Supporting Information

A new dehydrogenative [4+1] annulation between *para*-quinone methides (*p*-QMs) and iodonium ylides for the synthesis of 2,3-dihydrobenzofurans

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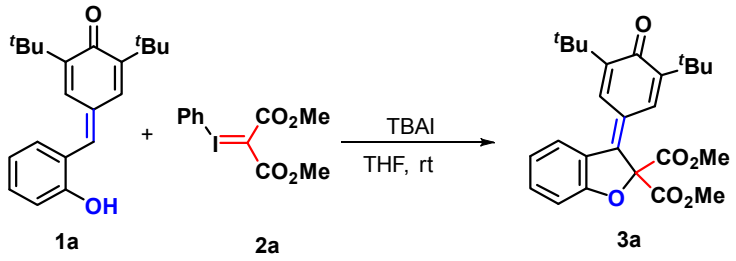
Context

General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (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 (APCI) 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.

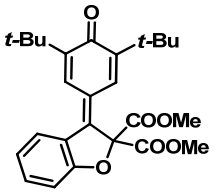
General Procedure for the Synthesis of Products 3

Example for the synthesis of 3a:



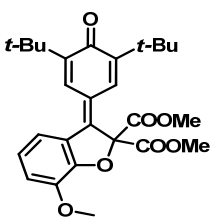
Under the air conditions, TBAI (0.8 mmol, 295 mg), 2,6-di-tert-butyl-4-(2-hydroxybenzylidene)cyclohexa-2,5-dien-1-one (**1a**, 0.4 mmol, 124 mg) and phenyl iodonium ylide **2a** (0.8 mmol, 267 mg) were added into a 10-mL reaction vial. Then, THF (4.0 mL) was added into the reaction system. The mixture was stirred at room temperature for 5 hours. After completion of the reaction (TLC monitored), the reaction system was removed to give the crude product which was purified by flash column chromatography (eluent, petroleum ether/ethyl acetate = 35:1) to afford the desired compound **3a** as pale red solid.

Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-ylidene)benzofuran-2,2(3H)-dicarboxylate (**3a**)



Pale red solid; 96 mg, 55% yield; mp 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.85 (d, J = 2.8 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.42-7.40 (m, 1H), 7.35 (d, J = 2.8 Hz, 1H), 7.15-7.09 (m, 2H), 3.86 (s, 6H), 1.37 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) δ 186.0, 166.1, 163.8, 148.9, 147.9, 142.0, 133.0, 130.7, 128.1, 127.4, 126.4, 124.0, 123.5, 111.7, 91.8, 54.0, 35.8, 35.8, 29.7, 29.7. IR (KBr, v, cm^{-1}) 2953, 1742, 1640, 1606, 1541, 1487, 1367, 878, 792. HRMS (ESI -TOF) m/z calcd for $C_{26}H_{30}O_6Na$ $[M+Na]^+$ 461.1940; found 461.1953.

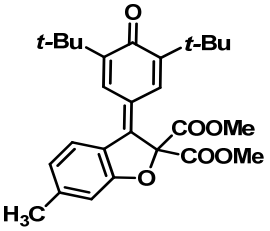
Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-7 methoxybenzofuran-2,2(3H)-dicarboxylate (**3b**)



Pale red solid; 109 mg, 58% yield; mp 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.86 (d, J = 2.8 Hz, 1H), 7.43-7.38 (m, 2H), 7.12-7.08 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 3.98 (s, 3H), 3.87 (s, 6H), 1.39 (s, 9H), 1.32 (s,

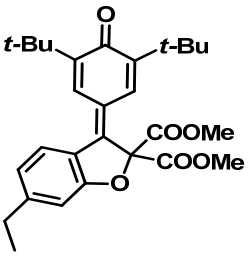
9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 165.9, 153.0, 148.8, 147.9, 145.5, 142.4, 130.7, 128.0, 127.4, 125.1, 124.1, 117.9, 114.7, 92.0, 56.2, 54.0, 35.8, 29.7, 29.6. IR (KBr, ν, cm^{-1}) 2954, 1738, 1700, 1616, 1544, 1445, 1365, 910, 885, 749. HRMS (ESI -TOF) m/z calcd for $C_{27}H_{32}O_7Na$ $[M+Na]^+$ 491.2046; found 491.2014.

Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-methylbenzofuran-2,2(3H)-dicarboxylate (**3c**)



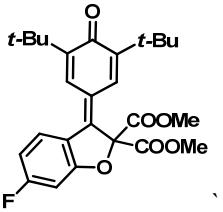
Pale red solid; 105 mg, 58% yield; mp 180-181 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.82 (d, J = 2.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 3.85 (s, 6H), 2.41 (s, 3H), 1.37 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 166.1, 164.2, 148.5, 147.5, 144.8, 142.3, 130.7, 127.5, 127.0, 126.0, 124.9, 121.5, 112.1, 91.8, 53.9, 35.7, 35.7, 29.7, 29.7, 22.0. IR (KBr, ν, cm^{-1}) 2959, 1700, 1616, 1541, 1476, 1377, 884, 809, 739. HRMS (ESI -TOF) m/z calcd for $C_{27}H_{32}O_6Na$ $[M+Na]^+$ 475.2097; found 475.2081.

Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-ethylbenzofuran-2,2(3H) dicarboxylate (**3d**)



Pale red solid; 97 mg, 52% yield; mp 152-153 ºC; ^{1}H NMR(400 MHz, $CDCl_3$; δ, ppm) 7.84 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.34 (s, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.94 (s, 1H), 3.85 (s, 6H), 2.73-2.67 (m, 2H), 1.37 (s, 9H), 1.30 (s, 9H), 1.30-1.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 166.1, 164.3, 151.1, 148.5, 147.5, 142.4, 130.7, 127.5, 127.0, 126.2, 123.8, 121.6, 110.8, 91.8, 53.9, 35.7, 35.7, 29.7, 29.7, 29.2, 14.9. IR (KBr, ν, cm^{-1}) 2958, 1710, 1615, 1540, 1475, 1578, 880, 810, 740. HRMS (ESI -TOF) m/z calcd for $C_{28}H_{34}O_6Na$ $[M+Na]^+$ 489.2253; found 489.2270.

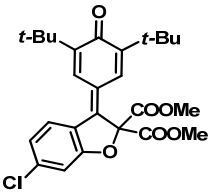
Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-fluorobenzofuran-2,2(3H)-dicarboxylate (**3e**)



Pale red solid; 113 mg, 60% yield; mp 160-161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77-7.73 (m, 2H), 7.32 (d, J = 2.8 Hz, 1H), 6.89-6.84 (m, 1H), 6.82-6.79 (m, 1H), 3.87 (s, 6H), 1.36 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 166.8 (^1J = 254.2 Hz), 165.7, 165.1, 165.0, 164.3, 149.1, 147.9, 140.4, 130.5, 127.5,

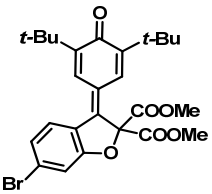
127.5(^4J = 14.2 Hz), 127.4(^5J = 10.7 Hz), 127.3, 127.1, 120.5(^6J = 2.8 Hz), 111.5(^3J = 23.4 Hz), 111.3, 100.0(^2J = 26.5 Hz), 99.8, 92.6, 54.1, 35.8, 35.8, 29.7, 29.6. IR (KBr, ν, cm^{-1}) 2970, 1730, 1695, 1610, 1545, 1440, 1285, 910, 745. HRMS (ESI -TOF) m/z calcd for $C_{26}H_{29}FO_6Na$ $[M+Na]^+$ 479.1846; found 479.1850

Dimethyl 6-chloro-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2,2(3H)-dicarboxylate (**3f**)



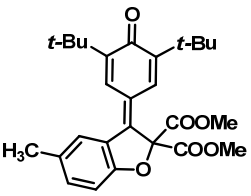
Pale red solid; 113 mg, 60% yield; mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.73 (d, J = 2.8 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 2.8 Hz, 1H), 7.27 (d, J = 1.6 Hz, 1H), 7.26-7.25 (m, 1H), 3.86 (s, 6H), 1.36 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 165.7, 163.9, 149.2, 148.2, 140.3, 130.4, 128.5, 127.0, 126.9, 126.9, 126.8, 123.3, 115.2, 92.1, 54.1, 35.8, 35.8, 29.7, 29.6. IR (KBr, ν, cm^{-1}) 2966, 1734, 1698, 1609, 1541, 1438, 1286, 904, 748. HRMS (ESI -TOF) m/z calcd for $C_{26}H_{29}ClO_6Na$ $[M+Na]^+$ 495.1550; found 495.1564.

Dimethyl 6-bromo-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2,2(3H)-dicarboxylate (**3g**)



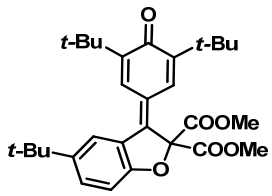
Pale red solid; 128 mg, 62% yield; mp 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) δ 7.74-7.72 (m, 1H), 7.70-7.61 (m, 1H), 7.32-7.31 (m, 1H), 7.28-7.26 (m, 1H), 7.12-7.09 (m, 1H), 3.86 (s, 6H), 1.36 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) δ 185.9, 165.7, 164.0, 163.9, 149.2, 148.2, 148.1, 140.3, 138.7, 130.4, 128.5, 128.3, 127.0, 126.9, 126.9, 126.8, 126.7, 124.0, 123.3, 122.8, 115.2, 112.3, 92.2, 92.1, 54.1, 35.8, 29.7, 29.6. IR (KBr, ν, cm^{-1}) 2956, 1742, 1601, 1536, 1437, 1368, 1257, 905, 810, 741 HRMS (ESI -TOF) m/z calcd for $C_{26}H_{29}BrO_6Na$ $[M+Na]^+$ 539.1045; found 539.1056.

Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-methylbenzofuran-2,2(3H)-dicarboxylate (**3h**)



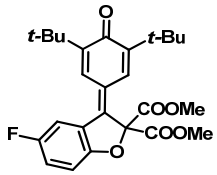
Pale red solid; 72 mg, 40% yield; mp 137-138 °C; ^{1}H NMR(100 MHz, $CDCl_3$; δ, ppm) 7.85 (d, J = 2.8 Hz, 1H), 7.60 (s, 1H), 7.34 (d, J = 2.8 Hz, 1H), 7.23-7.21 (m, 1H), 6.99 (d, J = 8.4 Hz, 1H), 3.85 (s, 6H), 2.39 (s, 3H), 1.38 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 166.1, 162.2, 148.7, 147.7, 142.3, 134.0, 132.9, 130.8, 127.8, 127.5, 126.6, 124.0, 111.3, 91.8, 53.9, 35.8, 35.7, 29.7, 29.6, 21.3. IR (KBr, ν, cm^{-1}) 2954, 1756, 1740, 1604, 1533, 1482, 1366, 885, 812, 744. HRMS (ESI-TOF) m/z calcd for $C_{27}H_{32}O_6Na$ $[M+Na]^+$ 475.2097; found 475.2094.

Dimethyl 5-(tert-butyl)-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2,2(3H)-dicarboxylate (**3i**)



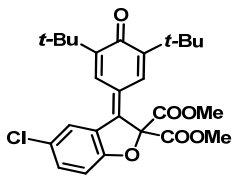
Pale red solid; 105 mg, 53% yield; mp 192-193 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.94 (d, J = 2.8 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.48-7.45 (m, 1H), 7.35 (d, J = 2.8 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 3.85 (s, 6H), 1.39 (s, 9H), 1.35 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.8, 166.2, 162.0, 148.5, 147.7, 146.4, 131.0, 130.7, 127.6, 127.6, 123.5, 123.2, 111.0, 91.9, 53.9, 35.8, 34.8, 31.5, 29.7. IR (KBr, v, cm^{-1}) 2953, 1755, 1738, 1653, 1616, 1482, 1366, 1263, 884, 785 HRMS (ESI -TOF) m/z calcd for $C_{30}H_{38}O_6Na$ $[M+Na]^+$ 517.2566; found 517.2552.

Dimethyl 3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-fluorobenzofuran-2,2(3H)-dicarboxylate (**3j**)



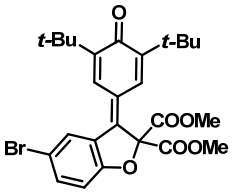
Pale red solid; 104 mg, 57% yield; mp 140-141 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69 (d, J = 2.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.31 (d, J = 2.8 Hz, 1H), 7.14-7.09 (m, 1H), 7.04-7.01 (m, 1H), 3.86 (s, 6H), 1.37 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 165.9, 158.6 (^{1}J = 228.2 Hz), 149.4, 148.3, 140.8 (^{6}J = 3.9 Hz), 140.7, 130.4, 129.0, 128.7, 124.8 (^{3}J = 9.4 Hz), 124.7, 119.8 (^{3}J = 25.2 Hz), 112.6 (^{2}J = 26.7 Hz), 112.2 (^{3}J = 8.8 Hz), 92.3, 54.0, 35.8, 35.8, 29.7, 29.6. IR (KBr, v, cm^{-1}) 2955, 1746, 1610, 1537, 1477, 1367, 1069, 883, 819, 737. HRMS (ESI -TOF) m/z calcd for $C_{26}H_{29}FO_6Na$ $[M+Na]^+$ 479.1846; found 479.1858.

Dimethyl 5-chloro-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2,2(3H)-dicarboxylate (**3k**)



Pale red solid; 110 mg, 58% yield; pale red solid; mp 160-161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.73 (d, J = 2.0 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H), 7.36-7.33 (m, 1H), 7.31 (d, J = 2.8 Hz, 1H), 7.02 (d, J = 8.8 Hz, 1H), 3.86 (s, 6H), 1.37 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 165.7, 162.0, 149.5, 148.4, 140.0, 132.5, 130.3, 129.1, 128.5, 126.8, 126.0, 125.5, 112.5, 92.1, 77.3, 77.2, 77.0, 76.7, 54.1, 35.9, 35.8, 29.6. IR (KBr, v, cm^{-1}) 2955, 1756, 1741, 1635, 1533, 1465, 1366, 882, 792; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{29}ClO_6Na$ $[M+Na]^+$ 495.1550; found 495.1564.

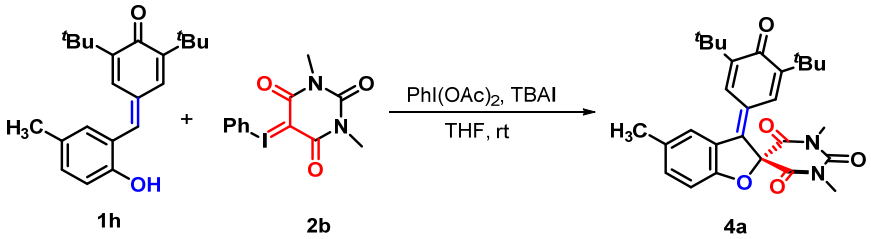
Dimethyl 5-bromo-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2,2(3H)-dicarboxylate (**3l**)



Pale red solid; 124 mg, 60% yield; mp 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (d, J = 2.0 Hz, 1H), 7.70 (d, J = 2.8 Hz, 1H), 7.49-7.47 (m, 1H), 7.31 (d, J = 2.8 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 3.86 (s, 6H), 1.37 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.9, 165.7, 162.5, 149.5, 148.4, 139.9, 135.3, 130.3, 129.1, 129.1, 126.8, 126.1, 115.7, 113.0, 92.0, 54.1, 35.9, 35.8, 29.6, 29.6. IR (KBr, v, cm^{-1}) 2957, 1756, 1736, 1606, 1533, 1462, 1366, 1241, 881, 815 HRMS (ESI -TOF) m/z calcd for $C_{26}H_{29}BrO_6Na$ $[M+Na]^+$ 539.1045; found 539.1027.

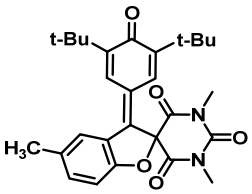
General Procedure for the Synthesis of Products 4

Example for the synthesis of **4a**:



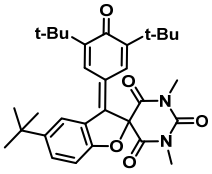
Under the air conditions, TBAI (0.8 mmol, 295 mg), $PhI(OAc)_2$ (0.4 mmol, 129 mg), 2,6-di-*tert*-butyl-4-(2-hydroxy-5-methylbenzylidene)cyclohexa-2,5-dien-1-one (**1h**, 0.4 mmol, 124 mg) and cyclic phenyl iodonium ylide **2b** (0.8 mmol, 267 mg) were added into a 10-mL reaction vial. Then, THF (4.0 mL) was added into the reaction system. The mixture was stirred at room temperature for 5 hour. After completion of the reaction (TLC monitored), the reaction system was removed to give the crude product which was purified by flash column chromatography (eluent, petroleum ether/ethyl acetate = 35:1) to afford the desired compound **4a** as pale red solid.

3-(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1',3',5-trimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4a**)



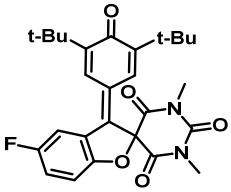
Pale red solid; 101 mg, 53% yield; mp 242-243 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.87 (d, J = 2.8 Hz, 1H), 7.64 (s, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.35 (d, J = 2.8 Hz, 1H), 3.45 (s, 6H), 2.41 (s, 3H), 1.36 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.2, 164.8, 163.3, 149.7, 149.5, 149.1, 145.4, 134.7, 133.5, 127.2, 127.0, 126.5, 125.2, 124.8, 111.3, 35.8, 35.4, 29.5, 29.3, 21.4. IR (KBr, v, cm^{-1}) 2958, 1737, 1691, 1614, 1540, 1480, 1378, 884, 749. HRMS (ESI -TOF) m/z calcd for $C_{28}H_{32}N_2O_5Na$ $[M+Na]^+$ 499.2209; found 499.2157

5-(Tert-butyl)-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4b**)



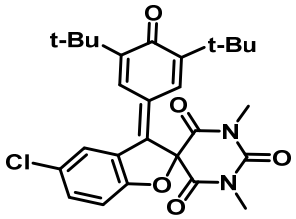
Pale red solid; 124 mg, 60% yield; mp 272-273 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96 (d, J = 2.8 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.49-7.46 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.36 (d, J = 2.8 Hz, 1H), 3.46 (s, 6H), 1.36 (s, 18H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 164.9, 149.8, 149.4, 148.9, 147.0, 145.8, 144.8, 131.8, 127.3, 127.0, 125.0, 123.0, 121.5, 111.1, 100.0, 35.8, 35.4, 34.8, 31.4, 29.5, 29.3.IR (KBr, v, cm^{-1}) 2961, 1734, 1690, 1653, 1615, 1541, 1458, 1363, 881, 749 HRMS (ESI -TOF) m/z calcd for $C_{31}H_{38}N_2O_5Na$ $[M+Na]^+$ 541.2678; found 541.2685.

3-(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-fluoro-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4c**)



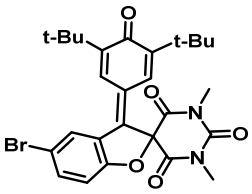
Pale red solid; 96 mg, 50% yield; mp 211-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.71 (d, J = 2.8 Hz, 1H), 7.50-7.47 (m, 1H), 7.13-7.11 (m, 1H), 6.95-6.92 (m, 1H), 6.32 (d, J = 2.4 Hz, 1H), 3.45 (s, 6H), 1.35 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.1, 164.6, 160.8, 160.2(^{1}J = 240.3 Hz), 157.8, 150.2, 149.8, 149.6, 143.8(^{4}J = 3.8 Hz), 143.8(^{1}J = 3.8 Hz), 143.7, 126.7(^{3}J = 23.2 Hz), 126.5, 126.4, 125.6(^{4}J = 9.6 Hz), 125.5, 120.5(^{2}J = 25.4 Hz), 120.3, 112.5, 112.2(^{5}J = 8.6 Hz), 112.1, 84.9, 77.3, 77.2, 77.0, 76.7, 35.8, 35.5, 29.5, 29.4, 29.3. IR (KBr, v, cm^{-1}) 2954, 1748, 1615, 1540, 1478, 1368, 1068, 885, 820, 735 HRMS (ESI -TOF) m/z calcd for $C_{27}H_{29}FN_2O_5Na$ $[M+Na]^+$ 503.1958; found 503.1936.

5-Chloro-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4d**)



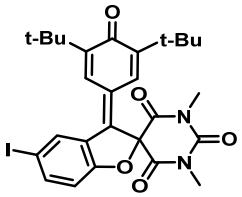
Pale red solid; 101 mg, 51% yield; mp 231-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.78 (d, J = 2.0 Hz, 1H), 7.73 (d, J = 2.8 Hz, 1H), 7.38-7.35 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 2.8 Hz, 1H), 3.45 (s, 6H), 1.36 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.1, 164.5, 163.1, 150.2, 149.6, 143.1, 133.1, 129.2, 126.6, 126.5, 126.2, 125.9, 112.5, 100.0, 35.9, 35.5, 29.5, 29.4, 29.3. IR (KBr, v, cm^{-1}) 2957, 1741, 1701, 1615, 1541, 1440, 1376, 888, 751. HRMS (ESI -TOF) m/z calcd for $C_{27}H_{29}ClN_2O_5Na$ $[M+Na]^+$ 519.1663; found 519.1644.

5-Bromo-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4e**)



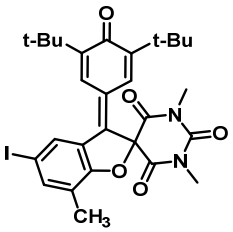
Pale red solid; 97 mg, 45% yield; mp 239-240 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; *δ,* ppm) 7.94 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.51-7.48 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 3.45 (s, 6H), 1.36 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ,* ppm) 185.1, 164.5, 163.6, 150.2, 149.9, 149.6, 143.0, 135.9, 128.9, 126.8, 126.6, 126.5, 116.3, 113.0, 35.9, 35.5, 29.5, 29.4, 29.3. IR (KBr, *v*, cm^{-1}); HRMS (ESI -TOF) m/z calcd for $C_{27}H_{29}BrN_2O_5Na$ $[M+Na]^+$ 563.1158; found 563.1119

3-(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4f**)



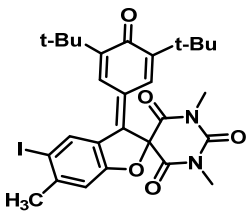
Pale red solid; 129 mg, 55% yield; mp 239-240 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; *δ,* ppm) 7.87-7.85 (m, 2H), 7.44-7.40 (m, 1H), 7.20-7.16 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 2.8 Hz, 1H), 3.46 (s, 6H), 1.35 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ,* ppm) 185.5, 164.1, 149.7, 149.6, 149.3, 145.1, 133.6, 127.1, 127.0, 126.3, 125.6, 124.8, 124.1, 111.8, 84.2, 35.8, 35.4, 29.5, 29.3. IR (KBr, *v*, cm^{-1}) 2957, 1734, 1690, 1614, 1543, 1441, 1271, 885, 749 HRMS (ESI -TOF) m/z calcd for $C_{28}H_{29}IN_2O_5Na$ $[M+Na]^+$ 611.1019; found 611.1009.

3-(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1',3',7-trimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4g**)



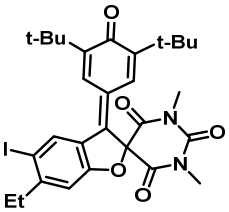
Pale red solid; 80 mg, 42% yield; mp 175-176 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; *δ,* ppm) 7.99 (s, 1H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.51 (s, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 3.46 (s, 6H), 2.20 (s, 3H), 1.35 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ,* ppm) 185.1, 164.6, 163.2, 150.0, 149.7, 149.6, 143.7, 142.6, 132.5, 126.7, 126.6, 126.6, 126.2, 124.3, 86.3, 84.2, 35.9, 35.5, 29.4, 29.4, 29.3, 14.6. IR (KBr, *v*, cm^{-1}) 2960, 1710, 1615, 1540, 1475, 1375, 880, 810, 740. HRMS (ESI -TOF) m/z calcd for $C_{28}H_{31}IN_2O_5Na$ $[M+Na]^+$ 625.1175; found 625.1164.

