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Iron Catalyzed Peroxidation of Fluorenes and 9-Alkyl-9H-Fluorenes and Oxidative Cleavage of C=C Bond in 9-Alkylidene-Fluorenes

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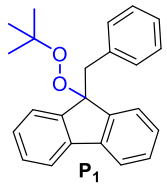
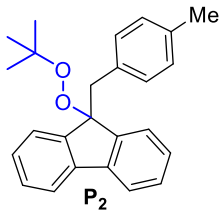
NMR data of peroxidative products:

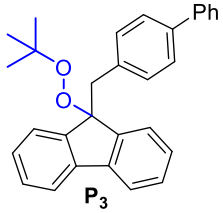
The following products are obtained by α-alkylation of fluorene with primary and secondary alcohols using the standard catalytic protocol. Known compounds are characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies and new compounds are characterized by ^{1}H, $^{13}C\{^{1}H\}$ NMR spectroscopies and HRMS.



9-benzyl-9-(tert-butylperoxy)-9H-fluorene (P_1):[1] The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_1** as a white semisolid (0.063 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 4H), 7.27 – 7.21 (m, 2H), 7.18 – 7.09 (m, 3H), 7.02 (d, *J* = 7.3 Hz, 2H), 3.48 (s, 2H), 1.17 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 145.1, 140.4, 136.4, 131.1, 128.9, 127.4, 126.9, 126.3, 125.9, 119.7, 90.8, 79.7, 42.3, 26.7.

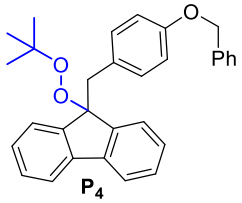


9-(tert-butylperoxy)-9-(4-methylbenzyl)-9H-fluorene (P_2):[1] The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_2** as a yellow semisolid (0.057 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.26 – 7.20 (m, 4H), 7.17 – 7.09 (m, 2H), 6.84 – 6.76 (m, 4H), 3.32 (s, 2H), 2.16 (s, 3H), 1.04 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 145.3, 140.5, 135.7, 133.3, 130.9, 128.8, 128.2, 126.9, 125.9, 119.7, 90.8, 79.6, 41.8, 26.7, 21.2.

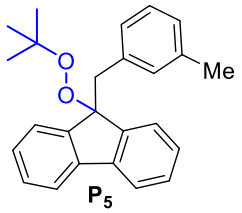


9-([1,1'-biphenyl]-4-ylmethyl)-9-(tert-butylperoxy)-9H-fluorene (P_3): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_3** as a yellow semisolid (0.068 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.2, 4.4 Hz, 2H), 7.34 – 7.18 (m, 5H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 3.40 (s, 1H), 1.06 (s, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3) δ 145.1, 141.0, 140.4, 138.9, 135.6, 131.5,

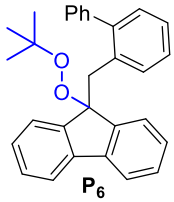
128.9, 128.8, 127.1, 127.0, 126.9, 126.1, 125.9, 119.8, 90.7, 79.8, 41.8, 26.7. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^+$ calcd for $C_{26}H_{19}$, 331.1487; found, 331.1475.



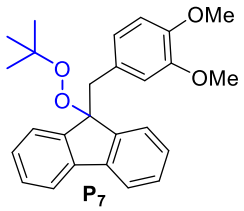
9-(4-(benzyloxy)benzyl)-9-(tert-butylperoxy)-9H-fluorene (P4): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P4** as a yellow semisolid (0.068 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.11 (m, 9H), 7.08 (t, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 2H), 3.27 (s, 2H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 157.4, 145.2, 140.4, 137.2, 132.0, 129.2, 128.8, 128.6, 127.9, 127.6, 126.9, 125.8, 119.7, 113.9, 90.8, 79.6, 69.9, 41.4, 26.7. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^+$ calcd for $C_{27}H_{21}O$, 361.1592; found, 361.1594.



9-(tert-butylperoxy)-9-(3-methylbenzyl)-9H-fluorene (P5):[1] The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P5** as a yellow solid (0.059 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 3.40 (s, 2H), 2.21 (s, 3H), 1.15 (s, 9H). ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 145.2, 140.4, 136.8, 136.3, 132.1, 128.8, 128.1, 127.3, 127.0, 126.9, 125.9, 119.7, 90.7, 79.7, 42.2, 26.7, 21.4.

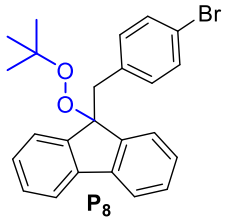


9-([1,1'-biphenyl]-2-ylmethyl)-9-(tert-butylperoxy)-9H-fluorene (P6): The crude product was purified by column chromatography (hexane/EtOAc 9.5:0.5 as eluent) to give pure product **P6** as a yellow semisolid (0.065 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.24 – 7.13 (m, 4H), 7.07 – 6.95 (m, 6H), 6.92 (d, *J* = 7.5 Hz, 2H), 6.62 – 6.51 (m, 2H), 3.34 (s, 2H), 1.03 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.6, 143.4, 141.7, 140.1, 134.6, 131.5, 130.0, 129.5, 128.7, 127.7, 127.0, 126.6, 126.4, 126.3, 125.7, 119.6, 90.9, 79.6, 37.5, 26.7. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^+$ calcd for $C_{26}H_{19}$, 331.1487; found, 331.1482.



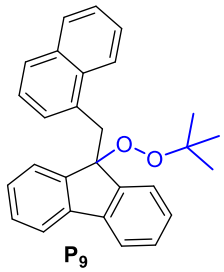
P_7

9-(tert-butylperoxy)-9-(3,4-dimethoxybenzyl)-9H-fluorene (P_7): The crude product was purified by column chromatography (hexane/EtOAc 9.5:0.5 as eluent) to give pure product **P_7** as a yellow semisolid (0.061 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 6.60 (d, *J* = 8.2 Hz, 1H), 6.53 (s, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 3.66 (s, 3H), 3.44 (s, 2H), 1.17 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 147.8, 147.4, 145.1, 140.5, 128.9, 128.8, 126.9, 125.8, 123.2, 119.8, 113.9, 110.1, 91.0, 79.7, 55.8, 55.6, 41.7, 26.7. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^+$ calcd for $C_{20}H_{19}O_2$, 315.1385; found, 315.1372.



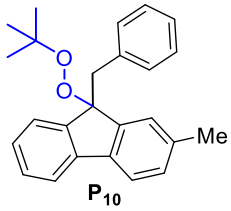
P_8

9-(4-bromobenzyl)-9-(tert-butylperoxy)-9H-fluorene (P_8): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_8** as a white solid (0.066 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 4H), 7.15 – 7.09 (m, 4H), 6.76 (d, *J* = 8.3 Hz, 2H), 3.31 (s, 2H), 1.04 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.7, 140.4, 135.4, 132.7, 130.6, 129.1, 127.0, 125.8, 120.4, 119.9, 90.5, 79.9, 41.5, 26.7. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^+$ calcd for $C_{20}H_{14}Br$, 333.0279; found, 333.0273.



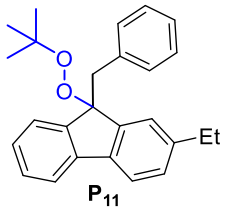
P_9

9-(tert-butylperoxy)-9-(naphthalen-1-ylmethyl)-9H-fluorene (P_9): The crude product was purified by column chromatography (hexane/EtOAc 9.5:0.5 as eluent) to give pure product **P_9** as a yellow semisolid (0.058 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.27 (m, 6H), 7.08 – 7.00 (m, 4H), 3.79 (s, 2H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.0, 133.5, 133.4, 129.8, 129.3, 128.7, 128.4, 127.4, 126.8, 125.9, 125.4, 125.2, 125.2, 124.9, 119.7, 90.9, 79.5, 38.8, 26.7. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^+$ calcd for $C_{24}H_{17}$, 305.1330; found, 305.1339.



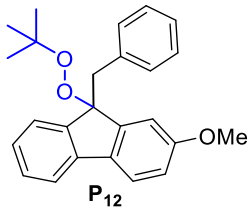
P_{10}

9-benzyl-9-(tert-butylperoxy)-2-methyl-9H-fluorene (P_{10}): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_{10}** as a pale yellowish oil (0.056 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.22 – 7.09 (m, 6H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.52 – 3.40 (m, 2H), 2.39 (s, 3H), 1.17 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.2, 145.0, 140.5, 137.8, 136.7, 136.6, 131.1, 129.6, 128.8, 127.4, 126.6, 126.4, 126.3, 126.0, 119.4, 119.3, 90.7, 79.7, 42.2, 26.8, 21.8. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^{+}$ calcd for $C_{21}H_{18}$, 270.1408; found, 270.1404.



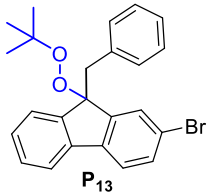
P_{11}

9-benzyl-9-(tert-butylperoxy)-2-ethyl-9H-fluorene (P_{11}): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_{11}** as a colourless oil (0.057 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.23 – 7.11 (m, 5H), 7.14 – 7.00 (m, 3H), 3.53 – 3.37 (m, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.16 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.2, 145.1, 143.2, 140.5, 138.0, 136.7, 131.2, 128.8, 128.5, 127.4, 126.5, 126.3, 125.9, 125.6, 119.5, 119.4, 90.7, 79.7, 42.2, 29.2, 26.7, 16.0. HRMS (ESI-TOF) m/z: [M + H_2O]$^{+}$ calcd for $C_{26}H_{30}O_3$, 390.2194; found, 390.2206.



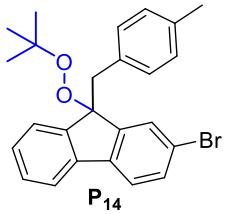
P_{12}

9-benzyl-9-(tert-butylperoxy)-2-methoxy-9H-fluorene (P_{12}): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_{12}** as a pale yellowish oil (0.055 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.19 – 7.12 (m, 4H), 7.09 – 7.03 (m, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 3.57 – 3.32 (m, 2H), 1.17 (s, 9H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 159.1, 146.9, 145.0, 140.4, 136.5, 133.2, 131.2, 128.9, 127.5, 126.4, 125.8, 125.7, 120.4, 119.0, 114.8, 111.6, 90.5, 79.7, 55.6, 42.4, 26.8. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^{+}$ calcd for $C_{21}H_{18}O$, 286.1358; found, 286.1366.



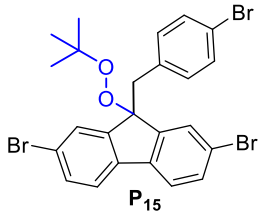
P13

9-benzyl-2-bromo-9-(tert-butylperoxy)-9H-fluorene (P13):[1] The crude product was purified by column chromatography (hexane/EtOAc 9.8:0.2 as eluent) to give pure product **P13** as a white solid (0.069 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 3H), 7.42 – 7.33 (m, 2H), 7.32 – 7.25 (m, 2H), 7.19 (d, *J* = 5.0 Hz, 3H), 7.09 – 7.00 (m, 2H), 3.50 (d, *J* = 13.9 Hz, 1H), 3.44 (d, *J* = 13.6 Hz, 1H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.4, 144.7, 139.34, 139.3, 135.8, 131.8, 131.0, 129.1, 128.9, 127.6, 127.4, 126.6, 125.8, 121.1, 120.7, 119.8, 90.6, 79.9, 42.3, 26.7.



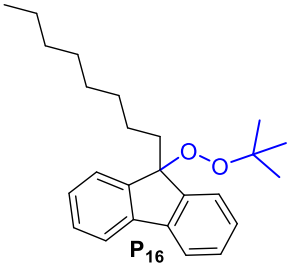
P14

2-bromo-9-(tert-butylperoxy)-9-(4-methylbenzyl)-9H-fluorene (P14):[1] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.9:0.1 as eluent) to give pure product **P14** as yellow solid (0.068 g, 78%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 10.9, 2.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.15 (t, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 3.27 (m, 2H), 2.17 (s, 3H), 1.04 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.5, 144.8, 139.4, 139.3, 136.0, 132.7, 131.8, 130.9, 129.1, 129.0, 128.3, 127.3, 125.9, 121.1, 120.7, 119.8, 90.6, 79.9, 41.9, 26.7, 21.2.

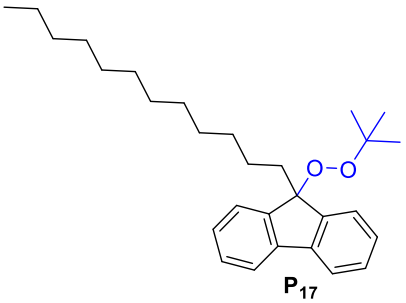


P15

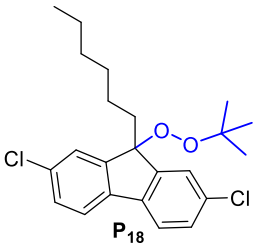
2,7-dibromo-9-(4-bromobenzyl)-9-(tert-butylperoxy)-9H-fluorene (P15): The crude product was purified by column chromatography (hexane/EtOAc 9.8:0.2 as eluent) to give pure product **P15** as a yellow semisolid (0.086 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.34 (s, 2H), 1.16 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.6, 138.1, 137.7, 134.2, 132.3, 130, 129.6, 129.1, 121.8, 121.3, 89.9, 80.5, 41.8, 26.6. HRMS (ESI-TOF) m/z: $[M - OOtBu]^+$ calcd for $C_{20}H_{12}Br_3$, 490.8469; found, 490.8466.



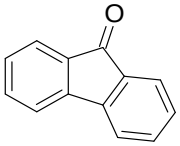
9-(tert-butylperoxy)-9-octyl-9H-fluorene (P_{16}):[1] The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_{16}** as a yellow oil (0.056 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 2.35 – 2.26 (m, 2H), 1.32 – 1.14 (m, 10H), 1.12 (s, 9H), 0.88 – 0.80 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.7, 140.8, 128.8, 127.3, 125.0, 119.7, 91.2, 79.3, 35.6, 31.9, 30.0, 29.3, 29.3, 26.6, 23.7, 22.7, 14.2.



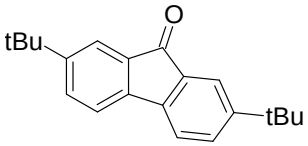
9-(tert-butylperoxy)-9-dodecyl-9H-fluorene (P_{17}): The crude product was purified by column chromatography (hexane/EtOAc mixture 9.9:0.1 as eluent) to give pure product **P_{17}** as yellow oily liquid (0.064 g, 76%).^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 2.30 – 2.27 (m, 2H), 1.31 – 1.12 (m, 18H), 1.10 (s, 9H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.86 – 0.81 (m, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 145.7, 140.8, 128.8, 127.3, 125.0, 119.8, 91.3, 79.3, 35.7, 32.0, 30.0, 29.8, 29.7, 29.6, 29.5, 29.4, 26.7, 23.7, 22.8, 14.3. HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ calcd for $C_{29}H_{42}O_2Na$, 445.3082; found, 445.3086.



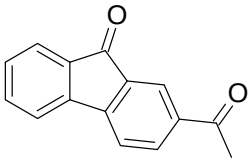
9-(tert-butylperoxy)-2,7-dichloro-9-hexyl-9H-fluorene (P_{18}): The crude product was purified by column chromatography (hexane/EtOAc 9.9:0.1 as eluent) to give pure product **P_{18}** as a yellow oil (0.059 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 9.0, 4.8 Hz, 4H), 7.35 (dd, *J* = 8.0, 1.7 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.29 – 1.13 (m, 6H), 1.11 (s, 9H), 0.84 – 0.81 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 147.6, 138.2, 133.4, 129.2, 125.3, 120.8, 90.8, 79.8, 35.7, 31.6, 29.6, 26.6, 23.5, 22.7, 14.1. HRMS (ESI-TOF) m/z: [M - OO*t*Bu]$^{+}$ calcd for $C_{19}H_{19}Cl_2$, 317.0864; found, 317.0848.



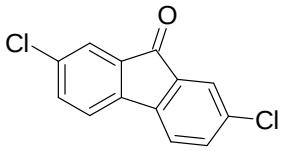
9H-fluoren-9-one (Q_1):[2] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.5:0.5 as eluent) to give pure product **Q_1** as yellow solid (0.033 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.36 (m, 4H), 7.22 – 7.16 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.0, 144.5, 134.8, 134.2, 129.2, 124.4, 120.4.



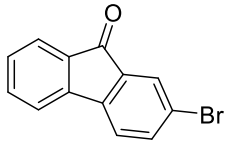
2,7-di-tert-butyl-9H-fluoren-9-one (Q_2):[2] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.8:0.2 as eluent) to give pure product **Q_2** as yellow solid (0.052 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.4 Hz, 2H), 7.40 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 1.26 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 152.4, 142.0, 134.7, 131.6, 121.7, 120.0, 35.1, 31.3.



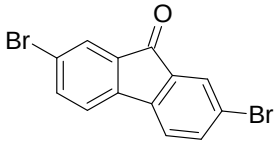
2-acetyl-9H-fluoren-9-one (Q_3):[3] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.0:1.0 as eluent) to give pure product **Q_3** as yellow solid (0.040 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.13 (d, *J* = 7.8, 1.3 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR$\{^1H\}$ (101 MHz, $CDCl_3$) δ 196.7, 192.9, 148.6, 143.4, 137.9, 135.2, 135.0, 134.9, 134.4, 130.3, 124.8, 124.3, 121.4, 120.6, 26.9.



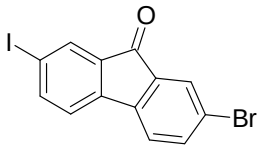
2,7-dichloro-9H-fluoren-9-one (Q_4):[2] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.5:0.5 as eluent) to give pure product **Q_4** as yellow solid (0.041 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.3 Hz, 2H), 7.44 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.2, 141.9, 135.5, 135.4, 134.7, 125.1, 121.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.3 Hz, 1H), 7.43 (dt, *J* = 16.5, 4.8 Hz, 2H).



2-bromo-9H-fluoren-9-one (Q_5):[3] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.5:0.5 as eluent) to give pure product **Q_5** as yellowish solid (0.044 g, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 (d, *J* = 3.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.29 (m, 1H). ^{13}C(^{1}H) NMR (101 MHz, $CDCl_3$) δ 192.5, 143.7, 143.0, 137.2, 135.8, 135.1, 133.7, 129.5, 127.6, 124.7, 123.0, 121.8, 120.5.



2,7-dibromo-9H-fluoren-9-one (Q_6):[3] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.5:0.5 as eluent) to give pure product **Q_6** as yellow solid (0.053 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.2 Hz, 2H), 7.59 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 142.3, 137.6, 135.3, 127.9, 123.4, 122.



2-bromo-7-iodo-9H-fluoren-9-one (Q_7):[4] The crude product was purified by column chromatography (hexane/EtOAc mixture 9.5:0.5 as eluent) to give pure product **Q_7** as yellowish solid (0.062 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 1.2 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.0, 143.6, 142.9, 142.4, 137.5, 135.3, 135.0, 133.7, 127.9, 123.6, 122.2, 122, 94.

^{1}H and ^{13}C NMR spectra of products:

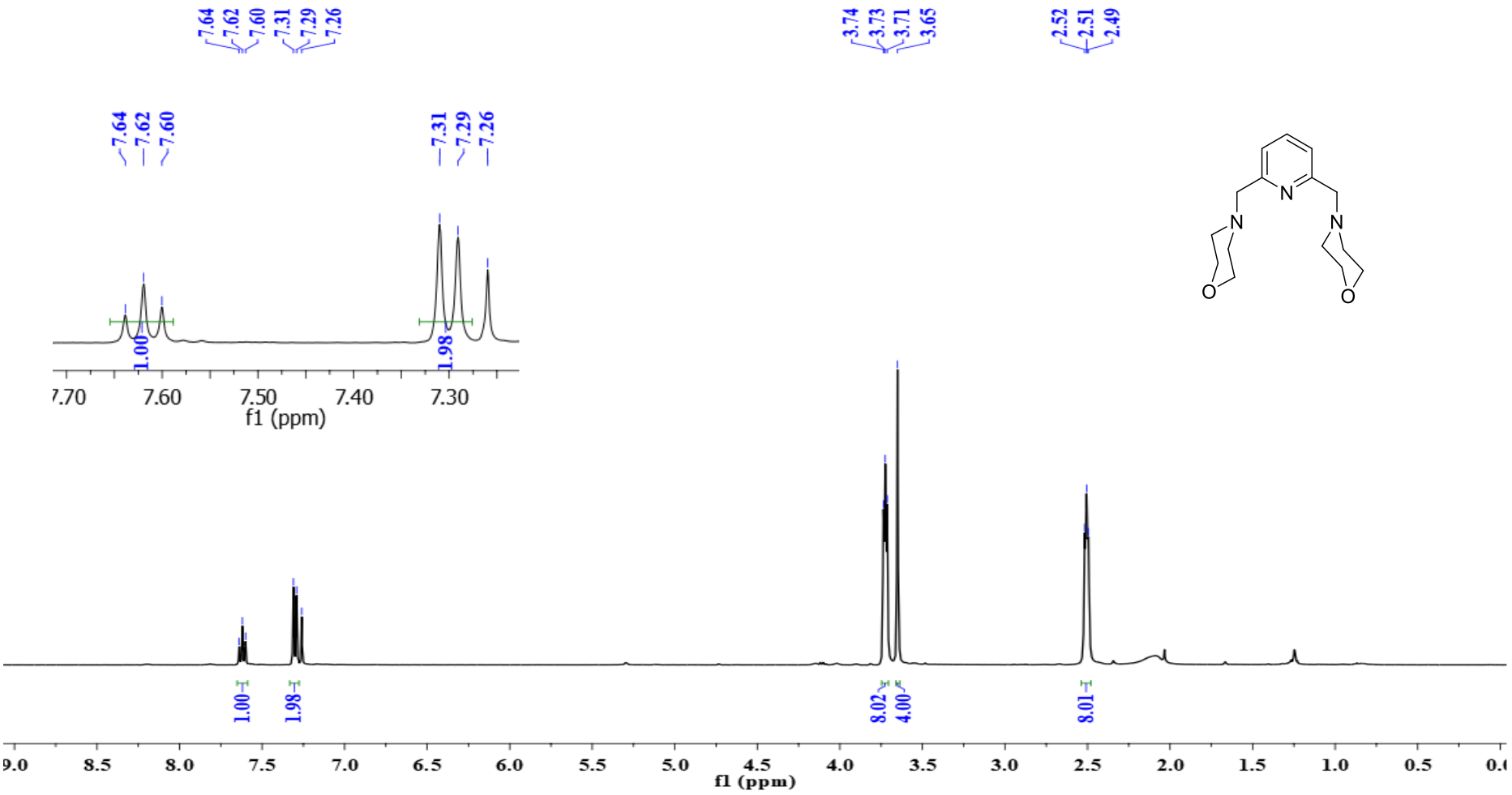


Figure S01. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,6-bis(morpholinomethyl)pyridine (**L_1**).

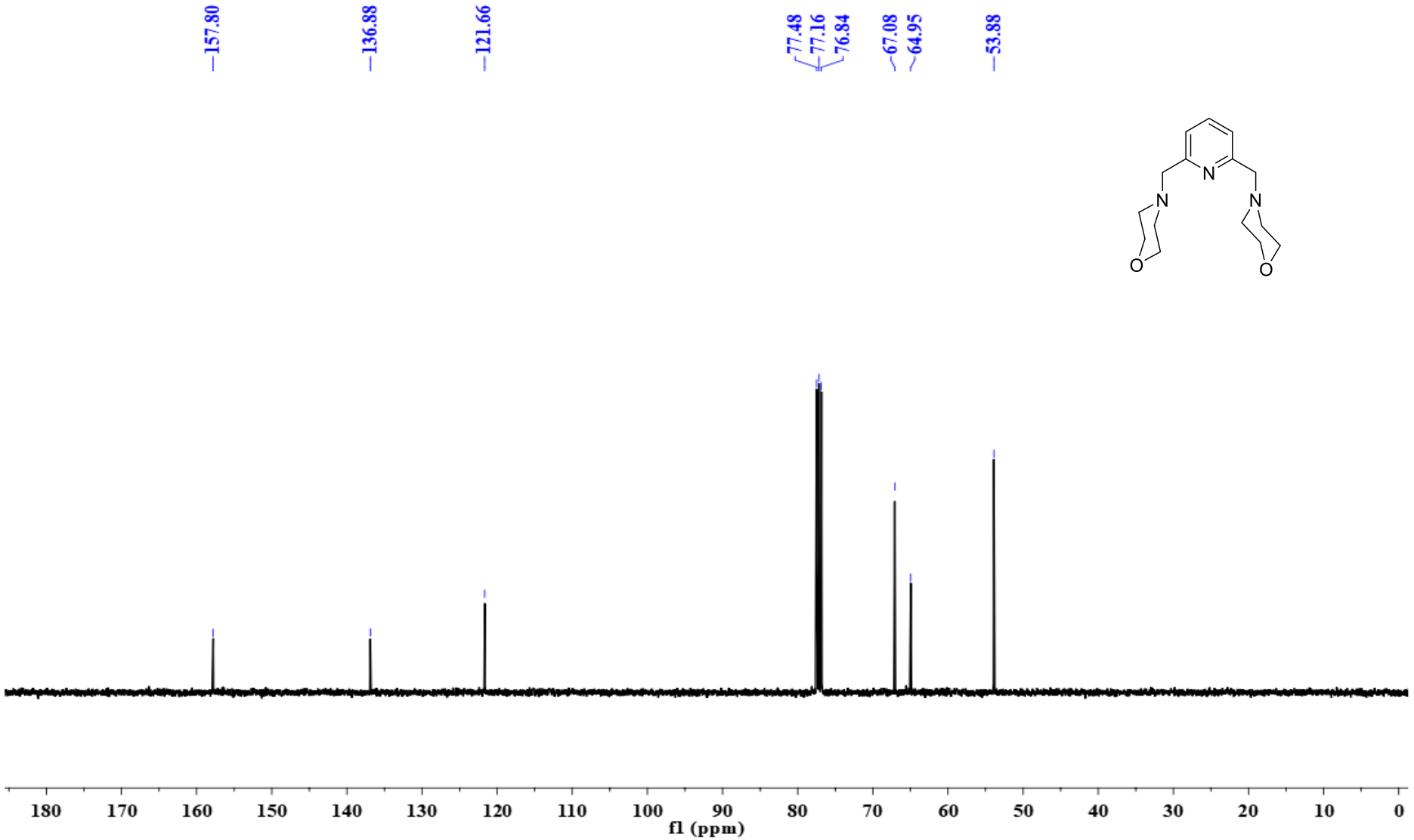


Figure S02. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,6-bis(morpholinomethyl)pyridine (**L_1**).

