Supporting Informations

A facile noncatalytic pathway for nitrene transfer process: expeditious access to aziridines

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CONTENTS

Preparation of NN-dibromo-p-toluene sulfonamide

The reagent NN-dibromo-p-toluene sulfonamide was prepared from Chloramine-T by following literature procedure[1] as follows.

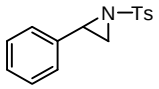
Bromine (2 ml) was added drop wise to a solution of Chloramine-T.$3H_2O$ (10 g) in water (200 ml) with constant stirring. The golden yellow precipitate of NN-dibromo-*p*-toluene sulfonamide was filtered under suction, washed with water and dried in a desiccator over P_2O_5 for 24 h.

General procedure for synthesis of aziridine: To a solution of olefin (1 mmol) and K_2CO_3 (2.5 mmol), in dry ethyl acetate (5 ml), a solution of $TsNBr_2$ (1.2 mmol) in dry ethyl acetate (5 mL) was added with the aid of a dropping funnel under nitrogen atmosphere. The reaction was stirred at room temperature under nitrogen atmosphere for appropriate time (TLC). After completion of the reaction, an aqueous solution of 10% sodium thiosulfate (5 mL) was added and the organic layer separated. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with brine and dried over anhydrous sodium sulfate and concentrated. The crude product was purified by flash chromatography on silica gel (230–400 mesh) with petroleum ether/ethyl acetate as eluent.

Procedure for synthesis of *N*-(*p*-tosy1)-l *H*-azepine: A mixture of $TsNBr_2$ (0.33 g, 1 mmol) and K_2CO_3 (0.28 g, 2 mmol) of was taken in a schlenk tube. It was evacuated and then back-filled with nitrogen. Then dry benzene (5 mL) was added under nitrogen atmosphere and the tube was sealed properly. Then the reaction set up was heated to 150 ^{o}C for 5 hrs. After completion of the reaction, an aqueous solution of sodium thiosulfate was added and the organic layer was separated. The aqueous layer was extracted with 1:1 petroleum ether - benzene, and the combined organic layer was washed with brine and dried over anhydrous sodium sulfate and concentrated. The crude product was purified by flash chromatography on silica gel (230–400 mesh) with petroleum ether/benzene (1:1) as eluent (Yield 54 mg, 22 %).

Experimental data:

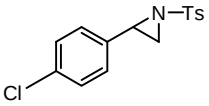
(1b) 2- Phenyl-1-(toluene-4-sulfonyl)-aziridine[2]



^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.81 (d, *J* = 8.4 Hz, 2H), 7.27-7.14(m, 7H), 3.71 (dd, *J* = 4.6 Hz, 7.1 Hz, 1H), 2.92 (d, *J* =7.2, 1H), 2.36 (s, 3H) 2.32 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100MHz) δ: 152.9, 143.2, 143.1, 137.9, 136.7, 136.5, 136.1, 134.7, 49.2, 44.1, 29.8.

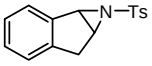
(2b) 2-(4-Chloro-phenyl)-1-(toluene-4-sulfonyl)-aziridine[2,3]



^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.86 (d, *J* =8.4 Hz, 2H), 7.35-7.14 (m, 6H), 3.73 (dd, *J* = 4.4Hz, 4.7Hz, 1H,), 2.98 (d, *J* =9.2 Hz, 1H), 2.44 (s, 3H) 2.34 (d, *J* = 4.4Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz)δ: 144.8, 134.7, 133.5, 129.8, 128.7, 127.9, 127.9, 40.2, 36.0, 30.9, 21.7.

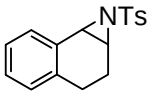
(3b) 1-[(4-methylphenyl)sulfonyl]-1,1a,6,6a-tetrahydroindeno[1,2-*b*]azirene [4]



^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.82 (d, *J*=8.1 Hz, 2H), 7.39 (d, *J*= 7.4 Hz, 1H), 7.31 (d, *J*= 8.1 Hz, 2H), 7.24-7.23 (m, 3H), 4.29 (d, *J*= 5.3 Hz, 1H), 3.15-3.12 (m, 2H), 2.43 (s, 3H).

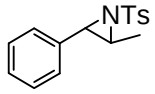
^{13}C NMR ($CDCl_3$, 100 MHz)δ: 144.4, 143.5, 138.2, 135.5, 129.7, 128.7, 127.7, 126.7, 125.6, 125.1, 50.1, 44.9, 34.6, 21.6.

(4b) 1-[(4-methylphenyl)sulfonyl]-1a,2,3,7b-tetrahydro-1*H*-naphtho[1,2-*b*]azirene[3,4]



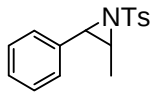
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.81 (d, *J*= 8.4 Hz, 2H), 7.34-7.1 (m, 6H), 7.12-7.04 (m, 2H), 7.04 (d, *J*=7.4 Hz, 1H), 3.81 (d, *J*= 7.1 Hz, 1H), 3.60-3.50 (m, 1H), 2.85-2.68 (m, 1H), 2.58-2.48 (m, 1H), 2.41 (s, 3H), 2.30-2.18 (m, 1H), 1.72-1.60 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz)δ: 144.2, 136.6, 135.6, 130.0, 129.7, 129.4, 128.6, 128.4, 127.6, 126.3, 42.1, 41.7, 24.7, 21.6, 20.0

(5b) *trans*-**2-Methyl-1-[(4-methylphenyl)sulfonyl]-3-phenylaziridine**[5]



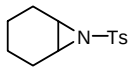
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.75 (d, *J*= 8.3 Hz, 2H), 7.32-7.12 (m, 5H), 7.12-7.04 (m, 2H), 3.72 (d, *J*=4.3 Hz, 1H), 2.90-2.75 (m, 1H), 2.32 (s, 3H), 1.77 (d, *J*=5.9 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz)δ: 143.9, 137.9, 135.6, 129.5, 128.5, 128.1, 127.2, 126.3, 49.1, 21.6, 14.1.

(6b). *cis*-**2-Methyl-1-[(4-methylphenyl)sulfonyl]-3-phenylaziridine**[5]



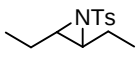
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.85 (d, *J*= 8.1 Hz, 2H), 7.40-7.14 (m, 7H), 3.89 (d, *J*=7.4 Hz), 3.18-3.10 (m, 1H), 2.40 (s, 3H), 0.99 (d, *J*=5.6 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz)δ: 144.4, 135.3, 132.7, 129.7, 128.23, 127.8, 127.5, 126.2, 46.1, 41.5, 21.6, 11.9.

(7b). 7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptane[2,3]



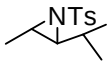
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.78 (d, *J*= 8.1 Hz, 2H,), 7.29 (d, *J*=7.9 Hz, 2H), 2.98-2.88 (m, 2H), 2.41 (s, 3H), 1.82-1.65 (m,4H), 1.40-1.10 (m, 4H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.9, 135.8, 129.5, 127.5, 39.7, 21.5.

(8b). 2,3-diethyl-1-[(4-methylphenyl)sulfonyl]aziridine[5]



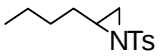
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.82 (d, *J*= 8.4 Hz, 2H,), 7.29 (d, *J*=8.1 Hz, 2H), 2.64-2.56 (m, 2H), 2,41 (s, 3H), 1.82-1.65 (m,4H), 0.91 (t, *J*=7.4 Hz, 6H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.7, 138.0, 129.4, 127.4, 50.9, 23.2, 21.6, 11.7.

