Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz, with either TMS (δ=0) or the signal for residual $CHCl_3$ in the $CDCl_3$ solvent (δ7.24) as internal standards. *J* values are reported in Hz. High resolution mass spectra were measured by using FAB method. Flash column chromatography was performed with Kieselgel 60 Art 9385 (230-400 mesh). All solvents used were purified according to standard procedures.

5-Bromo-3-[(triisopropylsilanyl)-ethynyl]-pyran-2-one (**2a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 1.14 – 1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 148.7, 147.1, 114.5, 101.9, 100.1, 98.7, 18.7, 11.3; FT-IR ($CHCl_3$) 3030, 2963, 2384, 2152, 1742, 1602, 1215 cm^{-1}; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_{16}H_{24}BrSiO_2$ 355.0729, found 355.0729.

5-Bromo-3-phenylethynyl-pyran-2-one (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 4H), 7.37 – 7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 149.2, 147.1, 132.4, 129.9, 128.9, 122.2, 115.0, 101.0, 98.4, 82.8; FT-IR ($CHCl_3$) 3139, 2922, 2206, 1736, 1604 cm^{-1}; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_{13}H_8BrO_2$ 274.9708, found 274.9707.

5-Bromo-3-(3-hydroxy-prop-1-ynyl)-pyran-2-one (4a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 4.50 (s, 2H), 2.34 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 159.4, 149.5, 148.1, 114.5, 101.1, 97.1, 52.1, 30.5; FT-IR ($CHCl_3$) 3429, 3078, 2924, 2855, 2375, 2098, 1944, 1828, 1743, 1602 cm^{-1}; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_8H_6BrO_3$ 228.9500, found 228.9500.

5-Bromo-3-(3-phenyl-prop-1-ynyl)-pyran-2-one (5a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.24 (m, 5H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 148.2, 146.6, 135.2, 128.5, 127.8, 126.8, 114.7, 100.3, 97.2, 75.5, 26.1; FT-IR ($CHCl_3$) 2923, 2403, 2256, 1735, 1601 cm^{-1}; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_{14}H_{10}BrO_2$ 288.9864, found 288.9864.

5-Bromo-3-hex-1-ynyl-pyran-2-one (6a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 2.45 (t, *J* = 6.8 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.50 – 1.41 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 147.7, 145.9, 114.9, 100.2, 100.1, 73.5, 30.2, 21.9, 19.4, 13.5; FT-IR ($CHCl_3$) 2958, 2931, 2229, 1743, 1603 cm^{-1}; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_{11}H_{12}BrO_2$ 255.0021, found 255.0021.

5-Bromo-3-cyclohex-1-enylethynyl-2-pyran-2-one (7a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.8 Hz, 1H), 7.43 (d, *J* = 2.8 Hz, 1H), 6.33 – 6.30 (m, 1H), 2.21 – 2.15 (m, 4H), 1.68 – 1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 158.4, 147.9, 145.5, 138.3, 119.8, 114.9, 100.4, 100.1, 79.8, 28.7, 26.0, 22.2, 21.4; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_{13}H_{12}BrO_2$ 279.0021, found 279.0020.

5-Bromo-3-octa-1,7-diynyl-pyran-2-one (8a): ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 7.53 (d, *J* = 2.8 Hz, 1H), 7.43 (d, *J* = 2.8 Hz, 1H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.25 (td, J_1 = 7.0, J_2 = 2.8 Hz, 2H), 1.97 (t, *J* = 2.8 Hz, 1H), 1.75 – 1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 158.8, 148.0, 146.3, 114.9, 100.3, 99.5, 83.9, 74.0, 68.7, 27.6, 27.2, 19.4, 18.1; FT-IR ($CHCl_3$) 2944, 2229, 1738, 1603 cm^{-1}; HRMS (FAB) m/z $(M+1)^+$ calcd for $C_{13}H_{12}BrO_2$ 279.0021, found 279.0023.

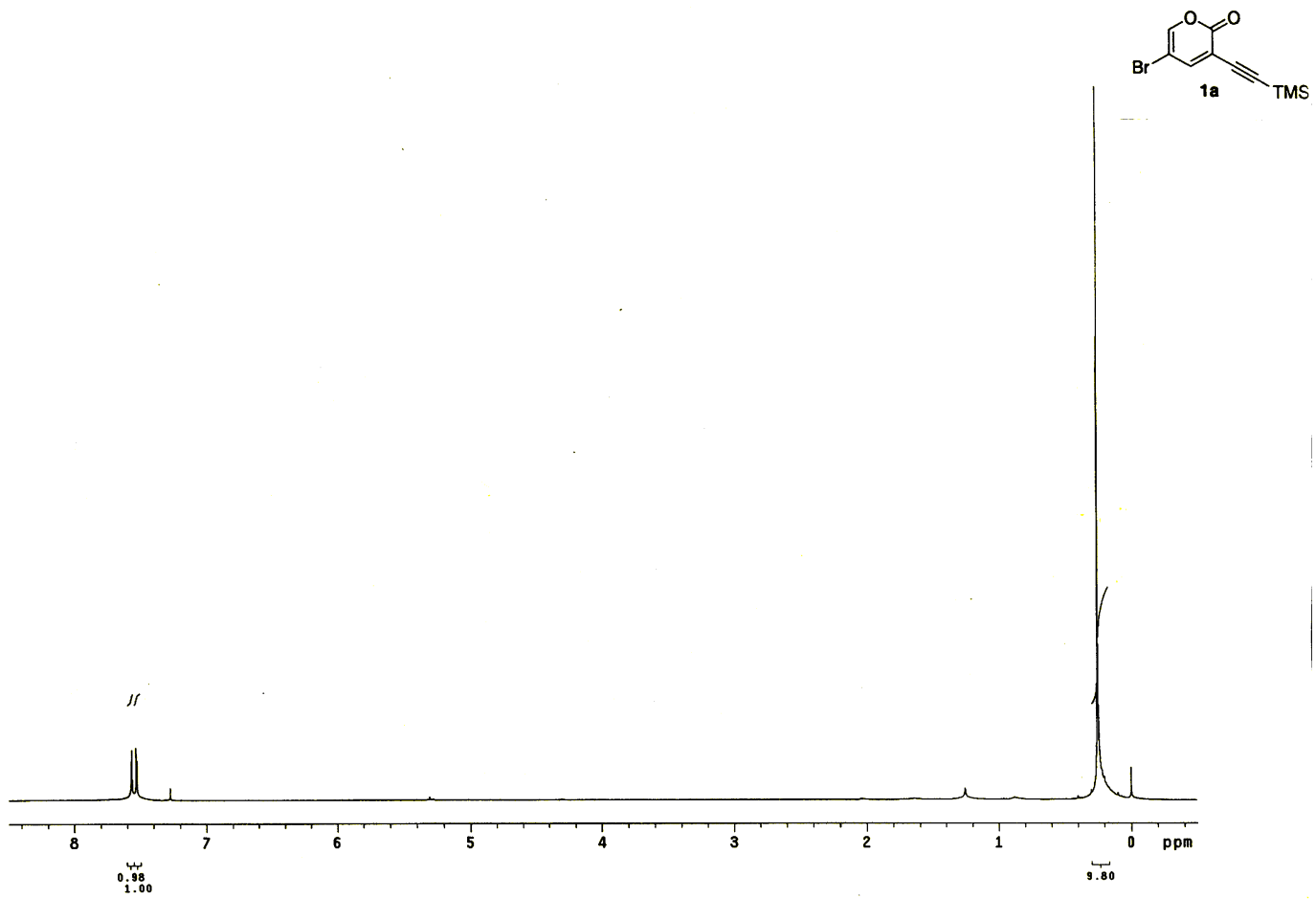
3-Bromo-5-(trimethylstannyl)-2H-pyran-2-one (**9**): To a solution of 3,5-dibromo-2-pyrone (30 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (5 mol%) in 1 mL of toluene was added HMDT (50 mg, 1.3 equiv.). After 1h at 80^{o}C, the reaction mixture was filtered through a thin layer of silica gel with EtOAc. The filtrate was concentrated and purified by flash column chromatography (30: 1 hexanes: EtOAc) to give the 3-(trimethylstannyl)-2-pyrone 9 in 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 7.49 (d, *J* = 2.4 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 162.5, 152.7, 149.0, 134.7, 102.1, -9.1.

3, 5-Bis-(trimethylstannyl)-2H-pyran-2-one (**10**): The same procedure for 9 was used except the solvent (THF) and equivalency of HMDT (2.6 equiv.). Isolated yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 7.29 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 0.30 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 164.6, 155.7, 154.4, 132.6, 113.6, -9.3.

5-[(Triisopropylsilanyl)-ethynyl]-3-trimethylsilanylethynyl-pyran-2-one (11): To a mixture of **1a** (23 mg, 0.085 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (5 mol %) and 1 mL of 1,4-dioxane were added Et_3N (1.2 eq.) and triisopropylsilyl acetylene (2 eq.) at RT. After stirring for 2h at RT under Ar, the reaction mixture was filtered through a plug of celite with ether. The filtrate was washed with H_2O, dried over $MgSO_4$, concentrated and chromatographed (80:1 hexanes: EtOAc) to give Compound **9** (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 2.4 Hz, 1H), 1.093-1.090 (m, 21H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.2, 147.3, 112.6, 104.9, 103.2, 97.5, 96.9, 95.2, 18.6, 11.2, -0.2; FT-IR ($CHCl_3$) 2944, 2865, 2158, 1753, 1618, 1537, 1463 cm^{-1}; HRMS (CI) m/z $(M+1)^+$ calcd for $C_{21}H_{33}Si_2O_2$ 373.2019, found 373.2021.

3-Ethynyl-5-[(triisopropylsilanyl)-ethynyl]-pyran-2-one (12): To a solution of **9a** (50 mg, 0.134 mmol) in 3 mL of mixture of THF/acetic acid (10:1 v/v) was slowly added 0.13 mL of 1 M TBAF solution in THF (1 eq.) at rt. The mixture was stirred at RT for 2 hr, whereupon water was added to complete the reaction. The organic layer was dried over $MgSO_4$ after usual workup. After removal of the solvent, the residue was purified by flash chromatography leading to **10** in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 3.38 (s, 1H), 1.13-1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 158.5, 154.6, 148.1, 111.8, 104.9, 97.3, 95.7, 84.7, 76.3, 18.7, 11.2; FT-IR ($CHCl_3$) 2944, 2866, 2360, 3161, 1746, 1463 cm^{-1}; HRMS (CI) m/z $(M+1)^+$ calcd for $C_{18}H_{25}SiO_2$ 301.1625, found 301.1617.

