Supporting Information

For

MeOTf-induced Carboannulation of Arylnitriles and Aromatic Alkynes: A New Metal-free Strategy to Construct Indenones

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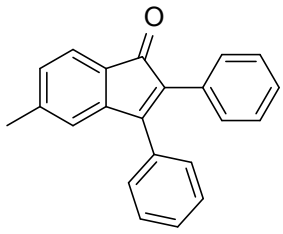
General Considerations

All manipulations were conducted in sealed tubes under an atmosphere of nitrogen. Unless otherwise noted, all starting materials were commercially available and were used without further purification. DCE was dried by 4Å molecule sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on JOEL 300MHz and 400MHz NMR spectrometer with TMS as internal standard. GC-MS spectra were recorded on Hewlett Packard GC-MS system. Single-crystal X-ray diffraction analysis for **4a** was carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo Kα radiation (λ= 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption.

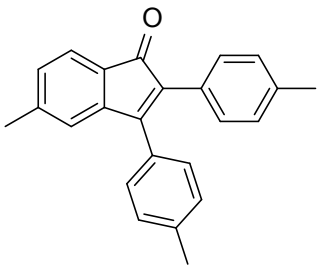
Experimental Procedures

Typical procedure for reaction of benzonitrile, MeOTf, and alkynes. To a 25 mL tube charged with nitrogen, was added *p*-tolunitrile **1a** (0.75 mmol), MeOTf (1.5 mmol), diphenylacetylene **2a** (0.5 mmol), DCE 2 mL. The tube was sealed and stirred for 12 h at 150 ^{o}C. The reaction mixture was quenched with 3M HCl and extracted with ethyl acetate (EA). Removing the solvent of reaction mixture and subsequent purification by column chromatography on silica gel (petroleum ether/ethyl acetate: 10:1) afforded **3aa** in 69% isolated yield.



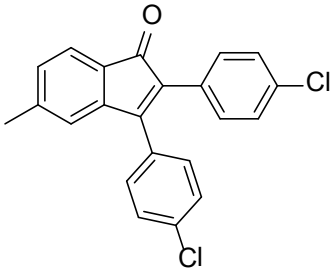
5-Methyl-2,3-diphenyl-1*H*-inden-1-one (**3aa)** [1]

69% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.35 (m, 5H), 7.27 – 7.22 (m, 6H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.93 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.3, 155.1, 145.9, 144.5, 133.1, 133.0, 131.0, 130.1, 129.3, 129.1, 128.9, 128.7, 128.5, 128.2, 127.8, 123.2, 122.7, 22.2. GC-MS: 296.



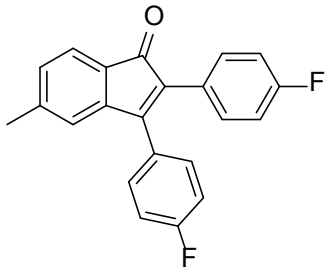
5-Methyl-2,3-di-p-tolyl-1*H*-inden-1-one (**3ab)** [2]

70% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.44 (d, *J* = 7.2 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.05 (m, 3H), 6.93 (s, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 196.6, 154.5, 146.0, 144.3, 139.3, 137.5, 132.5, 130.2, 130.0, 129.6, 128.9, 128.8, 128.7, 128.6, 128.2, 123.0, 122.5, 22.2, 21.6, 21.5. GC-MS: 324.



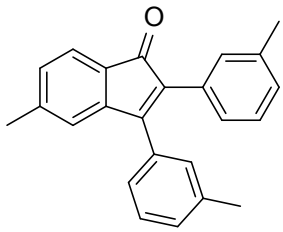
2,3-Bis(4-chlorophenyl)-5-methyl-1*H*-inden-1-one (**3ac)**

67% yield. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.33 – 7.16 (m, 6H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.90 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 195.6, 154.0, 145.2, 144.8, 135.5, 134.0, 132.0, 131.3, 131.1, 130.0, 129.5, 129.1, 128.6, 128.2, 123.5, 122.6, 22.2. GC-MS: 364. HRMS (ESI mode) calcd for $C_{22}H_{14}Cl_2O+H^+$ 365.0500, found 365.0497.



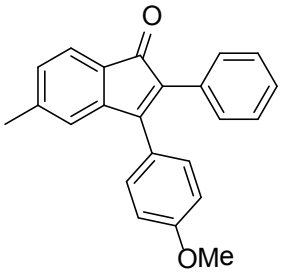
2,3-Bis(4-fluorophenyl)-5-methyl-1*H*-inden-1-one (**3ad)**

56% yield. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.27 – 7.20 (m, 2H), 7.17 – 7.06 (m, 3H), 7.00-6.93 (m, 2H), 6.91 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 196.0, 164.5 (d, *J* = 58.0 Hz), 161.2 (d, *J* = 56.2 Hz), 153.8, 145.5, 144.7, 132.0, 131.8 (d, *J* = 8.0 Hz), 130.6 (d, *J* = 8.2 Hz), 129.2, 128.7 (d, *J* = 3.3 Hz), 128.2, 126.8 (d, *J* = 3.4 Hz), 123.3, 122.5, 116.3 (d, *J* = 21.7 Hz), 115.4 (d, *J* = 21.4 Hz), 22.2. GC-MS: 332. HRMS (ESI mode) calcd for $C_{22}H_{14}F_2O+H^+$ 333.1091, found 333.1090.



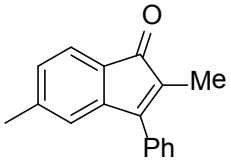
5-Methyl-2,3-di-m-tolyl-1*H*-inden-1-one (**3ae)**

65% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.32 – 6.98 (m, 9H), 6.92 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.5, 155.1, 146.0, 144.4, 138.5, 137.5, 133.0, 132.9, 130.9, 130.7, 130.0, 129.5, 128.9, 128.7, 128.5, 127.9, 127.1, 125.7, 123.0, 122.6, 22.2, 21.6, 21.6. GC-MS: 324. HRMS (ESI mode) calcd for $C_{24}H_{20}O+H^+$ 325.1592, found 325.1589.



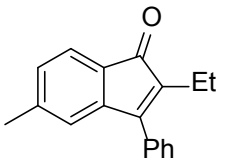
3-(4-Methoxyphenyl)-5-methyl-2-phenyl-1*H*-inden-1-one (**3ag)**

31% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 6.5 Hz, 2H), 7.29 – 7.22 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.99 (s, 1H), 6.93 (d, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.4, 160.5, 154.9, 145.8, 144.3, 132.2, 132.86, 131.4, 130.3, 130.2, 129.0, 128.8, 128.2, 127.7, 125.1, 123.0, 122.7, 114.3, 55.4, 22.3. GC-MS: 326. HRMS (ESI mode) calcd for $C_{23}H_{18}O_2$+H^+ 327.1385, found 327.1387.



2,5-Dimethyl-3-phenyl-1*H*-inden-1-one (**3ah)**

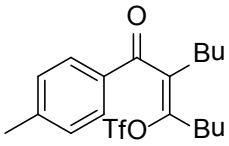
45% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.54 – 7.43 (m, 5H), 7.36 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.85 (s, 1H), 2.30 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 198.1, 154.3, 146.3, 144.1, 132.9, 131.6, 129.7, 129.1, 128.8, 128.2, 128.1, 122.7, 121.9, 22.1, 8.7. GC-MS: 234. HRMS (ESI mode) calcd for $C_{17}H_{14}O$+H^+ 235.1123, found 235.1123.



2-Ethyl-5-methyl-3-phenyl-1*H*-inden-1-one (**3ai)**

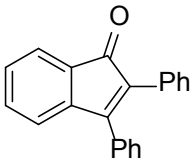
50% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.53 – 7.42 (m, 5H), 7.35 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.79 (s, 1H), 2.34 (q, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 198.0, 154.3, 146.4, 144.1, 137.2, 133.0, 129.1, 128.8, 128.7, 128.2, 127.9, 122.6, 122.0,

22.1, 16.8, 14.1. GC-MS: 248. HRMS (ESI mode) calcd for $C_{18}H_{16}O+H^+$ 249.1279, found 249.1274.



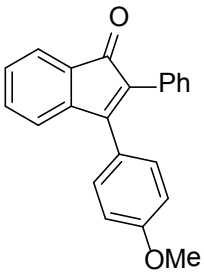
6-(4-Methylbenzoyl)dec-5-en-5-yl trifluoromethanesulfonate (**3aj)**

26% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.50 – 2.42 (m, 5H), 2.18 – 2.12 (t, *J* = 7.6 Hz, 2H), 1.53 – 1.16 (m, 8H), 0.88 – 0.78 (m, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 194.9, 148.2, 145.5, 134.1, 133.3, 129.9, 129.7, 118.5 (q, *J* = 313.7 Hz), 32.4, 29.6, 29.5, 28.5, 22.5, 21.9, 21.8, 13.6, 13.6. HRMS (ESI mode) calcd for $C_{19}H_{24}F_3O_4S+H^+$ 406.1426, found 406.1423.



2,3-Diphenyl-1*H*-inden-1-one (**3ba)** [1]

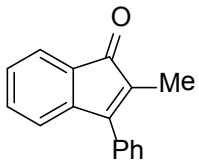
64% yield (160 °C). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.58 (d, *J* = 7.0 Hz, 1H), 7.46 – 7.33 (m, 6H), 7.32 – 7.20 (m, 6H), 7.14 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.6, 155.5, 145.4, 133.6, 132.9, 132.6, 130.9, 130.1, 129.4, 129.1, 128.9, 128.6, 128.2, 127.9, 123.1, 121.4. GC-MS: 282.



3-(4-Methoxyphenyl)-2-phenyl-1*H*-inden-1-one (**3bg)** [3]

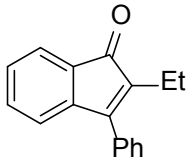
21% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.18–7.37 (m, 11 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 3.85 (s, 3 H). ^{13}C NMR (101 MHz,

CHLOROFORM-D) δ196.7, 160.6, 155.3, 145.3, 133.4, 131.8, 131.2, 130.4, 130.1, 129.0, 128.2, 127.7, 124.9, 123.0, 121.4, 114.3, 55.4. GC-MS: 312.



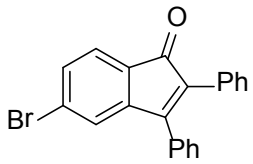
2-Methyl-3-phenyl-1*H*-inden-1-one (**3bh)** [1]

27% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.54 – 7.42 (m, 6H), 7.28 (td, *J* = 7.7, 1.2 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 198.4, 154.8, 145.8, 133.2, 132.8, 131.2, 131.1, 129.3, 128.8, 128.2, 128.1, 122.6, 120.5, 8.7. GC-MS: 220.



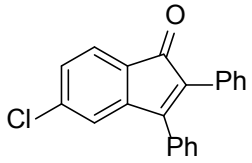
2-Ethyl-3-phenyl-1*H*-inden-1-one (**3bi)**

28% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.53 – 7.42 (m, 6H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 198.4, 154.8, 146.0, 136.8, 133.3, 133.0, 131.2, 129.3, 128.9, 128.3, 127.9, 122.6, 120.7, 16.8, 14.1. GC-MS: 234. HRMS (ESI mode) calcd for $C_{17}H_{14}O+H^{+}$ 235.1123, found 235.1121.



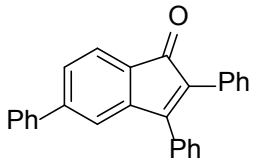
5-Bromo-2,3-diphenyl-1*H*-inden-1-one (**3ca)** [1]

70% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.45 – 7.40 (m, 5H), 7.36 – 7.33 (m, 2H), 7.25 – 7.26 (m, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 195.3, 154.2, 147.4, 133.5, 132.2, 131.7, 130.3, 130.1, 129.7, 129.4, 129.1, 128.5, 128.4, 128.2, 128.2, 124.8, 124.2. GC-MS: 360, 362.



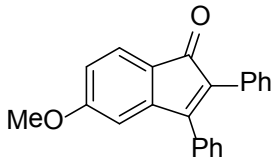
5-Chloro-2,3-diphenyl-1*H*-inden-1-one (**3da)** [1]

67% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.37 – 7.33 (m, 2H), 7.28 – 7.24 (m, 6H), 7.11 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 195.1, 154.1, 147.3, 139.8, 133.6, 132.3, 130.4, 130.1, 129.7, 129.1, 129.0, 128.6, 128.5, 128.2, 128.2, 124.0, 122.1. GC-MS: 316.



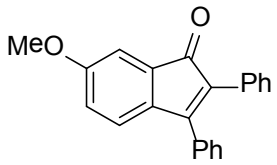
2,3,5-Triphenyl-1*H*-inden-1-one (**3ea)** [1]

72% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.66 (d, *J* = 7.4 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.50 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.47 – 7.37 (m, 8H), 7.36 (d, *J* = 1.0 Hz, 1H), 7.33 – 7.23 (m, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.1, 154.9, 146.8, 146.2, 140.4, 133.3, 132.8, 130.9, 130.1, 129.6, 129.4, 129.0, 128.6, 128.4, 128.2, 127.9, 127.6, 127.3, 123.5, 120.6. GC-MS: 358.



5-Methoxy-2,3-diphenyl-1*H*-inden-1-one (**3ha)** [1]

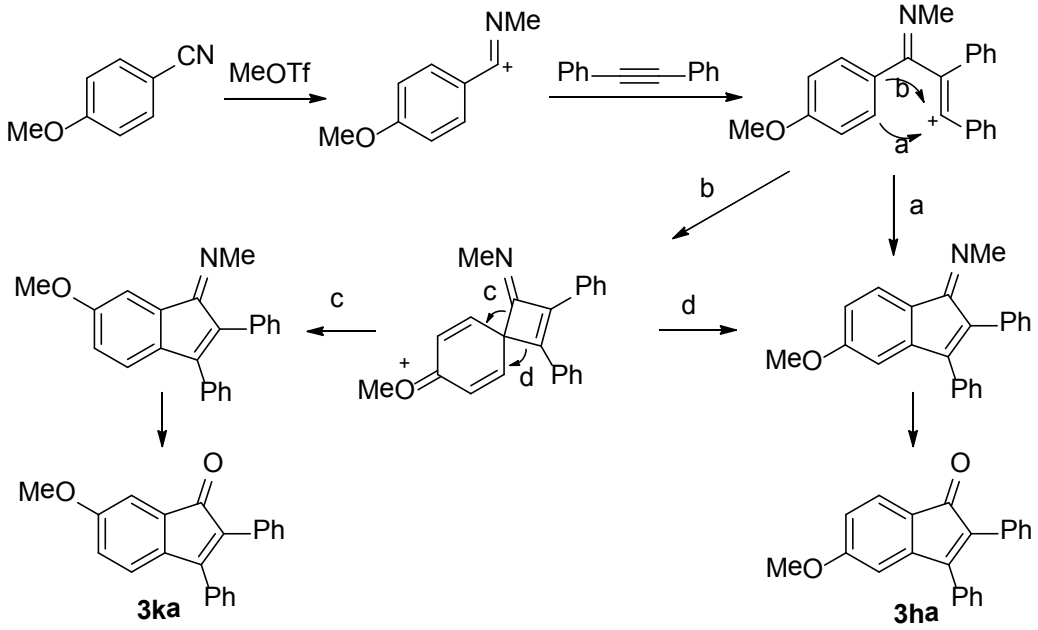
22% yield . ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.32 (m, 5H), 7.26 – 7.23 (m, 5H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.66 (dd, *J* = 7.9, 2.1 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 195.2, 164.6, 153.3, 148.1, 134.0, 132.8, 131.0, 130.1, 129.3, 128.9, 128.7, 128.2, 127.9, 125.0, 123.6, 110.6, 110.4, 55.9. GC-MS: 312.

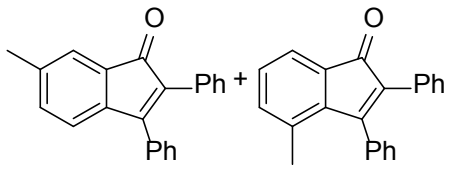


6-Methoxy-2,3-diphenyl-1*H*-inden-1-one (**3ka**) [4]

10% yield from *p*-MeO-C_6H_4-CN and 31% yield from *m*-MeO-C_6H_4-CN. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.42 – 7.34 (m, 5H), 7.27 – 7.20 (m, 5H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.78 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.2, 161.2, 156.5, 137.0, 133.0, 131.5, 131.1, 129.9, 129.4, 128.8, 128.5, 128.1, 127.7, 127.6, 122.3, 116.4, 110.7, 55.9. GC-MS: 312.

Plausible mechanism of reaction of *p*-MeO-C_6H_4-CN with diphenylacetylene

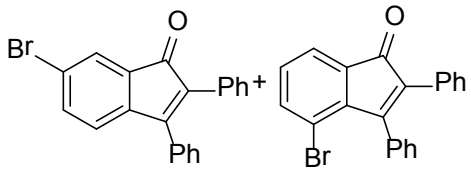




4-Methyl-2,3-diphenyl-1*H*-inden-1-one (**3ia**) and 6-methyl-2,3-diphenyl-1*H*-inden-1-one (**3ia′**) (3:1) [1]

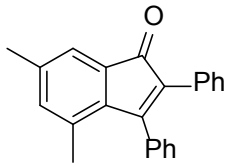
65% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.45 – 7.37 (m), 7.33 – 7.11 (m), 7.08 (d, *J* = 7.8 Hz, 0.3H), 7.02 (d, *J* = 7.4 Hz, 1H), 2.37 (s, 3H), 1.79 (s, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 196.8, 158.3, 155.7, 142.5, 142.1,

139.4, 137.9, 136.1, 133.4, 133.1, 133.0, 131.9, 131.2, 131.0, 130.8, 130.0, 129.9, 129.3, 129.0, 128.8, 128.6, 128.5, 128.1, 127.9, 127.9, 127.7, 127.6, 124.2, 121.2, 121.0, 21.5, 19.6. GC-MS: 296.



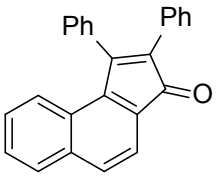
4-Bromo-2,3-diphenyl-1*H*-inden-1-one (**3ja)** and 6-bromo-2,3-diphenyl-1*H*-inden-1-one (**3ja′)** (1:1.5) [1]

63% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (d, *J* = 1.7 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 1.5H), 7.49 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1.5H), 7.43 – 7.37 (m), 7.33 (ddd, *J* = 9.6, 5.9, 2.3 Hz, 6H), 7.25 (s), 7.20 (s), 7.13 – 7.07 (t, *J* = 7.6 Hz, 1.5H), 7.01 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 195.3, 195.2, 157.3, 155.2, 143.9, 142.4, 139.9, 135.8, 135.1, 133.4, 132.9, 132.5, 132.4, 132.3, 130.4, 130.2, 130.0, 129.7, 129.0, 128.8, 128.8, 128.6, 128.5, 128.3, 128.1, 128.0, 126.4, 123.0, 122.7, 122.0, 116.8. GC-MS: 360, 362.



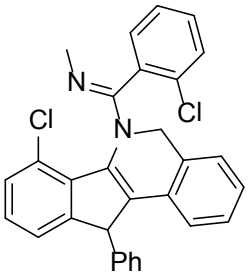
4,6-Dimethyl-2,3-diphenyl-1*H*-inden-1-one (**3la)**

68% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.44 – 7.35 (m, 3H), 7.31 – 7.26 (m, 3H), 7.21 – 7.15 (m, 5H), 6.89 (s, 1H), 2.31 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 197.2, 158.6, 139.4, 139.2, 137.8, 136.2, 133.1, 132.9, 131.4, 131.0, 129.9, 128.9, 128.5, 127.9, 127.4, 122.2, 21.2, 19.4. GC-MS: 310. HRMS (ESI mode) calcd for $C_{23}H_{18}O+H^{+}$ 311.1436, found 311.1433.



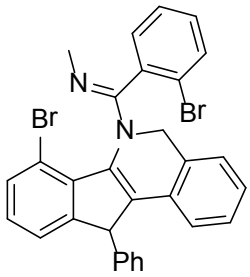
1,2-Diphenyl-3*H*-cyclopenta[a]naphthalen-3-one (**3ma)**

46% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.44 – 7.35 (m, 3H), 7.25 – 7.18 (m, 6H), 7.17 – 7.11 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 197.8, 156.9, 143.2, 138.4, 135.9, 132.5, 130.7, 130.1, 129.9, 129.4, 128.9, 128.9, 128.6, 128.0, 127.9, 127.6, 127.5, 127.0, 126.8, 125.0, 119.2. GC-MS: 332. HRMS (ESI mode) calcd for $C_{25}H_{16}O+H^{+}$ 333.1279, found 333.1272.



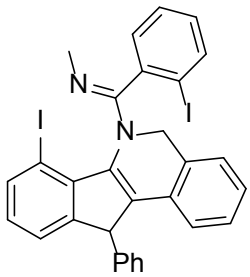
(*E*)-*N*-((7-Chloro-11-phenyl-5*H*-indeno[1,2-*c*]isoquinolin-6(11*H*)-yl)(2-chlorophenyl) methylene)methanamine (**4a)**

46% yield based on nitrile. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.77 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.56 – 7.41 (m, 3H), 7.29 – 7.16 (m, 6H), 7.15 – 6.99 (m, 6H), 5.20 (s, 1H), 4.36 (d, *J* = 15.2 Hz, 1H), 4.32 (d, *J* = 15.2 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.0, 150.6, 142.2, 139.8, 137.5, 135.2, 133.7, 133.1, 131.3, 130.6, 129.6, 129.5, 128.9, 128.1, 127.6, 127.1, 126.8, 126.5, 125.5, 123.4, 123.0, 52.0, 50.9, 38.5. HRMS (ESI mode) calcd for $C_{30}H_{22}Cl_2N_2+H^{+}$ 481.1238, found 481.1235.



(*E*)-*N*-((7-Bromo-11-phenyl-5*H*-indeno[1,2-*c*]isoquinolin-6(11*H*)-yl)(2-bromophenyl) methylene)methanamine (**4b)**

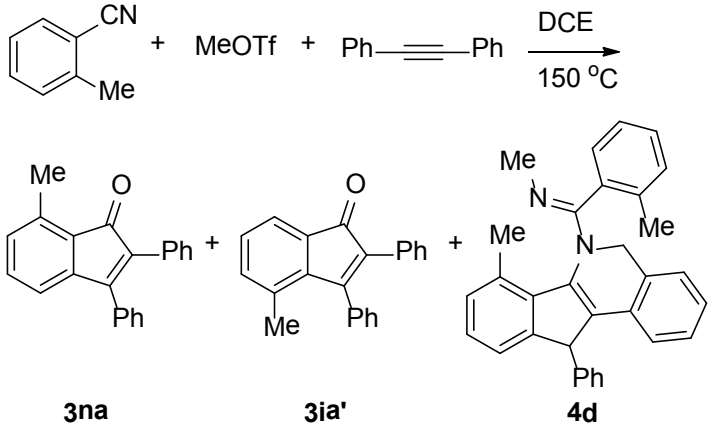
39% yield based on nitrile. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.86 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 – 6.92 (m, 11H), 5.21 (s, 1H), 4.37 (d, *J* = 15.2 Hz, 1H), 4.31 (d, *J* = 15.3 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 158.5, 150.8, 139.6, 135.0, 133.0, 132.3, 131.7, 130.8, 130.5, 129.6, 129.0, 128.2, 127.6, 127.2, 127.1, 127.0, 125.7, 123.6, 123.5, 123.2, 114.8, 52.1, 51.1, 38.5. HRMS (ESI mode) calcd for $C_{30}H_{22}Br_2N_2$+H^+ 571.0208, found 571.0210.



(*E*)-*N*-((7-Iodo-11-phenyl-5*H*-indeno[1,2-*c*]isoquinolin-6(11*H*)-yl)(2-iodophenyl)met hylene)methanamine (**4c)**

43% yield based on nitrile. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.15 (m, 7H), 7.11 – 7.07 (m, 3H), 7.03 – 6.96 (m, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 5.18 (s, 1H), 4.34 (d, *J* = 15.4 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 1H), 2.88 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 160.9, 150.4, 139.7, 139.6, 139.1, 132.4, 130.6, 130.5, 129.2, 128.9, 128.6, 128.2, 127.6, 127.1, 127.0, 126.0, 124.3, 123.6, 97.7, 86.7, 52.0, 51.2, 38.5. HRMS (ESI mode) calcd for $C_{30}H_{22}I_2N_2$+H^+ 664.9951, found 664.9952.

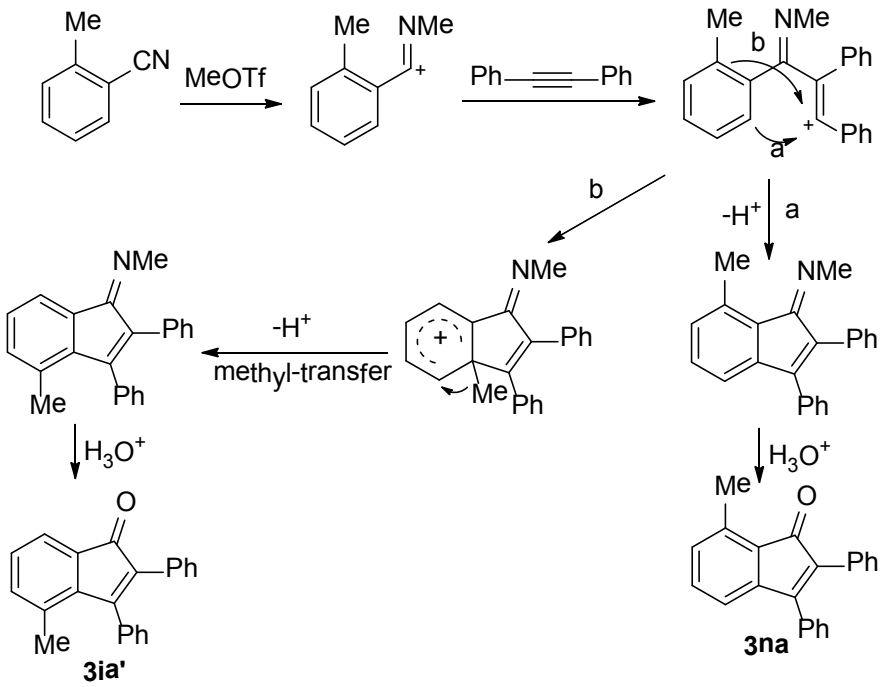
When *p*-tolunitrile was employed as substrate, the reaction yielded a mixture of indenones and indeno[1,2-*c*]isoquinoline. The normal product indenone **3na** and rearranged indenone **3ia′** were isolated in 36% combined yield and indeno[1,2-*c*]isoquinoline **5d** was observed in about 10% NMR yield.



4-Methyl-2,3-diphenyl-1*H*-inden-1-one **(3na)** and 7-methyl-2,3-diphenyl-1*H*-inden-1-one **(3ia′)** (1:1.2) [5]

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 – 7.33 (m), 7.32 – 7.12 (m), 7.08 (d, *J* = 7.8 Hz, 1.2H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 2.62 (s, 3H), 1.79 (s, 3.6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 197.7, 196.9, 158.3, 154.4, 145.8, 142.1, 138.1, 137.9, 136.0, 133.7, 133.1, 133.0, 132.7, 132.5, 132.3, 131.0, 130.9, 130.8, 130.1, 129.9, 129.2, 128.9, 128.8, 128.7, 128.5, 128.1, 127.9, 127.7, 127.6, 121.0, 119.3, 19.6, 17.5. GC-MS: 296.

