

Supporting Information

For

Ruthenium catalyzed *N*-alkylation of amino-1,3,5-triazines using alcohols

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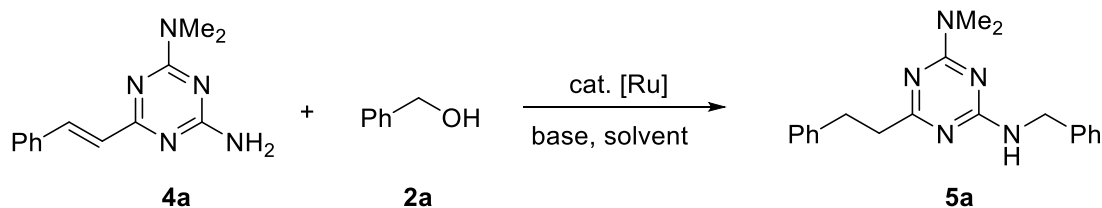
General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions were performed in a heating mantle in a sealed tube otherwise noted. Thin layer chromatography (TLC) was performed using silica gel 60 F254 and visualized using UV light. Column chromatography was performed with silica gel (mesh 300-400). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 500 MHz or 600 MHz spectrometer in CDCl₃ with Me₄Si as an internal standard. Data were reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet), coupling constant in hertz (Hz) and integration. IR spectra were recorded on an FT-IR spectrometer, and only major peaks are reported in cm⁻¹. HRMS and mass data were recorded by ESI on a TOF mass spectrometer.

General procedure for the synthesis of 3. To a Schlenk tube were added 1,3,5-triazine **1** (0.5 mmol), alcohol **2** (1.5 mmol), *t*-BuOK (1.0 mmol), dioxane (2 mL), and RuCl₂(PPh₃)₃ (0.01 mmol). The mixture was stirred at 120 °C (oil bath) under N₂. After completion, the mixture was cooled to room temperature, water was added to the mixture and extracted with EtOAc (3 x 20 mL). The organic phase was dried over anhydrous Na₂SO₄. The mixture was evaporated under vacuum, and the residue was purified by flash chromatography with petroleum ether and EtOAc as the eluent to give the pure product **3**.

General procedure for the synthesis of 4. To a Schlenk tube were added 1,3,5-triazine **4** (0.5 mmol), alcohol **2** (1.5 mmol), *t*-BuOK (1.0 mmol), dioxane (2 mL), and Ru(PPh₃)₃Cl₂ (0.015 mmol). The mixture was stirred at 120 °C (oil bath) under N₂. After completion, the mixture was cooled to room temperature, water was added to the mixture and extracted with EtOAc (3 x 20 mL). The organic phase was dried over anhydrous Na₂SO₄. The mixture was evaporated under

vacuum, and the residue was purified by flash chromatography with petroleum ether and EtOAc as the eluent to give the pure product **4**.

Table 3-SI Optimization of the reaction conditions



Entry	Catalyst	Base	Time (h)	Temp. (°C)	Solvent	Yield (%) ^a
1	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	24	120	dioxane	54
2	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	24	160	dioxane	58
3	Ru ₃ (CO) ₁₂	<i>t</i> -BuOK	24	160	dioxane	25
4	[Ru(<i>p</i> -cymene)Cl ₂] ₂	<i>t</i> -BuOK	24	160	dioxane	44
5 ^b	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	24	160	dioxane	54
6 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	160	dioxane	85
7 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	7	160	dioxane	45
8 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	120	dioxane	88
9 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	100	dioxane	25
10 ^{c,d}	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	120	dioxane	75
11 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	reflux	THF	28
12 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	120	MeCN	trace
13 ^c	RuCl ₂ (PPh ₃) ₃	<i>t</i> -BuOK	12	120	toluene	84
14 ^c	RuCl ₂ (PPh ₃) ₃	NaH	12	120	dioxane	56
15 ^c	RuCl ₂ (PPh ₃) ₃	KOH	12	120	dioxane	66

^[a] Reaction conditions: **4a** (0.5 mmol), **2a** (1.5 mmol), catalyst (2 mol%), base (1.0 mmol), solvent (2 mL), under N₂; isolated yields are shown. ^[b] **2a** (2.0 mmol). ^[c] RuCl₂(PPh₃)₃ (3 mol%). ^[d] *t*-BuOK (1.5 mmol).

N²-benzyl-N⁴,N⁴-dimethyl-1,3,5-triazine-2,4-diamine (3a)

white solid, 107.4 mg, yield: 93%; Mp: 143-144 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.01 (s, 1H), 7.34-7.31 (m, 4H), 7.29-7.26 (m, 1H), 6.00 (br, 1H), 4.61 (d, *J* = 5.2 Hz, 2H), 3.15 (s, 3H), 3.12 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.15, 164.84, 164.62, 138.93, 128.58, 127.57, 127.28, 44.63, 36.26, 36.05. IR (KBr, cm⁻¹): 3449, 3232, 1554, 1507, 1433, 1406, 1189, 1093, 813. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₂H₁₆N₅ 230.1406, found 230.1364.

N²,N²-dimethyl-N⁴-(3-methylbenzyl)-1,3,5-triazine-2,4-diamine (3b): white solid, 122.7 mg, 99%; mp: 121-123 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.97 (s, 1H), 7.23 (t, *J* = 7.5 Hz, 1H),

7.13-7.15 (m, 2H), 7.09 (s, 1H), 6.21 (br, 1H), 4.57 (d, $J = 5.2$ Hz, 2H), 3.15 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.08, 164.75, 164.56, 138.81, 138.19, 128.45, 128.34, 128.00, 124.65, 44.52, 36.24, 36.03, 21.39. IR (KBr, cm^{-1}): 3441, 3229, 1605, 1574, 1507, 1405, 1364. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{N}_5$ 244.1562, found 244.1560.

***N*²,*N*²-dimethyl-*N*⁴-(4-methylbenzyl)-1,3,5-triazine-2,4-diamine (3c)**: white solid, 122.0 mg, 99%; mp: 172-173 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.96 (s, 1H), 7.25 (d, $J = 7.8$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 6.31 (br, 1H), 4.55 (d, $J = 5.6$ Hz, 2H), 3.14 (s, 3H), 3.07 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.05, 164.73, 164.55, 136.86, 135.87, 129.21, 127.57, 44.30, 36.21, 36.04, 21.08. IR (KBr, cm^{-1}): 3448, 3236, 1587, 1558, 1508, 1403, 811. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{N}_5$ 244.1562, found 244.1555.

***N*²-(4-methoxybenzyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (3d)**: white solid, 121.7 mg, 94%; mp: 144-146 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.97 (s, 1H), 7.26 (d, $J = 8.65$ Hz, 2H), 6.86 (d, $J = 8.65$ Hz, 2H), 6.16 (br, 1H), 4.52 (d, $J = 5.4$ Hz, 2H), 3.80 (s, 3H), 3.10 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.97, 164.63, 164.52, 158.81, 131.00, 128.89, 113.90, 55.24, 43.99, 36.20, 36.02. IR (KBr, cm^{-1}): 3448, 3230, 3003, 1605, 1583, 1558, 1400, 1247, 1179, 985, 809. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{N}_5\text{O}$ 260.1511, found 260.1489.

***N*²-(4-chlorobenzyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (3e)**: white solid, 85.50 mg, 64%; mp: 142-144 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.11 (s, 1H), 7.30 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 8.6$ Hz, 2H), 6.37 (br, 1H), 4.56 (d, $J = 5.5$ Hz, 2H), 3.14 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.00, 164.71, 164.45, 137.57, 132.90, 128.82, 128.63, 43.87, 36.27, 36.05. IR (KBr, cm^{-1}): 3454, 3228, 1582, 1551, 1503, 1403, 985, 808. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{15}\text{ClN}_5$ 264.1016, found 264.1019.

***N*²-(4-fluorobenzyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (3f)**: yellow solid, 67.60 mg, 54%; mp: 149-150 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.33-7.28 (m, 2H), 7.02-6.98 (m, 2H), 6.55 (br, 1H), 4.55 (d, $J = 5.3$ Hz, 2H), 3.14 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.96, 164.68, 164.49, 162.01 (d, $J = 243.3$ Hz), 134.76, 129.17 (d, $J = 7.9$ Hz), 115.33 (d, $J = 21.3$ Hz), 43.84, 36.24, 36.01. IR (KBr, cm^{-1}): 3456, 3225, 1597, 1582, 1505, 1406, 1222, 814. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{15}\text{FN}_5$ 248.1311, found 248.1328.

***N*²,*N*²-dimethyl-*N*⁴-(3-(trifluoromethyl)benzyl)-1,3,5-triazine-2,4-diamine (3g)**: white solid, 136.5 mg, 91%; mp: 108-112 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.61 (s, 1H), 7.52 (d,

$J = 7.6$ Hz, 2H), 7.47-7.41 (m, 1H), 6.63 (br, 1H), 4.60-4.79 (m, 2H), 3.14 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.18, 164.92, 164.57, 140.19, 130.80, 130.79, 129.01(q, $J = 3.5$ Hz), 124.43 (q, $J = 33.4$ Hz), 124.11 (q, $J = 270.5$ Hz), 124.08 (q, $J = 4.1$ Hz), 37.58, 36.23, 36.02. IR (KBr, cm^{-1}): 3451, 3255, 1613, 1581, 1558, 1505, 1402, 1110, 809. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{N}_5$ 298.1280, found 298.1251.

***N*²-(furan-2-ylmethyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (3h)**: white solid, 49.30 mg, 45%; mp: 138-139 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.00 (s, 1H), 7.36 (d, $J = 1.9$ Hz, 1H), 6.53 (br, 1H), 6.32 (dd, $J = 3.0, 1.9$ Hz, 1H), 6.24 (d, $J = 3.0$ Hz, 1H), 4.59 (d, $J = 5.0$ Hz, 2H), 3.15 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.52, 165.00, 164.46, 152.06, 142.01, 110.33, 107.05, 37.58, 36.23, 36.02; IR (KBr, cm^{-1}): 3460, 3238, 1587, 1499, 1434, 1406, 1334, 812. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}$ 220.1198, found 220.1203.

***N*²,*N*²-dimethyl-*N*⁴-(thiophen-2-ylmethyl)-1,3,5-triazine-2,4-diamine (3i)**: yellow solid, 86.00 mg, 73%; mp: 145-147 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.94 (s, 1H), 7.21 (dd, $J = 5.1, 1.1$ Hz, 1H), 7.00 (dd, $J = 3.5, 1.1$ Hz, 1H), 6.95 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.65 (br, 1H), 4.75 (d, $J = 5.4$ Hz, 2H), 3.12 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.08, 164.49, 164.44, 141.82, 126.67, 125.64, 124.94, 39.37, 36.28, 36.13. IR (KBr, cm^{-1}): 3465, 3233, 1602, 1578, 1504, 1432, 1190, 812, 707. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{N}_5\text{S}$ 236.0970, found 236.0994.

***N*²,*N*²-dimethyl-*N*⁴-(pyridin-3-ylmethyl)-1,3,5-triazine-2,4-diamine (3j)**: yellow solid, 89.70 mg, 77%; mp: 156-158 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.60 (s, 1H), 8.50 (d, $J = 4.8$ Hz, 1H), 7.95 (s, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.24 (dd, $J = 7.8, 4.8$ Hz, 1H), 6.76 (br, 1H), 4.66-4.50 (m, 2H), 3.13 (s, 3H), 3.07 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.90, 164.68, 164.41, 149.24, 148.63, 135.14, 134.60, 123.41, 42.11, 36.25, 36.04. IR (KBr, cm^{-1}): 3465, 3245, 1616, 1584, 1557, 1402, 1371, 810. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{15}\text{N}_6$ 231.1358, found 231.1321.

***N*-benzyl-4-morpholino-1,3,5-triazin-2-amine (3k)**: white solid, 130.3 mg, 95%; mp: 149-150 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.37-7.31 (m, 4H), 7.30-7.29 (m, 1H), 6.07 (br, 1H), 4.58 (d, $J = 4.4$ Hz, 2H), 3.80 (t, $J = 4.9$ Hz, 4H), 3.71 (t, $J = 4.9$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.34, 164.94, 164.05, 138.60, 128.60, 127.56, 127.36, 66.67, 44.64, 43.38. IR (KBr, cm^{-1}): 3448, 3235, 2860, 1576, 1532, 1495, 1431, 1227, 1111, 814. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{N}_5\text{O}$ 272.1511, found 272.1501.

***N*²-benzyl-*N*⁴,*N*⁴-dimethyl-6-propyl-1,3,5-triazine-2,4-diamine (3l)**: white solid, 115.7 mg,

86%; mp: 82-84 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.30 (m, 4H), 7.29-7.23 (m, 1H), 5.68 (br, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 3.16 (s, 3H), 3.12 (s, 3H), 2.53-2.38 (m, 2H), 1.75 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 177.70, 165.64, 165.38, 139.36, 128.44, 127.48, 127.07, 44.60, 40.88, 35.99, 20.96, 13.99. IR (KBr, cm⁻¹): 3250, 2962, 1609, 1555, 1509, 1405, 1355, 1208. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₅H₂₂N₅ 272.1875, found 272.1894.

***N*²-benzyl-*N*⁴,*N*⁴-dimethyl-6-phenyl-1,3,5-triazine-2,4-diamine (3m)**: white solid, 149.6 mg, 96%; mp: 96-97 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.46-8.38 (m, 2H), 7.51-7.43 (m, 3H), 7.37-7.32 (m, 4H), 7.29-7.26 (m, 1H), 5.71 (br, 1H), 4.80-4.68 (m, 1H), 3.31 (s, 3H), 3.19 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.33, 166.18, 165.73, 139.33, 137.46, 131.04, 128.49, 128.17, 128.10, 127.63, 127.13, 44.80, 36.12. IR (KBr, cm⁻¹): 3471, 3275, 2915, 1596, 1539, 1505, 1405, 981, 704. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₈H₂₀N₅ 306.1719, found 306.1718.

***N*²-benzyl-6-(3-methoxyphenyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (3n)**: white solid, 155.0 mg, 93%; mp: 105-107 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.94-7.98 (m, 2H), 7.42-7.31 (m, 5H), 7.29-7.26 (m, 1H), 7.04 (t, *J* = 8.1 Hz, 1H), 5.58 (br, 1H), 4.78-4.68 (m, 2H), 3.89 (s, 3H), 3.30 (s, 3H), 3.19 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.17, 165.73, 159.54, 139.35, 138.96, 129.12, 128.53, 127.66, 127.19, 120.72, 117.29, 112.87, 55.32, 44.84, 36.13. IR (KBr, cm⁻¹): 3264, 2913, 1602, 1541, 1507, 1406, 1046, 789. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₉H₂₂N₅O 336.1824, found 336.1852.

***N*-benzyl-4,6-diphenyl-1,3,5-triazin-2-amine (3o)**: yellow oil, 143.9 mg, 85%; ¹H NMR (500 MHz, CDCl₃) δ 8.67 (d, *J* = 7.2 Hz, 2H), 8.60 (d, *J* = 7.2 Hz, 2H), 7.63-7.53 (m, 6H), 7.41-7.40 (m, 2H), 7.39-7.34 (m, 2H), 7.34-7.28 (m, 1H), 6.21 (t, *J* = 5.9 Hz, 1H), 4.85 (d, *J* = 6.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 171.57, 171.33, 166.52, 138.56, 136.74, 136.54, 131.95, 131.86, 128.78, 128.72, 128.58, 128.38, 127.73, 127.52, 45.07. IR (KBr, cm⁻¹): 3421, 1590, 1536, 1495, 1416, 771. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₁₉N₄ 339.1610, found 339.1616.

***N*²-benzyl-*N*⁴,*N*⁴-dimethyl-6-phenethyl-1,3,5-triazine-2,4-diamine (5a)**: white solid, 148.0 mg, 88%; mp: 85-86 °C (lit.¹ 88-89 °C); ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.30 (m, 4H), 7.30-7.24 (m, 5H), 7.23-7.17 (m, 1H), 5.70 (br, 1H), 4.64 (d, *J* = 5.0 Hz, 2H), 3.19 (s, 3H), 3.13 (s, 3H), 3.11-3.02 (m, 2H), 2.98-2.74 (m, 2H).

***N*²,*N*²-dimethyl-*N*⁴-(4-methylbenzyl)-6-phenethyl-1,3,5-triazine-2,4-diamine (5b)**: white solid, 148.3 mg, 84%; mp: 102-103 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.26 (m, 4H), 7.24 (d, *J* =

7.9 Hz, 2H), 7.22-7.17 (m, 1H), 7.15 (d, $J = 7.9$ Hz, 2H), 5.55 (br, 1H), 4.59 (d, $J = 5.0$ Hz, 2H), 3.16 (s, 6H), 3.11-3.01 (m, 2H), 2.91-2.77 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.70, 165.58, 165.38, 141.98, 136.74, 136.20, 129.15, 128.44, 128.24, 127.54, 125.73, 44.41, 40.25, 36.01, 33.34, 21.07. IR (KBr, cm^{-1}): 3447, 3257, 1624, 1560, 1513, 1398, 1012, 810. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{N}_5$ 348.2188, found 348.2191.

***N*²-(4-methoxybenzyl)-*N*⁴,*N*⁴-dimethyl-6-phenethyl-1,3,5-triazine-2,4-diamine (5c)**: white solid, 152.1 mg, 83%; mp: 101-103 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.31-7.26 (m, 6H), 7.22-7.17 (m, 1H), 6.89-6.85 (m, 2H), 5.46 (br, 1H), 4.55 (d, $J = 5.0$ Hz, 2H), 3.81 (s, 3H), 3.17 (s, 6H), 3.11-2.99 (m, 2H), 2.87-2.74 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.57, 165.55, 165.40, 158.82, 142.00, 131.34, 128.90, 128.45, 128.26, 125.75, 113.91, 55.28, 44.16, 40.27, 36.04, 33.37. IR (KBr, cm^{-1}): 3462, 3250, 1617, 1556, 1509, 1400, 1246, 810. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{N}_5\text{O}$ 364.2137, found 364.2128.

***N*²-(4-bromobenzyl)-*N*⁴,*N*⁴-dimethyl-6-phenethyl-1,3,5-triazine-2,4-diamine (5d)**: white solid, 173.6 mg, 84%; mp: 148-149 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 8.4$ Hz, 2H), 7.31-7.23 (m, 4H), 7.23-7.15 (m, 3H), 5.62 (br, 1H), 4.57 (d, $J = 4.9$ Hz, 2H), 3.17 (s, 3H), 3.09 (s, 3H), 3.07-3.05 (m, 2H), 2.88-2.76 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.86, 165.57, 165.33, 141.91, 138.45, 131.54, 129.20, 128.44, 128.28, 125.79, 120.90, 44.05, 40.22, 36.05, 33.30. IR (KBr, cm^{-1}): 3249, 2917, 1609, 1557, 1506, 1399, 1009, 813. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{BrN}_5$ 412.1137, found 412.1139.