3-Ethynyl-5-[(triisopropylsilanyl)-ethynyl]-pyran-2-one dimer (13): A solution of copper triflate benzene complex (16.2 mg, 0.6 eq.) in 1 mL 1,4-dioxane was added to a stirred suspension of $CaCO_3$ (21.5mg, 4 eq.) and starting **1a** (20 mg, 0.0537mmol) in 2 mL 1,4-dioxane at 80°C under Ar atmosphere. The reaction mixture was heated for 4 hr at the same temperature, cooled to RT and quenched with NH_4Cl (aq.). The aqueous layer was extracted with EtOAc and the organic layer was collected, then dried over $MgSO_4$. The residue was purified by flash chromatography (hexanes : EtOAc = 100 : 1) to allow the dimeric compound **11** in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.4 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 1.13-1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 157.9, 155.1, 149.3, 111.4, 105.3, 97.0, 96.1, 80.2, 76.7, 18.7, 11.3; FT-IR ($CHCl_3$) 2942.8, 2278, 1748 cm^{-1}; HRMS (CI) m/z $(M+1)^+$ calcd for $C_{36}H_{47}Si_2O_4$ 599.3014, found 599.3011.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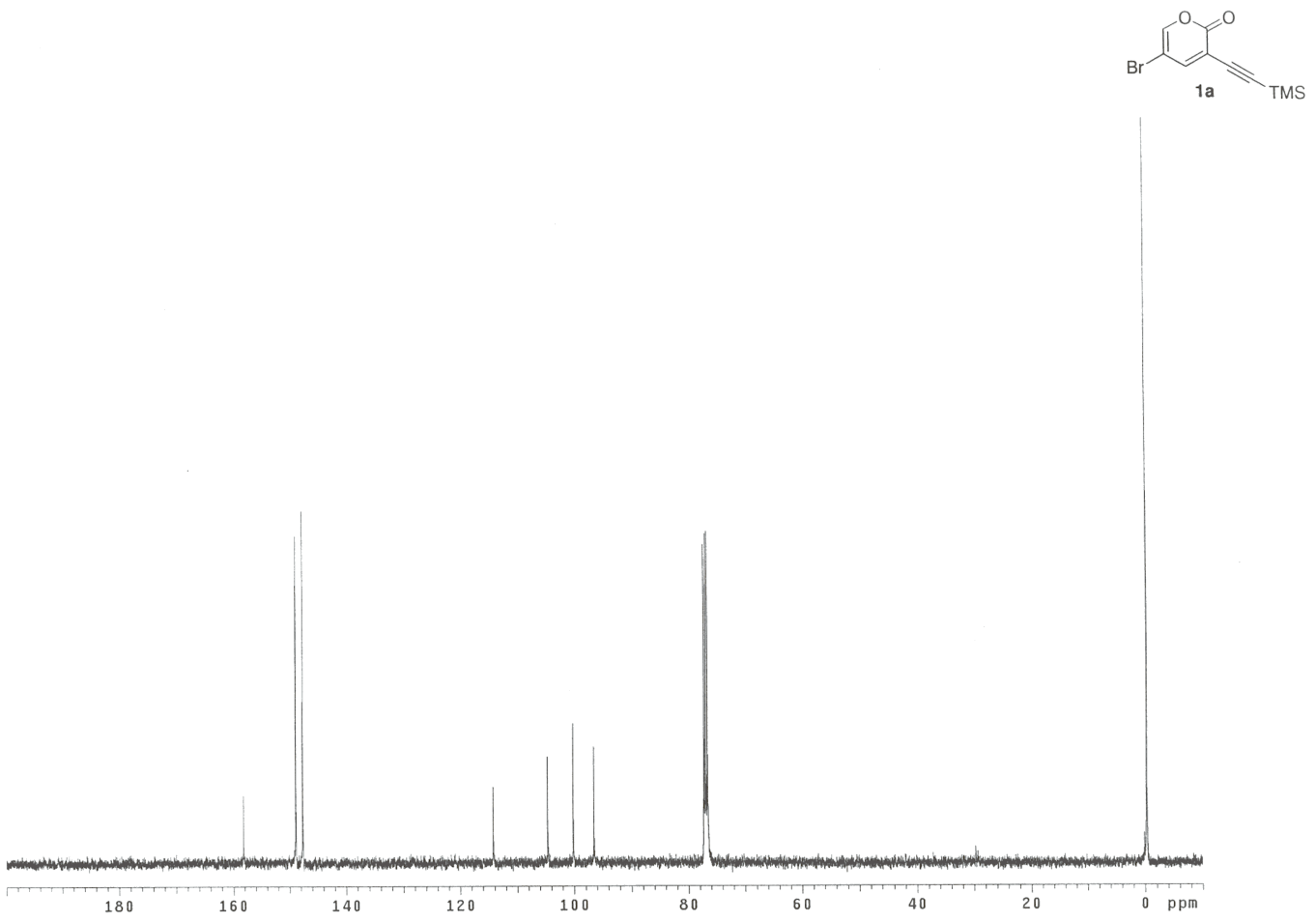
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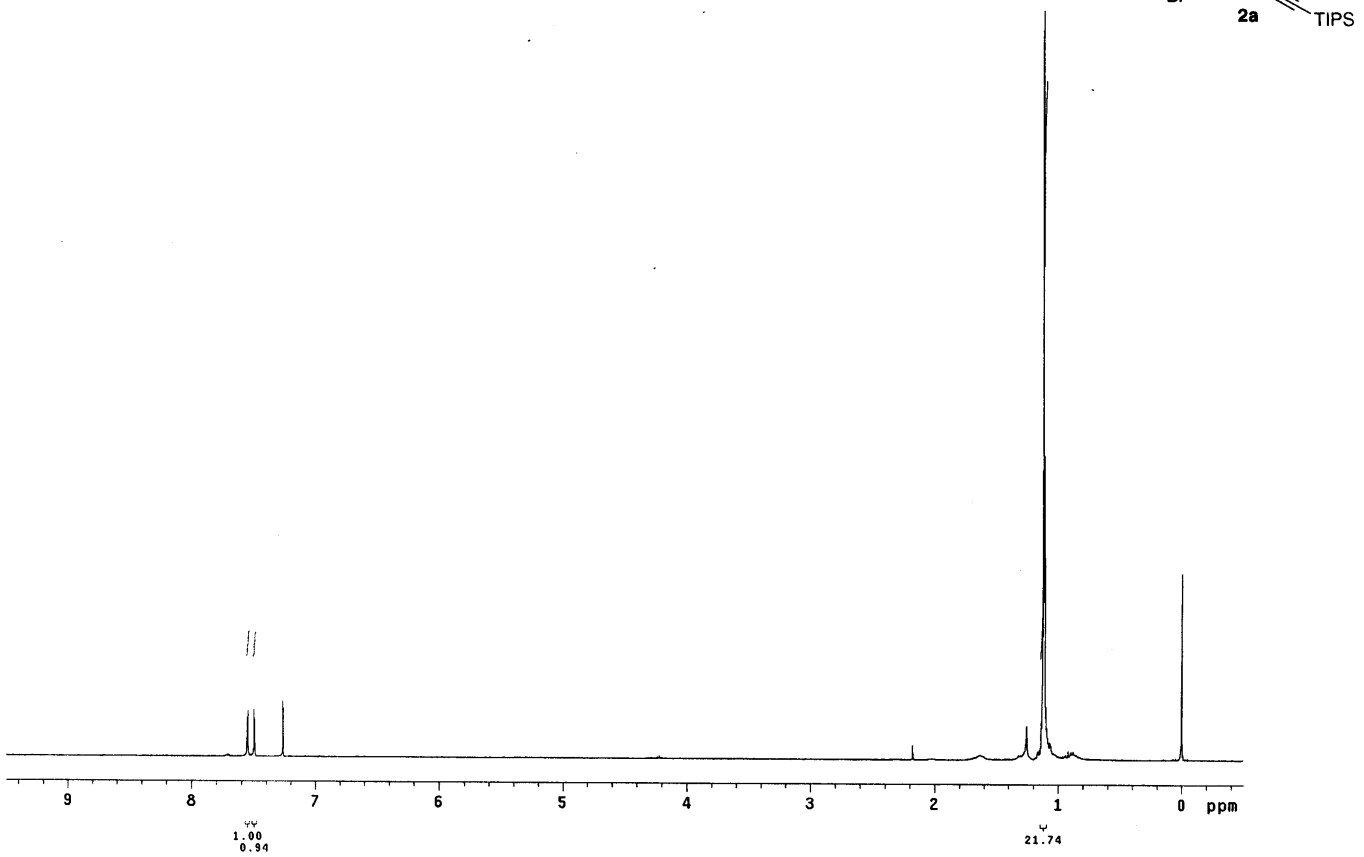
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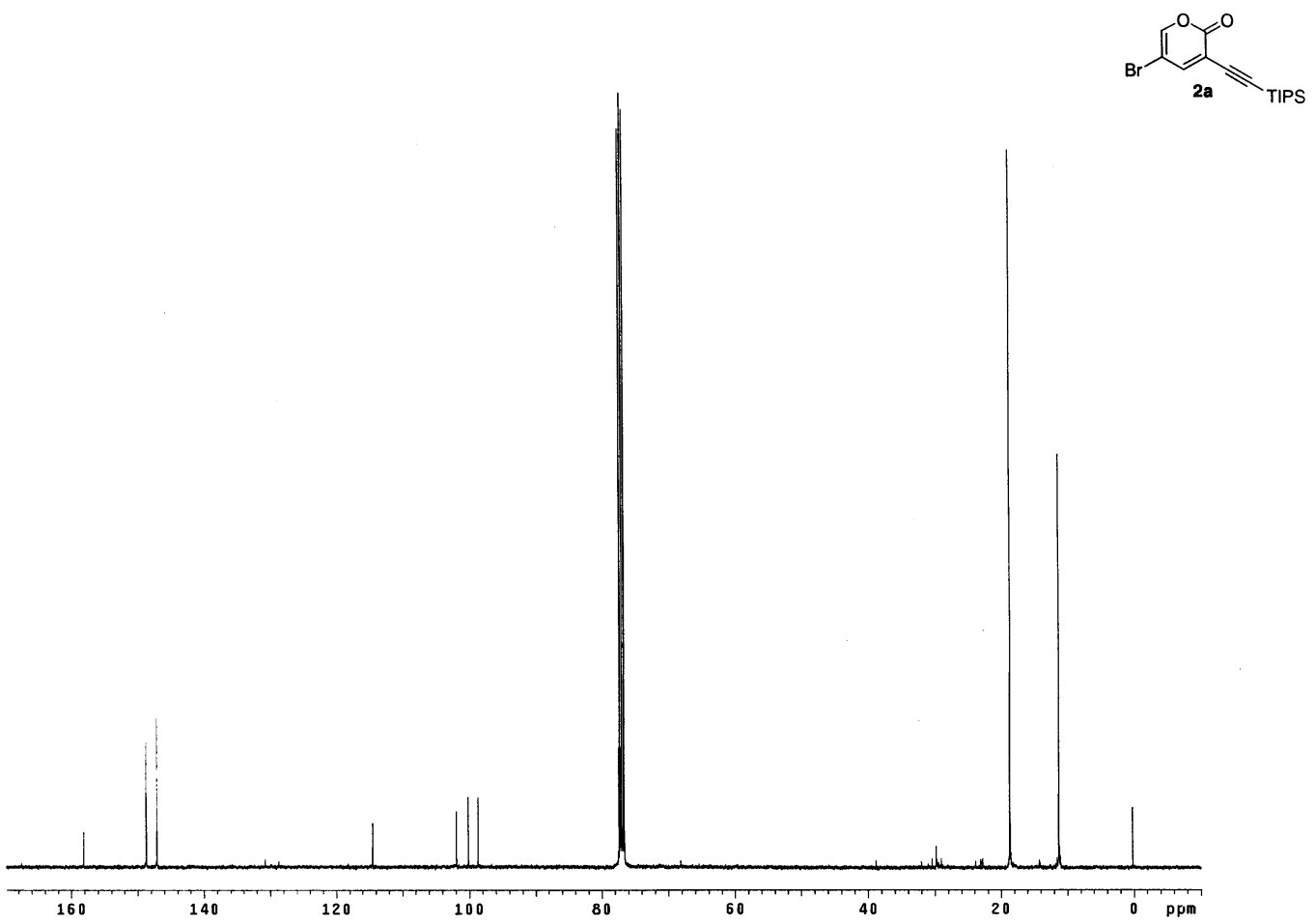
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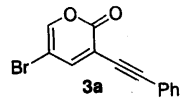

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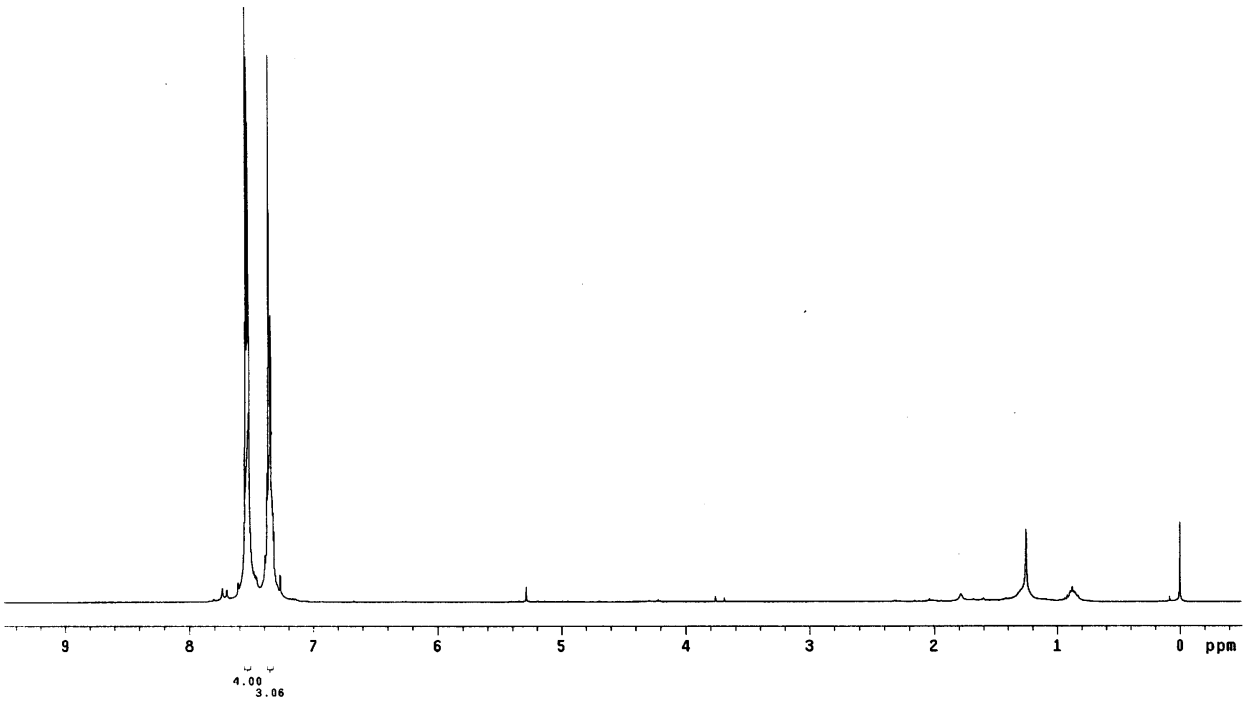