Plausible mechanism of for the formation of **3na** and **3ia′**



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2. Y. Kuninobu, T. Matsuki and K. Takai, *Org. Lett.* 2010, **12**, 2948.

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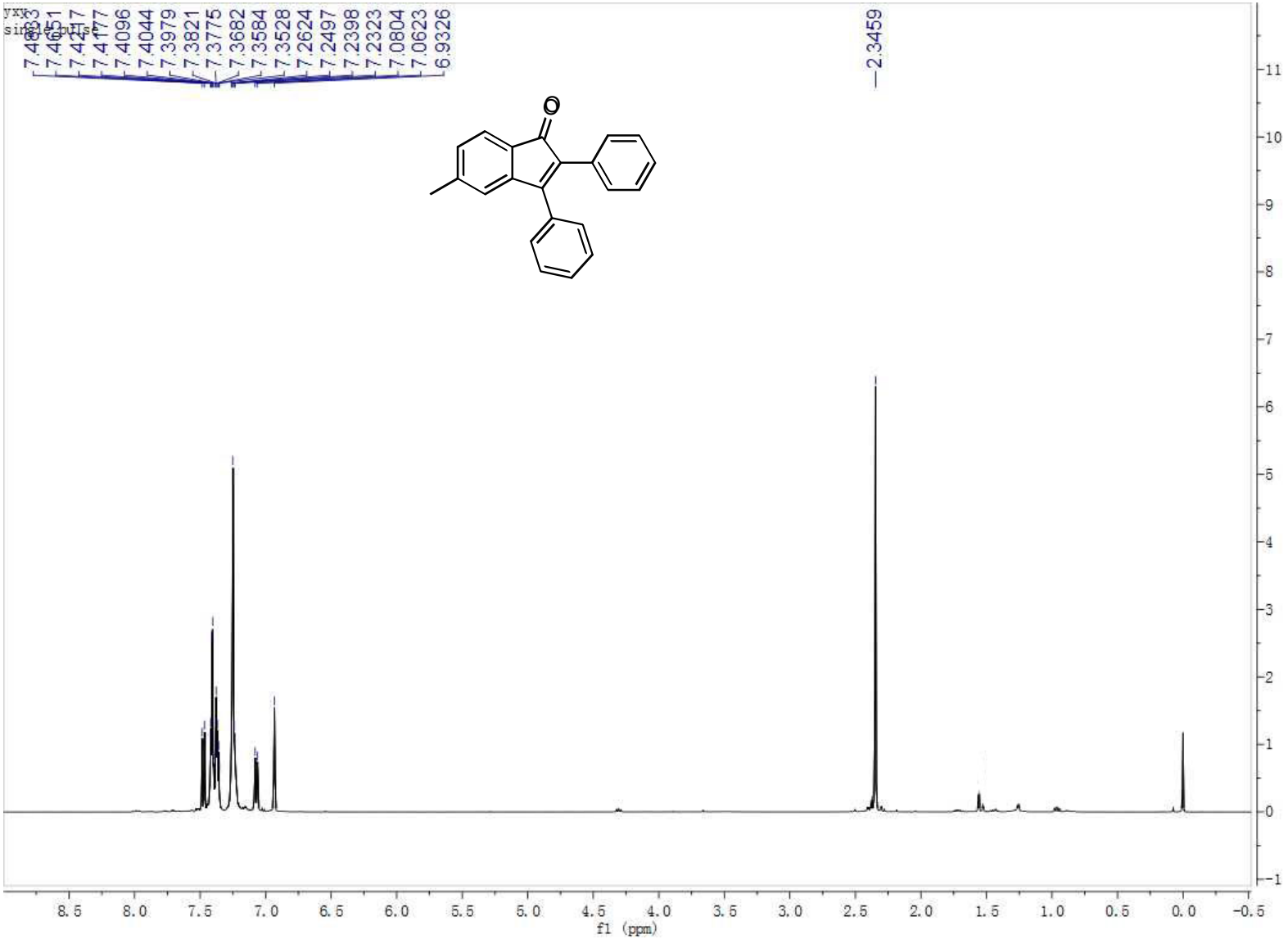
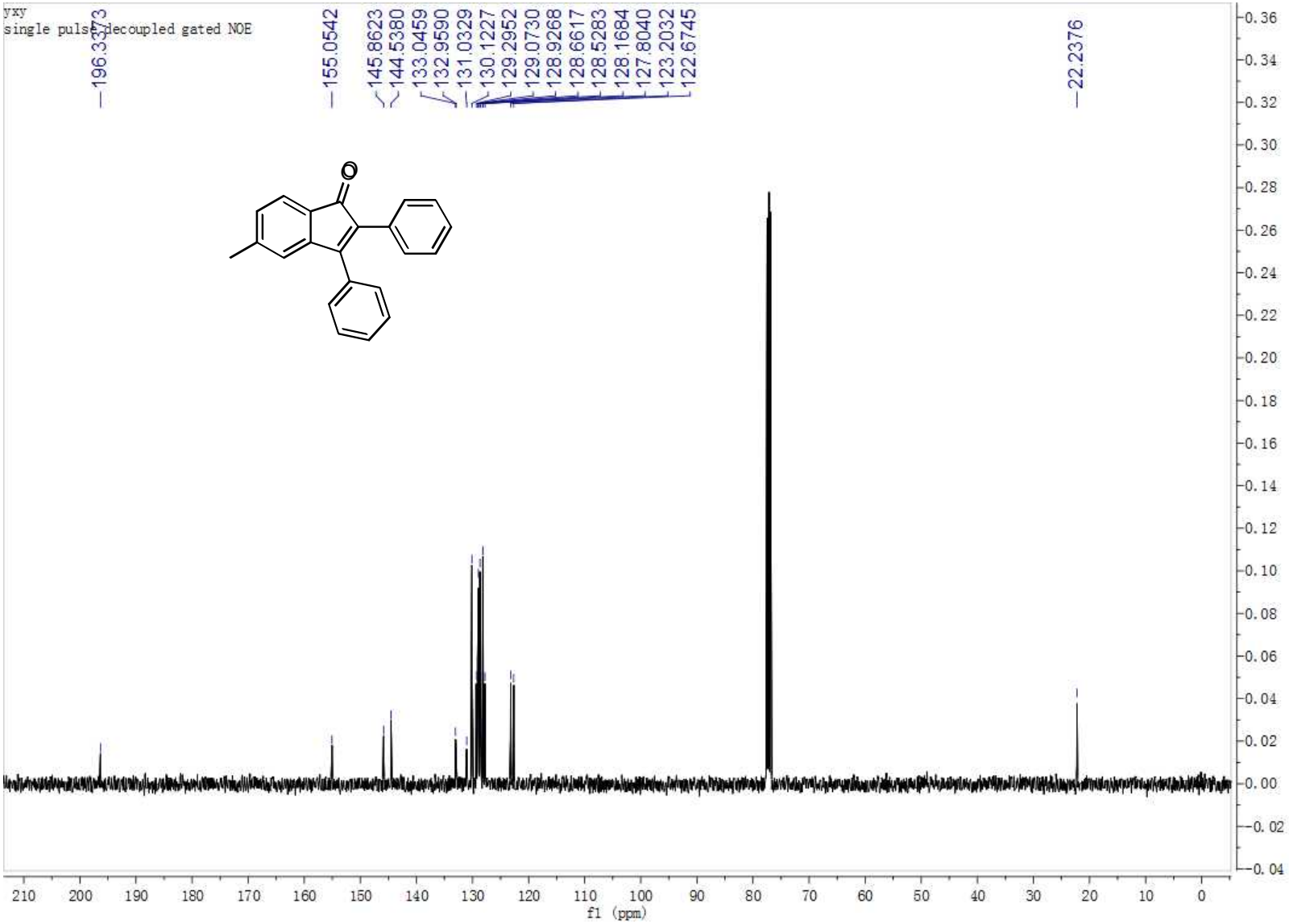
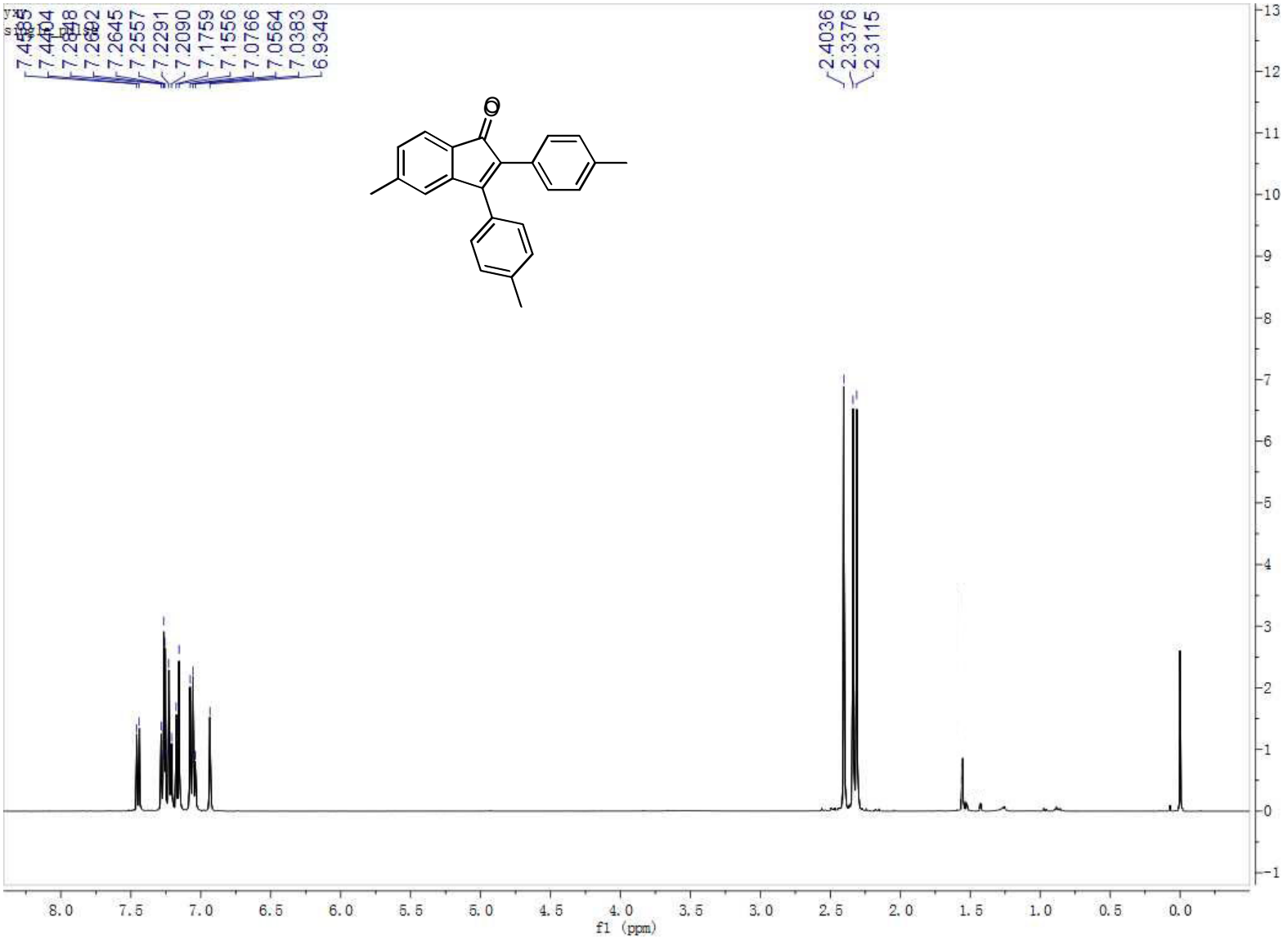
Copies of ^{1}H and ^{13}C NMR Spectra



