

Accessing Bridged Bicyclic Compounds or Meta Carbon-Functionalized Anilines from Dearomatization of Anilines

*Linfei Wang,^a Shuo-En Wang,^a Weibin Wang^{*b} and Renhua Fan^{*a}*

Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, China

Department of General Surgery, Peking Union Medical College Hospital, Chinese Academy of
Medical Science and Peking Union Medical College, No. 1 Shuai Fu Yuan, Dongcheng District,
Beijing, 100730, China.

Supporting Information

1. General experimental methods (S2)
2. Table 1. Condition Evaluation for the Reaction between Pentane-2,4-dione and
N-Ts-4-methoxy-4-methylcyclohexa-2,5-dienimine (S3)
3. Characterization Data (S4-S13)
4. Copies of ¹H, ¹³C NMR spectra of products (S14-S62)

General experimental methods:

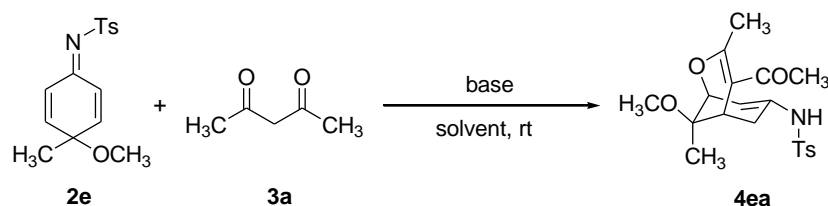
All reactions were performed in test tubes under air. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

EXPERIMENTAL SECTION

Typical procedure for the oxidative dearomatization and domino Michael addition.

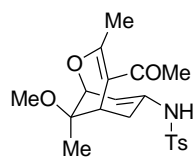
PhI(OAc)₂ (354 mg, 1.1 mmol) was added into the solution of *N*-Ts *p*-toluidine (261 mg, 1 mmol) in MeOH (5 mL) at 25 °C. After 15 min, the reaction mixture was quenched with saturated NaHCO₃ (50 mL), and extracted by ethyl acetate (50 mL x 3). The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was dissolved in CH₃OH (5 mL) and treated with acetylacetone (300 mg, 3 mmol) and CH₃ONa (27 mg, 0.5 mmol) at room temperature. The mixture was stirred over 4 hours. Upon completion determined by TLC, the reaction mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2:1) to afford the pure product **4ea** (355 mg, 91% yield).

Table 1. Condition Evaluation for the Reaction between Pentane-2,4-dione and *N*-Ts-4-methoxy-4-methylcyclohexa-2,5-dienimine

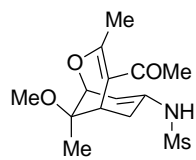


entry	base (equiv)	solvent	yield (%) ^{a,b}
1	CH ₃ ONa (0.5)	CH ₃ OH	98
2	<i>t</i> -BuOK (0.5)	CH ₃ OH	93
3	K ₂ CO ₃ (0.5)	CH ₃ OH	80
4	K ₃ PO ₄ (0.5)	CH ₃ OH	91
5	CH ₃ COONa (0.5)	CH ₃ OH	75
6	DMAP (0.5)	CH ₃ OH	69
7	DABCO (0.5)	CH ₃ OH	30
8	CH ₃ ONa (0.5)	THF	56
9	CH ₃ ONa (0.5)	CH ₃ CN	79
10	CH ₃ ONa (0.5)	ClCH ₂ CH ₂ Cl	90
11	CH ₃ ONa (0.5)	toluene	<5
12	CH ₃ ONa (0.5)	hexane	85
13	CH ₃ ONa (0.5)	DMF	0
14	CH ₃ ONa (0.2)	CH ₃ OH	80
15	CH ₃ ONa (0.1)	CH ₃ OH	51
16 ^c	CH ₃ ONa (0.5)	CH ₃ OH	82
16 ^d	CH ₃ ONa (0.5)	CH ₃ OH	87

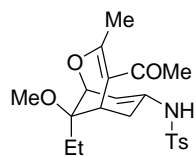
^aReaction conditions: compound **2e** (0.2 mmol), pentane-2,4-dione (0.6 mmol), solvent (3 mL), unless noted. ^bIsolated yield based on compound **2e**. ^c2 equivalents of pentane-2,4-dione was used. ^dThe reaction was conducted in a 5 mmol scale.



N-(4-acetyl-9-methoxy-3,9-dimethyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4ea: colorless solid; m.p. 141-142 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 1 H), 7.72 (d, $J = 7.8$ Hz, 2 H), 7.29 (d, $J = 7.3$ Hz, 2 H), 5.53 (d, $J = 6.4$ Hz, 1 H), 4.36 (d, $J = 6.8$ Hz, 1 H), 3.12 (s, 3 H), 2.90 (s, 1 H), 2.42 (s, 3 H), 2.19- 2.32 (m, 4 H), 2.05- 2.14 (m, 4 H), 1.00 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 164.0, 143.8, 138.5, 136.1, 129.4, 127.4, 114.5, 104.8, 72.6, 69.5, 48.9, 35.2, 33.9, 30.5, 21.4, 21.3, 16.1; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598, 1422 cm^{-1} ; HRMS m/z calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 392.1526, found 392.1518.

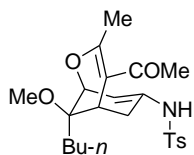


N-(4-acetyl-9-methoxy-3,9-dimethyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)methanesulfonamide 4da: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (s, 1 H), 5.56 (d, $J = 6.0$ Hz, 1 H), 4.52 (d, $J = 6.0$ Hz, 1 H), 3.20 (s, 3 H), 2.98-3.11 (m, 4 H), 2.53 (d, $J = 17.4$ Hz, 1 H), 2.34 (s, 3 H), 2.25 (s, 3 H), 2.16 (d, $J = 17.4$ Hz, 1 H), 1.32 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 164.5, 139.1, 114.9, 102.4, 73.0, 69.7, 49.3, 39.4, 35.6, 34.0, 31.0, 21.7, 16.8; IR (KBr) 3355, 3054, 2968, 2927, 2854, 2305, 1664, 1590, 1426, 1381 cm^{-1} ; HRMS m/z calcd for $\text{C}_{14}\text{H}_{22}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 316.1213, found 316.1214.



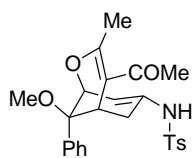
N-(4-acetyl-9-ethyl-9-methoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4fa: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.8$ Hz, 2 H), 7.48 (s, 1 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 5.53 (d, $J = 6.4$ Hz, 1 H), 4.40 (d, $J = 6.8$

Hz, 1 H), 3.07 (s, 3 H), 2.90 (s, 1 H), 2.43 (s, 3 H), 2.25 (s, 3 H), 2.15- 2.20 (m, 1 H), 2.11 (s, 3 H), 2.05- 2.25 (m, 1 H), 1.25 (q, $J = 7.3$ Hz, 2 H), 0.75 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 164.0, 143.9, 138.8, 136.1, 129.4, 127.6, 114.7, 105.0, 71.2, 71.1, 48.5, 35.0, 32.2, 30.6, 21.5, 21.3, 20.0, 6.8; IR (KBr) 3259, 3055, 2984, 2825, 2299, 1717, 1666, 1599, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{21}\text{H}_{27}\text{NNaO}_5\text{S}$ ($[\text{M}+\text{Na}]^+$): 428.1508, found 428.1501.



***N*-(4-acetyl-9-butyl-9-methoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-**

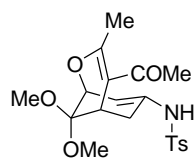
yl)-4-methylbenzenesulfonamide 4ga: colorless solid; m.p. 156-157 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.3$ Hz, 2 H), 7.42 (s, 1 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 5.54 (d, $J = 6.0$ Hz, 1 H), 4.40 (d, $J = 5.5$ Hz, 1 H), 3.08 (s, 3 H), 2.91 (s, 1 H), 2.42 (s, 3 H), 2.26 (s, 3 H), 2.00- 2.18 (m, 5 H), 1.15-1.25 (m, 6 H), 0.75 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 164.3, 144.0, 138.9, 136.1, 129.6, 127.7, 114.9, 104.7, 71.2, 71.1, 48.8, 35.2, 32.7, 30.9, 27.2, 24.7, 22.9, 21.6, 21.5, 14.0; IR (KBr) 3399, 2916, 1656, 1571, 1472, 1438 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{31}\text{NNaO}_5\text{S}$ ($[\text{M}+\text{Na}]^+$): 456.1821, found 456.1819.



***N*-(4-acetyl-9-methoxy-3-methyl-9-phenyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-**

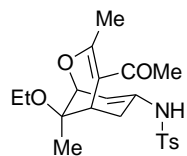
yl)-4-methylbenzenesulfonamide 4ha: colorless solid; m.p. 188-190 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.8$ Hz, 2 H), 7.23-7.27 (m, 4 H), 7.12-7.14 (m, 3 H), 5.72 (d, $J = 6.4$ Hz, 1 H), 5.04 (d, $J = 6.0$ Hz, 1 H), 3.18 (s, 1 H), 3.08 (s, 3 H), 2.84 (s, 3 H), 2.47 (s, 3 H), 2.27 (s, 3 H), 2.19 (s, 3 H), 1.91 (d, $J = 17.0$ Hz, 1 H), 1.68 (d, $J = 17.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 164.2, 143.7, 139.1, 137.1, 136.2, 129.5, 127.9, 127.8, 127.5, 126.9, 115.0, 103.3, 73.8, 68.5, 49.9, 37.2, 34.7, 30.8, 21.6, 21.4; IR (KBr) 3259, 3055, 2984, 2825, 2299,

1717, 1666, 1599, 1422 cm^{-1} ; HRMS m/z calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 454.1683, found 454.1693.



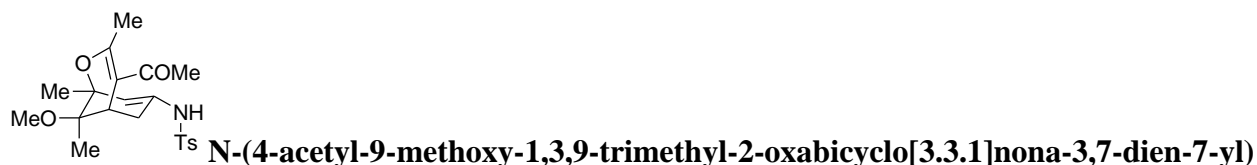
N-(4-acetyl-9,9-dimethoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4ia: colorless solid; m.p. 143-144 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3)

δ 7.71 (d, $J = 7.8$ Hz, 2 H), 7.28 (d, $J = 7.8$ Hz, 2 H), 7.17 (s, 1 H), 5.49 (d, $J = 6.4$ Hz, 1 H), 4.47 (d, $J = 6.8$ Hz, 1 H), 3.18 (s, 3 H), 3.09 (s, 3 H), 2.38-2.45 (m, 4 H), 2.18- 2.26 (m, 4 H), 2.08 (s, 3 H), 1.93 (d, $J = 12.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 163.4, 143.7, 139.6, 136.1, 129.4, 127.4, 114.8, 103.9, 95.2, 68.9, 48.9, 48.1, 34.6, 32.4, 30.4, 21.4, 21.1; IR (KBr) 3360, 3256, 2925, 1664, 1597, 1435 cm^{-1} ; HRMS m/z calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 408.1481, found 408.1460.



Methyl-9-ethoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3

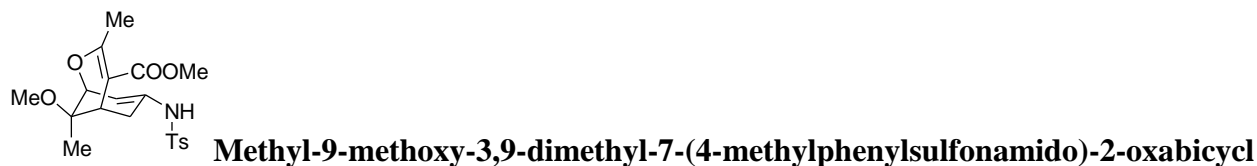
.3.1]nona-3,7-diene-4-carboxylate 4ja: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.3$ Hz, 2 H), 7.28 (d, $J = 7.3$ Hz, 2 H), 6.49 (s, 1 H), 5.43 (d, $J = 6.4$ Hz, 1 H), 4.32 (d, $J = 6.4$ Hz, 1 H), 3.65 (s, 3 H), 3.35 (q, $J = 6.8$ Hz, 1 H), 3.29 (q, $J = 6.8$ Hz, 1 H), 2.81 (s, 1 H), 2.43 (s, 3 H), 2.30 (d, $J = 17.0$ Hz, 1 H), 2.20 (d, $J = 17.0$ Hz, 1 H), 1.04-1.08 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 163.7, 144.2, 138.4, 129.7, 127.5, 106.5, 102.7, 72.7, 69.4, 56.5, 51.0, 35.3, 34.6, 21.6, 19.8, 17.1, 16.0; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm^{-1} ; HRMS m/z calcd for $\text{C}_{21}\text{H}_{27}\text{NNaO}_6\text{S}$ ($[\text{M}+\text{Na}]^+$): 444.1457, found 444.1445.



-4-methylbenzenesulfonamide 4ka: colorless solid; m.p. 148-149 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.8$ Hz, 2 H), 7.43 (s, 1 H), 7.26 (d, $J = 8.2$ Hz, 2 H), 5.25 (s, 1 H), 3.05 (s, 1 H), 3.01 (s, 3 H), 2.39 (s, 3 H), 2.14- 2.22 (m, 4 H), 1.99- 2.07 (m, 4 H), 1.27 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 165.2, 143.9, 136.3, 136.0, 129.4, 127.6, 114.5, 111.6, 78.8, 71.0, 48.8, 34.8, 33.5, 30.8, 21.7, 21.5, 19.7, 16.2; IR (KBr) 3358, 2924, 1666, 1582 cm^{-1} ; HRMS m/z calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 406.1677, found 406.1662.

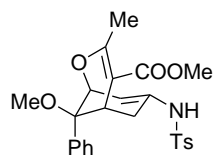


colorless solid; m.p. 170-171 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 6.9$ Hz, 2 H), 7.27- 7.33 (m, 5 H), 6.81 (s, 2 H), 6.25 (s, 1 H), 4.34 (s, 1 H), 3.17 (s, 3 H), 3.03 (s, 1 H), 2.74 (s, 2 H), 2.46 (s, 3 H), 2.26 (s, 3 H), 2.16 (m, 3 H), 1.28 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 162.2, 144.1, 136.5, 136.2, 134.1, 129.4, 128.3, 127.1, 114.0, 77.2, 69.2, 49.0, 34.8, 34.1, 29.9, 21.5, 20.8, 16.3; IR (KBr) 3328, 2947, 1702, 1613, 1492, 1434 cm^{-1} ; HRMS m/z calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 468.1834, found 468.1810.



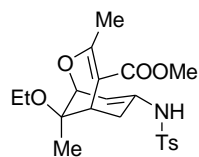
colorless solid; m.p. 132-133 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.8$ Hz, 2 H), 7.28 (d, $J = 7.3$ Hz, 2 H), 7.09 (s, 1 H), 5.44 (s, 1 H), 4.32 (s, 1 H), 3.65 (s, 3 H), 3.14 (s, 3 H), 2.82 (s, 1 H), 2.42 (s, 3 H), 2.20- 2.31 (m, 2 H), 2.08 (s,

3 H), 1.01 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 163.4, 143.9, 138.5, 135.7, 129.5, 129.3, 127.3, 106.0, 102.6, 77.2, 72.2, 69.5, 50.9, 48.9, 35.0, 34.0, 21.4, 19.8, 16.2; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm^{-1} ; HRMS m/z calcd for $\text{C}_{20}\text{H}_{25}\text{NNaO}_6\text{S}$ ($[\text{M}+\text{Na}]^+$): 430.1300, found 430.1304.



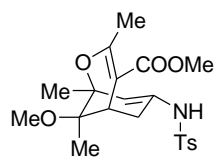
Methyl-9-methoxy-3-methyl-7-(4-methylphenylsulfonamido)-9-phenyl-2-ox

abicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4hb: colorless solid; m.p. 188-189 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.8$ Hz, 2 H), 7.23-7.27 (m, 3 H), 7.16 (m, 4 H), 6.44 (s, 1 H), 5.65 (d, $J = 6.4$ Hz, 1 H), 5.03 (d, $J = 6.4$ Hz, 1 H), 3.66 (s, 3 H), 3.13 (s, 1 H), 2.86 (s, 3 H), 2.47 (s, 3 H), 2.43 (s, 1 H), 2.06 (d, $J = 17.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 163.8, 143.9, 138.9, 137.1, 135.8, 129.7, 128.0, 127.9, 127.3, 126.8, 126.3, 104.6, 102.9, 73.8, 68.1, 51.0, 50.1, 37.4, 34.8, 21.6, 19.9; IR (KBr) 3247, 2937, 2891, 1681, 1450, 1332 cm^{-1} ; HRMS m/z calcd for $\text{C}_{25}\text{H}_{27}\text{NNaO}_6\text{S}$ ($[\text{M}+\text{Na}]^+$): 492.1457, found 492.1461.

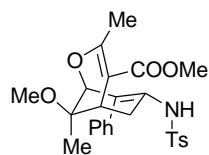


Methyl-9-ethoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[

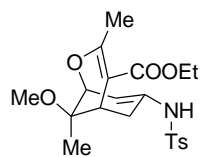
3.3.1]nona-3,7-diene-4-carboxylate 4jb: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.3$ Hz, 2 H), 7.28 (d, $J = 7.3$ Hz, 2 H), 6.49 (s, 1 H), 5.43 (d, $J = 6.4$ Hz, 1 H), 4.32 (d, $J = 6.4$ Hz, 1 H), 3.65 (s, 3 H), 3.35 (q, $J = 6.8$ Hz, 1 H), 3.29 (q, $J = 6.8$ Hz, 1 H), 2.81 (s, 1 H), 2.43 (s, 3 H), 2.30 (d, $J = 17.0$ Hz, 1 H), 2.20 (d, $J = 17.0$ Hz, 1 H), 1.04-1.08 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 163.7, 144.2, 138.4, 129.7, 127.5, 106.5, 102.7, 72.7, 69.4, 56.5, 51.0, 35.3, 34.6, 21.6, 19.8, 17.1, 16.0; IR (KBr) 3352, 3054, 2986, 2319, 1612, 1422 cm^{-1} ; HRMS m/z calcd for $\text{C}_{21}\text{H}_{27}\text{NNaO}_6\text{S}$ ($[\text{M}+\text{Na}]^+$): 444.1457, found 444.1445.



Methyl-9-methoxy-1,3,9-trimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4kb: colorless solid; m.p. 161-163 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.3$ Hz, 2 H), 7.28 (d, $J = 7.3$ Hz, 2 H), 6.60 (s, 1 H), 5.18 (s, 1 H), 3.66 (s, 3 H), 3.06 (s, 3 H), 2.98 (s, 1 H), 2.43 (s, 3 H), 2.19 (s, 2 H), 2.07 (s, 3 H), 1.28 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 164.7, 144.1, 136.2, 135.7, 129.6, 129.6, 127.4, 113.0, 102.1, 78.2, 70.9, 50.9, 48.8, 34.8, 32.7, 21.5, 20.1, 19.7, 16.3; IR (KBr) 3249, 2924, 2845, 1651, 1607, 1434 cm^{-1} ; HRMS m/z calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 422.1632, found 422.1629.

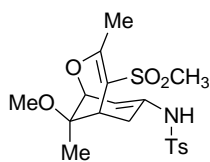


Methyl-9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-8-phenyl-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4lb: colorless solid; m.p. 161-162 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 7.3$ Hz, 2 H), 7.28-7.34 (m, 5 H), 6.79 (d, $J = 3.7$ Hz, 2 H), 6.25 (s, 1 H), 4.32 (s, 1 H), 3.72 (s, 3 H), 2.98 (s, 1 H), 2.90 (d, $J = 18.8$ Hz, 1 H), 2.66 (dd, $J = 18.8$ Hz, $J = 4.1$ Hz, 1 H), 2.47 (s, 3 H), 2.18 (s, 3 H), 1.25 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 162.8, 144.1, 136.6, 136.0, 134.4, 129.7, 129.5, 128.4, 127.1, 120.3, 103.4, 69.3, 51.0, 49.1, 34.3, 33.9, 21.6, 19.6, 16.3; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm^{-1} ; HRMS m/z calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 484.1788, found 484.1791.



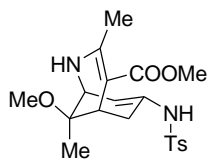
Ethyl 9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4ec: colorless solid; m.p. 135-136 °C; ^1H NMR

(400 MHz, CDCl₃) δ 7.70 (d, $J = 7.3$ Hz, 2 H), 7.29 (d, $J = 7.3$ Hz, 2 H), 6.82 (s, 1 H), 5.44 (d, $J = 6.0$ Hz, 1 H), 4.33 (d, $J = 6.0$ Hz, 1 H), 4.12 (q, $J = 6.8$ Hz, 2 H), 3.15 (s, 3 H), 2.83 (s, 1 H), 2.42 (s, 3 H), 2.21-2.33 (m, 2 H), 2.09 (s, 3 H), 1.25 (t, $J = 6.8$ Hz, 3 H), 1.03 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 163.1, 144.0, 138.4, 135.8, 129.6, 127.3, 106.1, 102.8, 77.2, 72.2, 69.6, 59.6, 49.0, 35.1, 34.1, 21.5, 19.8, 16.2, 14.3; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm⁻¹; HRMS m/z calcd for C₂₁H₂₈NO₆S ([M+H]⁺): 422.1637, found 422.1630.



N-(9-methoxy-3,9-dimethyl-4-(methylsulfonyl)-2-oxabicyclo[3.3.1]nona-3,7-

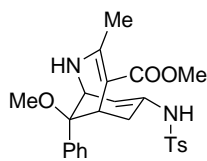
dien-7-yl)-4-methylbenzenesulfonamide 4ed: colorless solid; m.p. 181-182 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, $J = 7.8$ Hz, 2 H), 7.40 (s, 1 H), 7.30 (d, $J = 7.8$ Hz, 2 H), 5.51 (d, $J = 6.0$ Hz, 1 H), 4.38 (d, $J = 6.0$ Hz, 1 H), 3.17 (s, 3 H), 2.91 (s, 3 H), 2.69 (s, 1 H), 2.57 (d, $J = 17.8$ Hz, 1 H), 2.42 (s, 3 H), 2.33 (d, $J = 17.8$ Hz, 1 H), 2.08 (s, 3 H), 1.01 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 143.9, 138.4, 135.9, 129.6, 127.5, 110.9, 103.8, 72.6, 69.4, 49.1, 43.5, 36.1, 35.8, 21.5, 18.3, 15.9; IR (KBr) 3388, 2932, 1651, 1614, 1452 cm⁻¹; HRMS m/z calcd for C₁₉H₂₅NNaO₆S₂ ([M+Na]⁺): 450.1021, found 450.1015.



Methyl-9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-azabicycl

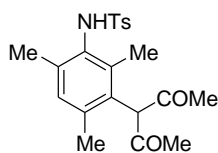
o[3.3.1]nona-3,7-diene-4-carboxylate 4ee: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, $J = 7.8$ Hz, 2 H), 7.31 (d, $J = 7.8$ Hz, 2 H), 5.83 (s, 1 H), 5.67 (d, $J = 10.0$ Hz, 1 H), 5.55 (d, $J = 10.0$ Hz, 1 H), 4.77 (s, 1 H), 3.17 (s, 3 H), 3.13 (s, 1 H), 2.44 (s, 3 H), 2.04 (s, 3 H), 1.93 (d, $J = 11.4$ Hz, 1 H), 1.76 (d, $J = 9.6$ Hz, 1 H), 1.19 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9,

146.9, 143.9, 139.1, 133.4, 129.7, 127.0, 125.9, 97.6, 79.6, 66.3, 51.1, 50.7, 39.2, 32.9, 22.4, 21.5, 20.4; IR (KBr) 3404, 2924, 2839, 1648, 1457 cm^{-1} ; HRMS m/z calcd for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 407.1641, found 407.1632.



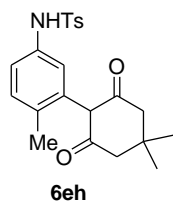
Methyl-9-methoxy-3-methyl-7-(4-methylphenylsulfonamido)-9-phenyl-2-aza

bicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4he: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.3$ Hz, 2 H), 7.21-7.22 (m, 7 H), 6.02 (d, $J = 10.0$ Hz, 1 H), 5.97 (d, $J = 10.0$ Hz, 1 H), 5.60 (s, 1 H), 4.77 (s, 1 H), 3.75 (s, 3 H), 3.35 (s, 1 H), 2.89 (s, 3 H), 2.45 (s, 3 H), 2.10 (s, 3 H), 1.64 (d, $J = 11.9$ Hz, 1 H), 1.46 (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 147.2, 143.9, 141.8, 139.3, 129.9, 128.4, 128.1, 127.8, 127.6, 127.1, 98.1, 84.3, 66.4, 50.9, 42.1, 31.6, 29.8, 21.7, 20.2; IR (KBr) 3376, 2926, 2849, 1659, 1596, 1478 cm^{-1} ; HRMS m/z calcd for $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 469.1797, found 469.1780.



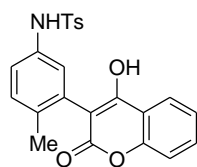
N-(3-(2-hydroxy-4-oxopent-2-en-3-yl)-2,4,6-trimethylphenyl)-4-methylbenz

enesulfonamide 6na: colorless solid; m.p. 185-187 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 7.8$ Hz, 2 H), 7.22 (d, $J = 7.8$ Hz, 2 H), 6.99 (s, 1 H), 6.46 (s, 1 H), 2.42 (s, 3 H), 2.15 (s, 3 H), 2.08 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.5, 143.7, 137.7, 137.5, 137.4, 134.1, 130.8, 130.5, 129.6, 127.2, 111.7, 23.0, 21.5, 20.2, 18.8, 16.2; IR (KBr) 3253, 2978, 2840, 1598, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 388.1577, found 388.1574.



