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Supporting Information

Access to Dihydropyridinones and Spirooxindoles: Application of *N*-Heterocyclic Carbene-Catalyzed [3 + 3] Annulation of Enals and Oxindole-Derived Enals with 2−Aminoacrylates

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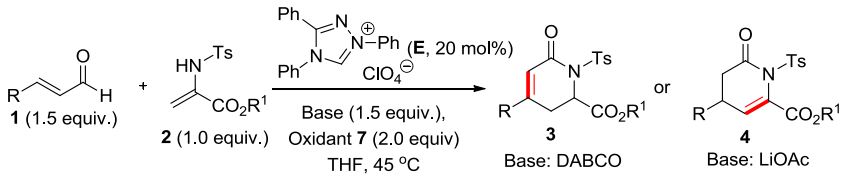
Table of Contents

1. General Information

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in an oven-dried sealed tube, with dry, freshly distilled solvents in anhydrous conditions. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90^{o}C. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 MHz instrument in $CDCl_3$, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. Data collections for crystal structure were performed at room temperature (293 K) using Mo Kα radiation on a Bruker APEXII diffractometer. The determination of enantiomeric excess was performed via chiral HPLC analysis (RIGOL) L-3000 HPLC workstation. Optical rotations were measured by Rudolph Autopol-I instrument. Enals **1** were were obtained from commercial suppliers or synthesized by aldol condensation. Isatin-derived enals **6** were were prepared according to the literature.[1]

2. Experimental Section

General experimental procedure for the synthesis of 3,4-dihydropyridinones 3a, 5,6-dihydropyridinones 4a and spirocyclic oxindoles 6.

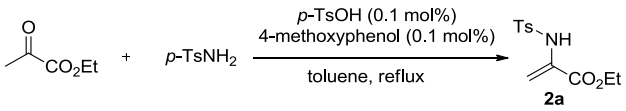


A dry 25 mL Schlenk tube with stir bar was charged with 2-aminoacrylate **2** (0.2 mmol, 1.0 equiv), NHC **E** (0.04 mol, 20 mol %), base (DABCO or LiOAc) (0.30 mol, 1.5 equiv.), oxidant **7** (0.4 mol, 2.0 equiv.). The tube was evacuated, and refilled with nitrogen. Then enals **1** (0.3 mmol, 1.5 equiv) was added and the mixture was dissolved with newly distilled solvent THF (2.0 mL). The mixture was stirred at 45^{o}C for 12 hours when the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford corresponding

products .

Spirooxindoles **6** were generated in the same way as described above by using isatin-derived enals **5** (1.0 equiv), 2-aminoacrylate **2** (1.5 equiv) as the starting material and LiOAc (20 mol%) as the base.

The preparation of 2-aminoacrylate 2a.[2]

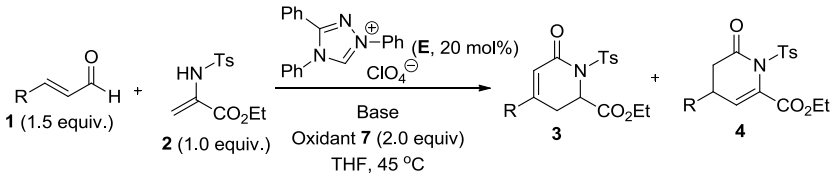


A round-bottom flask equipped with a Dean-Stark trap was charged with *p*-$TsNH_2$ (25 mmol), ethyl pyuvate (0.9 equiv), a catalytic amount of *p*-TsOH, 4-methoxyphenol (0.1 mol %) and toluene (50 mL). The stirred mixture was heated under reflux for 48 h then concentrated in vacuo. The resulting yellow oil was taken up in DCM (100 mL), washed with saturated $NaHCO_3$ (100 mL) and H_2O (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography to afford the desired product **2a** in 40% yield as white solid.

Optimization of the bases to further reduce the isomerization for enals 1c, 1h and 1o

Since the **4**:**3** ratios are not good enough in Table 2, entries 3, 8, and 17, several experiments are carried out to test whether the isomerization could be further reduced by other bases. And the experimental results are summarized in Table 1. From the experimental results we could see that employing $C_6H_5CO_2Na$ (1.5 equiv.) as the base could improve the ratio of **4**:**3**, but the yields were reduced.

Table 1. Optimization of bases.[a]



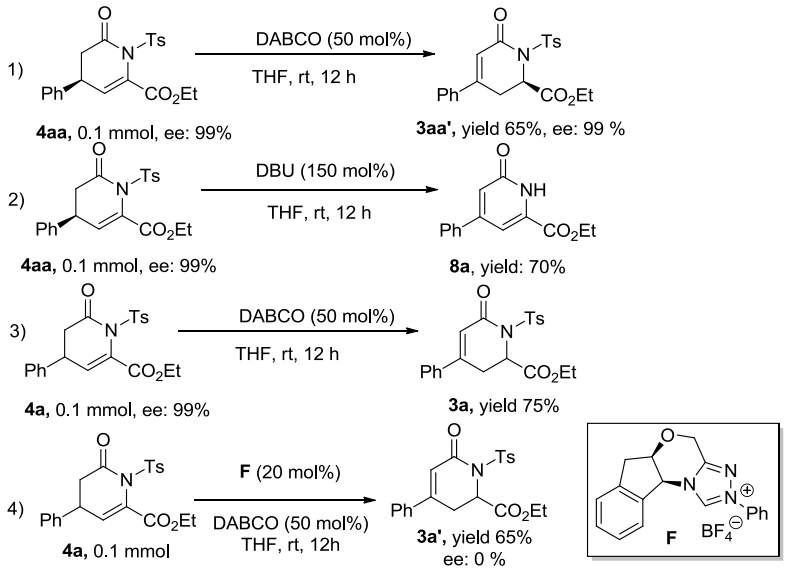
Entry	R	Base	Products[b]	Yield (%) [c]
1	**1c**, 4-$MeOC_6H_4$	LiOAc (0.2 equiv.)	**4c**:**3c** = 3:1	23
2	**1c**, 4-$MeOC_6H_4$	$C_6H_5CO_2Na$ (0.2 equiv)	**4c**:**3c** = 3:1	23
3	**1c**, 4-$MeOC_6H_4$	$C_6H_5CO_2Na$ (1.5 equiv)	**4c**:**3c** = 3.5:1	22
4	**1c**, 4-$MeOC_6H_4$	$Mg(OAc)_2$ (1.5 equiv)	N.R.	-
5	**1h**, 2-MeC_6H_4	LiOAc (0.2 equiv.)	**4h**:**3h** > 25:1	68
6	**1h**, 2-MeC_6H_4	$C_6H_5CO_2Na$ (0.2 equiv)	**4h**:**3h** > 25:1	73

7	**1h**, 2-MeC_6H_4	$C_6H_5CO_2Na$ (1.5 equiv)	**4h**:**3h** > 25:1	65
8	**1h**, 2-MeC_6H_4	$Mg(OAc)_2$ (1.5 equiv)	N.R.	-
9	**1o,** 3- thienyl	LiOAc (0.2 equiv.)	**4o**:**3o** = 6:1	33
10	**1o,** 3- thienyl	$C_6H_5CO_2Na$ (0.2 equiv)	**4o**:**3o** = 18:1	40
11	**1o,** 3- thienyl	$C_6H_5CO_2Na$ (1.5 equiv)	**4o**:**3o** = 20:1	32
12	**1o,** 3- thienyl	$Mg(OAc)_2$ (1.5 equiv)	N.R.	-

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), THF (2 mL). [b] The ratio of 4:3 are determined by ^{1}HNMR. [c] Yield of isolated product.

3. Control Experiments

We demonstrated that the formation of 3,4-dihydropyridinones **3** was most likely to undergo carbon-carbon double bonds migration from 5,6-dihydropyridinones **4** when DABCO was employed as the base. To test our hypothesis, several additional reactions were carried out and the results were summarized in scheme 1.



Scheme 1

The transformation of 4aa to 3aa'.

A dry 25 mL Schlenk tube with stir bar was charged with **4aa** (40 mg, 0.1 mmol, 1.0 equiv), DABCO (5 mg, 50 mol %). The tube was evacuated, and refilled with nitrogen. Then the mixture was dissolved with newly distilled solvent THF (1.0 mL). The mixture was stirred at rt for 12h until the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford desired product **3aa** in 65% yield as white solid.

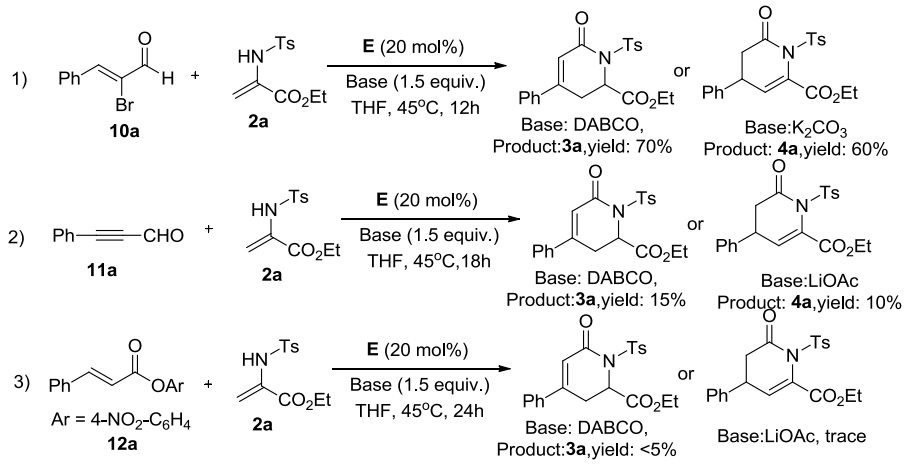
The transformations of **4a** to **3a**, **4a** to **3a'** were carried out in the same way as described above. For the transformation of **4a** to **3a'**, 20 mol% chiral triazolium salt **F** was added.

The transformation of 4aa to 8a.

A dry 25 mL Schlenk tube with stir bar was charged with **4aa** (40 mg, 0.1 mmol, 1.0 equiv), DBU (23 mg, 50 mol %). The tube was evacuated, and refilled with nitrogen. Then the mixture was dissolved with newly distilled solvent THF (1.0 mL). The mixture was stirred at rt for 12h until the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford desired product **8a** in 70% yield as white solid.

The application of 2-bromoenal, ynal or ester in the NHC-catalyzed [3 + 3] annulation strategy.

To further explore the reaction mechanism, the application of 2-bromoenal, ynal or ester with 2-aminoacrylates **2a** as the starting materials to synthesis of dihydropyridinones was also carried out and the results were summarized in scheme 2.



Scheme 2

General experimental procedure: A dry 25 mL Schlenk tube with stir bar was charged with 2-aminoacrylate **2a** (0.2 mmol, 1.5 equiv), NHC **E** (0.04 mol, 20 mol %), corresponding base (DABCO, LiOAc or K_2CO_3) (0.30 mol, 1.5 equiv.). The tube was evacuated, and refilled with nitrogen. Then the corresponding 2-bromoenal, ynal or ester (**10a**, **11a** or **12a**) (0.3 mmol, 1.5 equiv) was added and the mixture was dissolved with newly distilled solvent THF (2.0 mL). The mixture was stirred at 45°C (monitored by TLC). The reaction mixture was concentrated under

vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding products.

3. Characterization of Products

Ethyl 2-(4-methylphenylsulfonamido)acrylate (2a). White solid; Mp 66.3-68.0 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.13 (s, 1H), 5.65 (s, 2H), 4.20 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 163.1, 144.3, 135.5, 131.1, 129.7, 126.5, 106.7, 62.5, 21.6, 14.0.

Ethyl 6-oxo-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3a). White solid; Mp 111.3-112.9 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.47-7.45 (m, 2H), 7.43-7.41 (m, 3H), 7.33(d, J = 8.4 Hz, 2H), 6.16 (d, J = 3.0 Hz, 1H), 5.53 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 1H), 4.16-4.05 (m, 2H), 3.50 (dd, J_1 = 18.0 Hz, J_2 = 1.8 Hz, 1H), 3.22-3.18 (m, 1H), 2.44 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 169.7, 162.4, 151.8, 144.9, 136.0, 135.6, 130.6, 129.7, 129.0, 128.95, 126.2, 119.4, 62.4, 56.3, 30.7, 21.7, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{22}O_5NS^+$, $[M+H]^+$400.1213, Found: 400.1216.

Ethyl 6-oxo-4-phenyl-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4a). Light yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.34-7.28(m, 5H), 7.17 (d, J = 7.2Hz, 2H), 6.66 (d, J = 4.2 Hz, 1H), 4.42-4.32 (m, 2H), 3.91-3.88 (m, 1H), 2.81-2.72 (m, 2H), 2.44 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 169.5, 162.9, 145.3, 139.1, 135.7, 132.9, 129.5, 129.2, 129.1, 128.8, 127.7, 127.0, 62.1, 41.4, 36.8, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{21}H_{22}O_5NS^+$, $[M+H]^+$400.1213, Found: 400.1215.

Ethyl 6-oxo-4-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3b). White solid; Mp 150.6-152.2 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.14 (d, J = 2.4Hz, 1H), 5.52 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.15-4.04 (m, 2H), 3.49 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.19-3.15 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 162.5, 151.7, 144.8, 141.2, 135.8, 133.1, 129.7, 128.9, 126.2, 118.4, 62.3, 56.3, 30.6, 21.6, 21.3, 13.9 ppm; **HRMS** (ESI): calculated for $C_{22}H_{24}O_5NS^+$, $[M+H]^+$ 414.1370, Found: 414.1374.

Ethyl 6-oxo-4-(p-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4b). Light yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 9.0 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.8

Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 4.2 Hz, 1H), 4.42-4.32 (m, 2H), 3.87-3.84 (m, 1H), 2.78-2.69 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 163.0, 145.2, 137.4, 136.0, 135.7, 132.8, 129.8, 129.5, 129.2, 129.1, 62.1, 41.5, 36.5, 21.7, 21.0, 14.0 ppm; **HRMS** (ESI): calculated for $C_{22}H_{24}O_5NS^+$, $[M+H]^+$ 414.1370, Found: 414.1376.

Ethyl 4-(4-methoxyphenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3c). White solid; Mp 132.5-133.9 ^oC; ^1H NMR (600 MHz, CDCl3) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.10 (d, *J* = 3.0 Hz, 1H), 5.51 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.15-4.04 (m, 2H), 3.83 (s, 3H), 3.50 (dd, J_1 = 17.4 Hz, J_2 = 1.8 Hz, 1H), 3.17-3.13 (m, 1H), 2.43 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 169.7, 162.6, 161.7, 151.2, 144.7, 135.8, 129.7, 128.9, 128.1, 127.8, 117.2, 114.4, 62.3, 56.2, 55.4, 30.5, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{22}H_{24}NO_6S^+$, $[M+H]^+$ 430.1319, Found 430.1317.

Ethyl 4-(4-methoxyphenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4c). Light yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.85 (dd, J_1 =12.0 Hz, J_2 = 2.4 Hz, 2H), 6.65 (d, *J* = 4.8 Hz, 1H), 4.42-4.32 (m, 2H), 3.86-3.83 (m, 1H), 3.80 (s, 3H), 2.78-2.69 (m, 2H), 2.44 (s, 3H), 1.38 (t, *J* = 7.2Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 163.0, 159.0, 145.2, 135.7, 132.7, 131.0, 129.5, 129.2, 129.1, 128.0, 114.5, 62.1, 55.3, 41.6, 36.0, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{22}H_{24}NO_6S^+$, $[M+H]^+$ 430.1319, Found 430.1320.

Ethyl 4-(4-chlorophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3d). White solid; Mp 151.1-152.8 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.41-7.37 (m, 4H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.14 (d, *J* = 2.4 Hz, 1H), 5.53 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.16-4.05 (m, 2H), 3.45 (J_1 = 18.0 Hz, J_2 = 1.8 Hz, 1H), 3.21-3.17 (m, 1H), 2.44 (s, 3H), 1.10 (t, *J* = 7.2Hz, 3H); **^{13}CNMR** (150 MHz, $CDCl_3$) δ 169.6, 162.1, 150.5, 144.9, 136.8, 135.6, 134.4, 129.7, 129.2, 129.0, 127.5, 119.6, 62.4, 56.2, 30.6, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}ClNO_5S^+$, $[M+H]^+$ 434.0823, Found 434.0825.

Ethyl 4-(4-chlorophenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4d). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.30-7.26 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 5.4Hz, 1H), 4.43-4.32 (m, 2H), 3.88-3.85 (m, 1H), 2.79 (dd, J_1 =16.2

Hz, J_2 = 5.4 Hz, 1H), 2.72 (dd, J_1 =16.2 Hz, J_2 = 9.0 Hz, 1H), 2.44 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 169.1, 162.8, 145.4, 137.4, 135.4, 133.6, 133.3, 129.5, 129.3, 129.1, 128.3, 127.8, 62.2, 41.1, 36.0, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}ClNO_5S^+$, $[M+H]^+$ 434.0823, Found 434.0820.

Ethyl 4-(4-bromophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3e). White solid; Mp 171.6-173.4 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03(d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.34-7.32 (m, 4H), 6.14 (d, J = 3.0 Hz, 1H), 5.52 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.16-4.05 (m, 2H), 3.44 (dd, J_1 = 17.4 Hz, J_2 = 1.8 Hz, 1H), 3.21-3.12 (m, 1H), 2.44 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 162.1, 150.6, 144.9, 135.6, 134.9, 132.2, 129.7, 129.0, 127.7, 125.1, 119.7, 62.5, 56.2, 30.6, 21.7, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}BrNO_5S^+$, $[M+H]^+$ 478.0318, Found 478.0321.

Ethyl 4-(4-bromophenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4e). Light yellow oil; ^{1}H NMR (600 MHz, CDCl3) δ 7.97 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 4.8 Hz, 1H), 4.42-4.32 (m, 2H), 3.86-3.83 (m, 1H), 2.78 (dd, J_1 =16.2 Hz, J_2 = 5.4 Hz, 1H), 2.72 (dd, J_1 =16.2 Hz, J_2 = 9.0 Hz, 1H), 2.44 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl3) δ 169.1, 162.8, 145.4, 138.0, 135.5, 133.4, 132.2, 129.5, 129.1, 128.7, 127.6, 121.6, 62.2, 41.0, 36.0, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}BrNO_5S^+$, $[M+H]^+$ 478.0318, Found 478.0320.

Ethyl 4-(4-fluorophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3f). White solid; Mp 110.1-111.7 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03(d, J =8.4 Hz, 2H), 7.47-7.45 (m, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.10 (t, J = 8.4 Hz, 2H), 6.11 (d, J = 2.4 Hz, 1H), 5.53 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.16-4.05 (m, 2H), 3.46 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.21-3.16 (m, 1H), 2.43 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 164.9, 163.2, 162.2, 150.7, 144.8, 135.5, 132.2 (d, J = 3.0 Hz), 129.6, 128.9, 128.2 (d, J = 9.0 Hz), 119.0, 116.0 (d, J = 21.0 Hz), 62.4, 56.1, 30.7, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}FNO_5S^+$, $[M+H]^+$ 418.1119, Found 418.1116.

Ethyl 6-oxo-1-tosyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (3g). White solid; Mp 138.5-140.3 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.34(d, J = 8.4 Hz, 2H), 6.20(d, J = 2.4 Hz, 1H), 5.55 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.17-4.07 (m, 2H), 3.47 (dd, J_1 = 18.0 Hz, J_2 = 1.8 Hz, 1H),

3.27-3.22 (m, 1H), 2.44 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150MHz, CDCl3) δ 169.5, 161.9, 150.3, 145.0, 139.6, 135.4, 132.2 (q, *J* = 33.0 Hz), 129.7, 129.0, 126.6, 125.9 (q, *J* = 3.0 Hz), 123.6 (q, *J* = 270 Hz), 121.1, 62.5, 56.2, 30.7, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{22}H_{21}F_3NO_5S^+$, $[M+H]^+$ 468.1087, Found 68.1088.

Ethyl 6-oxo-4-(o-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4h). White solid; Mp 119.7-121.6 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.19-7.16 (m, 3H), 7.06 (d, *J* = 6.6 Hz, 1H), 6.59 (d, *J* = 4.2 Hz, 1H), 4.42-4.32 (m, 2H), 4.12-4.08 (m, 1H), 2.77-2.69 (m, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.8, 162.9, 145.3, 137.2, 135.7 , 135.5, 133.0 , 131.0, 129.6, 129.2, 129.1 , 127.6 , 126.8 , 126.0 , 62.1 , 40.7, 33.4, 21.7 , 19.5 , 14.0 ppm; **HRMS** (ESI): calculated for $C_{21}H_{22}O_5NS^+$, $[M+H]^+$400.1213, Found: 400.1212.

Ethyl 4-(2-bromophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3i). White solid; Mp 148.4-150.0 ^oC; **^{1}H NMR** (600 MHz, CDCl3) δ: 8.02 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.34-7.31 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8Hz, 1H), 5.90 (d, *J* = 3.0 Hz, 1H), 5.49 (dd, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1H), 4.24-4.18 (m, 1H), 4.10-4.04 (m, 1H), 3.38-3.34 (m, 1H), 3.22 (dd, J_1 = 18.0 Hz, J_2 = 1.8 Hz, 1H), 2.44 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 161.8, 152.9, 144.9, 138.7, 135.3, 133.3, 130.4, 129.6, 129.0, 128.9, 127.7, 124.1, 120.5, 62.3, 56.2, 32.7, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}BrNO_5S^+$, $[M+H]^+$ 478.0318, Found 478.0324.

Ethyl 4-(2-bromophenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4i). White solid; Mp 150.1-151.3 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08(d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 1H), 7.17-7.14 (m, 2H), 6.64 (d, *J* = 4.8 Hz, 1H), 4.42-4.36 (m, 2H), 4.32-4.29 (m, 1H), 2.84-2.75 (m, 2H), 2.44 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 162.9, 145.4, 137.7, 135.7, 133.5, 133.5, 129.6, 129.3, 129.2, 128.2, 128.0, 126.9, 124.0, 62.2, 40.0, 36.5. 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}BrNO_5S^+$, $[M+H]^+$ 478.0318, Found 478.0322.

Ethyl 6-oxo-4-(m-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3j). White solid; Mp 118.7-120.5 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03(d, *J* = 8.4 Hz, 2H), 7.34-7.23 (m, 6H), 6.14 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.16-4.05 (m, 2H), 3.50 (dd, J_1 = 17.4 Hz, J_2 = 1.8 Hz, 1H), 3.21-3.16 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C**

NMR (150 MHz, $CDCl_3$) δ 169.7, 162.4, 152.0, 144.8, 138.7, 136.0, 135.7, 131.4, 129.6, 128.9, 128.8, 126.8, 123.3, 119.1, 62.3, 56.2, 30.7, 21.6, 21.3, 13.9 ppm; **HRMS** (ESI): calculated for $C_{22}H_{24}O_5NS^+$, $[M+H]^+$ 414.1370, Found: 414.1372.

Ethyl 6-oxo-4-(m-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4j). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 6.96-6.95 (m, 2H), 6.66 (d, J = 4.8 Hz, 1H), 4.42-4.32 (m, 2H), 3.86-3.83 (m, 1H), 2.78-2.70 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 162.9, 145.2, 139.0, 138.8, 135.7, 132.7, 129.4, 129.1, 129.0, 128.96, 128.4, 127.6, 123.9, 62.0, 41.3, 36.7, 21.6, 21.3, 14.0 ppm; **HRMS** (ESI): calculated for $C_{22}H_{24}O_5NS^+$, $[M+H]^+$ 414.1370, Found: 414.1374.

Ethyl 4-(3-fluorophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3k). White solid; Mp 121.8-123.5 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03(d, J = 8.4 Hz, 2H), 7.39 (dd, J_1 = 13.8 Hz, J_2 = 7.8 Hz, 1H), 7.33(d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.8 Hz, 1H), 7.15-7.12 (m, 2H), 6.15 (d, J = 2.4 Hz, 1H), 5.53 (d, J=2.4 Hz, 1H), 4.17-4.06 (m, 2H), 3.44 (dd, J_1 = 17.4 Hz, J_2 = 1.2 Hz, 1H), 3.22-3.18 (m, 1H), 2.44(s, 3H), 1.12 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 163.8, 162.1 (d, J = 12.0 Hz), 150.4 (d, J = 3.0 Hz), 145.0, 138.3 (d, J = 7.5 Hz), 135.5, 130.6 (d, J = 9.0 Hz), 129.7, 129.0, 121.9 (d, J = 3.0 Hz), 120.3, 117.4(d, J = 21.0 Hz), 113.2 (d, J = 22.5 Hz), 62.5, 56.2, 30.7, 21.7, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}FNO_5S^+$, $[M+H]^+$ 418.1119, Found 418.1116.

Ethyl 4-(3-fluorophenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4k). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.32-7.28 (m, 3H), 6.99-6.96 (m, 2H), 6.86 (d, J = 9.6 Hz, 1H), 6.64 (d, J =4.8 Hz, 1H), 4.43-4.33 (m, 2H), 3.91-3.88 (m, 1H), 2.80 (dd, J_1 =16.2 Hz, J_2 = 5.4 Hz, 1H), 2.72 (dd, J_1 =16.2 Hz, J_2 = 9.6 Hz, 1H), 2.43 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.1, 163.2 (d, J = 246 Hz), 162.8, 145.4, 141.5 (d, J = 6.0 Hz), 135.4, 133.2, 130.7 (d, J = 7.5 Hz), 129.4, 129.1, 127.6, 122.7 (d, J = 3.0 Hz), 114.6 (d, J = 21.0 Hz), 114.0 (d, J = 21.0 Hz), 62.2, 41.0, 36.4, 21.6, 14.0 ppm; **HRMS** (ESI): calculated for $C_{21}H_{21}FNO_5S^+$, $[M+H]^+$ 418.1119, Found 418.1121.

Ethyl 4-(3,5-difluorophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3l). White solid; Mp 171.2-173.0 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 6.0 Hz, 2H), 6.88 (t, J = 8.0 Hz, 1H), 6.14 (d, J = 2.4 Hz, 1H), 5.53

(dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.18-4.07 (m, 2H), 3.38 (dd, J_1 = 17.4 Hz, J_2 = 1.8 Hz, 1H), 3.22-3.17 (m, 1H), 2.44 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.4, 164.0 (d, J = 13.5 Hz), 162.3 (d, 12.6 Hz), 161.7, 149.3, 145.1, 139.3 (t, J = 9.0 Hz), 135.4, 129.7, 129.0, 121.2, 109.4 (d, J = 4.5 Hz), 109.2 (d, J = 4.5 Hz), 105.7 (t, J = 25.5 Hz), 62.5, 56.1, 30.6, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{20}F_2NO_5S^+$, $[M+H]^+$ 436.1025, Found 436.1028.

Ethyl 4-(3,5-difluorophenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4l). White solid; Mp 151.5-153.2 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.73-6.68 (m, 1H), 6.60 (d, J = 4.8 Hz, 1H), 4.43-4.33 (m, 2H), 3.89-3.86 (m, 1H), 2.81 (dd, J_1 =16.8 Hz, J_2 = 5.4 Hz, 1H), 2.70 (dd, J_1 =16.8 Hz, J_2 = 9.6 Hz, 1H), 2.43 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.7, 164.1 (d, J = 12.0 Hz), 162.7, 162.4 (d, J=13.5 Hz), 145.5, 142.8 (t, J = 7.5 Hz), 135.2, 133.6, 129.5, 129.1, 126.4, 110.2 (d, J = 6.0 Hz), 110.1 (d, J = 6.0 Hz), 103.2 (t, J = 25.5 Hz), 62.3, 40.7, 36.3, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{20}F_2NO_5S^+$, $[M+H]^+$ 436.1025, Found 436.1029.

Ethyl 4-(3-bromo-4-fluorophenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3m). White solid; Mp 157.4-158.8 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.8 Hz, 2H), 7.65 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.16 (t, J = 8.4 Hz, 1H), 6.10 (d, J = 2.4 Hz, 1H), 5.53 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.17-4.07 (m, 2H), 3.41 (dd, J_1 = 15.0 Hz, J_2 = 1.8 Hz, 1H), 3.20-3.16 (m, 1H), 2.44(s, 3H), 1.12(t, J = 7.2Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 161.8, 160.2 (d, J = 255 Hz), 149.4, 145.0, 135.5, 133.7 (d, J = 3.0 Hz), 131.6, 129.7, 129.0, 127.0 (d, J = 7.5 Hz), 120.2, 117.0 (d, J = 18.0 Hz), 110.0 (d, J = 21.0 Hz), 62.5, 56.1, 30.8, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{21}H_{20}BrFNO_5S^+$, $[M+H]^+$ 496.0224, Found 496.0229.

Ethyl 4-(3-bromo-4-fluorophenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4m). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.36 (dd, J_1 =6.0 Hz, J_2 = 1.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.11-7.05 (m, 2H), 6.62 (d, J = 4.8 Hz, 1H), 4.44-4.33 (m, 2H), 3.87-3.84 (m, 1H), 2.81 (dd, J_1 =10.8 Hz, J_2 = 5.4 Hz, 1H), 2.71 (dd, J_1 =16.2 Hz, J_2 = 9.0 Hz, 1H), 2.44 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.8, 162.7, 158.5 (d, J = 255 Hz), 145.5, 136.4 (d, J = 3.0 Hz), 135.4, 133.5, 132.1, 129.5, 129.2, 127.6 (d, J = 7.5 Hz), 127.1, 117.0 (d, J = 21.0 Hz), 109.7 (d, J = 21.0 Hz), 62.3, 41.1, 35.6, 21.7, 14.0

ppm; **HRMS** (ESI): calculated for $C_{21}H_{20}BrFNO_5S^+$, $[M+H]^+$ 496.0224, Found 496.0227.

Ethyl 4-(3,4-dimethylphenyl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3n). White solid; Mp 113.8-115.4 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03(d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.23 (s, 1H), 7.23-7.20 (m, 1H), 7.16 (d, J = 7.8 Hz, 2H), 6.13 (d, J =2.4 Hz, 1H), 5.51(dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 1H), 4.15-4.03(m, 2H), 3.50 (dd, J_1 = 17.4 Hz, J_2 = 1.8 Hz, 1H), 3.18-3.14 (m, 1H), 2.43 (s, 3H), 2.78(s, 6H), 1.10(t, J = 7.2Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 162.6, 151.9, 144.7, 139.9, 137.3, 135.7, 133.4, 130.2, 129.6, 128.9, 127.3, 123.7, 118.2, 62.3, 56.2, 30.6, 21.6, 19.8, 19.7, 13.9 ppm; **HRMS** (ESI): calculated for $C_{23}H_{26}NO_5S^+$, $[M+H]^+$ 428.1526, Found 428.1530.

Ethyl 4-(3,4-dimethylphenyl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4n). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 7.8 Hz, 1H), 6.93 (s, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 4.8 Hz, 1H), 4.42-4.32 (m, 2H), 3.84-3.81 (m, 1H), 2.77-2.69 (m, 2H), 2.44 (s, 3H), 2.24 (s, 6H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 163.0, 145.2, 137.4, 136.5, 136.1, 135.8, 132.7, 130.3, 129.5, 129.1, 128.2, 124.2, 62.1, 41.6, 36.5, 21.7, 19.8, 19.3, 14.0 ppm; **HRMS** (ESI): calculated for $C_{23}H_{26}NO_5S^+$, $[M+H]^+$ 428.1526, Found 428.1532.

Ethyl 6-oxo-4-(thiophen-3-yl)-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3o). White solid; Mp 141.4-143.1 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.55 (m, 1H), 7.37(dd, J_1 = 4.8 Hz, J_2 = 2.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.25 (dd, J_1 = 4.8 Hz, J_2 = 2.4 Hz, 1H), 6.12 (d, J = 2.4 Hz, 1H), 5.51 (dd, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 1H), 4.15-4.03 (m, 2H), 3.46 (dd, J_1 = 17.4 Hz, J_2 = 1.8 Hz, 1H), 3.22-3.17 (m, 1H), 2.43 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 162.7, 145.6, 144.8, 138.1, 135.7, 129.6, 128.9, 127.4, 126.0, 124.9, 117.6, 62.4, 56.0, 30.7, 21.6, 13.9 ppm; **HRMS** (ESI): calculated for $C_{19}H_{20}NO_5S_2^+$, $[M+H]^+$ 406.0777, Found 406.0779.

Ethyl 6-oxo-4-(thiophen-3-yl)-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4o). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.33 (dd, J_1 = 4.8 Hz, J_2 = 3.0 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 4.8 Hz, 1H), 6.69 (d, J = 4.8 Hz, 1H), 4.40-4.34 (m, 2H), 3.95 (m, 1H), 2.82 (dd, J_1 =16.2 Hz, J_2 = 2.4 Hz, 1H), 2.43 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.4, 162.9, 145.2, 139.1, 135.5, 132.8, 129.4, 129.1, 127.8, 127.1, 126.2, 121.3, 62.1, 40.6, 32.2, 21.6, 14.0 ppm; **HRMS** (ESI):

calculated for $C_{19}H_{20}NO_5S_2^+$, $[M+H]^+$ 406.0777, Found 406.0780.

Ethyl 4-(furan-2-yl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3p). White solid; Mp 65.1-66.8 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 1.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 6.74 (d, J = 3.6 Hz, 1H), 6.51 (dd, J_1 = 3.0 Hz, J_2 = 1.2 Hz, 1H), 6.19 (d, J = 2.4 Hz, 1H), 5.50 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 1H), 4.14-4.03 (m, 2H), 3.35 (dd, J_1 = 17.4 Hz, J_2 = 2.4 Hz, 1H), 3.14-3.10 (m, 1H), 2.43 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 162.5, 150.0, 145.8, 144.8, 139.3, 135.7, 129.6, 128.9, 114.8, 113.4, 112.5, 62.4, 56.0, 28.6, 21.7, 13.8 ppm; **HRMS** (ESI): calculated for $C_{19}H_{20}NO_6S^+$, $[M+H]^+$ 390.1006, Found 390.1003

Ethyl 4-(furan-2-yl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4p). Red solid, Mp 143.5-145.2 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01(d, J = 8.4 Hz, 2H), 7.31(d, J = 7.8 Hz, 3H), 6.65 (d, J = 5.4 Hz, 1H), 6.28 (dd, J_1 = 3.0 Hz, J_2 = 1.8 Hz, 1H), 6.08 (d, J = 3.0 Hz, 1H), 4.41-4.33 (m, 2H), 3.95-3.92 (m, 1H), 2.83-2.75 (m, 2H), 2.44 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.0, 162.8, 151.2, 145.3, 142.5, 135.5, 133.2, 129.6, 129.1, 125.1, 110.4, 106.4, 62.2, 38.6, 30.8, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{19}H_{20}NO_6S^+$, $[M+H]^+$ 390.1006, Found 390.1008.

Ethyl 4-(naphthalen-1-yl)-6-oxo-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3q). White solid; Mp 125.6-128.3; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 2H), 7.87 (t, J = 7.8 Hz, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.53-7.46 (m, 3H), 7.36 (d, J = 8.4Hz, 2H), 7.29 (d, J = 7.2 Hz, 1H), 6.05 (d, J = 2.4 Hz, 1H), 5.56 (dd, J_1 = 6.6 Hz, J_2 = 2.4 Hz, 1H), 4.29-4.24 (m, 1H), 4.20-4.14 (m, 1H), 3.45-3.35 (m, 2H), 2.46 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.9, 162.0, 152.9, 145.0, 135.9, 135.6, 133.8, 129.8, 129.79, 129.7, 129.66, 129.0, 128.7, 126.9, 126.4, 125.1, 125.0, 124.4, 124.2, 62.3, 56.5, 34.2, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{25}H_{24}NO_5S^+$, $[M+H]^+$ 450.1370, Found 450.1374.

Ethyl 4-(naphthalen-1-yl)-6-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4q). White solid; Mp 177.6-179.3 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 7.90 (dd, J_1 = 7.4 Hz, J_2 = 2.4 Hz, 2H), 7.79 (d, J = 7 Hz, 1H), 7.59-7.56 (m, 1H), 7.54-7.52 (m,1H), 7.39 (t, J=7.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.25 (s, 1H), 6.73 (d, J = 4.8 Hz, 1H), 4.65-4.62 (m, 1H), 4.42-4.32 (m, 2H), 2.95 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.8, 162.9, 145.3, 135.7, 134.1, 134.0, 133.1, 130.6, 129.6, 129.3, 129.2, 128.6,

128.5, 126.8, 126.0, 125.4, 123.8, 122.5, 62.1, 40.3, 33.0, 21.7, 14.0 ppm; **HRMS** (ESI): calculated for $C_{25}H_{24}NO_5S^+$, $[M+H]^+$ 450.1370, Found 450.1372.

(E)-ethyl 6-oxo-4-styryl-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3r). White solid; Mp 157.5-159.1 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.39-7.31 (m, 5H), 6.95 (d, J = 17.2 Hz, 1H), 6.81 (d, J = 17.2 Hz, 1H), 5.86 (d, J = 1.8 Hz, 1H), 5.51 (dd, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 1H), 4.16-4.04 (m, 2H), 3.39 (dd, J_1 = 17.4 Hz, J_2 = 1.2 Hz, 1H), 3.03-2.99 (m, 1H), 2.43 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 162.6, 149.1, 144.8, 136.4, 135.7, 135.3, 129.7, 128.94, 128.92, 127.4, 126.3, 121.6, 62.4, 56.1, 28.1, 21.7, 13.9 ppm; **HRMS** (ESI): calculated for $C_{23}H_{24}NO_5S^+$, $[M+H]^+$ 426.1370, Found 426.1366.

(E)-ethyl 6-oxo-4-styryl-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4r). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.32-7.30 (m, 2H), 7.27-7.25 (m, 3H), 7.13 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 6.0 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 5.97 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 4.41-4.35 (m, 2H), 3.42-3.39 (m, 1H), 2.71 (dd, J_1 = 16.2 Hz, J_2 = 6.0 Hz, 1H), 2.57 (dd, J_1 = 16.2 Hz, J_2 = 6.6 Hz, 1H), 2.33 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 163.0, 145.2, 136.0, 135.4, 133.1, 132.3, 129.6, 129.1, 128.6, 128.0, 126.9, 126.4, 126.0, 62.1, 39.5, 34.0, 21.6, 14.0 ppm; **HRMS** (ESI): calculated for $C_{23}H_{24}NO_5S^+$, $[M+H]^+$ 426.1370, Found 426.1372.

Methyl 6-oxo-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine-2-carboxylate (3s). White solid; Mp 182.5-183.5 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.47-7.41 (m, 5H), 7.33 (d, J = 7.8 Hz, 2H), 6.16(d, J = 2.4 Hz, 1H), 5.55 (dd, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 1H), 3.64 (s, 3H), 3.50 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.22-3.18 (m, 1H), 2.44 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.2, 162.2, 151.8, 144.9, 135.9, 135.5, 130.6, 129.7, 128.94, 128.91, 126.2, 119.24, 119.23, 56.1, 53.0, 30.6, 21.6 ppm; **HRMS** (ESI): calculated for $C_{20}H_{20}NO_5S^+$, $[M+H]^+$ 386.1057, Found 386.1058.

Methyl 6-oxo-4-phenyl-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate (4s). Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.32-7.30 (m, 2H), 7.27-7.25 (m, 3H), 7.13 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 6.0 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 5.97 (dd, J_1 = 16.2 Hz, J_2 = 7.2 Hz, 1H), 4.41-4.35 (m, 2H), 3.42-3.39 (m, 1H), 2.71 (dd, J_1 = 16.2 Hz, J_2 = 6.0 Hz, 1H), 2.57 (dd, J_1 = 16.2 Hz, J_2 = 6.6 Hz, 1H), 2.33 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150

MHz, $CDCl_3$) δ 169.5, 163.0, 145.2, 136.0, 135.4, 133.1, 132.3, 129.6, 129.1, 128.6, 128.0, 126.9, 126.4, 126.0, 62.1, 39.5, 34.0, 21.6, 14.0 ppm; **HRMS** (ESI): calculated for $C_{20}H_{20}NO_5S^+$, $[M+H]^+$ 386.1057, Found 386.1059.

Ethyl 1-benzyl-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6a). White solid; Mp 216.8-217.9 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 2H), 7.43 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.30-7.27 (m, 4H), 7.22 (td, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.31 (s, 1H), 4.91 (s, 2H), 4.44-4.39 (m, 1H), 4.36-4.31 (m, 1H), 3.16 (d, J = 16.2 Hz, 1H), 2.68 (d, J = 16.2 Hz, 1H), 2.47 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.6, 167.7, 162.7, 145.7, 141.7, 135.2, 135.0, 134.7, 130.0, 129.7, 129.2, 128.9, 128.0, 127.9, 127.2, 124.2, 124.0, 122.6, 109.8, 62.4, 47.1, 44.2, 42.2, 21.7, 14.0 ppm; HRMS (ESI): calculated for $C_{29}H_{26}N_2NaO_6S^+$, $[M+Na]^+$ 553.1404, Found 553.1402

Ethyl 1-benzyl-5-methyl-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6b). White solid; Mp 225.4-226.4 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.33-7.31 (m, 3H), 7.29-7.24 (m, 3H), 7.02 (d, J = 7.8 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 6.31 (s, 1H), 4.88 (s, 2H), 4.45-4.39 (m, 1H), 4.36-4.31 (m, 1H), 3.1 5 (d, J = 16.8 Hz, 1H), 2.66 (d, J = 16.8 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.5, 167.8, 162.7, 145.5, 139.3, 135.3, 135.1, 134.5, 133.8, 129.94, 129.9, 129.2, 128.9, 128.0, 127.8, 127.2, 125.0, 122.7, 109.5, 62.3, 47.1, 44.2, 42.2, 21.7, 20.9, 13.9 ppm; HRMS (ESI): calculated for $C_{30}H_{28}N_2NaO_6S^+$, $[M+Na]^+$ 567.1560, Found 567.1560.

Ethyl 1-benzyl-5-methoxy-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6c). White solid; Mp 229.3-230.1 ^oC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.34-7.32 (m, 3H), 7.29-7.23 (m, 4H), 6.77 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.66 (d, J = 9.0 Hz, 1H), 6.38 (s, 1H), 4.91-4.86 (m, 2H), 4.45-4.40 (m, 1H), 4.35-4.30 (m, 1H), 3.79 (s, 3H), 3.21 (d, J = 16.2 Hz, 1H), 2.66 (d, J = 16.2 Hz, 1H), 2.46 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.4, 167.9, 162.6, 157.0, 145.6, 135.14, 135.07, 134.7, 134.4, 129.8, 129.2, 128.9, 128.8, 127.9, 127.1, 123.2, 115.8, 110.5, 109.9, 62.3, 56.1, 47.5, 44.2, 42.3, 21.7, 14.0 ppm; HRMS (ESI): calculated for $C_{30}H_{28}N_2NaO_7S^+$, $[M+Na]^+$

583.1509, Found 583.1507.

ethyl 1-benzyl-5-bromo-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6d). White solid; Mp 219.3-246.0 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, J =8.4 Hz, 2H), 7.55 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.35-7.32 (m,3H), 7.29 (m,1H), 7.23 (d, J = 7.2 Hz, 2H), 6.62 (d, J = 8.4 Hz, 1H), 6.25 (s, 1H), 4.88 (s, 2H), 4.45-4.33 (m, 2H), 3.10 (d, J = 16.8 Hz, 1H), 2.69 (d, J = 16.2 Hz, 1H), 2.46 (s,3H), 1.40 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.9, 167.2, 162.6, 145.7, 140.8, 135.1, 135.0, 134.5, 132.6, 130.0, 129.3, 129.2, 129.0, 128.9, 128.1, 127.3, 127.2, 127.1, 121.4, 116.5, 111.3, 62.5, 47.0, 44.2, 41.9, 21.8, 13.9 ppm; HRMS (ESI): calculated for $C_{29}H_{25}BrN_2NaO_6S^+$, $[M+Na]^+$ 631.0509, Found 631.0511.

Ethyl 1-benzyl-5-chloro-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6e). White solid; Mp 224.7-226.5 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.40 (d, J =8.4 Hz, 3H), 7.35-7.32(m, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 2H), 7.19 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.25 (s, 1H), 4.89 (s, 2H), 4.45-4.33 (m, 2H), 3.12 (d, J = 16.2 Hz, 1H), 2.68 (d, J = 16.2 Hz, 1H), 2.46 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 167.2, 162.6, 145.8, 140.3, 135.1, 134.9, 134.5, 130.0, 129.7, 129.6, 129.3, 129.0, 128.1, 127.1, 124.6, 121.4, 110.8, 62.5, 47.1, 44.3, 41.9, 21.8, 14.0 ppm; HRMS (ESI): calculated for $C_{29}H_{25}ClN_2NaO_6S^+$, $[M+Na]^+$ 587.1014, Found 587.1017.

Ethyl 1-benzyl-5-fluoro-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6f). White solid; Mp 244.5-246.0 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.35-7.33 (m, 2H), 7.31-7.28 (m, 1H), 7.24 (d, J = 7.2 Hz, 2H), 6.92 (td, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 6.67(dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, 1H), 6.27 (s, 1H), 4.89 (s, 2H), 4.45-4.40 (m, 1H), 4.38-4.33 (m, 1H), 3.17 (d, J = 16.2 Hz, 1H), 2.67 (d, J = 16.8 Hz, 1H), 2.47 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.3, 167.3, 162.6, 160.5, 158.8, 145.9, 137.6, 135.0, 134.8, 134.6, 130.0, 129.4, 129.35 129.3, 129.0, 128.1, 127.1, 121.8, 116.1 (d, J = 9.0 Hz), 112.4 (d, J = 27.0 Hz), 110.5 (d, J = 7.5 Hz), 62.5, 47.3, 44.3, 42.0, 21.8, 14.0 ppm; **HRMS** (ESI): calculated for $C_{29}H_{25}FN_2NaO_6S+^+$, $[M+Na]^+$ 571.1310, Found 571.1312.

Ethyl

1-benzyl-5,7-dimethyl-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-

6'-carboxylate (6g). White solid; Mp 223.5-224.7 ^{o}C; **^{1}H NMR** (600 MHz, CDCl3) δ 8.21 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 7.33 (m, 2H), 7.27-7.25 (m, 2H), 7.18 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 6.81 (s, 1H), 6.30 (s, 1H), 5.18-5.12 (dd, J_1 = 19.8 Hz, J_2 = 11.4 Hz, 2H), 4.45-4.39 (m,1H), 4.36-4.31 (m, 1H), 3.16 (d, J = 16.2 Hz, 1H), 2.70 (d, J = 16.8 Hz, 1H), 2.46 (s,3H), 2.26 (s, 3H), 2.21 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 176.5, 167.8, 162.8, 145.6, 137.2, 136.9, 135.2, 134.4, 134.0, 133.8, 129.9, 129.2, 128.9, 128.8, 127.4, 125.4, 122.9, 122.8, 120.2, 62.3, 46.6, 45.3, 42.5, 21.7, 20.6, 18.5, 14.0 ppm; HRMS (ESI): calculated for $C_{31}H_{30}N_2NaO_6S^+$, $[M+Na]^+$ 581.1717, Found 581.1716.

Ethyl

1-benzyl-6-bromo-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carb oxylate (6h). White solid; Mp 183.7-185.1 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.39-7.34 (m, 4H), 7.31 (d, J = 7.2 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 1H), 6.91 (d, J = 0.6 Hz, 1H), 6.27 (s, 1H), 4.87 (s, 1H), 4.43-4.39 (m, 1H), 4.36-4.32 (m, 1H), 3.13 (d, J = 16.8 Hz, 1H), 2.64 (d, J = 16.8 Hz, 1H), 2.46 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.4, 167.3, 162.5, 145.7, 143.0, 134.9, 134.87, 134.4, 130.0, 129.2, 129.1, 128.1, 127.1, 126.9, 126.8, 125.5, 123.4, 121.8, 113.1, 62.4, 46.7, 44.2, 42.0, 21.7, 13.9 ppm; HRMS (ESI): calculated for $C_{29}H_{25}BrN_2NaO_6S^+$, $[M+Na]^+$ 631.0509, Found 631.0513.

Ethyl

1-methyl-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6i). White solid; Mp 185.0-186.4 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.45(s, 1H), 7.39-7.34 (m, 3H), 7.13-7.10 (m, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.26 (s, 1H), 4.42-4.30 (m, 2H), 3.23 (s, 3H), 3.08 (dd, J_1 = 16.2 Hz, J_2 = 1.2 Hz, 1H), 2.63 (d, J = 16.2 Hz, 1H), 2.47 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.4, 167.9, 162.7, 145.6, 142.6, 135.1, 134.5, 130.0, 129.2, 128.0, 126.4, 124.1, 124.0, 122.7, 108.7, 62.3, 47.0, 42.0, 26.7, 21.8, 14.0 ppm; HRMS (ESI): calculated for $C_{23}H_{22}N_2NaO_6S^+$, $[M+Na]^+$ 477.1091, Found 477.1093.

Ethyl

1-allyl-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6j). White solid; Mp 161.5-162.3 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.45 (s,1H), 7.39 (d, J = 8.4 Hz, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.87 (d, J = 8.4

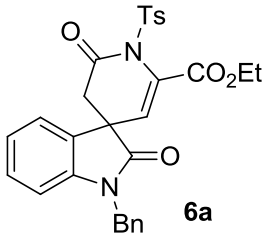
Hz, 1H), 6.27 (s, 1H), 5.86-5.79 (m, 1H), 5.27-5.22 (m, 2H), 4.43-4.35 (m, 1H), 4.34-4.30 (m, 3H), 3.11 (d, *J* = 16. 2Hz, H), 2.64 (d, *J* = 16.2 Hz, 1H), 2.47 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.1, 167.8, 162.6, 145.6, 141.8, 135.1, 134.5, 130.7, 130.0, 129.6, 129.2, 128.0, 124.2, 123.9, 122.6, 118.2, 109.6, 62.3, 46.9, 42.7, 42.1, 21.7, 13.9 ppm; HRMS (ESI): calculated for $C_{25}H_{24}N_2NaO_6S^+$, $[M+Na]^+$ 503.1247, Found 503.1247.

Methyl 1-benzyl-5-methyl-2,2'-dioxo-1'-tosyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-6'-carboxylate (6k). White solid; Mp 203.9-205.2 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.34-7.24 (m, 6H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 1H), 5.29 (s, 1H), 4.88 (dd, J_1 = 19.2 Hz, J_2 = 15.6 Hz, 2H), 3.91 (s, 3H), 3.15 (d, *J* = 16.2 Hz, 1H), 2.67 (d, *J* = 16.2Hz, 1H), 2.47 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 175.4, 167.8, 163.1, 145.7, 139.2, 135.14, 135.1, 134.2, 133.8, 129.9, 129.3, 128.9, 127.9, 127.85, 127.1, 124.9, 123.3, 109.5, 52.9, 47.1, 44.1, 42.2, 21.7, 21.0 ppm; HRMS (ESI): calculated for $C_{29}H_{26}N_2NaO_6S^+$, $[M+Na]^+$ 553.1404, Found 553.1403.