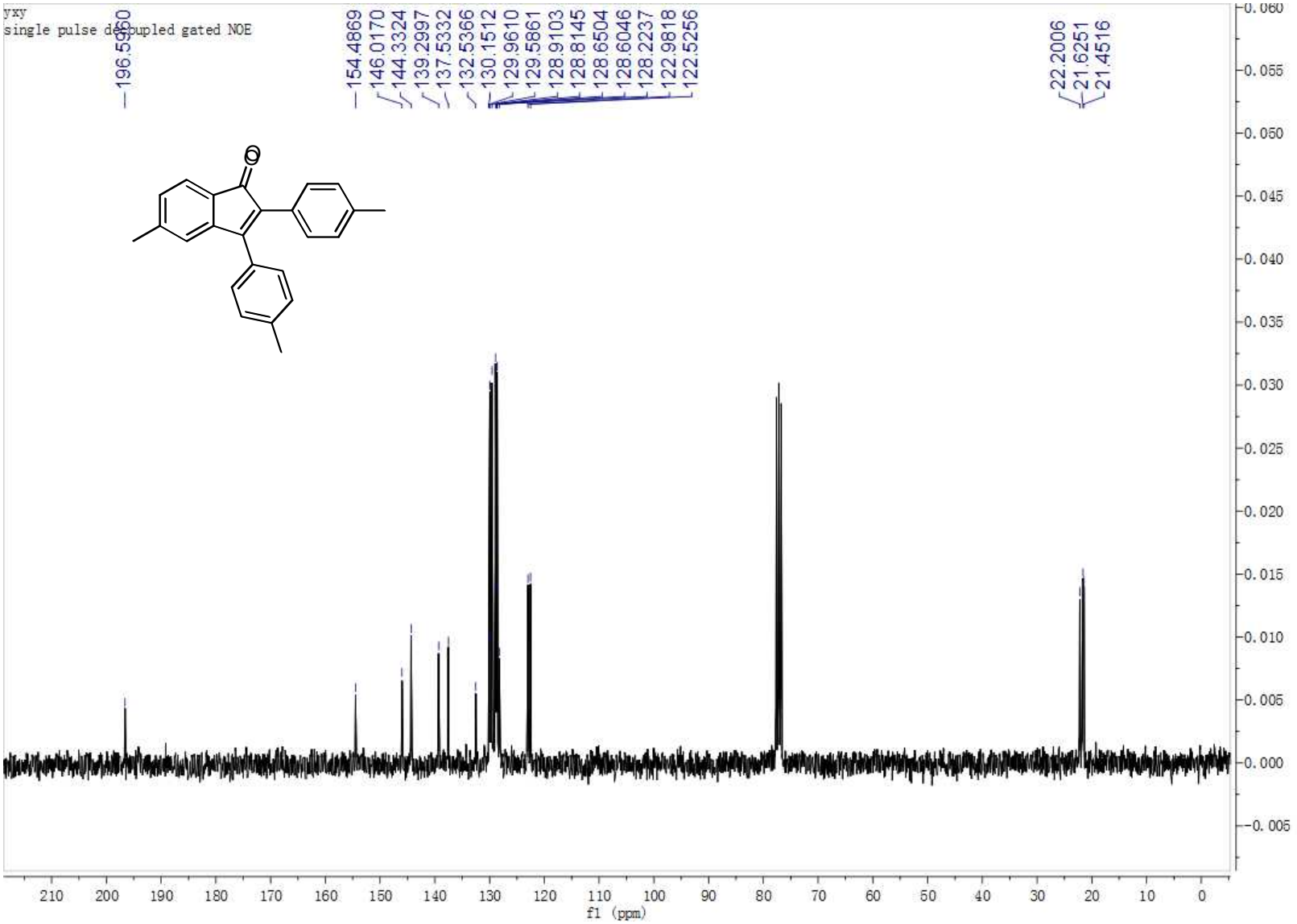
^{1}H NMR for compound **3aa**



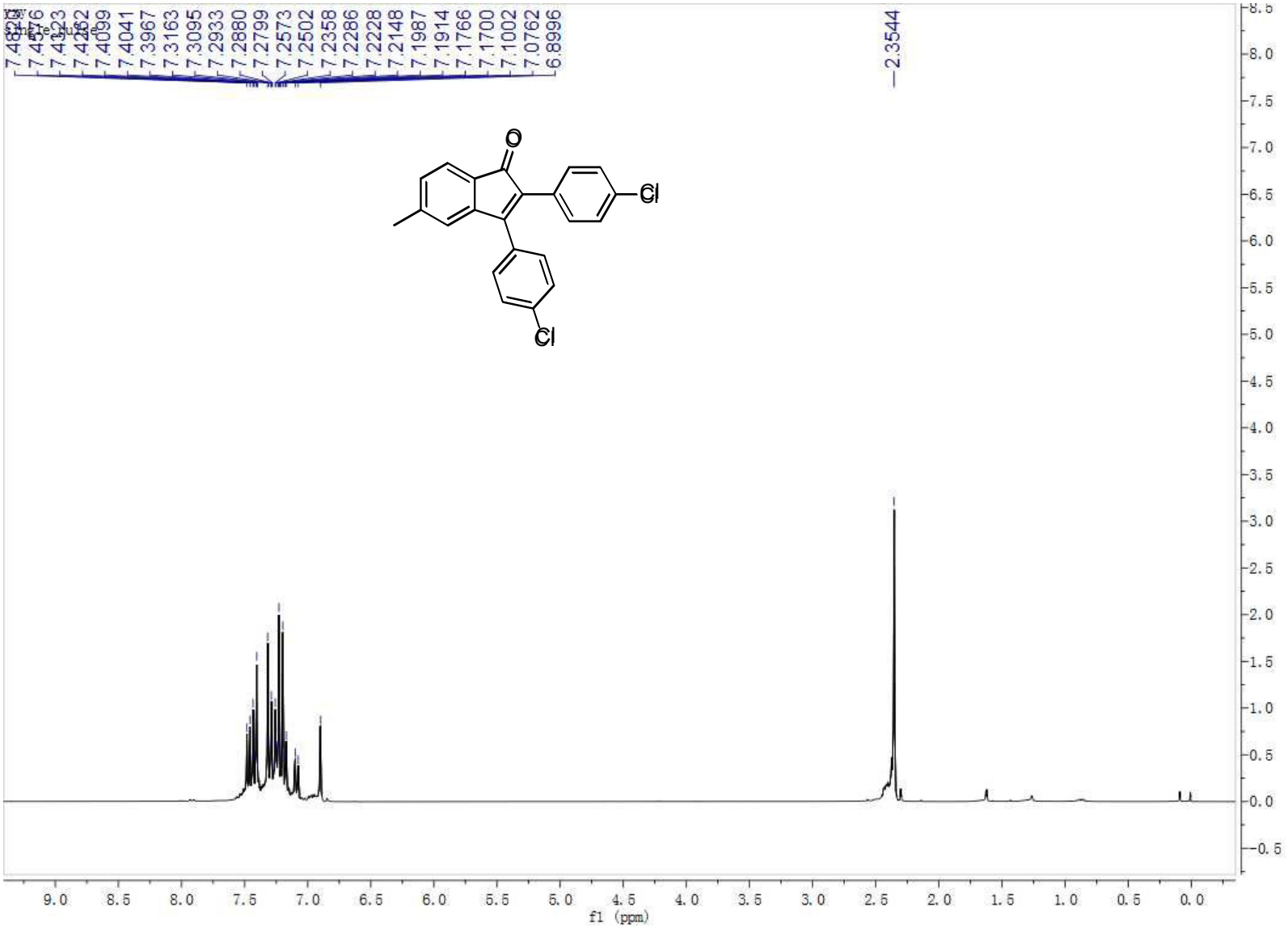
^{13}C NMR for compound **3aa**



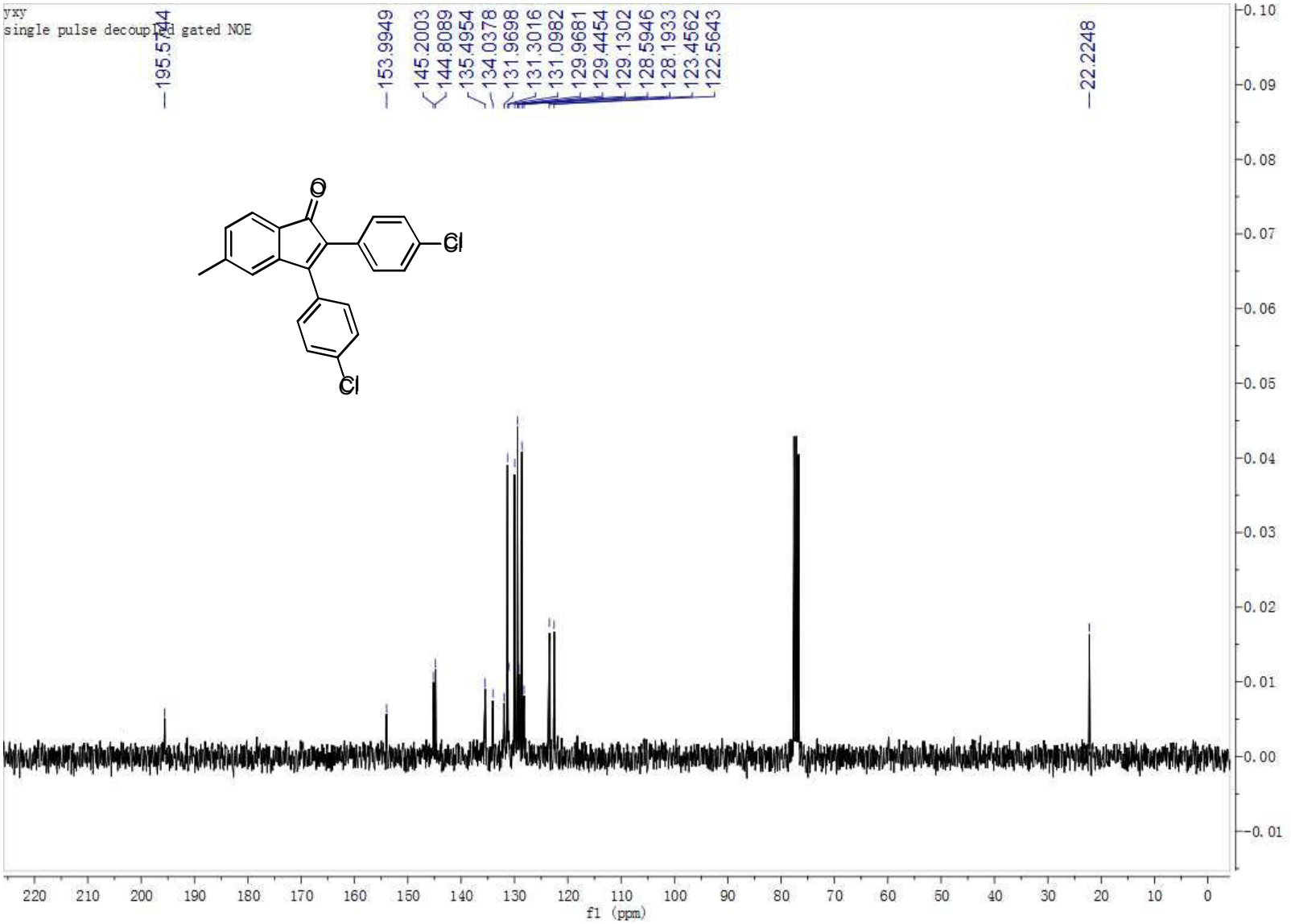
^{1}H NMR for compound **3ab**



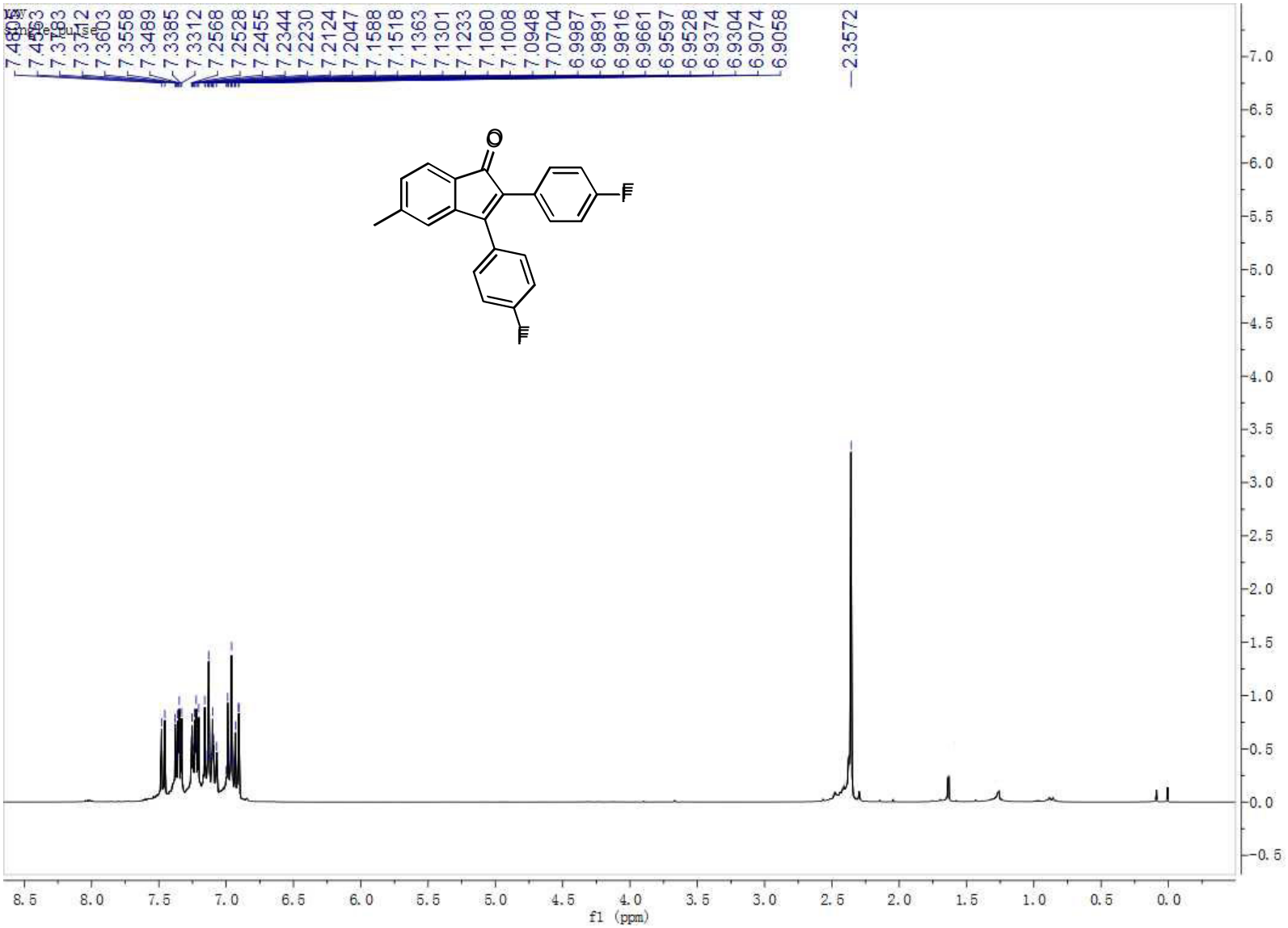
^{13}C NMR for compound **3ab**



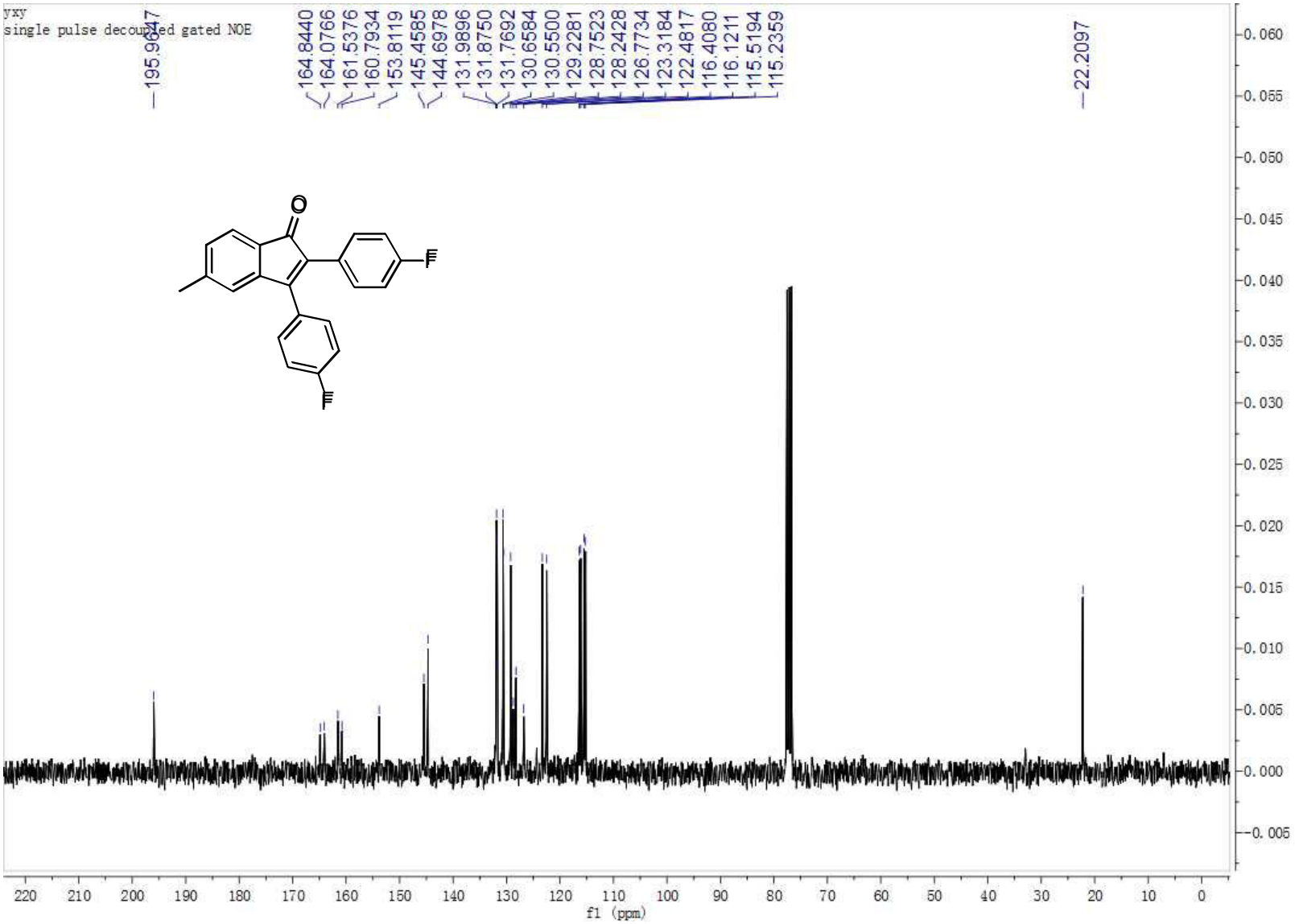
^{1}H NMR for compound **3ac**



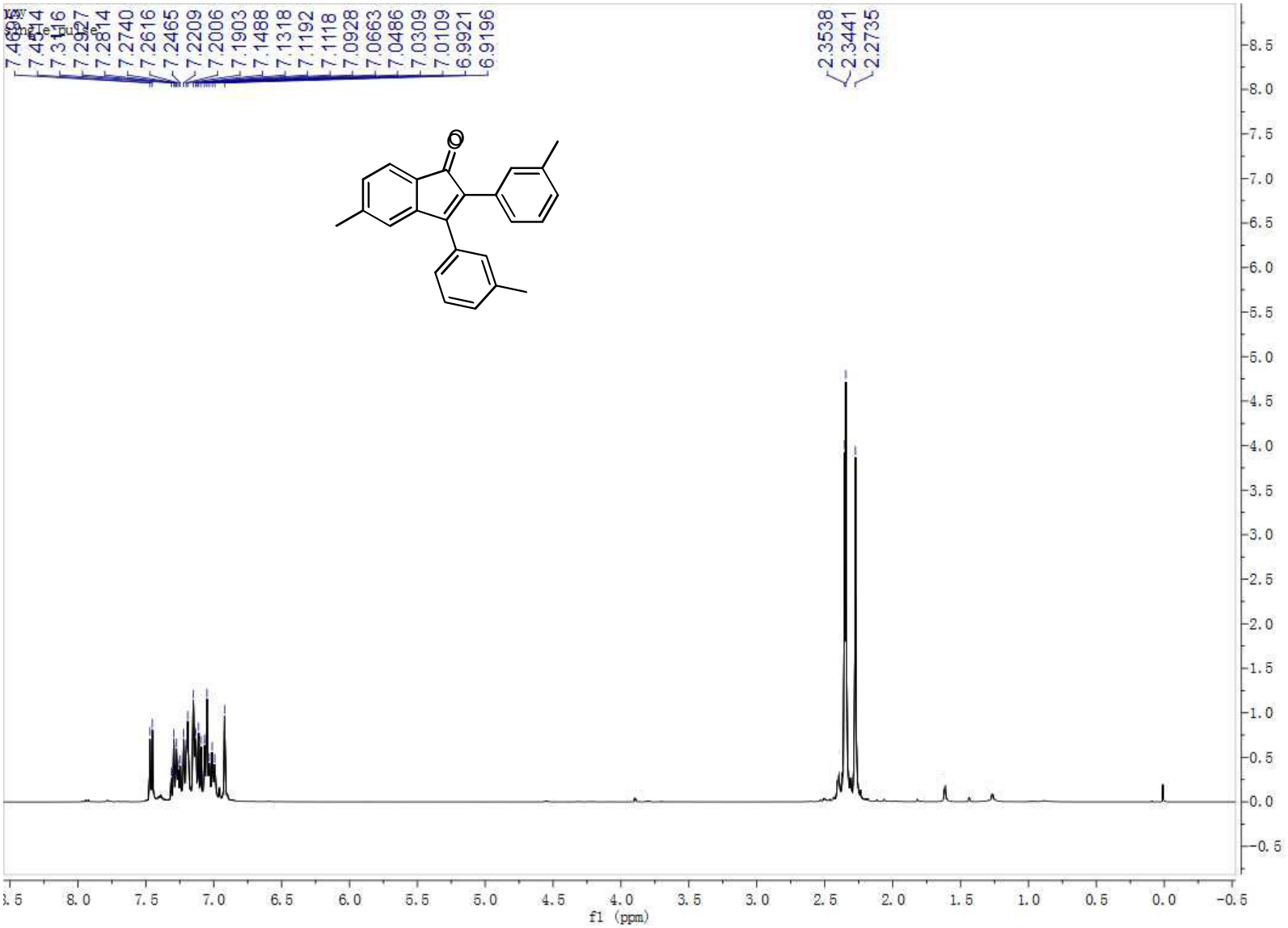
^{13}C NMR for compound **3ac**



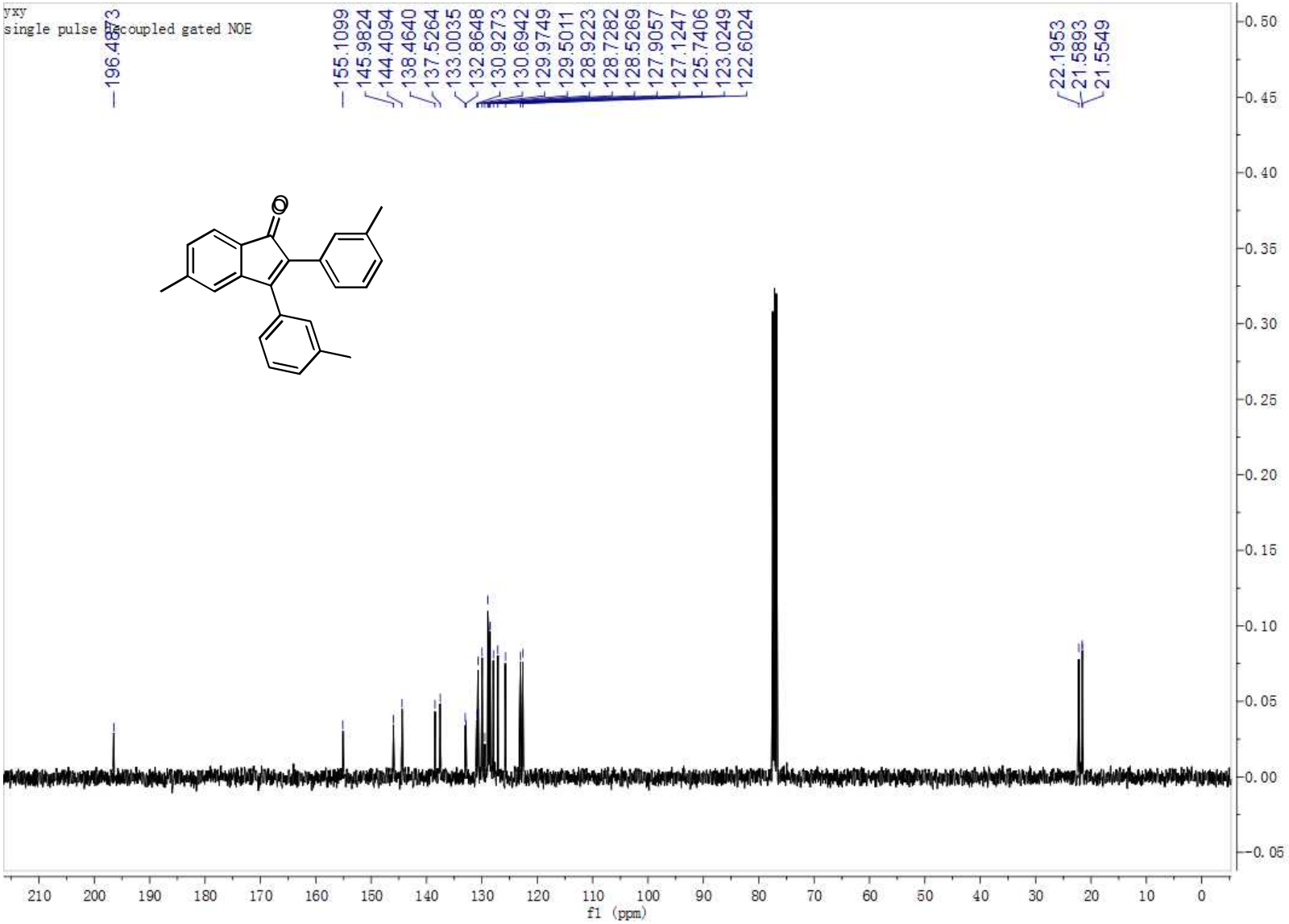
^{1}H NMR for compound **3ad**



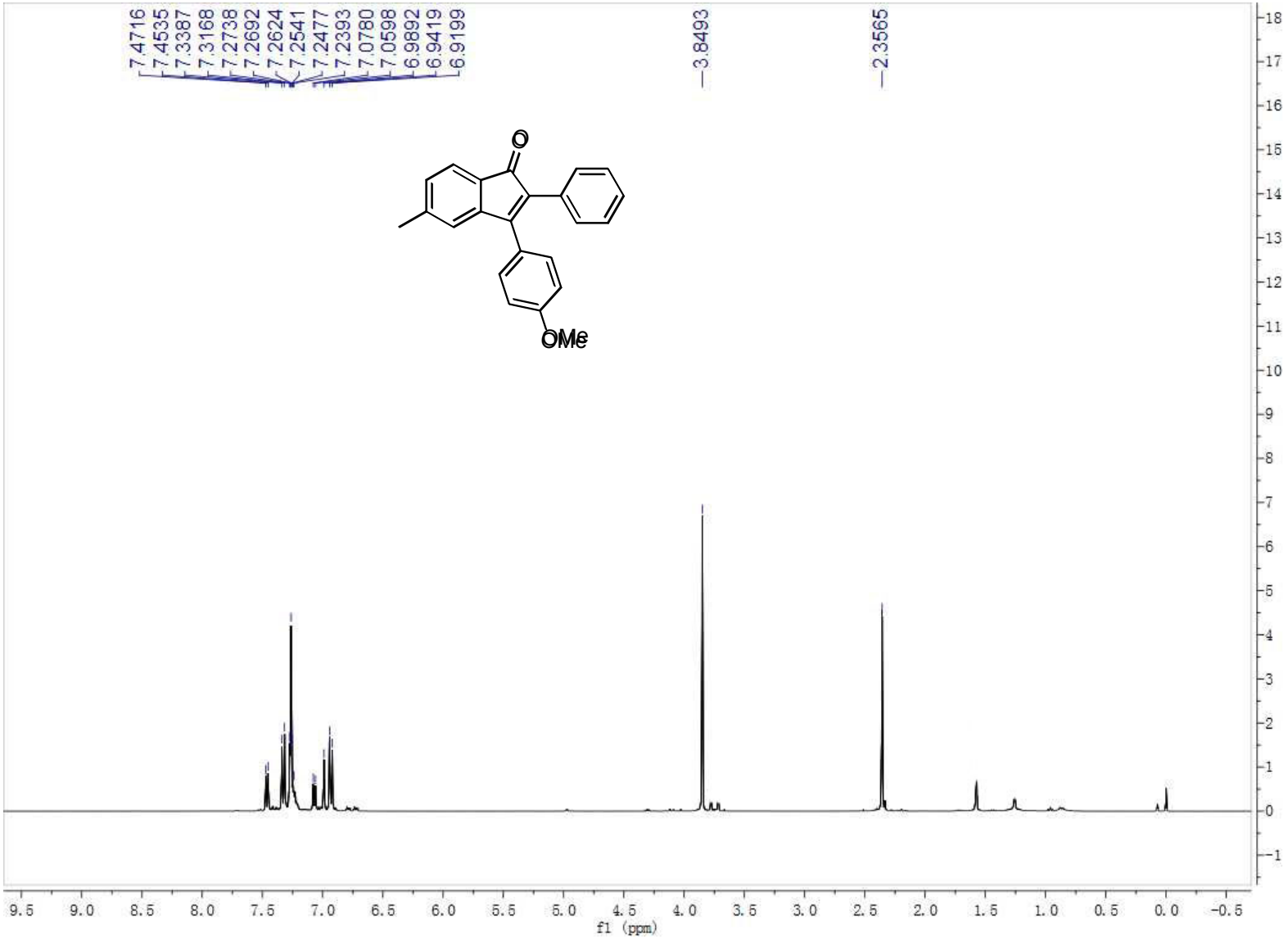