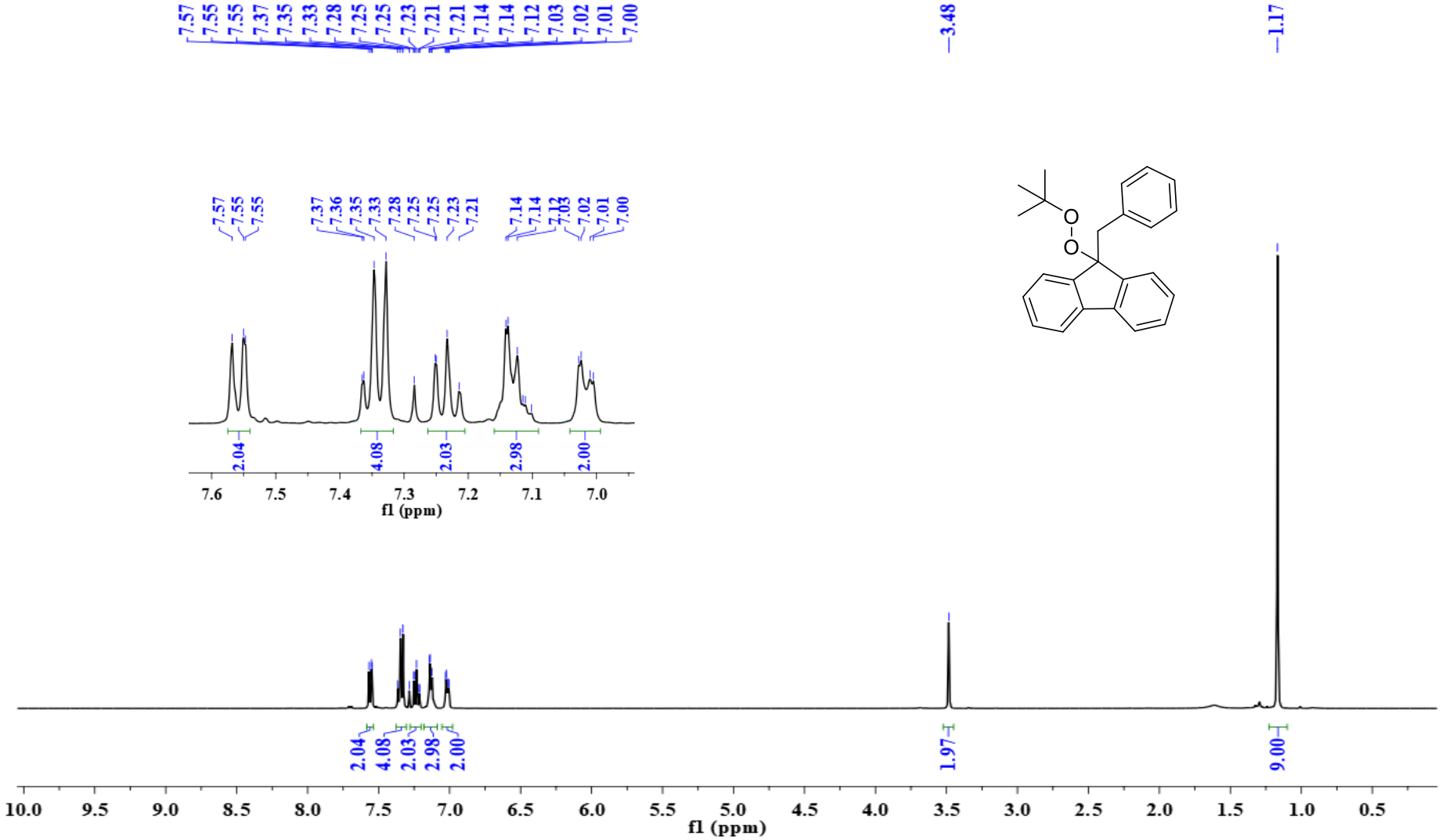


Figure S03. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-9H-fluorene (**P₁**).

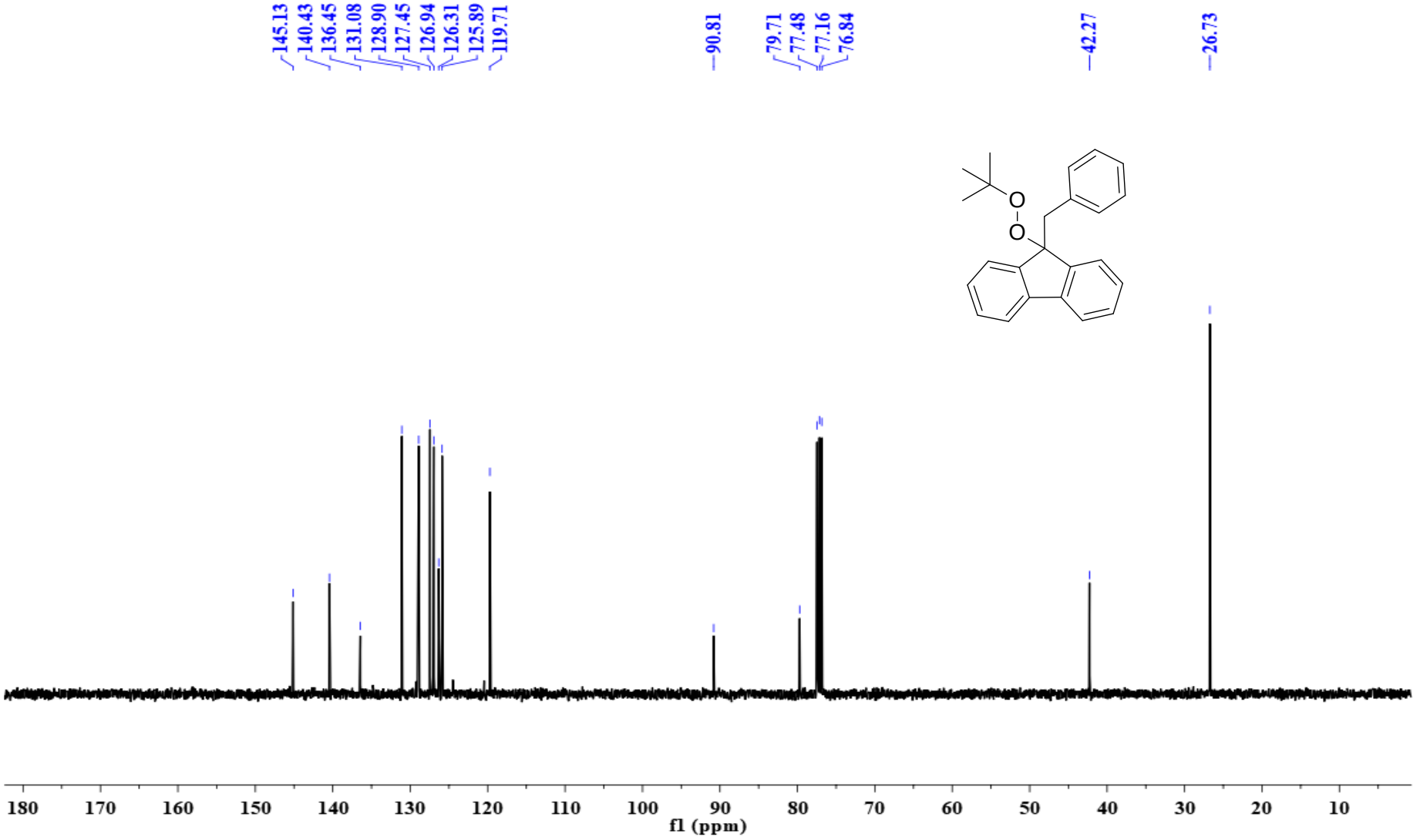


Figure S04. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-9H-fluorene (**P_1**).

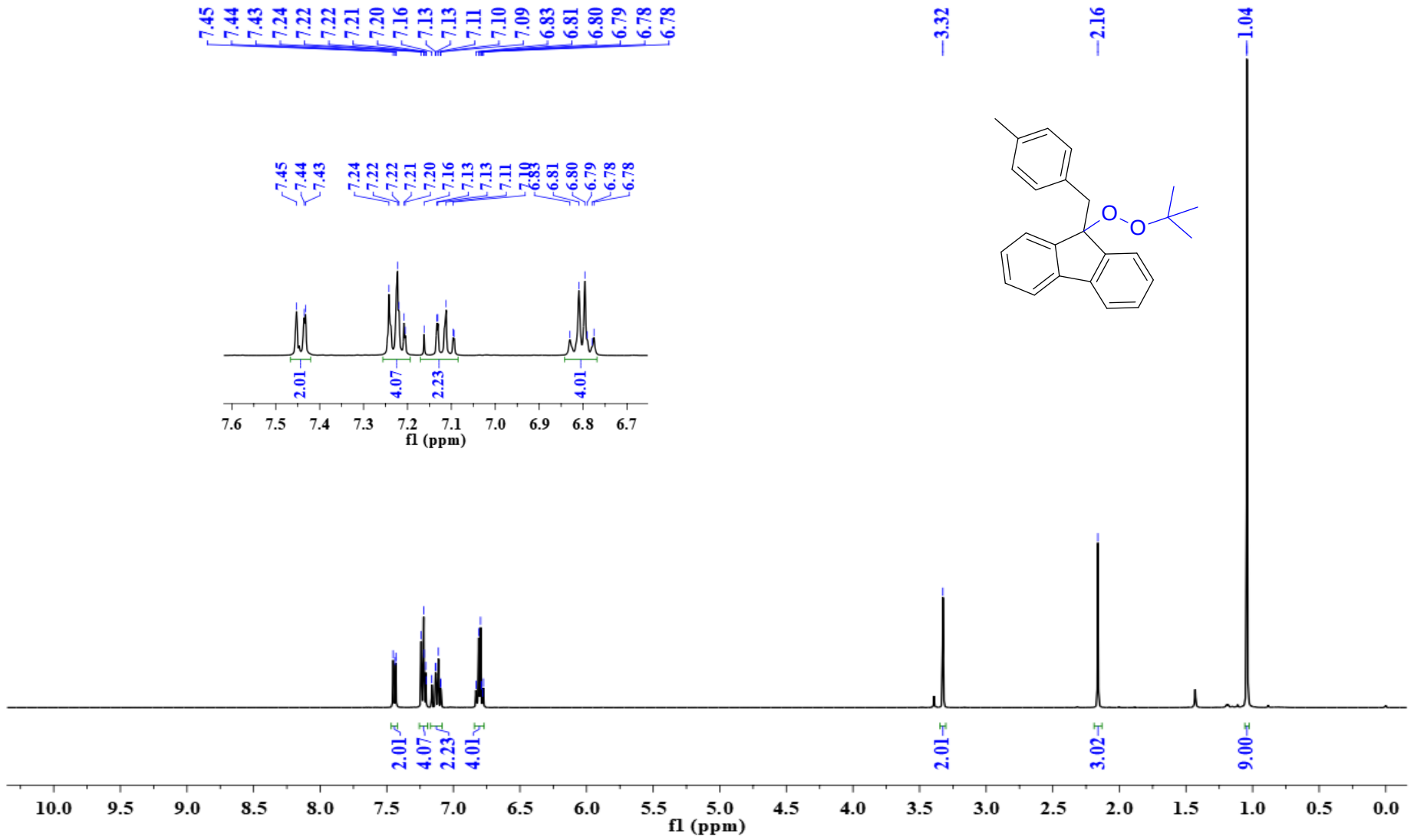


Figure S05. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(4-methylbenzyl)-9H-fluorene (**P_2**).

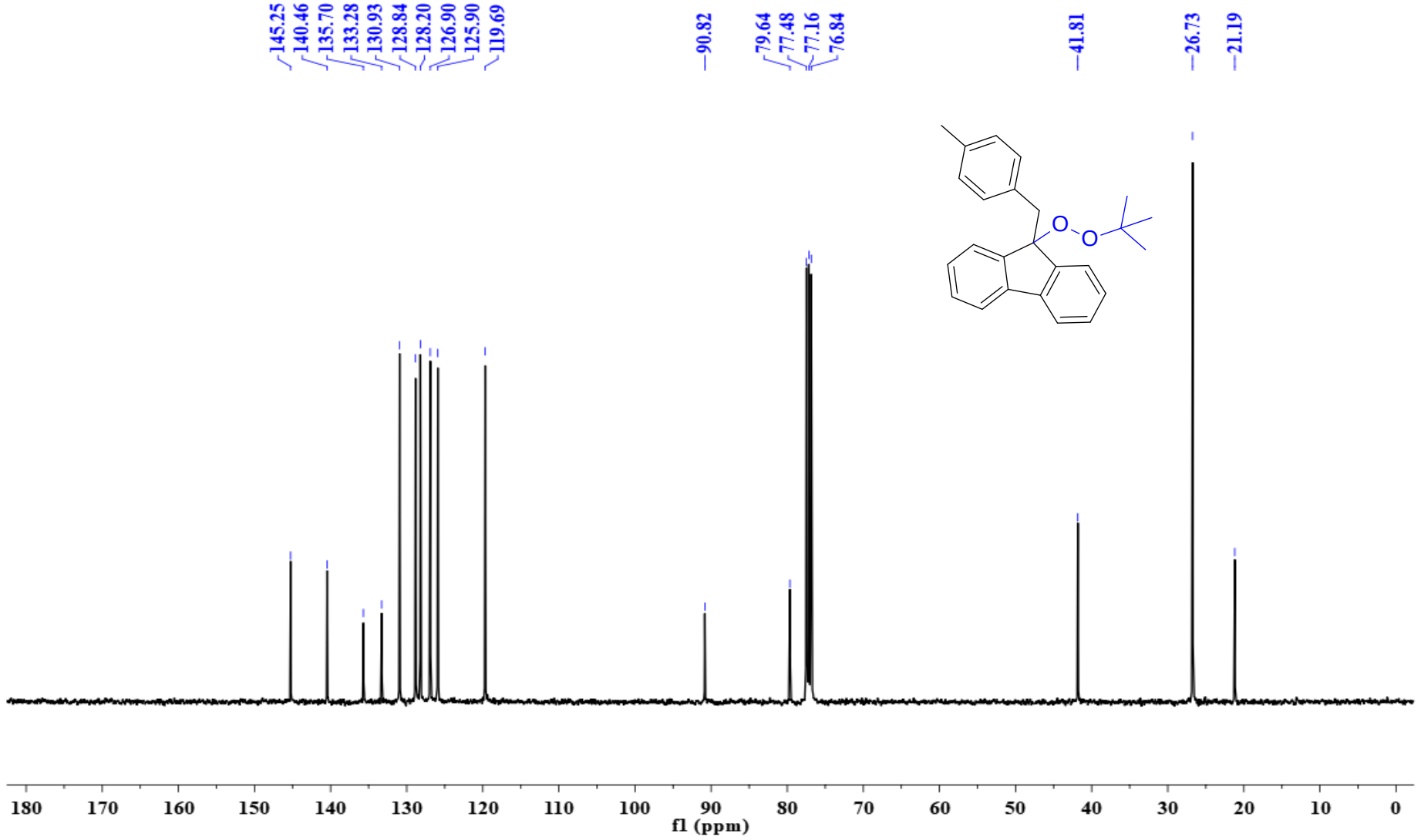


Figure S06. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(4-methylbenzyl)-9H-fluorene (**P_2**).

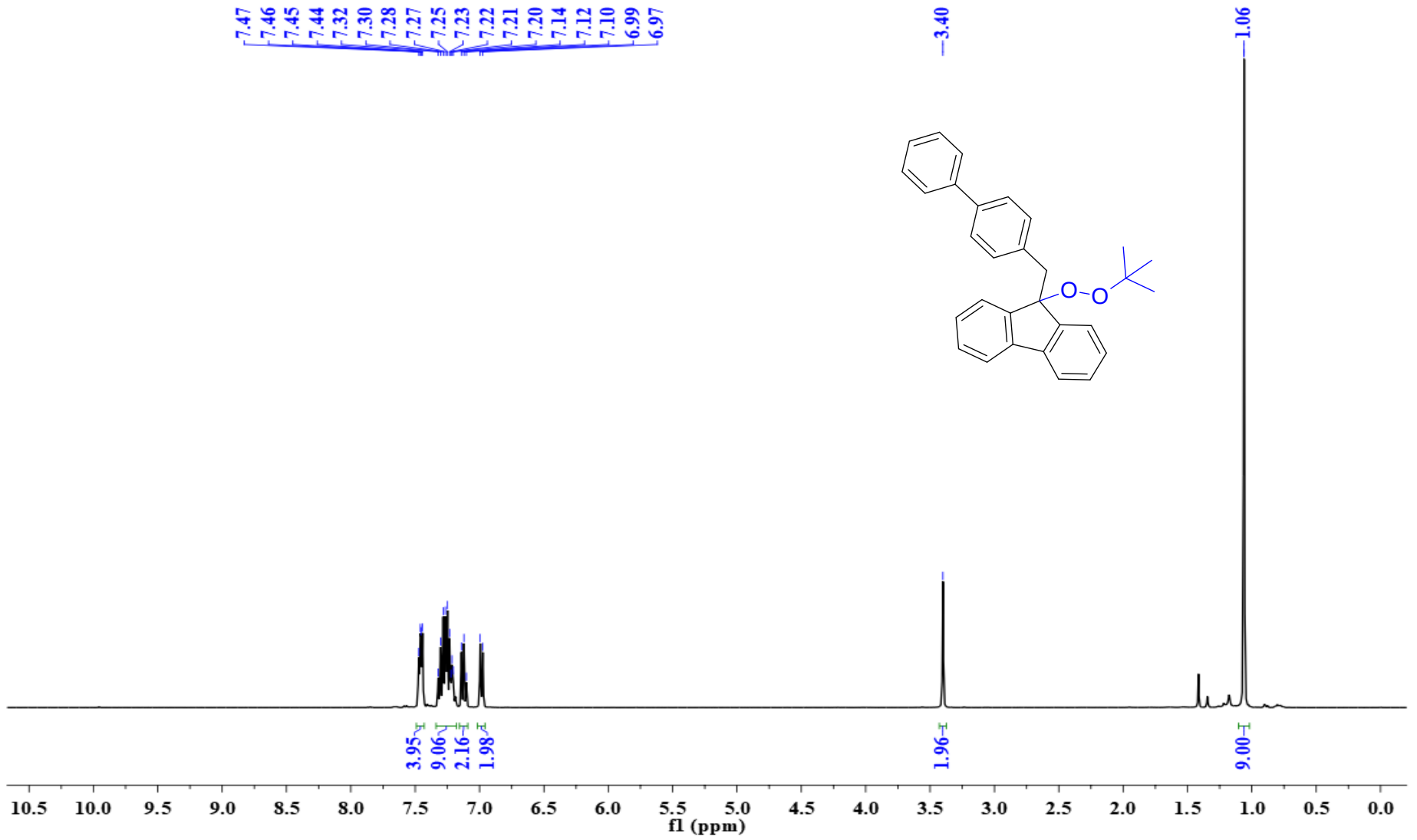


Figure S07. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-4-ylmethyl)-9-(tert-butylperoxy)-9H-fluorene (**P_3**).

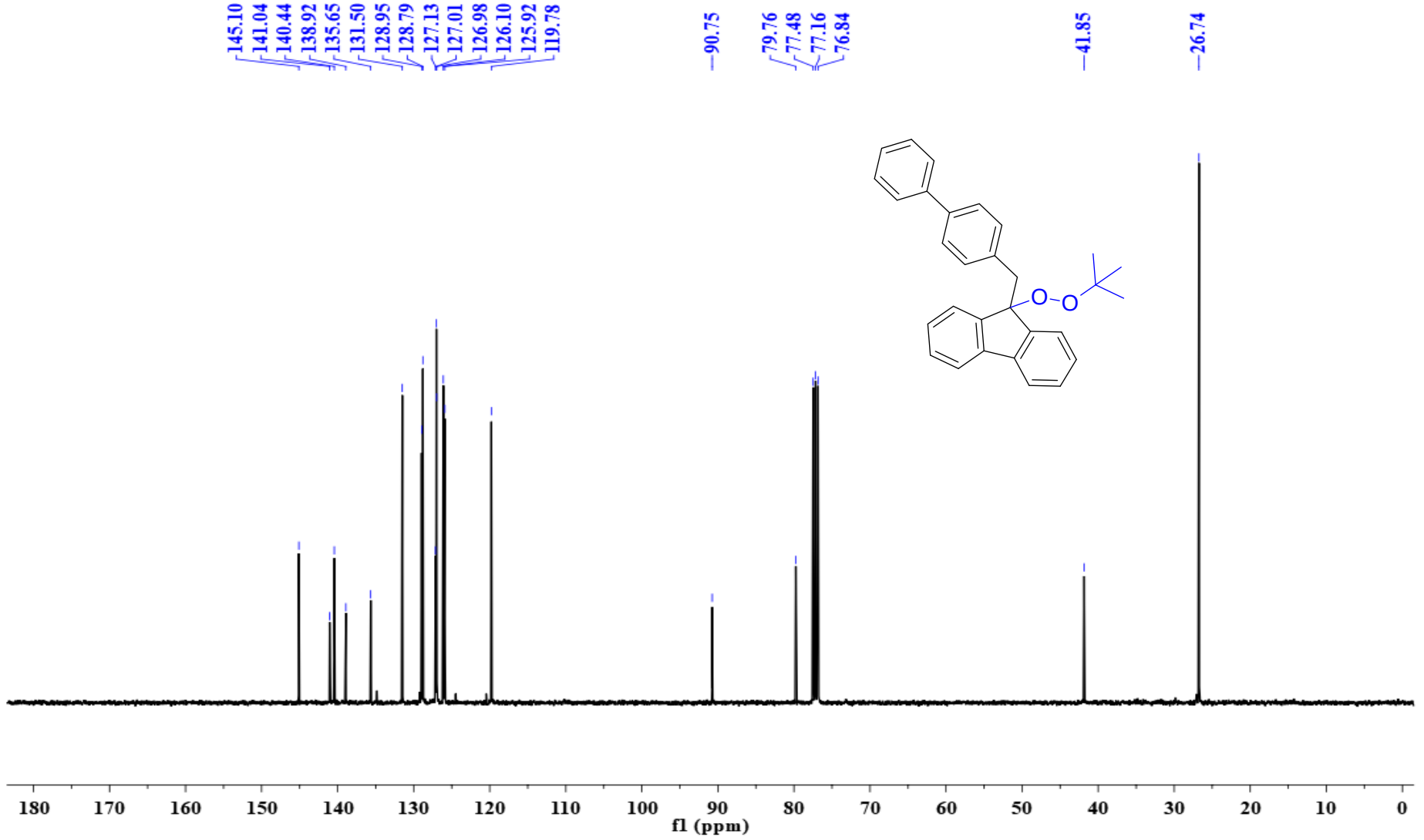


Figure S08. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-4-ylmethyl)-9-(tert-butylperoxy)-9H-fluorene (**P_3**).

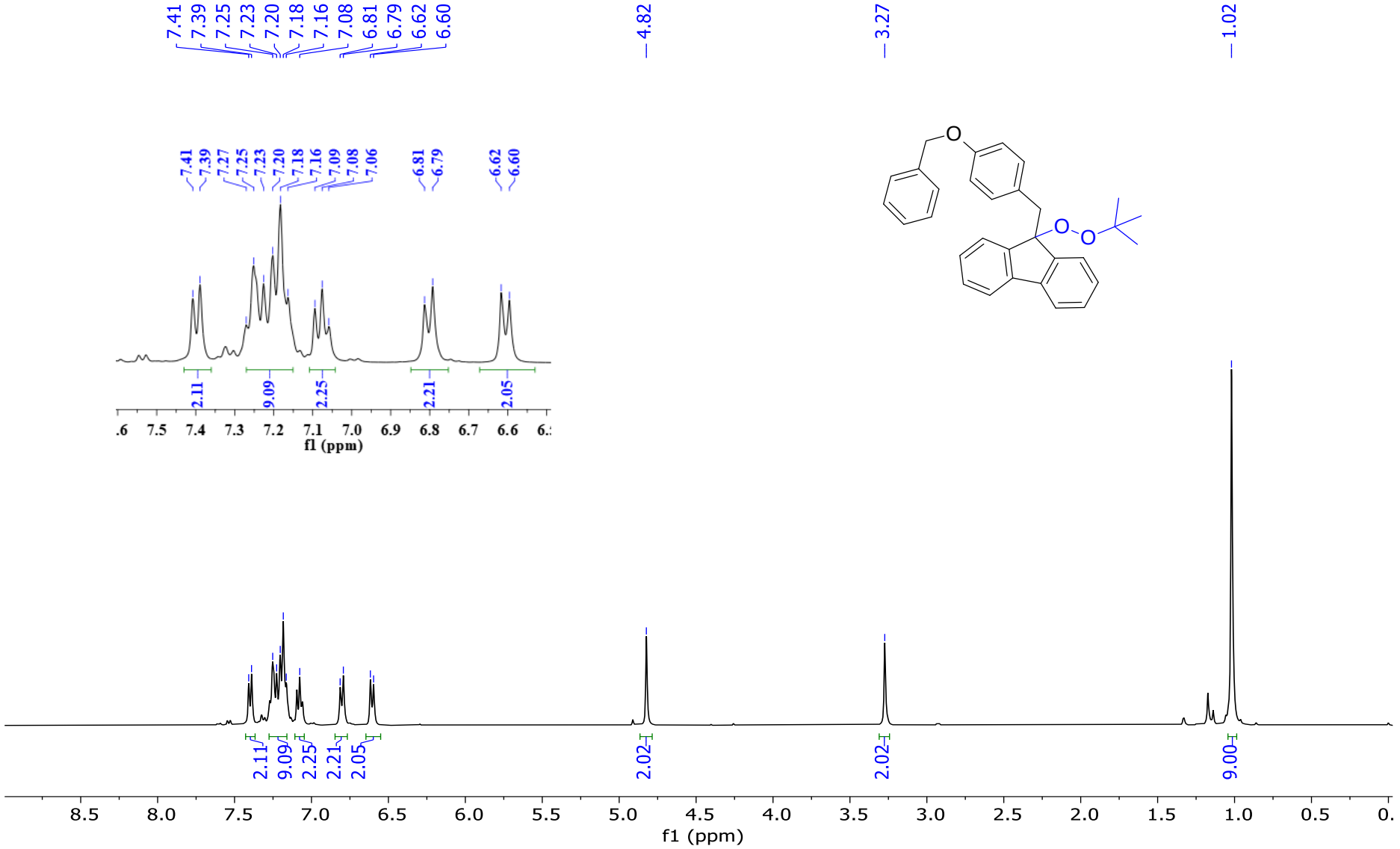


Figure S09. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(4-(benzyloxy)benzyl)-9-(tert-butylperoxy)-9H-fluorene (**P4**).