(9b). **2-Isopropyl- 3- methyl-1-tosylaziridine**[6]



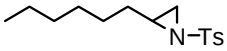
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.77 (d, 2H, *J*=8,24 Hz), 7.24 (d, 2H, *J*= 7.8), 2.62-2.61 (m, 1H,), 2.49-2.47 (m, 1H), 2.36 (s,3H), 1.59 (d, 3H, *J*= 4.12) 1.39 (m, 1H), 0.81 (d, 3H, *J*= 6.88), 0.66 (d, 3H, *J*=6.88) ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.7, 137.9, 129.3, 127.4, 54.9, 45.3, 30.0, 21.4, 19.7, 19.3, 14.2

(10b). 2-butyl-1-[(4-methylphenyl)sulfonyl]aziridine



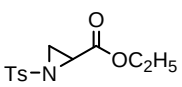
^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.81 (d, *J* = 8.4 Hz, 2H,), 7.32 (d, *J* = 8.1 Hz, 2H), 2.75-2.65 (m, 1H), 2.61 (d, *J* = 6.9 Hz, 1H,) 2.43 (s, 3H), 2.04 (d, *J* = 4.6 Hz, 1H,) 1.58-1.45 (m, 1H), 1.38-1.14 (m, 5H), 0.79 (t, *J*= 6.9 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 144.4, 135.2, 129.6, 128.0, 40.4, 33.8, 31.0, 28.8, 22.1, 21.6, 13.8.

(**11b**). **2-hexyl-1-[(4-methylphenyl)sulfonyl]aziridine**[7]



^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.82 (d, *J* = 8.4 Hz, 2H,), 7.32 (d, *J* = 8.1 Hz, 2H), 2.75-2.65 (m, 1H), 2.62 (d, *J* = 7.1 Hz, 1H,) 2.43 (s, 3H), 2.04 (d, *J* = 4.6 Hz, 1H,) 1.58-1.44 (m, 1H), 1.37-1.15 (m, 9H), 0.84 (t, *J*= 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 144.4, 135.2, 129.6, 128.0, 40.5, 33.8, 31.6, 31.3, 28.7, 26.7, 22.4, 21.6, 14.0.

(12b). Ethyl-1-tosylaziridine-2-carboxylate[8]



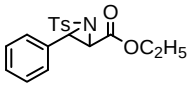
IR (KBr, cm^{-1}) ν: 2086, 1734, 1643, 1332, 1214, 1162, 1091, 1027; ^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.75-7.22 (m, 4H), 4.09-4.06 (m, 2H), 3.28-3.21 (m, 1H), 2.66-2.47 (m, 2H), 2.34 (s, 3 H) 1.14 (t, 3H, *J*=7.32); ^{13}C NMR ($CDCl_3$, 100 MHz)δ: 166.6, 145.1, 133.4, 129.7, 129.6, 62.3, 35.6, 31.8, 21.3, 13.5; GCMS (M/Z %): 29 (26), 41 (21), 58 (40), 65 (39), 86 (100), 91 (87), 114 (70), 155 (26), 196 (5), 205 (4), 224 (4), 270 (5)

(13b). 7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-one

^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.80 (d, *J* = 8.1 Hz, 2H,), 7.34 (d, *J* = 8.1 Hz, 2H), 3.48-3.38 (m, 1H), 3.13 (d, *J* = 6.6 Hz, 1H), 2.48-2.34 (m, 4H,), 2.20-2.10 (m, 1H), 2.05-1.95 (m, 1H), 1.90-1.78 (m, 2H), 1.70-1.56 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 201.4, 145.1, 134.4, 129.9, 127.9, 43.9, 40.9, 37.0, 21.8, 21.6, 17.1.

(14b) trans-N-(p-Tolylsulfonyl)-3-phenyl-2-aziridinecarboxylicacid,ethylester[3]

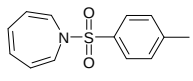


IR (KBr, cm^{-1}) ν: 2979, 2925, 2852, 1746, 1461, 1427, 1370, 1338, 1287, 1243, 1202, 1095, 1027, 894, 815, 759, 698, 599, 518

^{1}HNMR ($CDCl_3$, 300 MHz) δ: 7.78 (d, 2H, *J*=8.4 Hz), 7.31-7.24(m, 7H), 4.44(d, 1H, *J*=4.4), 4.33-4.30 (m, 2H), 3.52 (d, 1H, *J*=4 Hz), 2.41 (s, 3H) 1.34 (t, 3H, *J*=7. 2).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 165.8, 144.3, 137.1, 132.6, 129.6, 128.9, 128.6, 127.5, 127.3, 62.5, 47.7, 47.1, 30.8, 21.6, 13.9.

(15) 1-[(4-methylphenyl)sulfonyl]-1*H*-azepine[9]



^{1}HNMR ($CDCl_3$, 300 MHz) δ: 7.84 (d, *J*= 7.9 Hz, 2H), 7.55 (d, *J*= 7.9 Hz, 2H), 6.45-6.15 (m, 6H), 2.44 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): 143.5, 136.7, 133.2, 130.2, 128.5, 122.6, 112.8, 21.6.

Mass (ES, m/z): 248.9 (M +1).

(16b). 4-methyl-*N*-(triphenylphosphoranylidene)benzenesulfonamide[10]

$TsN{=}PPh_3$

^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.78-7.66 (m, 6H), 7.60-7.52 (m, 3H), 7.52-7.39 (m, 8H), 6.99 (d, *J*= 7.9 Hz, 2H), 2.29 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.4, 140.4, 133.2, 133.1, 132.72, 132.69, 132.5, 132.1, 132.0, 131.1, 128.7, 128.61, 128.57, 127.9, 126.8, 125.7, 21.3.

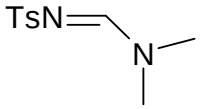
(17b). **Triethyl (4-methylphenyl)sulfonylimidophosphate[10]**

$TsN{=}P(OEt)_3$

^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.82 (d, *J*=8.1 Hz, 2H), 7.21 (d, *J*=7.9 Hz, 2H), 4.26-4.15 (m, 6H), 2.37 (s, 3H), 1.31 (dt, *J* = 7.1, 1.1 Hz, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 142.9, 141.7, 129.3, 126.3, 66.3, 66.2, 21.8, 16.2, 16.1.

(18). *N*-[(1*E*)-(dimethylamino)methylene]-4-methylbenzenesulfonamide[11]



^{1}HNMR ($CDCl_3$, 400 MHz) δ: 8.06, 7.70 (d, *J*=8.4 Hz, 2H), 7.19 (d, *J*=8.1 Hz, 2H), 3.05 (s, 3H), 2.94 (s, 3H), 2.33 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.1, 142.4, 139.5, 129.3, 126.5, 41.4, 35.5, 21.4.

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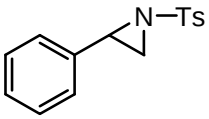
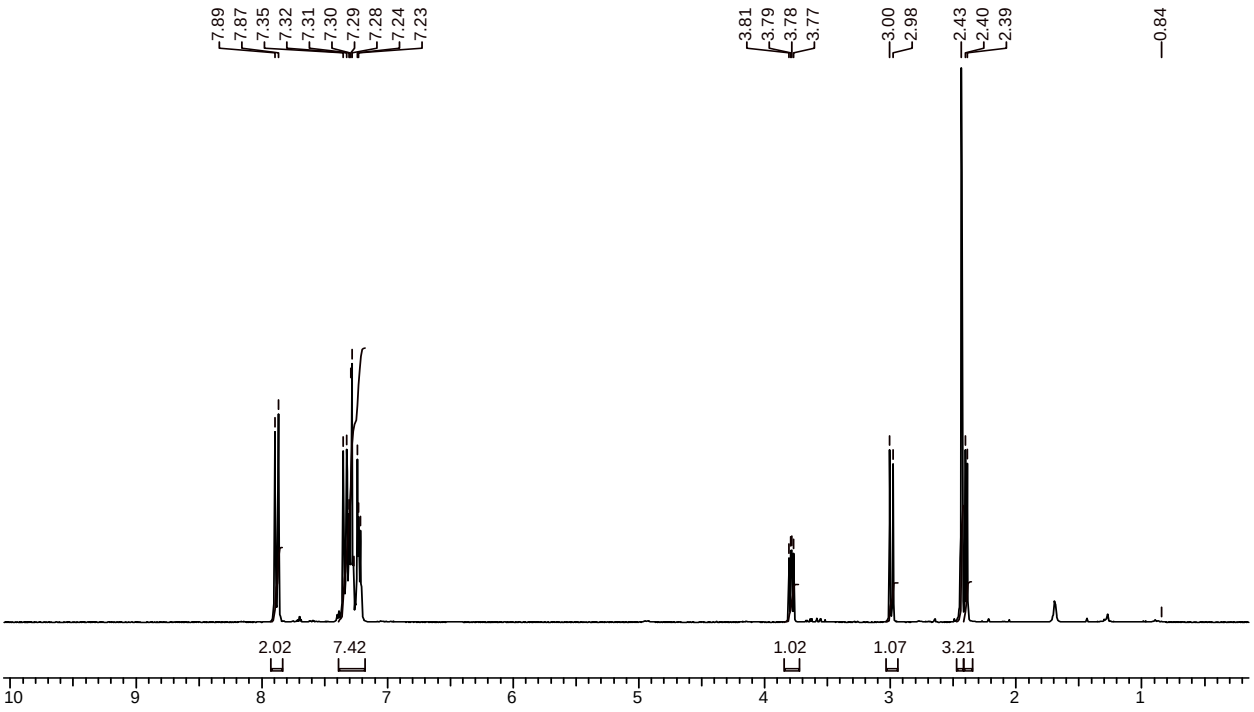