^{13}C NMR for compound **3ad**



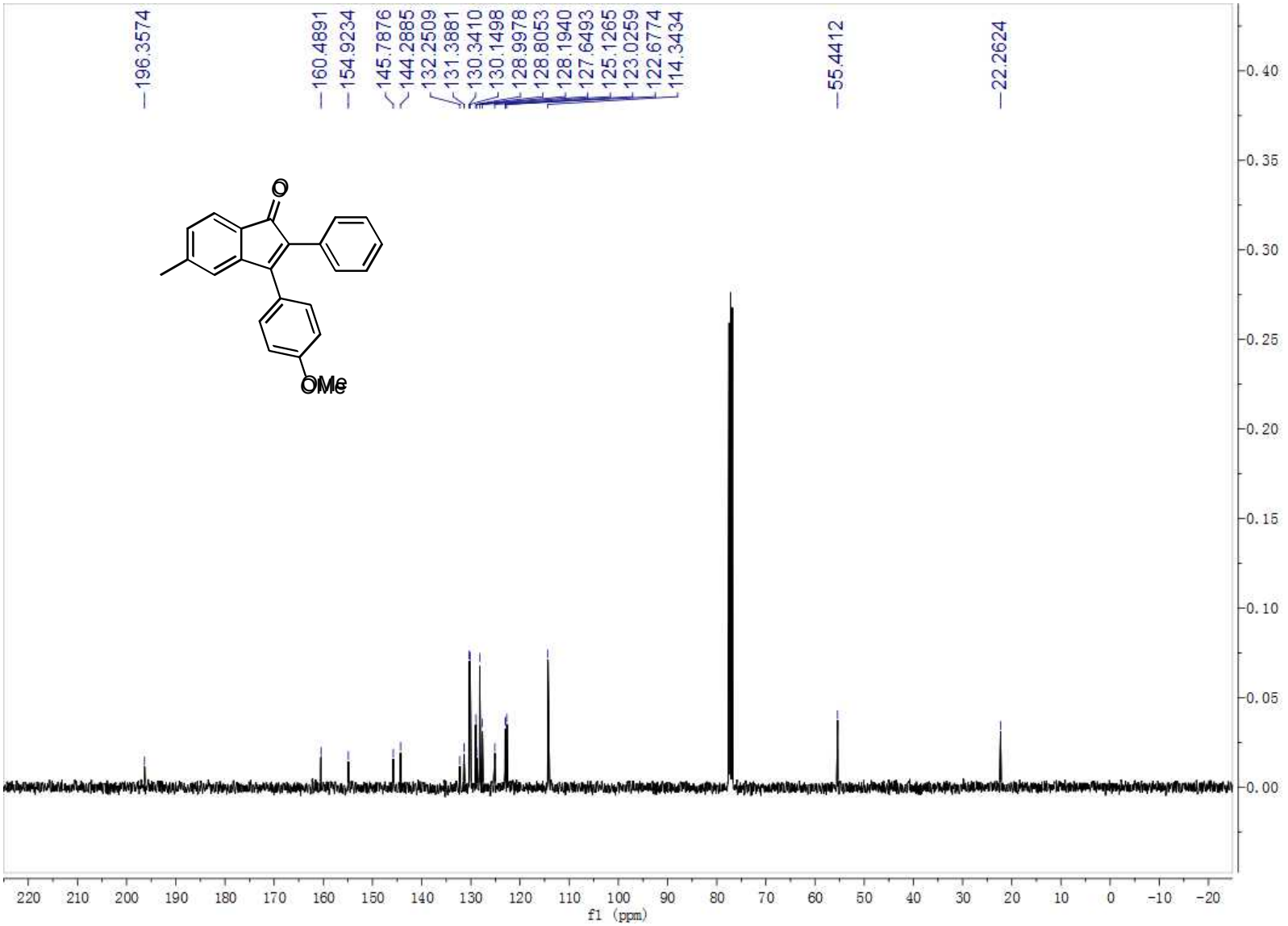
^{1}H NMR for compound **3ae**



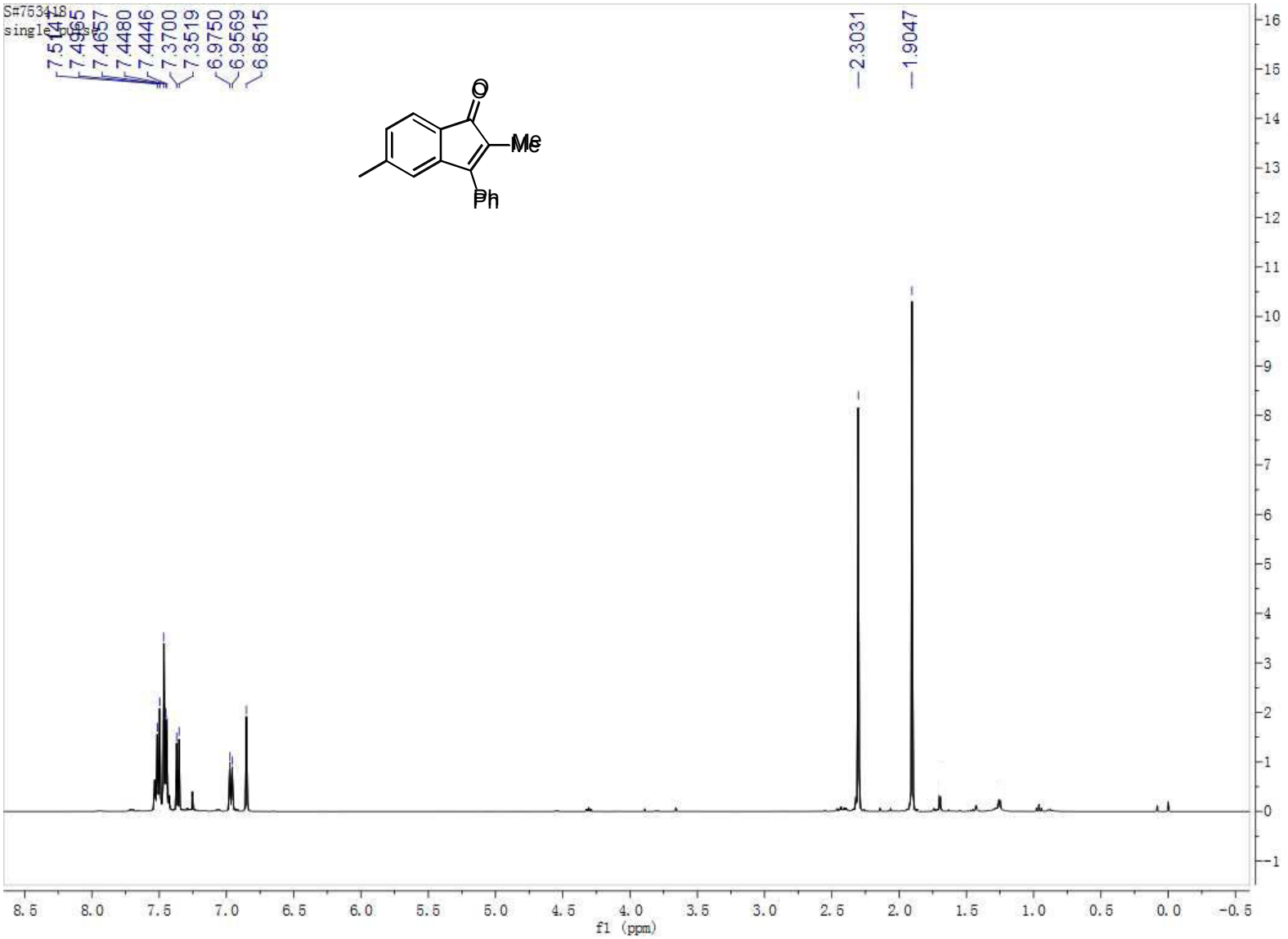
^{13}C NMR for compound **3ae**



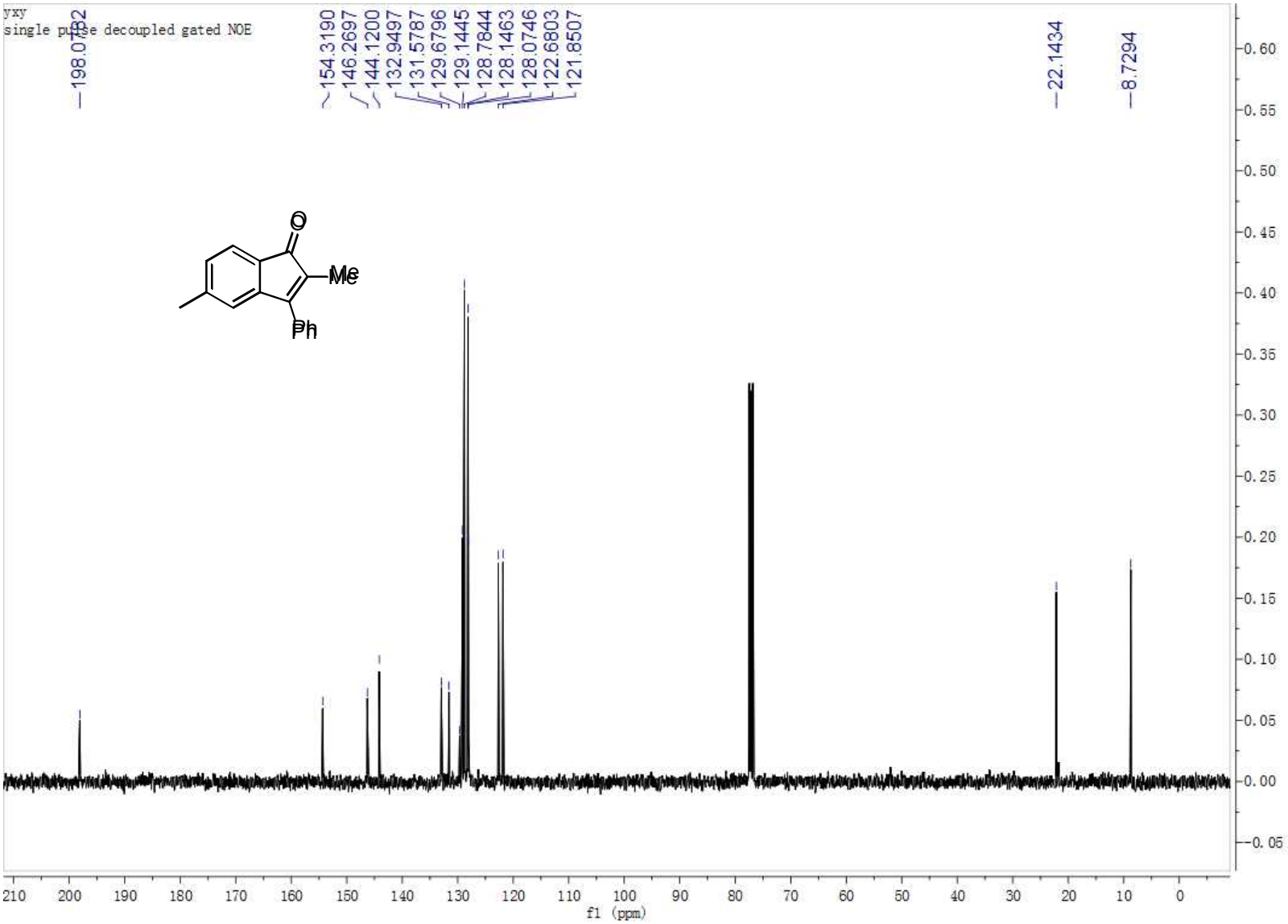
^{1}H NMR for compound **3ag**



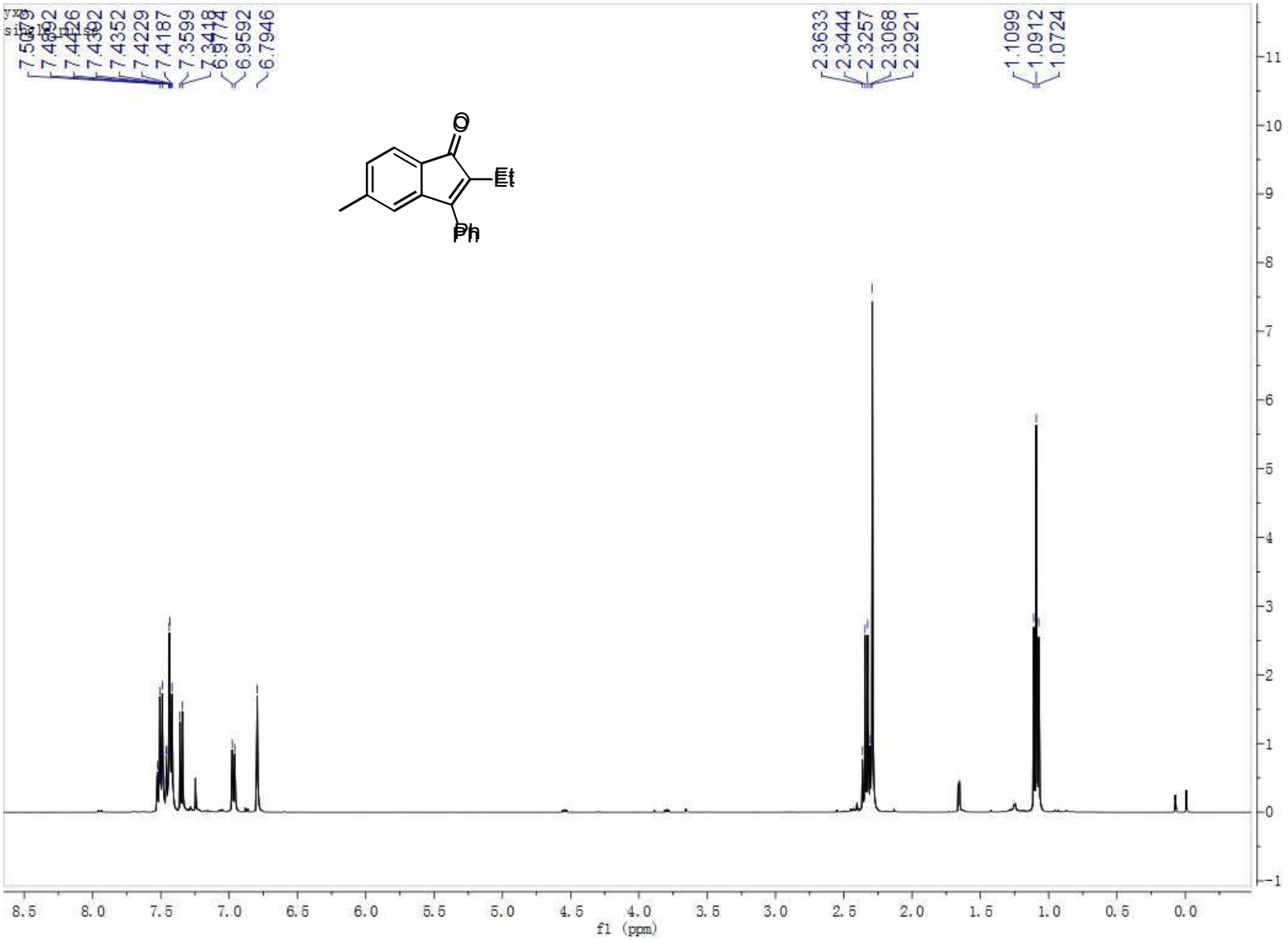
^{13}C NMR for compound **3ag**



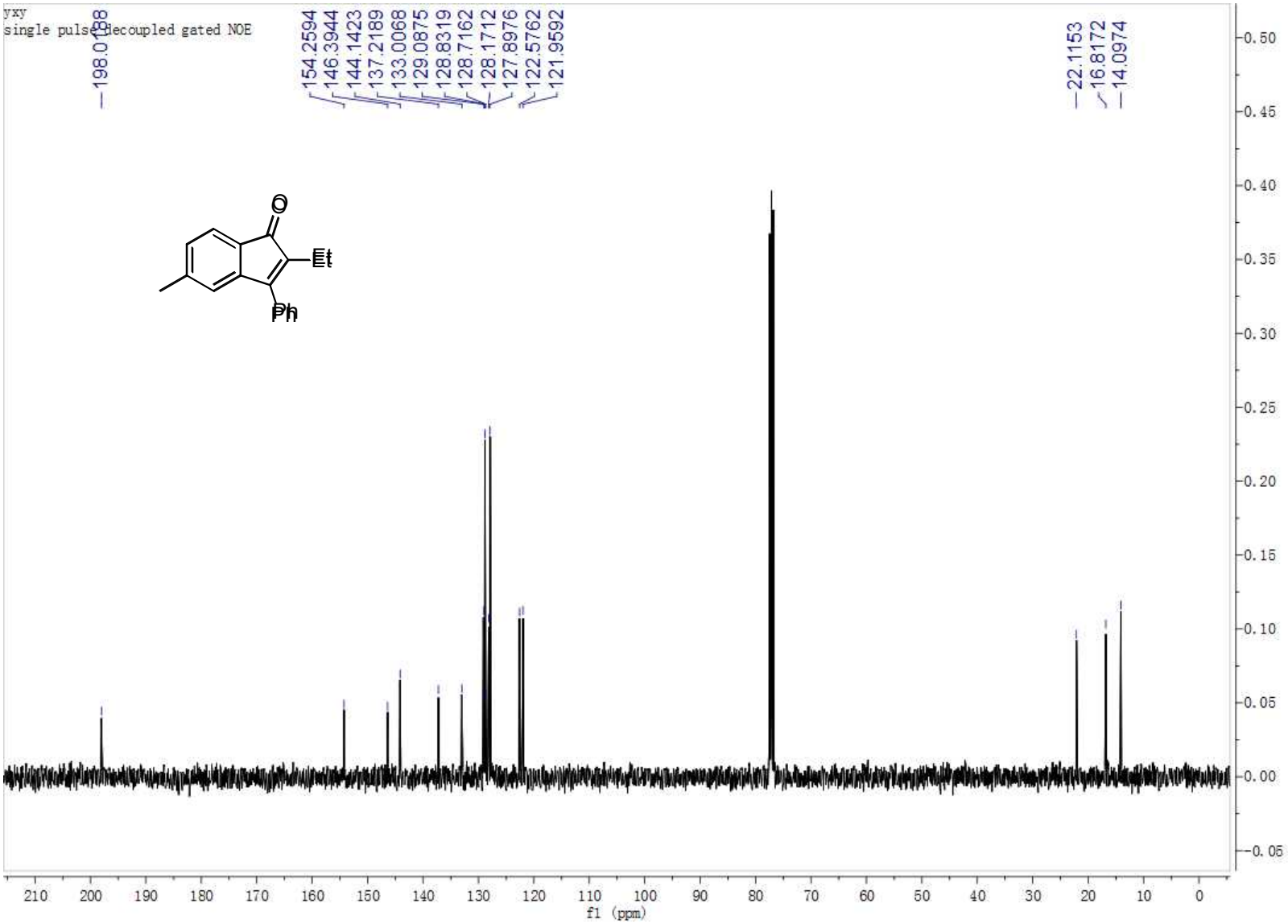
^{1}H NMR for compound **3ah**



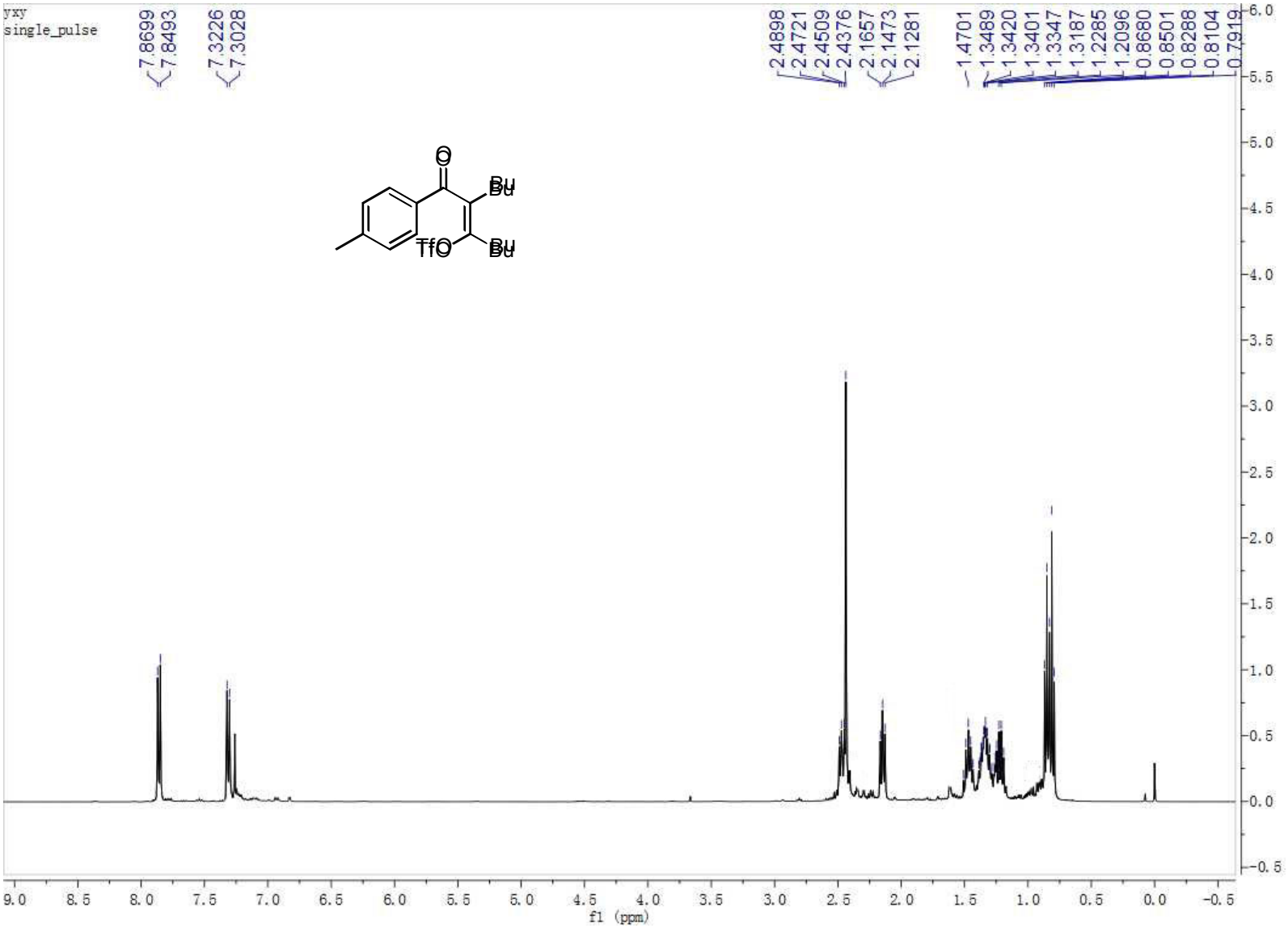
^{13}C NMR for compound **3ah**



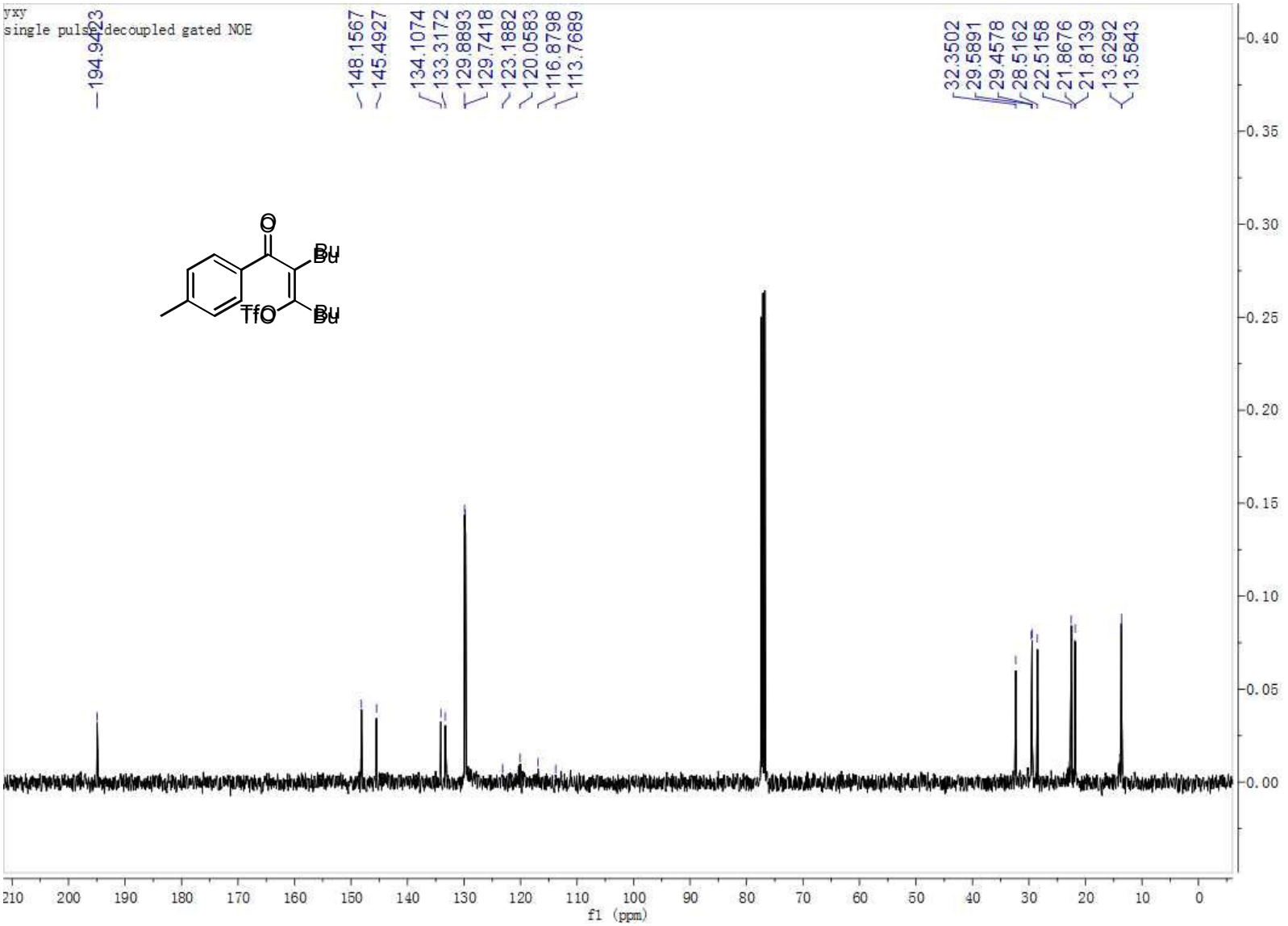
^{1}H NMR for compound **3ai**



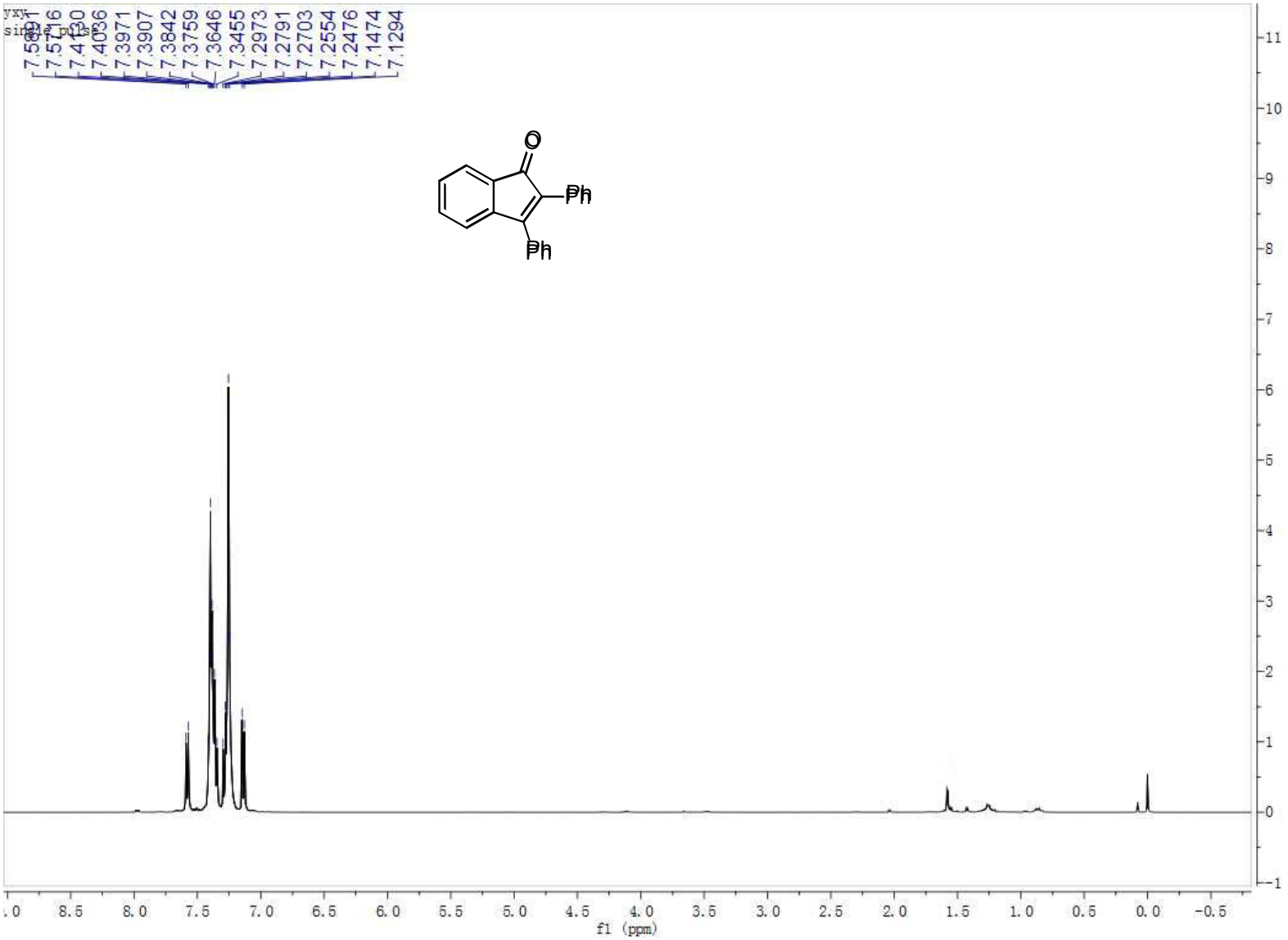