***N*²-benzyl-6-(4-methoxyphenethyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (5e)**: white solid, 134.7 mg, 74%; mp: 124-126 °C (lit.¹ 113-115-89 °C); ^1H NMR (600 MHz, CDCl_3) δ 7.38-7.30 (m, 4H), 7.28-7.21 (m, 1H), 7.17 (d, $J = 8.5$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 5.35 (br, 1H), 4.62 (d, $J = 4.0$ Hz, 2H), 3.78 (s, 3H), 3.16 (s, 3H), 3.11 (s, 3H), 2.99 (t, $J = 7.9$ Hz, 2H), 2.83-2.65 (m, 2H).

***N*²-benzyl-6-(4-chlorophenethyl)-*N*⁴,*N*⁴-dimethyl-1,3,5-triazine-2,4-diamine (5f)**: white solid; 164.2 mg, 89%; mp: 104-105 °C (lit.¹ 109-110 °C); ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.30 (m 4H), 7.30-7.26 (m, 1H), 7.23 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 5.50 (br, 1H), 4.62 (d, $J = 5.4$ Hz, 2H), 3.16 (s, 3H), 3.13 (s, 3H), 3.04 (t, $J = 7.2$ Hz, 2H), 2.92-2.64 (m, 2H).

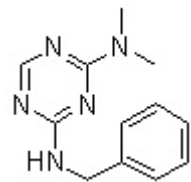
(trifluoromethyl)phenethyl)-1,3,5-triazine-2,4-diamine (5g): white solid, 148.4 mg, 74%; mp: 93-94 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.63 (s, $J = 7.9$ Hz, 1H), 7.47-7.42 (m, 1H), 7.40 (s, $J =$

7.5 Hz, 1H), 7.37-7.30 (m, 4H), 7.30-7.24 (m, 2H), 5.66 (br, 1H), 4.64 (d, $J = 5.9$ Hz, 1H), 3.33-3.22 (m, 2H), 3.15 (s, 6H), 2.94-2.76 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.20, 165.61, 165.32, 140.78, 139.27, 131.68, 130.78, 128.48 (q, $J = 38.5$ Hz), 128.45 (q, $J = 6.1$ Hz), 128.36, 127.74 (q, $J = 259.5$ Hz), 127.63, 127.14, 125.82 (q, $J = 5.7$ Hz), 44.65, 39.75, 36.07, 35.98, 29.60. IR (KBr, cm^{-1}): 3446, 3259, 2945, 1603, 1557, 1515, 1408, 1117. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{N}_5$ 402.1906, found 402.1915.

Ref.

1) Su, C. W.; Zeng, M.; Zhang, C.; Cui, D.-M. *Eur. J. Org. Chem.* **2020**, 4942-4949.

xzp180829-86 CDC13 0831



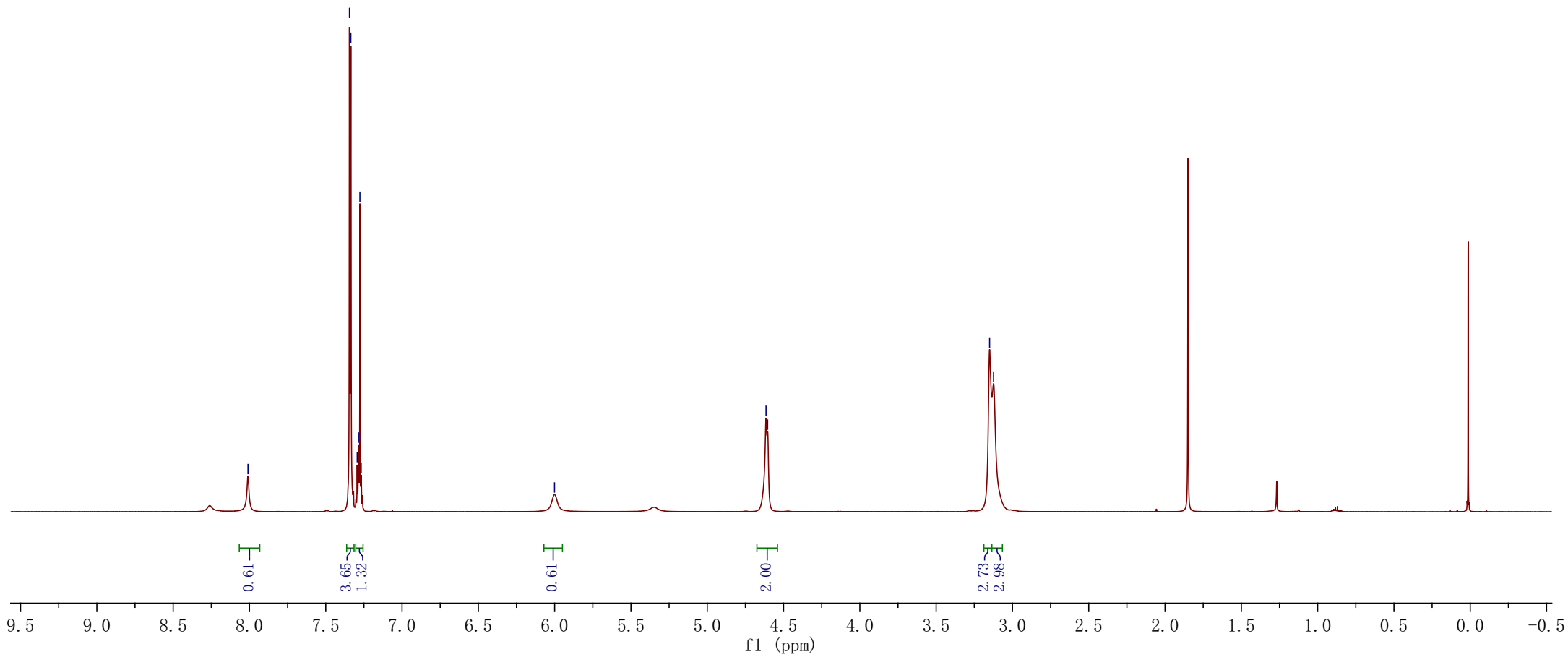
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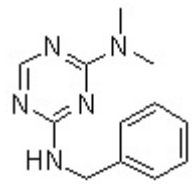
6.0008

4.6148
4.6014

3.1496
3.1236



180903
XZP-180829-86 0903



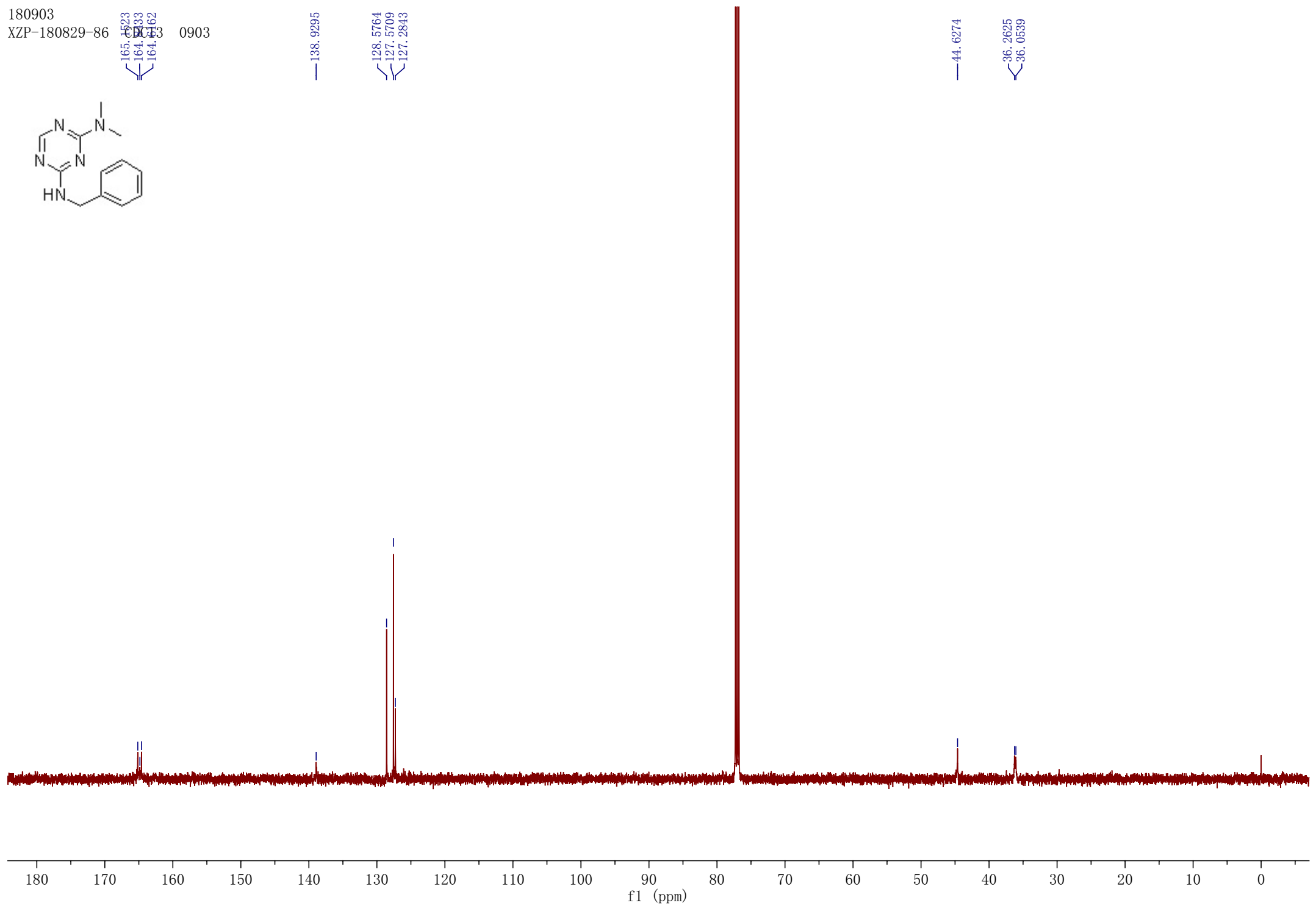
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181126
xzq181114-152

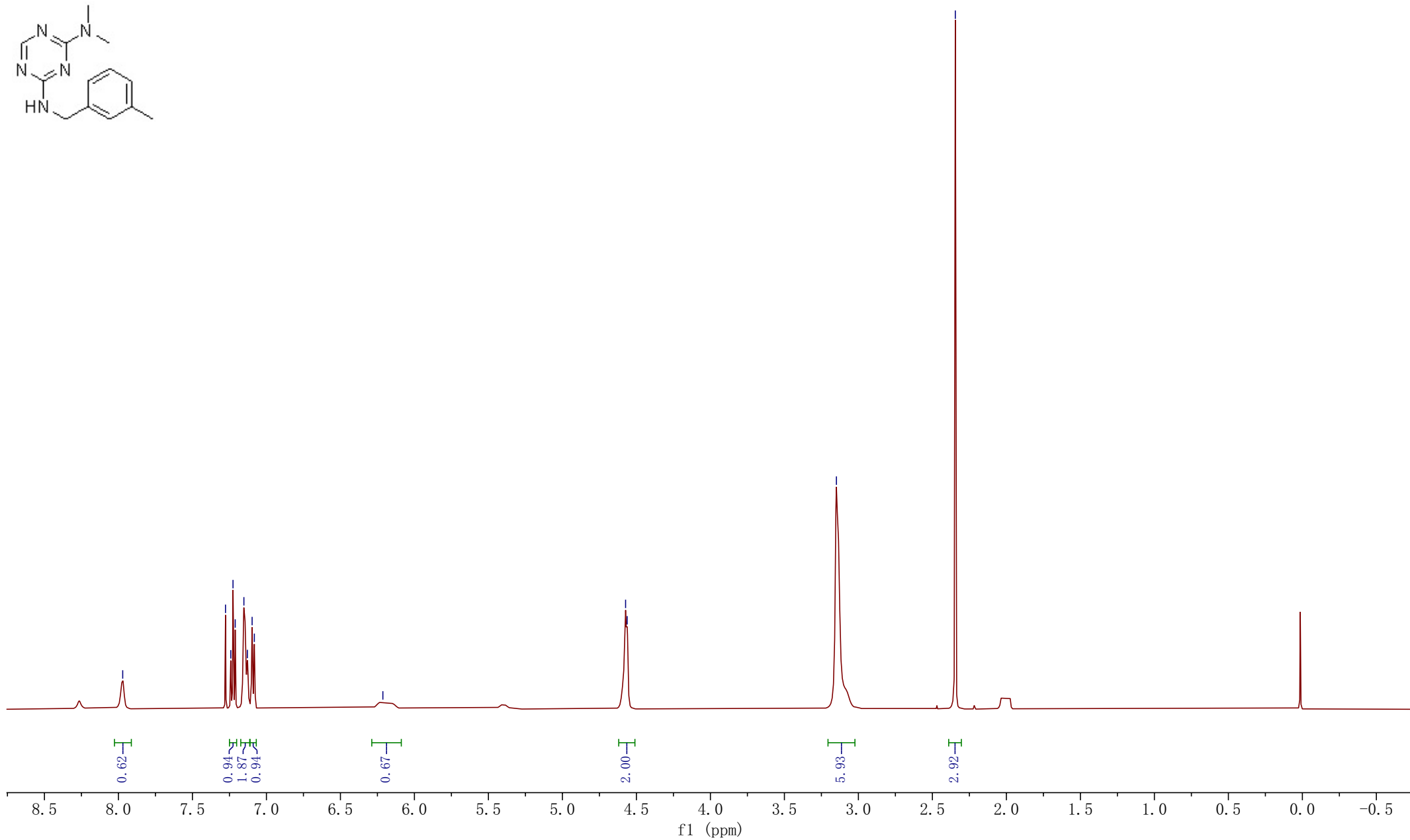
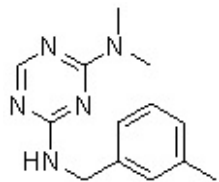
CDC13

6.2131

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3.1486

2.3451



181210
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CDC13 1210

165.801
164.7509
164.5687

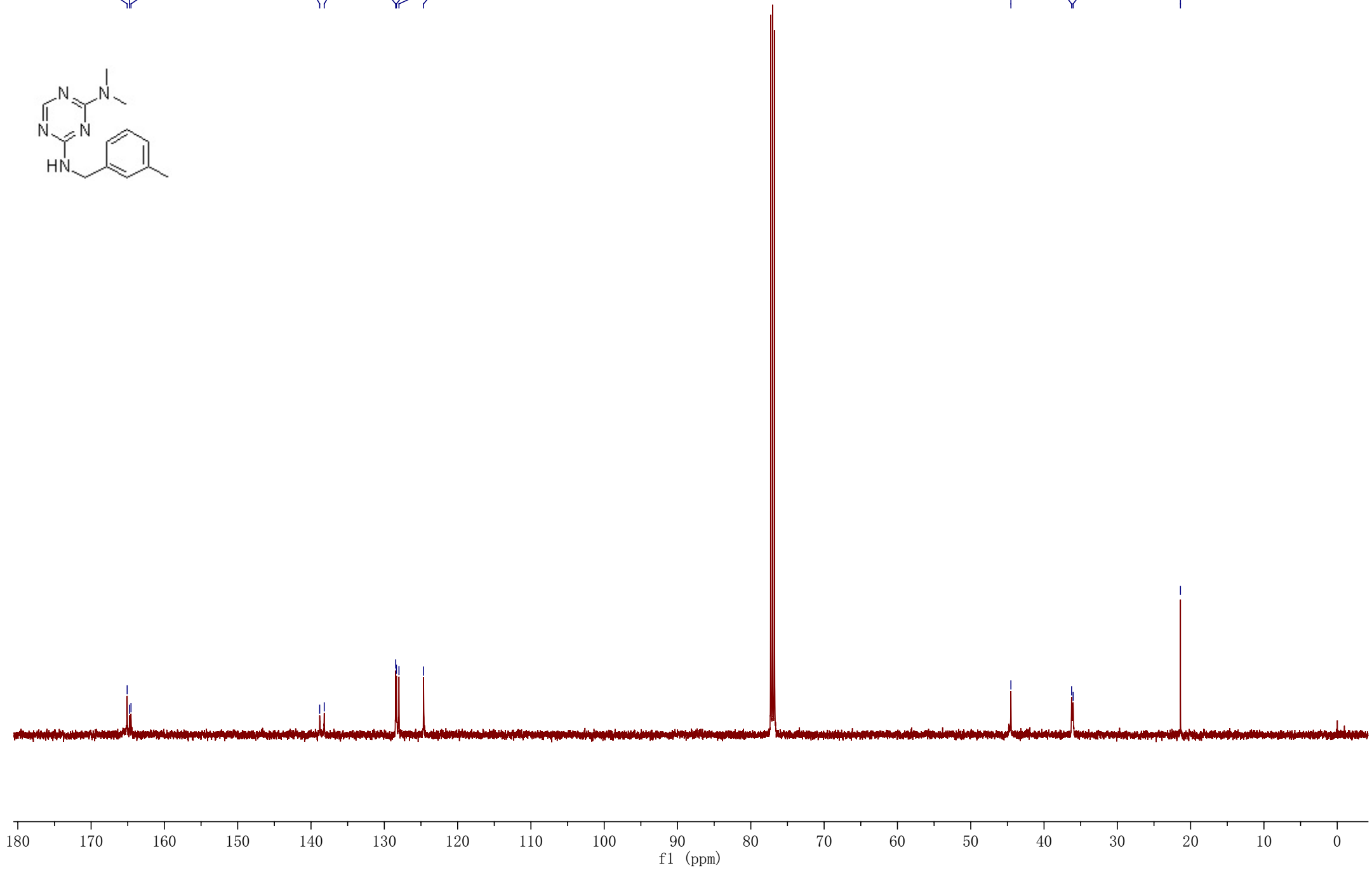
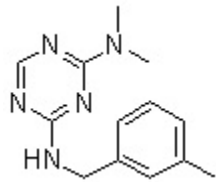
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36.0331

