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Graphical Abstract

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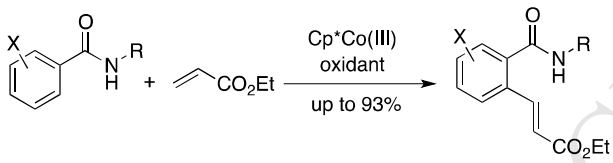

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Cp*Co(III)-catalyzed oxidative C-H alkenylation of benzamides with ethyl acrylate

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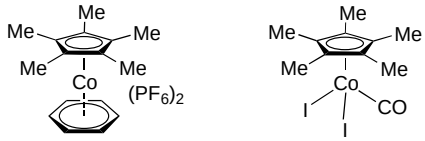
ABSTRACT

The utility of Cp*Co(III)-catalysts was expanded to oxidative C-C bond-forming reaction. *In situ*-generated Cp*Co(III)-catalyst, rather than a preformed cationic Cp*Co(III)-complex, was effective. Oxidative alkenylation of benzamides and acetanilide with ethyl acrylate proceeded with silver acetate as a stoichiometric oxidant, giving products in up to 93% yield.

1. Introduction

Functionalization of ubiquitous unreactive C-H bonds has attracted considerable attention in the field of organic synthesis.[1] The C-H functionalization process provides new opportunities for developing atom-[2] and step-economical[3] synthetic routes of natural products, biologically active compounds, functional organic materials, and other useful organic molecules. Regio- and chemoselective activation of a specific C-H bond among numerous C-H bonds in a molecule is essential for this purpose. Directing group-assisted C-H bond activation under transition metal catalysis is the most successful and widely used strategy, and various catalysts have been developed over the last two decades. Among them, cationic Cp*Rh(III) complexes are widely applied for various oxidative as well as redox neutral C-C, C-N, and other C-X bond-forming reactions.[4] Despite their high catalytic activity and broad reaction scope, however, the use of expensive rhodium metal has disadvantages for future application in large-scale synthesis. Thus, the development of an alternative catalyst with readily available base metal sources is highly desirable.[5-7] Since our report on the utility of a cationic Cp*Co(III)-arene complex **1a** in 2013 (Fig. 1),[8] we and others have attempted to broaden the scope of Cp*Co(III)-catalysis.[9,10] Cp*Co(III) complexes were successfully applied for a variety of redox neutral C-C and C-N bond formations. Cp*Co(III) was found to be superior to Cp*Rh(III) in some nucleophilic addition reactions[9b] as well as in some formally nucleophilic substitution reactions.[10b] On the other hand, there are no reports of oxidative C-C bond-forming reactions with external oxidants under Cp*Co(III)-catalysis.[11] Studies of oxidative C-H functionalizations are, therefore, important toward broadening the scope of Cp*Co(III)-catalysis. Herein, we demonstrate oxidative alkenylation of arenes with ethyl acrylate. The appropriate cationic Cp*Co(III) complex promoted the alkenylation reaction in the presence of silver oxidant, affording products in up to 93% yield.



1a **1b**

Fig. 1. Structures of Cp*Co(III)-complexes **1a** and **1b**.

2. Results and discussion

Transition metal-catalyzed oxidative alkenylation reactions of arenes, especially those using Pd, Rh, and Ru-catalysts, have been studied extensively.[12,13] Thus, we selected the reaction of arenes and acrylate as a model reaction to evaluate the feasibility

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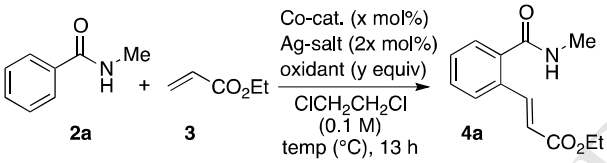
of oxidative C-C bond-forming processes under Cp*Co(III)-catalysis. Optimization studies of benzamide **2a** and ethyl acrylate **3** are summarized in Table 1. Our original cationic Cp*Co(III)-arene complex **1a** gave trace, if any, amounts of the desired product **4a** in the presence of silver acetate as a stoichiometric oxidant (entry 1). On the other hand, *in situ*-generated Co(III)-catalyst by mixing Cp*Co(CO)I_2 **1b** and $AgPF_6$ gave the product in 54% yield. The selection of the counter ion affected the reactivity of the Co(III)-catalyst, and $AgSbF_6$ afforded the best reactivity among silver salts screened (entries 2-6). The results were not improved by the use of any other oxidants screened. The use of benzoquinone as an oxidant led to only trace amounts of the product (entry 7). $Cu(OAc)_2$, which is often used for oxidative reactions under Cp*Rh(III)-catalysis, resulted in a lower yield than AgOAc (entry 8, 48%). We assume that the selection of a suitable oxidant is important for efficient catalyst turnover to regenerate catalytically active Cp*Co(III), while suppressing undesirable catalyst de-activation from the relatively unstable Cp*Co(I) species. Ag_2CO_3 also resulted in a low yield (entry 9, 16%), possibly because the acetate ion is important to efficiently assist the C-H activation step. The reaction proceeded smoothly even at 40 °C, but resulted in a slightly lower yield (entry 10, 73%). Thus, we selected the conditions in entry 6 as optimum for oxidative alkenylation. Negative control experiments in entries 11-15 suggested that the use of the well-defined cationic Cp*Co(III)-catalyst is required for present C-H functionalization.

Table 1. Optimization studies of Cp*Co(III)-catalyzed oxidative alkenylation.



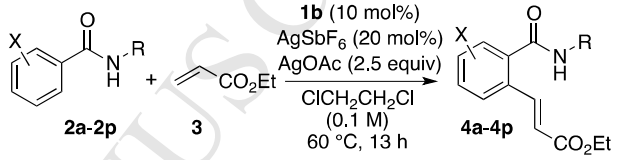
Entry	Co-cat. (x mol%)	Ag-salt (2x mol%)	Oxidant (y equiv)	Temp (°C)	Yield[a] (%)
1	**1a** (10)	none	AgOAc (2.5)	60	trace
2	**1b** (10)	$AgPF_6$ (20)	AgOAc (2.5)	60	54
3	**1b** (10)	AgOTf (20)	AgOAc (2.5)	60	60
4	**1b** (10)	$AgNTf_2$ (20)	AgOAc (2.5)	60	72
5	**1b** (10)	$AgBF_4$ (20)	AgOAc (2.5)	60	74
6	**1b** (10)	$AgSbF_6$ (20)	AgOAc (2.5)	60	84 (80)[b]
7	**1b** (10)	$AgSbF_6$ (20)	BQ (1.3)	60	trace
8	**1b** (10)	$AgSbF_6$ (20)	$Cu(OAc)_2$ (2.5)	60	47
9	**1b** (10)	$AgSbF_6$ (20)	Ag_2CO_3 (1.3)	60	16
10	**1b** (10)	$AgSbF_6$ (20)	AgOAc (2.5)	40	73
11	none	$AgSbF_6$ (20)	AgOAc (2.5)	60	0
12	CoI_2 (10)	$AgSbF_6$ (20)	AgOAc (2.5)	60	0
13	$Co(OAc)_2$(10)	none	AgOAc (2.5)	60	0
14	$Co(acac)_3$ (10)	none	AgOAc (2.5)	60	0
15	$Co(NH_3)_6Cl_3$(10)	none	AgOAc (2.5)	60	0

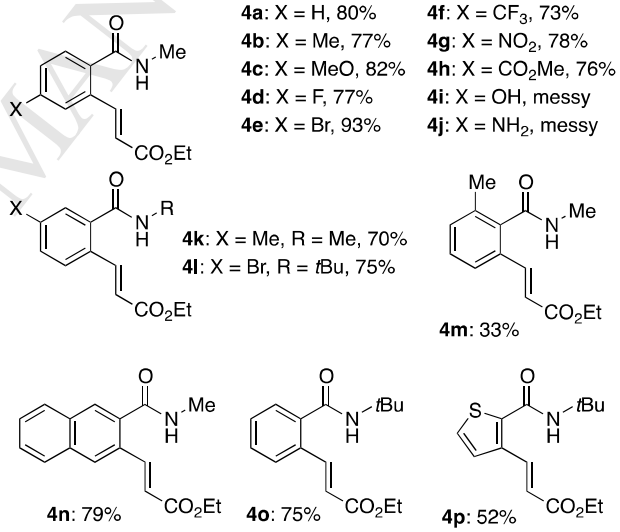
[a] Yield of **4a** determined by ^{1}H NMR analysis of crude mixture with an internal standard.

[b] Isolated yield of **4a** after purification by silica gel column chromatography.

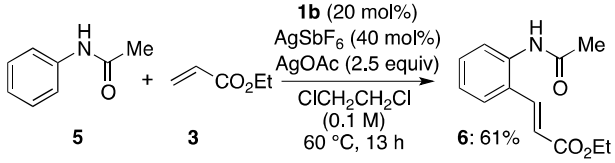
We then investigated the scope and limitations of Cp*Co(III)-catalyzed oxidative alkenylation reactions. The scope of benzamides is summarized in Table 2. Various functional groups at the *para*-position, such as Me, MeO, F, Br, CF_3, NO_2, and CO_2Me, were compatible (**4b**-**4h**, 73-93%), while phenol and aniline units (**4i** and **4j**) gave complex mixtures of byproducts. Substituents at the *meta*-position also gave the products in good yield (**4k** and **4l**). Good regioselectivity with *meta*-substituted substrates can be explained based on the steric factor. C-H metalation occurred selectively at the sterically less hindered position. With an *ortho*-substituted substrate, the reactivity decreased significantly, and product **4m** was obtained in only 33% yield. The *ortho*-substituent would destabilize a planar metalacyclic intermediate due to steric repulsion. In addition to other benzamide derivatives **4n** and **4o**, the C-H bond of thiophenyl unit was also functionalized, albeit in moderate yield (**4p**, 52%). As shown in Scheme 1, acetanilide (**5**) also reacted with ethyl acrylate, although 20 mol % of Cp*Co(III) was required to obtain product **6** in 61% yield.

Table 2. Cp*Co(III)-catalyzed oxidative alkenylation of benzamides.[a]





[a] Reaction was run using **4** (0.10 mmol) and **3** (0.15 mmol). Isolated yields of **4** after purification by silica gel column chromatography are shown in Table 2.



Scheme 1. Cp*Co(III)-catalyzed oxidative alkenylation of acetanilide **5**.

A plausible catalytic cycle is shown in Fig. 2. Initial halide abstraction from Cp*Co(CO)I_2 **1b** by $AgSbF_6$ in the presence of the AgOAc would form a neutral Cp*Co(III)$(OAc)_2$ complex, which would be a resting complex. On the basis of our previous mechanistic studies,[9b] we speculate that mono-cationic $[Cp^*Co(III)(OAc)]^+$ **I** would be a catalytically active species. We

assume that the concentration of the catalytically active species would be different depending on silver salts, which led to the reactivity difference observed in Table 1, entries 2-6. A key C-H bond activation step to afford metalacycle **II** would proceed via concerted metalation-deprotonation (CMD)[14] assisted by the acetate ion. Insertion into acrylate (**III**), followed by β-hydride elimination and reductive elimination, would afford product **4**, AcOH, and Cp*Co(I). Oxidation of Cp*Co(I) by silver salt regenerated the Cp*Co(III)-catalyst.

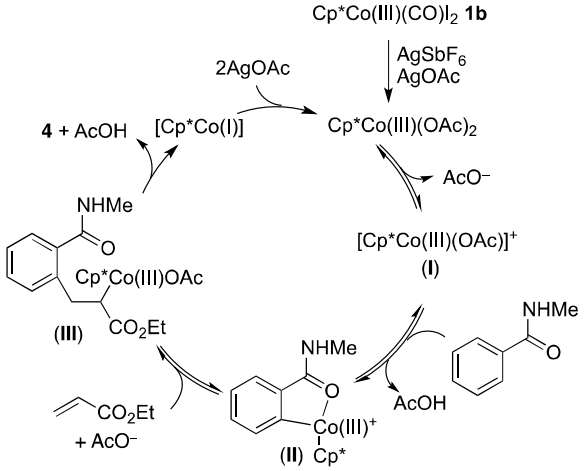


Fig. 2. Plausible catalytic cycle.

3. Conclusion

In conclusion, we report the first successful application of a Cp*Co(III)-catalyst to oxidative C-H alkenylation with an external oxidant, thereby expanding the utility of Cp*Co(III)-catalysis. The present protocol can be further improved, however, with regard to the use of precious silver salt as a stoichiometric oxidant and the limited substrate scope. Additional studies to improve the Cp*Co(III)-catalyzed oxidative process, including the use of environmentally benign oxidant, are ongoing in our group.

4. Experimental Section

4.1. General Procedure *(Table 2)*

To a dried screw-capped vial were added benzamide **2** (0.10 mmol), ethyl acrylate **3** (0.15 mmol), **1b** (4.8 mg, 0.01 mmol), $AgSbF_6$ (6.8mg, 0.02 mmol), AgOAc (41.7 mg, 0.25 mmol) and 1,2-dichloroethane (1.0 mL) under Ar atmosphere. The vial was capped and the mixture was heated at 60 °C for 13 h with stirring. After the mixture was cooled to room temperature, saturated EDTA·2Na *aq.* was added following dilution with CH_2Cl_2. Organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (x 2). Combined organic layers were dried over Na_2SO_4. After filtration and evaporation, obtained crude mixture was purified by silica gel column chromatography (CH_2Cl_2/EtOAc) to give product **3**.

*4.1.1. (E)-Ethyl 3-(2-(methylcarbamoyl)phenyl)acrylate (**4a**).*

A colorless solid; IR (KBr) ν 3085, 2979, 1714, 1703, 1635, 1557, 1270, 1048, 980, 767 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 2.99 (d, *J* = 4.6 Hz, 3H), 4.23 (q, *J* = 7.3 Hz, 2H), 5.98 (brs, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 7.34-7.50 (m, 3H), 7.59 (s, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.0, 60.7, 120.9, 127.2, 127.7, 129.9, 130.4, 132.8, 137.3, 141.9, 166.6, 169.5; HRMS (ESI): *m/z* calculated for $C_{13}H_{15}NNaO_3^+$ $[M+Na]^+$: 256.0944, found: 256.0956.

*4.1.2. (E)-Ethyl 3-(5-methyl-2-(methylcarbamoyl)phenyl)acrylate (**4b**).*

A colorless solid; IR (KBr) ν 2982, 1714, 1643, 1550, 1317, 1178, 1037, 976, 862 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 5.5 Hz , 3 H), 2.38 (s, 3H), 3.00 (d, *J* = 4.1 Hz, 3H), 4.23 (q, *J* = 5.5 Hz, 2H), 5.78 (brs, 1H), 6.36 (d, *J* = 12.4 Hz, 1H), 7.19 (d, *J* = 6.4 Hz, 1H), 7.34-7.42 (m, 2H), 8.00 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 21.4, 27.0, 60.7, 120.7, 127.8, 127.8, 130.6, 132.9, 134.5, 140.5, 142.3, 166.7, 169.5; HRMS (ESI): *m/z* calculated for $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$: 270.1101, found: 270.1092.

*4.1.3. (E)-Ethyl 3-(5-methoxy-2-(methylcarbamoyl)phenyl)acrylate (**4c**).*

A colorless solid; IR (KBr) ν 2985, 2942, 1715, 16641, 1625, 1546, 1314, 1293, 1228, 1182, 1034, 974, 862 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 7.3 Hz , 3 H), 2.98 (d, *J* = 5.0 Hz, 3H), 3.83 (s, 3H), 4.24 (q, *J* = 7.3 Hz, 2H), 5.88 (brs, 1H), 6.33 (d, *J* = 16.7 Hz, 1H), 6.89 (dd, *J* = 2.3, 8.7 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1s) 8.02 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 55.6, 60.8, 112.2, 115.4, 121.1, 129.5, 129.7, 135.0, 142.3, 161.0, 166.6, 169.2; HRMS (ESI): *m/z* calculated for $C_{14}H_{17}NNaO_4^+$ $[M+Na]^+$: 286.1050, found: 286.1054.

*4.1.4. (E)-Ethyl 3-(5-fluoro-2-(methylcarbamoyl)phenyl)acrylate (**4d**).*

A colorless solid; IR (KBr) ν 3082, 2984, 1721, 1635, 1558, 1321, 1182, 1034, 971, 855 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, *J* = 6.8 Hz , 3 H), 2.99 (d, *J* = 5.0 Hz, 3H), 4.24 (q, *J* = 6.8 Hz, 2H), 5.95 (brs, 1H), 6.34 (d, *J* = 16.5 Hz, 1H), 7.04 (ddd, *J* = 2.8, 8.7, 8.7 Hz, 1H), 7.25 (dd, *J* = 2.8, 10.1 Hz, 1H), 7.44 (dd, *J* = 6.0, 8.7 Hz, 2H), 7.91 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 60.9, 113.9 (d, *J* = 22.9 Hz), 116.8 (d, *J* = 22.9 Hz), 122.1, 130.6 (d, *J* = 9.5 Hz), 133.4 (d, *J* = 2.9 Hz), 135.5 (d, *J* = 7.6 Hz), 140.8 (d, *J* = 2.9 Hz), 163.5 (d, *J* = 254.7 Hz), 166.3, 168.6; HRMS (ESI): *m/z* calculated for $C_{13}H_{14}FNNaO_3^+$ $[M+Na]^+$: 274.0850, found: 274.0844.

*4.1.5. (E)-Ethyl 3-(5-bromo-2-(methylcarbamoyl)phenyl)acrylate (**4e**).*

A colorless solid; IR (KBr) ν 3079, 2975, 2935, 1719, 1642, 1561, 1316, 1190, 1032, 979, 862 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 7.5 Hz , 3 H), 3.00 (d, *J* = 5.2 Hz, 3H), 4.23 (q, *J* = 7.5 Hz, 2H), 5.88 (brs, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.74 (s, 1H) 7.90 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 60.1, 122.1, 124.1, 124.7, 129.3, 130.1, 132.7, 134.9, 135.8, 140.5, 166.2, 168.5; HRMS (ESI): *m/z* calculated for $C_{13}H_{14}BrNNaO_3^+$ $[M+Na]^+$: 334.0049, found: 334.0050.

*4.1.6. (E)-Ethyl 3-(2-(methylcarbamoyl)-5-(trifluoromethyl)phenyl)acrylate (**4f**).*

A colorless solid; IR (KBr) ν 3084, 2974, 1717, 1642, 1551, 1337, 1292, 1159, 1122, 1042, 989, 924, 843 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 6.9 Hz , 3 H), 3.04 (d, *J* = 4.6 Hz, 3H), 4.24 (q, *J* = 6.9 Hz, 2H), 5.88 (brs, 1H), 6.45 (d, *J* =

16.0 Hz, 1H), 7.57-7.65 (m, 2H), 7.85 (s, 1H) 7.94 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 61.0, 122.6, 123.5 (q, *J* = 273.4 Hz), 124.1 (q, *J* = 3.8 Hz), 126.3 (q, *J* = 22.9 Hz), 128.4, 132.5 (q, *J* = 32.9 Hz), 133.7; HRMS (ESI): *m/z* calculated for $C_{14}H_{14}F_3NNaO_3^+$ $[M+Na]^+$: 324.0818, found: 324.0818.

*4.1.7. (E)-Ethyl 3-(2-(methylcarbamoyl)-5-nitrophenyl)acrylate (**4g**).*

A colorless solid; IR (KBr) ν 3085, 2977, 1713, 1643, 1556, 1522, 1352, 1282, 1040, 989, 825 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 3.03 (d, *J* = 5.0 Hz, 3H), 4.26 (q, *J* = 7.3 Hz, 2H), 6.14 (brs, 1H), 6.50 (d, *J* = 16.5 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 16.5 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 1H) 8.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.2, 61.2, 122.1, 123.7, 124.2, 134.7, 139.4, 142.3, 148.8, 165.9, 167.5; HRMS (ESI): *m/z* calculated for $C_{13}H_{14}N_2NaO_5^+$ $[M+Na]^+$: 301.0795, found: 301.0791.

*4.1.8. (E)-Methyl 3-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-(methylcarbamoyl)benzoate (**4h**).*

A colorless solid; IR (KBr) ν 3082, 2988, 2954, 1721, 1644, 1551, 1320, 1252, 1184, 1032, 976, 866, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 7.2 Hz , 3 H), 3.02 (d, *J* = 4.8 Hz, 3H), 3.94 (s, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.07 (brs, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 16.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 52.7, 60.9, 122.1, 122.1, 127.9, 128.4, 130.6, 131.9, 133.2, 140.8, 140.9, 166.0, 166.4, 168.6; HRMS (ESI): *m/z* calculated for $C_{15}H_{17}NNaO_5^+$ $[M+Na]^+$: 314.0999, found: 314.0993.

*4.1.9. (E)-Ethyl 3-(4-methyl-2-(methylcarbamoyl)phenyl)acrylate (**4k**).*

A colorless solid; IR (KBr) ν 2979, 1715, 1639, 1604, 1541, 1309, 1272, 1178, 1030, 977, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, *J* = 7.3 Hz , 3 H), 2.35 (s, 3H), 3.00 (d, *J* = 5.0 Hz, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 5.88 (brs, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 7.29-7.37 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 21.4, 27.0, 60.7, 119.9, 127.2, 128.4, 129.9, 131.1, 137.3, 140.4, 141.8, 166.8, 169.6; HRMS (ESI): *m/z* calculated for $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$: 270.1101, found: 270.1104.

