

Supporting Information

Gold self-relay catalysis for accessing functionalized cyclopentenones bearing an all-carbon quaternary stereocenter

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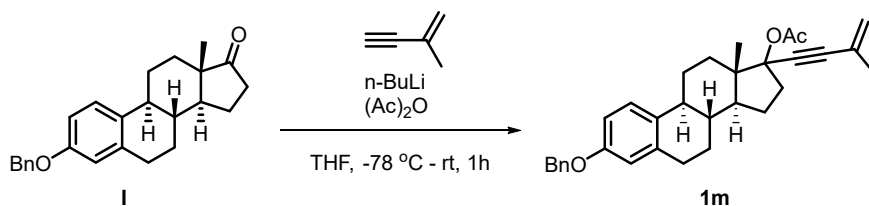
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Experimental

General Information

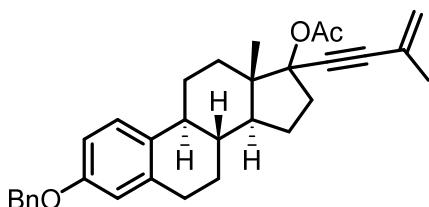
^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl_3 ($\text{DMSO}-d_6$) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General Procedure A for the Synthesis of Compounds **1m** and **1n**.



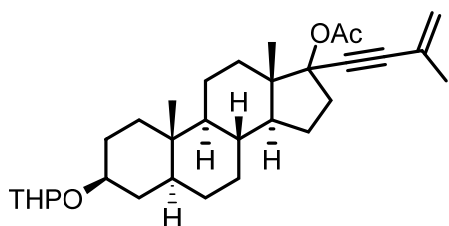
To a THF (0.5 M) solution of 2-methylbut-1-en-3-yne (1.0 equiv) was added *n*-BuLi (2.5 M in hexane, 1.1 equiv) at -78 °C, and the mixture was stirred at this temperature for 0.5 h. To this solution was added **I** (1.0 equiv) at -78 °C, and the reaction mixture was warmed to room temperature, and stirred for 1 h. The solution was added with acetic anhydride (1.2 equiv) and stirred for 1 h. To this reaction mixture was added, a saturated NH_4Cl solution, and the solution was extracted with diethyl ether (2 x 50mL) and washed with brine (30 mL). The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. The crude material was then purified by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate to give **1m**.

(8*R*,9*S*,13*S*,14*S*)-3-(Benzyloxy)-13-methyl-17-(3-methylbut-3-en-1-yn-1-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl acetate (1o)



colorless oil; 80% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.48-7.33 (m, 5H), 7.26 (d, $J = 8.0$ Hz, 1H), 6.84-6.81 (m, 1H), 6.76 (s, 1H), 5.34 (s, 1H), 5.25 (s, 1H), 5.06 (s, 2H), 2.89 (d, $J = 3.6$ Hz, 3H), 2.38 (s, 1H), 2.30-2.24 (m, 1H), 2.13 (s, 1H), 2.09 (d, $J = 6.0$ Hz, 3H), 2.03 (d, $J = 4.0$ Hz, 1H), 1.94 (s, 3H), 1.91-1.85 (m, 2H), 1.79-1.73 (m, 1H), 1.57-1.40 (m, 4H), 0.96 (d, $J = 4.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 169.5, 156.8, 138.0, 137.4, 132.8, 128.6, 127.9, 127.5, 126.6, 126.5, 121.9, 114.9, 112.4, 88.2, 87.8, 85.0, 70.0, 48.3, 48.1, 43.7, 39.2, 37.5, 3.4, 29.9, 27.4, 26.5, 23.6, 23.4, 21.6, 13.63; IR (KBr, ν , cm^{-1}): 2939, 1735, 1366, 1240, 1024, 903, 738; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{36}\text{O}_3$ 491.2562; Found 491.2553.

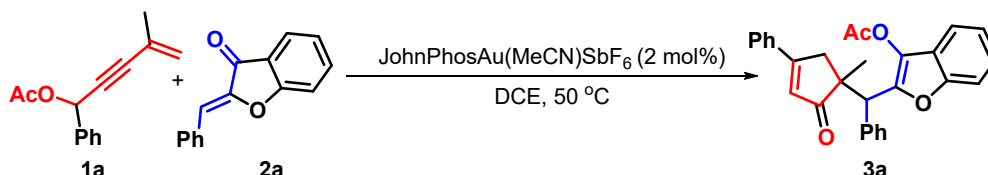
(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-(3-methylbut-3-en-1-yn-1-yl)-3-((tetrahydro-2*H*-pyran-2-yl)oxy)hexa-decahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acetate (1p)



colorless oil; 75% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 5.22 (s, 1H), 5.15 (s, 1H), 4.66 (d, $J = 2.8$ Hz, 1H), 3.88-3.83 (m, 1H), 3.67 (s, 3H), 3.55-3.51 (m, 1H), 3.43-3.40 (m, 1H), 2.67-2.57 (m, 1H), 1.96 (s, 3H), 1.83 (s, 3H), 1.78 (d, $J = 7.2$ Hz, 2H), 1.71-1.55 (m, 8H), 1.47 (s, 5H), 1.40-1.29 (m, 3H), 1.27-1.13 (m, 5H), 0.95-0.87 (m, 2H), 0.78 (d, $J = 9.6$ Hz, 6H), 0.64-0.57 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 169.4, 126.7, 121.7, 97.0, 96.7, 94.6, 88.4, 87.7, 85.2, 62.9, 54.1, 49.1, 48.1, 45.1, 44.8, 43.6, 37.6, 36.0, 35.9, 35.8, 34.4, 33.4, 31.8, 31.4, 28.7, 25.7, 23.8, 23.6, 21.6, 21.0, 20.1, 13.7, 12.41; IR (KBr, ν , cm^{-1}): 2956, 1668, 1491, 1322, 1113, 811, 759; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{46}\text{O}_4$ 505.3294; Found 505.3294.

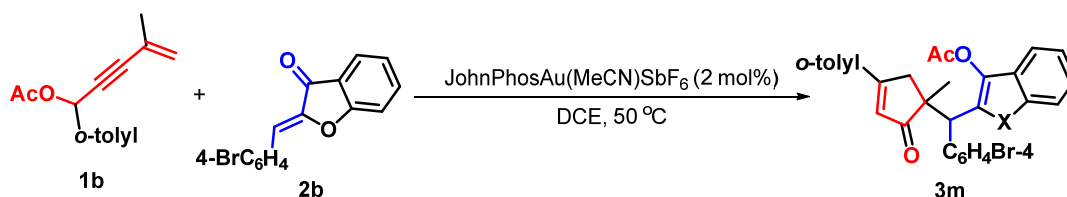
General Procedure for the Synthesis of Products 3a-3v.

Example for the synthesis of **3a**:



To a 10 mL Schlenk tube under air conditions, 1,3-enyne esters (**1a**, 0.2 mmol, 1 equiv), oxodiene (**2a**, 0.2 mmol, 1 equiv), JohnPhosAu(MeCN)SbF₆ (2 mol%), 1,2-dichloroethane (2.5 mL) were successively added. The mixture was stirred at 50 °C. The reactions were monitored by TLC. After the reaction was completed (indicated by TLC, petroleum ether : ethyl acetate = 5:1), the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography to afford the desired pure product (**3a**, 55.9 mg, 64% yield) as yellowish oil.

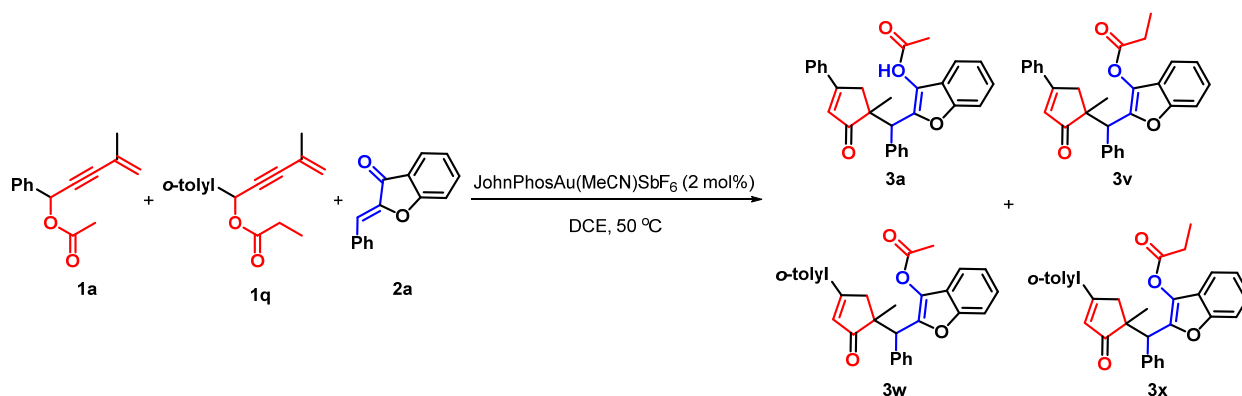
Gram-Scale Experiment for the Synthesis of Product 3b.



To a 50 mL Schlenk flask under air conditions, 1,3-enyne ester **1b** (3 mmol, 1 equiv), oxodiene **2b** (3 mmol, 1 equiv), JohnPhosAu(MeCN)SbF₆ (2 mol%), 1,2-dichloroethane (15 mL) were successively added. The mixture was stirred at 50 °C. The reactions were monitored by TLC. After the reaction was completed (indicated by TLC, petroleum ether: ethyl acetate = 5:1), the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography to afford the desired pure product (**3m**, 1.032g, 65% yield) as yellowish oil.

Crossover Experiments

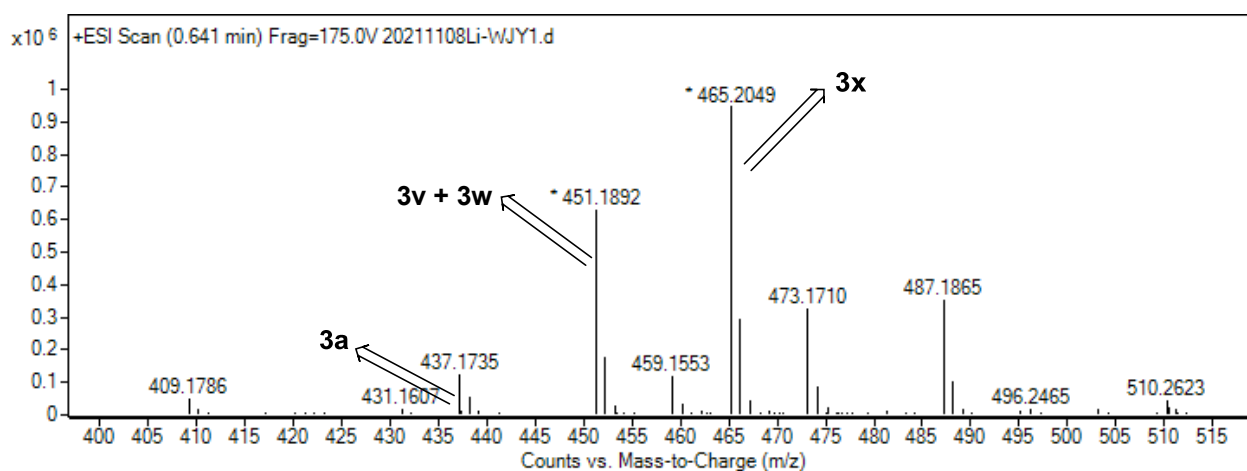
To a 10 mL Schlenk tube under air conditions, 1,3-enyne acetate (**1a**, 0.05 mmol, 1 equiv), 1,3-enyne propionate (**1q**, 0.05 mmol, 1 equiv), aurone (**2a**, 0.1 mmol, 2 equiv), JohnPhosAu(MeCN)SbF₆ (2 mol%), 1,2-dichloroethane (2.5 mL) were successively added. The mixture was stirred at 50 °C for 20 hours. After the reaction was completed (indicated by TLC, petroleum ether: ethyl acetate = 5:1), the reaction mixture was detected by HRMS analysis.



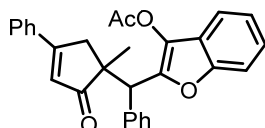
3a HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{25}\text{O}_4$ 437.1753; Found 451.1735

3v and **3w**: HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4$ 451.1909; Found 451.1892.

3x: HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{29}\text{O}_4$ 465.2066; Found 465.2049.

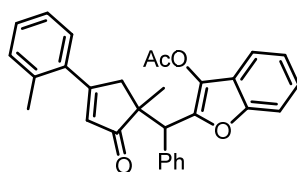


2-((1-Methyl-2-oxo-4-phenylcyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3a**, major)**



yellowish oil; 55.9 mg, 64% yield; ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 7.60 (d, $J = 7.2$ Hz, 4H), 7.44 (d, $J = 4.0$ Hz, 6H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.15-7.09 (m, 3H), 6.47 (s, 1H), 4.79 (s, 1H), 4.69 (s, 1H), 4.02 (d, $J = 17.6$ Hz, 1H), 2.84 (d, $J = 17.6$ Hz, 1H), 2.25 (s, 3H), 1.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 213.3, 171.8, 141.5, 139.0, 133.9, 133.2, 132.1, 131.4, 130.2, 128.9, 128.8, 128.2, 128.1, 127.8, 127.7, 127.0, 125.7, 56.3 (4° C), 52.6 (3° C), 40.5 (2° C), 26.5 (1° C), 26.3 (1° C); IR (KBr, ν , cm⁻¹): 3057, 2925, 1693, 1600, 1449, 1305, 1096, 736; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{24}\text{O}_4\text{Na}$ 459.1572; Found 459.1575.

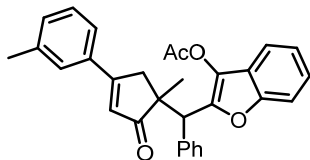
2-((1-Methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3b**, major)**



white solid; 67.6 mg, 75% yield; mp: 156.7-163.5 °C; ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 7.56 (d, $J = 7.6$ Hz, 2H),

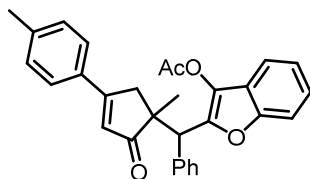
7.40-7.36 (m, 2H), 7.34-7.27 (m, 4H), 7.25 (d, $J = 2.4$ Hz, 2H), 7.23-7.14 (m, 3H), 6.16 (s, 1H), 4.65 (s, 1H), 4.00 (d, $J = 18.4$ Hz, 1H), 2.76 (d, $J = 18.4$ Hz, 1H), 2.24 (s, 3H), 2.18 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 212.1, 173.8, 168.1, 152.2, 145.7, 137.4, 135.9, 135.6, 131.2, 130.6, 130.0, 129.8, 129.5, 128.5, 127.4, 127.1, 126.0, 124.3, 122.9, 122.9, 119.0, 111.4, 51.9 (4°C), 48.0 (3°C), 44.3 (2°C), 24.7 (1°C), 20.9 (1°C), 20.4 (1°C); HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{27}\text{O}_4$ 451.1909; Found 451.1908.

2-((1-Methyl-2-oxo-4-(*m*-tolyl)cyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3c, major)



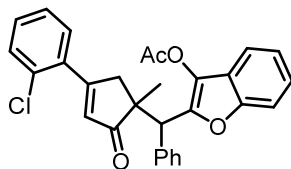
yellowish oil; 53.2 mg, 59% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.59 (d, $J = 7.2$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 4H), 7.36-7.32 (m, 4H), 7.28 (s, 1H), 7.14-7.12 (m, 2H), 6.45 (s, 1H), 4.67 (s, 1H), 3.98 (d, $J = 17.9$ Hz, 1H), 2.83 (d, $J = 17.6$ Hz, 1H), 2.41 (s, 3H), 2.24 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 211.8, 171.9, 168.2, 152.3, 145.9, 138.6, 137.7, 134.2, 132.1, 130.1, 129.2, 128.6, 127.6, 124.8, 124.2, 122.9, 118.9, 111.6, 52.4 (4°C), 47.9 (3°C), 40.8 (2°C), 25.1 (1°C), 21.5 (1°C), 20.5 (1°C); IR (KBr, ν , cm^{-1}): 3060, 2926, 1775, 1695, 1453, 1197, 1095, 743; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{27}\text{O}_4$ 451.1909; Found 451.1907.

2-((1-Methyl-2-oxo-4-(*p*-tolyl)cyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3d, major)



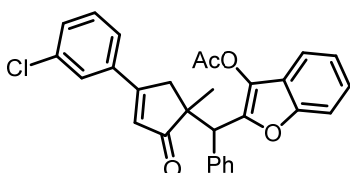
yellowish oil; 48.7 mg, 54% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.55-7.51 (m, 3H), 7.44-7.35 (m, 3H), 7.24 (d, $J = 8.0$ Hz, 4H), 7.14-7.07 (m, 3H), 6.42 (s, 1H), 4.67 (s, 1H), 3.99 (d, $J = 18.0$ Hz, 1H), 2.81 (d, $J = 18.0$ Hz, 1H), 2.40 (s, 3H), 2.25 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 211.8, 204.6, 171.7, 168.2, 152.4, 145.9, 141.9, 137.8, 131.5, 130.7, 129.6, 128.6, 128.3, 127.0, 124.3, 124.0, 122.9, 122.9, 118.9, 111.6, 52.3 (4°C), 46.5 (3°C), 40.7 (2°C), 25.2 (1°C), 21.7 (1°C), 20.5 (1°C); IR (KBr, ν , cm^{-1}): 3062, 2928, 1767, 1698, 1454, 1195, 1096, 748; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{27}\text{O}_4$ 451.1909; Found 451.1907.

2-((4-(2-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3e, major)



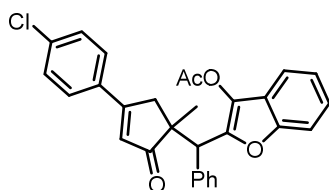
white solid; 64.0 mg, 68% yield; mp: 129.6-134.1 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.53 (d, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.39-7.35 (m, 2H), 7.33-7.28 (m, 4H), 7.25 (s, 1H), 7.22-7.13 (m, 2H), 6.41 (s, 1H), 4.64 (s, 1H), 4.03 (d, $J = 18.4$ Hz, 1H), 2.83 (d, $J = 18.4$ Hz, 1H), 2.20 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 212.0, 171.2, 168.1, 152.3, 145.7, 137.5, 135.0, 132.4, 130.0, 129.1, 128.6, 127.5, 127.0, 124.4, 123.0, 122.9, 119.0, 111.6, 52.2 (4°C), 48.1 (3°C), 43.7 (2°C), 24.7 (1°C), 20.4 (1°C); IR (KBr, ν , cm^{-1}): 2927, 1773, 1702, 1601, 1367, 1197, 1097, 744; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{23}\text{ClO}_4\text{Na}$ 493.1183; Found 493.1170.

2-((4-(3-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3f, major)



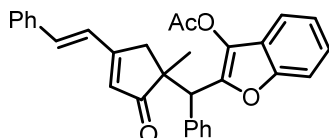
white solid; 65.9 mg, 70% yield; mp: 144.8-151.7 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.59 (s, 2H), 7.48 (d, *J* = 4.8 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.25-7.21 (m, 1H), 7.14-7.11 (m, 3H), 6.44 (s, 1H), 4.65 (s, 1H), 3.96 (d, *J* = 18.0 Hz, 1H), 2.78 (d, *J* = 18.0 Hz, 1H), 2.24 (s, 3H), 1.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 211.5, 169.9, 168.2, 152.3, 145.6, 137.5, 136.0, 135.1, 131.1, 130.0, 128.7, 127.5, 126.9, 125.1, 123.0, 119.0, 111.6, 52.5 (4° C), 47.9 (3° C), 40.8 (2° C), 25.0 (1° C), 20.5 (1° C); IR (KBr, ν, cm⁻¹): 3061, 2927, 1775, 1698, 1453, 1368, 1197, 741; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₃ClO₄Na 493.1183; Found 493.1165.

2-((4-(4-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl acetate (3g, major)



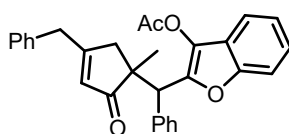
white solid; 66.9 mg, 71% yield; mp: 101.0-106.5 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.63-7.60 (m, 4H), 7.46-7.44 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.22-7.18 (m, 3H), 6.46 (s, 1H), 4.69 (s, 1H), 4.02 (d, *J* = 18.0 Hz, 1H), 2.83 (d, *J* = 17.6 Hz, 1H), 2.29 (s, 3H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 211.6, 170.1, 168.2, 152.3, 145.7, 137.5, 132.6, 130.0, 129.2, 128.7, 128.3, 125.3, 124.4, 123.0, 111.5, 52.5 (4° C), 47.9 (3° C), 40.7 (2° C), 25.0 (1° C), 20.5 (1° C); IR (KBr, ν, cm⁻¹): 3061, 2927, 1774, 1698, 1453, 1197, 1090, 740; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₃ClO₄Na 493.1183; Found 493.1166.

(E)-2-((4-Bromophenyl)(1-methyl-2-oxo-4-styrylcyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3h, major)



yellowish oil; 53.1 mg, 49% yield; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.53 (d, *J* = 8.0 Hz, 4H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.42-7.35 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.19-7.07 (m, 4H), 6.03 (s, 1H), 4.59 (s, 1H), 3.75 (d, *J* = 17.2 Hz, 1H), 2.67 (d, *J* = 17.2 Hz, 1H), 2.30 (s, 3H), 1.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 211.3, 169.5, 168.2, 152.4, 145.2, 136.9, 136.7, 135.6, 131.8, 130.7, 129.7, 129.0, 128.3, 127.7, 124.5, 124.1, 123.0, 122.7, 121.5, 119.0, 111.6, 51.9 (4° C), 47.3 (3° C), 38.9 (2° C), 25.0 (1° C), 20.5 (1° C); IR (KBr, ν, cm⁻¹): 2926, 1772, 1694, 1623, 1489, 1195, 1010, 749; HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₂₆BrO₄ 541.1014; Found 541.0978.

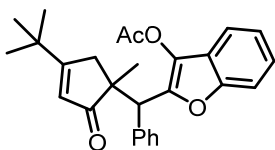
2-((4-Benzyl-1-methyl-2-oxocyclopent-3-en-1-yl)(4-bromophenyl)methyl)benzofuran-3-yl acetate (3i, major)



yellowish oil; 69.9 mg, 66% yield; mp: 139.1-140.6 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.47 (d, *J* = 8.4 Hz, 2H), 7.33-7.27 (m, 6H), 7.25 (s, 3H), 7.18 (d, *J* = 7.2 Hz, 3H), 6.99 (d, *J* = 7.2 Hz, 2H), 5.83 (s, 1H), 5.34-5.32 (m, 1H), 4.54 (s, 1H), 3.64 (s, 1H), 3.52 (d, *J* = 15.6 Hz, 1H), 3.46 (d, *J* = 18.4 Hz, 1H), 2.32 (d, *J* = 18.4 Hz, 1H), 2.28 (s, 3H), 1.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 211.9, 178.5, 168.2, 152.4, 145.1, 136.7, 136.5, 131.7, 131.4, 128.8, 128.8,

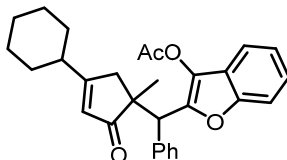
127.0, 124.5, 123.1, 122.8, 121.4, 119.1, 111.7, 52.4 (4° C), 47.2 (2° C), 42.9 (3° C), 40.0 (2° C), 24.5 (1° C), 20.5 (1° C); IR (KBr, ν , cm^{-1}): 3061, 1778, 1701, 1454, 1368, 1196, 1011, 748; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{BrO}_4\text{Na}$ 551.0834; Found 551.0833.

2-((4-Bromophenyl)(4-(tert-butyl)-1-methyl-2-oxocyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3j, major)



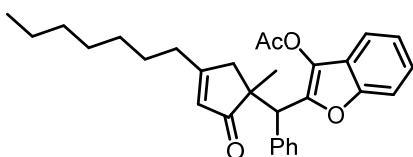
white solid; 54.5 mg, 55% yield; mp: 131.8-132.9 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.49 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.29 (s, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 5.79 (s, 1H), 4.51 (s, 1H), 3.61 (d, $J = 18.4$ Hz, 1H), 2.40 (s, 1H), 2.29 (s, 3H), 1.09 (s, 9H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 212.5, 188.9, 168.0, 152.3, 145.2, 136.7, 131.7, 130.9, 124.7, 123.3, 123.0, 121.4, 119.1, 111.4, 51.9 (4° C), 47.2 (4° C), 39.6 (3° C), 35.1 (1° C), 28.7 (2° C), 24.6 (1° C), 20.5 (1° C); IR (KBr, ν , cm^{-1}): 2965, 2870, 1779, 1701, 1454, 1368, 1194, 746; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}^+]$ Calcd for $\text{C}_{27}\text{H}_{28}\text{BrO}_4$ 495.1171; Found 495.1162.

2-((4-Bromophenyl)(4-cyclohexyl-1-methyl-2-oxocyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3k, major)



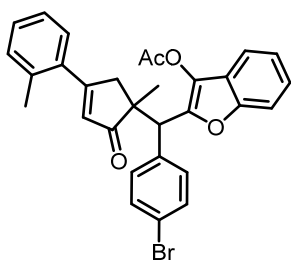
yellowish oil; 73.0 mg, 70% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 3.6$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 5.77 (s, 1H), 4.50 (s, 1H), 3.58 (d, $J = 18.4$ Hz, 1H), 2.35 (s, 1H), 2.28 (s, 3H), 2.23 (d, $J = 11.6$ Hz, 1H), 1.78-1.71 (m, 5H), 1.31-1.22 (m, 5H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 212.3, 185.3, 168.1, 152.3, 145.2, 136.8, 131.6, 131.2, 125.4, 124.5, 123.0, 122.7, 121.4, 119.1, 111.4, 51.5 (4° C), 47.2 (3), 41.9 (3° C), 41.46 (2° C), 31.1 (2° C), 25.9 (2° C), 24.6 (1° C), 20.5 (1° C); IR (KBr, ν , cm^{-1}): 2928, 2853, 1779, 1700, 1453, 1368, 1196, 746; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{30}\text{BrO}_4$ 521.1327; Found 521.1326.

2-((4-Bromophenyl)(4-hexyl-1-methyl-2-oxocyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3l, major)



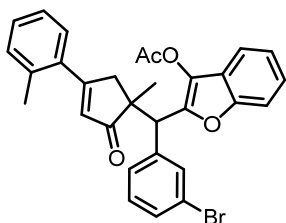
yellowish oil; 52.4 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 5.79 (s, 1H), 4.53 (s, 1H), 3.53 (d, $J = 18.4$ Hz, 1H), 2.34 (d, $J = 8.4$ Hz, 1H), 2.29 (s, 3H), 1.28-1.23 (m, 10H), 1.01 (s, 3H), 0.88-0.85 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 212.1, 181.1, 168.1, 152.4, 145.2, 136.7, 131.7, 131.3, 127.0, 124.5, 123.0, 122.8, 121.4, 119.1, 111.4, 52.0 (4° C), 47.2 (3° C), 43.3 (2° C), 33.6 (2° C), 31.7 (2° C), 29.2 (2° C), 29.1 (2° C), 27.2 (2° C), 24.6 (2° C), 22.7 (2° C), 20.5 (1° C), 14.2 (1° C); IR (KBr, ν , cm^{-1}): 2928, 2857, 1779, 1701, 1617, 1454, 1195, 746; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{32}\text{BrO}_4$ 523.1484; Found 523.1461.

2-((4-Bromophenyl)(1-methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3m, major)



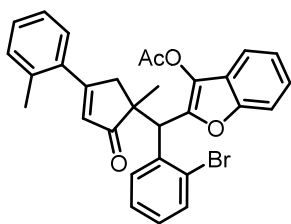
yellowish oil; 77.3 mg, 77% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm): 7.52 (d, $J = 4.0$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 4H), 7.25-7.20 (m, 4H), 6.16 (s, 1H), 4.64 (s, 1H), 3.97 (d, $J = 18.0$ Hz, 1H), 2.77 (d, $J = 18.4$ Hz, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 1.17 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm): 211.8, 173.9, 168.1, 152.4, 145.1, 136.6, 136.0, 135.5, 131.8, 131.3, 130.7, 129.8, 127.2, 126.1, 124.6, 123.1, 122.8, 121.6, 119.1, 111.5, 51.8 (4°C), 47.5 (3°C), 44.2 (2°C), 24.6 (1°C), 21.0 (1°C), 20.6 (1°C); IR (KBr, ν , cm^{-1}): 3062, 2962, 1776, 1698, 1454, 1368, 1194, 747; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{BrO}_4\text{Na}$ 551.0834; Found 551.0842.

2-((3-Bromophenyl)(1-methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3n, major)



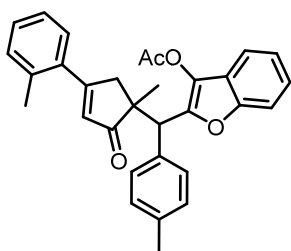
yellowish oil; 46.0 mg, 73% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm): 7.52 (d, $J = 3.9$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 7.3$ Hz, 4H), 7.25-7.20 (m, 4H), 6.16 (s, 1H), 4.64 (s, 1H), 3.97 (d, $J = 18.3$ Hz, 1H), 2.97 (d, $J = 19.2$ Hz, 1H), 2.77 (d, $J = 18.3$ Hz, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 1.17 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm): 212.1, 175.7, 168.1, 152.8, 144.9, 139.8, 135.9, 135.5, 132.0, 131.3, 130.6, 130.2, 129.9, 129.7, 128.8, 127.1, 126.1, 124.6, 123.1, 122.7, 119.2, 111.6, 51.9 (4°C), 47.7 (3°C), 44.20 (2°C), 24.7 (1°C), 20.9 (1°C), 20.5 (1°C); IR (KBr, ν , cm^{-1}): 3062, 2927, 1778, 1698, 1368, 1193, 1094, 746; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{BrO}_4\text{Na}$ 551.0834; Found 551.0851.

2-((2-Bromophenyl)(1-methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)methyl)benzofuran-3-yl acetate (3o, major)



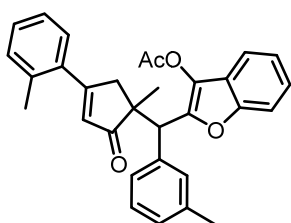
white solid; 79.4 mg, 75% yield; mp: 171.1-177.9 $^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm): 7.82 (d, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.37-7.33 (m, 1H), 7.29 (d, $J = 4.4$ Hz, 4H), 7.25-7.20 (m, 3H), 7.17 (d, $J = 8.8$ Hz, 2H), 6.19 (s, 1H), 5.51 (s, 1H), 4.05 (d, $J = 18.4$ Hz, 1H), 2.83 (d, $J = 18.0$ Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 1.25 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm): 211.3, 173.5, 168.3, 152.5, 144.9, 137.1, 135.9, 135.6, 133.5, 131.3, 130.6, 129.9, 129.6, 128.9, 127.7, 127.2, 126.6, 126.1, 124.5, 123.1, 122.9, 119.2, 111.5, 52.5 (4°C), 45.6 (3°C), 44.8 (2°C), 23.9 (1°C), 21.0 (1°C), 20.5 (1°C); IR (KBr, ν , cm^{-1}): 3061, 2963, 1774, 1701, 1454, 1197, 1025, 745; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{BrO}_4\text{Na}$ 551.0834; Found 551.0831.

2-((1-Methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)(p-tolyl)methyl)benzofuran-3-yl acetate (3p, major)



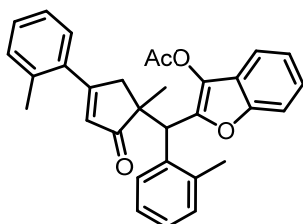
yellowish oil; 44.6 mg, 48% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm): 7.44 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 6.0$ Hz, 4H), 7.22-7.17 (m, 6H), 6.15 (s, 1H), 4.62 (s, 1H), 3.81 (d, $J = 19.2$ Hz, 1H), 2.76 (d, $J = 18.4$ Hz, 1H), 2.40 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H), 1.17 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm): 212.3, 173.9, 168.2, 152.3, 146.0, 137.1, 135.9, 134.4, 131.3, 129.9, 129.3, 129.0, 127.2, 126.1, 124.3, 122.9, 119.0, 111.5, 51.95 (4°C), 47.6 (3°C), 44.4 (2°C), 24.7 (1°C), 21.2 (1°C), 21.0 (1°C), 20.7 (1°C); IR (KBr, ν , cm^{-1}): 3023, 2925, 1778, 1698, 1454, 1368, 1196, 748; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{29}\text{O}_4$ 465.2066; Found 465.2065.

2-((1-Methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)(m-tolyl)methyl)benzofuran-3-yl acetate (3q, major)



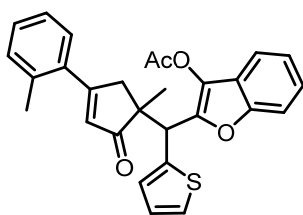
yellowish oil; 58.5 mg, 63% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm): 7.54 (d, $J = 8.4$ Hz, 1H), 7.34 (s, 1H), 7.30-7.27 (m, 6H), 7.17 (d, $J = 9.2$ Hz, 4H), 6.17 (s, 1H), 4.64 (s, 1H), 3.85 (d, $J = 19.2$ Hz, 1H), 2.78 (d, $J = 18.4$ Hz, 1H), 2.41 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 1.18 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm): 212.3, 175.6, 168.2, 152.3, 145.9, 138.2, 137.4, 135.9, 131.3, 130.9, 129.9, 129.5, 128.5, 128.2, 127.1, 126.1, 124.1, 123.2, 123.0, 119.0, 111.5, 51.9 (4°C), 48.0 (3°C), 44.5 (2°C), 24.8 (1°C), 21.7 (1°C), 20.9 (1°C), 20.5 (1°C); IR (KBr, ν , cm^{-1}): 3059, 2926, 1779, 1698, 1454, 1190, 1095, 747; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{29}\text{O}_4$ 465.2066; Found 465.2065.

2-((1-Methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)(o-tolyl)methyl)benzofuran-3-yl acetate (3r, major)



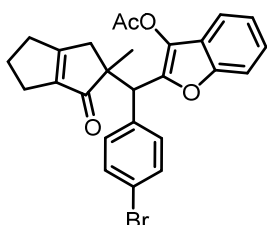
white solid; 71.1 mg, 69% yield; mp: 102.1-107.9 $^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm): 7.67 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 10.0$ Hz, 2H), 7.26-7.21 (m, 7H), 7.19 (d, $J = 4.4$ Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 1H), 6.22 (s, 1H), 5.10 (s, 1H), 4.02 (d, $J = 18.4$ Hz, 1H), 2.91 (d, $J = 18.4$ Hz, 1H), 2.49 (s, 3H), 2.18 (s, 3H), 2.17 (s, 3H), 1.18 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm): 212.5, 173.9, 168.3, 152.3, 145.5, 137.9, 135.9, 131.2, 131.0, 129.8, 129.5, 129.1, 127.2, 127.1, 126.2, 126.0, 124.4, 122.9, 118.9, 111.6, 52.3 (4°C), 45.1 (3°C), 42.9 (2°C), 24.1 (1°C), 20.9 (1°C), 20.4 (1°C), 20.3 (1°C); IR (KBr, ν , cm^{-1}): 3061, 2961, 1775, 1700, 1454, 1368, 1190, 742; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{29}\text{O}_4$ 465.2066; Found 465.2069.

2-((1-Methyl-2-oxo-4-(o-tolyl)cyclopent-3-en-1-yl)(thiophen-2-yl)methyl)benzofuran-3-yl acetate (3s, major)



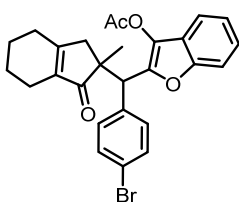
yellowish solid; 76.7 mg, 84% yield; mp: 115.9-120.5 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.51 (d, *J* = 8.0 Hz, 1H), 7.31-7.28 (m, 5H), 7.19 (d, *J* = 3.2 Hz, 3H), 7.10 (d, *J* = 5.2 Hz, 1H), 6.86-6.84 (m, 1H), 6.17 (s, 1H), 4.99 (s, 1H), 3.91 (d, *J* = 19.2 Hz, 1H), 2.89 (d, *J* = 18.8 Hz, 1H), 2.44 (s, 3H), 2.20 (s, 3H), 1.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 212.2, 175.6, 168.2, 152.7, 145.3, 139.3, 136.0, 135.5, 135.5, 131.3, 130.5, 129.7, 128.0, 127.2, 126.5, 126.1, 124.9, 124.8, 123.3, 122.6, 119.3, 111.5, 52.2 (4° C), 44.2 (3° C), 42.5 (2° C), 24.2 (1° C), 21.1 (1° C), 20.7 (1° C); IR (KBr, ν, cm⁻¹): 2973, 2899, 1711, 1601, 1457, 1362, 821, 758; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₂₈H₂₄O₄SNa 479.1293; Found 479.1267.

2-((4-Bromophenyl)(2-methyl-1-oxo-1,2,3,4,5,6-hexahydropentalen-2-yl)methyl)benzofuran-3-yl acetate (3t, major)



white solid; 56.6 mg, 59% yield; mp: 192.6-193.4 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.50 (d, *J* = 8.4 Hz, 1H), 7.39-7.27 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.57 (s, 1H), 3.23 (d, *J* = 19.2 Hz, 1H), 2.42 (s, 1H), 2.38 (s, 3H), 2.35-2.09 (m, 6H), 1.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 206.3, 168.1, 152.6, 147.2, 146.1, 137.2, 131.2, 130.8, 124.7, 123.3, 122.7, 121.2, 119.1, 111.8, 58.6 (4° C), 46.3 (3° C), 37.2 (2° C), 32.0 (2° C), 27.3 (2° C), 24.6 (2° C), 24.5 (1° C), 20.7 (1° C); IR (KBr, ν, cm⁻¹): 2960, 1779, 1695, 1455, 1368, 1193, 1011, 747; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₂₆H₂₃BrO₄Na 501.0677; Found 501.0648.

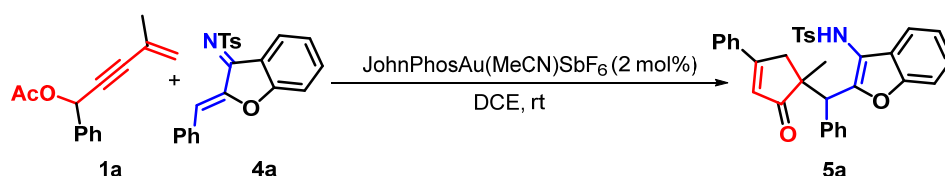
2-((4-Bromophenyl)(2-methyl-1-oxo-2,3,4,5,6,7-hexahydro-1H-inden-2-yl)methyl)benzofuran-3-yl acetate (3u, major)



white solid; 63.2 mg, 64% yield; mp: 127.3-128.7 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.56 (d, *J* = 8.4 Hz, 1H), 7.44-7.32 (m, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.57 (s, 1H), 3.24 (d, *J* = 18.8 Hz, 1H), 2.48 (s, 1H), 2.43 (s, 3H), 2.19-1.87 (m, 4H), 1.72-1.58 (m, 4H), 1.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 211.2, 172.9, 168.1, 152.6, 146.1, 137.4, 137.1, 131.1, 130.6, 124.7, 123.3, 122.7, 121.1, 119.1, 111.8, 46.5 (4° C), 41.9 (3° C), 28.3 (2° C), 23.9 (2° C), 22.1 (2° C), 21.6 (2° C), 20.7 (1° C), 20.1 (1° C); IR (KBr, ν, cm⁻¹): 2928, 1779, 1695, 1455, 1368, 1193, 1010, 747; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₂₇H₂₅BrO₄Na 515.0834; Found 515.0833.

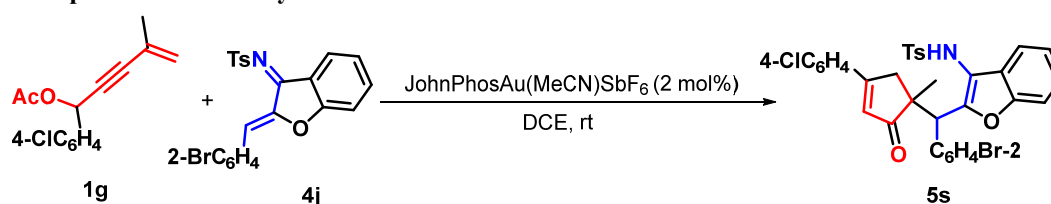
General Procedure for the Synthesis of Products 5.

Example for the synthesis of **5a**:



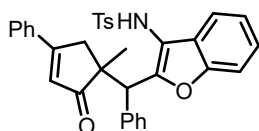
To a 10 mL Schlenk tube under air conditions, 1,3-enyne esters (**1a**, 0.2 mmol, 1 equiv), azadiene (**2a**, 0.2 mmol, 1 equiv), JohnPhosAu(MeCN)SbF₆ (2 mol%), 1,2-dichloroethane (2.5 mL) were successively added. The mixture was stirred at room temperature. The reactions were monitored by TLC. After the reaction was completed (indicated by TLC, petroleum ether : ethyl acetate = 5:1), the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography to afford the desired pure product (**5a**, 87.7 mg, 80% yield) as white solid.

Gram-Scale Experiment for the Synthesis of Product 5o



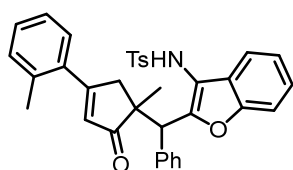
To a 50 mL Schlenk flask under air conditions, 1,3-enyne esters (**1g**, 3 mmol, 1 equiv), azadiene (**4j**, 3 mmol, 1 equiv), JohnPhosAu(MeCN)SbF₆ (2 mol%), 1,2-dichloroethane (15 mL) were successively added. The mixture was stirred at room temperature. The reactions were monitored by TLC. After the reaction was completed (indicated by TLC, petroleum ether: ethyl acetate = 5:1), the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography to afford the desired pure product (**5s**, 1.646g, 83% yield) as white solid.

4-Methyl-N-(2-((1-methyl-2-oxo-4-phenylcyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (**5a**, major)



white solid; 87.7 mg, 80% yield; mp: 118.4-119.1 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.78-7.72 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.49-7.40 (m, 3H), 7.25-7.13 (m, 8H), 7.08-7.02 (m, 2H), 6.27 (s, 1H), 4.00 (d, *J* = 14.0 Hz, 2H), 2.76 (d, *J* = 18.0 Hz, 1H), 2.41 (s, 3H), 1.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 214.1, 174.0, 153.6, 151.4, 143.6, 136.8, 136.3, 133.6, 131.9, 129.9, 129.8, 129.0, 128.2, 127.5, 127.4, 127.1, 125.6, 124.5, 124.2, 123.3, 121.4, 114.6, 111.0, 53.6 (4° C), 46.6 (3° C), 40.1 (2° C), 25.6 (1° C), 21.7 (1° C); IR (KBr, ν, cm⁻¹): 3243, 1677, 1570, 1452, 1342, 1166, 737, 574; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₄H₂₉NO₄SNa 570.1715; Found 570.1715.

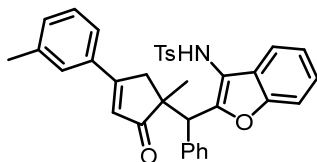
4-Methyl-N-(2-((1-methyl-2-oxo-4-(*o*-tolyl)cyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (**5b**, major)



white solid; 70.8 mg, 63% yield; mp: 127.6-128.5 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.77-7.75 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 2H), 7.26-7.19 (m, 8H), 7.14-7.03 (m, 6H), 5.97 (s, 1H), 4.07 (d, *J* = 18.4 Hz, 1H), 3.98 (s, 1H), 2.64 (d, *J* = 18.4 Hz, 1H), 2.39 (s, 3H), 2.10 (s, 3H), 1.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 214.4,

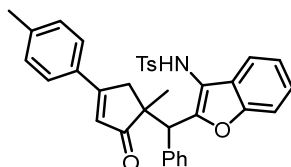
176.3, 153.6, 151.6, 143.6, 136.7, 136.1, 136.0, 135.1, 131.4, 130.0, 129.9, 129.8, 129.1, 128.2, 127.5, 127.2, 126.2, 124.66, 123.4, 121.5, 114.6, 110.9, 53.0 (4° C), 46.7 (3° C), 43.7 (2° C), 25.1 (1° C), 21.7 (1° C), 21.1 (1° C); IR (KBr, ν , cm^{-1}): 3253, 1682, 1454, 1166, 1093, 750, 566; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{31}\text{NO}_4\text{SNa}$ 584.1871; Found 584.1874.

4-Methyl-N-(2-((1-methyl-2-oxo-4-(*m*-tolyl)cyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (5c, major)



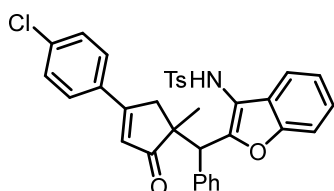
white solid; 82.1 mg, 73% yield; mp: 119.5-120.3 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.78-7.74 (m, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 10.0$ Hz, 2H), 7.33-7.27 (m, 4H), 7.26-7.20 (m, 2H), 7.20-7.13 (m, 4H), 7.07-7.04 (m, 2H), 6.25 (s, 1H), 3.97 (d, $J = 15.6$ Hz, 2H), 2.77 (d, $J = 16.0$ Hz, 1H), 2.40 (d, $J = 10.0$ Hz, 6H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 214.1, 174.3, 153.6, 151.4, 143.5, 138.7, 136.8, 136.3, 133.6, 132.6, 129.9, 129.8, 128.9, 128.2, 127.7, 127.5, 127.3, 125.6, 124.5, 124.3, 124.1, 123.2, 121.4, 114.6, 111.0, 53.6 (4° C), 46.5 (3° C), 40.2 (2° C), 25.6 (1° C), 21.7 (1° C), 21.5 (1° C); IR (KBr, ν , cm^{-1}): 3242, 1677, 1596, 1453, 1166, 1093, 871, 668; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{31}\text{NO}_4\text{SNa}$ 584.1871; Found 584.1852.

4-Methyl-N-(2-((1-methyl-2-oxo-4-(*p*-tolyl)cyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (5d, major)



white solid; 64.9 mg, 57% yield; mp: 149.8-150.9 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.76 (d, $J = 6.8$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.29 (s, 1H), 7.26-7.20 (m, 5H), 7.19-7.14 (m, 4H), 7.07-7.01 (m, 2H), 6.23 (s, 1H), 3.99-3.94 (m, 2H), 2.75 (d, $J = 18.0$ Hz, 1H), 2.40 (d, $J = 8.8$ Hz, 6H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 214.1, 174.0, 153.6, 151.4, 143.5, 142.6, 136.8, 136.4, 130.9, 129.9, 129.8, 129.7, 128.2, 127.5, 127.3, 127.2, 125.7, 124.5, 123.3, 123.2, 121.4, 114.6, 111.0, 53.5 (4° C), 46.6 (3° C), 40.1 (2° C), 25.6 (1° C), 21.7 (1° C), 21.7 (1° C); IR (KBr, ν , cm^{-1}): 3225, 1673, 1593, 1453, 1166, 1093, 815, 564; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{31}\text{NO}_4\text{SNa}$ 584.1871; Found 584.1846.

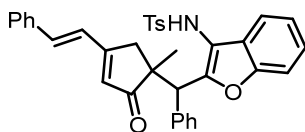
N-(2-((4-(4-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5e, major)



white solid; 102.4 mg, 88% yield; mp: 140.2-141.8 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.75-7.73 (m, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 3H), 7.39 (d, $J = 8.4$ Hz, 3H), 7.19-7.16 (m, 4H), 7.06-7.02 (m, 3H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.23 (s, 1H), 3.95 (d, $J = 18.4$ Hz, 2H), 2.71 (d, $J = 18.4$ Hz, 1H), 2.40 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 213.8, 172.3, 153.6, 151.4, 143.6, 137.9, 136.2, 129.9, 129.8, 129.3, 128.4, 128.2, 127.5, 125.6, 124.6, 123.3, 121.4, 114.7, 111.0, 53.7 (4° C), 46.5 (3° C), 40.1 (2° C), 25.5 (1° C), 21.7 (1° C); IR (KBr, ν , cm^{-1}): 3243,

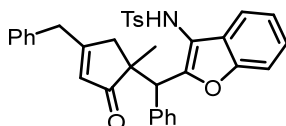
1676, 1490, 1328, 1166, 1091, 828, 574; HRMS (ESI -TOF) m/z : $[M+Na]^+$ Calcd for $C_{34}H_{28}ClNO_4SNa$ 604.1325; Found 604.1320.

(E)-4-Methyl-N-(2-((1-methyl-2-oxo-4-styrylcyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (5f, major)



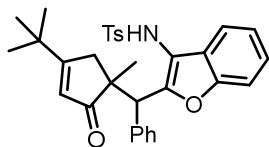
white solid; 66.6 mg, 58% yield; mp: 76.3-77.4 °C; 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 7.79-7.77 (m, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 6.4$ Hz, 2H), 7.41-7.36 (m, 3H), 7.34-7.27 (m, 3H), 7.26 (s, 2H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 3H), 7.09-7.03 (m, 3H), 5.86 (s, 1H), 3.96 (s, 1H), 3.80 (d, $J = 17.6$ Hz, 1H), 2.63 (d, $J = 17.6$ Hz, 1H), 2.41 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 214.1, 171.9, 153.7, 151.5, 143.6, 138.0, 136.3, 135.4, 130.0, 129.9, 129.8, 129.1, 128.2, 127.9, 127.6, 127.5, 127.4, 125.7, 124.5, 123.8, 123.3, 121.5, 114.6, 111.1, 53.3 (4° C), 46.6 (3° C), 38.4 (2° C), 25.6 (1° C), 21.7 (1° C); IR (KBr, ν , cm^{-1}): 3233, 1674, 1579, 1352, 1166, 1093, 751, 667; HRMS (ESI -TOF) m/z : $[M+Na]^+$ Calcd for $C_{36}H_{31}NO_4SNa$ 596.1871; Found 596.1868.

N-(2-((4-Benzyl-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5g, major)



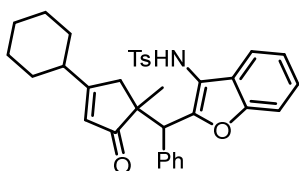
white solid; 60.7 mg, 54% yield; mp: 77.2-78.1 °C; 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 7.81-7.75 (m, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.28 (s, 1H), 7.26-7.16 (m, 7H), 7.13 (d, $J = 8.4$ Hz, 3H), 6.94-6.91 (m, 4H), 5.63 (s, 1H), 3.87 (s, 1H), 3.59 (d, $J = 22.8$ Hz, 3H), 2.40 (s, 3H), 2.25 (d, $J = 18.8$ Hz, 1H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 214.7, 181.5, 153.5, 151.4, 143.6, 136.3, 136.1, 129.8, 128.9, 128.8, 128.1, 127.5, 127.1, 124.5, 123.3, 121.5, 114.5, 111.1, 53.7 (4° C), 46.4 (2° C), 42.6 (3° C), 40.2 (2° C), 25.0 (1° C), 21.7 (1° C); IR (KBr, ν , cm^{-1}): 3251, 1683, 1454, 1344, 1166, 1093, 736, 668; HRMS (ESI -TOF) m/z : $[M+Na]^+$ Calcd for $C_{35}H_{31}NO_4SNa$ 584.1871; Found 584.1869.

N-(2-((4-(tert-Butyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5h, major)



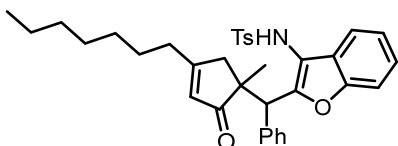
white solid; 55.9 mg, 53% yield; mp: 90.2-91.8 °C; 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 7.78-7.76 (m, 1H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.31-7.28 (m, 1H), 7.26-7.18 (m, 5H), 7.14-7.06 (m, 3H), 6.98 (d, $J = 6.0$ Hz, 2H), 5.62 (s, 1H), 3.86 (s, 1H), 3.66 (d, $J = 18.4$ Hz, 1H), 2.38 (s, 3H), 2.30 (d, $J = 18.8$ Hz, 1H), 1.06 (s, 9H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 215.3, 191.9, 153.6, 151.6, 143.5, 136.7, 136.2, 129.8, 128.1, 127.4, 125.6, 124.6, 124.2, 123.3, 121.5, 114.4, 110.8(1), 110.8(0), 53.2 (4° C), 46.5 (4° C), 39.2 (3° C), 35.4 (1° C), 28.6 (2° C), 25.0 (1° C), 21.7 (1° C); IR (KBr, ν , cm^{-1}): 3258, 2967, 1683, 1598, 1454, 1167, 738, 565; HRMS (ESI -TOF) m/z : $[M+Na]^+$ Calcd for $C_{32}H_{33}NO_4SNa$ 550.2028; Found 550.2028.

