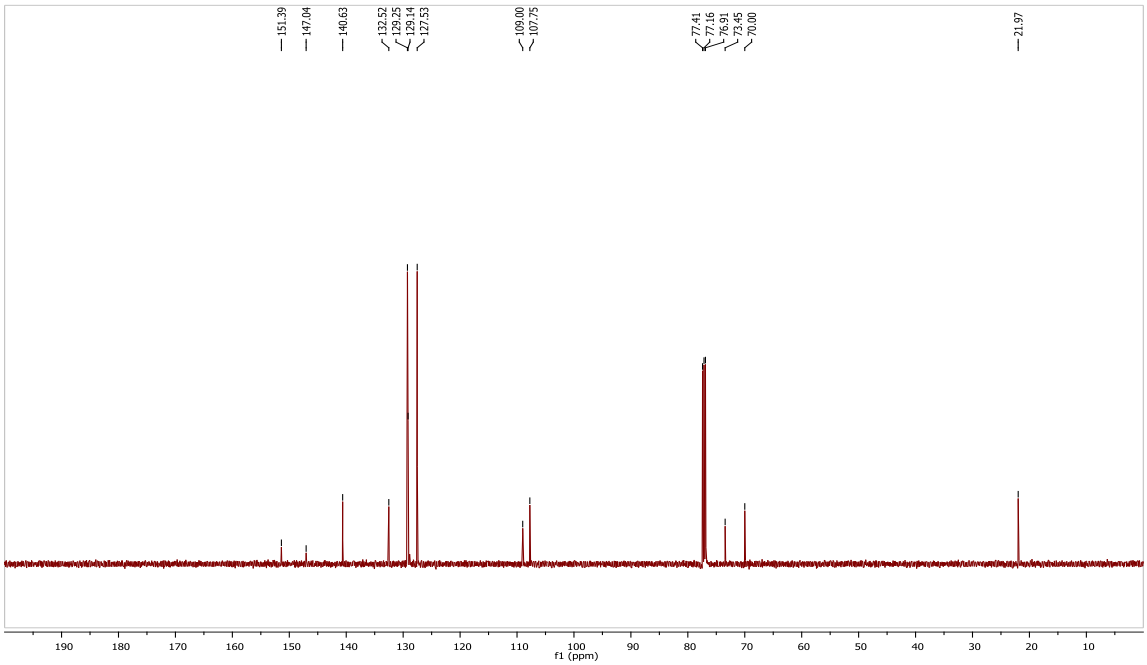

7.56
7.54
7.46
7.43
7.41
7.34
7.32
7.29
7.28
7.27
7.26
6.84
6.81
6.65
6.62
5.55
5.37
4.67
2.45
1.85
1.12
3.02
0.90
0.91
0.97
0.96
1.96
2.97
f1 (ppm)


161.52
155.98
143.65
139.38
138.13
128.41
127.84
126.45
115.45
115.40
106.18
77.58
77.16
76.74
59.12
24.25
f1 (ppm)

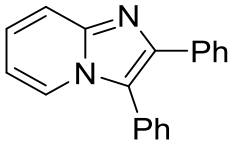
(4b)

