Supporting Information

Iron(III) Tetra(pentafluorophenyl)porpholactone Catalyzes Nitrogen Atom Transfer to C=C and C-H Bonds with Organic Azides

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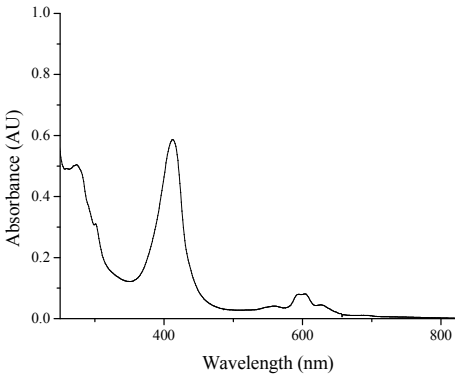
1. General Information

All reactions were performed under oxygen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. Dichloromethane (DCM), 1,2-dichloroethane (DCE), acetonitrile, and Chlorobenzene were distilled over calcium hydride, THF and toluene were distilled over sodium. For chromatography, 200-300 mesh silica gel (Qindao, China) was employed. ^{1}H NMR spectra were recorded at 300 MHz with Varian Mercury 300 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. FTIR spectra were obtained in the range of 4000−600 cm^{-1} on a Nicolet Magna 750 FT/IR spectrometer. ESI-MS spectra were recorded with Bruker Apex IV FTMS spectrometer. UV-Vis spectra were recorded with Agilent 8453 UV-vis spectrometer. **Caution! Organic azides are potentially explosive and should be handled with great care.** N-Tosyliminophenyliodinane (PhINTs)[1], Organic azides[2], [Fe(F_{20}TPPL)Cl], [Mn(F_{20}TPP)Cl][3] were prepared by the literature methods.

Synthesis of [Fe(F_{20}-TPPL)Cl]: Preparation of H_2F_{20}TPPL was according to Gouterman's method[4] using gold salt to replace $AgNO_3$. [Fe(F_{20}TPPL)Cl] was obtained by refluxing the metal-free base with ferrous chloride in acetic acid. UV-vis: 412 nm, 558, 592, 603 and 628 nm. HRMS (ESI) m/z for $C_{43}H_6F_{20}N_4O_2Fe$ (M^+) calcd 1045.9516, found 1045.9525.

UV-vis



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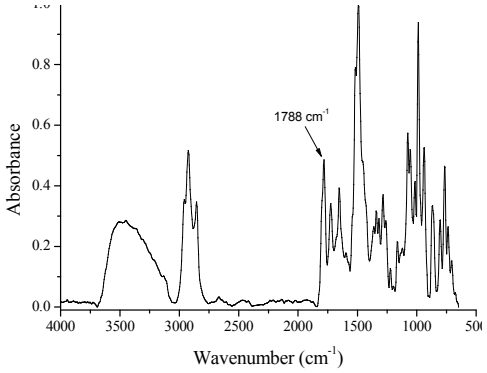
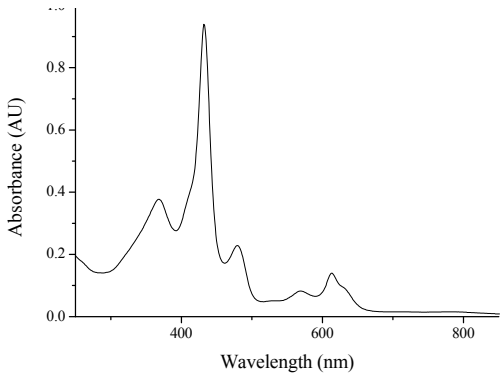
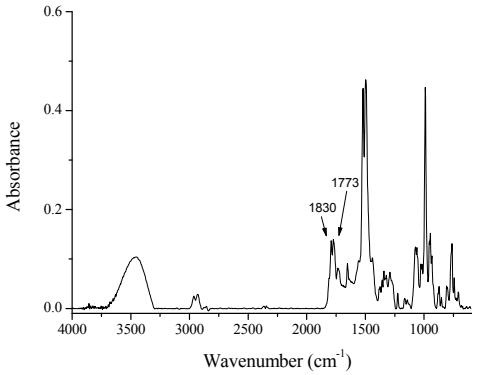


Synthesis of [Mn(F_{20}-TPPL)Cl]: [Mn(F_{20}TPPL)Cl] was obtained by refluxing the metal-free base with manganese(II) chloride in DMF. UV-vis: 368, 432, 479, 569 and 613nm. HRMS (ESI) m/z for $C_{43}H_6F_{20}N_4O_2Mn$ (M^+) calcd 1044.9546, found 1044.9529.

UV-vis



FTIR



2. Experimental procedure

2.1 Typical procedures of [Fe(F_{20}TPPL)Cl] catalytic reactions

General procedure for aziridination of alkenes: 1,2-Dichloroethane (2 mL) was added to a mixture of alkene (0.60 mmol), azide (0.20 mmol), catalyst (0.001 mmol), and 4Å molecular sieves (120 mg). Then the reaction mixture was heated to 80^{o}C under nitrogen atmosphere. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (PE: EA = 10:1).

General procedure for aziridination of Fullerene: 1,2-Dichloroethane (2 mL) was added to a mixture of Fullerene (0.20 mmol), azide (0.20 mmol), catalyst (0.001 mmol), and 4Å molecular sieves (120 mg). Then the reaction mixture was heated to 80^{o}C under nitrogen atmosphere. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (Toluene: Petroleum ether = 1:1) to get *N*-tosyl[1,2]aziridino[60]fullerene.

General procedure for aziridination of alkanes and thioanisole: 1,2-Dichloroethane (2 mL) was added to a mixture of alkane/thioanisole (1.00 mmol), azide (0.20 mmol), catalyst (0.001 mmol), and 4Å molecular sieves (120 mg). Then the reaction mixture was heated to 80^{o}C under nitrogen atmosphere. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (PE: EA = 10:1).

2.2 Optimization of reaction condition for aziridination of styrene

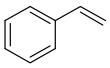
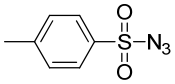
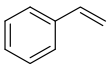
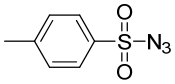
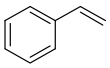
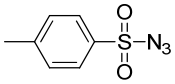
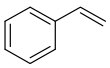
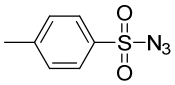
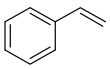
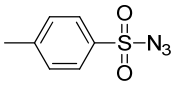
Table S1. Optimization and typical procedure for aziridination of styrene[a]

Entry	Cat	mol(%)	solvent[b]	T (^{o}C)	Time(h)	Yield (%)[c]
1	Fe(F_{20}-TPPL)Cl	0.5	DCE	80	12	**87**
2	Fe(F_{20}-TPPL)Cl	1	DCE	80	12	88
3	Fe(F_{20}-TPPL)Cl	0.5	DCE	80	24	84
4	Fe(F_{20}-TPPL)Cl	0.5	DCE	80	6	50
5	Fe(F_{20}-TPPL)Cl	0.5	DCM	40	12	23
6	Fe(F_{20}-TPPL)Cl	0.5	CH_3CN	60	12	33
7	Fe(F_{20}-TPPL)Cl	0.5	Toluene	100	12	36
8	Fe(F_{20}-TPPL)Cl	0.5	C_6H_5Cl	100	12	43
9	Fe(F_{20}-TPPL)Cl	0.5	DCE	30	12	15
10	Fe(F_{20}-TPPL)Cl	0.5	DCE	60	12	50

[a] Performed under N_2 in the presence of 4Å molecule sieves: [styrene] =2.0 mmol/2 mL; styrene/azide = 3:1. [b] DCE = 1,2-dichloroethane, DCM = dichloromethane. [c] isolated yields.

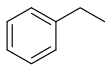
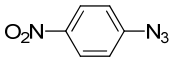
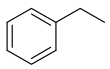
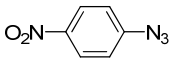
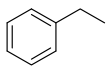
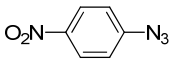
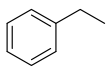
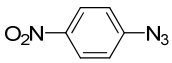
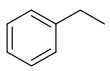
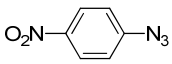
2.3 Control experiments and comparison of different catalysts

Table S2. Control Experiments of aziridination of styrene[a]

Entry	Substrate	Azide	Catalyst	T/□	Light	Yield(%)[b]
1			/	80	√	30
2			$FeCl_3$	80	√	56
3			$Fe(F_{20}TPPL)Cl$	20	√	14
4			$Fe(F_{20}TPPL)Cl$	80	√	87
5			$Fe(F_{20}TPPL)Cl$	80	In darkness	86

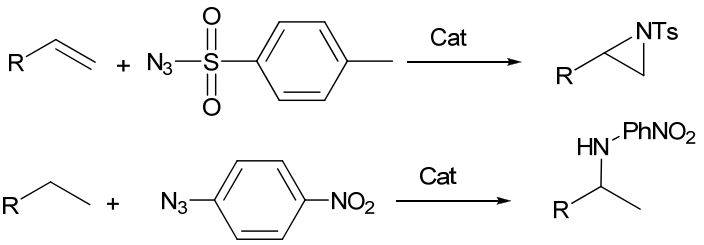
[a] Performed under N_2 in the presence of 4Å molecule sieves: [styrene] =1.0 mmol/mL; styrene/azide = 3:1 in DCE. [b] isolated yields.

Table S3. Control experiments of amidation of ethylbenzene[a]

Entry	Substrate	Azide	Catalyst	T/□	Light	Yield(%)[b]
1			/	80	√	0
2			$FeCl_3$	80	√	0
3			$Fe(F_{20}TPPL)Cl$	20	√	0
4			$Fe(F_{20}TPPL)Cl$	80	√	88
5			$Fe(F_{20}TPPL)Cl$	80	In darkness	85

[a] Performed under N_2 in the presence of 4Å molecule sieves: [styrene] =1.0 mmol/mL; alkane/azide = 5:1 in DCE. [b] isolated yields.

Table S4. Comparison of catalytic activity of [Fe(F_{20}TPPL)Cl], [Fe(F_{20}TPP)Cl] and [Fe(F_{15}TPC)] towards N atom transfer to C=C and C-H bonds.[a]



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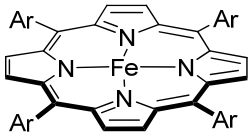
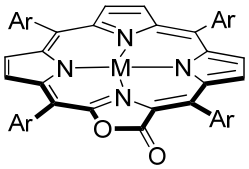
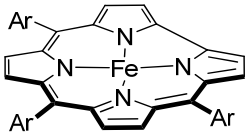


[Fe(F_{20}-TPP)Cl]



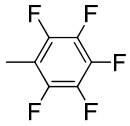
M= Fe, [Fe(F_{20}-TPPL)Cl]

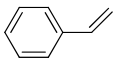
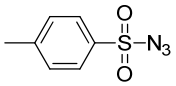
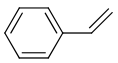
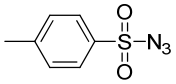
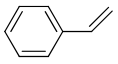
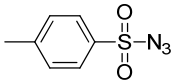
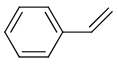
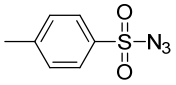
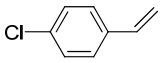
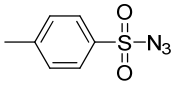
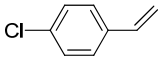
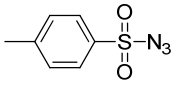
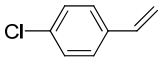
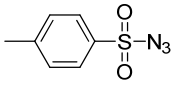
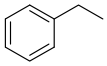
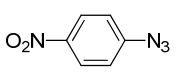
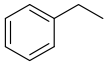
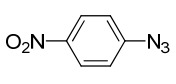
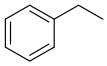
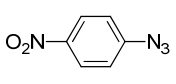
Mn, [Mn(F_{20}-TPPL)Cl]



[Fe(F_{15}-TPC)]

Ar=



Entry	Substrate	Azide	Catalyst[a]	T/□	Time/h	Yield(%)[b]
1[c]			Fe(F_{20}-TPPL)Cl	80	12	**88**
2[c]			Fe(F_{20}-TPP)Cl	80	12	76
3[c]			Fe(F_{15}-TPC)	80	12	59
4[c]			Mn(F_{20}-TPPL)Cl	80	12	53
5[d]			Fe(F_{20}-TPPL)Cl	80	12	**80**
6[d]			Fe(F_{20}-TPP)Cl	80	12	39
7[d]			Fe(F_{15}-TPC)	80	12	<10
8[d]			Fe(F_{20}-TPPL)Cl	80	12	**88**
9[d]			Fe(F_{20}-TPP)Cl	80	12	46
10[d]			Fe(F_{15}-TPC)	80	12	65

[a] Performed in DCE (1,2-dichloroethane) under N_2 in the presence of 4Å molecule sieves: [substrate] = 2.0 mmol/2 mL; alkene/azide = 3:1, alkane/azide = 5:1. [b] isolated yields. [c] 1 mol% catalyst based on azide was used. [d] 0.5 mol% catalyst was added.

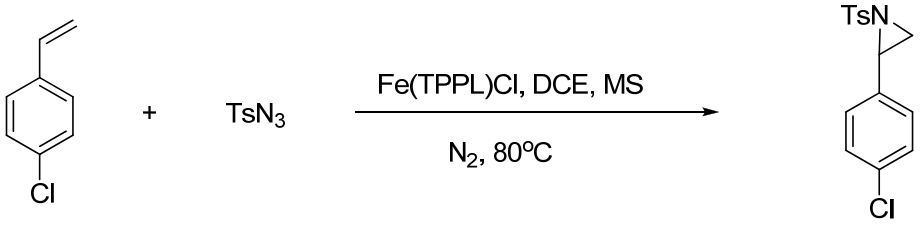
2.4 Calculation of TON by external standard

Procedure: 1,2-Dichloroethane (2 mL) was added to a mixture of *p*-chlorostyrene (2.34 mmol), azide (0.47 mmol), catalyst (0.0022 mmol), and 4Å molecular sieves (120 mg). The reaction mixture was heated to 80°C under nitrogen atmosphere. After complete consumption of the azide as monitored by TLC, the mixture was concentrated under reduced pressure. 23.8mg 4-cyanopyridine (0.229mmol) as external standard was added. This reaction mixture dissolved in 2 ml $CDCl_3$ and then filtered MS. The integration (I) of protons of aziridines (a, b, and c) and protons of 4-cyanopyridine in this ^{1}HNMR of $CDCl_3$ was used to calculated TON.

$$TON = [2\times(I_{aziridine\ (3,75\ ppm)} / I_{4\text{-}cyanopyridine\ (8.81\ ppm)})\times M_{4\text{-cyanopyridine}}]/[cat.]$$

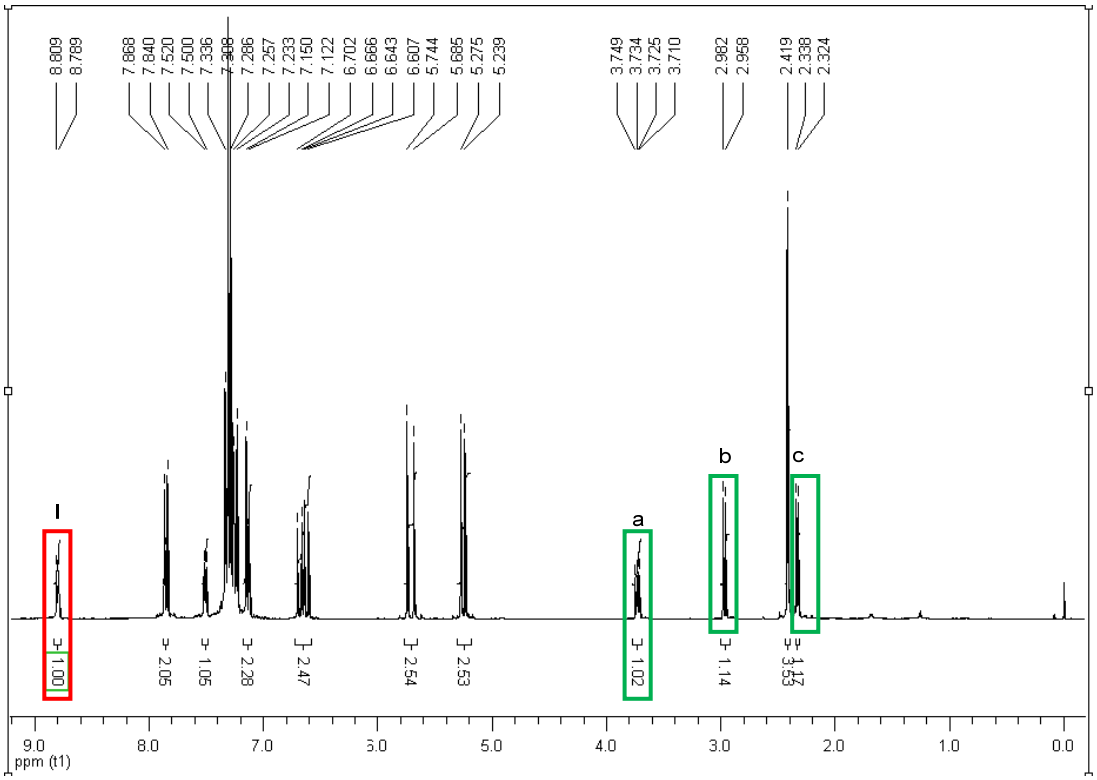
$$= [2\times(1.02/1.00) \times 0.229]/0.0022$$

$$\approx 200$$



n	2.34mmol	0.47mmol	2.21umol

After 12h, 4-cyanopyridine is added to the filtrate as internal reference. ^{1}HNMR spectrum is shown as following:


8.809
8.789
7.868
7.840
7.520
7.500
7.336
7.288
7.286
7.257
7.233
7.150
7.122
6.702
6.666
6.643
6.607
5.744
5.685
5.275
5.239
3.749
3.734
3.725
3.710
2.982
2.958
2.419
2.338
2.324
I
a
b
c
1.00
2.05
1.05
2.28
2.47
2.54
2.53
1.02
1.14
3.53
ppm (t1)

2.5 Time–course for aziridination of styrene by [Fe(F_{20}TPPL)Cl] and [Fe(F_{20}TPP)Cl]

Procedure: 1,2-Dichloroethane (2 mL) was added to a mixture of *p*-chlorostyrene (5 mmol), azide (2 mmol), catalyst (0.005 mmol), and 4Å molecular sieves (120 mg). The reaction mixture was heated to 80^{o}C under nitrogen atmosphere. 0.2 ml of the reaction solution was taken out every 2 hours and then concentrated under reduced pressure. 4-cyanopyridine was used as external standard. The integration (I) of protons of aziridines (a, b, and c) and protons of 4-cyanopyridine in this ^{1}HNMR of $CDCl_3$ was used to calculated TON.