E**thyl 6-oxo-4-phenyl-1,6-dihydropyridine-2-carboxylate (8a)**. Brown solid; Mp 157.6-159.3 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.55 (bs, 1H), 7.62-7.60 (m, 2H), 7.50-7.45 (m, 3H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.02 (d, *J* = 1.2 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.0, 160.9, 152.3, 136.7, 133.9, 129.9, 129.1, 126.8, 122.5, 109.3, 62.8, 14.1

4. Crystal data and crystal structure of 6a

XRD Data for Compound 6a (CCDC No. 1526708)



6a

Bond precision: C-C = 0.0036 A Wavelength=0.71073

Cell: a=11.4870(4) b=25.8357(6) c=9.2054(3)
alpha=90 beta=110.444(4) gamma=90
Temperature: 290 K

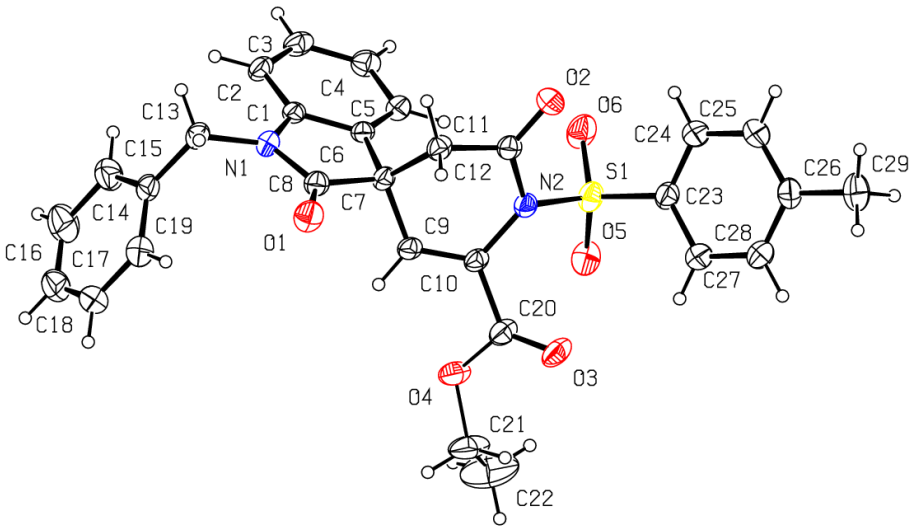
	Calculated	Reported
Volume	2559.86(15)	2559.85(14)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C29 H26 N2 O6 S	C29 H26 N2 O6 S
Sum formula	C29 H26 N2 O6 S	C29 H26 N2 O6 S
Mr	530.58	530.58
Dx,g cm-3	1.377	1.377
Z	4	4
Mu (mm-1)	0.174	0.174
F000	1112.0	1112.0
F000'	1113.03	
h,k,lmax	14,31,11	14,31,11
Nref	5041	5033
Tmin,Tmax	0.959,0.976	0.843,1.000
Tmin'	0.959	

Correction method= # Reported T Limits: Tmin=0.843 Tmax=1.000
AbsCorr = MULTI-SCAN

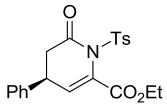
Data completeness= 0.998 Theta(max)= 26.020

R(reflections)= 0.0511(3638) wR2(reflections)= 0.1268(5033)

S = 1.045 Npar= 373

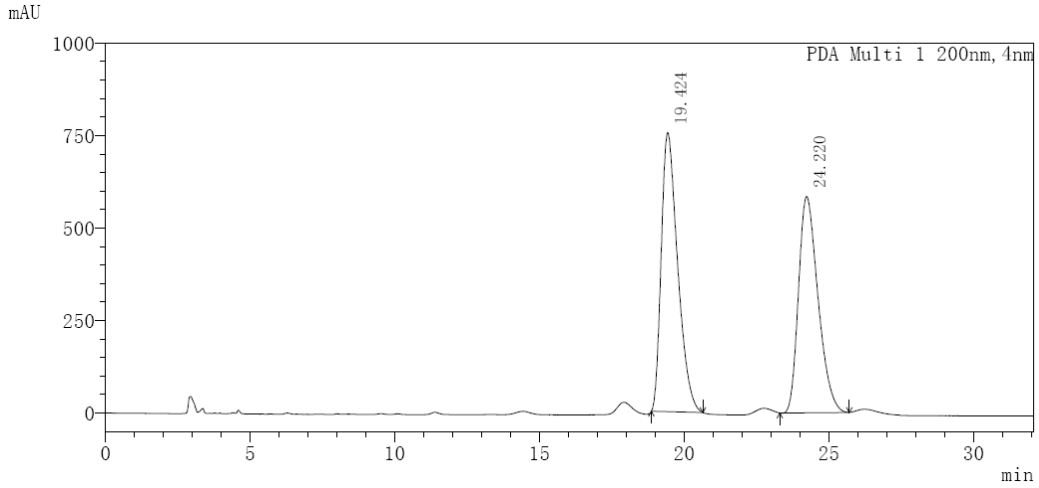

C3
C2
C4
C1
C5
C13
C11
O2
O6
C25
C24
C15
N1
C6
C12
N2
S1
C26
C29
C8
C7
C23
C14
C19
O1
C9
O5
C28
C16
C17
C10
C27
C20
C18
O3
O4
C21
C22

5. HPLC spectra of 3aa, 4aa and 6aa



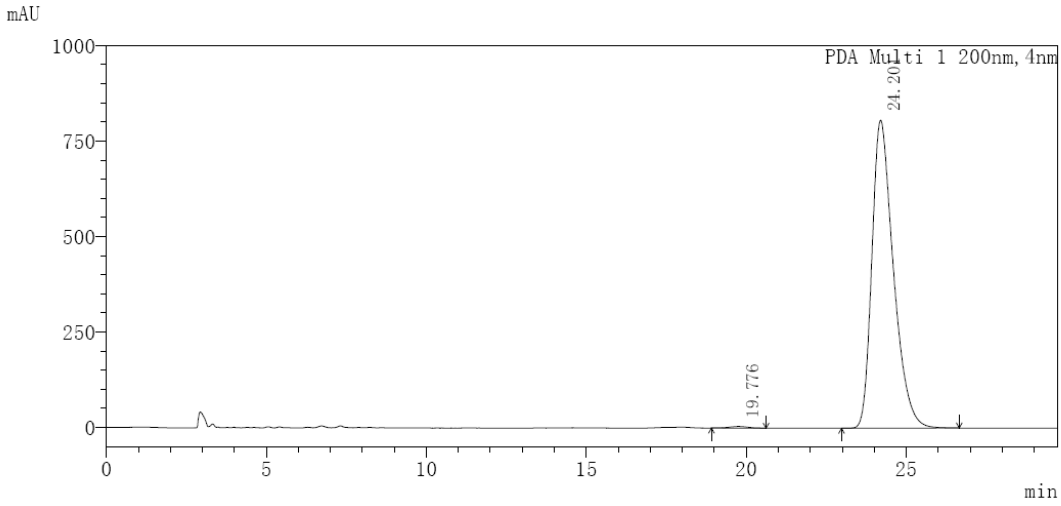
4aa

$[\alpha]^{25}_{D}$ = -133.2 (c = 1.0 in $CHCl_3$); HPLC analysis: 99% ee., [CHIRALPAK OD column; 1.0 mL/min; solvent system: i-PrOH/hexane = 90:10; retention times: 19.8 min (minor), 24.2 min (major)].



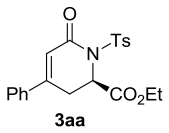
PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.424	29692651	754418	51.992	56.351
2	24.220	27417339	584367	48.008	43.641
Total		57109990	1338786	100.000	100.000



PDA Ch1 200nm

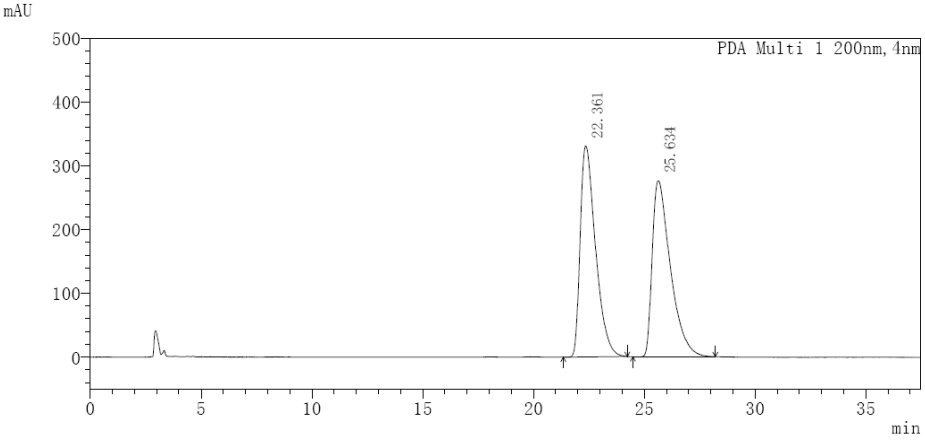
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.776	171905	4383	0.454	0.541
2	24.201	37678427	805897	99.546	99.459
Total		37850332	810280	100.000	100.000



3aa

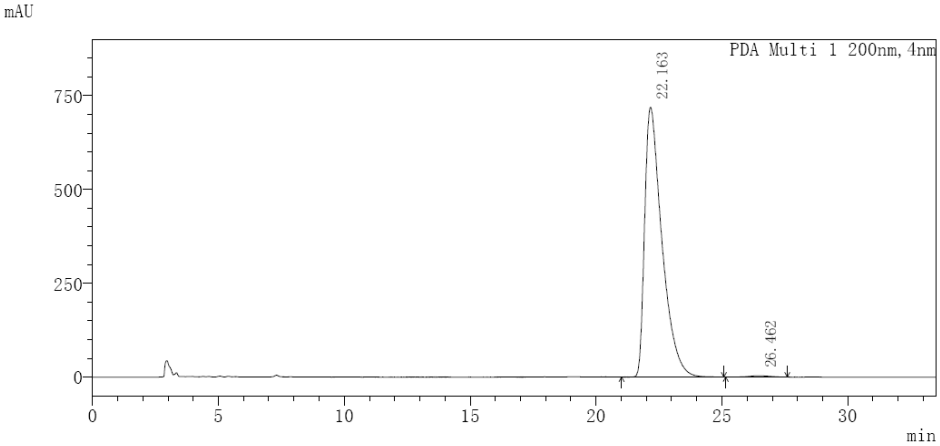
The asymmetric synthesis of **3aa** using chiral triazolium salt **F** as the precatalyst under condition **A**. (Scheme 3, Eqn 1).

$[\alpha]^{25}_{D}$ = -46 (c = 1.0 in $CHCl_3$); $[\alpha]^{25}_{D}$ = -148 (c = 1.0 in CH_2Cl_2) [3]; HPLC analysis: 99% ee., [CHIRALPAK OD column; 1.0 mL/min; solvent system: i-PrOH/hexane = 90:10; retention times: 22.2 min (major), 26.5 min (minor)].



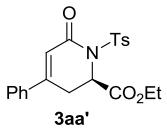
PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.361	15890120	330804	50.272	54.527
2	25.634	15717915	275876	49.728	45.437
Total		31608035	606680	100.000	100.000



PDA Ch1 200nm

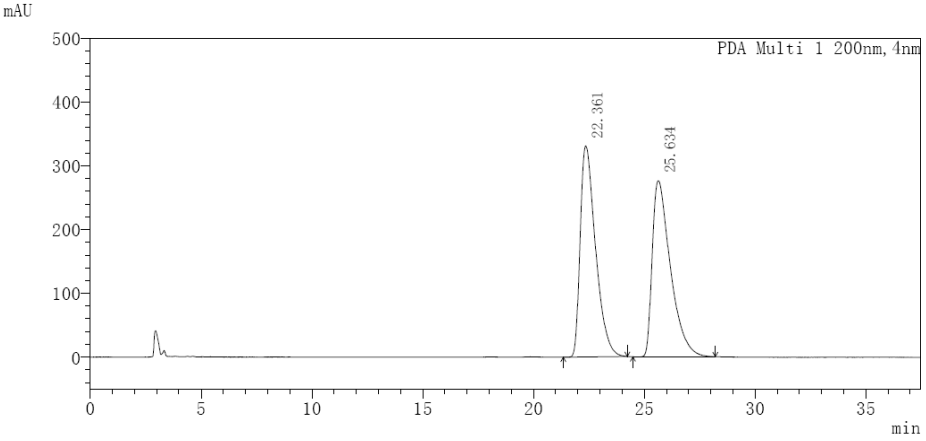
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.163	34353868	718885	99.428	99.518
2	26.462	197498	3484	0.572	0.482
Total		34551366	722369	100.000	100.000



3aa'

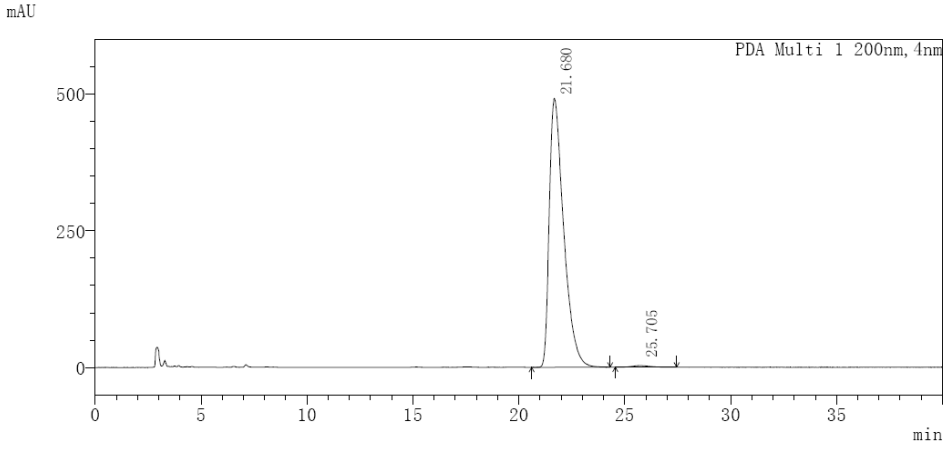
The HPLC spectra for the transformation of **4aa** to **3aa'** using DABCO as the base. (Scheme 5, Eqn 1)

$[\alpha]^{25}_{D}$ = -143 (c = 1.0 in CH_2Cl_2); HPLC analysis: 99% ee., [CHIRALPAK OD column; 1.0 mL/min; solvent system: i-PrOH/hexane = 90:10; retention times: 21.7 min (major), 25.7 min (minor)].



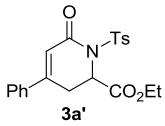
PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.361	15890120	330804	50.272	54.527
2	25.634	15717915	275876	49.728	45.437
Total		31608035	606680	100.000	100.000



PDA Ch1 200nm

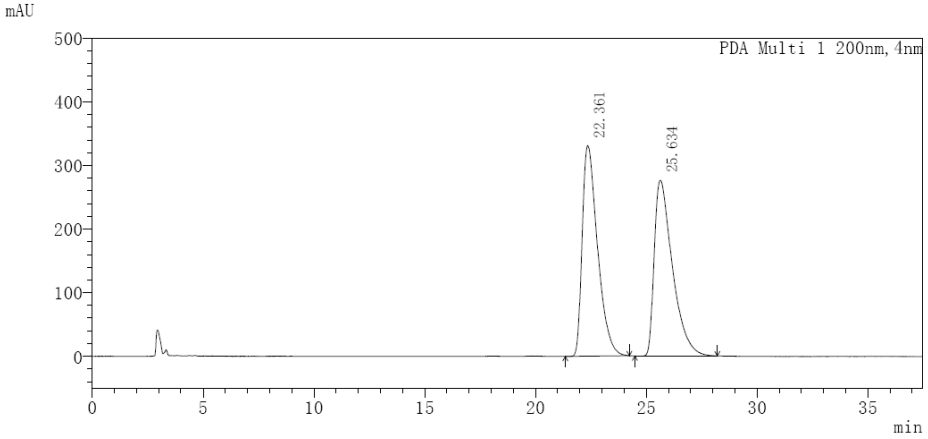
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.680	23173304	491032	99.294	99.409
2	25.705	164840	2919	0.706	0.591
Total		23338144	493951	100.000	100.000



3a'

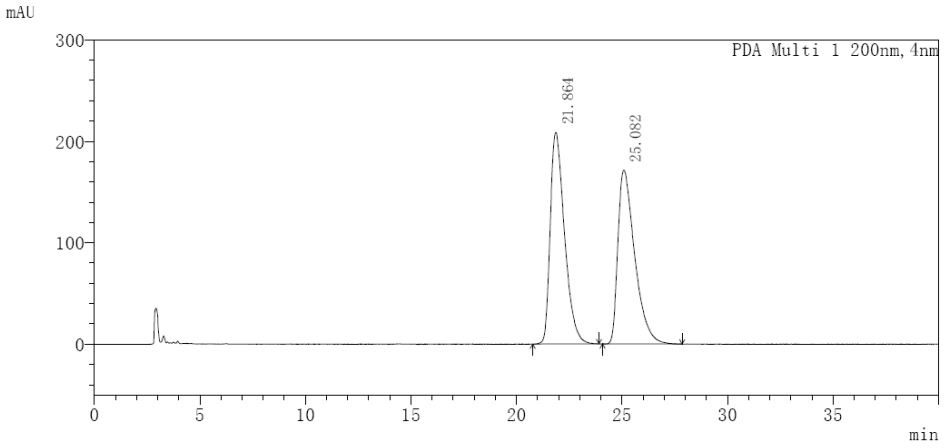
The HPLC spectra for the transformation of racemic **4a** to **3a'** in the presence of chiral triazolium salt **F.** (Scheme 5, Eqn 2)

HPLC analysis: 0% ee., [CHIRALPAK OD column; 1.0 mL/min; solvent system: i-PrOH/hexane = 90:10]



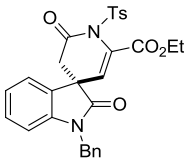
PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.361	15890120	330804	50.272	54.527
2	25.634	15717915	275876	49.728	45.437
Total		31608035	606680	100.000	100.000



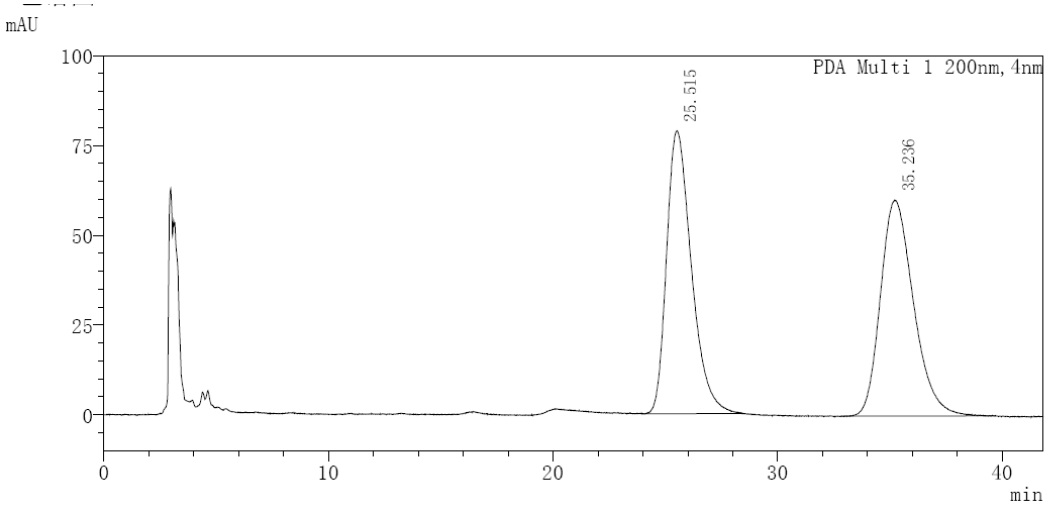
PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.864	9805427	208358	50.856	54.909
2	25.082	9475340	171100	49.144	45.091
Total		19280767	379459	100.000	100.000



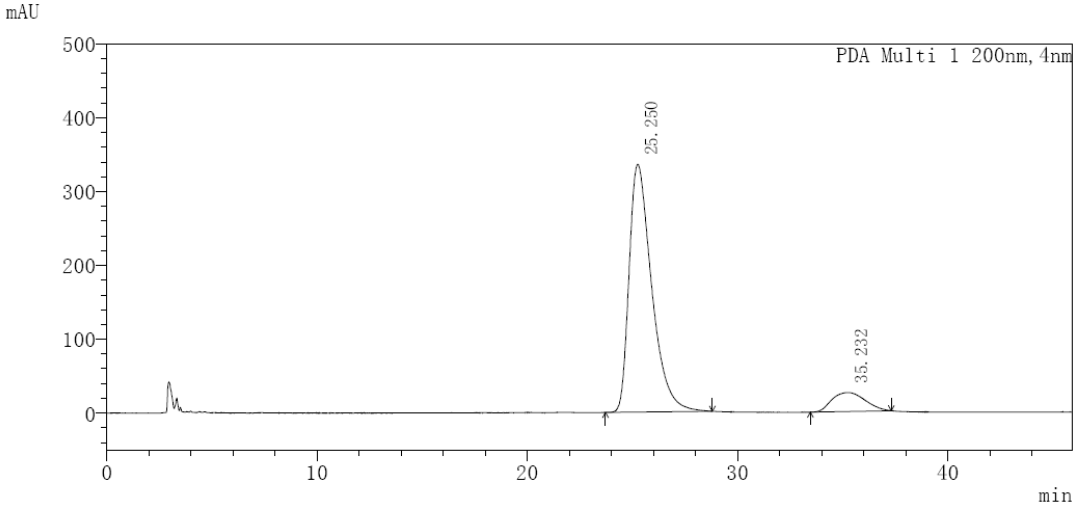
6aa

$[\alpha]^{25}_{D}$ = 112 (c = 1.0 in $CHCl_3$); HPLC analysis: 79.7 ee., [CHIRALPAK OD column; 1.0 mL/min; solvent system: i-PrOH/hexane = 90:10; retention times: 25.3 min (minor), 35.2 min (major)].



PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.525	6072085	78818	49.624	56.731
2	35.236	6164140	60116	50.376	43.269
Total		12236224	138933	100.000	100.000



PDA Ch1 200nm

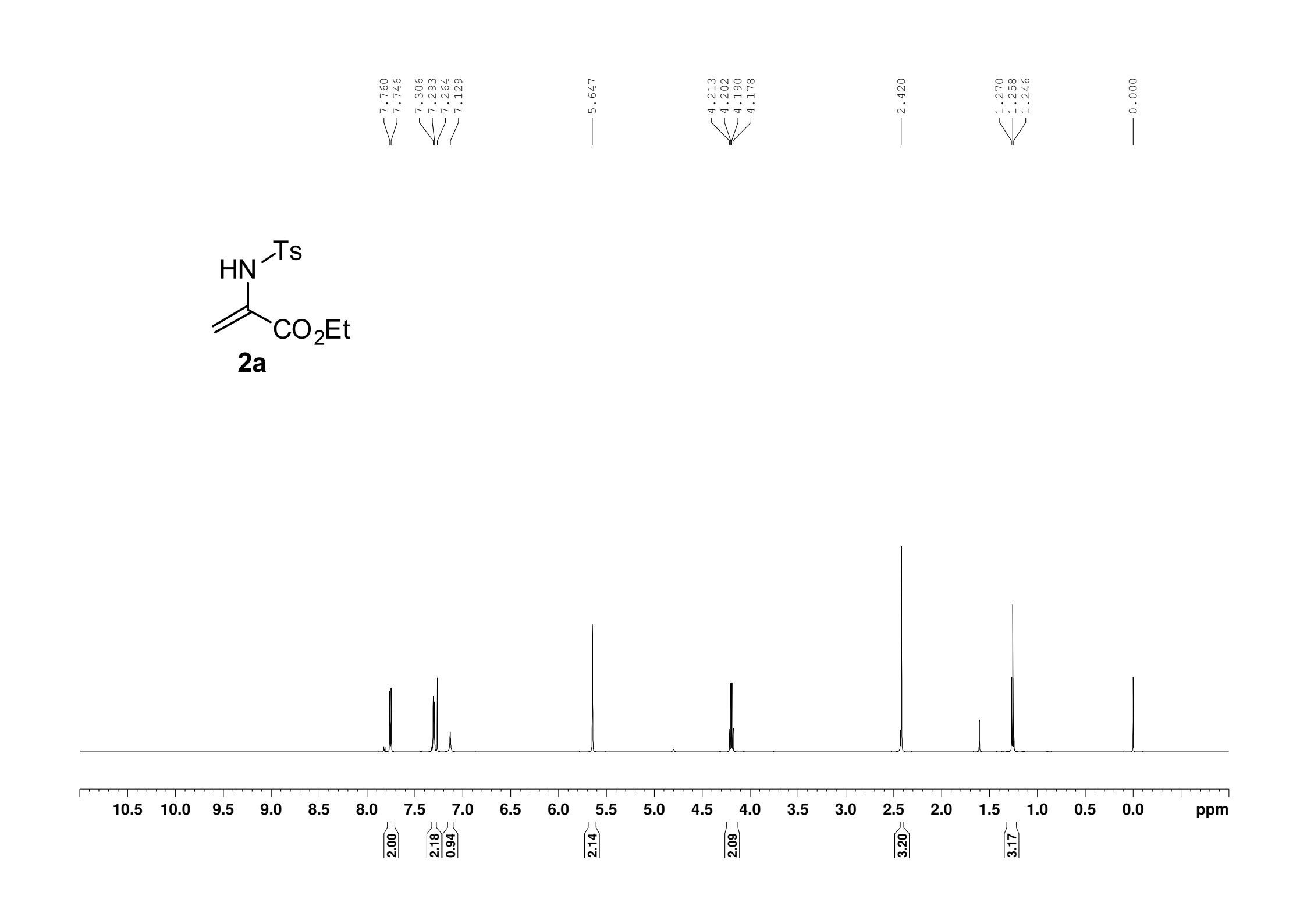
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.250	25052613	335466	89.878	92.873
2	35.232	2821278	25742	10.122	7.127
Total		27873891	361209	100.000	100.000

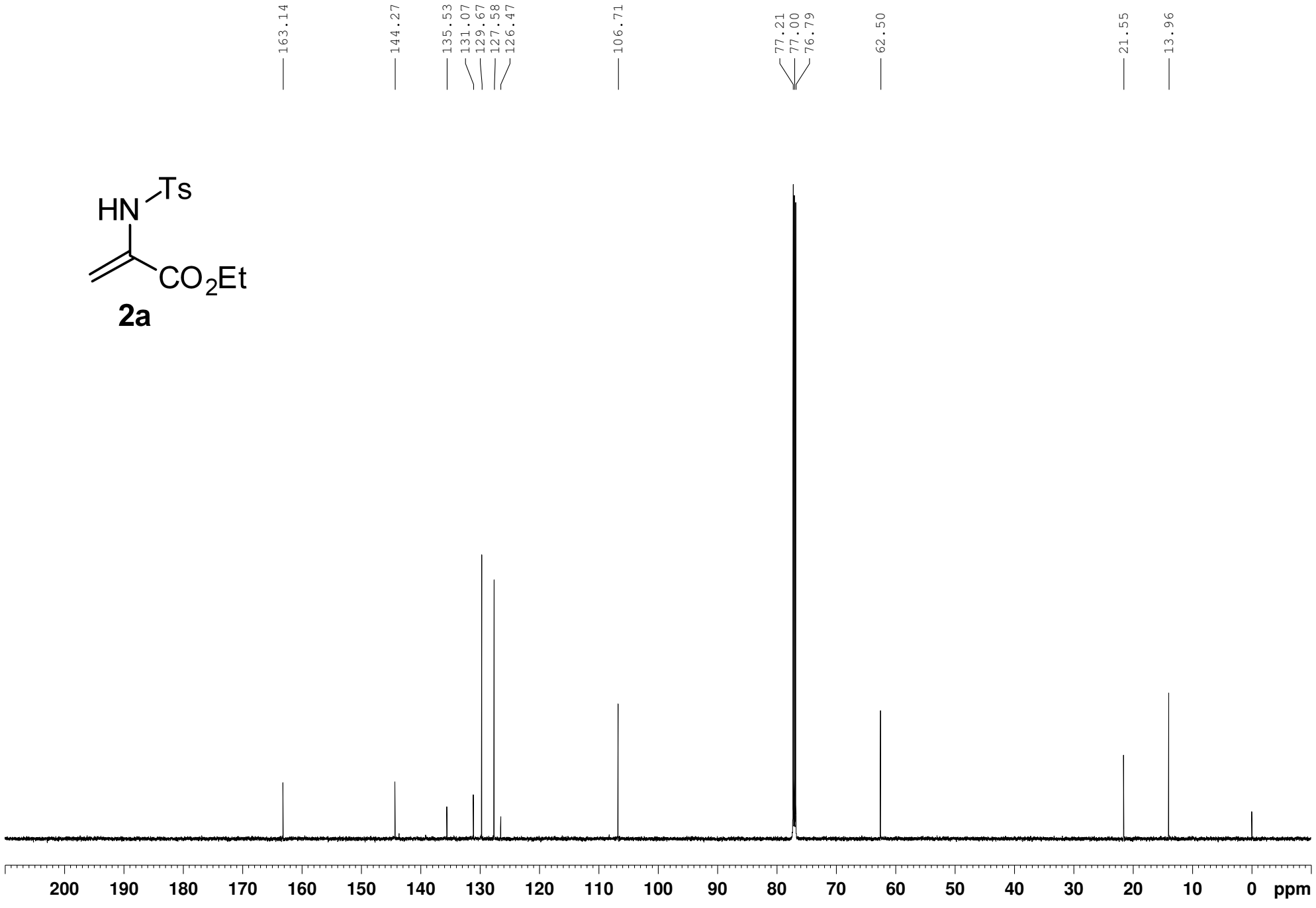
References

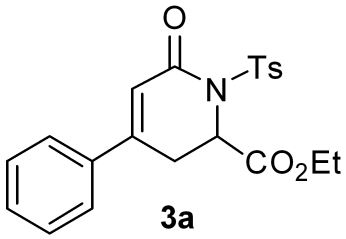
1. T. Mukaiyama, K. Ogata, I. Sato, Y. Hayashi, *Chem. Eur. J.* 2014, **20**, 13583 – 13588.

2. B. Li, N. Wang, Y. Liang, S. Xu, B.Wang, *Org. Lett.*, 2013, **15**, 136–139.

3. W.-Q. Jia, X.-Y. Chen, L.-H. Sun, S. Ye, *Org. Biomol. Chem.*, 2014, **12**, 2167-2171.


7.760
7.746
7.306
7.293
7.264
7.129
5.647
4.213
4.202
4.190
4.178
2.420
1.270
1.258
1.246
0.000
HN
Ts
CO2Et
2a
10.5 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 0.0 ppm
2.00
2.18
0.94
2.14
2.09
3.20
3.17


163.14
144.27
135.53
131.07
129.67
127.58
126.47
106.71
77.21
77.00
76.79
62.50
21.55
13.96
HN
Ts
CO2Et
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3a

8.041
8.028
7.468
7.465
7.456
7.452
7.432
7.422
7.410
7.337
7.323
7.262
6.162
6.157
5.538
5.535
5.527
5.524
4.162
4.150
4.144
4.138
4.132
4.126
4.120
4.108
4.104
4.092
4.086
4.080
4.074
4.069
4.062
4.051
3.519
3.516
3.489
3.486
3.228
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3.183
2.437
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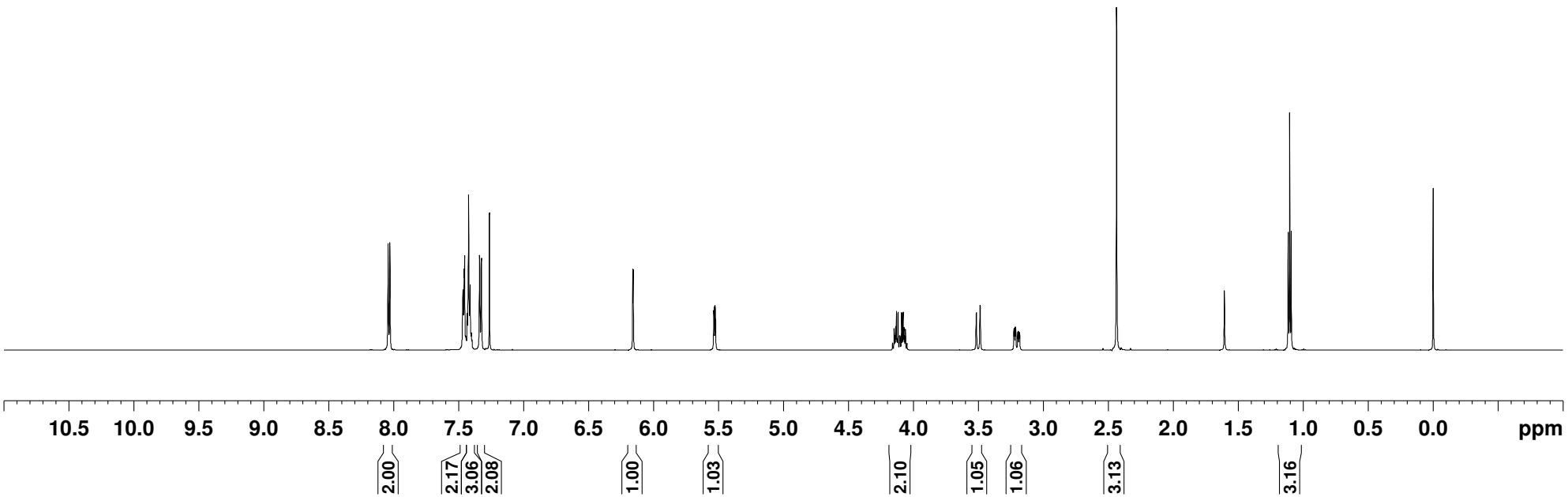
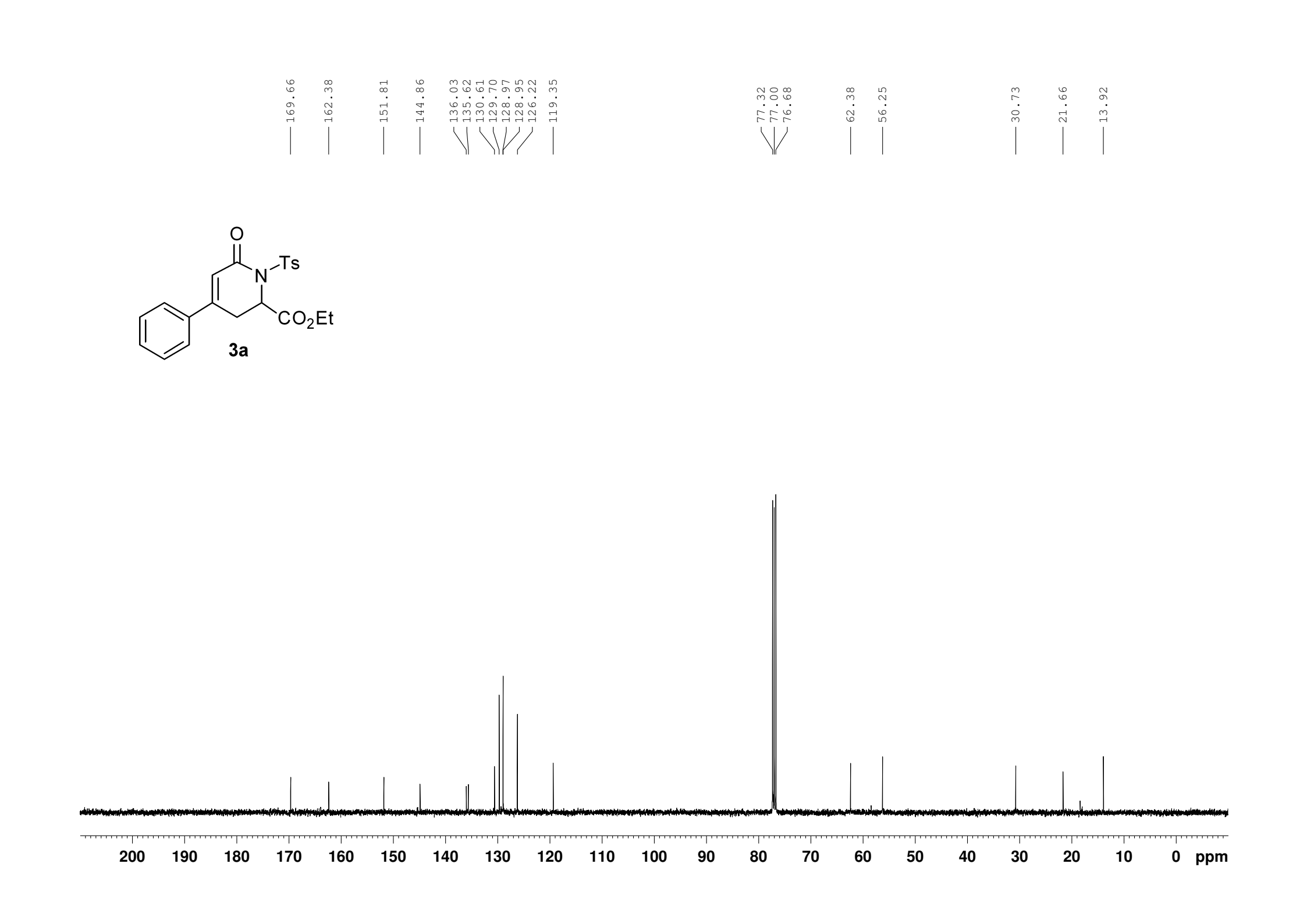
1.093
0.000

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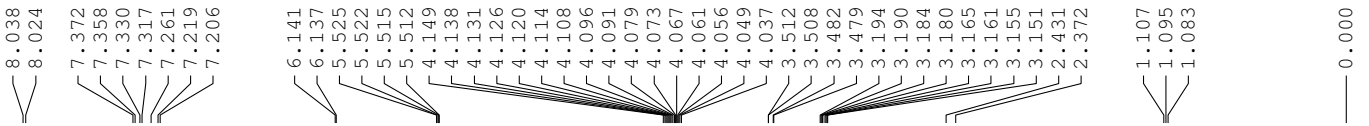
162.38
151.81
144.86
136.03
135.62
130.61
129.70
128.97
128.95
126.22
119.35
77.32
77.00
76.68
62.38
56.25
30.73
21.66
13.92
O
N
Ts
CO2Et
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.038
8.024
7.372
7.358
7.330
7.317
7.261
7.219
7.206
6.141
6.137
5.525
5.522
5.515
5.512
4.149
4.138
4.131
4.126
4.120
4.114
4.108
4.096
4.091
4.079
4.073
4.067
4.061
4.056
4.049
4.037
3.512
3.508
3.482
3.479
3.194
3.190
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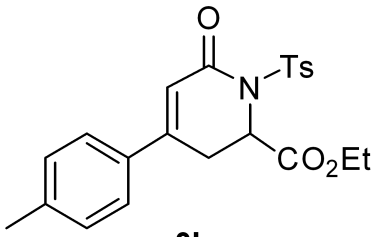
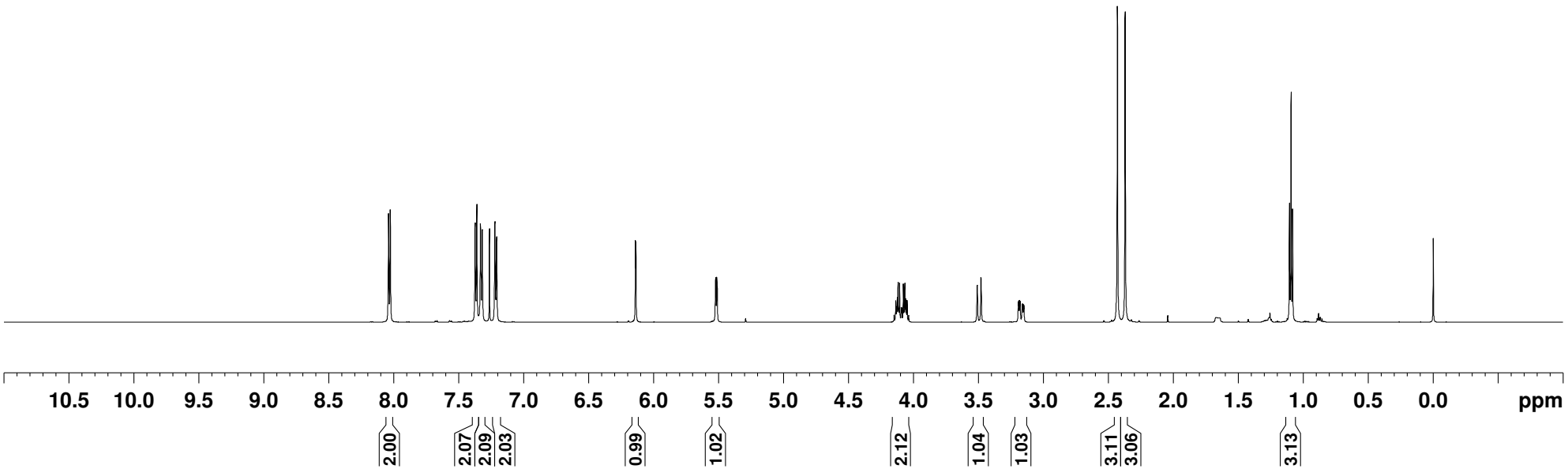
3.151
2.431
2.372
1.107
1.095
1.083
0.000


O
N
Ts
CO2Et

3b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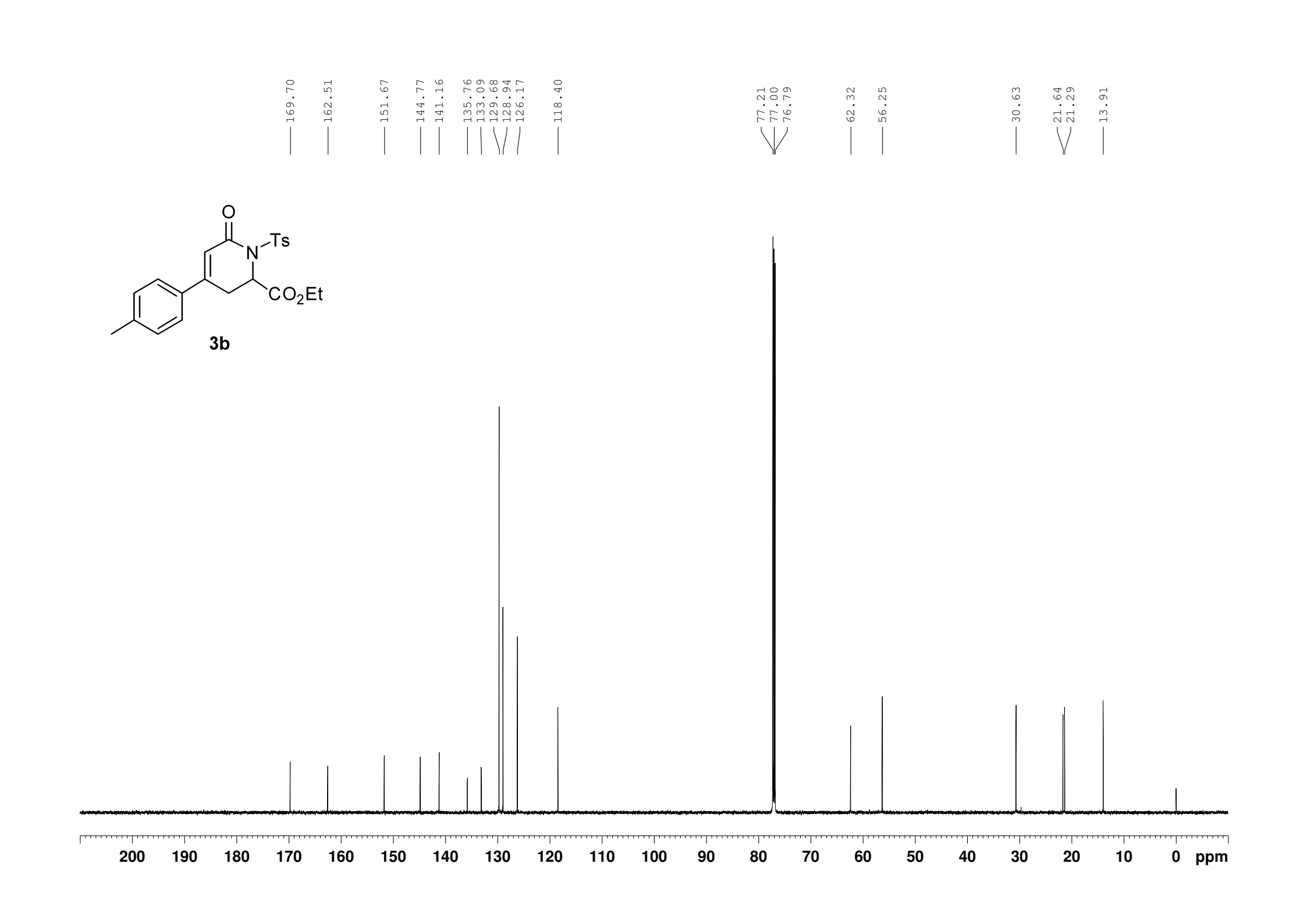
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
2.07
2.09
2.03
0.99
1.02
2.12
1.04
1.03
3.11
3.06
3.13


169.70
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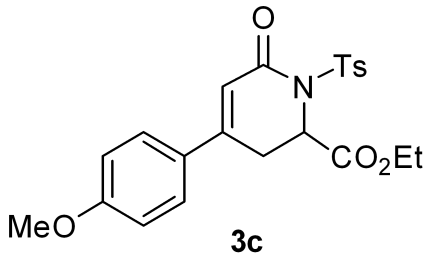
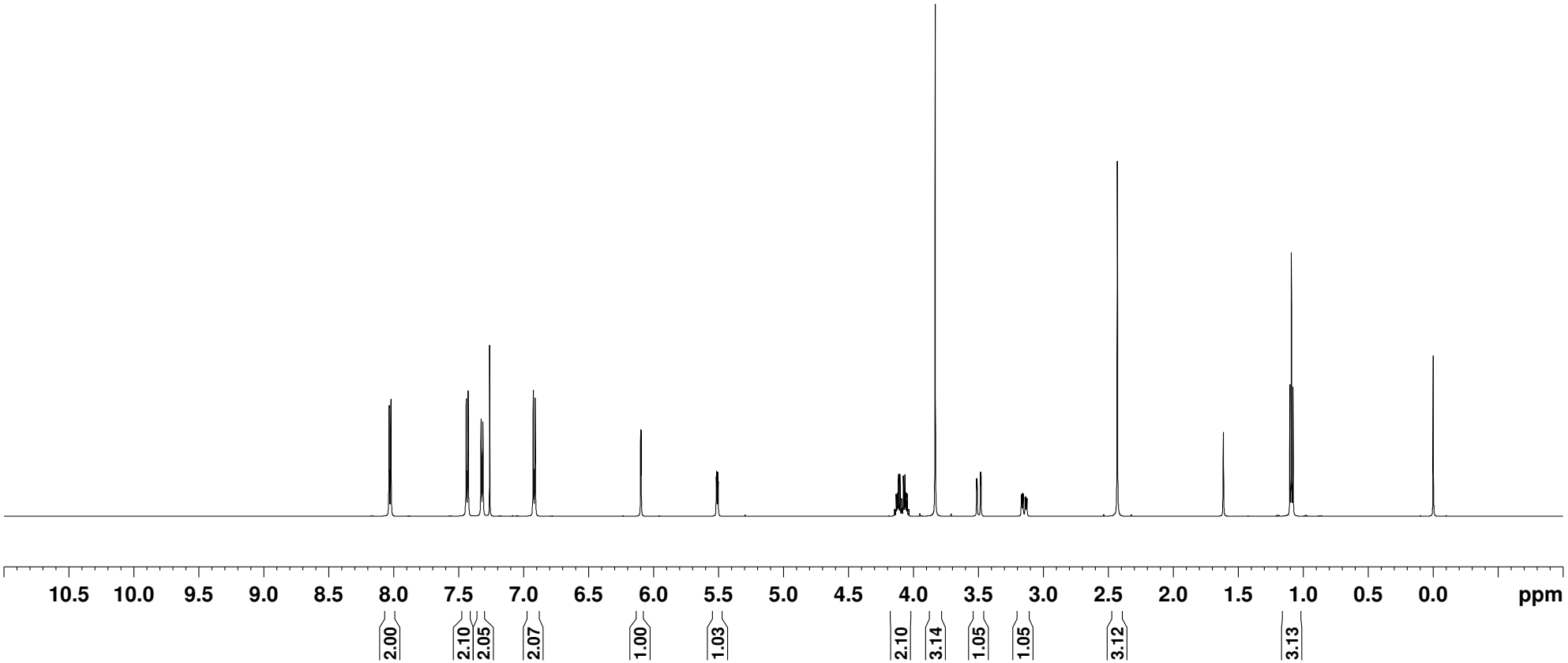
144.77
141.16
135.76
133.09
129.68
128.94
126.17
118.40
77.21
77.00
76.79
62.32
56.25
30.63
21.64
21.29
13.91
O
N
Ts
CO2Et
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
Ts
CO2Et
MeO