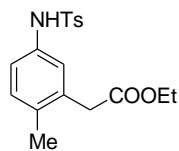
N-(3-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-4-methylphenyl)-4-methy

lbenzenesulfonamide 6eh: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 2 H), 7.33 (s, 1 H), 7.08 (d, $J = 7.8$ Hz, 1 H), 6.90 (d, $J = 7.8$ Hz, 1 H), 6.66 (s, 1 H), 6.00 (s, 1 H), 2.37 (s, 1 H), 2.35 (s, 4 H), 2.03 (s, 3 H), 1.15 (s, 3 H), 1.15 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 136.3, 135.9, 135.0, 131.7, 131.1, 129.6, 127.4, 124.7, 122.3, 115.9, 32.0, 29.0, 27.9, 21.6, 19.3; IR (KBr) 3054, 2968, 1651, 1438 cm^{-1} ; HRMS m/z calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 400.1583, found 400.1586.



N-(3-(4-hydroxy-2-oxo-2H-chromen-3-yl)-4-methylphenyl)-4-methylbenzenes

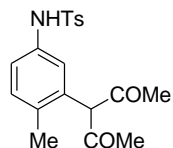
ulfonamide 6ei: colorless solid; m.p. 120-122 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.8$ Hz, 2 H), 7.56-7.65 (m, 4 H), 7.32 (d, $J = 7.8$ Hz, 2 H), 7.17 (d, $J = 7.8$ Hz, 2 H), 7.09 (d, $J = 8.2$ Hz, 1 H), 7.00 (d, $J = 7.8$ Hz, 1 H), 6.91 (s, 1 H), 2.31 (s, 3 H), 2.11 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 160.4, 152.9, 143.8, 135.9, 135.1, 132.5, 131.8, 129.6, 129.3, 127.2, 124.2, 124.1, 123.7, 122.7, 116.5, 115.0, 104.9, 60.5, 21.4, 20.9, 18.9, 14.1; IR (KBr) 3250, 2911, 2845, 1680, 1610, 1568, 1496 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 422.1062, found 422.1065.



Methyl 2-(2-methyl-5-(4-methylphenylsulfonamido)phenyl)acetate 6ef:

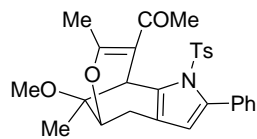
colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.3$ Hz, 2 H), 7.20 (d, $J = 7.3$ Hz, 2 H),

7.01 (d, $J = 7.8$ Hz, 1 H), 6.95 (d, $J = 8.7$ Hz, 2 H), 6.87 (d, $J = 7.8$ Hz, 1 H), 6.12 (q, $J = 6.9$ Hz, 2 H), 3.52 (s, 2 H), 2.36 (s, 3 H), 2.21 (s, 3 H), 1.22 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 143.6, 136.1, 134.4, 134.1, 133.8, 131.0, 129.5, 127.2, 123.8, 120.8, 60.9, 39.1, 21.4, 18.9, 18.9, 14.1; IR (KBr) 3259, 2982, 2876, 1731, 1615, 1504, 1467 cm^{-1} ; HRMS m/z calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 348.1264, found 348.1271.



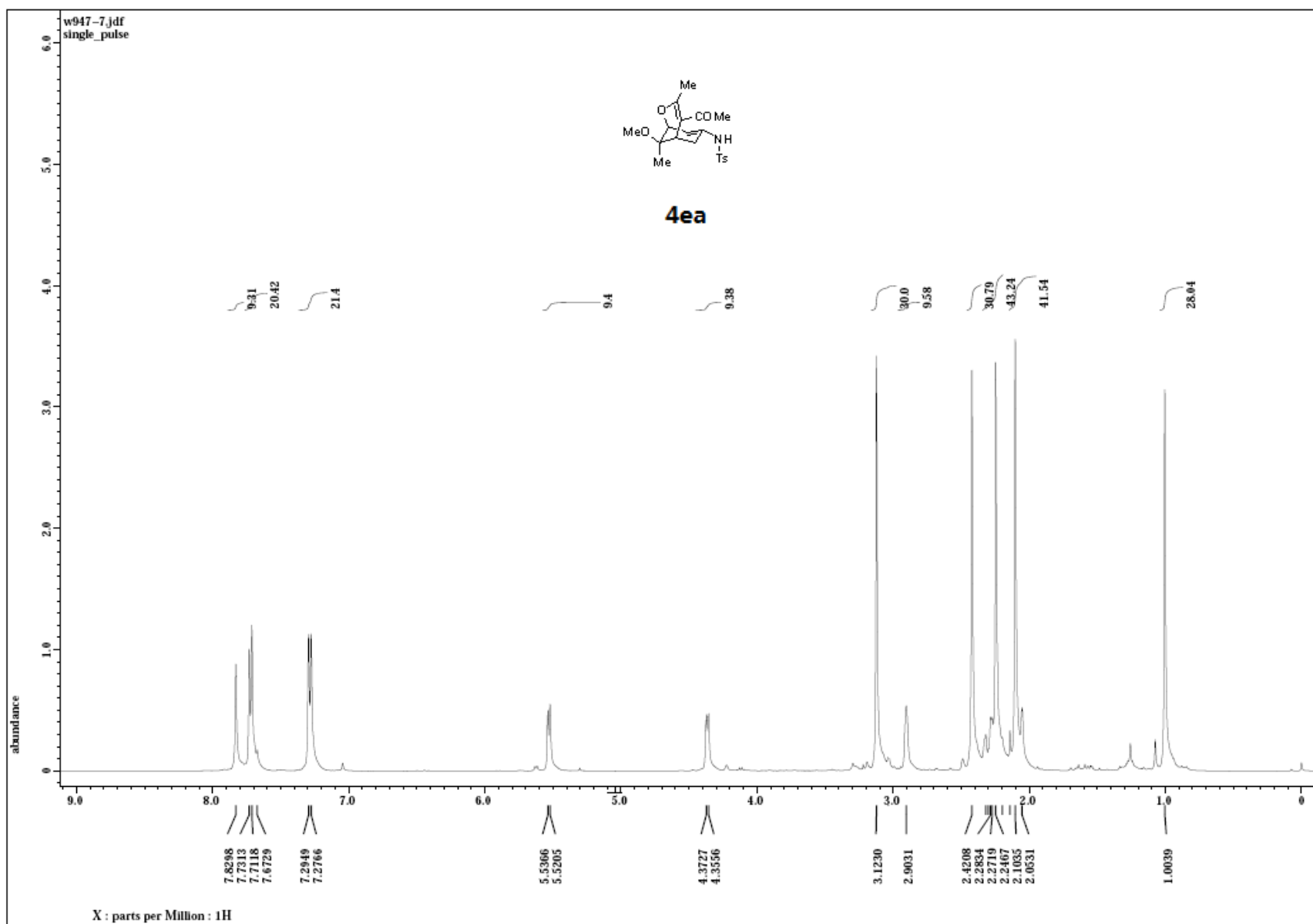
***N*-(3-(2-hydroxy-4-oxopent-2-en-3-yl)-4-methylphenyl)-4-methylbenzenesulfonamide**

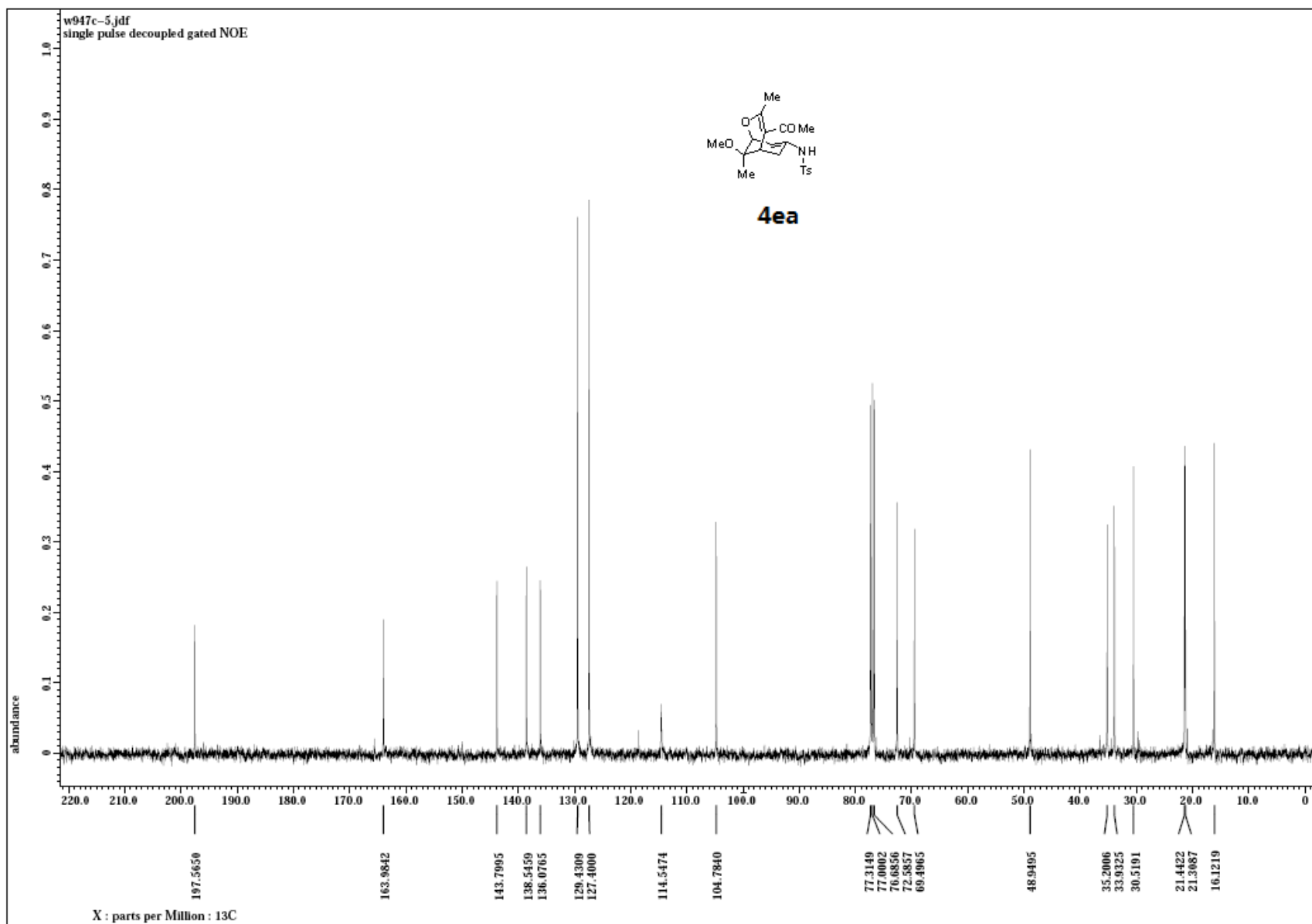
amide 6ea: colorless solid; m.p. 176-178 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.3$ Hz, 2 H), 7.14-7.27 (m, 3 H), 7.07 (d, $J = 7.8$ Hz, 1 H), 6.75 (s, 1 H), 2.36 (s, 3 H), 2.08 (s, 3 H), 1.65 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.6, 144.0, 137.0, 135.7, 135.4, 134.8, 131.4, 129.7, 127.5, 125.1, 122.5, 112.9, 23.6, 21.6, 19.3; IR (KBr) 3236, 2922, 2850, 1597, 1495, 1375, 1320 cm^{-1} ; HRMS m/z calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 360.1270, found 360.1257.

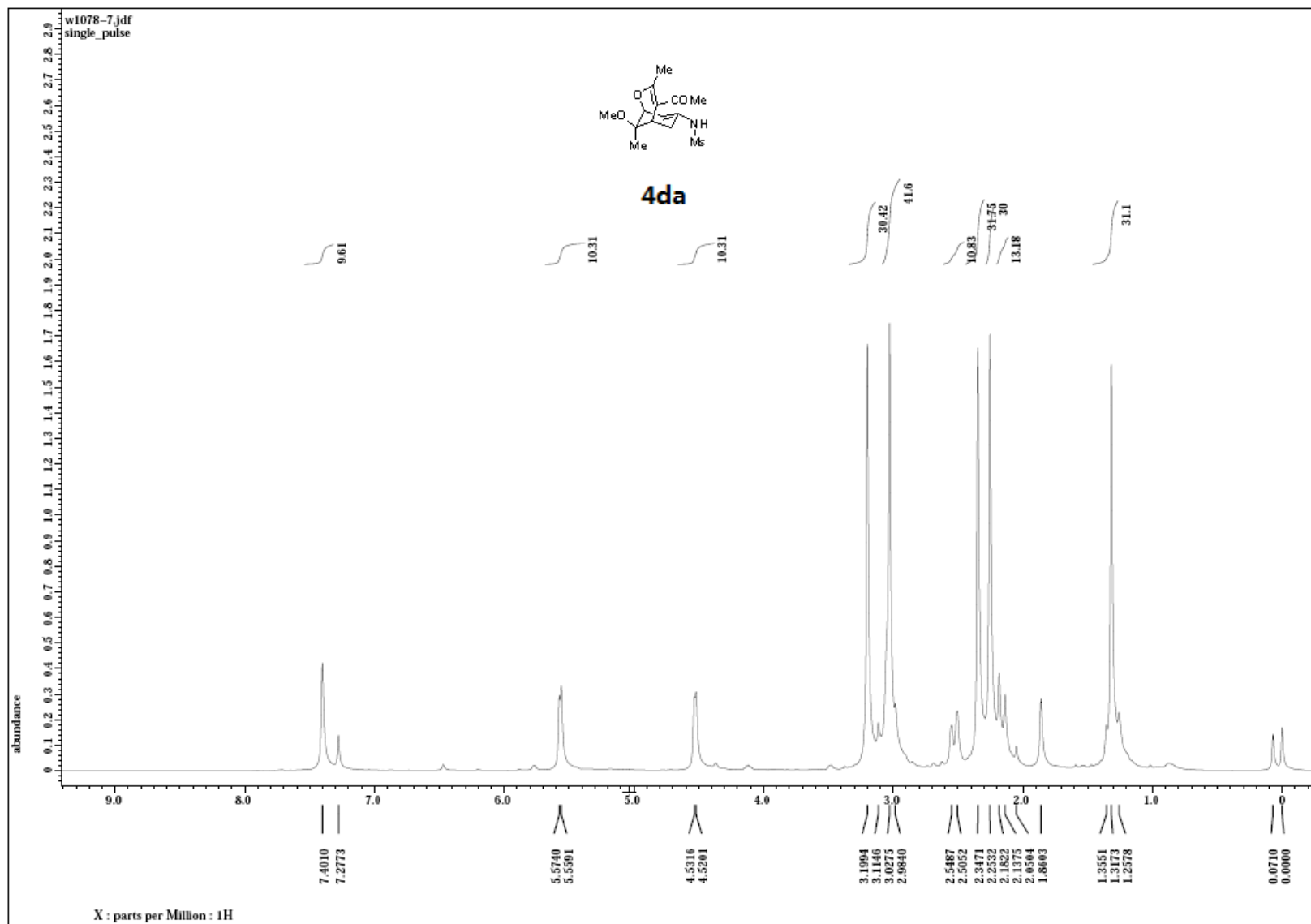


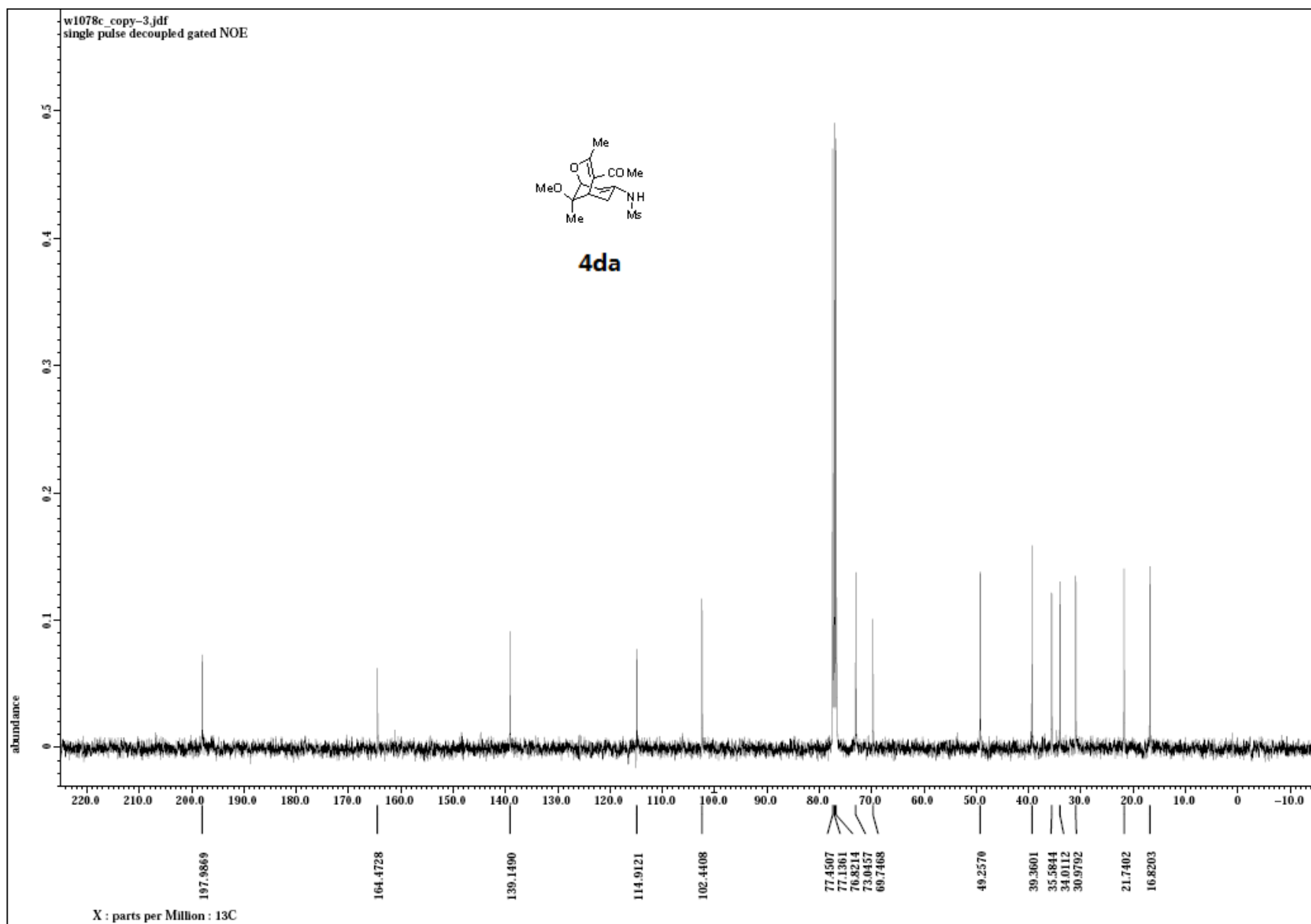
5ma: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.35 (m, 5 H), 7.17

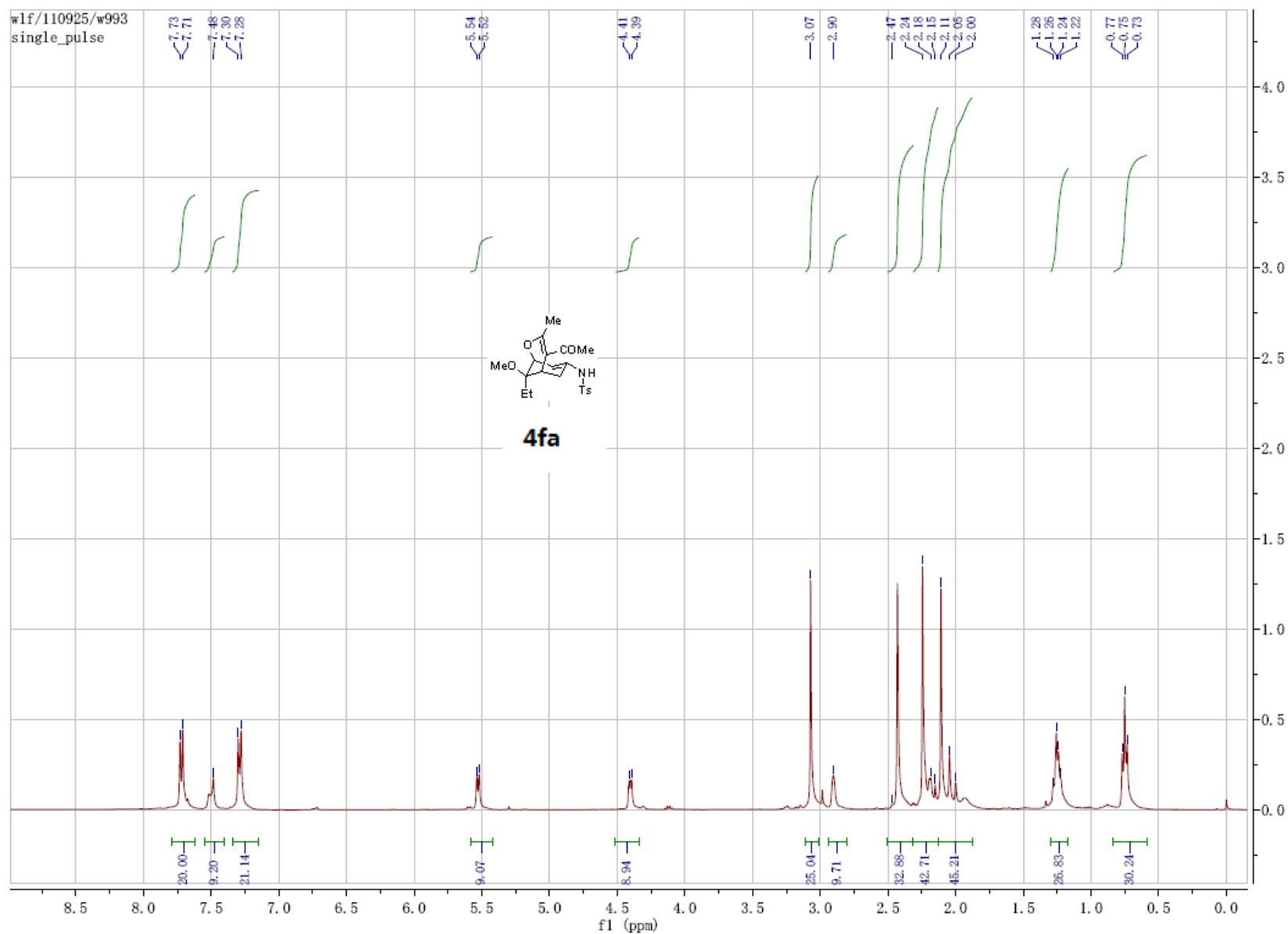
(d, $J = 8.5$ Hz, 2 H), 7.13 (d, $J = 8.5$ Hz, 2 H), 6.14 (s, 1 H), 4.78 (s, 1 H), 3.26 (s, 3 H), 3.19 (s, 2 H), 3.09 (d, $J = 4.8$ Hz, 1 H), 2.37 (s, 3 H), 2.30 (s, 3 H), 2.10 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 162.6, 144.7, 138.6, 133.7, 132.2, 130.5, 129.5, 128.2, 127.4, 126.4, 122.1, 115.4, 113.9, 71.7, 70.7, 49.3, 35.7, 31.9, 30.1, 21.6, 21.1, 16.3; IR (KBr) cm^{-1} ; HRMS m/z calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 492.1839, found 492.1842.