N-(2-((4-Cyclohexyl-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5i, major)



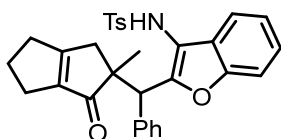
white solid; 83.1 mg, 75% yield; mp: 53.2-54.8 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 8.19 (s, 1H), 7.90 (d, *J* = 6.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.38-7.29 (m, 4H), 7.12-7.02 (m 3H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 6.0 Hz, 2H), 5.92 (s, 1H), 4.71 (s, 1H), 3.27 (d, *J* = 19.6 Hz, 1H), 2.42-2.36 (m, 1H), 2.16 (s, 3H), 2.10 (d, *J* = 11.6 Hz, 1H), 1.69-1.57 (m, 5H), 1.27-1.08 (m, 4H), 0.90 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 214.8, 188.6, 153.6, 137.8, 135.8, 129.2, 128.7, 127.8, 127.0, 126.5, 124.6, 123.4, 121.5, 111.1, 52.1 (4° C), 46.1 (3° C), 42.0 (3° C), 41.3 (2° C), 31.2 (2° C), 25.9 (2° C), 23.8 (1° C), 21.7 (1° C); IR (KBr, ν, cm⁻¹): 2928, 2852, 1674, 1453, 1338, 1166, 1093, 737; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₄H₃₅NO₄SNa 576.2184; Found 576.2167.

***N*-(2-((4-Heptyl-1-methyl-2-oxocyclopent-3-en-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5j, major)**



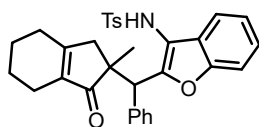
white solid; 78.6 mg, 69% yield; mp: 74.6-75.8 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.85-7.80 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.38-7.36 (m, 1H), 7.31-7.27 (m, 4H), 7.24 (d, *J* = 2.8 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.03-7.00 (m, 2H), 5.69 (s, 1H), 3.93 (s, 1H), 3.66 (d, *J* = 18.8 Hz, 1H), 2.44 (s, 3H), 2.38-2.33 (m, 2H), 2.28 (d, *J* = 7.2 Hz, 1H), 1.49-1.44 (m, 2H), 1.31-1.19 (m, 7H), 0.97 (s, 3H), 0.94-0.90 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.7, 173.4, 144.3, 143.4, 136.2, 135.5, 131.5, 130.5, 129.7, 128.6, 128.3, 127.3, 126.9, 126.6, 126.2, 123.8, 47.9 (4° C), 45.7 (3° C), 41.8 (2° C), 37.2 (2° C), 36.9 (2° C), 32.0 (2° C), 24.1 (2° C), 23.9 (2° C), 21.9 (2° C), 21.6 (2° C), 21.2 (2° C), 14.1 (1° C), 13.7 (1° C); IR (KBr, ν, cm⁻¹): 2928, 1675, 1454, 1343, 1167, 1092, 749, 669; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₅H₃₉NO₄SNa 592.2497; Found 592.2496.

***4*-Methyl-*N*-(2-((2-methyl-1-oxo-1,2,3,4,5,6-hexahydropentalen-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (5k, major)**



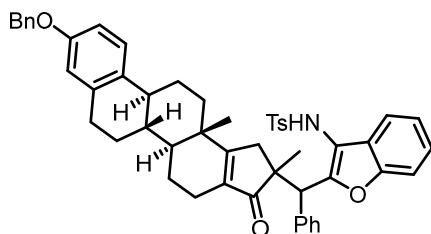
white solid; 44.0 mg, 43% yield; mp: 78.4-79.7 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.81-7.76 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 1H), 7.25-7.19 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.98-6.92 (m, 2H), 3.86 (s, 1H), 3.47 (d, *J* = 18.8 Hz, 1H), 2.42 (d, *J* = 18.0 Hz, 1H), 2.40 (s, 3H), 2.38-2.34 (m, 1H), 2.25-2.15 (m, 3H), 2.05-2.01 (m, 2H), 0.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 208.7, 187.6, 153.5, 151.5, 145.9, 143.5, 136.7, 136.2, 129.8, 129.7, 128.0, 127.4, 127.2, 125.7, 124.4, 123.2, 121.4, 114.4, 110.8, 59.8 (4° C), 46.8 (3° C), 37.3 (2° C), 32.3 (2° C), 27.0 (2° C), 25.2 (2° C), 24.5 (1° C), 21.7 (1° C); IR (KBr, ν, cm⁻¹): 3237, 2961, 1677, 1452, 1380, 1166, 1093, 747; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₁H₂₉NO₄SNa 534.1715; Found 534.1724.

***4*-Methyl-*N*-(2-((2-methyl-1-oxo-2,3,4,5,6,7-hexahydro-1H-inden-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (5l, major)**



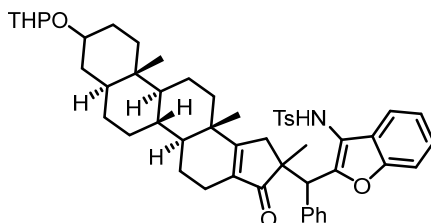
white solid; 62.0 mg, 59% yield; mp: 55.7-56.9 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.81-7.75 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.35-7.33 (m, 1H), 7.25-7.18 (m, 5H), 7.16-7.10 (m, 3H), 6.97 (d, *J* = 6.8 Hz, 2H), 3.83 (s, 1H), 3.42 (d, *J* = 18.0 Hz, 1H), 2.39 (s, 3H), 2.17 (d, *J* = 18.4 Hz, 3H), 1.91 (d, *J* = 16.0 Hz, 1H), 1.72 (d, *J* = 17.2 Hz, 1H), 1.57-1.52 (m, 1H), 1.43 (s, 2H), 1.17 (d, *J* = 11.2 Hz, 1H), 0.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.8, 174.6, 153.6, 151.6, 143.6, 143.5, 136.7, 136.2, 129.9, 129.8, 128.0, 127.4, 127.2, 125.8, 124.5, 123.3, 121.4, 114.3, 110.9, 110.8, 52.7 (4° C), 46.9 (3° C), 41.9 (2° C), 28.7 (2° C), 24.6 (2° C), 21.9 (2° C), 21.7 (2° C), 21.2 (1° C), 19.8 (1° C); IR (KBr, ν, cm⁻¹): 3246, 2929, 1682, 1496, 1166, 1093, 738, 662; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₂H₃₁NO₄SNa 548.1871; Found 548.1885.

N-(2-(((5*aS*,5*bS*,11*bS*,13*aS*)-9-(benzyloxy)-2,13*a*-dimethyl-3-oxo-2,3,4,5,5*a*,5*b*,6,7,11*b*,12,13,13*a*-dodecahydro-1*H*-cyclopenta[*a*]chrysen-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5*m*, major)



white solid; 120.8 mg, 74% yield; mp: 63.2-66.1 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.79-7.77 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.45-7.32 (m, 6H), 7.24-7.21 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 7.00 (d, *J* = 6.4 Hz, 2H), 6.83-6.80 (m, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 5.05 (s, 2H), 3.85 (s, 1H), 3.55-3.48 (m, 1H), 2.84-2.77 (m, 2H), 2.41 (d, *J* = 5.6 Hz, 1H), 2.39 (s, 3H), 2.22-2.08 (m, 3H), 2.02-1.97 (m, 2H), 1.83-1.78 (m, 1H), 1.66-1.54 (m, 3H), 1.37-1.29 (m, 1H), 1.21-1.04 (m, 2H), 0.94 (d, *J* = 11.2 Hz, 6H), 0.74-0.69 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 214.7, 182.6, 157.0, 153.5, 151.6, 143.5, 138.0, 137.3, 136.7, 136.2, 133.9, 132.8, 129.9, 129.8, 128.7, 128.1, 128.0, 127.5, 127.4, 127.3, 126.2, 125.8, 124.5, 123.4, 121.4, 114.6, 114.3, 112.6, 110.9, 70.1 (4° C), 52.8 (3° C), 47.0 (3° C), 46.8 (3° C), 43.4 (3° C), 38.3 (4° C), 37.6 (2° C), 36.6 (3° C), 35.2 (2° C), 30.0 (2° C), 26.5 (2° C), 25.9 (2° C), 24.3 (2° C), 21.7 (1° C), 20.4 (2° C), 19.2 (1° C), 18.2 (1° C); IR (KBr, ν, cm⁻¹): 2926, 1679, 1498, 1379, 1249, 1166, 1027, 737; HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₅₃H₅₄NO₅S 802.3566; Found 802.3572.

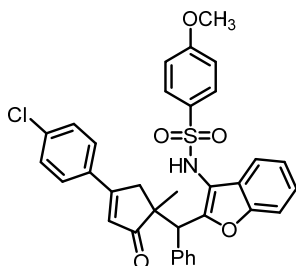
4-methyl-*N*-(2-(phenyl((5*aS*,5*bR*,7*aS*,11*aS*,11*bS*,13*aS*)-2,11*a*,13*a*-trimethyl-3-oxo-9-((tetrahydro-2*H*-pyran-2-yl)oxy)-2,3,4,5,5*a*,5*b*,6,7,7*a*,8,9,10,11,11*a*,11*b*,12,13,13*a*-octadecahydro-1*H*-cyclopenta[*a*]chrysen-2-yl)methyl)benzofuran-3-yl)benzenesulfonamide (5*n*, major)



white solid; 83.2 mg, 51% yield; mp: 54.2-55.8 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.77-7.75 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.36-7.32 (m, 1H), 7.26-7.16 (m, 5H), 7.15-7.08 (m, 3H), 6.96 (d, *J* = 6.4 Hz, 2H), 4.73 (s, 1H), 3.82 (d, *J* = 2.4 Hz, 1H), 3.62-3.41 (m, 2H), 2.38 (s, 3H), 2.14 (d, *J* = 18.0 Hz, 1H), 2.03 (s, 2H), 1.92-1.45 (m, 14H), 1.42-1.12 (m, 7H), 1.10-0.94 (m, 3H), 0.89 (d, *J* = 7.2 Hz, 6H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.63-0.45 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 214.7, 182.7, 170.8, 153.5, 151.6, 143.5, 136.7, 136.2, 133.8, 129.9, 129.8, 128.0, 127.4, 127.2, 125.8,

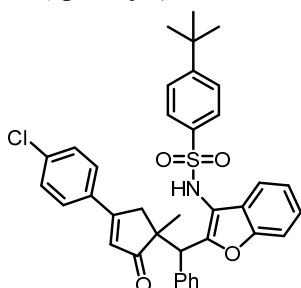
124.4, 123.3, 121.4, 114.3, 111.0, 73.6 (4° C), 53.7 (2° C), 52.8 (4° C), 47.8 (3° C), 47.0 (3° C), 44.2 (3° C), 37.5 (4° C), 36.7 (2° C), 35.9 (3° C), 35.7 (4° C), 35.3 (3° C), 34.6 (2° C), 33.9 (2° C), 31.4 (2° C), 31.0, (2° C) 28.4 (2° C), 27.5 (2° C), 25.6 (2° C), 24.3 (2° C), 21.7 (2° C), 21.6 (1° C), 20.4 (2° C), 20.2 (2° C), 19.1 (1° C), 18.2 (1° C), 12.3 (1° C); IR (KBr, ν , cm^{-1}): 2936, 1730, 1635, 1452, 1351, 1167, 1027, 737; HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{51}\text{H}_{61}\text{NO}_6\text{SNa}$ 838.4117; Found 838.4119.

3-(4-Chlorophenyl)-5-((3-((4-methoxyphenyl)amino)benzofuran-2-yl)(phenyl)methyl)-5-methylcyclopent-2-en-1-one (5o, major)



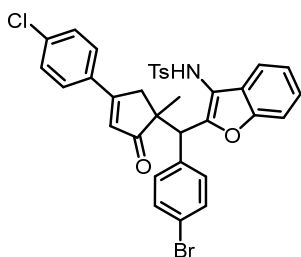
white solid; 49.0 mg, 41% yield; mp: 55.1-56.3 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.77-7.71 (m, 1H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 2.0$ Hz, 2H), 7.18 (d, $J = 6.8$ Hz, 3H), 7.09 (d, $J = 4.4$ Hz, 3H), 6.76 (d, $J = 8.8$ Hz, 2H), 6.23 (s, 1H), 3.98-3.94 (m, 2H), 3.80 (s, 3H), 2.69 (d, $J = 18.0$ Hz, 1H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 213.7, 172.2, 163.1, 153.6, 151.4, 137.9, 136.2, 132.1, 131.1, 129.9, 129.5, 129.3, 128.4, 128.2, 127.4, 125.6, 124.6, 123.3, 121.4, 114.8, 114.3, 111.0, 55.6 (4° C), 53.7 (1° C), 46.6 (3° C), 40.0 (2° C), 25.5 (1° C); IR (KBr, ν , cm^{-1}): 3244, 1679, 1596, 1454, 1262, 1092, 830, 738; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{28}\text{ClNO}_5\text{SNa}$ 620.1274; Found 620.1266.

5-((3-((4-tert-Butyl)phenyl)amino)benzofuran-2-yl)(phenyl)methyl)-3-(4-chlorophenyl)-5-methylcyclopent-2-en-1-one (5p, major)



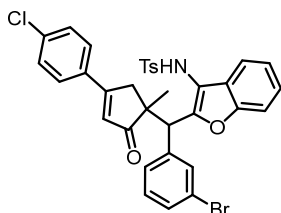
white solid; 98.6 mg, 79% yield; mp: 59.1-60.5 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.77 (d, $J = 8.8$ Hz, 2H), 7.58-7.51 (m, 3H), 7.46-7.38 (m, 5H), 7.28 (s, 1H), 7.19-7.12 (m, 5H), 7.10 (s, 1H), 6.27 (s, 1H), 4.18 (s, 1H), 3.96 (d, $J = 18.0$ Hz, 1H), 2.76 (d, $J = 17.6$ Hz, 1H), 1.35 (s, 9H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 213.8, 172.2, 156.6, 153.5, 151.7, 137.9, 137.3, 136.5, 132.1, 129.9, 129.3, 128.5, 128.4, 127.5, 126.2, 125.7, 124.6, 124.5, 123.2, 121.1, 114.6, 111.0, 53.7 (4° C), 46.7 (3° C), 40.3 (2° C), 35.3 (4° C), 31.3 (1° C), 25.6 (1° C); IR (KBr, ν , cm^{-1}): 3239, 2965, 1678, 1328, 1169, 1090, 829, 738; HRMS (ESI -TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{37}\text{H}_{34}\text{ClNO}_4\text{SNa}$ 646.1795; Found 646.1782.

N-(2-((3-Bromophenyl)(4-(4-chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5q, major)



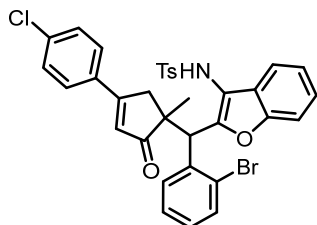
white solid; 89.9 mg, 68% yield; mp: 84.8-85.3 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.70-7.66 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.41-7.36 (m, 4H), 7.18 (d, *J* = 4.0 Hz, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.22 (s, 1H), 3.96 (s, 1H), 3.88 (d, *J* = 18.0 Hz, 1H), 2.67 (d, *J* = 17.6 Hz, 1H), 2.40 (s, 3H), 1.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.3, 172.2, 153.6, 150.9, 143.7, 138.1, 136.7, 135.3, 132.0, 131.5, 131.4, 129.8, 129.4, 128.4, 127.5, 125.5, 124.8, 124.6, 123.5, 121.4, 115.0, 111.0, 53.5 (4° C), 46.0 (3° C), 39.9 (2° C), 25.4 (1° C), 21.8 (1° C); IR (KBr, ν, cm⁻¹): 2925, 1683, 1596, 1489, 1165, 1091, 747; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₄H₂₇BrClNO₄SNa 682.0430; Found 682.0421.

***N*-(2-((3-Bromophenyl)(4-(4-chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5r, major)**



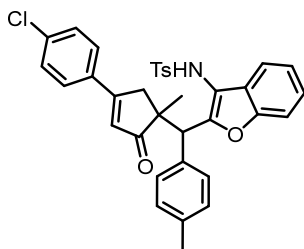
white solid; 104.4 mg, 79% yield; mp: 89.8-91.2 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.73 (d, *J* = 6.4 Hz, 1H), 7.67-7.60 (m, 3H), 7.44-7.38 (m, 5H), 7.23-7.15 (m, 7H), 6.92-6.84 (m, 1H), 6.25 (d, *J* = 12.8 Hz, 1H), 5.30 (s, 1H), 4.02 (s, 1H), 3.91 (d, *J* = 17.6 Hz, 1H), 2.75 (d, *J* = 18.0 Hz, 1H), 2.41 (s, 3H), 1.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.6, 174.0, 153.6, 150.6, 143.8, 138.7, 136.8, 133.5, 132.7, 132.0, 130.6, 129.8, 129.0, 128.5, 127.4, 127.2, 125.5, 124.7, 124.2, 123.4, 122.3, 121.4, 115.0, 111.1, 53.5 (4° C), 46.2 (3° C), 39.9 (2° C), 25.6 (1° C), 21.9 (1° C); IR (KBr, ν, cm⁻¹): 3243, 1676, 1596, 1453, 1166, 1092, 749; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₄H₂₇BrClNO₄SNa 682.0430; Found 682.0419.

***N*-(2-((2-Bromophenyl)(4-(4-chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (5s, major)**



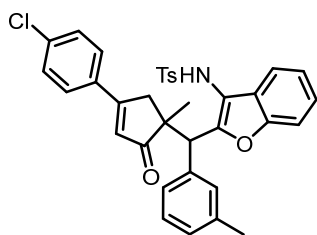
white solid; 121.6 mg, 92% yield; mp: 118.7-119.1 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 8.08-8.05 (m, 1H), 7.65-7.60 (m, 3H), 7.59-7.55 (m, 3H), 7.47-7.39 (m, 3H), 7.26-7.17 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 1H), 6.30 (s, 1H), 5.26 (s, 1H), 4.05-4.00 (m, 1H), 2.76-2.71 (m, 1H), 2.36 (s, 3H), 1.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 212.4, 171.3, 153.5, 150.2, 143.6, 137.8, 137.0, 136.3, 133.5, 132.3, 130.8, 129.6, 129.3, 128.3, 127.4, 126.8, 125.0, 123.3, 121.7, 115.7, 111.0, 54.8 (4° C), 43.7 (3° C), 40.7 (2° C), 24.8 (1° C), 21.6 (1° C); IR (KBr, ν, cm⁻¹): 3244, 1682, 1597, 1454, 1327, 1164, 738, 565; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₄H₂₇BrClNO₄SNa 682.0430; Found 682.0430.

***N*-2-((4-(4-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(*p*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (**5t**, major)**



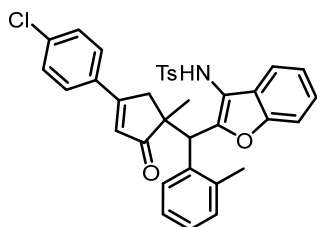
white solid; 71.5 mg, 60% yield; mp: 107.6-108.0 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.76-7.70 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.19-7.12 (m, 5H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 4.03-3.81 (m, 2H), 2.72-2.67 (m, 1H), 2.38 (d, *J* = 22.4 Hz, 6H), 1.02 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.9, 172.3, 153.6, 151.7, 143.6, 137.9, 137.0, 136.8, 133.1, 132.1, 129.8, 129.3, 128.9, 128.4, 127.5, 124.5, 123.3, 121.4, 114.5, 111.0, 53.7 (4° C), 46.2 (3° C), 40.1 (2° C), 25.5 (1° C), 21.7 (1° C), 21.2 (1° C); IR (KBr, ν, cm⁻¹): 3224, 1660, 1591, 1436, 1166, 1091, 750; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₅H₃₀ClNO₄SNa 618.1482; Found 618.1460.

***N*-2-((4-(4-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(*m*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (**5u**, major)**

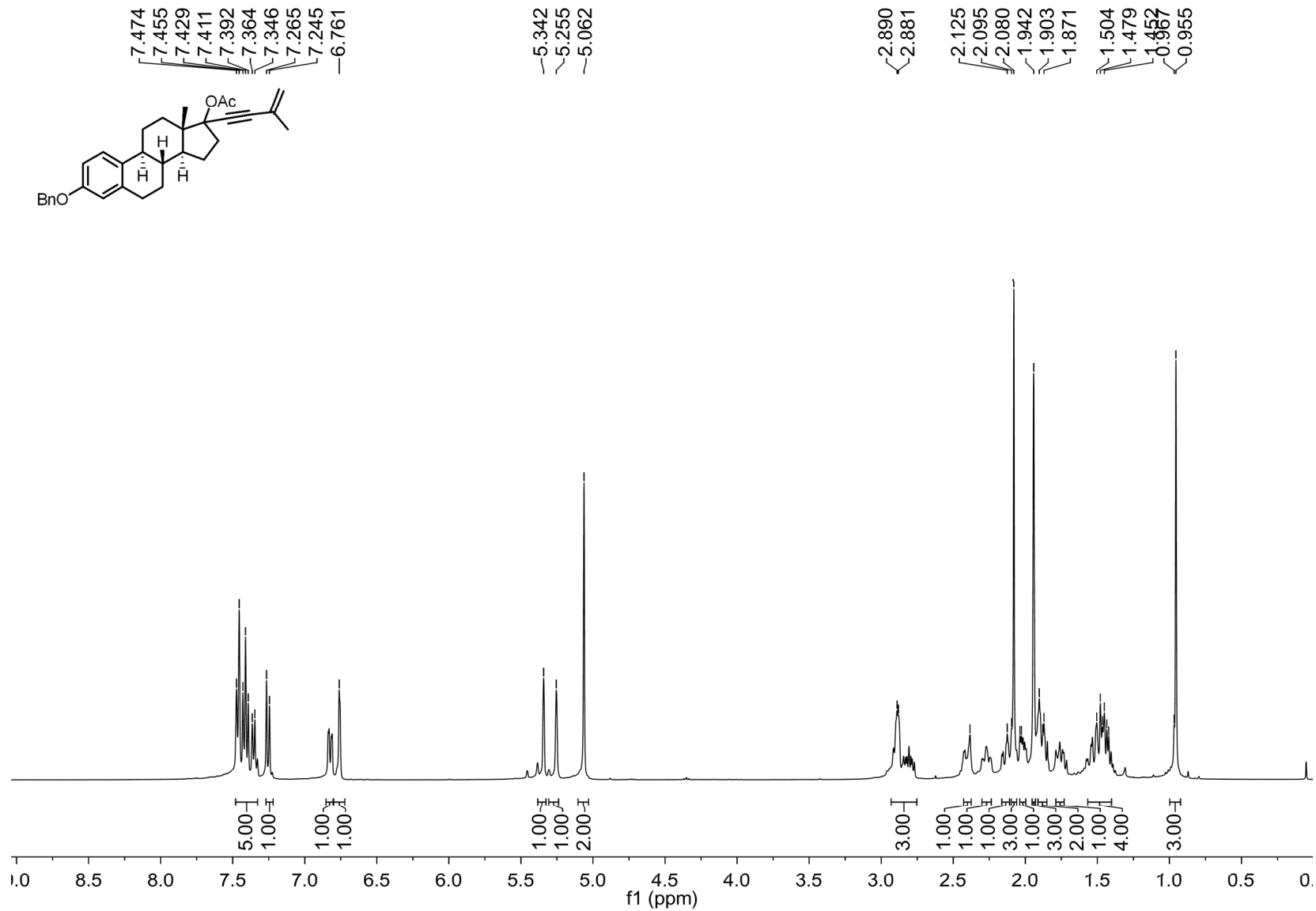


white solid; 77.5 mg, 65% yield; mp: 125.4-126.7 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.78-7.76 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.26-7.16 (m, 7H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.29 (s, 1H), 5.35 (s, 1H), 4.04 (s, 1H), 4.01-3.94 (m, 1H), 2.76 (d, *J* = 18.0 Hz, 1H), 2.42 (d, *J* = 10.4 Hz, 6H), 1.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.9, 172.3, 153.6, 151.5, 143.5, 137.8, 136.9, 136.1, 132.2, 130.4, 129.7, 129.3, 128.4, 128.2, 128.1, 127.5, 127.0, 125.7, 124.61, 123.3, 121.4, 114.6, 111.0, 53.6 (4° C), 46.5 (3° C), 40.2 (2° C), 25.5 (1° C), 21.8 (1° C), 21.7 (1° C); IR (KBr, ν, cm⁻¹): 3231, 1679, 1454, 1165, 1091, 748, 667; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₅H₃₀ClNO₄SNa 618.1482; Found 618.1465.

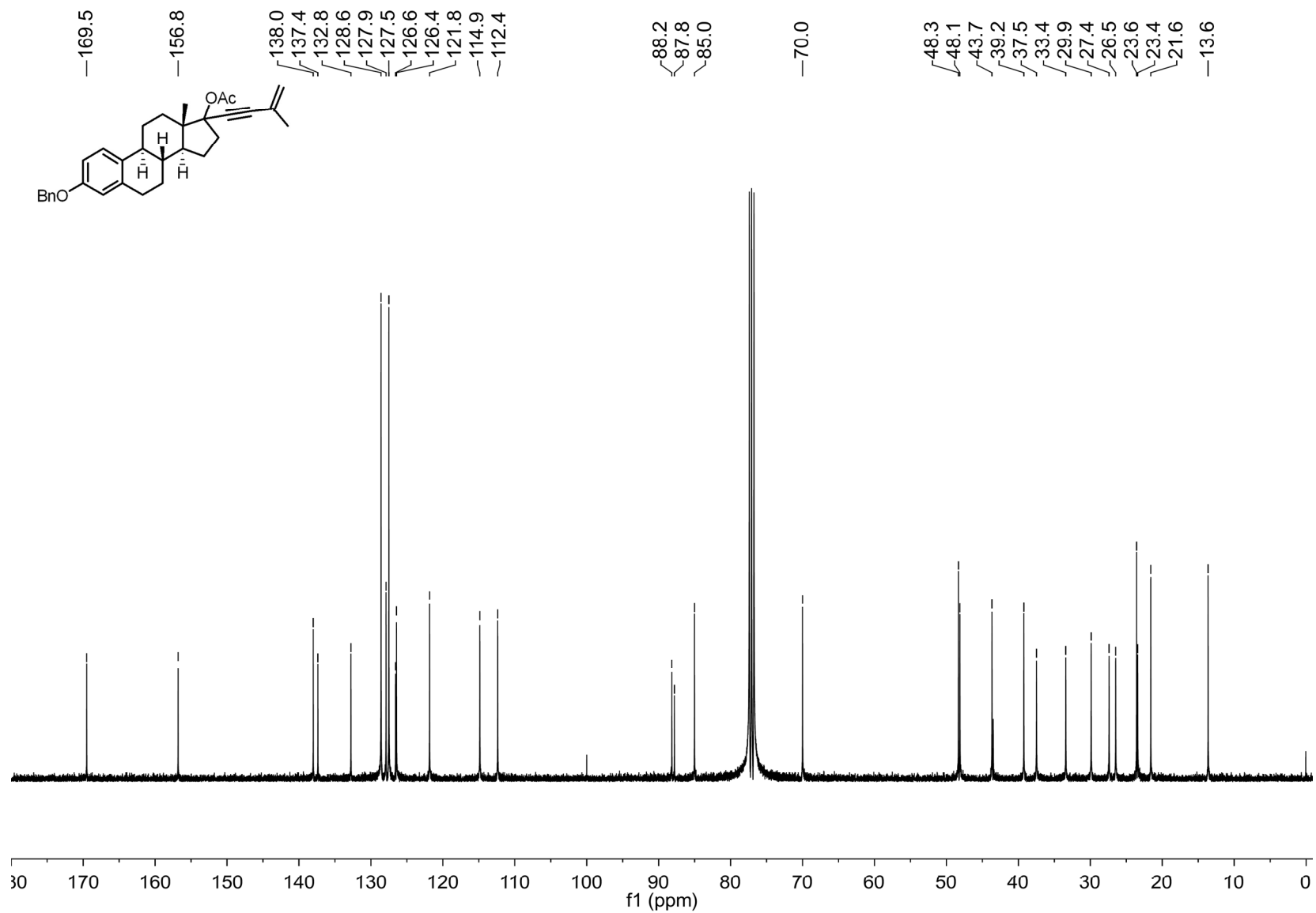
***N*-2-((4-(4-Chlorophenyl)-1-methyl-2-oxocyclopent-3-en-1-yl)(*o*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (**5v**, major)**



white solid; 81.1 mg, 68% yield; mp: 80.8-81.4 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.96 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.30 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.21-7.19 (m, 1H), 7.17-7.09 (m, 5H), 7.067.03 (m, 1H), 6.28 (s, 1H), 4.95 (s, 1H), 4.05 (d, *J* = 17.6 Hz, 1H), 2.79 (d, *J* = 18.0 Hz, 1H), 2.39 (s, 3H), 2.15 (s, 3H), 1.12 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 213.7, 172.0, 153.4, 152.1, 143.7, 138.0, 137.6, 135.2, 132.2, 131.0, 129.7, 129.3, 128.4, 127.3, 126.2, 124.5, 123.0, 120.8, 114.8, 111.1, 54.8 (4° C), 40.8 (3° C), 40.6 (2° C), 24.8 (1° C), 21.6 (1° C), 20.5 (1° C); IR (KBr, ν, cm⁻¹): 3245, 1682, 1597, 1327, 1164, 1013, 740, 667; HRMS (ESI -TOF) *m/z*: [M+Na]⁺ Calcd for C₃₅H₃₀ClNO₄SNa 618.1482; Found 618.1479.

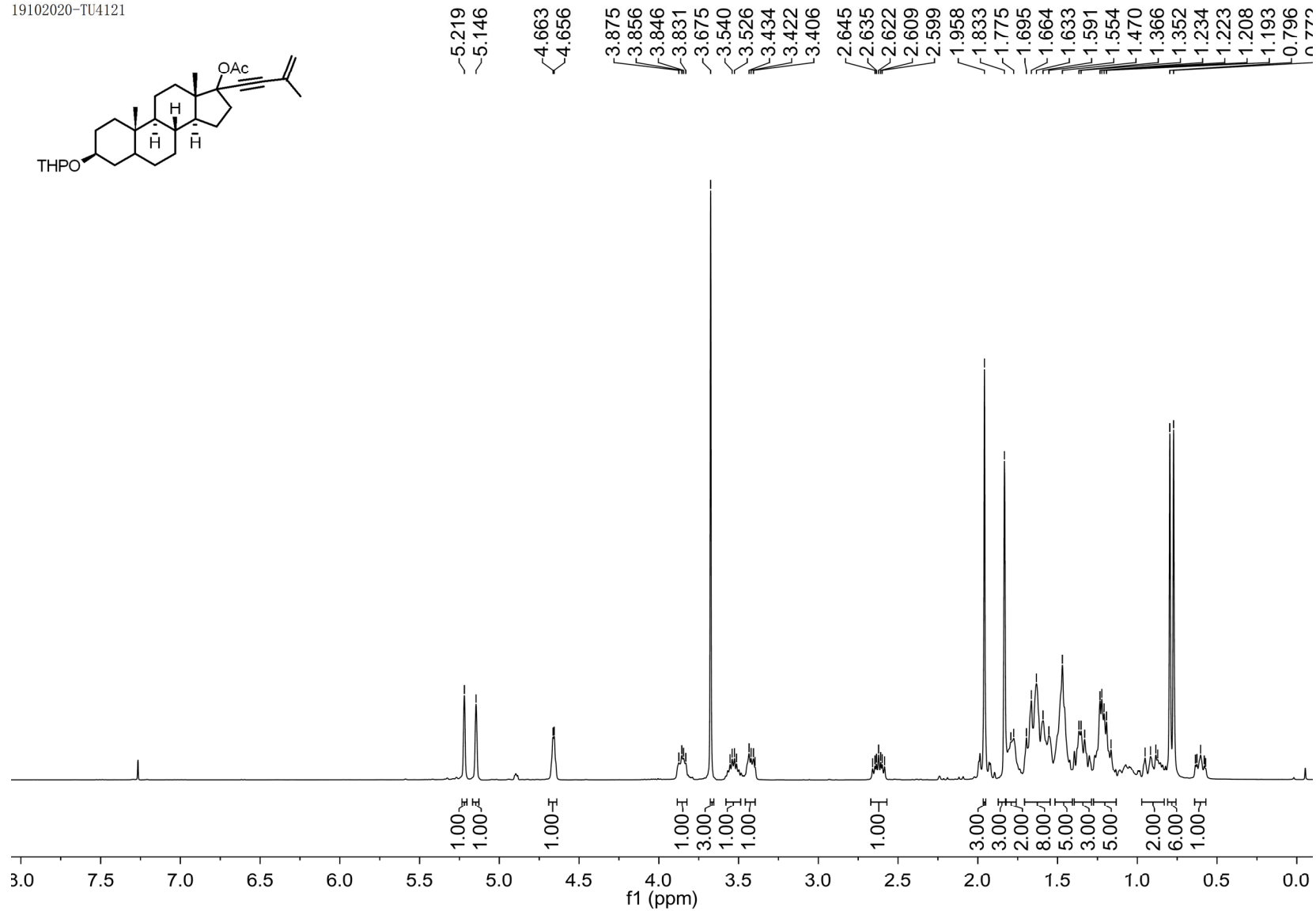


¹H NMR Spectrum of Compound 1o

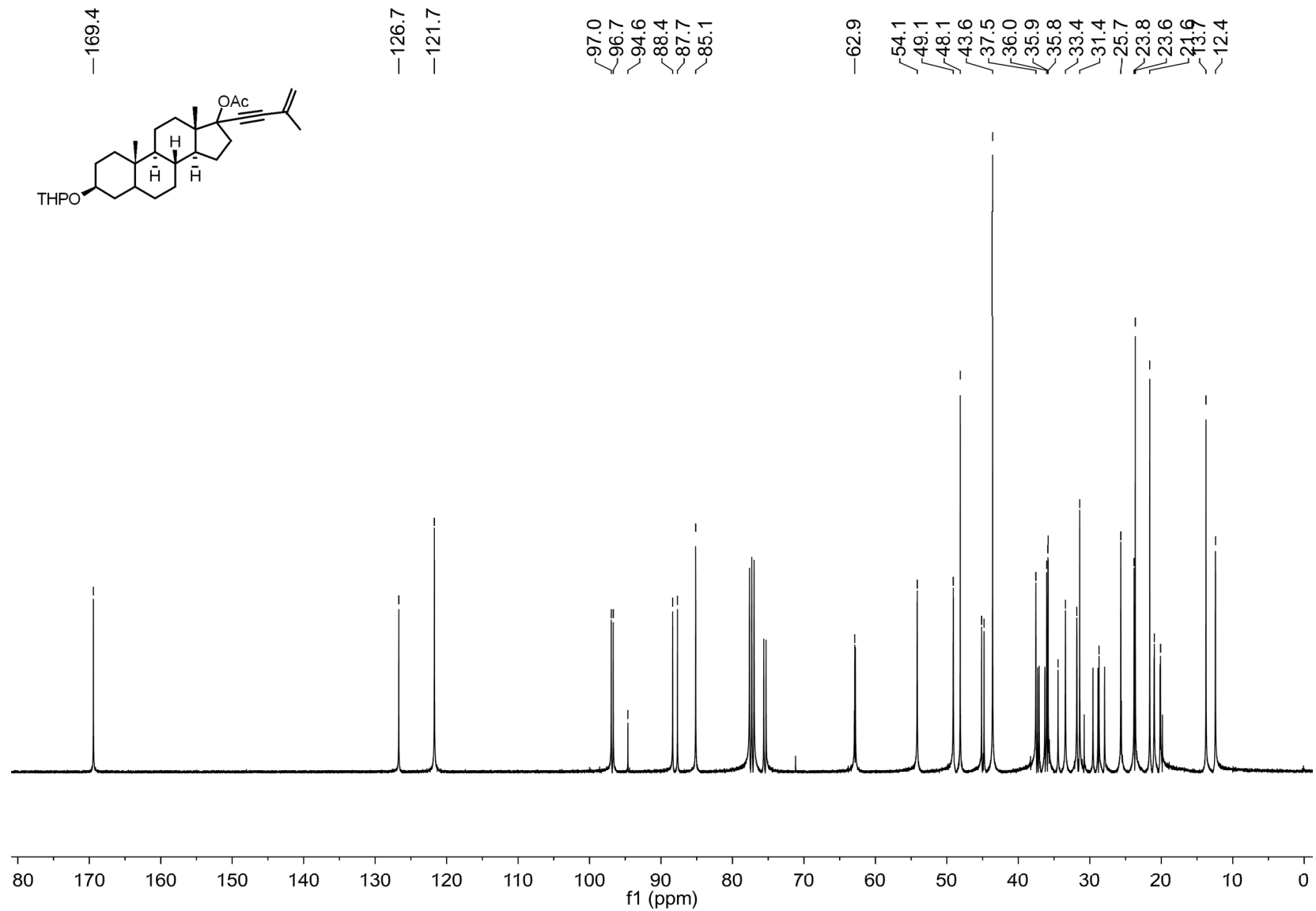


¹³C NMR Spectrum of Compound 10

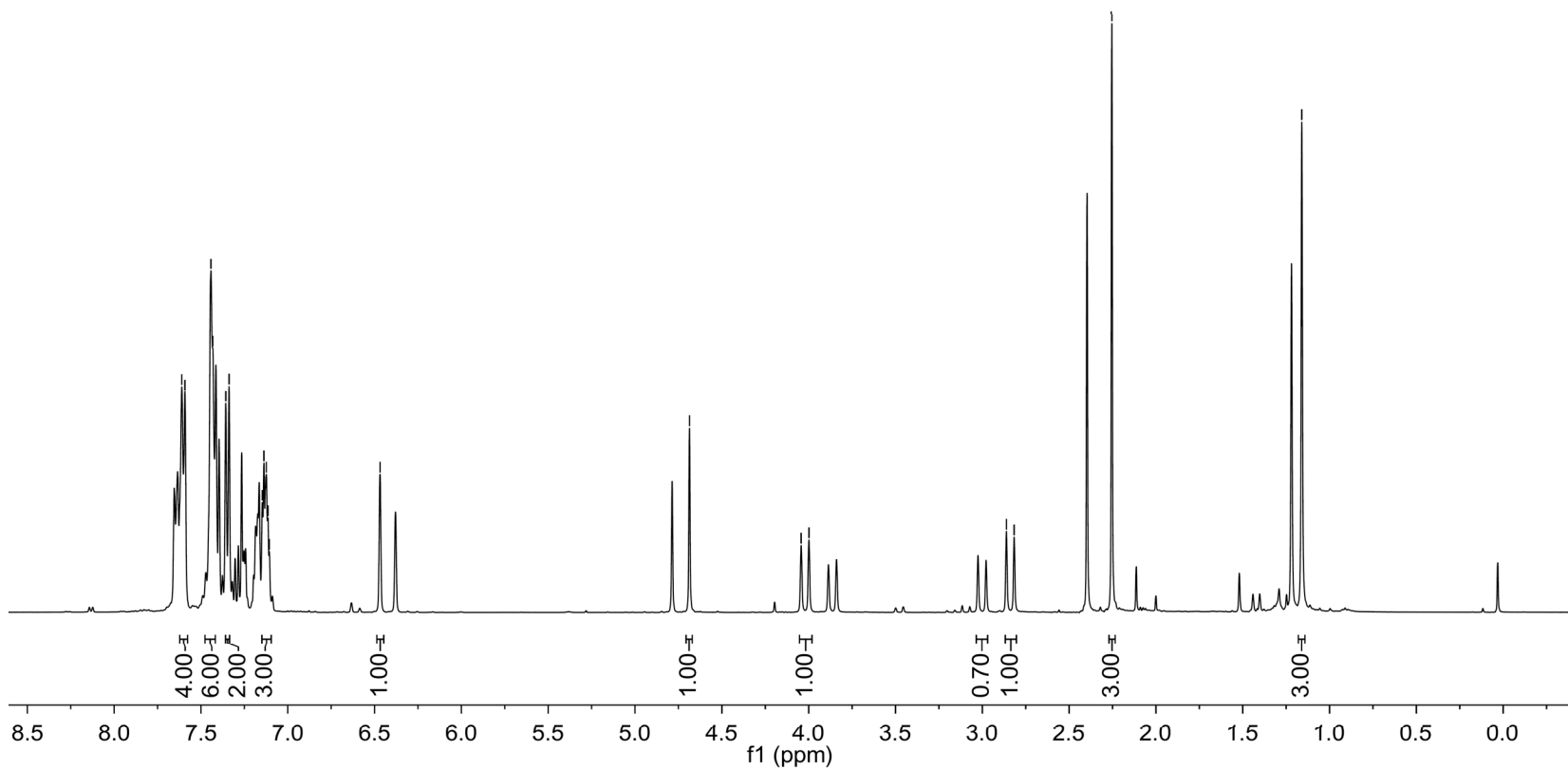
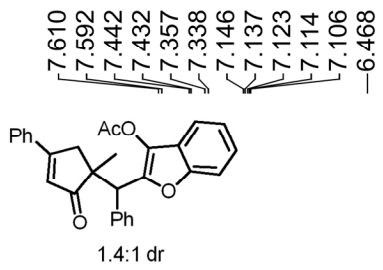
19102020-TU4121



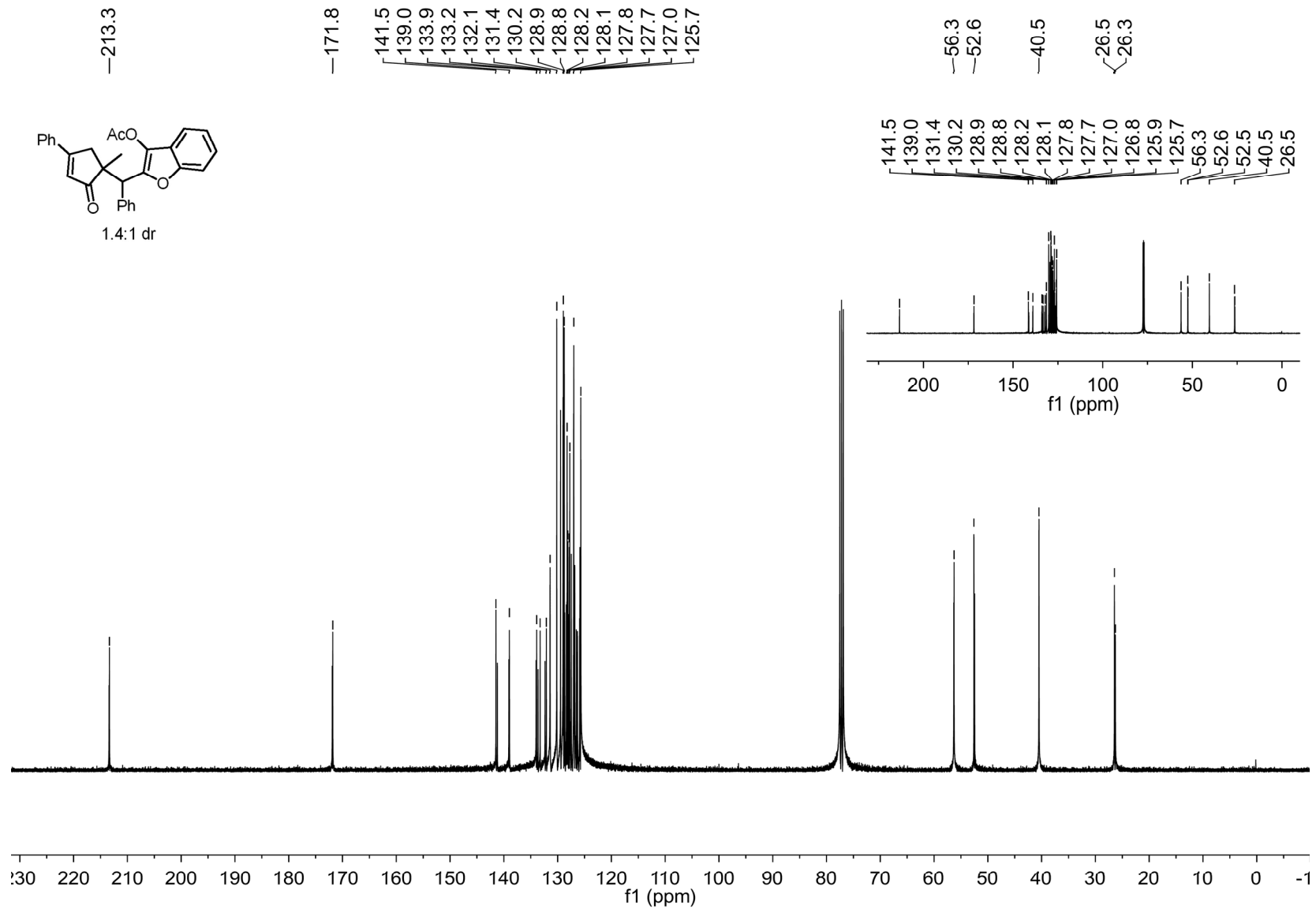
¹H NMR Spectrum of Compound 1p



¹³C NMR Spectrum of Compound 1p



¹H NMR Spectrum of Compound 3a



¹³C NMR Spectrum of Compound 3a

7.565
7.546
7.379
7.360
7.331
7.312
7.306
7.289
7.274
7.252
7.247
7.227
7.208
7.189
6.162

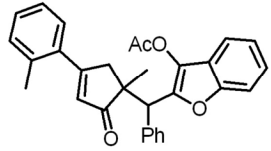
4.650

4.023
3.977

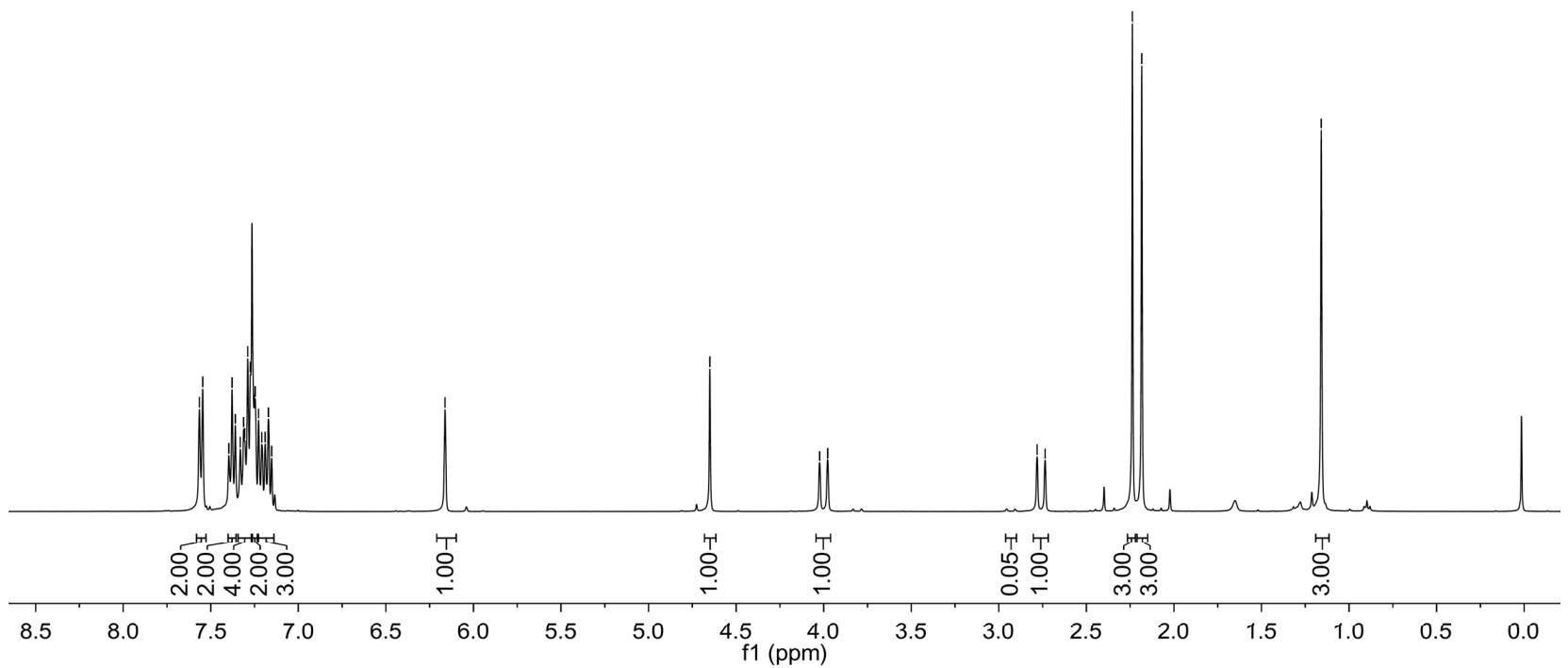
2.781
2.735

2.237
2.184

1.159

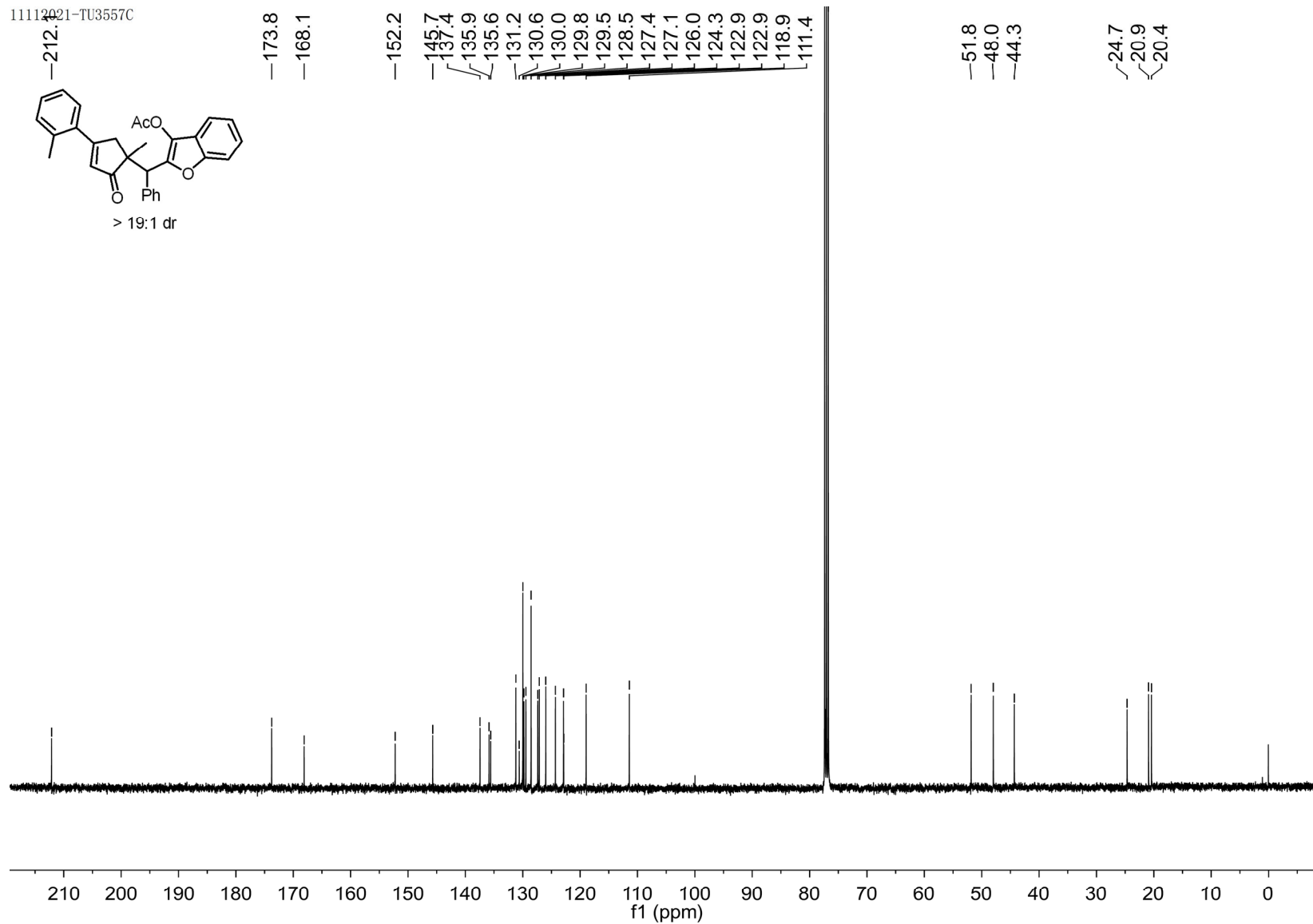


> 19:1 dr

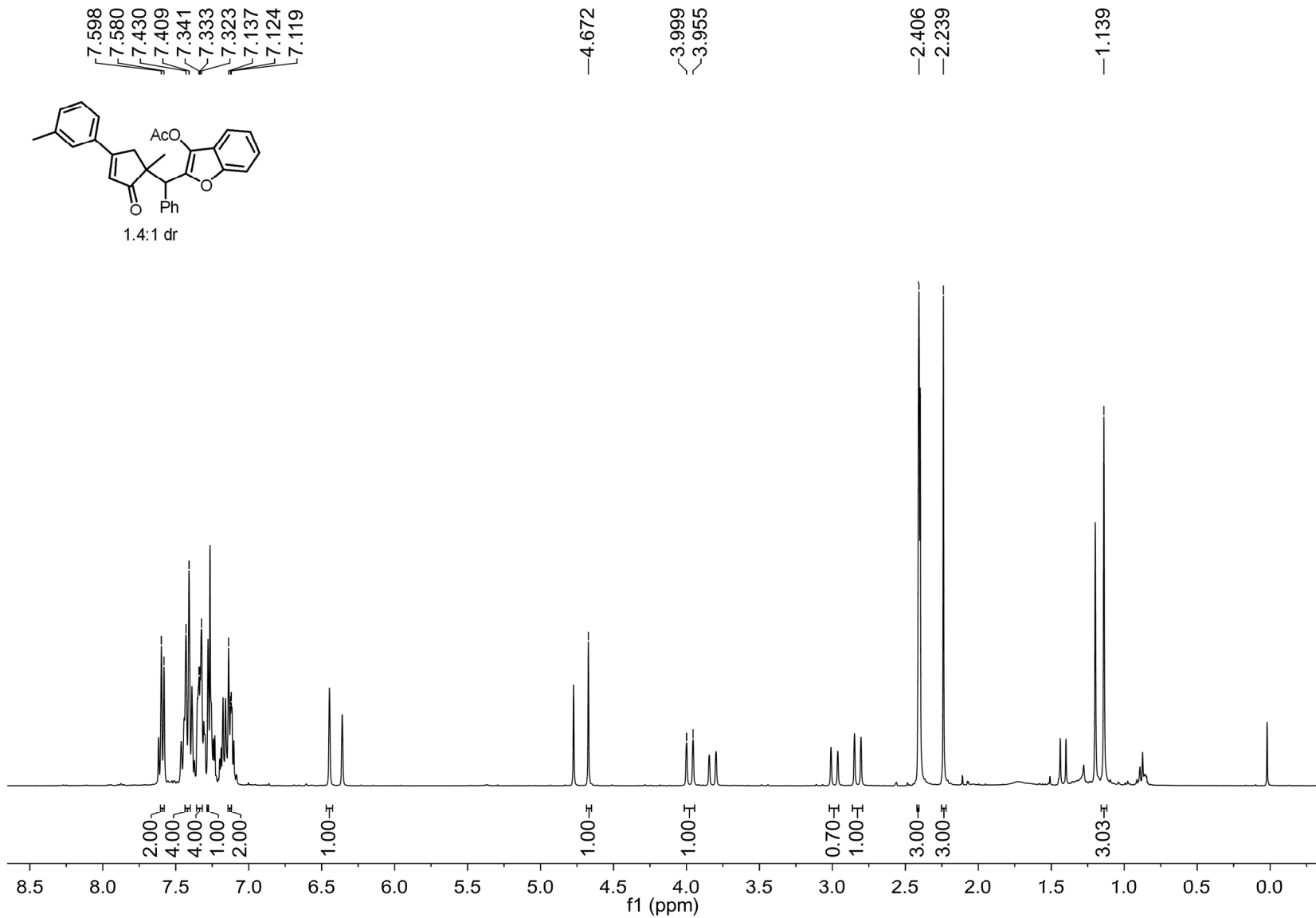
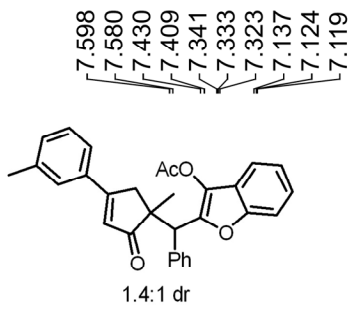