3-(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-iodo-1',3',6-trimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4h**)



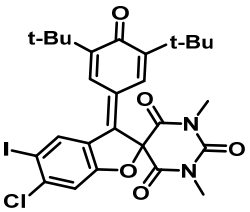
Pale red solid; 57 mg, 30% yield; mp 237-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.29 (s, 1H), 7.72 (d, J = 2.8 Hz, 1H), 6.92 (s, 1H), 6.33 (d, J = 2.8 Hz, 1H), 3.45 (s, 6H), 2.48 (s, 3H), 1.36 (s, 9H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.1, 165.1, 164.5, 149.8, 149.6, 147.6, 143.1, 136.1, 126.8, 126.5, 125.5, 124.9, 112.4, 93.6, 84.6, 35.8, 35.5, 29.4, 29.4, 29.3, 29.2. IR (KBr, ν, cm^{-1}) 2958, 1701, 1618, 1541, 1478, 1376, 884, 810, 740. HRMS (ESI -TOF) m/z calcd for $C_{28}H_{31}IN_2O_5Na$ $[M+Na]^+$ 625.1175; found 625.1186.

3-(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-ethyl-5-iodo-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4i**)



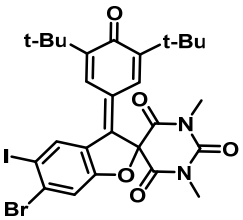
Pale red solid; 78 mg, 40% yield; mp 263-264 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.32 (s, 1H), 7.75 (d, J = 2.4 Hz, 1H), 6.92 (s, 1H), 6.36 (d, J = 2.4 Hz, 1H), 3.47 (s, 6H), 2.81-2.75 (m, 2H), 1.38 (s, 9H), 1.27-1.24 (m, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.1, 165.4, 164.6, 152.6, 149.8, 149.6, 149.6, 143.1, 136.5, 126.8, 126.5, 125.6, 124.9, 111.1, 100.0, 93.0, 84.6, 35.8, 35.5, 35.0, 29.4, 29.4, 29.3, 13.9. IR (KBr, ν, cm^{-1}) 2960, 1760, 1740, 1615, 1540, 1420, 1370, 810, 745. HRMS (ESI -TOF) m/z calcd for $C_{29}H_{33}IN_2O_5Na$ $[M+Na]^+$ 639.1332; found 639.1343.

6-Chloro-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-iodo-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4j**)



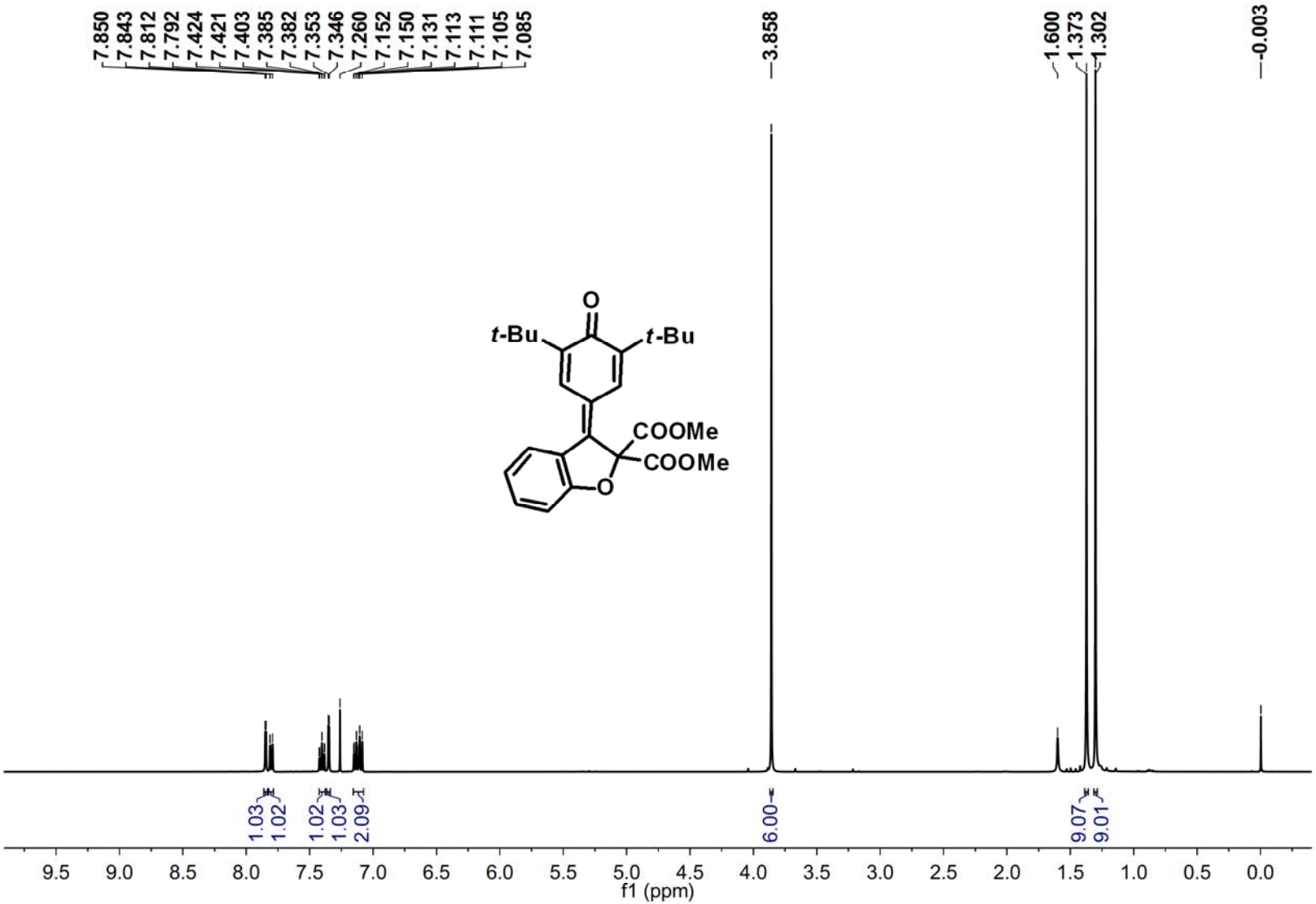
Pale red solid; 79 mg, 40% yield; mp 278-279 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.31 (s, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.31 (s, 1H), 6.31 (d, J = 2.8 Hz, 1H), 3.45 (s, 6H), 1.35 (s, 9H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.1, 164.4, 164.2, 150.4, 150.1, 149.5, 141.4, 136.5, 134.2, 126.9, 126.4, 115.7, 94.0, 84.8, 35.9, 35.6, 31.6, 29.4, 29.3, 22.7, 14.1. IR (KBr, ν, cm^{-1}) 2958, 1751, 1737, 1608, 1540, 1421, 1370, 807, 742. HRMS (ESI -TOF) m/z calcd for $C_{27}H_{28}ClIN_2O_5Na$ $[M+Na]^+$ 645.0629; found 645.0638.

6-Bromo-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-iodo-1',3'-dimethyl-1'H,3H-spiro[benzofuran-2,5'-pyrimidine]-2',4',6'(3'H)-trione (**4k**)

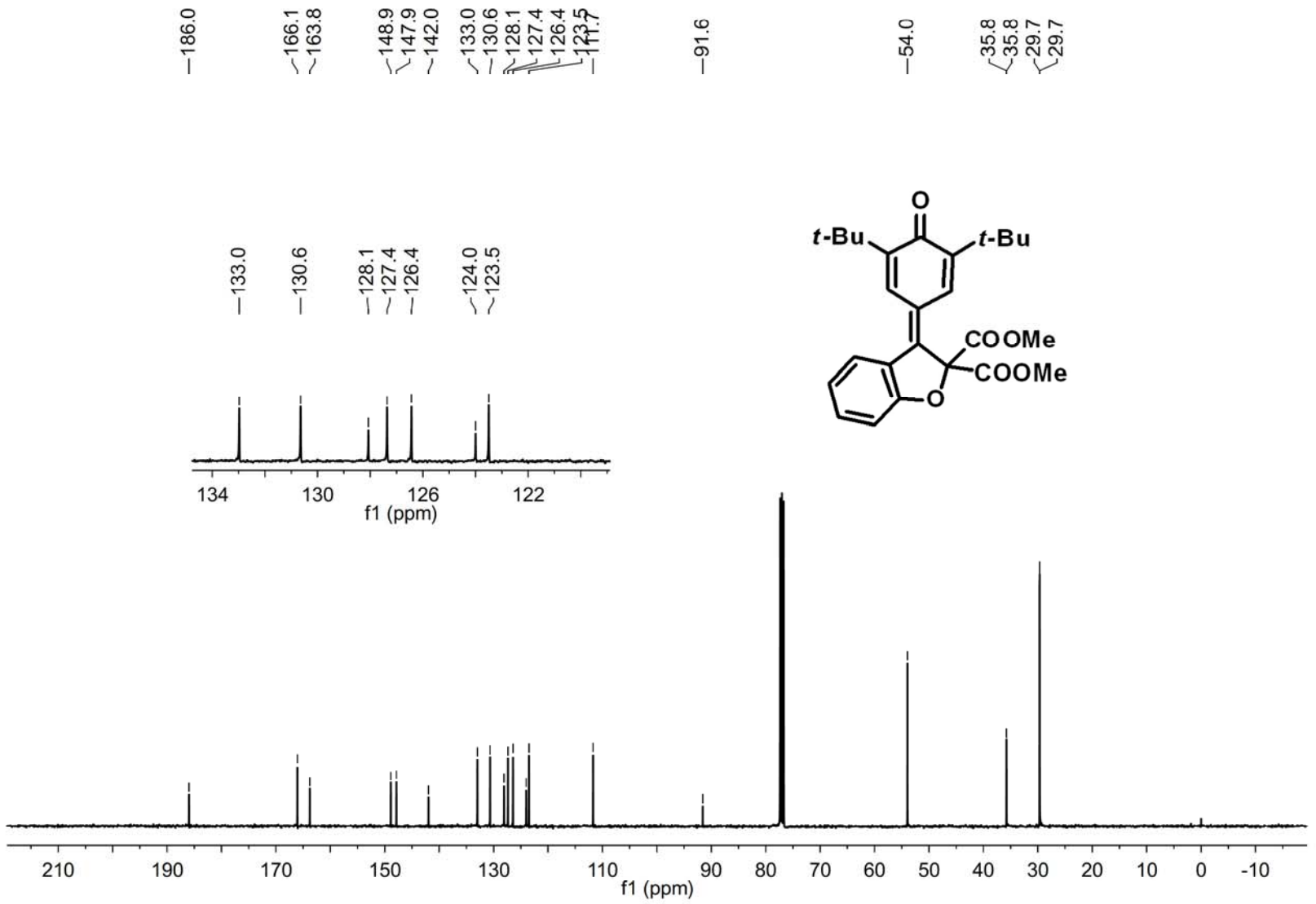


Pale red solid; 97 mg, 45% yield; mp 259-260 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.31 (s, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.13 (s, 1H), 6.31 (d, J = 2.4 Hz, 1H), 3.45 (s, 6H), 1.35 (s, 9H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.1, 164.7, 164.2, 150.4, 150.2, 149.5, 142.9, 141.3, 136.6, 126.7, 126.3, 125.9, 112.4, 91.0,

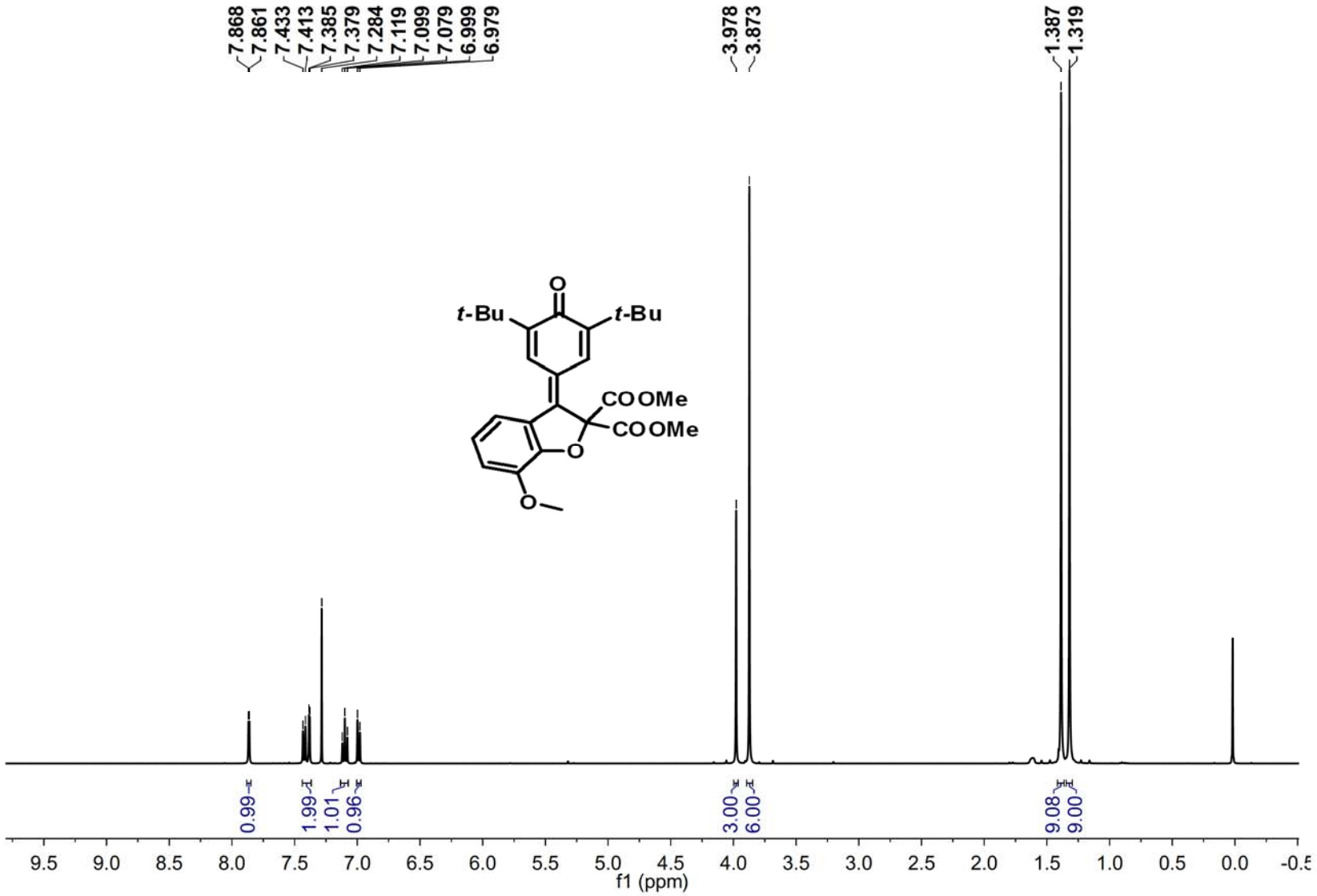
85.0, 35.9, 35.5, 29.4, 29.4, 29.3. IR (KBr, *v*, cm^{-1}) 2959, 1700, 1616, 1541, 1476, 1377, 884, 809, 739. HRMS (ESI -TOF) m/z calcd for $C_{27}H_{28}BrIN_2O_5Na$ $[M+Na]^+$ 689.0124; found 689.0130.