*4.1.10. (E)-Ethyl 3-(4-bromo-2-(tert-butylcarbamoyl)phenyl)acrylate (**4l**).*

A colorless oil; IR (neat) ν 3065, 2973, 1714, 1641, 1541, 1312, 1263, 1178, 1097, 1041, 976, 895, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 1.47(s, 9H), 4.24 (q, *J* = 7.3 Hz, 2H), 5.64 (brs, 1H), 6.35 (d, *J* = 16.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 2.3, 7.8 Hz, 1H), 7.57 (s, *J* = 2.3 Hz, 1H), 7.85 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 28.8, 52.7, 60.8, 121.3,124.0, 128.5, 130.7, 131.2, 133.1, 140.0, 140.7, 166.3, 166.7; HRMS (ESI): *m/z* calculated for $C_{16}H_{20}BrNNaO_3^+$ $[M+Na]^+$: 376.0519, found: 376.0520.

*4.1.11. (E)-Ethyl 3-(3-methyl-2-(methylcarbamoyl)phenyl)acrylate (**4m**).*

A colorless oil; IR (neat) ν 2980, 1710, 1638, 1543, 1313, 1233, 1090, 1039, 979, 867, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 2.34 (s, 3H), 3.04 (d, *J* = 5.0 Hz, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 5.72 (brs, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.70 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 19.3, 26.8, 60.7, 120.8, 124.0, 1293, 131.7, 121.9, 135.6, 138.2, 141.6, 166.7, 169.8; HRMS (ESI): *m/z* calculated for $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$: 270.1101, found: 270.1102.

*4.1.12. (E)-Ethyl 3-(3-(methylcarbamoyl)naphthalen-2-yl)acrylate (**4n**).*

A colorless solid; IR (KBr) ν 2981, 1715, 1644, 1622, 1551, 1304, 1177, 1033, 976, 863, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.3 Hz , 3 H), 3.05 (d, *J* = 5.0 Hz, 3H), 4.26 (q, *J* = 7.3 Hz, 2H), 6.14 (brs, 1H), 6.44 (d, *J* = 16.5 Hz, 1H), 7.50-7.57 (m, 2H), 7.76-7.87 (m, 2H), 7.91 (s, 1H), 8.01 (s, 1H), 8.23 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.5, 27.1, 60.7, 120.8, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 130.4, 133.0, 133.6, 134.4, 142.5, 166.7, 169.5; HRMS (ESI): *m/z* calculated for $C_{17}H_{17}NNaO_3^+$ $[M+Na]^+$: 306.1101, found: 306.1105.

*4.1.13. (E)-Ethyl 3-(2-(tert-butylcarbamoyl)phenyl)acrylate (**4o**).*

A colorless oil; IR (neat) ν 3063, 2971, 1712, 1639, 1538, 1314, 1177, 1094, 1042, 977, 879, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.3 Hz , 3 H), 1.49 (s, 9H), 4.26 (q, *J* = 7.3 Hz, 2H), 5.55 (brs, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 7.36-7.50 (m, 3H), 7.59 (s, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 28.9, 52.4, 60.7, 120.8, 127.0, 127.7, 130.0, 130.1, 132.3, 138.7, 142.0, 166.6, 168.3; HRMS (ESI): *m/z* calculated for $C_{16}H_{20}BrNNaO_3^+$ $[M+Na]^+$: 298.1414, found: 298.1423.

*4.1.14. (E)-Ethyl 3-(2-(methylcarbamoyl)thiophen-3-yl)acrylate (**4p**).*

A colorless solid; IR (neat) ν 2979, 1707, 1632, 1536, 1244, 1178, 1037, 987, 867, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 6.9 Hz , 3 H), 3.01 (s, 3H), 4.26 (q, *J* = 6.9 Hz, 2H), 6.33 (d, *J* = 16.5 Hz, 1H), 5.84 (brs, 1H), 7.29 (d, *J* = 5.5 Hz, 1H), 7.33 (d, *J* = 5.5 Hz, 1H), 8.26 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.5,27.2, 60.8, 121.7, 127.0, 127.2, 136.4, 136.5, 138.6, 162.8, 162.9; HRMS (ESI): *m/z* calculated for $C_{11}H_{13}NNaO_3S^+$ $[M+Na]^+$: 262.0508, found: 262.0513.

*4.1.15. (E)-Ethyl 3-(2-acetamidophenyl)acrylate (**6**) (Scheme 2).*

To a dried screw-capped vial were added acetanilide **5** (0.10 mmol), ethyl acrylate **3** (0.15 mmol), **1b** (9.6 mg, 0.02 mmol), $AgSbF_6$ (13.6mg, 0.04 mmol), AgOAc (41.7 mg, 0.25 mmol) and 1,2-dichloroethane (1.0 mL) under Ar atmosphere. The vial was capped and the mixture was heated at 60 °C for 13 h with stirring. After the mixture was cooled to room temperature, saturated EDTA·2Na *aq.* was added following dilution with CH_2Cl_2. Organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (x 2). Combined organic layers were dried over Na_2SO_4. After filtration and evaporation, obtained crude mixture was purified by silica gel column chromatography (CH_2Cl_2/EtOAc) to give product **6**. A colorless solid; IR (KBr) ν 2978, 1712, 1659, 1537, 1455, 1302, 1270, 1045, 971, 764, 743 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.6 Hz , 3 H),

2.23 (s, 3H), 4.26 (q, J = 7.6 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 7.20 (m, 1H), 7.29-7.43 (m, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.70-7.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 24.4, 60.9, 120.9, 125.3, 126.0, 127.3, 127.7, 130.9, 136.0, 139.4, 166.9, 169.0; HRMS (ESI): m/z calculated for $C_{13}H_{15}NNaO_3^+$ $[M+Na]^+$: 256.0944, found: 256.0936

Acknowledgments

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Supplementary Material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.xxxxxxxxx

Supplementary Material

Cp*Co(III)-catalyzed oxidative C-H alkenylation of benzamides with ethyl acrylate

Yudai Suzuki, Bo Sun, Tatsuhiko Yoshino, Motomu Kanai* and Shigeki Matsunaga *

Experimental Section

General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on JEOL JNM-ECS400 spectrometers, operating at 400 MHz for ^{1}H NMR and 98.52 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ was reported in the scale relative to $CHCl_3$ (7.26 ppm for ^{1}H NMR) and $CDCl_3$ (77.16 ppm for ^{13}C NMR) as an internal reference. ESI mass spectra for HRMS were measured on a JEOL JMS-T100LC AccuTOF spectrometer. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). 1,2-Dichloroethane (DCE) was distilled from CaH_2, purged with argon for over 30 min and stored over activated molecular sieves 4A under argon atmosphere. Cp*Co(CO)I_2 was synthesized according to the literature.[1] All benzamides **2** were prepared by the same procedure as described in the literature.[2,3] Acetanilide was purchased from Aldrich and used without purification. Commercially available ethyl acrylate (TCI) was purified by distillation before use.

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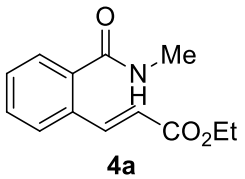
General Procedure of Cobalt(III)-Catalyzed Alkenylation

To a dried screw-capped vial were added benzamide **2** (0.10 mmol), ethyl acrylate **3** (0.15 mmol), **1b** (4.8 mg, 0.01 mmol), $AgSbF_6$ (6.8mg, 0.02 mmol), AgOAc (41.7 mg, 0.25 mmol) and 1,2-dichloroethane (1.0 mL) under Ar atmosphere. The vial was capped and the mixture was heated at 60 °C for 13 h with stirring. After the mixture was cooled to room temperature, saturated EDTA·2Na *aq.* was added following dilution with CH_2Cl_2. Organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (x 2). Combined organic layers were dried over Na_2SO_4. After filtration and evaporation, obtained crude mixture was purified by silica gel column chromatography (CH_2Cl_2/EtOAc) to give a corresponding product **3**.

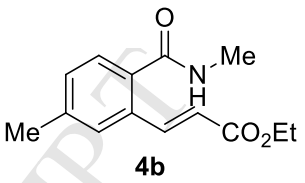


4a

(*E*)-ethyl 3-(2-(methylcarbamoyl)phenyl)acrylate (4a): a colorless solid; IR (KBr) ν 3085, 2979, 1714, 1703, 1635, 1557, 1270, 1048, 980, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 2.99 (d, *J* = 4.6 Hz, 3H), 4.23 (q, *J* = 7.3 Hz, 2H), 5.98 (brs, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 7.34-7.50 (m, 3H), 7.59 (s, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.0, 60.7, 120.9, 127.2, 127.7, 129.9,

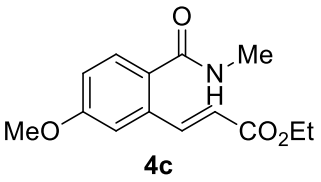
130.4, 132.8, 137.3, 141.9, 166.6, 169.5; HRMS (ESI): *m/z* calculated for $C_{13}H_{15}NNaO_3^+$ $[M+Na]^+$: 256.0944, found: 256.0956

(*E*)-ethyl 3-(5-methyl-2-(methylcarbamoyl)phenyl)acrylate (4b): a colorless solid; IR (KBr) ν 2982, 1714, 1643, 1550, 1317, 1178, 1037, 976, 862 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 5.5 Hz , 3 H), 2.38 (s, 3H), 3.00 (d, *J* = 4.1 Hz, 3H), 4.23 (q, *J* = 5.5 Hz, 2H), 5.78 (brs, 1H), 6.36 (d, *J* = 12.4 Hz, 1H), 7.19 (d, *J* = 6.4 Hz, 1H), 7.34-7.42 (m, 2H), 8.00 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 21.4, 27.0, 60.7, 120.7, 127.8, 127.8, 130.6, 132.9, 134.5, 140.5, 142.3, 166.7, 169.5; HRMS (ESI): *m/z* calculated for $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$: 270.1101, found: 270.1092



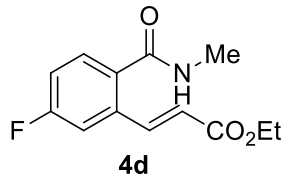
4b

(*E*)-ethyl 3-(5-methoxy-2-(methylcarbamoyl)phenyl)acrylate (4c): a colorless solid; IR (KBr) ν 2985, 2942, 1715, 16641, 1625, 1546, 1314, 1293, 1228, 1182, 1034, 974, 862 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 7.3 Hz , 3 H), 2.98 (d, *J* = 5.0 Hz, 3H), 3.83 (s, 3H), 4.24 (q, *J* = 7.3 Hz, 2H), 5.88 (brs, 1H), 6.33 (d, *J* = 16.7 Hz, 1H), 6.89 (dd, *J* = 2.3, 8.7 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1s) 8.02 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 55.6, 60.8, 112.2, 115.4, 121.1, 129.5, 129.7, 135.0, 142.3, 161.0, 166.6, 169.2; HRMS (ESI): *m/z* calculated for $C_{14}H_{17}NNaO_4^+$ $[M+Na]^+$: 286.1050, found: 286.1054



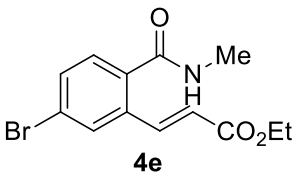
4c

(*E*)-ethyl 3-(5-fluoro-2-(methylcarbamoyl)phenyl)acrylate (4d): a colorless solid; IR (KBr) ν 3082, 2984, 1721, 1635, 1558, 1321, 1182, 1034, 971, 855 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, *J* = 6.8 Hz , 3 H), 2.99 (d, *J* = 5.0 Hz, 3H), 4.24 (q, *J* = 6.8 Hz, 2H), 5.95 (brs, 1H), 6.34 (d, *J* = 16.5 Hz, 1H), 7.04 (ddd, *J* = 2.8, 8.7, 8.7 Hz, 1H), 7.25 (dd, *J* = 2.8, 10.1 Hz, 1H), 7.44 (dd, *J* = 6.0, 8.7 Hz, 2H), 7.91 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 60.9, 113.9 (d, *J* = 22.9 Hz), 116.8 (d, *J* = 22.9 Hz), 122.1, 130.6 (d, *J* = 9.5 Hz), 133.4 (d, *J* = 2.9 Hz), 135.5 (d, *J* = 7.6 Hz), 140.8 (d, *J* = 2.9 Hz), 163.5 (d, *J* = 254.7 Hz), 166.3, 168.6; HRMS (ESI): *m/z* calculated for $C_{13}H_{14}FNNaO_3^+$ $[M+Na]^+$: 274.0850, found: 274.0844



4d

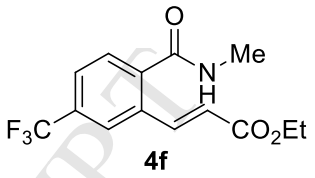
(*E*)-ethyl 3-(5-bromo-2-(methylcarbamoyl)phenyl)acrylate (4e): a colorless solid; IR (KBr) ν 3079, 2975, 2935, 1719, 1642, 1561, 1316, 1190, 1032, 979, 862 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 7.5 Hz , 3 H), 3.00 (d, *J* = 5.2 Hz, 3H), 4.23 (q, *J* = 7.5 Hz, 2H), 5.88 (brs, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.74 (s, 1H) 7.90 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$,



4e

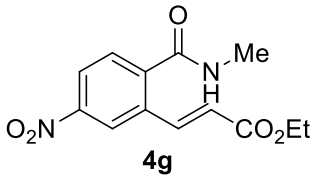
100 MHz) δ 14.4, 27.1, 60.1, 122.1, 124.1, 124.7, 129.3, 130.1, 132.7, 134.9, 135.8, 140.5, 166.2, 168.5; HRMS (ESI): *m/z* calculated for $C_{13}H_{14}BrNNaO_3^+$ $[M+Na]^+$: 334.0049, found: 334.0050

(*E*)-ethyl 3-(2-(methylcarbamoyl)-5-(trifluoromethyl)phenyl)acrylate (4f): a colorless solid; IR (KBr) ν 3084, 2974, 1717, 1642, 1551, 1337, 1292, 1159, 1122, 1042, 989, 924, 843 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 6.9 Hz , 3 H), 3.04 (d, *J* = 4.6 Hz, 3H), 4.24 (q, *J* = 6.9 Hz, 2H), 5.88 (brs, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 7.57-7.65 (m, 2H), 7.85 (s, 1H) 7.94 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 61.0, 122.6, 123.5 (q, *J* = 273.4 Hz), 124.1 (q, *J* = 3.8 Hz), 126.3 (q, *J* = 22.9 Hz), 128.4, 132.5 (q, *J* = 32.9 Hz), 133.7; HRMS (ESI): *m/z* calculated for $C_{14}H_{14}F_3NNaO_3^+$ $[M+Na]^+$: 324.0818, found: 324.0818



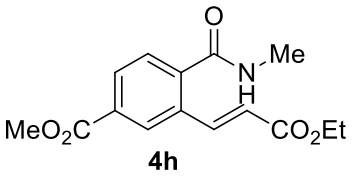
4f

(*E*)-ethyl 3-(2-(methylcarbamoyl)-5-nitrophenyl)acrylate (4g): a colorless solid; IR (KBr) ν 3085, 2977, 1713, 1643, 1556, 1522, 1352, 1282, 1040, 989, 825 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 3.03 (d, *J* = 5.0 Hz, 3H), 4.26 (q, *J* = 7.3 Hz, 2H), 6.14 (brs, 1H), 6.50 (d, *J* = 16.5 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 16.5 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 1H) 8.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.2, 61.2, 122.1, 123.7, 124.2, 134.7, 139.4, 142.3, 148.8, 165.9, 167.5; HRMS (ESI): *m/z* calculated for $C_{13}H_{14}N_2NaO_5^+$ $[M+Na]^+$: 301.0795, found: 301.0791



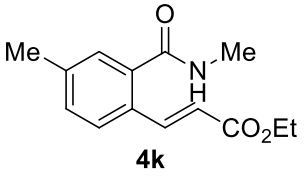
4g

(*E*)-methyl 3-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-(methylcarbamoyl)benzoate (4h): a colorless solid; IR (KBr) ν 3082, 2988, 2954, 1721, 1644, 1551, 1320, 1252, 1184, 1032, 976, 866, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, *J* = 7.2 Hz , 3 H), 3.02 (d, *J* = 4.8 Hz, 3H), 3.94 (s, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.07 (brs, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 16.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 27.1, 52.7, 60.9, 122.1, 122.1, 127.9, 128.4, 130.6, 131.9, 133.2, 140.8, 140.9, 166.0, 166.4, 168.6; HRMS (ESI): *m/z* calculated for $C_{15}H_{17}NNaO_5^+$ $[M+Na]^+$: 314.0999, found: 314.0993



4h

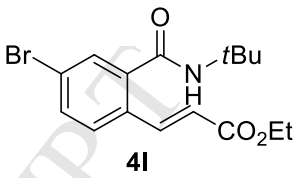
(*E*)-ethyl 3-(4-methyl-2-(methylcarbamoyl)phenyl)acrylate (4k): a colorless solid; IR (KBr) ν 2979, 1715, 1639, 1604, 1541, 1309, 1272, 1178, 1030, 977, 822 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, *J* = 7.3 Hz , 3 H), 2.35 (s, 3H), 3.00 (d, *J* = 5.0 Hz, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 5.88 (brs, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 7.29-7.37 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100



4k

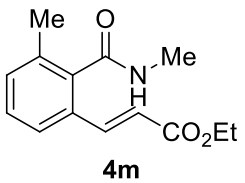
MHz) δ 14.4, 21.4, 27.0, 60.7, 119.9, 127.2, 128.4, 129.9, 131.1, 137.3, 140.4, 141.8, 166.8, 169.6; HRMS (ESI): *m*/*z* calculated for $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$: 270.1101, found: 270.1104

(*E*)-ethyl 3-(4-bromo-2-(tert-butylcarbamoyl)phenyl)acrylate (4l): a colorless oil; IR (neat) ν 3065, 2973, 1714, 1641, 1541, 1312, 1263, 1178, 1097, 1041, 976, 895, 816 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 1.47(s, 9H), 4.24 (q, *J* = 7.3 Hz, 2H), 5.64 (brs, 1H), 6.35 (d, *J* = 16.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 2.3, 7.8 Hz, 1H), 7.57 (s, *J* = 2.3 Hz, 1H), 7.85 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 28.8, 52.7, 60.8, 121.3,124.0, 128.5, 130.7, 131.2, 133.1, 140.0, 140.7, 166.3, 166.7; HRMS (ESI): *m*/*z* calculated for $C_{16}H_{21}NNaO_3^+$ $[M+Na]^+$: 376.0519, found: 376.0520



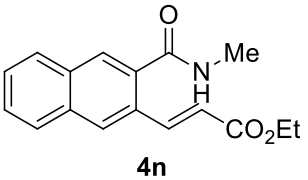
4l

(*E*)-ethyl 3-(3-methyl-2-(methylcarbamoyl)phenyl)acrylate (4m): a colorless oil; IR (neat) ν 2980, 1710, 1638, 1543, 1313, 1233, 1090, 1039, 979, 867, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.3 Hz , 3 H), 2.34 (s, 3H), 3.04 (d, *J* = 5.0 Hz, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 5.72 (brs, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.70 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 19.3, 26.8, 60.7, 120.8, 124.0, 1293, 131.7, 121.9, 135.6, 138.2, 141.6, 166.7, 169.8; HRMS (ESI): *m*/*z* calculated for $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$: 270.1101, found: 270.1102



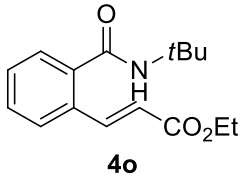
4m

(*E*)-ethyl 3-(3-(methylcarbamoyl)naphthalen-2-yl)acrylate (4n): a colorless solid; IR (KBr) ν 2981, 1715, 1644, 1622, 1551, 1304, 1177, 1033, 976, 863, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.3 Hz , 3 H), 3.05 (d, *J* = 5.0 Hz, 3H), 4.26 (q, *J* = 7.3 Hz, 2H), 6.14 (brs, 1H), 6.44 (d, *J* = 16.5 Hz, 1H), 7.50-7.57 (m, 2H), 7.76-7.87 (m, 2H), 7.91 (s, 1H), 8.01 (s, 1H), 8.23 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.5, 27.1, 60.7, 120.8, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 130.4, 133.0, 133.6, 134.4, 142.5, 166.7, 169.5; HRMS (ESI): *m*/*z* calculated for $C_{17}H_{17}NNaO_3^+$ $[M+Na]^+$: 306.1101, found: 306.1105



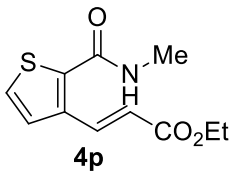
4n

(*E*)-ethyl 3-(2-(*tert*-butylcarbamoyl)phenyl)acrylate (4o): a colorless oil; IR (neat) ν 3063, 2971, 1712, 1639, 1538, 1314, 1177, 1094, 1042, 977, 879, 764 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.3 Hz , 3 H), 1.49 (s, 9H), 4.26 (q, *J* = 7.3 Hz, 2H), 5.55 (brs, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 7.36-7.50 (m, 3H), 7.59 (s, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 28.9, 52.4, 60.7, 120.8, 127.0, 127.7, 130.0, 130.1, 132.3, 138.7, 142.0, 166.6, 168.3; HRMS (ESI): *m*/*z* calculated for $C_{16}H_{20}BrNNaO_3^+$ $[M+Na]^+$: 298.1414, found: 298.1423