21.3900



190102
xzp181127-161 CDC 23 0102

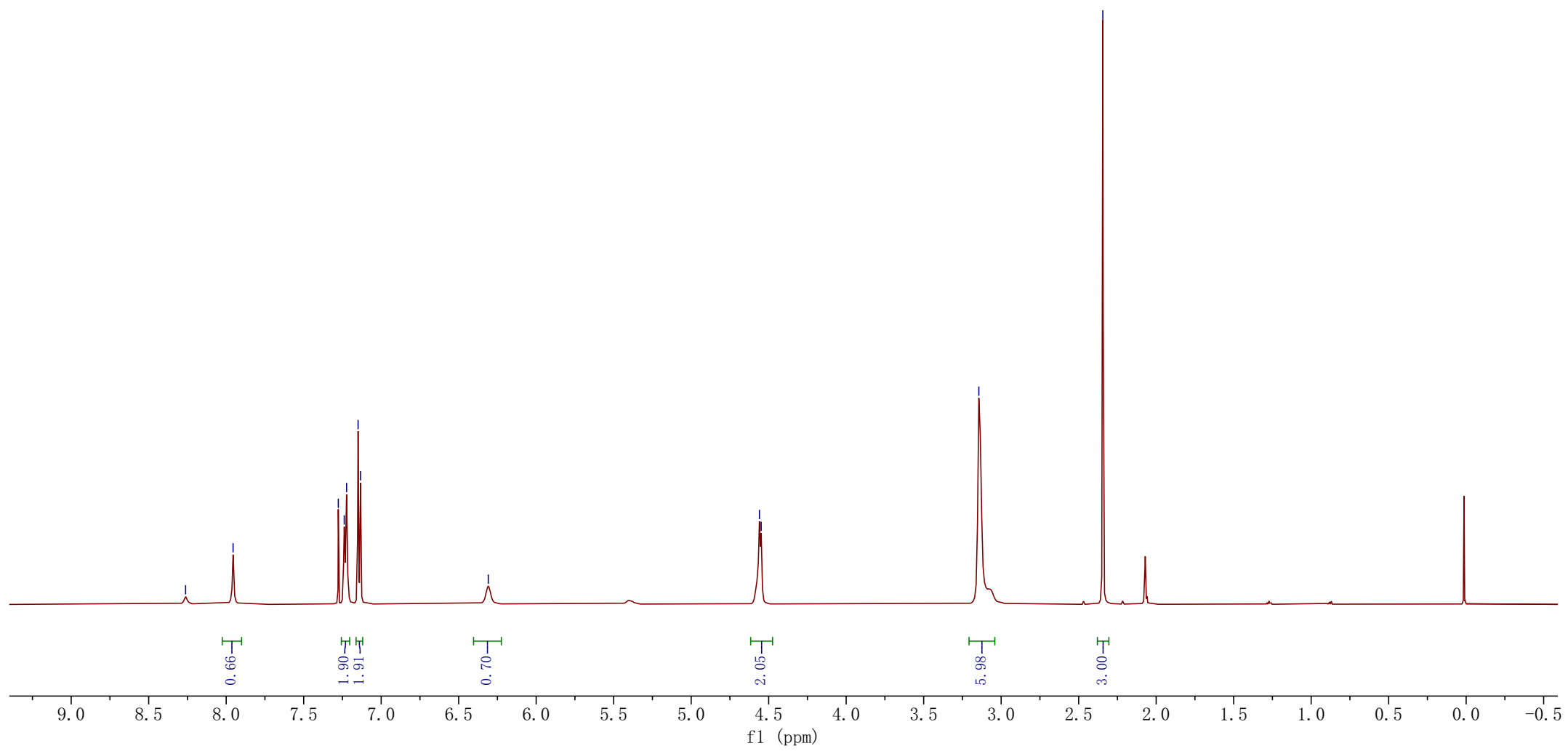
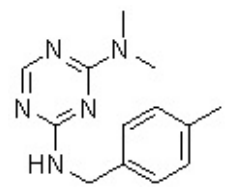
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7.2230
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7.1332

6.3091

4.5595
4.5184

3.1440

2.3441



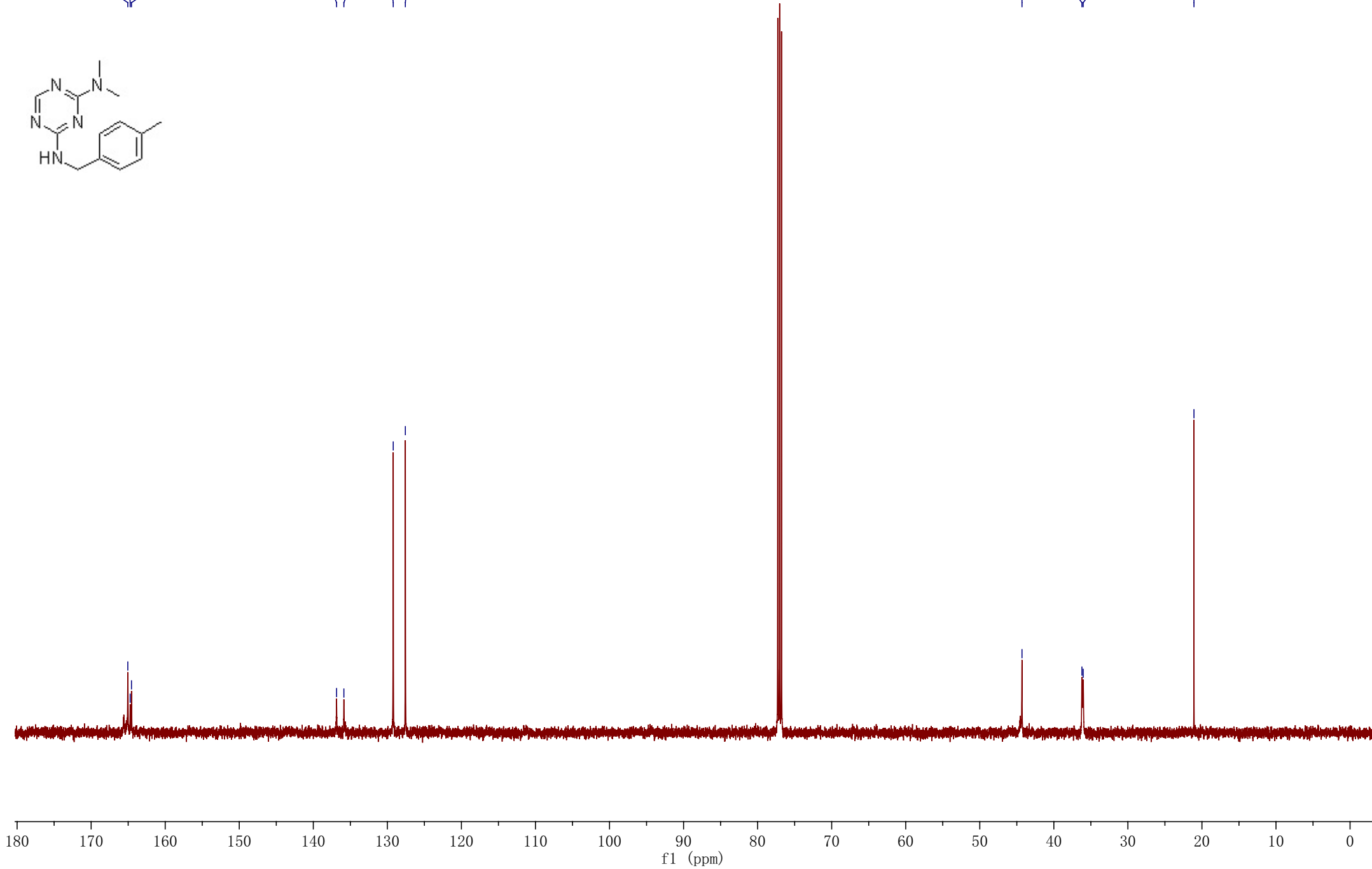
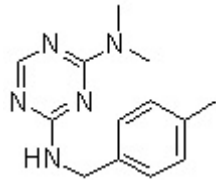
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130.13
0115

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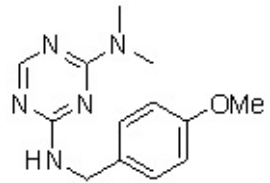
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36.2084
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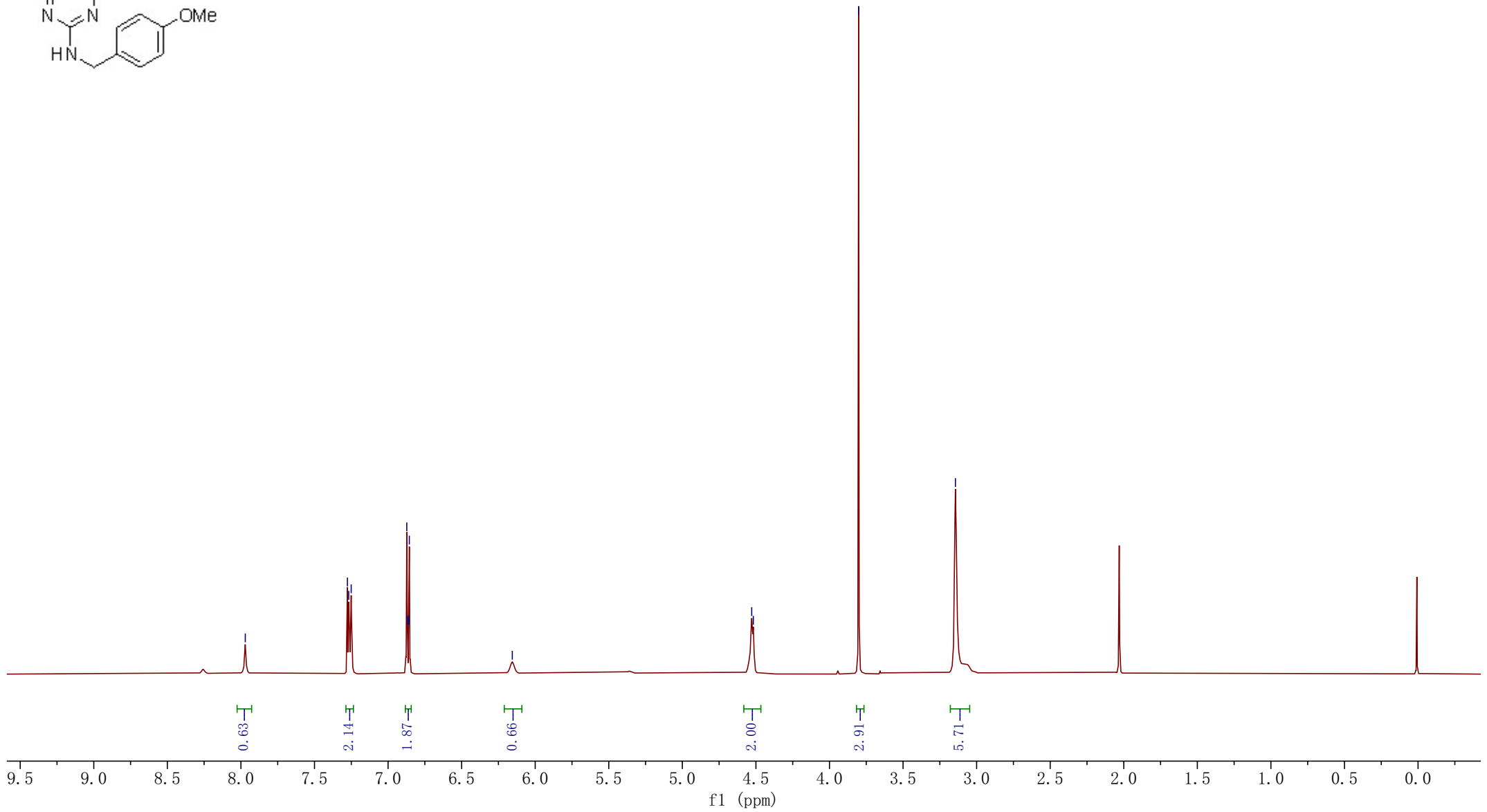
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6.1557

4.5286
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3.1441



190121
xzp181122 CDC13 0121

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164.5214

158.8117

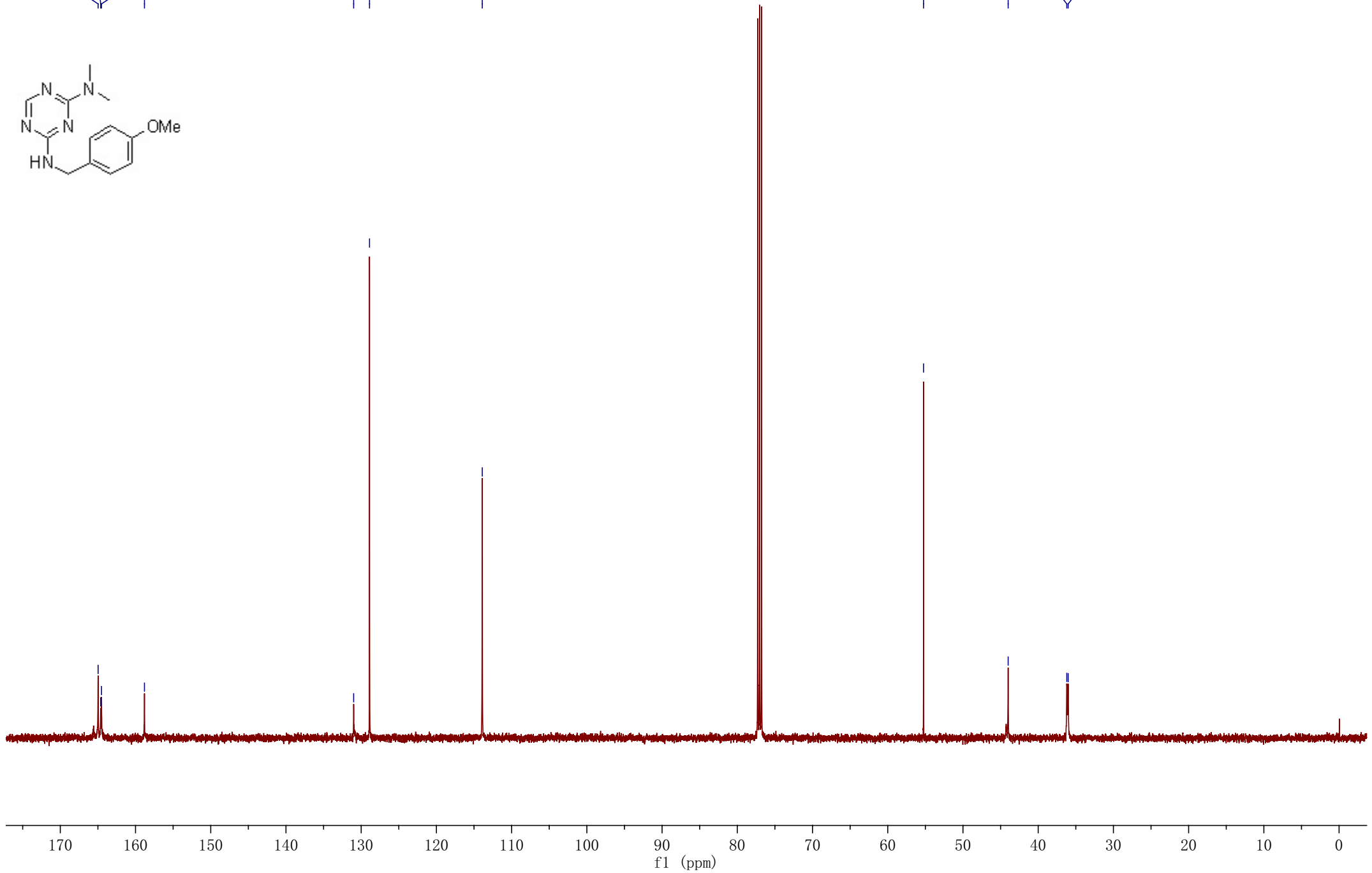
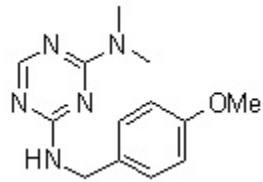
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190107
xzp181122-160