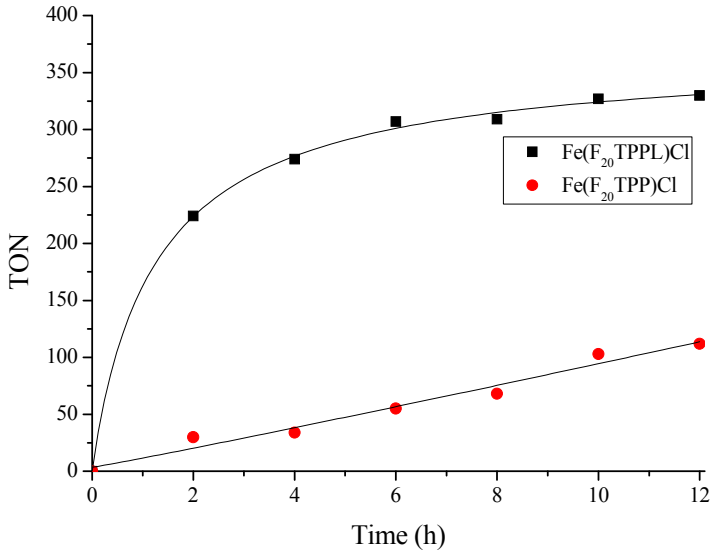


Figure S1 Time-course for aziridination of styrene by [Fe(F_{20}TPPL)Cl] and [Fe(F_{20}TPP)Cl]

3. Stability of [Fe(F_{20}TPPL)Cl] and [Fe(F_{20}TPP)Cl] toward oxidants

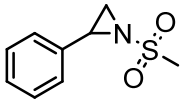
Procedure:

In 2ml CH_2Cl_2 solution of [Fe(F_{20}TPPL)Cl] or [Fe(F_{20}TPP)Cl] (1~5×10^{-5}M) was added 100 equiv. oxidant. After 4h, $Na_2S_2O_6$ was added to quench the excess oxidants or active species. The solution was diluted 5 times for UV-vis spectra and compared with the initial UV-vis spectra.

Entry	Oxidant	Decomposed [Fe(F_{20}TPPL)Cl] %	Decomposed [Fe(F_{20}TPP)Cl] %
1	H_2O_2	46	16
2	NaClO	80	25
3	Oxone®	76	24
4	TBHP	25	15
5	*m*-CPBA	100	35
6	PhIO	90	22
7	PhINTs	84	20

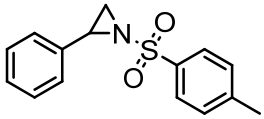
4. Characterization of selected compounds

N-methylsulfonyl-2-phenylaziridine (Table 1, entry 2)[5]



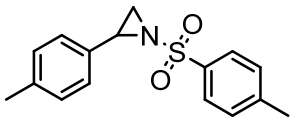
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.37 (m, 5H), 3.70 (dd, 1H), 3.07 (s, 3H), 2.94 (d, J = 7.2 Hz, 1H), 2.42 (d, J = 4.5 Hz, 1H). HRMS (ESI) m/z for $C_9H_{12}NO_2S(M+H^+)$ calcd 198.0583, found 198.0581.

N-(*p*-Tolylsulfonyl)-2-phenylaziridine (Table 2, entry 1)[5]



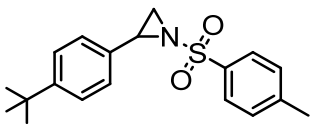
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.27-7.30 (m, 3H), 7.20-7.24 (m, 2H), 3.78 (dd, 1H), 2.99 (d, J = 7.2 Hz, 1H), 2.44 (s, 3H), 2.39 (d, J = 4.5 Hz, 1H). ^{13}C NMR (300MHz, $CDCl_3$) δ 21.71, 36.00, 41.09, 126.62, 127.99, 128.36, 128.62, 129.83, 135.02, 135.09, 144.72. HRMS (ESI) m/z for $C_{15}H_{16}NO_2S(M+H^+)$ calcd 274.0896, found 274.0895. m.p 90 ^{o}C.

N-(*p*-Tolylsulfonyl)-2-(*p*-methylphenyl)aziridine (Table 2, entry 2)[5]



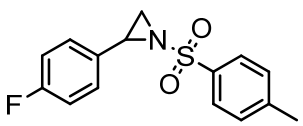
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.10 (s, 4H), 3.74 (dd, 1H), 2.97 (d, J = 7.2 Hz, 1H), 2.43 (s, 3H), 2.38 (d, J = 4.5 Hz, 1H), 2.31 (s, 3H). HRMS (ESI) m/z for $C_{16}H_{18}NO_2S(M+H^+)$ calcd 288.1053, found 288.1050.

N-(*p*-Tolylsulfonyl)-2-(*p*-tert-butylphenyl)aziridine (Table 2, entry 3)[6]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 2H), 7.31-7.35 (m, 4H), 7.16 (d, J = 8.4 Hz, 2H), 3.78 (dd, 1H), 2.97 (d, J = 7.2 Hz, 1H), 2.43 (s, 3H), 2.39 (d, J = 4.5 Hz, 1H), 1.29 (s, 9H). HRMS (ESI) m/z for $C_{19}H_{24}NO_2S(M+H^+)$ calcd 330.1522, found 330.1520.

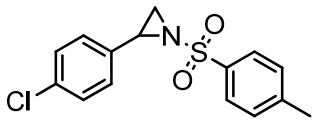
N-(*p*-Tolylsulfonyl)-2-(*p*-fluorophenyl)aziridine (Table 2, entry 4)[7]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.17-7.21 (m, 2H), 6.95-7.01 (m, 2H), 3.76 (dd, 1H), 2.97 (d, J = 7.2 Hz, 1H), 2.44 (s, 3H), 2.35 (d, J = 4.5 Hz,

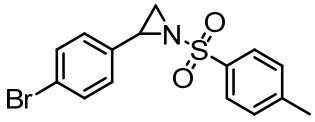
1H). HRMS (ESI) m/z for $C_{15}H_{15}FNO_2S(M+H^+)$ calcd 292.0802, found 292.0801. m.p 98 ^oC.

N-(*p*-Tolylsulfonyl)-2-(*p*-chlorophenyl)aziridine (Table 2, entry 5)[5]



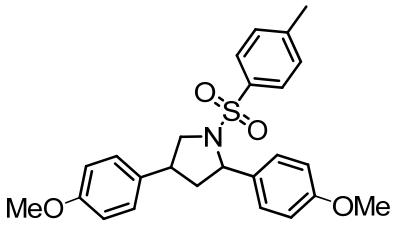
^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.25-7.28 (m, 2H), 7.14-7.17 (m, 2H), 3.74 (dd, 1H), 2.98 (d, J = 7.2 Hz, 1H), 2.44 (s, 3H), 2.35 (d, J = 4.5 Hz, 1H). ^{13}C NMR (300MHz, $CDCl_3$) δ 21.71, 36.10, 40.30, 127.98, 128.80, 129.88, 133.70, 134.20, 134.81, 144.88. HRMS (ESI) m/z for $C_{15}H_{15}ClNO_2S(M+H^+)$ calcd 308.0506, found 308.0503. m.p 122 ^oC.

N-(*p*-Tolylsulfonyl)-2-(*p*-bromophenyl)aziridine (Table 2, entry 6)[8]



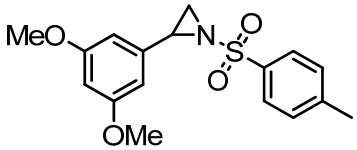
^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 3.72 (dd, 1H), 2.98 (d, J = 6.9 Hz, 1H), 2.44 (s, 3H), 2.34 (d, J = 4.2 Hz, 1H). ^{13}C NMR (300MHz, $CDCl_3$) δ 21.70, 36.04, 40.32, 122.30, 127.95, 128.27, 129.86, 131.70, 134.21, 134.75, 144.86. HRMS (ESI) m/z for $C_{15}H_{15}BrNO_2S(M+H^+)$ calcd 352.0001, found 352.0008. m.p 136 ^oC.

2,4-bis(4-methoxyphenyl)-1-tosylpyrrolidine (Table 2, entry 7)



^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.26-7.29 (m, 4H), 7.04 (d, J = 8.4 Hz, 2H), 6.80-6.86 (m, 4H), 4.73 (dd, 1H), 4.10 (m, 1H), 3.81(s, 3H), 3.77 (s, 3H), 3.45 (t, 1H), 2.82-2.92 (m, 1H), 2.56-2.64 (m, 1H), 2.43 (s, 3H), 1.97-2.05 (m, 1H). ^{13}C NMR (400MHz, $CDCl_3$) δ 21.67, 21.70, 40.88, 42.96, 44.68, 55.40, 55.44, 56.10, 62.69, 64.20, 76.84, 77.16, 77.36, 77.48, 113.91, 113.98, 114.14, 114.19, 127.15, 127.39, 127.56, 127.74, 127.82, 128.08, 128.10, 129.54, 129.67, 129.77, 130.79, 131.29, 131.72, 134.69, 134.93, 135.21, 136.01, 143.35, 143.56, 158.71, 158.77, 158.87, 159.02. HRMS (ESI) m/z for $C_{25}H_{28}NO_4S(M+H^+)$ calcd 438.1734, found 438.1732.

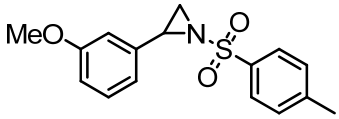
N-(*p*-Tolylsulfonyl)-2-(3,5-dimethoxyphenyl)aziridine (Table 2, entry 8)



^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 6.35 (s, 3H),

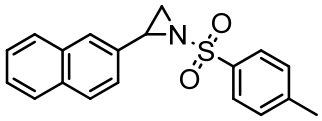
3.72 (s, 6H), 3.67 (dd,1H), 2.96 (d, J = 7.2 Hz, 1H), 2.42 (s, 3H), 2.37 (d, J = 4.5 Hz, 1H). MS (ESI) *m/z* 334 ($M+H^+$); HRMS (ESI) m/z for $C_{17}H_{20}NO_4S(M+H^+)$ calcd 334.1108, found 334.1102.

N-(*p*-Tolylsulfonyl)-2-(*m*-methoxyphenyl)aziridine (Table 2, entry 9)



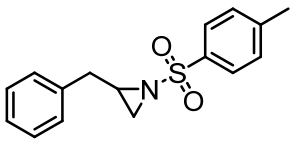
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.34-7.35 (d, J = 8.4 Hz, 2H), 7.20 (t, 1H), 6.81-6.83 (m, 2H), 6.72 (m, 1H), 3.75 (s, 3H), 3.72 (dd, 1H), 2.97(d, J = 6.0 Hz, 1H), 2.43(s, 3H), 2.36-2.40 (d, J = 4.2 Hz, 1H). HRMS (ESI) m/z for $C_{16}H_{18}NO_3S(M+H^+)$ calcd 304.1002, found 304.0997.

N-(*p*-Tolylsulfonyl)-2-(naphthalen-2-yl)aziridine (Table 2, entry 10)[9]



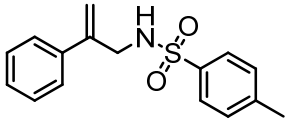
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.73-7.81 (m, 4H), 7.45-7.48 (m, 2H), 7.26-7.34 (m, 3H), 3.93 (dd, 1H), 3.07 (d, J = 7.2 Hz, 1H), 2.50 (d, J = 4.5 Hz, 1H), 2.42 (s, 3H). HRMS (ESI) m/z for $C_{19}H_{18}NO_2S(M+H^+)$ calcd 324.1053, found 324.1052.

2-benzyl-1-tosylaziridine (Table 2, entry 11)[10]



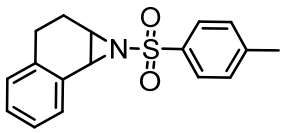
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.14-7.22 (m, 5H), 7.02-7.05 (m, 2H), 2.90-2.98 (m, 1H), 2.81 (dd, 1H), 2.64-2.72 (m, 2H), 2.42 (s, 3H), 2.16 (d, J = 4.5 Hz, 1H). HRMS (ESI) m/z for $C_{16}H_{18}NO_2S(M+H^+)$ calcd 288.1053, found 288.1054.

4-methyl-N-(2-phenylallyl)benzenesulfonamide (Table 2, entry 12)[11]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.21-7.29 (m, 7H), 5.36 (s, 1H), 5.20 (s, 1H), 4.71(t, 1H), 3.98 (d, J = 6.3 Hz, 2H), 2.43 (s, 3H). HRMS (ESI) m/z for $C_{16}H_{18}NO_2S(M+H^+)$ calcd 288.1053, found 288.1050.

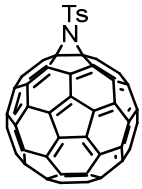
1-tosyl-1a,2,3,7b-tetrahydro-1H-naphtho[1,2-b]azirine (Table 2, entry 13)[6]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-8.09 (m, 3H), 7.29-7.44 (m, 3H), 7.04-7.24 (m, 2H), 3.41 (m,

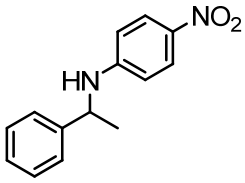
2H), 2.90 (t, 2H), 2.45 (s, 3H), 2.07 (m, 2H). HRMS (ESI) m/z for $C_{17}H_{18}NO_2S(M+H^+)$ calcd 300.1053, found 300.1049.

_N_-tosyl[1,2]aziridino[60]fullerene[12]



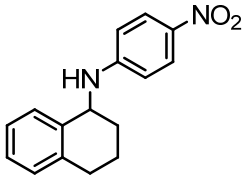
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.22 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (400MHz, $CDCl_3/CS_2$) δ 21.91, 79.84, 128.56, 130.18, 135.61, 140.92, 141.39, 141.88, 142.18, 142.80, 143.11, 143.16, 143.26, 143.91, 143.98, 144.18, 144.53, 145.02, 145.08, 145.16, 145.33, 145.66. MS (MALDI) *m/z* 889 (M^+).

4-nitro-N-(1-phenylethyl)aniline (Table 3, entry 1)[13]



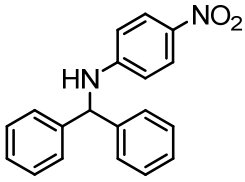
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 9.1 Hz, 2H), 7.31 (m, 4H), 6.46 (d, J = 9.1 Hz, 2H), 4.89 (br, 1H), 4.60 (m, 1H), 1.65 (m, 3H). HRMS (ESI) m/z for $C_{14}H_{15}N_2O_2(M+H^+)$ calcd 243.1128, found 243.1124.