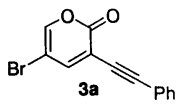

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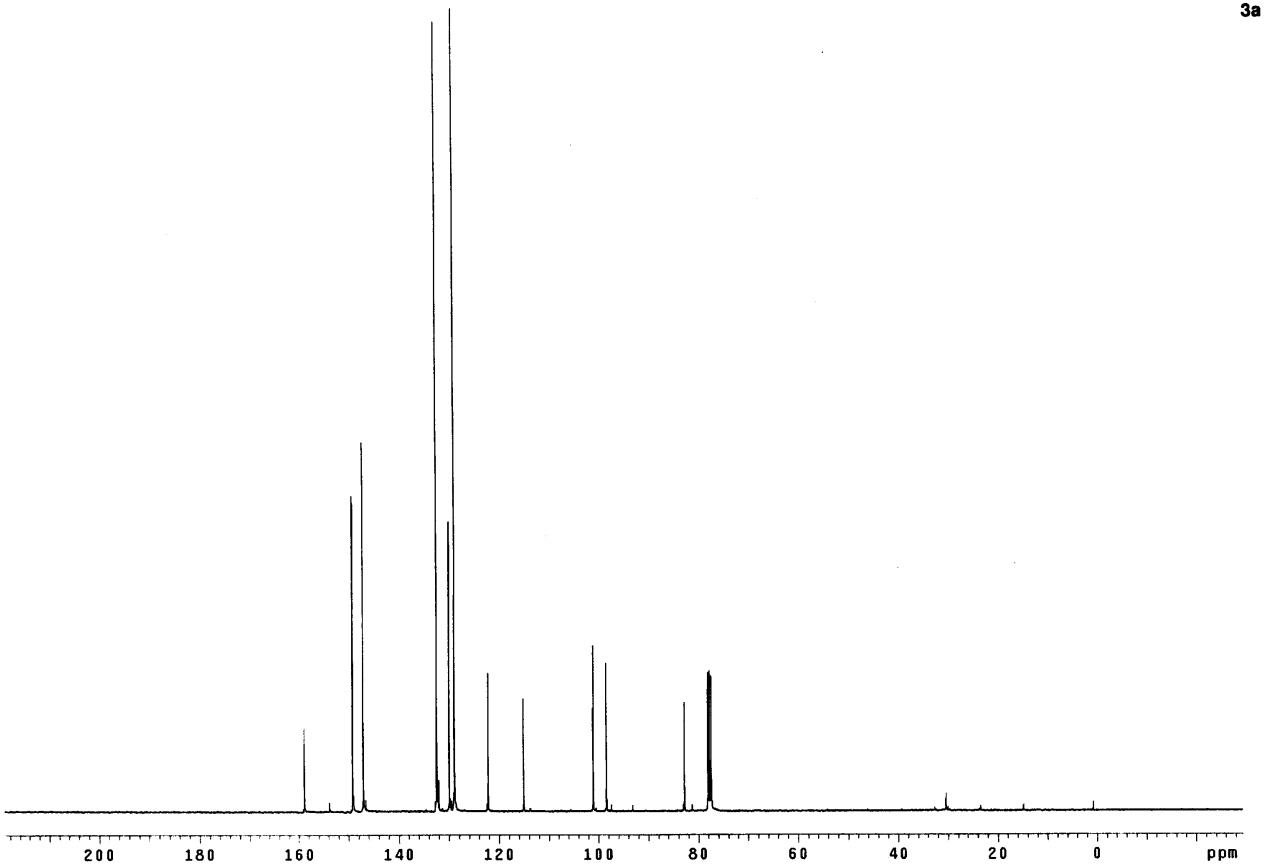

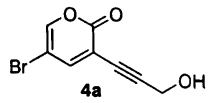

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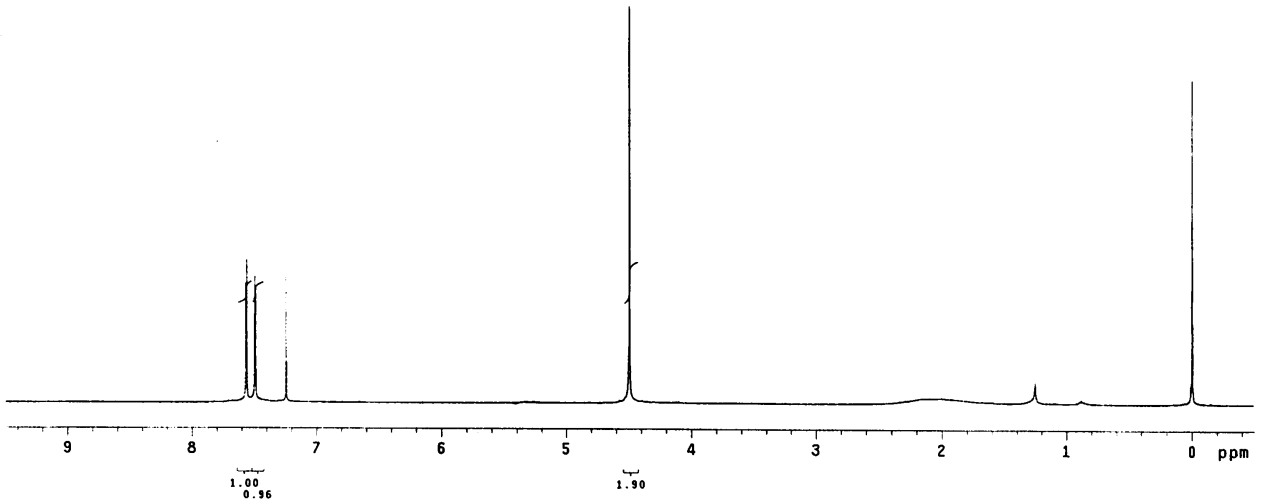

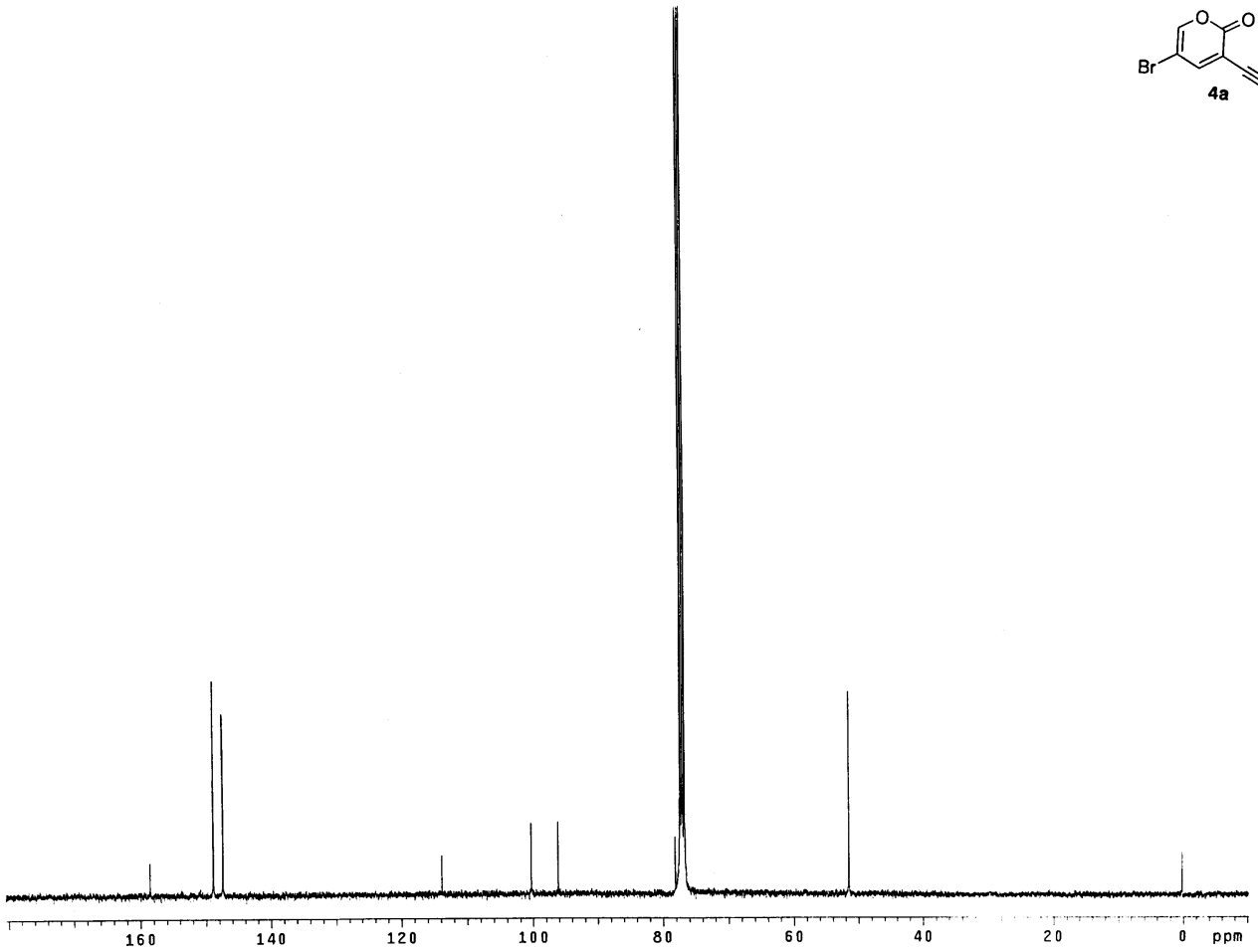
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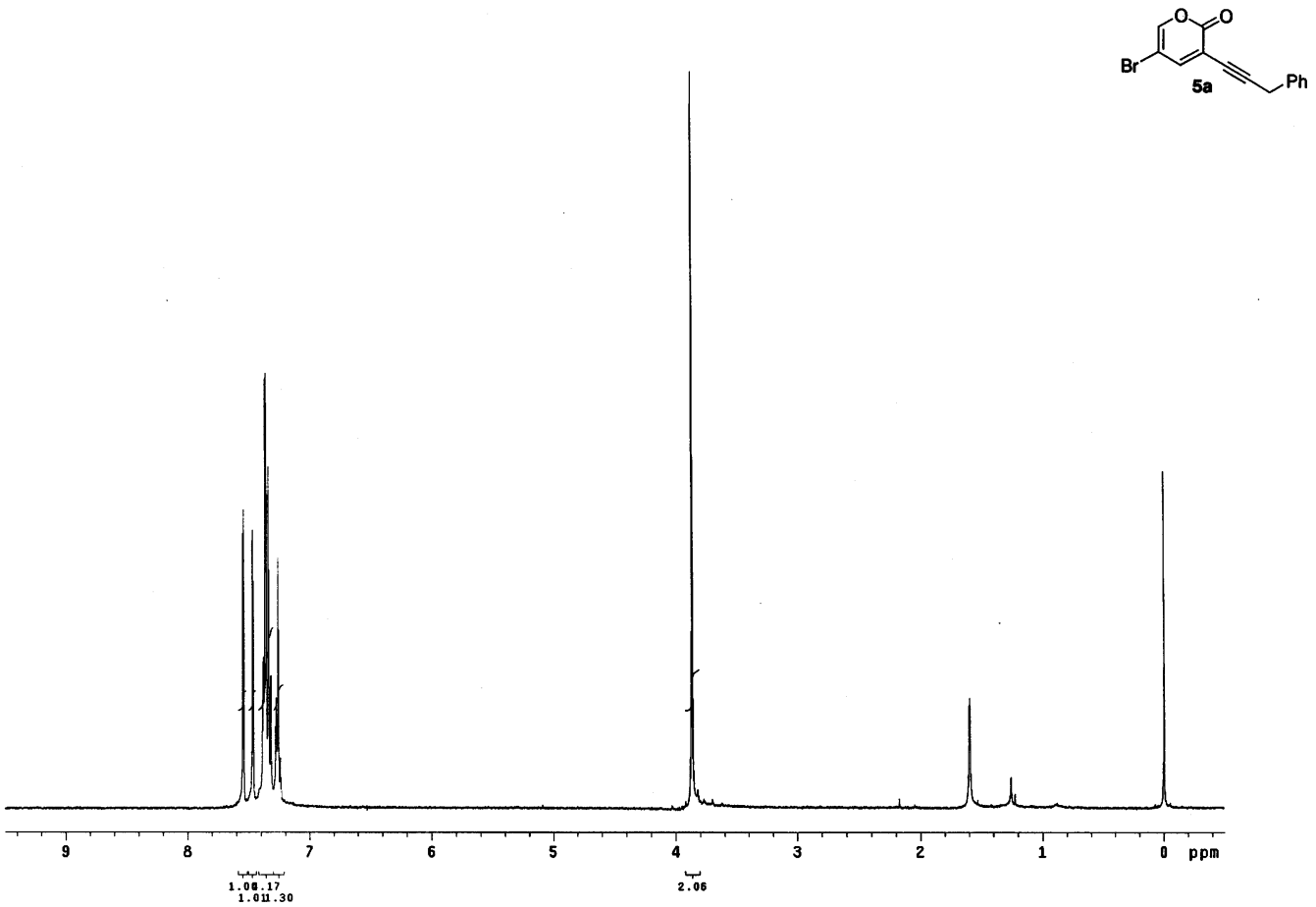
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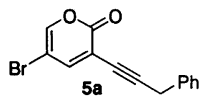