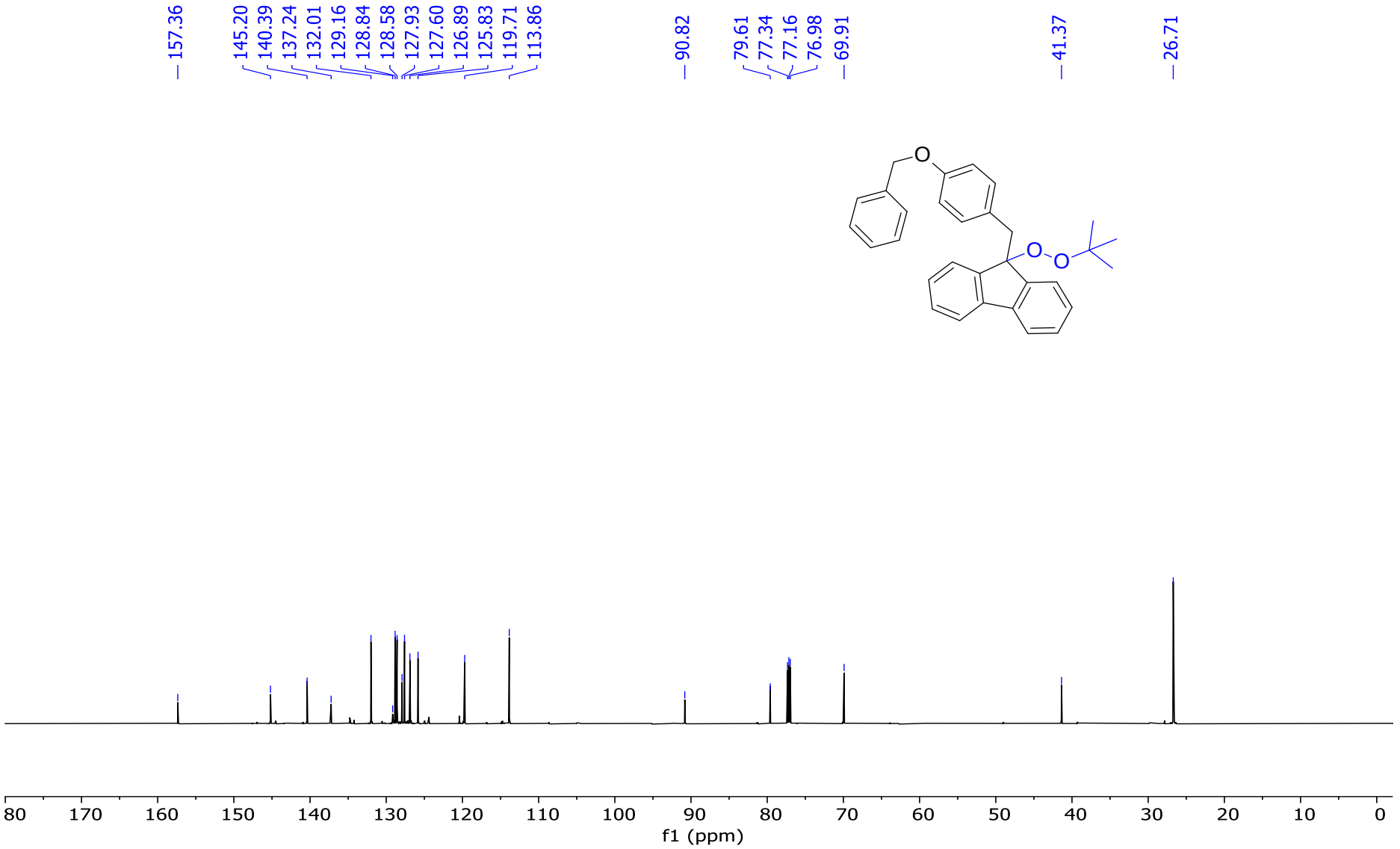


Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-(benzyloxy)benzyl)-9-(tert-butylperoxy)-9H-fluorene (**P4**).

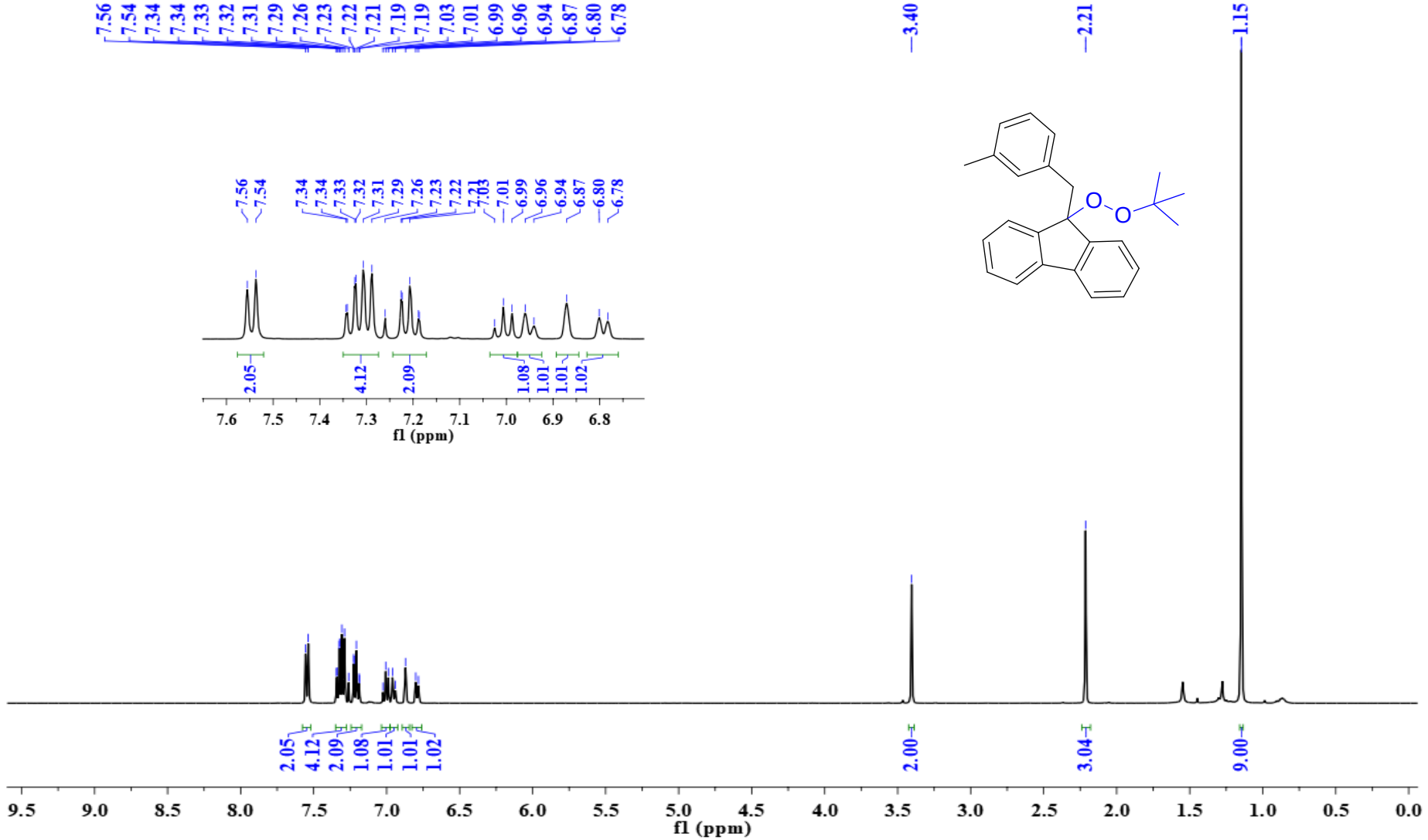


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(3-methylbenzyl)-9H-fluorene (**P_5**).

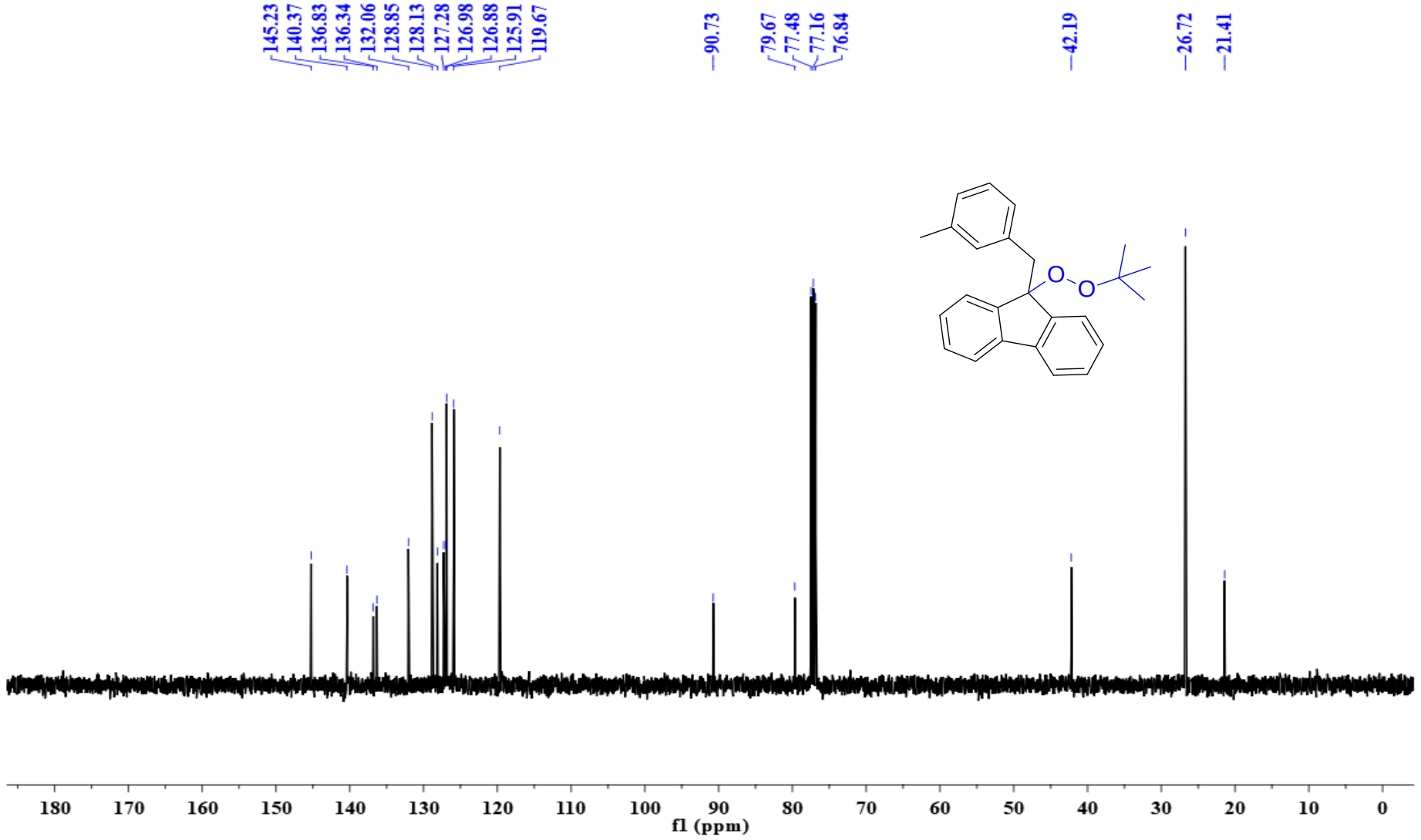


Figure S12. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(3-methylbenzyl)-9H-fluorene (**P_5**).

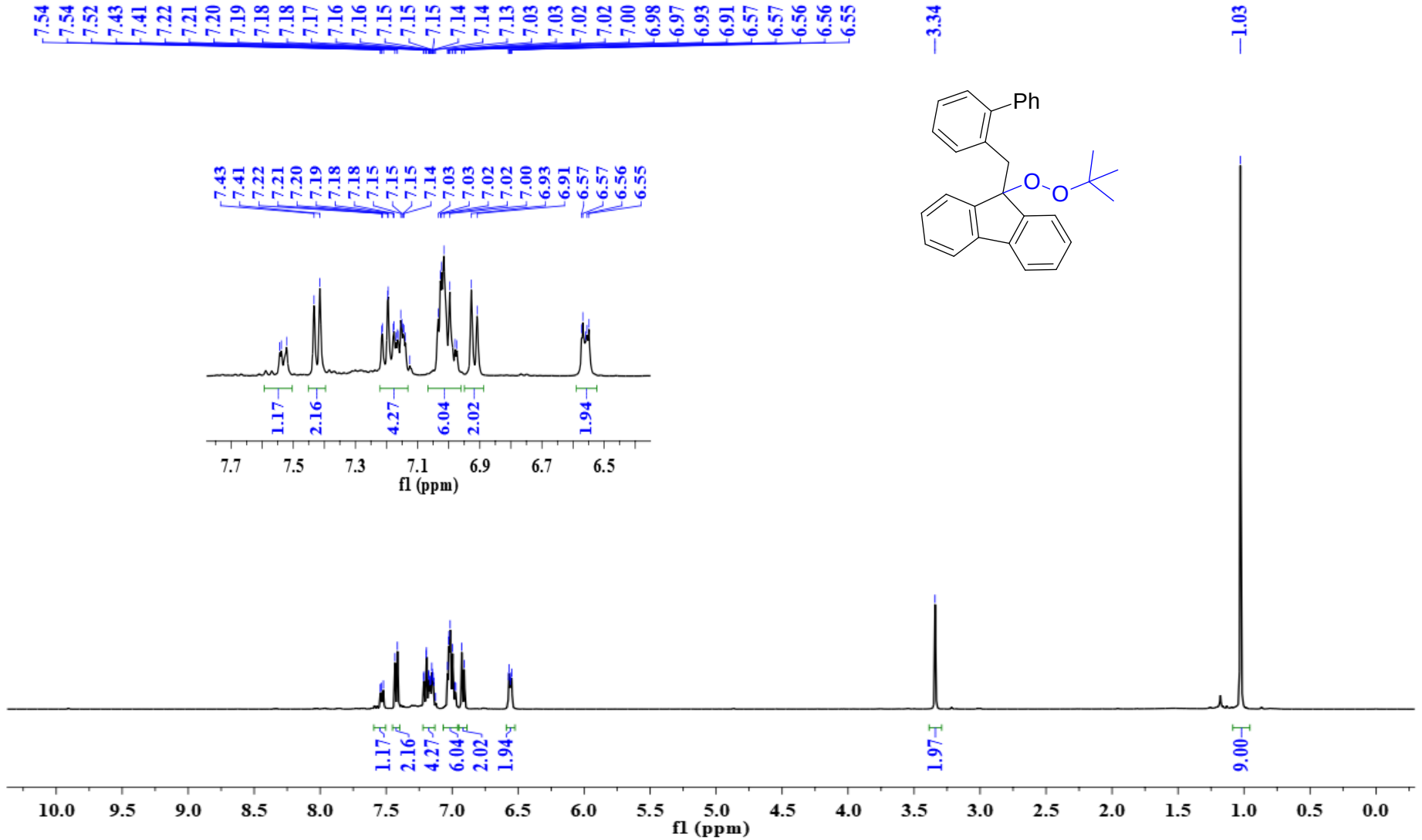


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-2-ylmethyl)-9-(tert-butylperoxy)-9H-fluorene (**P_6**).

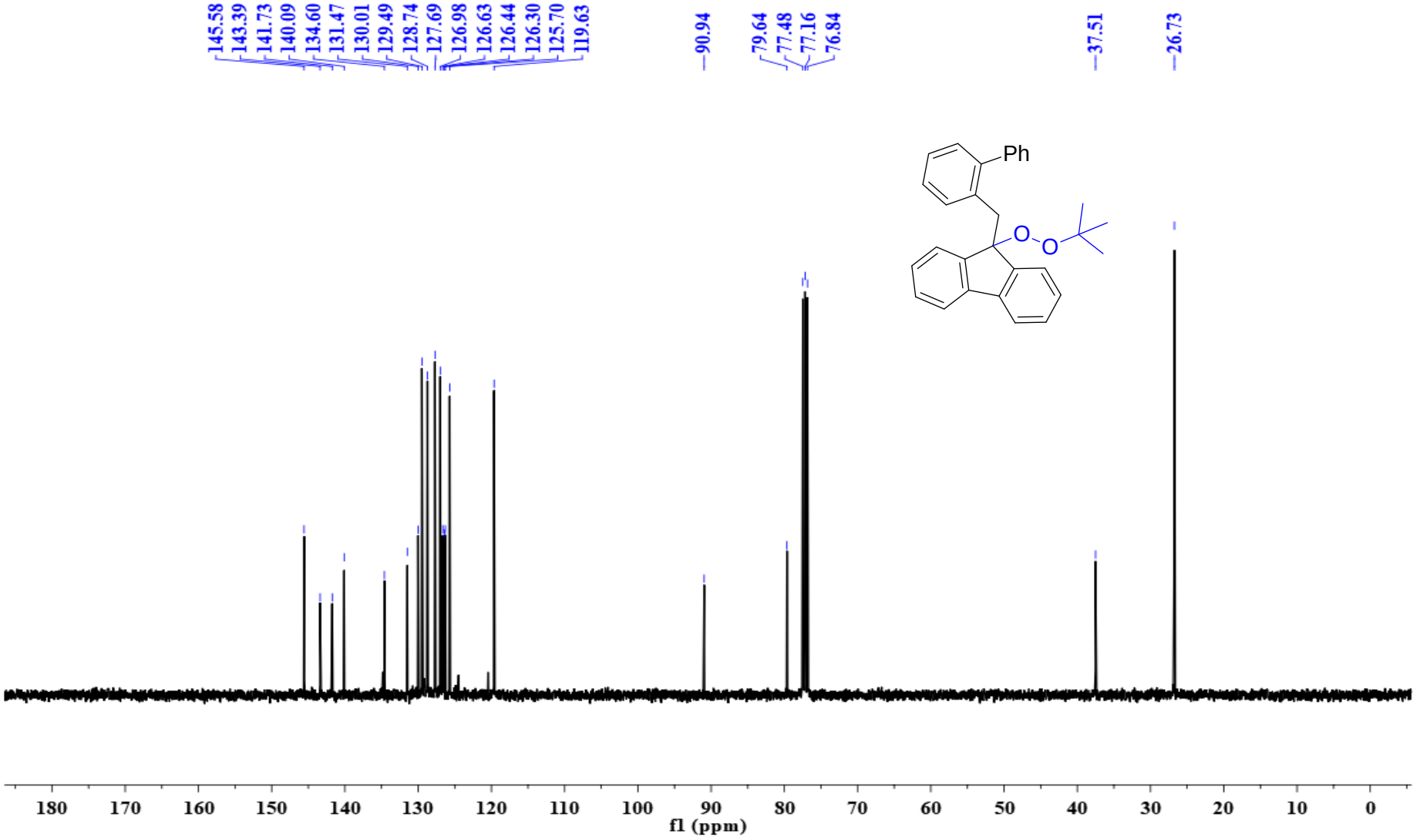


Figure S14. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-2-ylmethyl)-9-(tert-butylperoxy)-9H-fluorene (**P$_6$**).

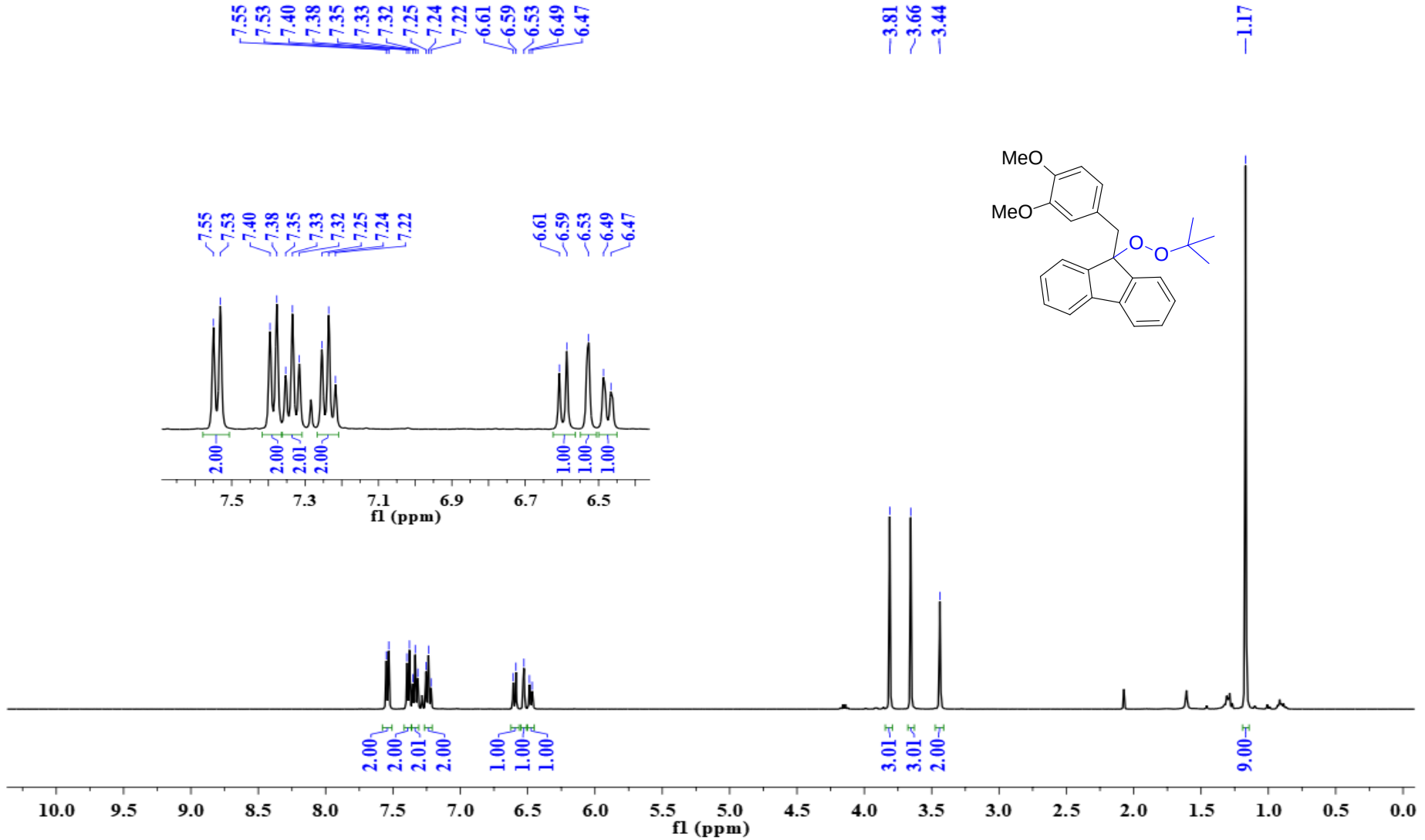


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(3,4-dimethoxybenzyl)-9H-fluorene (**P_7**).

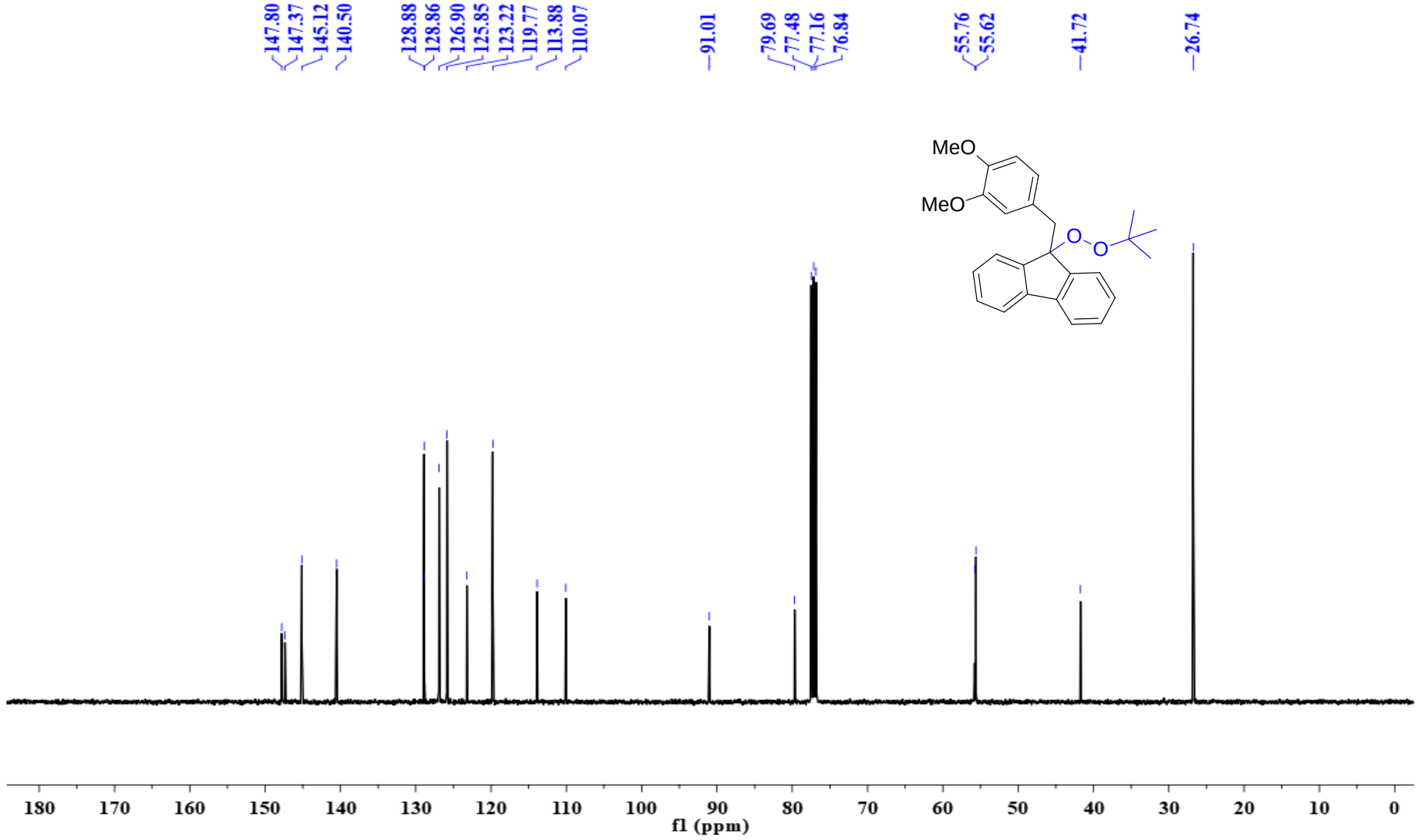


Figure S16. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(3,4-dimethoxybenzyl)-9H-fluorene (**P**$_7$).