1,2,3,4-tetrahydro-N-(4-nitrophenyl)-1-naphthalenamine (Table 3, entry 2)[14]



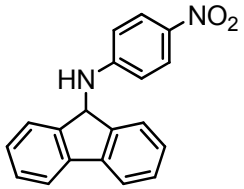
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 9.1 Hz, 2H), 7.20 (m, 4H), 6.60 (d, J = 9.1 Hz, 2H), 4.74 (m, 1H), 2.85 (m, 2H), 2.06 (m, 2H), 1.85 (m, 2H). HRMS (ESI) m/z for $C_{16}H_{16}N_2NaO_2$ ($M+Na^+$) calcd 291.1104, found 291.1101.

N-benzhydryl-4-nitrobenzenamine (Table 3, entry 3)[14]



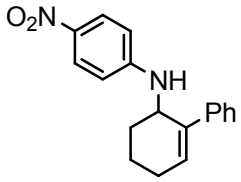
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 2H), 7.32 (m, 10H), 6.50 (d, J = 8.3 Hz, 2H), 5.63 (s, 1H), 5.02 (s, 1H). HRMS (ESI) m/z for $C_{19}H_{16}N_2NaO_2(M+Na^+)$ calcd 327.1104, found 327.1102.

N-(4-nitrophenyl)-9H-fluoren-9-amine (Table 3, entry 4)[14]



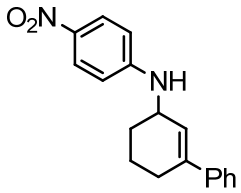
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.1 Hz, 2H), 7.54 (d, J = 7.1 Hz, 2H), 7.45 (m, 2H), 7.30 (m, 2H), 6.68 (d, J = 8.0 Hz, 2H), 5.72 (s, 1H), 4.97 (br s, 1H). MS (ESI) *m/z* 303 (M+ H^+).

4-nitro-N-(2-phenylcyclohex-2-enyl)aniline (Table 3, entry 5)



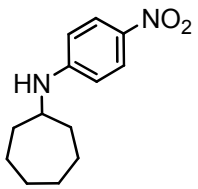
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 9.3 Hz, 2H), 7.29-7.37 (m, 5H), 6.55 (d, J = 9.3 Hz, 2H), 6.41 (m, 1H), 4.59 (m, 2H), 2.32 (m, 2H), 1.75 (m, 3H). HRMS (ESI) m/z for $C_{18}H_{19}N_2O_2$(M+H^+) calcd 295.1441, found 295.1436.

4-nitro-N-(3-phenylcyclohex-2-enyl)aniline (Table 3, entry 5)



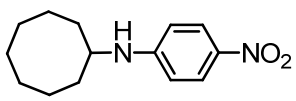
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 9.3 Hz, 2H), 7.28-7.42 (m, 5H), 6.58 (d, J = 9.3 Hz, 2H), 6.06 (m, 1H), 4.59 (m, 1H), 4.30 (m, 1H), 2.51 (m, 2H), 1.73-2.04 (m, 3H). HRMS (ESI) m/z for $C_{18}H_{19}N_2O_2$(M+H^+) calcd 295.1441, found 295.1436.

N-(4-nitrophenyl)cycloheptanamine (Table 3, entry 6)[14]



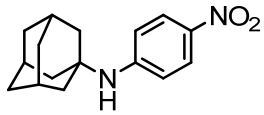
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 9.2 Hz, 2H), 6.45 (d, J = 9.2 Hz, 2H), 3.55 (m, 1H), 2.05 (m, 2H), 1.72-1.40 (m, 10H). HRMS (ESI) m/z for $C_{13}H_{19}N_2O_2$(M+H^+) calcd 235.1441, found 235.1438.

N-(4-nitrophenyl)cyclooctanamine (Table 3, entry 7)[14]



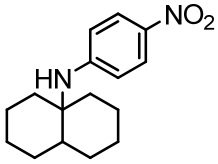
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 9.2 Hz, 2H), 6.45 (d, J = 9.2 Hz, 2H), 4.45 (br s, 1H), 3.59 (m, 1H), 1.92 (m, 2H), 1.75 (m, 2H), 1.66-1.40 (m, 10H). HRMS (ESI) m/z for $C_{14}H_{21}N_2O_2(M+H^+)$ calcd 249.1598, found 249.1592.

N-(4-nitrophenyl)-1-Adamantanamine (Table 3, entry 8)[14]



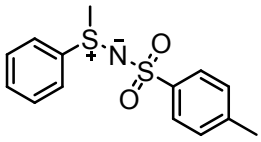
^{1}H NMR (300 MHz, CDCl3) δ 8.05 (d, J = 9.2 Hz, 2H), 6.63 (d, J = 9.2 Hz, 2H), 2.17 (br s, 3H), 2.00 (br s, 6H), 1.73 (m, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 126.11, 111.45, 42.39, 36.26, 29.54. HRMS (ESI) m/z for $C_{16}H_{20}N_2NaO_2(M+Na^+)$ calcd 295.1417, found 295.1412.

N-(4-nitrophenyl)decahydronaphthalen-4a-amine (Table 3, entry 9)

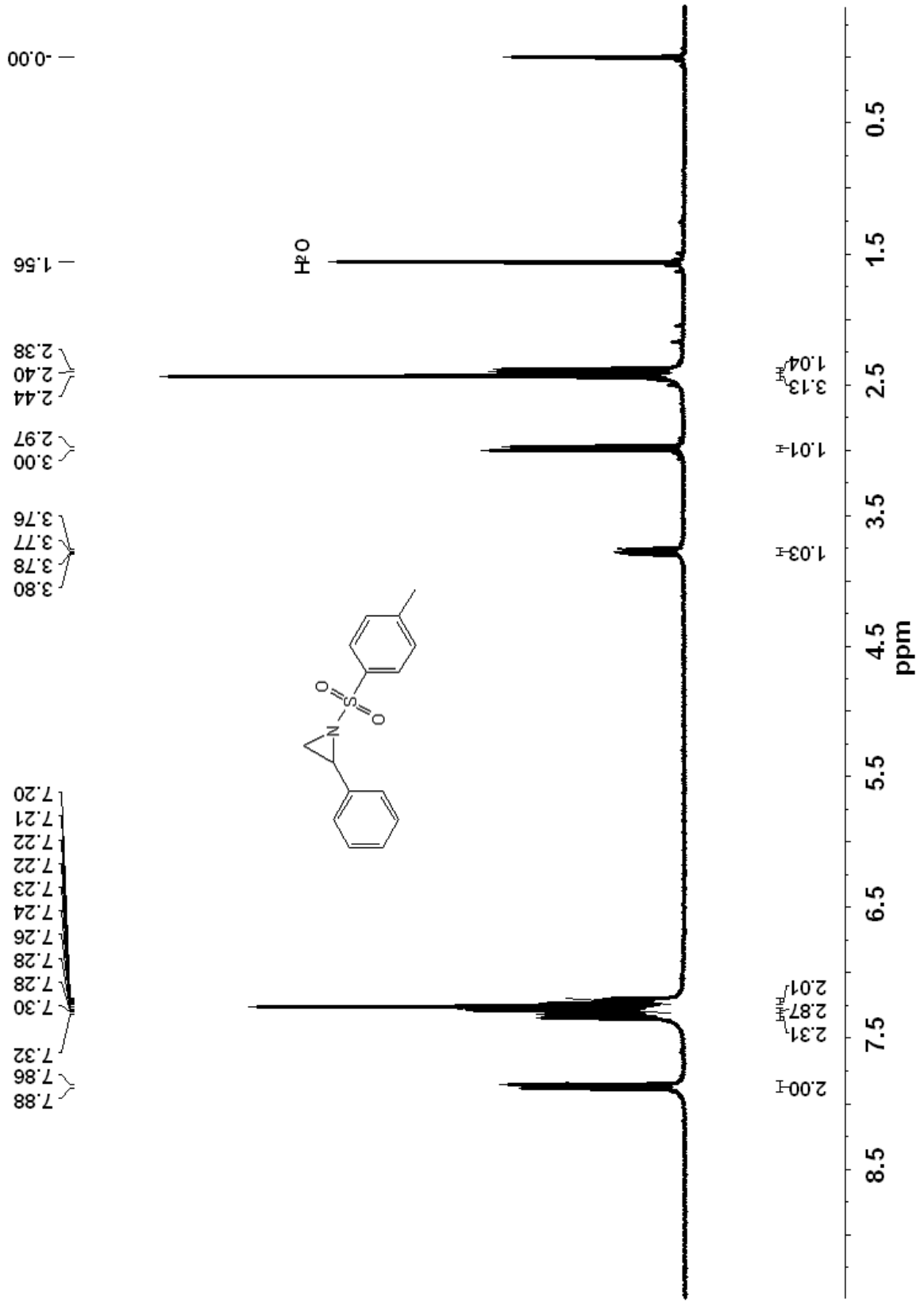


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 9.3 Hz, 2H), 6.63 (d, J = 9.3 Hz, 2H), 4.50 (s, 1H), 1.32-2.04 (m, 17 H). ^{13}C NMR (400MHz, $CDCl_3$) δ 22.30, 27.66, 40.15, 57.28, 113.27, 126.24, 137.22, 152.43. MS (ESI) *m/z* 275 ($M+H^+$); HRMS (ESI) m/z for $C_{16}H_{23}N_2O_2(M+H^+)$ calcd 275.1754, found 275.1754.

4-methyl-N-(methylphenyl-λ4-sulfanylidene)-benzenesulfonamide (Table 3, entry 10)[15]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.75 (m, 4H), 7.49-7.55 (m, 3H), 7.17 (d, J = 7.8 Hz, 2H), 2.84 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (300MHz, $CDCl_3$) δ 21.44, 39.12, 125.86, 126.29, 129.29, 130.03, 132.48, 136.06, 141.27, 141.78. HRMS (ESI) m/z for $C_{14}H_{16}NO_2S_2(M+H^+)$ calcd 294.0617, found 294.0616. m.p 124 ^{o}C.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2.40
2.44
2.97
3.00
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3.77
3.78
3.80
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7.21
7.22
7.22
7.23
7.24
7.26
7.28
7.28
7.30
7.32
7.86
7.88
2.00
2.01
2.87
2.31
1.03
3.13
1.04
1.01
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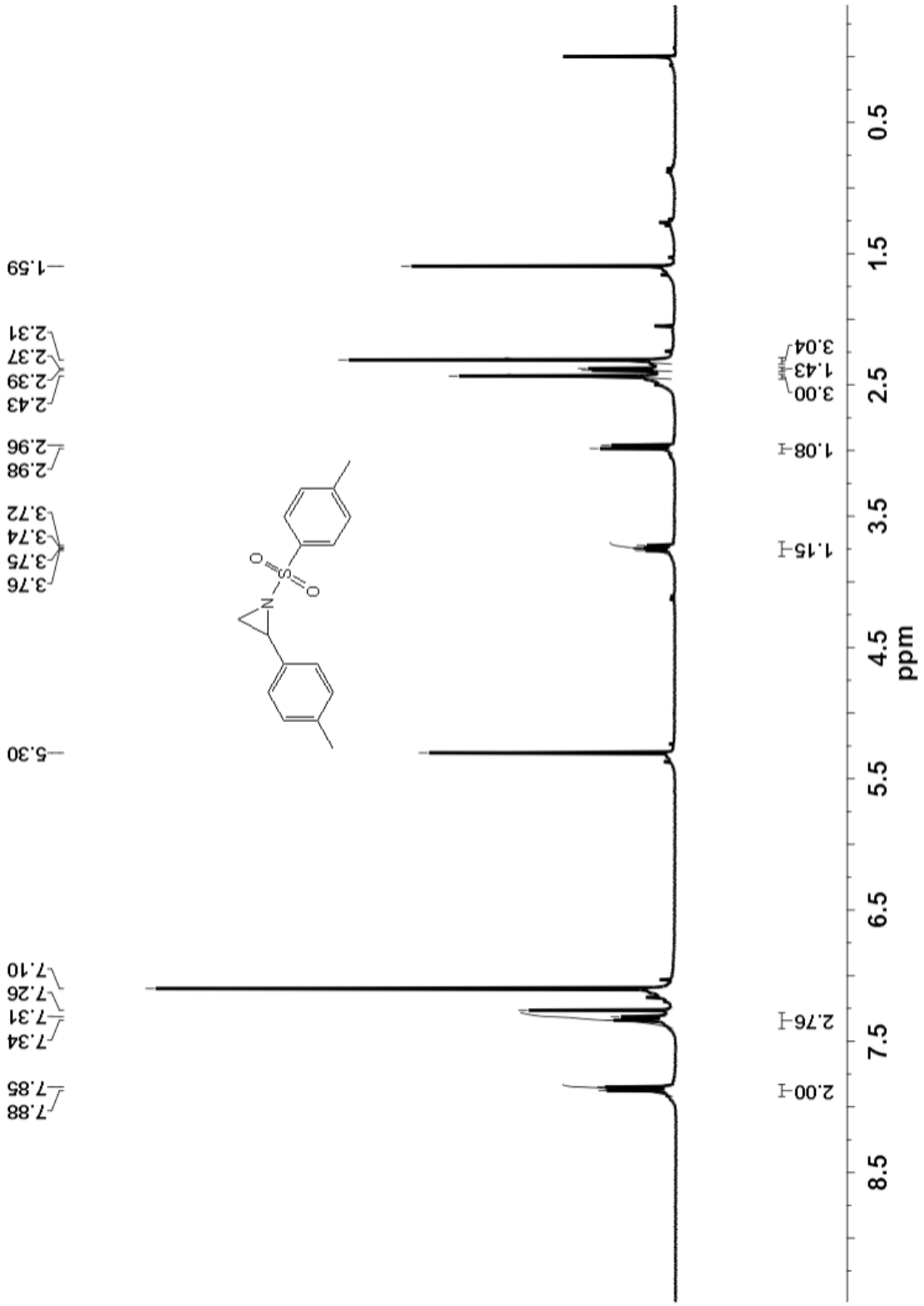
3.5
4.5
5.5
6.5
7.5
8.5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7.26
7.31
7.34
7.85
7.88
3.04
1.43
3.00
1.08
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5.5
6.5
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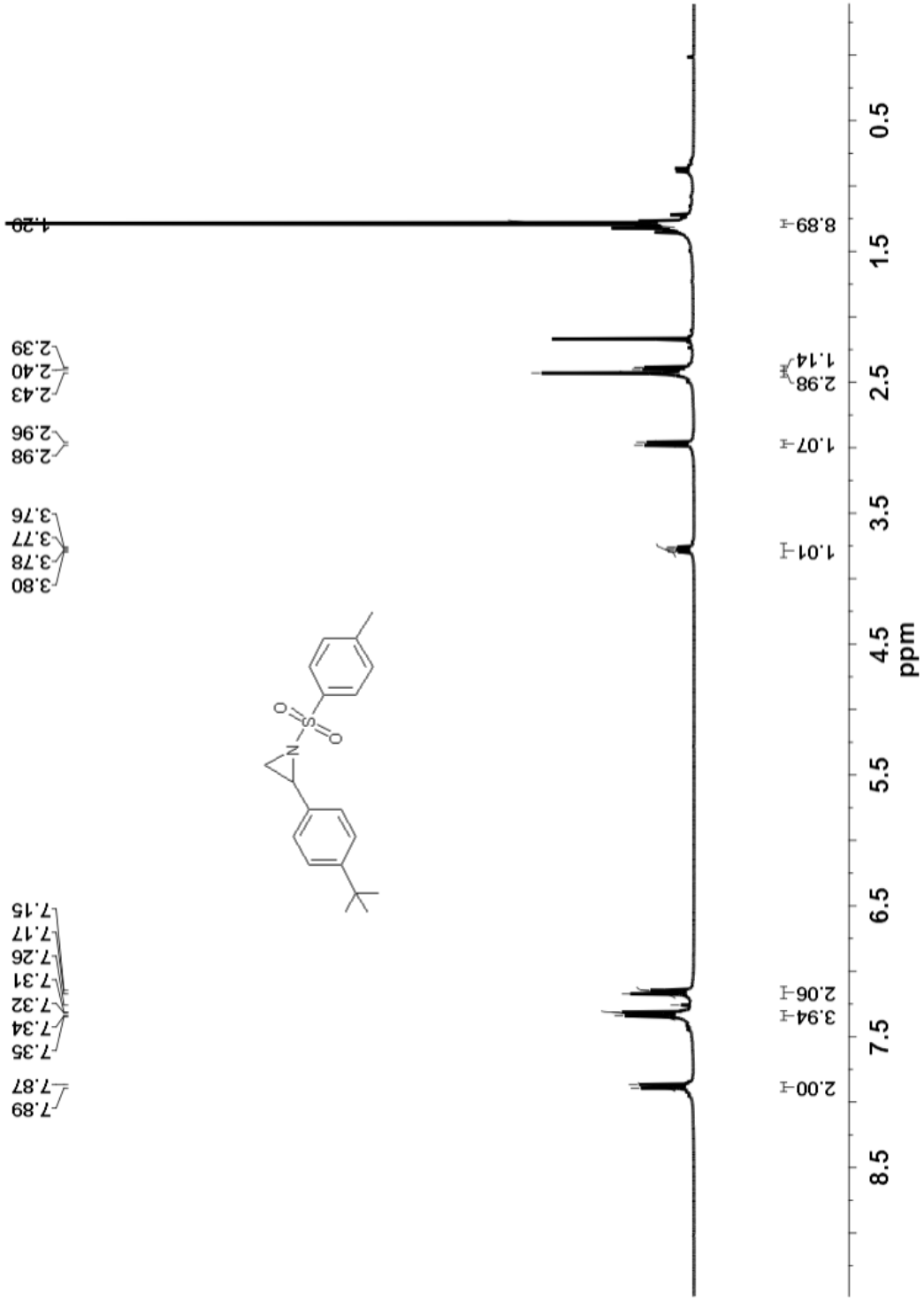
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7.34
7.35
7.87
7.89
8.89
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2.98
1.07
1.01
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7.5
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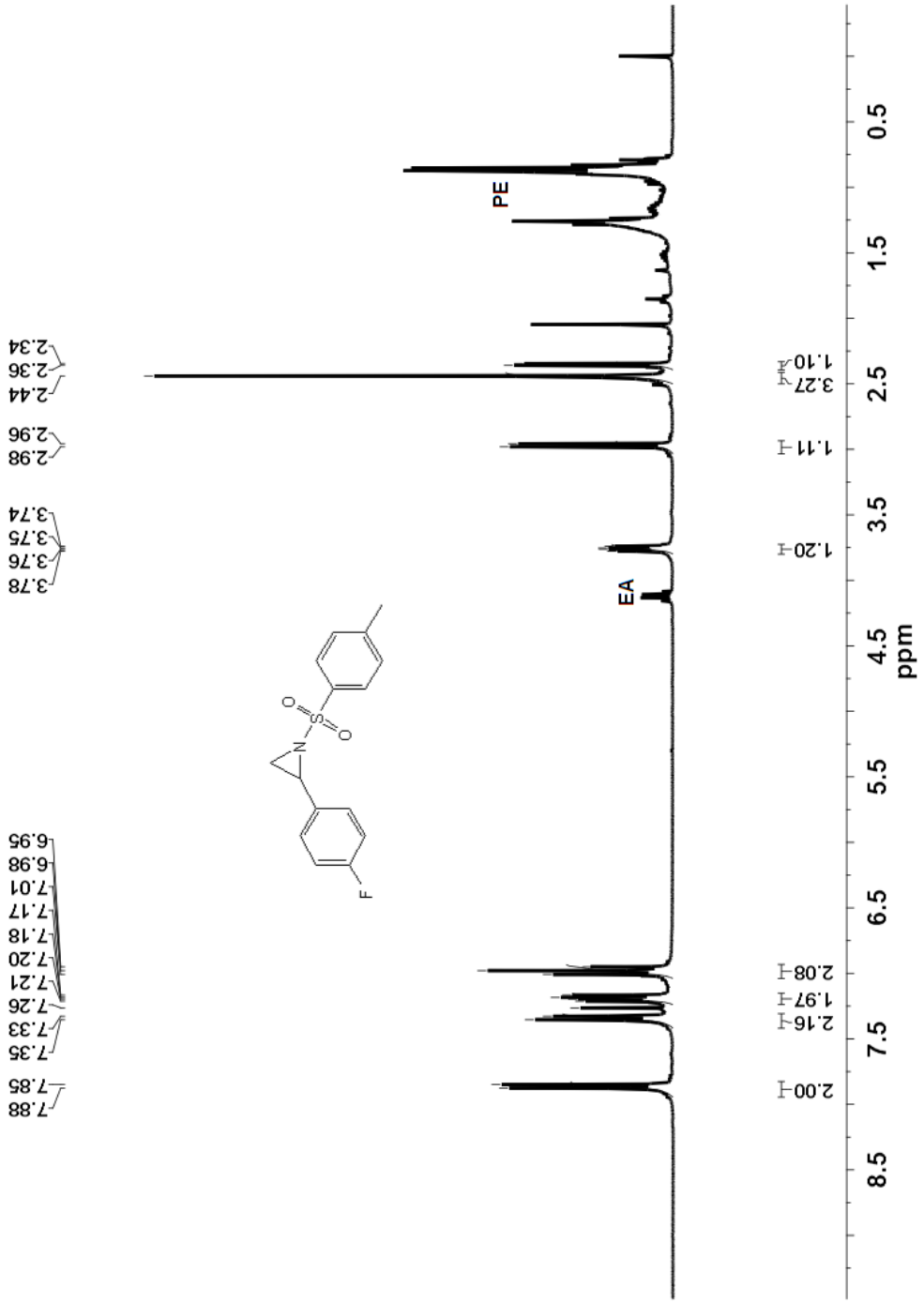

