Rh(III)-Catalyzed Cascade Annulation Reaction of *N*,*N*-Dimethyl Enaminones with Iodonium Ylides to Give Substituted Isocoumarins.

Mingshuai Zhang,[a] Longkun Chen,[a] Donghan Liu,[a] Zhuoyuan Liu,[a] Jiuzhong Huang,[*b] Xiang Li,[*c]

Fuchao Yu,[*a]

[a]*Faculty of Life Science and Technology, Kunming University of Science and Technology, Kunming, 650504, P. R. China.*
[b]*School of Pharmacy, Key Laboratory of Prevention and Treatment of Cardiovascular and Cerebrovascular Diseases of Ministry of Education, Gannan Medical University, Ganzhou 341000, PR China.*

Supporting Information

Table of Contents

1. General information.

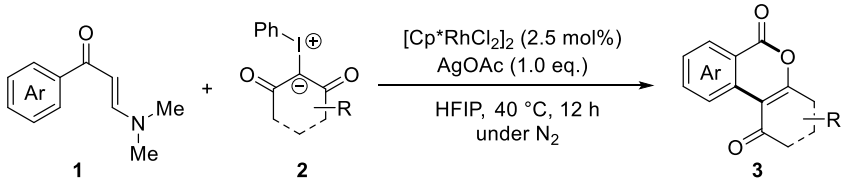
All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a DRX600 (^{1}H: 600 MHz, ^{13}C: 150 MHz), chemical shifts (δ) are expressed in ppm, and J values are given in Hz, and deuterated $CDCl_3$ and DMSO-d_6 were used as solvent. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/MS TOF instrument.

All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

N,*N*-Dimethyl enaminones **1** were prepared according to the literature[1], iodonium ylides **2** were prepared according to the literature[2]. Other reagents were purchased from Energy Chemical and Adamas-beta®.

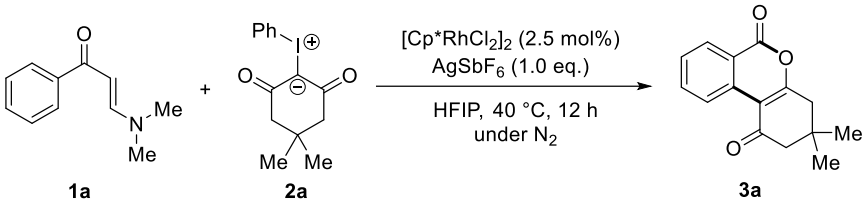
2. General procedure.

2.1 Typical procedure for the synthesis of isocoumarins 3.



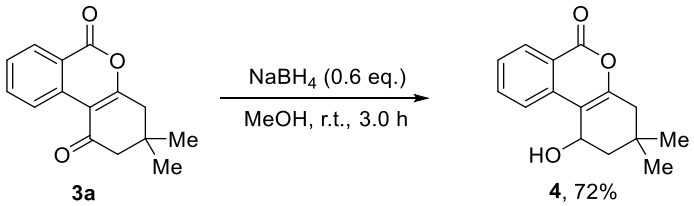
N,*N*-Dimethyl enaminones **1** (0.5 mmol), iodonium ylides **2** (0.75 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgOAc (1.0 eq.) and HFIP (1.0 mL) were charged into a 10 mL Ace Glass pressure tubes under N_2, and the mixture was stirred at 40 °C for 12.0 h until *N*,*N*-dimethyl enaminones were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford isocoumarins **3**.

2.2 Gram-synthesis of isocoumarin 3a.



N,*N*-Dimethyl enaminones **1** (5.0 mmol), iodonium ylides **2** (7.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgOAc (1.0 eq.) and HFIP (10 mL) were charged into a 100 mL Ace Glass pressure tubes under N_2, and the mixture was stirred at 40 °C for 12.0 h until *N*,*N*-dimethyl enaminones were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford isocoumarin **3a** in 90% yield (1.1 g).

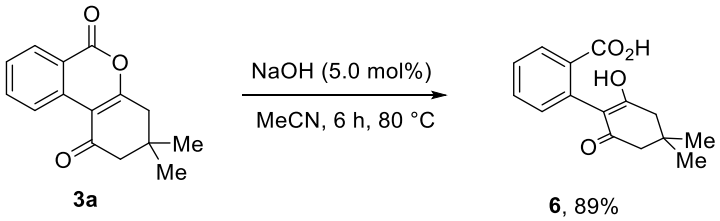
2.3 Derivatization of isocoumarin 3a.



Isocoumarin **3a** (5.0 mmol), $NaBH_4$ (0.3 mmol) and MeOH (2.0 mL) were charged into

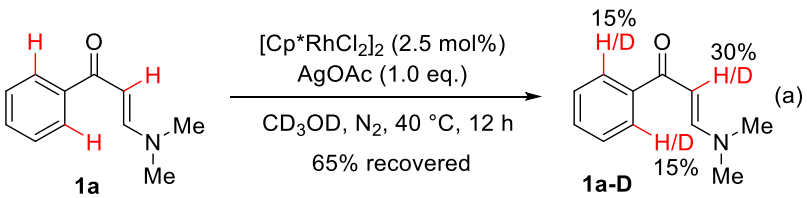
a 10 mL Ace Glass pressure tubes, and the mixture was stirred at room temperature for 3.0 h until isocoumarin were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford the reductive product **4** in 72% yield.

Isocoumarin **3a** (5.0 mmol), benzylamine (0.6 mmol) and DCM (2.0 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 12.0 h until isocoumarin were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford 2-benzylisoquinolin-1(2*H*)-one **5** in 60% yield.



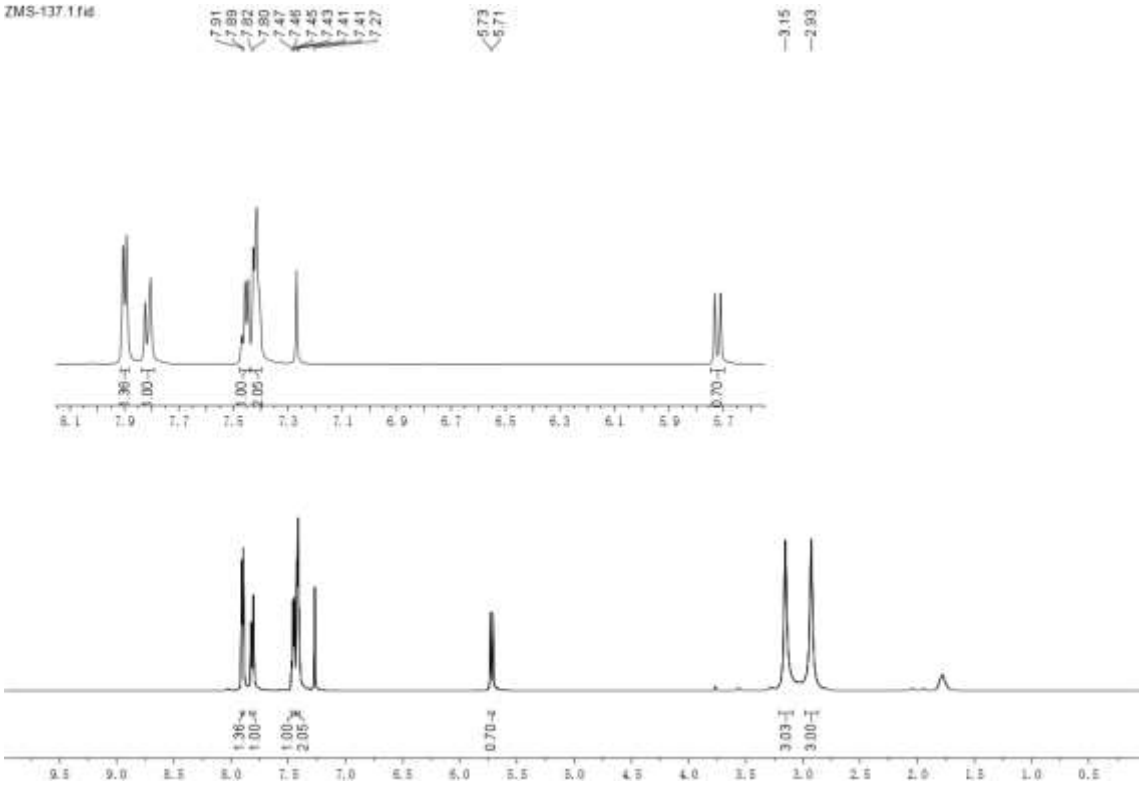
Isocoumarin **3a** (5.0 mmol), NaOH (5.0 mmol%) and MeCN (2.0 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 6.0 h until isocoumarin were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford the carboxylic acid product **6** in 89% yield.

2.4 Isotopic labeling experiments.



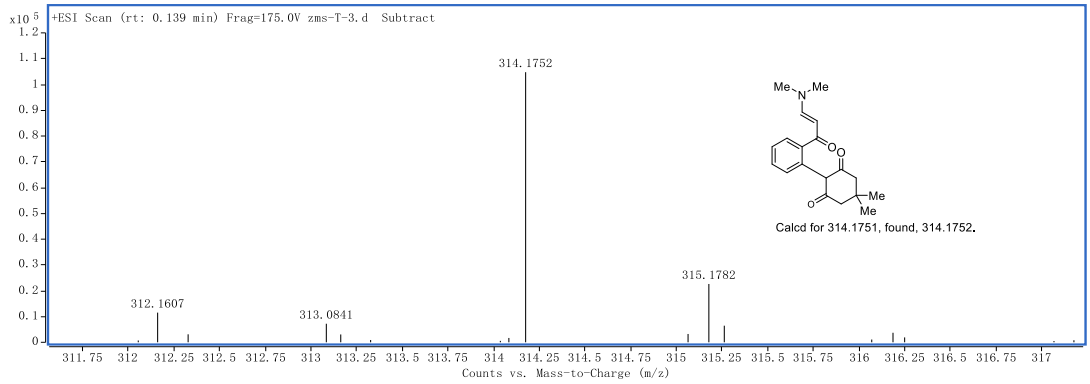
N,*N*-Dimethyl enaminone **1a** (2.0 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgOAc (1.0 eq.) and CD_3OD (3.0 eq.) were charged into a 10 mL Ace Glass pressure tubes under N_2, and

the mixture was stirred at 40 °C for 12.0 h. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford **1a-D** by ^1H NMR identification.



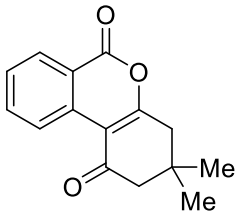
2.4 The mechanistic investigation.

With regard to the standard conditions, the intermediate **E** in the Scheme 4 was successfully detected by LC-HRMS during the crude reaction mixture.



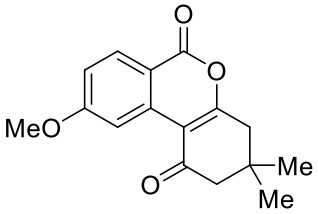
3. Spectroscopic data.

3,3-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3a)



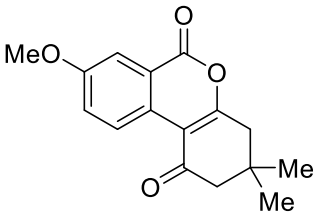
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; Yellow solid: 117mg (96%); mp = 143–144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.04 (d, *J* = 8.3 Hz, 1H, ArH), 8.22 (d, *J* = 7.9 Hz, 1H, ArH), 7.79 (t, *J* = 7.7 Hz, 1H, ArH), 7.52 (t, *J* = 7.6 Hz, 1H, ArH), 2.79 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.1, 168.1, 160.9, 135.8, 134.0, 129.7, 128.5, 125.9, 119.8, 110.7, 53.0, 42.6, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{15}H_{14}O_3$ [$(M+H)^+$], 243.1016, found, 243.1008.

9-Methoxy-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3b)



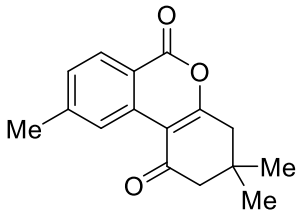
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 8:1, R_f = 0.2; Yellow solid: 130mg (96%); mp = 127–128 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.58 (s, 1H, ArH), 8.18 (d, *J* = 8.8 Hz, 1H, ArH), 7.05–7.03 (m, 1H, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.78 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.4, 169.1, 165.6, 160.6, 136.4, 131.8, 117.2, 112.7, 110.4, 108.0, 55.9, 53.0, 42.7, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{16}H_{16}O_4$ [$(M+H)^+$], 273.1121, found, 273.1122.

8-Methoxy-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3c)



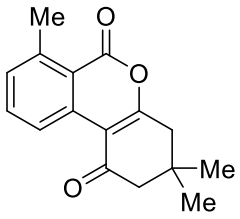
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 128mg (94%); mp = 126–127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.59 (s, 1H, ArH), 8.18 (d, *J* = 8.8 Hz, 1H, ArH), 7.07–7.03 (m, 1H, ArH), 3.95 (s, 3H, $ArOCH_3$), 2.79 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.4, 169.1, 165.6, 160.6, 136.4, 131.8, 117.3, 112.7, 110.5, 108.0, 55.9, 53.0, 42.8, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{16}H_{16}O_4$ [$(M+H)^+$], 273.1121, found, 273.1121.

3,3,9-Trimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3d)



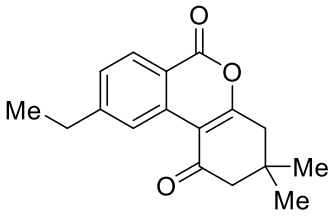
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 118mg (93%); mp = 135–136 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.85 (s, 1H, ArH), 8.16 (d, J = 8.1 Hz, 1H, ArH), 7.34 (d, J = 7.9 Hz, 1H, ArH), 2.78 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 2.50 (s, 3H, $ArCH_3$), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.3, 168.2, 161.0, 147.2, 134.0, 129.8, 129.7, 126.0, 117.4, 110.7, 53.0, 42.7, 32.1, 28.3, 22.7, 22.7; HRMS (TOF ES+): m/z calcd for $C_{16}H_{16}O_3$ [$(M+H)^+$], 257.1172, found, 257.1176.

3,3,7-Trimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3e)



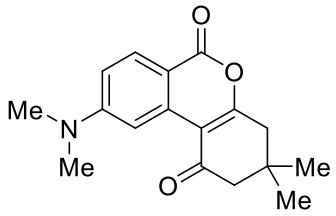
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 75mg (58%); mp = 111–112 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.96 (d, J = 8.4 Hz, 1H, ArH), 7.64 (t, J = 7.9 Hz, 1H, ArH), 7.33 (d, J = 7.5 Hz, 1H, ArH), 2.80 (s, 3H, $ArCH_3$), 2.77 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.1, 168.1, 160.0, 143.6, 135.5, 135.0, 131.6, 123.8, 118.3, 110.7, 53.2, 42.6, 32.0, 28.3, 28.3, 24.0; HRMS (TOF ES+): m/z calcd for $C_{16}H_{16}O_3$ [$(M+H)^+$], 257.1172, found, 257.1176.

9-Ethyl-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3f)



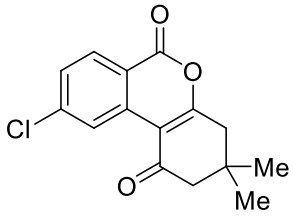
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; Yellow solid: 129mg (96%); mp = 108–109 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.89 (s, 1H, ArH), 8.20 (d, J = 7.6 Hz, 1H, ArH), 7.37 (d, J = 8.1 Hz, 1H, ArH), 2.81 (d, J = 7.3 Hz, 2H, CH_2), 2.79 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 1.30 (t, J = 6.9 Hz, 3H, CH_3), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.3, 168.2, 161.0, 153.3, 134.1, 129.9, 128.7, 125.0, 117.5, 110.7, 53.1, 42.7, 32.1, 29.9, 28.3, 15.4, 15.4; HRMS (TOF ES+): m/z calcd for $C_{17}H_{18}O_3$ [$(M+H)^+$], 271.1329, found, 271.1332.

9-(Dimethylamino)-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3g)



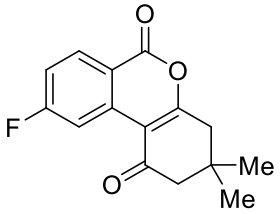
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 8:1, R_f = 0.2; Yellow solid: 106mg (74%); mp = 168–169 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.28 (s, 1H, ArH), 8.08 (d, J = 9.0 Hz, 1H, ArH), 6.80 (dd, J = 9.0, 2.2 Hz, 1H, ArH), 3.13 (s, 6H, CH_3), 2.75 (s, 2H, CH_2), 2.49 (s, 2H, CH_2), 1.15 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.8, 169.0, 161.1, 155.0, 135.4, 131.6, 112.4, 110.6, 107.1, 105.9, 53.2, 42.9, 40.3, 40.3, 32.0, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{17}H_{19}NO_3$ [$(M+H)^+$], 286.1438, found, 286.1440.

9-Chloro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3h)



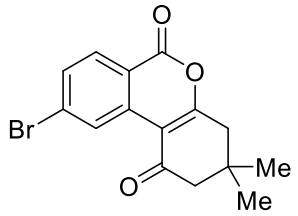
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 122mg (88%); mp = 159–160 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.10 (s, 1H, ArH), 8.20 (d, J = 8.5 Hz, 1H, ArH), 7.48 (d, J = 8.4 Hz, 1H, ArH), 2.80 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.7, 169.2, 160.1, 142.9, 135.2, 131.2, 129.1, 125.9, 118.2, 109.9, 52.8, 42.7, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{15}H_{13}ClO_3$ [$(M+H)^+$], 277.0626, found, 277.0628.

9-Fluoro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3i)



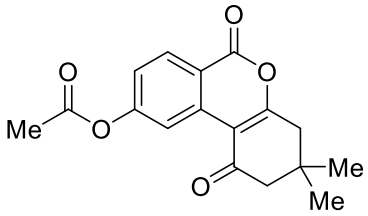
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.2; Yellow solid: 120mg (92%); mp = 119–120 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.79 (d, J = 10.9 Hz, 1H, ArH), 8.30 (t, J = 6 Hz, 1H, ArH), 7.22 (t, J = 7.5 Hz, 1H, ArH), 2.80 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 1.18 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.8, 169.3, 167.4 (C–F, J = 256.1 Hz), 159.9, 136.9 (C–F, J = 12.2 Hz), 132.8 (C–F, J = 10.5 Hz), 116.8 (C–F, J = 23.6 Hz), 116.3 (C–F, J = 2.3 Hz), 112.6 (C–F, J = 26.1 Hz), 110.1 (C–F, J = 3 Hz), 52.8, 42.6, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{15}H_{13}FO_3$ [$(M+H)^+$], 261.0921, found, 261.0924.

9-Bromo-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3j)



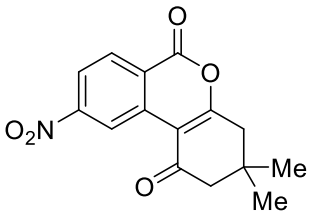
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 148mg (92%); mp = 149–150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.28 (s, 1H, ArH), 8.11 (d, J = 8.4 Hz, 1H, ArH), 7.67–7.63 (m, 1H, ArH), 2.80 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.7, 169.2, 160.3, 135.2, 132.0, 131.9, 131.1, 128.9, 118.5, 109.8, 52.8, 42.7, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{15}H_{13}BrO_3$ [$(M+H)^+$], 321.0121, found, 321.0123.

3,3-Dimethyl-1,6-dioxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-9-yl acetate (3k)



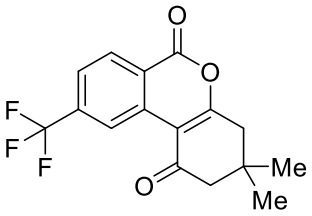
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 4:1, R_f = 0.2; Yellow solid: 112mg (74%); mp = 229–230 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.58 (s, 1H, ArH), 8.17 (d, J = 8.8 Hz, 1H, ArH), 7.04 (dd, J = 8.9, 2.6 Hz, 1H, ArH), 3.94 (s, 3H, CH_3), 2.78 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.4, 169.1, 165.6, 160.6, 136.4, 131.8, 117.2, 117.2, 112.7, 110.4, 108.0, 55.9, 53.0, 42.7, 32.1, 28.2, 28.2; HRMS (TOF ES+): m/z calcd for $C_{17}H_{16}O_5$ [$(M+H)^+$], 301.1071, found, 301.1075.

3,3-Dimethyl-9-nitro-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3l)



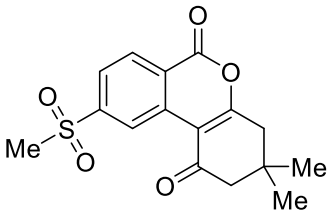
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 125mg (87%); mp = 170–171 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.94 (s, 1H, ArH), 8.45 (d, J = 8.7 Hz, 1H, ArH), 8.30–8.28 (m, 1H, ArH), 2.85 (s, 2H, CH_2), 2.57 (s, 2H, CH_2), 1.20 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.3, 169.8, 159.2, 152.3, 135.3, 131.4, 123.9, 122.6, 121.6, 109.8, 52.6, 42.6, 32.2, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{15}H_{13}NO_5$ [$(M+H)^+$], 288.0866, found, 288.0870.

3,3-Dimethyl-9-(trifluoromethyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione(3m)



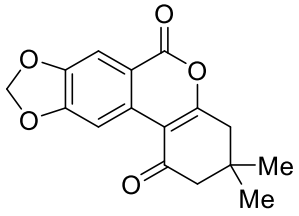
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; Yellow solid: 125mg (84%); mp = 168–169 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.42 (s, 1H, ArH), 8.40 (d, *J* = 8.3 Hz, 1H, ArH), 7.76 (d, *J* = 8.2 Hz, 1H, ArH), 2.83 (s, 2H CH_2), 2.55 (s, 2H, CH_2), 1.19 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.7, 169.2, 159.8, 137.0 (*J* = 32.7 Hz), 134.5, 130.5, 124.9 (*J* = 3,4 Hz), 123.5 (*J* = 3.9 Hz), 122.6, 122.3, 110.0, 52.8, 42.6, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{16}H_{13}F_3O_3$ [$(M+H)^+$], 311.0890, found, 311.0888.

3,3-Dimethyl-9-(methylsulfonyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3n)



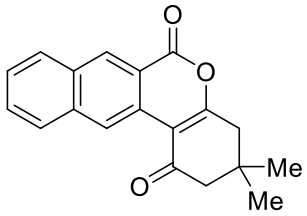
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 4:1, R_f = 0.2; White solid: 147 mg (91%); mp = 244–245 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.69 (s, 1H, ArH), 8.47 (d, *J* = 8.3 Hz, 1H, ArH), 8.09–8.06 (m, 1H, ArH), 3.16 (s, 3H, Me), 2.85 (s, 2H, CH_2), 2.57 (s, 2H, CH_2), 1.20 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.3, 169.5, 159.3, 146.8, 134.8, 131.0, 126.1, 125.5, 123.3, 109.8, 52.5, 44.0, 42.5, 32.1, 28.1, 28.1; HRMS (TOF ES+): m/z calcd for $C_{16}H_{16}O_5S$ [$(M+H)^+$], 321.0791, found, 321.0799.

3,3-Dimethyl-3,4-dihydro-1*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]chromene-1,6(2*H*)-dione (3o)



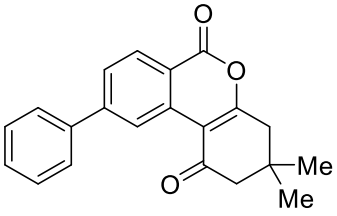
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.2; Yellow solid: 109mg (76%); mp = 164–165 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.7 Hz, 1H, ArH), 7.18 (d, *J* = 8.7 Hz, 1H, ArH), 6.18 (s, 2H, , CH_2), 3.13 (s, 2H, CH_2), 2.65 (s, 2H, CH_2), 1.19 (s, 6H, Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.9, 168.6, 151.4, 144.4, 142.4, 121.5, 120.4, 120.1, 119.2, 110.2, 101.9, 52.4, 39.5, 34.0, 29.0, 29.0; HRMS (TOF ES+): m/z calcd for $C_{16}H_{14}O_5$ [$(M+H)^+$], 287.0914, found, 287.0916.

3,3-Dimethyl-3,4-dihydro-1*H*-naphtho[2,3-*c*]chromene-1,6(2*H*)-dione (3p)



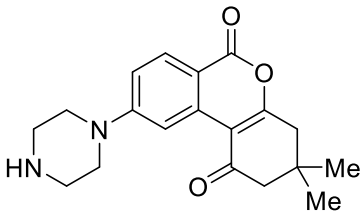
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 8:1, R_f = 0.2; Yellow solid: 124mg (85%); mp = 188–189 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.53 (s, 1H, ArH), 8.91 (s, 1H, ArH), 8.01 (dd, *J* = 17.0, 8.3 Hz, 2H, ArH), 7.66 (t, *J* = 7.5 Hz, 1H, ArH), 7.58 (t, *J* = 7.5 Hz, 1H, ArH), 2.82 (s, 2H, CH_2), 2.57 (s, 2H, CH_2), 1.21 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.5, 167.0, 161.2, 137.0, 132.2, 131.9, 129.7, 129.4, 129.2, 127.9, 127.4, 125.5, 118.1, 110.7, 53.0, 42.7, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{19}H_{16}O_3$ [$(M+H)^+$], 293.1172, found, 293.1174.

3,3-Dimethyl-9-phenyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3q)



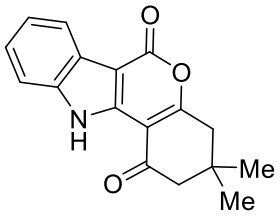
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; Yellow solid: 144mg (91%); mp = 153–154 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.34 (s, 1H, ArH), 8.34 (d, *J* = 8.3 Hz, 1H, ArH), 7.77 (d, *J* = 9.6 Hz, 1H, ArH), 7.72 (d, *J* = 7.3 Hz, 2H, ArH), 7.50 (t, *J* = 7.5 Hz, 2H, ArH), 7.43 (t, *J* = 7.3 Hz, 1H, ArH), 2.81 (s, 2H, CH_2), 2.54 (s, 2H, CH_2), 1.19 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.2, 168.5, 160.8, 148.4, 139.7, 134.4, 130.3, 129.2, 129.2, 128.9, 127.8, 127.8, 127.3, 124.3, 118.5, 110.7, 53.0, 42.7, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{21}H_{18}O_3$ [$(M+H)^+$], 319.1329, found, 319.1328.

3,3-Dimethyl-9-(piperazin-1-yl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3r)



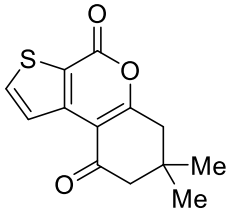
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.2; Yellow solid: 128mg (79%); mp = 176–177 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.57 (s, 1H, ArH), 8.16–8.13 (m, H, ArH), 7.02 (dd, *J* = 9.1, 2.5 Hz, 1H, ArH), 3.72 (t, *J* = 5.2 Hz, 2H, CH_2), 3.58–3.54 (m, 2H, CH_2), 3.54–3.50 (m, 2H, CH_2), 3.48 (t, *J* = 5.4 Hz, 2H, CH_2), 2.77 (s, 2H, CH_2), 2.50 (s, 2H, CH_2), 1.16 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.8, 169.4, 161.0, 160.5, 155.2, 135.8, 131.7, 115.2, 110.4, 109.3, 53.1, 48.2, 47.1, 45.1, 42.9, 39.8, 32.1, 28.2, 28.2; HRMS (TOF ES+): m/z calcd for $C_{19}H_{22}N_2O_3$ [$(M+H)^+$], 327.1703, found, 327.1707.

9-(Dimethylamino)-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3s)



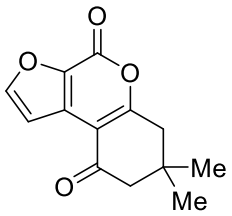
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 4:1, R_f = 0.2; White solid: 73mg (50%); mp = 223–224 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.26 (s, 1H, NH), 8.15 (d, *J* = 7.7 Hz, 1H, ArH), 7.52 (d, *J* = 7.9 Hz, 1H, ArH), 7.42–7.34 (m, 2H, ArH), 2.86 (s, 2H, CH_2), 2.55 (s, 2H, CH_2), 1.21 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.2, 172.4, 157.8, 141.9, 137.1, 125.3, 123.6, 123.2, 121.2, 112.0, 106.4, 99.4, 50.9, 42.0, 33.3, 28.5, 28.5; HRMS (TOF ES+): m/z calcd for $C_{17}H_{15}NO_3$ [$(M+H)^+$], 282.1125, found, 282.1131.

7,7-Dimethyl-7,8-dihydro-4*H*-thieno[2,3-*c*]chromene-4,9(6*H*)-dione (3t)



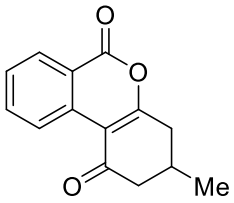
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.2; White solid: 107mg (87%); mp = 128–129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 5.2 Hz, 1H, C=CH), 7.91 (d, *J* = 5.2 Hz, 1H, C=CH), 2.82 (s, 2H, CH_2), 2.50 (s, 2H, CH_2), 1.18 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.3, 169.5, 157.0, 143.6, 138.0, 126.2, 123.0, 111.6, 51.6, 41.9, 32.6, 28.4, 28.4; HRMS (TOF ES+): m/z calcd for $C_{13}H_{12}O_3S$ [$(M+H)^+$], 249.0580, found, 249.0581.

7,7-Dimethyl-7,8-dihydro-4*H*-furo[2,3-c]chromene-4,9(6*H*)-dione (3u)



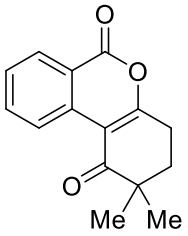
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.2; Yellow solid: 89mg (77%); mp = 145–146 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 (s, 1H, C=CH), 7.37 (d, *J* = 1.9 Hz, 1H, C=CH), 2.79 (s, 2H, CH_2), 2.48 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.3, 169.2, 152.2, 151.5, 136.9, 132.6, 110.3, 109.3, 51.1, 41.7, 33.0, 28.4, 28.4; HRMS (TOF ES+): m/z calcd for $C_{13}H_{12}O_4$ [$(M+Na)^+$], 255.0628, found, 255.0628.

3-Methyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3x)



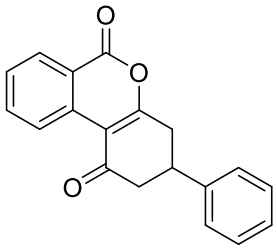
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 108mg (95%); mp = 123–124 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.05 (d, *J* = 8.3 Hz, 1H, ArH), 8.28 (dd, *J* = 8.0, 1.5 Hz, 1H, ArH), 7.81–7.76 (m, 1H, ArH), 7.53 (t, *J* = 7.5 Hz, 1H, ArH), 2.97–2.91 (m, 1H, C-CH), 2.74–2.63 (m, 2H, CH_2), 2.48–2.34 (m, 2H, CH_2), 1.18 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.1, 169.1, 160.7, 135.8, 134.1, 129.7, 128.6, 126.0, 119.9, 111.3, 47.3, 37.0, 27.8, 20.9; HRMS (TOF ES+): m/z calcd for $C_{14}H_{14}O_3$ [$(M+H)^+$], 229.0859, found, 229.0863.

2,2-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3y)



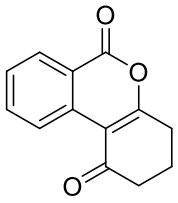
V $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; White solid: 115mg (95%); mp = 142–143 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.04 (d, *J* = 8.3 Hz, 1H, ArH), 8.28 (d, *J* = 7.9 Hz, 1H, ArH), 7.79 (t, *J* = 7.7 Hz, 1H, ArH), 7.53 (t, *J* = 7.6 Hz, 1H, ArH), 2.80 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 1.17 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.2, 168.1, 160.9, 135.8, 134.0, 129.7, 128.5, 125.9, 119.9, 110.7, 53.0, 42.6, 32.1, 28.3, 28.3; HRMS (TOF ES+): m/z calcd for $C_{14}H_{14}O_3$ [$(M+H)^+$], 243.1016, found, 243.1022.

3-Phenyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3z)



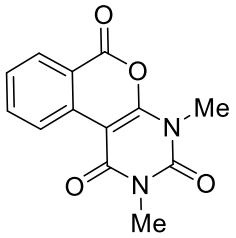
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.2; Yellow solid: 124mg (78%); mp = 118–119 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.10 (d, *J* = 8.3 Hz, 1H, ArH), 8.31 (d, *J* = 7.9 Hz, 1H, ArH), 7.82 (t, *J* = 7.7 Hz, 1H, ArH), 7.56 (t, *J* = 7.6 Hz, 1H, ArH), 7.40 (t, *J* = 7.5 Hz, 2H, ArH), 7.31 (dd, *J* = 12.5, 7.4 Hz, 3H, ArH), 3.61–3.54 (m, 1H, C-CH), 3.23–3.12 (m, 2H, CH_2), 2.98–2.87 (m, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.3, 168.7, 160.6, 141.5, 135.9, 133.9, 129.8, 129.2, 129.2, 128.8, 127.7, 126.7, 126.7, 126.1, 119.9, 111.5, 46.0, 38.1, 36.5; HRMS (TOF ES+): m/z calcd for $C_{19}H_{14}O_3$ [$(M+H)^+$], 291.1016, found, 291.1019.