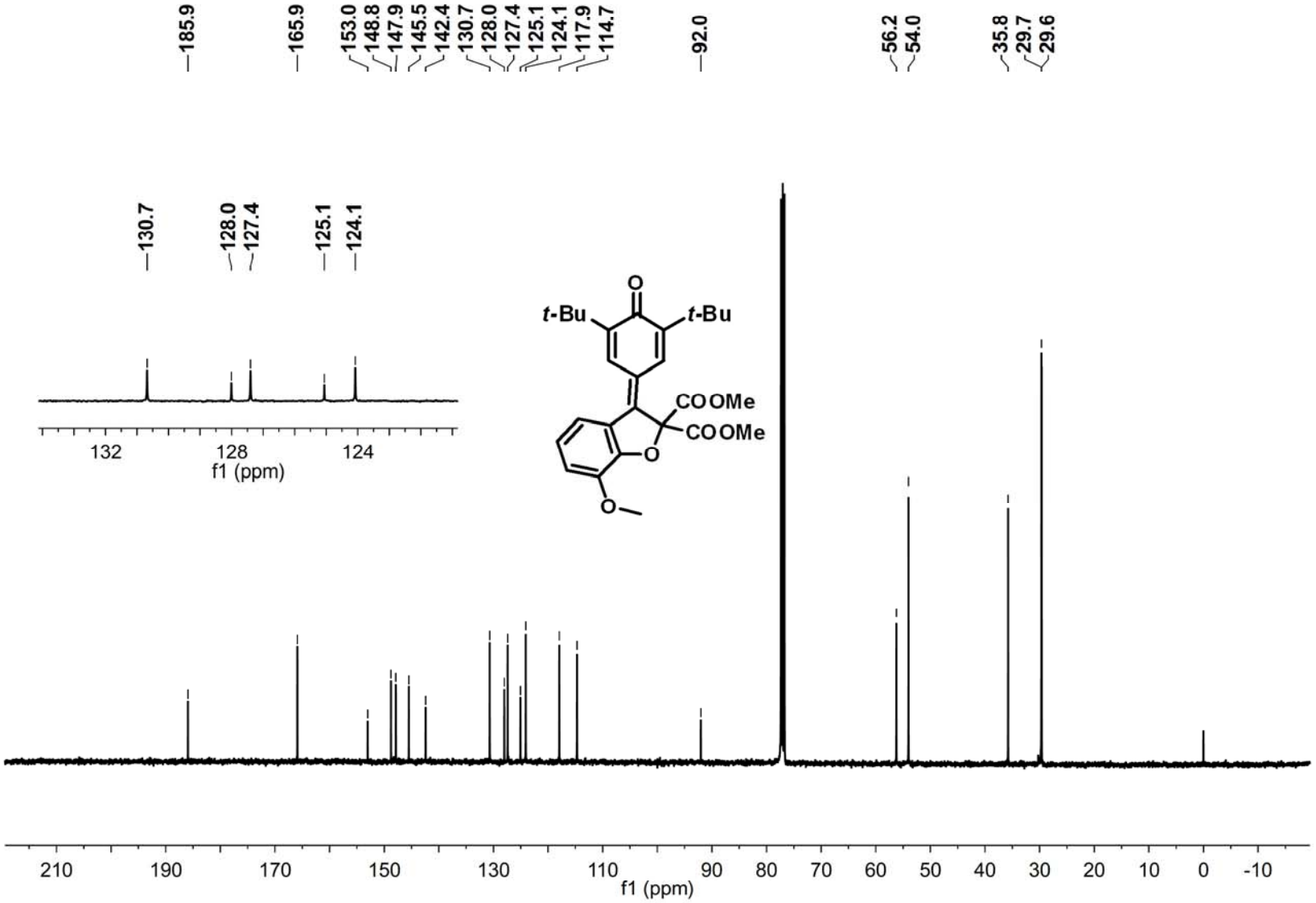
^{1}H NMR Spectrum of Compound 3a



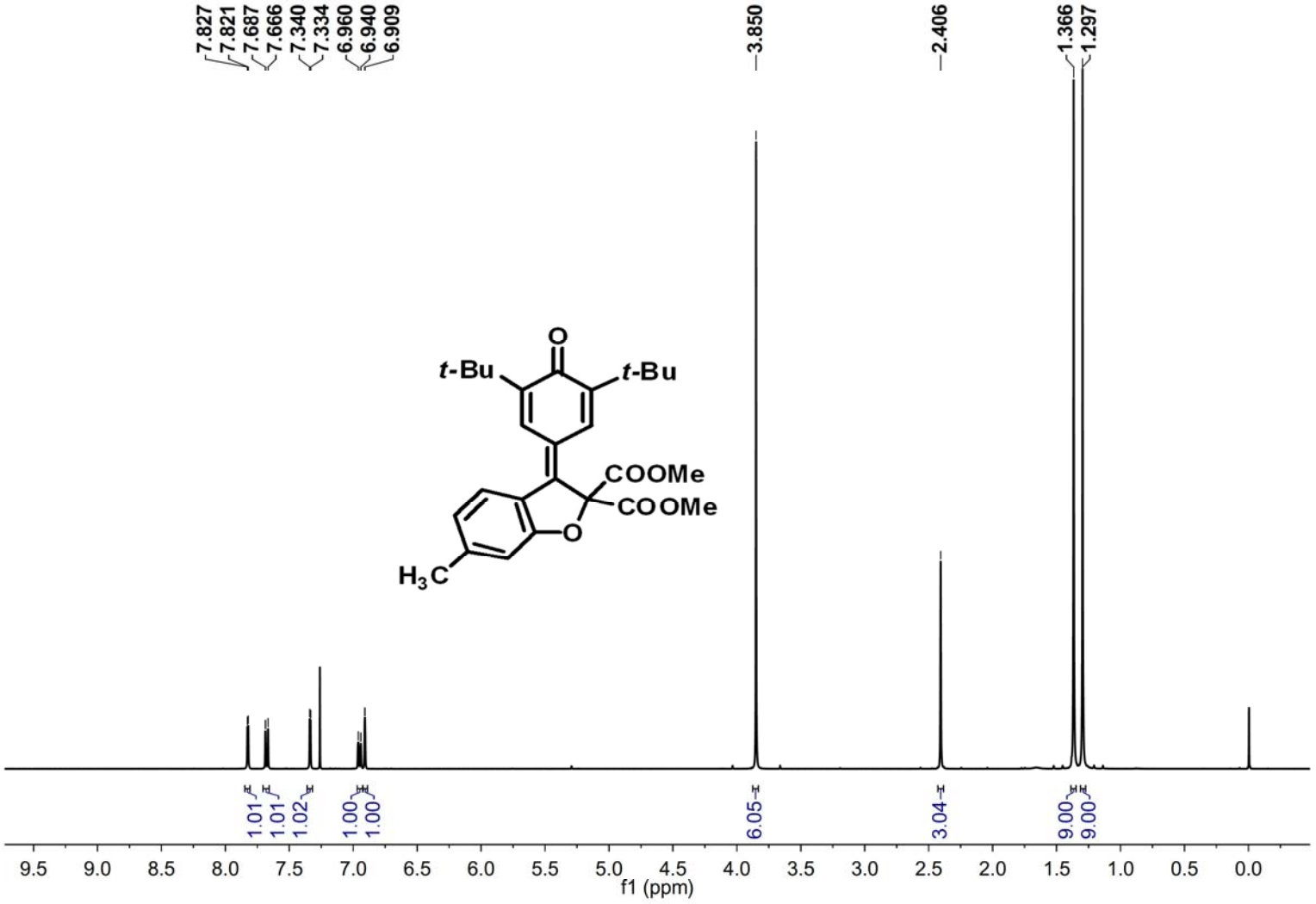
^{13}C NMR Spectrum of Compound 3a



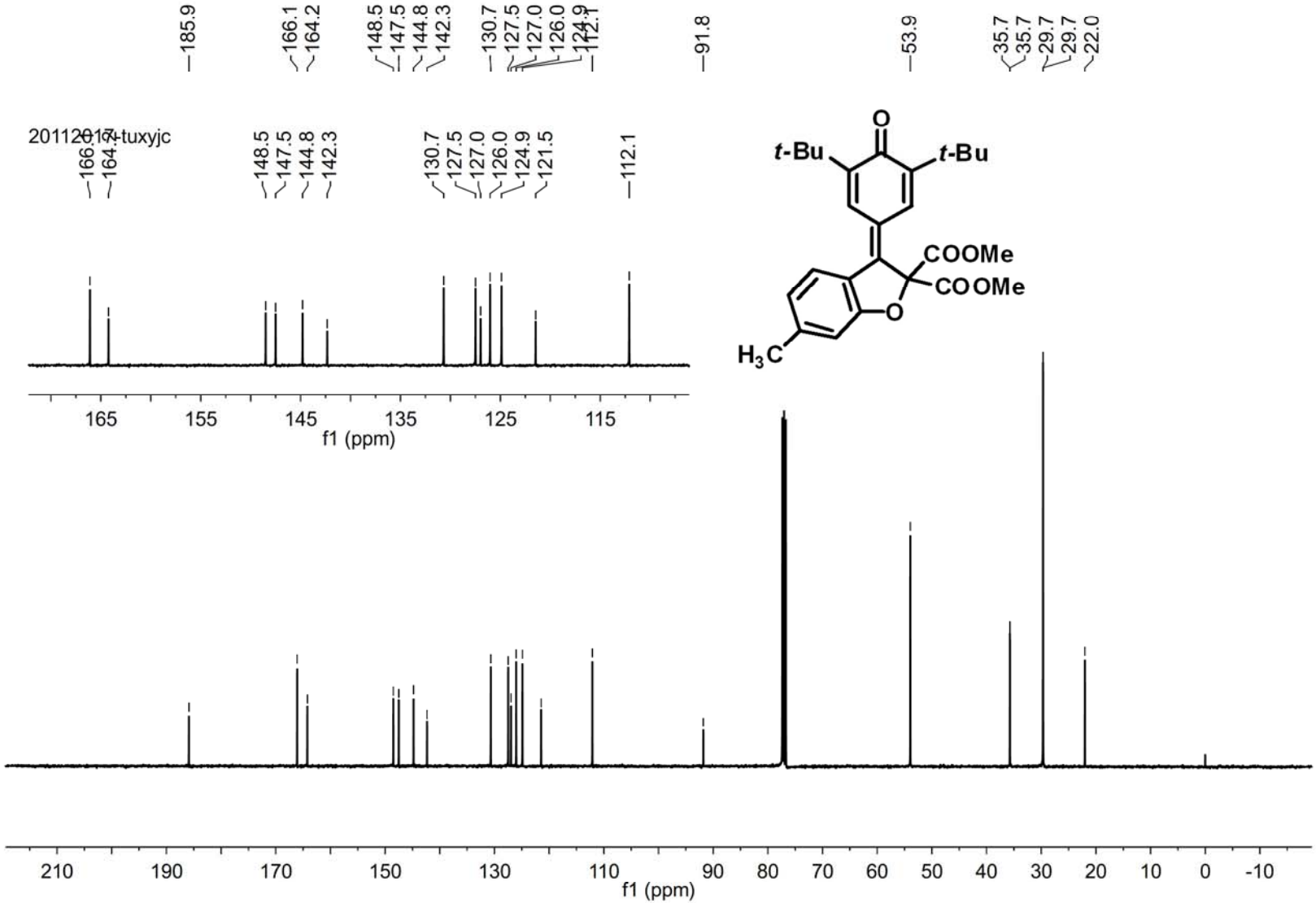
^{1}H NMR Spectrum of Compound 3b



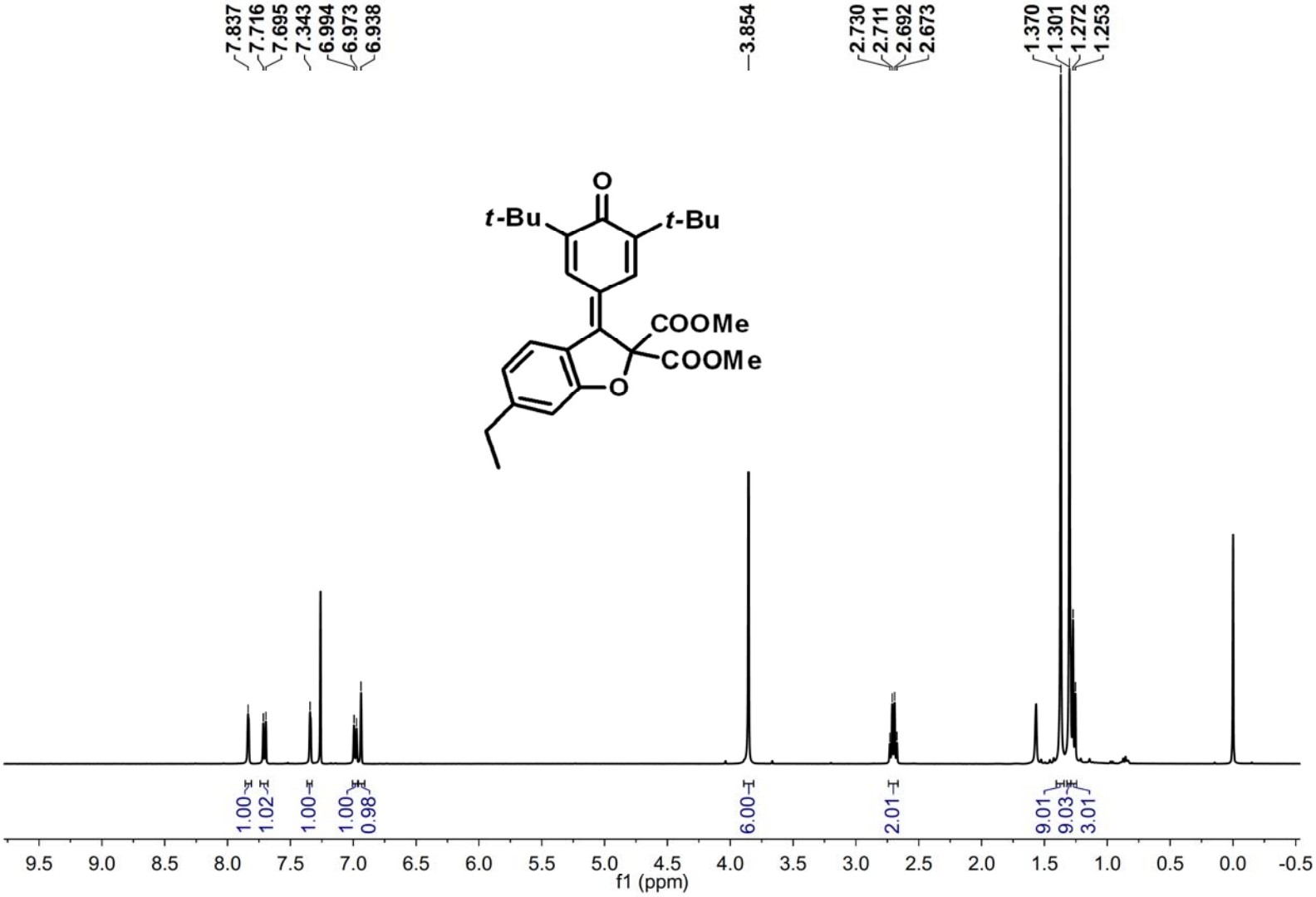
^{13}C NMR Spectrum of Compound 3b



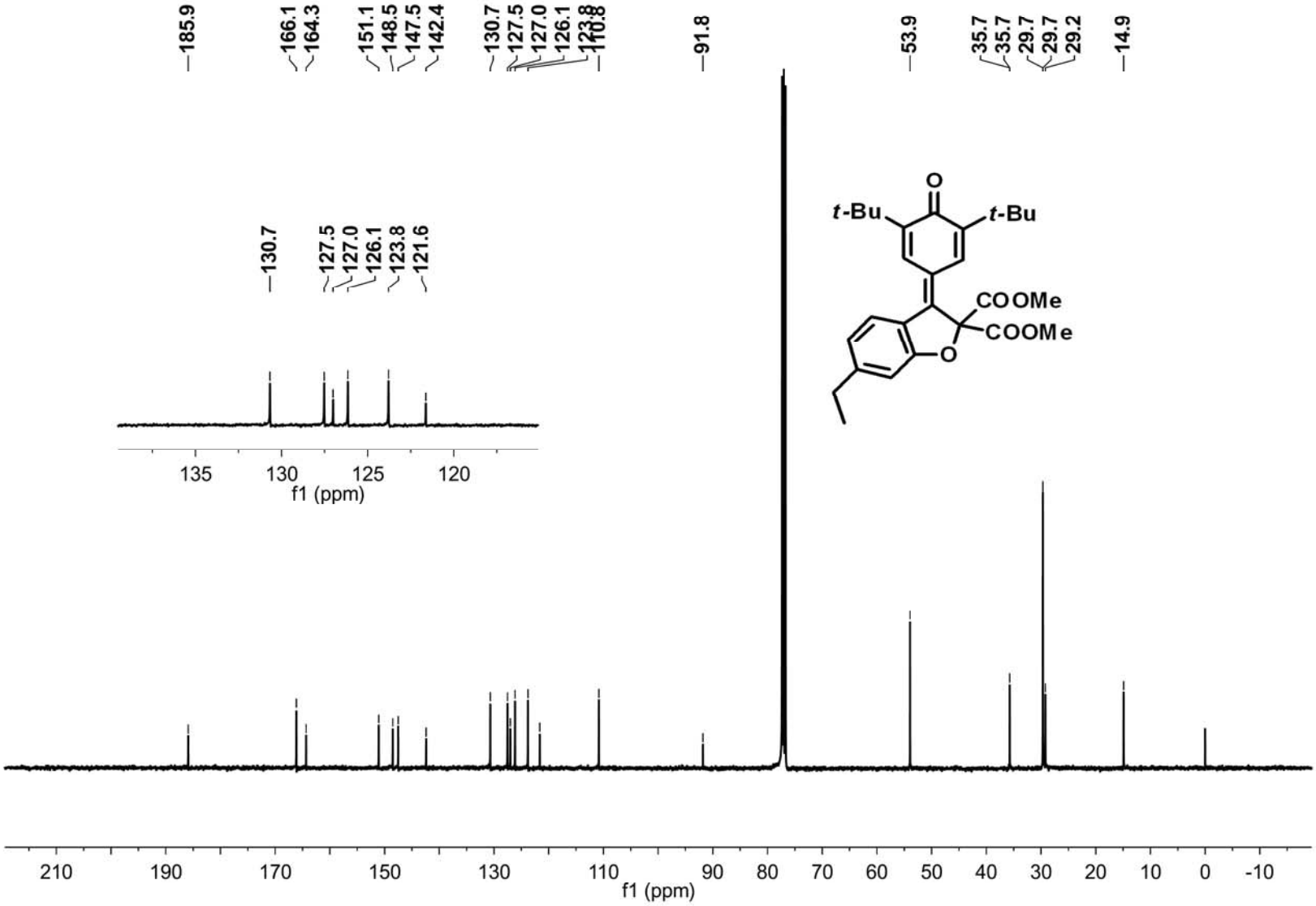
^{1}H NMR Spectrum of Compound 3c



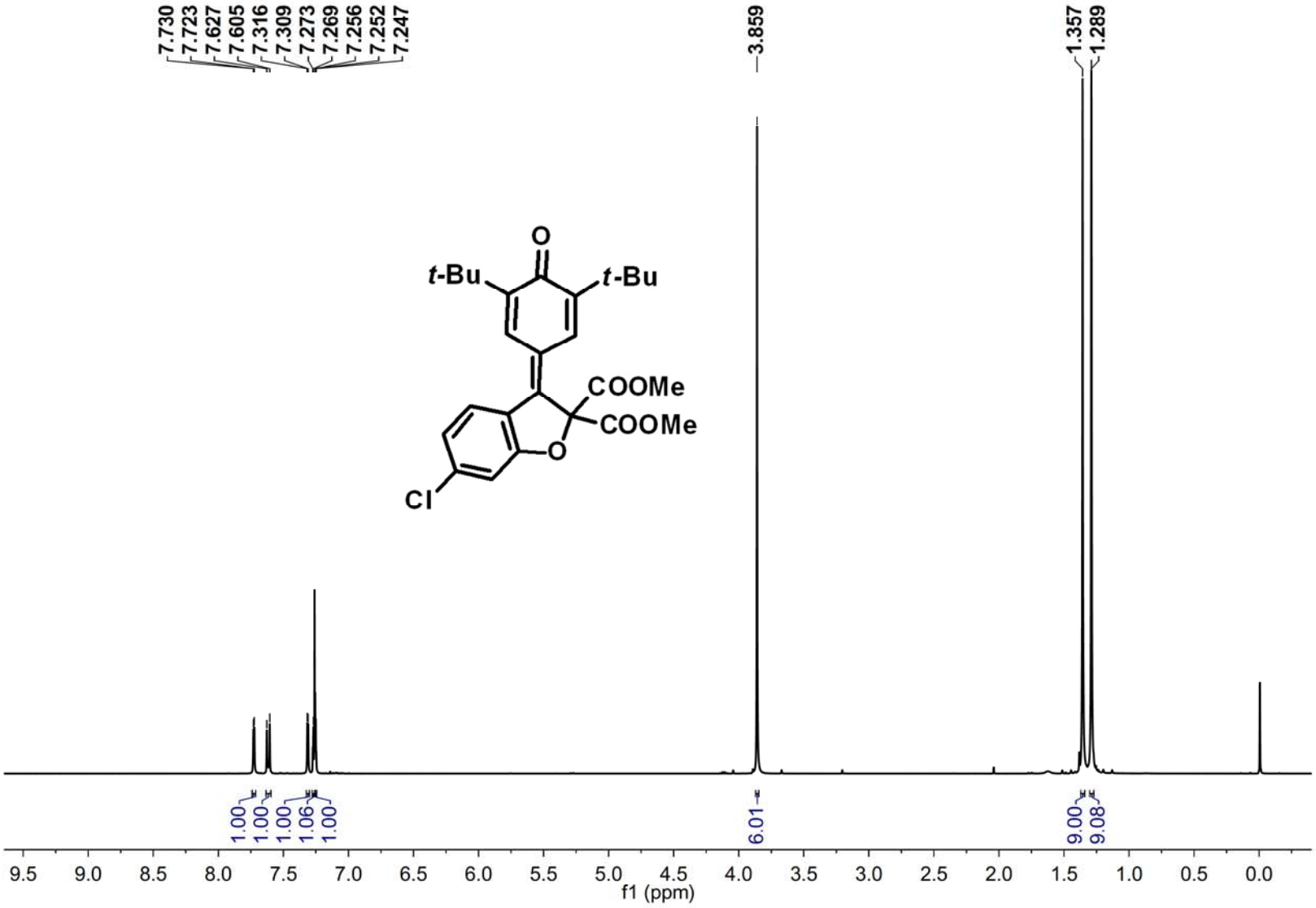
^{13}C NMR Spectrum of Compound 3c



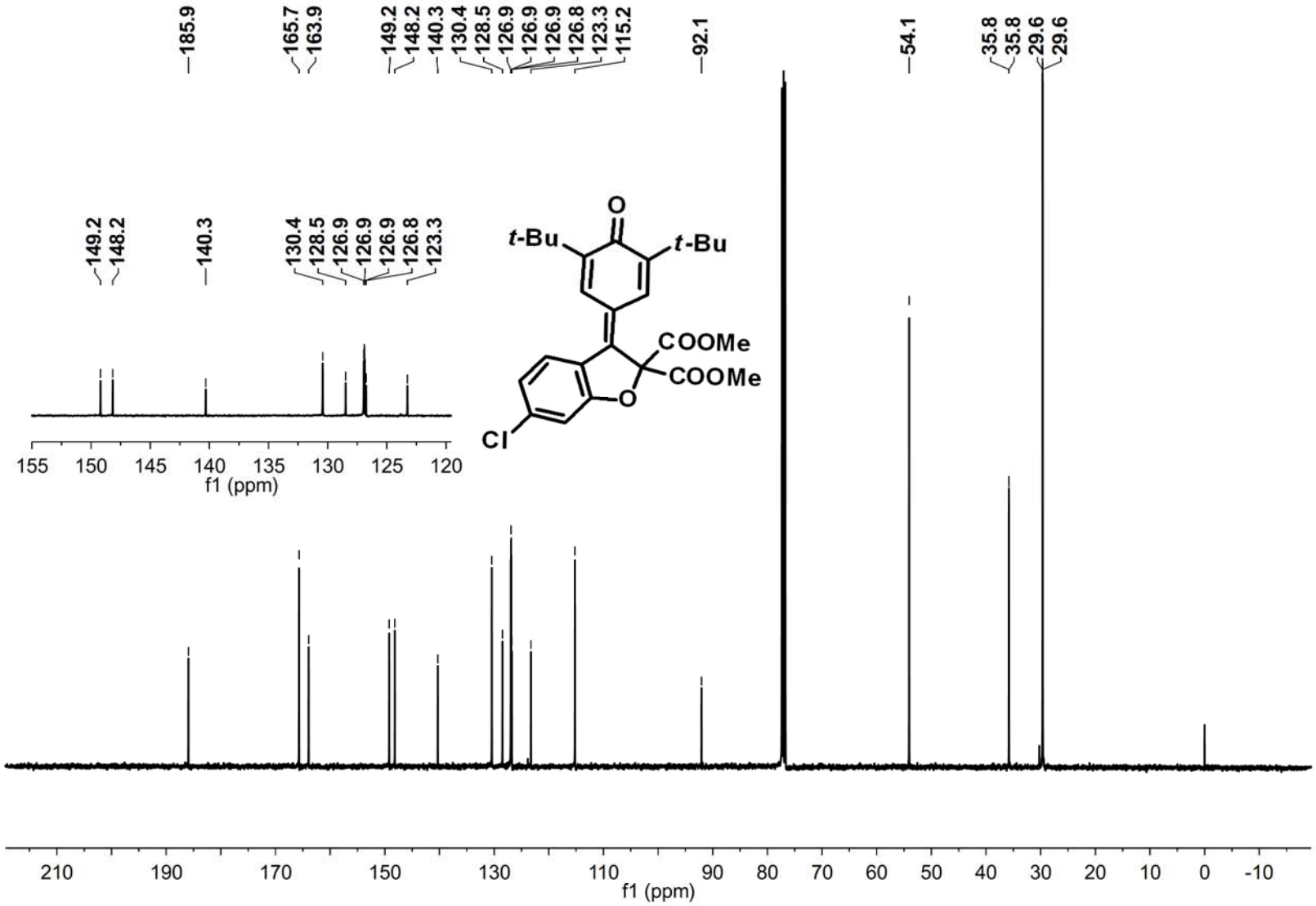
^{1}H NMR Spectrum of Compound 3d