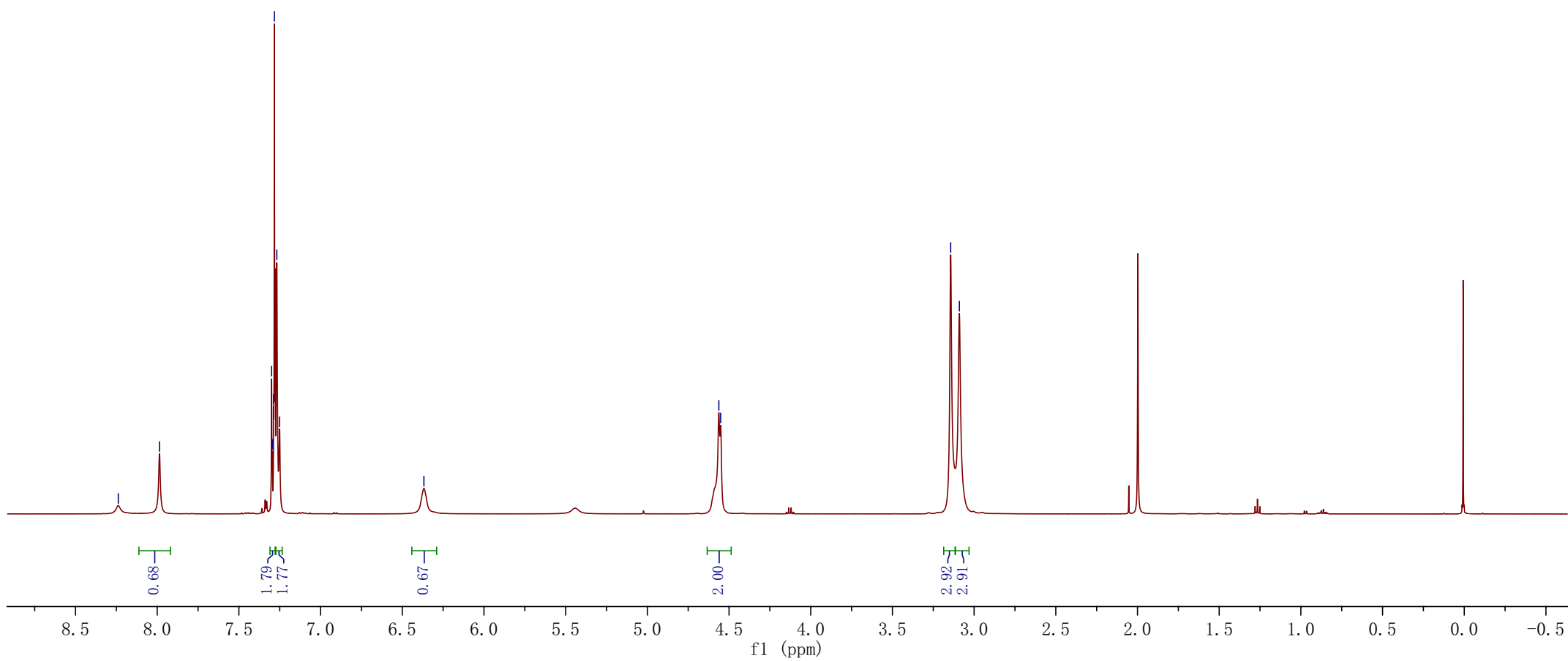
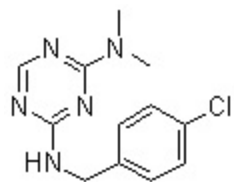
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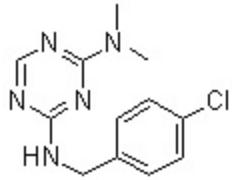
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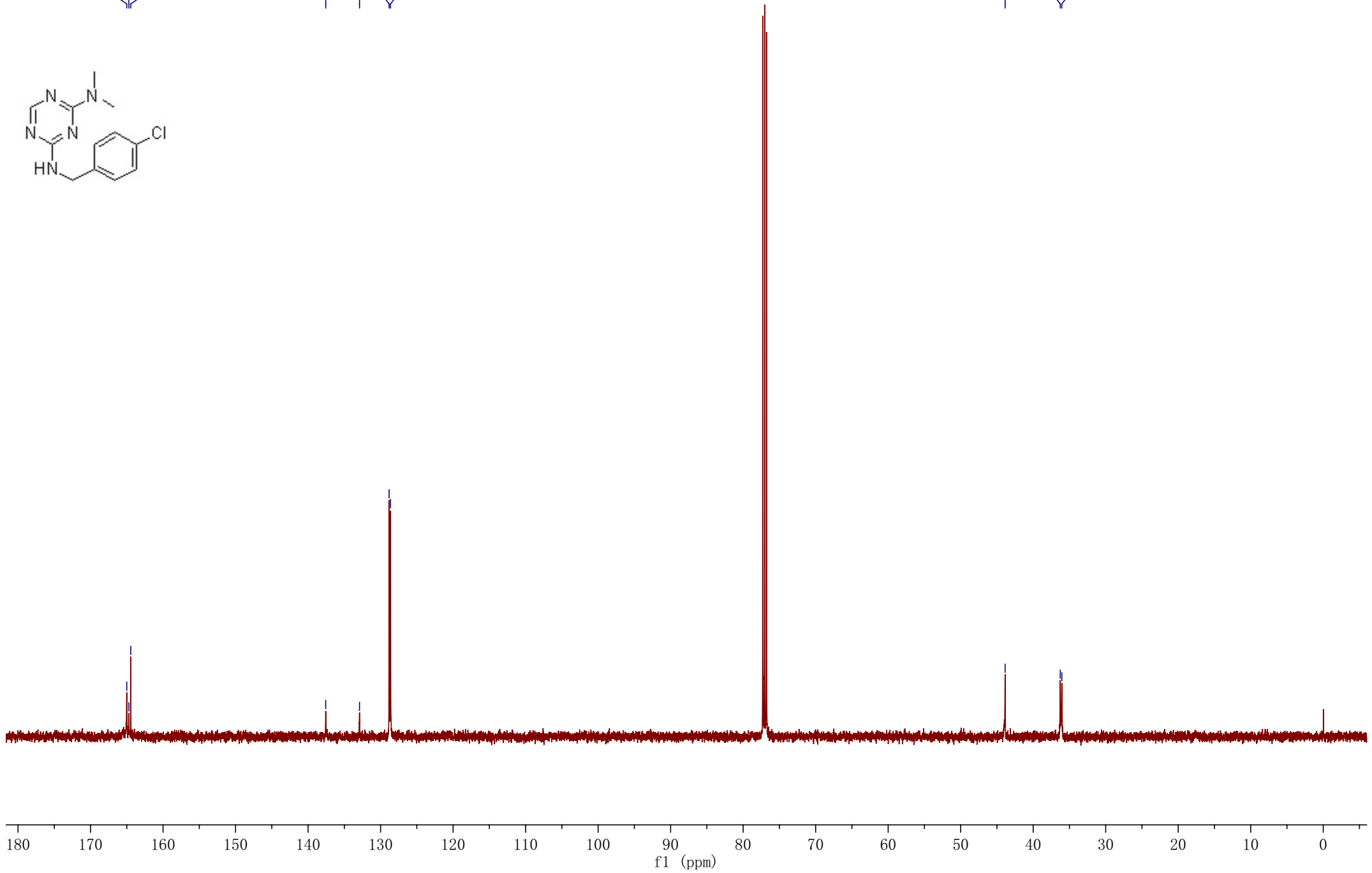
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36.2670
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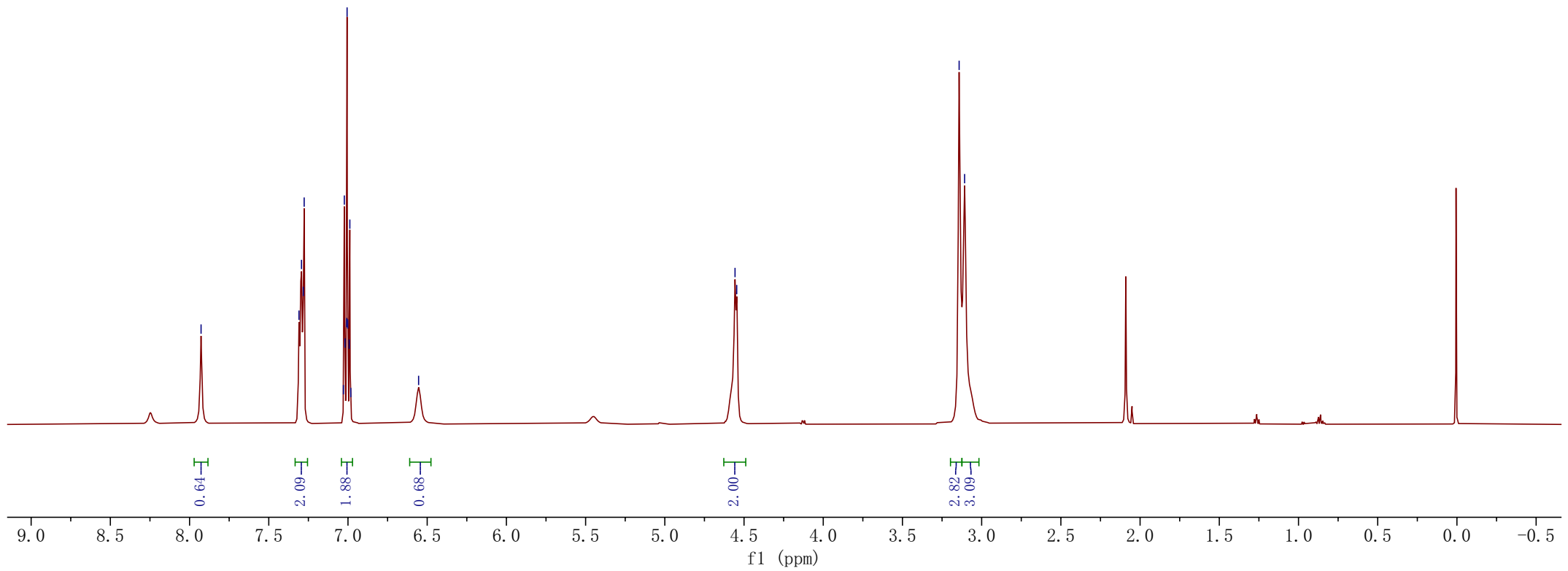
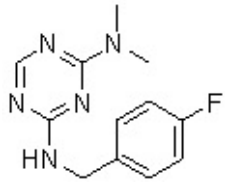


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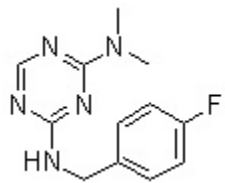
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7.2765
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4.5568
4.5461

3.1422
3.1077



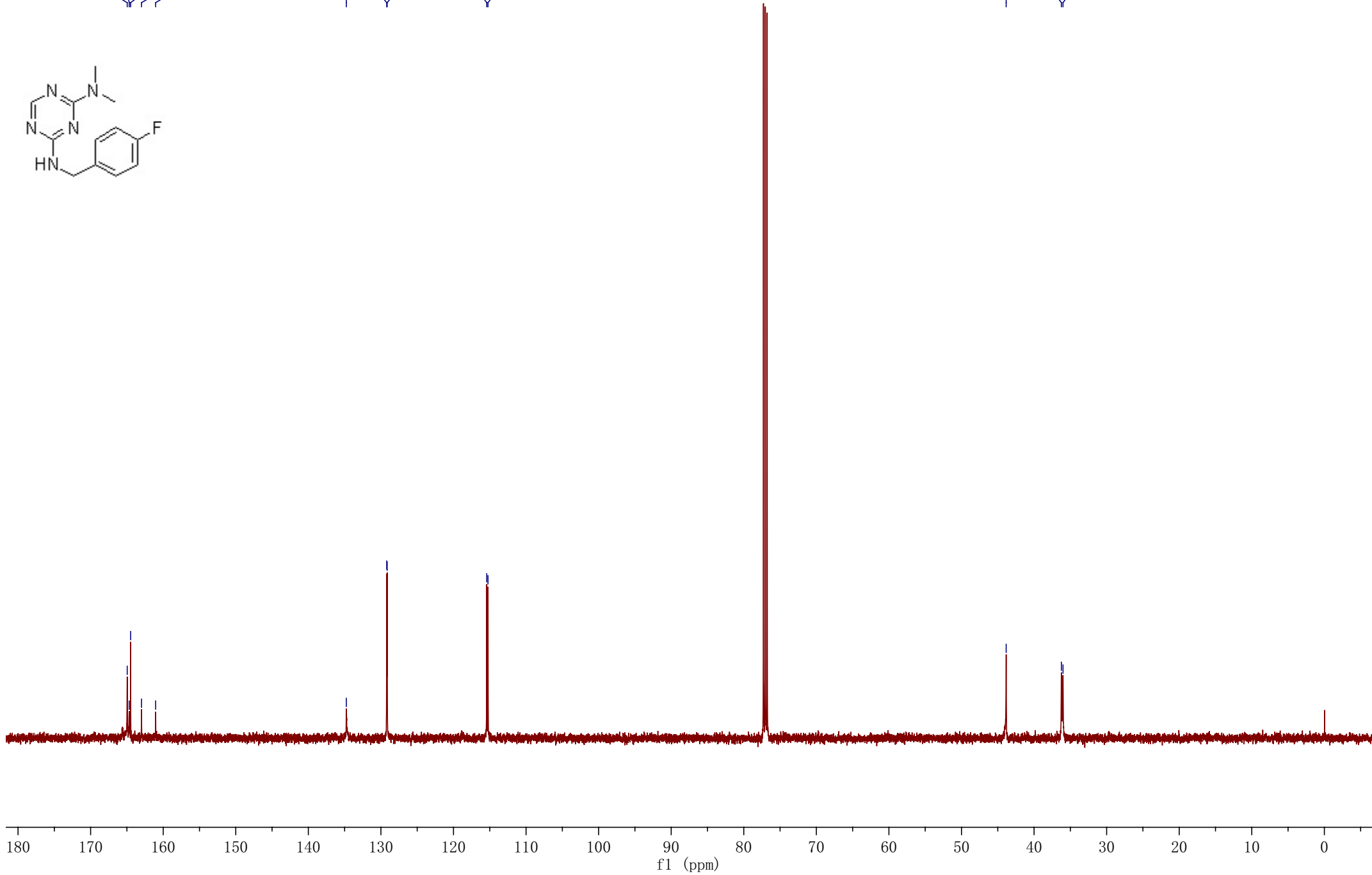
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164.6656
162.3877
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43.8435
36.2355
36.0105



190423

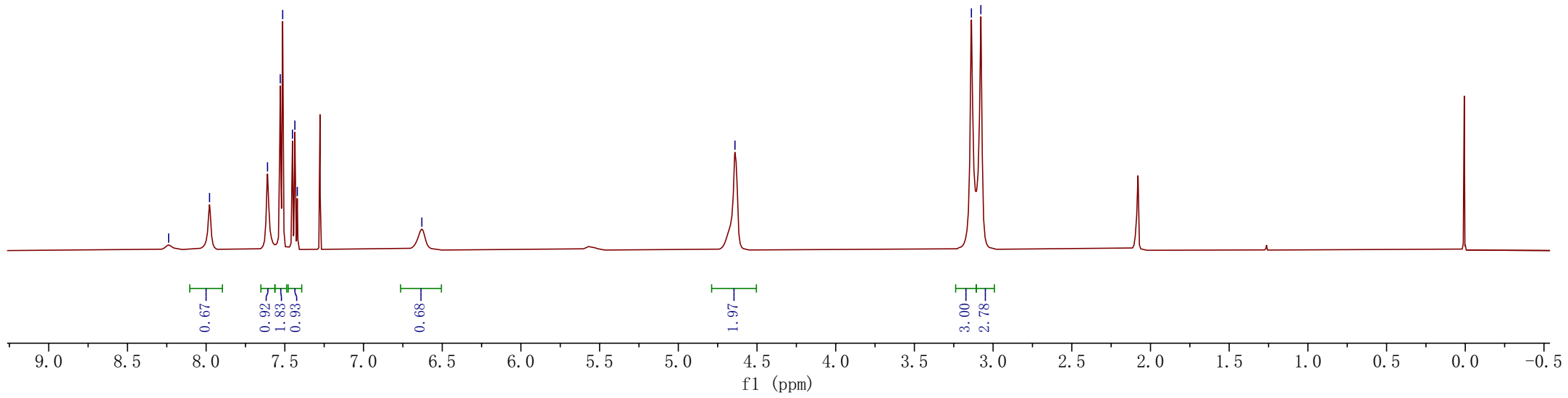
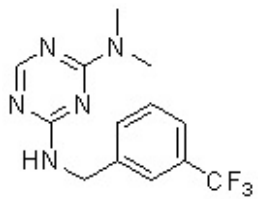
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6.6296

4.6401

3.1379
3.0778



190522
xzp19043

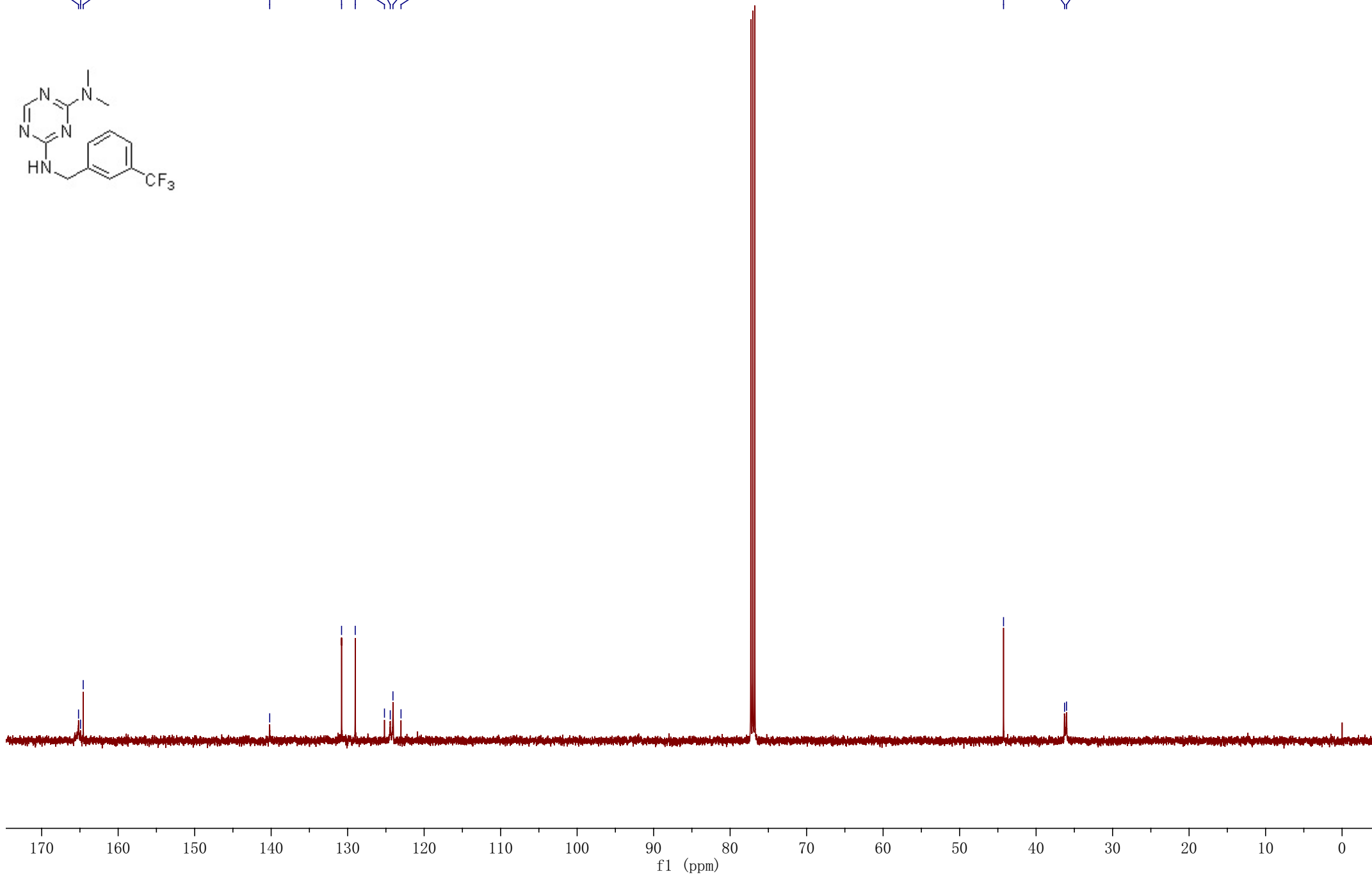
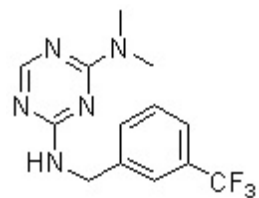
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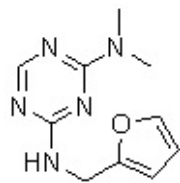
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123.0239

