SUPPORTING INFORMATION

for

Interception Of Benzyne With Thioethers: A Facile Access To Sulfur Ylides In Mild Conditions

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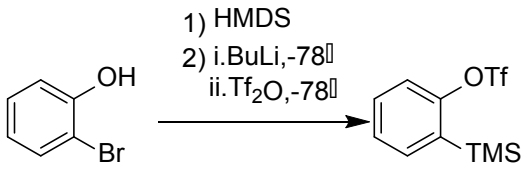
General Information

Unless otherwise stated, all commercial reagents were used without additional purification. CH_3CN was freshly distilled from calcium hydride prior to use. Benzyne precursors *o*-Trialkylsilylaryl triflates and thioethers were prepared according to literature procedures .[1,2] **I**satins were methylated with CH_3I. All reactions were performed under an argon atmosphere in an oven-dried flask. ^1H NMR spectra were recorded on 500 MHz or 400 MHz spectrometer. ^{13}C NMR spectra were recorded on 125 MHz or 100 MHz spectrometer. Chemical shifts are reported in ppm with the internal standard tetramethylsilane (δ = 0 ppm) for ^1H NMR and $CDCl_3$ (δ = 77.00 ppm) for ^{13}C NMR. HRMS: (ESI) Mass Spectra were obtained on a IonSpec FT-ICR mass spectrometer.

Preparation of starting materials:

Benzyne precursors *o*-Trialkylsilylaryl triflates and thioethers were prepared according to literature procedures .[1,2] Iatins were methylated with CH_3I.

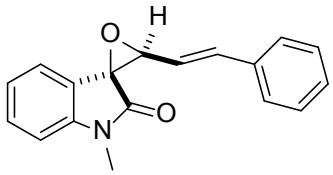
Scheme SI 1: Preparation of *o*-Trialkylsilylaryl triflates



General procedure for the on pot synthesis of spiro epoxyoxindole: To a 25 mL flask was introduced *N*-methylisatin (0.25 mmol), thioether (0.38 mmol, 1.5 equiv.), and CsF (0.76 mmol, 3.0 equiv.), The flask was then sealed with a rubber septum, evacuated and backfilled with argon three times. Then anhydrous CH_3CN (10 mL) was syringed. The mixture was stirred vigorously under 40 ℃ for 5 min before *o*-Trimethylsilylphenyl triflate (1.2 equiv.) was added in one portion, the reaction mixture was stirred at 40℃ overnight. Upon the completion of the reaction (monitored by TLC), the volatiles were removed under reduced pressure. Purification by flash column chromatography on silica gel (15% ethyl acetate in petroleum) gave the spiro epoxyoxindole**.**

(1) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E.; *Synthesis*. **2002**, 9, 1454–1458.

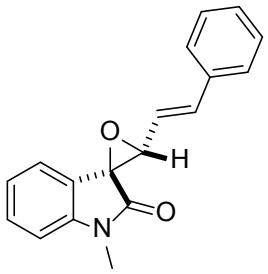
(2) Yu, M.; Xie, Y.; Xie, C.; Zhang ,Y. *Org. Lett.* **2012**, 14 (8), 2164–2167.



cis-**4aa**

1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4aa**):

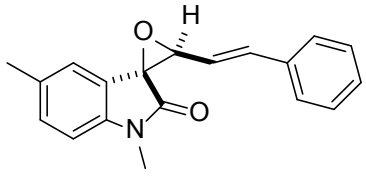
Yellowish solid. mp:138.4-138.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 7.27 (d, *J* = 2.0 Hz, 2H), 6.92 (d, *J* = 16.2 Hz, 1H), 6.80 (dd, *J* = 19.2, 8.4 Hz, 2H), 4.19 (d, *J* = 8.5 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 143.5, 138.5, 135.7, 132.9, 128.7, 127.0, 125.4, 124.9, 121.2, 115.5, 110.1, 67.4, 61.8, 26.7. HRMS calcd for $C_{18}H_{15}NO_2Na$ $[M+Na]^+$ 300.1000, found 300.0990.



trans-**4aa**

1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4aa**):

Yellowish solid. mp:141.2-143.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.50 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.37 (dd, *J* = 7.6, 2.2 Hz, 3H), 7.35 – 7.27 (m, 2H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.21 (dd, *J* = 16.0, 7.5 Hz, 1H), 4.30 (d, *J* = 7.5 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.3, 144.3, 138.6, 135.4, 132.9, 128.9, 128.8, 127.1, 126.8, 123.5, 120.4, 115.4, 110.3, 65.8, 62.0, 26.8. HRMS: calcd for $C_{18}H_{15}NO_2Na$ $[M+Na]^+$: 300.0995, found 300.1019.

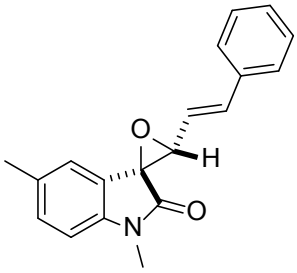


cis-**4ab**

1,5-dimethyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ab**):

Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.46 (d, *J* = 7.2 Hz, 2H),

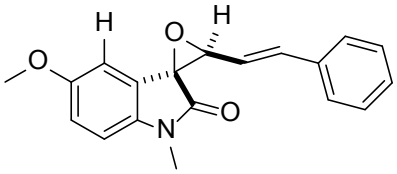
7.34-7.26 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.92-6.82 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.18 (dd, *J* =6.8, 1.2 Hz, 1H), 3.24 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.1, 142.2, 137.9, 135.9, 132.5, 130.4, 128.6, 128.5, 126.9, 123.3, 122.4, 121.9, 108.5, 67.1, 62.3, 26.6, 21.0. HRMS: calcd for $C_{19}H_{17}NO_2Na$ $[M+Na]^+$: 314.1151, found 314.1145.



trans-**4ab**

1,5-dimethyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-4ab):

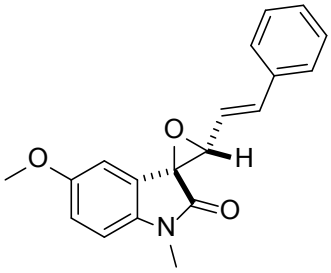
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42-7.40 (m, 2H), 7.37-7.29 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 7.00 (d, *J* = 16 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.29 (d, *J* = 7.6 Hz, 1H), 3.26 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.8, 143.0, 138.0, 135.7, 132.3, 130.4, 128.8, 128.7, 126.7, 124.8, 121.4, 121.3, 108.7, 65.5, 62.4, 26.7, 21.2. HRMS: calcd for $C_{19}H_{17}NO_2Na$ $[M+Na]^+$: 314.1151, found 314.1153.



cis-**4ac**

5-methoxy-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ac**):

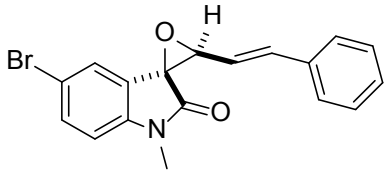
Yellowish semisolid . ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 7.2 Hz, 2H), 7.32 (dd, *J* = 14.9, 7.4 Hz, 4H), 6.89 (d, *J* = 2.7 Hz, 2H), 6.87 – 6.75 (m, 2H), 4.17 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.25 (d, *J* = 4.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.9, 156.4, 138.1, 137.9, 135.8, 128.6, 128.5, 127.0, 124.3, 121.7, 114.9, 109.3, 108.6, 67.3, 62.4, 55.9, 26.7. HRMS: calcd for $C_{19}H_{17}NO_3Na$ $[M+Na]^+$: 330.1106, found 330.1101.



trans-**4ac**

5-methoxy-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4ac**):

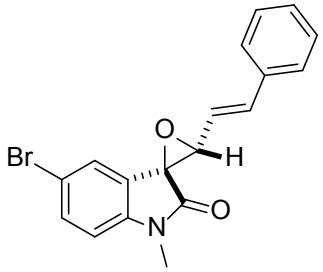
Yellowish semisolid . ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.28 (m, 3H), 6.99 (d, *J* = 15.9 Hz, 1H), 6.89 (d, *J* = 11.1 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.40 – 6.10 (m, 1H), 4.30 (d, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 3.33 – 3.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.5, 155.9, 138.7, 137.9, 135.6, 128.8, 128.7, 126.7, 122.6, 120.9, 114.4, 111.6, 109.3, 65.4, 62.5, 55.9, 26.8. HRMS: calcd for $C_{19}H_{17}NO_3Na$ $[M+Na]^+$: 330.1106, found 330.1107.



cis-**4ad**

5-bromo-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ad**):

Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.72 (s, 1H), 7.58 – 7.41 (m, 4H), 7.33 (s, 2H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.80 (dd, *J* = 17.0, 8.1 Hz, 2H), 4.37 (d, *J* = 5.8 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.4, 150.1, 143.5, 138.5, 135.7, 135.6, 132.9, 132.1, 128.7, 127.0, 121.2, 116.2, 115.5, 110.1, 67.4, 62.7, 61.6, 26.7. HRMS: calcd for $C_{18}H_{14}BrNO_2$ Na $[M+Na]^+$: 378.0100; found 378.0103.

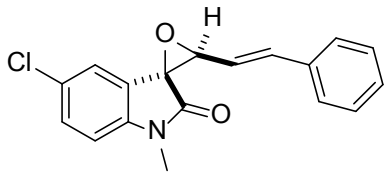


trans-**4ad**

5-bromo-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4ad**):

Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (d, *J* = 8.0 Hz, 1H),

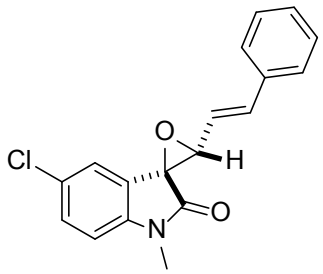
7.42 (d, *J* = 6.5 Hz, 2H), 7.36 (s, 4H), 7.00 (d, *J* = 15.9 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.21 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ ppm 171.3, 144.3, 138.6, 135.4, 132.9, 128.9, 128.8, 127.1, 126.8, 123.5, 120.4, 115.4, 110.3, 65.8, 61.9, 53.2, 26.8. HRMS: calcd for $C_{18}H_{14}BrNO_2Na$ $[M+Na]^+$: 378.0106, found 378.0119.



cis-**4ae**

5-chloro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ae**):

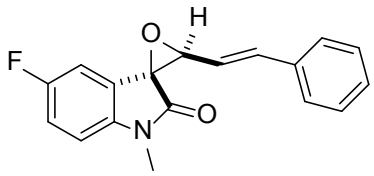
Yellowish solid. mp:118.4-119.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.38 (d, *J* = 7.2 Hz, 2H), 7.27-7.18 (m, 4H), 7.05 (s, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.76 (dd, *J* = 14.8, 7.2 Hz, 2H), 4.12 (d, 8.4 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.6, 143.0, 138.5, 135.7, 130.0, 128.7, 128.4, 127.0, 125.1, 122.2, 121.2, 109.7, 67.4, 61.9, 26.8. HRMS: calcd for $C_{18}H_{14}ClNO_2Na$ $[M+Na]^+$: 334.0605, found 334.0608.



trans-**4ae**

5-chloro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4ae**):

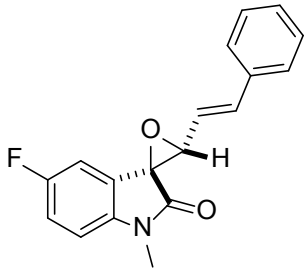
Yellowish solid. mp:123.1-123.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42-7.40 (m, 2H), 7.37-7.30 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.01 (d, *J* = 15.6 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.26 (dd, *J* = 15.6, 7.2 Hz, 1H), 4.31 (dd, *J* = 7.2, 0.4 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.4, 143.8, 138.6, 135.4, 130.0, 128.9, 128.8, 128.2, 126.8, 124.3, 120.4, 109.8, 65.8, 62.1, 26.8. HRMS: calcd for $C_{18}H_{14}ClNO_2Na$ $[M+Na]^+$: 334.0605, found 334.0622.



cis-**4af**

5-fluoro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4af**):

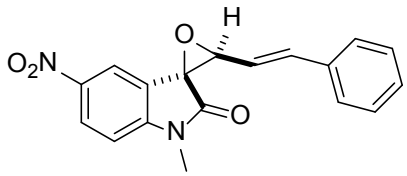
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (d, *J* = 7.3 Hz, 2H), 7.25 – 7.16 (m, 3H), 6.99 (t, *J* = 8.8 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.75 (dd, *J* = 15.2, 8.8 Hz, 2H), 4.09 (d, *J* = 8.2 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 160.5, 158.1, 140.4, 138.4, 135.7, 128.6, 126.9, 125.0 (d, *J* = 8.4 Hz), 121.2, 116.4 (d, *J* = 23.6 Hz), 109.6 (dd, *J* = 49.7, 16.8 Hz), 67.3, 62.1, 26.7. HRMS: calcd for $C_{18}H_{14}NO_2Na$ $[M+Na]^+$: 318.0901, found 318.0902.



trans-**4af**

5-fluoro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4af**):

Yellowish semisolid.^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.08 (t, *J* = 8.8 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.84 (dd, *J* = 8.4, 3.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 7.3 Hz, 1H), 4.31 (d, *J* = 7.3 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.7, 160.3, 157.9, 141.4, 138.5, 135.5, 129.0, 129.0, 126.9, 123.2 (d, *J* = 8.5 Hz), 120.6, 116.6 (d, *J* = 23.7 Hz), 112.4, 112.2, 109.6 (d, *J* = 8.1 Hz), 65.8, 62.4, 26.8. HRMS: calcd for $C_{18}H_{14}NO_2Na$ $[M+Na]^+$: 318.0901,found 318.0908.

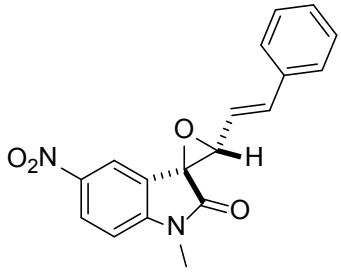


cis-**4ag**

1-methyl-5-nitro-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ag**):

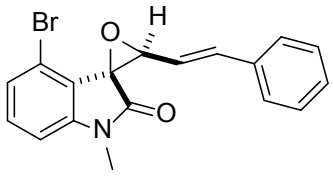
Yellowish solid. mp:147.3-148.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.33 (d, *J* = 8.6 Hz, 1H), 8.04 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.02 – 6.92

(m, 2H), 6.76 (dd, *J* = 16.1, 8.7 Hz, 1H), 4.32 (d, *J* = 8.6 Hz, 1H), 3.33 (s, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.2, 149.7, 143.6, 139.2, 135.5, 128.9, 128.7, 127.0, 124.4, 120.4, 117.6, 108.4, 67.7, 61.5, 29.7, 27.1. HRMS: calcd for $C_{18}H_{14}N_2O_4Na$ $[M+Na]^+$: 345.0846, found 345.0843.



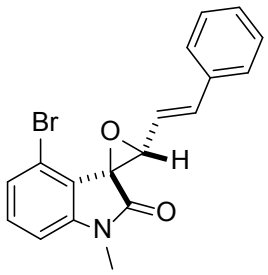
trans-**4ag**

1-methyl-5-nitro-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4ag**): Yellowish semisolid. ^{1}H NMR (400 MHz, DMSO): δ ppm 8.38 (d, *J* = 8.8 Hz, 1H), 8.24 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.40-7.32 (m, 4H), 7.17 (d, *J* = 16 Hz, 1H), 6.62 (dd, *J* = 15.6, 6.8 Hz, 1H), 4.37 (d, *J* = 7.2 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ ppm 171.3, 151.2, 142.7, 138.0, 135.3, 128.7, 128.6, 127.1, 126.9, 121.9, 121.0, 119.0, 109.7, 65.7, 61.4, 27.0. HRMS: calcd for $C_{18}H_{14}N_2O_4Na$ $[M+Na]^+$: 345.0846, found 345.0845.



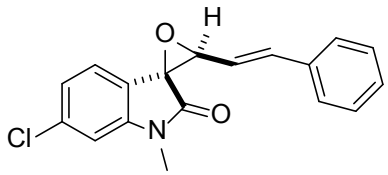
cis-**4ah**

4-bromo-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ah**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.47-7.45 (m, 2H), 7.34-7.27 (m, 3H), 7.22-7.17 (m, 2H), 6.98-6.86 (m, 2H), 6.84 (dd, *J* = 6.4, 2.4 Hz, 1H), 5.00 (d, *J* = 8.0 Hz, 1H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.5, 145.4, 137.5, 134.9, 130.1, 127.6, 127.5, 126.3, 125.9, 120.1, 119.7, 116.6, 106.7, 62.2, 61.0, 25.7. HRMS: calcd for $C_{18}H_{14}BrNO_2Na$ $[M+Na]^+$: 378.0100, found 378.0100.



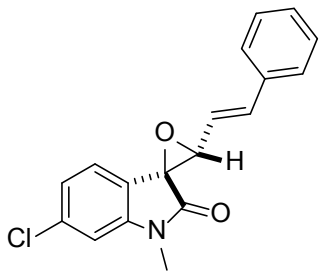
trans-**4ah**

4-bromo-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (trans-**4ah**): Yellowish semisolid.^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.41-7.39 (m, 2H), 7.35-7.28 (m, 3H), 7.25-7.20 (m, 2H), 7.08 (dd, *J* = 16, 8.8 Hz, 1H), 6.92-6.86 (m, 2H), 4.22 (d, *J* = 9.2 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.8, 146.9, 139.0, 135.6, 131.1, 128.7, 128.2, 126.7, 122.8, 120.4, 117.9, 108.0, 69.2, 64.6, 26.8. HRMS: calcd for $C_{18}H_{14}BrNO_2Na$ $[M+Na]^+$: 378.0100, found 378.0097.



cis-**4ai**

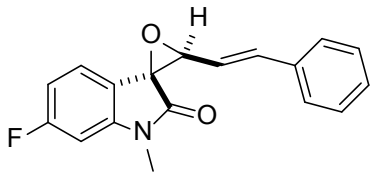
6-chloro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ai**): Yellowish solid. mp:140.7-141.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39 (d, *J* = 7.2 Hz, 2H), 7.27-7.20 (m, 3H), 7.00 (s, 2H), 6.86-6.82 (m, 2H), 6.77 (dd, *J* = 16.4, 8.4 Hz, 1H), 4.12 (d, *J* = 8.4 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.2, 145.7, 138.3, 136.0, 135.5, 128.6, 126.9, 122.6, 122.5, 121.6, 121.2, 109.5, 67.2, 62.0, 26.7. HRMS: calcd for $C_{18}H_{14}ClNO_2Na$ $[M+Na]^+$: 334.0605,found 334.0602.



trans-**4ai**

6-chloro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4ai**): Yellowish solid. mp:138.8-139.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42 (d, *J* = 7.2Hz, 2H), 7.37-7.31 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 1H),

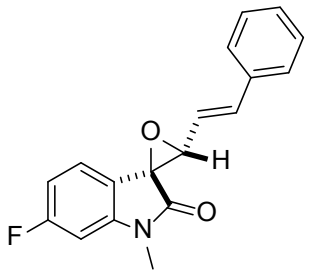
7.01 (d, *J* = 15.6 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.26 (dd, *J* = 16.0, 7.2 Hz, 1H), 4.31 (d, *J* = 7.2 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 172.0, 146.6, 138.2, 136.4, 135.6, 129.0, 128.9, 126.9, 124.9, 122.7, 120.8, 109.9, 65.6, 62.2, 26.9. HRMS: calcd for $C_{18}H_{14}ClNO_2Na$ $[M+Na]^+$: 334.0605, found 334.0615.



cis-**4aj**

6-fluoro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4aj**):

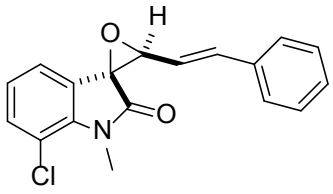
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39 (d, J = 6.4 Hz, 2H), 7.28-7.19 (m, 3H), 7.03 (d, J = 4.0 Hz, 1H), 6.86 (d, J = 16.4 Hz, 1H), 6.72-6.68 (m, 2H), 6.59 (d, J = 8.8 Hz, 1H), 4.12 (d, J = 8.0 Hz, 1H), 3.18 (s, 3H)); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 165.6, 163.2, 146.1, 138.3, 135.8, 130.9, 128.7, 126.9, 123.0 (d, *J* = 10.1 Hz), 121.4, 109.0 (d, *J* = 22.7 Hz), 97.8 (d, *J* = 27.8 Hz), 67.1, 61.9, 26.8. HRMS: calcd for $C_{18}H_{14}FNO_2Na$ $[M+Na]^+$: 318.0901; found 318.0917.



trans-**4aj**

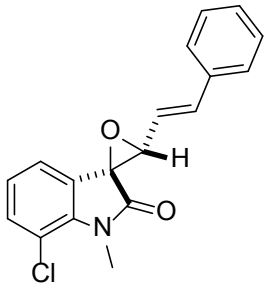
6-fluoro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4aj**):

Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.35 (d, J = 6.4 Hz, 2H), 7.30-7.24 (m, 3H), 7.14 (dd, J = 7.2, 4.0 Hz, 1H), 6.94 (d, J = 16.0 Hz, 1H), 6.70 (t, J = 8.4 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 6.20 (dd, J = 16.0, 6.8 Hz), 4.23 (d, J = 6.8 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 172.2, 165.6, 163.2, 147.0, 138.0, 135.5, 128.8, 126.8, 125.3 (d, *J* = 10.0 Hz), 120.8, 116.7, 109.0 (d, *J* = 22.7 Hz), 98.0 (d, *J* = 27.8 Hz), 65.3, 62.0, 26.8. HRMS: calcd for $C_{18}H_{14}FNO_2Na$ $[M+Na]^+$: 318.0901, found 318.0921.



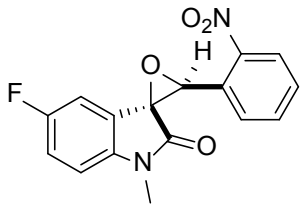
cis-**4ak**

7-chloro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ak**): Yellowish solid. mp:146.0-148.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.46-7.44 (d, *J* = 8.0 Hz, 2H), 7.35-7.30 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.04-6.98 (m, 2H), 6.93 (d, *J* = 16 Hz, 1H), 6.83 (dd, *J* = 16.4, 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.3, 140.2, 138.5, 135.7, 132.4, 128.7, 127.0, 126.2, 123.6, 121.2, 120.0, 116.3, 67.8, 61.7, 29.9. HRMS: calcd for $C_{18}H_{14}ClNO_2Na$ $[M+Na]^+$: 334.0605, found 334.0607.



trans-**4ak**

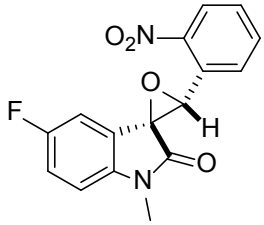
7-chloro-1-methyl-3'-((E)-styryl)spiro[indoline-3,2'-oxiran]-2-one (*trans*-**4ak**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40 (d, *J* = 6.8 Hz, 2H), 7.36-7.28 (m, 4H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.00-6.96 (m, 2H), 6.26 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.31 (d, *J* = 7.2 Hz, 1H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 172.2, 141.0, 138.4, 135.5, 132.4, 128.8, 126.8, 124.3, 123.4, 122.4, 120.4, 116.5, 66.2, 61.8, 30.2. HRMS: calcd for $C_{18}H_{14}ClNO_2Na$ $[M+Na]^+$: 334.0605, found 334.0615.



cis-**4bf**

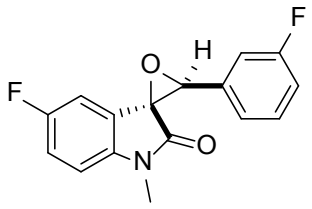
5-fluoro-1-methyl-3'-(2-nitrophenyl)spiro[indoline-3,2'-oxiran]-2-one (*cis*-**4bf**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.6 Hz, 1H), 8.00 (s, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.12 (dd, *J* = 12.2, 5.4 Hz, 1H),

7.07 – 7.01 (m, 1H), 6.83 (dd, *J* = 8.4, 3.8 Hz, 1H), 5.06 (s, 1H), 3.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): ppm 169.4, 160.6, 158.3, 146.5, 140.8, 133.8, 130.4, 129.7, 124.5, 121.9, 117.0, 116.8, 110.5, 110.2, 109.6, 109.5, 62.3, 65.1, 26.7. HRMS: calcd for $C_{16}H_{11}FN_2O_4Na$ $[M+Na]^+$: 337.0601 ,found 337.0617.



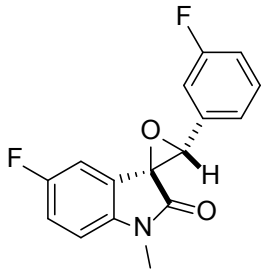
tran-**4bf**

5-fluoro-1-methyl-3'-(2-nitrophenyl)spiro[indoline-3,2'-oxiran]-2-one (*tran*-**4bf**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 10.7 Hz, 1H), 8.07 – 8.01 (m, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.00 – 6.91 (m, 1H), 5.82 – 5.71 (m, 1H), 5.16 (s, 1H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm170.7, 159.7, 157.3, 146.8, 141.5, 134.5, 130.4, 129.5, 125.1, 122.0, 116.9, 116.7, 110.7, 110.4, 109.6, 109.5, 64.4, 61.7, 26.9. HRMS: calcd for $C_{16}H_{11}FN_2O_4Na$ $[M+Na]^+$: 337.0601 ,found 337.0617.



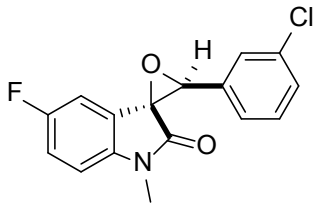
cis-**4df**

5-fluoro-3'-(3-fluorophenyl)-1-methylspiro[indoline-3,2'-oxiran]-2-one (*cis*-**4df**): Yellowish solid. mp:158.0-158.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.34 (s, 3H), 7.12-7.03 (m, 2H), 6.97-6.95 (m, 1H), 6.83 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.60 (s, 1H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.3, 163.6, 160.8(d, *J* = 62.4 Hz), 158.1, 140.5, 133.9 (d, *J* = 7.7 Hz), 129.3 (d, *J* = 8.1 Hz), 124.9 (d, *J* = 8.4 Hz), 123.1 (d, *J* = 2.9 Hz), 116.3 (dd, *J* = 70.8, 22.4 Hz), 114.7(d, *J* = 23.1 Hz), 109.6 (dd, *J* = 53.4, 16.7 Hz), 66.8, 61.8, 26.6. HRMS: calcd for $C_{16}H_{11}NO_2F_2Na$ $[M+Na]^+$: 310.0656 ,found 310.0654 .



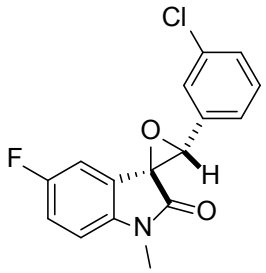
trans-**4df**

5-fluoro-3'-(3-fluorophenyl)-1-methylspiro[indoline-3,2'-oxiran]-2-one(*trans*-**4df**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.43 (dd, *J* = 13.6, 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 9.2 Hz, 1H), 7.12 (t, *J* = 8.4 Hz, 1H), 7.02-6.97 (m, 1H), 6.82 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.23 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.80 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.0, 164.1, 161.6, 159.9, 157.5, 141.3, 135.4, 135.3, 130.5 (d, *J* = 8.4 Hz), 122.3 (t, *J* = 5.3 Hz), 116.4 (dd, *J* = 58.0, 22.4 Hz), 113.8 (d, *J* = 23.1 Hz), 111.8 (d, *J* = 26.4 Hz), 109.3 (d, *J* = 8.1 Hz), 64.5(d, *J* = 2.6 Hz), 61.5, 26.8. HRMS: calcd for $C_{16}H_{11}NO_2F_2Na$ $[M+Na]^+$: 310.0656 ,found 310.0659 .



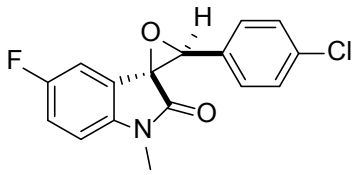
cis-**4ef**

3'-(3-chlorophenyl)-5-fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ef**): Yellowish solid. mp:179.8-180.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.57 (s, 1H), 7.49 (d, *J* = 3.2 Hz, 1H), 7.32 (d, *J* = 4.4 Hz, 2H), 7.12 (td, *J* = 8.8, 2.0 Hz, 1H), 6.97 (dd, *J* = 7.2, 2.4 Hz, 1H), 6.83 (dd, , *J* = 8.4, 3.6 Hz, 1H), 4.58 (s, 1H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.3, 160.5, 158.1, 140.5, 133.8, 133.4, 129.1 (d, *J* = 6.6 Hz), 127.6, 125.6, 124.8 (d, *J* = 8.1 Hz), 116.7 (d, *J* = 23.8 Hz), 109.9 (d, *J* = 25.7 Hz), 109.4 (d, *J* = 8.1 Hz), 66.7, 61.8, 26.7. HRMS: calcd for $C_{16}H_{11}NO_2FClNa$ $[M+Na]^+$: 326.0360 , found 326.0352 .



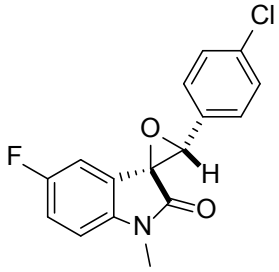
trans-**4ef**

3'-(3-chlorophenyl)-5-fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one(*trans*-**4ef**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.44 (s, 1H), 7.38-7.32 (m, 3H), 7.03 (td, *J* = 8.8, 2.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.23 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.78 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.0, 159.9, 157.5, 141.3, 134.8, 130.0, 129.3, 126.8, 124.7, 122.2 (d, *J* = 8.8 Hz), 116.7 (d, *J* = 23.5 Hz), 111.8 (d, *J* = 26.4 Hz), 109.3 (d, *J* = 8.1 Hz), 64.4, 61.5, 26.8. HRMS: calcd for $C_{16}H_{11}NO_2FClNa$ $[M+Na]^+$: 326.0360 , found 326.0351 .



cis-**4ff**

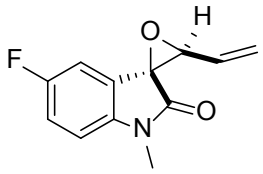
3'-(4-chlorophenyl)-5-fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one (*cis*-**4ff**): Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.54 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 6.0 Hz, 1H), 6.83 (dd, *J* = 8.0, 3.2 Hz, 1H), 4.58 (s, 1H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.4, 160.5, 158.1, 140.5 (d, *J* = 1.8 Hz), 134.9, 129.8, 128.9, 128.0, 124.93 (d, *J* = 8.1 Hz), 116.58 (d, *J* = 23.5 Hz), 110.0, 109.37 (d, *J* = 7.7 Hz), 67.0, 61.8, 26.6. HRMS: calcd for $C_{16}H_{11}NO_2FClNa$ $[M+Na]^+$: 326.0360, found 326.0368 .



trans-**4ff**

3'-(4-chlorophenyl)-5-fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one(*trans*-**4ff**)
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42-7.37 (m, 4H), 7.02 (t, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 4.78 (s, 1H),

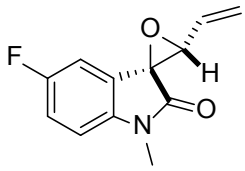
3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.1, 159.9, 157.5, 141.2, 135.0, 131.3, 129.0, 128.0, 122.3 (d, *J* = 8.8 Hz), 116.6 (d, *J* = 23.8 Hz), 111.8 (d, *J* = 26.4 Hz), 109.3 (d, *J* = 8.1 Hz), 64.6, 61.5, 26.8. HRMS: calcd for $C_{16}H_{11}NO_2FClNa$ $[M+Na]^+$: 326.0360 , found 326.0353 .



cis-**4gf**

5-fluoro-1-methyl-3'-vinylspiro[indoline-3,2'-oxiran]-2-one (*cis*-**4gf**):

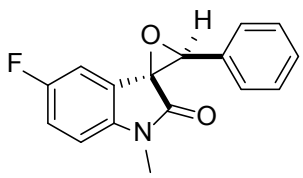
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.09 (t, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 0.8 Hz, 1H), 6.84 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.50-6.41 (m, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.55 (d, *J* = 10.4 Hz, 1H), 4.01 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.7, 160.5, 158.1, 140.4, 130.6, 124.9 (d, *J* = 8.4 Hz), 123.8, 116.4 (d, *J* = 23.5 Hz), 109.9 (d, *J* = 25.7 Hz), 109.4 (d, *J* = 8.1 Hz), 67.0, 61.7, 16.8. HRMS: calcd for $C_{12}H_{10}FNO_2Na$ $[M+Na]^+$: 242.0593, found 242.0599.



trans-**4gf**

5-fluoro-1-methyl-3'-vinylspiro[indoline-3,2'-oxiran]-2-one (*trans*-**4gf**):

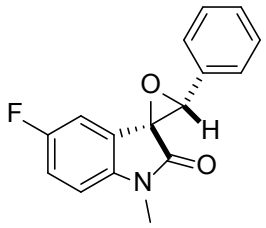
Yellowish solid. mp:137.0-137.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.12 (t, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.86 (dd, *J* = 8.4, 3.6 Hz, 1H), 5.98 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.76 (d, *J* = 17.2 Hz, 1H), 5.62 (d, *J* = 10.8 Hz, 1H), 4.16 (d, *J* = 6.8 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.5, 160.1, 157.7, 141.2, 129.9, 123.6, 122.9, 122.8, 116.4 (d, *J* = 23.5 Hz), 112.3 (d, *J* = 26.4 Hz), 109.4 (d, *J* = 8.1 Hz), 65.2, 61.6, 26.8. HRMS: calcd for $C_{12}H_{10}FNO_2Na$ $[M+Na]^+$: 242.0593 ,found 242.0592.



cis-**4hf**

5-fluoro-1-methyl-3'-phenylspiro[indoline-3,2'-oxiran]-2-one (*cis*-**4hf**):

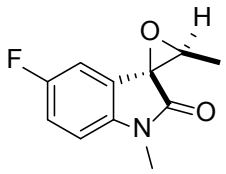
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, *J* = 7.2Hz, 2H), 7.42-736 (m, 3H), 7.12 (t, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.83-6.81 (m, 1H), 4.64 (s, 1H), 3.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.6, 160.5, 158.1, 140.5, 131.3, 129.0, 127.6 (d, *J* = 30.0 Hz), 125.3 (d, *J* = 8.4 Hz), 116.4 (d, *J* = 23.6 Hz), 109.9(d, *J* = 25.4 Hz), 109.3(d, *J* = 7.9 Hz), 67.7, 61.9, 26.6. HRMS: calcd for $C_{16}H_{12}FNO_2Na$ $[M+Na]^+$: 292.0744, found 292.0764.



trans-**4hf**

5-fluoro-1-methyl-3'-phenylspiro[indoline-3,2'-oxiran]-2-one (trans-**4hf**):

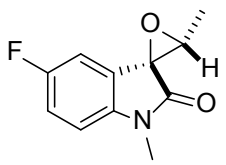
Yellowish semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.43-7.40 (m, 5H), 7.00 (t, J = 8.4 Hz, 1H), 6.80-6.78 (m, 1H), 6.22 (d, J = 8.0 Hz, 1H), 4.84 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.4, 159.9, 157.5, 141.2, 132.7, 128.8 (d, *J* = 36.2 Hz), 122.7 (d, *J* = 8.8 Hz), 122.7, 122.6, 116.4 (d, *J* = 23.8 Hz), 111.9 (d, *J* = 26.3 Hz), 109.1 (d, *J* = 8.1 Hz), 65.2, 61.5, 26.8. HRMS: calcd for $C_{16}H_{12}NO_2FNa$ $[M+Na]^+$: 292.0750, found 292.0733.



cis-**4if**

5-fluoro-1,3'-dimethylspiro[indoline-3,2'-oxiran]-2-one (*cis*-**4if**):

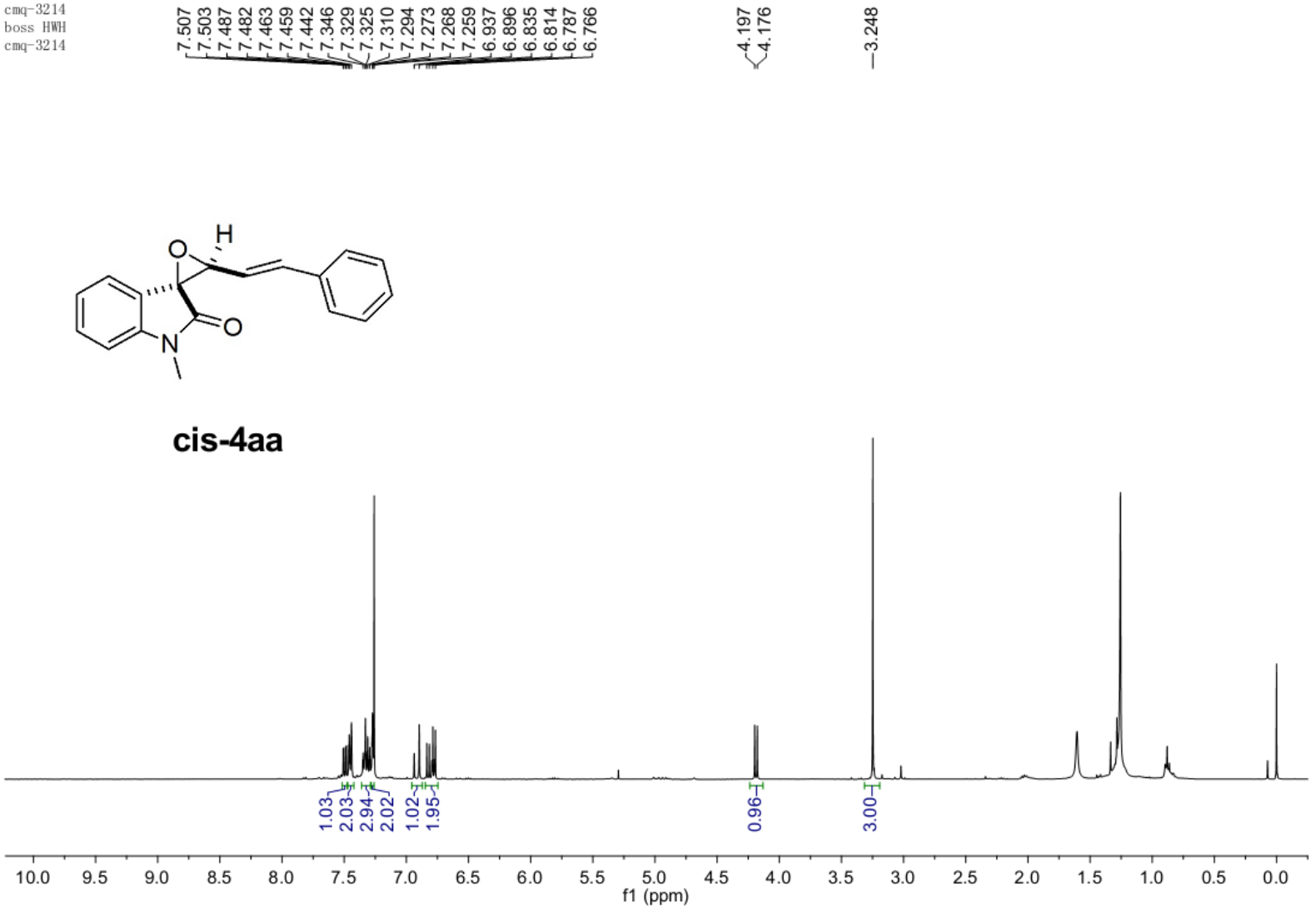
Yellowish solid. mp:143.5-143.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.07 (t, *J* = 8.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 2H), 3.71-3.68 (m, 1H), 3.25 (s, 3H), 1.73 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.4, 160.5, 158.1, 140.3, 125.88 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 23.8 Hz), 109.5 (dd, *J* = 61.3, 16.9 Hz), 63.4, 59.6, 26.7, 12.2. HRMS: calcd for $C_{11}H_{10}FNO_2Na$ $[M+Na]^+$: 230.0588, found 230.0604.