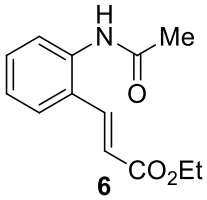
4o

(*E*)-ethyl 3-(2-(methylcarbamoyl)thiophen-3-yl)acrylate (4p): a colorless solid; IR (neat) ν 2979, 1707, 1632, 1536, 1244, 1178, 1037, 987, 867, 774 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 6.9 Hz , 3 H), 3.01 (s, 3H), 4.26 (q, *J* = 6.9 Hz, 2H), 6.33 (d, *J* = 16.5 Hz, 1H), 5.84 (brs, 1H), 7.29 (d, *J* = 5.5 Hz, 1H), 7.33 (d, *J* = 5.5 Hz, 1H), 8.26 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.5,27.2, 60.8, 121.7, 127.0, 127.2, 136.4, 136.5, 138.6, 162.8, 162.9; HRMS (ESI): *m*/*z* calculated for $C_{11}H_{13}NNaO_3S^+$ $[M+Na]^+$: 262.0508, found: 262.0513



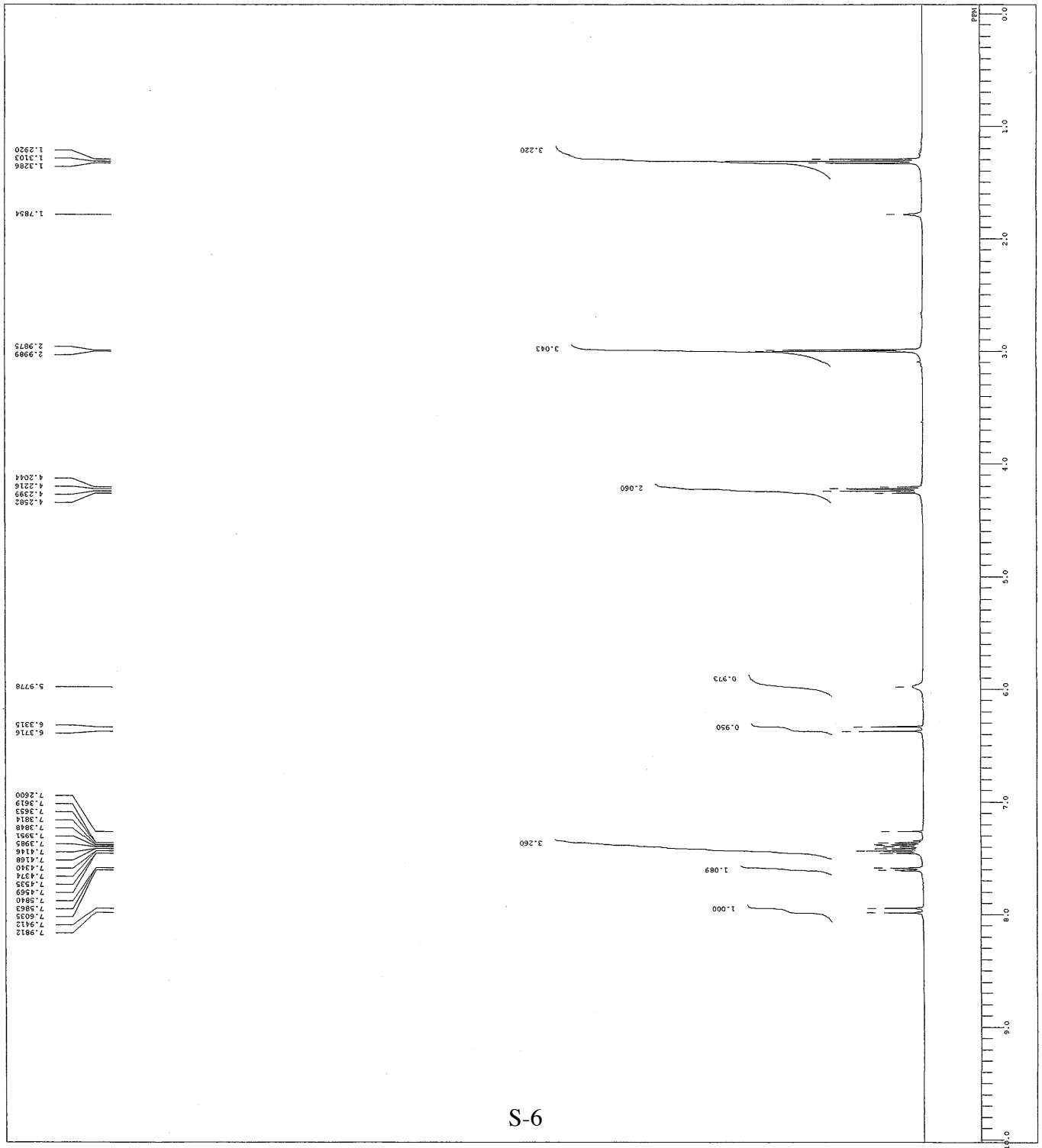
4p

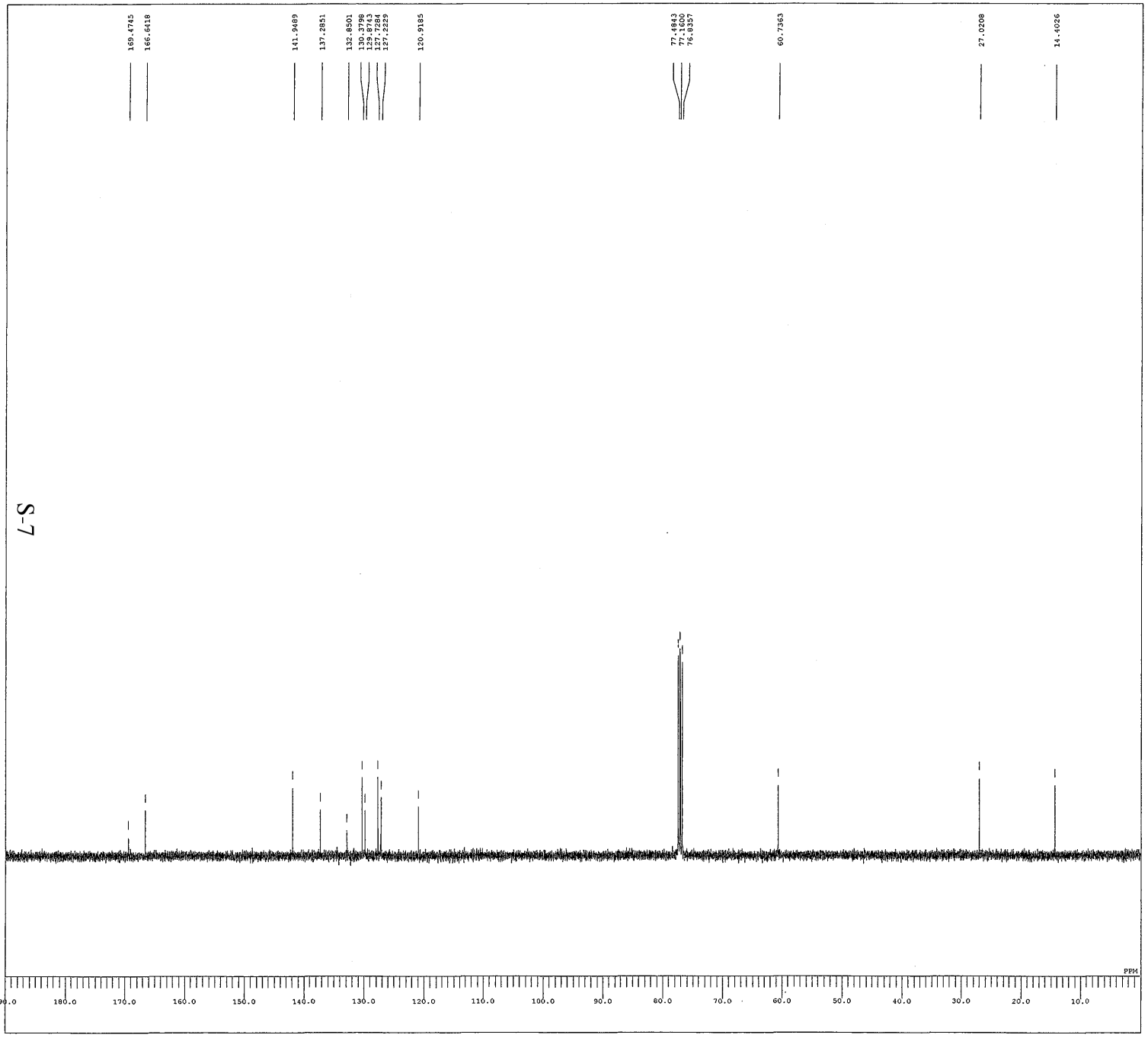
(*E*)-ethyl 3-(2-acetamidophenyl)acrylate: a colorless solid; IR (KBr) ν 2978, 1712, 1659, 1537, 1455, 1302, 1270, 1045, 971, 764, 743 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.6 Hz , 3 H), 2.23 (s, 3H), 4.26 (q, *J* = 7.6 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 7.20 (m, 1H), 7.29-7.43 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.70-7.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 24.4, 60.9, 120.9, 125.3, 126.0, 127.3, 127.7, 130.9, 136.0, 139.4, 166.9, 169.0; HRMS (ESI): *m*/*z* calculated for $C_{13}H_{15}NNaO_3^+$ $[M+Na]^+$: 256.0944, found: 256.0936



6

oxidative Heck N-methyl amide



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OBSET         4.64 KHz
OBFIN         8.74 Hz
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FREQU     24630.54 Hz
SCANS          227
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PD          3.0000 sec
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SLVNT  CDCL3
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RGAIN           60
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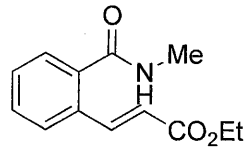
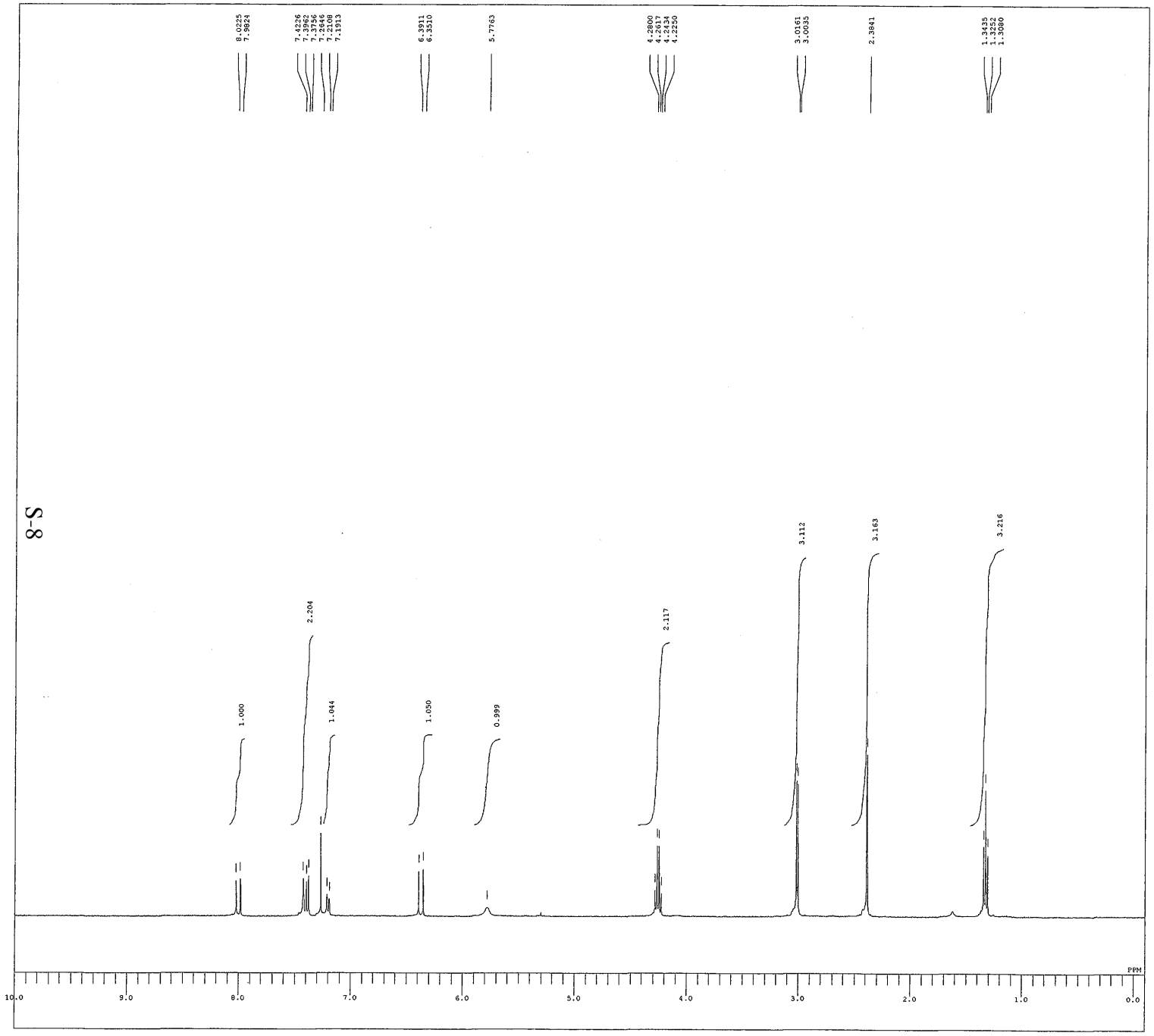


4a

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COMNT  ys-oxidative Heck N-methyl p-Me amide
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FREQU       5878.90 Hz
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PD             5.0000 sec
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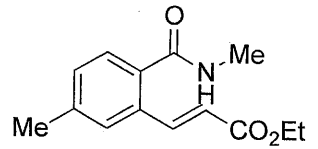
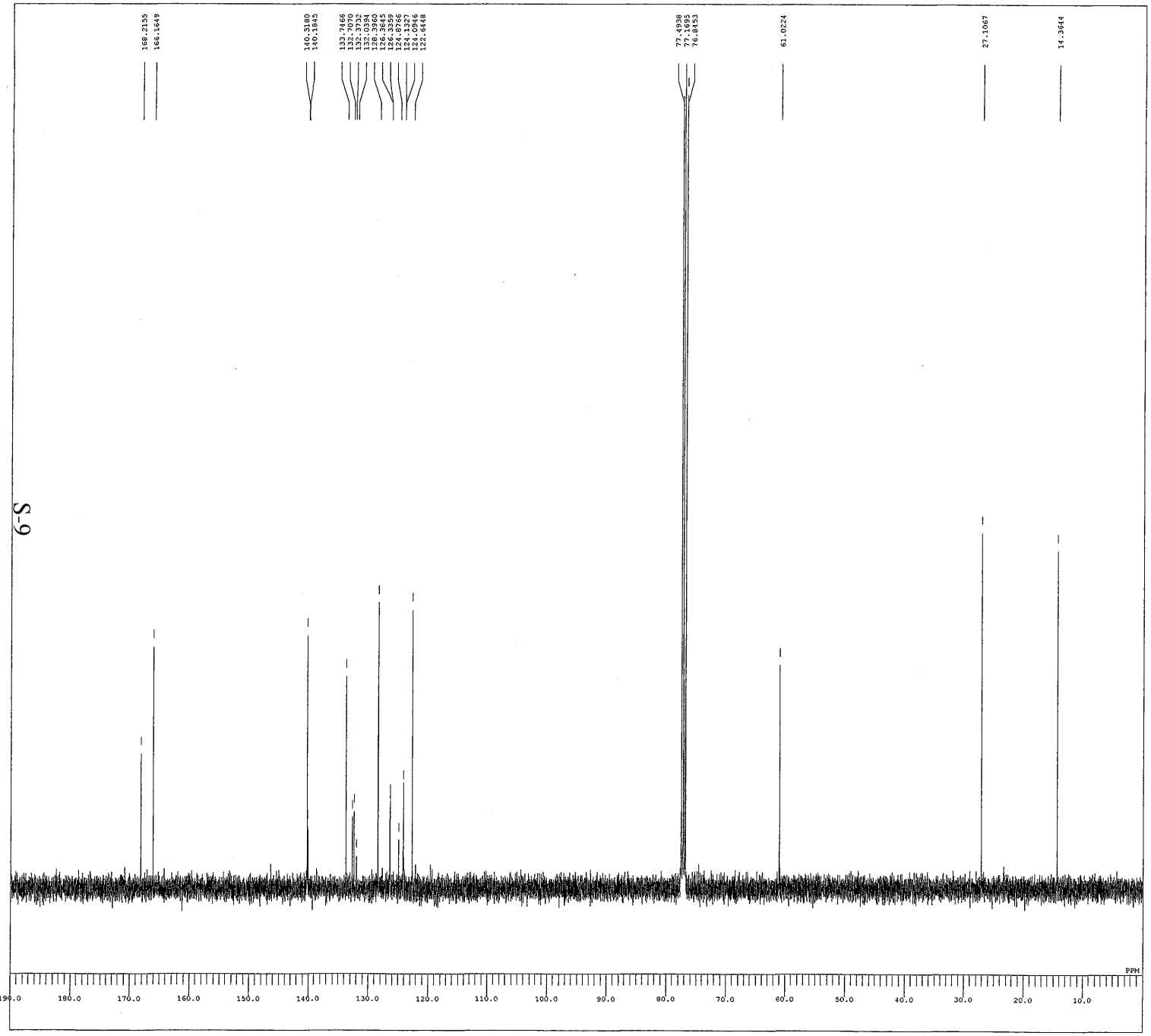