44.2572

36.2797
36.0233



190102
xzp181101-139 CDC13 0108



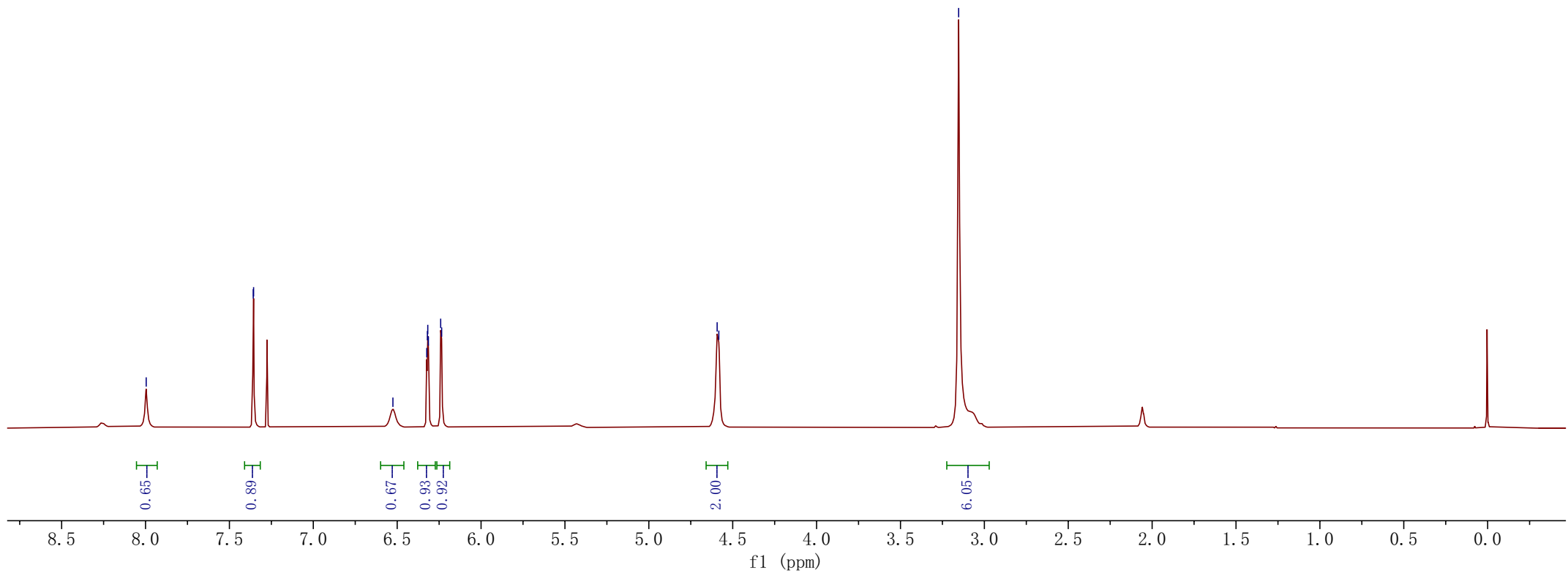
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6.2349

4.5928
4.5829

3.1533



190115

xzpl81101-139

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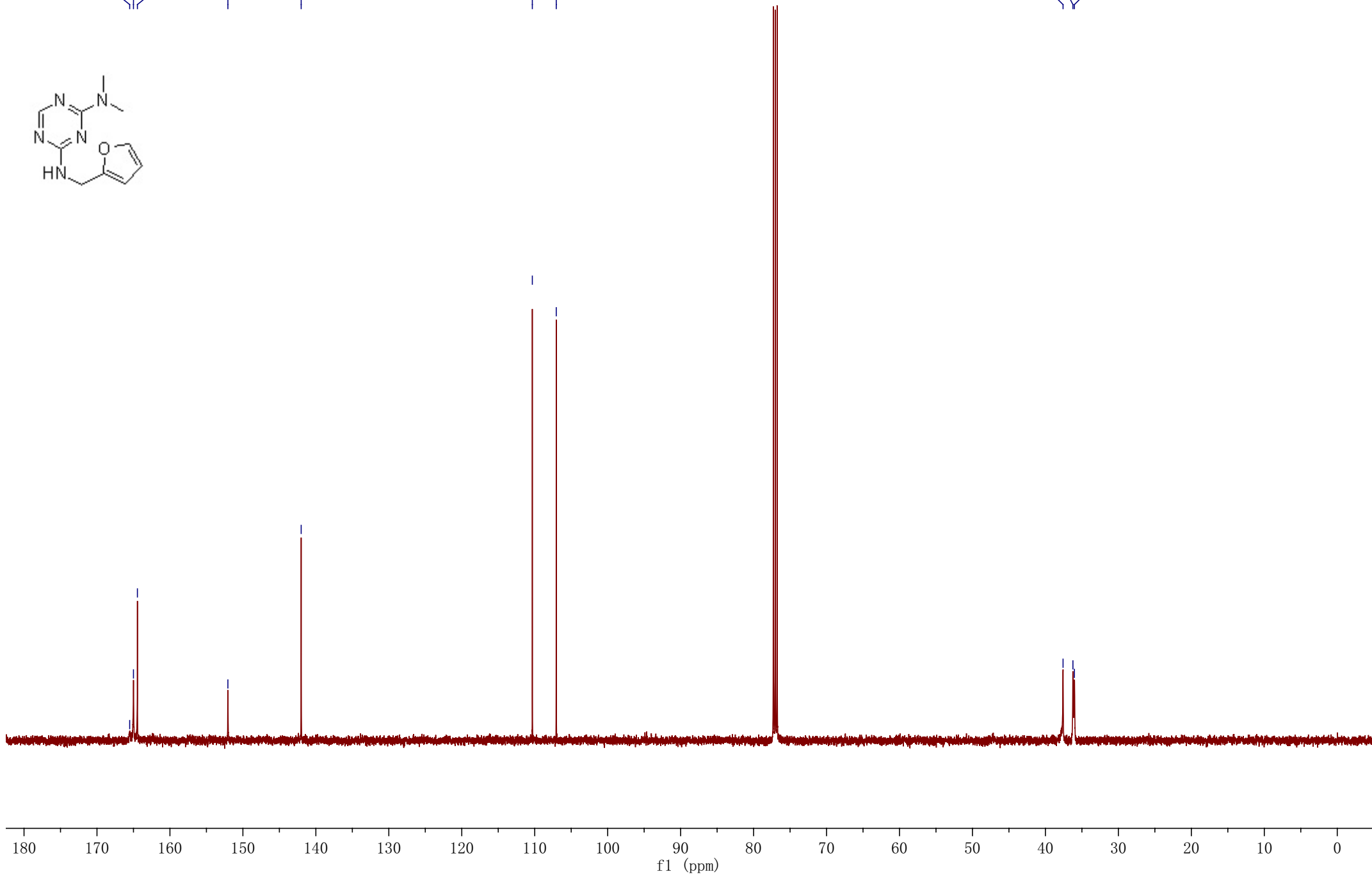
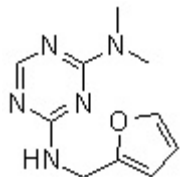
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110.3280

107.0488

37.5845
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36.0238

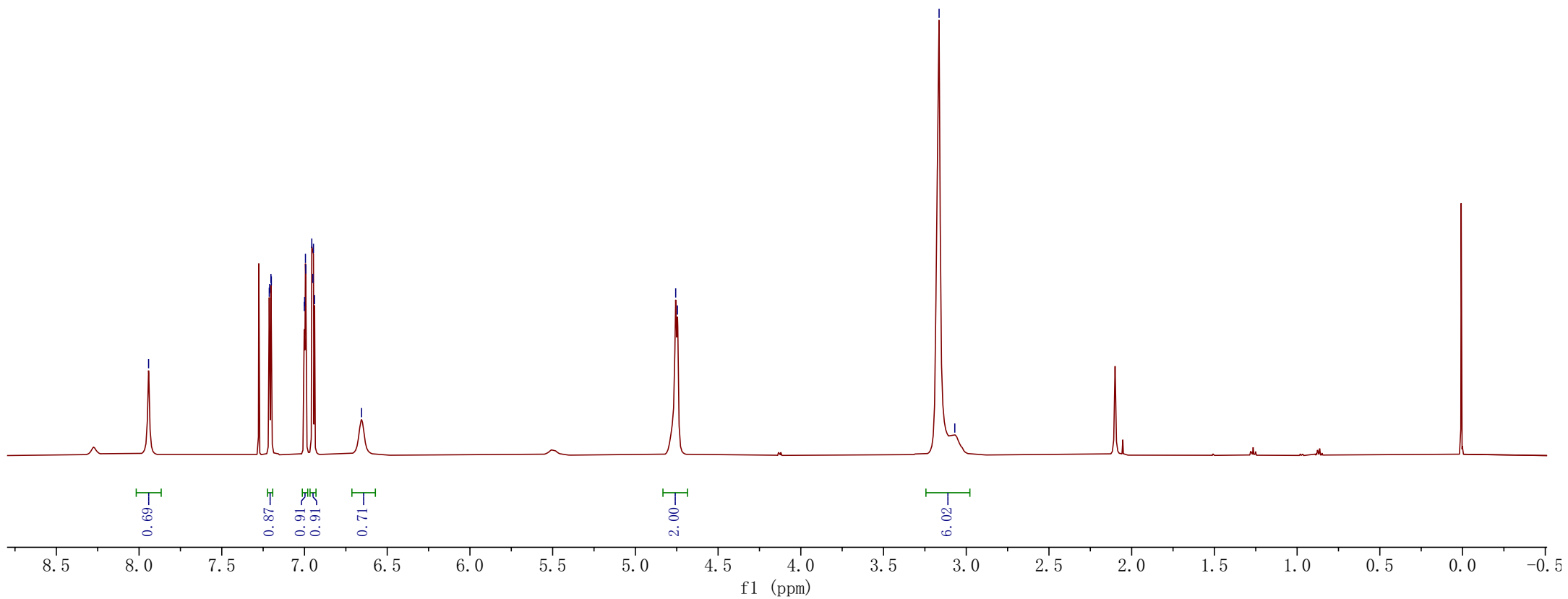
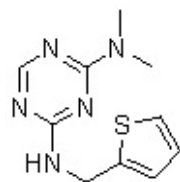


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6.6549

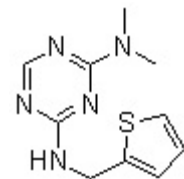
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190121
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CDC13 0121

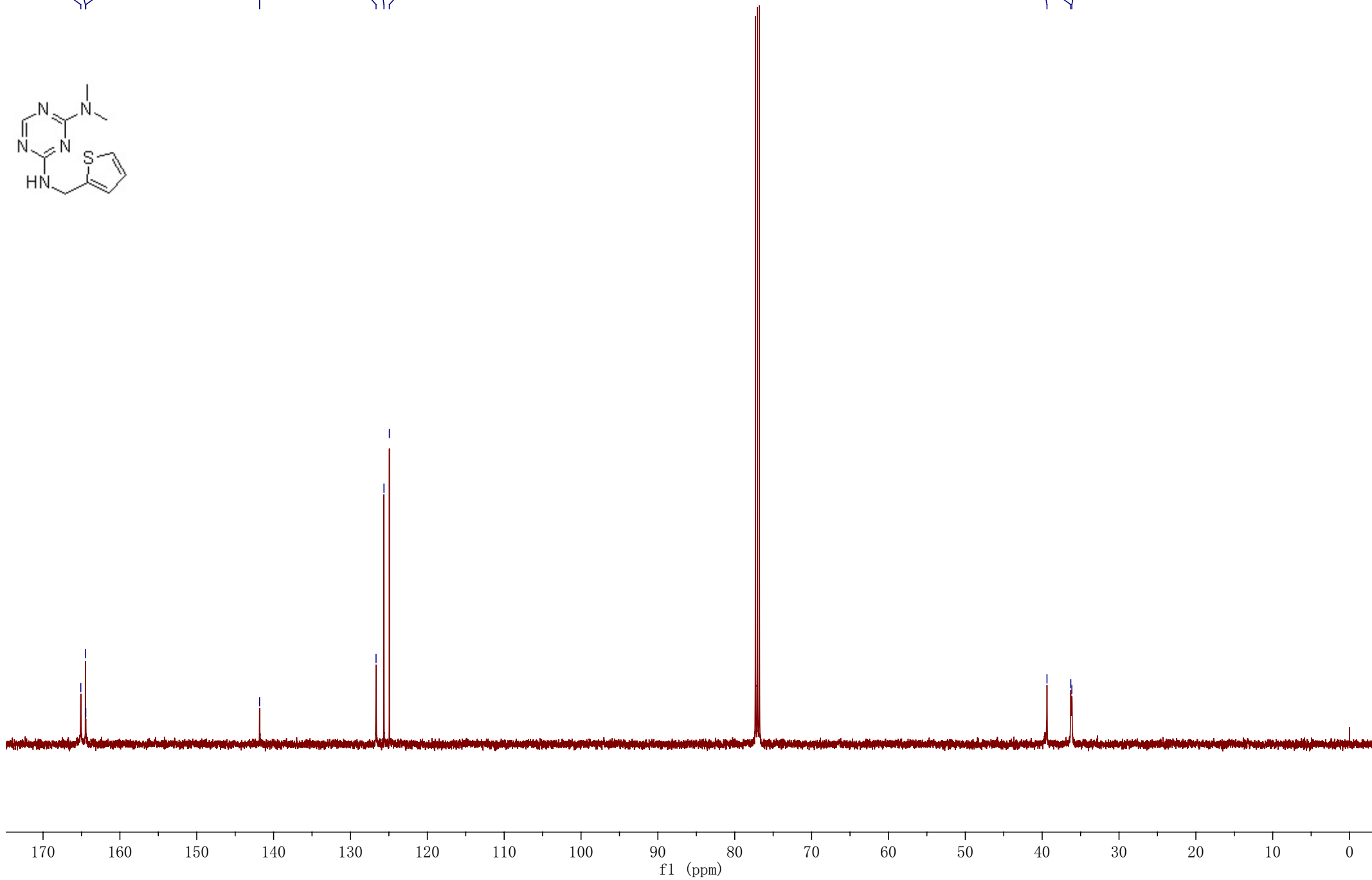


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141.8238

126.6701
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124.9430

39.3729
36.2755
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191031

xzpz191025-103

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8.8956

1033
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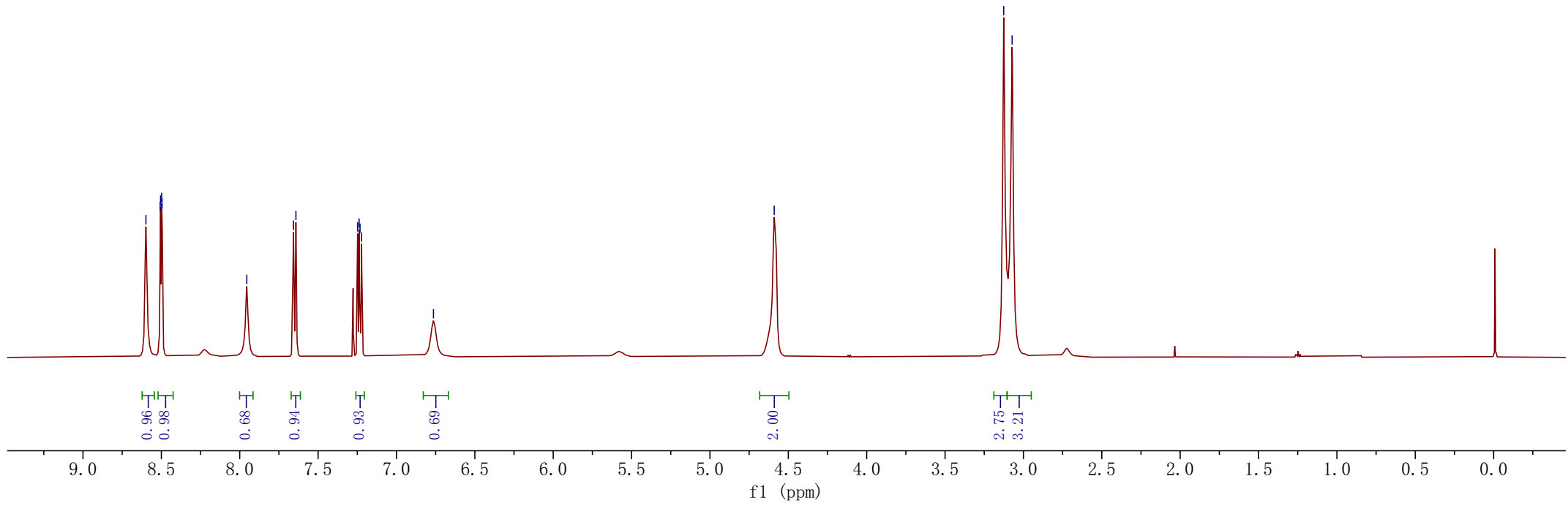
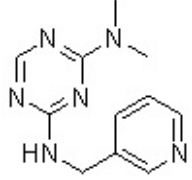
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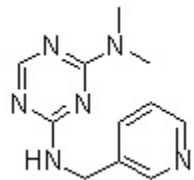
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191105
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149.2379
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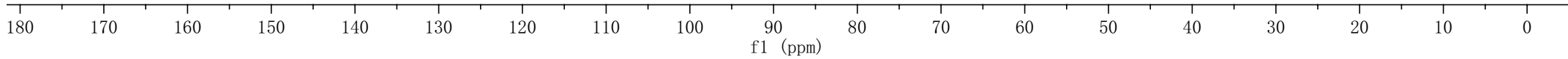
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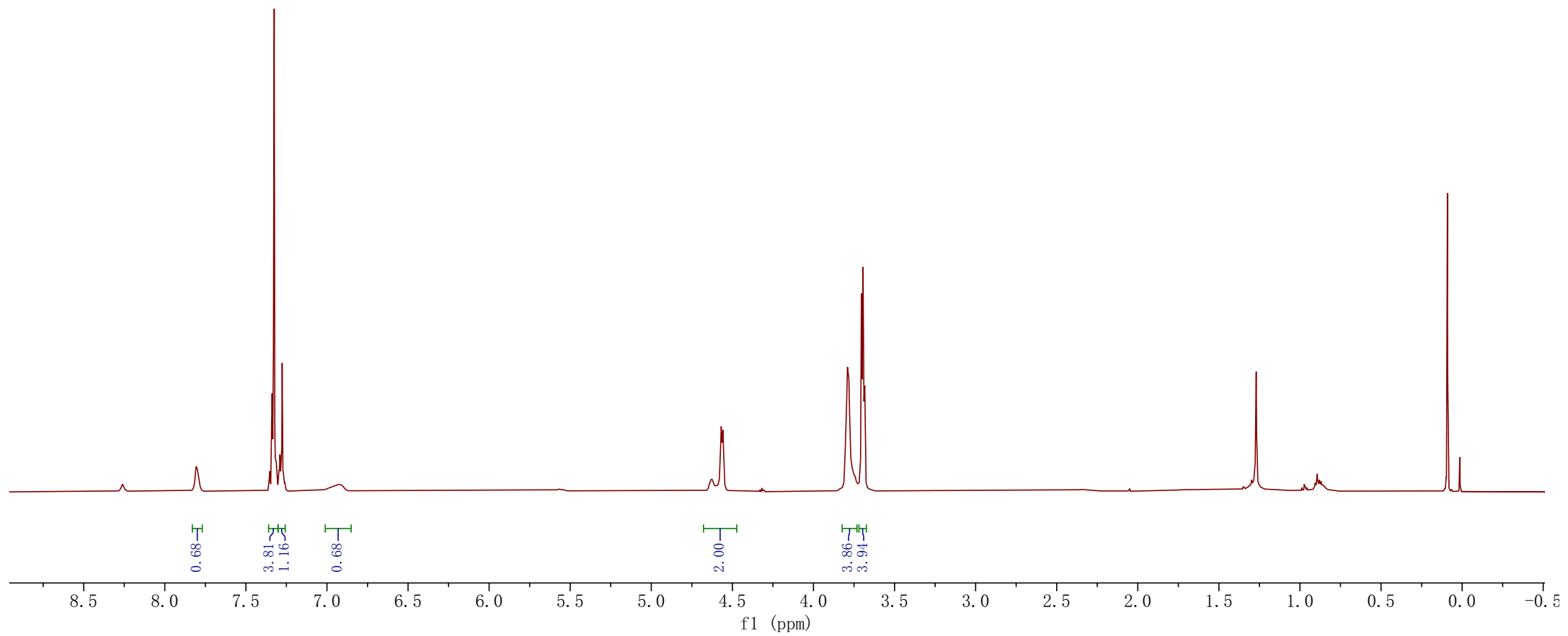
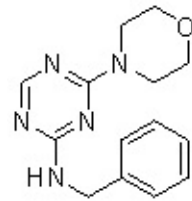
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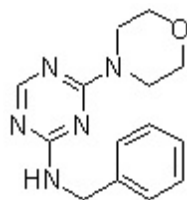