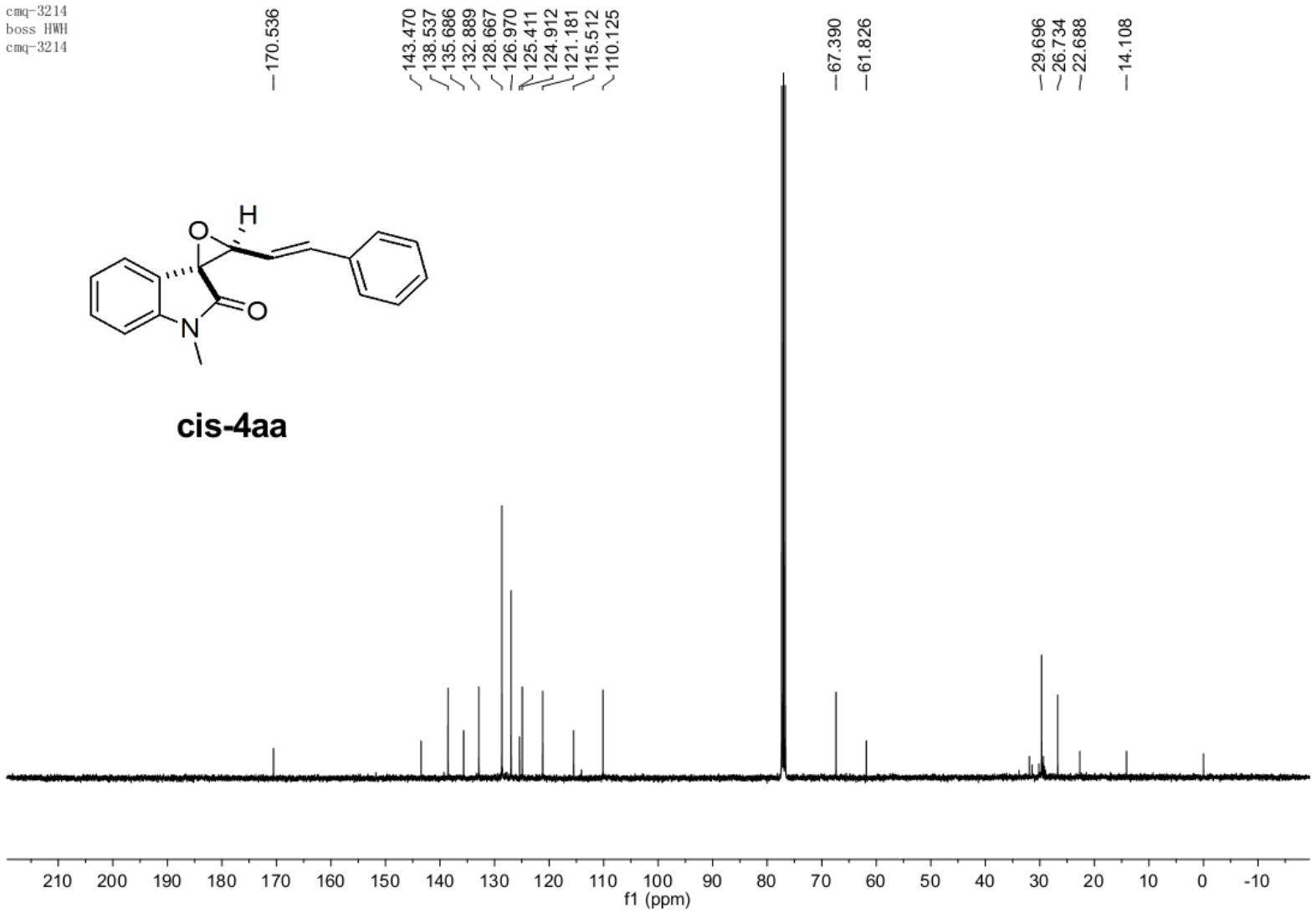


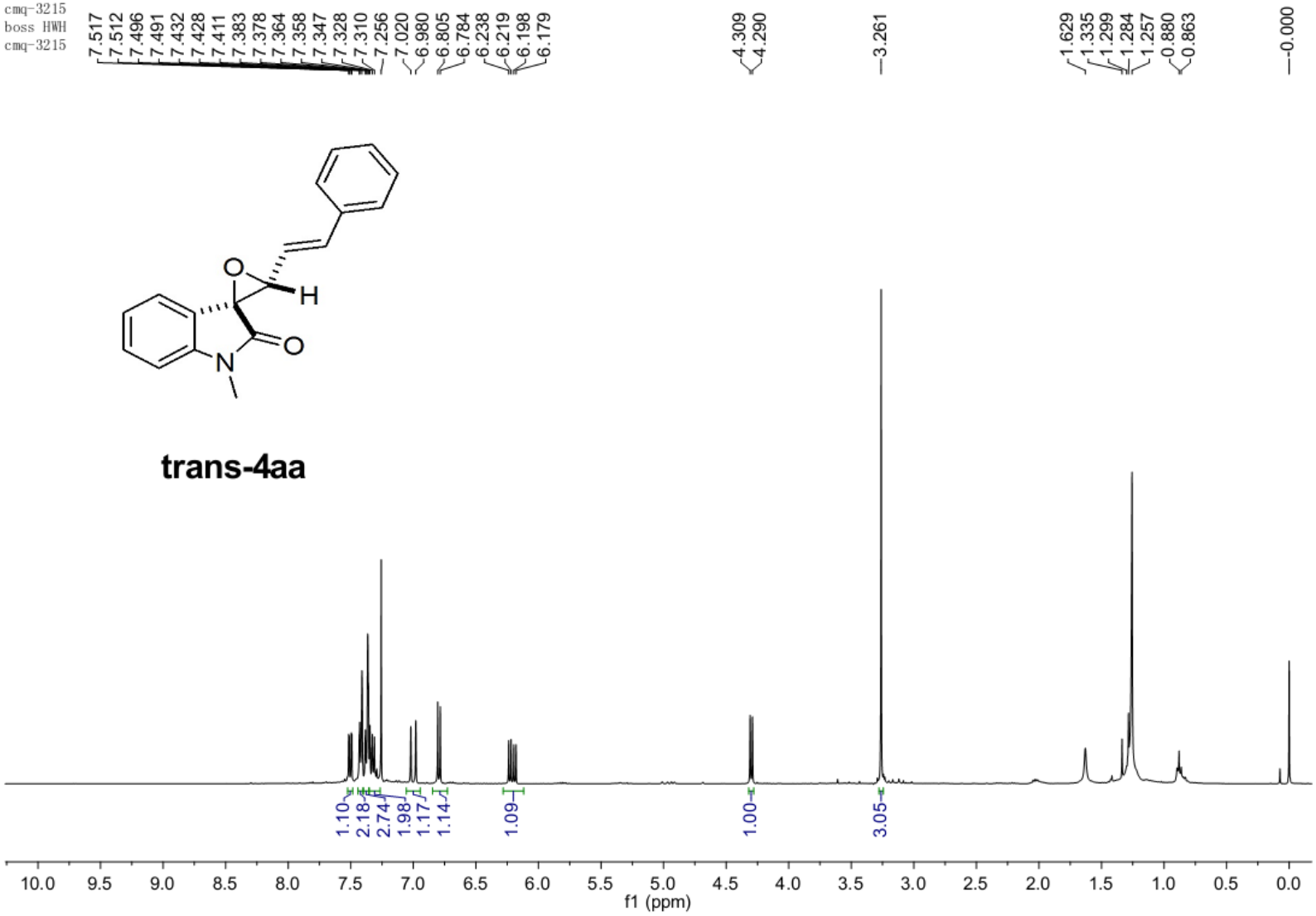
trans-**4if**

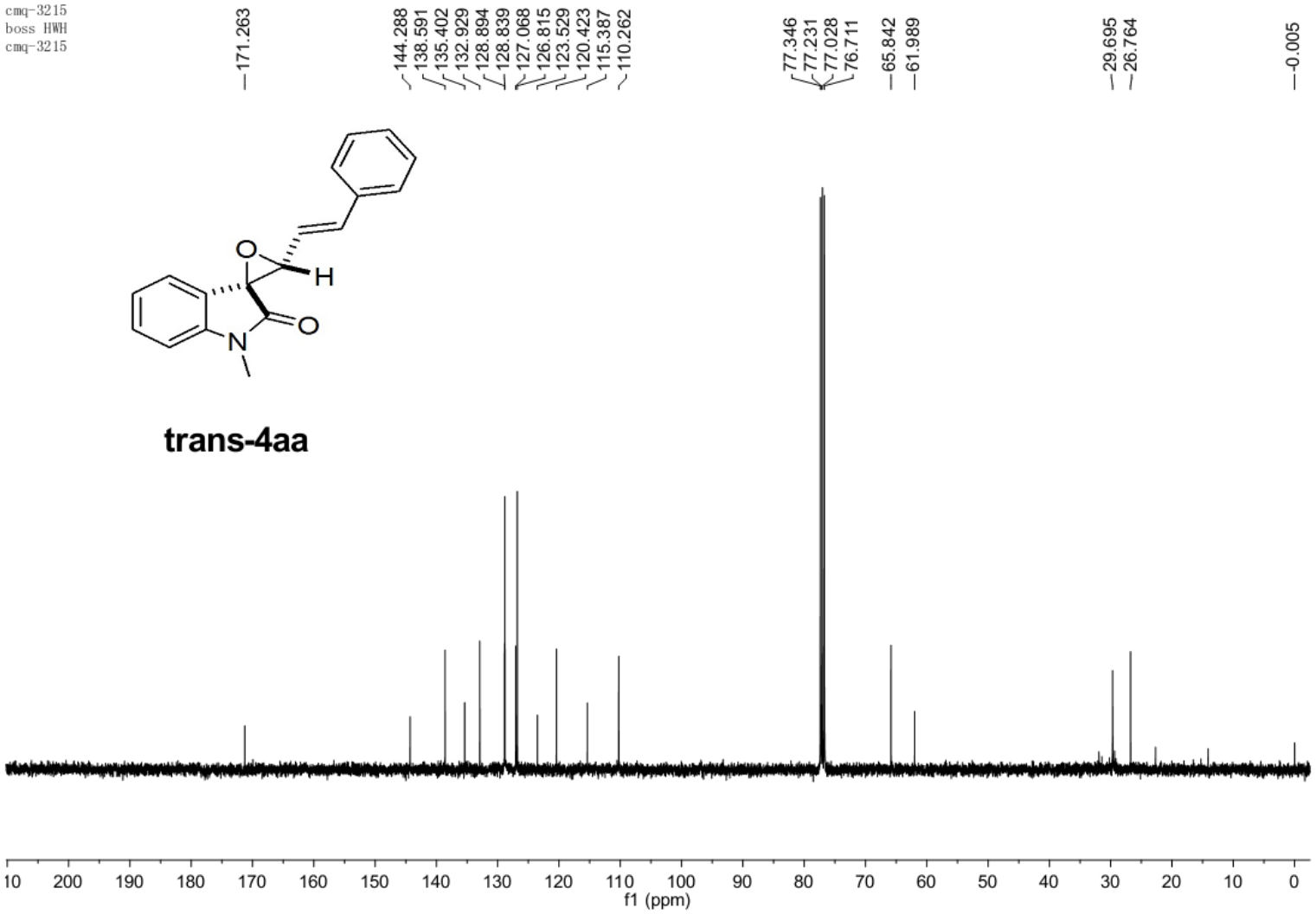
5-fluoro-1,3'-dimethylspiro[indoline-3,2'-oxiran]-2-one (*trans*-**4if**):

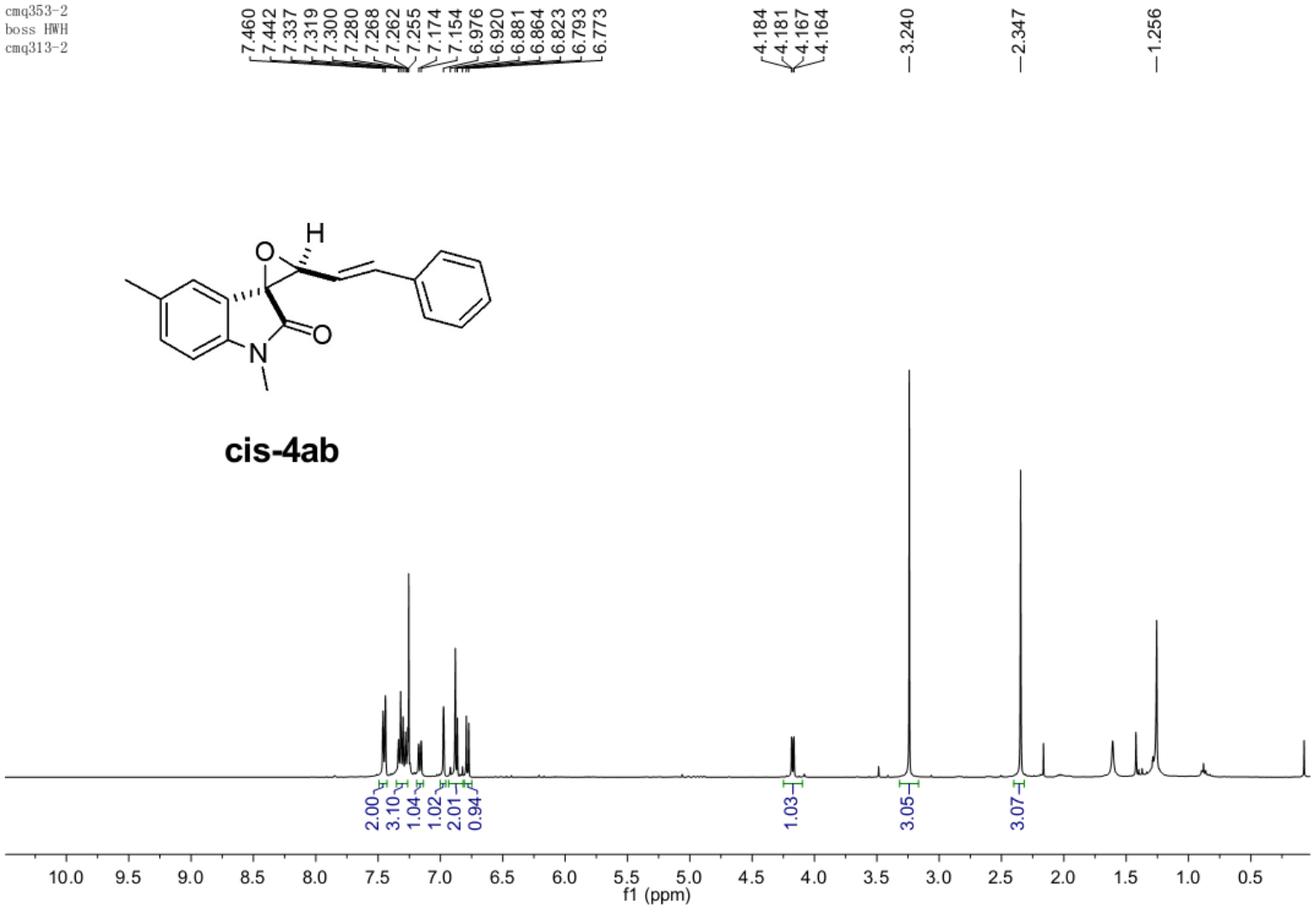
Yellowish semsolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.12 (t, J = 8.8 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.88-6.85 (m, 1H), 3.79 (q, J = 5.2 Hz, 1H), 3.26 (s, 3H), 1.59 (d, J = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 172.3, 160.2, 157.8, 141.3, 123.6 (d, J = 8.4 Hz), 116.2 (d, J = 23.8 Hz), 112.2 (d, J = 25.7 Hz), 109.3 (d, J = 8.1 Hz), 61.5, 60.5, 26.7, 13.6. HRMS: calcd for $C_{11}H_{10}FNO_2Na$ $[M+Na]^+$: 230.0588, found 230.0593.