4b

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POINT        26214
FRQU      24630.54 Hz
SCANS          515
ACQTM       1.0643 sec
PD          3.0000 sec
PW1          3.60 usec
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SLVNT  CDCL3
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RGAIN          60
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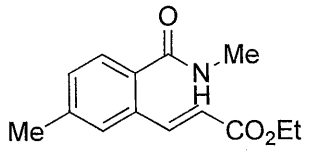
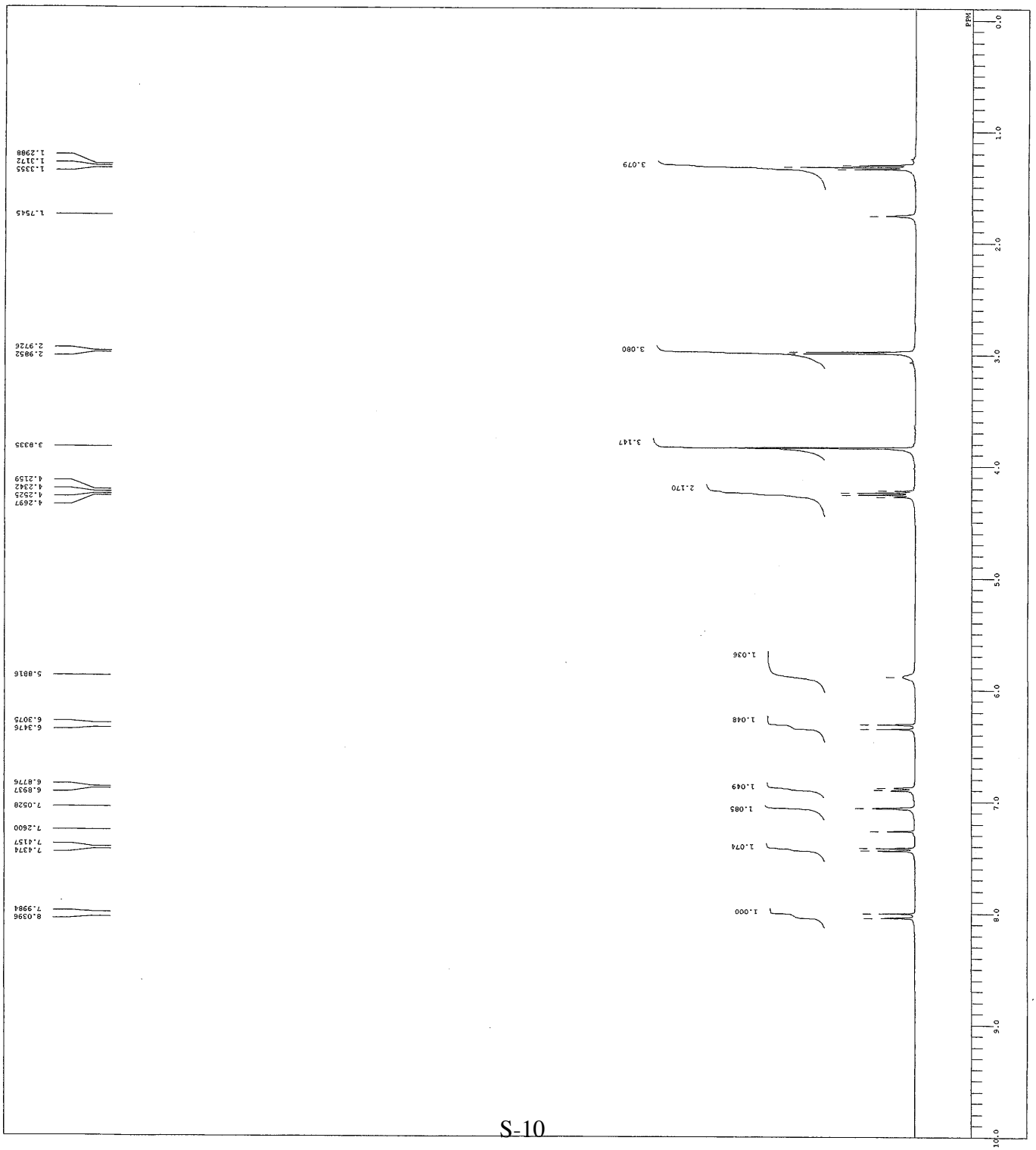
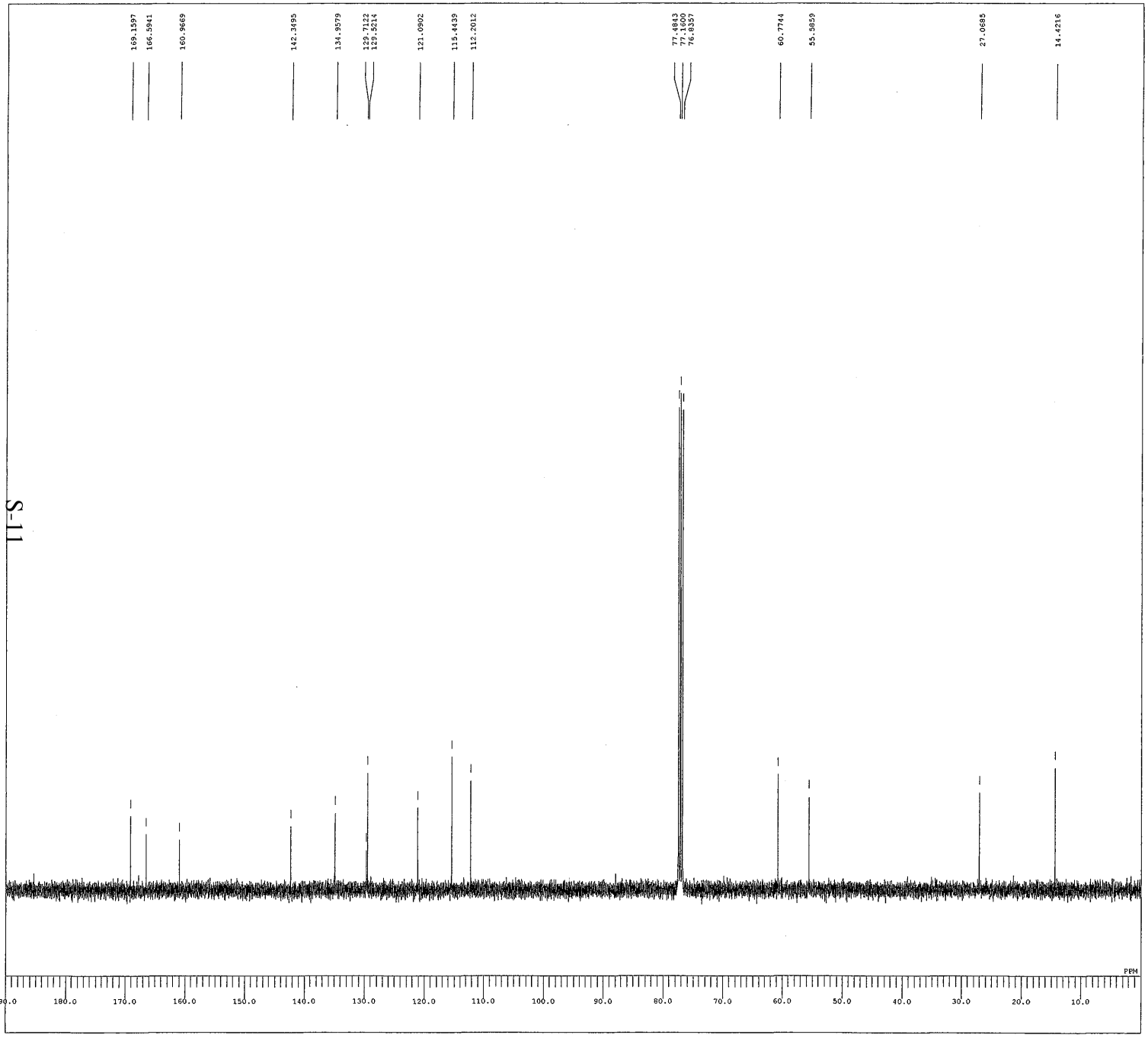


4b



oxidative Heck N-methyl pOMe amide

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COMNT  oxidative Heck N-methyl pOMe amide C
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OBFIN         8.74 Hz
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FREQU     24630.54 Hz
SCANS          391
ACQTM       1.0643 sec
PD          3.0000 sec
PW1            3.60 usec
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SLVNT  CDCL3
EXREF        77.16 ppm
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RGAIN           60
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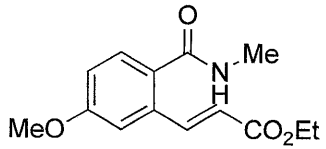
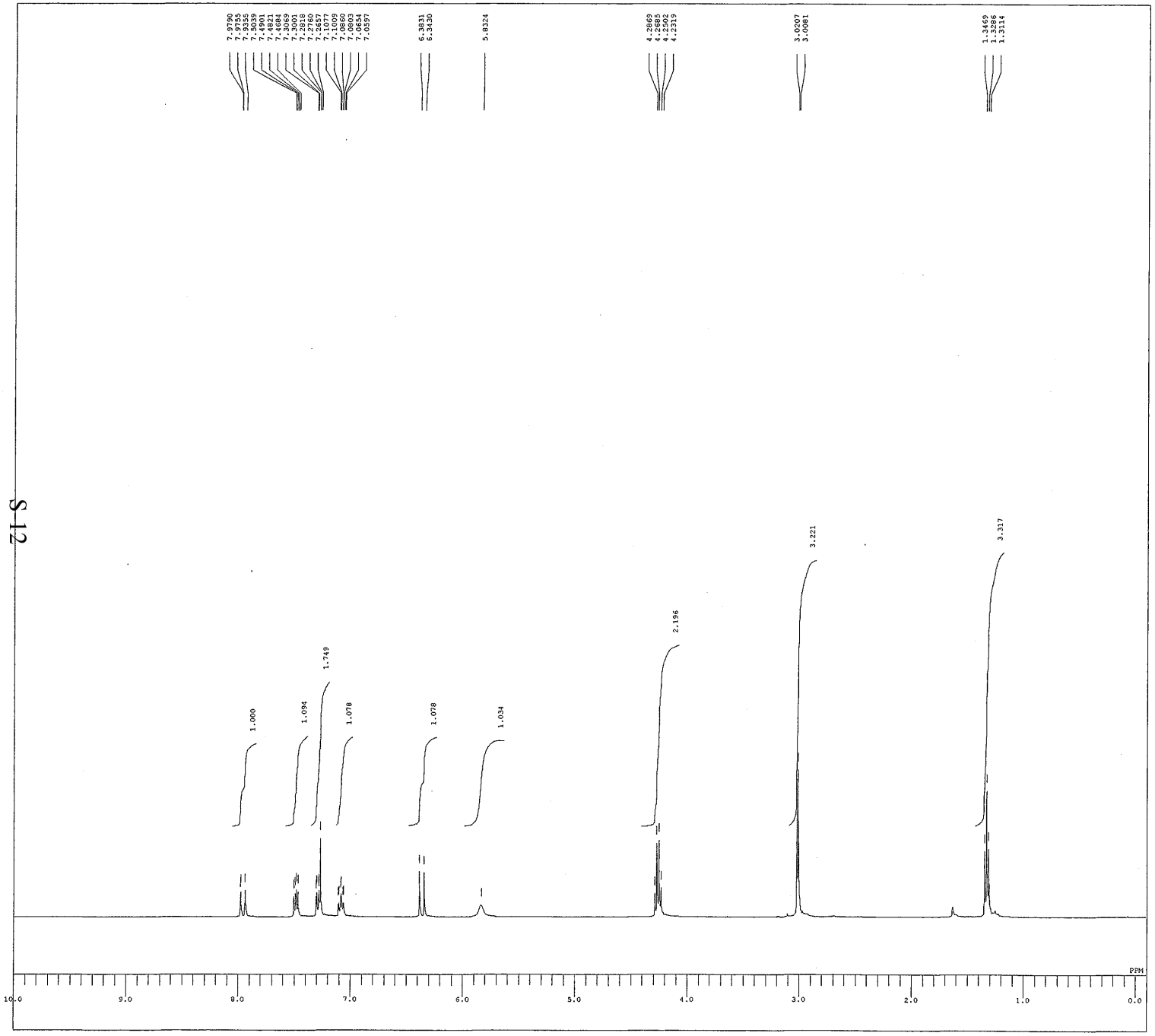


4c

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COMNT  oxidative Heck N-methyl p-F amide
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OBFIN          3.34 Hz
POINT         13107
FREQU       5878.90 Hz
SCANS             8
ACQTM          2.2295 sec
PD             5.0000 sec
PW1            5.07 usec
IRNUC  1H
CTEMP         22.7 c
SLVNT  CDCL3
EXREF         7.26 ppm
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RGAIN            44
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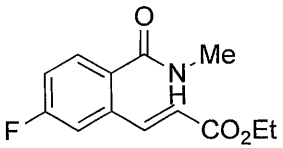
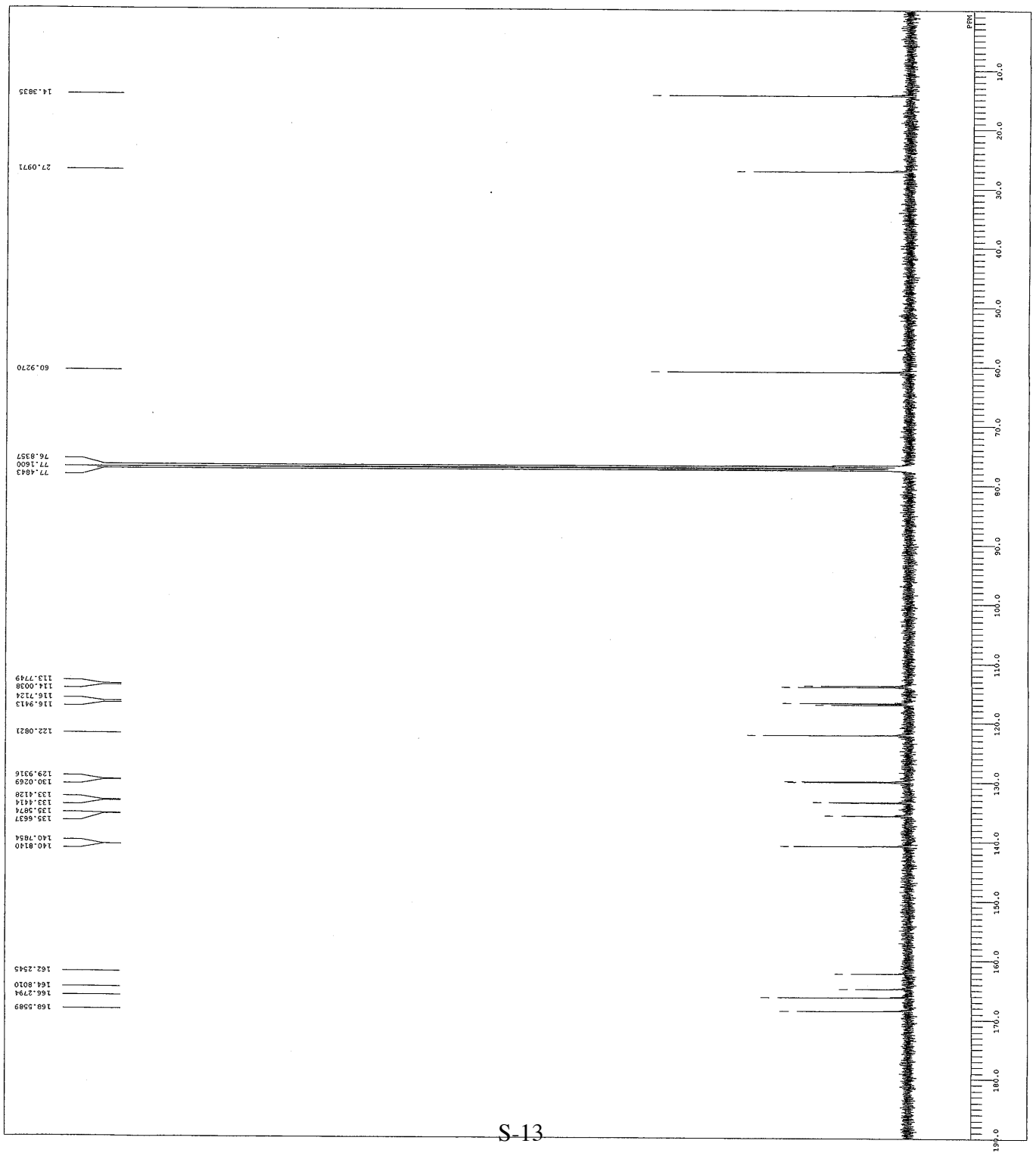
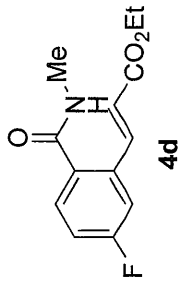


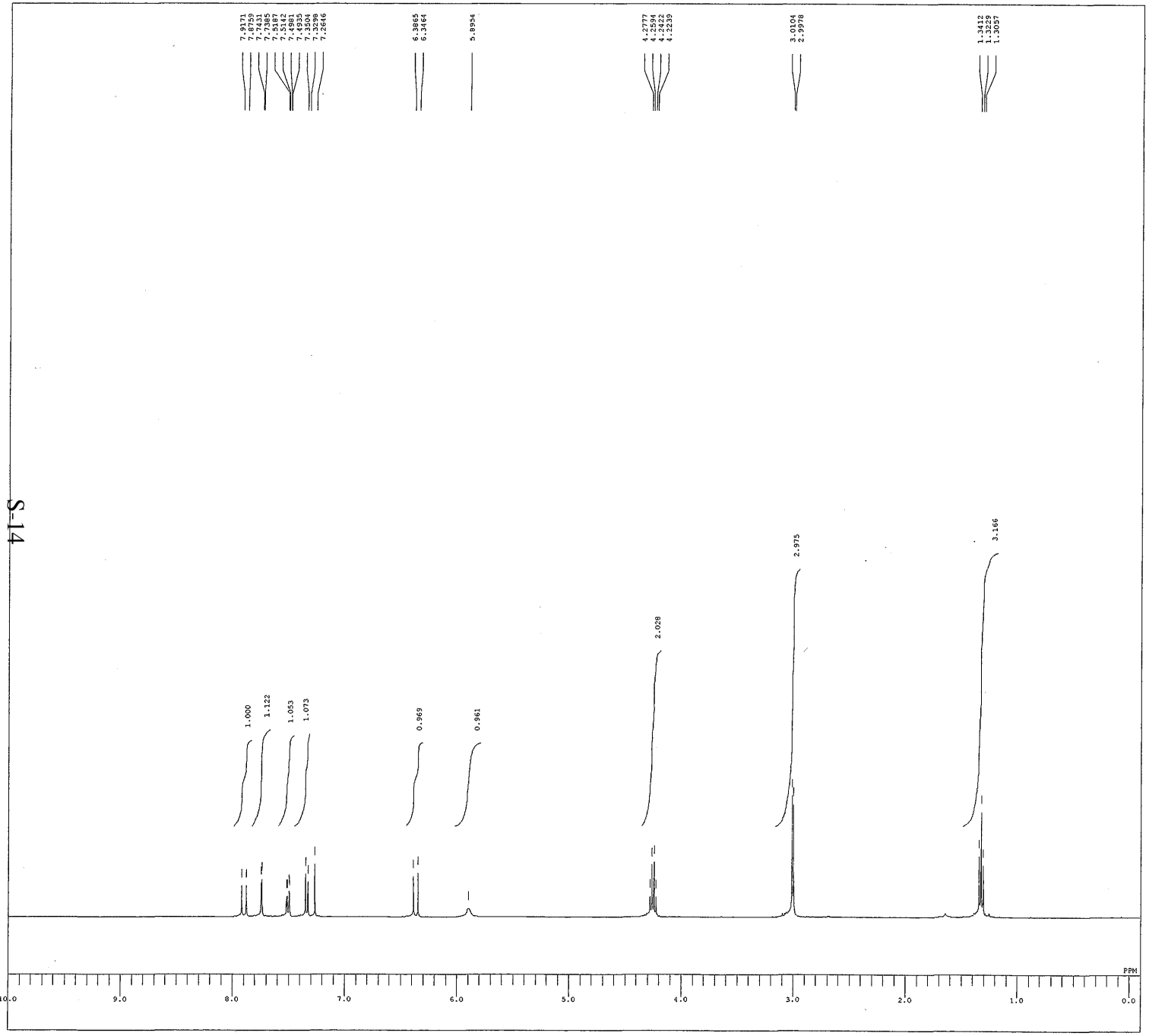
4d



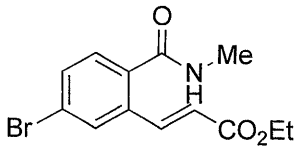


4d

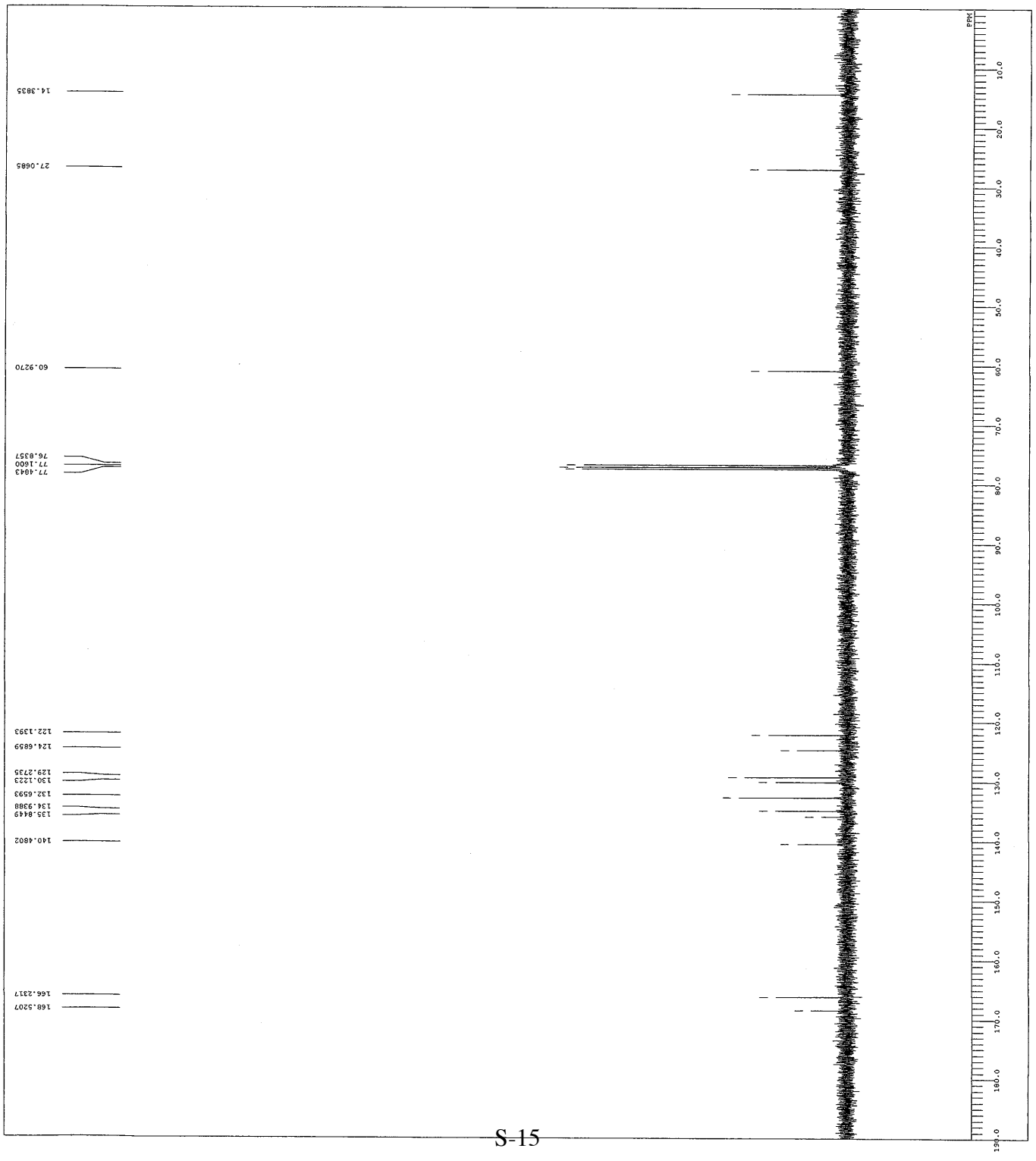
oxidative Heck N-methyl pF amide C

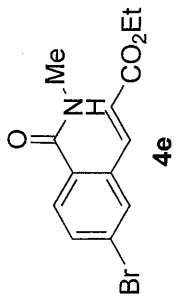



```
DFILE   ys-oxidative Heck N-methyl p-Br amide-1-1.als
COMNT   ys-oxidative Heck N-methyl p-Br amide
DATIM   14-01-2015 09:21:52
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         391.78 MHz
OBSET           8.51 KHz
OBFIN           3.34 Hz
POINT          13107
FREQU        5078.90 Hz
SCANS             8
ACQTM          2.2295 sec
PD             5.0000 sec
PW1            5.07 usec
IRNUC   1H
CTEMP          22.4 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            44
```