¹H NMR Spectrum of Compound 3b

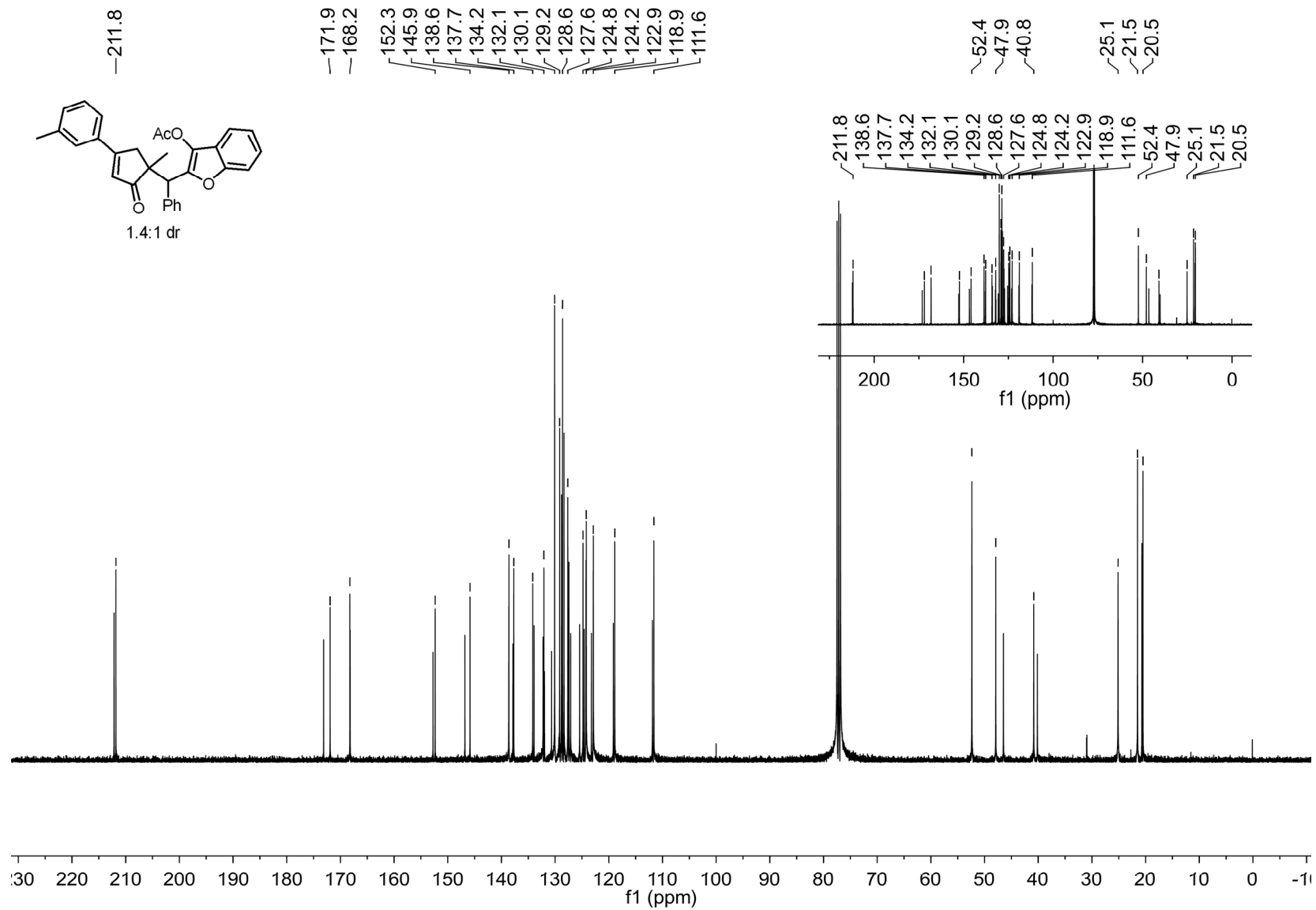
11112021-TU3557C



¹³C NMR Spectrum of Compound 3b

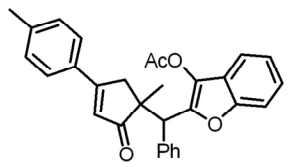


¹H NMR Spectrum of Compound 3c

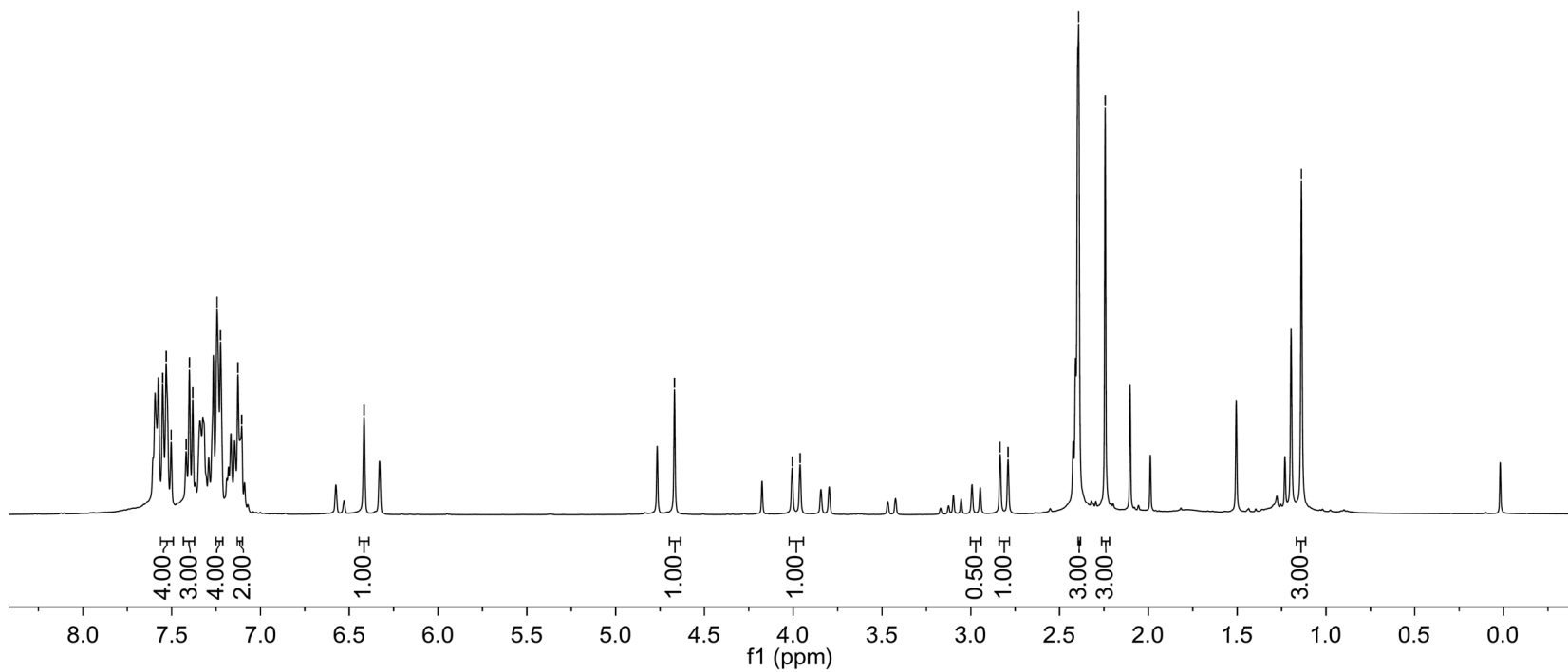


¹³C NMR Spectrum of Compound 3c

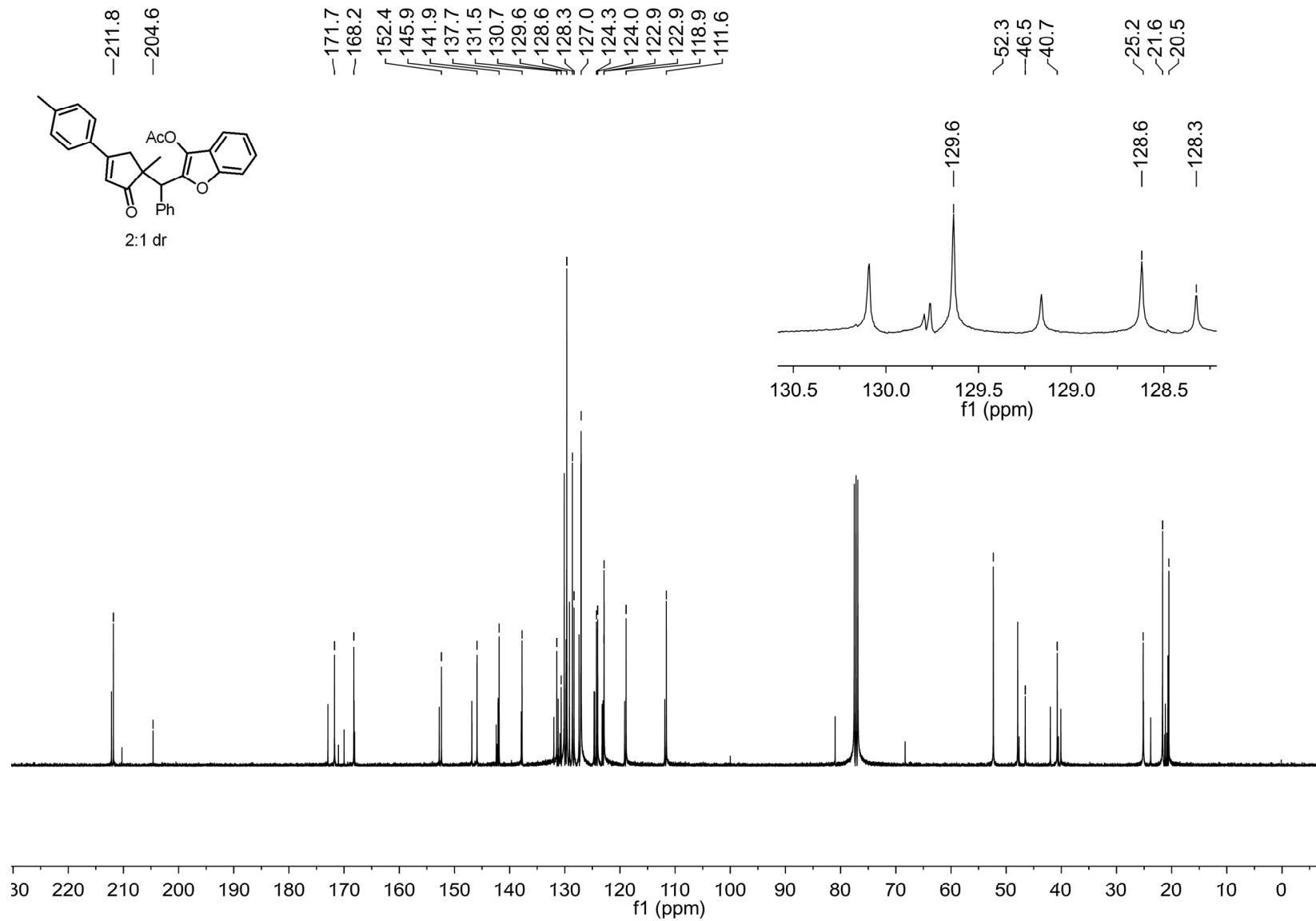
7.551
7.531
7.503
7.419
7.400
7.381
7.244
7.225
7.127
7.106
—6.416
—4.669
—4.006
—3.961
—2.835
—2.790
—2.393
—2.243
—1.138



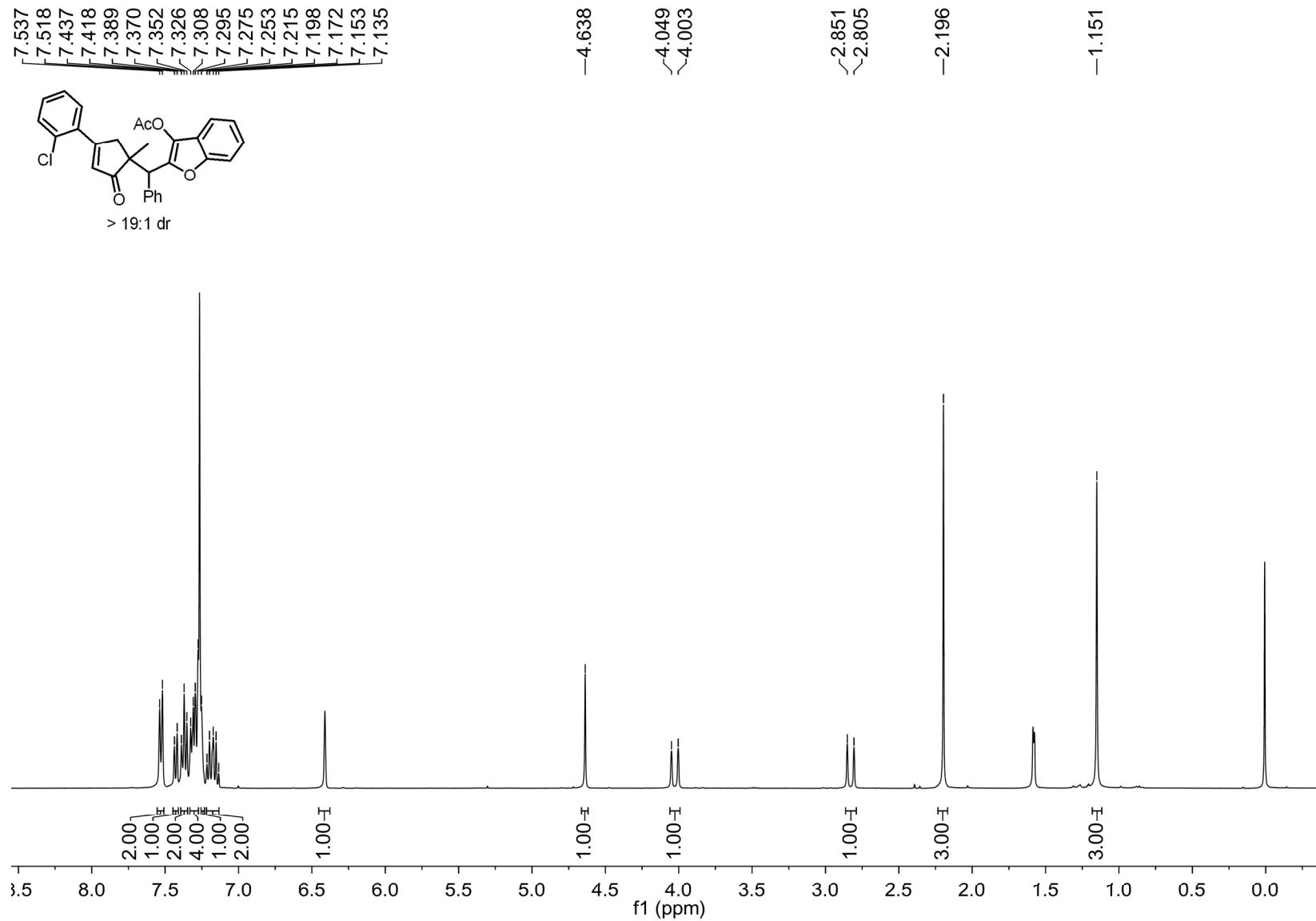
2:1 dr



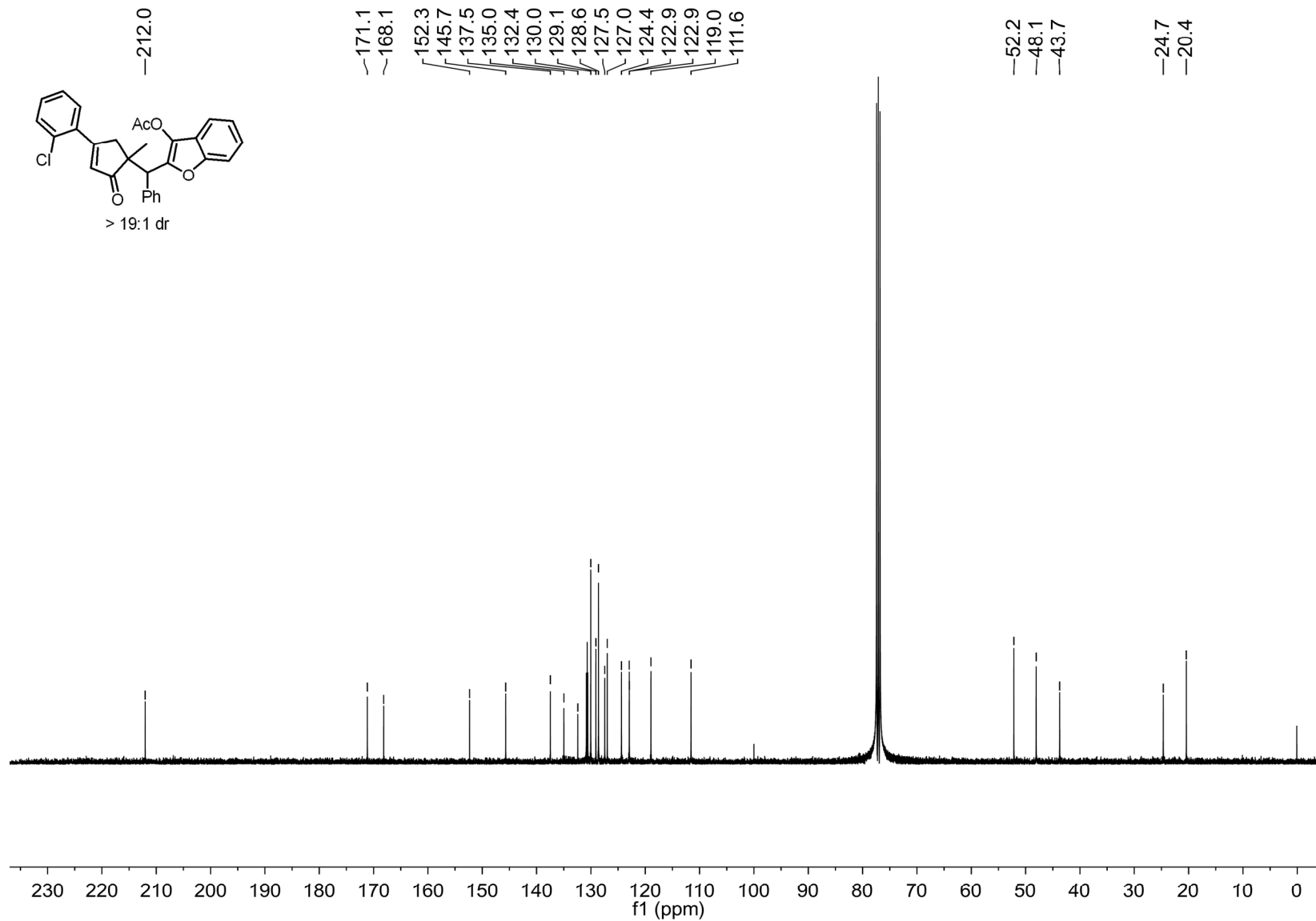
¹H NMR Spectrum of Compound 3d



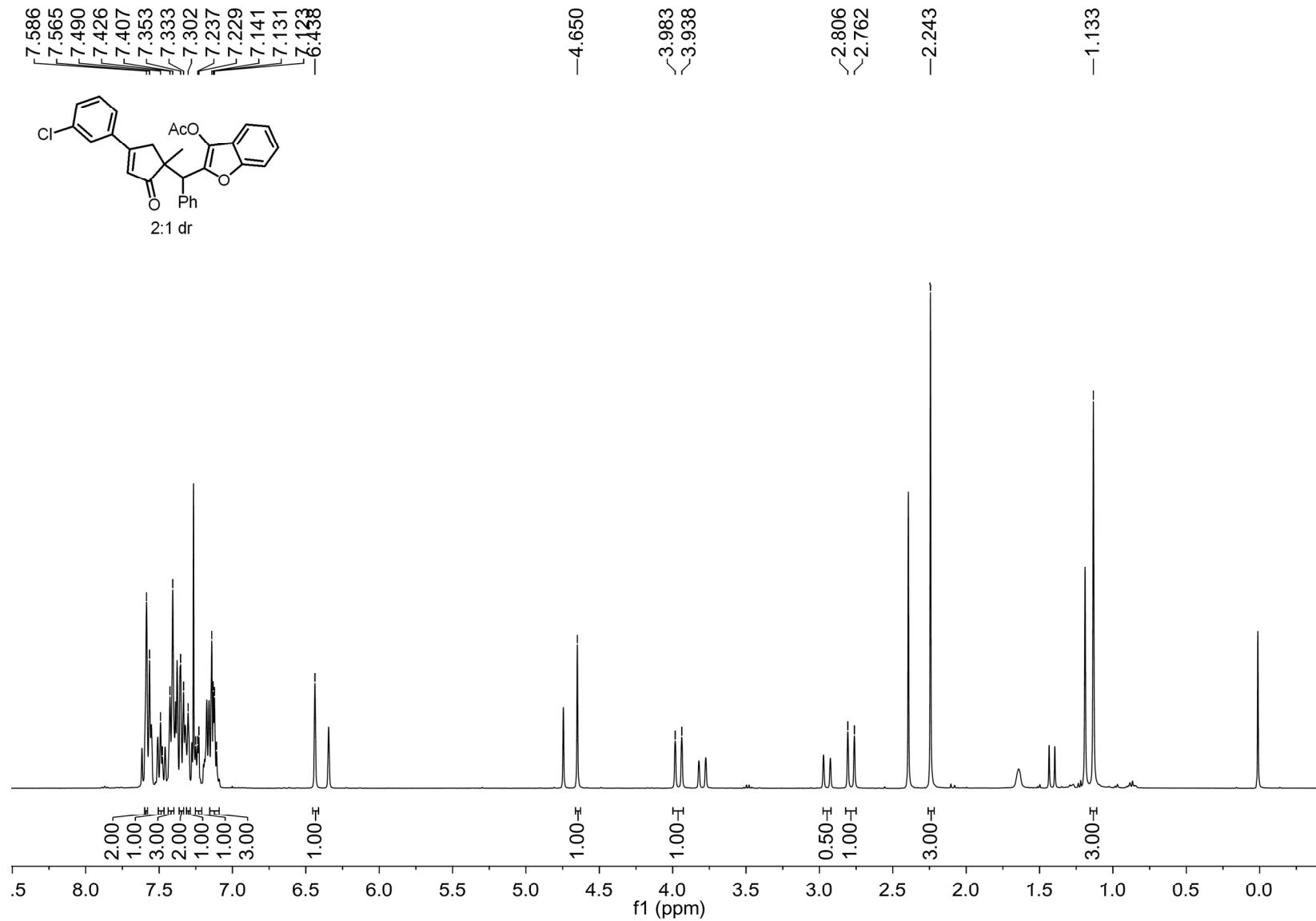
¹³C NMR Spectrum of Compound 3d



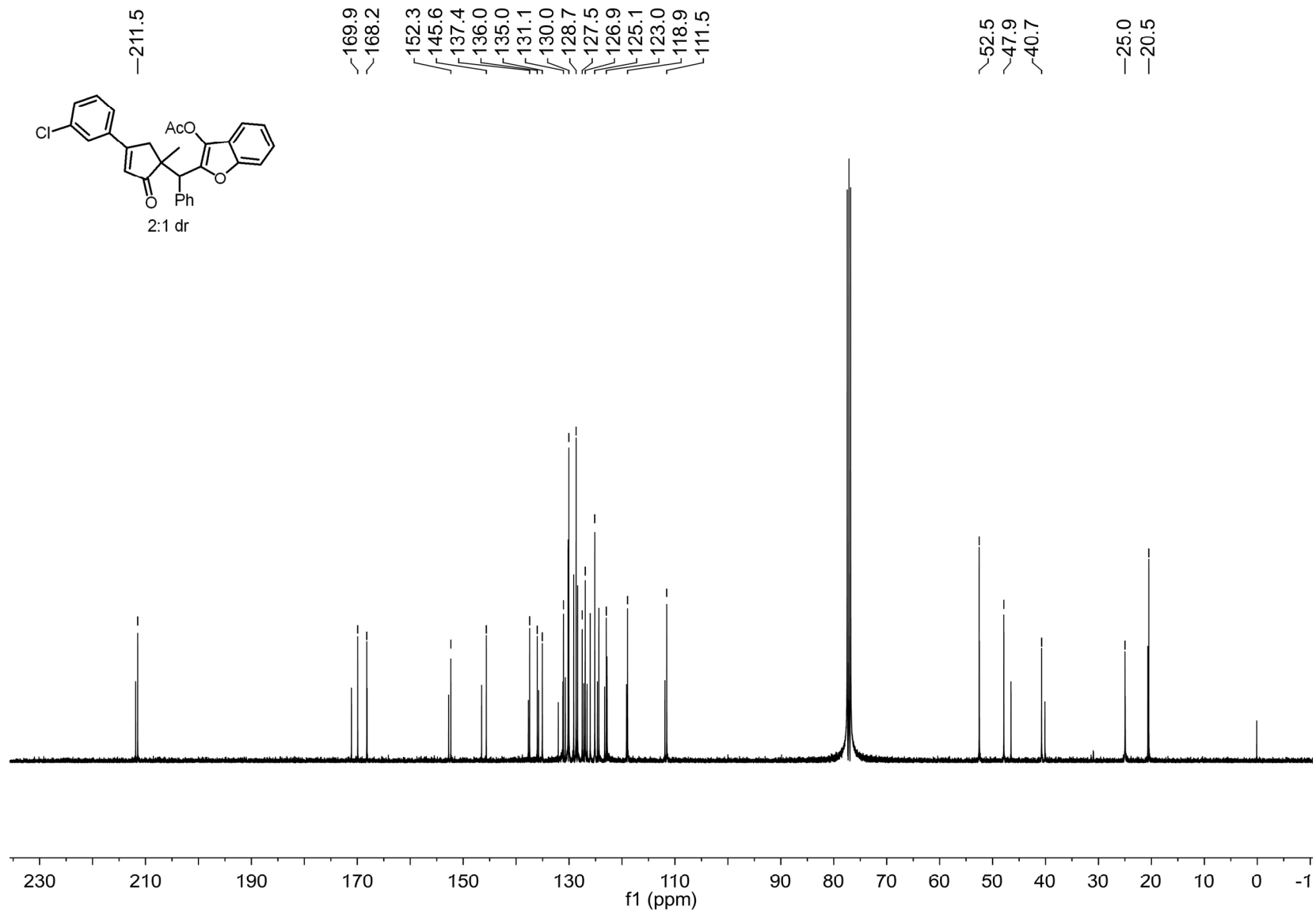
¹H NMR Spectrum of Compound 3e



¹³C NMR Spectrum of Compound 3e



¹H NMR Spectrum of Compound 3f



¹³C NMR Spectrum of Compound 3f

7.619
7.608
7.597
7.461
7.454
7.442
7.361
7.342
7.215
7.198
7.183
-6.463

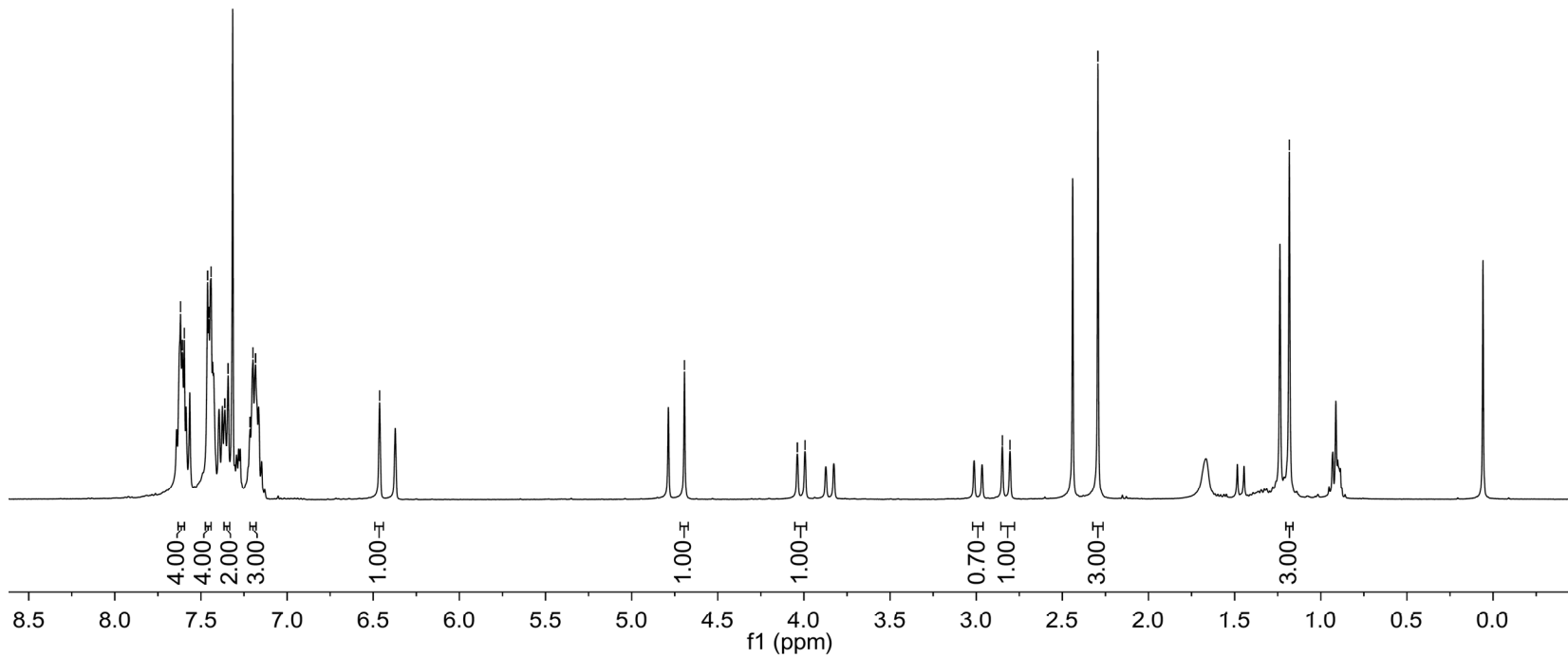
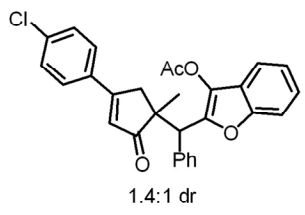
-4.693

4.039
3.994

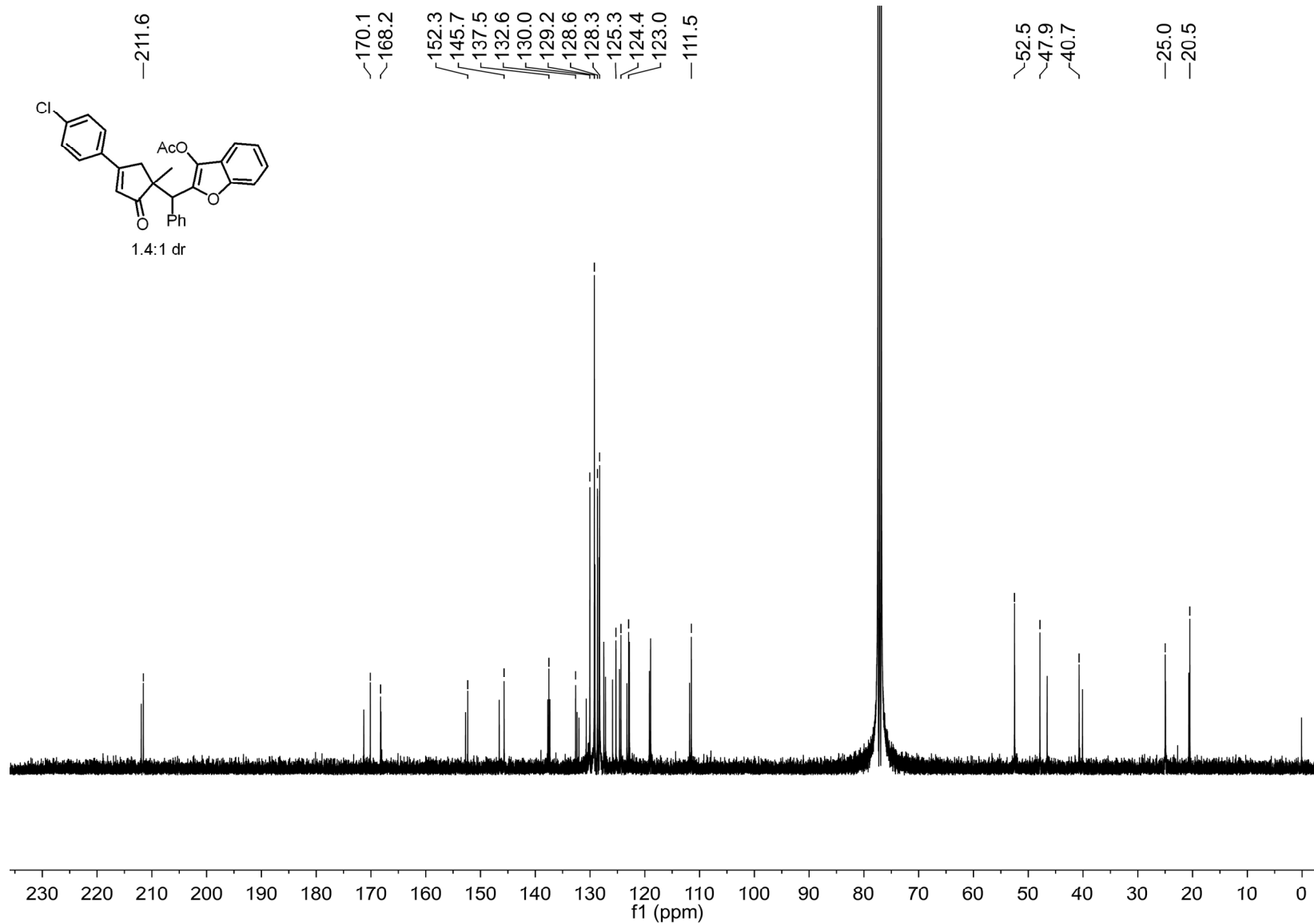
2.848
2.804

-2.293

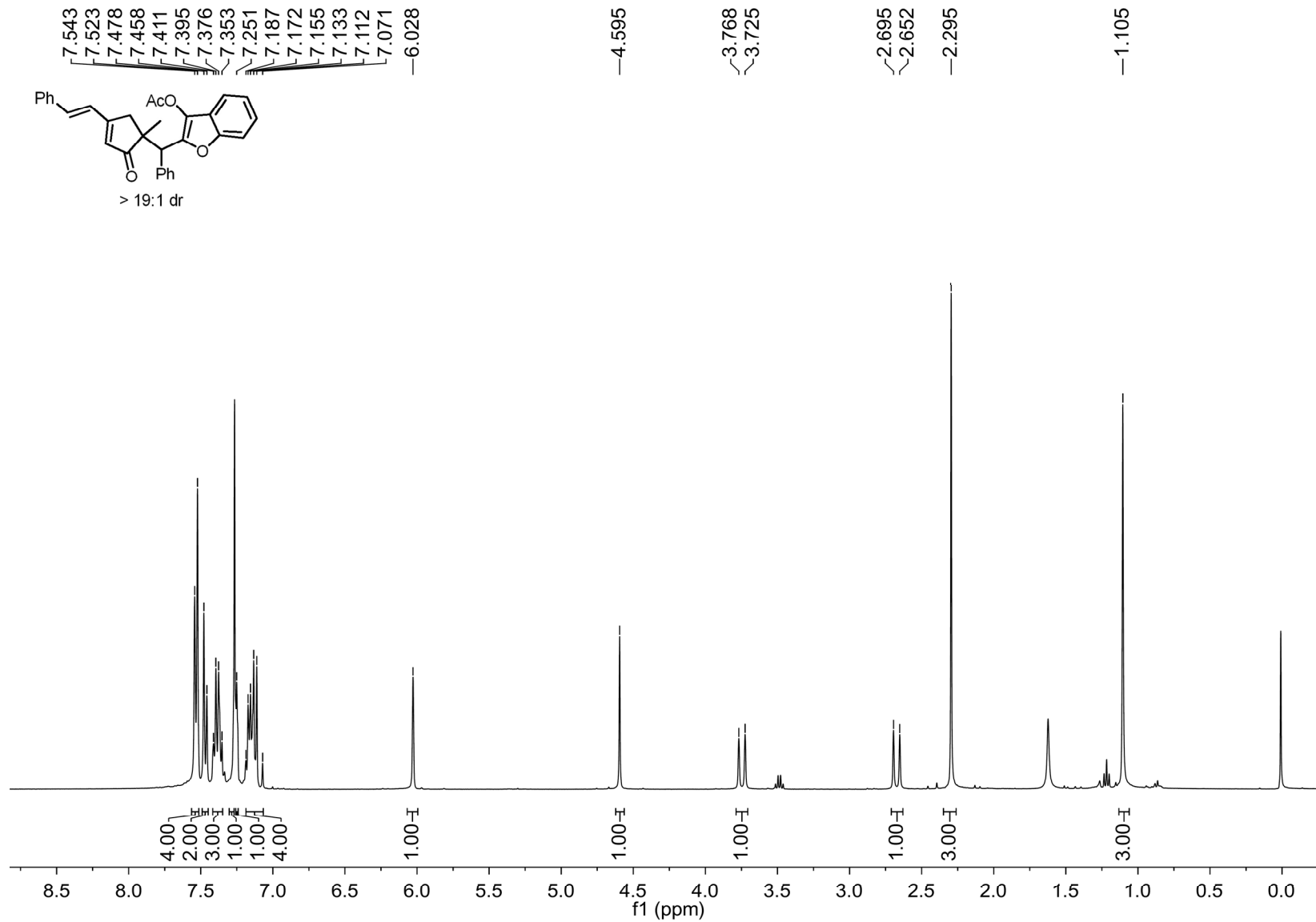
-1.183



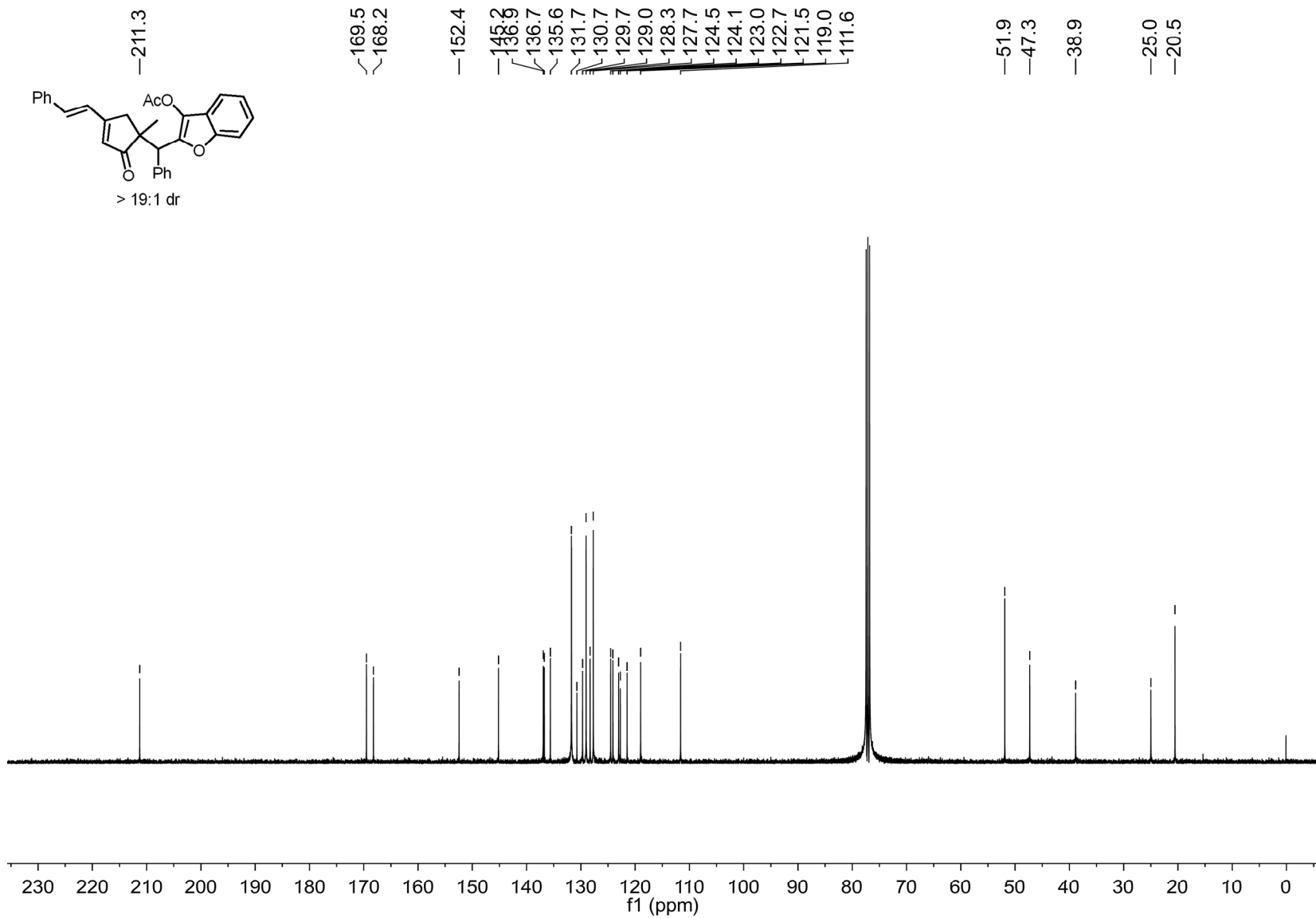
¹H NMR Spectrum of Compound 3g



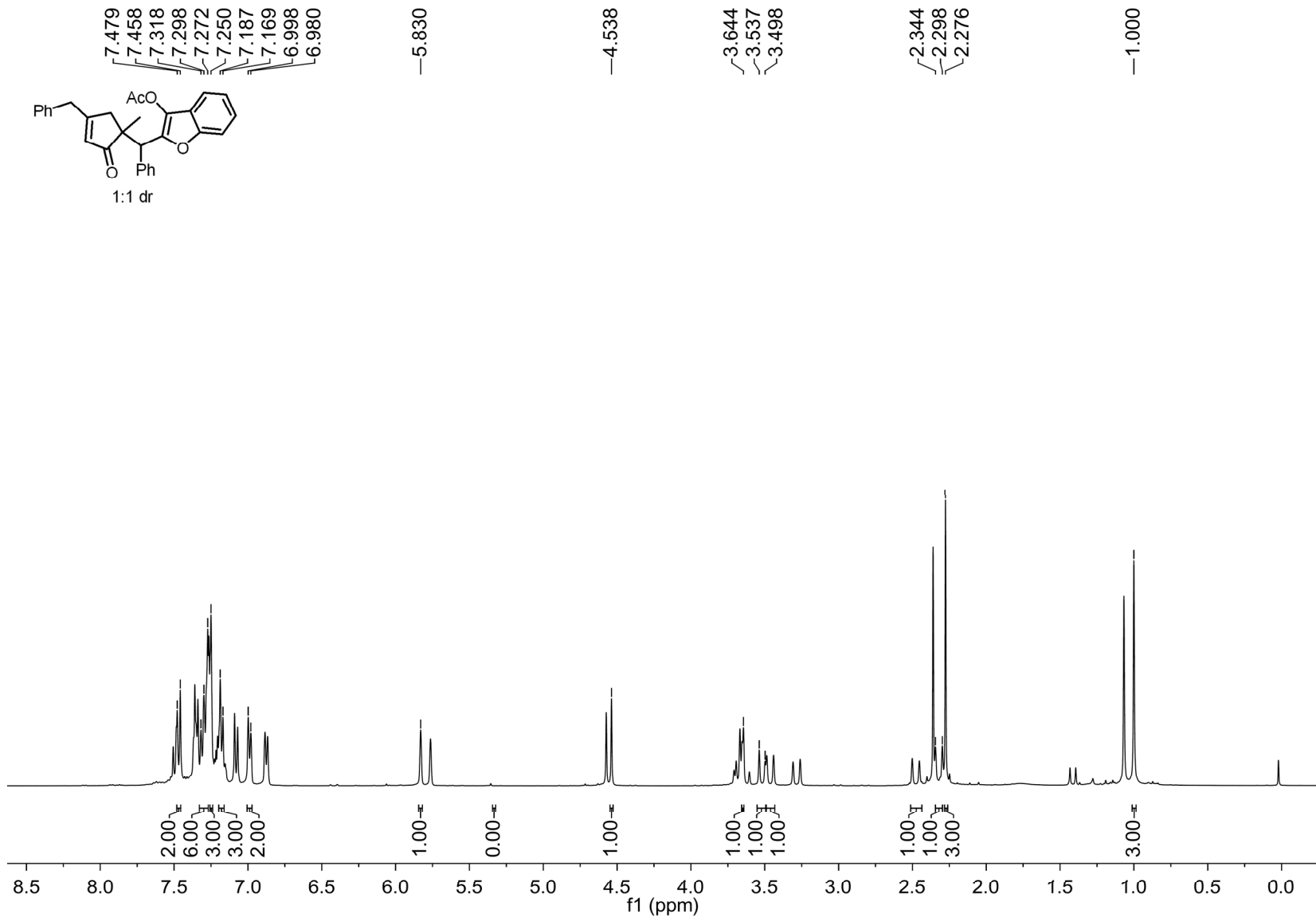
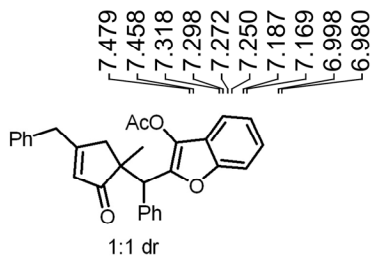
¹³C NMR Spectrum of Compound 3g



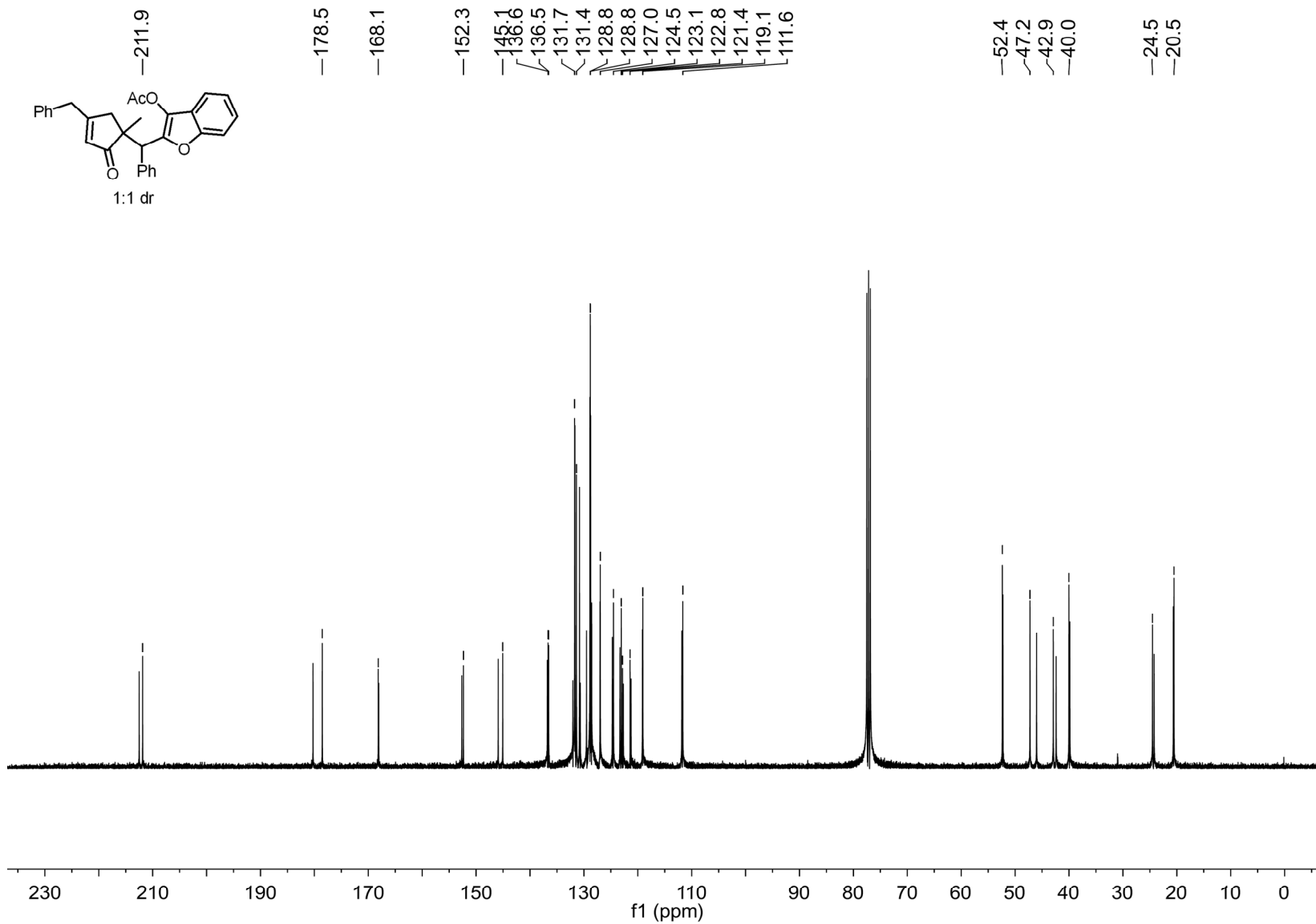
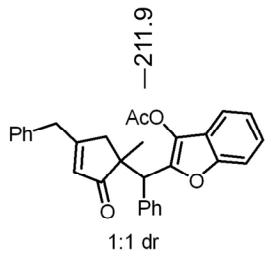
¹H NMR Spectrum of Compound 3h



