Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Nickel-catalyzed [3 + 2] cycloaddition of diynes with methyleneaziridines via C–C bond cleavage

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1. General information

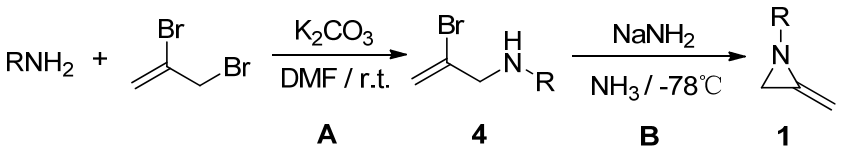
Ni(cod)$_2$ was ordered from Aldrich. 2-Methyleneaziridines **1a~1g** were prepared according to literature procedures[1-3]. Diynes were prepared according to literature procedures[4-7].

Commercially available reagents were used throughout without further purification. All solvents were purified according to the standard procedures.

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques, unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX–400 or Bruker DRX–500 spectrometers (400 MHz or 500 MHz for ^{1}H NMR, 100 MHz or 125 MHz for ^{13}C NMR, see details of each compound) using $CDCl_3$, CD_3COCD_3 or C_6D_6 as solvent. Tetramethylsilane (δ=0), $CDCl_3$ (7.27ppm), CD_3COCD_3 (2.05ppm) or C_6D_6 (7.16ppm) serves as the internal standard for ^{1}H NMR and $CDCl_3$ (77.16ppm), CD_3COCD_3 (29.84ppm) or C_6D_6 (128.06ppm) for ^{13}C NMR. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Chromatography was performed on silica gel (300–400 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica.

2. Experiment Procedures and Characterization Data

2.1 The Preparation of 2-Methyleneaziridines

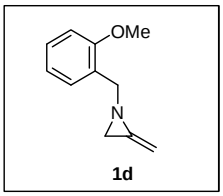


General Method A[1]: Preparation of Allylic Amines 4. To a stirred solution of amines (9.5mmol) and 2,3-dibromo-1-propene (10.4mmol) in DMF (20ml) was added K_2CO_3 (19.0mmol) at room temperature, and stirring was continued for 1 h. The reaction mixture was worked up by adding water (30 ml), extracting with CH_2Cl_2 (4×20 ml), washing the combined organic phases with brine (30 ml), and drying with Na_2SO_4. The crude product obtained after removal of CH_2Cl_2 contained much DMF. It was purified by chromatography on a silica gel column eluting with a mixture of petroleum ether/CH_3CO_2Et to give Allylic Amines **4**.

General Method B[2-3]: Synthesis of 2-Methyleneaziridines 1. A three-necked flask was fitted with a cold-finger condenser and a gas inlet. The system was purged with dry ammonia then sodium amide (2.5 eq.) was added and the system again flushed with ammonia. After ammonia (50ml) was condensed into the flask. After cooling to –78°C, the allylamine **4** (50% w/v in diethyl ether) was added slowly to the mixture, which was subsequently stirred for 1 h. The mixture was diluted with diethyl ether (10ml) and quenched by the dropwise addition of water (5ml) (CAUTION). After the ammonia had evaporated, diethyl ether (50ml) was added and the mixture was stirred

for 2 min. The organic phase was separated and washed 0.1M acetic acid (5×50ml), then 10% NaOH (2×50ml) and finally brine (50ml), then dried ($MgSO_4$). Removal of the solvent under reduced pressure and subsequent bulb-to-bulb distillation yielded the product.

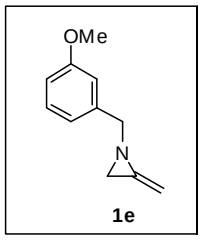
1-(2-methoxybenzyl)-2-methyleneaziridine 1d.



1d

Sodium amide (732mg, 18.7mmol) in ammonia (50ml) and subsequent reaction with corresponding amine **4** (2.40 g, 9.4mmol) for 1 h at –78 ºC as described in General Method B, followed by workup and bulb-to-bulb distillation gave **1d** (1.15g, 70%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J*=7.4, 1H), 7.31 (dd, *J*=10.7, 1H), 7.00 (t, *J*=7.4, 1H), 6.91 (d, *J*=8.2, 1H), 4.88 – 4.66 (m, 2H), 3.87 (s, 3H), 3.76 (s, 2H), 2.19 (s, 2H); ^{13}C (125 MHz, $CDCl_3$) 157.3, 137.4, 129.5, 128.5, 126.8, 120.5, 110.2, 83.5, 57.5, 55.4, 30.9; HRMS calcd for $C_{11}H_{13}NONa$ $[M+Na]^+$ 198.0895, found 198.0888.

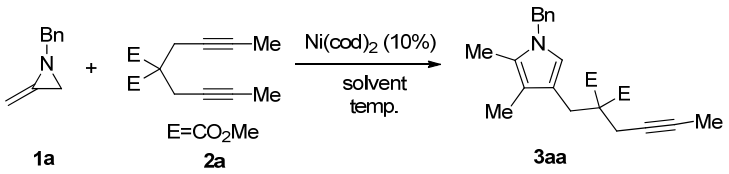
1-(3-methoxybenzyl)-2-methyleneaziridine 1e.



1e

Sodium amide (853mg, 21.9mmol) in ammonia (70 ml) and subsequent reaction with corresponding amine 4 (2.80 g, 10.9mmol) for 1 h at –78 ºC as described in General Method B, followed by workup and bulb-to-bulb distillation gave **1e** (1.55g, 81%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (dd, *J*=9.2, 6.4, 1H), 7.00 – 6.93 (m, 2H), 6.90 – 6.84 (m, 1H), 4.77 (d, *J*=1.0, 2H), 3.85 (s, 3H), 3.71 (s, 2H), 2.18 (s, 2H); ^{13}C (126 MHz, $CDCl_3$) 159.8, 139.9, 137.1, 129.5, 120.6, 113.7, 113.1, 83.7, 62.9, 55.3, 30.8; HRMS calcd for $C_{11}H_{14}NO$ $[M+H]^+$ 176.1075, found 176.1069.

2.2 Optimization of Solvent and Temperature



1a **2a** **3aa**

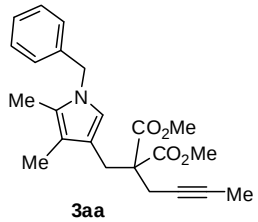
Entry	Solvent	Temp. (°C)	Isolated yield (%)
1	DMF	rt	20
2	DCE	rt	3
3	CH_3CN	rt	24
4	THF	rt	36
5	Benzene	rt	40
6	Toulene	rt	49
7	1,4-dioxane	rt	60
8	1,4-dioxane	10	30
9	1,4-dioxane	60	34
10	1,4-dioxane	80	11

2.3 General Procedure for Ni(0)-Catalyzed [3+ 2] Cycloadditions

Under an argon atmosphere, 2-Methyleneaziridines **1** (0.5mmol), dyines **2** (0.2mmol), $Ni(cod)_2$ (10mol %) and 1,4-dioxane (1ml) were added into a Schlenk tube. The reaction mixture was stirred at room temperature and monitored by TLC or GC. When the reaction was over, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (1% Et_3N was added in eluent).

Experimental data for cycloadducts

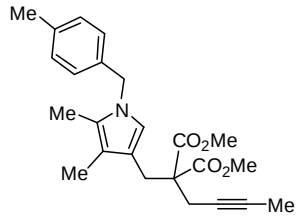
Dimethyl 2-((1-benzyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)-2-(but-2-yn-1-yl)malonate (3aa)



3aa

Colorless oil, ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.39 – 7.16 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.46 (s, 1H), 5.01 (s, 2H), 3.69 (s, 6H), 3.22 (s, 2H), 2.72 (d, *J* = 2.5 Hz, 2H), 1.98 (d, *J* = 9.7 Hz, 6H), 1.77 (t, *J* = 2.5 Hz, 3H).; ^{13}C (100MHz, Acetone-d_6) 171.2, 140.2, 129.3, 127.8, 127.1, 125.0, 119.8, 115.6, 115.3, 79.4, 75.2, 59.4, 52.6, 50.6, 28.2, 23.3, 9.8, 9.7, 3.2; HRMS calcd for $C_{23}H_{27}NO_4Na$ $[M+Na]^+$ 404.1838, found 404.1828.

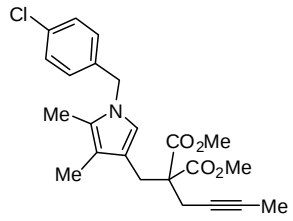
Dimethyl 2-(but-2-yn-1-yl)-2-((4,5-dimethyl-1-(4-methylbenzyl)-1H-pyrrol-3-yl)methyl)malonate (3ba)



3ba

Colorless oil, ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.11 (d, *J* = 7.1 Hz, 2H), 6.87 (d, *J* = 7.1 Hz, 2H), 6.39 (s, 1H), 4.95 (s, 2H), 3.66 (s, 6H), 3.13 (s, 2H), 2.63 (s, 2H), 2.28 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H), 1.75 (s, 3H); ^{13}C (100 MHz, Acetone-d_6) 171.3, 137.3, 137.2, 129.9, 127.2, 125.0, 119.8, 115.5, 115.2, 79.3, 75.1, 59.4, 52.6, 50.5, 28.1, 23.2, 21.0, 9.8, 9.6, 3.2; HRMS calcd for $C_{24}H_{29}NO_4Na$ $[M+Na]^+$ 418.1994, found 418.2004.

Dimethyl 2-(but-2-yn-1-yl)-2-((1-(4-chlorobenzyl)-4,5-dimethyl-1H-pyrrol-3-yl)methyl)malonate (3ca)

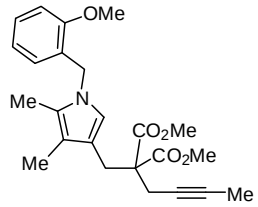


3ca

Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.34 (s, 1H), 4.92 (s, 2H), 3.73 (s, 6H), 3.24 (s, 2H), 2.74 (d, *J* = 2.3 Hz, 2H), 1.98 (s, 3H), 1.96 (s, 3H), 1.81 (t, *J* = 2.1 Hz, 3H); ^{13}C (100 MHz,

$CDCl_3$) 171.0, 137.4, 133.0, 128.9, 127.6, 124.7, 118.8, 115.6, 115.3, 79.0, 74.4, 58.8, 52.5, 49.8, 27.5, 22.9, 9.8, 9.4, 3.6; HRMS calcd for $C_{23}H_{26}NO_4NaCl$ $[M+Na]^+$ 438.1448, found 438.1438.

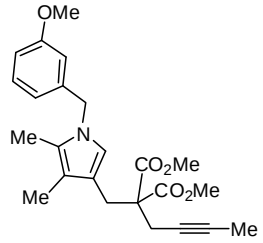
Dimethyl 2-(but-2-yn-1-yl)-2-((1-(2-methoxybenzyl)-4,5-dimethyl-1H-pyrrol-3-yl)methyl)malonate (3da)



3da

White solid, mp 124 – 125℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.42 (d, *J* = 7.0 Hz, 1H), 6.36 (s, 1H), 4.94 (s, 2H), 3.89 (s, 3H), 3.72 (s, 6H), 3.25 (s, 2H), 2.76 (s, 2H), 2.03 (s, 3H), 1.99 (s, 3H), 1.81 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) 171.2, 156.3, 128.2, 127.4, 127.2, 124.9, 120.9, 119.0, 117.9, 109.8, 78.9, 74.6, 58.9, 55.3, 52.5, 45.6, 27.7, 22.9, 9.7, 9.5, 3.7; HRMS calcd for $C_{24}H_{29}NO_5Na$ $[M+Na]^+$ 434.1943, found 434.1947.

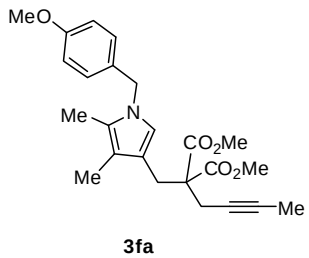
Dimethyl 2-(but-2-yn-1-yl)-2-((1-(3-methoxybenzyl)-4,5-dimethyl-1H-pyrrol-3-yl)methyl)malonate (3ea)



3ea

Yellow oil, ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 6.44 (s, 1H), 5.00 (s, 2H), 3.76 (s, 3H), 3.69 (s, 6H), 3.17 (s, 2H), 2.67 (d, *J* = 2.6 Hz, 2H), 1.98 (s, 3H), 1.93 (s, 3H), 1.77 (s, 3H); ^{13}C (100 MHz, Acetone-d_6) 171.3, 142.0, 130.4, 125.1, 119.9, 119.3, 115.6, 115.3, 113.4, 112.6, 76.4, 75.2, 59.4, 55.4, 52.7, 50.7, 28.2, 23.3, 9.8, 9.6, 3.2; HRMS calcd for $C_{24}H_{29}NO_5Na$ $[M+Na]^+$ 434.1943, found 434.1940.

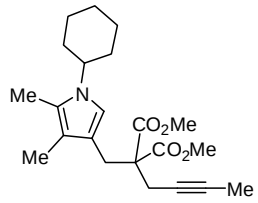
Dimethyl 2-(but-2-yn-1-yl)-2-((1-(4-methoxybenzyl)-4,5-dimethyl-1H-pyrrol-3-yl)methyl)malonate (3fa)



3fa

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.89 (q, *J*=8.8, 4H), 6.34 (s, 1H), 4.90 (s, 2H), 3.81 (s, 3H), 3.73 (s, 6H), 3.25 (s, 2H), 2.75 (d, *J*=2.4, 2H), 2.02 (s, 3H), 1.97 (s, 3H), 1.82 (t, *J*=2.3, 3H); ^{13}C (100 MHz, $CDCl_3$) 171.2, 158.9, 130.8, 127.7, 124.7, 118.8, 115.3, 114.9, 114.2, 78.9, 74.5, 58.9, 55.4, 52.5, 50.0, 27.6, 22.9, 9.9, 9.5, 3.7; HRMS calcd for $C_{24}H_{29}NO_5Na$ $[M+Na]+$ 434.1943, found 434.1946.

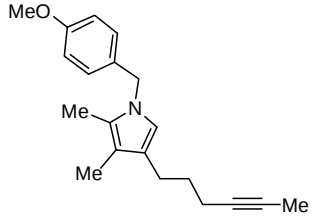
Dimethyl 2-(but-2-yn-1-yl)-2-((1-cyclohexyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)malonate (3ga)



3ga

Colorless oil, ^{1}H NMR (400 MHz, Acetone-d_6) δ = 6.58 (s, 1H), 4.01 (t, *J*=11.1, 1H), 3.92 (s, 6H), 3.33 (s, 2H), 2.81 (s, 2H), 2.30 (s, 3H), 2.12 (s, 4H), 2.08 (s, 2H), 2.00 (d, *J*=1.1, 3H), 1.98 – 1.38 (m, 7H); ^{13}C (125 MHz, Benzene-d_6) 171.2, 115.2, 114.5, 114.3, 103.8, 79.0, 75.5, 59.5, 55.0, 52.1, 34.6, 28.6, 26.1, 25.7, 23.5, 9.9, 9.7, 3.4; HRMS calcd for $C_{22}H_{31}NO_4Na$ $[M+Na]^+$ 396.2151, found 396.2146.

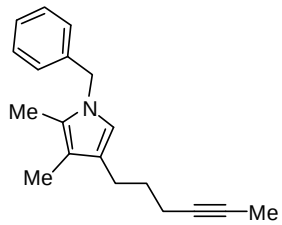
4-(hex-4-yn-1-yl)-1-(4-methoxybenzyl)-2,3-dimethyl-1H-pyrrole (3fb)



3fb

Yellow oil, ^{1}H NMR (500 MHz, Acetone-d_6) δ = 6.95 (d, *J*=8.8, 2H), 6.83 (d, *J*=8.7, 2H), 6.39 (s, 1H), 4.88 (s, 2H), 3.74 (s, 3H), 2.41 (t, *J*=7.4, 2H), 2.10 (dtd, *J*=7.3, 4.9, 2.6, 2H), 1.97 (s, 3H), 1.87 (s, 3H), 1.71 (t, *J*=2.6, 3H), 1.66 – 1.59 (m, 2H); ^{13}C (125 MHz, Acetone-d_6) 159.8, 132.4, 128.6, 125.0, 121.6, 117.9, 114.7, 114.2, 79.9, 75.9, 55.5, 50.2, 30.9, 25.4, 18.8, 9.8, 9.6, 3.3; HRMS calcd for $C_{20}H_{25}NONa$ $[M+Na]^+$ 318.1834, found 318.1823.

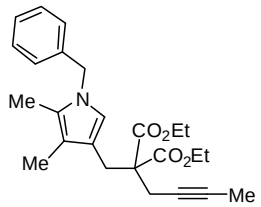
1-benzyl-4-(hex-4-yn-1-yl)-2,3-dimethyl-1H-pyrrole (3ab)



3ab

Yellow oil, ^{1}H NMR (400 MHz, C_6D_6) δ = 7.08 (dd, *J*=8.0, 5.3, 7H), 7.03 – 6.88 (m, 10H), 6.68 (d, *J*=7.4, 2H), 6.28 (s, 1H), 4.97 (d, *J*=4.2, 4H), 4.33 (s, 2H), 3.76 (s, 2H), 3.20 (s, 2H), 2.04 (s, 3H), 1.71 (s, 3H), 1.39 (t, *J*=2.2, 3H); ^{13}C (100 MHz, C_6D_6) 139.8, 128.8, 127.2, 126.4, 124.5, 121.6, 117.6, 114.3, 79.9, 75.7, 50.2, 30.6, 25.3, 18.9, 9.8, 9.7, 3.5; HRMS calcd for $C_{19}H_{23}NNa$ $[M+Na]^+$ 288.1728, found 288.1740.

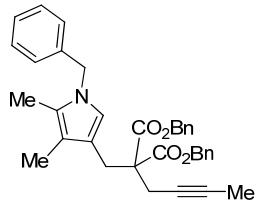
Diethyl 2-((1-benzyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)-2-(but-2-yn-1-yl)malonate (3ac)



3ac

Yellow oil, ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.43 – 7.28 (m, 3H), 7.04 (d, *J*=7.4, 2H), 6.43 (s, 1H), 5.02 (s, 2H), 4.29 – 4.15 (m, 4H), 3.22 (s, 2H), 2.73 (d, *J*=2.5, 2H), 2.08 (s, 3H), 2.01 (s, 3H), 1.86 (t, *J*=2.5, 3H), 1.31 (t, *J*=7.1, 6H); ^{13}C (100 MHz, CD_2Cl_2) 170.4, 138.9, 128.5, 127.0, 126.3, 124.4, 118.8, 115.1, 114.9, 78.5, 74.4, 61.1, 58.4, 50.2, 27.1, 22.5, 13.7, 9.4, 9.0, 3.1; HRMS calcd for $C_{26}H_{33}NO_5Na$ $[M+Na]^+$ 432.2151, found 432.2158.

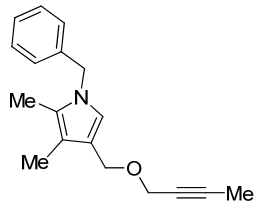
Dibenzyl 2-((1-benzyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)-2-(but-2-yn-1-yl)malonate (3ad)



3ad

Yellow oil, ^{1}H NMR (400 MHz, C_6D_6) δ = 7.08 (dd, *J*=8.0, 5.3, 7H), 7.03 – 6.88 (m, 10H), 6.68 (d, *J*=7.4, 2H), 6.28 (s, 1H), 4.97 (d, *J*=4.2, 4H), 4.33 (s, 2H), 3.76 (s, 2H), 3.20 (s, 2H), 2.04 (s, 3H), 1.71 (s, 3H), 1.39 (t, *J*=2.2, 3H); ^{13}C (100 MHz, C_6D_6) 170.4, 139.4, 136.3, 128.8, 128.6, 128.4, 128.2, 127.2, 126.4, 124.5, 119.6, 115.8, 115.5, 79.3, 75.4, 67.0, 59.7, 50.3, 28.3, 23.5, 9.9, 9.7, 3.4; HRMS calcd for $C_{35}H_{35}NO_4Na$ $[M+Na]^+$ 556.2464, found 556.2467.

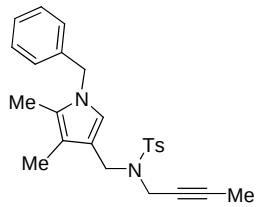
1-benzyl-4-((but-2-ynyloxy)methyl)-2,3-dimethyl-1H-pyrrole (3ae)



3ae

Yellow oil, ^{1}H NMR (400 MHz, C_6D_6) δ 6.99 – 6.89 (m, 3H), 6.69 (d, *J* = 7.3 Hz, 2H), 6.40 (s, 1H), 4.62 (s, 2H), 4.36 (s, 2H), 4.15 (d, *J* = 2.2 Hz, 2H), 2.10 (s, 3H), 1.72 (s, 3H), 1.46 (s, 3H); ^{13}C (125 MHz, Acetone-d6) 139.3, 128.5, 128.1, 127.0, 126.4, 120.1, 117.8, 114.5, 81.0, 76.0, 63.1, 55.7, 49.9, 8.7, 8.5, 2.3; HRMS calcd for C18H21NONa [M+Na]+ 290.1521, found 290.1524.

N-((1-benzyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)-N-(but-2-ynyl)-4-methylbenzenesulfonamide (3af)

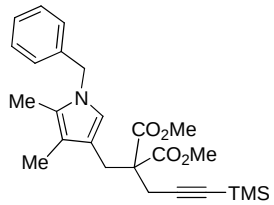


3af

Colorless oil, ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.82 – 7.76 (m, 2H), 7.42 (dd, *J* = 8.5, 0.5 Hz, 2H), 7.33 – 7.27 (m,

2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.01 (dd, *J* = 7.9, 0.9 Hz, 2H), 6.62 (s, 1H), 5.03 (s, 2H), 4.15 (s, 2H), 3.86 (q, *J* = 2.3 Hz, 2H), 2.44 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.47 (t, *J* = 2.4 Hz, 3H); ^{13}C (125 MHz, Acetone-d_6) 143.1, 139.2, 136.7, 129.1, 128.5, 128.0, 127.0, 126.3, 125.4, 120.5, 114.6, 114.2, 81.2, 71.7, 49.9, 41.7, 34.9, 20.5, 8.8, 8.5, 2.1; HRMS calcd for $C_{25}H_{28}N_2O_2NaS$ $[M+Na]^+$ 443.1769, found 443.1773.

