Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for Iron-catalyzed efficient intermolecular amination of C(sp^3)-H bonds with bromamine-T as nitrene source

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General Experimental Section: Reagents were obtained commercially and used without further purification unless indicated otherwise. Solvent was removed under reduced pressure and the residue obtained was chromatographed on a silica gel column (300-400 mesh) using a gradient solvent system (EtOAc / *n*-hexane as eluant unless specified otherwise). ^{1}H and ^{13}C NMR spectra were measured on Bruker DPX-400 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were determined on a Finnigan MAT 95 mass spectrometer.

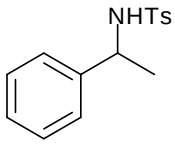
Synthesis of Iron complex [Fe(N4Py)(CH_3CN)](ClO_4)$_2$ (1)

Compound **1** was prepared according to published procedures. [M. Lubben, A. Meetsma, E. C. Wilkinson, B. Feringa, L. Que, Jr., *Angew. Chem. Int. Ed.*, 1995, **34**, 1512].

General Procedure for amination of C-H bond with TsNBrNa

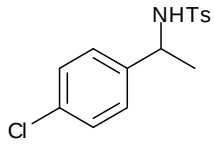
To a mixture of **2** (0.3 mmol) and complex **1** (5 mol %) in acetonitrile (2 mL) was added TsNBrNa (0.45 mmol). The reaction mixture was stirred at 40 ℃ for 8 h. Then the reaction mixture was extracted with ethyl acetate and washed by water and brine subsequently. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent.

Characterization Data



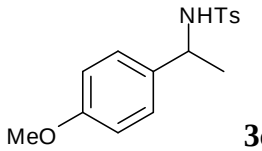
3a

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.62 (d, *J* = 10.2 Hz, 2H), 7.22 - 7.18 (m, 5H), 7.12 - 7.09 (m, 2H), 4.74 (br, 1H), 4.49 - 4.45 (m, 1H), 2.39 (s, 3H), 1.43 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.1, 142.0, 137.6, 129.5, 128.6, 127.5, 127.1, 126.1, 53.4, 23.2, 21.0.



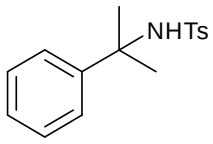
3b

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.59 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.19 (d, *J* = 6.8 Hz, 1H), 4.44 (q, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.3, 140.5, 137.4, 133.2, 129.4, 128.5, 127.6, 127.0, 53.1, 23.5, 21.5.



3c

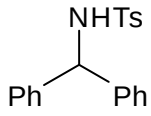
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.62 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 5.29 (d, *J* = 6.8 Hz, 1H), 4.40 (m, 1H), 3.73 (s, 3H), 2.38 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 158.5, 142.6, 137.6, 134.2, 129.1, 127.1, 126.8, 113.5, 54.9, 52.9, 23.2, 23.2.



3d

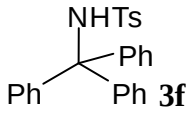
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.57 (d, *J* = 8.4 Hz, 2H), 7.37 - 7.19 (m, 7H), 5.02 (br, 1H), 2.40

(s, 3H), 1.63 (s, 6H).



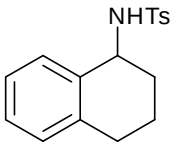
3e

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.56 (d, *J* = 8.3 Hz, 2H), 7.23 - 7.19 (m, 6H), 7.17 - 7.06 (m, 6H), 5.57 (d, *J* = 6.9 Hz, 1H), 5.05 (d, *J* = 7.0 Hz, 1H), 2.38 (s, 3H).



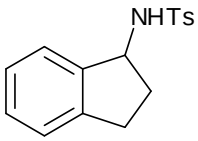
3f

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.36 - 7.30 (m, 6H), 7.21 - 7.16 (m, 9H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.87 (s, 1H), 2.33 (s, 3H).



3g

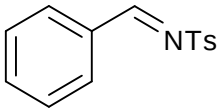
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.83 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 7.8, 7.0 Hz, 1H), 7.05 (dd, *J* = 9.8, 7.6 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 4.65 (d, *J* = 7.6 Hz, 1H), 4.45 (dt, *J* = 7.6, 4.9 Hz, 1H), 2.73 - 2.66 (m, 2H), 2.46 (s, 3H), 1.89 - 1.66 (m, 4H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.4, 137.6, 137.4, 135.6, 129.8, 129.2, 128.8, 127.6, 127.1, 126.3, 51.9, 30.8, 28.8, 21.6, 19.1.



3h

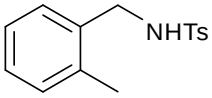
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.84 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.24 - 7.12 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 4.83 (dd, *J* = 15.9, 7.6 Hz, 1H), 4.71 (d, *J* = 7.9 Hz, 1H), 2.96 - 2.85 (m, 1H), 2.75 - 2.73 (m, 1H), 2.46 (s, 3H), 2.39 - 2.28 (m, 1H), 1.76 – 1.74 (m, 1H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.5, 142.9, 142.0, 138.2, 129.8, 128.3, 127.2, 126.9, 124.8,

124.1, 58.8, 34.8, 29.9, 21.5.



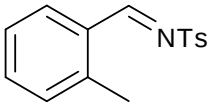
3i

^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.04 (s, 1H), 7.92 - 7.90 (m, 4H), 7.62 (t, *J* = 6.8 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 170.2, 144.6, 134.9, 132.4, 131.3, 129.8, 129.2, 128.1, 126.5, 21.5.



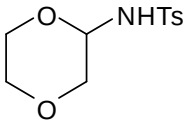
3ja

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.22 - 7.15 (m, 1H), 7.13 – 7.11 (m, 3H), 4.41 (m, 1H), 4.09 (d, *J* = 5.9 Hz, 2H), 2.45 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.6, 136.8, 136.6, 133.9, 130.6, 129.8, 128.8, 128.3, 127.2, 126.2, 45.3, 21.4, 18.6.



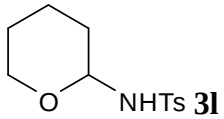
3jb

^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.35 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.26 (m, 2H), 2.61 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 168.7, 144.4, 142.2, 135.4, 134.6, 131.6, 130.6, 130.4, 129.8, 127.9, 126.6, 21.7, 19.5.



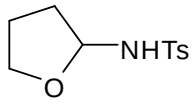
3k

^{1}H NMR (400 MHz, $CDCl_3$), δ: 2.41 (s, 3H), 3.40 - 3.44 (m, 2H), 3.51 - 3.60 (m, 3H), 3.77 - 3.81 (m, 1H), 4.96 (m, 1H), 6.17 (d, *J* = 9.6 Hz, 1H), 7.28 (d, *J*= 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.6, 138.4, 129.6, 127.1, 78.1, 69.5, 66.2, 62.4, 21.6.



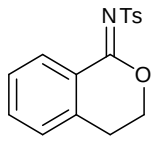
3l

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.78 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.36 (dr, 1H), 4.77 - 4.76 (m, 1H), 3.71 - 3.69 (m, 1H), 3.38 - 3.37 (m, 1H), 2.41 (s, 3H), 1.82 - 1.80 (m, 2H), 1.55 – 1.54 (m, 1H), 1.42 -1.70 (m, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.3, 138.8, 129.4, 127.1, 82.1, 66.3, 31.8, 24.6, 22.4, 21.6.