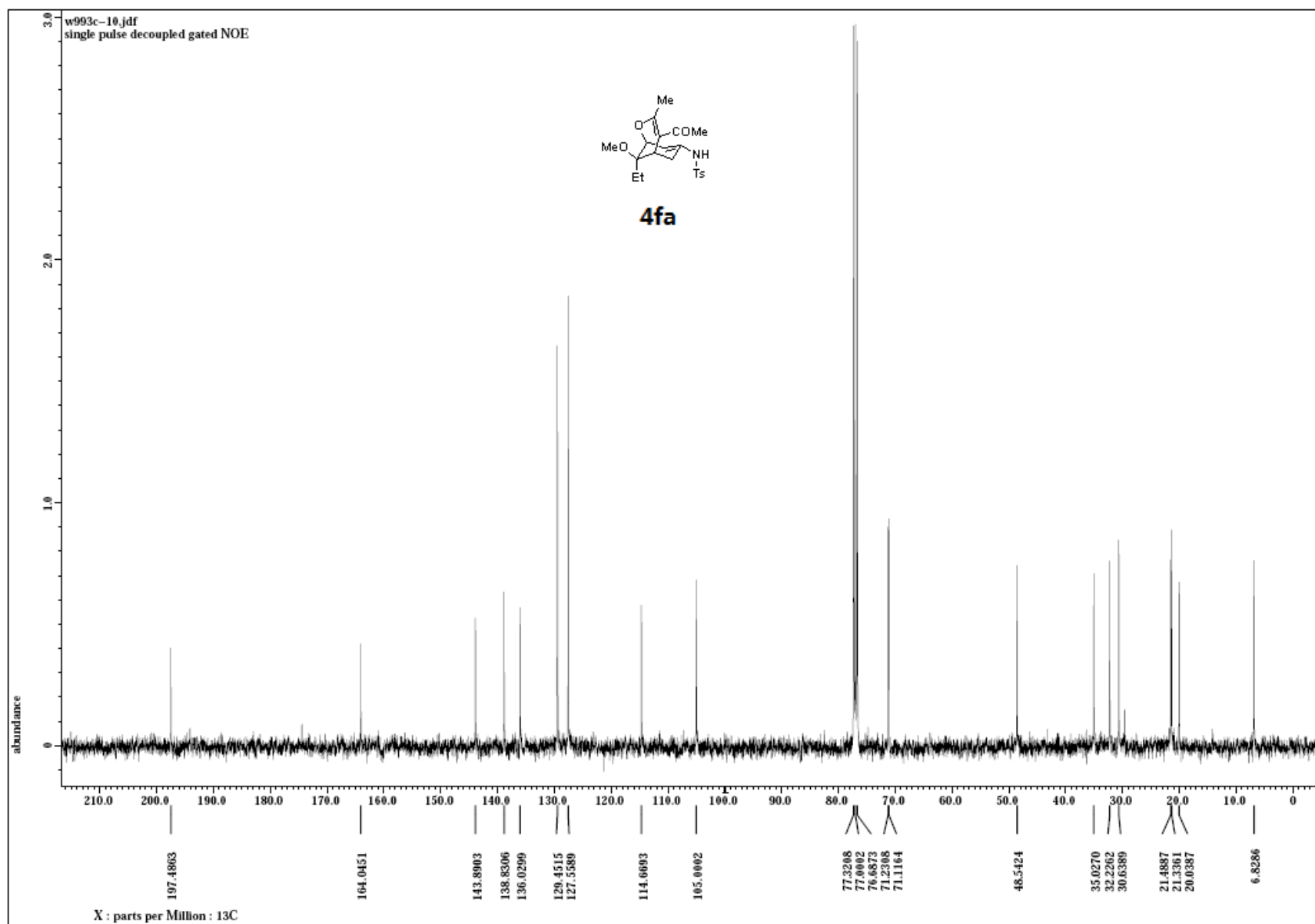


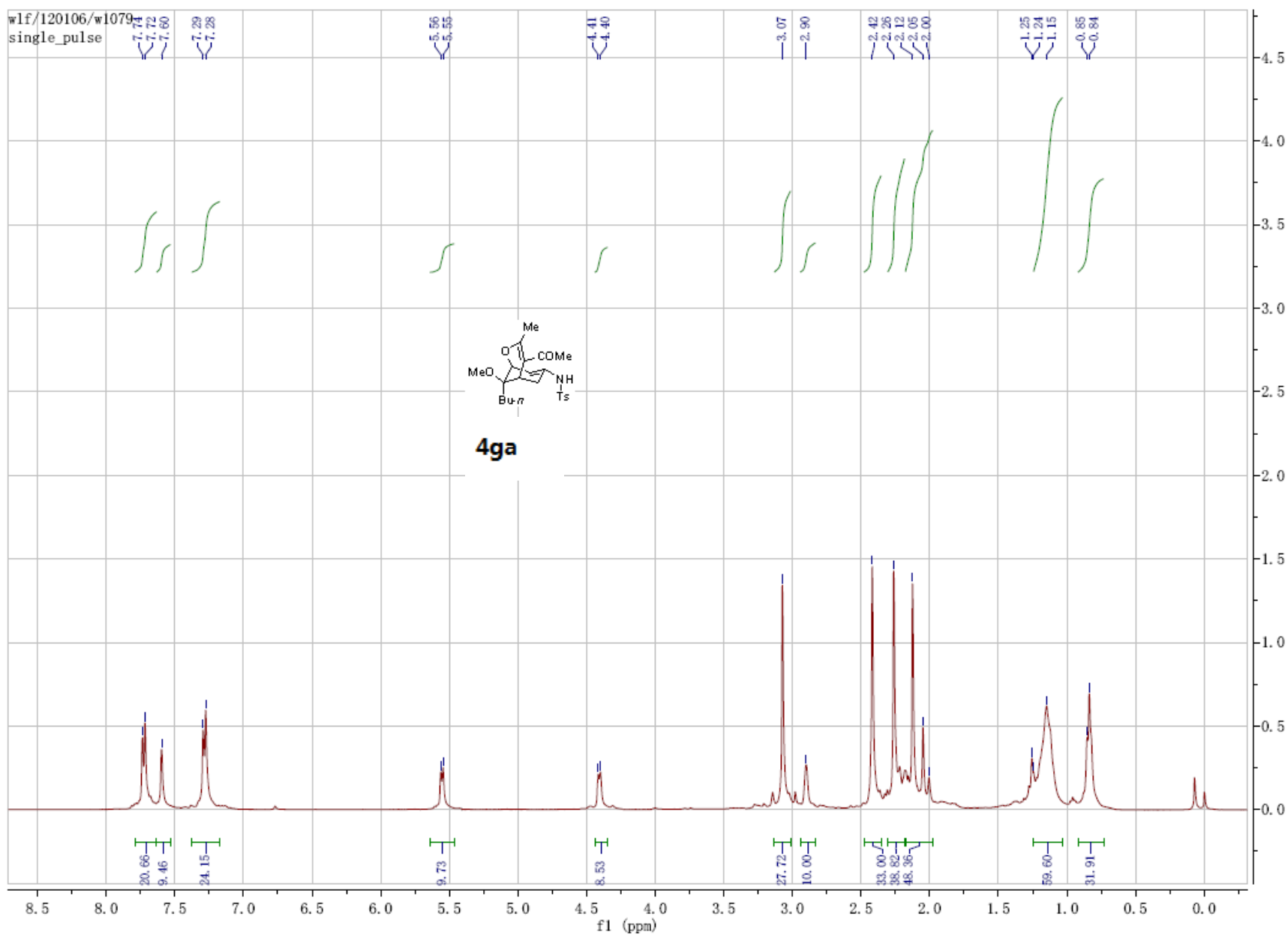


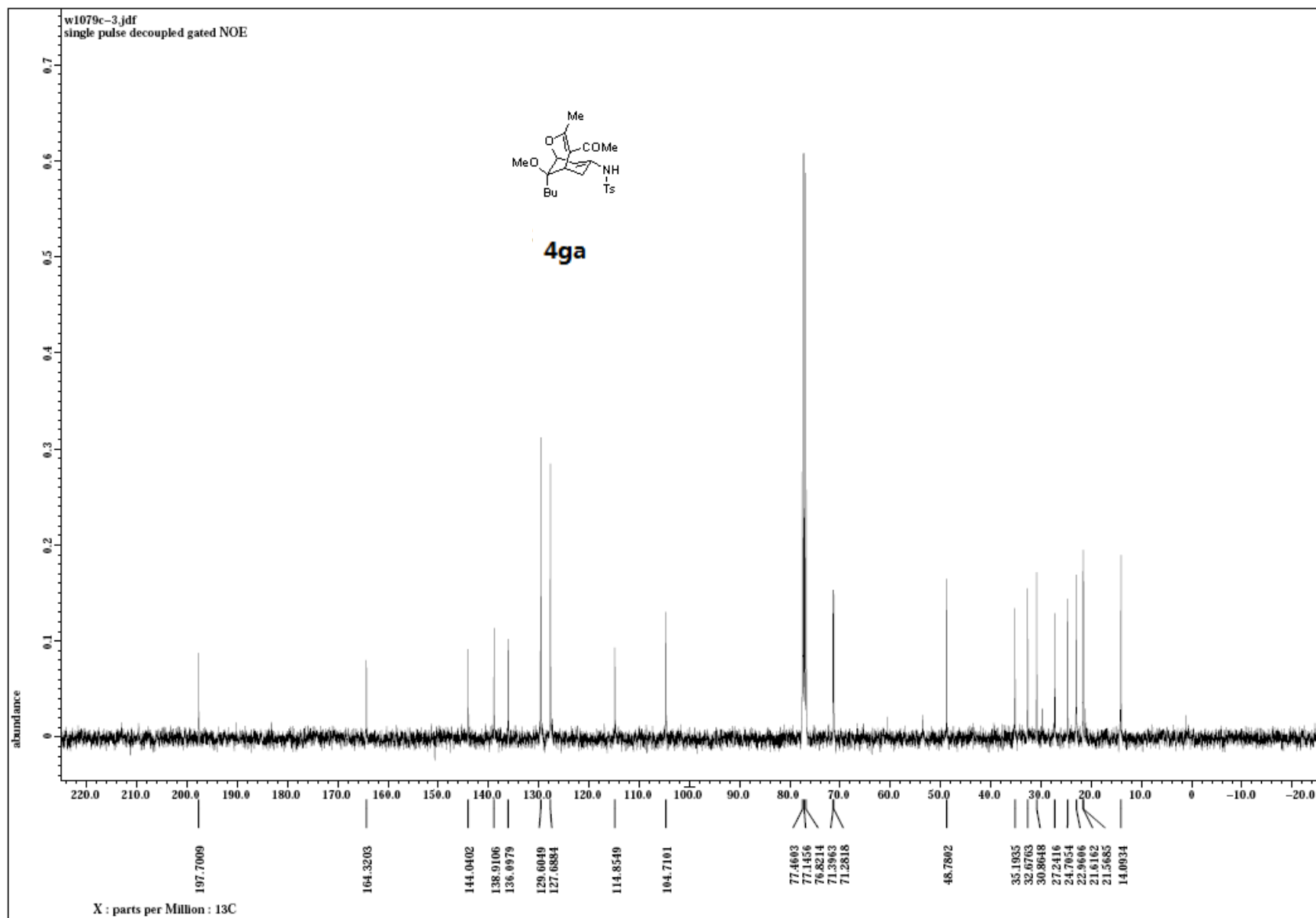


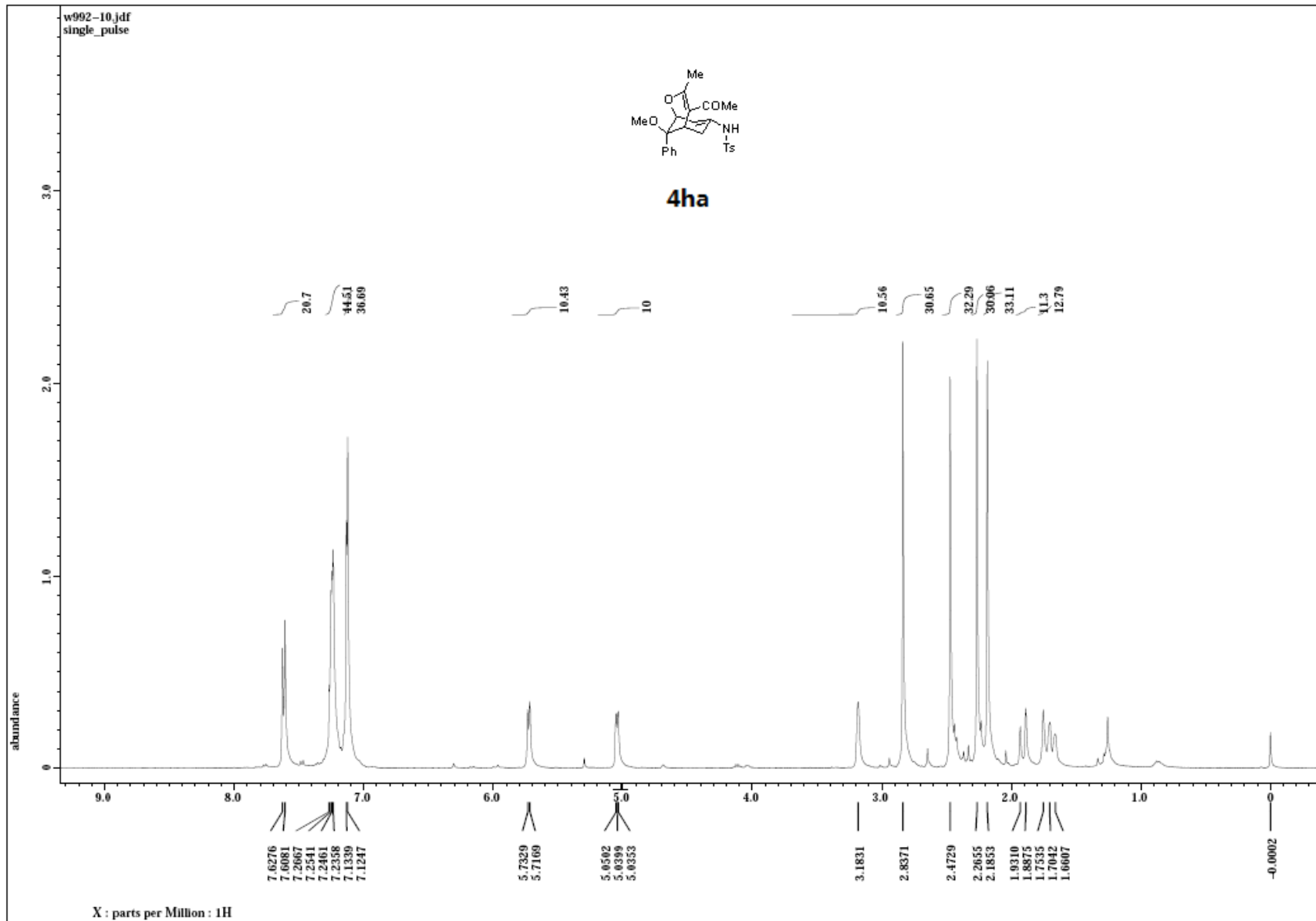


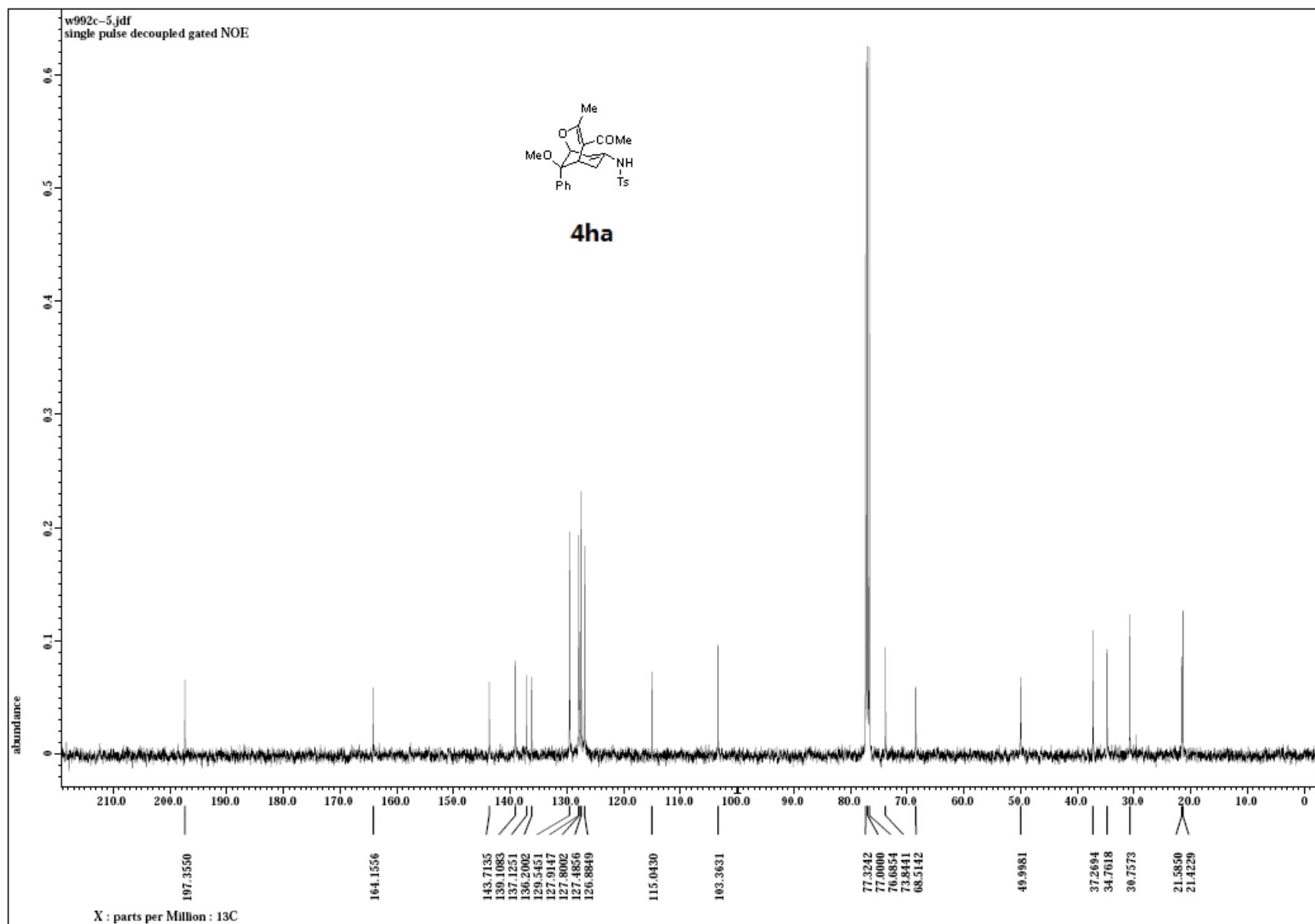


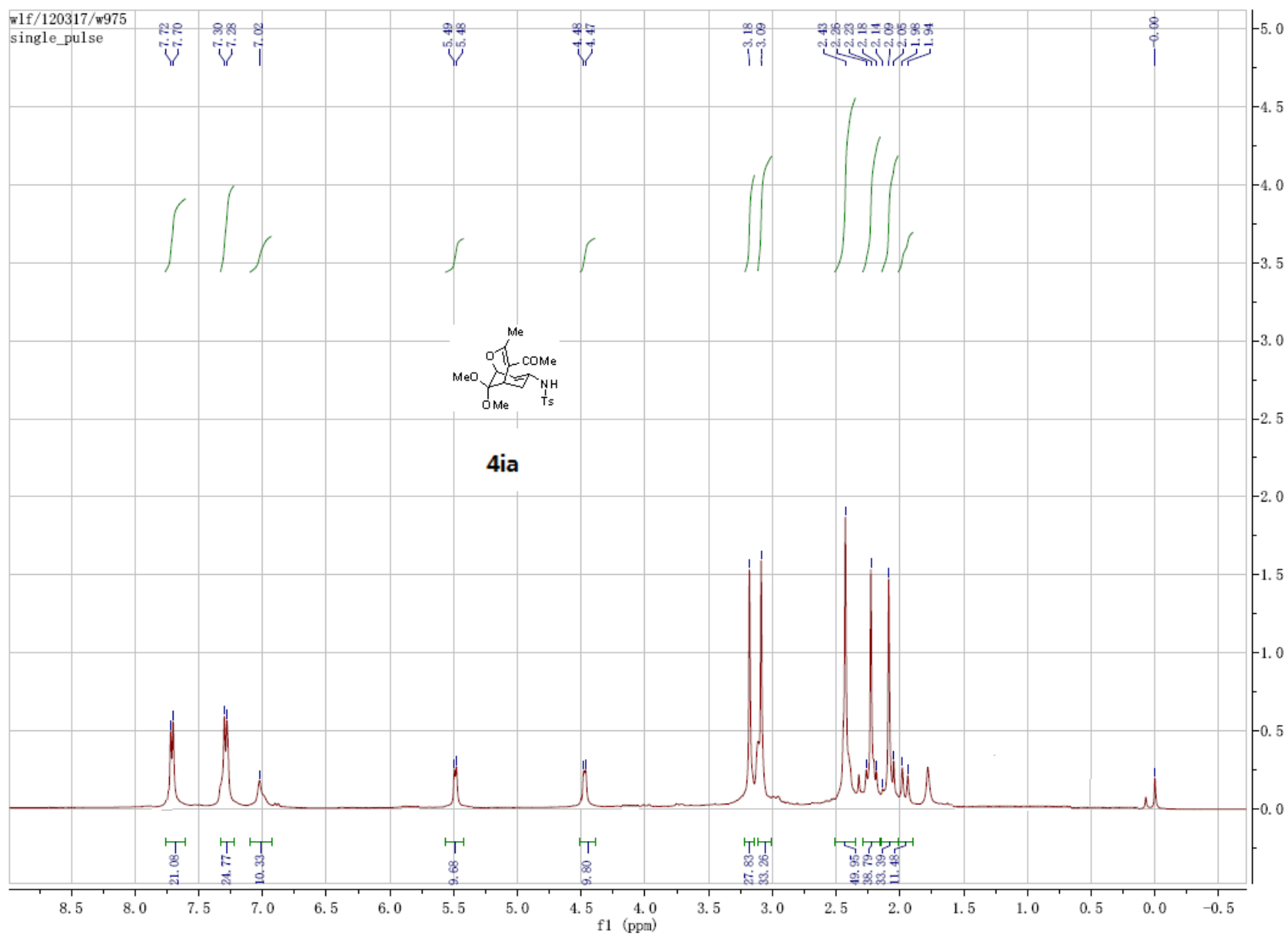


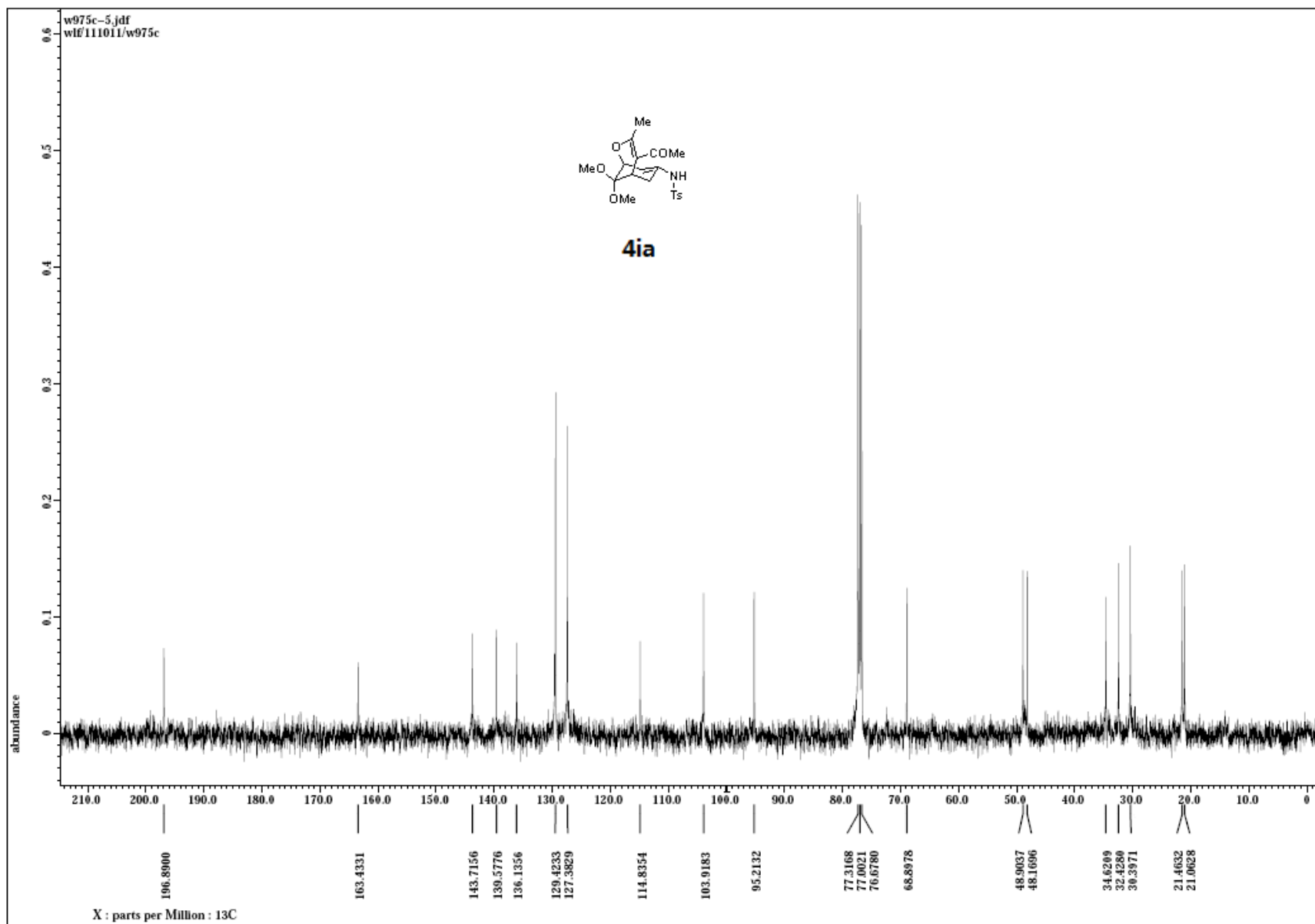