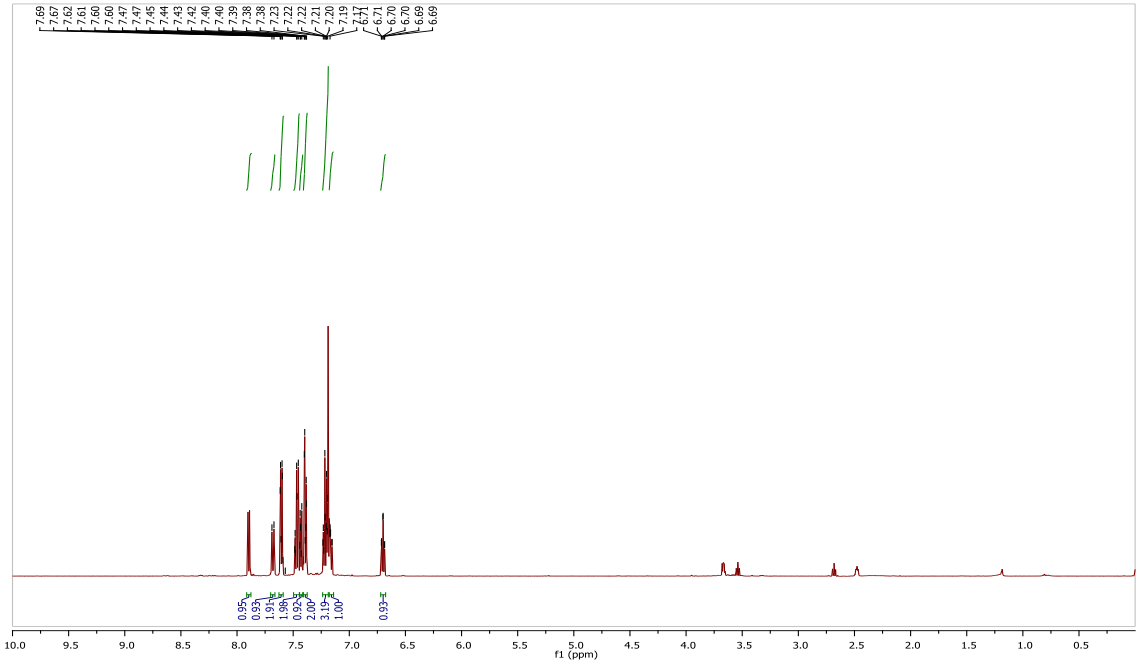

O
N
N
Ph
Ph

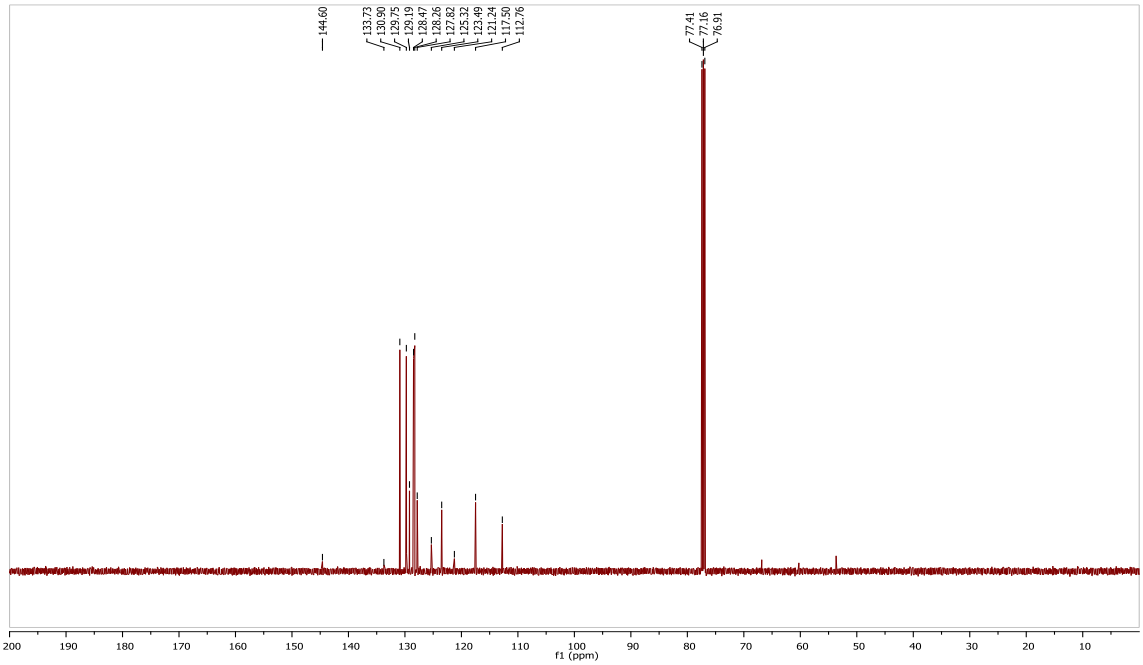

7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.26
7.26
7.25
7.24
7.24
6.62
6.61
5.73
5.73
5.71
4.65
2.14
6.01
4.29
2.00
1.00
2.03
3.04
f1 (ppm)


151.39
147.04
140.63
132.52
129.25
129.14
127.53
109.00
107.75
77.41
77.16
76.91
73.45
70.00
21.97
f1 (ppm)