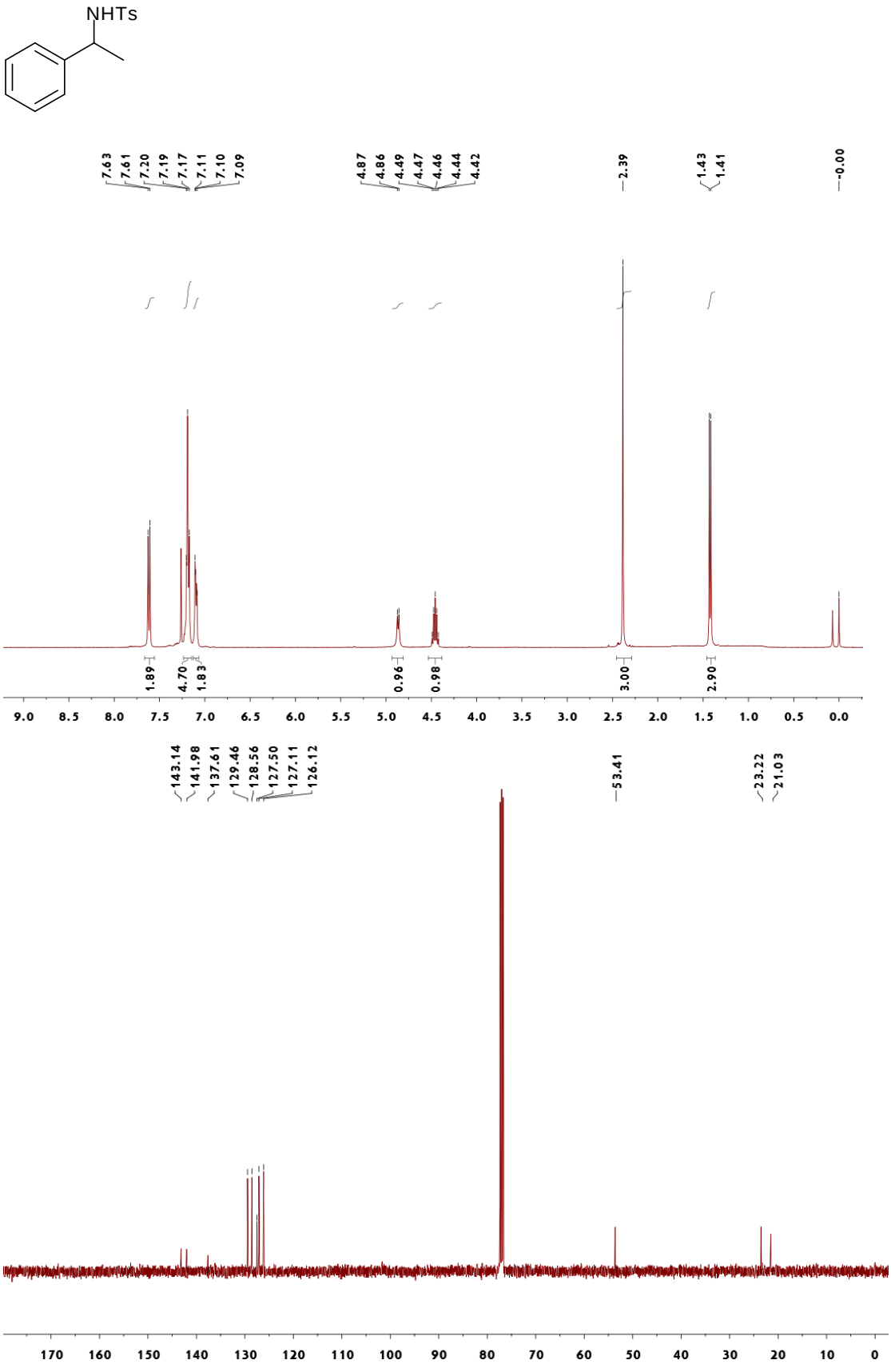
3m

^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.73 - 1.84 (m, 3H), 1.86 - 1.89 (m, 1H), 2.44 (s, 3H), 3.68 - 3.73 (m, 2H), 5.29 - 5.37 (m, 1H), 5.90 (br, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 143.3, 138.5, 129.5, 127.0, 84.9, 67.2, 32.5, 23.9, 21.4.



3n

^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.08 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.52 (td, *J* =1.2, 0.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.22 - 7.35 (m, 2H), 4.57 (t, *J* = 6.0 Hz, 2H), 3.07 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$), δ: 162.8, 142.9, 139.2, 137.9, 134.1, 130.1, 129.1, 127.8, 127.6, 127.3, 125.2, 68.6, 27.2, 21.5.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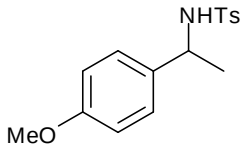
NHTs
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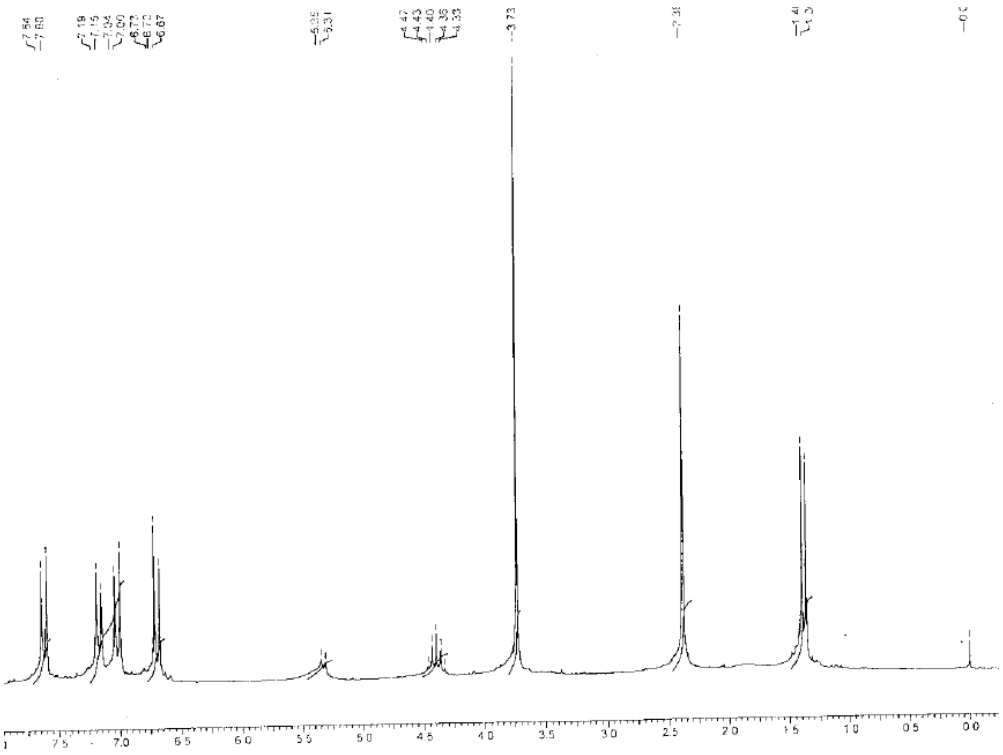