3,4-Dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3a')



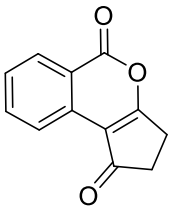
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 12:1, R_f = 0.2; Yellow solid: 101mg (95%); mp = 165–166 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.04 (d, J = 8.3 Hz, 1H, ArH), 8.27 (d, J = 7.6 Hz, 1H, ArH), 7.80–7.77 (m, 1H, ArH), 7.52 (t, J = 7.6 Hz, 1H, ArH), 2.93 (t, J = 6.3 Hz, 2H, CH_2), 2.65 (t, J = 6.5 Hz, 2H, CH_2), 2.20–2.15 (m, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.1, 169.6, 160.6, 135.8, 134.1, 129.7, 128.5, 126.2, 119.9, 111.7, 39.1, 29.1, 20.1; HRMS (TOF ES+): m/z calcd for $C_{13}H_{10}O_3$ [$(M+H)^+$], 215.0703, found, 215.0705.

2,4-Dimethyl-1*H*-isochromeno[3,4-*d*]pyrimidine-1,3,6(2*H*,4*H*)-trione (3b')



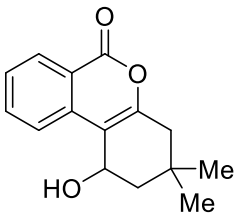
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 2:1, R_f = 0.2; Yellow solid: 82mg (63%); mp = 180–181 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, J = 7.0 Hz, 1H, ArH), 7.72 (s, 1H, ArH), 7.53–7.45 (m, 1H, ArH), 7.18 (d, J = 7.3 Hz, 1H, ArH), 3.42 (s, 3H, CH_3), 2.98 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 190.6, 169.1, 151.6, 148.3, 144.2, 138.2, 133.0, 130.4, 125.0, 120.9, 102.9, 30.0, 30.0; HRMS (TOF ES+): m/z calcd for $C_{19}H_{14}O_3$ [$(M+H)^+$], 259.0713, found, 259.0713.

2,3-Dihydrocyclopenta[*c*]isochromene-1,5-dione (3c')



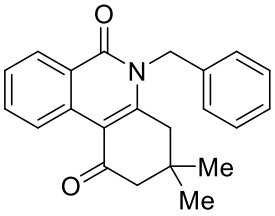
V $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.2; White solid: 93mg (93%); mp = 181–182 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.49 (d, J = 7.9 Hz, 1H, ArH), 8.27 (d, J = 7.9 Hz, 1H, ArH), 7.81 (t, J = 7.6 Hz, 1H, ArH), 7.57 (t, J = 7.7 Hz, 1H, ArH), 3.05–3.01 (m, 2H, CH_2), 2.77–2.74 (m, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.6, 180.6, 161.3, 136.0, 132,0, 130.6, 129.2, 123.4, 118.7, 114.7, 34.7, 25.9; HRMS (TOF ES+): m/z calcd for $C_{12}H_8O_3$ [$(M+H)^+$], 201.0546, found, 201.5055.

1-Hydroxy-3,3-dimethyl-1,2,3,4-tetrahydro-6*H*-benzo[*c*]chromen-6-one (4)



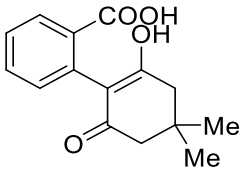
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 4:1, R_f = 0.2; White solid: 87mg (71%); mp = 100–101 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 7.9 Hz, 1H, ArH), 7.92 (d, *J* = 8.1 Hz, 1H, ArH), 7.74 (t, *J* = 7.7 Hz, 1H, ArH), 7.46 (t, *J* = 7.6 Hz, 1H, ArH), 5.04 (s, 1H, OH), 2.48 (d, *J* = 17.6 Hz, 1H, CH_2), 2.35 (d, *J* = 17.6 Hz, 1H, CH_2), 2.03 (dd, *J* = 13.8, 5.8 Hz, 1H, C-CH), 1.82–1.73 (m, 2H, CH_2), 1.19 (s, 3H, CH_3), 1.05 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.7, 153.8, 136.8, 134.9, 129.8, 127.7, 124.0, 120.8, 110.9, 65.0, 45.6, 41.5, 30.6, 29.3, 28.5; HRMS (TOF ES+): m/z calcd for $C_{15}H_{16}O_3$ [$(M+H)^+$], 245.1172, found, 245.1171.

5-Benzyl-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2*H*,5*H*)-dione (5)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 4:1, R_f = 0.2; White solid: 132mg (80%); mp = 125–126 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.29 (d, *J* = 8.47 Hz, 1H, ArH), 8.48 (d, *J* = 7.9 Hz, 1H, ArH), 7.77 (t, *J* = 7.7 Hz, 1H, ArH), 7.53 (t, *J* = 7.6 Hz, 1H, ArH), 7.33 (t, *J* = 7.4 Hz, 2H, ArH), 7.28 (s, 1H, ArH), 7.12 (d, *J* = 7.9 Hz, 2H, ArH), 5.52 (s, 2H, CH_2), 2.82 (s, 2H, CH_2), 2.48 (s, 2H, CH_2), 1.01 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.3, 163.2, 152.7, 136.2, 134.0, 133.9, 129.2, 129.2, 128.2, 127.7, 127.3, 126.2, 125.2, 125.9, 124.1, 111.1, 52.4, 47.3, 42.1, 32.2, 28.1, 28.1; HRMS (TOF ES+): m/z calcd for $C_{22}H_{21}NO_2$ [$(M+H)^+$], 332.1645, found, 332.1643.

6'-Hydroxy-4',4'-dimethyl-2'-oxo-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carboxylic acid (6)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 116mg (89%); mp = 176–177 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.41 (d, J = 8.3 Hz, 1H, ArH), 7.22 (t, J = 7.5 Hz, 1H, ArH), 7.14 (d, J = 6.5 Hz, 1H, ArH), 6.94 (d, *J* = 6.9 Hz, 1H, ArH), 2.19 (s, 2H, CH_2), 2.13 (s, 2H, CH_2), 1.04 (s, 6H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 197.6, 168.9, 160.4, 135.1, 132.9, 132.8, 130.9, 129.3, 126.5, 115.8, 52.3, 41.7, 31.9, 29.0, 27.8; HRMS (TOF ES+): m/z calcd for $C_{15}H_{16}O_4$ [$(M+H)^+$], 261.1121, found, 261.1126.

4. X-ray Structure and Data[3] of 3b (CCDC 2209204).

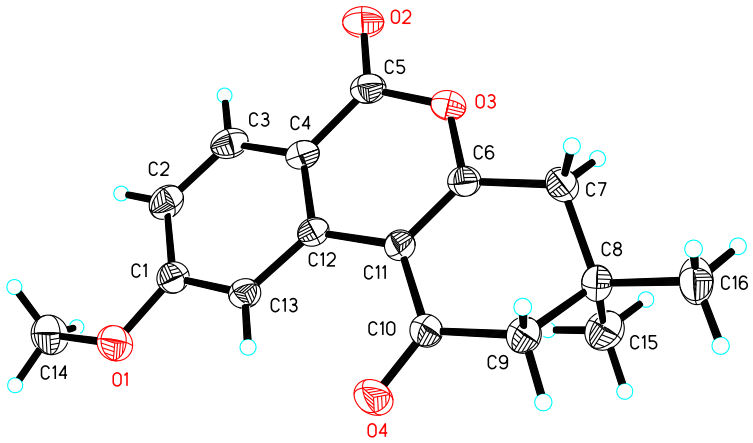


Figure S1 X-Ray crystal structure of 3b.

Table S1 Crystal data and structure refinement for **3b.**

Empirical formula	$C_{16}H_{16}O_4$
Formula weight	272.29
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.6765(5) A alpha = 90 deg.
	b = 13.7501(6) A beta = 105.149(5) deg.
	c = 10.5137(5) A gamma = 90 deg.
Volume	1350.27(11) A^3
Z, Calculated density	4, 1.339 Mg/m^3
Absorption coefficient	0.789 mm^-1
F(000)	576
Crystal size	0.230 x 0.220 x 0.200 mm
Theta range for data collection	5.418 to 67.240 deg.
Limiting indices	-11<=h<=11, -16<=k<=15, -12<=l<=9
Completeness to theta = 67.240	99.4%
Reflections collected / unique	4661 / 2415 [R(int) = 0.0249]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2415 / 0 / 184
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1194
R indices (all data)	R1 = 0.0554, wR2 = 0.1286
Extinction coefficient	n/a
Largest diff. peak and hole	0.153 and -0.194 e.A^-3

5. ^{1}H NMR and ^{13}C NMR spectra for spectroscopic data.