3c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7.315
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6.912
6.101
6.096
5.518
5.515
5.508
5.504
4.146
4.134
4.128
4.122
4.116
4.110
4.104
4.092
4.091
4.078
4.072
4.066
4.060
4.055
4.048
4.037
3.833
3.514
3.511
3.485
3.481
3.171
3.167
3.160
3.156
3.142
3.137
3.131
3.127
2.432
1.103
1.091
1.079
0.000
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2.07
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1.03
2.10
3.14
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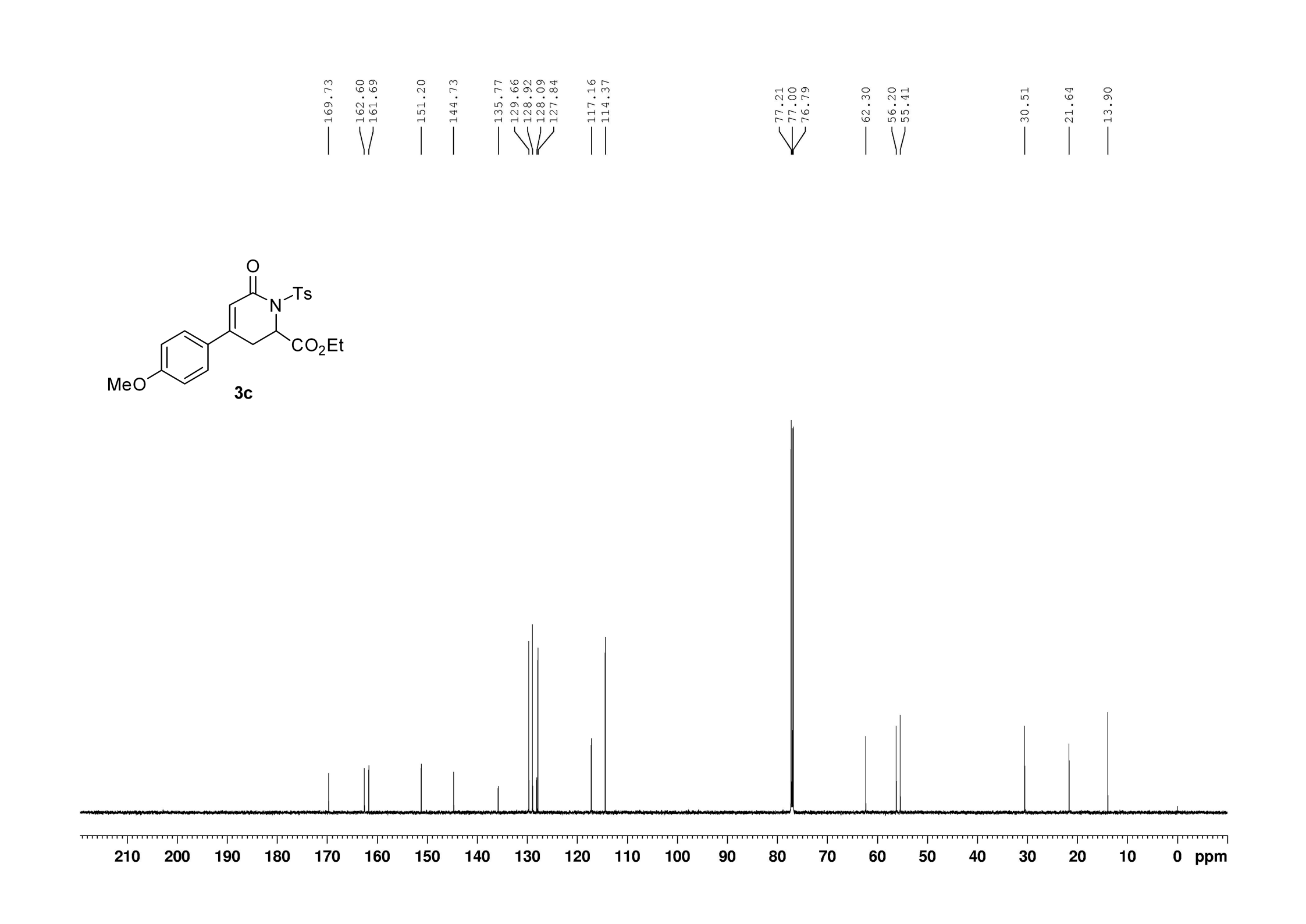
1.05
3.12
3.13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127.84
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114.37
77.21
77.00
76.79
62.30
56.20
55.41
30.51
21.64
13.90
O
N
Ts
CO2Et
MeO
3c
210
200
190
180
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150
140
130
120
110
100
90
80
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60
50
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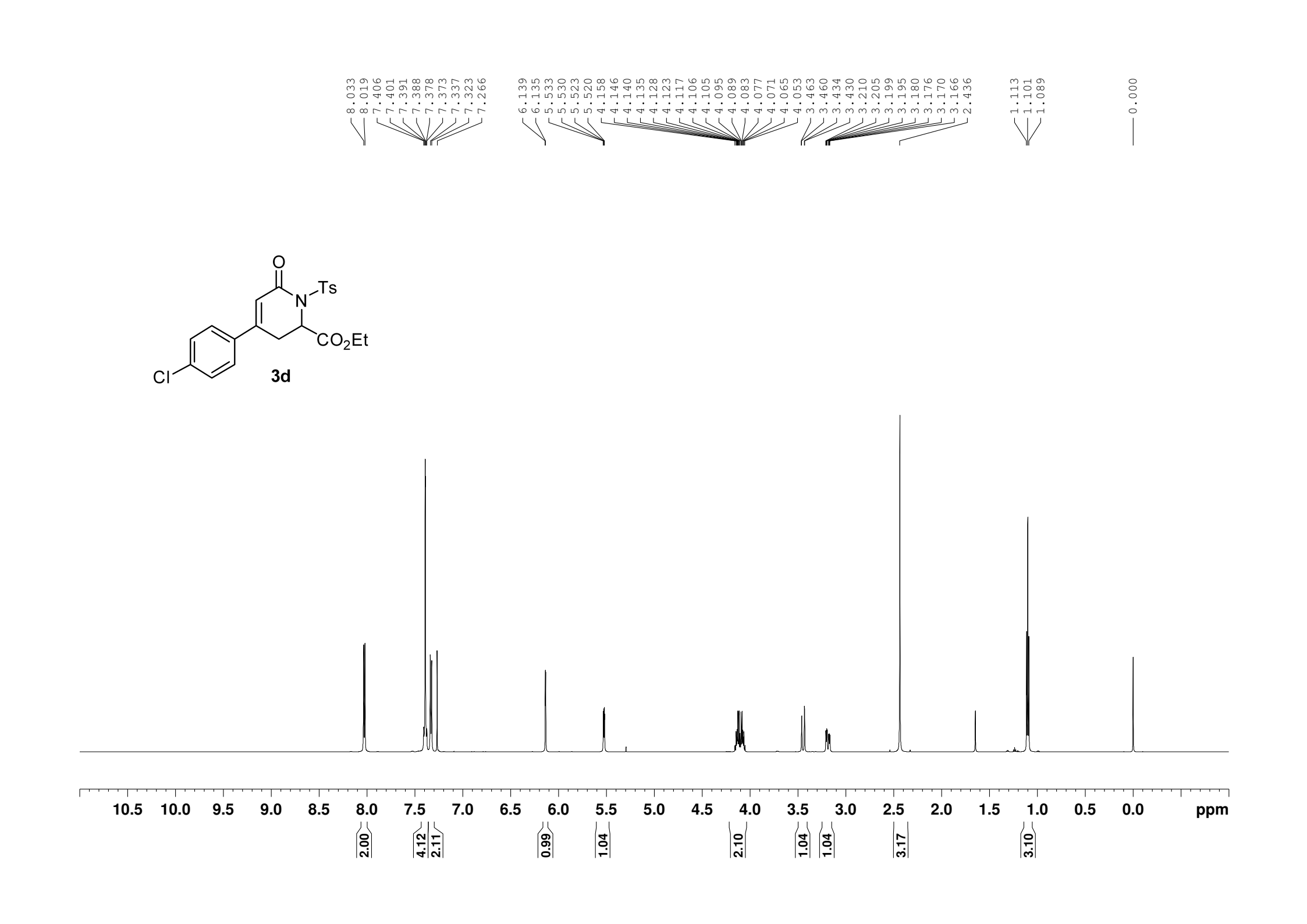
30
20
10
0
ppm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6.139
6.135
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5.530
5.523
5.520
4.158
4.146
4.140
4.135
4.128
4.123
4.117
4.106
4.105
4.095
4.089
4.083
4.077
4.071
4.065
4.053
3.463
3.460
3.434
3.430
3.210
3.205
3.199
3.195
3.180
3.176
3.170
3.166
2.436
1.113
1.101
1.089
0.000
O
N
Ts
CO2Et
Cl
3d
10.5 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 0.0 ppm
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2.10
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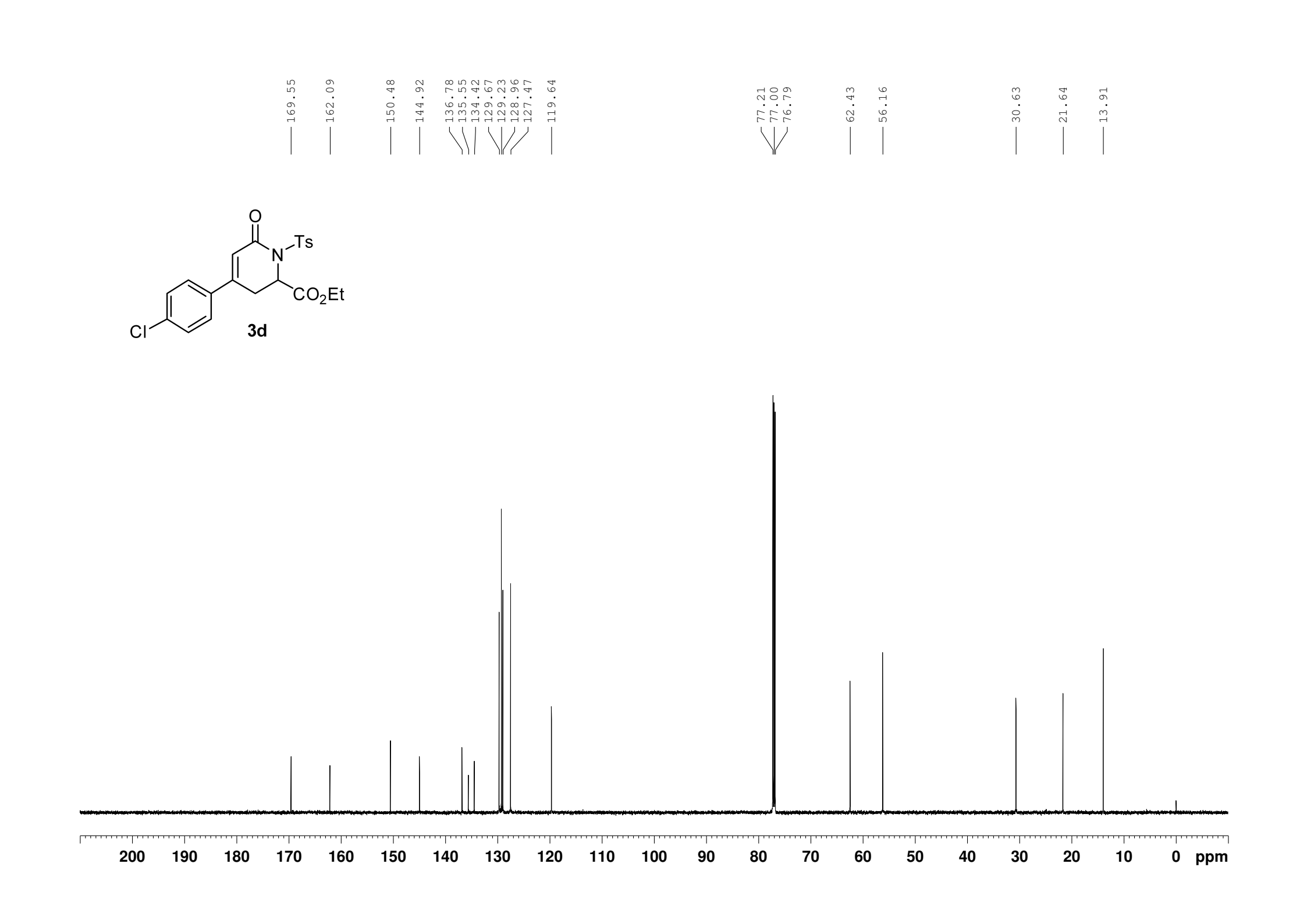
3.10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77.21
77.00
76.79
62.43
56.16
30.63
21.64
13.91
O
N
Ts
CO2Et
Cl
3d
200
190
180
170
160
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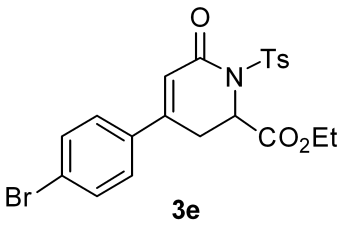
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
Ts
CO2Et
Br

3e

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7.324
7.316
7.265
6.146
6.141
5.531
5.528
5.521
5.518
4.158
4.146
4.140
4.135
4.128
4.123
4.117
4.106
4.094
4.088
4.083
4.077
4.071
4.065
4.053
3.456
3.453
3.427
3.424
3.212
3.208
3.202
3.198
3.183
3.179
3.173
3.168
2.438
1.114
1.102
1.090
0.000
10.5 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 0.0 ppm
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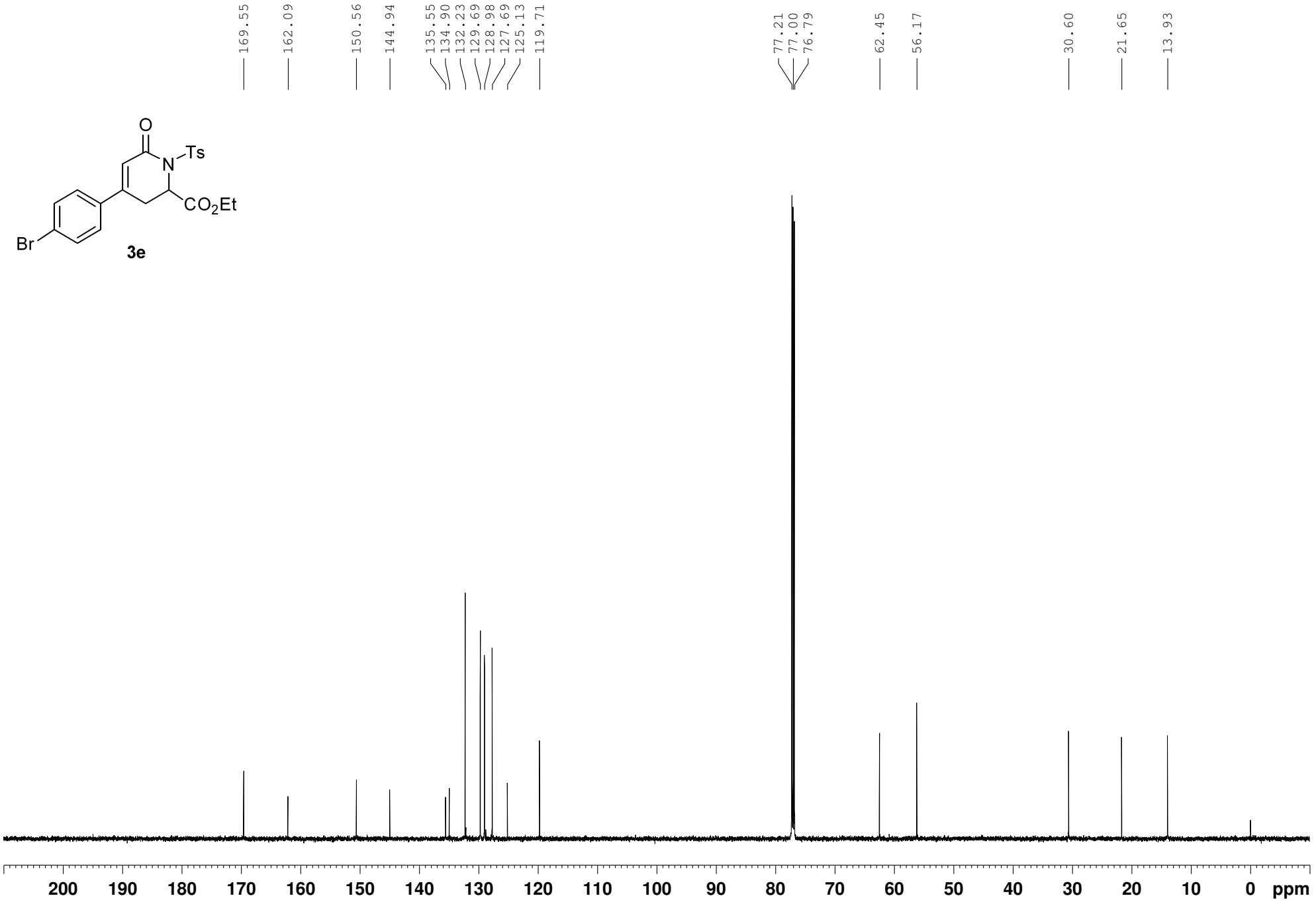
1.93
4.12
0.97
1.02
2.08
0.99
1.00
3.14
3.10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150.56
144.94
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129.69
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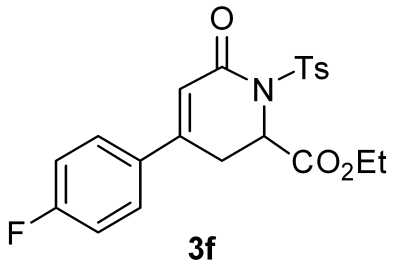
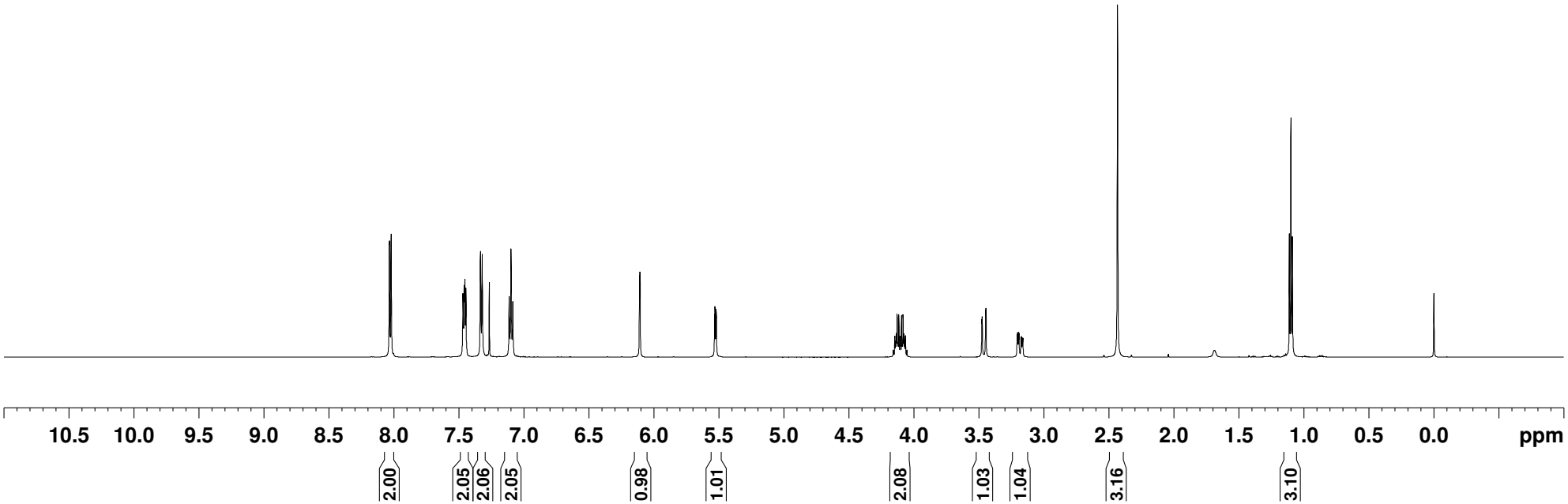
127.69
125.13
119.71
77.21
77.00
76.79
62.45
56.17
30.60
21.65
13.93
O
N
Ts
CO2Et
Br
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
Ts
CO2Et
F

3f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7.335
7.322
7.268
7.115
7.101
7.086
6.112
6.108
5.534
5.531
5.524
5.521
4.159
4.147
4.141
4.135
4.129
4.124
4.117
4.106
4.096
4.090
4.084
4.078
4.072
4.066
4.054
3.479
3.475
3.449
3.446
3.207
3.202
3.196
3.192
3.177
3.173
3.167
3.163
2.434
1.112
1.101
1.089
0.000
10.5 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 0.0 ppm
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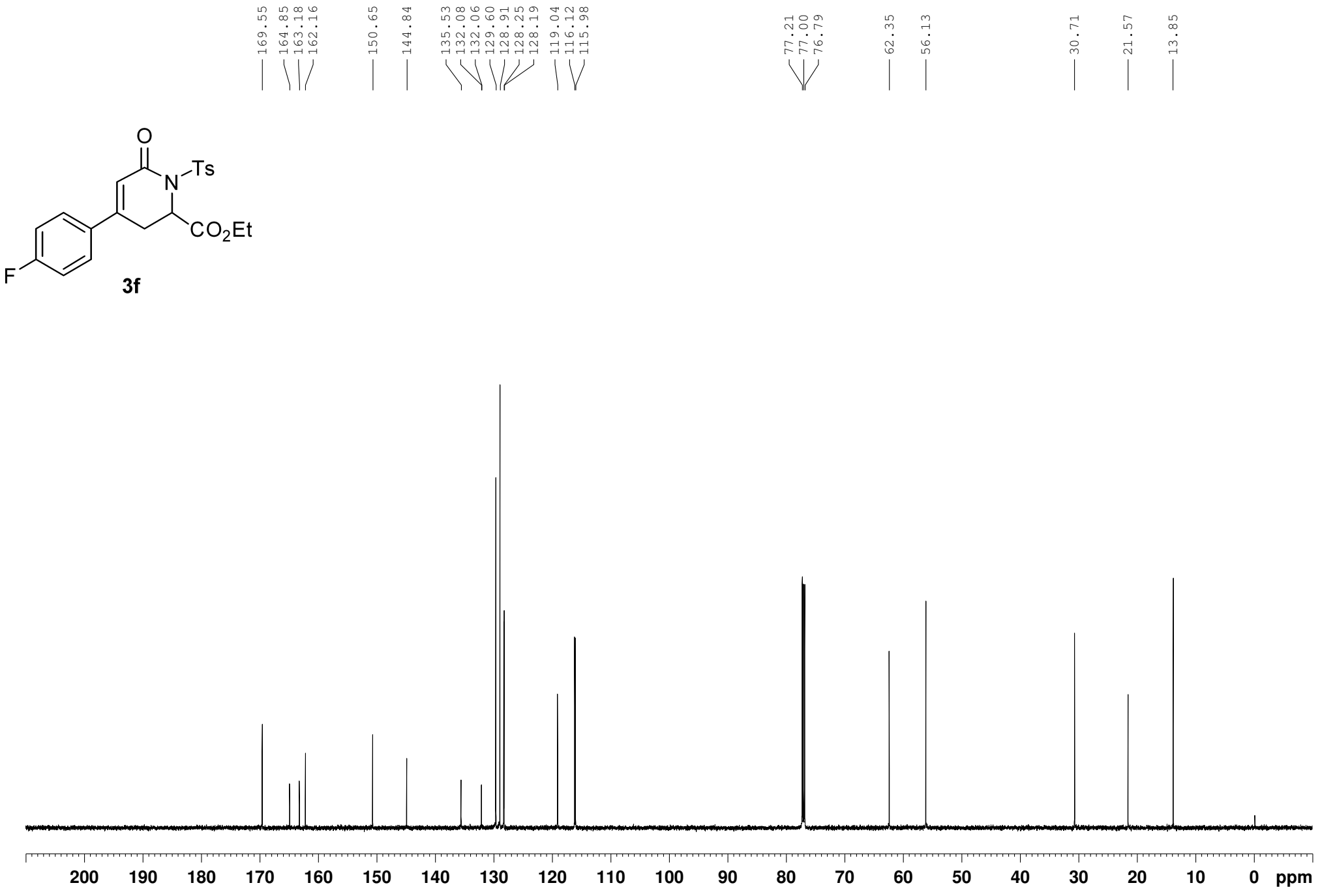
2.05
2.06
2.05
0.98
1.01
2.08
1.03
1.04
3.16
3.10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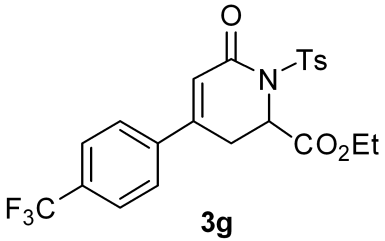
162.16
150.65
144.84
135.53
132.08
132.06
129.60
128.91
128.25
128.19
119.04
116.12
115.98
77.21
77.00
76.79
62.35
56.13
30.71
21.57
13.85
O
N
Ts
CO2Et
F
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
Ts
N
CO2Et
F3C

3g

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7.570
7.557
7.345
7.331
7.266
6.198
6.194
5.559
5.556
5.549
5.545
4.173
4.161
4.155
4.150
4.144
4.138
4.132
4.119
4.107
4.101
4.095
4.089
4.083
4.077
4.065
3.489
3.486
3.459
3.457
3.266
3.262
3.256
3.251
3.237
3.232
3.226
3.222
2.442
1.126
1.114
1.102
0.000
10.5 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 0.0 ppm
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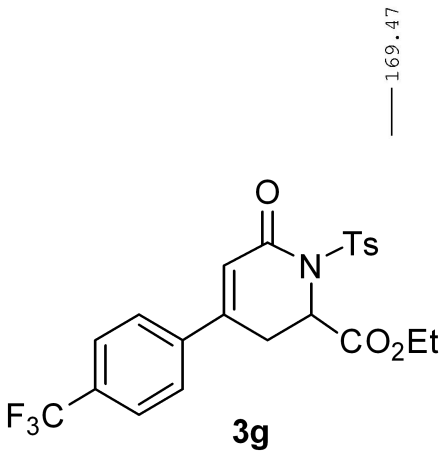
2.02
2.04
2.09
0.99
1.03
2.05
0.99
1.05
3.17
3.09


O
N
Ts
CO2Et
F3C

3g

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161.85
150.28
145.04
139.57
135.41
132.50
132.28
132.06
131.85
129.69
128.99
126.57
126.30
125.97
125.94
125.92
125.90
124.49
122.69
121.18
120.88
77.21
77.00
76.79
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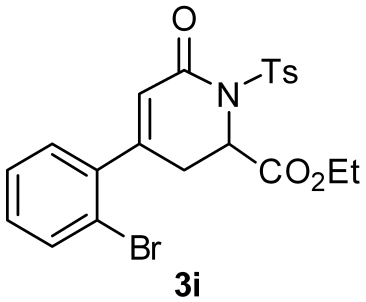
56.18
30.74
21.62
13.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
N
Ts
CO2Et
Br

3i

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7.329
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7.310
7.269
7.238
7.225
7.212
7.098
7.085
5.899
5.894
5.495
5.493
5.484
5.482
4.236
4.224
4.218
4.212
4.206
4.200
4.194
4.182
4.098
4.086
4.080
4.074
4.069
4.063
4.057
4.045
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3.379
3.372
3.368
3.353
3.349
3.342
3.338
3.241
3.238
3.211
3.208
2.440
1.179
1.167
1.155
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10.5
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
0.0
ppm
2.07
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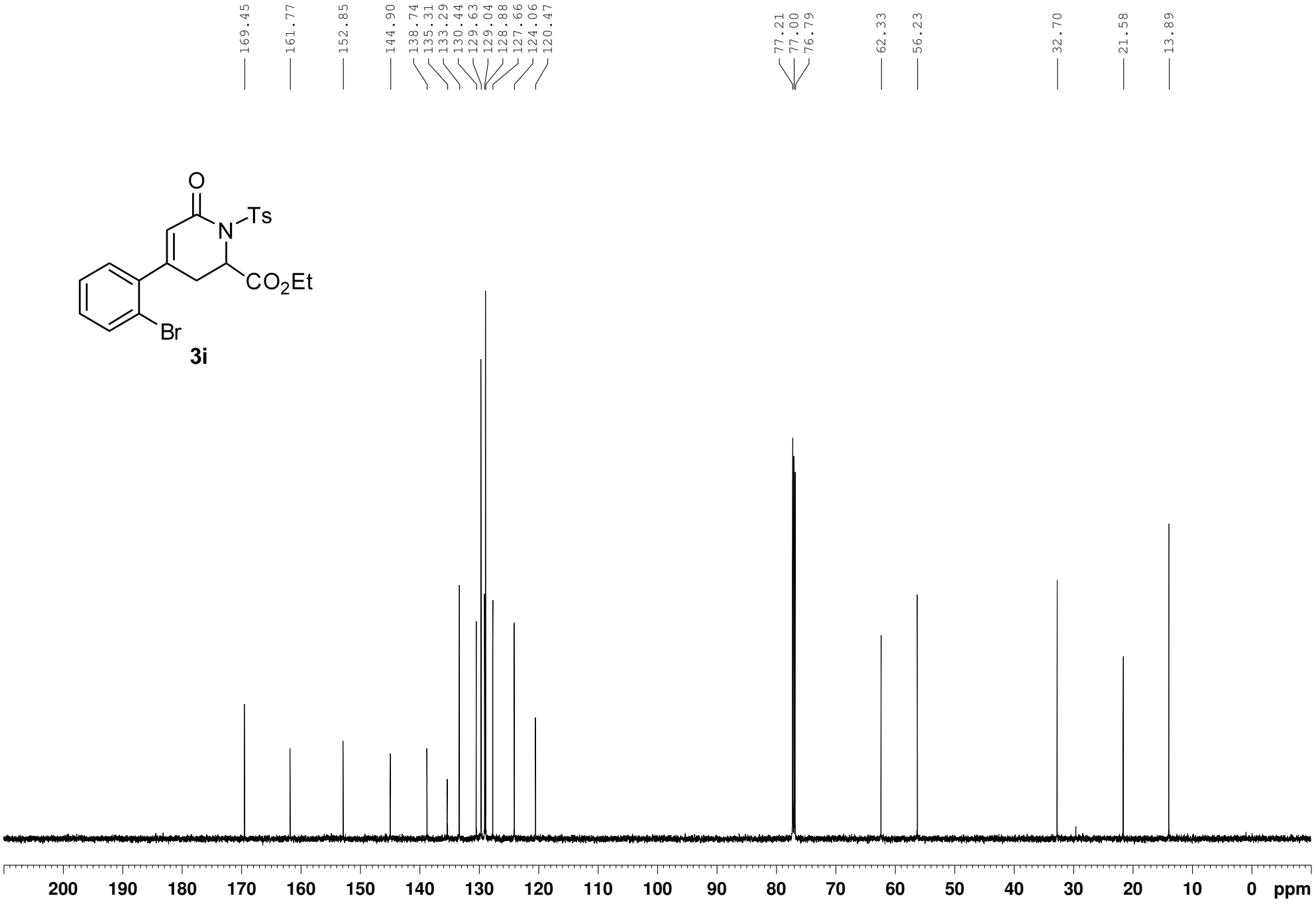
3.27
1.09
1.10
1.00
1.06
1.06
1.08
1.08
1.08
3.21
3.15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130.44
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129.04
128.88
127.66
124.06
120.47
77.21
77.00
76.79
62.33
56.23
32.70
21.58
13.89
O
N
Ts
CO2Et
Br
3i
200
190
180
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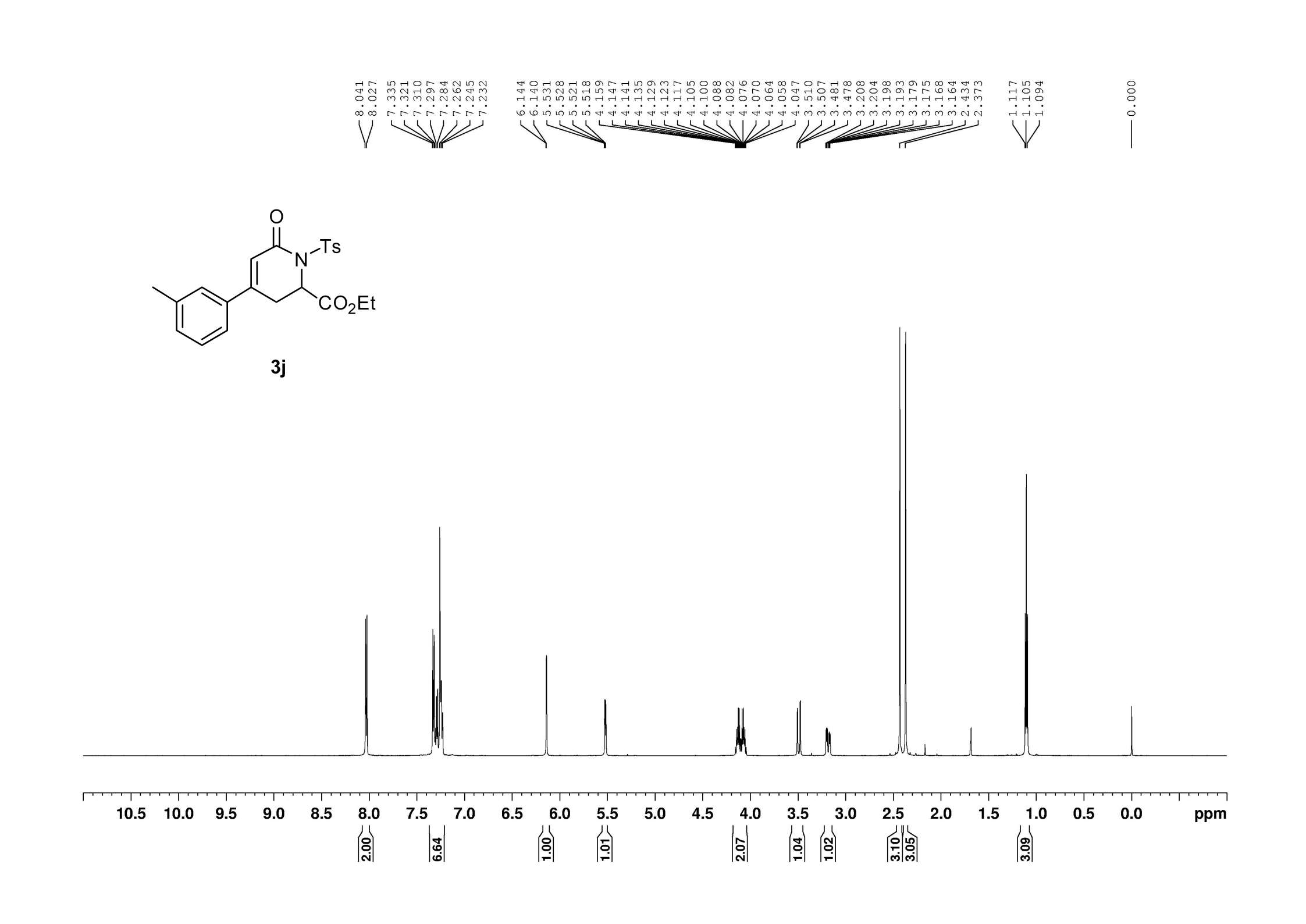
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.232
6.144
6.140
5.531
5.528
5.521
5.518
4.159
4.147
4.141
4.135
4.129
4.123
4.117
4.105
4.100
4.088
4.082
4.076
4.070
4.064
4.058
4.047
3.510
3.507
3.481
3.478
3.208
3.204
3.198
3.193
3.179
3.175
3.168
3.164
2.434
2.373
1.117
1.105
1.094
0.000
O
N
Ts
CO2Et
3j
10.5
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
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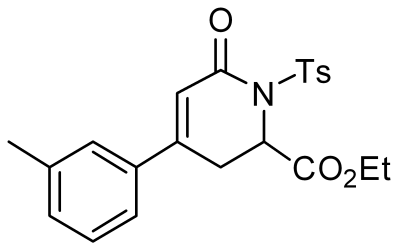
2.07
1.04
1.02
3.10
3.05
3.09


O
N
Ts
CO2Et

3j

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135.67
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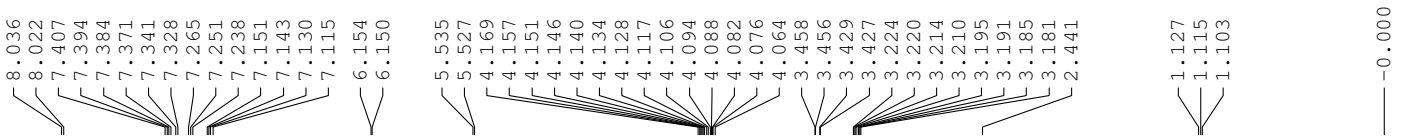
129.63
128.91
128.80
126.82
123.34
119.11
77.21
77.00
76.79
62.30
56.23
30.74
21.60
21.33
13.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.251
7.238
7.151
7.143
7.130
7.115
6.154
6.150
5.535
5.527
4.169
4.157
4.151
4.146
4.140
4.134
4.128
4.117
4.106
4.094
4.088
4.082
4.076
4.064
3.458
3.456
3.429
3.427
3.224
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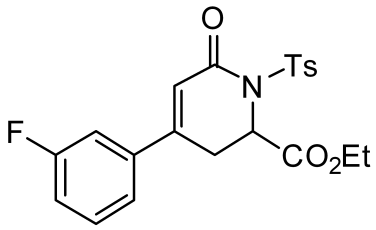
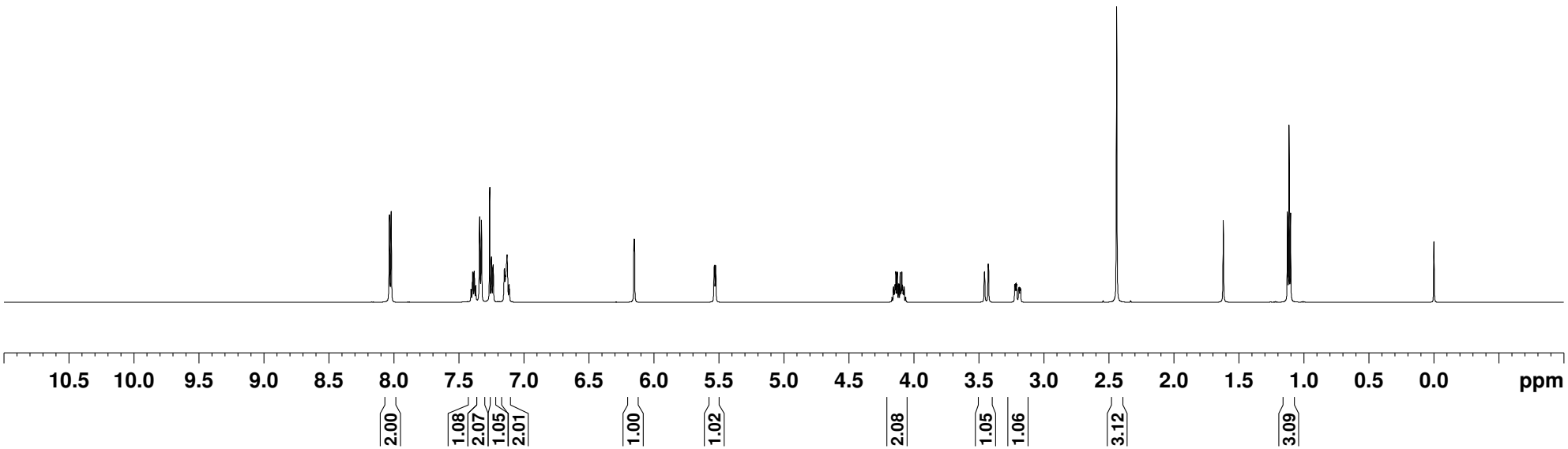

O
N
Ts
F
CO2Et

3k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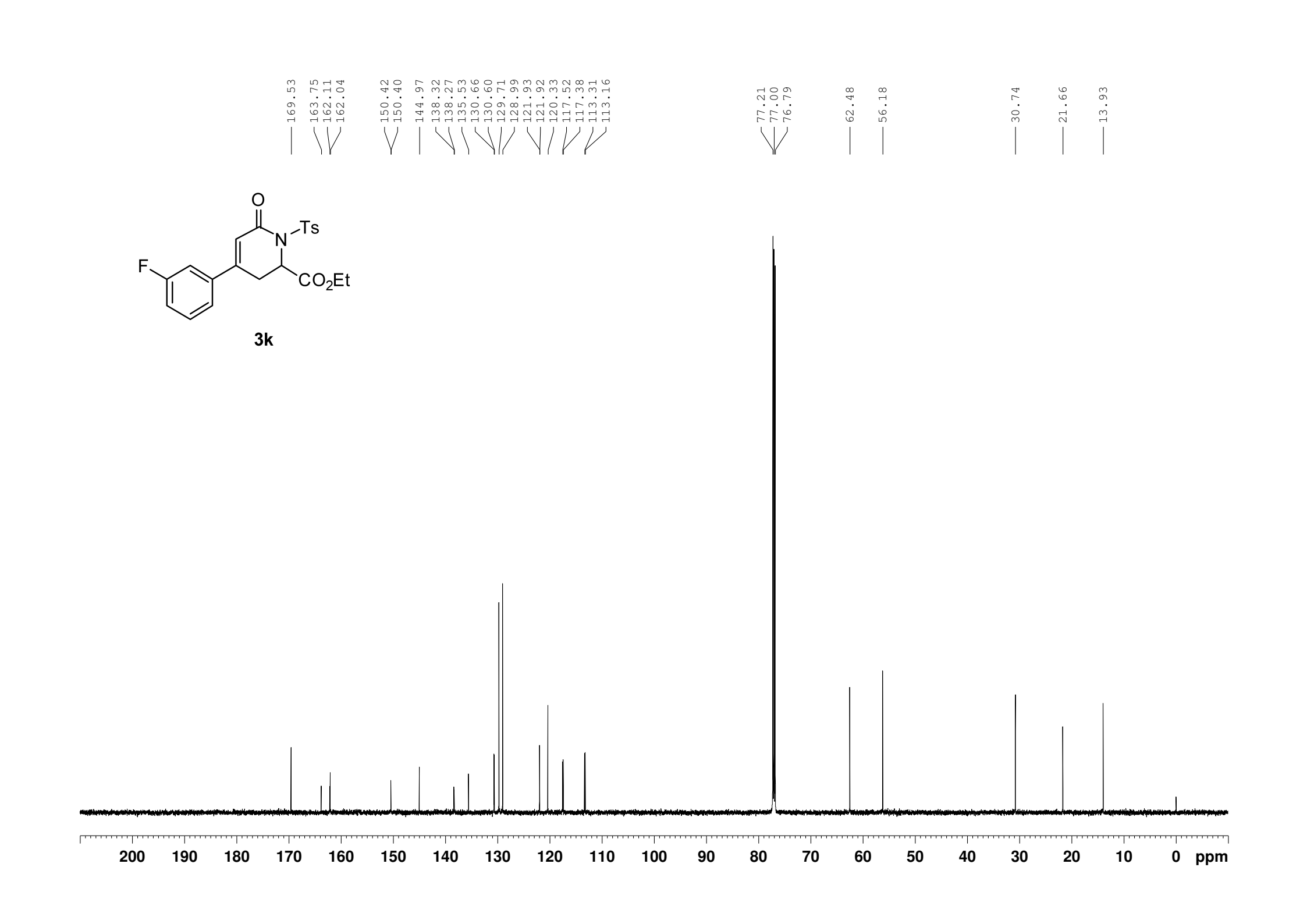
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.08
2.07
1.05
2.01
1.00
1.02
2.08
1.05
1.06
3.12
3.09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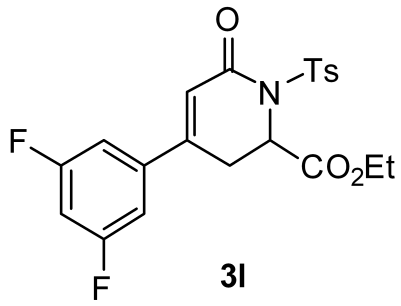
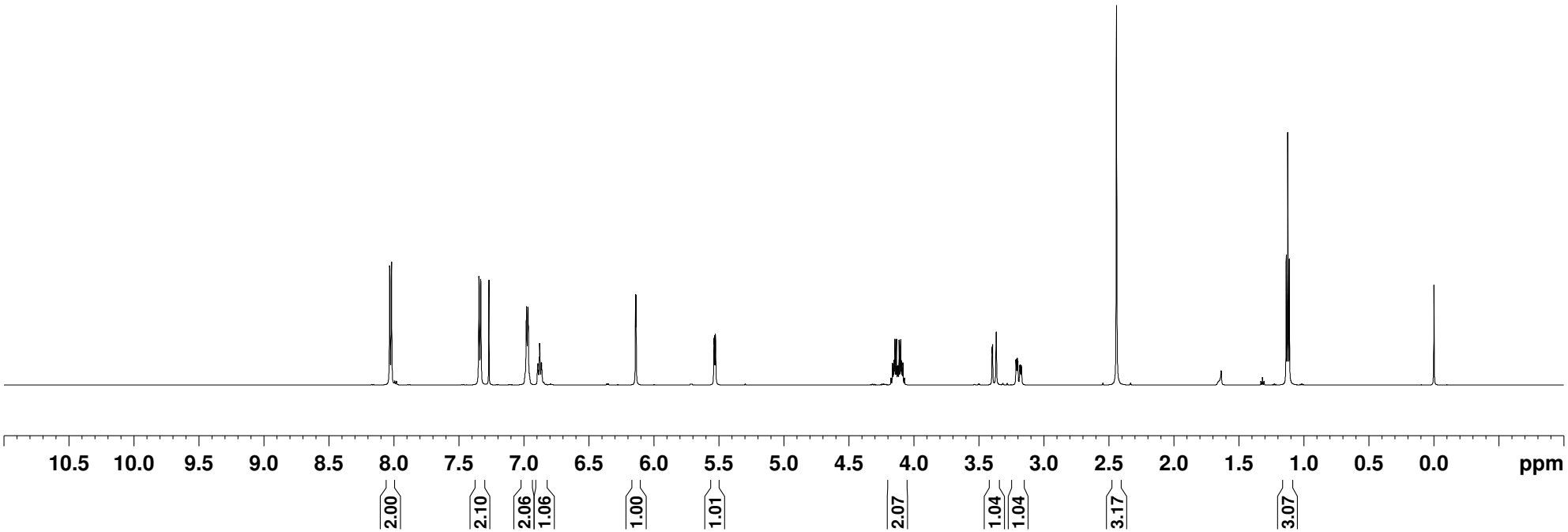
162.04
150.42
150.40
144.97
138.32
138.27
135.53
130.66
130.60
129.71
128.99
121.93
121.92
120.33
117.52
117.38
113.31
113.16
77.21
77.00
76.79
62.48
56.18
30.74
21.66
13.93
O
N
Ts
F
CO2Et
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
Ts
F
F
CO2Et

3l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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
0.0
ppm
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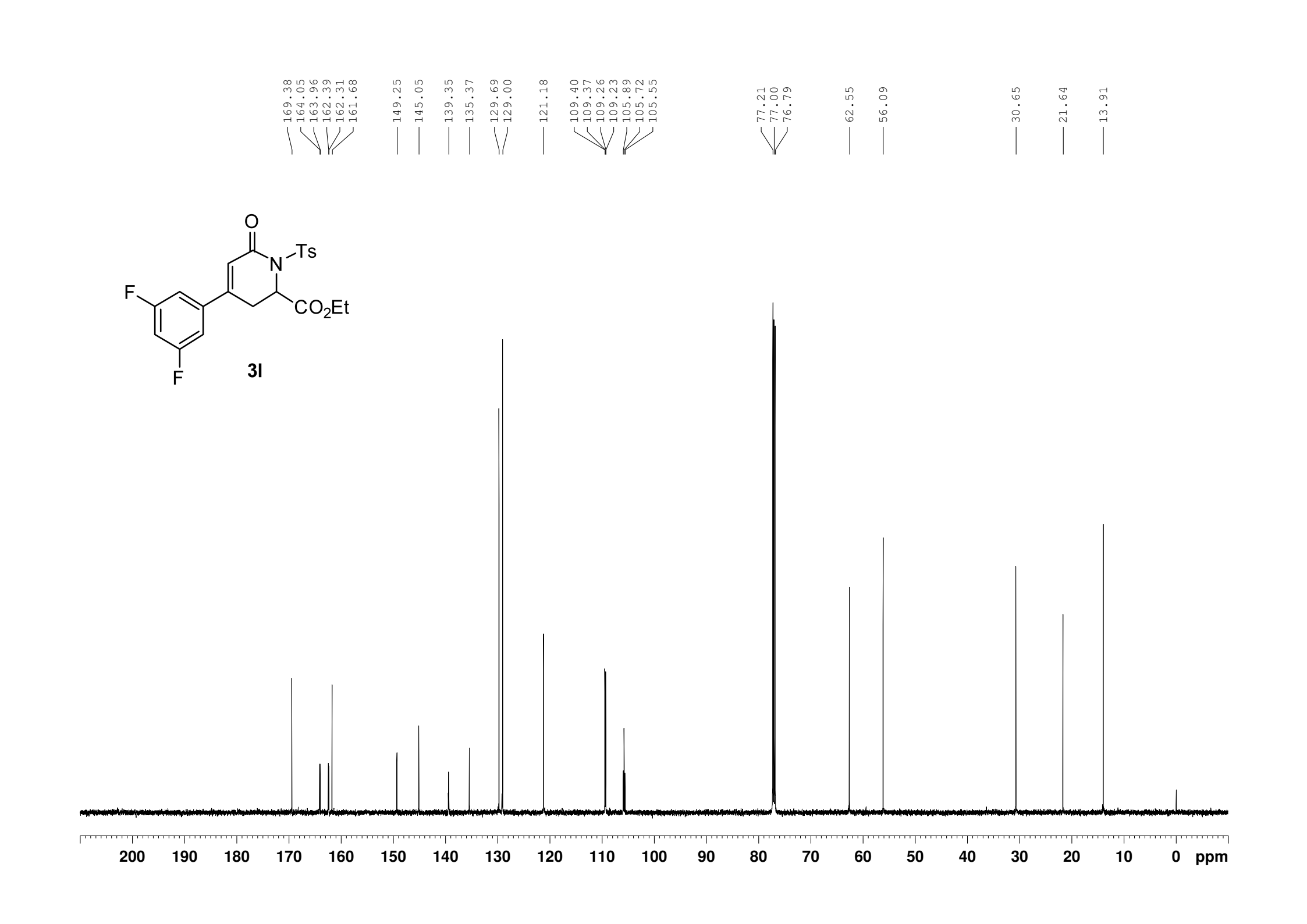
2.06
1.06
1.00
1.01
2.07
1.04
1.04
3.17
3.07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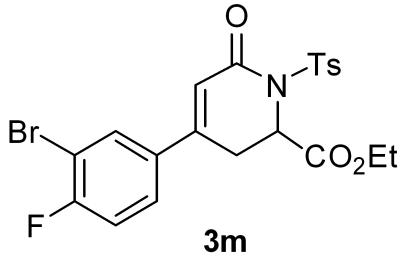
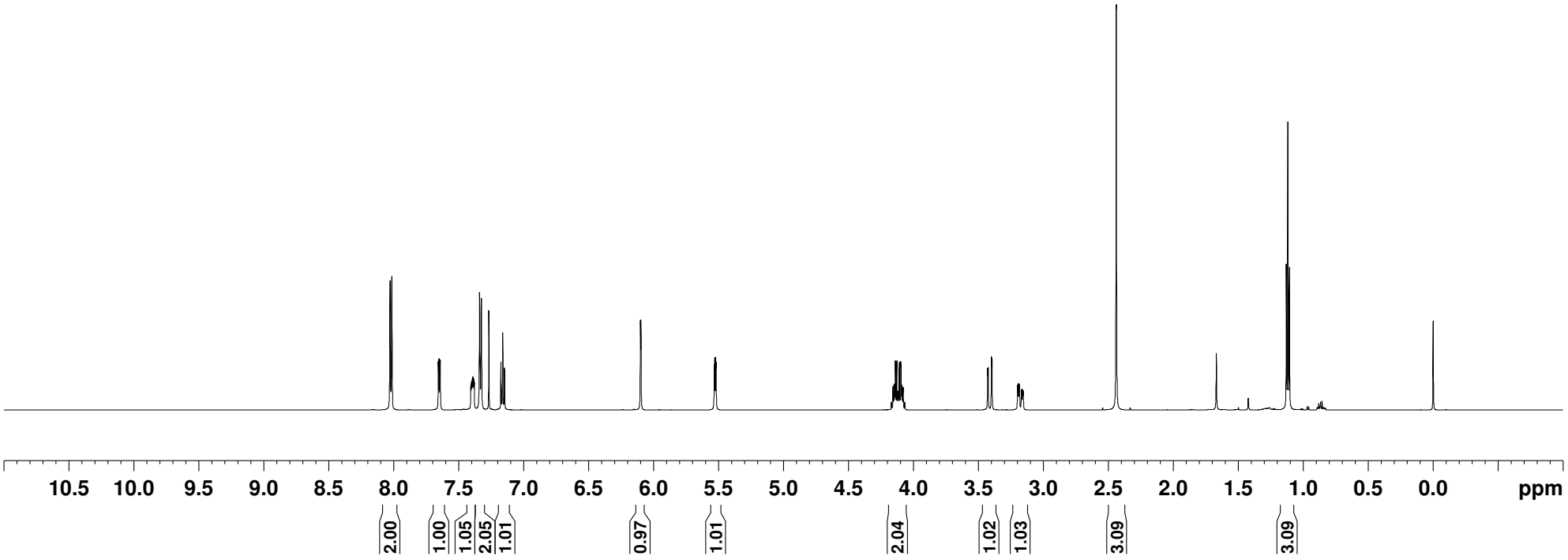
149.25
145.05
139.35
135.37
129.69
129.00
121.18
109.40
109.37
109.26
109.23
105.89
105.72
105.55
77.21
77.00
76.79
62.55
56.09
30.65
21.64
13.91
O
N
Ts
F
CO2Et
F
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
Ts
N
Br
CO2Et
F