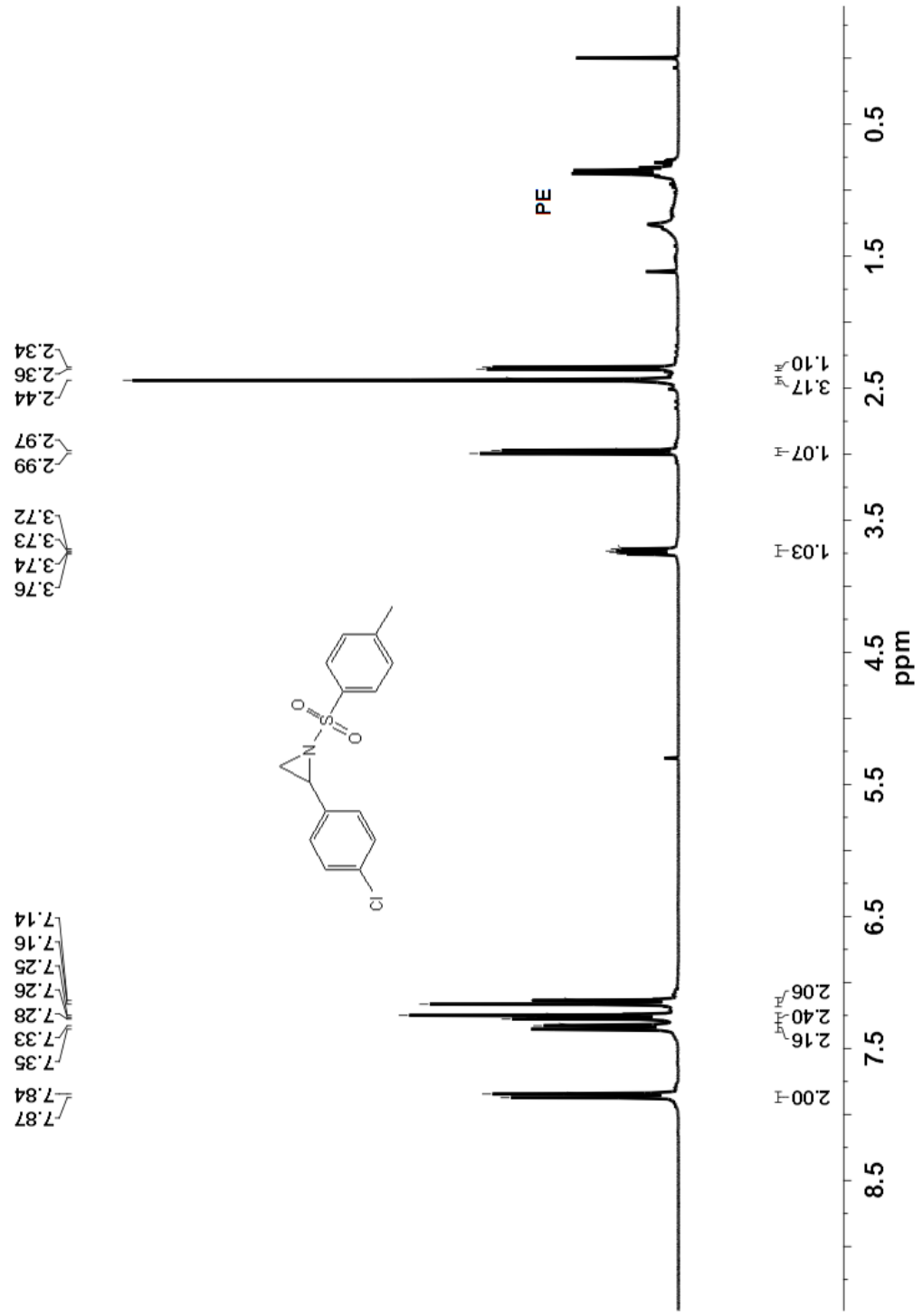
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7.14
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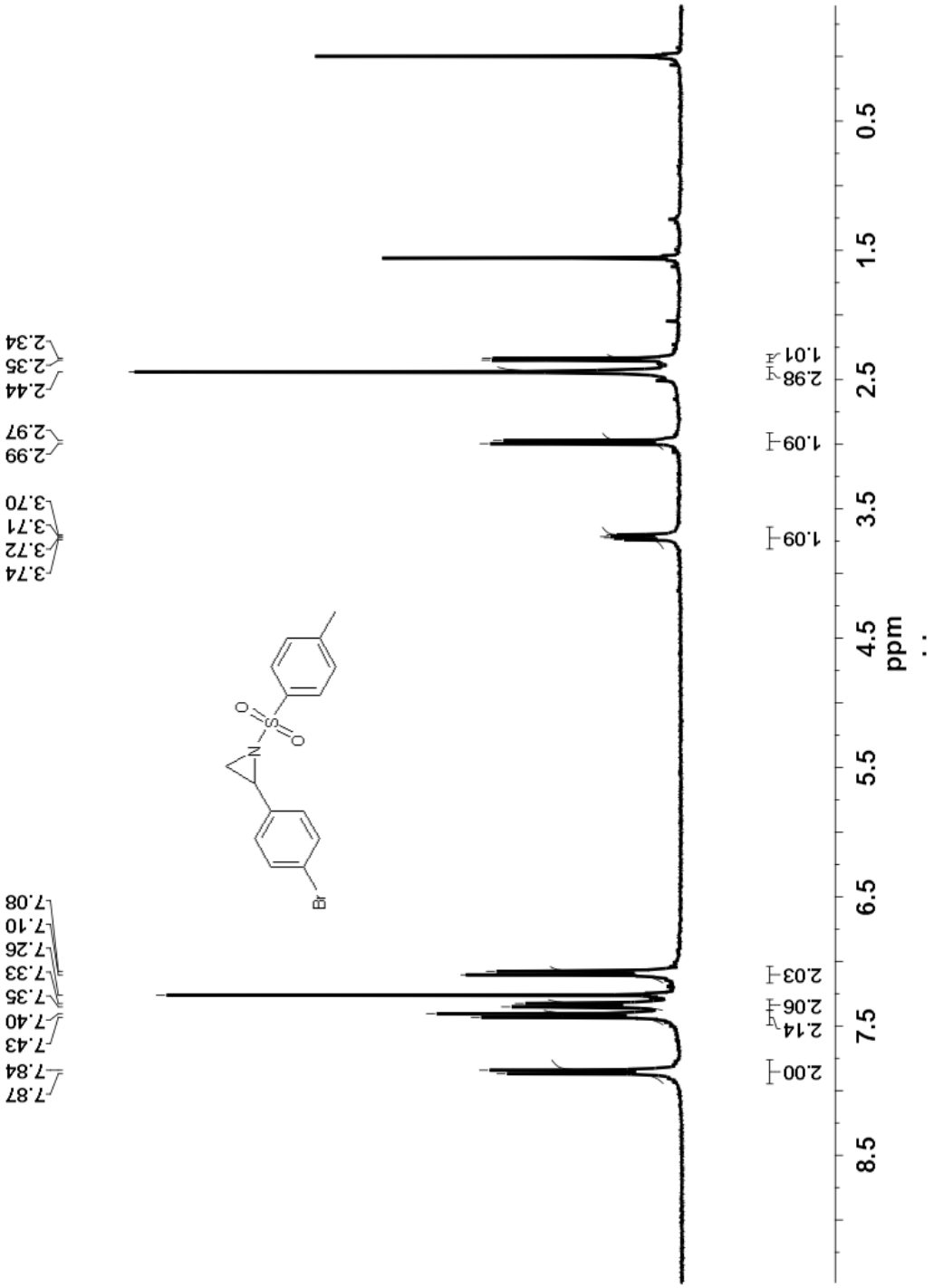
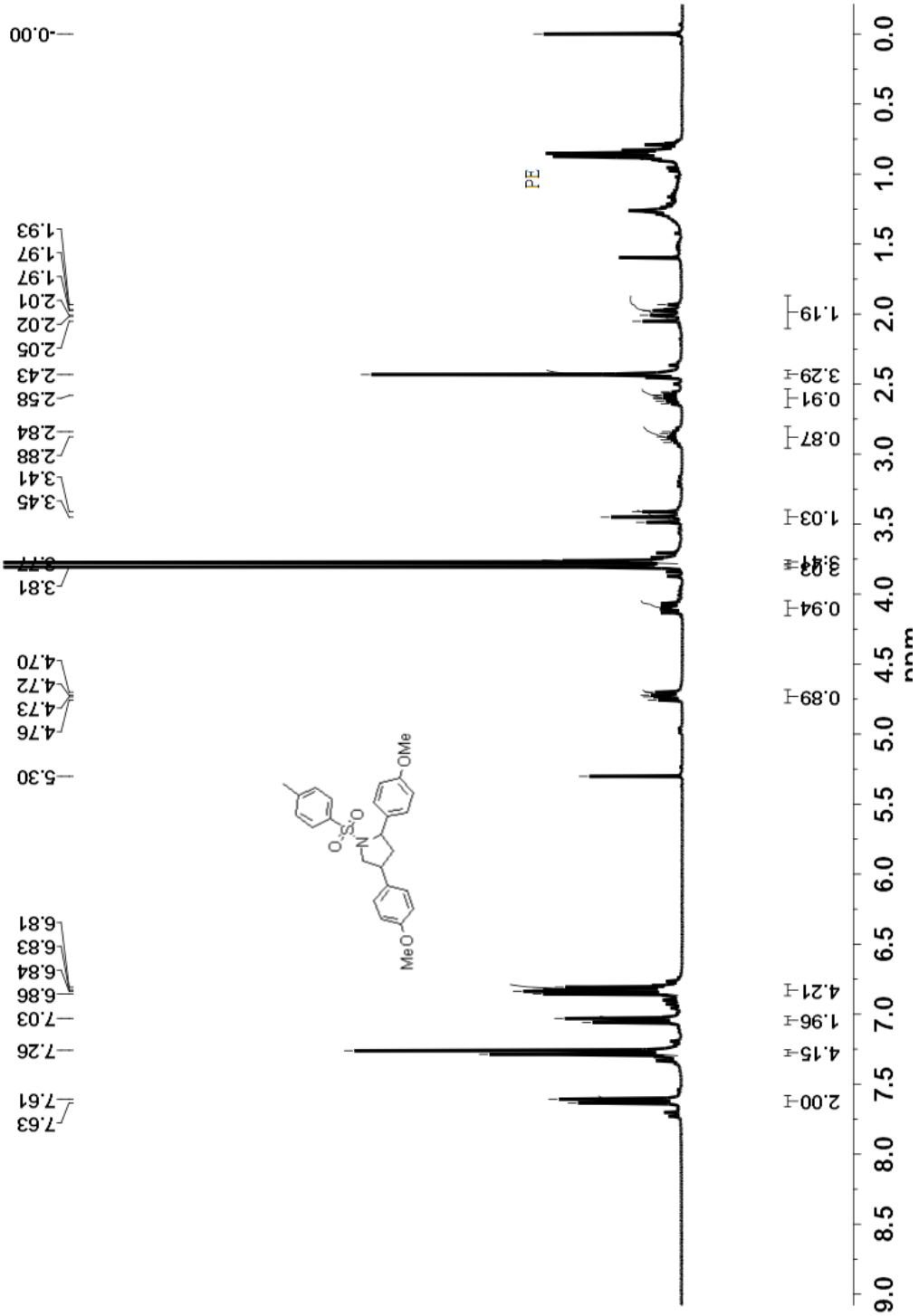
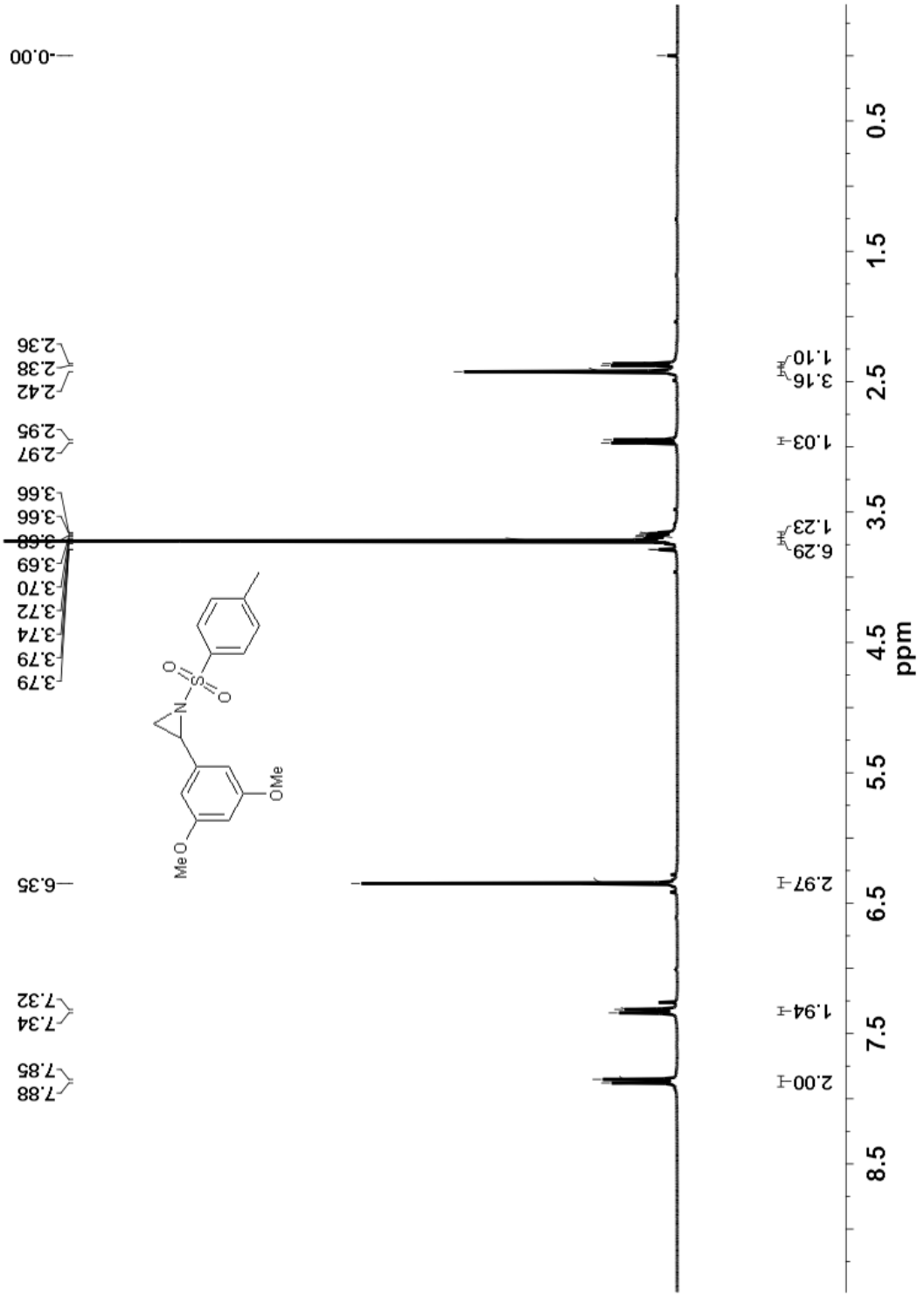