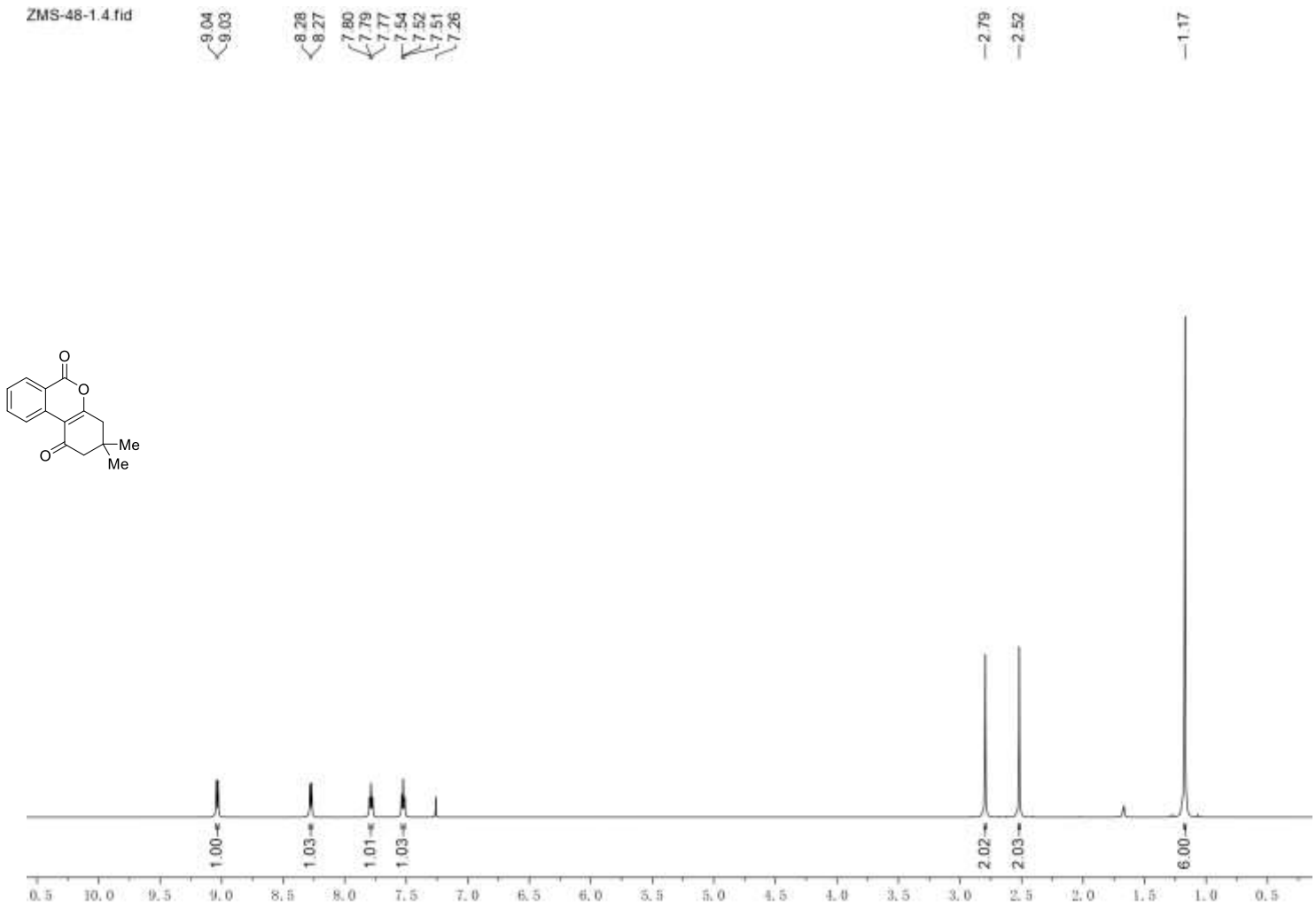


Figure S2. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3a**

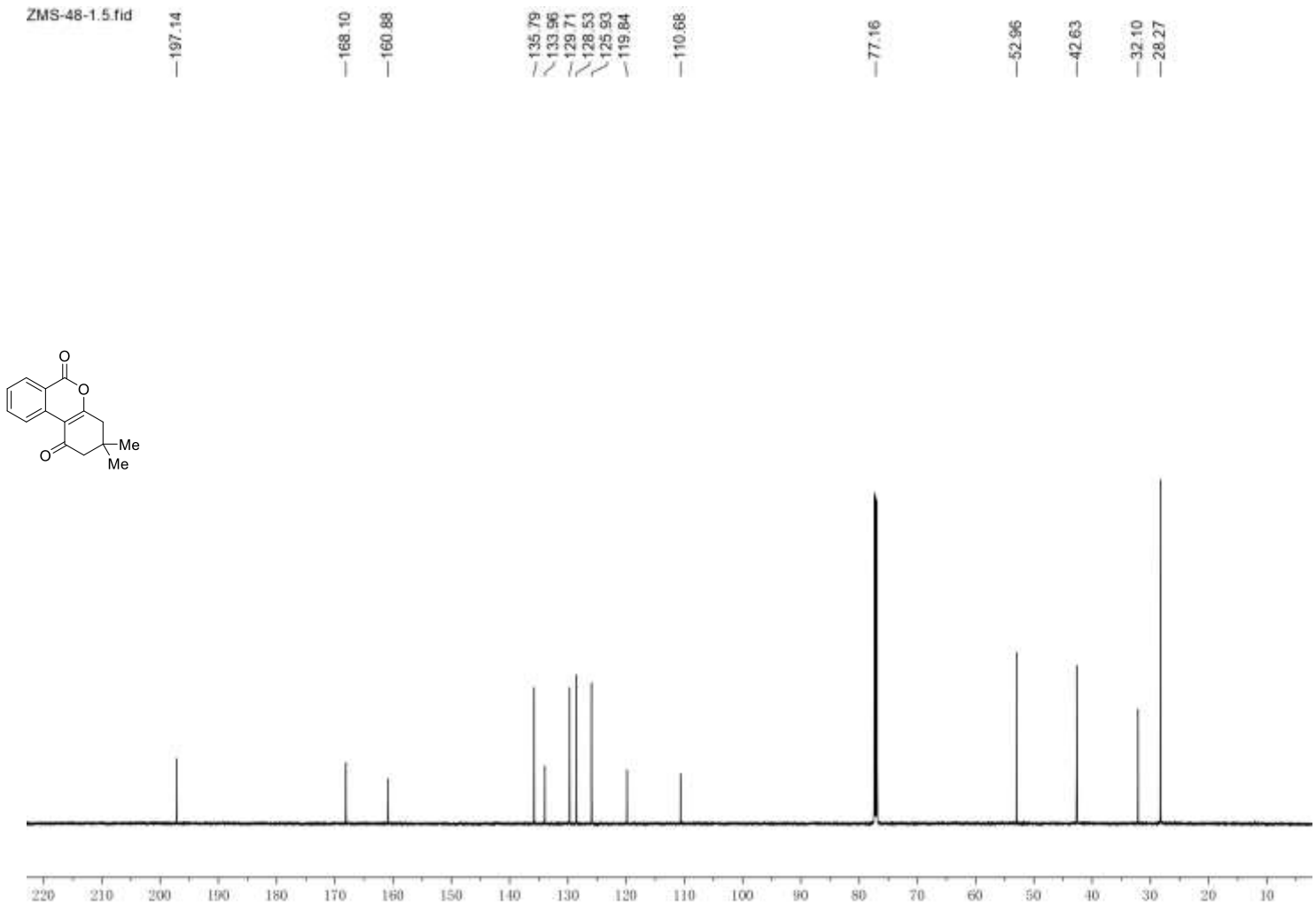


Figure S3. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3a**

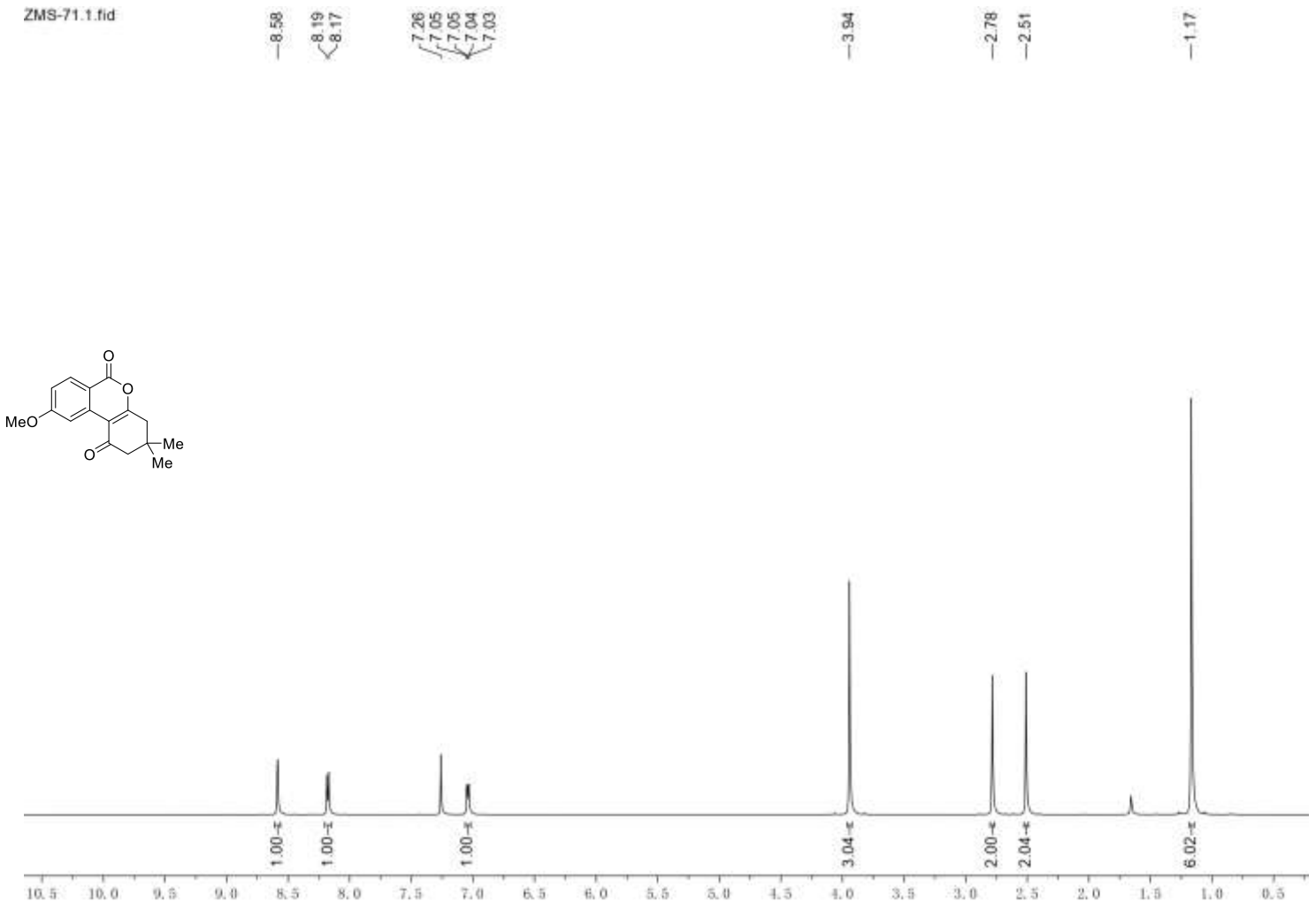


Figure S4. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3b**

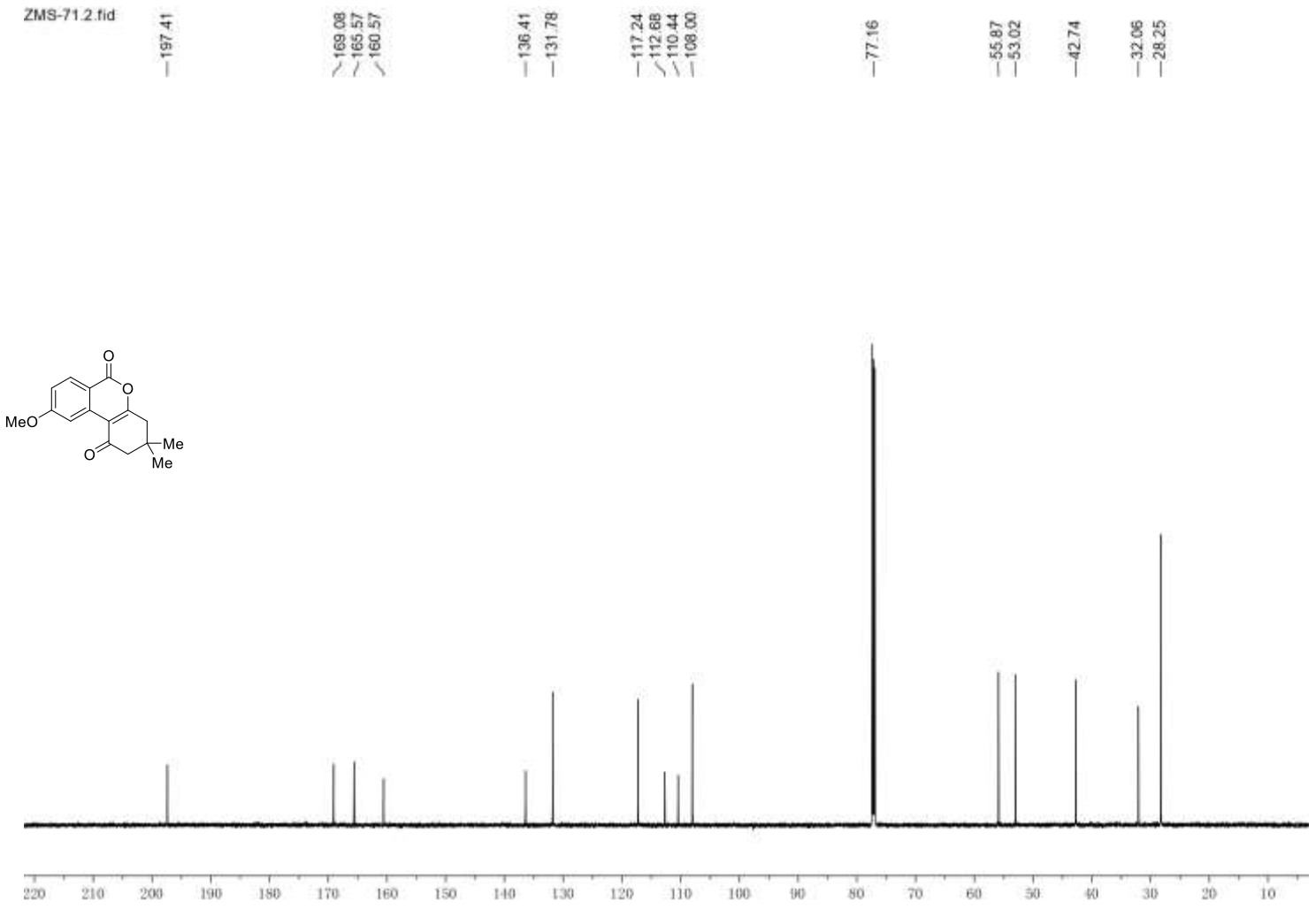


Figure S5. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3b**

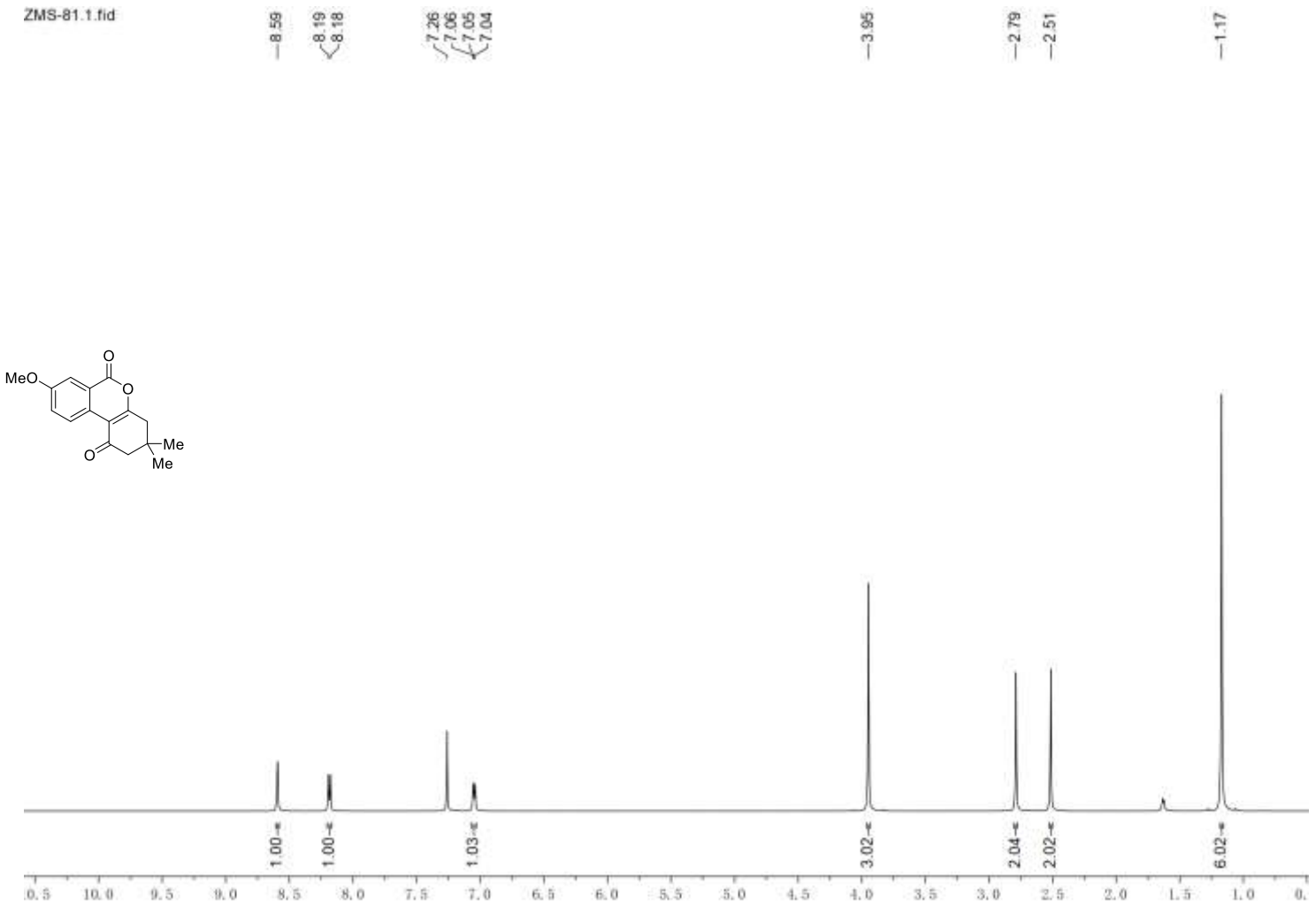


Figure S6. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3c**

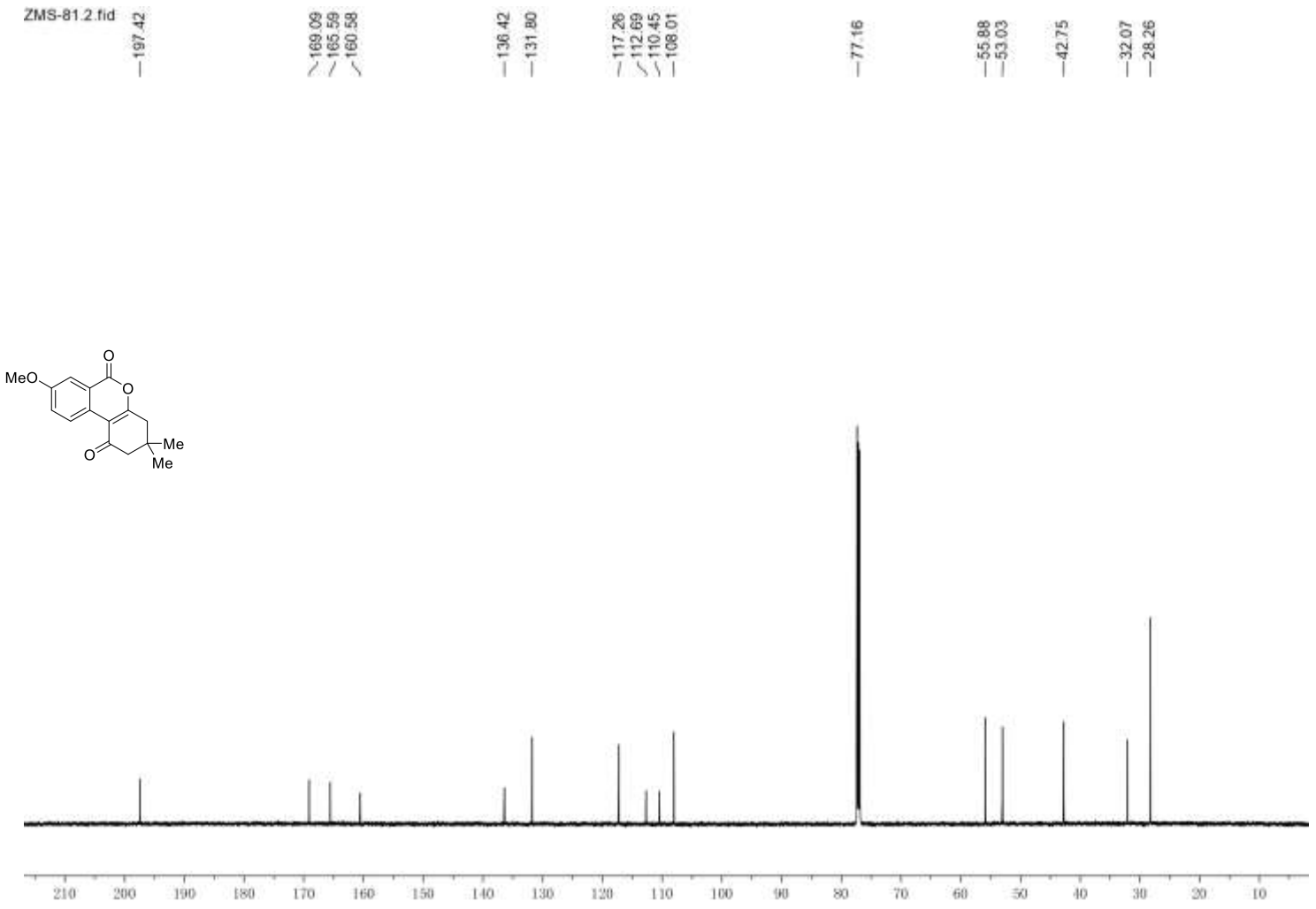


Figure S7. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3c**

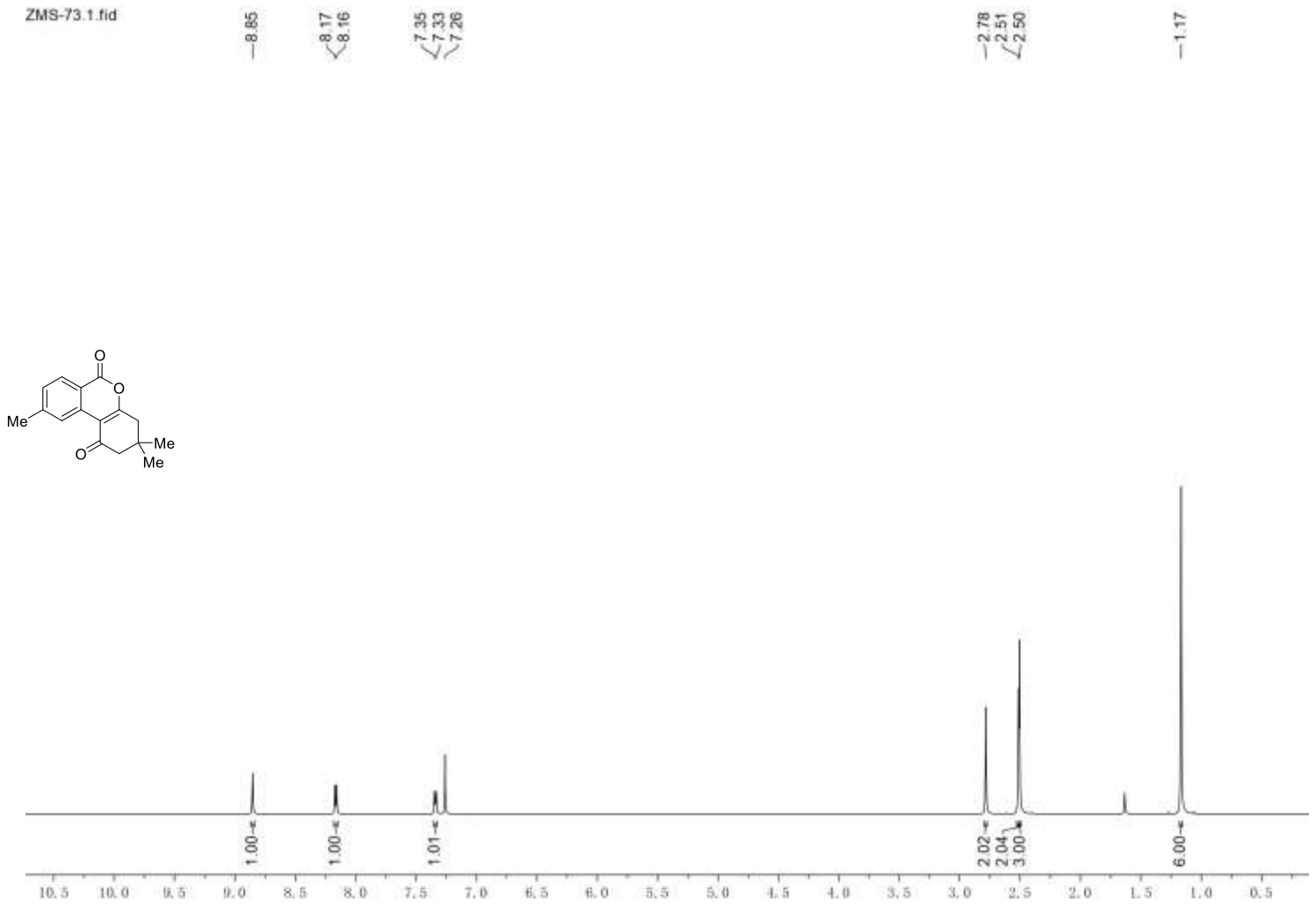


Figure S8. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3d**

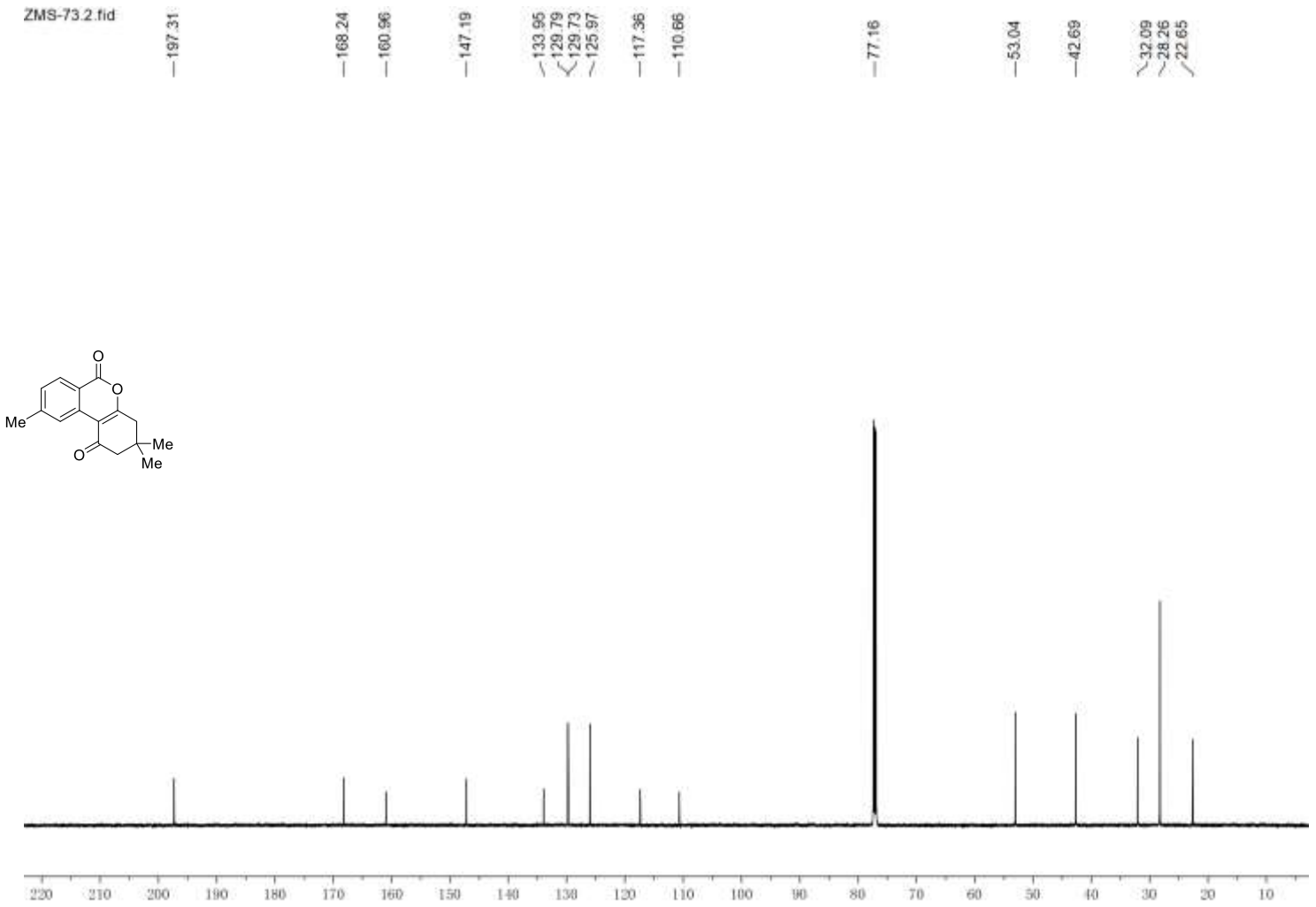


Figure S9. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3d**

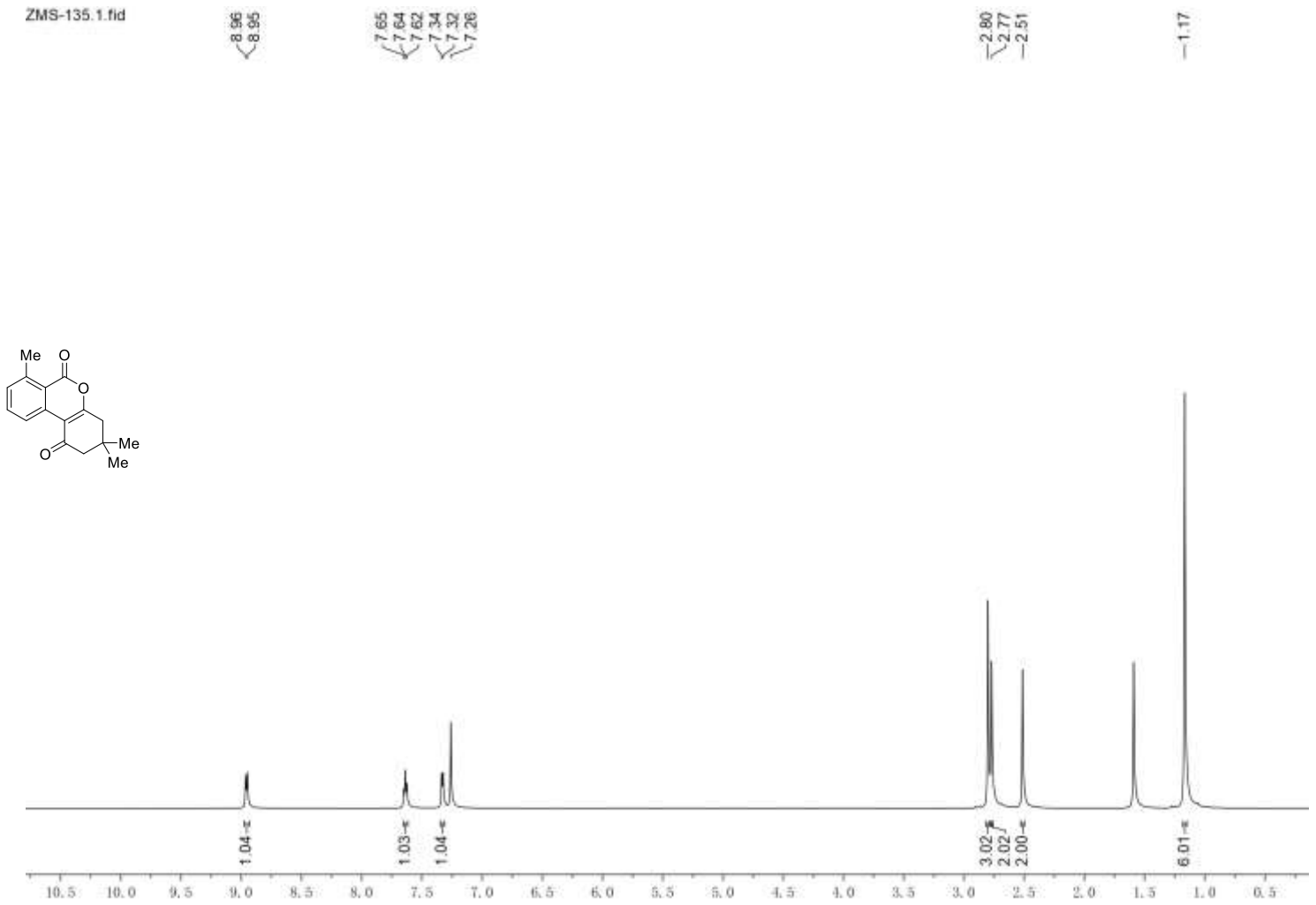


Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3e**

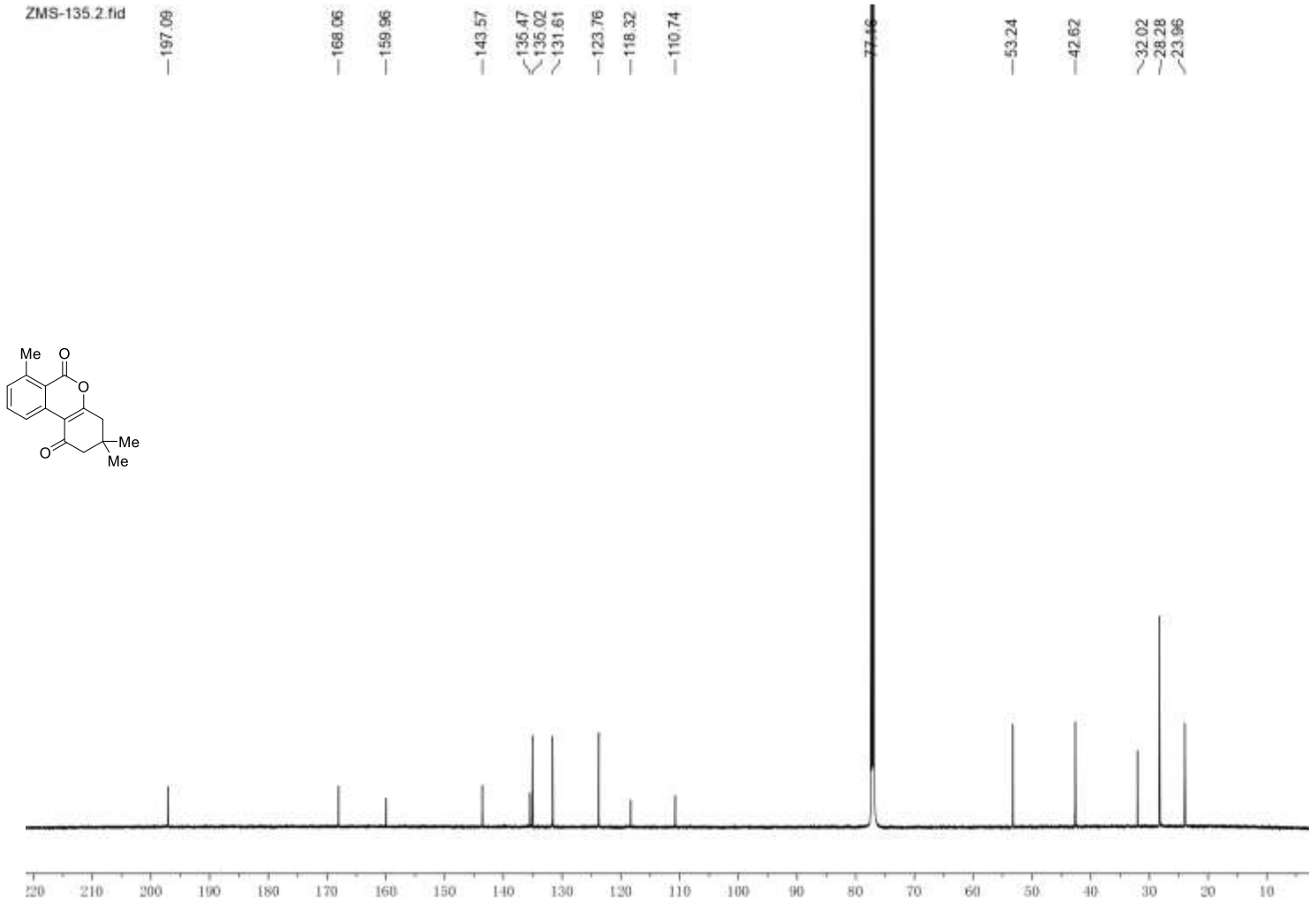


Figure S11. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3e**

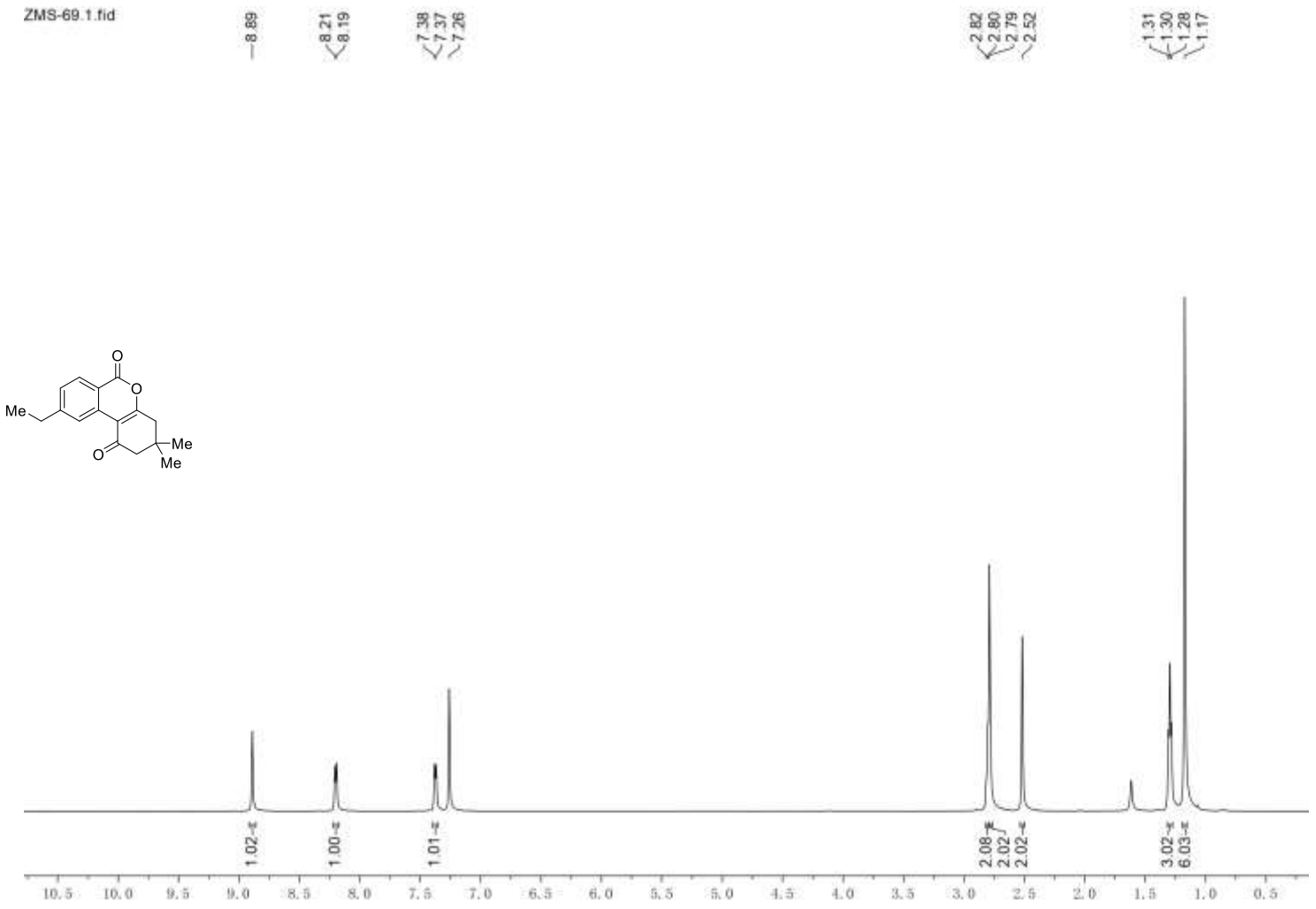


Figure S12. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3f**

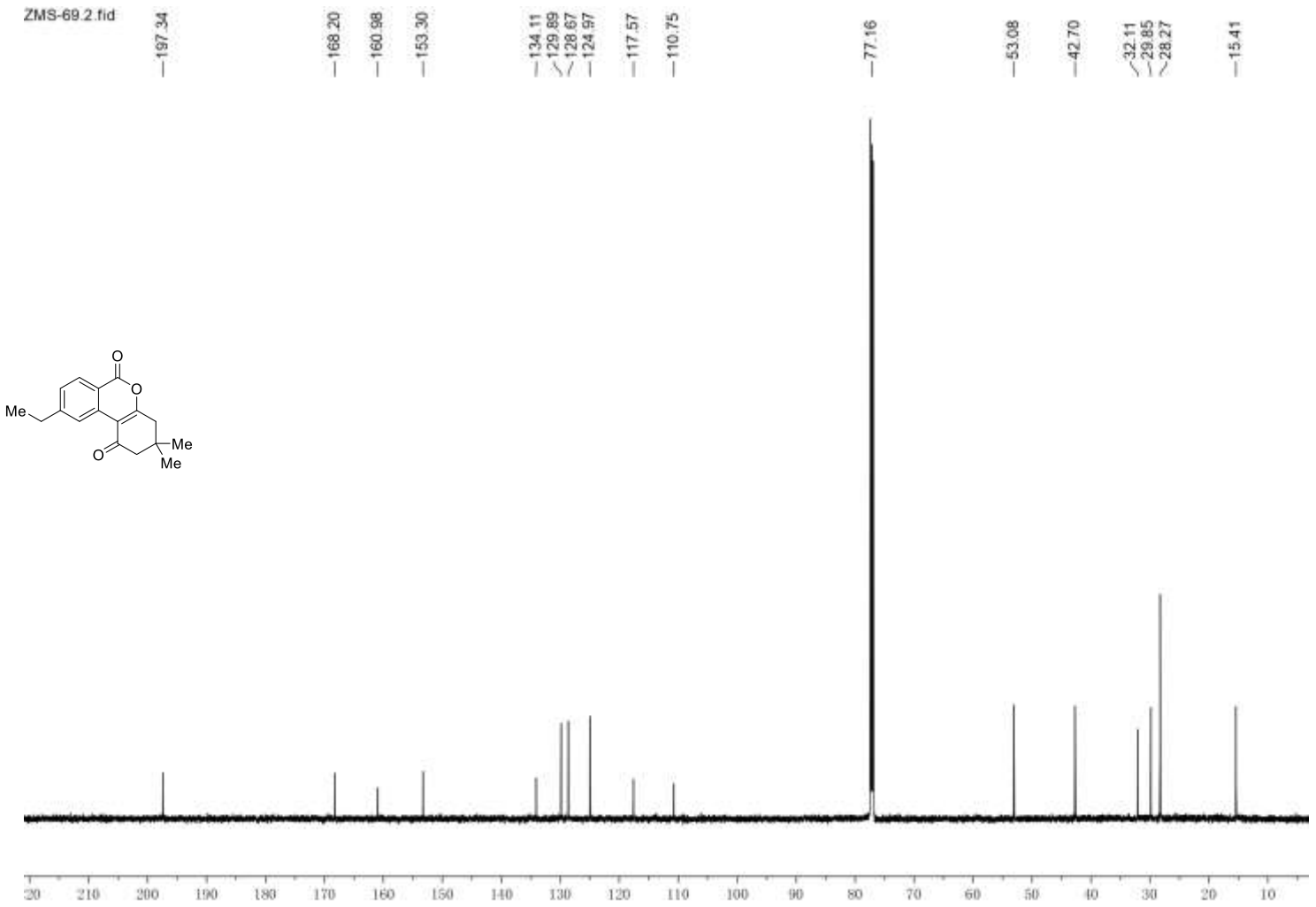


Figure S13. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3f**