^{13}C NMR for compound **3ai**



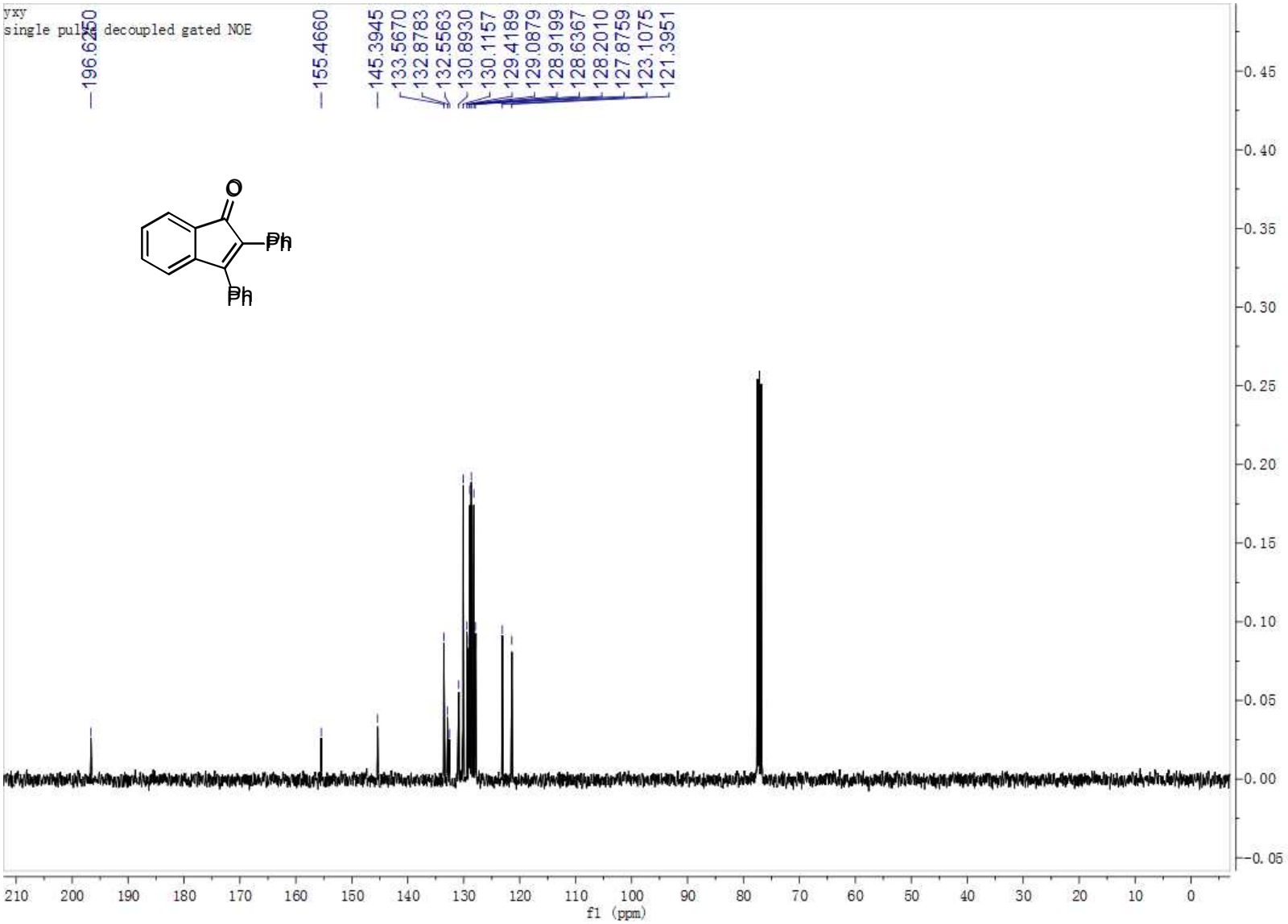
^{1}H NMR for compound **3aj**



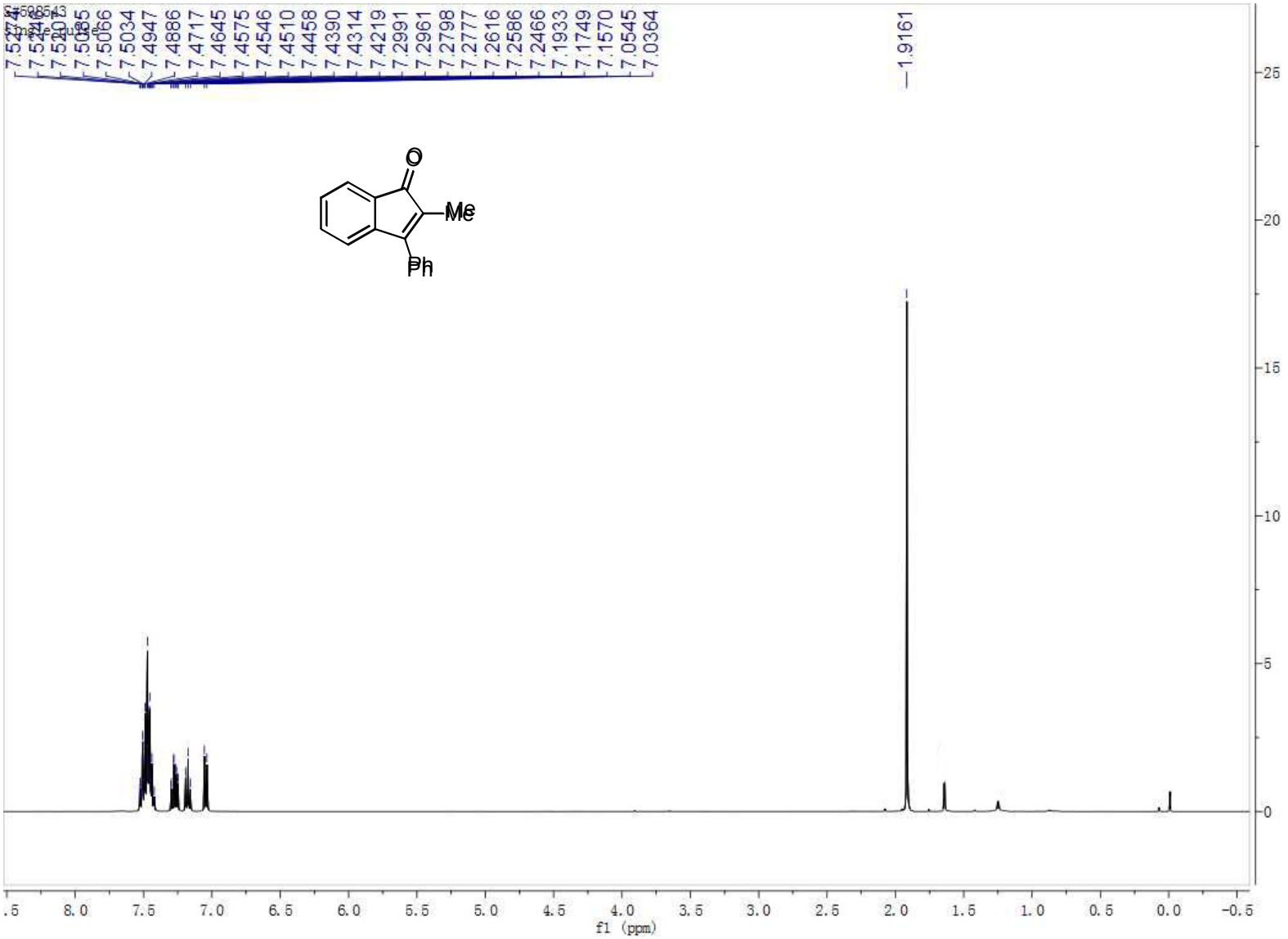
^{13}C NMR for compound **3aj**



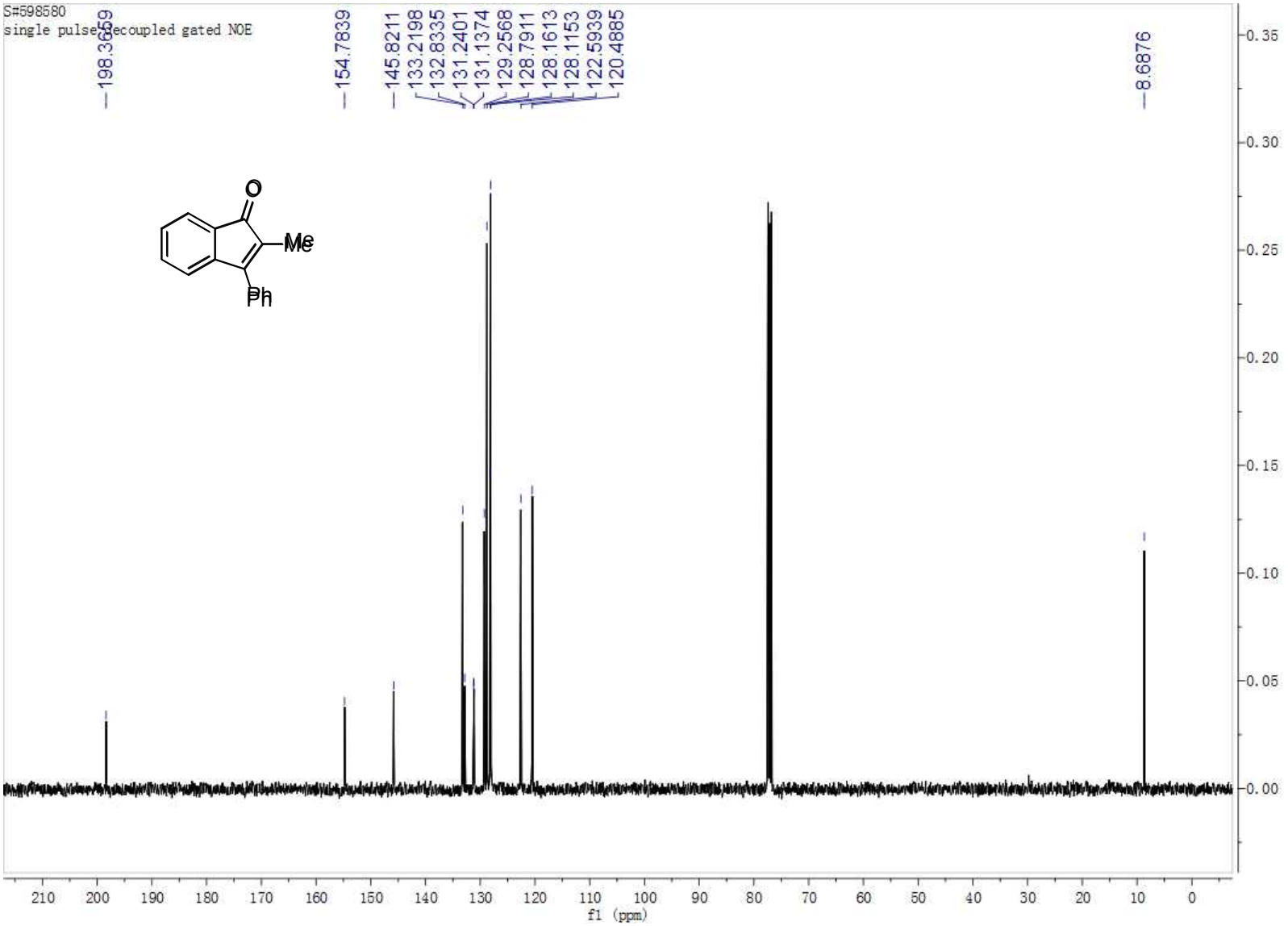
^{1}H NMR for compound **3ba**



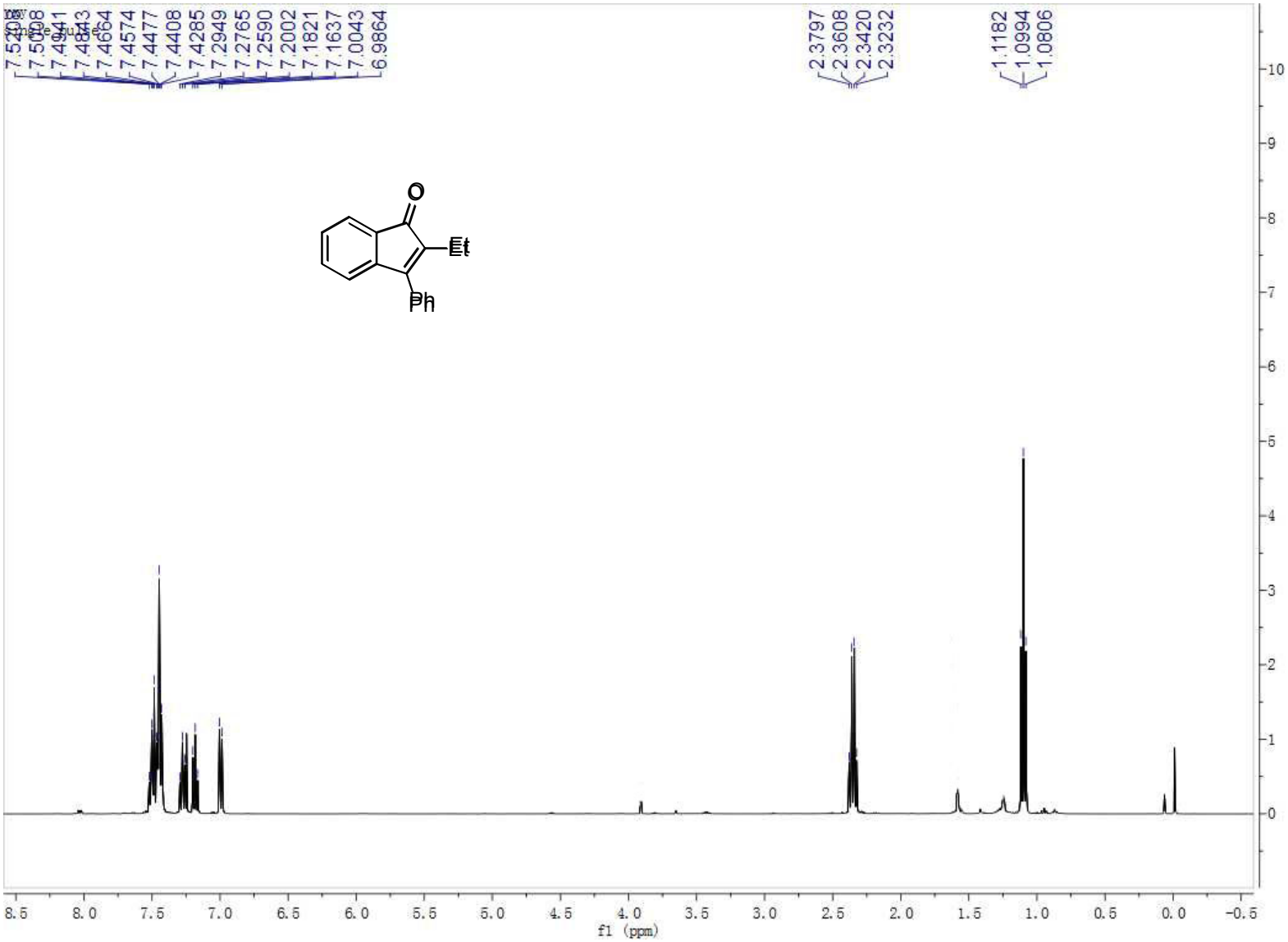
^{13}C NMR for compound **3ba**



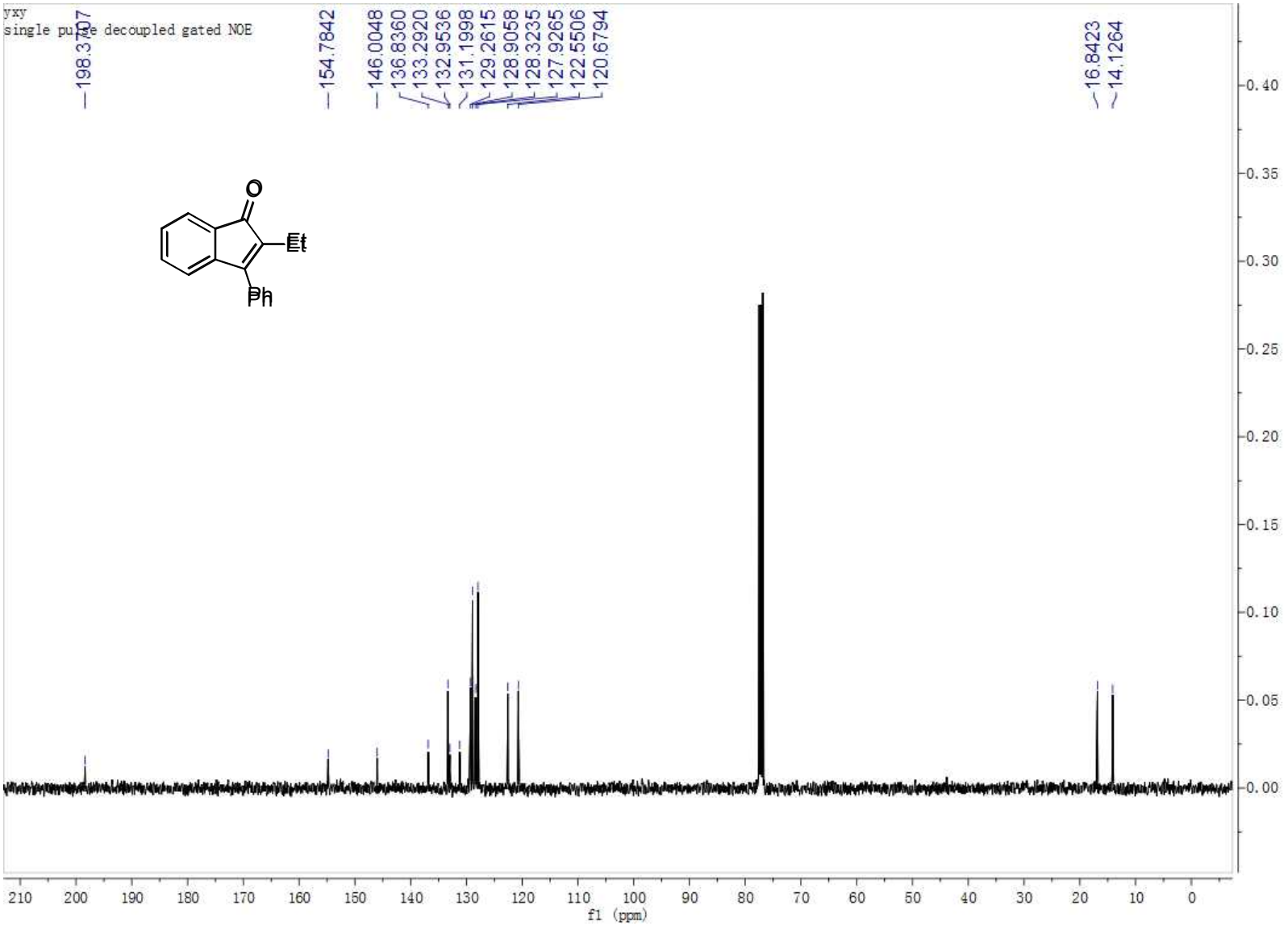
^{1}H NMR for compound **3bh**



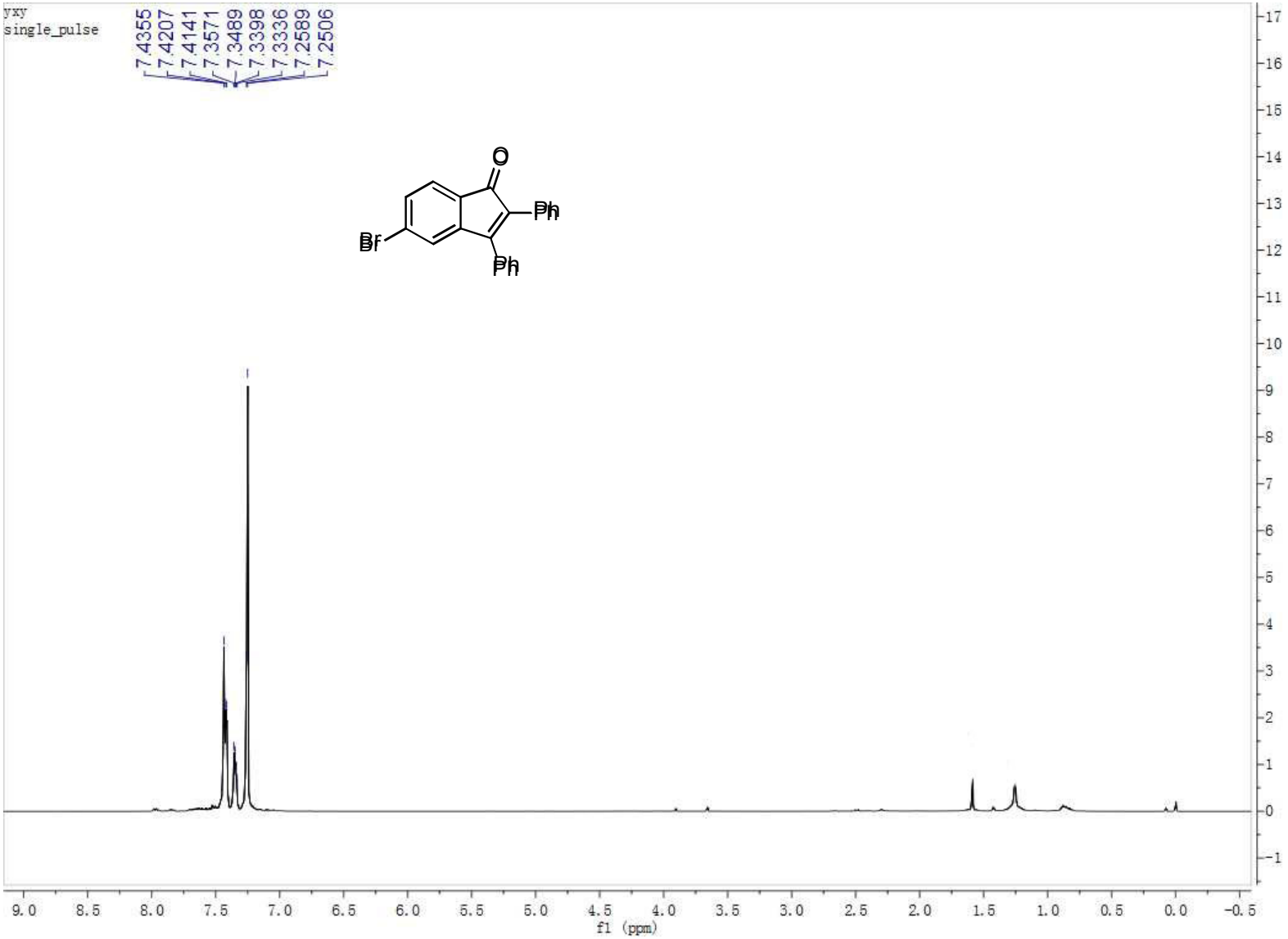
^{13}C NMR for compound **3bh**



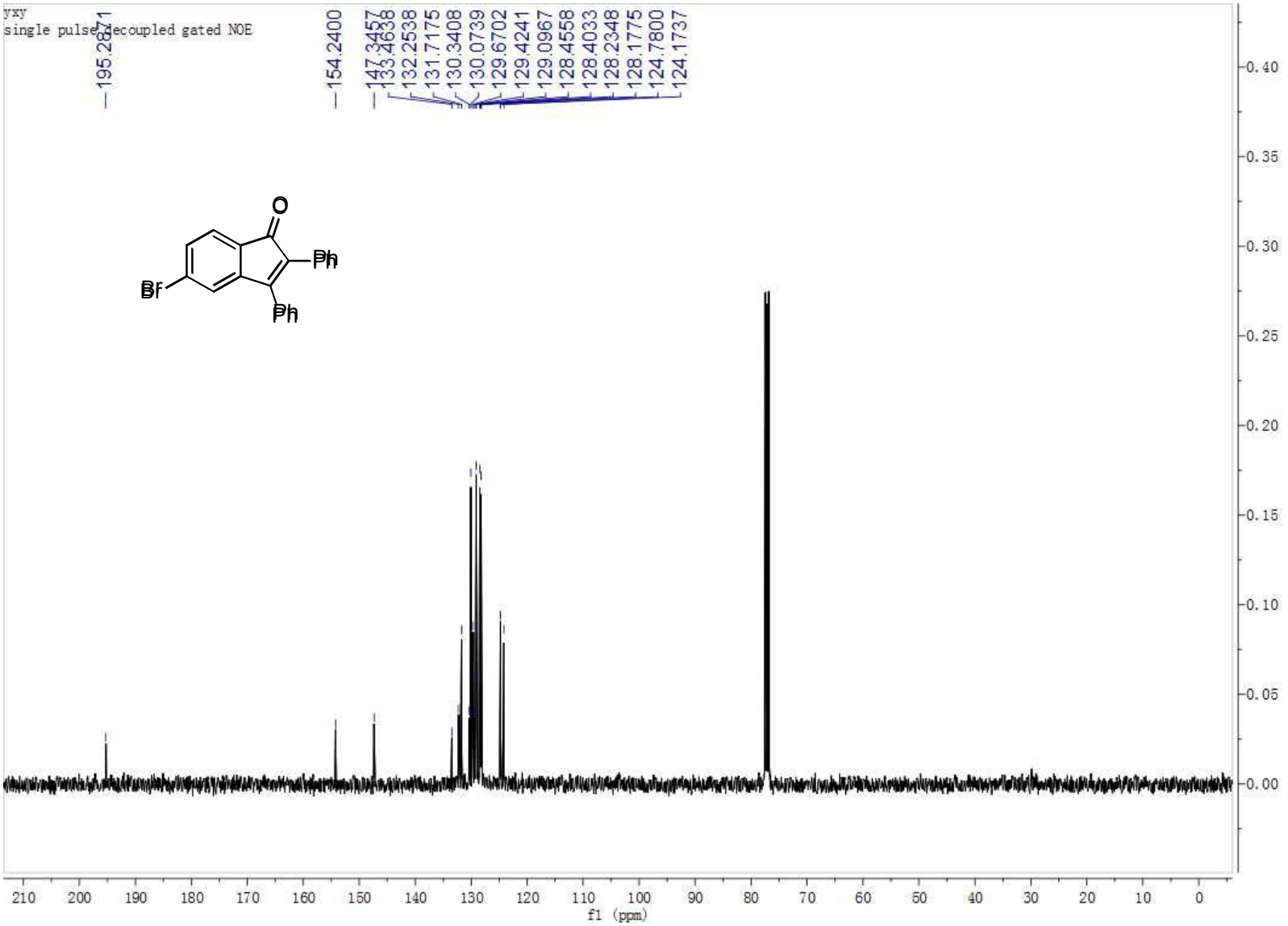
^{1}H NMR for compound **3bi**