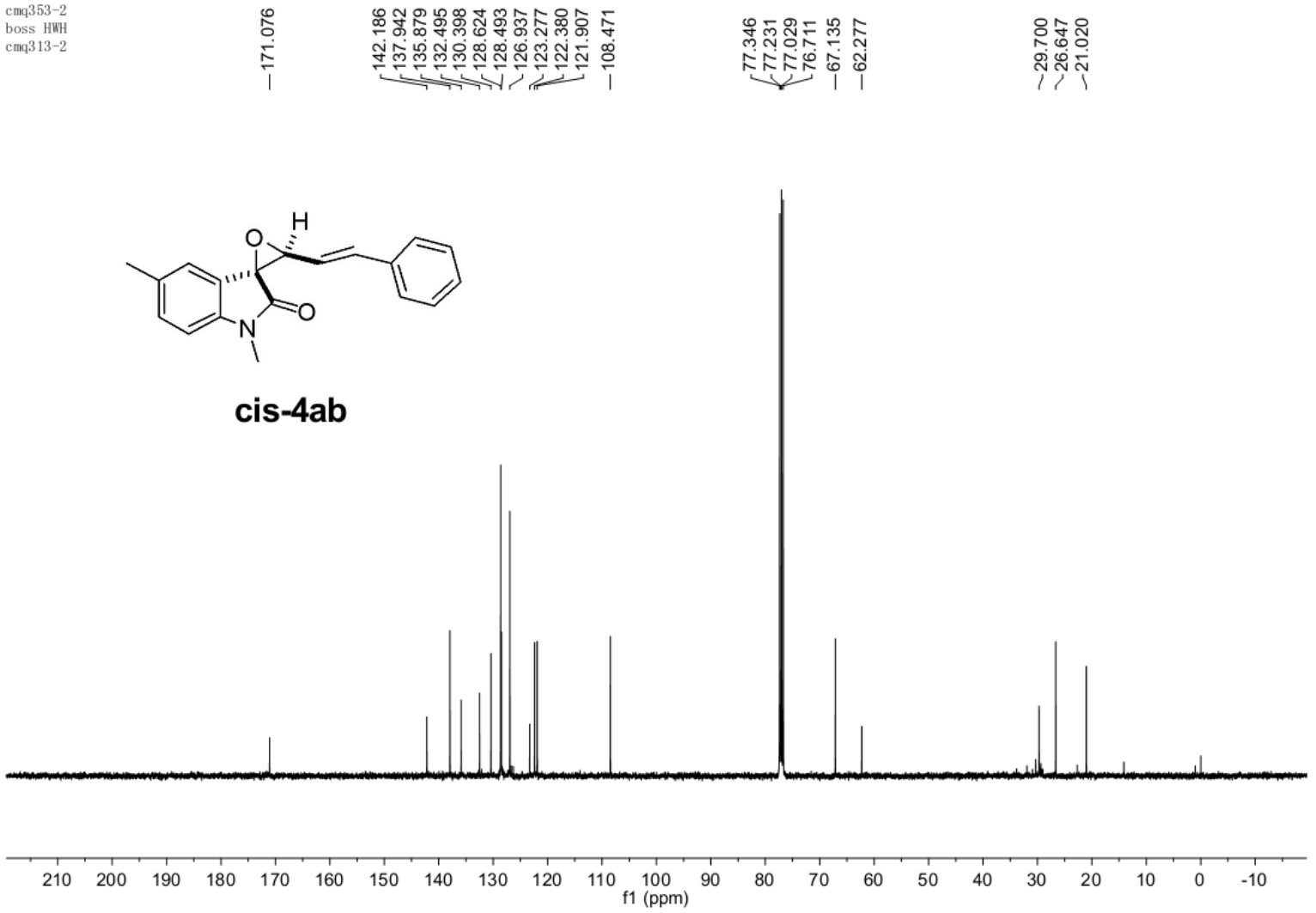


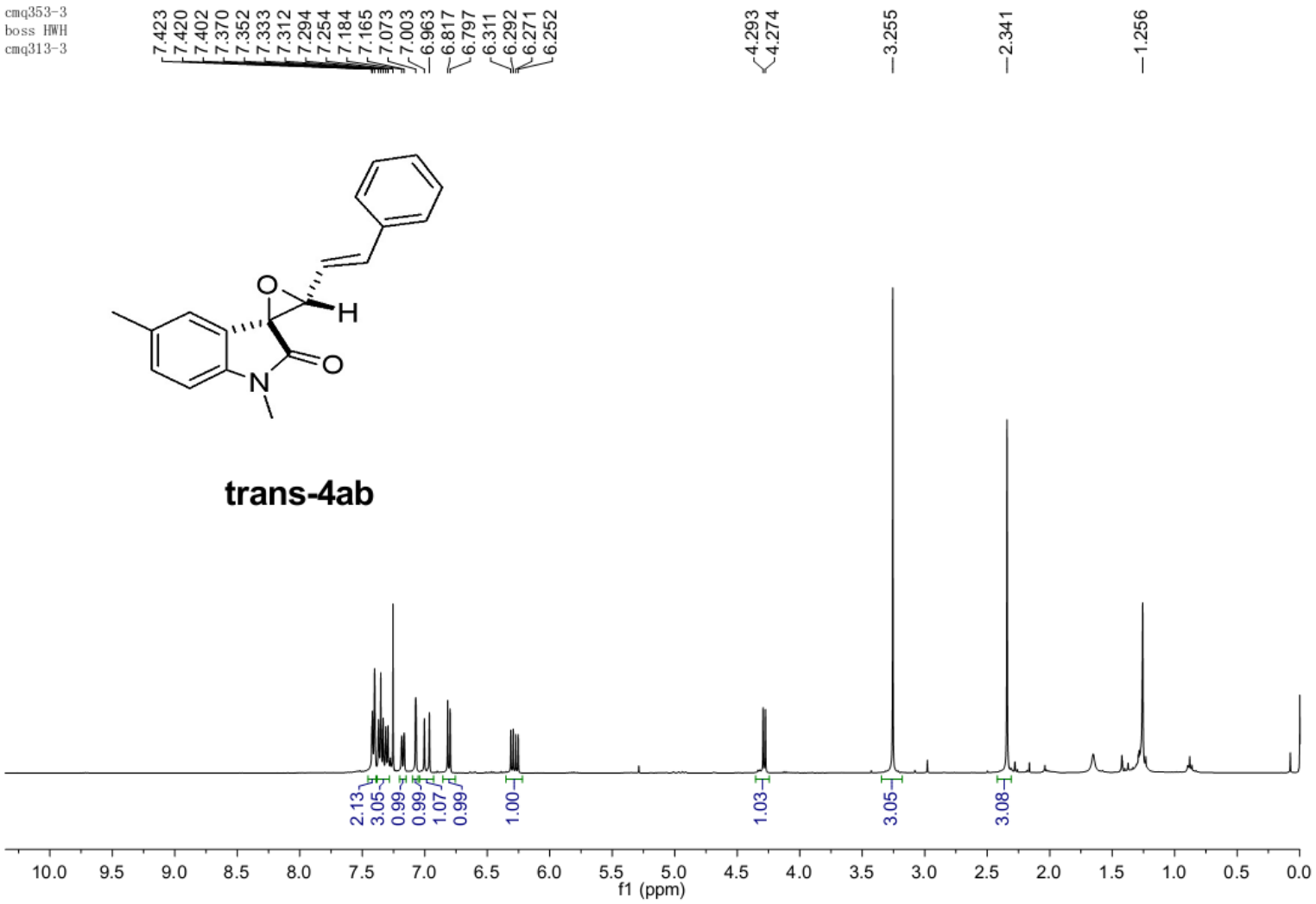




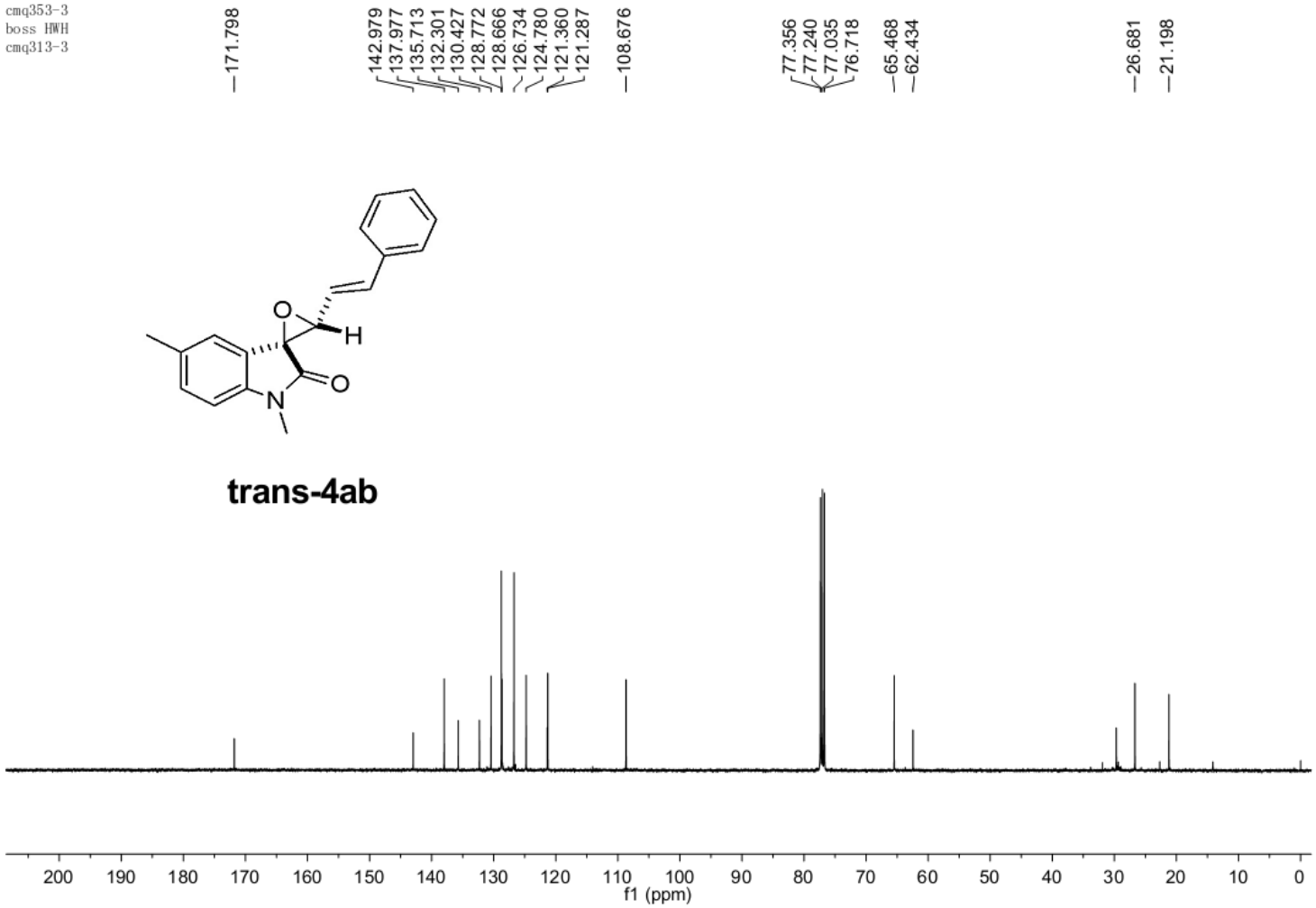


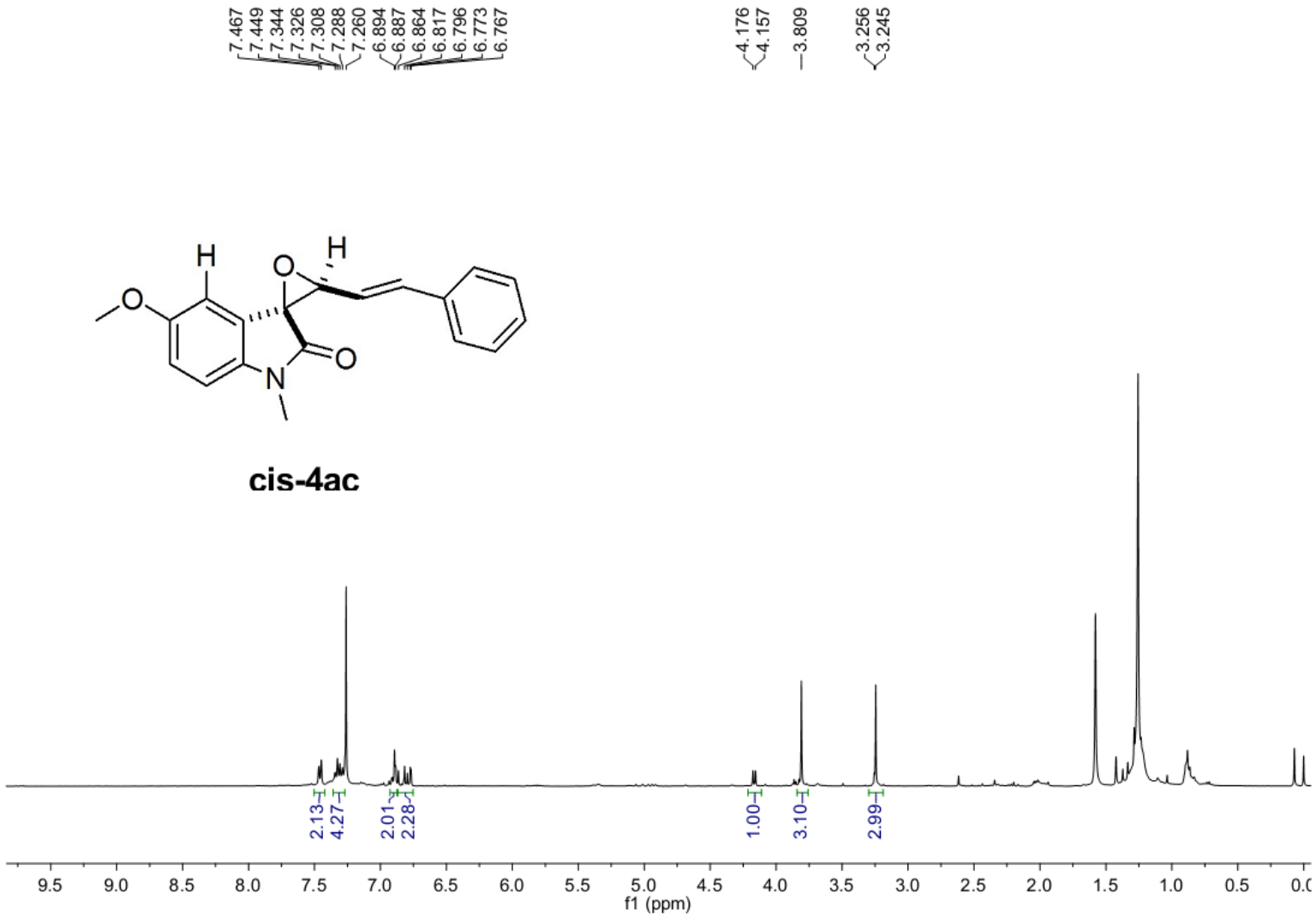


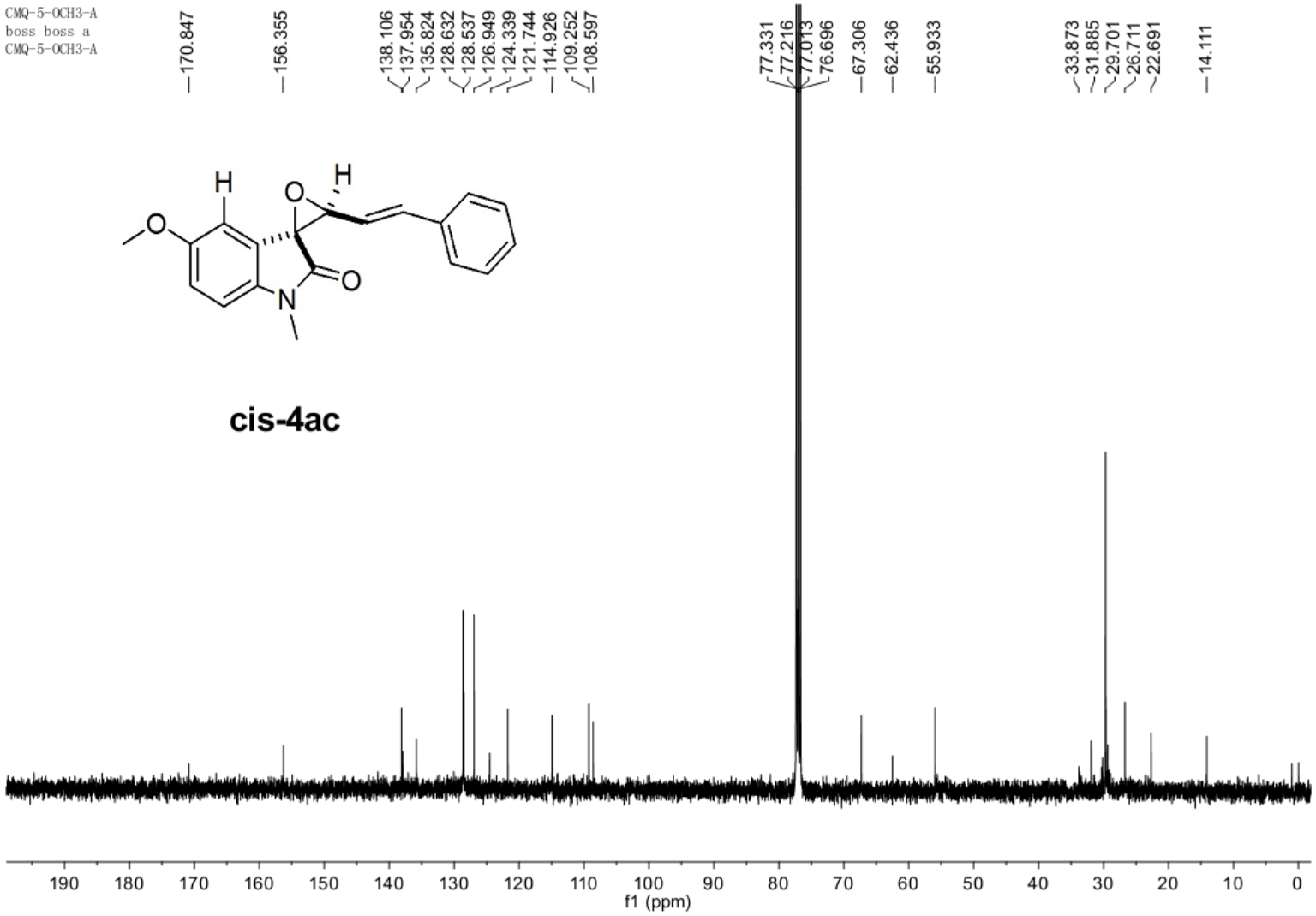


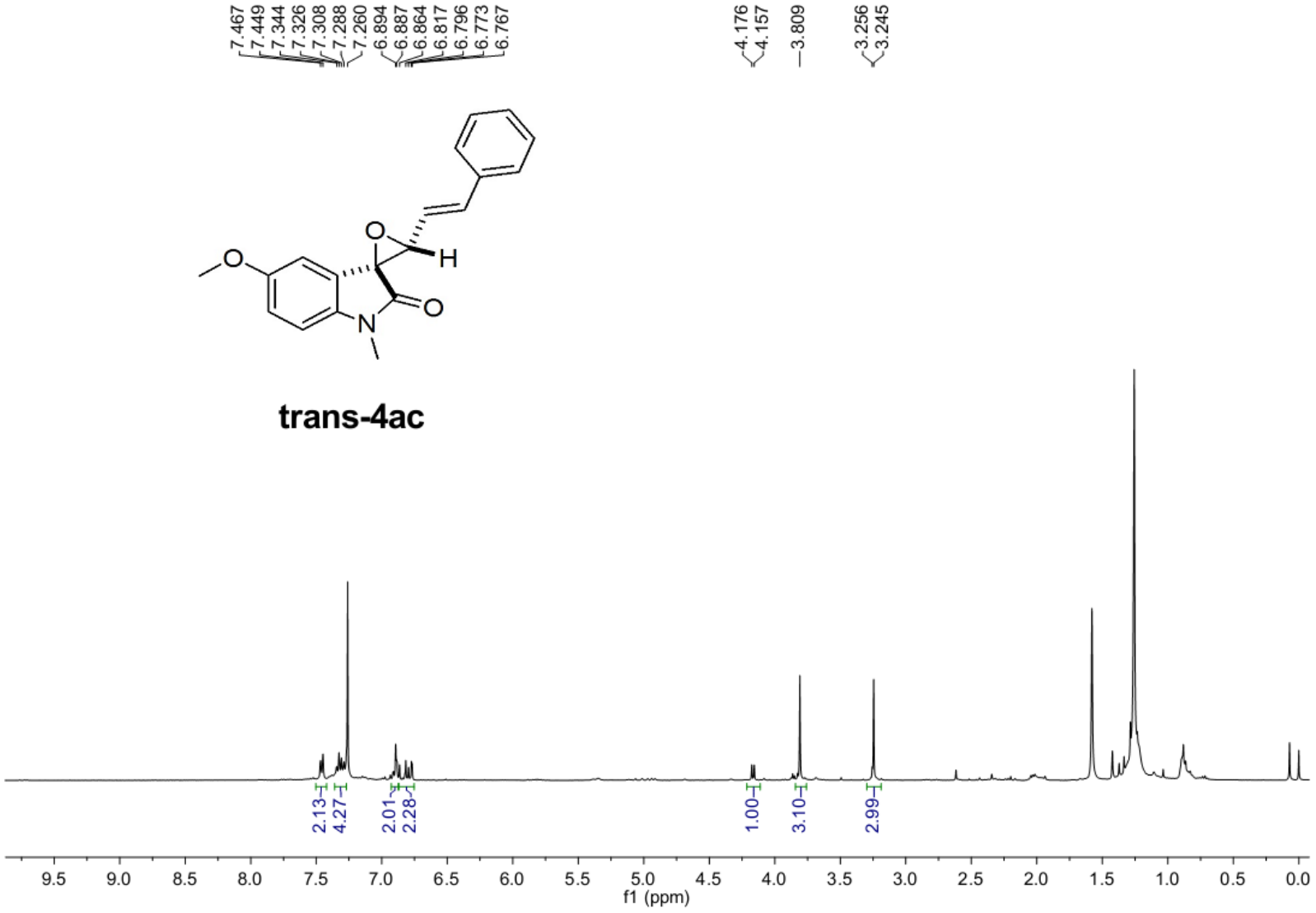


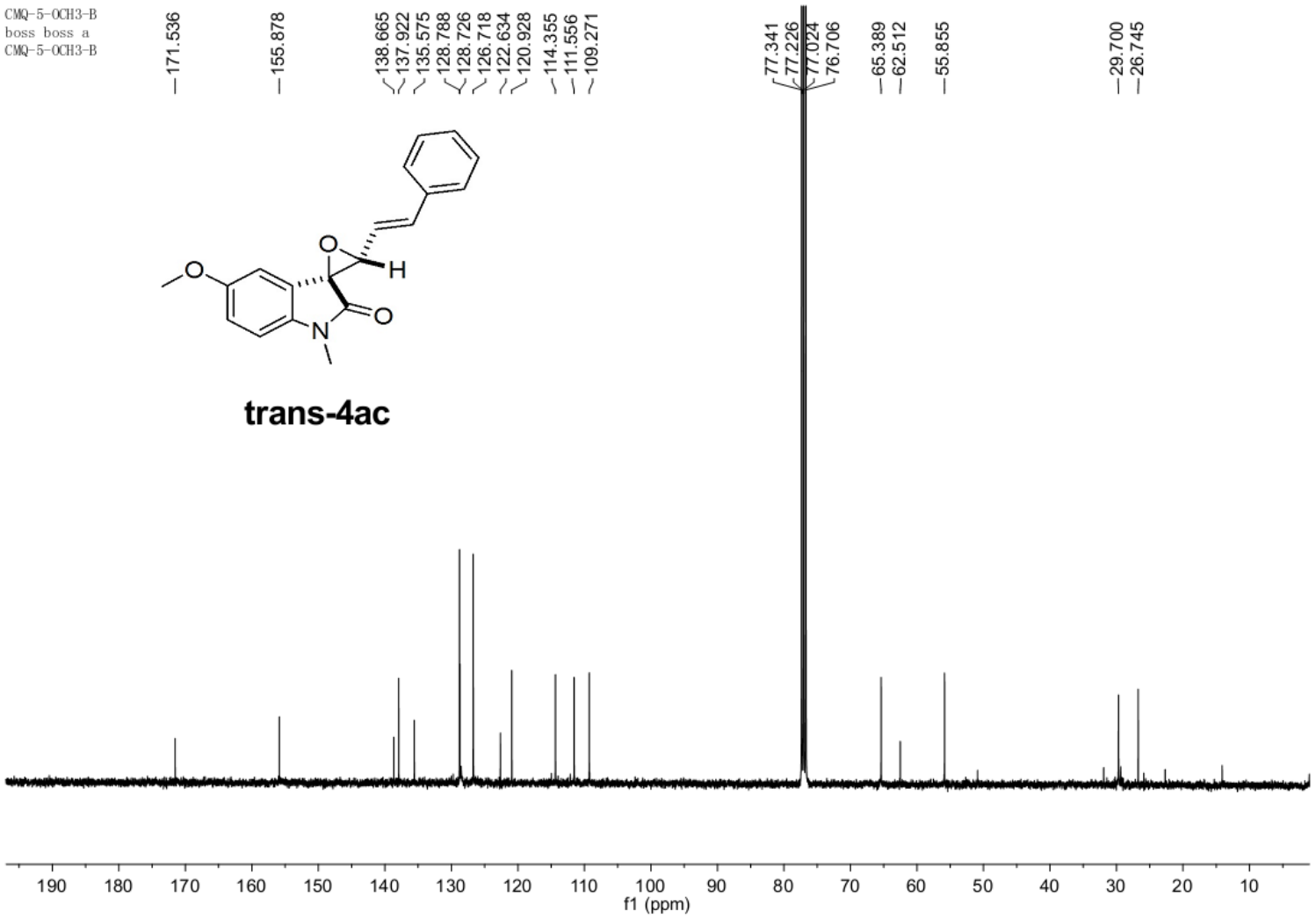
trans-4ab

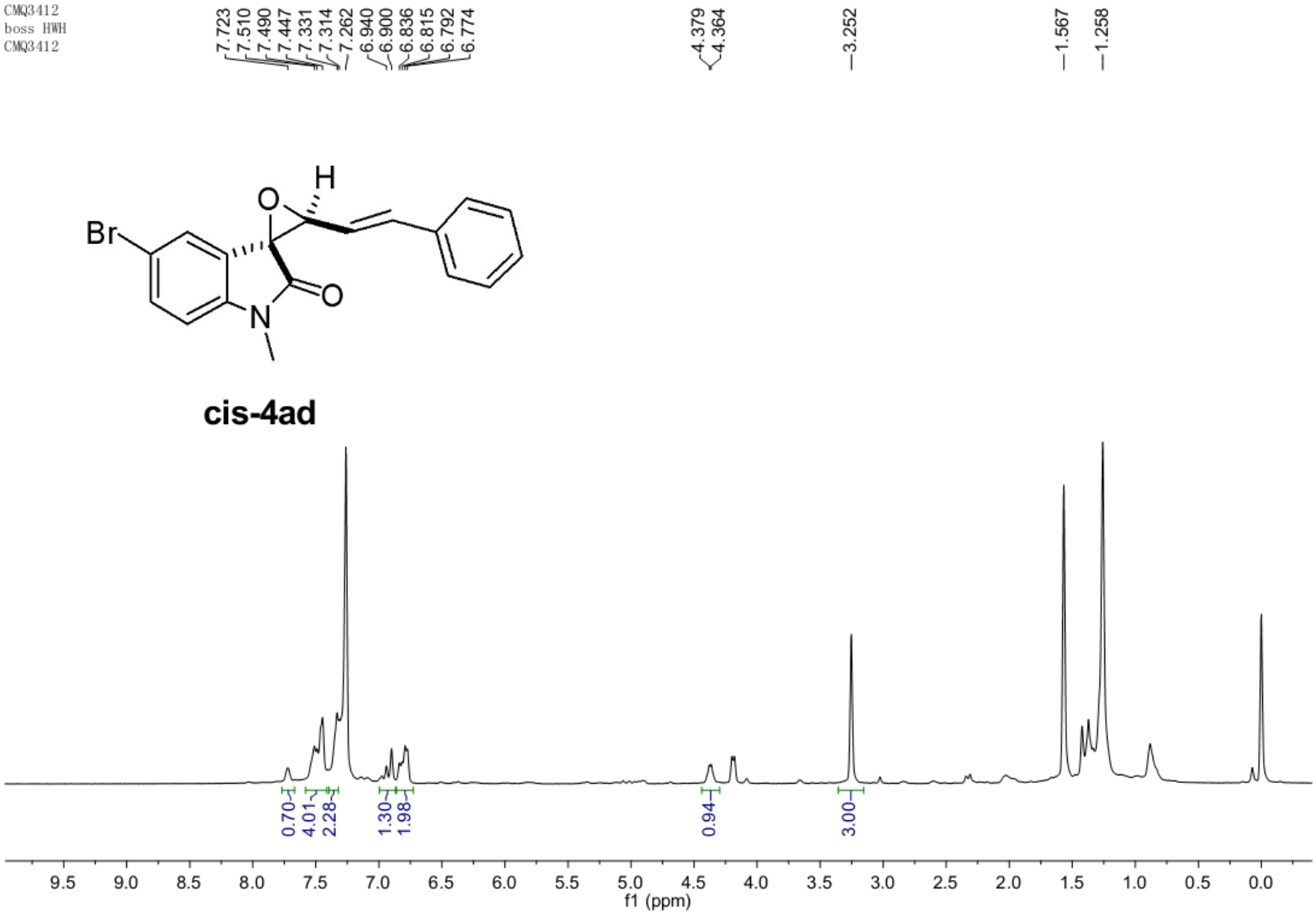


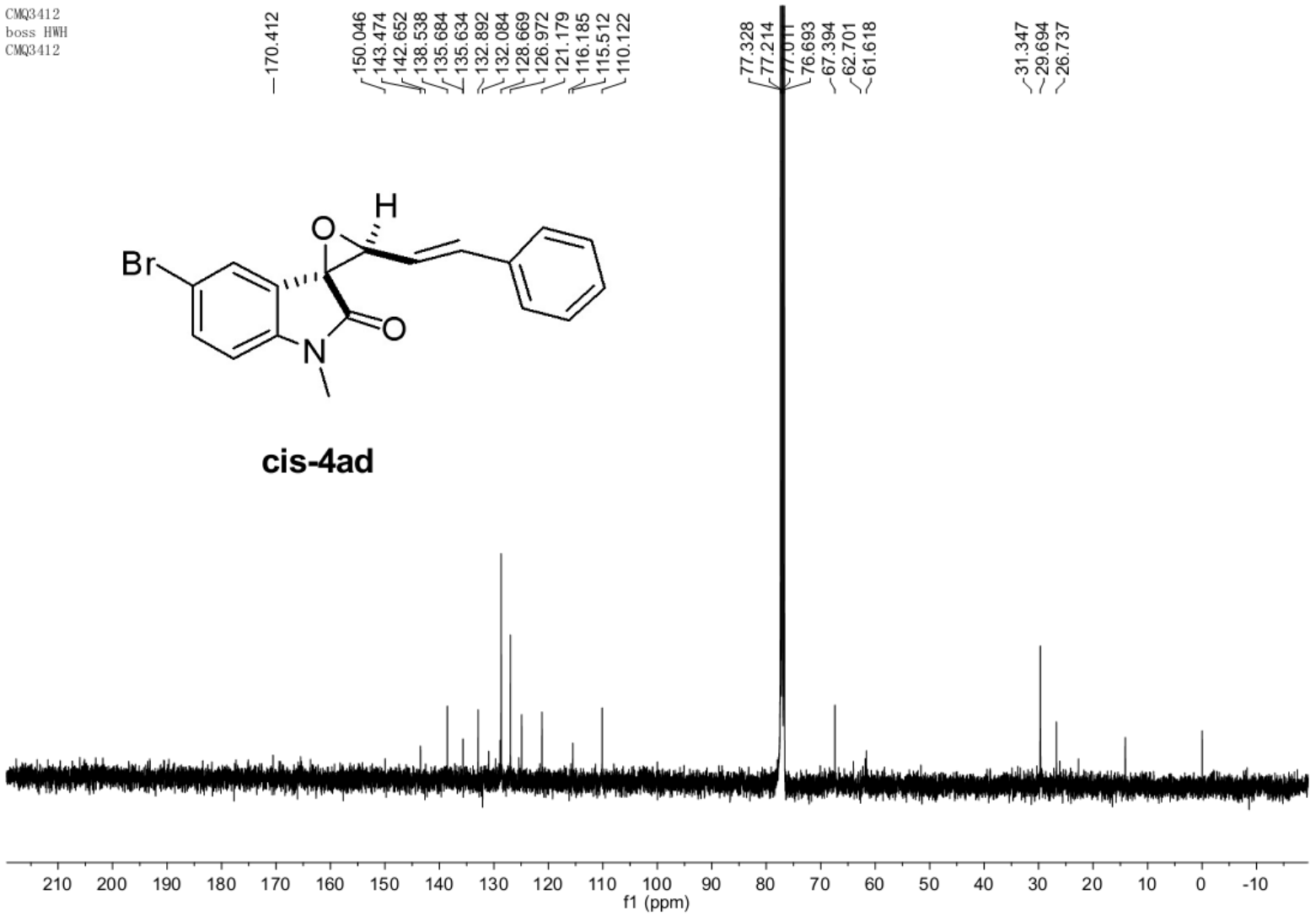












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cmq3413

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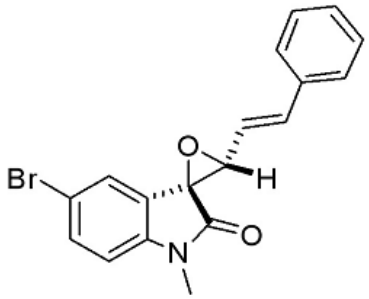

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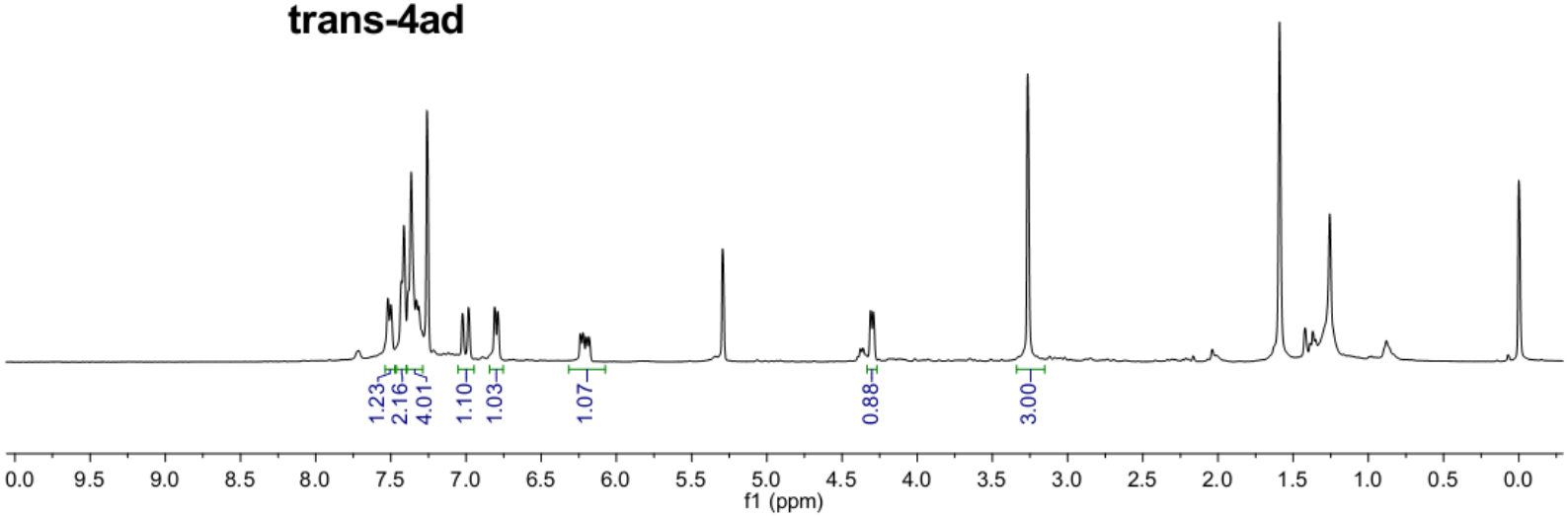
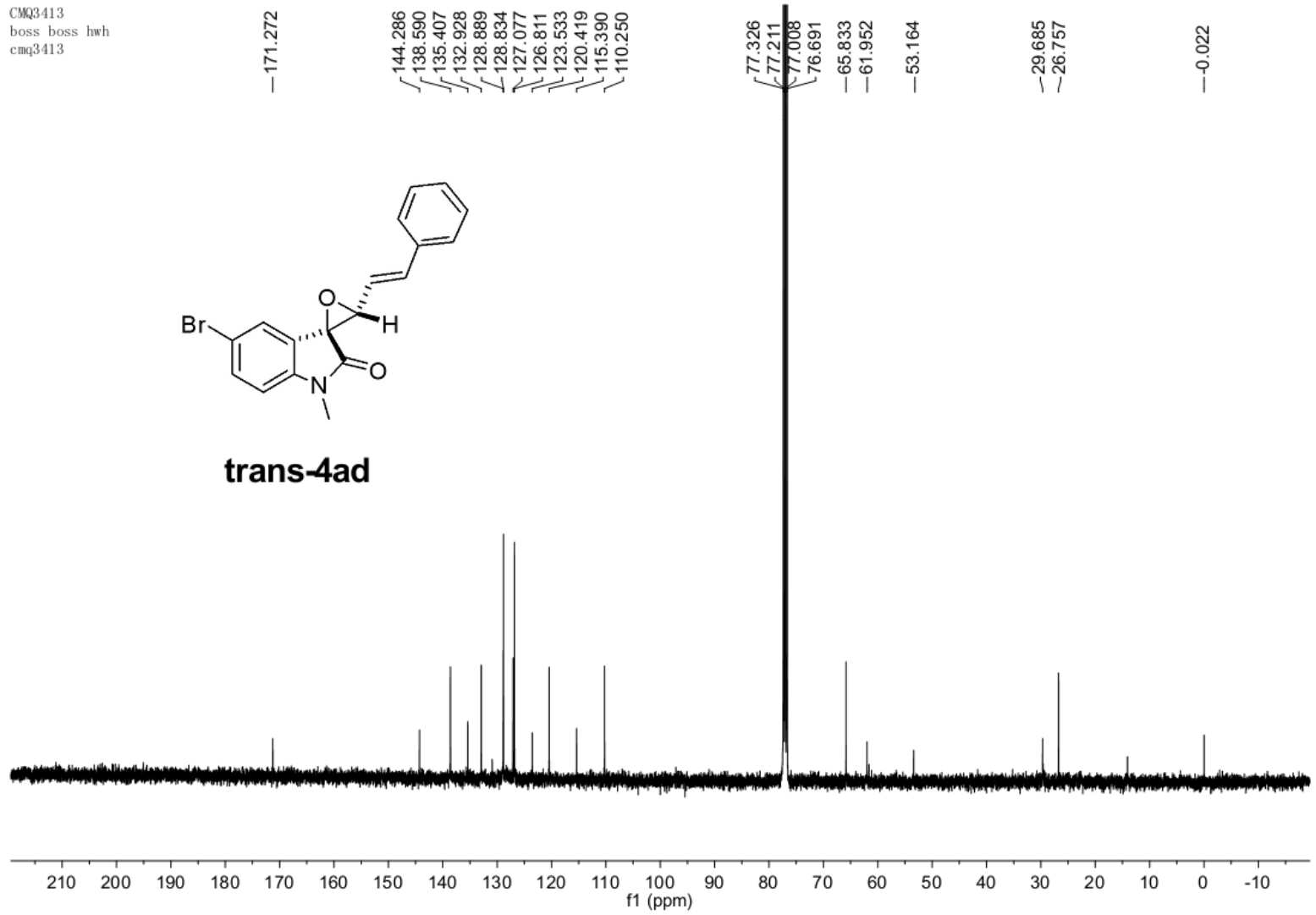
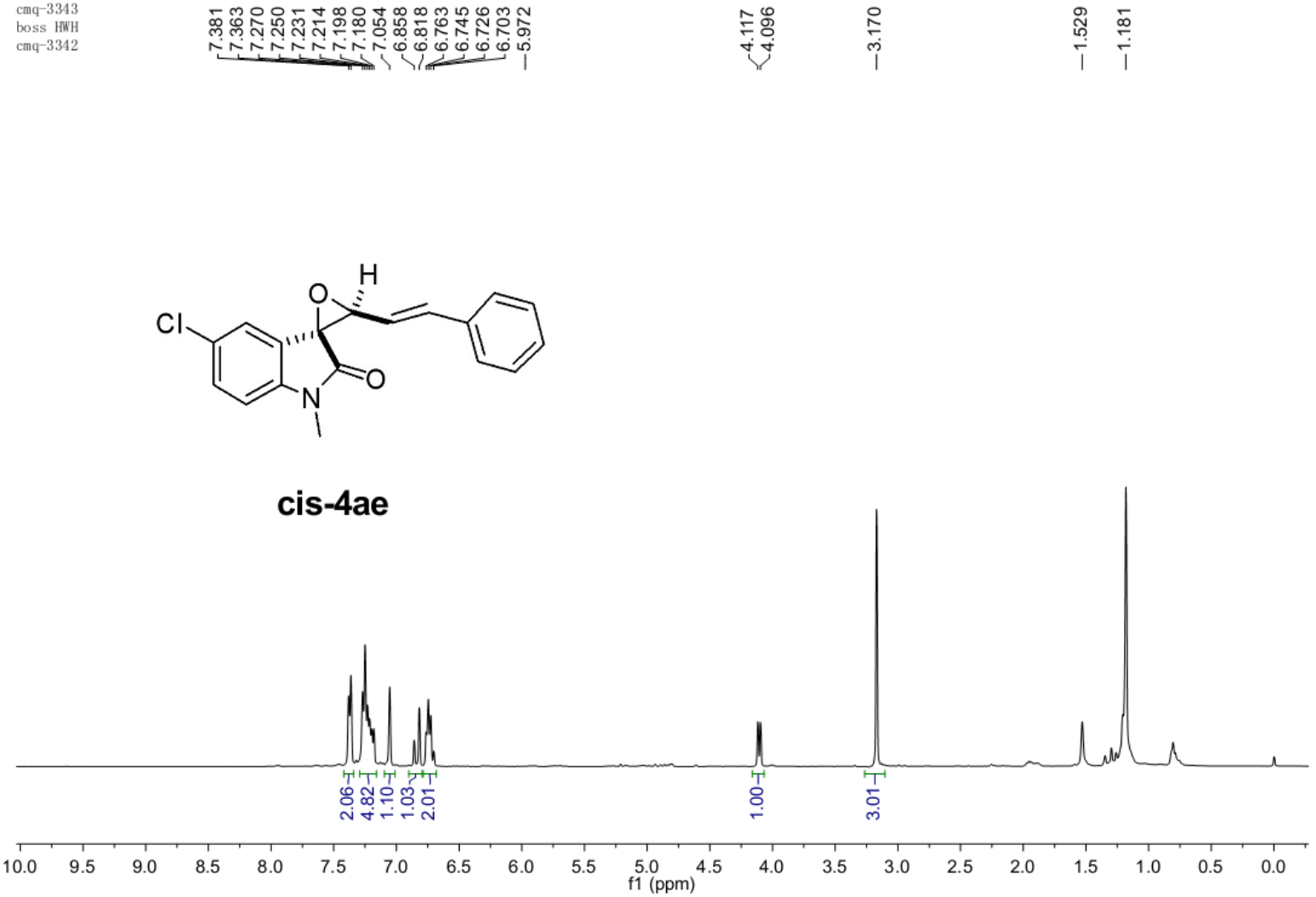
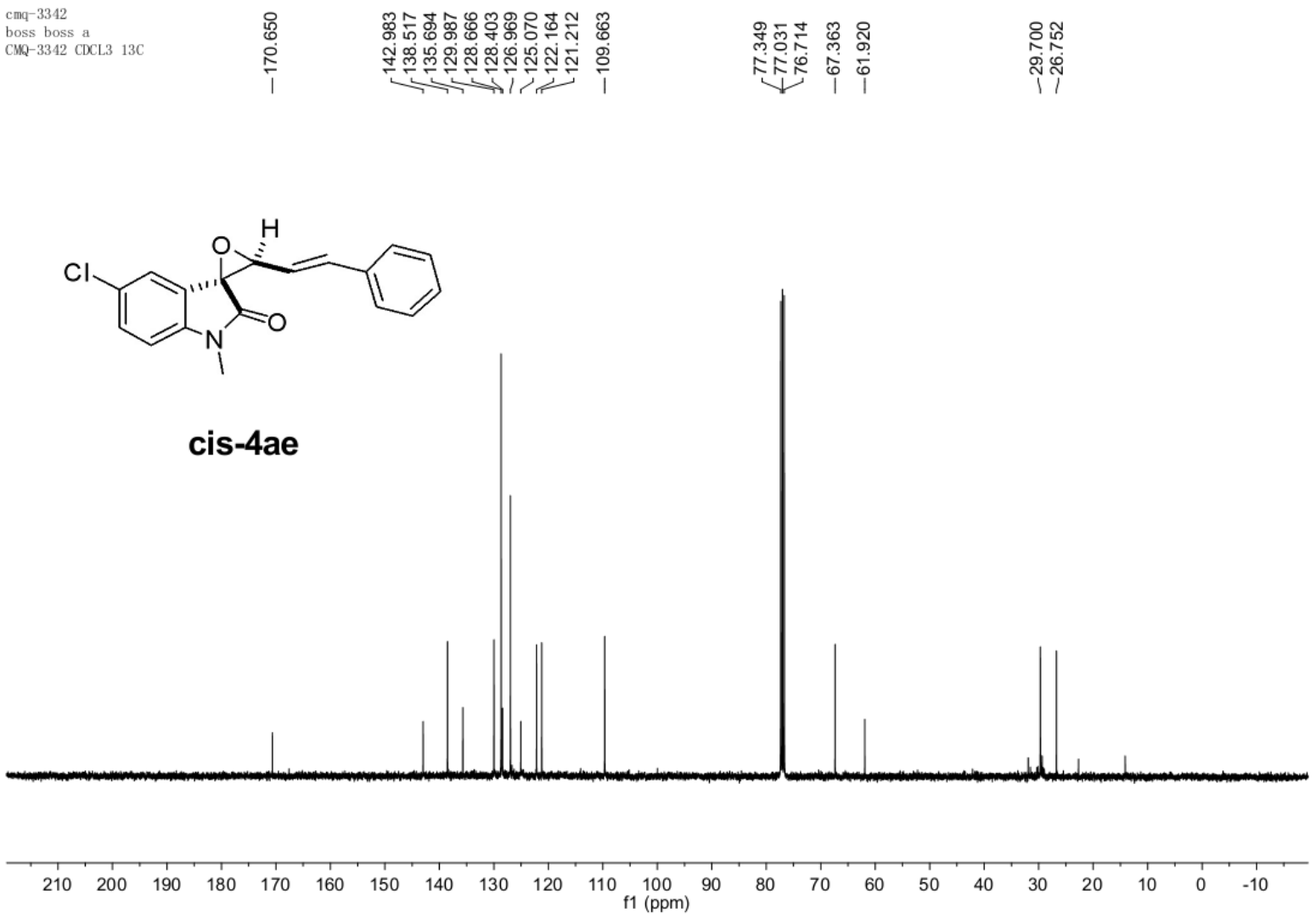
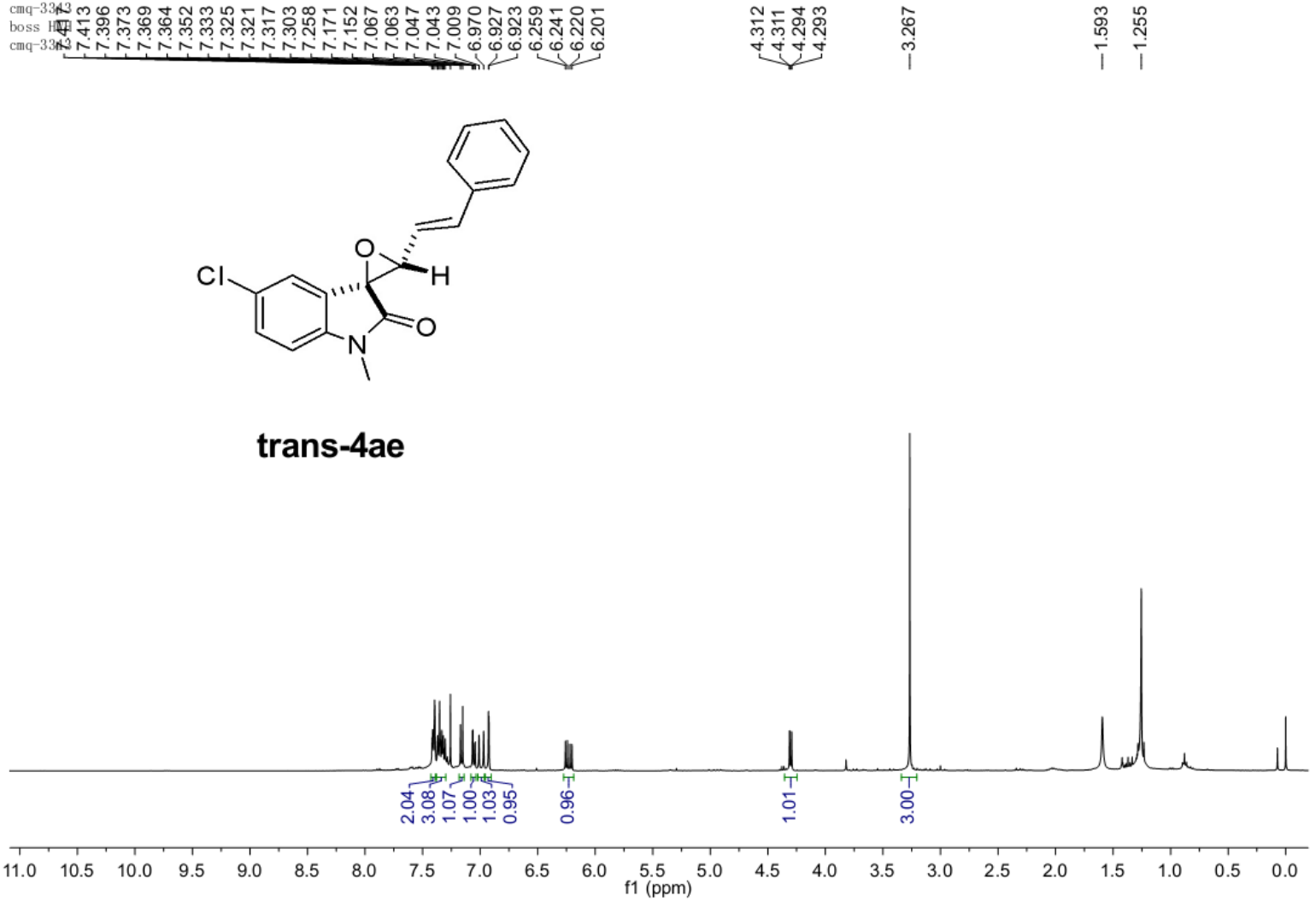
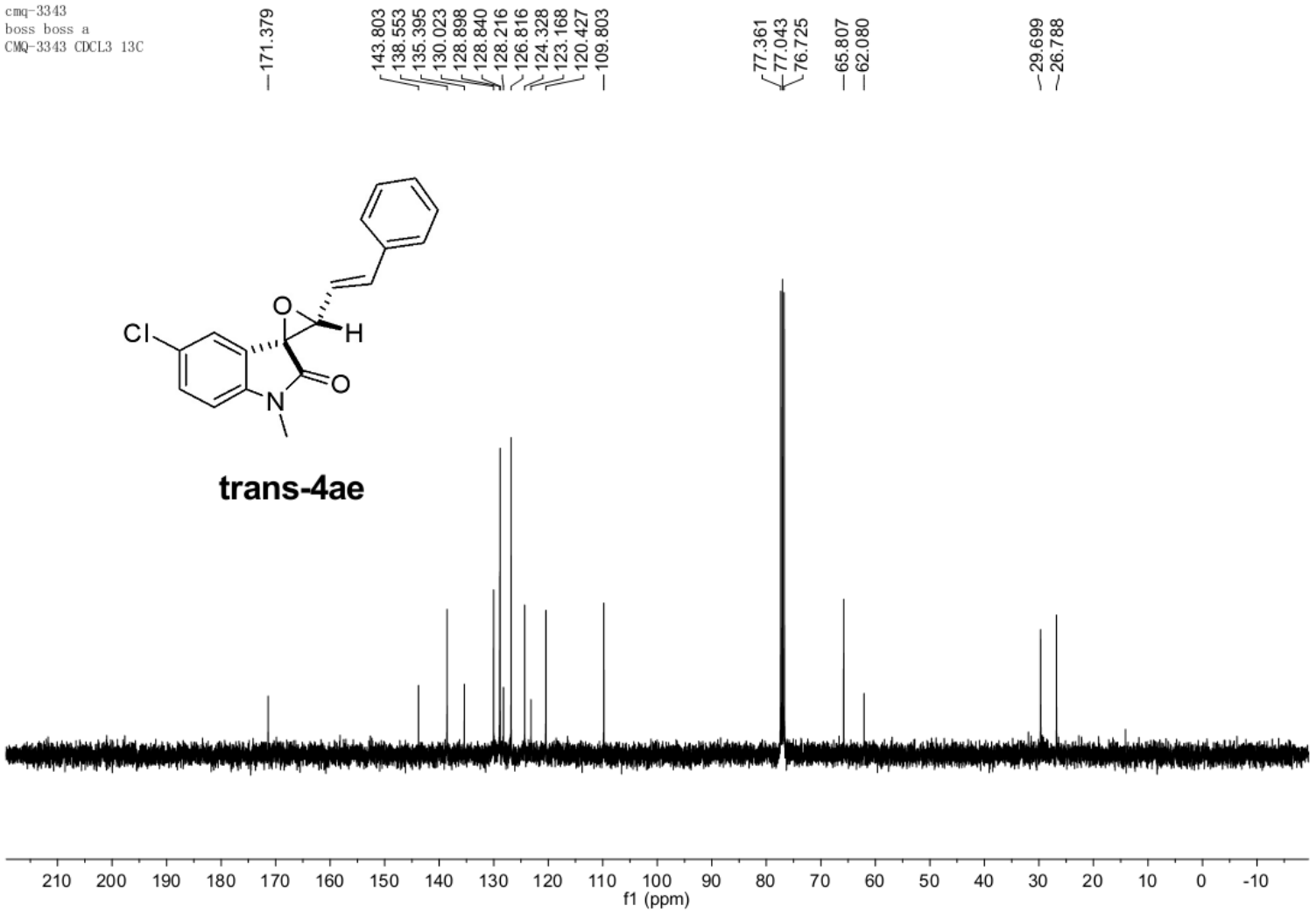