^{13}C NMR Spectrum of Compound 3h

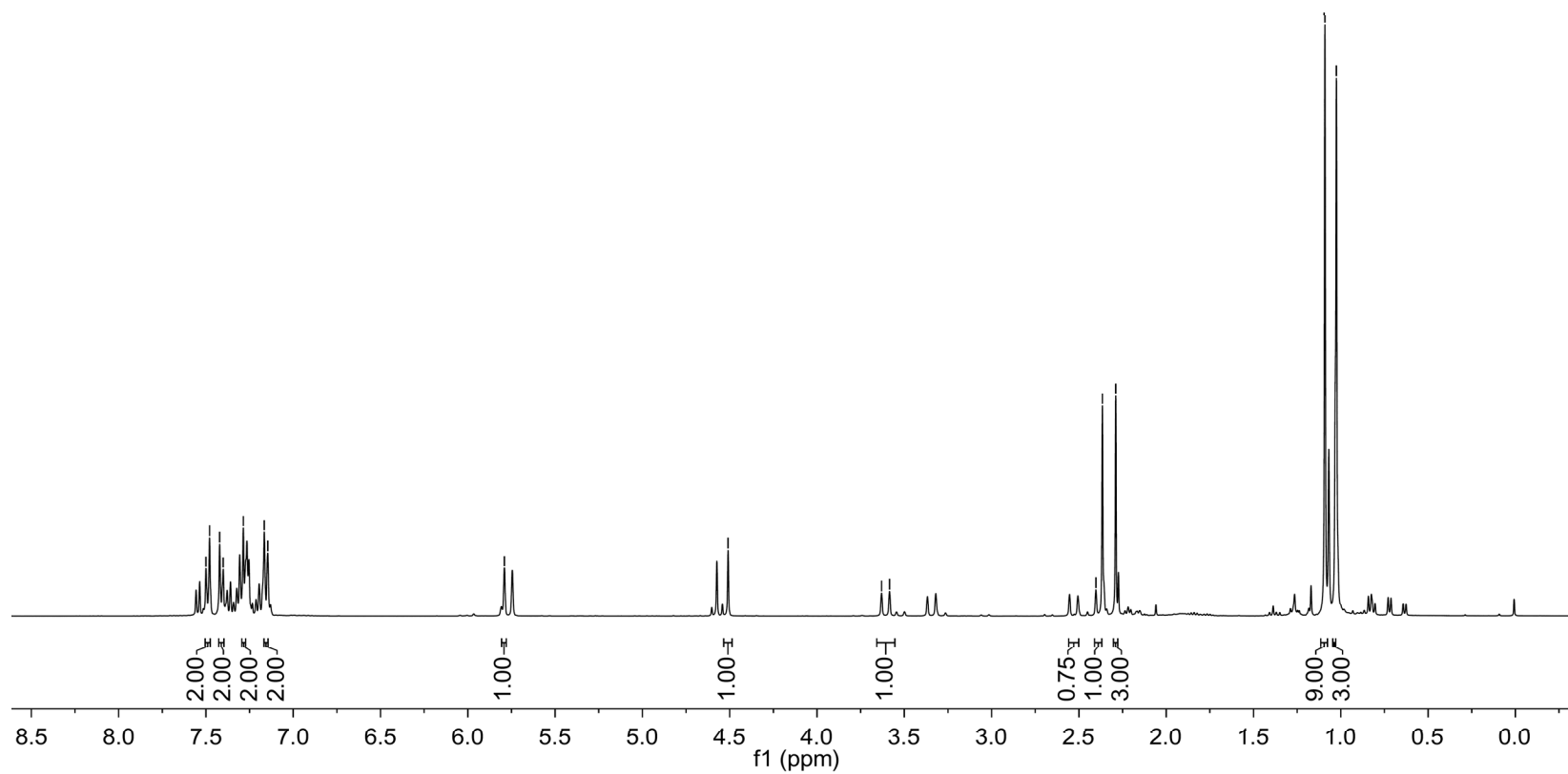
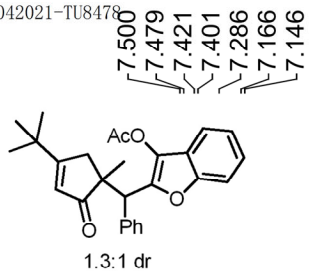


¹H NMR Spectrum of Compound 3i

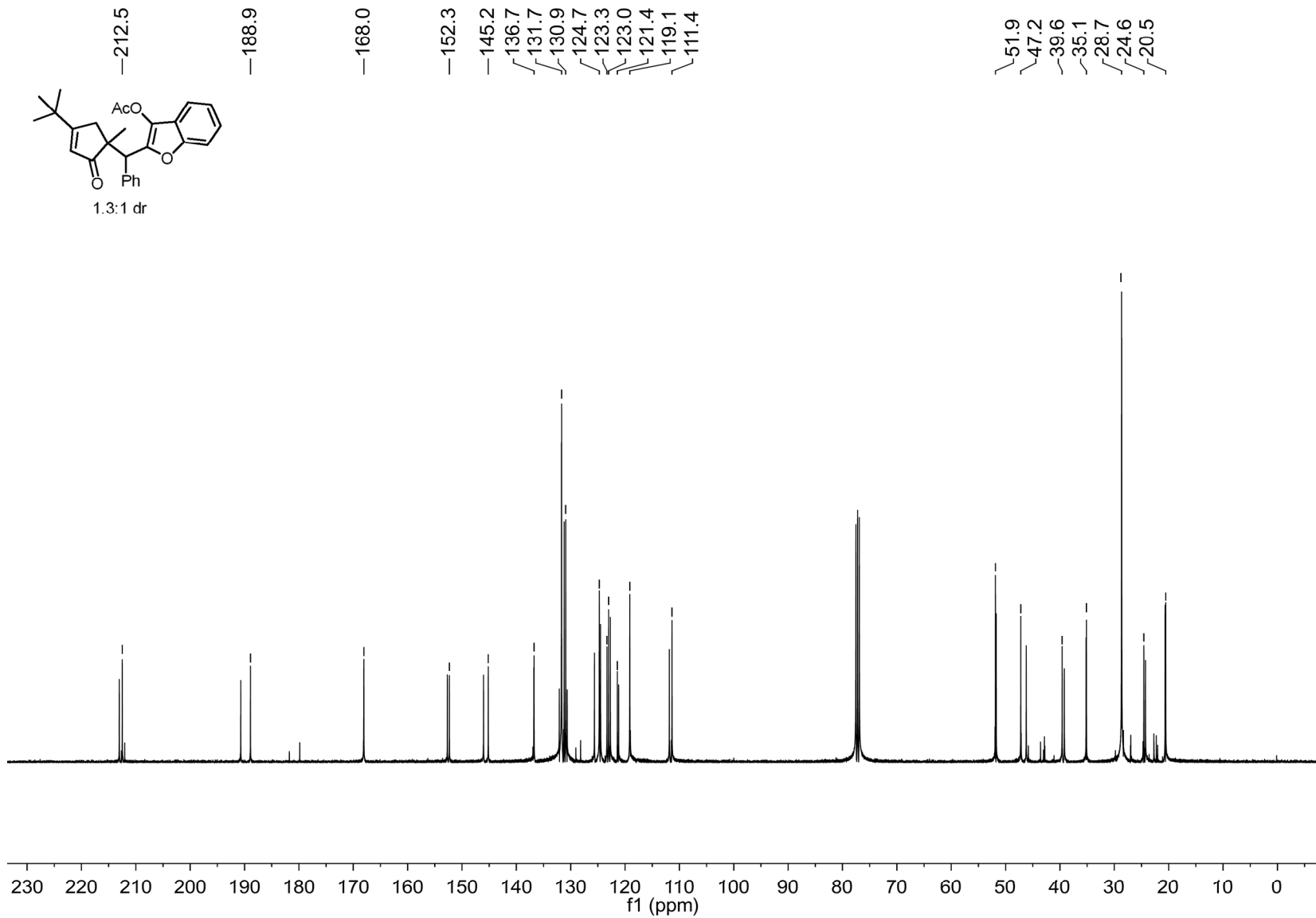
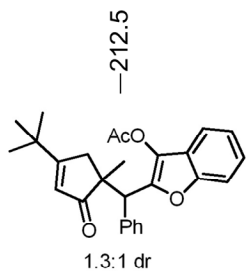


¹³C NMR Spectrum of Compound 3i

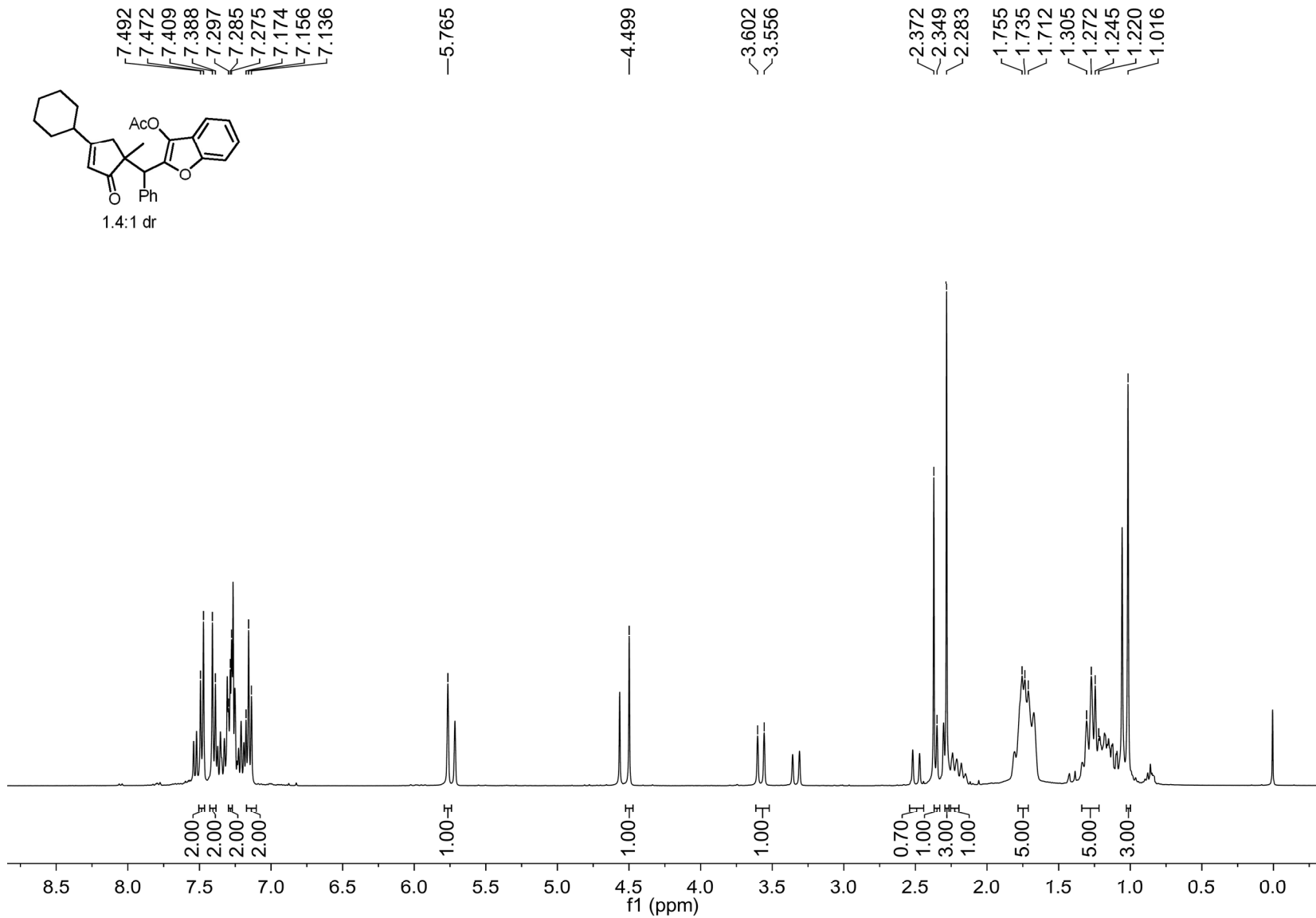
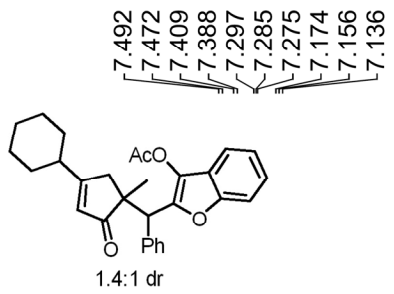
25042021-TU8478



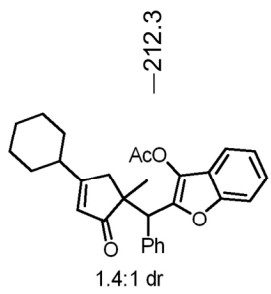
¹H NMR Spectrum of Compound 3j



¹³C NMR Spectrum of Compound 3j



¹H NMR Spectrum of Compound 3k



—212.3

—185.3

—168.1

—152.3

—145.2

—136.8

—131.6

—131.2

—125.4

—124.5

—123.0

—122.7

—121.4

—119.1

—111.4

~51.5

~47.2

~41.9

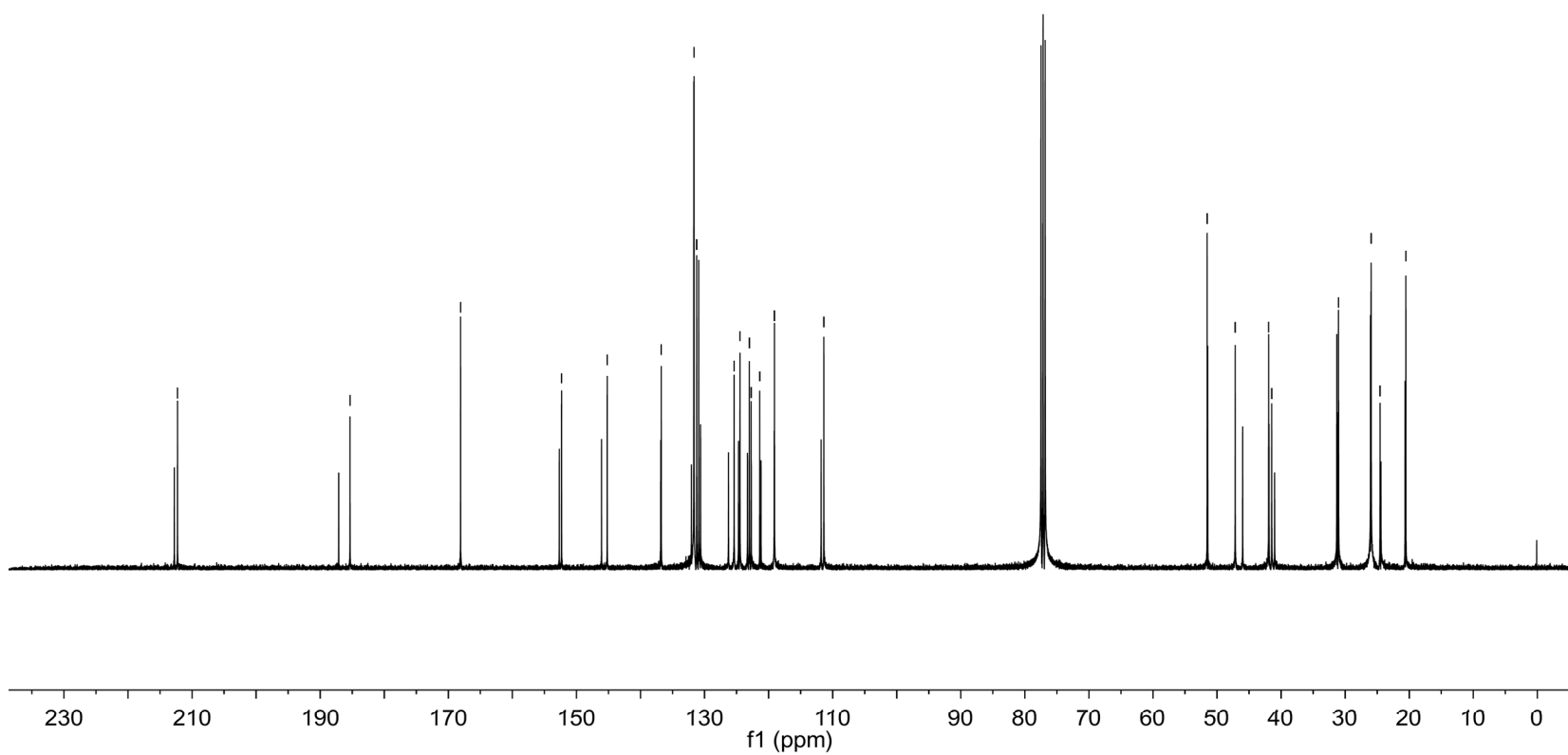
~41.5

~31.0

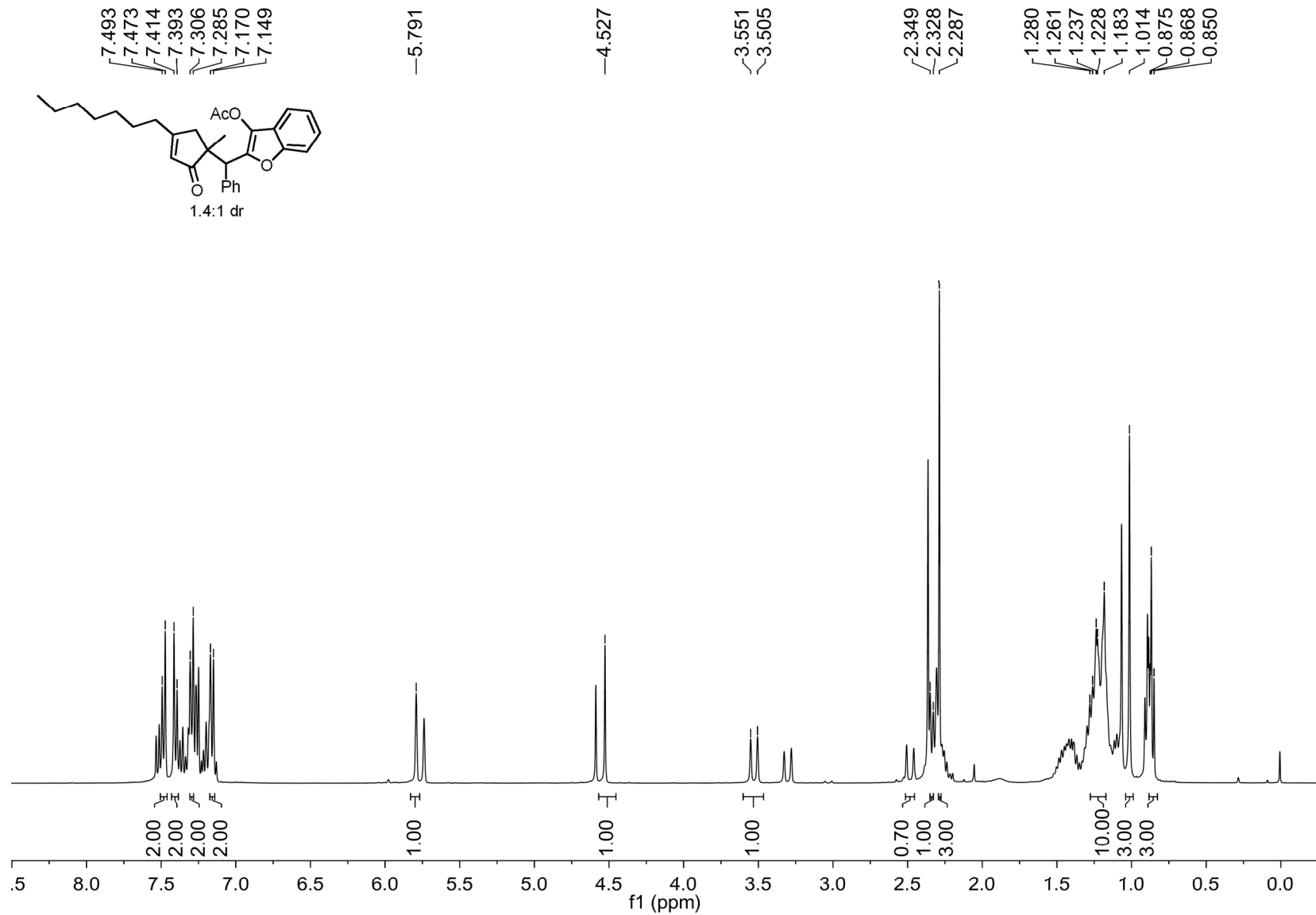
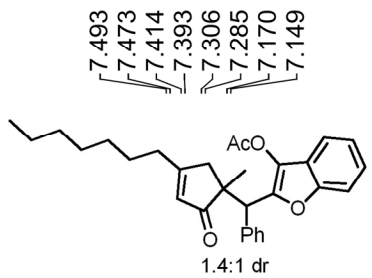
~25.9