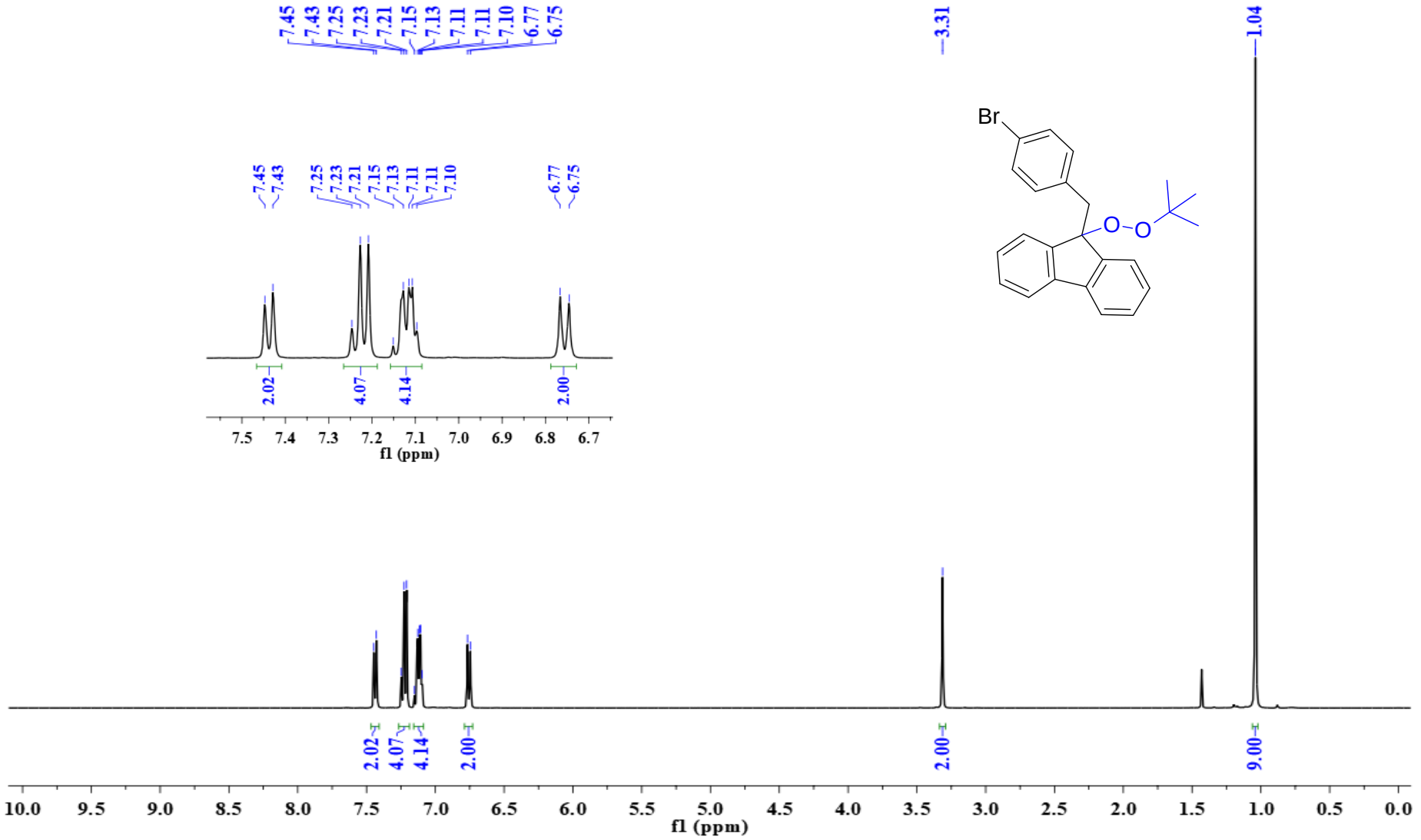


Figure S17. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-bromobenzyl)-9-(tert-butylperoxy)-9H-fluorene (**P_8**).

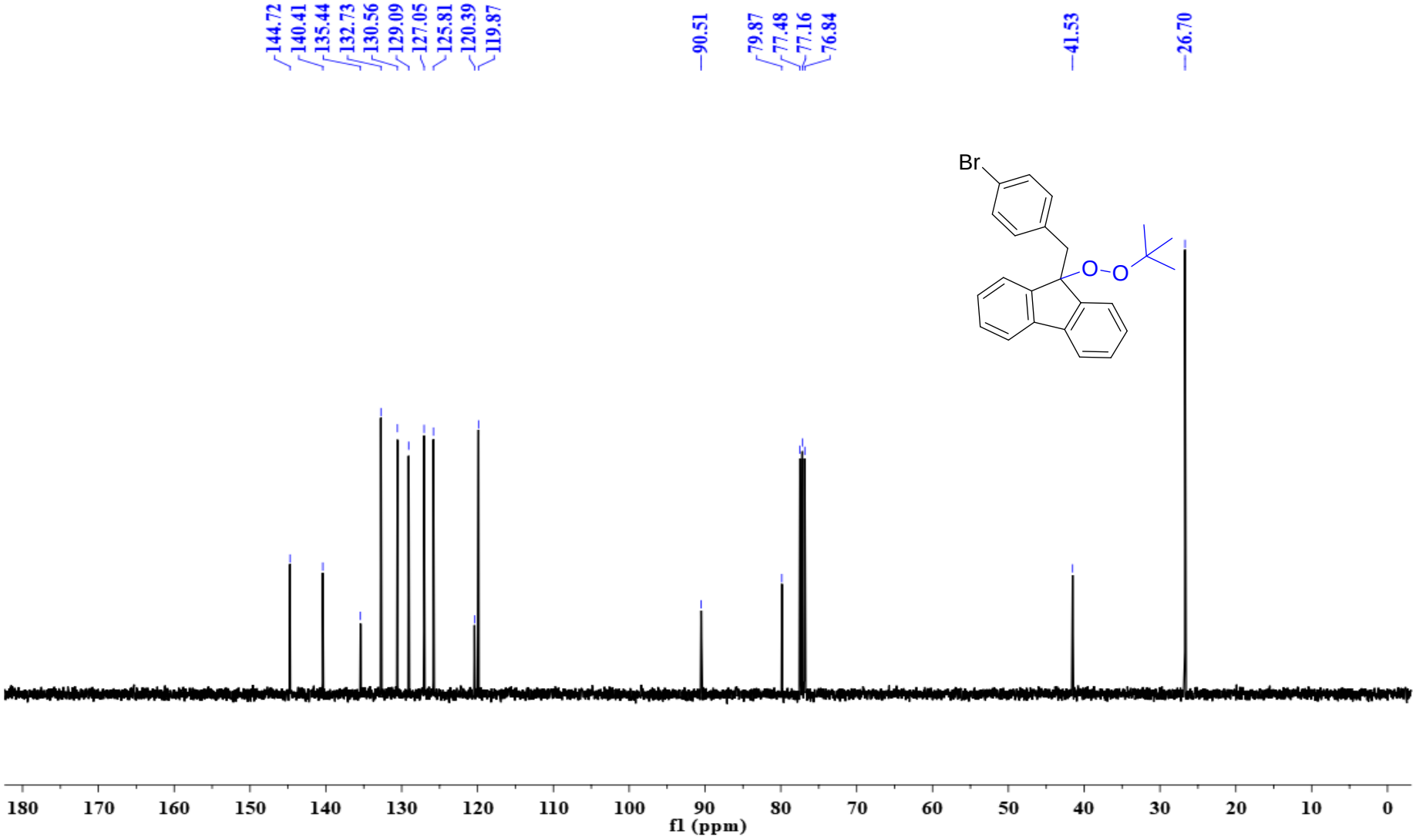


Figure S18. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-bromobenzyl)-9-(tert-butylperoxy)-9H-fluorene (**P8**).

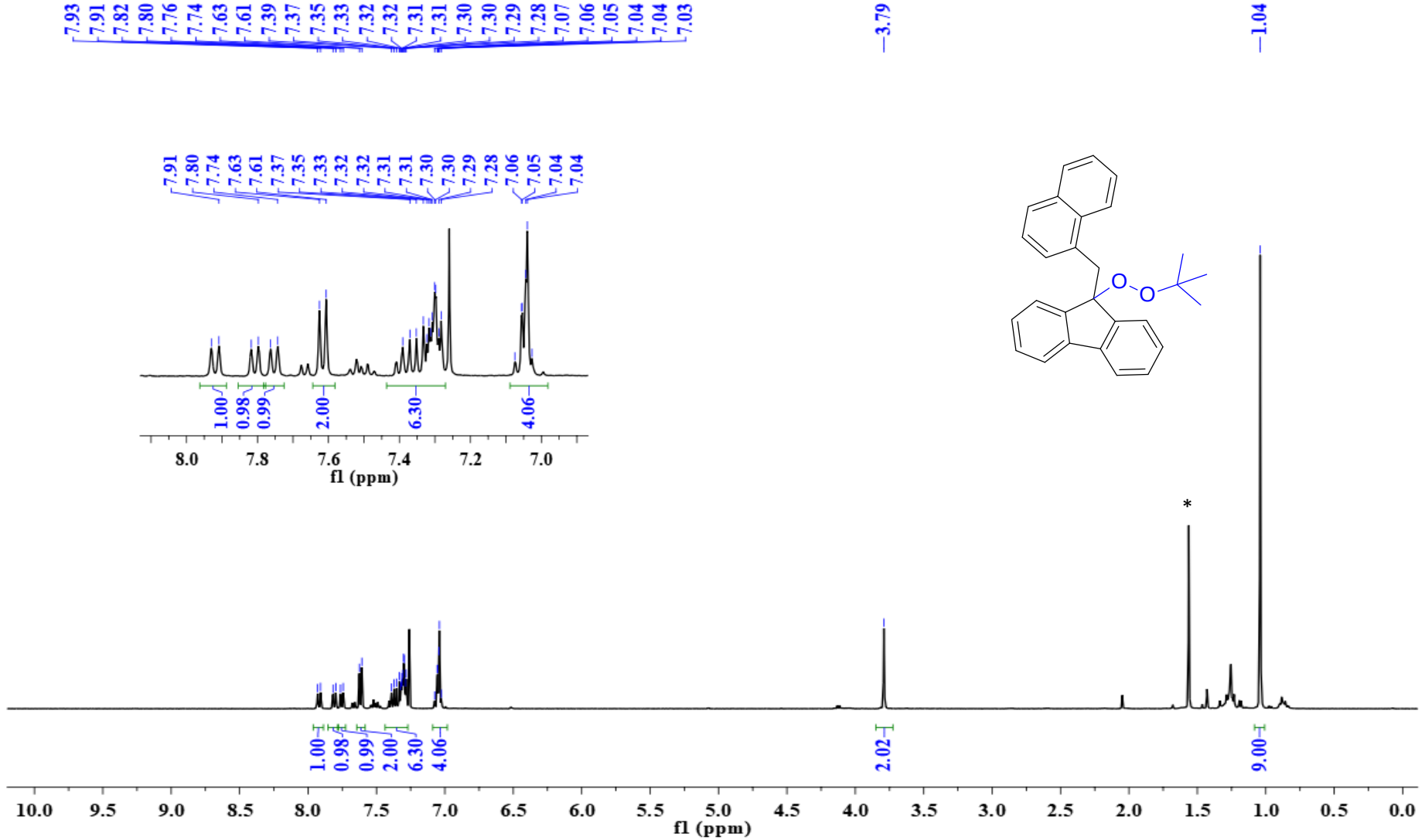


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(naphthalen-1-ylmethyl)-9H-fluorene (**P_9**). (* indicates H_2O)

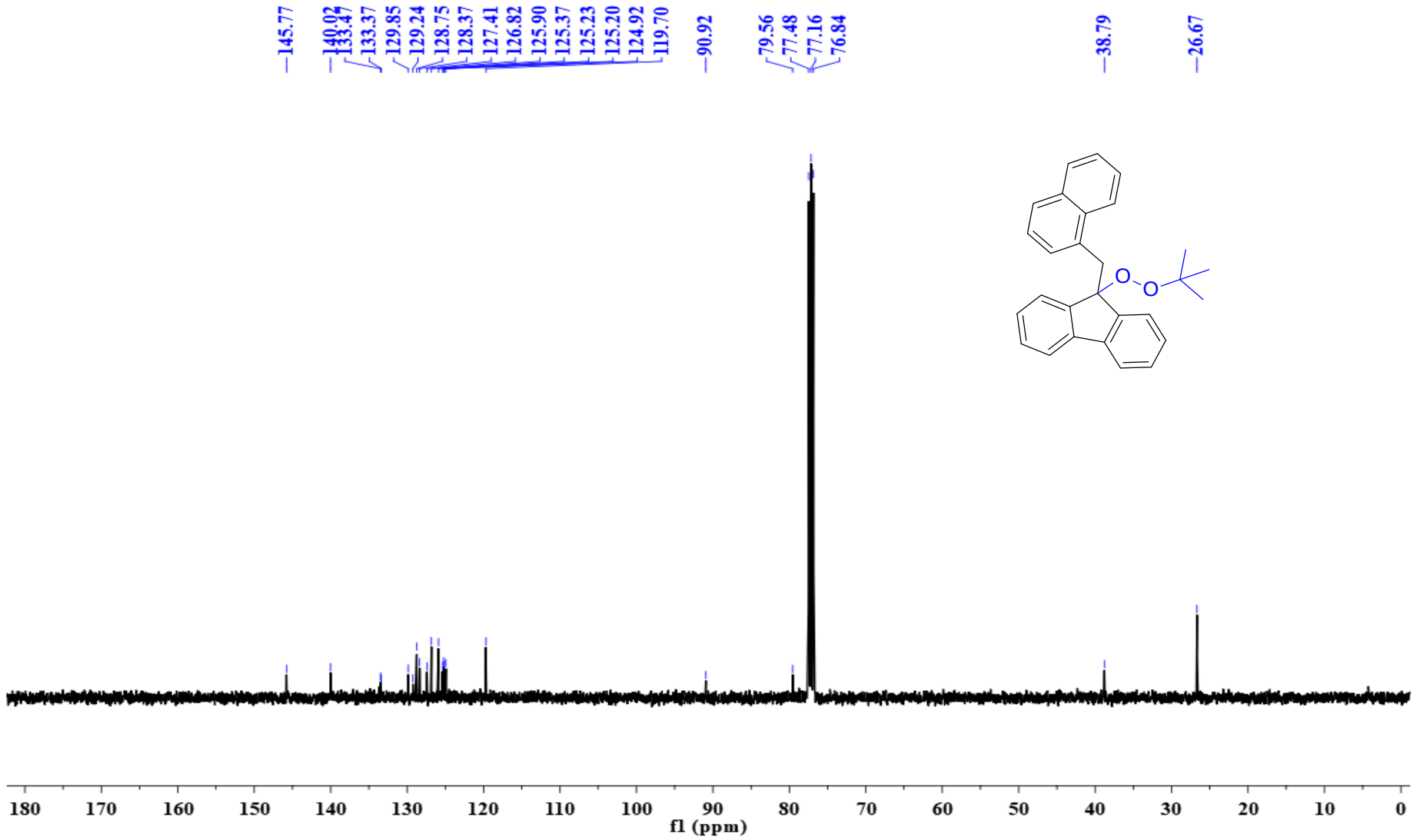


Figure S20. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-(naphthalen-1-ylmethyl)-9H-fluorene (**P₉**).

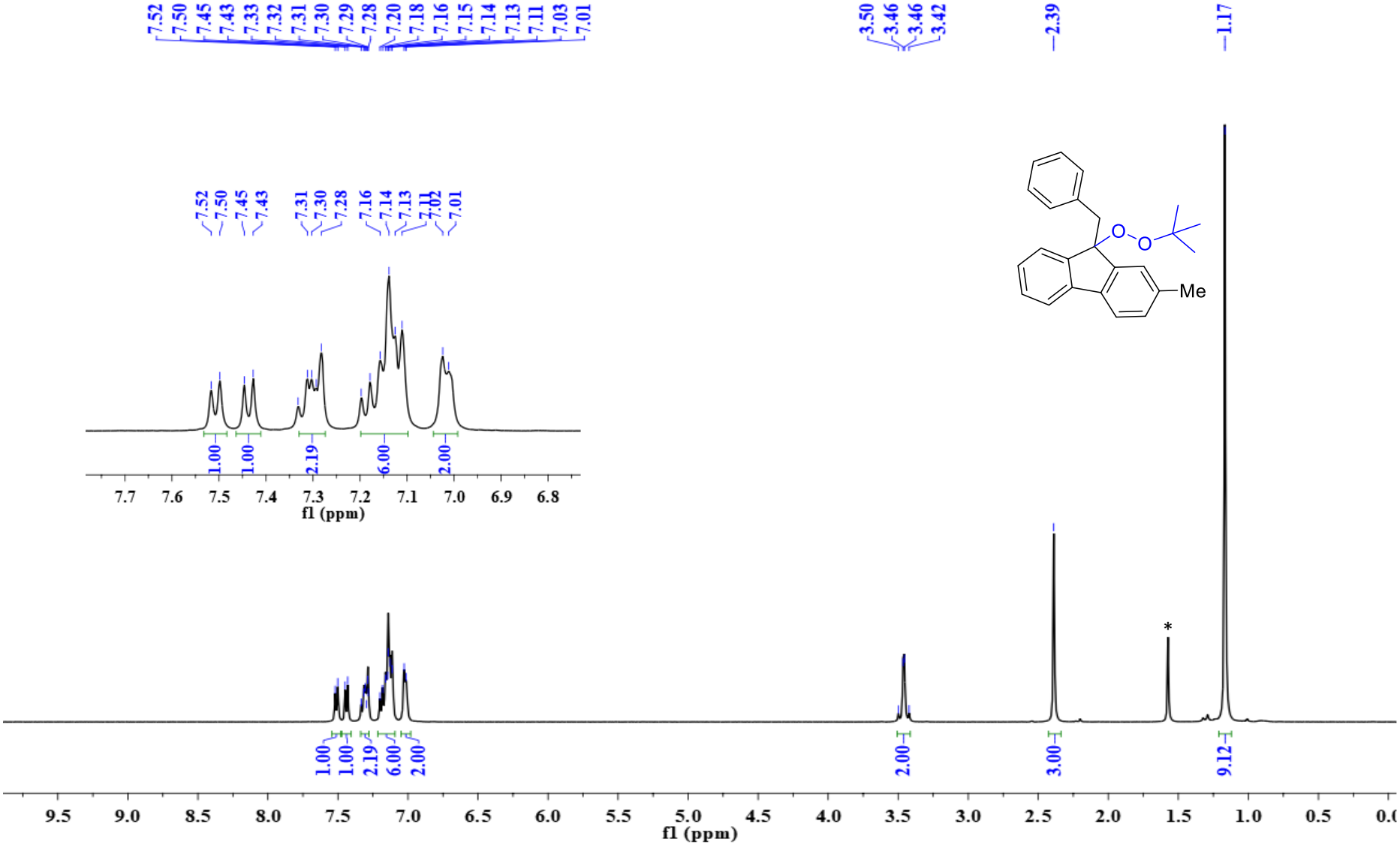


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-2-methyl-9H-fluorene (**P_{10}**). (* indicates H_2O)

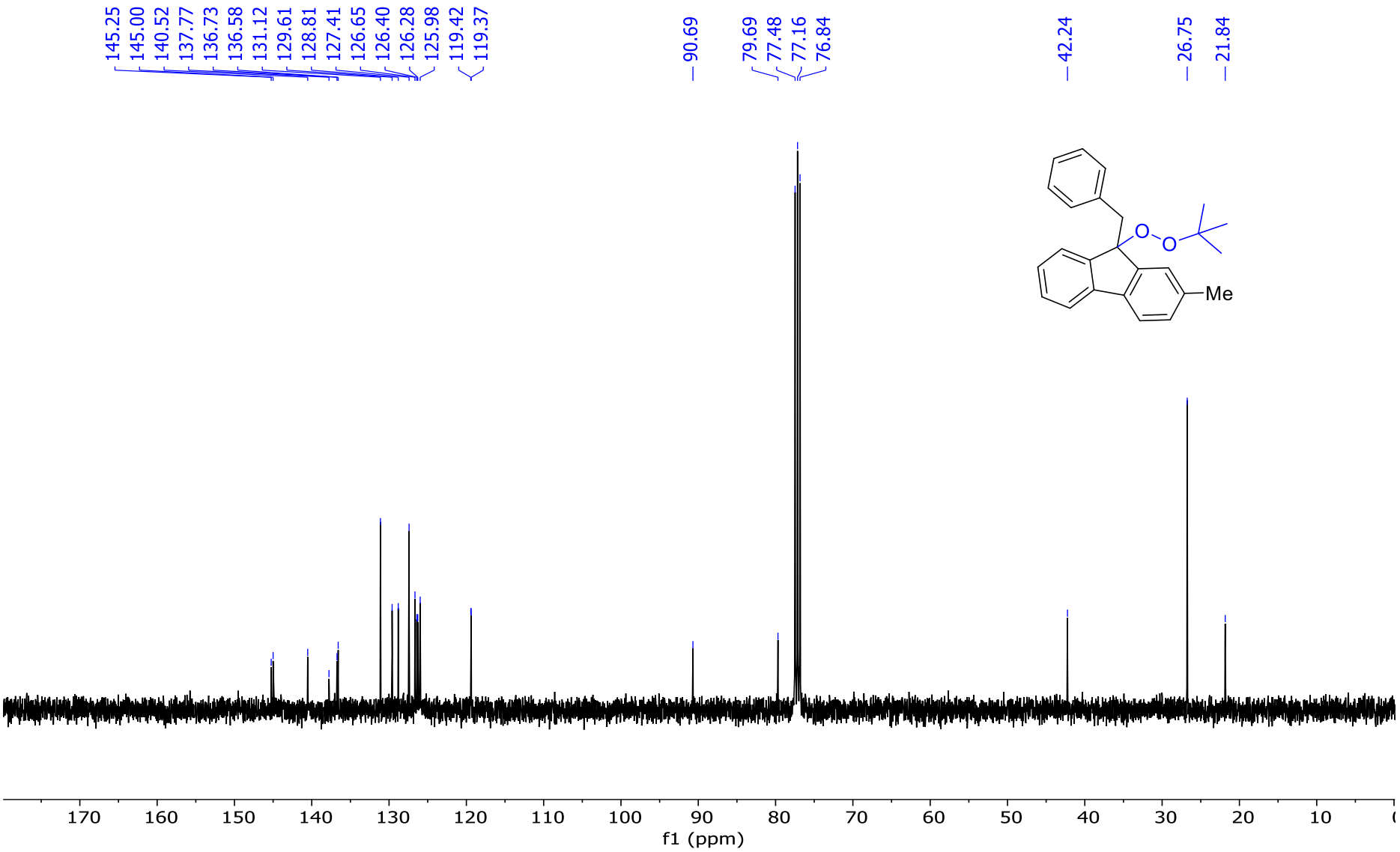


Figure S22. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-2-methyl-9H-fluorene (**P10**).

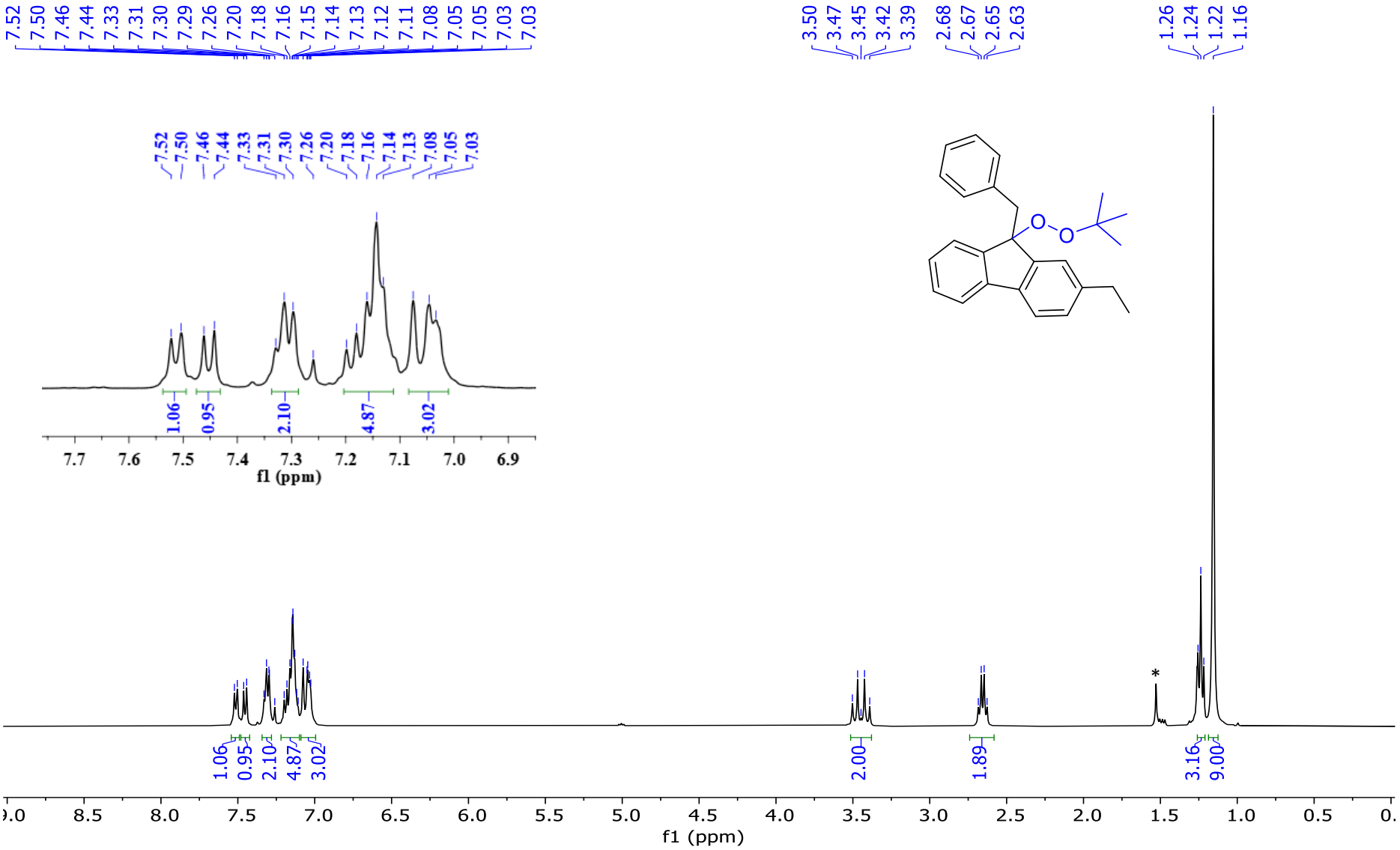


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-2-ethyl-9H-fluorene (**P_{11}**). (* indicates H_2O)

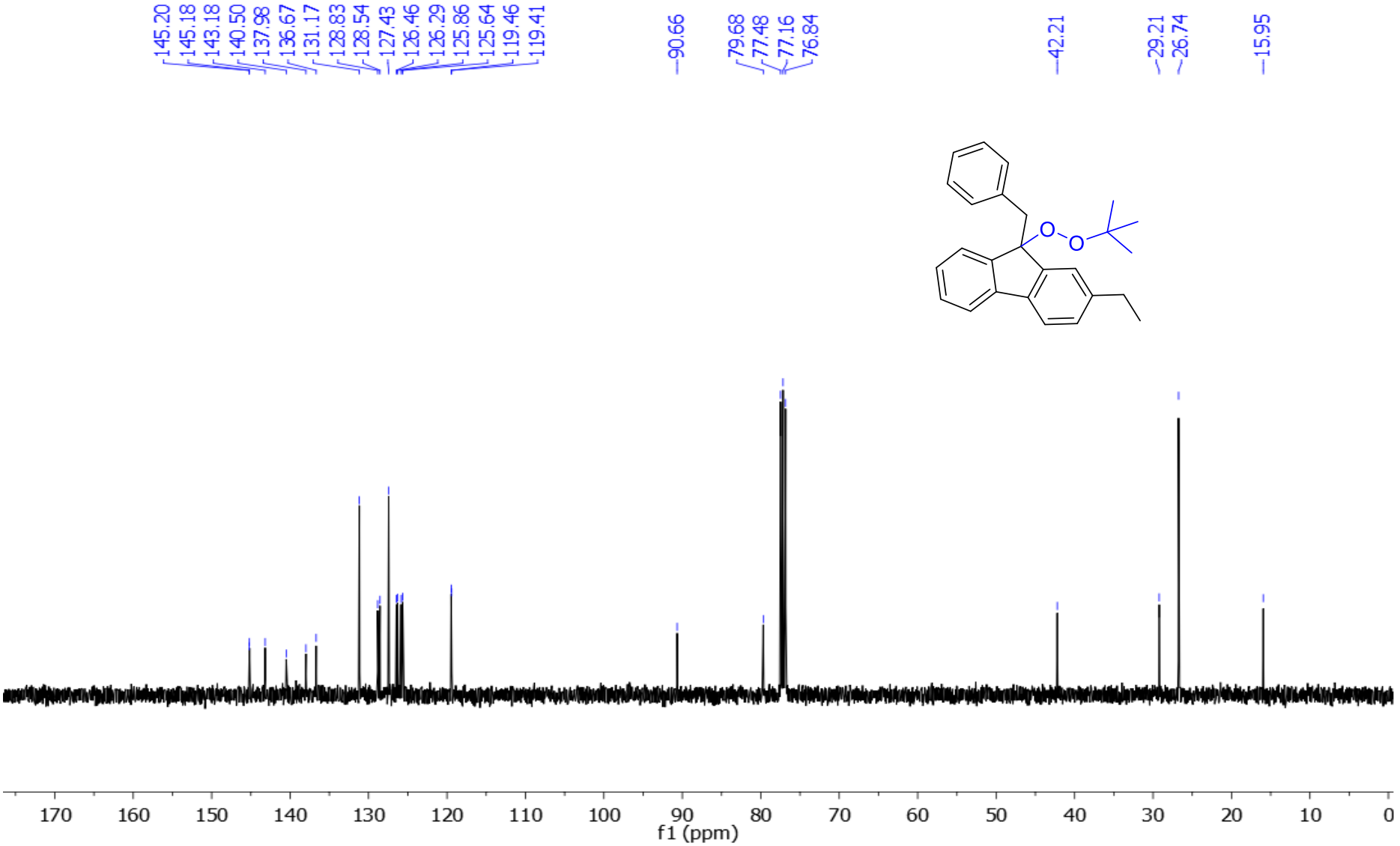


Figure S24. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-2-ethyl-9H-fluorene (**P_{11}**).