N—Ts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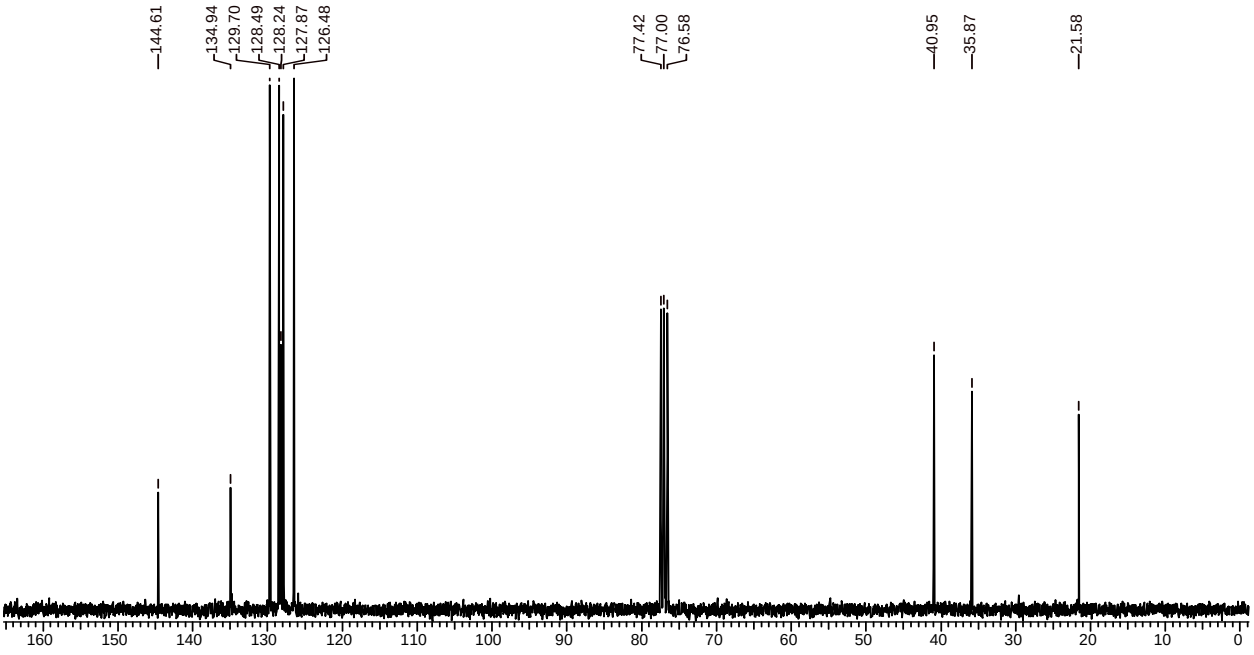
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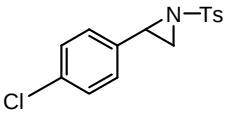
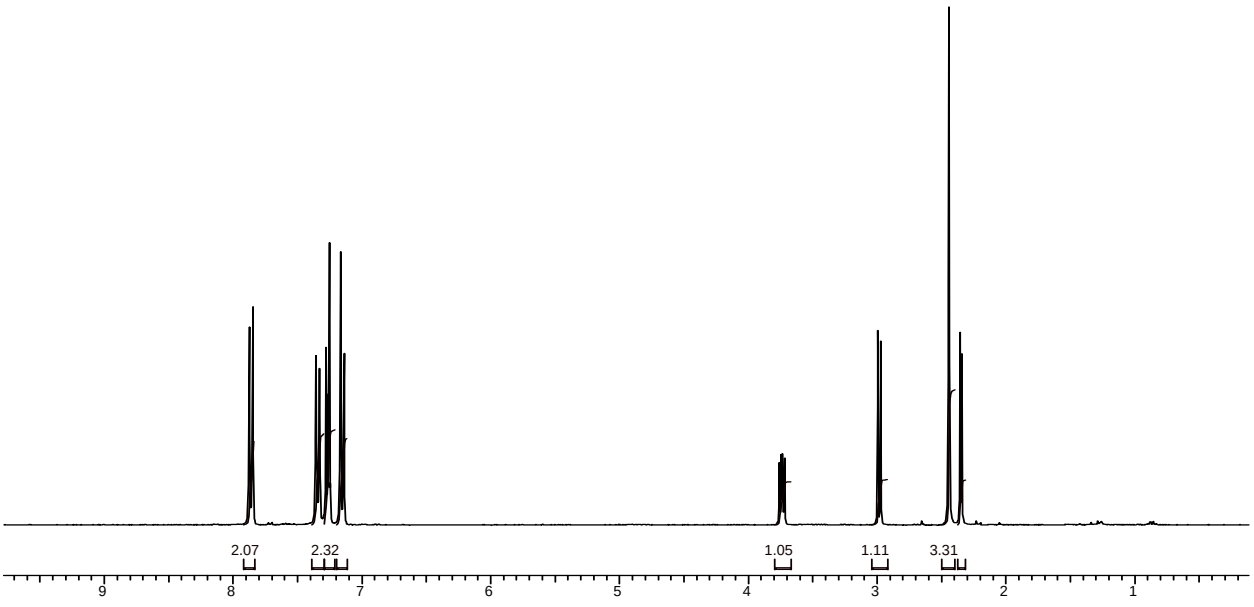