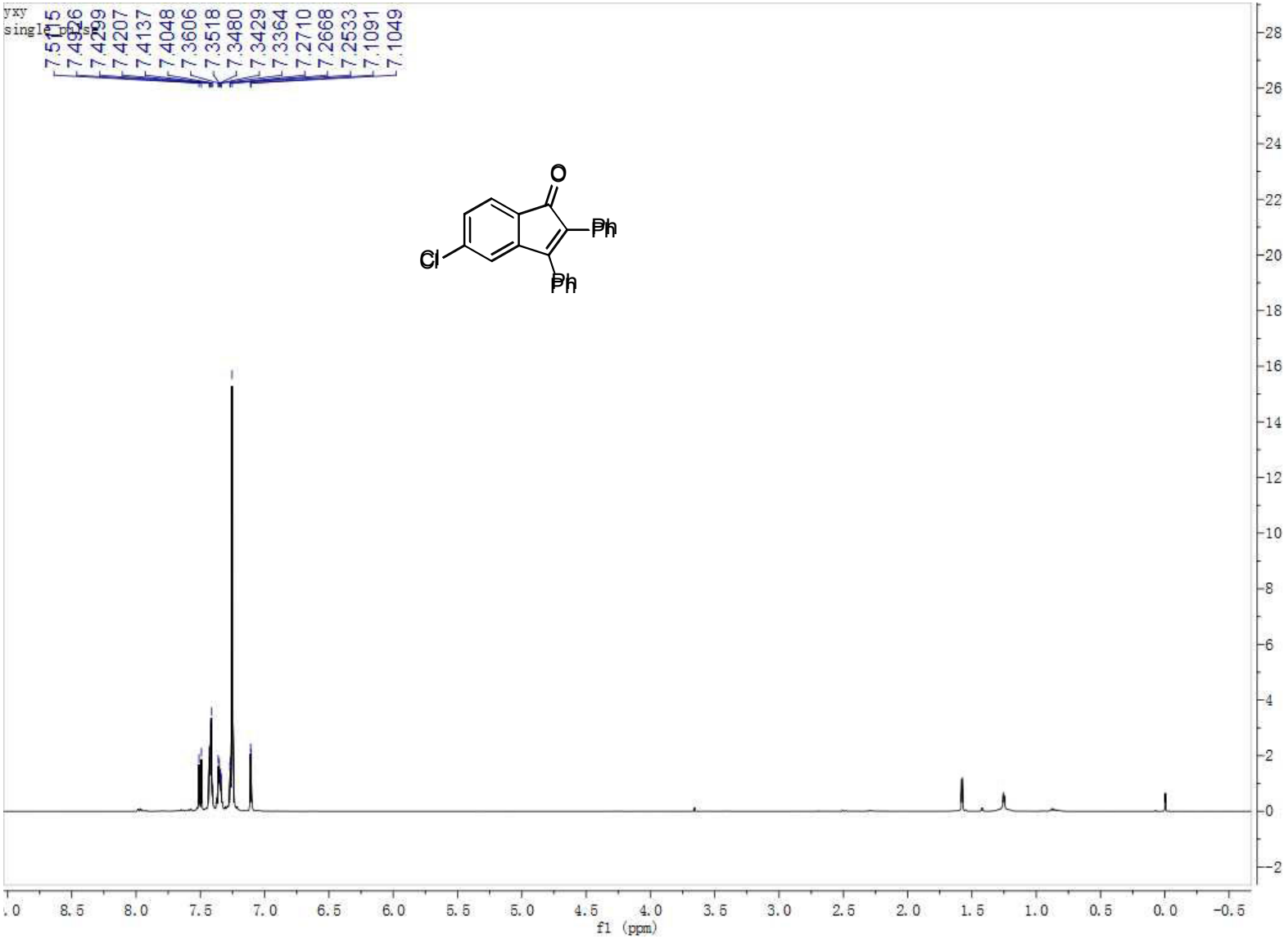
^{13}C NMR for compound **3bi**



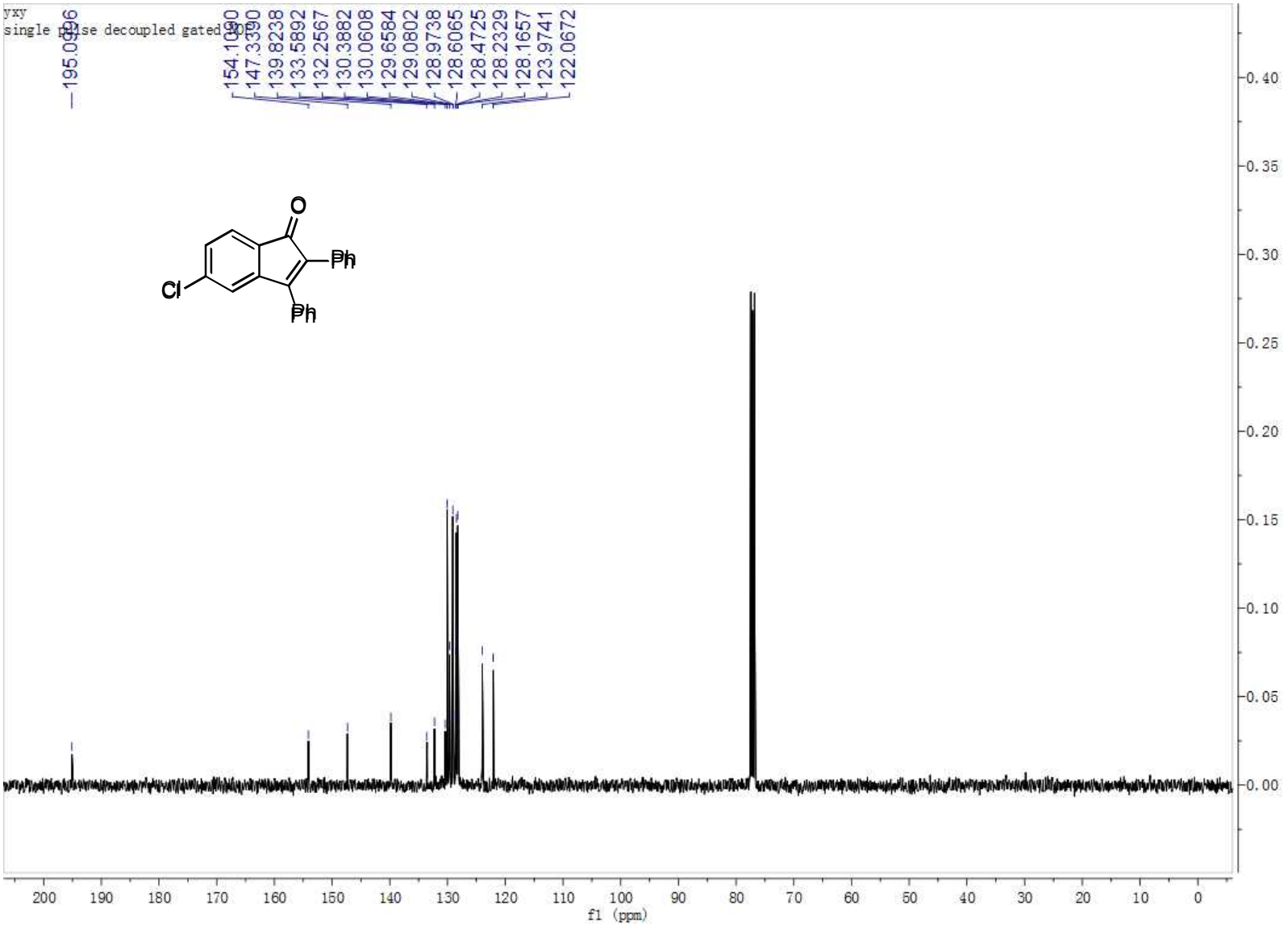
^{1}H NMR for compound **3ca**



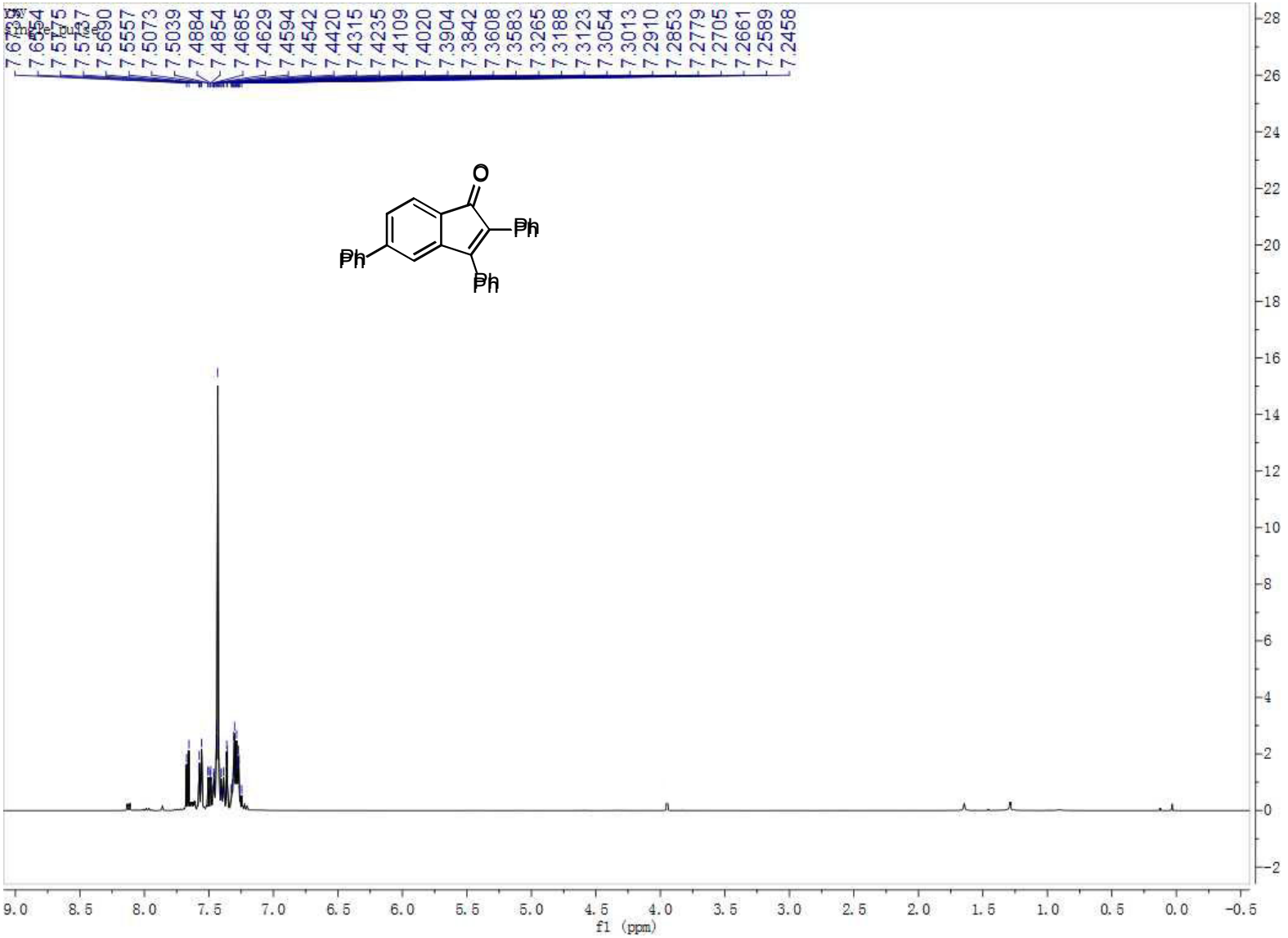
^{13}C NMR for compound **3ca**



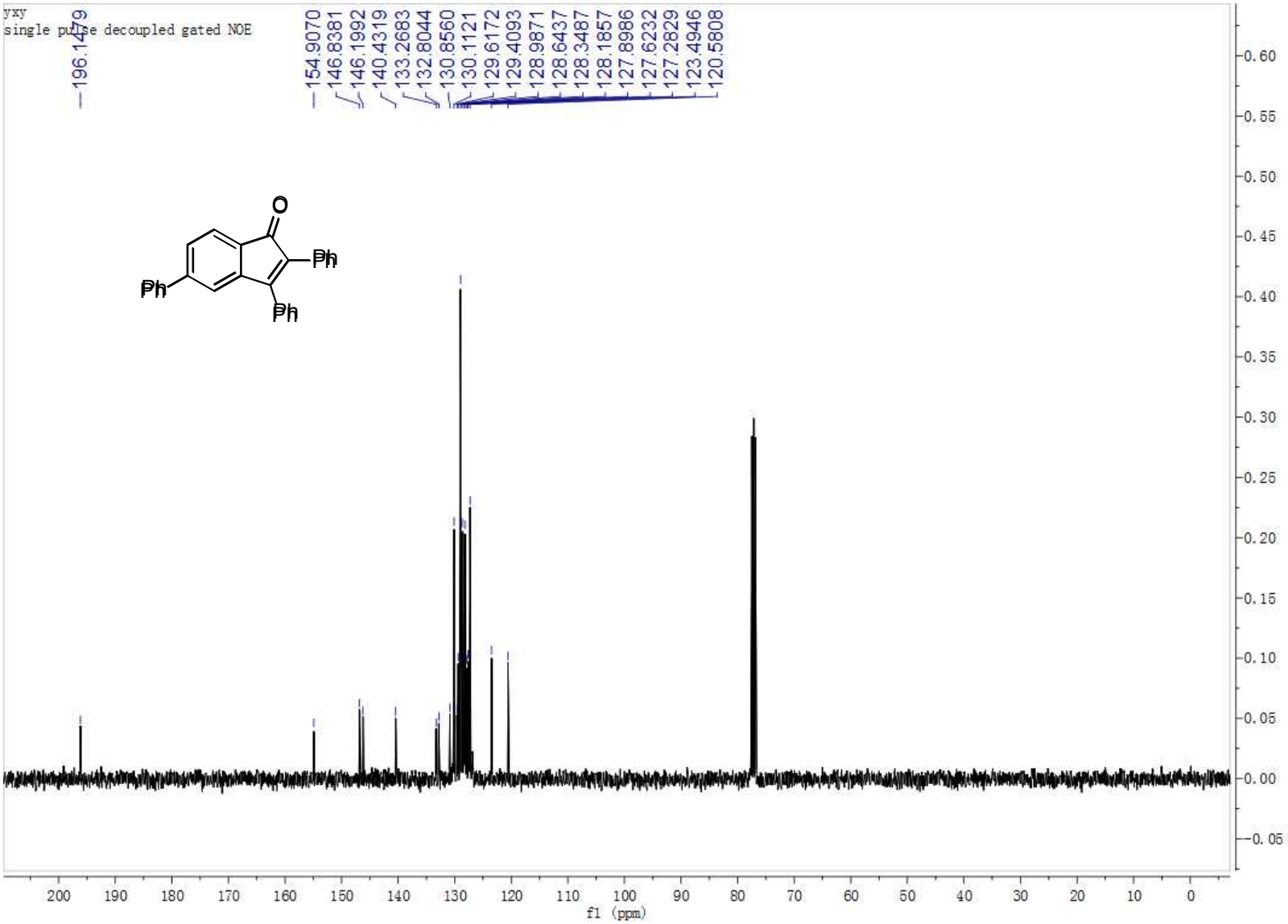
^{1}H NMR for compound **3da**



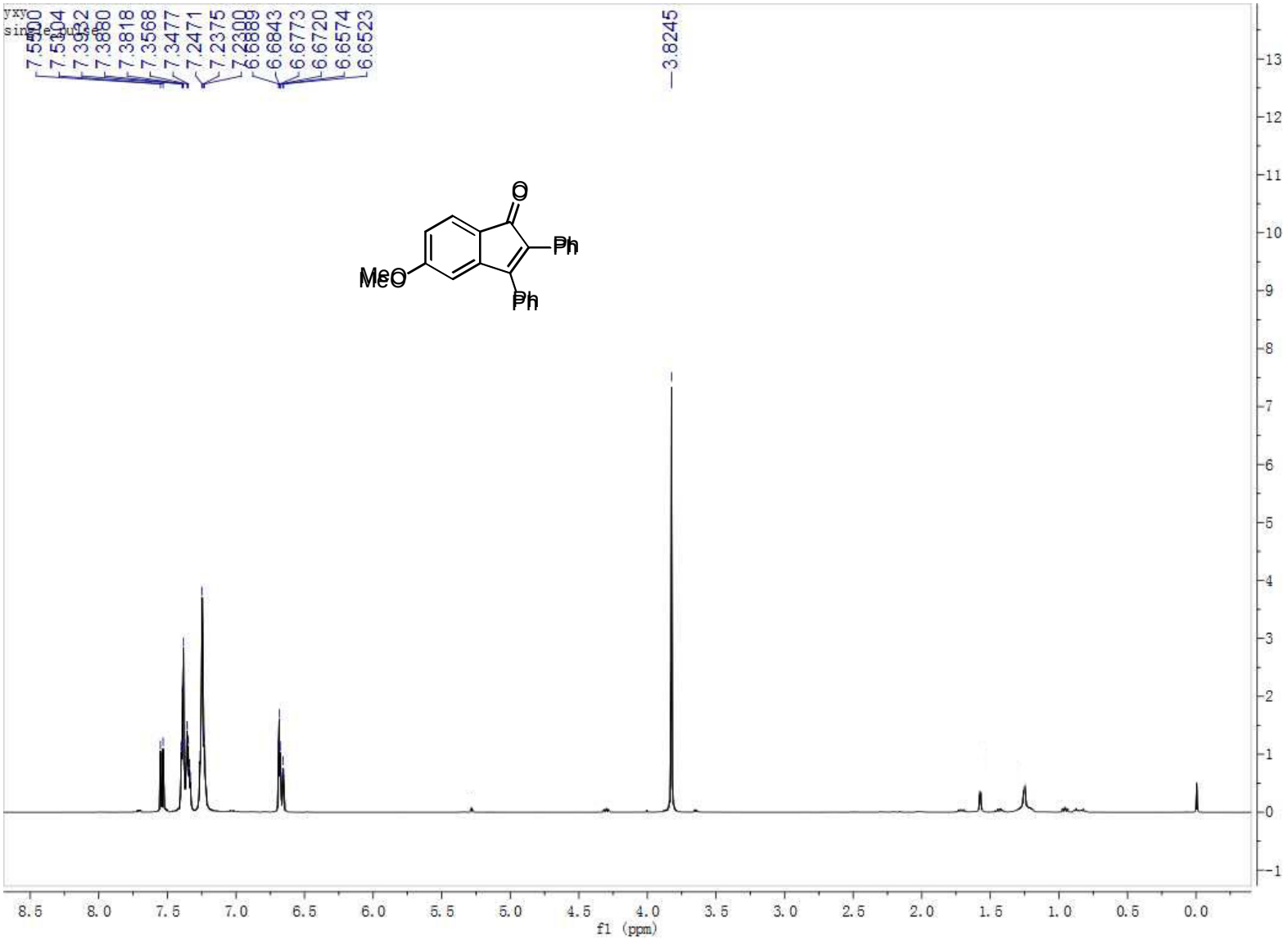
^{13}C NMR for compound **3da**



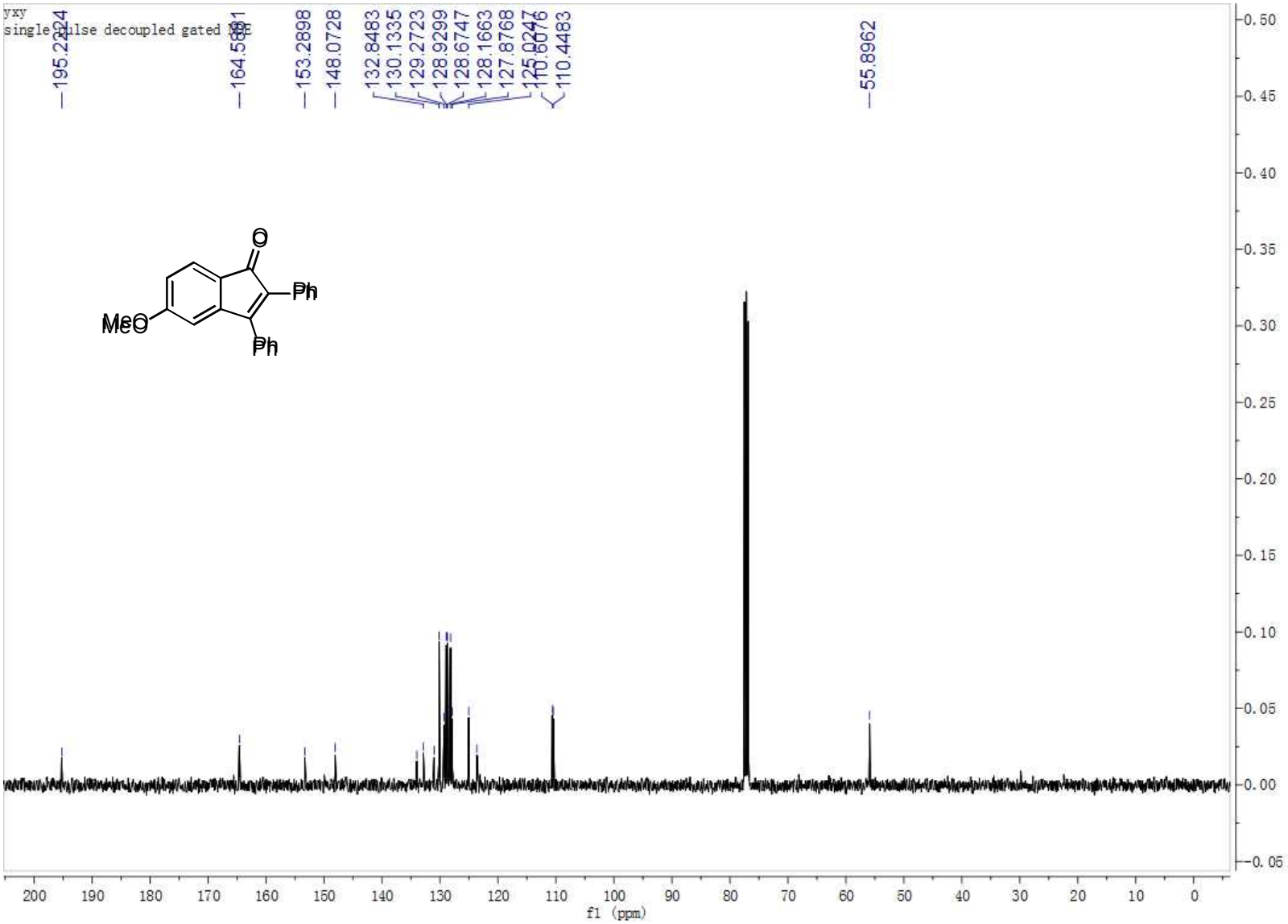
^{1}H NMR for compound **3ea**



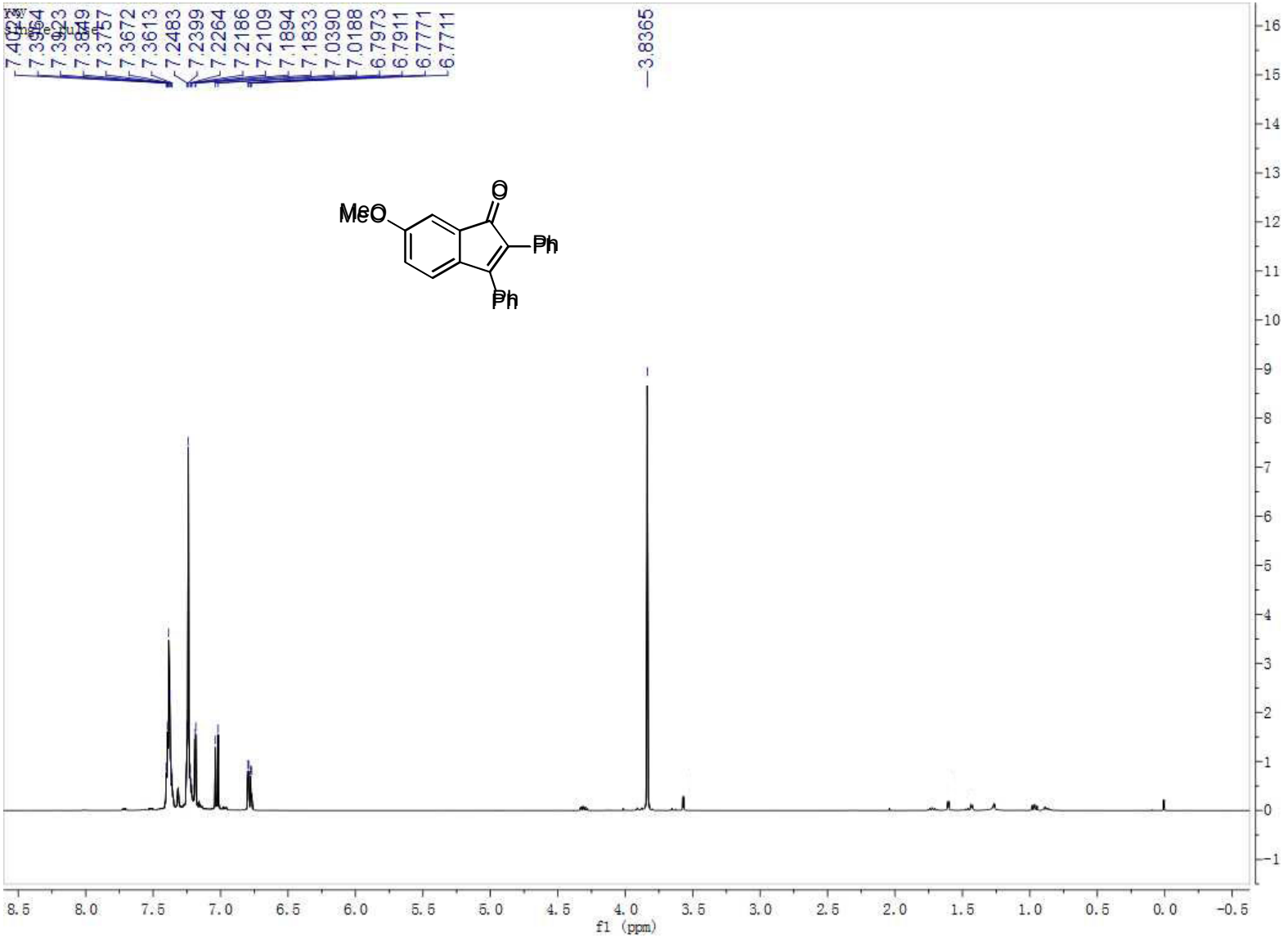
^{13}C NMR for compound **3ea**



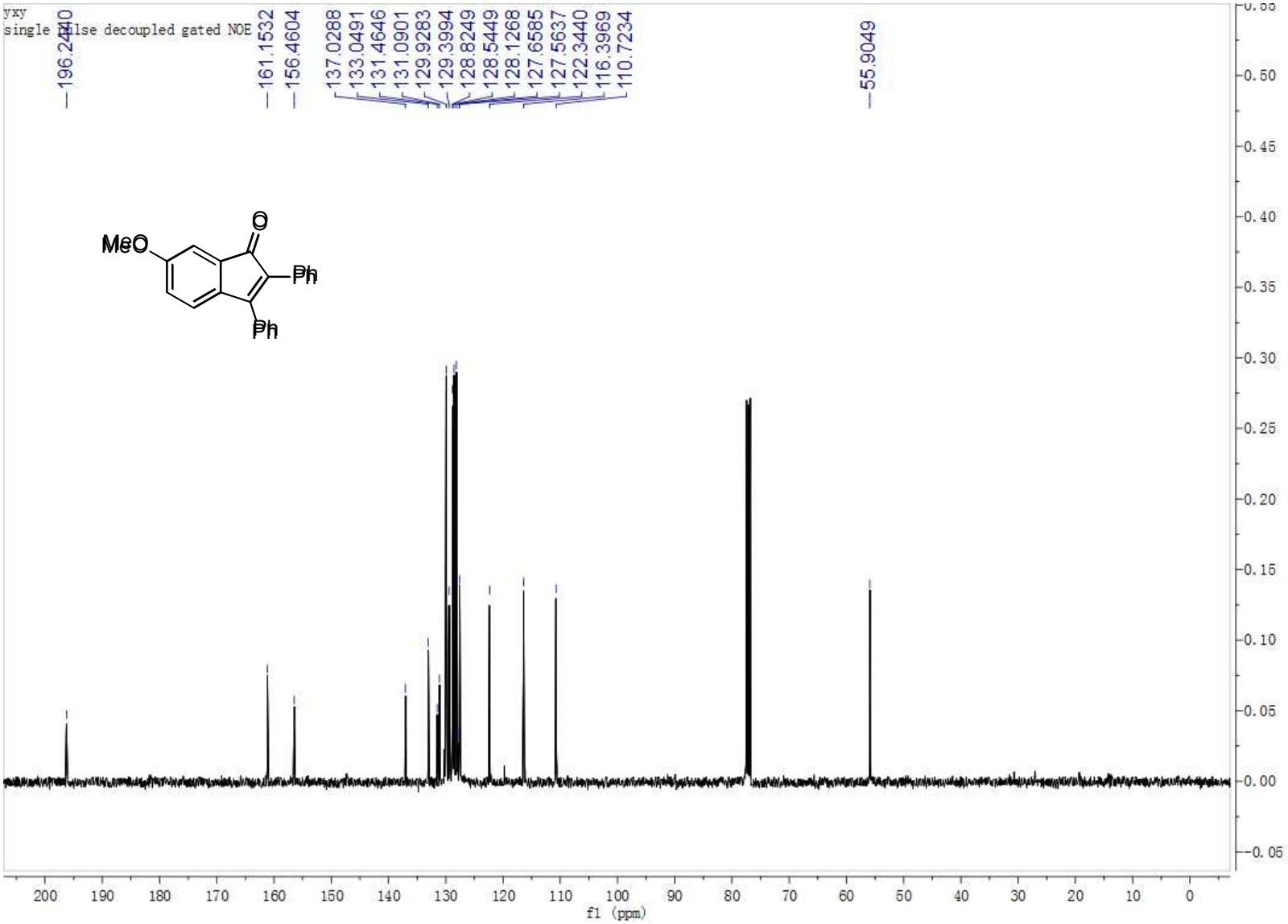
^{1}H NMR for compound **3ha**