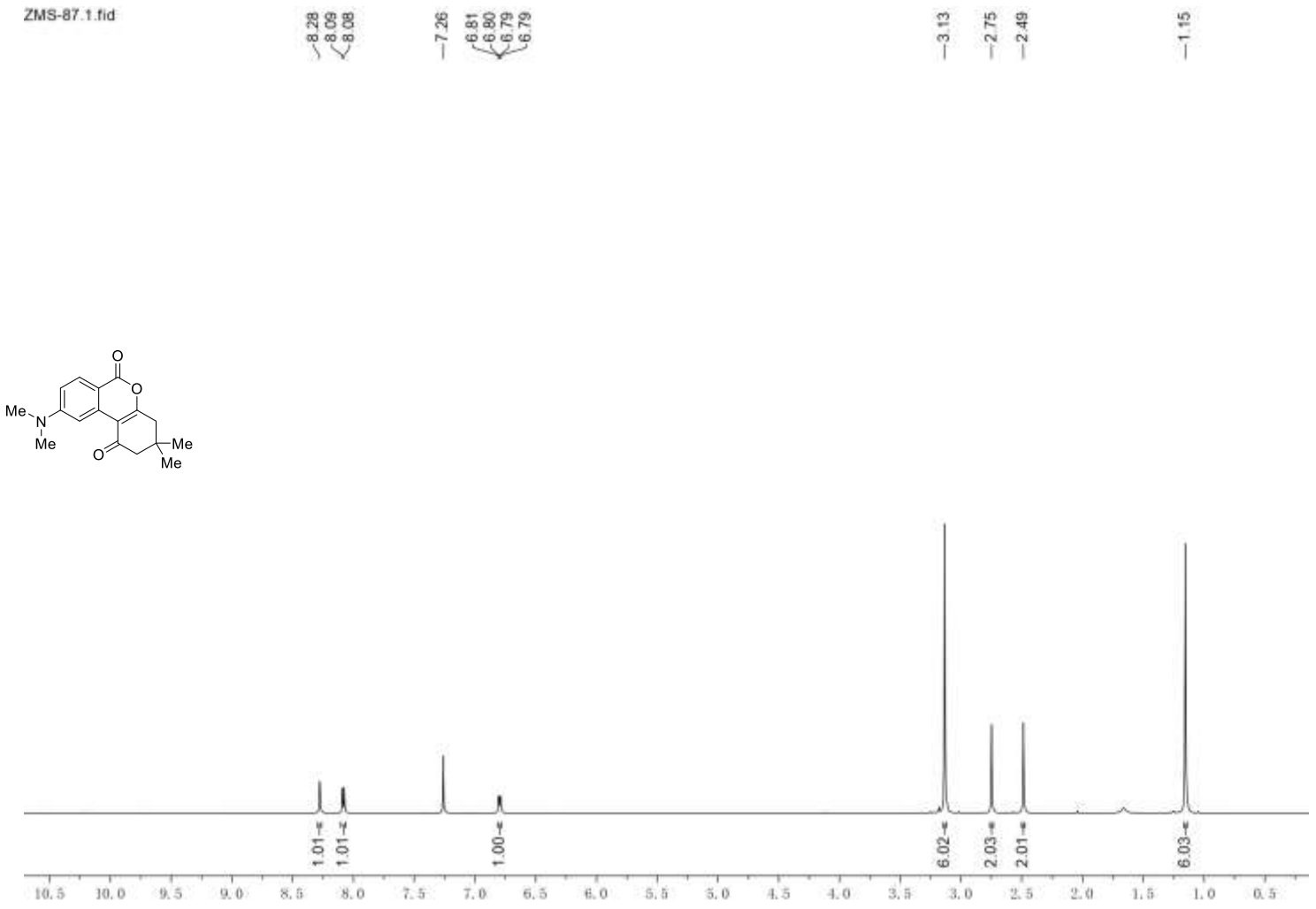


Figure S14. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3g**

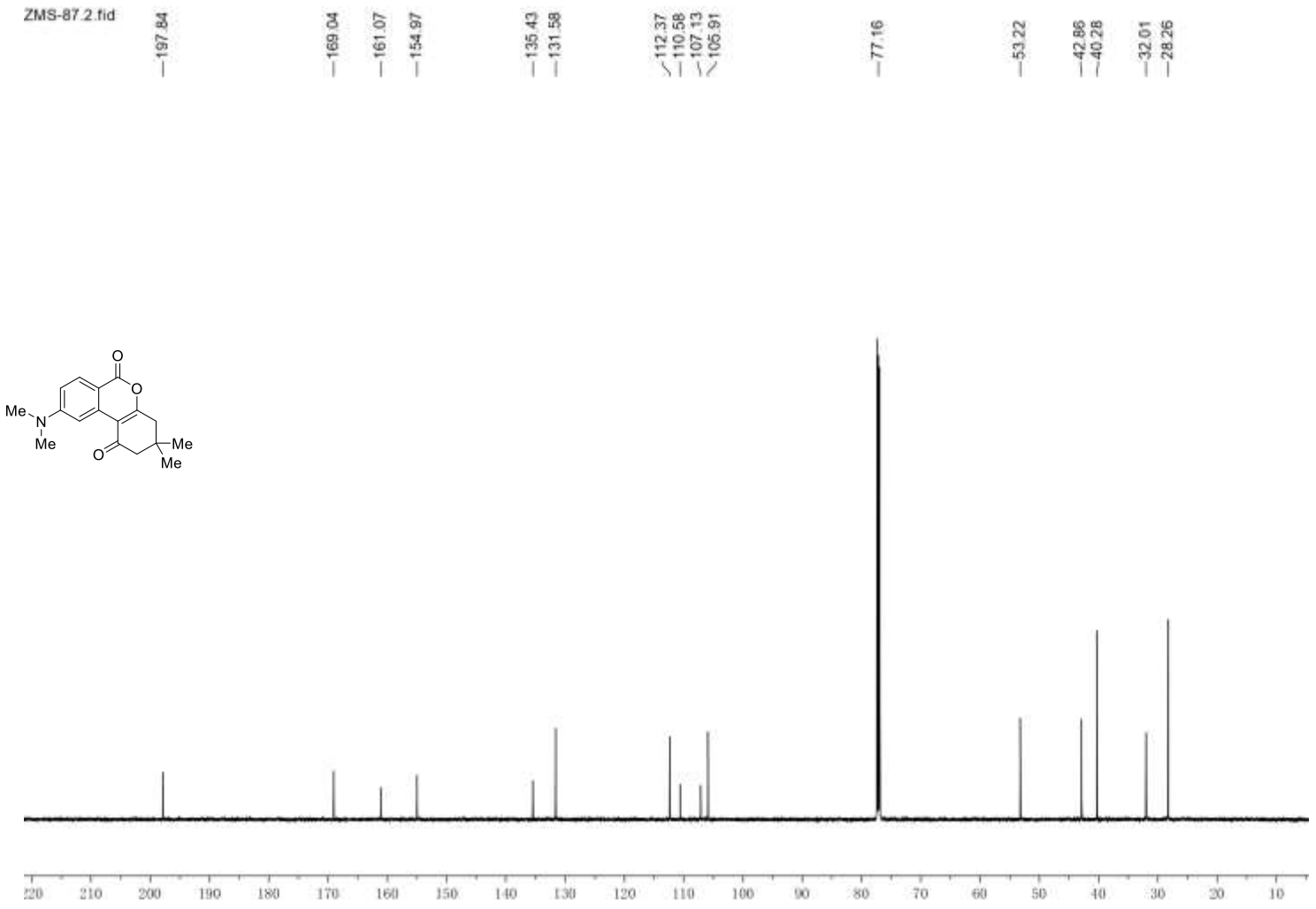


Figure S15. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3g**

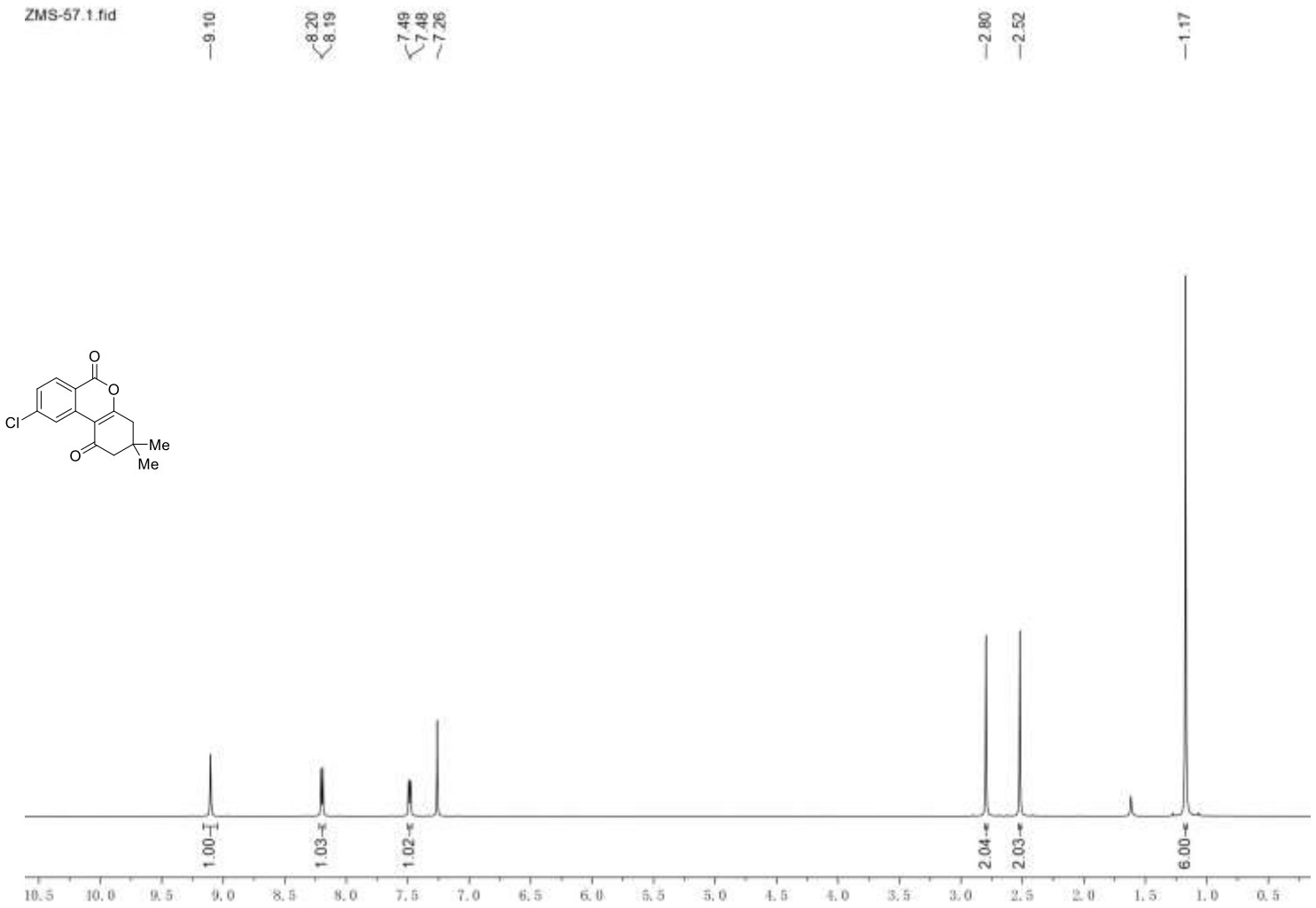


Figure S16. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3h**

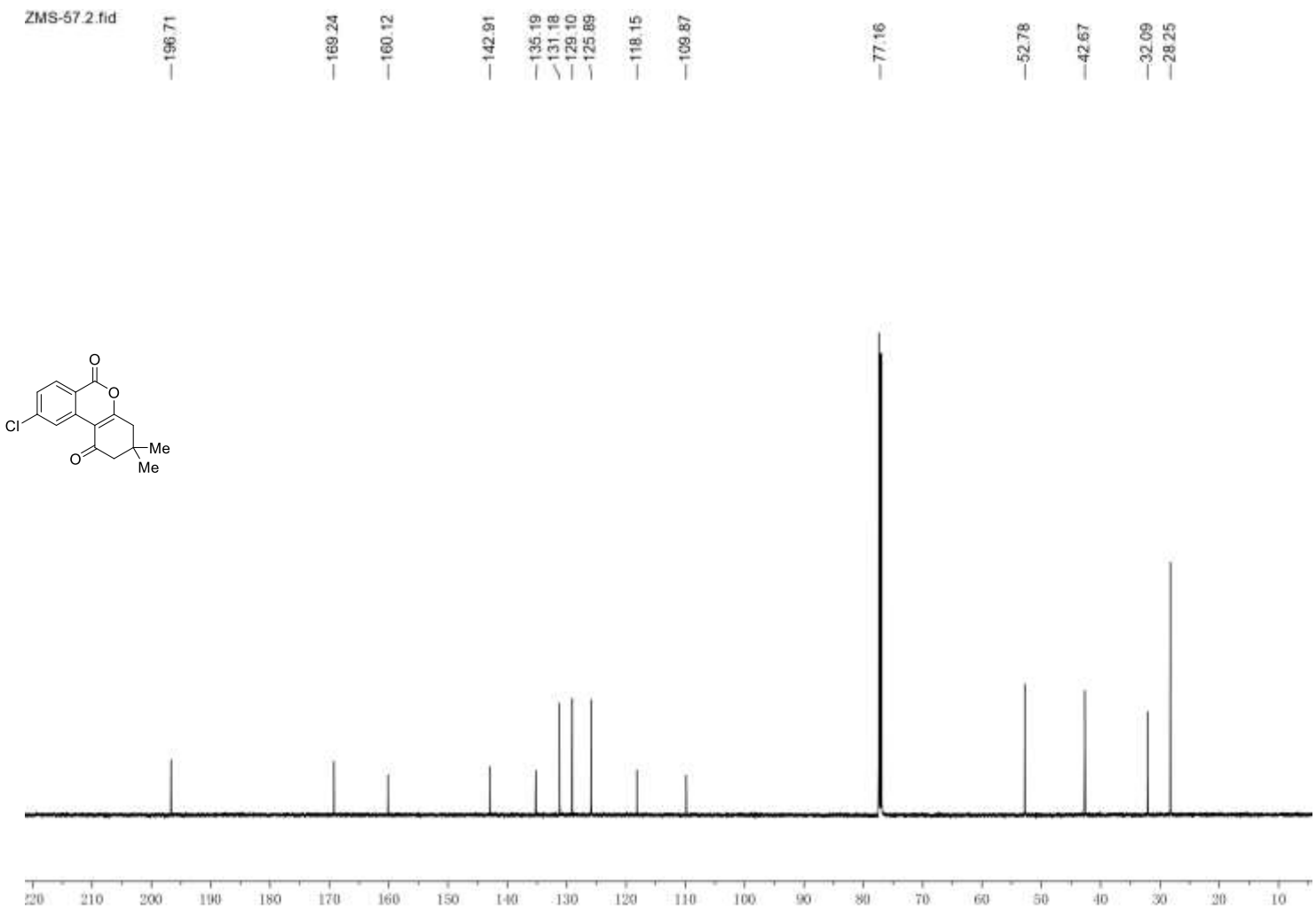


Figure S17. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3h**

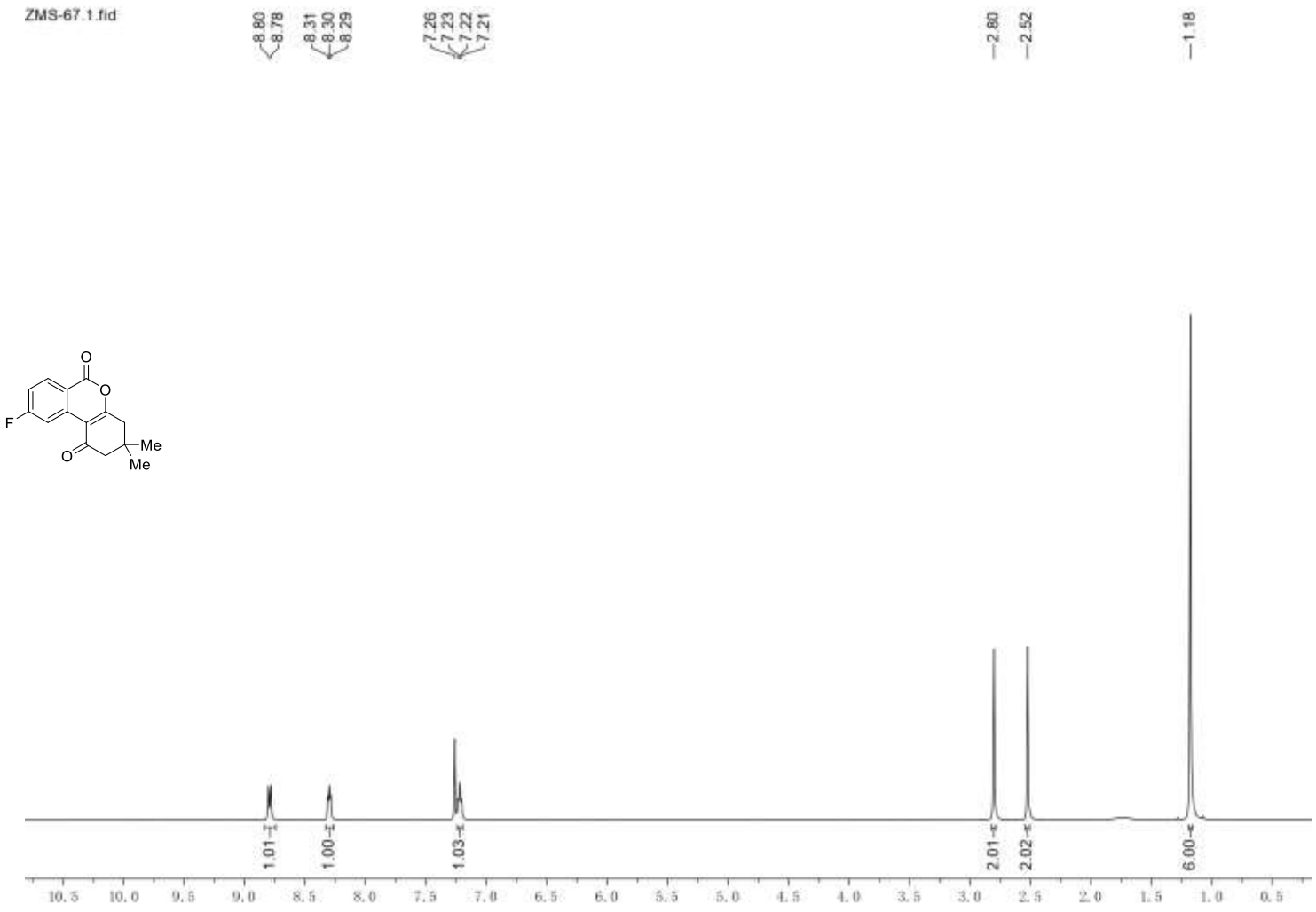


Figure S18. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3i**

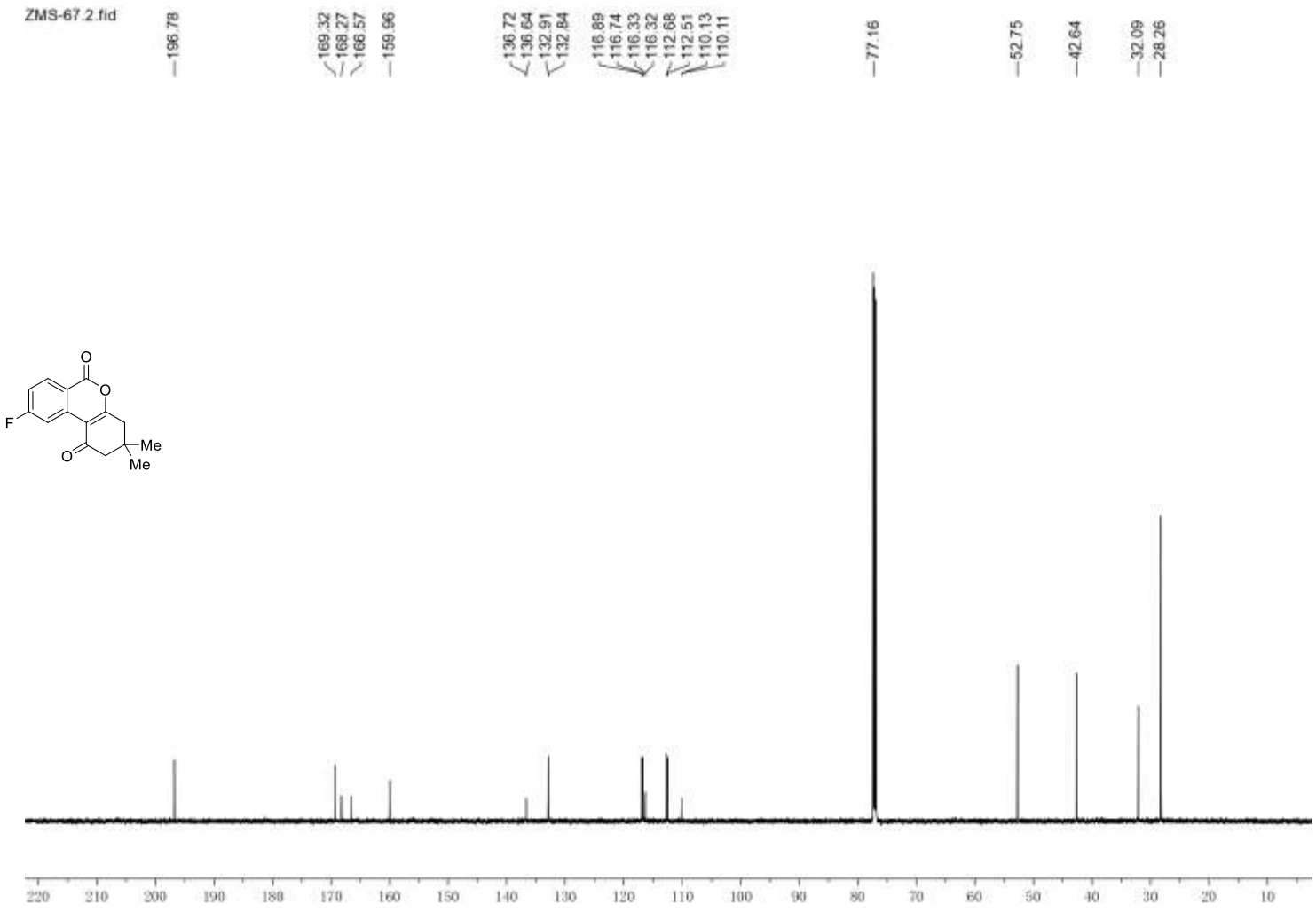


Figure S19. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3i**

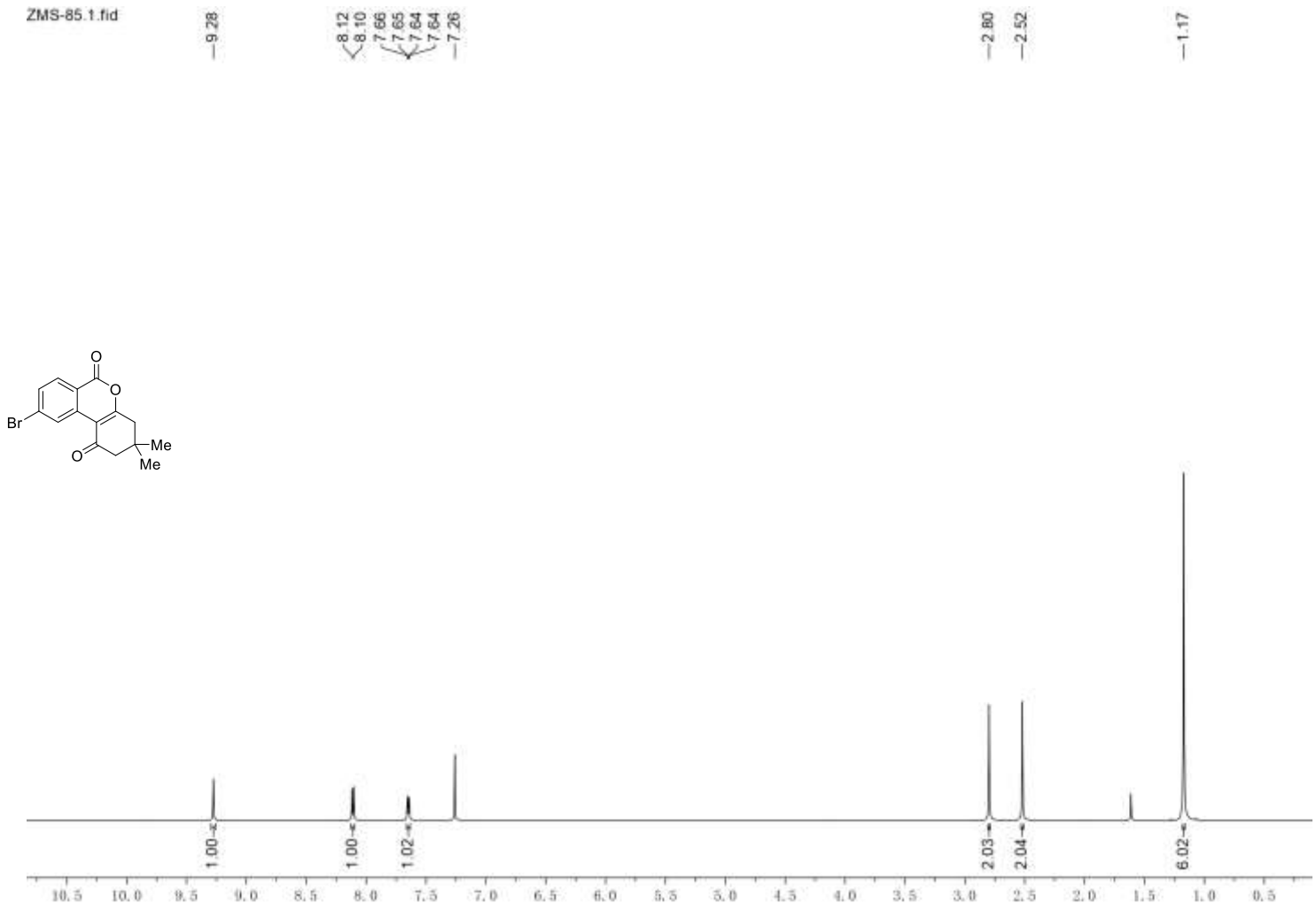


Figure S20. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3j**

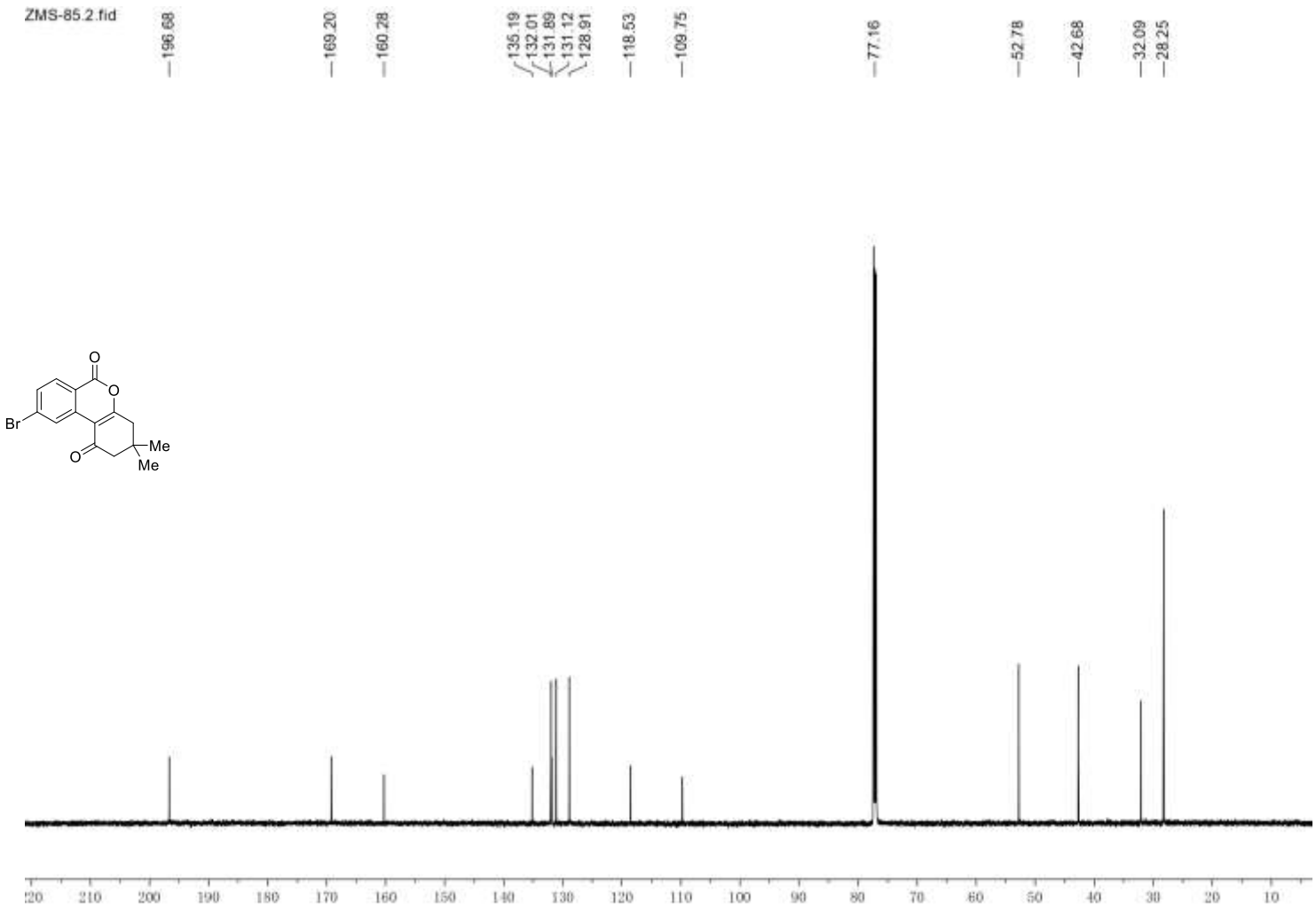


Figure S21. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3j**

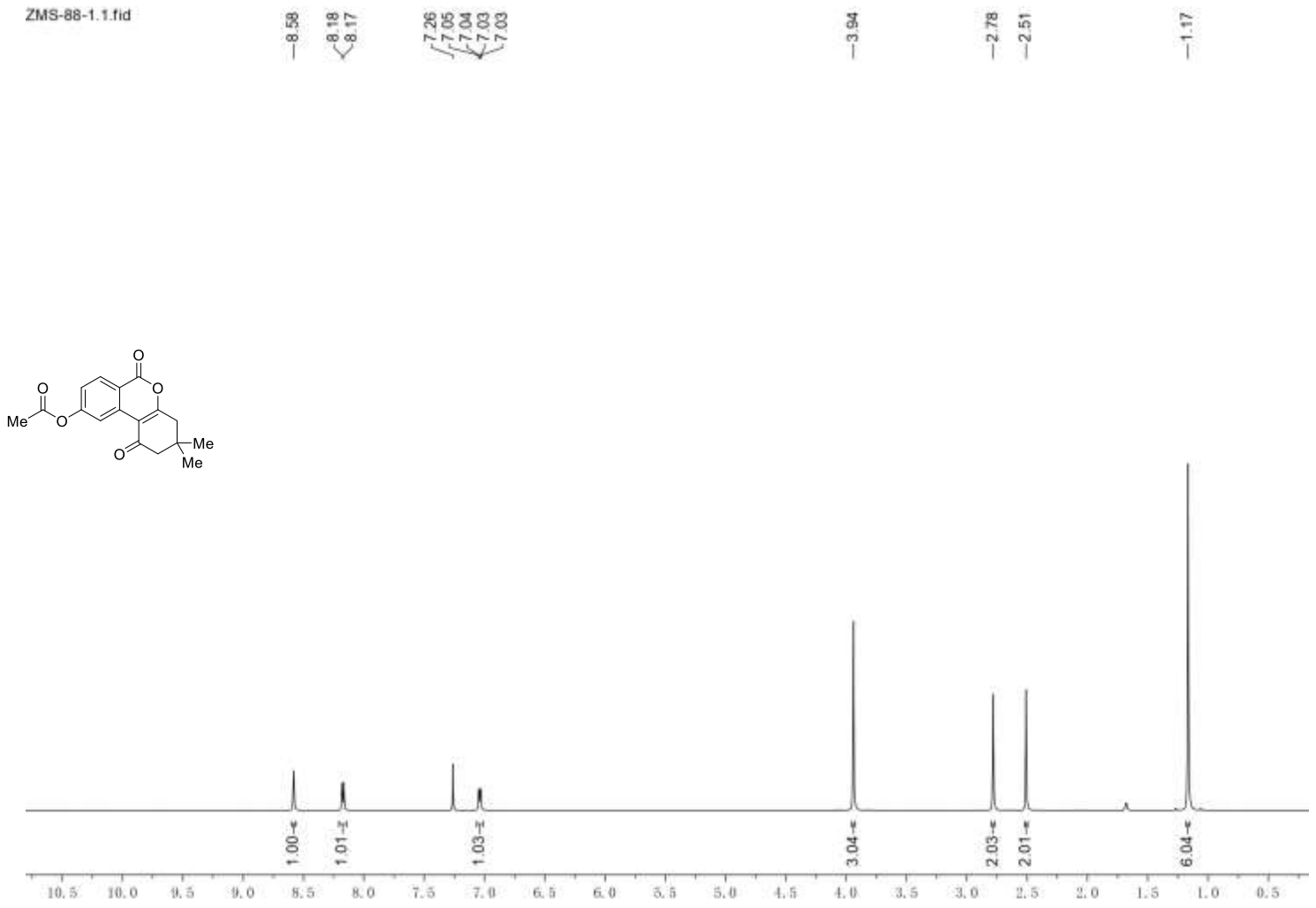


Figure S22. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3k**

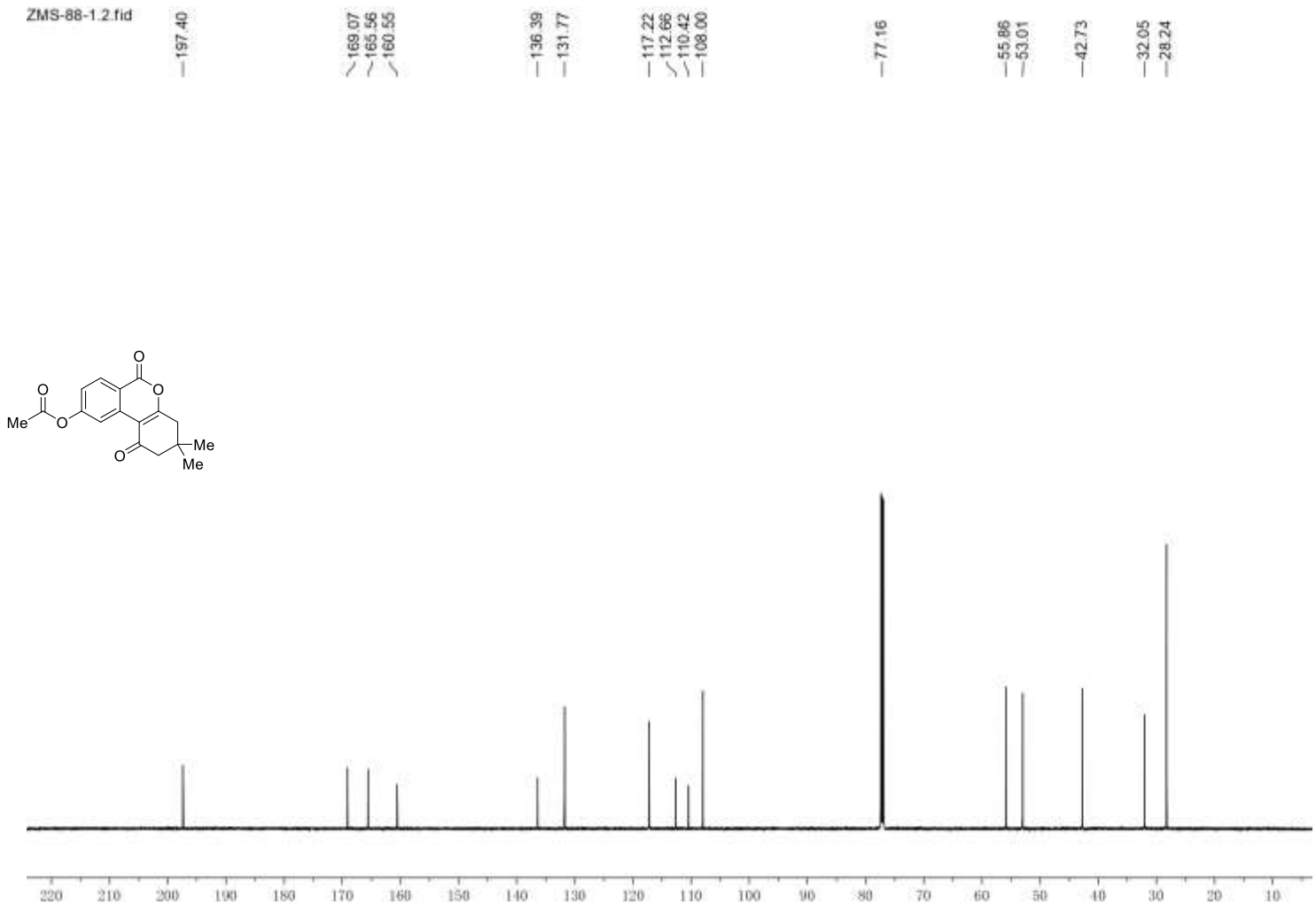


Figure S23. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3k**

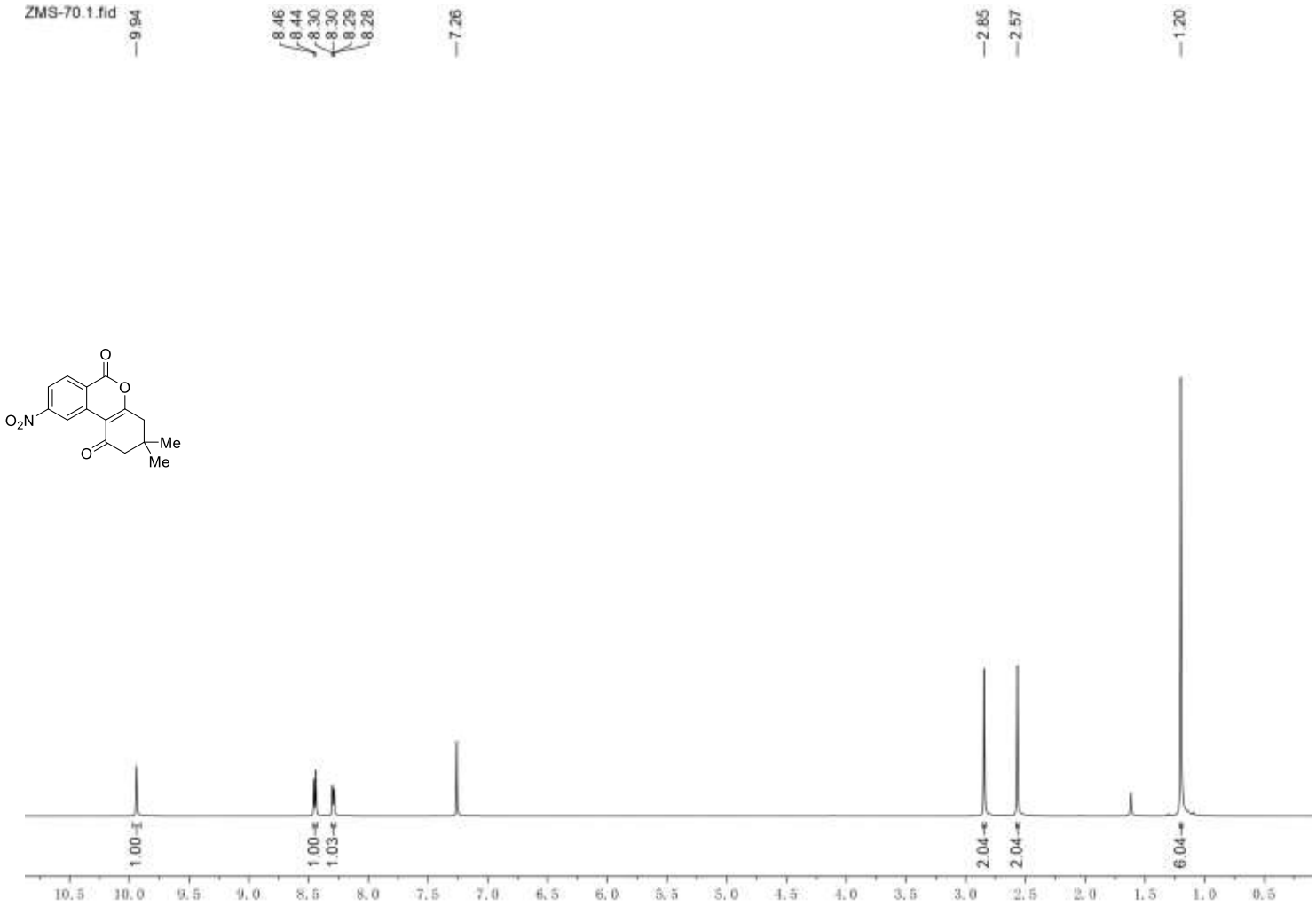


Figure S24. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3l**

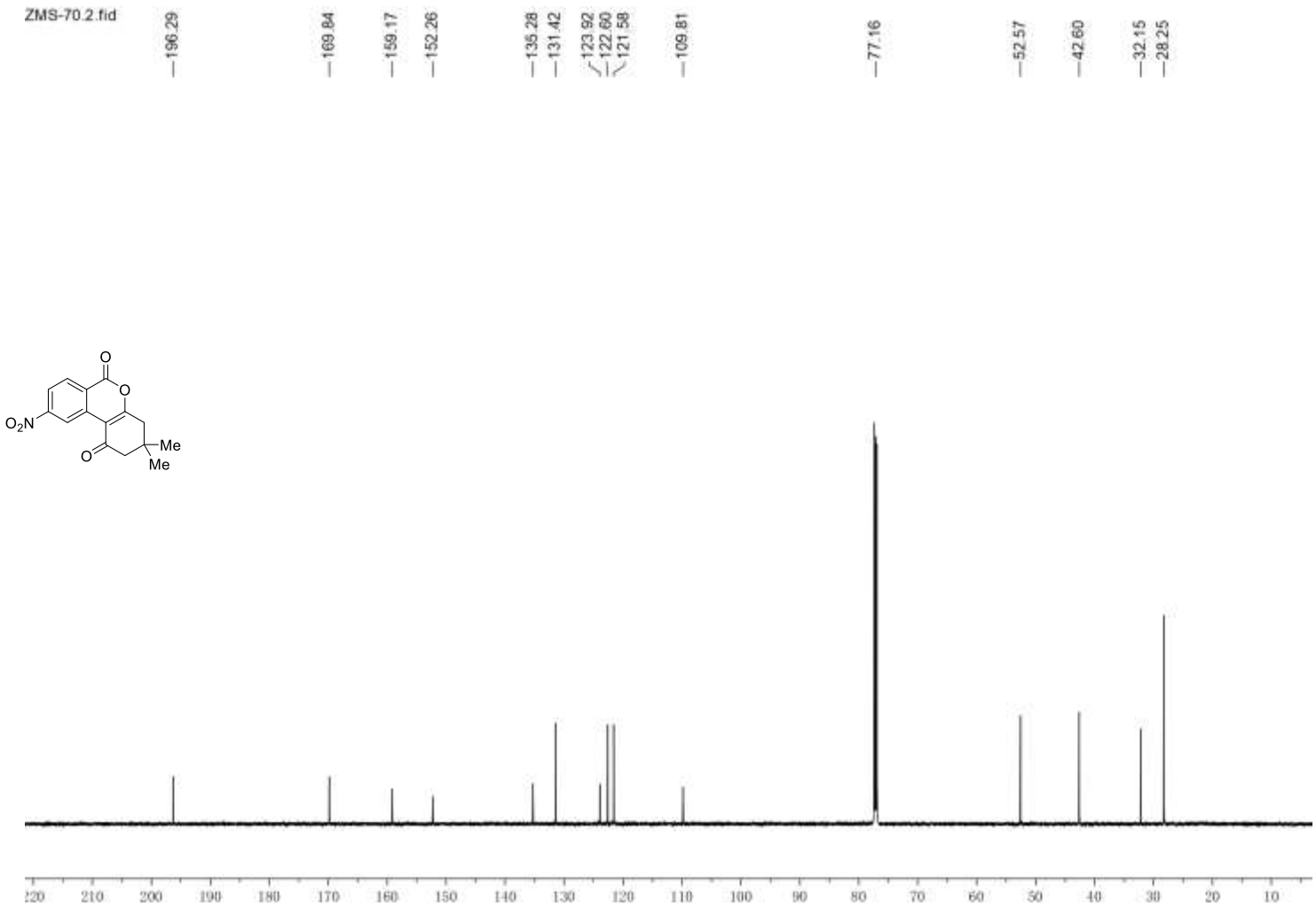


Figure S25. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3l**