N—Ts
Cl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9
8
7
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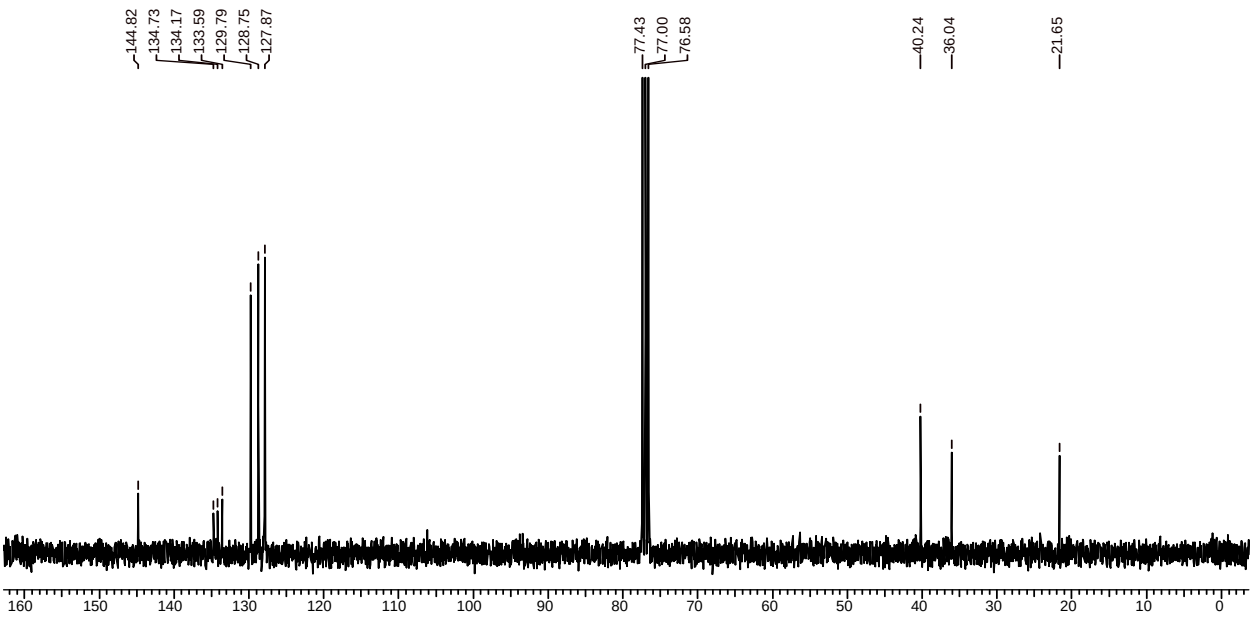
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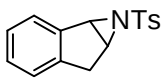
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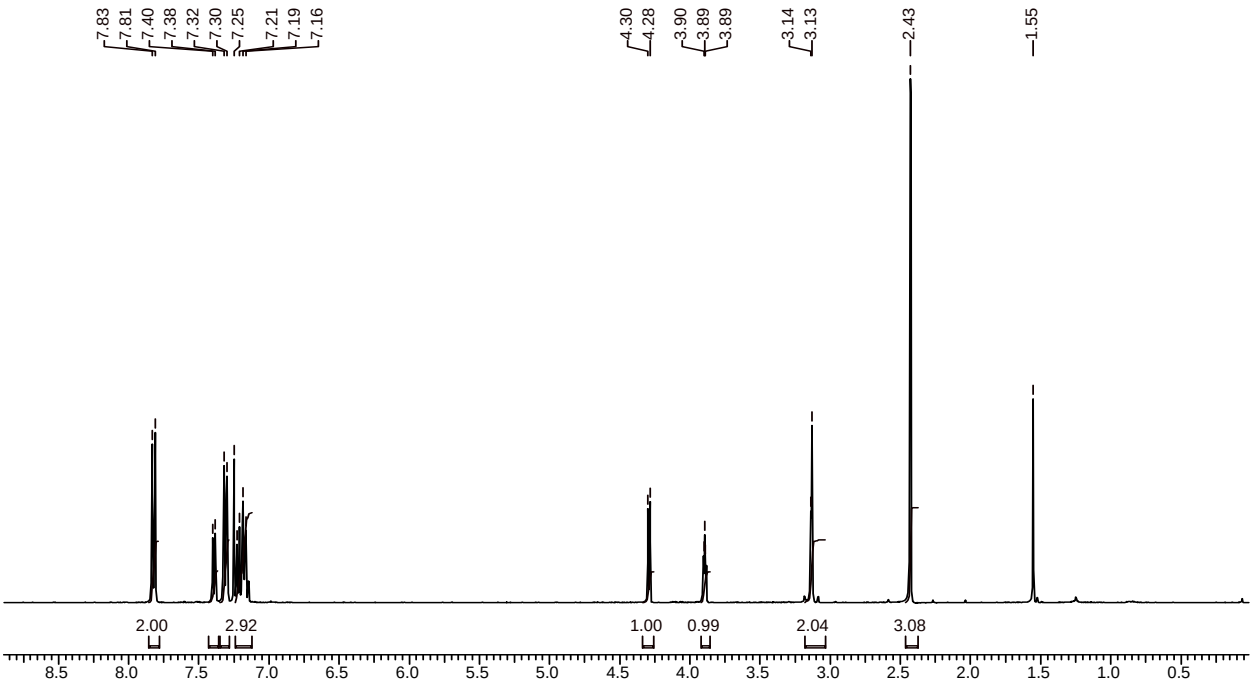