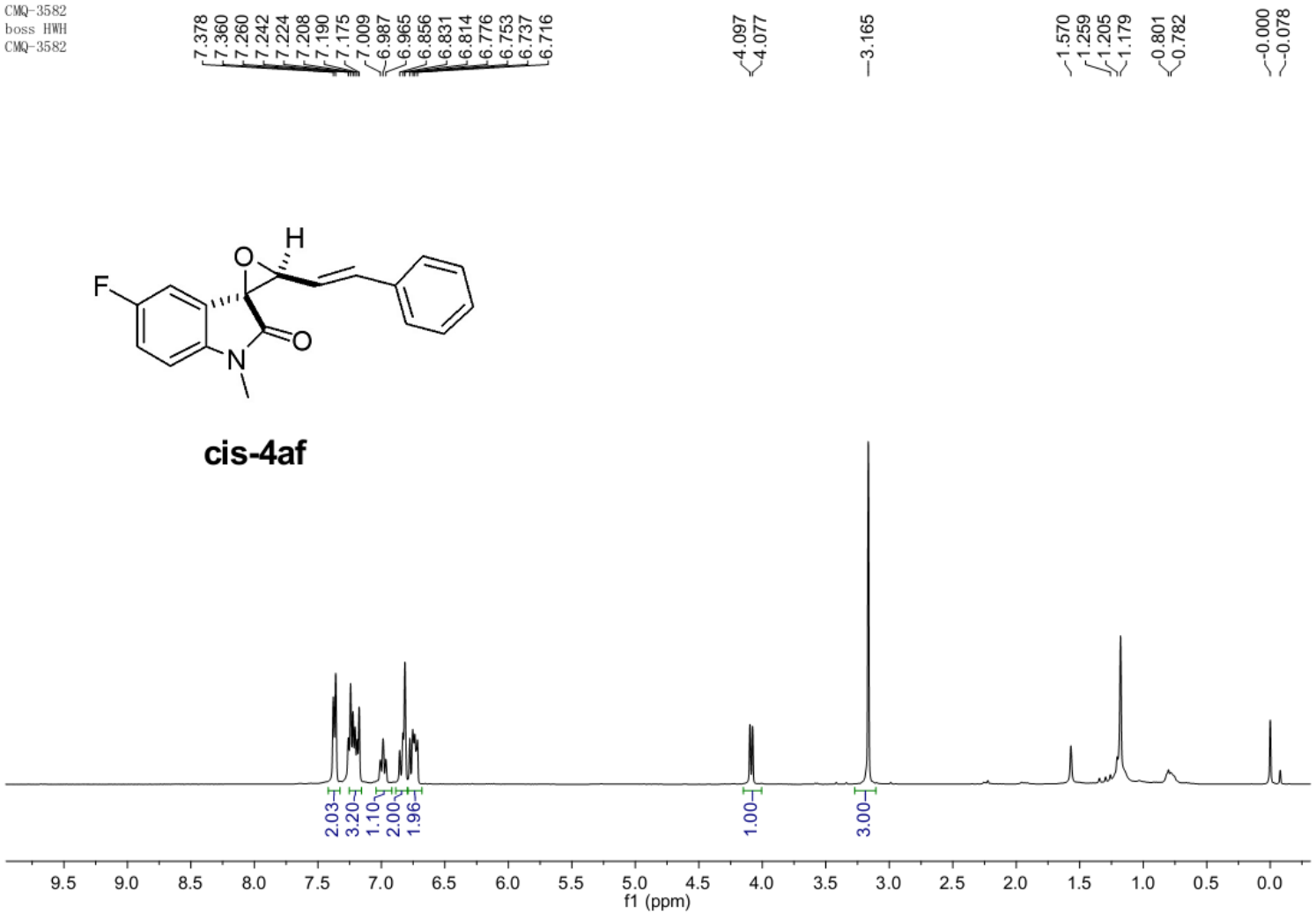


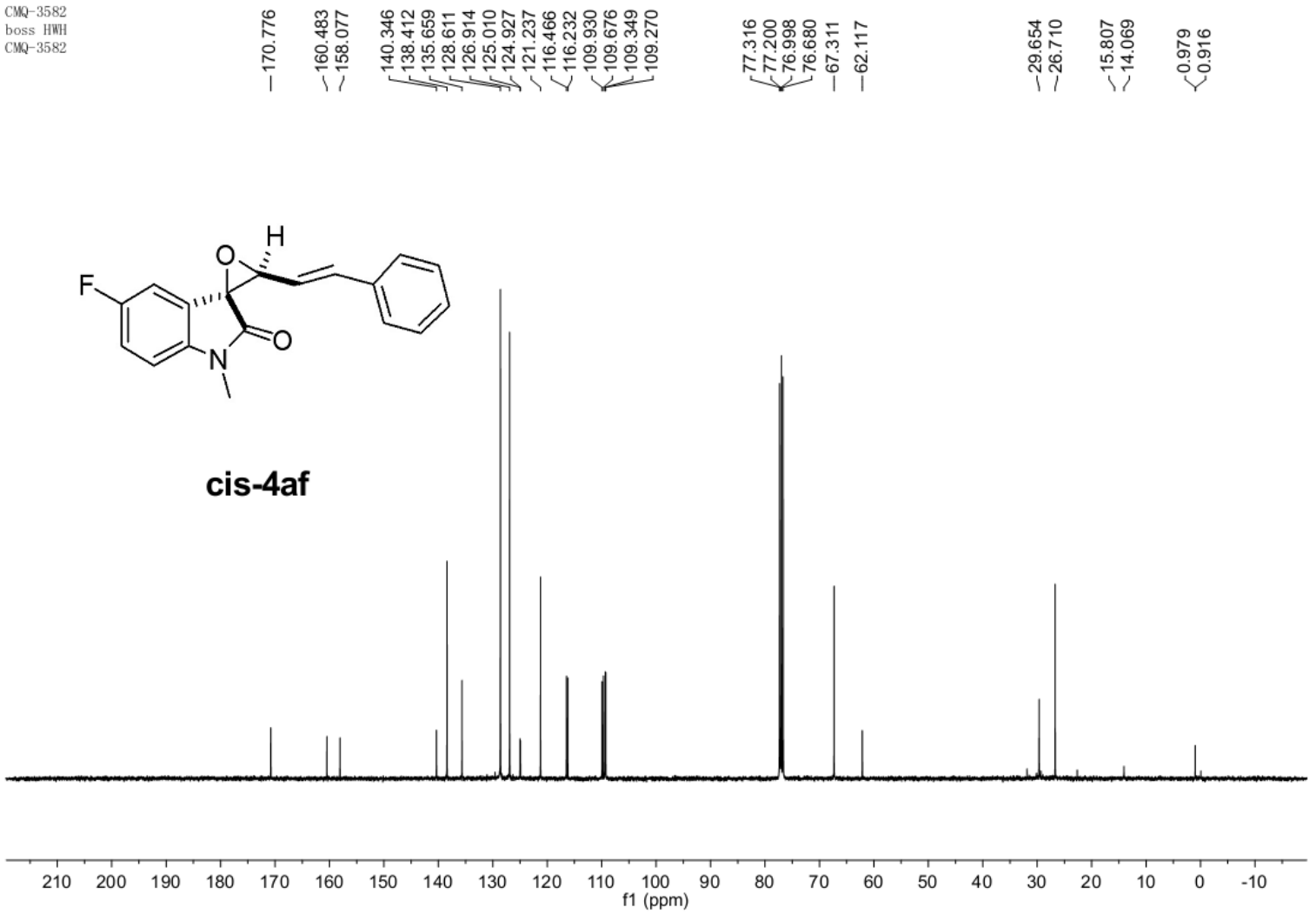


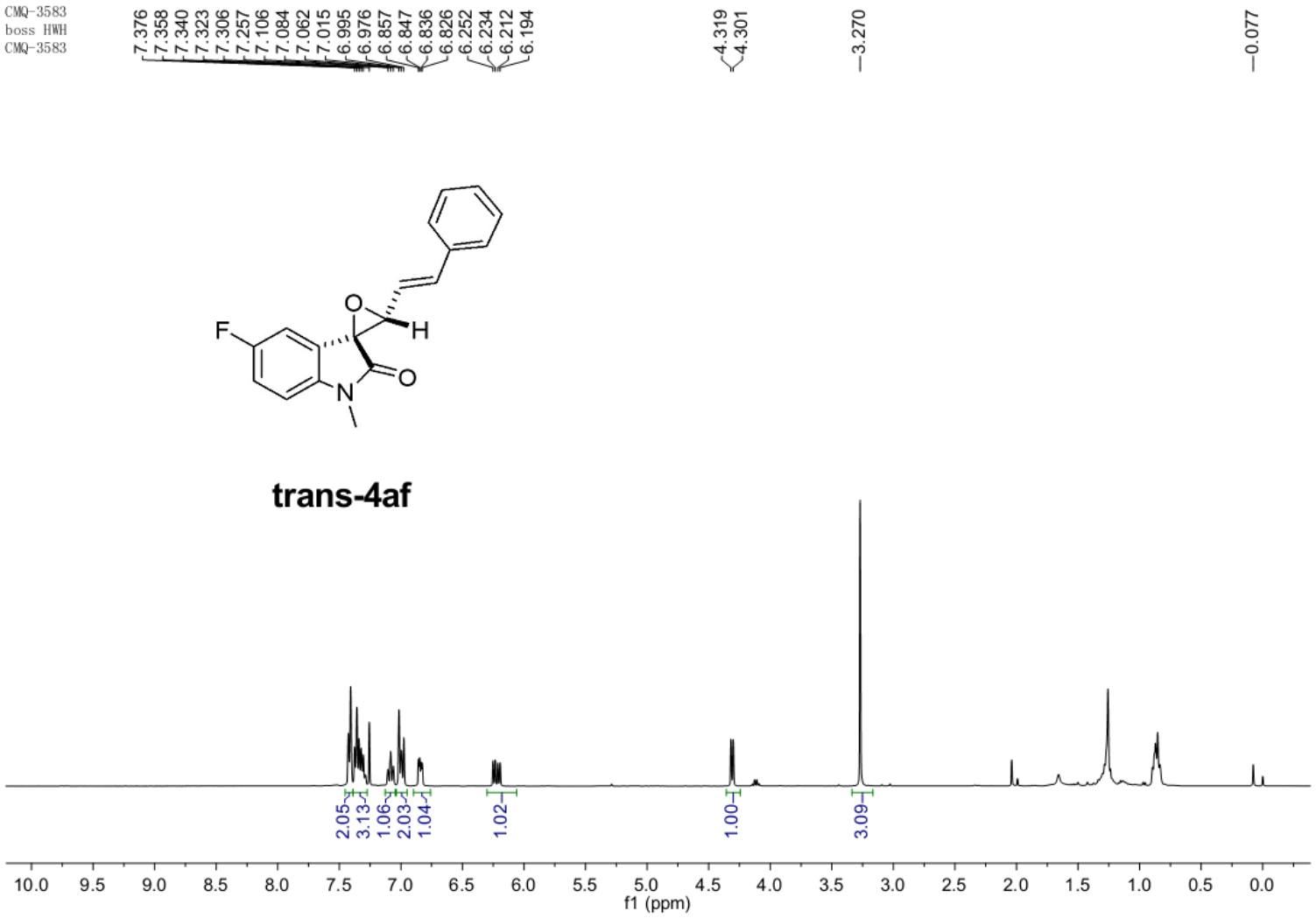


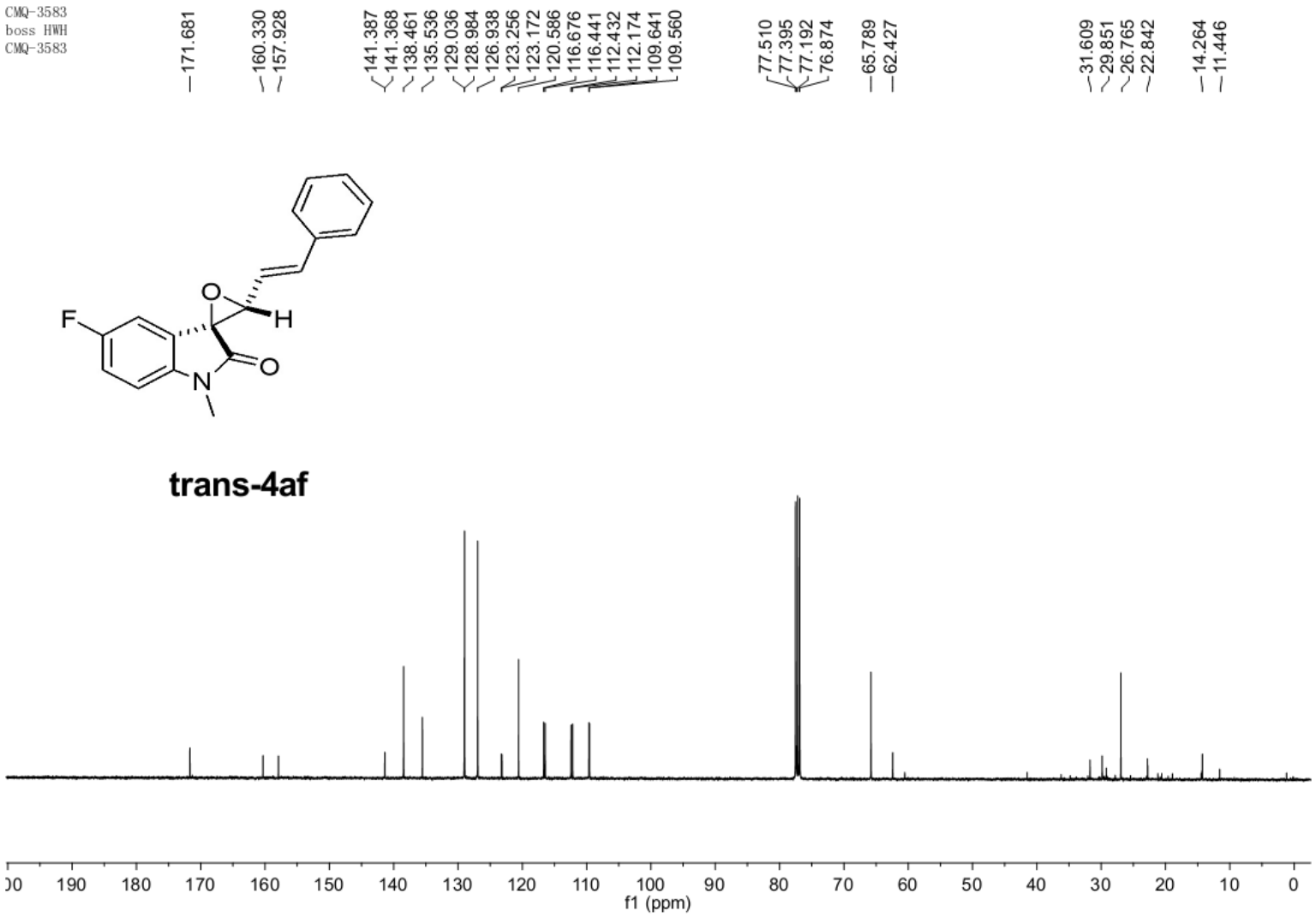


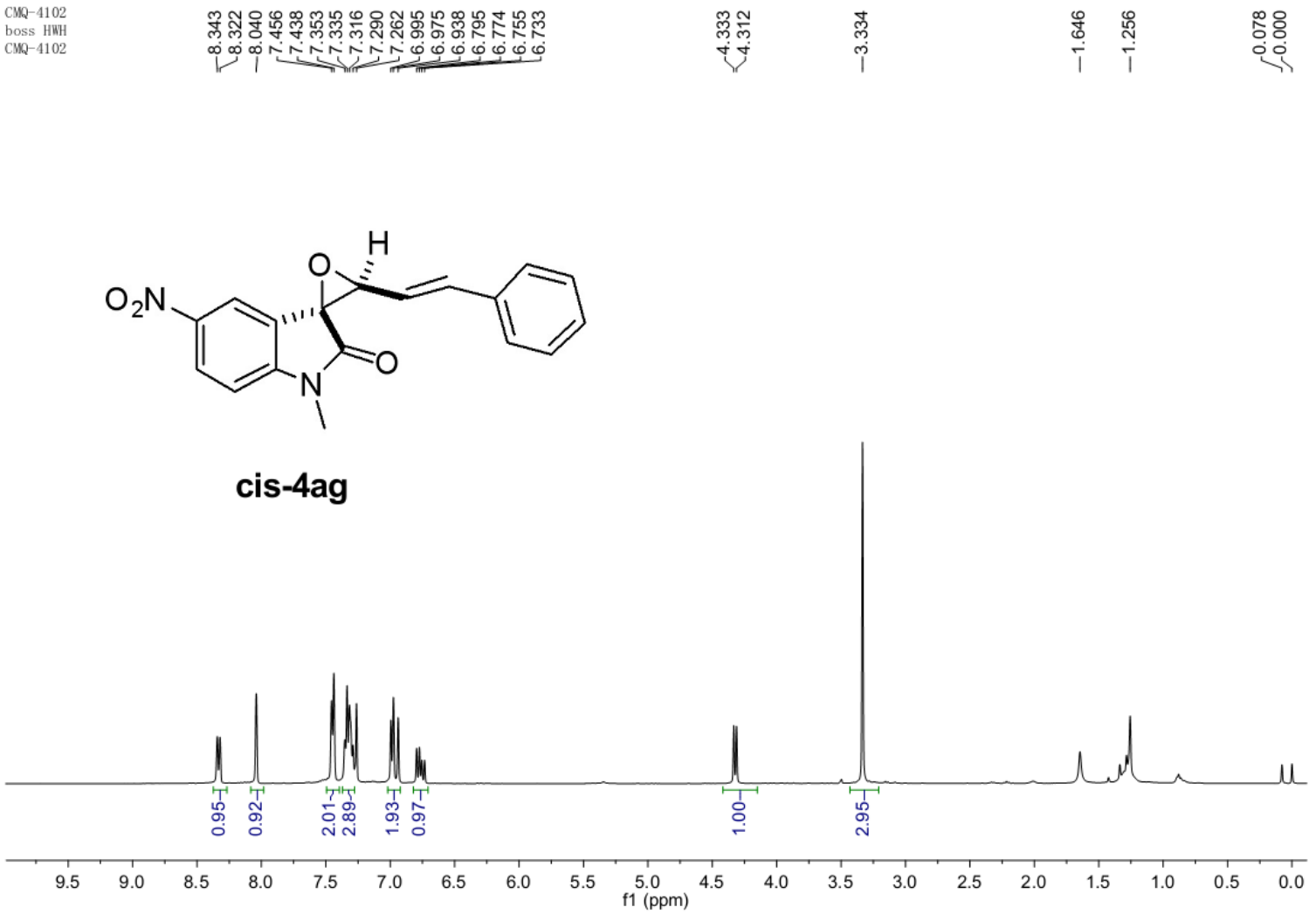


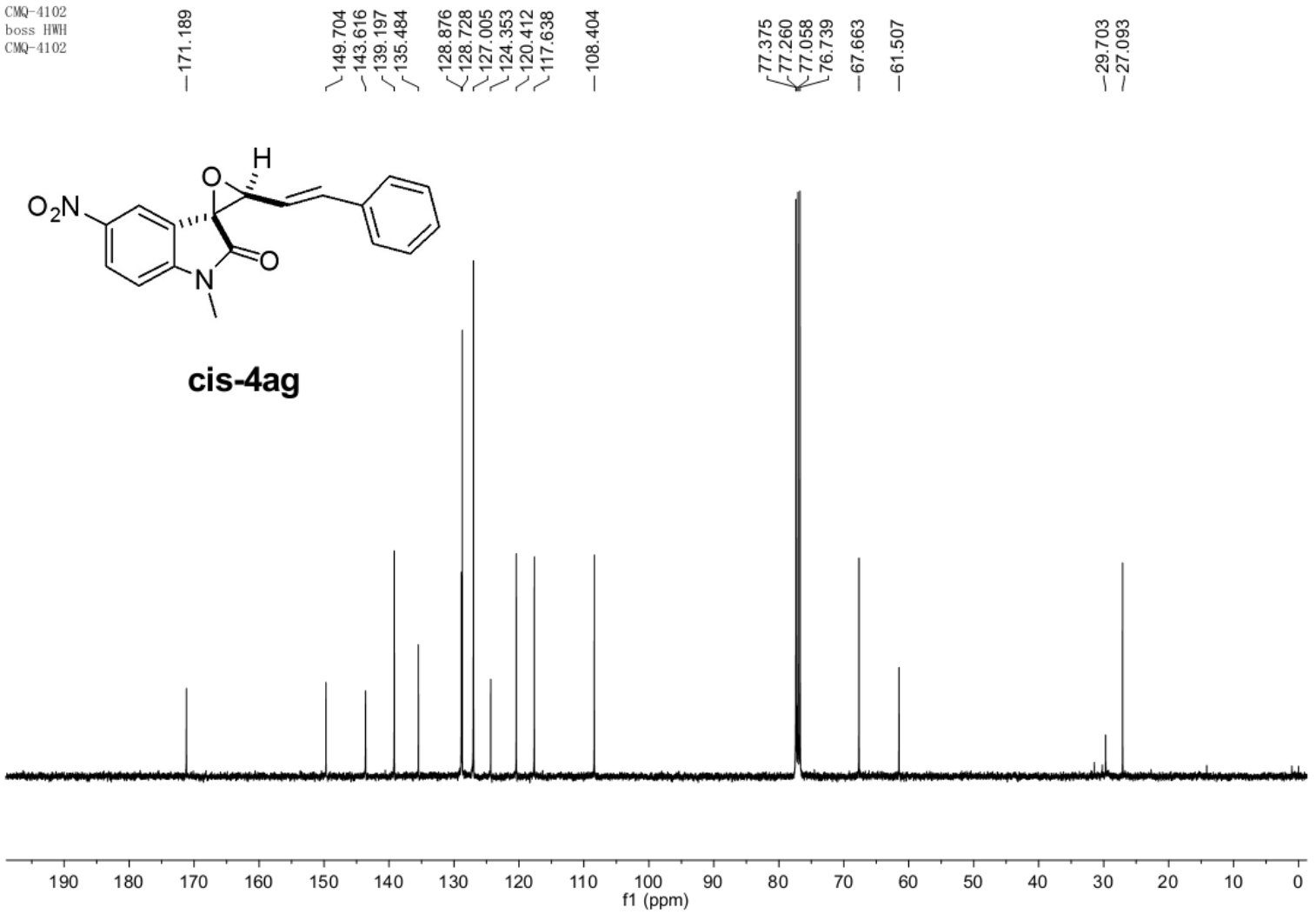


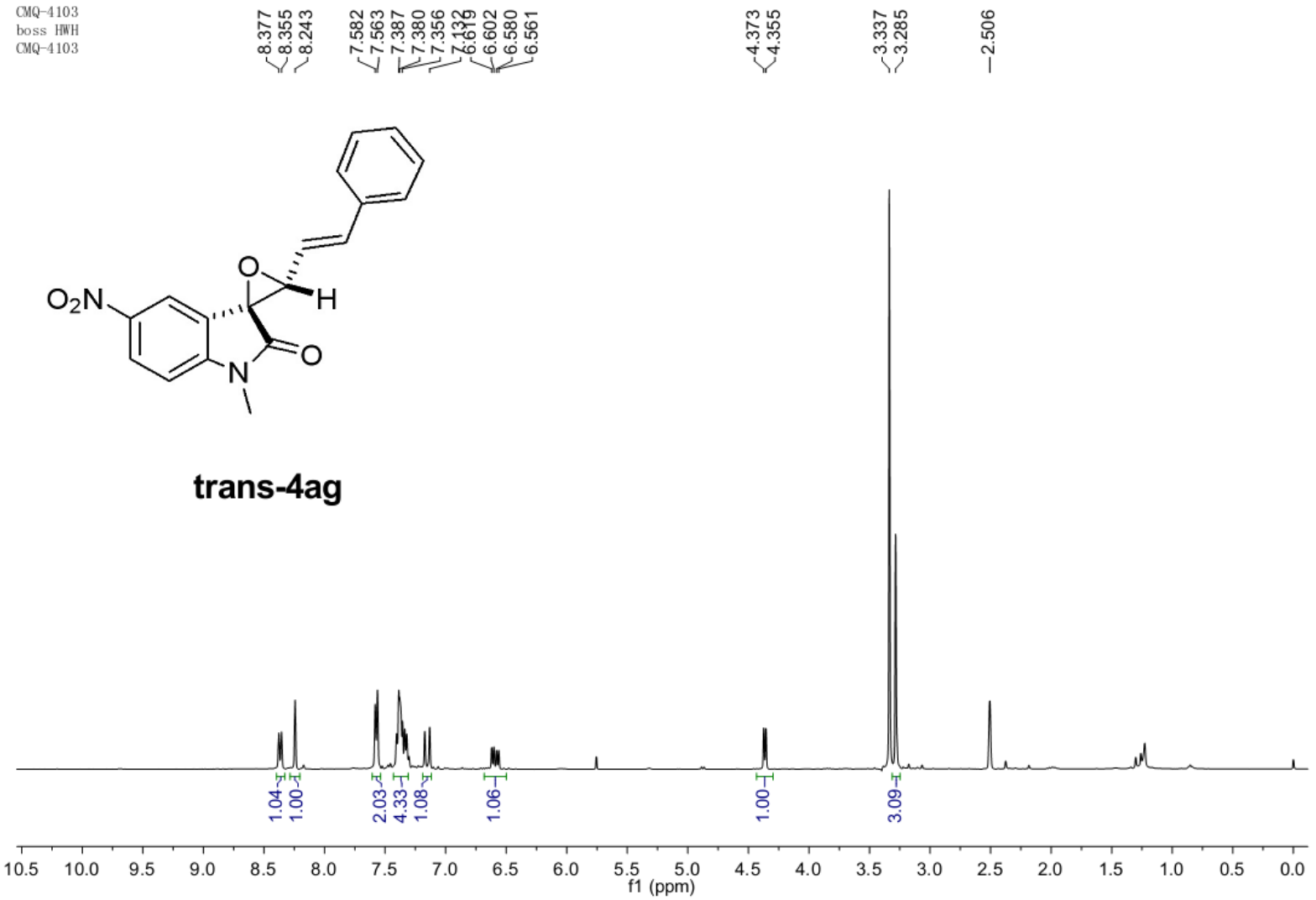


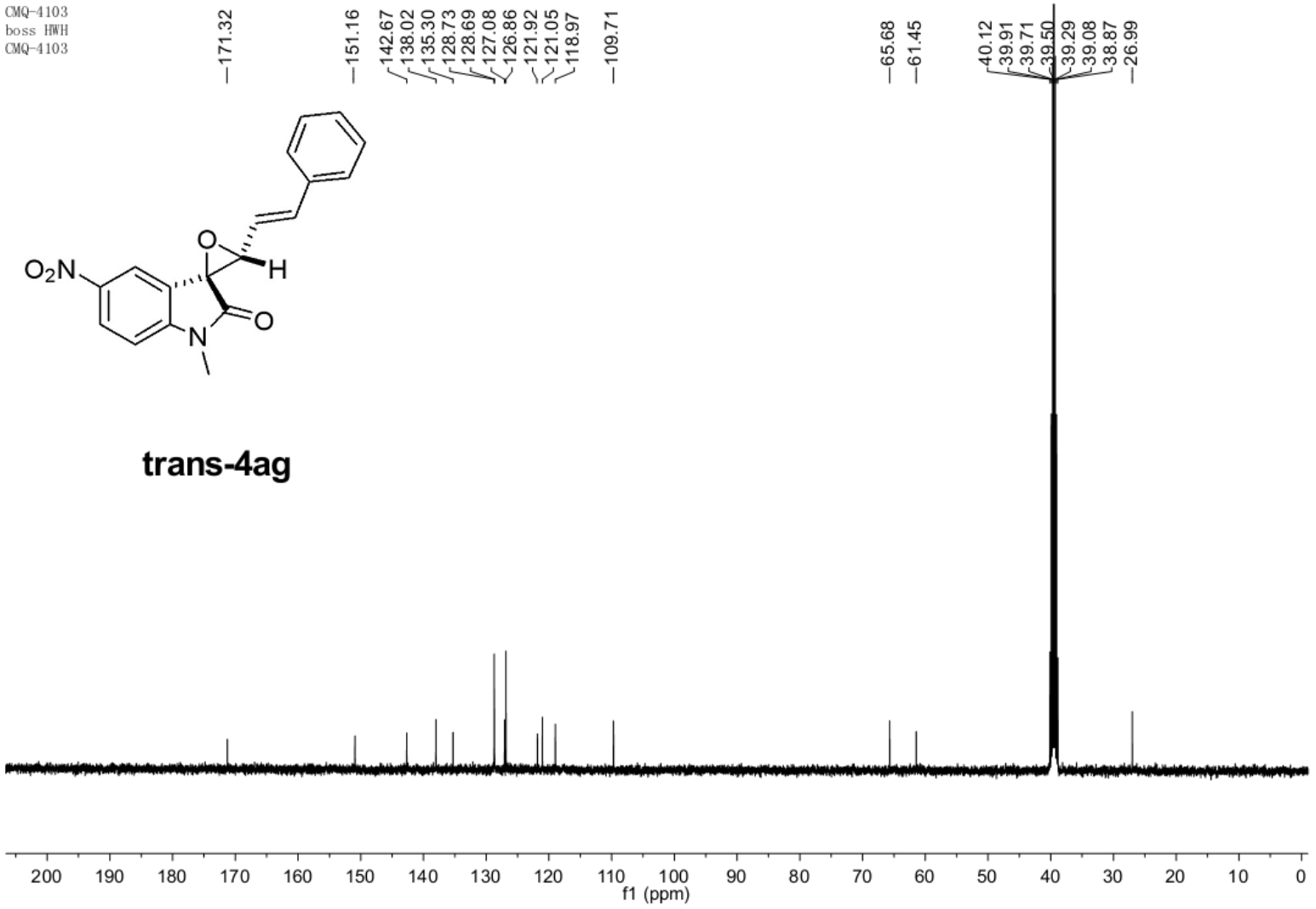


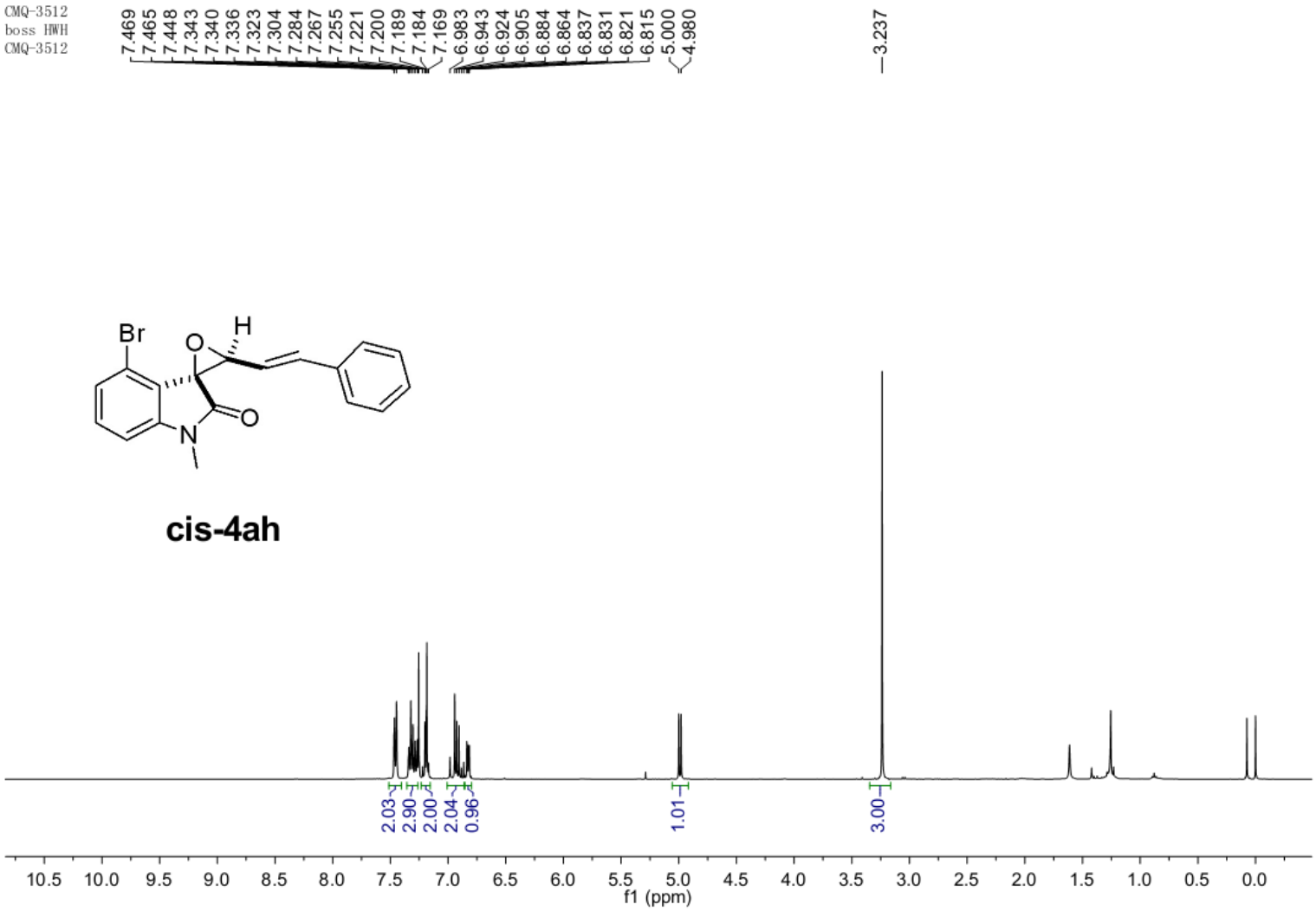




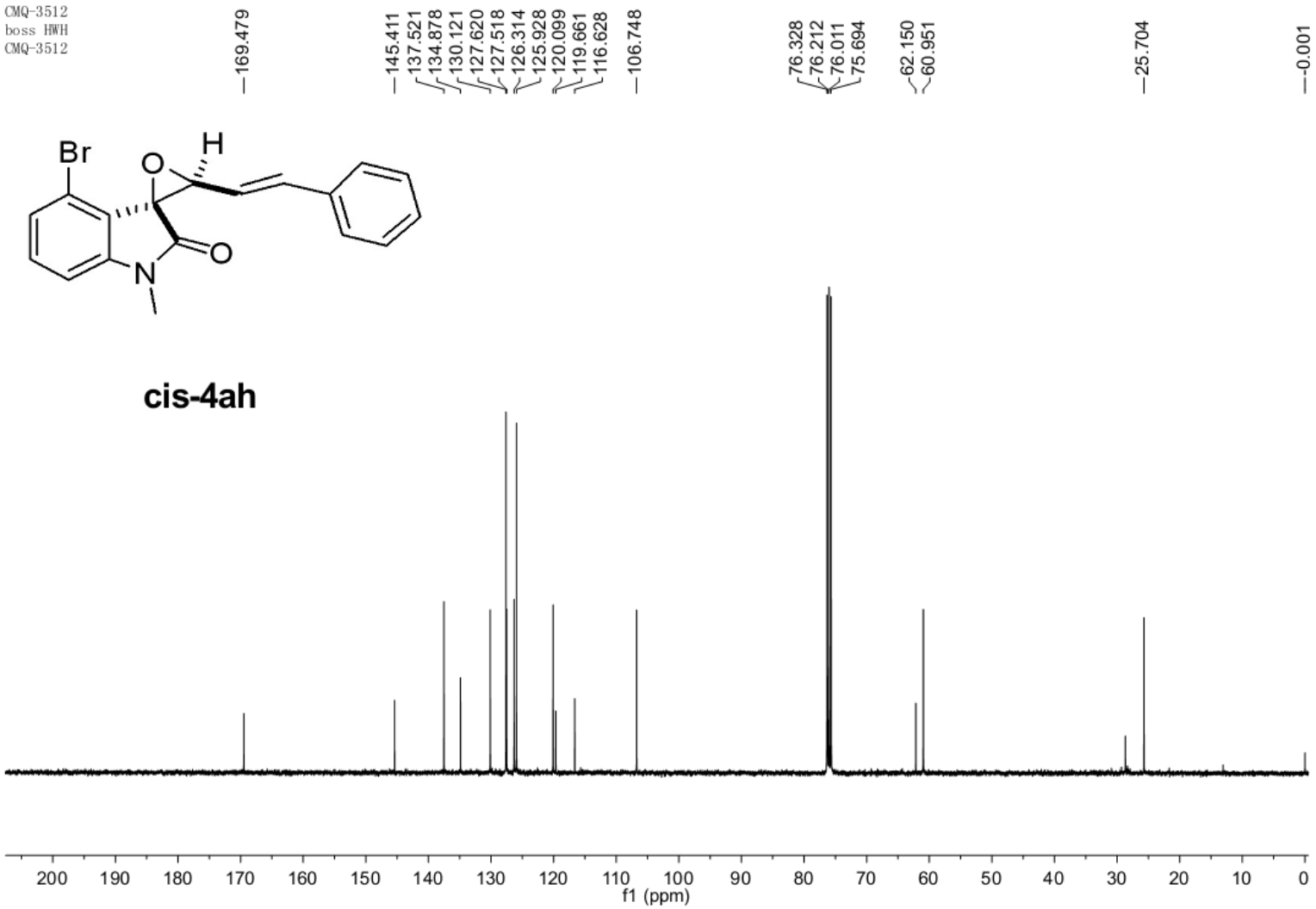


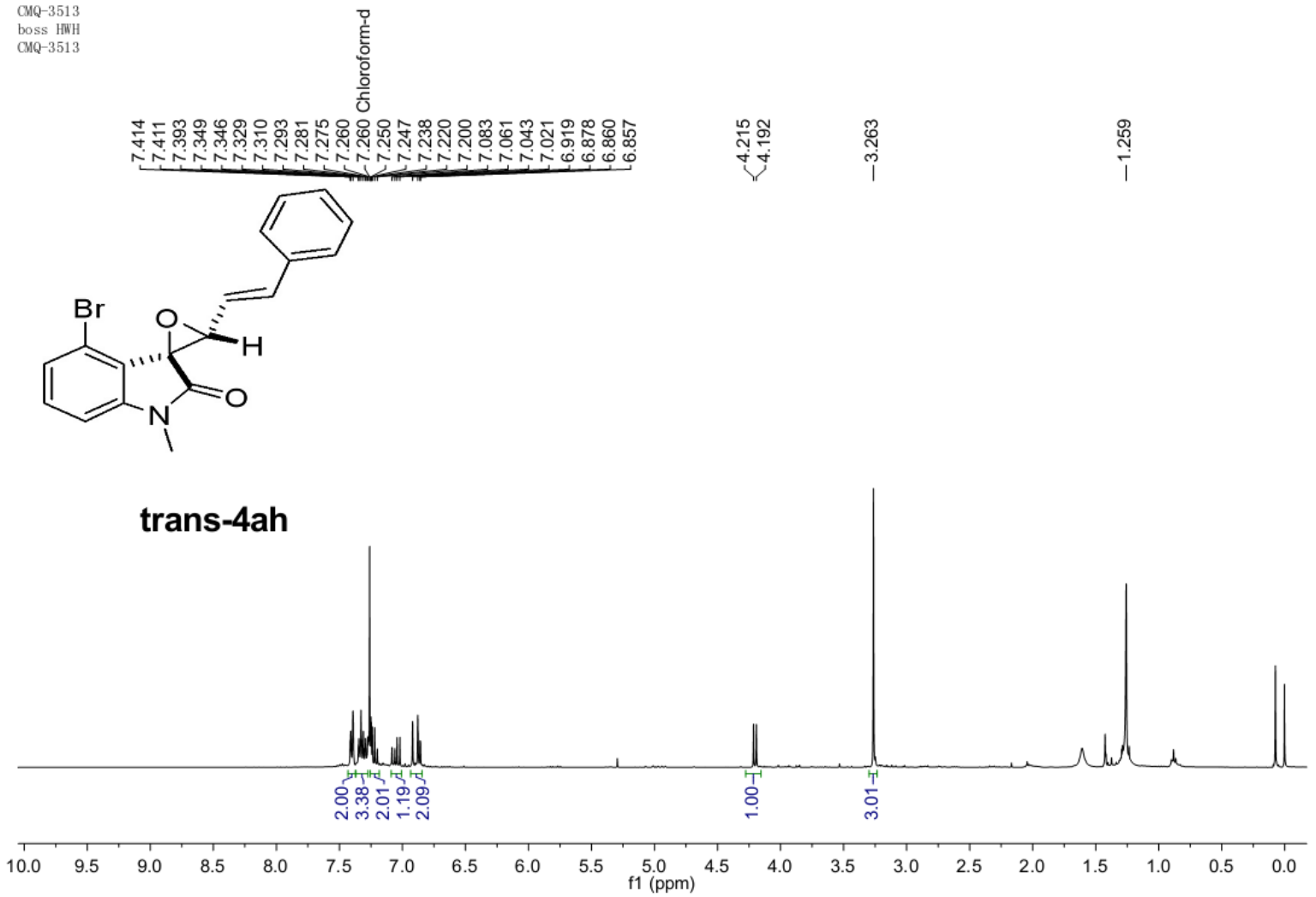


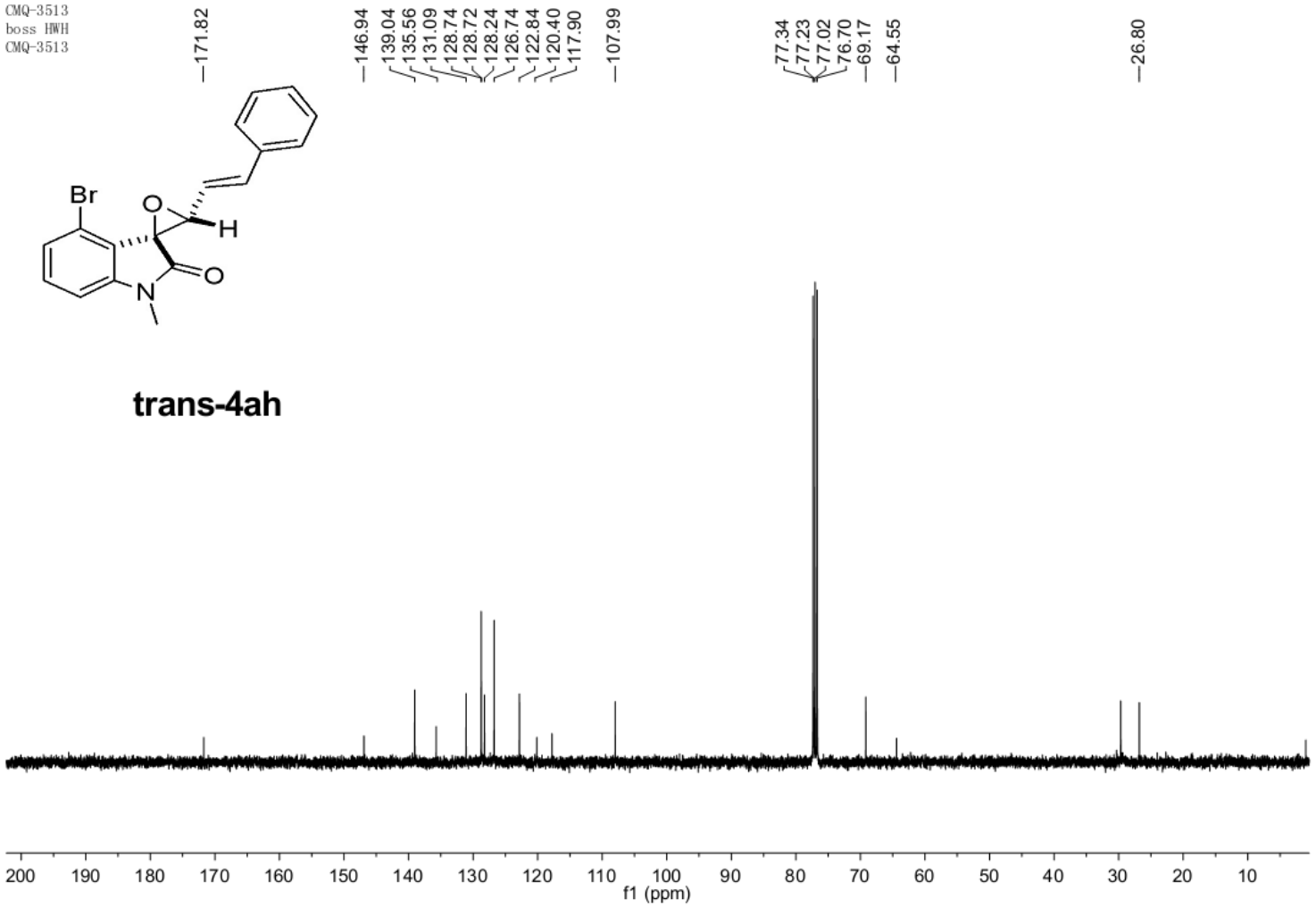




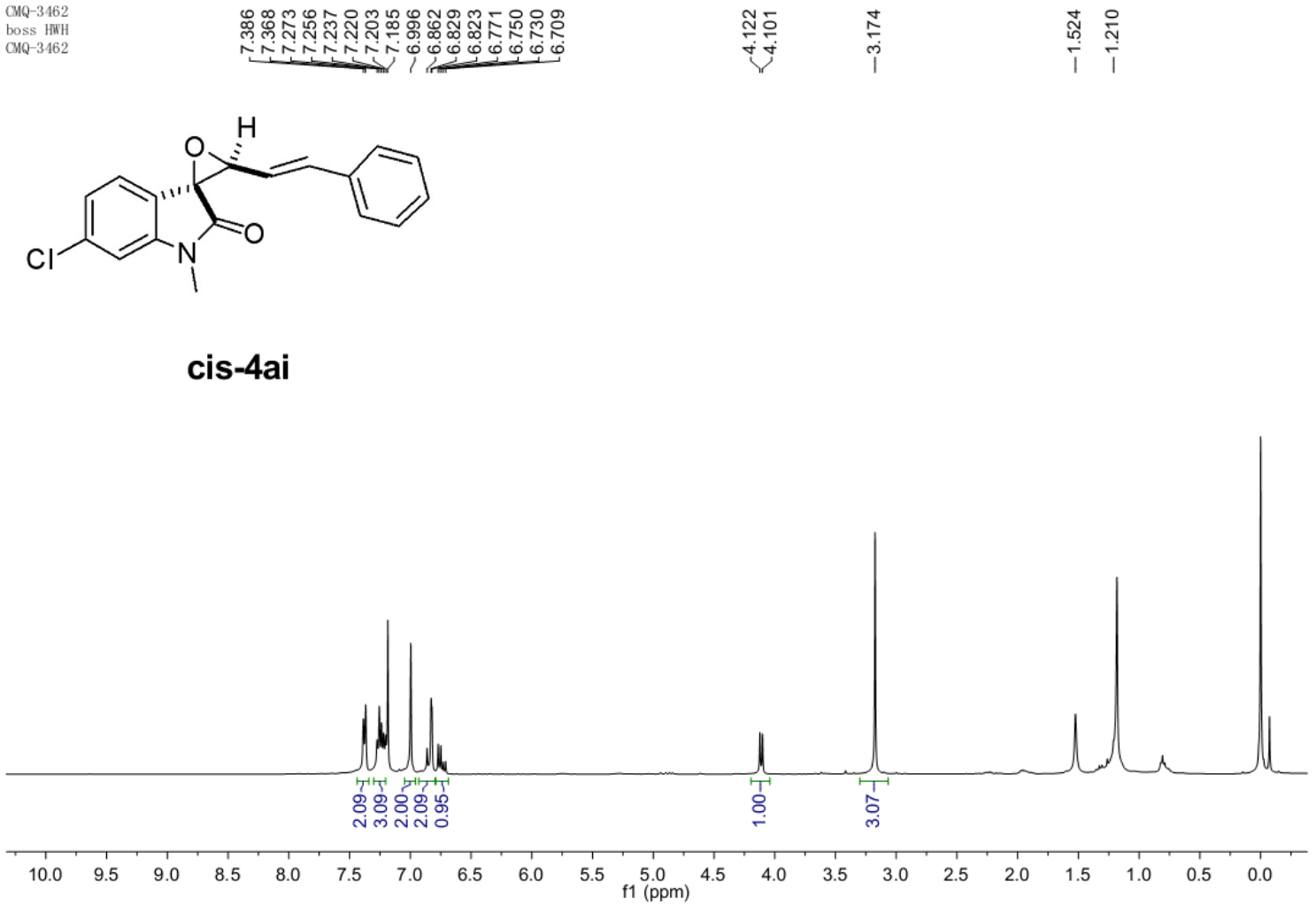