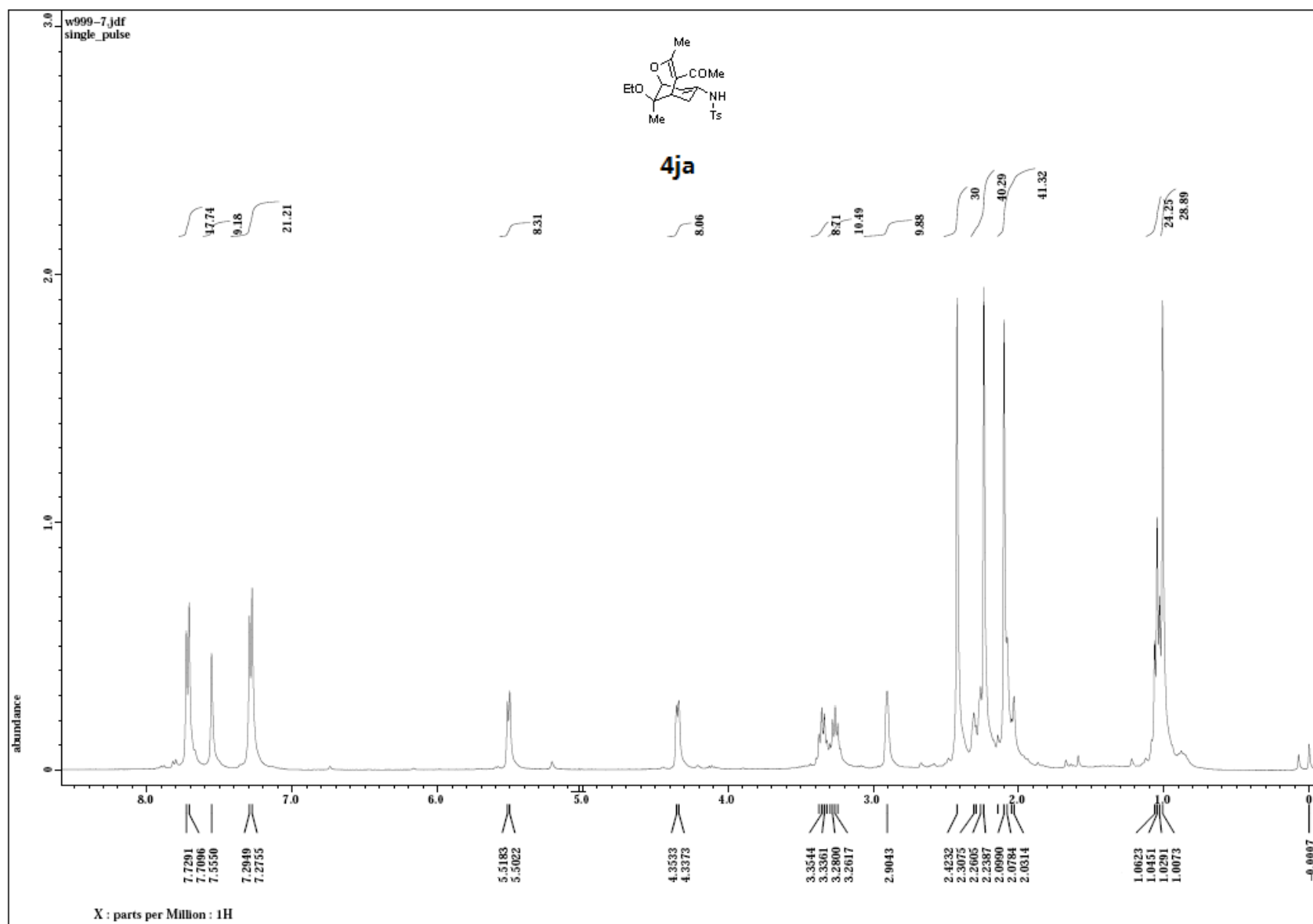


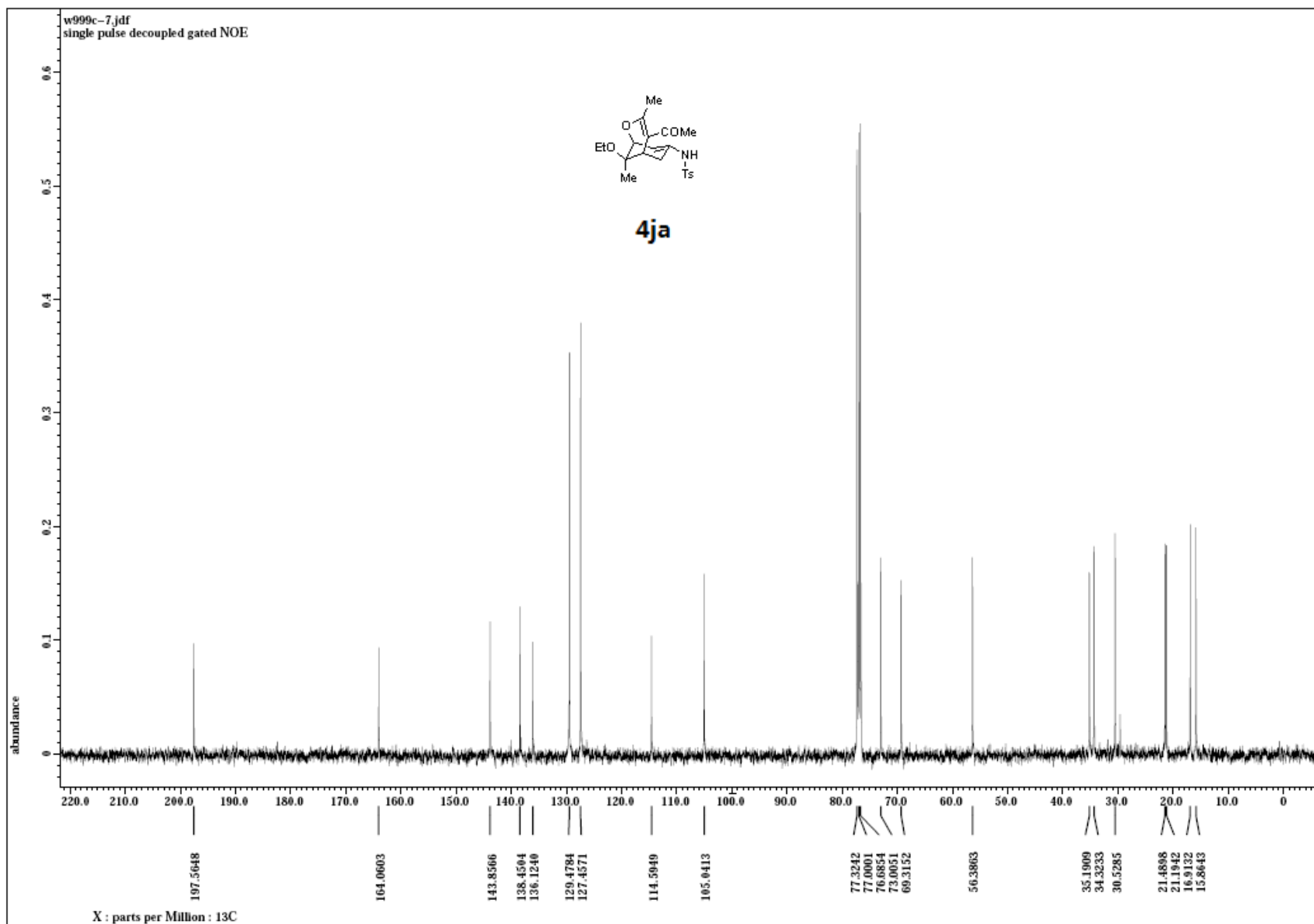


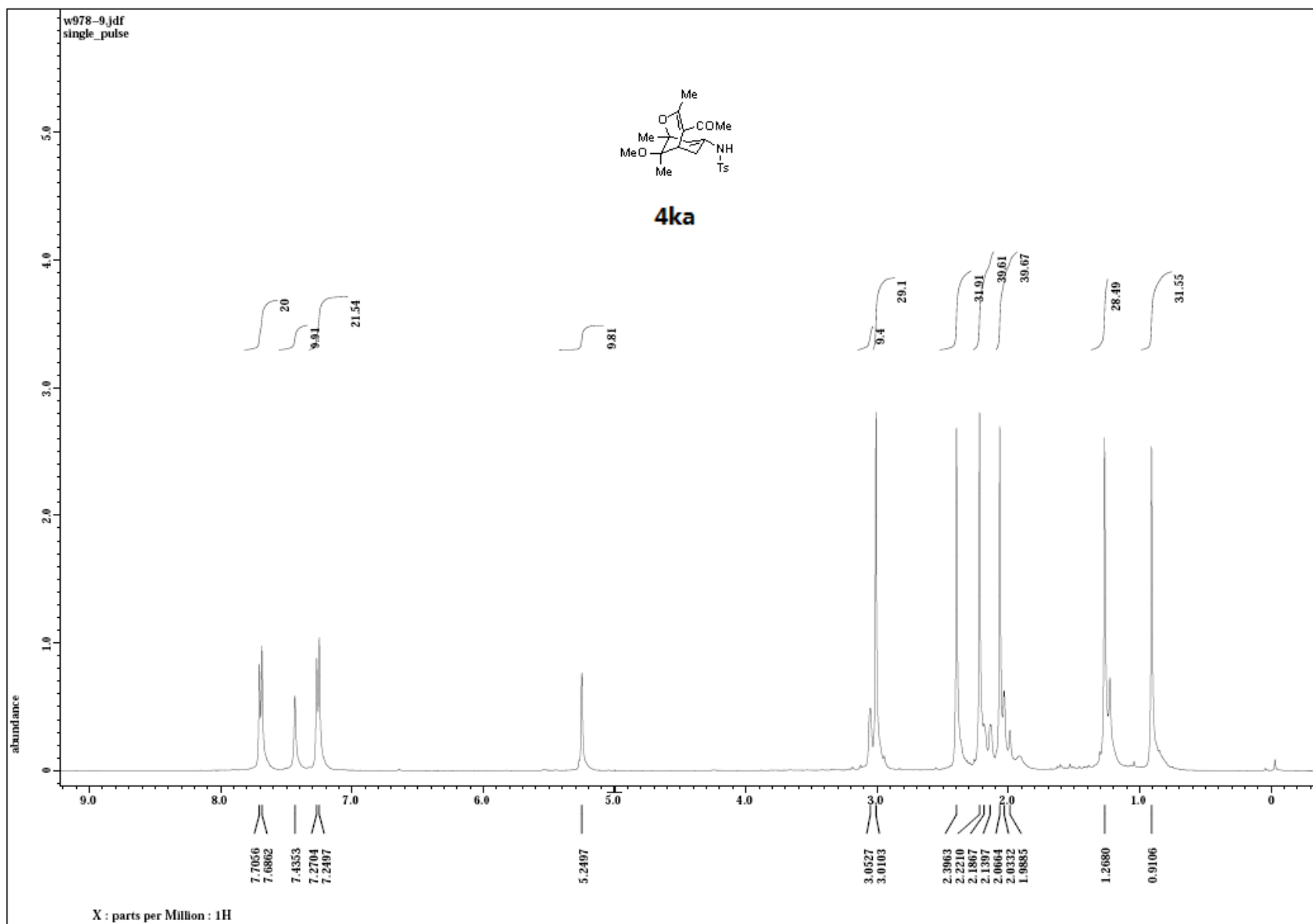


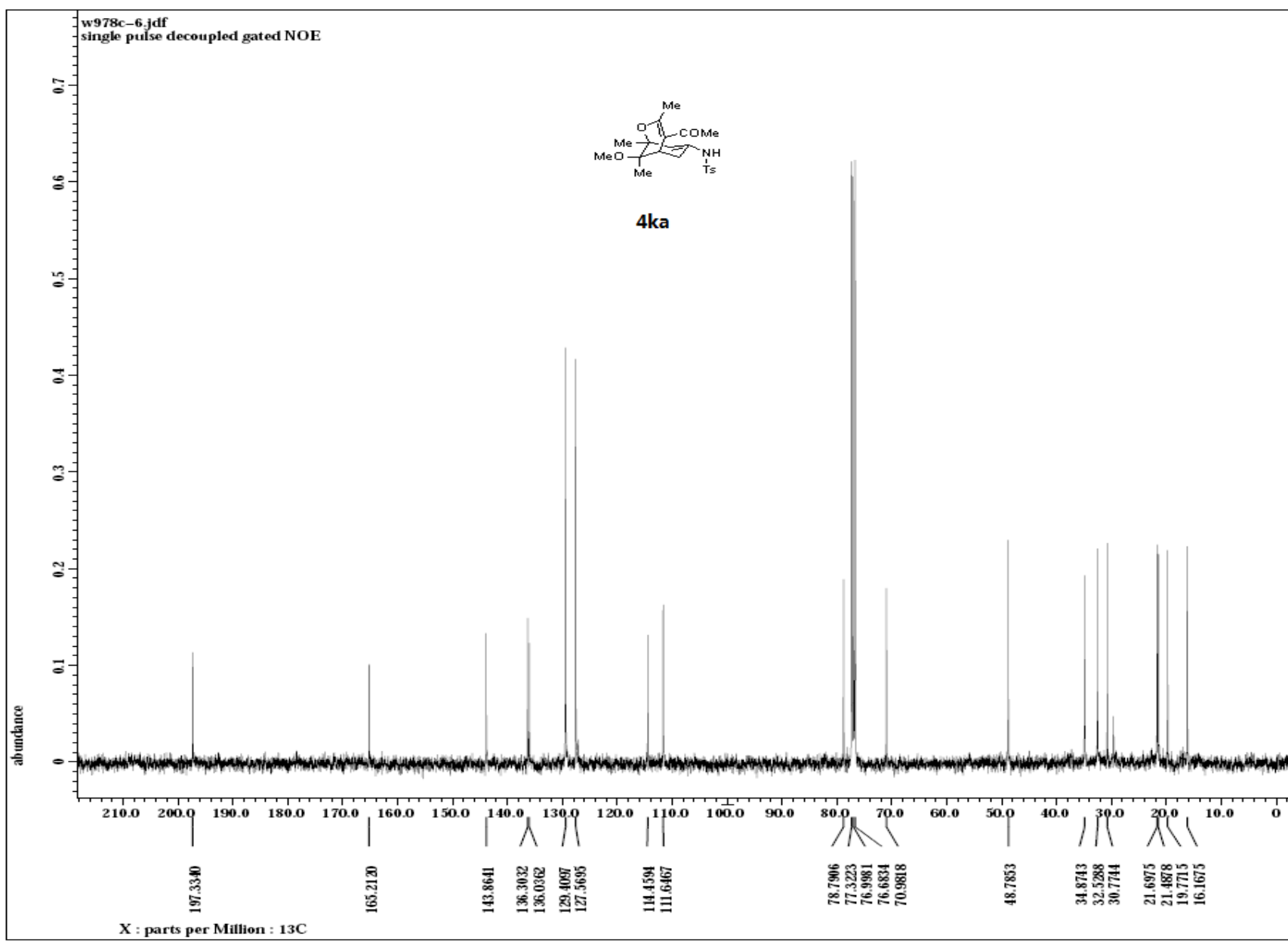


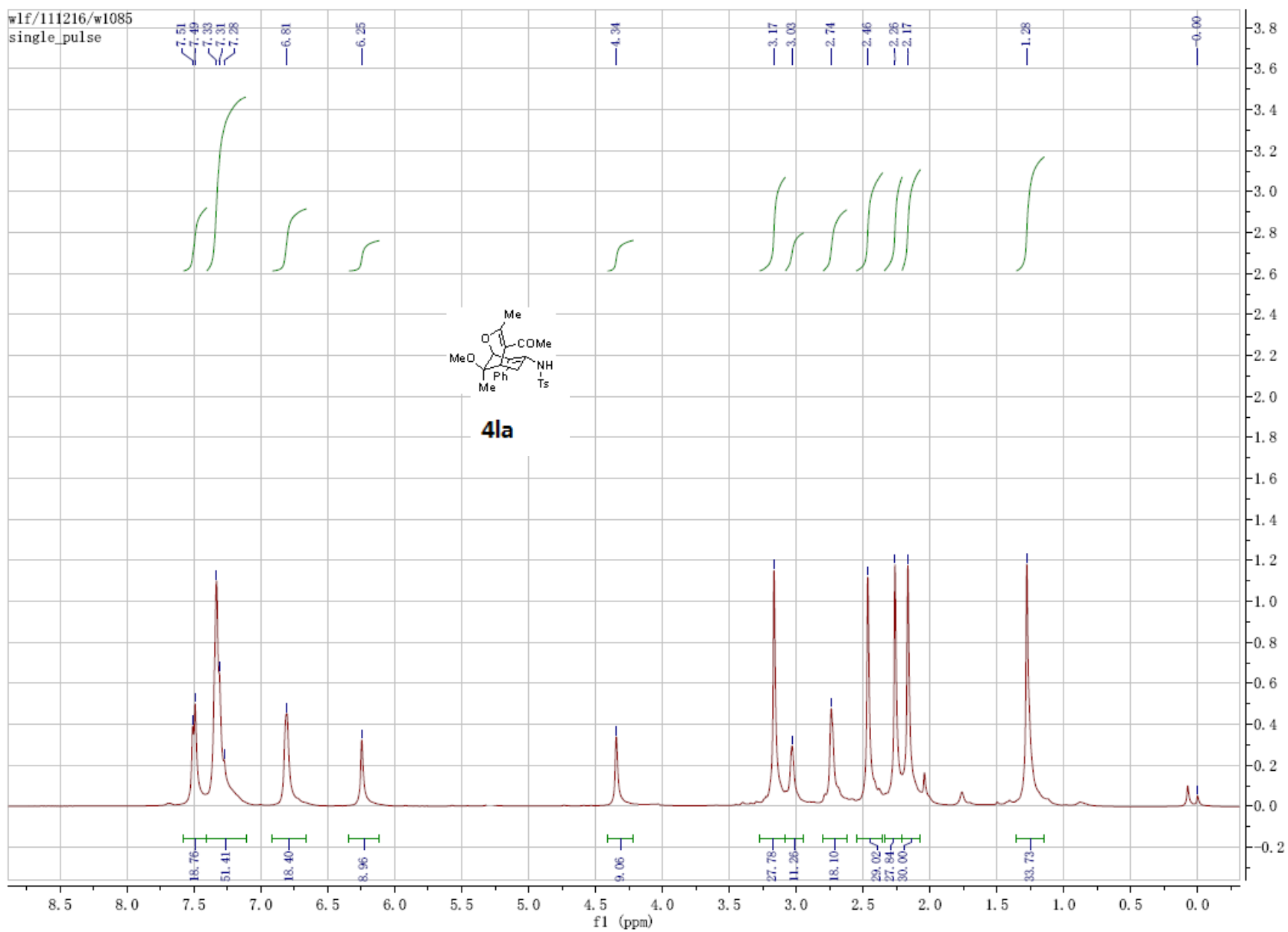


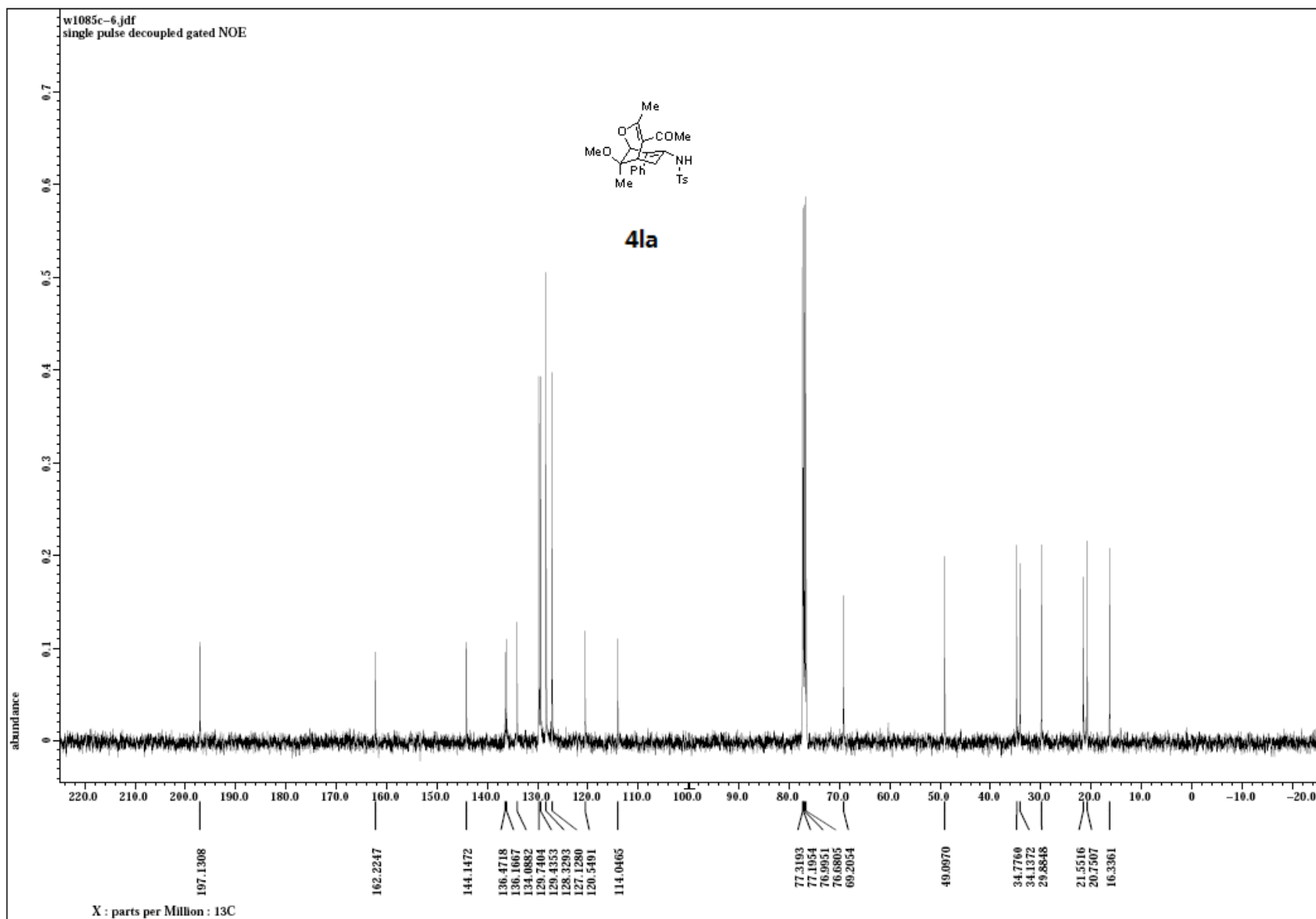




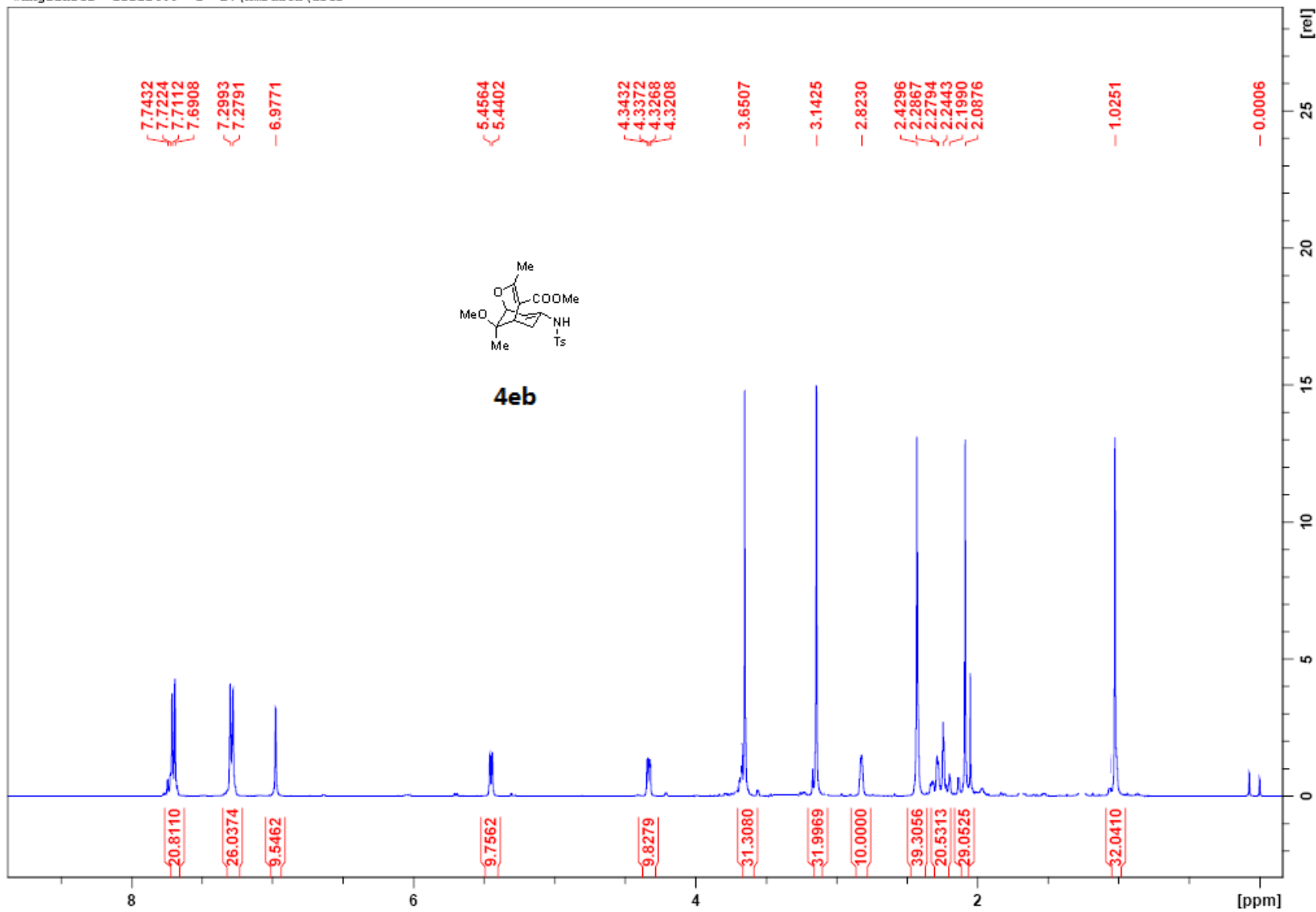


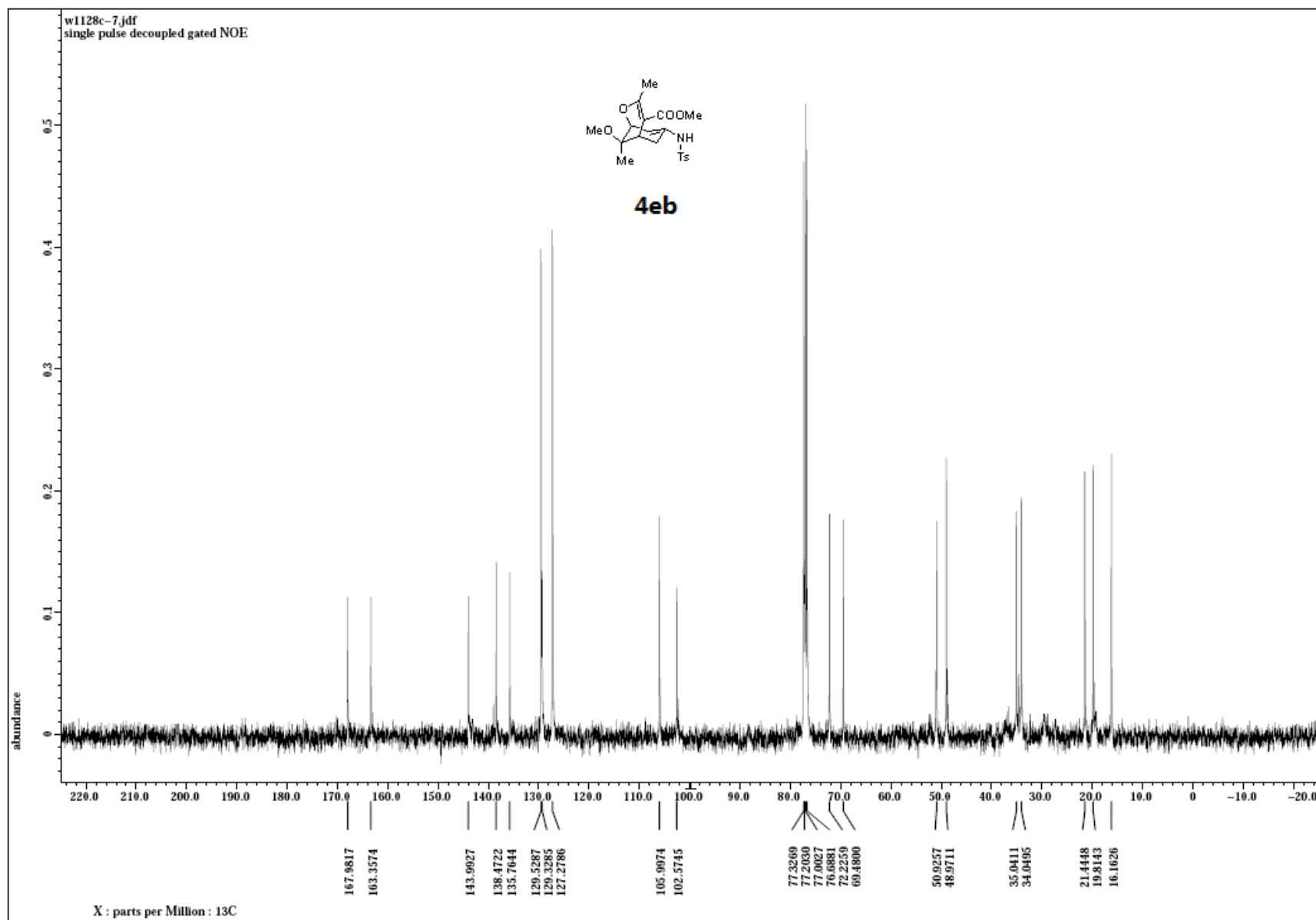