3m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4.0
3.5
3.0
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2.0
1.5
1.0
0.5
0.0
ppm
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1.00
1.05
2.05
1.01
0.97
1.01
2.04
1.02
1.03
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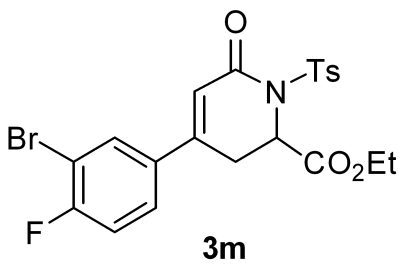
3.09


O
N
Ts
Br
CO2Et
F

3m

169.46
161.82
161.11
159.44
149.37
144.98
135.48
133.70
133.68
131.56
129.65
128.98
127.05
127.00
120.15
117.12
116.97
110.05
109.91
77.21
77.00
76.79
62.51
56.11
30.75
21.63
13.91
200
190
180
170
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140
130
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100
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60
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20
10
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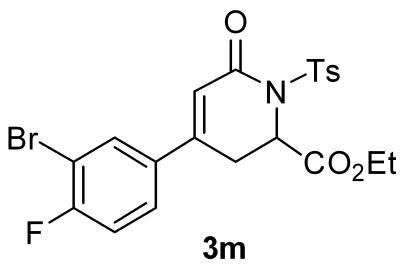
ppm


O
N
Ts
Br
CO2Et
F

3m

169.46
161.82
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77.21
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76.79
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56.11
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21.63
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200
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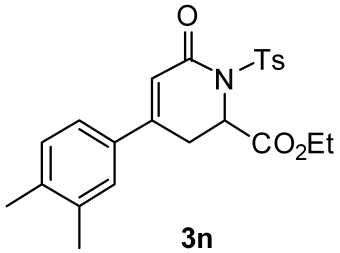

3n

8.038 8.024 7.330 7.317 7.260 7.231 7.215 7.212 7.202 7.199 7.169 7.156 6.134 6.130 5.520 5.517 5.509 5.506 4.149 4.137 4.131 4.125 4.119 4.114 4.107 4.096 4.086 4.074 4.068 4.063 4.057 4.051 4.045 4.033 3.515 3.511 3.485 3.482 3.183 3.179 3.173 3.169 3.154 3.150 3.144 3.139 2.432 2.278 1.110 1.098 1.086 0.000

10.5 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 0.0 ppm

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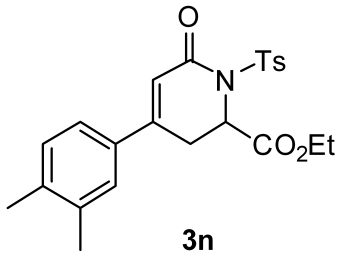

3n

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135.69
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127.34
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77.00
76.79
62.28
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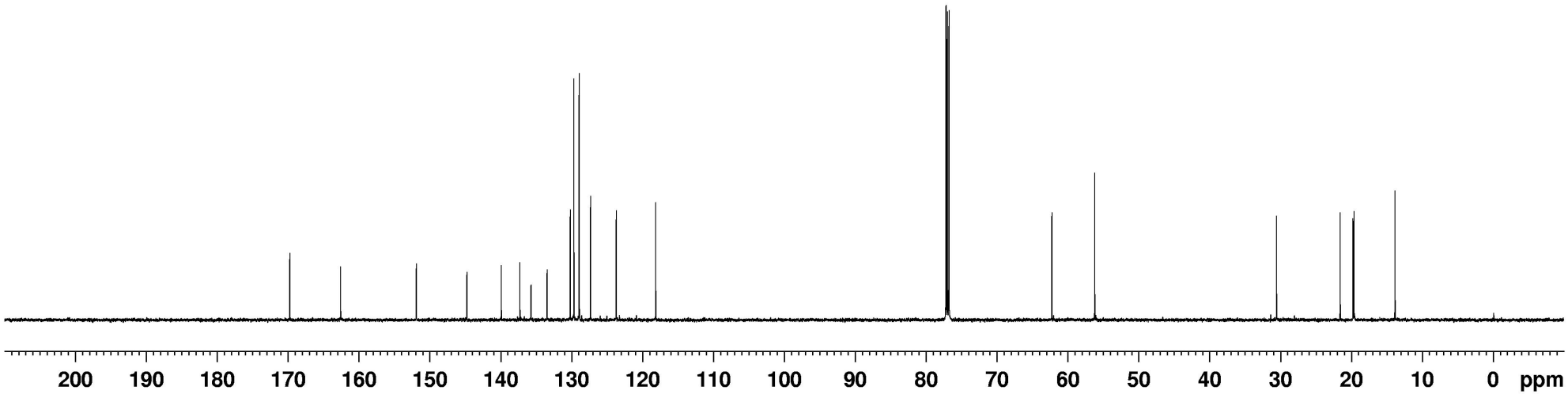
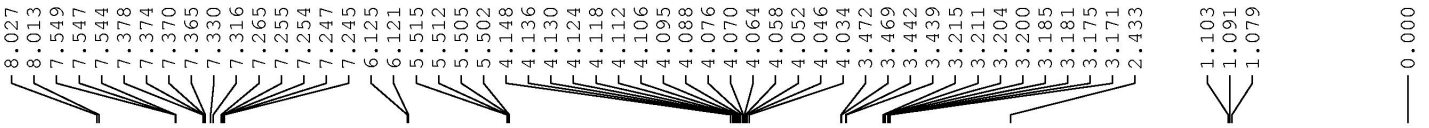
19.80
19.65
13.88

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7.265
7.255
7.254
7.247
7.245
6.125
6.121
5.515
5.512
5.505
5.502
4.148
4.136
4.130
4.124
4.118
4.112
4.106
4.095
4.088
4.076
4.070
4.064
4.058
4.052
4.046
4.034
3.472
3.469
3.442
3.439
3.215
3.211
3.204
3.200
3.185
3.181
3.175
3.171
2.433
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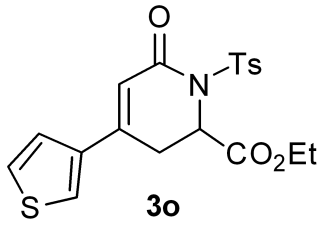
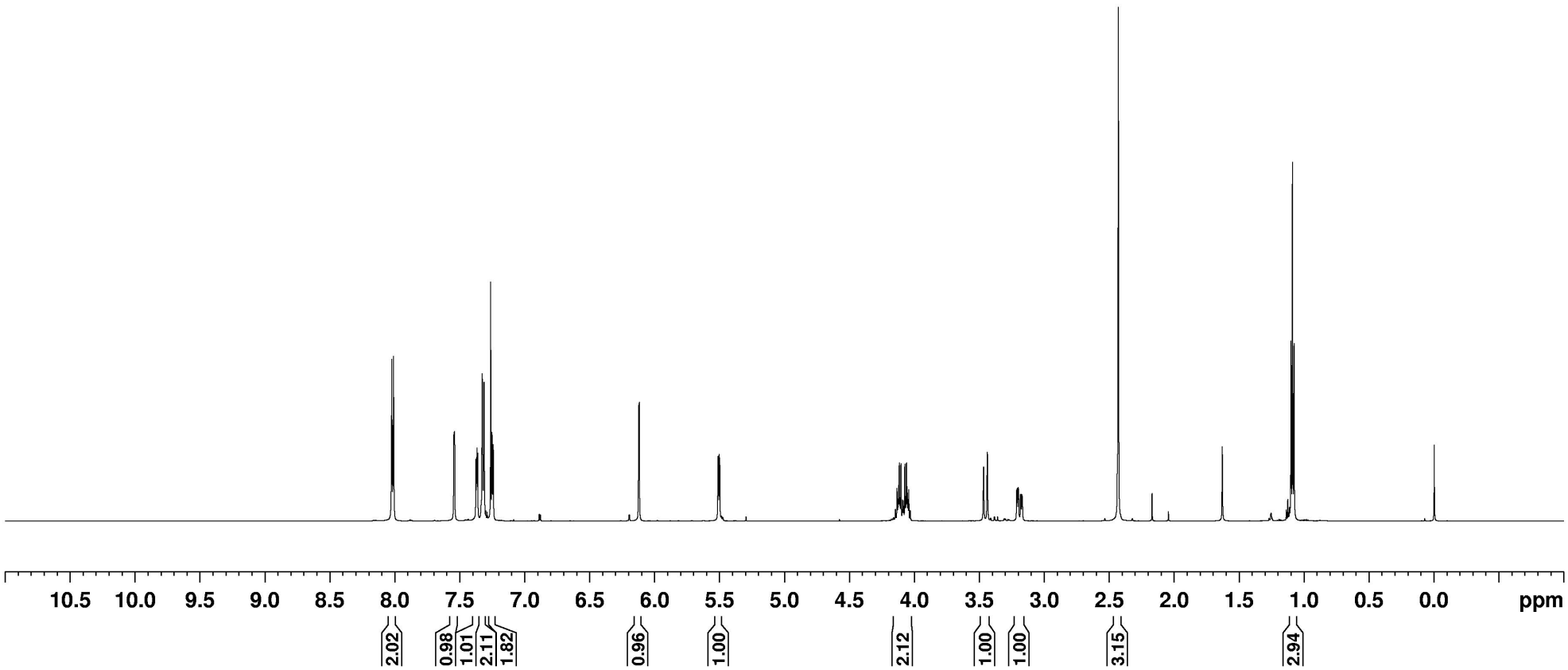
1.091
1.079
0.000


O
N
Ts
CO2Et
S

3o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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.01
2.11
1.82
0.96
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2.12
1.00
1.00
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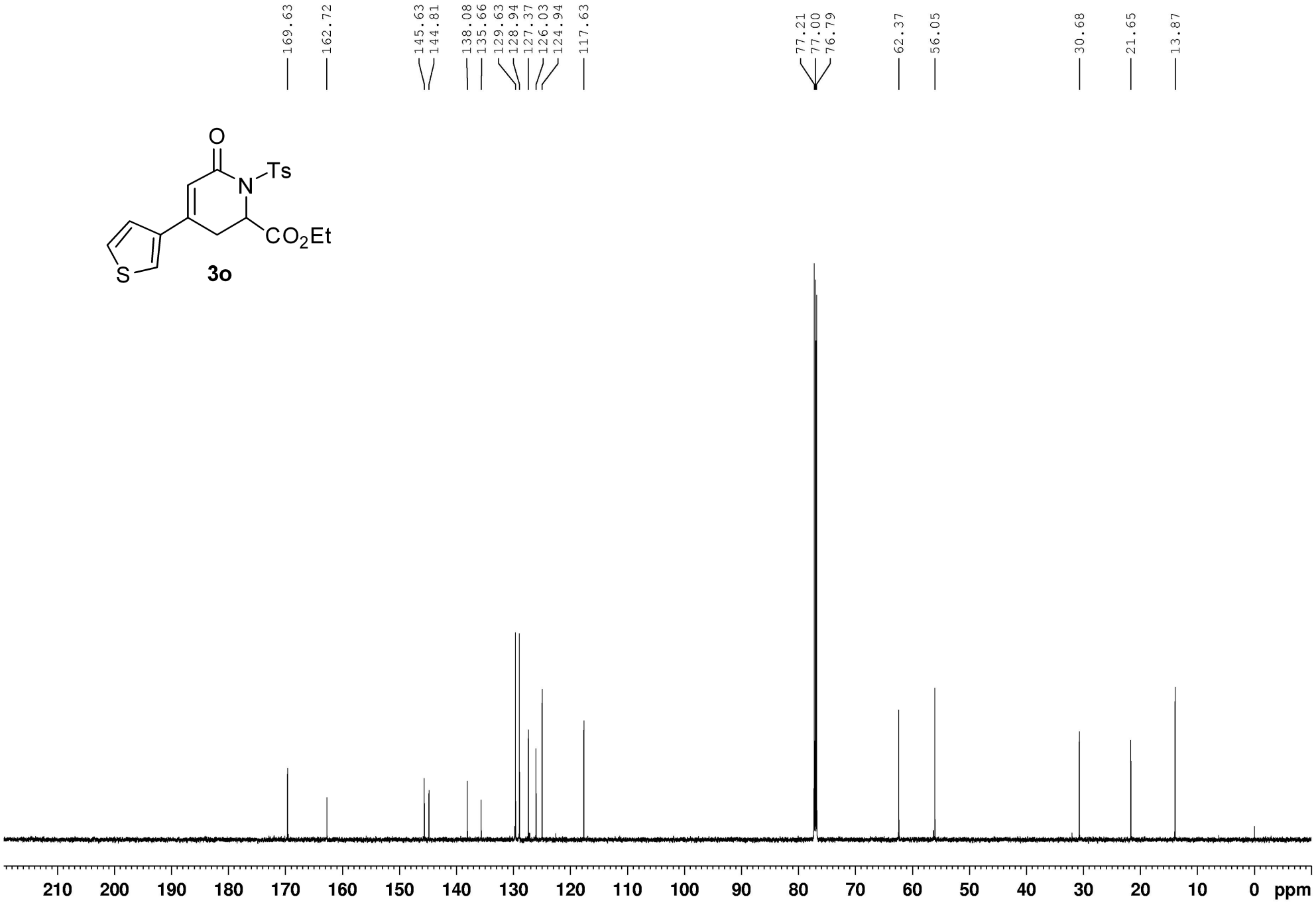
2.94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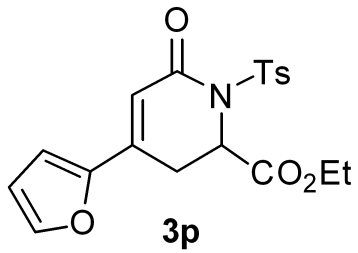
127.37
126.03
124.94
117.63
77.21
77.00
76.79
62.37
56.05
30.68
21.65
13.87
O
N
Ts
CO2Et
S
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
Ts
CO2Et
O

3p

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7.264
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6.733
6.510
6.508
6.505
6.502
6.190
6.186
5.507
5.504
5.496
5.493
4.144
4.132
4.126
4.120
4.114
4.108
4.102
4.090
4.085
4.073
4.067
4.061
4.055
4.049
4.043
4.031
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3.365
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3.337
3.138
3.134
3.128
3.124
3.110
3.105
3.099
3.095
2.431
1.098
1.086
1.075
0.000
10.5 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 0.0 ppm
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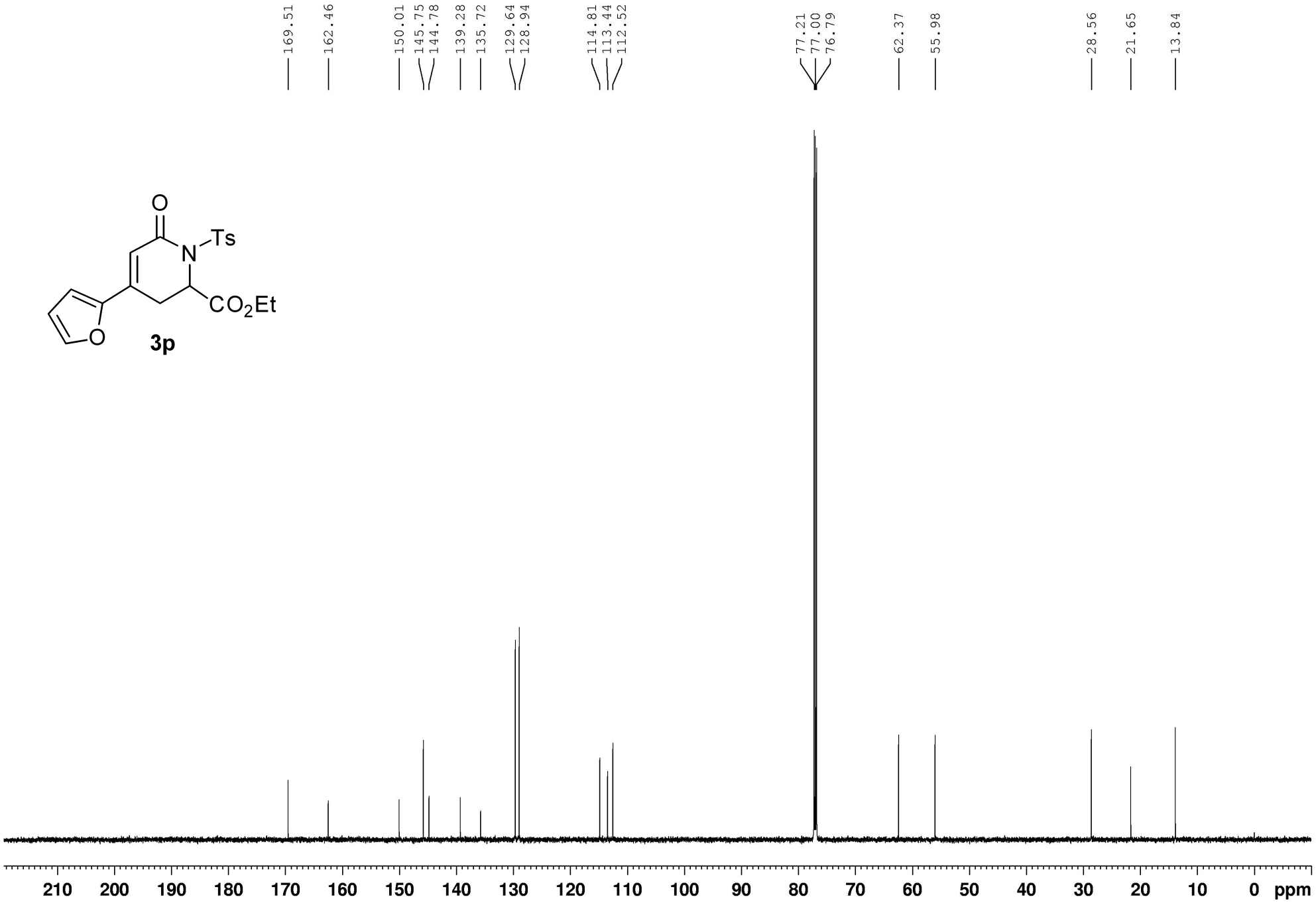
2.06
1.01
0.98
0.93
1.00
2.07
1.04
1.03
3.12
3.08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112.52
77.21
77.00
76.79
62.37
55.98
28.56
21.65
13.84
O
N
Ts
CO2Et
O
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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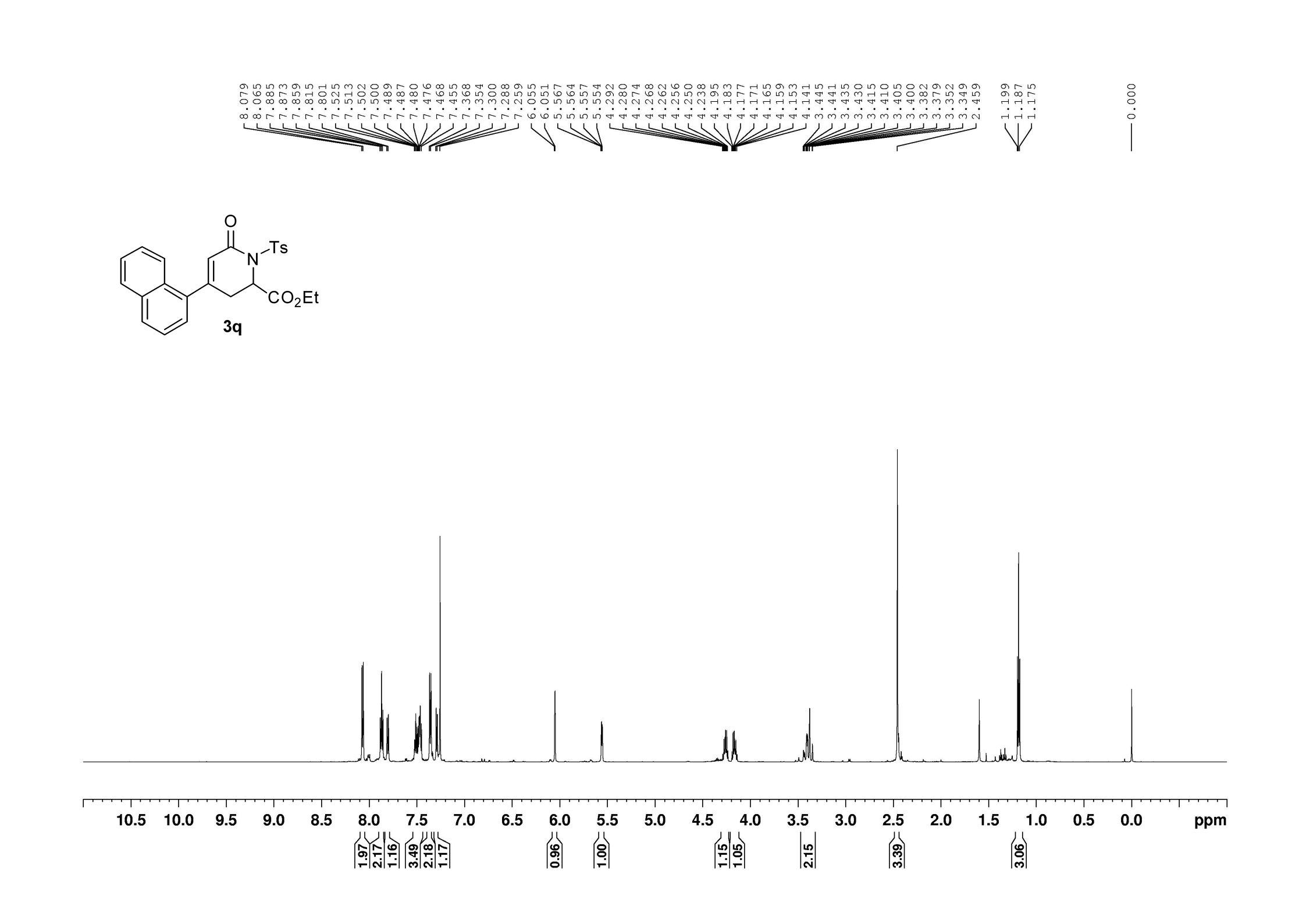
30
20
10
0
ppm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7.487
7.480
7.476
7.468
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7.368
7.354
7.300
7.288
7.259
6.055
6.051
5.567
5.564
5.557
5.554
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4.280
4.274
4.268
4.262
4.256
4.250
4.238
4.195
4.183
4.177
4.171
4.165
4.159
4.153
4.141
3.445
3.441
3.435
3.430
3.415
3.410
3.405
3.400
3.382
3.379
3.352
3.349
2.459
1.199
1.187
1.175
0.000
O
N
Ts
CO2Et
3q
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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
0.0
ppm
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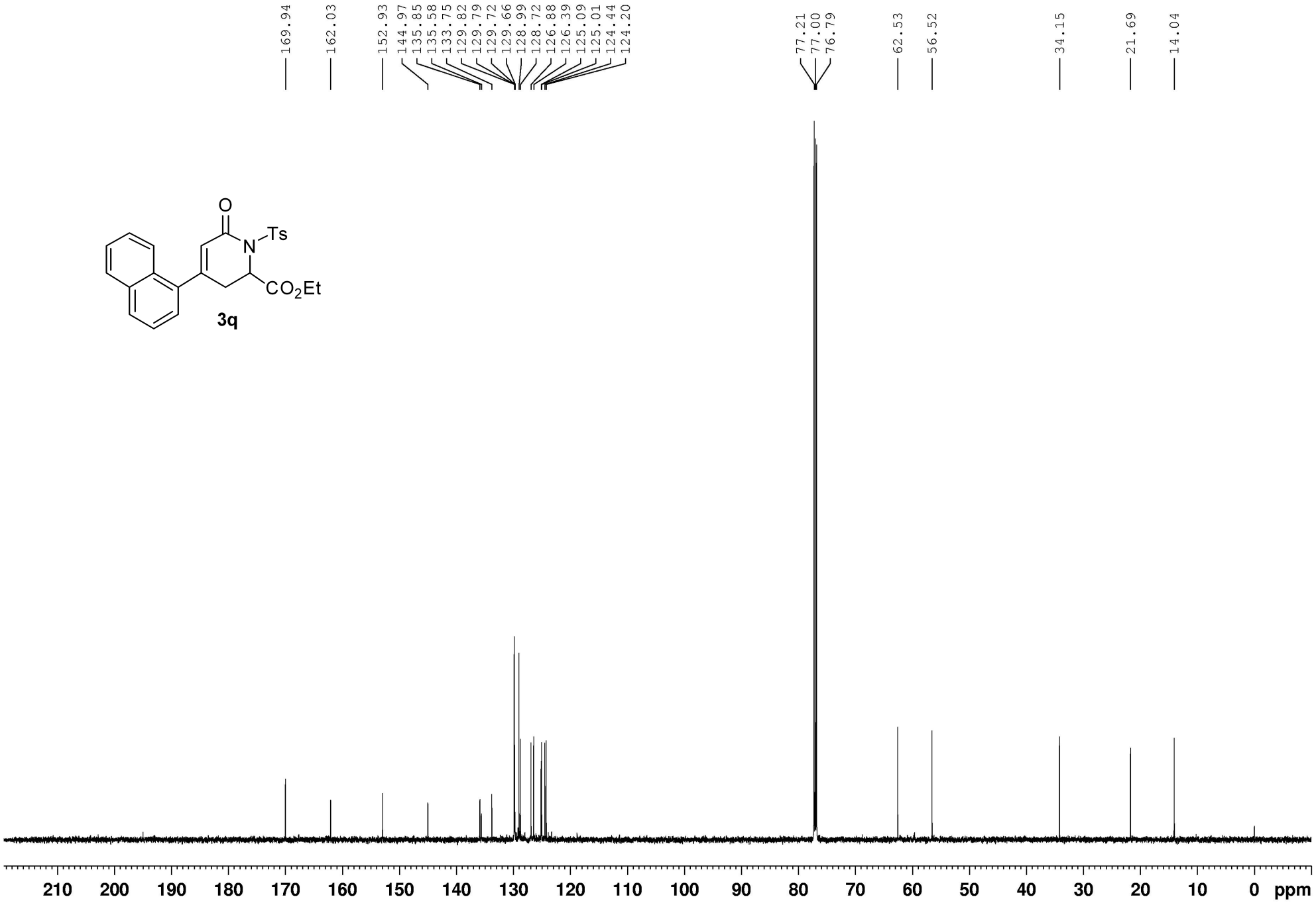
3.06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128.99
128.72
126.88
126.39
125.09
125.01
124.44
124.20
77.21
77.00
76.79
62.53
56.52
34.15
21.69
14.04
O
N
Ts
CO2Et
3q
210
200
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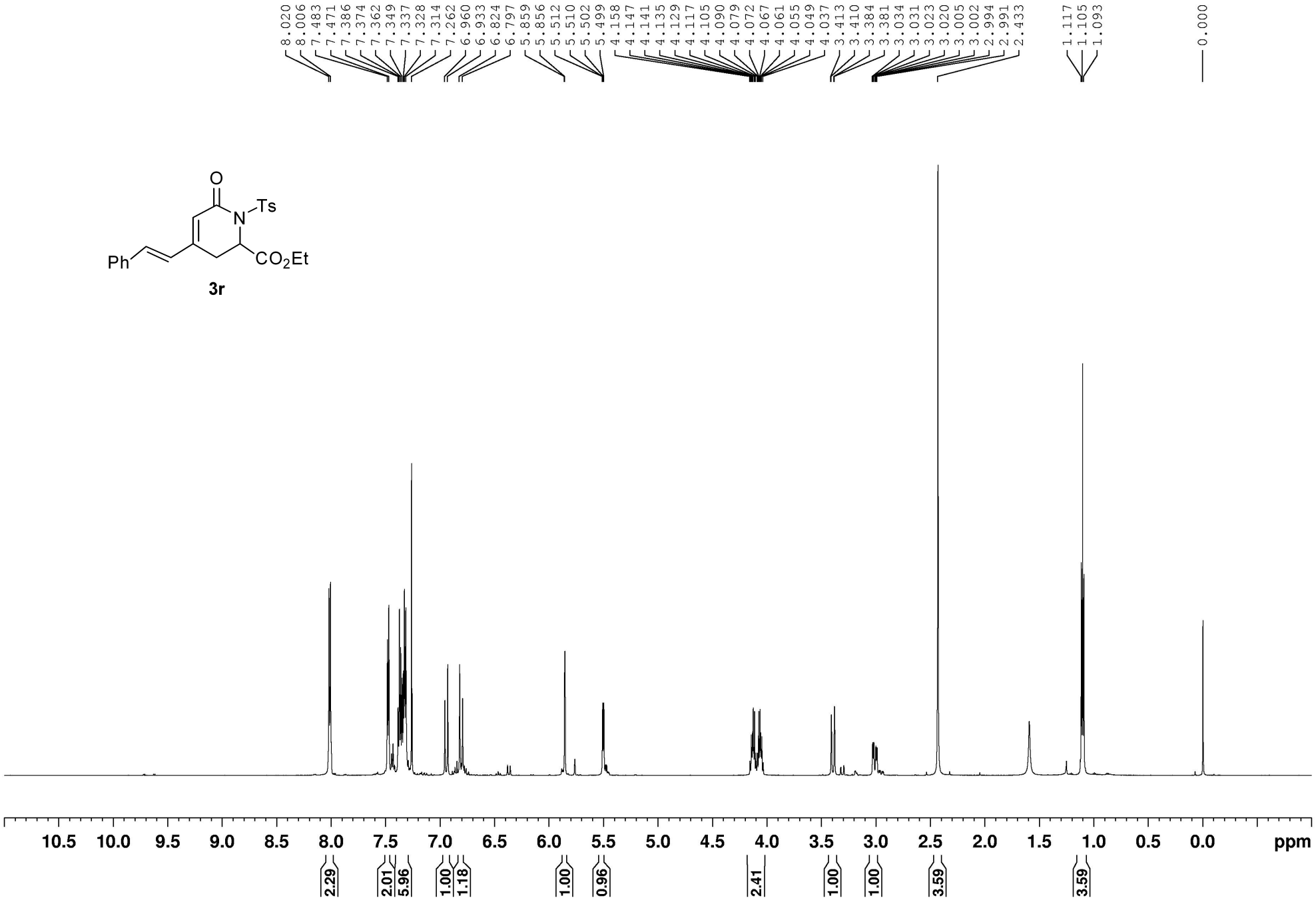
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.824
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5.859
5.856
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5.502
5.499
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4.141
4.135
4.129
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4.079
4.072
4.067
4.061
4.055
4.049
4.037
3.413
3.410
3.384
3.381
3.034
3.031
3.023
3.020
3.005
3.002
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2.991
2.433
1.117
1.105
1.093
0.000
O
N
Ts
Ph
CO2Et
3r
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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
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2.0
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1.0
0.5
0.0
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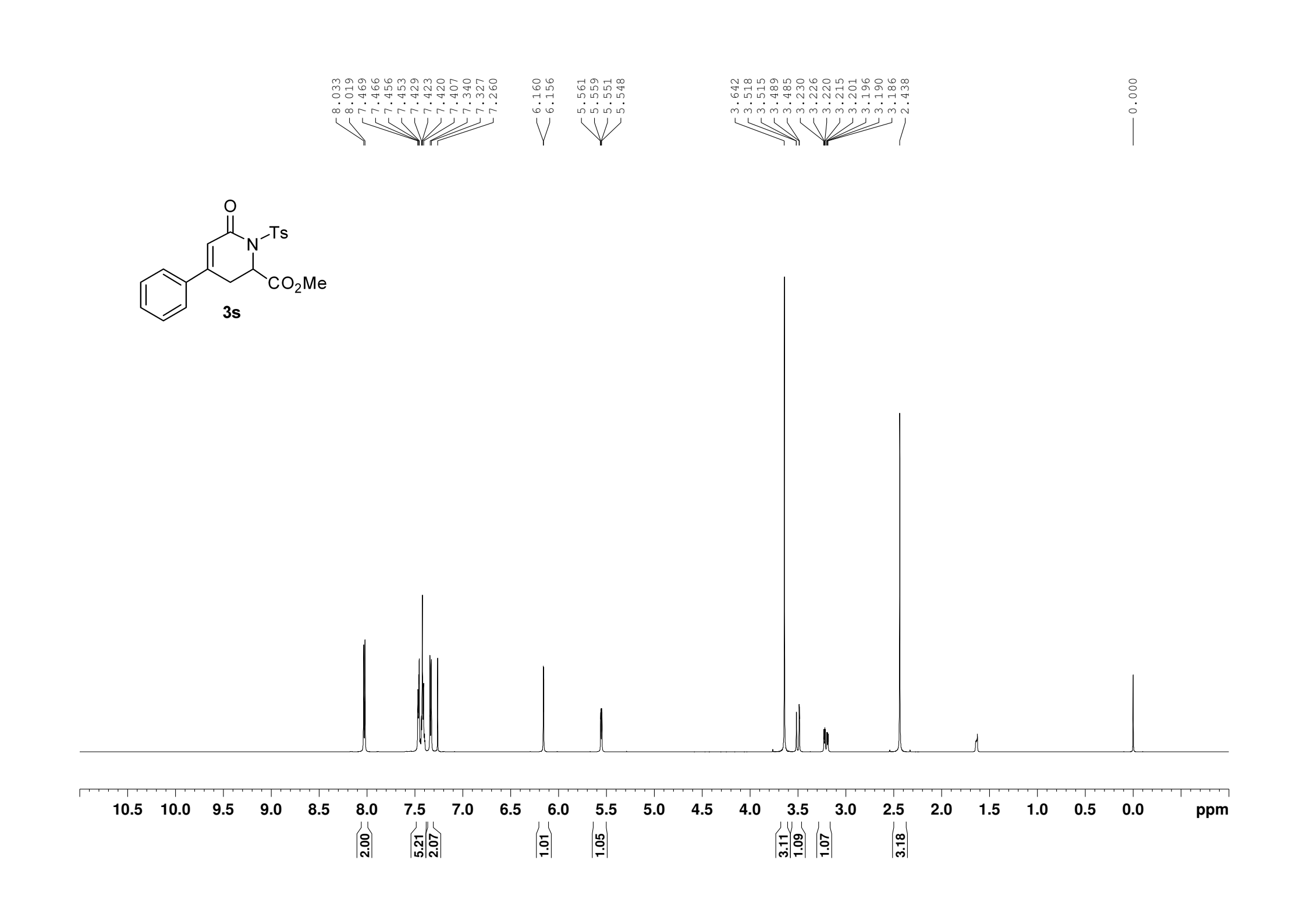
3.59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6.156
5.561
5.559
5.551
5.548
3.642
3.518
3.515
3.489
3.485
3.230
3.226
3.220
3.215
3.201
3.196
3.190
3.186
2.438
0.000
O
N
Ts
CO2Me
3s
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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1.05
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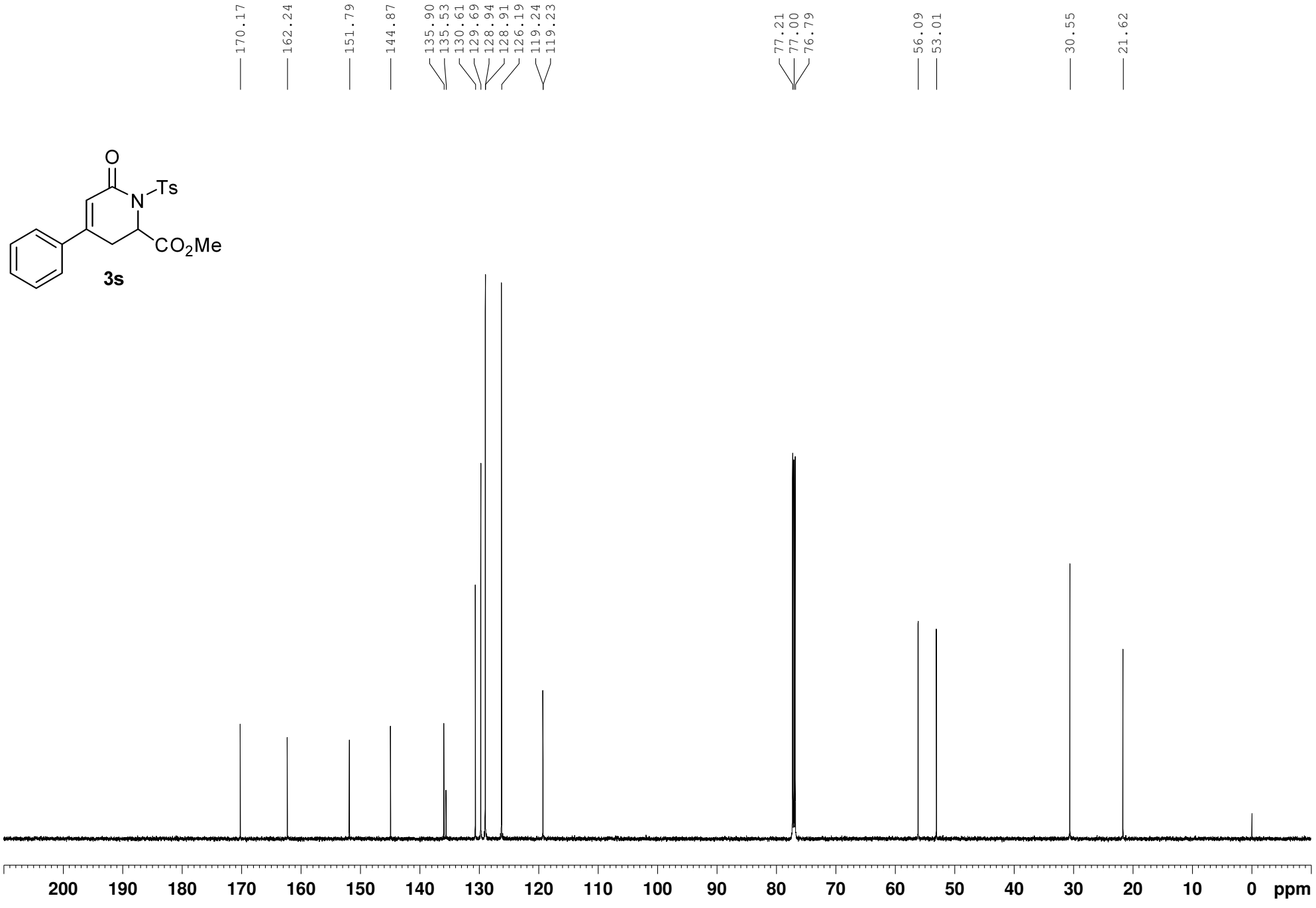
1.07
3.18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130.61
129.69
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128.91
126.19
119.24
119.23
77.21
77.00
76.79
56.09
53.01
30.55
21.62
O
N
Ts
CO2Me
3s
200
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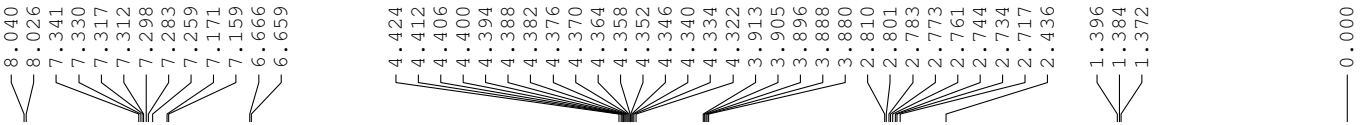
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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4.406
4.400
4.394
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4.382
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4.370
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4.352
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4.340
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3.905
3.896
3.888
3.880
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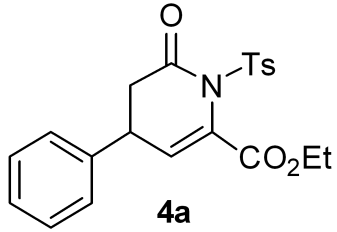
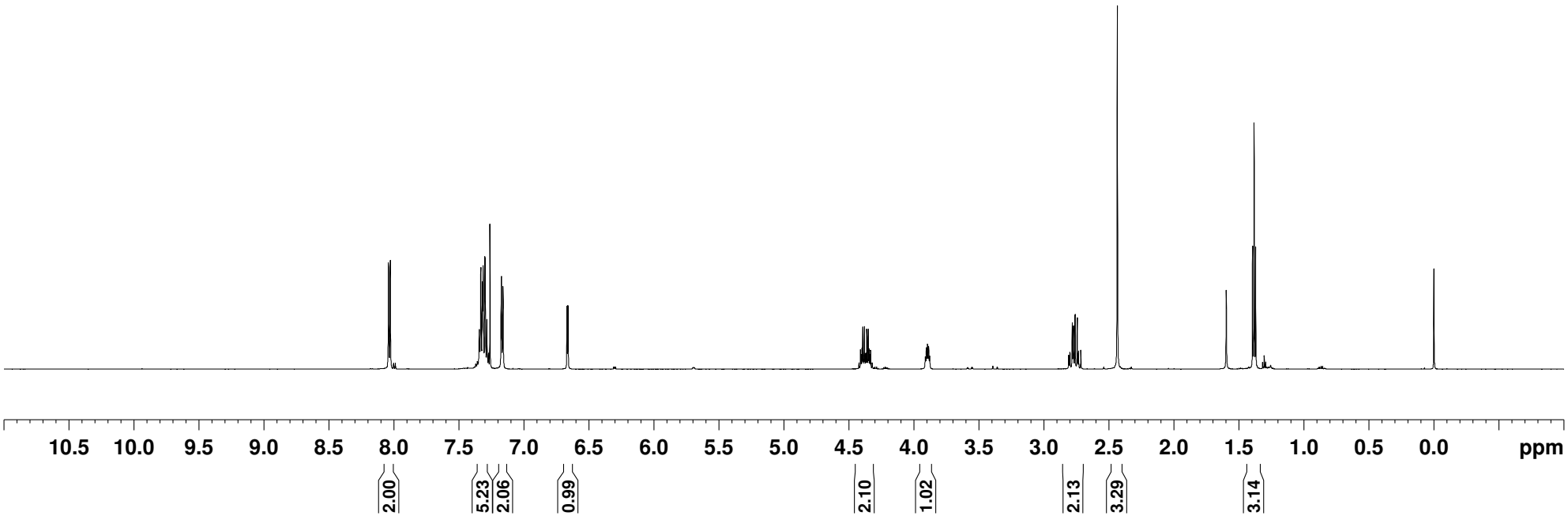
0.000