cis-4ah



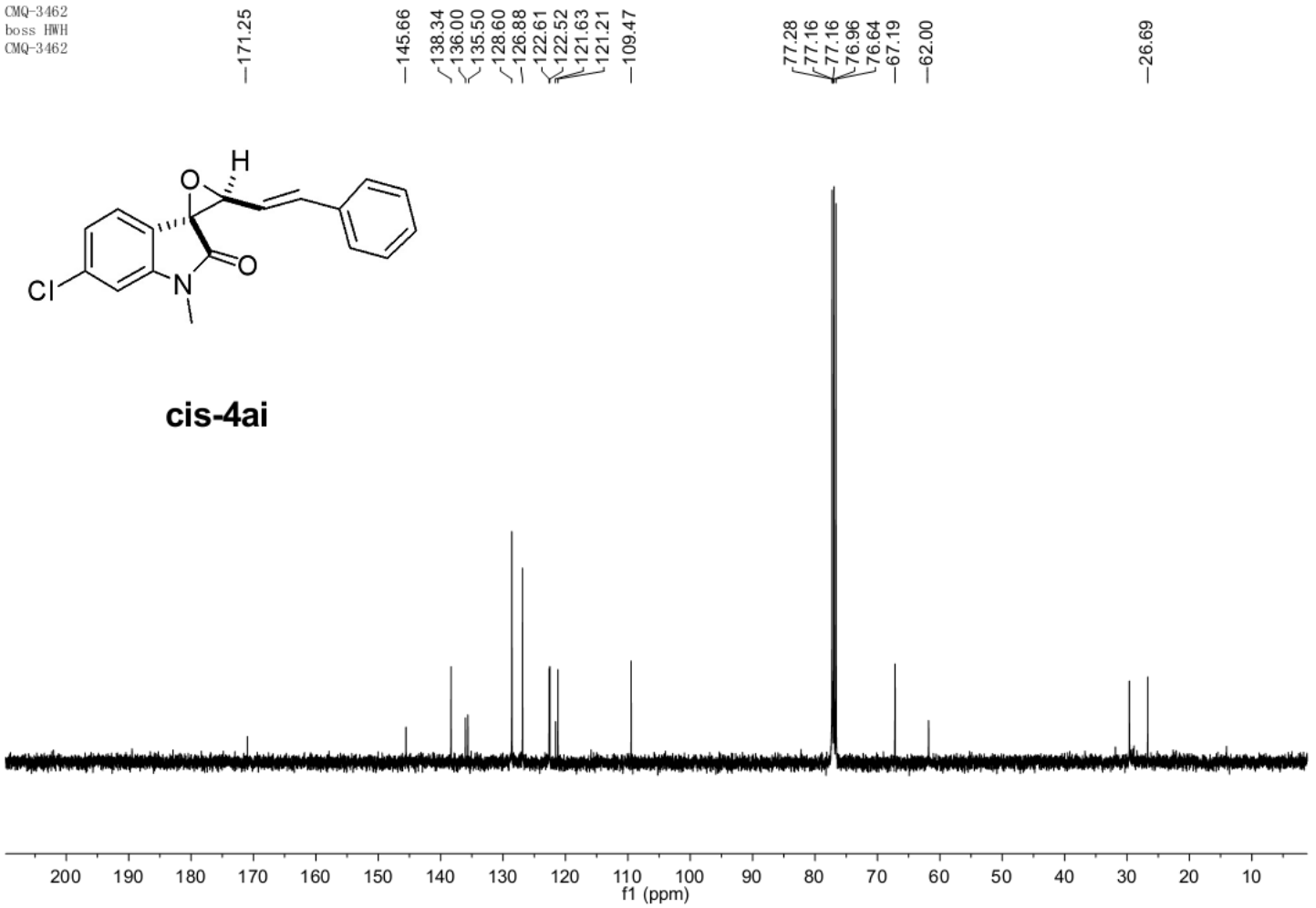




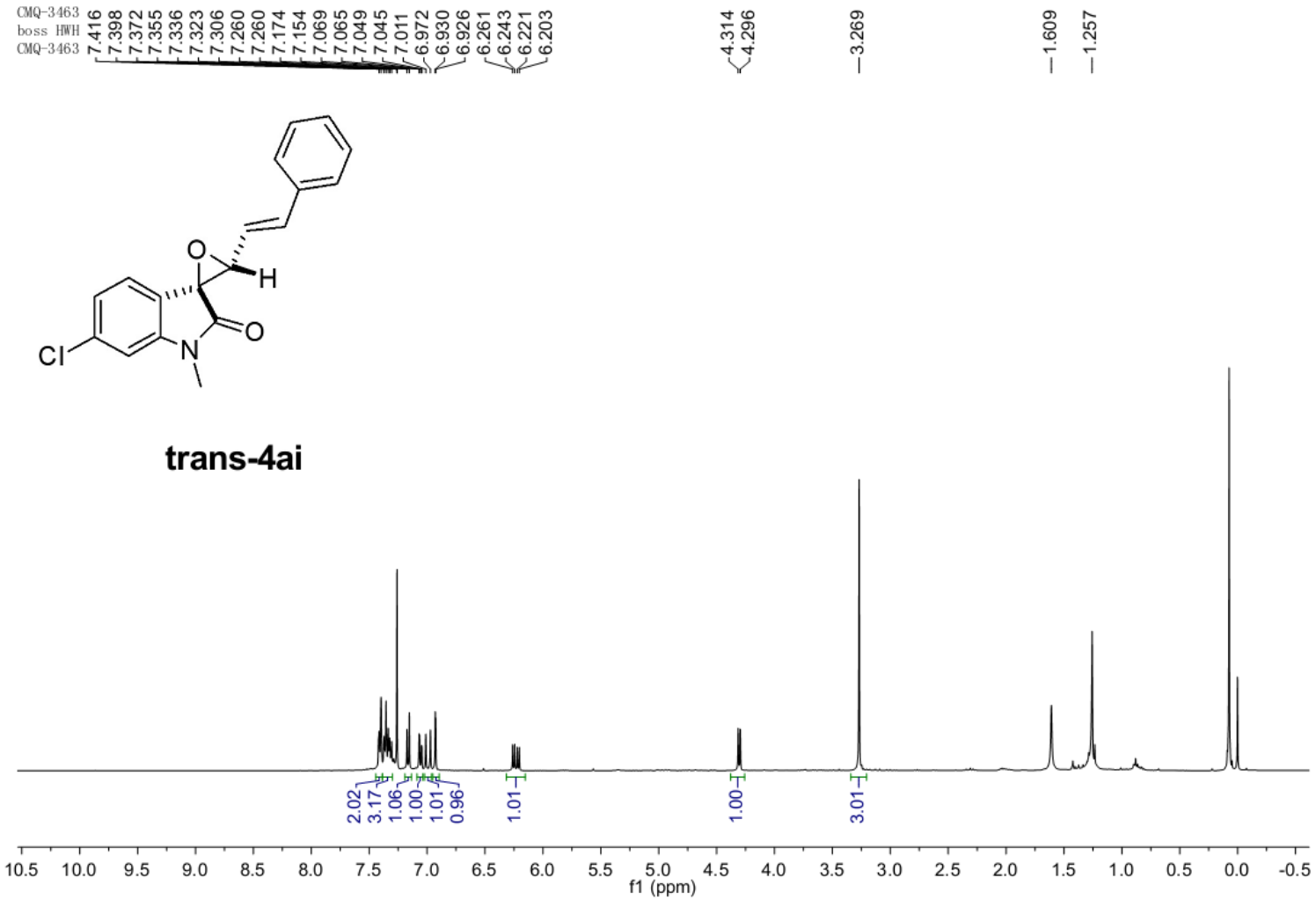
trans-4ah

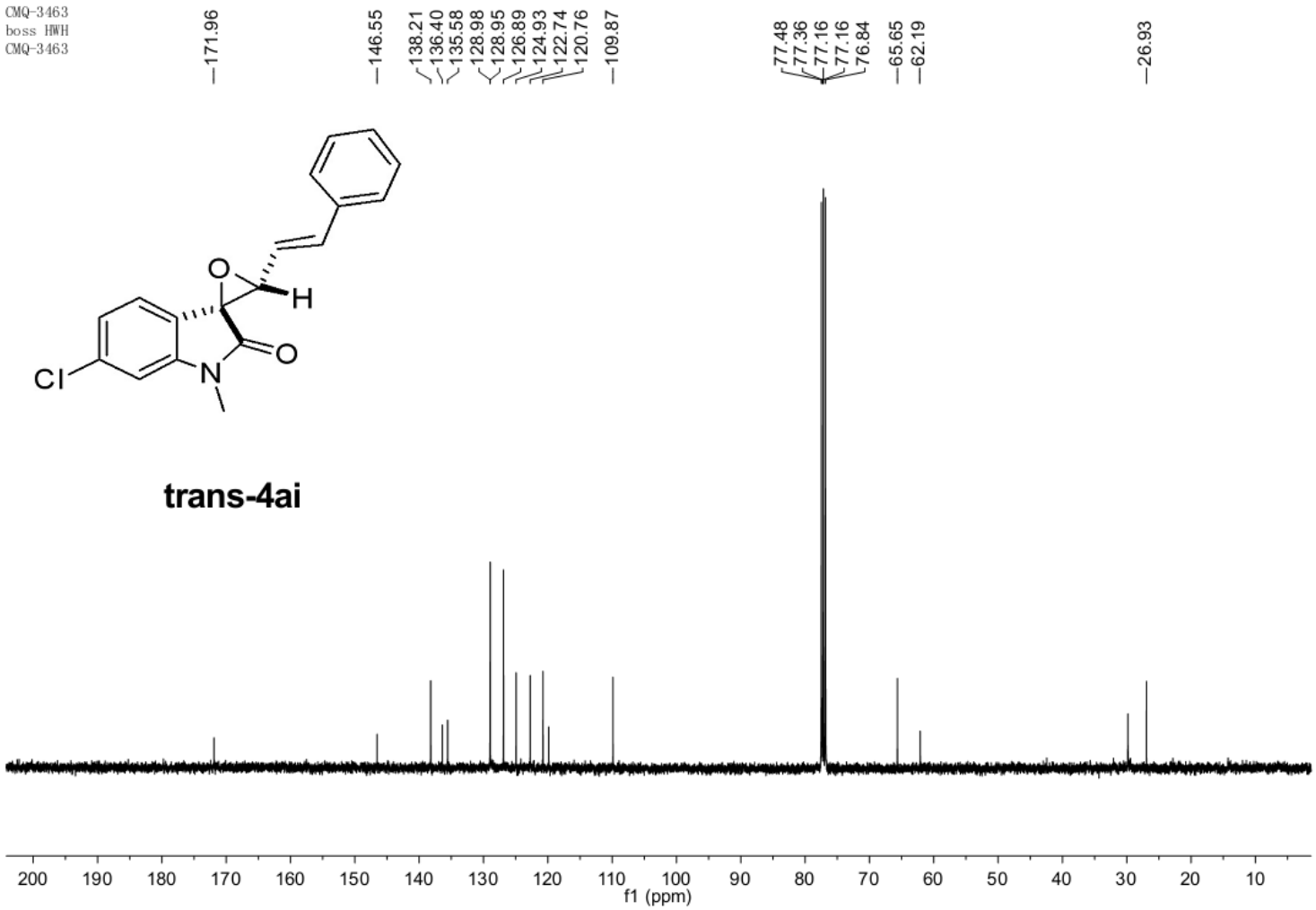


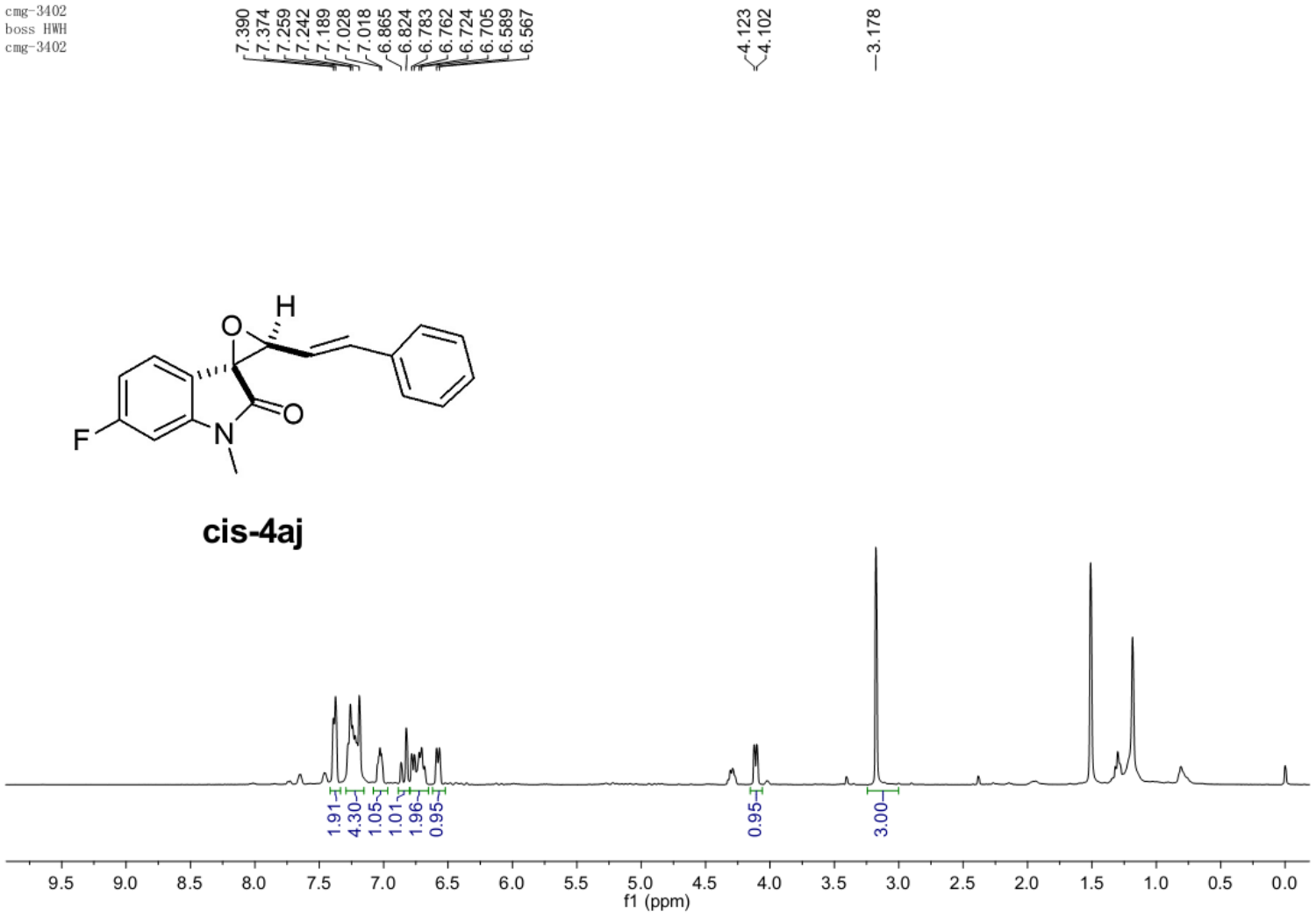
cis-4ai

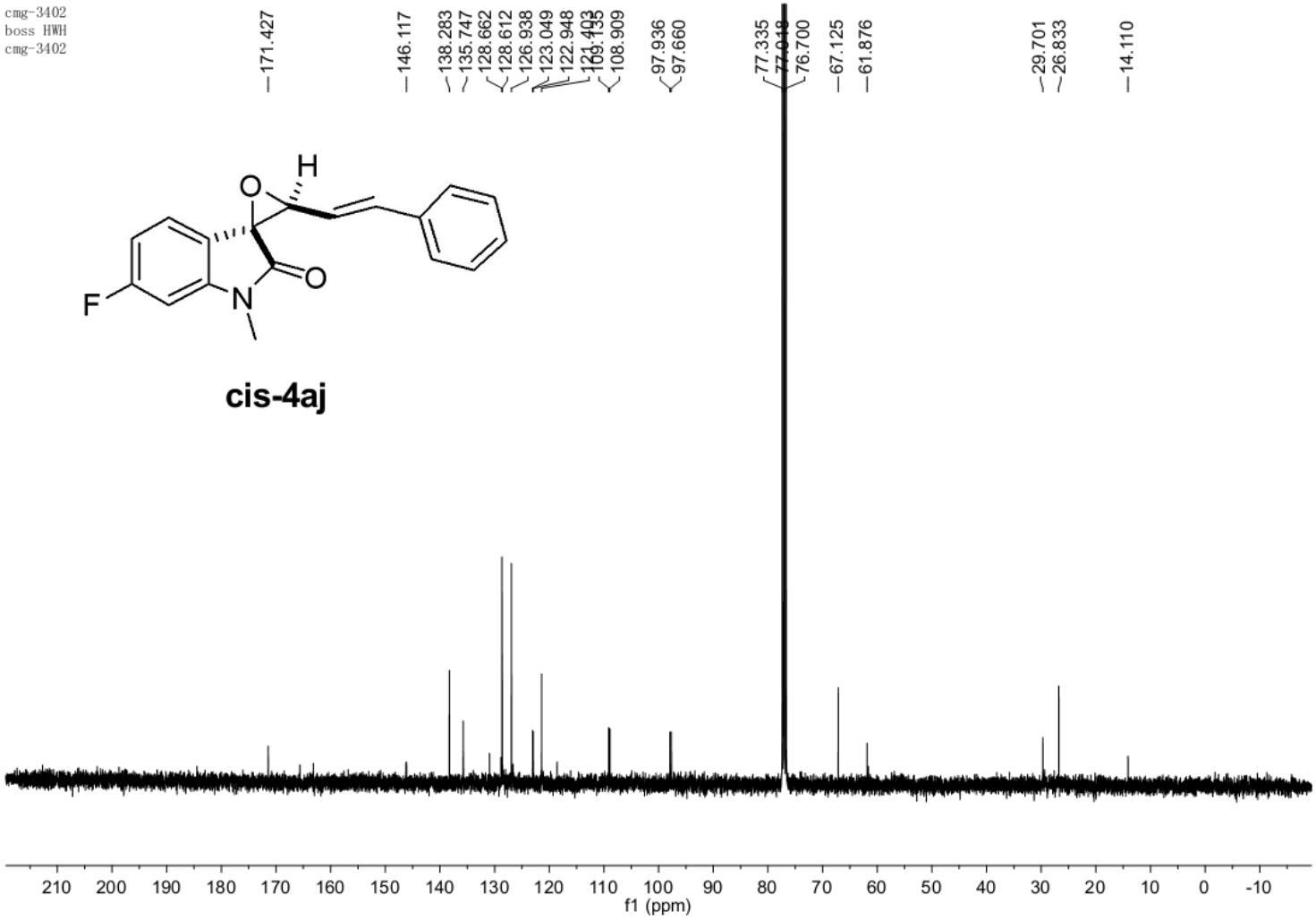


cis-4ai









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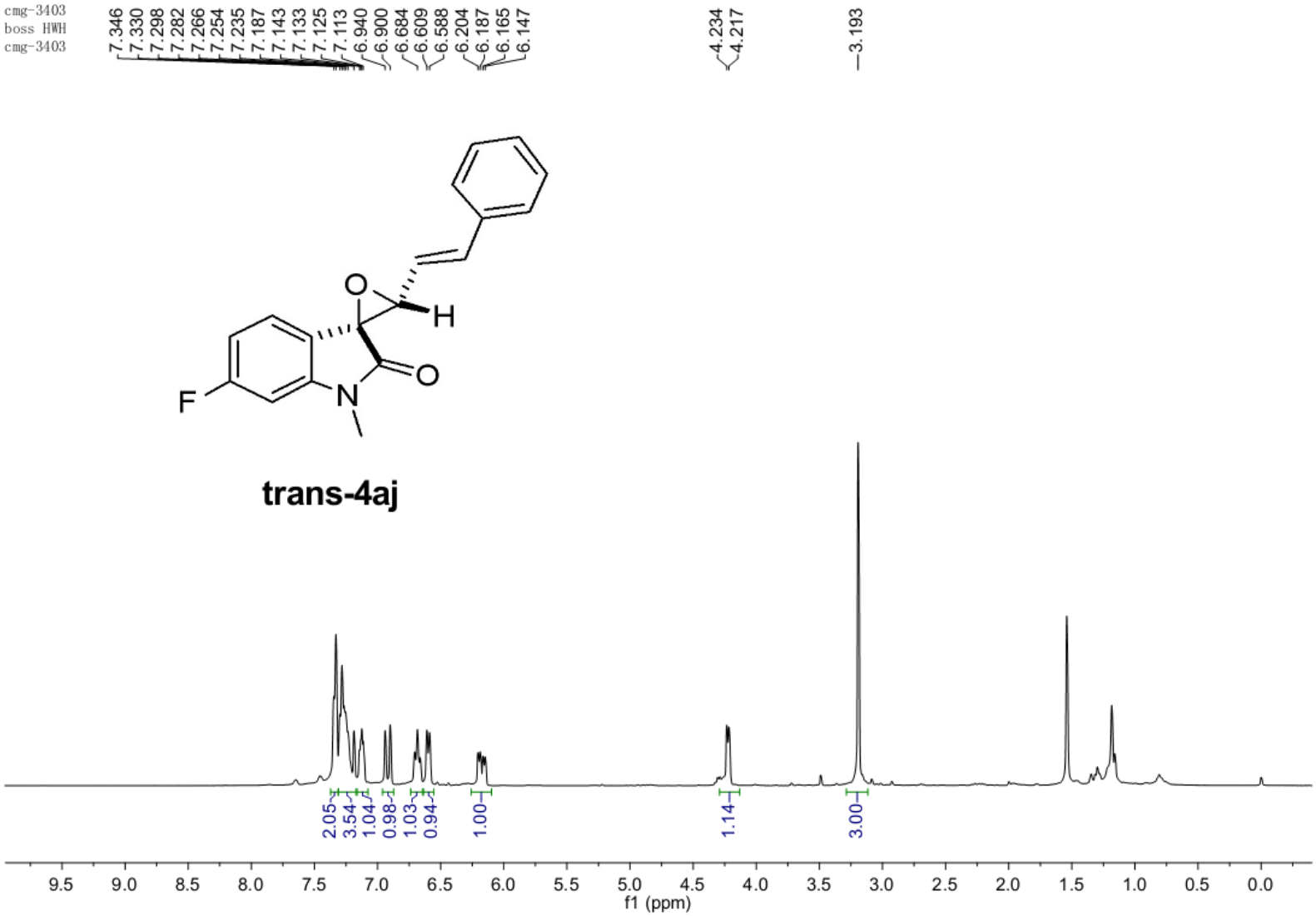
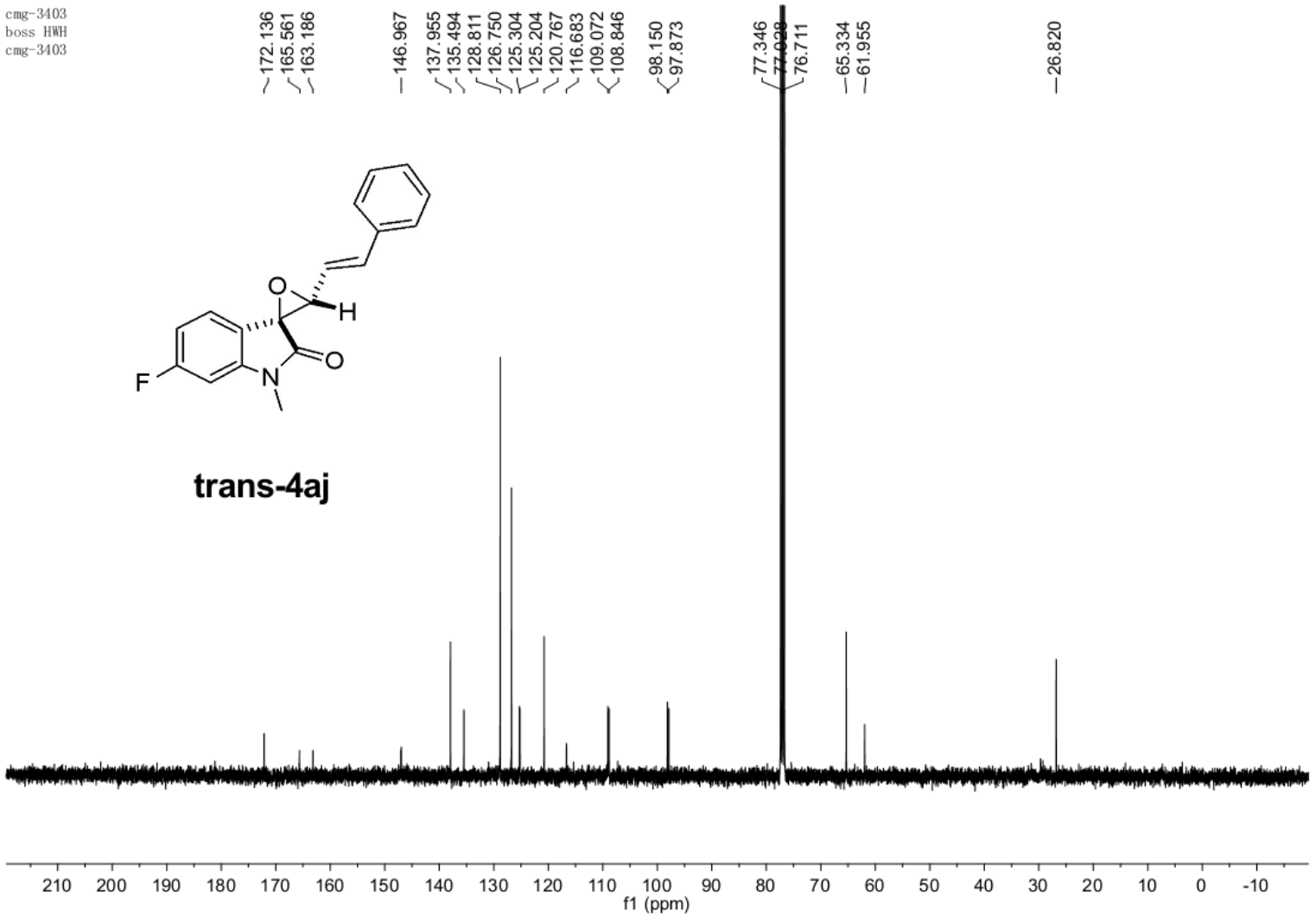
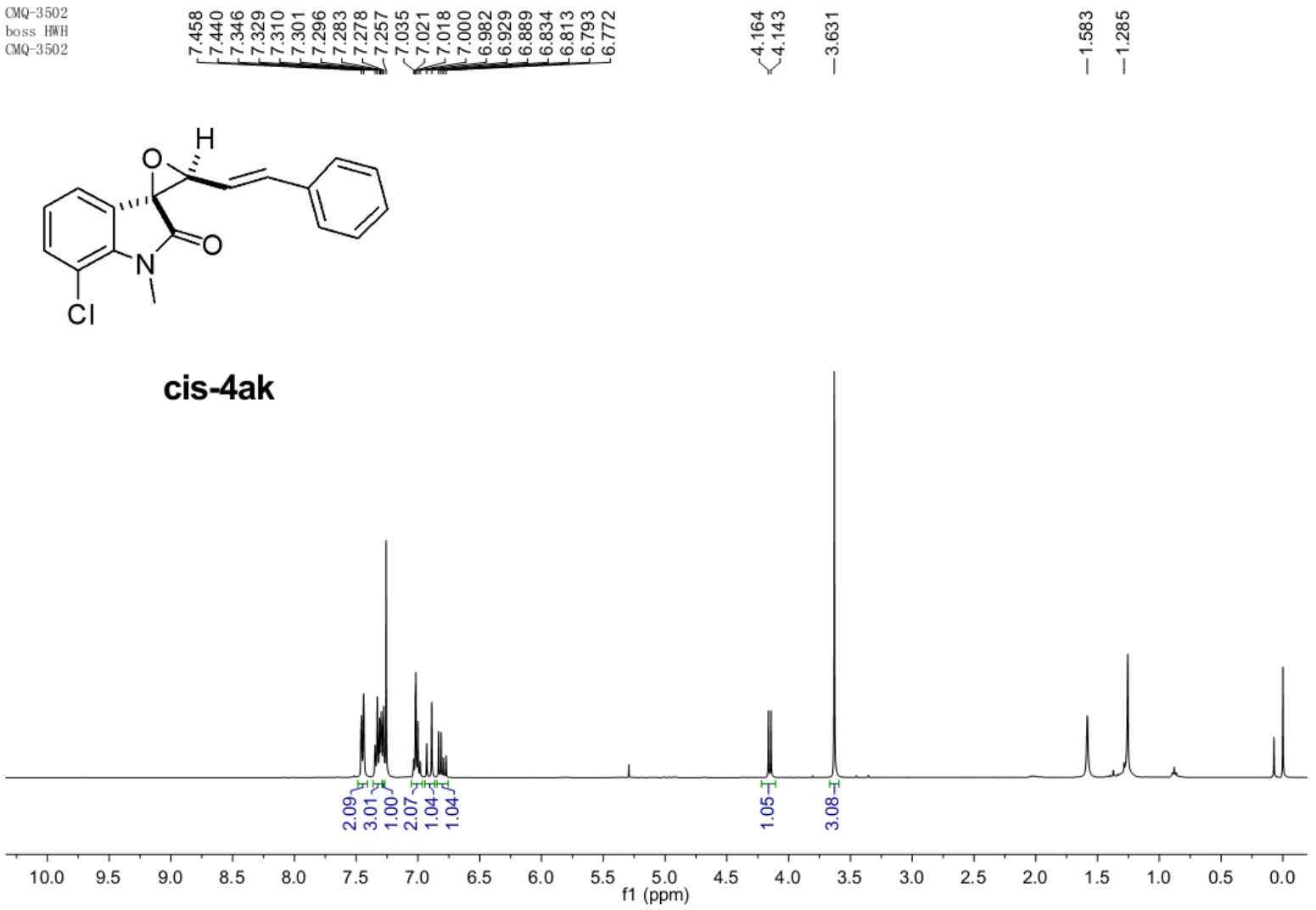
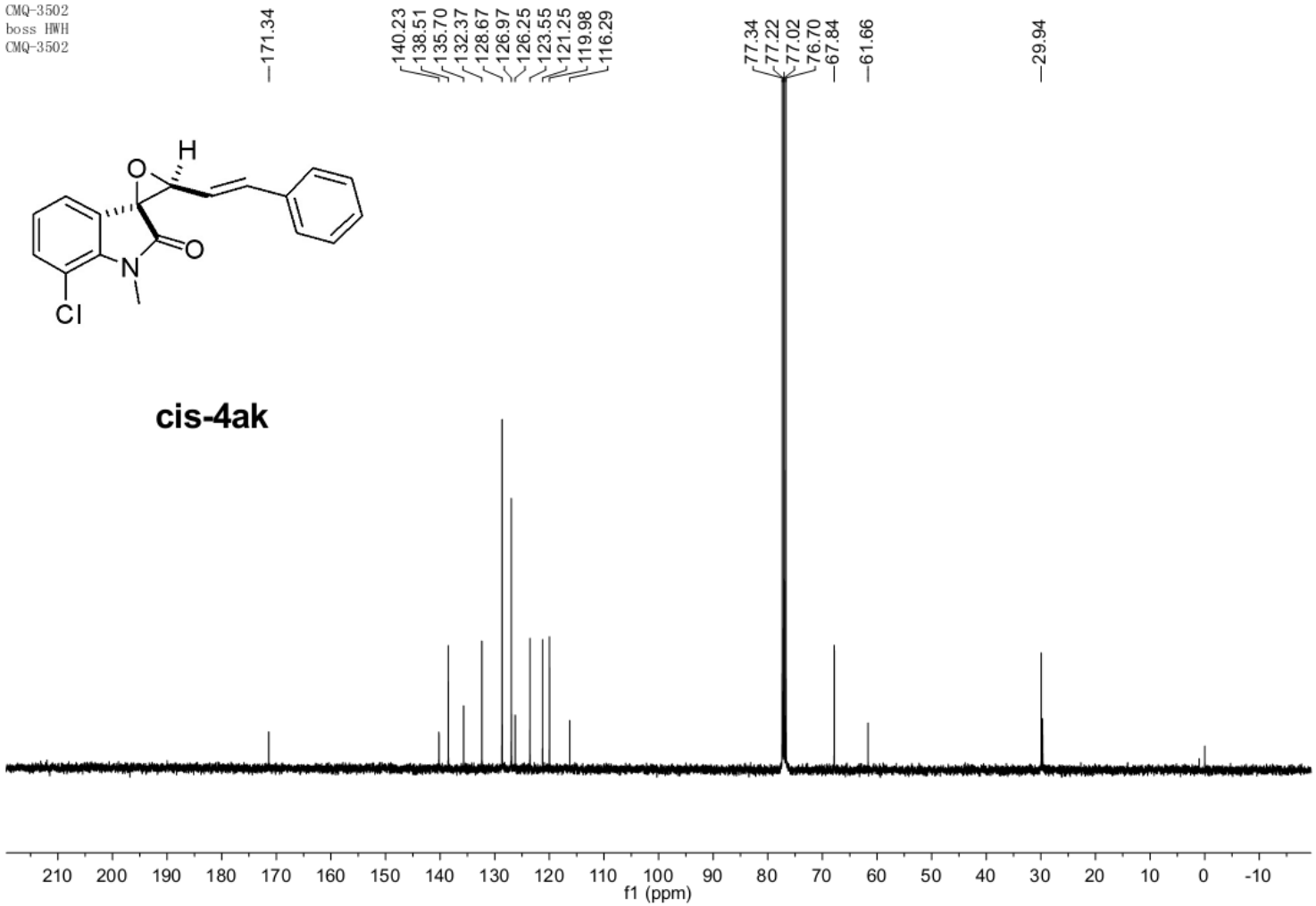
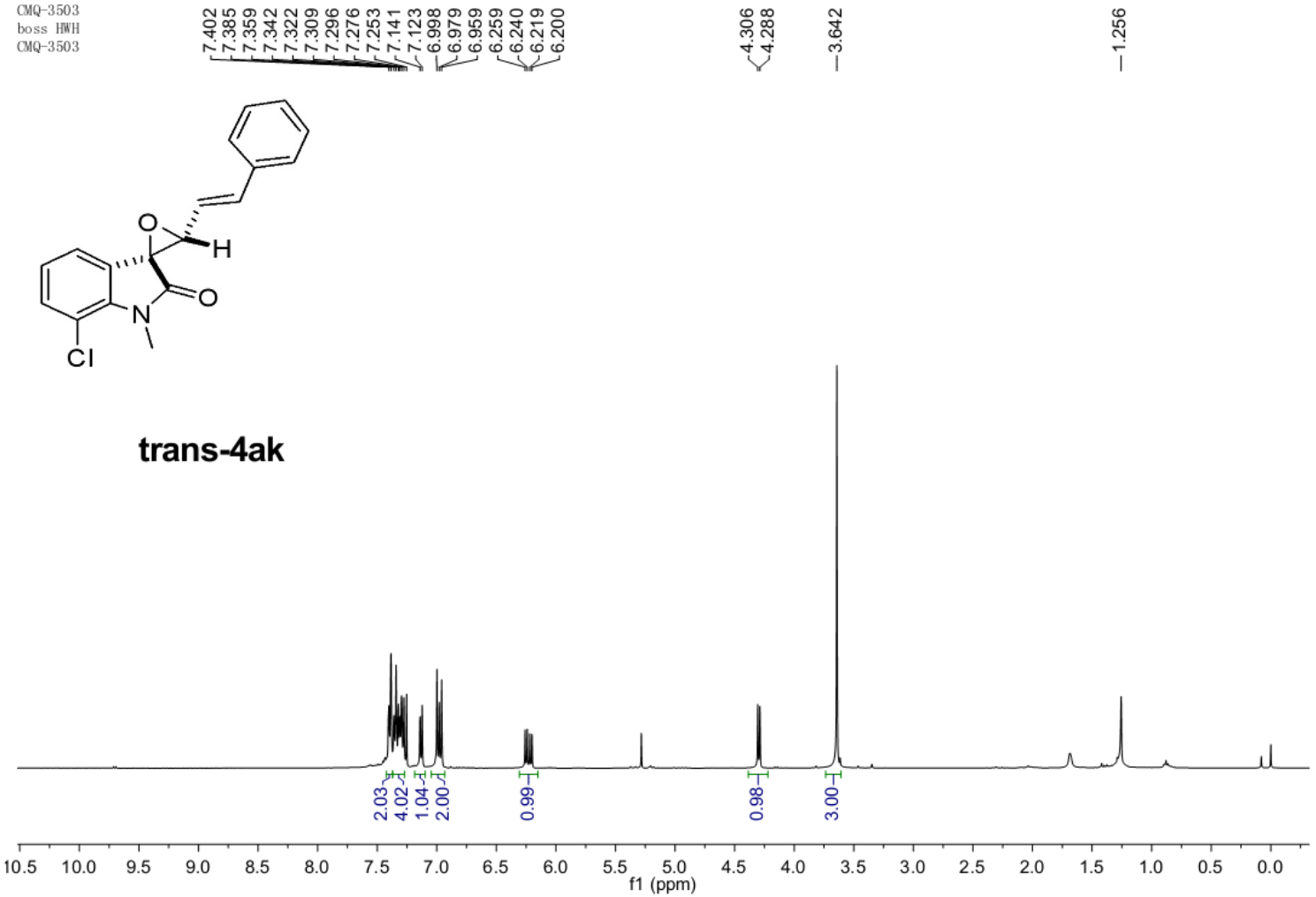