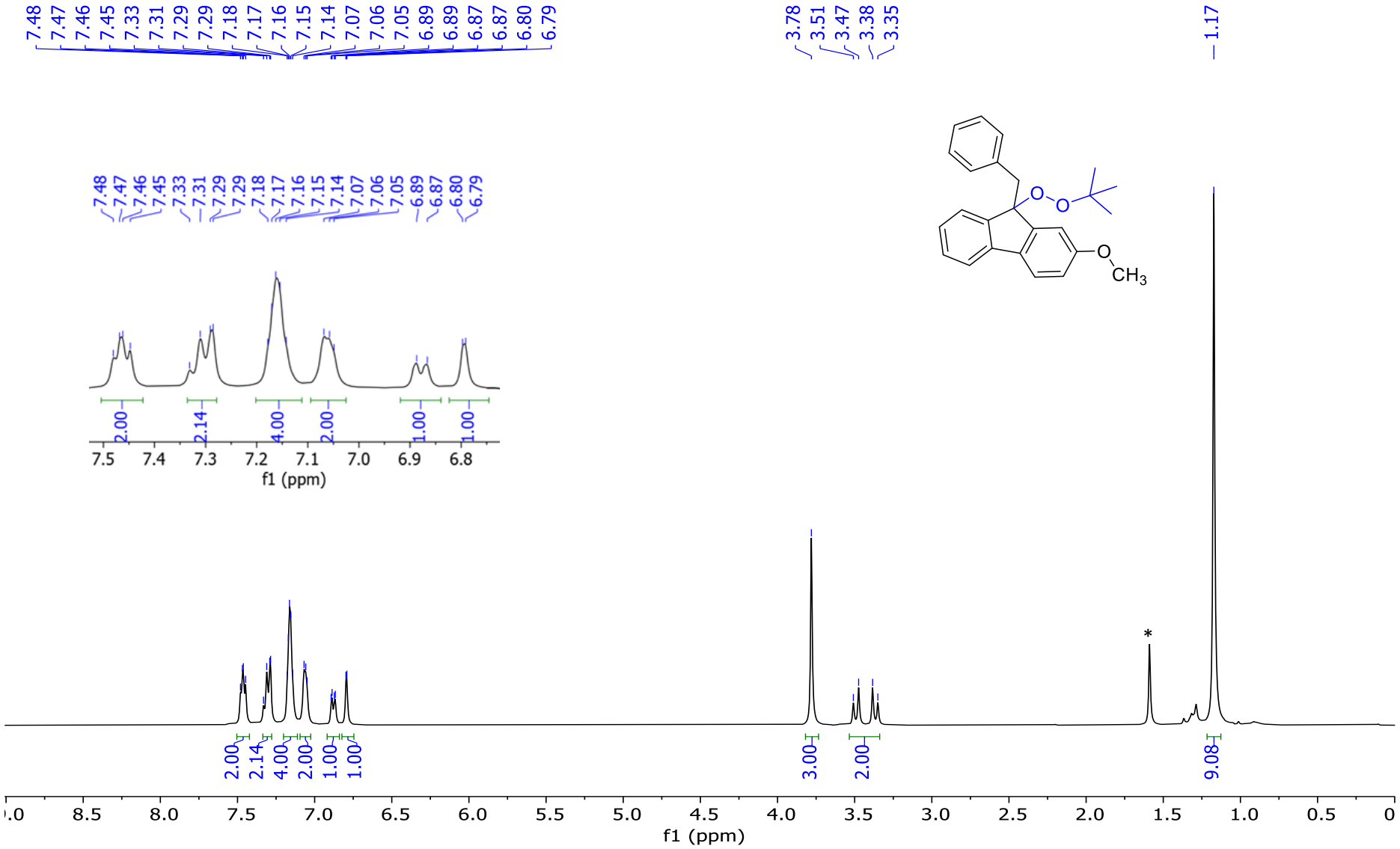


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-2-ethyl-9H-fluorene (**P12**). (* indicates H_2O)

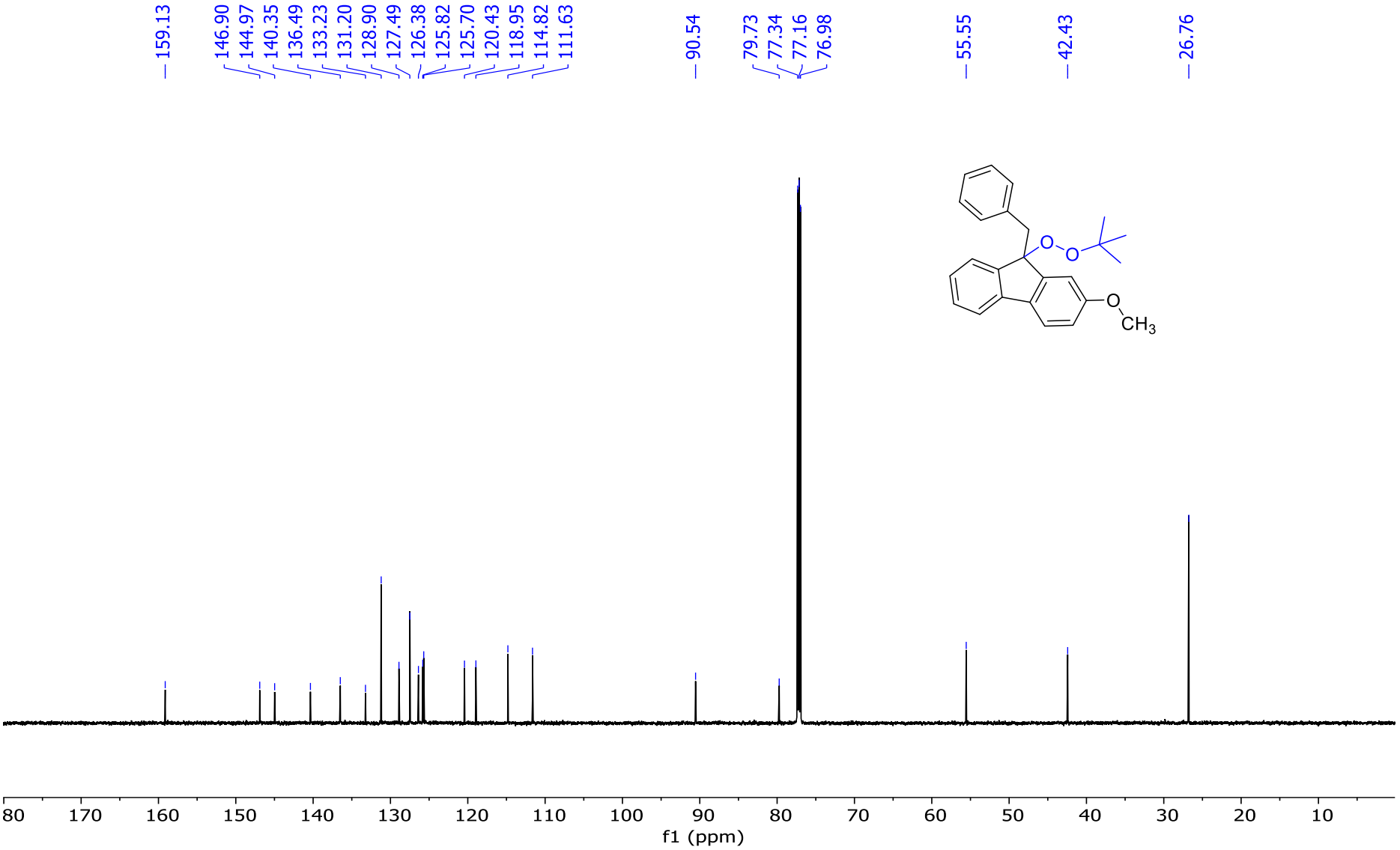


Figure S26. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-9-(tert-butylperoxy)-2-methoxy-9H-fluorene (**P12**).

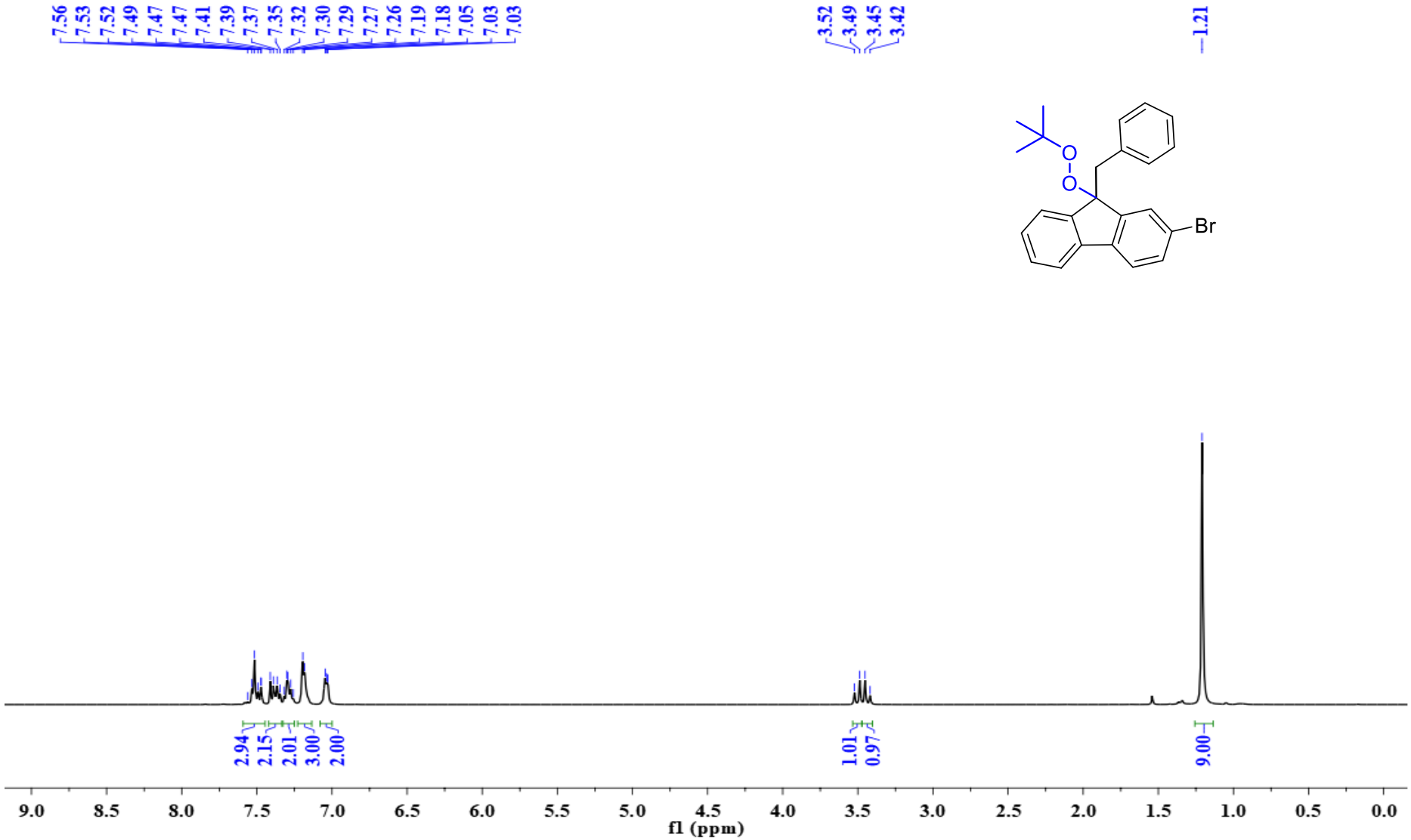


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-2-bromo-9-(tert-butylperoxy)-9H-fluorene (**P$_{13}$**).

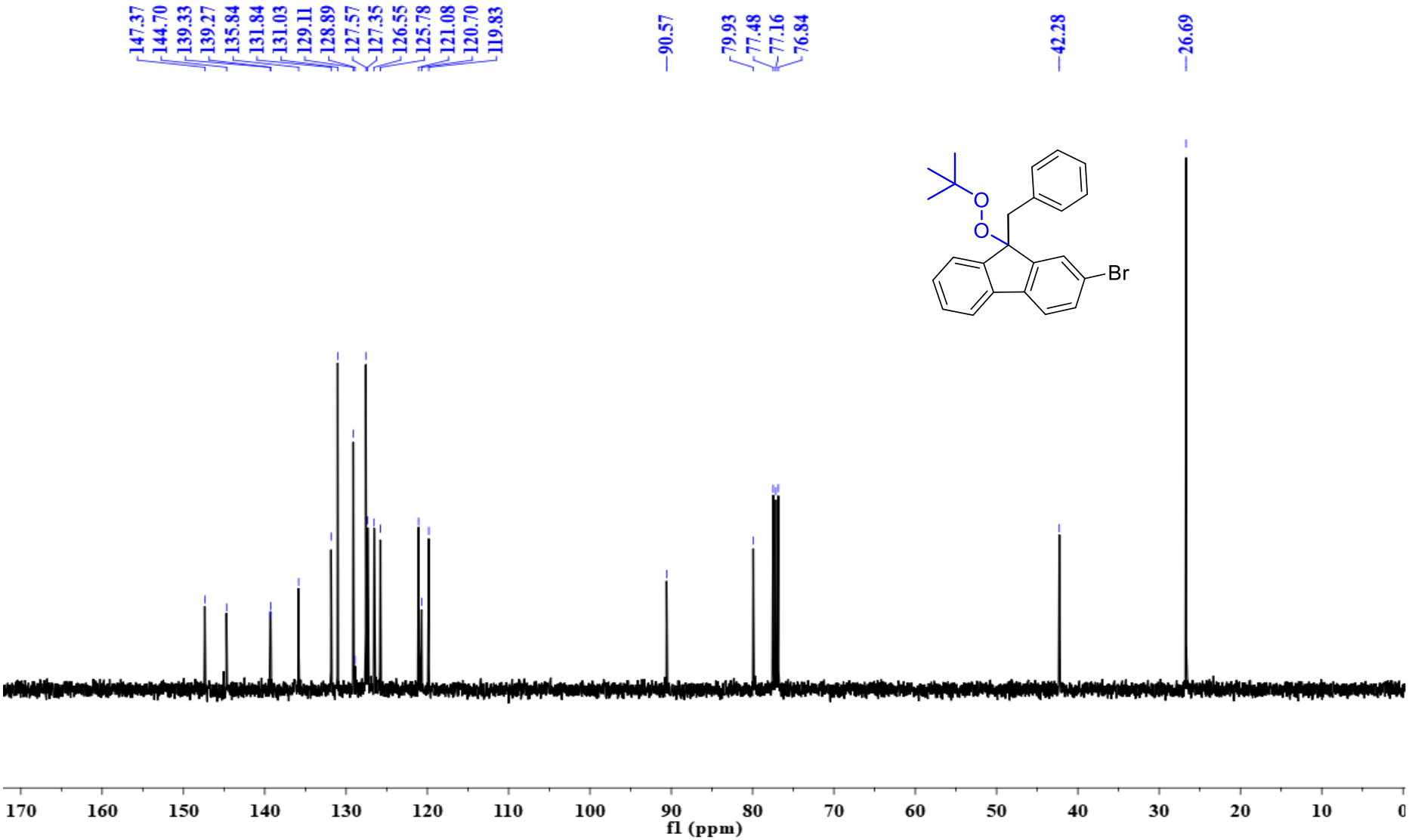


Figure S28. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-2-bromo-9-(tert-butylperoxy)-9H-fluorene (**P_{13}**).

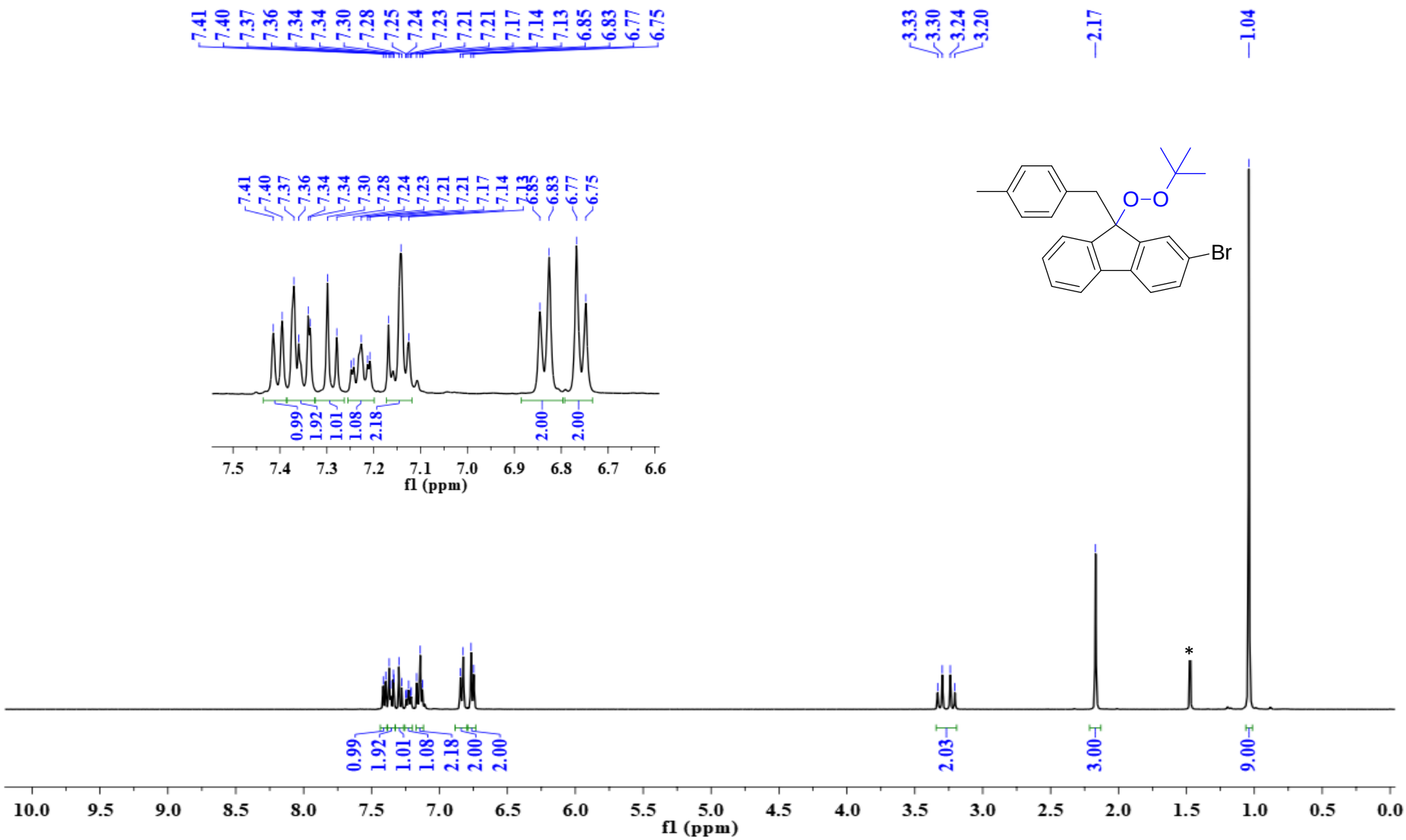


Figure S29. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-bromo-9-(tert-butylperoxy)-9-(4-methylbenzyl)-9H-fluorene (**P_{14}**). (* indicates H_2O)

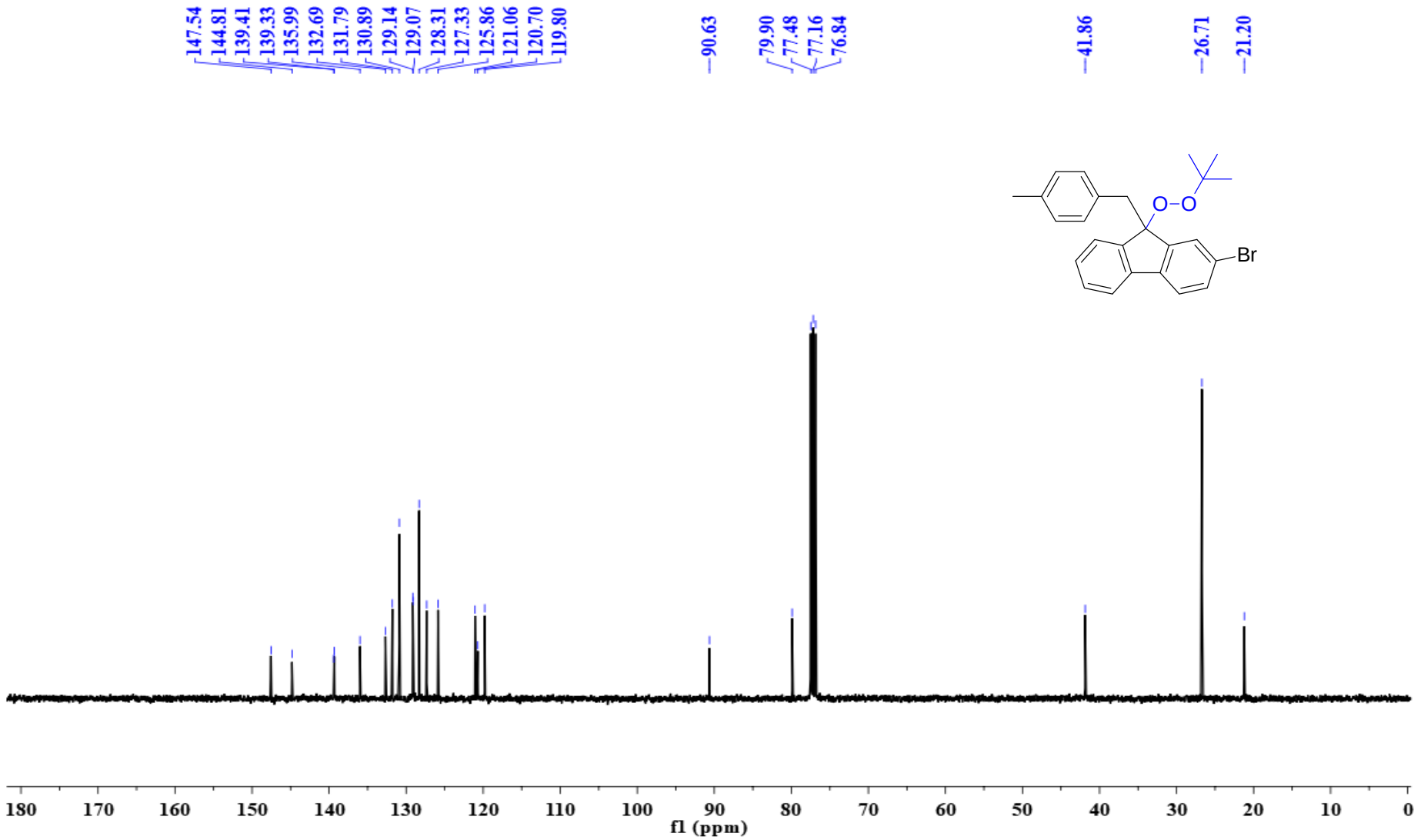


Figure S30. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-bromo-9-(tert-butylperoxy)-9-(4-methylbenzyl)-9H-fluorene (**P14**).