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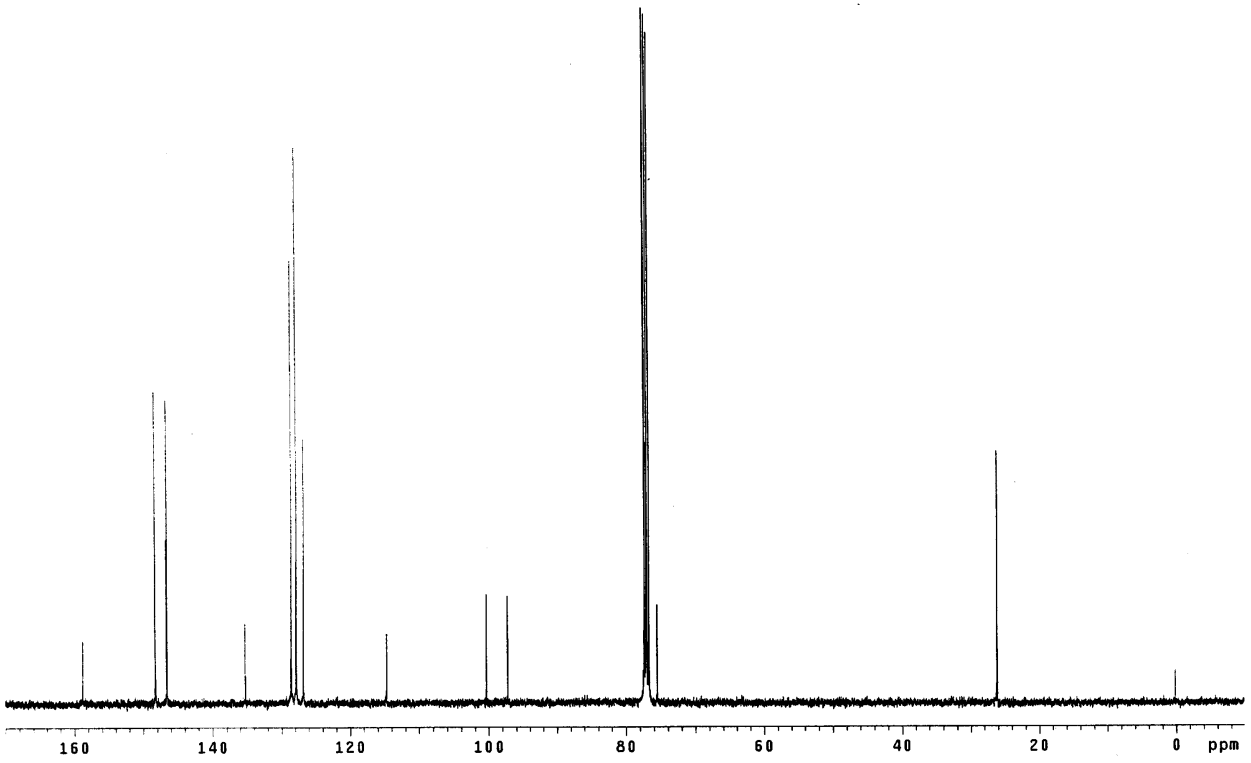

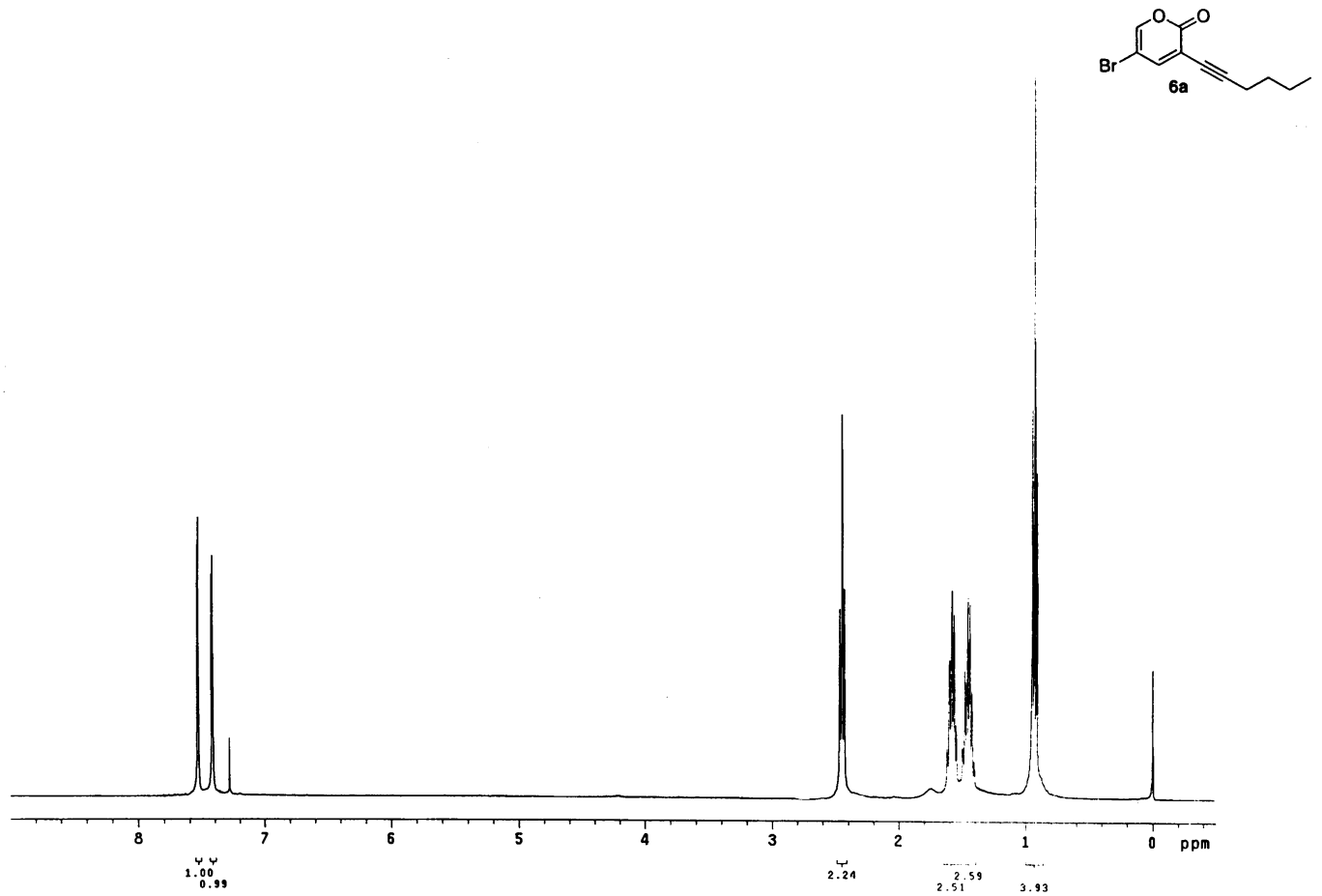
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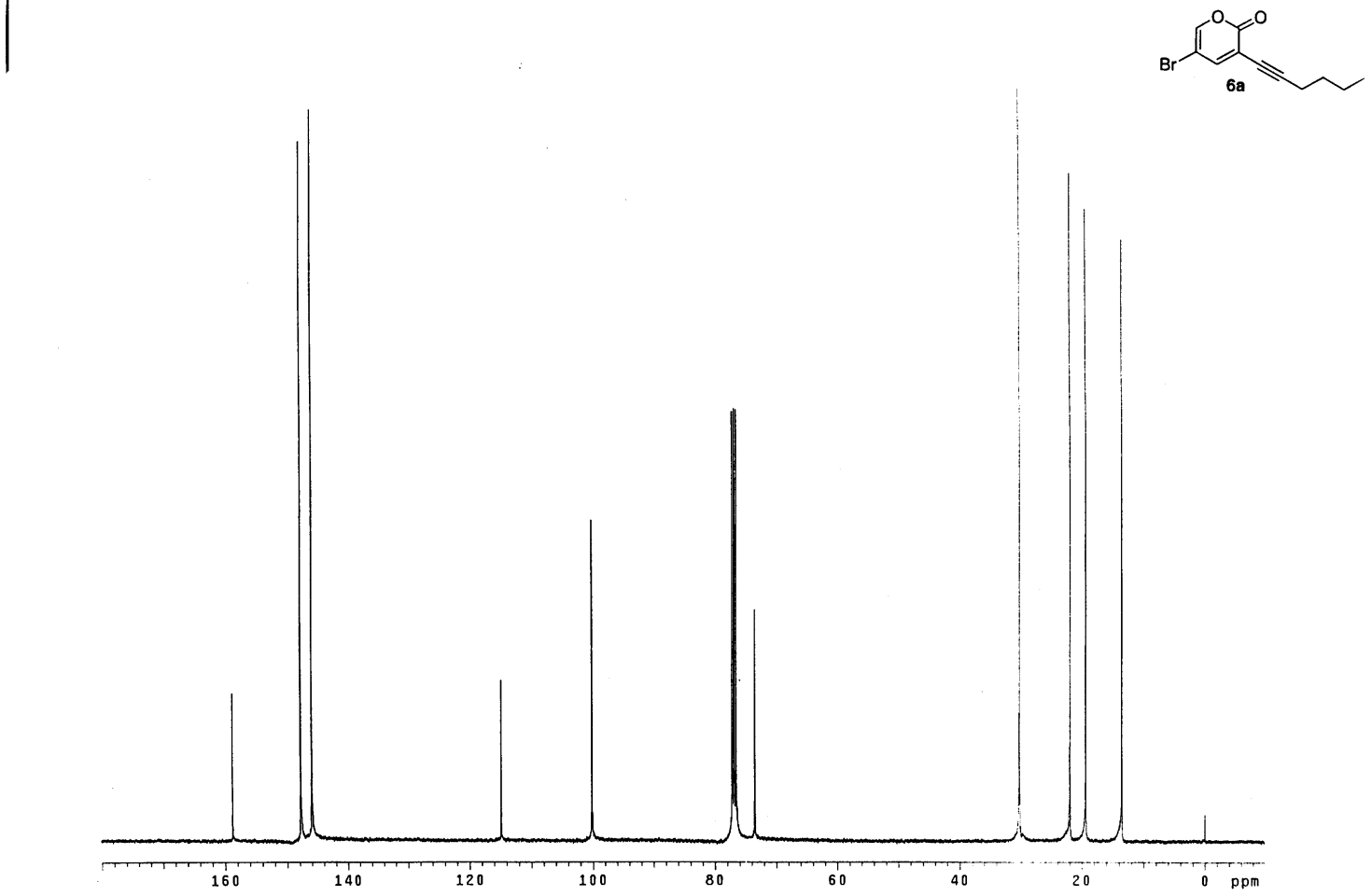
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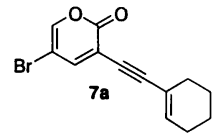