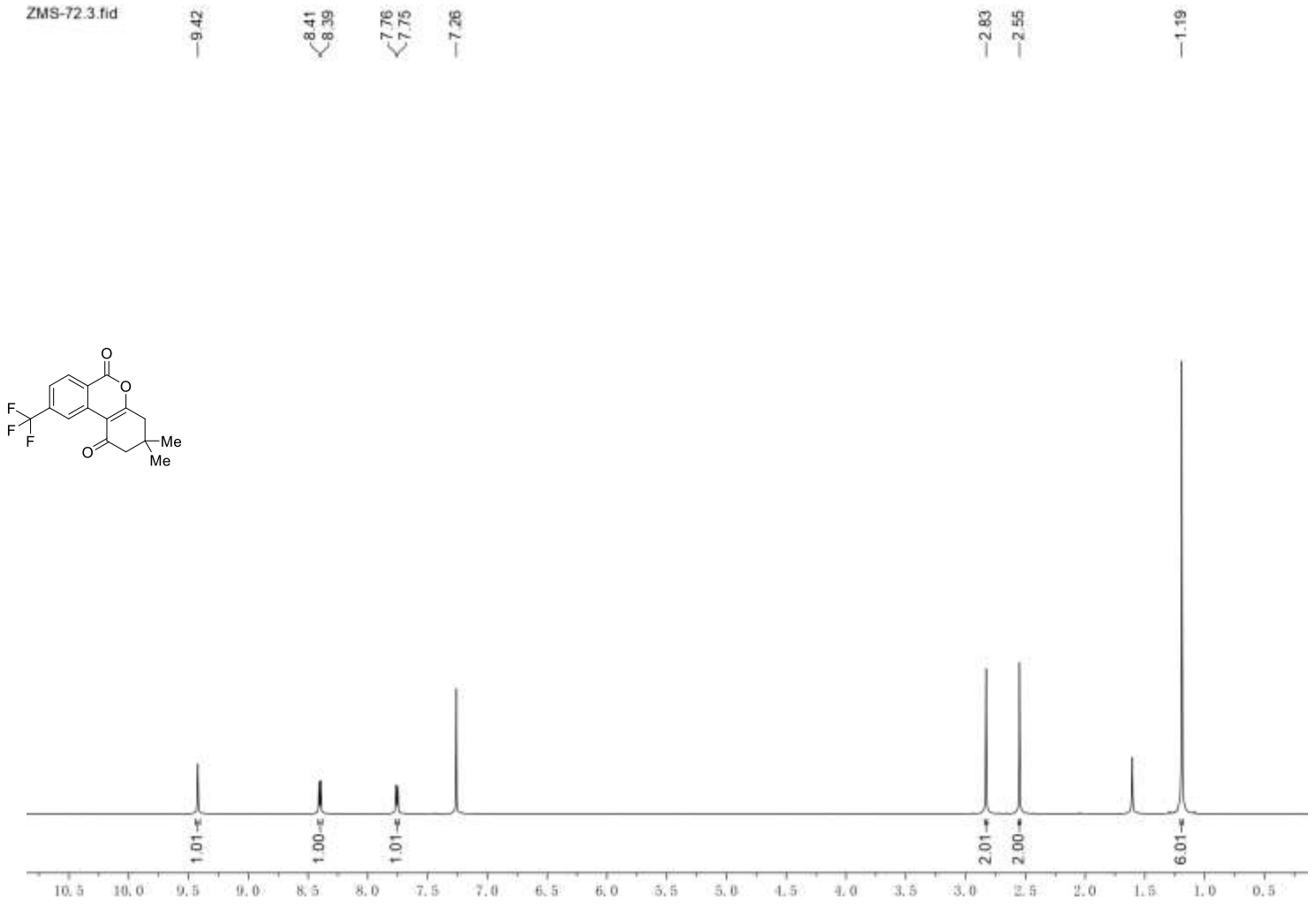


Figure S26. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3m**

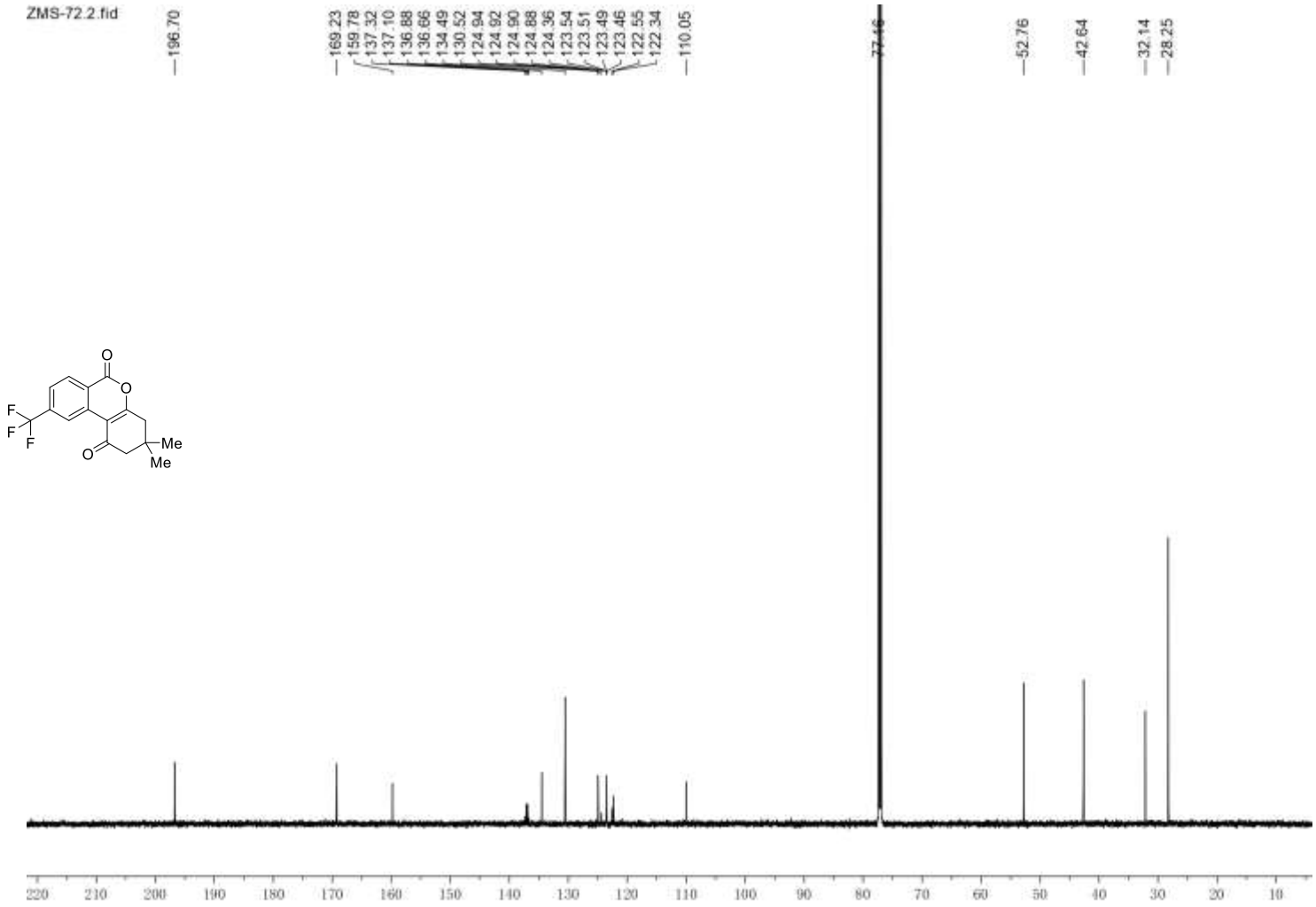


Figure S27. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3m**

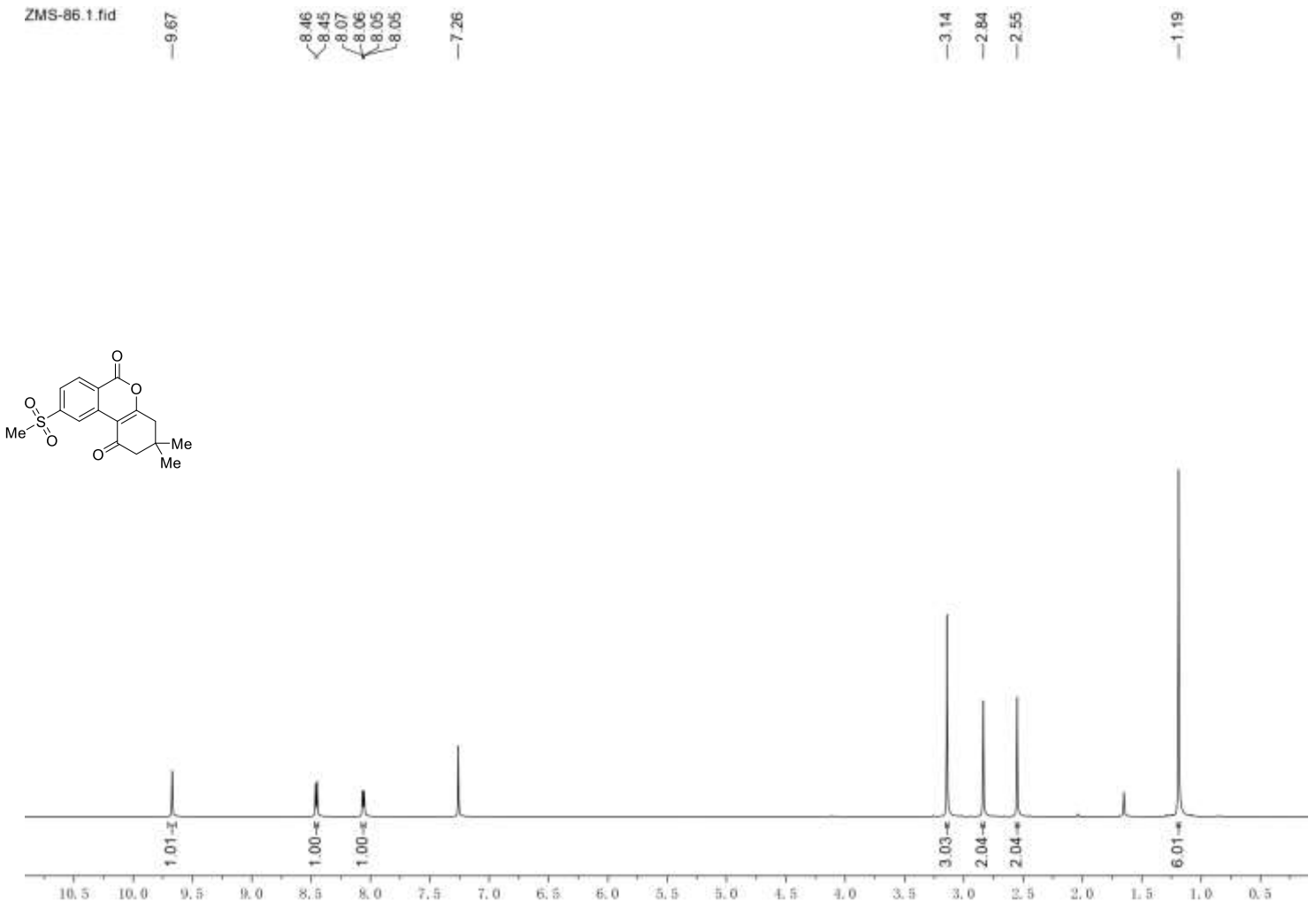


Figure S28. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3n**

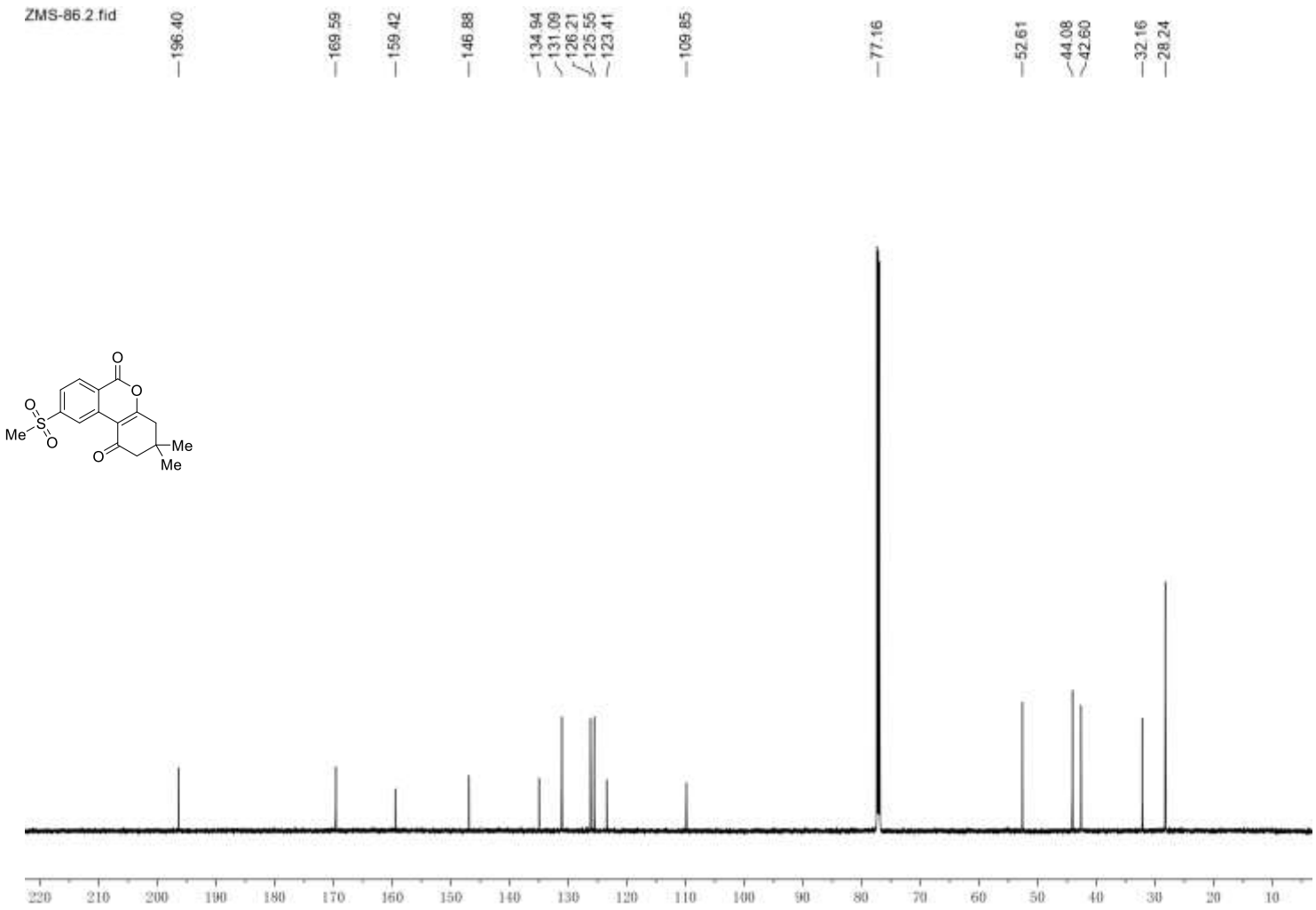


Figure S29. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3n**

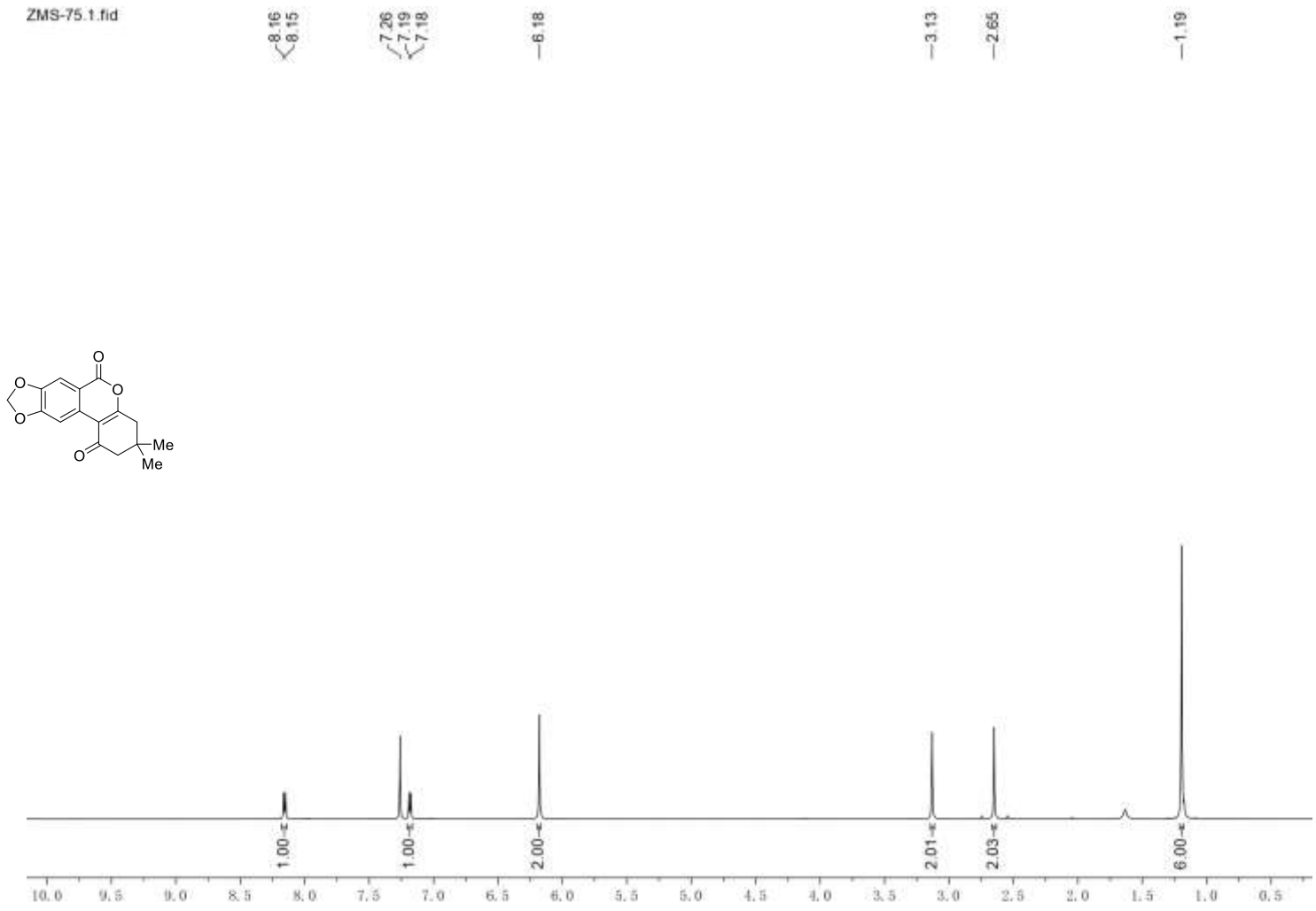


Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3o**

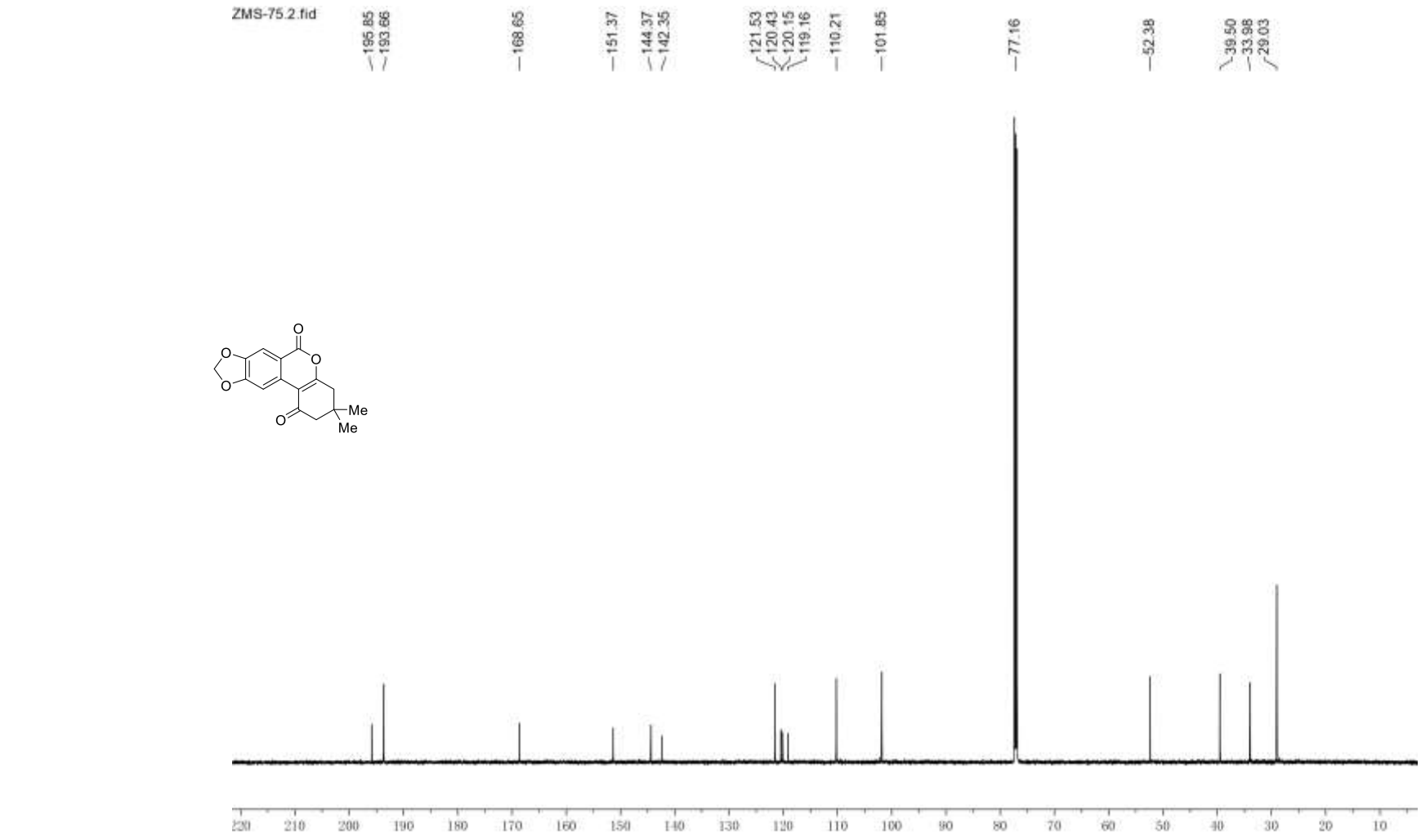


Figure S31. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3o**

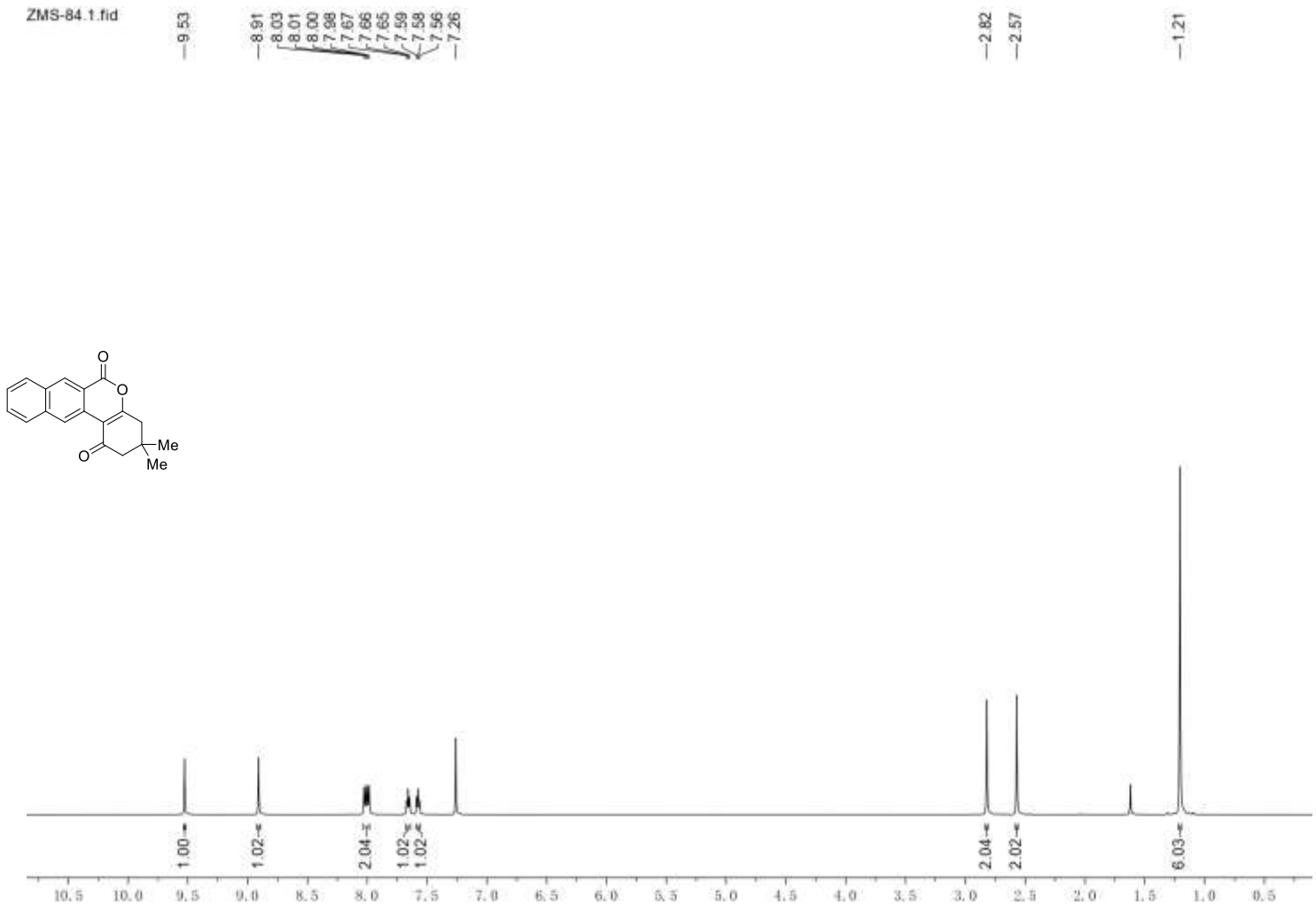


Figure S32. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3p**

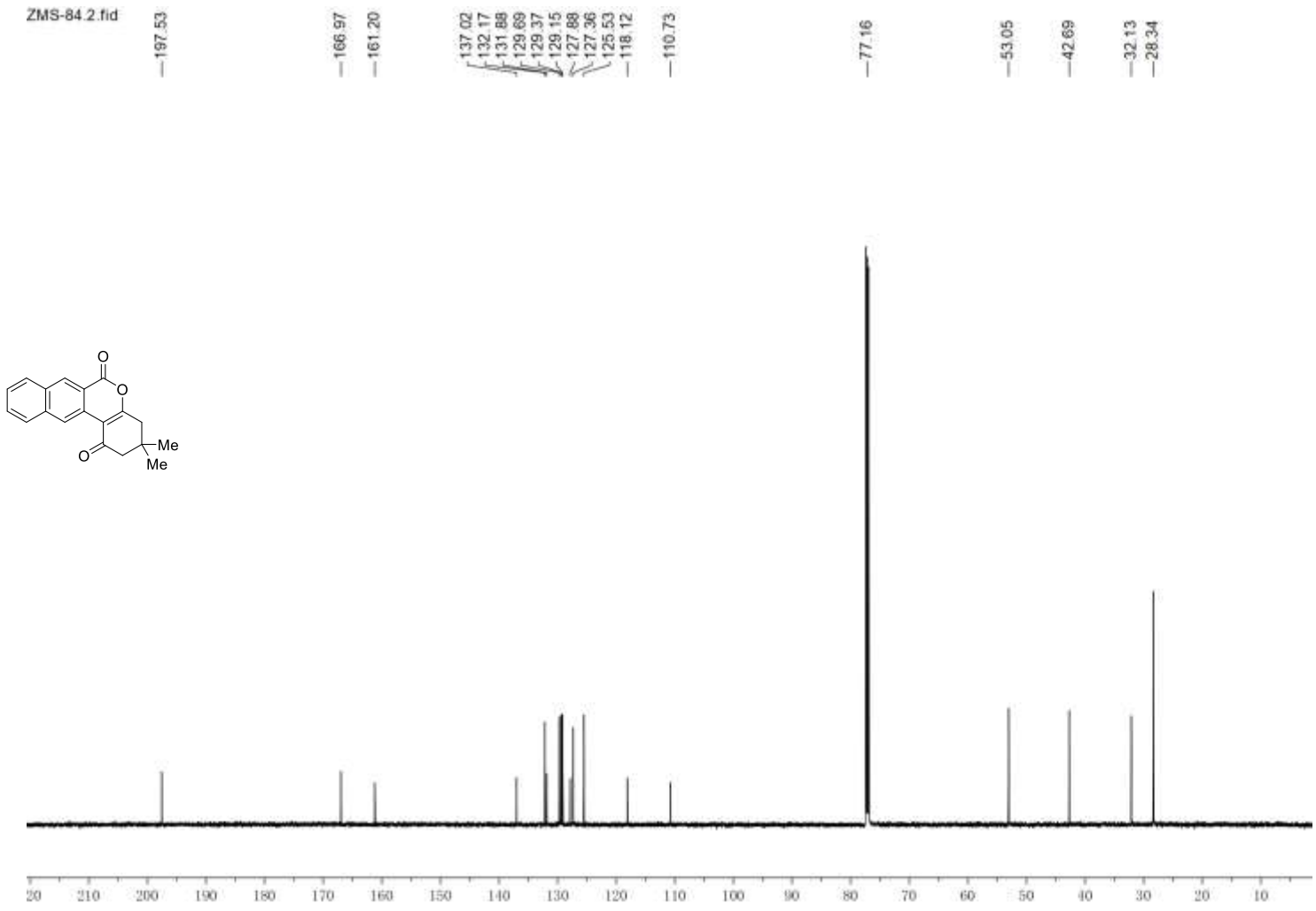


Figure S33. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3p**

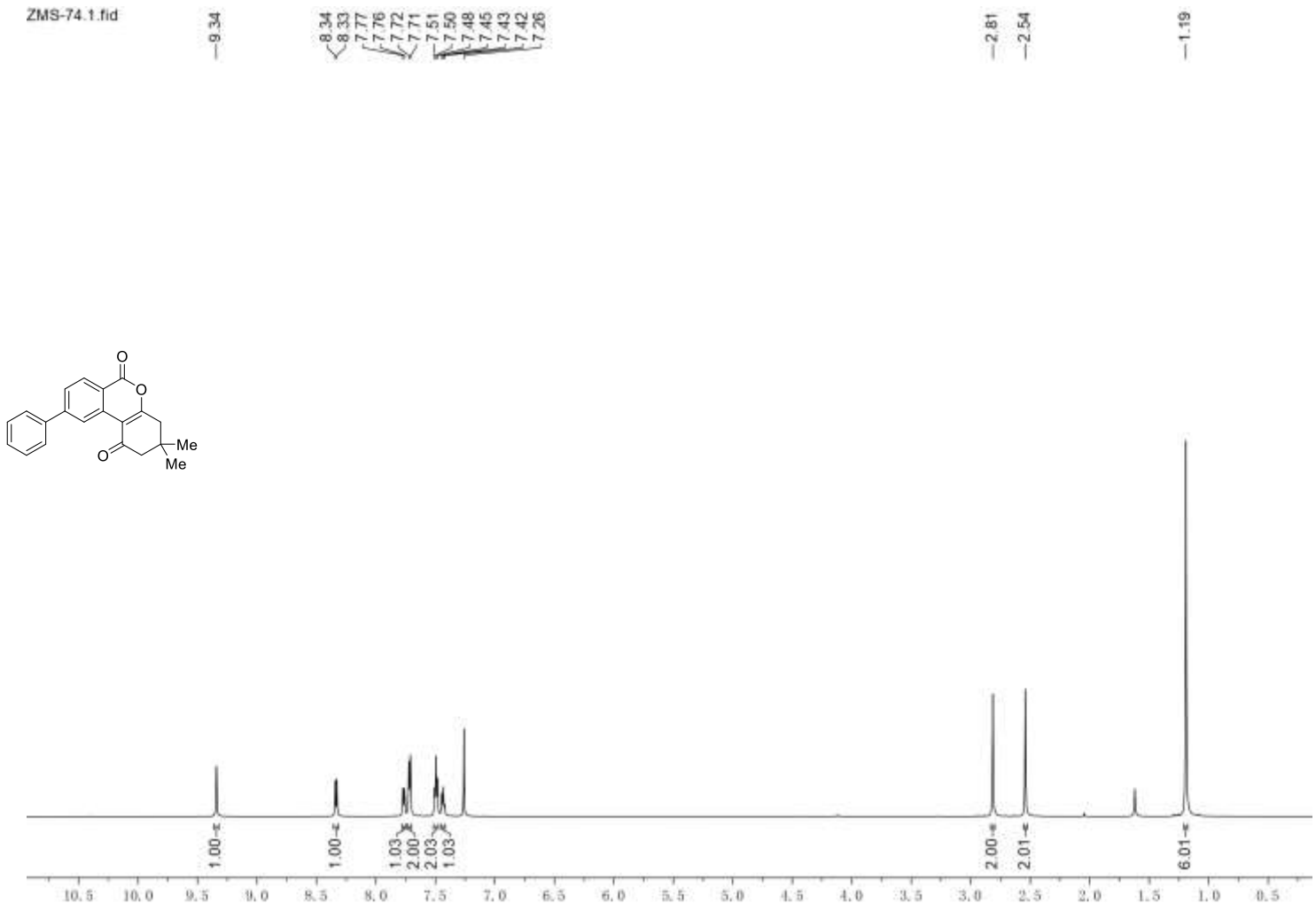


Figure S34. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3q**

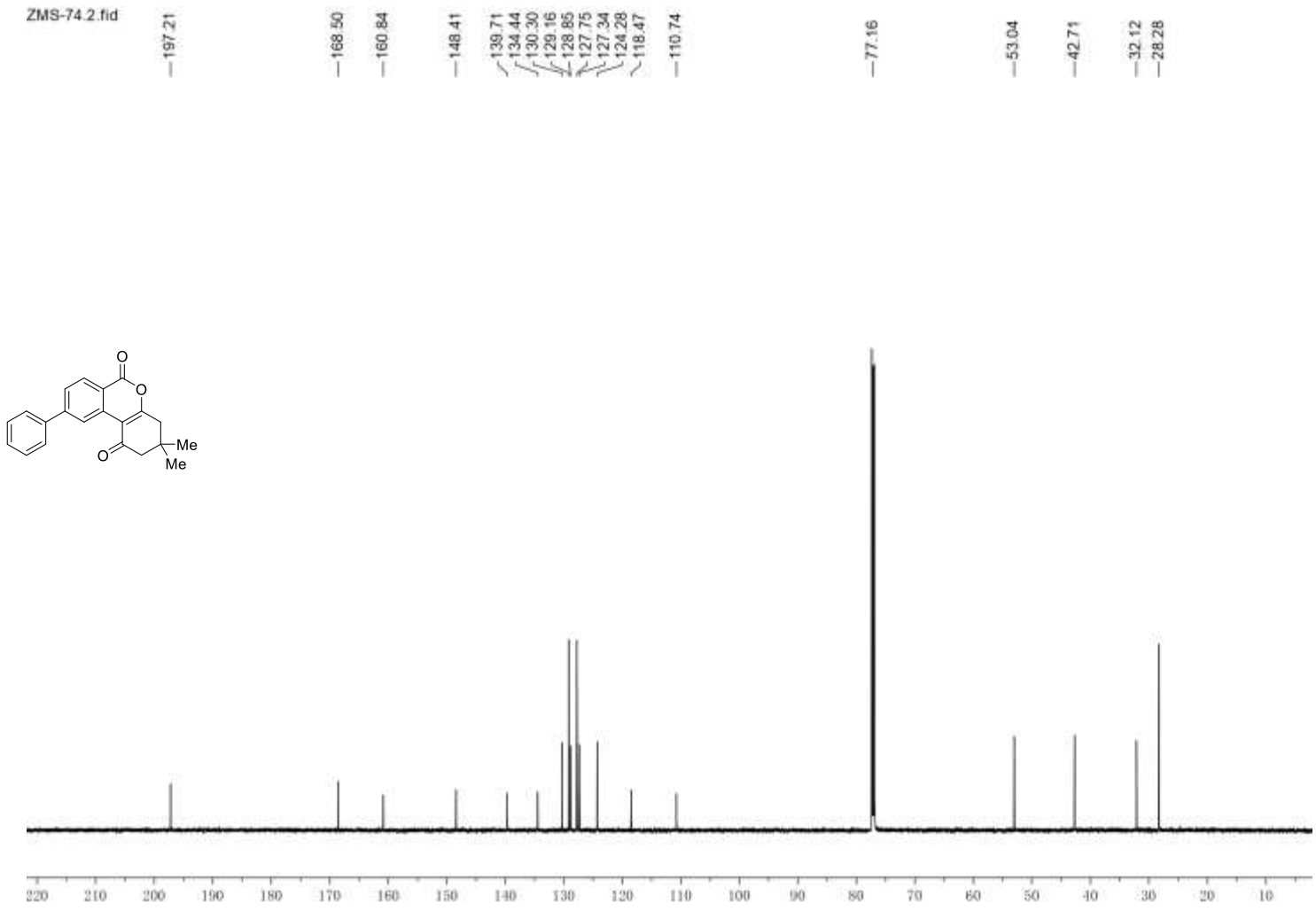


Figure S35. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3q**

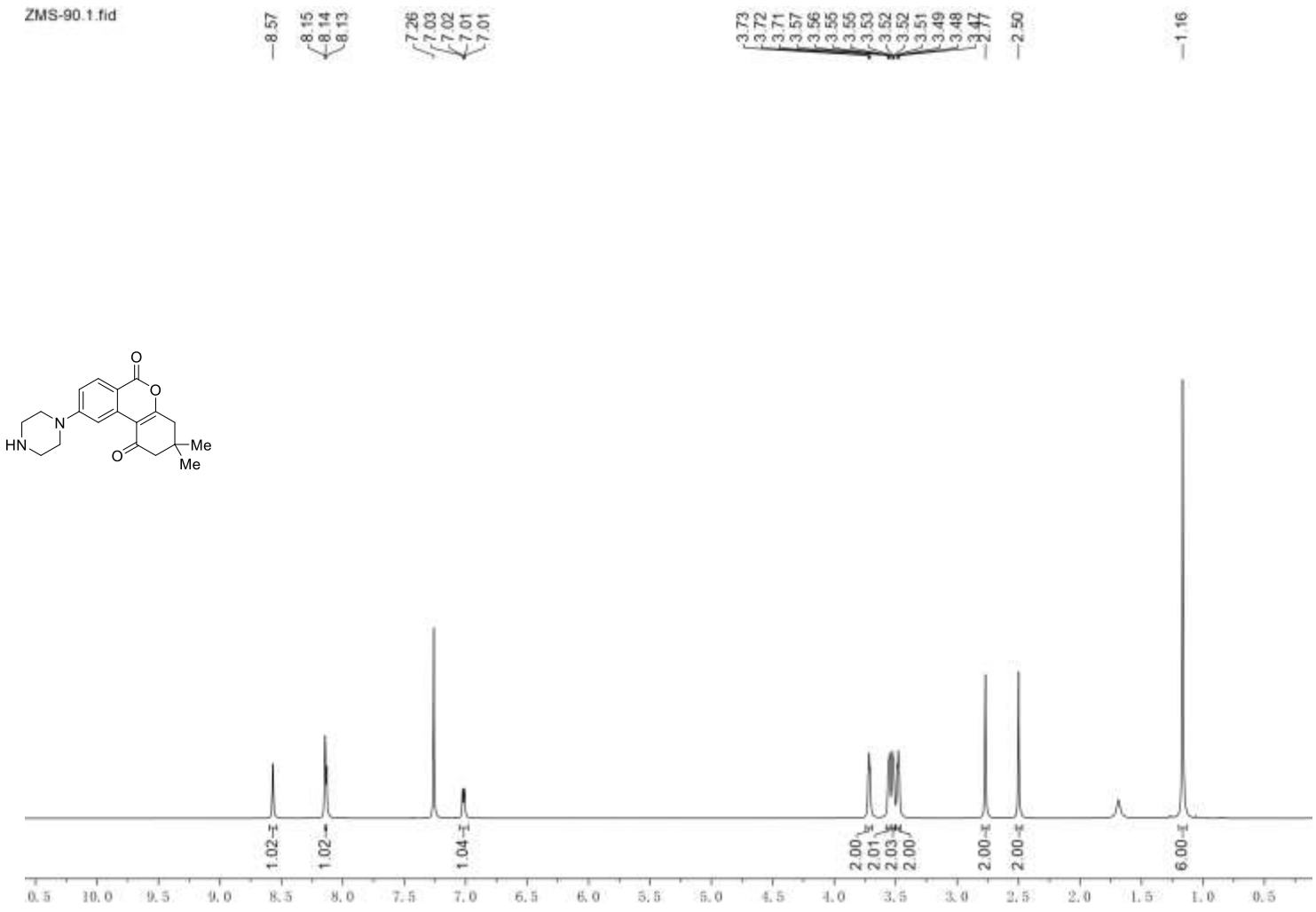


Figure S36. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3r**

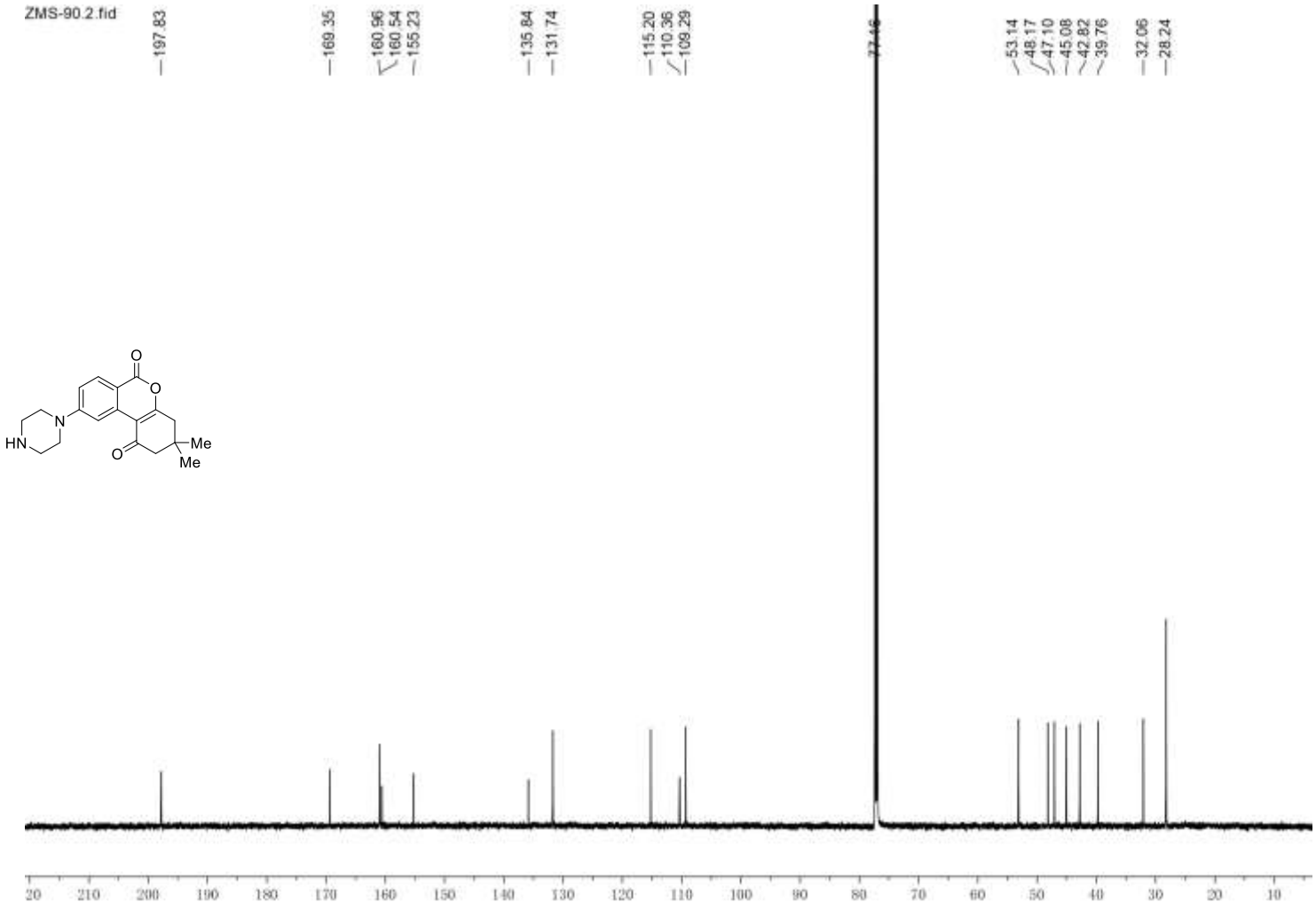


Figure S37. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3r**