4e

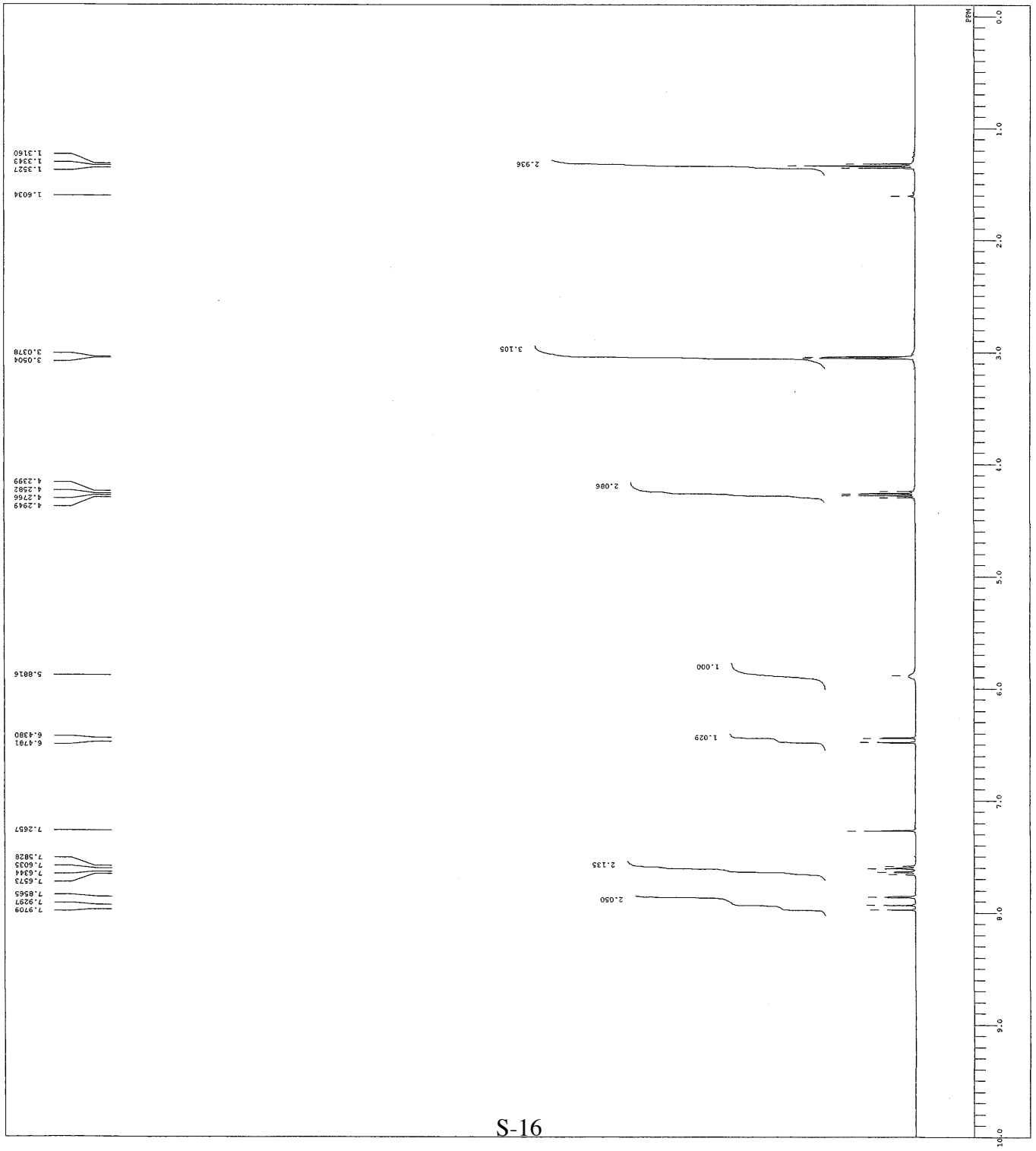


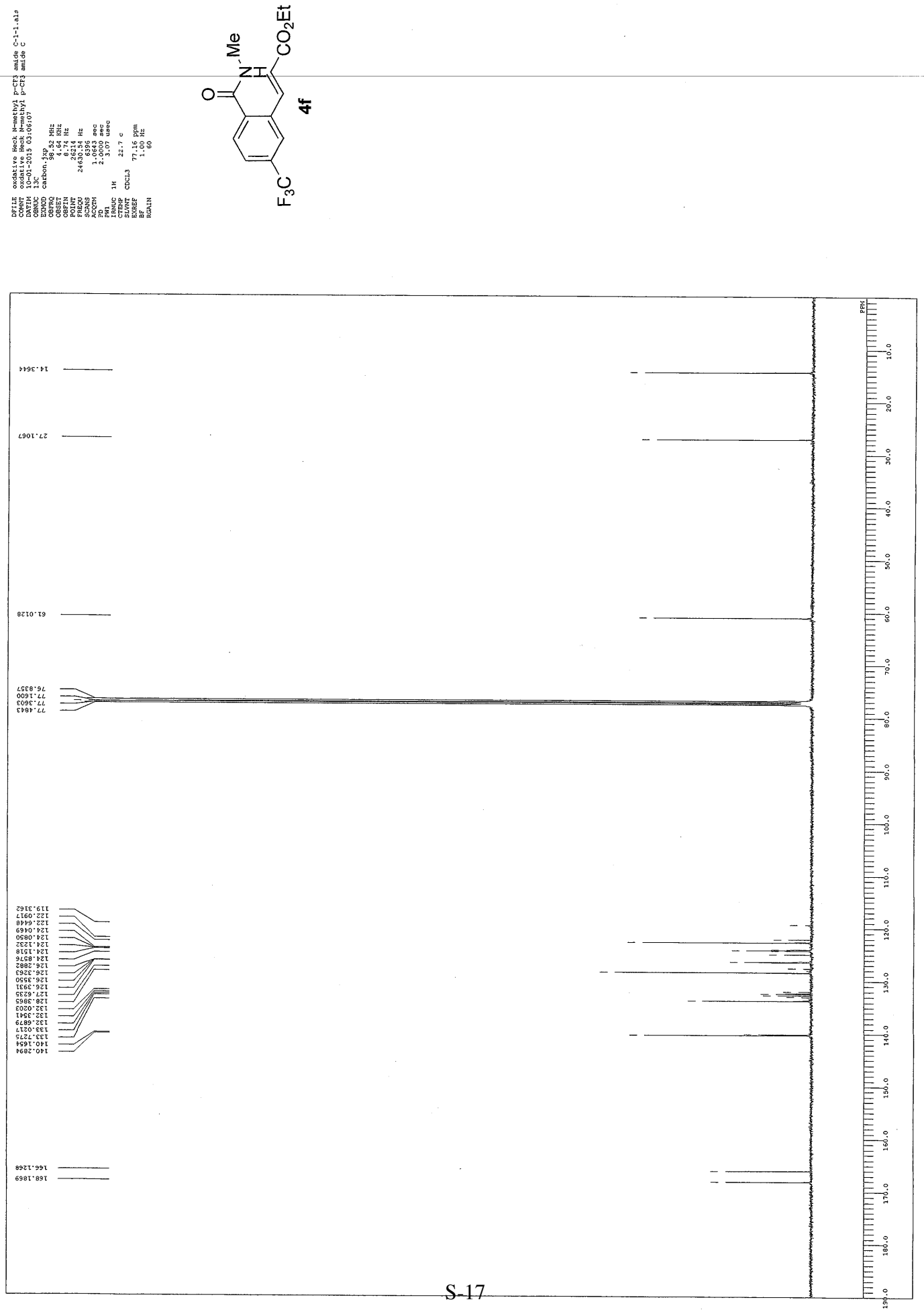



```
DTYIE  oxidative Heck N-methyl pBr amide C-1-1.als
CURDE  oxidative Heck N-methyl pBr amide C
DATIM  22-10-2014 00:04:59
OBNUC  13C
EXMOD  carbon.jxp
OBSFQ      90.52 MHz
OBSET      4.44 KHz
OBFIN      8.74 Hz
POINT     26214
FRQLO     24630.54 Hz
SCANS       128
ACQPN       1.0483 sec
PD          3.0000 sec
PWNUC       3.00 usec
IRNUC  1H
CTEMP      24.6 c
SOLVNT  CDCl3     77.16 ppm
EXREF       0.12 Hz
BF            60
RGAIN
```