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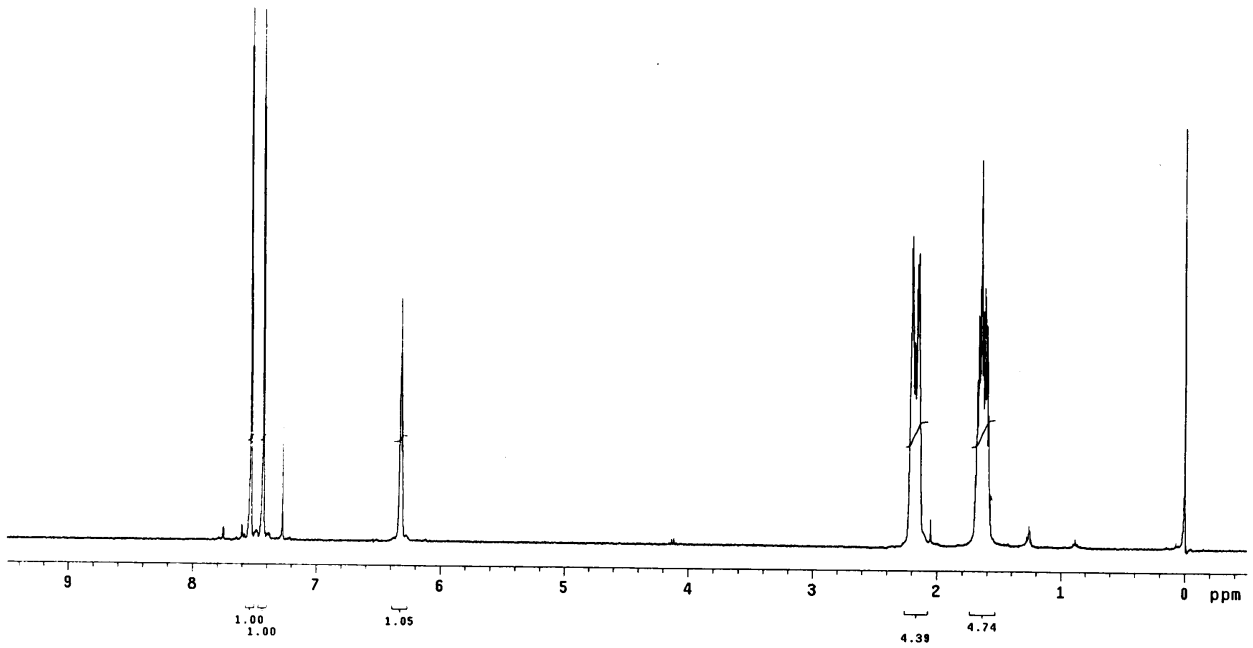

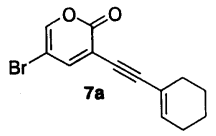

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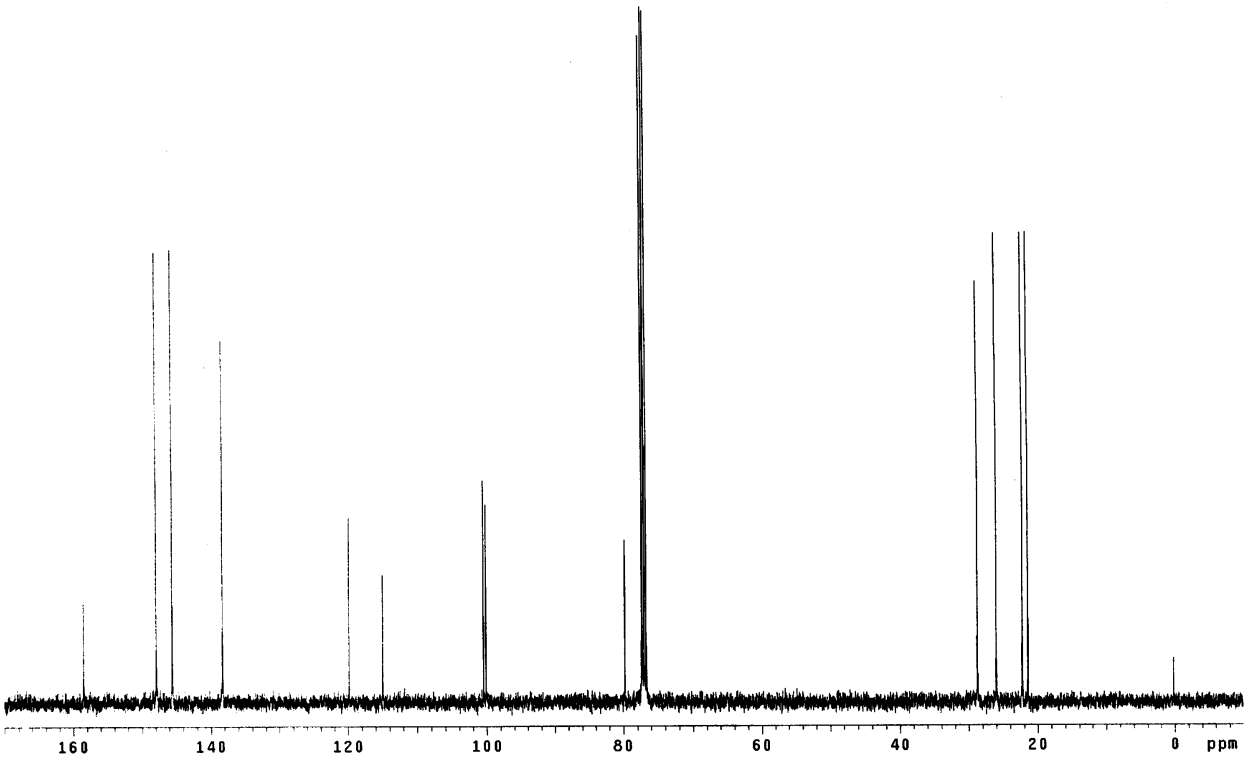

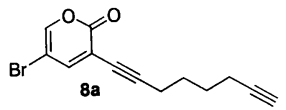

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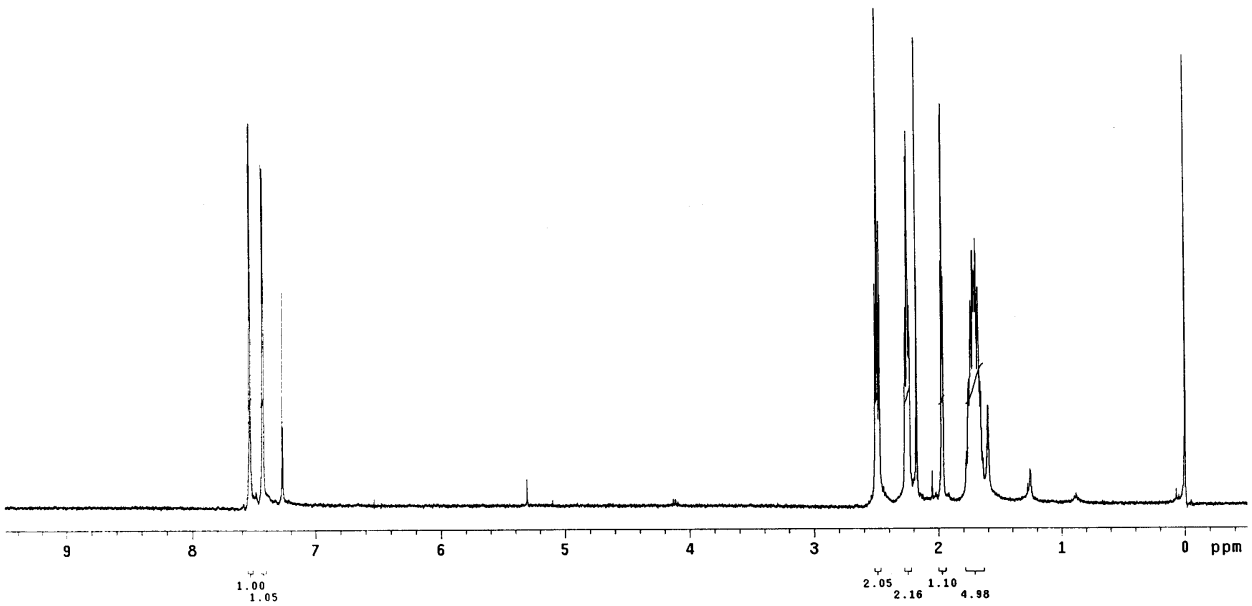

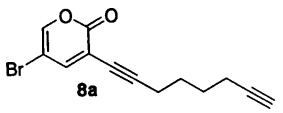

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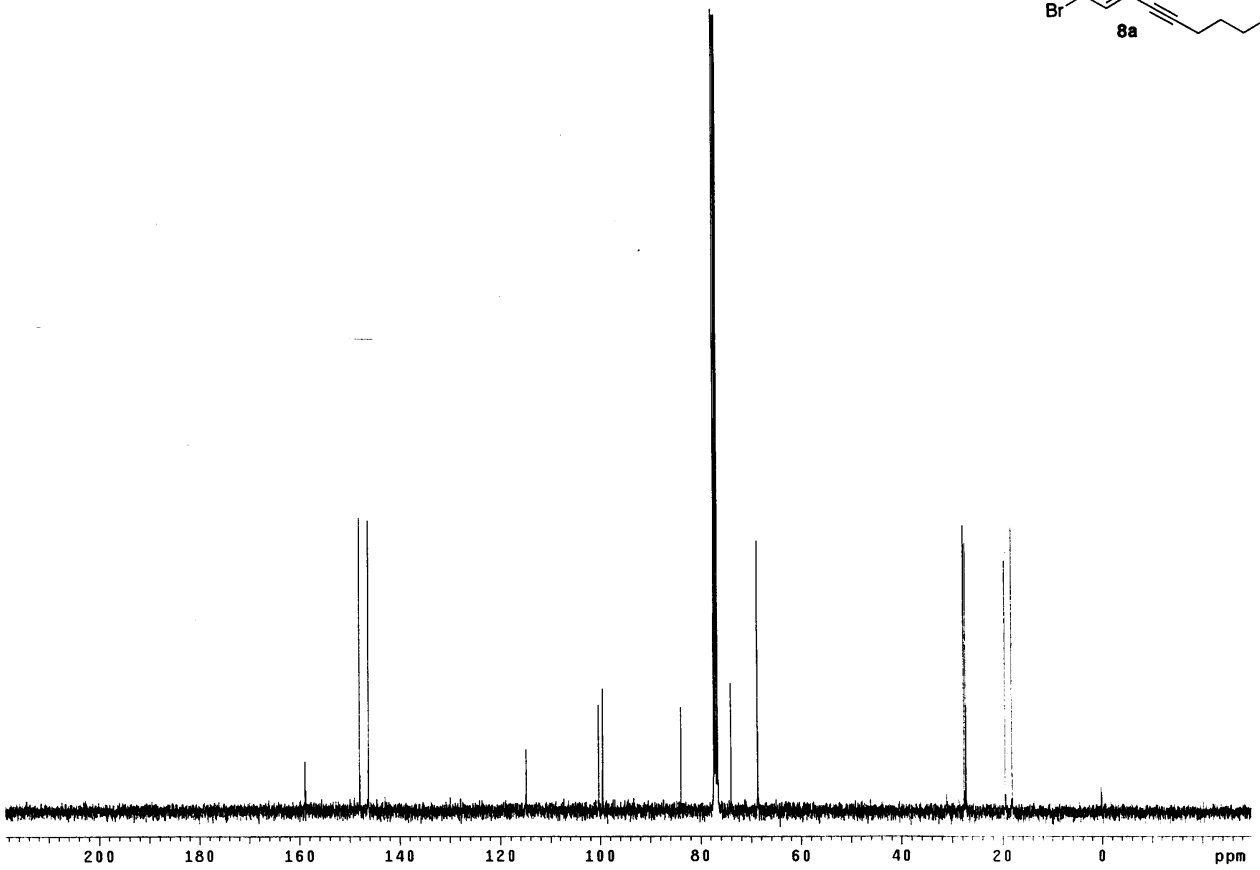