~24.6

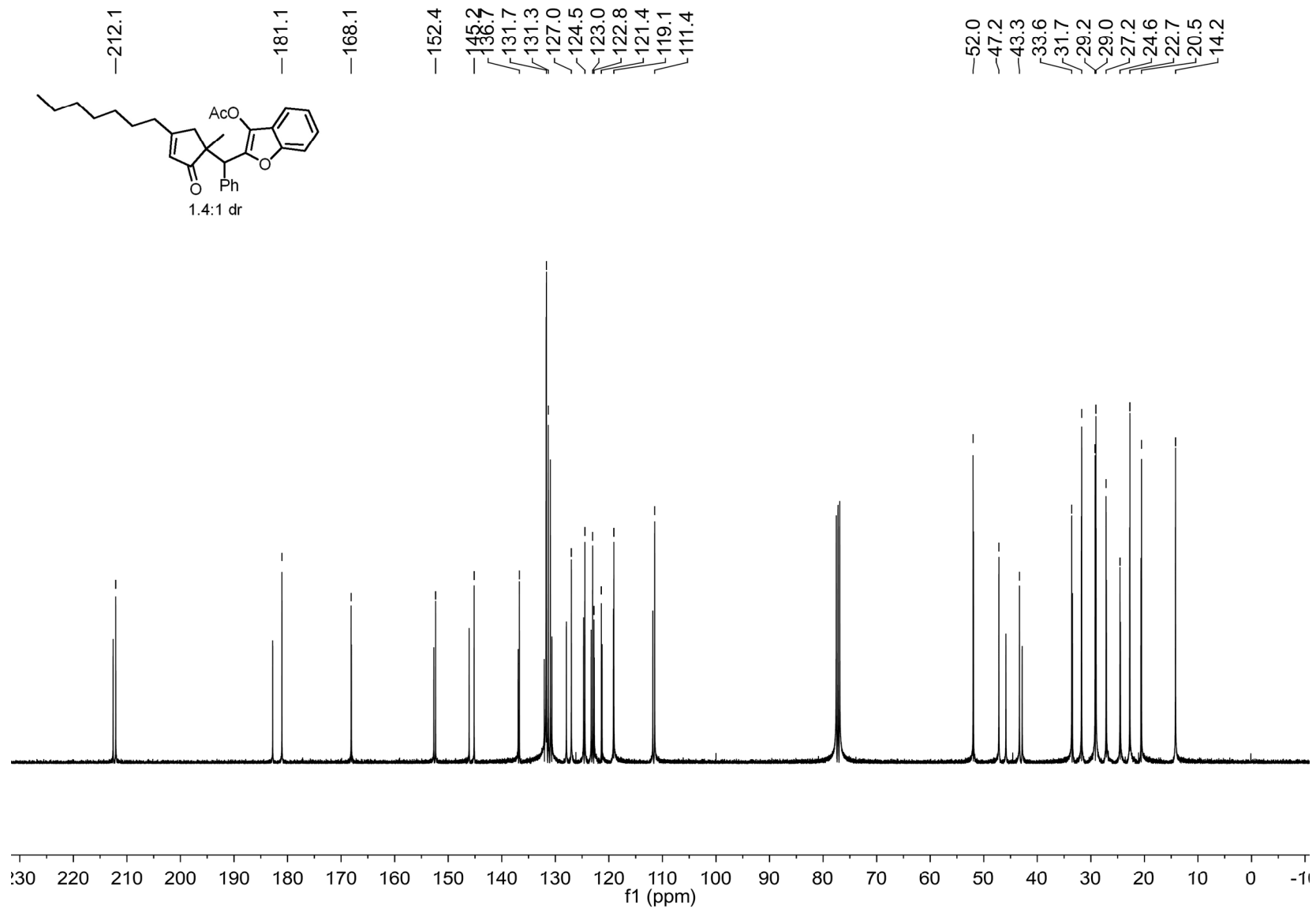
~20.5



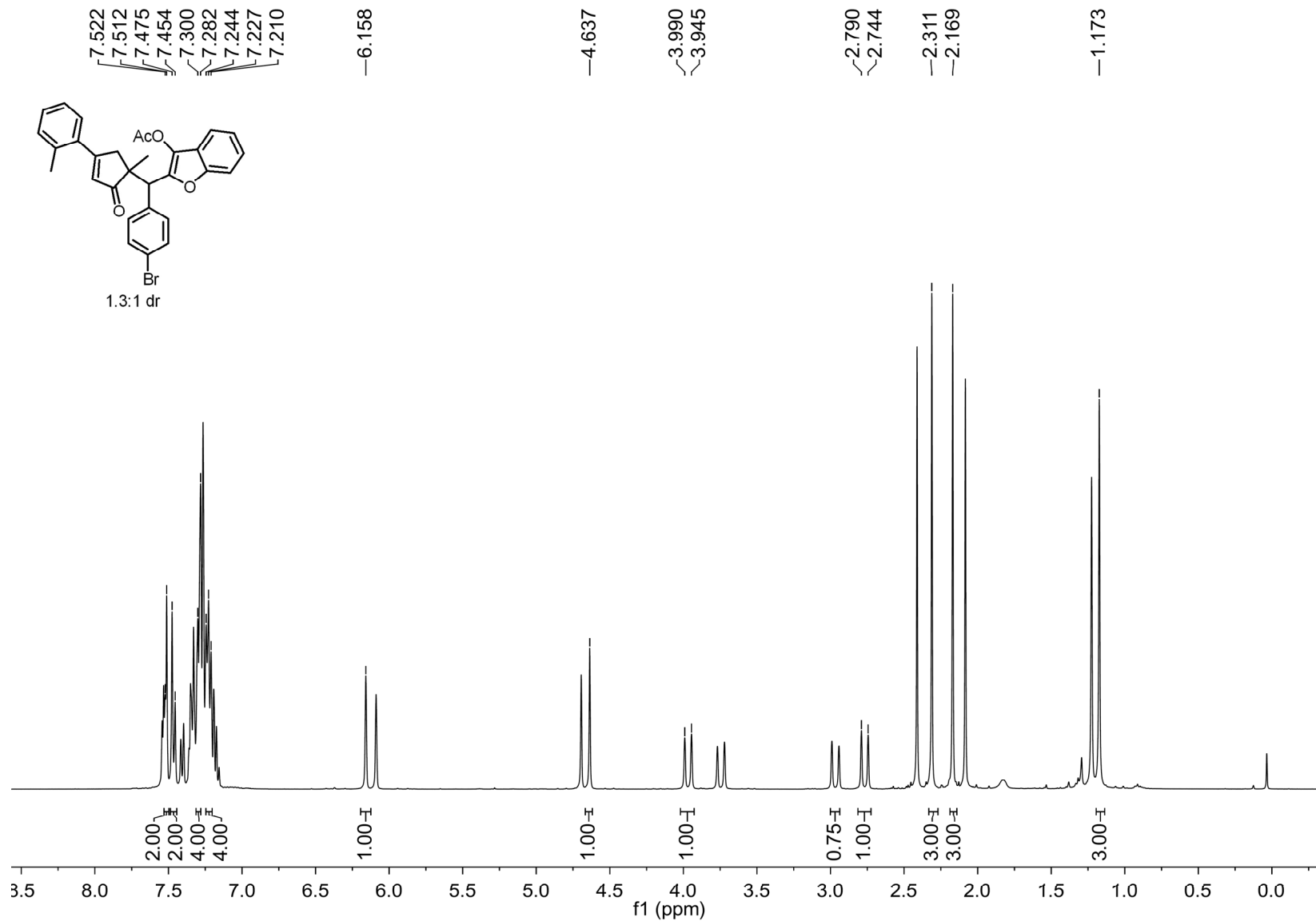
¹³C NMR Spectrum of Compound 3k



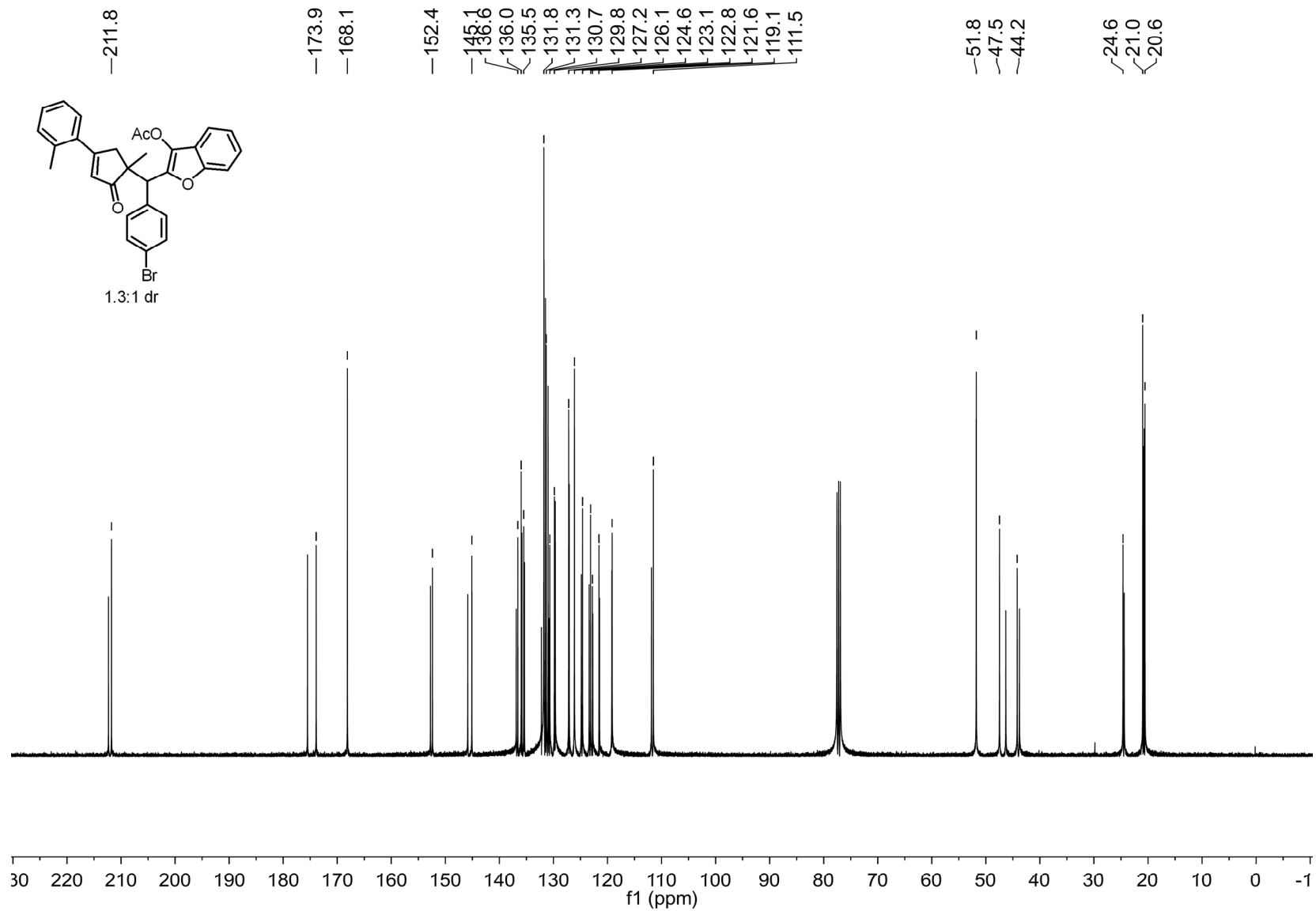
¹H NMR Spectrum of Compound 31



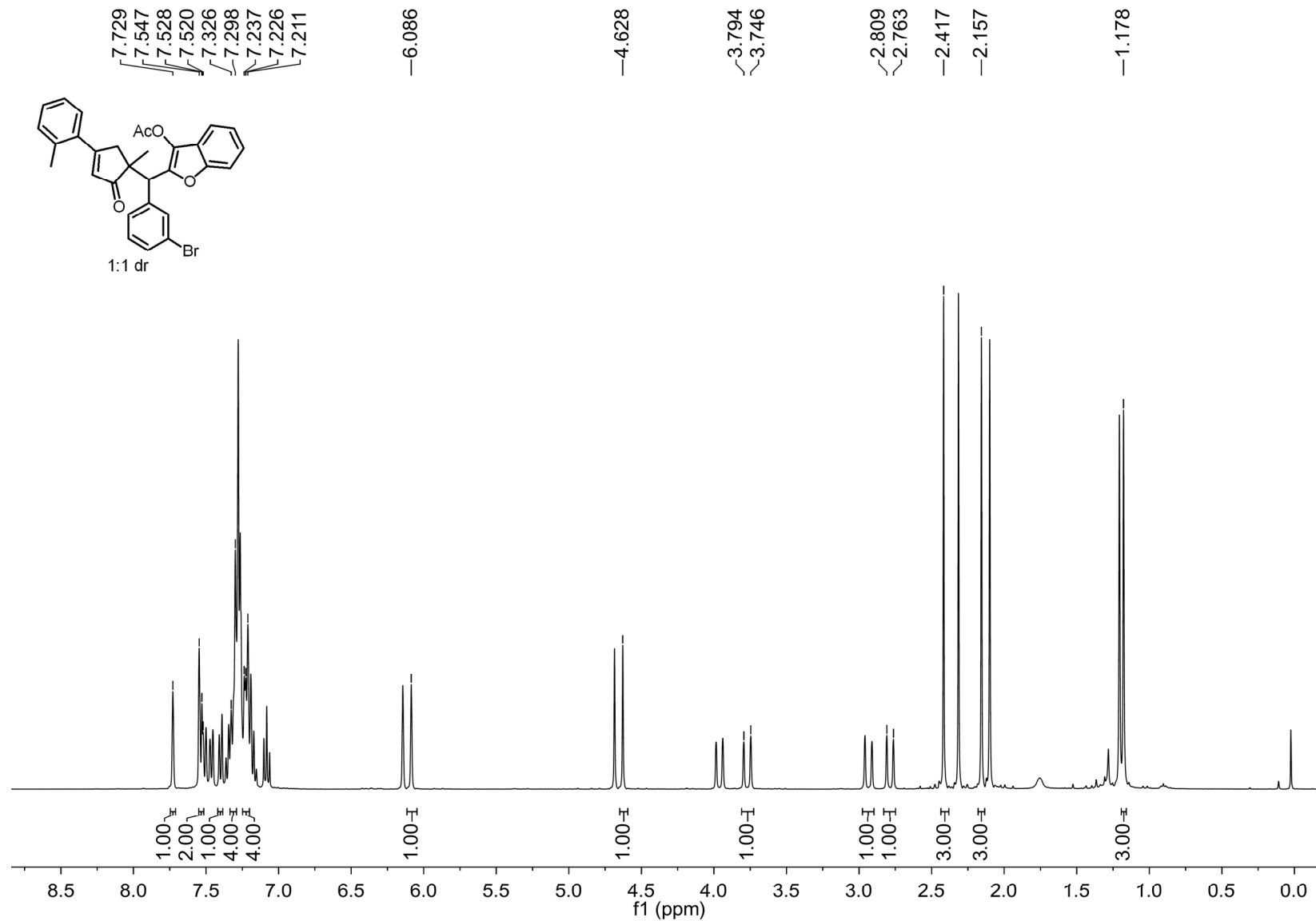
¹³C NMR Spectrum of Compound 31



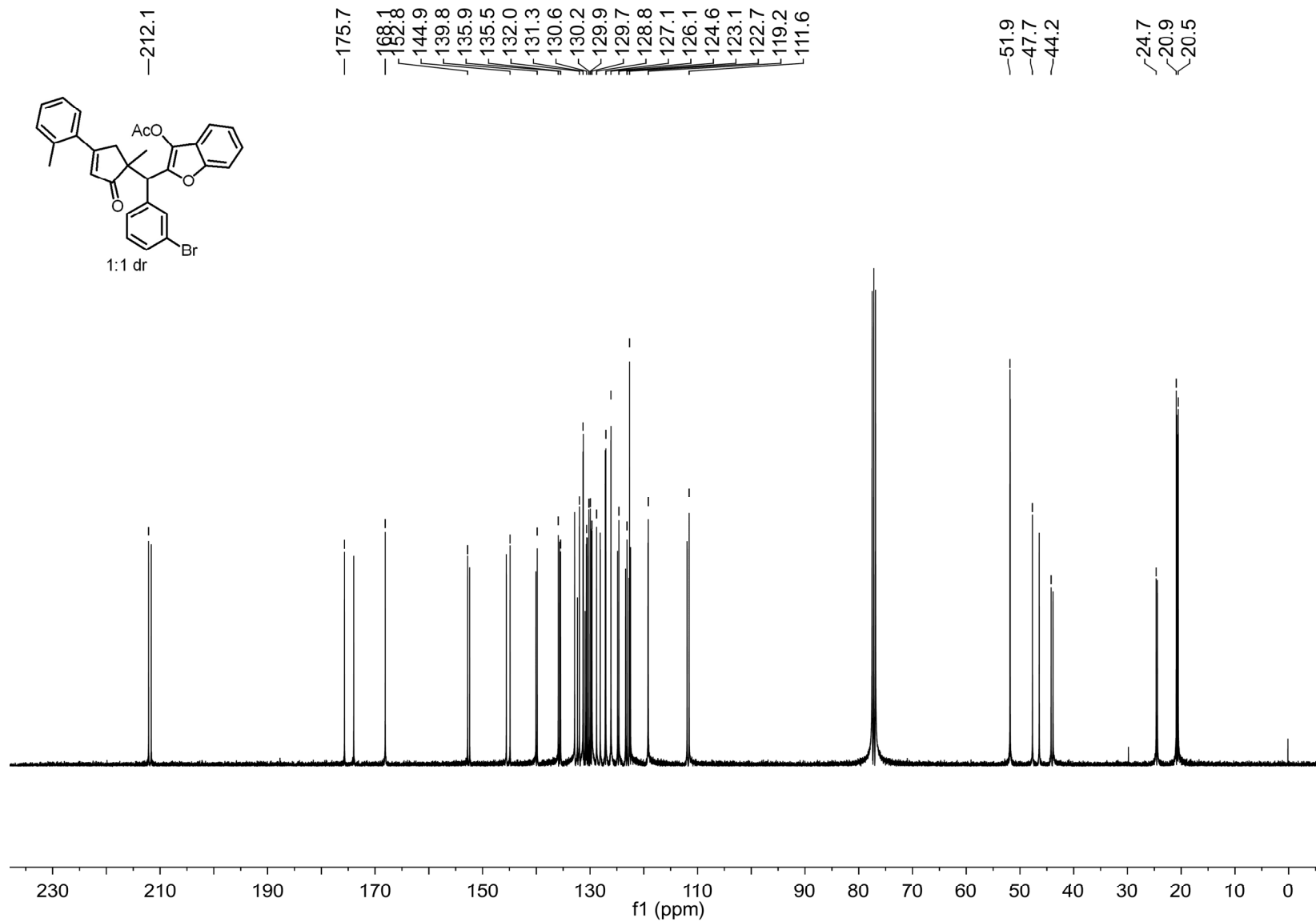
¹H NMR Spectrum of Compound 3m



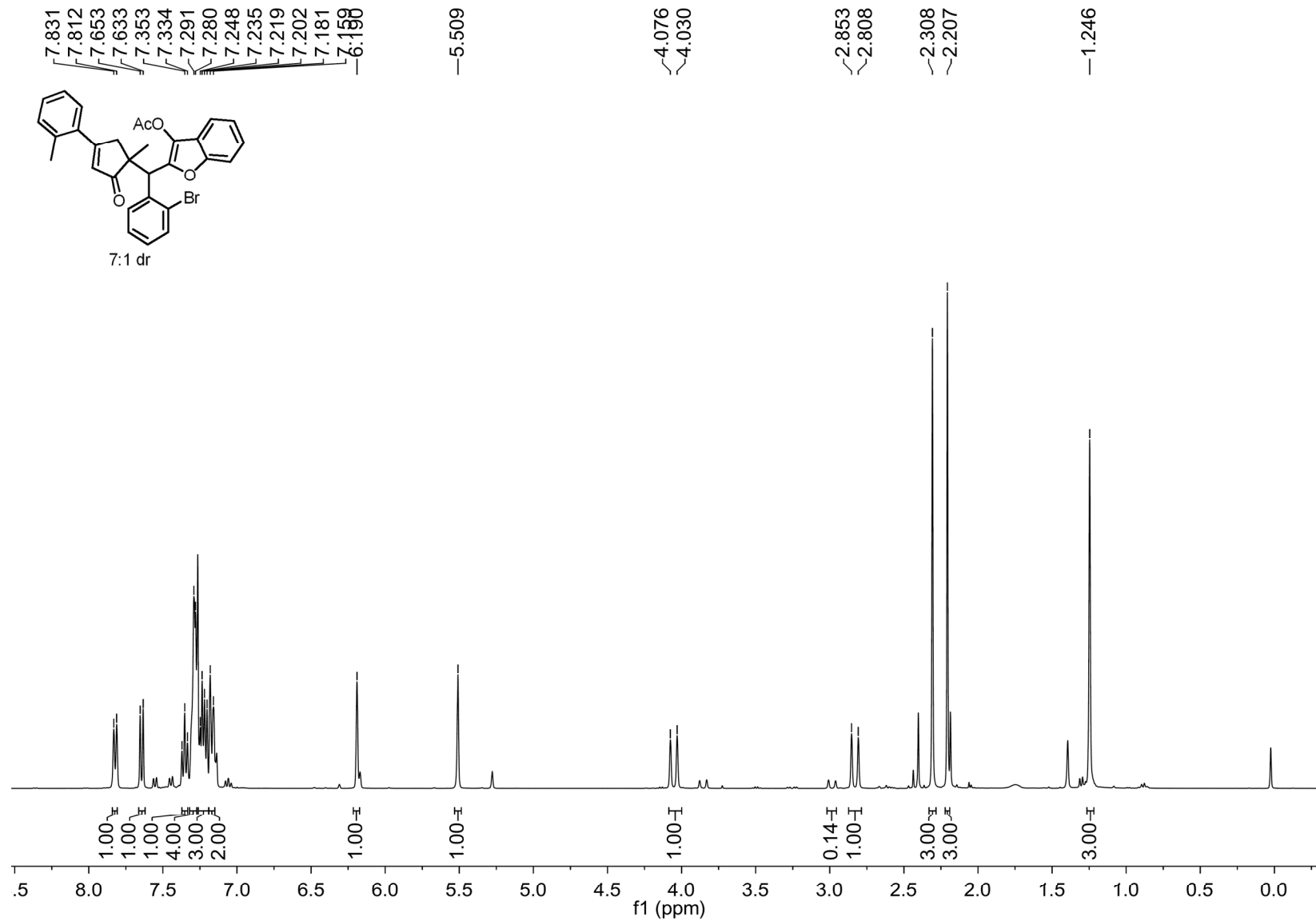
^{13}C NMR Spectrum of Compound 3m



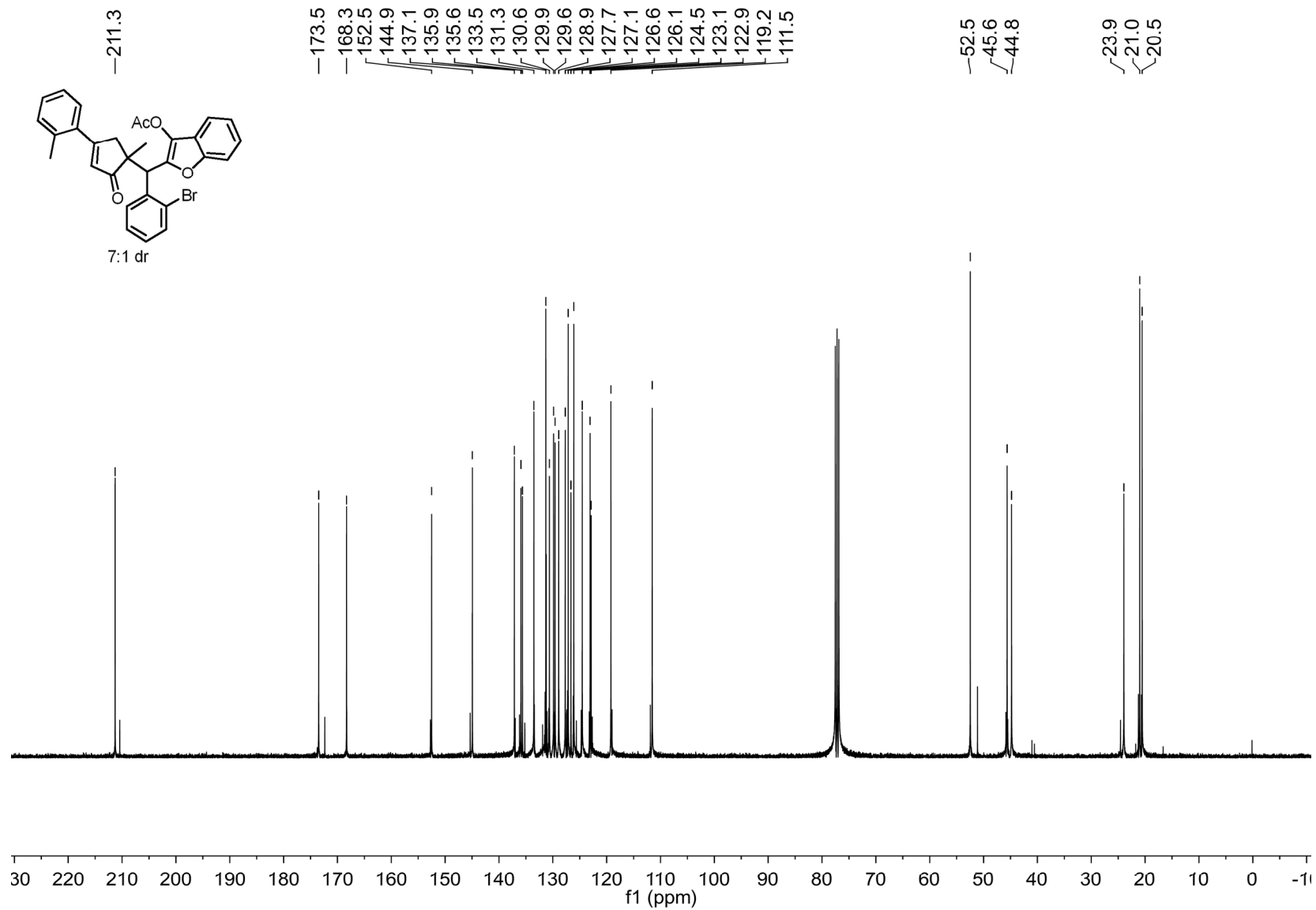
¹H NMR Spectrum of Compound 3n



^{13}C NMR Spectrum of Compound 3n

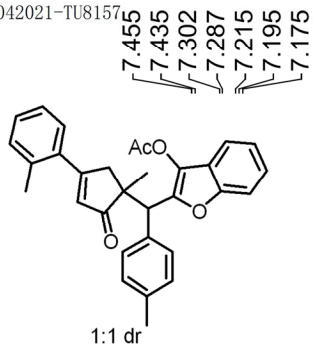


¹H NMR Spectrum of Compound 30



^{13}C NMR Spectrum of Compound 30

15042021-TU8157



7.455
7.435
7.302
7.287
7.215
7.195
7.175

-6.148

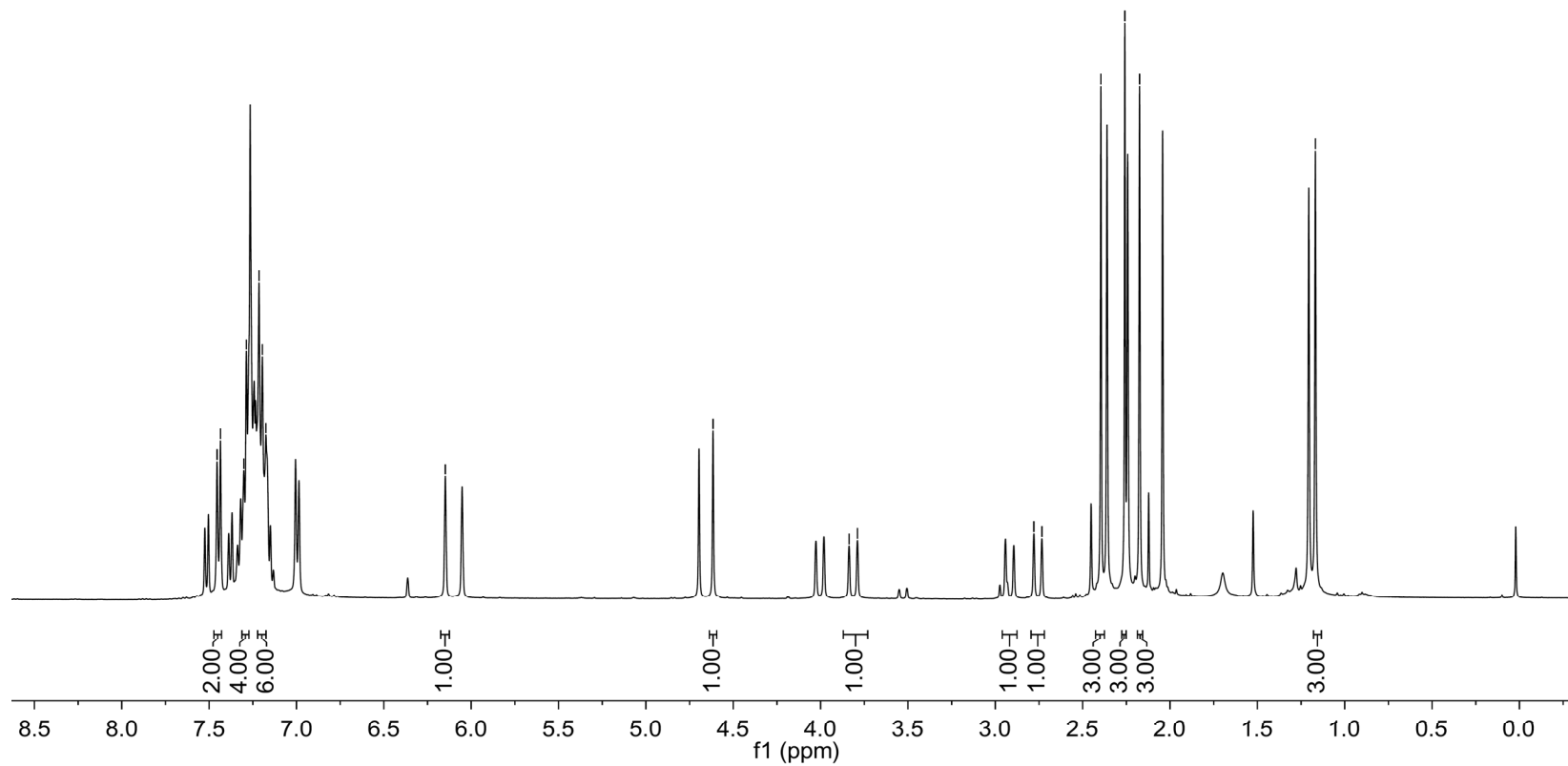
-4.616

3.837
3.789

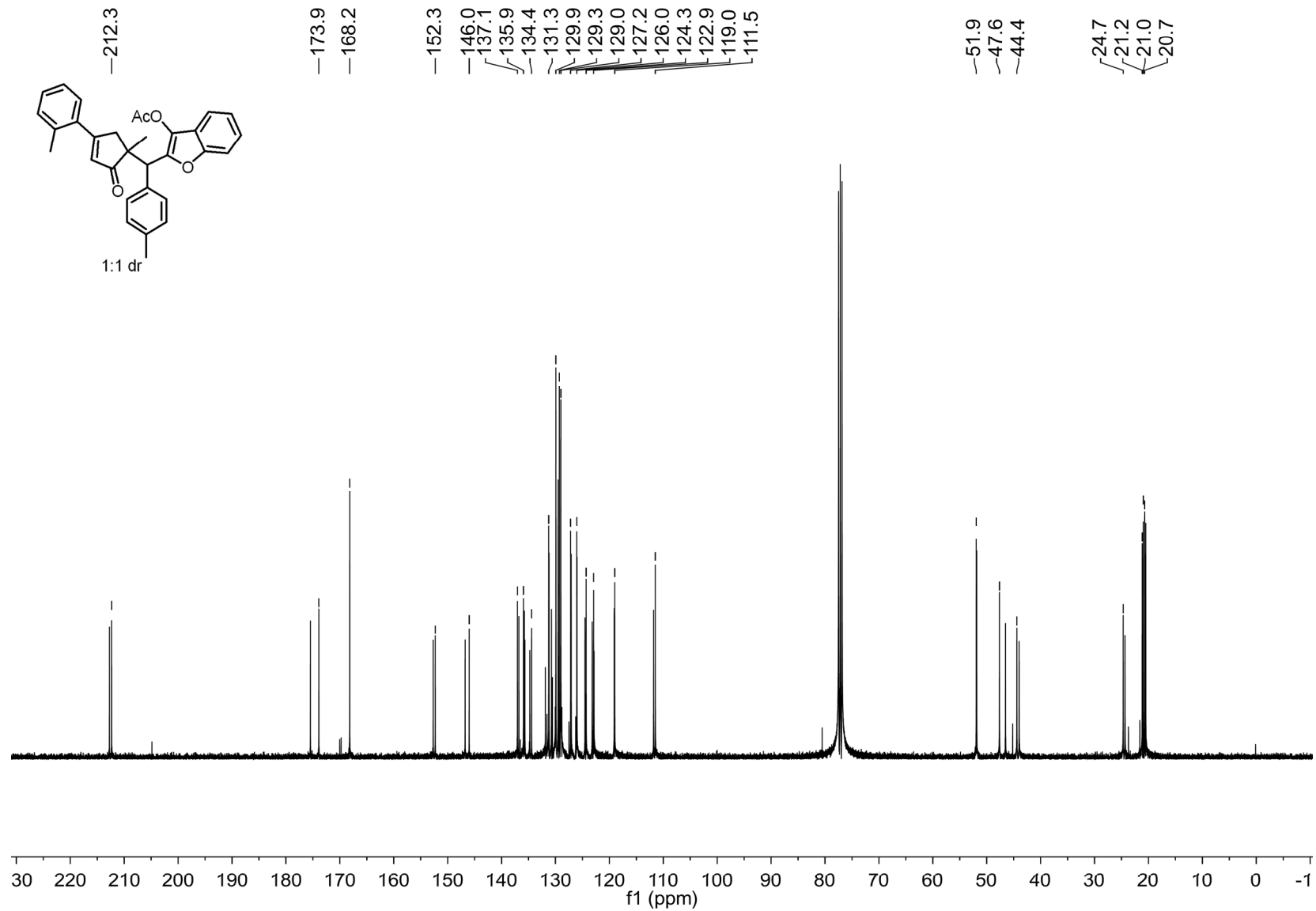
2.779
2.733

2.396
2.259
2.175

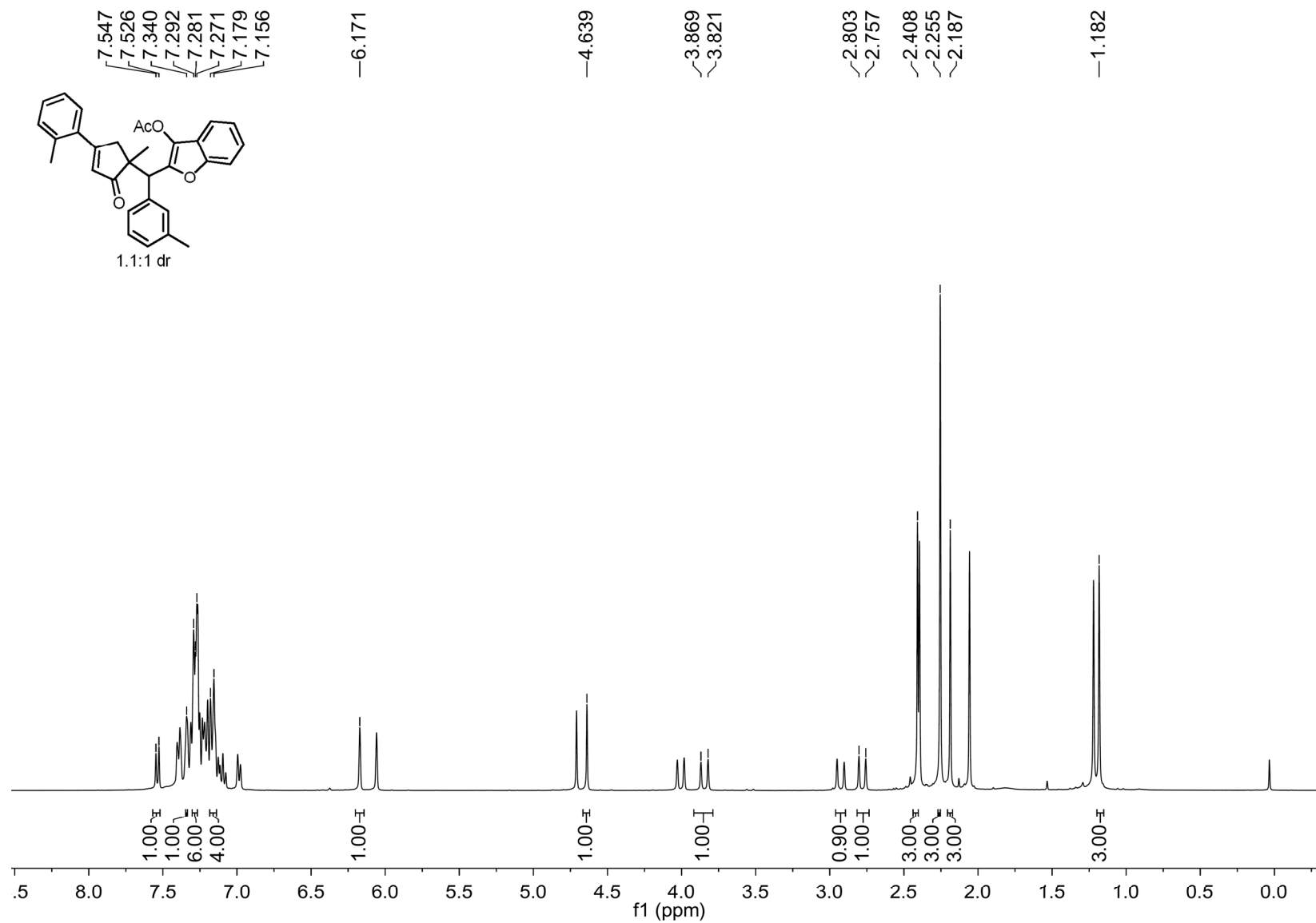
-1.168



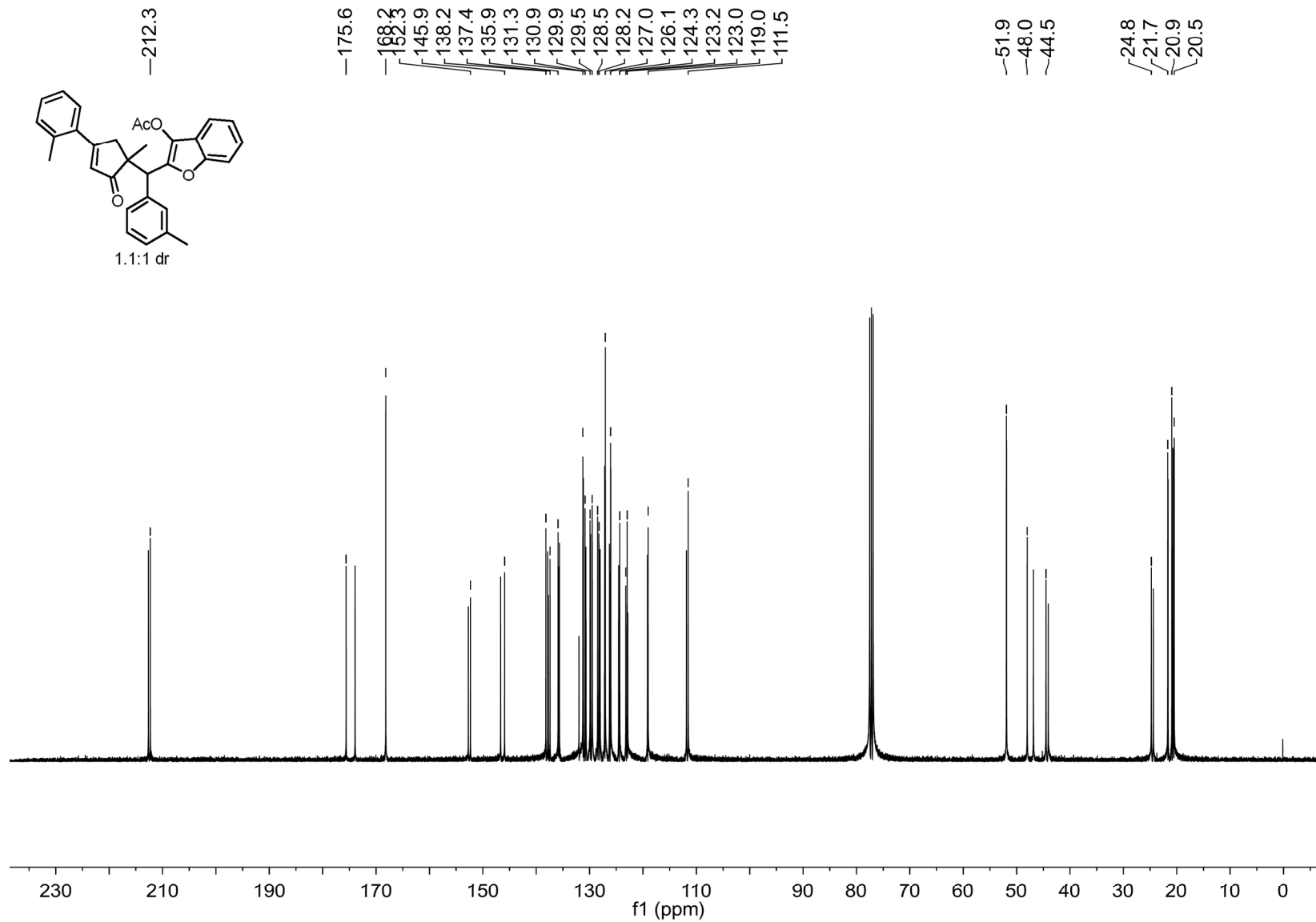
¹H NMR Spectrum of Compound 3p



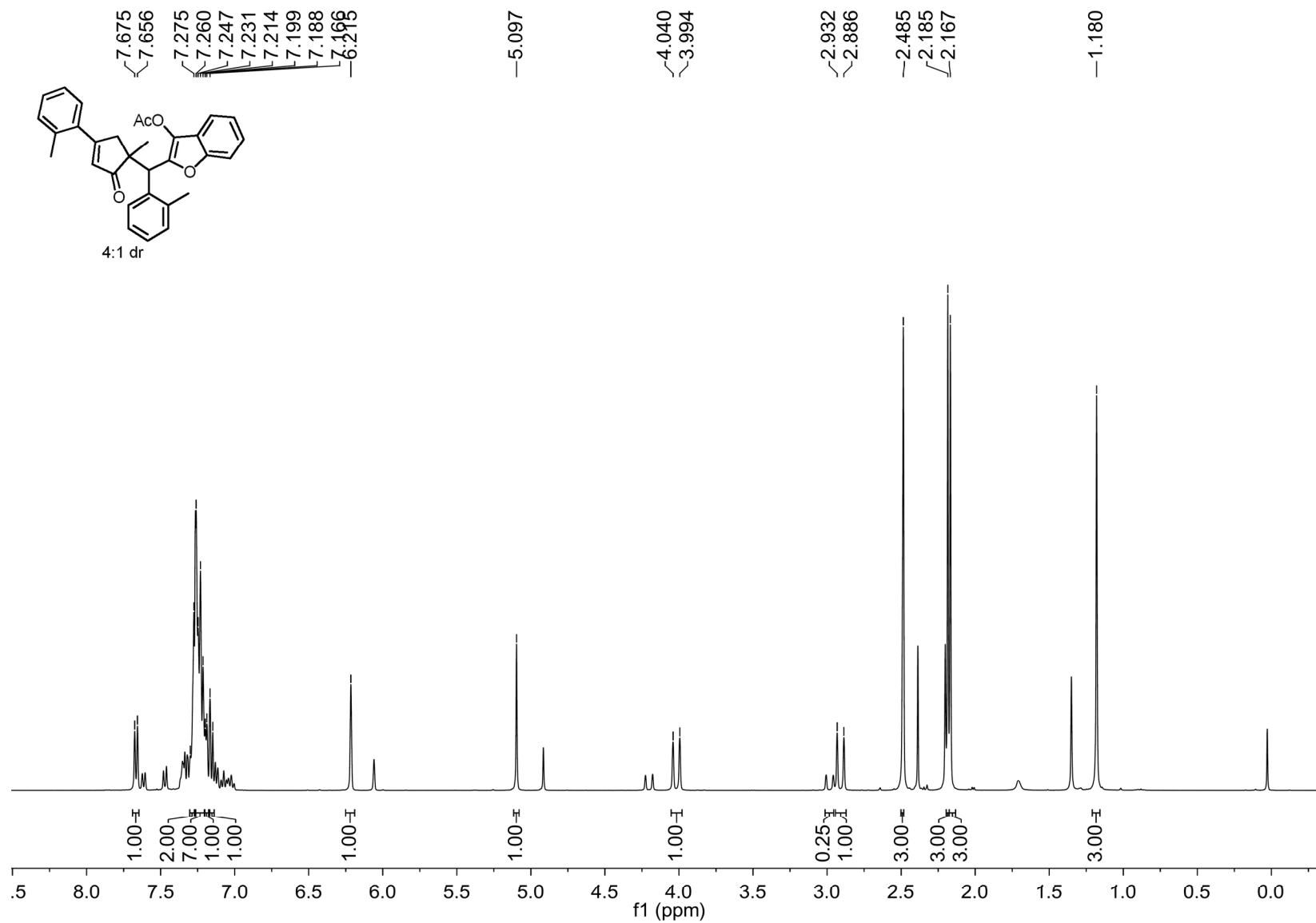
¹³C NMR Spectrum of Compound 3p



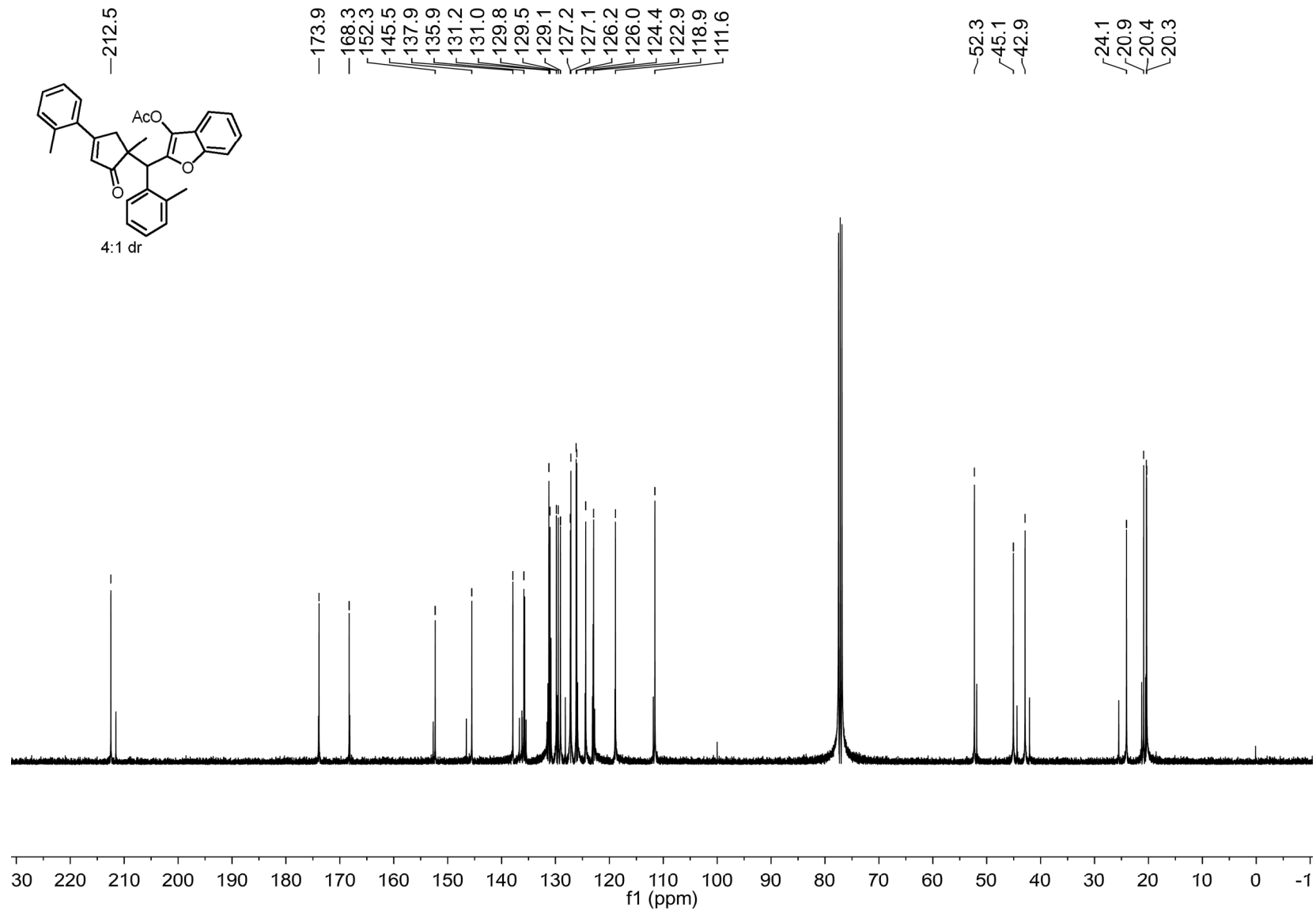
¹H NMR Spectrum of Compound 3q



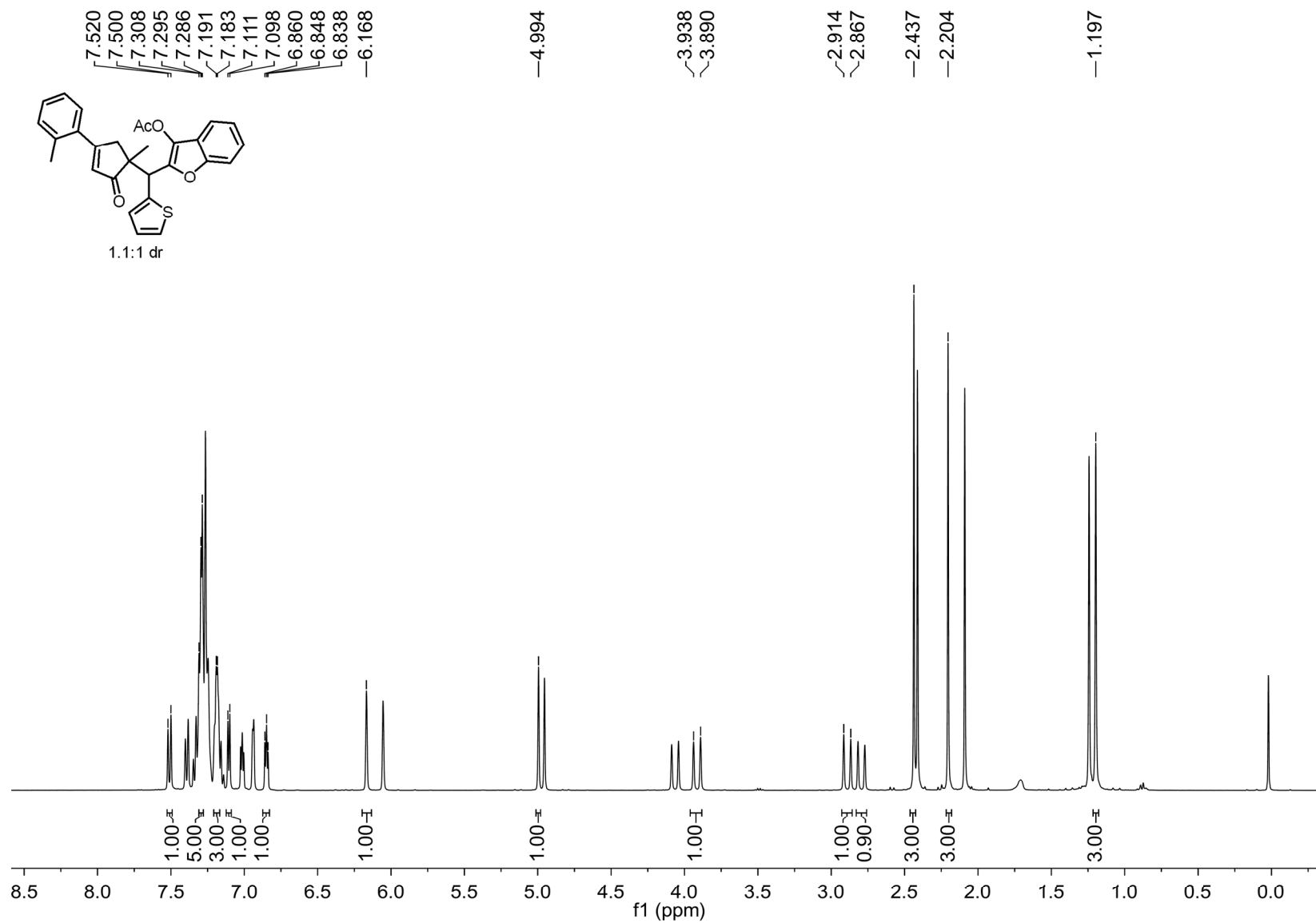
¹³C NMR Spectrum of Compound 3q



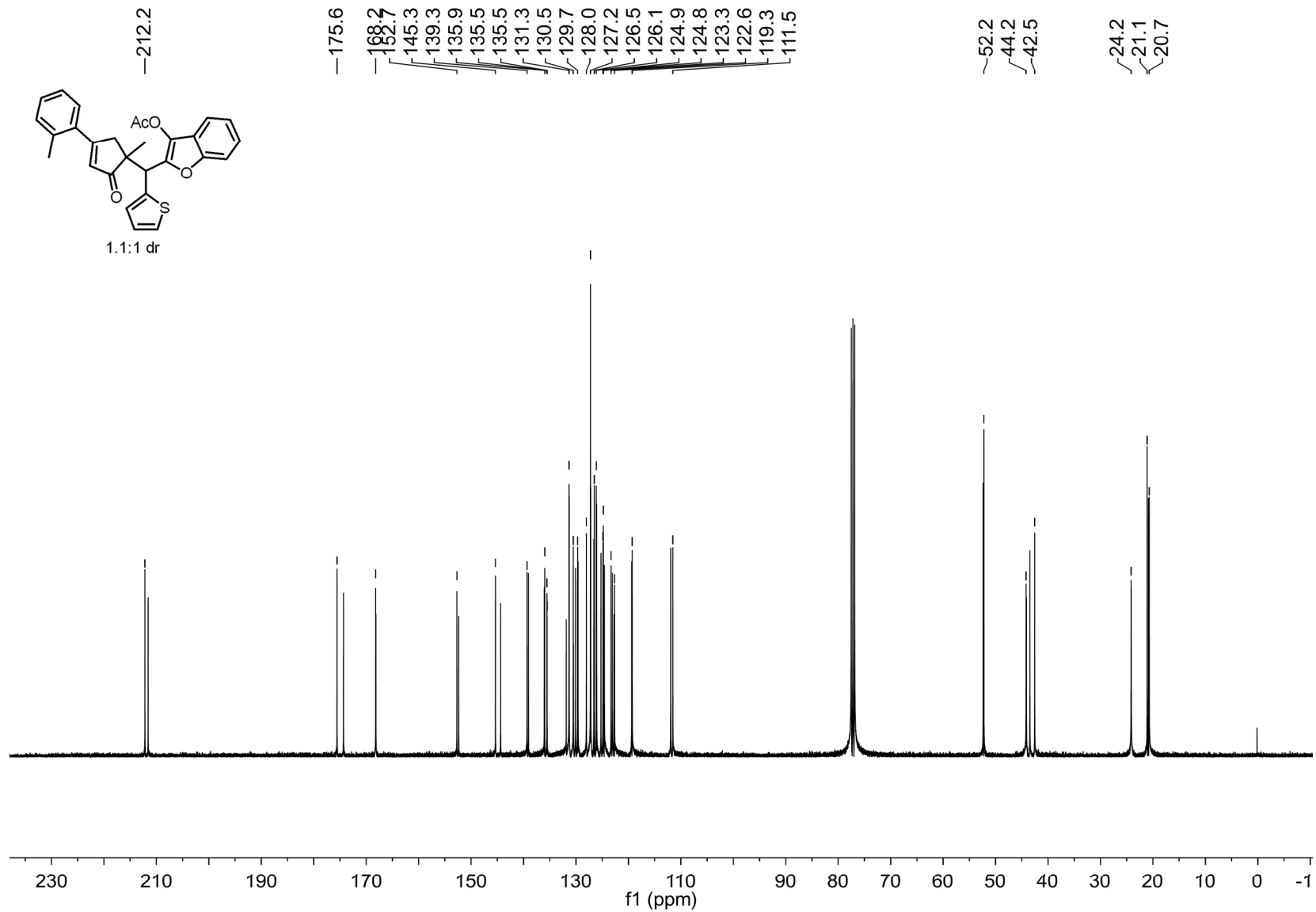
¹H NMR Spectrum of Compound 3r



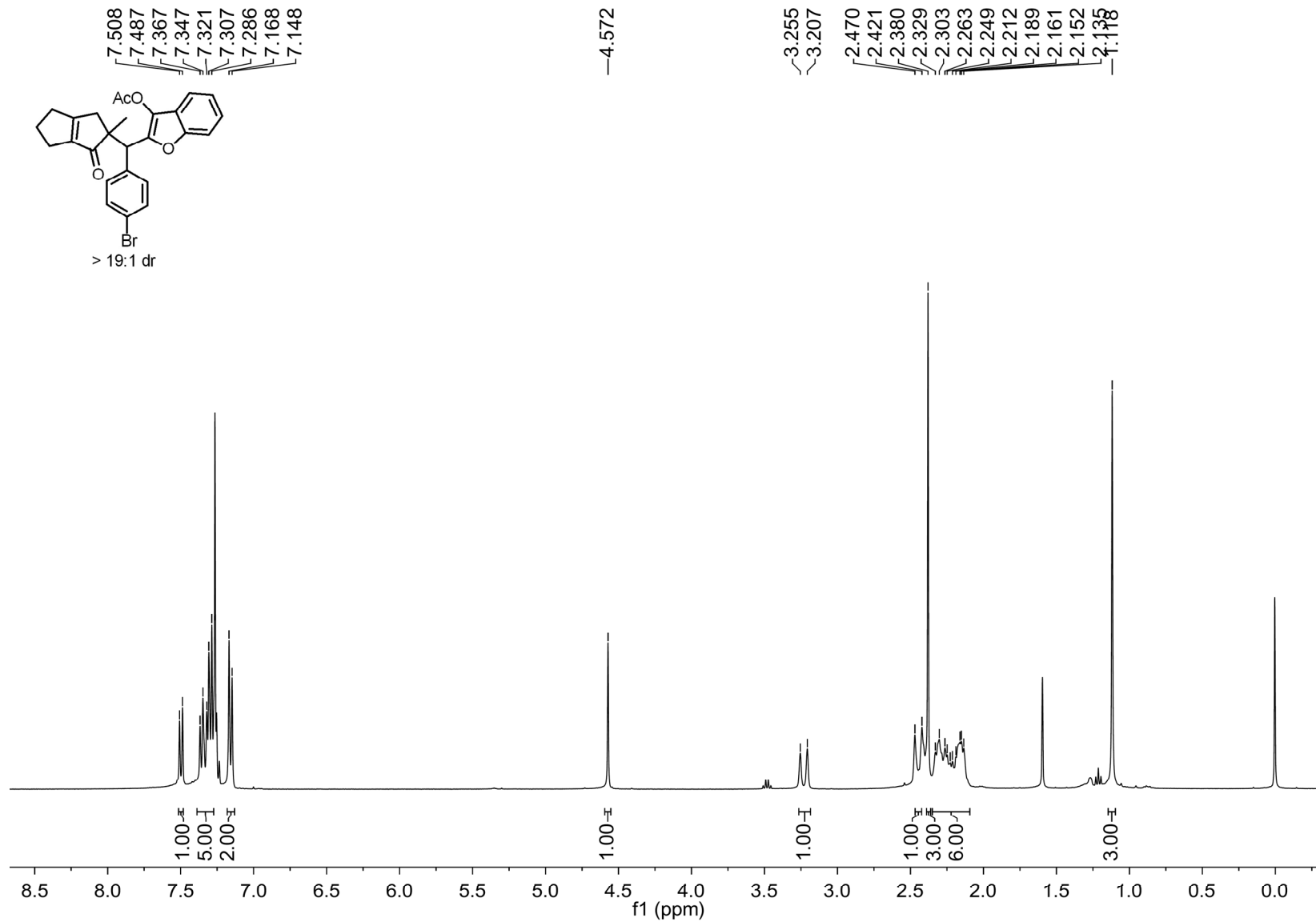
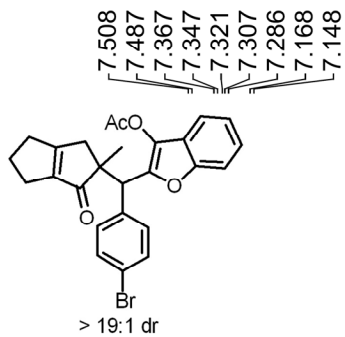
¹³C NMR Spectrum of Compound 3r



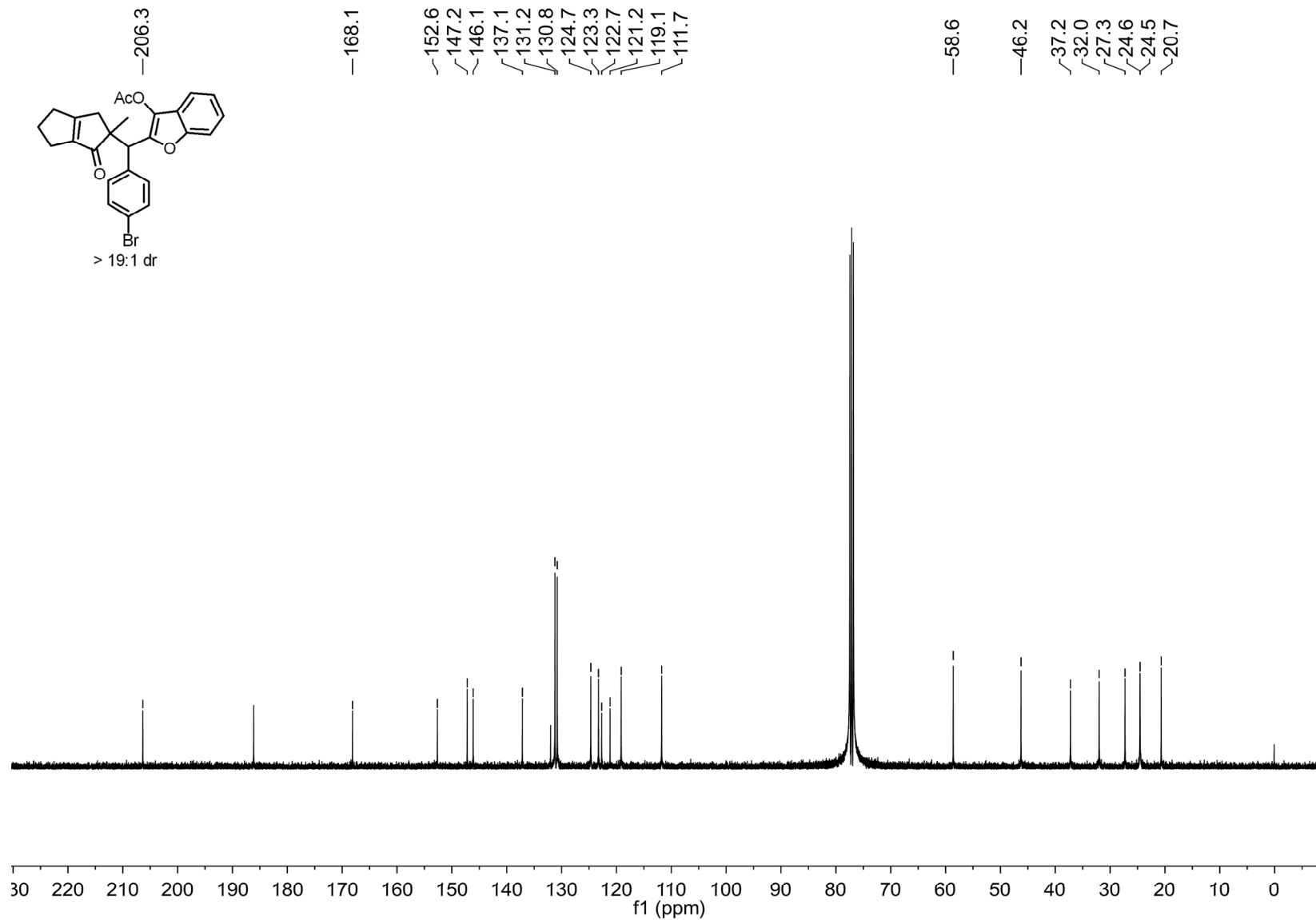
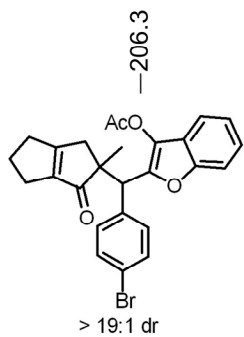
¹H NMR Spectrum of Compound 3s



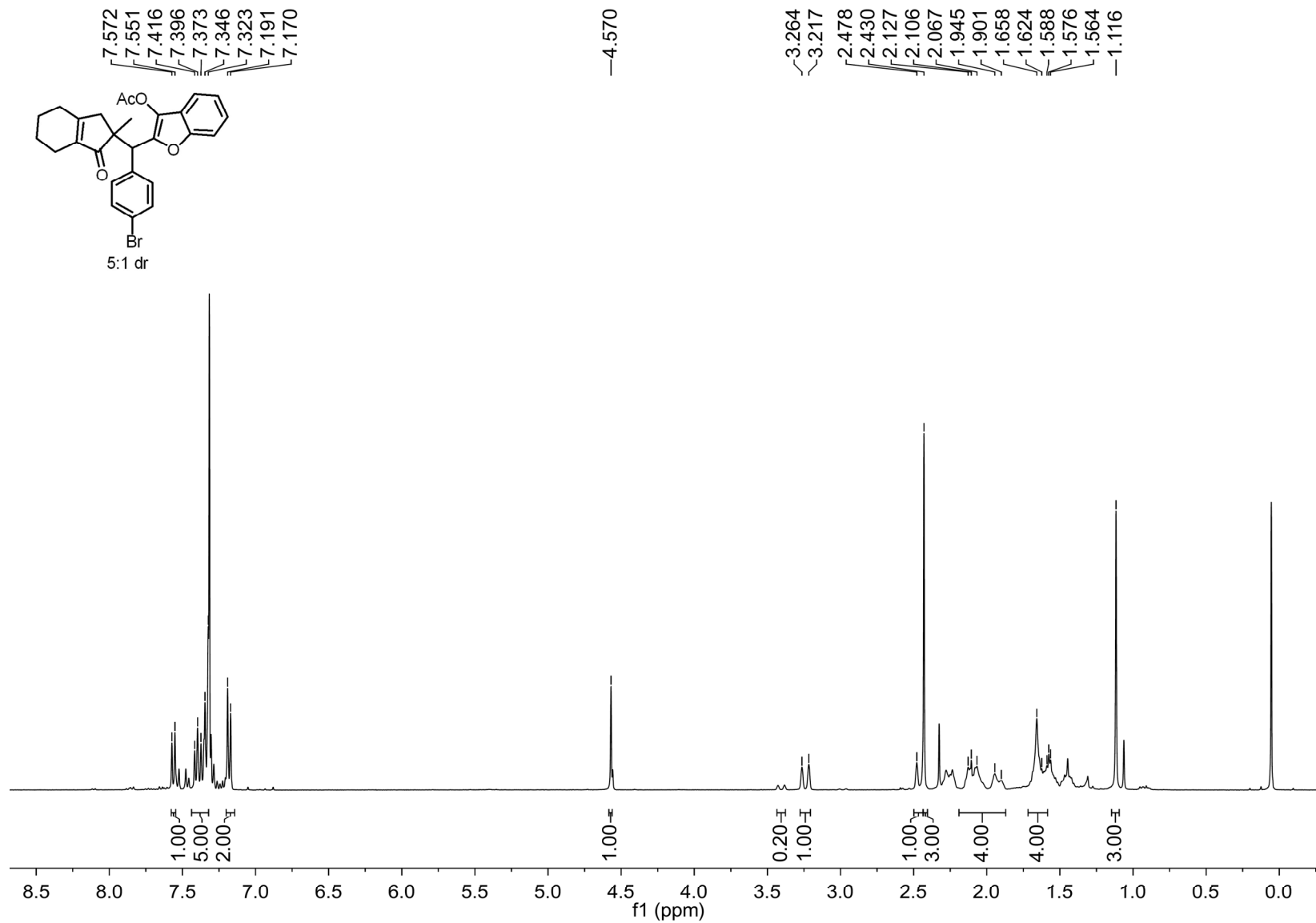
¹³C NMR Spectrum of Compound 3s



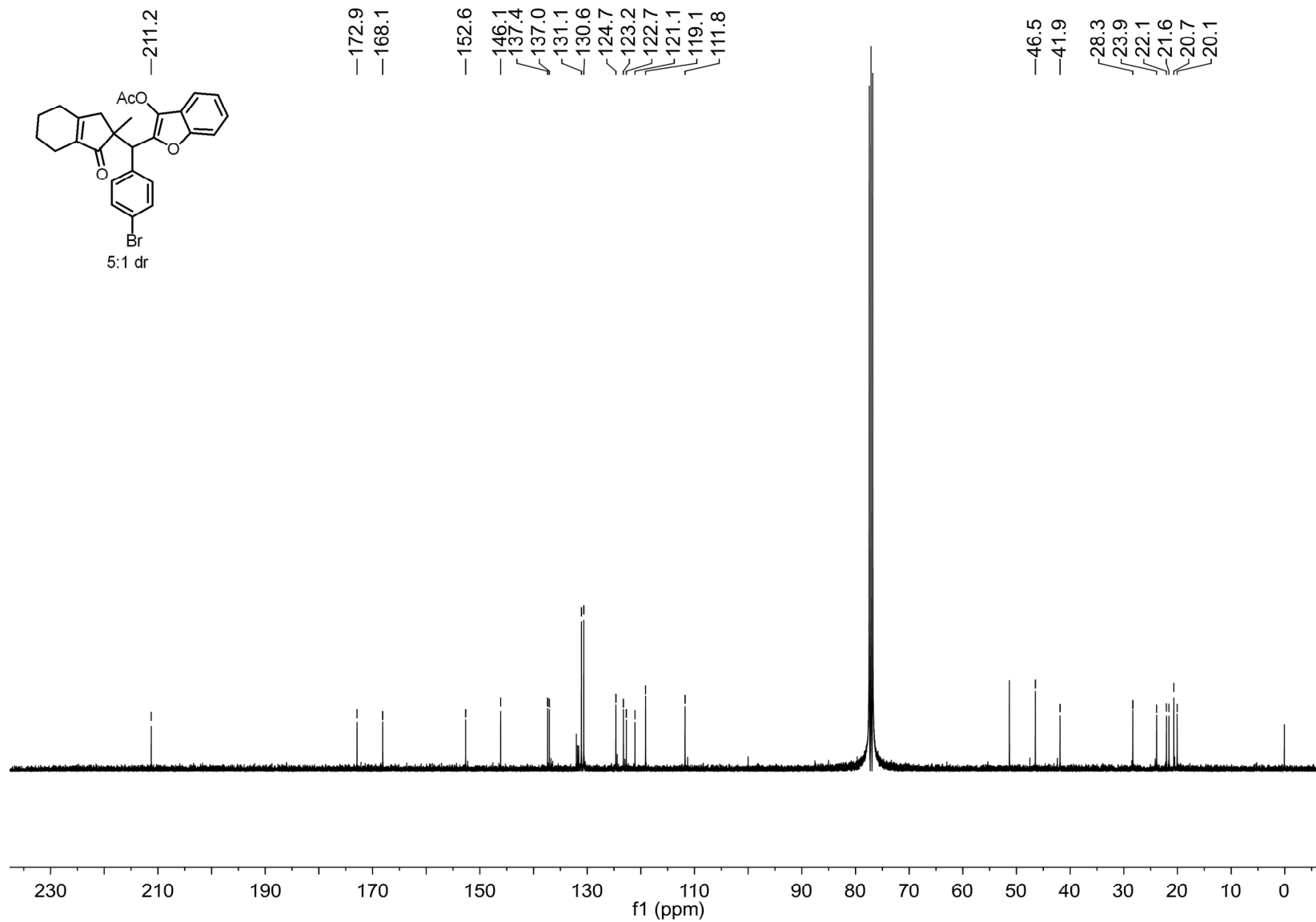
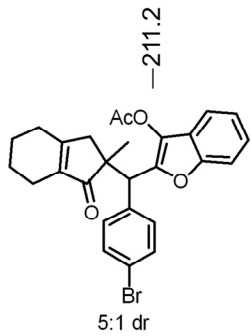
¹H NMR Spectrum of Compound 3t



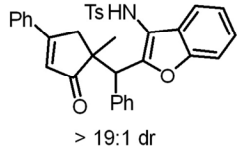
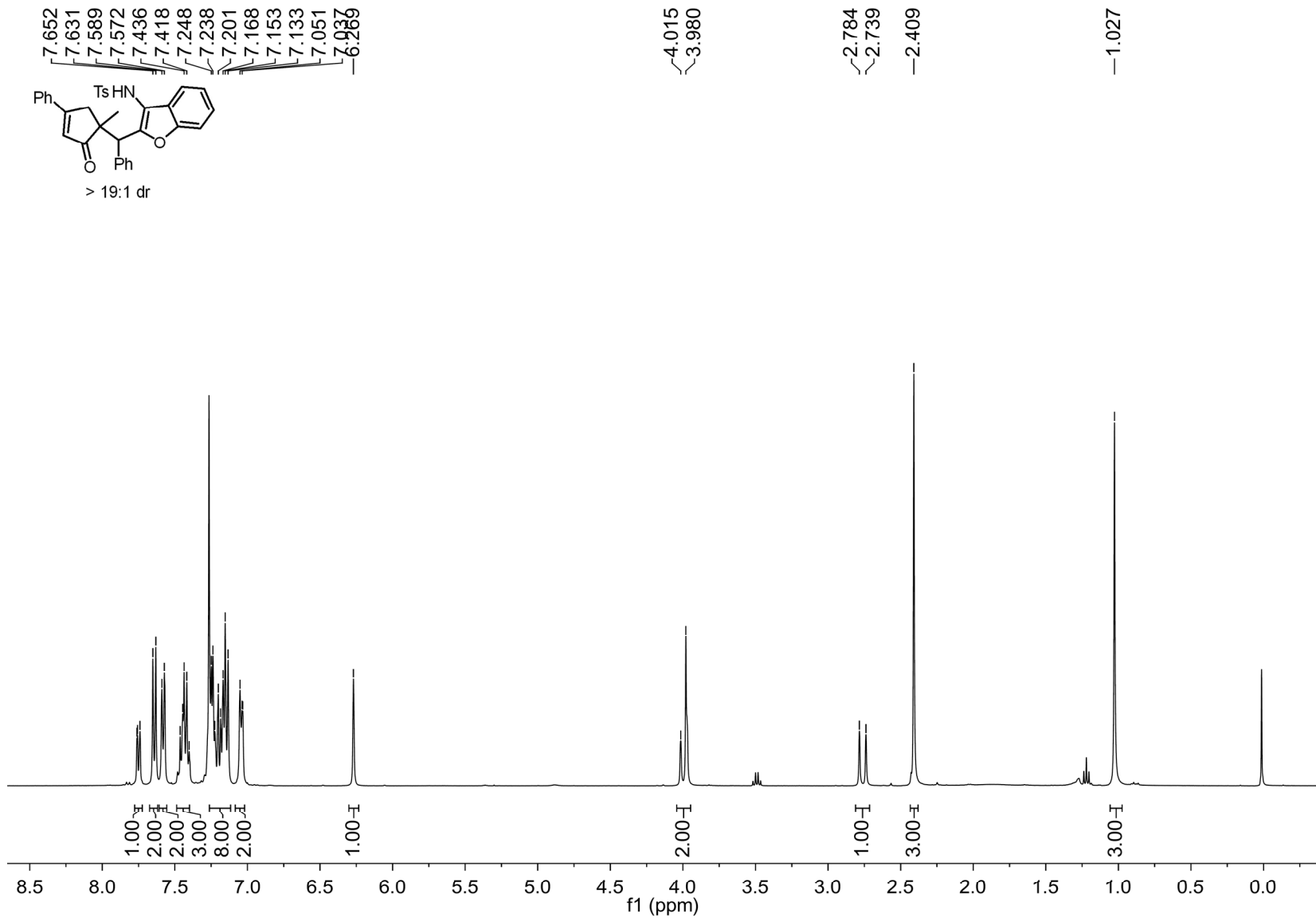
¹³C NMR Spectrum of Compound 3t



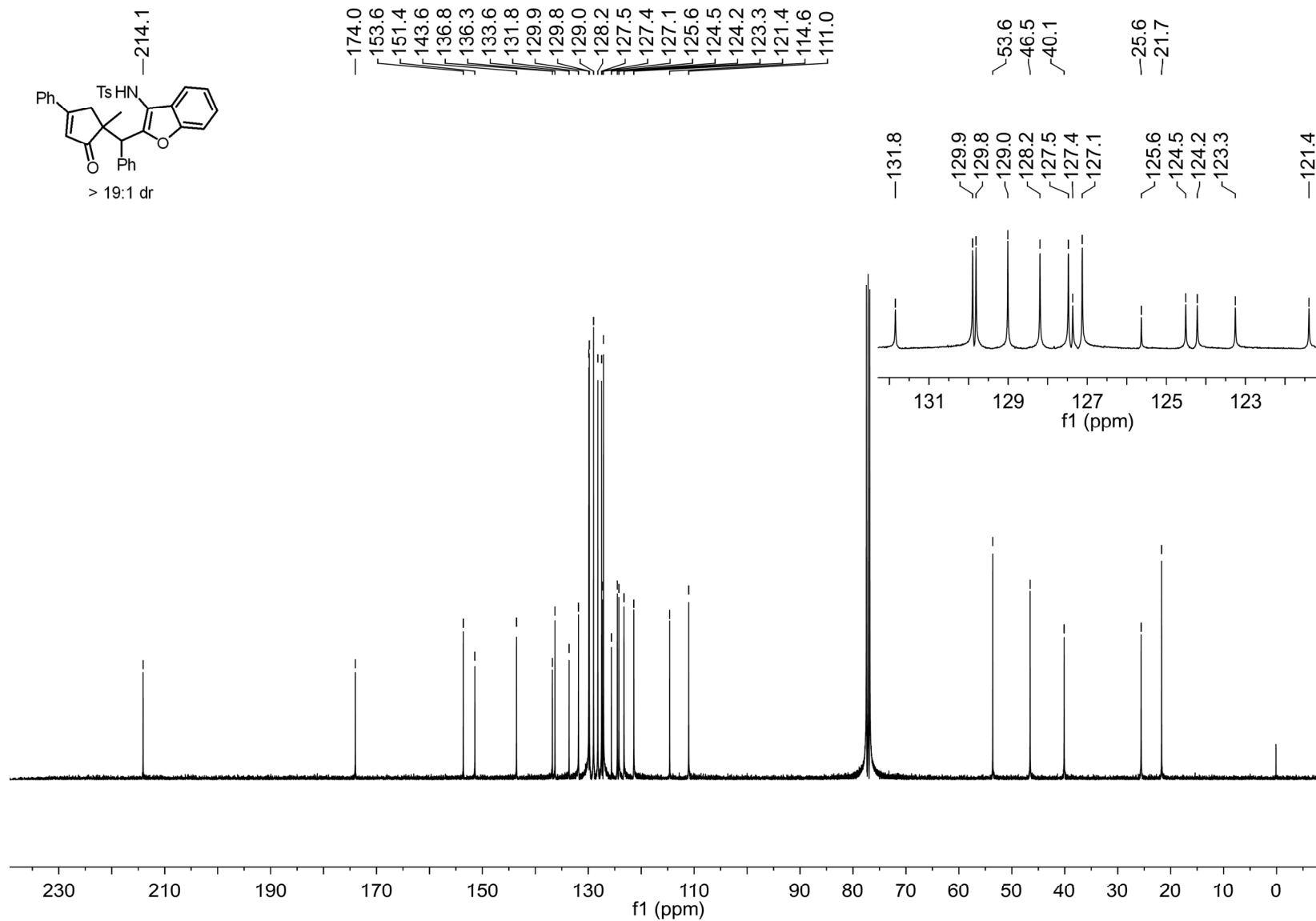
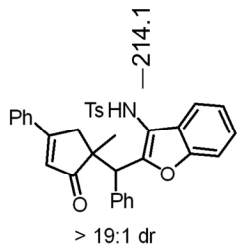
^1H NMR Spectrum of Compound 3u



¹³C NMR Spectrum of Compound 3u



¹H NMR Spectrum of Compound 5a



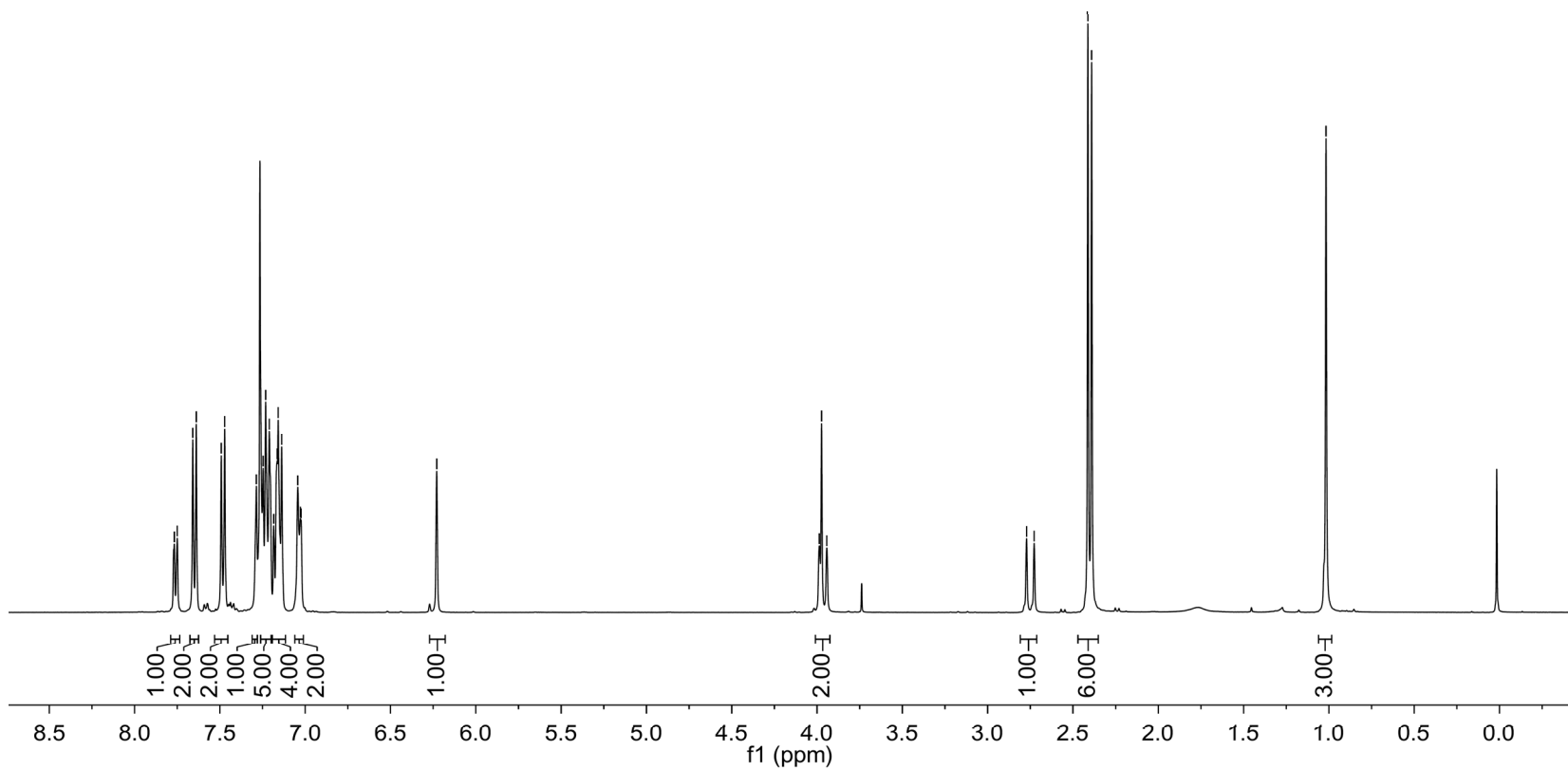
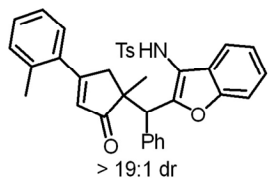
¹³C NMR Spectrum of Compound 5a