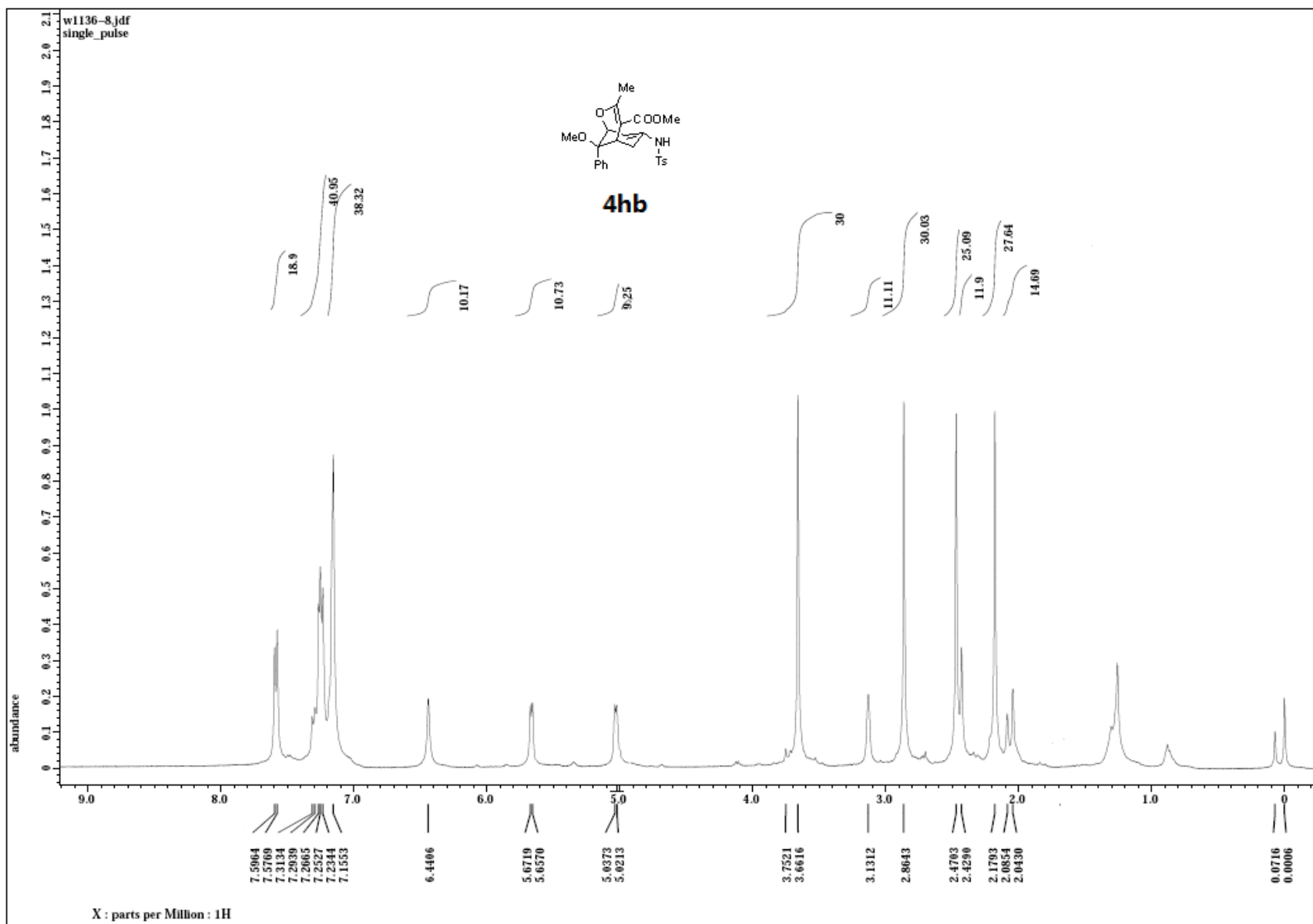


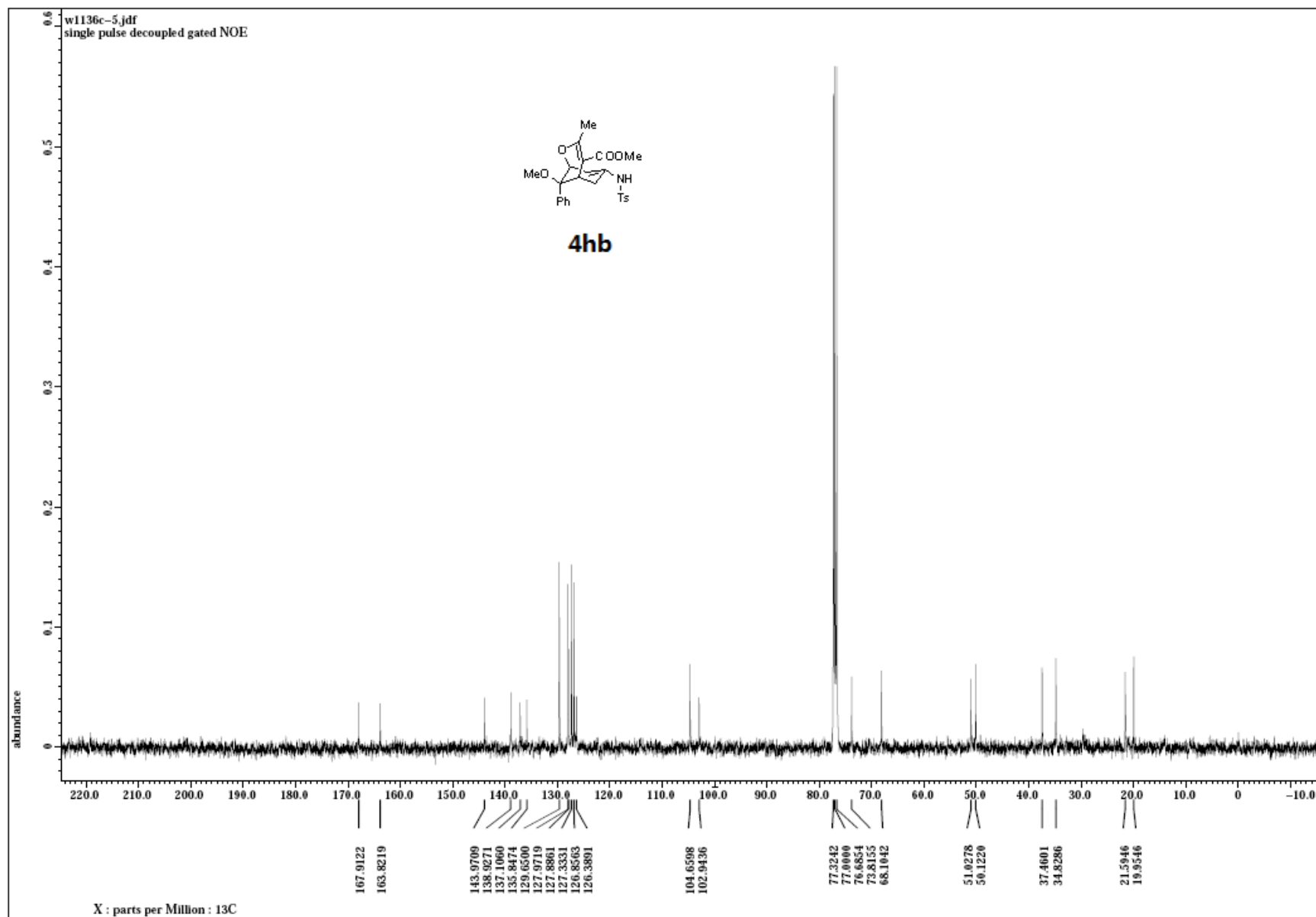


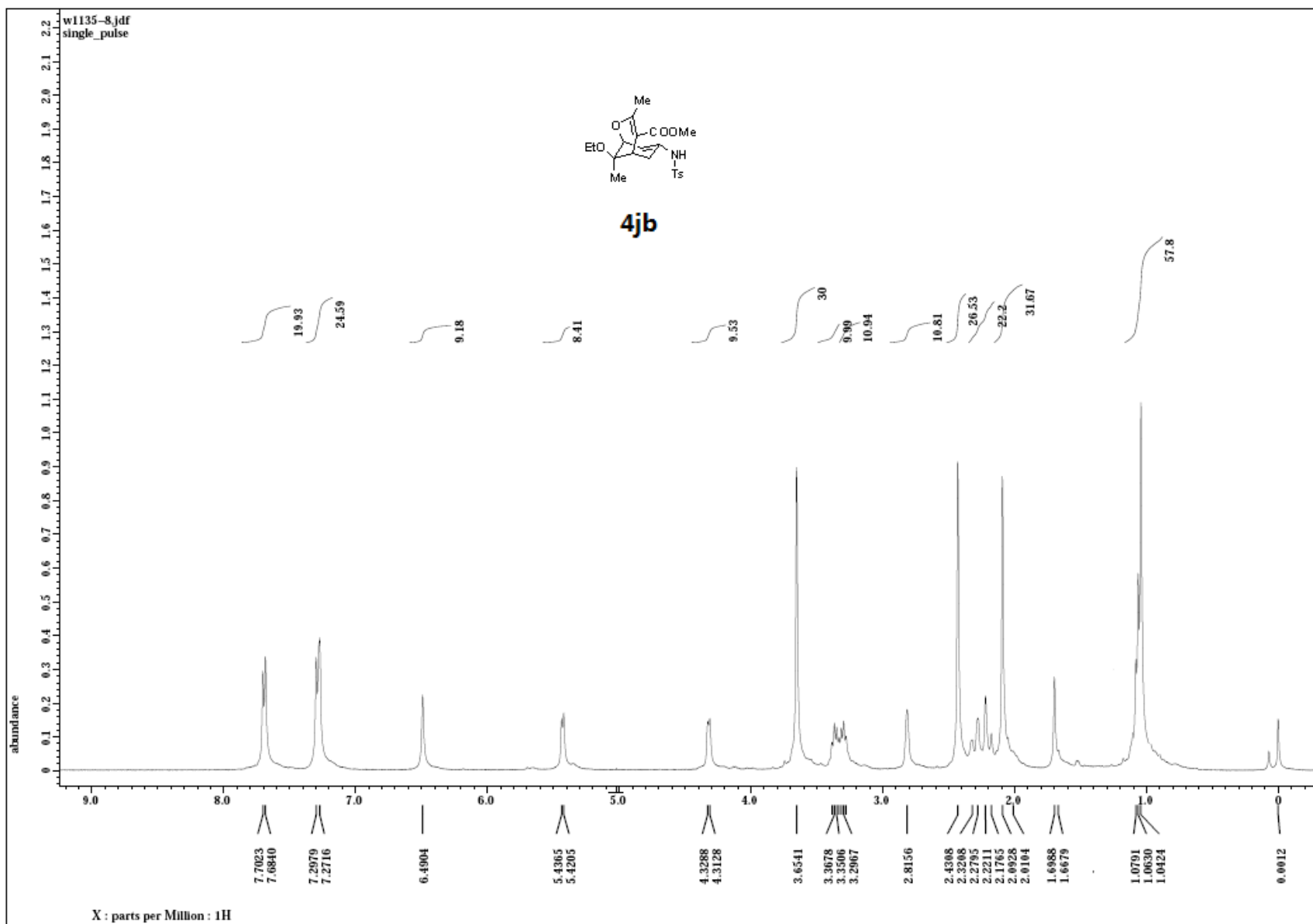
wanglinfei 12112406 1 E:\nmrdata\user

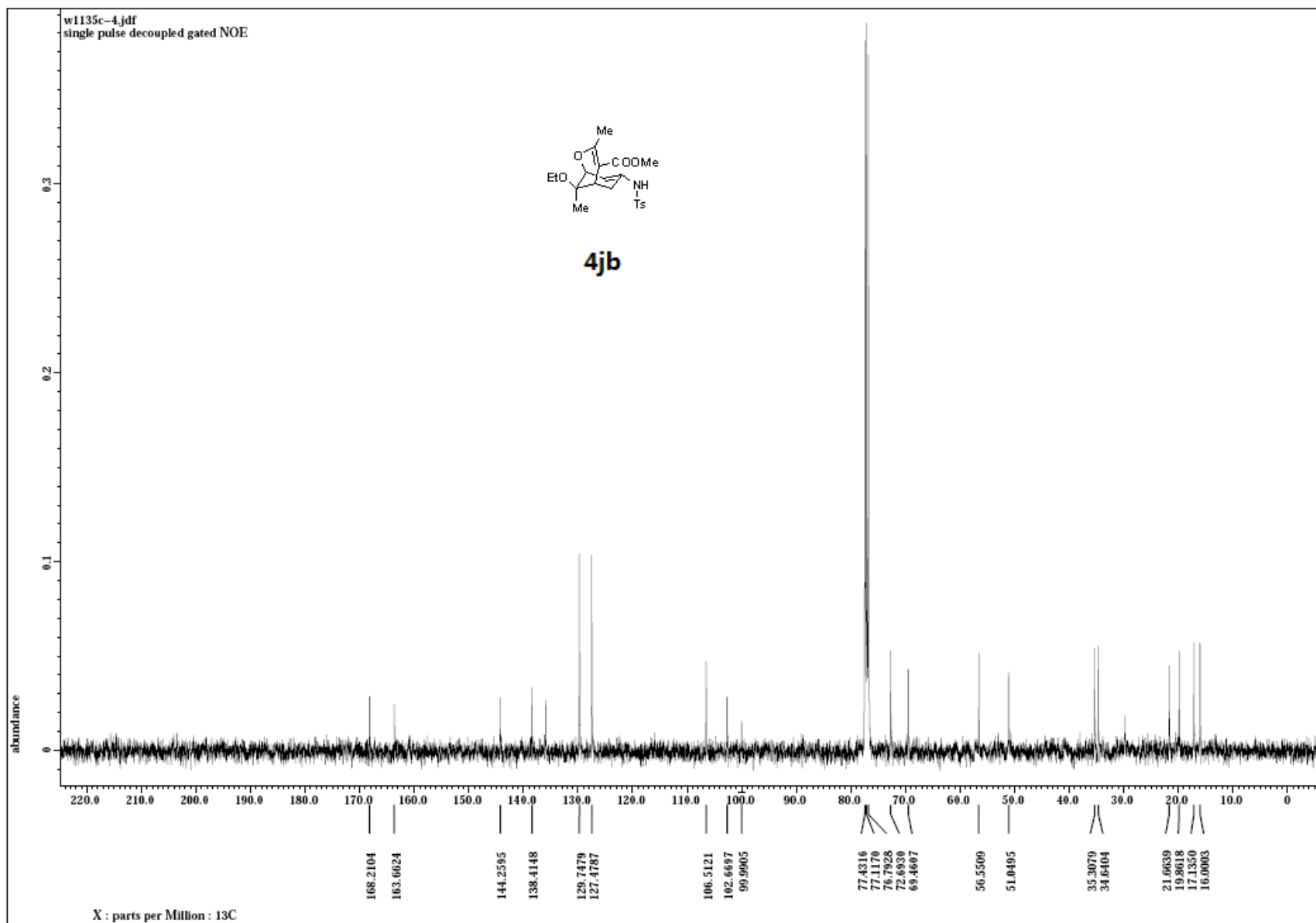


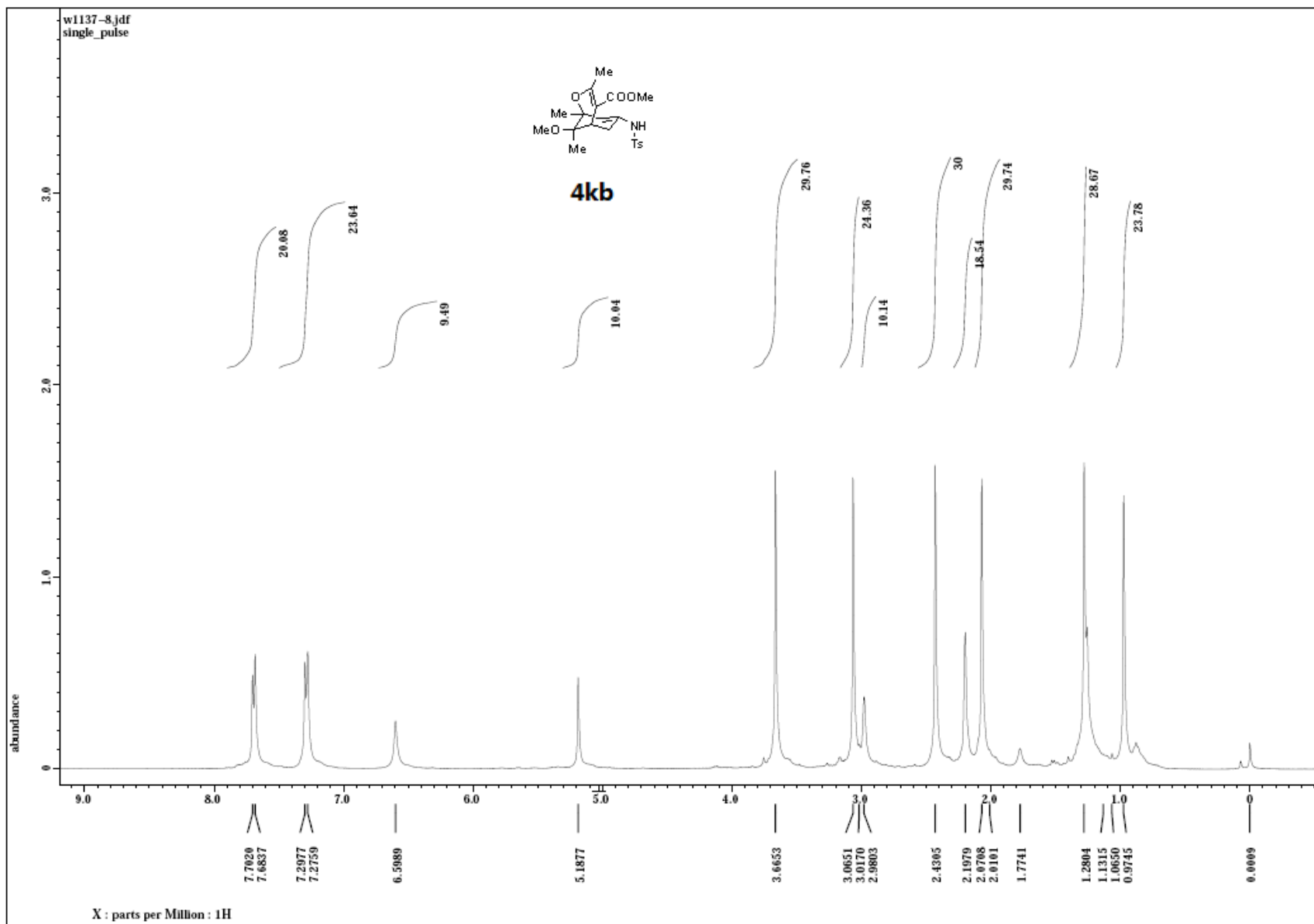


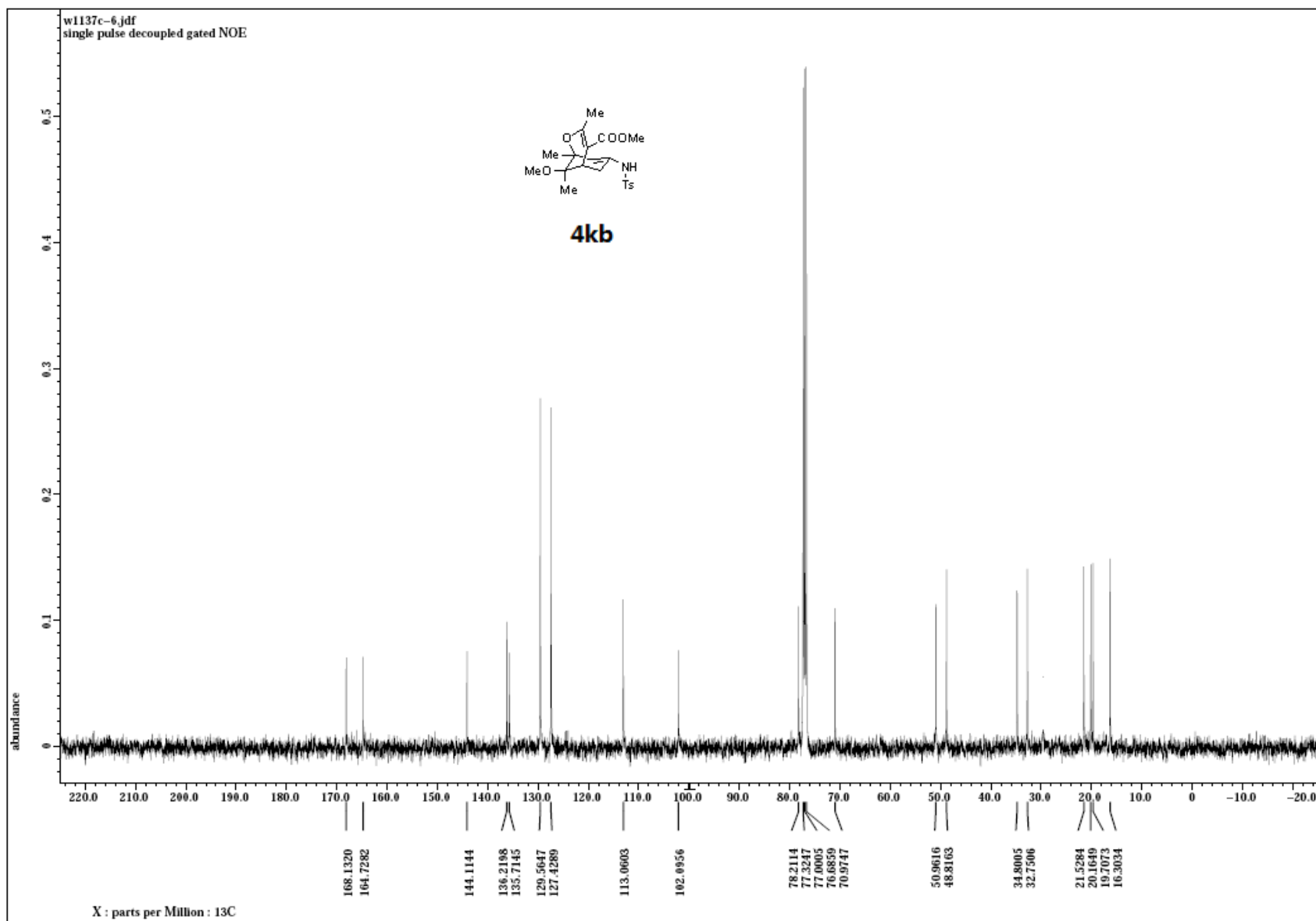


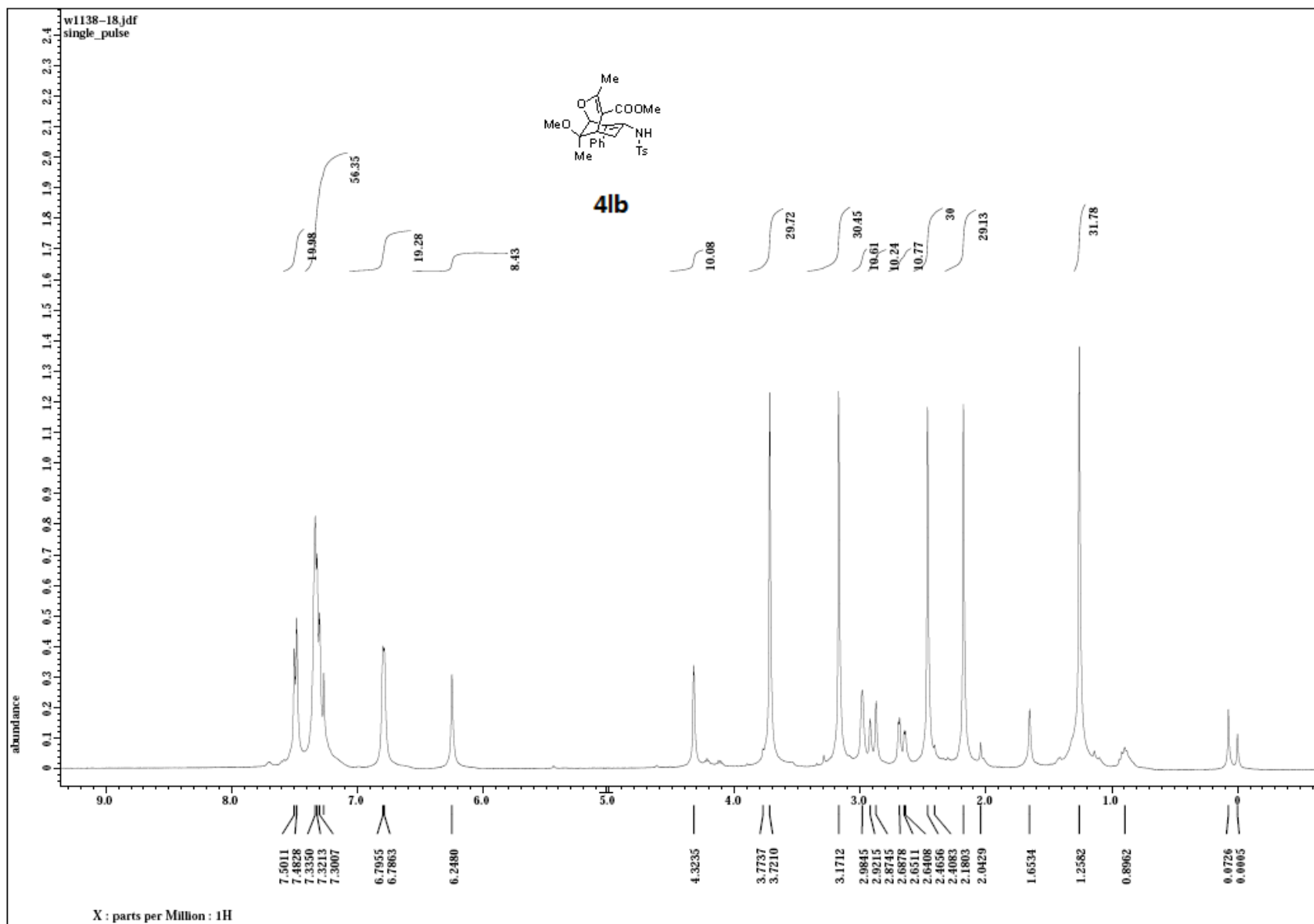