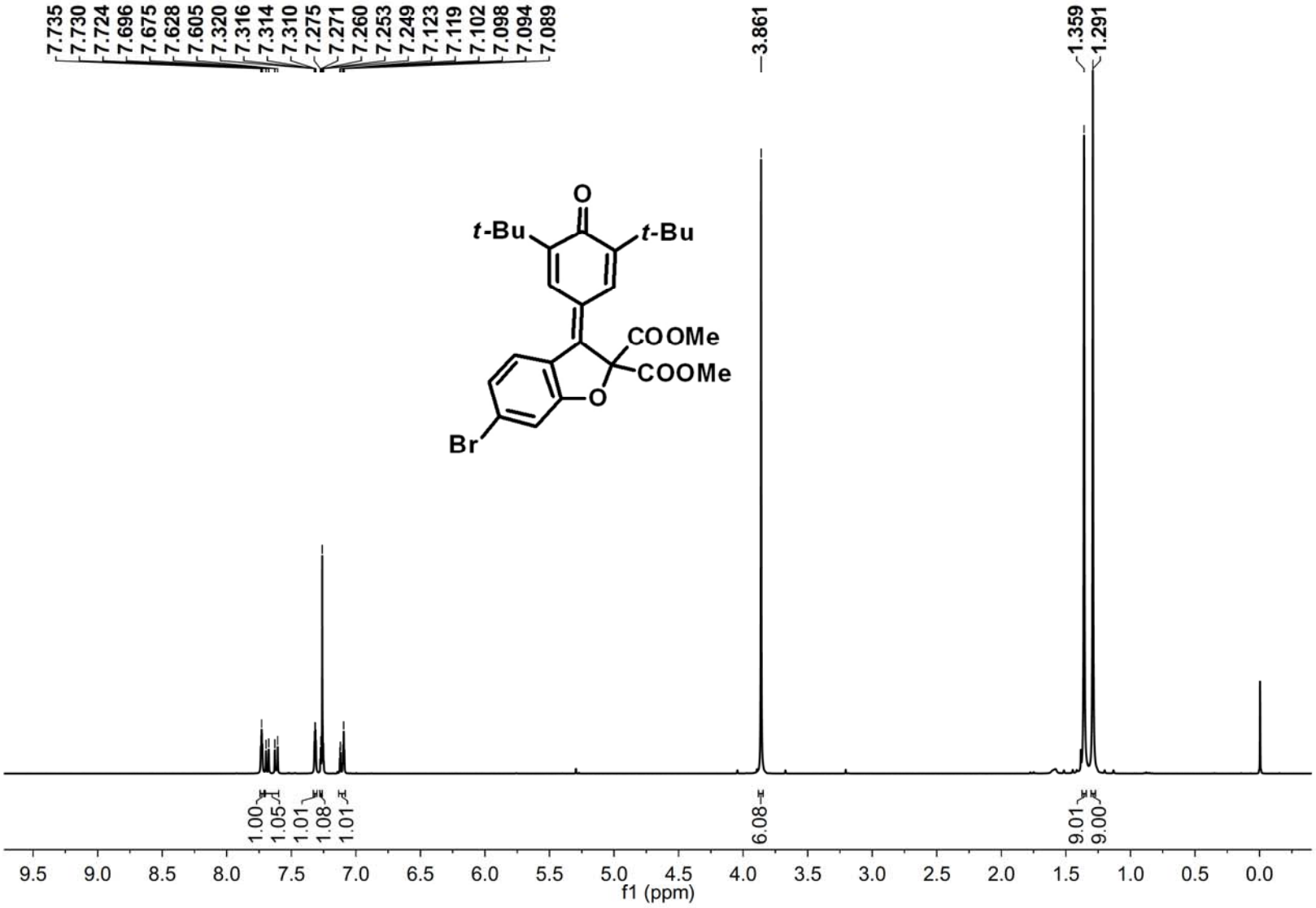
^{13}C NMR Spectrum of Compound 3d



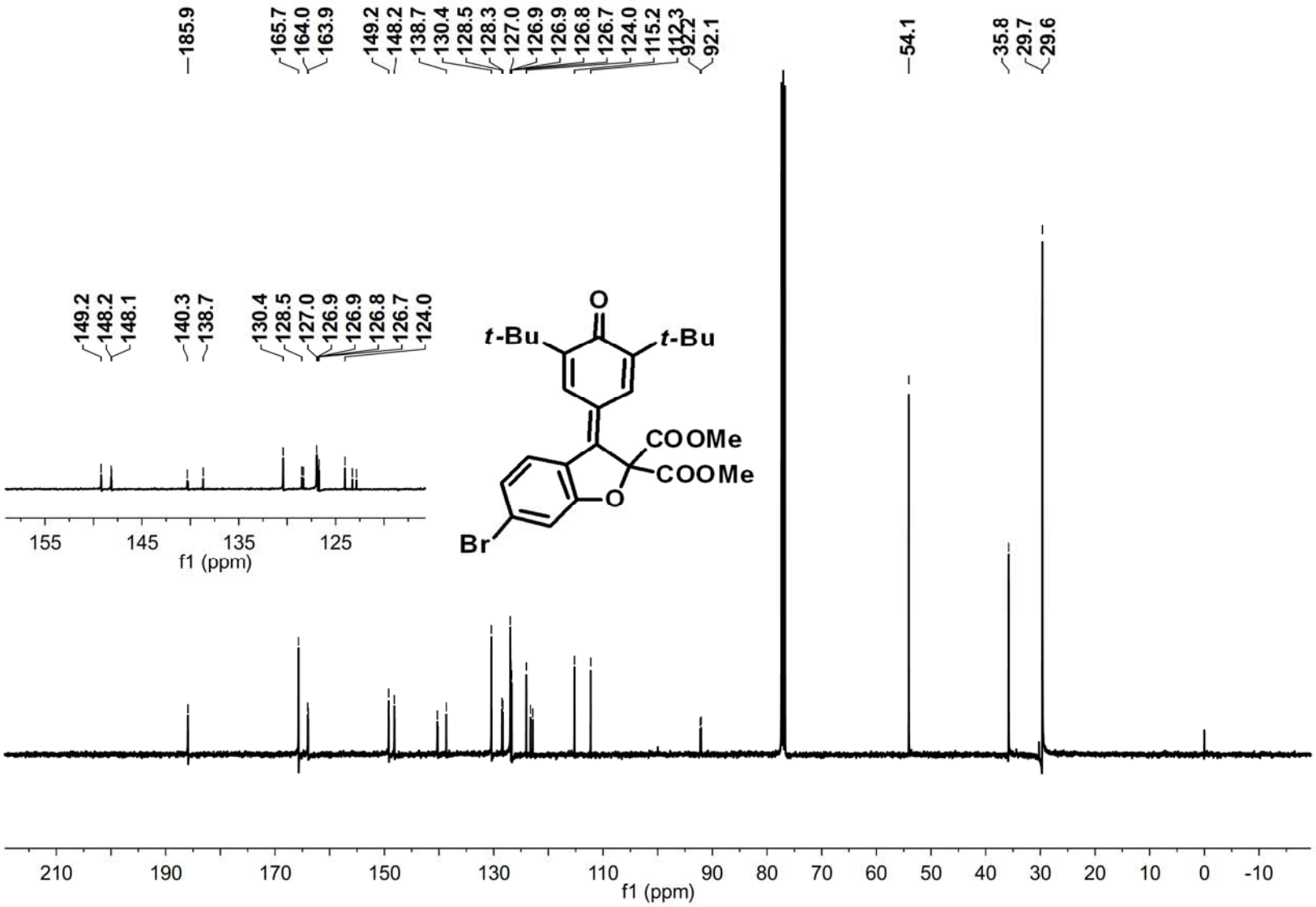
^{1}H NMR Spectrum of Compound 3e



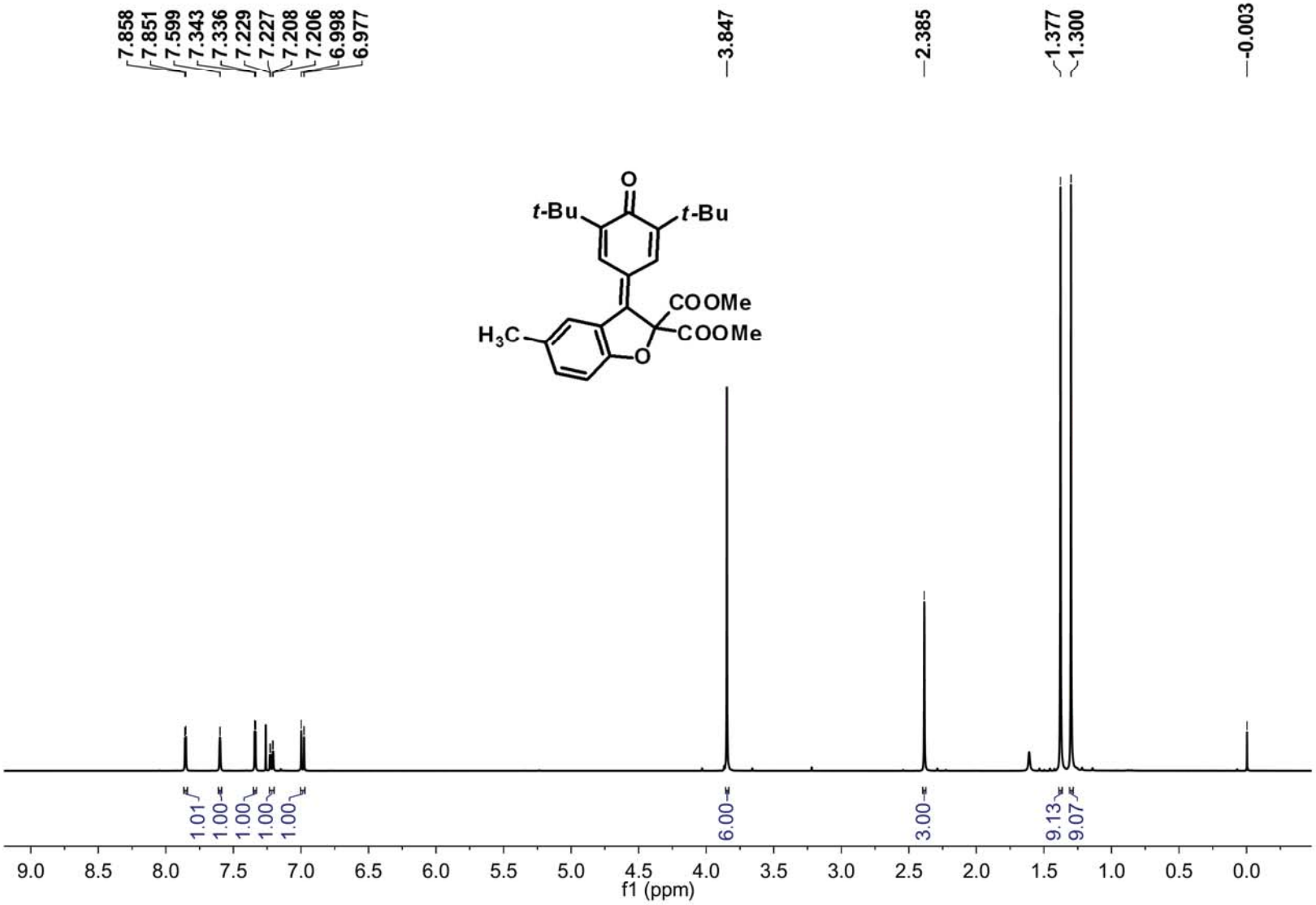
^{13}C NMR Spectrum of Compound 3e



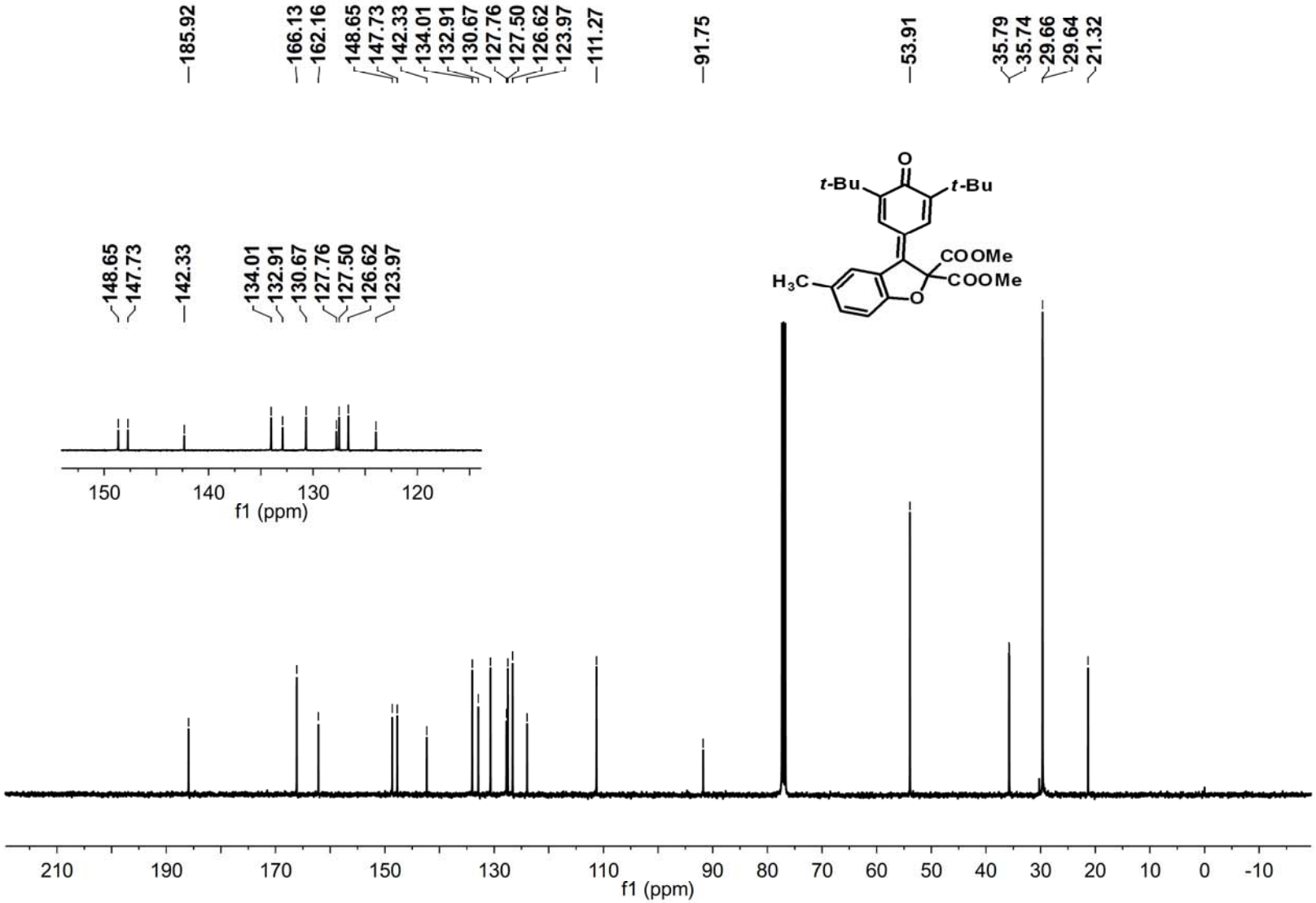
^{1}H NMR Spectrum of Compound 3f



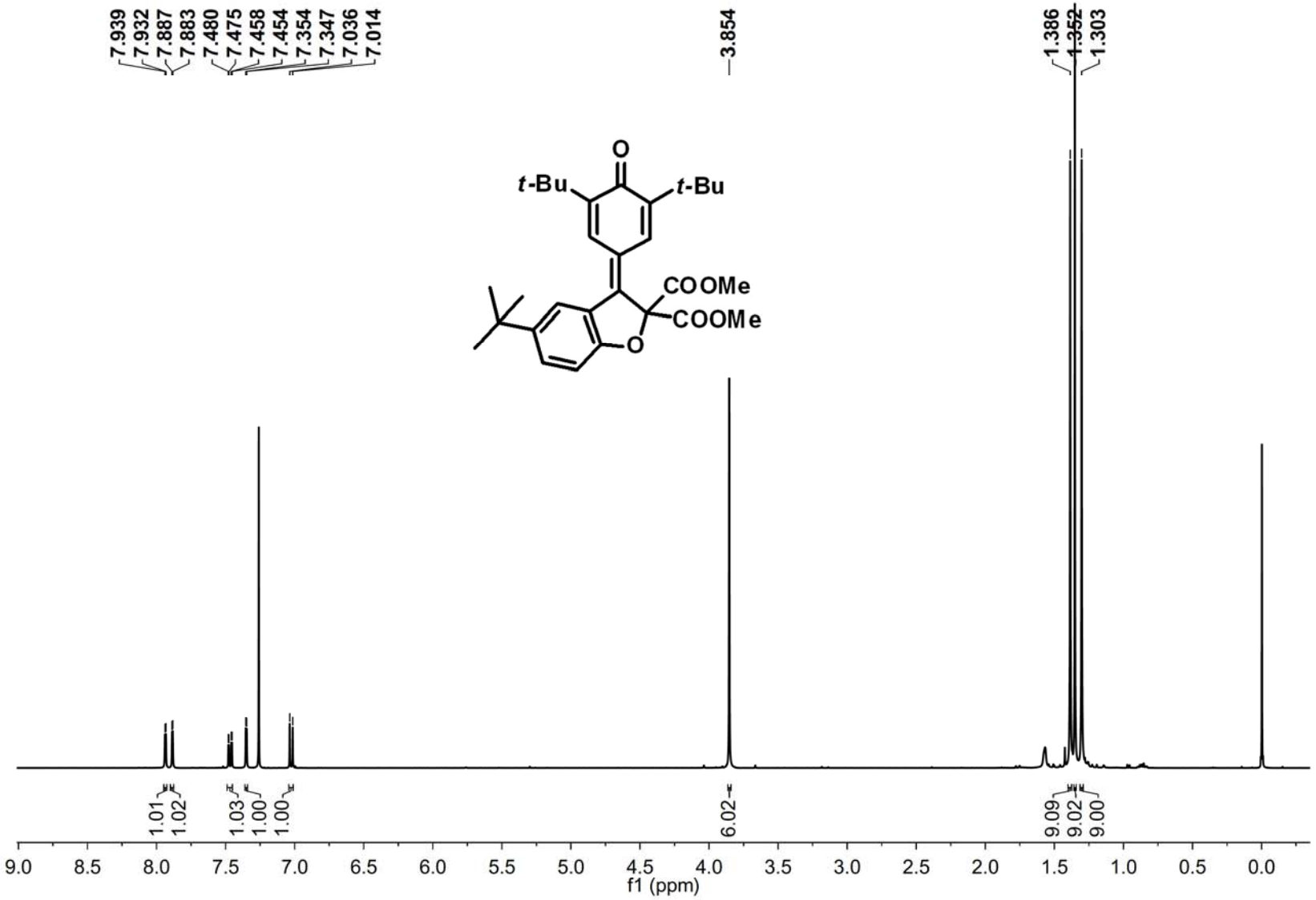
^{13}C NMR Spectrum of Compound 3f



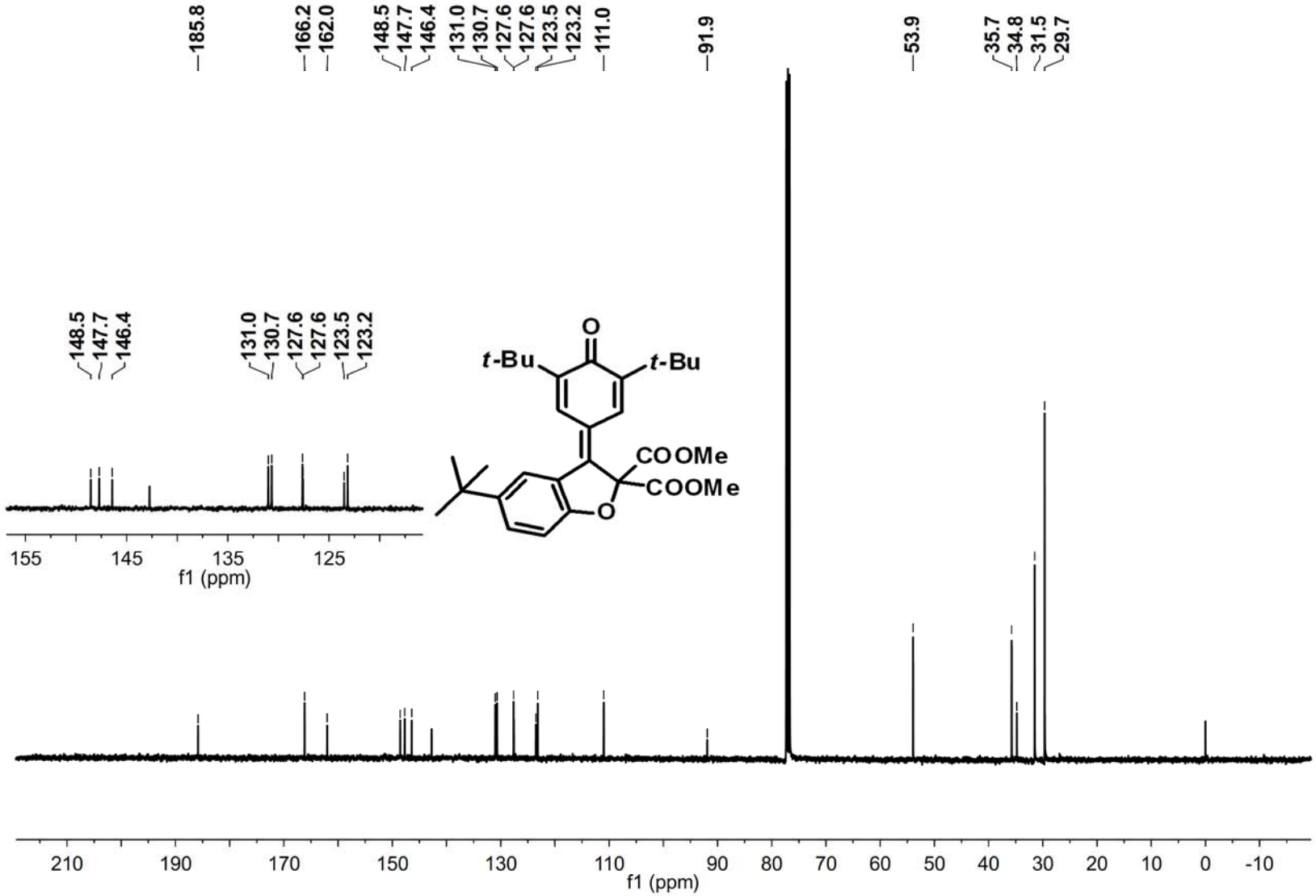
^{1}H NMR Spectrum of Compound 3g



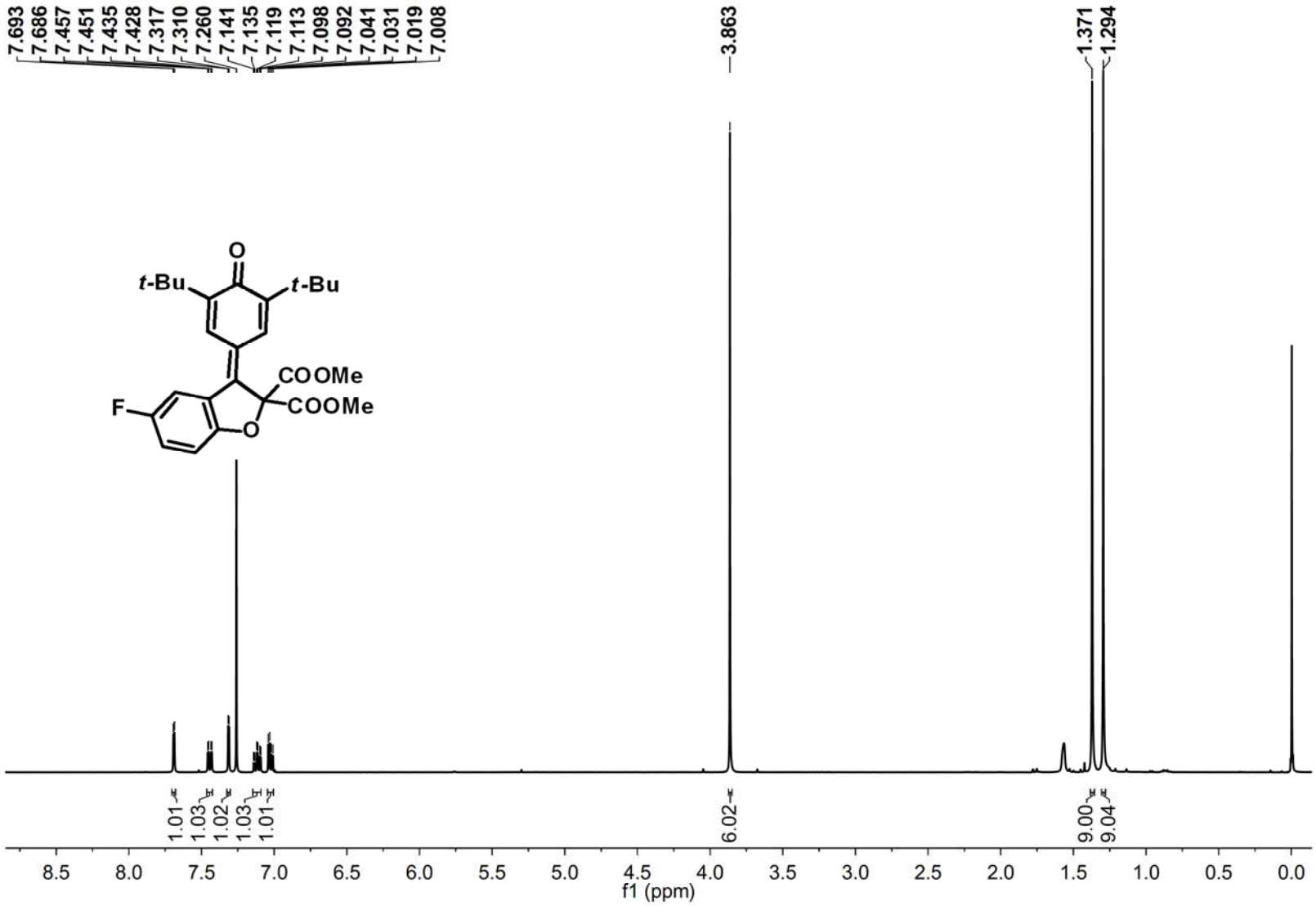
^{13}C NMR Spectrum of Compound 3g