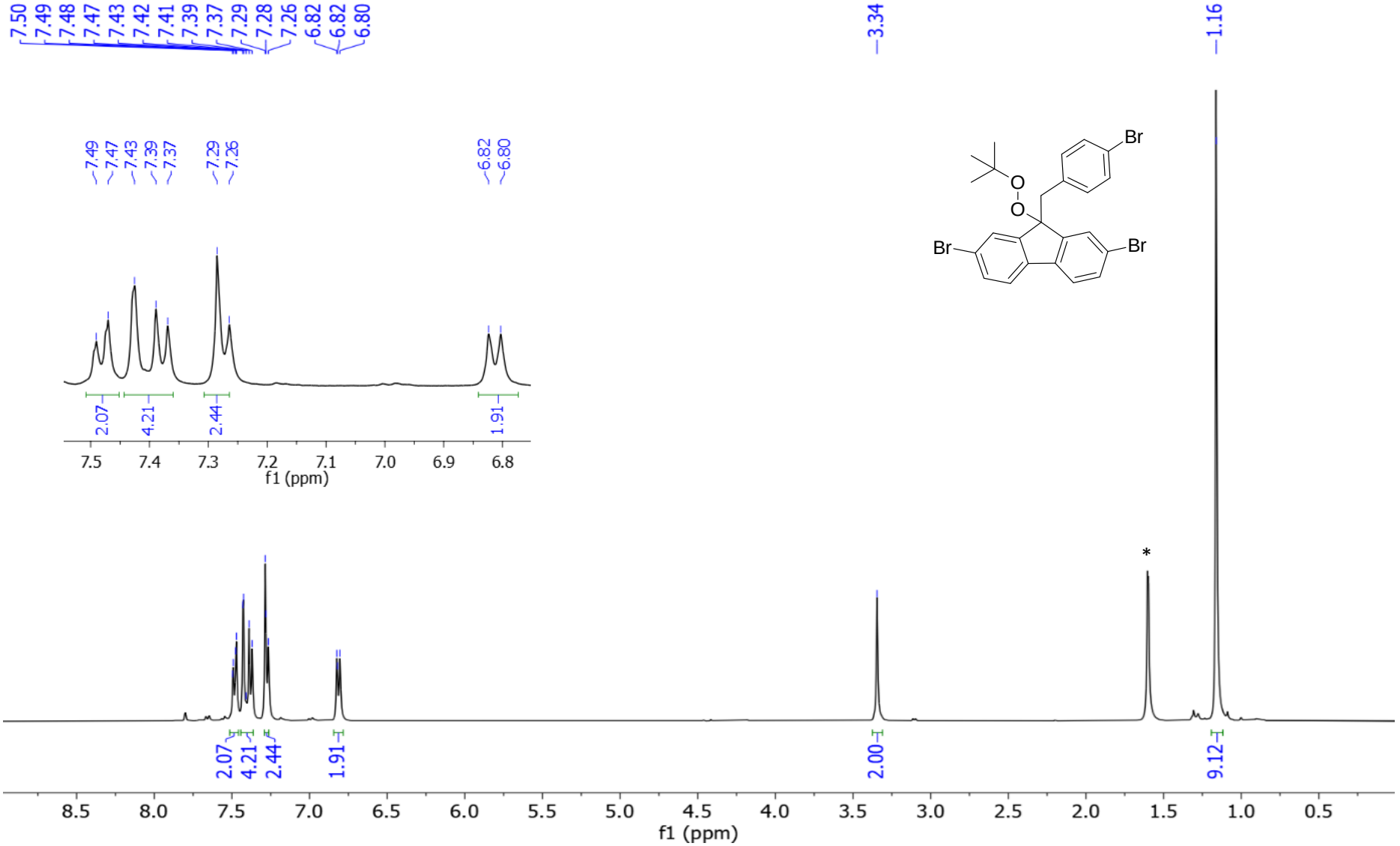


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-dibromo-9-(4-bromobenzyl)-9-(tert-butylperoxy)-9H-fluorene (**P$_{15}$**). (* indicates H_2O)

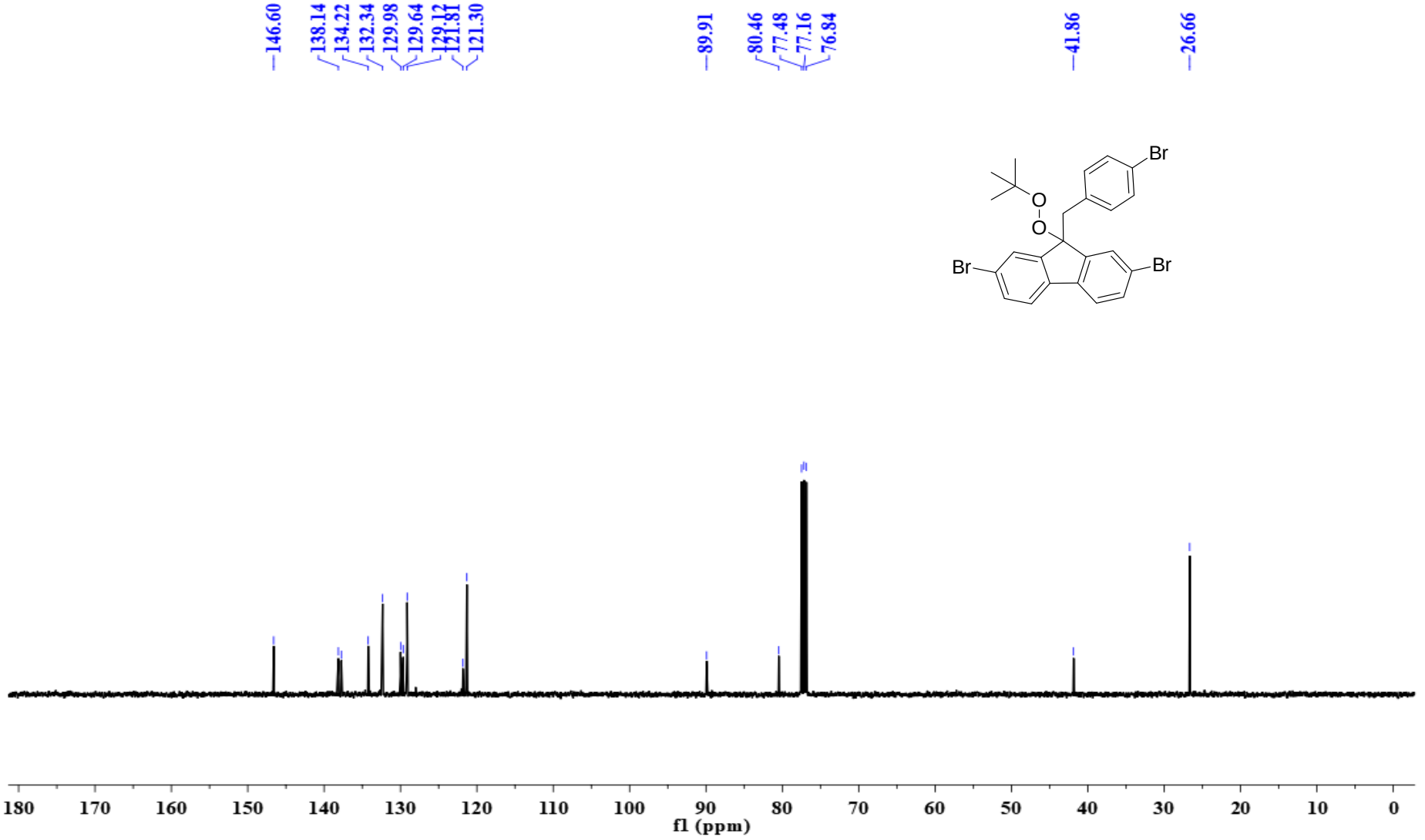


Figure S32. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-dibromo-9-(4-bromobenzyl)-9-(tert-butylperoxy)-9H-fluorene (**P_{15}**).

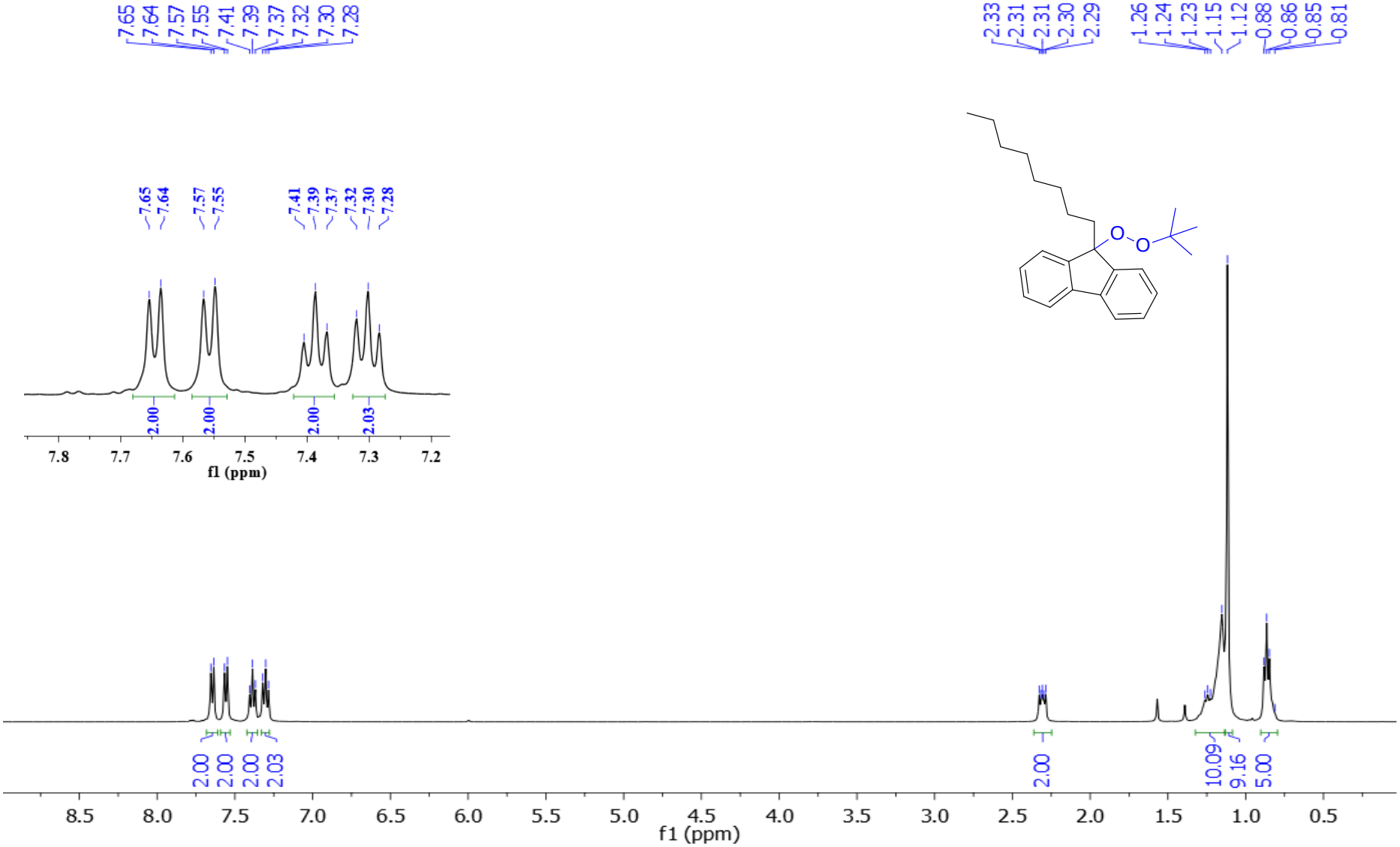


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-octyl-9H-fluorene (**P$_{16}$**).

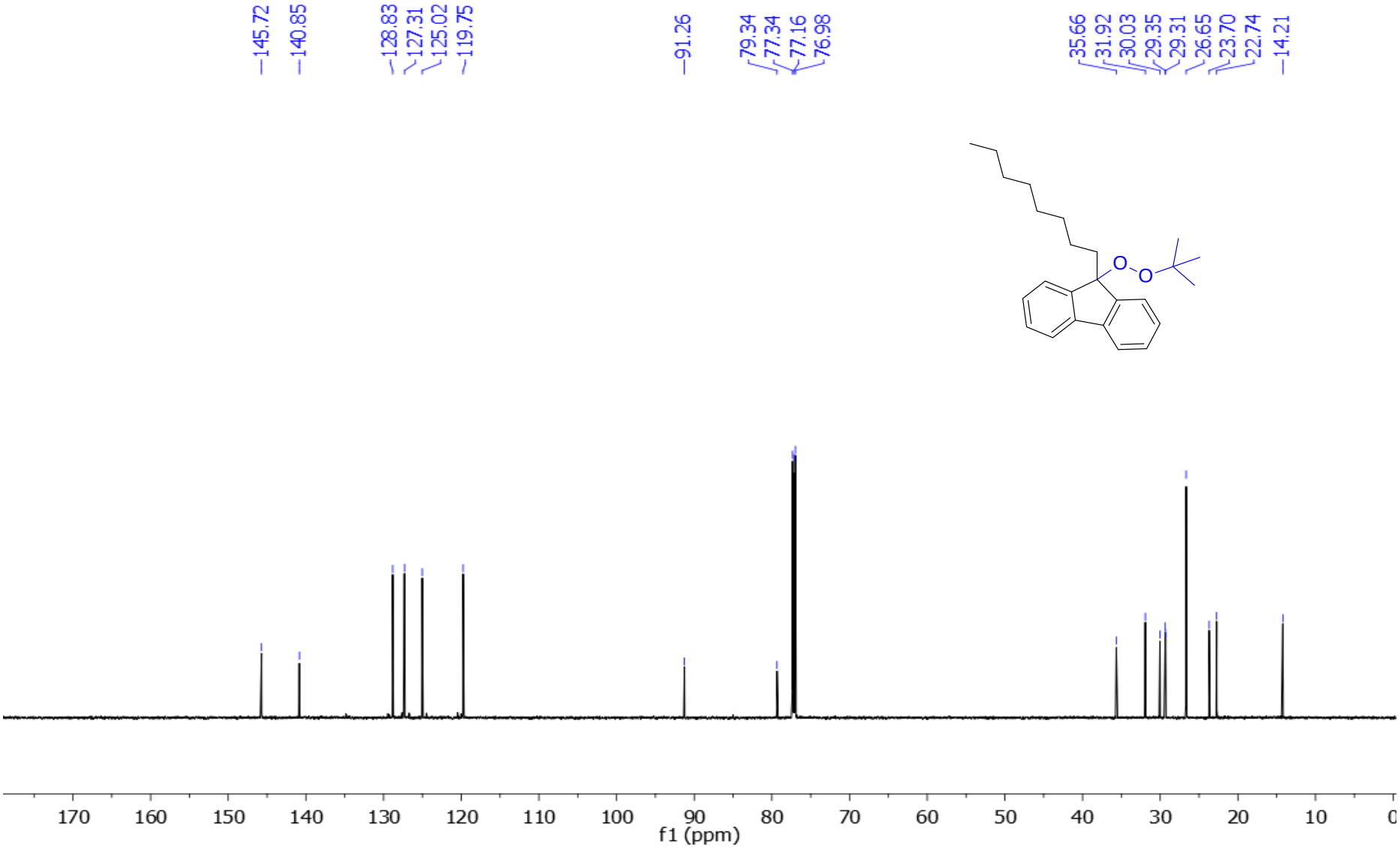


Figure S34. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-octyl-9H-fluorene (**P_{16}**).

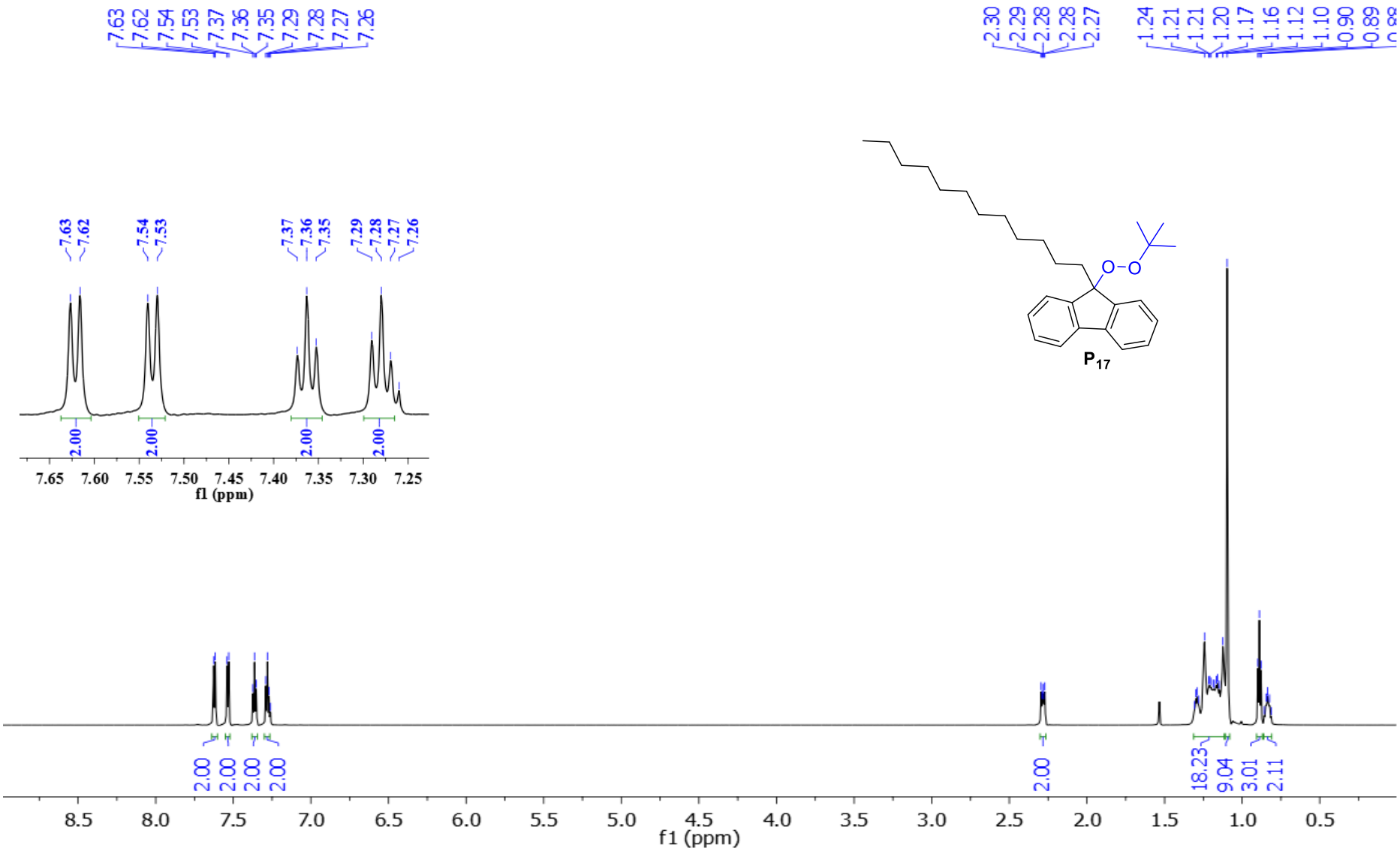


Figure S35. ^{1}H NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-dodecyl-9H-fluorene (**P$_{17}$**).

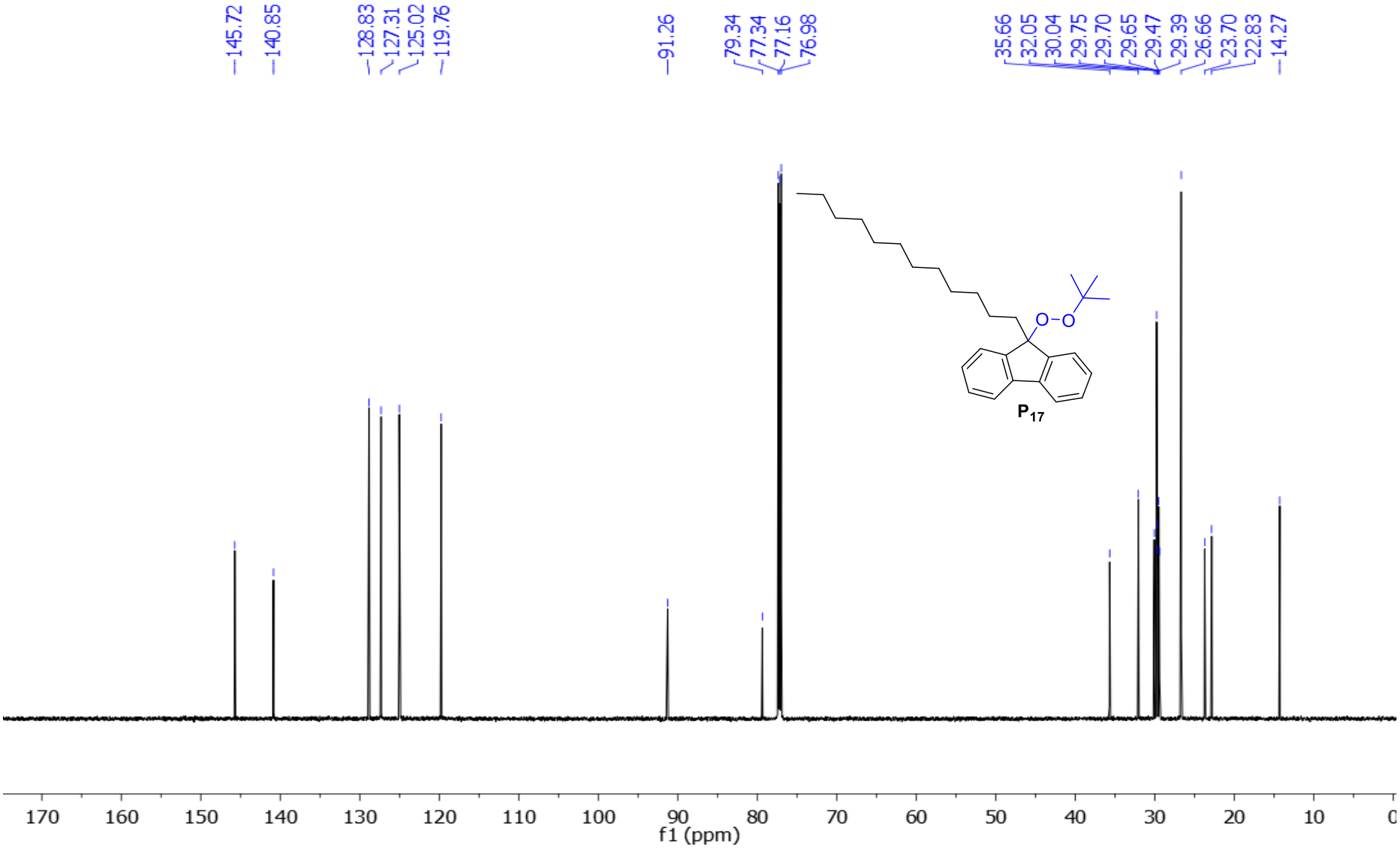


Figure S36. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-9-dodecyl-9H-fluorene (**P17**).

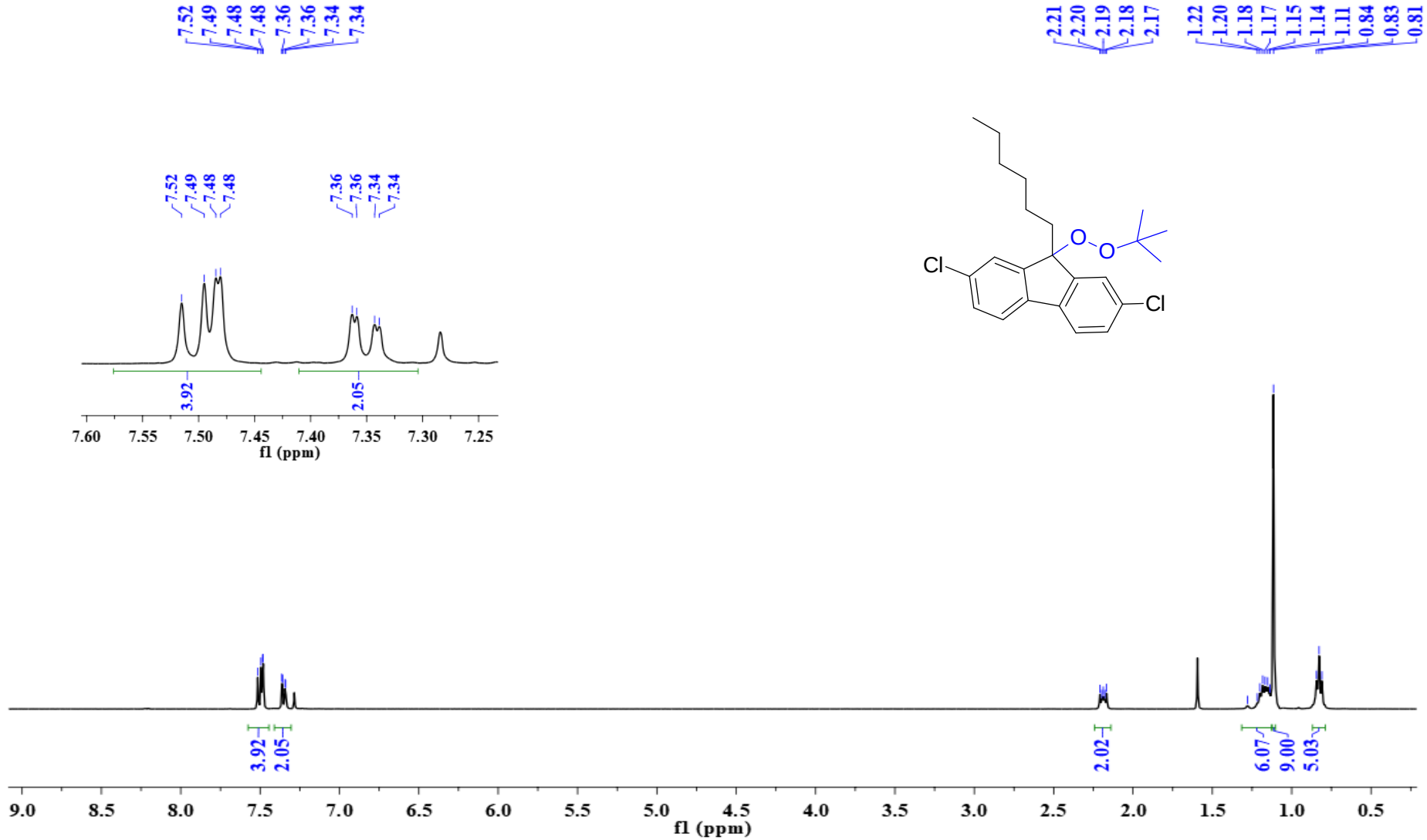


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-2,7-dichloro-9-hexyl-9H-fluorene (**P_{18}**).

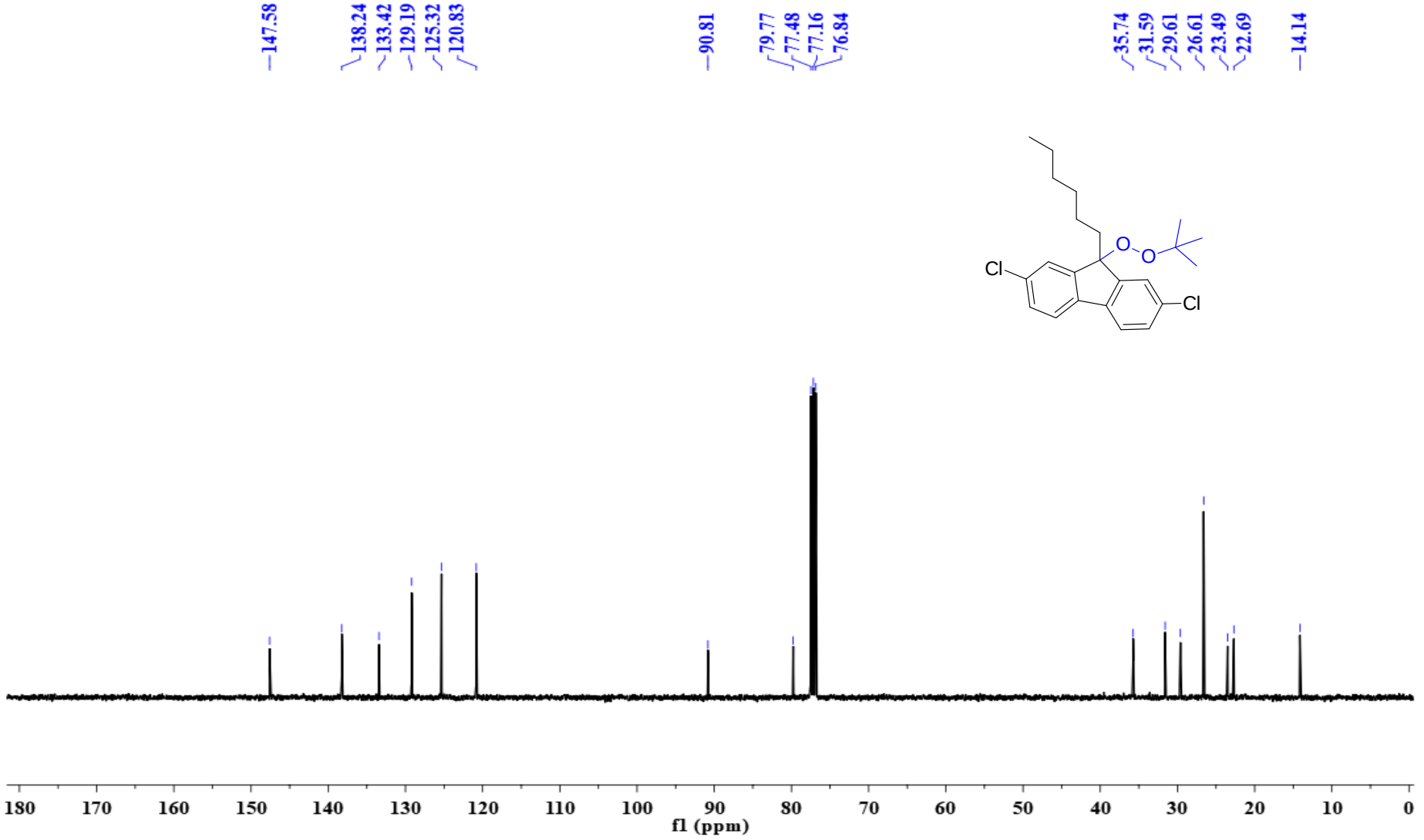


Figure S38. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(tert-butylperoxy)-2,7-dichloro-9-hexyl-9H-fluorene (**P_{18}**).