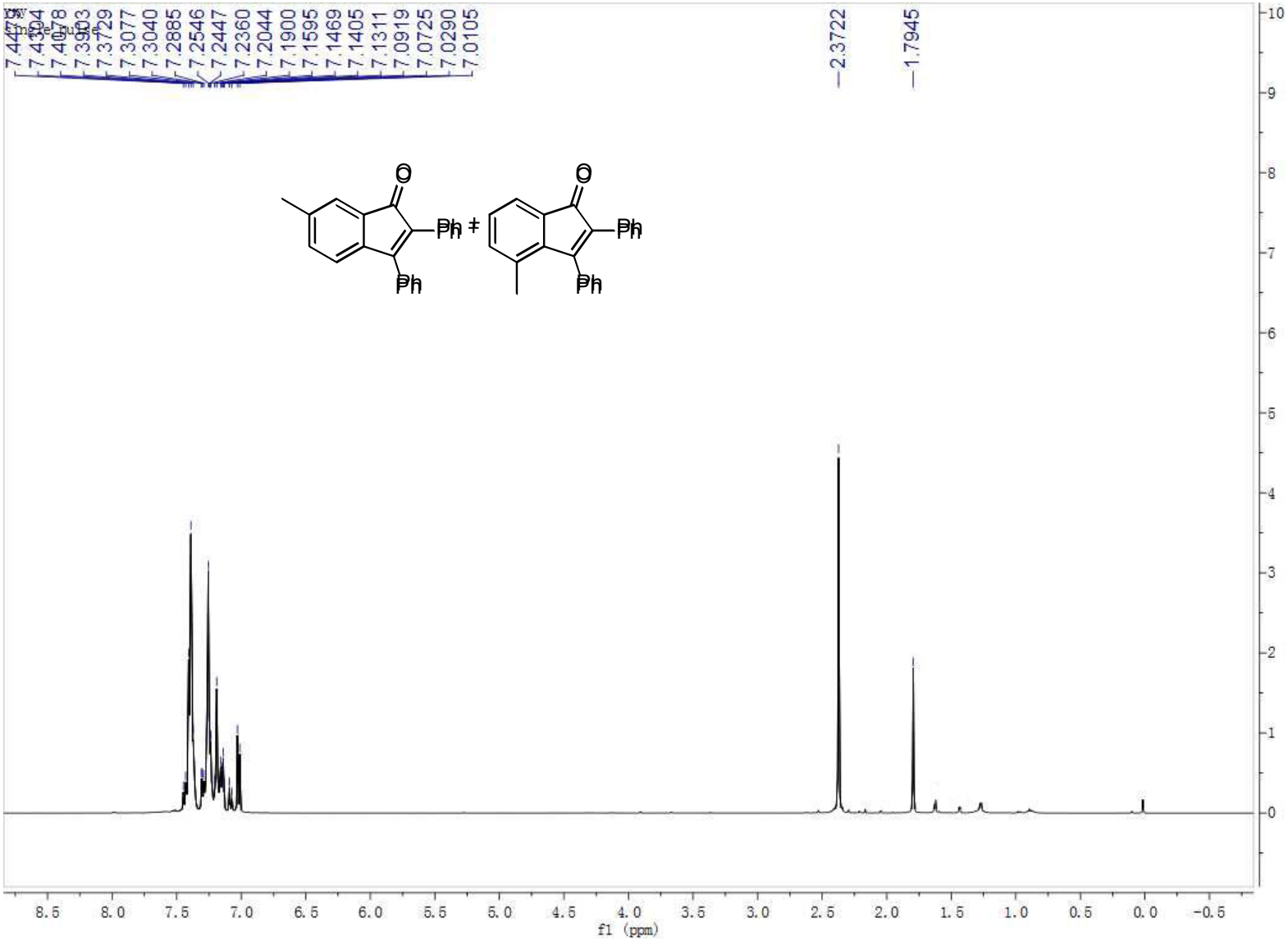
^{13}C NMR for compound **3ha**



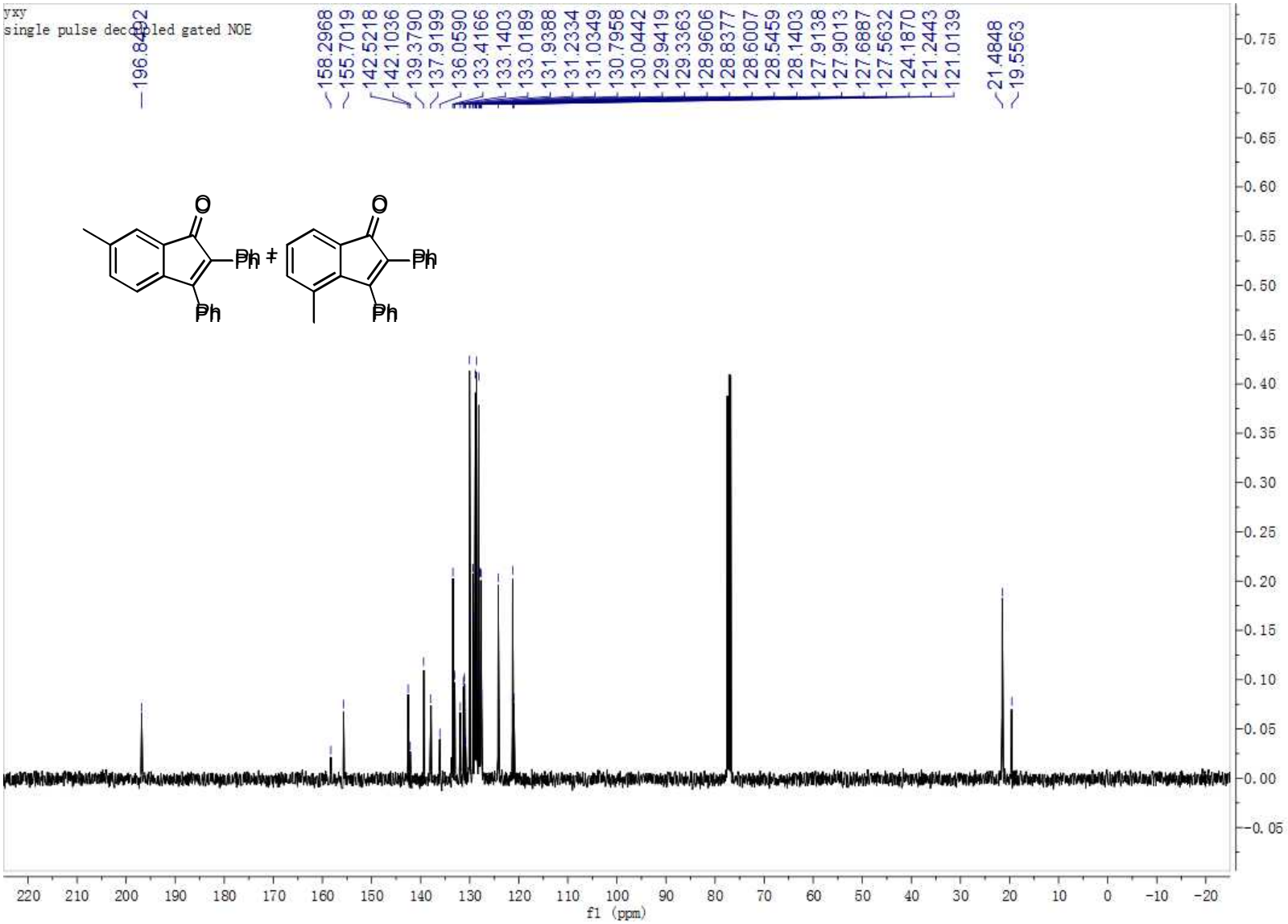
^{1}H NMR for compound **3ka**



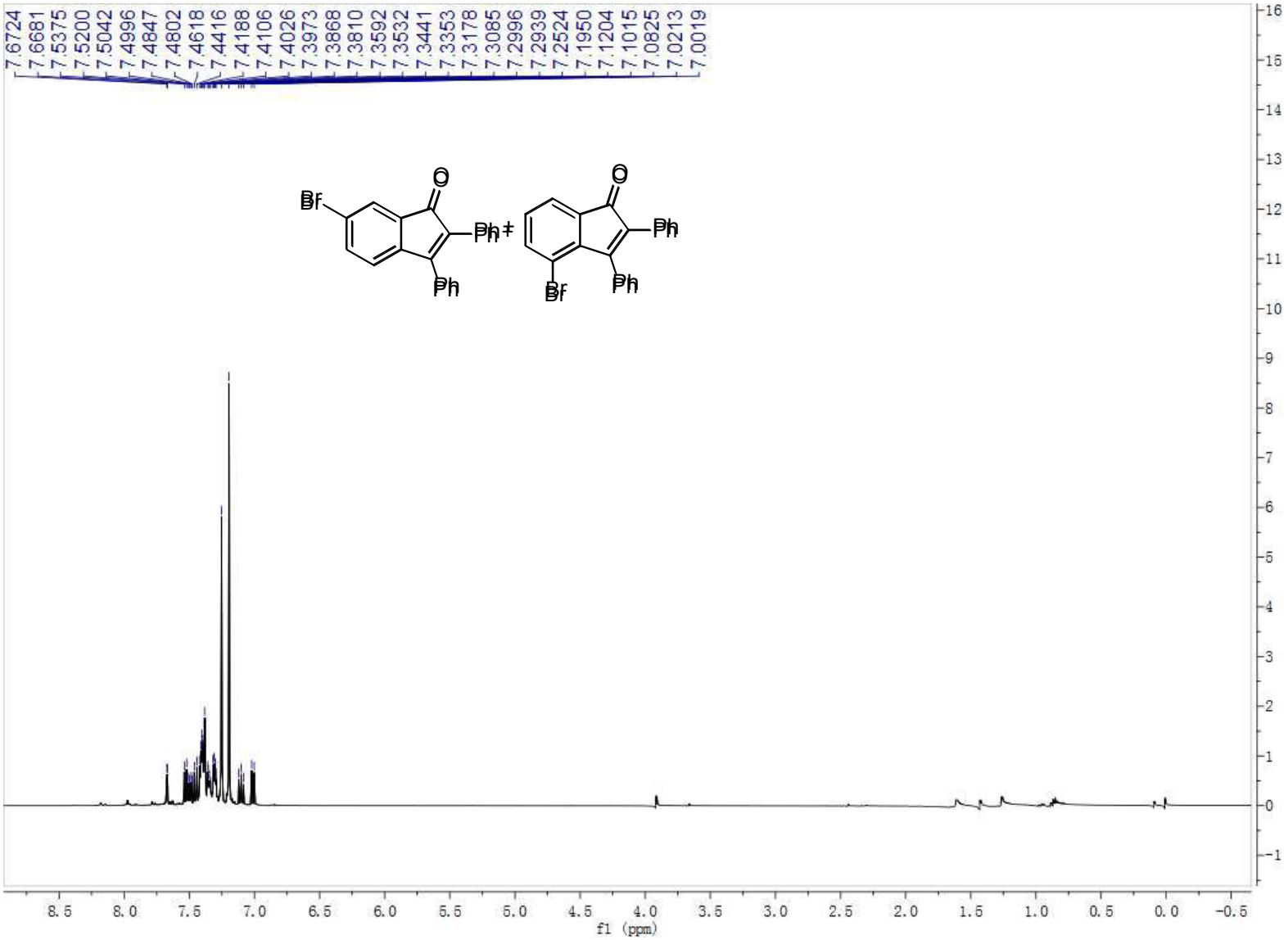
^{13}C NMR for compound **3ka**



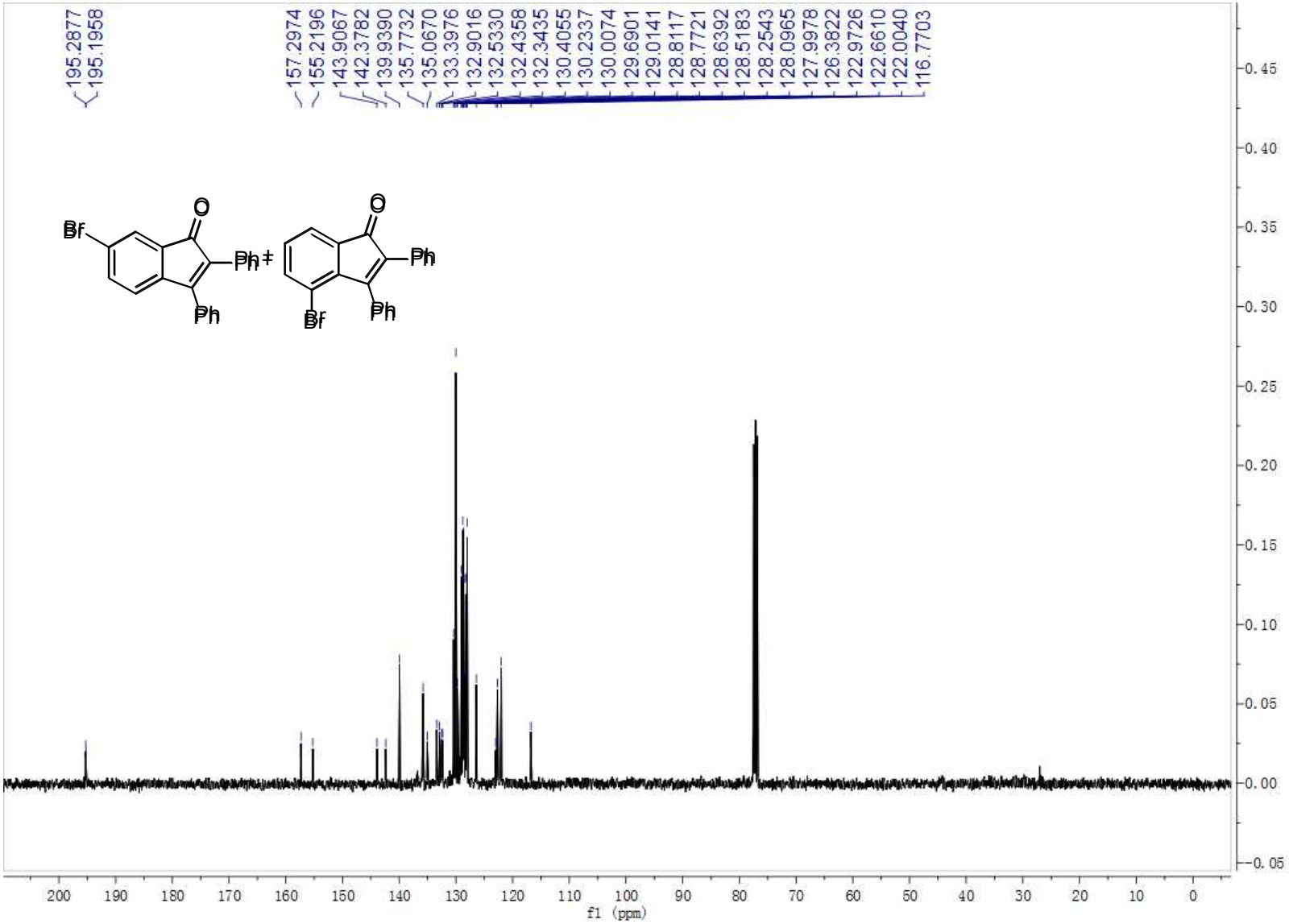
^{1}H NMR for compound **3ia** and **3ia′**



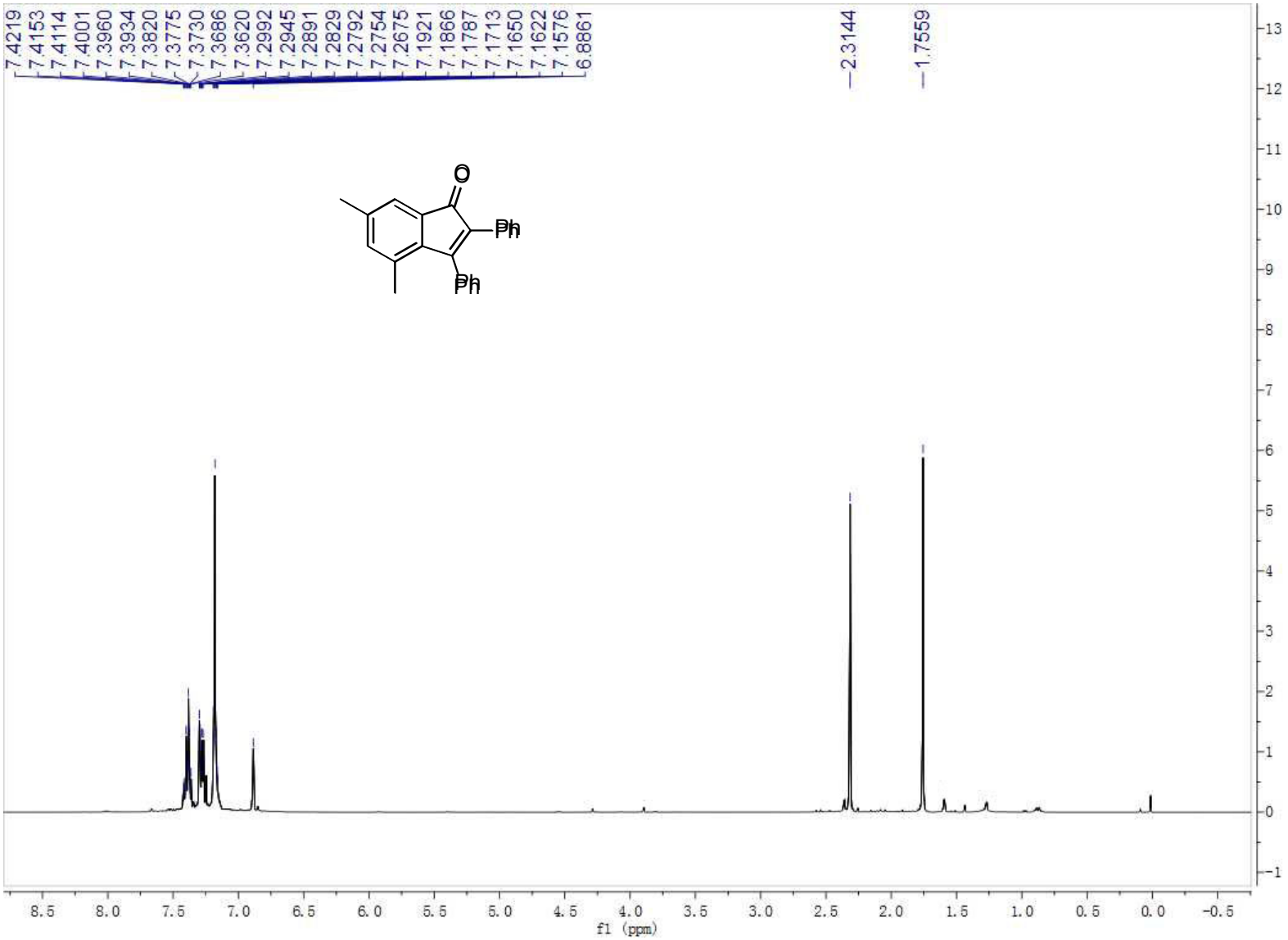
^{13}C NMR for compound **3ia** and **3ia′**



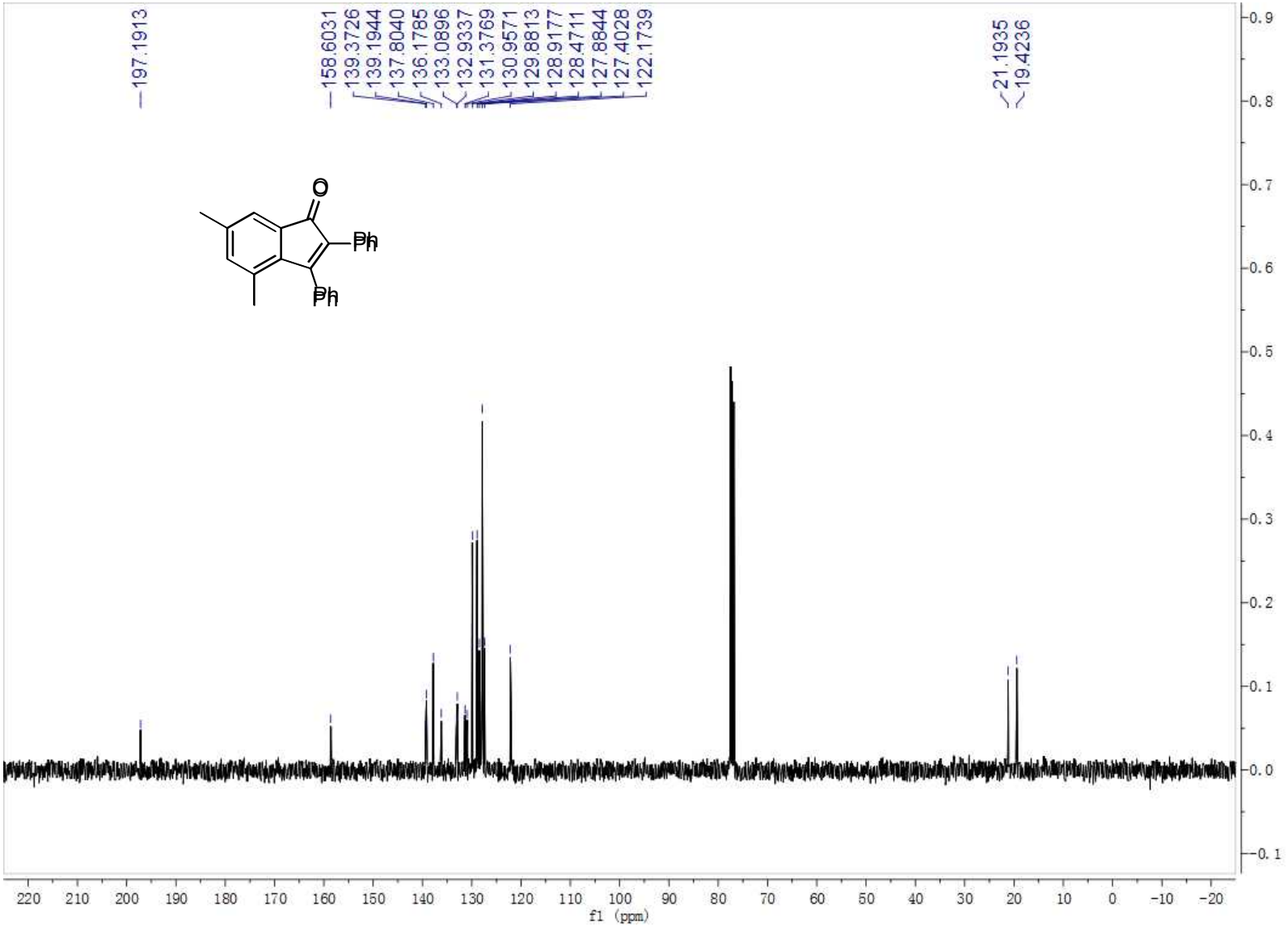
^{1}H NMR for compound **3ja** and **3ja′**



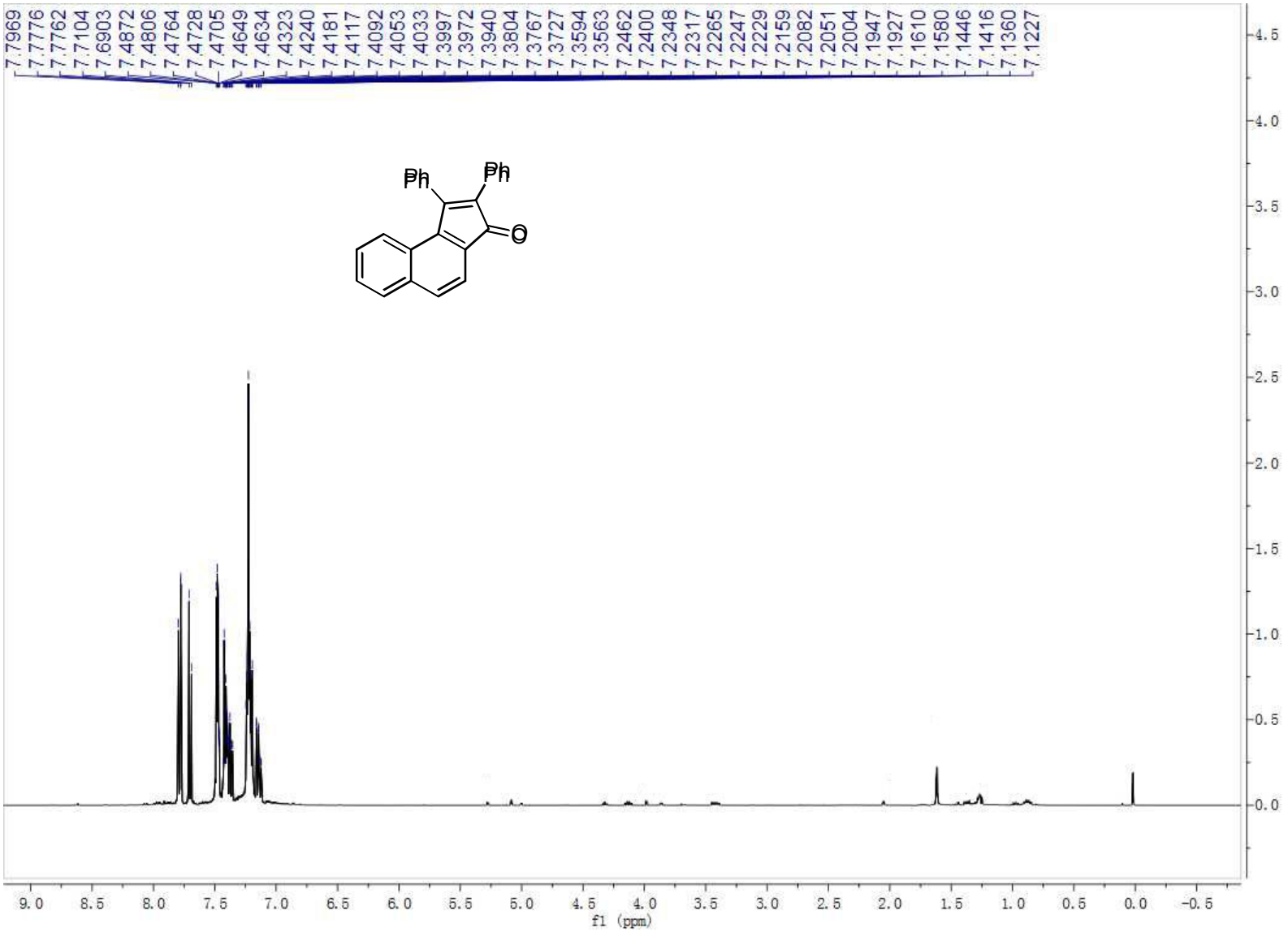
^{13}C NMR for compound **3ja** and **3ja′**