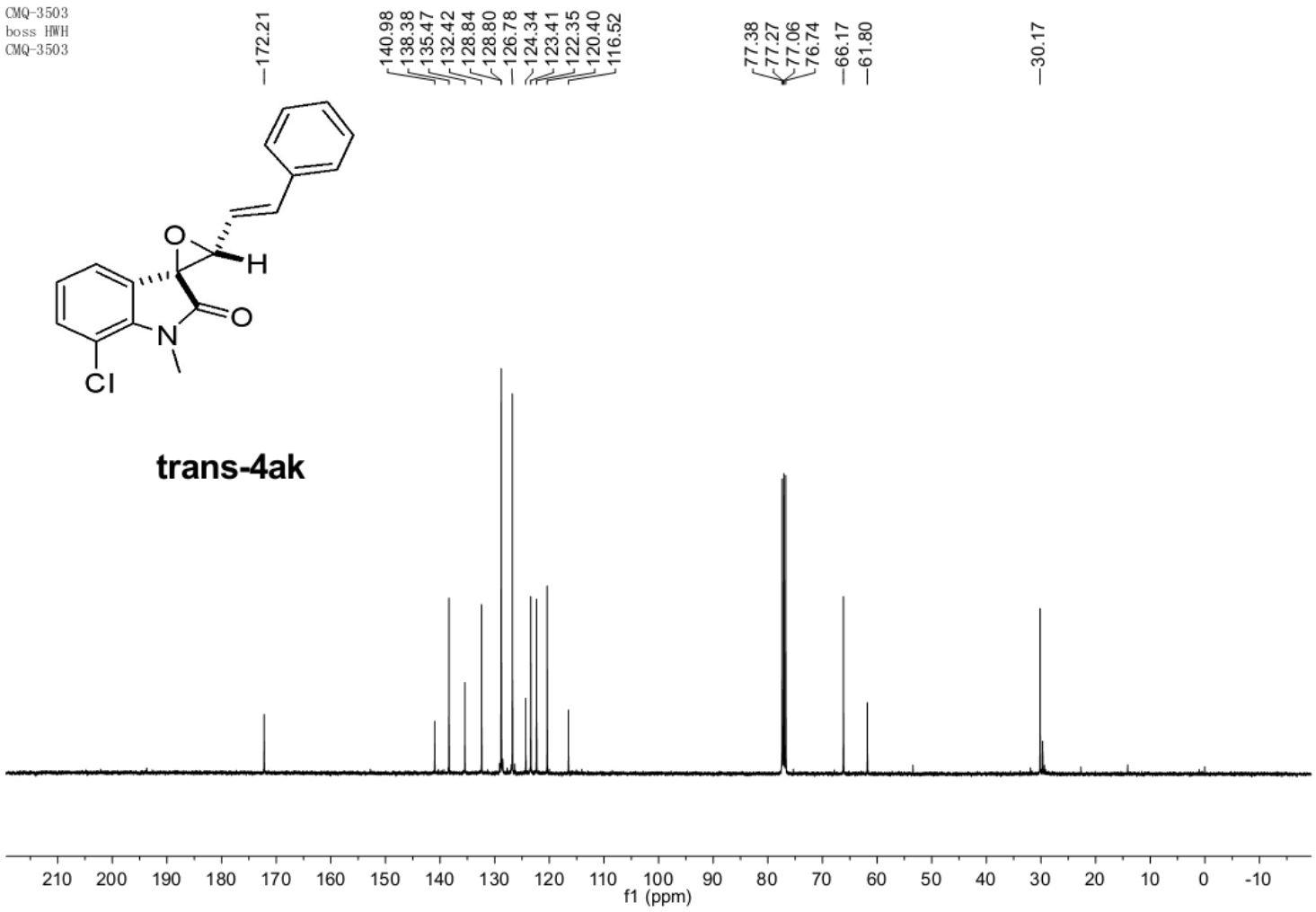
trans-4aj

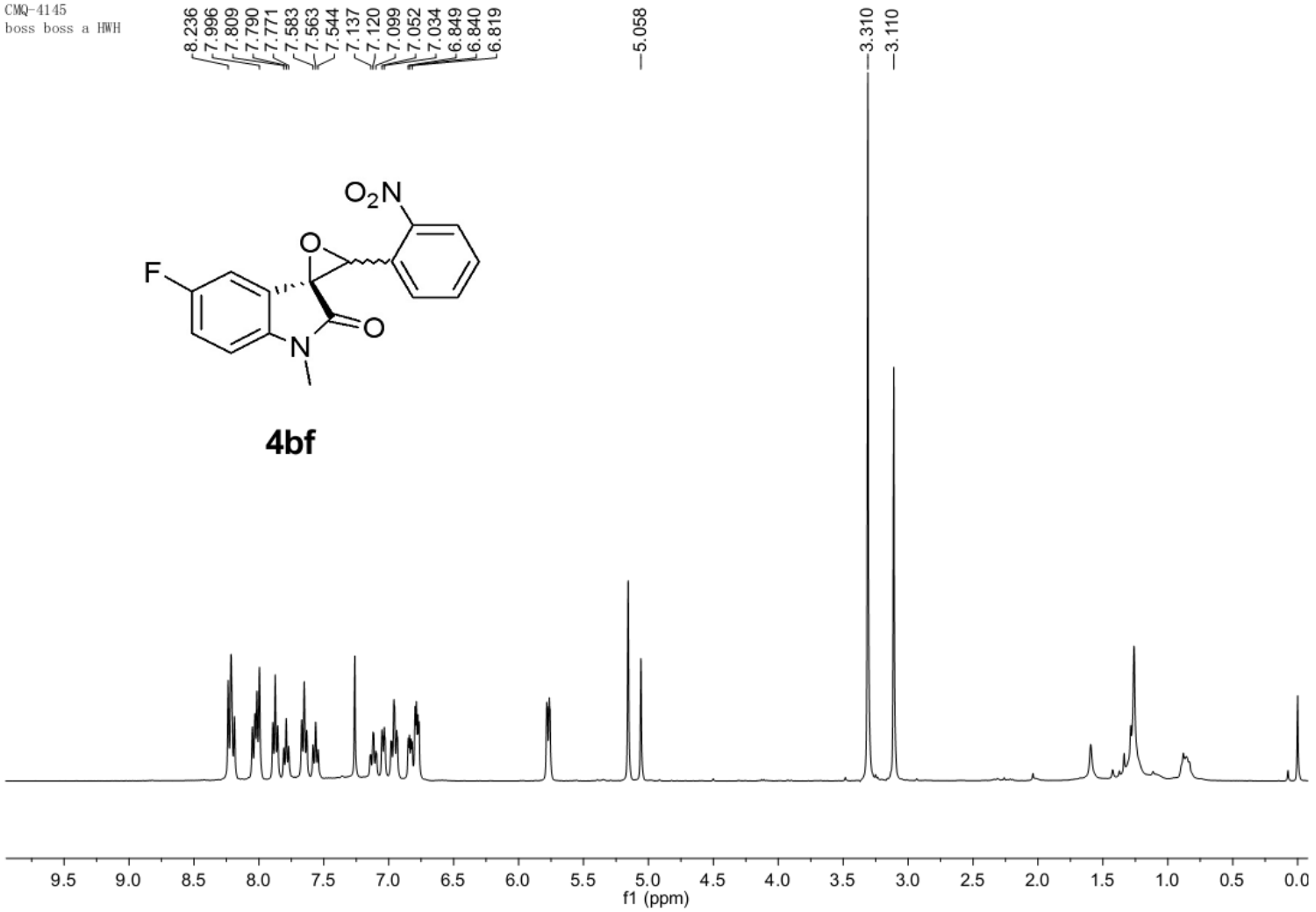


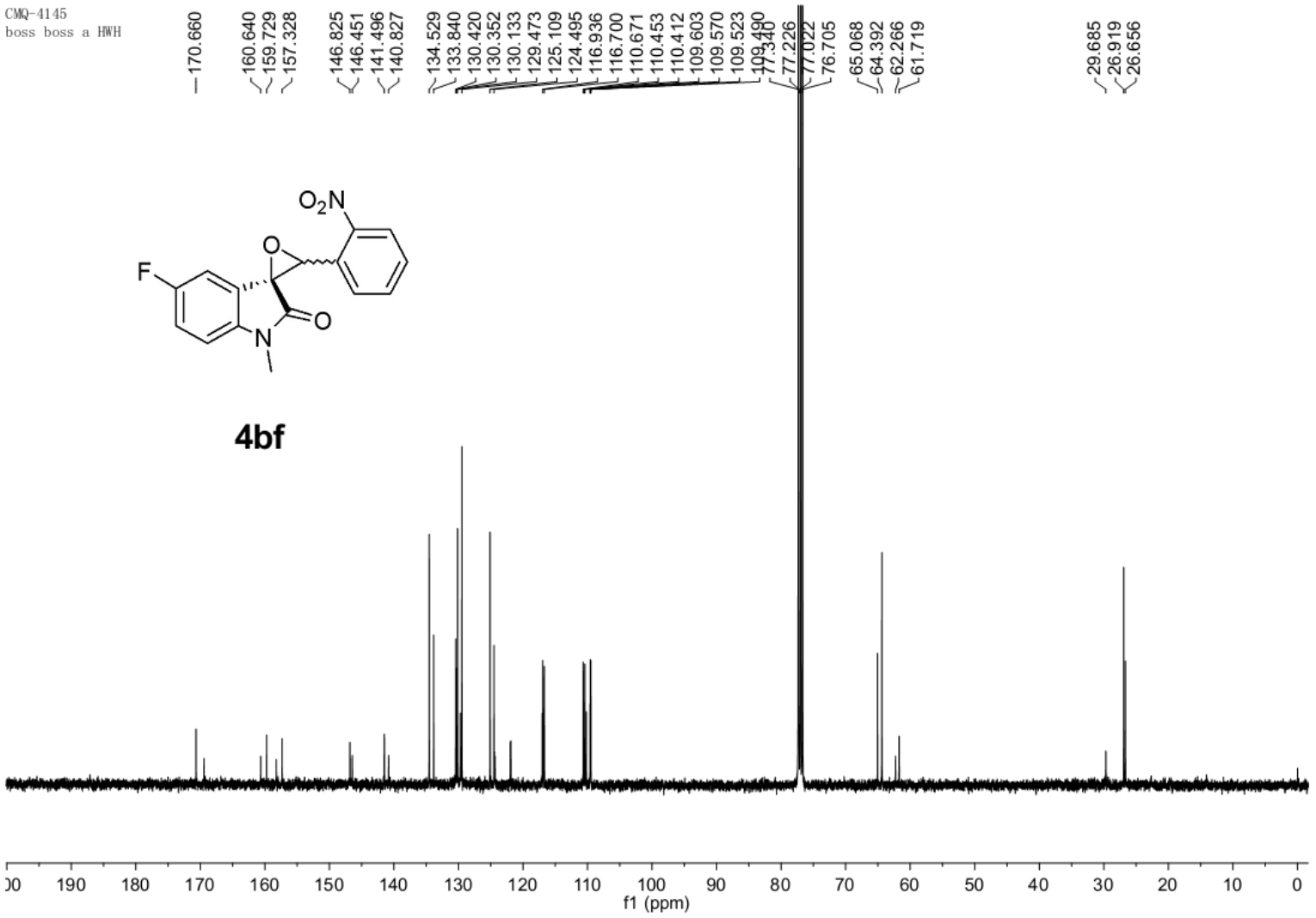


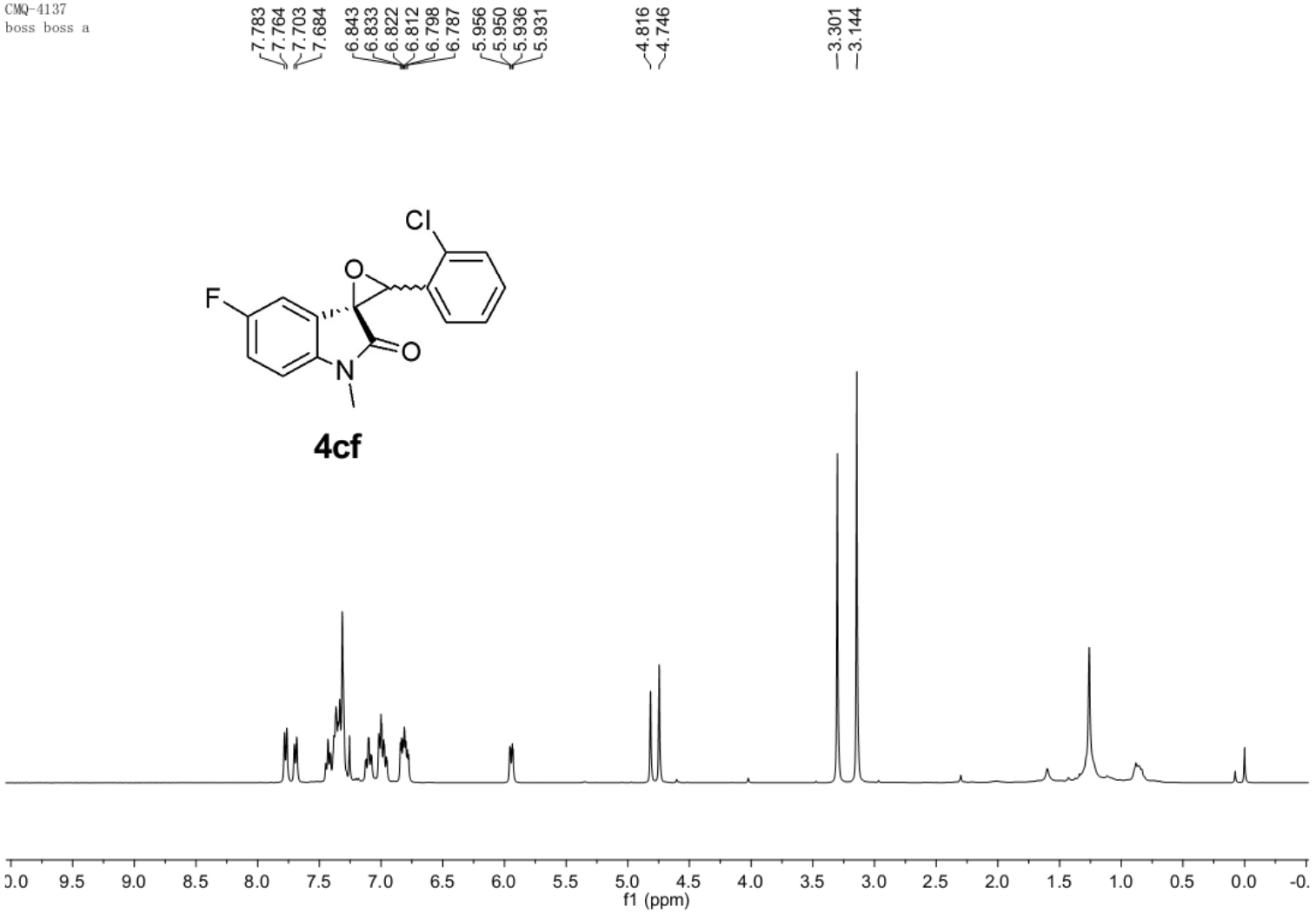


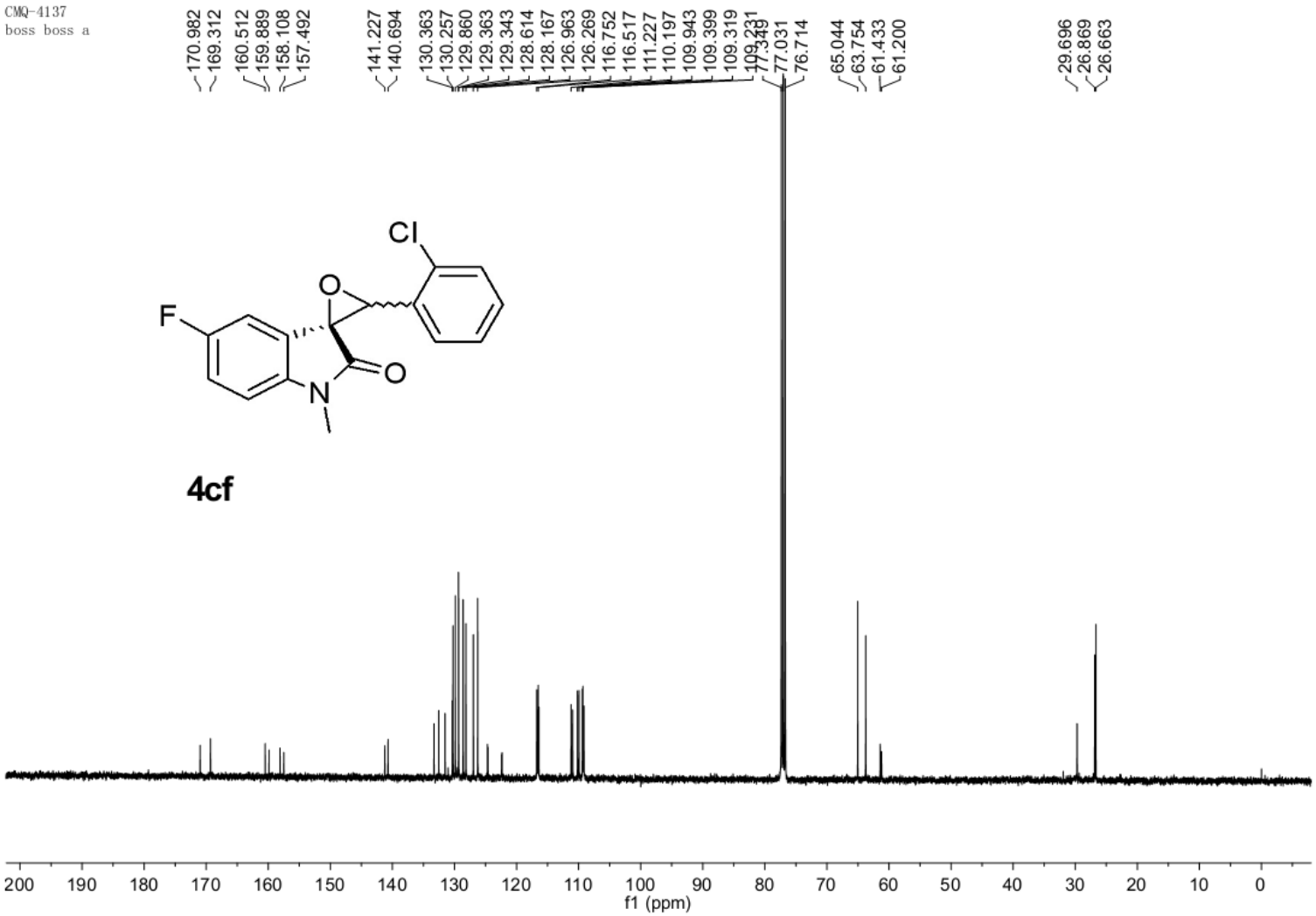


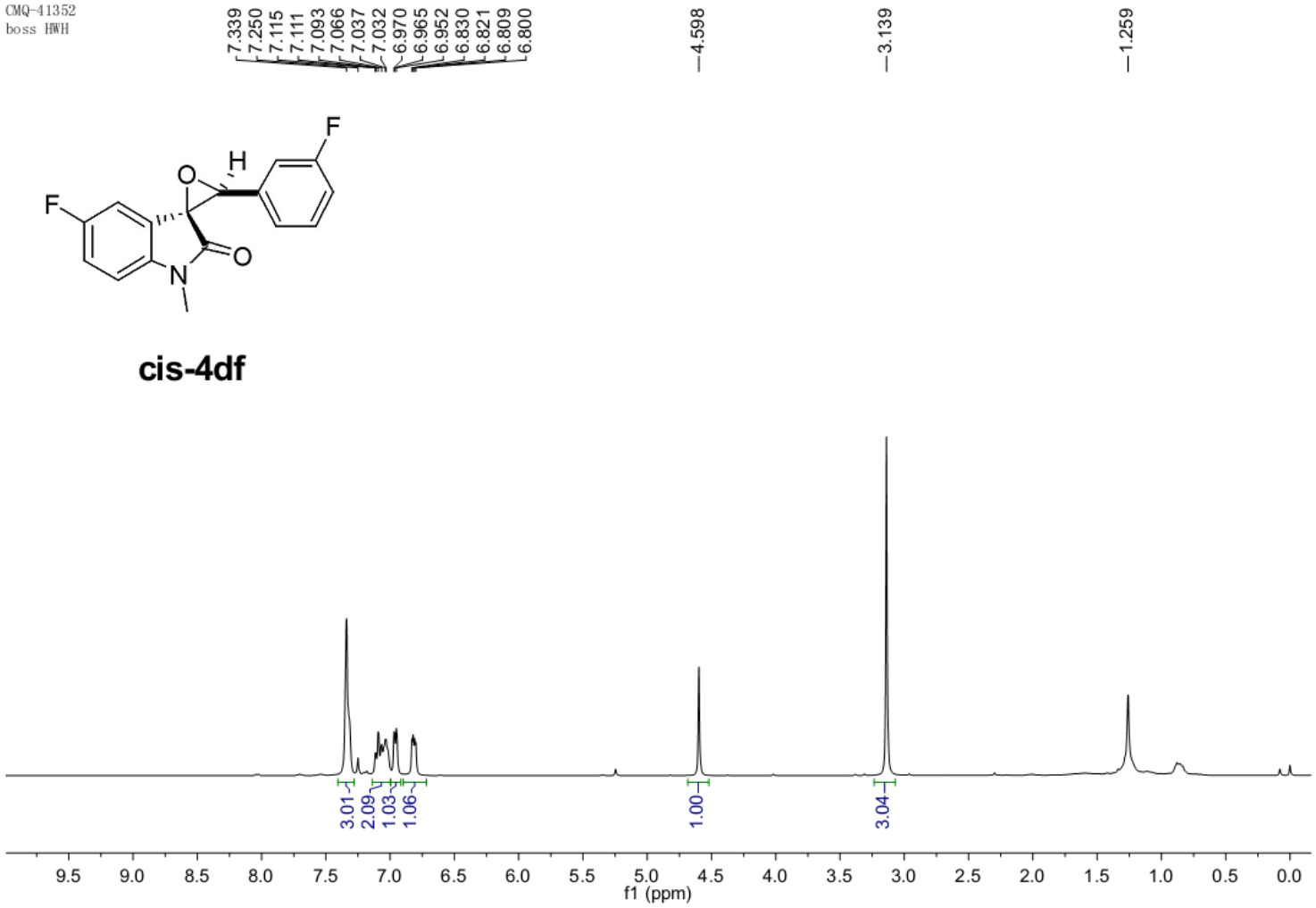












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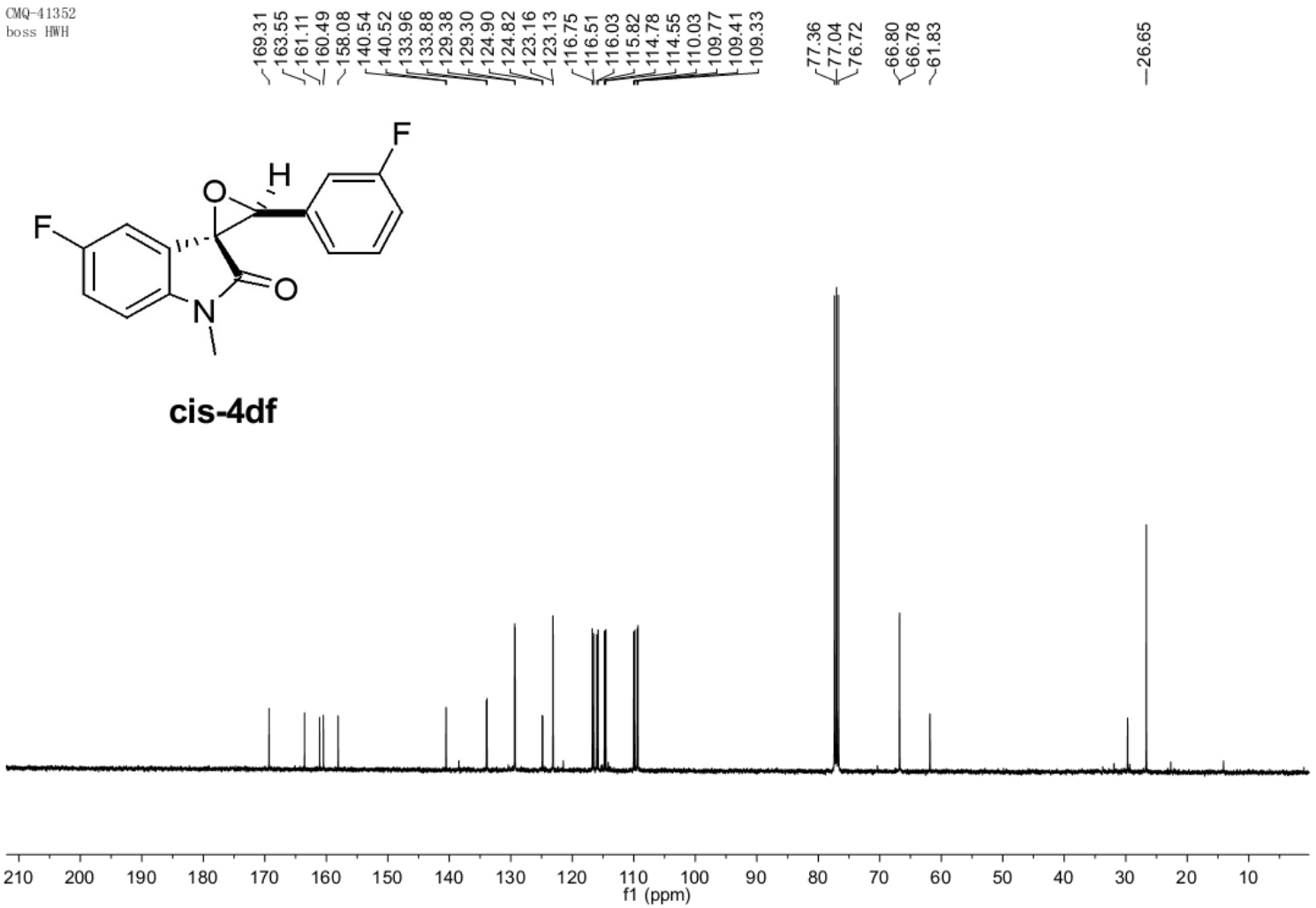

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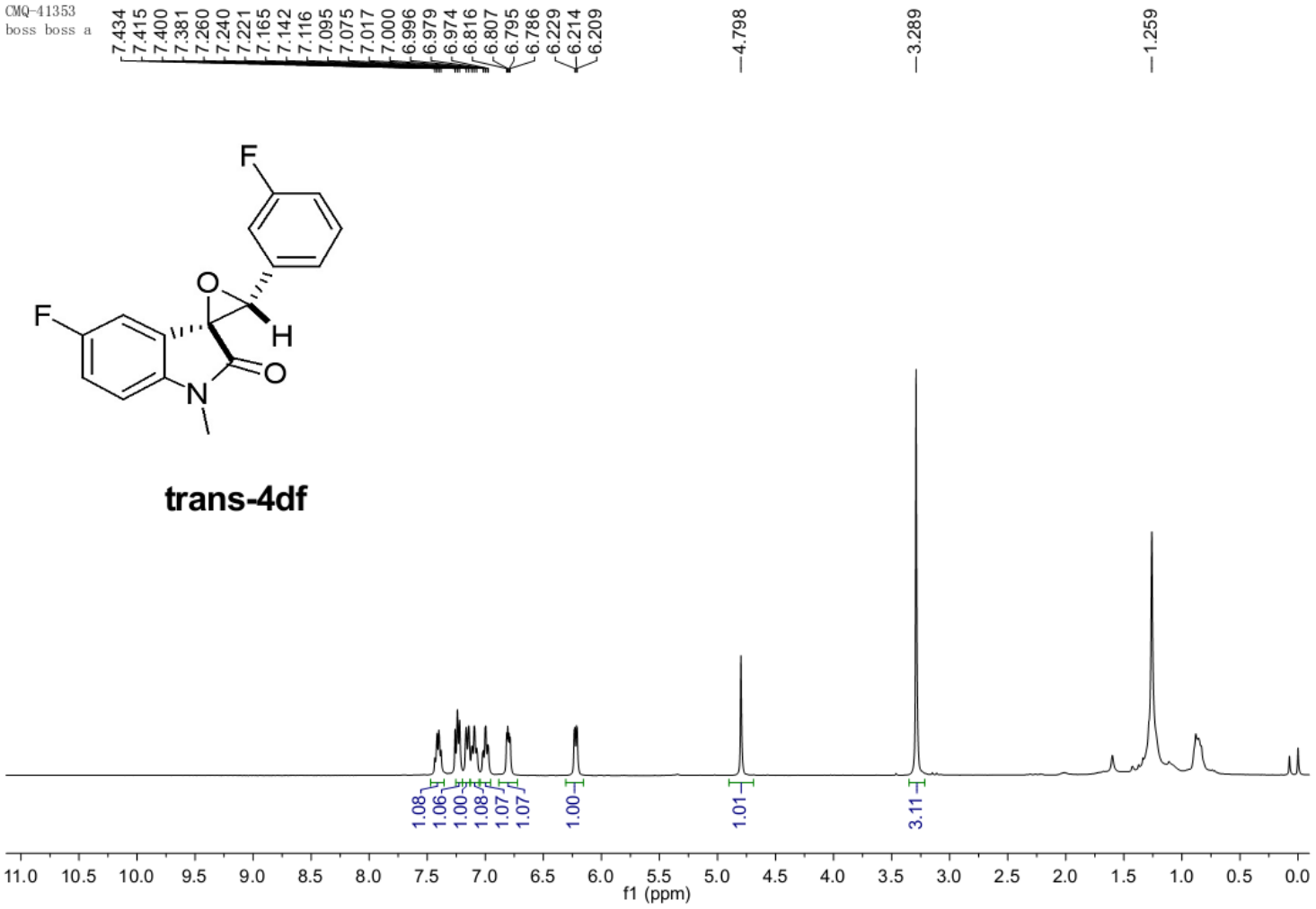