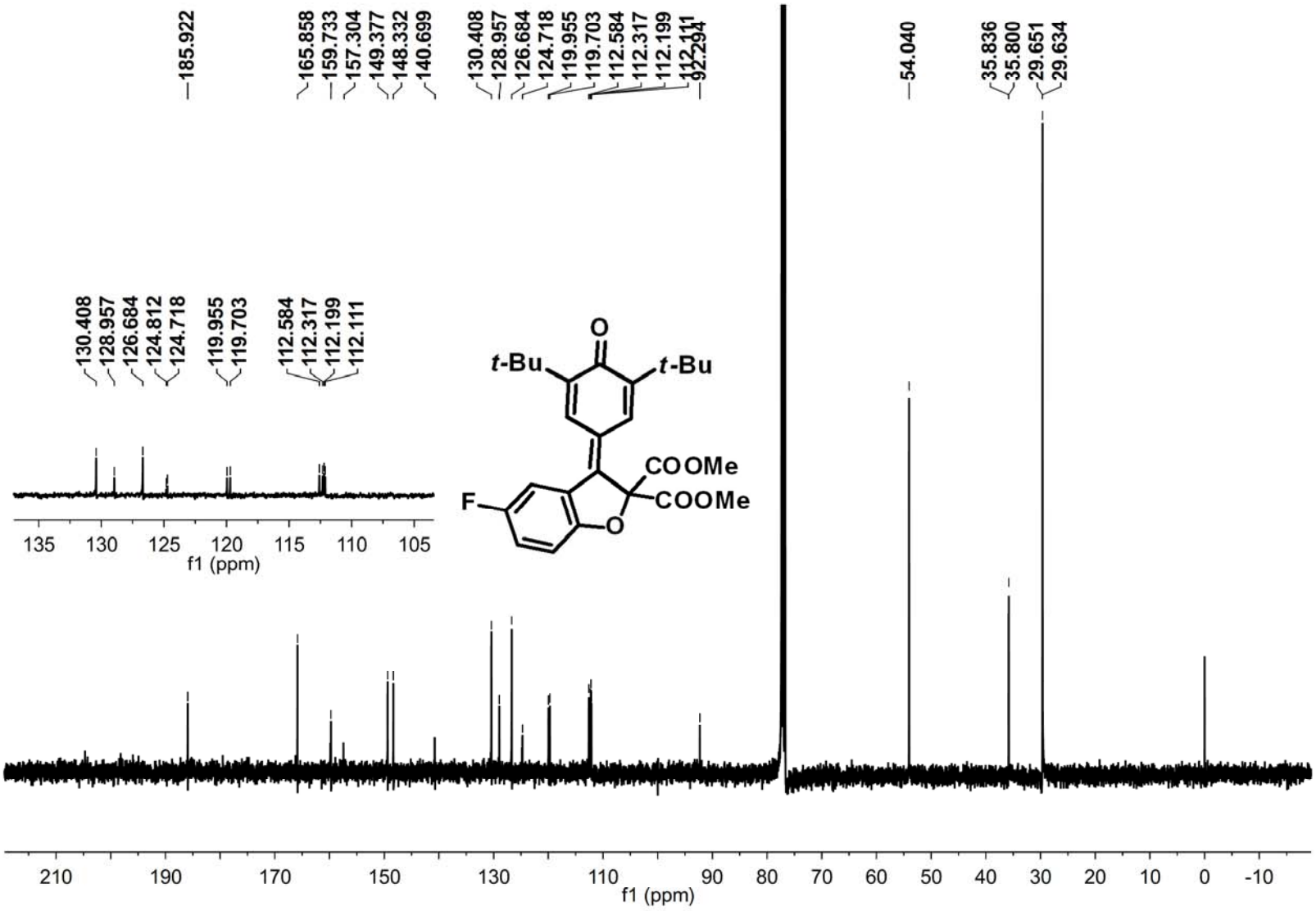
^{1}H NMR Spectrum of Compound 3h



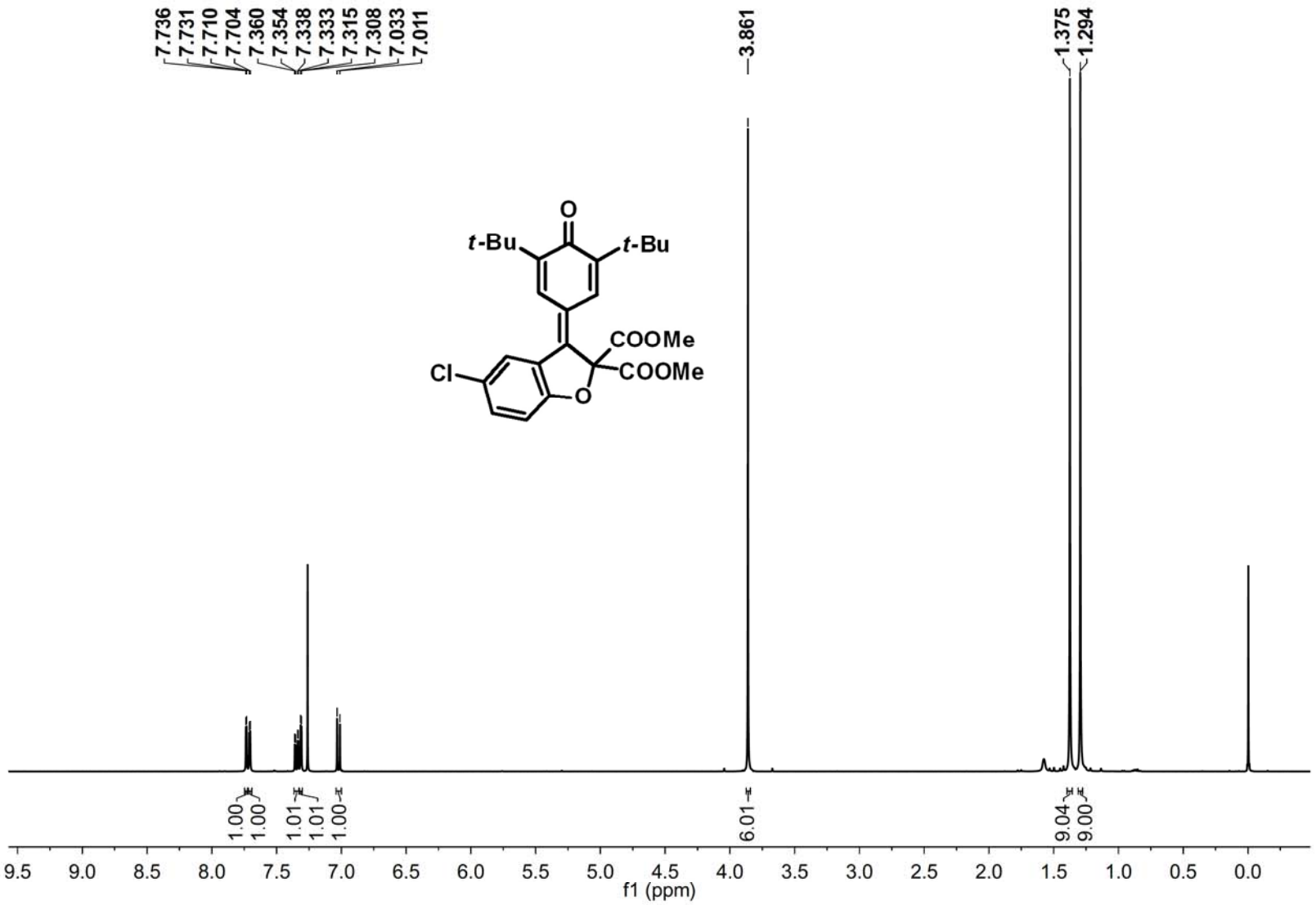
^{13}C NMR Spectrum of Compound 3h



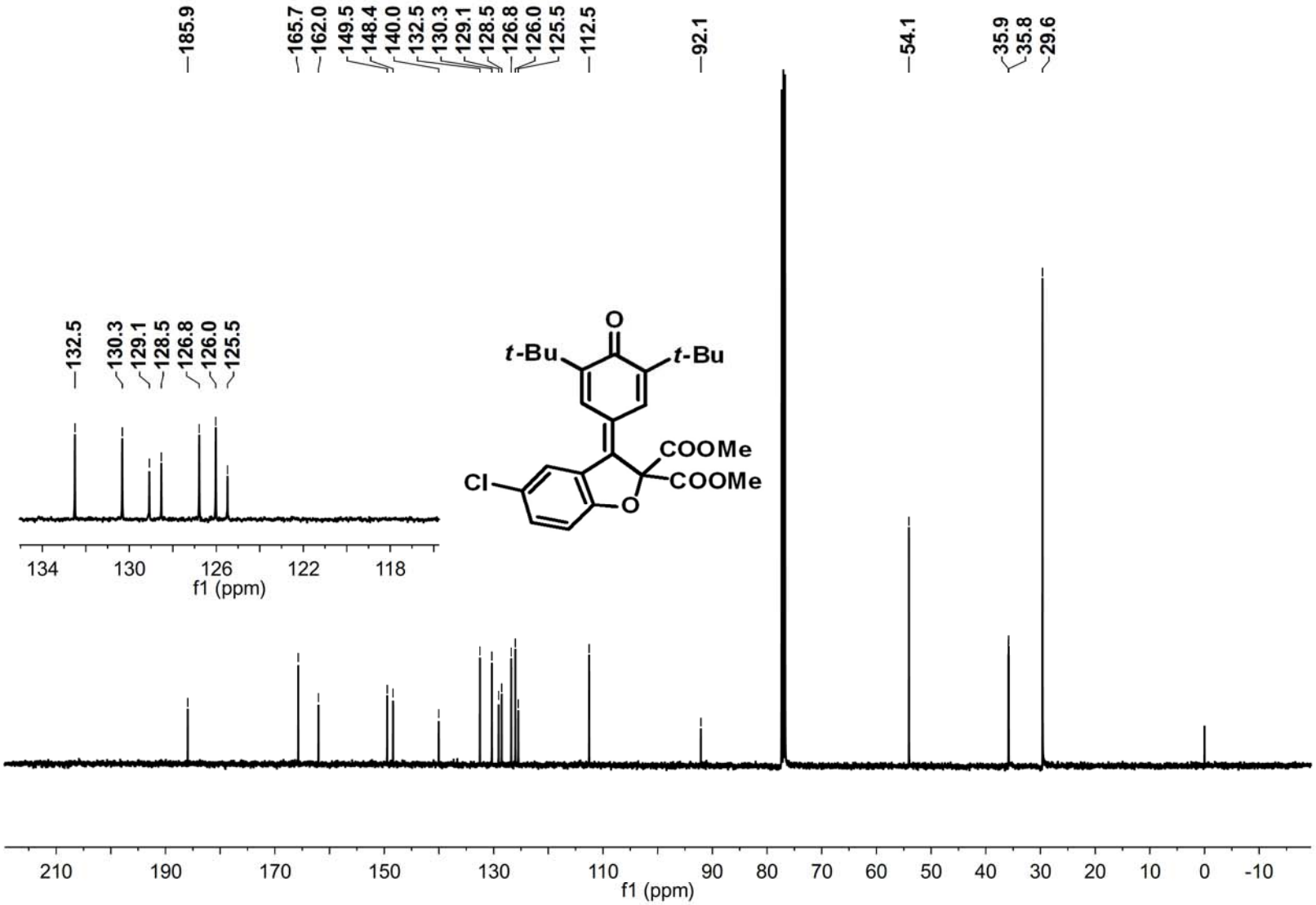
^{1}H NMR Spectrum of Compound 3i



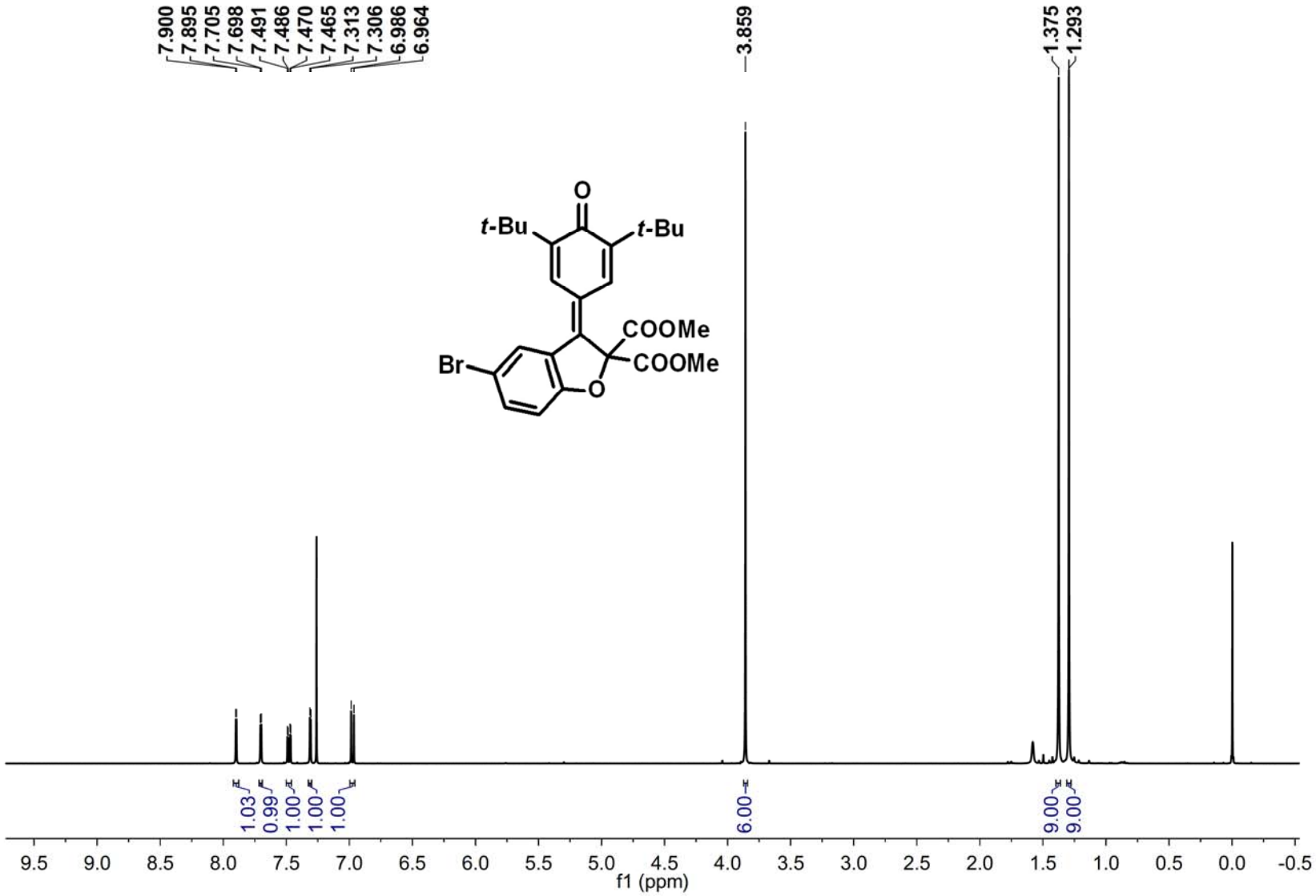
^{13}C NMR Spectrum of Compound 3i



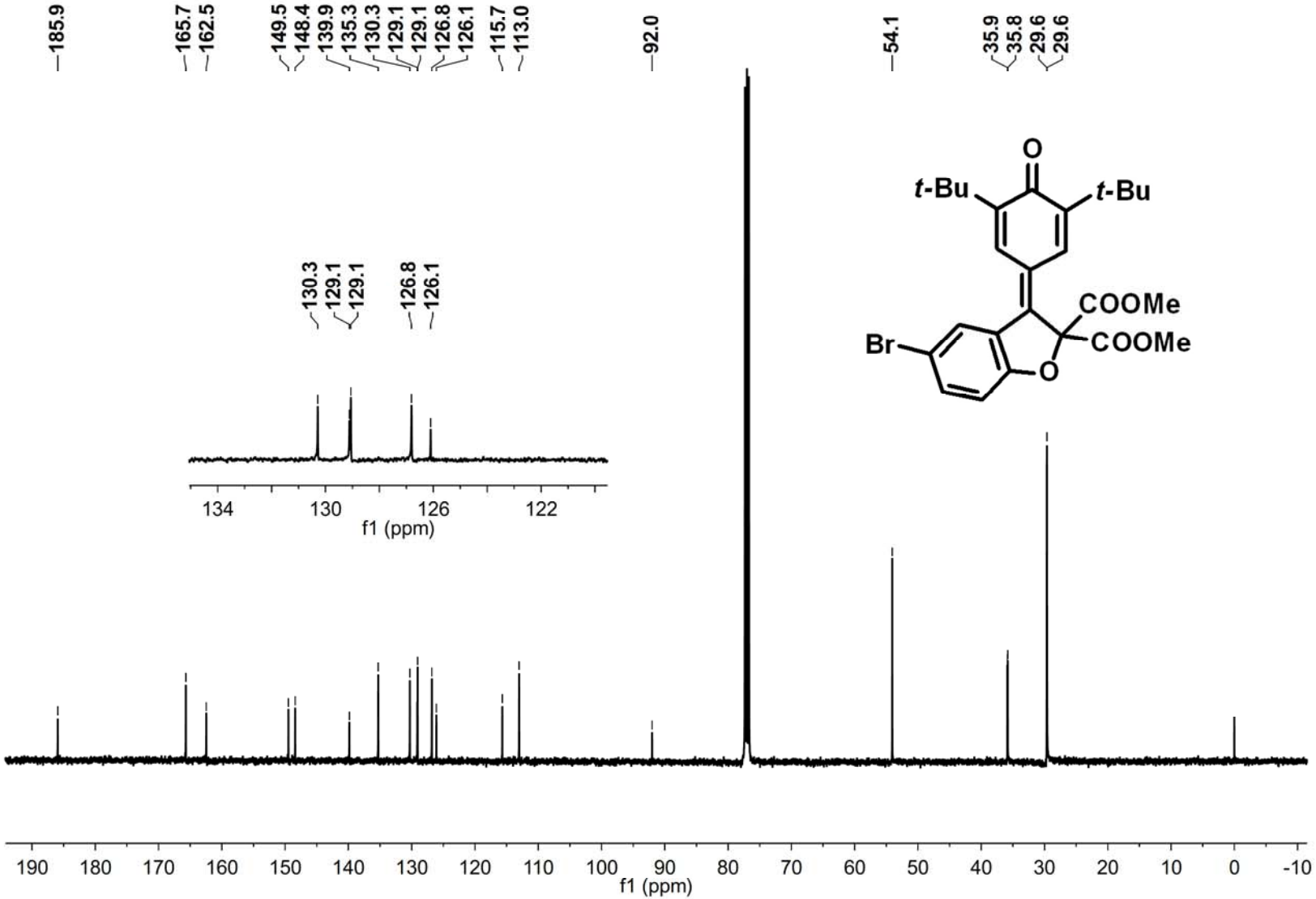
^{1}H NMR Spectrum of Compound 3j



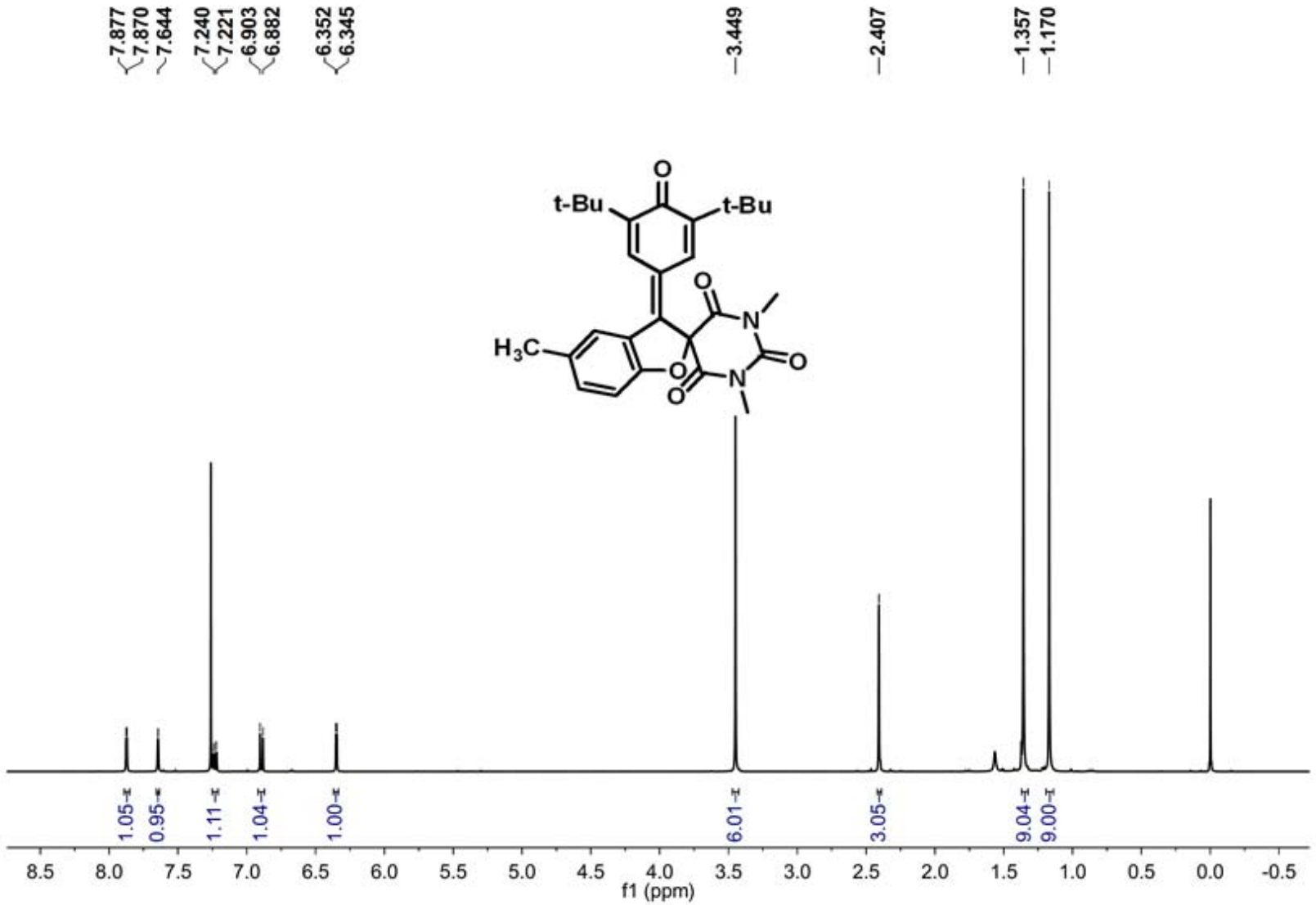
^{13}C NMR Spectrum of Compound 3k



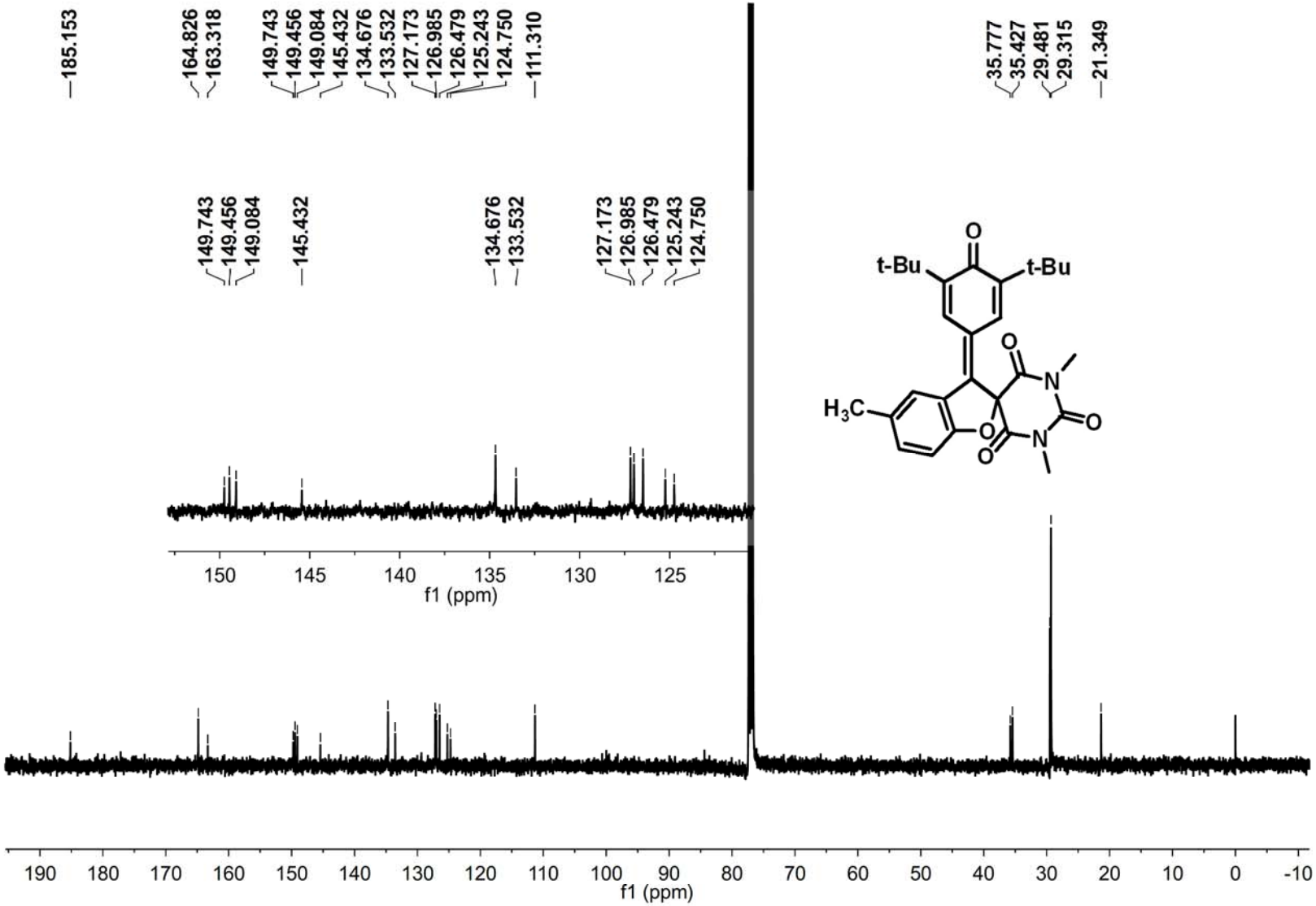
^{1}H NMR Spectrum of Compound 3l