7.659
7.639
7.492
7.472
7.286
7.246
7.232
7.210
7.185
7.164
7.158
7.138
7.043
7.028
6.924
6.926

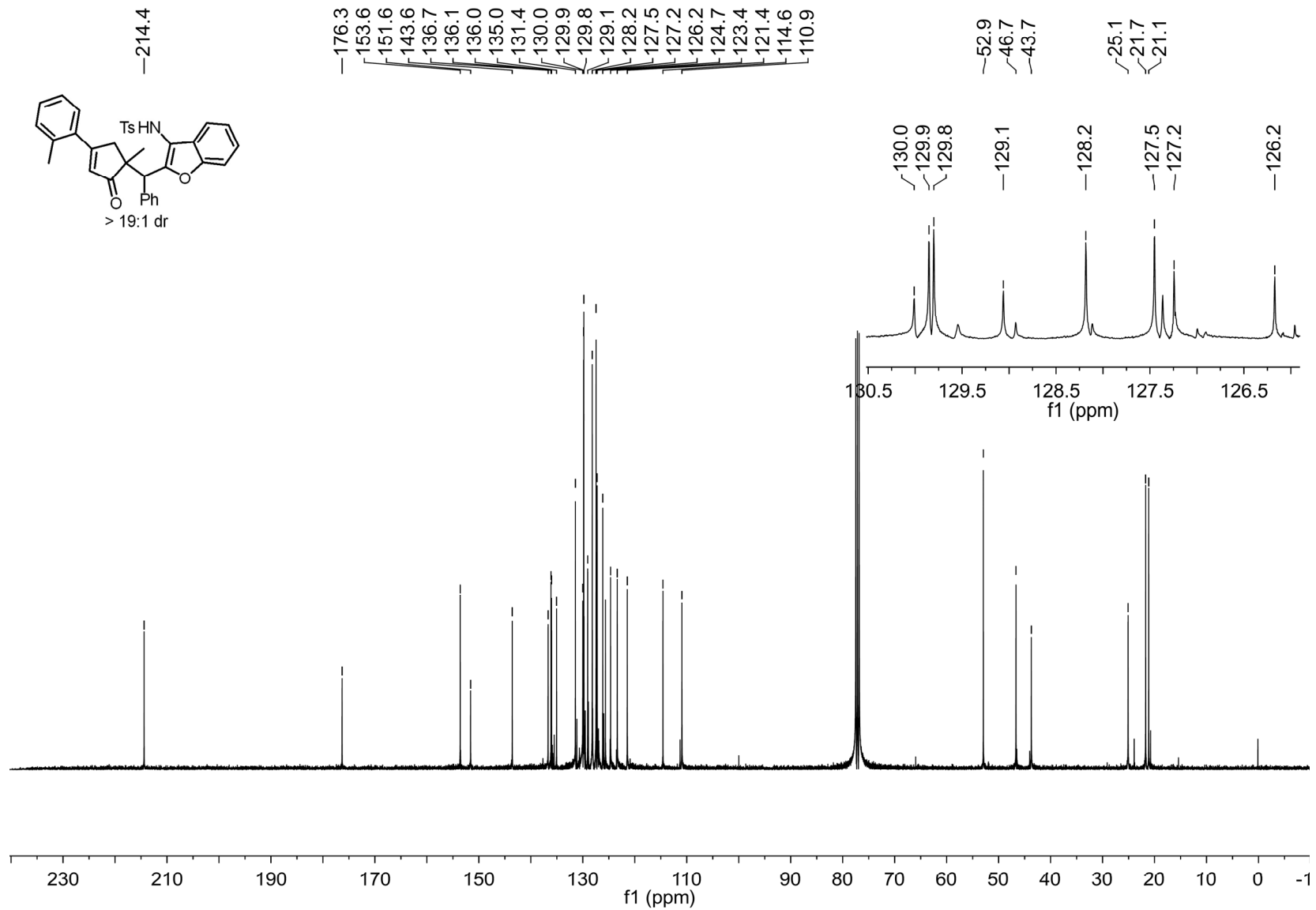
3.986
3.973
3.943

2.772
2.727
2.413
2.391

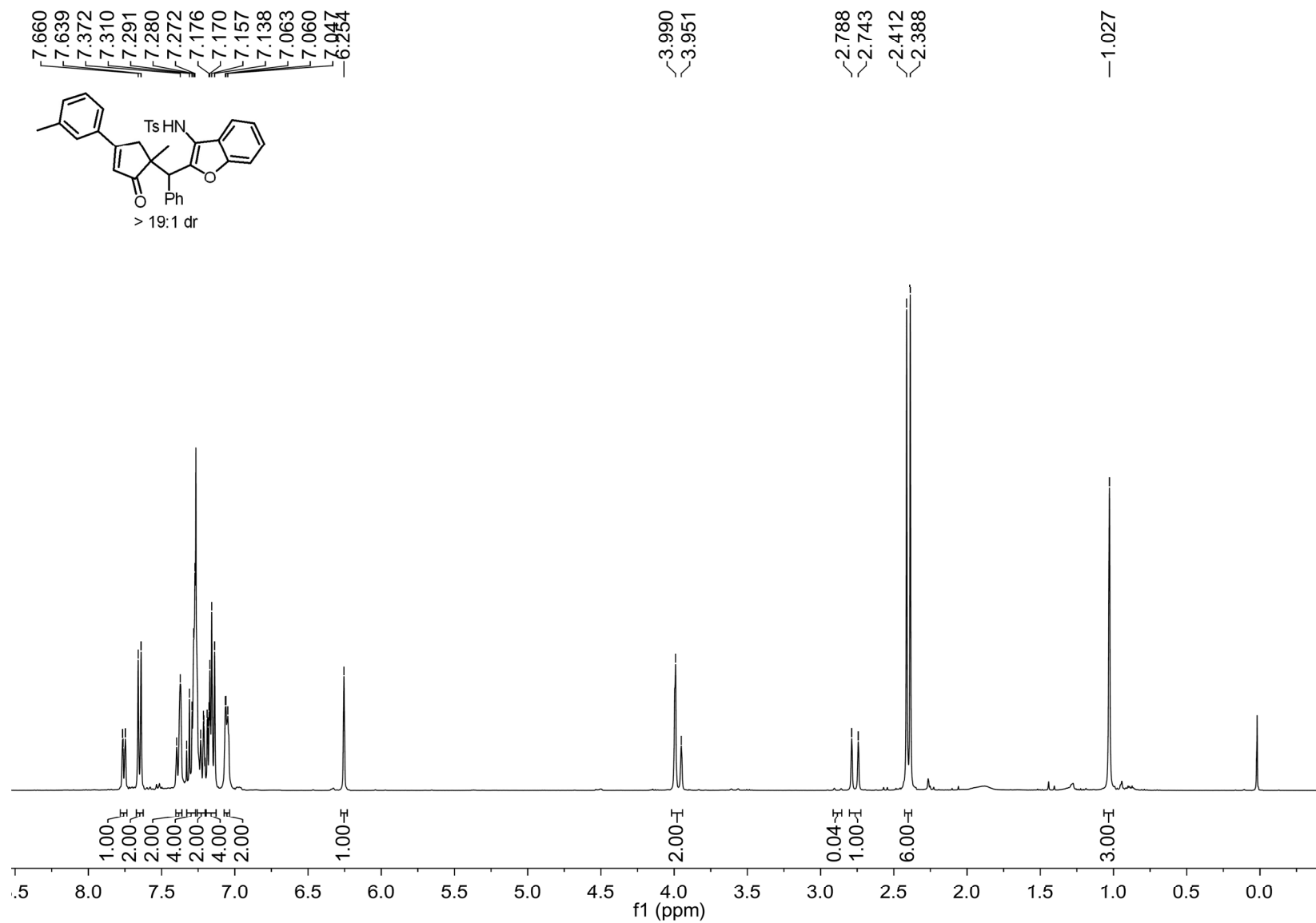
1.017



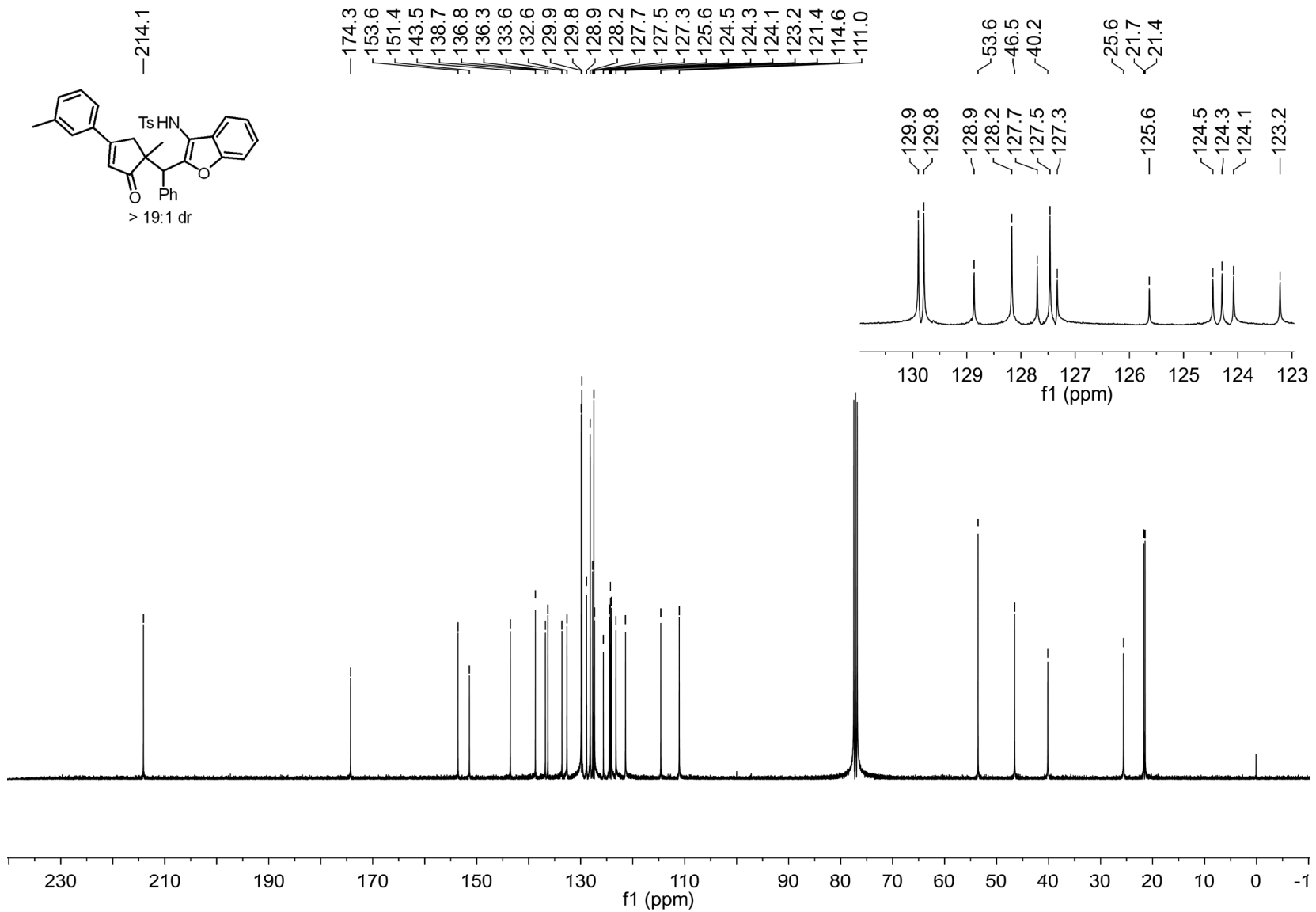
¹H NMR Spectrum of Compound 5b



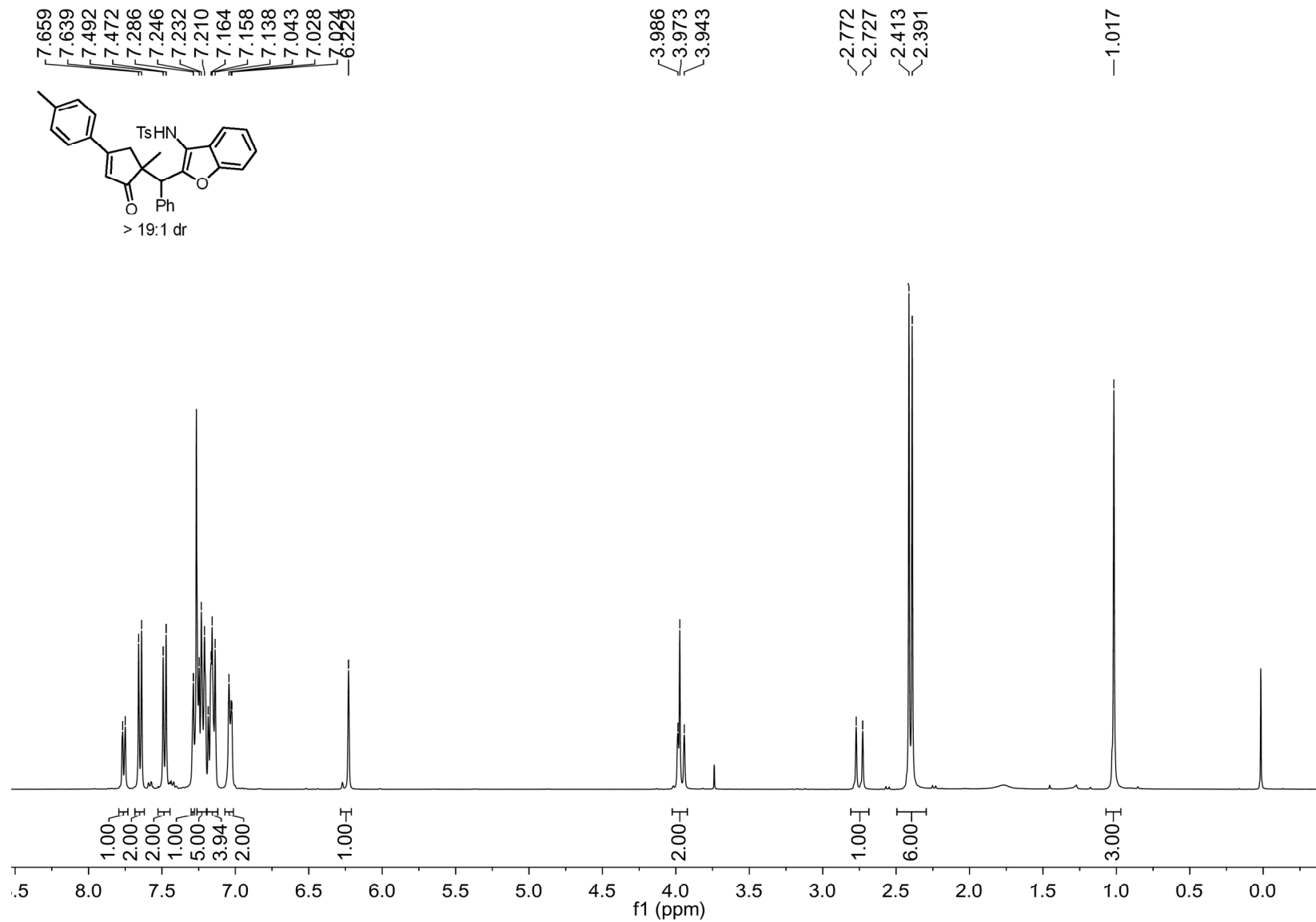
^{13}C NMR Spectrum of Compound 5b



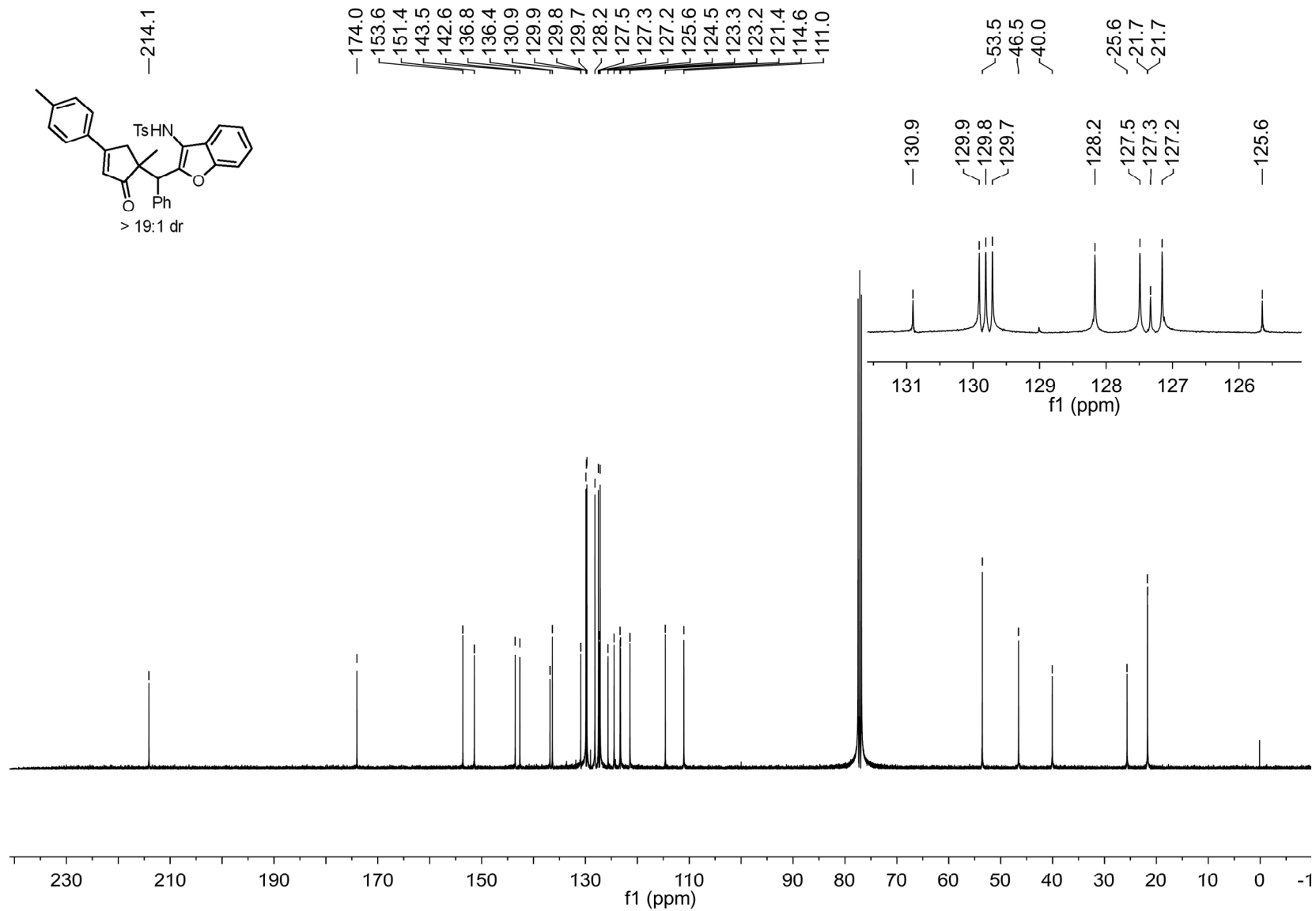
¹H NMR Spectrum of Compound 5c



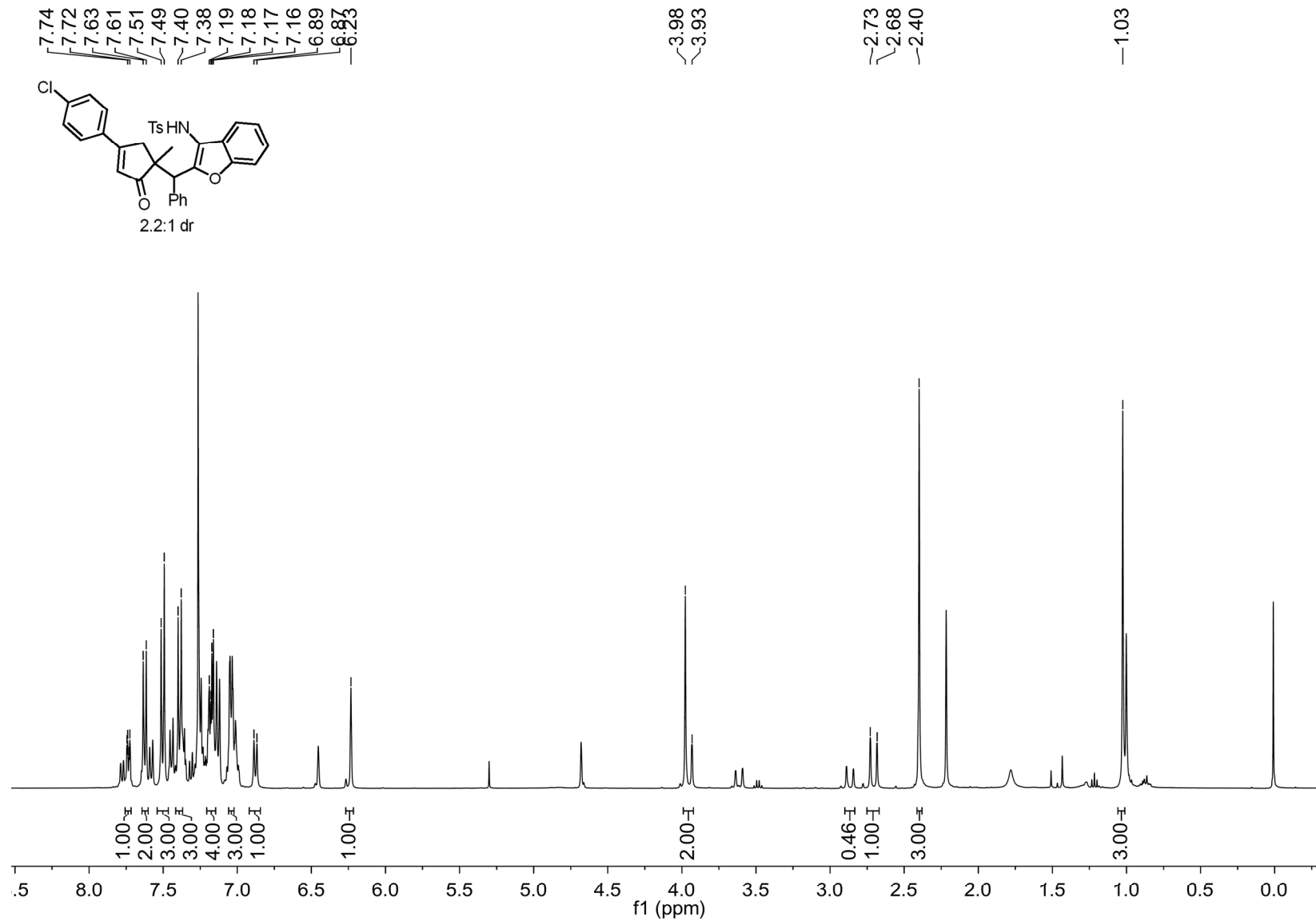
^{13}C NMR Spectrum of Compound 5c



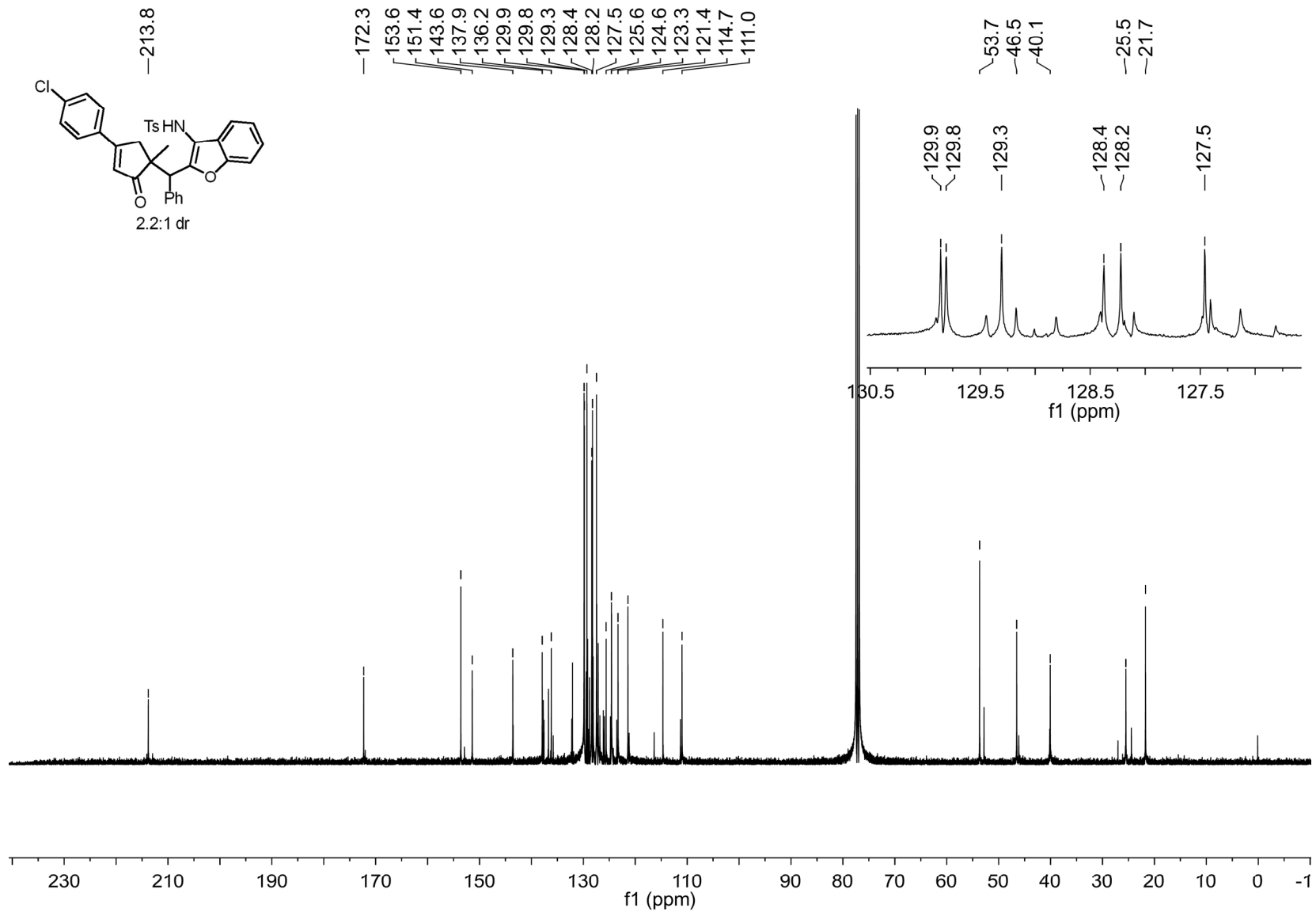
¹H NMR Spectrum of Compound 5d



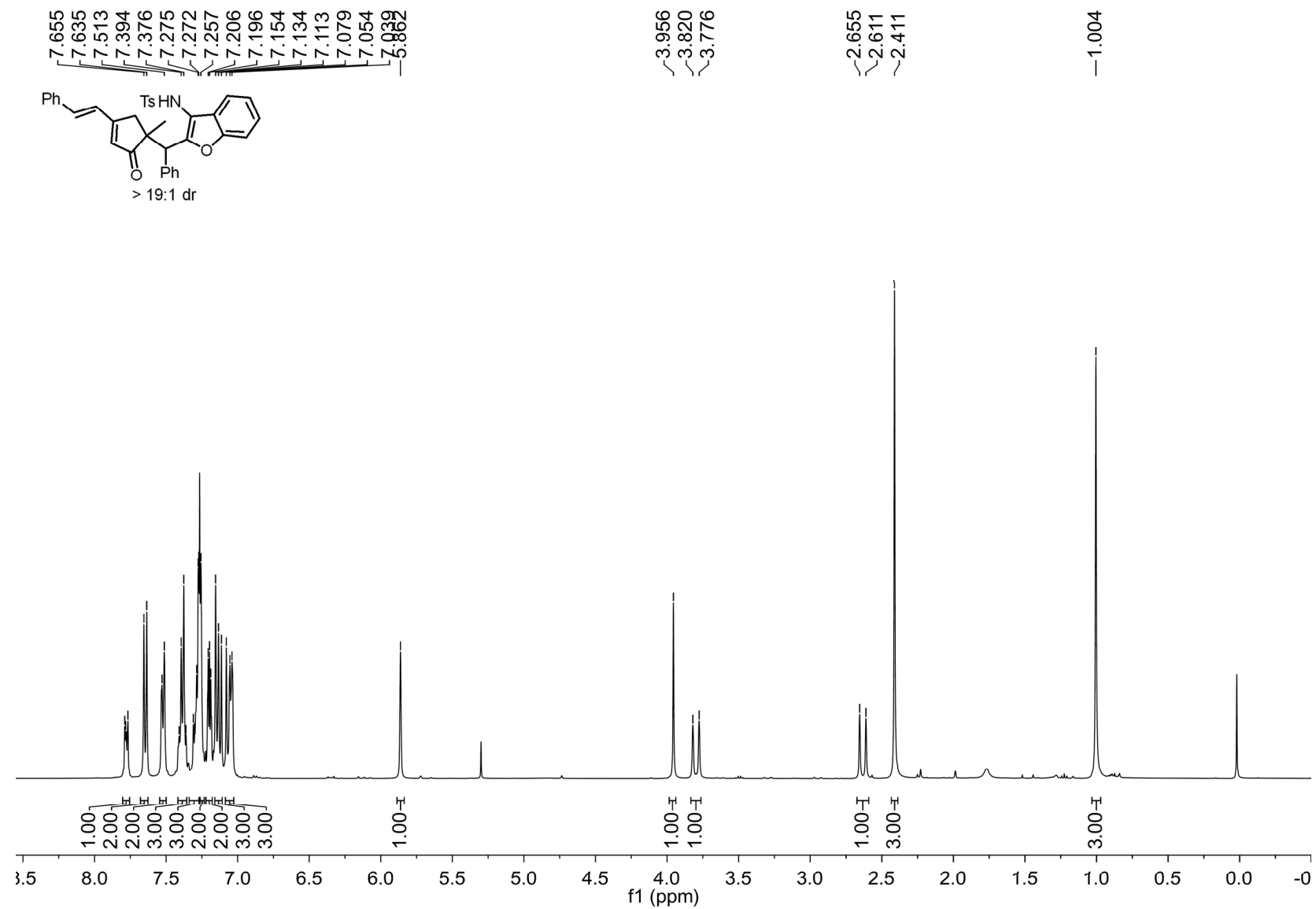
^{13}C NMR Spectrum of Compound 5d



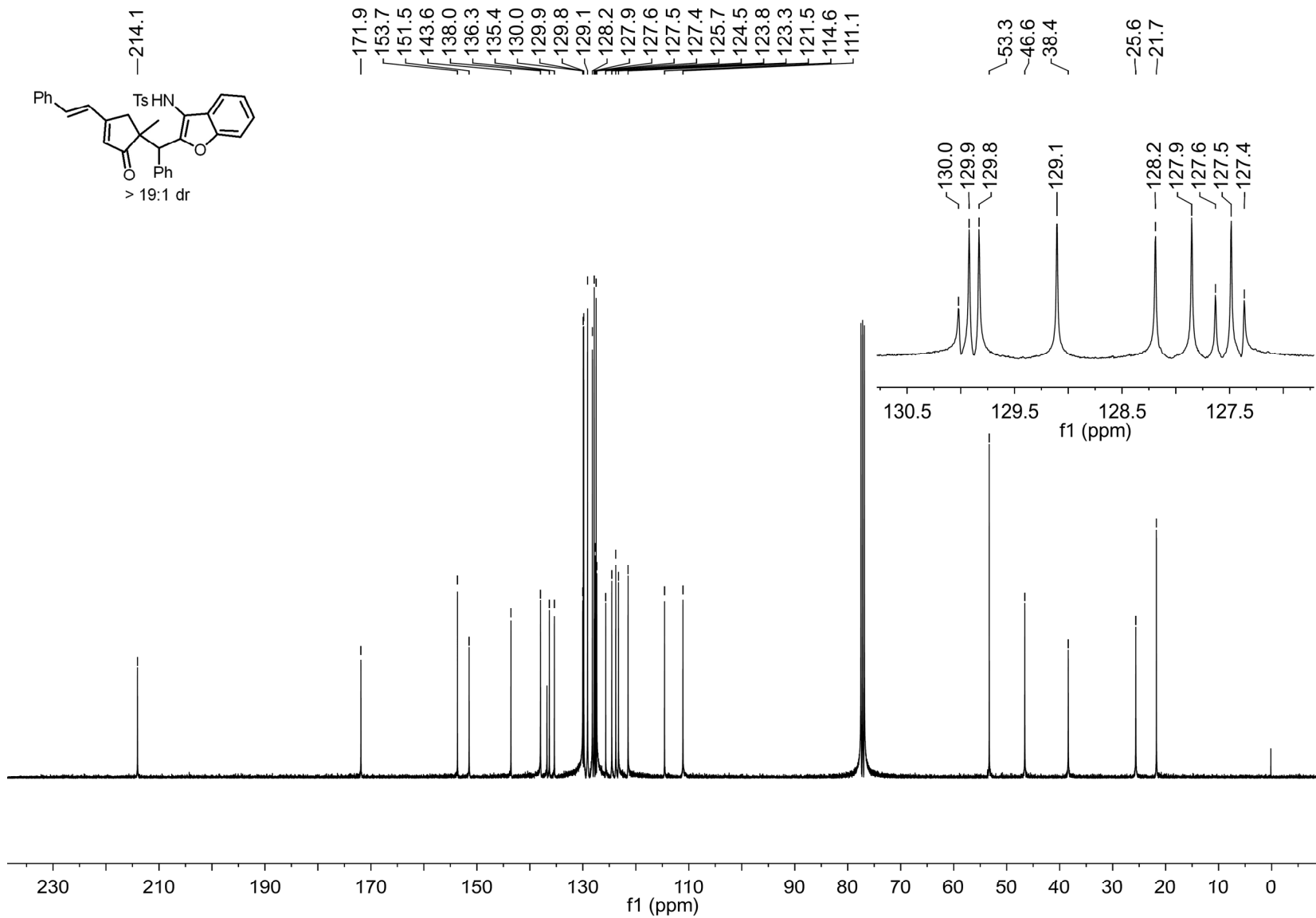
^1H NMR Spectrum of Compound 5e



^{13}C NMR Spectrum of Compound 5e



¹H NMR Spectrum of Compound 5f



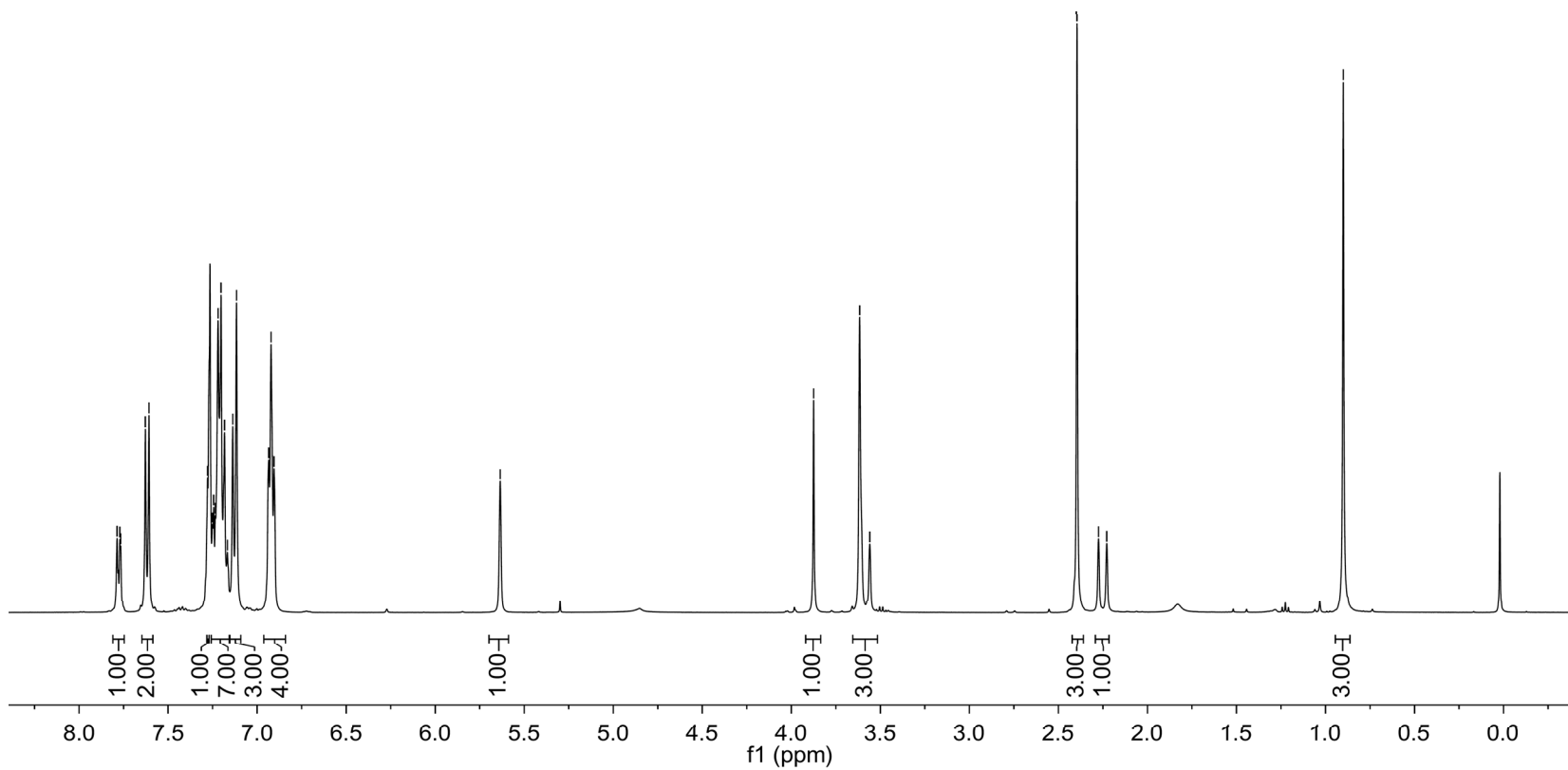
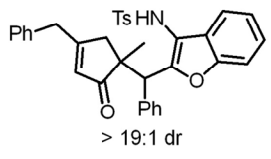
^{13}C NMR Spectrum of Compound 5f

7.786
7.771
7.766
7.628
7.607
7.278
7.244
7.234
7.219
7.202
7.183
7.137
7.116
6.935
6.922
6.895

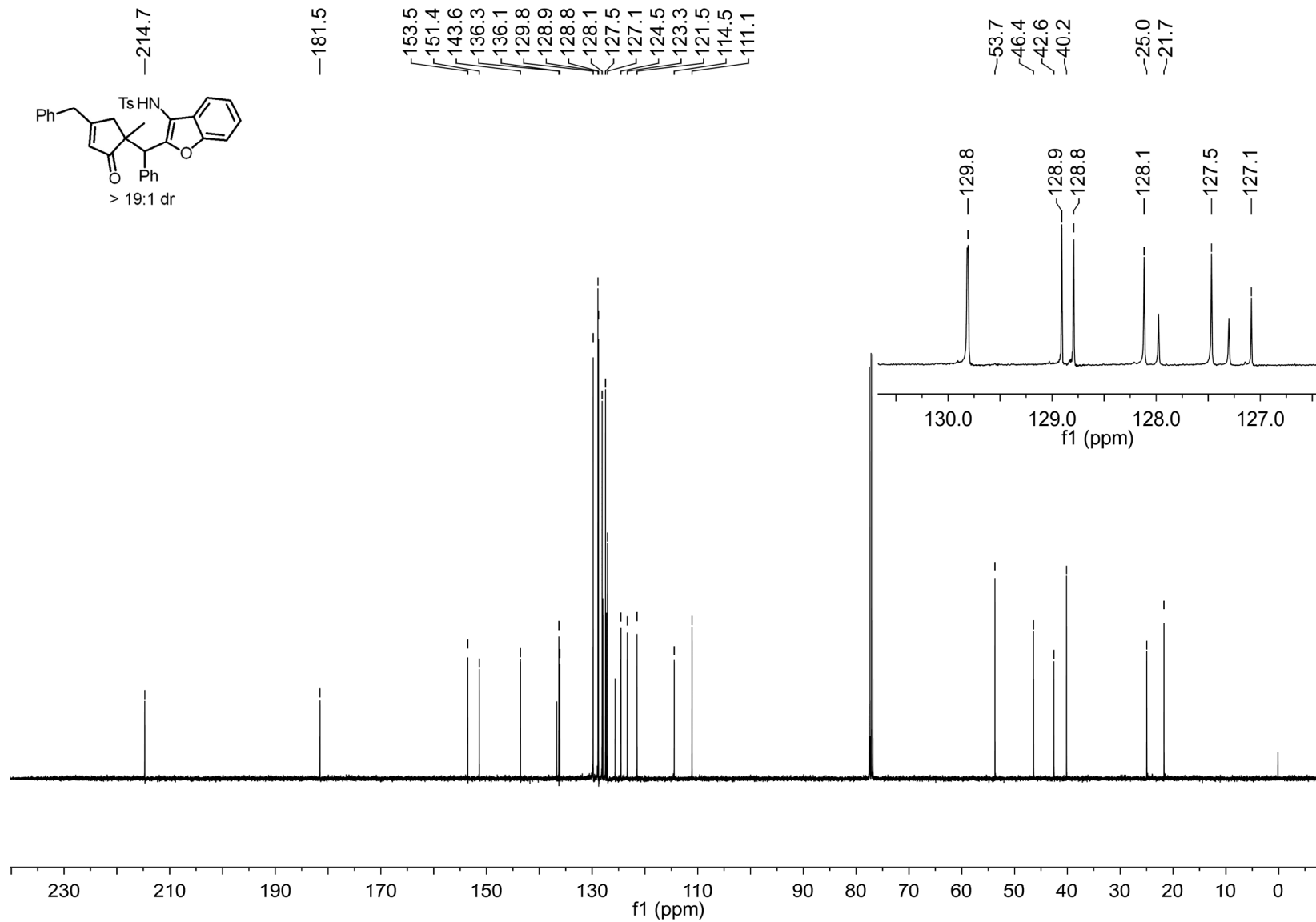
3.875
3.616
3.559

2.395
2.275
2.228

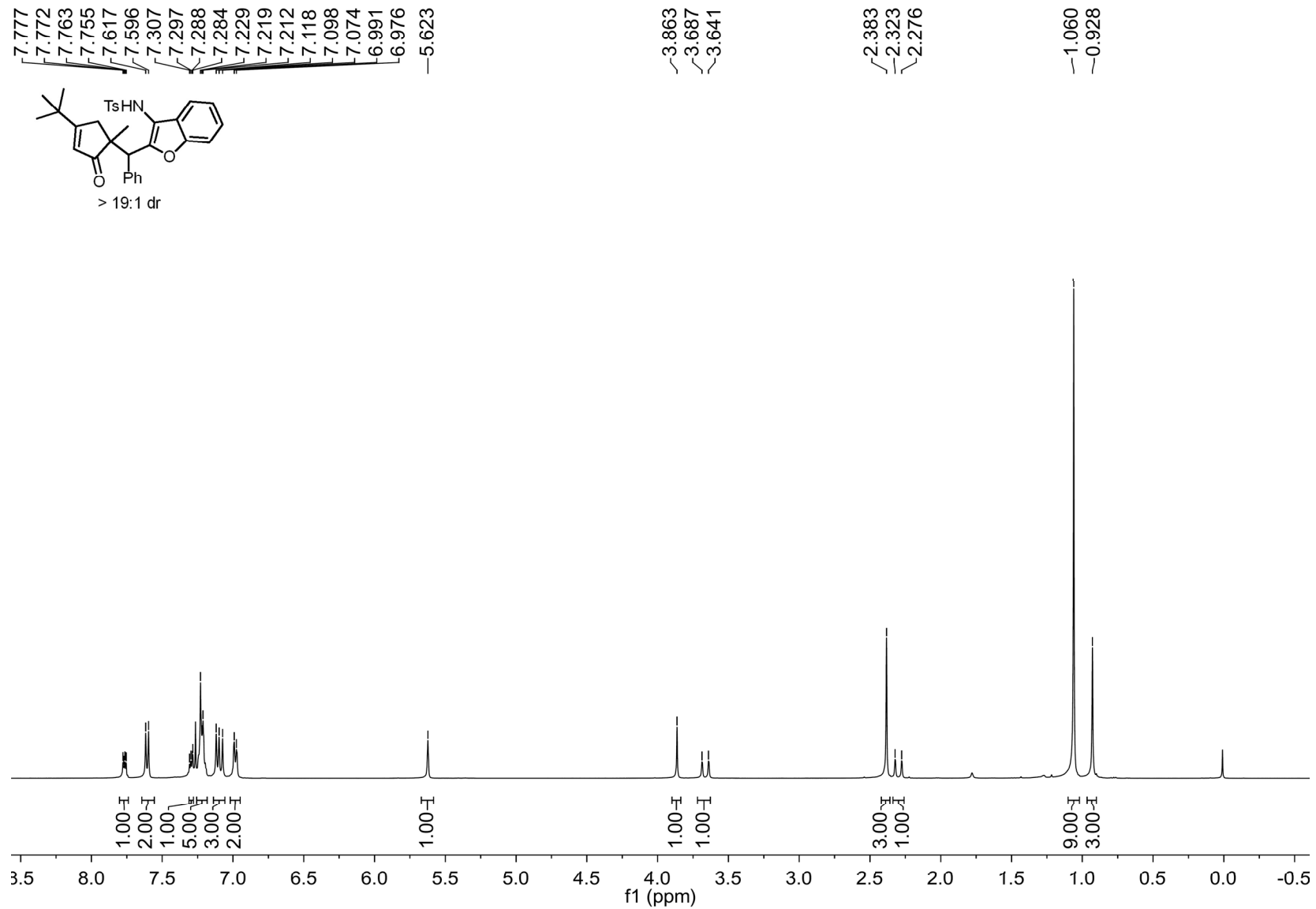
-0.900



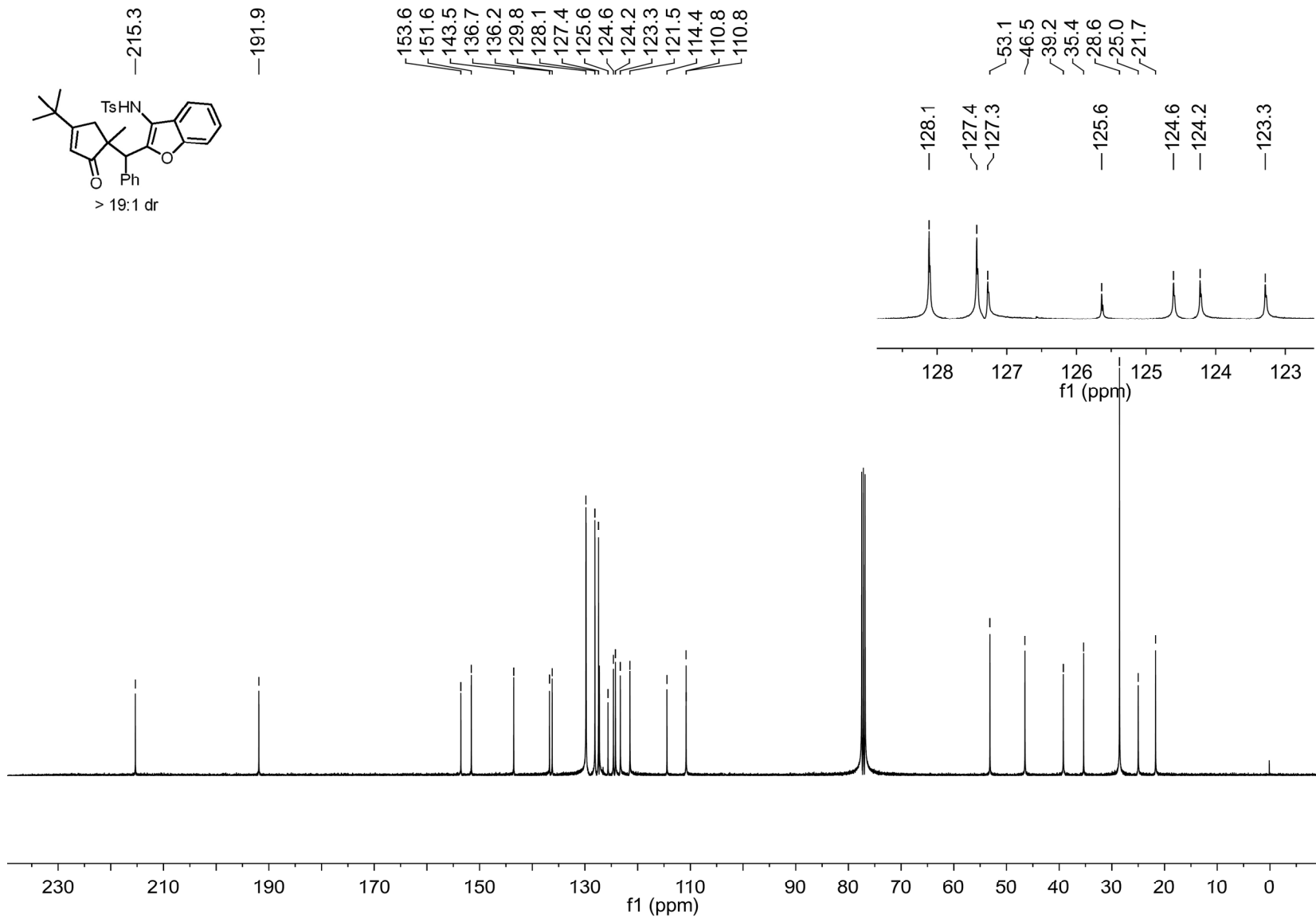
¹H NMR Spectrum of Compound 5g

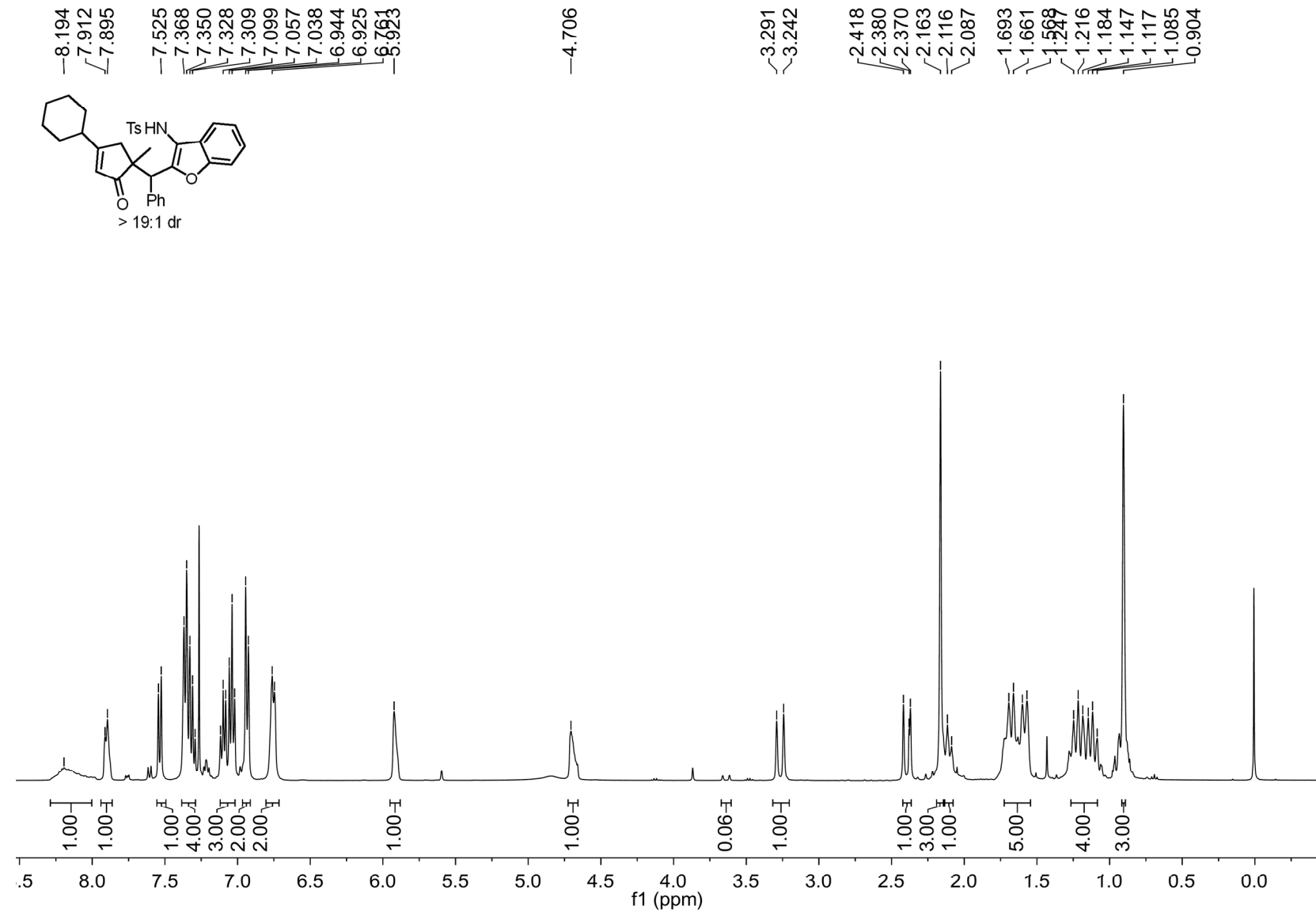
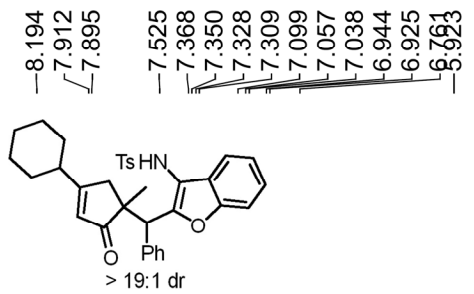