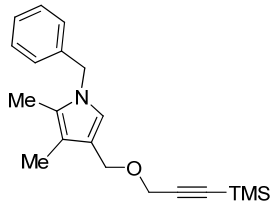
Dimethyl 2-((1-benzyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)
-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (3ai)



3ai

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.20 (m, 4H), 6.96 (d, *J*=7.1, 2H), 6.33 (s, 1H), 4.95 (s, 2H), 3.72 (s, 6H), 3.26 (s, 2H), 2.81 (s, 2H), 2.01 (s, 3H), 1.98 (s, 3H), 0.17 (s, 9H); ^{13}C (100 MHz, $CDCl_3$) 170.8, 138.8, 128.8, 127.3, 126.5, 124.9, 118.9, 115.4, 115.0, 102.8, 88.3, 59.0, 52.6, 50.5, 27.6, 23.9, 9.9, 9.5, 0.1; HRMS calcd for $C_{25}H_{33}NO_4NaSi$ $[M+Na]^+$ 462.2077, found 462.2071.

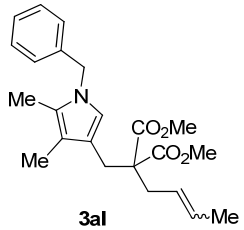
1-benzyl-2,3-dimethyl-4-(((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-1H-pyrrole (3aj)



3aj

Yellow oil, ^{1}H NMR (400 MHz, Acetone-d_6) δ = 6.94 (d, *J*=8.8, 2H), 6.86 (d, *J*=8.8, 2H), 6.37 (s, 1H), 4.92 (s, 2H), 3.76 (s, 3H), 3.68 (s, 6H), 3.16 (s, 2H), 2.82 (s, 2H), 2.70 (s, 2H), 1.97 (s, 3H), 1.92 (s, 3H), 0.14 (s, 9H); ^{13}C (100 MHz, Acetone-d_6) 140.1, 129.4, 127.9, 127.3, 125.8, 121.2, 118.3, 115.5, 104.1, 90.5, 64.1, 56.8, 50.8, 9.7, 9.5, 0.0; HRMS calcd for $C_{20}H_{27}NONaSi$ $[M+Na]^+$ 348.1760, found 348.1757.

Dimethyl 2-((1-benzyl-4,5-dimethyl-1H-pyrrol-3-yl)methyl)-2-(but-2-enyl)malonate (3al)



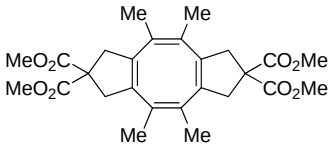
3al
(Z / E)

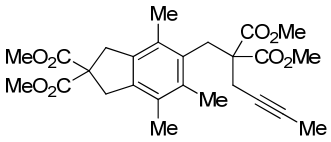
Yellow oil, ^{1}H, ^{13}C NMR see part 3

Note: (Z/E)-1-bromo-2-butene was used to prepare the 1,6-eneyne (**2l**)

Two homo-[2+2+2] cycloaddition products[8,9]

(Part 3 Copy of NMR Spectra)





2.4 Reference

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(2) J. Ince, T. M. Ross, M. Shipman, A. M. Z. Slawin, *Tetrahedron*. **1996**, *52*, 7037.
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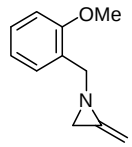
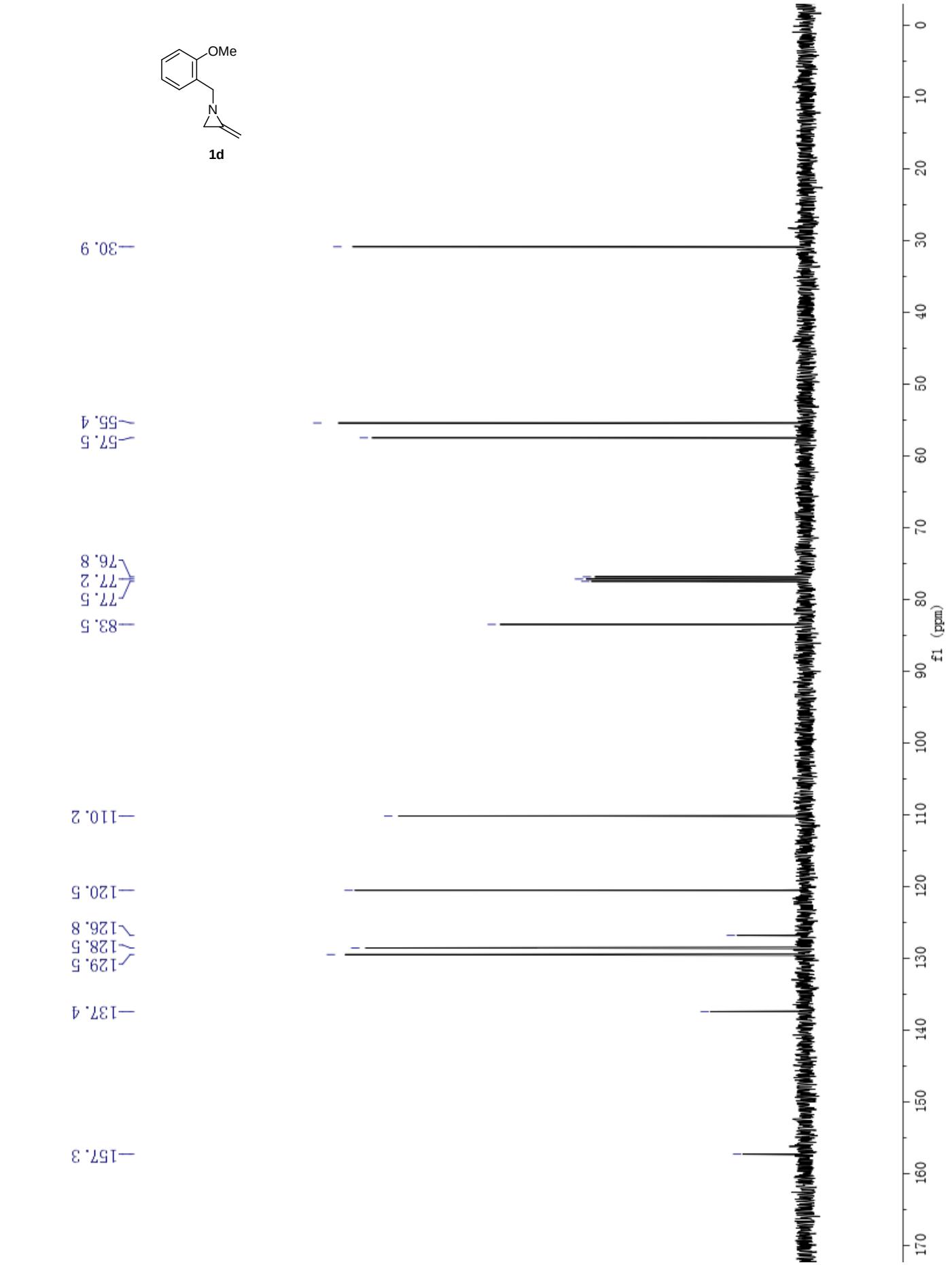
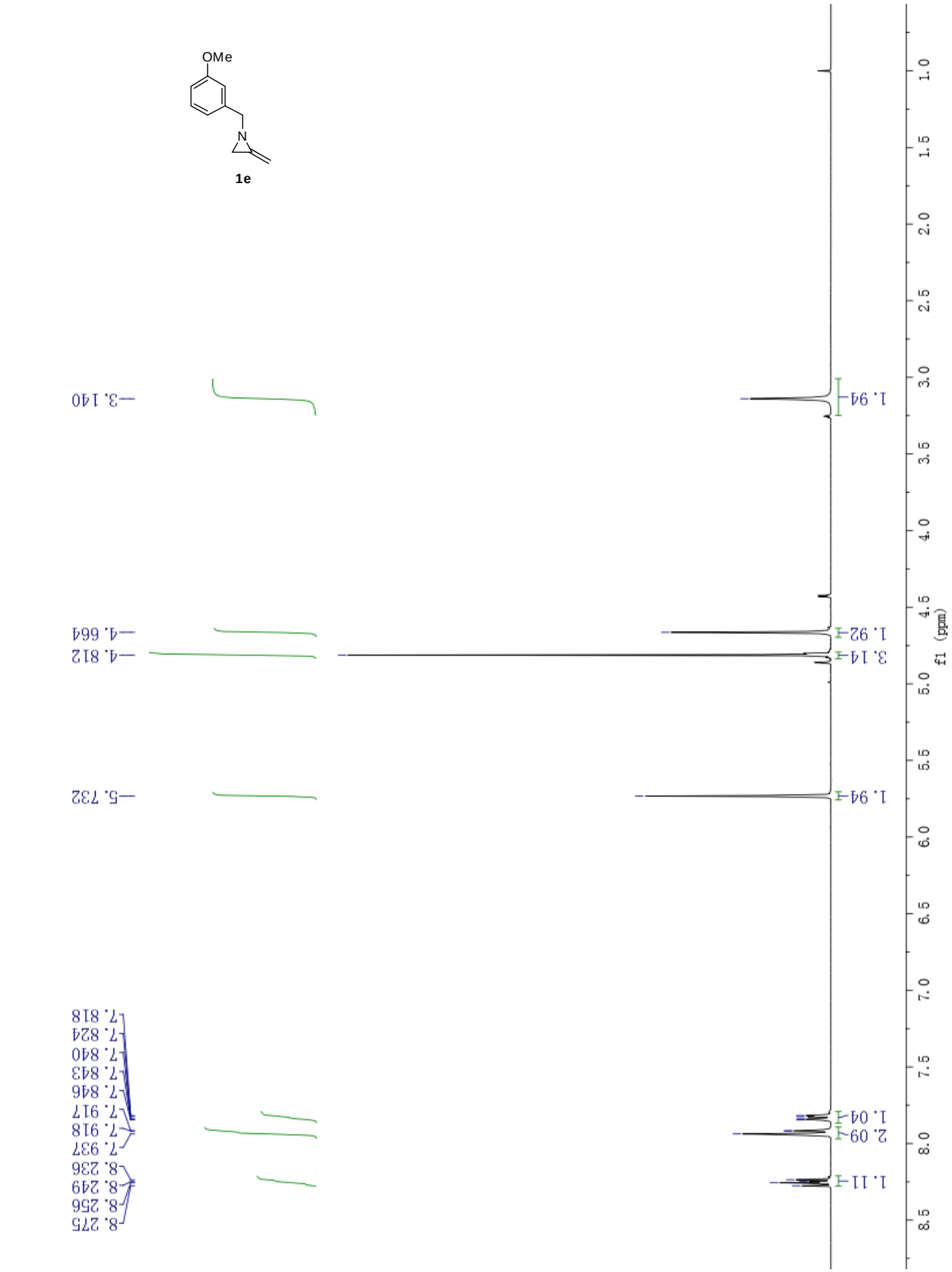
(5) M. Takimoto, T. Mizuno, M. Morib, Y. Sato, *Tetrahedron*. **2006**, *62*, 7589.
(6) C. Sperger, L. H. S. Strand, A. Fiksdahl, *Tetrahedron*. **2010**, *66*, 7749.
(7) M. Ishizaki, O. Hoshino, *Tetrahedron*. **2000**, *56*, 8813.
(8) P. A. Wender, J. P. Christy, *J. Am. Chem. Soc*. **2007**, *129*, 13402.
(9) P. A. Wender, J. P. Christy, A. B. Lesser, M. T. Gieseler, *Angew. Chem. Int. Ed.* **2009**, *48*, 7687.

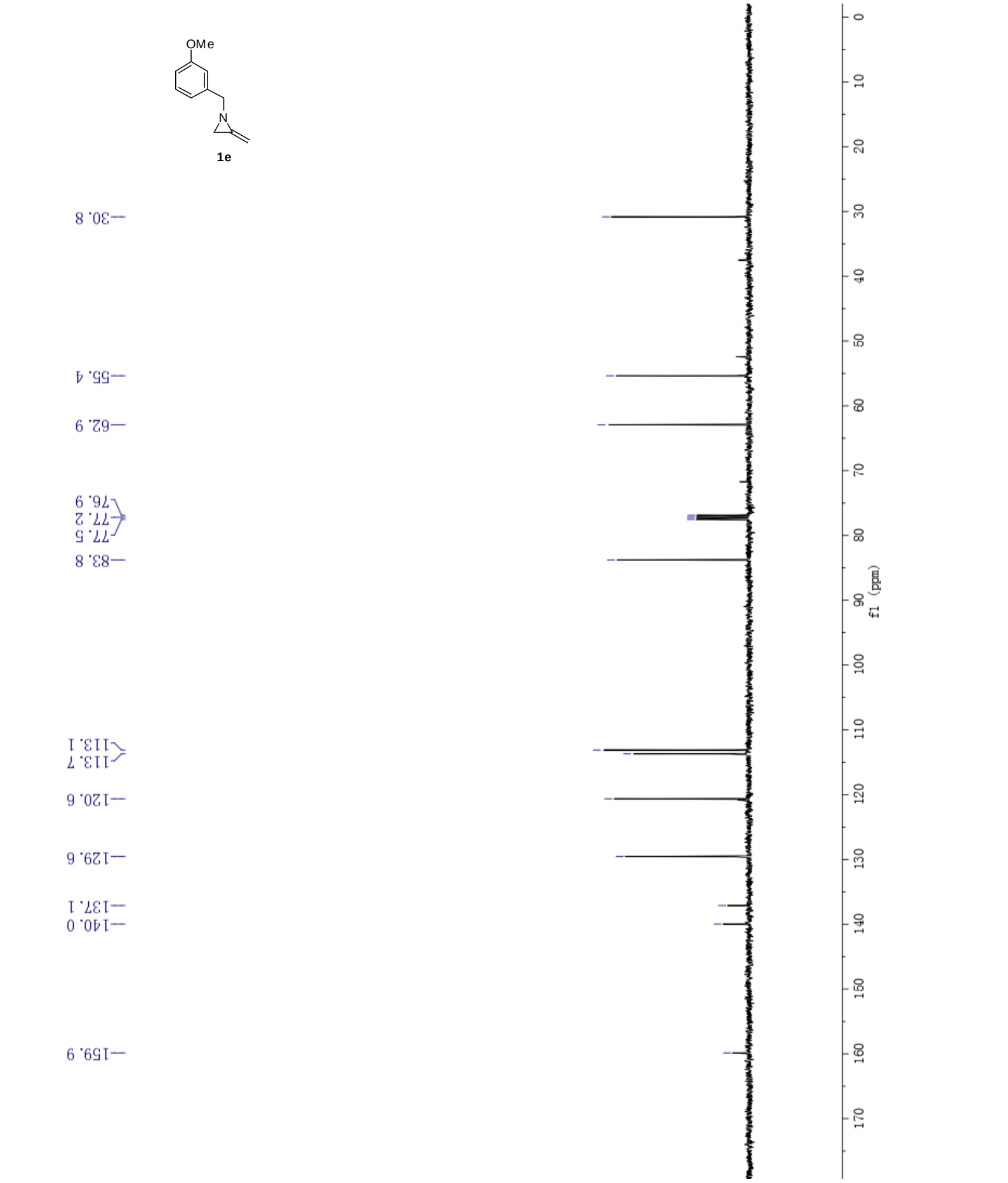
3. Copy of NMR Spectra

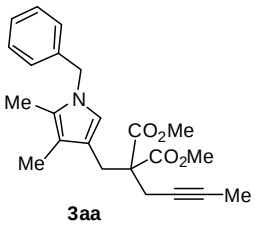


1d





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N
Me
CO2Me
CO2Me
Me

3aa

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1.781
1.966
1.990
2.714
2.720
3.219
3.686
5.014
6.460
6.991
7.009
7.251
7.303
7.322
3.12
3.01
3.09
2.11
2.05
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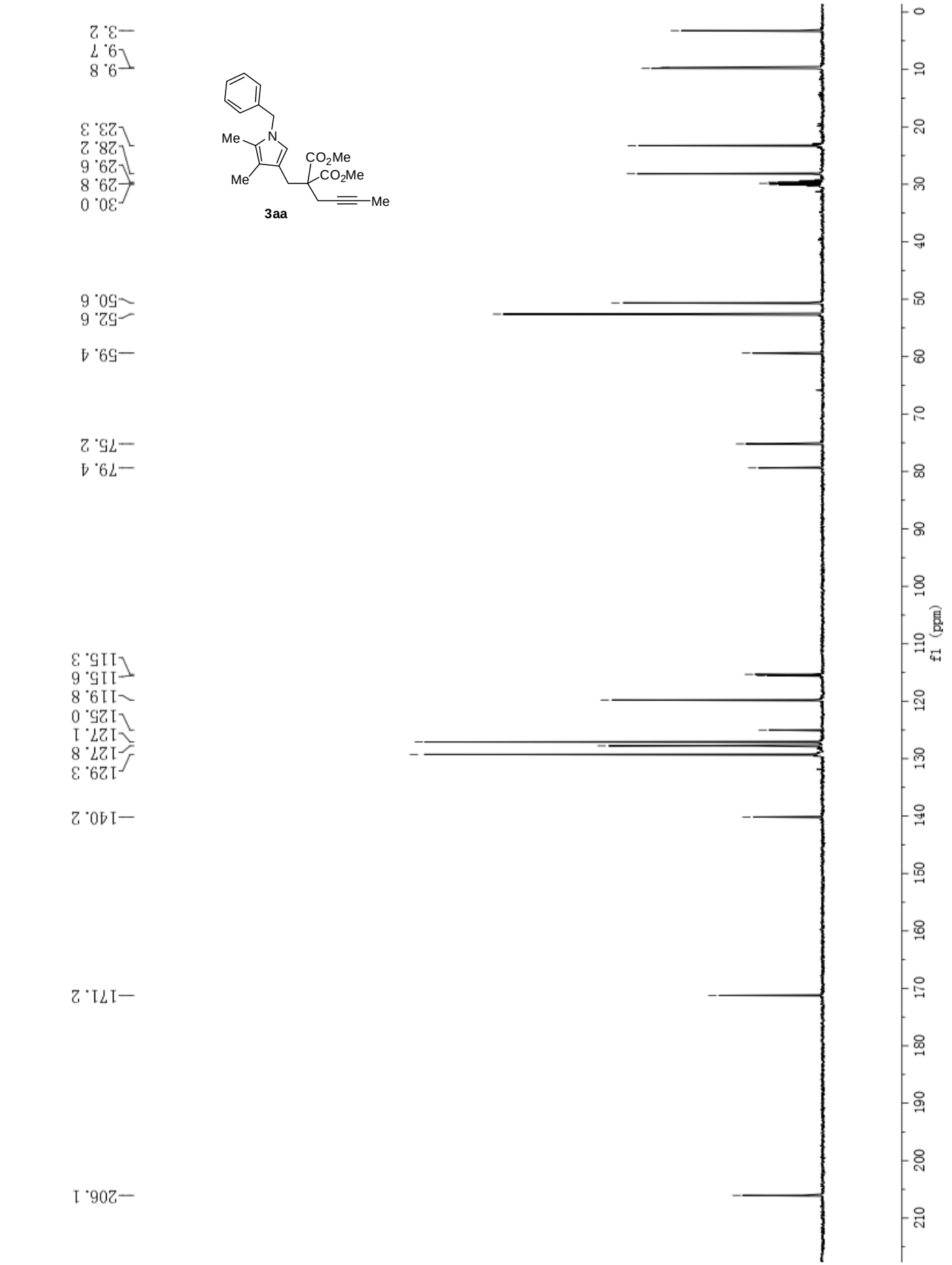
2.03
1.00
2.01
3.24
f1 (ppm)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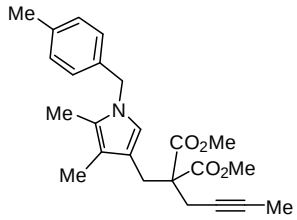
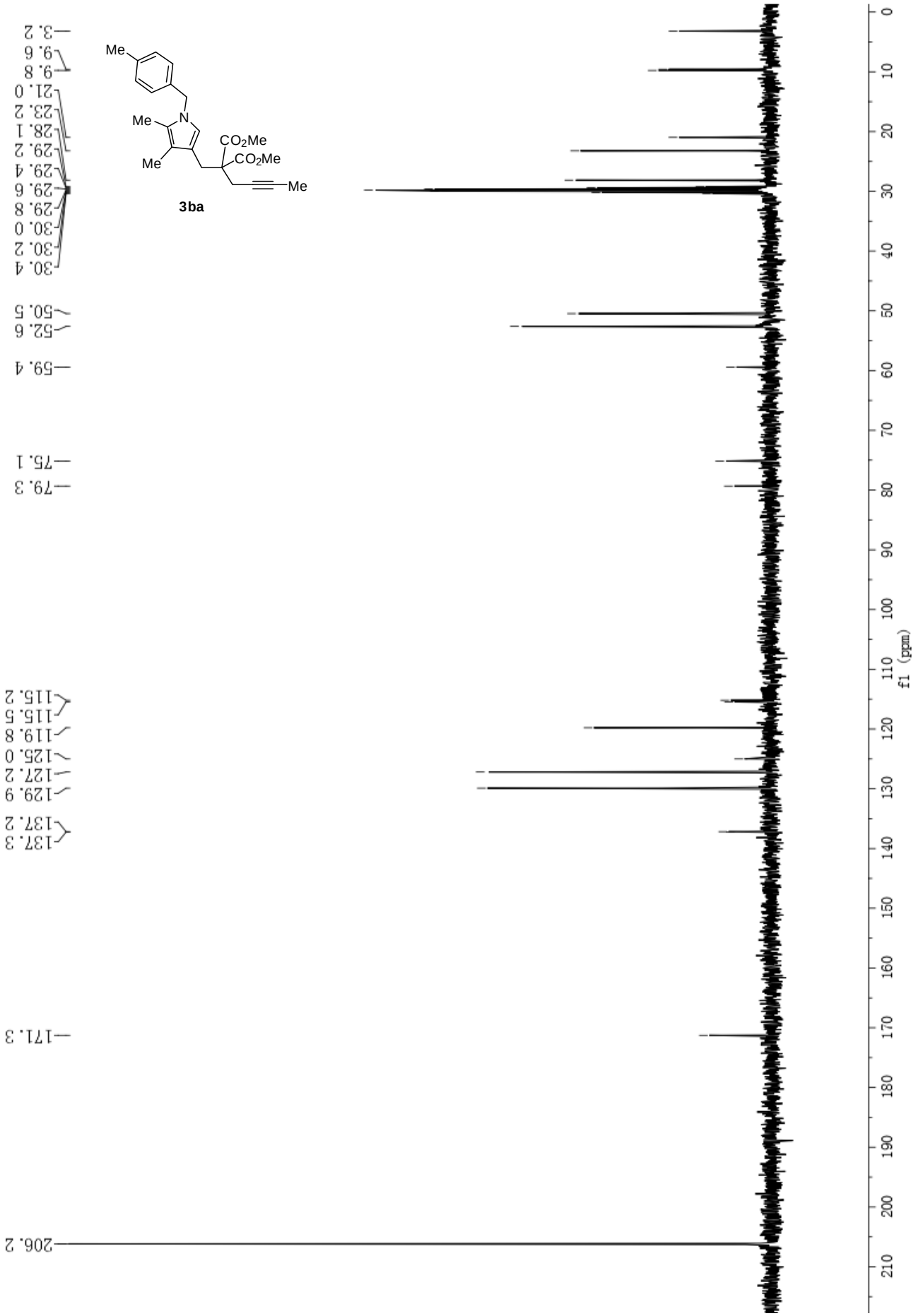
9.7
9.8
23.3
28.2
29.6
29.8
30.0
50.6
52.6
59.4
75.2
79.4
115.3
115.6
119.8
125.0
127.1
127.8
129.3
140.2
171.2
206.1
Me
N
Me
CO2Me
CO2Me
Me
3aa
f1 (ppm)