PE
OMe
MeO
ppm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7.32
7.34
7.85
7.88
1.10
3.16
1.03
1.23
6.29
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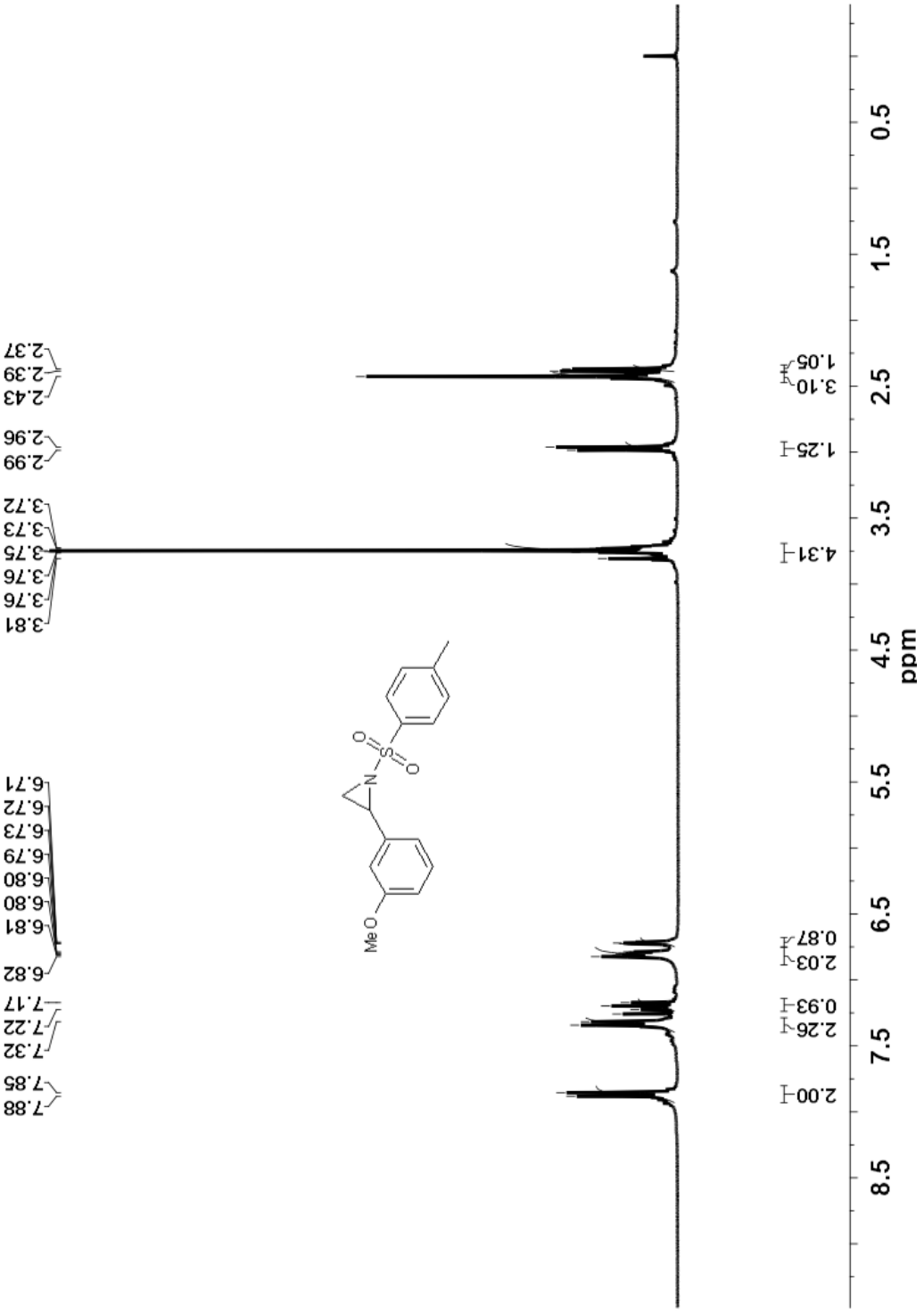
ppm
OMe
MeO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6.80
6.81
6.82
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7.32
7.85
7.88
1.05
3.10
1.25
4.31
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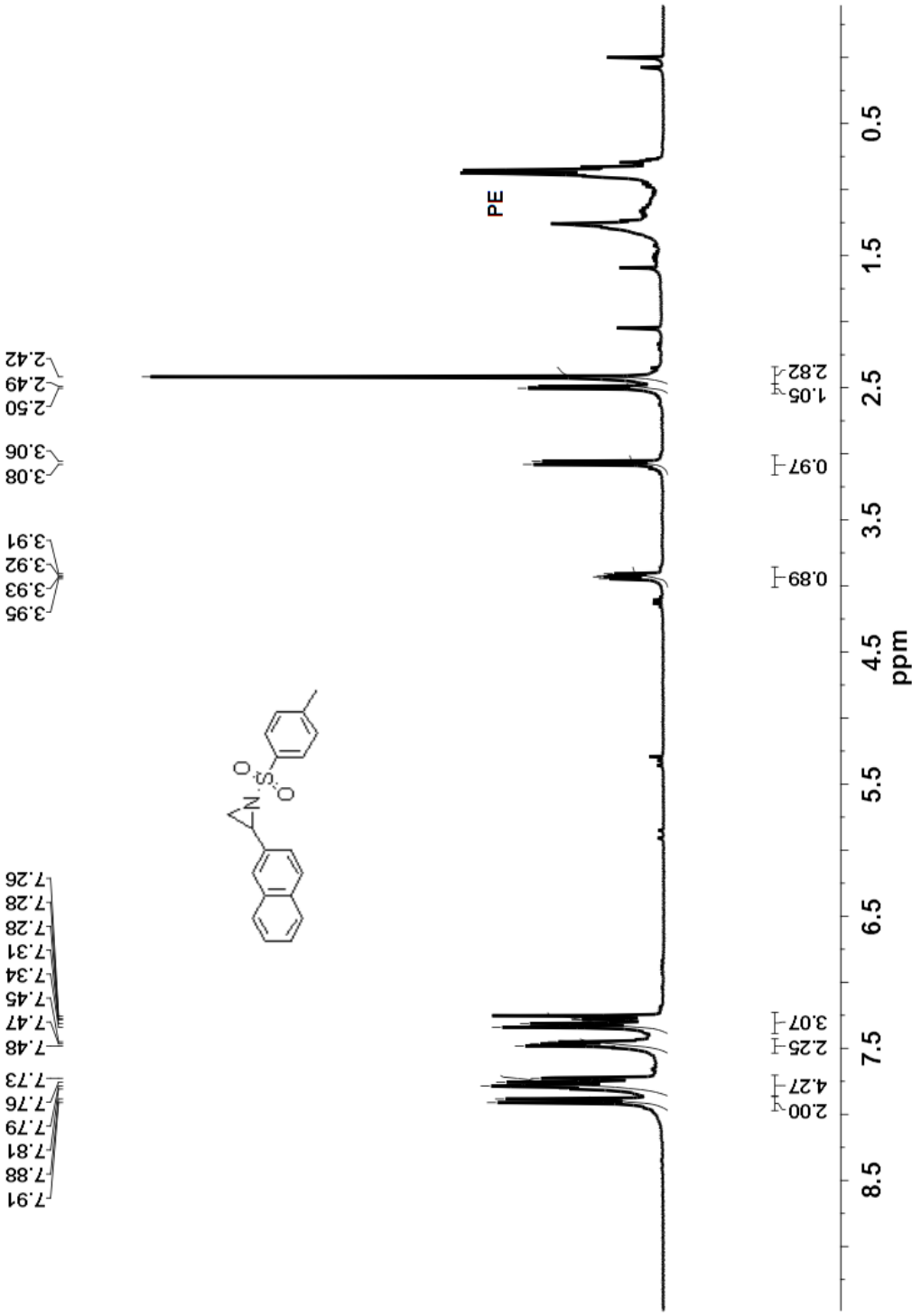
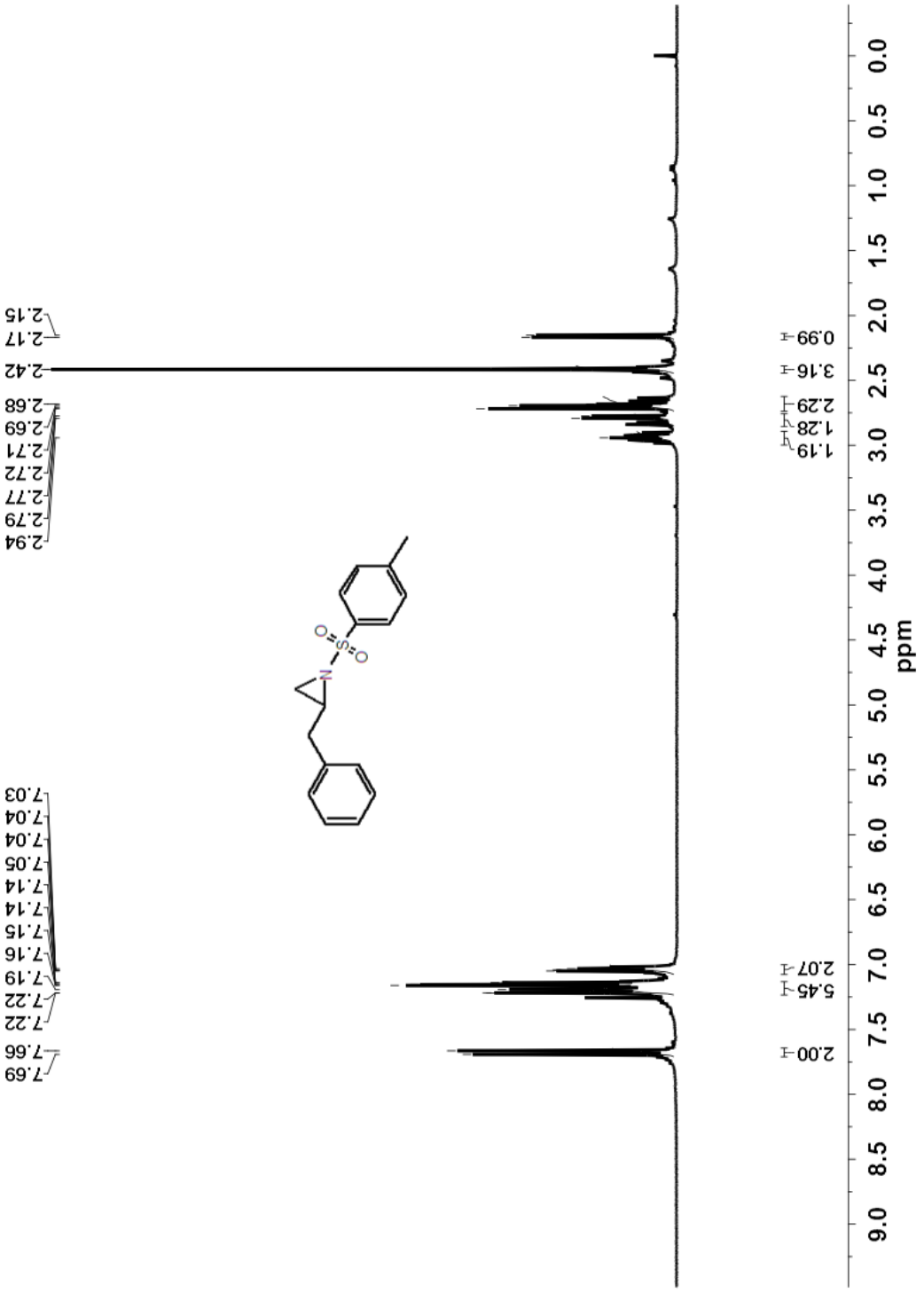
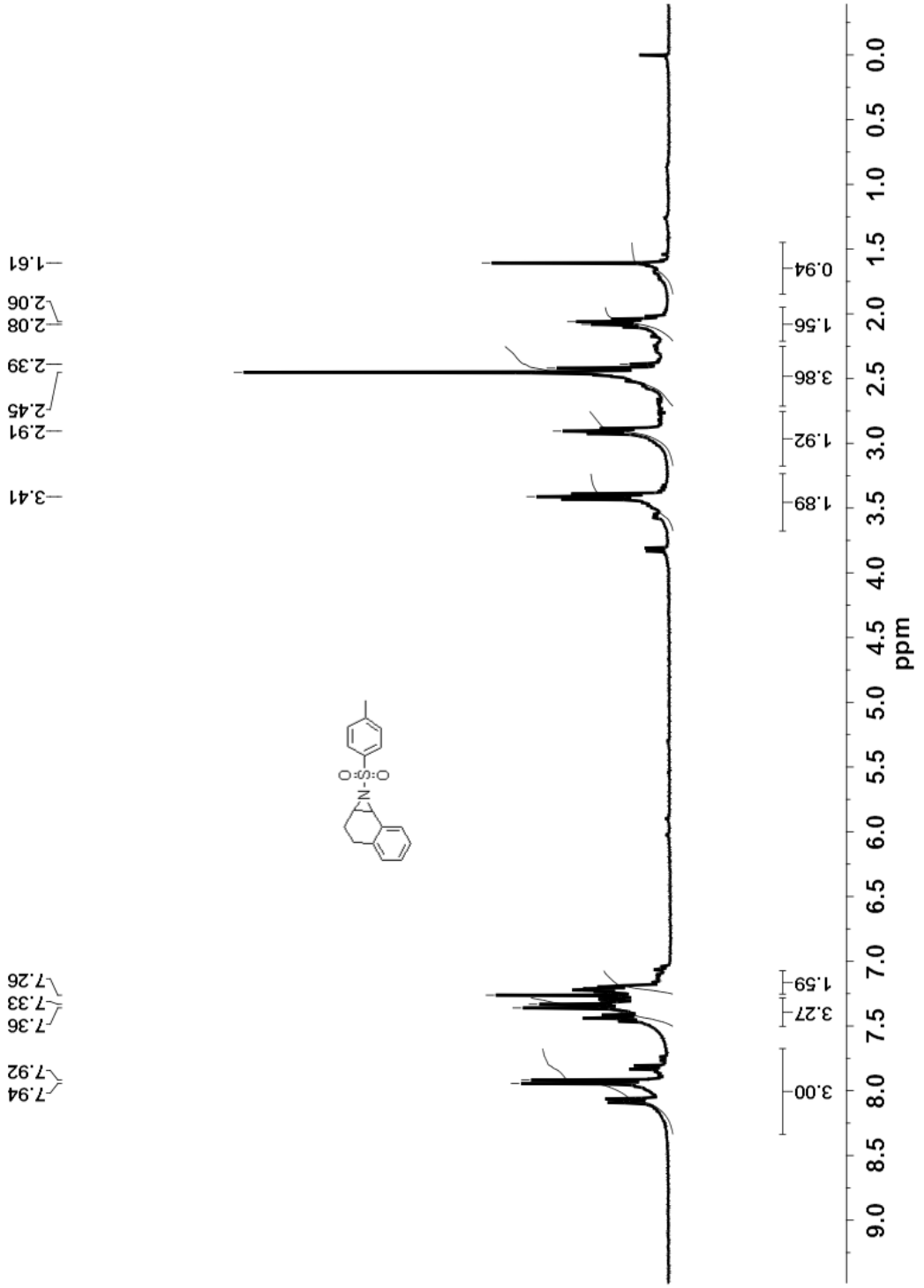
7.5
8.5
ppm
Me O