^{13}C NMR Spectrum of Compound 5g

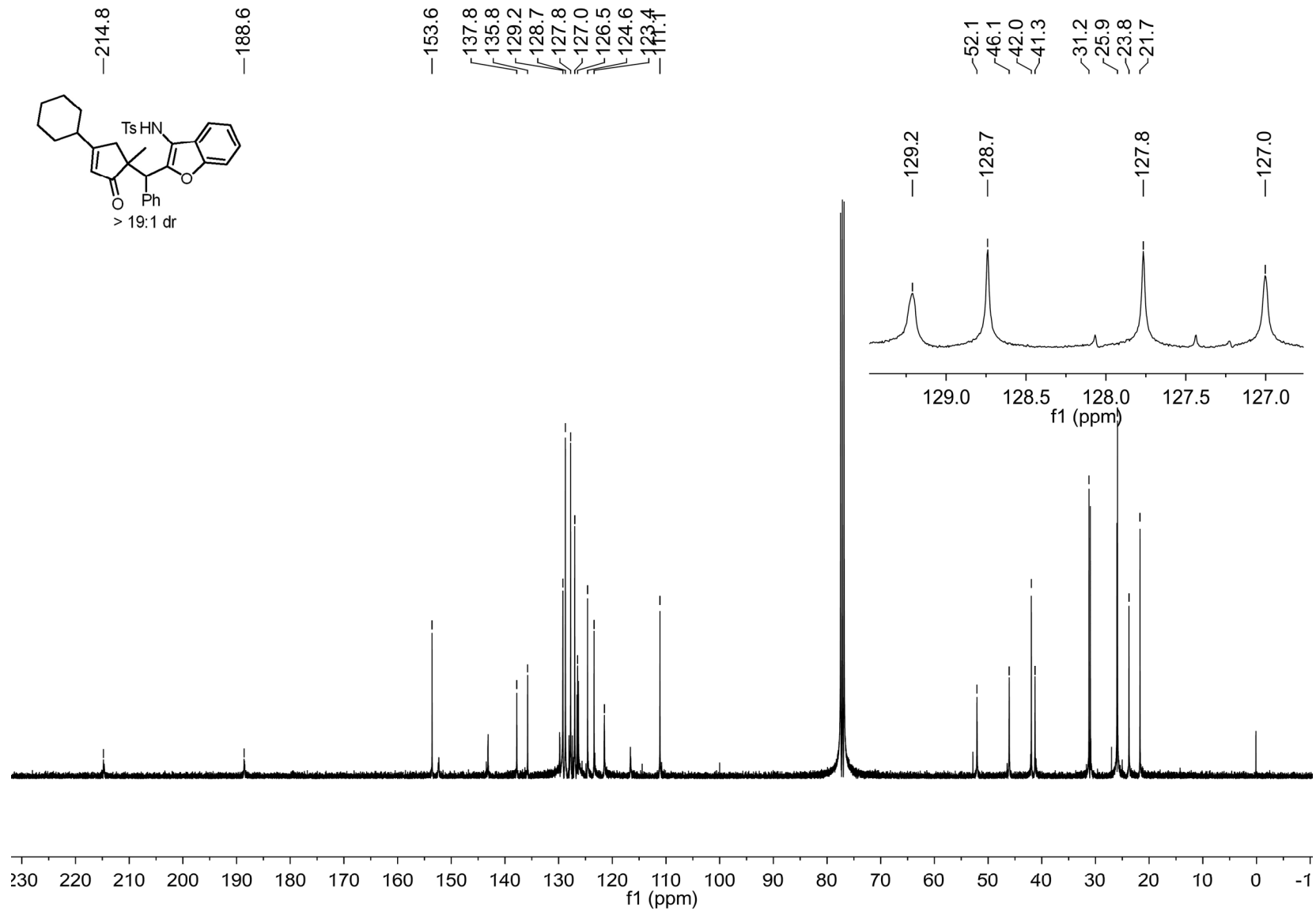


¹H NMR Spectrum of Compound 5h

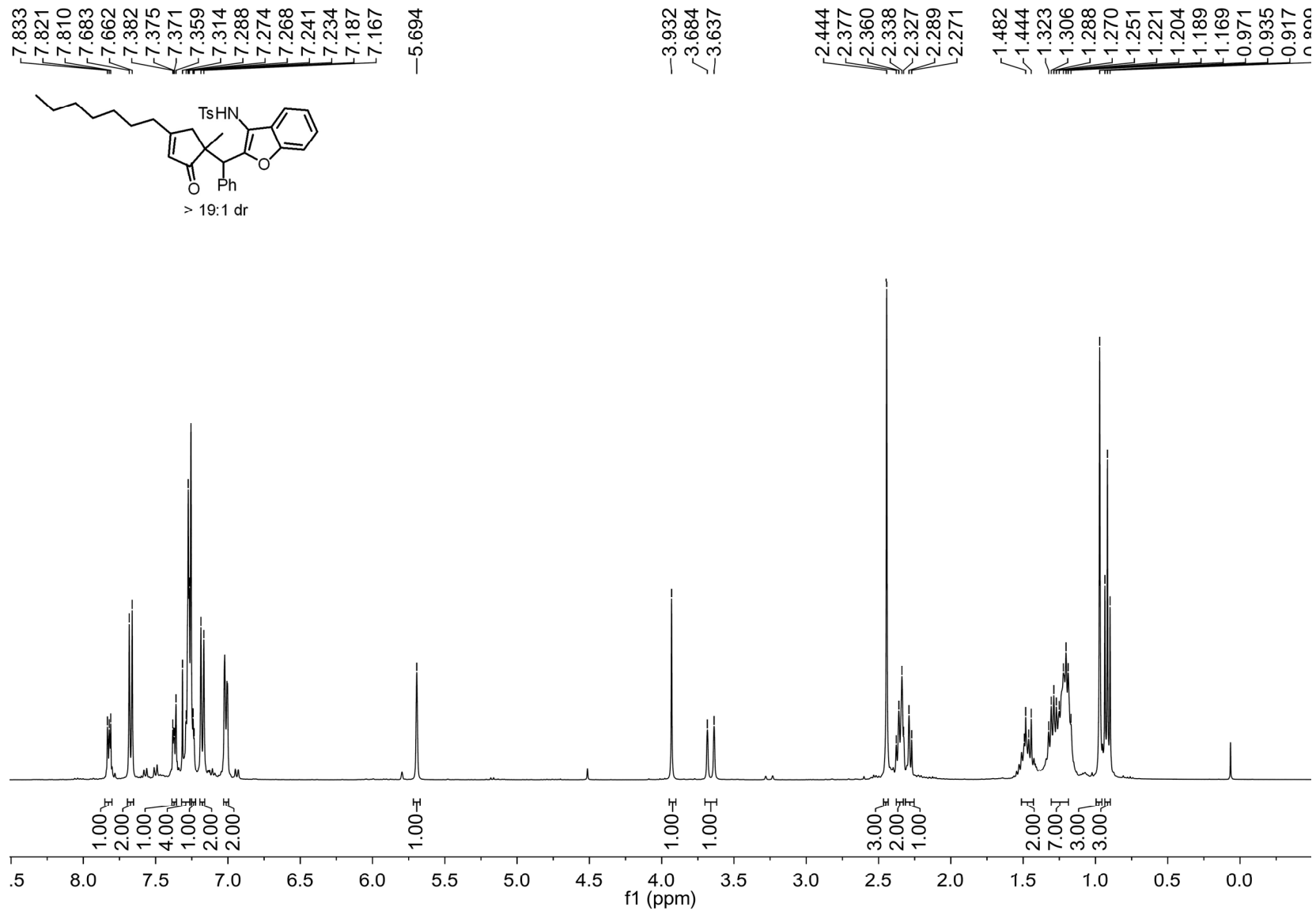




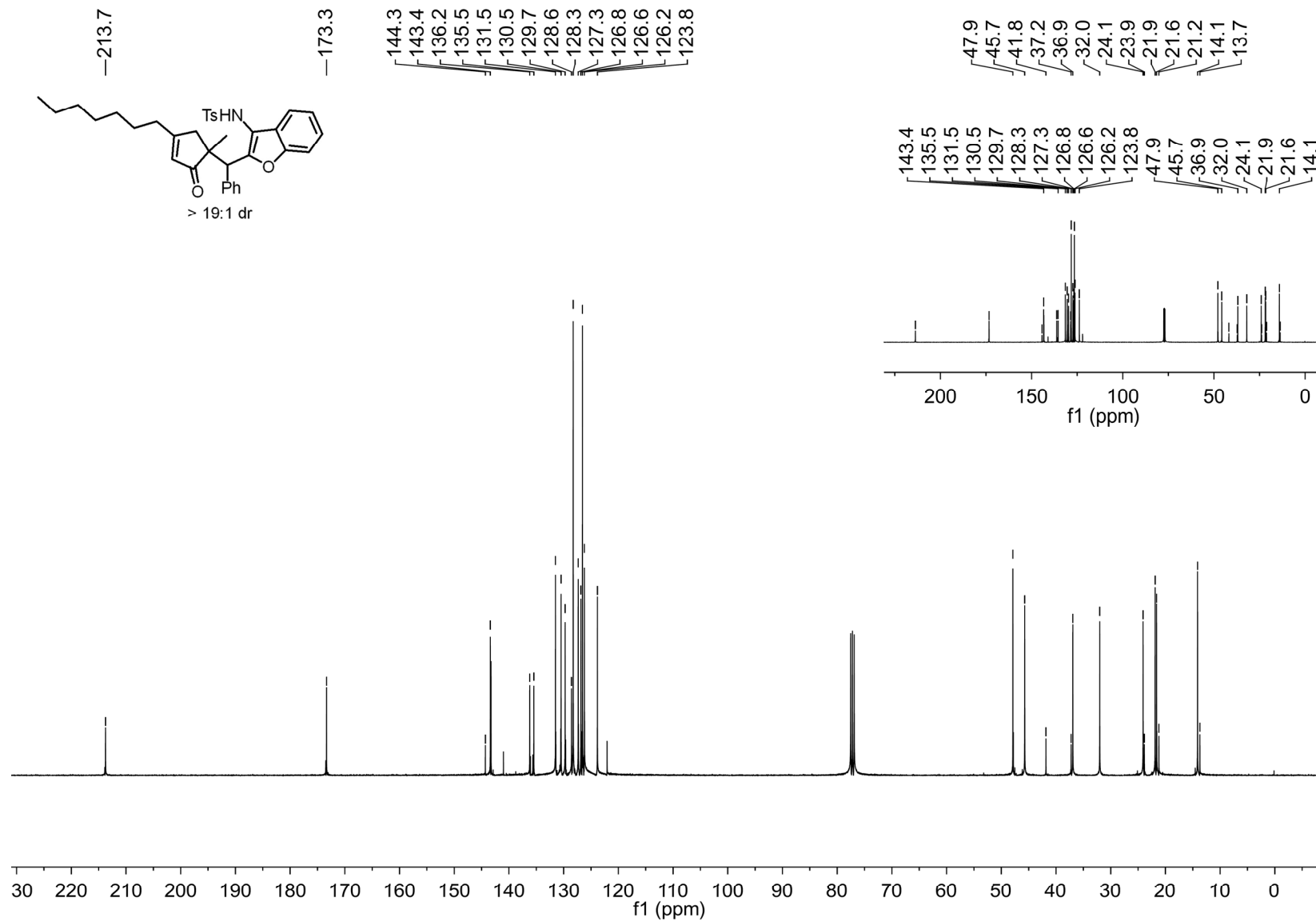
¹H NMR Spectrum of Compound 5i



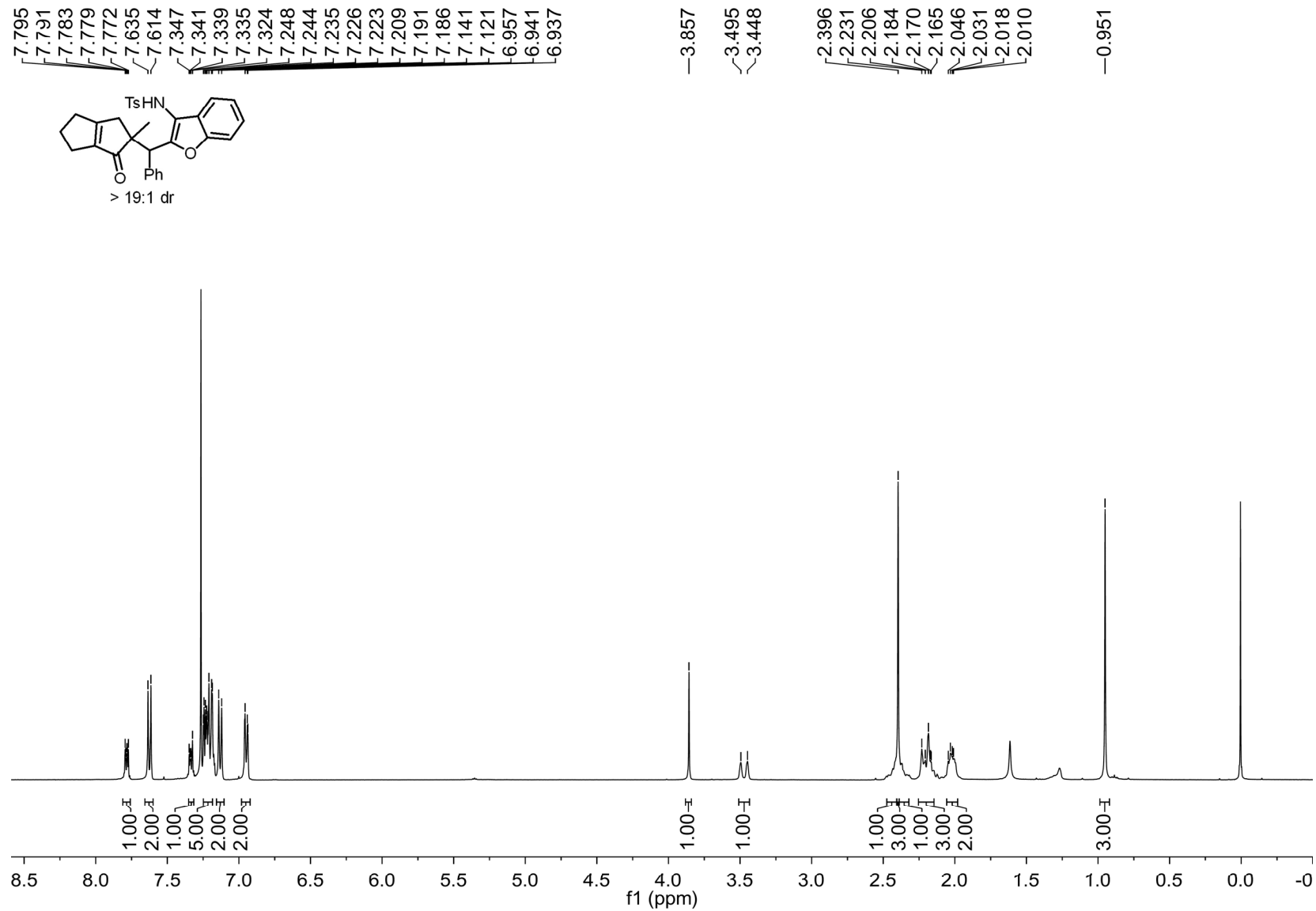
^{13}C NMR Spectrum of Compound 5i

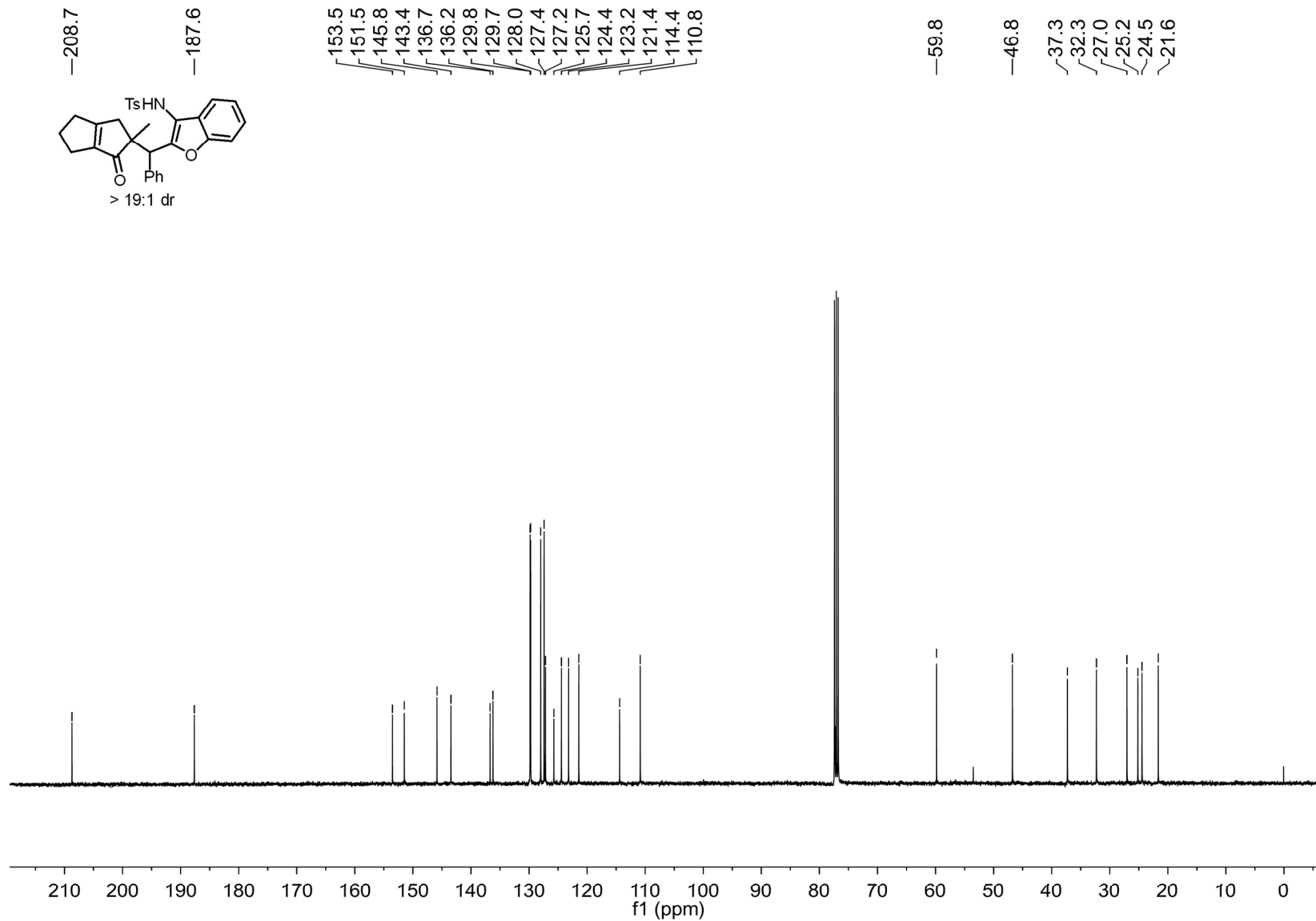


¹H NMR Spectrum of Compound 5j

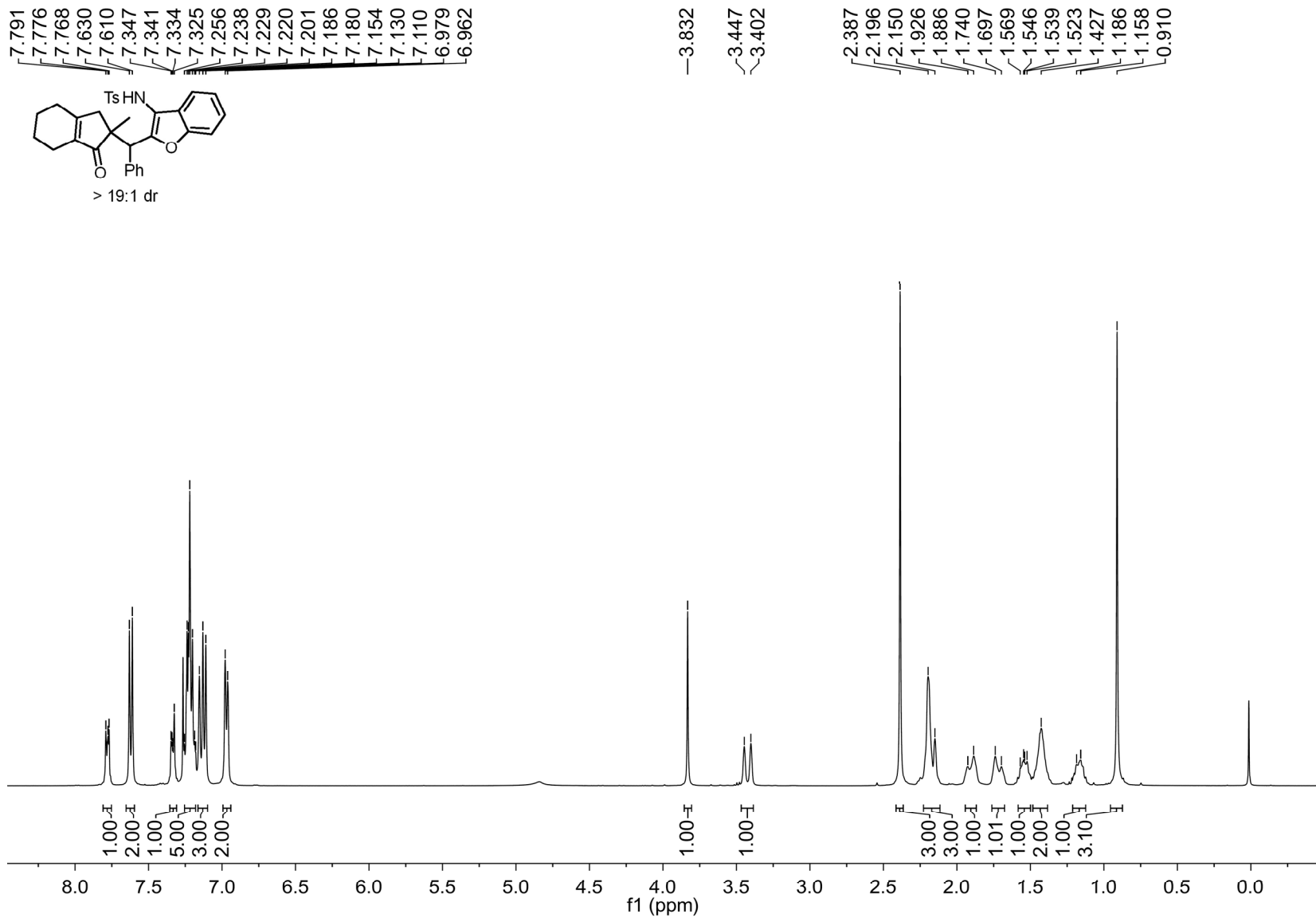


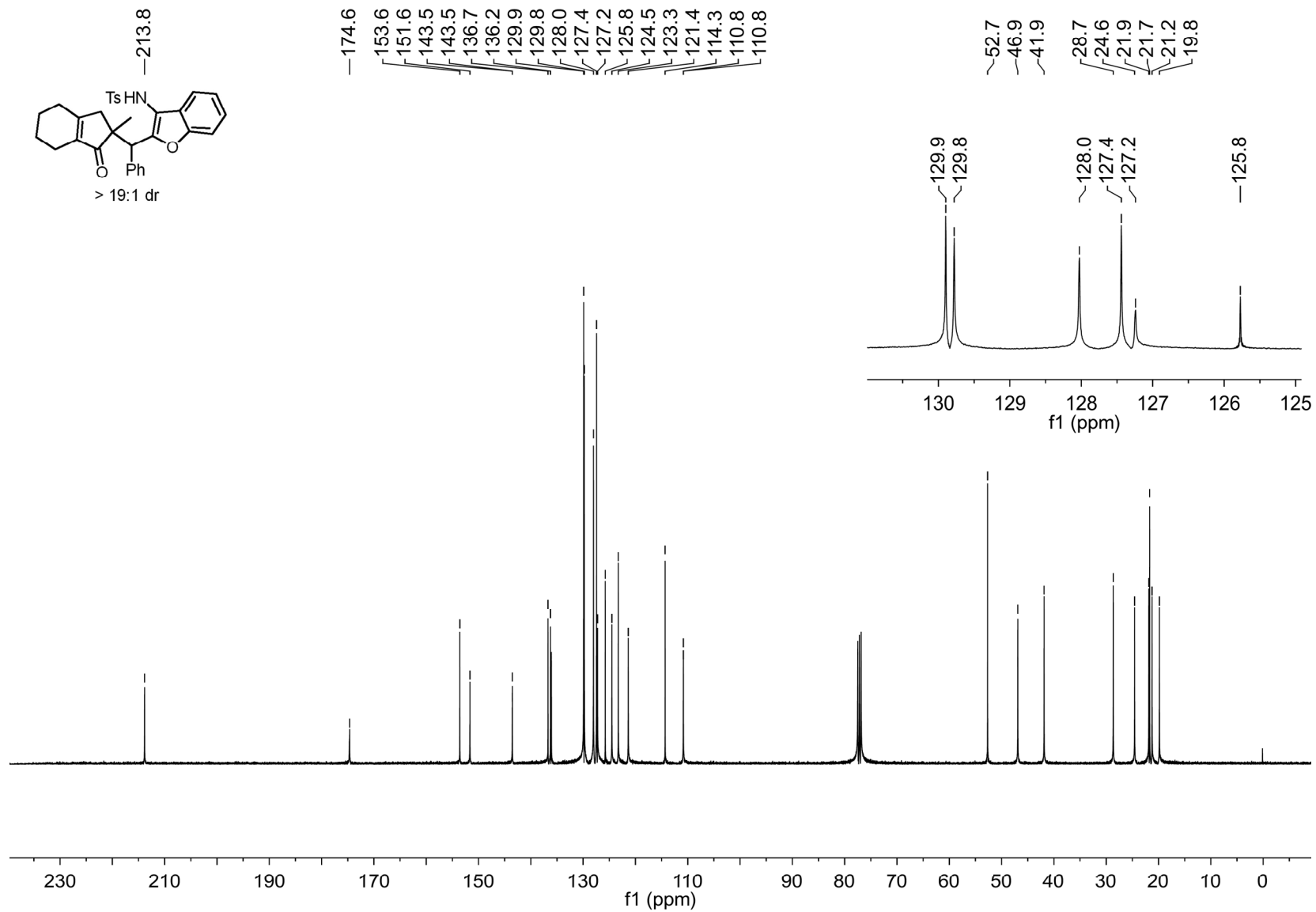
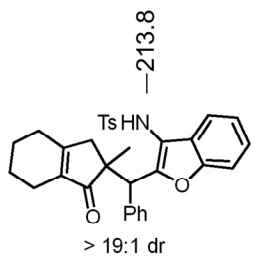
¹³C NMR Spectrum of Compound 5j