3ba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Me
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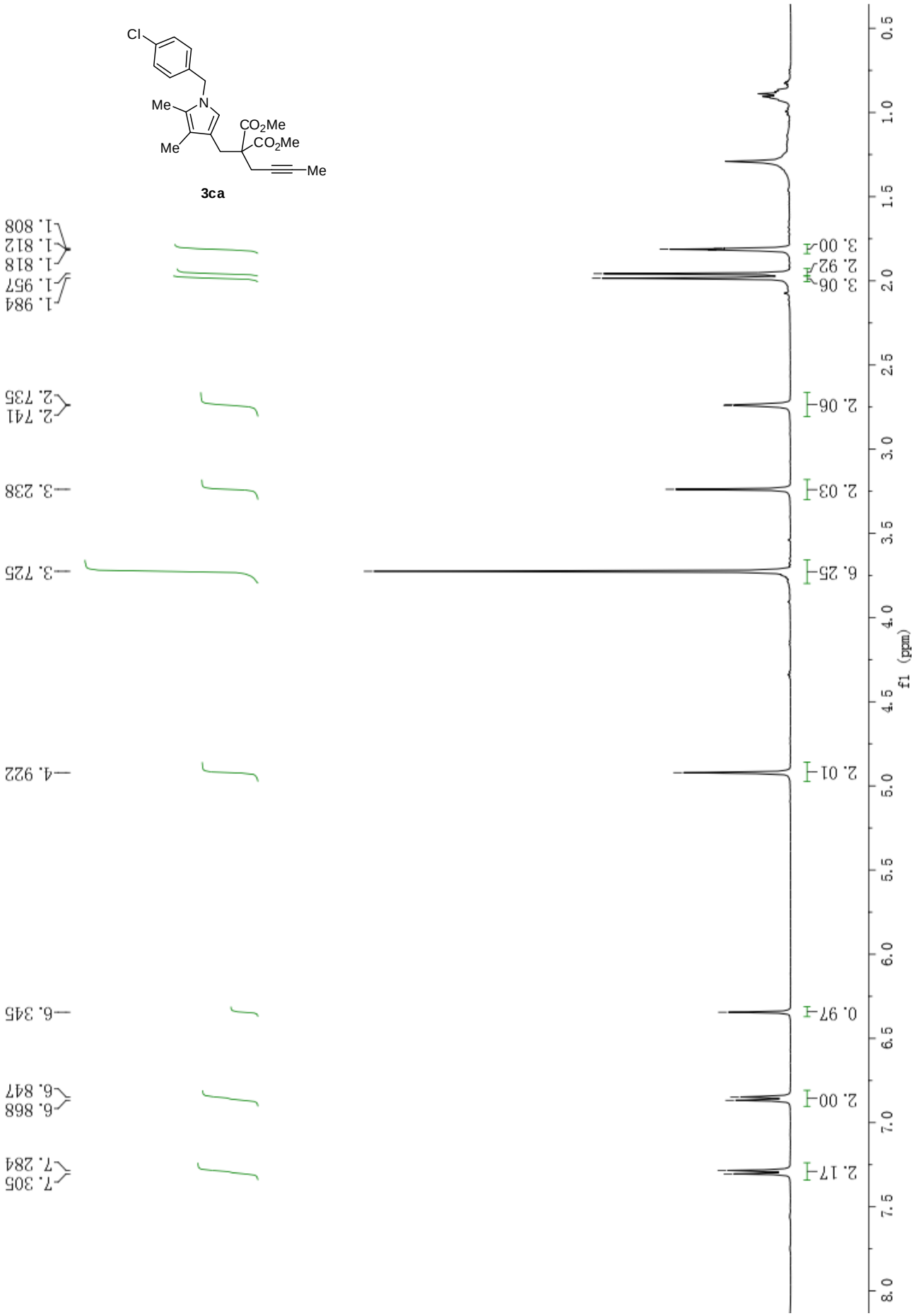
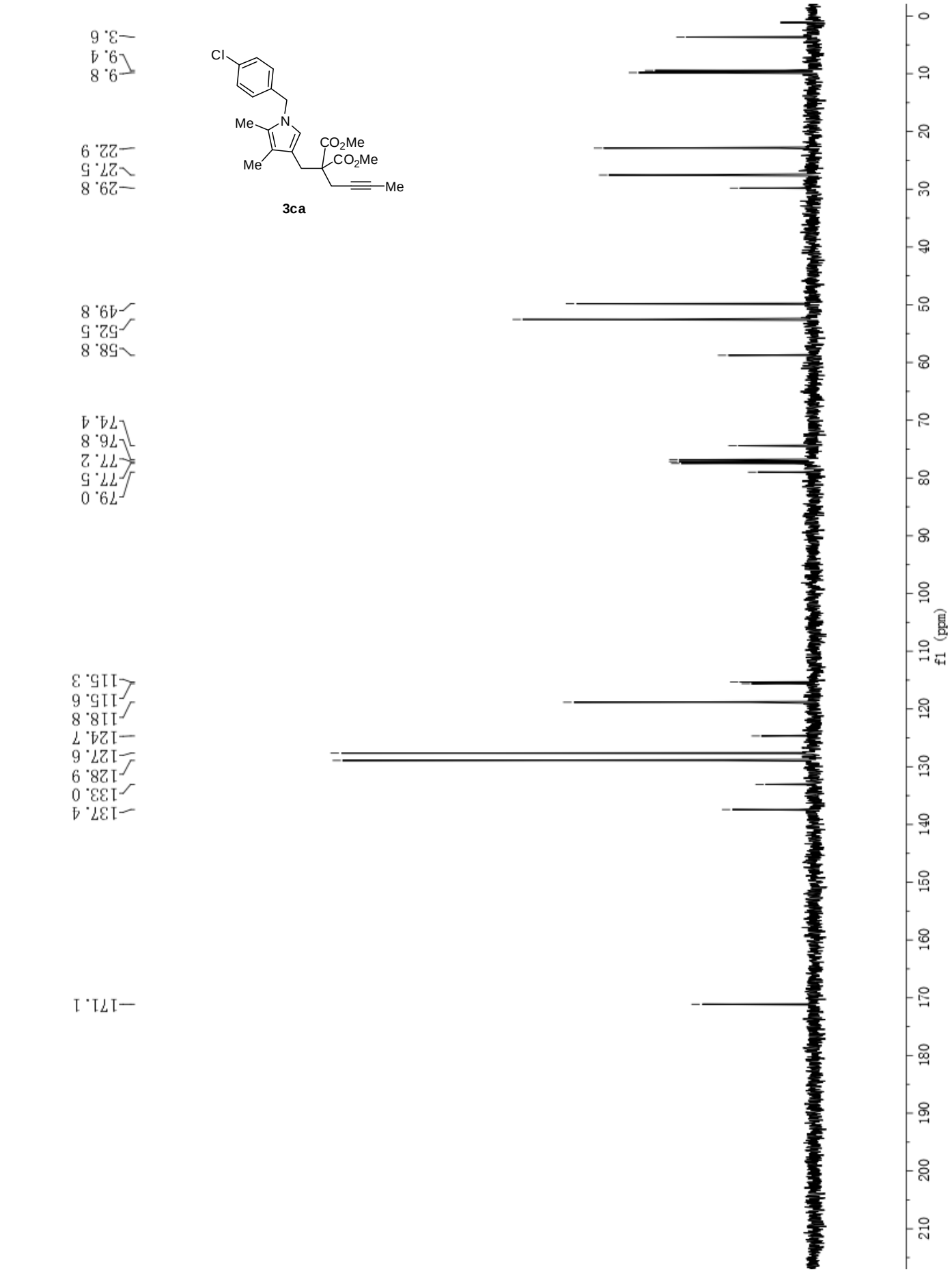
CO2Me
Me
3ba
f1 (ppm)

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CO2Me
Me
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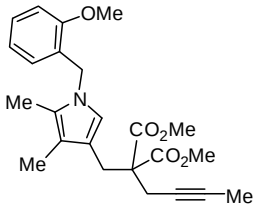
f1 (ppm)


OMe
Me
N
Me
CO_2Me
CO_2Me
Me

3da

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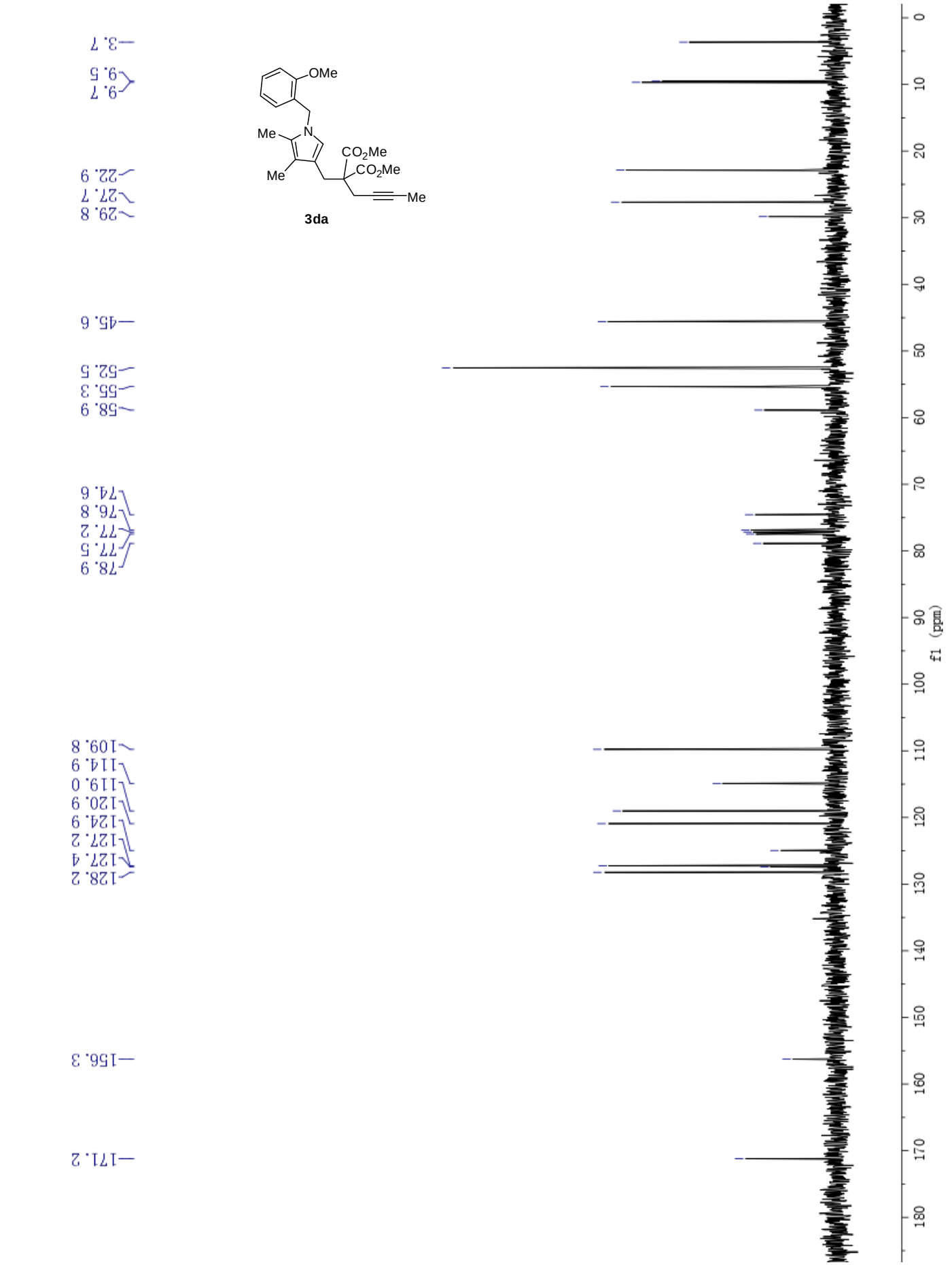
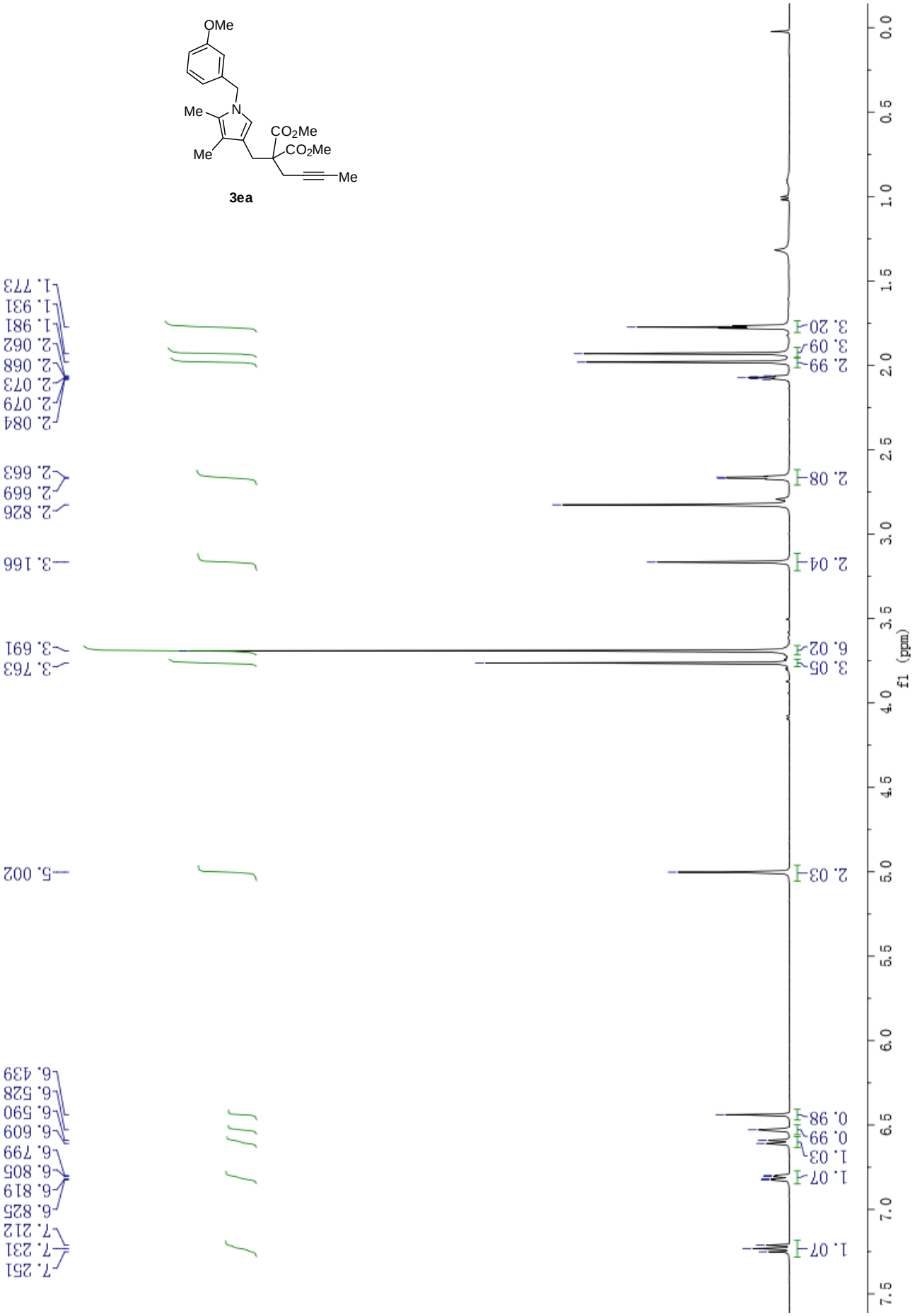
3.253
3.721
3.894
4.942
6.357
6.408
6.426
6.878
6.898
7.229
7.248
7.266
3.07
2.96
2.75
2.01
1.99
6.02
3.05
2.04
1.00
0.93
1.99
1.12
f1 (ppm)

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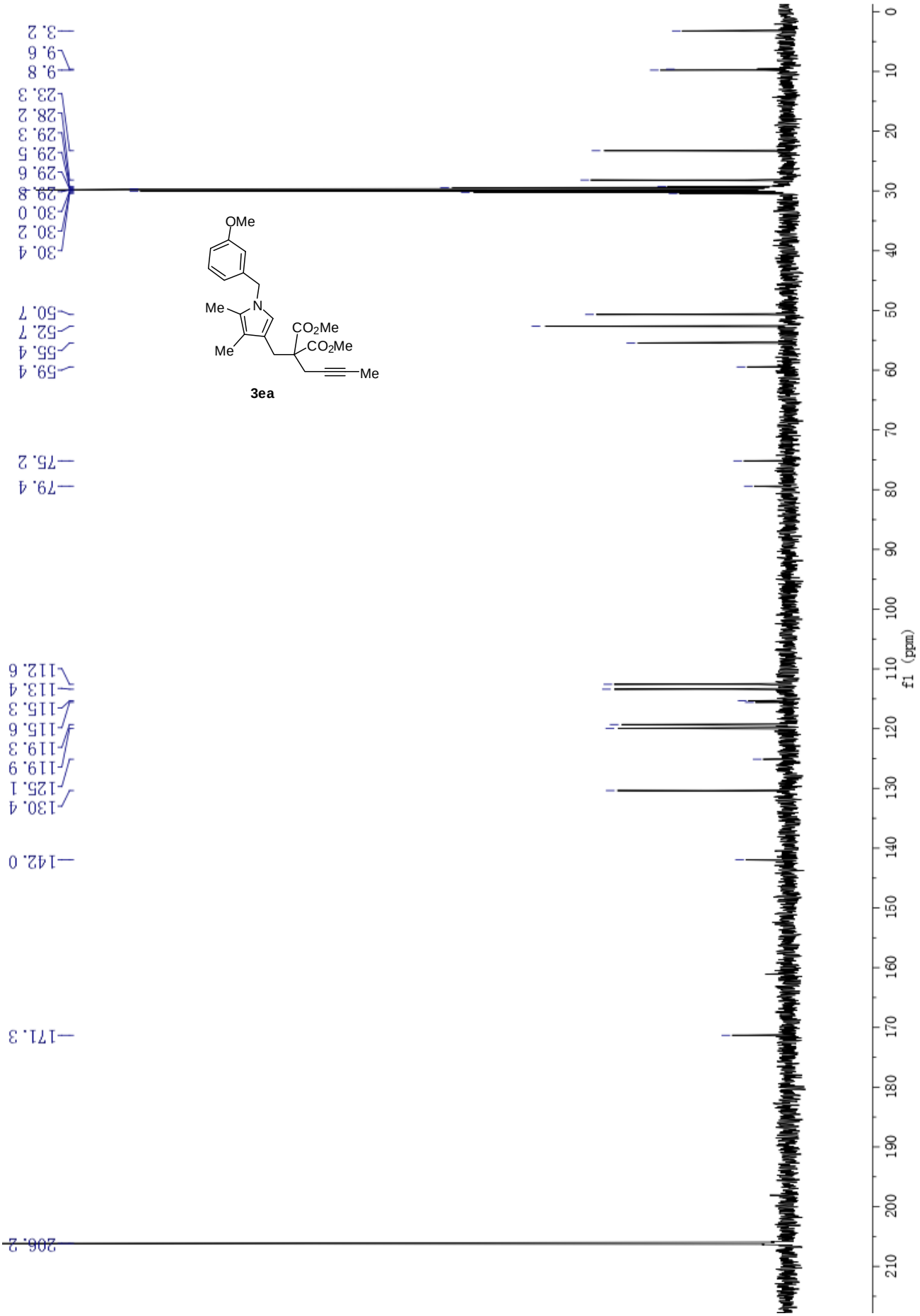
Me
N
Me
CO2Me
CO2Me
Me
3ea
f1 (ppm)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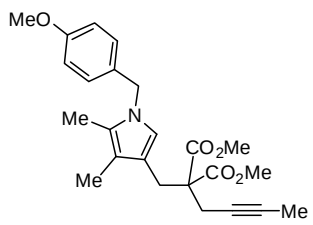
Me
N
Me
CO2Me
CO2Me
Me
3ea
f1 (ppm)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Me
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Me
CO2Me
CO2Me
Me