O
Ts
N
CO2Et

4a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4.0
3.5
3.0
2.5
2.0
1.5
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2.10
1.02
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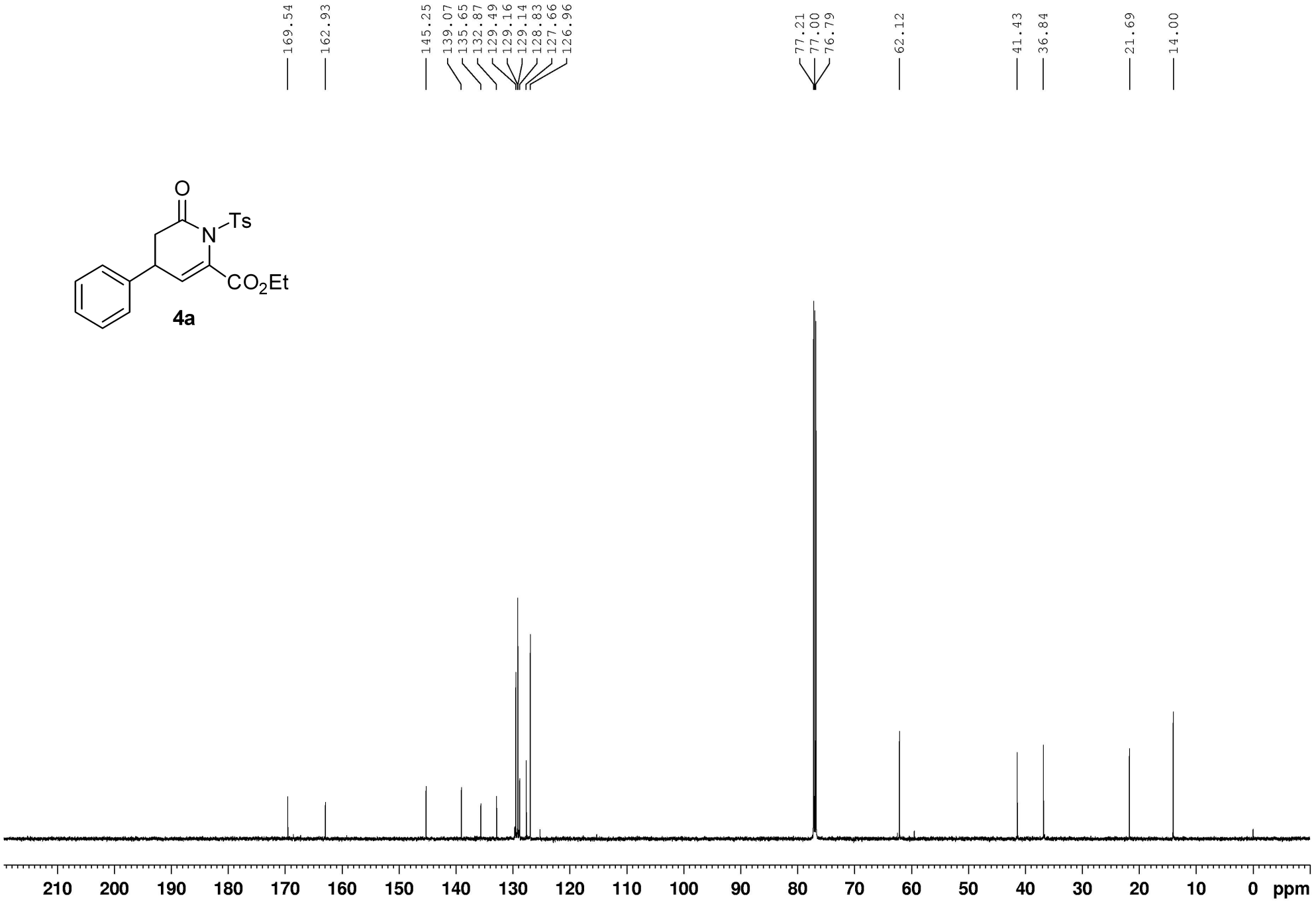
3.14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127.66
126.96
77.21
77.00
76.79
62.12
41.43
36.84
21.69
14.00
O
N
Ts
CO2Et
4a
210
200
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60
50
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30
20
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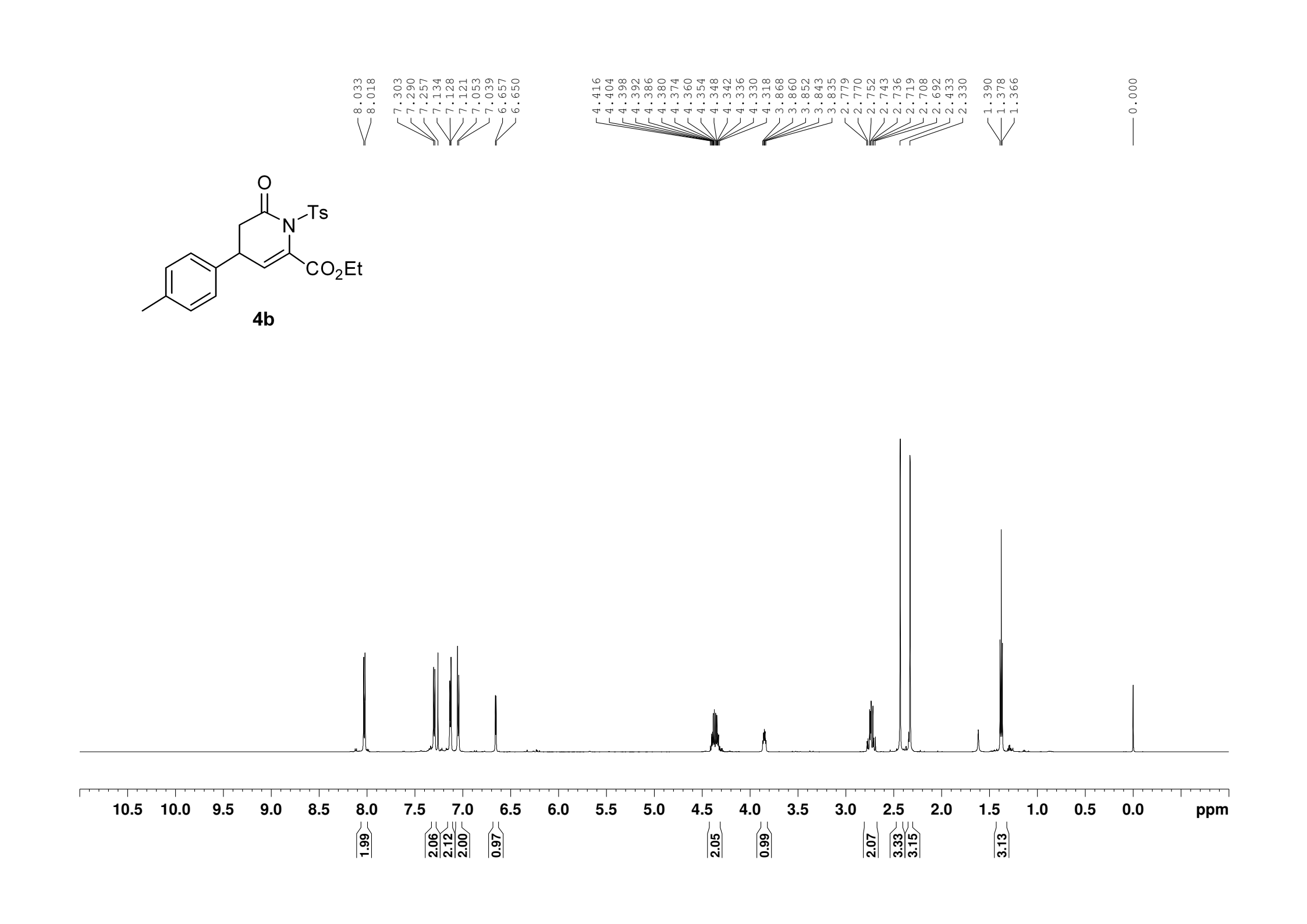
0
ppm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7.039
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4.404
4.398
4.392
4.386
4.380
4.374
4.360
4.354
4.348
4.342
4.336
4.330
4.318
3.868
3.860
3.852
3.843
3.835
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2.770
2.752
2.743
2.736
2.719
2.708
2.692
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2.330
1.390
1.378
1.366
0.000
O
N
Ts
CO2Et
4b
10.5 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 0.0 ppm
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2.12
2.00
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2.05
0.99
2.07
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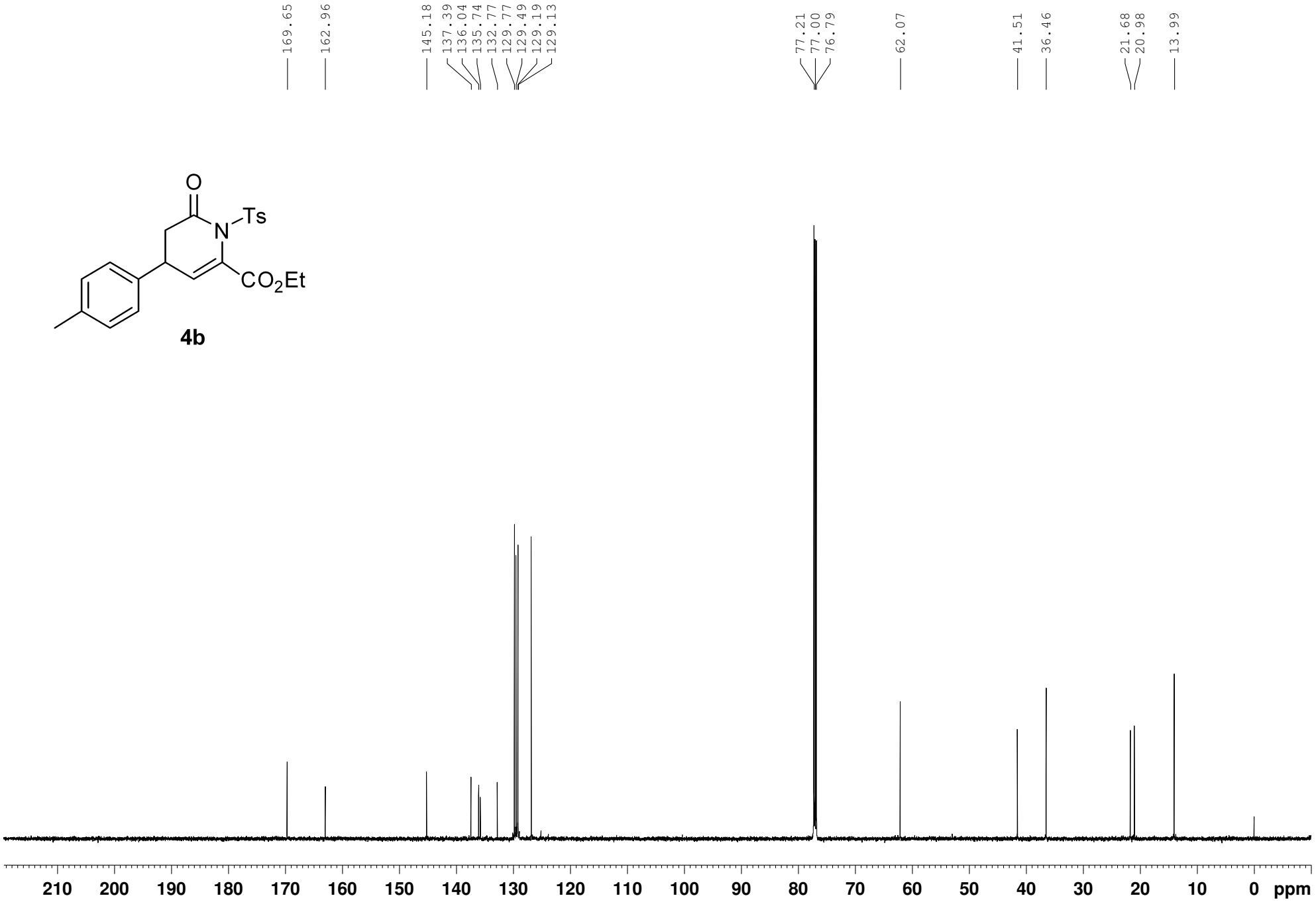
3.15
3.13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129.19
129.13
77.21
77.00
76.79
62.07
41.51
36.46
21.68
20.98
13.99
O
N
Ts
CO2Et
4b
210
200
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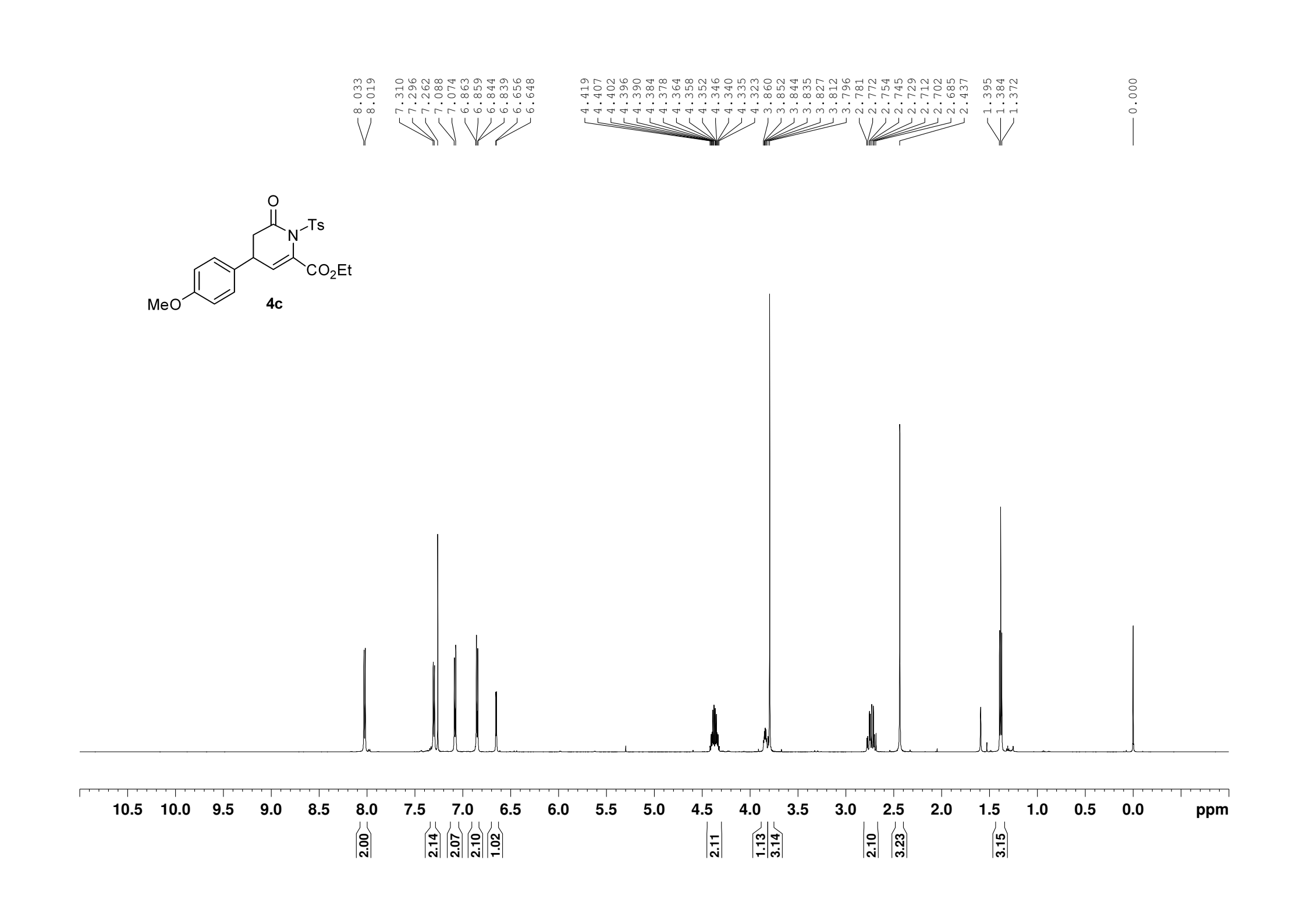
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4.407
4.402
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4.390
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4.378
4.364
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4.346
4.340
4.335
4.323
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3.852
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2.781
2.772
2.754
2.745
2.729
2.712
2.702
2.685
2.437
1.395
1.384
1.372
0.000
O
N
Ts
CO2Et
MeO
4c
10.5 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 0.0 ppm
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1.13
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2.10
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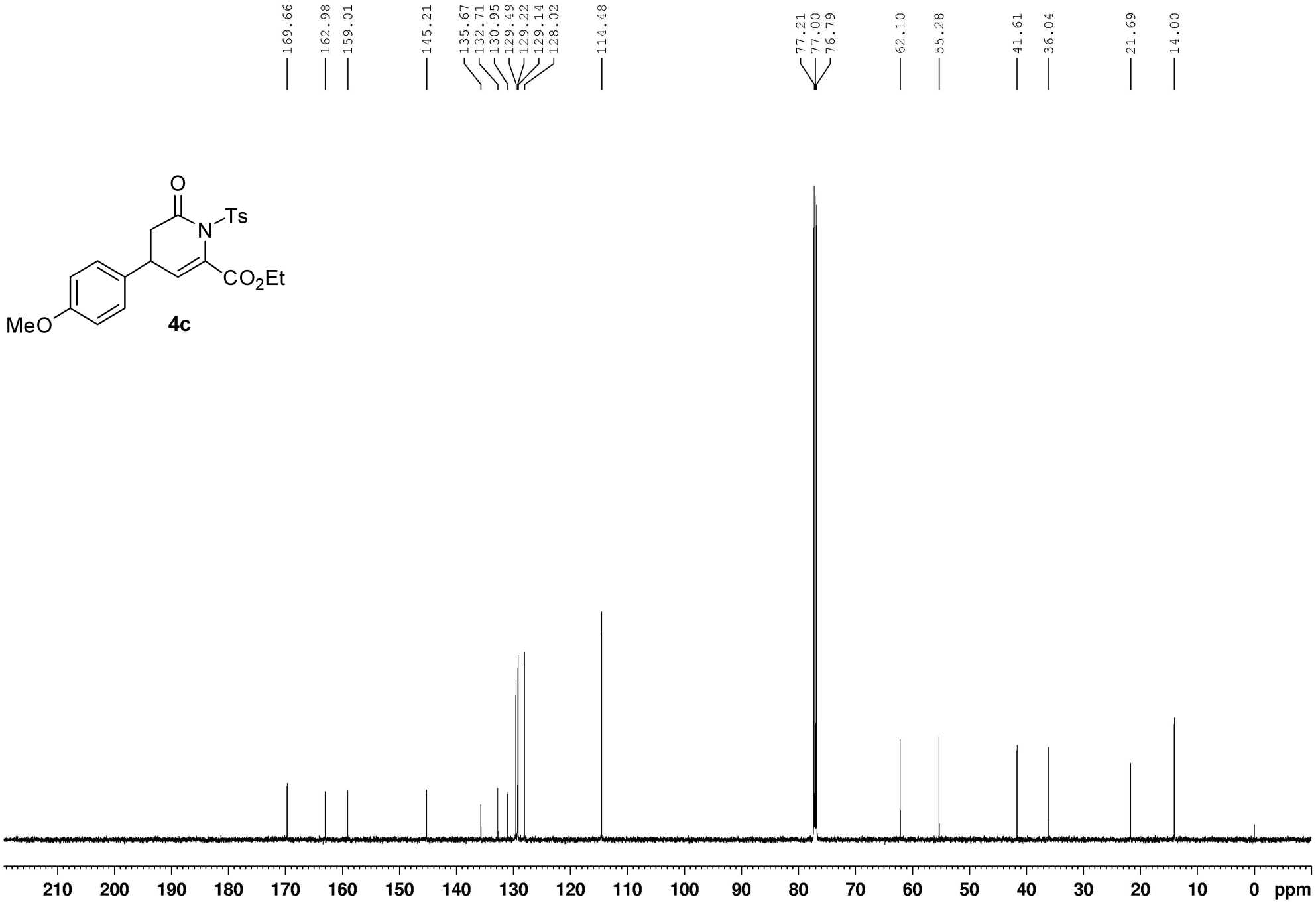
3.15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114.48
77.21
77.00
76.79
62.10
55.28
41.61
36.04
21.69
14.00
O
N
Ts
CO2Et
MeO
4c
210
200
190
180
170
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140
130
120
110
100
90
80
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60
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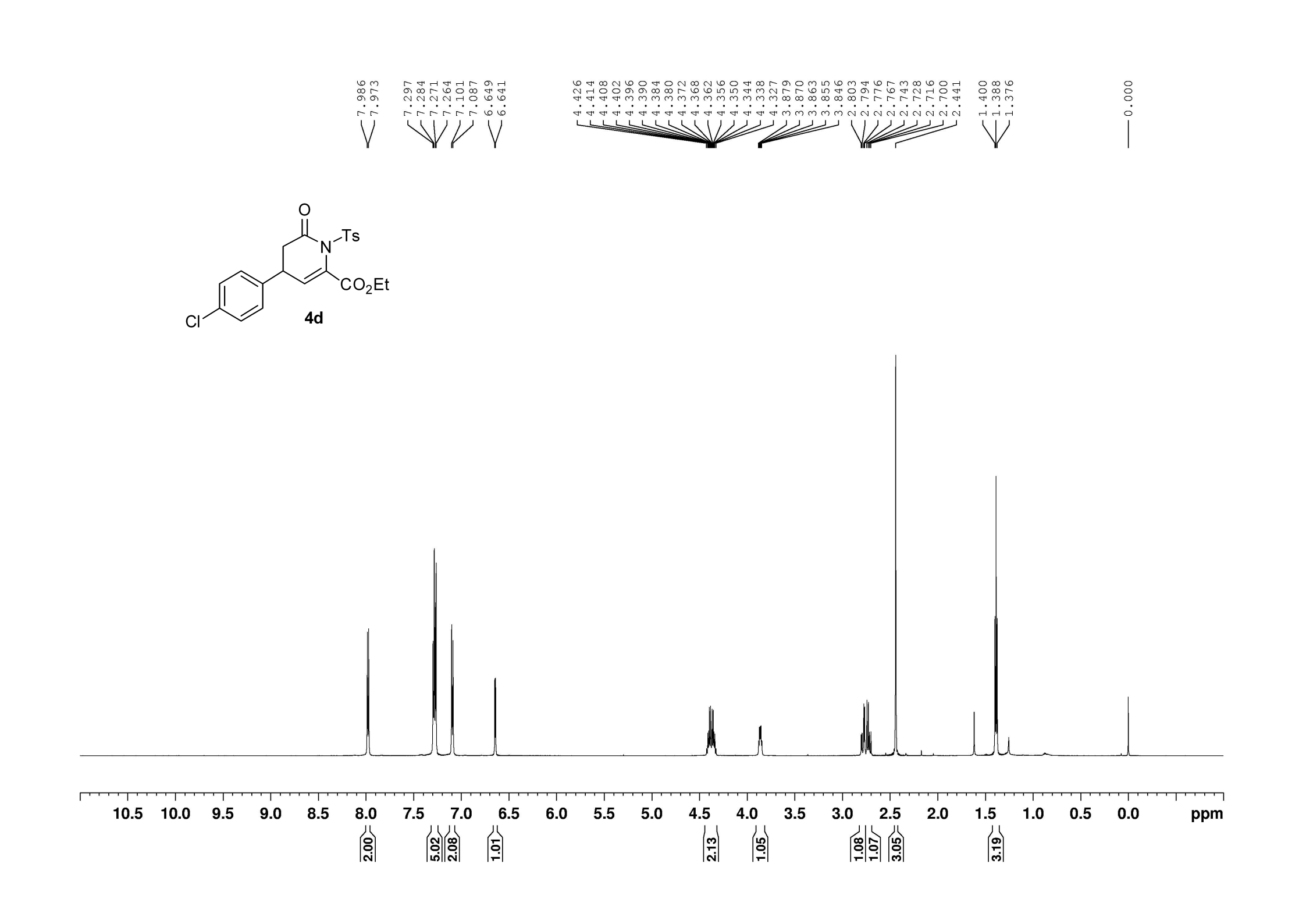
20
10
0
ppm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4.408
4.402
4.396
4.390
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4.380
4.372
4.368
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4.356
4.350
4.344
4.338
4.327
3.879
3.870
3.863
3.855
3.846
2.803
2.794
2.776
2.767
2.743
2.728
2.716
2.700
2.441
1.400
1.388
1.376
0.000
O
N
Ts
CO2Et
Cl
4d
10.5
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
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1.01
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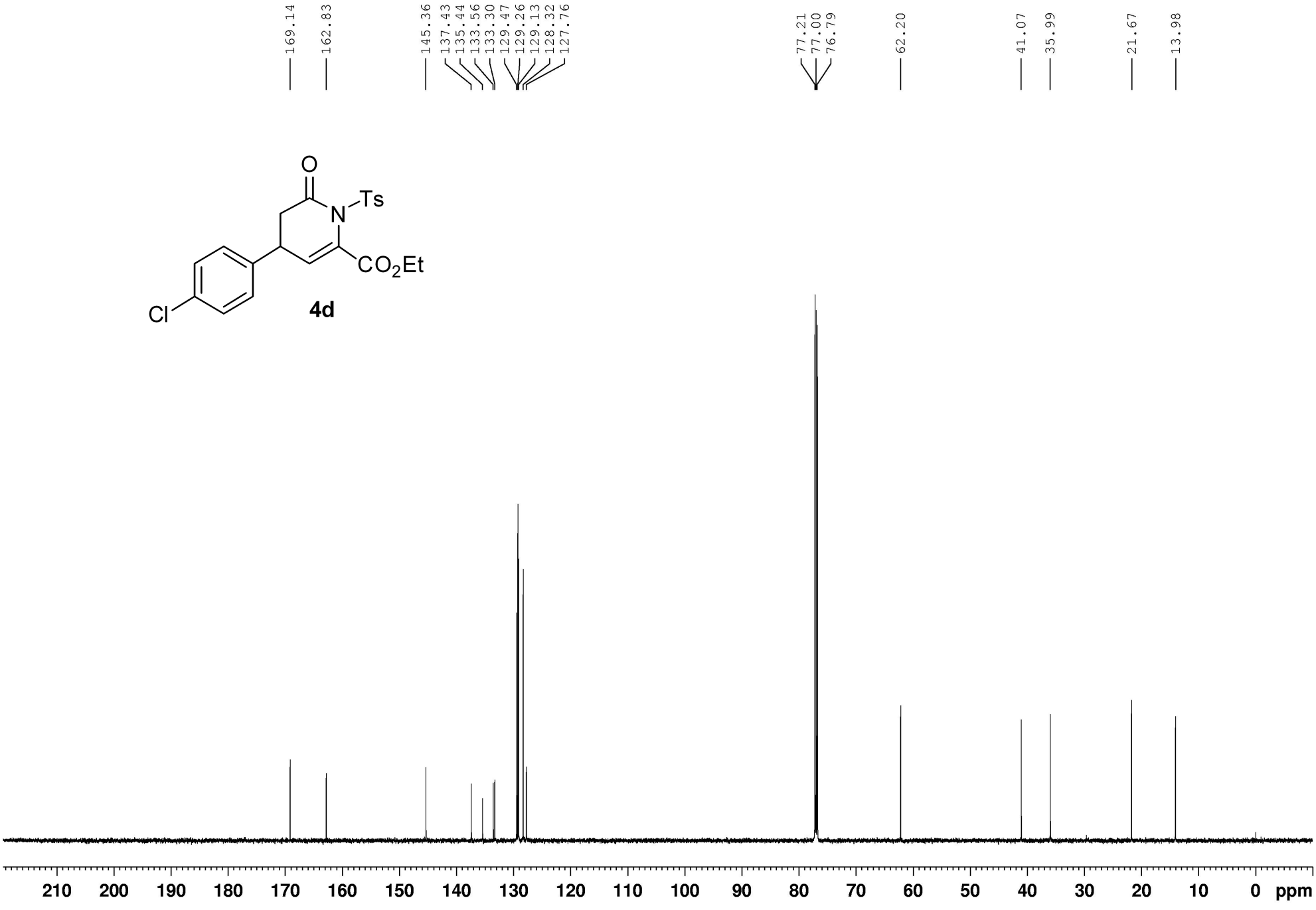
1.05
1.08
1.07
3.05
3.19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127.76
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77.00
76.79
62.20
41.07
35.99
21.67
13.98
O
N
Ts
CO2Et
Cl
4d
210
200
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140
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100
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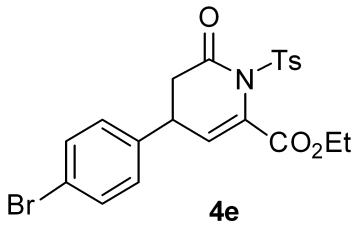
ppm


O
N
Ts
CO2Et
Br

4e

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7.026
6.647
6.639
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4.412
4.406
4.400
4.394
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4.366
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2.739
2.724
2.712
2.696
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1.386
1.374
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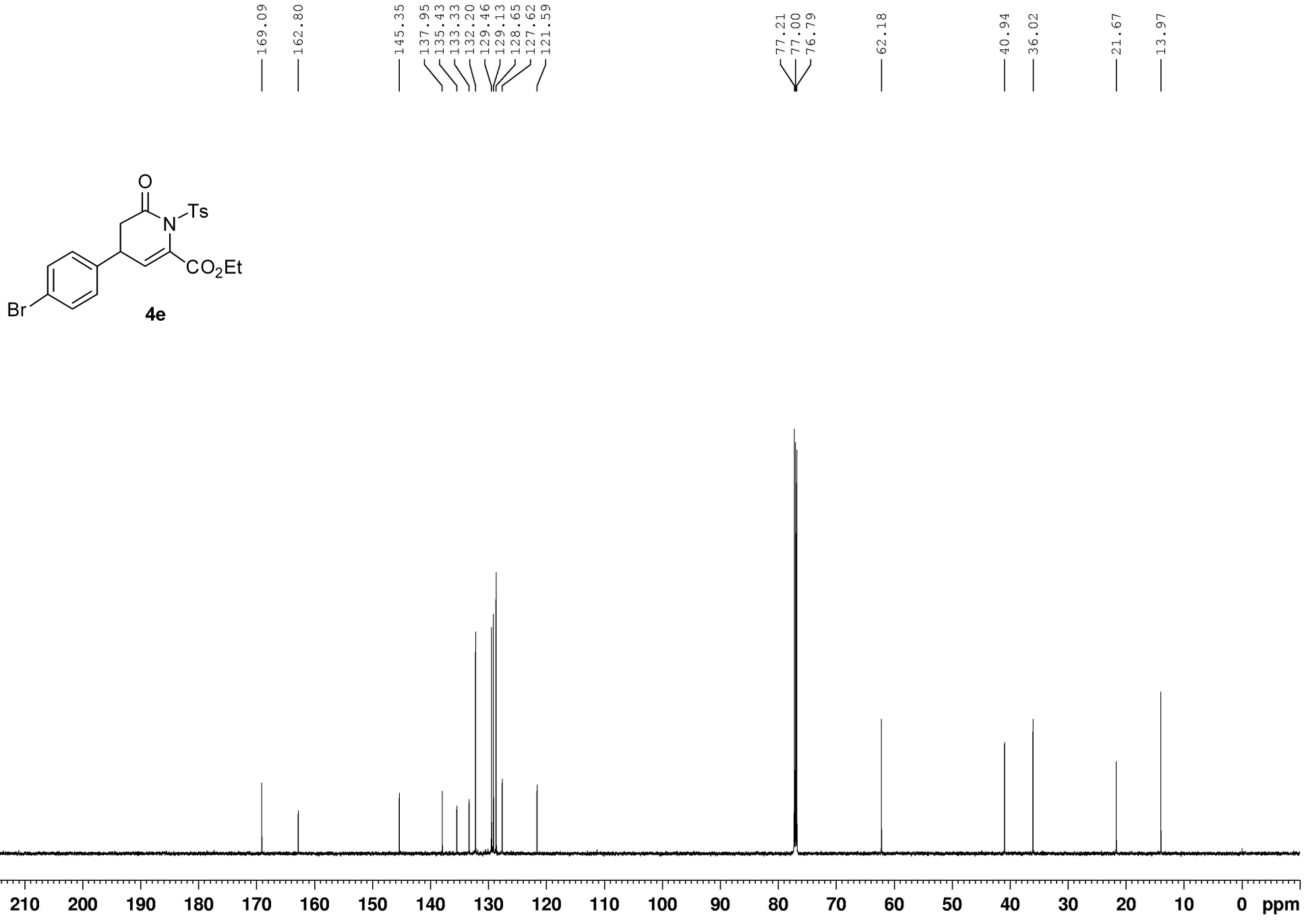
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127.62
121.59
77.21
77.00
76.79
62.18
40.94
36.02
21.67
13.97
O
N
Ts
CO2Et
Br
4e
210
200
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180
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140
130
120
110
100
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80
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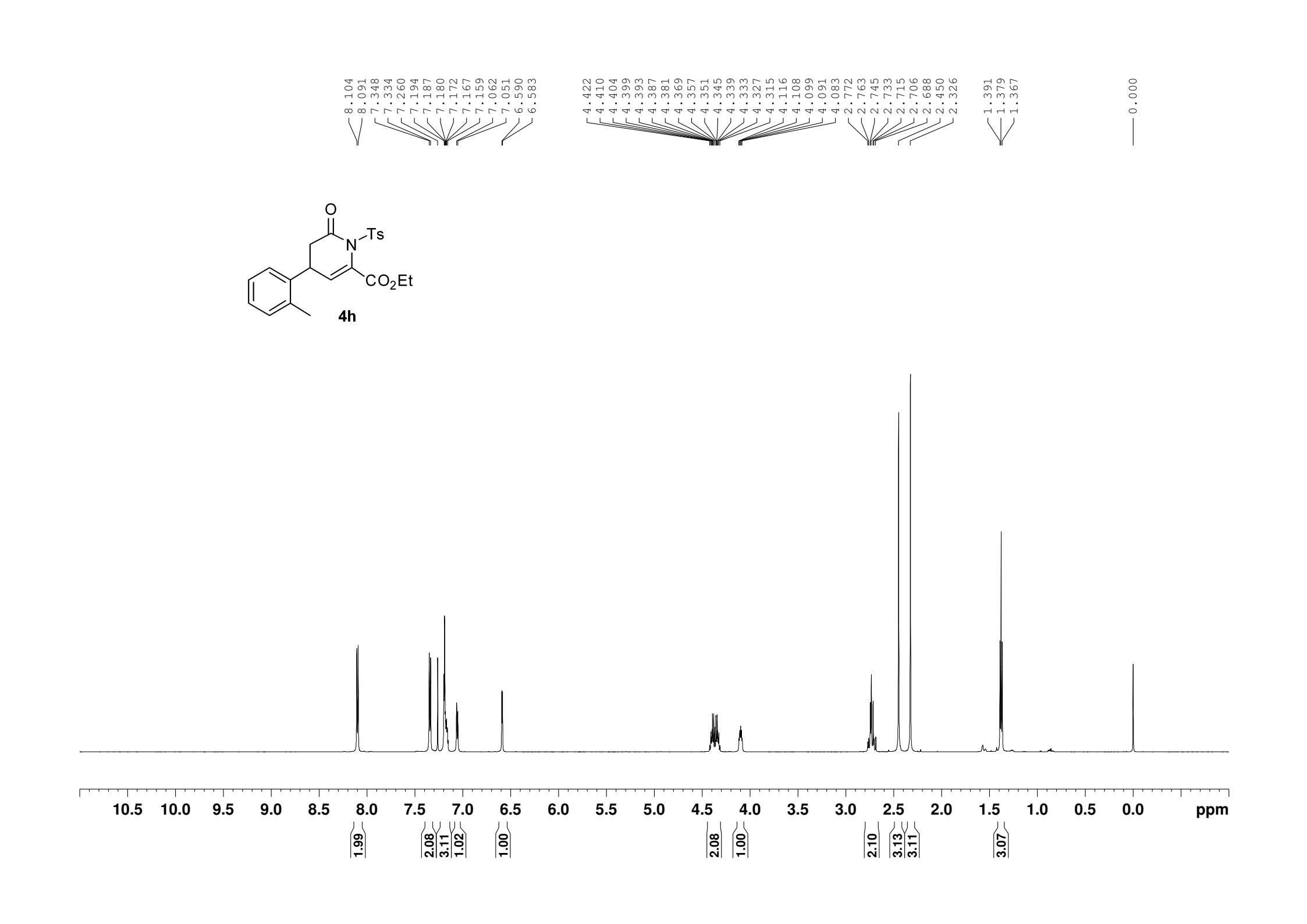
60
50
40
30
20
10
0
ppm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7.167
7.159
7.062
7.051
6.590
6.583
4.422
4.410
4.404
4.399
4.393
4.387
4.381
4.369
4.357
4.351
4.345
4.339
4.333
4.327
4.315
4.116
4.108
4.099
4.091
4.083
2.772
2.763
2.745
2.733
2.715
2.706
2.688
2.450
2.326
1.391
1.379
1.367
0.000
O
N
Ts
CO2Et
4h
10.5 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 0.0 ppm
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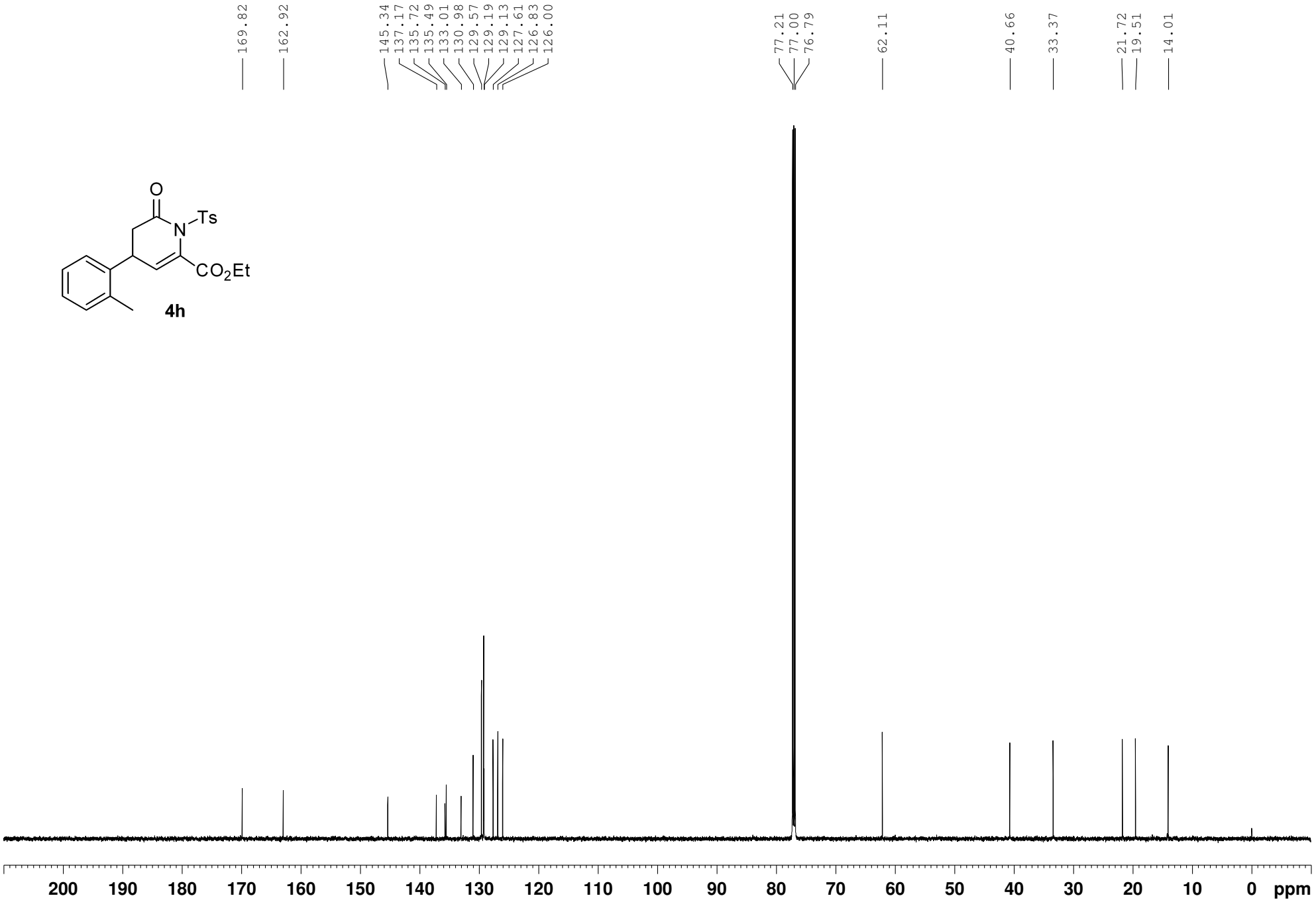
2.08
3.11
1.02
1.00
2.08
1.00
2.10
3.13
3.11
3.07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129.13
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126.83
126.00
77.21
77.00
76.79
62.11
40.66
33.37
21.72
19.51
14.01
O
N
Ts
CO2Et
4h
200
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180
170
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140
130
120
110
100
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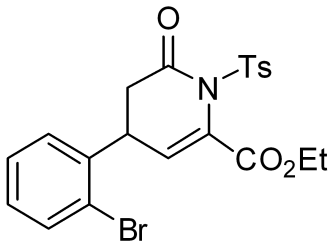
60
50
40
30
20
10
0
ppm


O
N
Ts
CO2Et
Br

4i

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4.404
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4.387
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4.345
4.319
4.310
4.305
4.301
4.296
4.287
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2.826
2.809
2.799
2.787
2.772
2.760
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2.443
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10.5 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 0.0 ppm
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1.00
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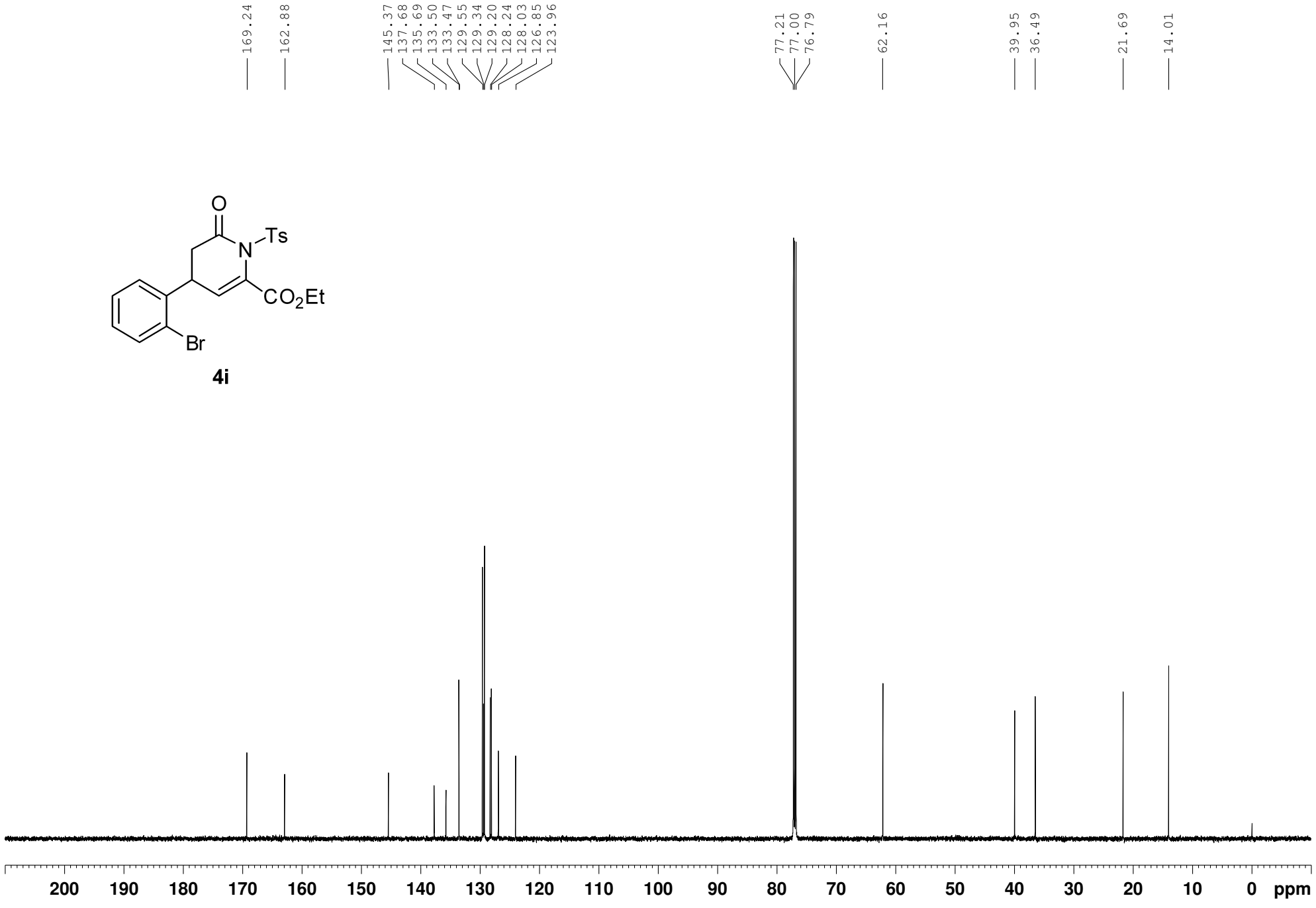
2.07
1.00
2.09
1.03
2.11
3.11
3.08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128.24
128.03
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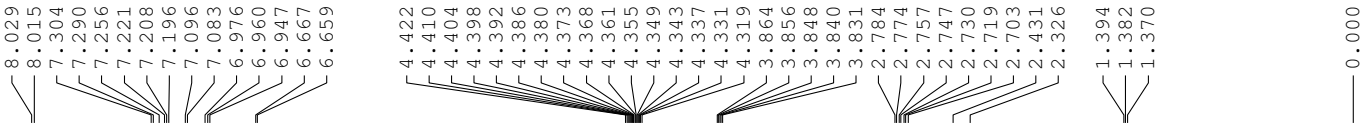
123.96
77.21
77.00
76.79
62.16
39.95
36.49
21.69
14.01
O
N
Ts
CO2Et
Br
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.083
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6.947
6.667
6.659
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4.404
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4.361
4.355
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4.331
4.319
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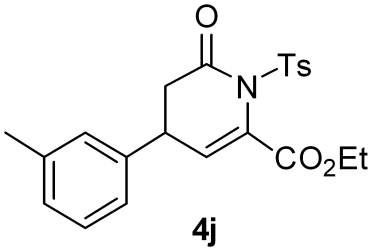
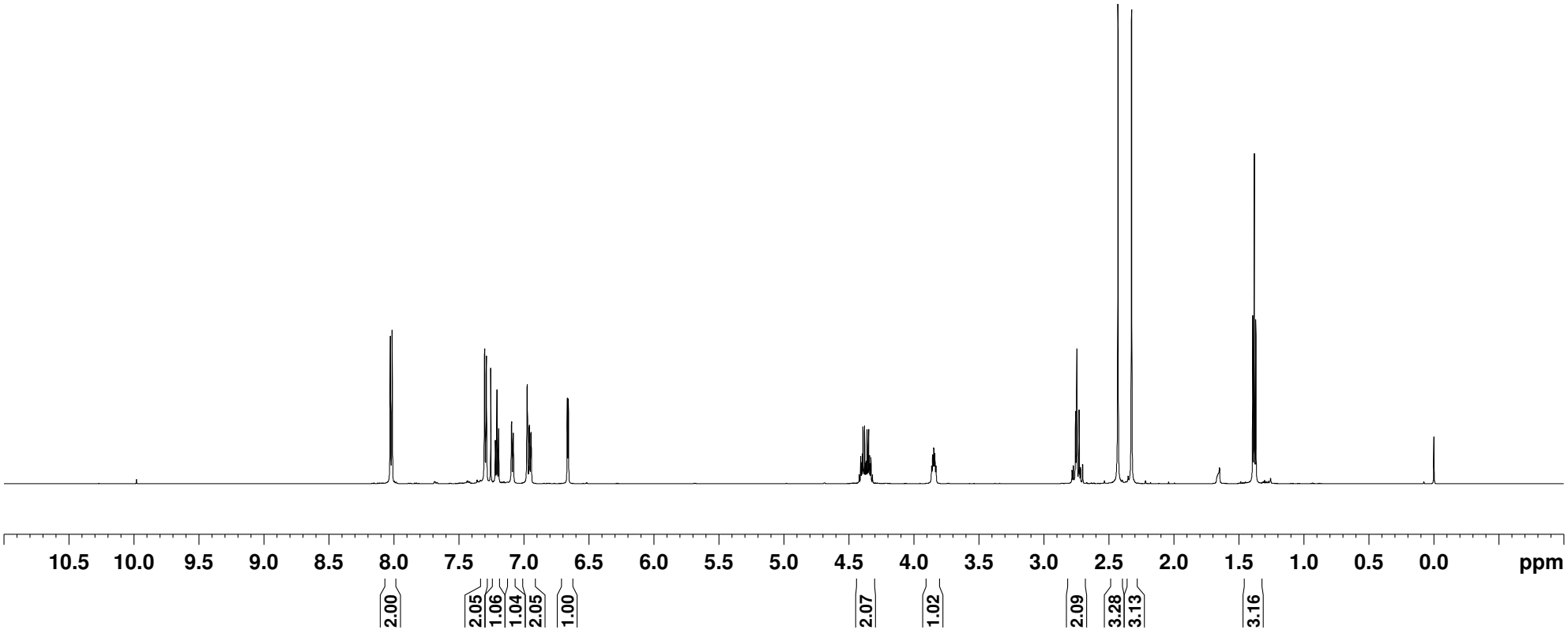
1.382
1.370
0.000


O
Ts
N
CO2Et

4j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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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1.04
2.05
1.00
2.07
1.02
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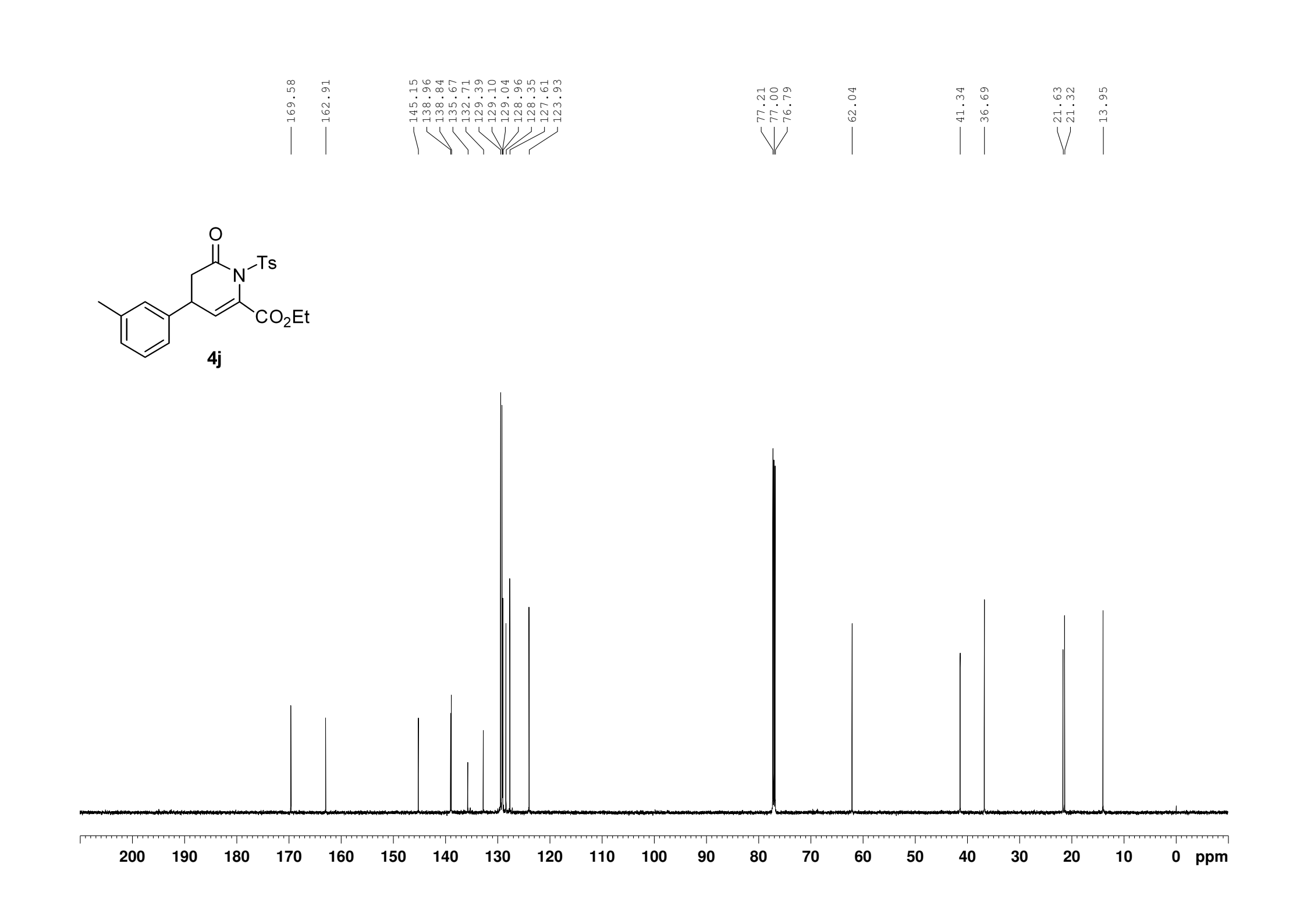
3.16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128.96
128.35
127.61
123.93
77.21
77.00
76.79
62.04
41.34
36.69
21.63
21.32
13.95
O
N
Ts
CO2Et
4j
200
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150
140
130
120
110
100
90
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60
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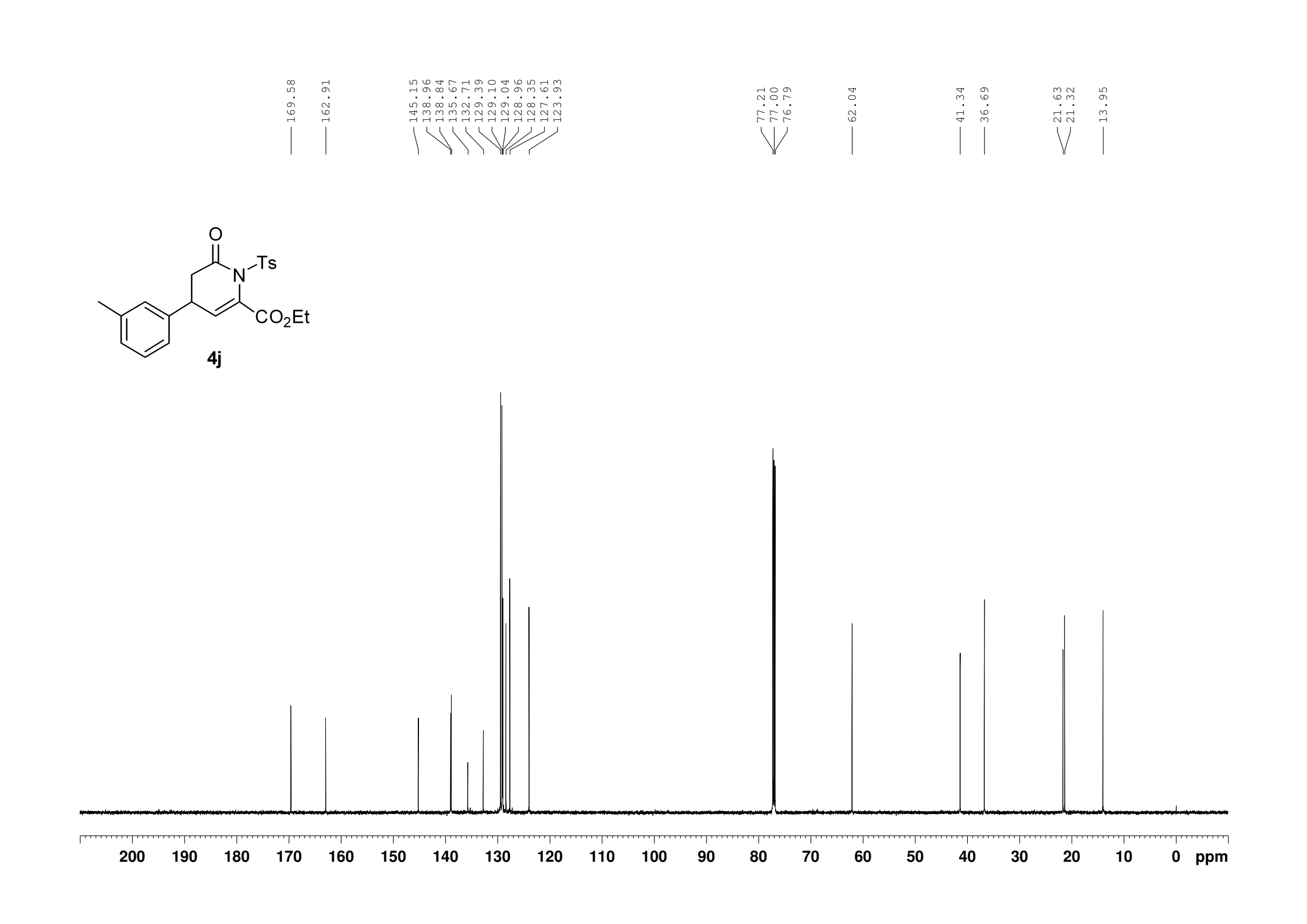
20
10
0
ppm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128.96
128.35
127.61
123.93
77.21
77.00
76.79
62.04
41.34
36.69
21.63
21.32
13.95
O
N
Ts
CO2Et
4j
200
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180
170
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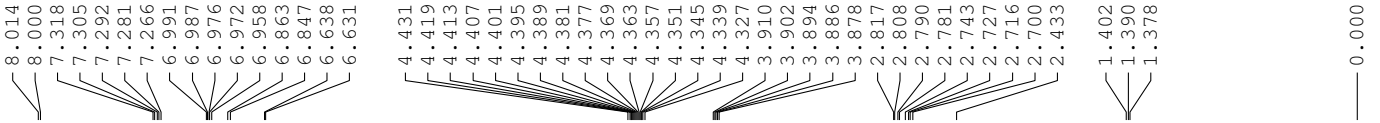
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.958
6.863
6.847
6.638
6.631
4.431
4.419
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4.407
4.401
4.395
4.389
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4.377
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4.363
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4.345
4.339
4.327
3.910
3.902
3.894
3.886
3.878
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2.700
2.433
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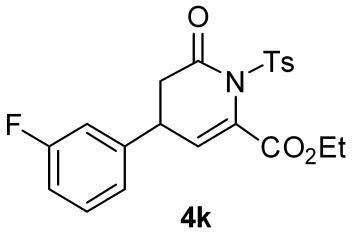
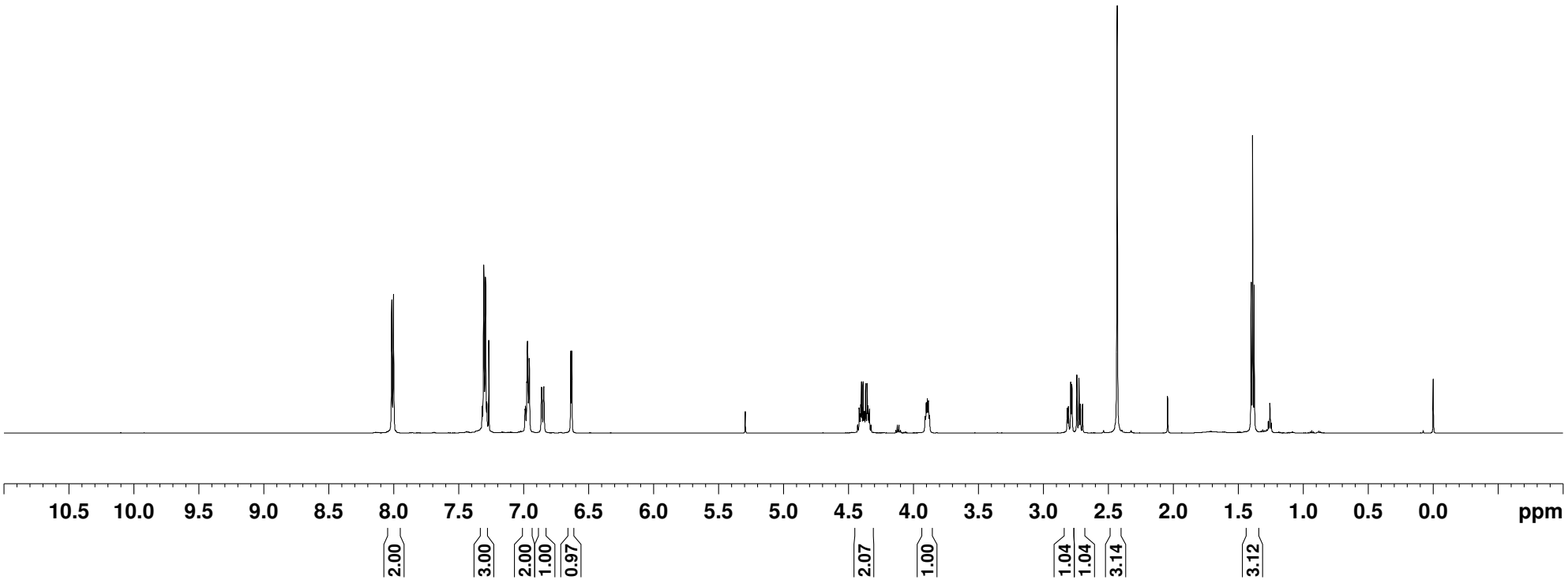
1.390
1.378
0.000