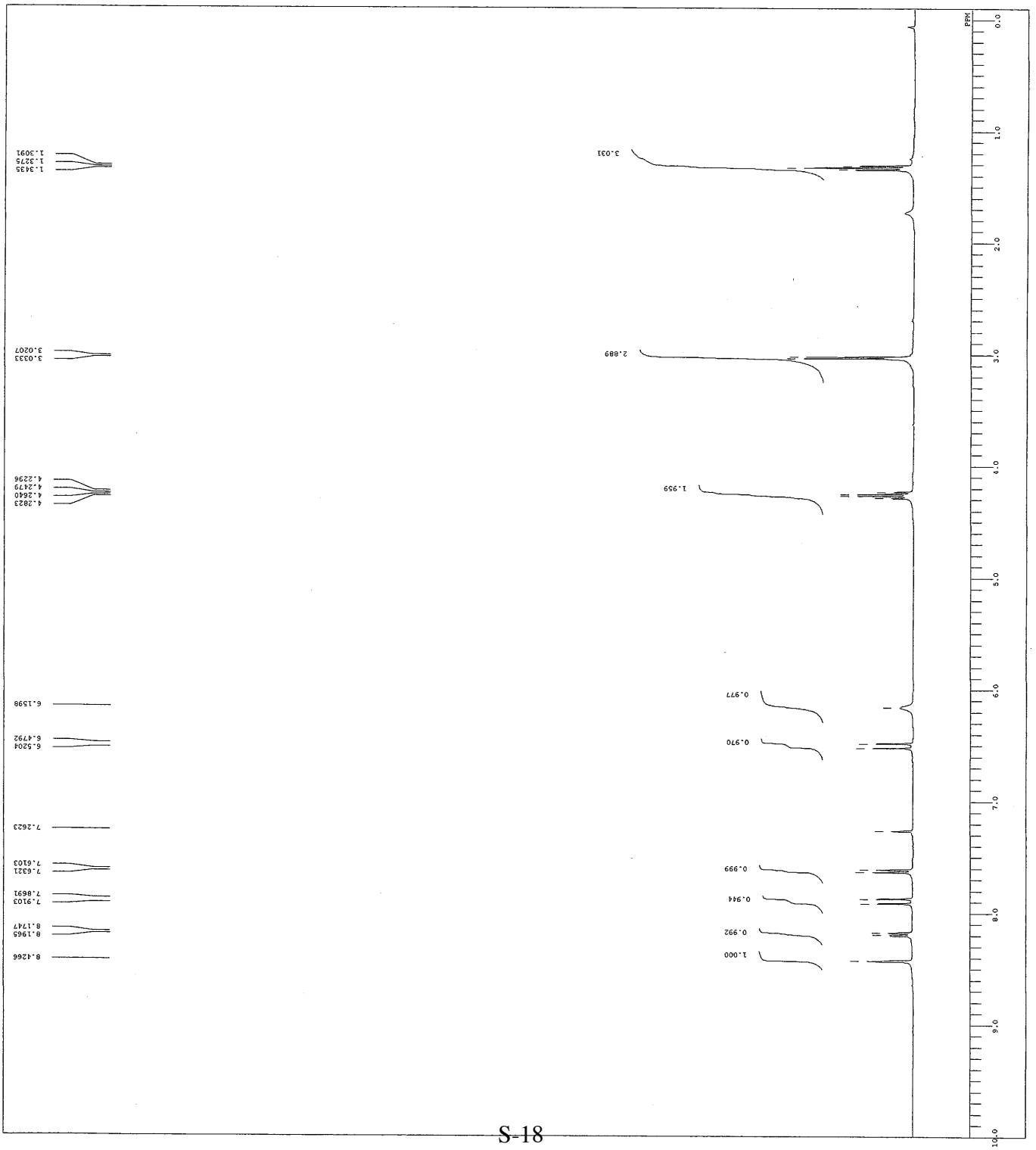
oxidative Heck N-methyl pBr amide C

ys-oxidative Heck N-methyl p-CF3 amide

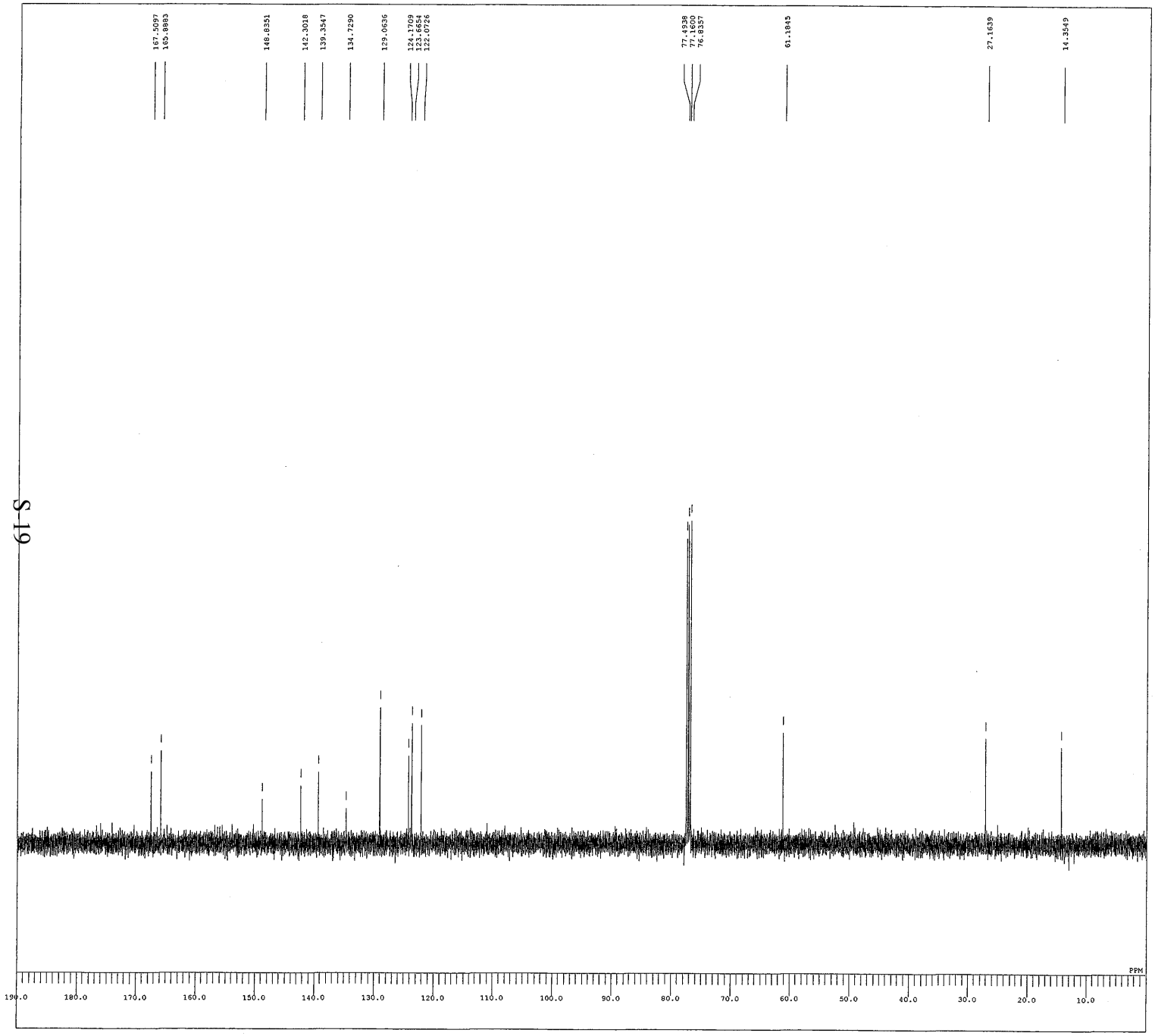




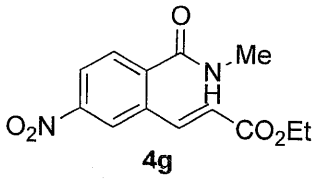
oxdative Heck N-methyl p-CF3 amide C



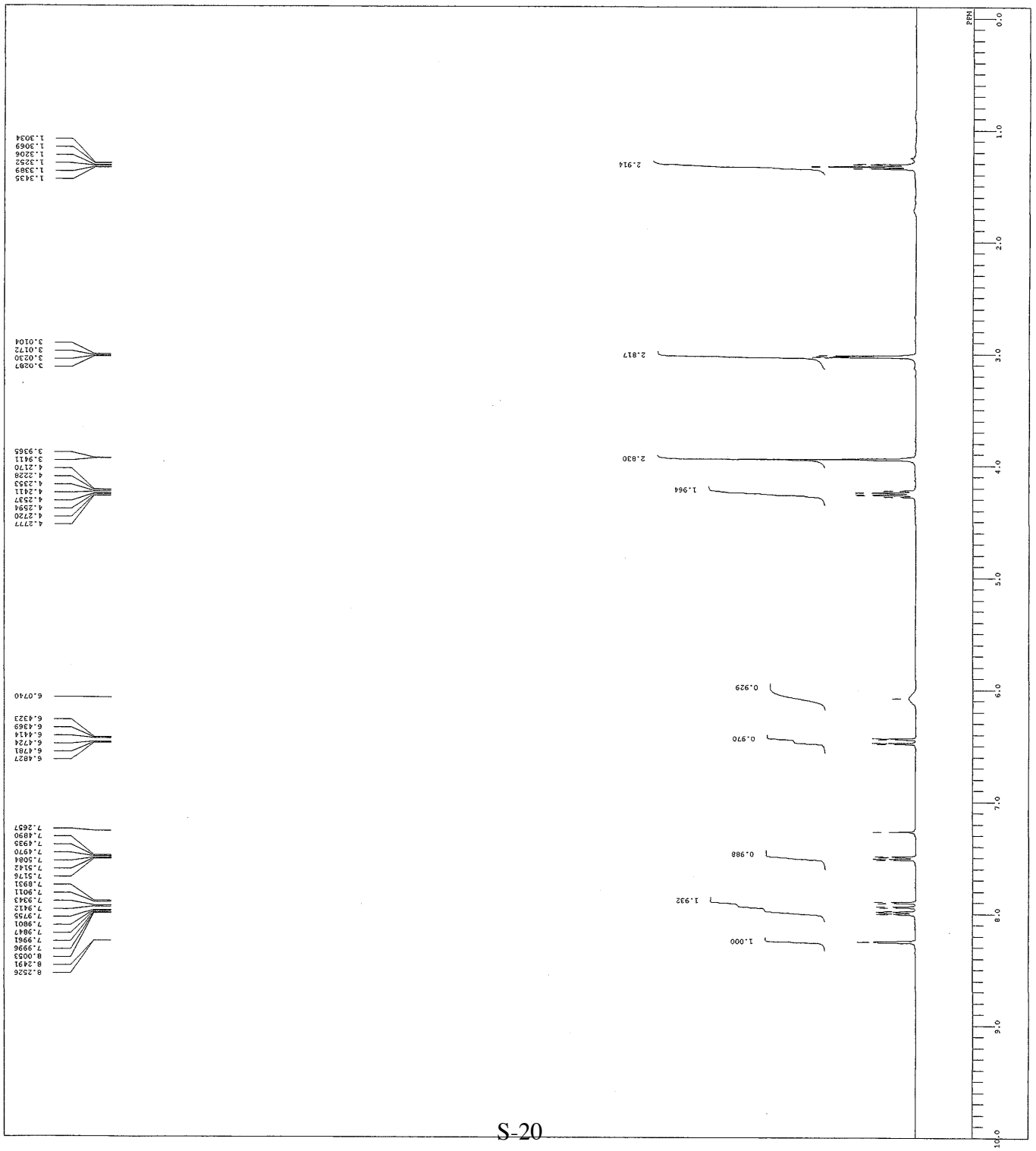
oxidative Heck N-methyl pNO2 amide

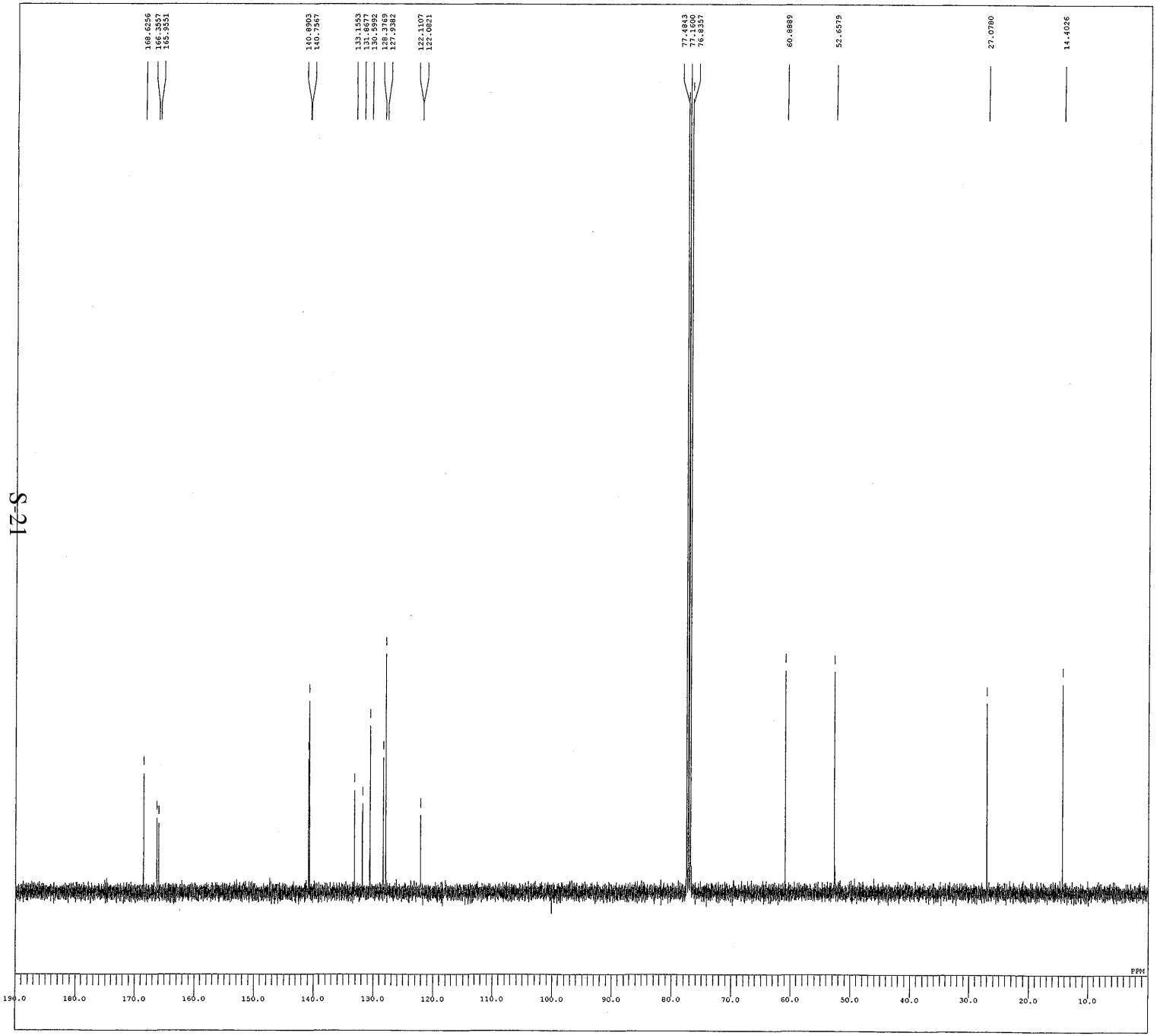



```
DFILE  oxidative Heck N-methyl pNO2 amide C-1-1.als
COMNT  oxidative Heck N-methyl pNO2 amide C
DATIM  22-10-2014 01:36:03
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.54 Hz
SCANS          109
ACQTM       1.0643 sec
PD          3.0000 sec
PW1            3.60 usec
IRNUC  1H
CTEMP         24.5 c
SLVNT  CDCL3
EXREF        77.16 ppm
BF            0.12 Hz
RGAIN           60
```

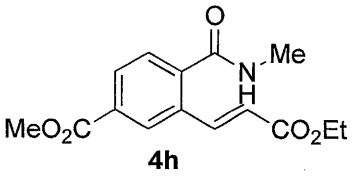


4g

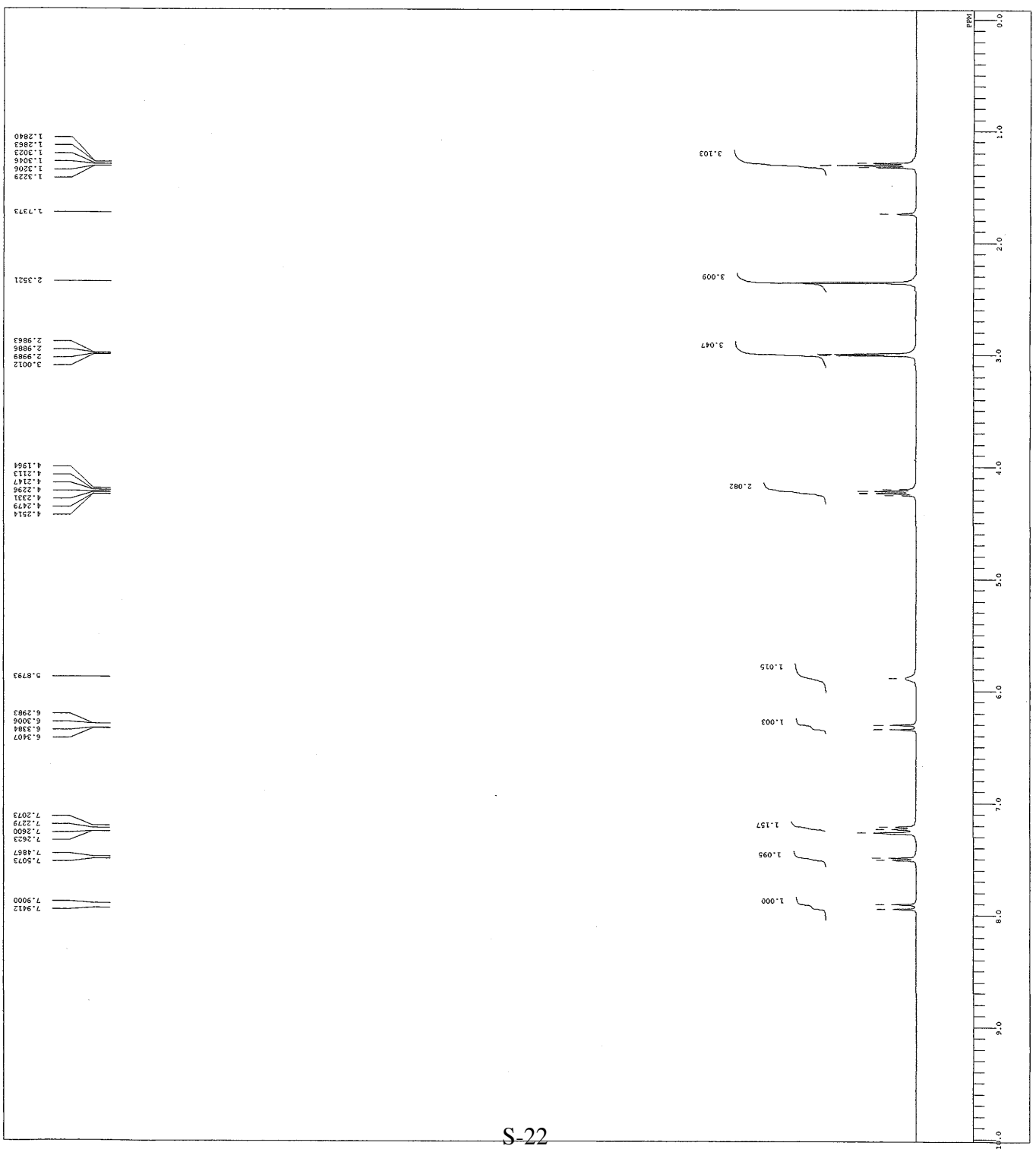

DFILE oxdative Heck N-methyl pCO2Me amide-1-1.als
COMNT oxdative Heck N-methyl pCO2Me amide
DATIM 09-01-2015 23:21:02
OBNUC 1H
EXMOD proton.jxp
OBFRQ 381.78 MHz
OBSET 8.51 KHz
OBFIN 1.34 Hz
POINT 131072
FREQU 5878.90 Hz
SCANS 4
ACQTM 2.2835 sec
PD 5.0000 sec
PW1 5.07 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 38
Me
N
H
O
CO2Et
MeO2C
4h
oxdative Heck N-methyl pCO2Me amide
PPM

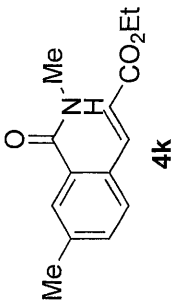



```
DFILE   oxdative Heck N-methyl pCO2Me amide C-1-1.als
COMNT   oxdative Heck N-methyl pCO2Me amide C
DATIM   09-01-2015 23:22:04
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         98.52 MHz
OBSET          4.64 KHz
OBFIN          9.74 Hz
POINT         26214
FREQU      24630.54 Hz
SCANS           742
ACQTM         1.0643 sec
PD            2.0000 sec
PW1              3.07 usec
IRNUC   1H
CTEMP         22.7 c
SLVNT   CDCL3
EXREF         77.16 ppm
BF             0.12 Hz
RGAIN            60
```