3fa

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1.824
1.968
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3.246
3.727
3.808
4.895
6.342
6.858
6.880
6.899
6.921
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2.87
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1.94
5.89
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1.92
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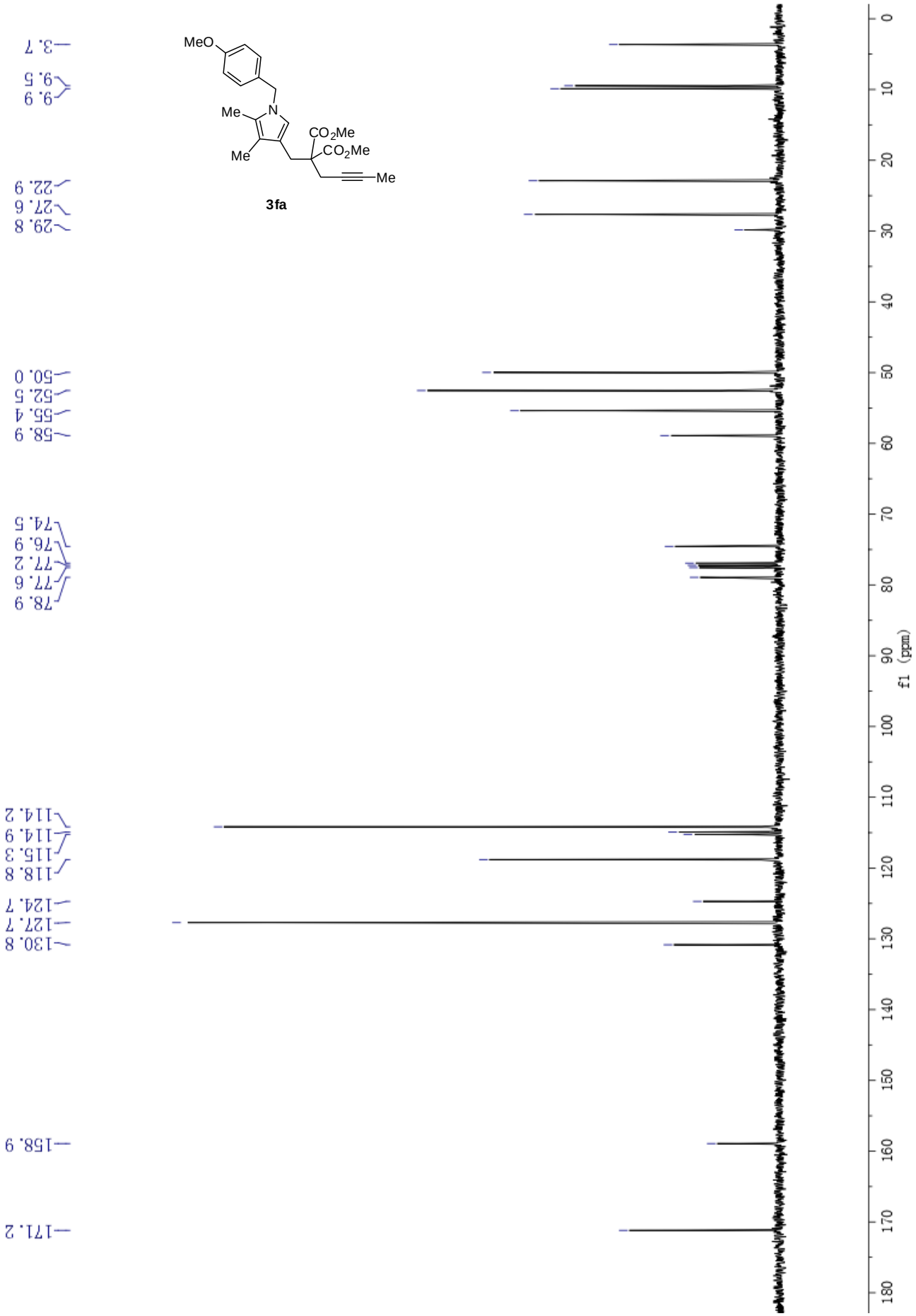
3.88
f1 (ppm)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CO2Me
CO2Me
Me
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50.0
52.5
55.4
58.9
74.5
76.9
77.2
77.6
78.9
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114.9
115.3
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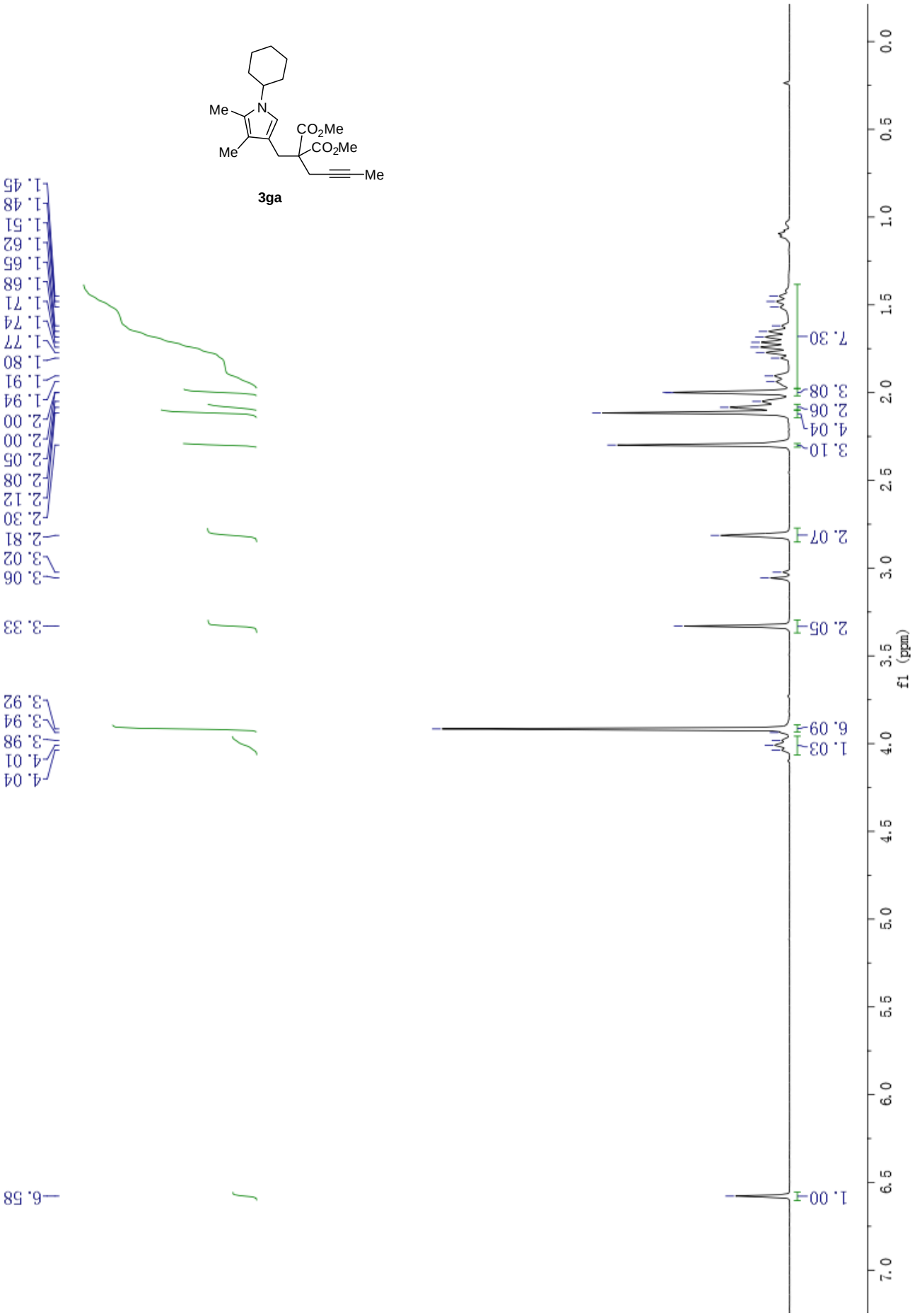
158.9
171.2
f1 (ppm)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CO2Me
Me
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1.80
1.91
1.94
2.00
2.00
2.05
2.08
2.12
2.30
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3.02
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3.33
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3.94
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4.01
4.04
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2.05
6.09
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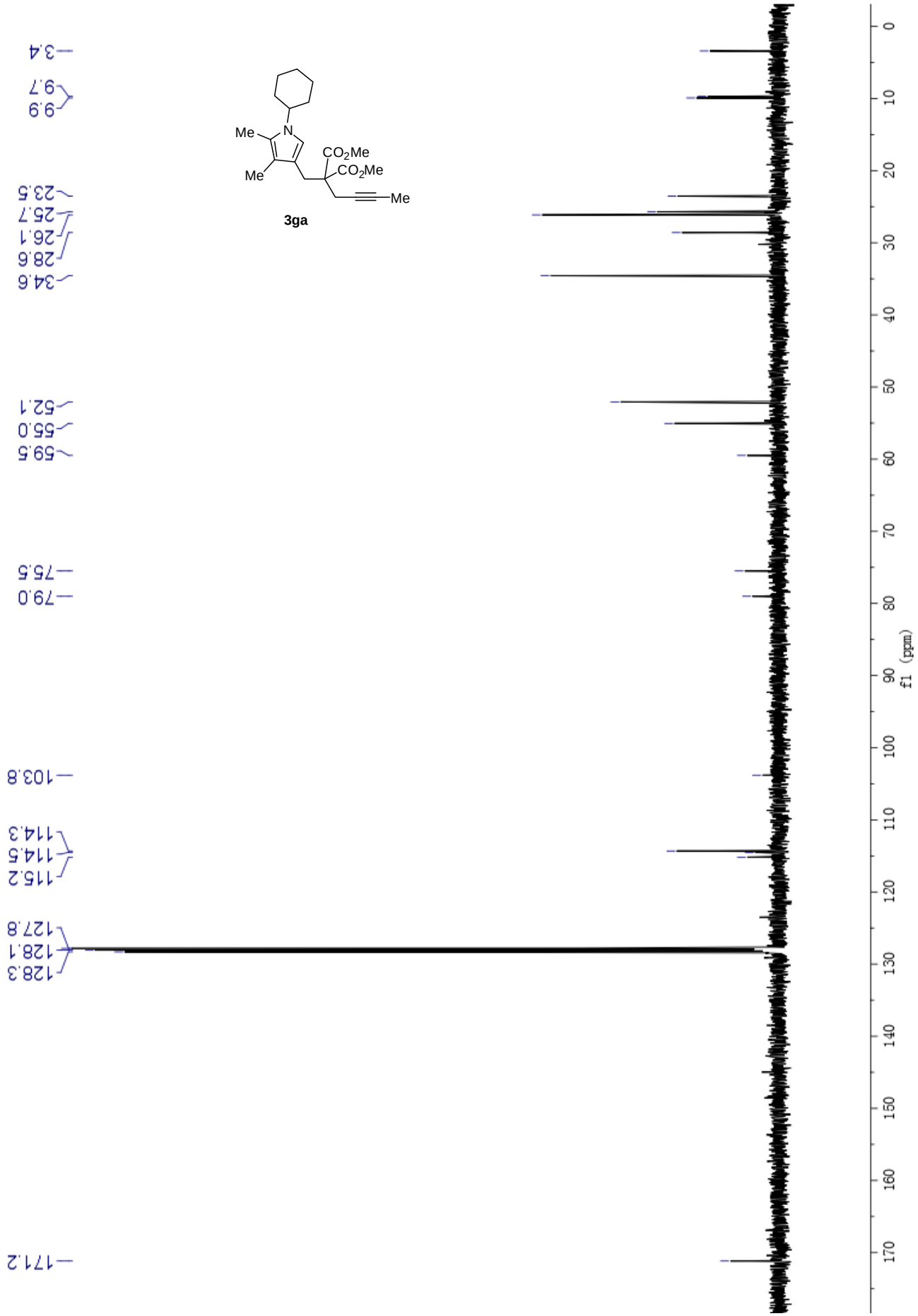
1.00
f1 (ppm)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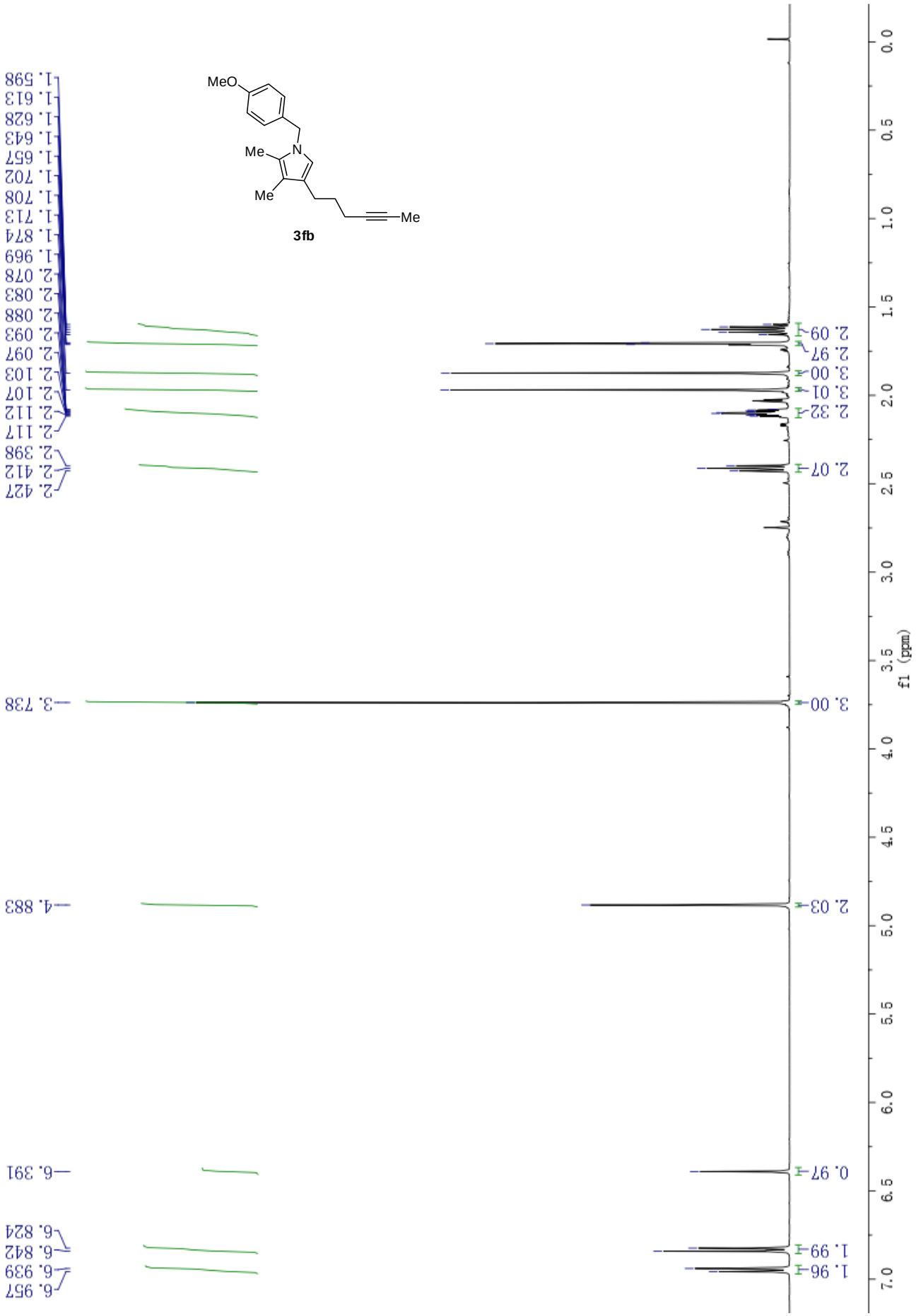
Me
CO2Me
CO2Me
Me
3ga
f1 (ppm)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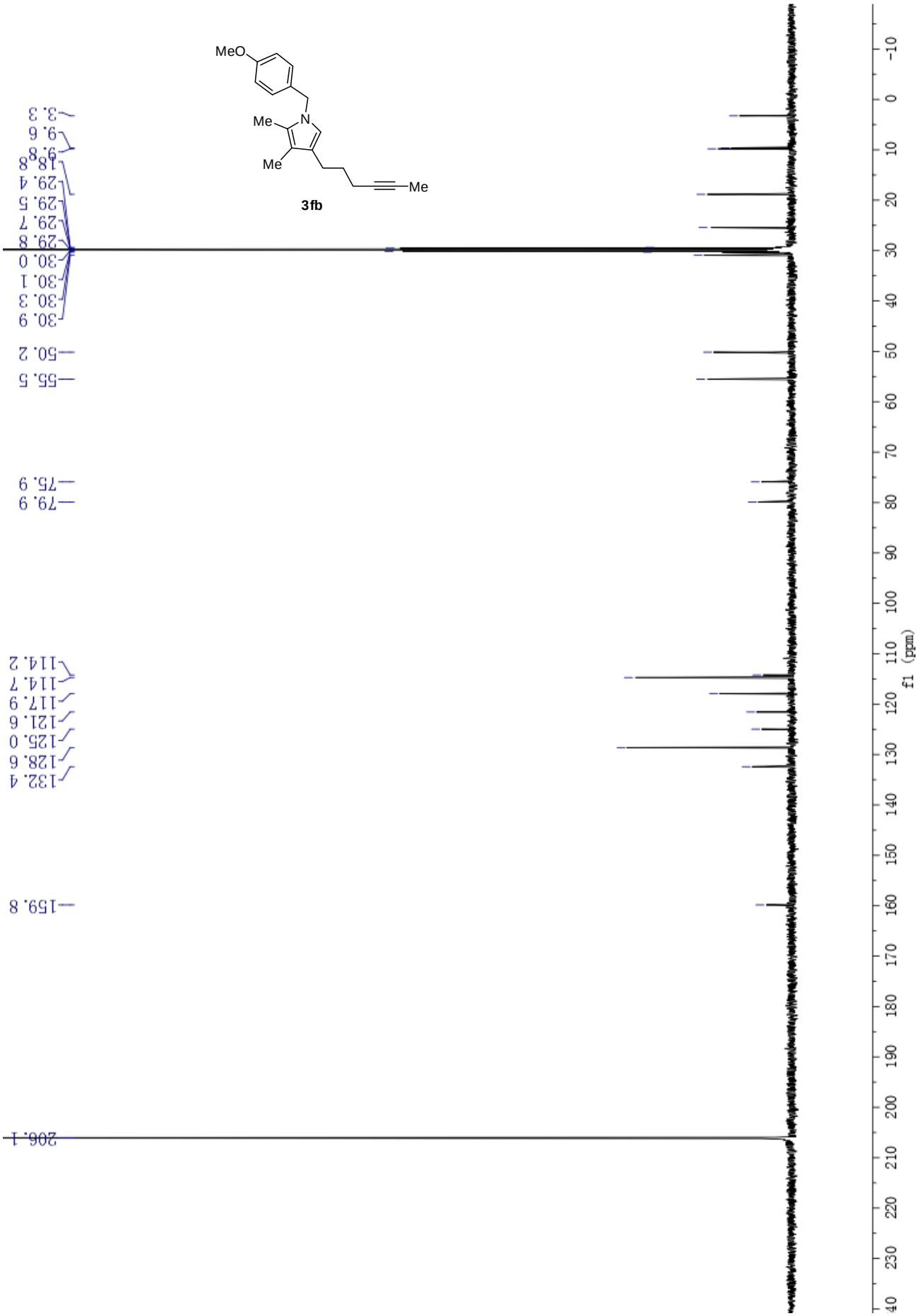
Me
Me
3fb
f1 (ppm)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30.0
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55.5
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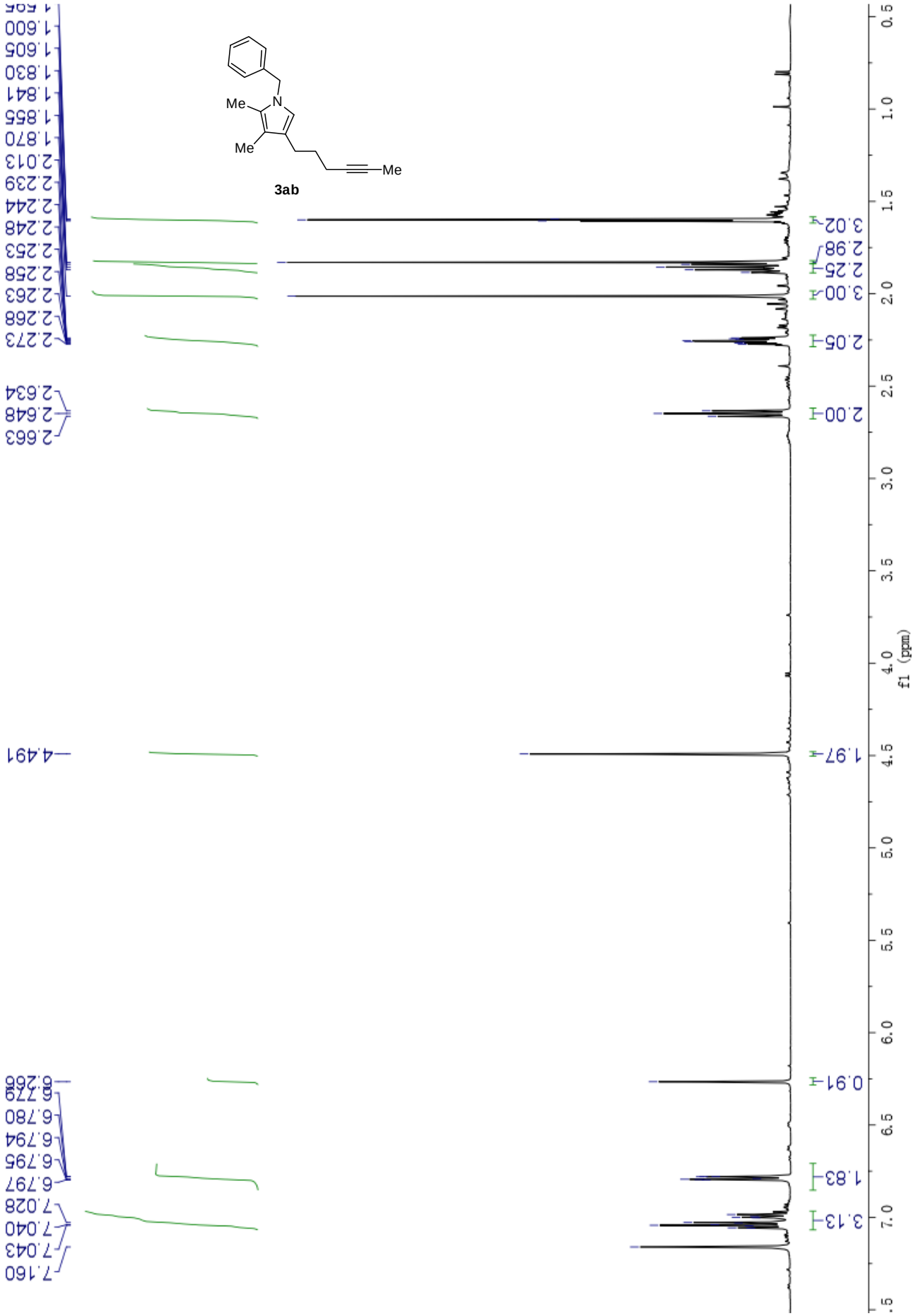
f1 (ppm)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N
Me
Me
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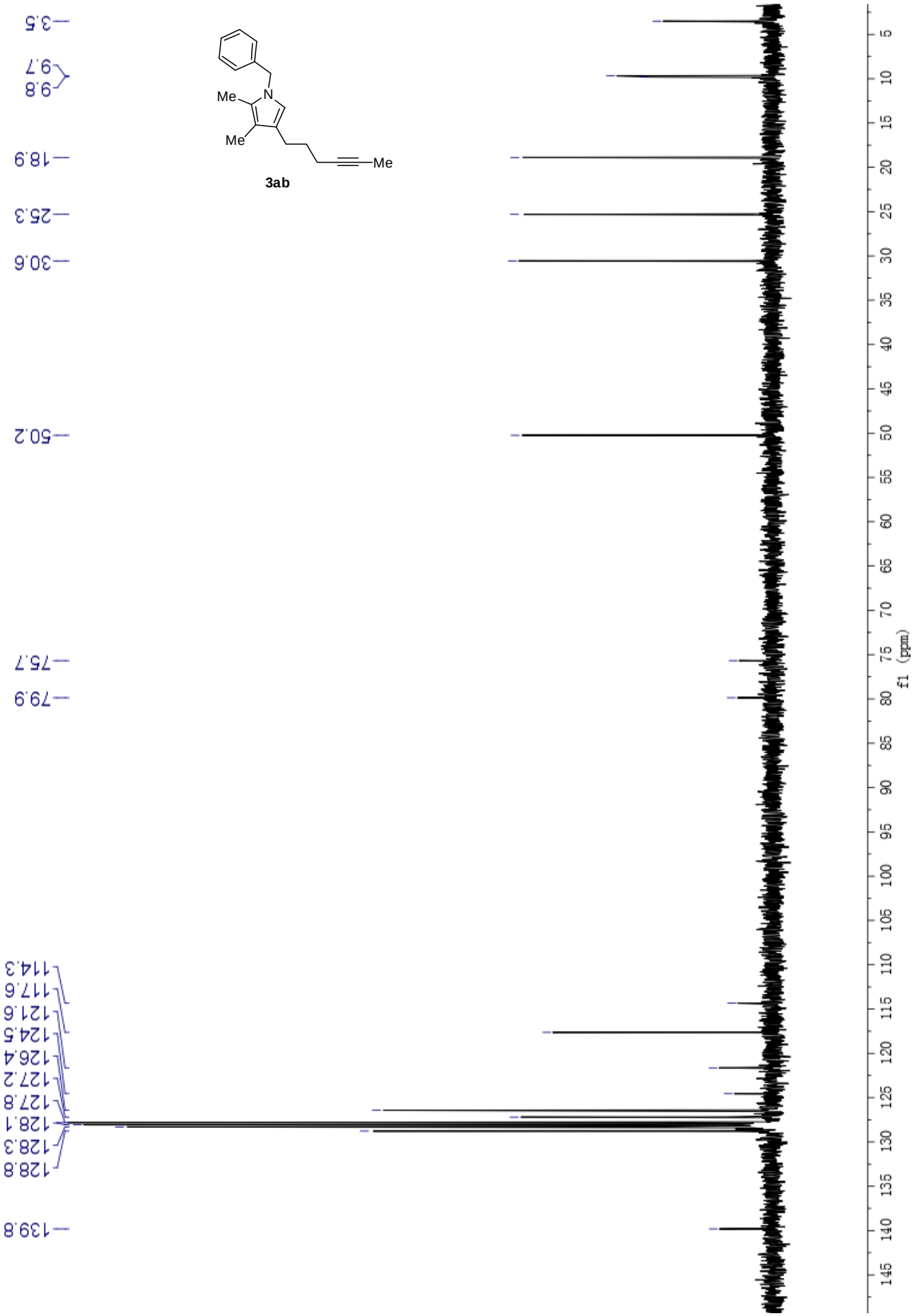
f1 (ppm)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N
Me
Me
3ab
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9.8
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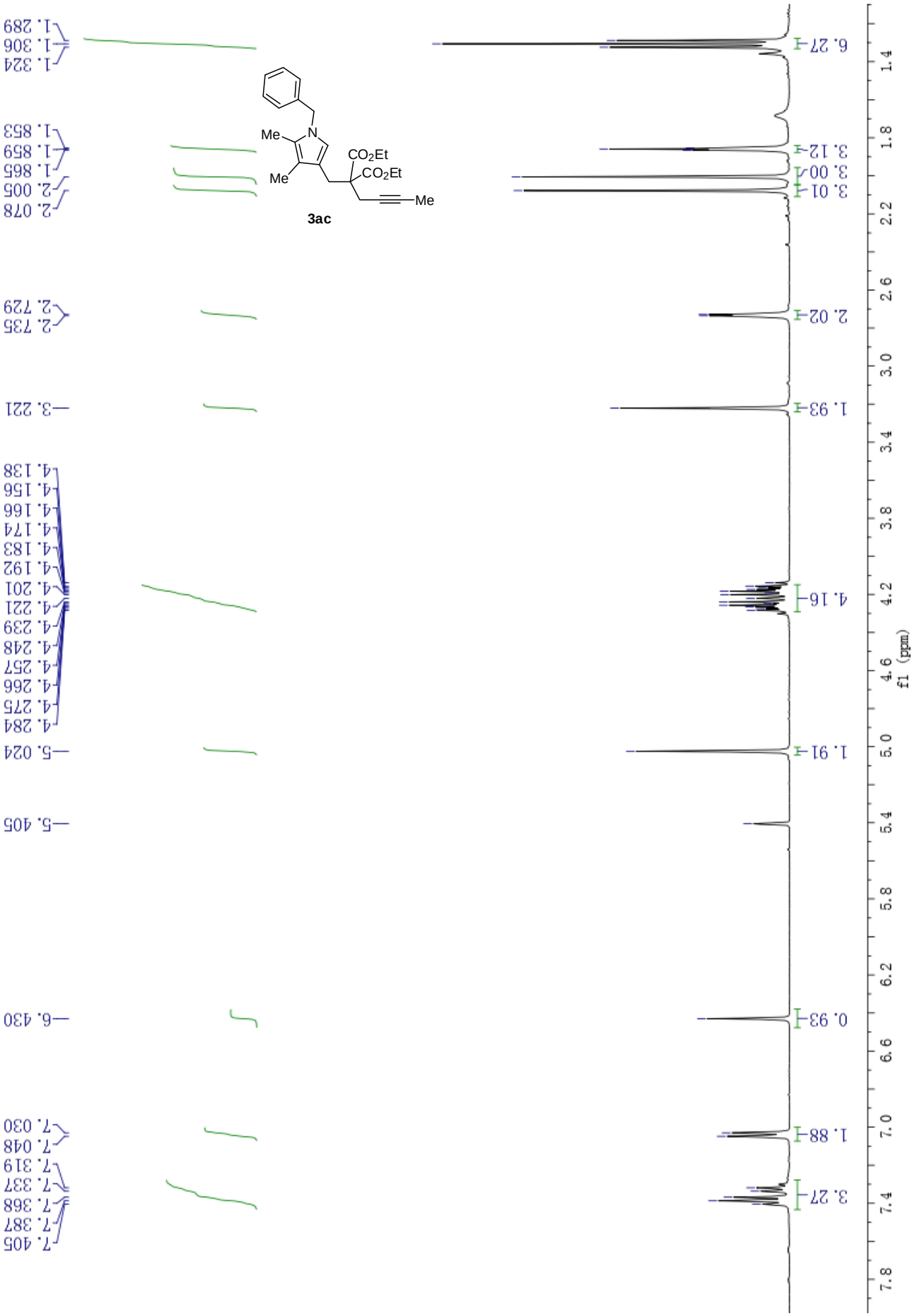
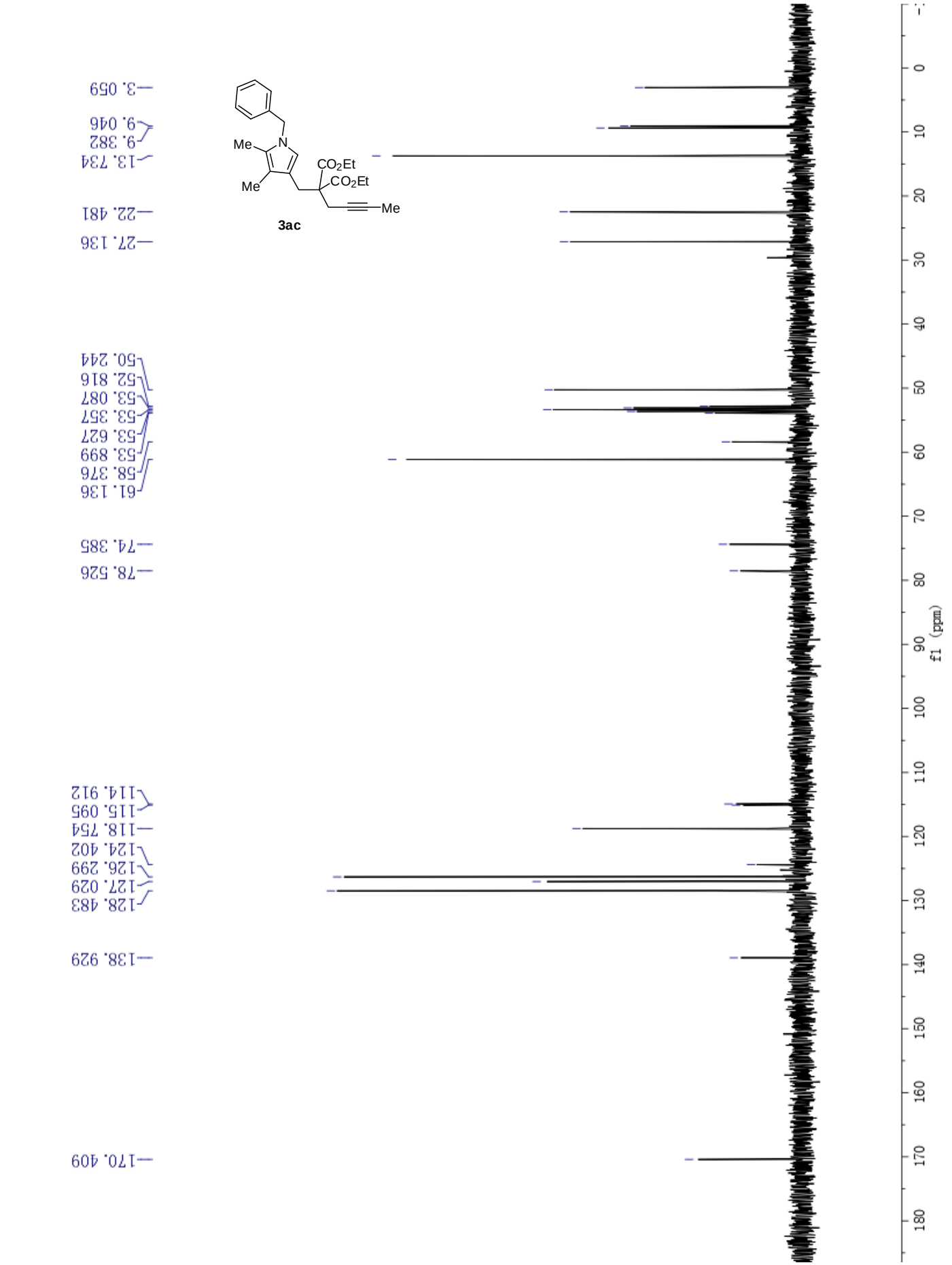
128.3
128.8
139.8
f1 (ppm)