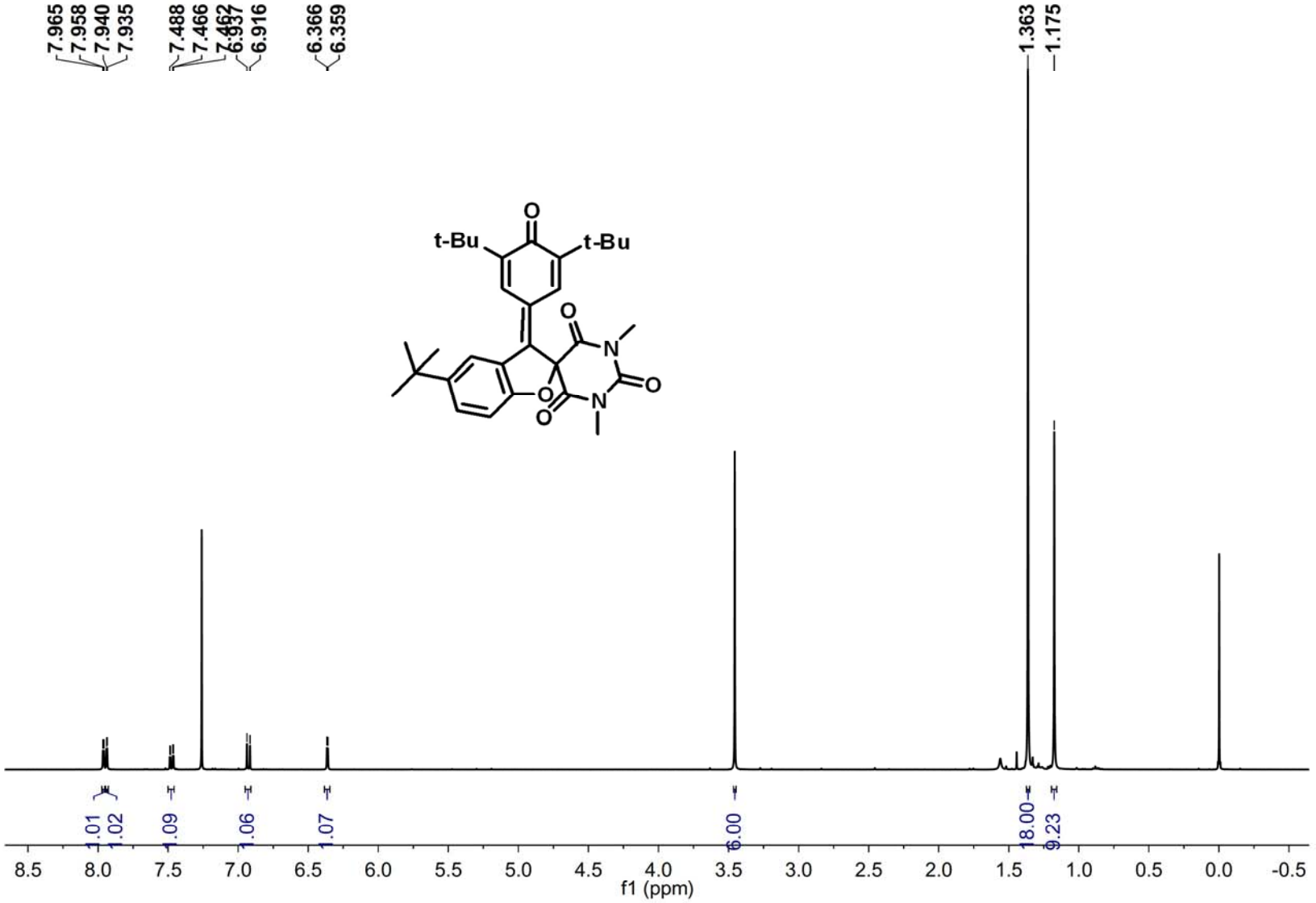
^{13}C NMR Spectrum of Compound 3l



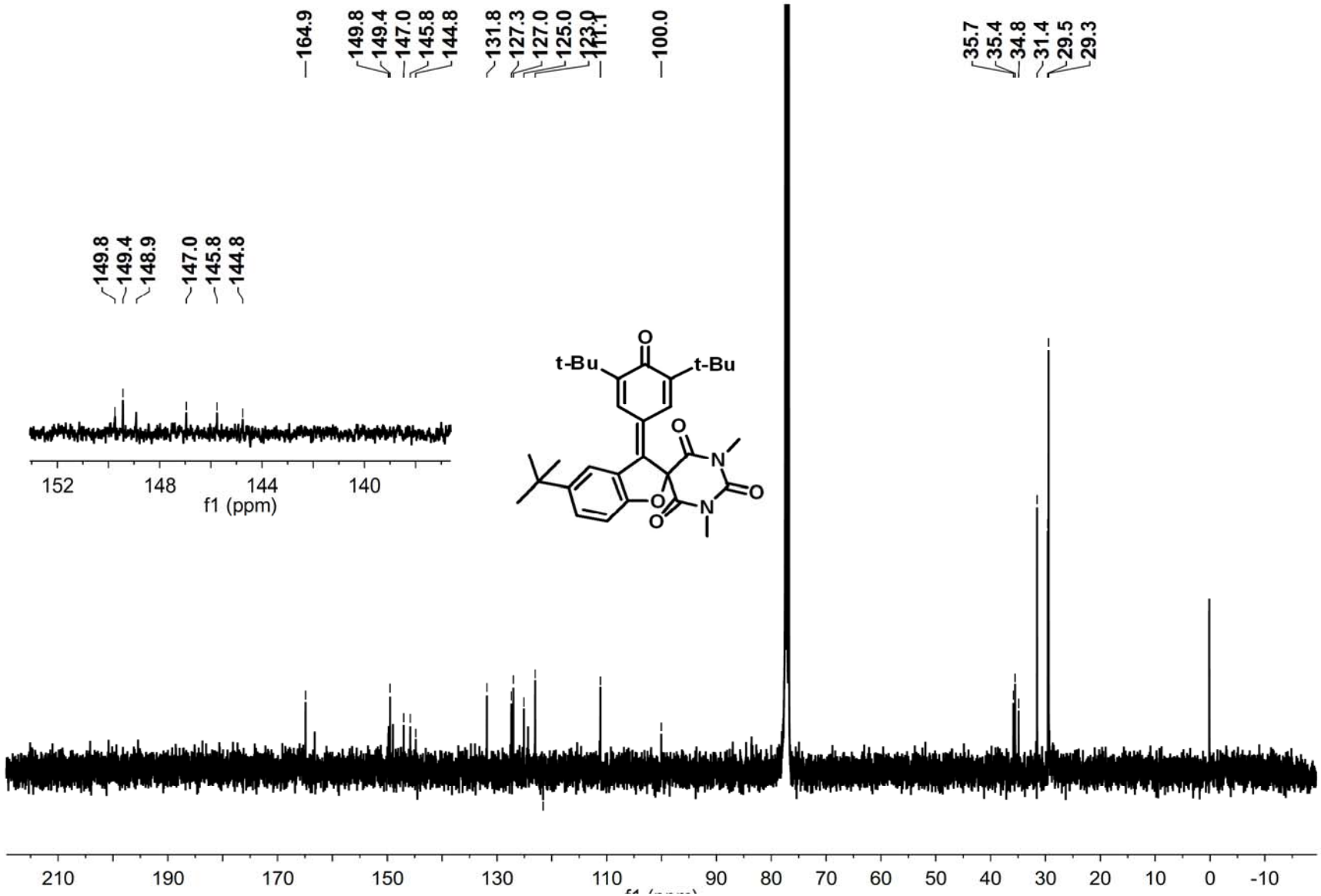
^{1}H NMR Spectrum of Compound 4a



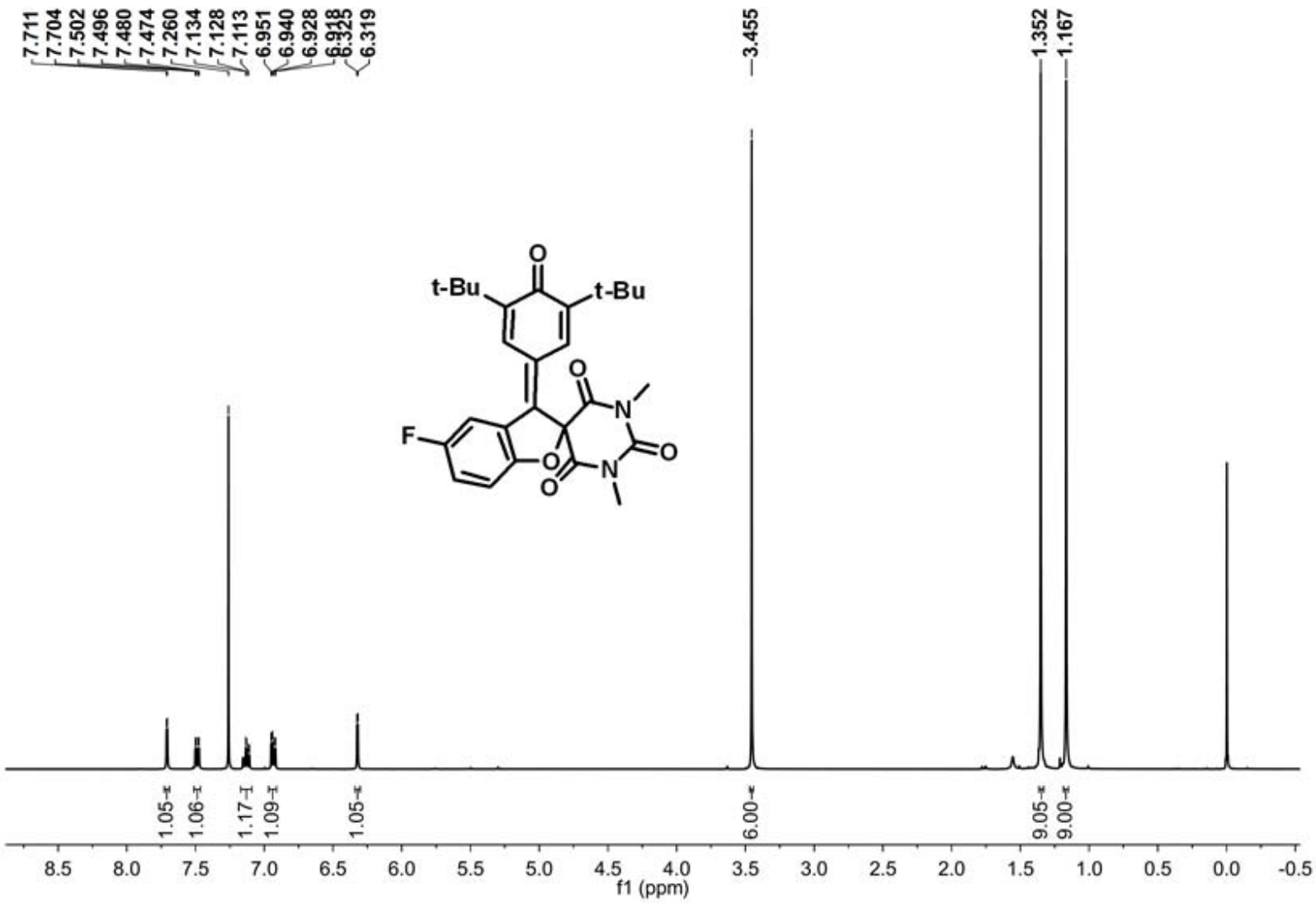
^{13}C NMR Spectrum of Compound 4a



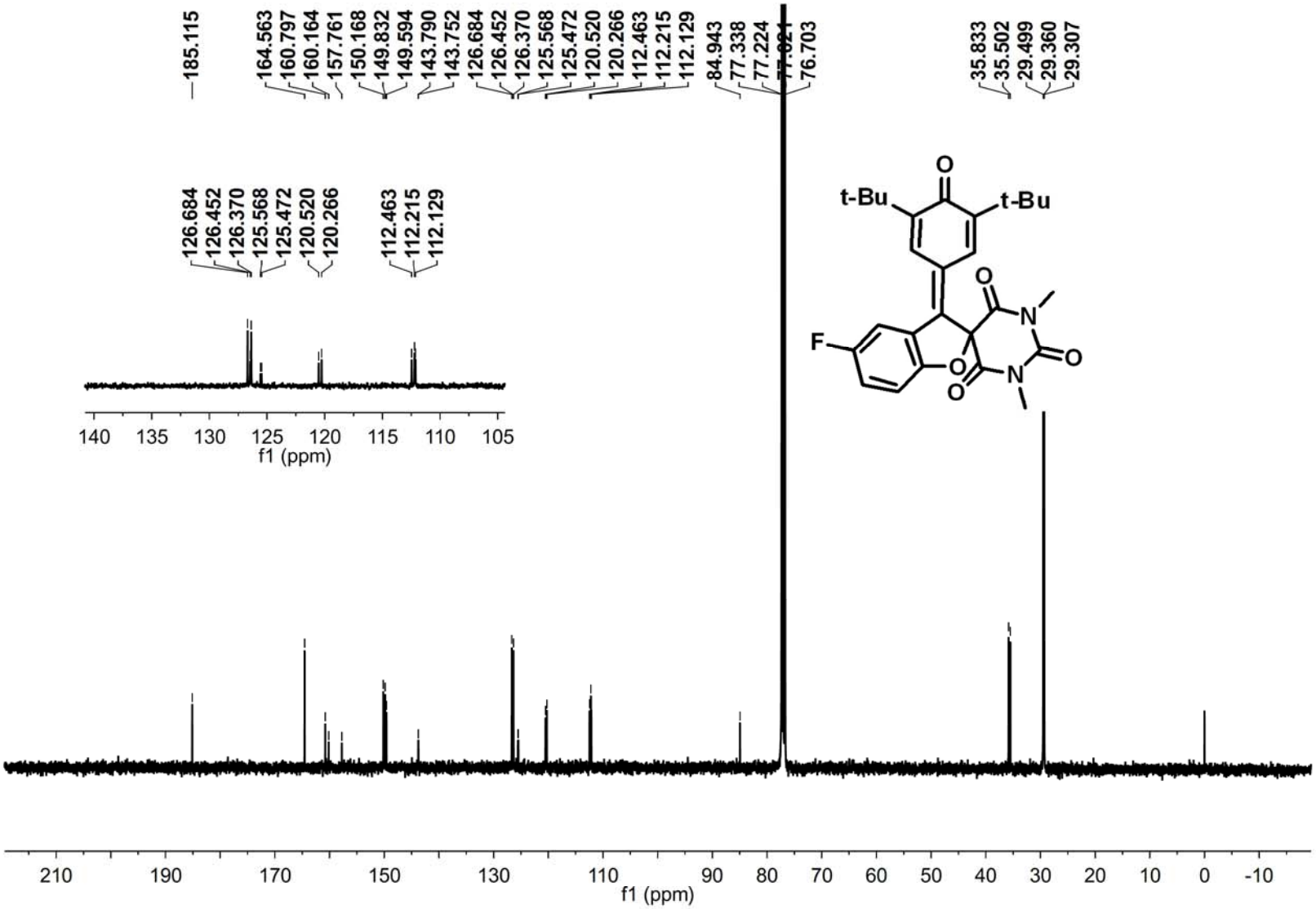
^{1}H NMR Spectrum of Compound 4b



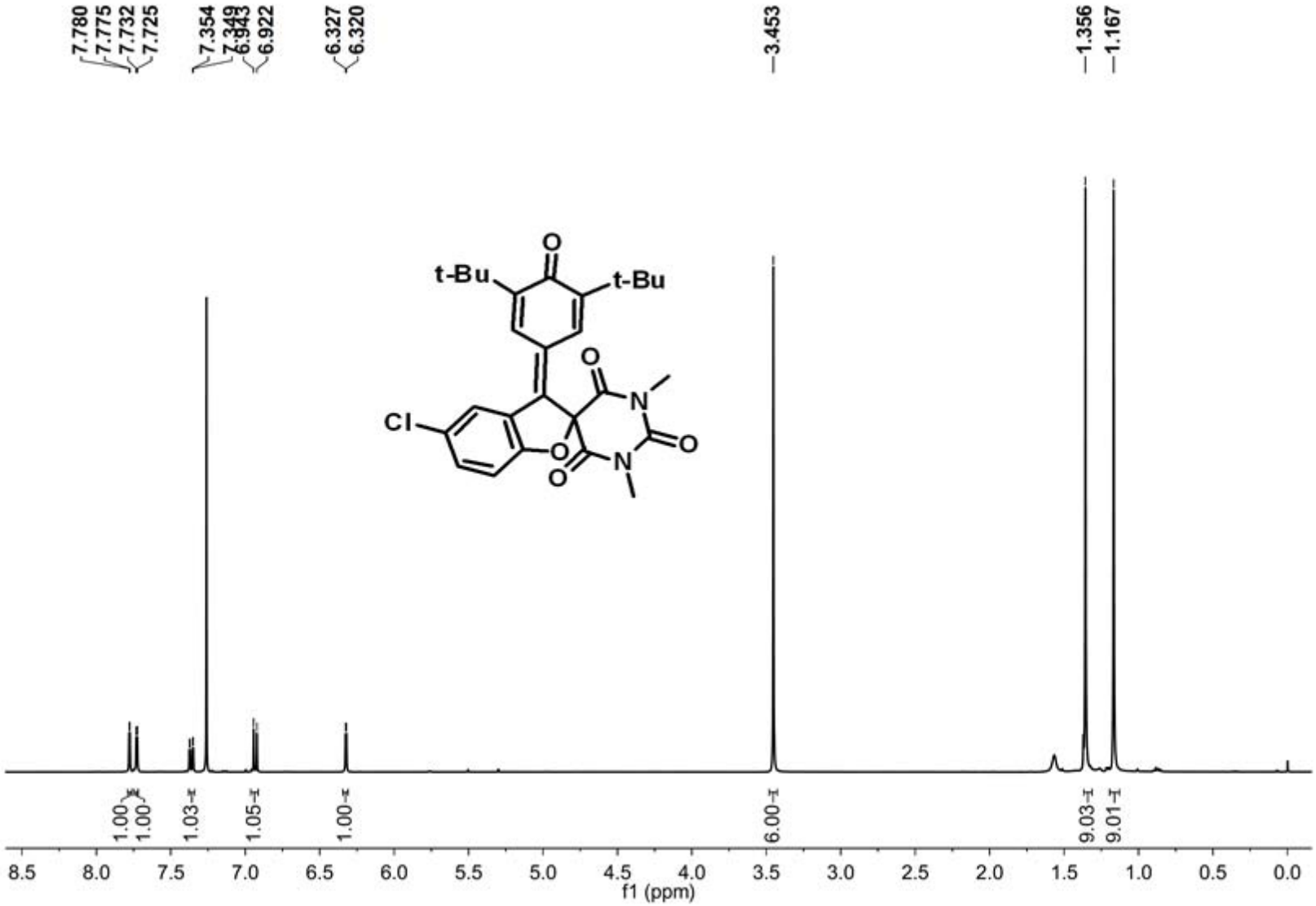
^{13}C NMR Spectrum of Compound 4b



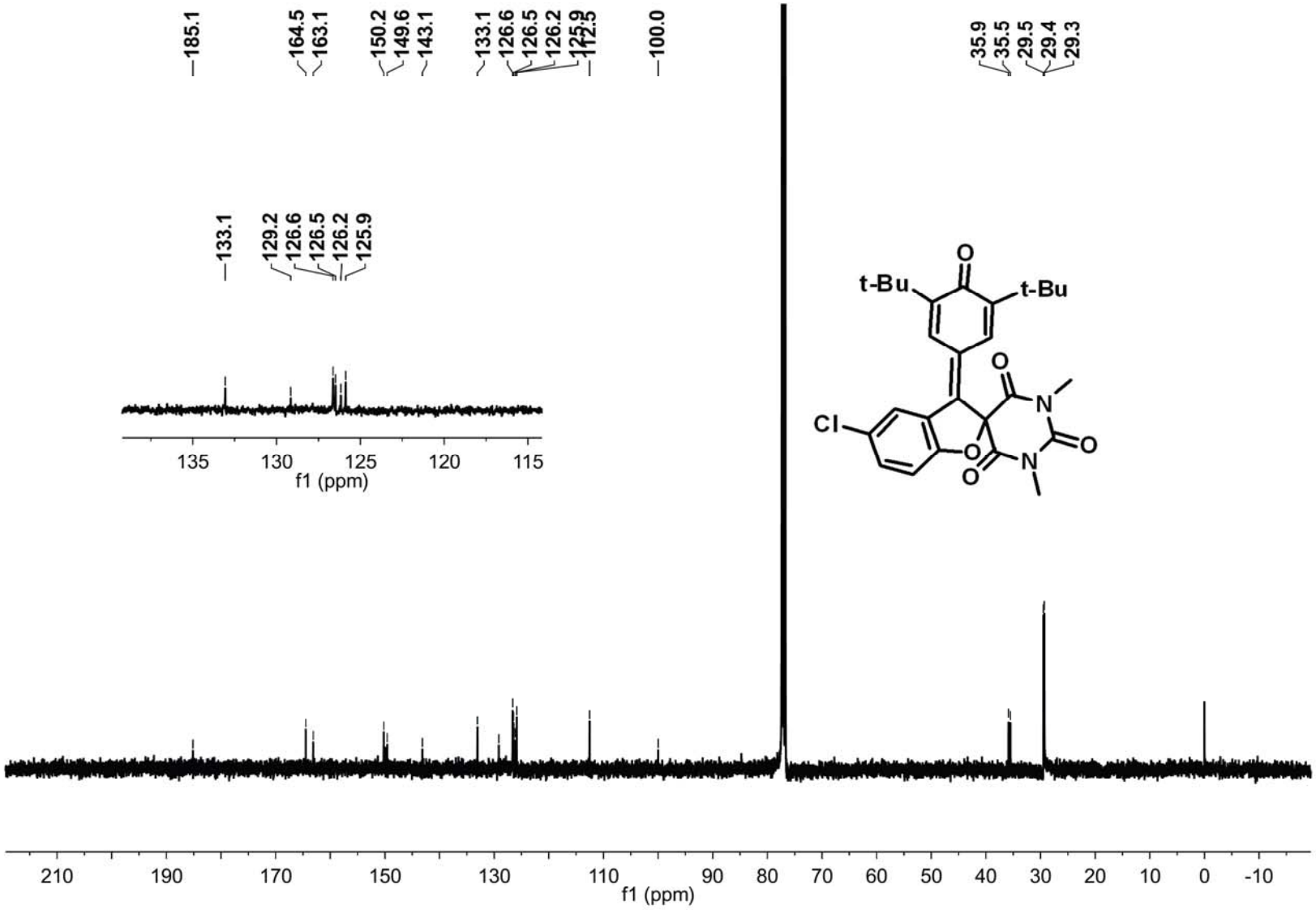
^{1}H NMR Spectrum of Compound 4c



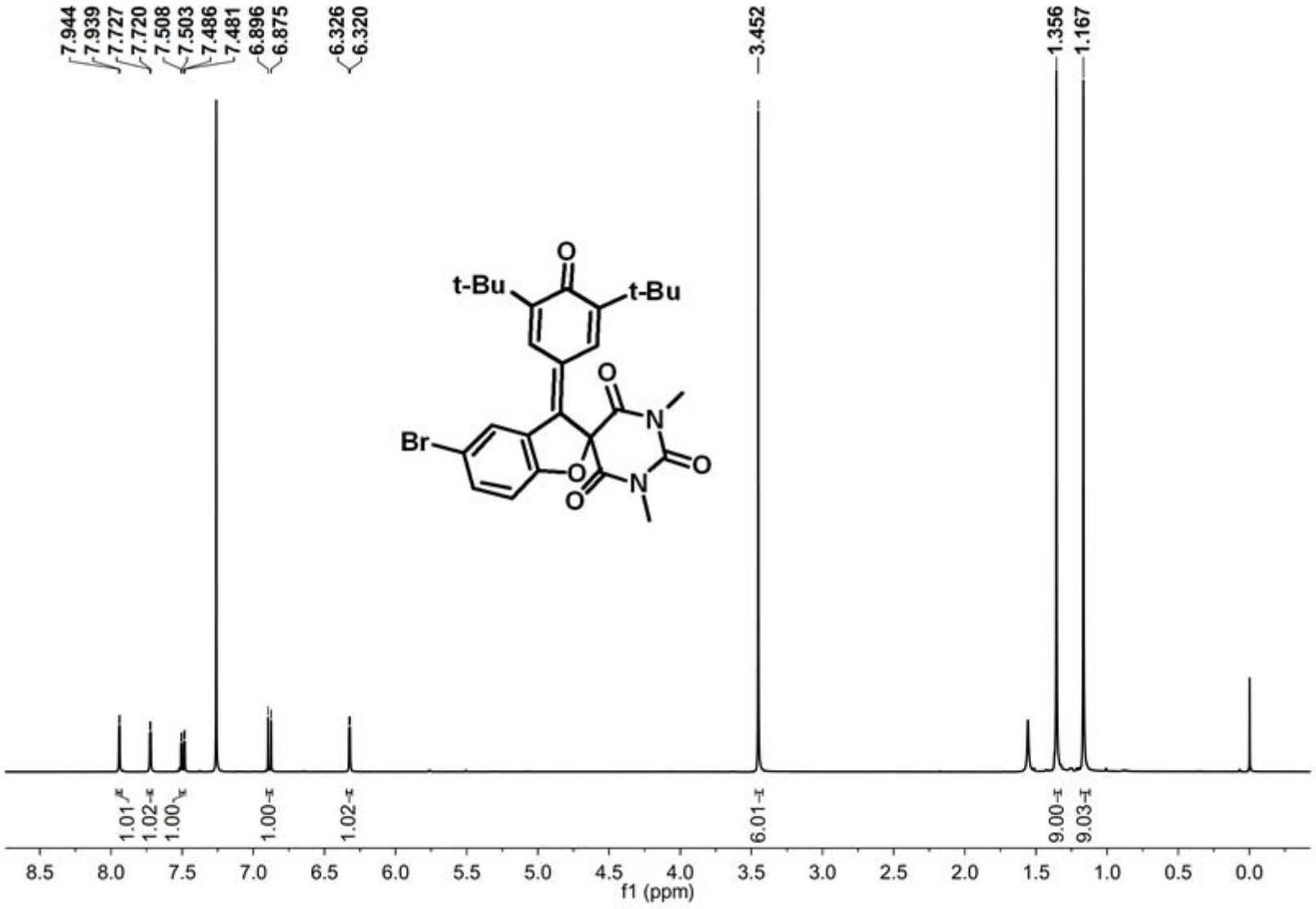
^{13}C NMR Spectrum of Compound 4c