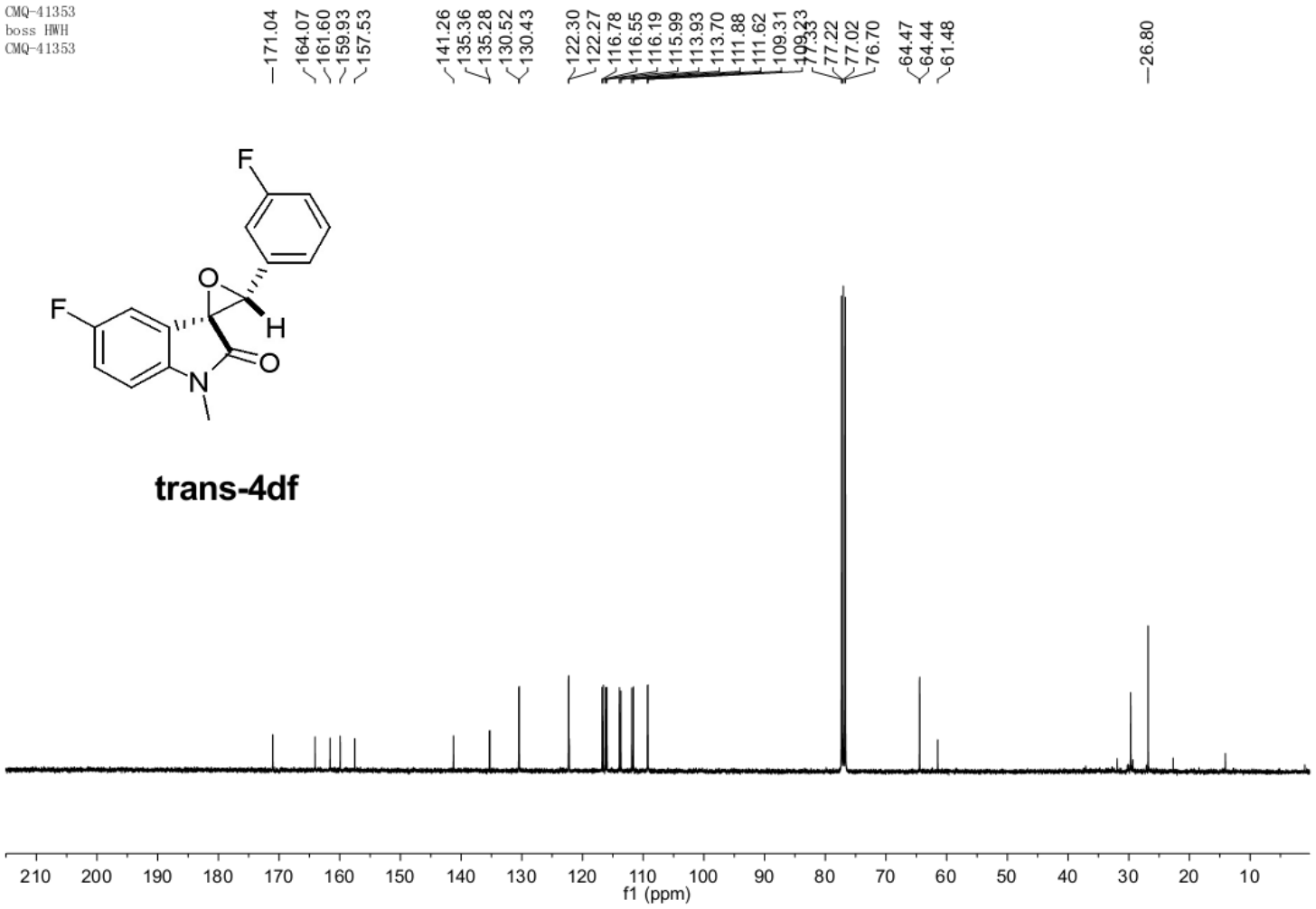

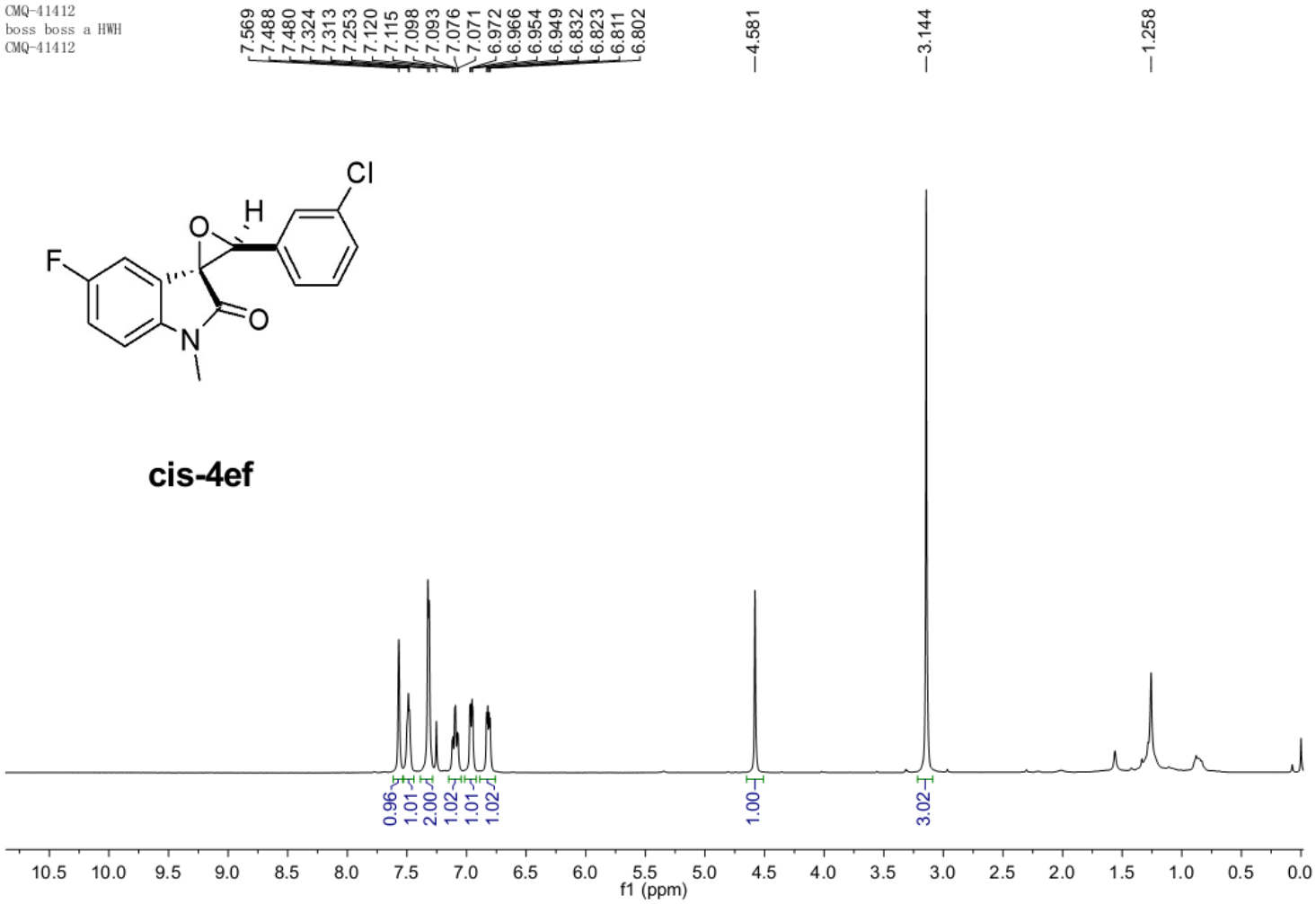

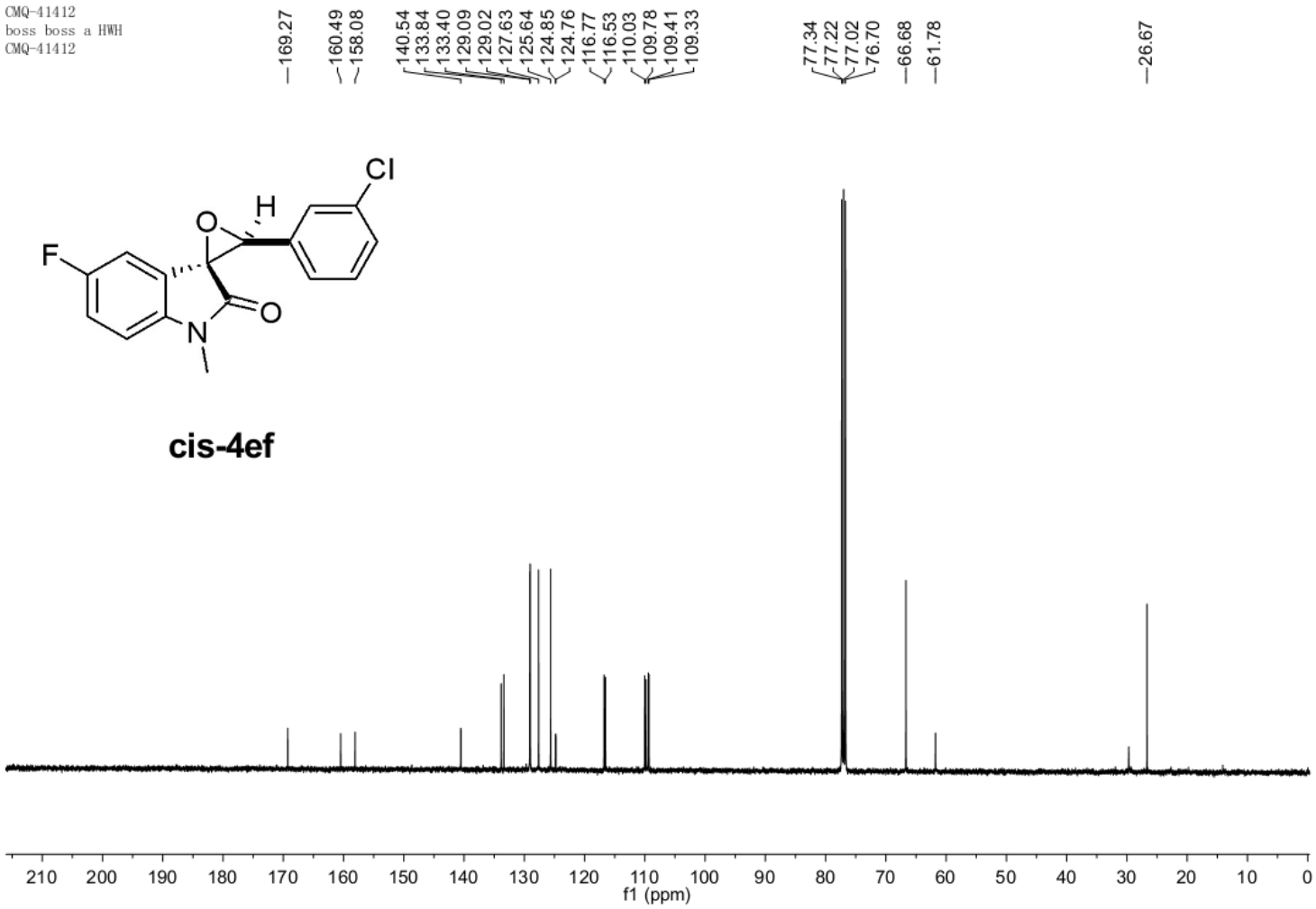

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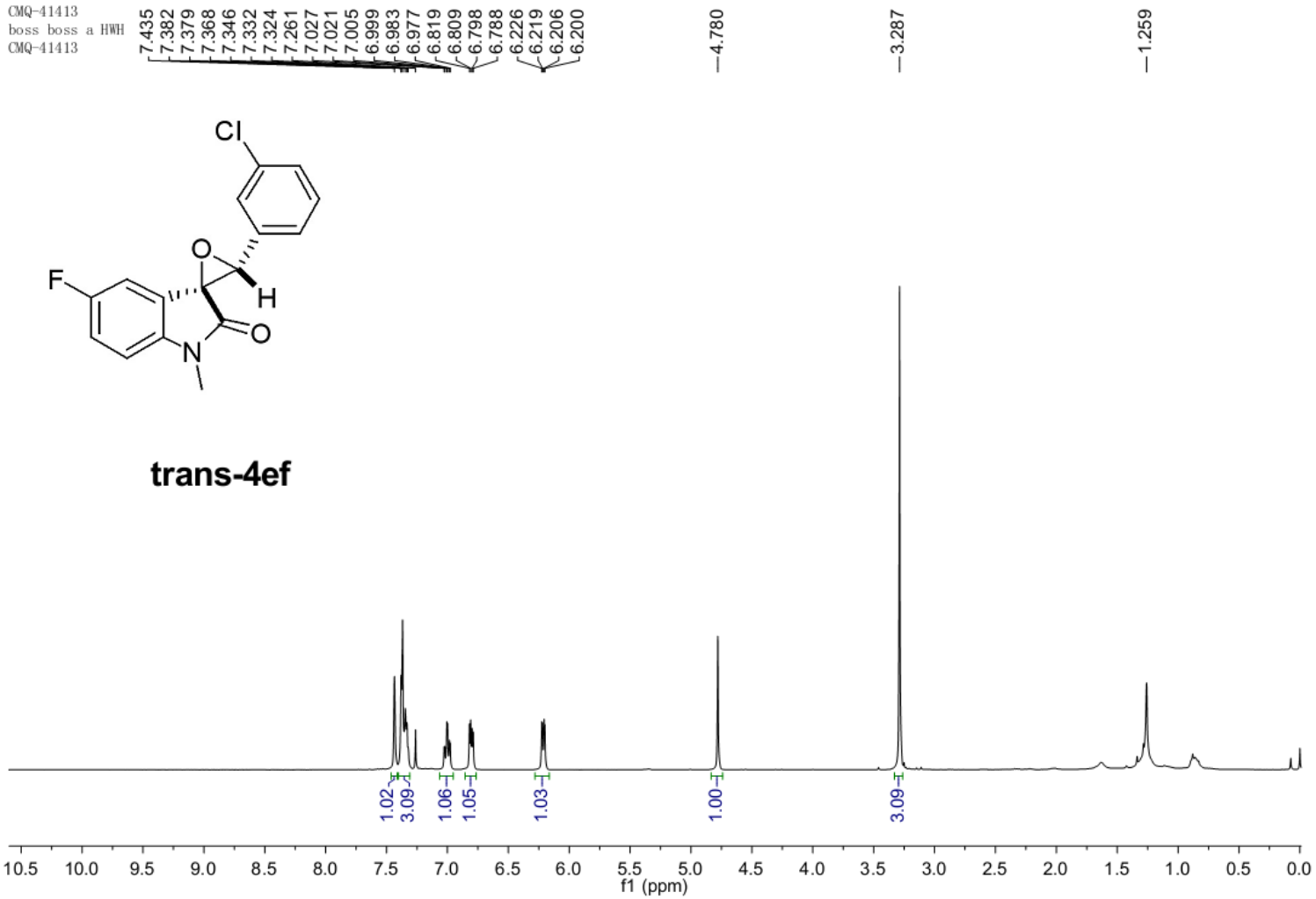

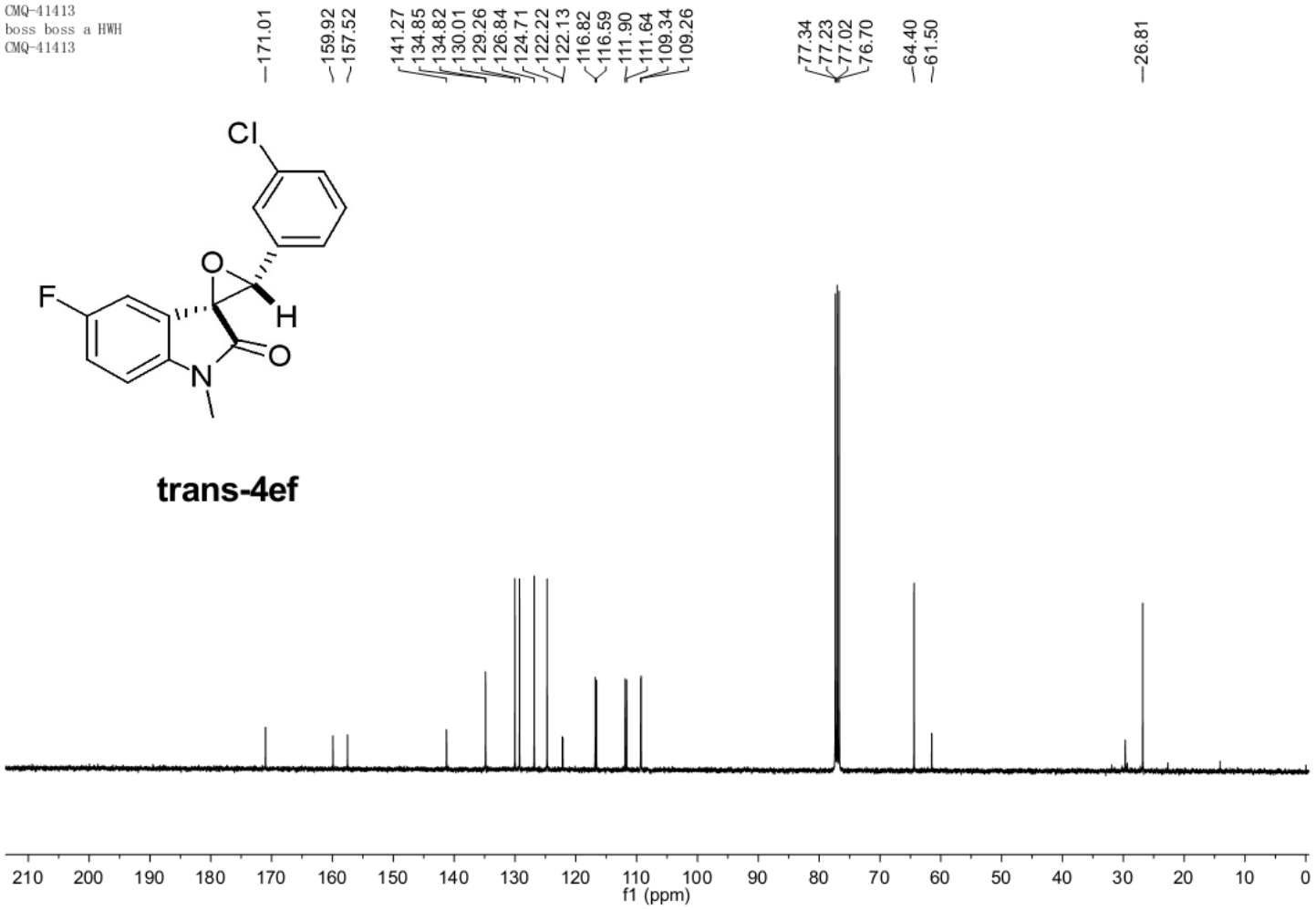

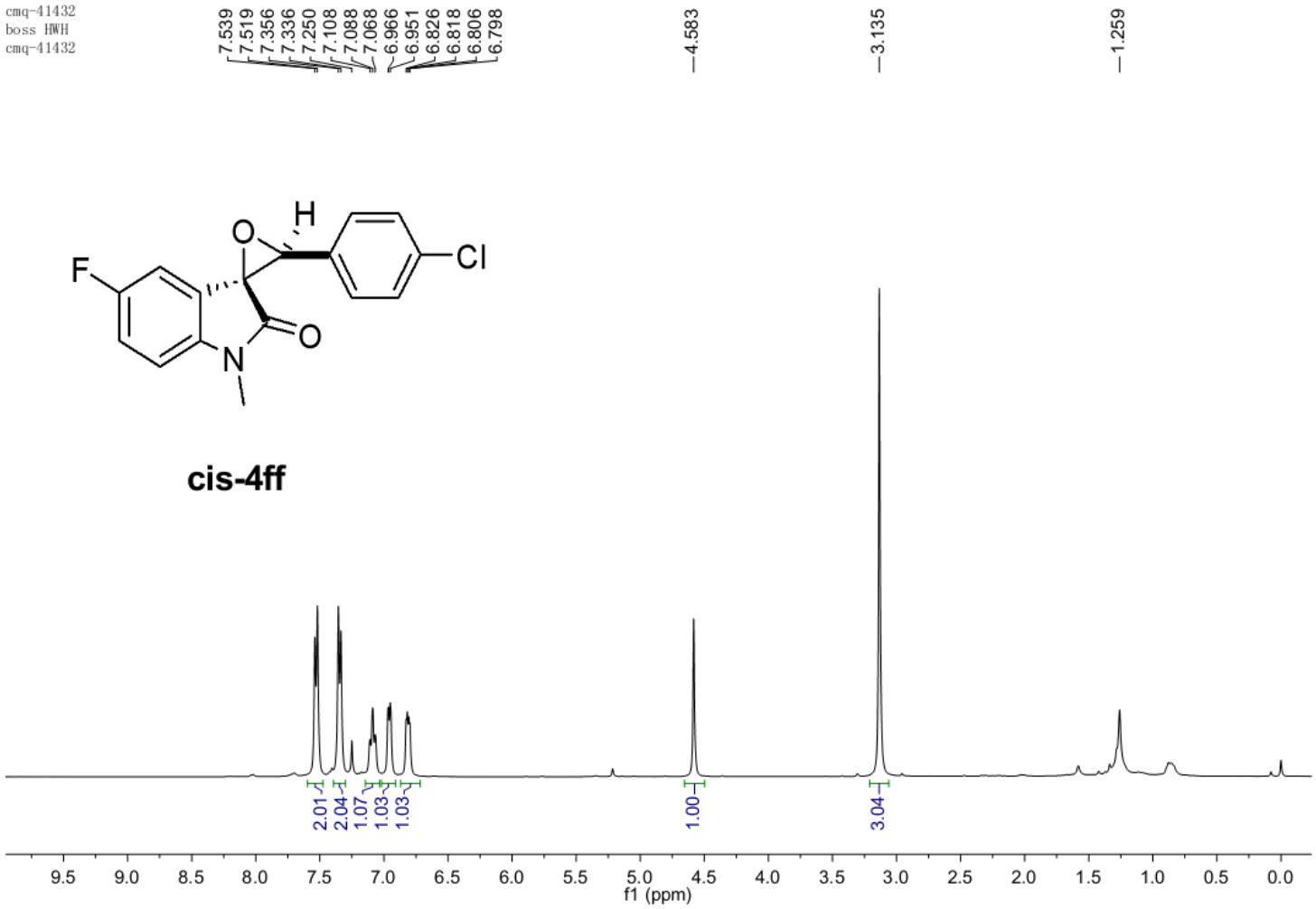

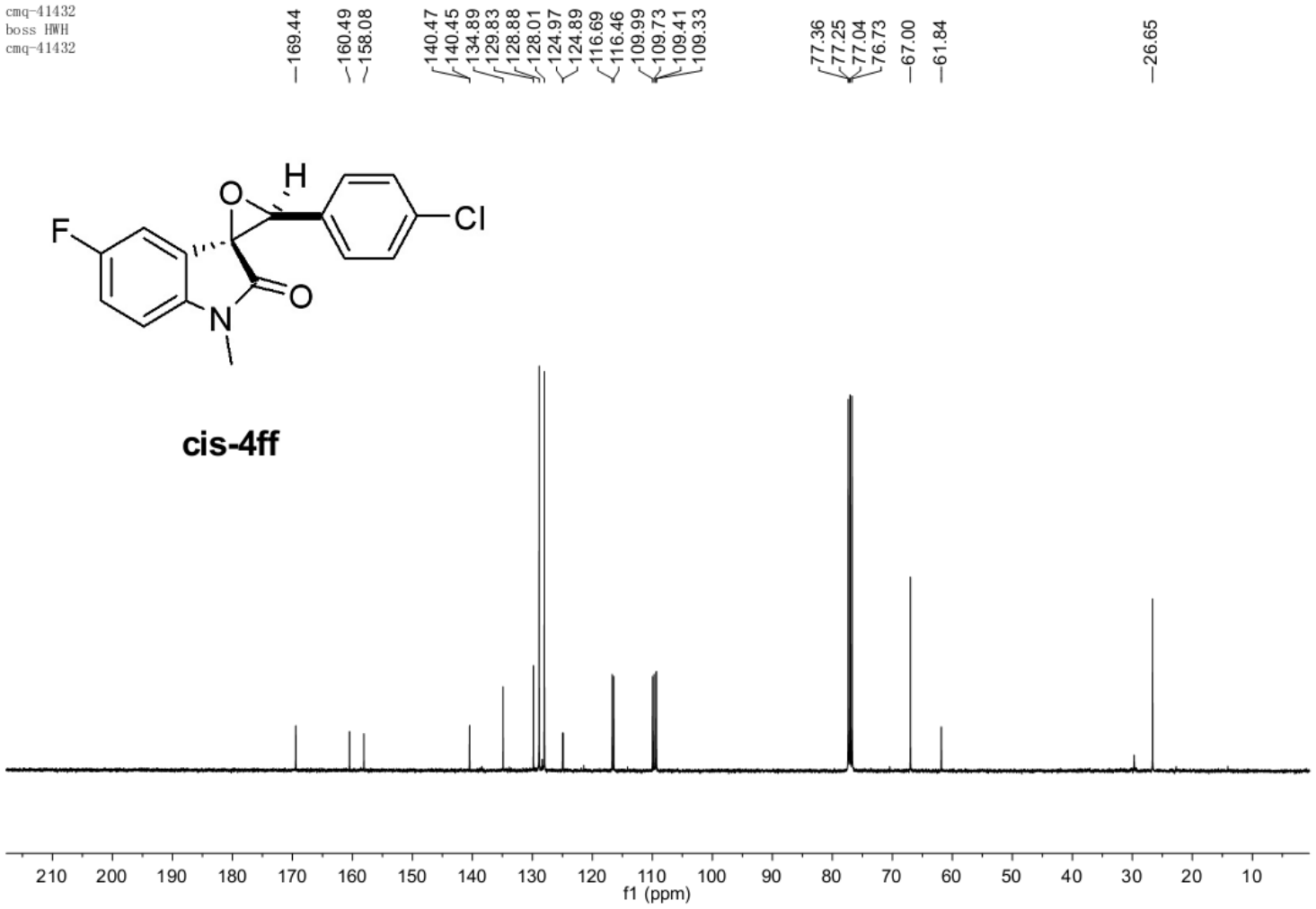

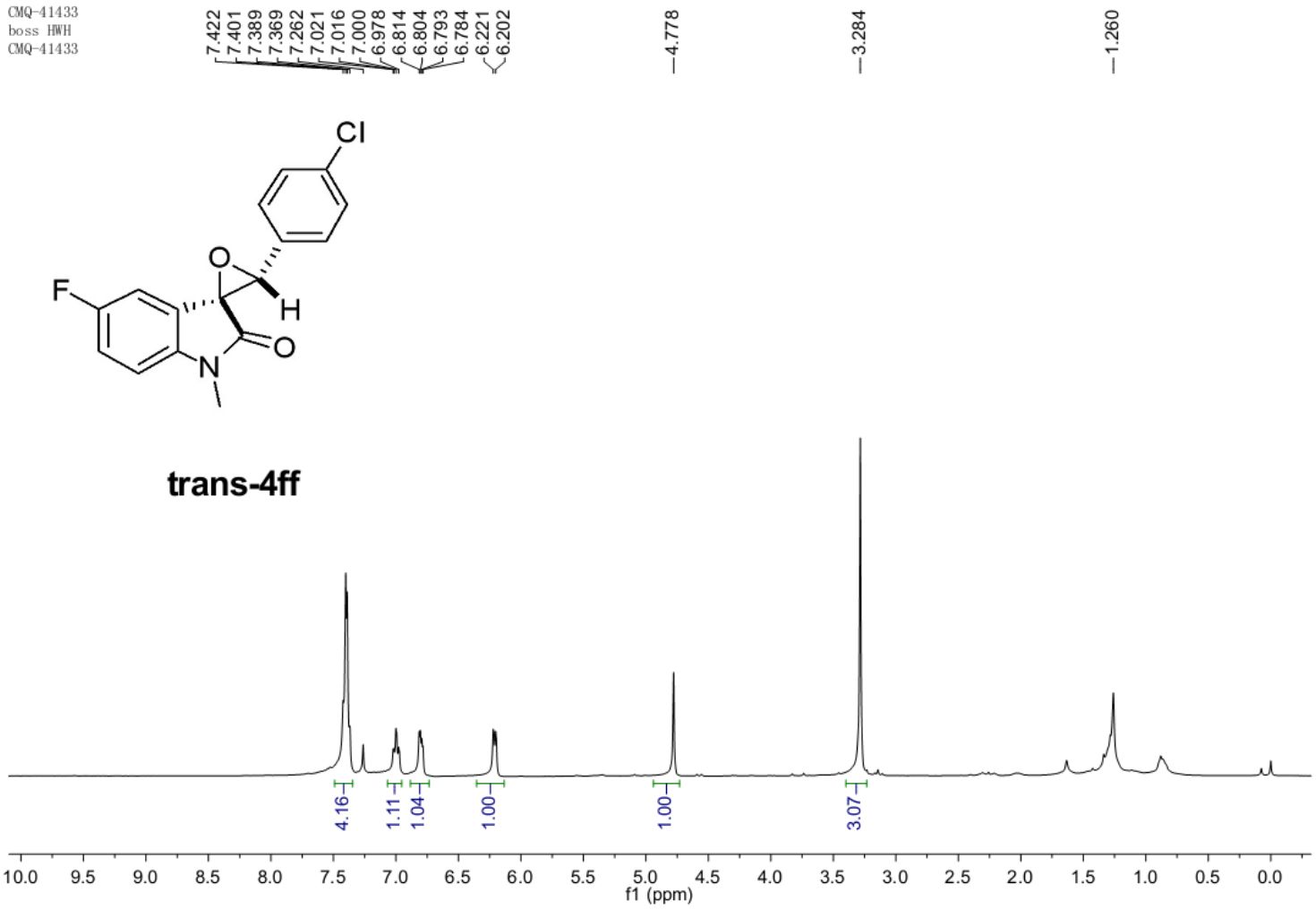

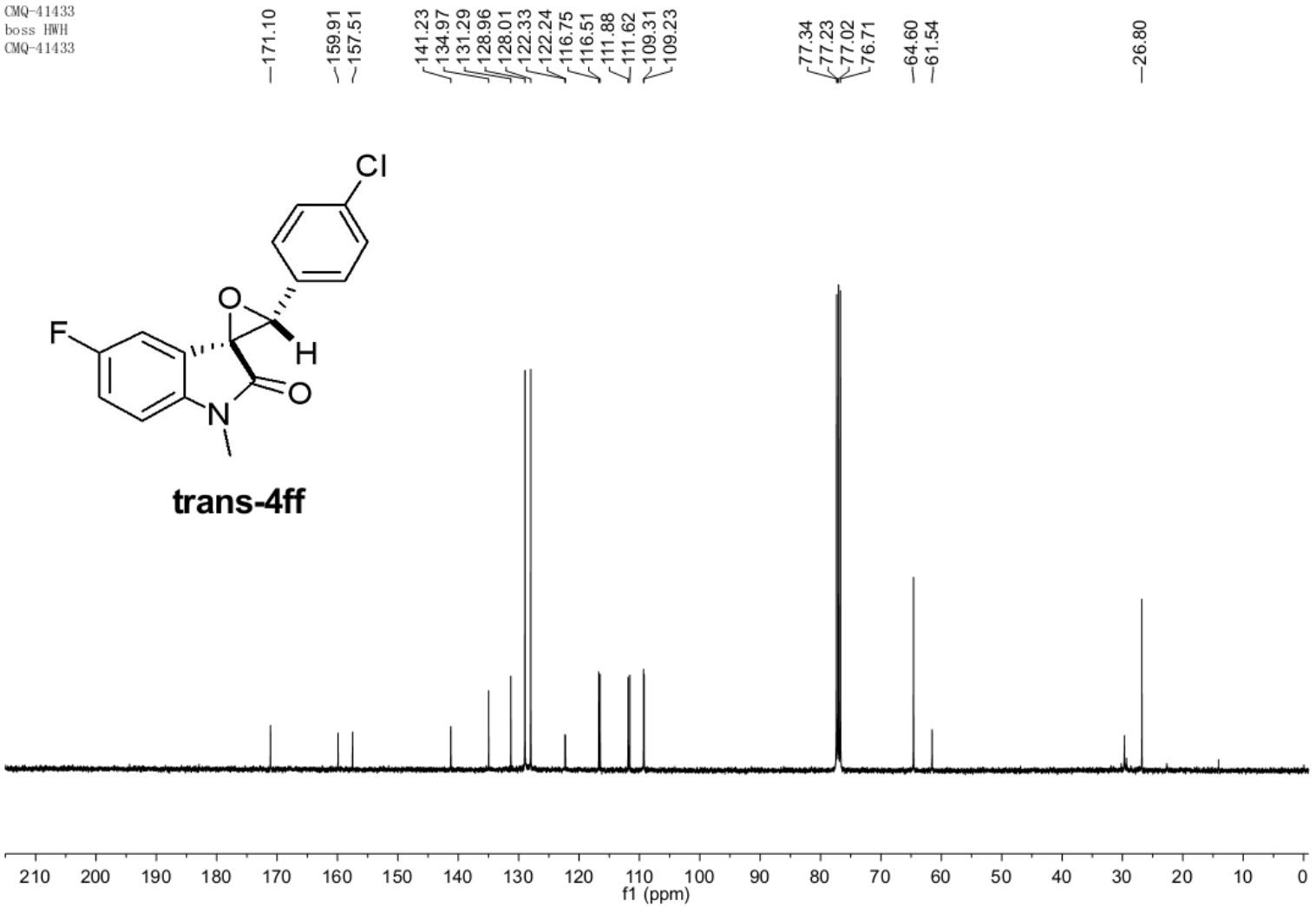

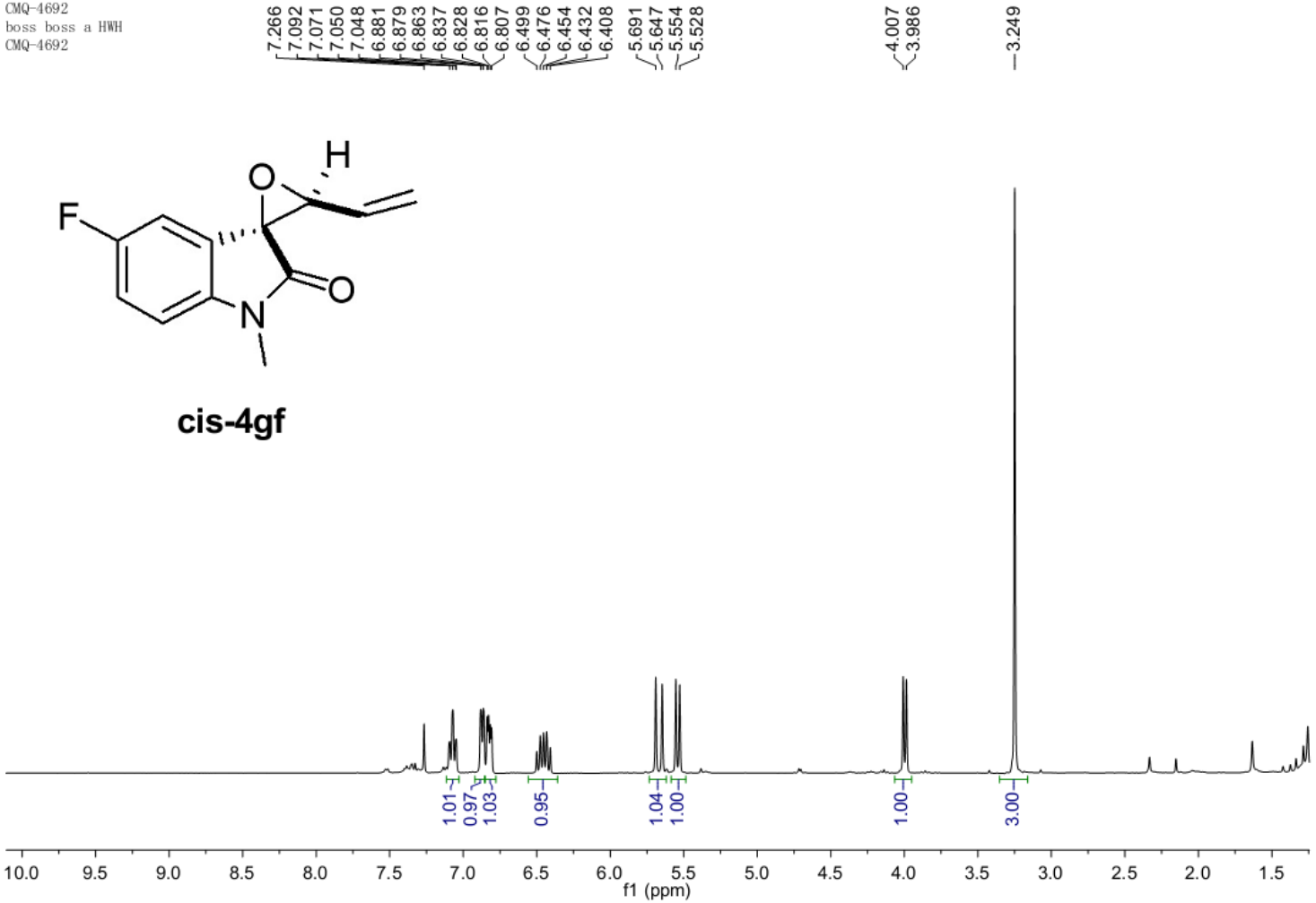

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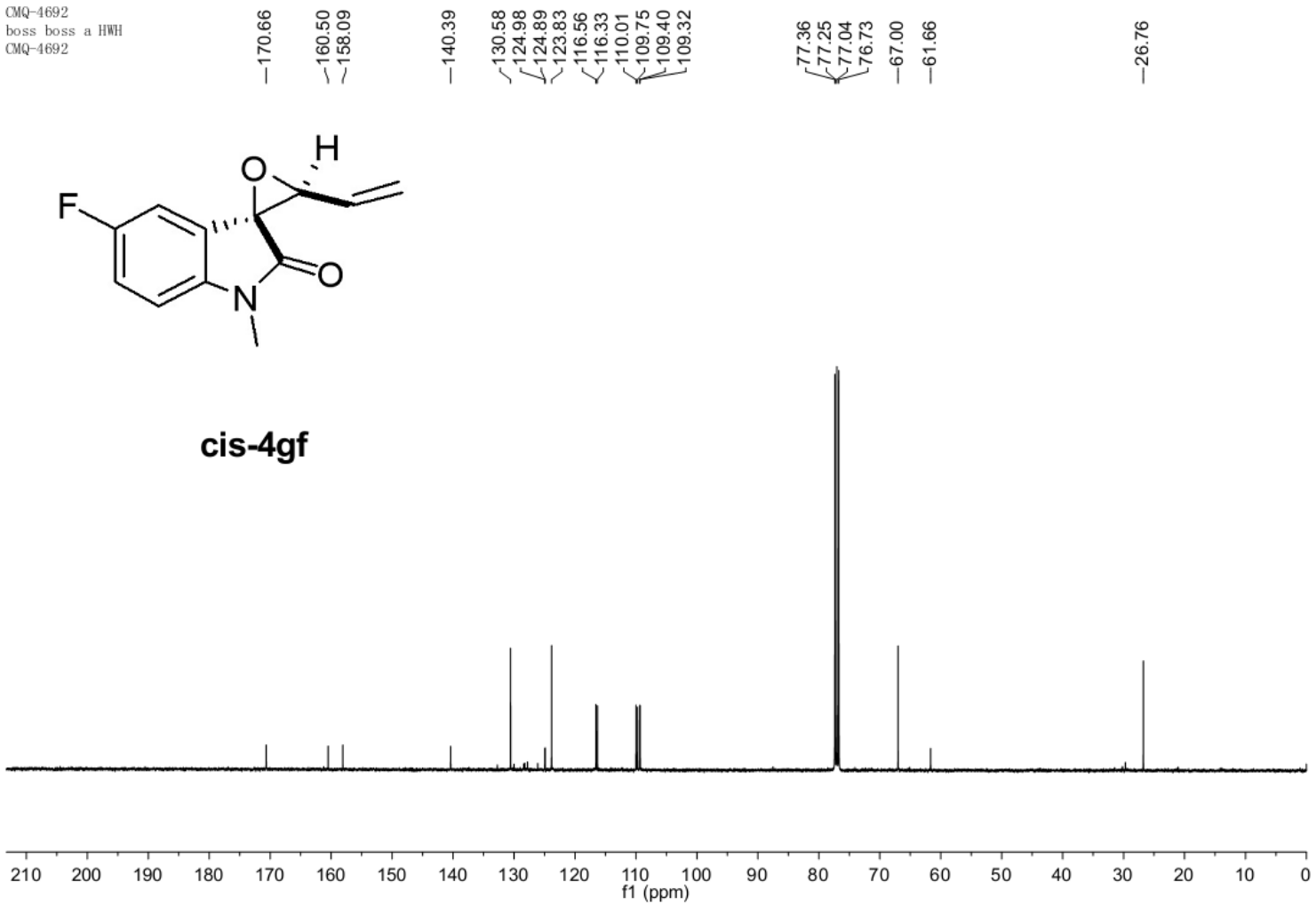