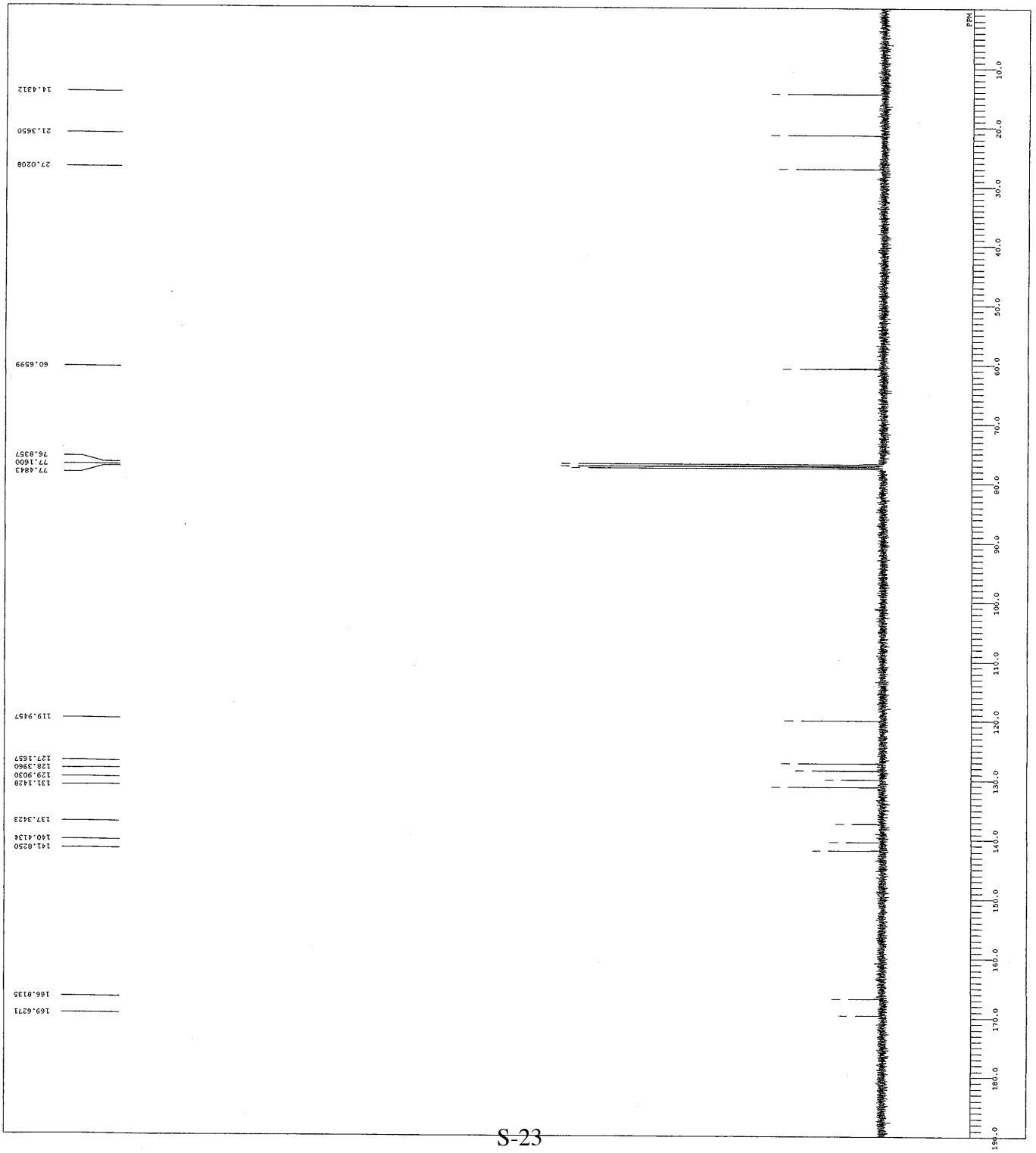
4h

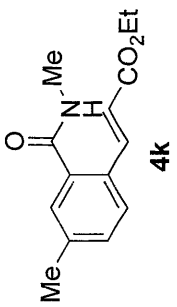




4k

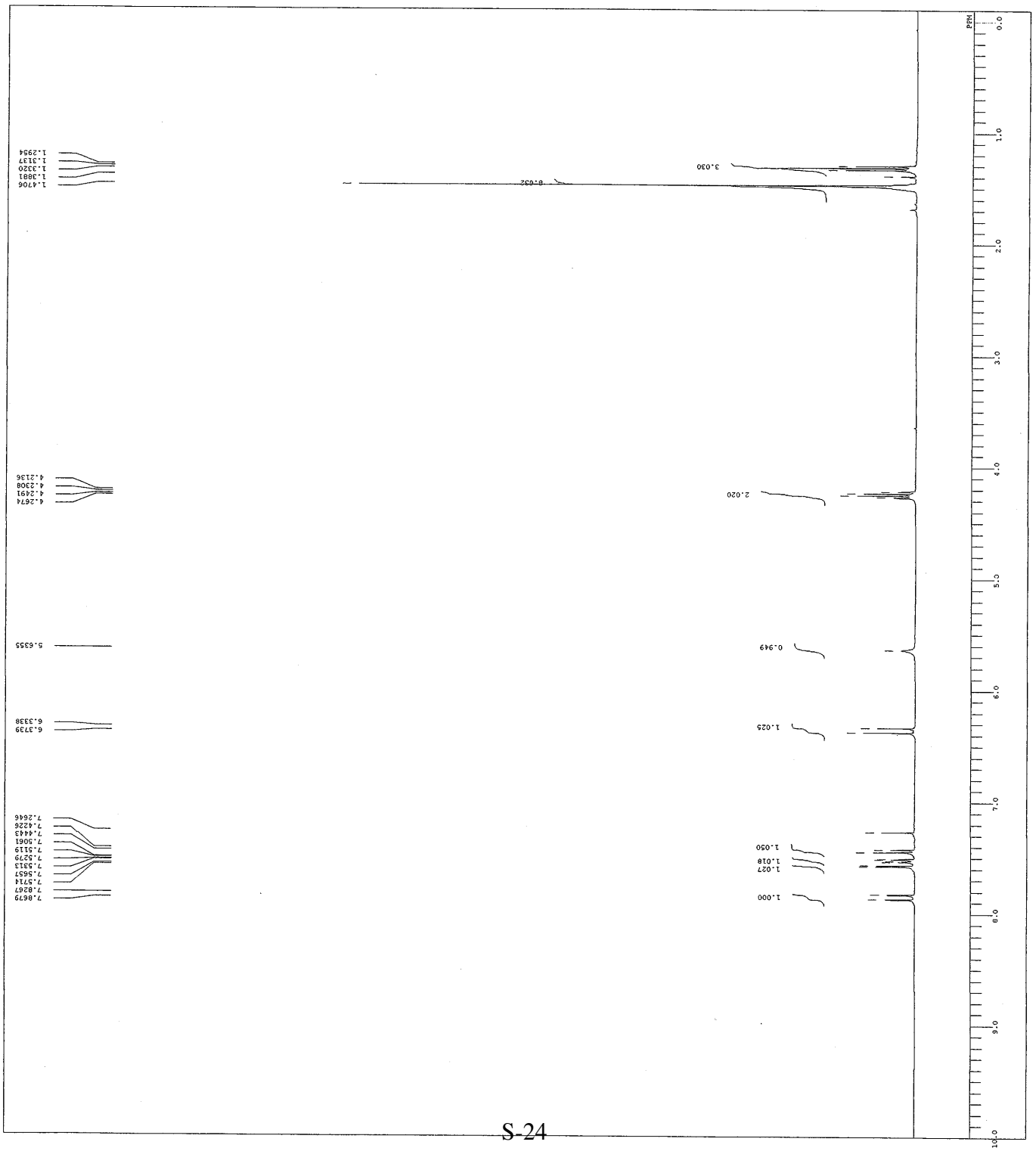
oxidative Heck N-methyl mMe amide



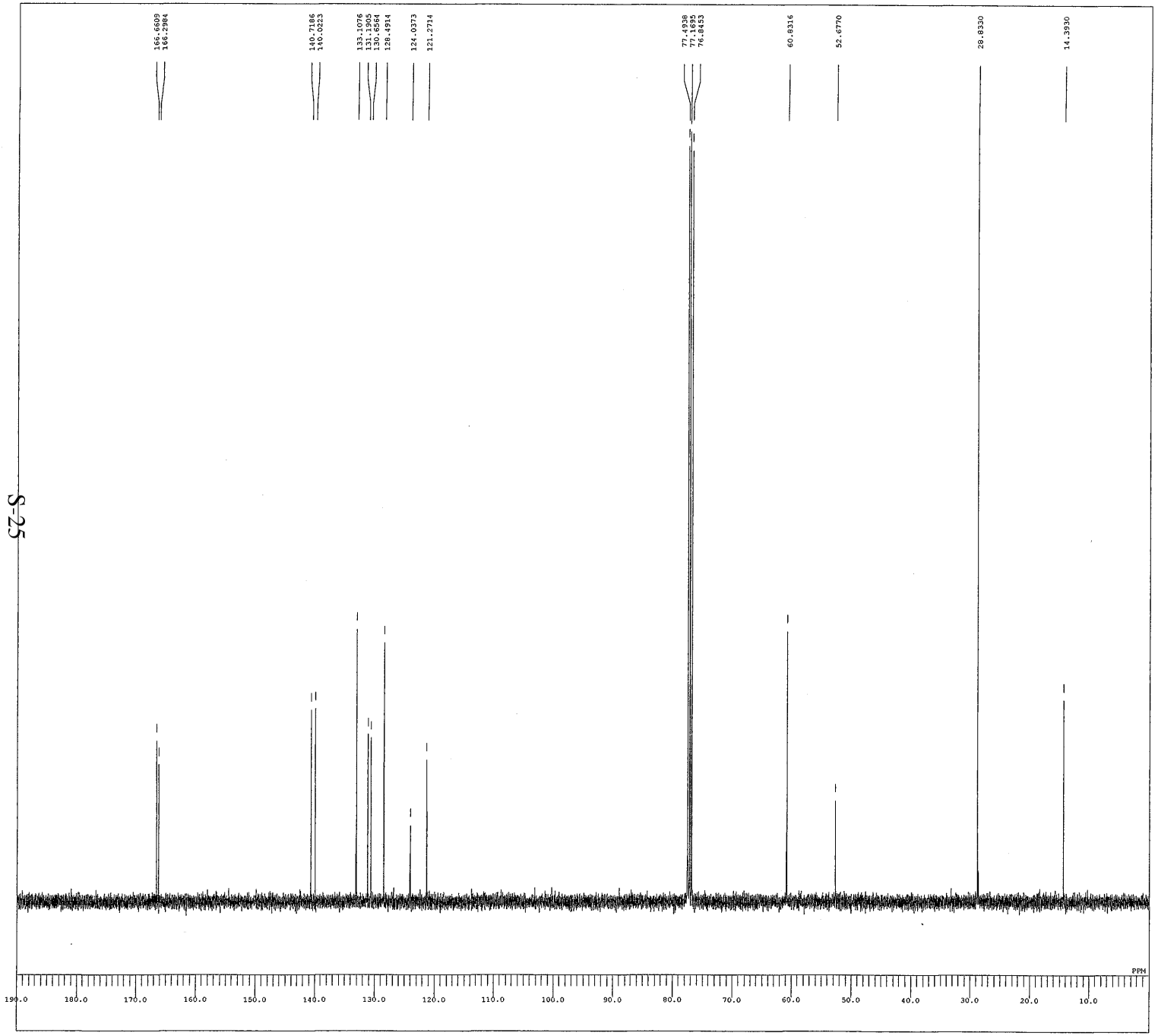


4k

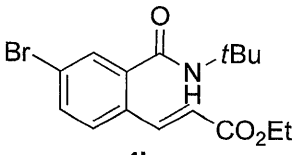
oxidative Heck N-methyl mMe amide



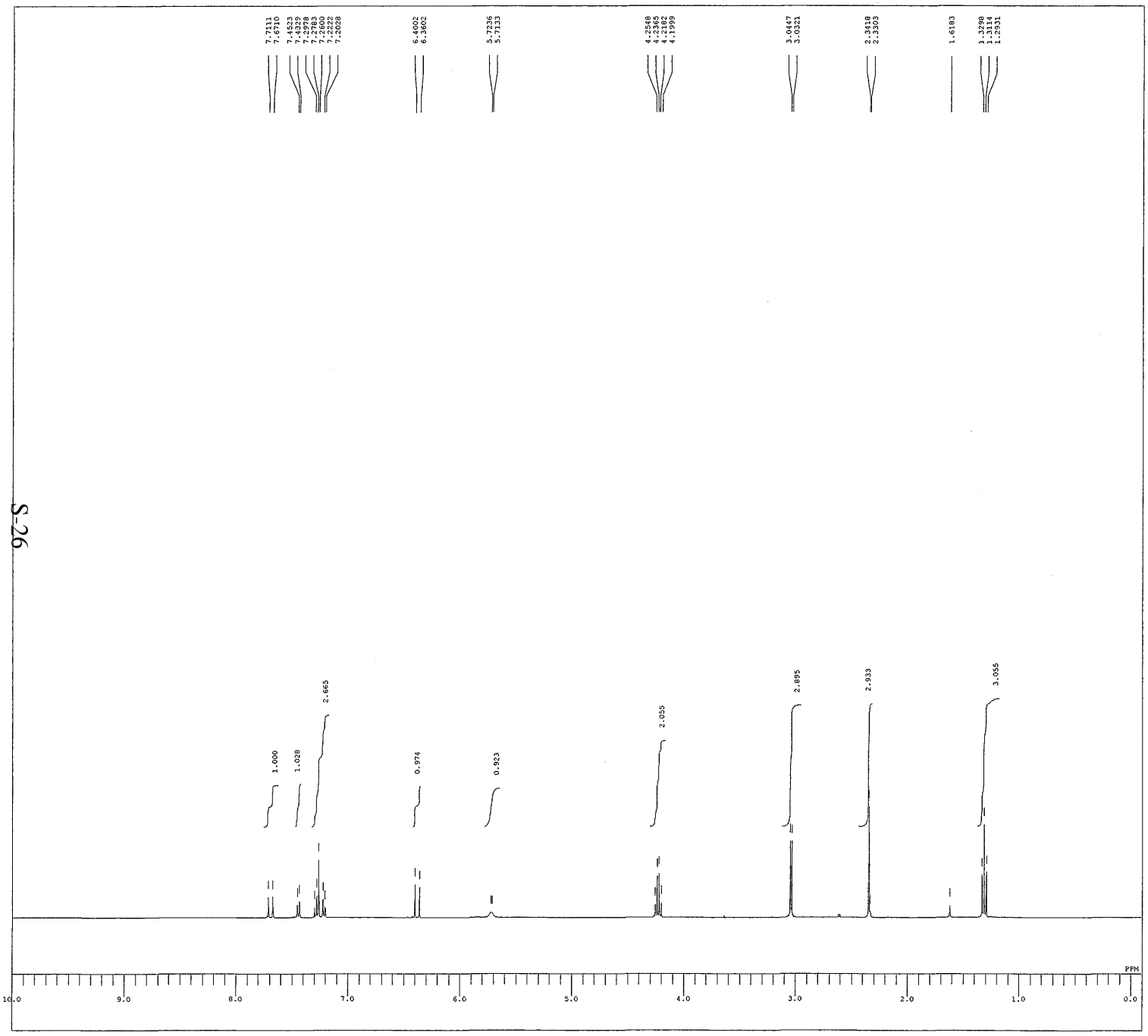
oxdative Heck N-tBu m-Br amide



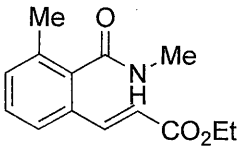

```
DFILE  oxdative Heck N-tBu m-Br amide C-1-1.als
COMNT  oxdative Heck N-tBu m-Br amide C
DATIM  10-01-2015 02:15:16
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.54 Hz
SCANS          919
ACQTM       1.0643 sec
PD          2.0000 sec
PW1            3.07 usec
IRNUC  1H
CTEMP         22.8 c
SLVNT  CDCL3
EXREF        77.16 ppm
BF            0.12 Hz
RGAIN           60
```



4l

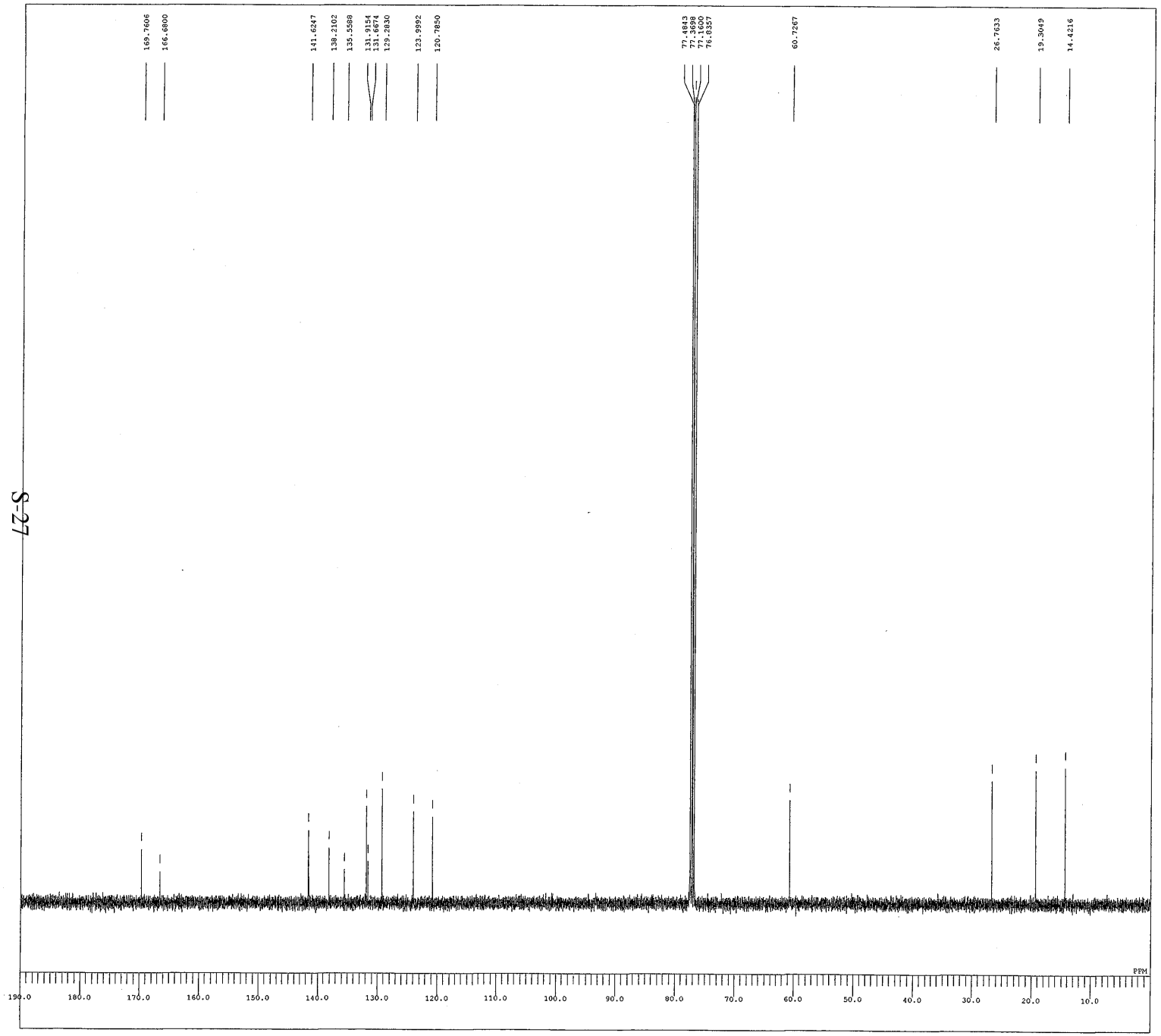



```
DFILE  oxdative Heck N-methyl o-methyl amide-1-1.als
COMNT  oxdative Heck N-methyl o-methyl amide
DATIM  10-01-2015 01:20:12
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        391.78 MHz
OBSET          6.51 KHz
OBFIN          3.34 Hz
POINT         13107
FREQU       5878.90 Hz
SCANS             8
ACQTM          2.2295 sec
PD             5.0000 sec
PW1               5.07 usec
IRNUC  1H
CTEMP            22.7 c
SLVNT  CDCL3
EXREF             7.26 ppm
BF                0.12 Hz
RGAIN               44
```

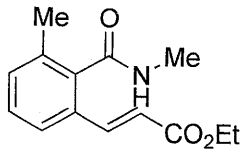


4m

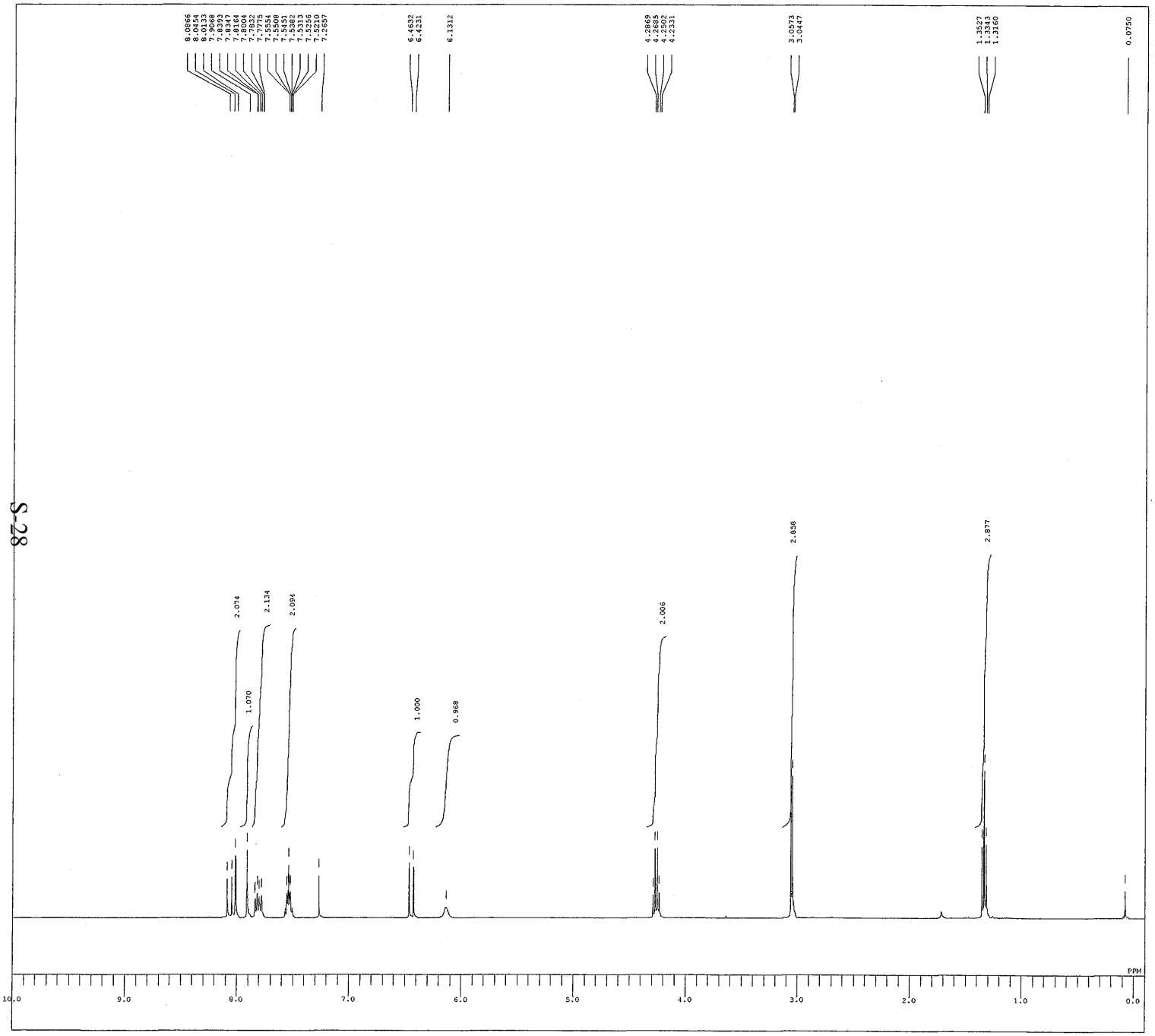
oxdative Heck N-methyl o-methyl amide C



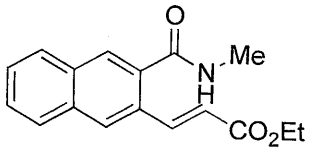

```
DFILE  oxdative Heck N-methyl o-methyl amide C-1-1.als
COMNT  oxdative Heck N-methyl o-methyl amide C
DATIM  10-01-2015 01:23:09
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.54 Hz
SCANS          950
ACQTM       1.0643 sec
PD          2.0000 sec
PW1            3.07 usec
IRNUC  1H
CTEMP         22.7 c
SLVNT  CDCL3
EXREF        77.16 ppm
BF            0.12 Hz
RGAIN           60
```



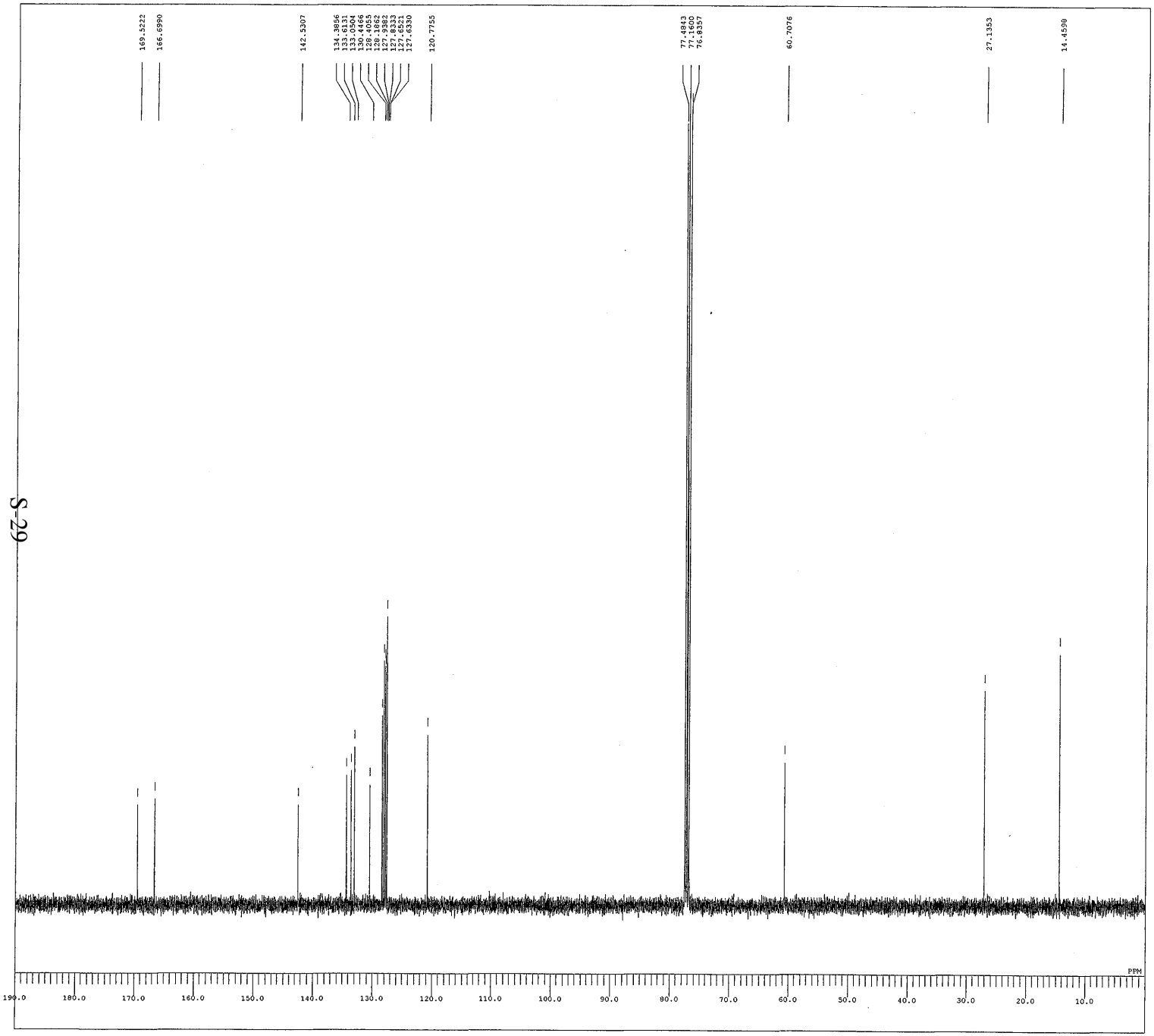
4m



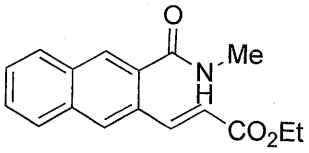

```
DFILE   oxdative Heck N-methyl 2-nap amide-1-1.als
COMNT   oxdative Heck N-methyl 2-nap amide
DATIM   10-01-2015 00:02:33
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         391.78 MHz
OBSET           8.51 KHz
OBFIN           3.34 Hz
POINT          13107
FREQU        5878.90 Hz
SCANS             8
ACQTM          2.2295 sec
PD             5.0000 sec
PW1               5.07 usec
IRNUC   1H
CTEMP          22.7 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            40
```