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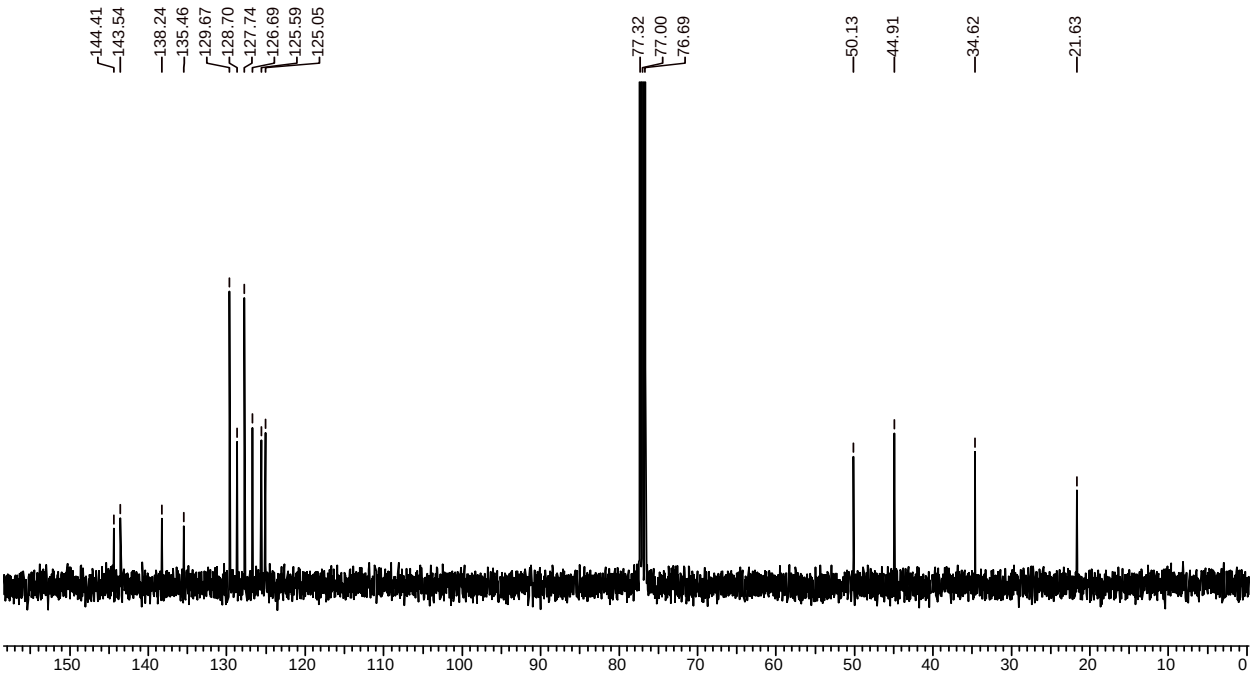
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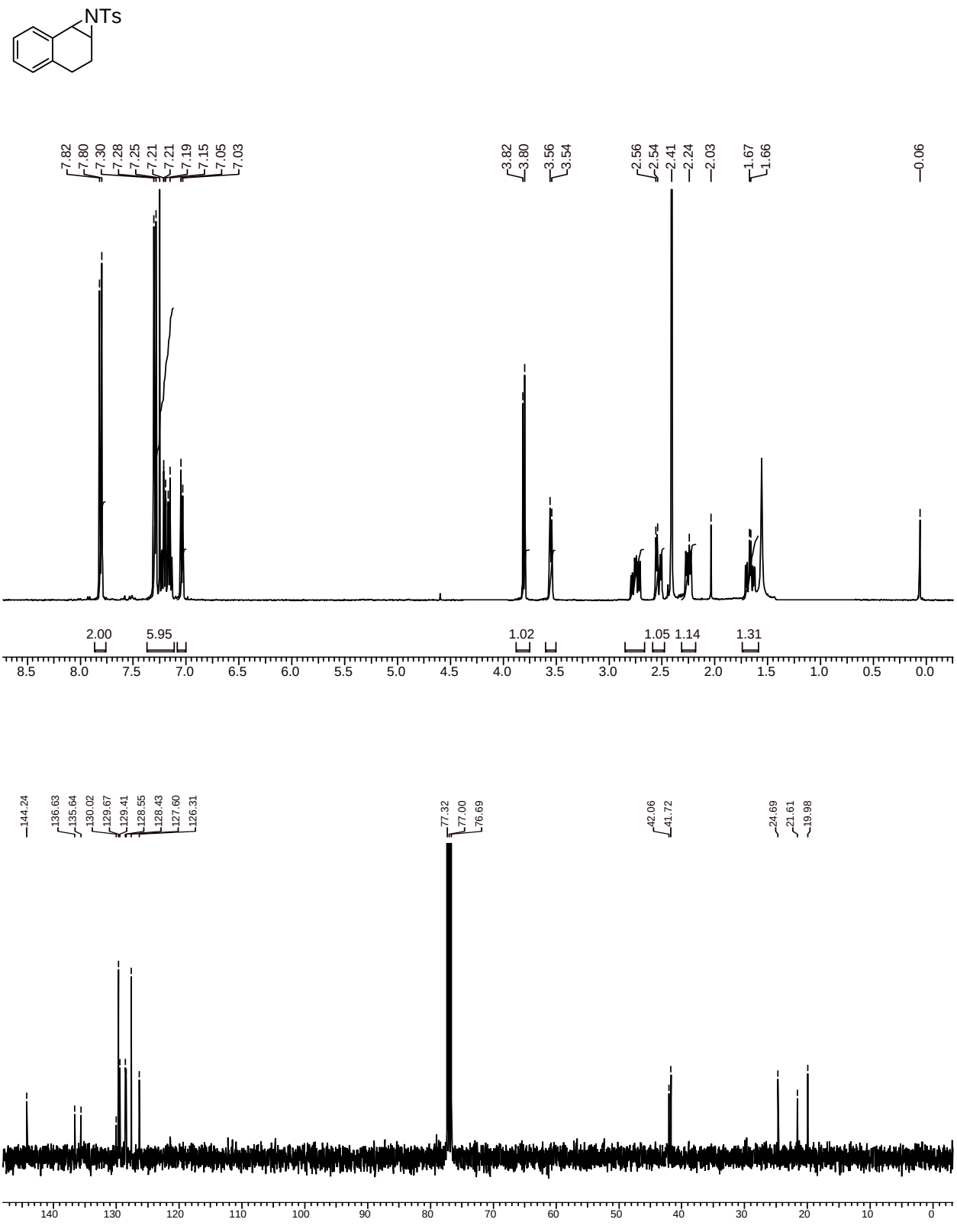
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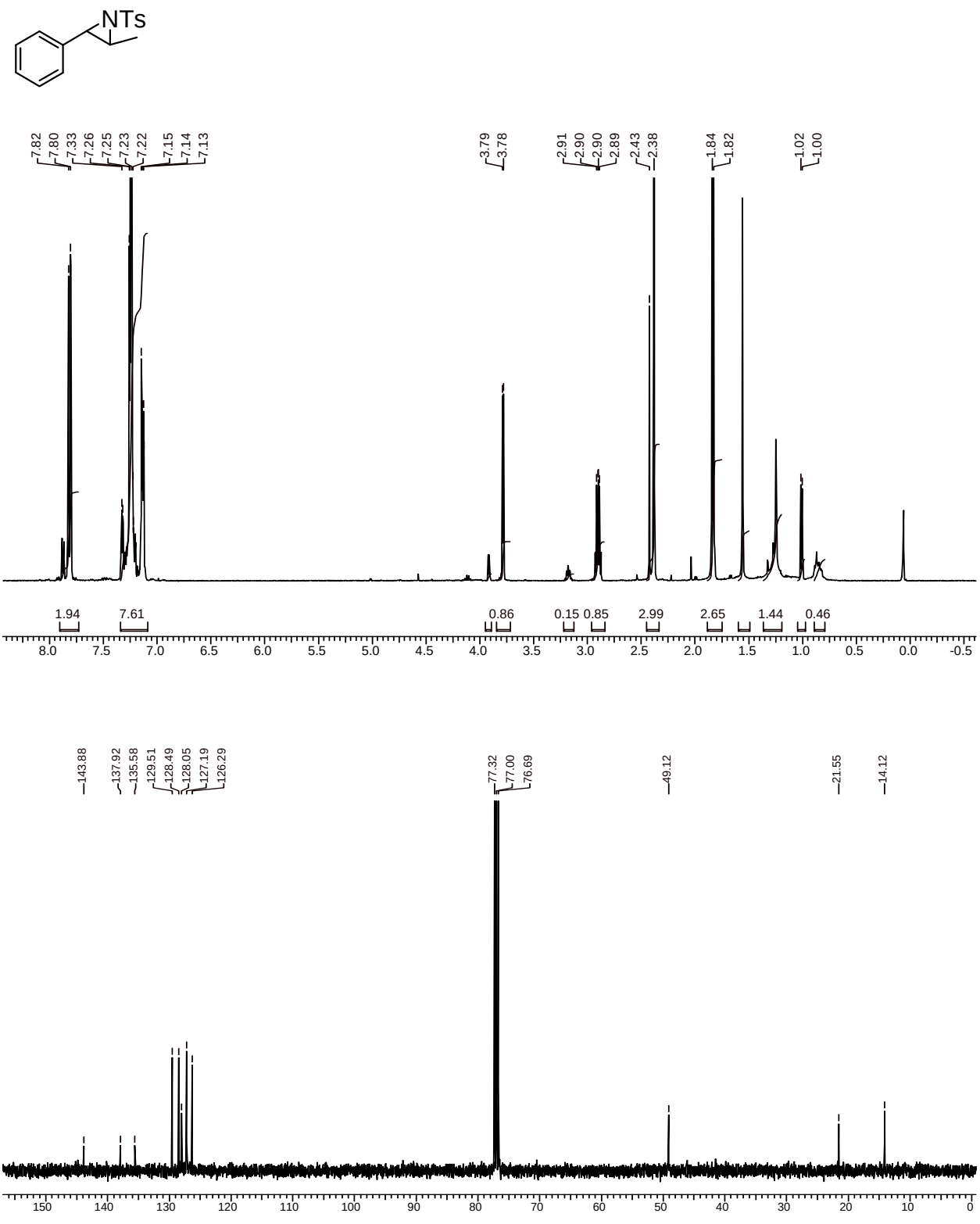
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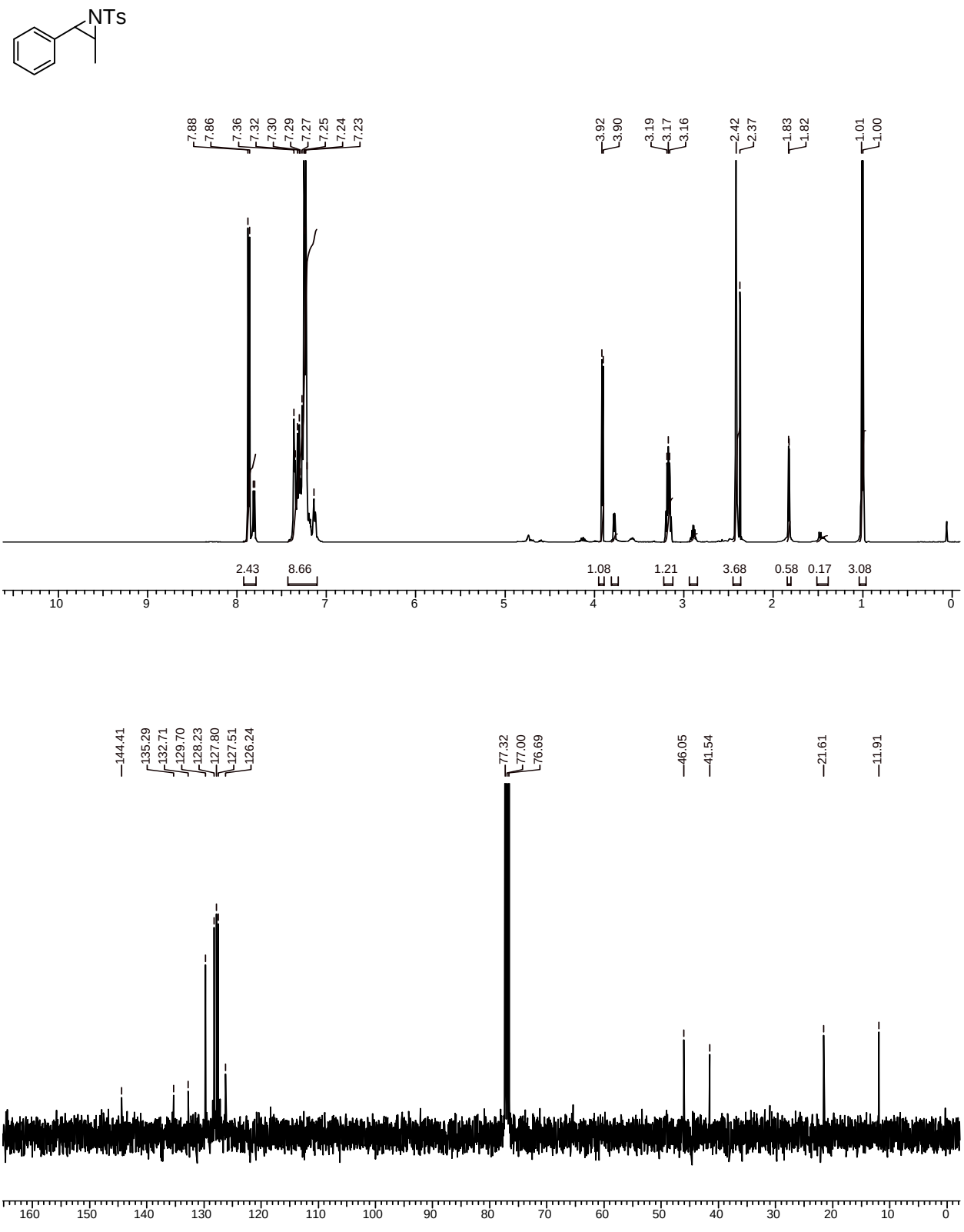