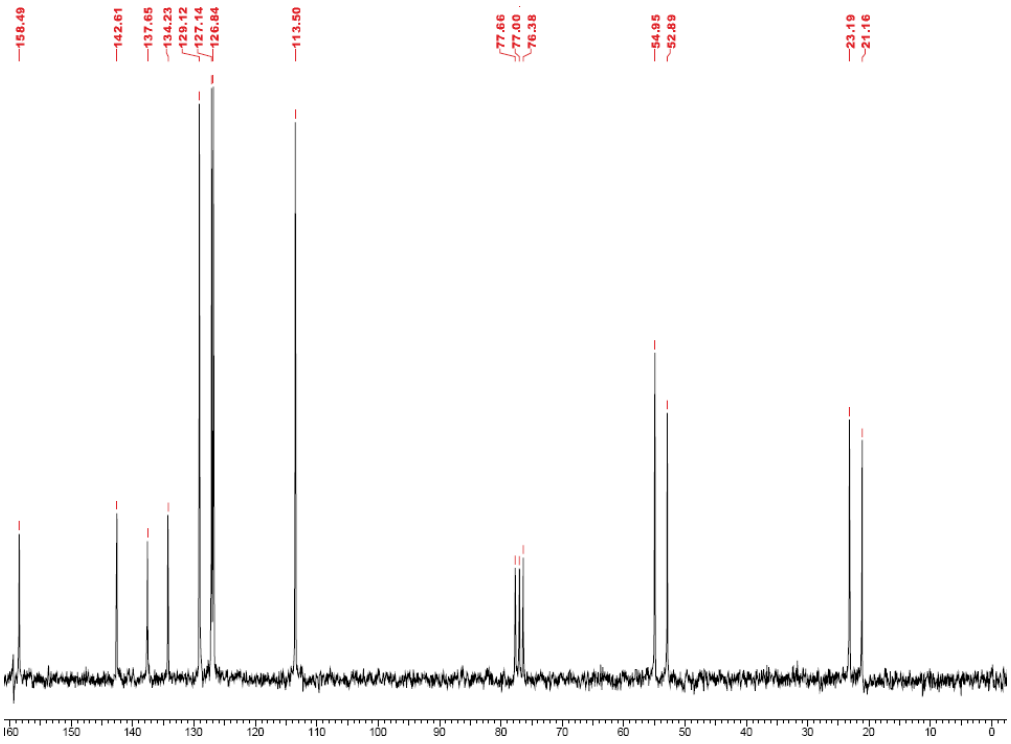

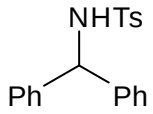
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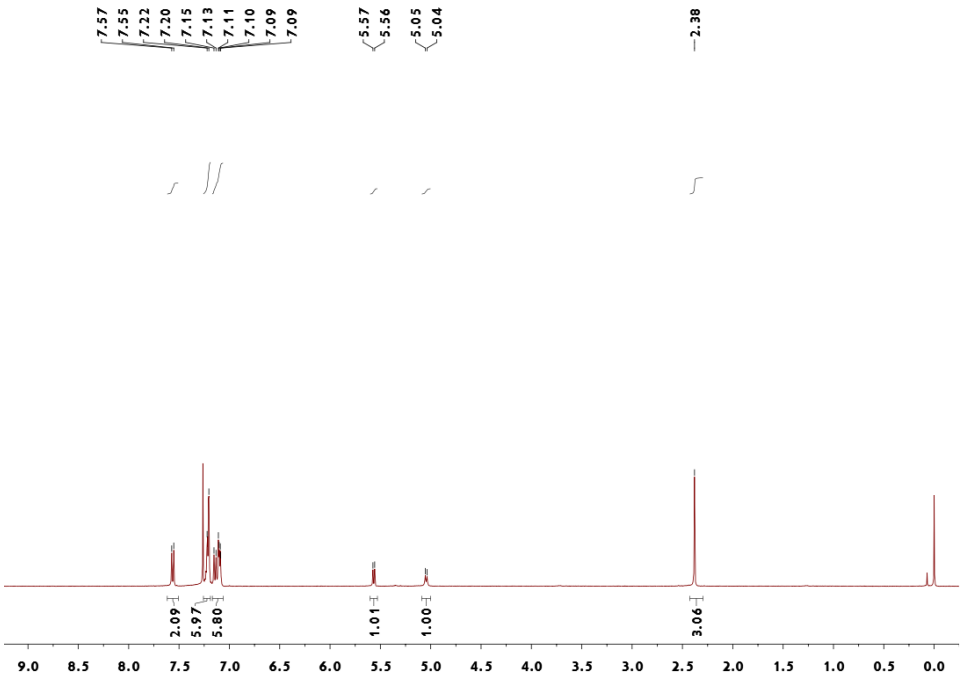
Ph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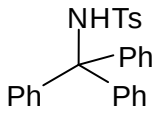
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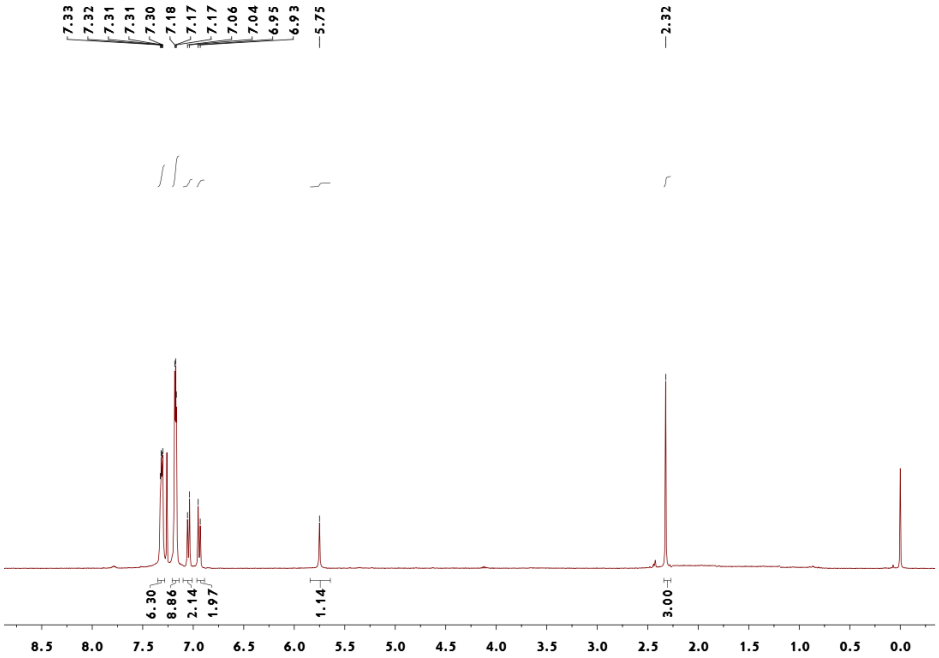
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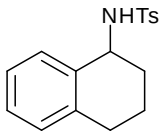