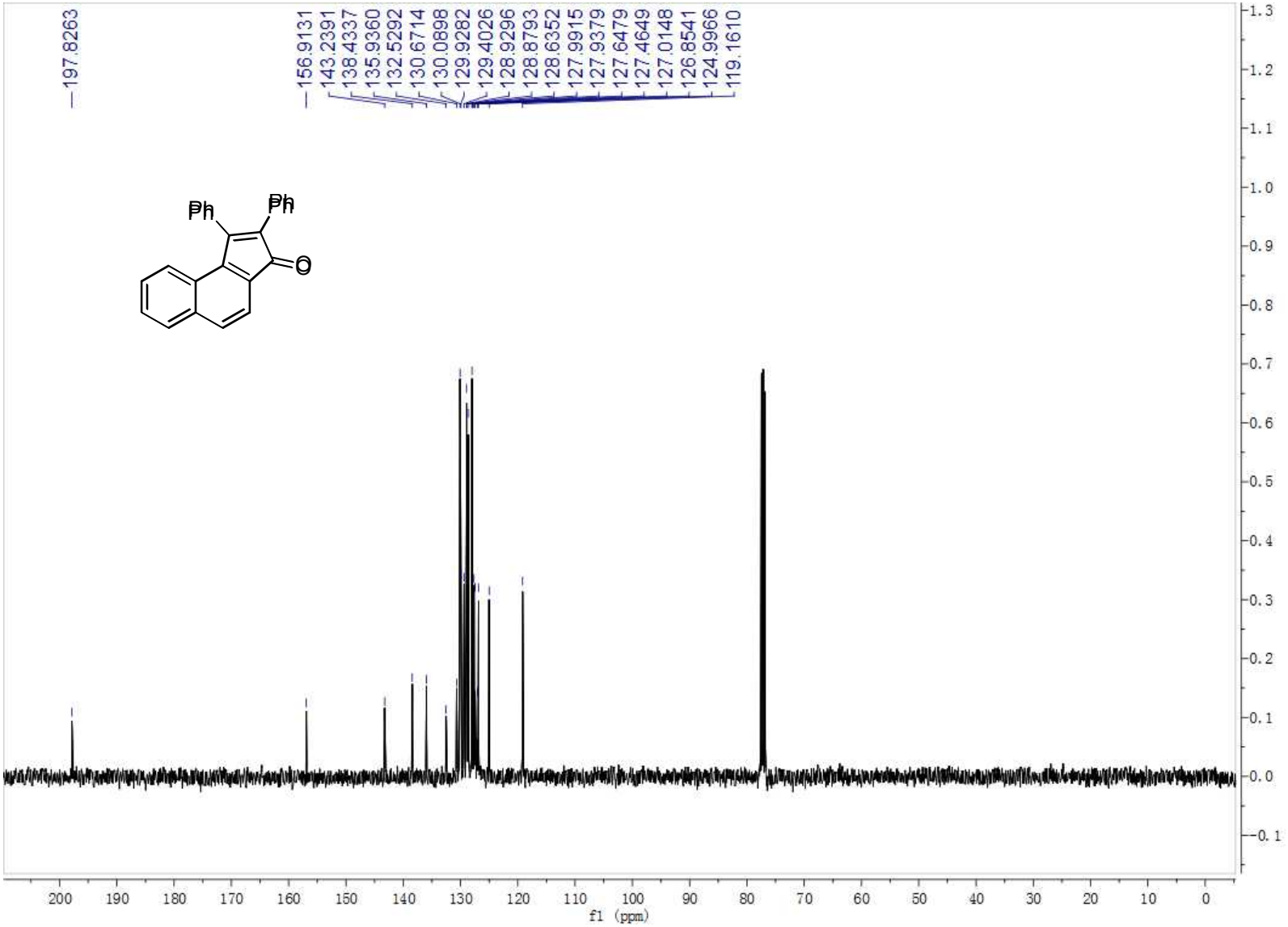
^{1}H NMR for compound **3la**



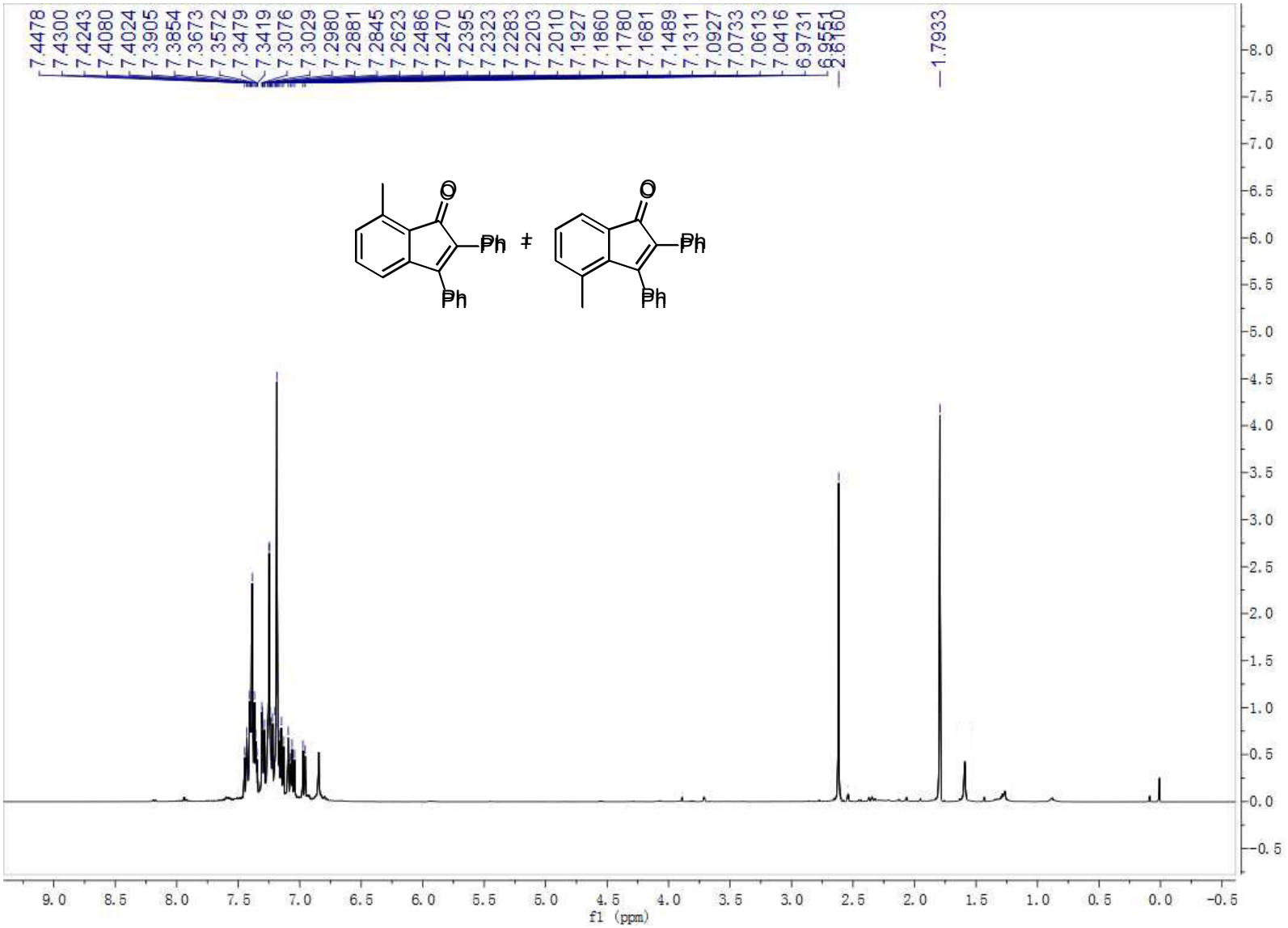
^{13}C NMR for compound **3la**



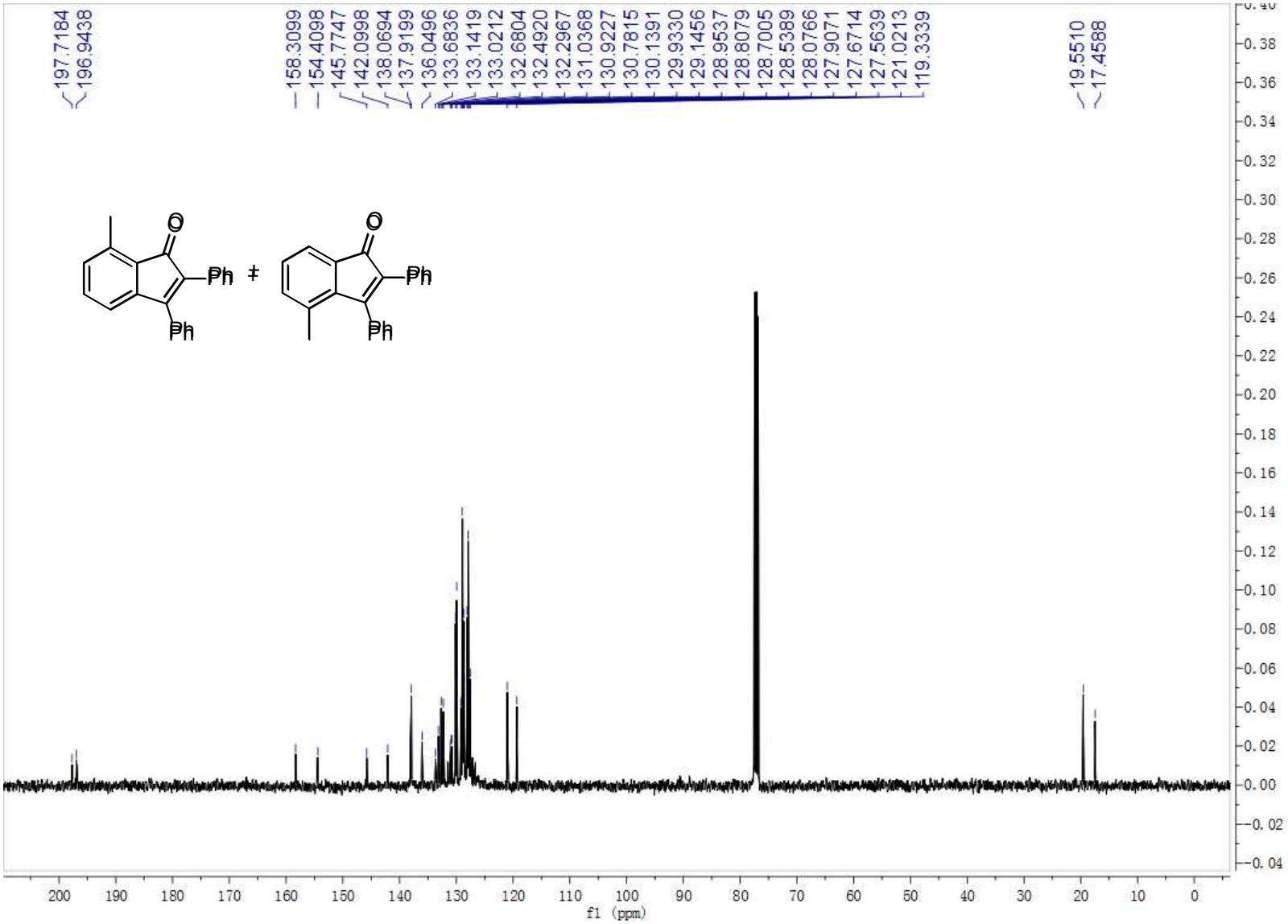
^{1}H NMR for compound **3ma**



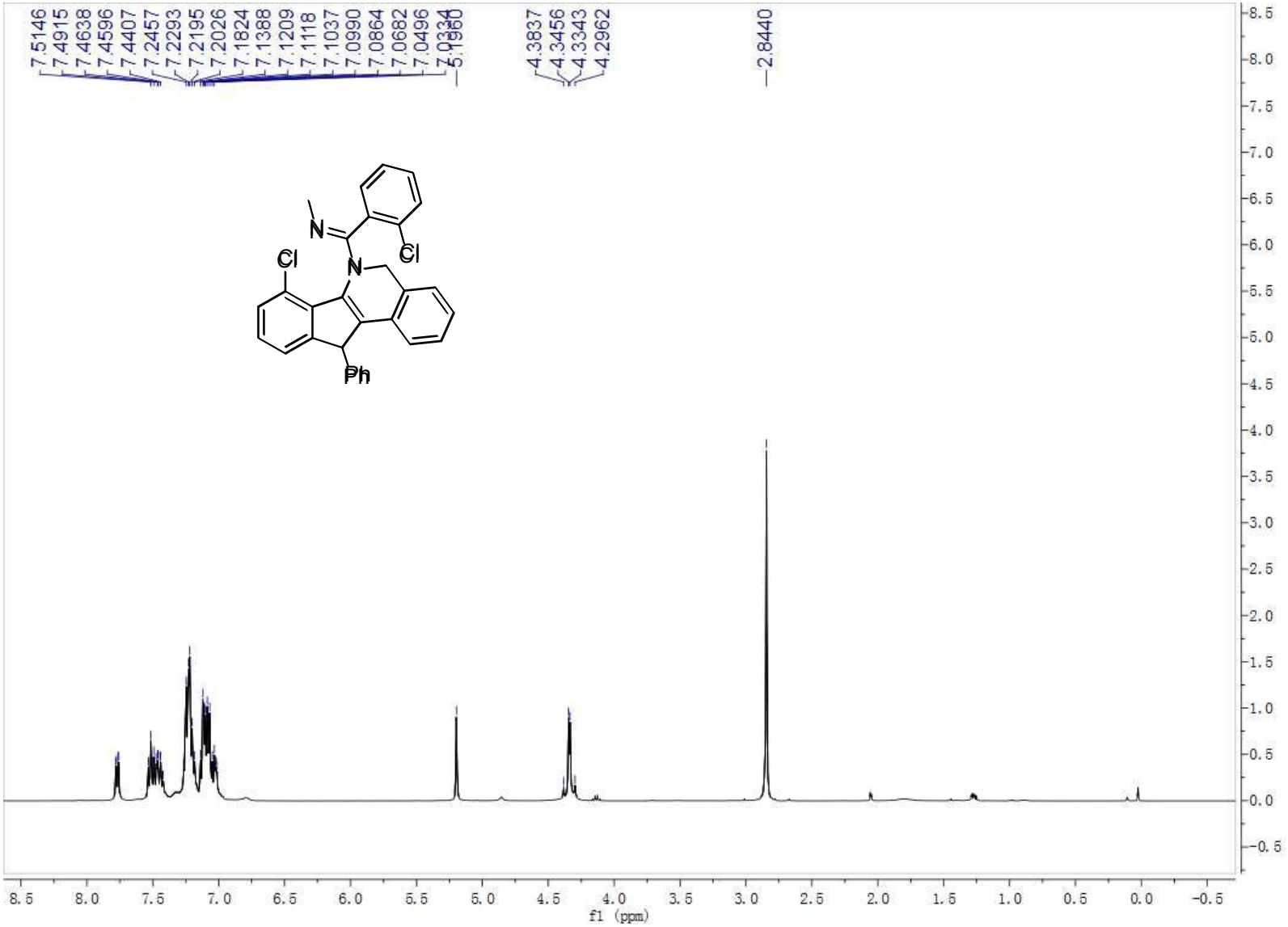
^{13}C NMR for compound **3ma**



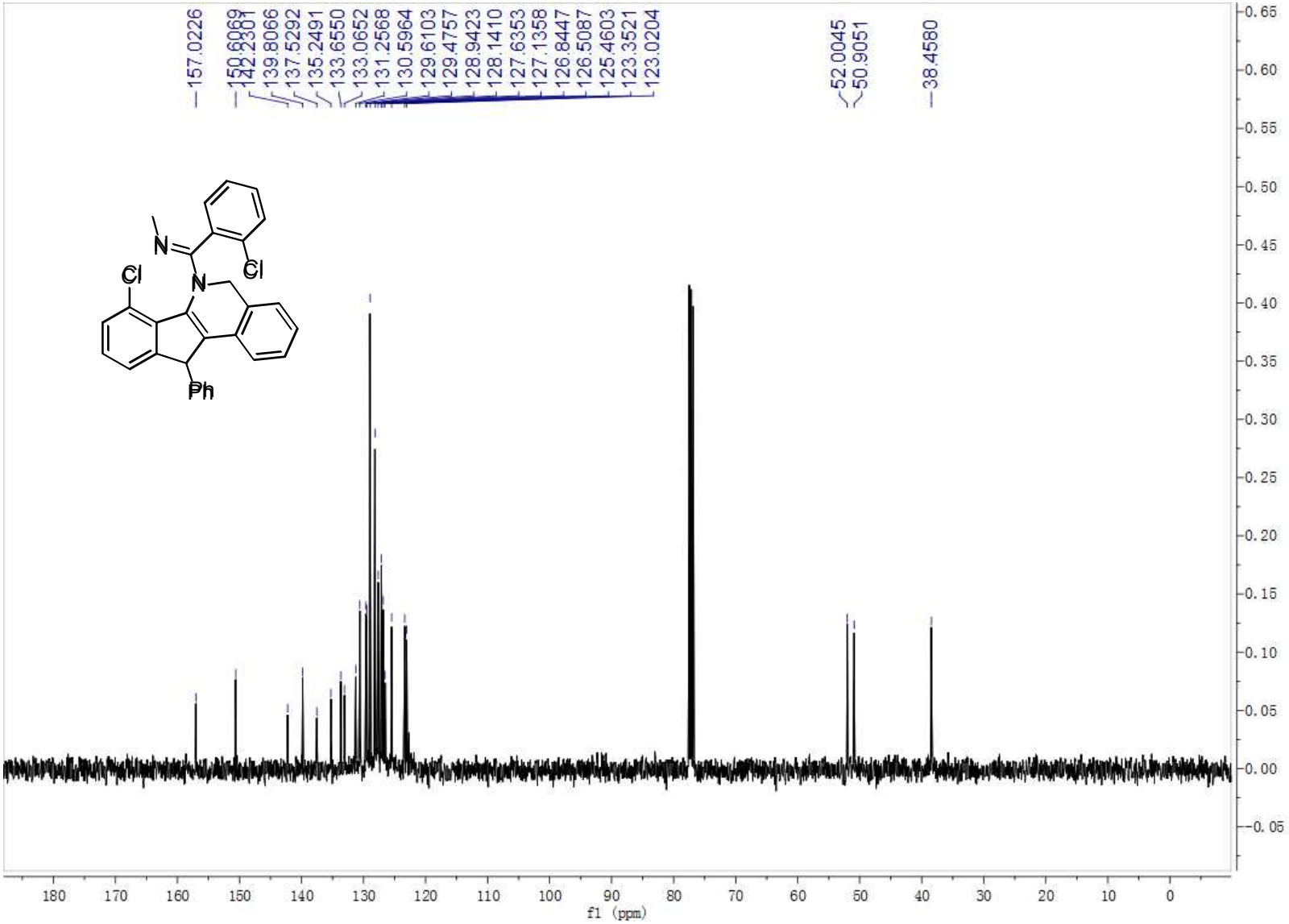
^{1}H NMR for compound **3na** and **3ia′**



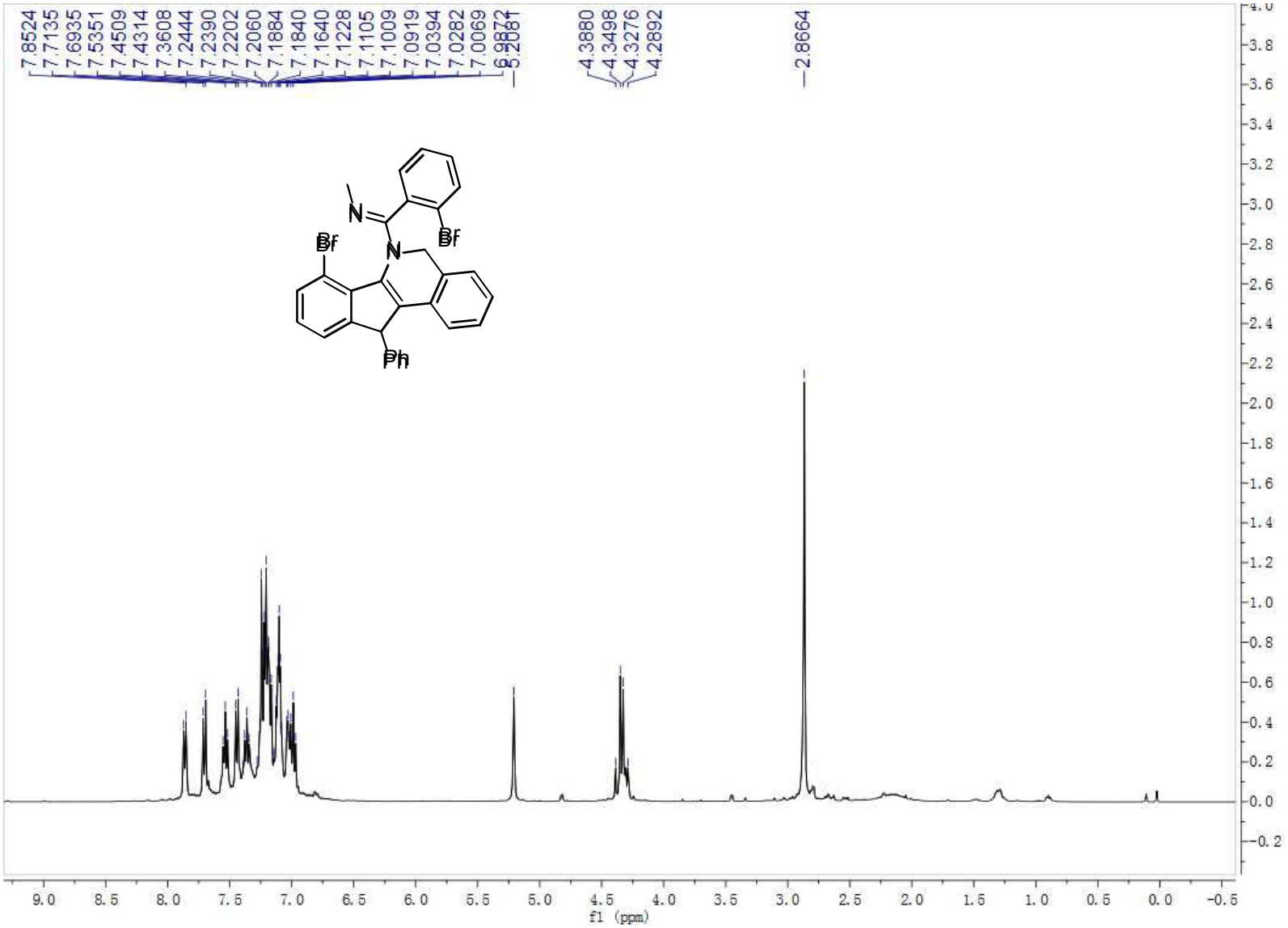
^{13}C NMR for compound **3na** and **3ia′**



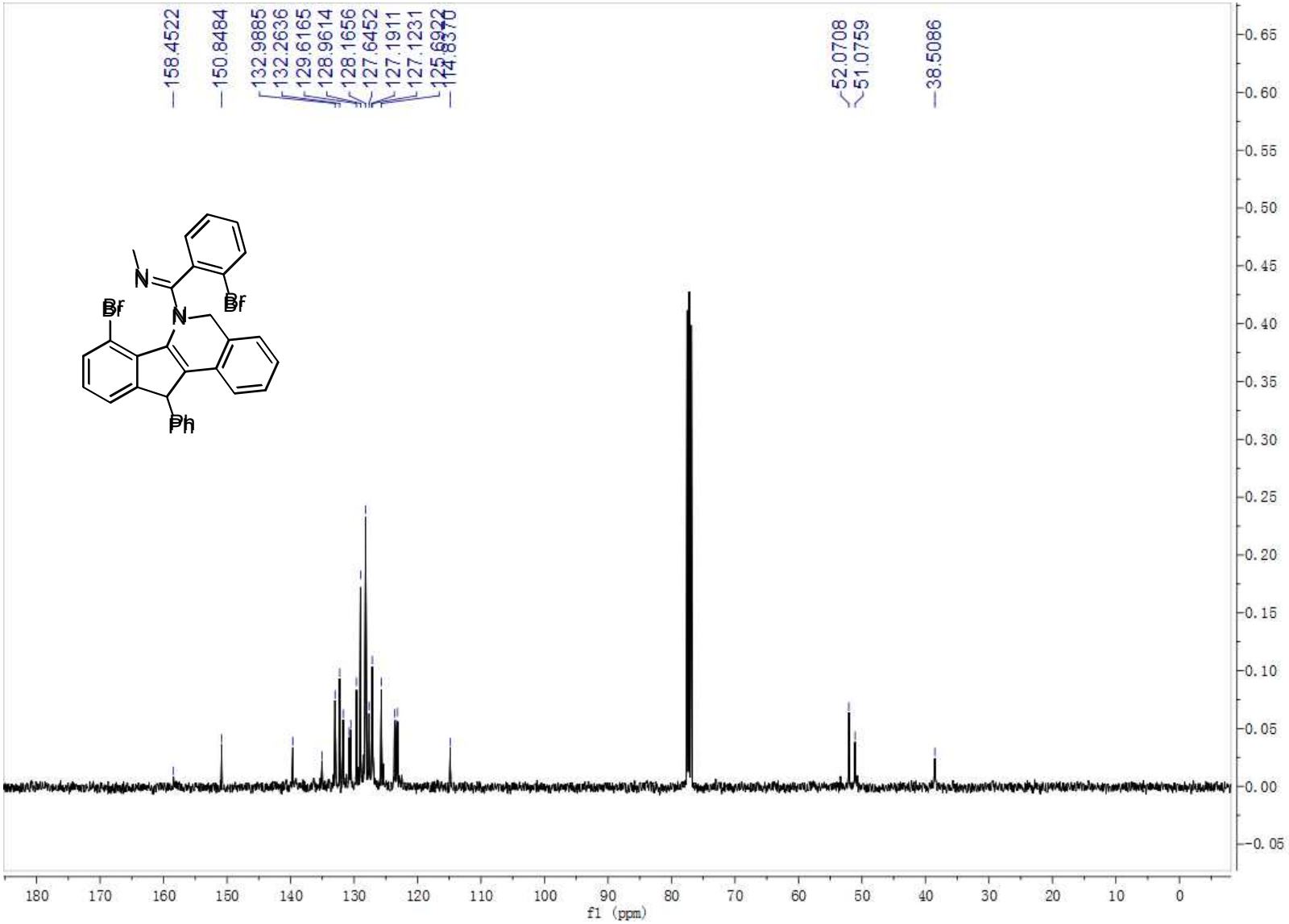
^{1}H NMR for compound **4a**



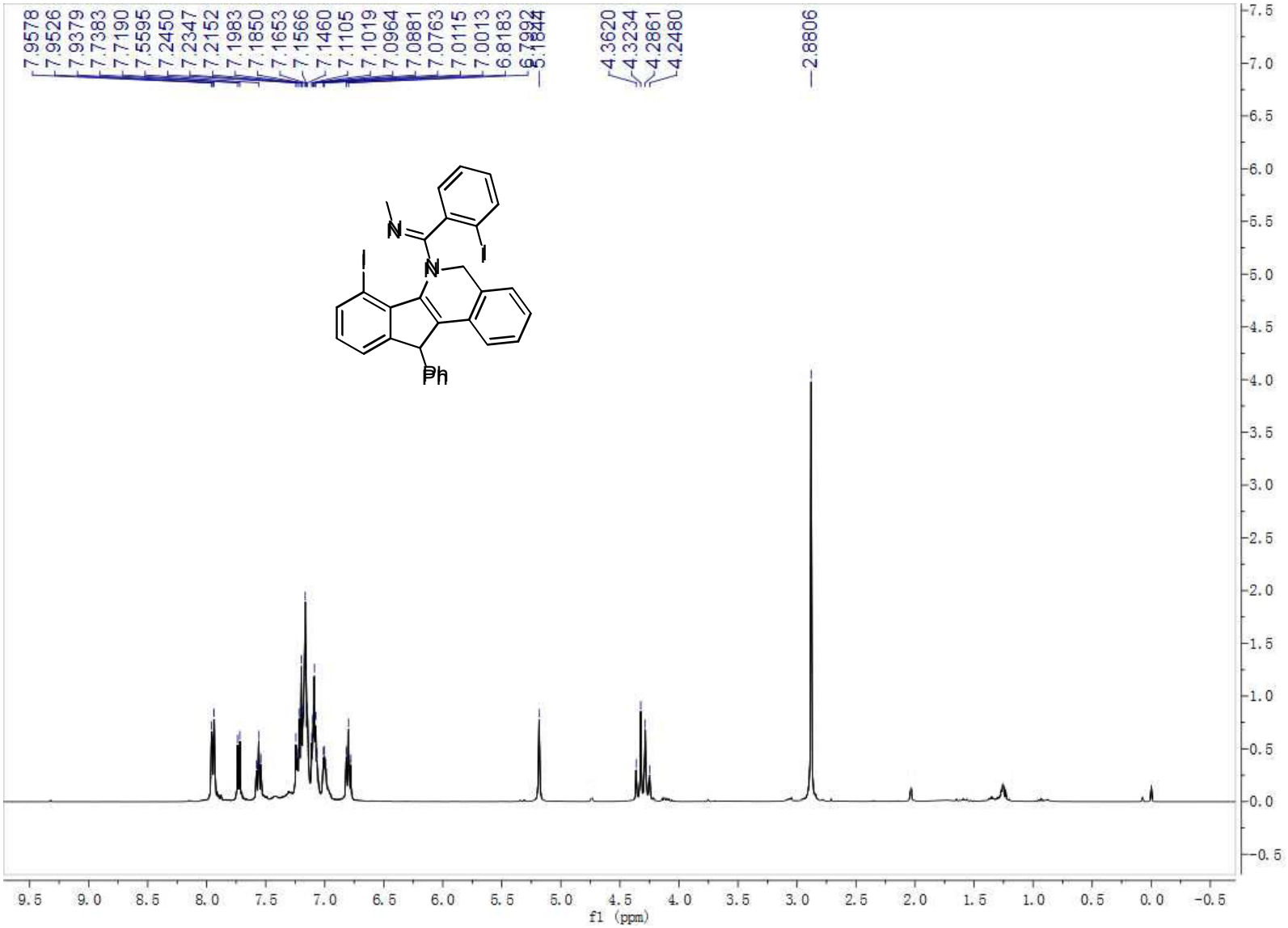
^{13}C NMR for compound **4a**



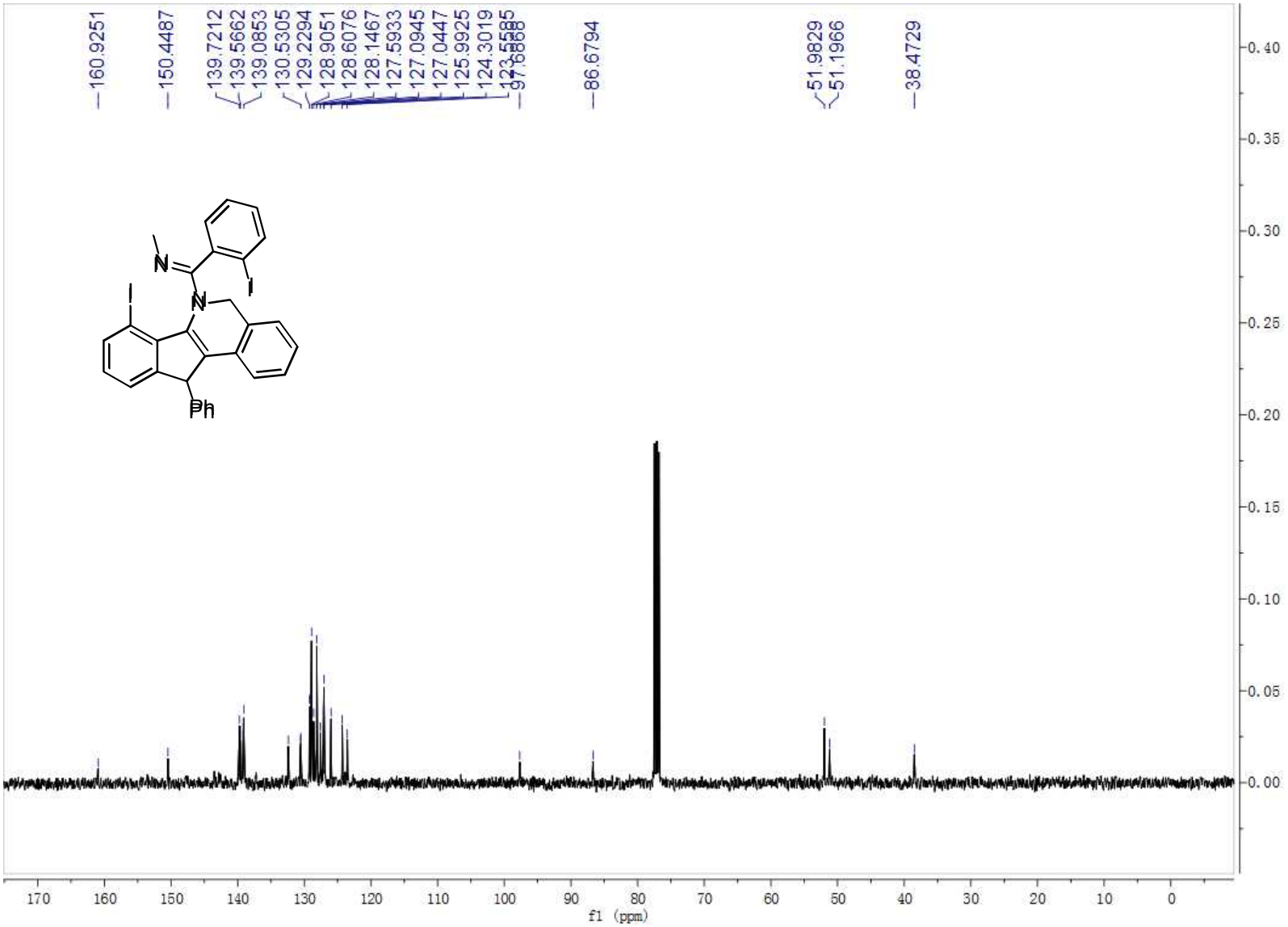
[1]H NMR for compound **4b**



^{13}C NMR for compound **4b**



^{1}H NMR for compound **4c**



^{13}C NMR for compound **4c**