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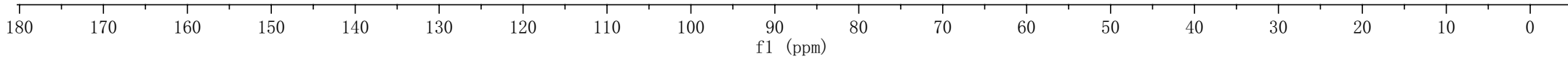
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190107
xzp181122-172

CDC13
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7.2431

5.6755

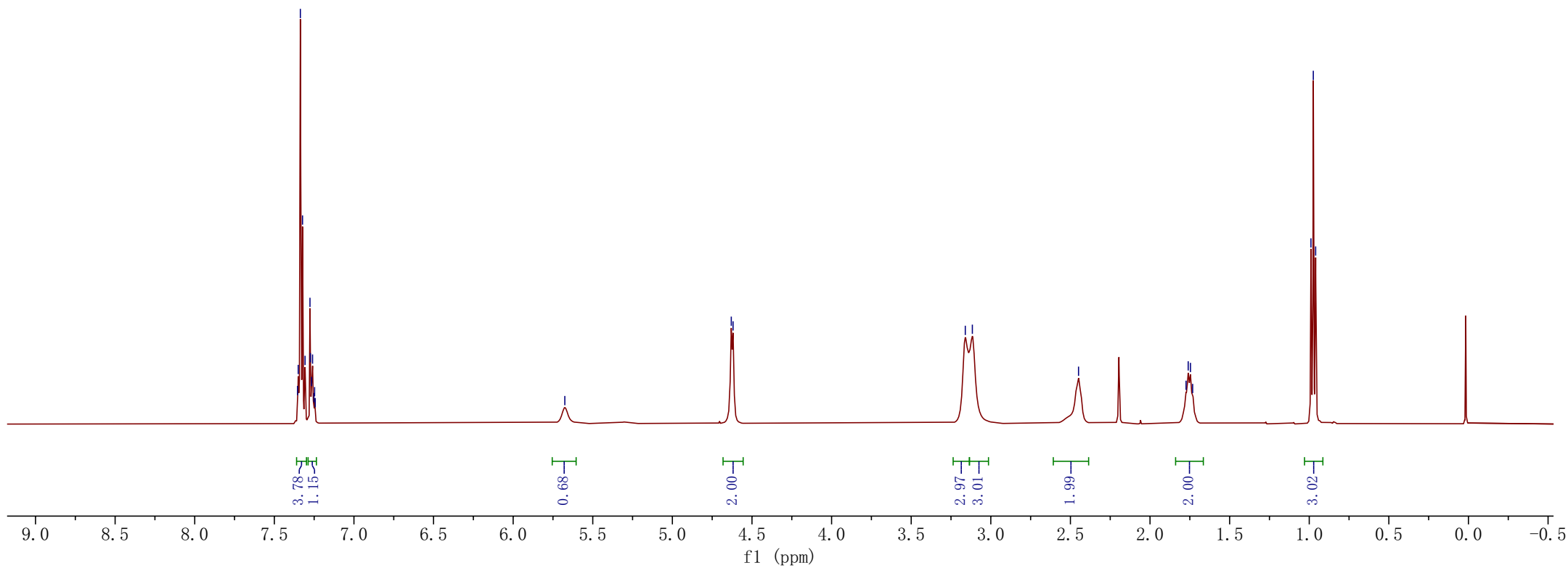
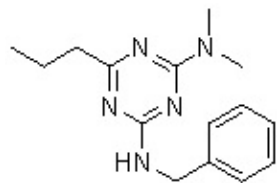
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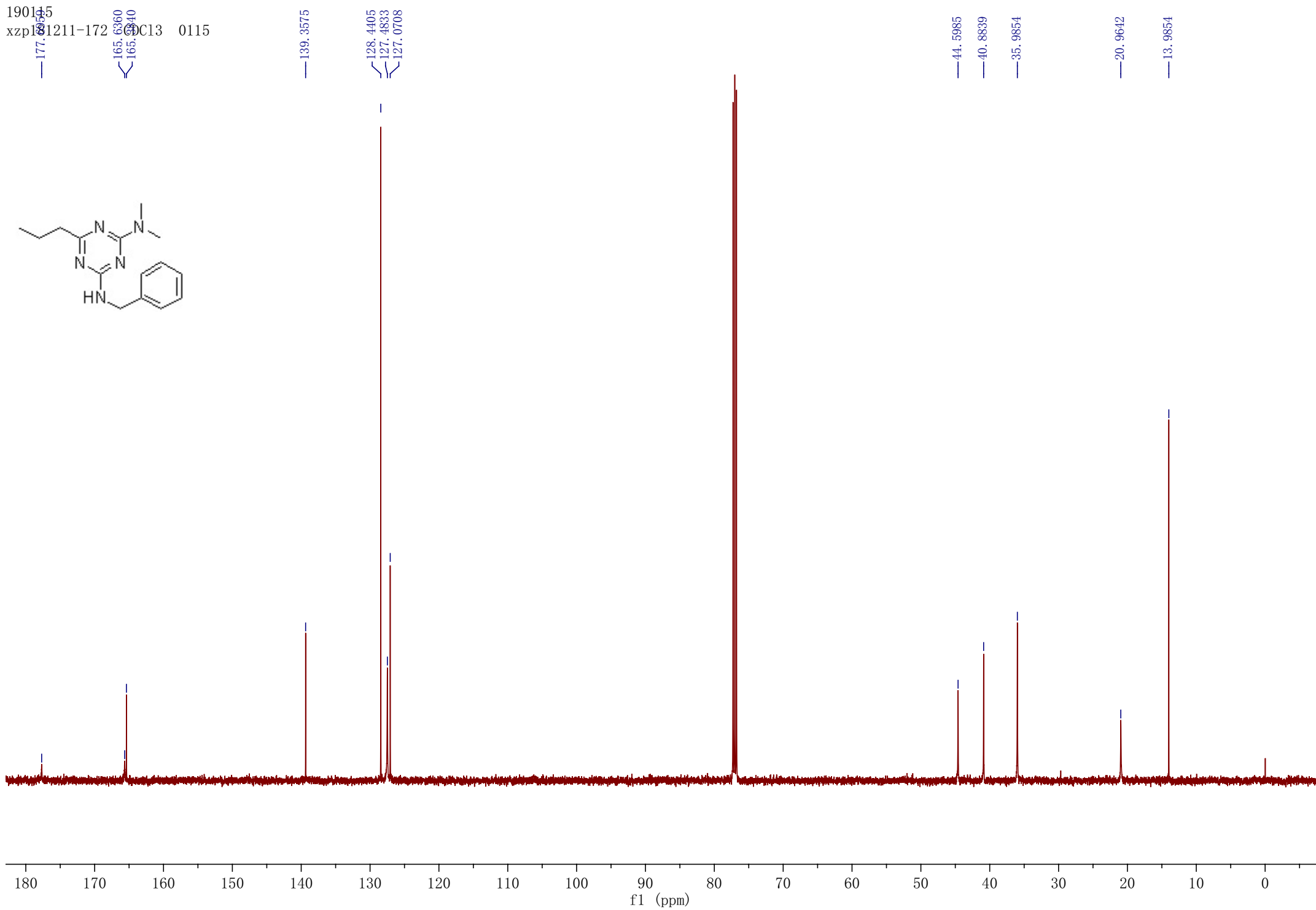
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0.9892
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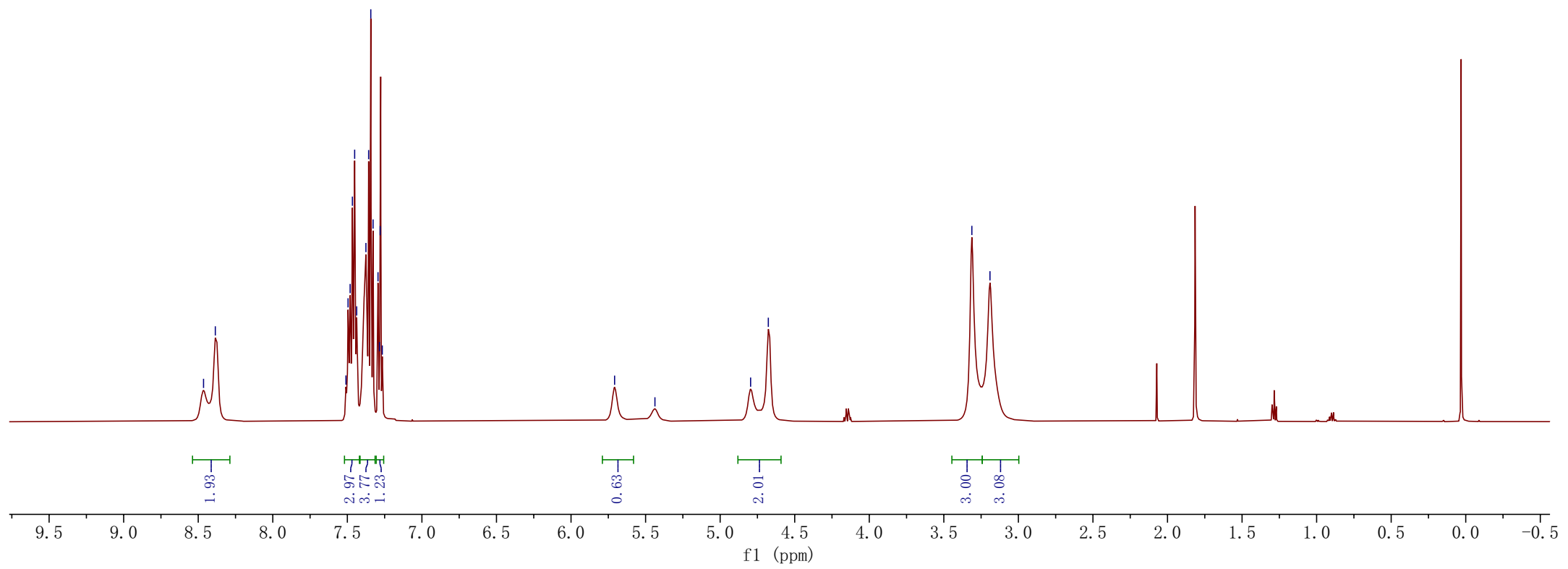
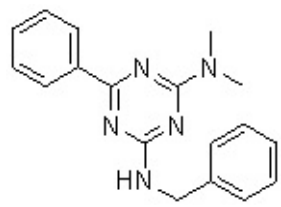
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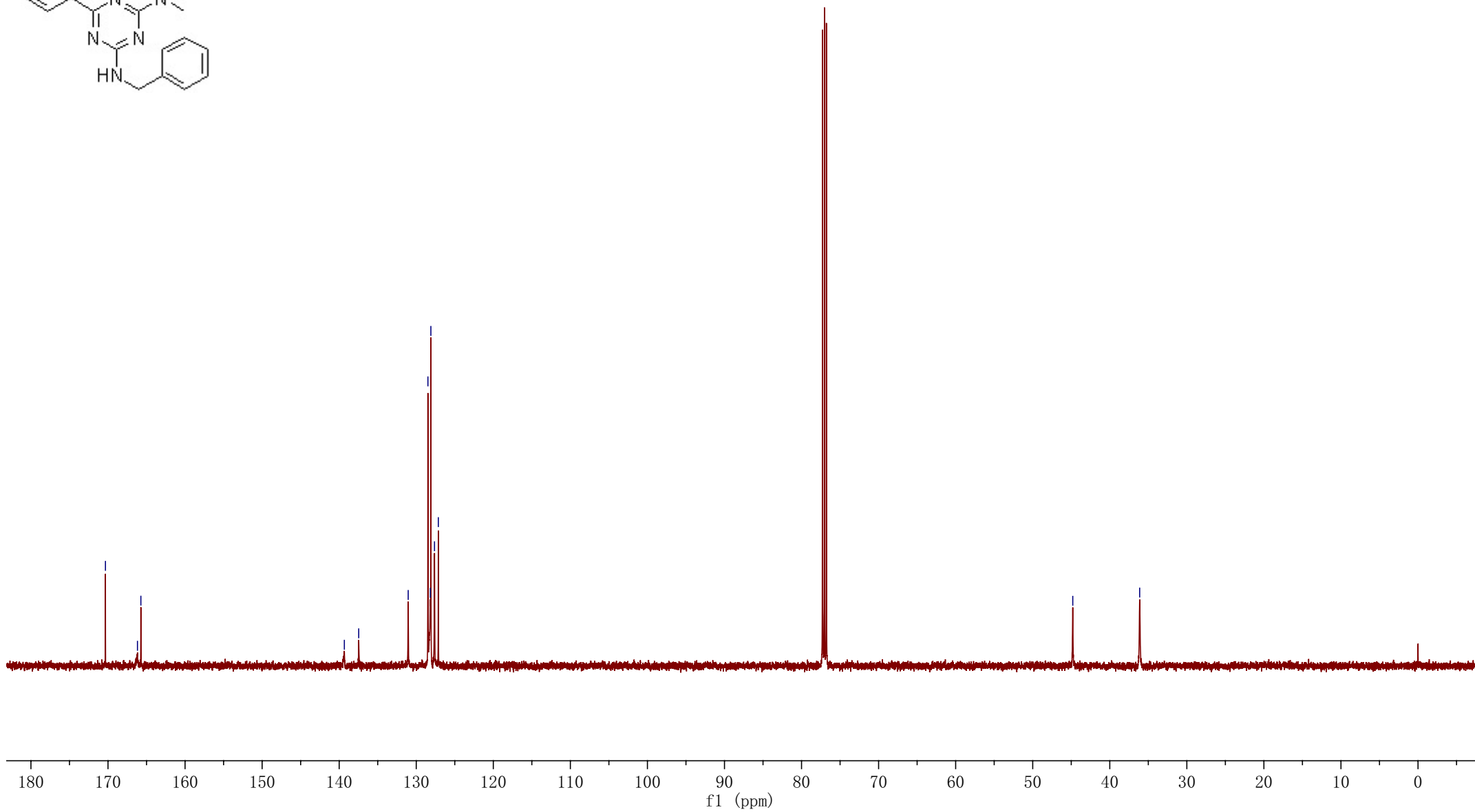
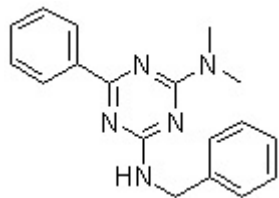
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181126

xzq181114-150

CDC13

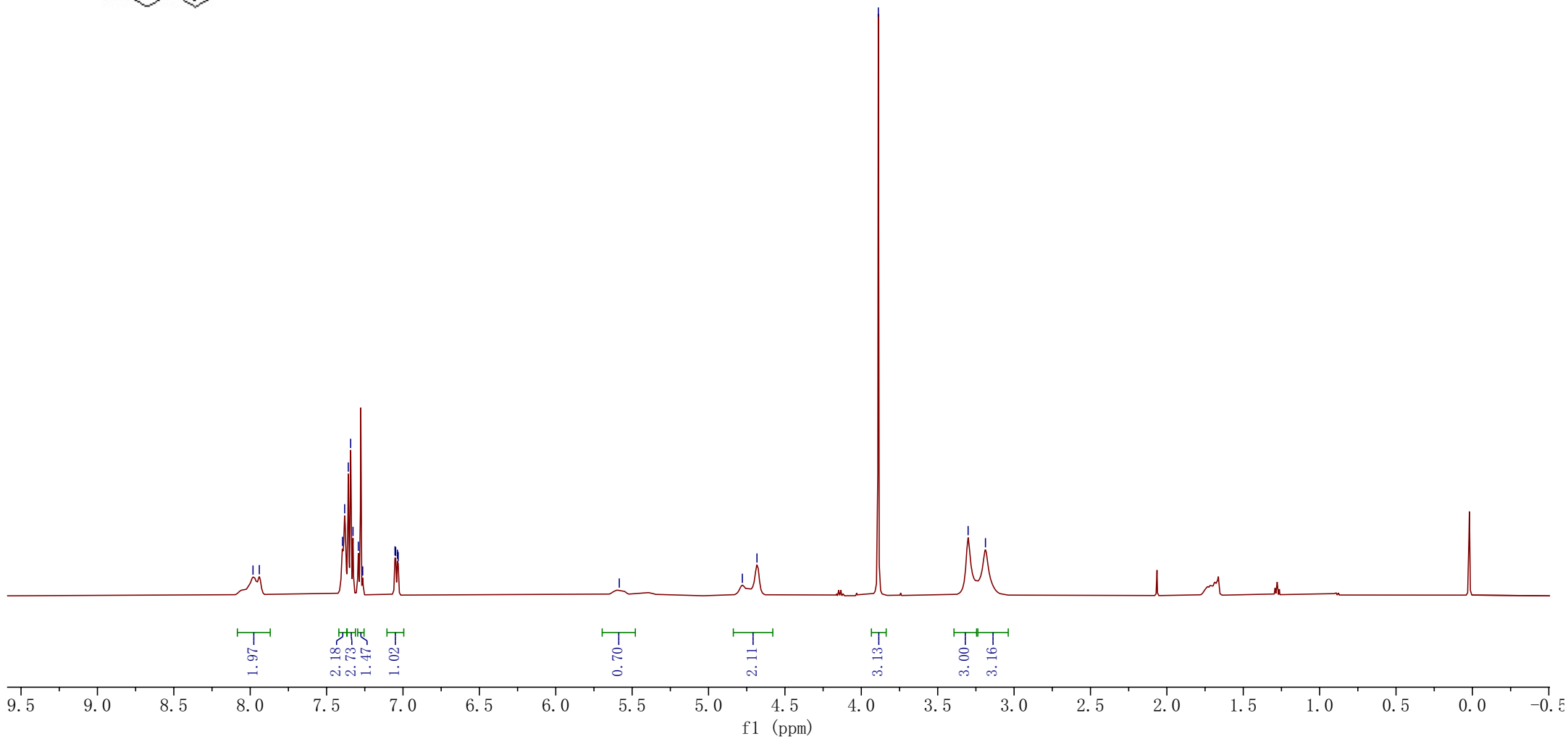
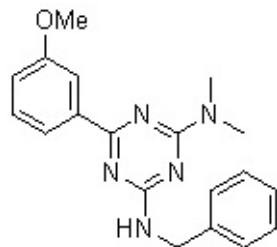
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3.3009
3.1874