O
N
Ts
F
CO2Et

4k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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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1.00
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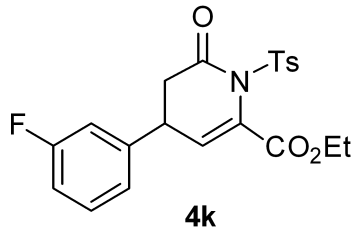
1.04
3.14
3.12


O
Ts
N
F
CO2Et

4k

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114.54
114.07
113.93
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77.00
76.79
62.17
41.02
36.35
21.63
13.95
200
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180
170
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140
130
120
110
100
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60
50
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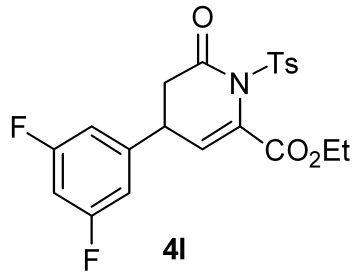
20
10
0
ppm


O
Ts
N
F
F
CO_2Et

4l

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6.723
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6.701
6.690
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6.600
6.592
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4.422
4.416
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4.404
4.399
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4.383
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4.348
4.342
4.330
3.892
3.884
3.876
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2.825
2.817
2.798
2.789
2.723
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2.696
2.680
2.433
1.406
1.394
1.382
10.5 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 0.0 ppm
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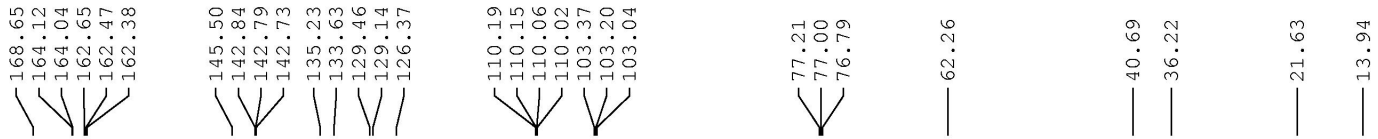
1.02
2.09
1.04
1.06
1.05
3.13
3.22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135.23
133.63
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129.14
126.37
110.19
110.15
110.06
110.02
103.37
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103.04
77.21
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76.79
62.26
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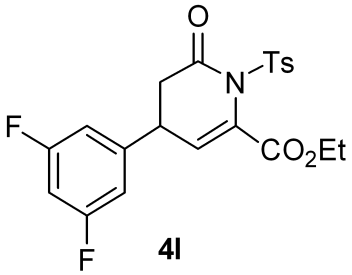
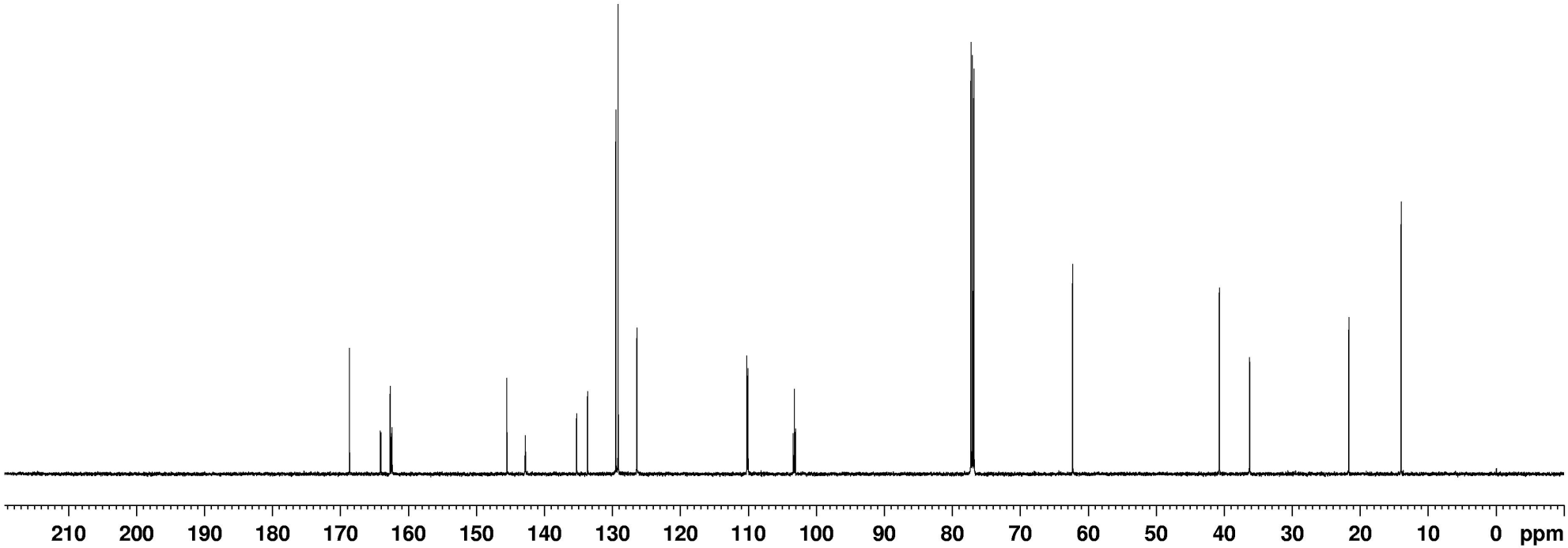
13.94


O
Ts
N
F
CO2Et
F

4l


210
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190
180
170
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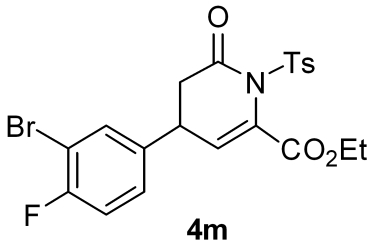
O
N
Ts
Br
CO2Et
F

4m

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7.266
7.112
7.108
7.104
7.098
7.094
7.090
7.087
7.078
7.064
7.050
6.625
6.616
4.435
4.423
4.417
4.411
4.405
4.399
4.393
4.385
4.382
4.373
4.367
4.361
4.355
4.349
4.343
4.332
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3.861
3.853
3.846
3.837
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2.800
2.782
2.773
2.733
2.718
2.706
2.691
2.437
1.407
1.395
1.383
0.000
10.5 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 0.0 ppm
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2.07
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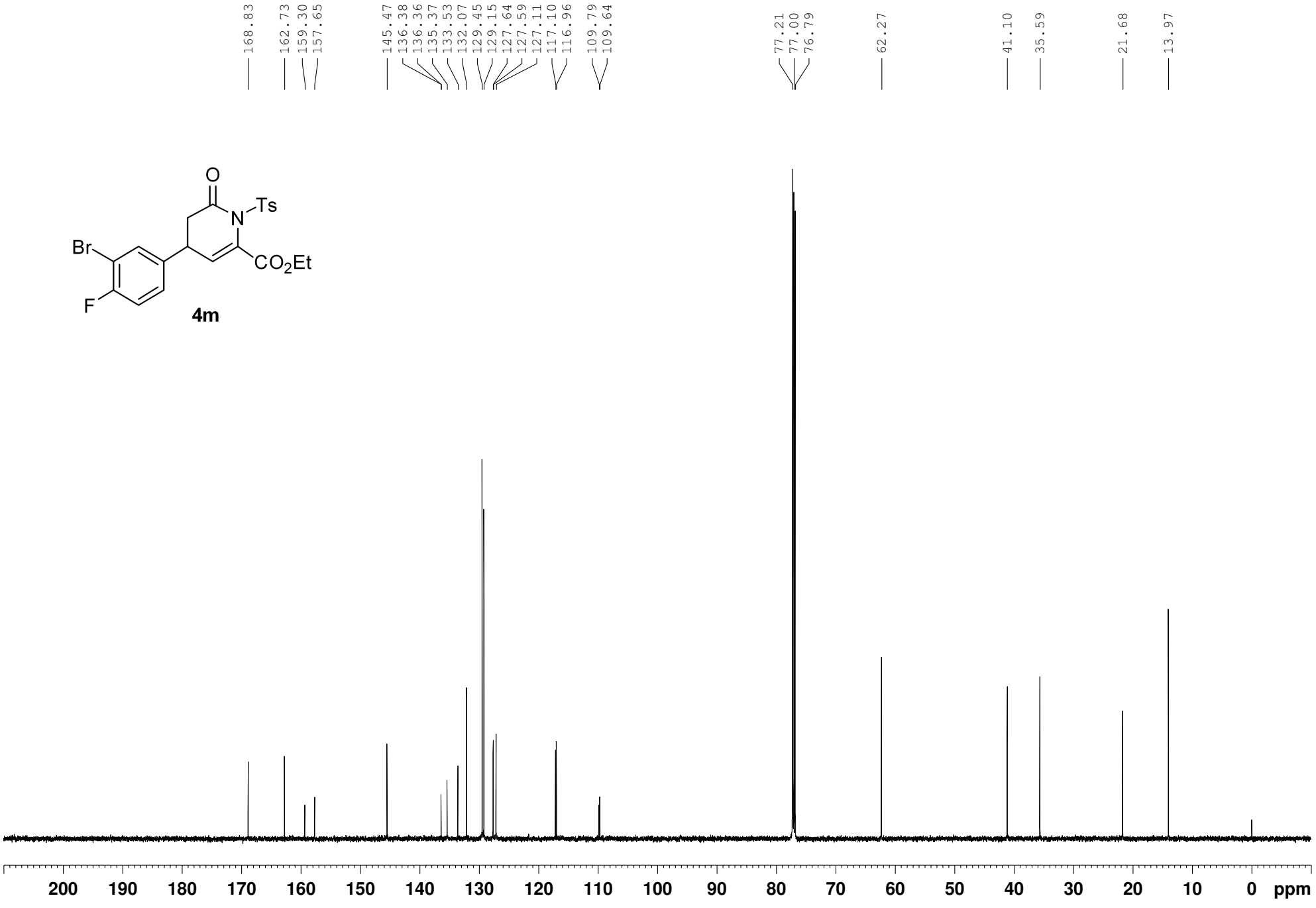
2.12
1.02
2.13
3.10
3.14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127.59
127.11
117.10
116.96
109.79
109.64
77.21
77.00
76.79
62.27
41.10
35.59
21.68
13.97
O
N
Ts
Br
CO2Et
F
4m
200
190
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140
130
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100
90
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60
50
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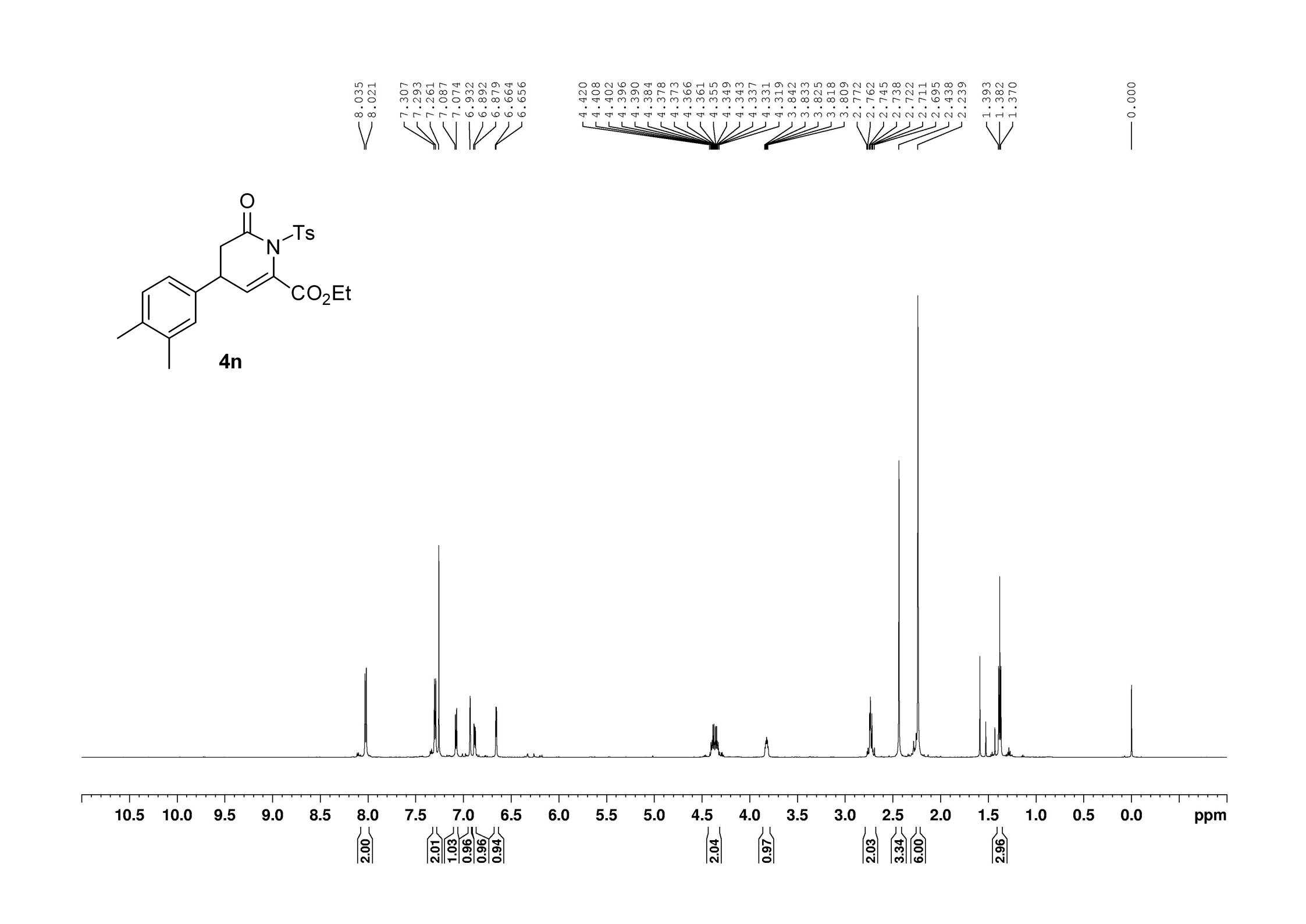
10
0
ppm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4.408
4.402
4.396
4.390
4.384
4.378
4.373
4.366
4.361
4.355
4.349
4.343
4.337
4.331
4.319
3.842
3.833
3.825
3.818
3.809
2.772
2.762
2.745
2.738
2.722
2.711
2.695
2.438
2.239
1.393
1.382
1.370
0.000
O
N
Ts
CO2Et
4n
10.5
10.0
9.5
9.0
8.5
8.0
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
0.0
ppm
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1.03
0.96
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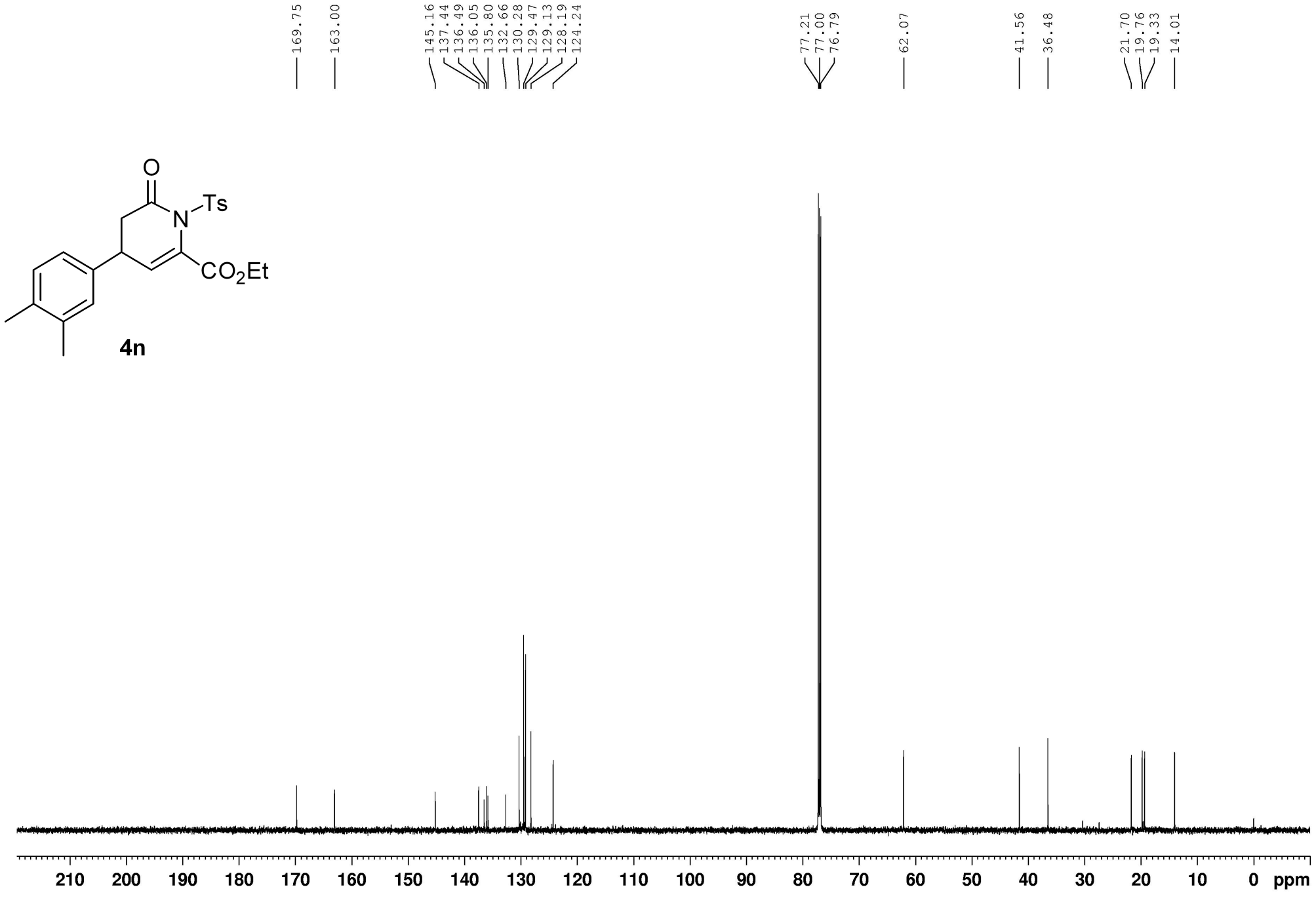
0.94
2.04
0.97
2.03
3.34
6.00
2.96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77.21
77.00
76.79
62.07
41.56
36.48
21.70
19.76
19.33
14.01
O
N
Ts
CO2Et
4n
210
200
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180
170
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140
130
120
110
100
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60
50
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20
10
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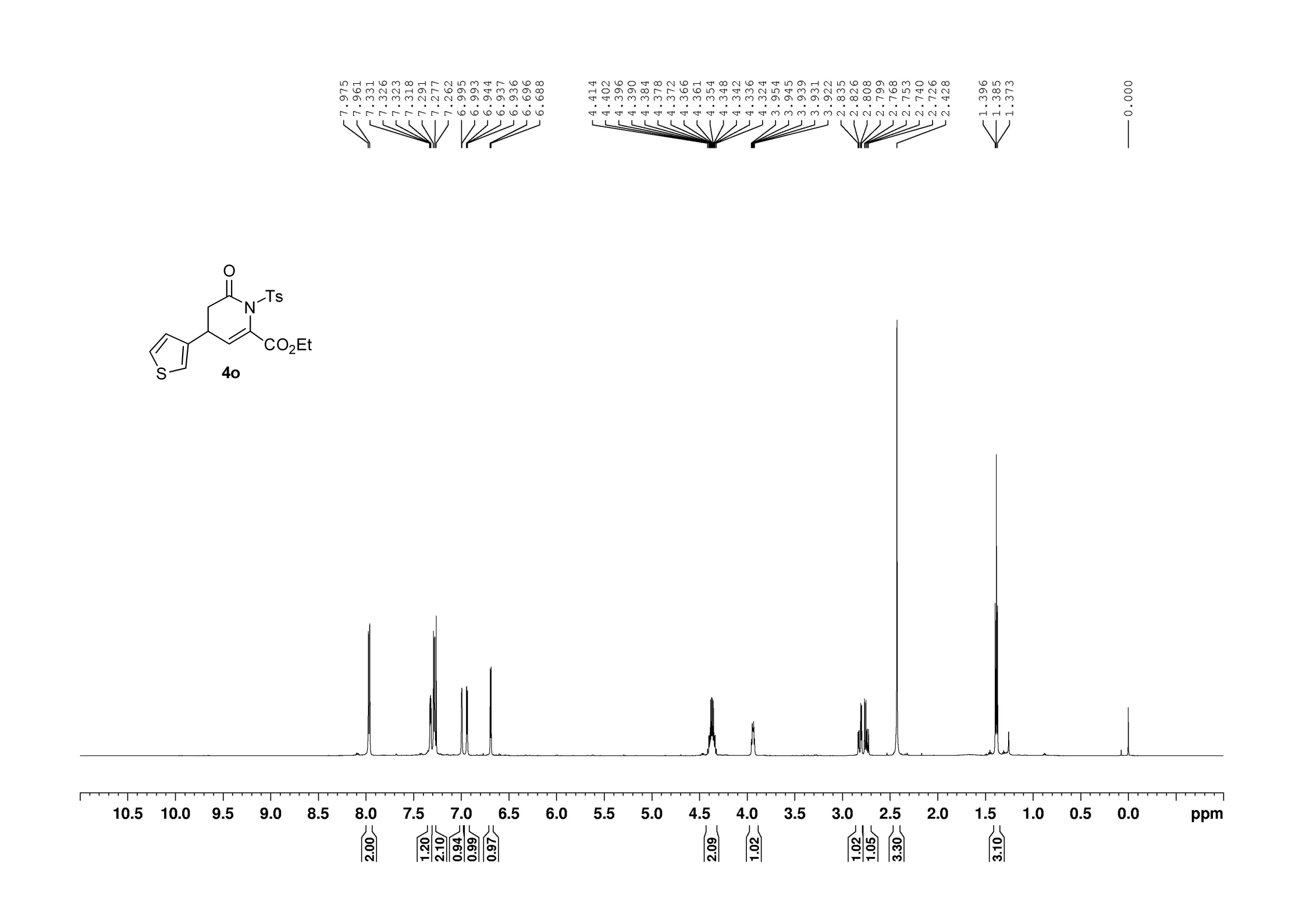
ppm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6.937
6.936
6.696
6.688
4.414
4.402
4.396
4.390
4.384
4.378
4.372
4.366
4.361
4.354
4.348
4.342
4.336
4.324
3.954
3.945
3.939
3.931
3.922
2.835
2.826
2.808
2.799
2.768
2.753
2.740
2.726
2.428
1.396
1.385
1.373
0.000
O
N
Ts
CO2Et
S
4o
10.5
10.0
9.5
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
0.0
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0.97
2.09
1.02
1.02
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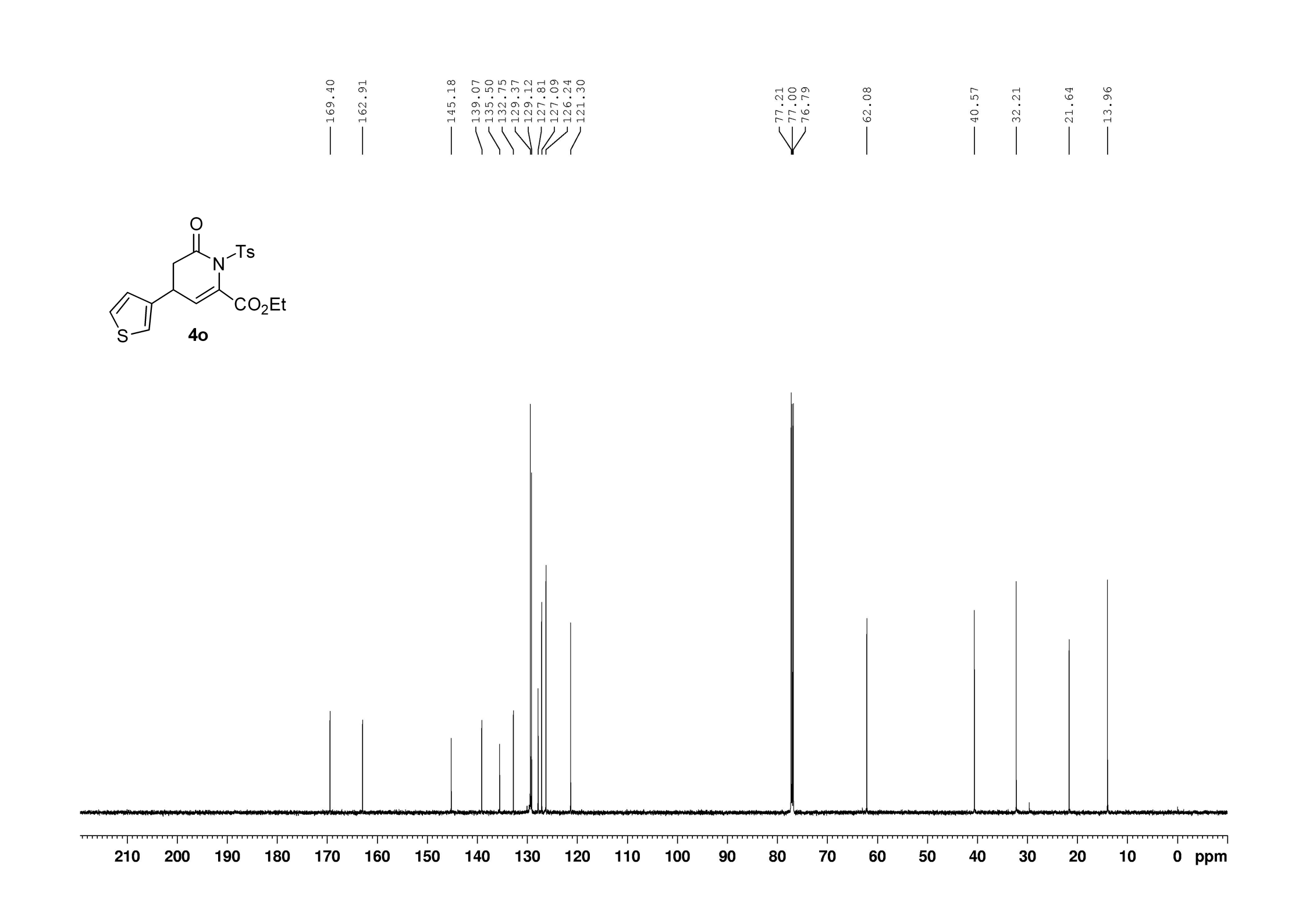
3.10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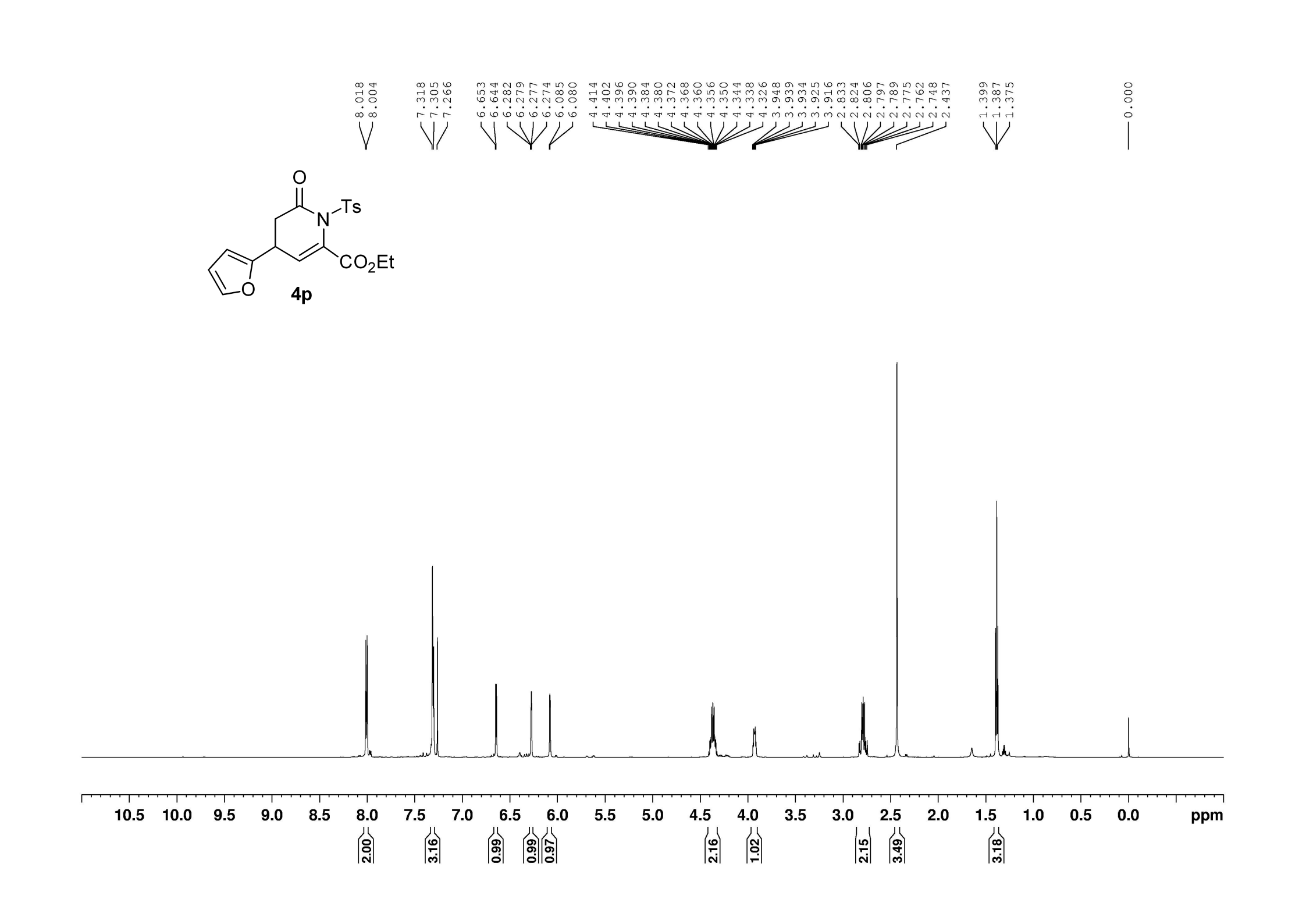
126.24
121.30
77.21
77.00
76.79
62.08
40.57
32.21
21.64
13.96
O
N
Ts
CO2Et
S
4o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.644
6.282
6.279
6.277
6.274
6.085
6.080
4.414
4.402
4.396
4.390
4.384
4.380
4.372
4.368
4.360
4.356
4.350
4.344
4.338
4.326
3.948
3.939
3.934
3.925
3.916
2.833
2.824
2.806
2.797
2.789
2.775
2.762
2.748
2.437
1.399
1.387
1.375
0.000
O
N
Ts
CO2Et
O
4p
10.5 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 0.0 ppm
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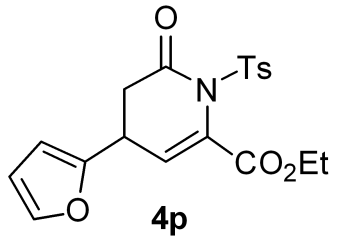
3.16
0.99
0.99
0.97
2.16
1.02
2.15
3.49
3.18



4p

169.04
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151.21
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142.52
135.54
133.22
129.56
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110.42
106.40
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62.15
38.63
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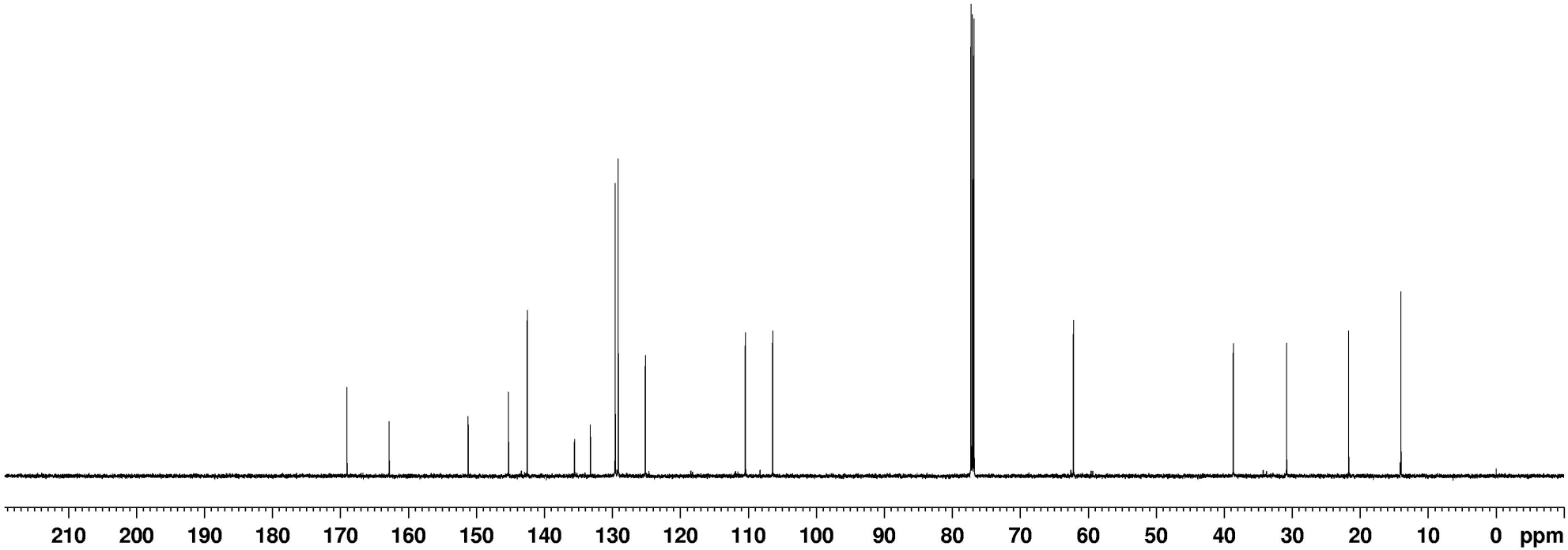
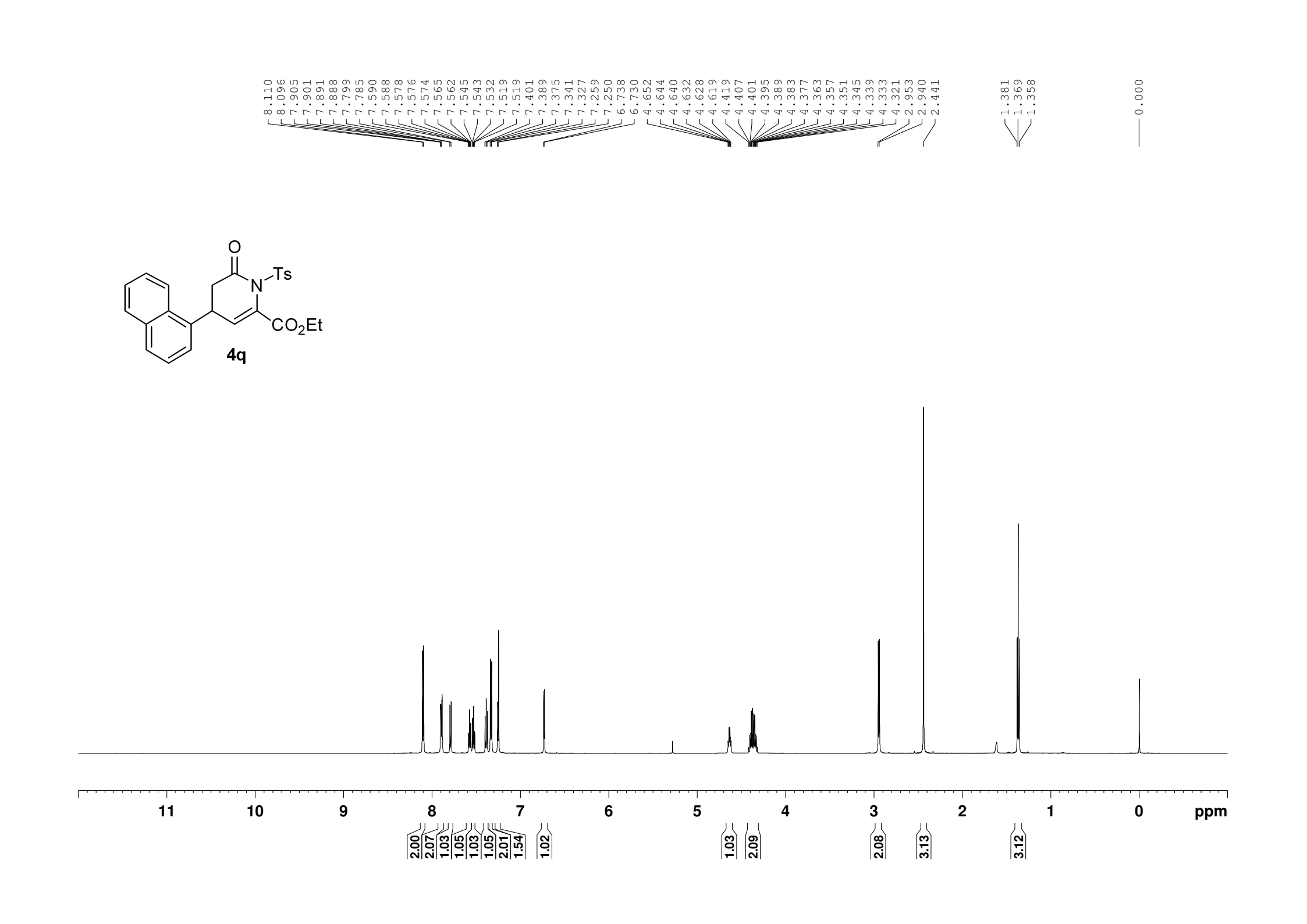
21.66
13.97

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7.588
7.578
7.576
7.574
7.565
7.562
7.545
7.543
7.532
7.519
7.519
7.401
7.389
7.375
7.341
7.327
7.259
7.250
6.738
6.730
4.652
4.644
4.640
4.632
4.628
4.619
4.419
4.407
4.401
4.395
4.389
4.383
4.377
4.363
4.357
4.351
4.345
4.339
4.333
4.321
2.953
2.940
2.441
1.381
1.369
1.358
0.000
O
N
Ts
CO2Et
4q
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.07
1.03
1.05
1.03
1.05
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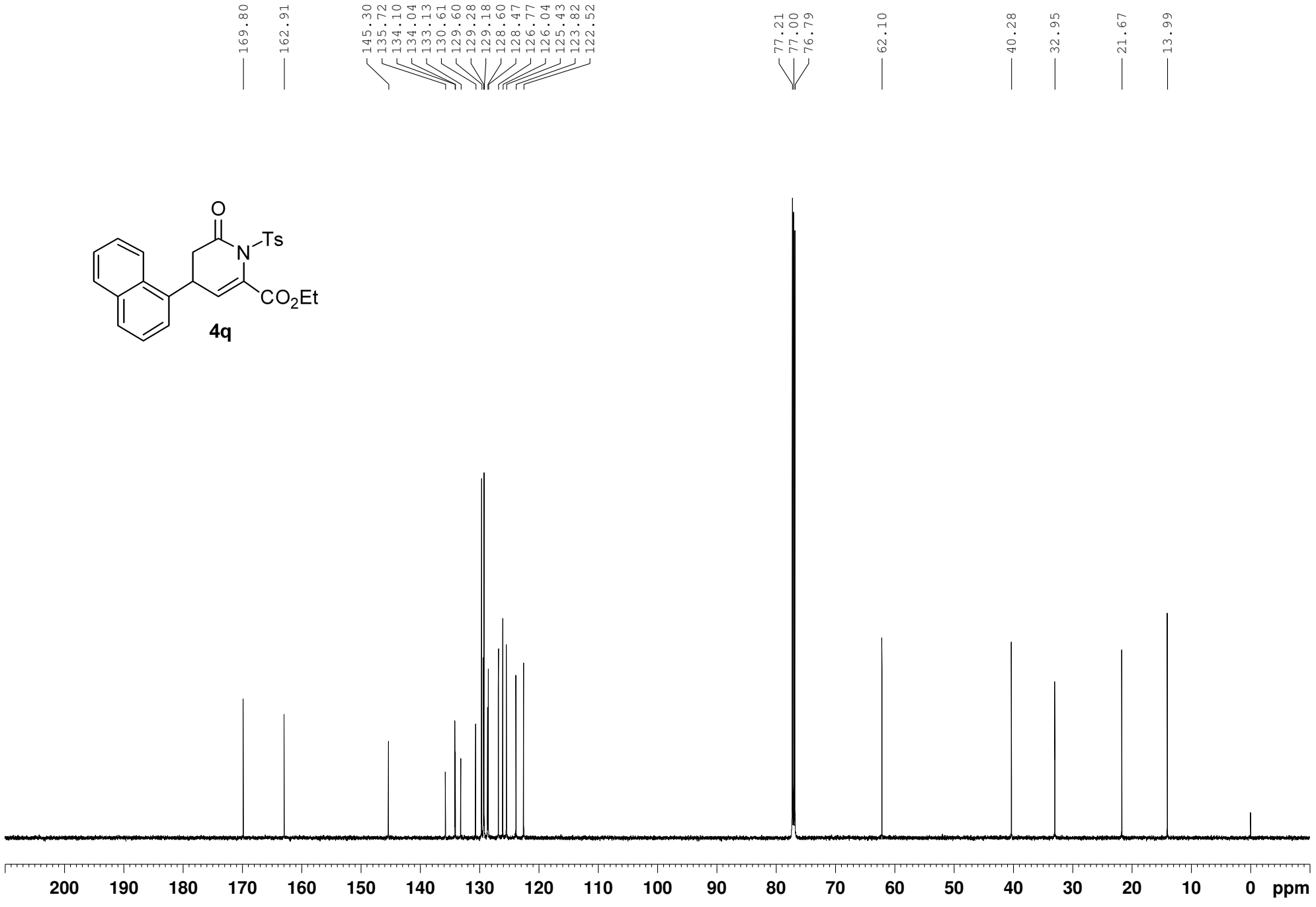
1.54
1.02
1.03
2.09
2.08
3.13
3.12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129.18
128.60
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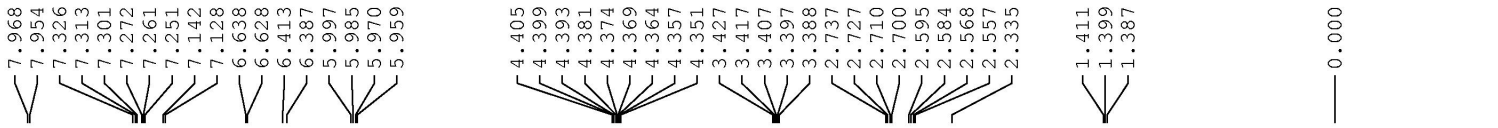
126.77
126.04
125.43
123.82
122.52
77.21
77.00
76.79
62.10
40.28
32.95
21.67
13.99
O
Ts
N
CO2Et
4q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.628
6.413
6.387
5.997
5.985
5.970
5.959
4.405
4.399
4.393
4.381
4.374
4.369
4.364
4.357
4.351
3.427
3.417
3.407
3.397
3.388
2.737
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2.335
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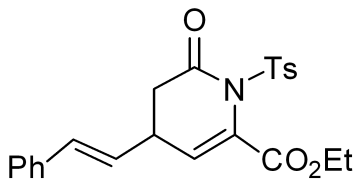
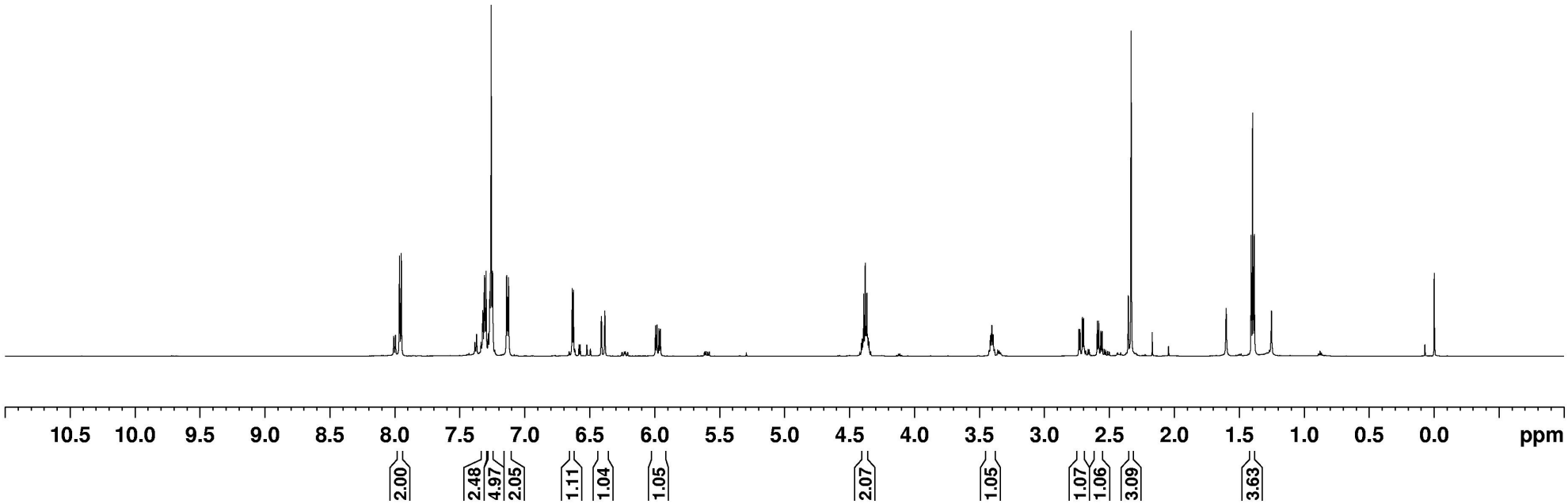
1.399
1.387
0.000