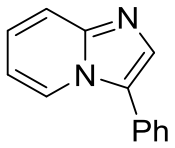
(5a)

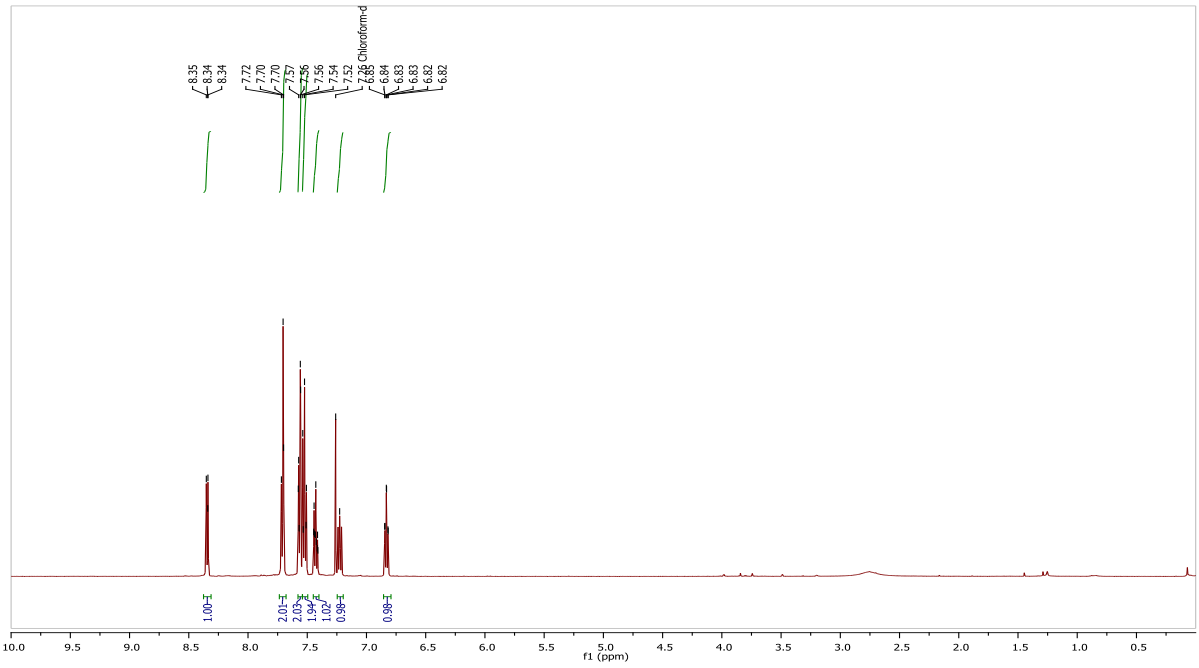

N
Ph
N
Ph

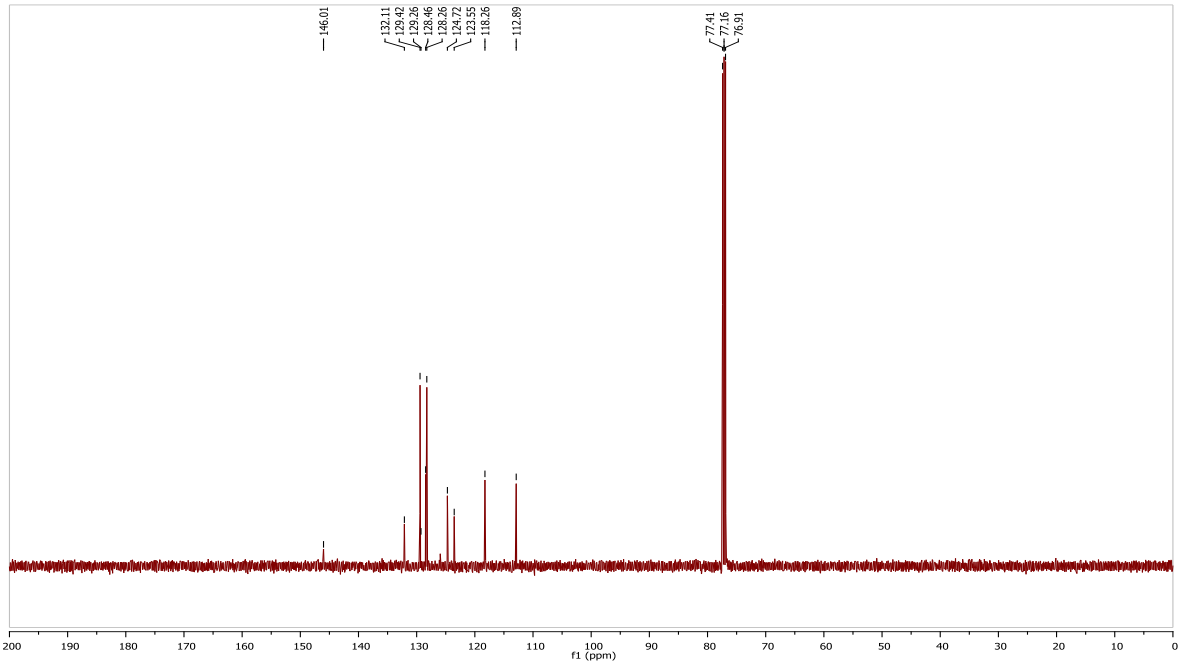

7.69
7.67
7.62
7.61
7.60
7.60
7.60
7.47
7.47
7.45
7.44
7.43
7.42
7.40
7.40
7.39
7.38
7.38
7.23
7.22
7.22
7.21
7.20
7.19
7.17
6.71
6.71
6.70
6.70
6.69
6.69
0.95
0.93
1.91
1.98
0.92
2.00
3.19
1.00
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


144.60
133.73
130.90
129.75
129.19
128.47
128.26
127.82
125.32
123.49
121.24
117.30
112.76
77.41
77.16
76.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

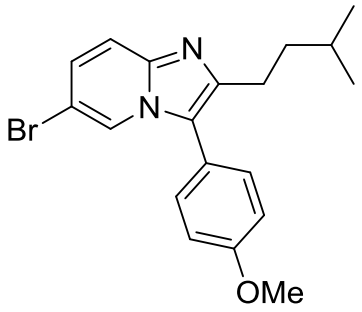
(5b)