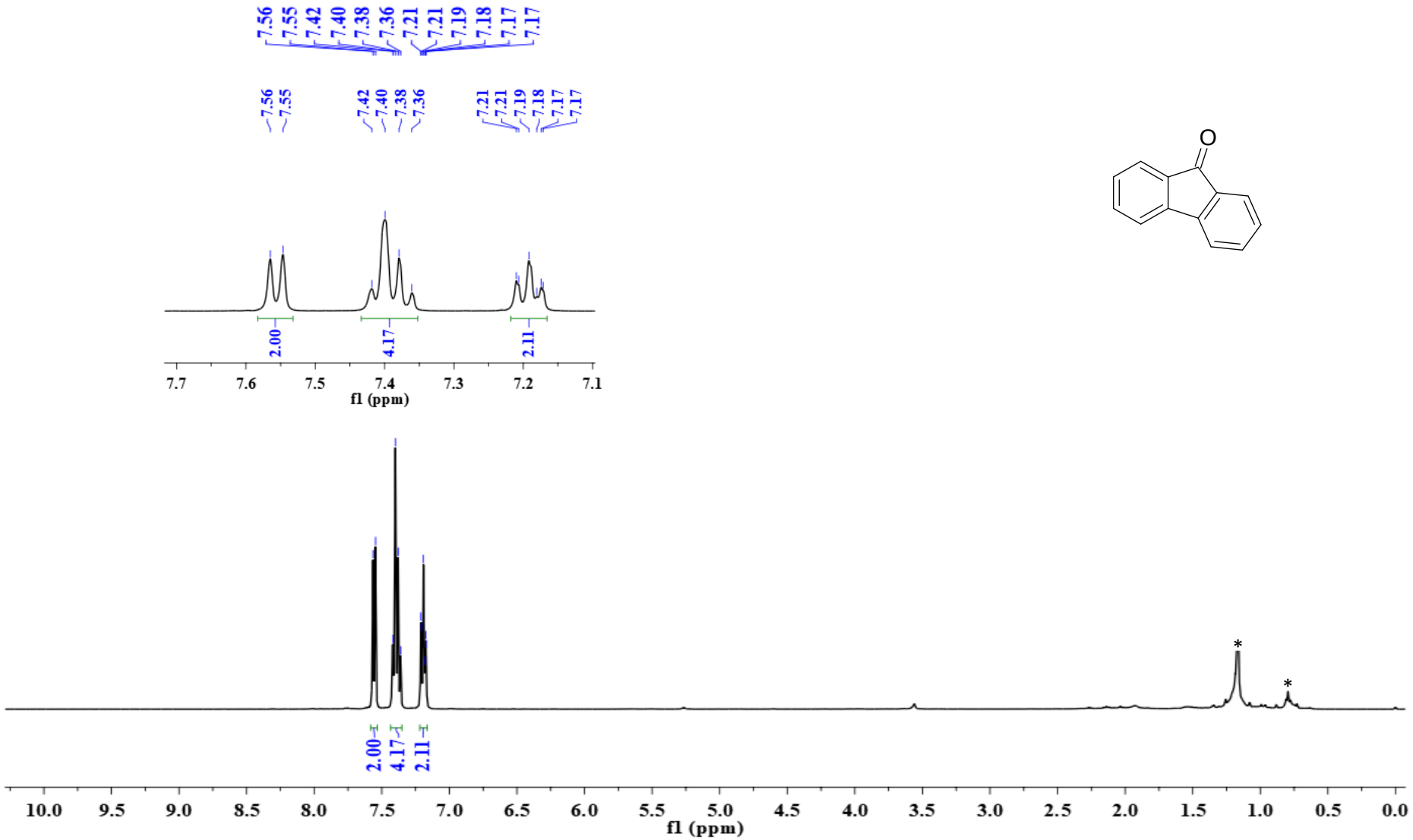


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of 9H-fluoren-9-one (**Q_1**). (* indicates H-grease))

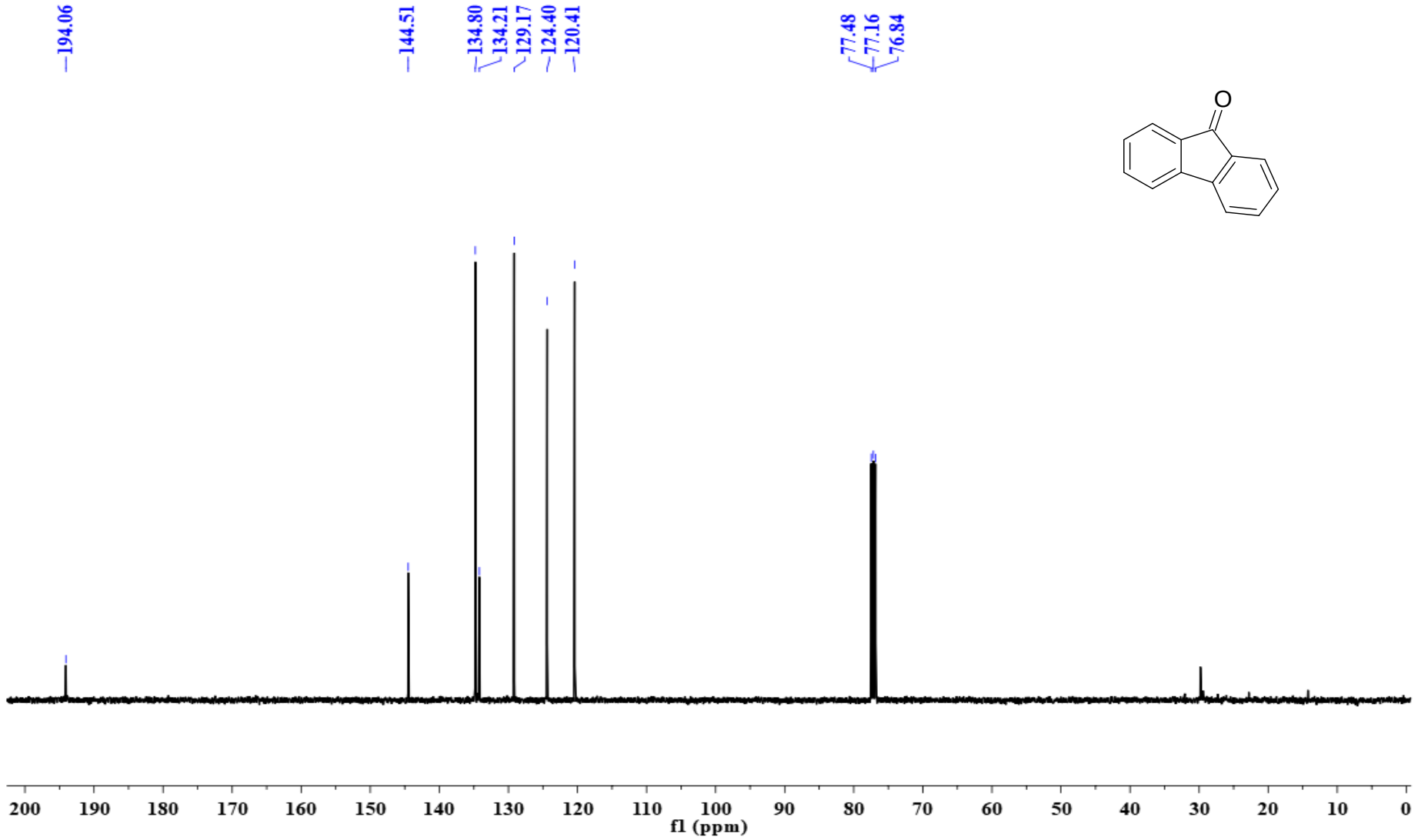


Figure S40. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9H-fluoren-9-one (**Q_1**).

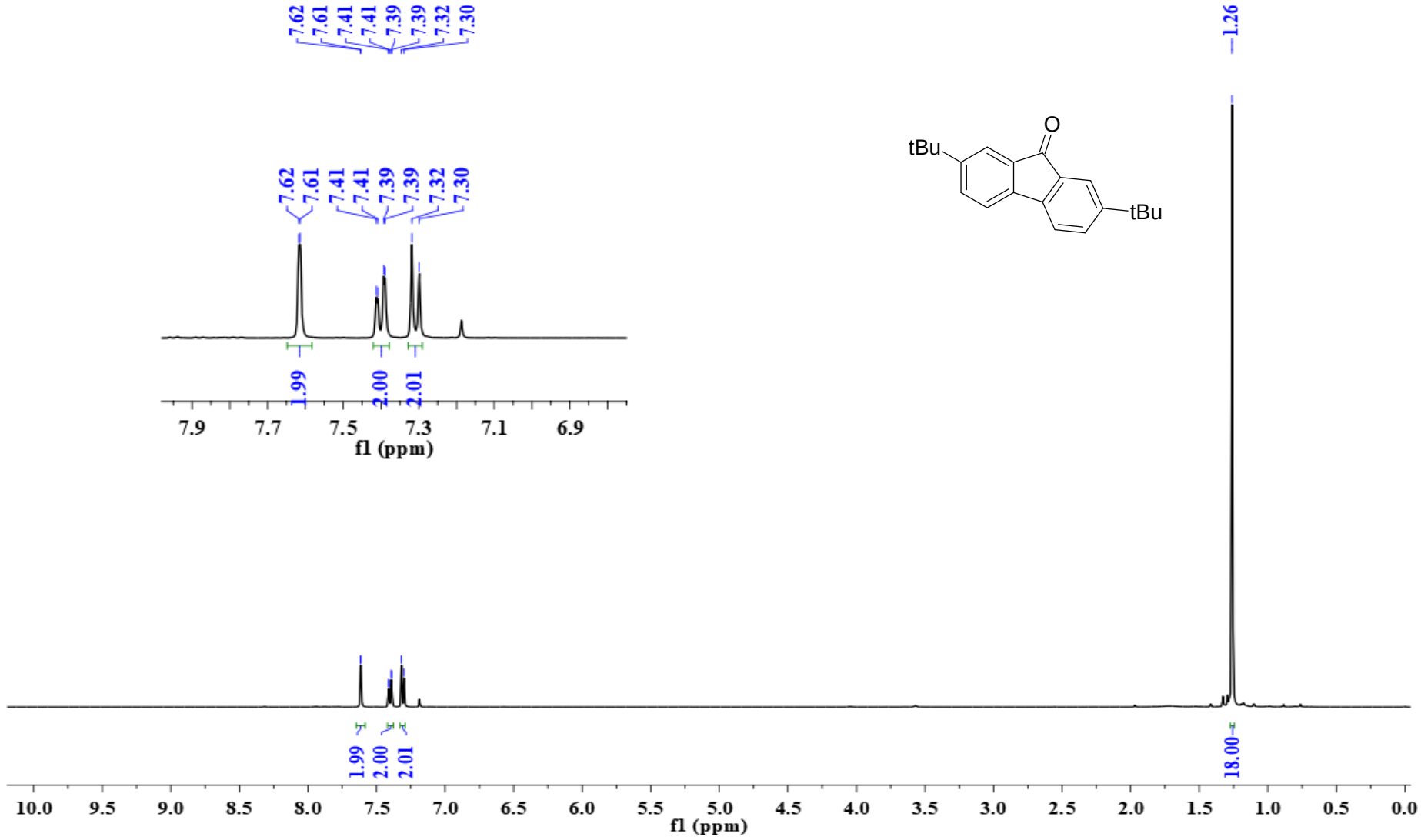


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-di-tert-butyl-9H-fluoren-9-one (**Q_2**).

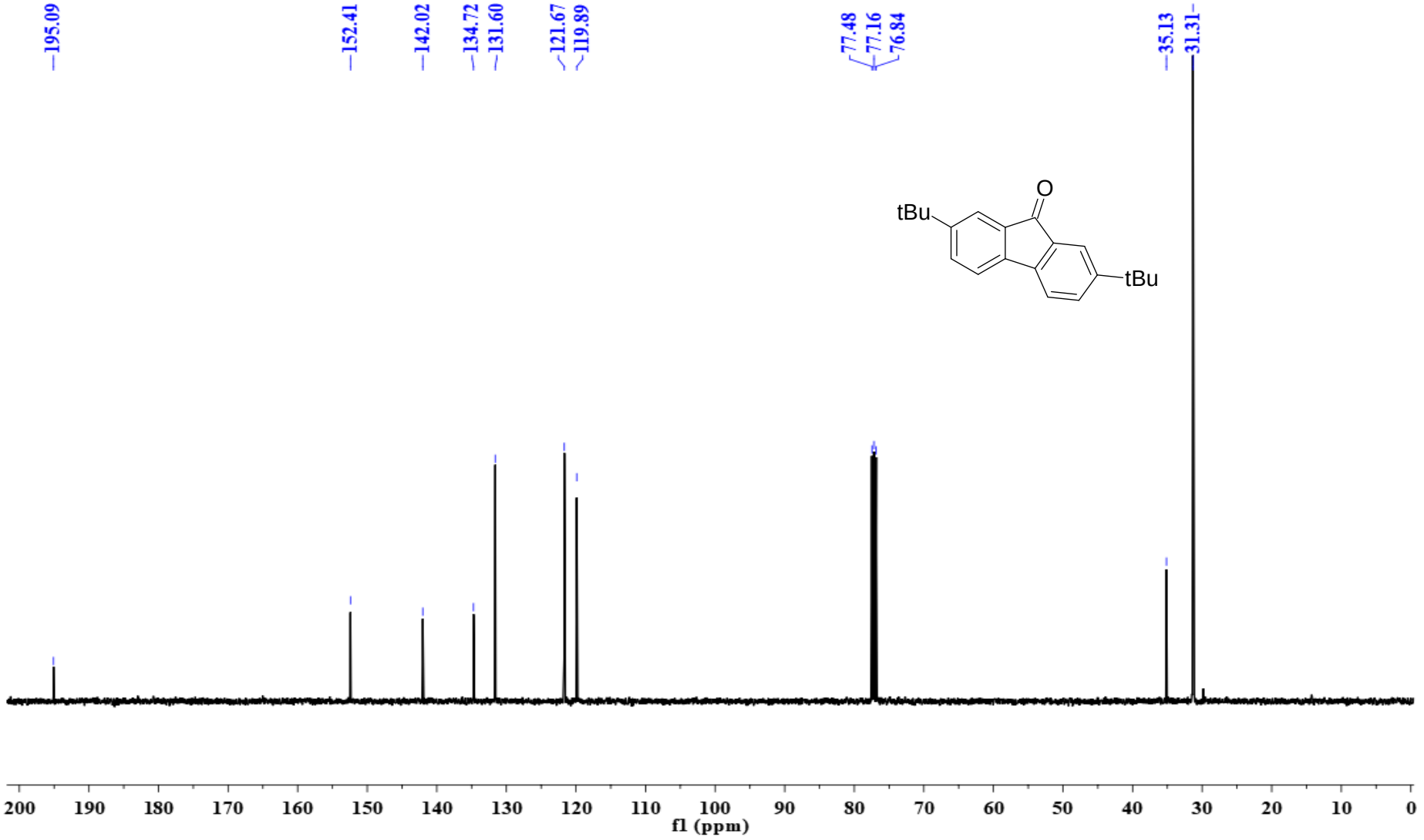


Figure S42. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-di-tert-butyl-9H-fluoren-9-one (**Q_2**).

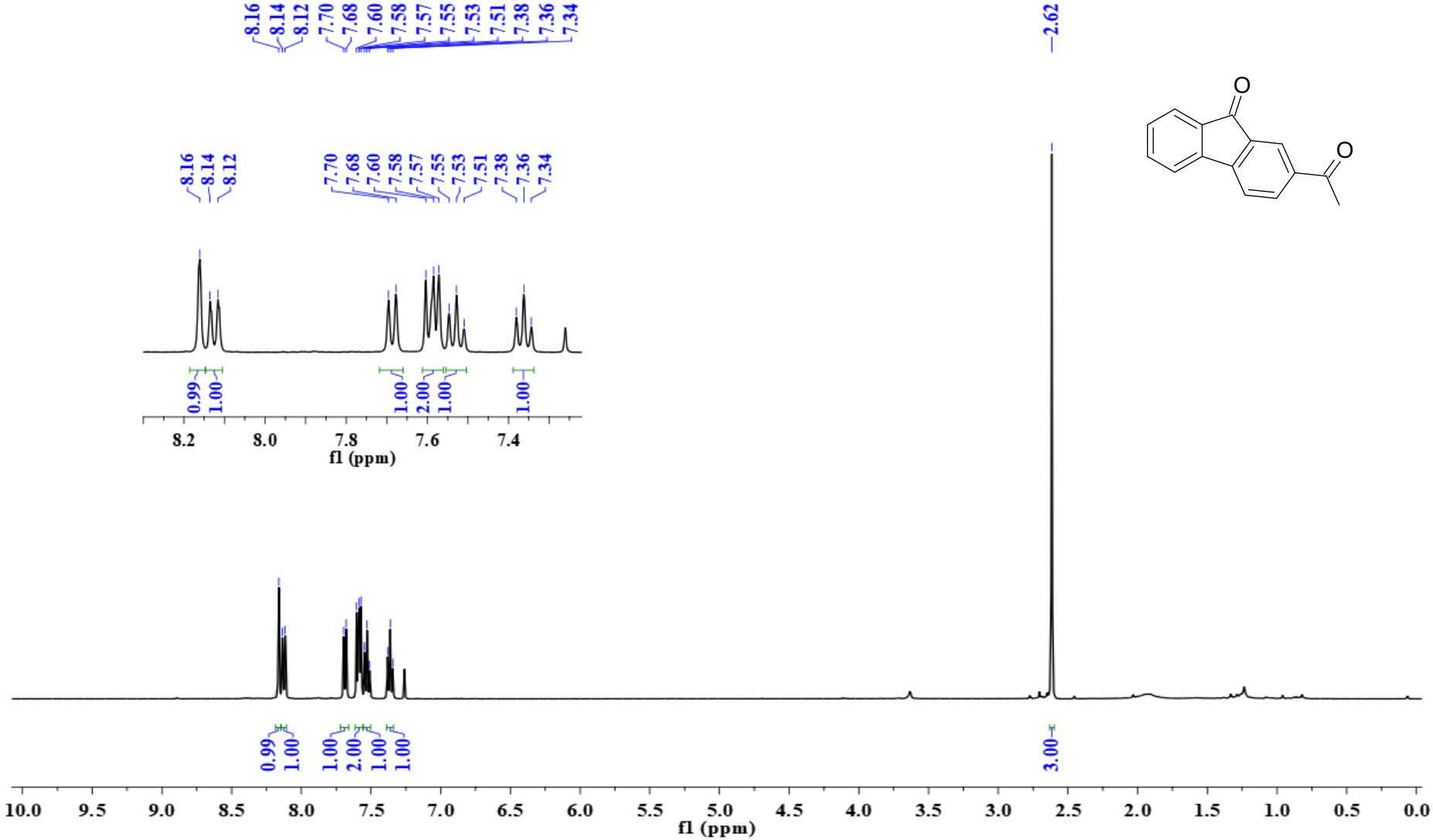


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-acetyl-9H-fluoren-9-one (**Q_3**).

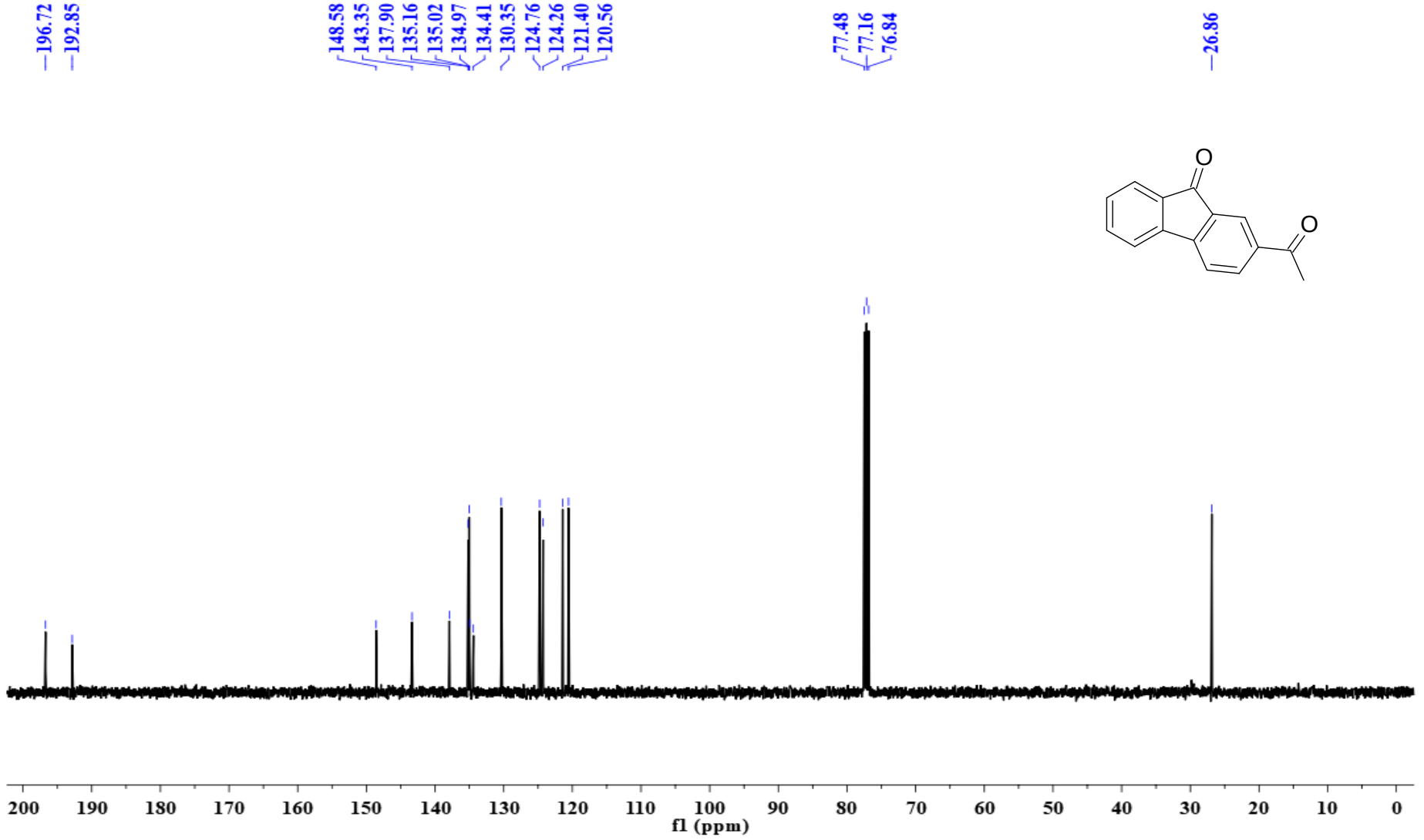


Figure S44. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-acetyl-9H-fluoren-9-one (**Q_3**).

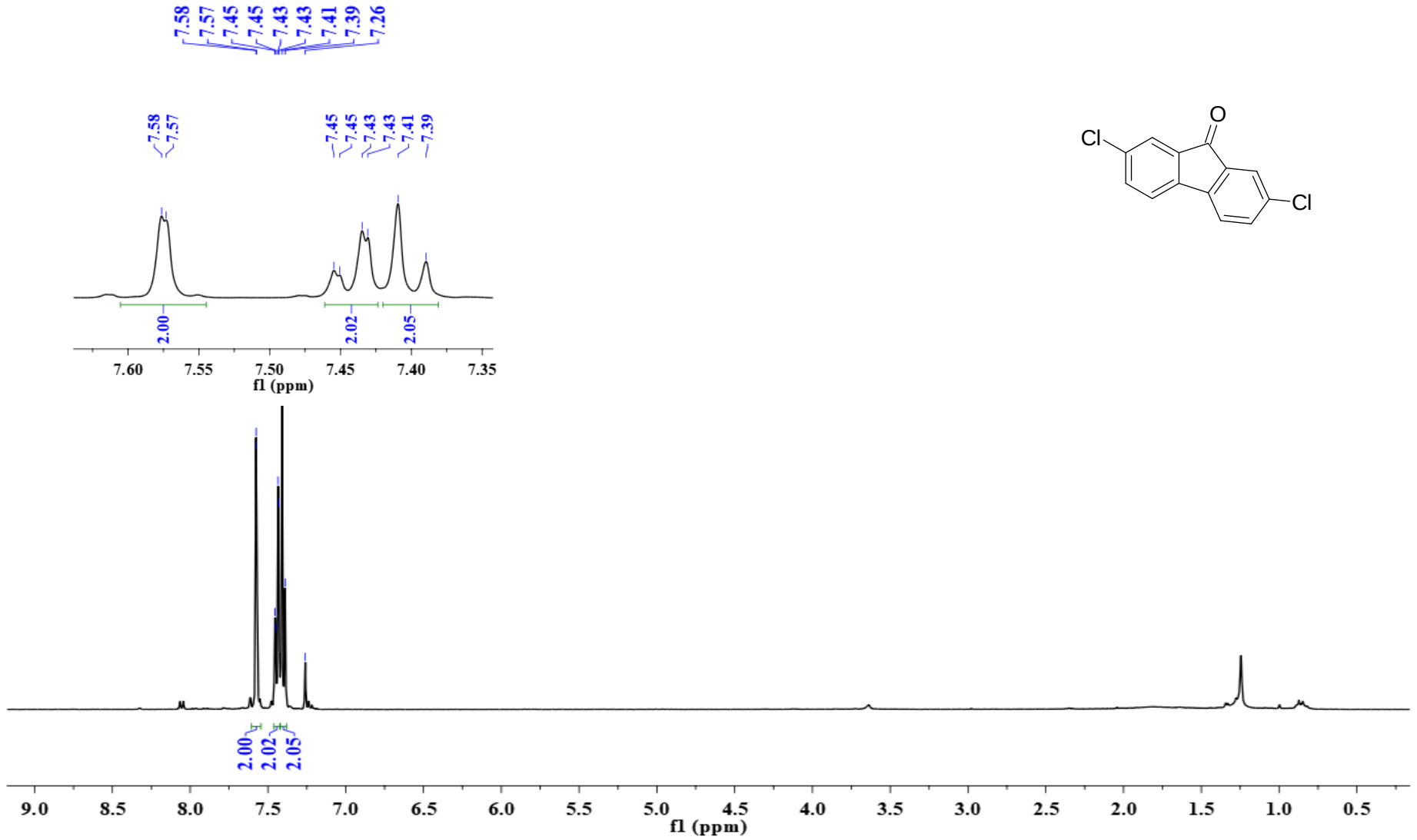


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-dichloro-9H-fluoren-9-one (**Q$_4$**).