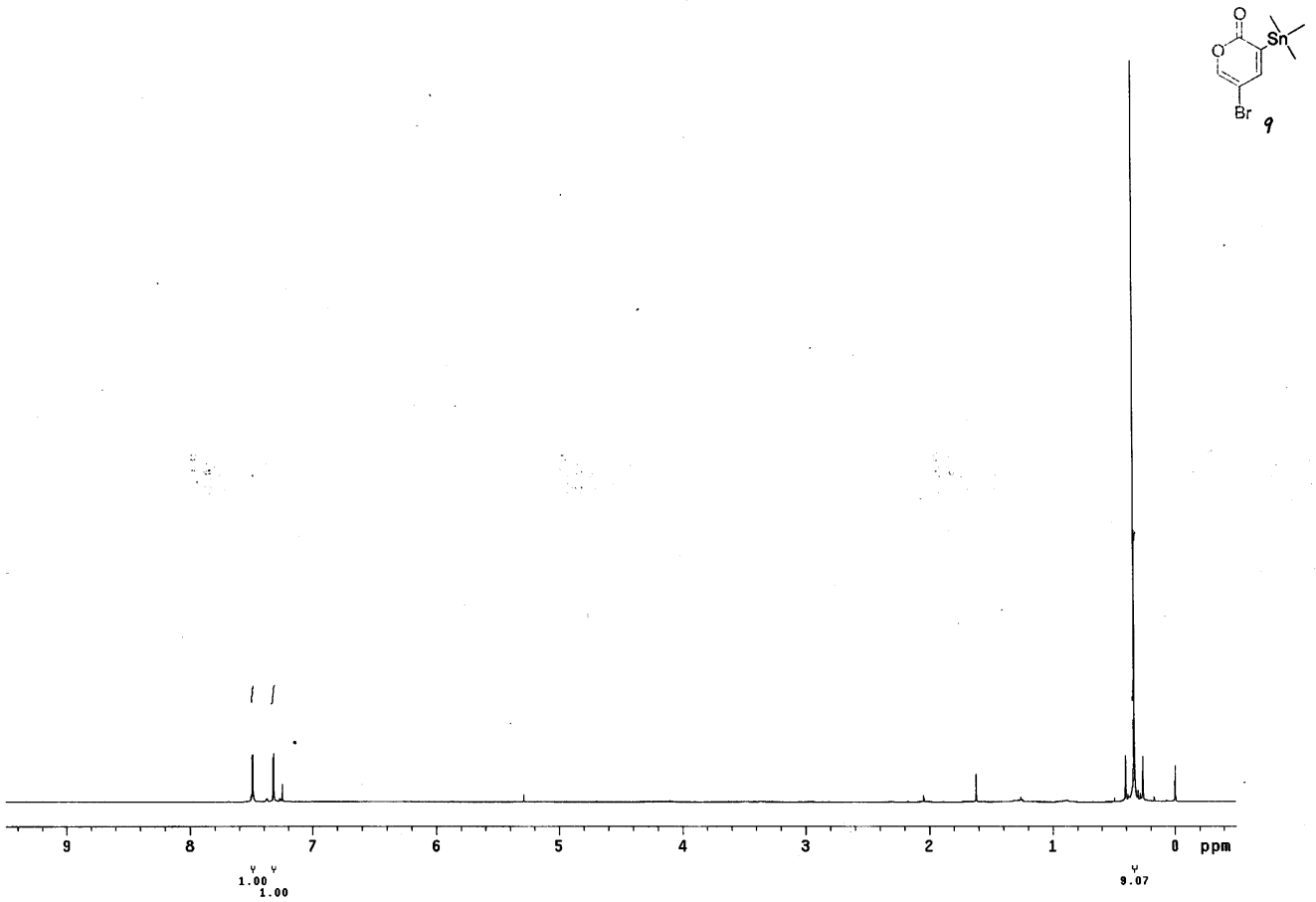
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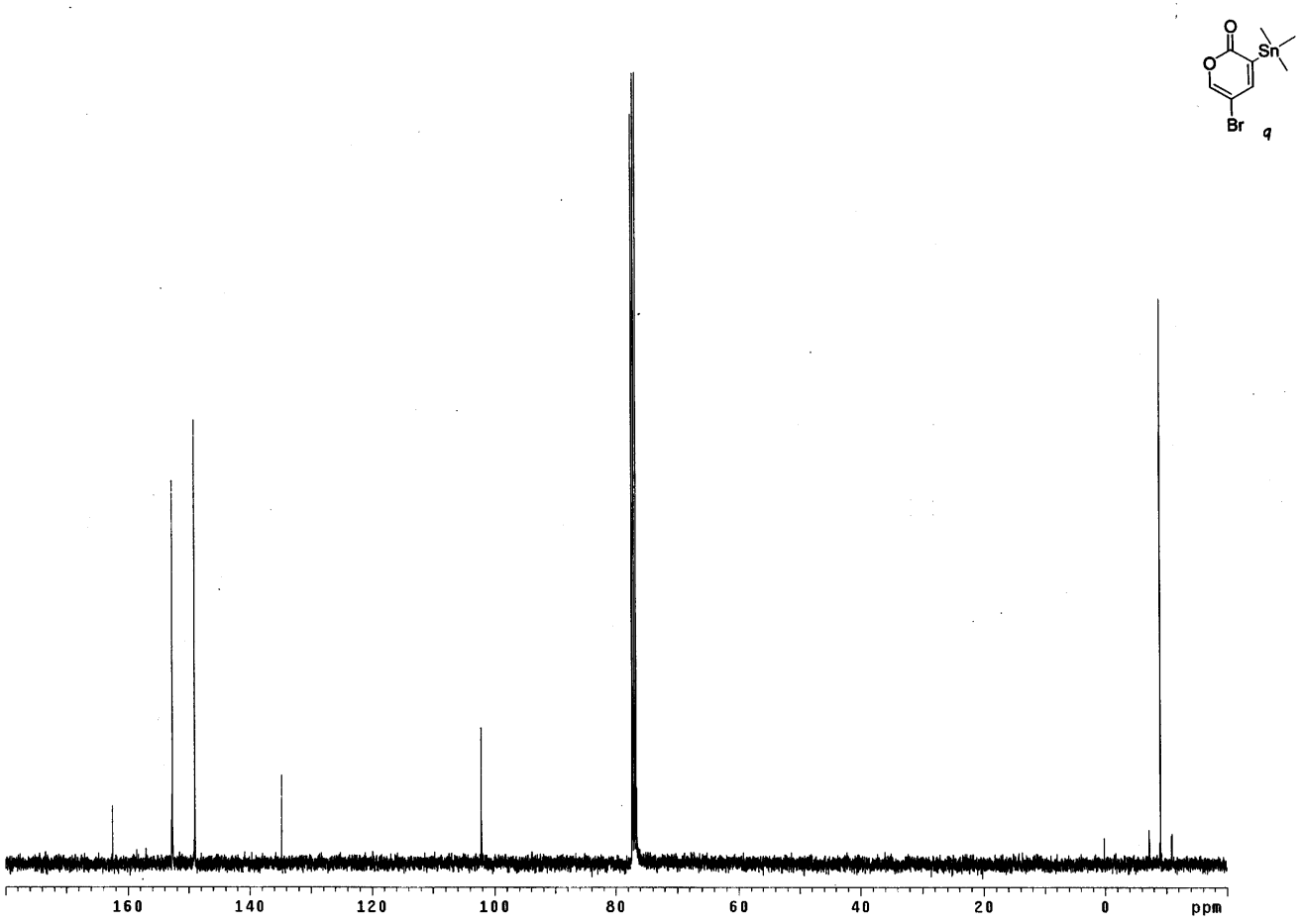
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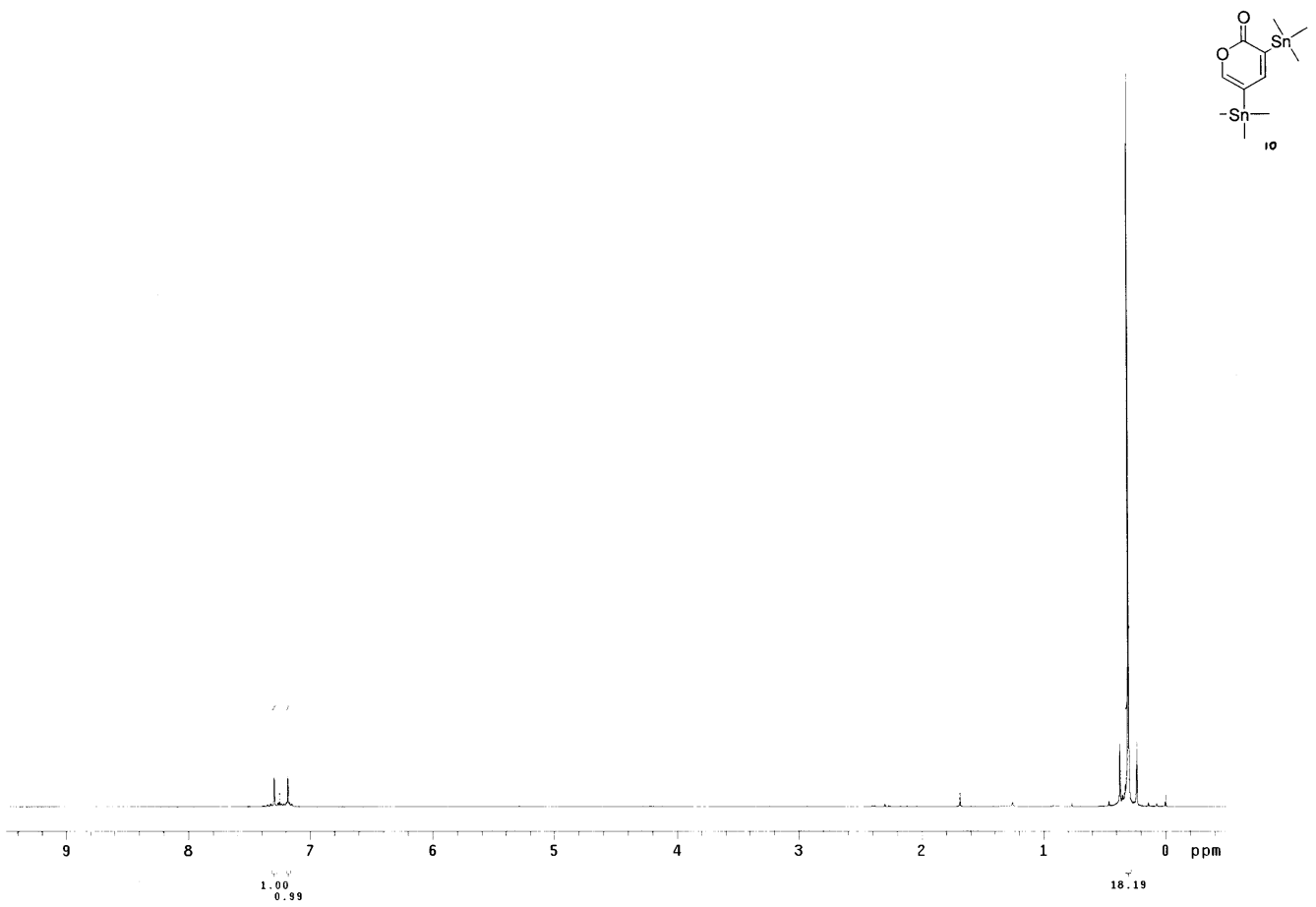
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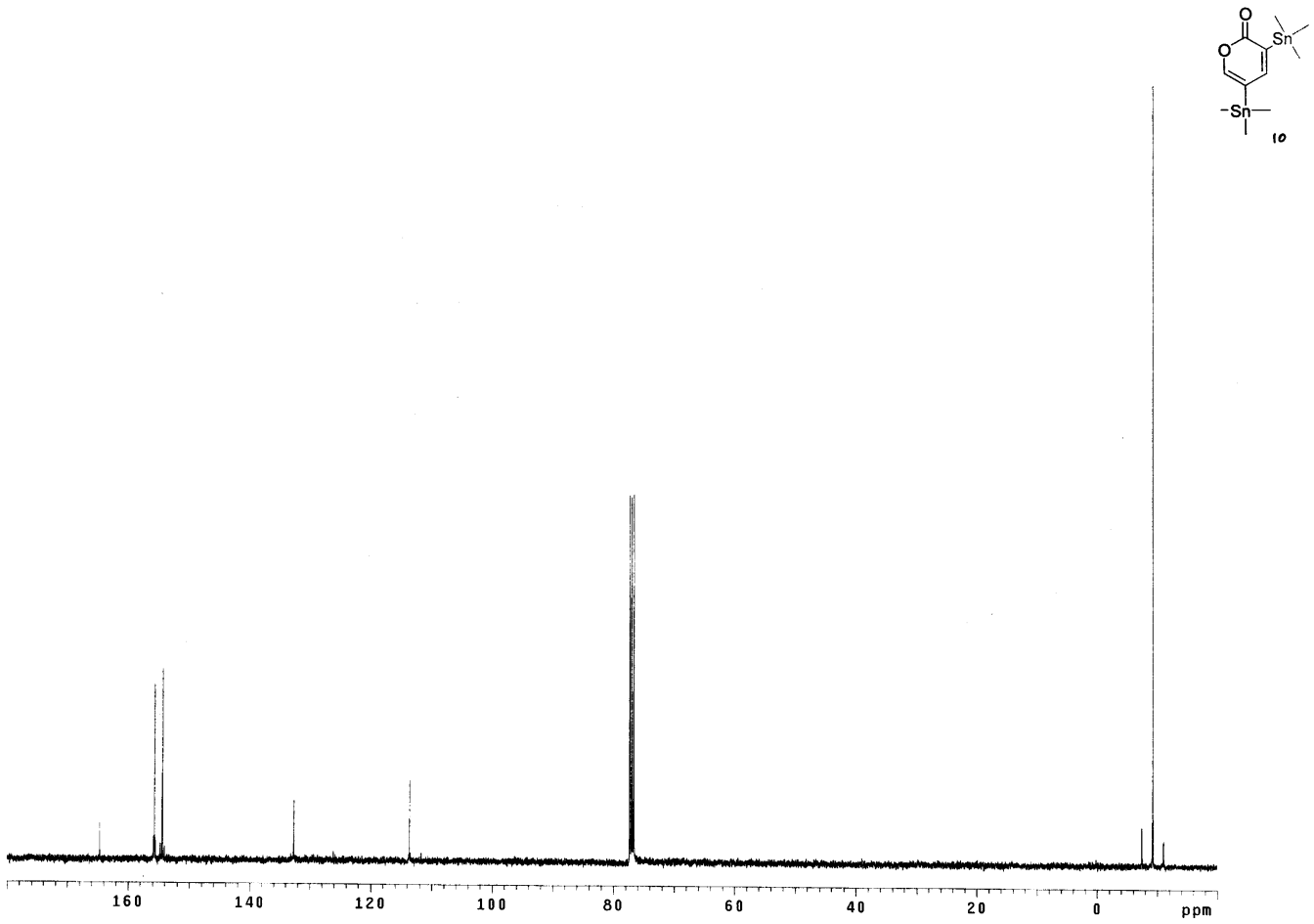
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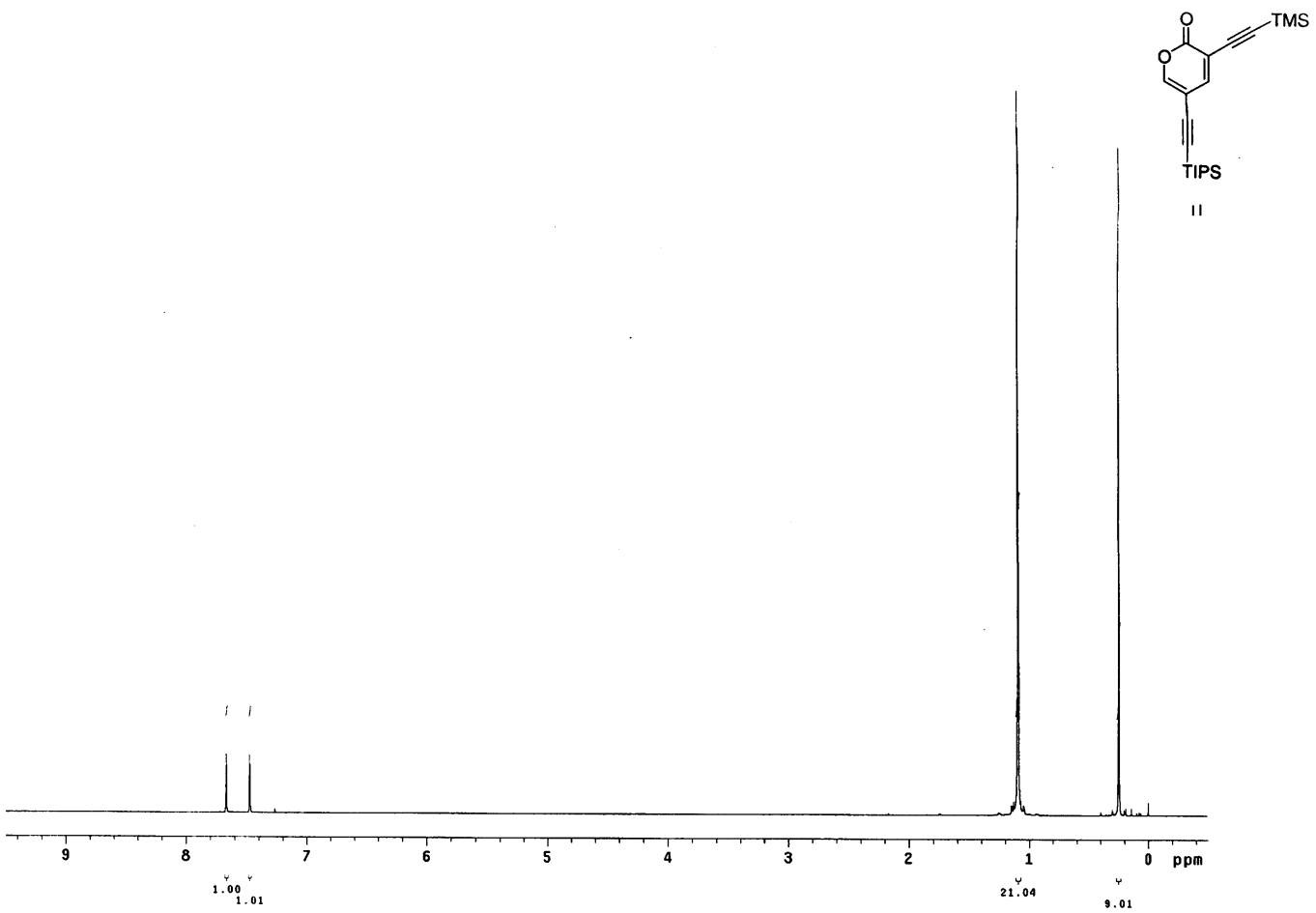