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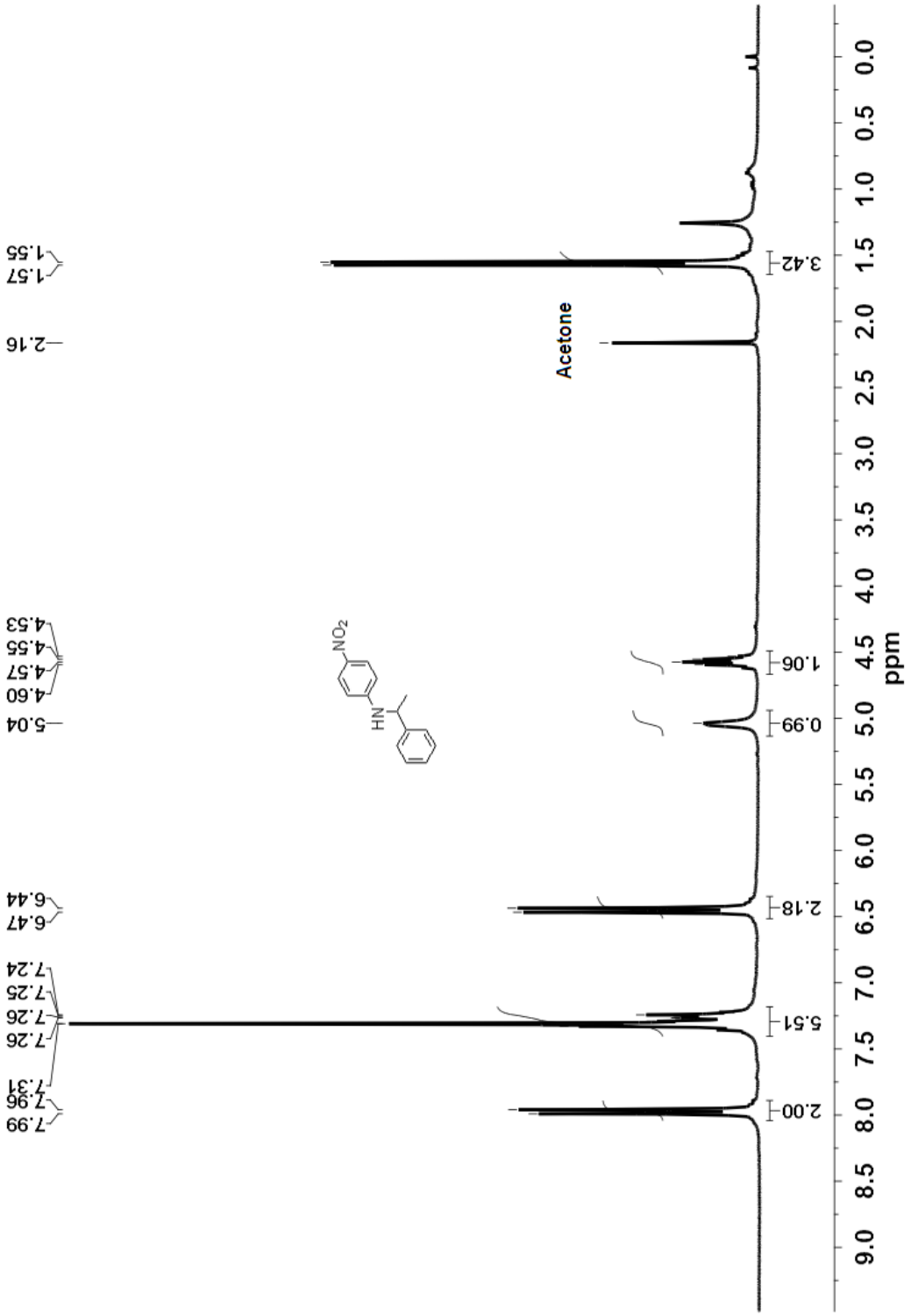