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74.385
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115.095
118.754
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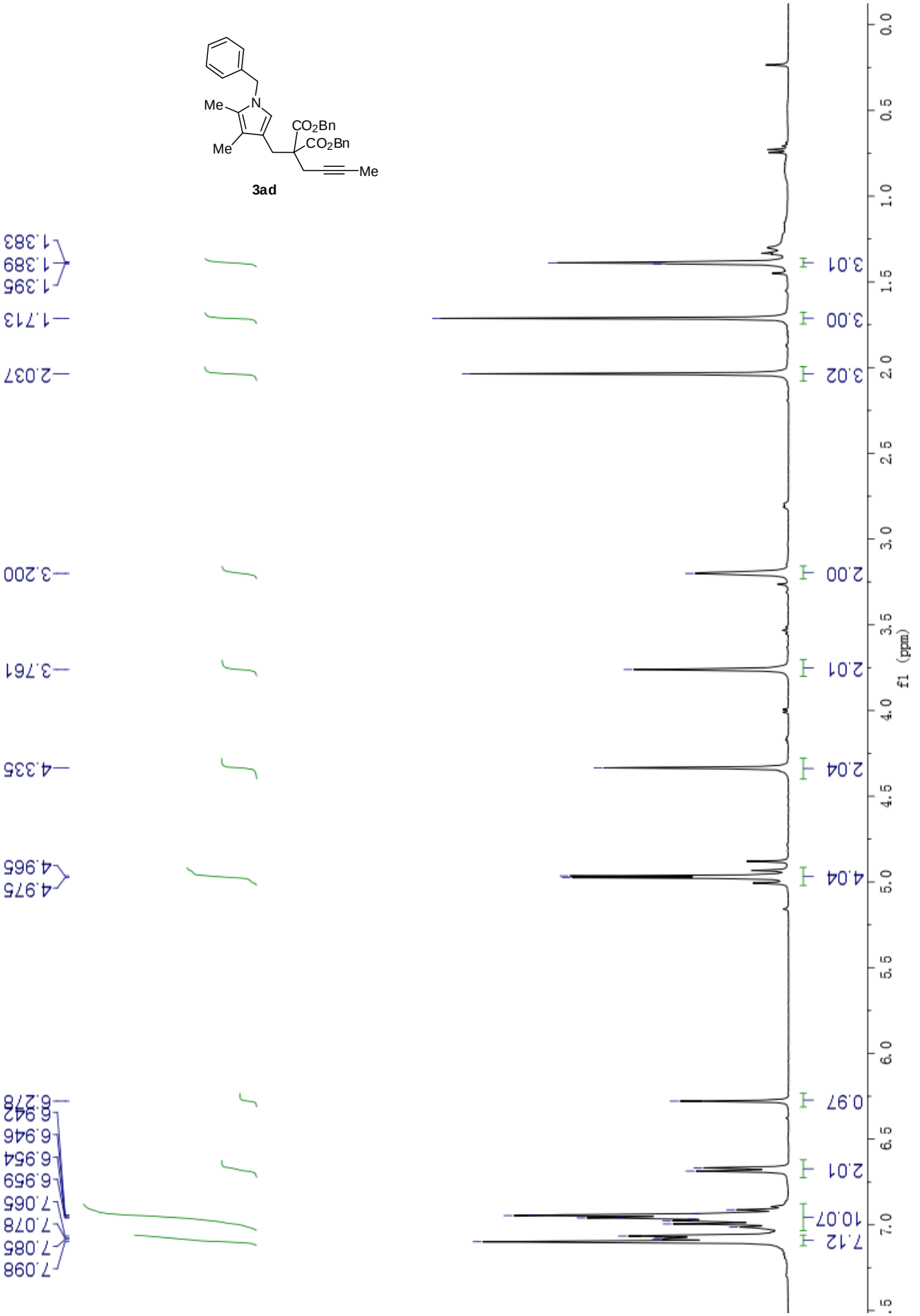
CO2Et
CO2Et
Me
3ac
f1 (ppm)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7.085
7.098
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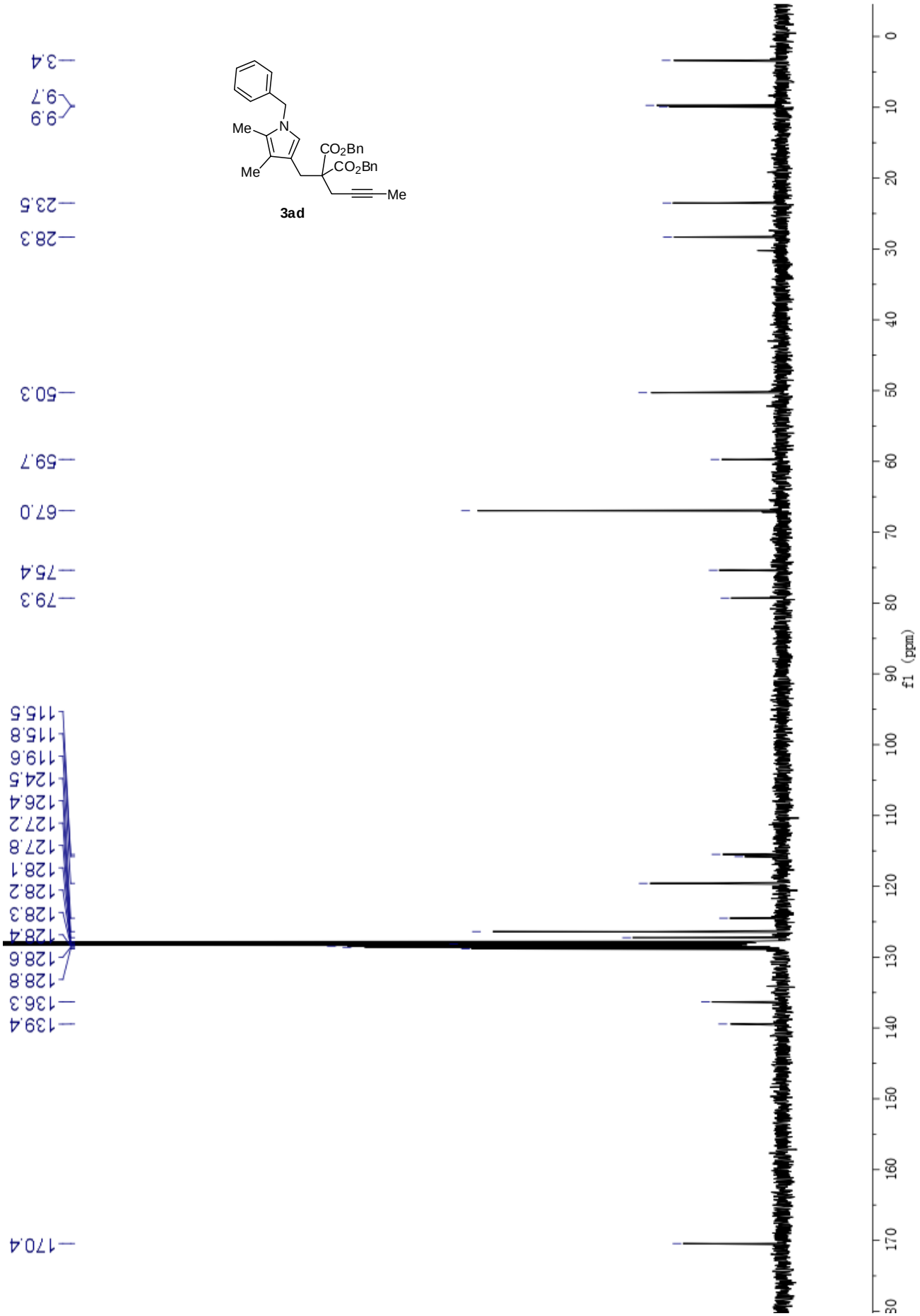
10.07
7.12
f1 (ppm)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139.4
170.4
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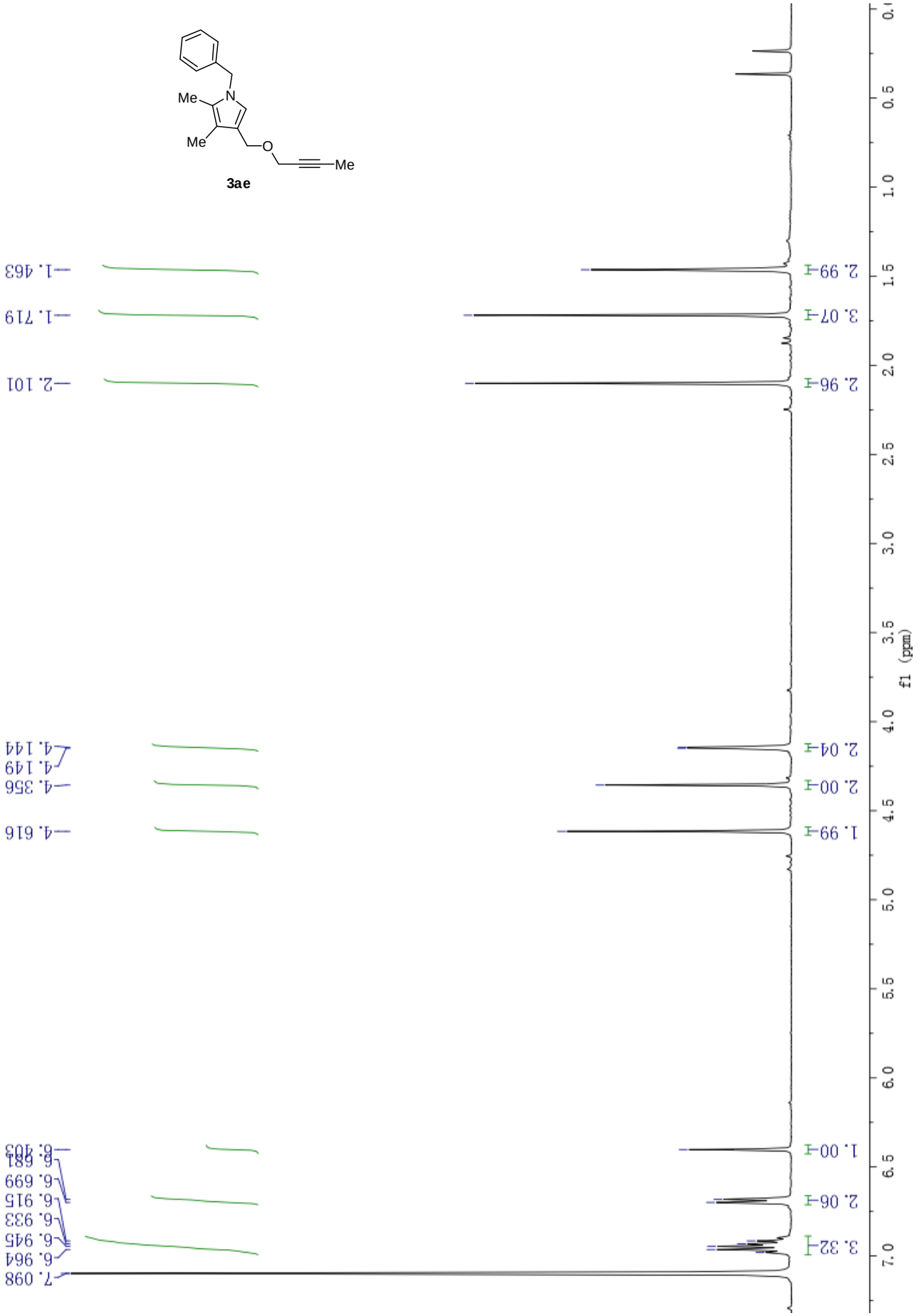
N
Me
CO2Bn
CO2Bn
Me
3ad
f1 (ppm)