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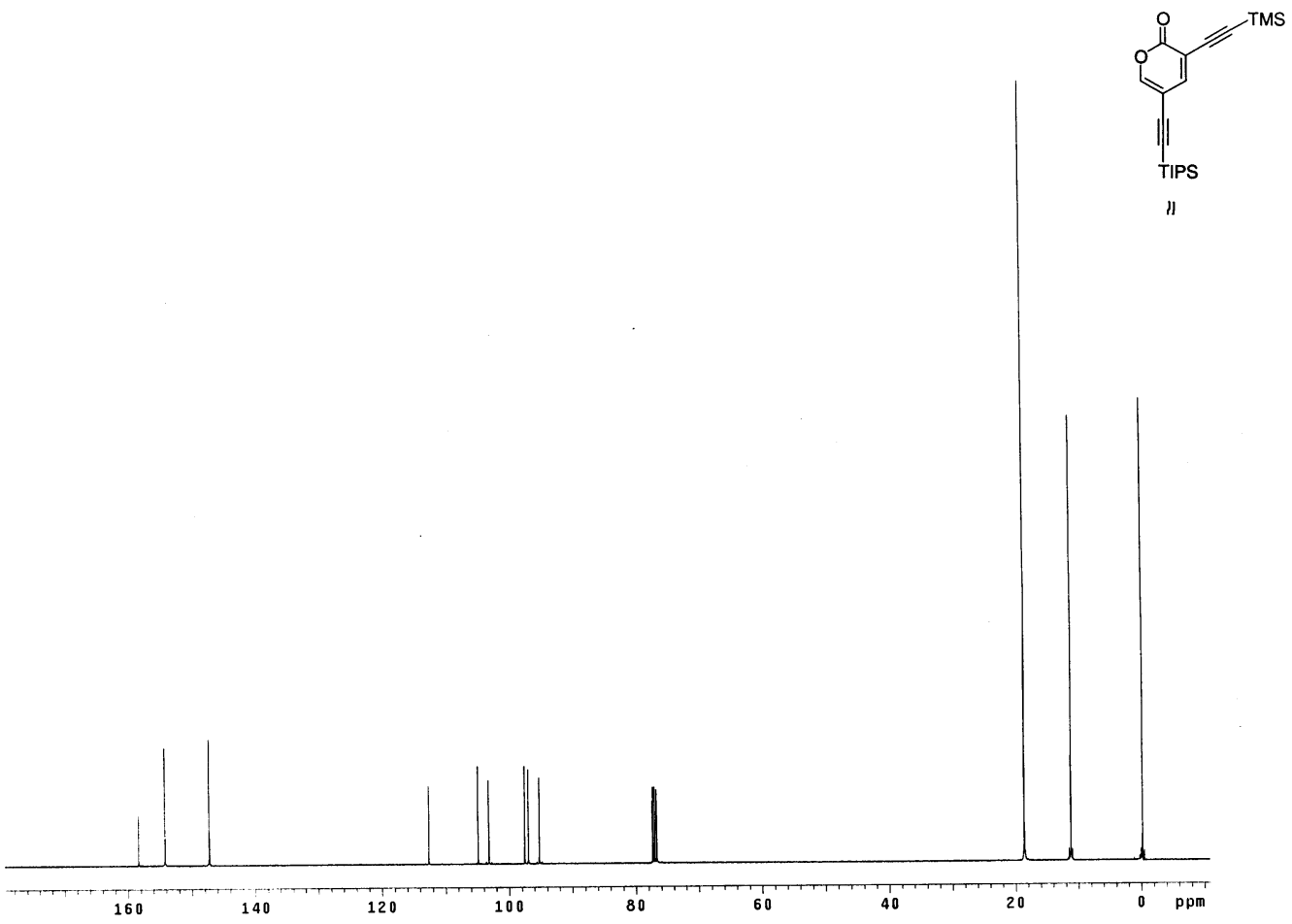
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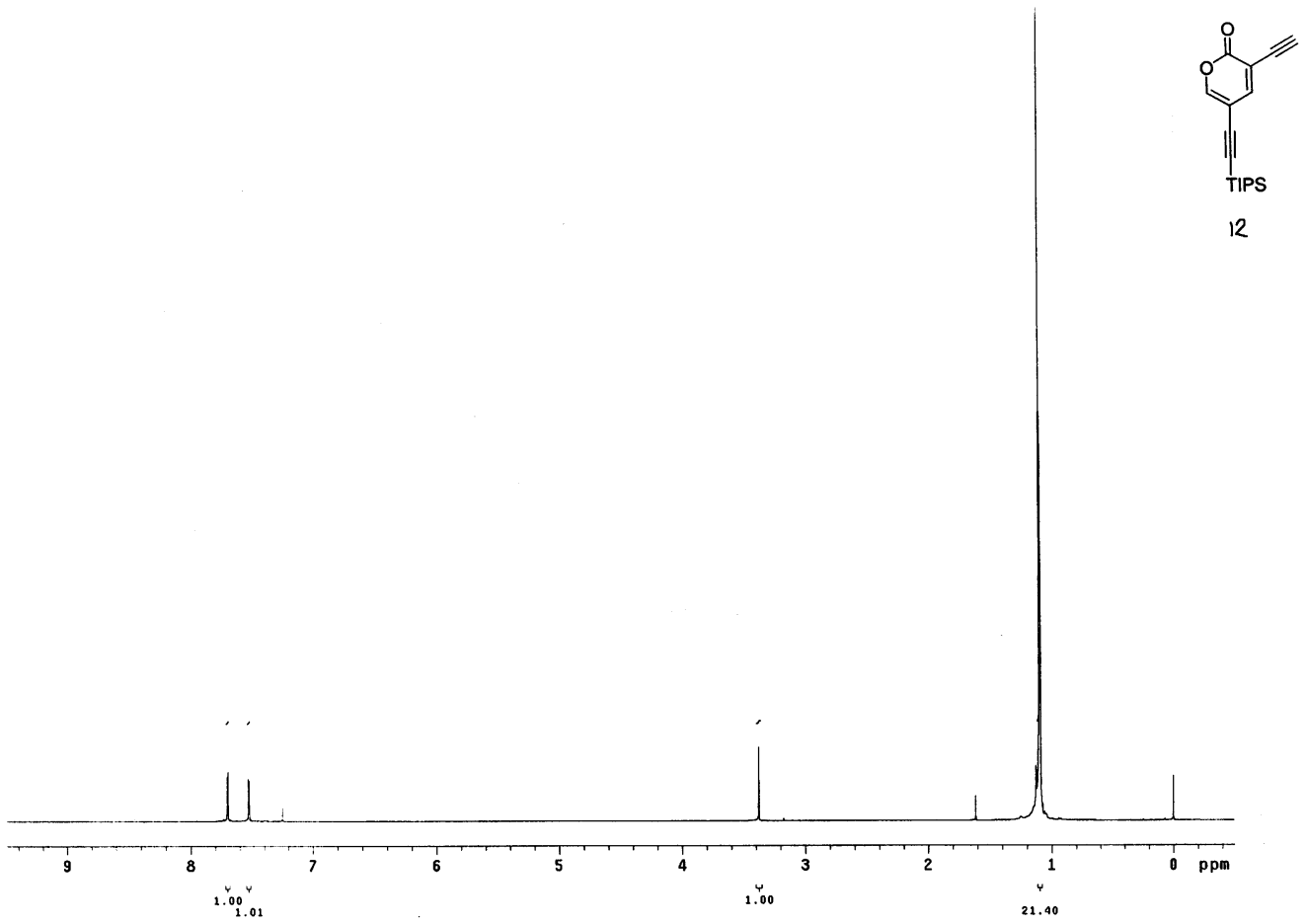
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O
TIPS
12
9
8
7
6
5
4
3
2
1
0
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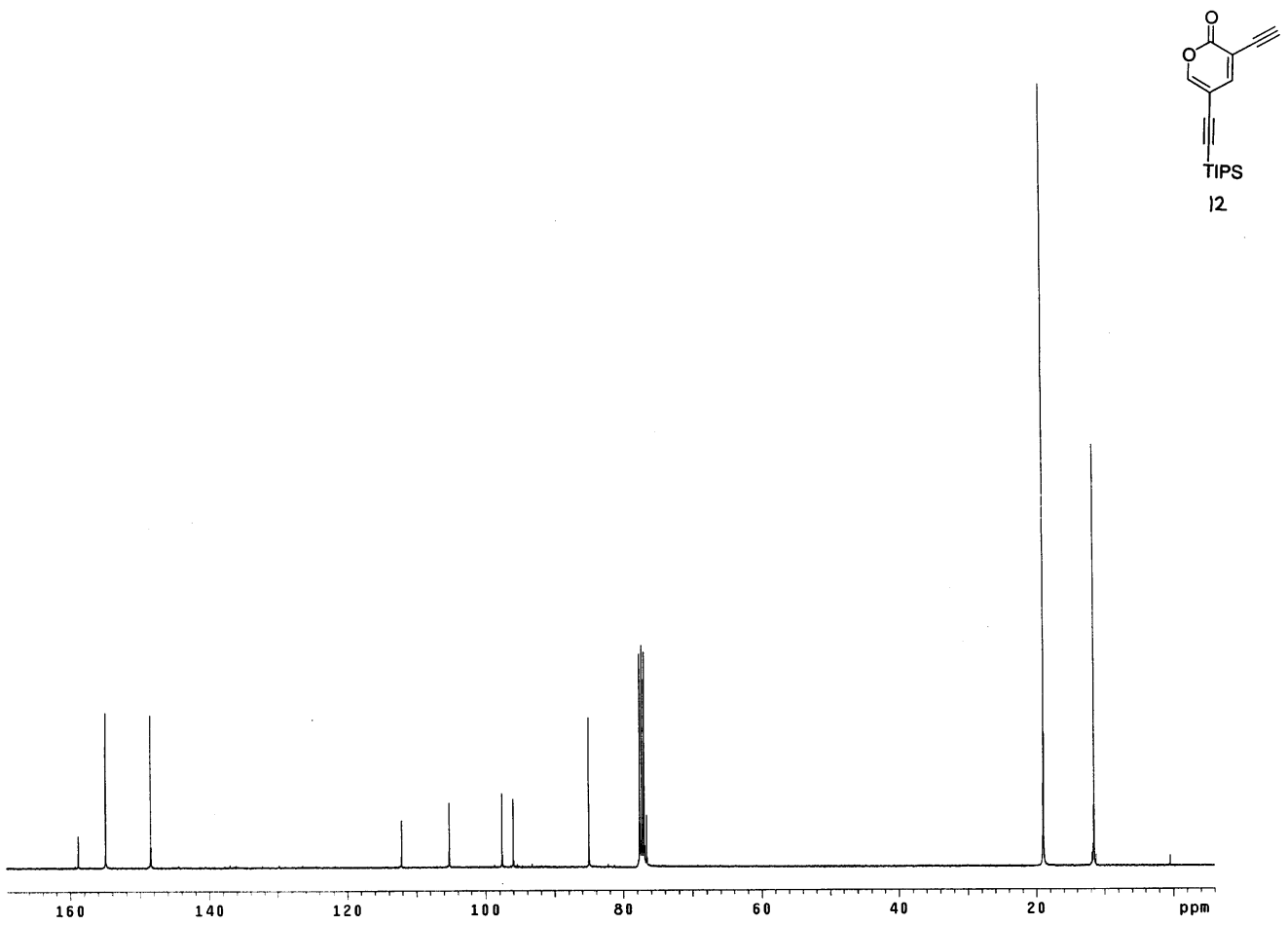
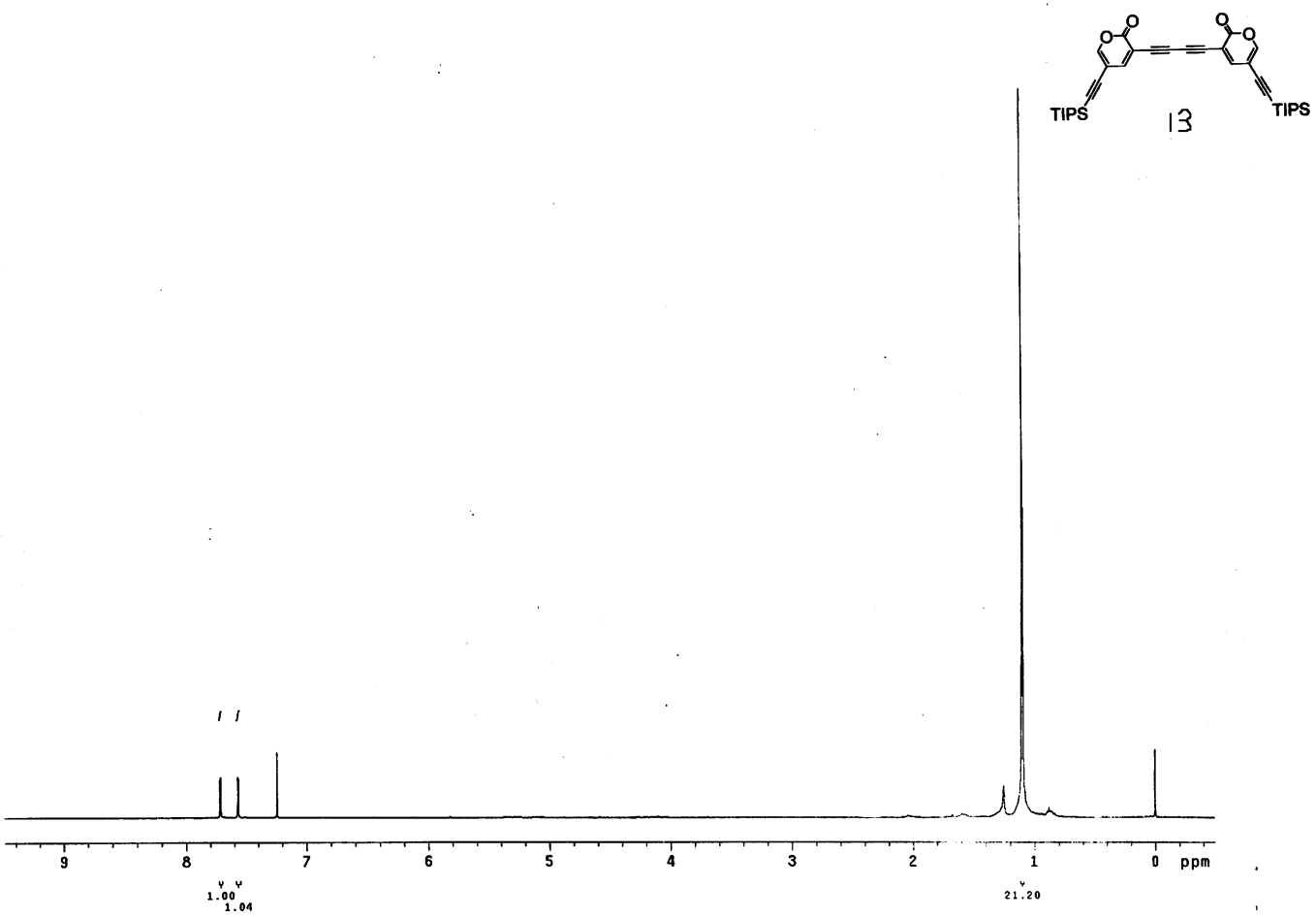
1.01
1.00
21.40