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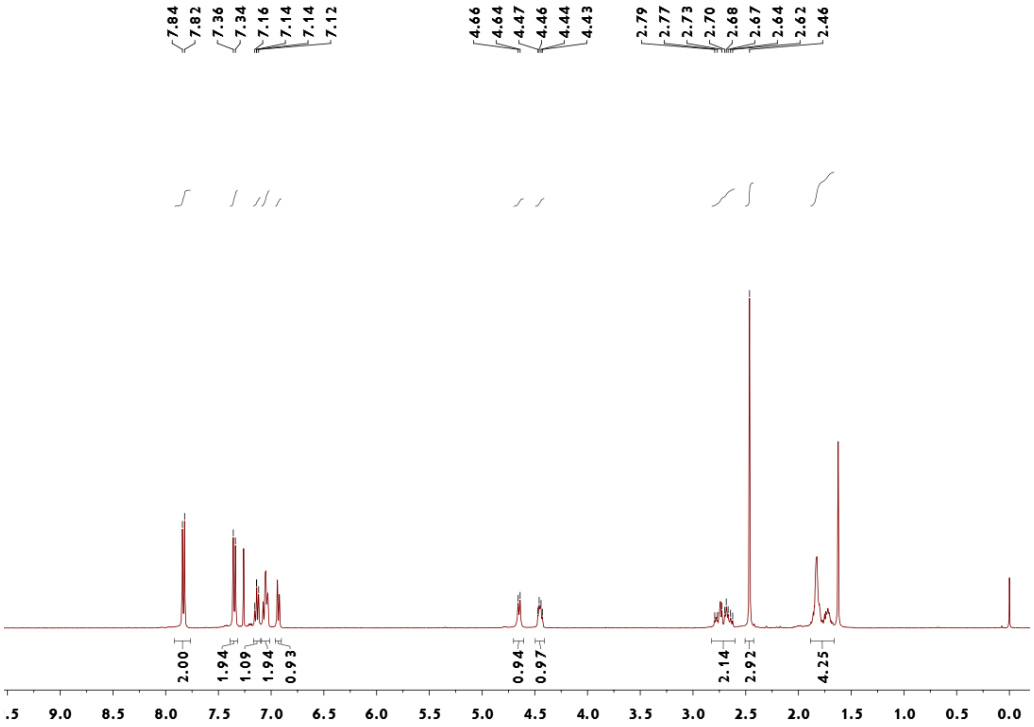
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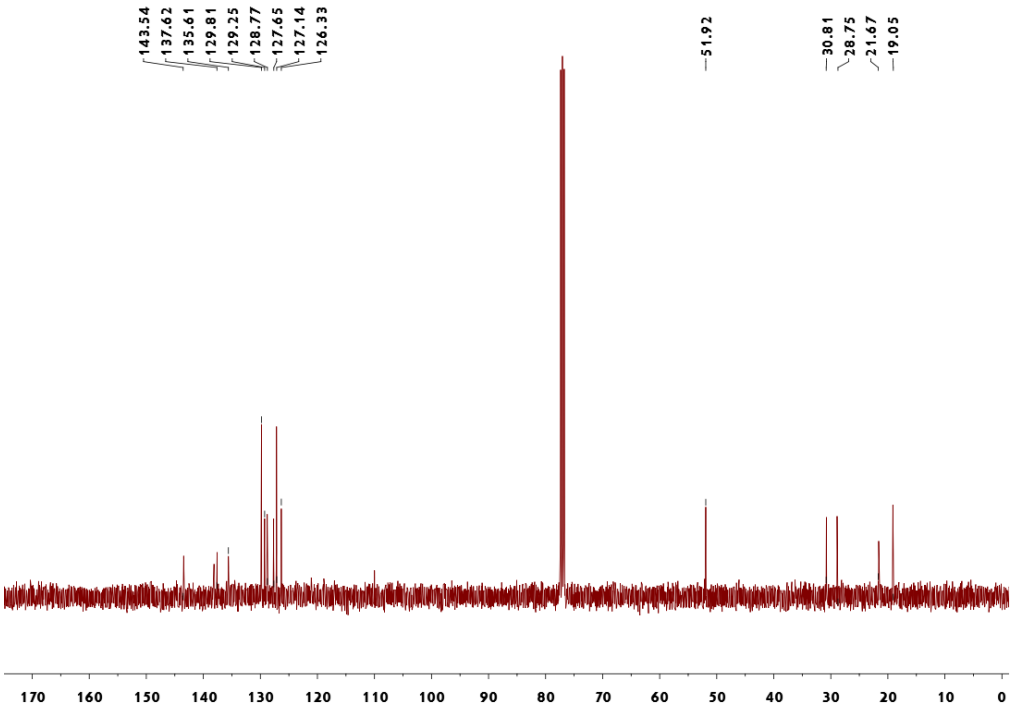
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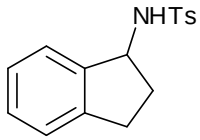
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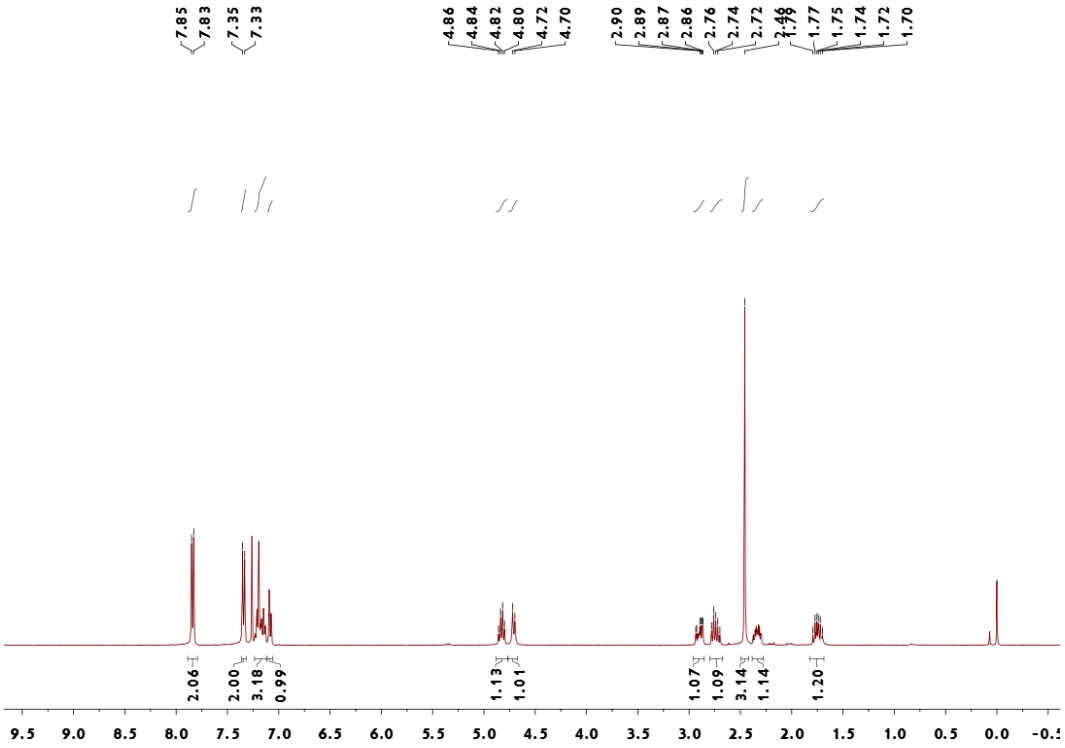
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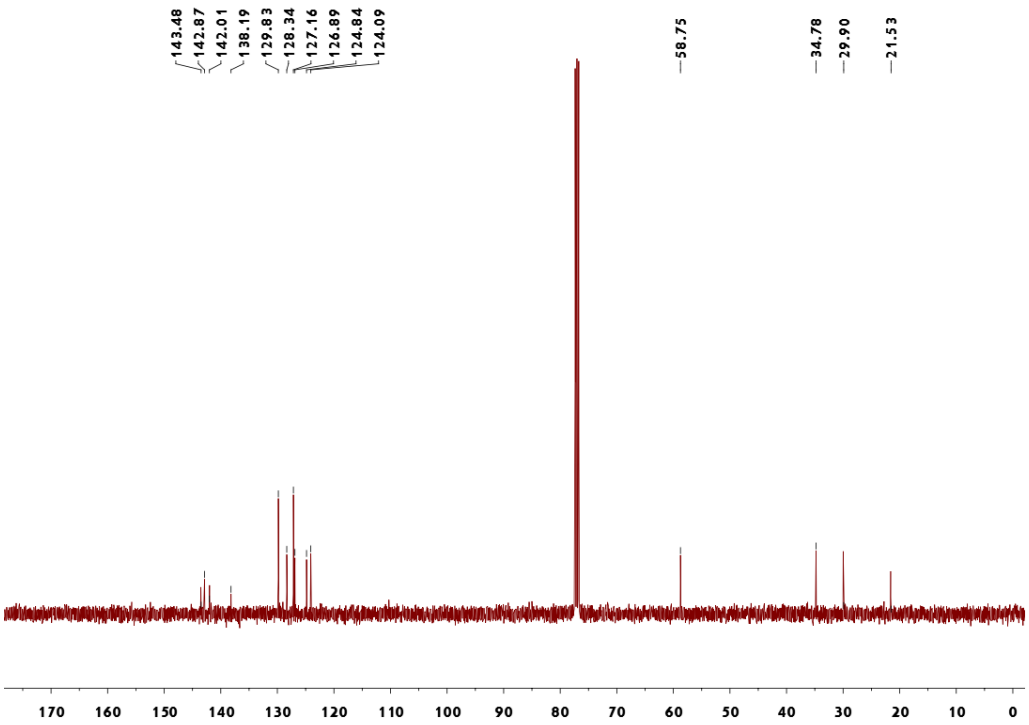