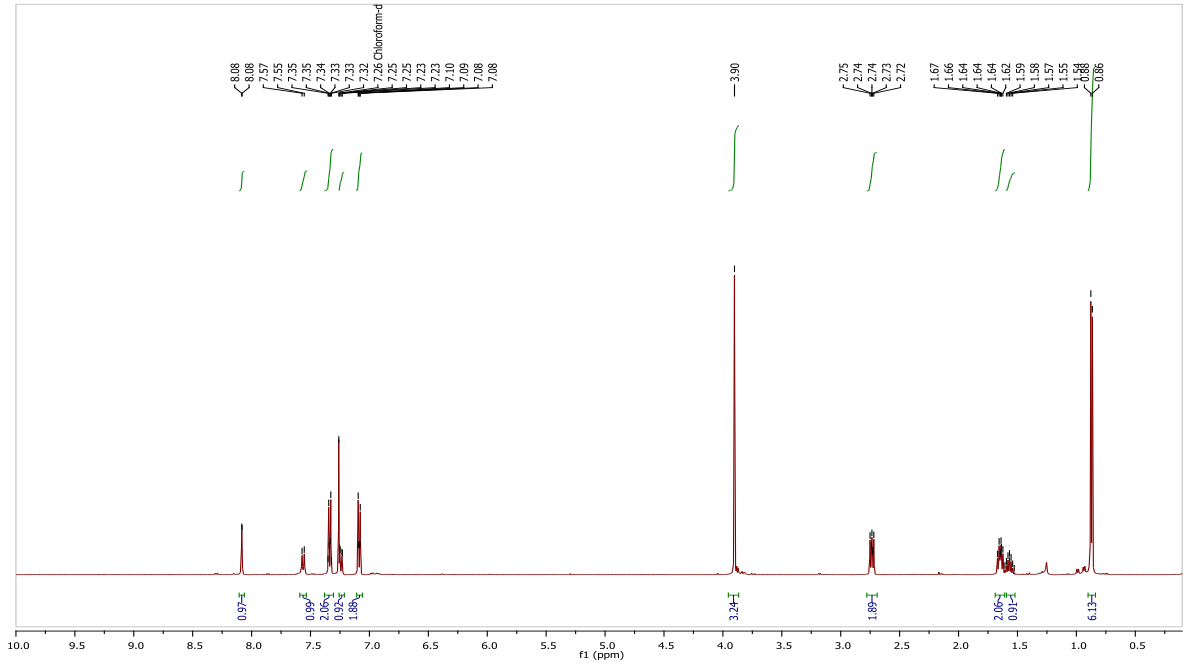

N
N
Ph

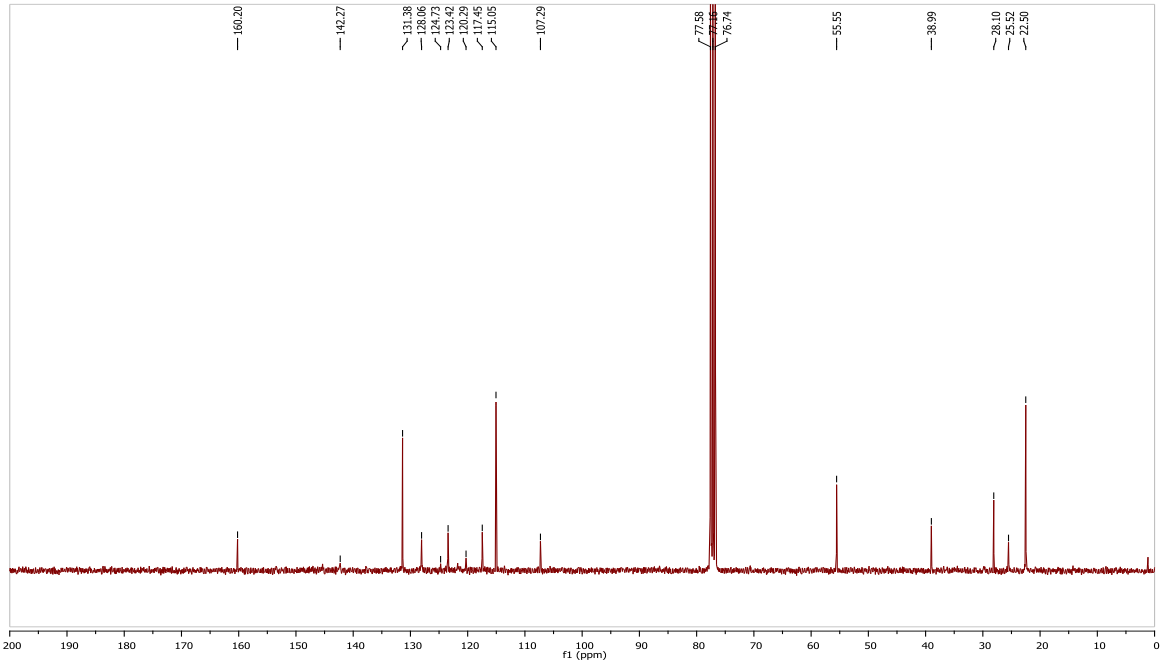

8.35
8.34
8.34
7.72
7.70
7.70
7.57
7.56
7.56
7.54
7.52
7.26 Chloroform-d
6.85
6.84
6.83
6.83
6.82
6.82
1.00
2.01
2.03
1.94
1.02
0.98
0.98
f1 (ppm)


146.01
132.11
129.42
129.26
128.46
128.26
124.72
123.55
118.26
112.89
77.41
77.16
76.91
f1 (ppm)

(5c)


N
N
Br
OMe


8.08
8.08
7.57
7.55
7.35
7.35
7.34
7.33
7.33
7.32
7.26 Chloroform-d
7.25
7.25
7.23
7.23
7.10
7.09
7.08
7.08
3.90
2.75
2.74
2.74
2.73
2.72
1.67
1.66
1.64
1.64
1.64
1.62
1.59
1.58
1.57
1.55
0.88
0.86
0.97
0.99
2.06
0.92
1.88
3.24
1.89
2.06
0.91
6.13
f1 (ppm)


160.20
142.27
131.38
128.06
124.73
123.42
120.29
117.45
115.05
107.29
77.58
77.16
76.74
55.55
38.99
28.10
25.52
22.50
f1 (ppm)