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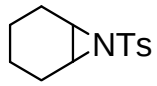
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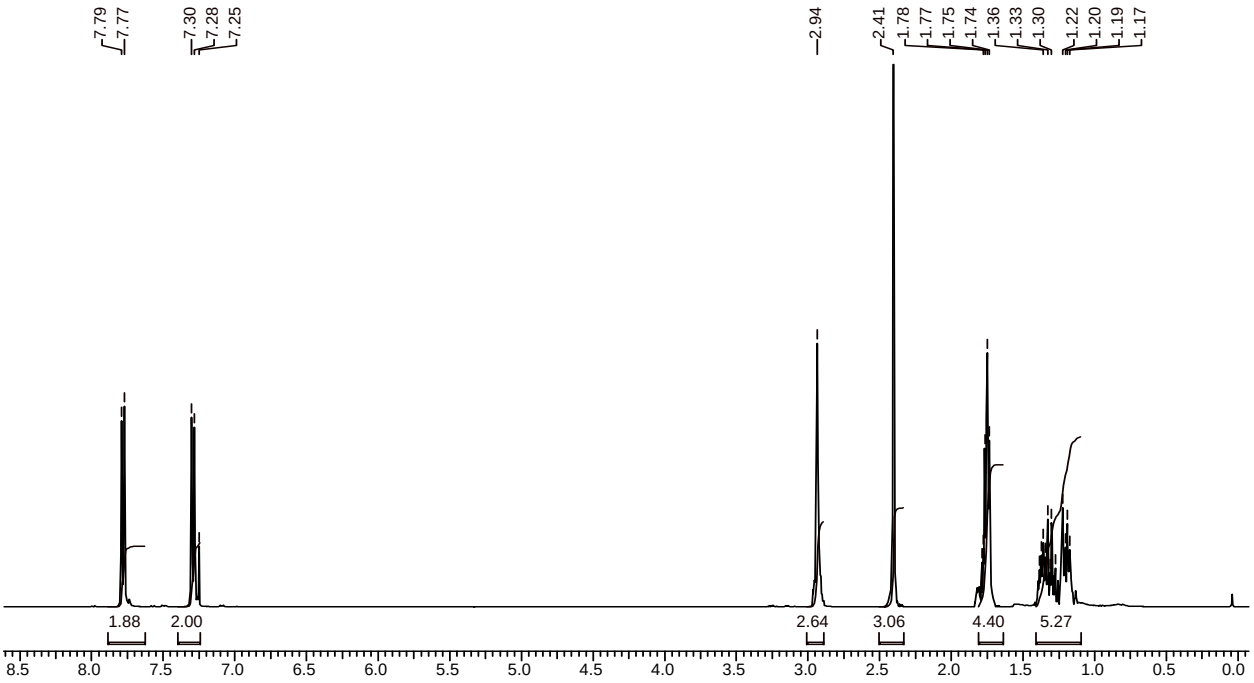
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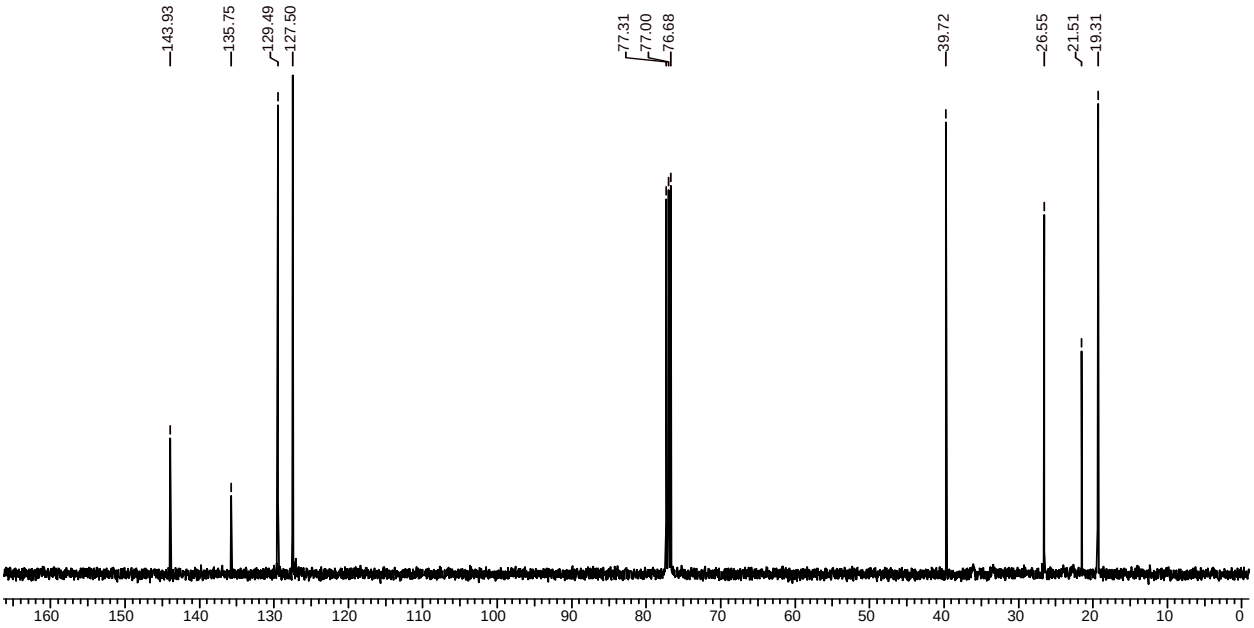
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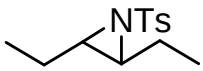