O
N
Ts
Ph
CO2Et

4r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7.0
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6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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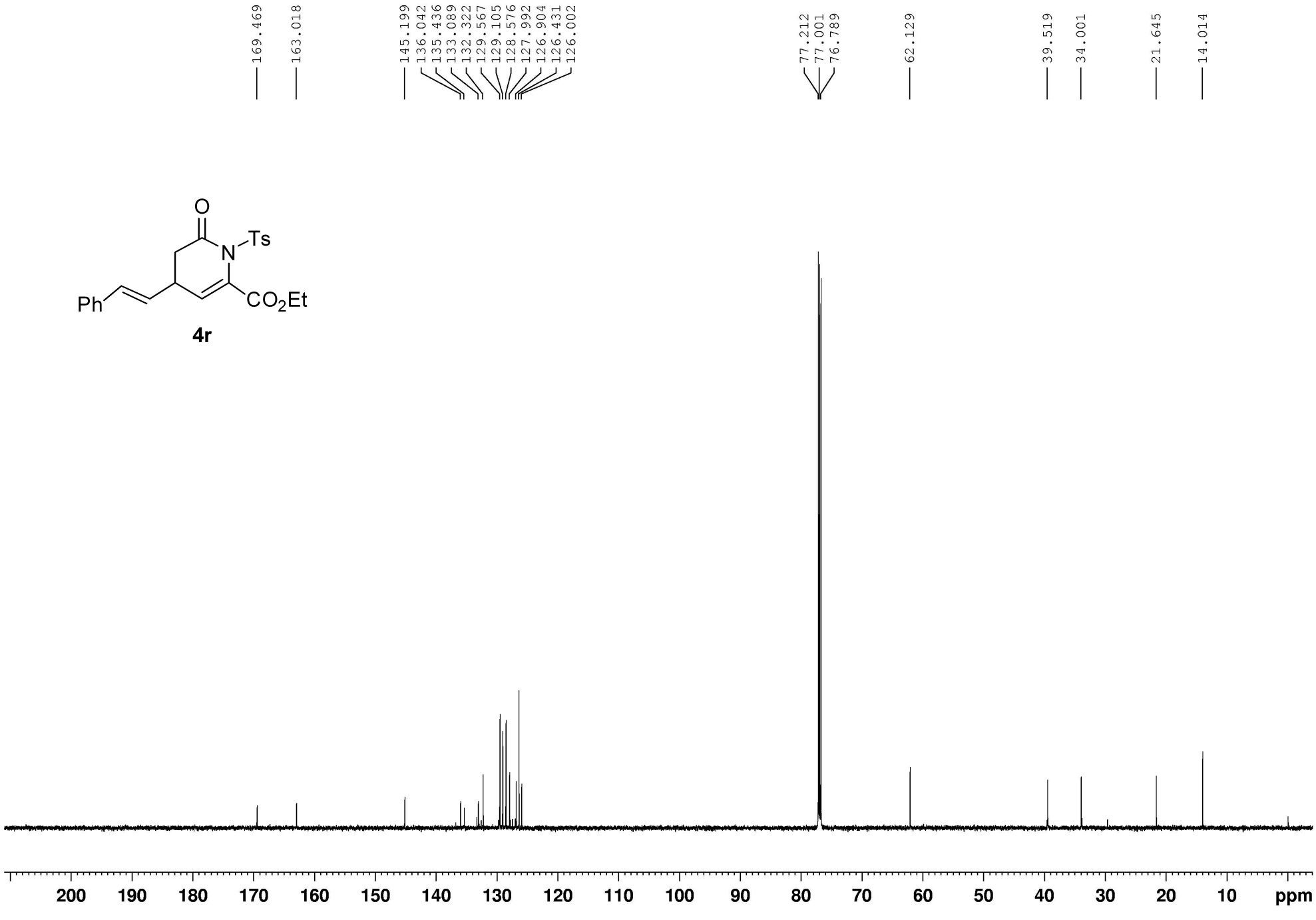
2.05
1.11
1.04
1.05
2.07
1.05
1.07
1.06
3.09
3.63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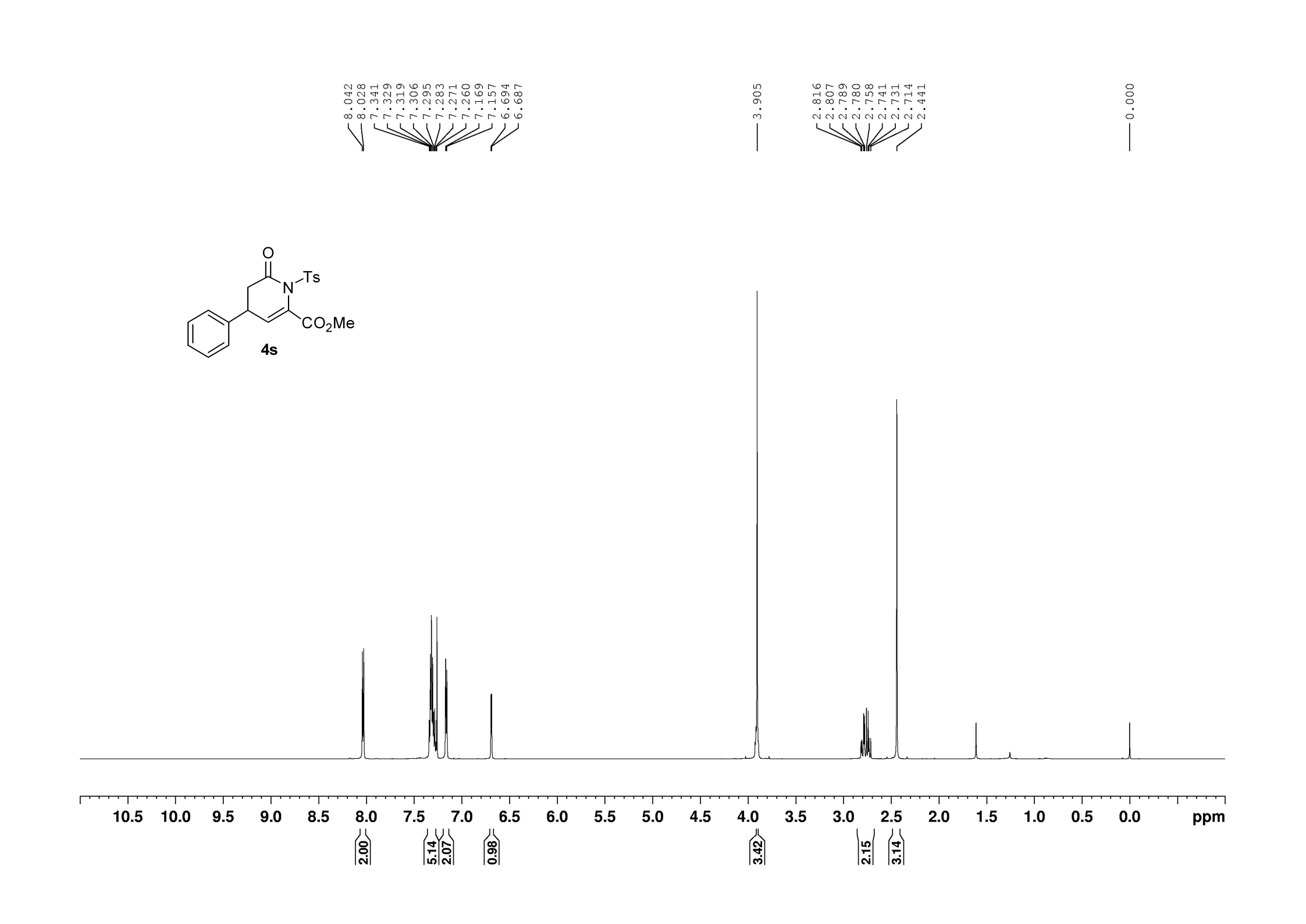
127.992
126.904
126.431
126.002
77.212
77.001
76.789
62.129
39.519
34.001
21.645
14.014
O
N
Ts
Ph
CO2Et
4r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.271
7.260
7.169
7.157
6.694
6.687
3.905
2.816
2.807
2.789
2.780
2.758
2.741
2.731
2.714
2.441
0.000
O
N
Ts
CO2Me
4s
10.5
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
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0.0
ppm
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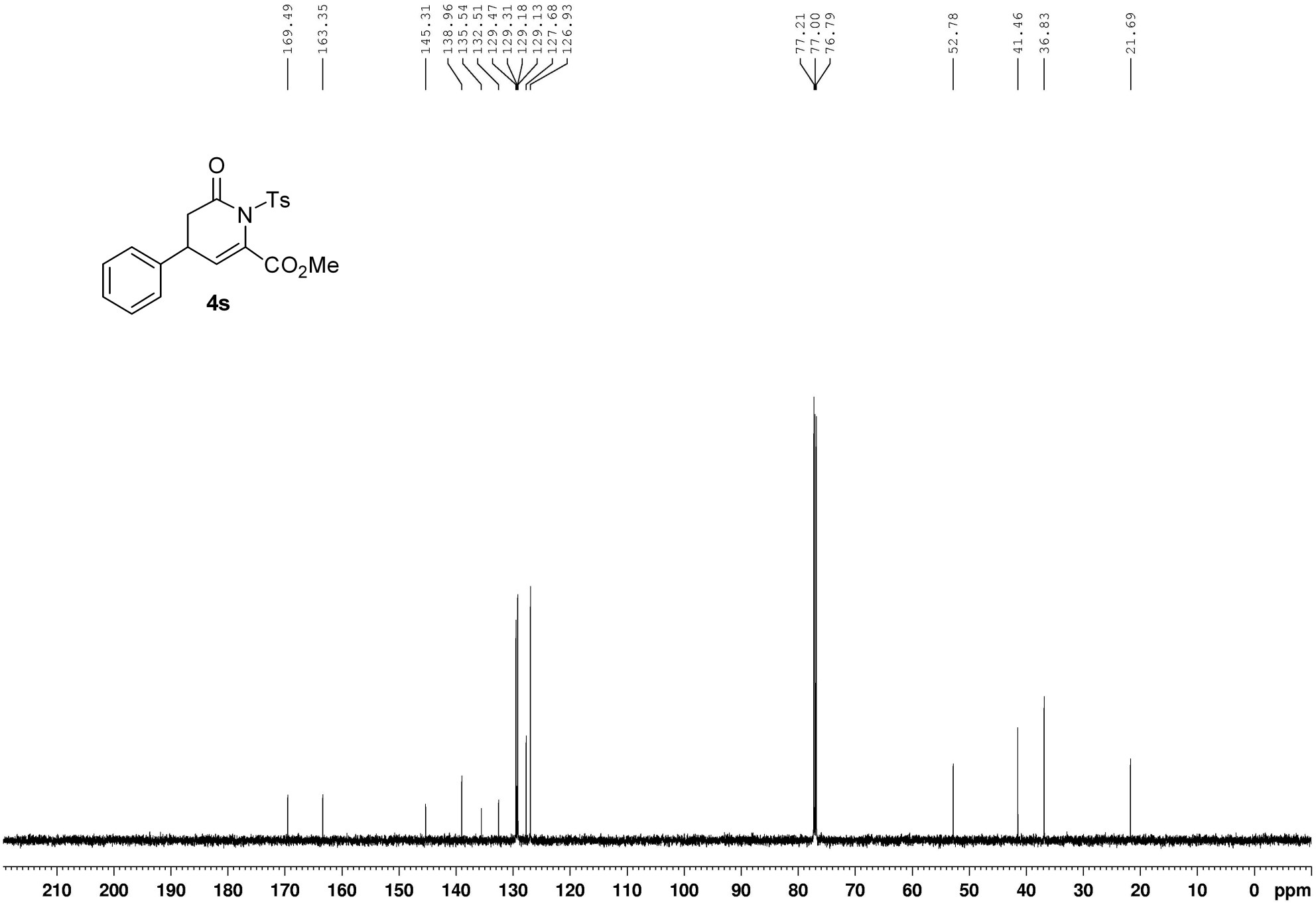
3.14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129.18
129.13
127.68
126.93
77.21
77.00
76.79
52.78
41.46
36.83
21.69
O
N
Ts
CO2Me
4s
210
200
190
180
170
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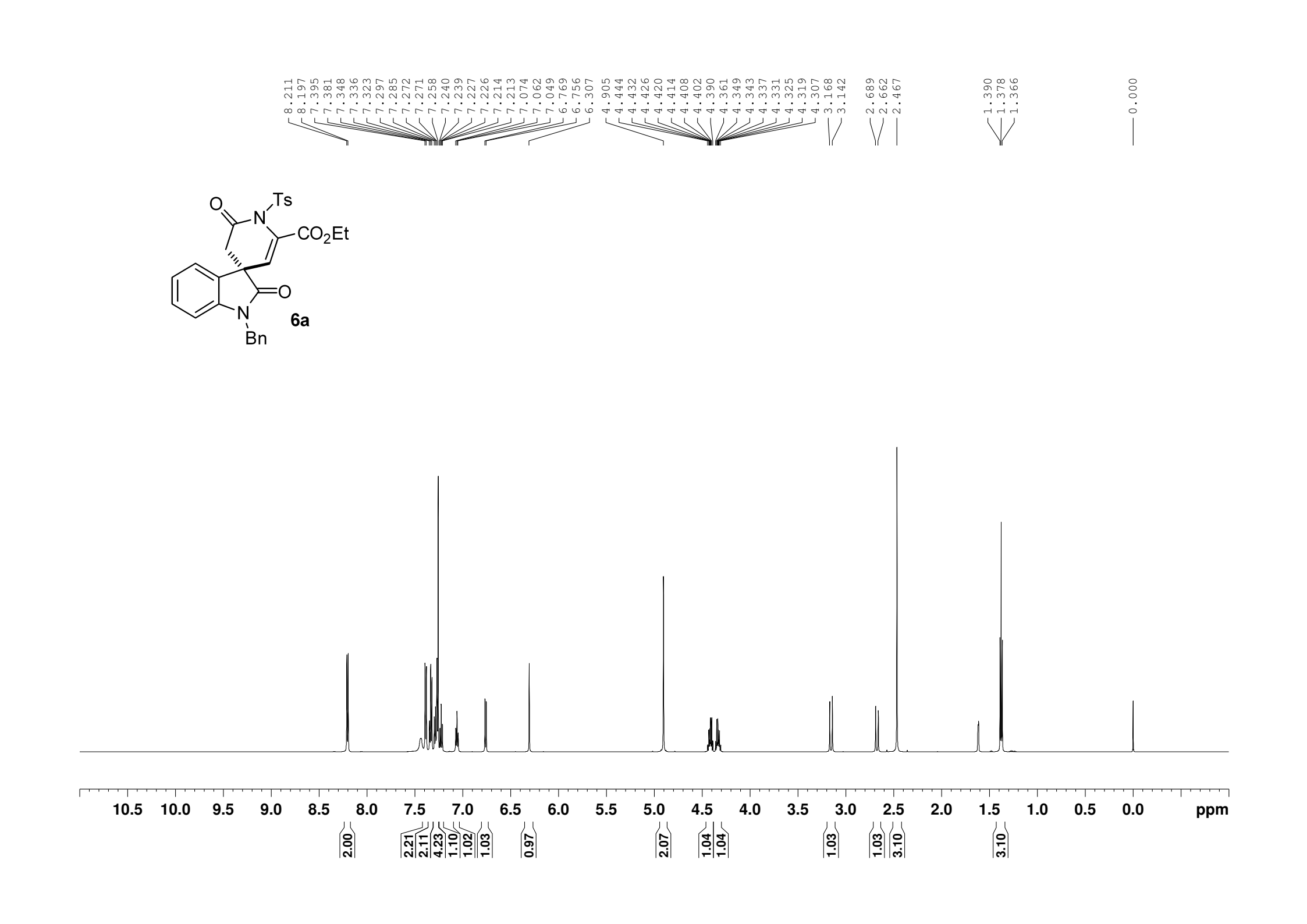
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.258
7.240
7.239
7.227
7.226
7.214
7.213
7.074
7.062
7.049
6.769
6.756
6.307
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4.432
4.426
4.420
4.414
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4.402
4.390
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4.349
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4.337
4.331
4.325
4.319
4.307
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3.142
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1.378
1.366
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Ts
N
O
CO2Et
O
N
Bn
6a
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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
0.0
ppm
2.00
2.21
2.11
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1.03
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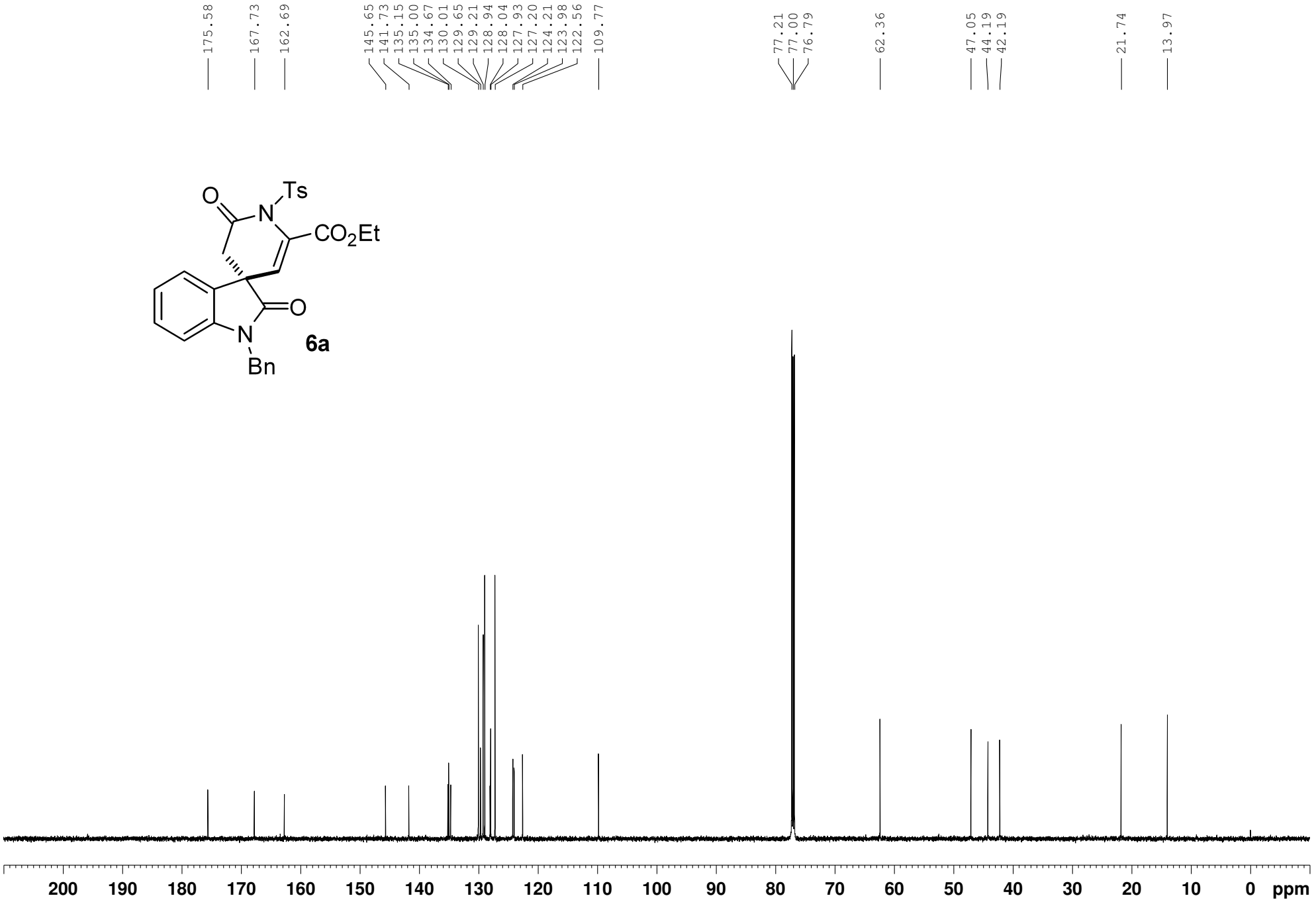
1.04
1.03
1.03
3.10
3.10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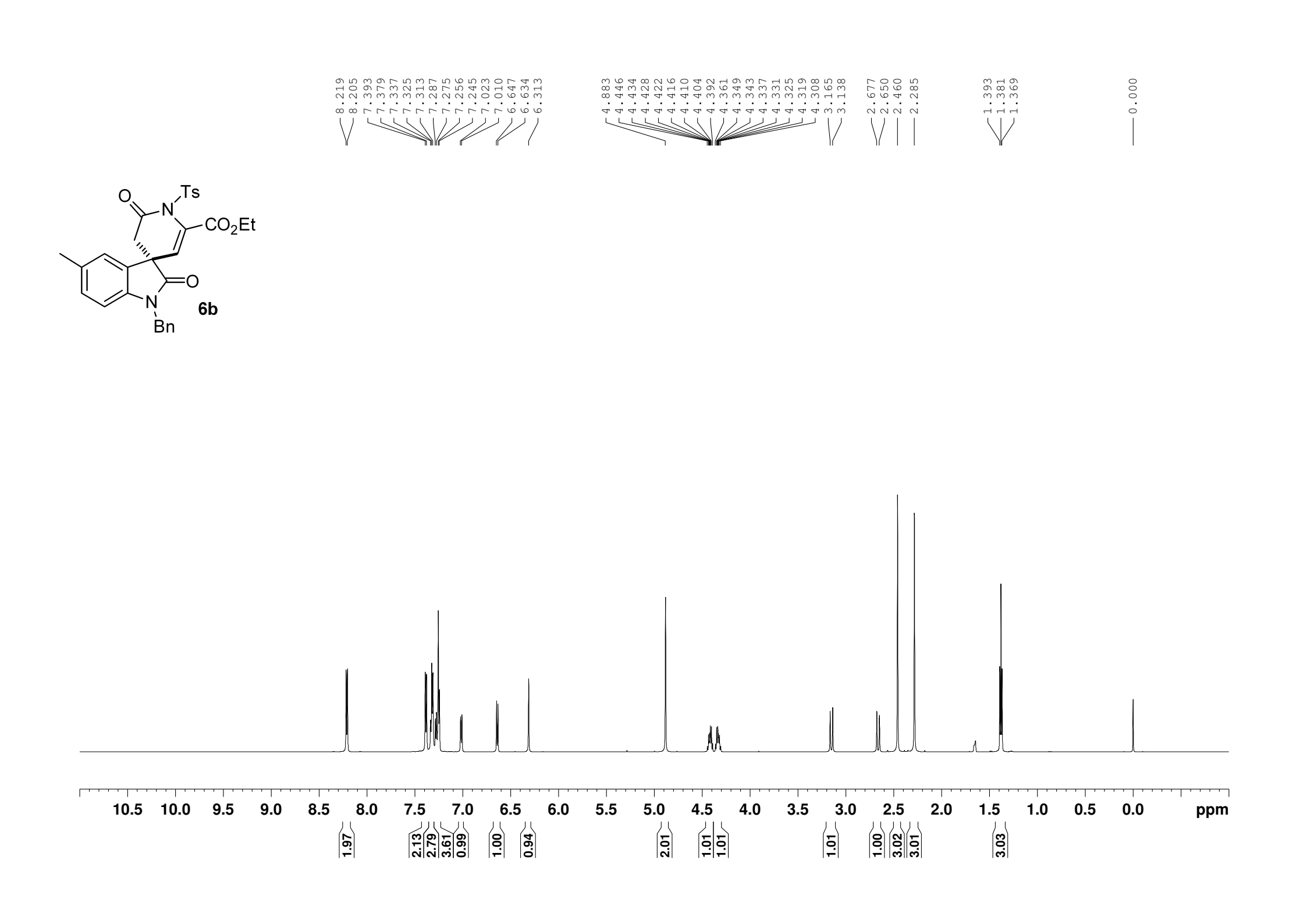
128.04
127.93
127.20
124.21
123.98
122.56
109.77
77.21
77.00
76.79
62.36
47.05
44.19
42.19
21.74
13.97
O
N
Ts
CO2Et
O
N
Bn
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.245
7.023
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6.634
6.313
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4.434
4.428
4.422
4.416
4.410
4.404
4.392
4.361
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4.343
4.337
4.331
4.325
4.319
4.308
3.165
3.138
2.677
2.650
2.460
2.285
1.393
1.381
1.369
0.000
Ts
CO2Et
O
N
O
N
Bn
6b
10.5 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 0.0 ppm
1.97
2.13
2.79
3.61
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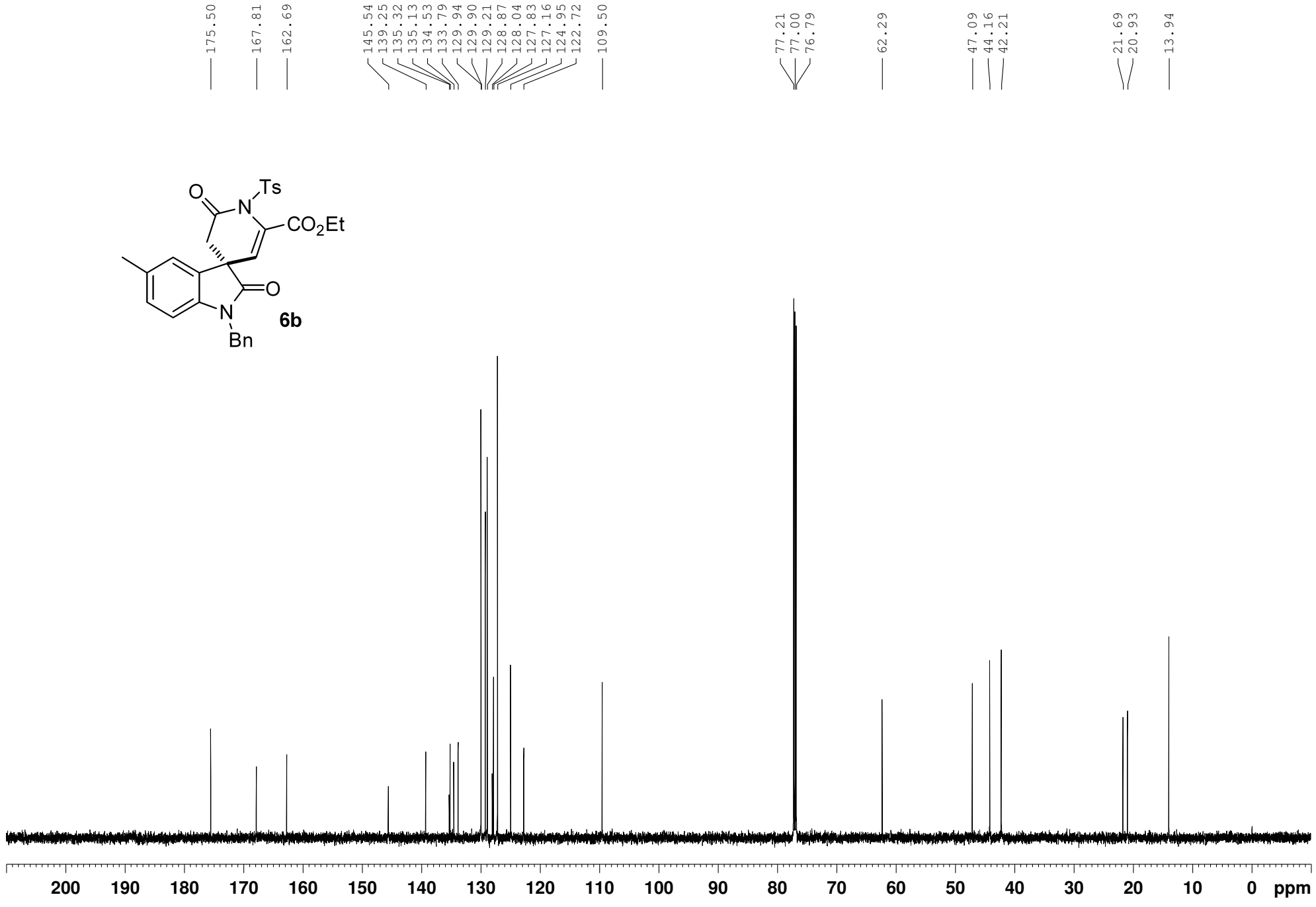
1.00
0.94
2.01
1.01
1.01
1.01
1.00
3.02
3.01
3.03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135.32
135.13
134.53
133.79
129.94
129.90
129.21
128.87
128.04
127.83
127.16
124.95
122.72
109.50
77.21
77.00
76.79
62.29
47.09
44.16
42.21
21.69
20.93
13.94
Ts
N
O
CO2Et
O
N
Bn
6b
200
190
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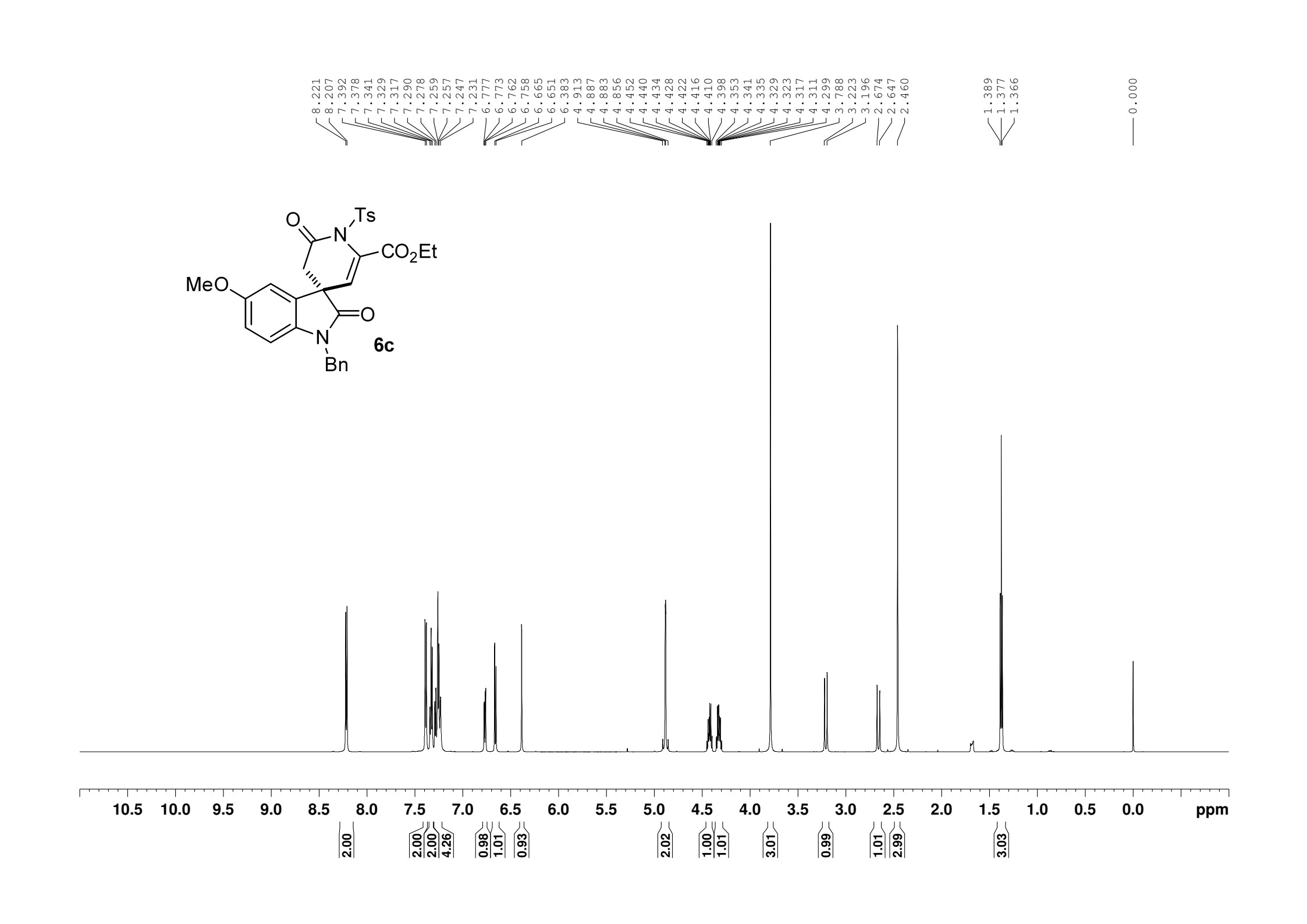
ppm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7.231
6.777
6.773
6.762
6.758
6.665
6.651
6.383
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4.887
4.883
4.856
4.452
4.440
4.434
4.428
4.422
4.416
4.410
4.398
4.353
4.341
4.335
4.329
4.323
4.317
4.311
4.299
3.788
3.223
3.196
2.674
2.647
2.460
1.389
1.377
1.366
0.000
O
N
Ts
CO2Et
MeO
O
N
Bn
6c
10.5
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
0.0
ppm
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2.00
2.00
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3.01
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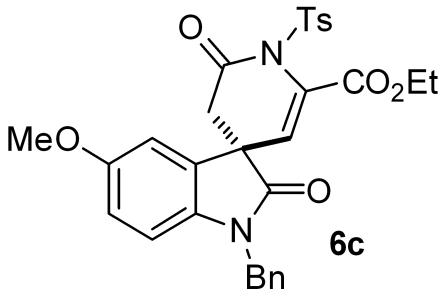
2.99
3.03



6c

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167.93
162.56
157.02
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135.14
135.07
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134.38
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129.24
128.88
128.75
127.85
127.13
123.21
115.81
110.50
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77.21
77.00
76.79
62.32
56.07
47.48
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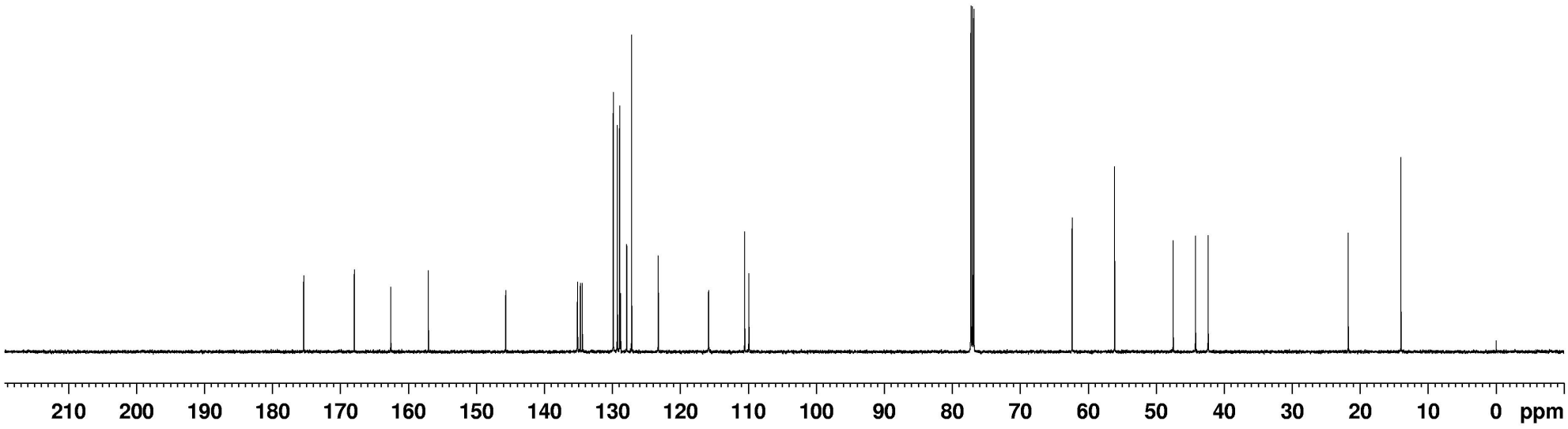
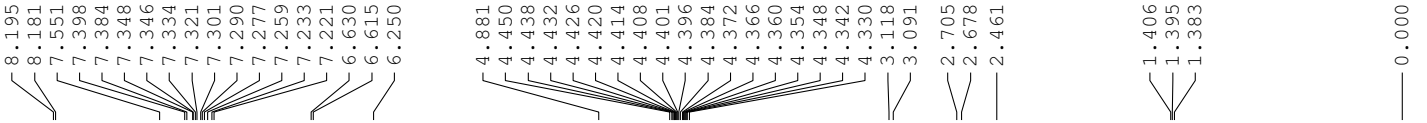
21.71
13.95

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7.277
7.259
7.233
7.221
6.630
6.615
6.250
4.881
4.450
4.438
4.432
4.426
4.420
4.414
4.408
4.401
4.396
4.384
4.372
4.366
4.360
4.354
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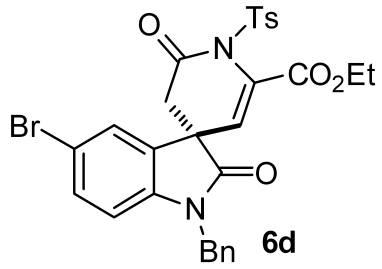
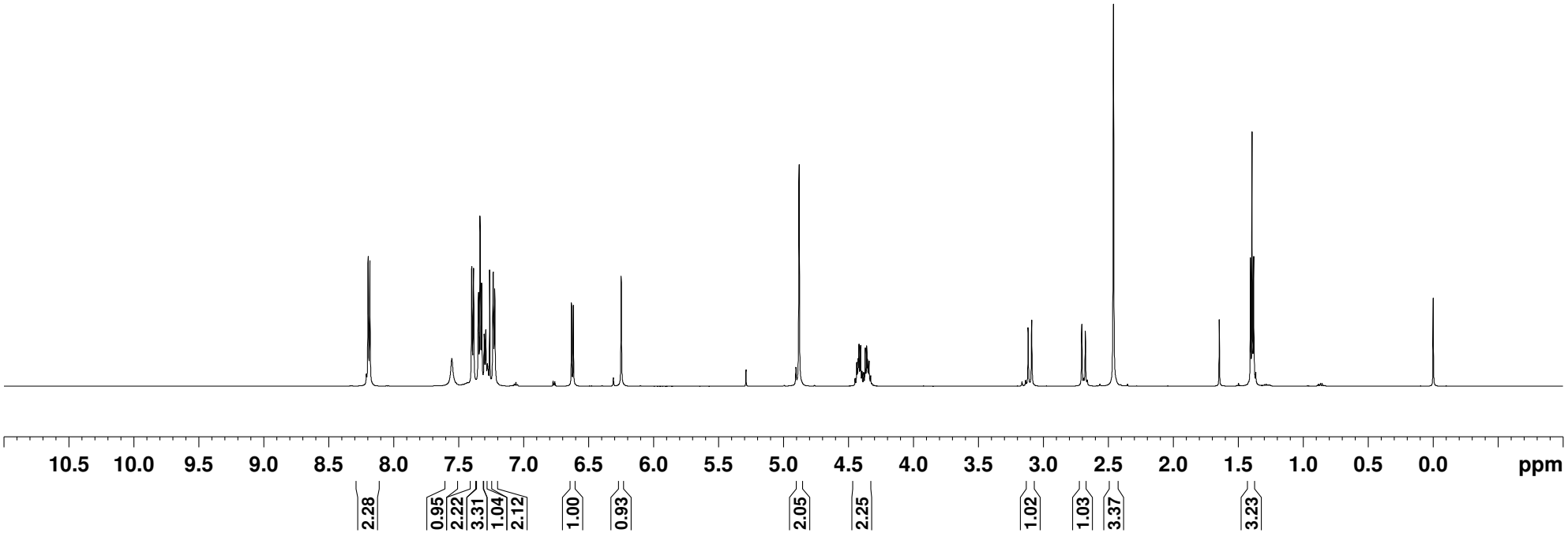
0.000


O
N
Ts
CO2Et
Br
O
N
Bn

6d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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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0.95
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2.12
1.00
0.93
2.05
2.25
1.02
1.03
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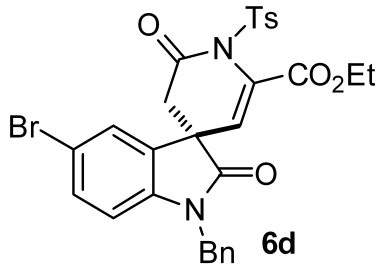
3.23



6d

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162.55
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140.79
135.09
134.95
134.48
132.63
129.97
129.29
129.18
128.99
128.90
128.06
127.29
127.17
127.11
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77.00
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47.00
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41.89
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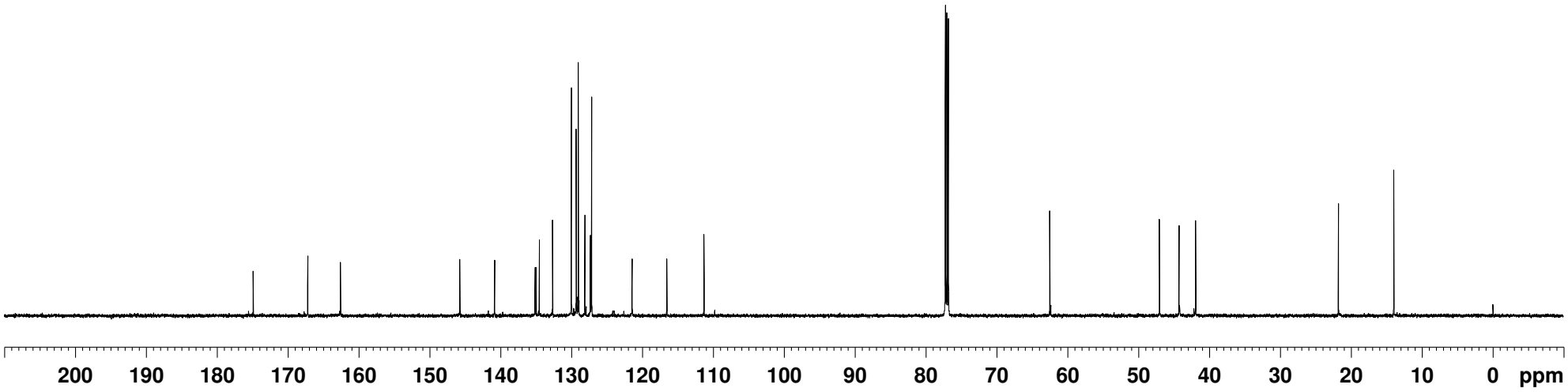
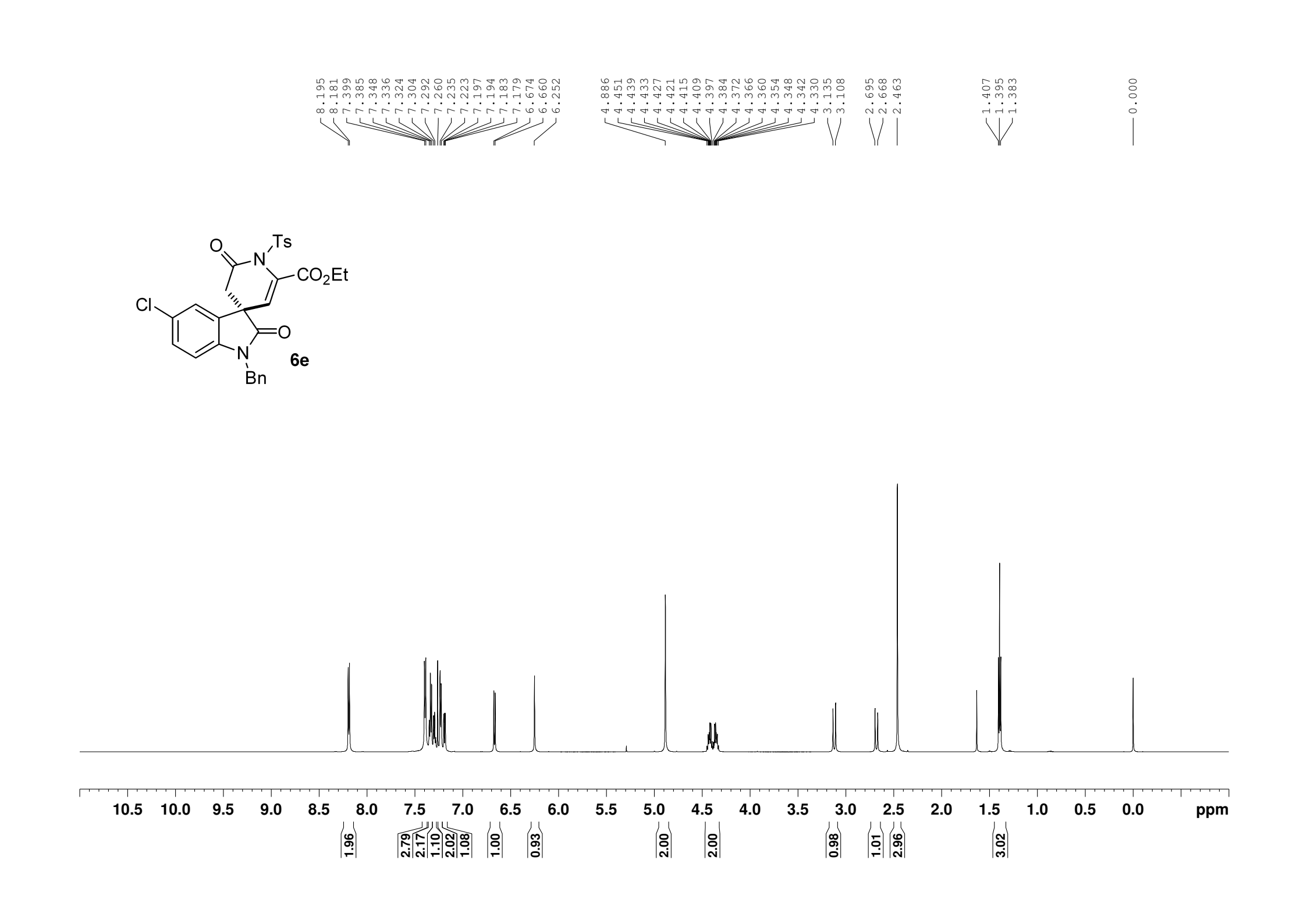
13.94