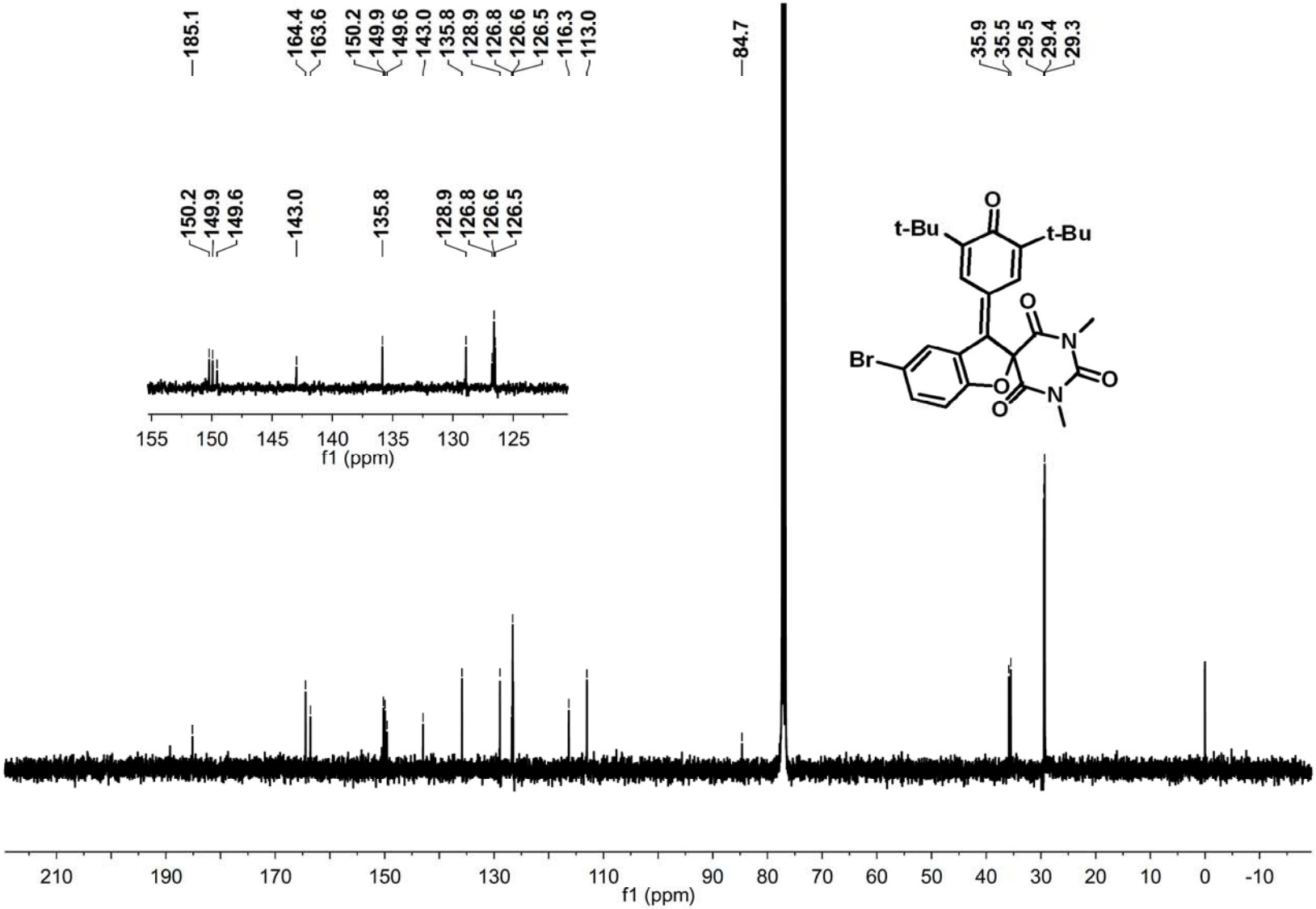
[1]H NMR Spectrum of Compound 4d



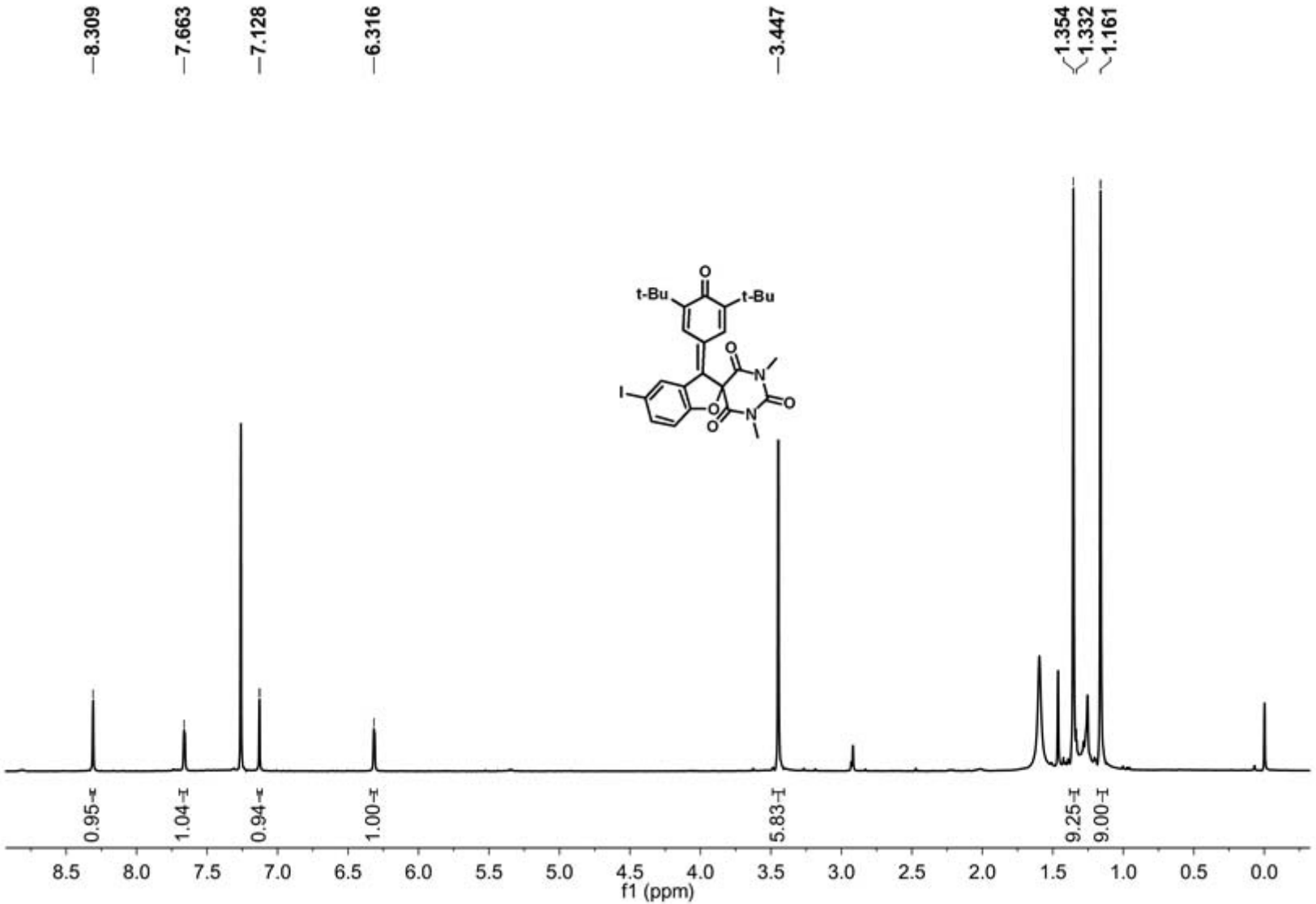
^{13}C NMR Spectrum of Compound 4d



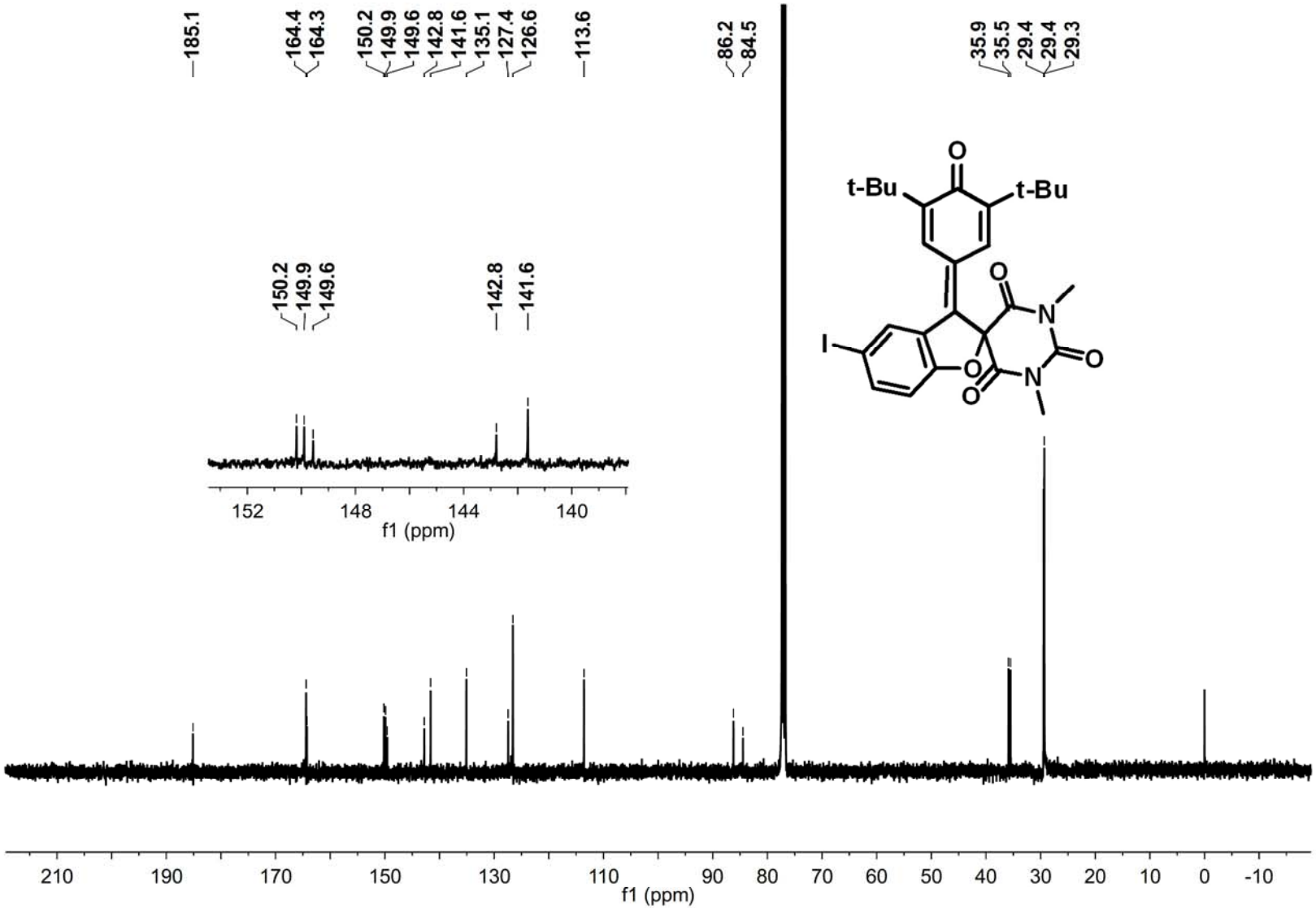
^{1}H NMR Spectrum of Compound 4e



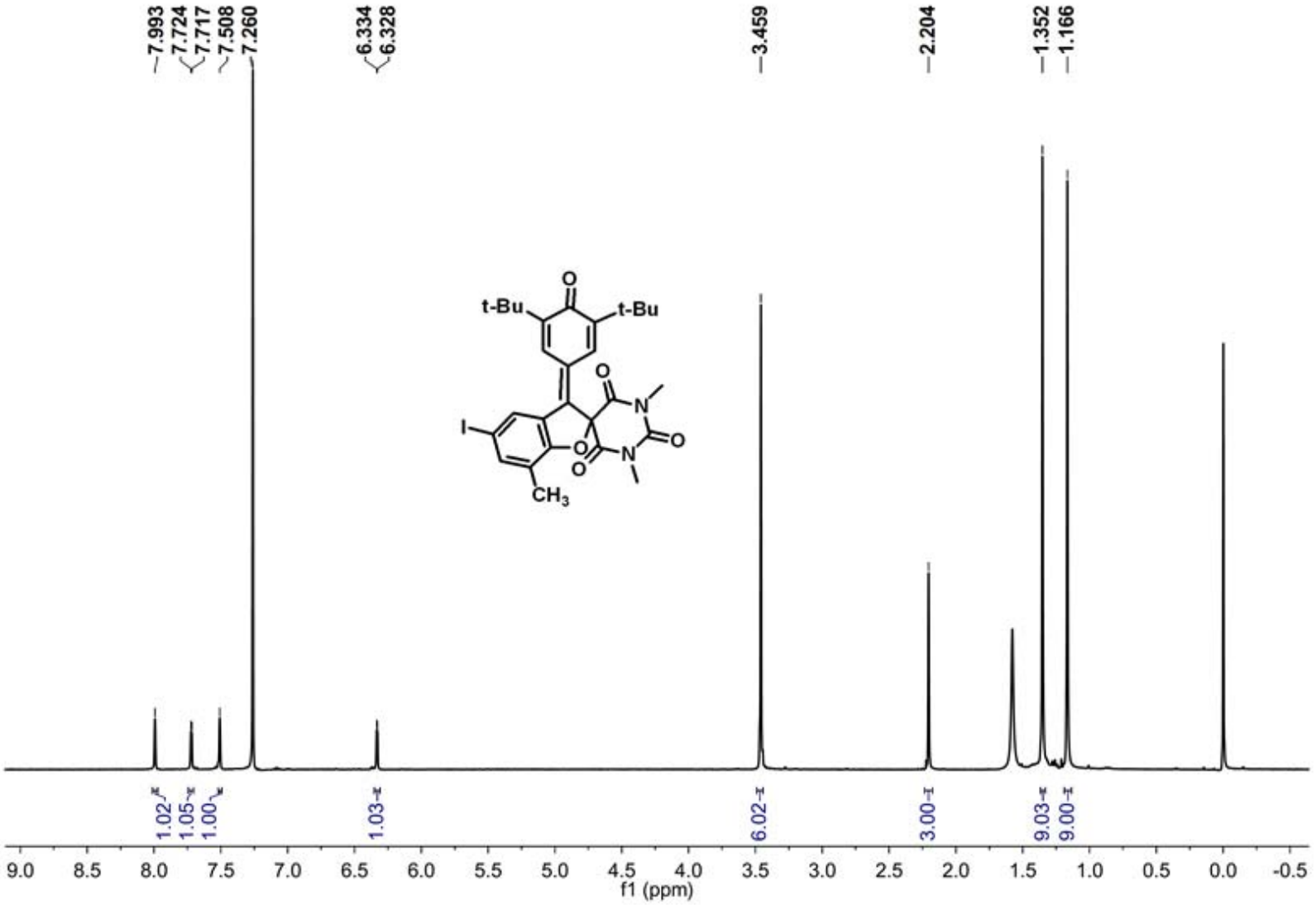
^{13}C NMR Spectrum of Compound 4e



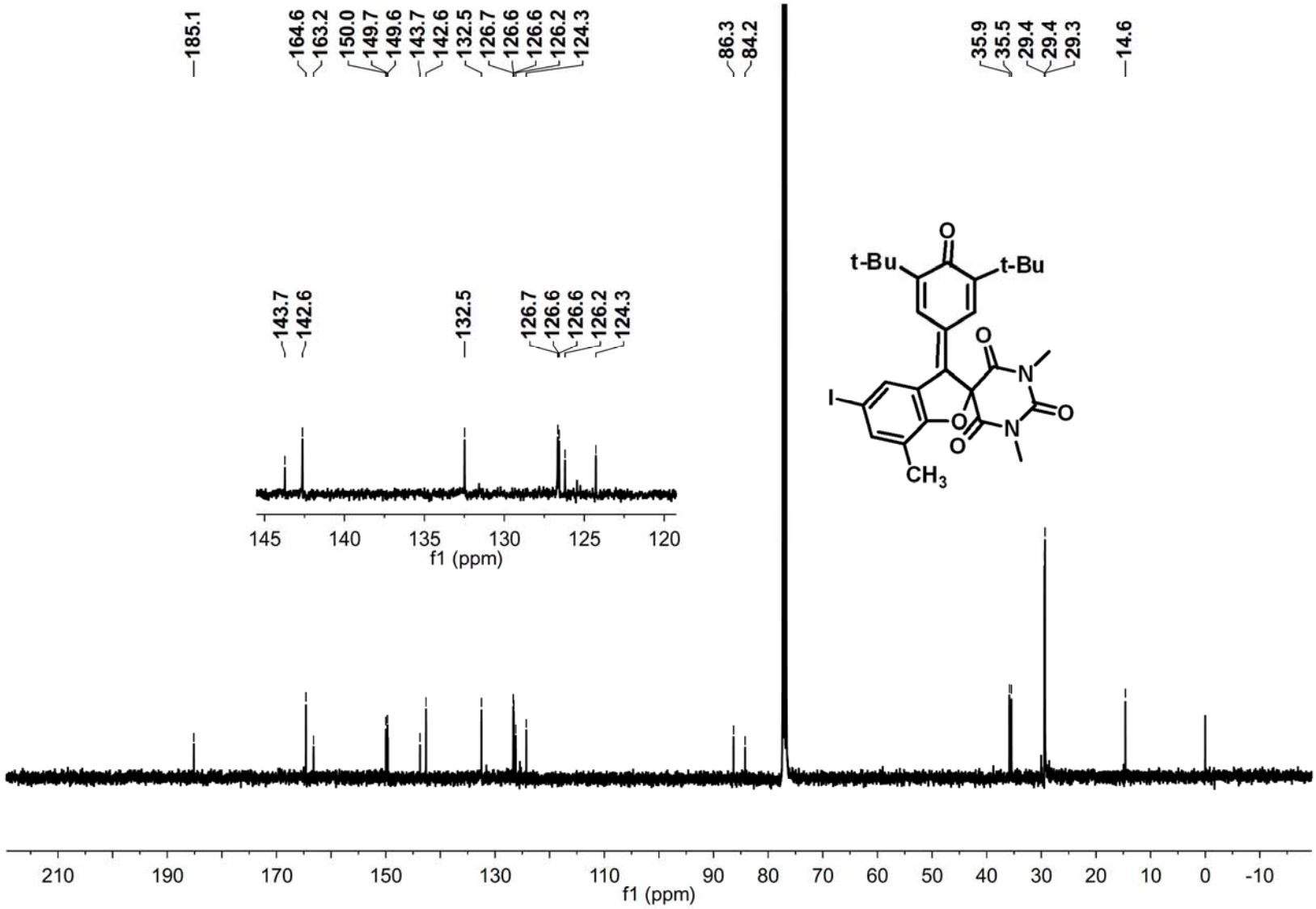
^{1}H NMR Spectrum of Compound 4f



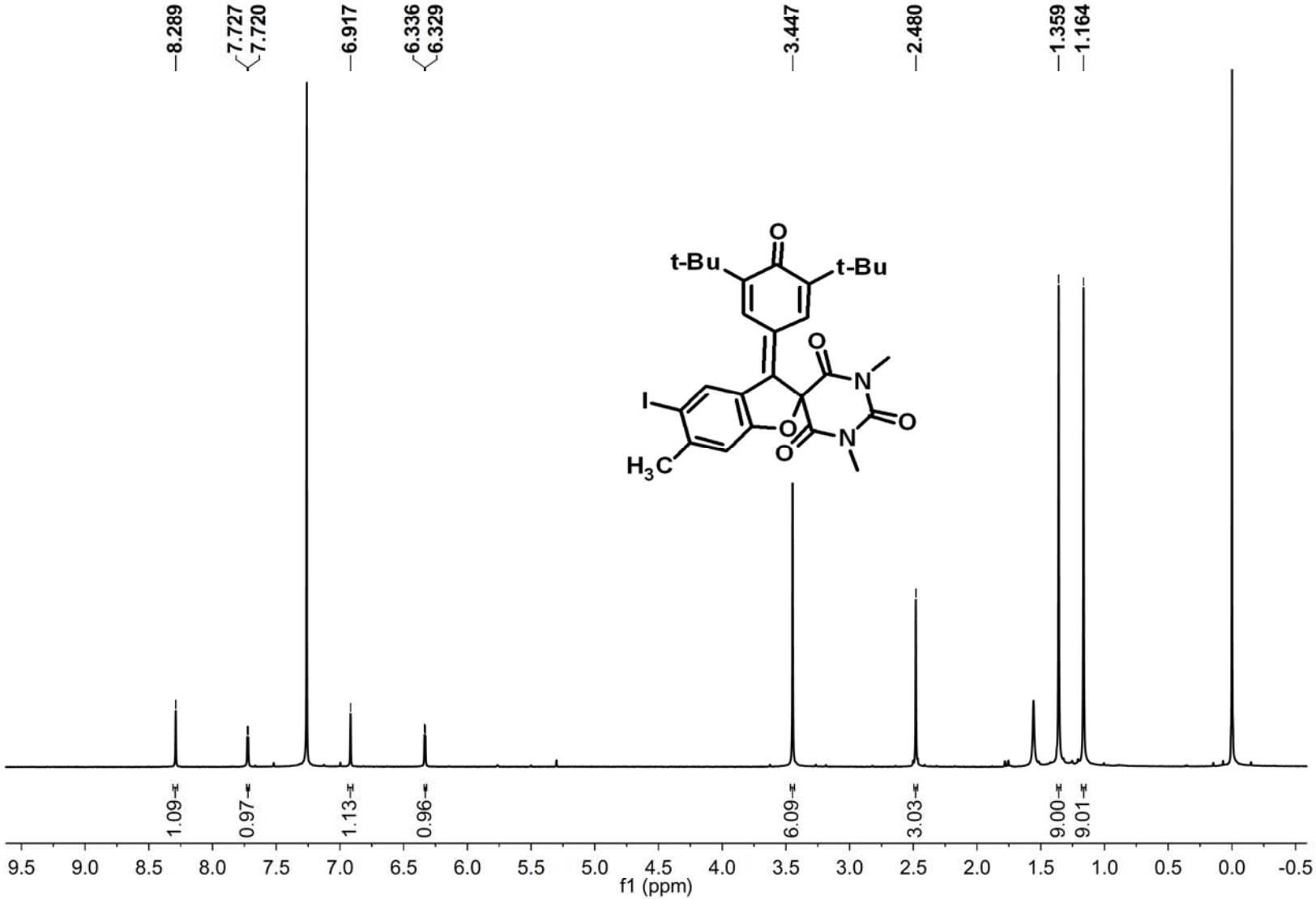
^{13}C NMR Spectrum of Compound 4f



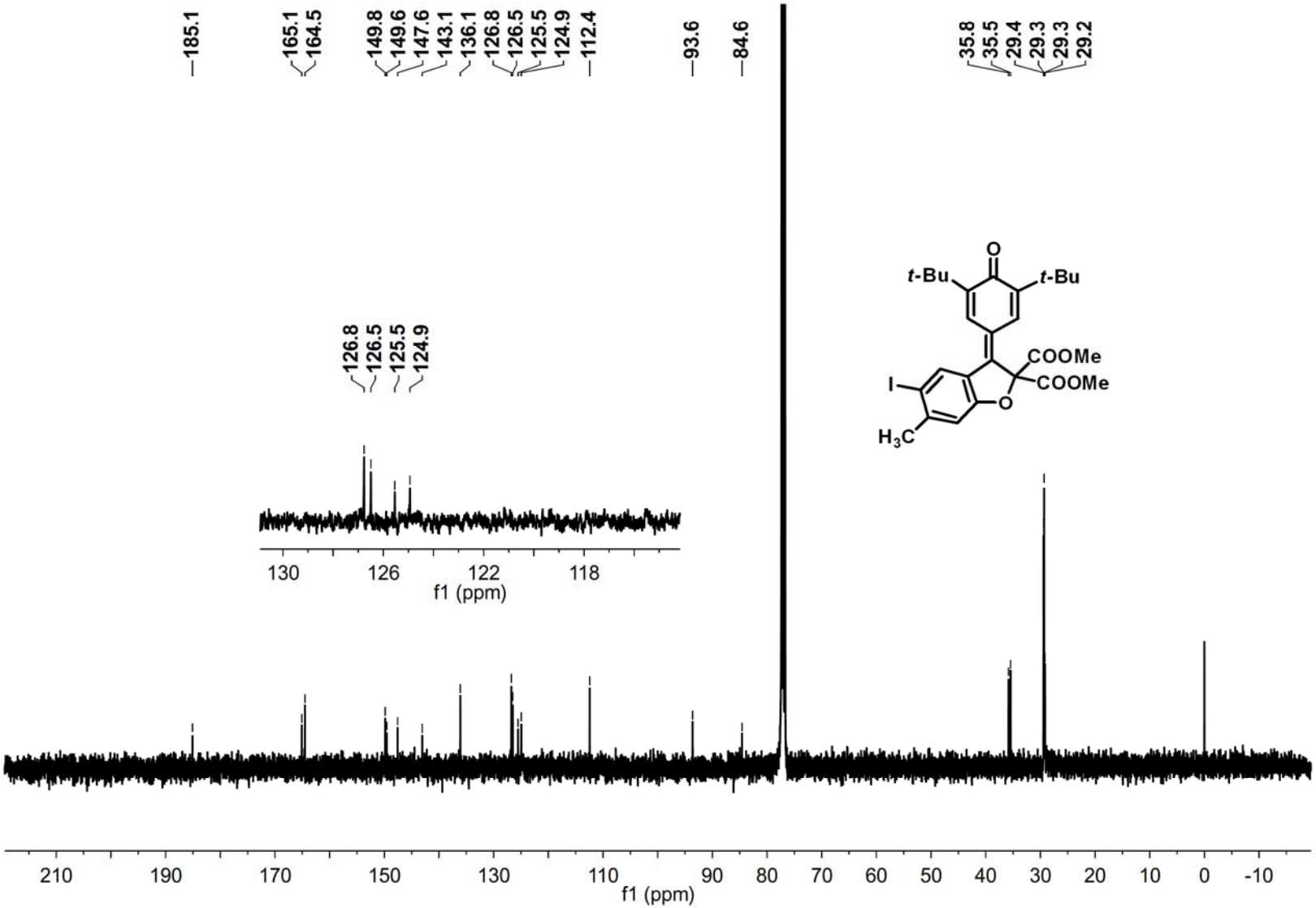
^{1}H NMR Spectrum of Compound 4g



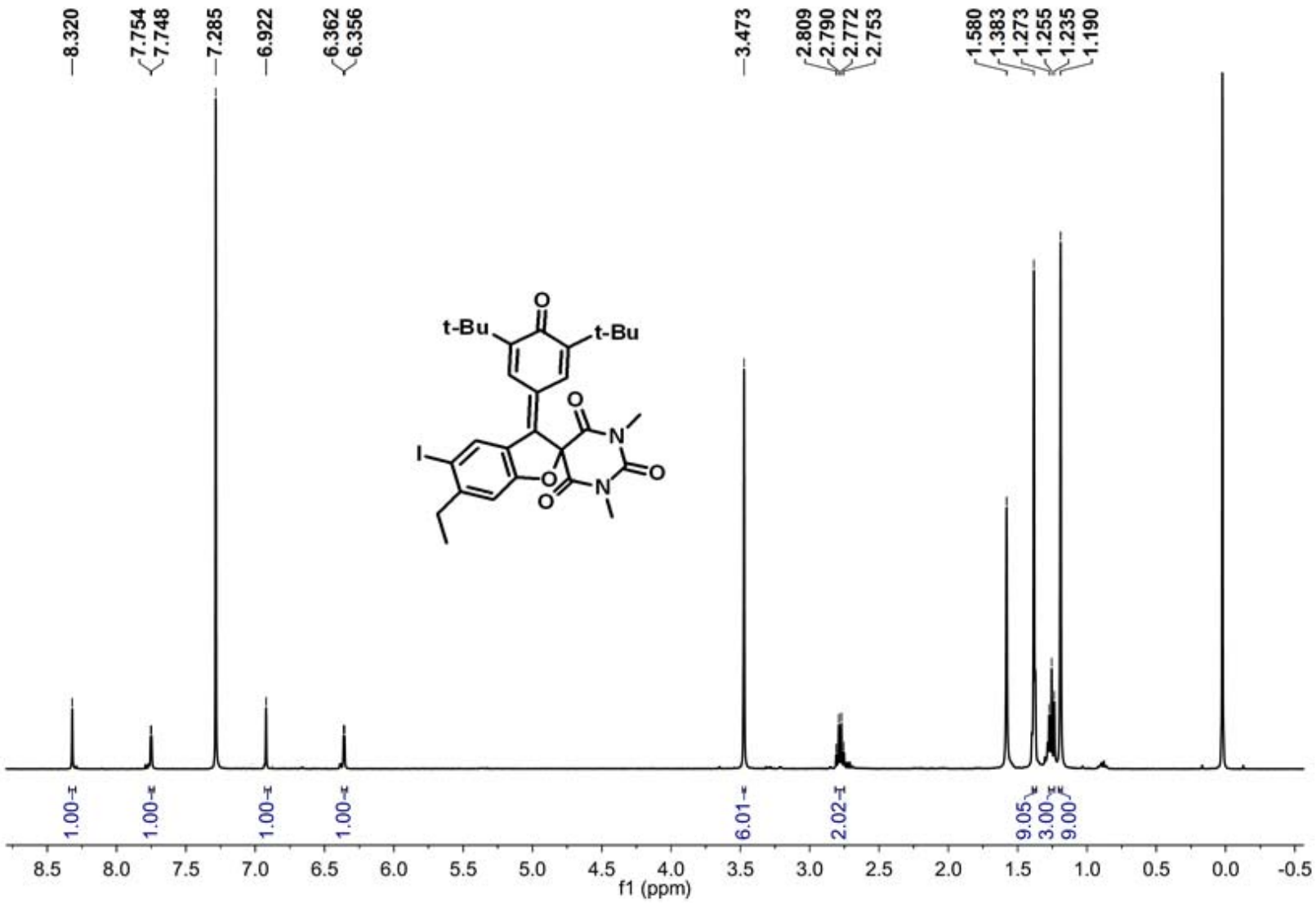