Me
N
Me
O
Me
3ae
7.098
6.964
6.945
6.933
6.915
6.699
6.681
6.405
4.616
4.356
4.149
4.144
2.101
1.719
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2.06
3.32
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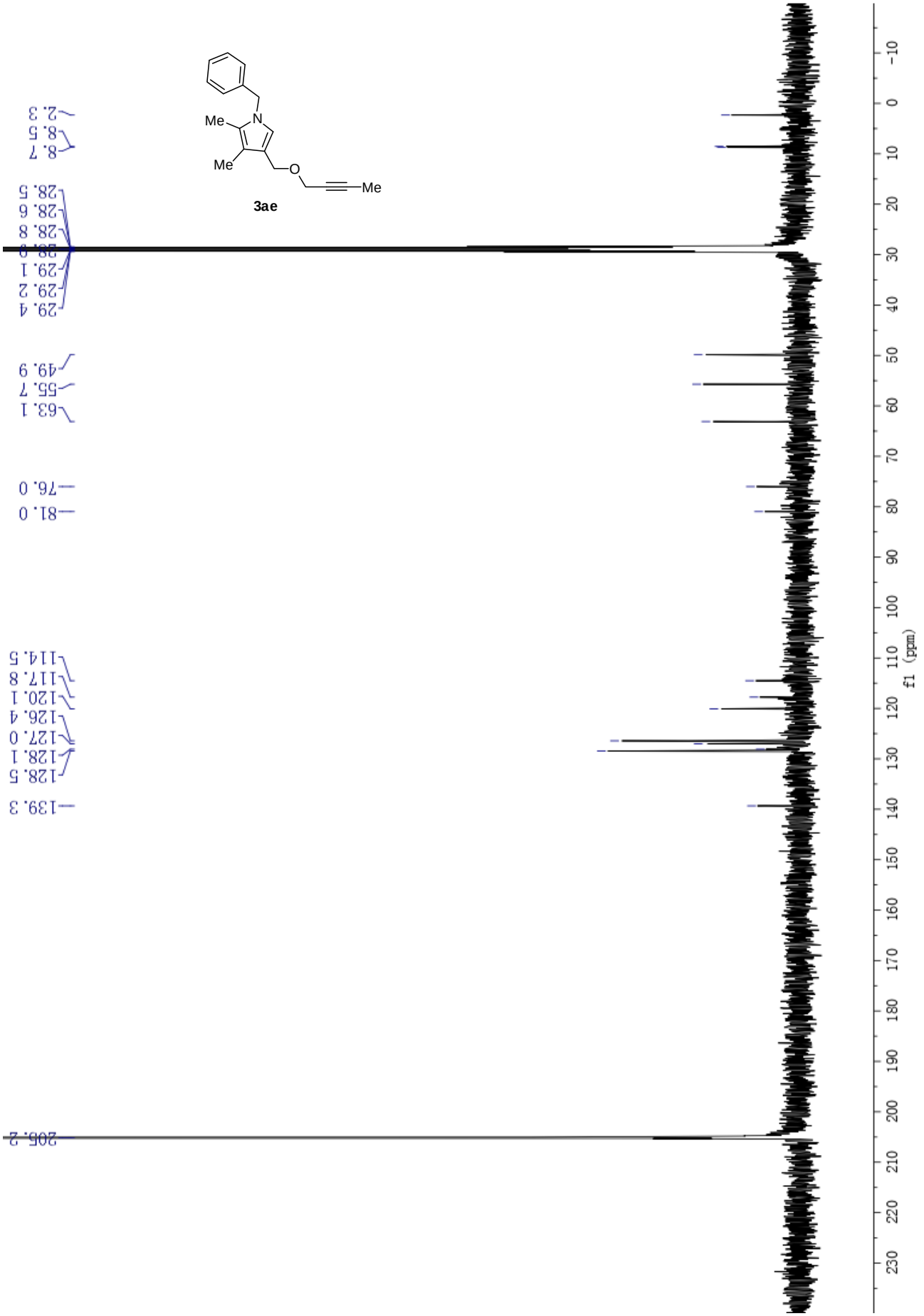
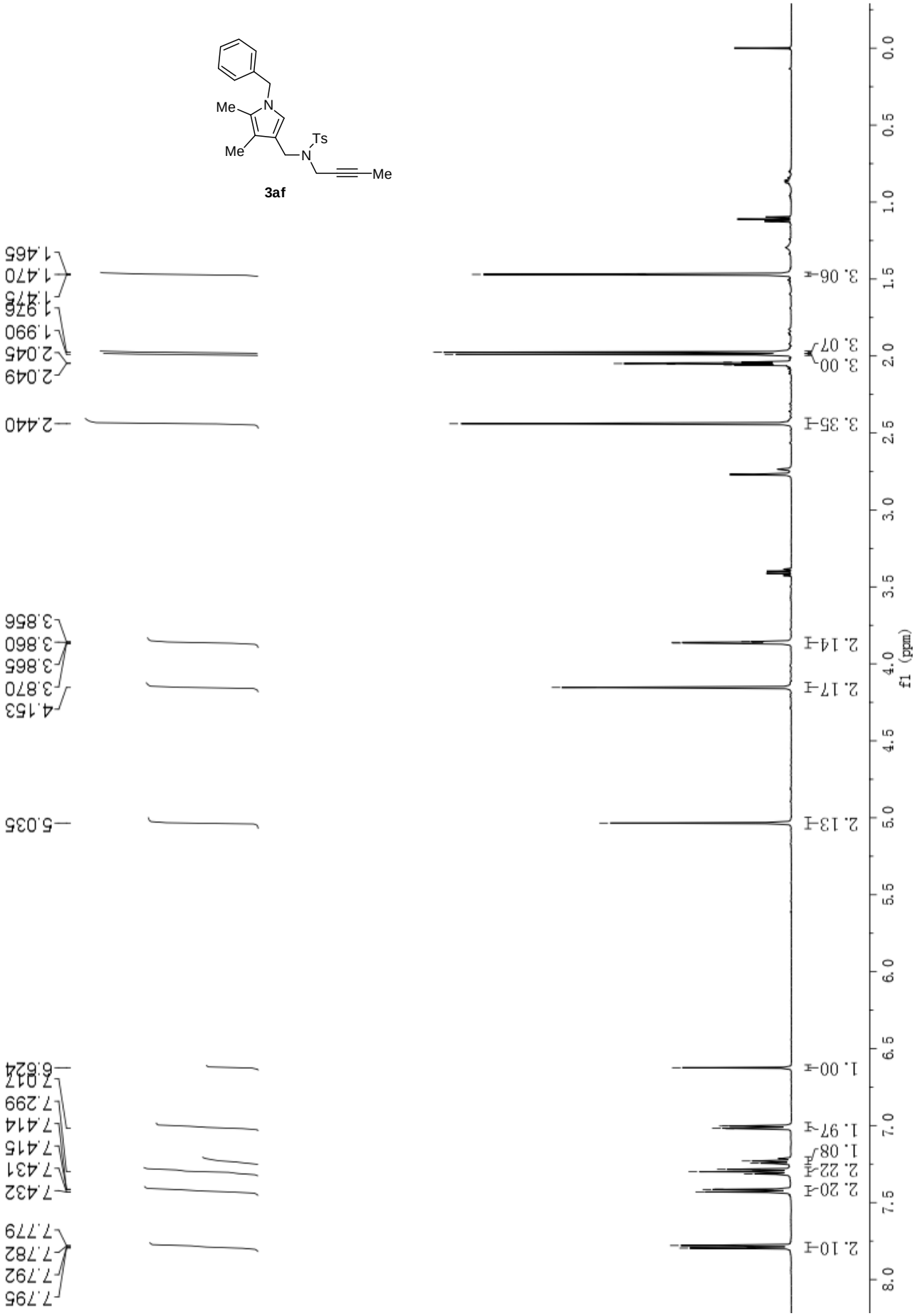
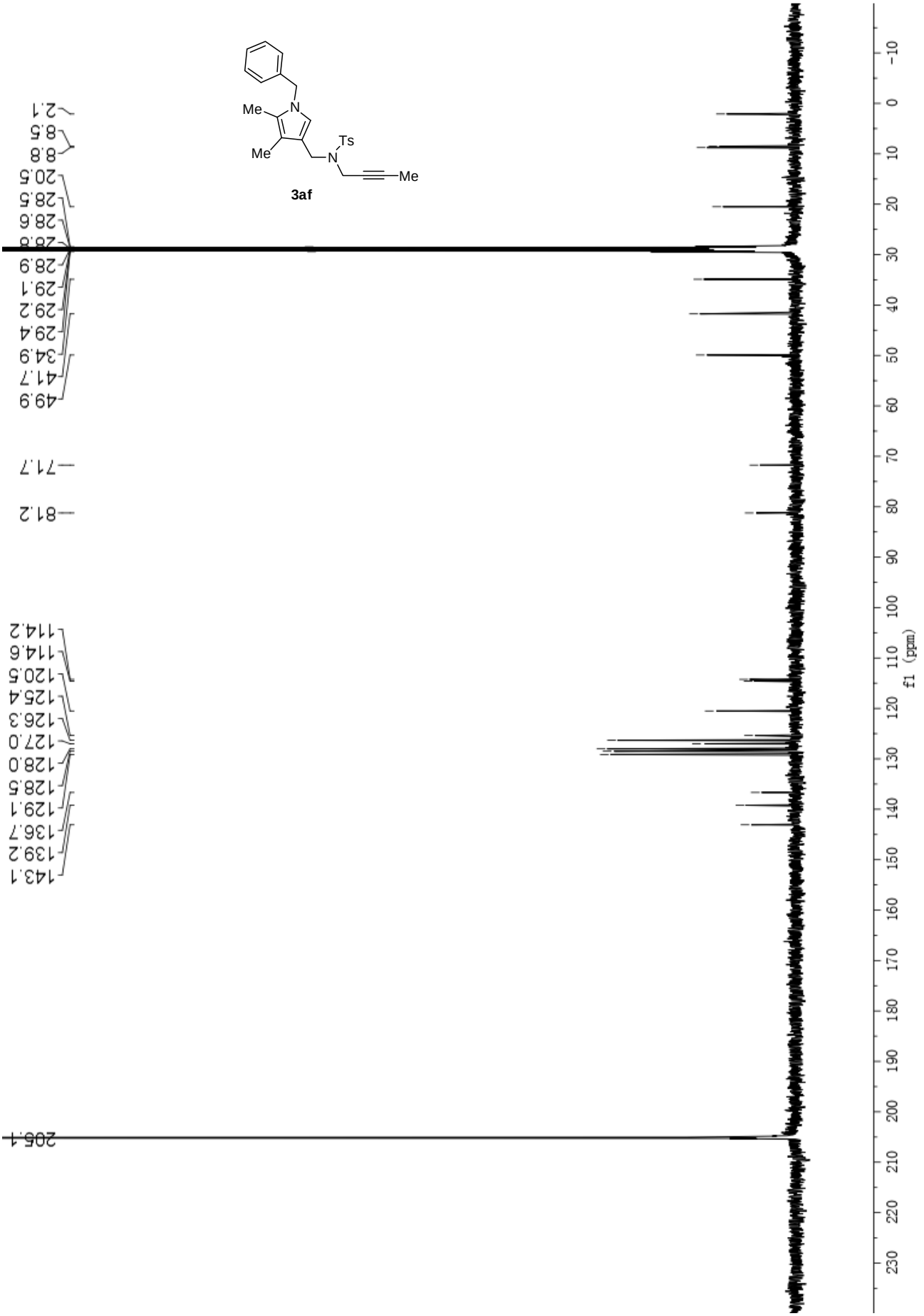
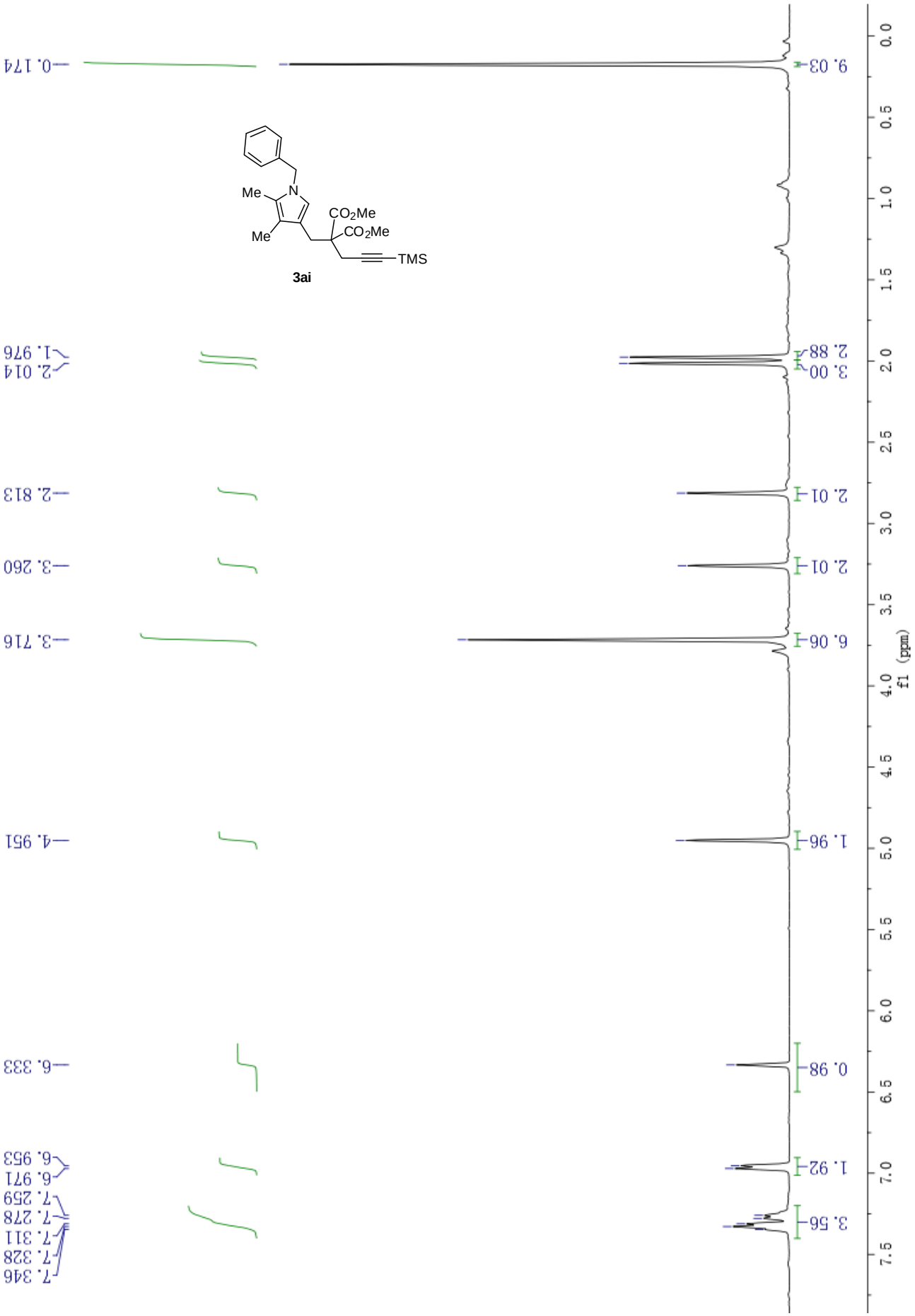
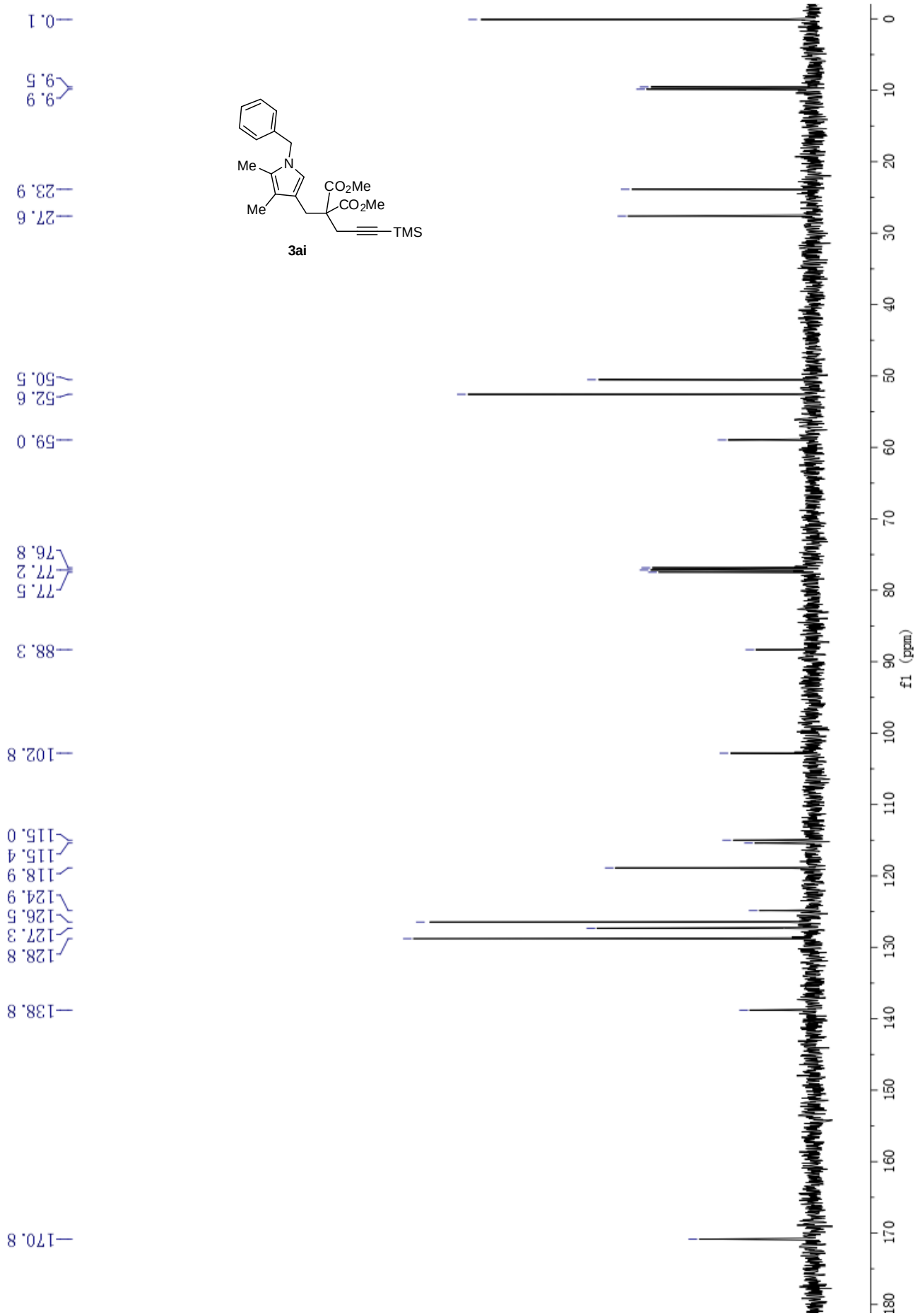
2.00
2.04
2.96
3.07
2.99
f1 (ppm)

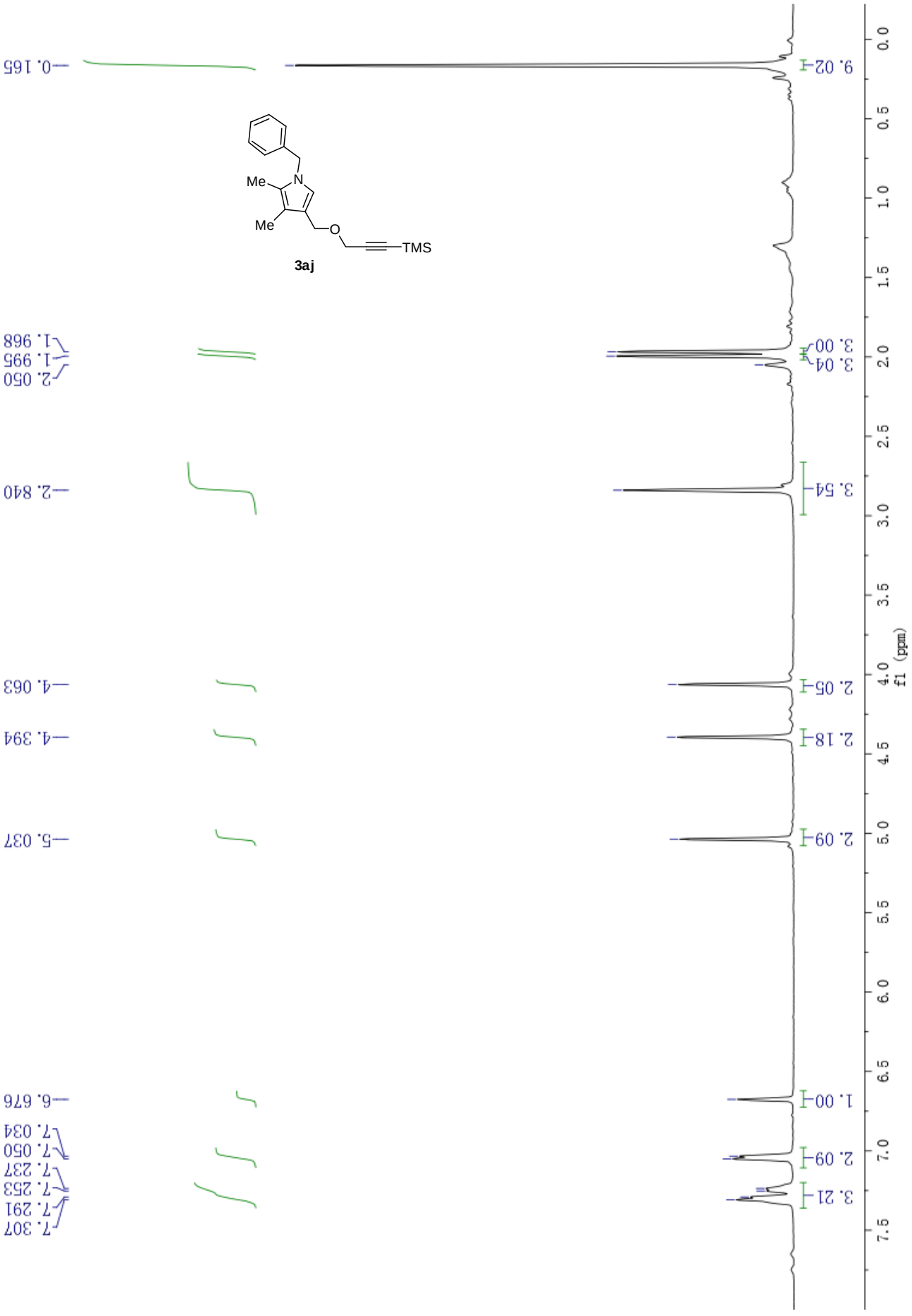

Me
N
Me
O
Me
3ae
f1 (ppm)

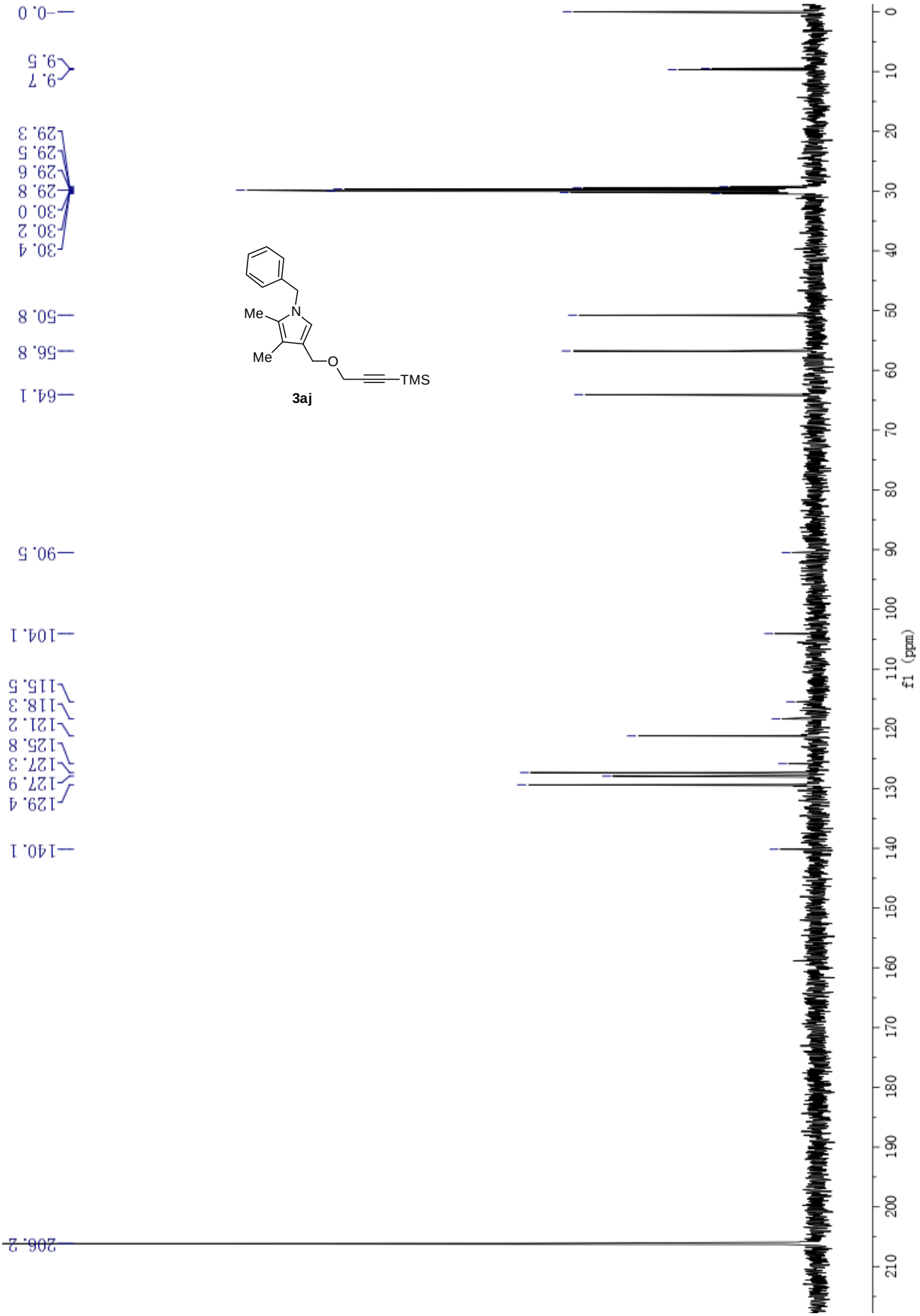

Me
N
Me
Ts
N
Me
3af
1.465
1.470
1.475
1.978
1.990
2.045
2.049
2.440
3.856
3.860
3.865
3.870
4.153
5.035
6.824
7.017
7.299
7.414
7.415
7.431
7.432
7.779
7.782
7.792
7.795
3.06
3.07
3.00
3.35
2.14
2.17
2.13
1.00
1.97
1.08
2.22
2.20
2.10
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

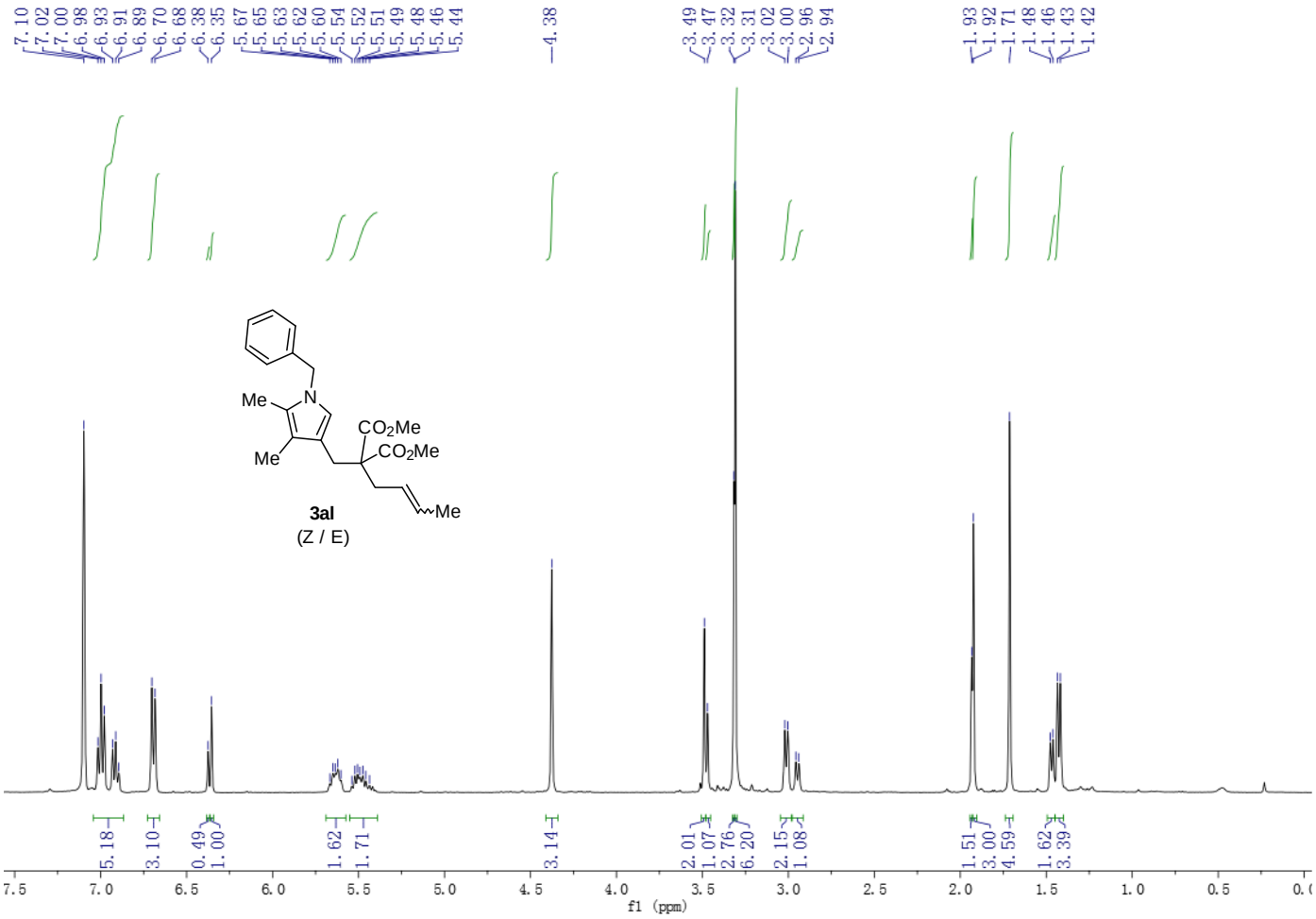

Me
N
Me
Ts
N
Me
3af
2.1
8.5
8.8
20.5
28.5
28.6
28.8
28.9
29.1
29.2
29.4
34.9
41.7
49.9
71.7
81.2
114.2
114.6
120.5
125.4
126.3
127.0
128.0
128.5
129.1
136.7
139.2
143.1
205.1
f1 (ppm)

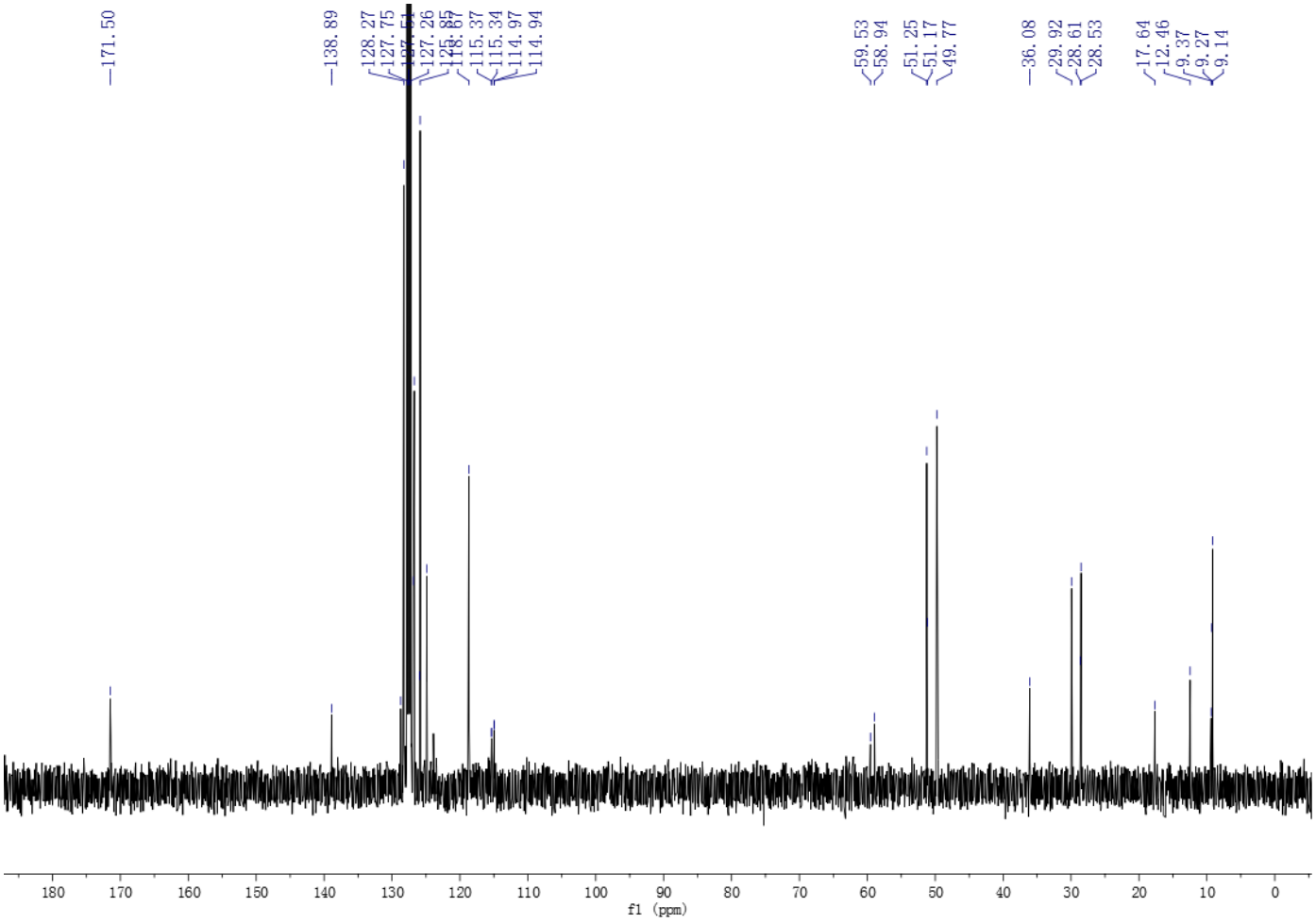

Me
N
Me
CO2Me
CO2Me
TMS
3ai
f1 (ppm)

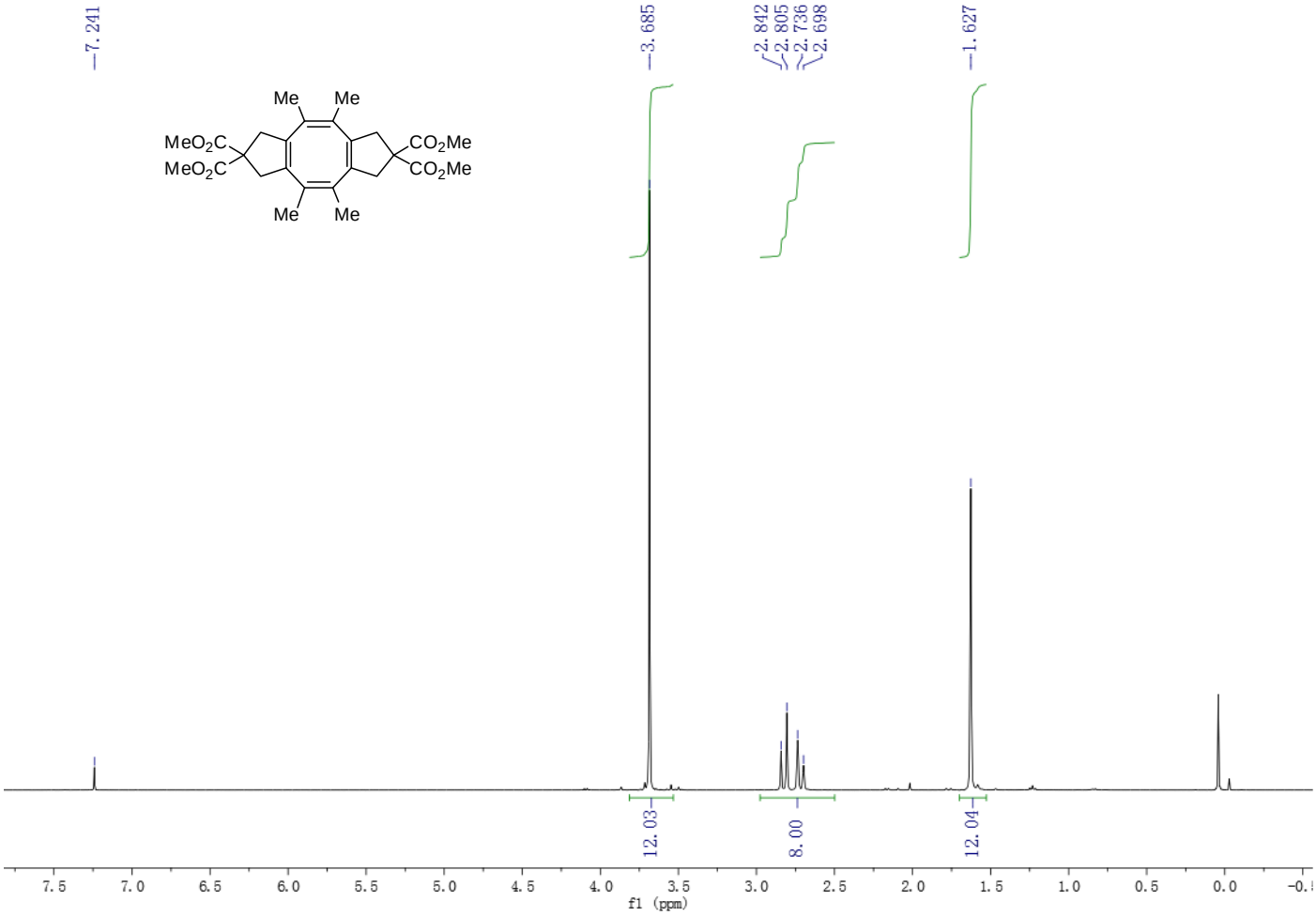

Me
N
Me
CO2Me
CO2Me
TMS
3ai
f1 (ppm)


Me
N
Me
O
TMS
3aj
0.165
9.02
3.00
3.04
1.968
1.995
2.050
2.840
3.54
4.063
2.05
4.394
2.18
5.037
2.09
6.676
1.00
7.034
7.050
7.237
7.253
7.291
7.307
2.09
3.21
f1 (ppm)


0.0
9.5
9.7
29.3
29.5
29.6
29.8
30.0
30.2
30.4
50.8
56.8
64.1
90.5
104.1
115.5
118.3
121.2
125.8
127.3
127.9
129.4
140.1
206.2
Me
N
Me
O
TMS
3aj
f1 (ppm)


7.10
7.02
7.00
6.98
6.93
6.91
6.89
6.70
6.68
6.38
6.35
5.67
5.65
5.63
5.62
5.60
5.54
5.52
5.51
5.49
5.48
5.46
5.44
4.38
3.49
3.47
3.32
3.31
3.02
3.00
2.96
2.94
1.93
1.92
1.71
1.48
1.46
1.43
1.42
Me
N
Me
CO2Me
CO2Me
Me
3al
(Z / E)
5.18
3.10
0.49
1.00
1.62
1.71
3.14
2.01
1.07
2.76
6.20
2.15
1.08
1.51
3.00
4.59
1.62
3.39
f1 (ppm)