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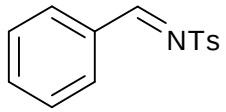
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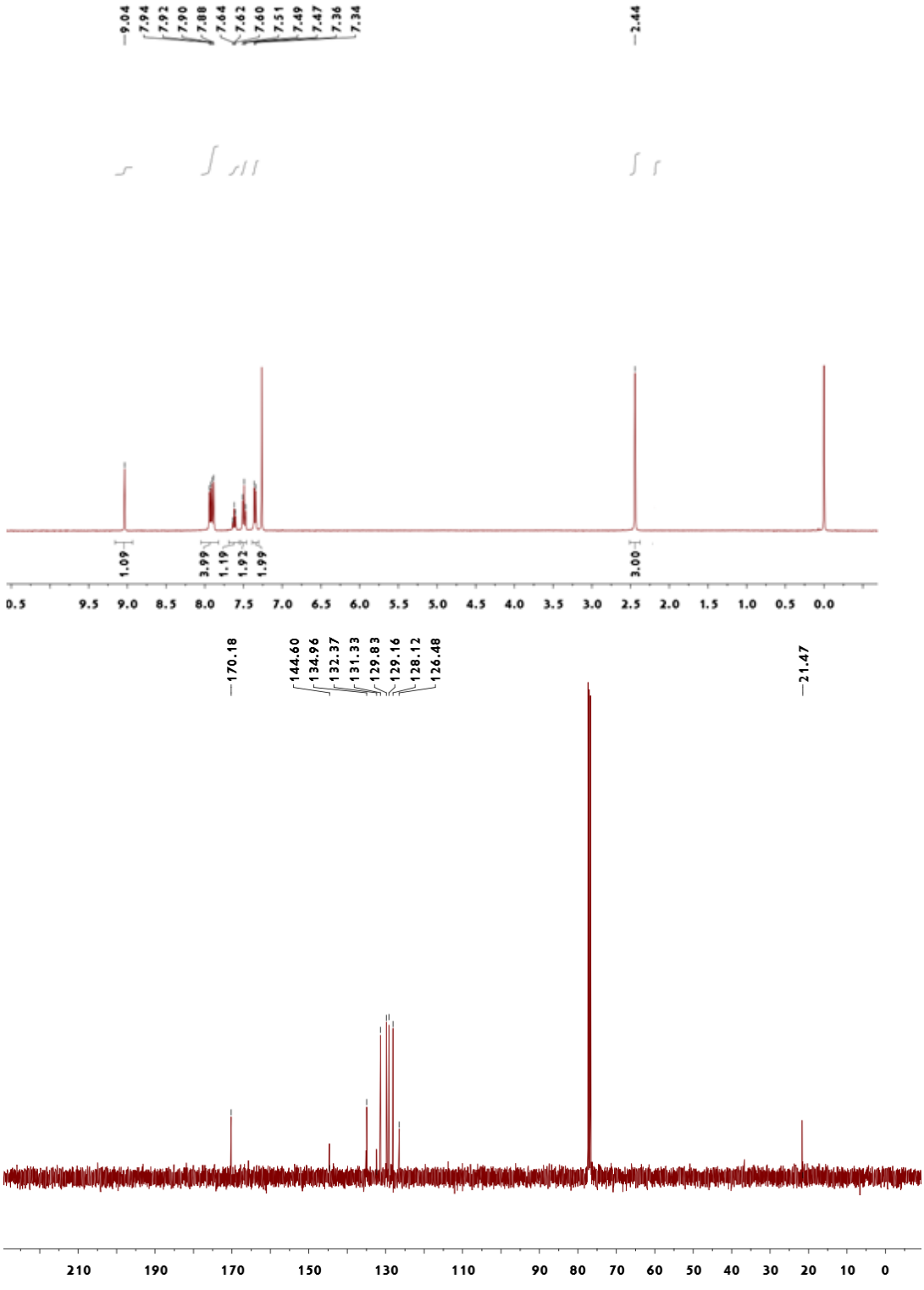
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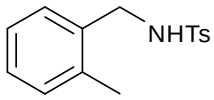
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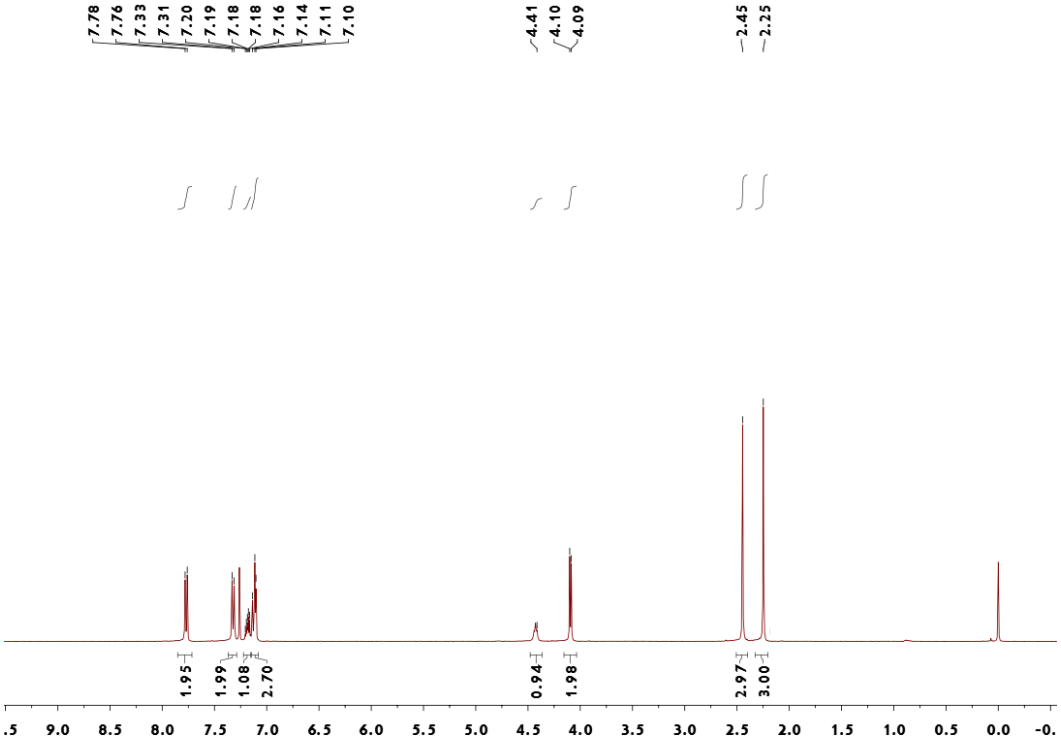
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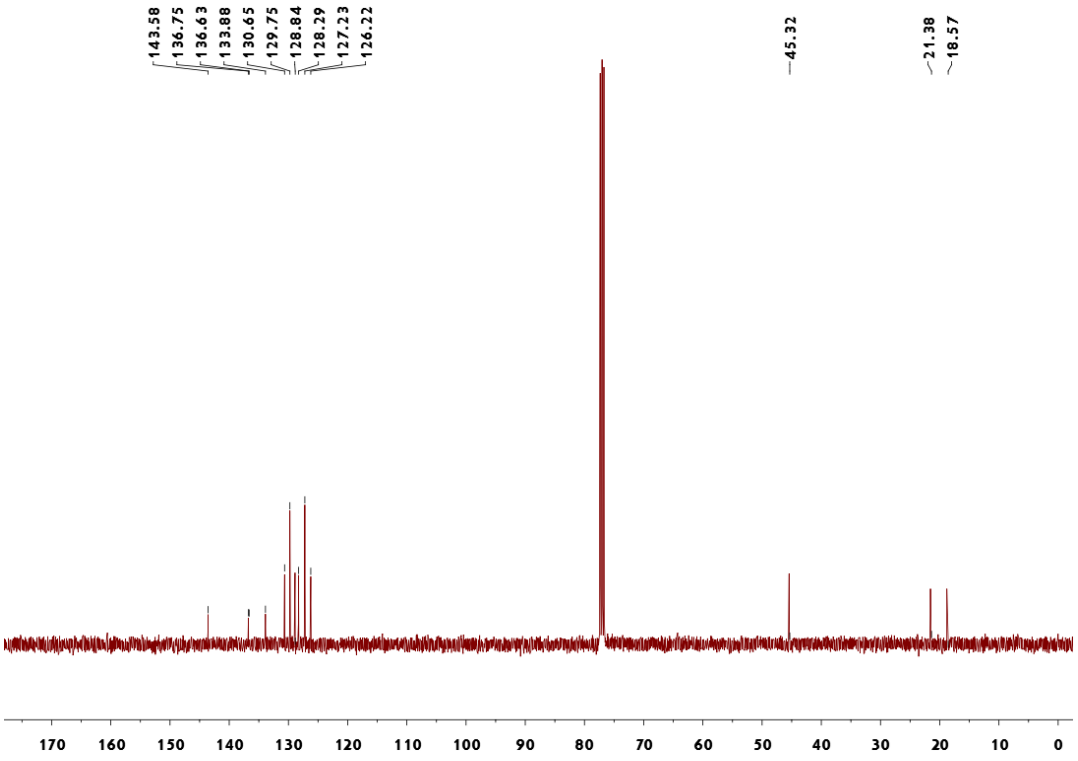