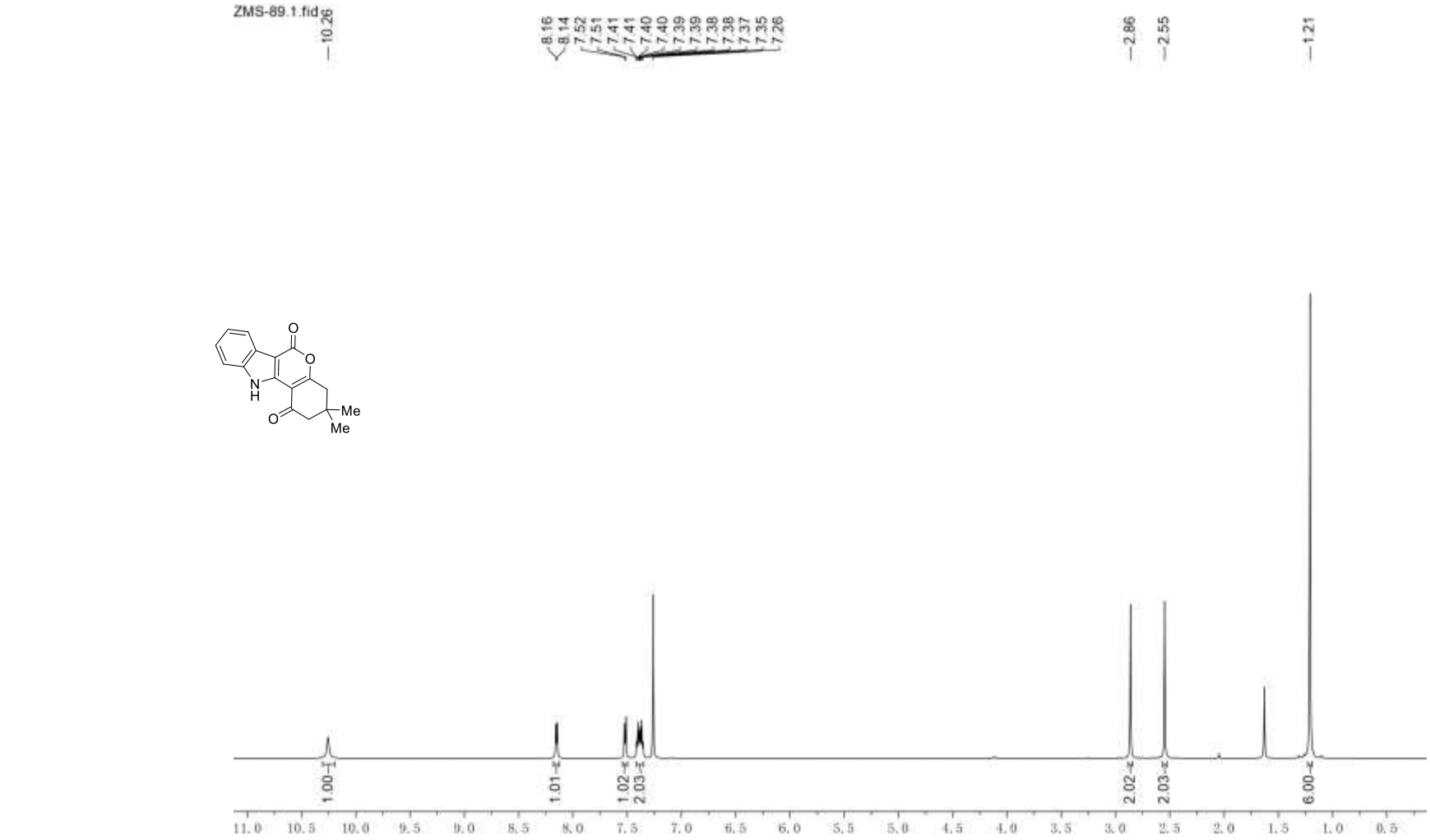


Figure S38. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3s**

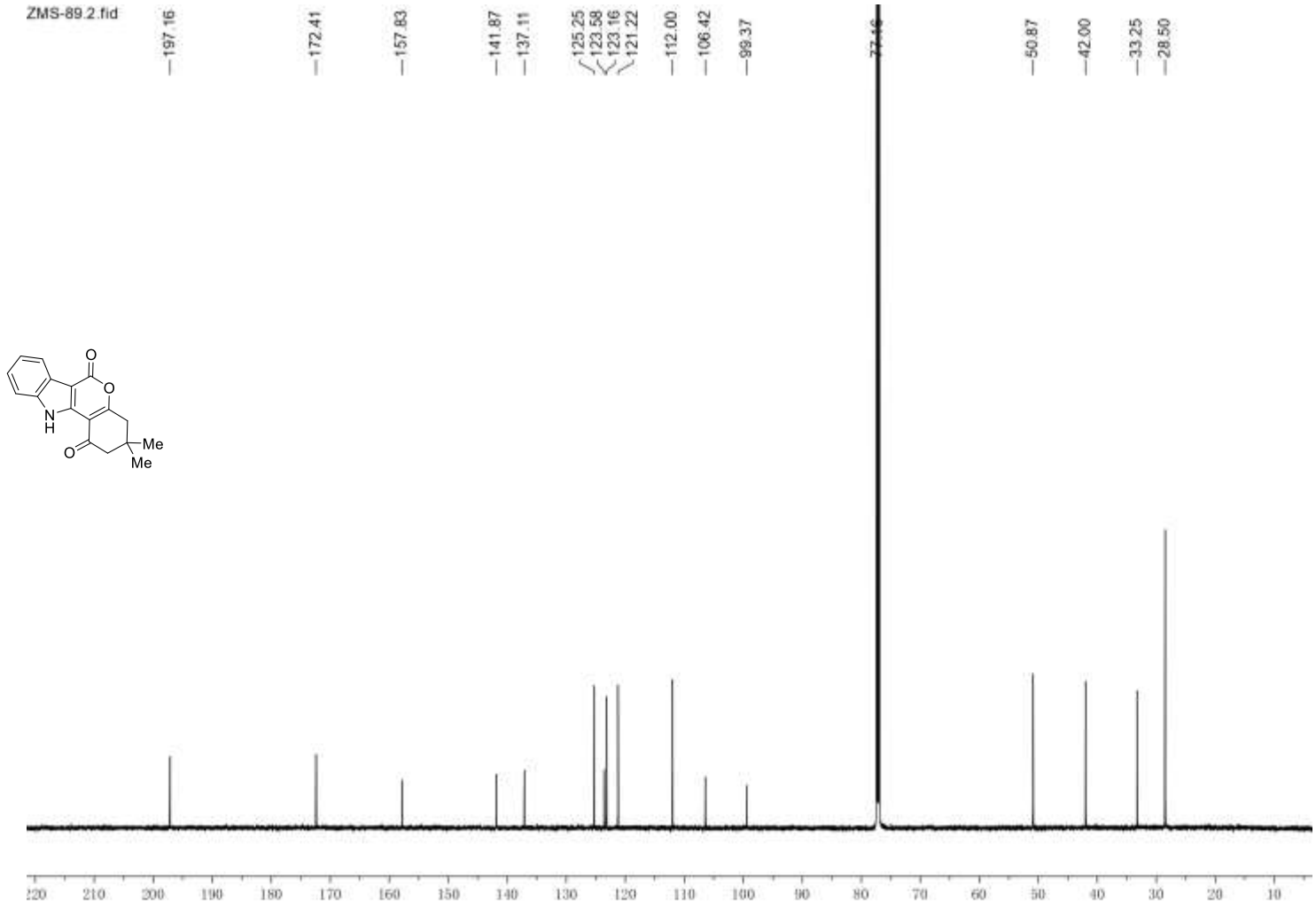


Figure S39. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3s**

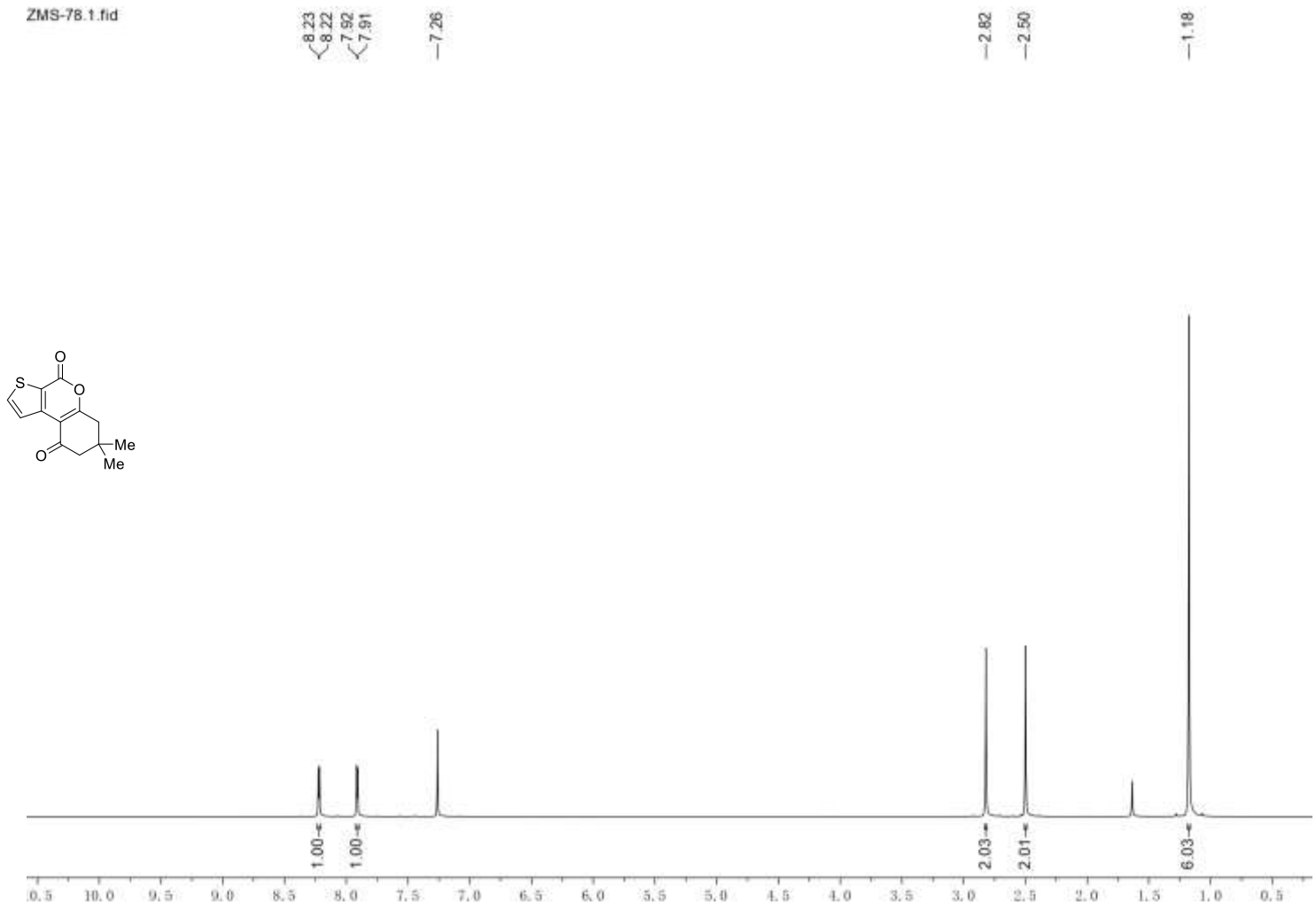


Figure S40. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3t**

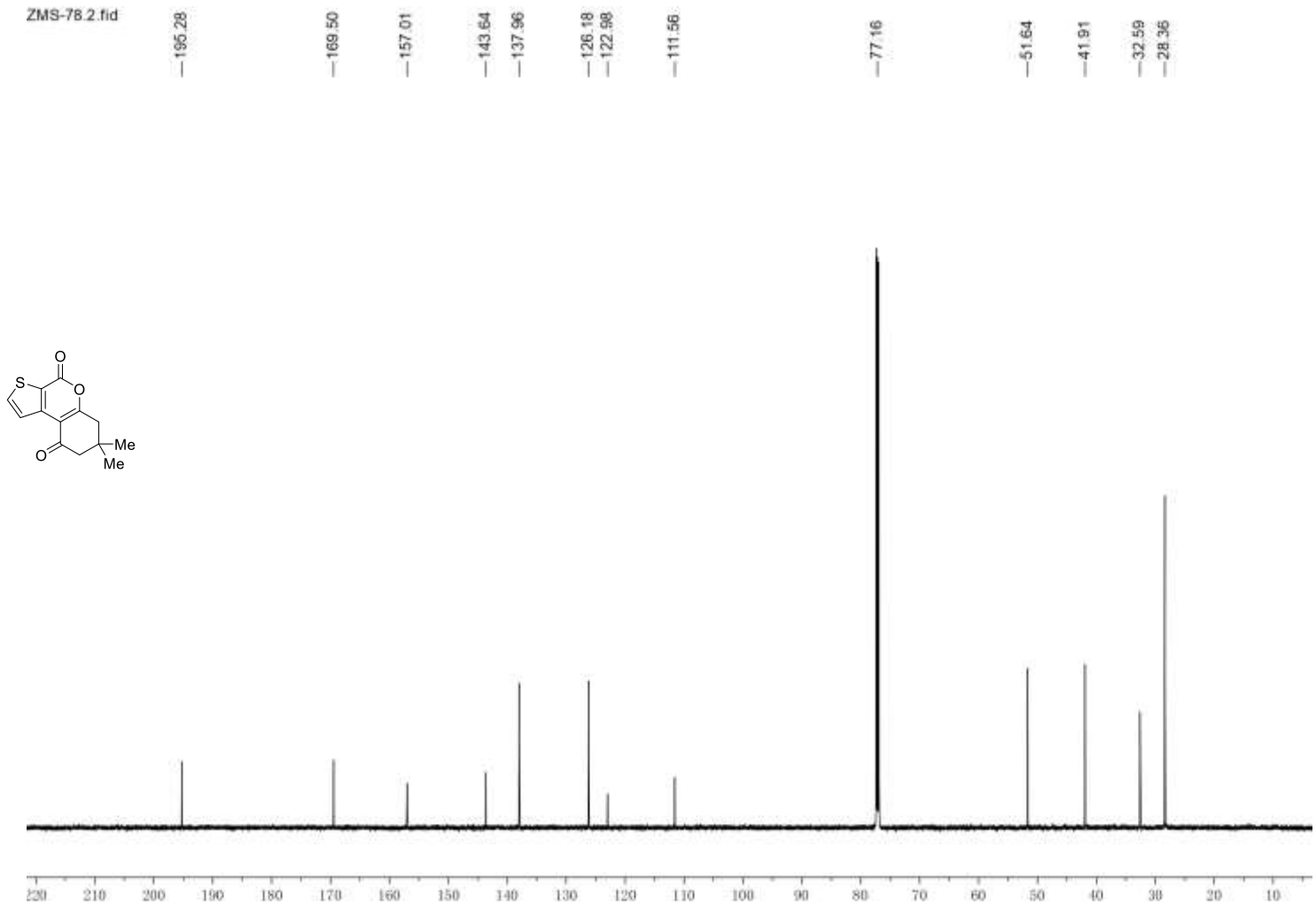


Figure S41. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3t**

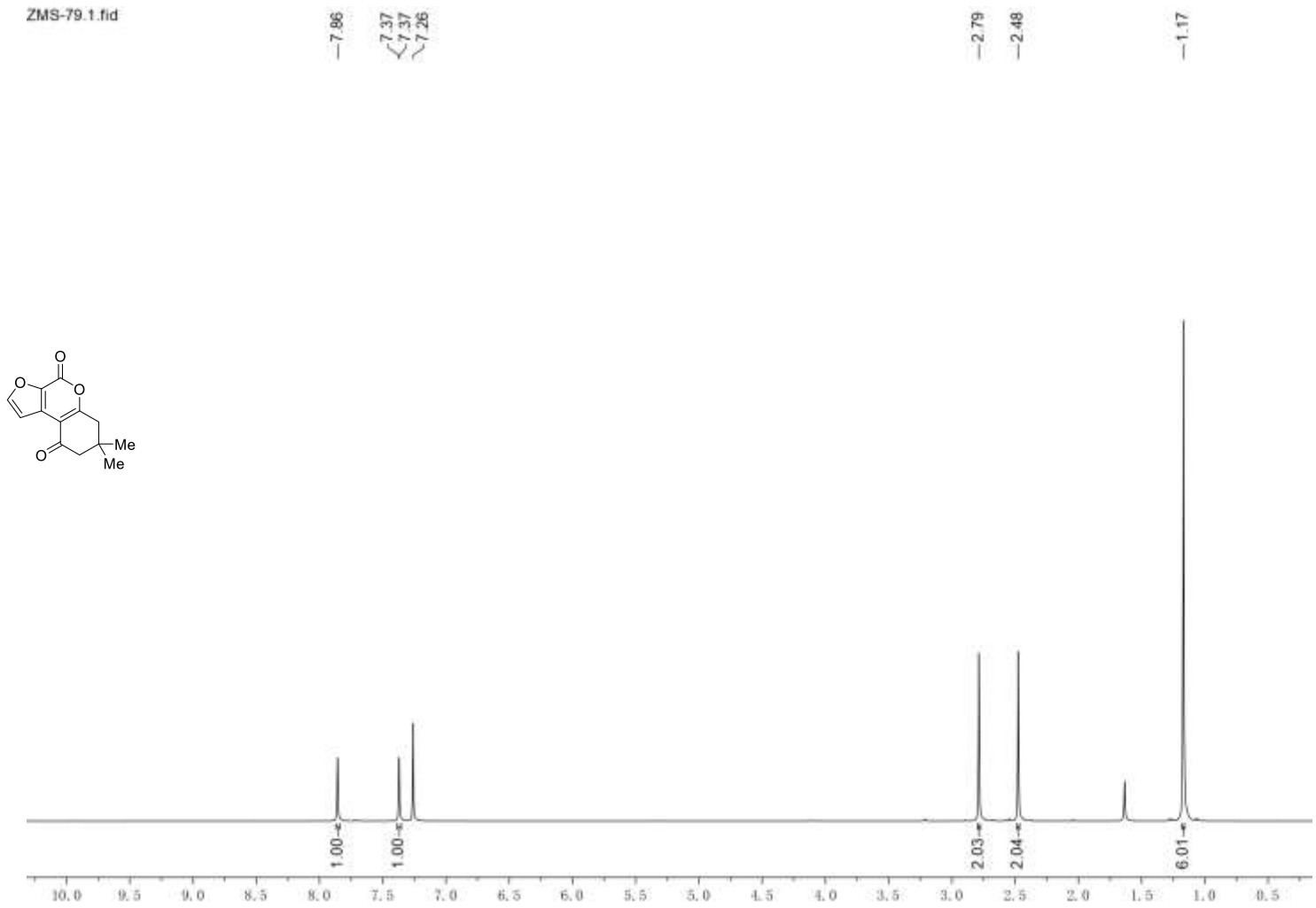


Figure S42. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3u**

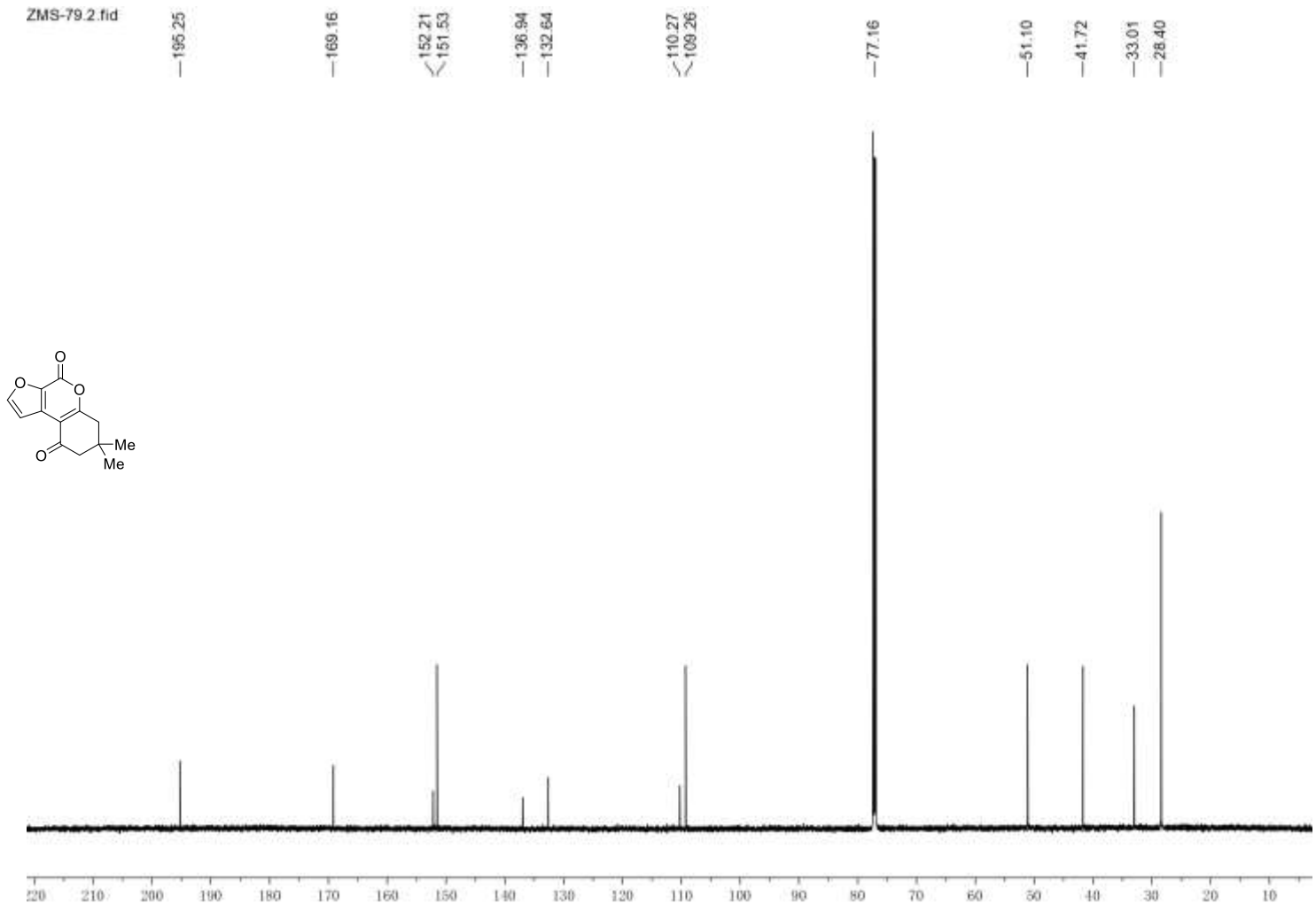


Figure S43. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3u**

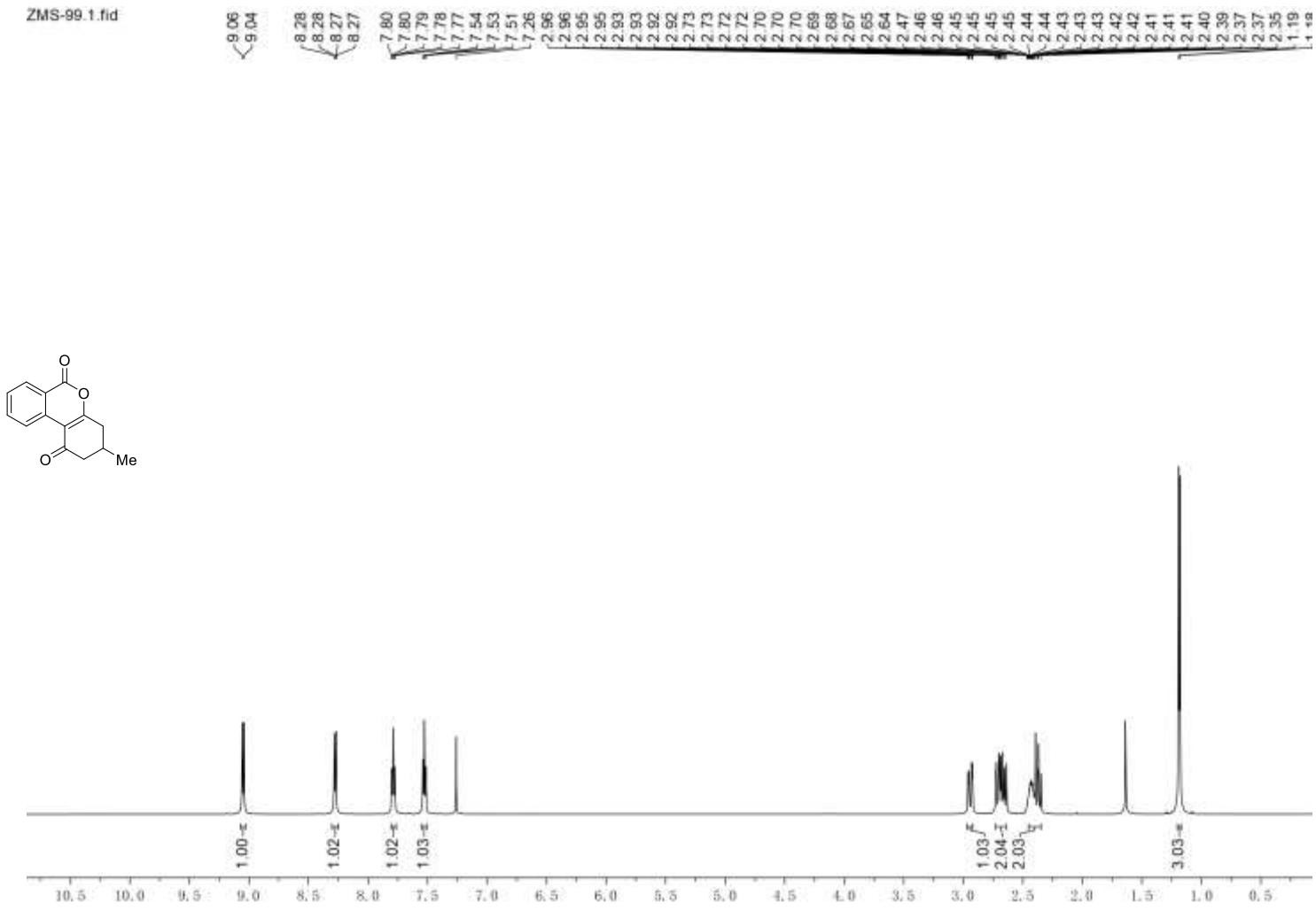


Figure S44. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3x**

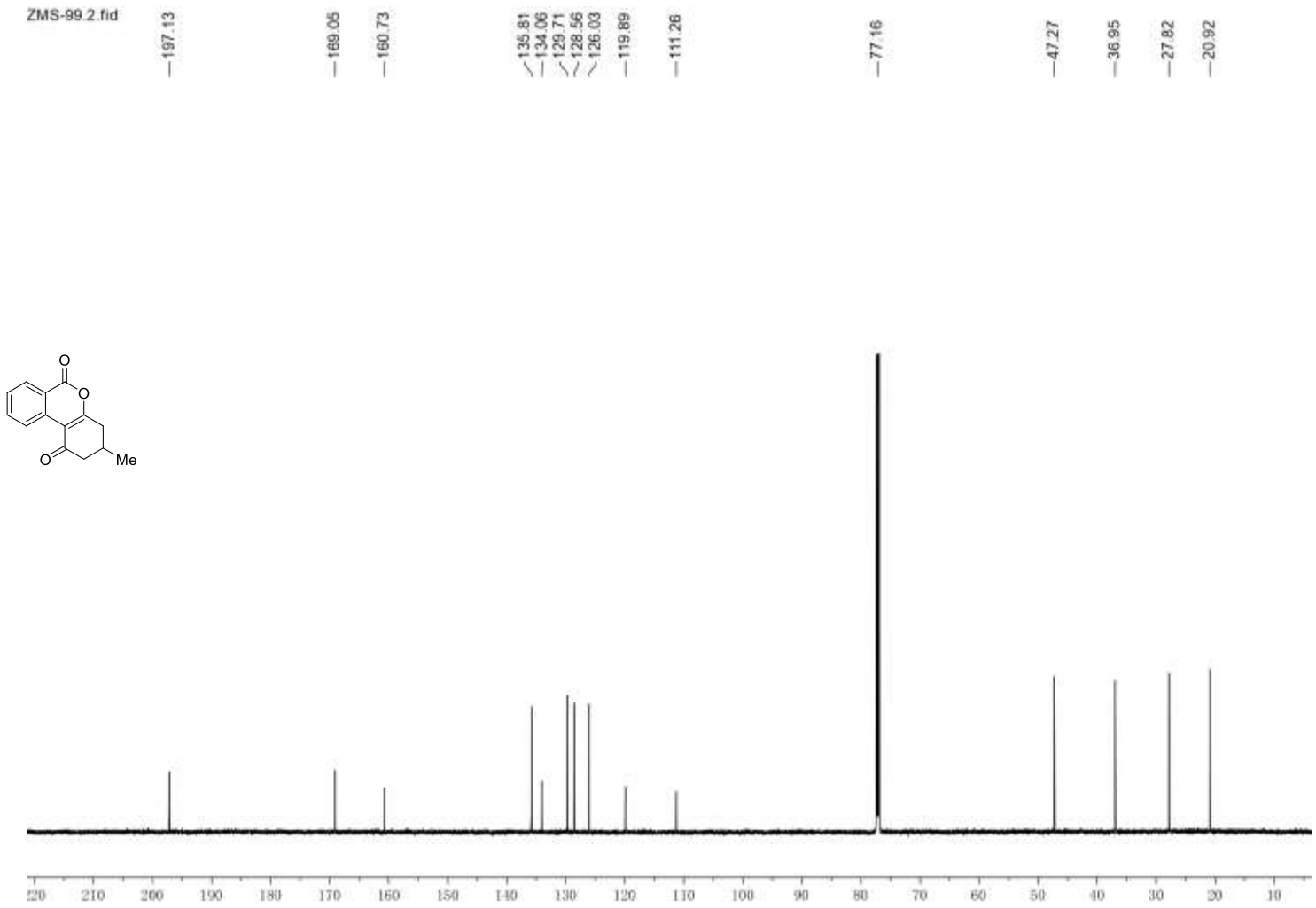


Figure S45. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3x**

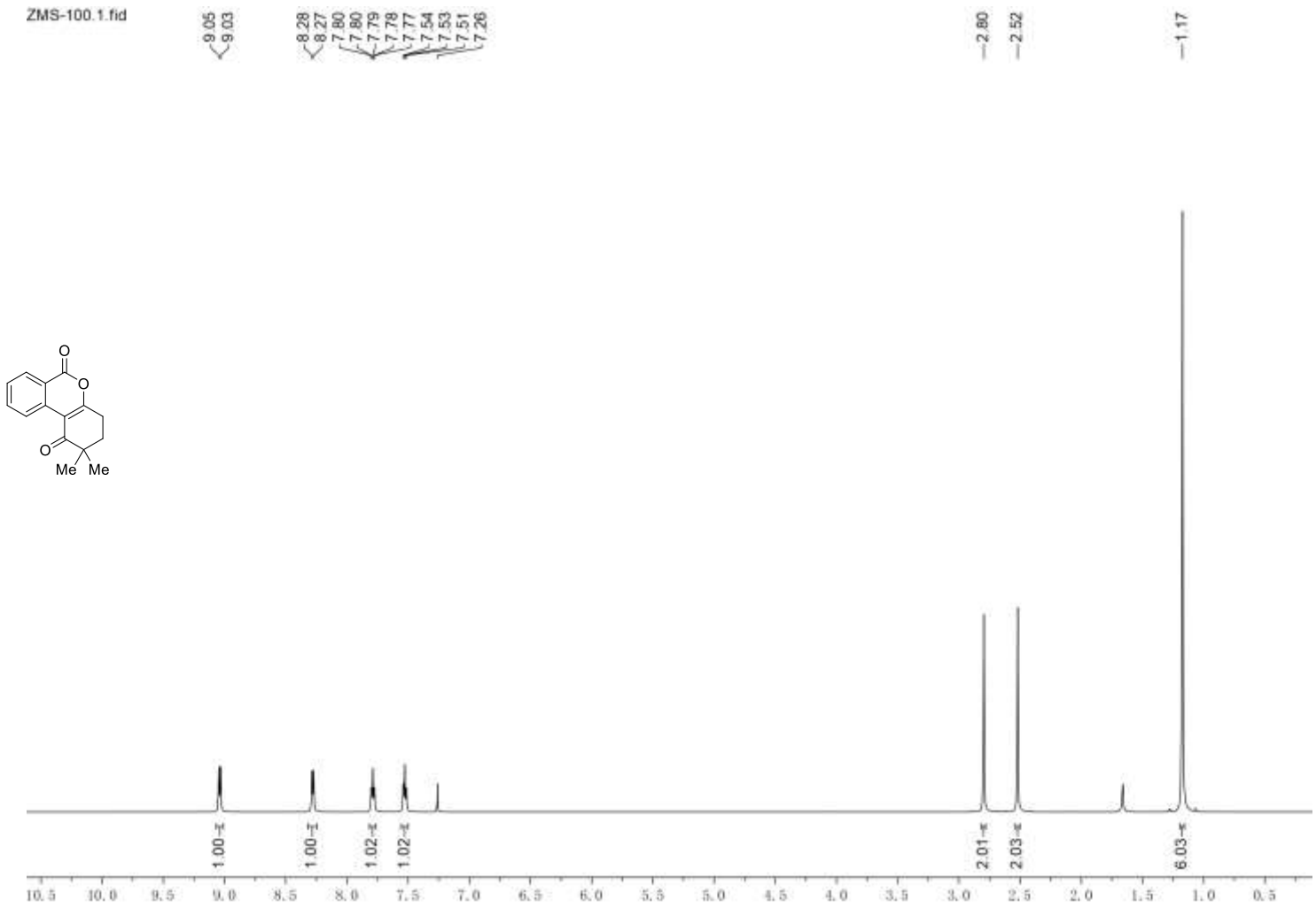


Figure S46. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3y**

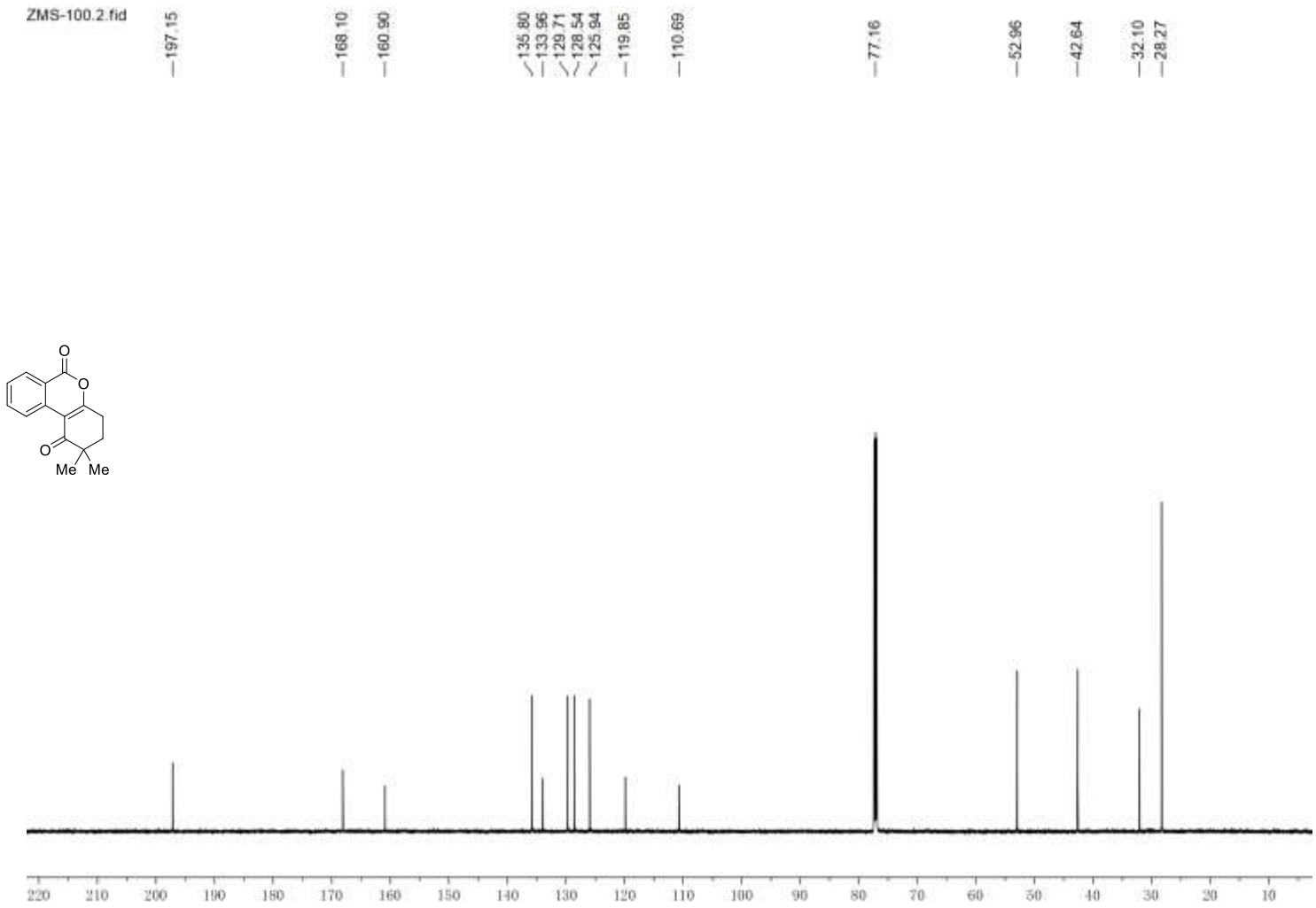


Figure S47. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3y**

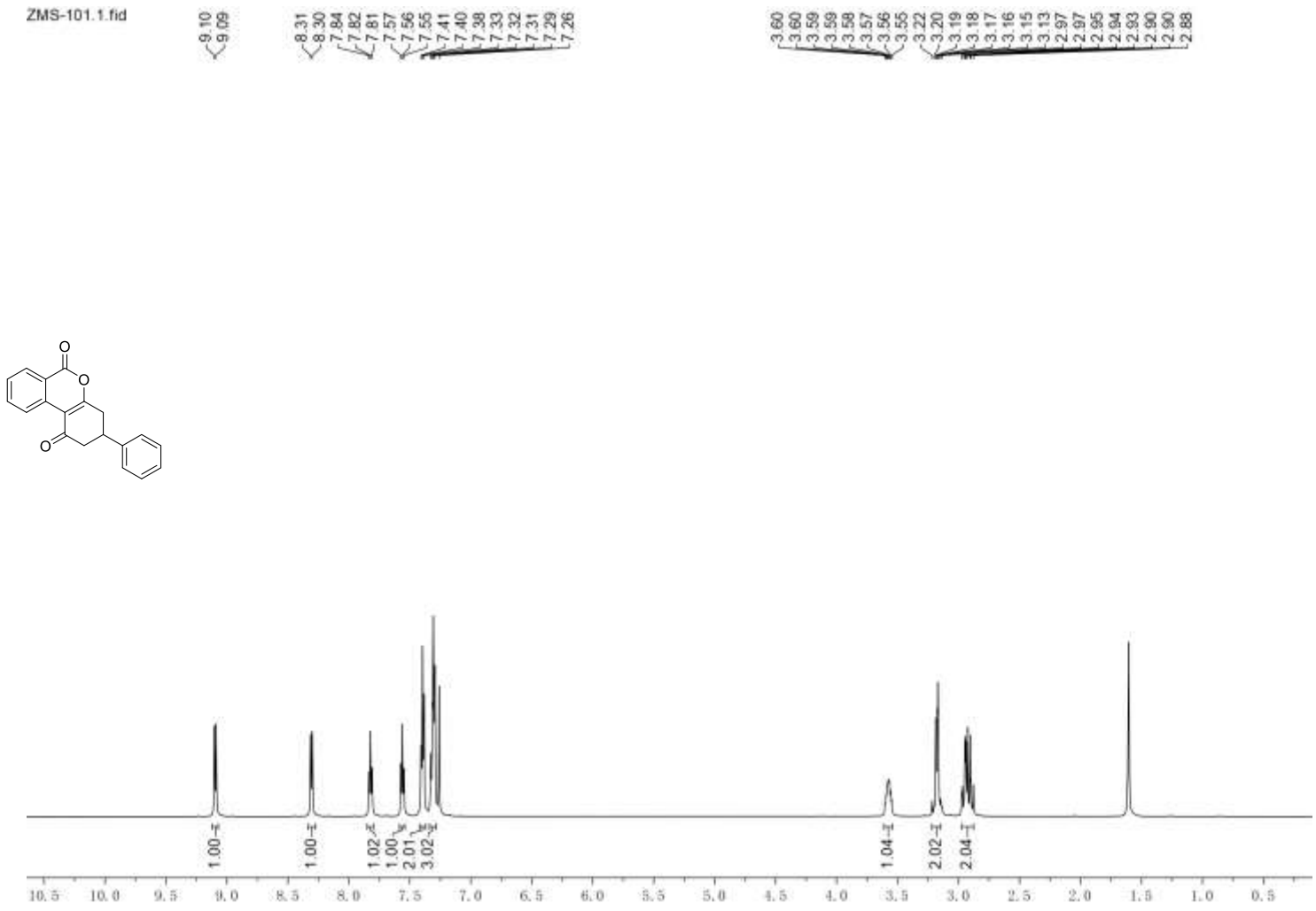


Figure S48. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3z**

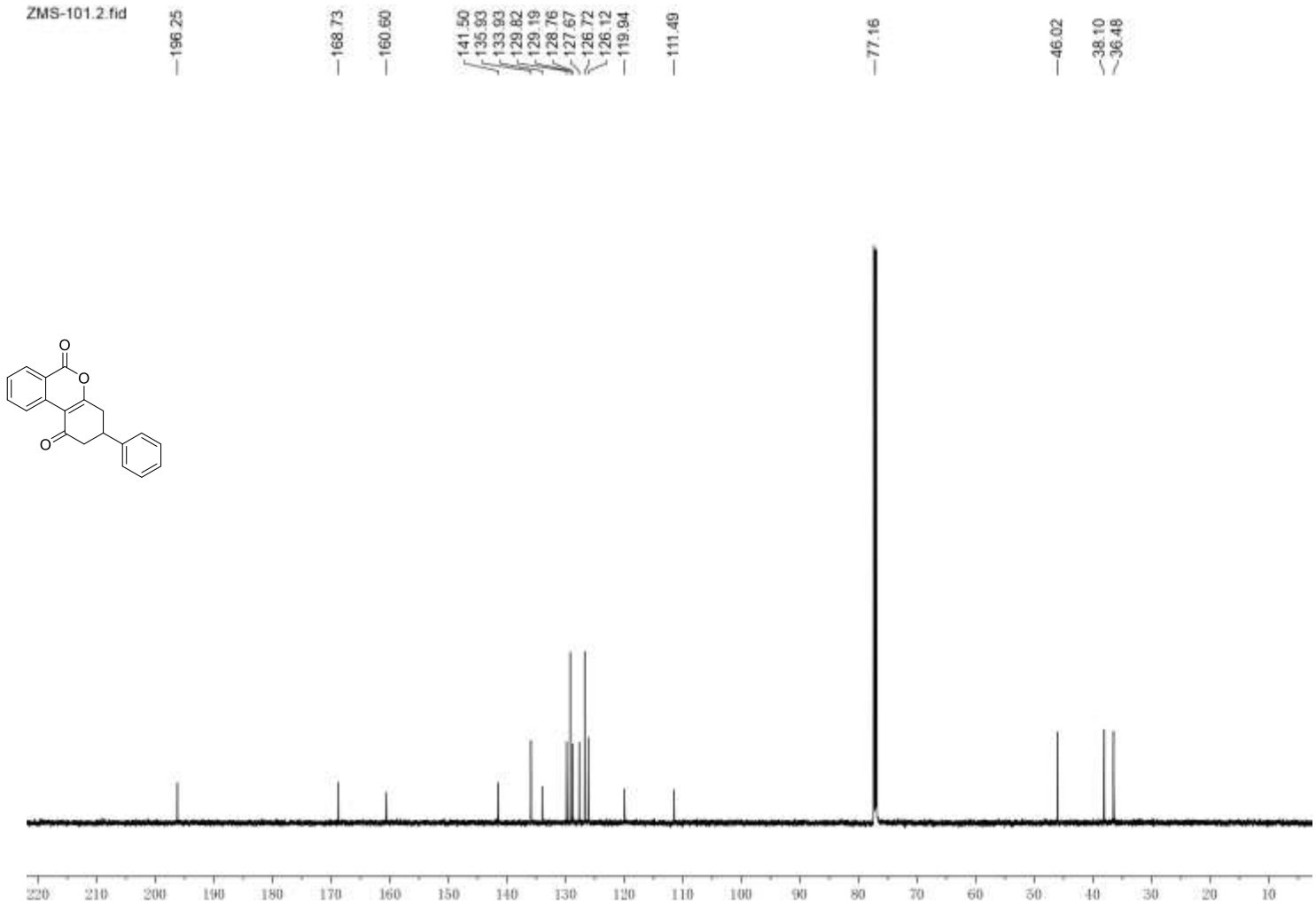