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7.304
7.292
7.260
7.235
7.223
7.197
7.194
7.183
7.179
6.674
6.660
6.252
4.886
4.451
4.439
4.433
4.427
4.421
4.415
4.409
4.397
4.384
4.372
4.366
4.360
4.354
4.348
4.342
4.330
3.135
3.108
2.695
2.668
2.463
1.407
1.395
1.383
0.000
Ts
N
O
CO2Et
Cl
O
N
Bn
6e
10.5
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
0.0
ppm
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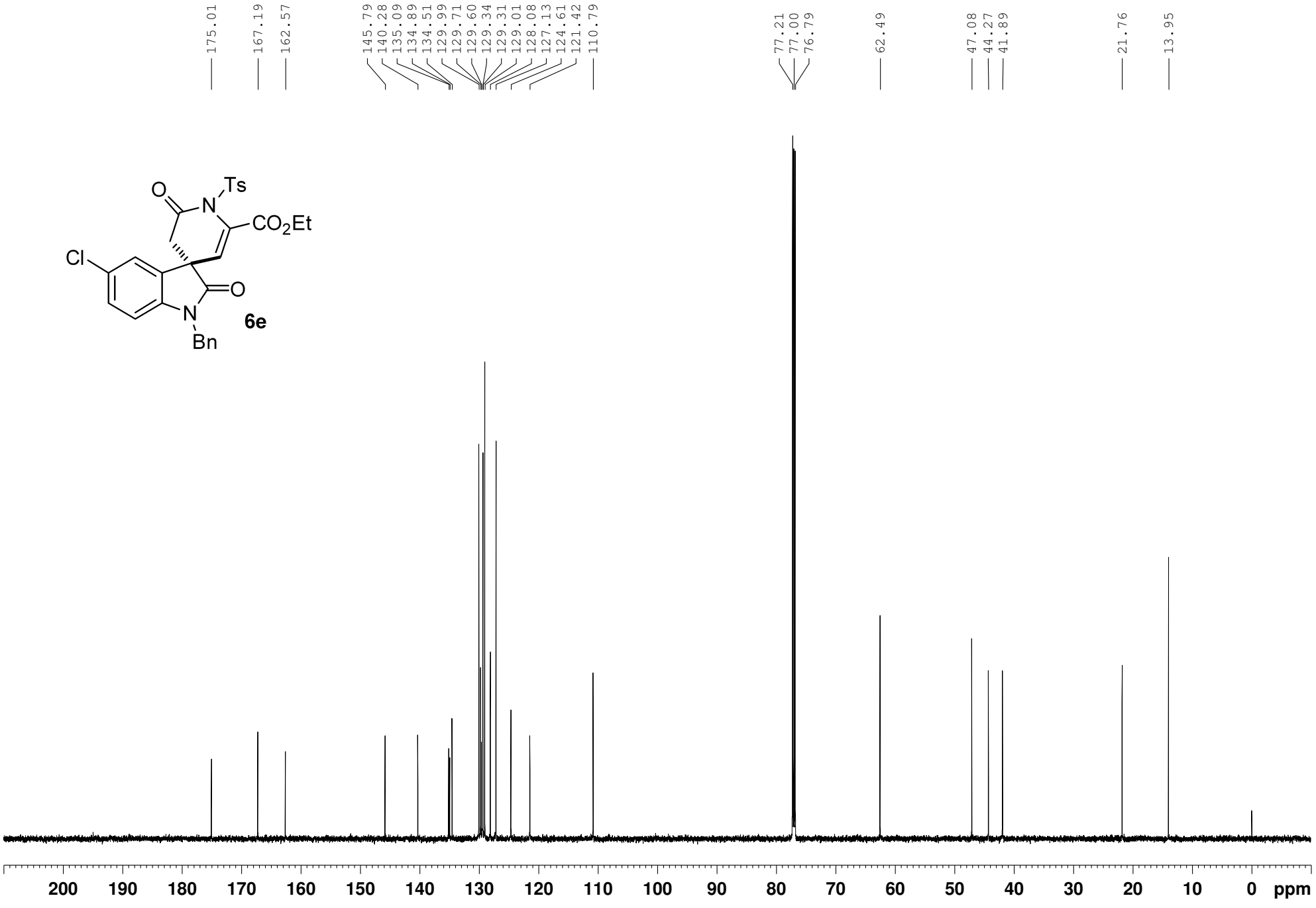
2.00
0.98
1.01
2.96
3.02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134.51
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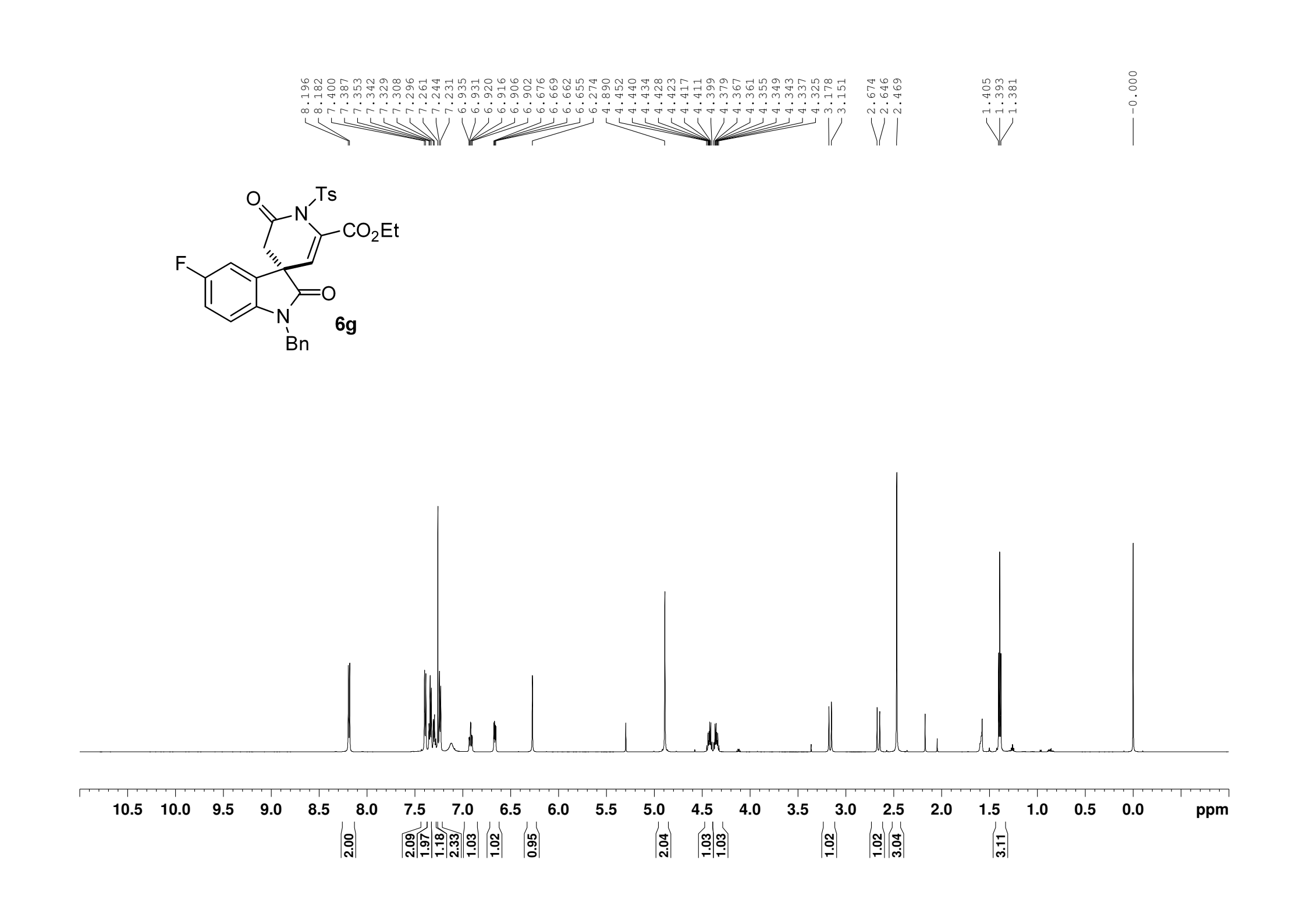
129.34
129.31
129.01
128.08
127.13
124.61
121.42
110.79
77.21
77.00
76.79
62.49
47.08
44.27
41.89
21.76
13.95
O
N
Ts
CO2Et
Cl
O
N
Bn
6e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.308
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7.261
7.244
7.231
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6.931
6.920
6.916
6.906
6.902
6.676
6.669
6.662
6.655
6.274
4.890
4.452
4.440
4.434
4.428
4.423
4.417
4.411
4.399
4.379
4.367
4.361
4.355
4.349
4.343
4.337
4.325
3.178
3.151
2.674
2.646
2.469
1.405
1.393
1.381
0.000
Ts
N
O
CO2Et
F
O
N
Bn
6g
10.5 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 0.0 ppm
2.00
2.09
1.97
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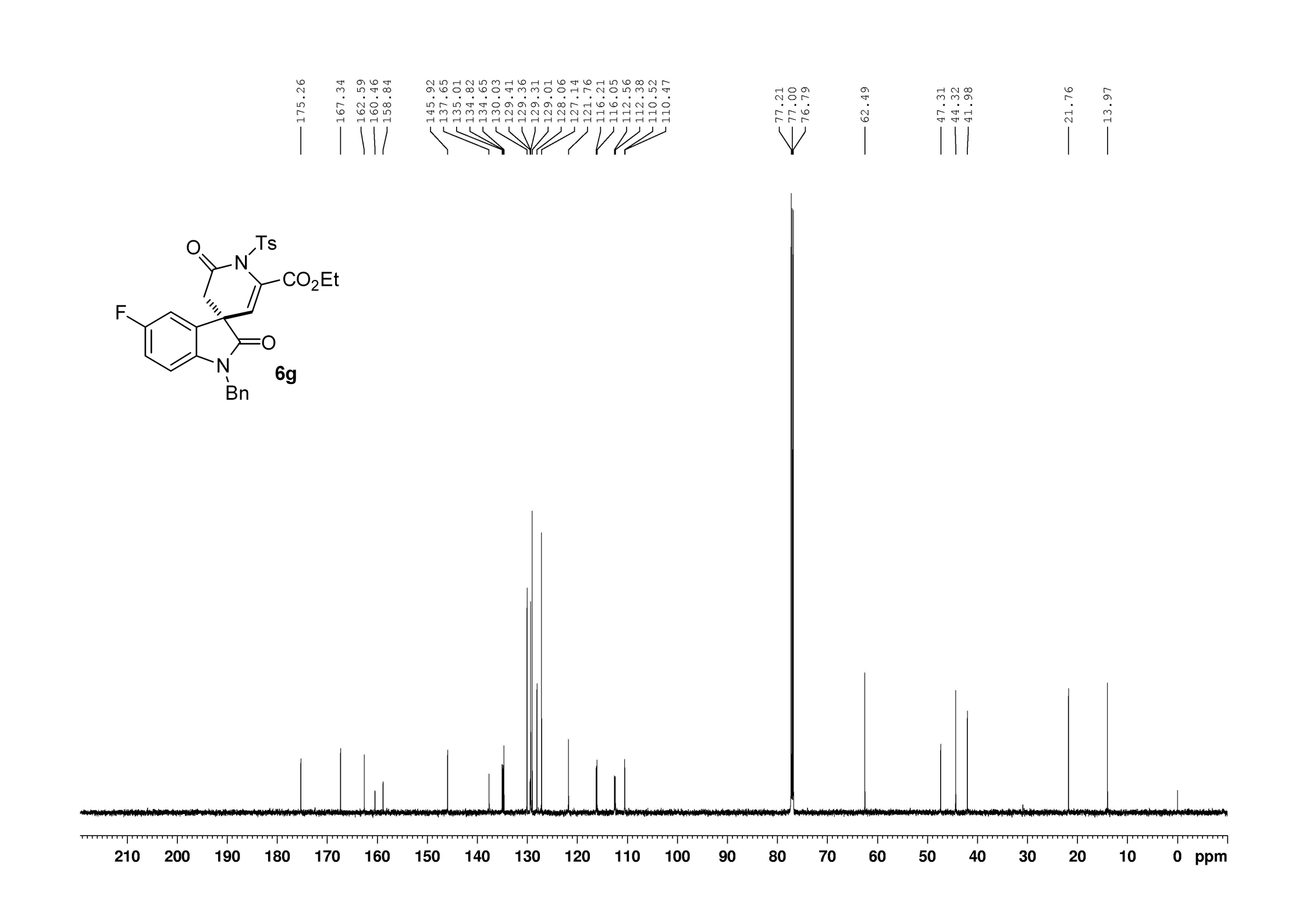
1.03
1.02
0.95
2.04
1.03
1.03
1.02
1.02
3.04
3.11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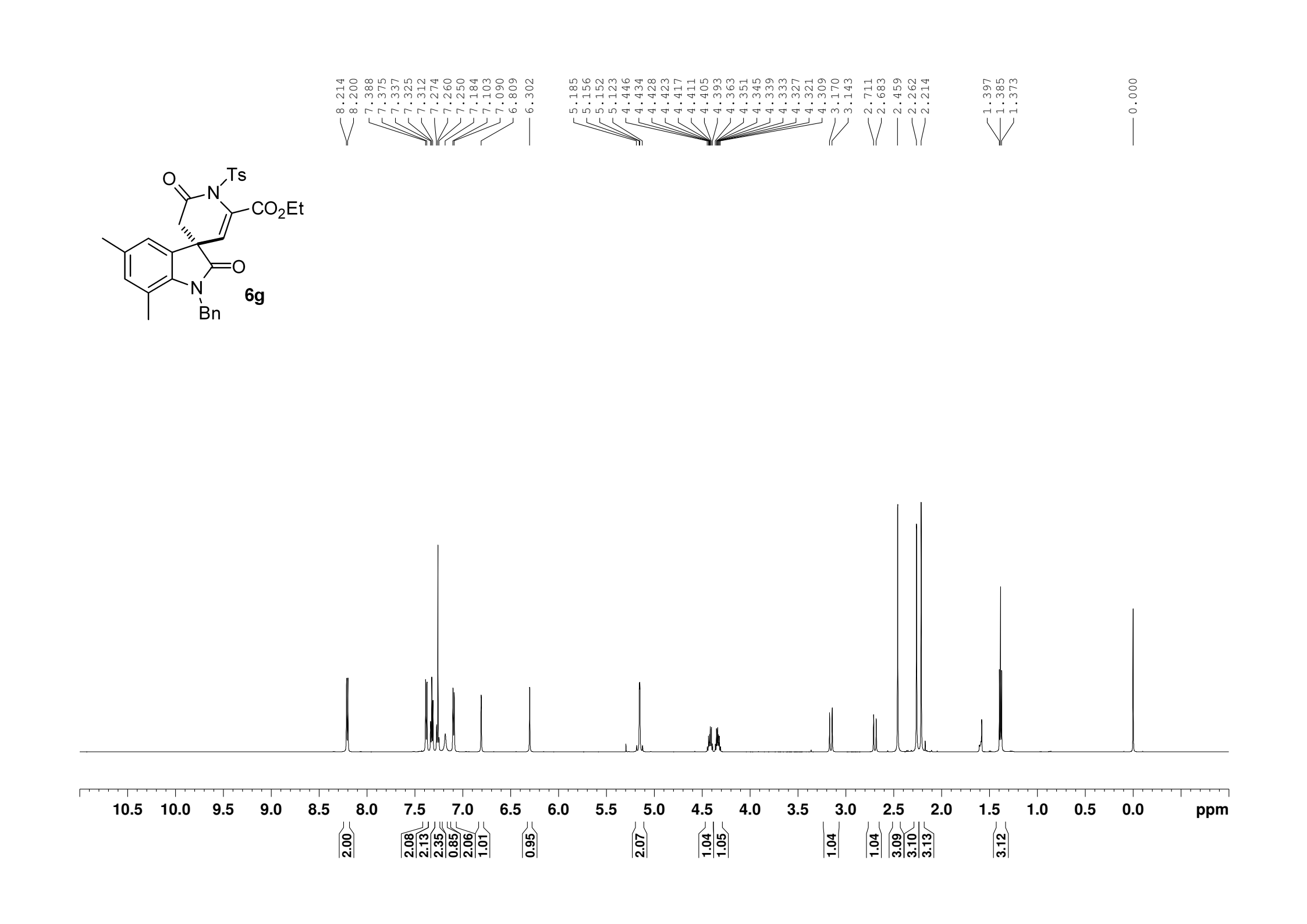
129.36
129.31
129.01
128.06
127.14
121.76
116.21
116.05
112.56
112.38
110.52
110.47
77.21
77.00
76.79
62.49
47.31
44.32
41.98
21.76
13.97
Ts
N
O
CO2Et
F
O
N
Bn
6g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.325
7.312
7.274
7.260
7.250
7.184
7.103
7.090
6.809
6.302
5.185
5.156
5.152
5.123
4.446
4.434
4.428
4.423
4.417
4.411
4.405
4.393
4.363
4.351
4.345
4.339
4.333
4.327
4.321
4.309
3.170
3.143
2.711
2.683
2.459
2.262
2.214
1.397
1.385
1.373
0.000
Ts
CO2Et
O
N
O
N
Bn
6g
10.5 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 0.0 ppm
2.00
2.08
2.13
2.35
0.85
2.06
1.01
0.95
2.07
1.04
1.05
1.04
1.04
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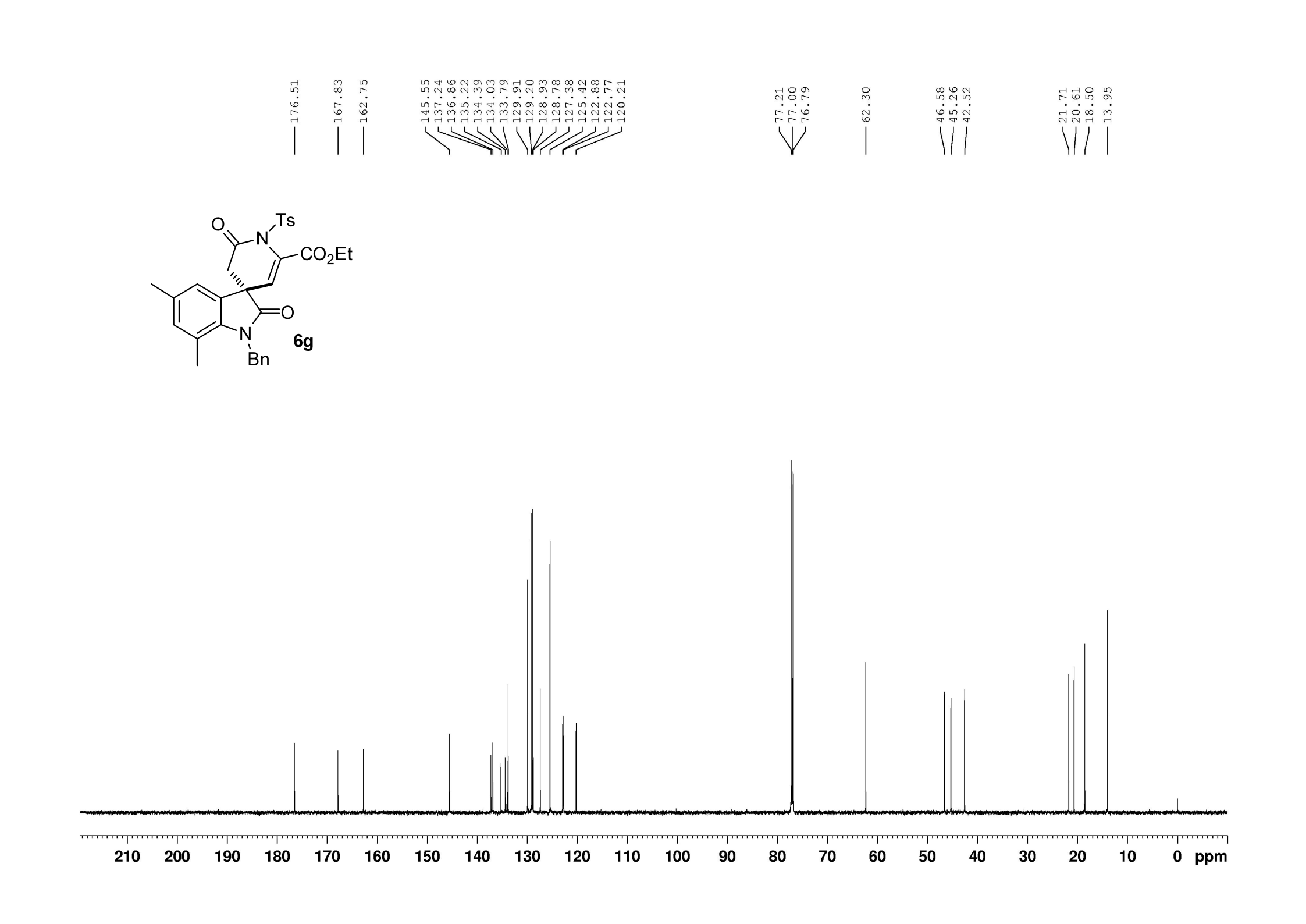
3.10
3.13
3.12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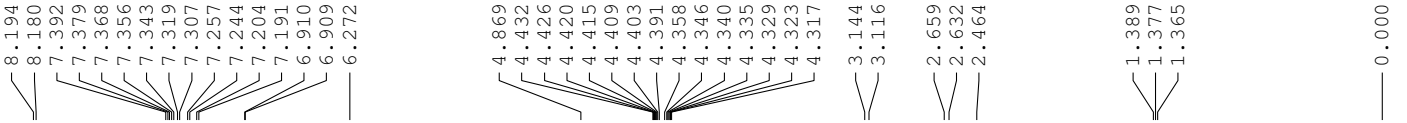
128.93
128.78
127.38
125.42
122.88
122.77
120.21
77.21
77.00
76.79
62.30
46.58
45.26
42.52
21.71
20.61
18.50
13.95
O
N
Ts
CO2Et
O
N
Bn
6g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.319
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7.257
7.244
7.204
7.191
6.910
6.909
6.272
4.869
4.432
4.426
4.420
4.415
4.409
4.403
4.391
4.358
4.346
4.340
4.335
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2.632
2.464
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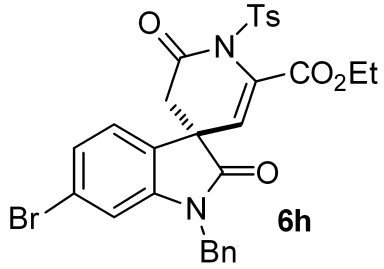
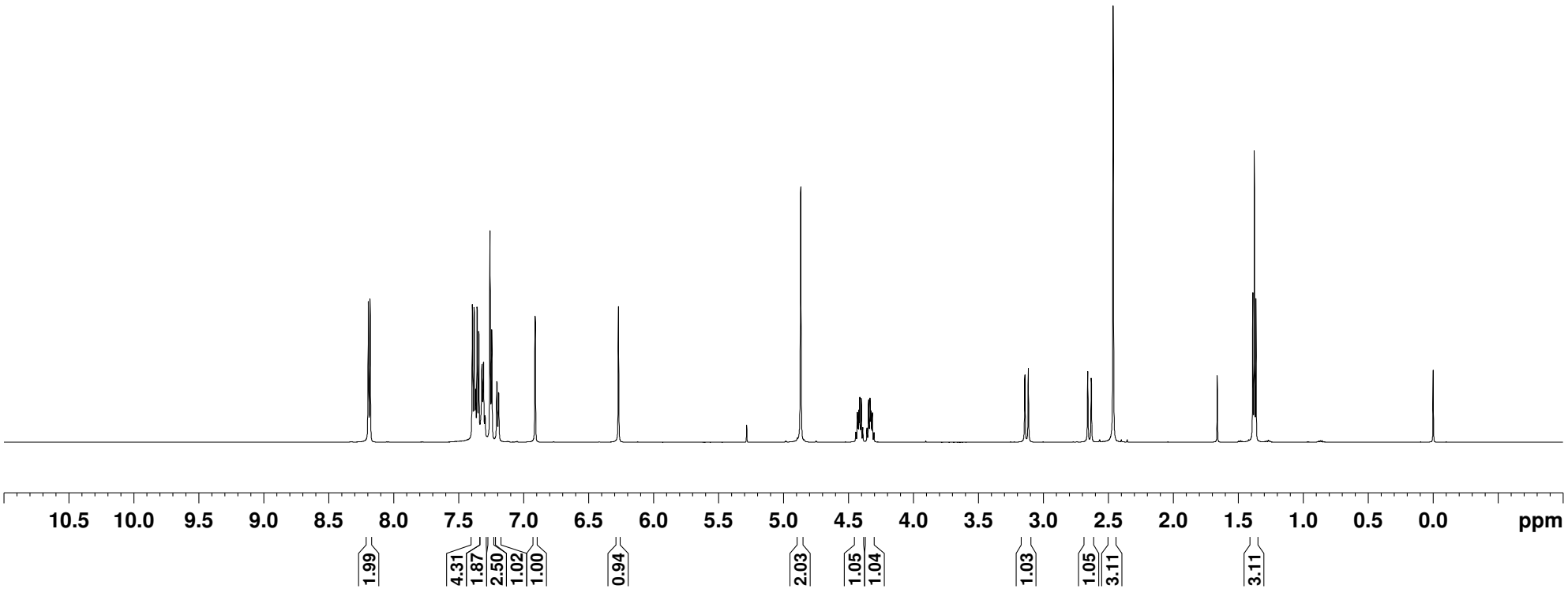
1.377
1.365
0.000


O
N
Ts
CO2Et
O
Br
N
Bn

6h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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
ppm
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4.31
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1.00
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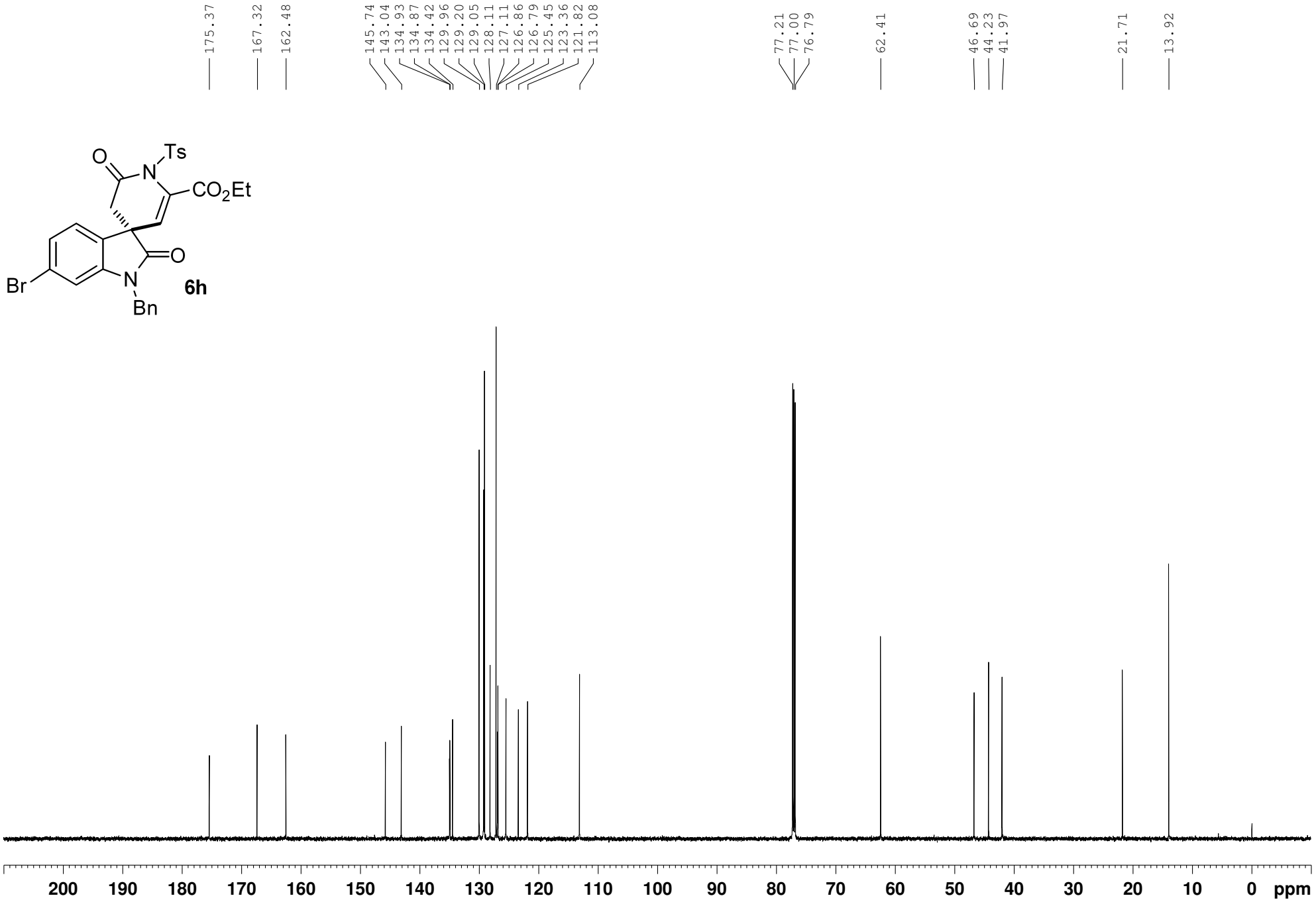
1.04
1.03
1.05
3.11
3.11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129.20
129.05
128.11
127.11
126.86
126.79
125.45
123.36
121.82
113.08
77.21
77.00
76.79
62.41
46.69
44.23
41.97
21.71
13.92
O
N
Ts
CO2Et
O
Br
N
Bn
6h
200
190
180
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150
140
130
120
110
100
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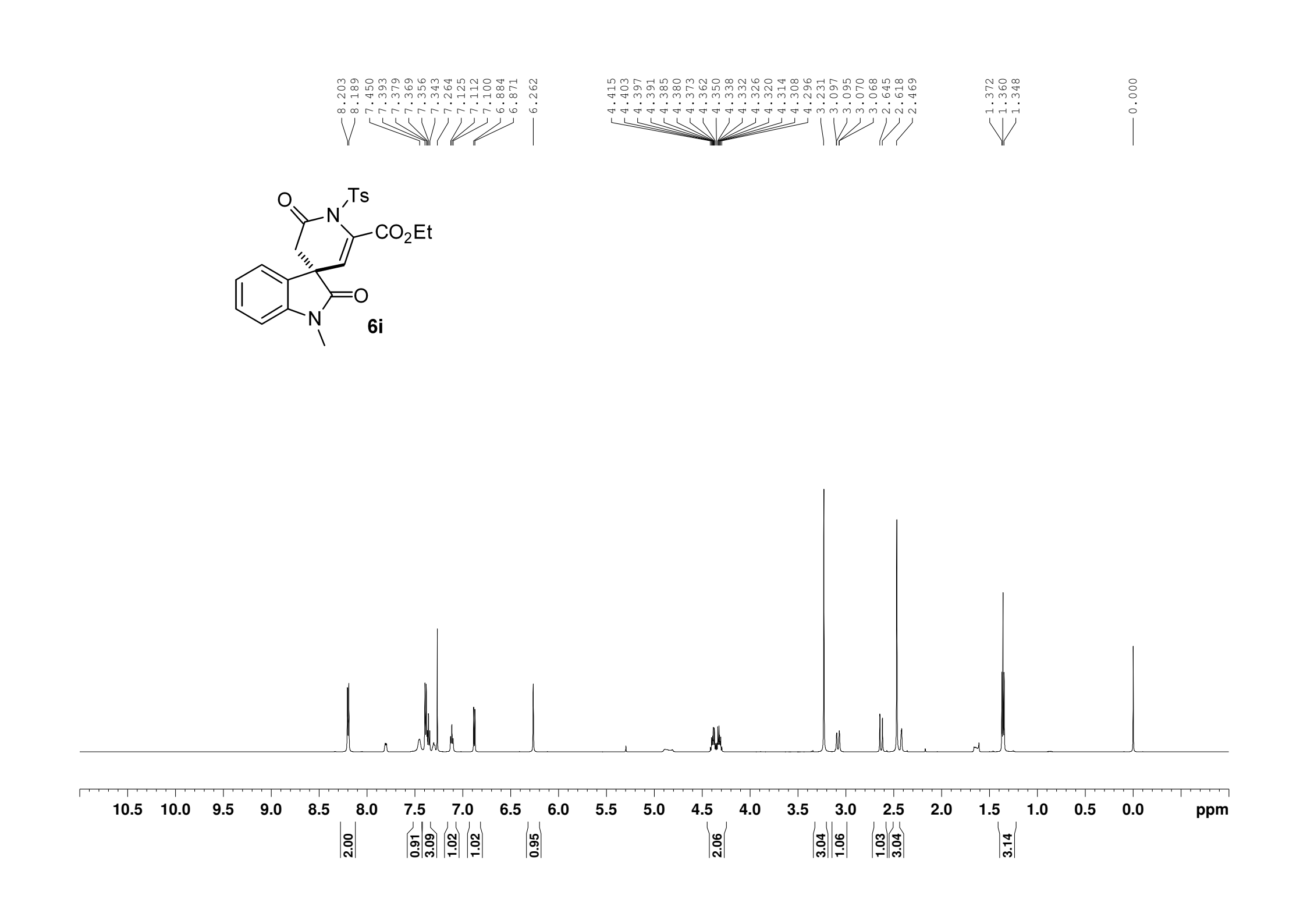
80
70
60
50
40
30
20
10
0
ppm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6.262
4.415
4.403
4.397
4.391
4.385
4.380
4.373
4.362
4.350
4.338
4.332
4.326
4.320
4.314
4.308
4.296
3.231
3.097
3.095
3.070
3.068
2.645
2.618
2.469
1.372
1.360
1.348
0.000
Ts
N
O
CO2Et
O
N
6i
10.5 10.0 9.5 9.0 8.5 8.0 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 0.0 ppm
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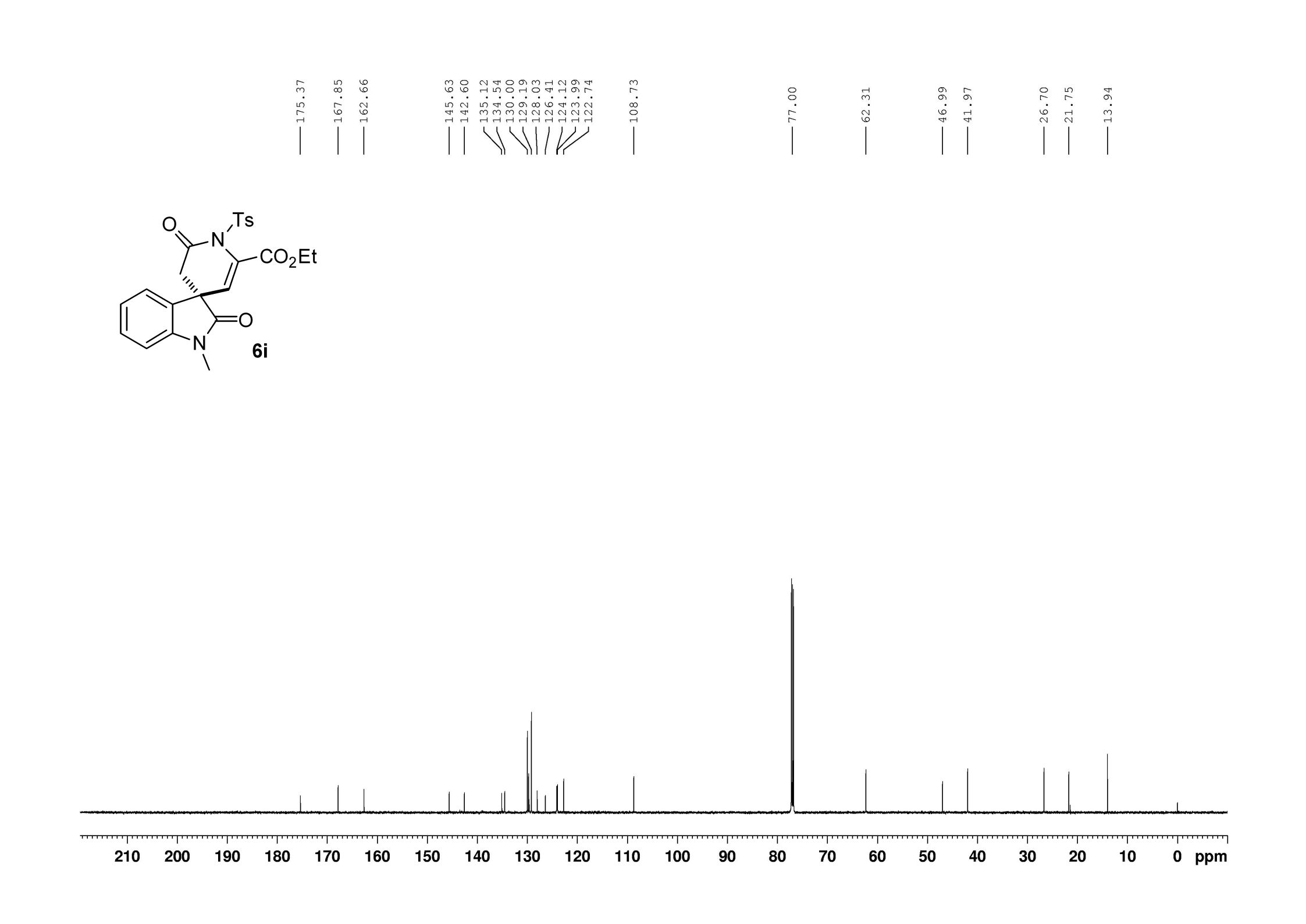
1.02
1.02
0.95
2.06
3.04
1.06
1.03
3.04
3.14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130.00
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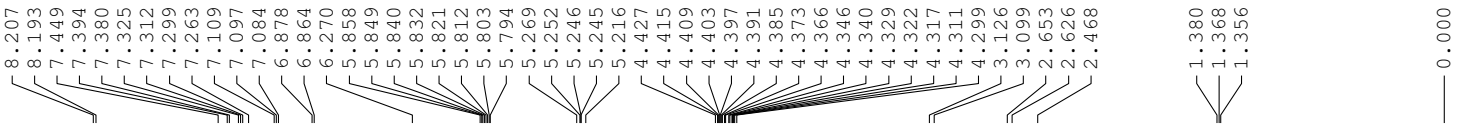
128.03
126.41
124.12
123.99
122.74
108.73
77.00
62.31
46.99
41.97
26.70
21.75
13.94
Ts
CO2Et
6i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.109
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5.812
5.803
5.794
5.269
5.252
5.246
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5.216
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4.403
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4.391
4.385
4.373
4.366
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4.322
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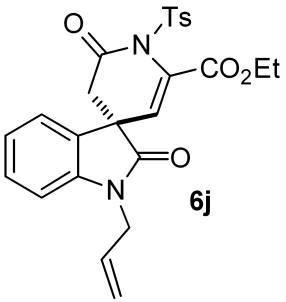
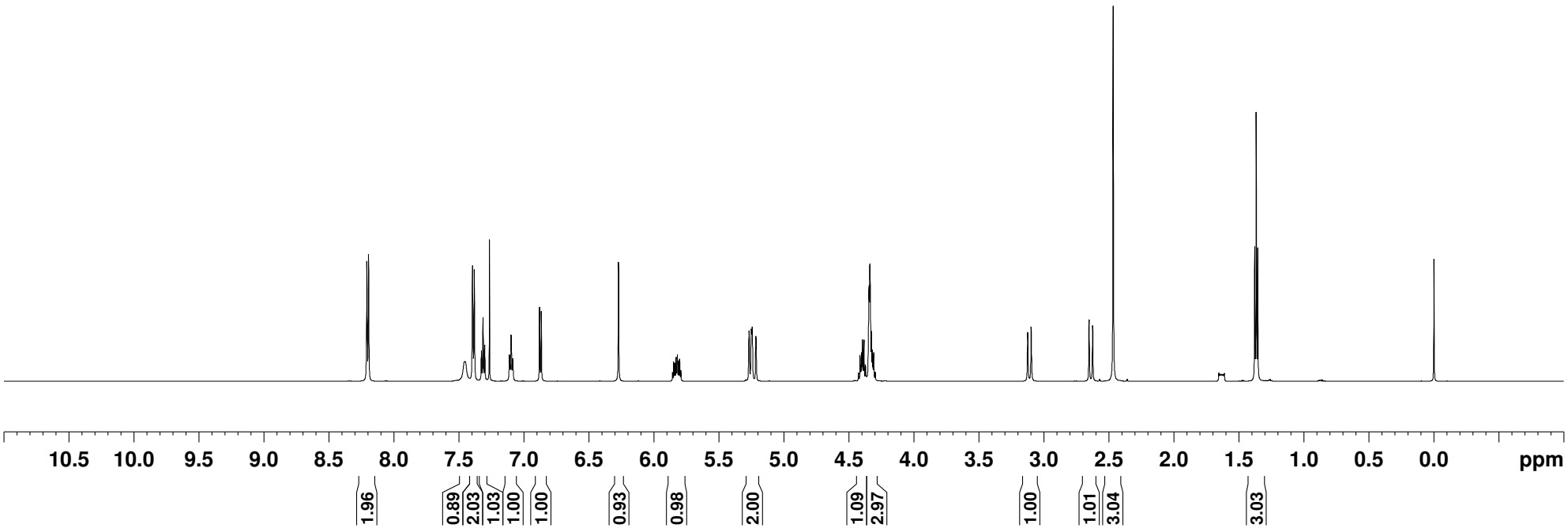

O
N
Ts
CO2Et
O
N

6j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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
0.5
0.0
ppm
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0.89
2.03
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0.93
0.98
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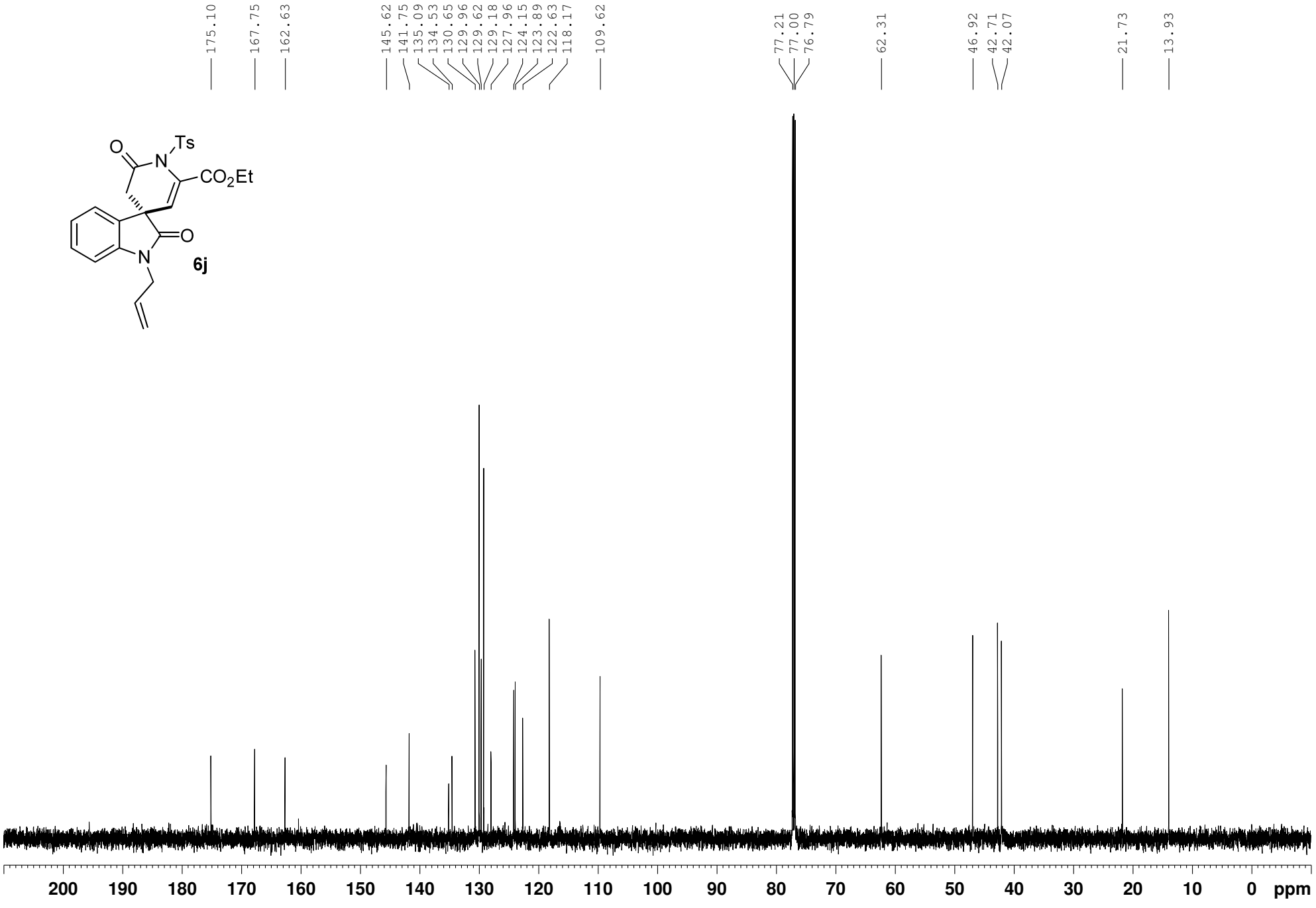
2.97
1.00
1.01
3.04
3.03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124.15
123.89
122.63
118.17
109.62
77.21
77.00
76.79
62.31
46.92
42.71
42.07
21.73
13.93
Ts
CO2Et
6j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.209
8.195
7.399
7.385
7.338
7.326
7.314
7.306
7.289
7.277
7.258
7.254
7.241
7.025
7.011
6.645
6.632
6.329
5.293
4.915
4.889
4.873
4.847
3.910
3.162
3.135
2.683
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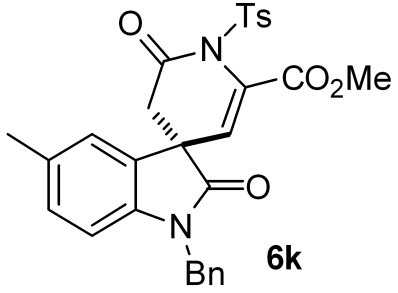
2.466
2.283
0.000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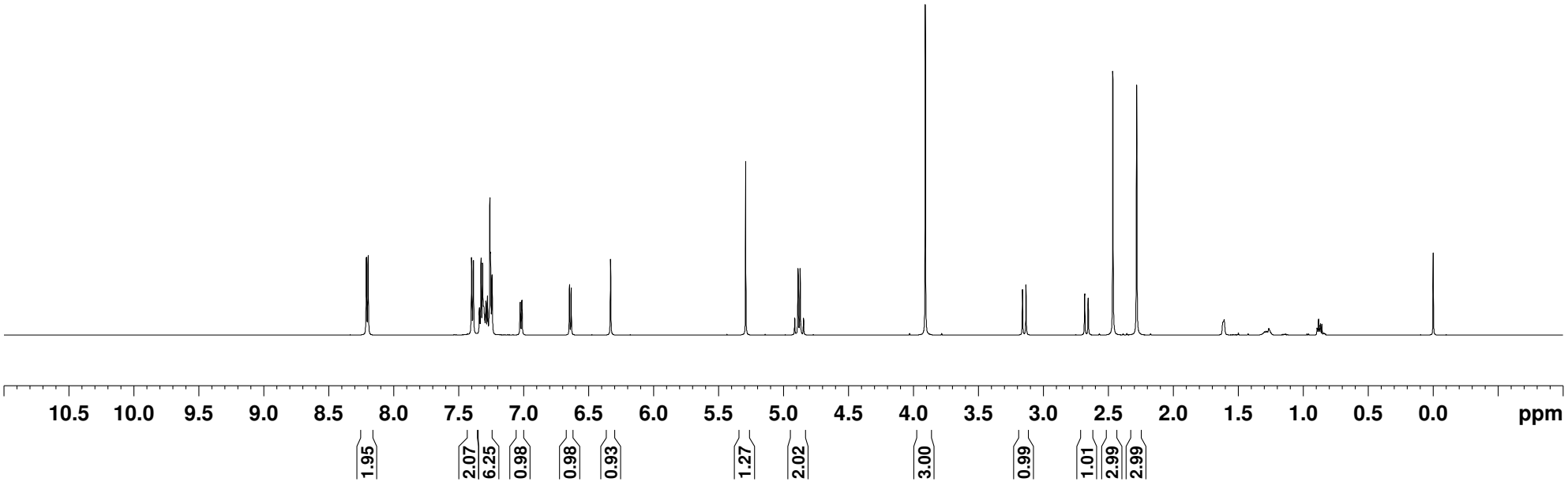
N
Ts
CO2Me
O
N
Bn

6k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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
0.0
ppm
1.95
2.07
6.25
0.98
0.98
0.93
1.27
2.02
3.00
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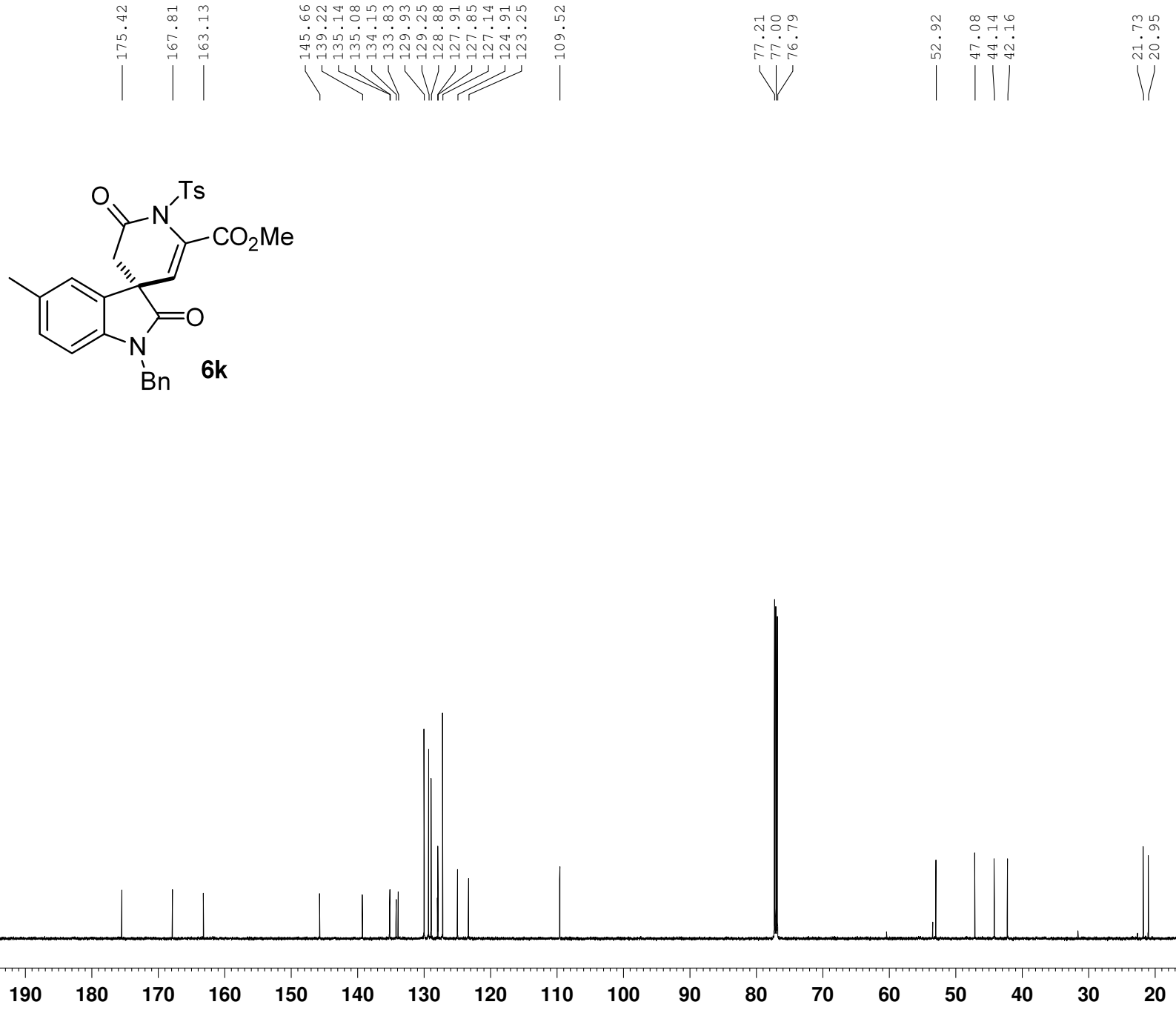
1.01
2.99
2.99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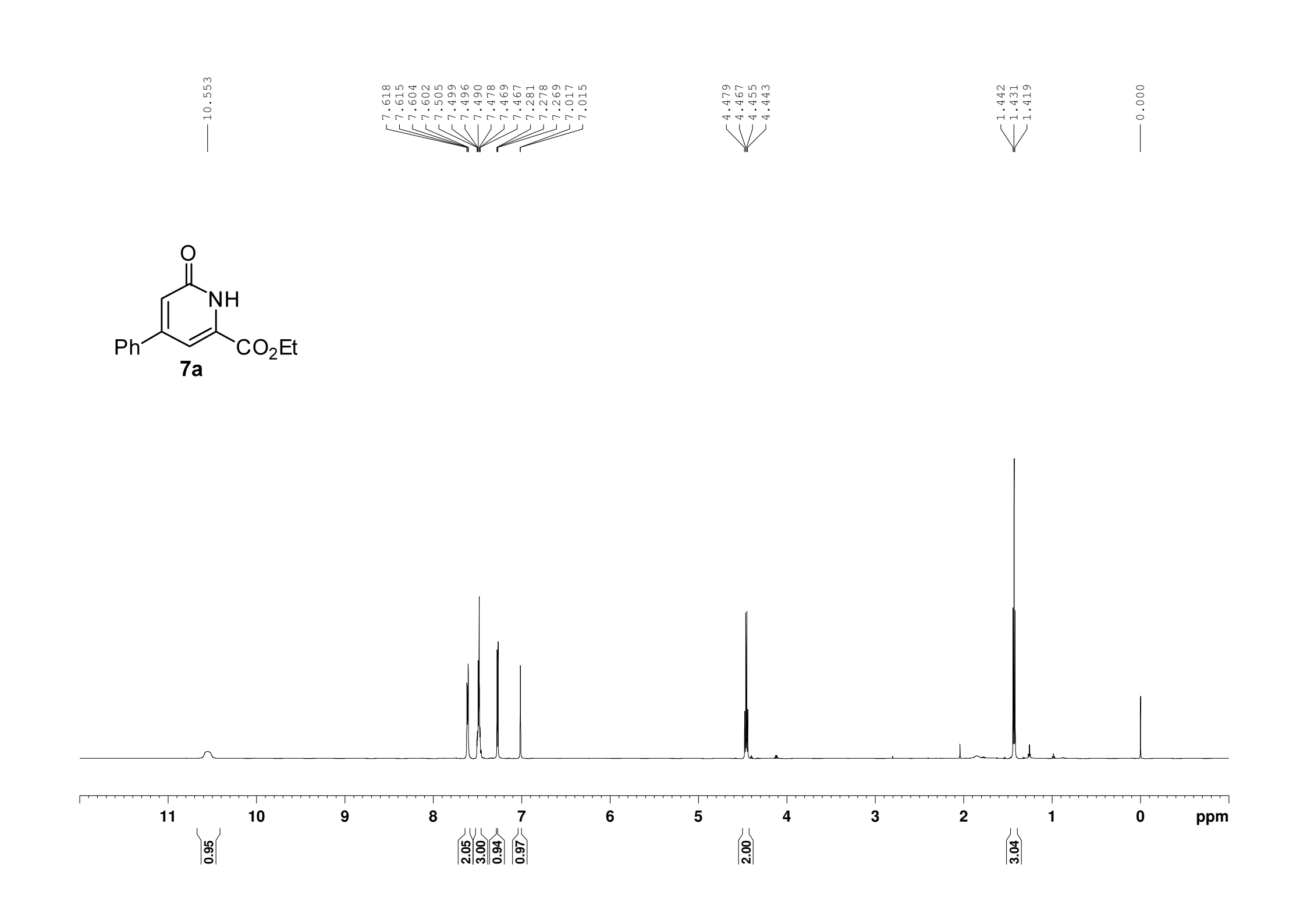
139.22
135.14
135.08
134.15
133.83
129.93
129.25
128.88
127.91
127.85
127.14
124.91
123.25
109.52
77.21
77.00
76.79
52.92
47.08
44.14
42.16
21.73
20.95
O
N
Ts
CO2Me
O
N
Bn
6k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.615
7.604
7.602
7.505
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7.496
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7.467
7.281
7.278
7.269
7.017
7.015
4.479
4.467
4.455
4.443
1.442
1.431
1.419
0.000
O
NH
Ph
CO2Et
7a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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2.05
3.00
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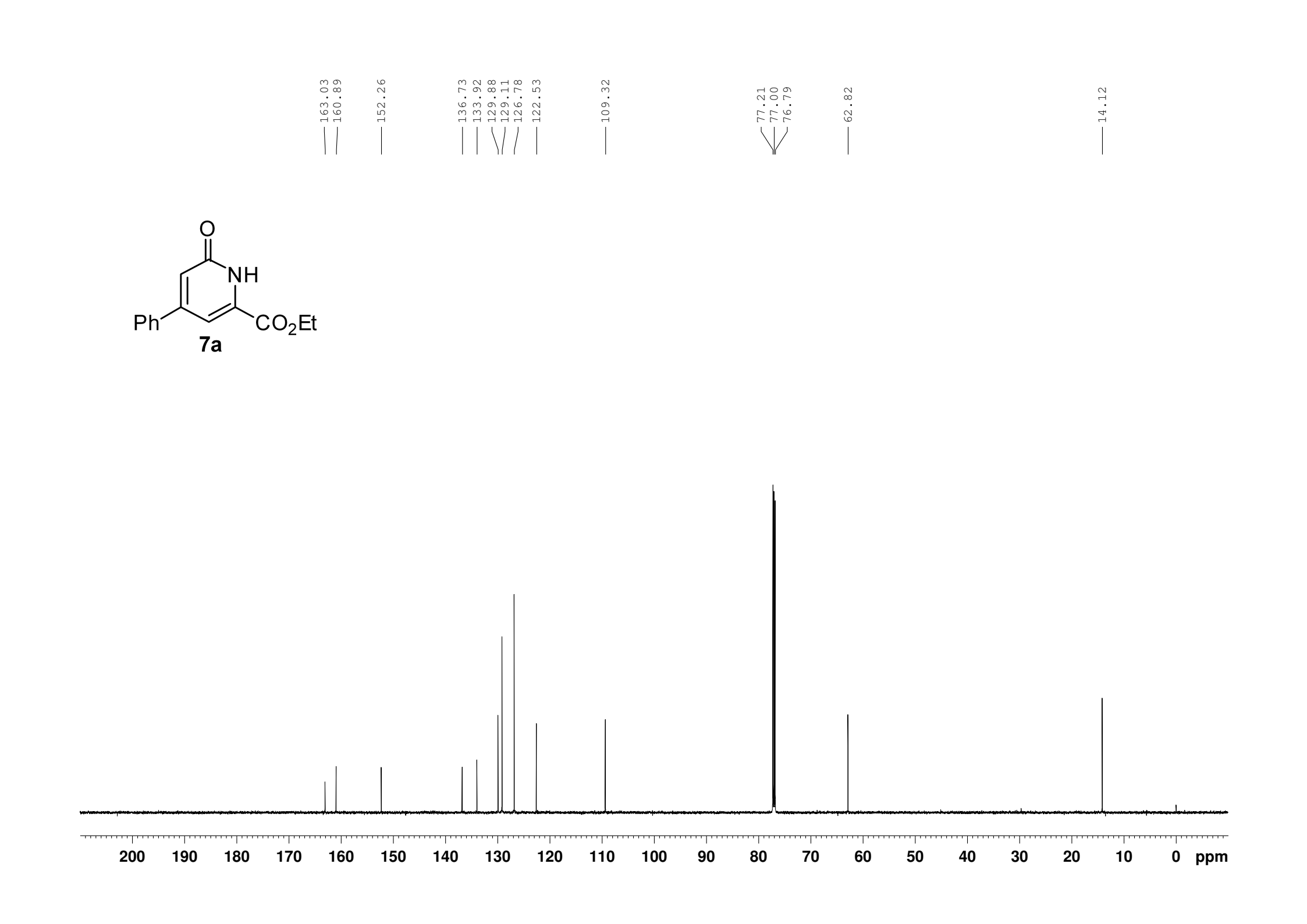
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129.88
129.11
126.78
122.53
109.32
77.21
77.00
76.79
62.82
14.12
O
NH
Ph
CO2Et
7a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm