Supporting Information

Copper-Catalyzed Stereoselective Alkylhydrazination of Alkynes

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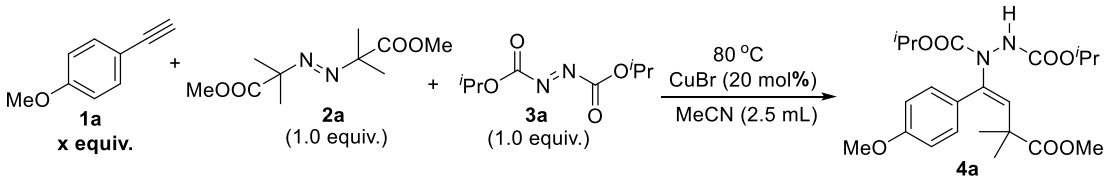
I. General Considerations

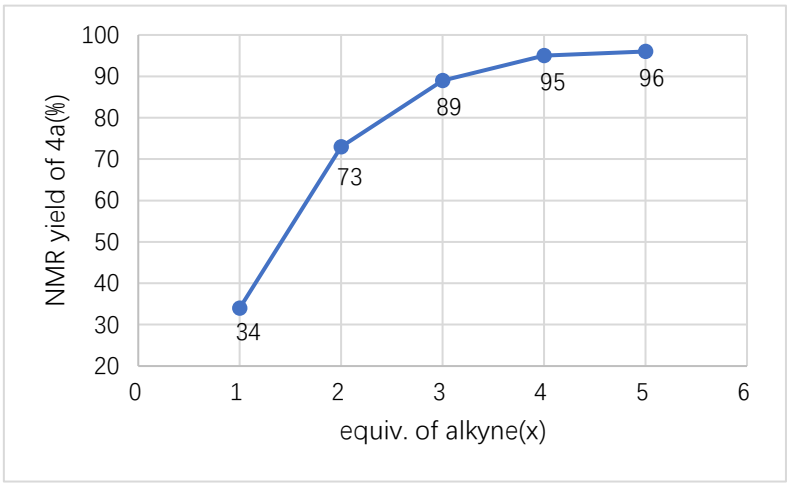
Reagents. Unless otherwise indicated, all reactions were carried out in Schlenk tube under an argon atmosphere with dry solvents. Anhydrous MeCN was purchased from Alfa Aesar and used as received. Ether/THF was dried and purified by distillation from sodium/benzophenone. MeOH and CH_2Cl_2 were distilled from CaH_2. CuBr was purchased from Aladdin. Other copper catalysts were purchased from Alfa Aesar, Strem, Aladdin or JK Chemical and used as received. All other reagents were purchased from commercial sources and used as received.

Analytical Methods. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. NMR spectra were recorded on a Bruker AV-400 or 500 MHz instrument in $CDCl_3$. All ^{1}H NMR spectra are reported in ppm downfield from tetramethylsilane (0 ppm). All ^{13}C NMR spectra are reported in ppm relative to residual $CHCl_3$ (77.0 ppm). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) using UV light as a visualizing agent. Flash chromatography was performed on silica gel 60 (200-300 mesh). High resolution mass spectra (HRMS) was obtained on an ESI-LC-MS/MS or APCI-LC-MS/MS spectrometer.

II. Optimization of Reaction Conditions

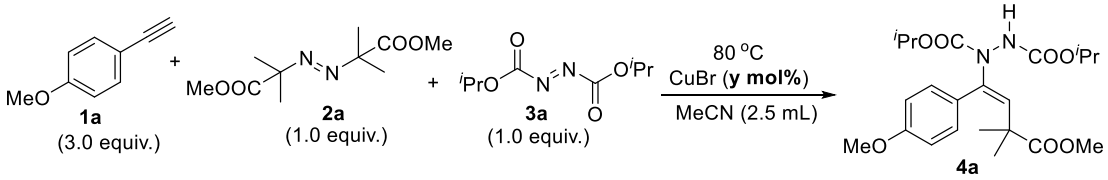
Screening of **equiv. of alkyne**

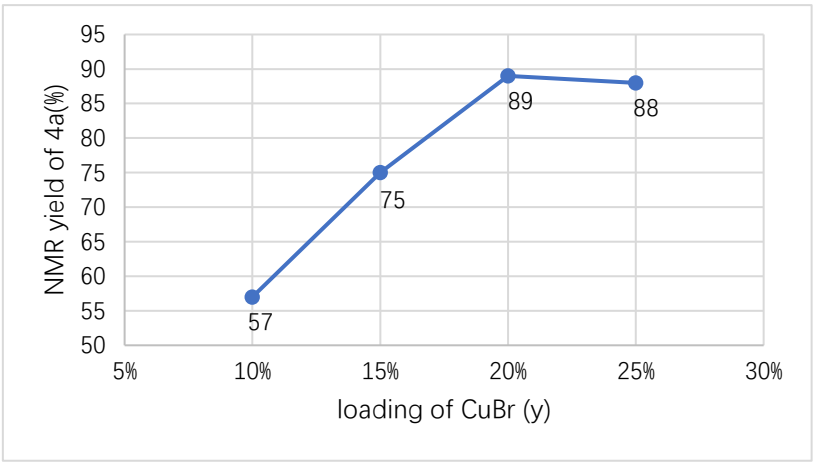




3.0 equiv. of alkyne was selected.

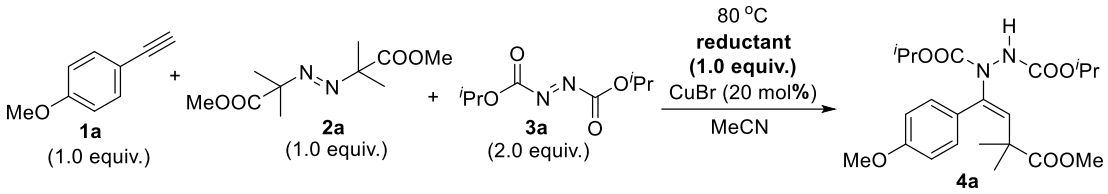
Screening of **loading of copper catalyst**





20 mol% CuBr was selected.

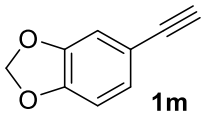
Screening of **reductant**



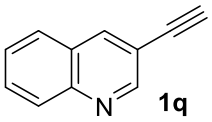
reductant	NMR yield(%)
Na_2SO_3	19
$Na_2S_2O_3•5H_2O$	38
$NaHSO_3$	20
$Na_2S_2O_5$	17
1,4-cyclohexadiene	28
Et_3SiH	22

III. Synthesis and characterization of alkynes

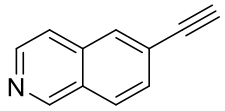
These alkynes were prepared according to the reported literatures. The ^{1}H NMR spectral data matched those of previous reported.



1m [1]



1q [2]



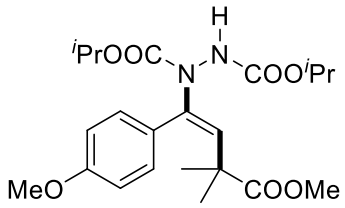
1r

6-Ethynylisoquinoline (1r): the title compound was prepared according to the previous reported protocols using 6-bromoisoquinoline as starting metarial;[2] a white solid, m.p. 115-117 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.55 (d, *J* = 6.0 Hz, 1H), 7.98 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.60 (d, *J* = 6.0 Hz, 1H), 3.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 143.8, 135.2, 130.6, 130.0, 127.8, 127.6, 124.1, 120.0, 83.0, 79.7; HRMS (ESI) calcd for $C_{11}H_8N^+$ $[M+H]^+$ 154.0651, found 154.0651.

IV. General procedure for the alkylhydrazination of alkynes

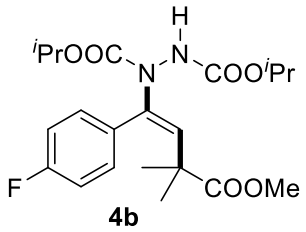
General Procedure: In an oven-dried resealable screw-cap test tube, CuBr (5.7 mg, 0.04 mmol, 20 mol%), alkyne (**1**) (0.6 mmol, 3.0 equiv.), dimethyl 2,2'-azobis(2-methylpropionate) or its analogues (**2**) (0.2 mmol, 1.0 equiv.) and azocarboxylic esters (**3**) (0.2 mmol, 1.0 equiv.) were mixed in anhydrous MeCN (2.5 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C oil path for 8 h. The mixture was cooled down to room temperature, filtered over Celite and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (silica gel) or preparative TLC to afford the related alkenylhydrazines.

V. Characterization data for the products and side products



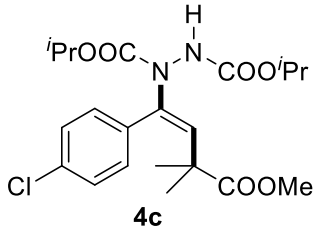
4a

Diisopropyl 1-[(*E*)-4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4a): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **4a** (67.2 mg, 77% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.56-6.12 (m, 1H, -N*H*), 5.93 (br s, 1H), 4.94 (sept, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 3.29 (br s, 3H), 1.27 (s, 6H), 1.23 (d, *J* = 6.0 Hz, 6H), 1.21 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 159.5, 155.6, 154.7, 137.5, 133.5, 130.9, 127.6, 113.2, 70.4, 69.7, 55.2, 51.6, 42.8, 27.3, 21.90, 21.88; $C_{22}H_{33}N_2O_7$ $[M+H]^+$ 437.2282, found 437.2284.



4b

Diisopropyl 1-[(*E*)-1-(4-fluorophenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4b): The representative procedure was followed using 4-fluorophenylacetylene (**1b**) (72.1 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **4b** (55.5 mg, 66% yield) as slightly yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.21 (m, 2H), 7.01 (dd, *J* = 9.0, 8.5 Hz, 2H), 6.64-6.22 (m, 1H, -N*H*), 5.96 (s, 1H), 4.99-4.86 (m, 2H), 3.32 (br s, 3H), 1.27 (s, 6H), 1.24 (d, *J* = 6.0 Hz, 6H), 1.23-1.16 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 162.6 (d, *J* = 246.5 Hz), 155.6, 154.5, 137.1, 133.7, 131.5 (d, *J* = 8.3 Hz), 114.8 (d, *J* = 21.5 Hz), 70.6, 69.9, 51.6, 42.8, 27.3, 21.9; HRMS (ESI) calcd for $C_{21}H_{30}FN_2O_6$ $[M+H]^+$ 425.2082, found 425.2086.

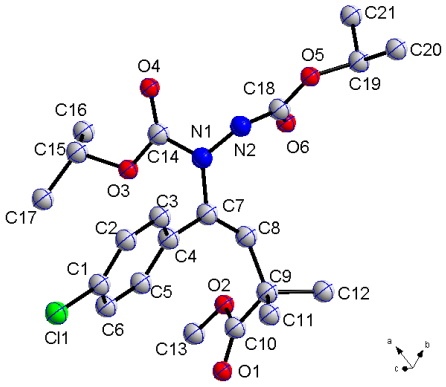


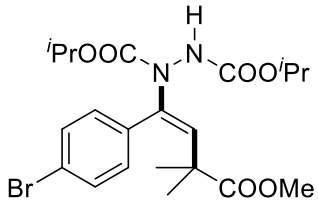
4c

Diisopropyl 1-[(*E*)-1-(4-chlorophenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4c): The representative procedure was followed using 4-chlorophenylacetylene (**1c**) (81.9 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **4c** (48.7 mg, 56% yield) as colorless solid, m.p. 105-109 °C. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, *2*H), 6.64-6.25 (m, 1H, -N*H*), 5.96 (s, 1H), 5.00-4.82

(m, 2H), 3.30 (br s, 3H), 1.26 (s, 6H), 1.23 (d, J = 6.5 Hz, 6H), 1.19 (d, J = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 155.6, 154.4, 137.0, 134.3, 133.9, 131.0, 128.0, 70.7, 70.0, 51.7, 42.8, 27.3, 21.9; HRMS (ESI) calcd for $C_{21}H_{30}ClN_2O_6$ $[M+H]^+$ 441.1787, found 441.1781.

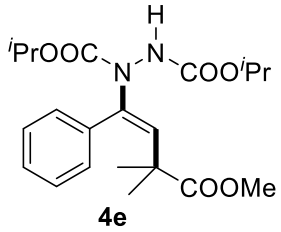
X-Ray structure of 4c (CCDC 1948643)





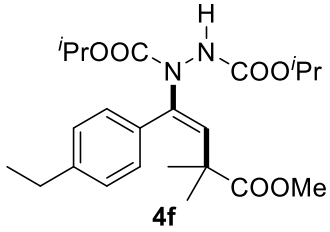
4d

Diisopropyl 1-[(*E*)-1-(4-bromophenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4d): The representative procedure was followed using 4-bromophenylacetylene (**1d**) (108.6 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **4d** (53.7 mg, 55% yield) as slightly yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.60-6.17 (m, 1H, -N*H*), 5.96 (s, 1H), 5.00-4.84 (m, 2H), 3.30 (br s, 3H), 1.26 (s, 6H), 1.23 (d, J = 6.5 Hz, 6H), 1.19 (d, J = 5.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 155.6, 154.4, 137.0, 134.4, 133.8, 131.3, 130.9, 122.5, 70.7, 69.9, 51.7, 42.8, 27.3, 21.8; HRMS (ESI) calcd for $C_{21}H_{30}BrN_2O_6$ $[M+H]^+$ 485.1282, found 485.1285.



4e

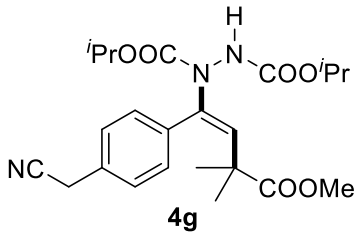
Diisopropyl 1-[(*E*)-4-methoxy-3,3-dimethyl-4-oxo-1-phenylbut-1-en-1-yl]-1,2-hydrazine-dicarboxylate (4e): The representative procedure was followed using phenylacetylene (**1e**) (61.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by preparative TLC (silica gel, 3:1 petroleum ether:EtOAc) to afford **4e** (18.4 mg, 23% yield) as colorless sticky, because the polarity of **4e** is very close to that of the byproduct **SP-1**. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 3H), 7.26-7.20 (m, 2H), 6.59-6.17 (m, 1H, -N*H*), 6.06-5.82 (br s, 1H), 5.02-4.83 (m, 2H), 3.23 (br s, 3H), 1.27 (s, 6H), 1.23 (d, *J* = 6.0 Hz, 6H), 1.19 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 155.6, 154.7, 137.6, 135.4, 133.8, 129.5, 128.4, 127.8, 70.5, 69.8, 51.5, 42.8, 27.4, 21.9; HRMS (ESI) calcd for $C_{21}H_{31}N_2O_6$ $[M+H]^+$ 407.2177, found 407.2182.



4f

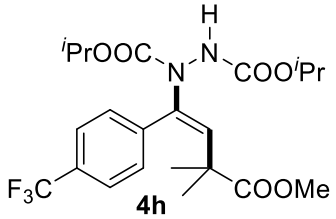
Diisopropyl 1-[(*E*)-1-(4-ethylphenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4f): The representative procedure was followed using 4-ethylphenylacetylene (**1f**) (78.1 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by preparative TLC (silica gel, 2.5:1 petroleum ether:EtOAc) to afford **4f** (54.5 mg, 63% yield) as slightly yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (br s, 4H), 6.60-

6.18 (m, 1H, -N*H*), 5.96 (br s, 1H), 4.94 (sept, *J* = 6.4 Hz, 2H), 3.22 (br s, 3H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.28 (s, 6H), 1.25-1.15 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 155.6, 154.7, 144.4, 137.6, 133.7, 132.6, 129.4, 127.3, 70.3, 69.7, 51.5, 42.7, 28.6, 27.3, 21.9, 15.5; HRMS (ESI) calcd for $C_{23}H_{35}N_2O_6$ $[M+H]^+$ 435.2490, found 435.2496.



4g

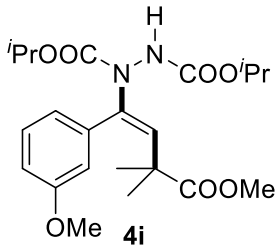
Diisopropyl 1-{(*E*)-1-[4-(cyanomethyl)phenyl]-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl}-1,2-hydrazinedicarboxylate (4g): The representative procedure was followed using 4-ethynylbenzeneacetonitrile (**1g**) (84.7 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methyl-propionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 200:1 dichloromethane:methanol) to afford **4g** (52.4 mg, 59% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (br s, 4H), 6.67-6.23 (m, 1H, -N*H*), 5.99 (s, 1H), 5.00-4.88 (m, 2H), 3.76 (s, 2H), 3.30 (br s, 3H), 1.28 (s, 6H), 1.25 (d, *J* = 6.5 Hz, 6H), 1.21 (d, *J* = 5.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 155.6, 154.5, 137.2, 135.5, 134.0, 130.5, 130.0, 127.4, 117.5, 70.7, 69.9, 51.6, 42.8, 27.3, 23.4, 21.9; HRMS (ESI) calcd for $C_{23}H_{32}N_3O_6$ $[M+H]^+$ 446.2286, found 446.2281.



4h

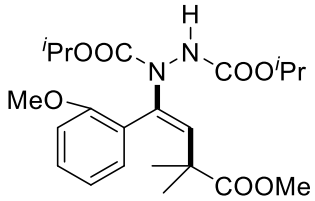
Diisopropyl 1-{(*E*)-4-methoxy-3,3-dimethyl-4-oxo-1-[4-(trifluoromethyl)phenyl]but-1-en-1-yl}-1,2-hydrazinedicarboxylate (4h): The representative procedure was followed using 4-

ethynyl-α,α,α-trifluorotoluene (**1h**) (102.1 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methyl-propionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 500:1 dichloromethane:methanol) to afford **4h** (37.3 mg, 39% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.47-7.37 (m, 2H), 6.68-6.25 (m, 1H, -N*H*), 6.01 (br s, 1H), 5.01-4.82 (m, 2H), 3.23 (br s, 3H), 1.28 (s, 6H), 1.27-1.10 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7, 155.6, 154.3, 139.3, 136.8, 134.1, 130.3 (q, *J* = 32.1 Hz), 130.0, 124.7 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.5 Hz), 70.8, 70.1, 51.6, 42.8, 27.4, 21.84, 21.81; HRMS (ESI) calcd for $C_{22}H_{30}F_3N_2O_6$ $[M+H]^+$ 475.2050, found 475.2044.



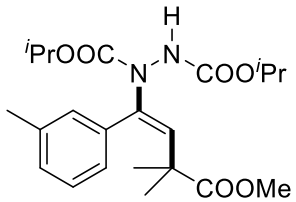
4i

Diisopropyl 1-[(*E*)-1-(3-methoxyphenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4i): The representative procedure was followed using 3-ethynylanisole (**1i**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **4i** (72.5 mg, 83% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.87-6.74 (m, 3H), 6.78 (br s, 1H), 6.58-6.17 (m, 1H, -N*H*), 5.98 (br s, 1H), 5.01-4.88 (m, 2H), 3.80 (s, 3H), 3.27 (br s, 3H), 1.29 (s, 6H), 1.24 (d, *J* = 6.5 Hz, 6H), 1.21 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 159.0, 155.6, 154.7, 137.4, 136.7, 133.9, 128.9, 121.8, 114.9, 114.1, 70.5, 69.8, 55.2, 51.5, 42.8, 27.3, 21.9; HRMS (ESI) calcd for $C_{22}H_{33}N_2O_7$ $[M+H]^+$ 437.2282, found 437.2275.



4j

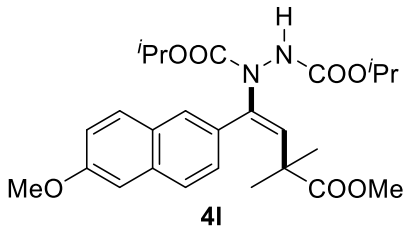
Diisopropyl 1-[(*E*)-4-methoxy-1-(2-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4j): The representative procedure was followed using 2-ethynylanisole (**1j**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **4j** (50.0 mg, 58% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.90 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 6.84 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.78-6.31 (m, 1H, -N*H*), 6.14-5.94 (m, 1H), 4.97 (sept, *J* = 6.0 Hz, 1H), 4.92-4.77 (m, 1H), 3.82 (s, 3H), 3.36-3.13 (m, 3H), 1.32-1.10 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 157.0, 155.7, 154.6, 136.3, 134.0, 133.0, 129.9, 124.0, 119.8, 110.1, 70.1, 69.5, 55.5, 51.4, 42.9, 27.2, 21.9, 21.7; HRMS (ESI) calcd for $C_{22}H_{33}N_2O_7$ $[M+H]^+$ 437.2282, found 437.2290.



4k

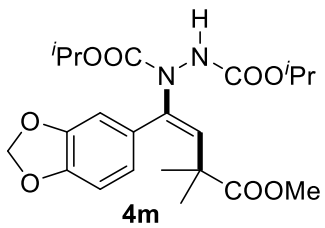
Diisopropyl 1-[(*E*)-1-(3-methylphenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4k): The representative procedure was followed using 3-ethynyltoluene (**1k**) (69.7 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by preparative TLC (silica gel, 2.5:1 petroleum ether:EtOAc) to afford **4k** (52.1 mg, 62% yield) as slightly yellow liquid. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.024 (d, *J* = 7.6 Hz, 1H), 7.015 (s, 1H), 6.58-6.17 (m, 1H, -N*H*),

6.04-5.78 (m, 1H), 4.95 (sept, J = 6.4 Hz, 2H), 3.23 (br s, 3H), 2.33 (s, 3H), 1.27 (s, 6H), 1.24 (d, J = 6.4 Hz, 6H), 1.21 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 155.6, 154.7, 137.7, 137.3, 135.2, 133.8, 130.1, 129.0, 127.7, 126.5, 70.4, 69.7, 51.4, 42.8, 27.3, 21.9, 21.3; HRMS (ESI) calcd for $C_{22}H_{32}N_2O_6Na$ $[M+Na]^+$ 443.2153, found 443.2159.



4l

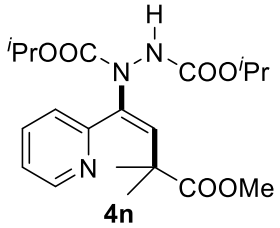
Diisopropyl 1-[(*E*)-4-methoxy-1-(6-methoxynaphthalen-2-yl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4l): The representative procedure was followed using 2-ethynyl-6-methoxynaphthalene (**1l**) (109.3 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **4l** (54.6 mg, 56% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.60 (s, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.14 (dd, J = 8.5, 2.5 Hz, 1H), 7.10 (d, J = 2.5 Hz, 1H), 6.62-6.23 (m, 1H, -N*H*), 6.11-5.89 (m, 1H), 5.00-4.88 (m, 2H), 3.92 (s, 3H), 3.25-2.99 (m, 3H), 1.30 (s, 6H), 1.25-1.14 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 158.0, 155.6, 154.8, 137.7, 134.2, 133.9, 130.4, 129.6, 128.9, 128.0, 127.3, 126.3, 119.1, 105.6, 70.5, 69.7, 55.2, 51.5, 42.9, 27.4, 21.88, 21.85; HRMS (ESI) calcd for $C_{26}H_{35}N_2O_7$ $[M+H]^+$ 487.2439, found 487.2445.



4m

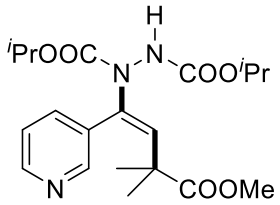
Diisopropyl 1-[(*E*)-1-(benzo[*d*][1,3]dioxol-5-yl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-

yl]-1,2-hydrazinedicarboxylate (4m): The representative procedure was followed using 5-ethynylbenzo[1,3]dioxole (**1m**) (87.7 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **4m** (68.8 mg, 77% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77-6.66 (m, 3H), 6.55-6.21 (m, 1H, -N*H*), 5.99-5.80 (m, 3H), 4.99-4.88 (m, 2H), 3.39 (br s, 3H), 1.27 (s, 6H), 1.25-1.19 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 155.5, 154.6, 147.5, 147.1, 137.3, 133.8, 129.0, 123.7, 109.8, 107.6, 101.1, 70.5, 69.8, 51.7, 42.7, 27.2, 21.92, 21.87; HRMS (ESI) calcd for $C_{22}H_{31}N_2O_8$ $[M+H]^+$ 451.2075, found 451.2082.



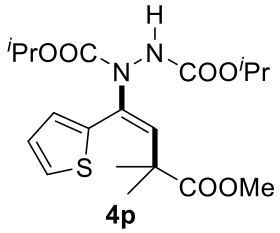
4n

Diisopropyl 1-[(*E*)-4-methoxy-3,3-dimethyl-4-oxo-1-(pyridin-2-yl)but-1-en-1-yl]-1,2-hydrazinedicarboxylate (4n): The representative procedure was followed using 2-ethynylpyridine (**1n**) (61.9 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 50:1 dichloromethane:methanol) to afford **4n** (34.1 mg, 42% yield) as brown sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (br s, 1H), 7.65 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.44 (br s, 1H), 7.19-7.13 (m, 1H), 7.04-6.63 (m, 1H, -N*H*), 6.12 (s, 1H), 5.08-4.93 (m, 1H), 4.93-4.80 (m, 1H), 3.28 (s, 3H), 1.38 (s, 6H), 1.27 (d, *J* = 5.5 Hz, 6H), 1.20-1.02 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 155.8, 155.0, 154.3, 148.5, 137.7, 136.6, 136.0, 122.8, 122.5, 70.5, 69.9, 51.4, 43.0, 27.4, 22.0, 21.8; HRMS (ESI) calcd for $C_{20}H_{30}N_3O_6$ $[M+H]^+$ 408.2129, found 408.2136.



4o

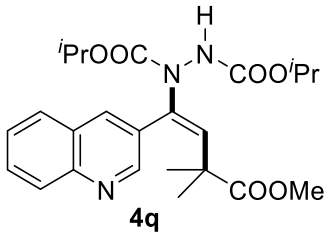
Diisopropyl 1-[(*E*)-4-methoxy-3,3-dimethyl-4-oxo-1-(pyridin-3-yl)but-1-en-1-yl]-1,2-hydrazinedicarboxylate (4o): The representative procedure was followed using 3-ethynylpyridine (**1o**) (61.9 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 50:1 dichloromethane:methanol) to afford **4o** (58.4 mg, 72% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72-8.36 (m, 2H), 7.66 (s, 1H), 7.33-7.21 (m, 1H), 7.03-6.62 (m, 1H, -N*H*), 6.08 (br s, 1H), 4.99-4.84 (m, 2H), 3.30 (br s, 3H), 1.27 (s, 6H), 1.25-1.13 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 155.6, 154.2, 150.4, 149.2, 137.3, 135.2, 131.5, 122.7, 70.8, 70.0, 51.8, 42.8, 27.4, 21.8; HRMS (ESI) calcd for $C_{20}H_{30}N_3O_6$ $[M+H]^+$ 408.2129, found 408.2130.



4p

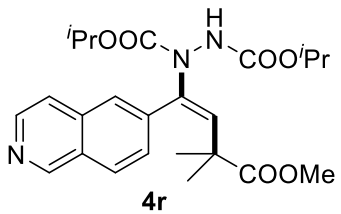
Diisopropyl 1-[(*E*)-4-methoxy-3,3-dimethyl-4-oxo-1-(thiophen-2-yl)but-1-en-1-yl]-1,2-hydrazinedicarboxylate (4p): The representative procedure was followed using 2-ethynylthiophene (**1p**) (64.9 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 500:1 dichloromethane:methanol) to afford **4p** (50.5 mg, 62% yield) as slightly brown sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.29 (m, 1H), 6.98-6.91 (m, 2H), 6.63-6.26 (m, 1H, -N*H*), 6.24-5.97 (m, 1H), 4.96 (sept, J = 6.5 Hz, 1H), 4.95

(sept, *J* = 6.5 Hz, 1H), 3.37 (br s, 3H), 1.34 (s, 6H), 1.25 (d, *J* = 6.5 Hz, 6H), 1.24 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 155.6, 154.6, 137.8, 136.6, 131.2, 129.3, 126.7, 126.6, 70.7, 69.9, 51.7, 42.9, 27.1, 21.9; HRMS (ESI) calcd for $C_{19}H_{29}N_2O_6S$ $[M+H]^+$ 413.1741, found 413.1743.



4q

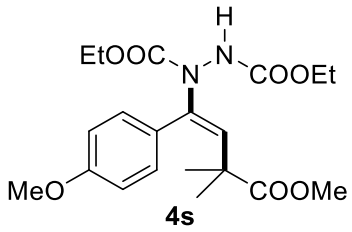
Diisopropyl 1-[(*E*)-4-methoxy-3,3-dimethyl-4-oxo-1-(quinolin-3-yl)but-1-en-1-yl]-1,2-hydrazinedicarboxylate (4q): The representative procedure was followed using 3-ethynylquinoline (**1q**) (91.9 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 2:1 petroleum ether:EtOAc) to afford **4q** (66.1 mg, 73% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.0 Hz, 1H), 8.13-7.93 (m, 2H), 7.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.70 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.54 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.25-6.83 (m, 1H, -N*H*), 6.31-6.02 (m, 1H), 5.06-4.83 (m, 2H), 3.12 (br s, 3H), 1.30 (s, 6H), 1.27-1.09 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 155.7, 154.4, 151.0, 147.1, 136.9, 135.8, 135.1, 129.9, 129.0, 128.6, 128.0, 127.0, 126.9, 70.8, 69.9, 51.7, 42.9, 27.4, 21.9, 21.8; HRMS (ESI) calcd for $C_{24}H_{32}N_3O_6$ $[M+H]^+$ 458.2286, found 458.2288.



4r

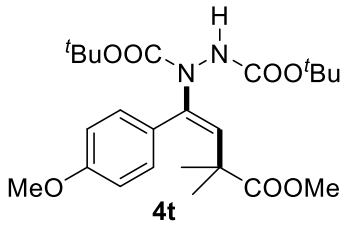
Diisopropyl 1-[(*E*)-1-(isoquinolin-6-yl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4r): The representative procedure was followed using 6-

ethynylisoquinoline (**1r**) (91.9 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 1:1 petroleum ether:EtOAc) to afford **4r** (60.2 mg, 66% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.50 (d, *J* = 5.6 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 5.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.01-6.76 (m, 1H, -N*H*), 6.09 (s, 1H), 5.01-4.83 (m, 2H), 3.09 (br s, 3H), 1.30 (s, 6H), 1.26-1.09 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 155.7, 154.5, 152.0, 143.4, 137.6, 137.2, 135.0, 134.5, 128.5, 127.9, 127.6, 127.1, 120.6, 70.7, 69.9, 51.5, 42.9, 27.4, 21.9; HRMS (ESI) calcd for $C_{24}H_{32}N_3O_6$ $[M+H]^+$ 458.2286, found 458.2284.



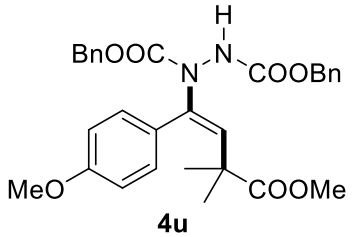
4s

Diethyl 1-[(*E*)-4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4s): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diethyl azodicarboxylate (**3b**) (34.8 mg, 0.2 mmol). The crude product was purified by preparative TLC (silica gel, 2.5:1 petroleum ether:EtOAc, twice) to afford **4s** (53.0 mg, 65% yield) as slightly yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.72-6.32 (m, 1H, -N*H*), 5.96 (br s, 1H), 4.20-4.13 (m, 4H), 3.80 (s, 3H), 3.29 (br s, 3H), 1.27 (s, 6H), 1.26-1.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 159.5, 155.9, 155.2, 137.4, 133.8, 130.8, 127.4, 113.2, 62.6, 61.9, 55.1, 51.6, 42.8, 27.3, 14.33, 14.28; HRMS (ESI) calcd for $C_{20}H_{29}N_2O_7$ $[M+H]^+$ 409.1969, found 409.1962.



4t

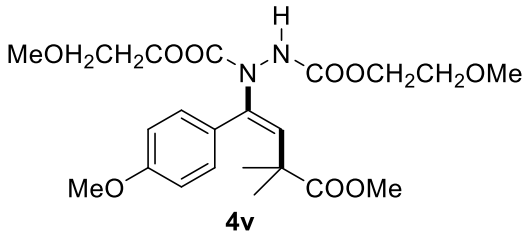
Di(*tert*-butyl) 1-[(*E*)-4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4t): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and di-*tert*-butyl azodicarboxylate (**3c**) (46.1 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 6:1 petroleum ether:EtOAc) to afford **4t** (48.4 mg, 52% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.44-5.95 (m, 1H, -N*H*), 5.89 (br s, 1H), 3.80 (s, 3H), 3.29 (br s, 3H), 1.44 (br s, 18H), 1.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 159.5, 155.0, 153.9, 138.0, 133.0, 130.8, 128.1, 113.1, 81.6, 81.1, 55.2, 51.6, 42.7, 28.2, 28.1, 27.4; HRMS (ESI) calcd for $C_{24}H_{37}N_2O_7$ $[M+H]^+$ 465.2595, found 465.2603.



4u

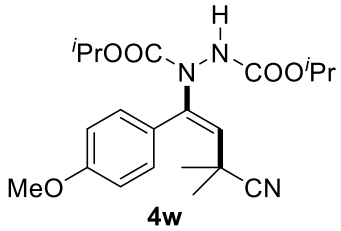
Dibenzyl 1-[(*E*)-4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4u): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and dibenzyl azodicarboxylate (**3d**) (59.3 mg, 0.2 mmol). The crude product was purified by preparative TLC (silica gel, 2:1 petroleum ether:EtOAc) to afford **4u** (50.7 mg, 48% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.25 (m, 10H), 7.17-7.00 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.72-6.34 (m, 1H, -N*H*), 6.09-5.72 (m, 1H), 5.16 (s, 2H), 5.12 (s, 2H), 3.77 (s,

3H), 3.23 (s, 3H), 1.22 (br s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 159.6, 155.6, 155.0, 137.2, 135.65, 135.60, 134.3, 130.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.0, 113.3, 68.3, 67.6, 55.1, 51.6, 42.7, 27.2; HRMS (ESI) calcd for $C_{30}H_{33}N_2O_7$ $[M+H]^+$ 533.2282, found 533.2288.



4v

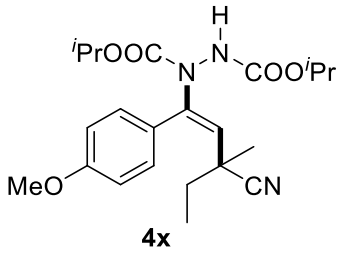
Di((2-methoxyethoxy)methyl) 1-[(*E*)-4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4v): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and di-2-methoxyethyl azodicarboxylate (**3e**) (46.8 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 150:1 dichloromethane:methanol) to afford **4v** (59.5 mg, 64% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.81-6.40 (m, 1H, -N*H*), 5.99 (s, 1H), 4.32-4.21 (m, 4H), 3.80 (s, 3H), 3.60-3.52 (m, 4H), 3.36 (s, 3H), 3.35 (s, 3H), 3.29 (s, 3H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 159.6, 155.4, 155.1, 137.1, 134.3, 130.9, 127.2, 113.2, 70.45, 70.36, 65.6, 64.9, 58.9, 58.8, 55.2, 51.6, 42.8, 27.2; HRMS (ESI) calcd for $C_{22}H_{33}N_2O_9$ $[M+H]^+$ 469.2181, found 469.2186.



4w

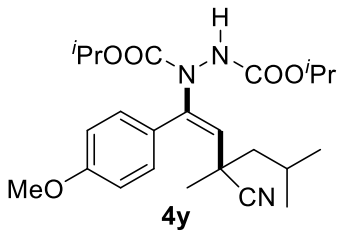
Diisopropyl 1-[(*E*)-3-cyano-1-(4-methoxyphenyl)-3-methylbut-1-en-1-yl]-1,2-hydrazine-dicarboxylate (4w): The representative procedure was followed using 4-ethynylanisole (**1a**)

(79.2 mg, 0.6 mmol), 2,2'-azobis(2-methylpropionitrile) (**2b**) (32.8 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **4w** (61.7 mg, 76% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.54-6.19 (m ,1H, -N*H*), 5.84-5.58 (m, 1H), 5.01-4.88 (m, 2H), 3.82 (s, 3H), 1.44 (s, 6H), 1.30-1.17 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 155.6, 154.4, 140.2, 131.2, 128.2, 126.3, 123.1, 113.6, 70.8, 70.1, 55.2, 31.1, 29.1, 21.91, 21.88; HRMS (ESI) calcd for $C_{21}H_{30}N_3O_5$ $[M+H]^+$ 404.2180, found 404.2184.



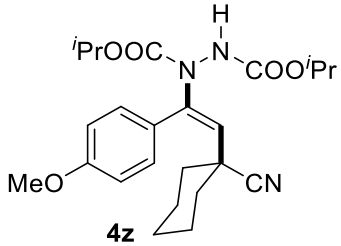
4x

Diisopropyl 1-[(*E*)-3-cyano-1-(4-methoxyphenyl)-3-methylpent-1-en-1-yl]-1,2-hydrazine-dicarboxylate (4x): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), 2,2'-azodi(2-methylbutyronitrile) (**2c**) (38.5 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **4x** (60.0 mg, 72% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.60-6.20 (m ,1H, -N*H*), 5.79-5.46 (m, 1H), 5.00-4.89 (m, 2H), 3.82 (s, 3H), 1.78-1.64 (m, 2H), 1.42 (s, 3H), 1.28-1.18 (m, 12H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 155.5, 154.4, 140.2, 131.2, 128.2, 126.3, 121.9, 113.4, 70.8, 69.9, 55.1, 36.6, 35.2, 26.8, 21.88, 21.85, 9.4; HRMS (ESI) calcd for $C_{22}H_{32}N_3O_5$ $[M+H]^+$ 418.2336, found 418.2334.



4y

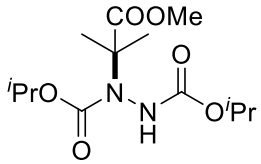
Diisopropyl 1-[(*E*)-3-cyano-1-(4-methoxyphenyl)-3,5-dimethylhex-1-en-1-yl]-1,2-hydrazinedicarboxylate (4y): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), 2,2'-azobis(2,4-dimethyl)valeronitrile (**2d**) (49.7 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **4y** (42.0 mg, 47% yield) as slightly yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.58-6.09 (m ,1H, -N*H*), 5.85-5.52 (m, 1H), 5.00-4.89 (m, 2H), 3.82 (s, 3H), 1.97-1.87 (m, 1H), 1.67-1.55 (m, 2H), 1.46 (s, 3H), 1.29-1.17 (m, 12H), 1.00 (d, *J* = 6.0 Hz, 3H), 0.98 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 155.6, 154.4, 139.4, 131.2, 129.2, 126.3, 122.3, 113.4, 70.8, 70.0, 55.2, 50.6, 35.2, 28.7, 25.7, 23.9, 23.4, 21.92, 21.89, 21.87; HRMS (ESI) calcd for $C_{24}H_{36}N_3O_5$ $[M+H]^+$ 446.2649, found 446.2643.



4z

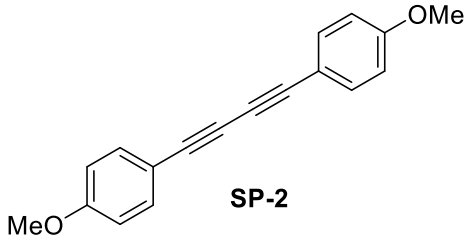
Diisopropyl 1-[(*E*)-2-(1-cyanocyclohexyl)-1-(4-methoxyphenyl)vinyl]-1,2-hydrazinedicarboxylate (4z): The representative procedure was followed using 4-ethynylanisole (**1a**) (79.2 mg, 0.6 mmol), 1,1'-azobis(cyclohexanecarbonitrile) (**2e**) (48.9 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol). The crude product was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **4z** (37.5 mg, 43% yield) as yellow sticky. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.51-6.13

(m ,1H, -N*H*), 5.82-5.53 (m, 1H), 4.94 (sept, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 1.93-1.85 (m, 2H), 1.65-1.46 (m, 7H), 1.28-1.18 (m, 13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 155.5, 154.5, 140.6, 131.0, 128.1, 126.8, 121.9, 113.6, 70.8, 70.0, 55.2, 36.8, 36.7, 24.8, 22.1, 21.9; HRMS (ESI) calcd for $C_{24}H_{34}N_3O_5$ $[M+H]^+$ 444.2493, found 444.2498.



SP-1

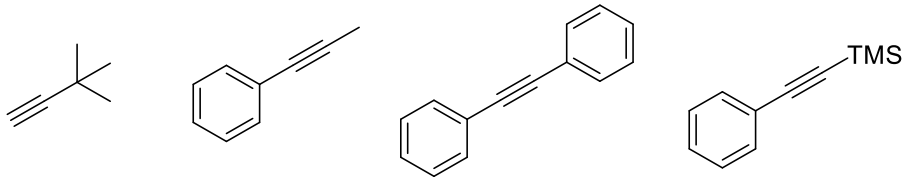
Diisopropyl 1-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1,2-hydrazinedicarboxylate (**SP-1**): the title product was purified by flash column chromatography (silica gel, 5:1 petroleum ether:EtOAc) to afford **SP-1** as slight yellow liquid. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52-6.20 (m, 1H, -N*H*), 5.07-4.84 (m, 2H), 3.72 (s, 3H), 1.68 (br s, 3H), 1.40 (s, 3H), 1.29 (d, *J* = 6.4 Hz, 3H), 1.27 (d, *J* = 6.4 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 156.6, 154.9, 70.4, 69.8, 64.1, 52.4, 24.9, 23.7, 21.9, 21.8; HRMS (ESI) calcd for $C_{13}H_{24}N_2O_6Na$ [M+Na]+ 327.1527, found 327.1530.



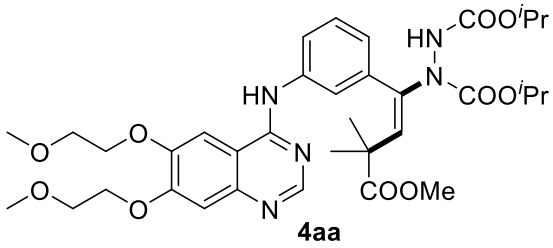
SP-2

1,4-bis(4-methoxyphenyl)buta-1,3-diyne (SP-2) the title product was purified by flash column chromatography (silica gel, 40:1 petroleum ether:EtOAc) to afford **SP-2** as slight yellow solid. ^{1}H, ^{13}C NMR spectral data matched those of previously reported.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 134.0, 114.1, 113.9, 81.2, 72.9, 55.3. HRMS (ESI) calcd for $C_{18}H_{15}O_2$ $[M+H]^+$ 263.1067, found 263.1065.

Substrates that didn't work:

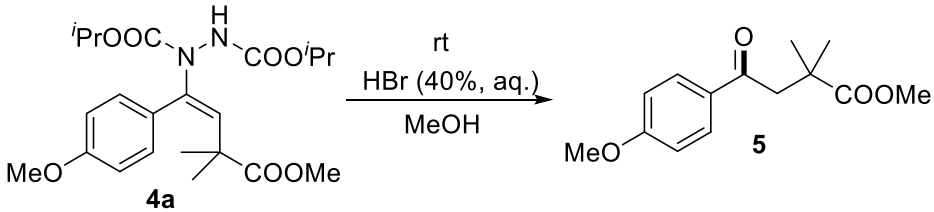


VI. Synthetic applications



4aa

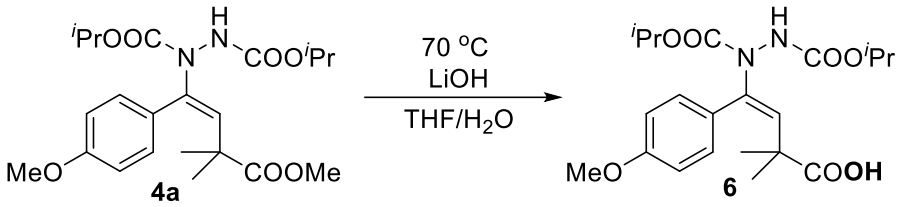
Erlotinib derivative (4aa): Following the general procedure of alkylhydrazination of alkynes, Erlotinib (236.1 mg, 0.6 mmol), dimethyl 2,2'-azobis(2-methylpropionate) (**2a**) (46.1 mg, 0.2 mmol) and diisopropyl azodicarboxylate (**3a**) (40.4 mg, 0.2 mmol) were used. The crude product was purified by flash chromatography (silica gel, 30:1 dichloromethane:methanol) to afford **4aa** (86.1 mg, 61% yield) as white gem. *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.12 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.52-7.41 (m ,1H, -N*H*CO), 7.37 (s, 1H), 7.27 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.16 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.10-5.86 (m, 1H), 5.03-4.81 (m, 2H), 4.31-4.10 (m, 4H), 3.89-3.67 (m, 4H), 3.41 (s, 3H), 3.40 (s, 3H), 3.29 (br s, 3H), 1.30 (s, 6H), 1.28-1.11 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 156.3, 155.7, 154.9, 154.1, 153.3, 148.5, 147.2, 138.7, 137.4, 135.9, 133.9, 128.1, 125.0, 122.5, 121.7, 109.2, 108.5, 102.8, 70.7, 70.5, 70.3, 69.6, 68.8, 68.1, 59.0, 51.6, 42.9, 27.1, 21.8; HRMS (ESI) calcd for $C_{35}H_{47}N_5O_{10}Na$ $[M+Na]^+$ 720.3215, found 720.3234.



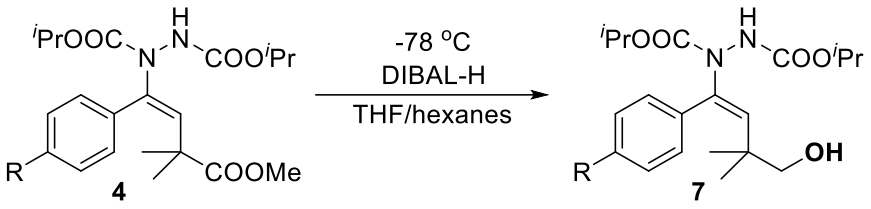
4a **5**

Methyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-oxobutyrate (**5**). **4a** (87.3 mg, 0.2 mmol) dissolved in MeOH (1.0 mL) was added 40% aqueous solution of HBr (2.0 mL). The mixture was stirred at room temperature for 10 min. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (20 mL) at 0 °C. After quenching the reaction, the mixture was allowed to warm to room temperature and was extracted with EtOAc (10 mL × 3). The organic layer was

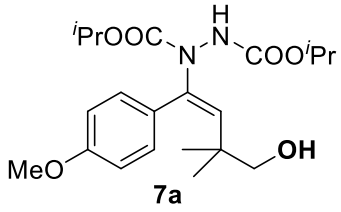
dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography (silica gel, 6:1 petroleum ether:EtOAc) to afford the desired compound **5** (49.1 mg, 98% yield) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H), 3.68 (s, 3H), 3.25 (s, 2H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 177.9, 163.4, 130.1, 130.0, 113.6, 55.4, 51.8, 48.2, 40.0, 25.7; HRMS (ESI) calcd for $C_{14}H_{19}O_4$ $[M+H]^+$ 251.1278, found 251.1280.



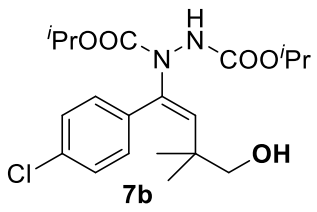
(*E*)-4-[1,2-bis(isopropoxycarbonyl)hydrazinyl]-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoic acid (**6**): To the solution of **4a** (87.3 mg, 0.2 mmol) in THF (2.0 mL) was added aqueous lithium hydroxide (1 M, 0.5 mL). The mixture was stirred at room temperature for 20 minutes and then stirred at 70 °C for 9 hours. After cooled to room temperature, the mixture was acidified to pH 1 with 10% HCl. Ethyl acetate (10 mL) was added to dilute the solution. The organic layer was seperated and the aqueous layer was extracted with EtOAc (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography (silica gel, gradient from 50:1 to 10:1 dichloromethane:methanol) to afford the corresponding compound as colorless sticky (81.1 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.13 (m, 2H), 6.82-6.60 (m, 3H), 6.02-5.83 (m, 1H), 5.00-4.83 (m, 2H), 3.77 (s, 3H), 1.34-1.11 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 159.7, 155.5, 154.8, 138.1, 132.6, 131.2, 127.4, 113.1, 70.5, 69.8, 55.1, 42.7, 26.8, 21.91, 21.88; HRMS (ESI) calcd for $C_{21}H_{31}N_2O_7$ $[M+H]^+$ 423.2126, found 423.2123.



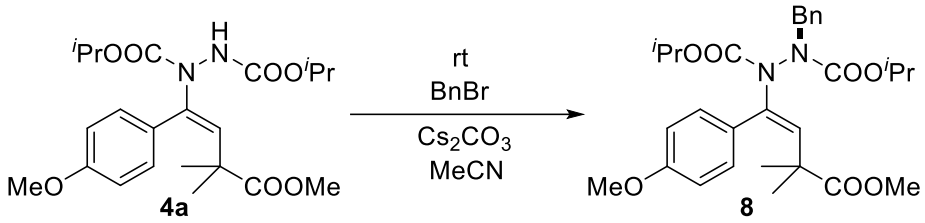
To a solution of the **4** (0.2 mmol, 1 equiv.) in dry THF (1.0 mL) was added DIBAL-H (1.0 mL, 1.0 M in hexanes, 5.0 equiv.) over 5 min at -78 °C. The reaction mixutre was stirred at -78 °C for 1 h, then slowly warmed to room temparature overnight and quenched with saturated NH_4Cl (5 mL). The precipitate was filtered off and washed with EtOAc (10 mL). The filtrate was dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography (silica gel, 100:1 dichloromethane:methanol) to afford the corresponding primary alcohol **7**.



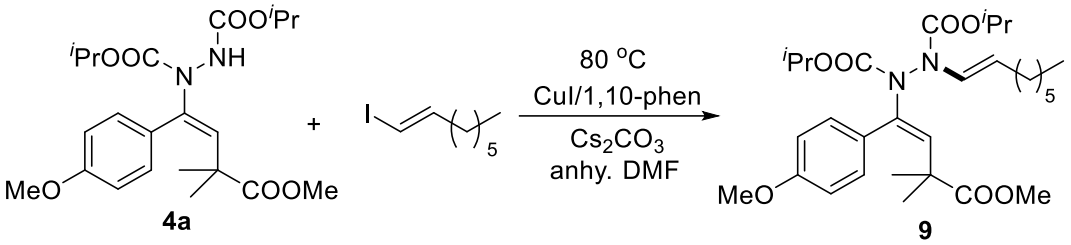
Diisopropyl 1-[(*E*)-4-hydroxy-1-(4-methoxyphenyl)-3,3-dimethylbut-1-en-1-yl]-1,2-hydrazinedicarboxylate (**7a**): colorless sticky (32.1 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.44-6.08 (m, 1H, -N*H*), 5.90-5.65 (m, 1H), 5.00 (sept, *J* = 6.4 Hz, 1H), 4.91 (sept, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 3.26 (s, 2H), 1.27 (d, *J* = 6.4 Hz, 6H), 1.21 (d, *J* = 6.4 Hz, 6H), 0.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.4, 155.2, 137.4, 136.9, 131.4, 127.9, 113.2, 72.7, 70.8, 69.7, 55.2, 38.7, 25.2, 22.1, 22.0, 21.9; HRMS (ESI) calcd for $C_{21}H_{32}N_2O_6Na$ $[M+Na]^+$ 431.2153, found 431.2153.



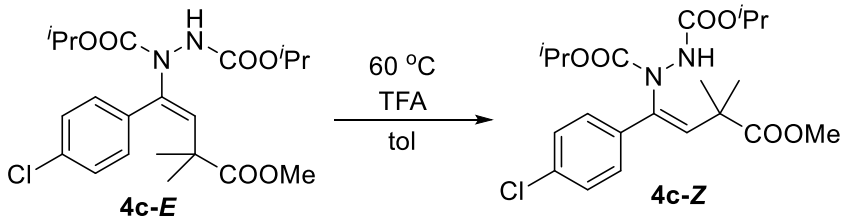
Diisopropyl 1-[(*E*)-4-hydroxy-1-(chlorophenylphenyl)-3,3-dimethylbut-1-en-1-yl]-1,2-hydrazinedicarboxylate (**7b**): colorless sticky (72.3 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 4H), 6.64-6.37 (m, 1H), 5.96-5.71 (m, 1H), 5.04-4.81 (m, 2H), 3.27 (s, 2H), 1.25 (d, *J* = 6.4 Hz, 6H), 1.23-1.14 (m, 6H), 0.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 155.0, 137.3, 136.6, 134.4, 134.3, 131.6, 127.9, 72.6, 70.9, 69.8, 38.6, 25.0, 21.9, 21.8; HRMS (ESI) calcd for $C_{20}H_{29}ClN_2O_5Na$ $[M+Na]^+$ 435.1657, found 435.1658.



Diisopropyl (*E*)-1-benzyl-2-[4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (**8**): To a solution of **4a** (87.3 mg, 0.2 mmol, 1.0 equiv.) in MeCN (2.0 mL) were added cesium carbonate (162.9 mg, 0.5 mmol, 2.5 equiv.) and benzyl bromide (68.4 mg, 0.4 mmol, 2.0 equiv.). The reaction mixture was stirred for 12 h at room temperature. The reaction was diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography (silica gel, 4:1 petroleum ether:EtOAc) to afford **8** (103.0 mg, 98% yield) as colorless sticky. *Tetrasubstituted hydrzines were reported and explained by the existence of up to four conformations, which have complicated ^{1}H and ^{13}C spectra.*[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.22 (m, 5H), 7.11-6.89 (m, 2H), 6.79-6.63 (m, 2H), 5.67-5.44 (m, 1H), 4.92-4.41 (m, 4H), 3.83-3.72 (m, 3H), 3.39-3.19 (m, 3H), 1.36-0.88 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 159.44, 159.39, 155.9, 154.1, 153.9, 137.0, 136.7, 136.2, 133.9, 131.3, 129.4, 128.8, 128.11, 128.07, 127.4, 127.3, 127.1, 112.9, 112.6, 70.2, 69.98, 69.93, 55.12, 55.09, 53.3, 51.6, 51.5, 42.7, 42.1, 27.5, 27.0, 22.0, 21.8, 21.5; HRMS (ESI) calcd for $C_{29}H_{38}N_2O_7Na$ $[M+Na]^+$ 549.2571, found 549.2576.



Diisopropyl 1-[(*E*)-4-methoxy-1-(4-methoxyphenyl)-3,3-dimethyl-4-oxobut-1-en-1-yl]-2-[(*E*)-oct-1-en-1-yl]-1,2-hydrazinedicarboxylate (**9**): To an oven-dried resealable screw-cap test tube, CuI (2.9 mg, 0.015 mmol, 10 mol%), 1,10-phenanthroline (5.4 mg, 0.03 mmol, 20 mol%), **4a** (68.7 mg, 0.16 mmol, 1.05 equiv.) and Cs_2CO_3 (48.9 mg, 0.15 mmol) were added. The tube was evacuated and backfilled with argon. The (*E*)-1-iodo-1-octene (35.7 mg, 0.15 mmol, 1.0 equiv.) and anhydrous DMF (0.8 mL) were added via syringe. The tube was sealed and stirred at 80 ºC for 48 h. The reaction mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (3×10 mL). The combined organic phases were washed with brine (3×10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography (silica gel, 6:1 petroleum ether:EtOAc) to afford **9** (47.0 mg, 57% yield) as slightly yellow sticky. *Tetrasubstituted hydrzines were reported and explained by the existence of up to four conformations, which have complicated ^1H and ^{13}C spectra.*[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.08 (m, 2H), 6.87-6.74 (m, 2H), 6.70-6.44 (m, 1H), 6.06-5.50 (m, 1H), 5.03-4.79 (m, 3H), 3.85-3.72 (m, 3H), 3.42-3.32 (m, 3H), 2.08-1.88 (m, 2H), 1.36-1.07 (m, 26H), 0.95-0.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 176.2, 159.52, 159.48, 153.1, 152.8, 151.7, 136.9, 136.1, 131.7, 131.5, 126.3, 125.0, 124.6, 112.8, 112.6, 111.1, 110.6, 70.7, 70.4, 70.1, 55.1, 51.65, 51.6, 42.7, 31.7, 30.2, 30.1, 29.5, 29.4, 28.7, 28.6, 27.5, 27.40, 27.37, 22.6, 21.98, 21.89, 21.81, 21.77, 21.67, 14.1; HRMS (ESI) calcd for $C_{30}H_{46}N_2O_7Na$ $[M+Na]^+$ 569.3197, found 569.3198.

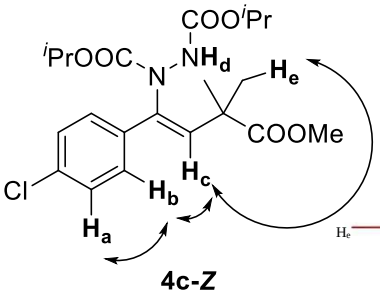


Diisopropyl 1-[(*Z*)-1-(4-chlorophenyl)-4-methoxy-3,3-dimethyl-4-oxobut-1-en-1-yl]-1,2-hydrazinedicarboxylate (4c-*Z*): To an oven-dried resealable screw-cap test tube, **4c-*E*** (88.2 mg, 0.2 mmol, 1 equiv.), dry toluene (2.0 mL), trifluoroacetic acid (68.4 mg, 0.6 mmol, 3.0 equiv.) was added. The reaction mixutre was stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature, then quenched with saturated $NaHCO_3$ (3 mL) and washed with EtOAc (3×10 mL). The combined organic phases were washed with brine (3×10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography (silica gel, 8:1 petroleum ether:EtOAc) to afford **4c-*Z*** as colorless sticky (43.8 mg, 50% yield); *Due to the presence of amide rotamers, the product gives two sets of NMR signals.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.40 (m, 2H), 7.32-7.21 (m, 2H), 7.02-6.55 (m, 1H, -N*H*, *deuterium exchange*), 5.71-5.51 (m, 1H), 5.01-4.76 (m, 2H), 3.79-3.62 (m, 3H), 1.43 (s, 6H), 1.35-0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 177.7, 155.3, 154.9, 154.0, 153.7, 138.4, 136.7, 135.7, 134.1, 133.9, 132.6, 128.9, 128.1, 128.0, 71.0, 70.8, 69.8, 69.6, 52.8, 52.6, 43.5, 26.5, 26.4, 21.9, 21.6; HRMS (ESI) calcd for $C_{21}H_{29}ClN_2O_6Na$ $[M+Na]^+$ 463.1606, found 463.1610.

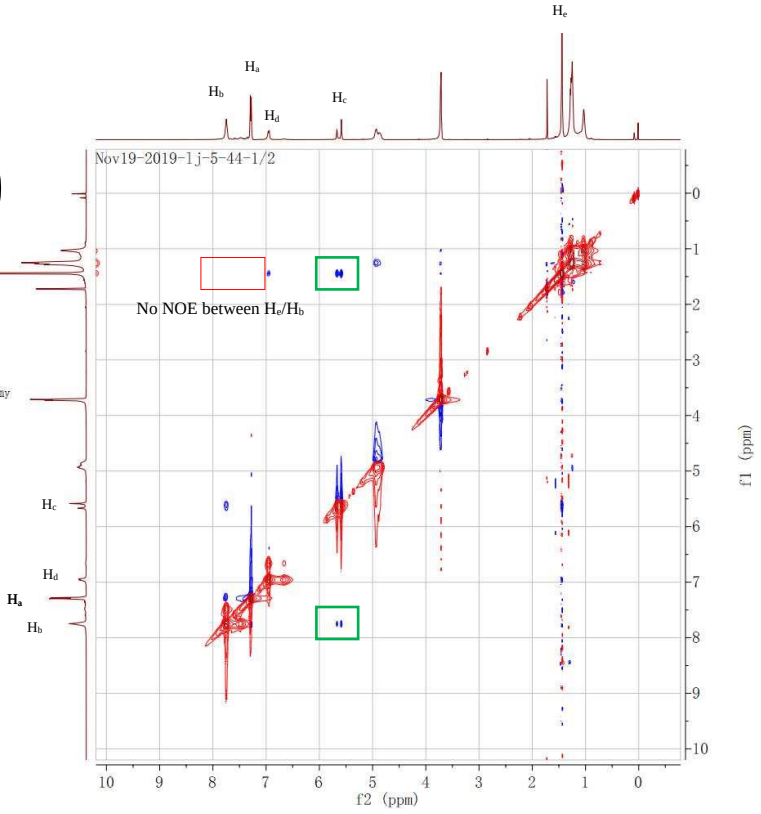
Analysis of stereochemistry of 4c-*Z* and 4c-*E*

The *E*-configuration of **4c** was confirmed through X-ray analysis. Examples in **scheme 3** and **scheme 4** also show similar NMR signals to **4c-*E***. (especially the signal of olefin hydrogen) So the configuration of these compounds were assigned as *E*-configuration. For *Z*-isomer, the chemical shifts of OMe (about 0.4 ppm shifts to the low fields), alkyl hydrogen, olefin hydrogen and aryl hydrogen varied. The NOESY experiments of **4c-*Z*** and **4c-*E*** were conducted to further check the configurations of the double bonds. For **4c-*Z***, NOE effect between olefin hydrogen and aryl hydrogen was observed. Meanwhile, no NOE effect was detected between methyl hydrogen and aryl hydrogen. For **4c-*E***, the results are contrast to **4c-*Z***. The following crude spectrum showed the stereoselectivity of the reaction.

NOESY of 4c-*Z* and 4c-*E*



4c-*Z*



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5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.8
11	Pulse Sequence	noesyphpr
12	Experiment	NOESY
13	Probe	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0166
14	Number of Scans	16
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16	Relaxation Delay	2.0000
17	Pulse Width	12.7500
18	Presaturation Frequency	
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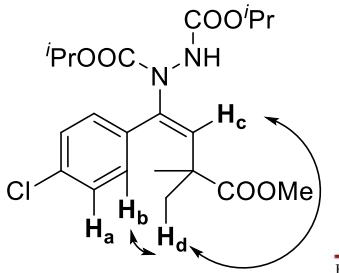
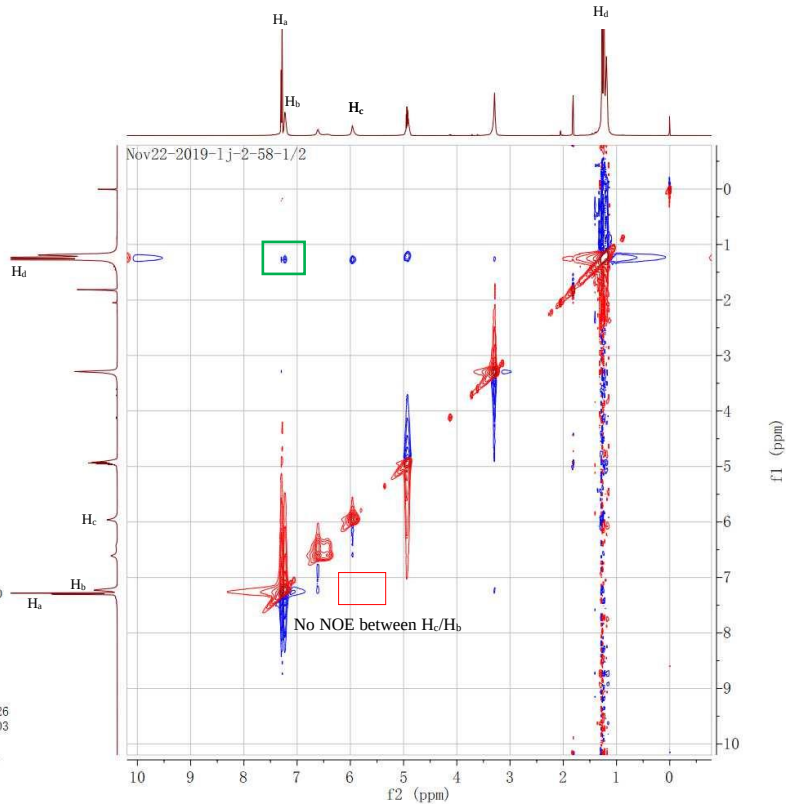
20	Acquisition Date	2019-11-20T01:44:56
21	Modification Date	2019-11-20T04:53:16
22	Class	
23	Spectrometer Frequency	(500.13, 500.13)
24	Spectral Width	(5498.5, 5500.6)
25	Lowest Frequency	(-398.7, -399.7)



4c-*E*



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6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.9
11	Pulse Sequence	noesyphpr
12	Experiment	NOESY
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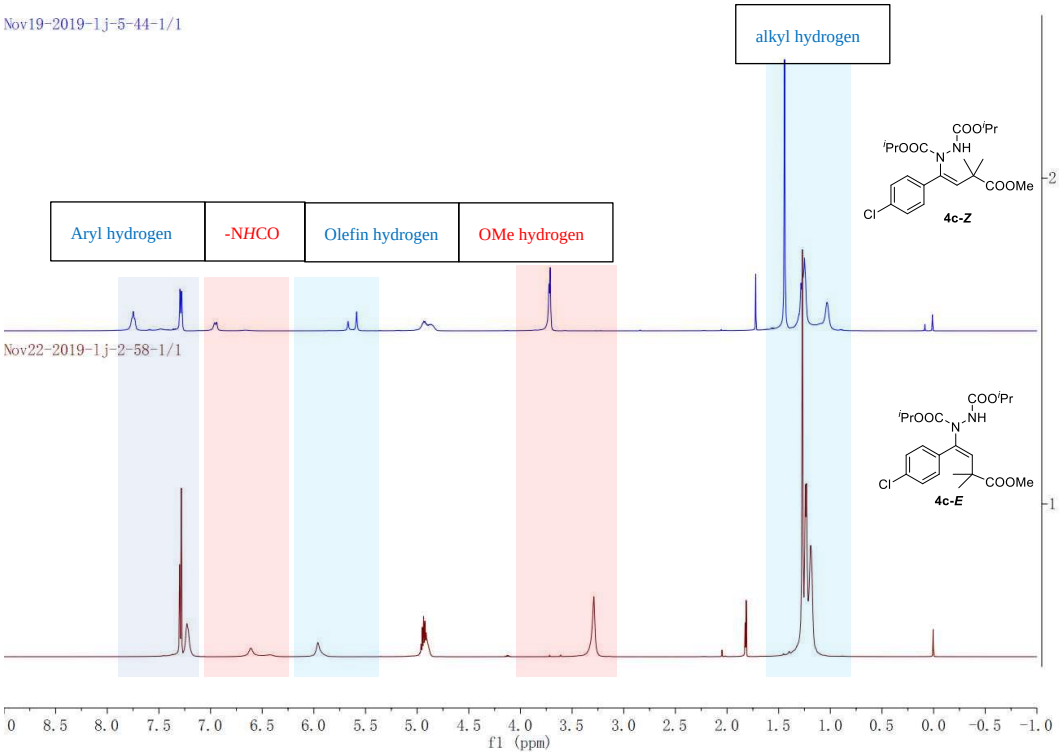
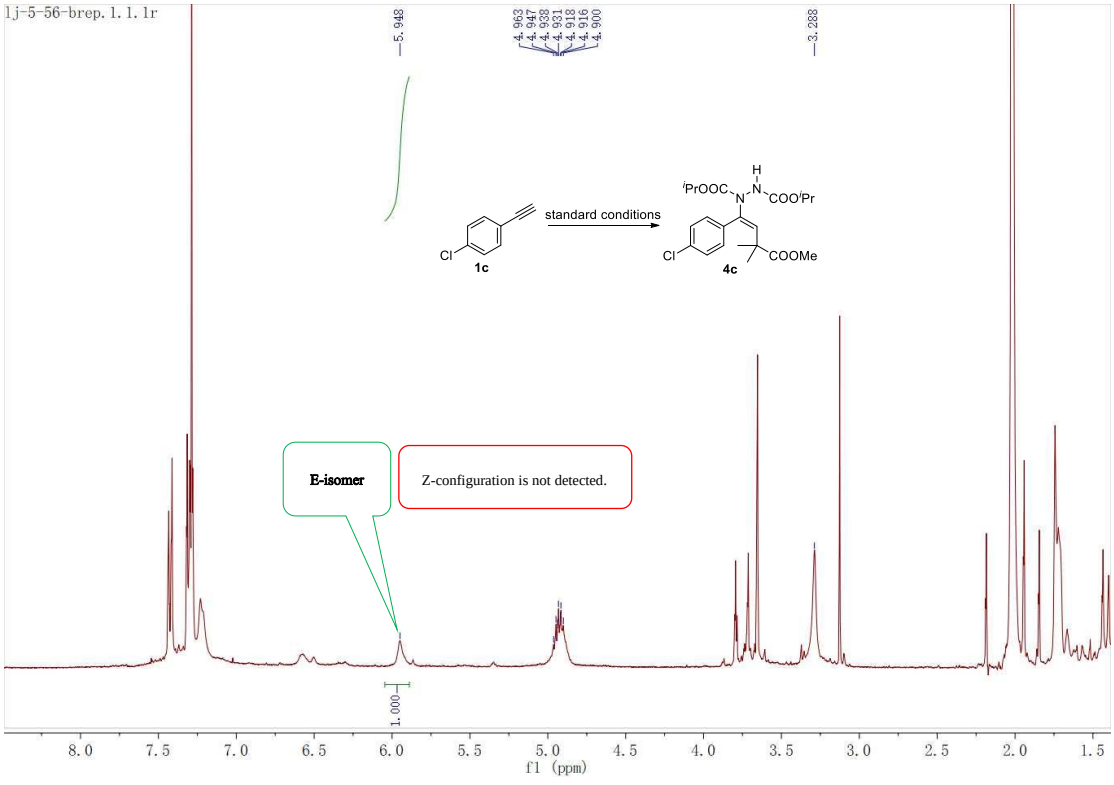
A comparation of ^{1}H NMR between 4c-*Z* and 4c-*E*

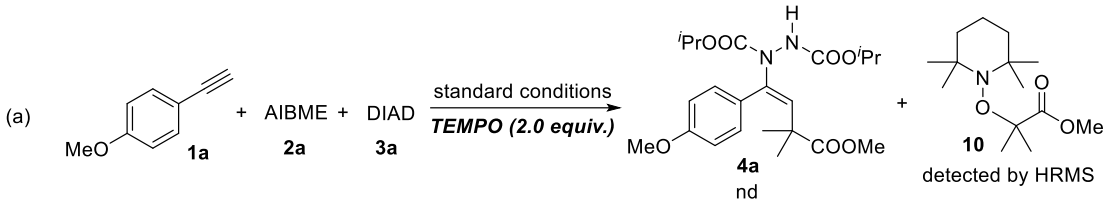


Crude ^{1}H NMR spectrum of standard conditions

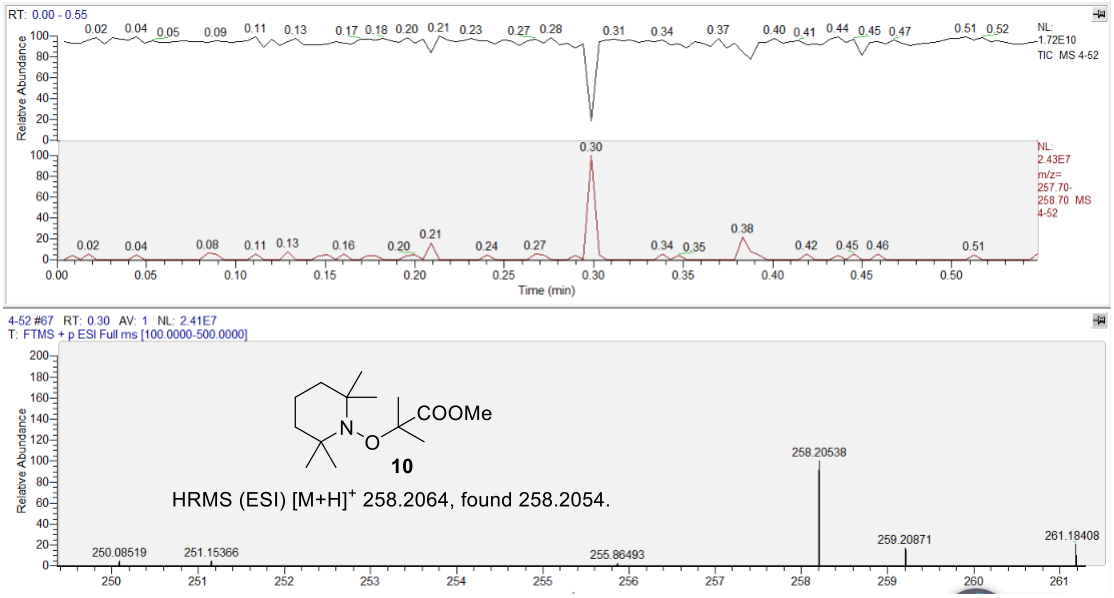


VII. Mechanistic study

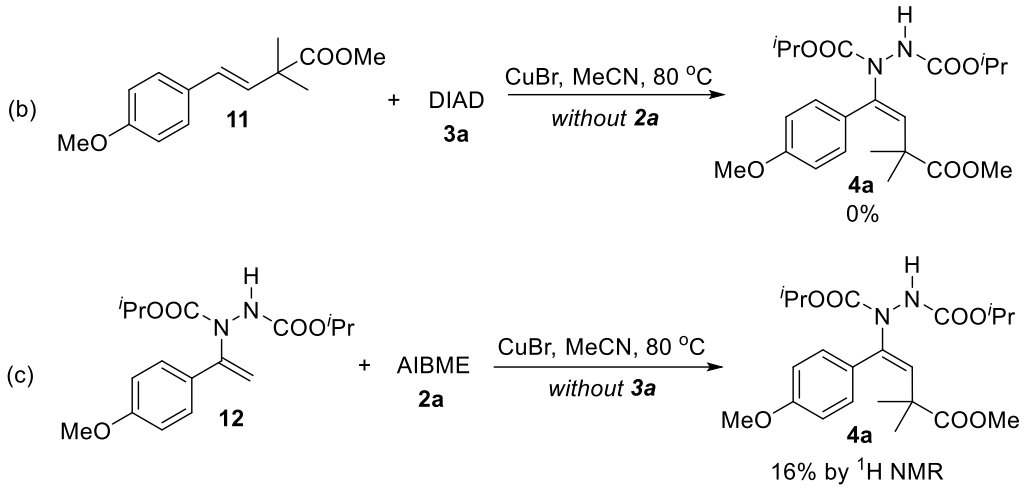
7.1 Radical inhibiting experiments



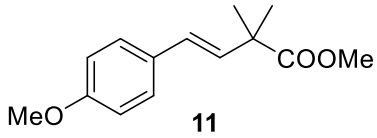
In an oven-dried resealable screw-cap test tube, CuBr (5.7 mg, 0.04 mmol, 20 mol%), alkyne **1a** (79.2 mg, 0.6 mmol, 3.0 equiv.), dimethyl 2,2'-azobis(2-methylpropionate) **2a** (0.2 mmol, 1.0 equiv.), DIAD **3a** (0.2 mmol, 1.0 equiv.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 62.5 mg, 0.40 mmol, 2.0 equiv.) were mixed in anhydrous MeCN (2.5 mL) under Ar atmosphere. The reaction mixture was stirred at 80 °C oil path for 8 h. The residue was detected on High Resolution Mass (MS) analysis. The reaction was totally inhibited, and **10** was detected by the HRMS.



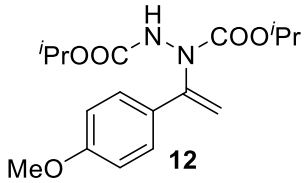
7.2 Possible intermediates



Preparation of starting material:



Methyl (*E*)-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (11). The title compound was prepared according to the previous reported protocols[6], and the ^{1}H NMR spectral data matched those of previously reported.



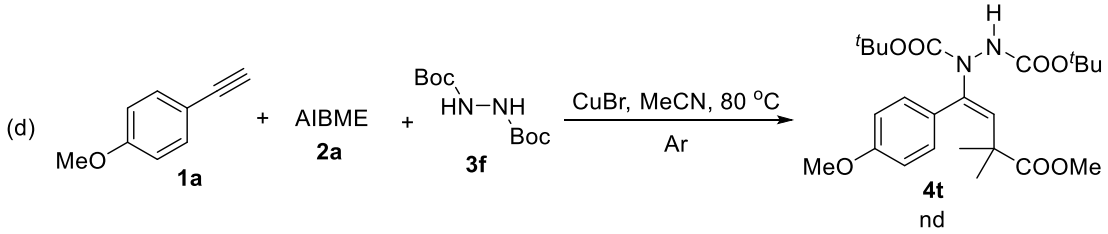
Diisopropyl 1-[1-(4-methoxyphenyl)vinyl]-1,2-hydrazinedicarboxylate (**12**). The title compound was prepared according to previous reported literature with 4-methoxyacetophenone as starting material.[7] To a solution of 4-methoxyacetophenone (1.50 g, 10.0 mmol) and DIAD (2.42 g, 12.0 mmol) in anhydrous THF (15 mL) was added dropwise PPh_3 (3.14 g, 12.0 mmol) in anhydrous THF (15 mL) at 0 °C under argen atmosphere. The solution was stirred at room temperture for 12 h. When the reaction was complete, the solution was concentrated and dissolved in petroleum ether/ EtOAc (3:1) until white solid precipitated, then the mixture was

filtered and the filtrate was concentrated. The crude material was purified by flash column chromatography (silica gel, 6:1 petroleum ether:EtOAc) to afford **12** as slightly yellow sticky. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 6.96-6.67 (m, 3H), 5.28 (s,1H), 5.25 (s, 1H), 5.06-4.94 (m, 1H), 4.89 (sept, *J* = 6.0 Hz, 1H), 3.81 (s, 3H), 1.32-1.22 (m, 6H), 1.19-1.05 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 155.7, 154.6, 146.6, 129.8, 127.4, 113.6, 108.1, 70.7, 69.9, 55.3, 21.9, 21.7; HRMS (ESI) calcd for $C_{17}H_{25}N_2O_5$ $[M+H]^+$ 337.1758, found 337.1763.

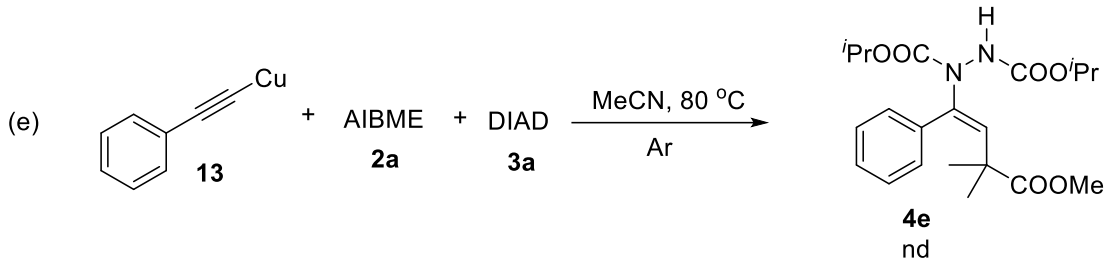
Procedure:

eq b: In an oven-dried resealable screw-cap test tube, CuBr (2.8 mg, 0.02 mmol, 20 mol%), **11** (24.3 mg, 0.1 mmol, 1.0 equiv.) and **3a** (20.2 mg, 0.1 mmol, 1.0 equiv.) were mixed in anhydrous MeCN (1.3 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C oil path for 8 h. No desired product was detected.

eq c: In an oven-dried resealable screw-cap test tube, CuBr (5.7 mg, 0.04 mmol, 20 mol%), **12** (67.3 mg, 0.2 mmol, 1.0 equiv.) and **2a** (46.1 mg, 0.2 mmol, 1.0 equiv.) were mixed in anhydrous MeCN (2.5 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C oil path for 8 h. After cooled to room temperature, internal standard *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added for ^{1}H NMR experiment, a 16% yield of **4a** was detected. Product was also isolated for checking the stereochemistry of new formed C-C double bond.



In an oven-dried resealable screw-cap test tube, CuBr (5.7 mg, 0.04 mmol, 20mol%), alkyne **1a** (79.2 mg, 0.6 mmol, 3.0 equiv.), dimethyl 2,2'-azobis(2-methylpropionate) **2a** (46.1 mg, 0.2 mmol, 1.0 equiv.) and **3f** (46.5 mg, 0.2 mmol, 1.0 equiv.) were mixed in anhydrous MeCN (2.5 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C oil path for 8 h. A messy TLC profile was observed and **4t** was not detected by ^{1}H NMR.



In an oven-dried resealable screw-cap test tube, commercially available **13** (98.8 mg, 0.6 mmol, 3.0 equiv.), dimethyl 2,2'-azobis(2-methylpropionate) **2a** (46.1 mg, 0.2 mmol, 1.0 equiv.) and **3a** (40.4 mg, 0.2 mmol, 1.0 equiv.) were mixed in anhydrous MeCN (2.5 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C oil path for 8 h. **4e** was not detected by TLC and ^{1}H NMR.

VIII. References

[1] L. S. Kocsis and K. M. Brummond, *Org. Lett.*, 2014, **16**, 4158.

[2] U. Dutta, D. W. Lupton and D. Maiti, *Org. Lett.*, 2016, **18**, 860.

[3] H. Zhu, S. Sun, H. Qiao, F. Yang, J. Kang, Y. Wu and Y. Wu, *Org. Lett.*, 2018, **20**, 620.

[4] D. Wang, J. Li, N. Li, T. Gao, S. Hou and B. Chen, *Green Chem.*, 2010, **12**, 45.

[5] (a) U. Maeorg, L. Grehn and U. Ragnarsson, *Angew. Chem., Int. Ed.*, 1996, **35**, 2626; (b) U. Maeorg, T. Pehk and U. Ragnarsson, *Acta Chem. Scand.*, 1999, **53**, 1127; (c) L. K. Rasmussen, *J. Org. Chem.*, 2006, **71**, 3627.

[6] B. Gao, Y. Xie, Z. Shen, L. Yang and H. Huang, *Org. Lett.*, 2015, **17**, 4968.

[7] Z.-J. Zhang, D. Yi, Q. Fu, W. Liang, S.-Y. Chen, L. Yang, F.-T. Du, J.-X. Ji and W. Wei, *Tetrahedron Lett.*, 2017, **58**, 2417.

IX. Copies of NMR spectra

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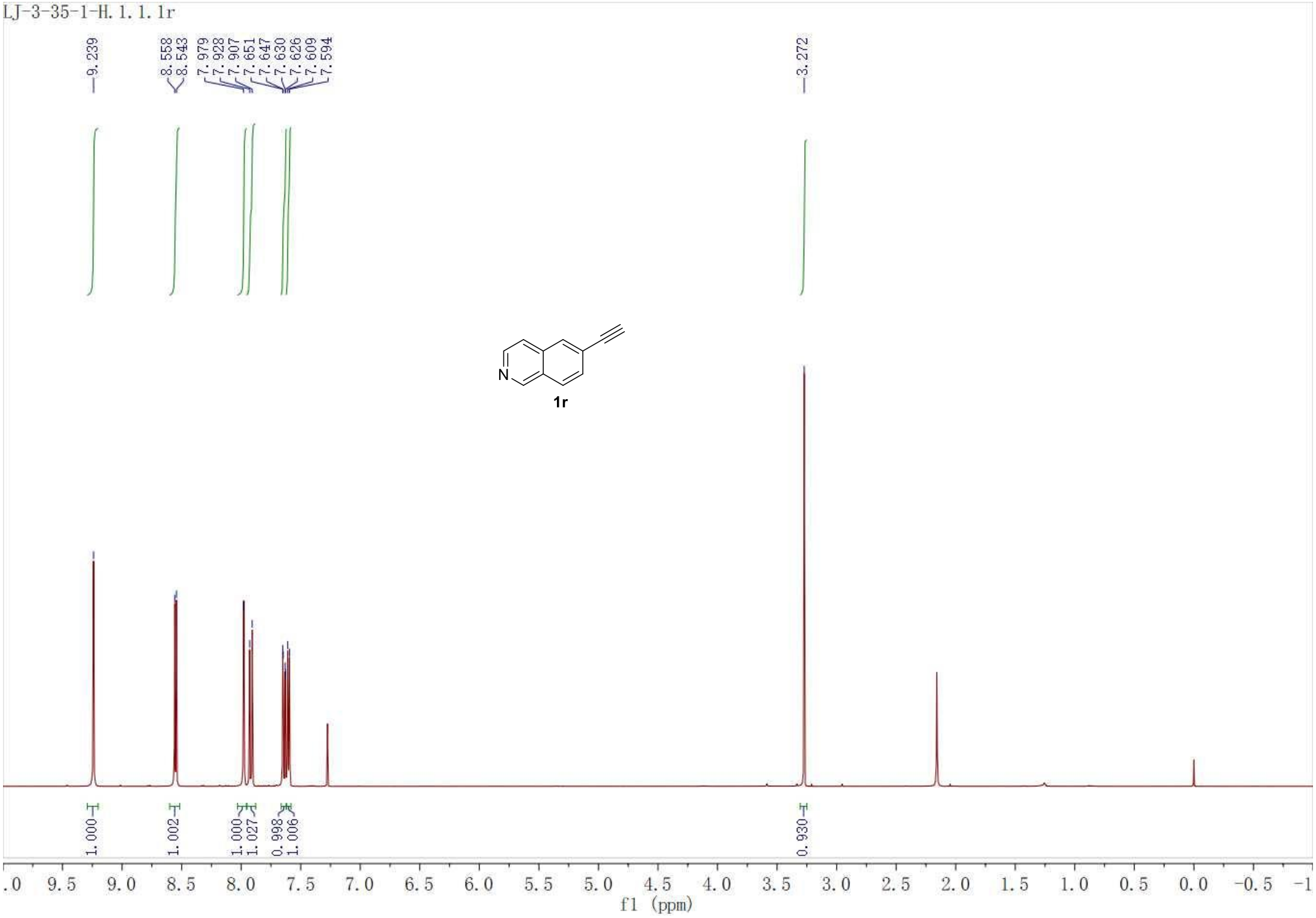

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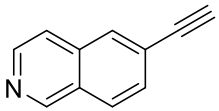
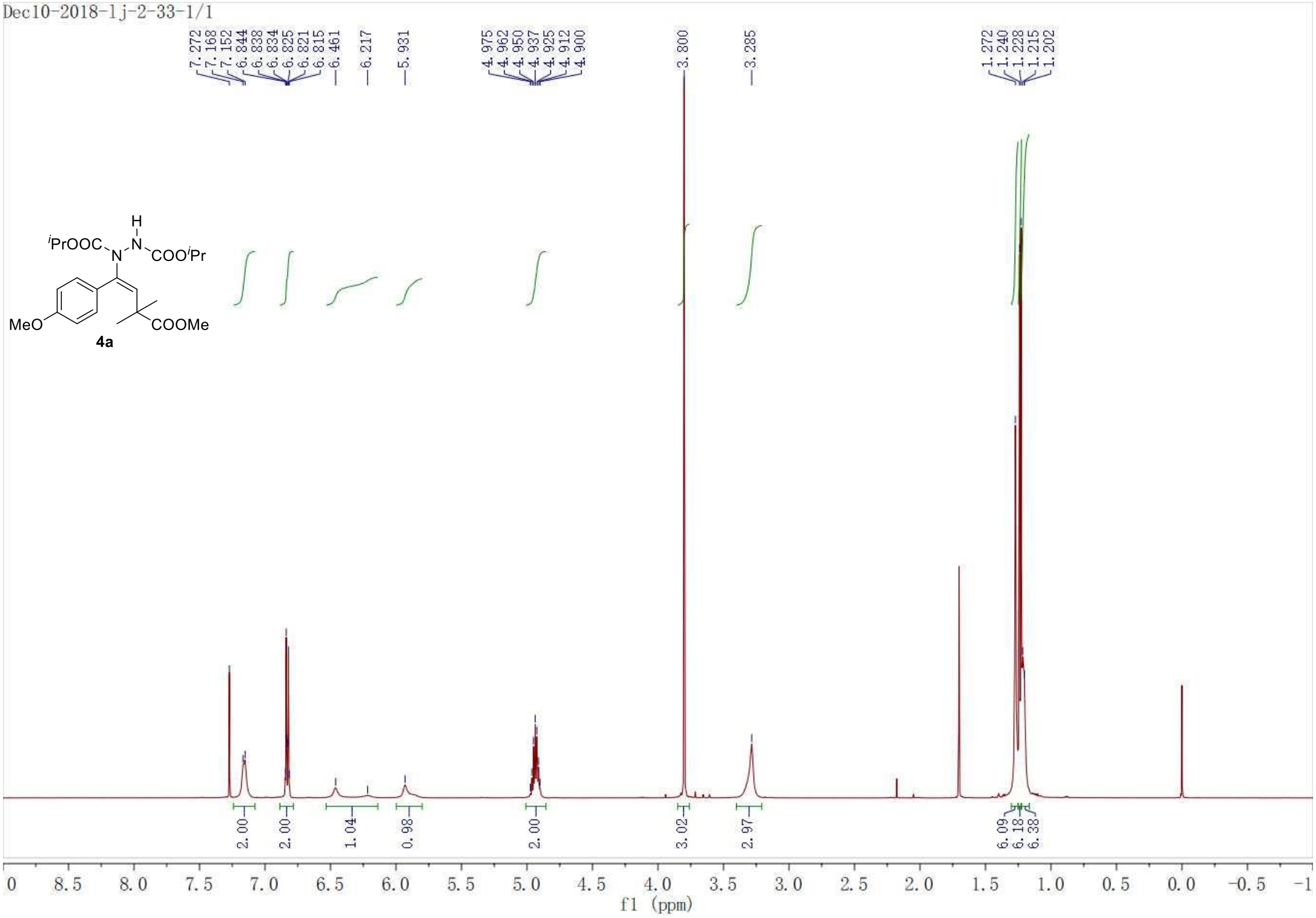


1r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6.834
6.825
6.821
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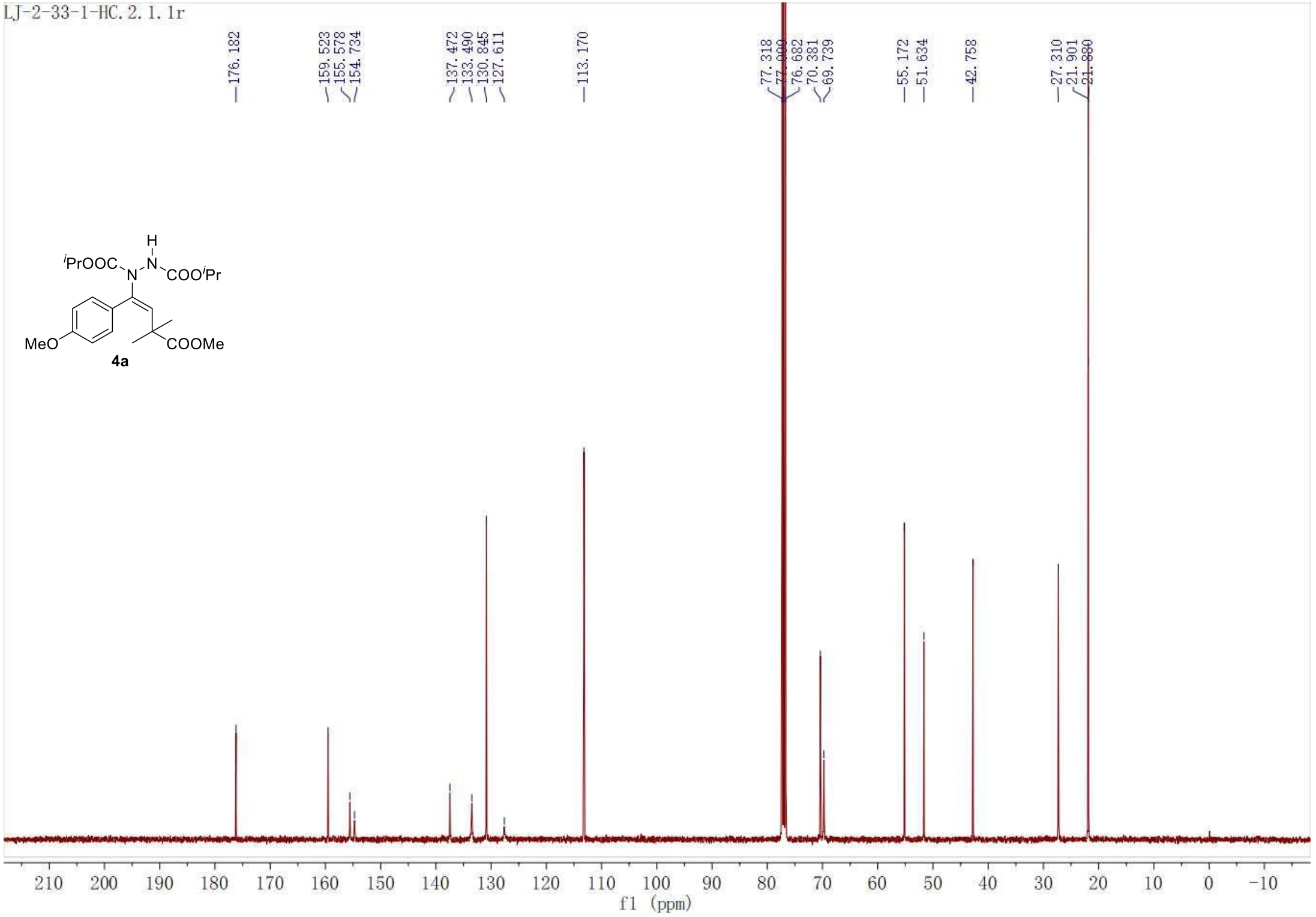
6.461
6.217
5.931
4.975
4.962
4.950
4.937
4.925
4.912
4.900
3.800
3.285
1.272
1.240
1.228
1.215
1.202
H
N
N
iPrOOC
COOiPr
MeO
COOMe
4a
2.00
2.00
1.04
0.98
2.00
3.02
2.97
6.09
6.18
6.38
f1 (ppm)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77.000
76.682
70.381
69.739
55.172
51.634
42.758
27.310
21.901
21.880
H
N
N
iPrOOC
COOiPr
MeO
COOMe
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
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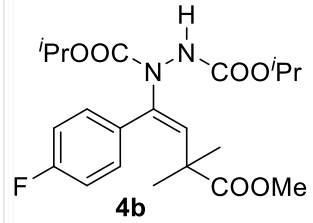
0
−10
f1 (ppm)

Jul31-2018-1j-2-57-1r



4b

7.284
7.264
7.028
7.024
7.010
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6.993
6.550
6.332
5.956
4.968
4.955
4.943
4.931
4.918
4.911
3.316
1.273
1.248
1.236
1.209
1.202

1.95
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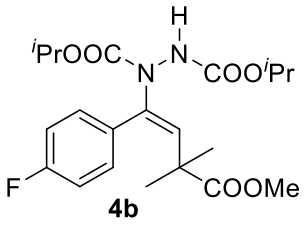
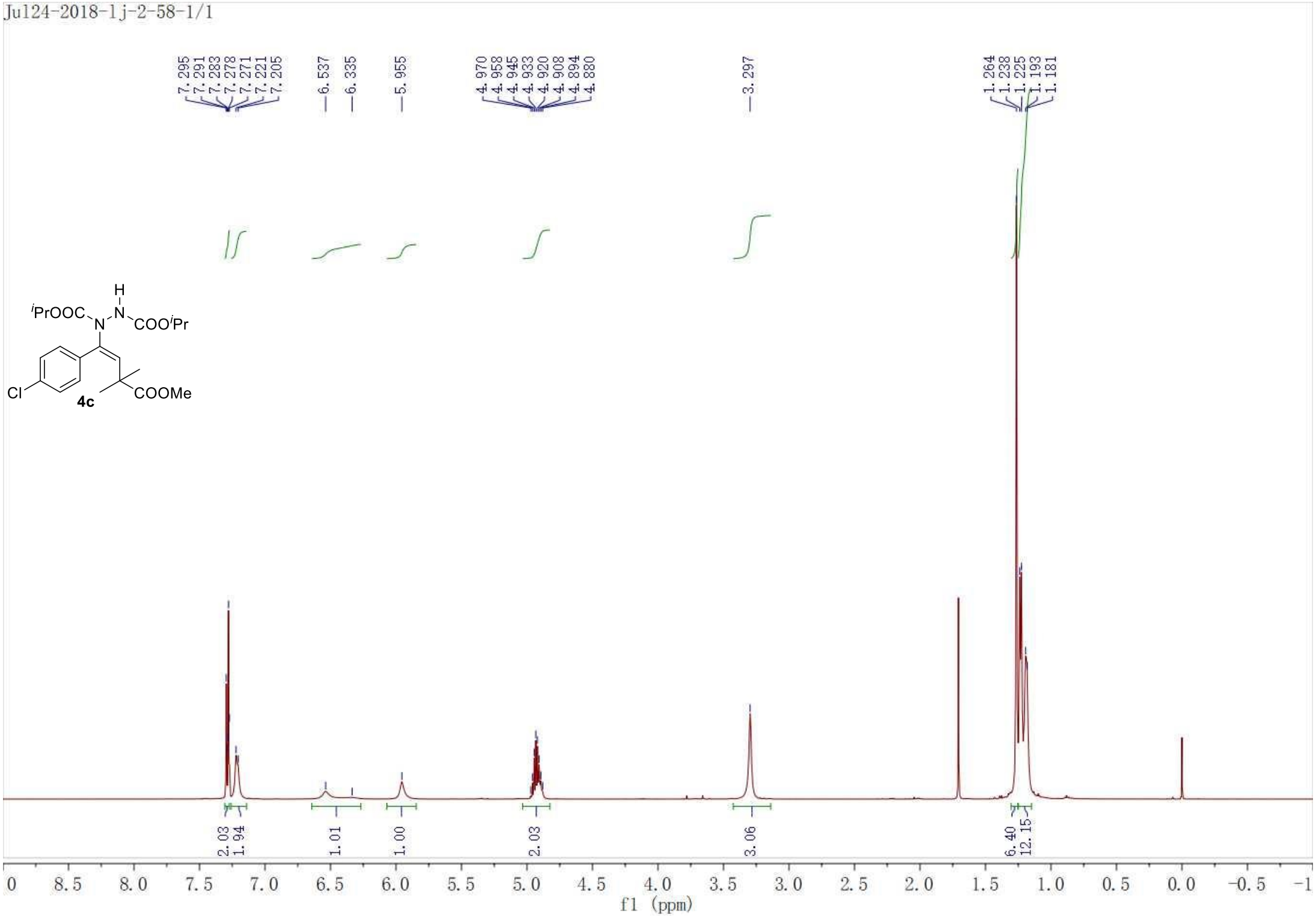
f1 (ppm)

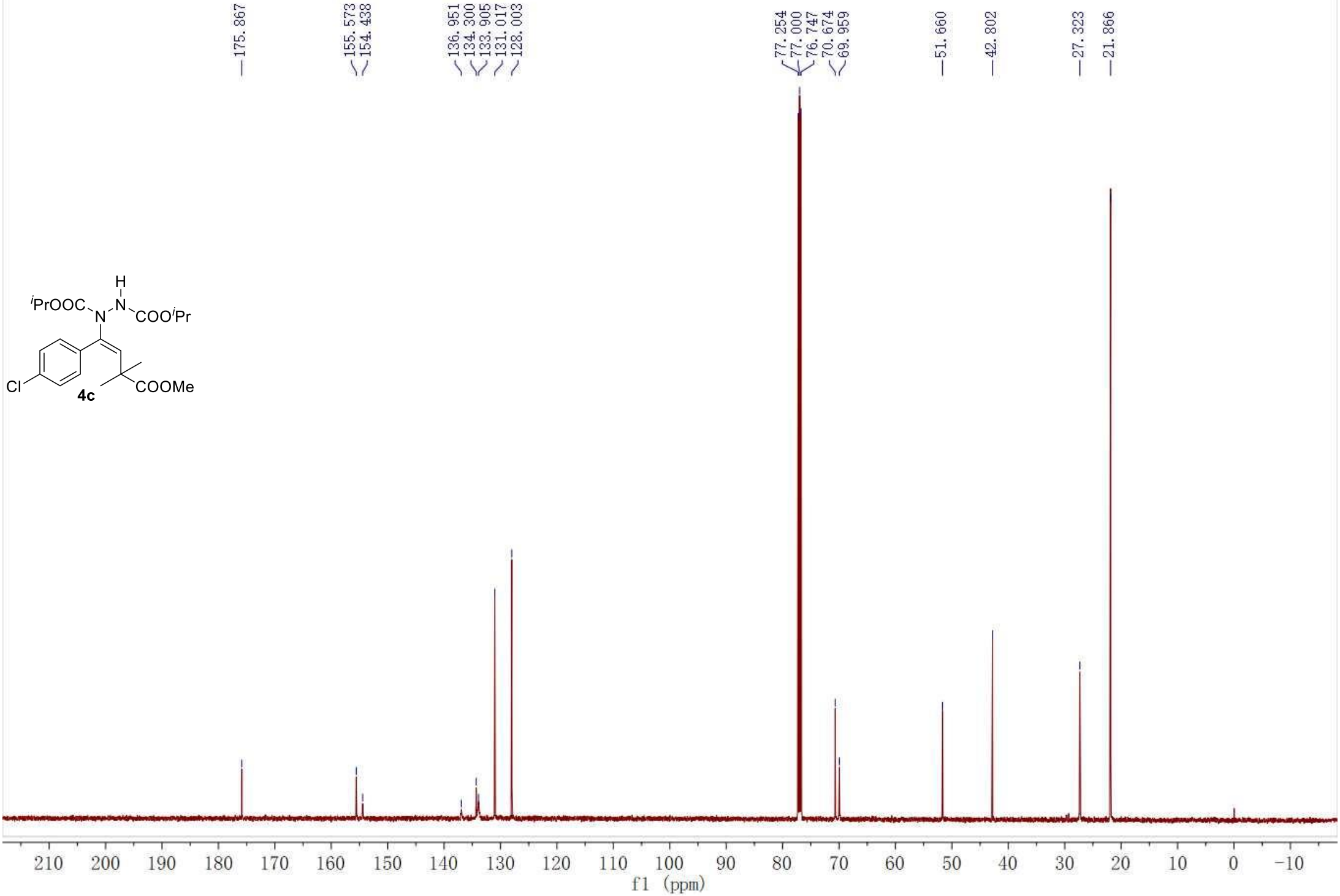
Aug02-2018-1j-57-1/1

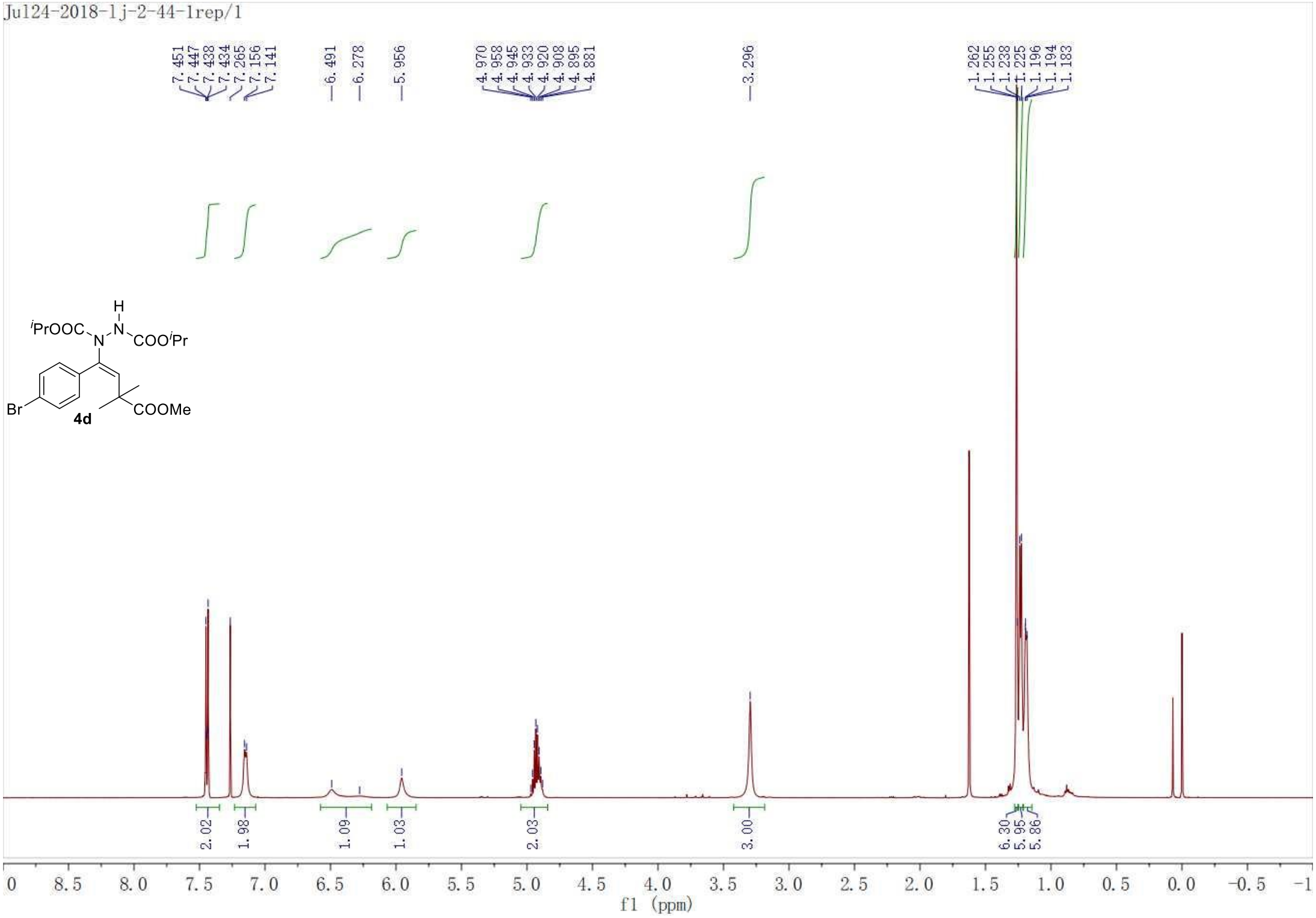


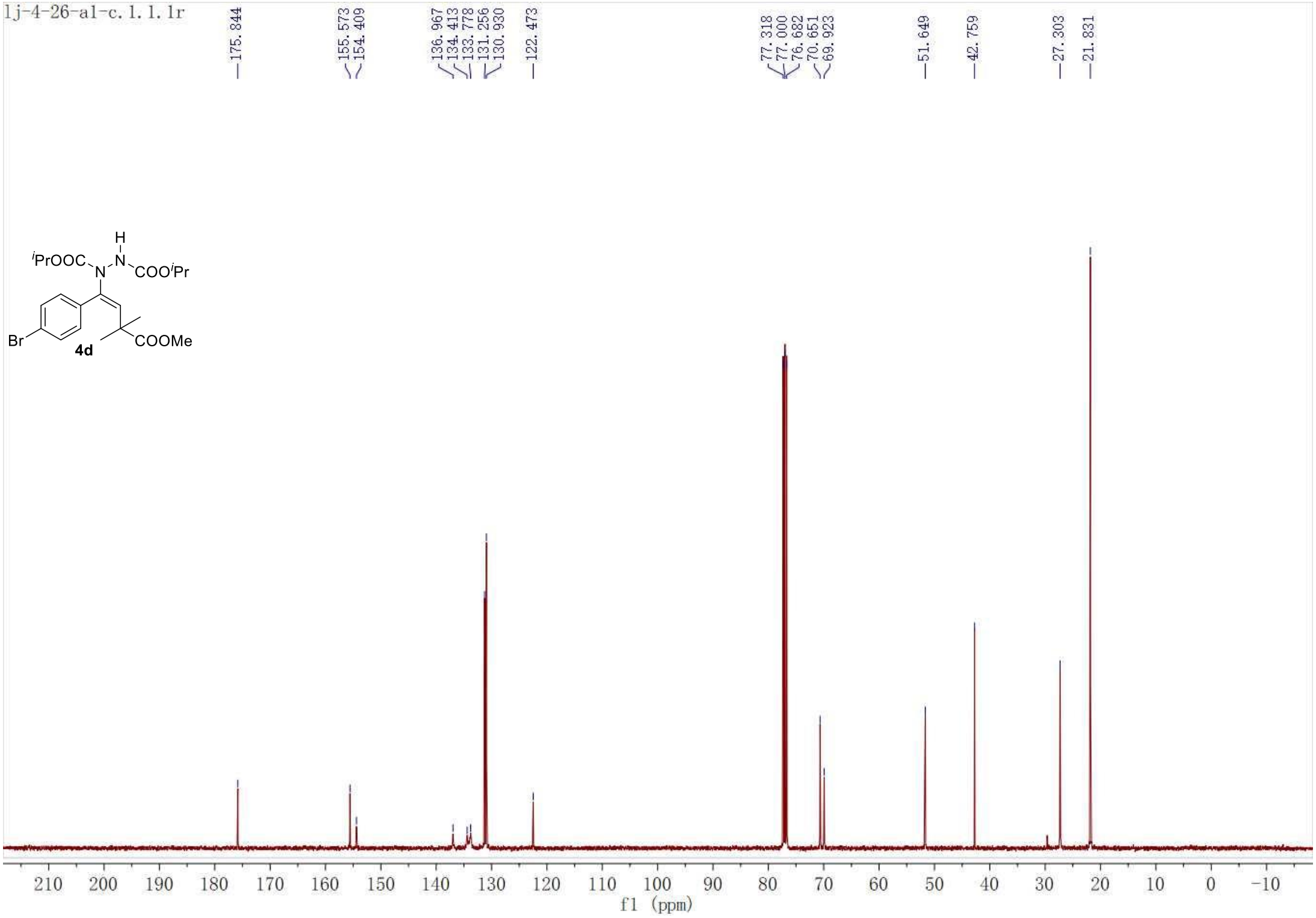
4b

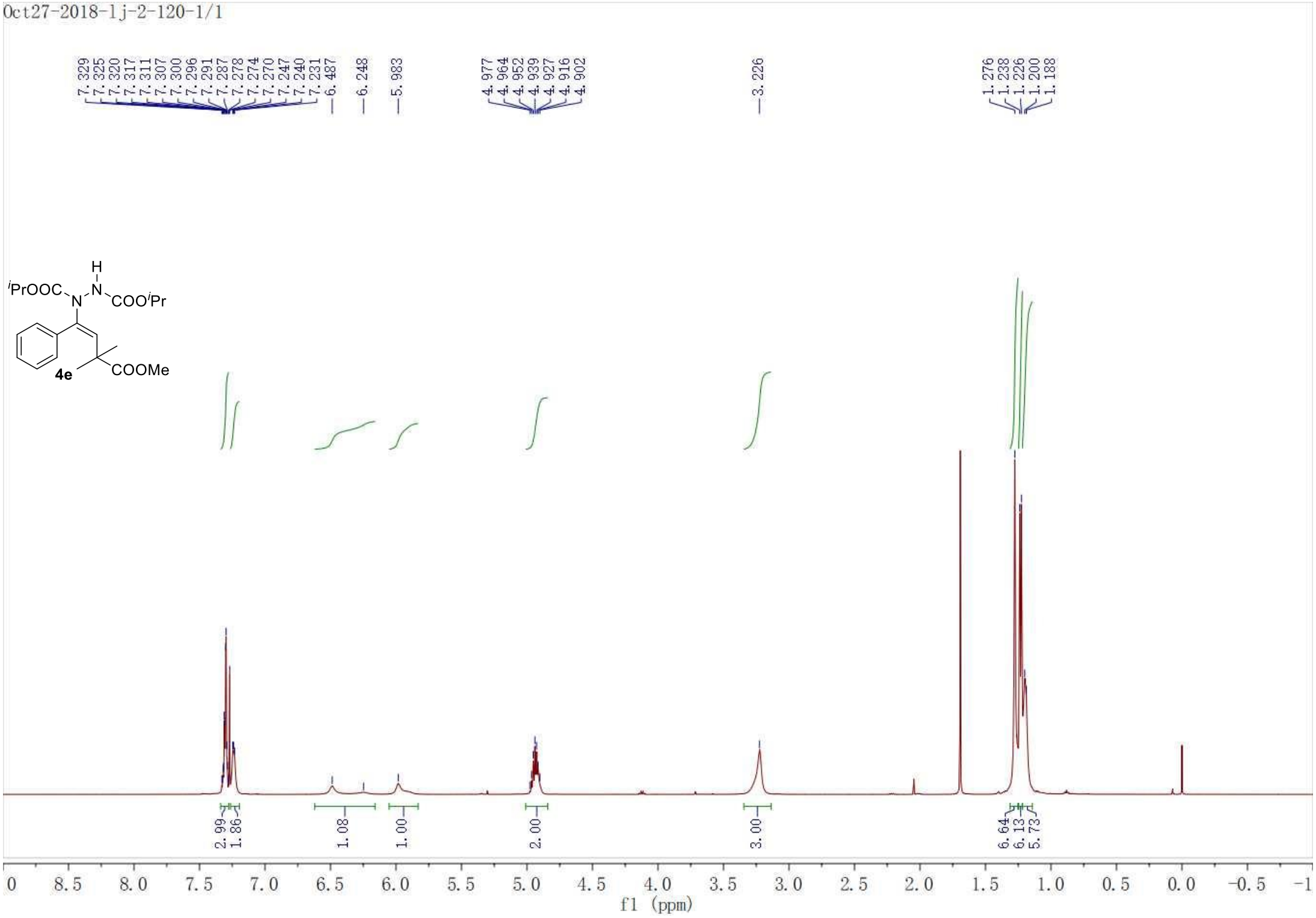

Jul24-2018-1j-2-58-1/1
7.295
7.291
7.283
7.278
7.271
7.221
7.205
6.537
6.335
5.955
4.970
4.958
4.945
4.933
4.920
4.908
4.894
4.880
3.297
1.264
1.238
1.225
1.193
1.181
H
N
N
iPrOOC
COOiPr
Cl
COOMe
4c
2.03
1.94
1.01
1.00
2.03
3.06
6.40
12.15
f1 (ppm)

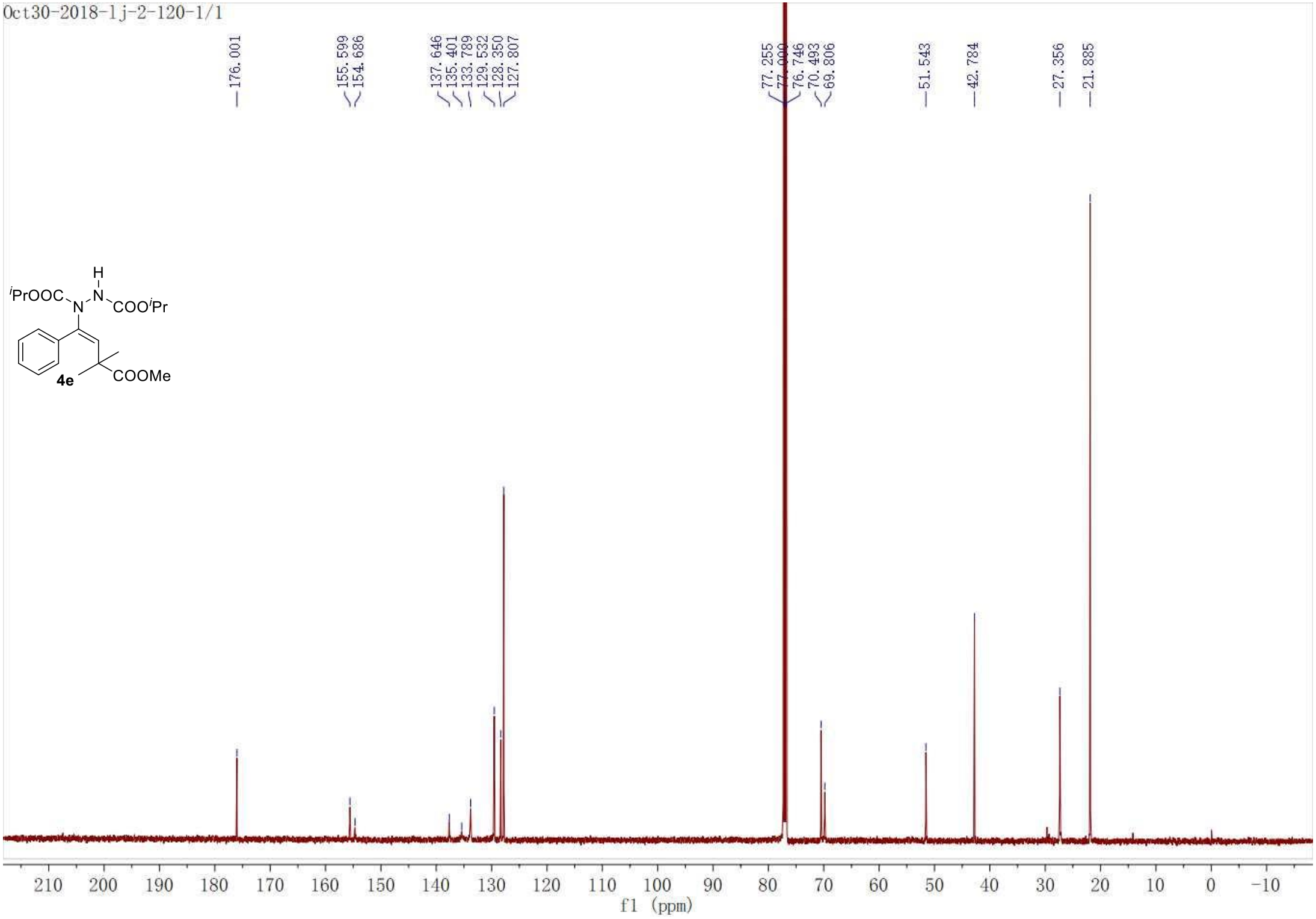
Jul26-2018-1j-2-58-1/1

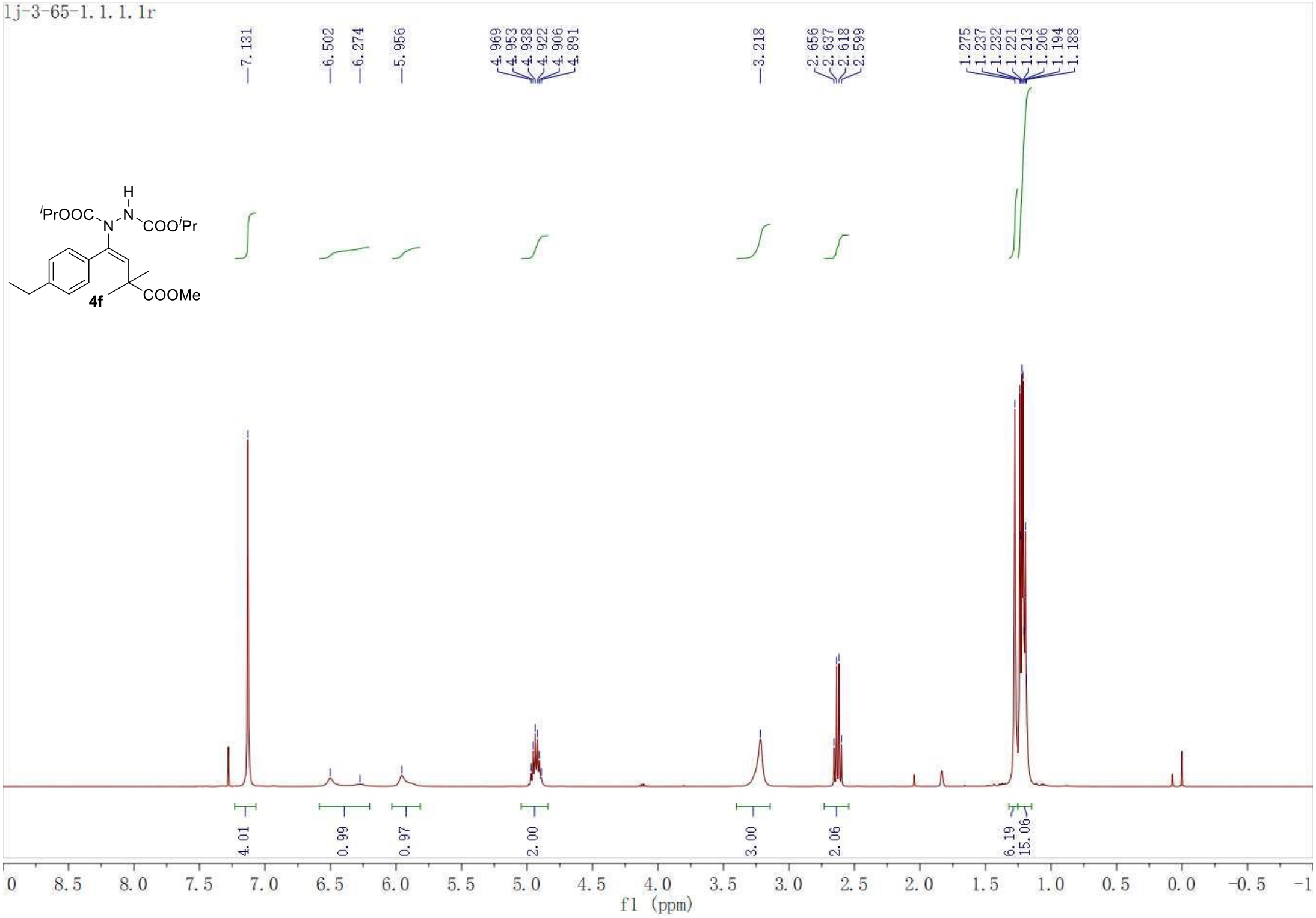


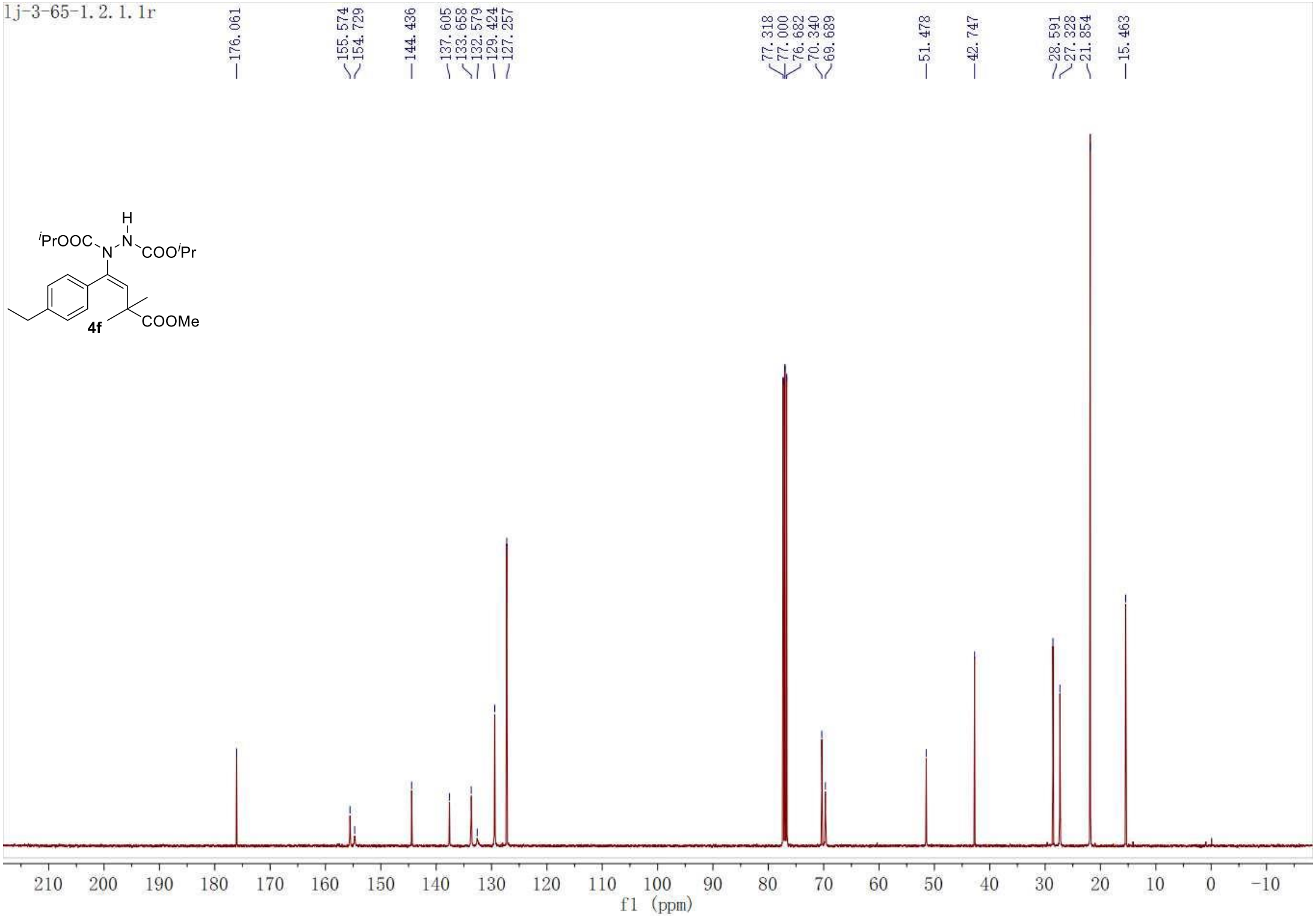

Jul24-2018-1j-2-44-1rep/1
7.451
7.447
7.438
7.434
7.265
7.156
7.141
6.491
6.278
5.956
4.970
4.958
4.945
4.933
4.920
4.908
4.895
4.881
3.296
1.262
1.255
1.238
1.225
1.196
1.194
1.183
H
iPrOOC
N
N
COOiPr
Br
COOMe
4d
2.02
1.98
1.09
1.03
2.03
3.00
6.30
5.95
5.86
f1 (ppm)

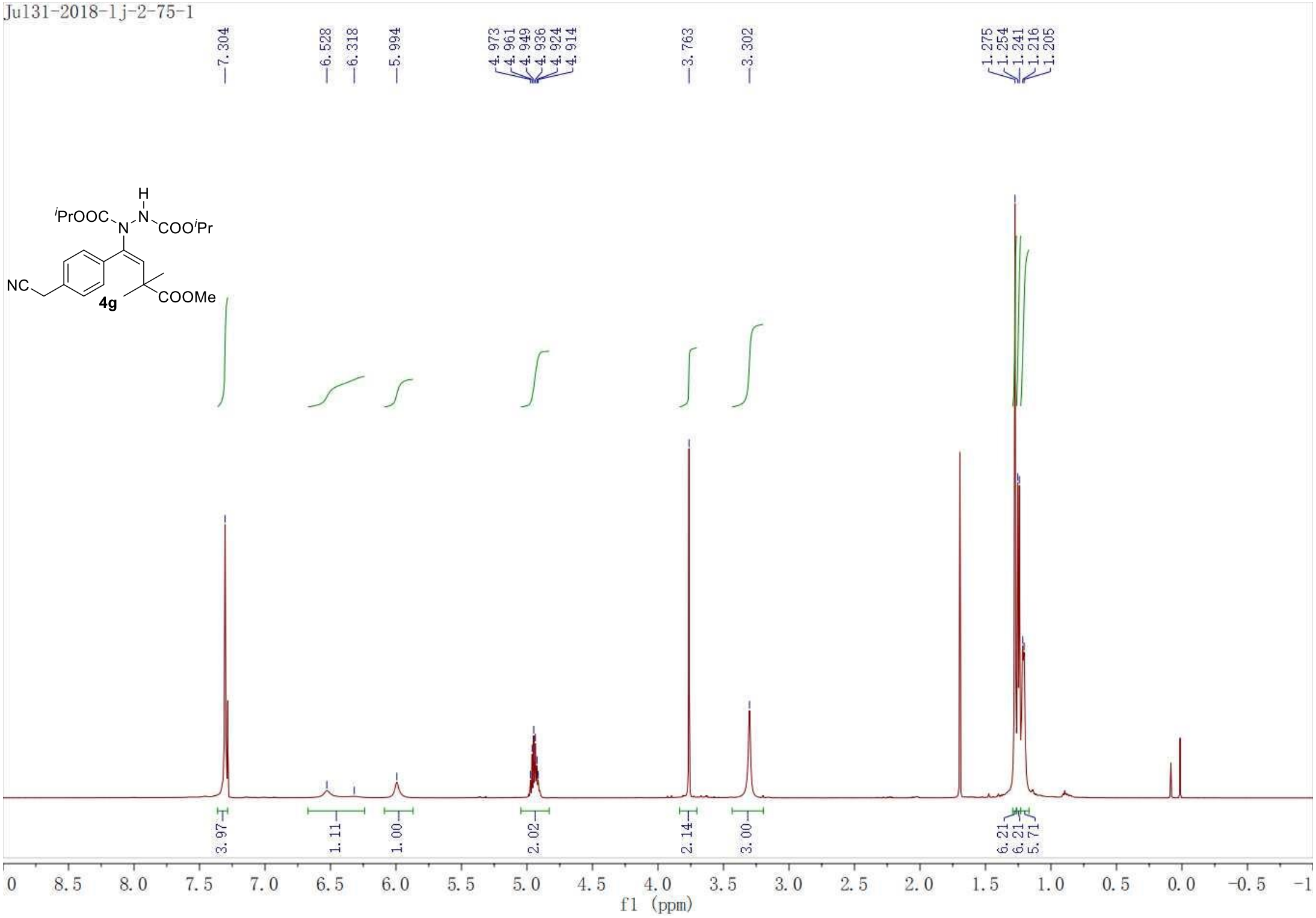

1j-4-26-a1-c.1.1.1r
175.844
155.573
154.409
136.967
134.413
133.778
131.256
130.930
122.473
77.318
77.000
76.682
70.651
69.923
51.649
42.759
27.303
21.831
H
N
N
iPrOOC
COOiPr
Br
COOMe
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

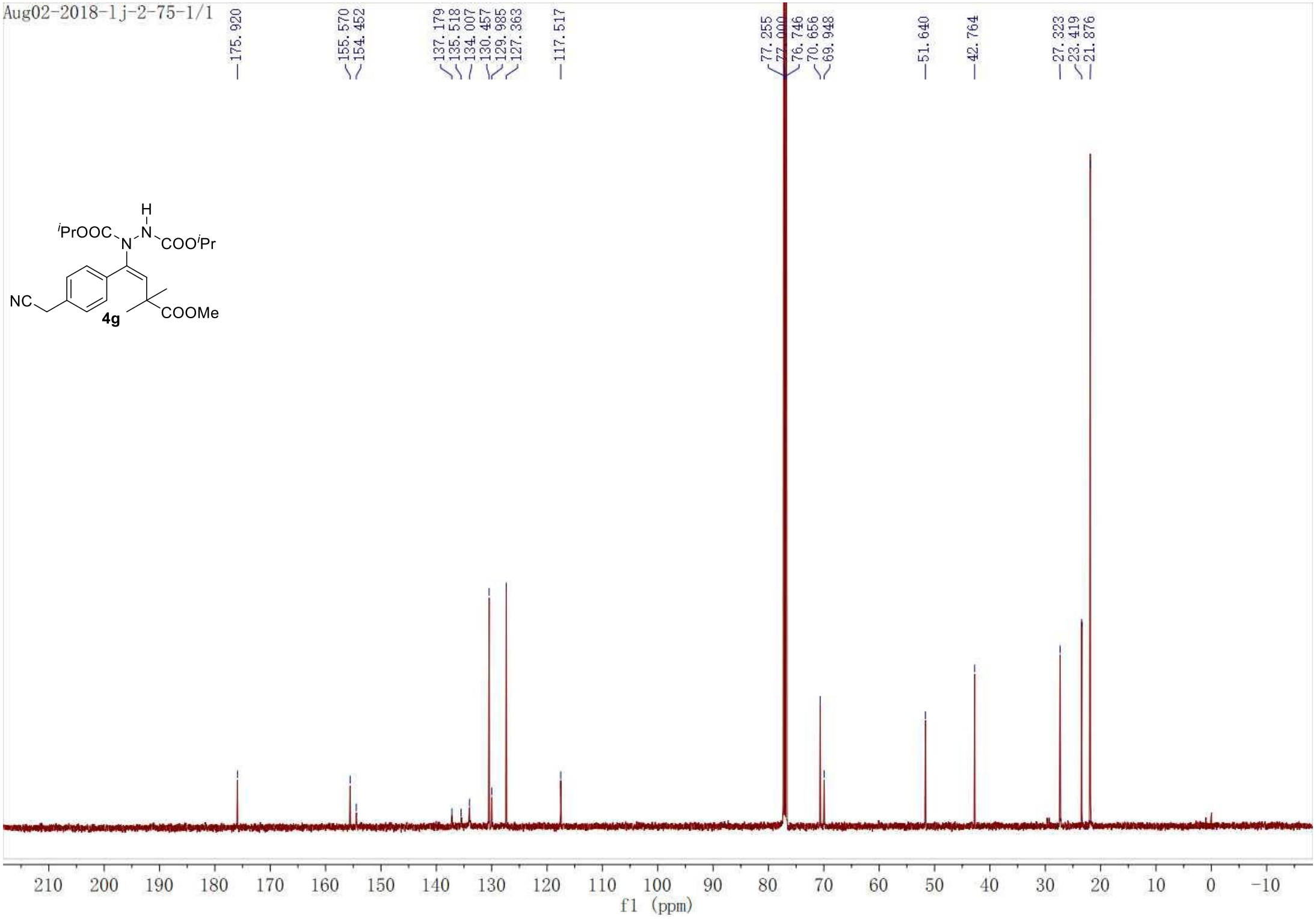

Oct27-2018-1j-2-120-1/1
7.329
7.325
7.320
7.317
7.311
7.307
7.300
7.296
7.291
7.287
7.278
7.274
7.270
7.247
7.240
7.231
6.487
6.248
5.983
4.977
4.964
4.952
4.939
4.927
4.916
4.902
3.226
1.276
1.238
1.226
1.200
1.188
H
iPrOOC
N
N
COOiPr
4e
COOMe
2.99
1.86
1.08
1.00
2.00
3.00
6.64
6.13
5.73
f1 (ppm)

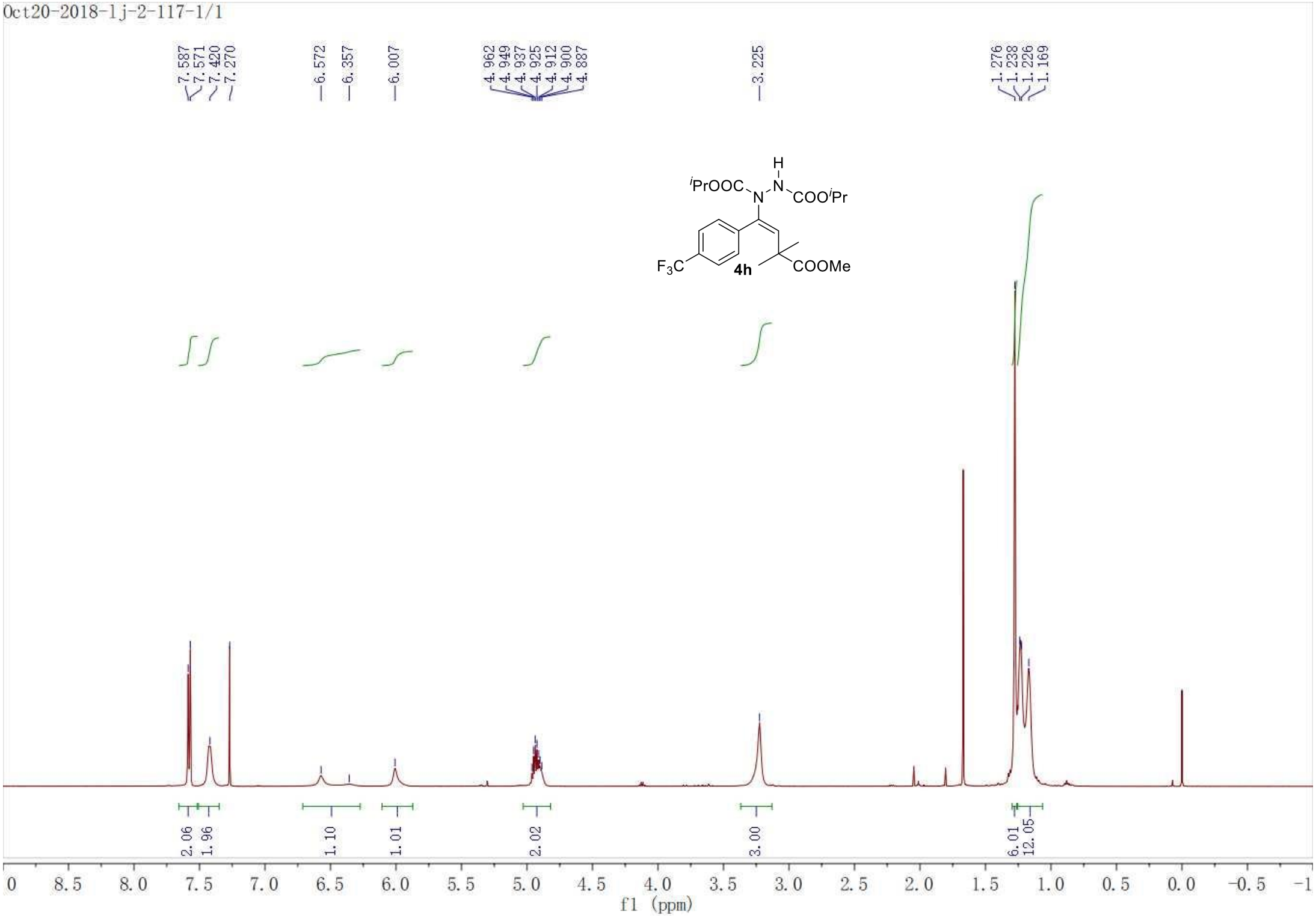

0ct30-2018-1j-2-120-1/1
176.001
155.599
154.686
137.646
135.401
133.789
129.532
128.350
127.807
77.255
77.000
76.746
70.493
69.806
51.543
42.784
27.356
21.885
iPrOOC
N
H
N
COOiPr
4e
COOMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

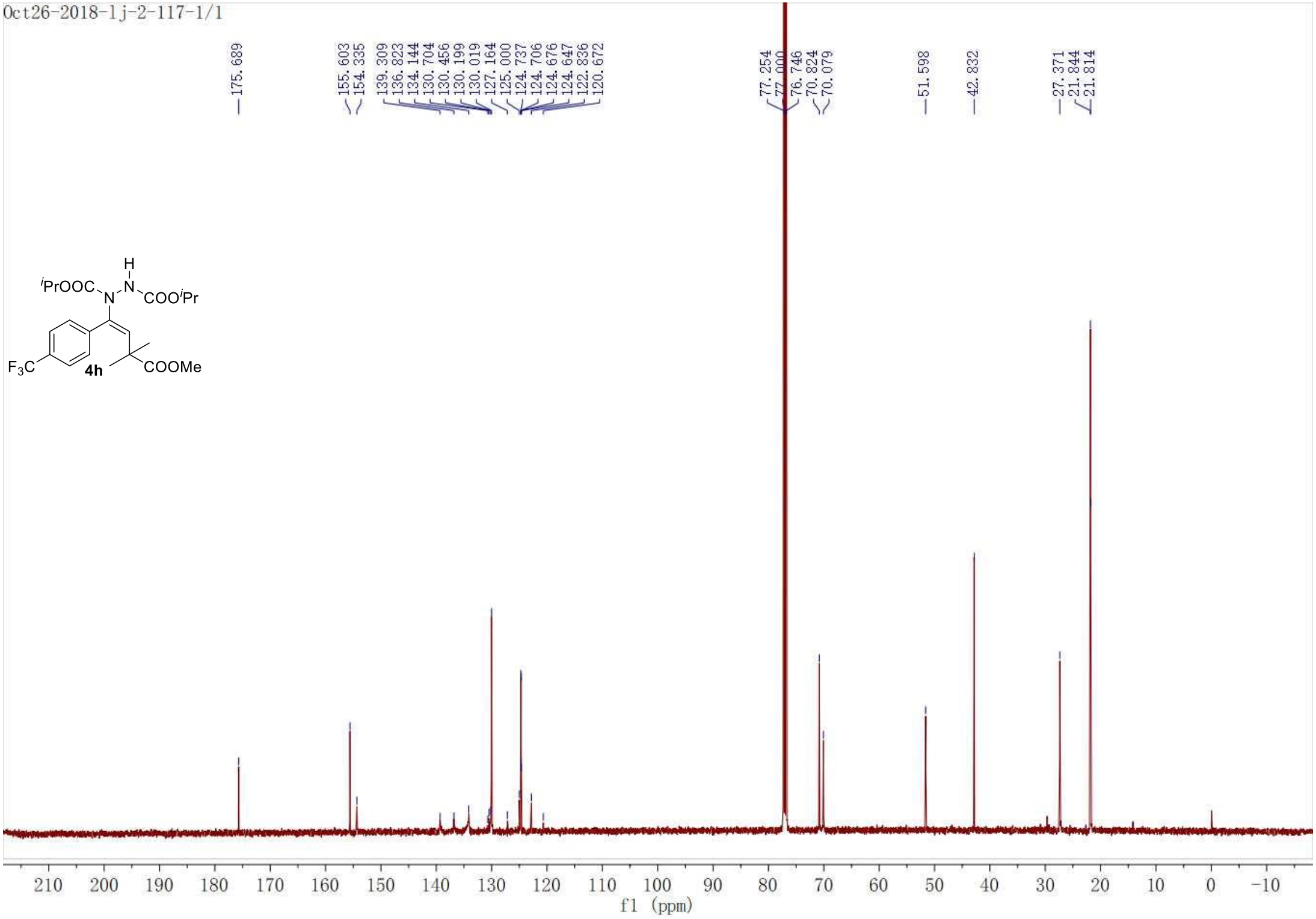

1j-3-65-1.1.1.1r
7.131
6.502
6.274
5.956
4.969
4.953
4.938
4.922
4.906
4.891
3.218
2.656
2.637
2.618
2.599
1.275
1.237
1.232
1.221
1.213
1.206
1.194
1.188
H
N
N
iPrOOC
COOiPr
COOMe
4f
4.01
0.99
0.97
2.00
3.00
2.06
6.19
15.06
f1 (ppm)

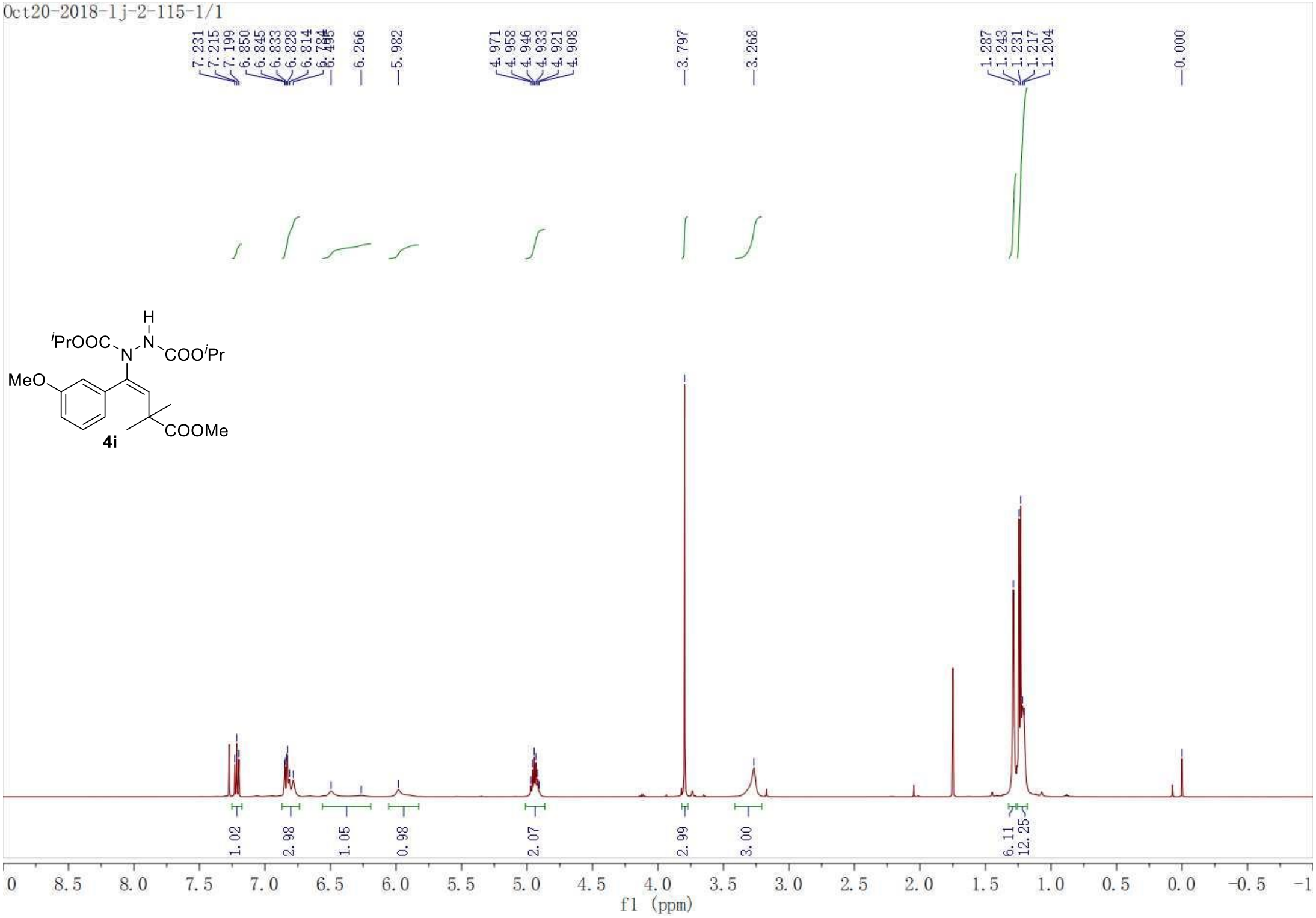

1j-3-65-1.2.1.1r
176.061
155.574
154.729
144.436
137.605
133.658
132.579
129.424
127.257
77.318
77.000
76.682
70.340
69.689
51.478
42.747
28.591
27.328
21.854
15.463
H
iPrOOC
N
N
COOiPr
COOMe
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

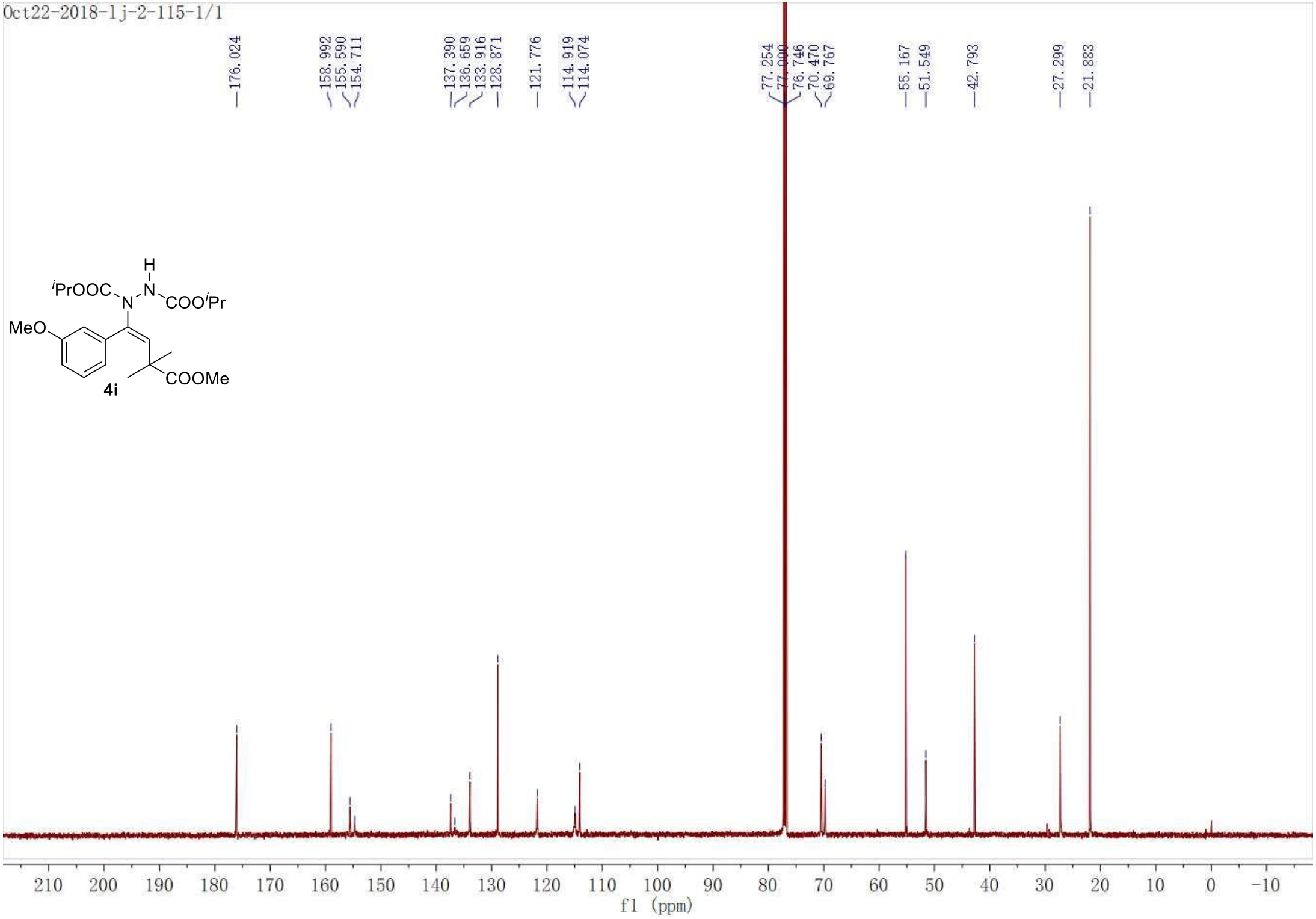

Jul31-2018-1j-2-75-1
7.304
6.528
6.318
5.994
4.973
4.961
4.949
4.936
4.924
4.914
3.763
3.302
1.275
1.254
1.241
1.216
1.205
H
N
N
iPrOOC
COOiPr
NC
COOMe
4g
3.97
1.11
1.00
2.02
2.14
3.00
6.21
6.21
5.71
f1 (ppm)

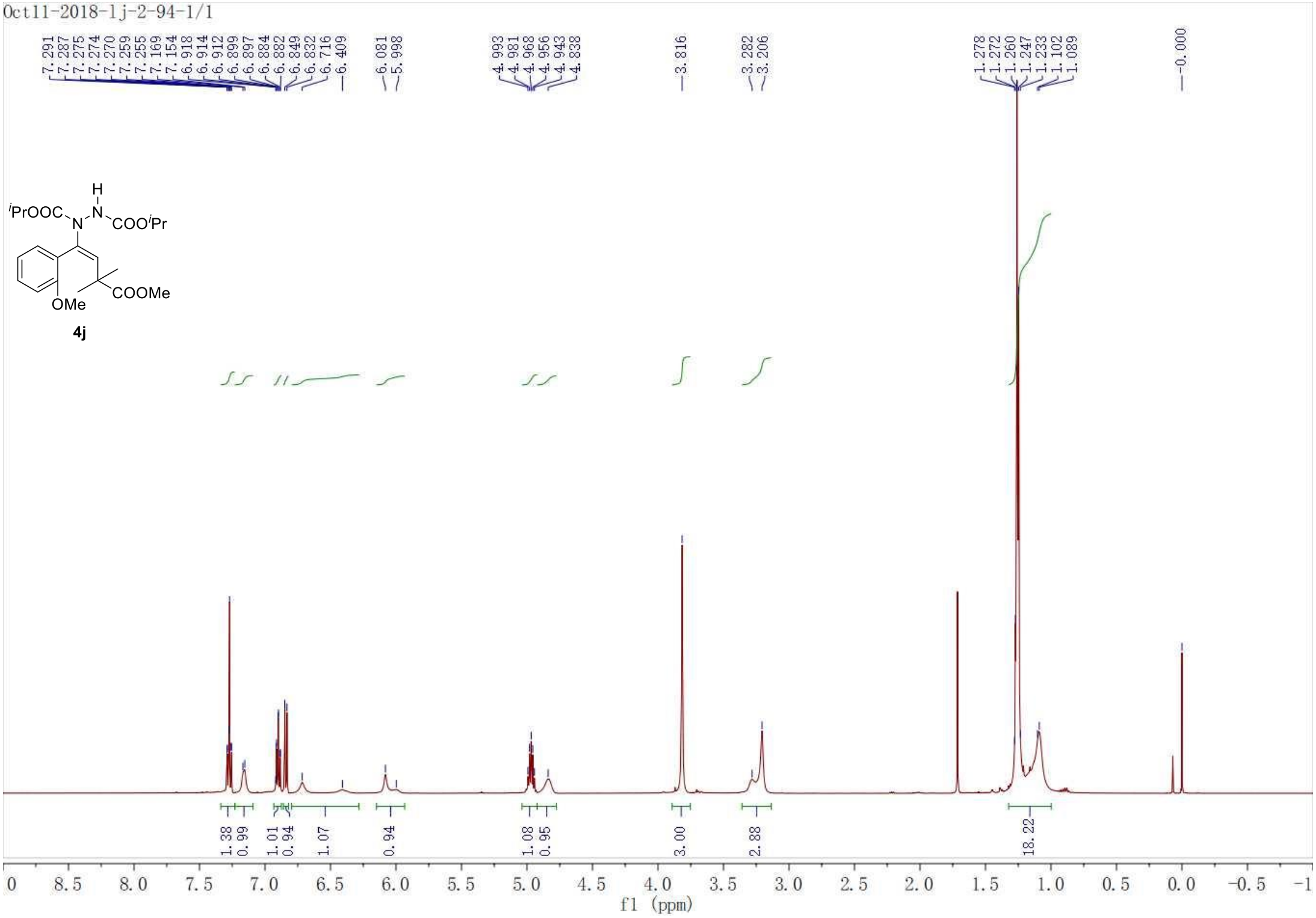

Aug02-2018-1j-2-75-1/1
175.920
155.570
154.452
137.179
135.518
134.007
130.457
129.985
127.363
117.517
77.255
77.000
76.746
70.656
69.948
51.640
42.764
27.323
23.419
21.876
H
N
N
iPrOOC
COOiPr
NC
COOMe
4g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

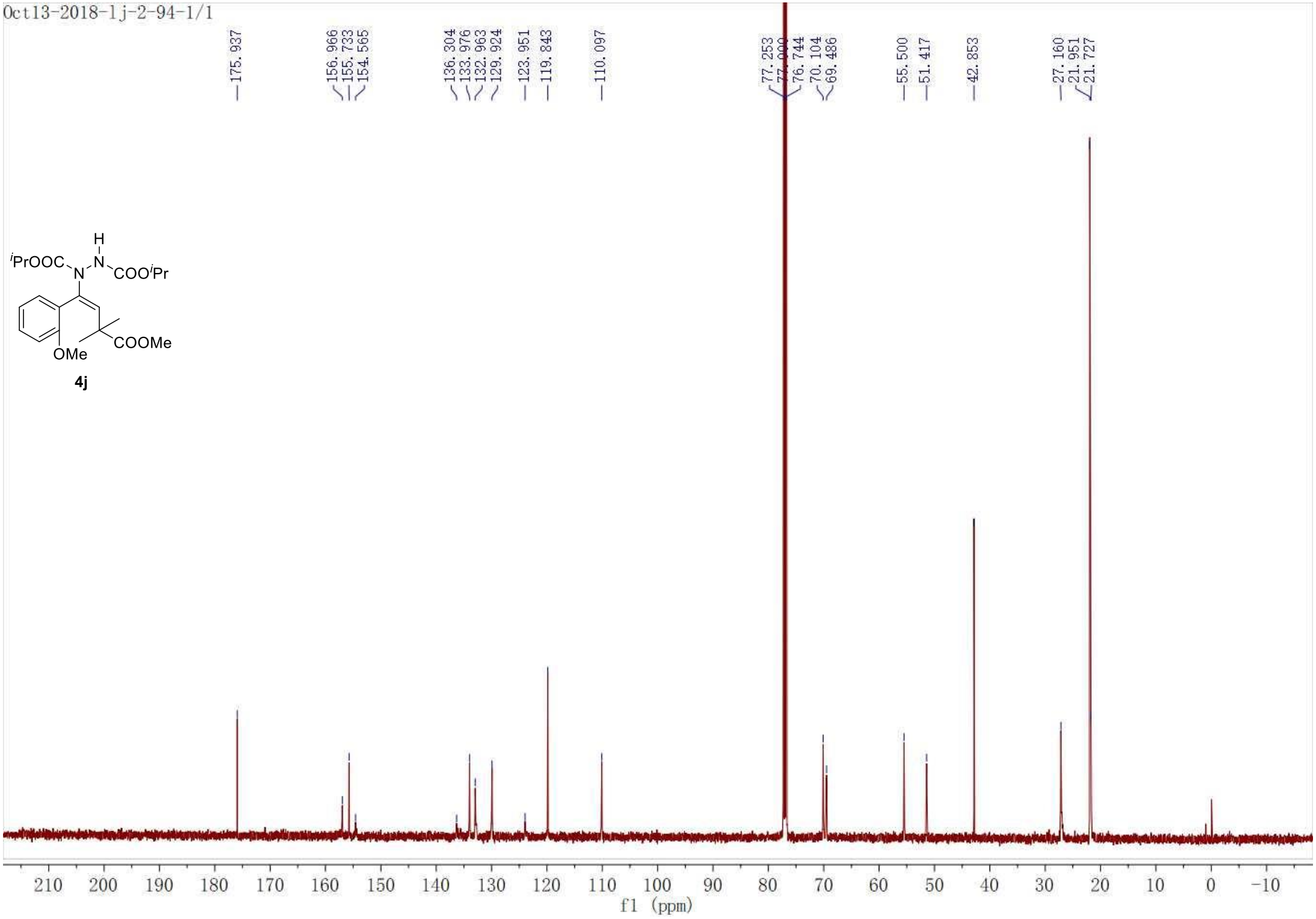

Oct20-2018-1j-2-117-1/1
7.587
7.571
7.420
7.270
6.572
6.357
6.007
4.962
4.949
4.937
4.925
4.912
4.900
4.887
3.225
1.276
1.238
1.226
1.169
H
N
N
iPrOOC
COOiPr
F3C
4h
COOMe
2.06
1.96
1.10
1.01
2.02
3.00
6.01
12.05
f1 (ppm)

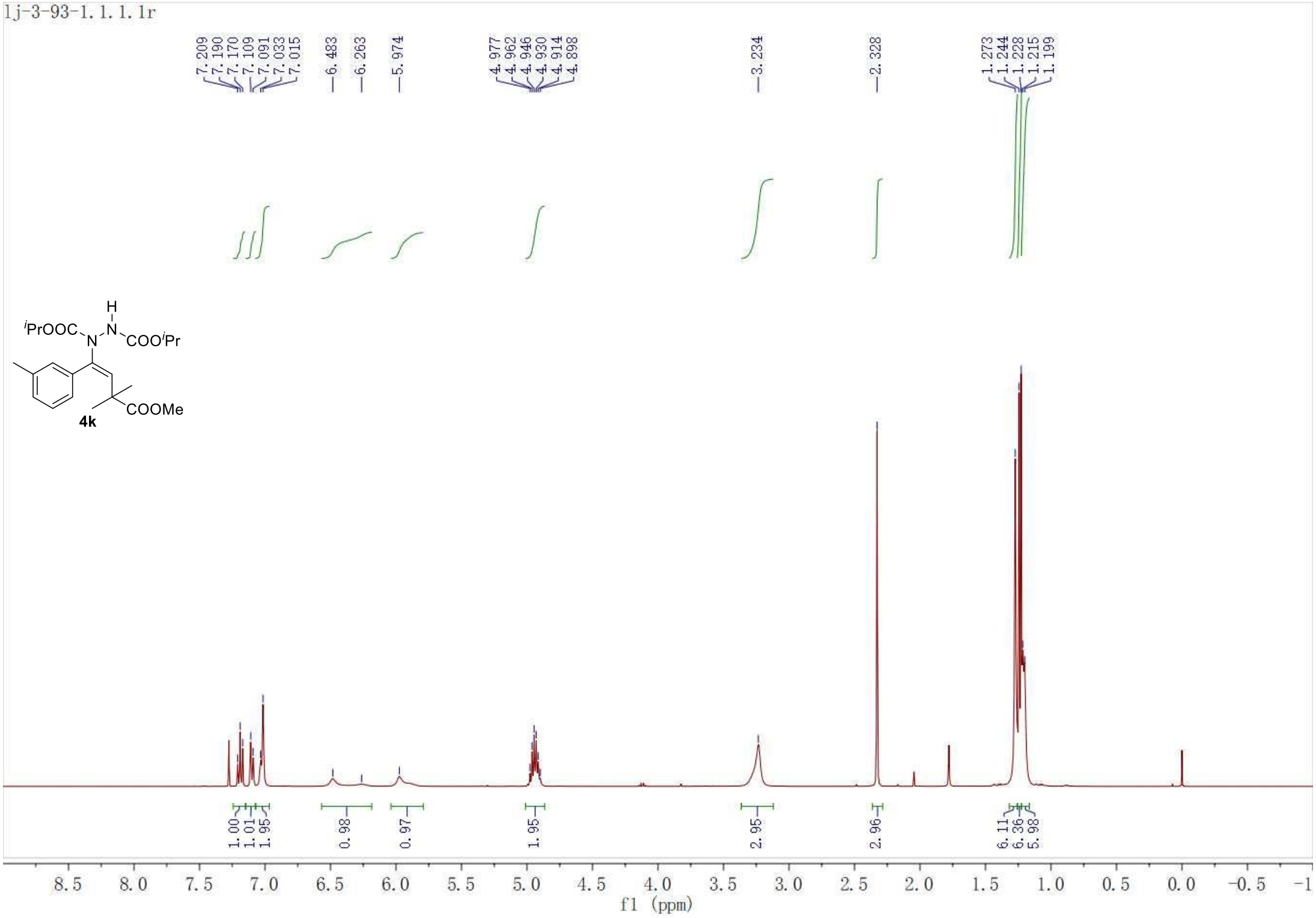

Oct26-2018-1j-2-117-1/1
175.689
155.603
154.335
139.309
136.823
134.144
130.704
130.456
130.199
130.019
127.164
125.000
124.737
124.706
124.676
124.647
122.836
120.672
77.254
77.000
76.746
70.824
70.079
51.598
42.832
27.371
21.844
21.814
H
N
N
iPrOOC
COOiPr
F3C
COOMe
4h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

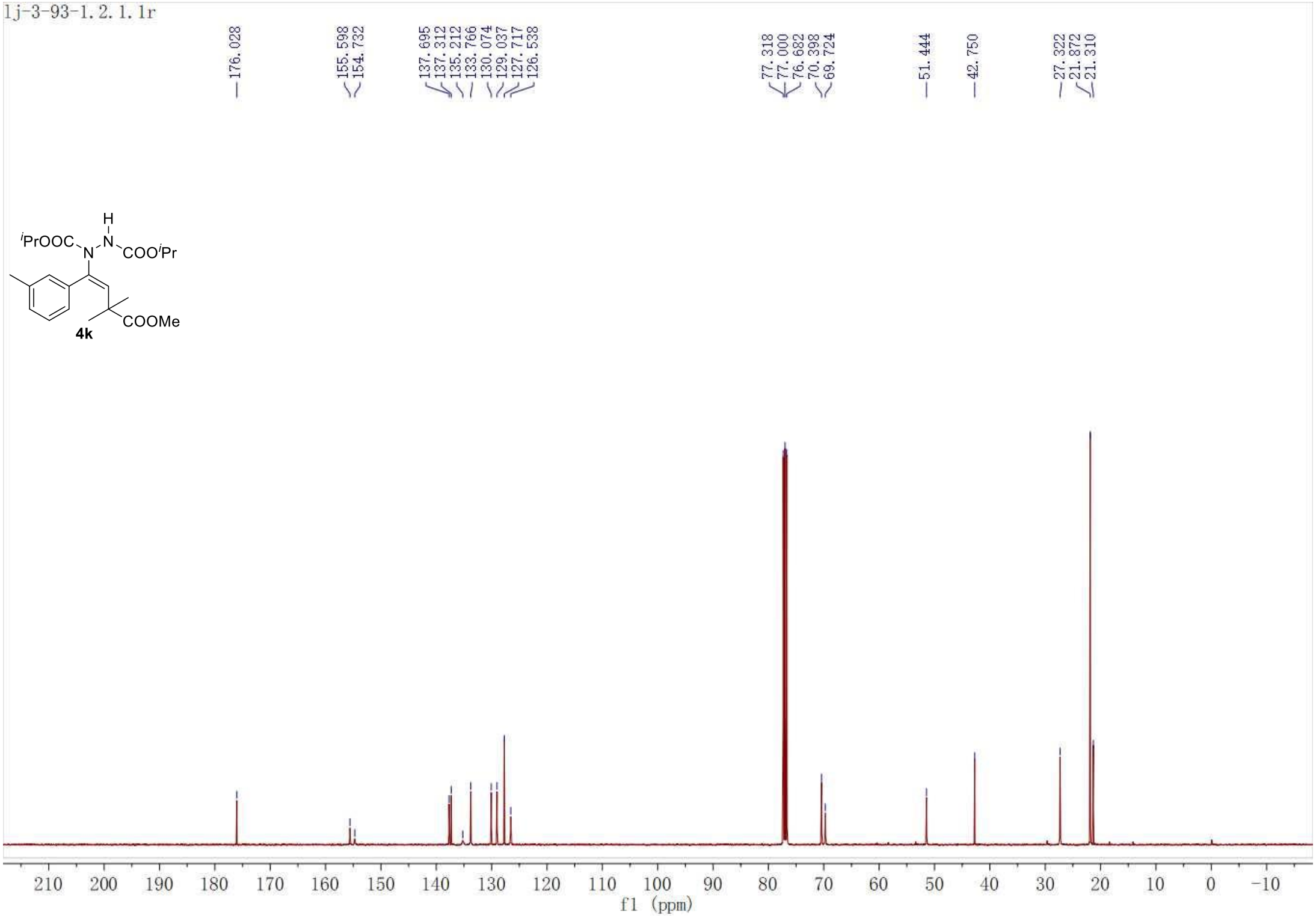

0ct20-2018-1j-2-115-1/1
7.231
7.215
7.199
6.850
6.845
6.833
6.828
6.814
6.266
5.982
4.971
4.958
4.946
4.933
4.921
4.908
3.797
3.268
1.287
1.243
1.231
1.217
1.204
0.000
H
N
N
iPrOOC
COOiPr
MeO
COOMe
4i
1.02
2.98
1.05
0.98
2.07
2.99
3.00
6.11
12.25
f1 (ppm)


Oct22-2018-1j-2-115-1/1
176.024
158.992
155.590
154.711
137.390
136.659
133.916
128.871
121.776
114.919
114.074
77.254
77.000
76.746
70.470
69.767
55.167
51.549
42.793
27.299
21.883
H
N
N
iPrOOC
COOiPr
MeO
COOMe
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

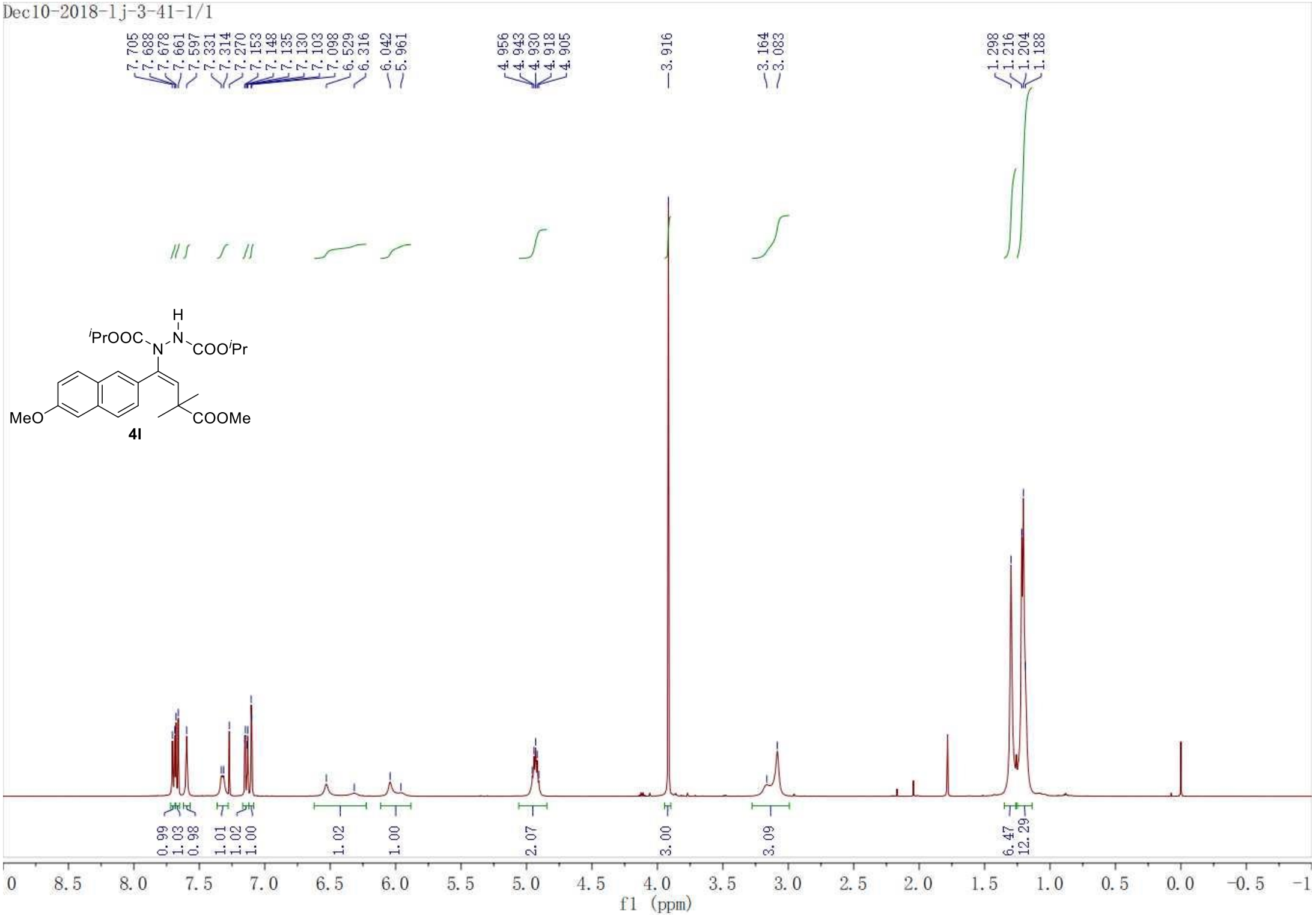

Oct11-2018-1j-2-94-1/1
7.291
7.287
7.275
7.274
7.270
7.259
7.255
7.169
7.154
6.918
6.914
6.912
6.899
6.897
6.884
6.882
6.849
6.832
6.716
6.409
6.081
5.998
4.993
4.981
4.968
4.956
4.943
4.838
3.816
3.282
3.206
1.278
1.272
1.260
1.247
1.233
1.102
1.089
-0.000
H
N
N
iPrOOC
COOiPr
COOMe
OMe
4j
1.38
0.99
1.01
0.94
1.07
0.94
1.08
0.95
3.00
2.88
18.22
f1 (ppm)


Oct13-2018-1j-2-94-1/1
175.937
156.966
155.733
154.565
136.304
133.976
132.963
129.924
123.951
119.843
110.097
77.253
77.000
76.744
70.104
69.486
55.500
51.417
42.853
27.160
21.951
21.727
H
iPrOOC
N
N
COOiPr
COOMe
OMe
4j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1j-3-93-1.1.1.1r
7.209
7.190
7.170
7.109
7.091
7.033
7.015
6.483
6.263
5.974
4.977
4.962
4.946
4.930
4.914
4.898
3.234
2.328
1.273
1.244
1.228
1.215
1.199
H
N
N
iPrOOC
COOiPr
COOMe
4k
1.00
1.01
1.95
0.98
0.97
1.95
2.95
2.96
6.11
6.36
5.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

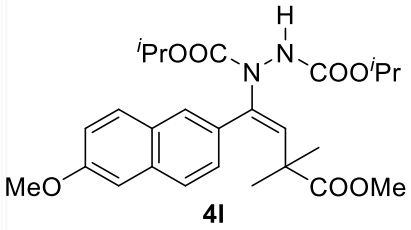

1j-3-93-1.2.1.1r
176.028
155.598
154.732
137.695
137.312
135.212
133.766
130.074
129.037
127.717
126.538
77.318
77.000
76.682
70.398
69.724
51.444
42.750
27.322
21.872
21.310
H
N
N
iPrOOC
COOiPr
COOMe
4k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Dec10-2018-1j-3-41-1/1

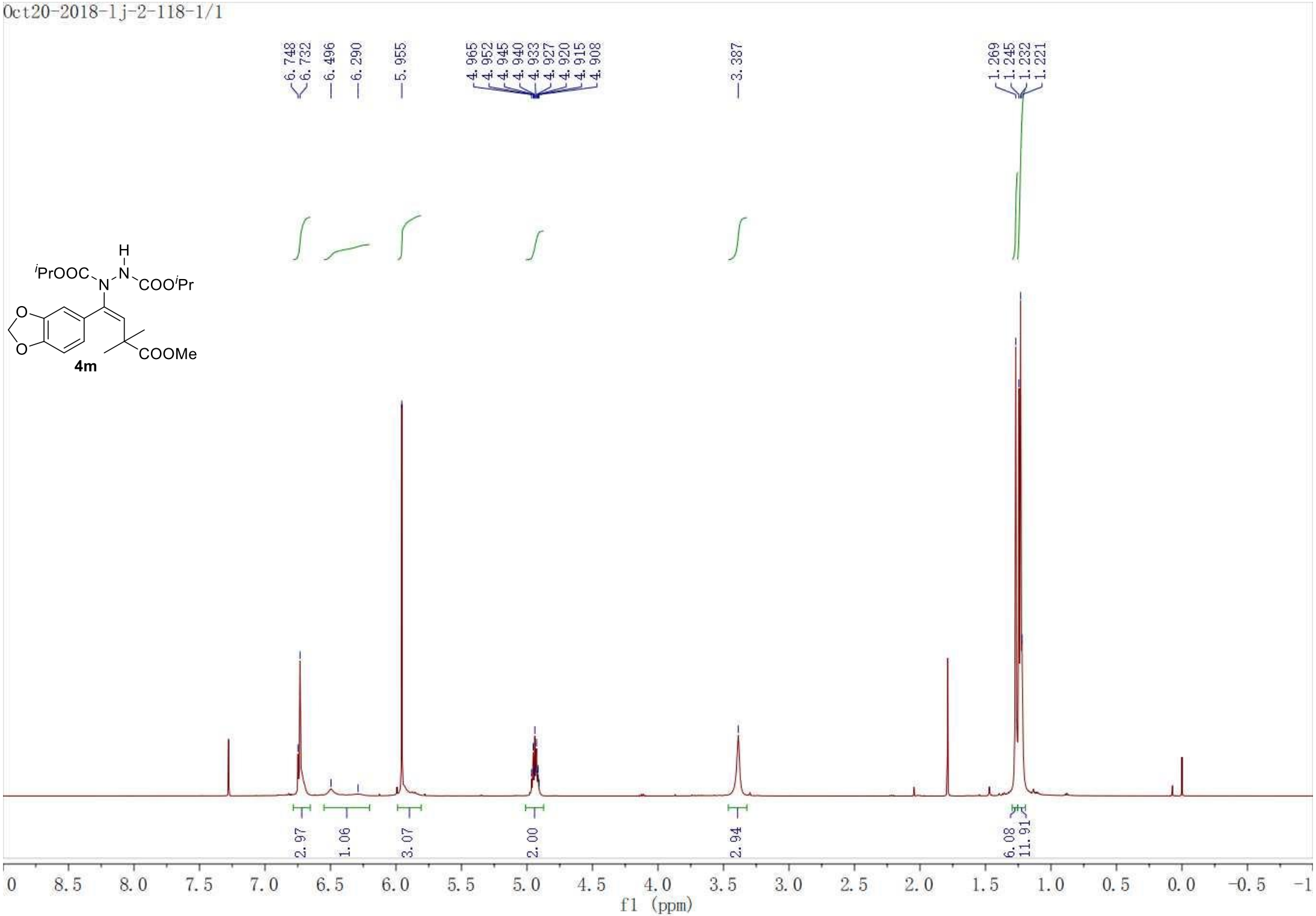


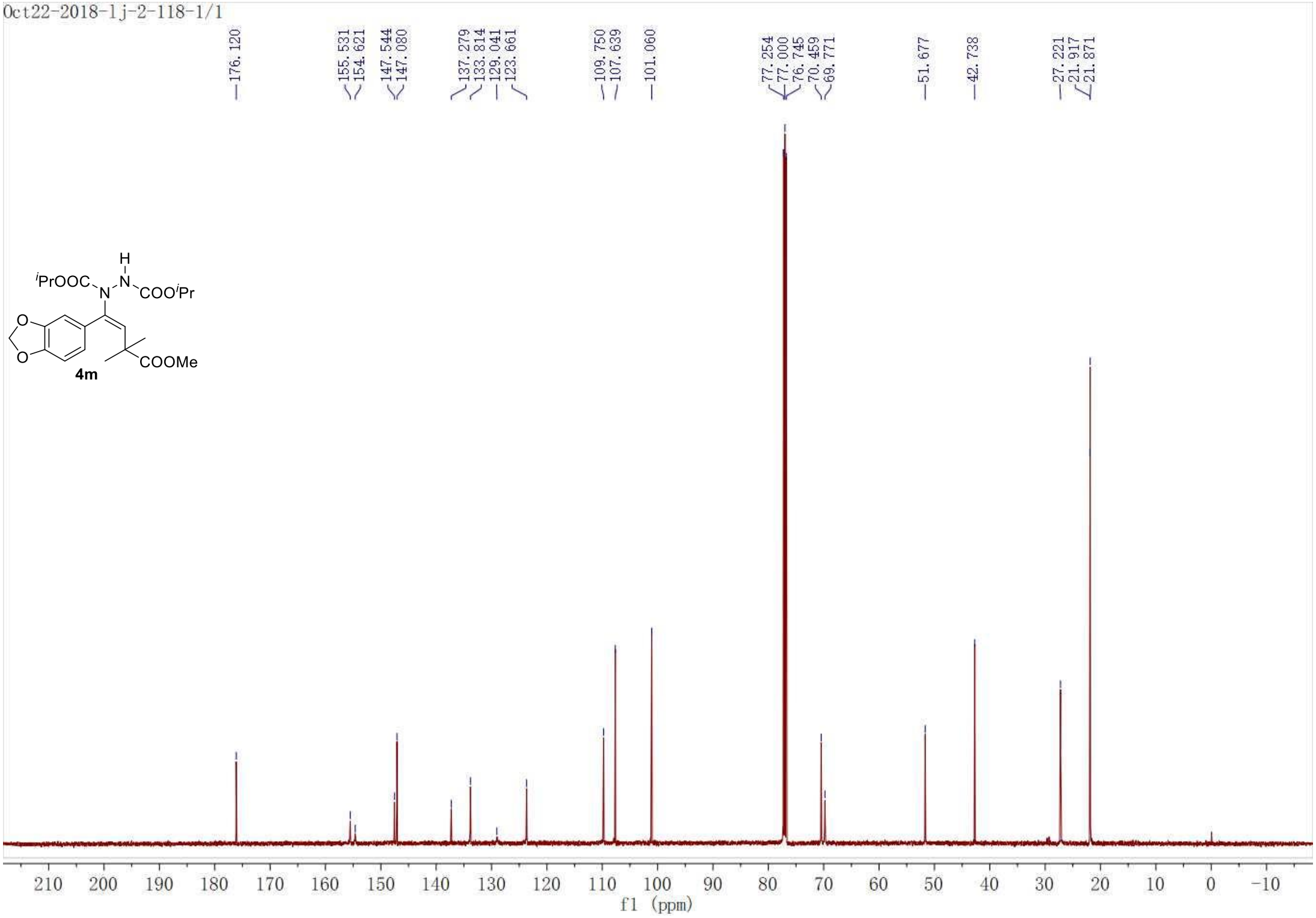
4l

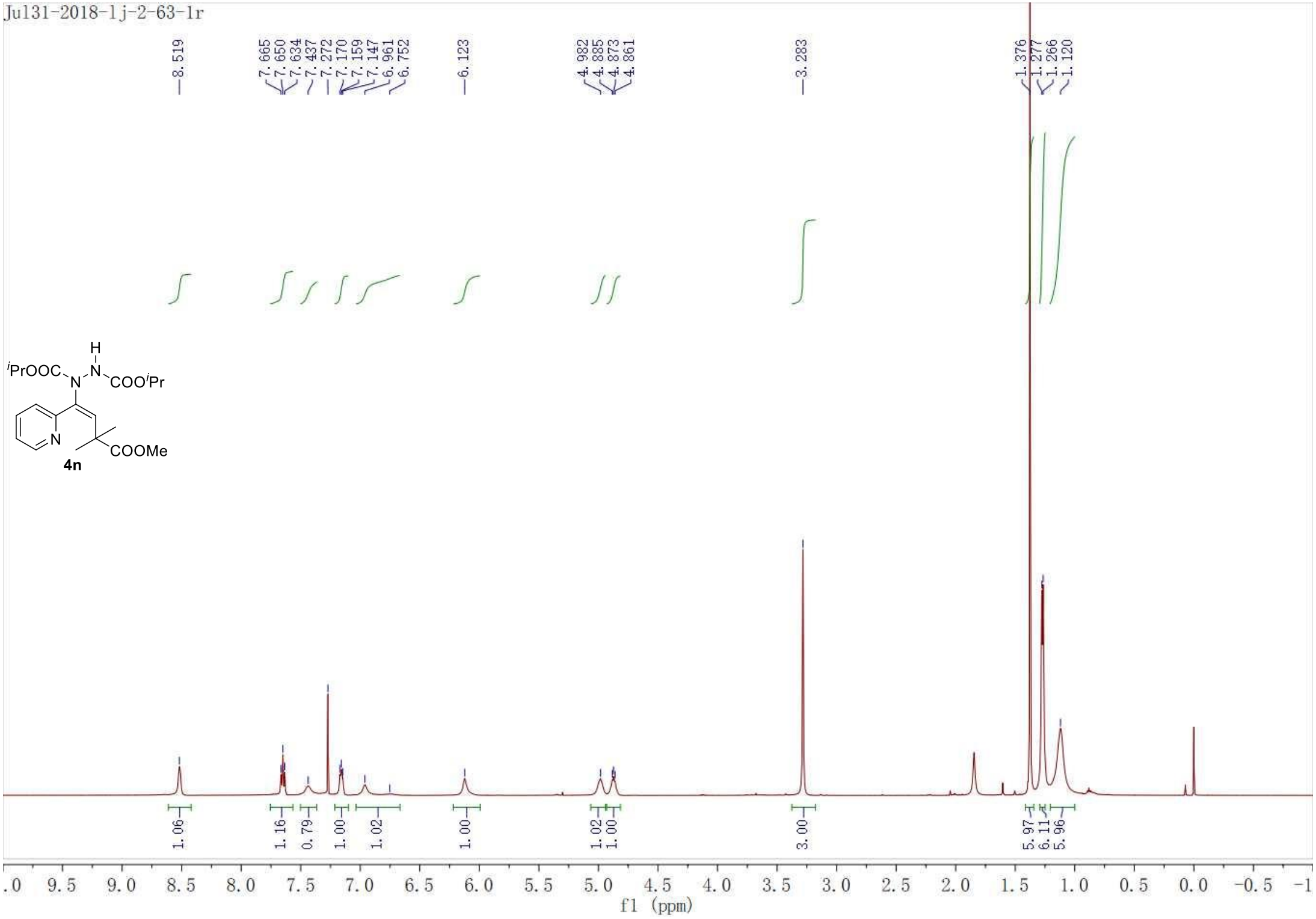
Dec12-2018-1j-3-41-1c-ok/1

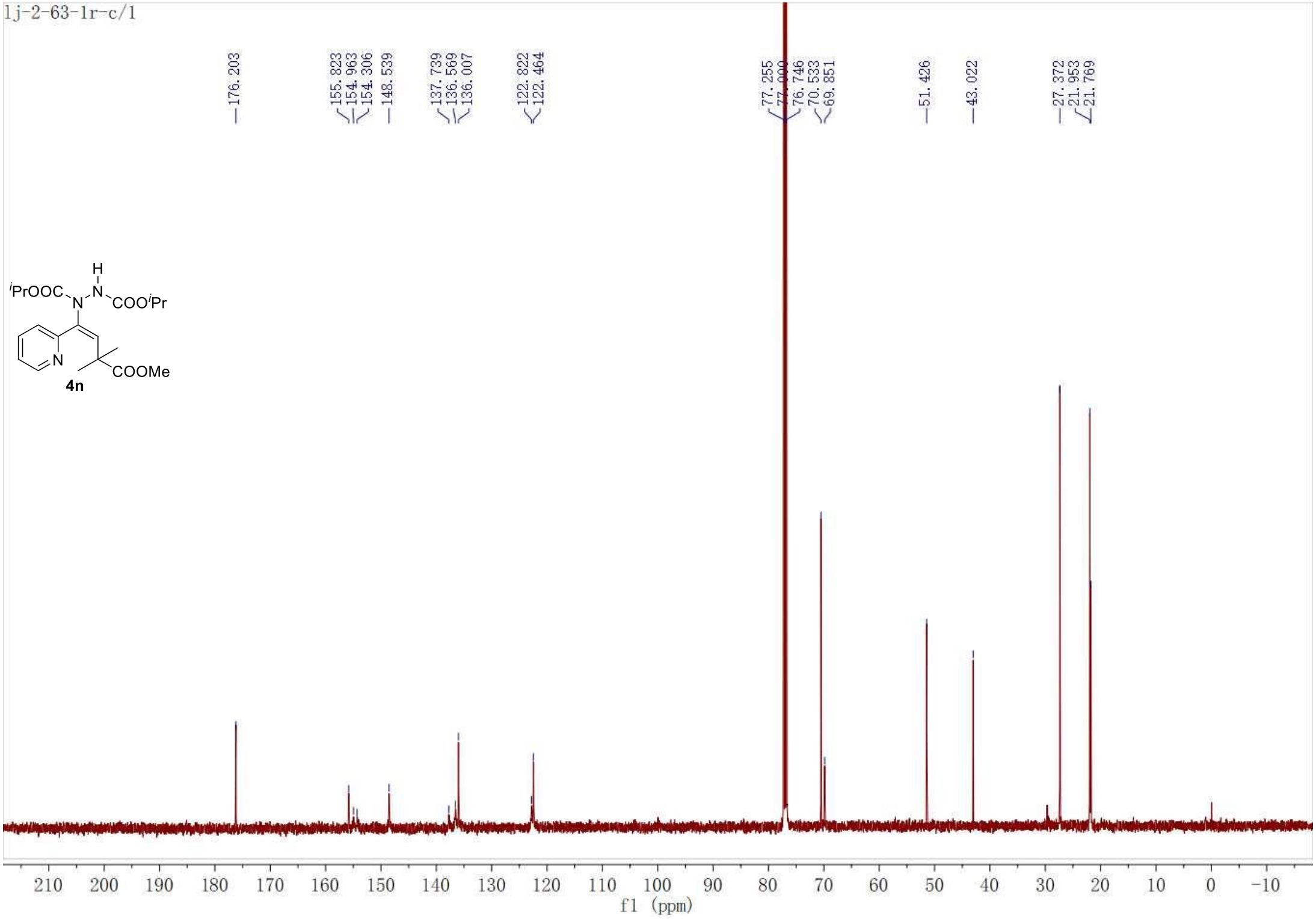


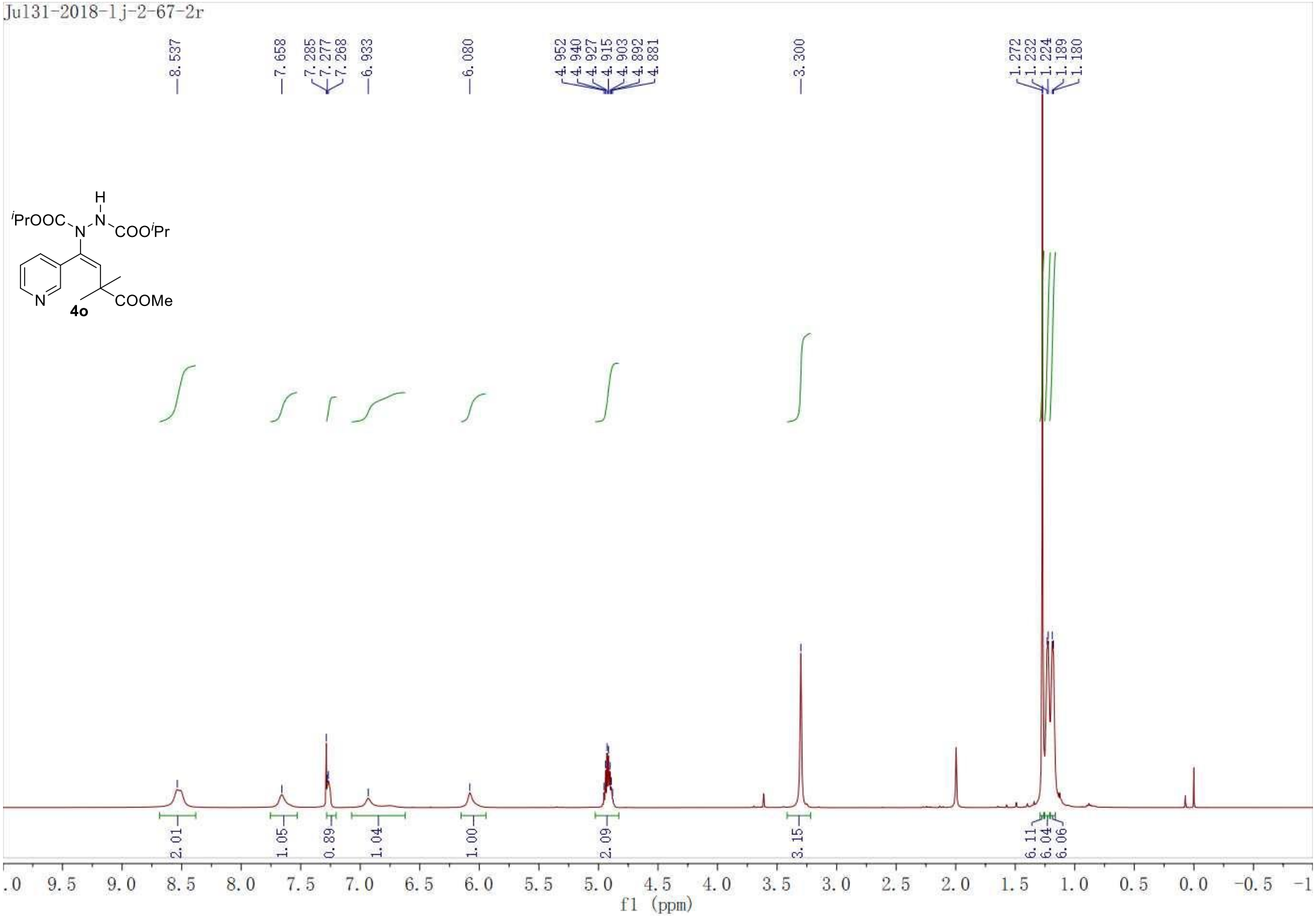
4l


Oct20-2018-1j-2-118-1/1
6.748
6.732
6.496
6.290
5.955
4.965
4.952
4.945
4.940
4.933
4.927
4.920
4.915
4.908
3.387
1.269
1.245
1.232
1.221
H
N
N
iPrOOC
COOiPr
O
O
COOMe
4m
2.97
1.06
3.07
2.00
2.94
6.08
11.91
f1 (ppm)

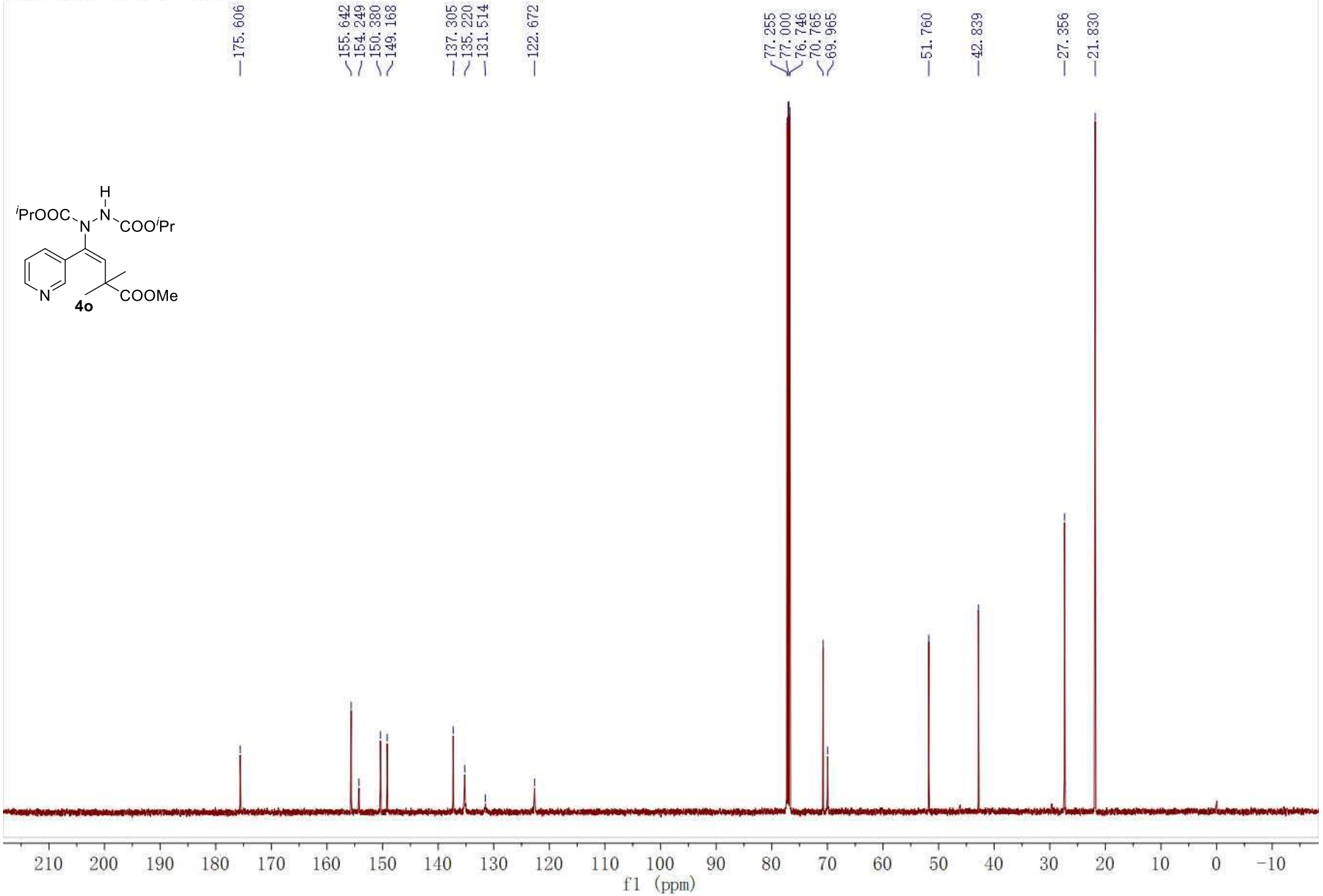

Oct22-2018-1j-2-118-1/1
176.120
155.531
154.621
147.544
147.080
137.279
133.814
129.041
123.661
109.750
107.639
101.060
77.254
77.000
76.745
70.459
69.771
51.677
42.738
27.221
21.917
21.871
H
N
N
iPrOOC
COOiPr
O
O
COOMe
4m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

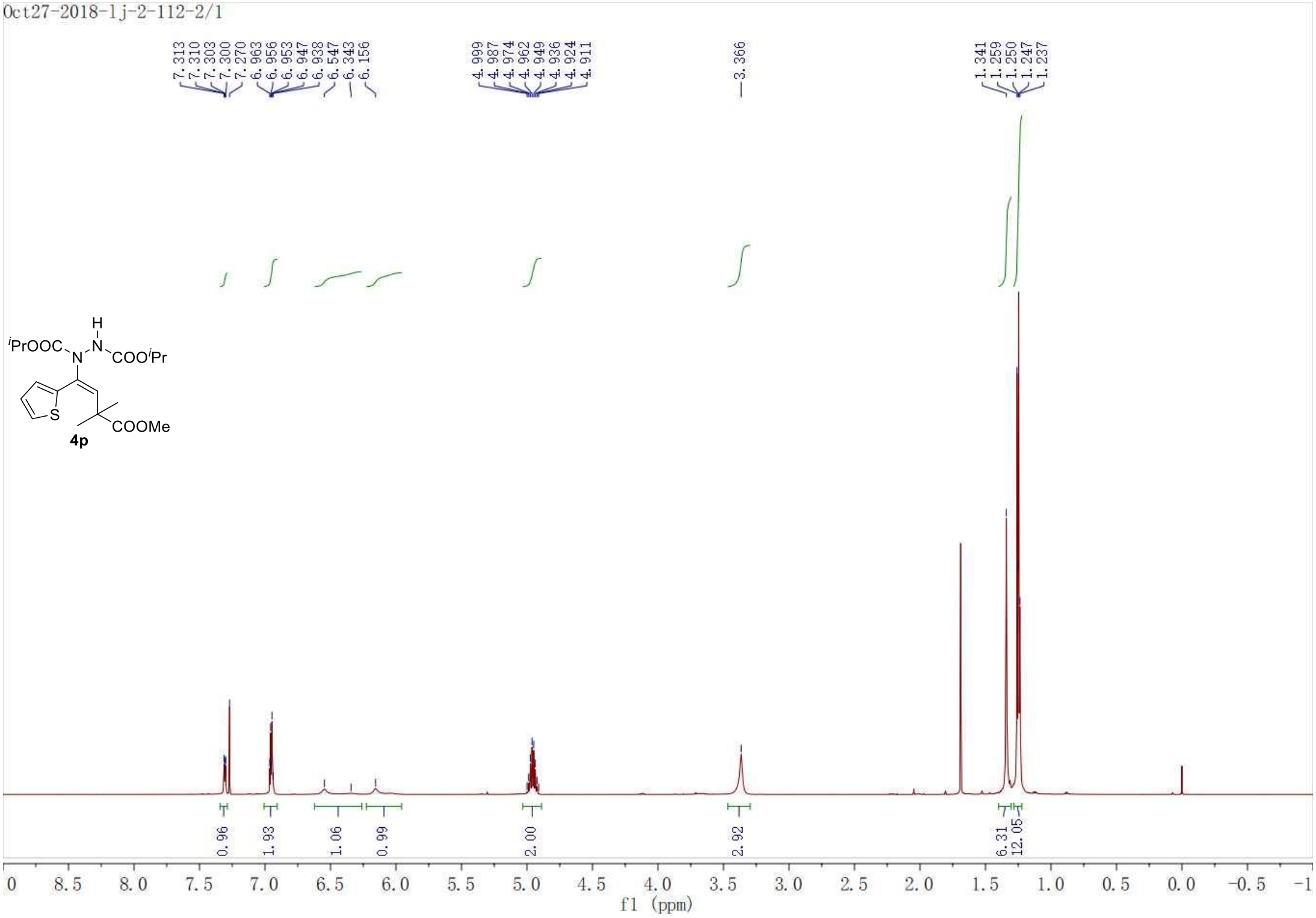

Jul31-2018-1j-2-63-1r
8.519
7.665
7.650
7.634
7.437
7.272
7.170
7.159
7.147
6.961
6.752
6.123
4.982
4.885
4.873
4.861
3.283
1.376
1.277
1.266
1.120
iPrOOC
N
H
N
COOiPr
N
COOMe
4n
1.06
1.16
0.79
1.00
1.02
1.00
1.02
1.00
3.00
5.97
6.11
5.96
f1 (ppm)

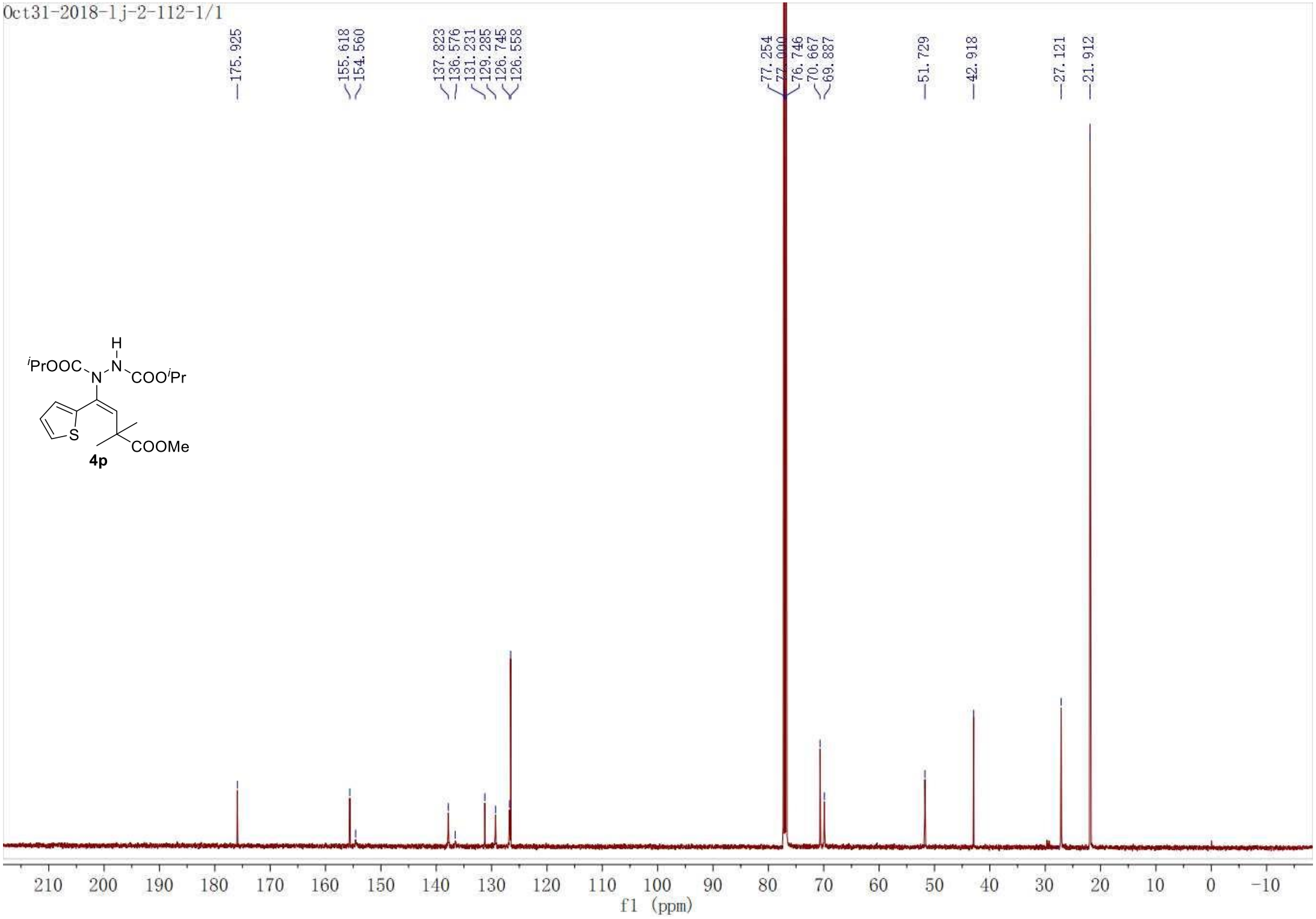

1j-2-63-1r-c/1
176.203
155.823
154.963
154.306
148.539
137.739
136.569
136.007
122.822
122.464
77.255
77.000
76.746
70.533
69.851
51.426
43.022
27.372
21.953
21.769
iPrOOC
N
H
N
COOiPr
N
COOMe
4n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Jul31-2018-1j-2-67-2r
8.537
7.658
7.285
7.277
7.268
6.933
6.080
4.952
4.940
4.927
4.915
4.903
4.892
4.881
3.300
1.272
1.232
1.224
1.189
1.180
iPrOOC
N
H
N
COOiPr
N
COOMe
4o
2.01
1.05
0.89
1.04
1.00
2.09
3.15
6.11
6.04
6.06
f1 (ppm)

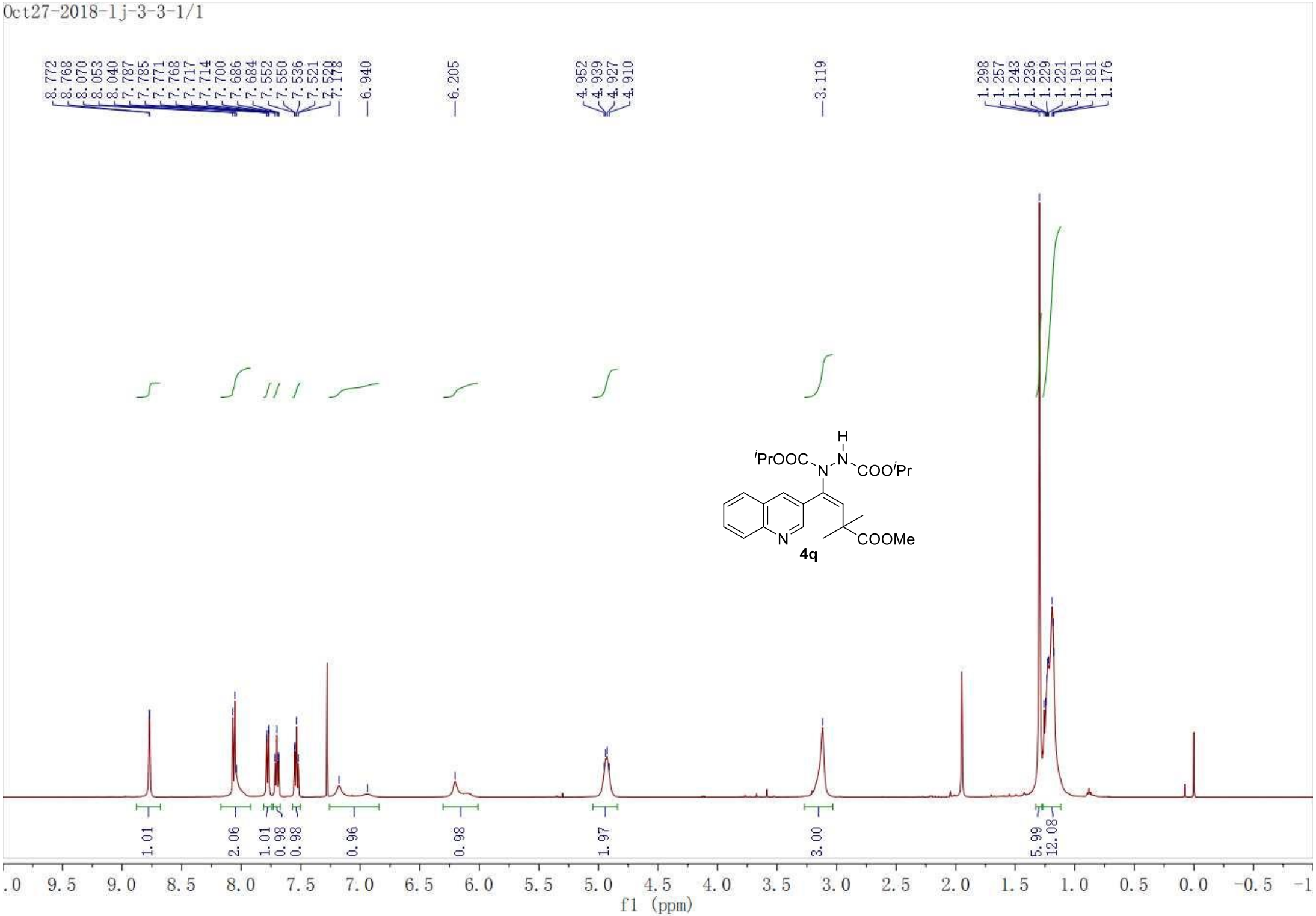
Aug02-2018-1j-2-67-2r/1



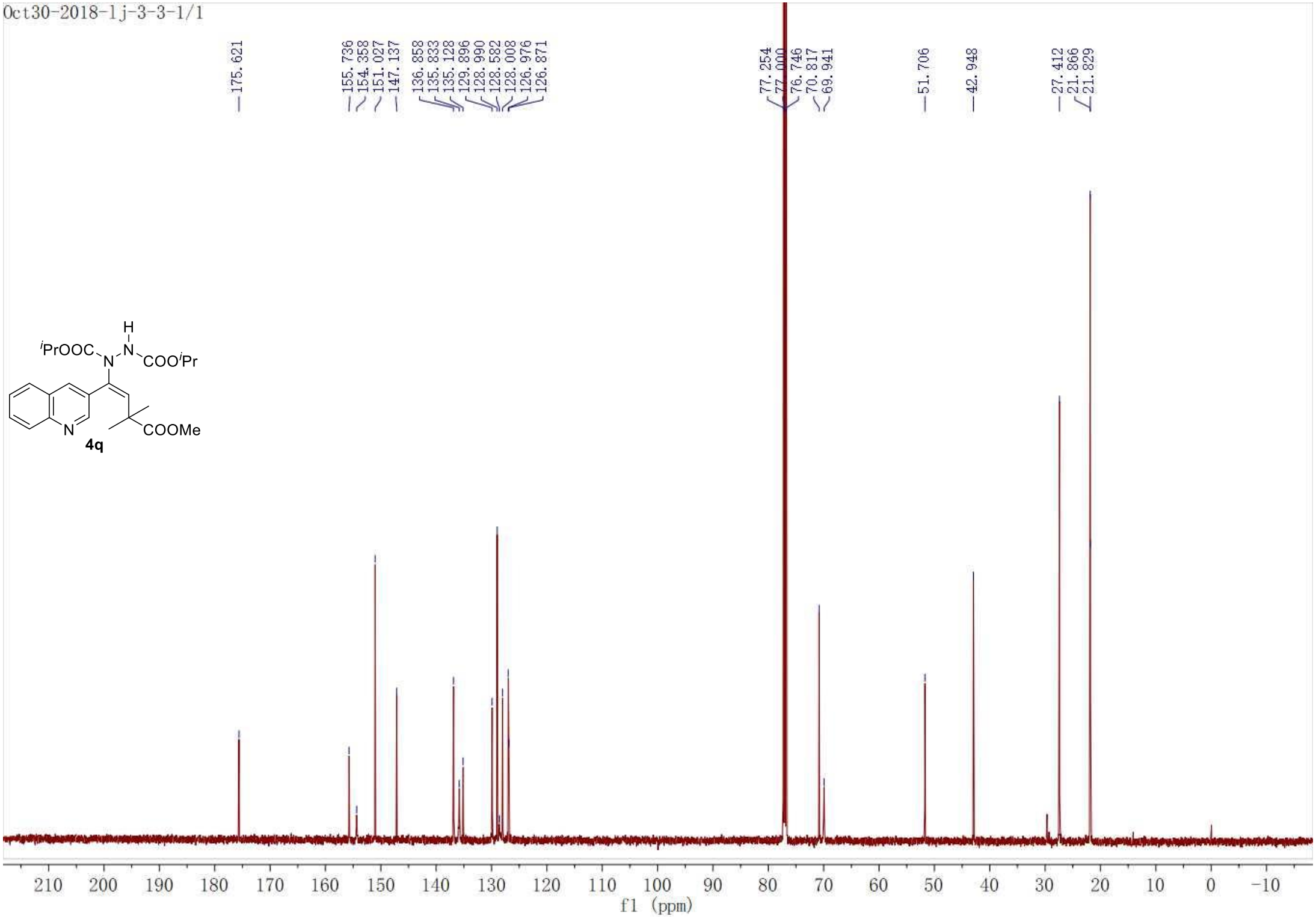

Oct27-2018-1j-2-112-2/1
7.313
7.310
7.303
7.300
7.270
6.963
6.956
6.953
6.947
6.938
6.547
6.343
6.156
4.999
4.987
4.974
4.962
4.949
4.936
4.924
4.911
3.366
1.341
1.259
1.250
1.247
1.237
H
iPrOOC
N
N
COOiPr
S
COOMe
4p
0.96
1.93
1.06
0.99
2.00
2.92
6.31
12.05
f1 (ppm)

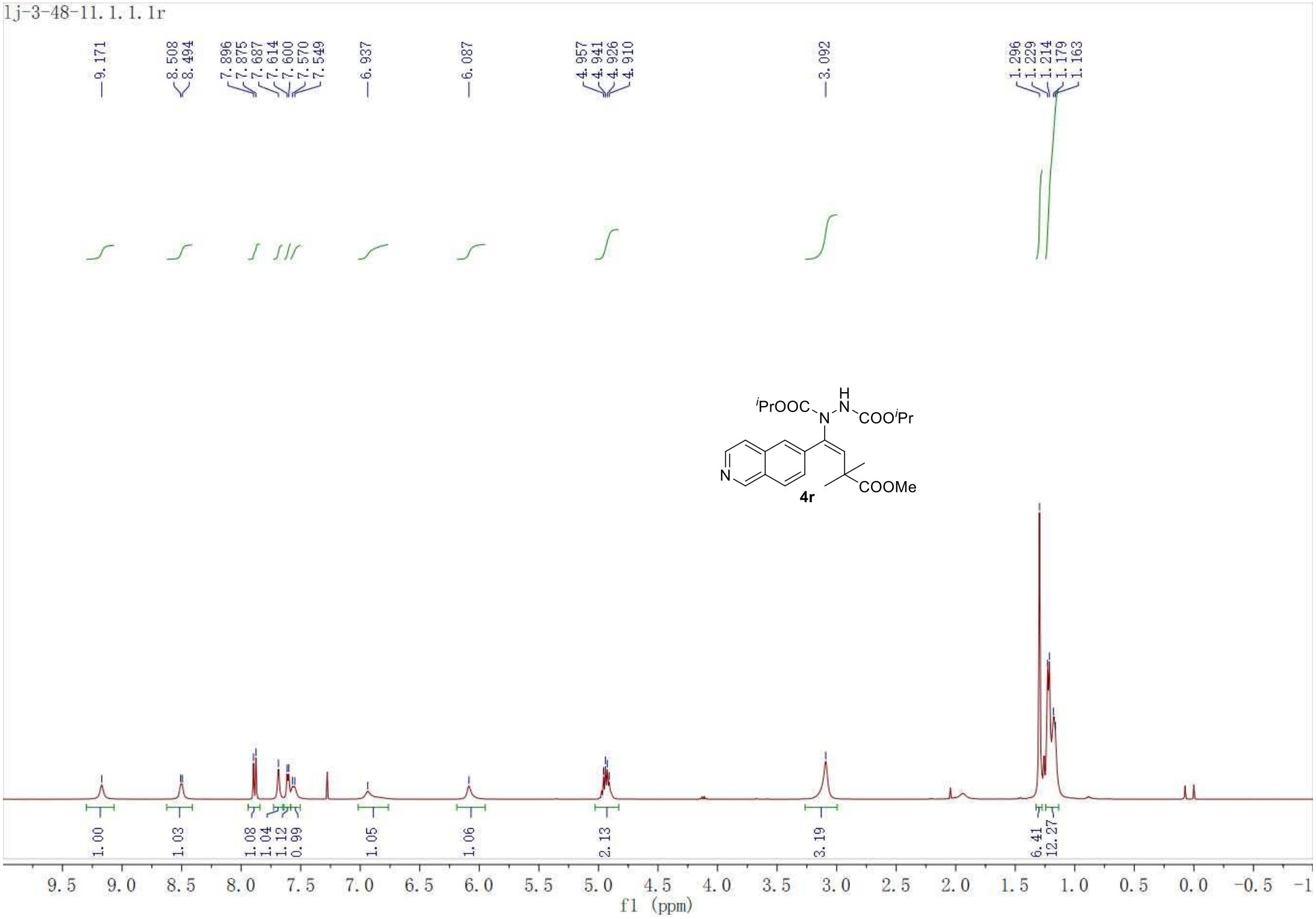

Oct31-2018-1j-2-112-1/1
175.925
155.618
154.560
137.823
136.576
131.231
129.285
126.745
126.558
77.254
77.000
76.746
70.667
69.887
51.729
42.918
27.121
21.912
H
N
N
iPrOOC
COOiPr
S
COOMe
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

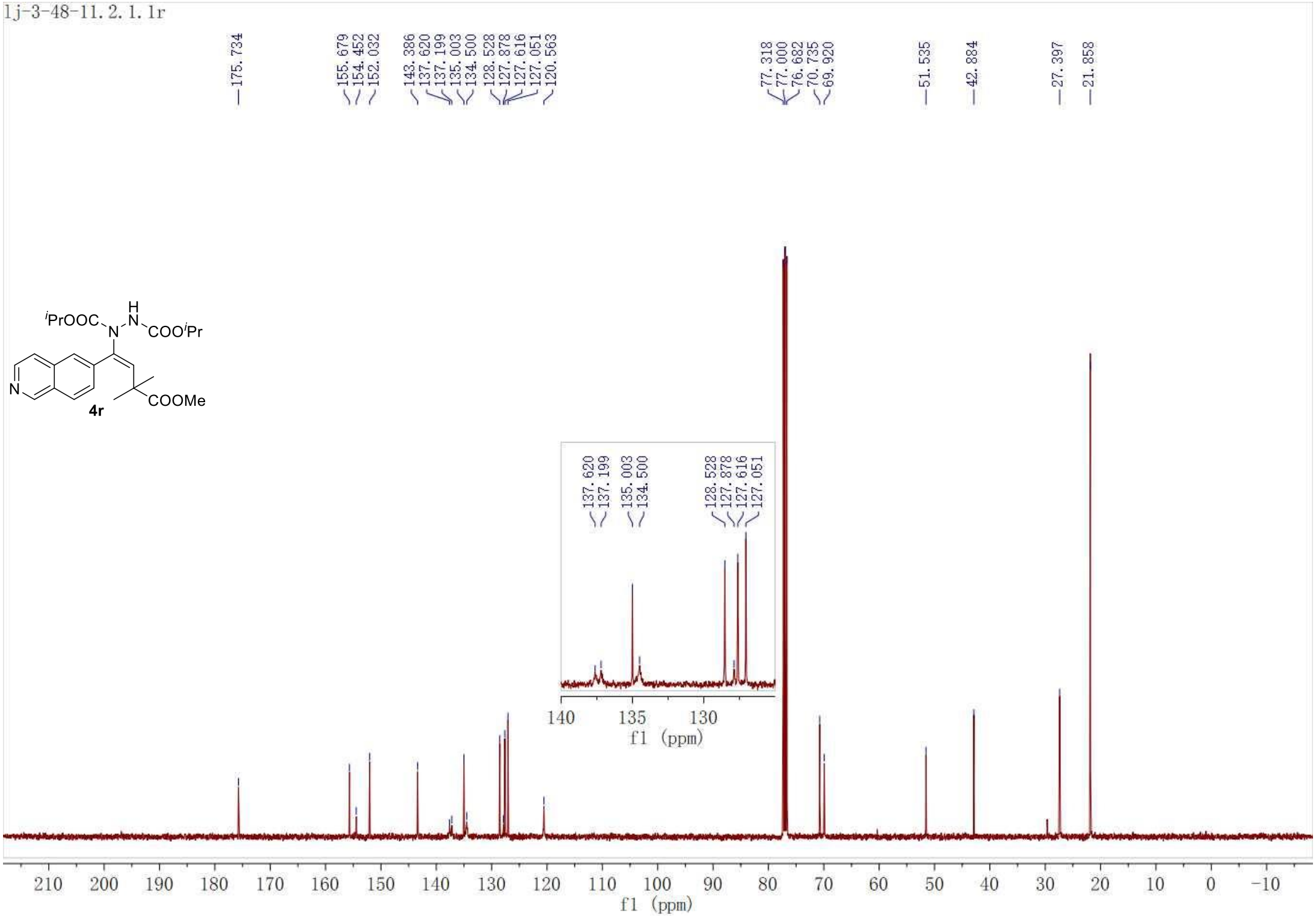
Oct27-2018-1j-3-3-1/1

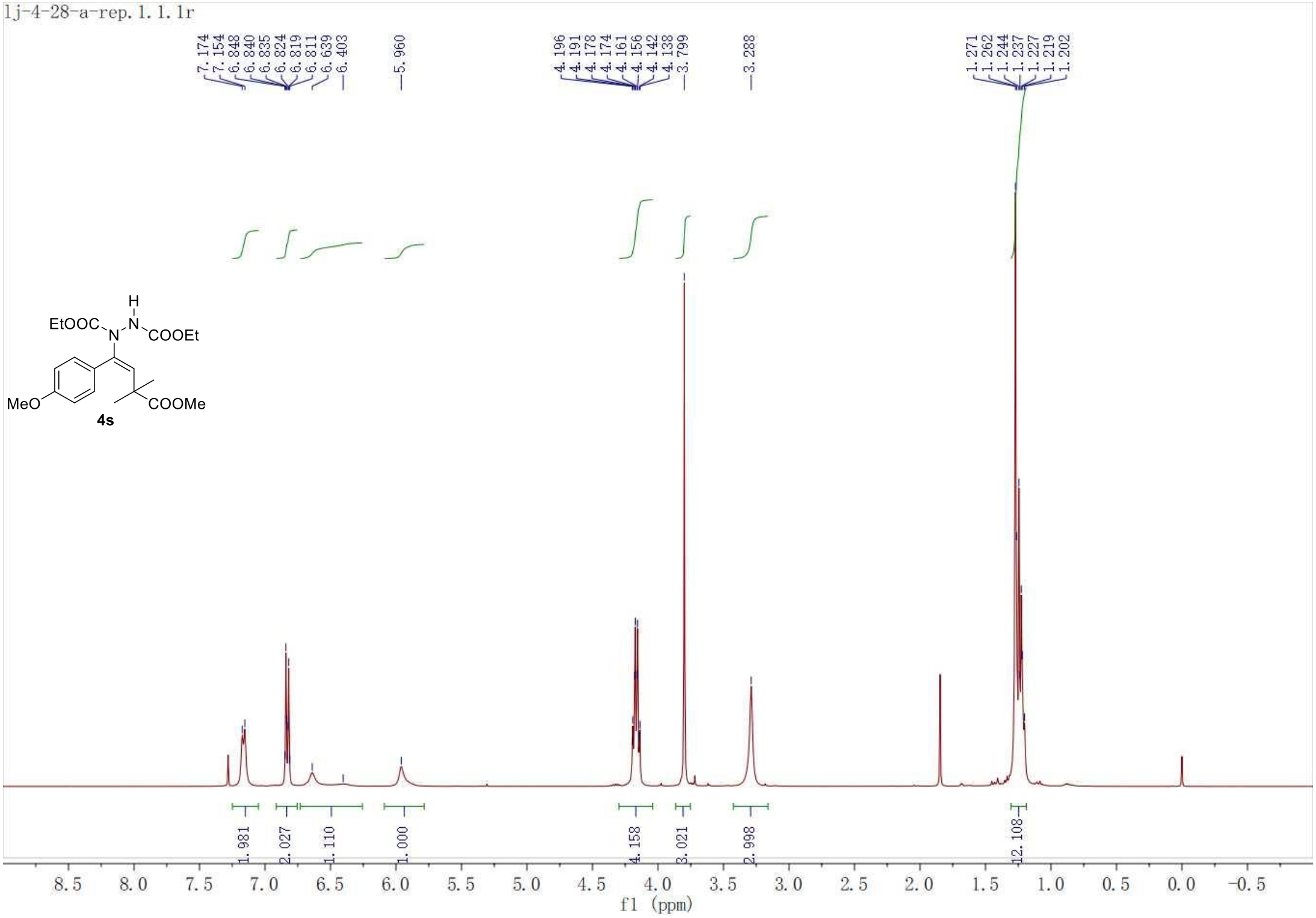


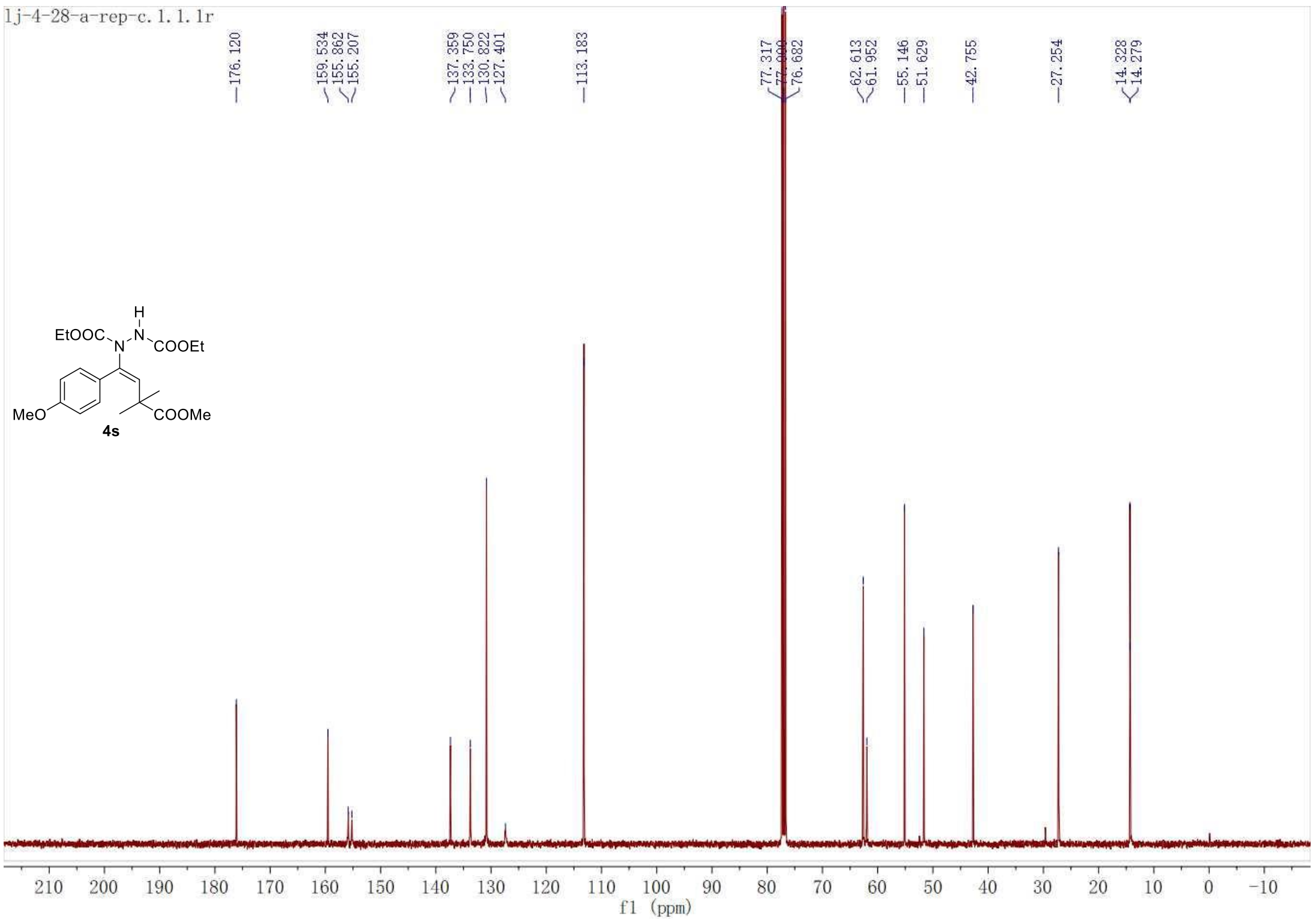
4q


Oct30-2018-1j-3-3-1/1
175.621
155.736
154.358
151.027
147.137
136.858
135.833
135.128
129.896
128.990
128.582
128.008
126.976
126.871
77.254
77.000
76.746
70.817
69.941
51.706
42.948
27.412
21.866
21.829
H
N
N
iPrOOC
COOiPr
N
COOMe
4q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

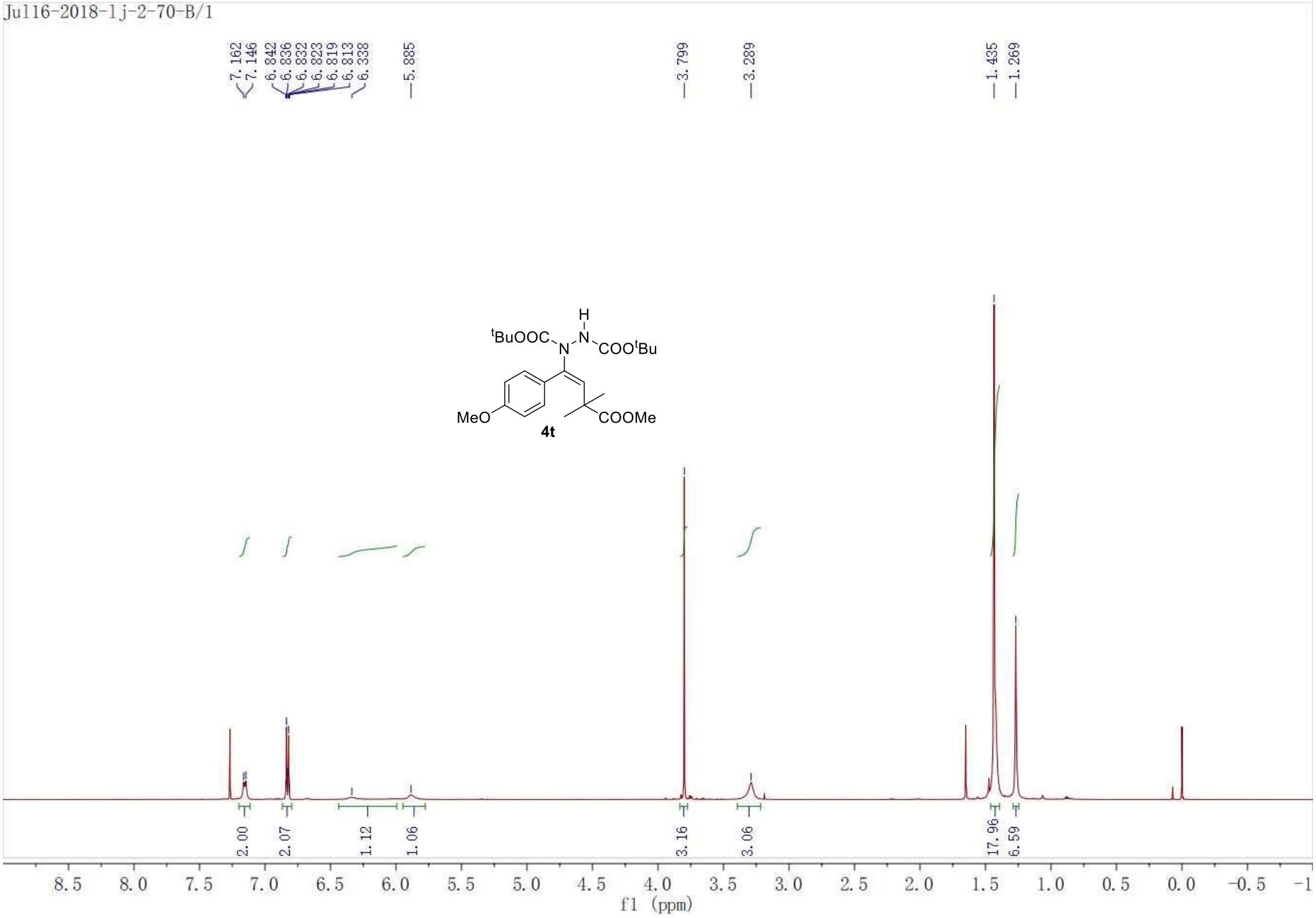

1j-3-48-11.1.1.1r
9.171
8.508
8.494
7.896
7.875
7.687
7.614
7.600
7.570
7.549
6.937
6.087
4.957
4.941
4.926
4.910
3.092
1.296
1.229
1.214
1.179
1.163
iPrOOC
N
H
N
COOiPr
N
COOMe
4r
1.00
1.03
1.08
1.04
1.12
0.99
1.05
1.06
2.13
3.19
6.41
12.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

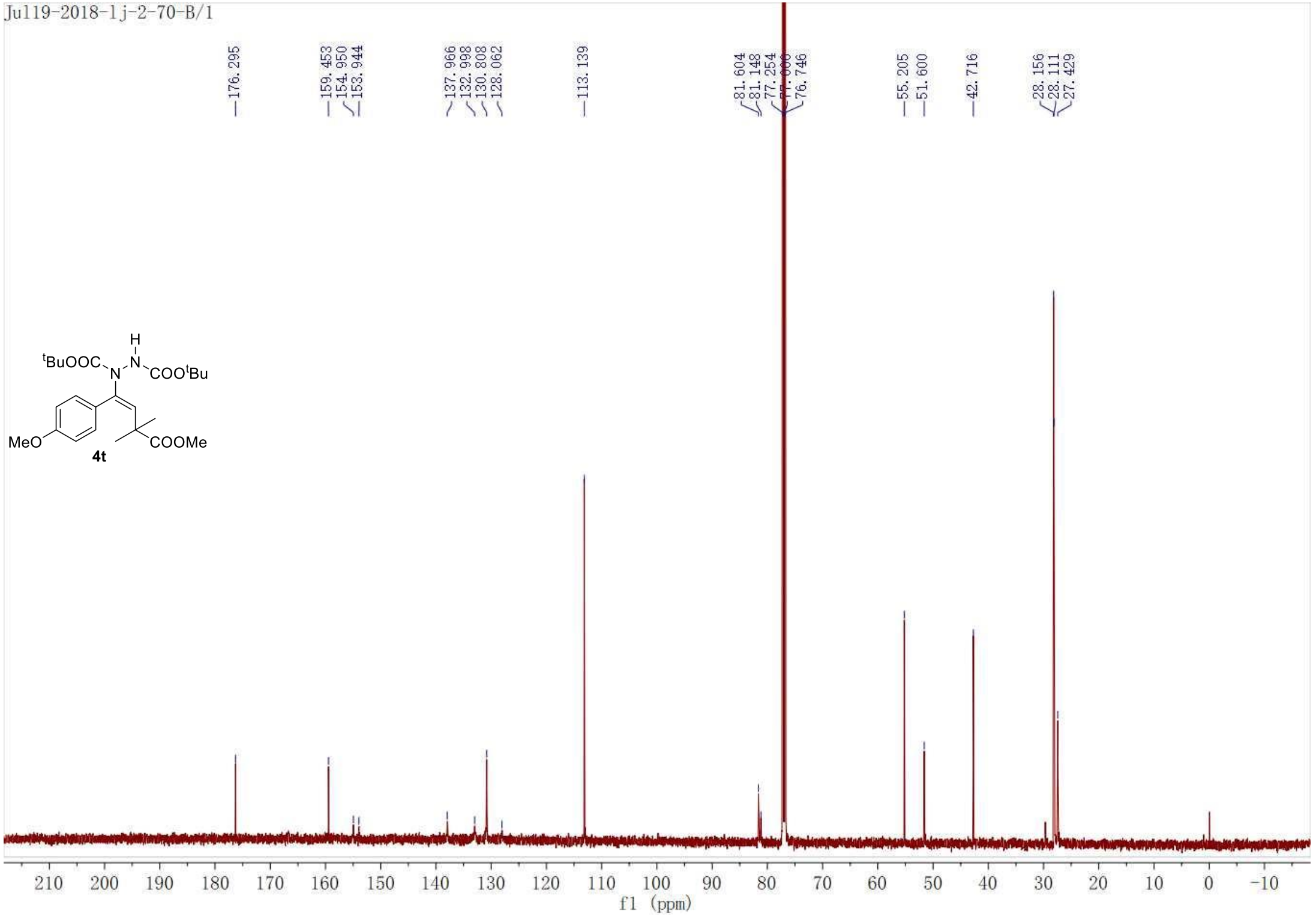

1j-3-48-11.2.1.1r
175.734
155.679
154.452
152.032
143.386
137.620
137.199
135.003
134.500
128.528
127.878
127.616
127.051
120.563
77.318
77.000
76.682
70.735
69.920
51.535
42.884
27.397
21.858
iPrOOC
N
H
N
COOiPr
N
COOMe
4r
137.620
137.199
135.003
134.500
128.528
127.878
127.616
127.051
140
135
130
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


1j-4-28-a-rep.1.1.1r
7.174
7.154
6.848
6.840
6.835
6.824
6.819
6.811
6.639
6.403
5.960
4.196
4.191
4.178
4.174
4.161
4.156
4.142
4.138
3.799
3.288
1.271
1.262
1.244
1.237
1.227
1.219
1.202
EtOOC
N
H
N
COOEt
MeO
COOMe
4s
1.981
2.027
1.110
1.000
4.158
3.021
2.998
12.108
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

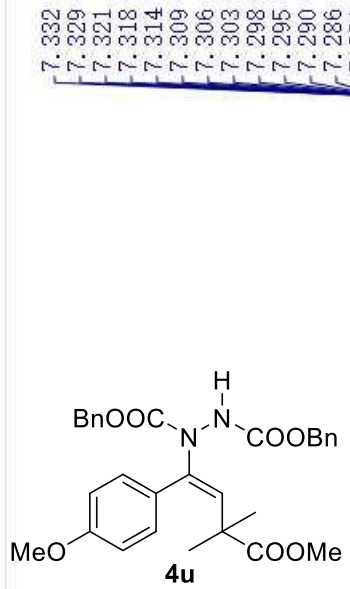

lj-4-28-a-rep-c.1.1.1r
176.120
159.534
155.862
155.207
137.359
133.750
130.822
127.401
113.183
77.317
77.000
76.682
62.613
61.952
55.146
51.629
42.755
27.254
14.328
14.279
EtOOC
N
H
N
COOEt
MeO
COOMe
4s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Jul16-2018-1j-2-70-B/1



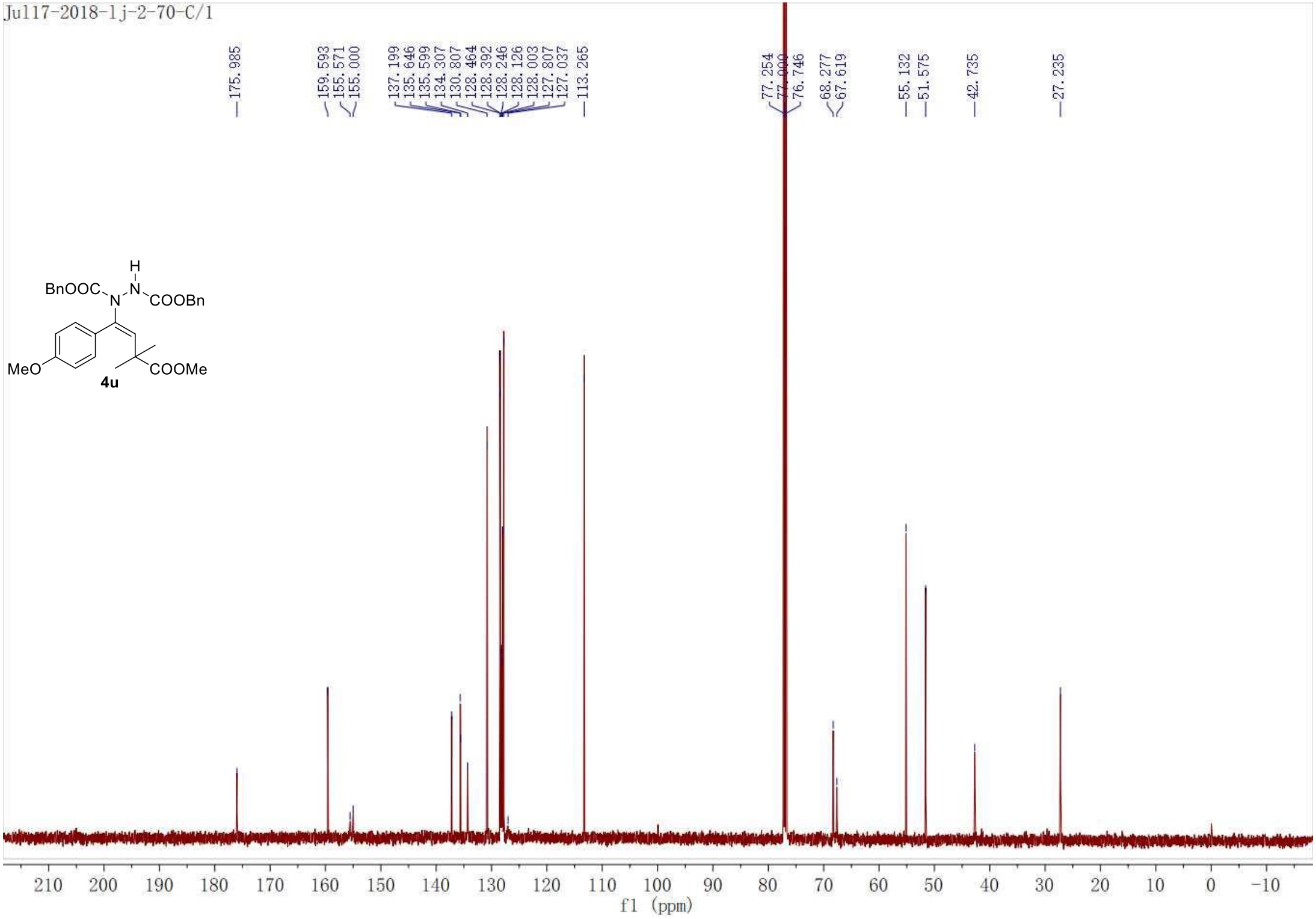

Jul19-2018-1j-2-70-B/1
176.295
159.453
154.950
153.944
137.966
132.998
130.808
128.062
113.139
81.604
81.148
77.254
77.000
76.746
55.205
51.600
42.716
28.156
28.111
27.429
H
tBuOOC
N
N
COOtBu
MeO
COOMe
4t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Jul16-2018-1j-2-70-C/1

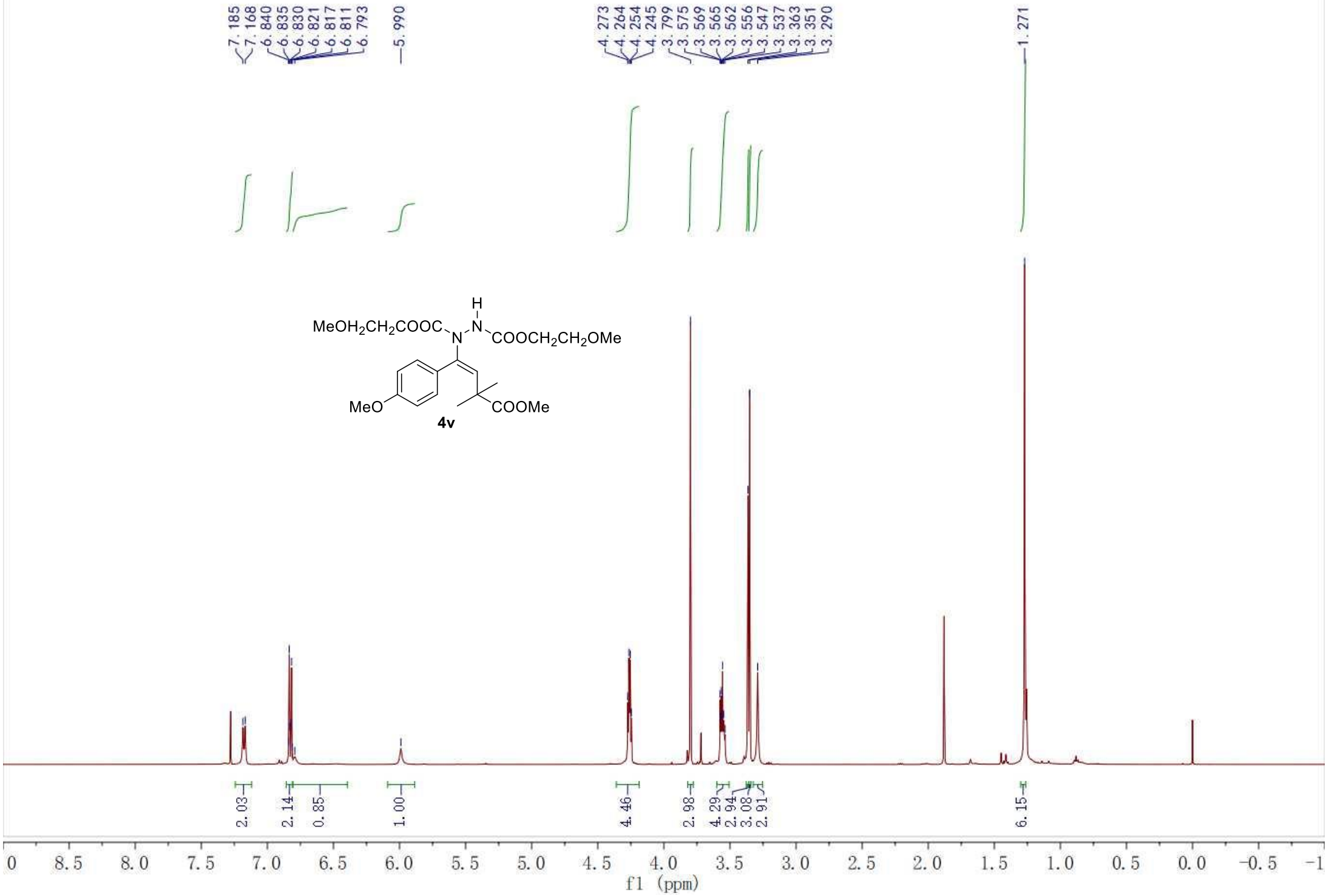


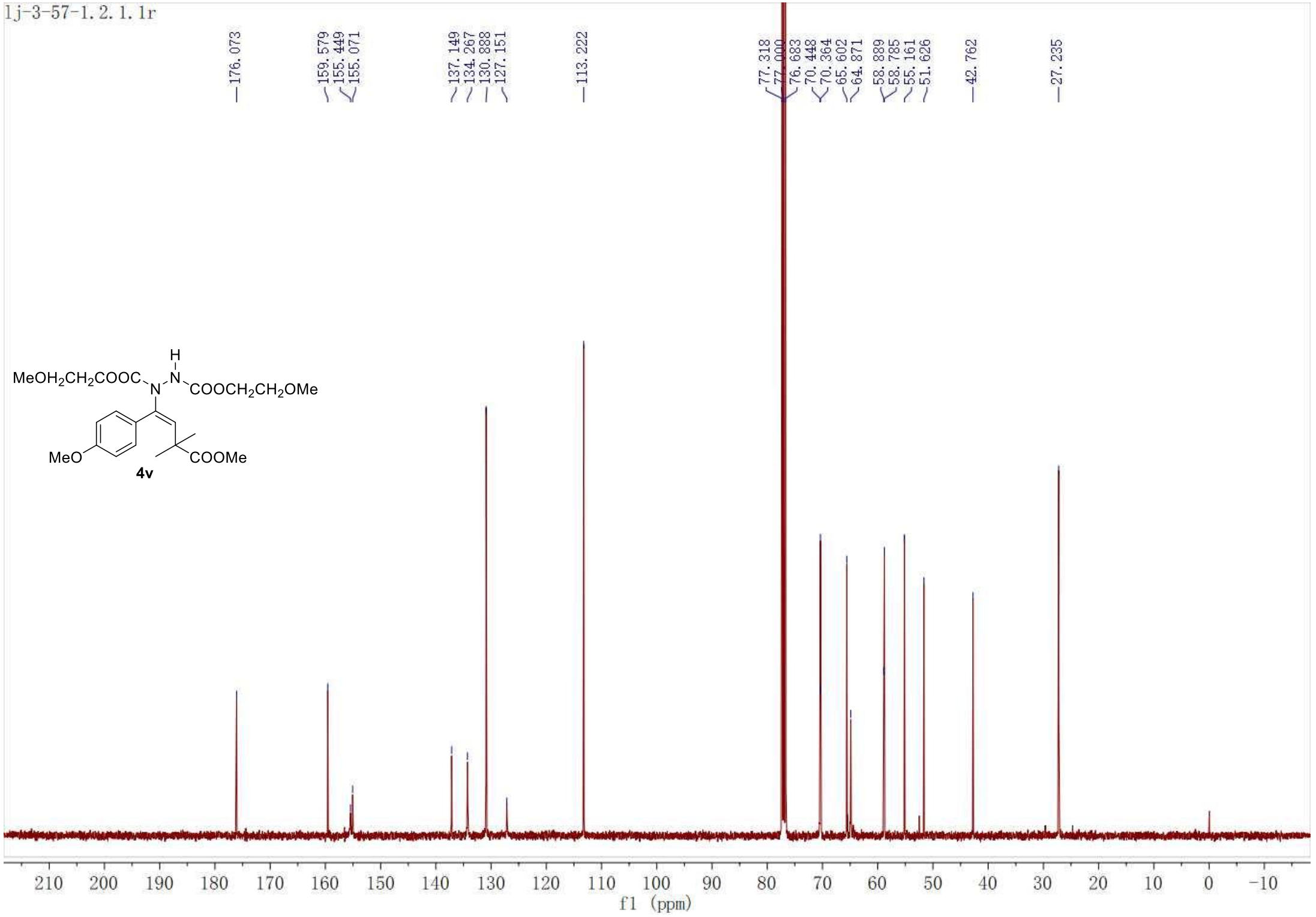
4u

f1 (ppm)

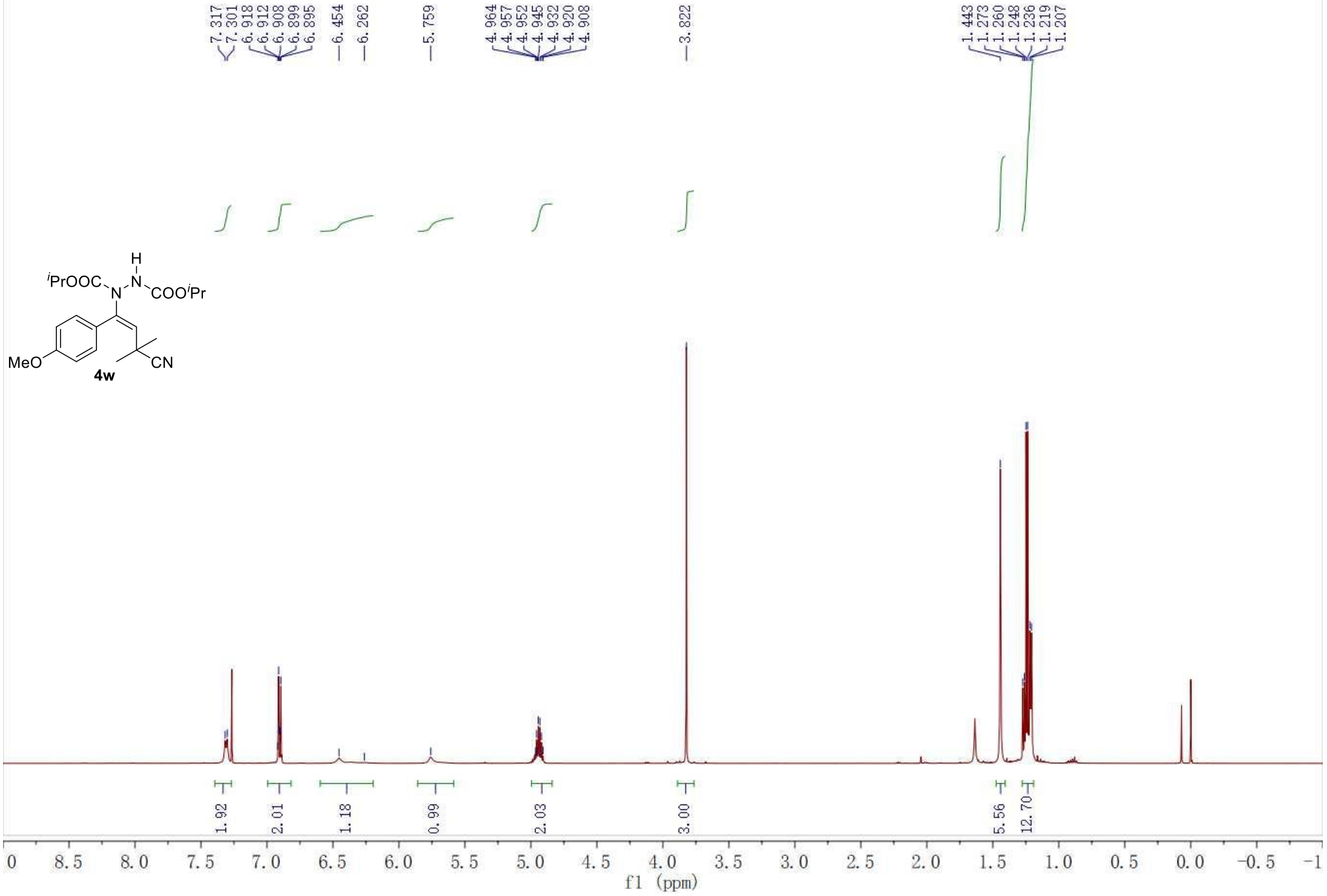

Jul17-2018-1j-2-70-C/1
175.985
159.593
155.571
155.000
137.199
135.646
135.599
134.307
130.807
128.464
128.392
128.246
128.126
128.003
127.807
127.037
113.265
77.254
77.000
76.746
68.277
67.619
55.132
51.575
42.735
27.235
BnOOC
N
H
N
COOBn
MeO
COOMe
4u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Sep08-2018-1j-2-84-2/1

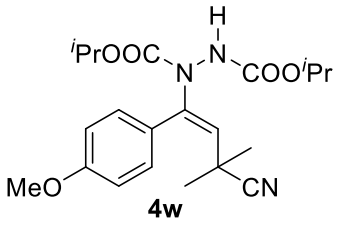



1j-3-57-1.2.1.1r
176.073
159.579
155.449
155.071
137.149
134.267
130.888
127.151
113.222
77.318
77.000
76.683
70.448
70.364
65.602
64.871
58.889
58.785
55.161
51.626
42.762
27.235
MeOH2CH2COOC
N
H
N
COOCH2CH2OMe
MeO
COOMe
4v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Sep08-2018-1j-2-85-1/1



Sep09-2018-1j-2-85-1/1



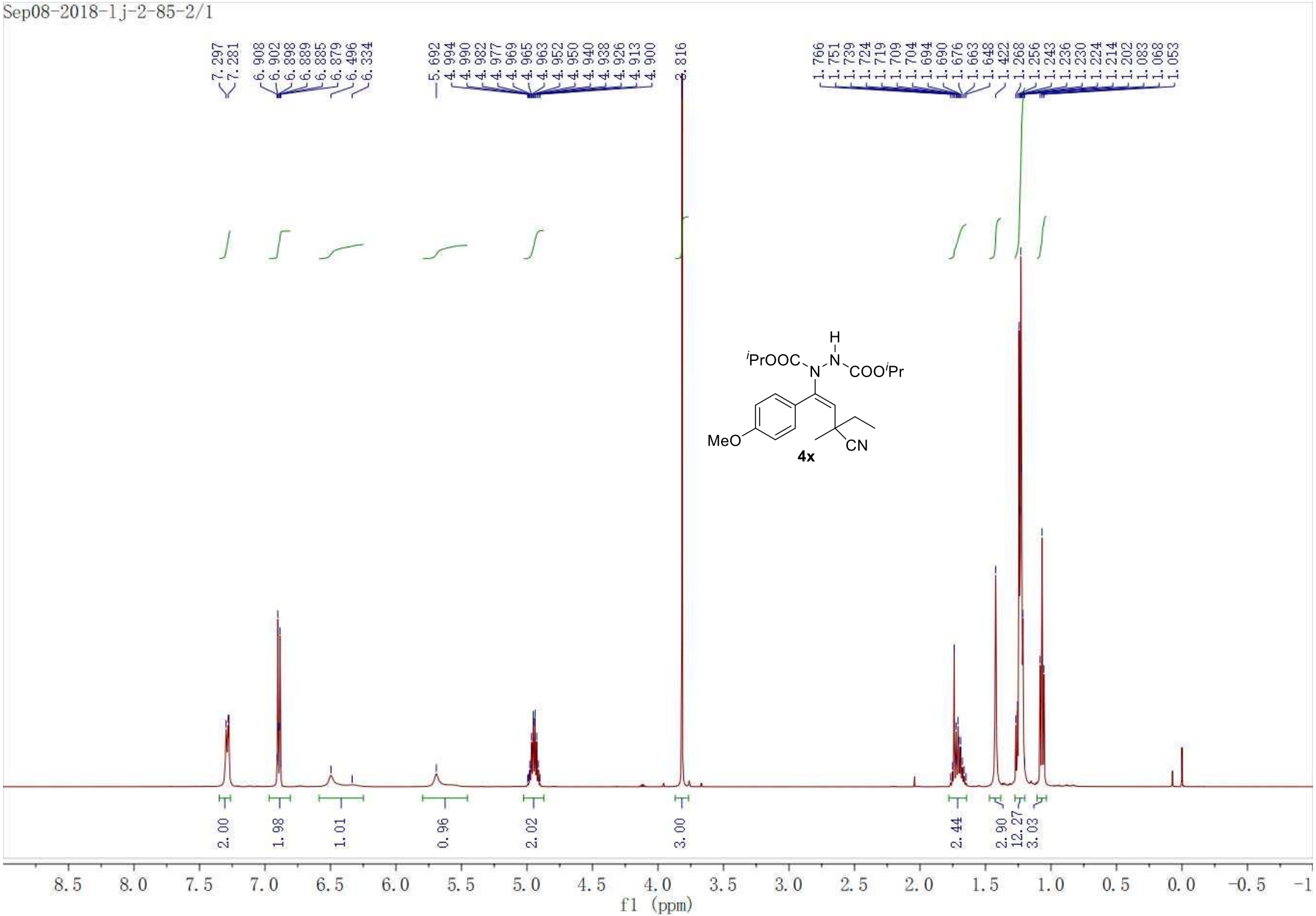
4w

160.28
155.55
154.41
140.24
131.17
128.22
126.33
123.09
113.56
77.25
77.00
76.75
70.84
70.01
55.21
31.14
29.11
21.91
21.88

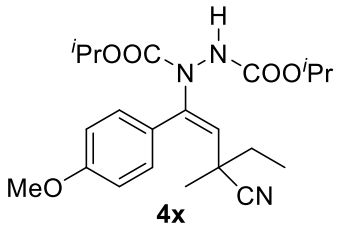
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

Sep08-2018-1j-2-85-2/1



Sep09-2018-1j-2-85-2/1



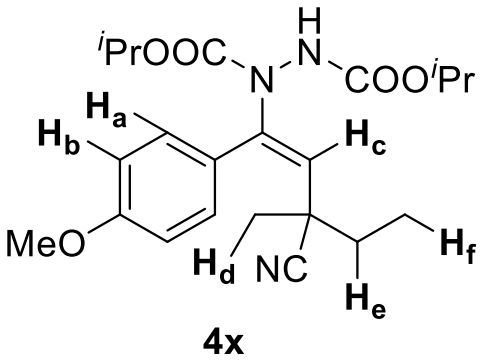
4x

160.198
155.486
154.420
140.224
131.175
128.193
126.202
121.874
113.421
77.255
77.000
76.746
70.752
69.882
55.143
36.567
35.169
26.762
21.877
21.851
9.423

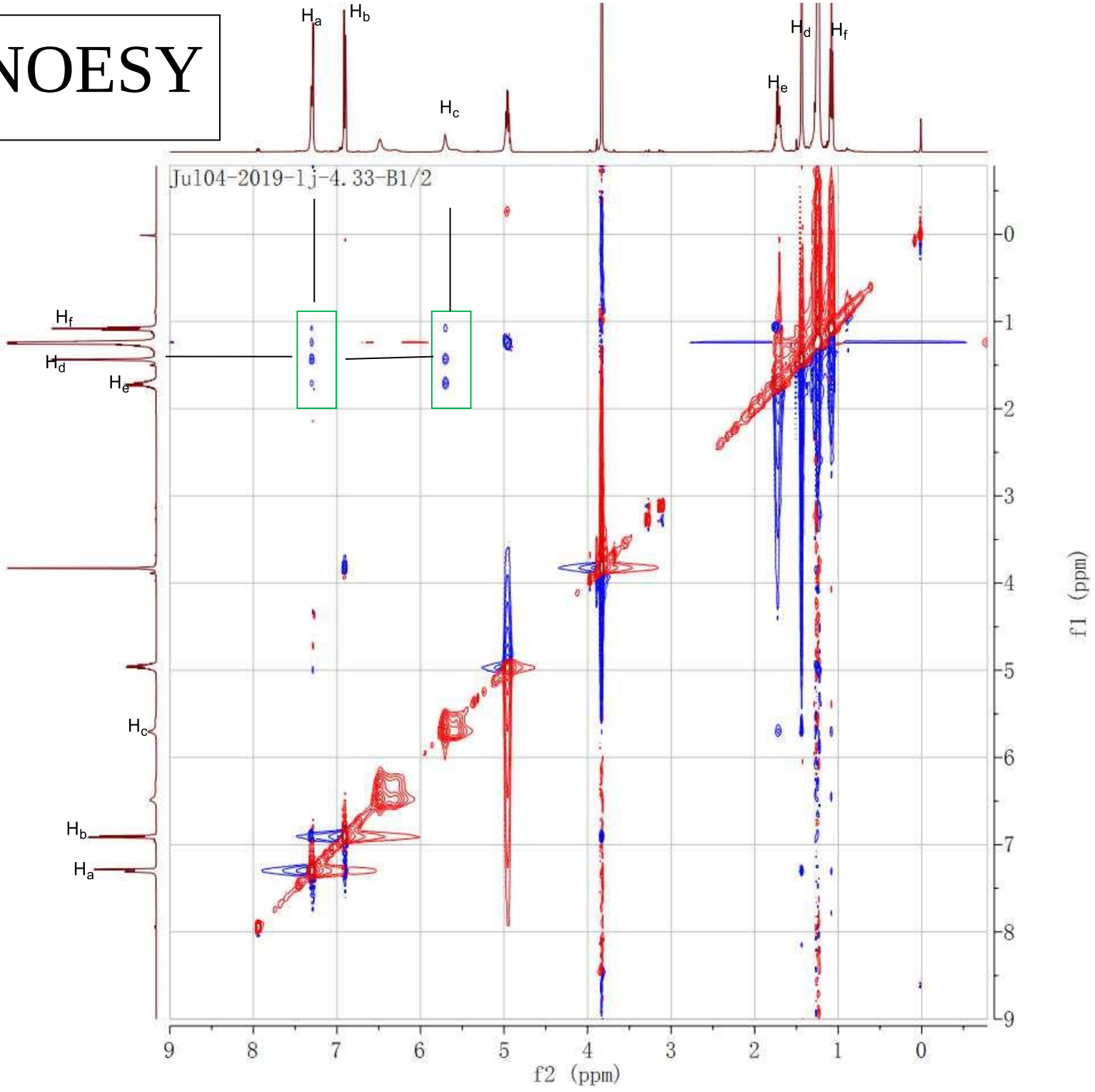
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

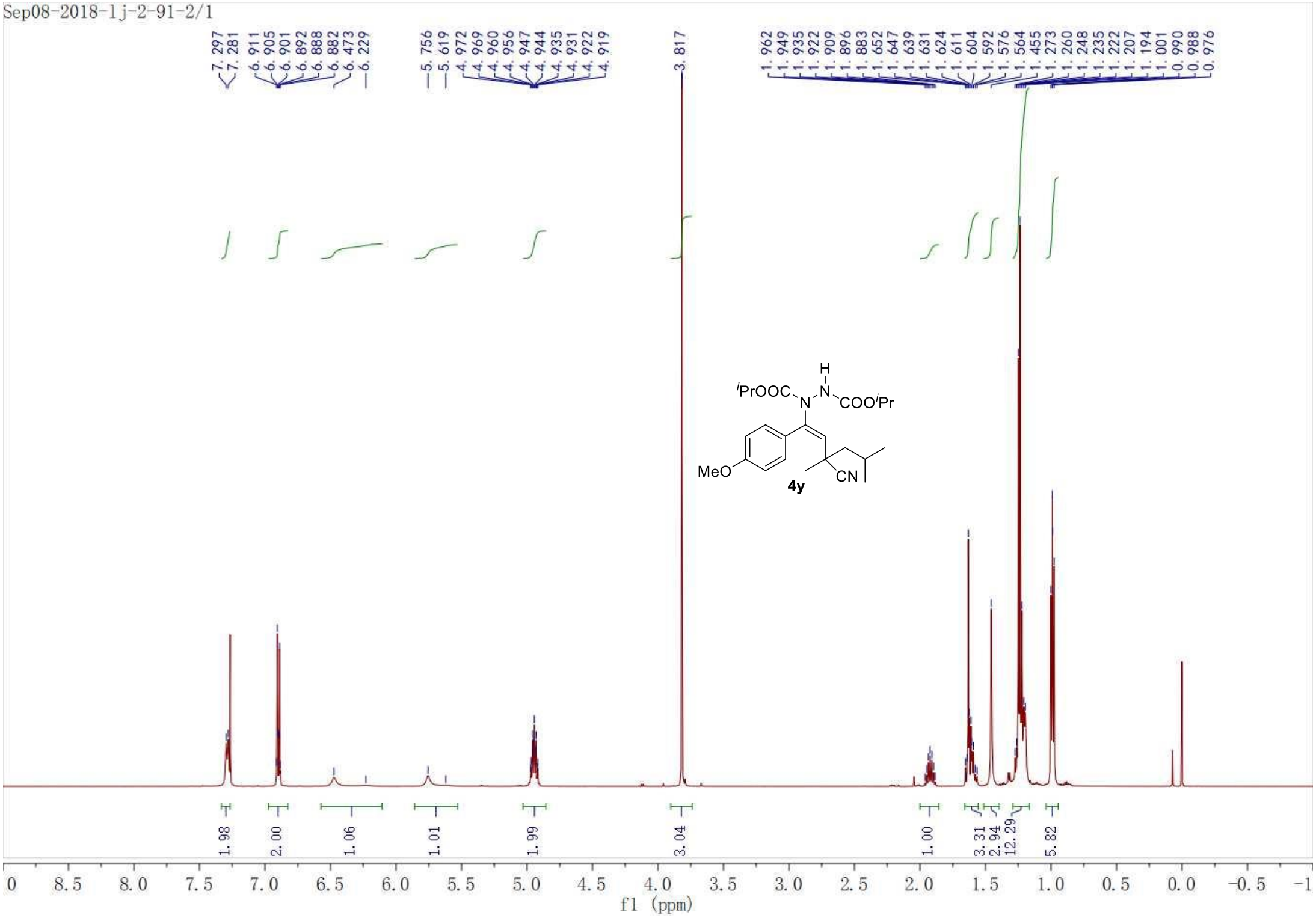
NOESY



4x

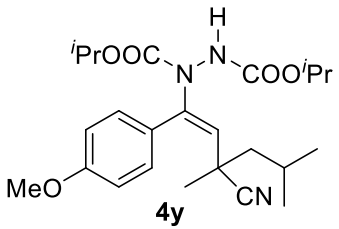


	Parameter	Value
1	Data File Name	D:/chemistry/research/my research/my group/NMR/Jul04-2019-1j-4.33-B1/2/ser
2	Title	Jul04-2019-1j-4.33-B1/2
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.1
11	Pulse Sequence	noesyphpr
12	Experiment	NOESY
13	Probe	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0166
14	Number of Scans	16
15	Receiver Gain	105
16	Relaxation Delay	2.0000
17	Pulse Width	12.7500
18	Presaturation Frequency	
19	Acquisition Time	0.1862
20	Acquisition Date	2019-07-04T23:34:26
21	Modification Date	2019-07-05T02:36:43
22	Class	
23	Spectrometer Frequency	


Sep08-2018-1j-2-91-2/1
7.297
7.281
6.911
6.905
6.901
6.892
6.888
6.882
6.473
6.229
5.756
5.619
4.972
4.969
4.960
4.956
4.947
4.944
4.935
4.931
4.922
4.919
3.817
1.962
1.949
1.935
1.922
1.909
1.896
1.883
1.652
1.647
1.639
1.631
1.624
1.611
1.604
1.592
1.576
1.564
1.455
1.273
1.260
1.248
1.235
1.222
1.207
1.194
1.001
0.990
0.988
0.976
H
N
N
iPrOOC
COOiPr
MeO
CN
4y
1.98
2.00
1.06
1.01
1.99
3.04
1.00
3.31
2.94
12.29
5.82
f1 (ppm)

Sep09-2018-1j-2-91-2/1

160.250
155.593
154.420
139.438
131.234
129.160
126.291
122.282
113.433
77.254
77.000
76.746
70.785
69.962
55.190
50.562
35.188
28.740
25.673
23.866
23.400
21.921
21.892
21.873

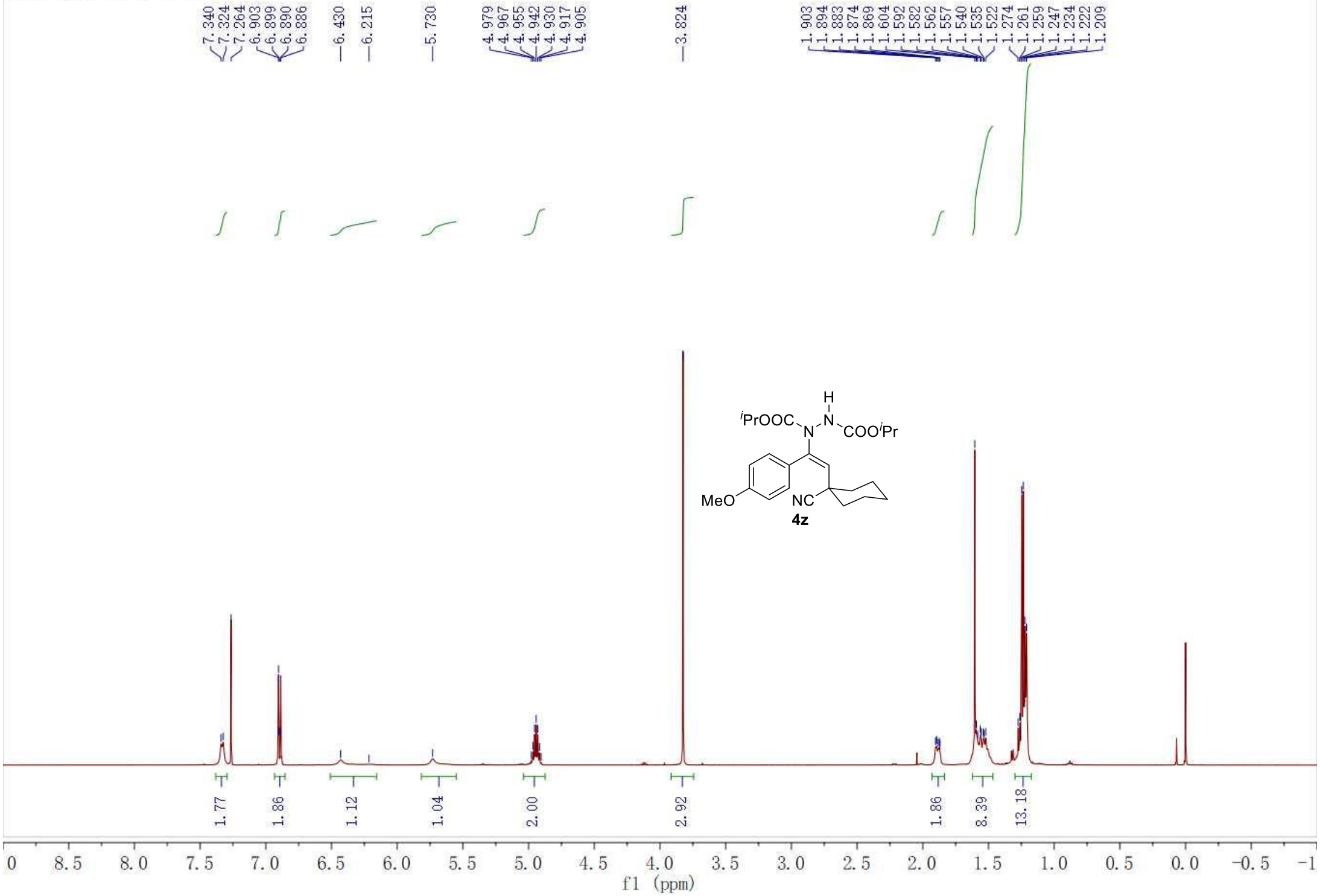


4y

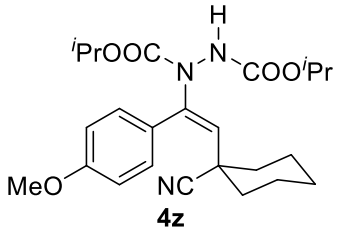
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

Sep08-2018-1j-2-91-1/1



Sep09-2018-1j-2-91-1/1

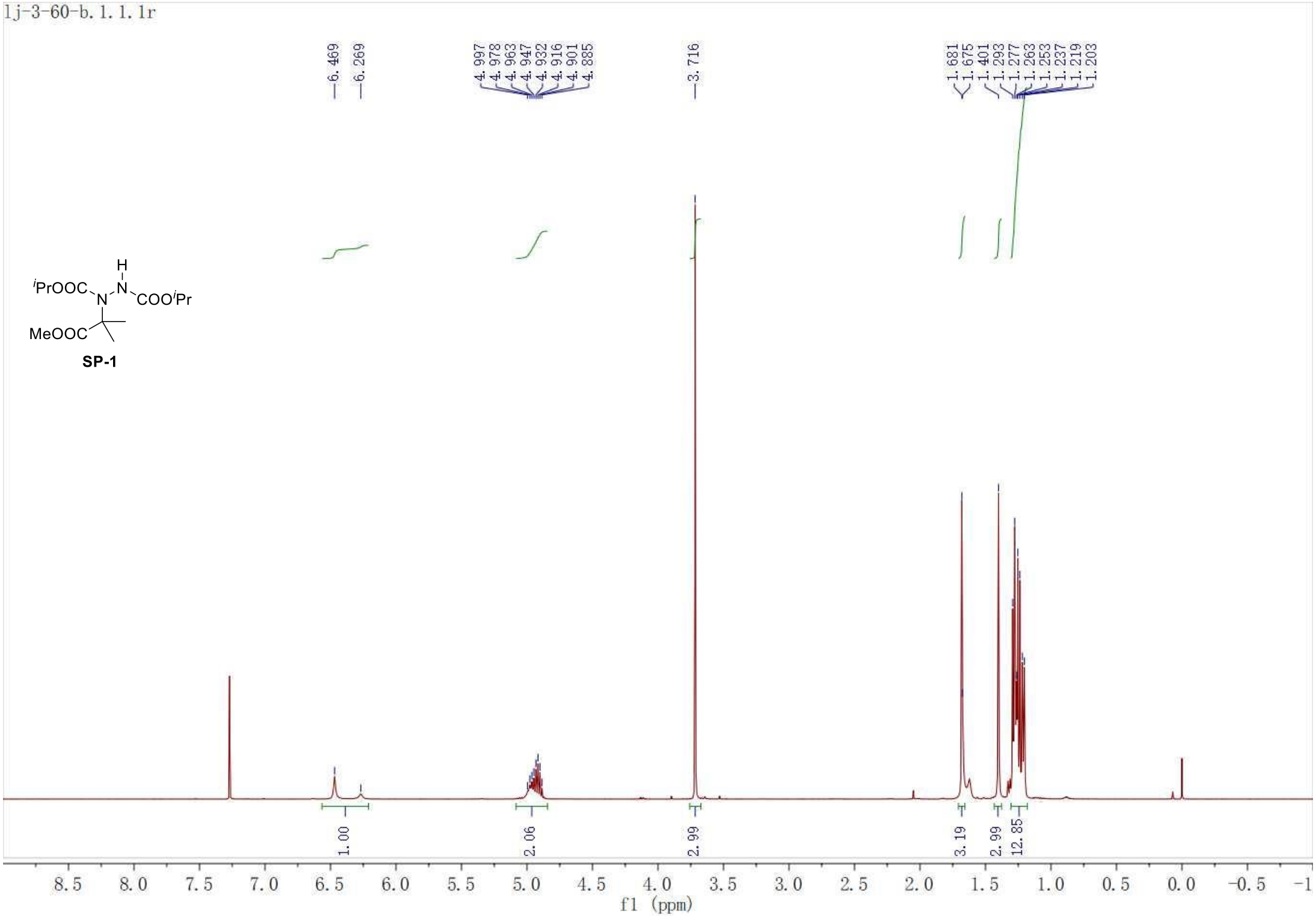


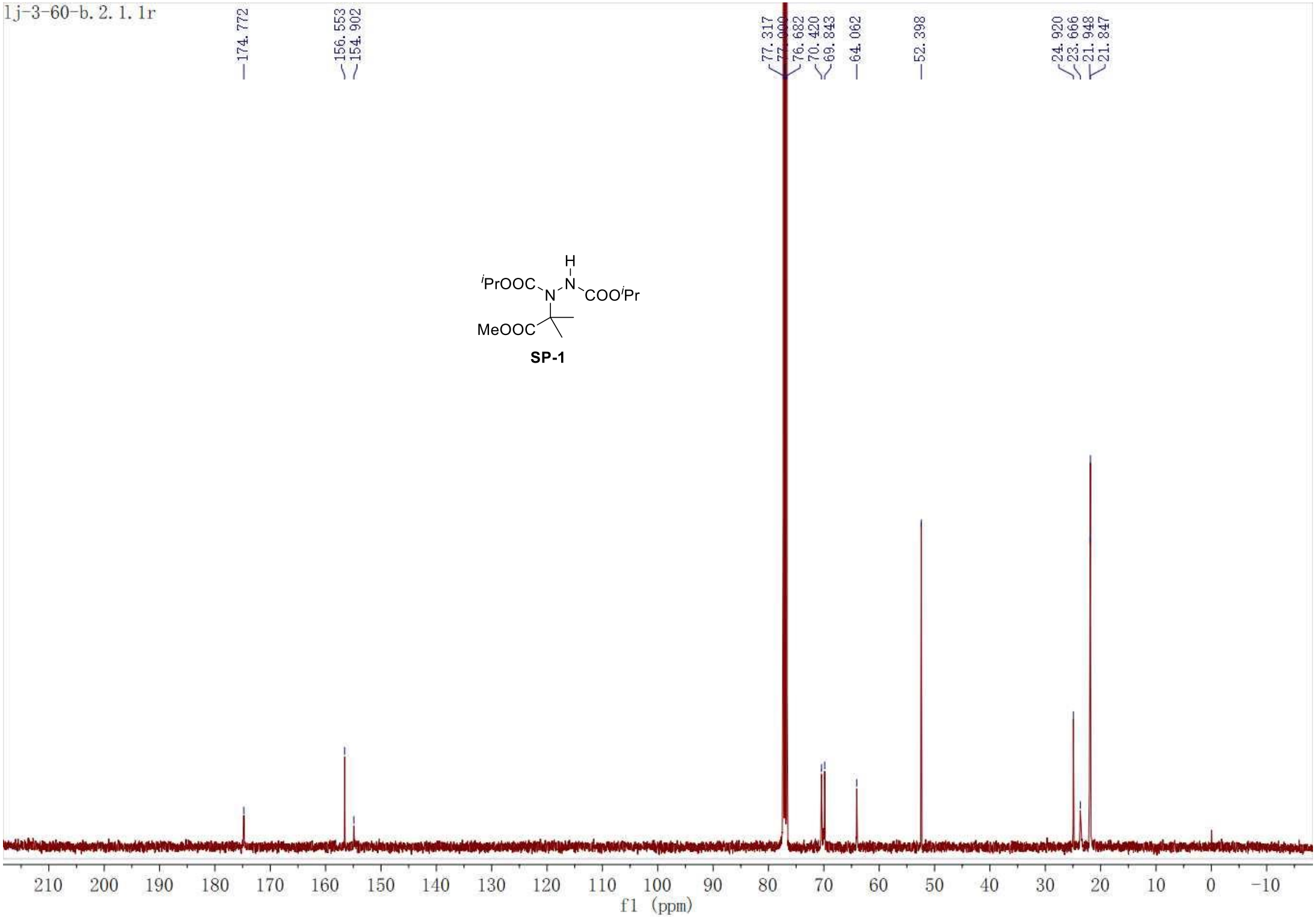
4z

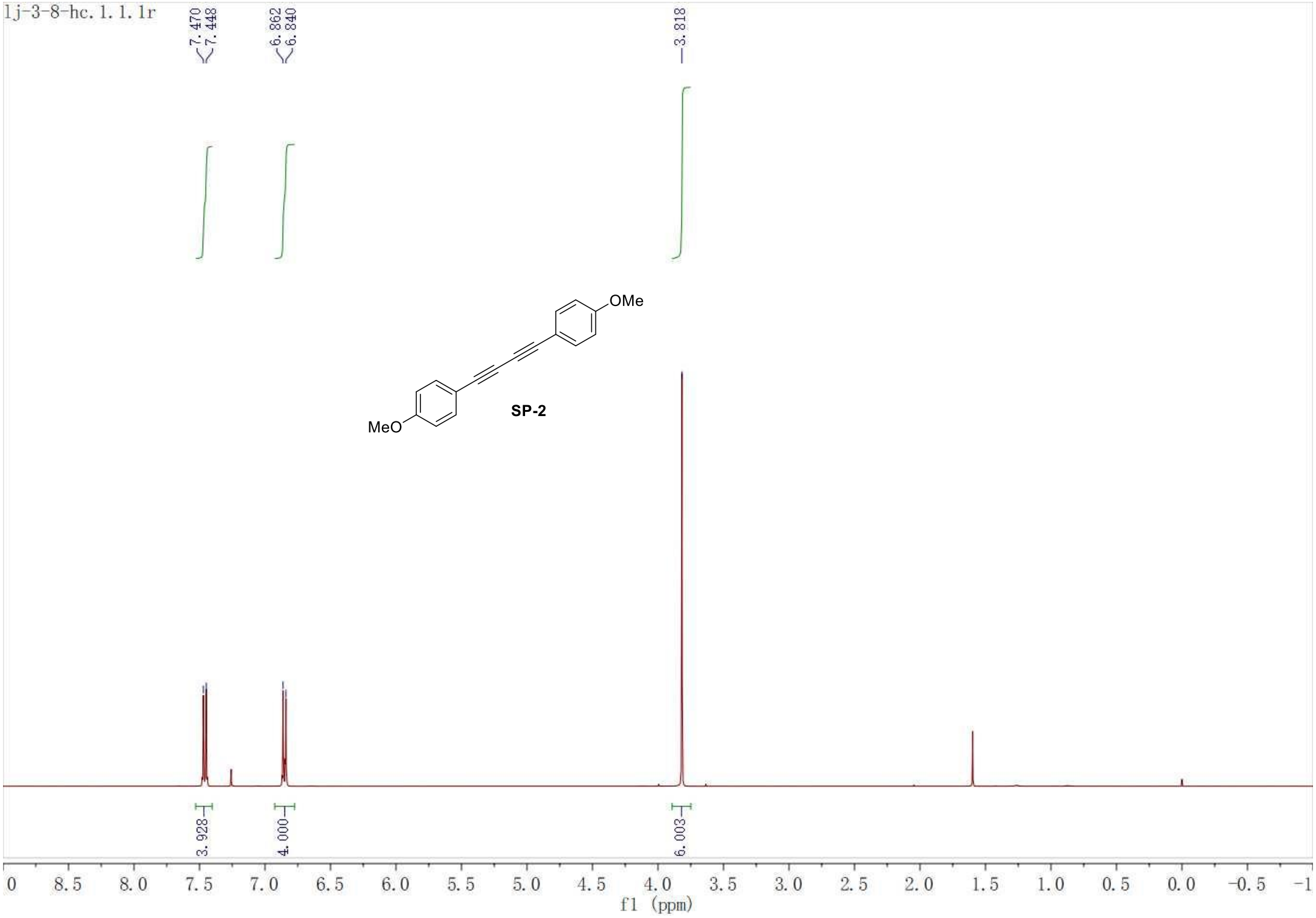
160.187
155.503
154.483
140.597
131.039
128.064
126.829
121.895
113.586
77.253
77.000
76.745
70.800
69.985
55.216
36.838
36.683
24.777
22.104
21.914

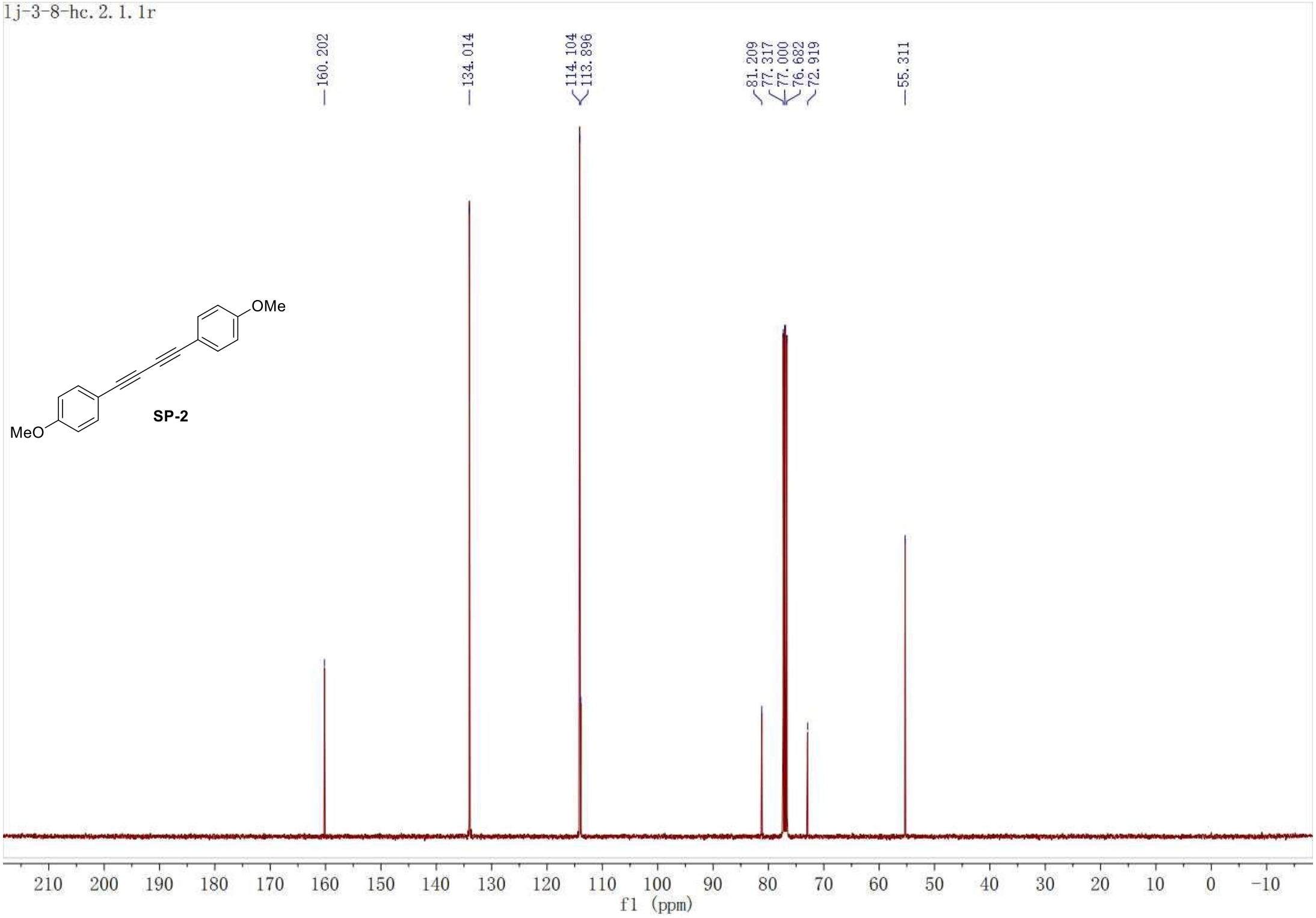
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

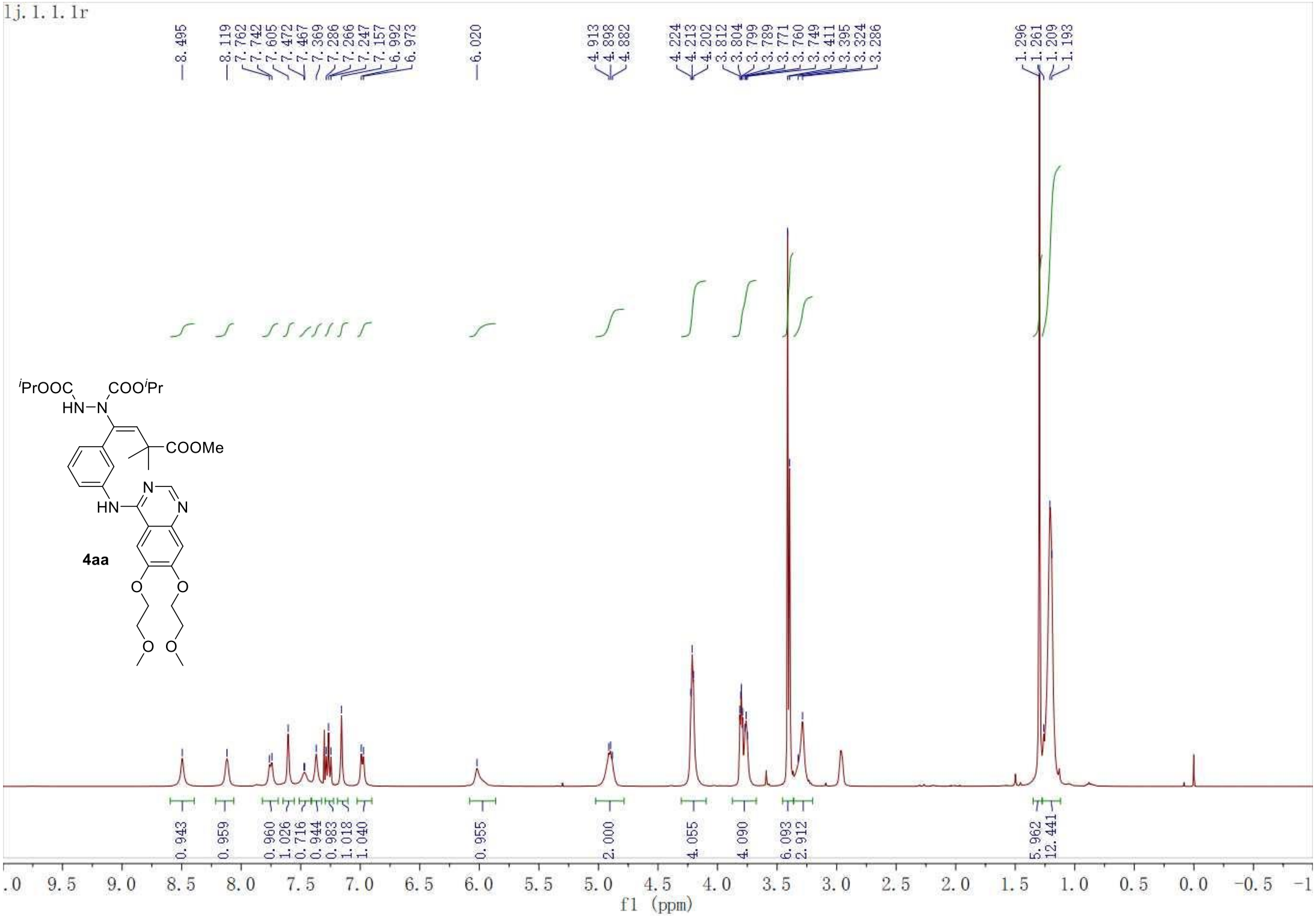
f1 (ppm)

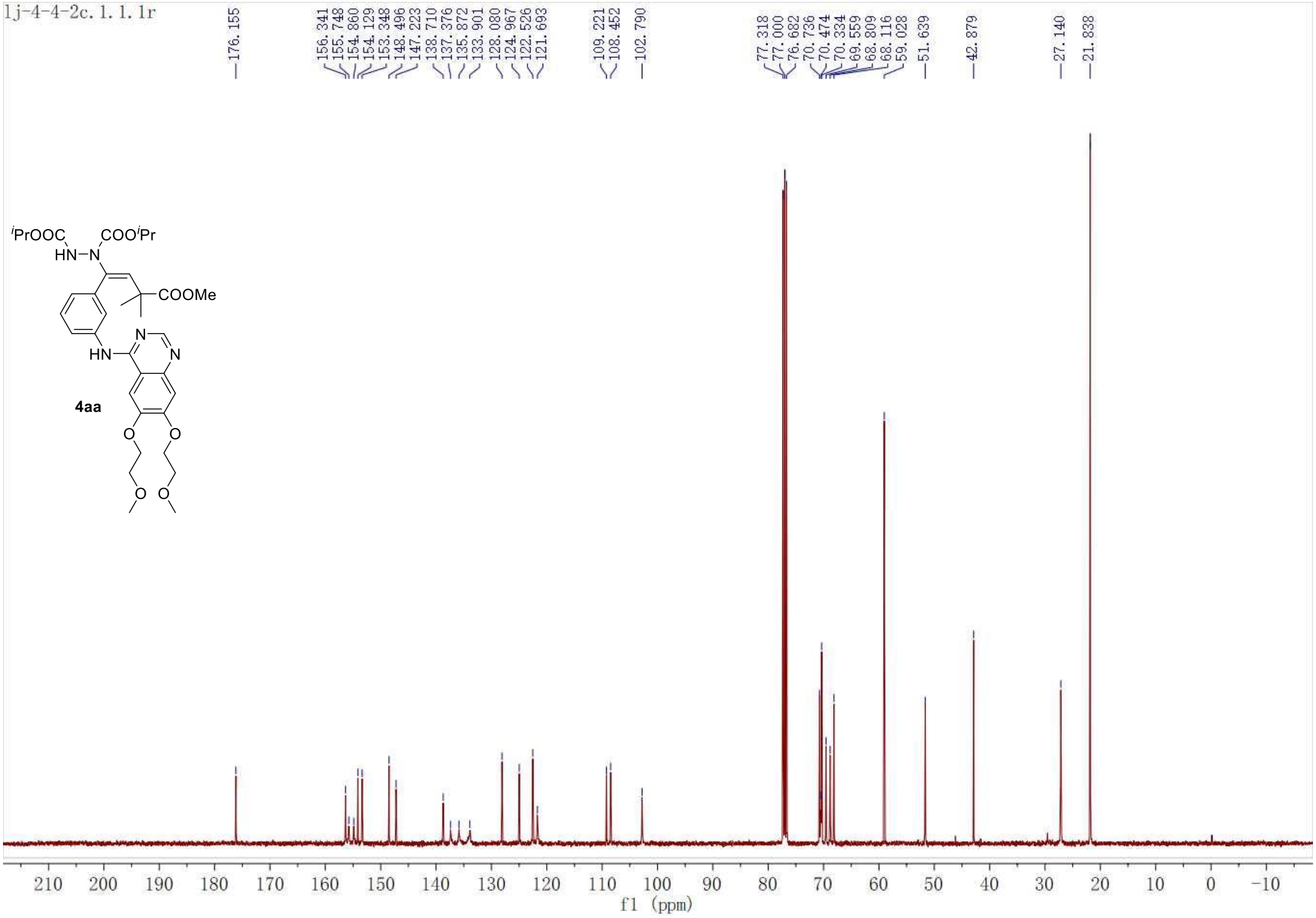

1j-3-60-b.1.1.1r
6.469
6.269
4.997
4.978
4.963
4.947
4.932
4.916
4.901
4.885
3.716
1.681
1.675
1.401
1.293
1.277
1.263
1.253
1.237
1.219
1.203
H
iPrOOC
N
N
COOiPr
MeOOC
SP-1
1.00
2.06
2.99
3.19
2.99
12.85
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


1j-3-60-b.2.1.1r
174.772
156.553
154.902
77.317
77.000
76.682
70.420
69.843
64.062
52.398
24.920
23.666
21.948
21.847
H
N
N
iPrOOC
COOiPr
N
MeOOC
SP-1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

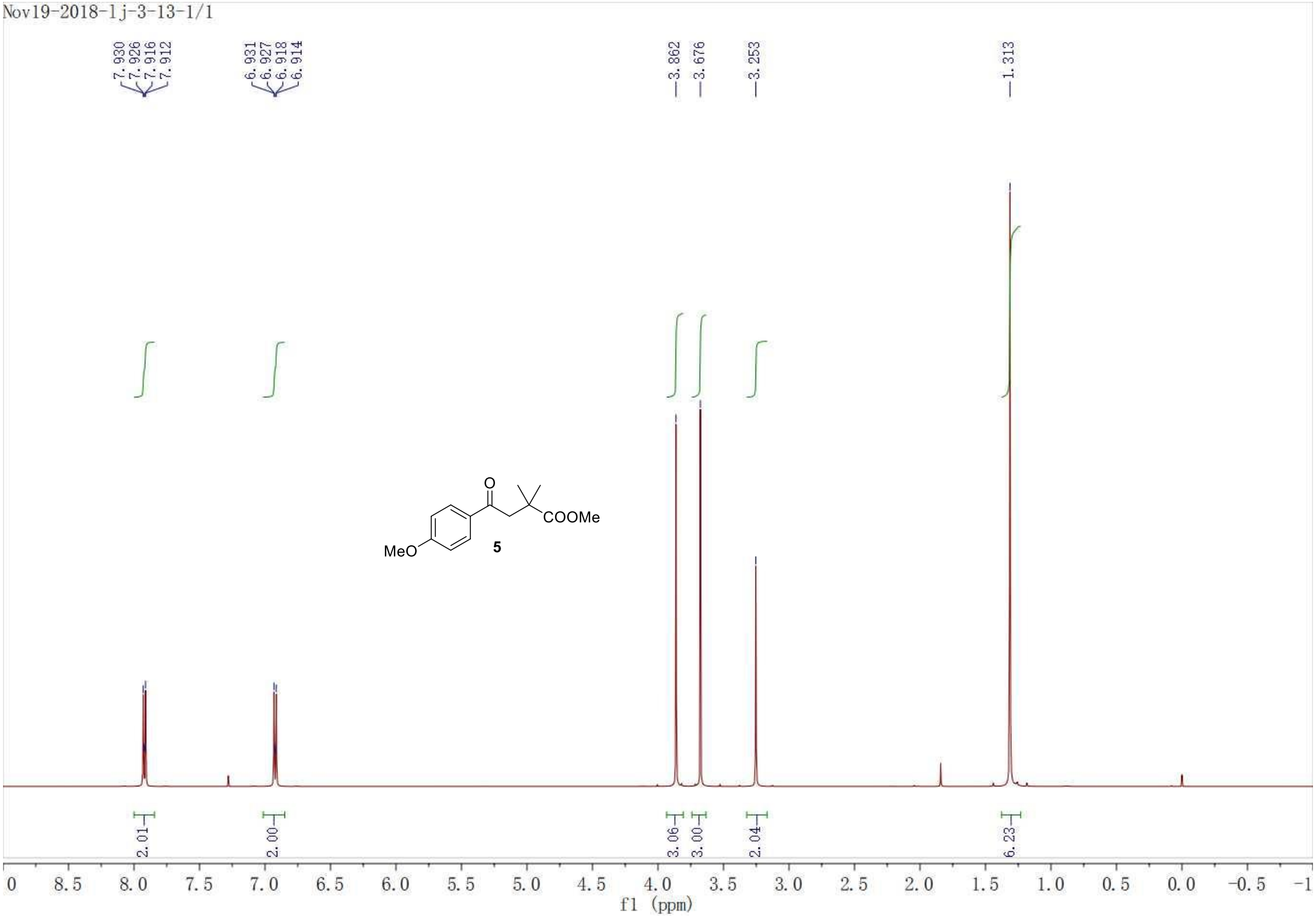

1j-3-8-hc.1.1.1r
7.470
7.448
6.862
6.840
3.818
OMe
MeO
SP-2
3.928
4.000
6.003
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


1j-3-8-hc.2.1.1r
160.202
134.014
114.104
113.896
81.209
77.317
77.000
76.682
72.919
55.311
OMe
MeO
SP-2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1j. 1. 1. 1r
8.495
8.119
7.762
7.742
7.605
7.472
7.467
7.369
7.286
7.266
7.247
7.157
6.992
6.973
6.020
4.913
4.898
4.882
4.224
4.213
4.202
3.812
3.804
3.799
3.789
3.771
3.760
3.749
3.411
3.395
3.324
3.286
1.296
1.261
1.209
1.193
iPrOOC
COOiPr
HN
N
COOMe
HN
N
N
4aa
O
O
O
O
0.943
0.959
0.960
1.026
0.716
0.944
0.983
1.018
1.040
0.955
2.000
4.055
4.090
6.093
2.912
5.962
12.441
f1 (ppm)


1j-4-4-2c.1.1.1r
176.155
156.341
155.748
154.860
154.129
153.348
148.496
147.223
138.710
137.376
135.872
133.901
128.080
124.967
122.526
121.693
109.221
108.452
102.790
77.318
77.000
76.682
70.736
70.474
70.334
69.559
68.809
68.116
59.028
51.639
42.879
27.140
21.838
iPrOOC
COOiPr
HN
N
COOMe
HN
N
4aa
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Nov19-2018-1j-3-13-1/1



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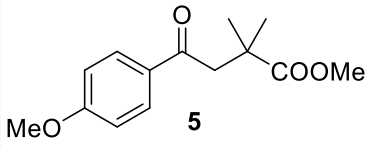
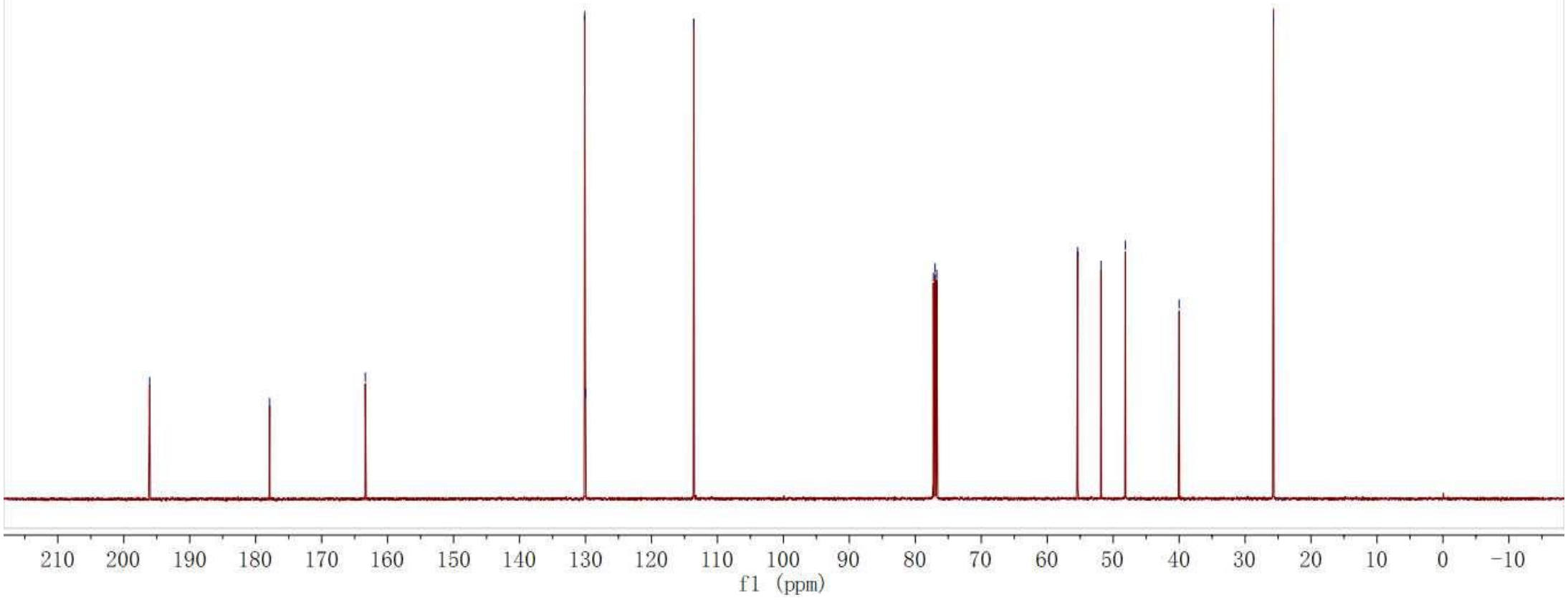
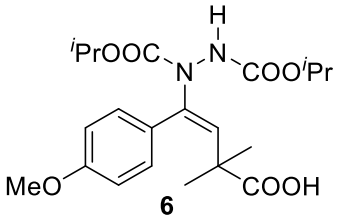
196.072
177.890
163.384
130.118
130.003
113.580
77.255
77.000
76.746
55.389
51.836
48.160
40.003
25.695



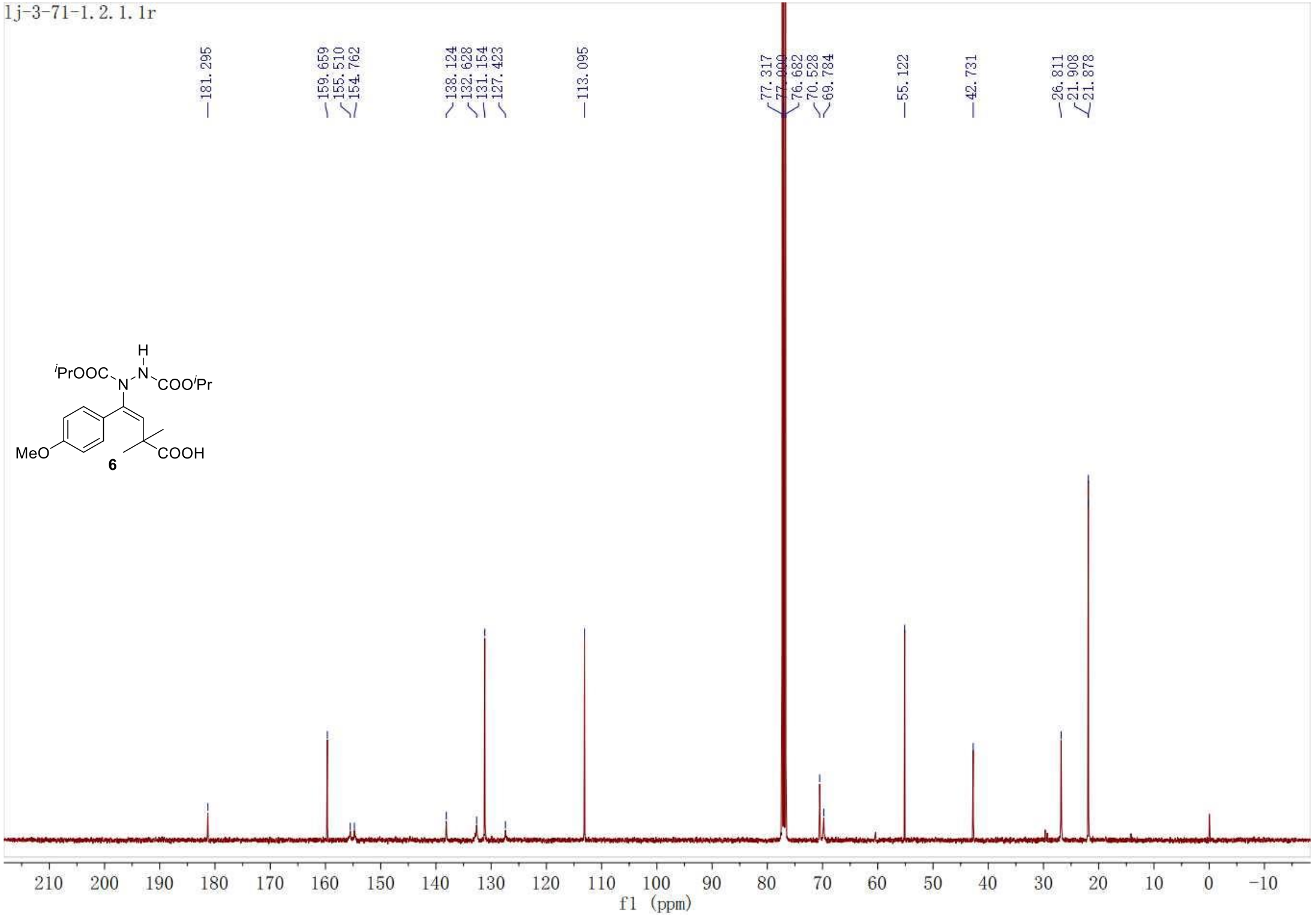
5

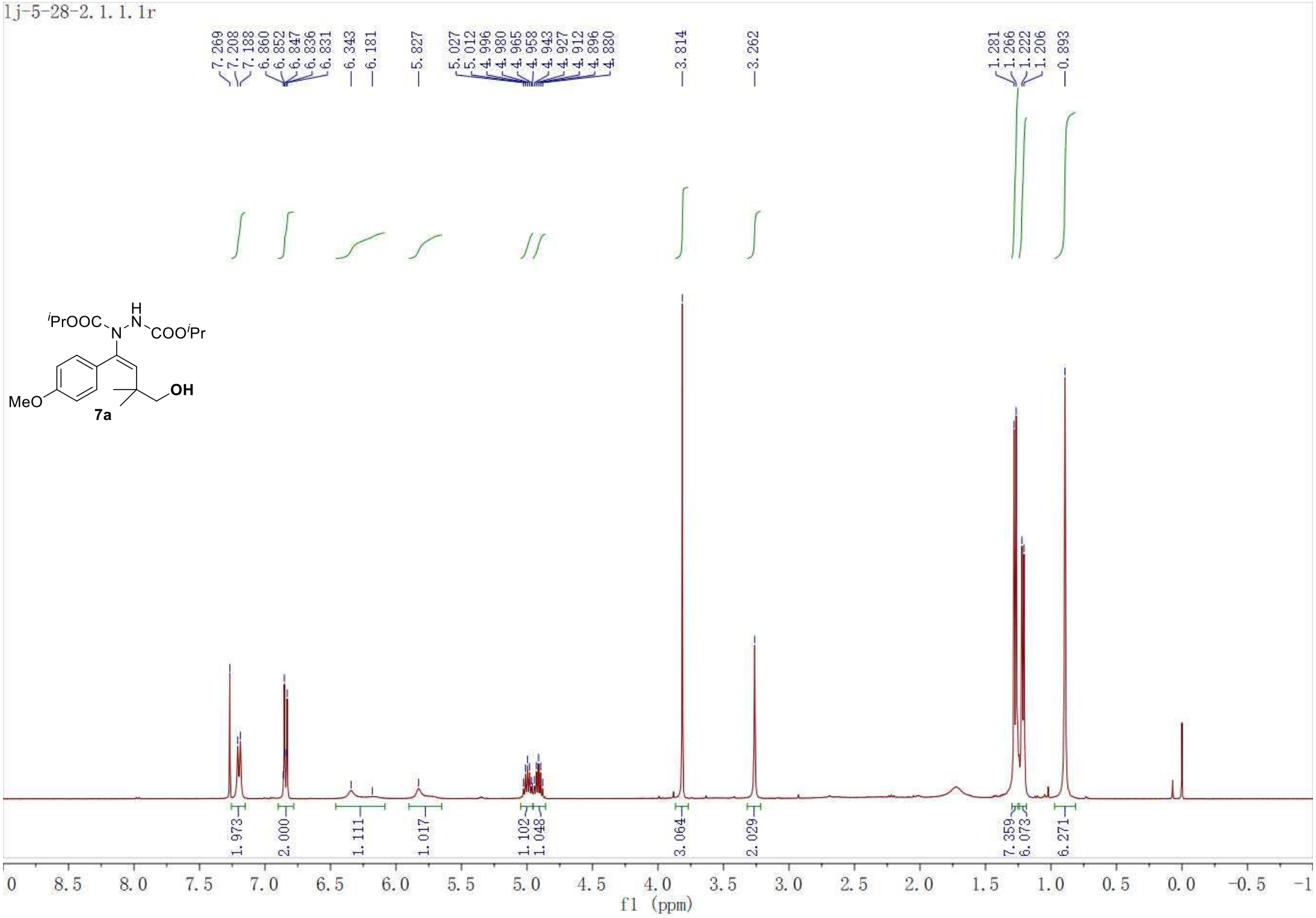


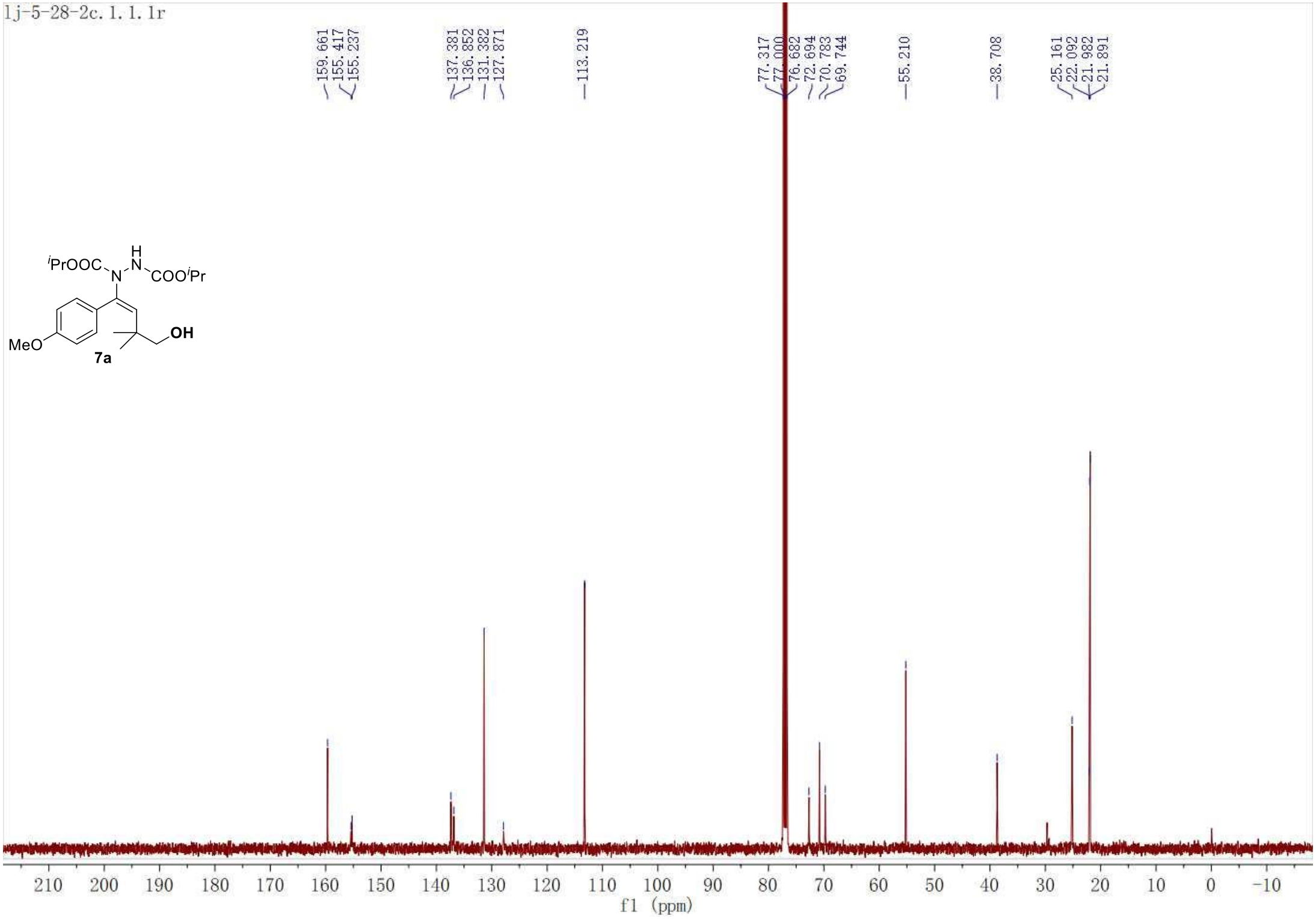
Dec10-2018-1j-3-37-1/1

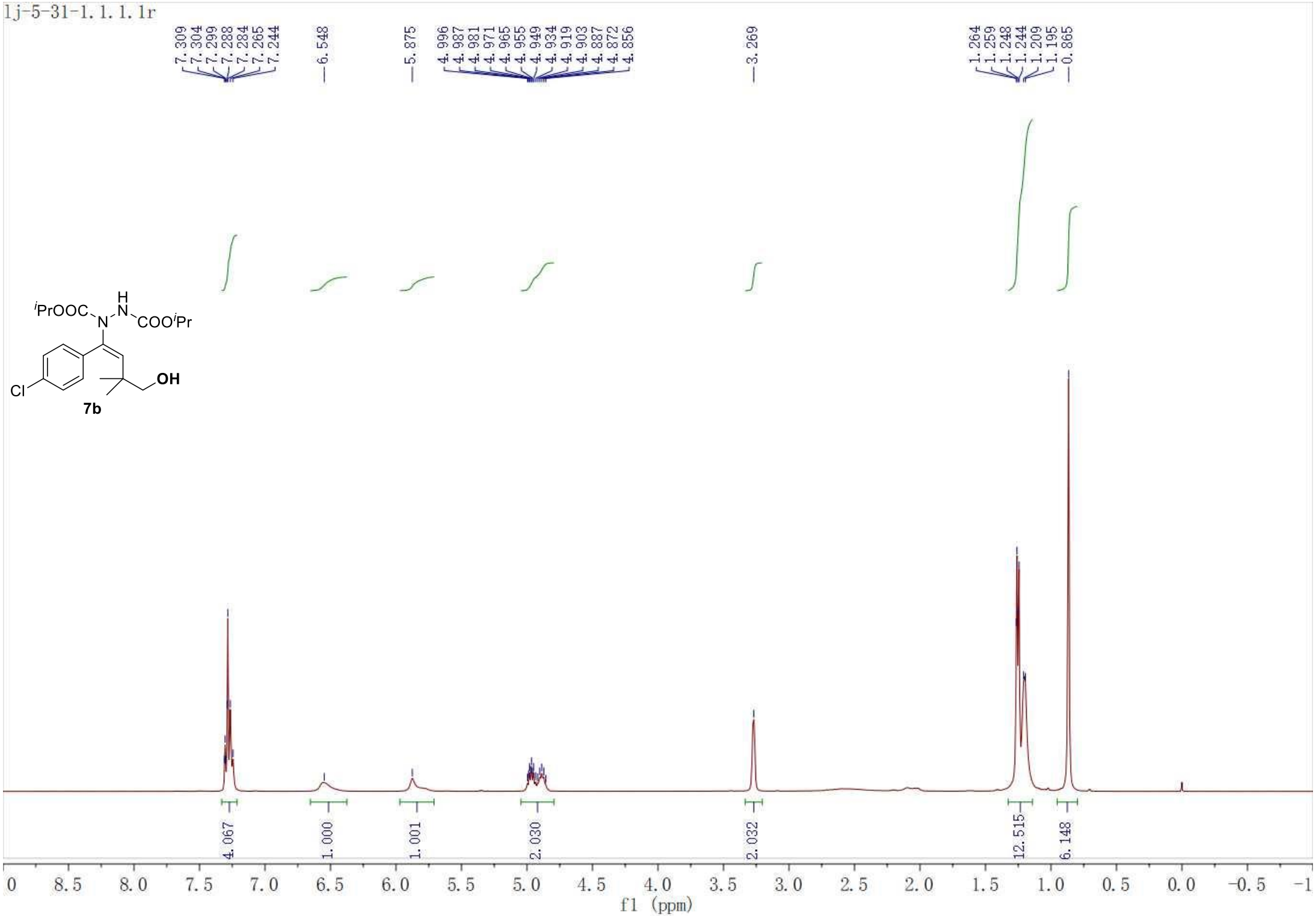


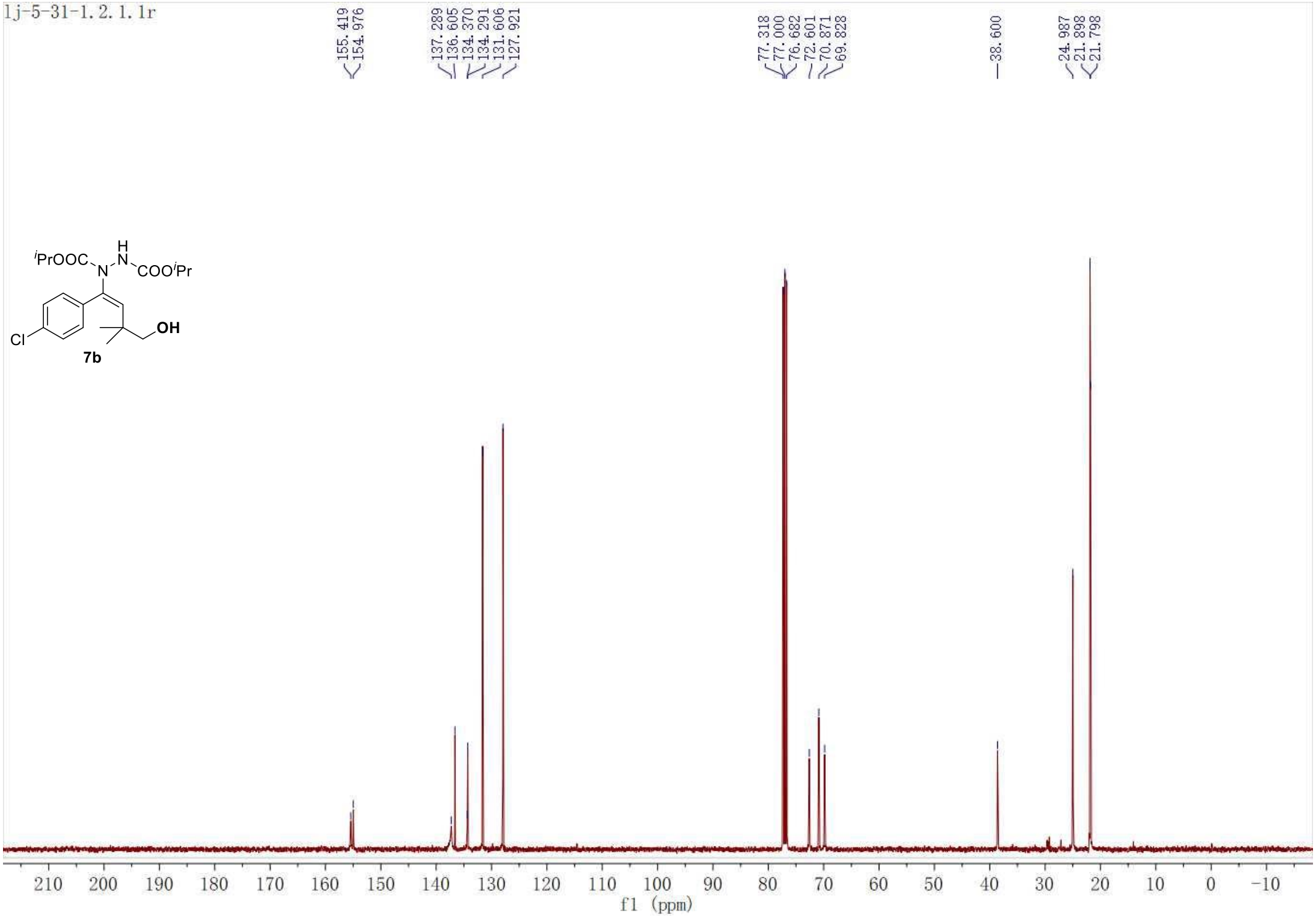
6

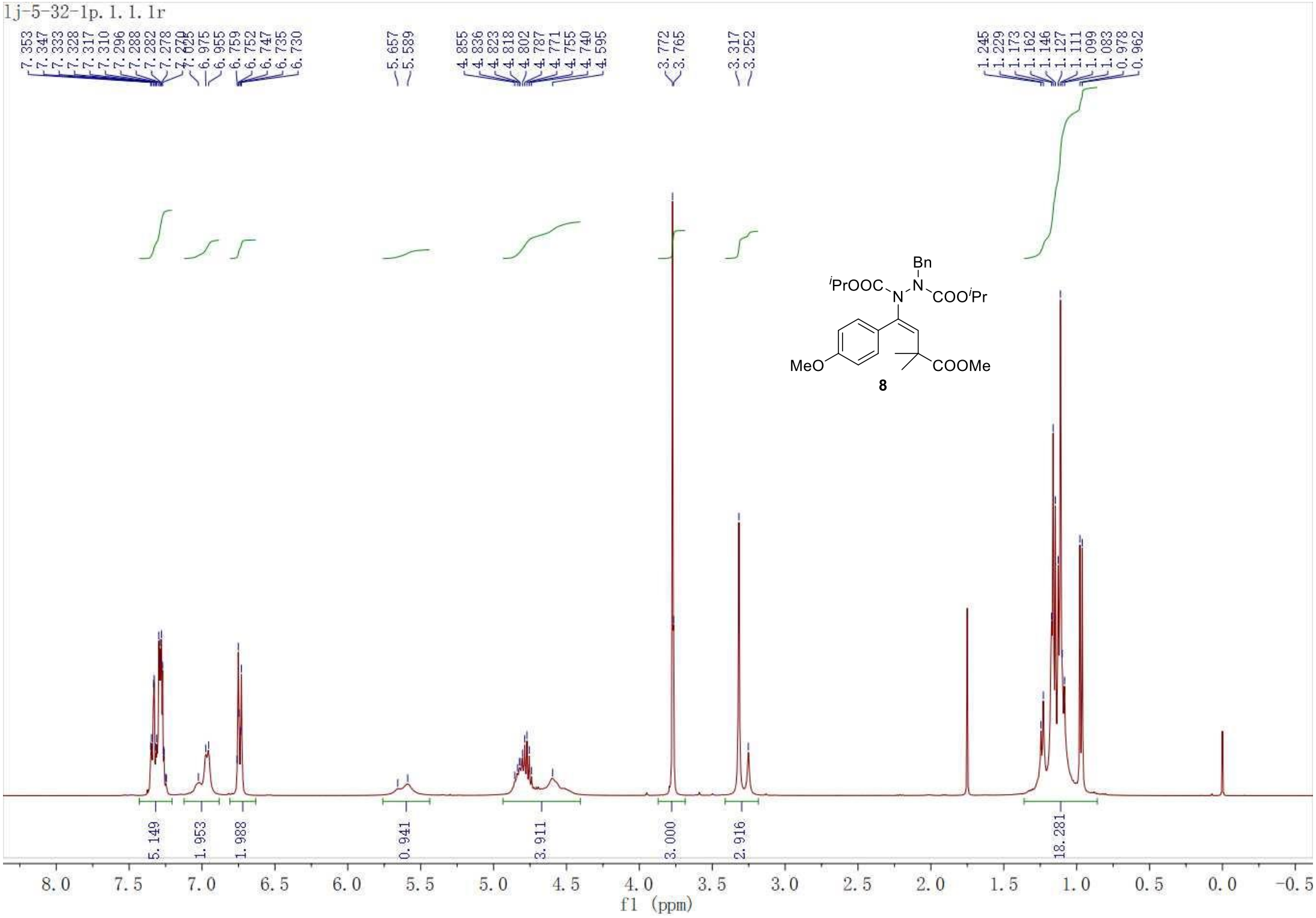

1j-3-71-1.2.1.1r
181.295
159.659
155.510
154.762
138.124
132.628
131.154
127.423
113.095
77.317
77.000
76.682
70.528
69.784
55.122
42.731
26.811
21.908
21.878
H
iPrOOC
N
N
COOiPr
MeO
COOH
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

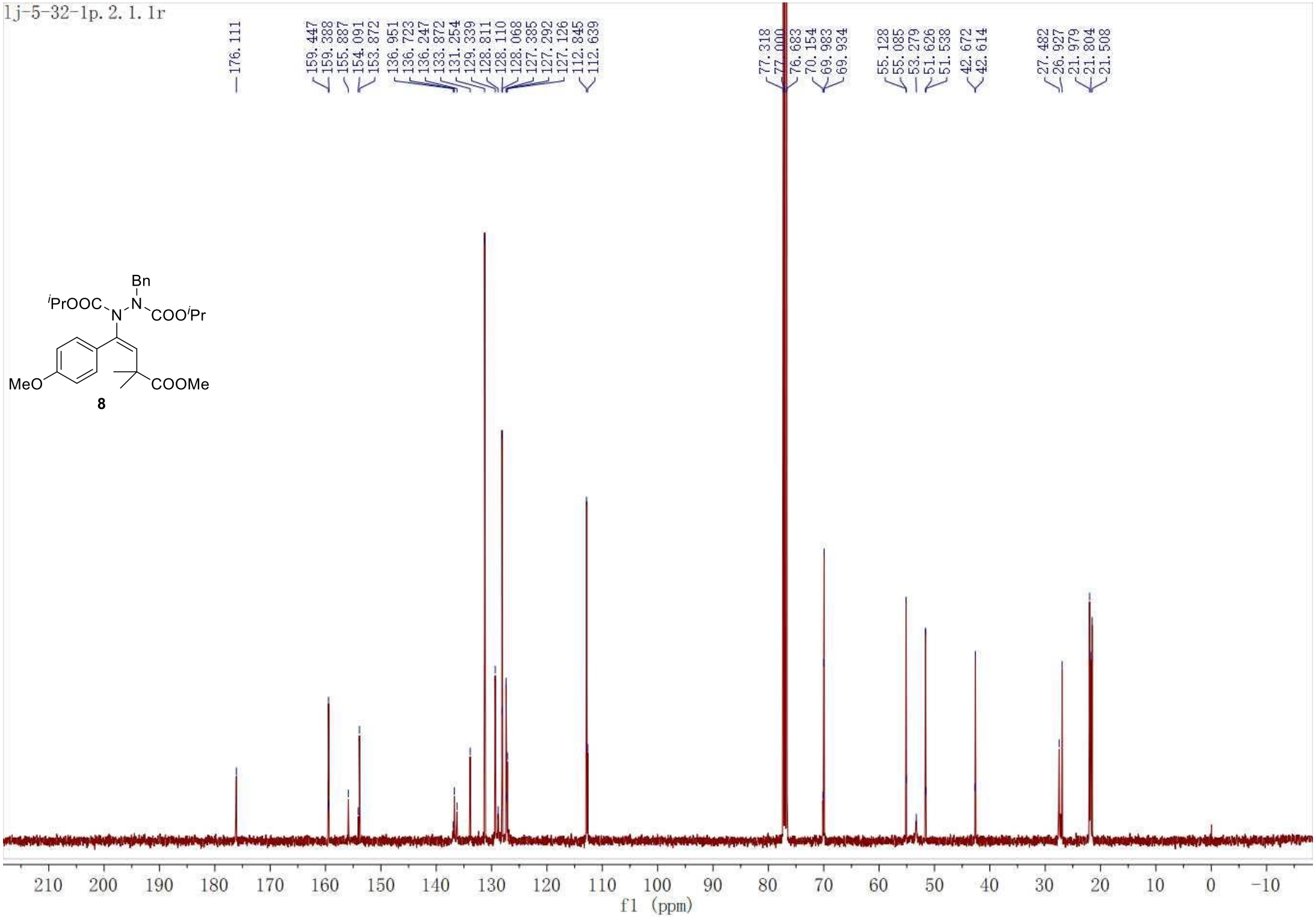

1j-5-28-2.1.1.1r
7.269
7.208
7.188
6.860
6.852
6.847
6.836
6.831
6.343
6.181
5.827
5.027
5.012
4.996
4.980
4.965
4.958
4.943
4.927
4.912
4.896
4.880
3.814
3.262
1.281
1.266
1.222
1.206
0.893
iPrOOC
N
H
N
COOiPr
MeO
OH
7a
1.973
2.000
1.111
1.017
1.102
1.048
3.064
2.029
7.359
6.073
6.271
f1 (ppm)

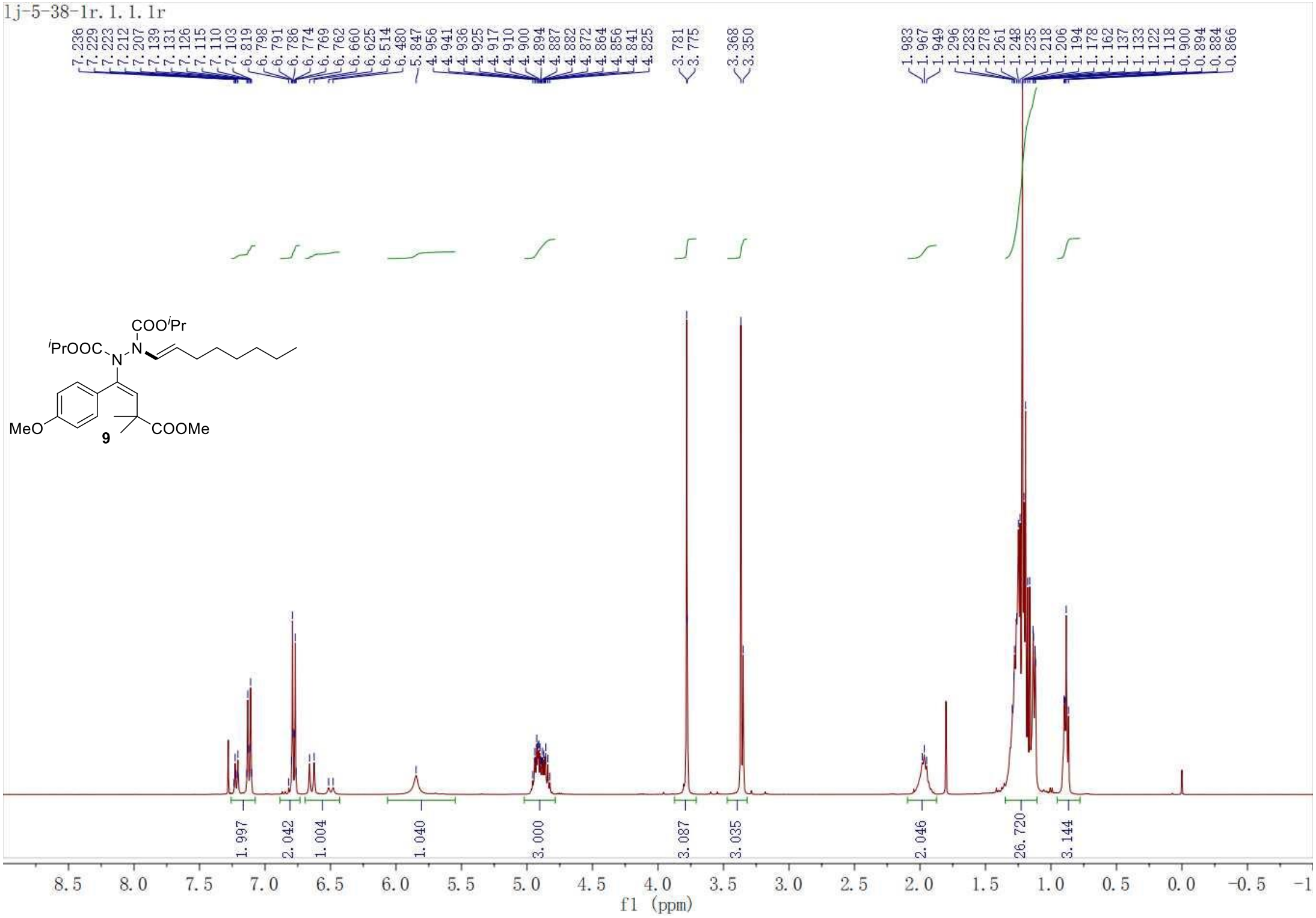

1j-5-28-2c.1.1.1r
159.661
155.417
155.237
137.381
136.852
131.382
127.871
113.219
77.317
77.000
76.682
72.694
70.783
69.744
55.210
38.708
25.161
22.092
21.982
21.891
iPrOOC
N
H
N
COOiPr
MeO
OH
7a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

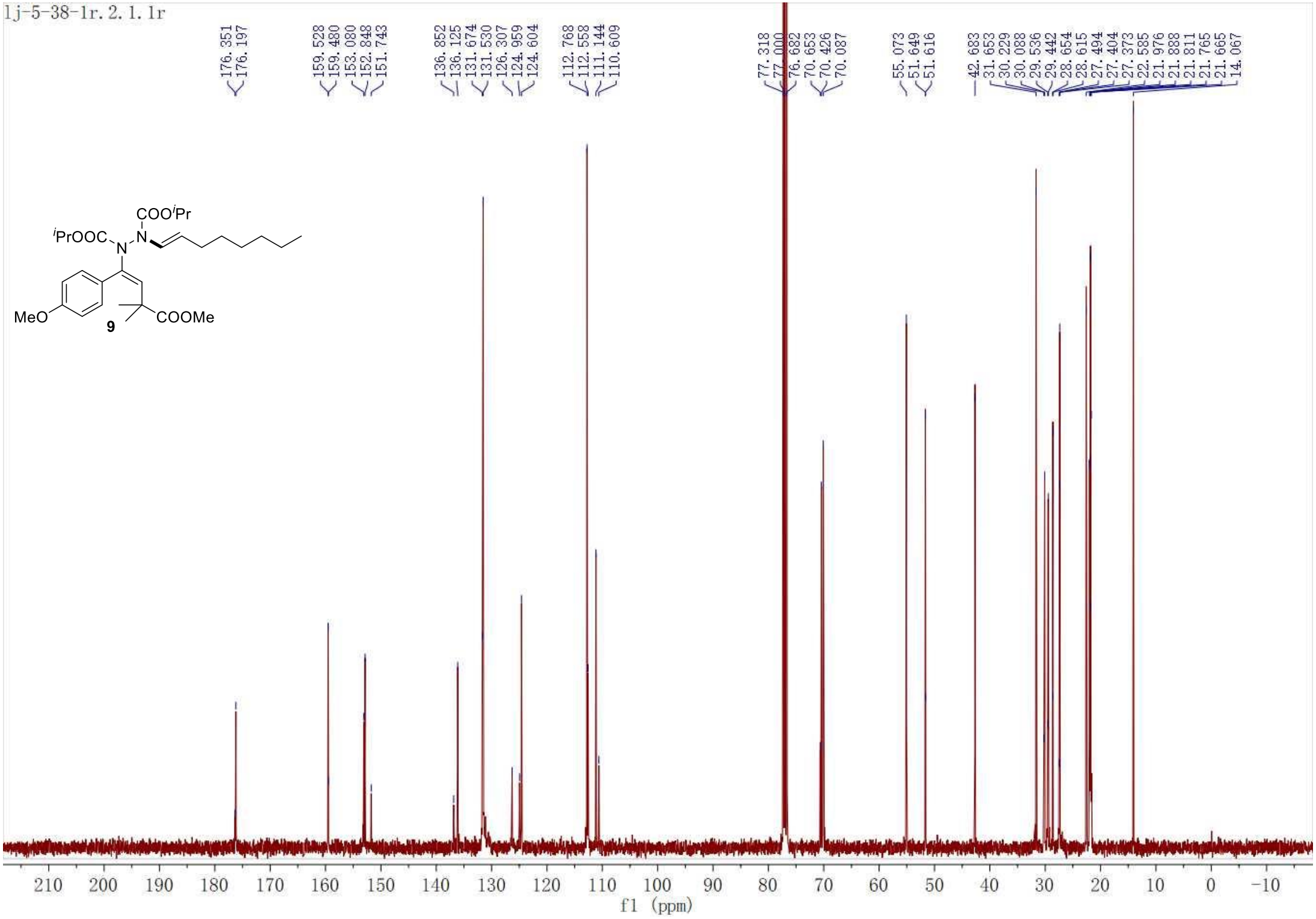

1j-5-31-1.1.1.1r
7.309
7.304
7.299
7.288
7.284
7.265
7.244
6.548
5.875
4.996
4.987
4.981
4.971
4.965
4.955
4.949
4.934
4.919
4.903
4.887
4.872
4.856
3.269
1.264
1.259
1.248
1.244
1.209
1.195
0.865
iPrOOC
N
H
N
COOiPr
Cl
OH
7b
4.067
1.000
1.001
2.030
2.032
12.515
6.148
f1 (ppm)

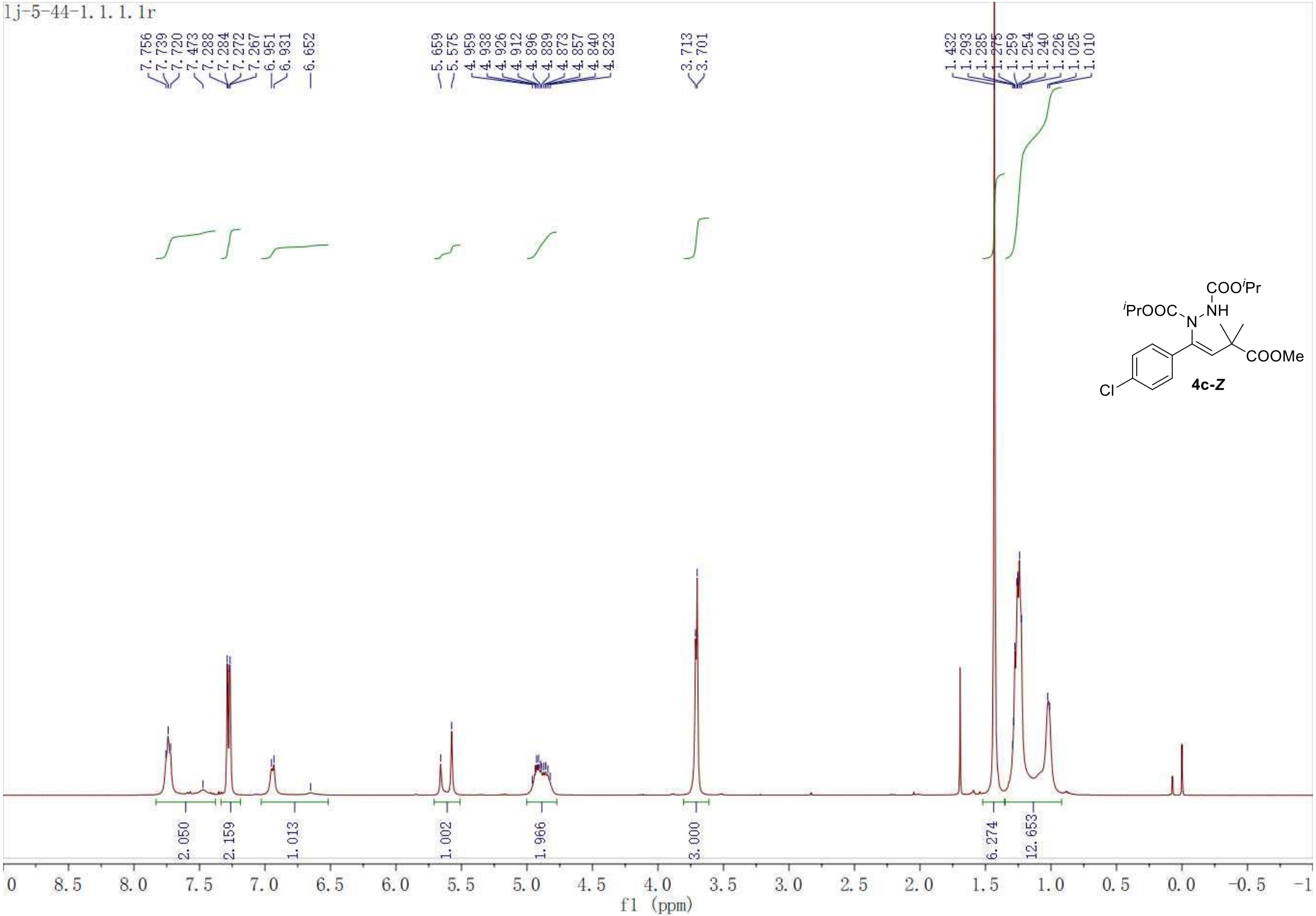

1j-5-31-1.2.1.1r
155.419
154.976
137.289
136.605
134.370
134.291
131.606
127.921
77.318
77.000
76.682
72.601
70.871
69.828
38.600
24.987
21.898
21.798
iPrOOC
N
H
N
COOiPr
Cl
OH
7b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

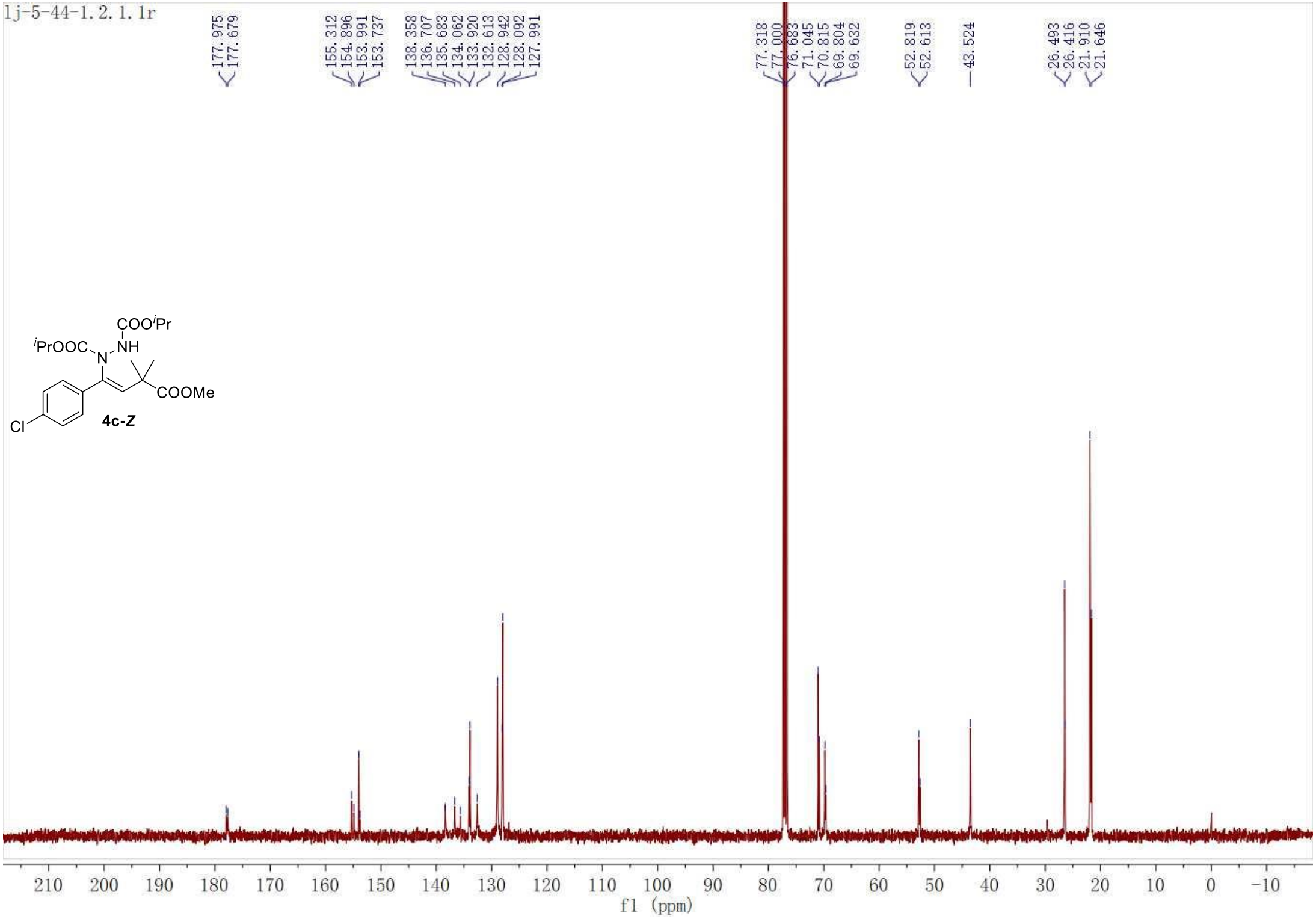

1j-5-32-1p.1.1.1r
7.353
7.347
7.333
7.328
7.317
7.310
7.296
7.288
7.282
7.278
6.975
6.955
6.759
6.752
6.747
6.735
6.730
5.657
5.589
4.855
4.836
4.823
4.818
4.802
4.787
4.771
4.755
4.740
4.595
3.772
3.765
3.317
3.252
1.245
1.229
1.173
1.162
1.146
1.127
1.111
1.099
1.083
0.978
0.962
Bn
iPrOOC
N
N
COOiPr
MeO
COOMe
8
5.149
1.953
1.988
0.941
3.911
3.000
2.916
18.281
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


1j-5-32-1p.2.1.1r
176.111
159.447
159.388
155.887
154.091
153.872
136.951
136.723
136.247
133.872
131.254
129.339
128.811
128.110
128.068
127.385
127.292
127.126
112.845
112.639
77.318
77.000
76.683
70.154
69.983
69.934
55.128
55.085
53.279
51.626
51.538
42.672
42.614
27.482
26.927
21.979
21.804
21.508
Bn
iPrOOC
N
N
COOiPr
MeO
COOMe
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

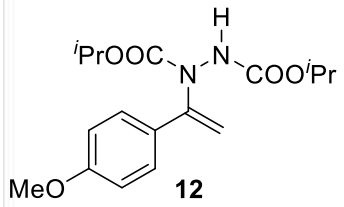

1j-5-38-1r.1.1.1r
7.236
7.229
7.223
7.212
7.207
7.139
7.131
7.126
7.115
7.110
7.103
6.819
6.798
6.791
6.786
6.774
6.769
6.762
6.660
6.625
6.514
6.480
5.847
4.956
4.941
4.936
4.925
4.917
4.910
4.900
4.894
4.887
4.882
4.872
4.864
4.856
4.841
4.825
3.781
3.775
3.368
3.350
1.983
1.967
1.949
1.296
1.283
1.278
1.261
1.248
1.235
1.218
1.206
1.194
1.178
1.162
1.137
1.133
1.122
1.118
0.900
0.894
0.884
0.866
COO^{i}Pr
^{i}PrOOC
N
N
MeO
COOMe
9
1.997
2.042
1.004
1.040
3.000
3.087
3.035
2.046
26.720
3.144
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


1j-5-38-1r.2.1.1r
176.351
176.197
159.528
159.480
153.080
152.848
151.743
136.852
136.125
131.674
131.530
126.307
124.959
124.604
112.768
112.558
111.144
110.609
77.318
77.000
76.682
70.653
70.426
70.087
55.073
51.649
51.616
42.683
31.653
30.229
30.088
29.536
29.442
28.654
28.615
27.494
27.404
27.373
22.585
21.976
21.888
21.811
21.765
21.665
14.067
COO^{i}Pr
^{i}PrOOC
N
N
MeO
COOMe
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


1j-5-44-1.1.1.1r
7.756
7.739
7.720
7.473
7.288
7.284
7.272
7.267
6.951
6.931
6.652
5.659
5.575
4.959
4.938
4.926
4.912
4.896
4.889
4.873
4.857
4.840
4.823
3.713
3.701
1.432
1.293
1.285
1.275
1.259
1.254
1.240
1.226
1.025
1.010
COO^{i}Pr
^{i}PrOOC
N
NH
COOMe
Cl
4c-Z
2.050
2.159
1.013
1.002
1.966
3.000
6.274
12.653
f1 (ppm)


1j-5-44-1.2.1.1r
177.975
177.679
155.312
154.896
153.991
153.737
138.358
136.707
135.683
134.062
133.920
132.613
128.942
128.092
127.991
77.318
77.000
76.683
71.045
70.815
69.804
69.632
52.819
52.613
43.524
26.493
26.416
21.910
21.646
COO^{i}Pr
^{i}PrOOC
N
NH
COOMe
Cl
4c-Z
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Nov19-2018-1j-3-9-26/1

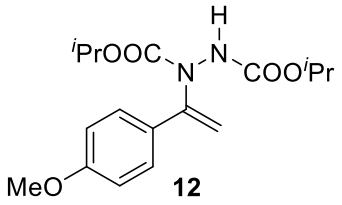


12

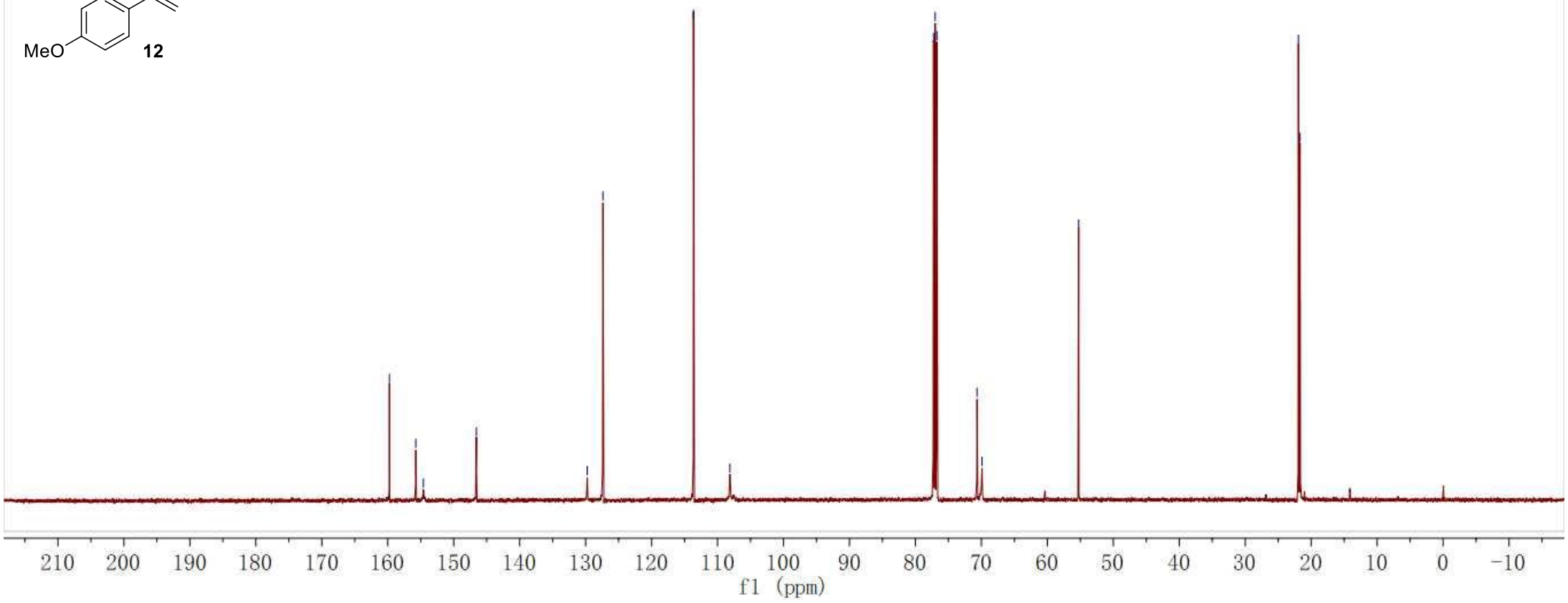
f1 (ppm)

Nov20-2018-1j-3-9-2b/1

159.742
155.748
154.593
146.568
129.761
127.371
113.639
108.133
77.255
77.000
76.747
70.656
69.909
55.256
21.940
21.688



12



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)