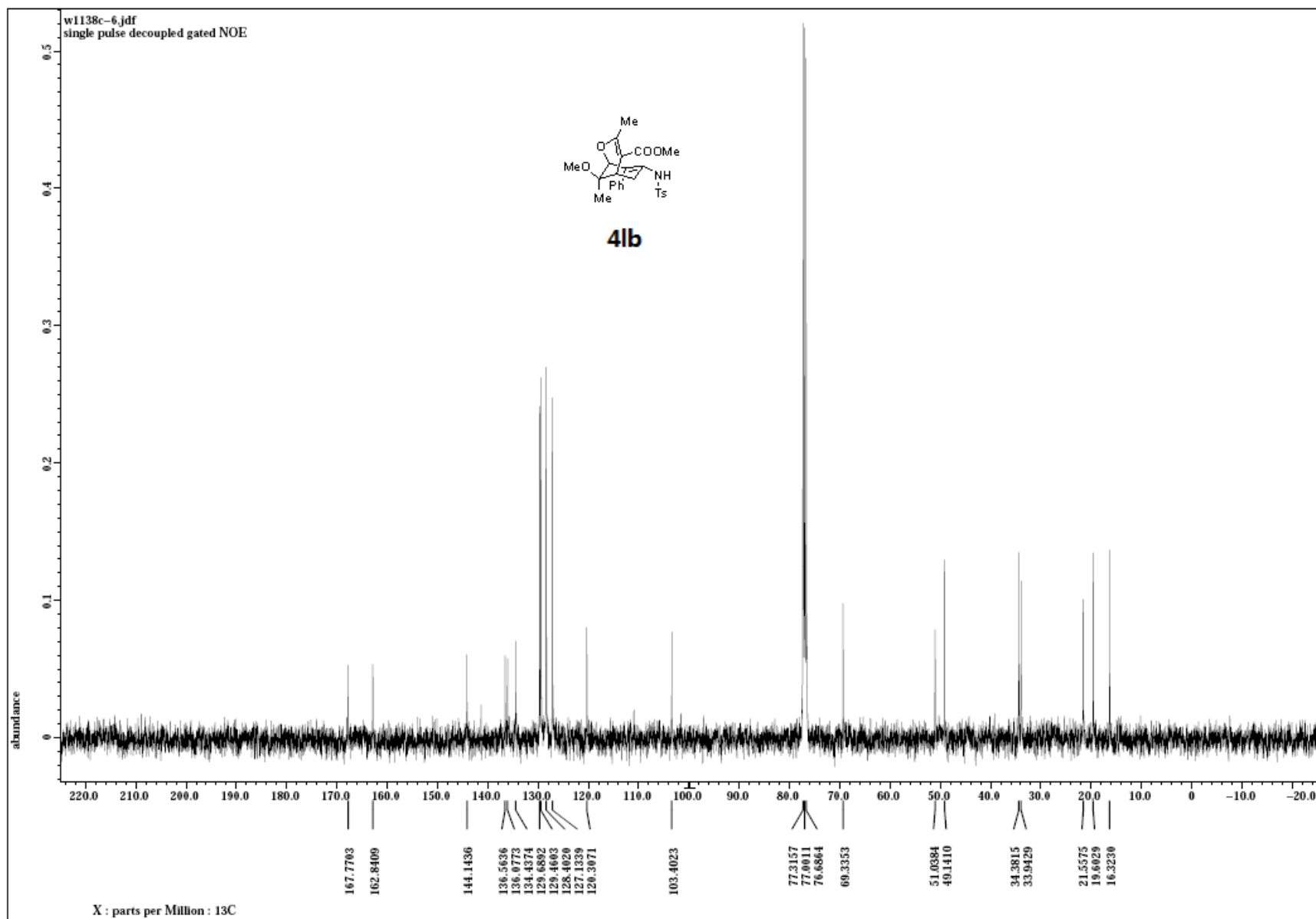


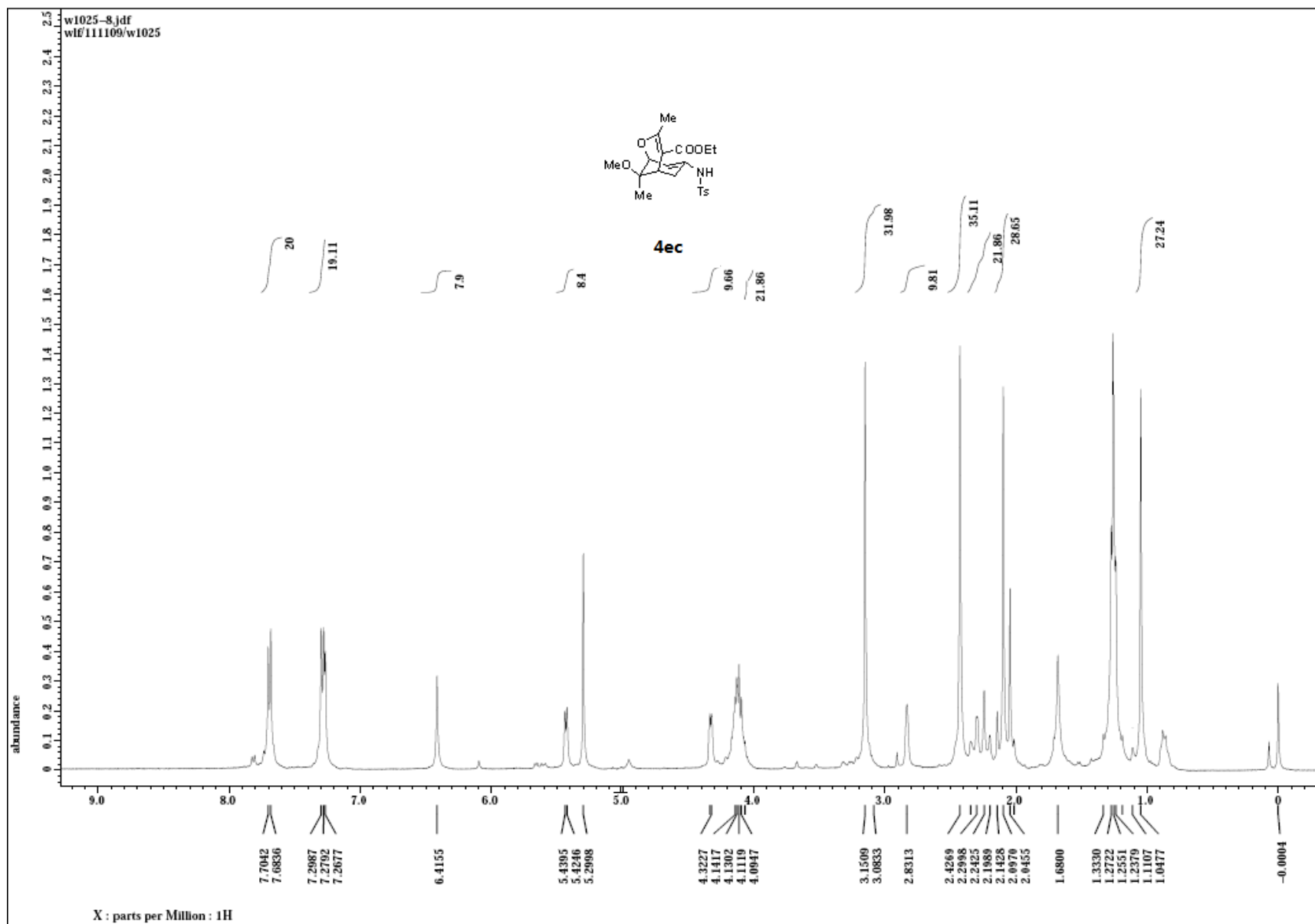


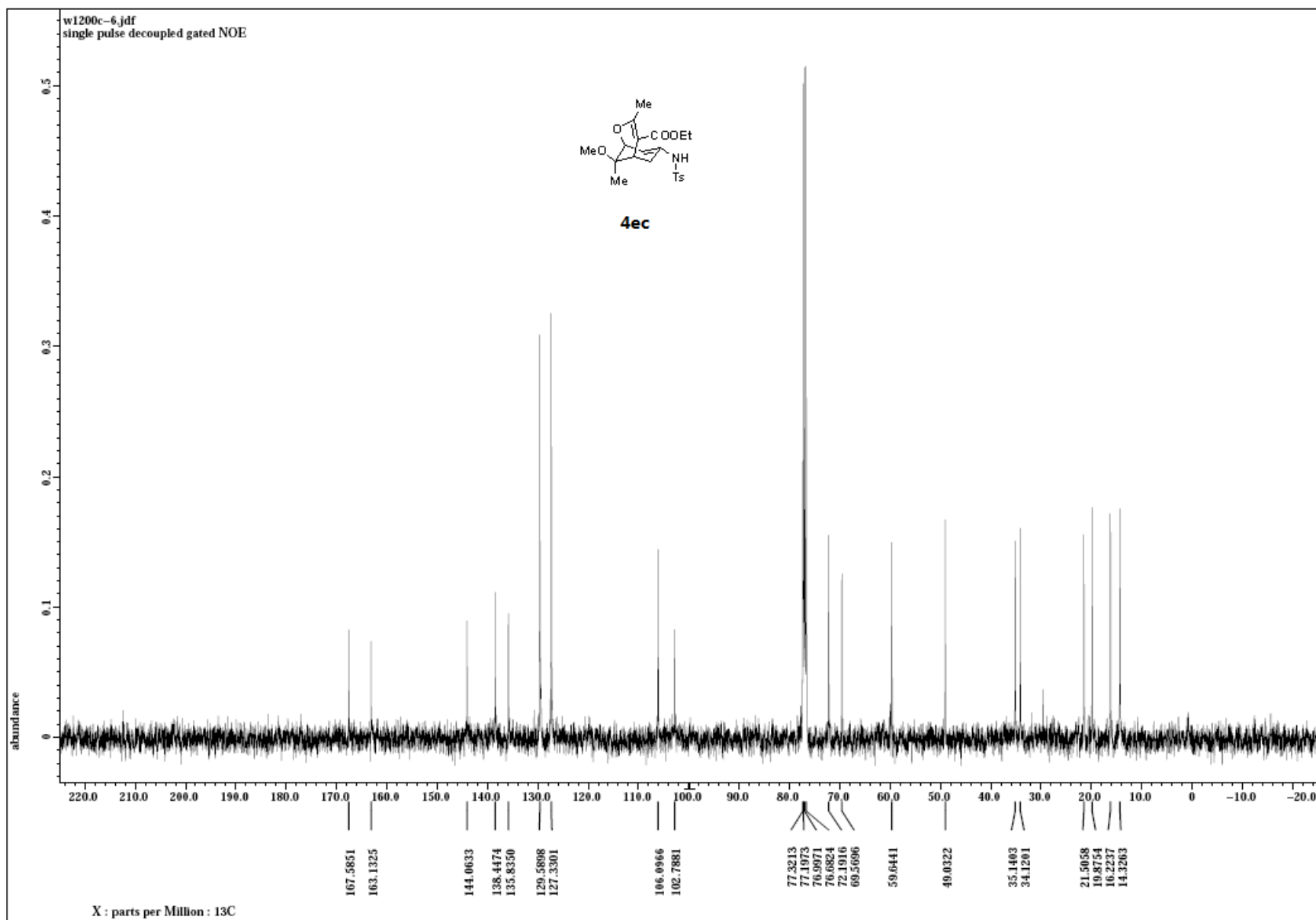


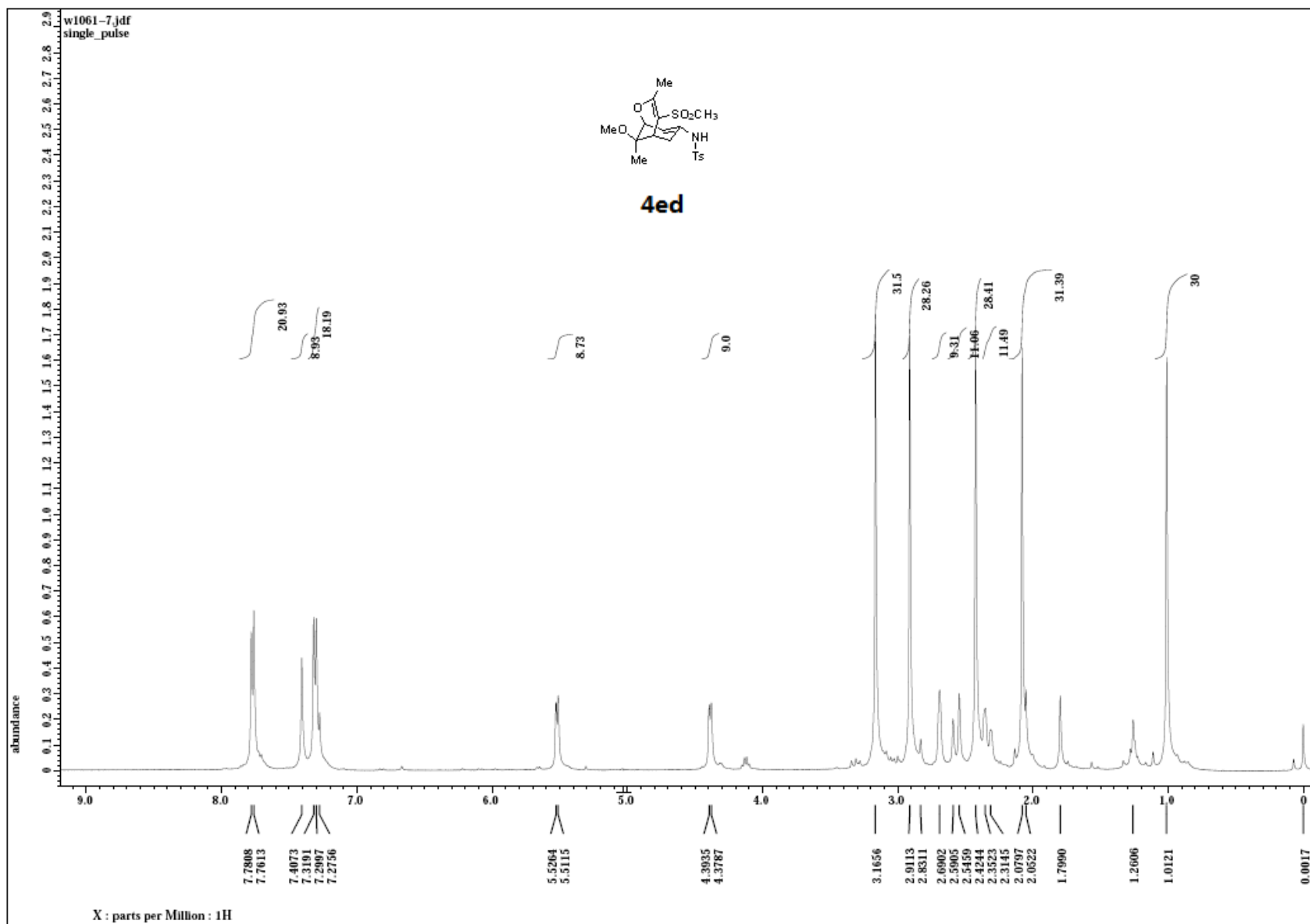


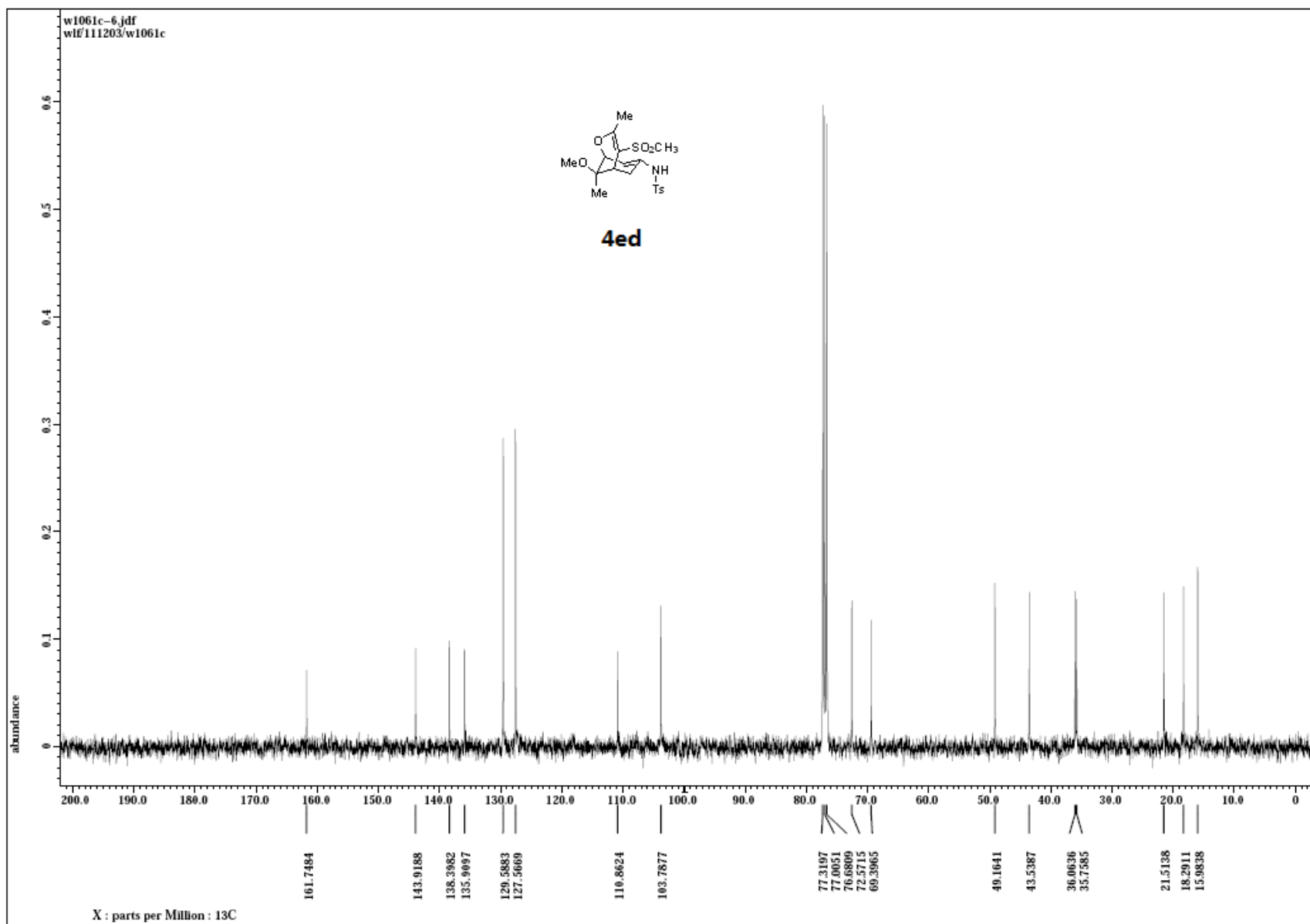


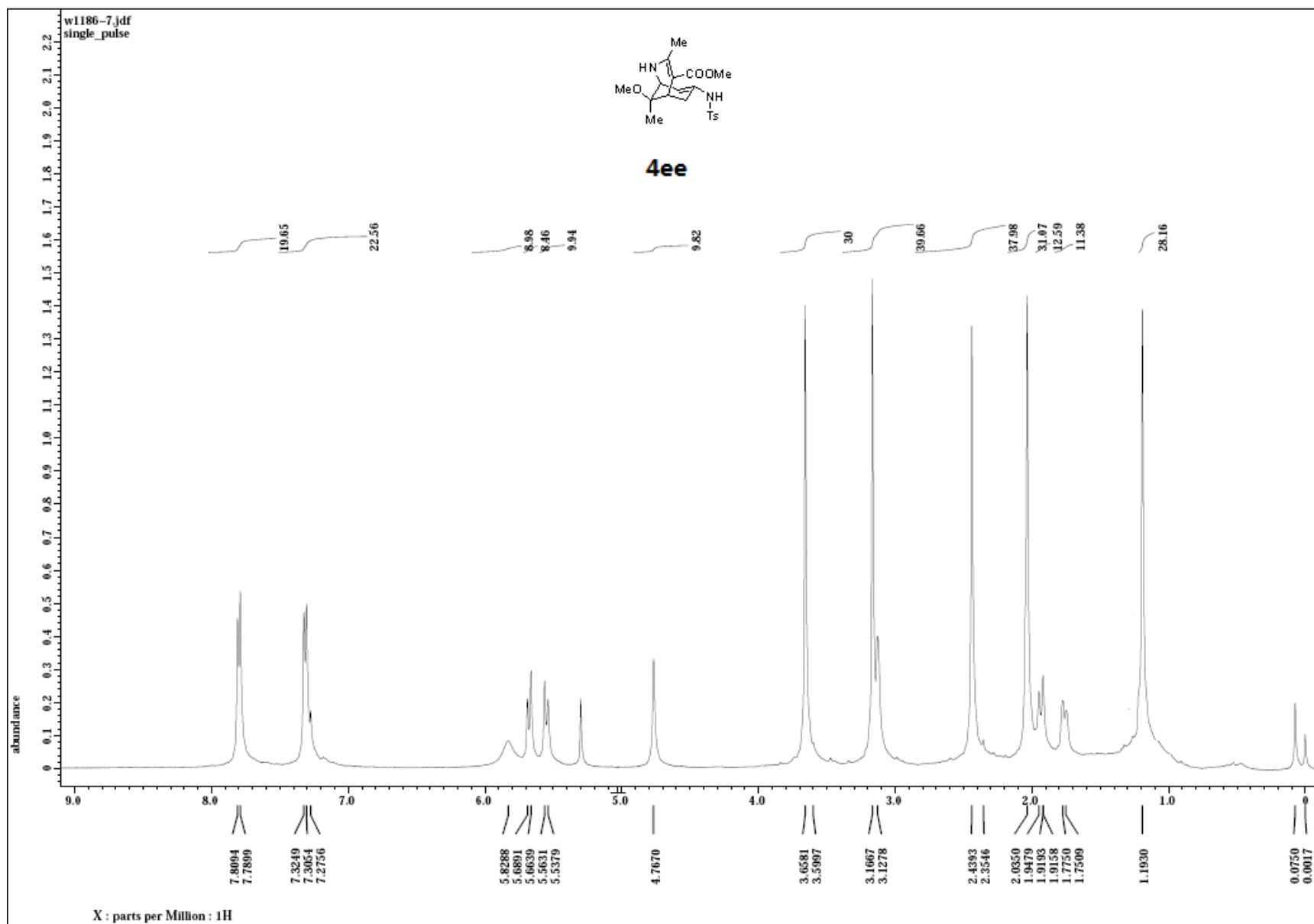


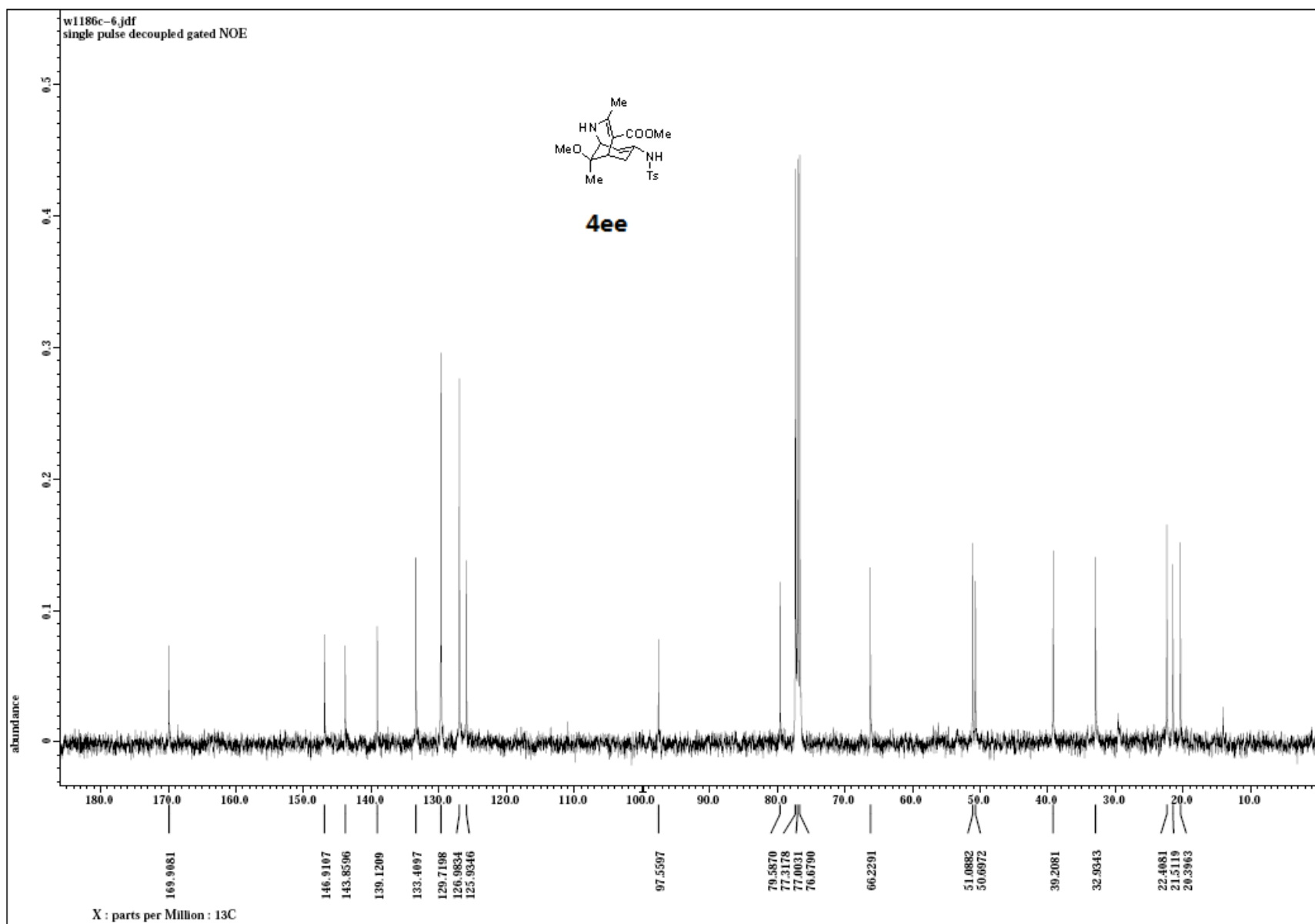