12


TIPS
TIPS
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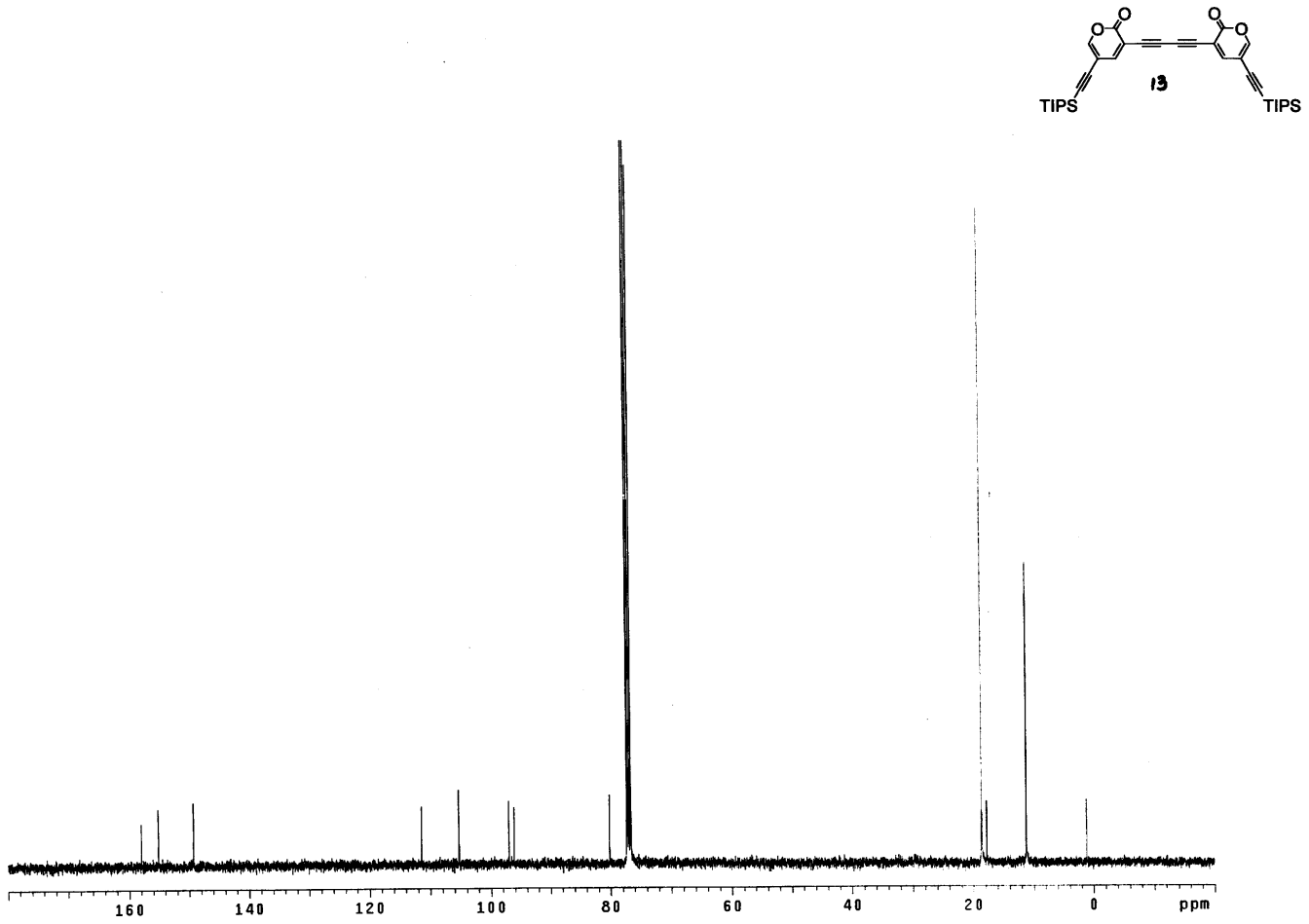
1.04
21.20


TIPS
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TIPS
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ppm