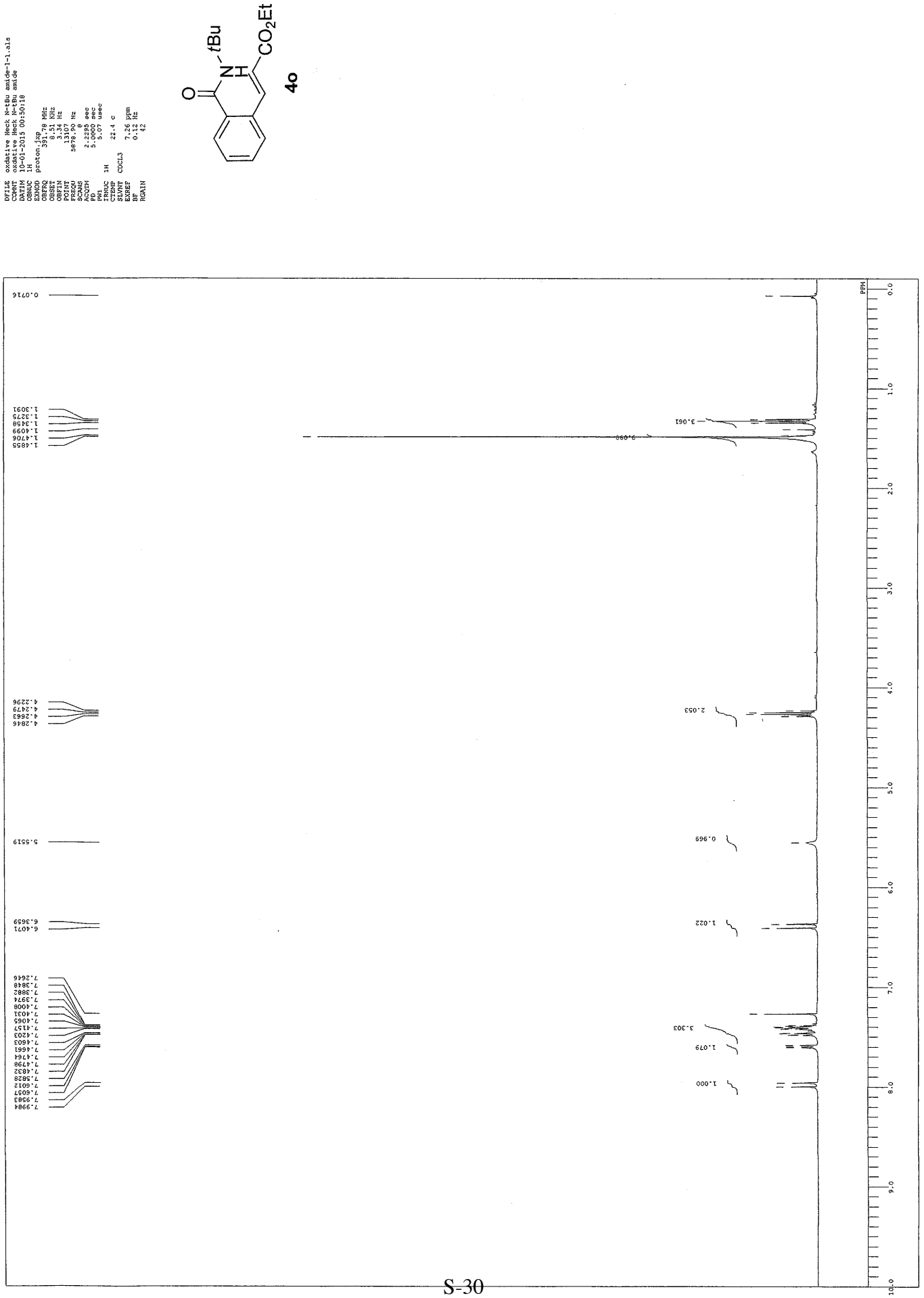
4n



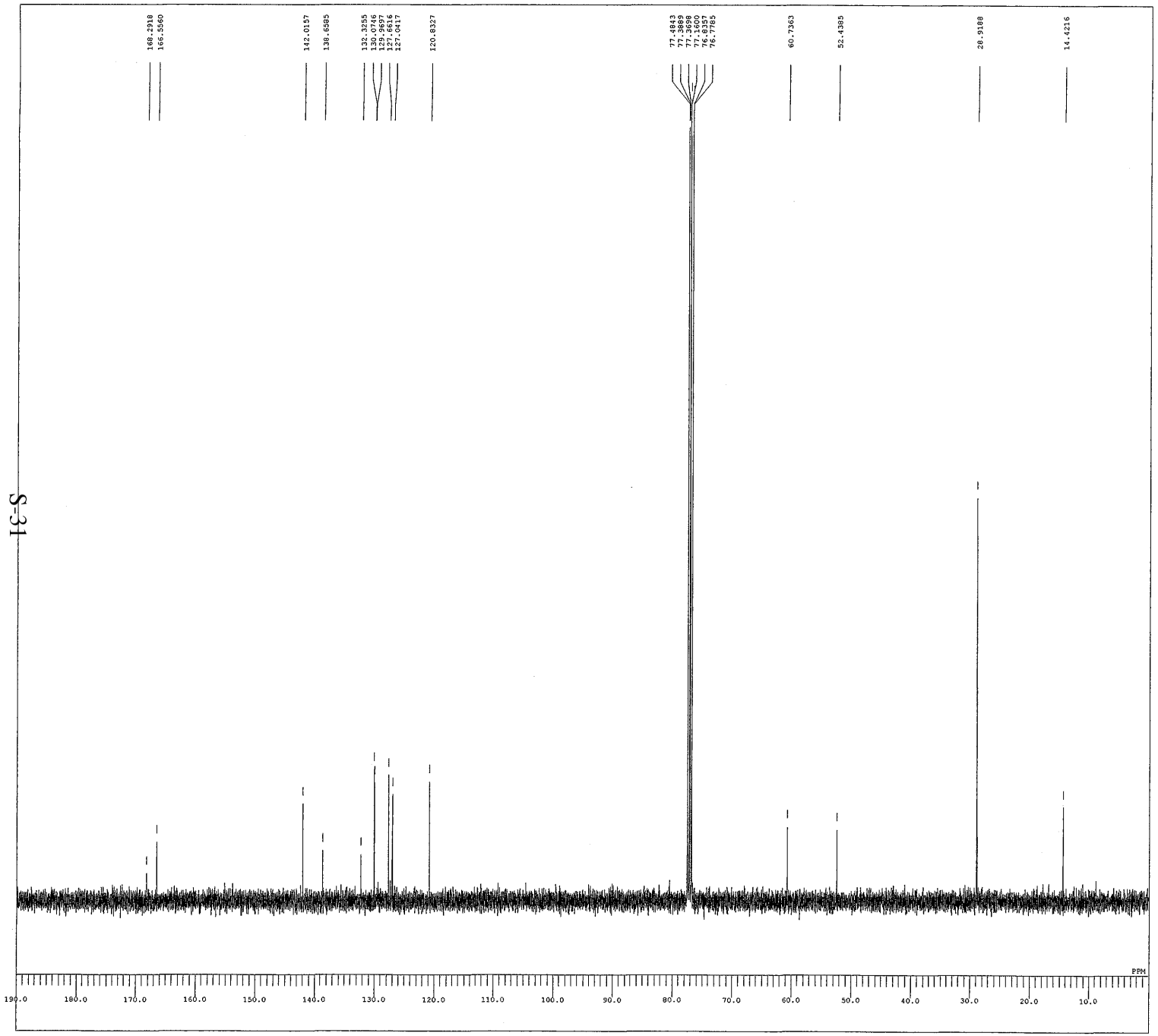

```
DFILE  oxdative Heck N-methyl 2-nap amide C-1-1.als
COMNT  oxdative Heck N-methyl 2-nap amide C
DATIM  10-01-2015 00:04:51
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         0.74 Hz
POINT        26214
FREQU     24630.54 Hz
SCANS          760
ACQTM       1.0643 sec
PD          2.0000 sec
PW1            3.07 usec
IRNUC  1H
CTEMP         22.7 c
SLVNT  CDCL3
EXREF       77.16 ppm
BF             0.12 Hz
RGAIN            60
```



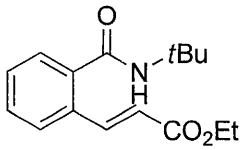
4n



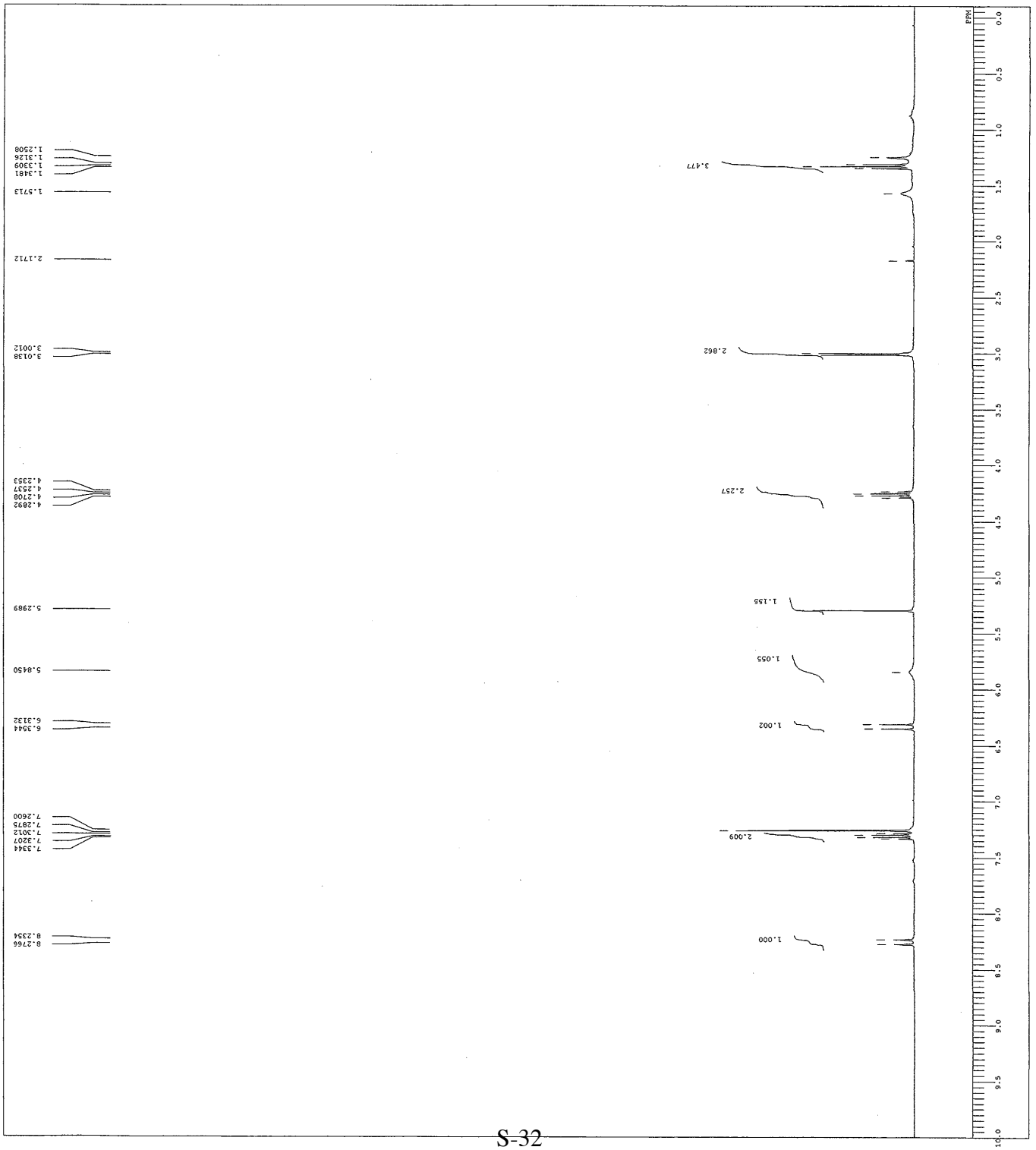
oxdative Heck N-tBu amide



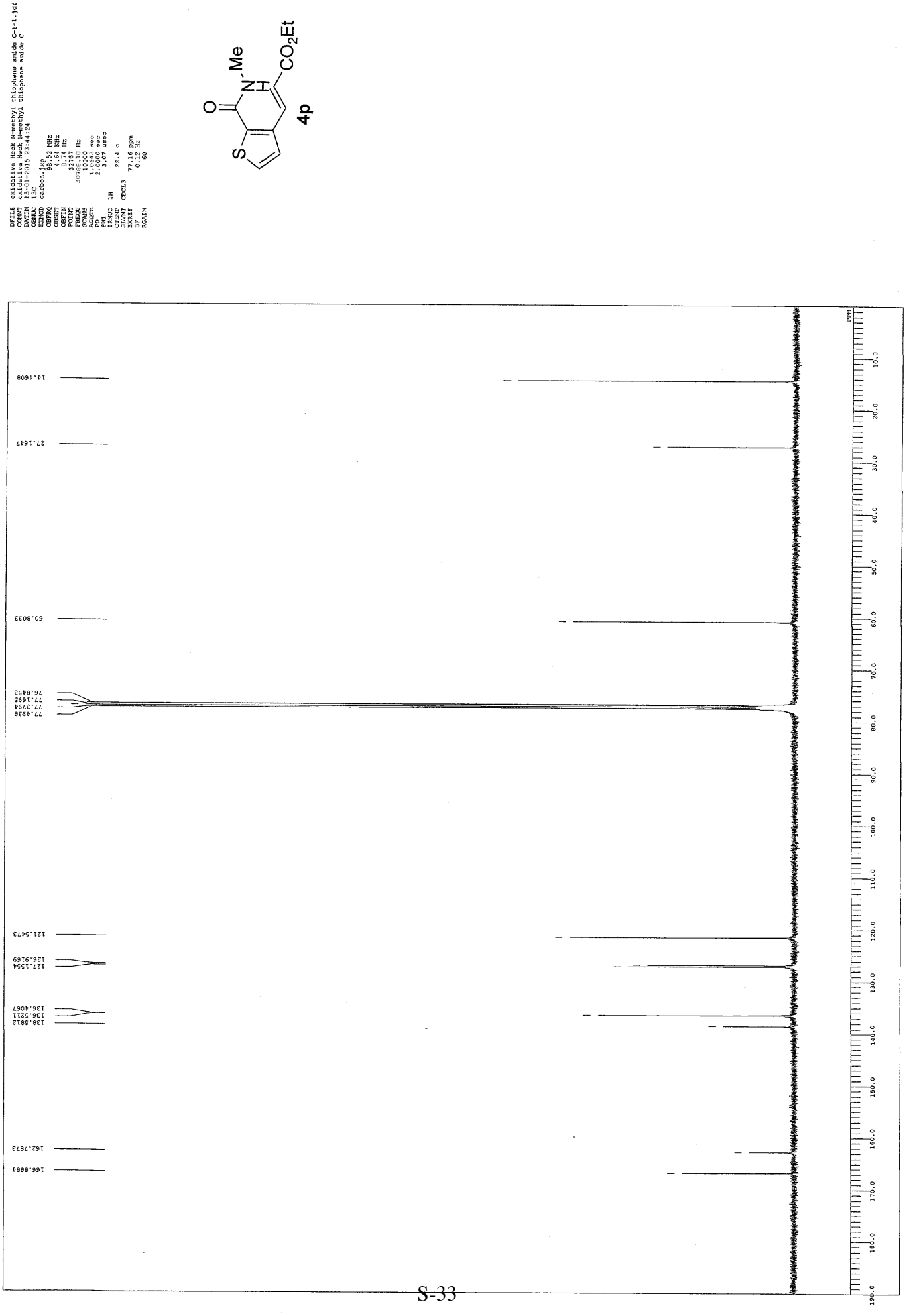

```
DFILE   oxdative Heck N-tBu amide C-1-1.als
COMNT   oxdative Heck N-tBu amide C
DATIM   10-01-2015 00:51:59
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         98.52 MHz
OBSET          4.64 KHz
OBFIN          8.74 Hz
POINT         26214
FREQU      24630.54 Hz
SCANS           500
ACQTM         1.0643 sec
PD            2.0000 sec
PW1           3.07 usec
IRNUC   1H
CTEMP         23.0 c
SLVNT   CDCL3
EXREF         77.16 ppm
BF             0.12 Hz
RGAIN            60
```

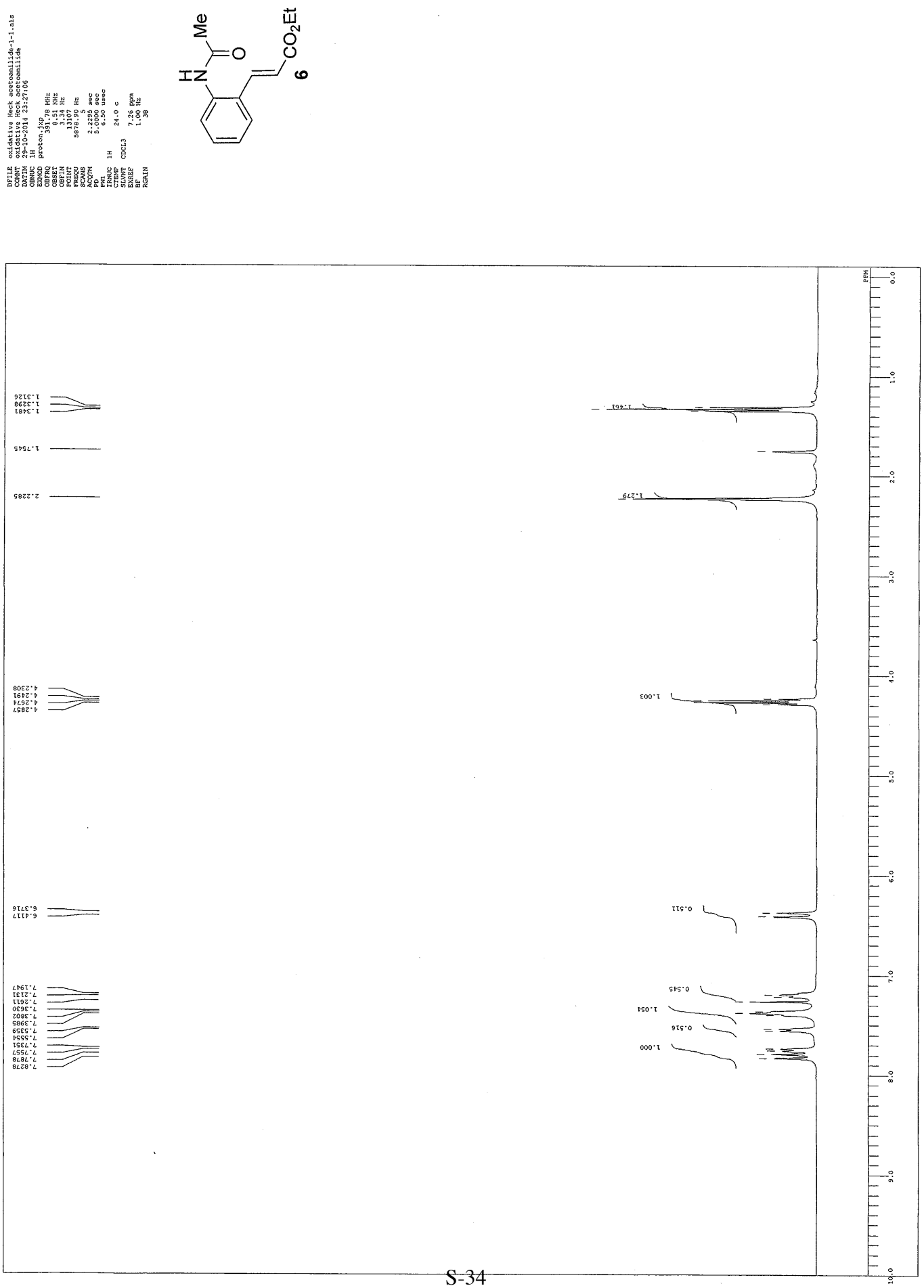


4o

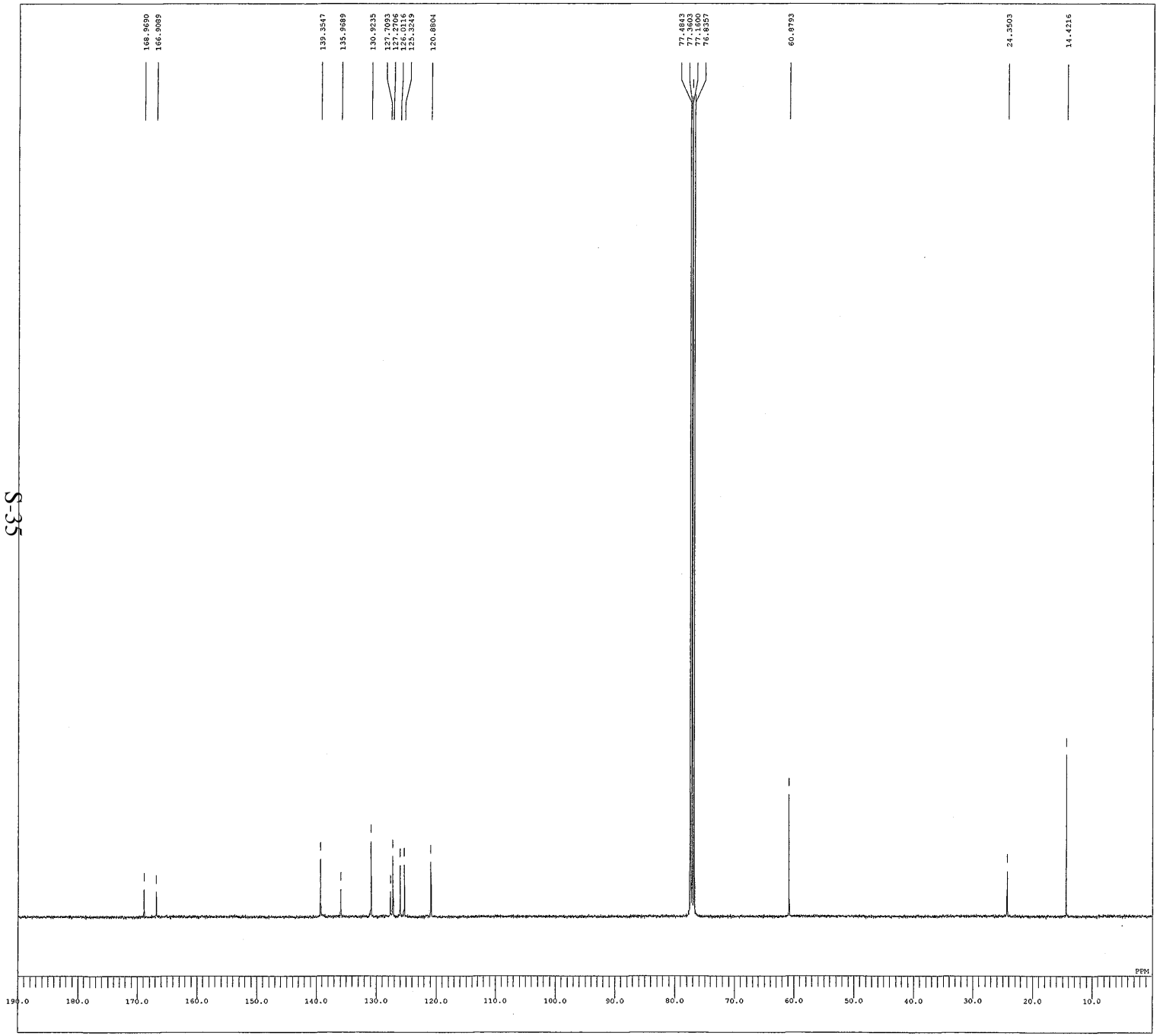

DFILE oxidative Heck N-methyl thiophene amide-1-ala
COMNT ys-oxidative Heck N-methyl thiophene amide
DATIM 13-01-2015 16:49:03
OBNUC 1H
EXMOD proton.jxp
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINTS 131072
FREQU 5878.90 Hz
SCANS 6
ACQTM 2.2295 sec
PD 5.0000 sec
PW1 5.07 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 59
Me
N
H
O
S
CO2Et
4p
8.2766
8.2354
7.3444
7.3273
7.3012
7.2875
7.2600
6.3444
6.3132
5.8450
5.2989
4.2892
4.2708
4.2537
4.2353
3.0138
3.0012
2.1712
1.5713
1.3481
1.3309
1.3126
1.2508
1.000
2.009
1.002
1.055
1.155
2.257
2.862
3.477
PPM

oxidative Heck N-methyl thiophene amide C

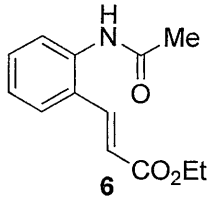




oxidative Heck acetoanilide




```
DFILE   oxidative Heck acetoanilide C-1-1.als
COMNT   oxidative Heck acetoanilide C
DATIM   29-10-2014 23:29:20
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         98.52 MHz
OBSET          4.64 KHz
OBFIN          8.74 Hz
POINT         26214
FREQU      24630.54 Hz
SCANS          8000
ACQTM        1.0643 sec
PD           3.0000 sec
PW1             3.60 usec
IRNUC   1H
CTEMP          23.4 c
SLVNT   CDCL3
EXREF         77.16 ppm
BF             1.00 Hz
RGAIN            60
```



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