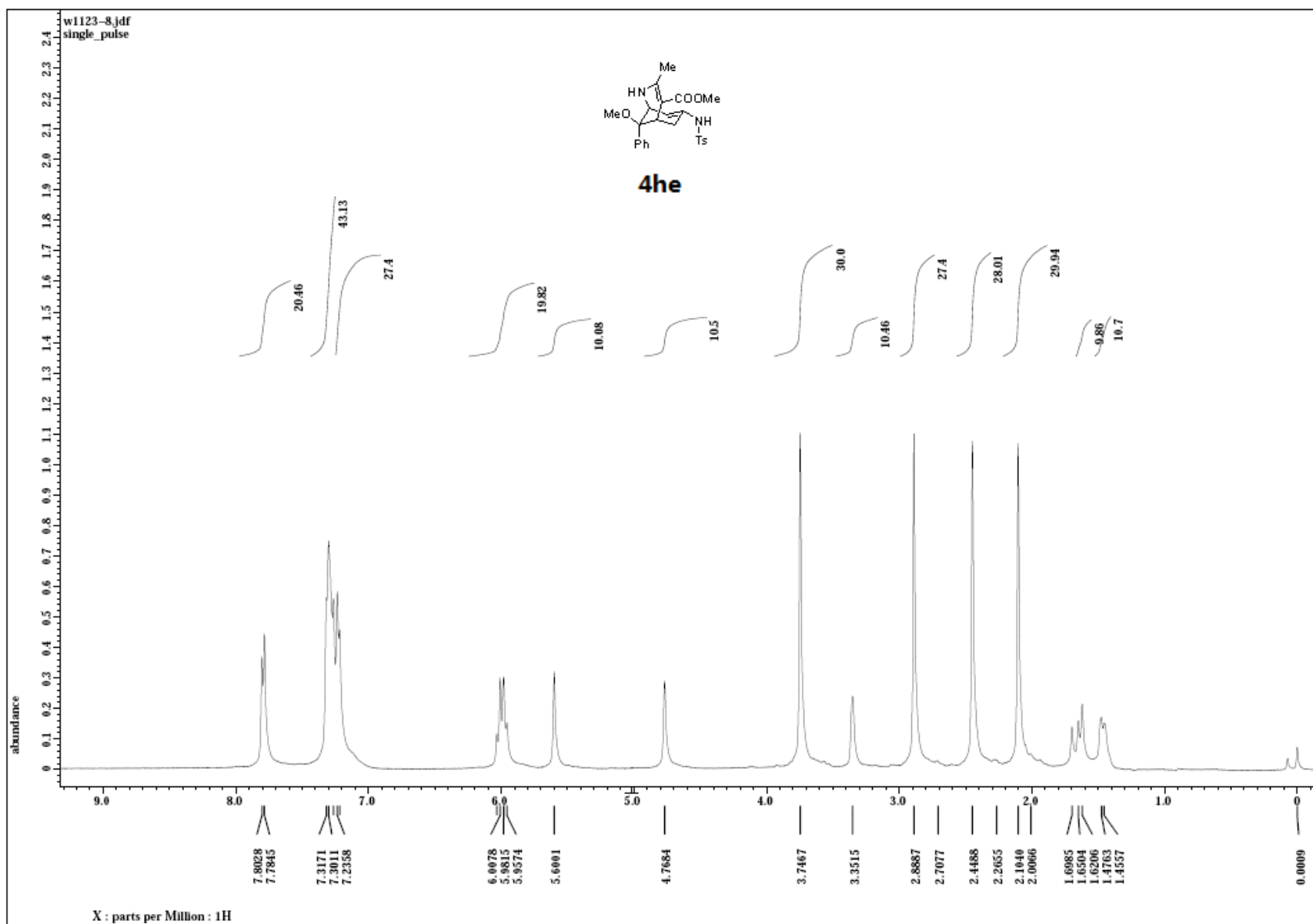


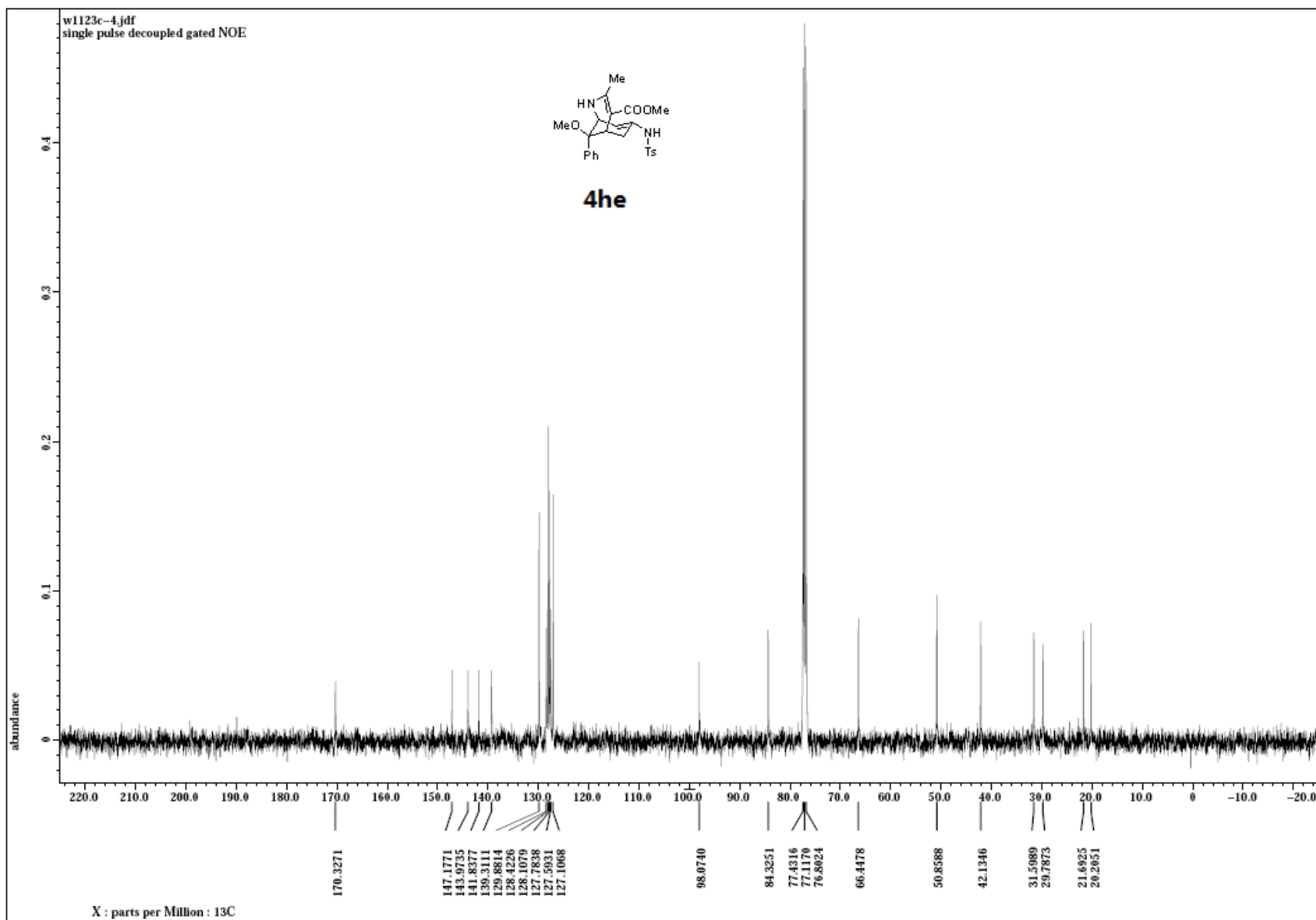


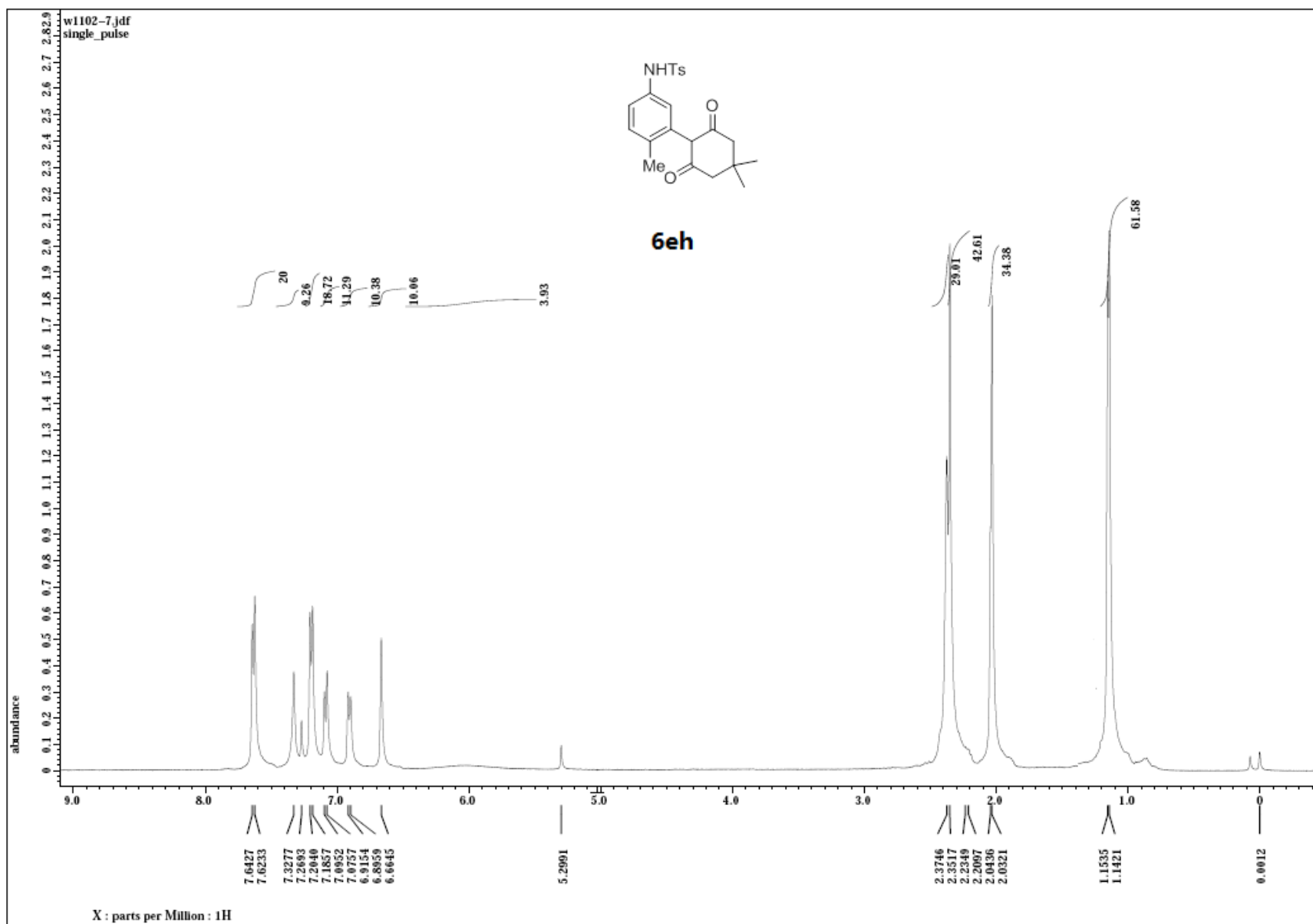


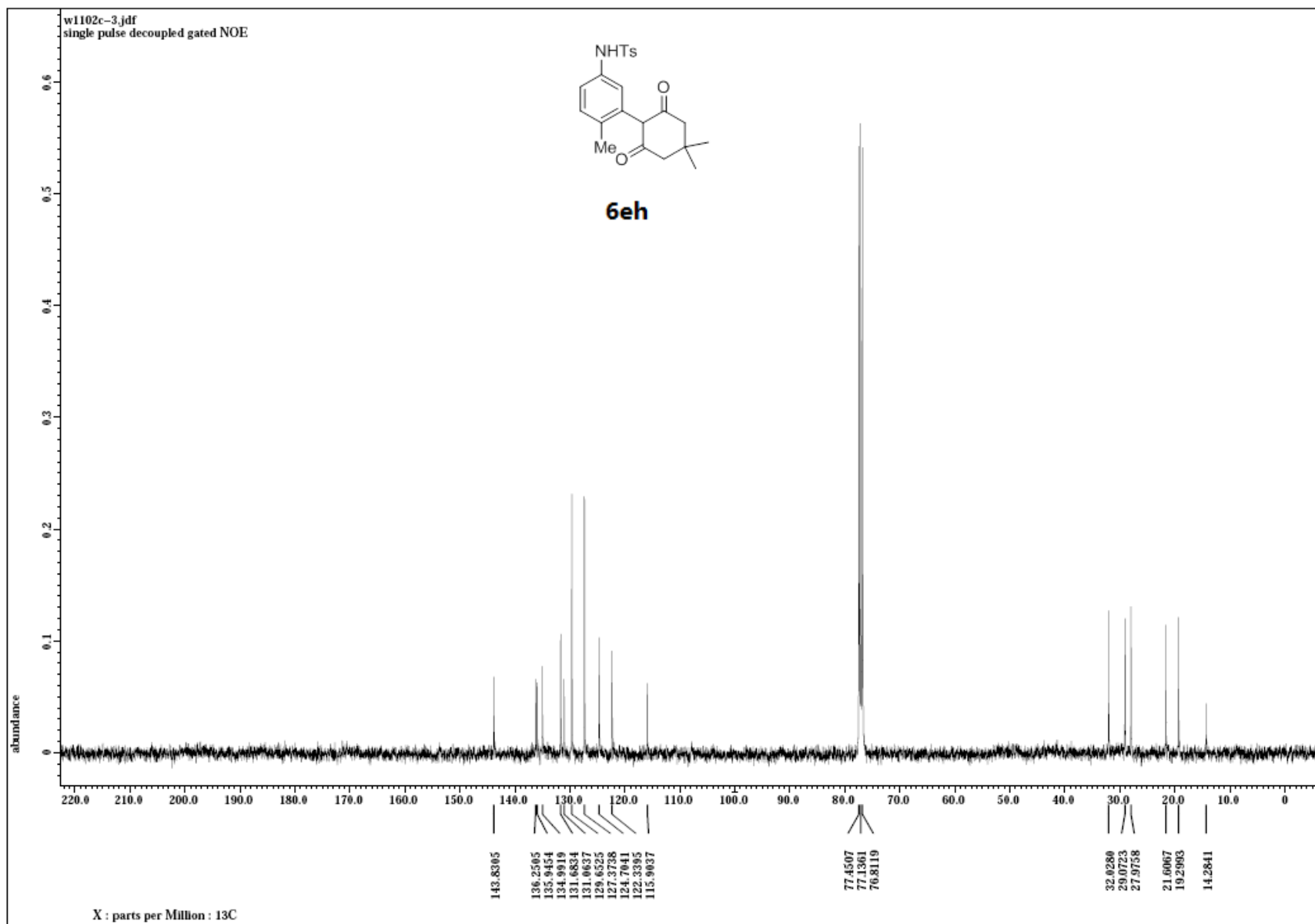


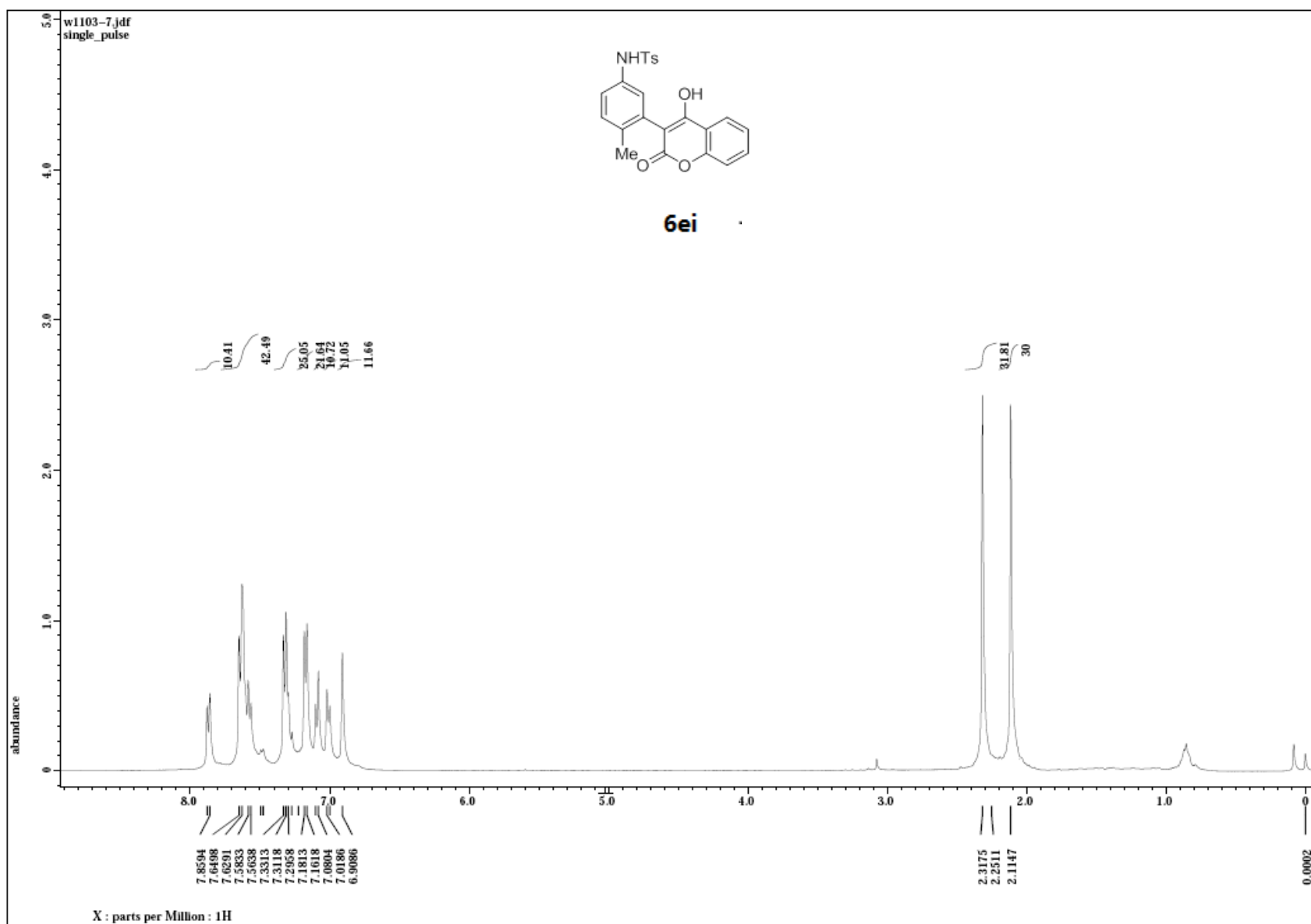


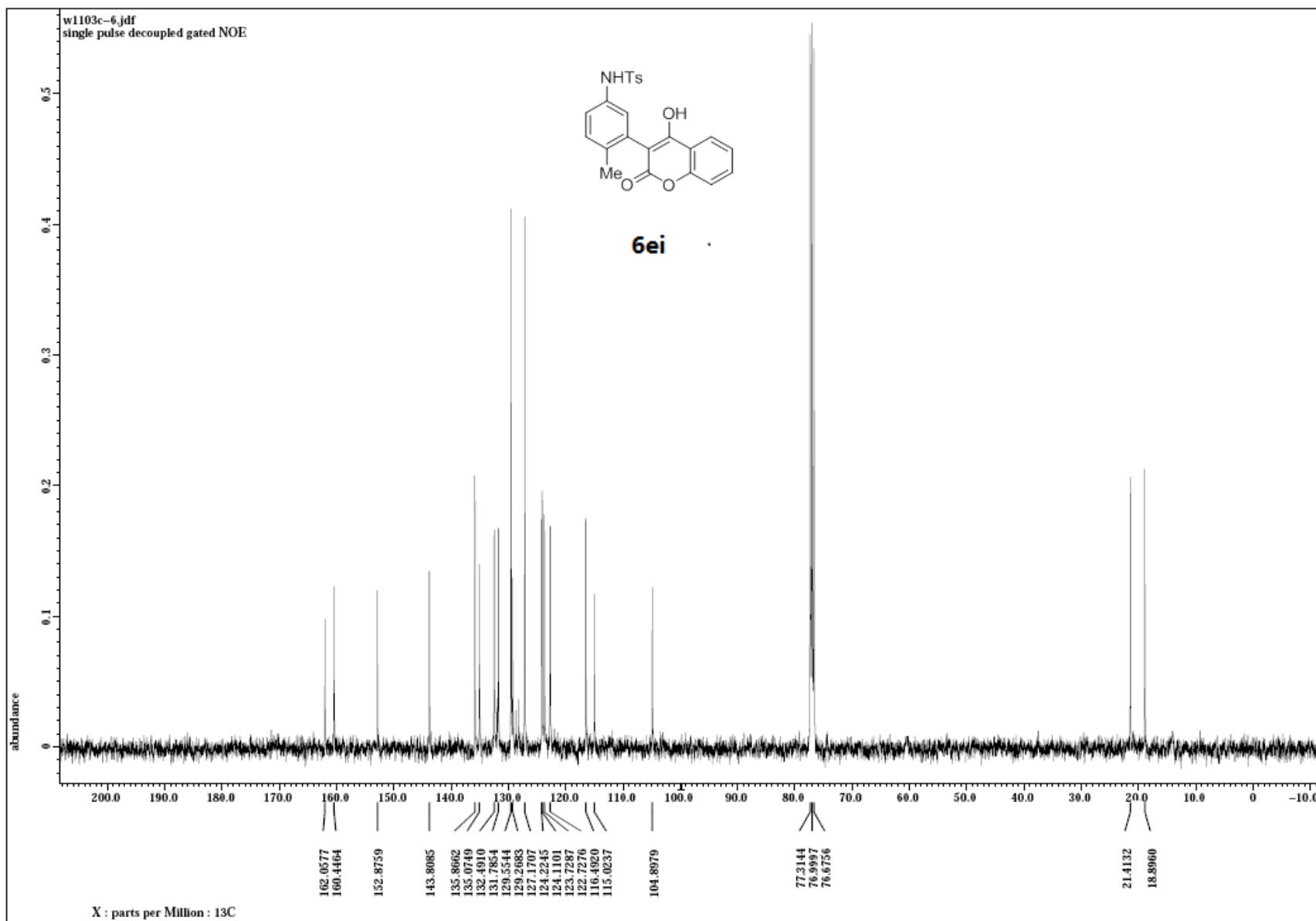


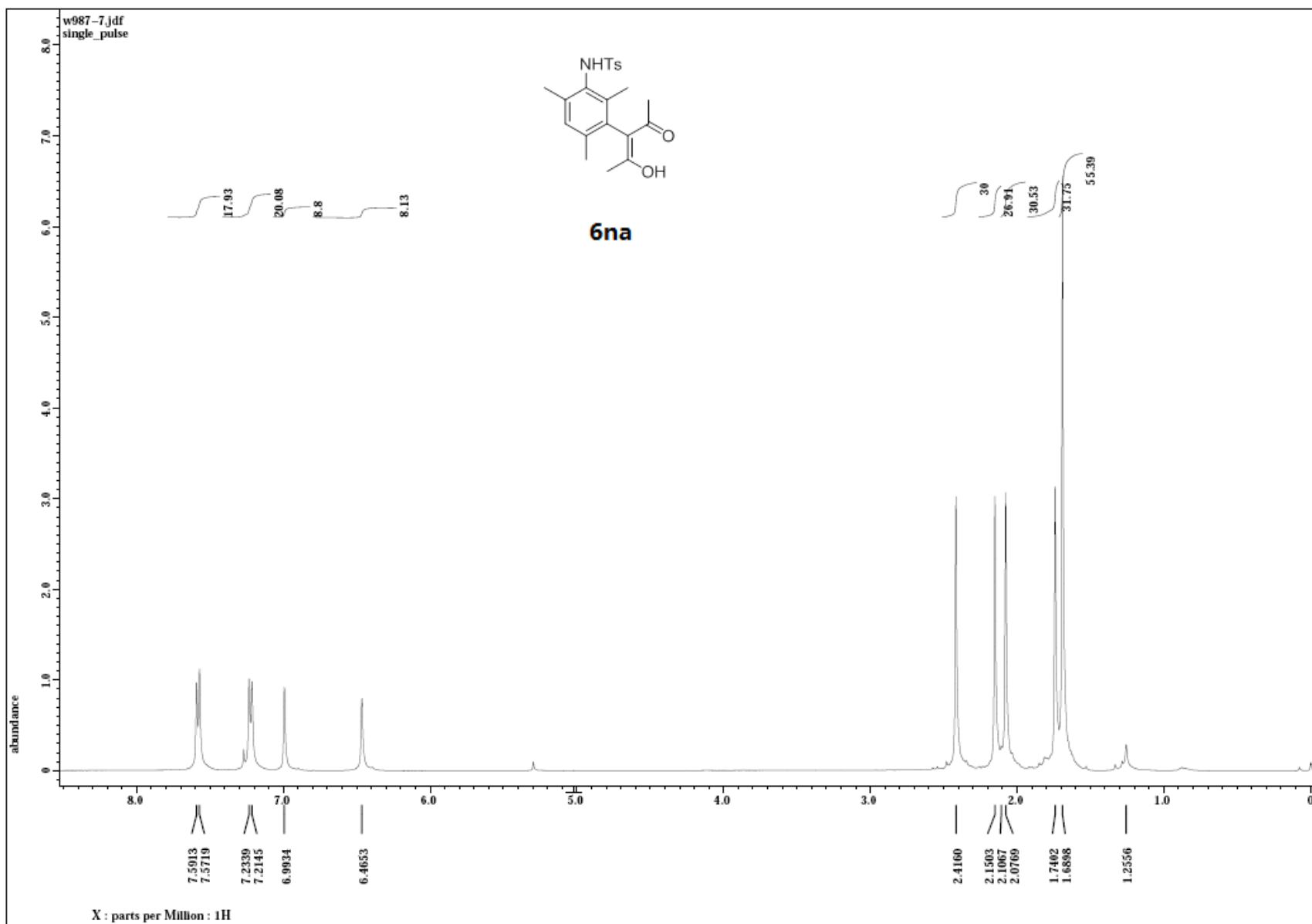


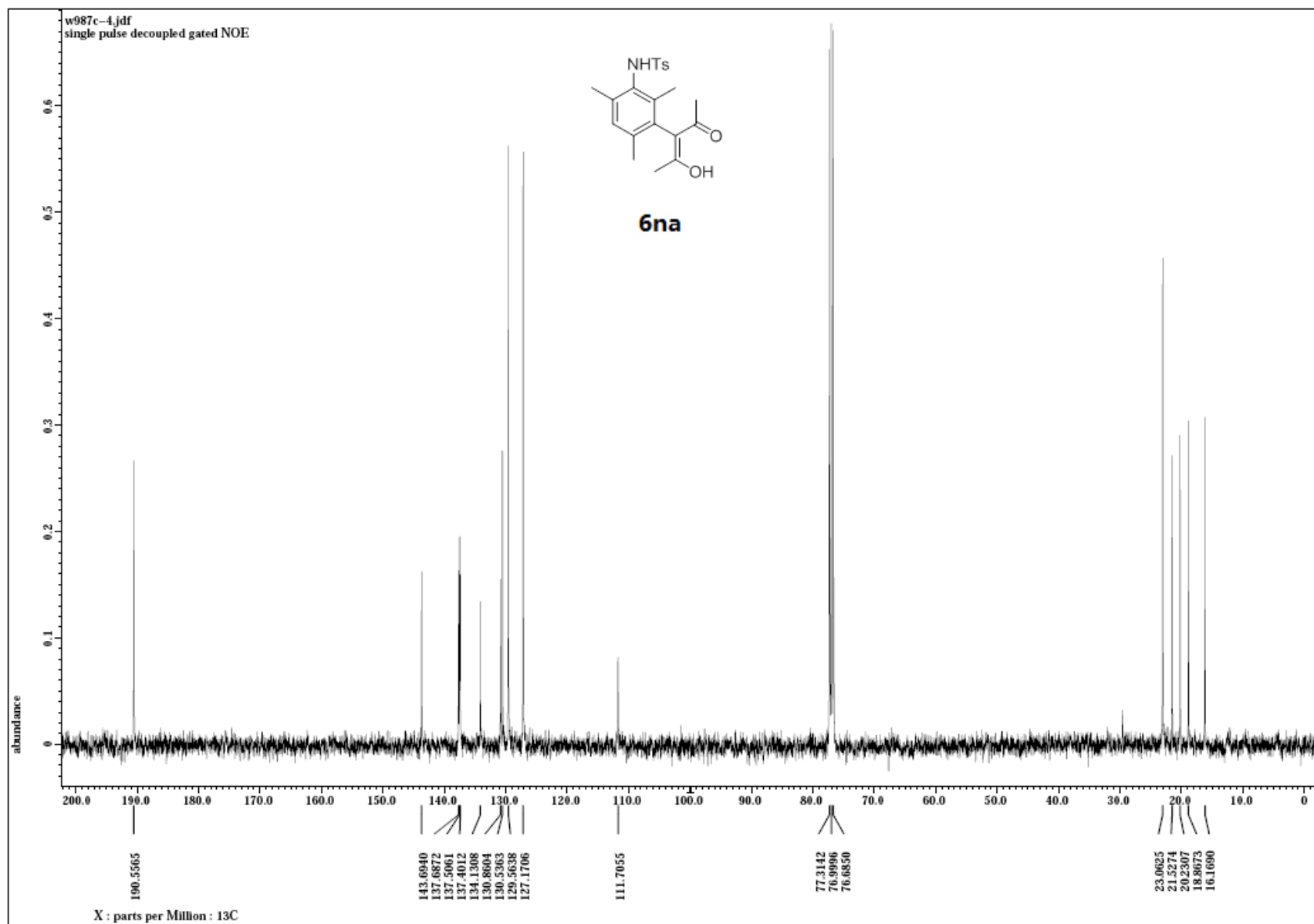