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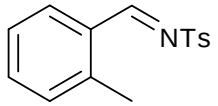
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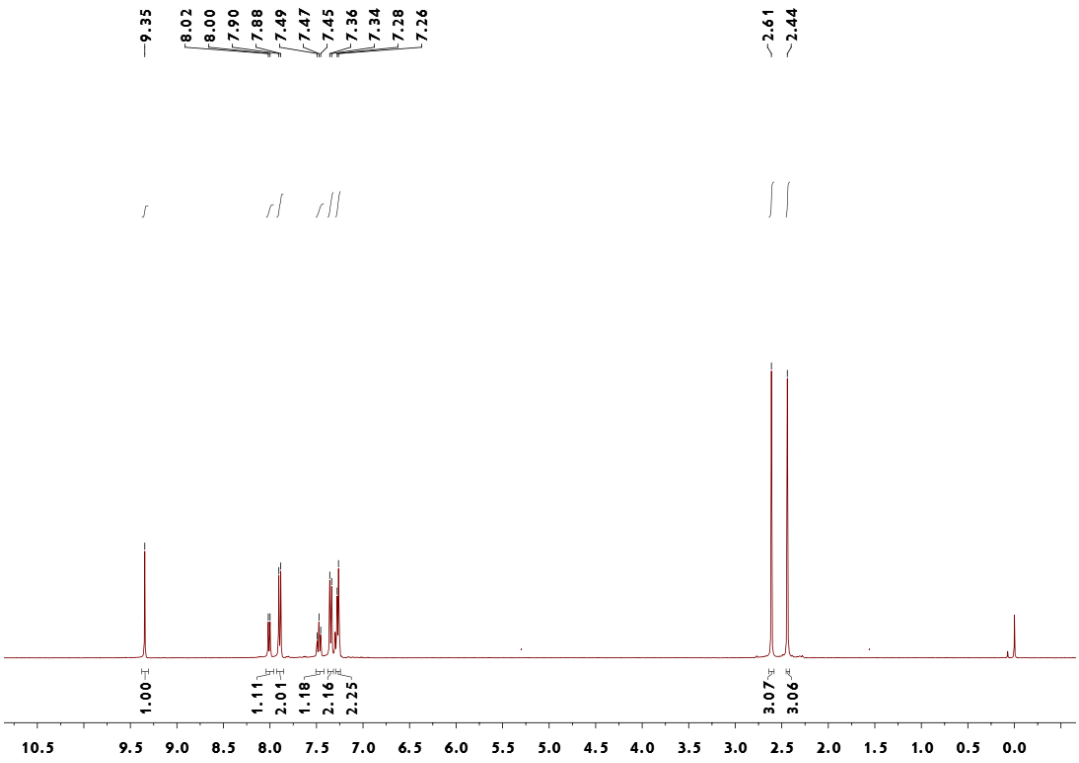
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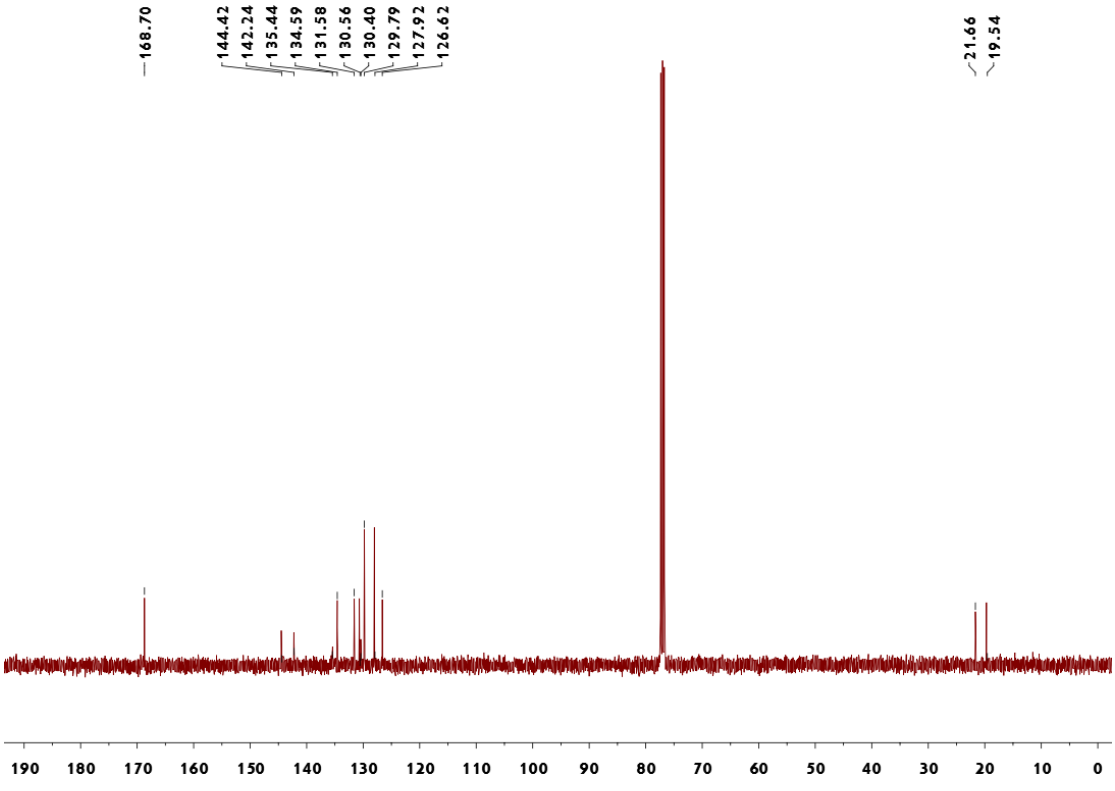
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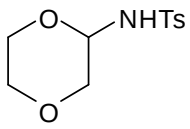
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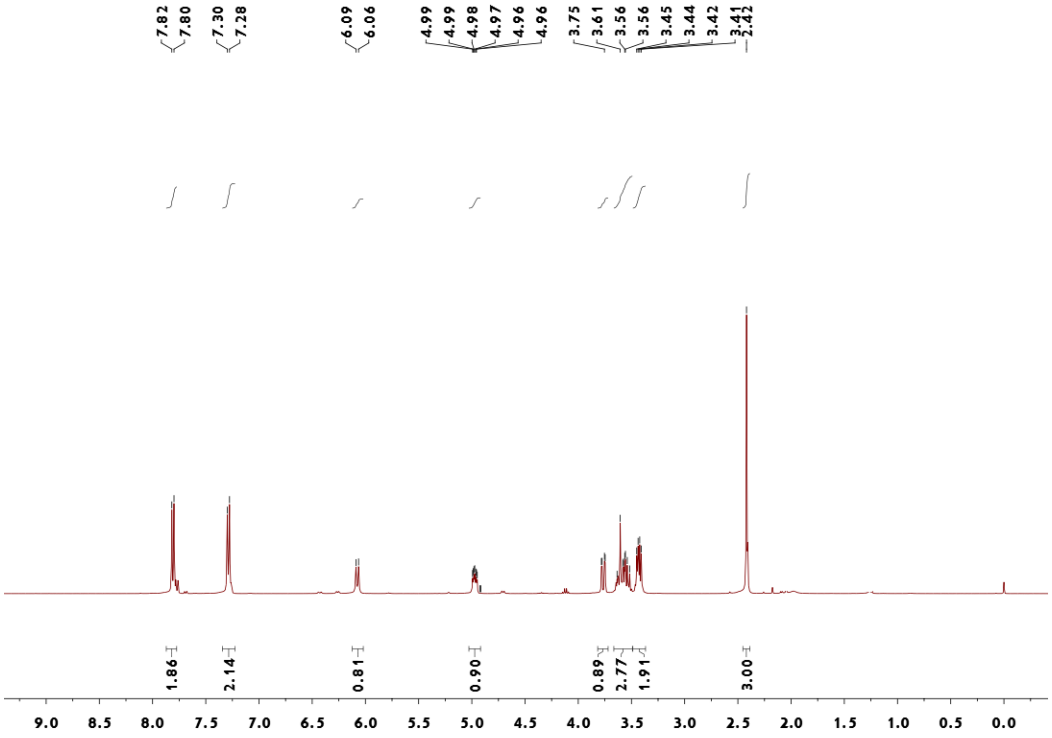