Figure S49. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3z**

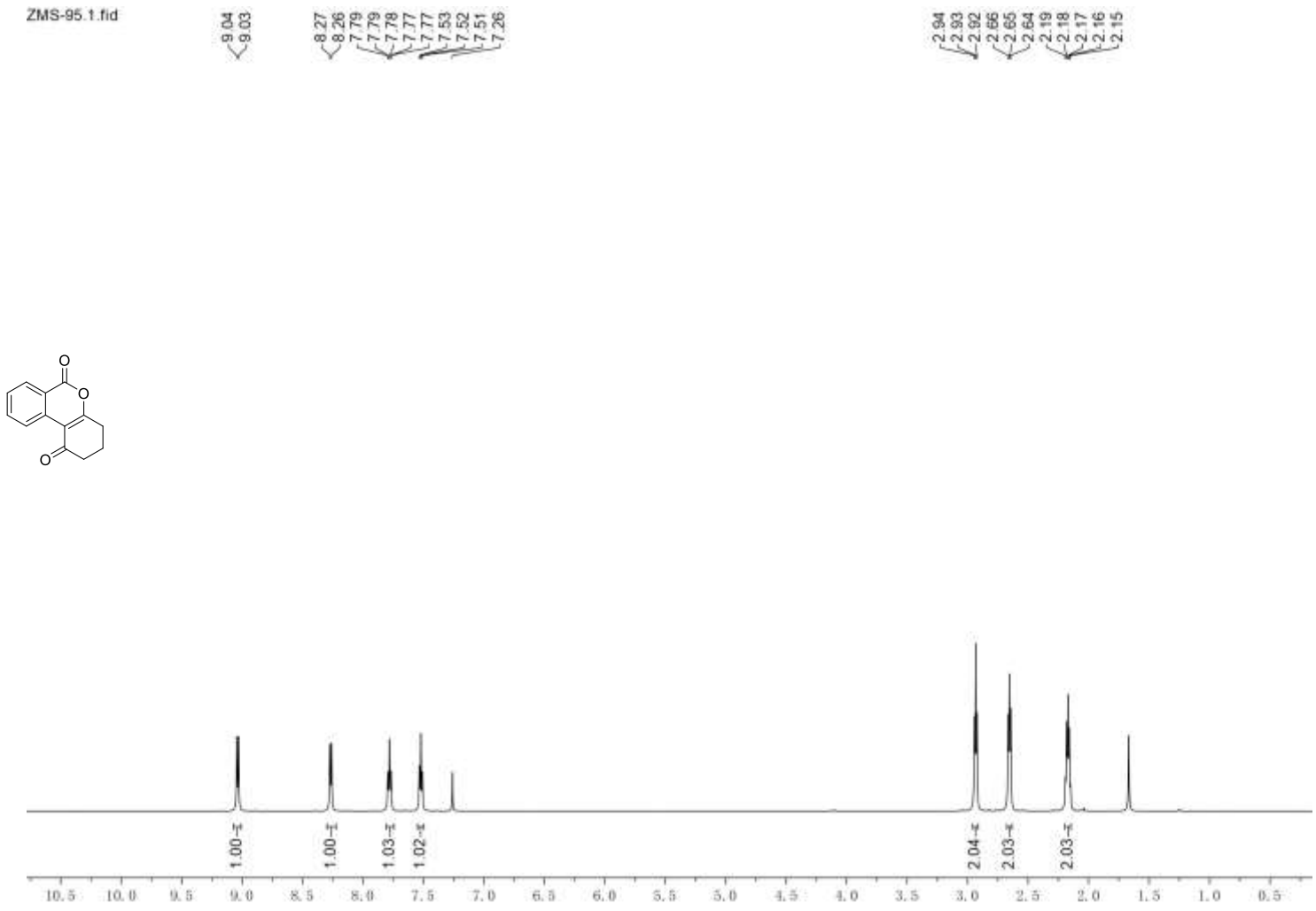


Figure S50. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3a'**

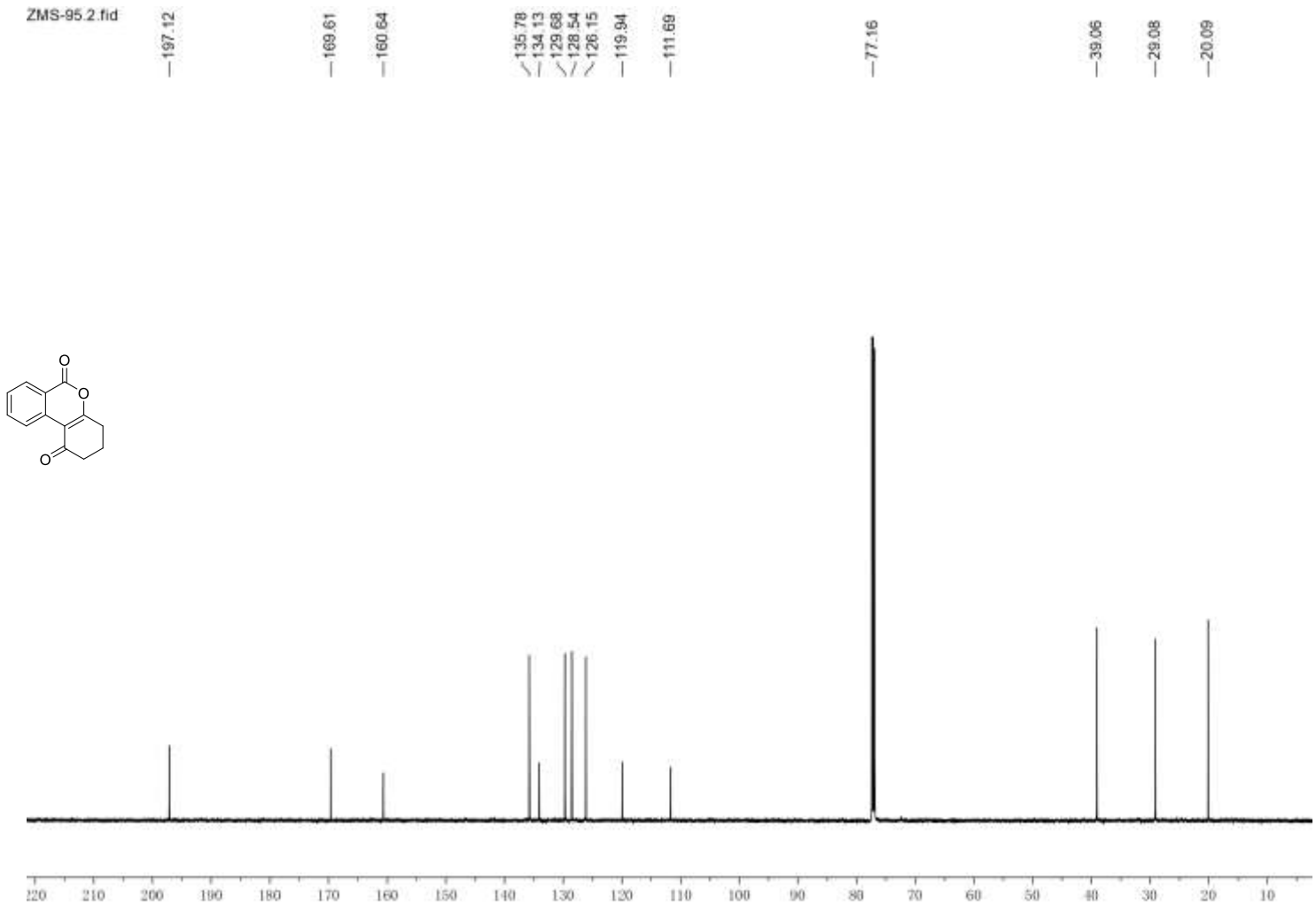


Figure S51. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3a'**

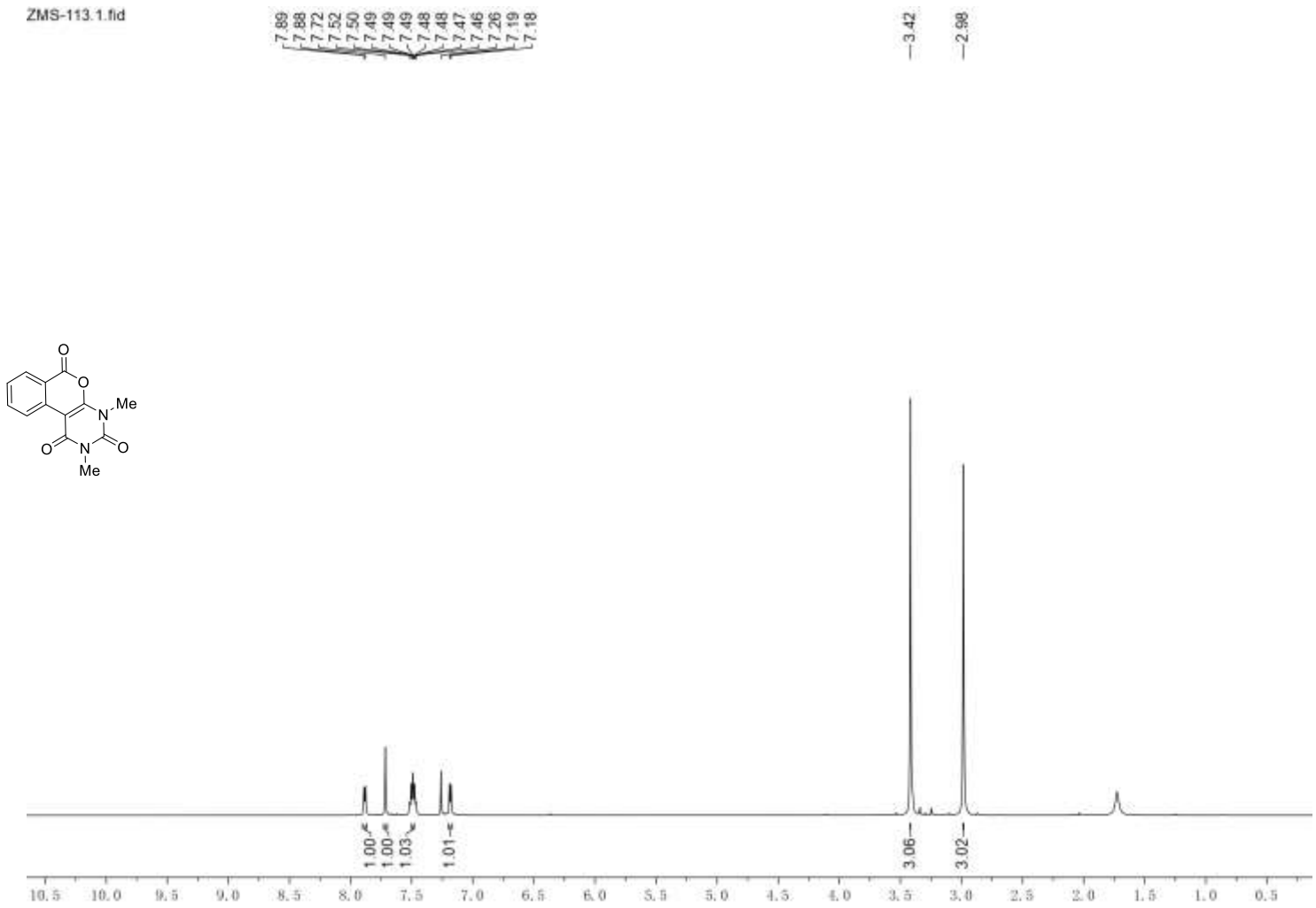


Figure S52. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3b'**

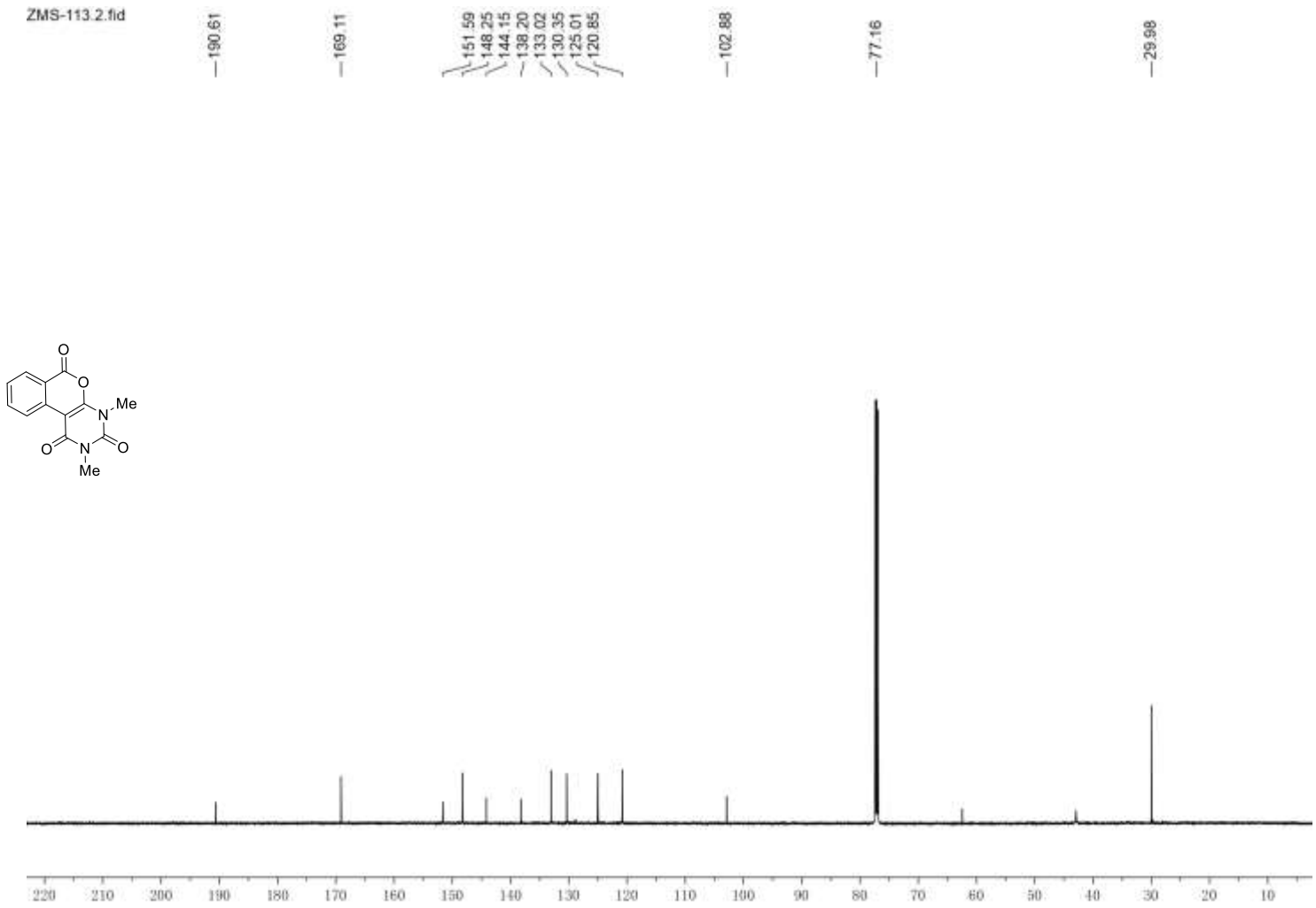


Figure S53. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3b'**

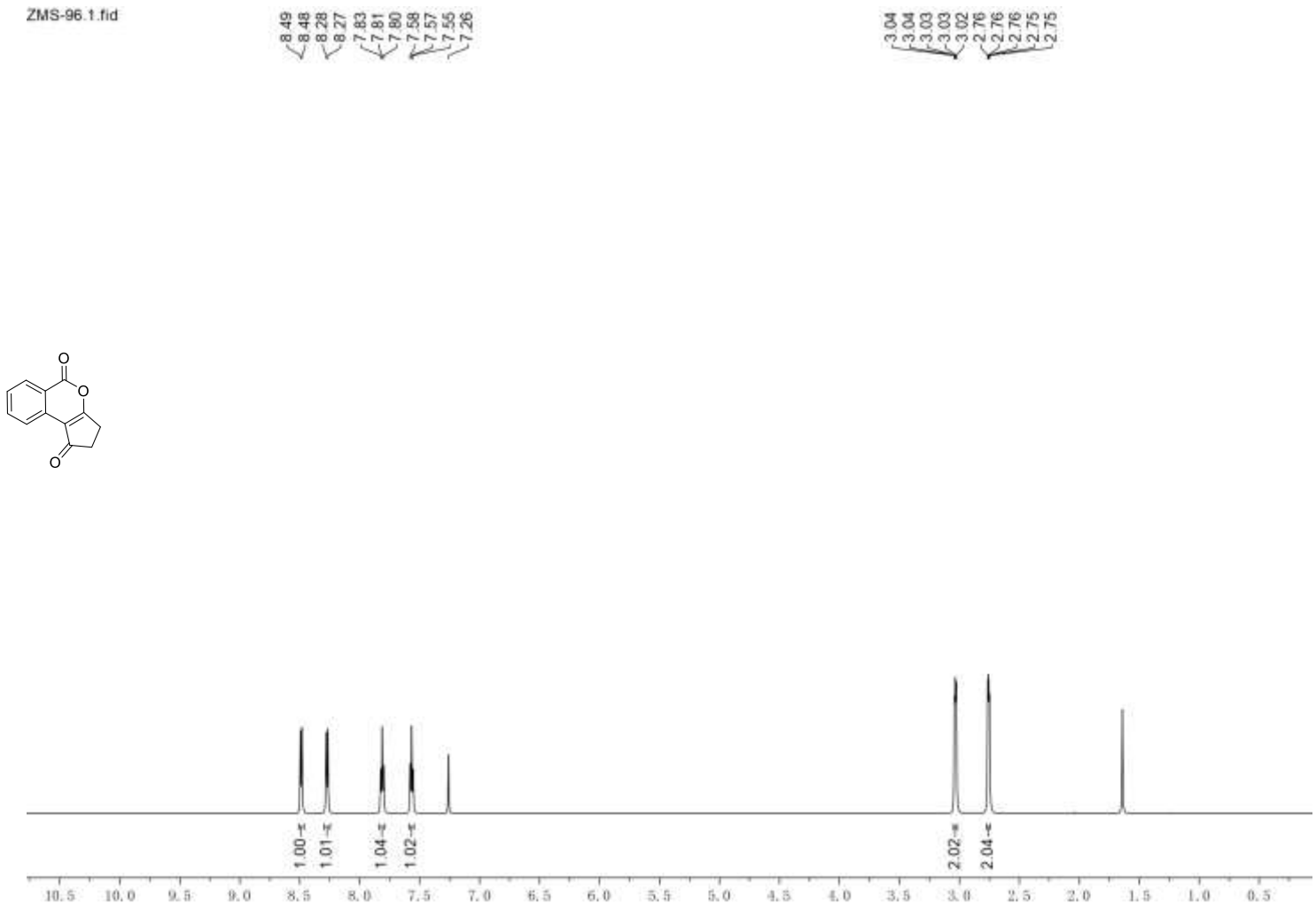


Figure S54. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3c'**

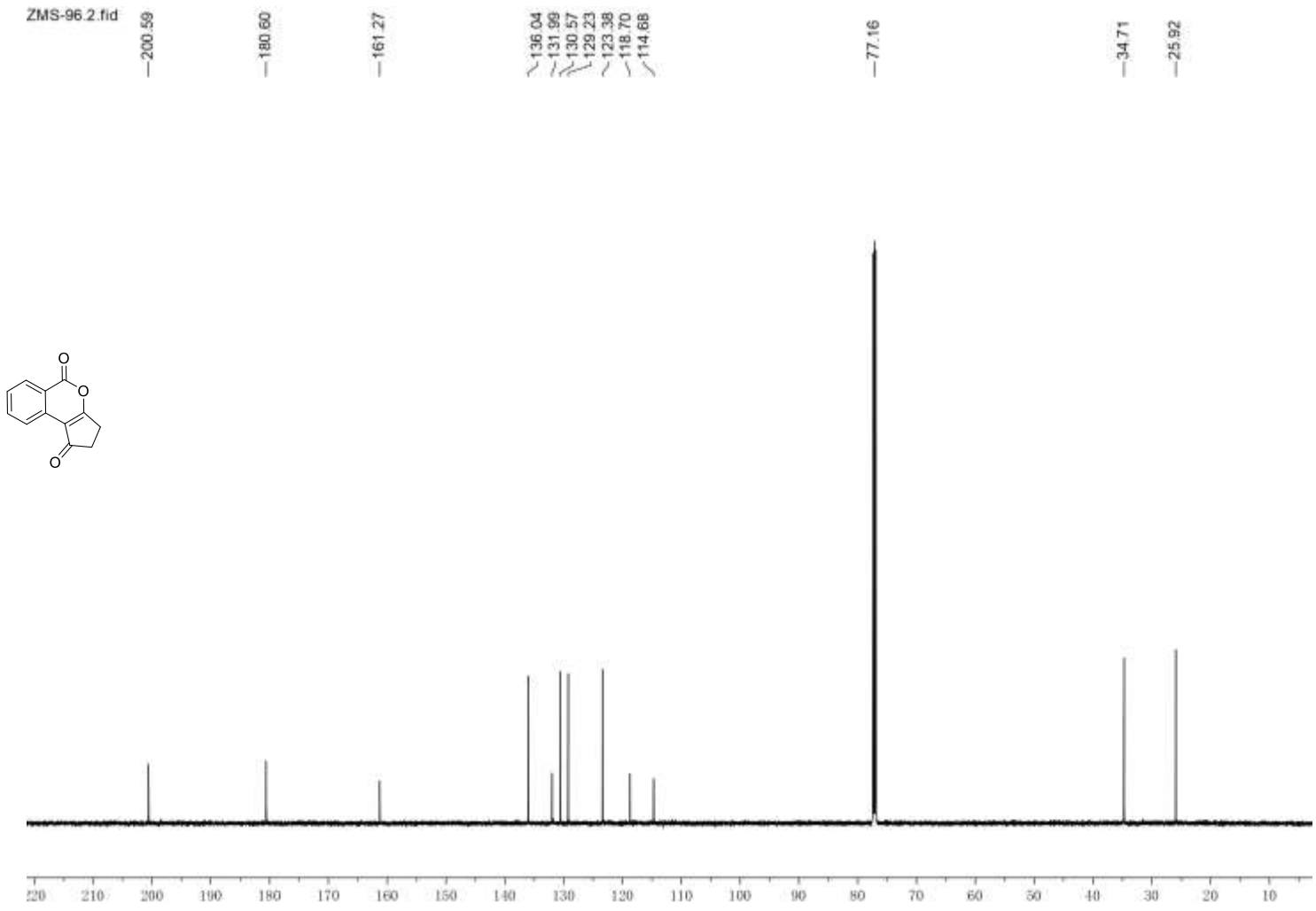


Figure S55. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3c'**

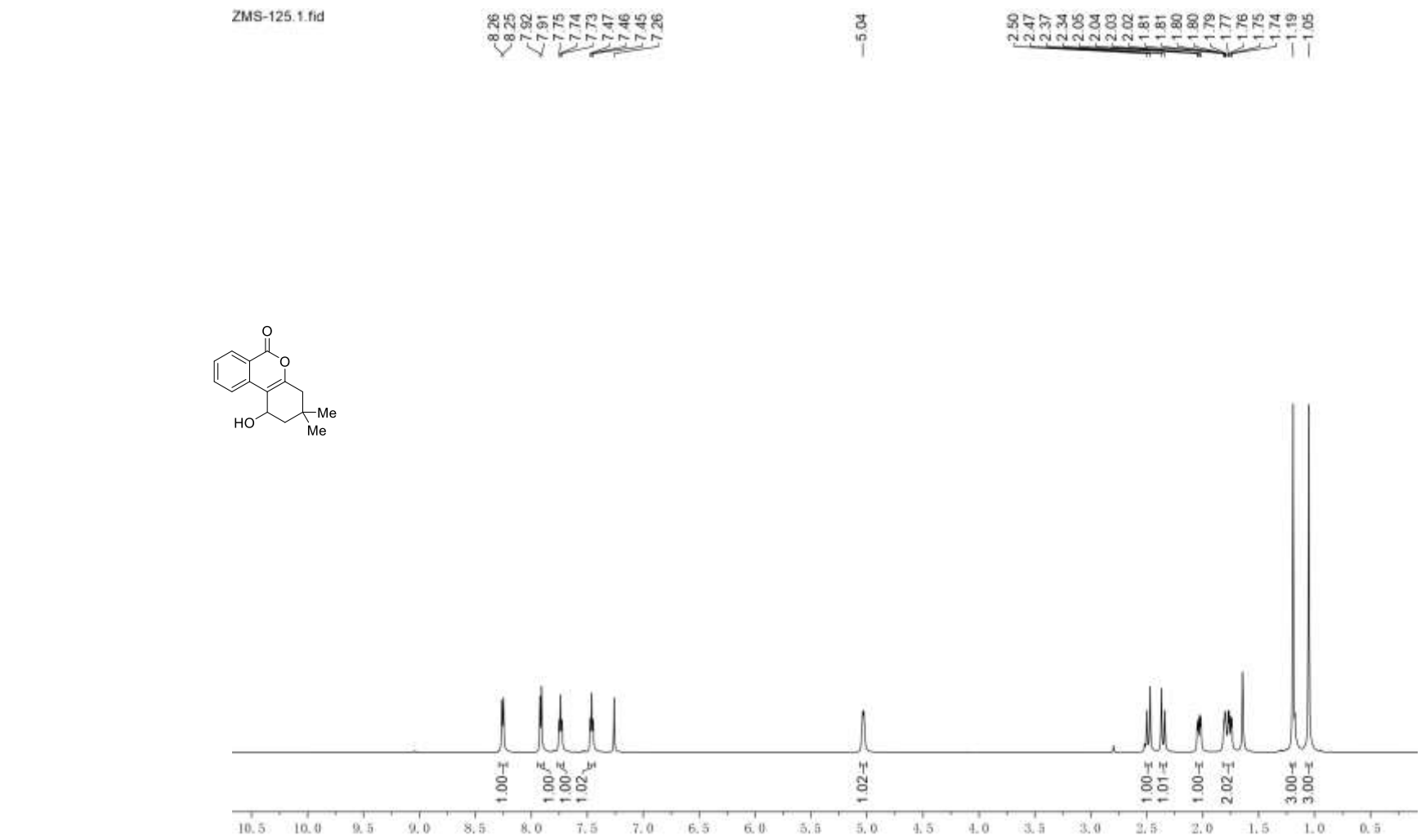


Figure S56. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4**

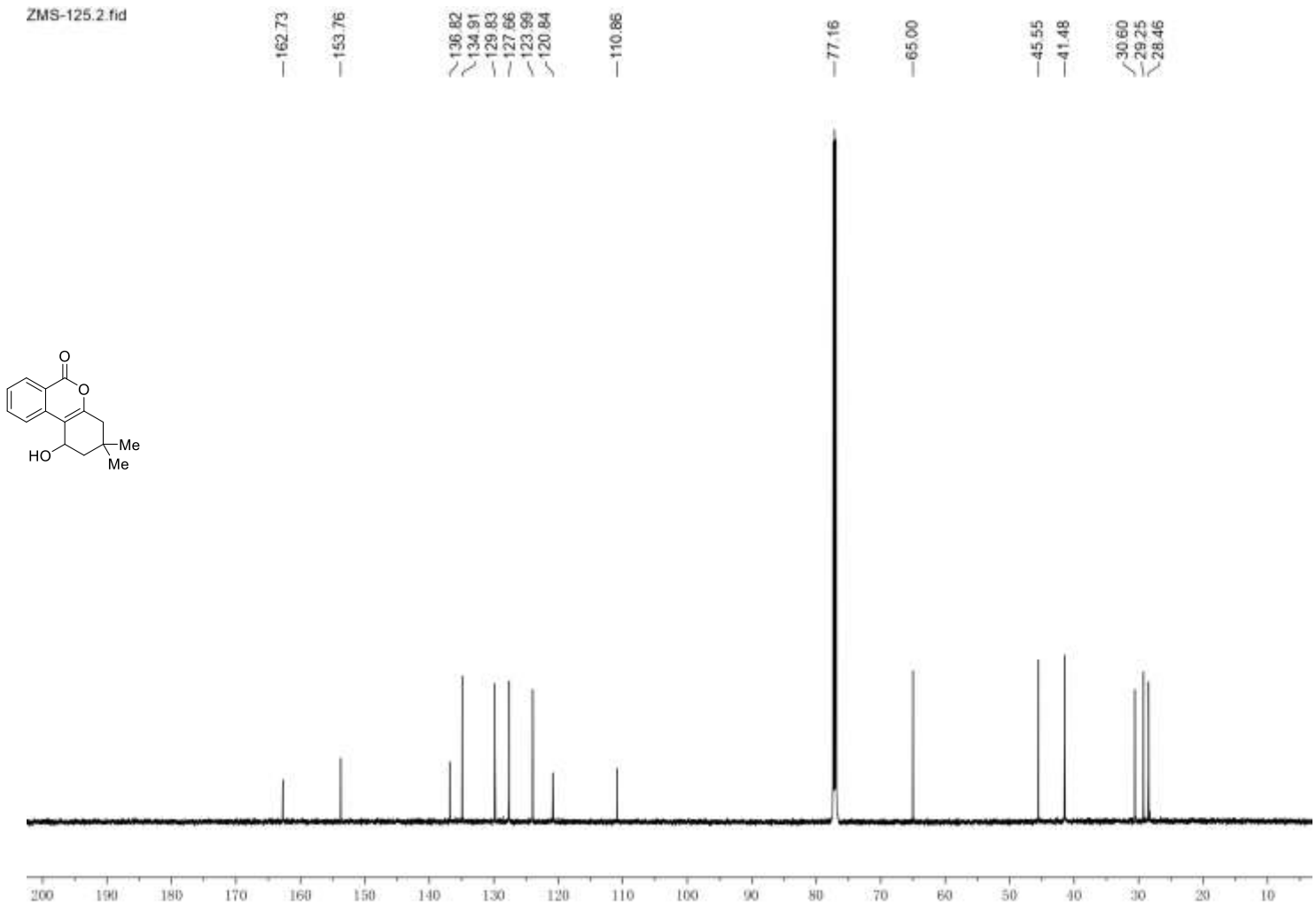


Figure S57. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **4**

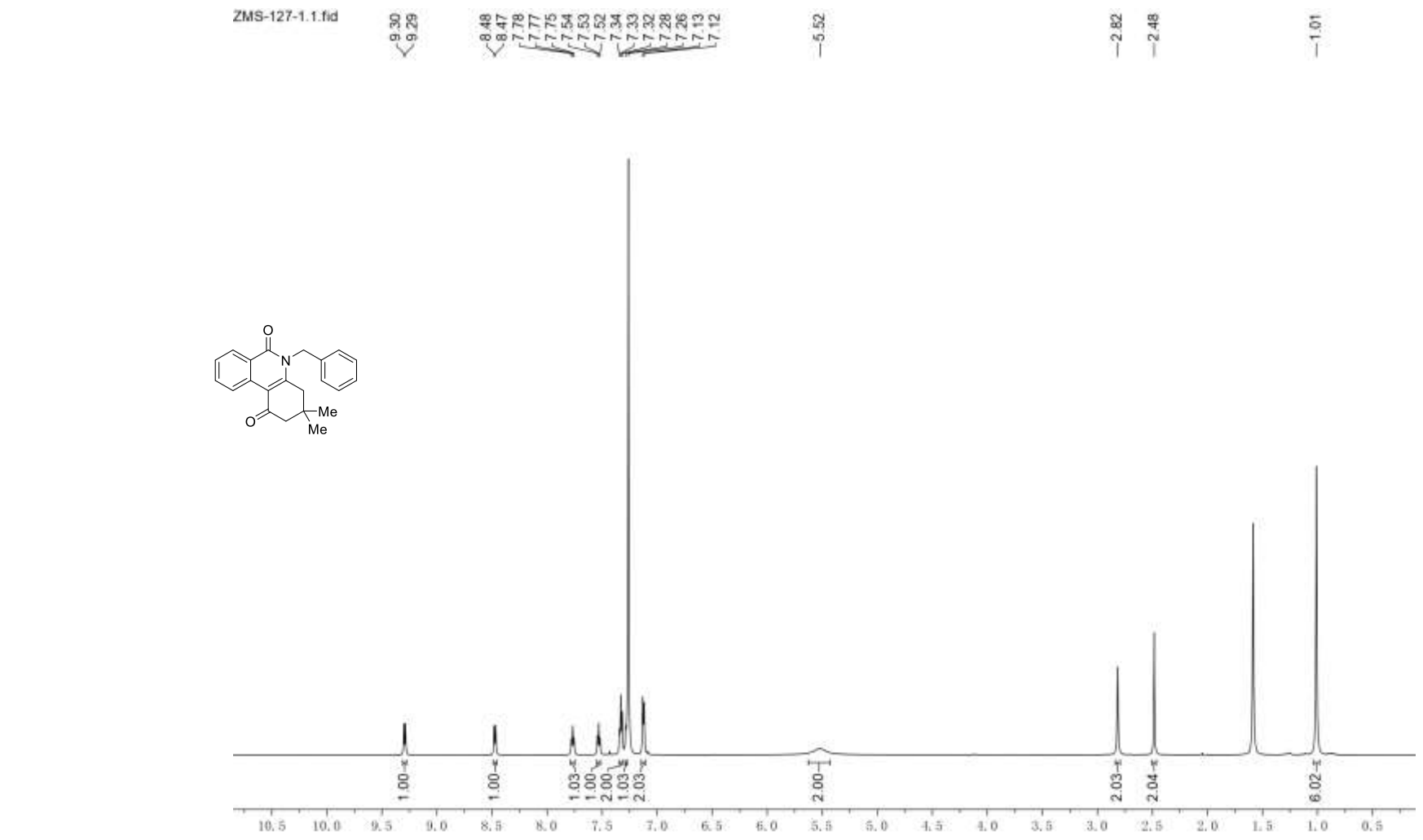


Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **5**

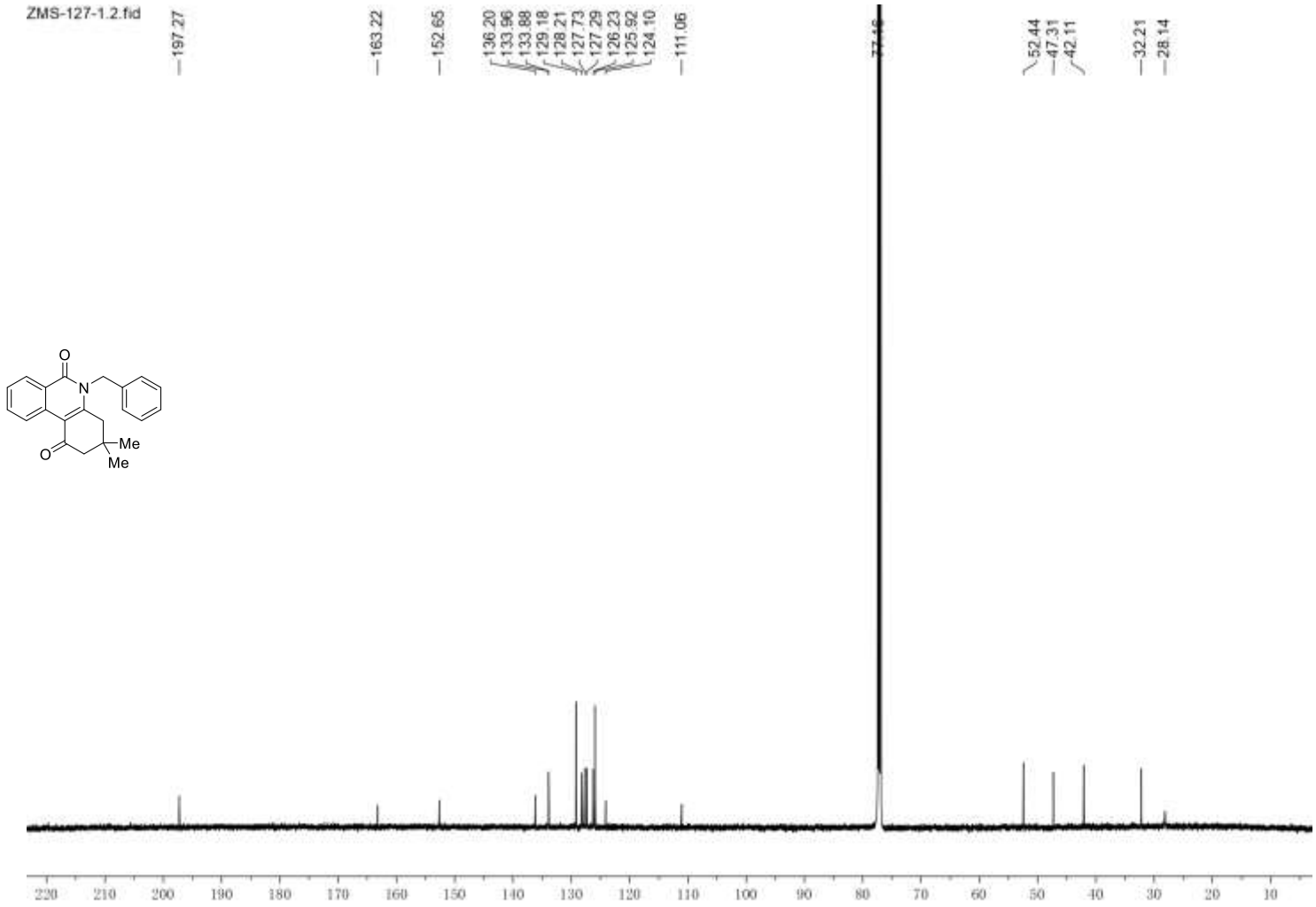


Figure S59. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **5**

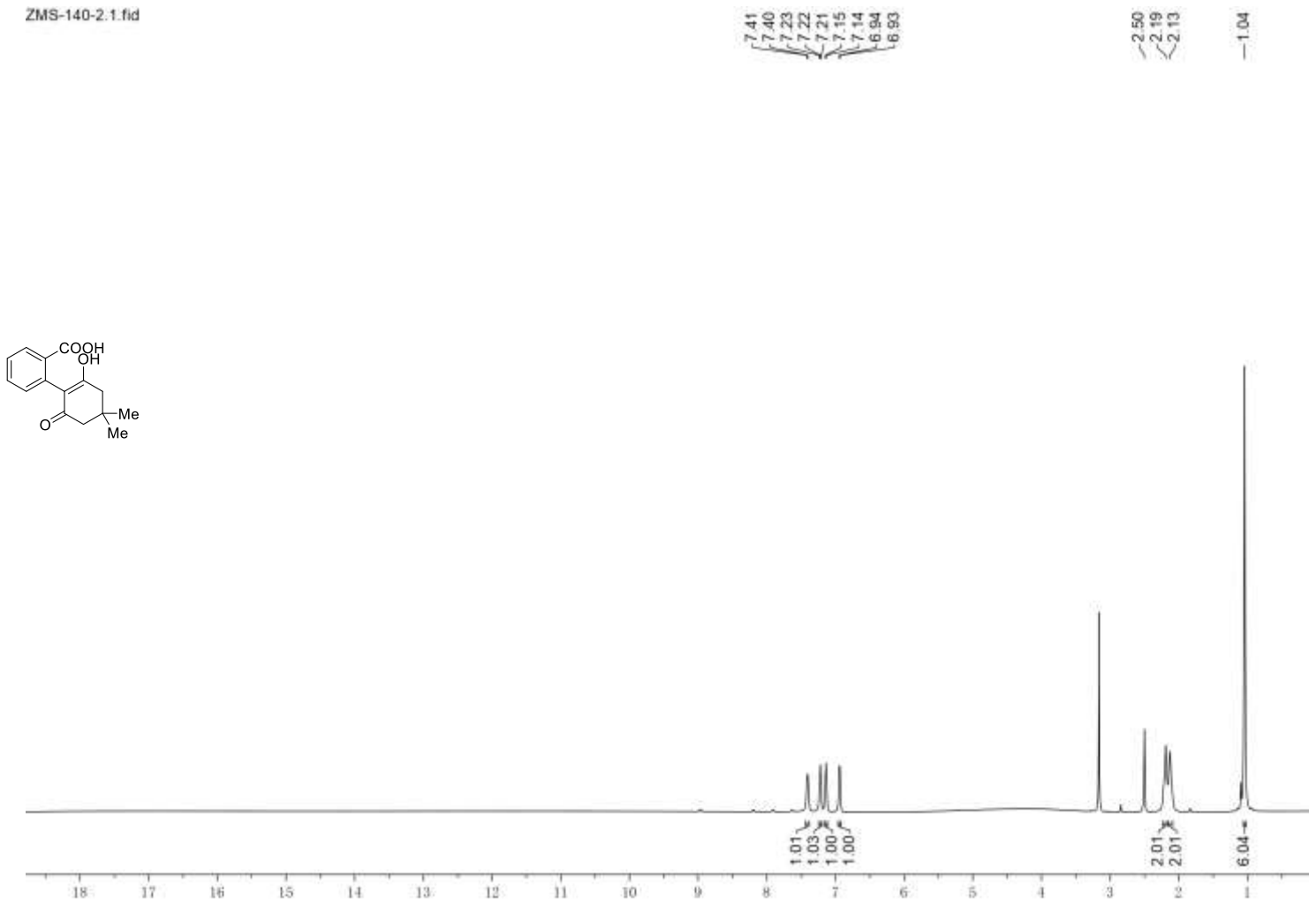


Figure S60. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **6**

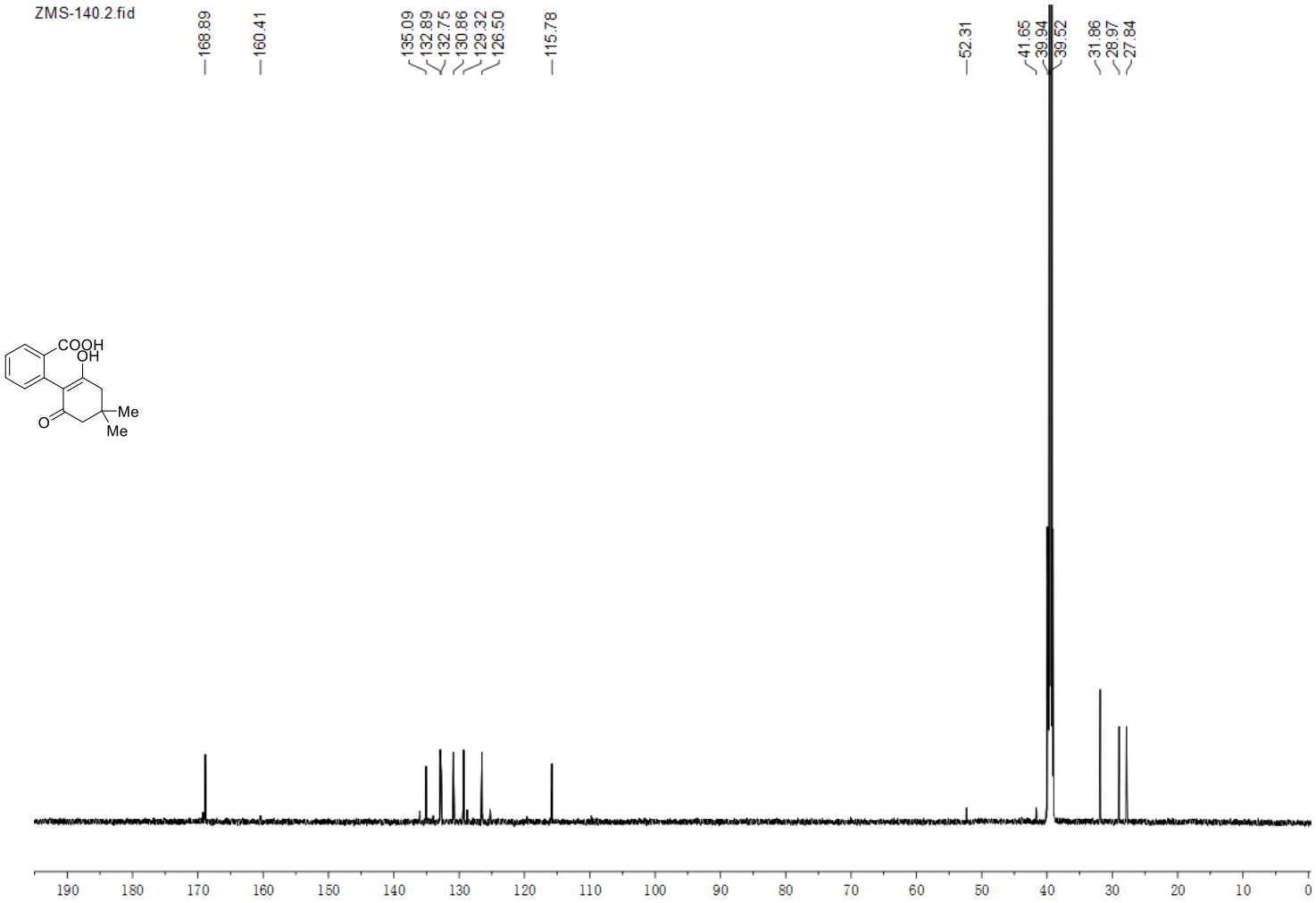