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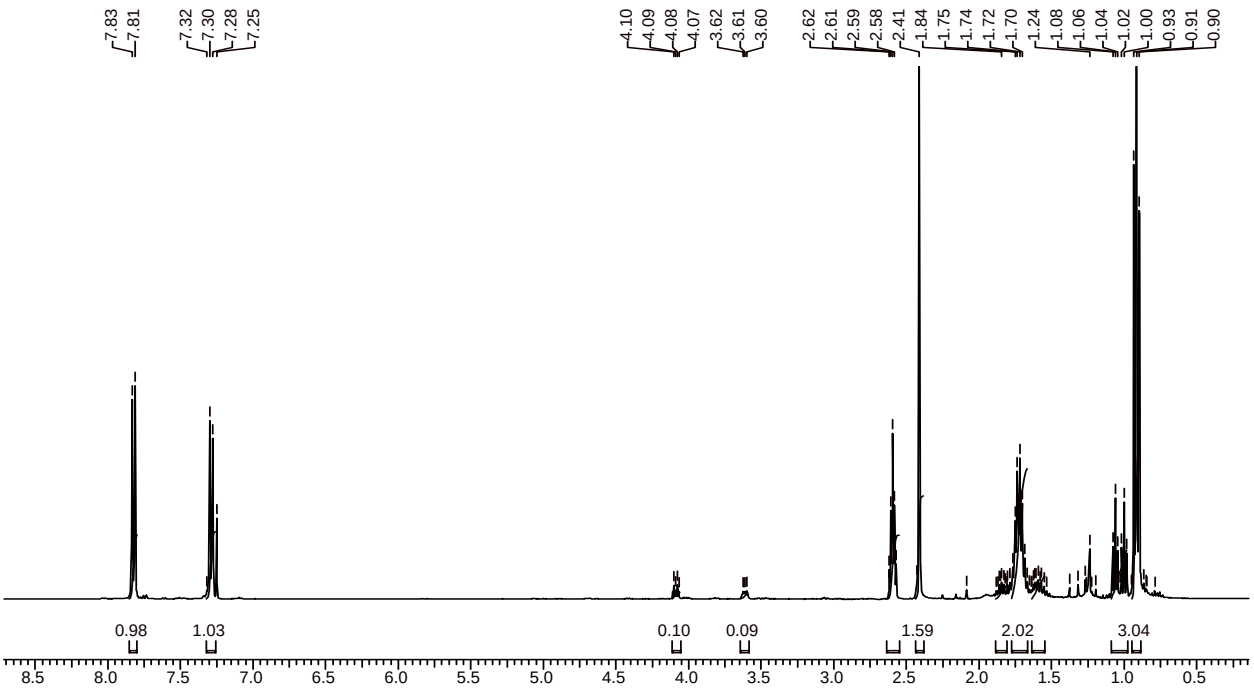
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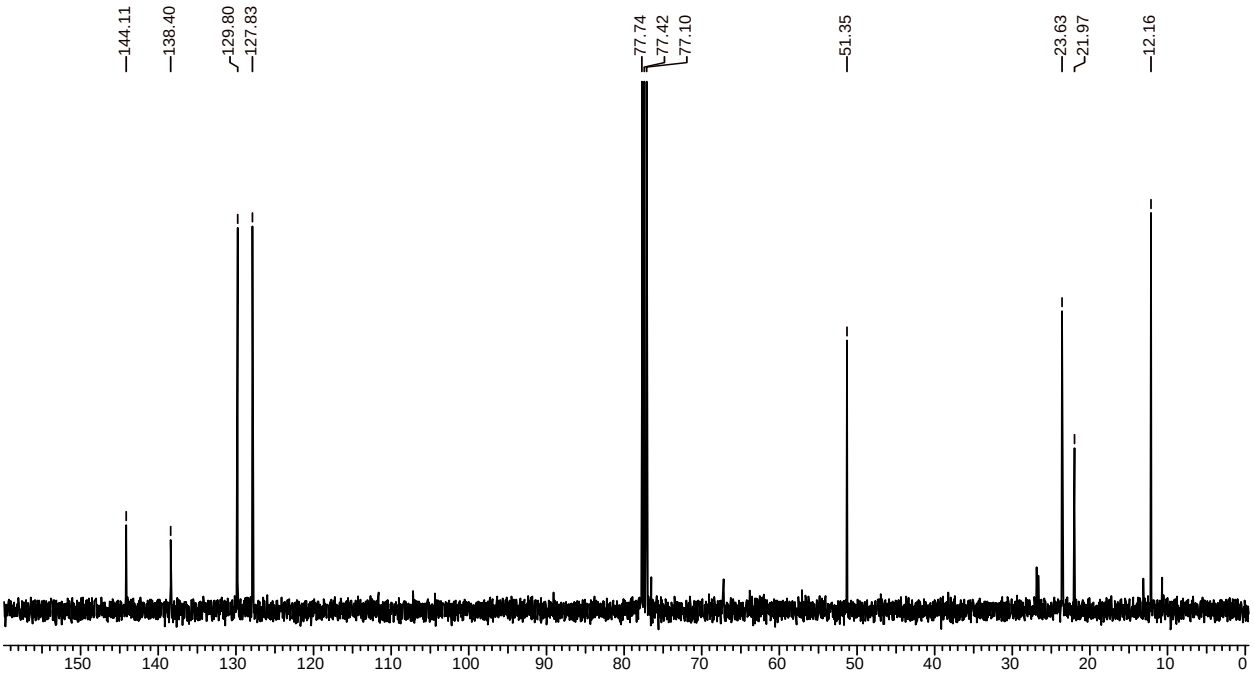
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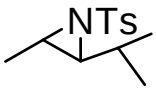
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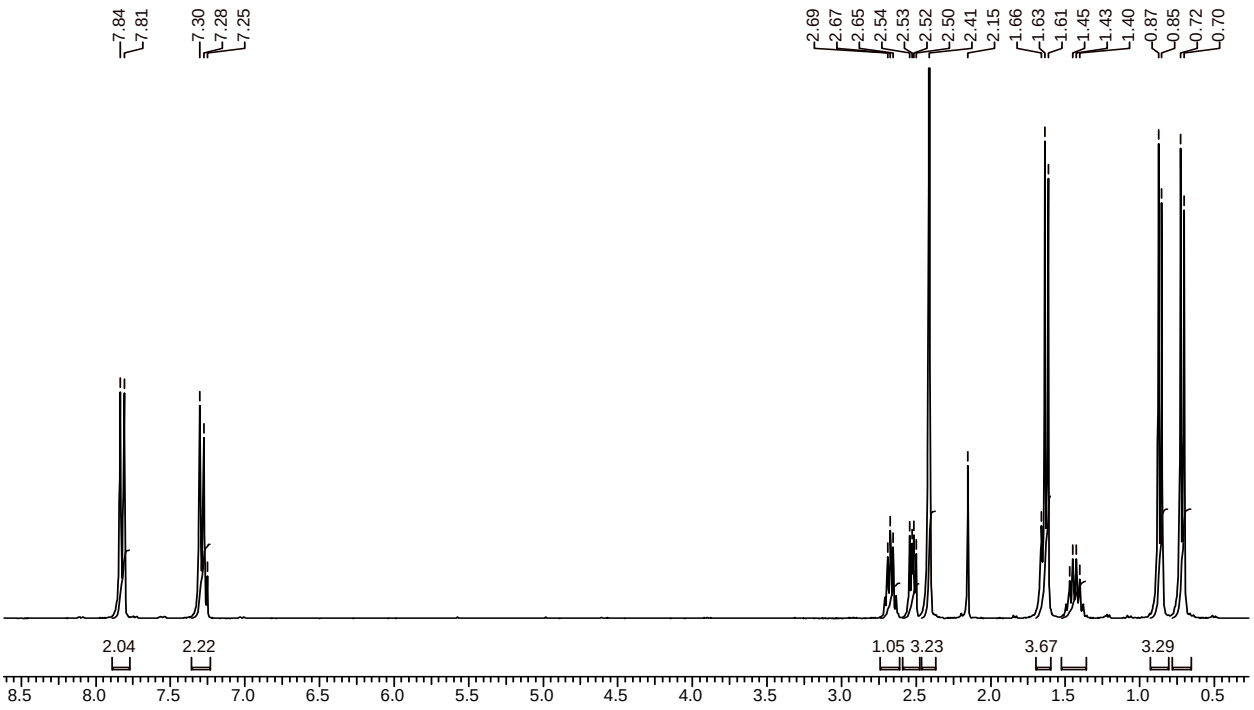
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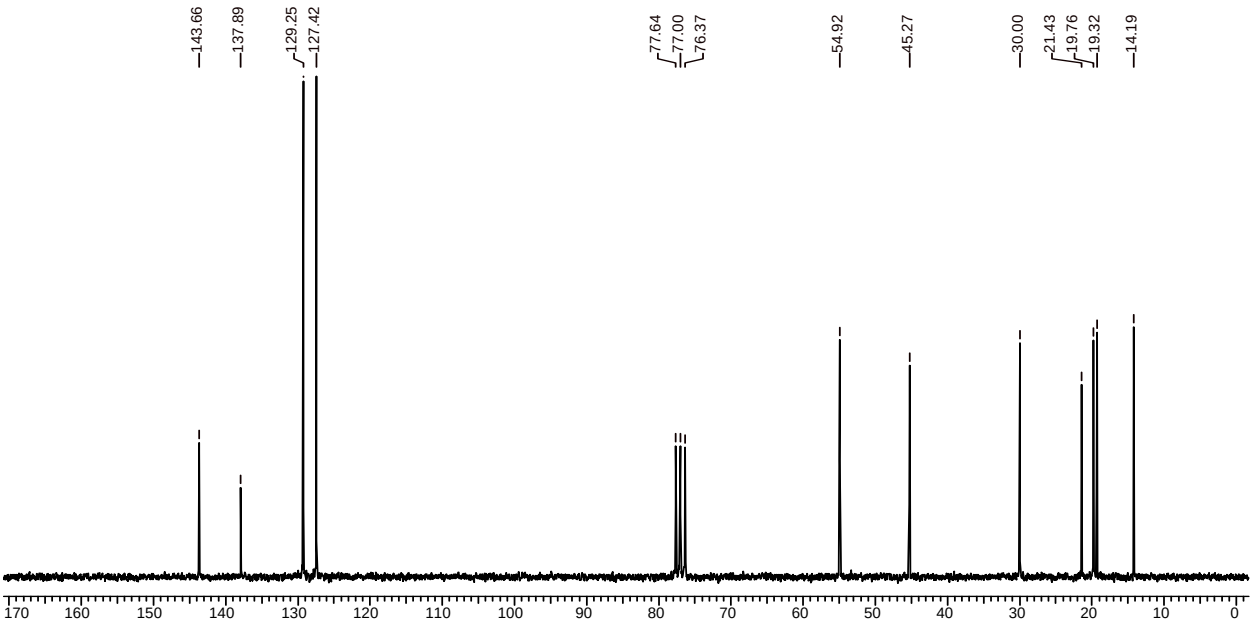