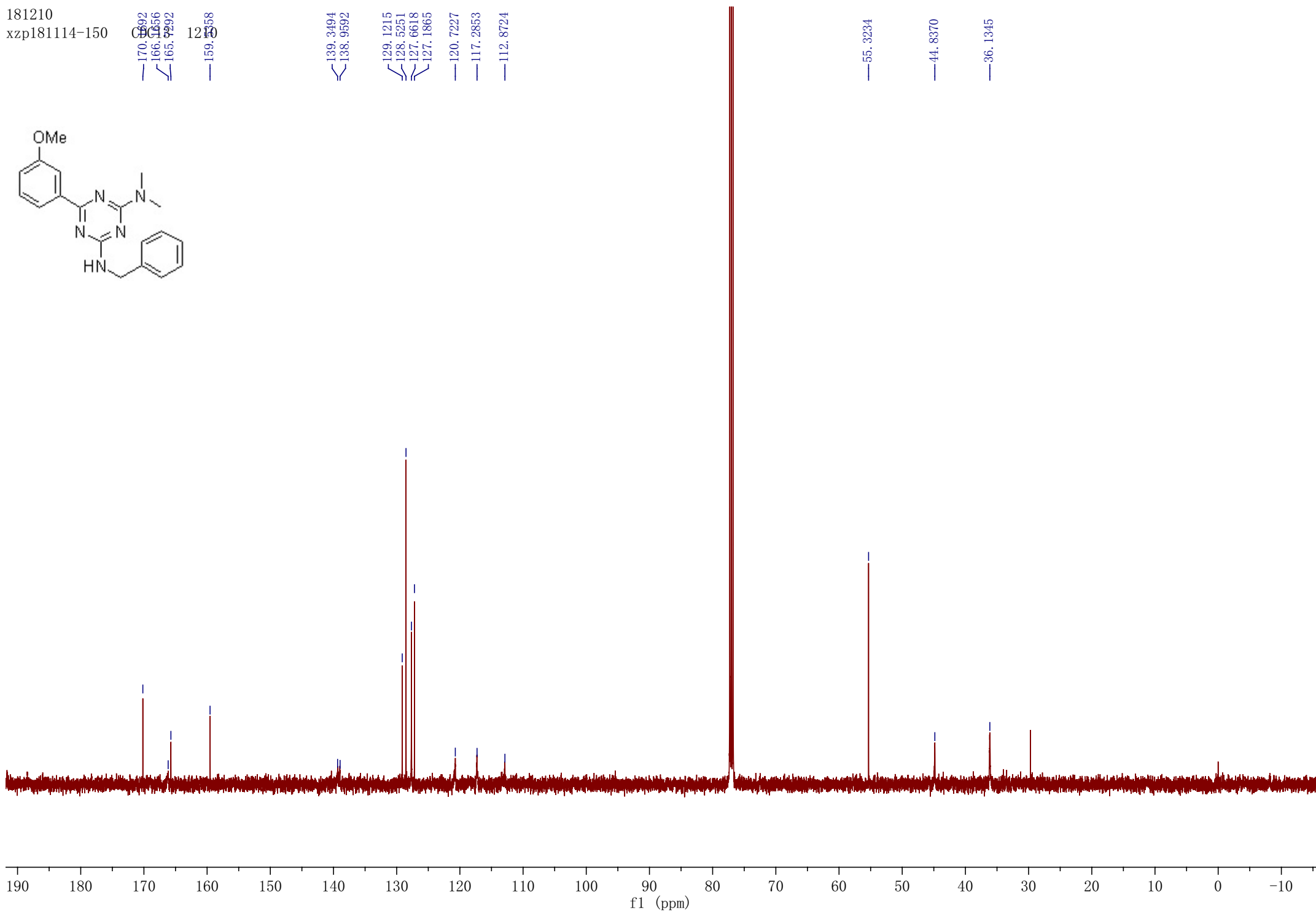
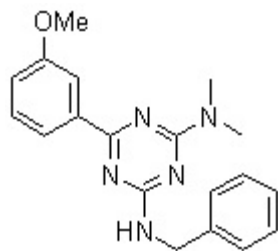


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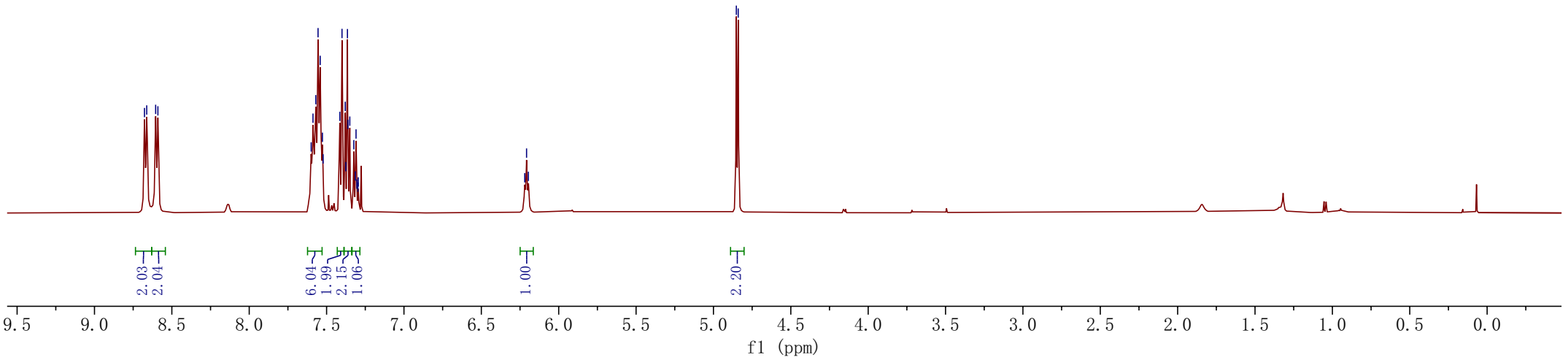
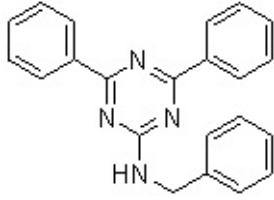
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XZP200113-141