171.50
138.89
128.27
127.75
127.26
115.37
115.34
114.97
114.94
59.53
58.94
51.25
51.17
49.77
36.08
29.92
28.61
28.53
17.64
12.46
9.37
9.27
9.14
f1 (ppm)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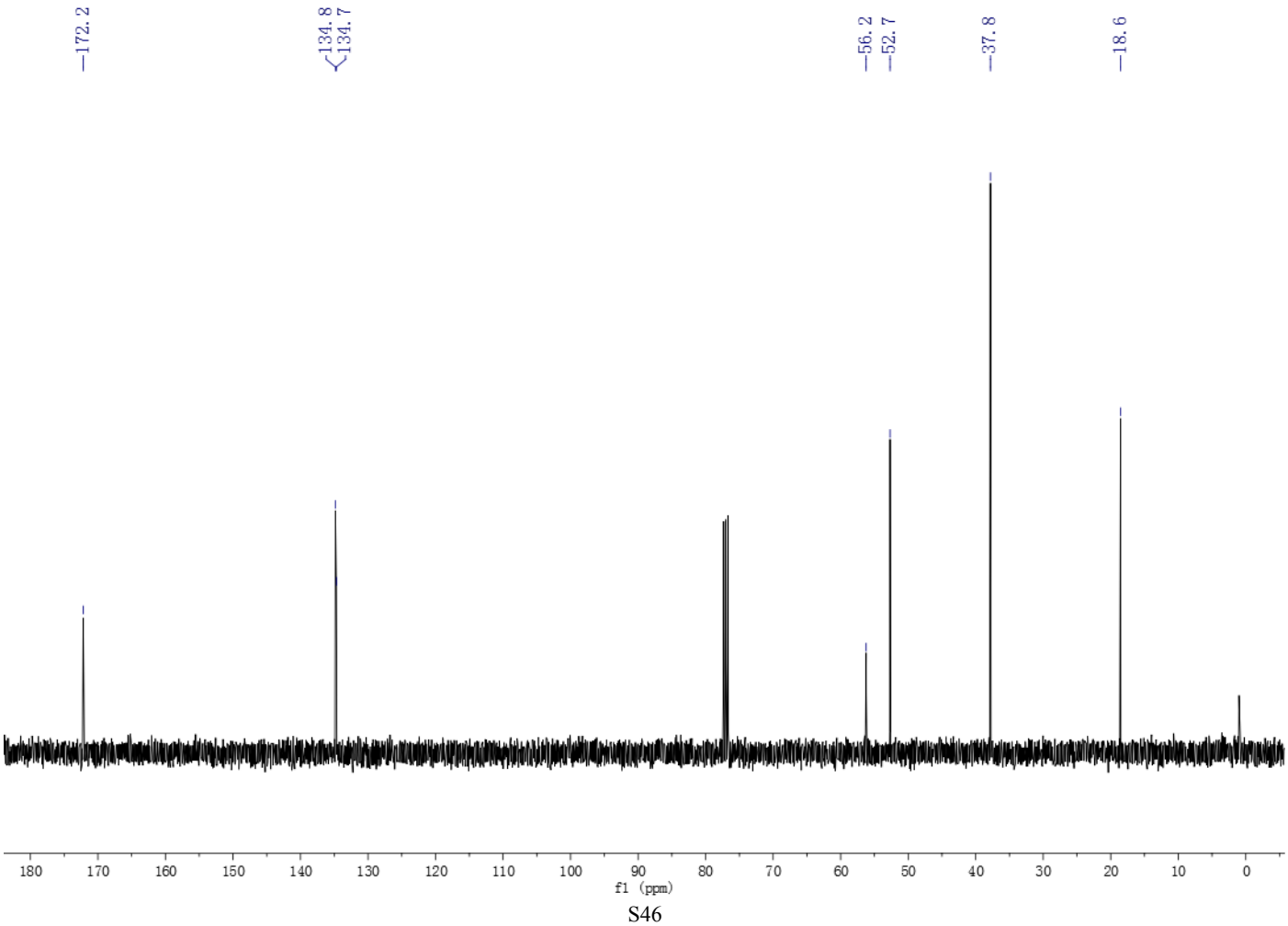
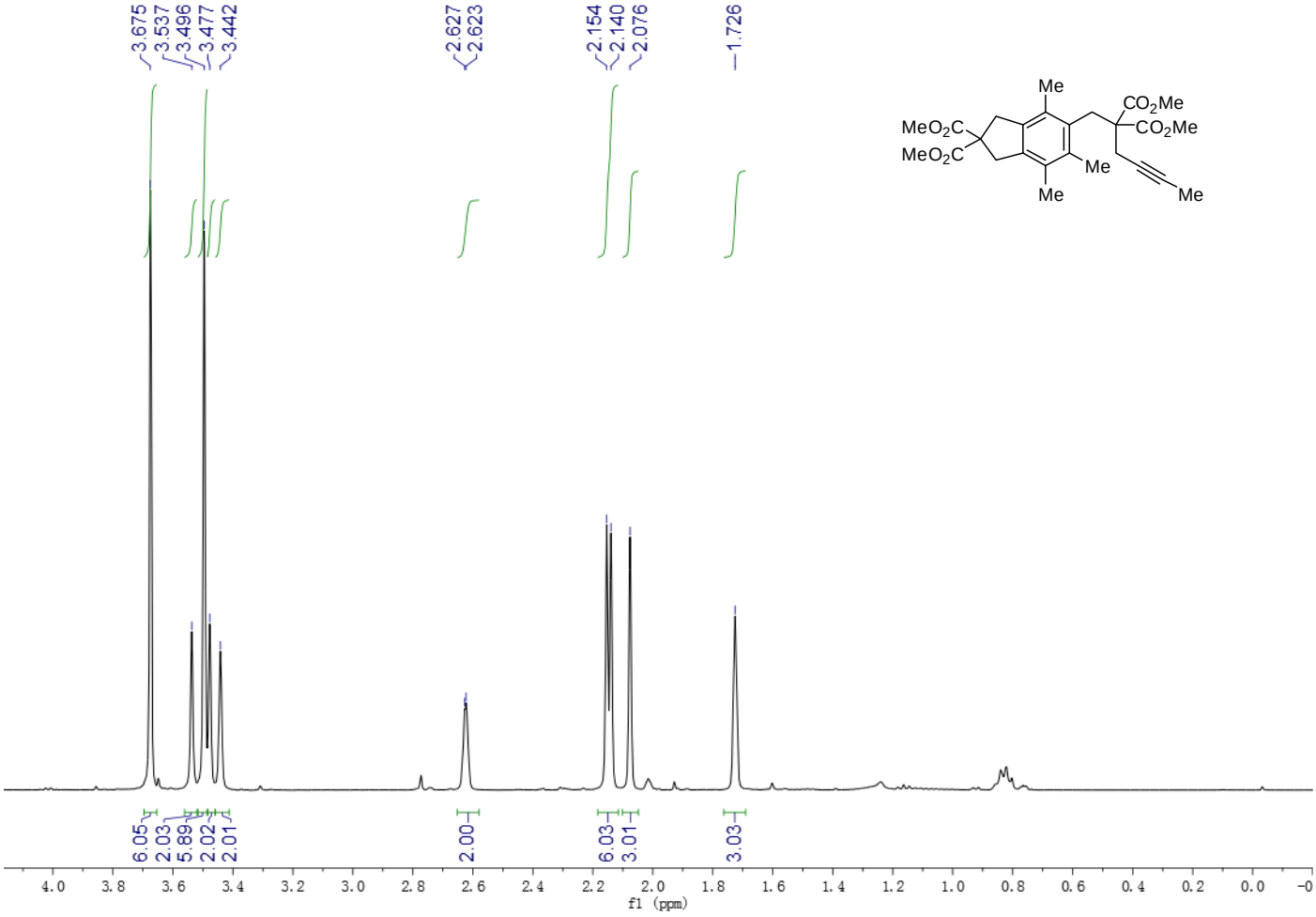
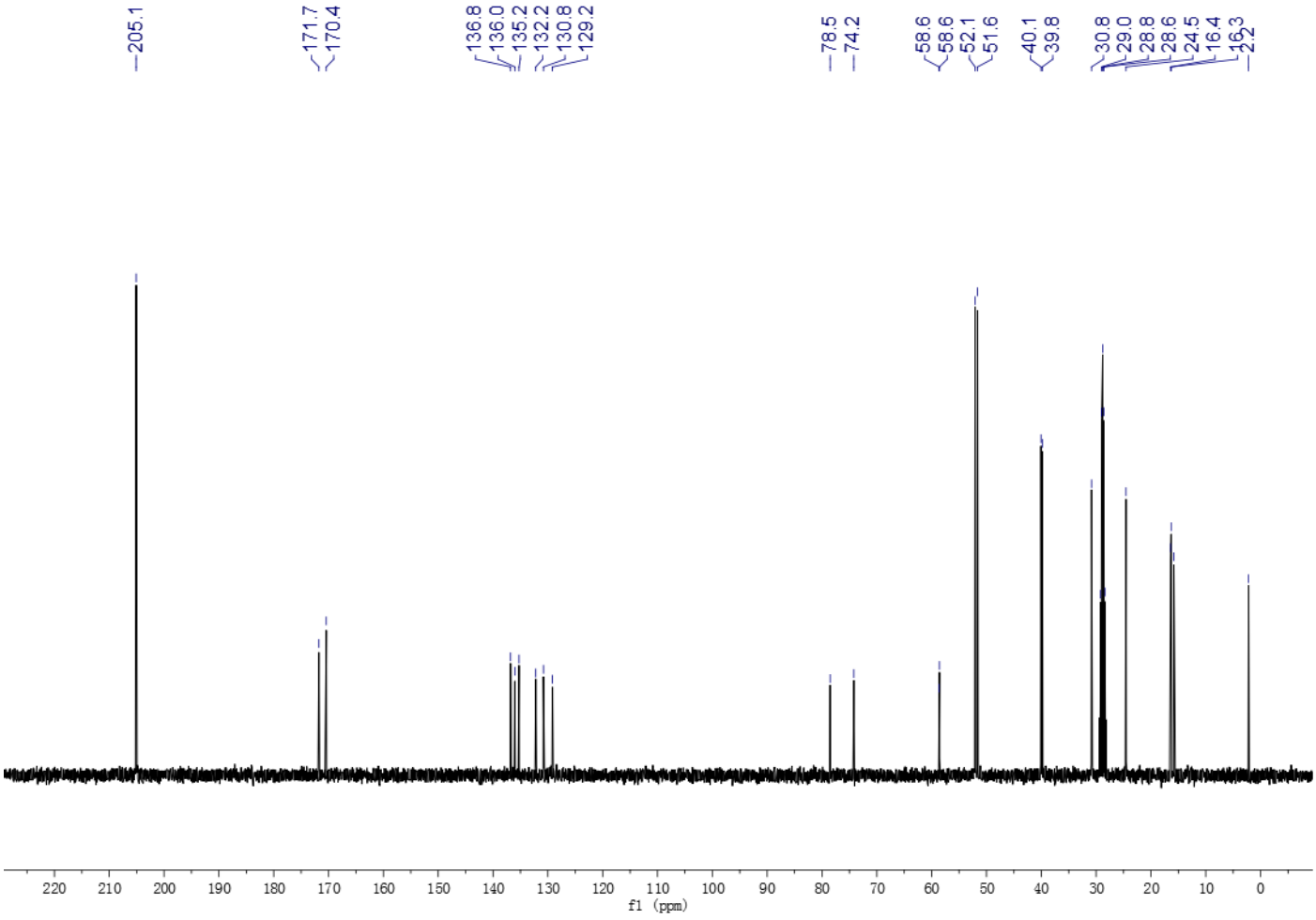
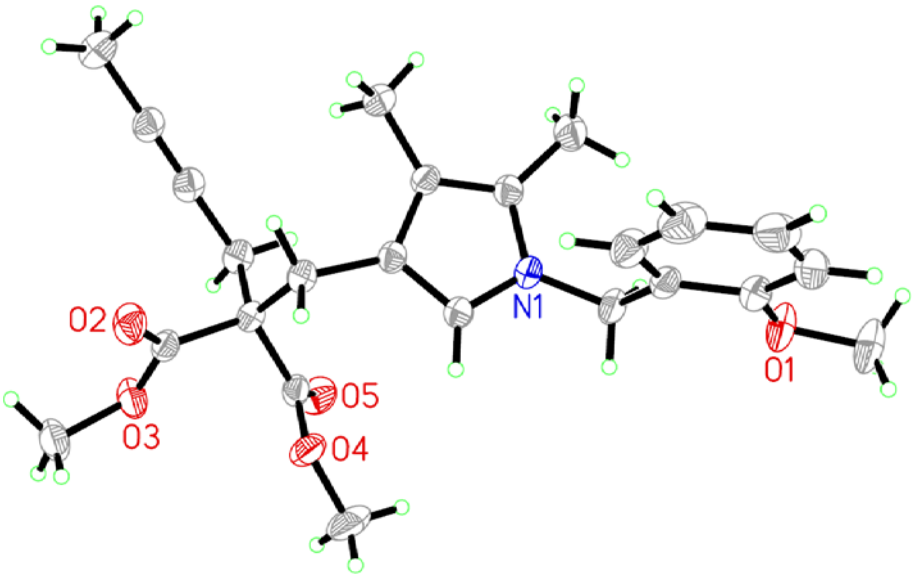
3.685
2.842
2.805
2.736
2.698
1.627
Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
Me
Me
12.03
8.00
12.04
f1 (ppm)


172.2
134.8
134.7
56.2
52.7
37.8
18.6
f1 (ppm)


3.675
3.537
3.496
3.477
3.442
2.627
2.623
2.154
2.140
2.076
1.726
Me
CO2Me
CO2Me
MeO2C
MeO2C
Me
Me
Me
6.05
2.03
5.89
2.02
2.01
2.00
6.03
3.01
3.03
f1 (ppm)


205.1
171.7
170.4
136.8
136.0
135.2
132.2
130.8
129.2
78.5
74.2
58.6
58.6
52.1
51.6
40.1
39.8
30.8
29.0
28.8
28.6
24.5
16.4
16.3
f1 (ppm)

4. Copy of X-ray of 3da



General	
Code	**3da**
Systematic name	dimethyl 2-(but-2-yn-1-yl)-2-((1-(2-methoxybenzyl)-4,5-dimethyl-1H-pyrrol-3-yl)methyl)malonate
Creation method	SHELXL-97
Phase data	
Formula sum	C24H29NO5
Formula weight	411.48 g/mol
Crystal system	triclinic
Space-group	P -1 (2)
Cell parameters	a=8.2459(8) Å b=8.7253(8) Å c=17.0434(15) Å α=98.293(7)° β=101.048(7)° γ=107.799(7)°
Cell ratio	a/b=0.9451 b/c=0.5119 c/a=2.0669
Cell volume	1118.59(18) $Å^3$
Z	2
Calc. density	1.2216 g/cm^3
RAll	0.0892
Pearson code	aP118
Formula type	NO5P24Q29
Wyckoff sequence	i59

Atomic parameters

Atom	Ox.	Wyck.	Site	S.O.F.	x / a	y / b	z / c	U [$Å^2$]
O2		2i	1		0.4659(2)	0.8876(2)	0.31837(11)	
O4		2i	1		0.9124(2)	0.9044(2)	0.32766(11)	
O3		2i	1		0.6798(2)	0.9807(2)	0.43396(11)	
N1		2i	1		0.8431(2)	0.3932(3)	0.19097(12)	
C11		2i	1		0.5923(3)	0.3363(3)	0.22918(14)	
O5		2i	1		0.9503(2)	0.7669(3)	0.42605(12)	
C15		2i	1		0.5852(3)	0.6377(3)	0.26109(14)	
H15A		2i	1		0.45870	0.58470	0.24990	0.0510

H15B	2i	1	0.60710	0.71850	0.22730	0.0510
C16	2i	1	0.6551(3)	0.7297(3)	0.35213(14)	
C17	2i	1	0.5865(3)	0.8725(3)	0.36400(14)	
C22	2i	1	0.8552(3)	0.8000(3)	0.37453(15)	
C9	2i	1	0.8162(3)	0.5388(3)	0.21081(14)	
H9A	2i	1	0.89000	0.64150	0.20800	0.0530
O1	2i	1	1.1641(3)	0.2507(3)	0.05967(12)	
C20	2i	1	0.4082(4)	0.5500(3)	0.40200(15)	
C12	2i	1	0.7046(3)	0.2669(3)	0.20084(14)	
C19	2i	1	0.5987(3)	0.6157(3)	0.41075(15)	
H19A	2i	1	0.64080	0.52390	0.40130	0.0570
H19B	2i	1	0.65550	0.67660	0.46670	0.0570
C10	2i	1	0.6630(3)	0.5098(3)	0.23552(13)	
C1	2i	1	0.9137(3)	0.3214(3)	0.05900(15)	
C21	2i	1	0.2555(4)	0.4936(3)	0.39749(15)	
C8	2i	1	0.9785(3)	0.3713(4)	0.15125(14)	
H8A	2i	1	1.01910	0.28750	0.17120	0.0600
H8B	2i	1	1.07780	0.47370	0.16610	0.0600
C2	2i	1	0.7616(3)	0.3366(4)	0.01706(17)	
H2A	2i	1	0.69510	0.37970	0.04620	0.0710
C14	2i	1	0.4217(3)	0.2431(3)	0.24628(17)	
H14A	2i	1	0.40510	0.12750	0.23630	0.0850
H14B	2i	1	0.32650	0.26080	0.21100	0.0850
H14C	2i	1	0.42440	0.28130	0.30240	0.0850
C4	2i	1	1.0121(4)	0.2577(3)	0.01339(17)	
C23	2i	1	0.0686(4)	0.4237(4)	0.39420(18)	
H23C	2i	1	0.03600	0.34920	0.34200	0.0780
H23A	2i	1	-0.00770	0.48460	0.37960	0.0780
H23B	2i	1	0.03080	0.34200	0.42520	0.0780
C3	2i	1	0.9552(4)	0.2081(4)	-0.07014(18)	
H3A	2i	1	1.02010	0.16380	-0.09980	0.0810
C13	2i	1	0.6921(4)	0.0920(4)	0.18133(19)	
H13A	2i	1	0.79370	0.08500	0.16340	0.0980
H13B	2i	1	0.58790	0.03070	0.13860	0.0980
H13C	2i	1	0.68680	0.04690	0.22930	0.0980
C18	2i	1	0.6443(4)	1.1324(4)	0.4496(2)	
H18A	2i	1	0.71720	1.19860	0.50180	0.1080
H18B	2i	1	0.52280	1.10820	0.44990	0.1080
H18C	2i	1	0.66910	1.19150	0.40750	0.1080
C5	2i	1	0.7051(4)	0.2898(4)	-0.06677(19)	
H5A	2i	1	0.60260	0.30260	-0.09400	0.0870
C6	2i	1	0.8012(5)	0.2241(4)	-0.10997(19)	
H6A	2i	1	0.76220	0.19010	-0.16670	0.0910
C7	2i	1	1.2792(5)	0.1985(6)	0.0179(2)	
H7A	2i	1	1.37830	0.19620	0.05720	0.1460

H7B	2i	1	1.31950	0.27410	-0.01570	0.1460
H7C	2i	1	1.21710	0.09020	-0.01600	0.1460
C39	2i	1	1.1014(3)	0.9803(5)	0.3445(2)	
H39A	2i	1	1.12980	1.05350	0.30830	0.1290
H39B	2i	1	1.15300	0.89630	0.33620	0.1290
H39C	2i	1	1.14680	1.04140	0.40020	0.1290

Anisotropic displacement parameters, in Å²

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O2	0.0513(11)	0.0654(13)	0.0655(12)	0.0341(10)	0.0058(9)	0.0108(10)
O4	0.0373(10)	0.0626(12)	0.0738(13)	0.0137(8)	0.0210(9)	0.0222(10)
O3	0.0578(11)	0.0587(12)	0.0598(12)	0.0315(9)	0.0026(9)	-0.0072(9)
N1	0.0419(11)	0.0494(13)	0.0461(12)	0.0175(10)	0.0190(9)	0.0081(9)
C11	0.0385(12)	0.0450(14)	0.0411(13)	0.0122(11)	0.0137(10)	0.0082(11)
O5	0.0458(11)	0.0793(15)	0.0742(13)	0.0271(10)	0.0042(10)	0.0238(11)
C15	0.0396(13)	0.0484(14)	0.0421(13)	0.0187(11)	0.0116(10)	0.0116(11)
C16	0.0352(12)	0.0464(14)	0.0422(13)	0.0165(10)	0.0119(10)	0.0105(11)
C17	0.0390(13)	0.0468(15)	0.0456(14)	0.0168(11)	0.0180(11)	0.0120(12)
C22	0.0384(13)	0.0468(15)	0.0484(14)	0.0197(11)	0.0120(11)	0.0065(12)
C9	0.0464(14)	0.0433(14)	0.0432(13)	0.0136(11)	0.0186(11)	0.0080(11)
O1	0.0685(13)	0.1088(18)	0.0664(13)	0.0502(13)	0.0347(11)	0.0152(12)
C20	0.0578(17)	0.0540(16)	0.0454(14)	0.0221(13)	0.0220(12)	0.0186(12)
C12	0.0476(14)	0.0457(14)	0.0420(13)	0.0164(11)	0.0152(11)	0.0086(11)
C19	0.0501(15)	0.0565(16)	0.0431(14)	0.0223(12)	0.0150(11)	0.0169(12)
C10	0.0404(13)	0.0466(14)	0.0366(12)	0.0162(11)	0.0123(10)	0.0077(11)
C1	0.0439(14)	0.0519(15)	0.0447(14)	0.0113(11)	0.0186(11)	0.0096(12)
C21	0.0567(17)	0.0549(16)	0.0495(15)	0.0209(13)	0.0253(12)	0.0171(13)
C8	0.0414(14)	0.0651(18)	0.0469(15)	0.0219(12)	0.0173(11)	0.0074(13)
C2	0.0472(15)	0.074(2)	0.0533(17)	0.0170(14)	0.0124(13)	0.0106(14)
C14	0.0506(16)	0.0512(16)	0.0697(18)	0.0122(12)	0.0271(13)	0.0129(14)
C4	0.0579(17)	0.0560(17)	0.0555(17)	0.0152(13)	0.0264(13)	0.0090(13)
C23	0.0536(17)	0.077(2)	0.0697(19)	0.0219(15)	0.0212(14)	0.0249(16)
C3	0.077(2)	0.067(2)	0.0525(18)	0.0131(16)	0.0305(16)	0.0030(15)
C13	0.0712(19)	0.0530(18)	0.080(2)	0.0254(14)	0.0325(16)	0.0139(15)
C18	0.069(2)	0.0598(19)	0.085(2)	0.0343(16)	0.0123(17)	-0.0095(16)
C5	0.0576(18)	0.086(2)	0.0585(19)	0.0090(16)	0.0057(15)	0.0161(17)
C6	0.082(2)	0.074(2)	0.0464(17)	-0.0049(18)	0.0154(17)	0.0054(15)
C7	0.089(3)	0.133(4)	0.101(3)	0.063(2)	0.059(2)	0.020(2)
C39	0.0375(16)	0.093(3)	0.121(3)	0.0056(16)	0.0281(17)	0.026(2)