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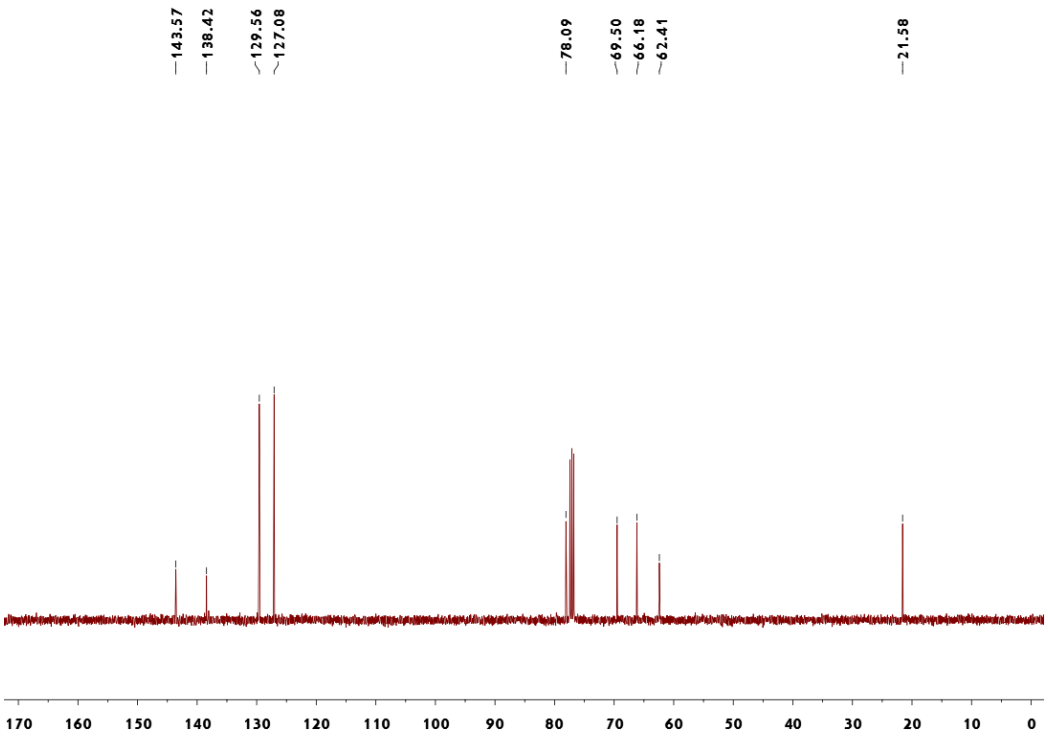
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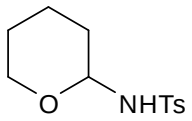
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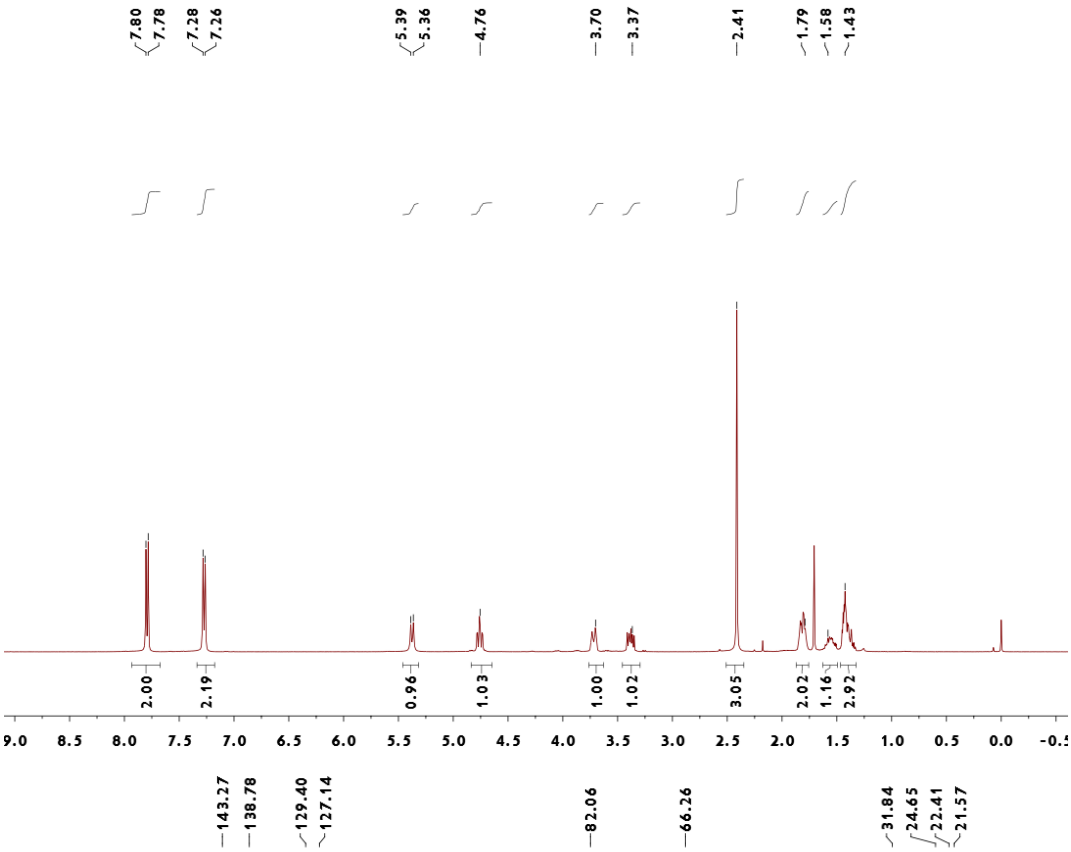
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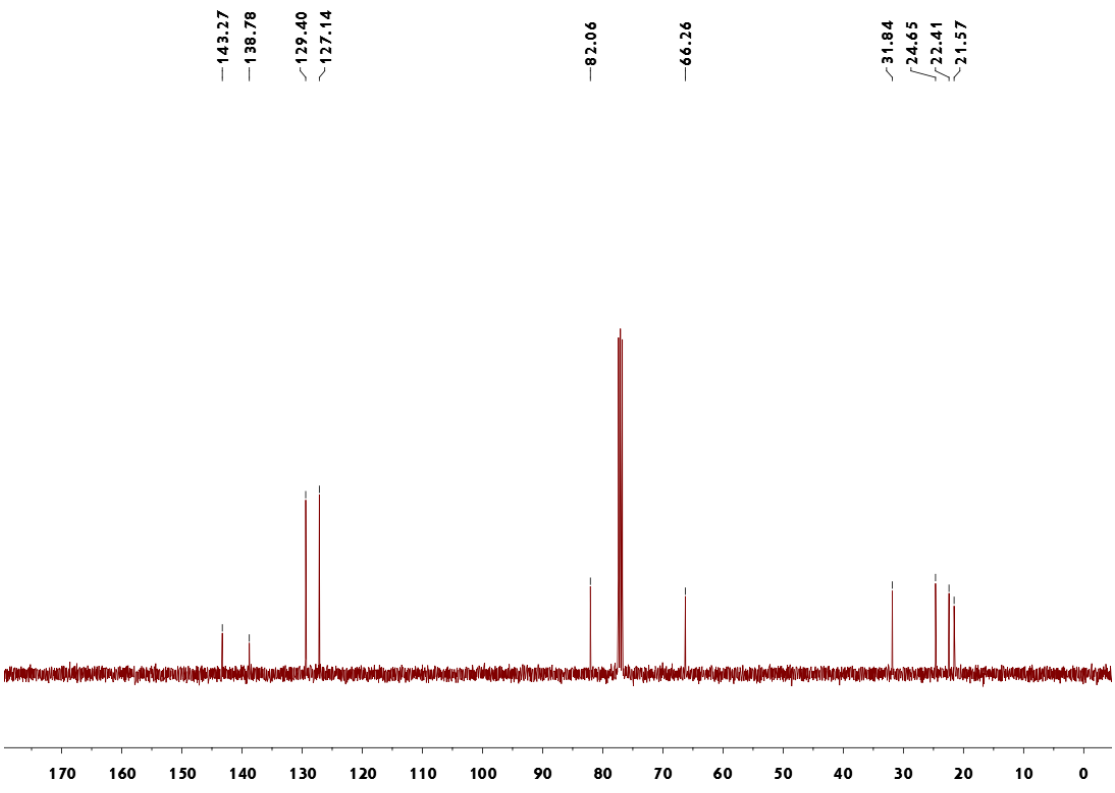
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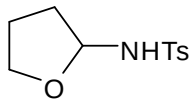