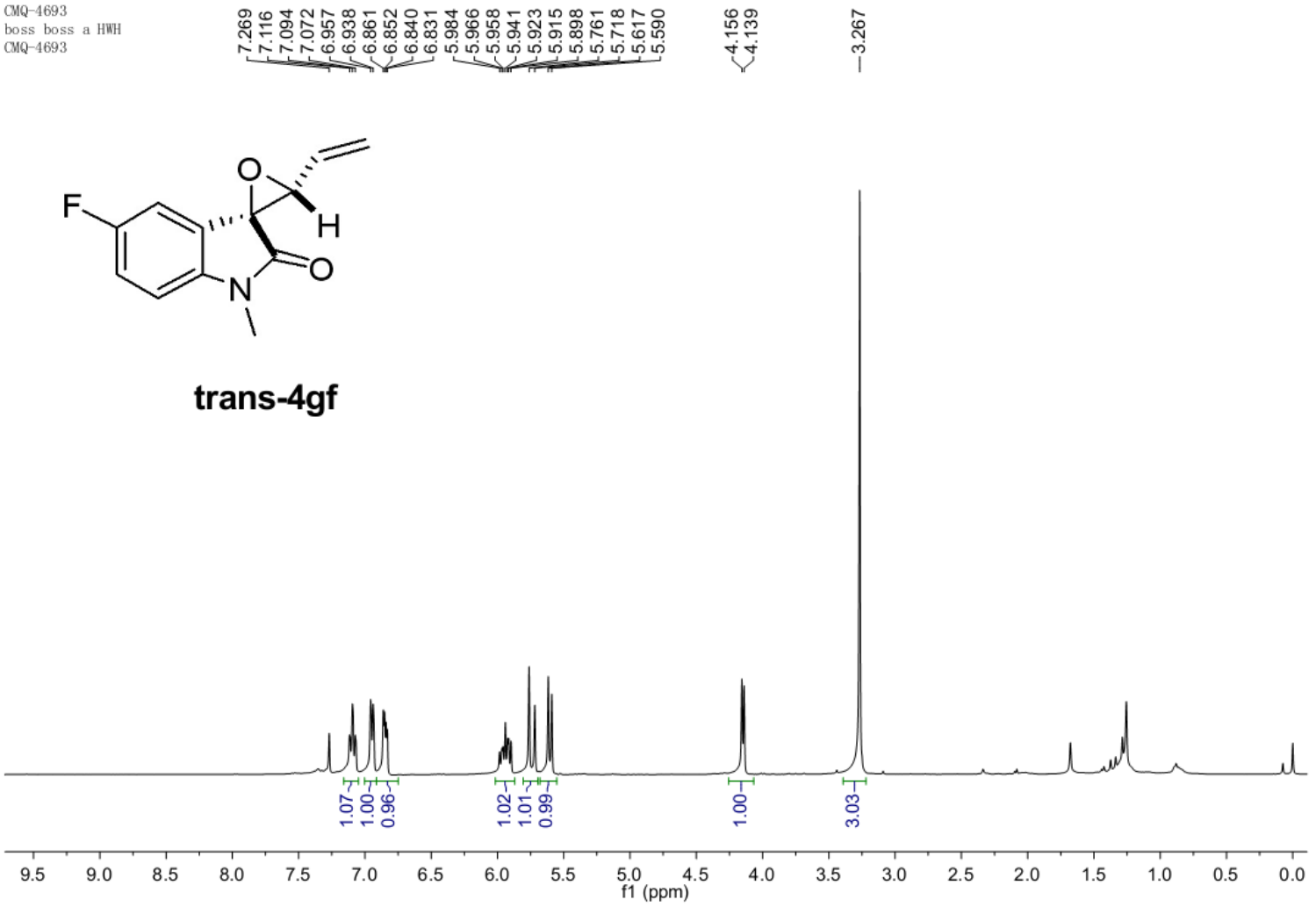

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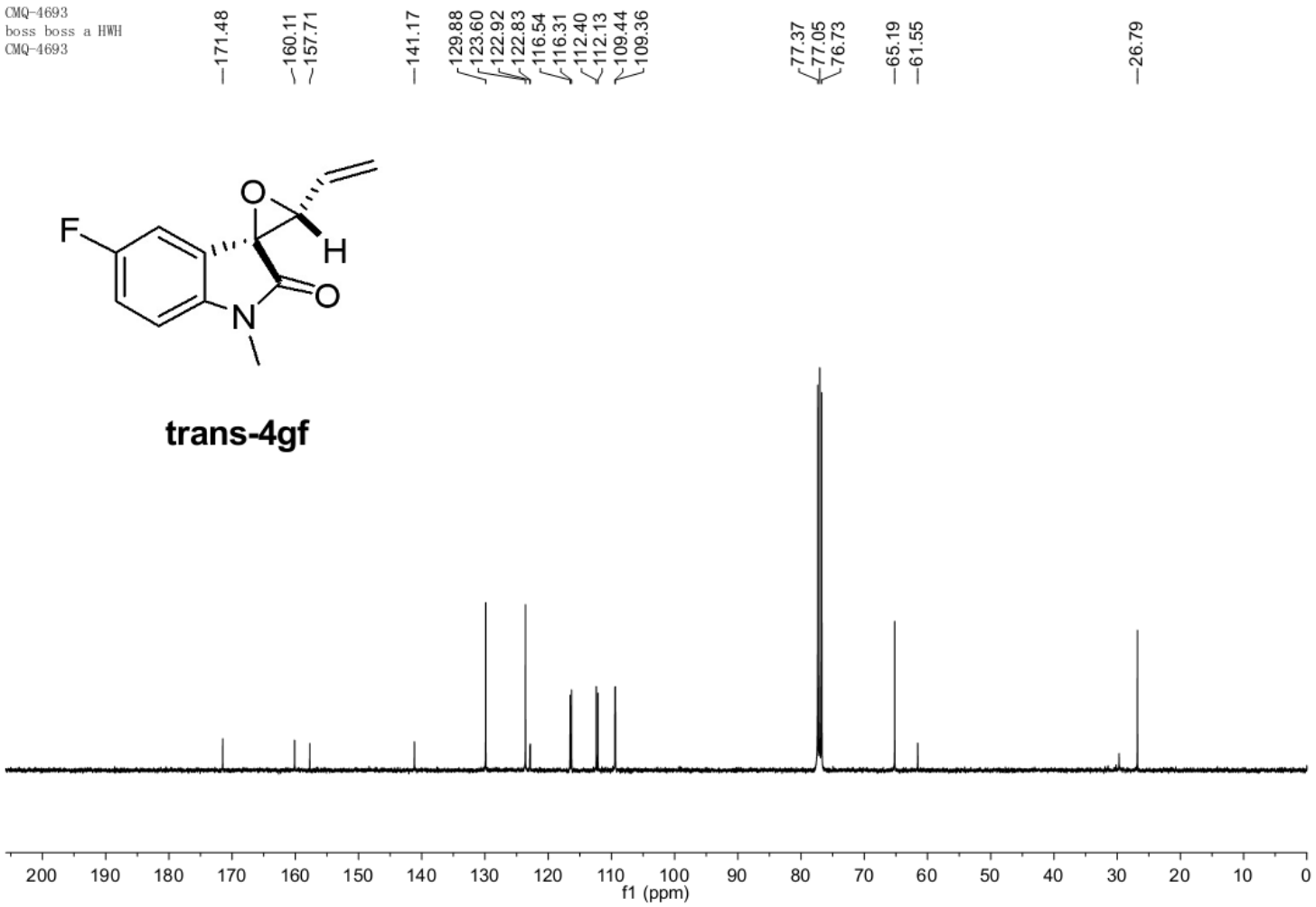

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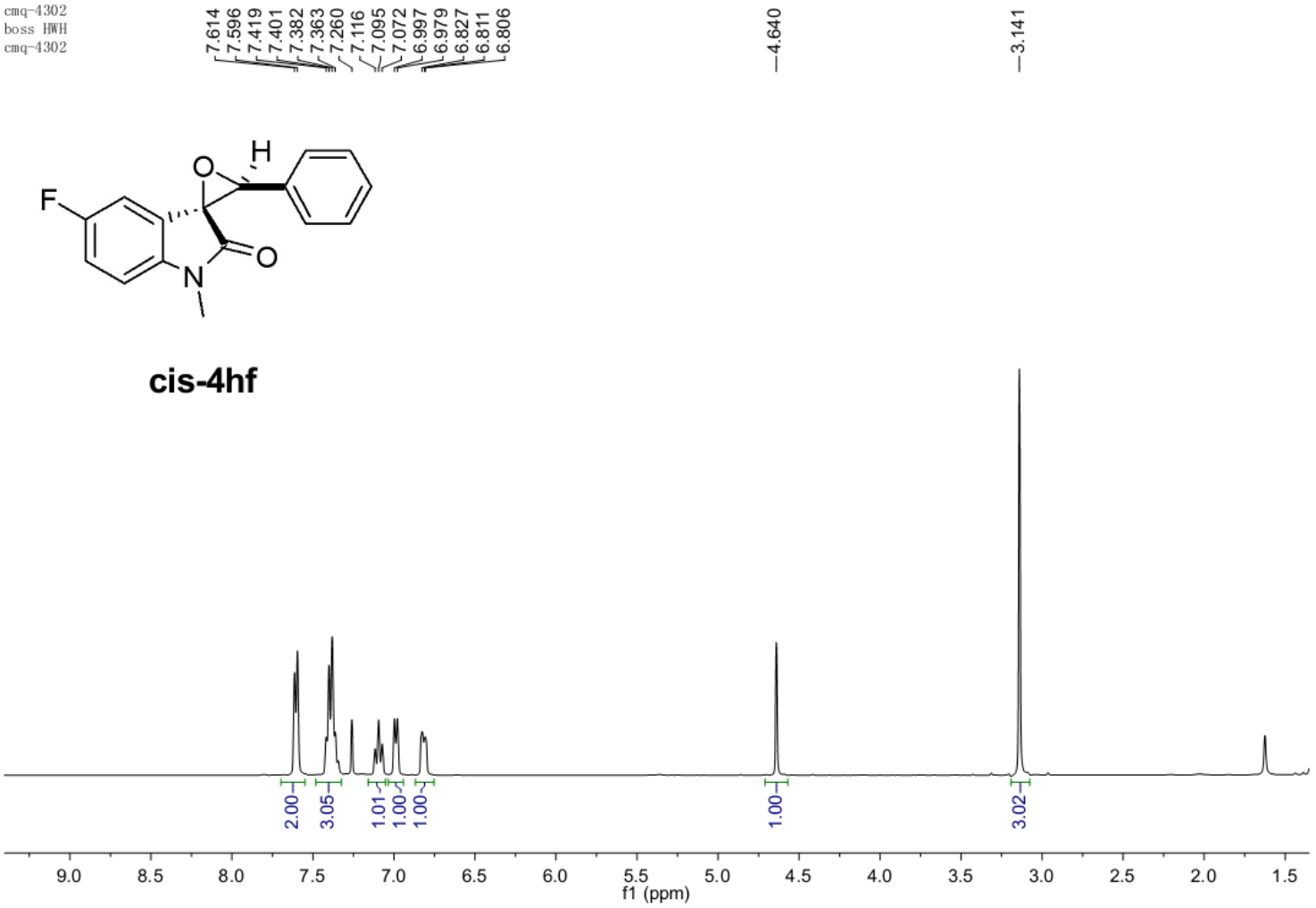
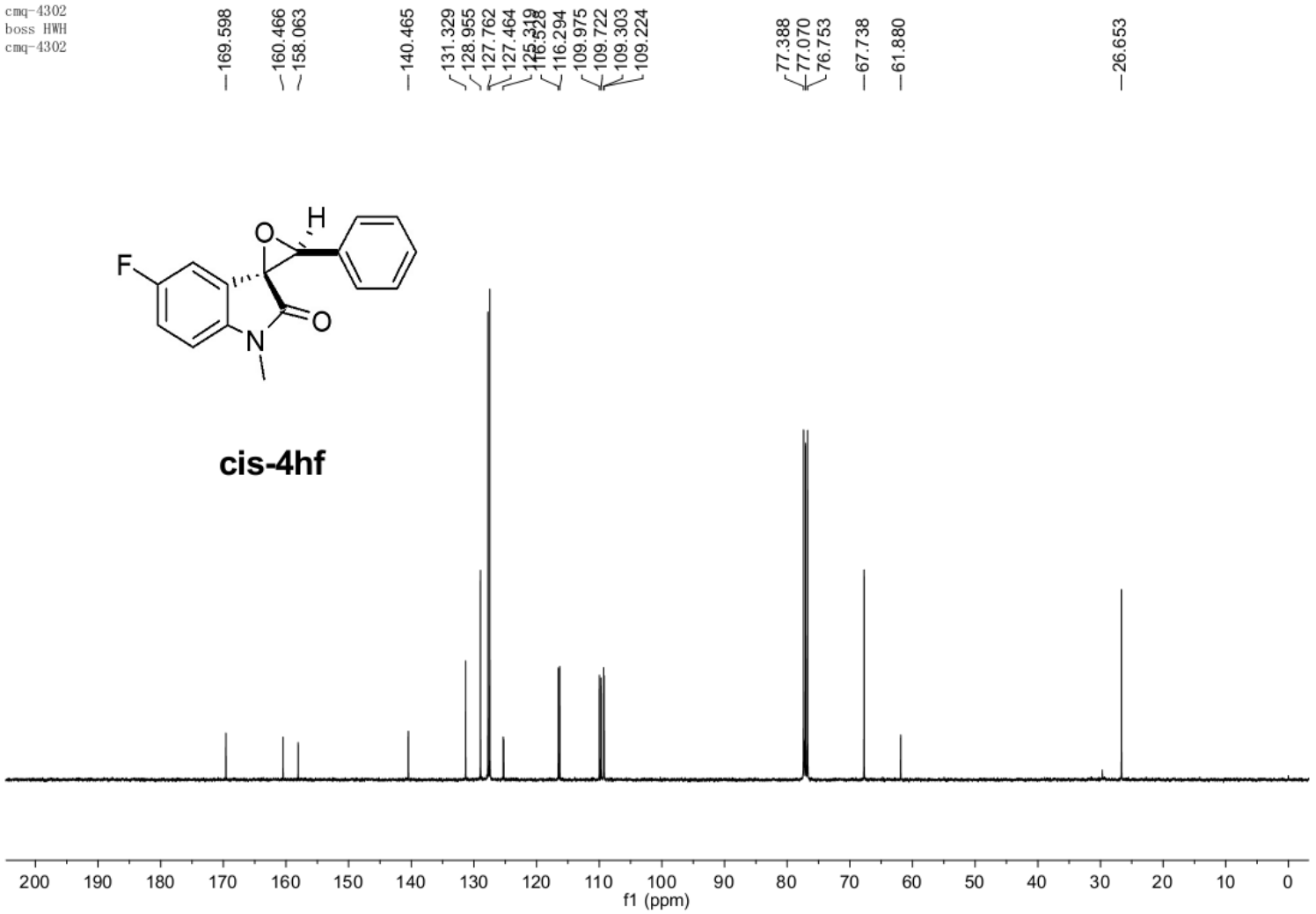
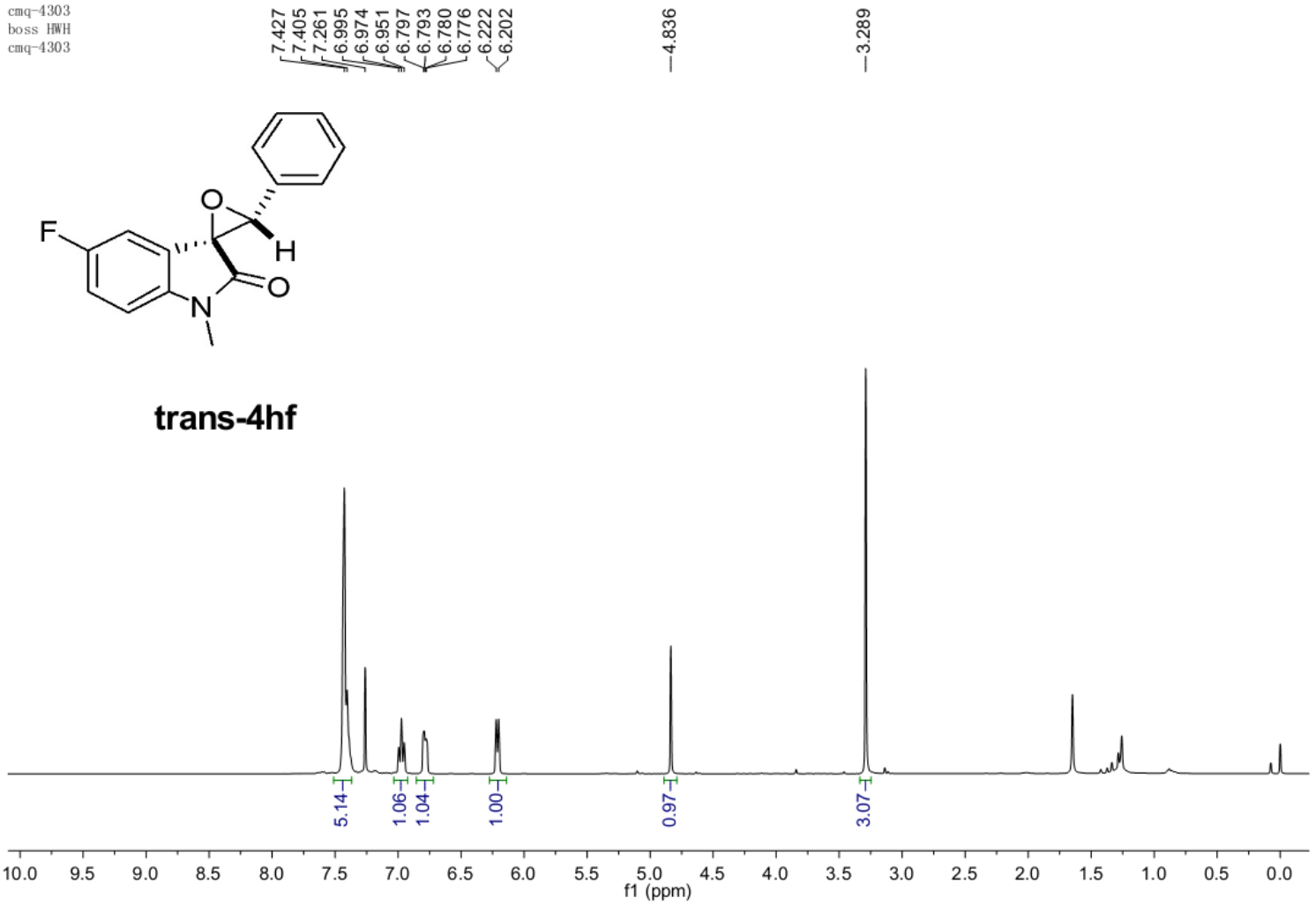
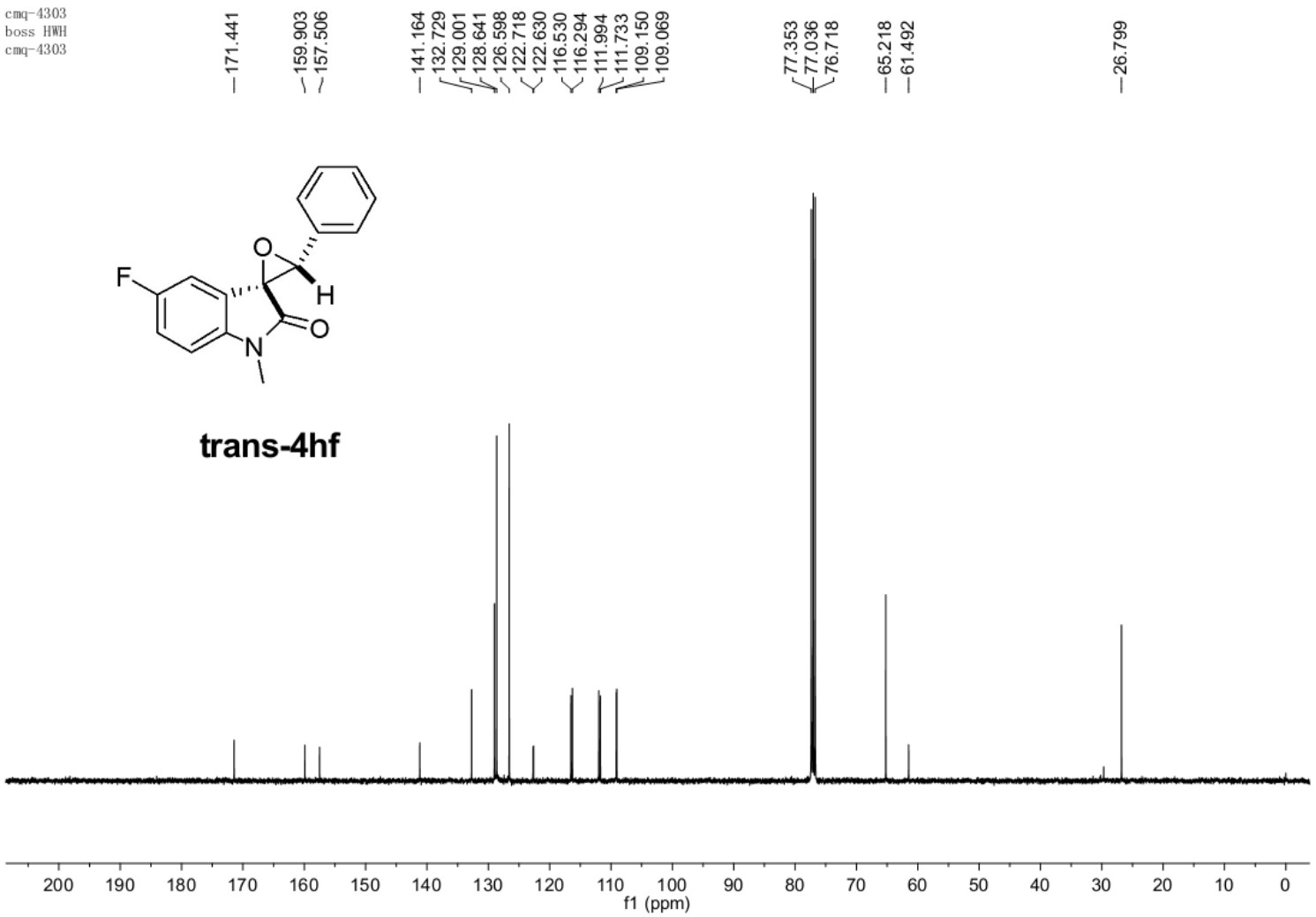
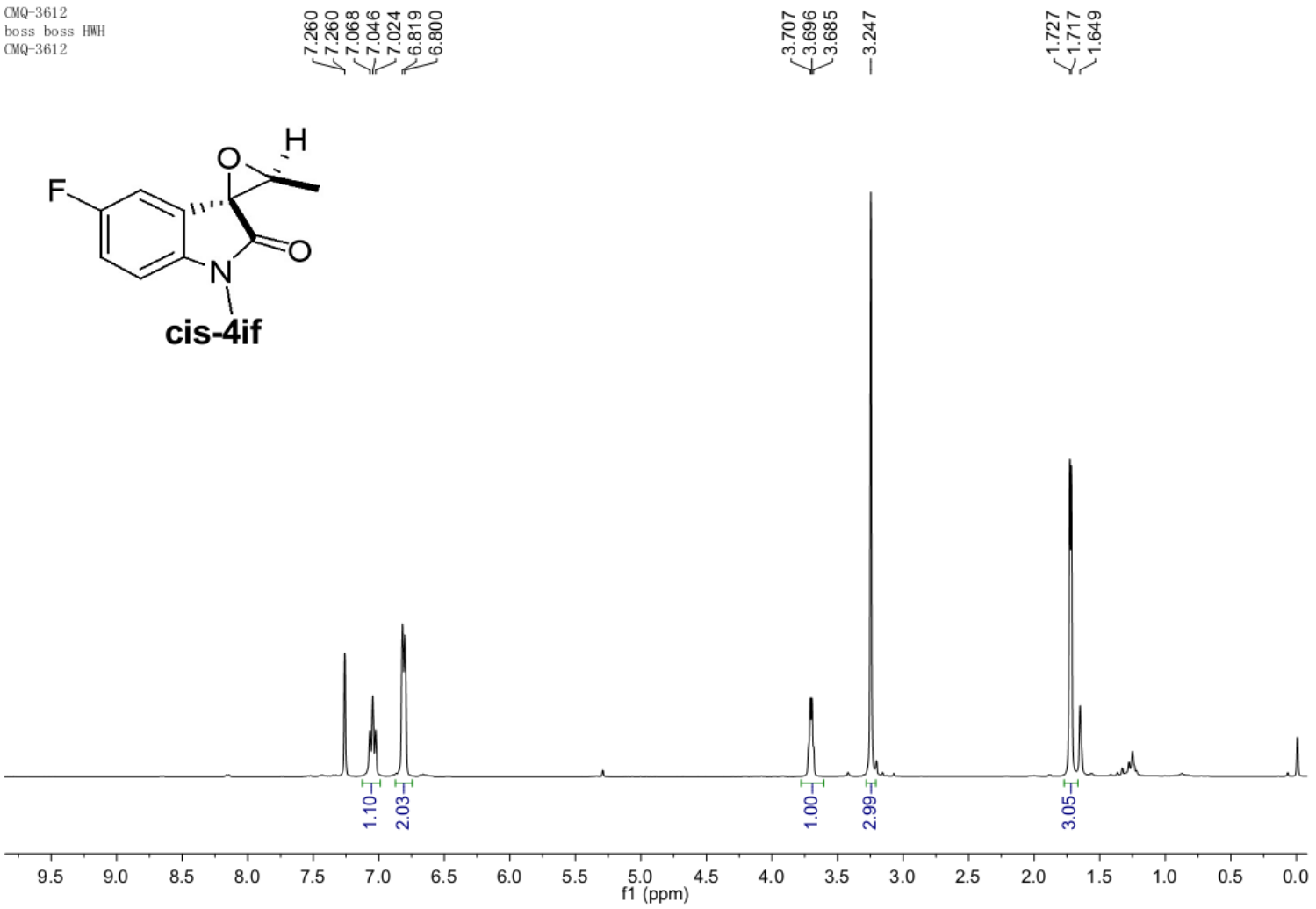
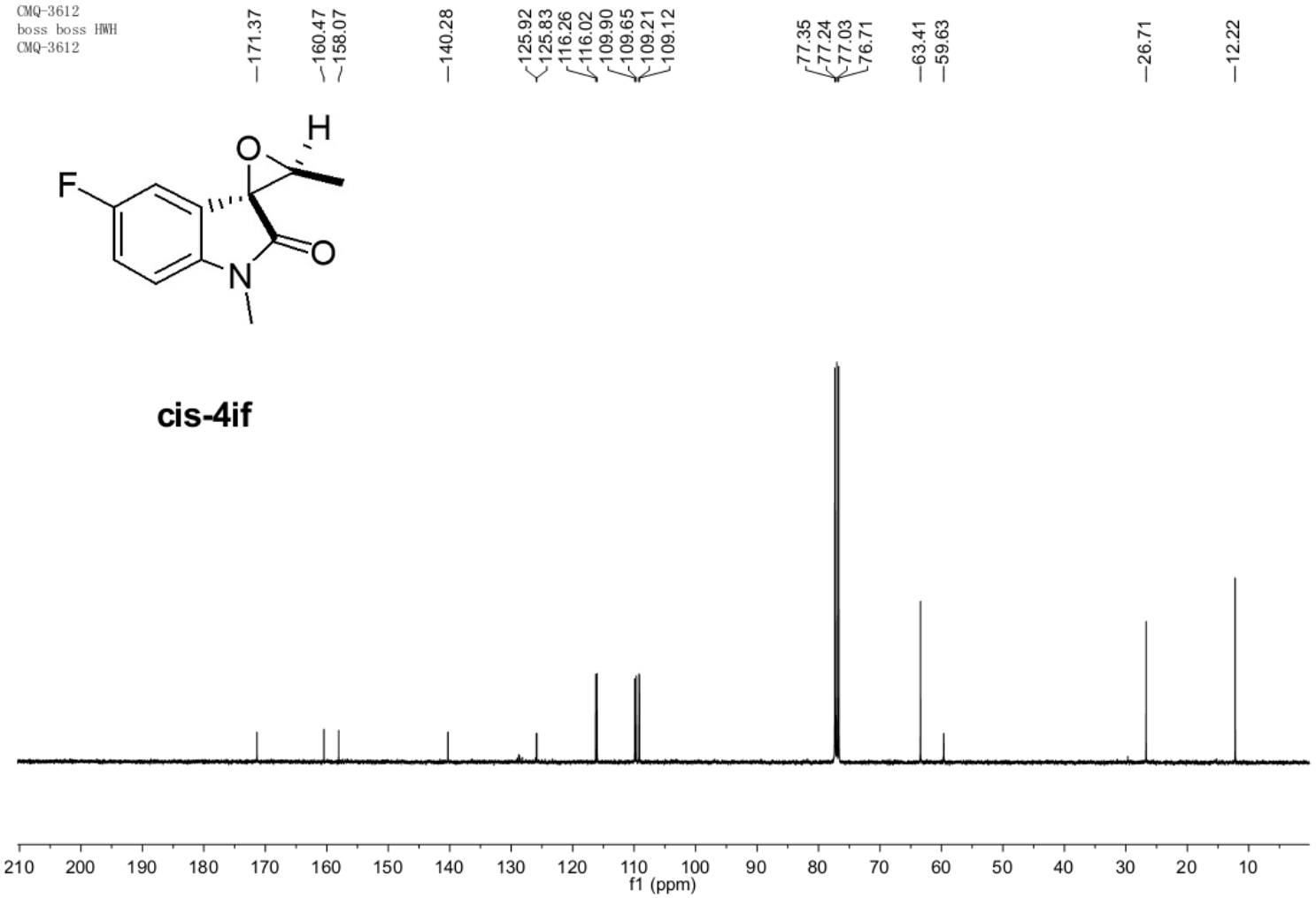


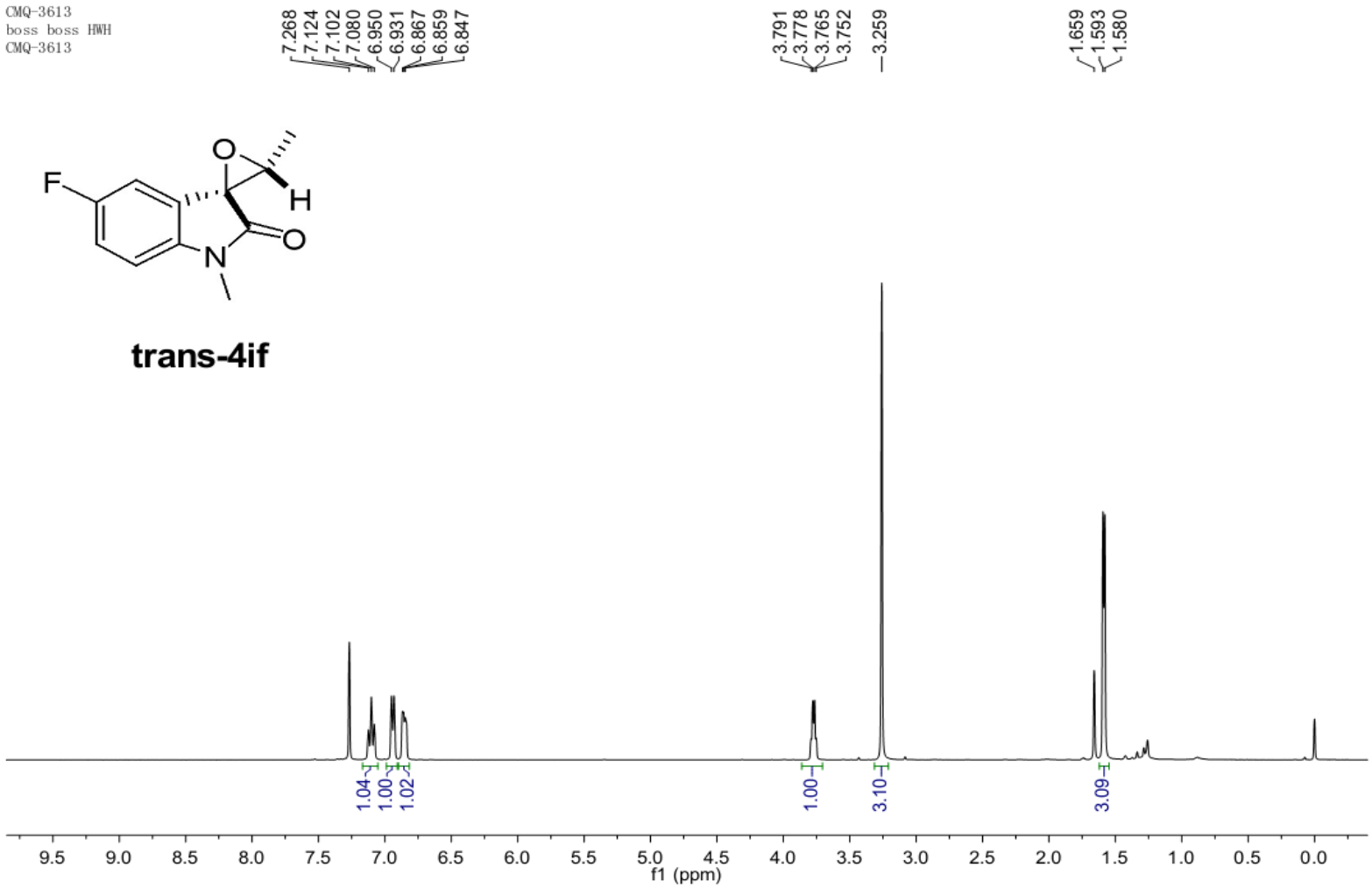




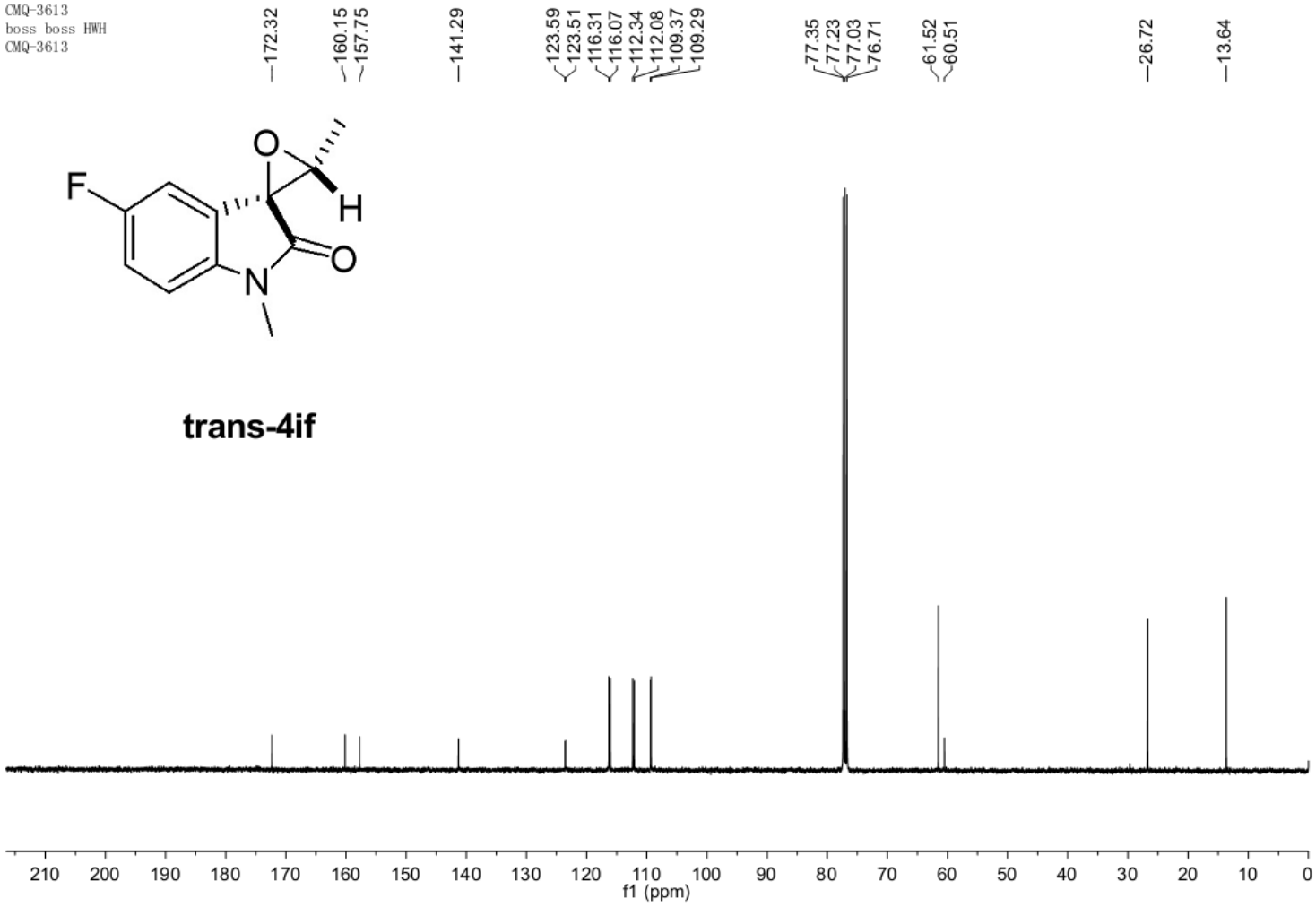








trans-4if



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