^{13}C NMR Spectrum of Compound 4g



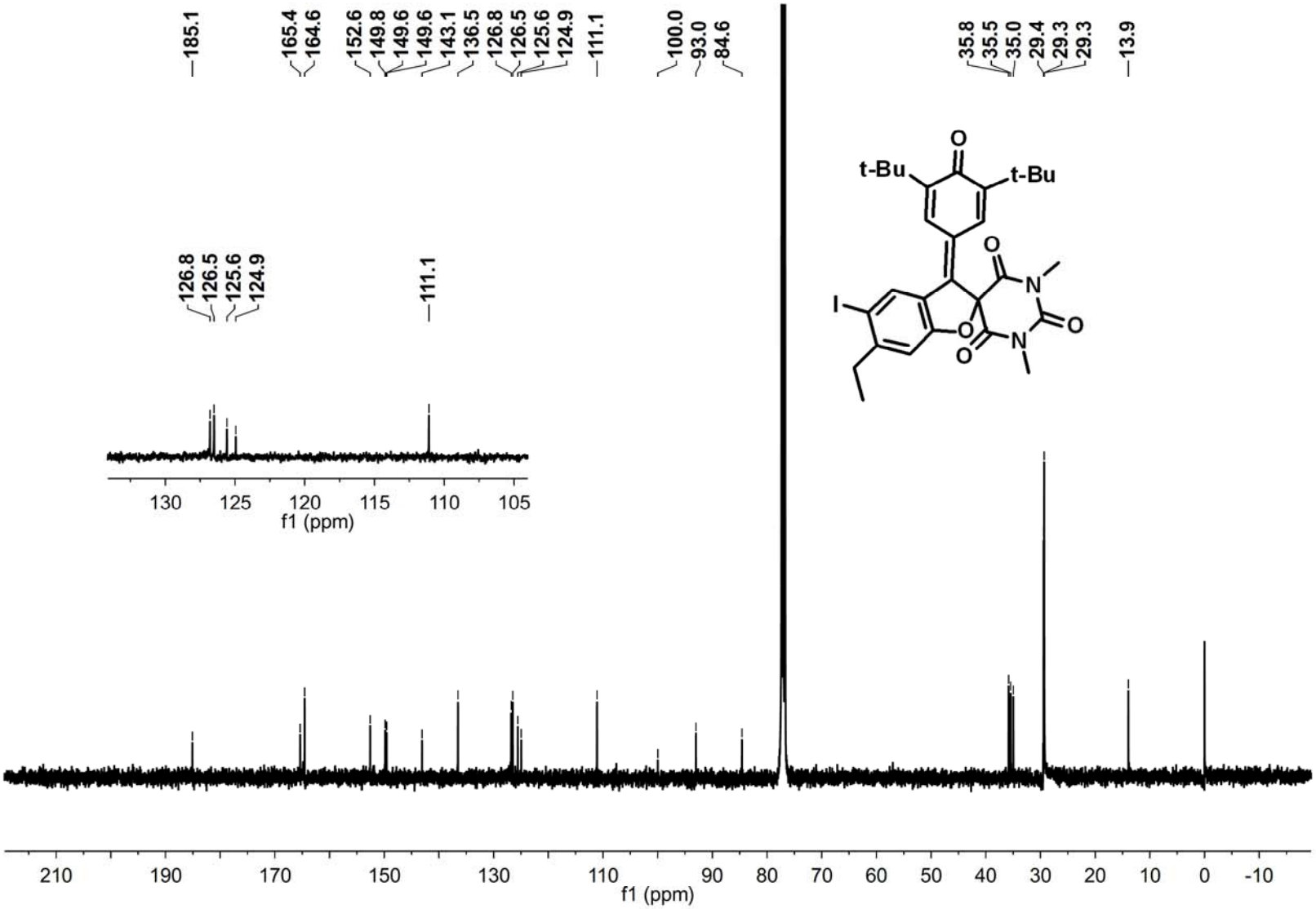
^{1}H NMR Spectrum of Compound 4h



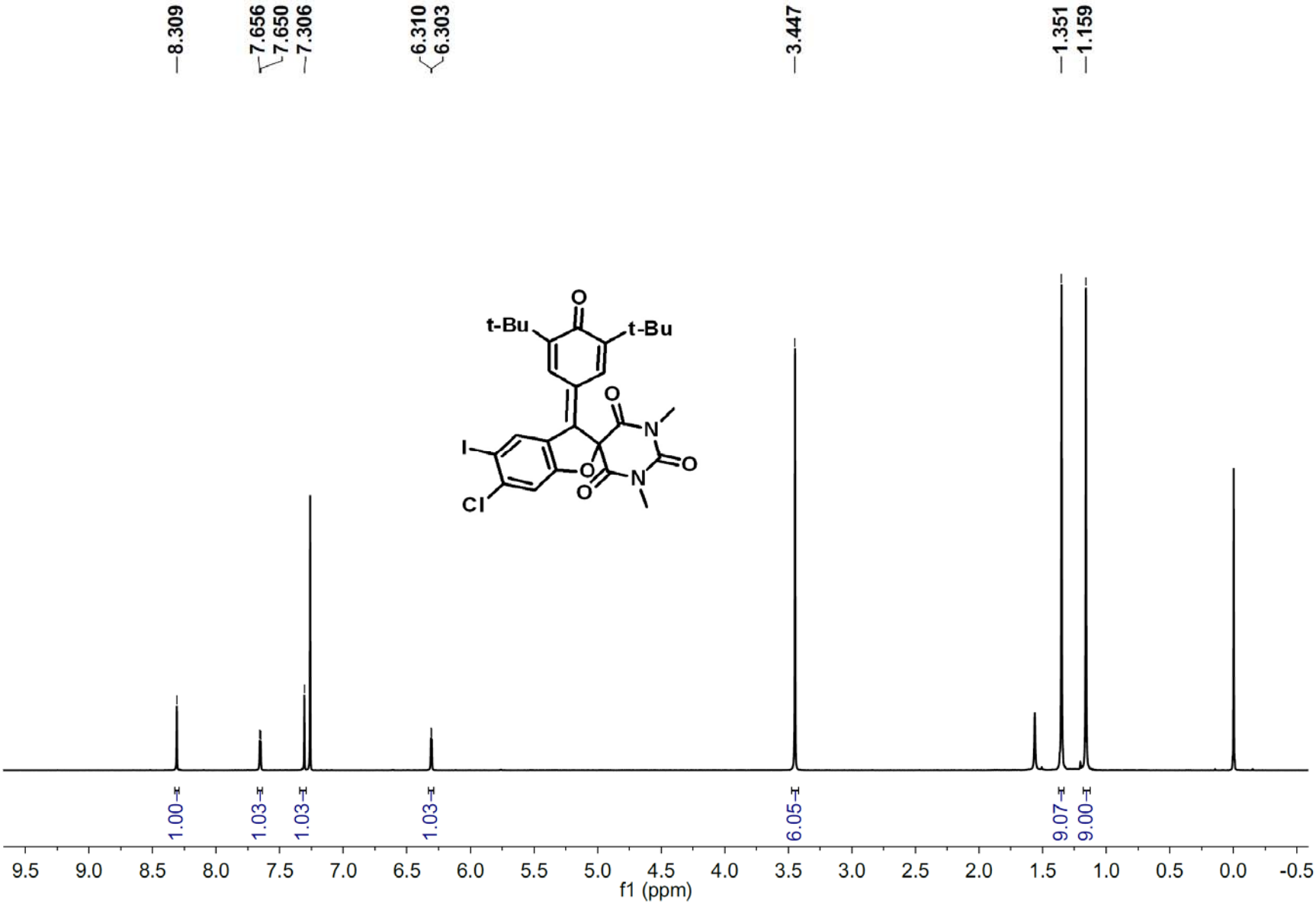
^{13}C NMR Spectrum of Compound 4h



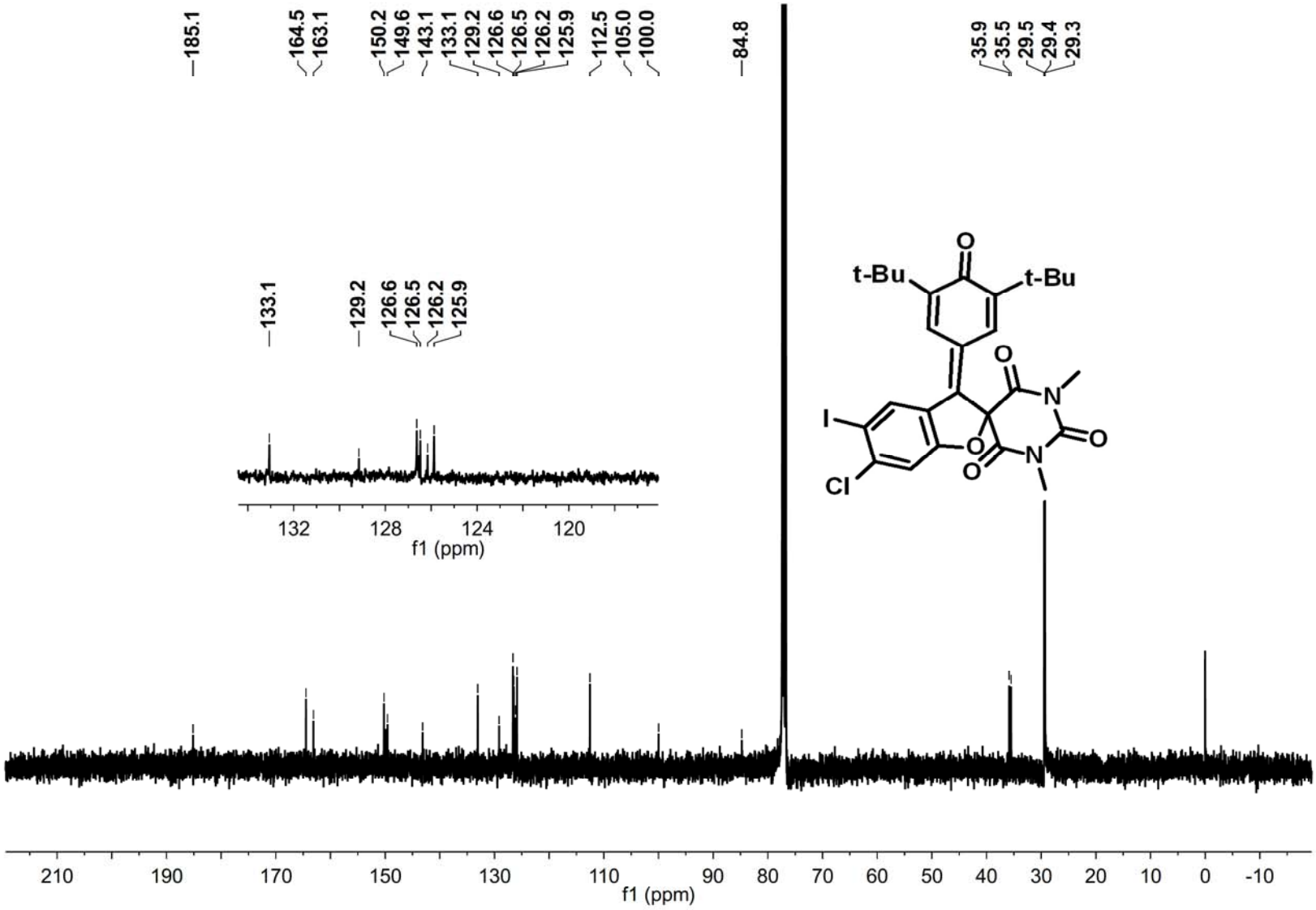
[1]H NMR Spectrum of Compound 4i



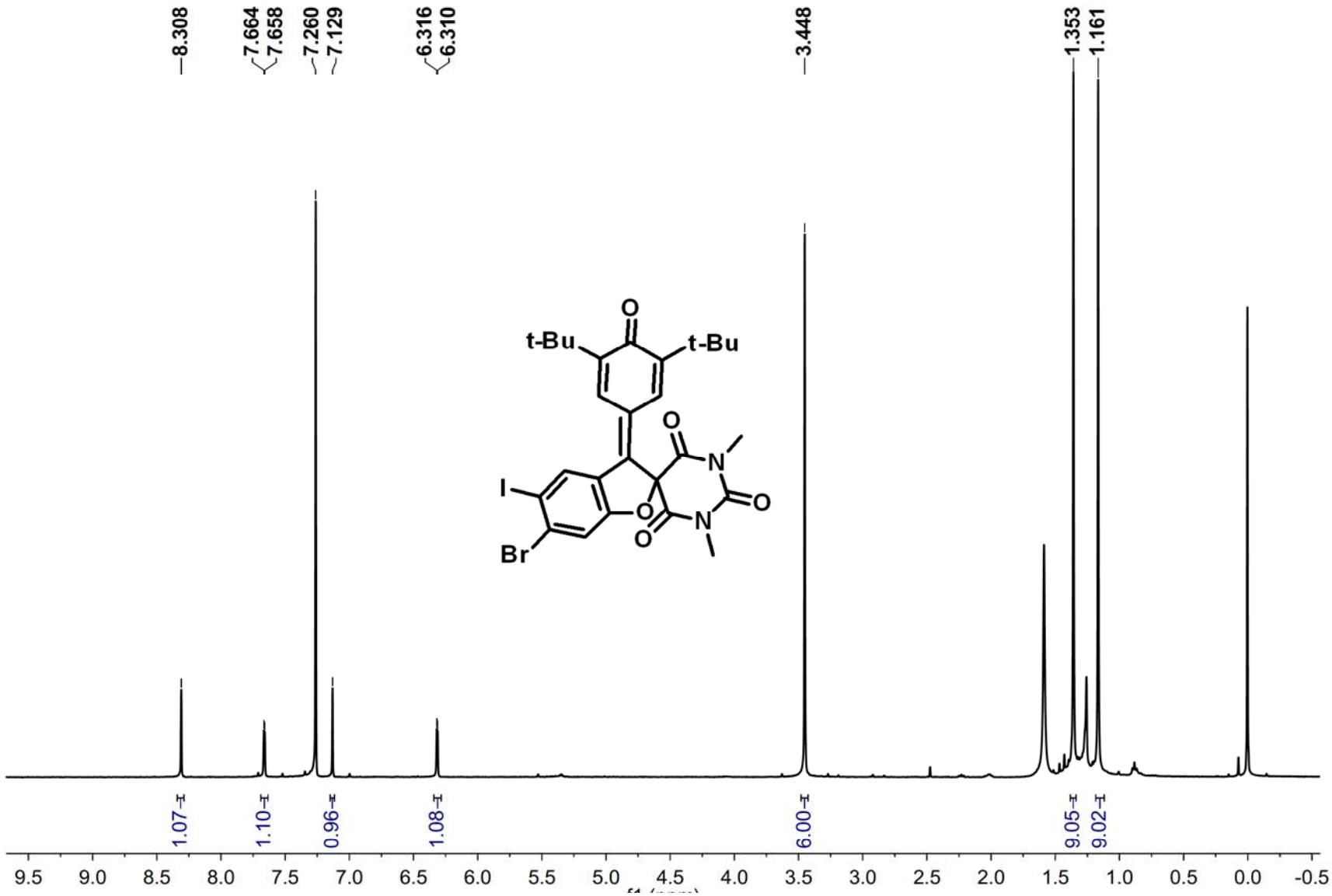
^{13}C NMR Spectrum of Compound 4i



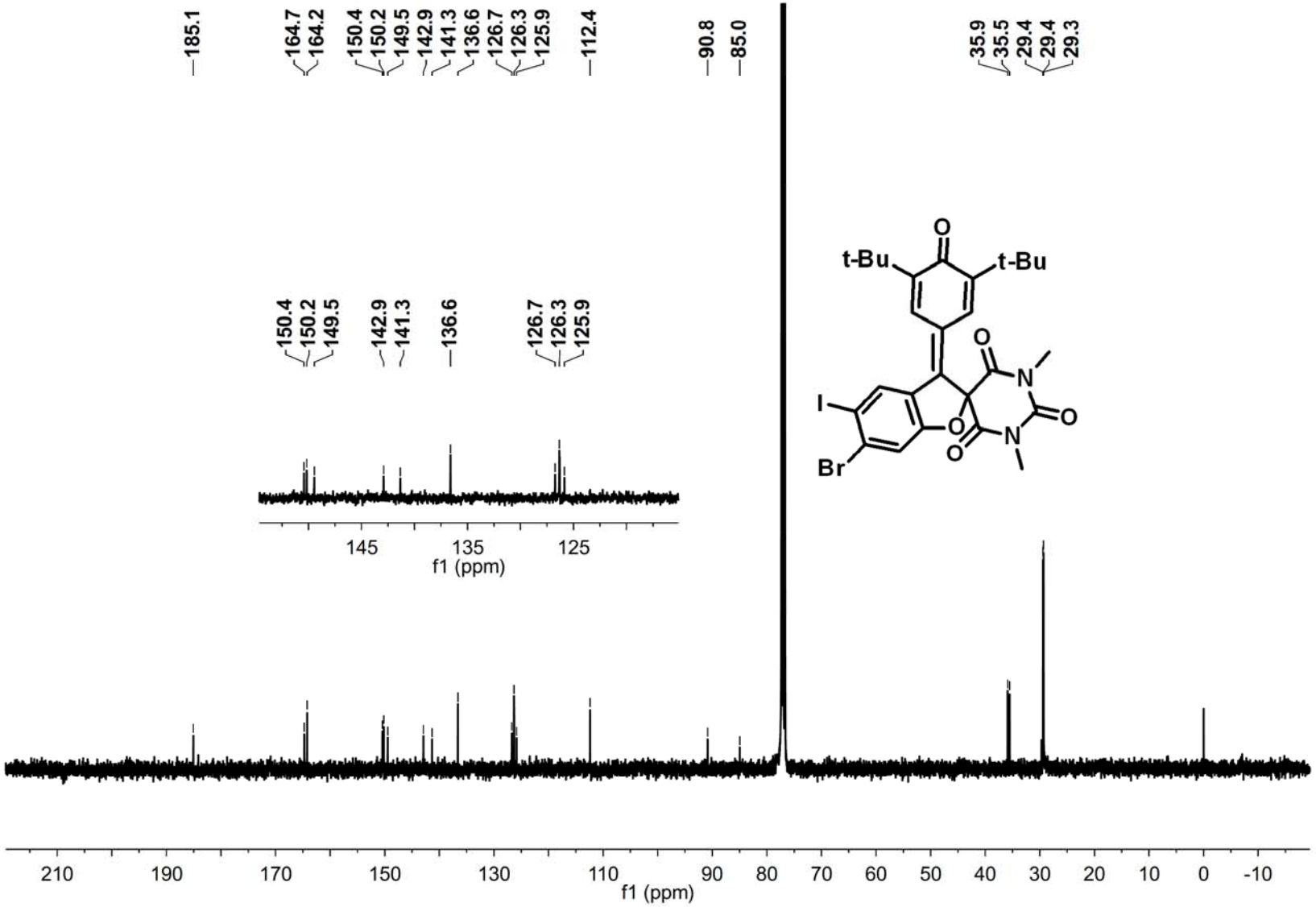
^{1}H NMR Spectrum of Compound 4j



^{13}C NMR Spectrum of Compound 4j



^{1}H NMR Spectrum of Compound 4k



^{13}C NMR Spectrum of Compound 4k