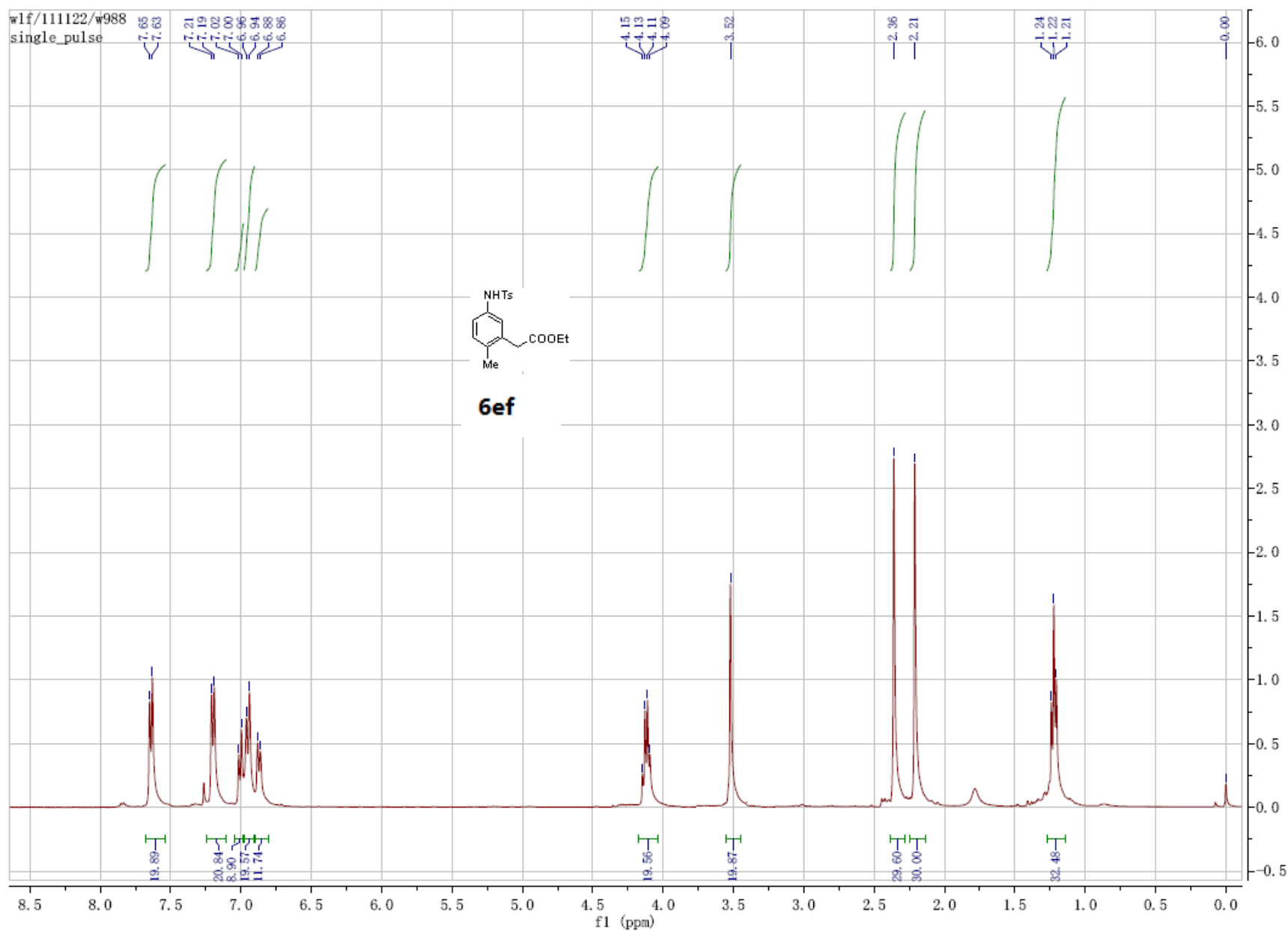


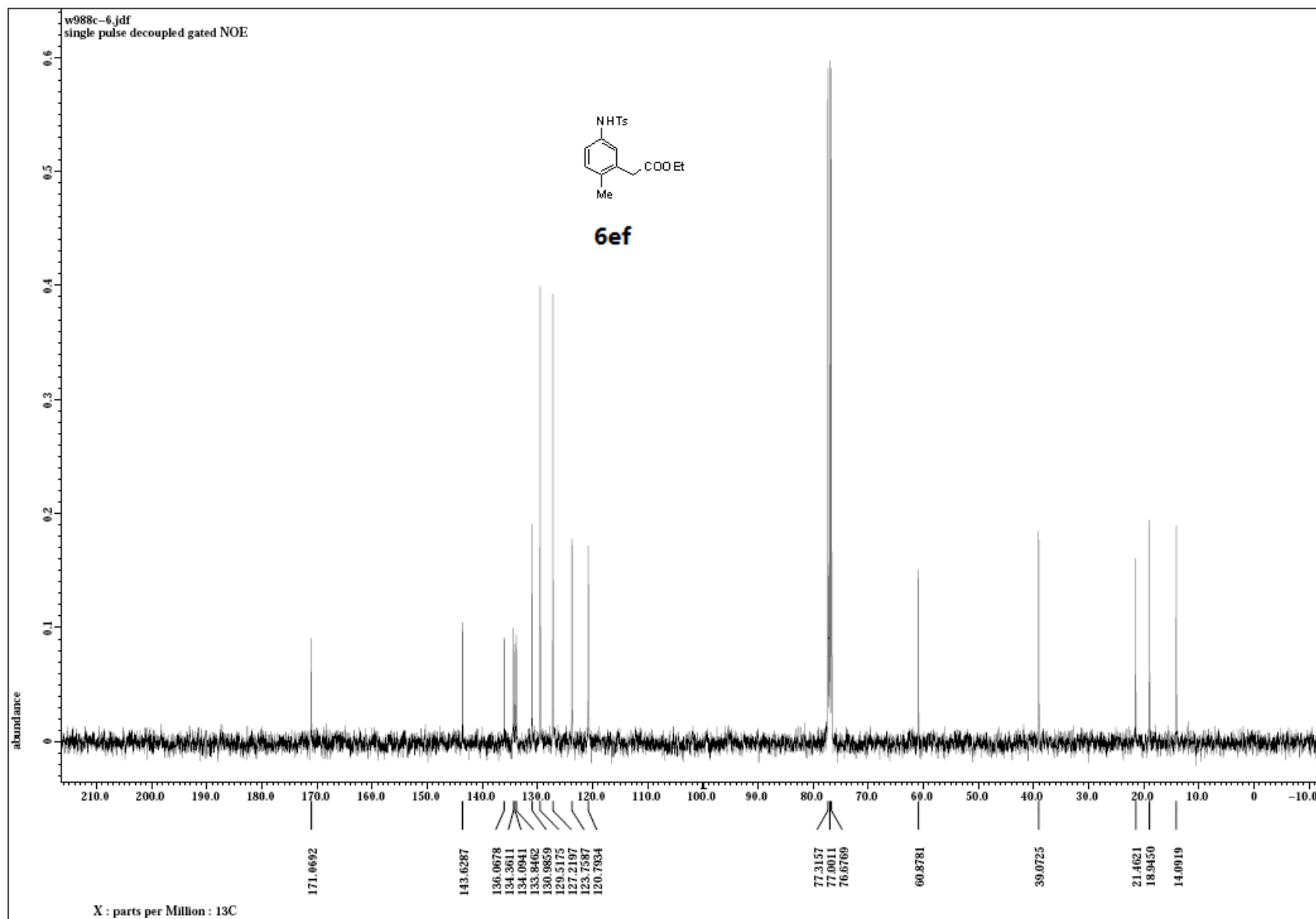


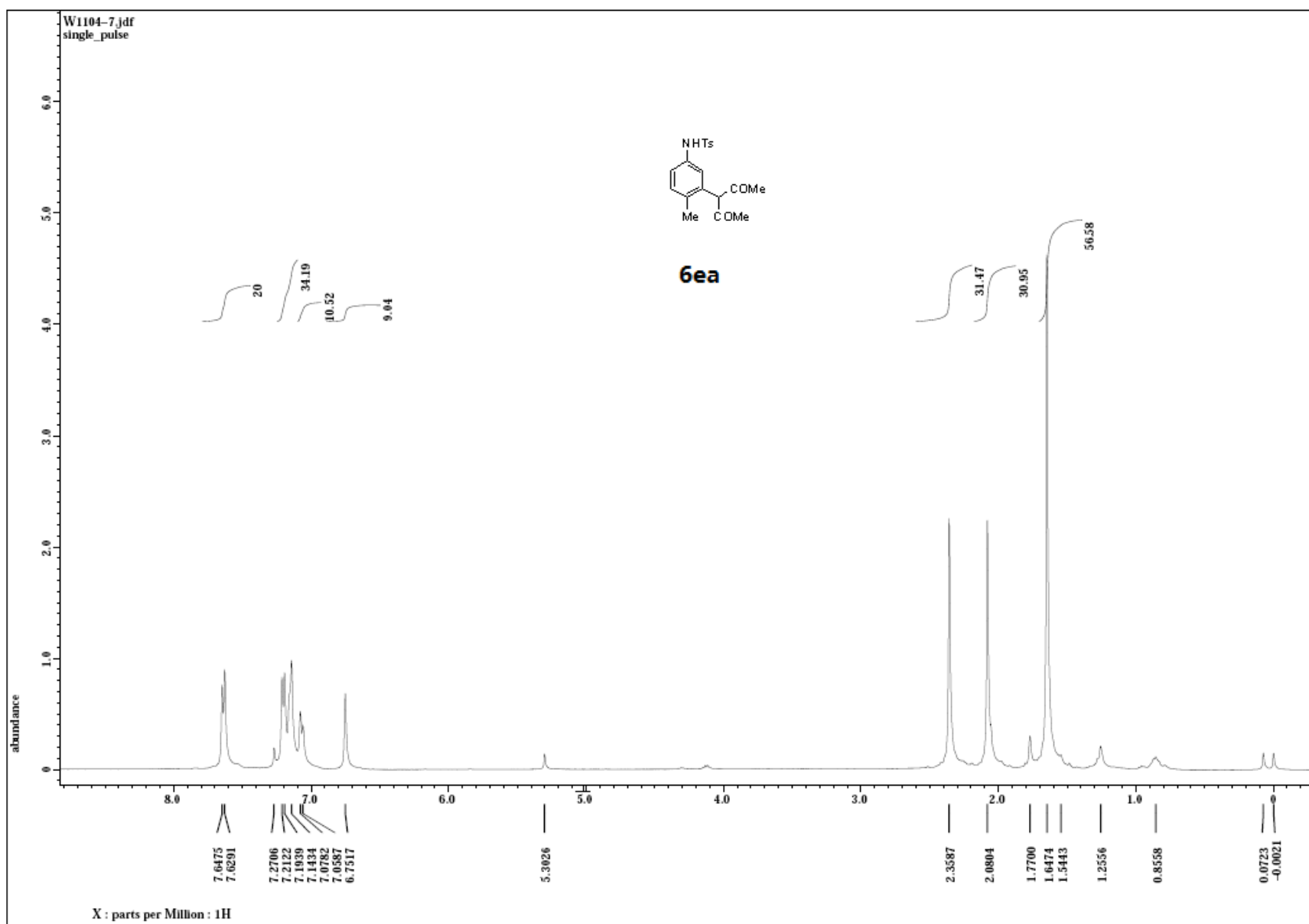


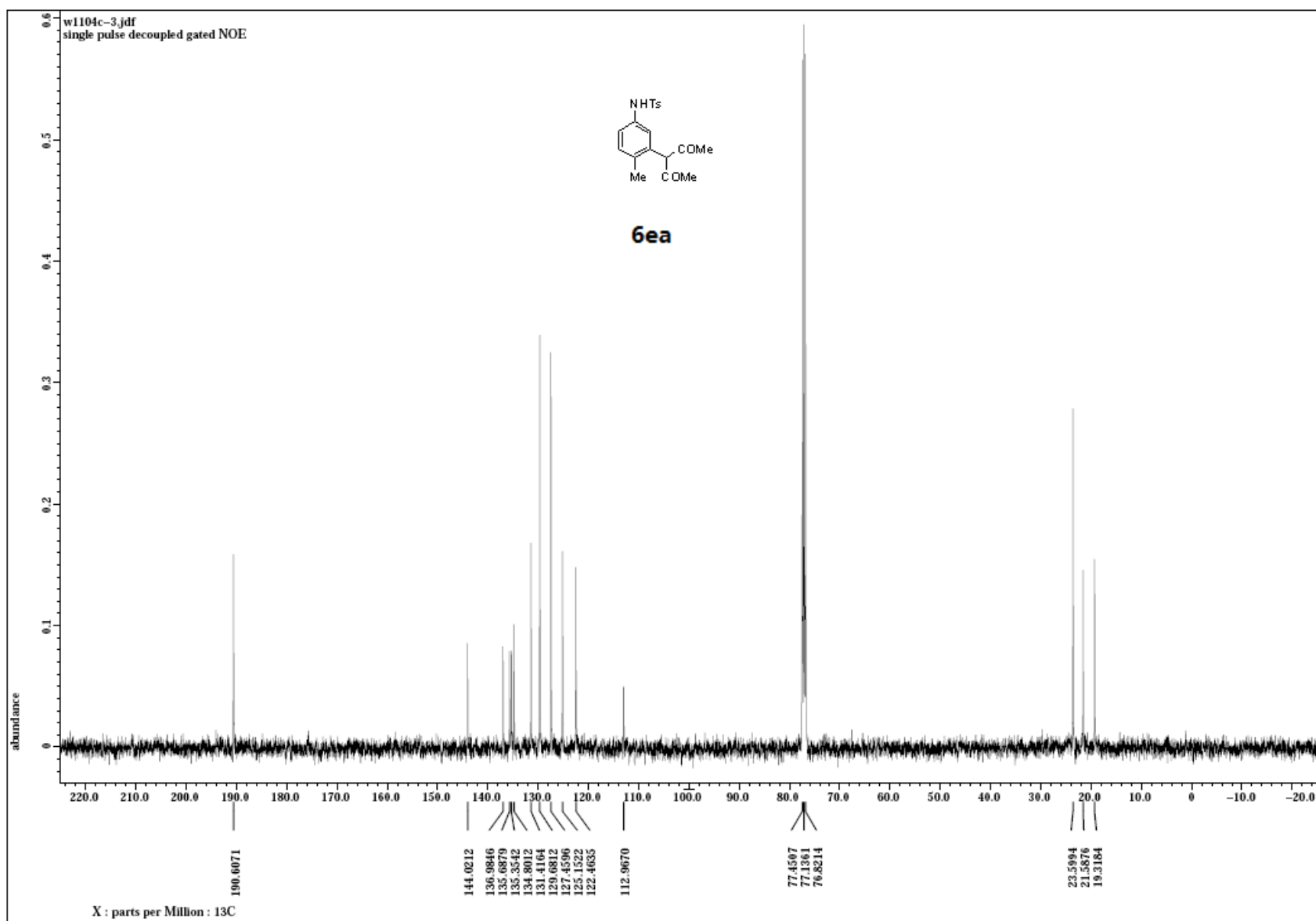




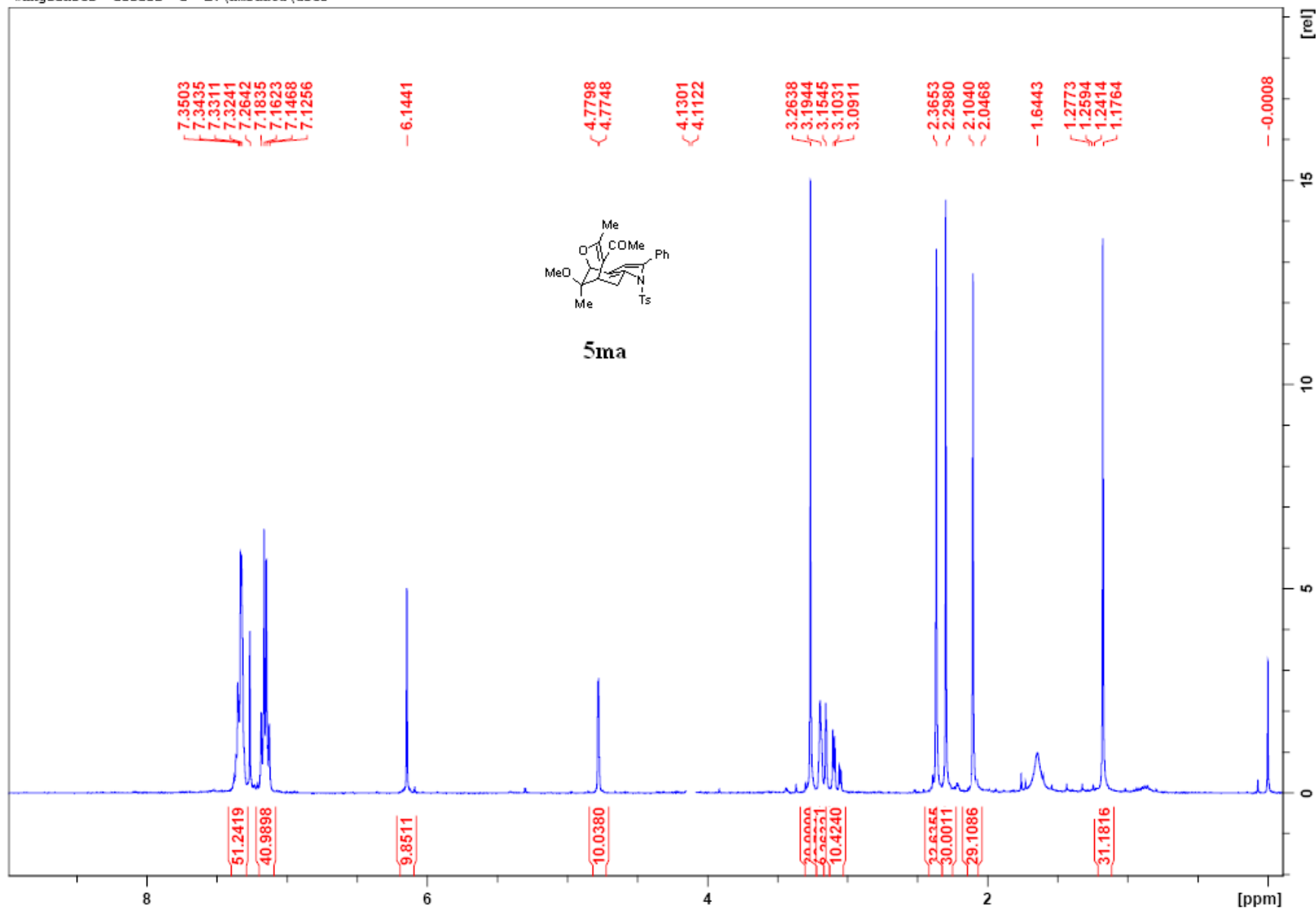








wanglinfei 121122 1 E:\nmrdata\user



wanglinfei 12112202 1 E:\nmrdata\user