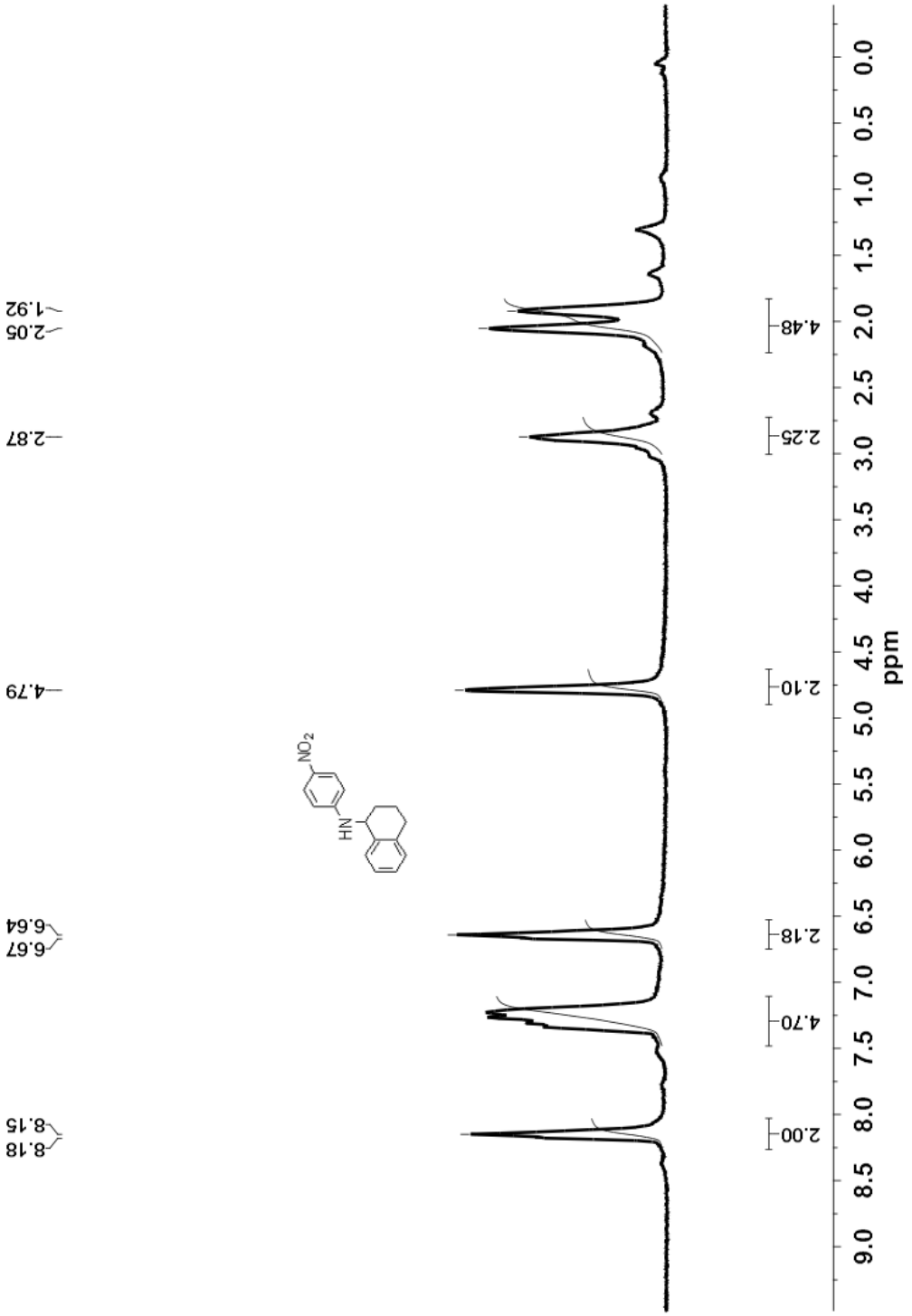
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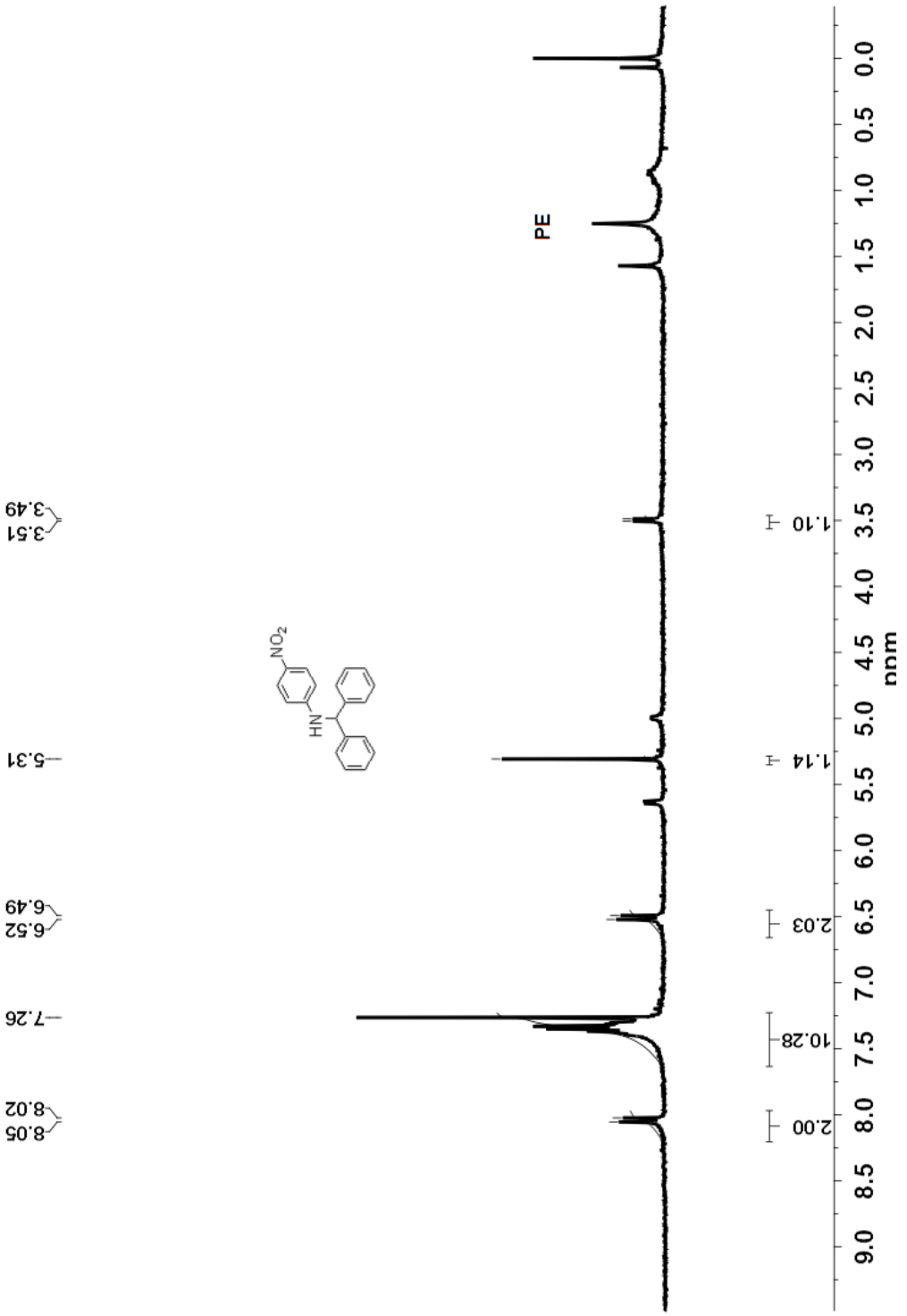
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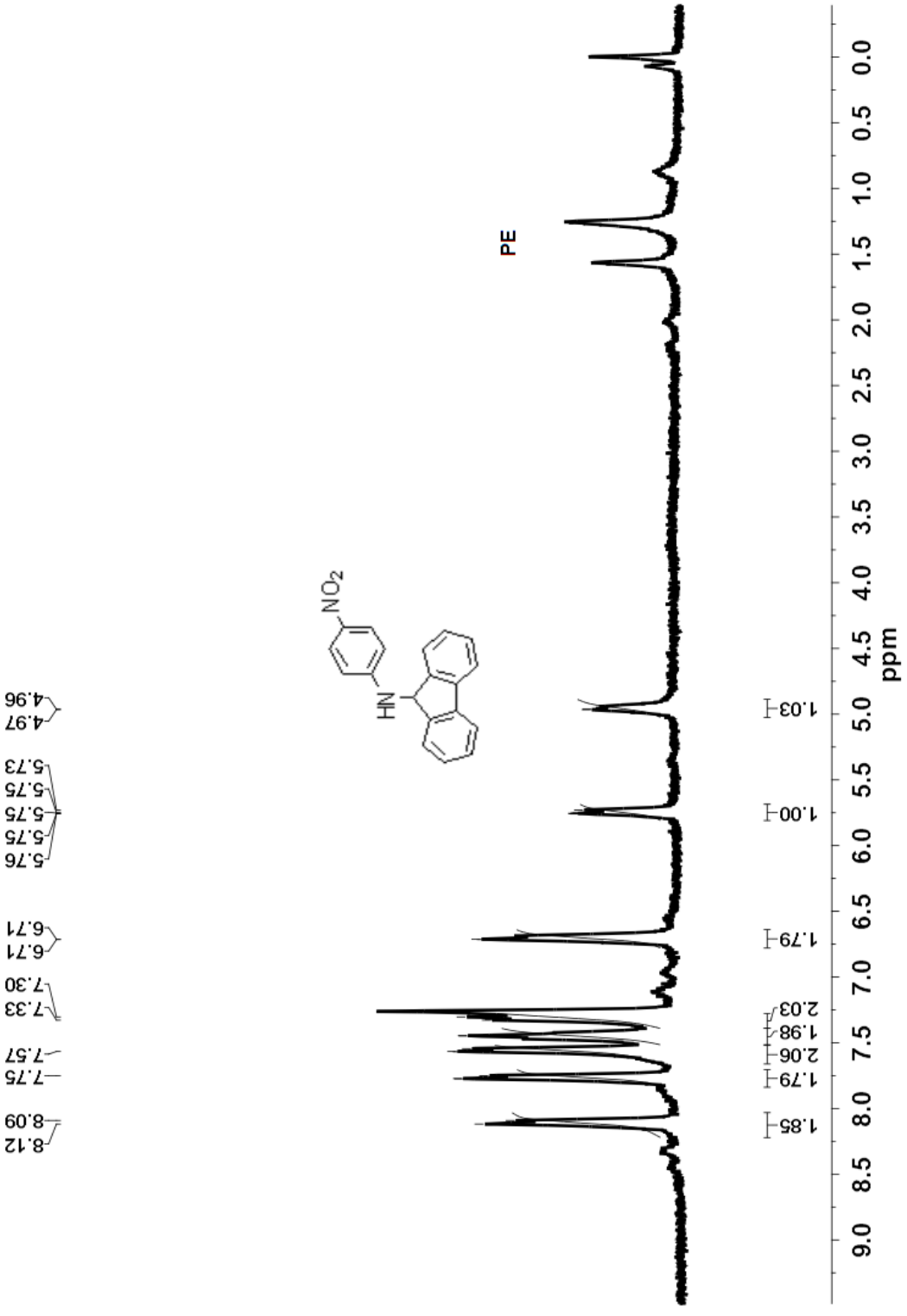
ppm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HN
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2.5
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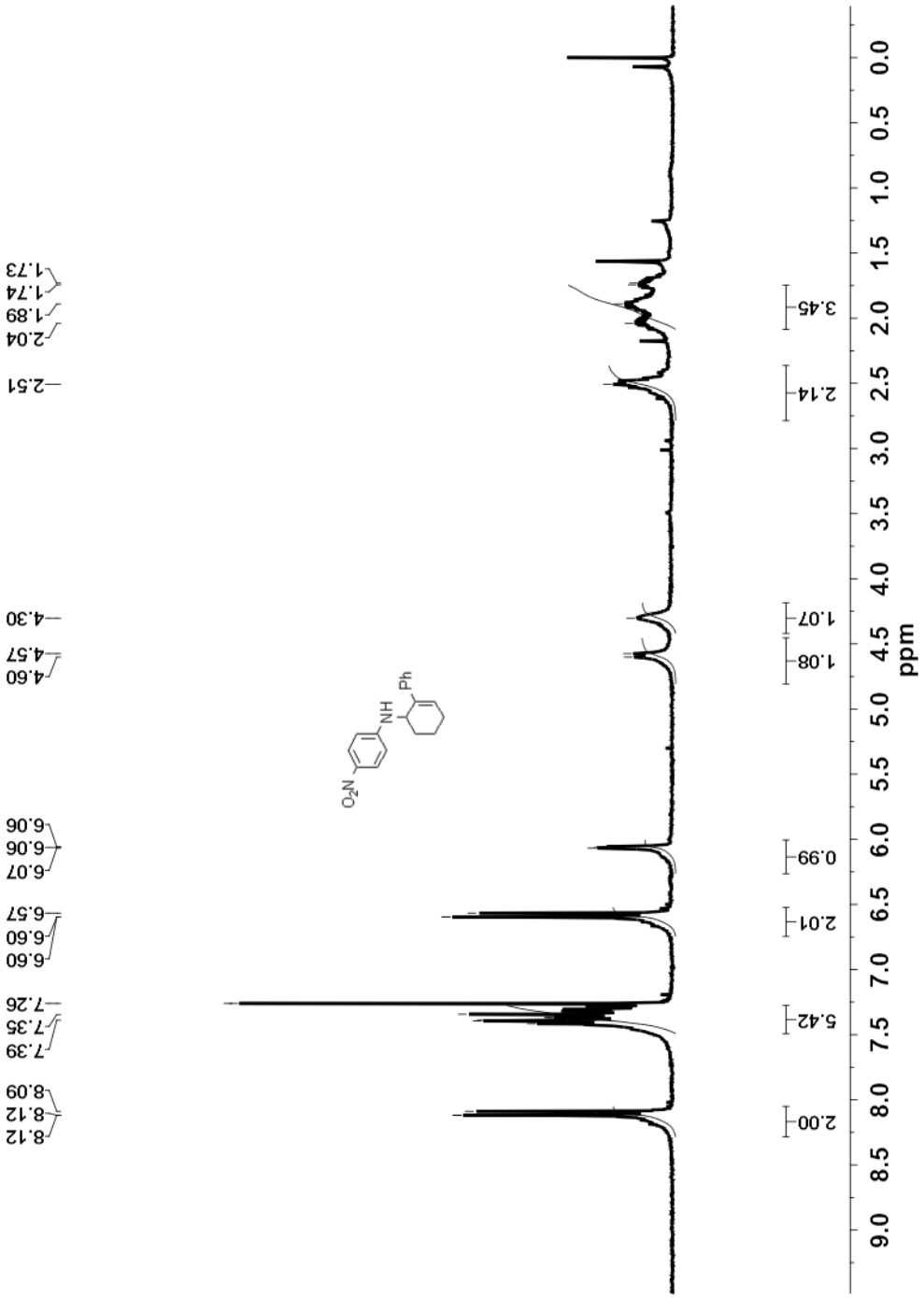
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
1.03
1.00
1.79
2.03
1.98
2.06
1.79
1.85
4.97
4.96
5.73
5.75
5.75
5.75
5.76
6.71
6.71
7.30
7.33
7.57
7.75
8.09
8.12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8.12
8.09
7.39
7.35
7.26
6.60
6.60
6.57
6.07
6.06
6.06
4.60
4.57
4.30
2.51
2.04
1.89
1.74
1.73
2.00
5.42
0.99
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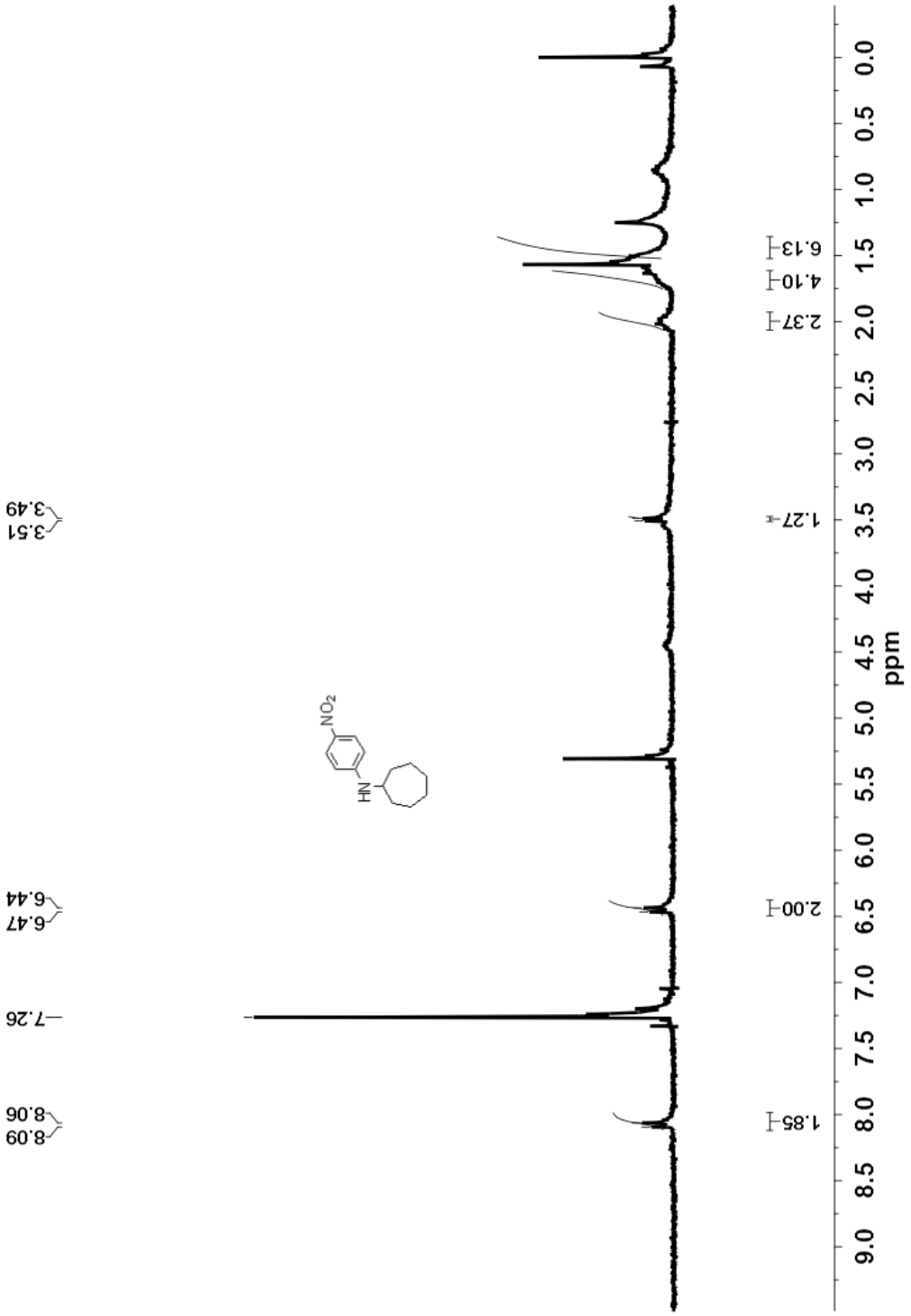
1.07
1.08
2.14
3.45
NH
Ph
O2N
ppm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8.06
7.26
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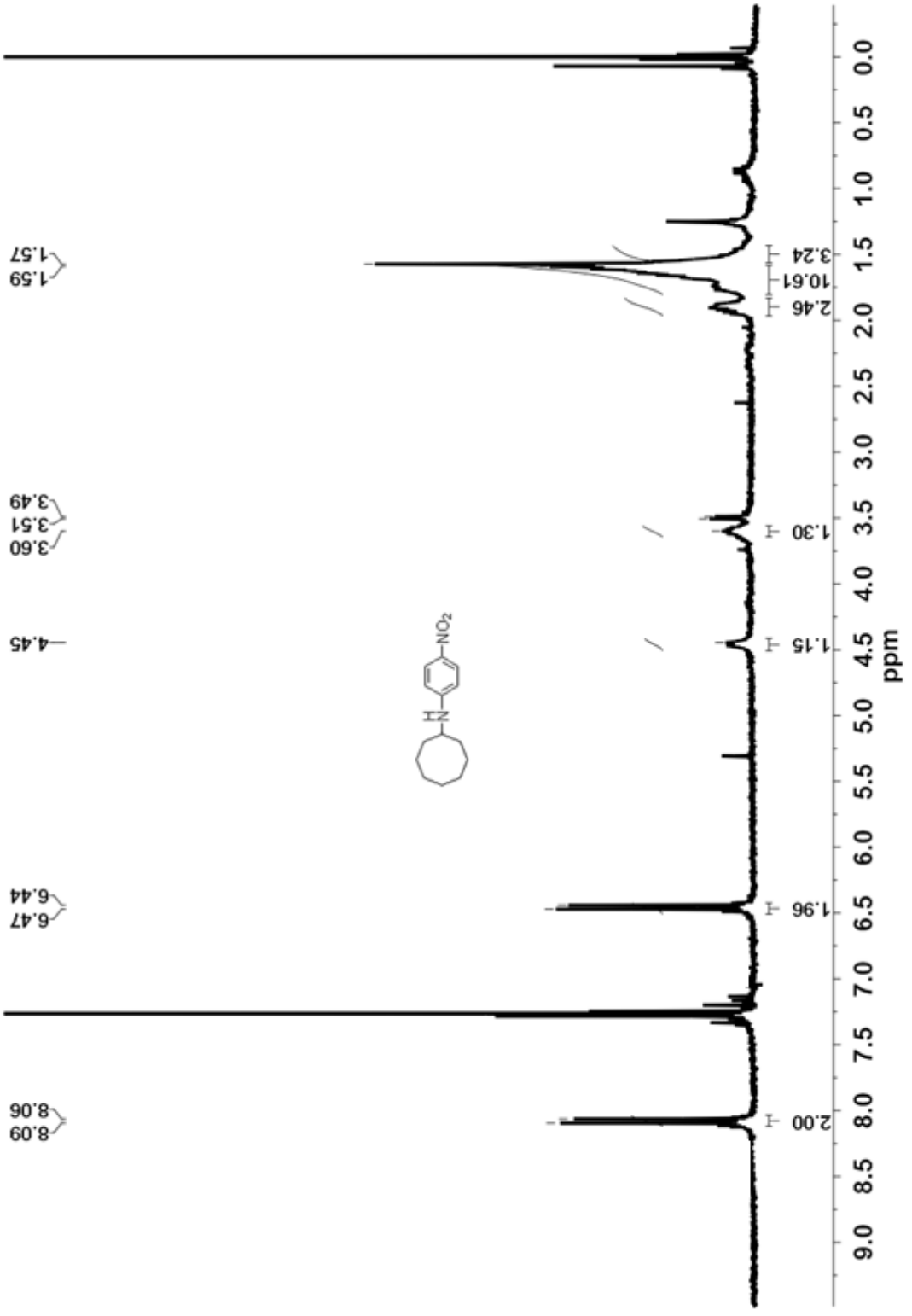
NO2
HN
ppm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8.06
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6.44
4.45
3.60
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1.30
3.24
10.61
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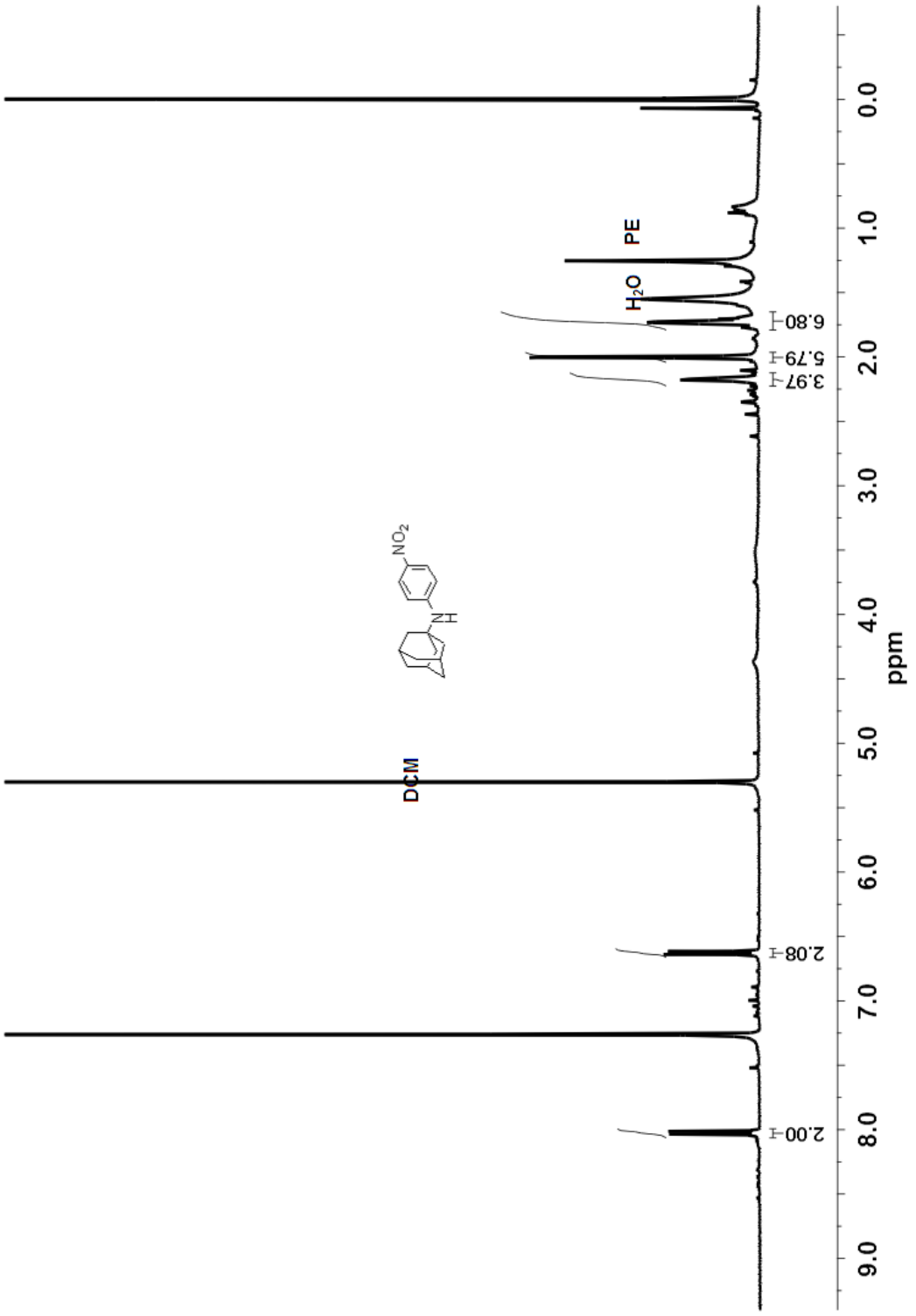
NO2
HN