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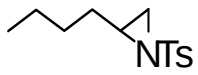
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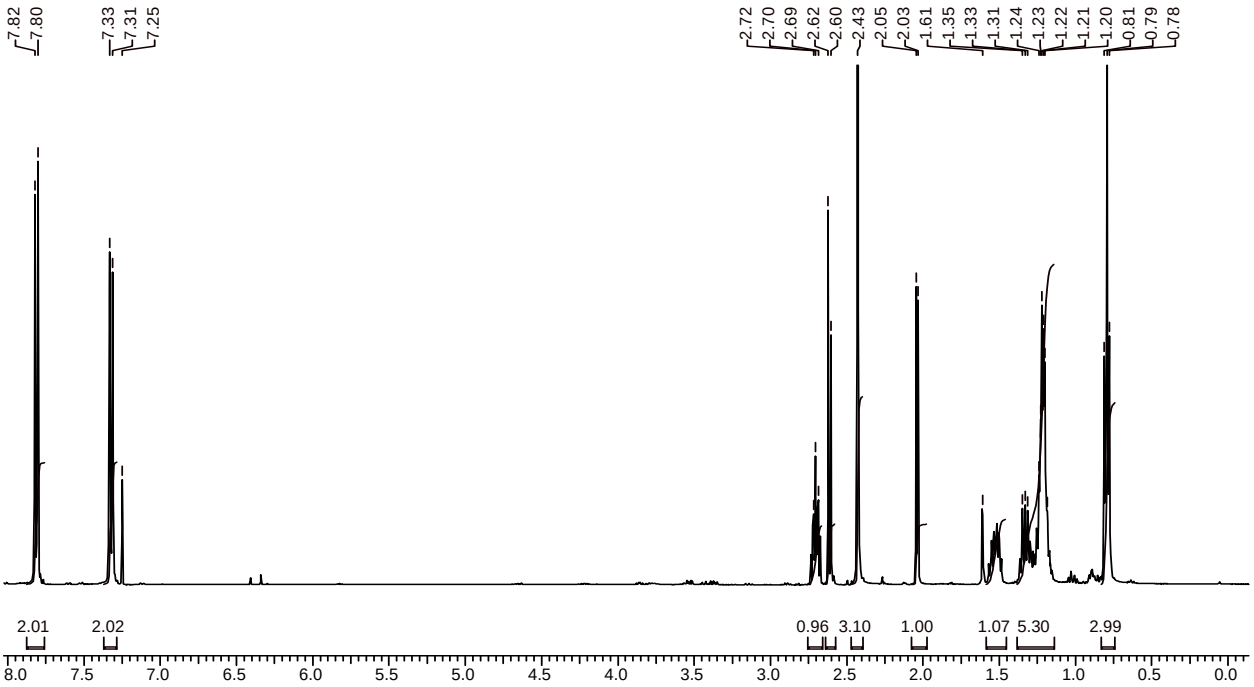
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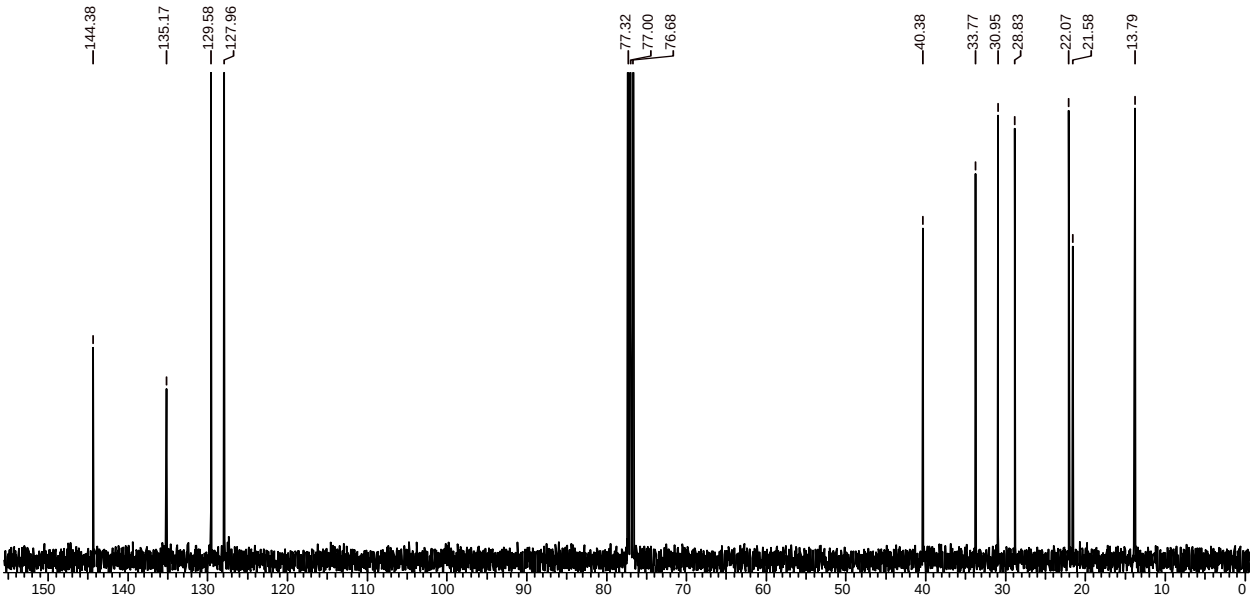
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