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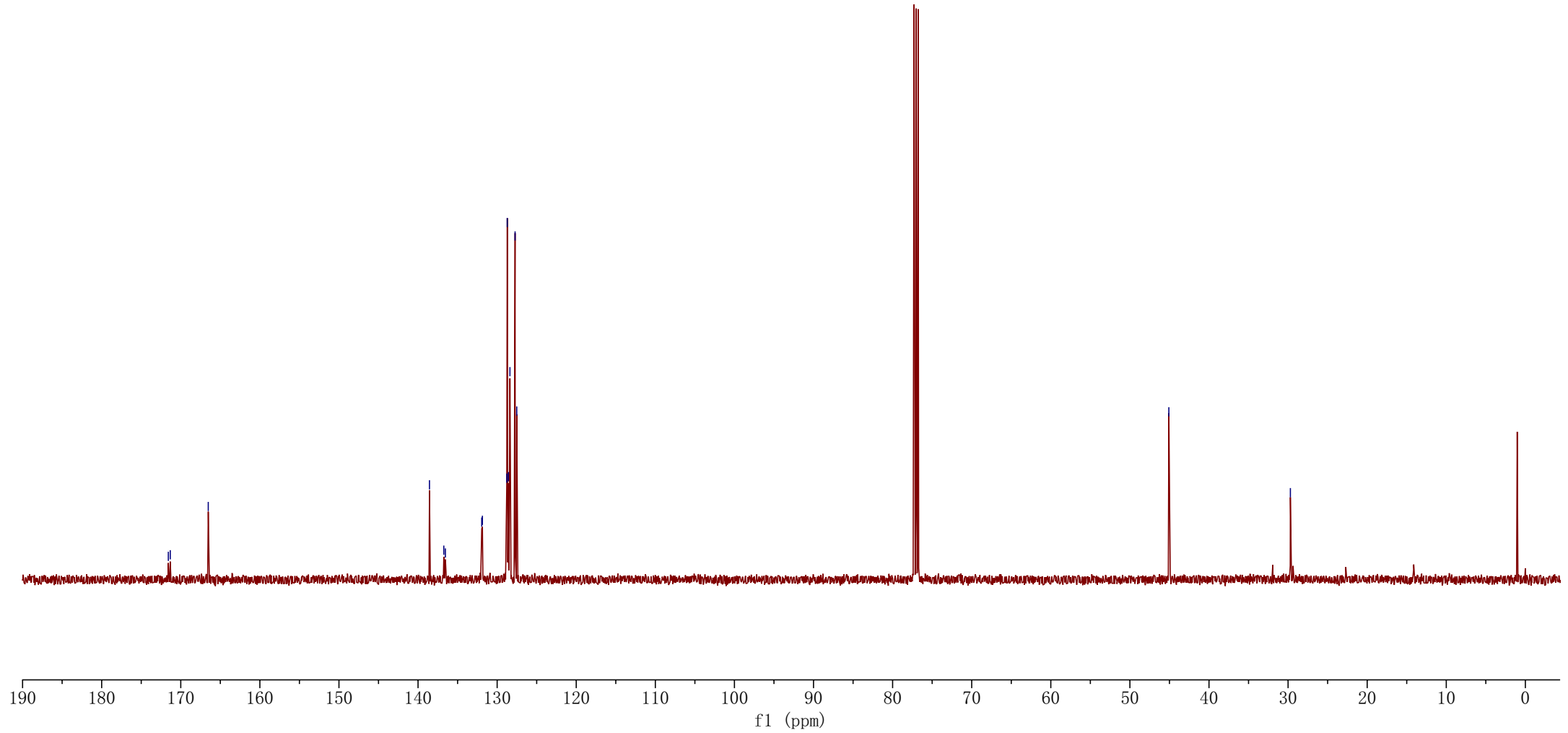
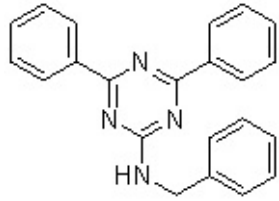
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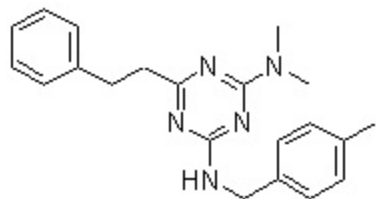
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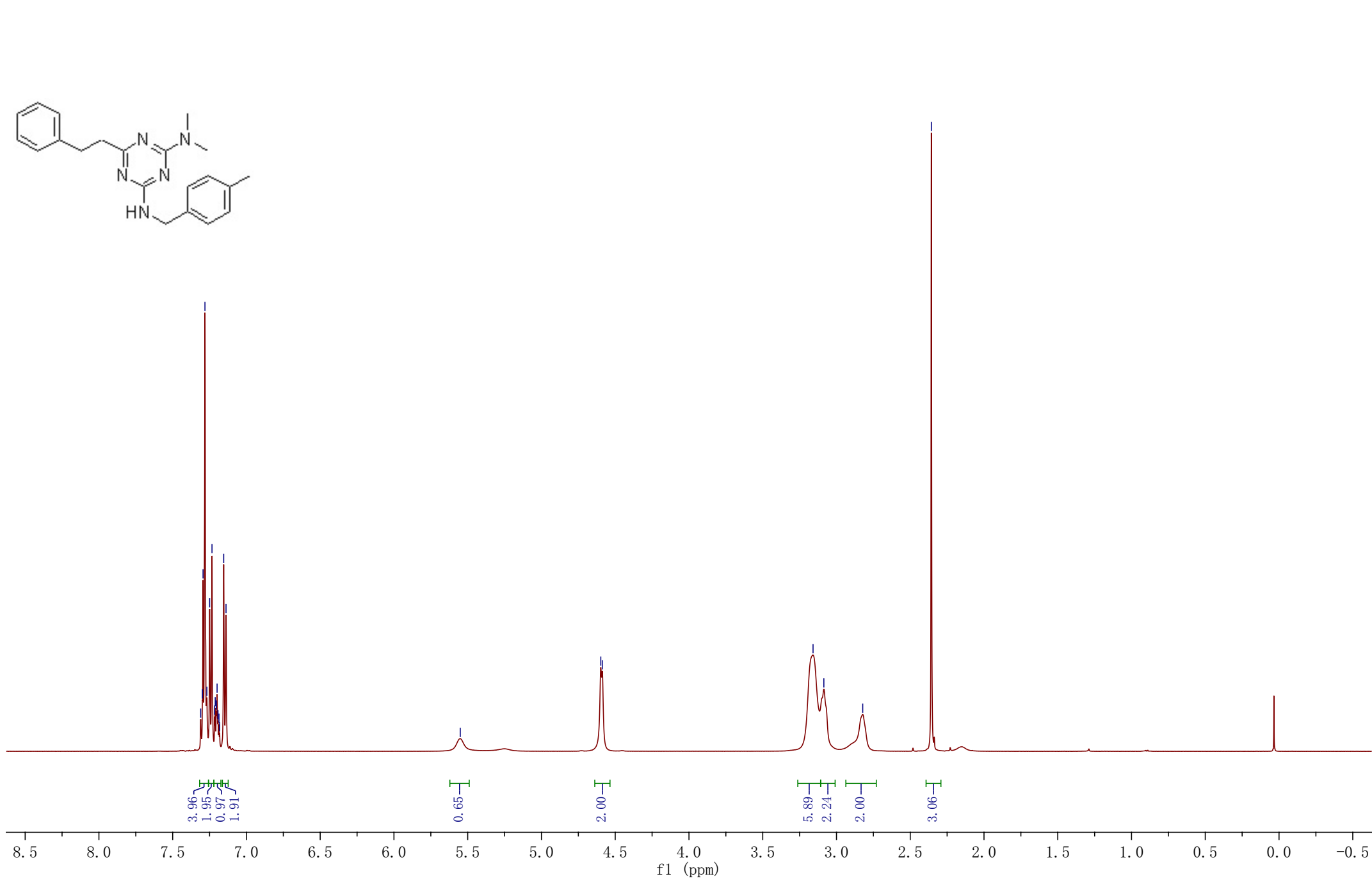
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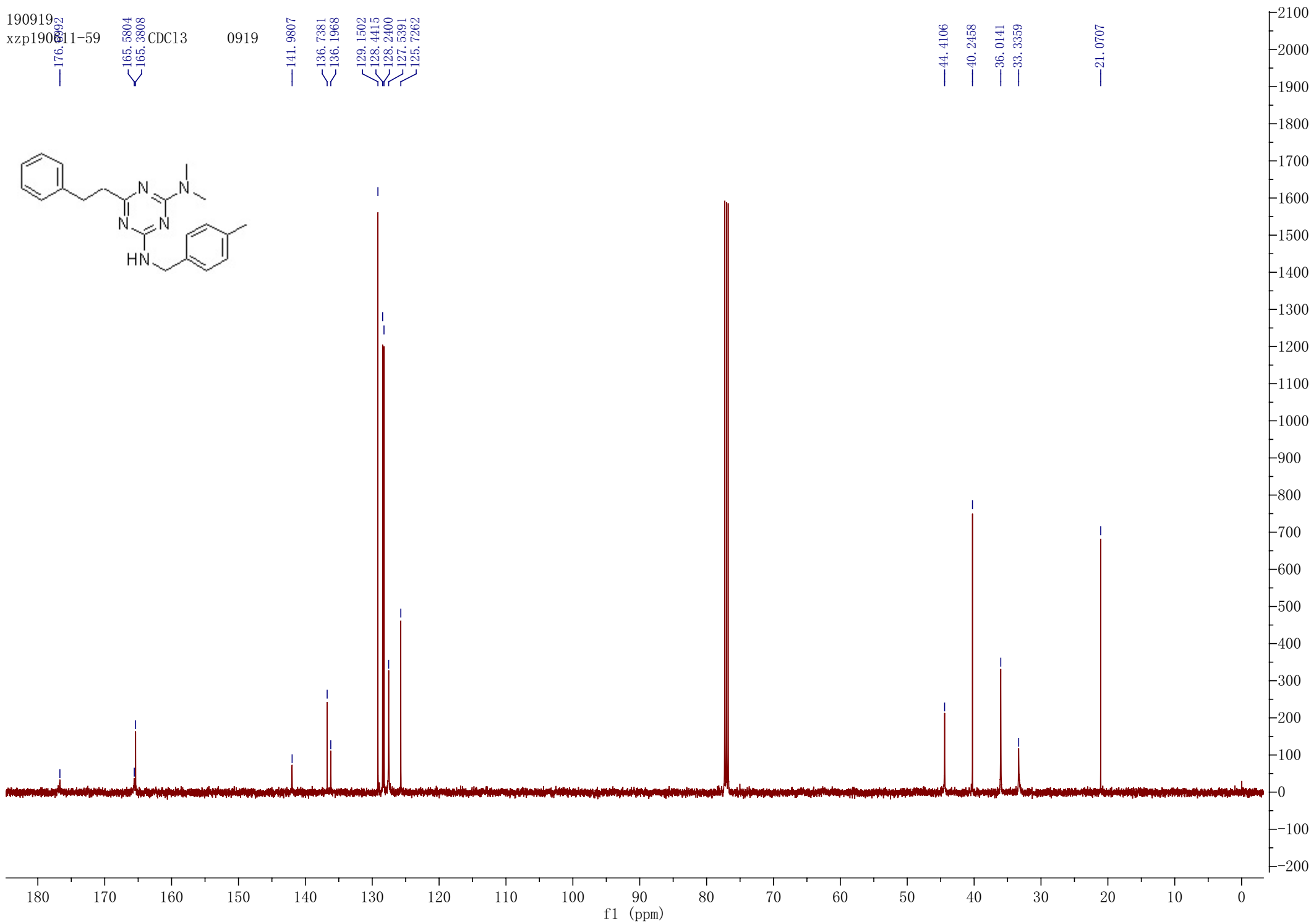
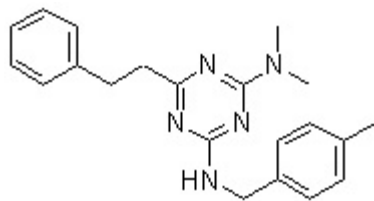
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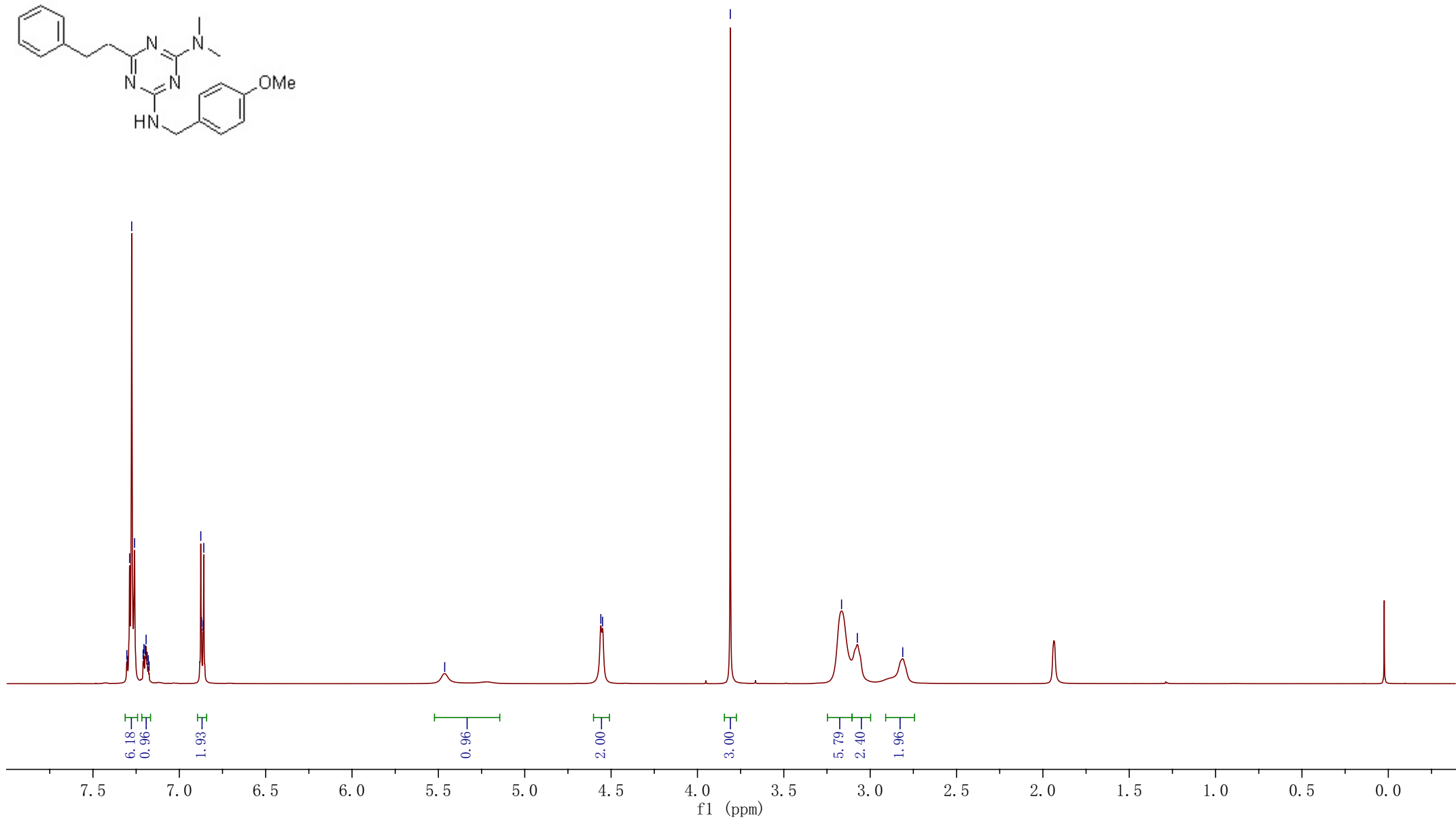
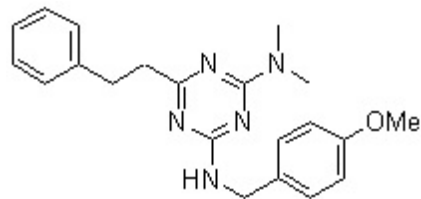
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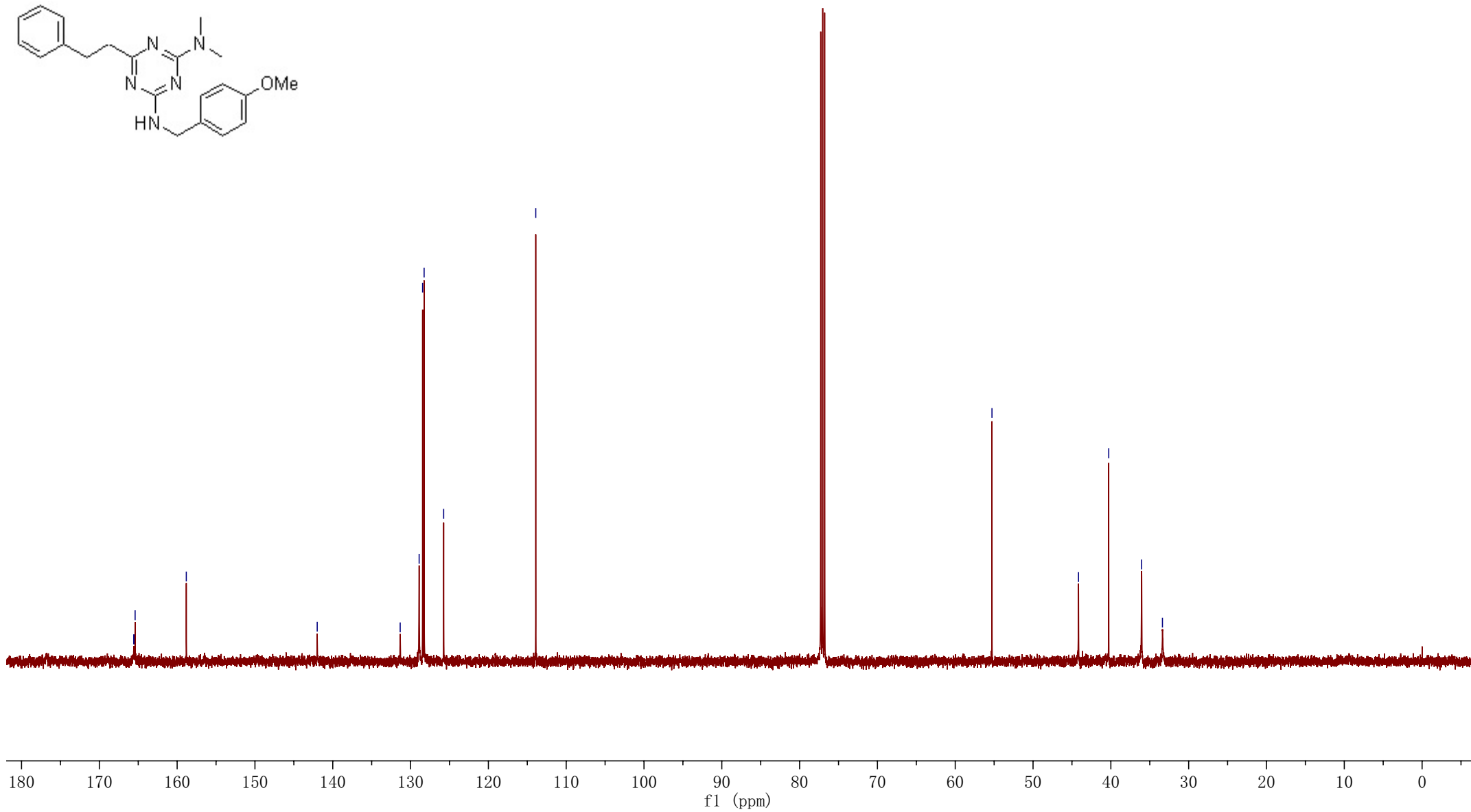
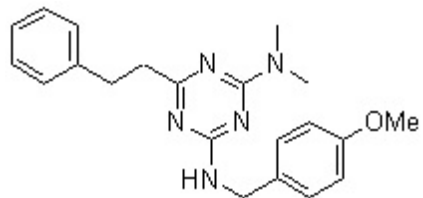
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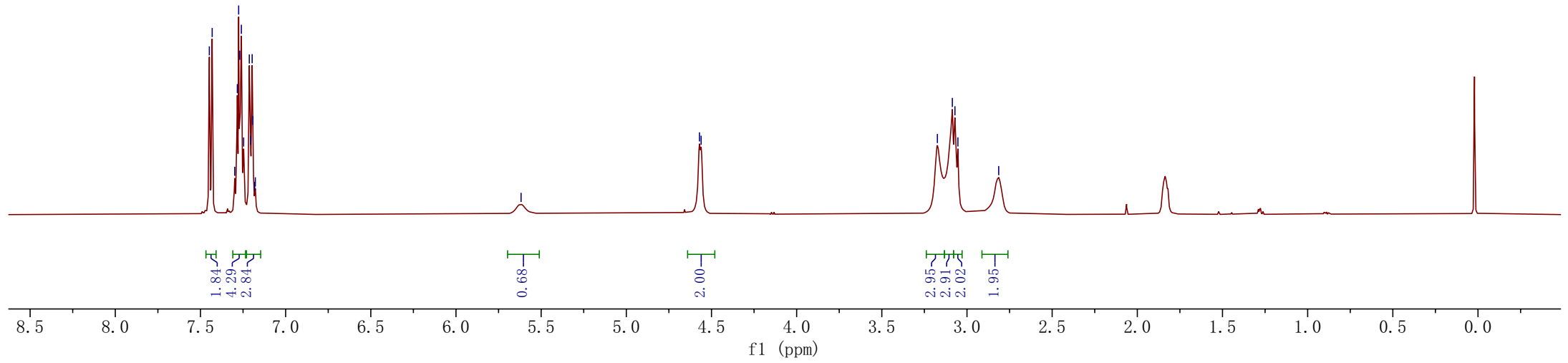
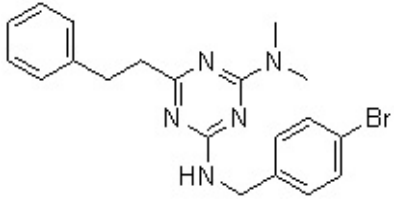
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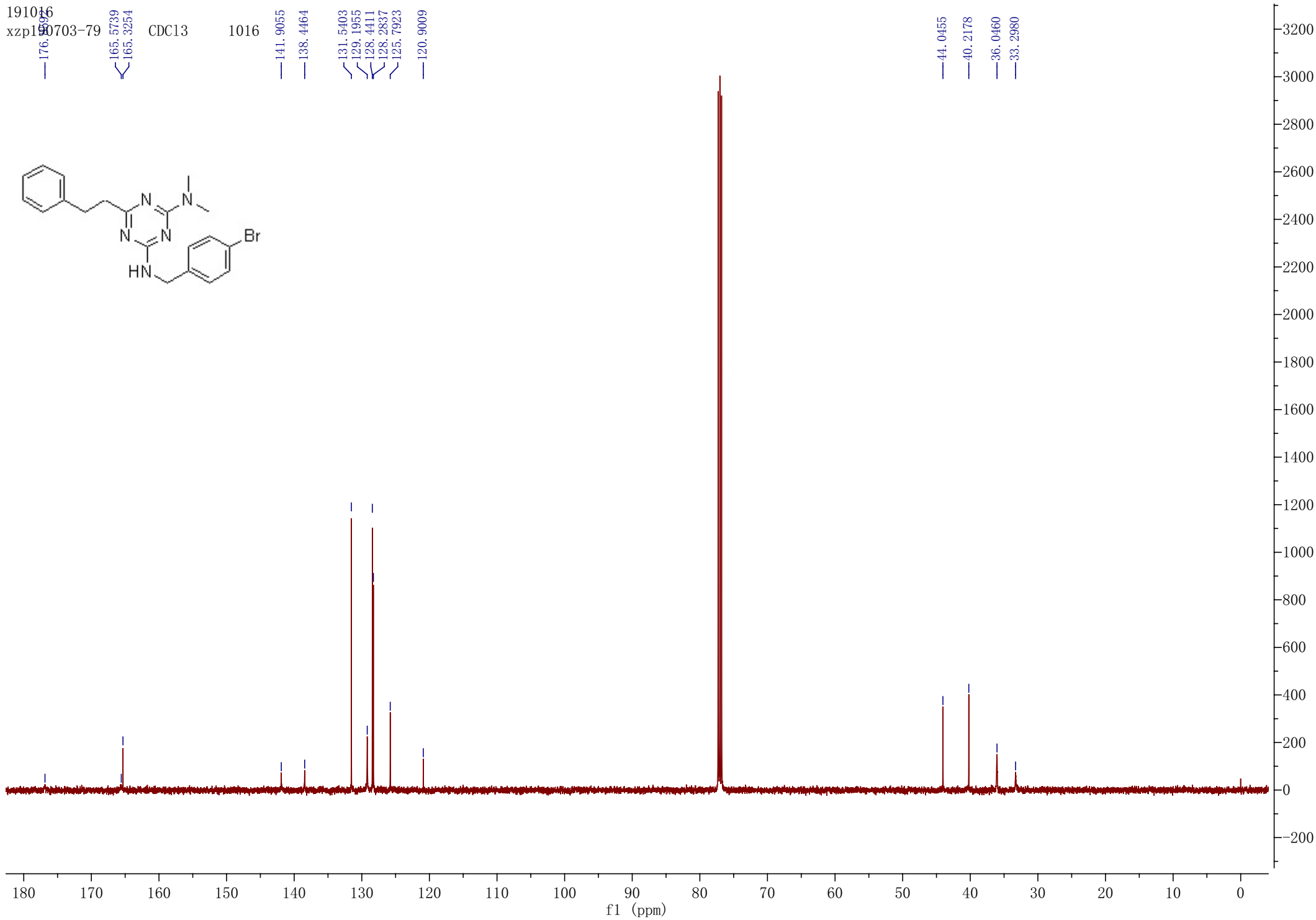
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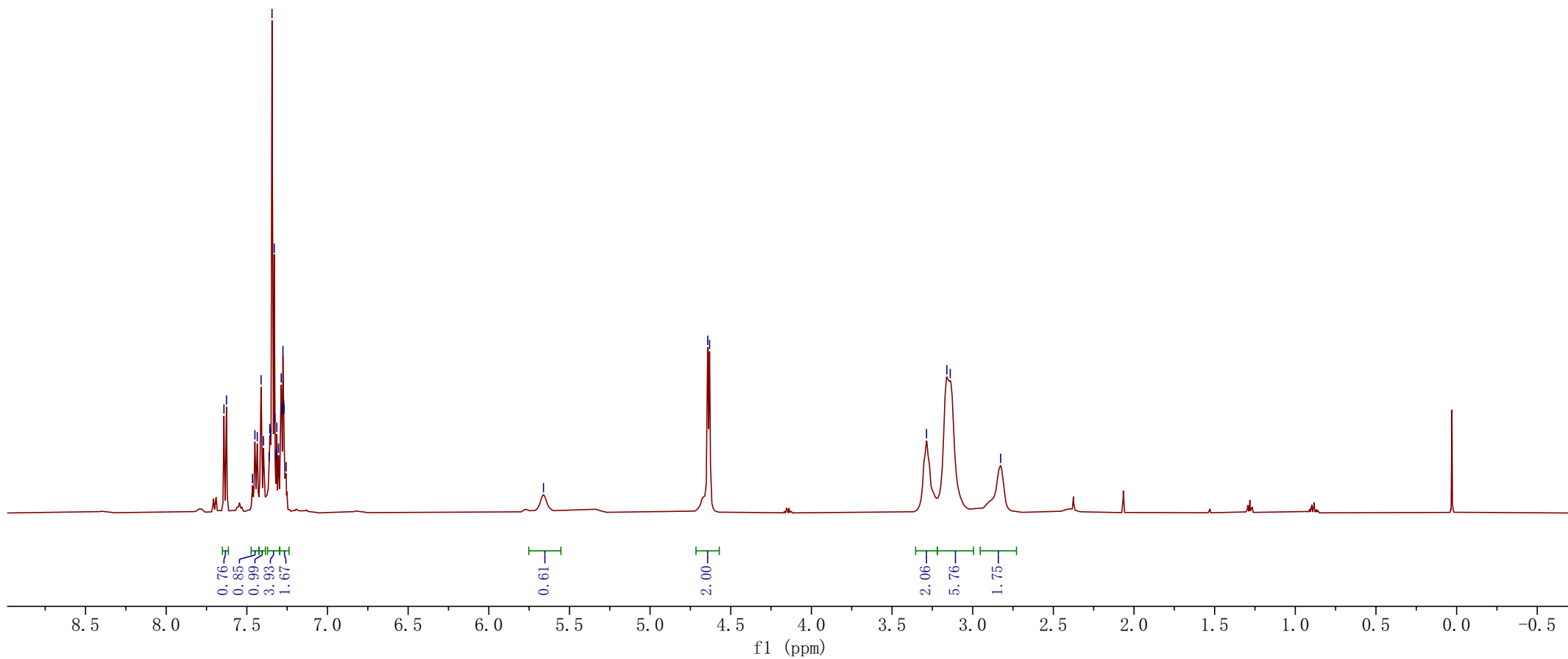
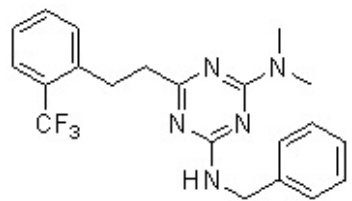
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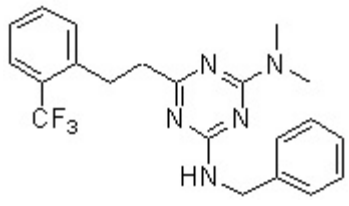
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