ppm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H
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2.08
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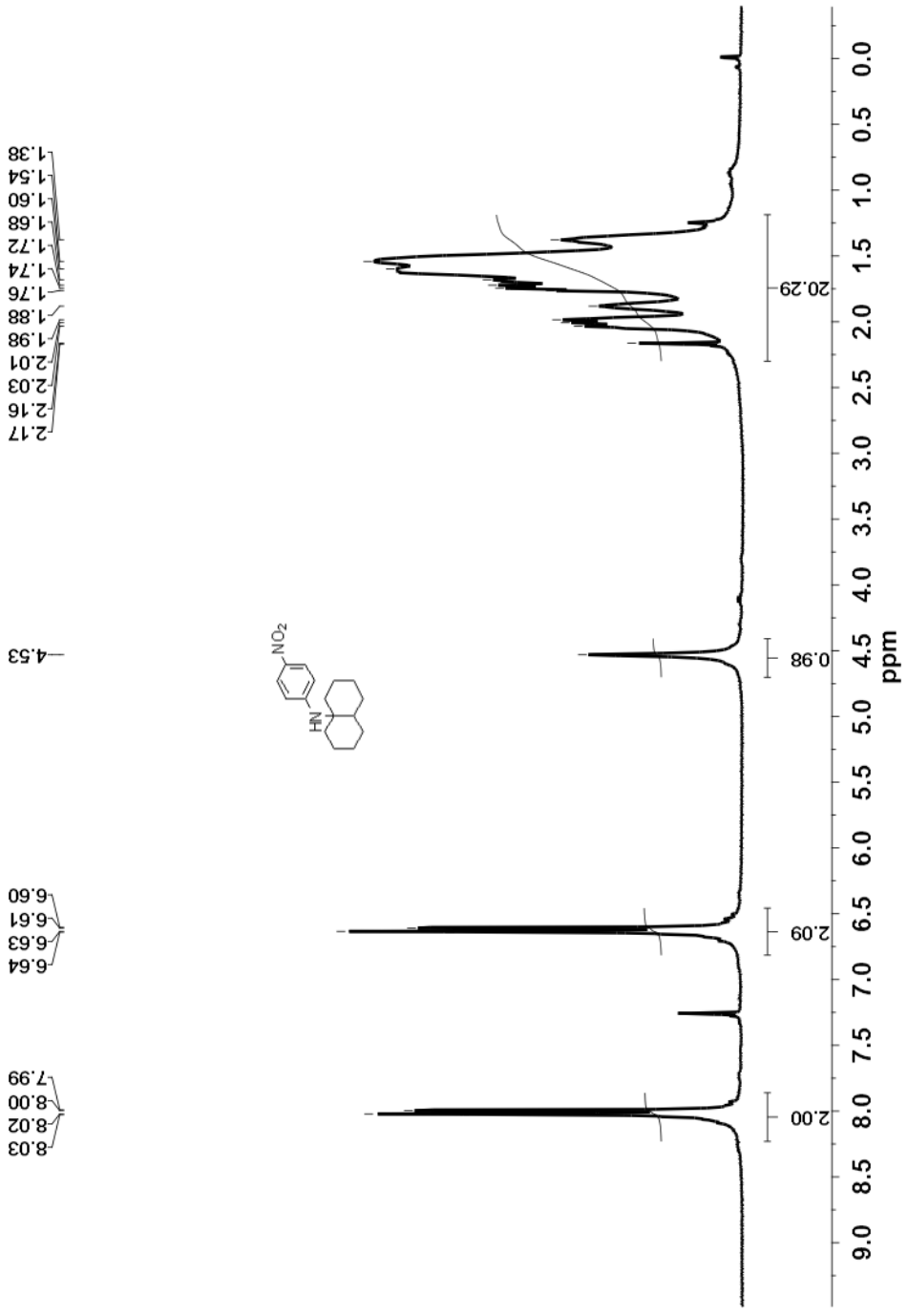
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm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1.60
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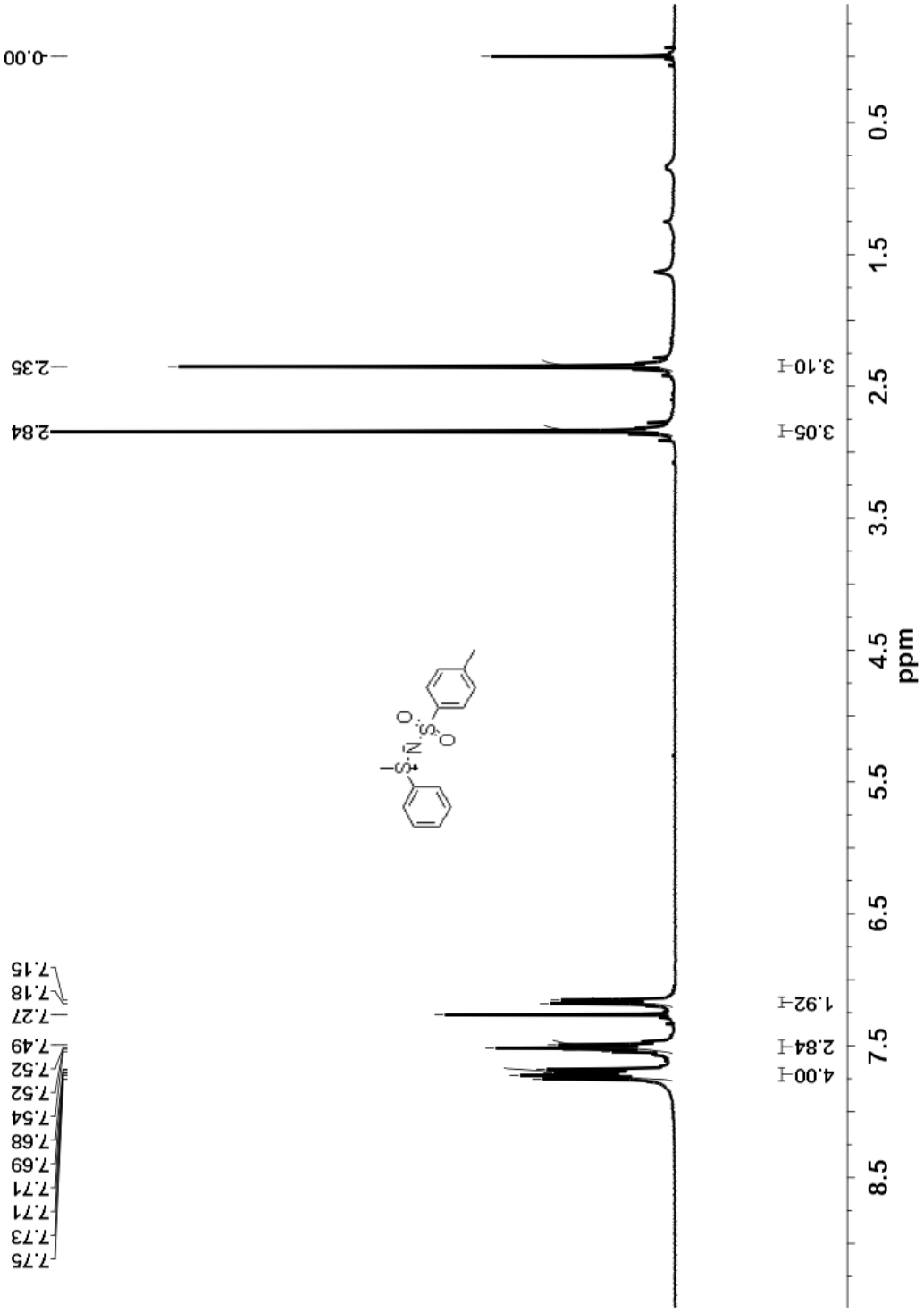
1.72
1.74
1.76
1.88
1.98
2.01
2.03
2.16
2.17
4.53
6.60
6.61
6.63
6.64
7.99
8.00
8.02
8.03
20.29
0.98
2.09
2.00
ppm
NO2
HN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7.27
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7.52
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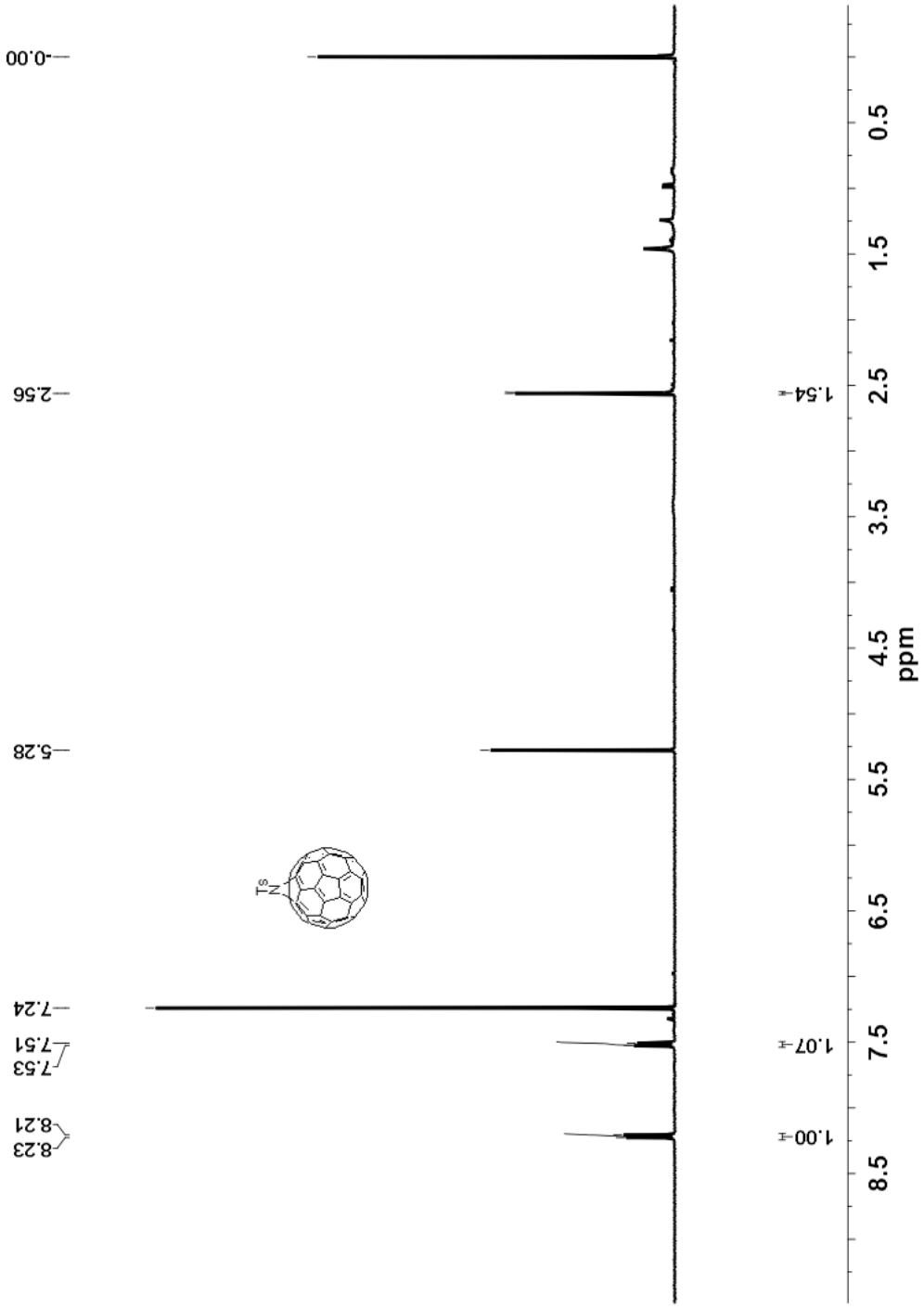
7.54
7.68
7.69
7.71
7.71
7.73
7.75
3.10
3.05
1.92
2.84
4.00
0.5
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
ppm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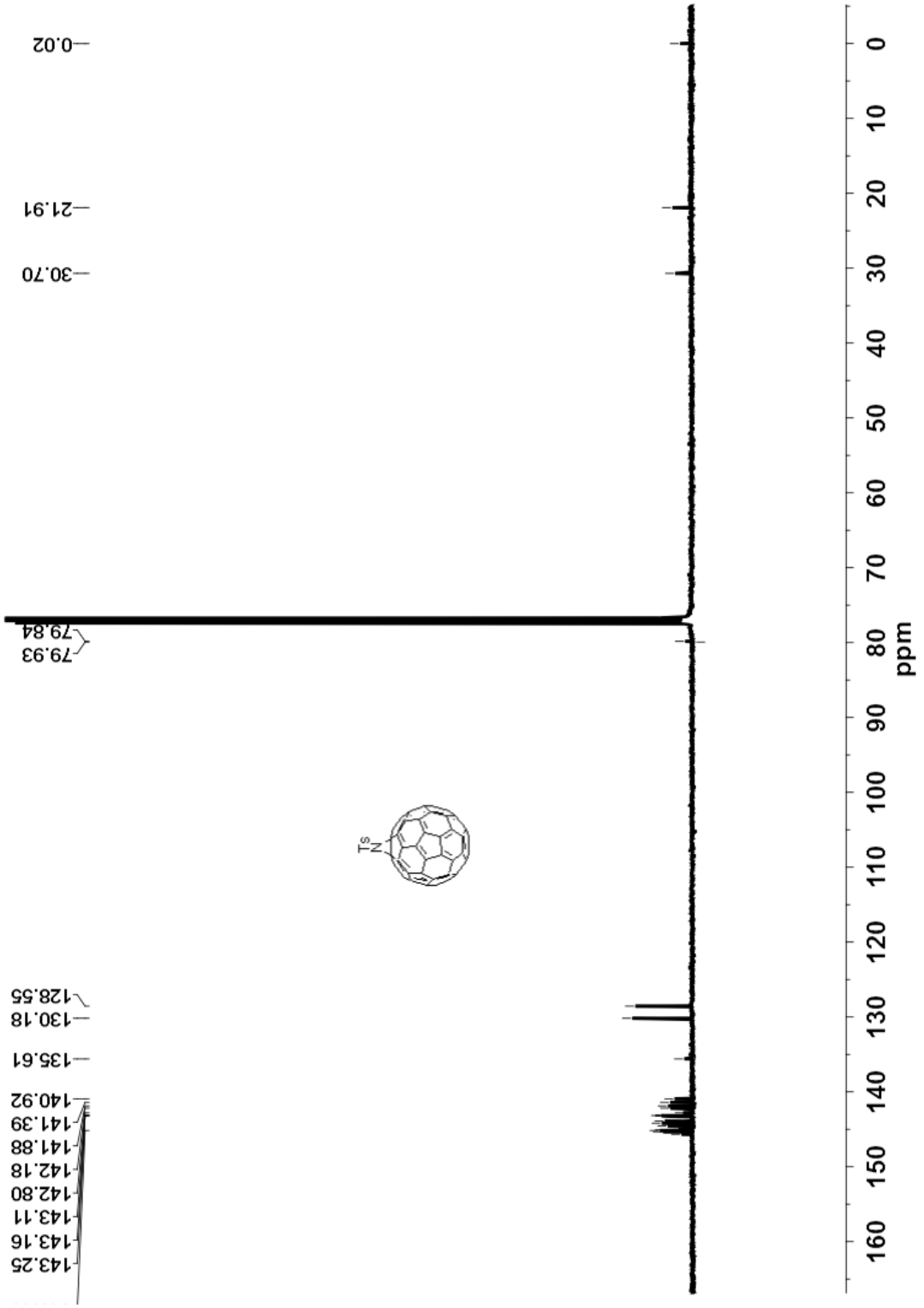
5.28
7.24
7.51
7.53
8.21
8.23
1.54
1.07
1.00
0.5
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
ppm
Ts
N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79.84
79.93
128.55
130.18
135.61
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141.39
141.88
142.18
142.80
143.11
143.16
143.25
Ts
N
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm

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