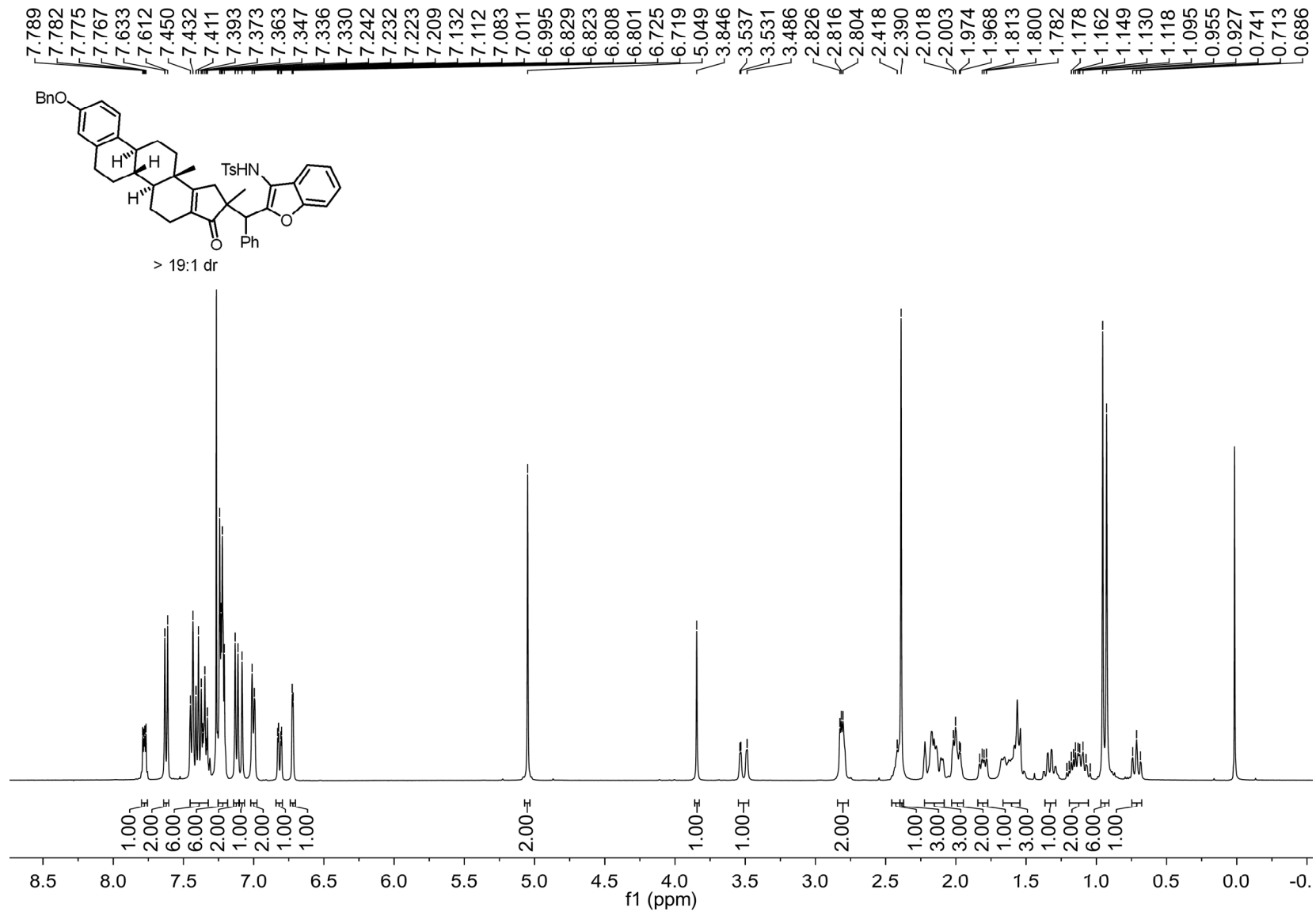


^{13}C NMR Spectrum of Compound 5k

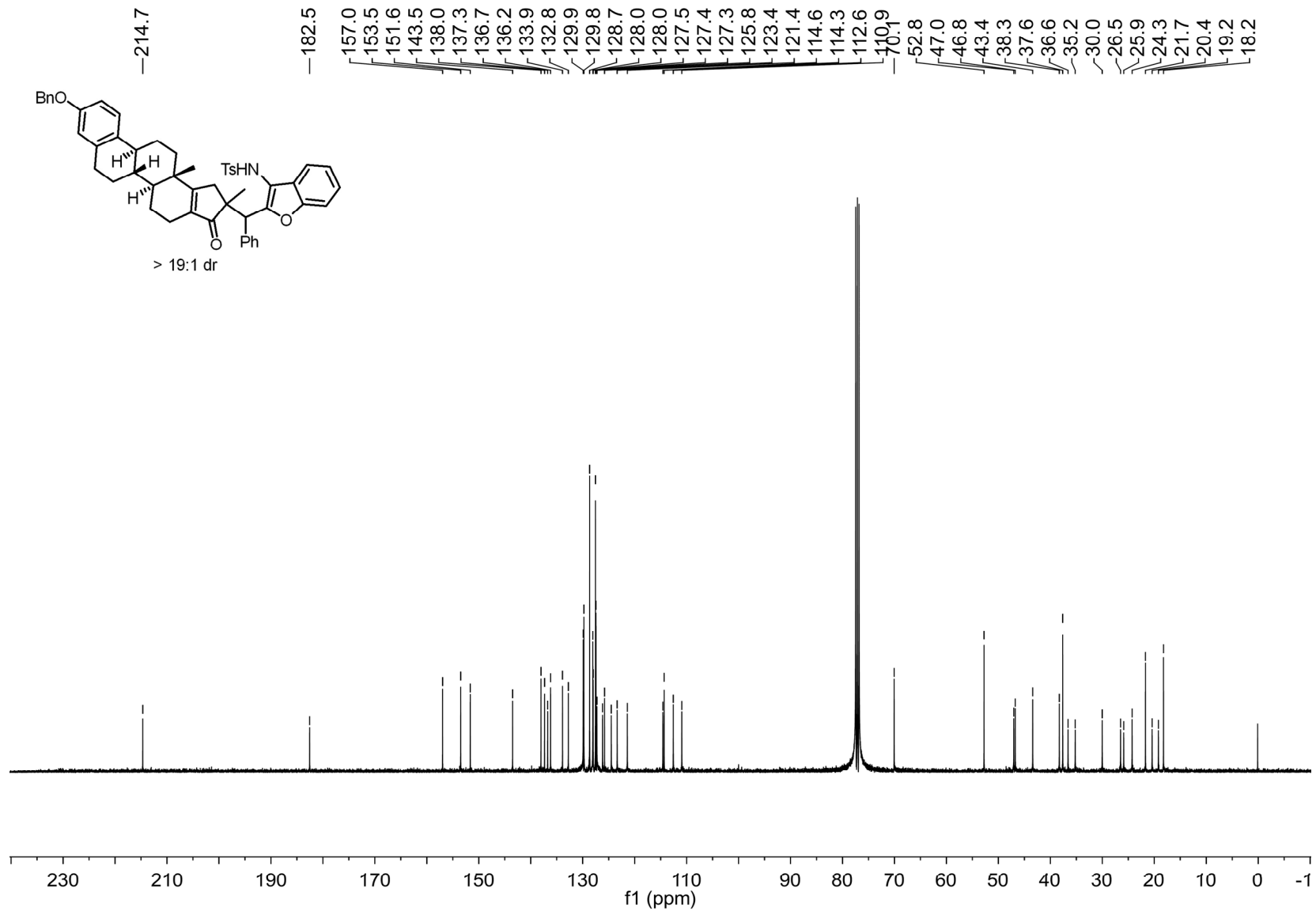




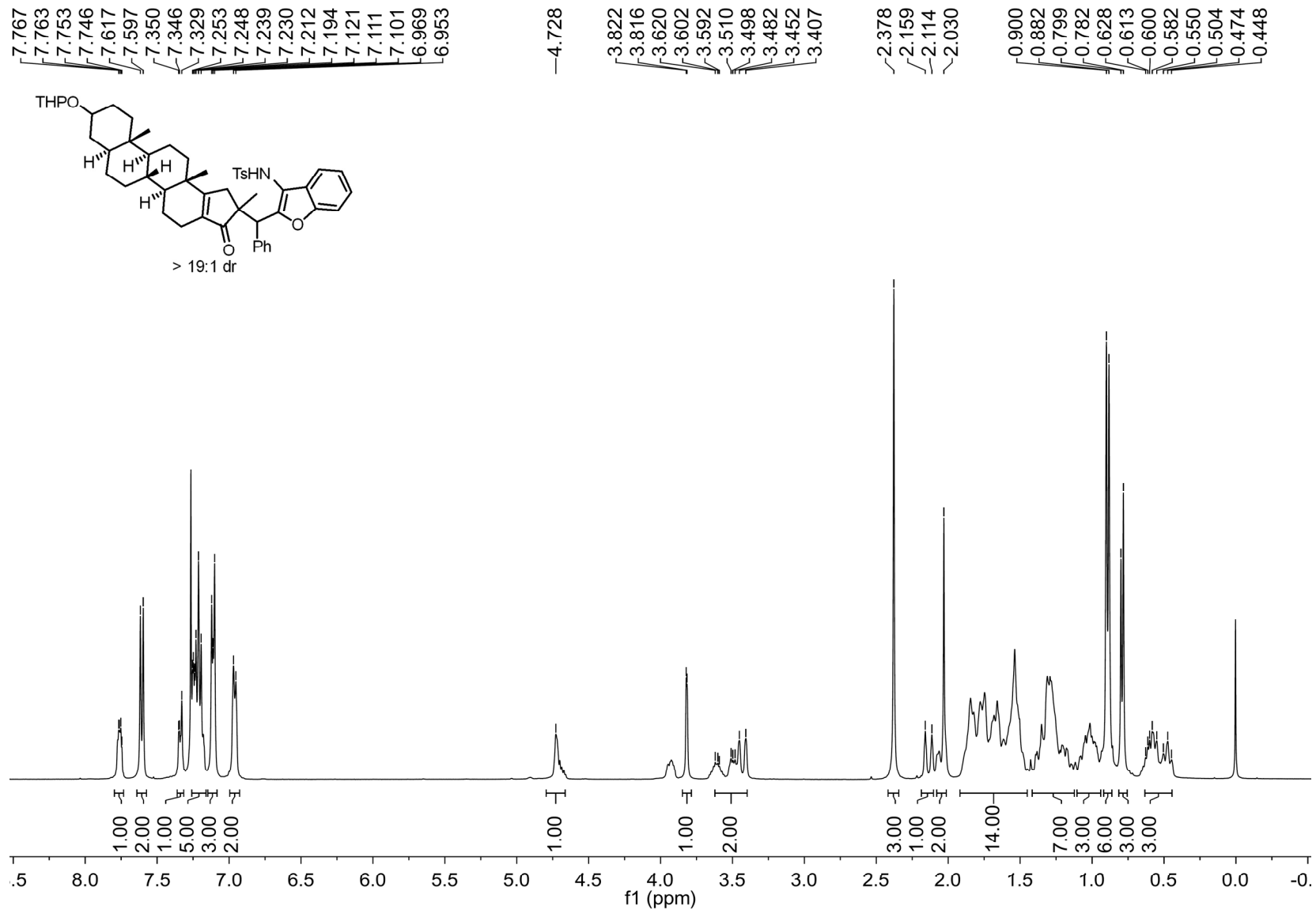
^{13}C NMR Spectrum of Compound 51



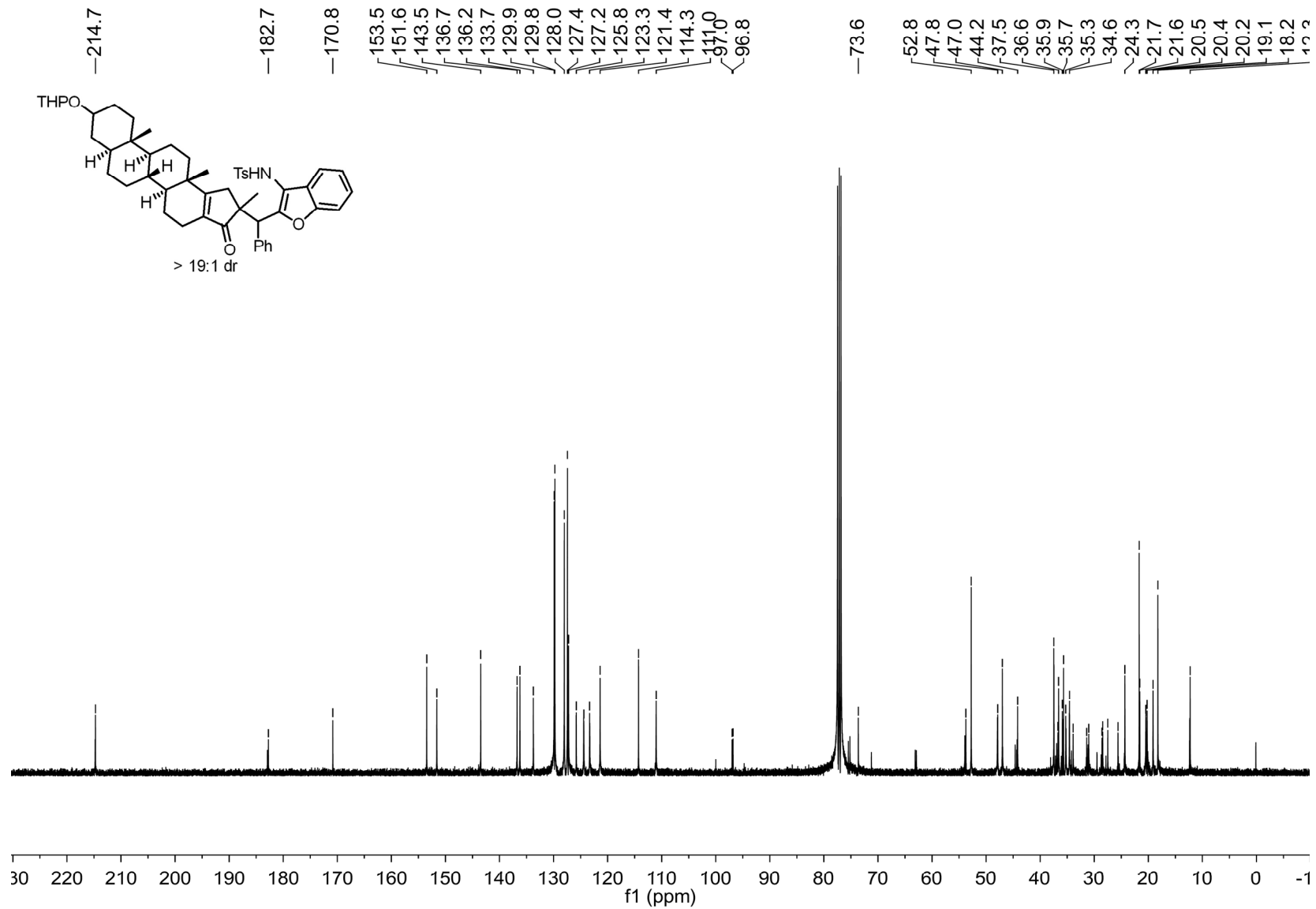
¹H NMR Spectrum of Compound 5m



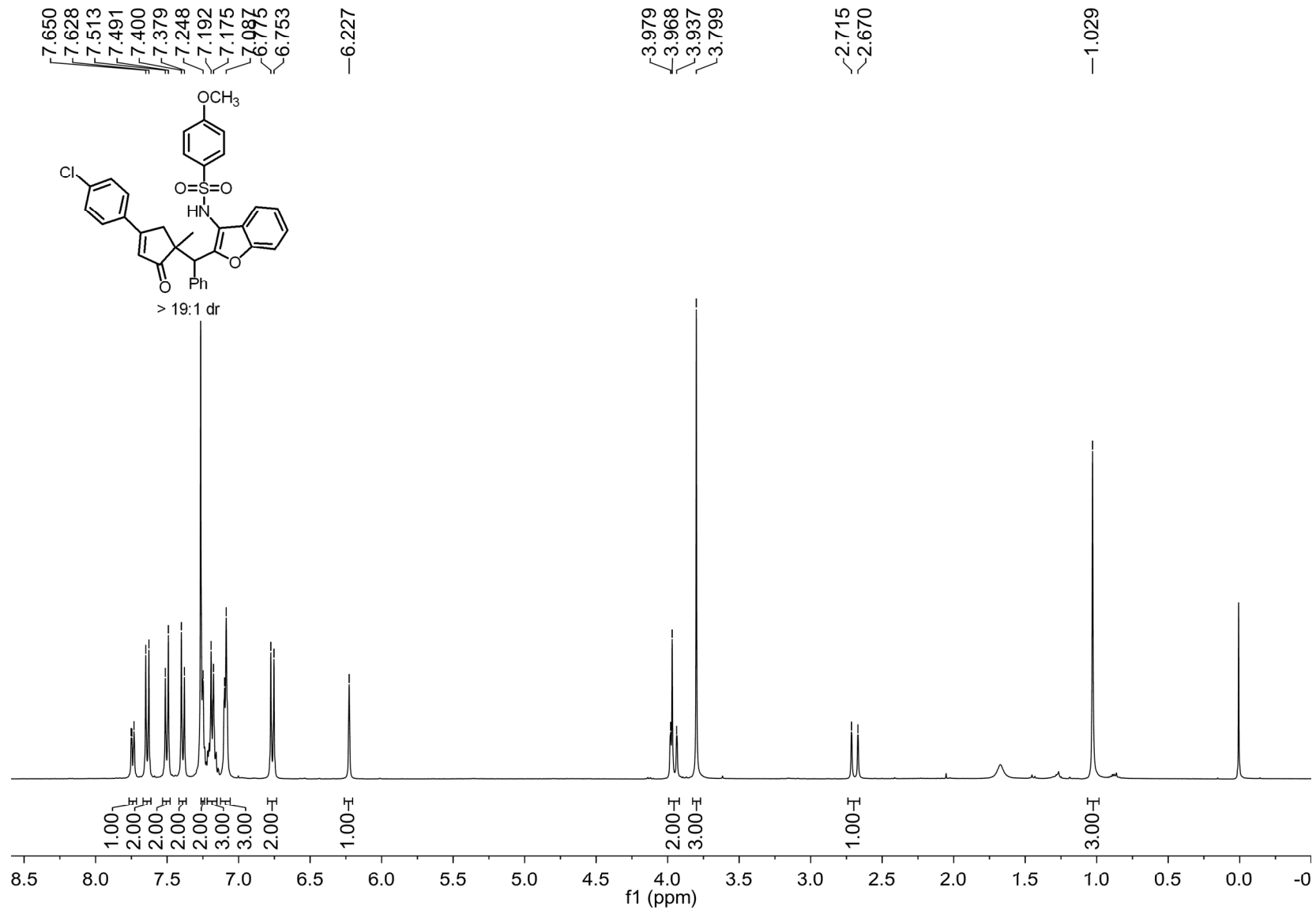
¹³C NMR Spectrum of Compound 5m



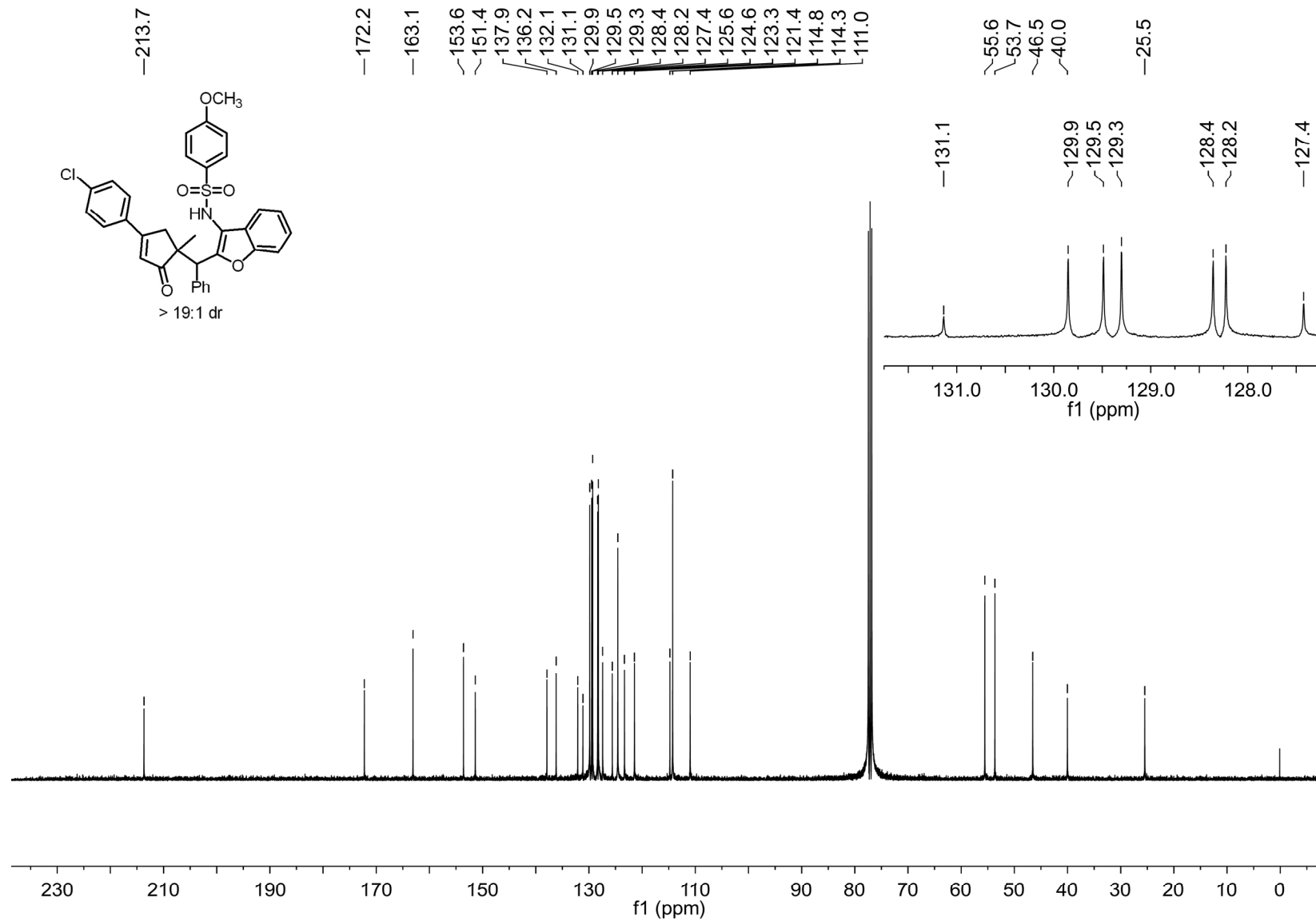
¹H NMR Spectrum of Compound 5n



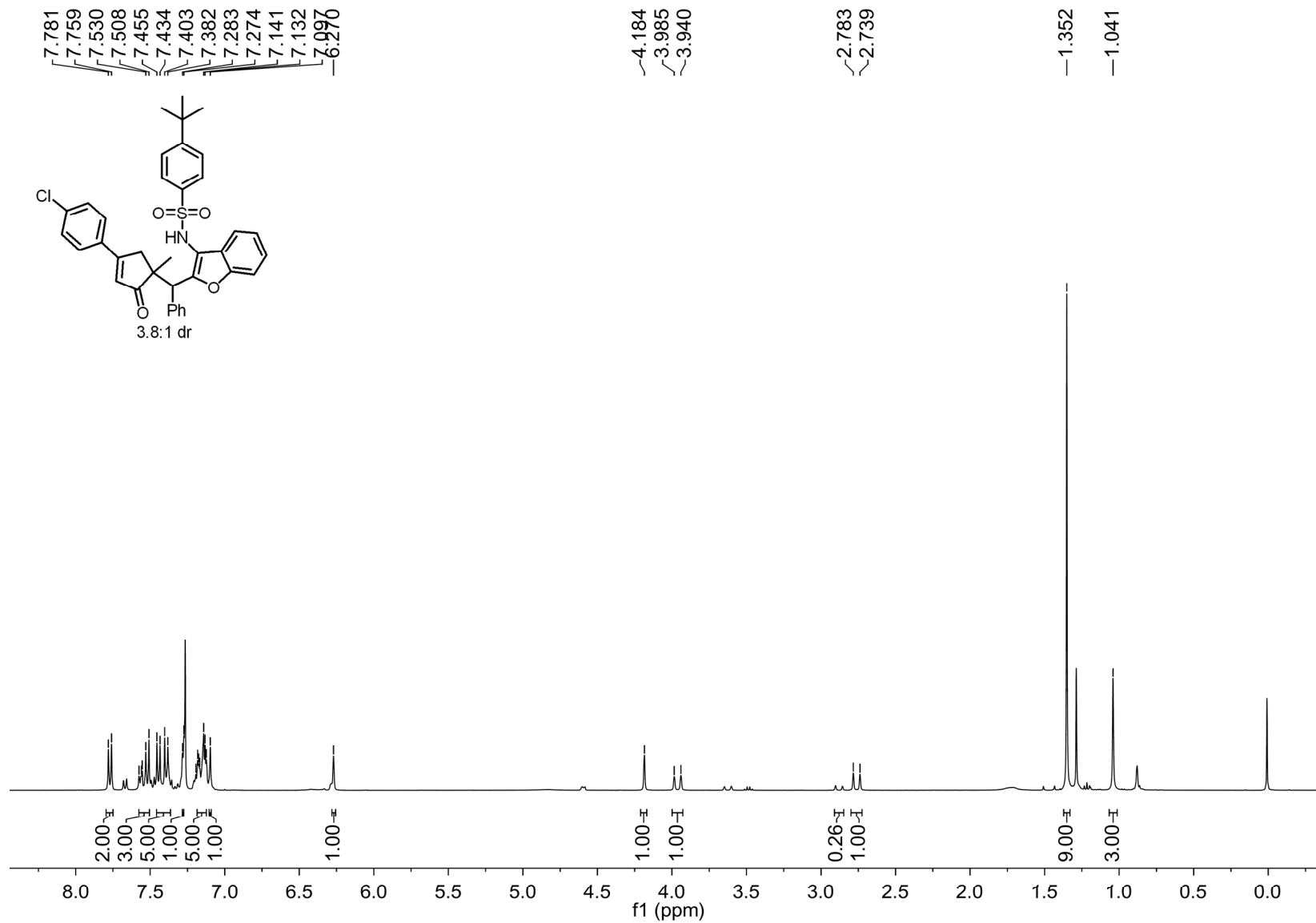
¹³C NMR Spectrum of Compound 5n



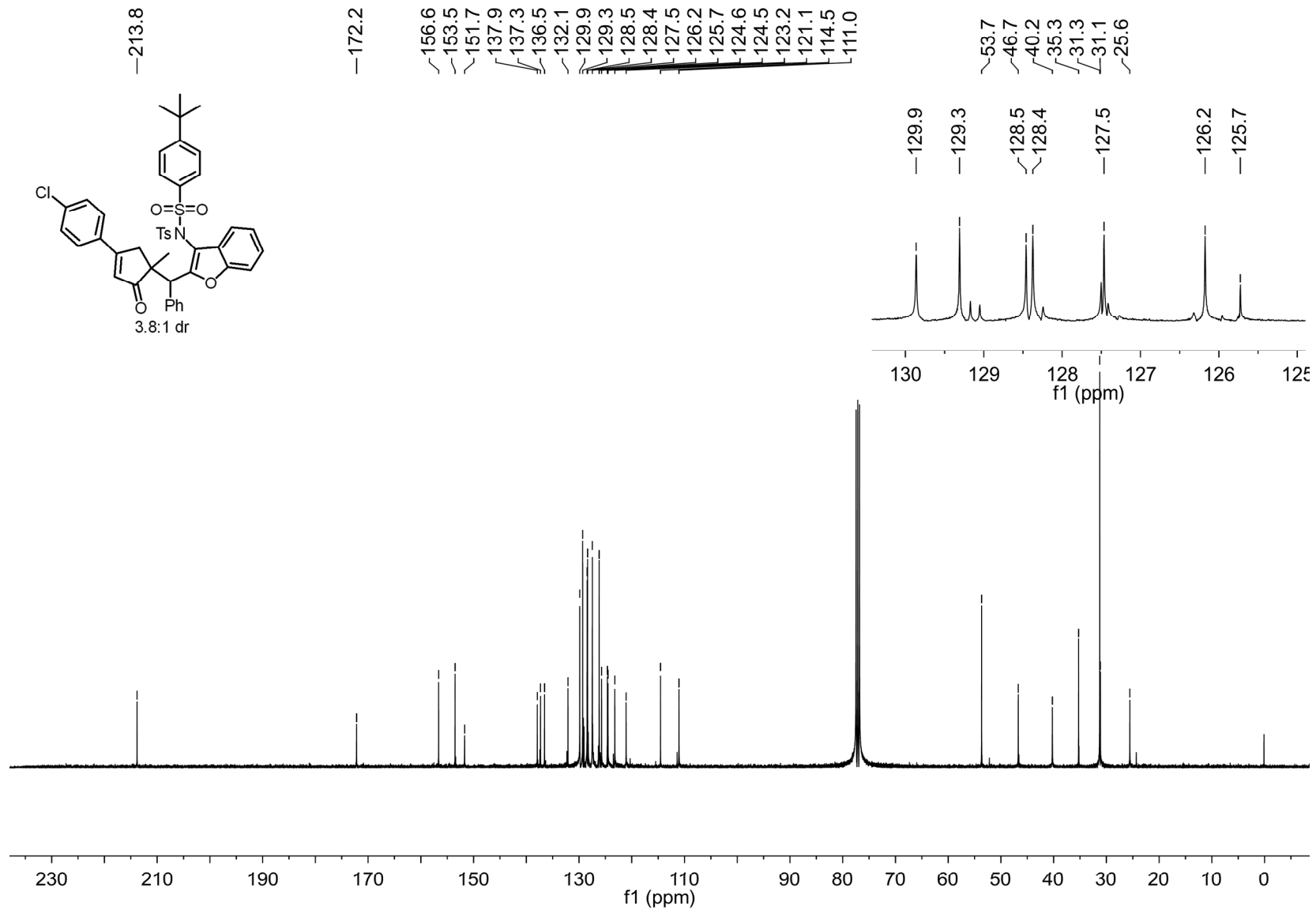
¹H NMR Spectrum of Compound 50



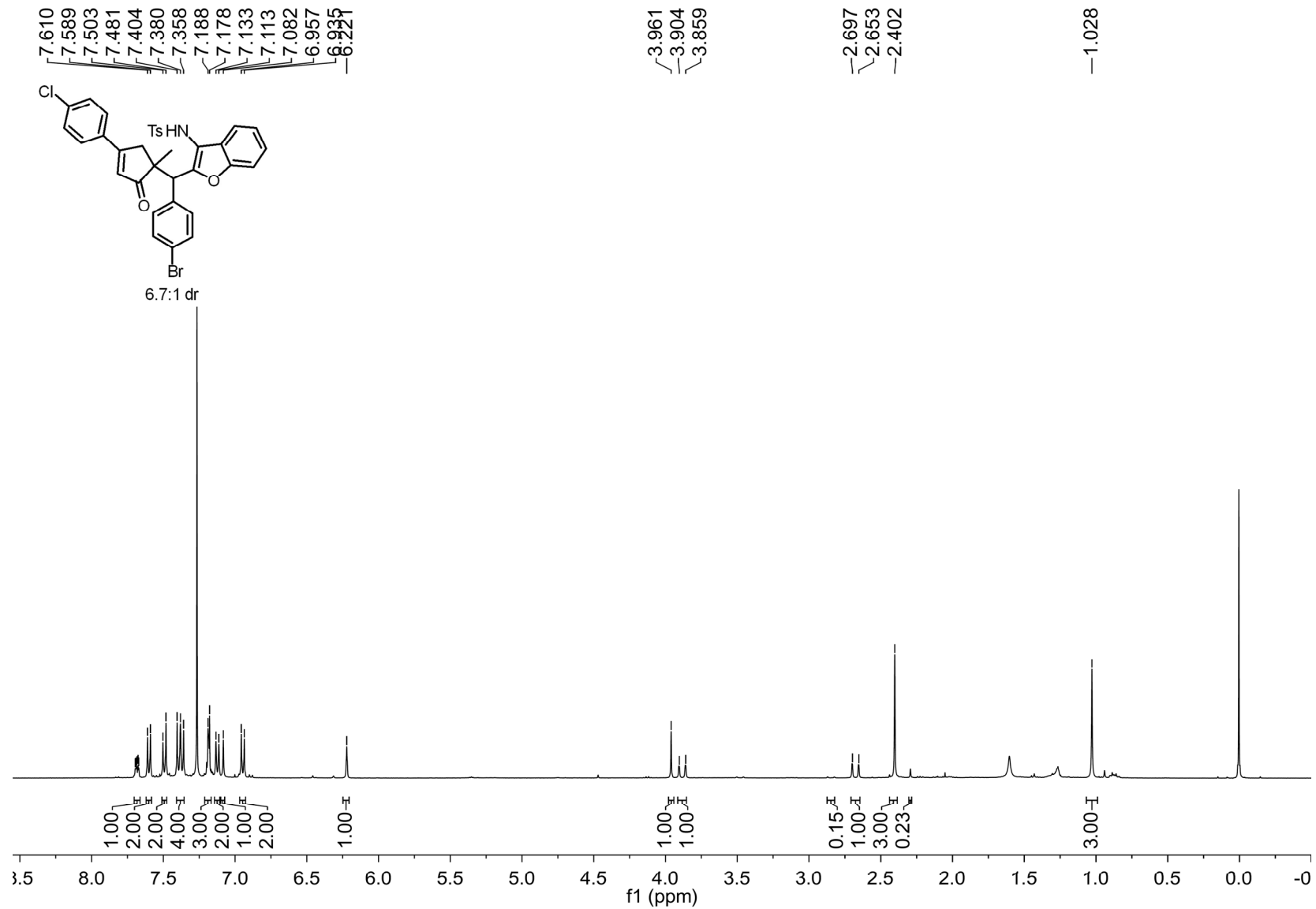
¹³C NMR Spectrum of Compound 50

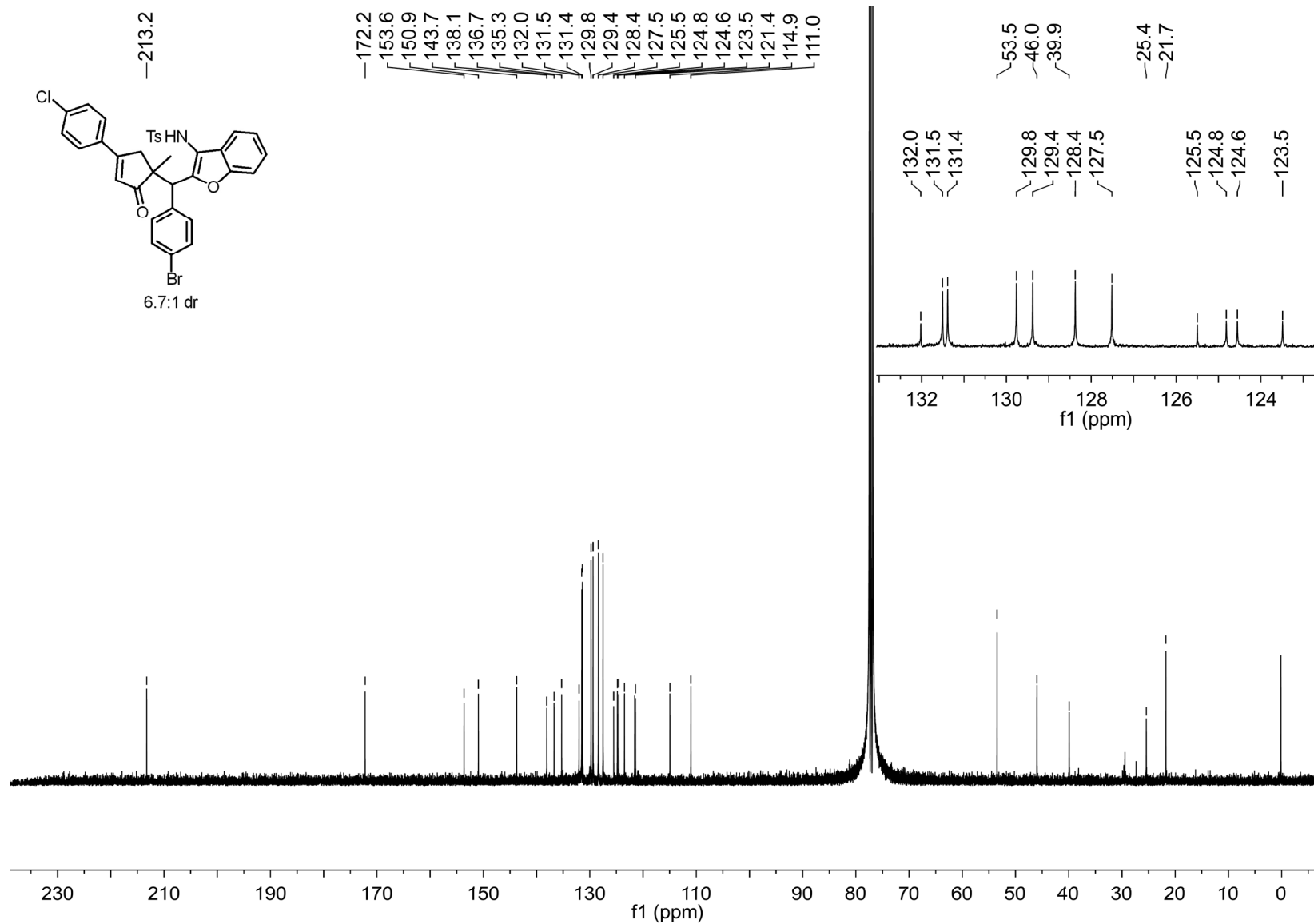


¹H NMR Spectrum of Compound 5p

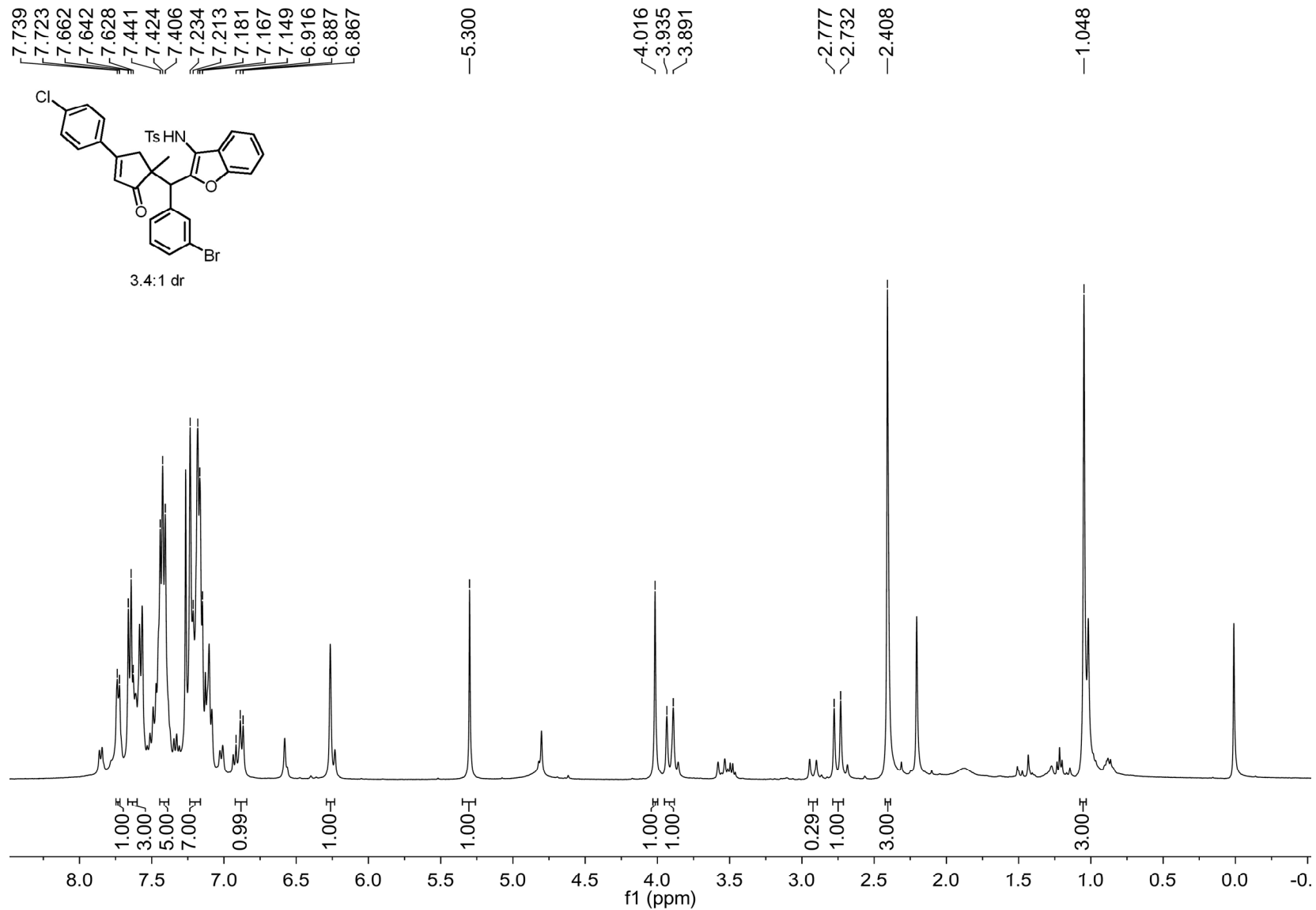


^{13}C NMR Spectrum of Compound 5p

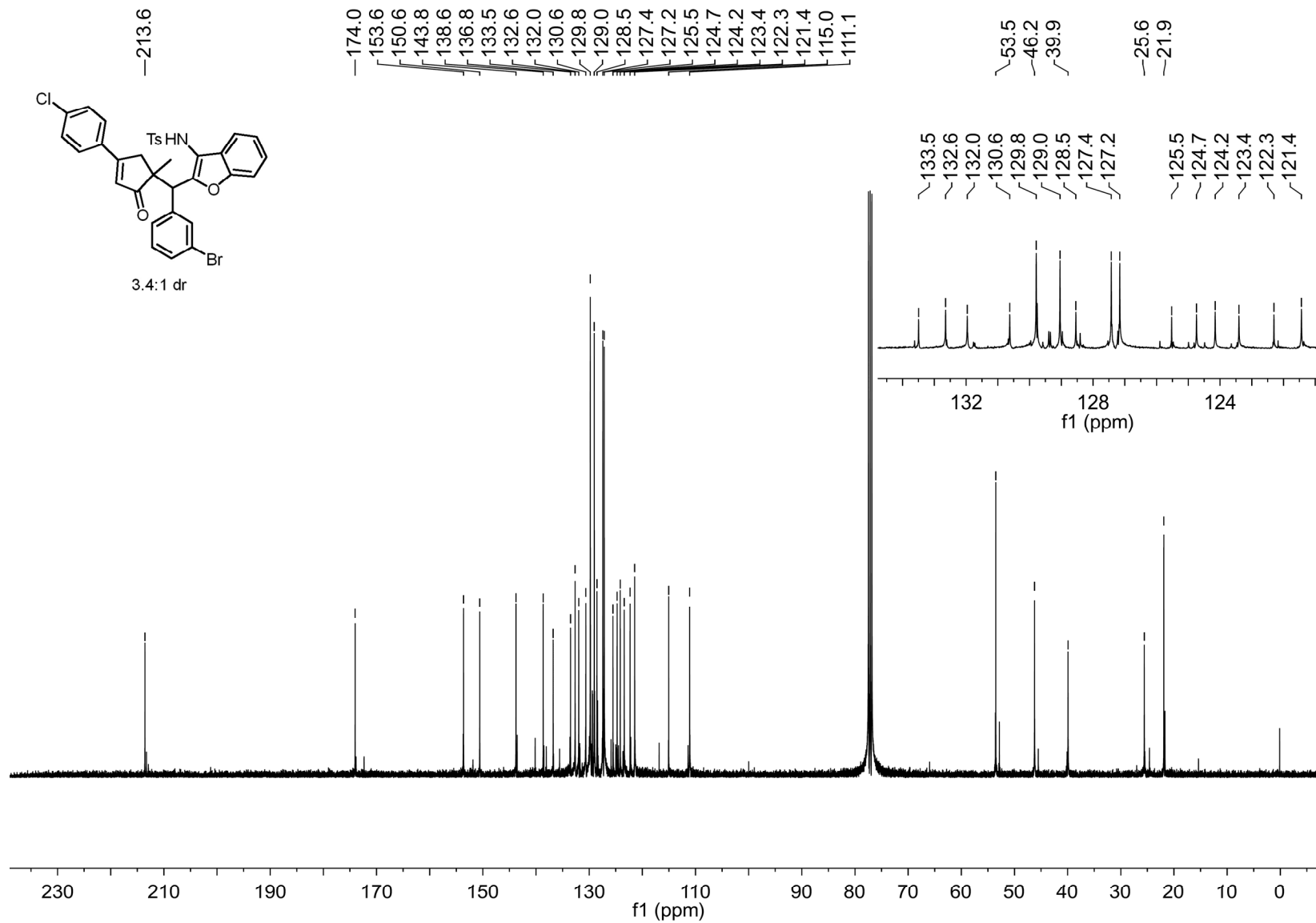




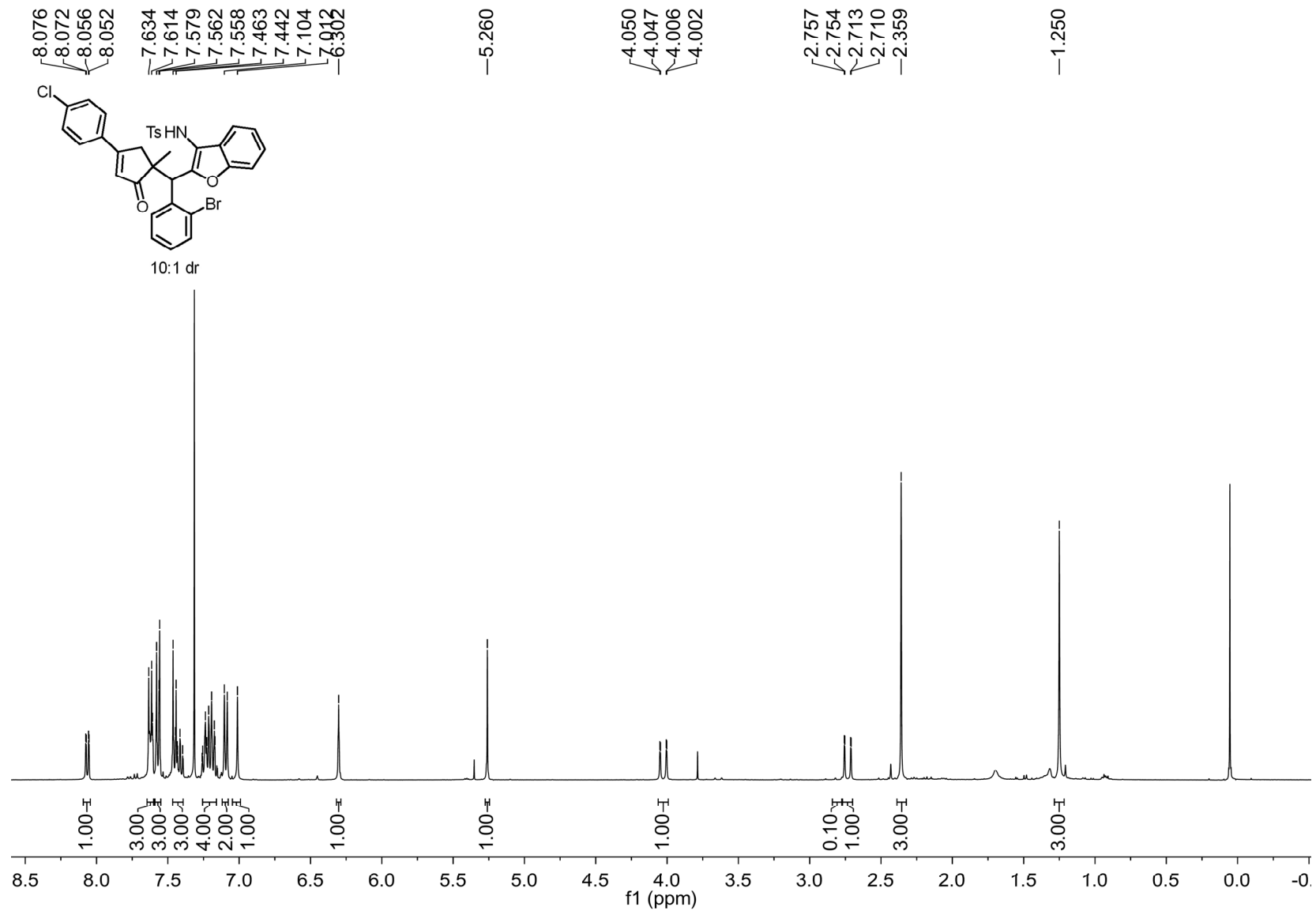
¹³C NMR Spectrum of Compound 5q



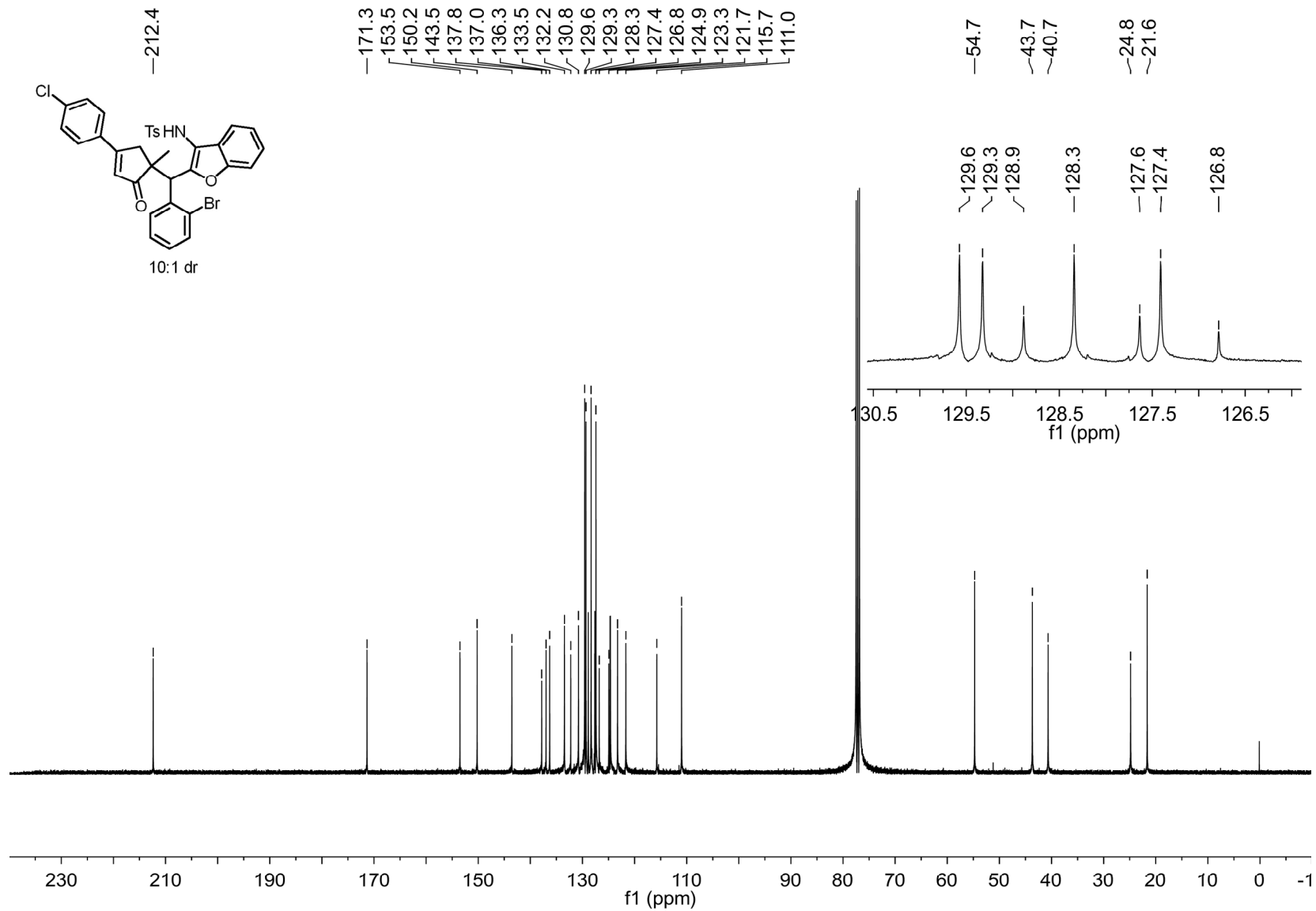
¹H NMR Spectrum of Compound 5r



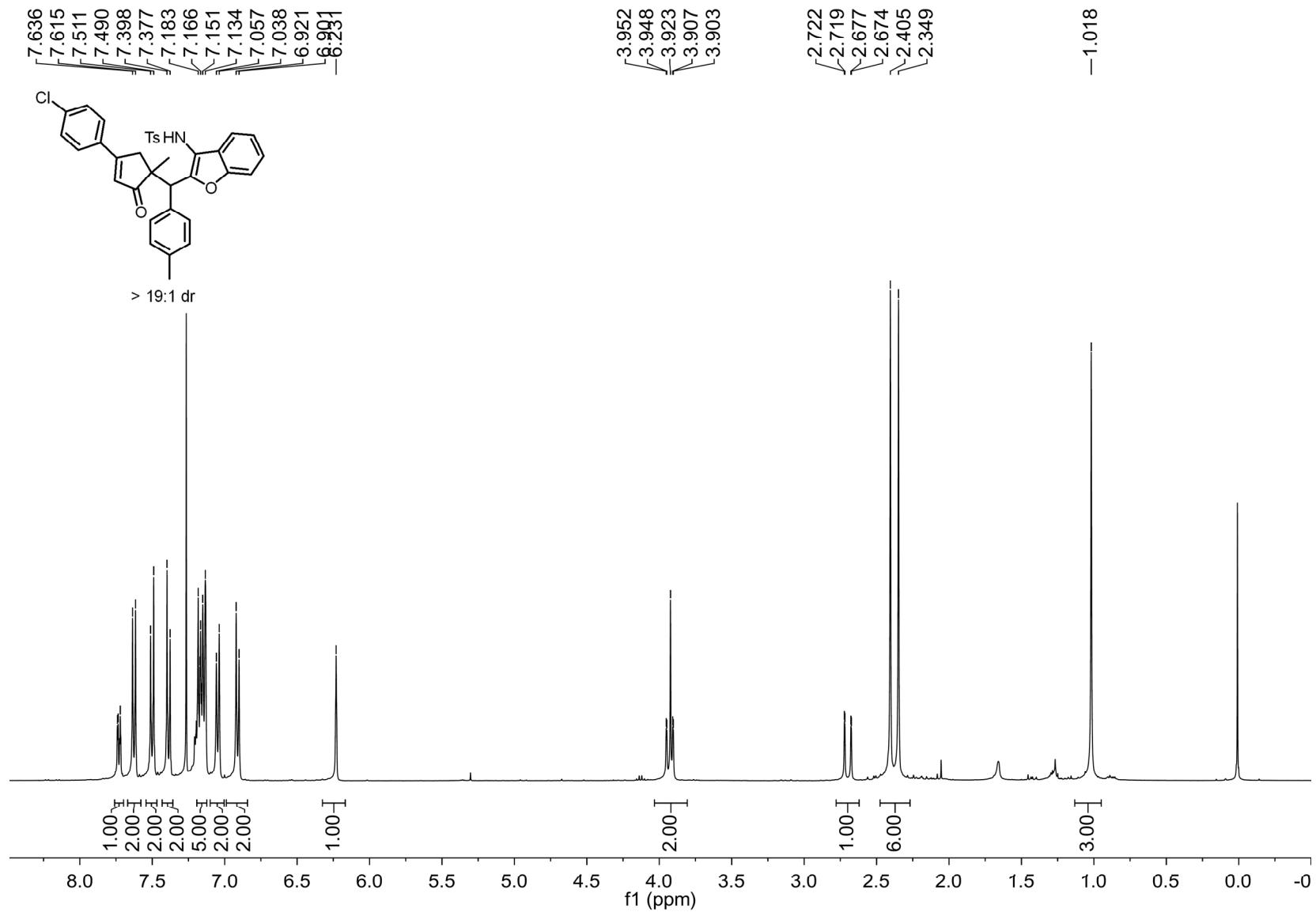
^{13}C NMR Spectrum of Compound 5r



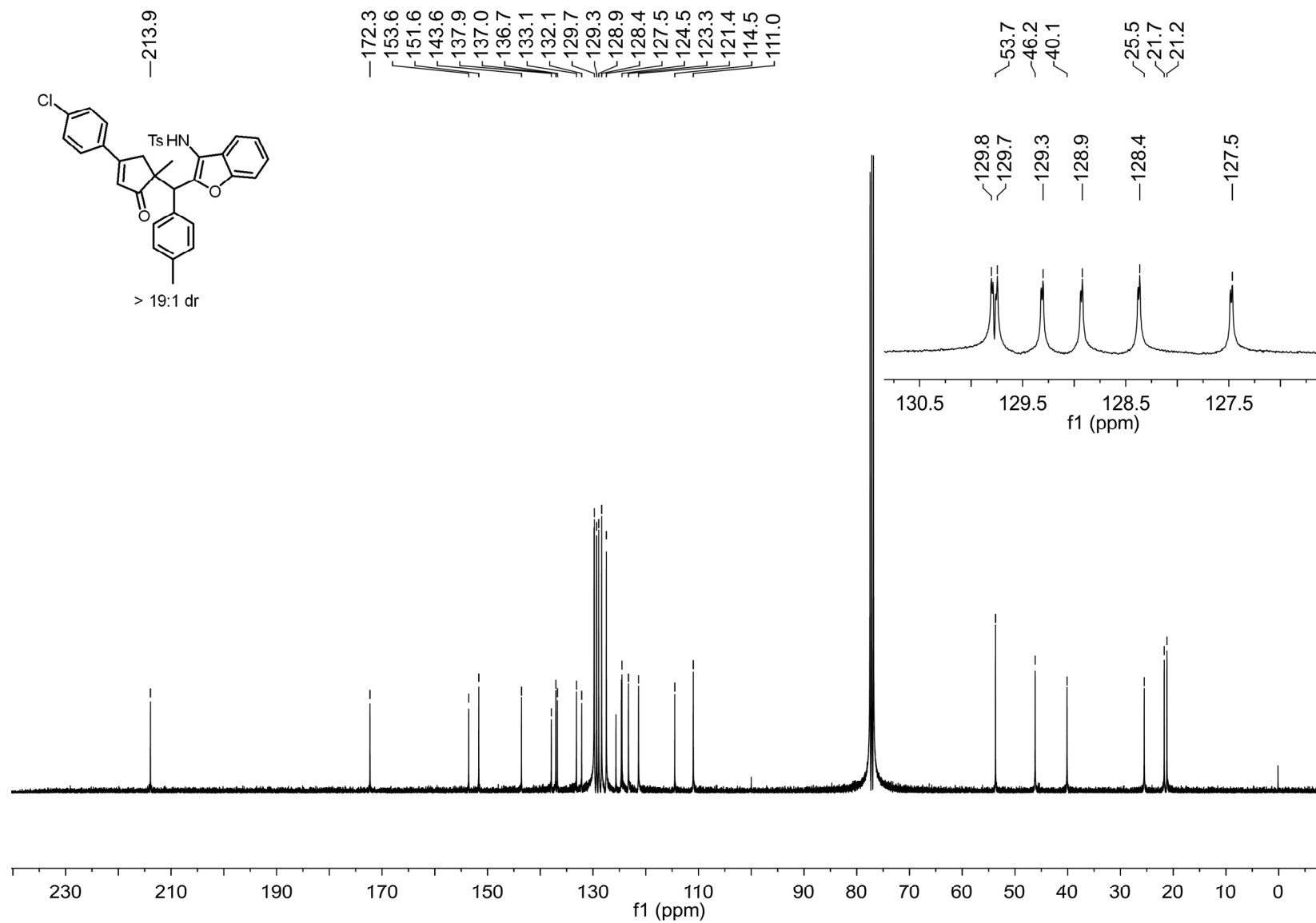
¹H NMR Spectrum of Compound 5s



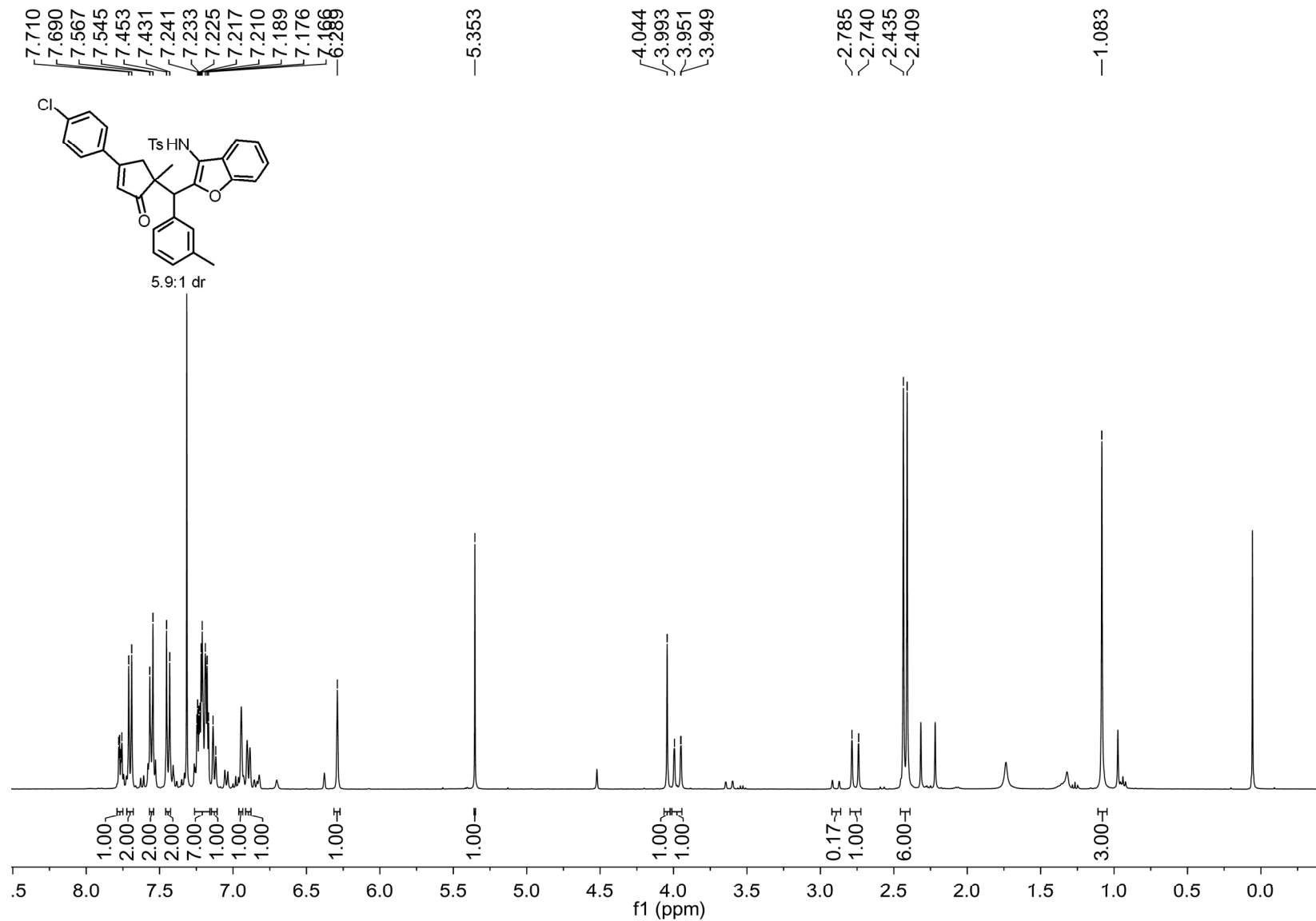
^{13}C NMR Spectrum of Compound 5s



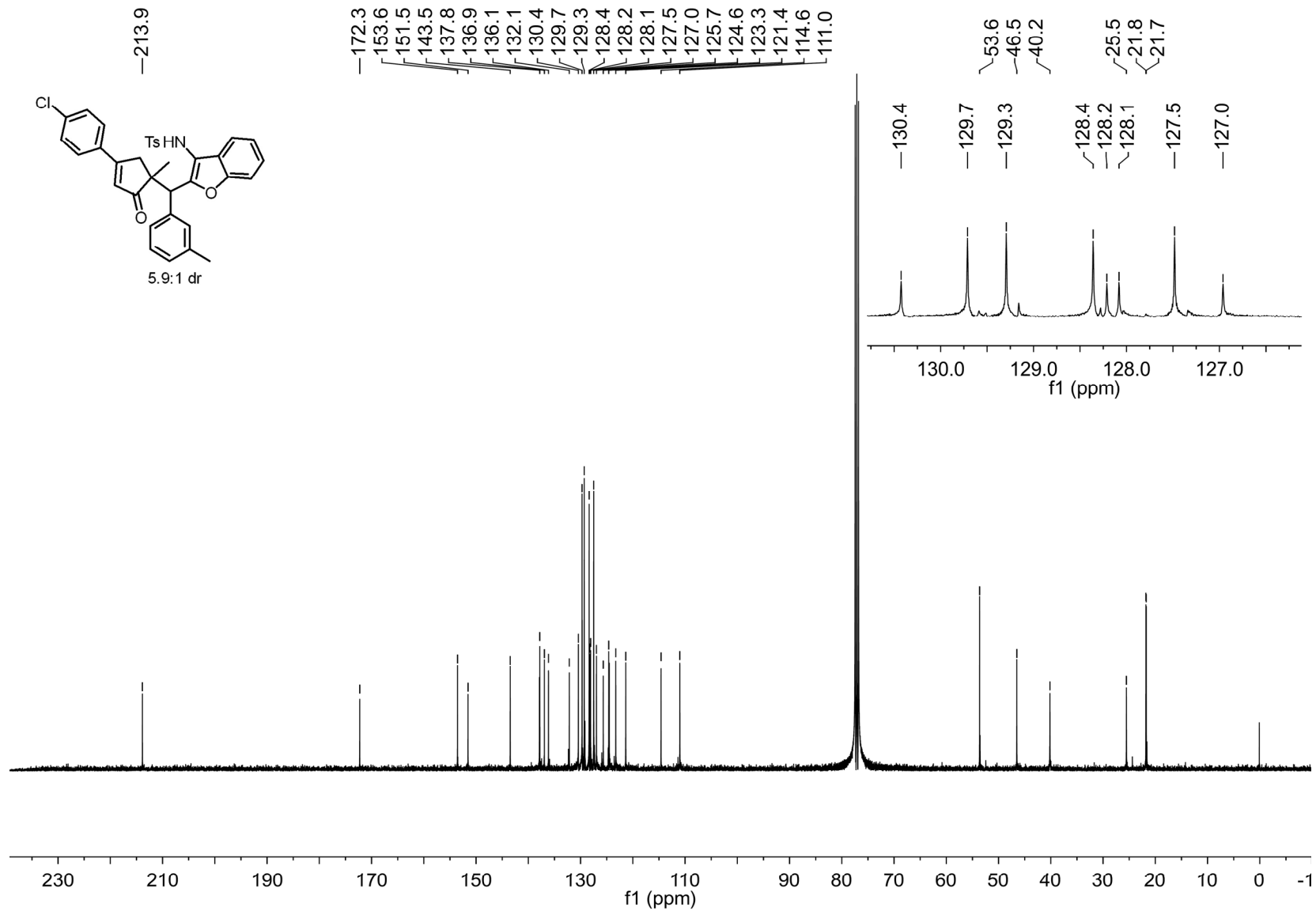
^1H NMR Spectrum of Compound 5t



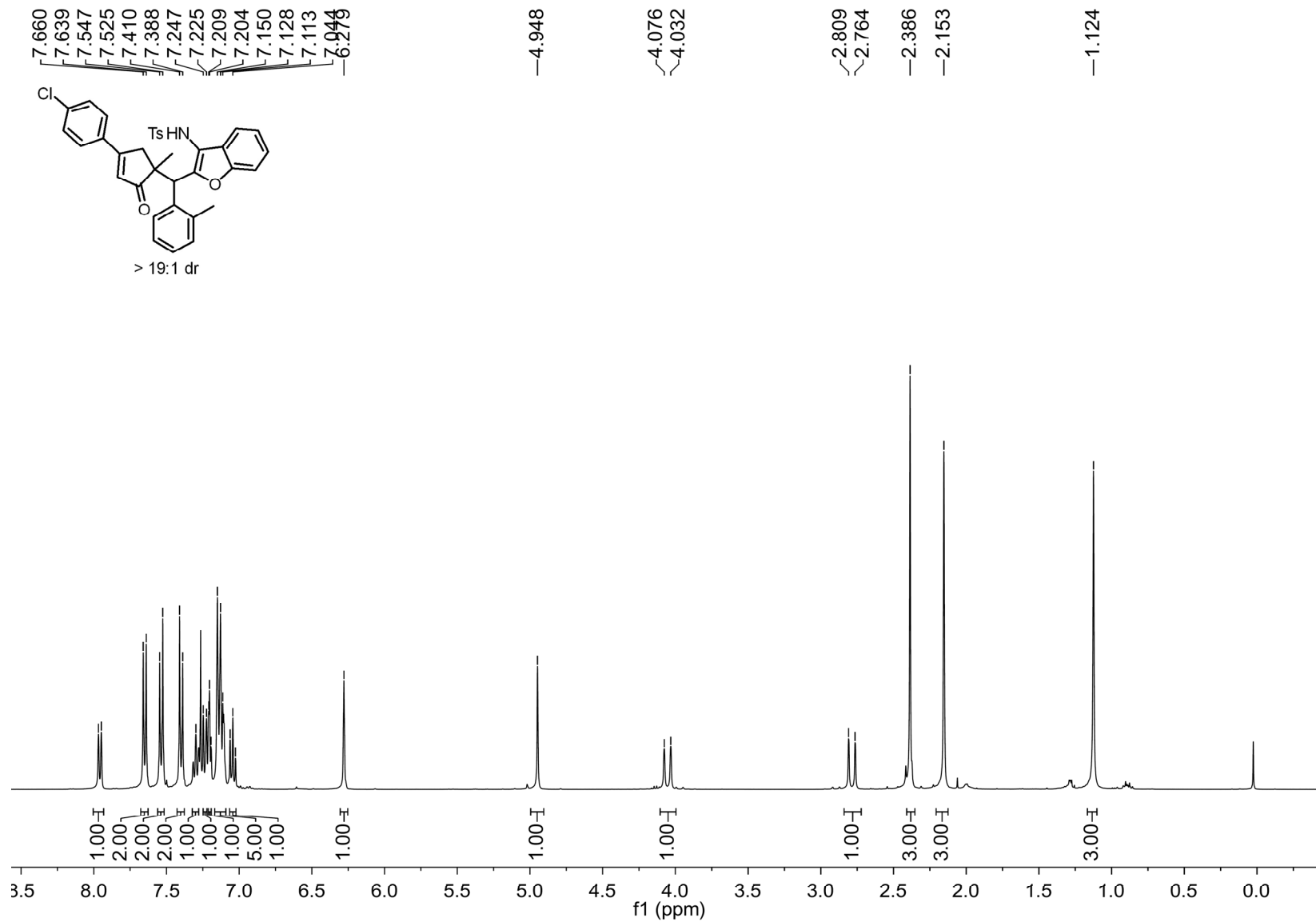
^{13}C NMR Spectrum of Compound 5t



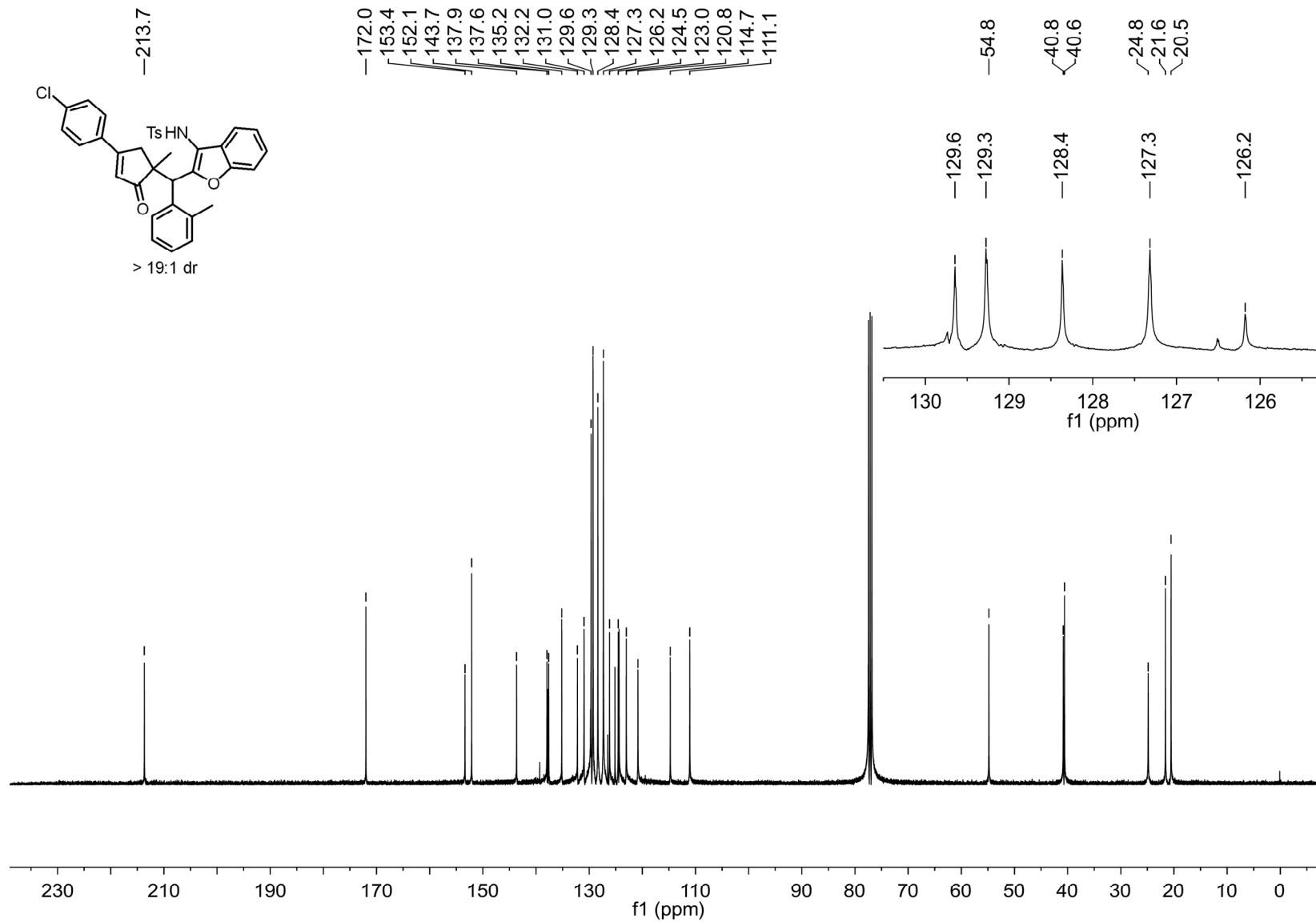
¹H NMR Spectrum of Compound 5u



¹³C NMR Spectrum of Compound 5u



^1H NMR Spectrum of Compound 5v



^{13}C NMR Spectrum of Compound 5v