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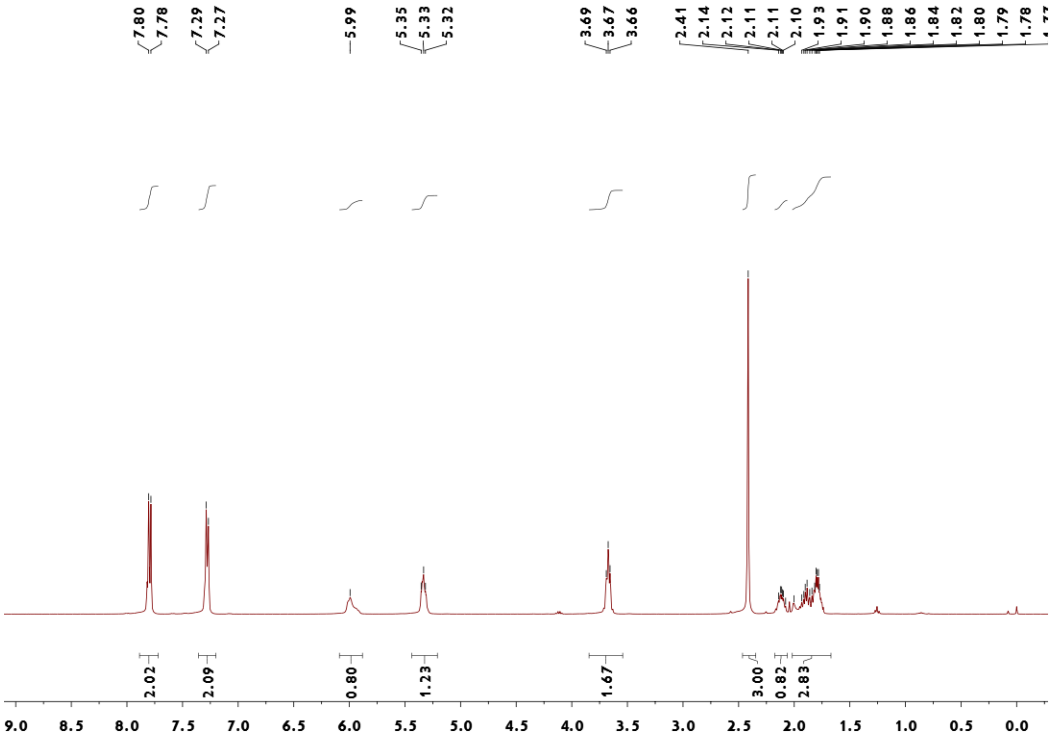
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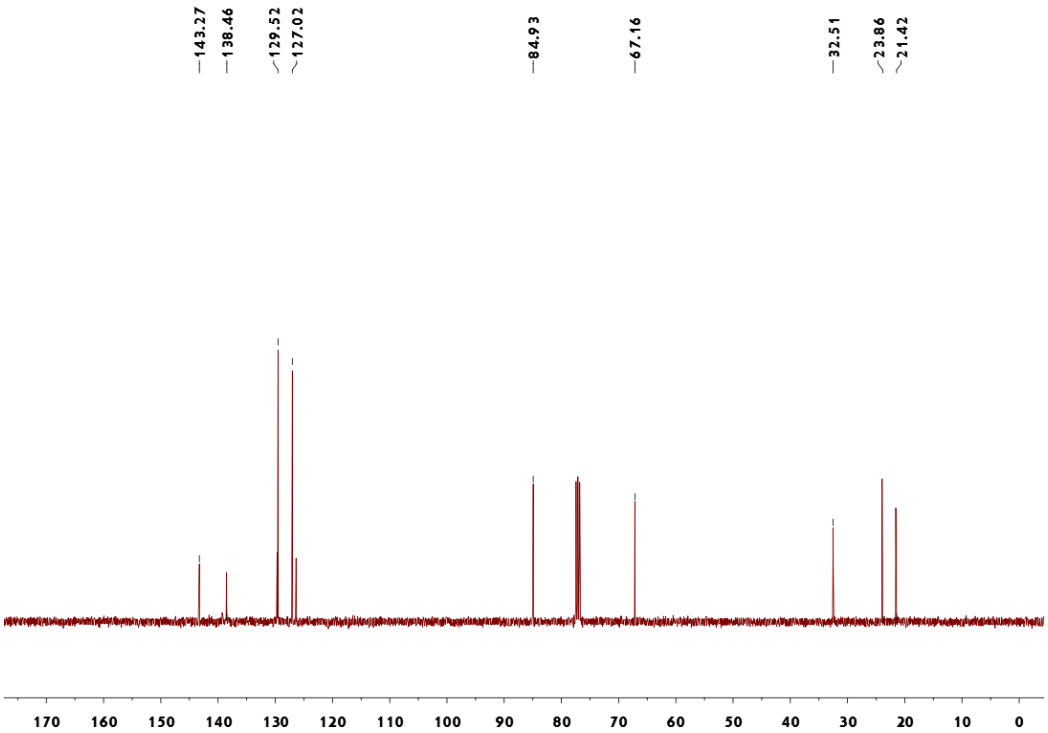
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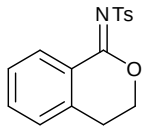
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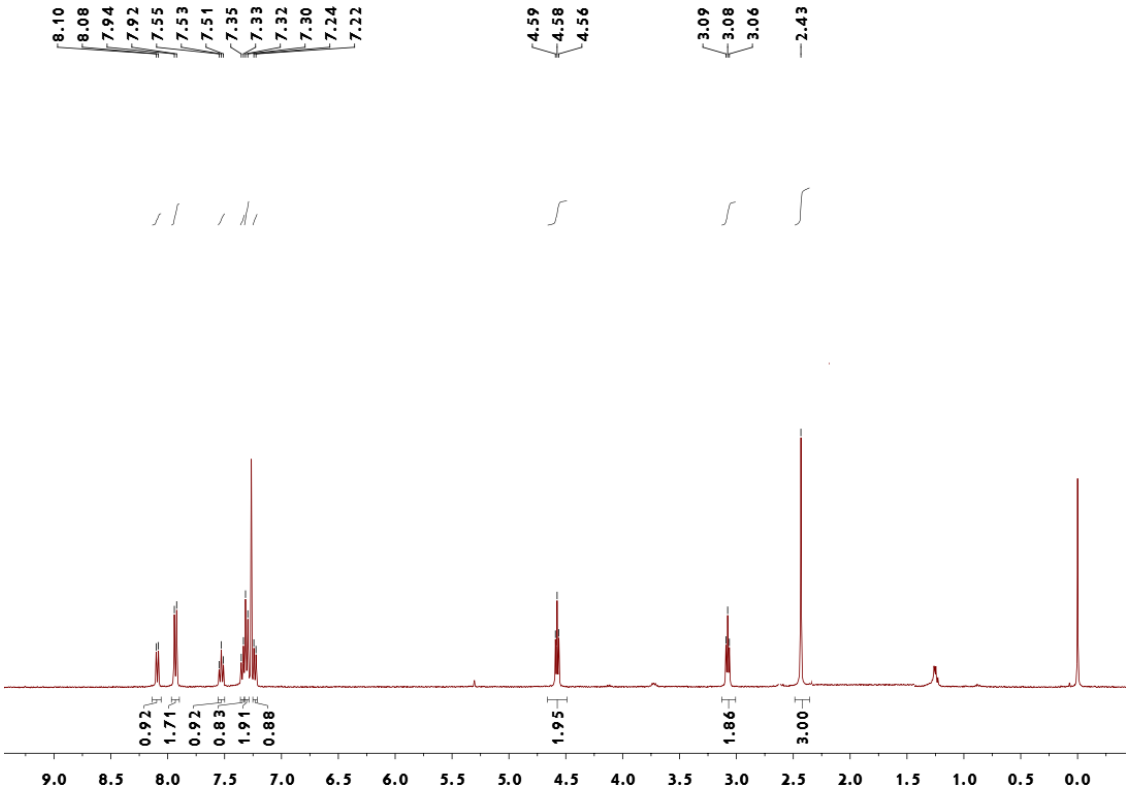
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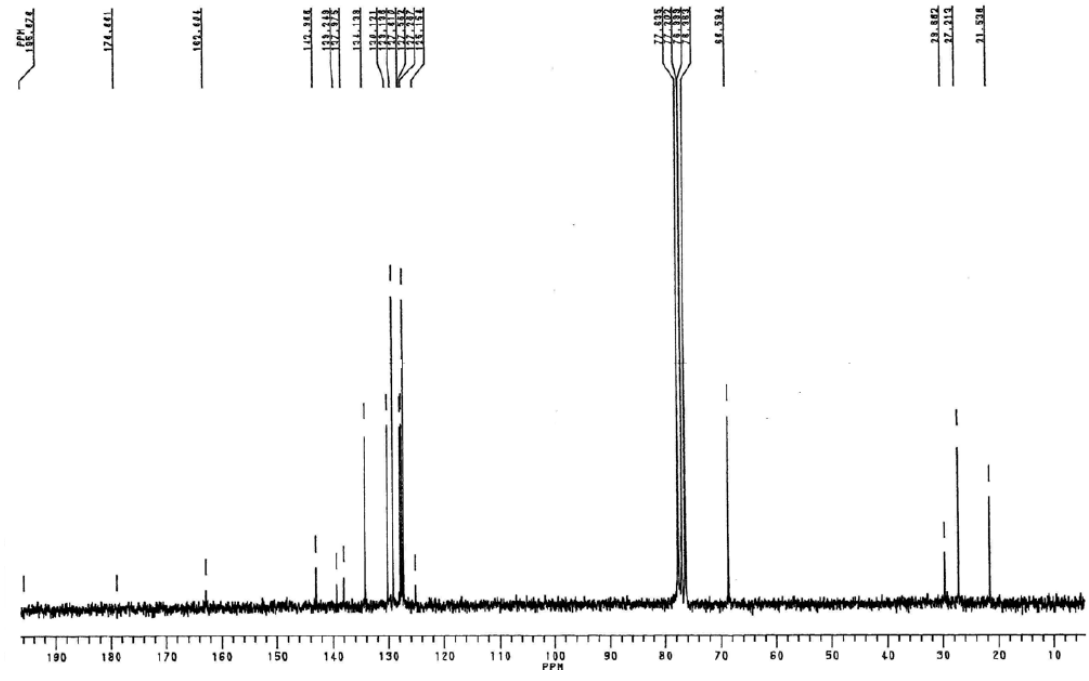
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