Figure S61. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **6**

6. References and notes.

1. (*a*) Tingoli, M.; Mazzella, M.; Panunzi, B.; Tuzi, A. L-Proline-catalyzed activation of methyl ketones or active methylene compounds and DMF-DMA for syntheses of (2E)-3-dimethylamino-2-propen-1-ones. *Eur. J. Org. Chem.* **2011**, 399. (*b*) Das, B.; enkateswarlu, K.; Majhi, V.; Reddy, M. R.; Reddy, K. N.; Yerra Rao, K.; Ravikumar, K.; Sridhar, B. Highly efficient, mild and chemo- and stereoselective synthesis of enaminones and enamino esters using silica supported perchloric acid under solvent-free conditions. *J. Mol. Catal. A: Chem.* **2006**, *246*, 276. (c) Liu, Y.; Zhou, R. Wan, J.-P. Water-promoted synthesis of enaminones. Mechanism investigation and application in multicomponent reactions. *Synth. Commun.* **2013**, *43*, 2475.
2. (a) Moriarty, R. M.; Tyagi, S.; Ivanov, D.; Constantinescu, M. The mechanism of 1,4 alkyl group migration in hypervalent halonium ylides: the stereochemical course. *J. Am. Chem. Soc.* **2008**, *130*, 7564. (b) Jiang, Y.; Li, P.; Zhao, J.; Liu, B.; Li, X. Iodonium ylides as carbene precursors in Rh(III)-catalyzed C–H activation. *Org. Lett.* **2020**, *22*, 7475.
3. CCDC 2209204 contain the supplementary crystallographic data for compound **3b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.