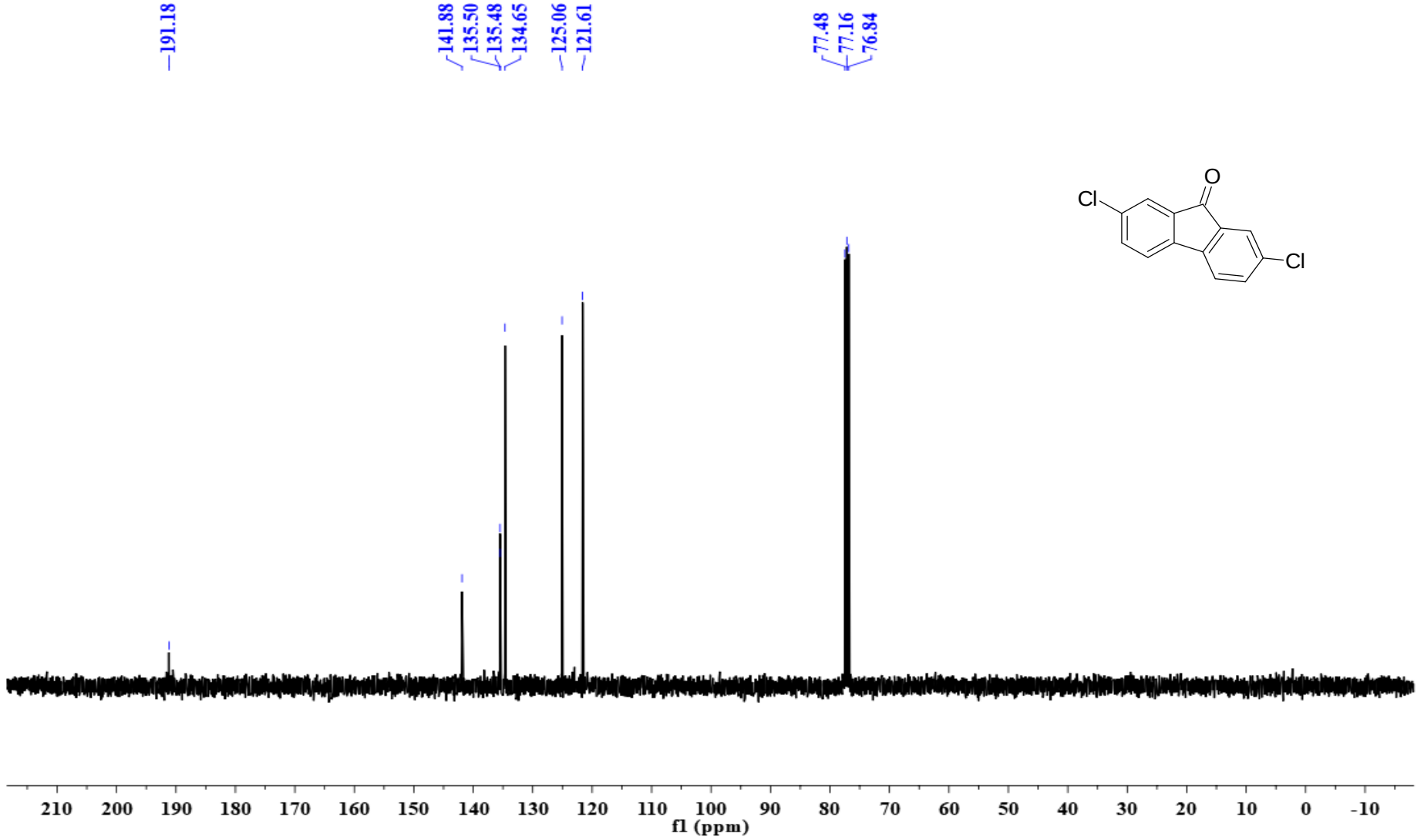


Figure S46. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-dichloro-9H-fluoren-9-one (**Q4**).

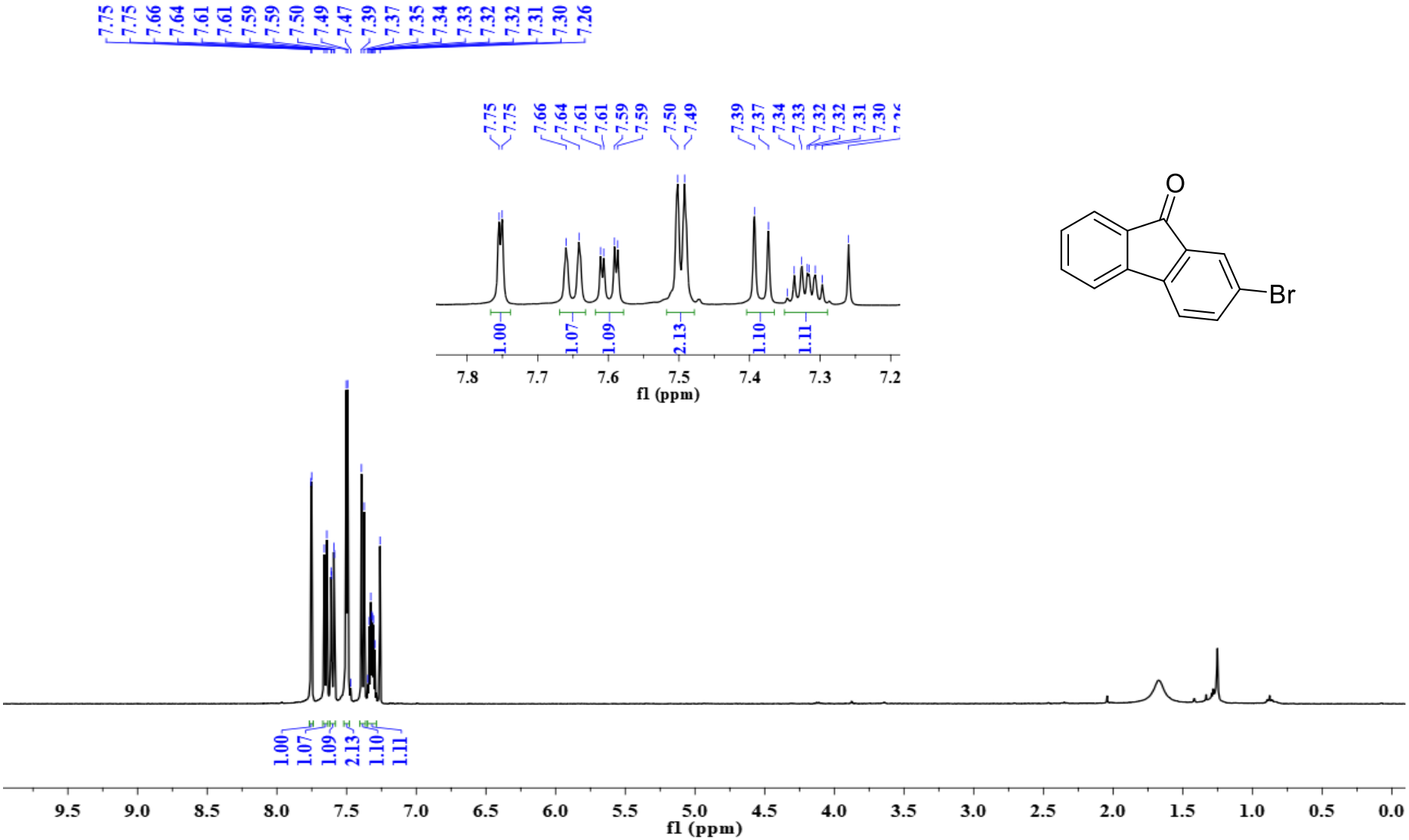


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-bromo-9H-fluoren-9-one (**Q_5**).

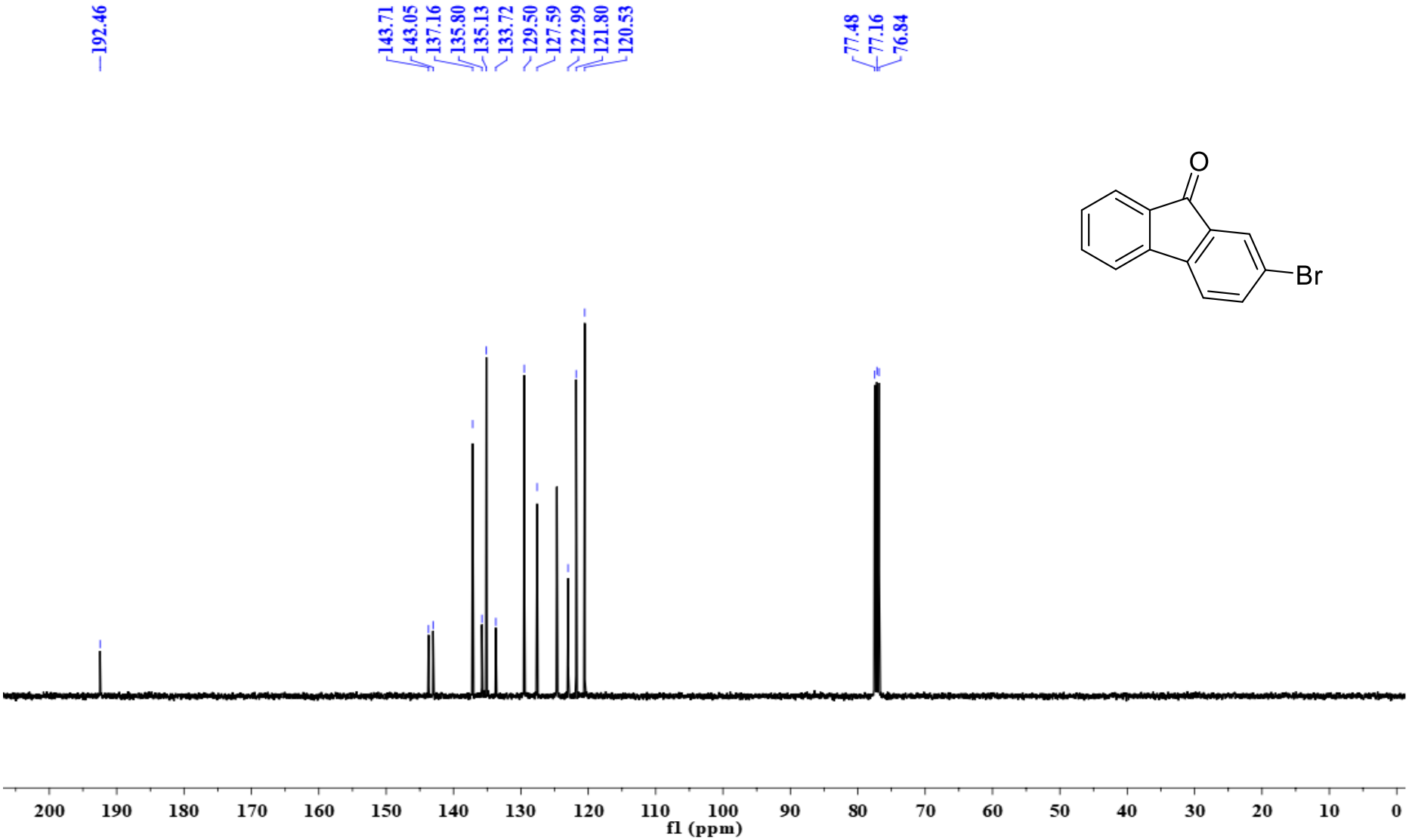


Figure S48. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-bromo-9H-fluoren-9-one (**Q_5**).

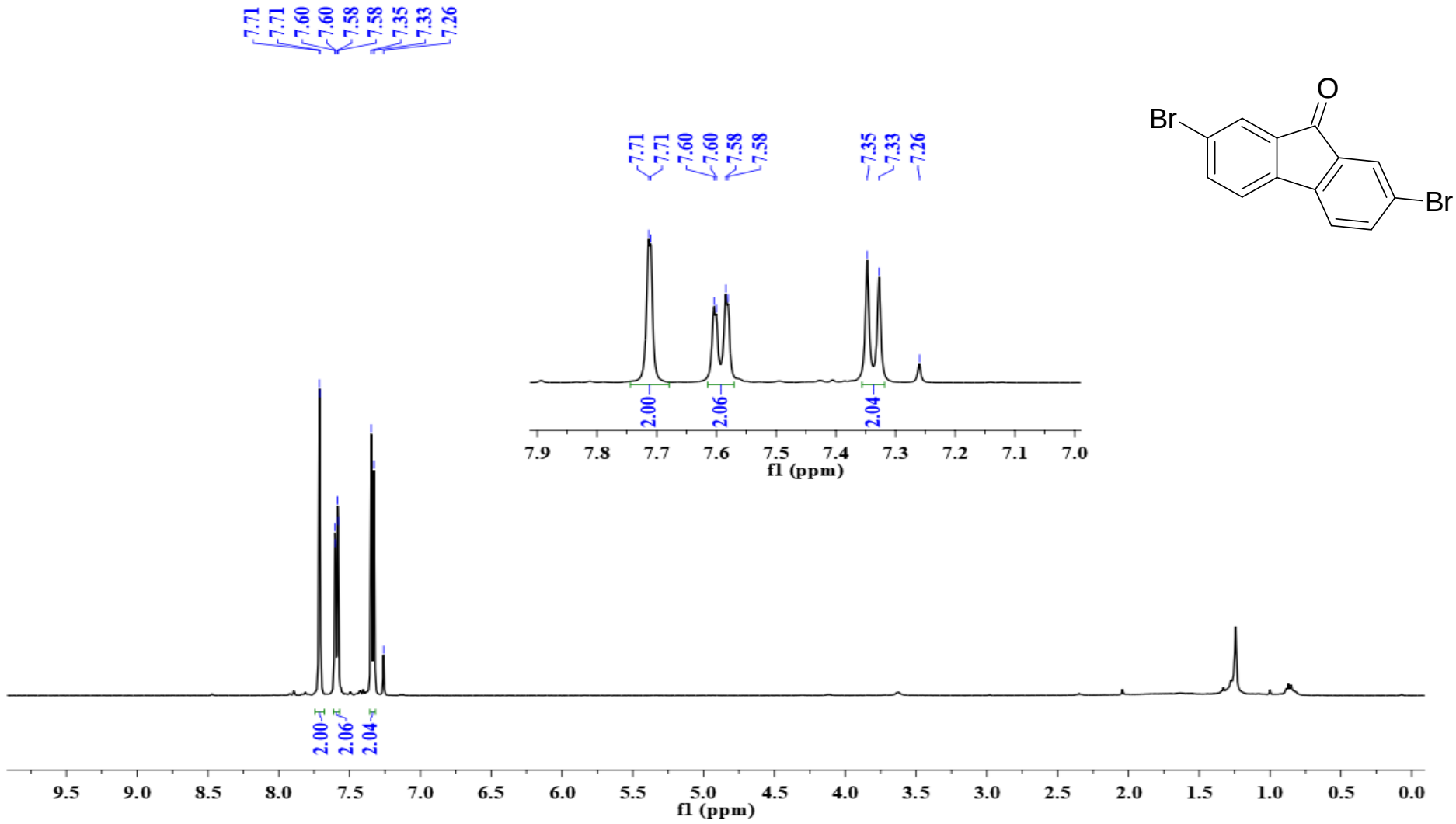


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-dibromo-9H-fluoren-9-one (**Q$_6$**).

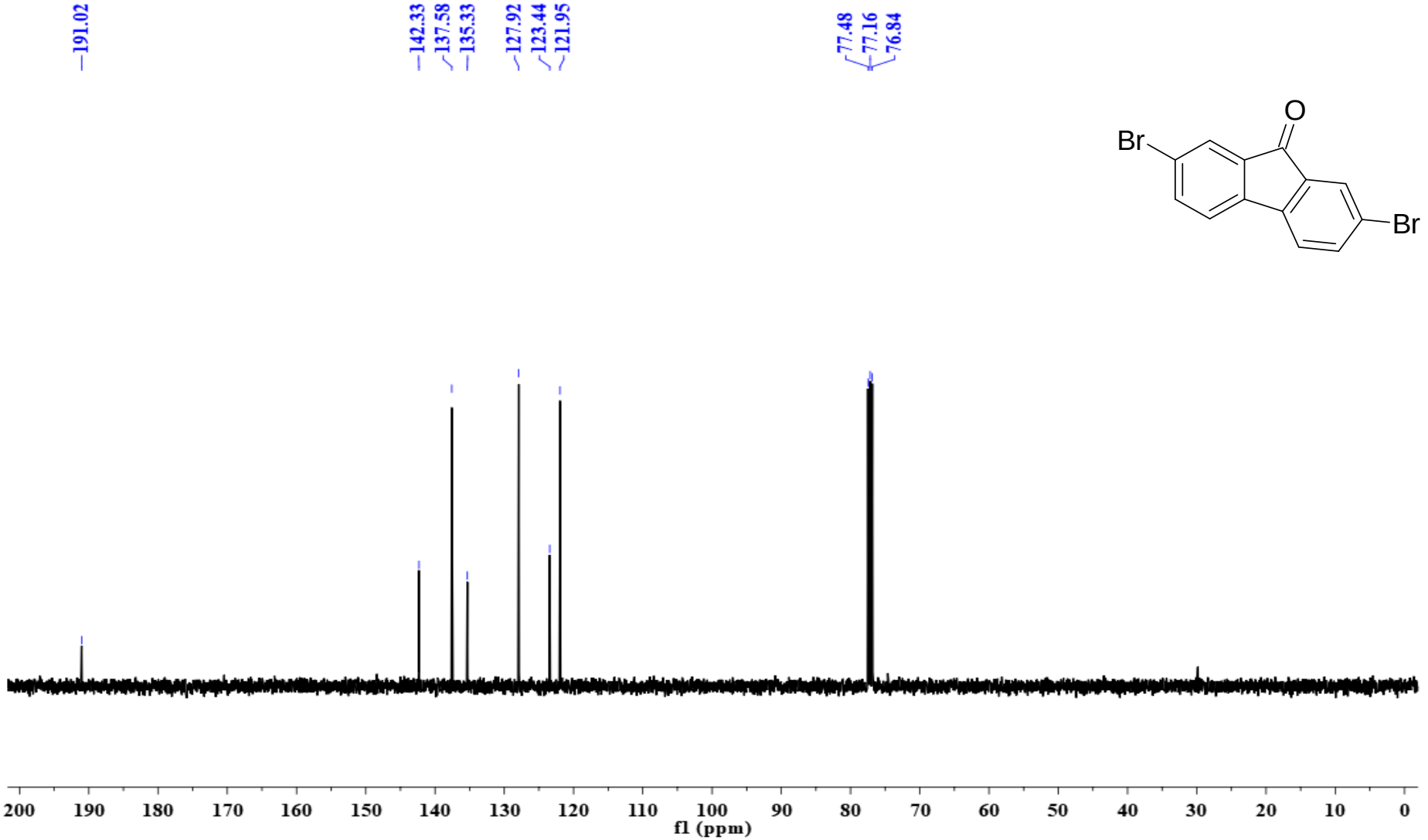


Figure S50. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-dibromo-9H-fluoren-9-one (**Q$_6$**).

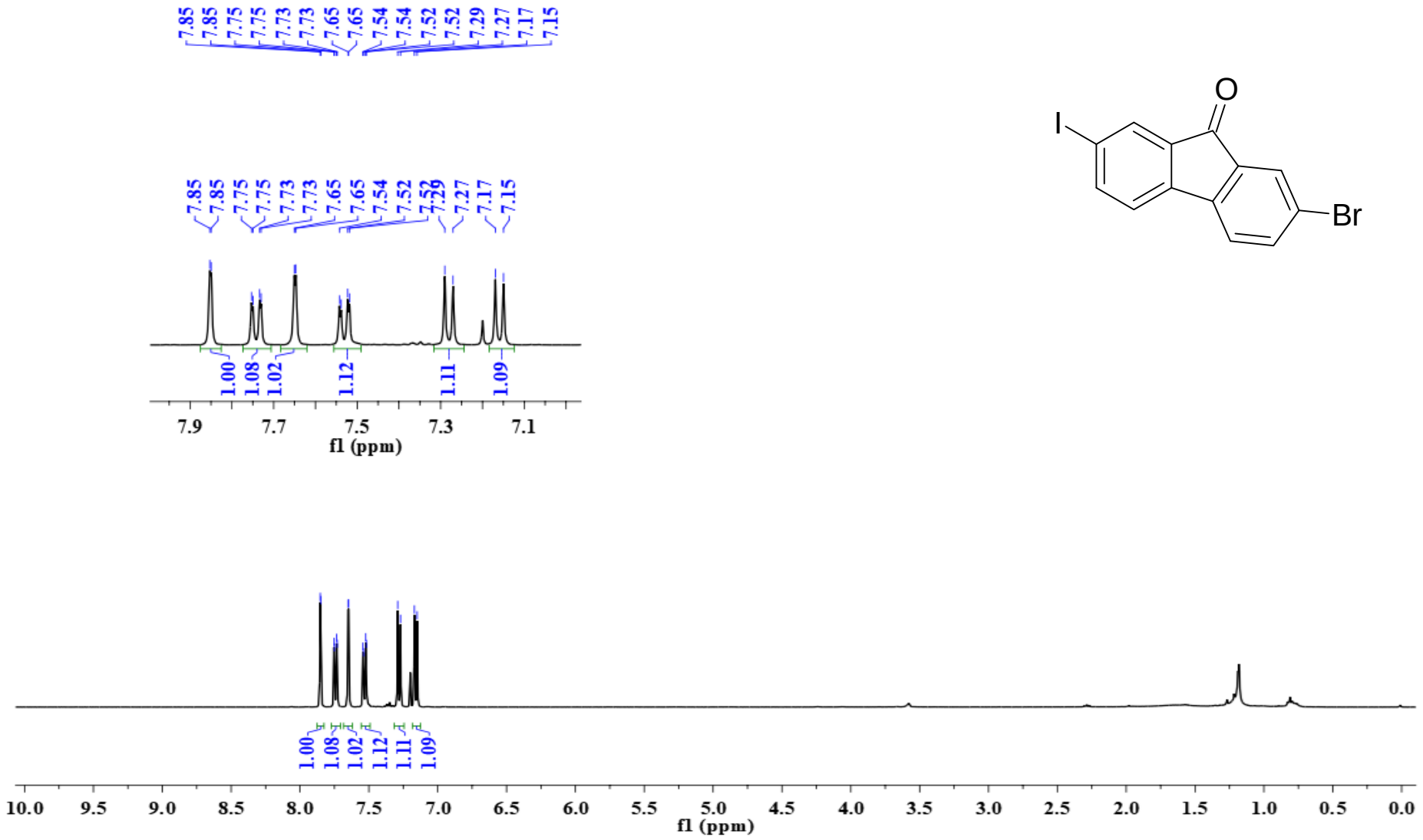


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-bromo-7-iodo-9H-fluoren-9-one (**Q**$_7$).

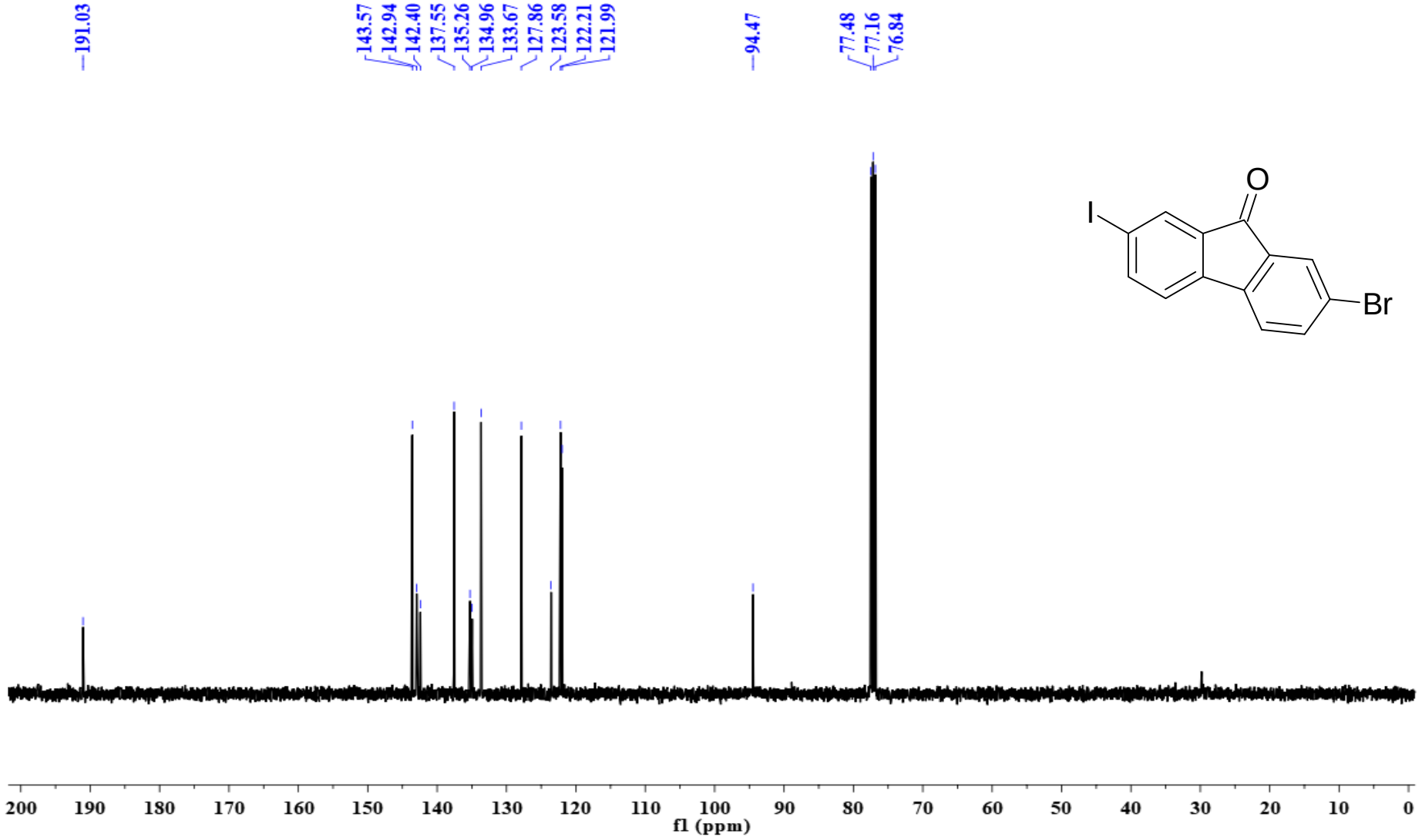


Figure S52. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-bromo-7-iodo-9H-fluoren-9-one (**Q**$_7$).

X-ray structure determination of complex 1

Crystallographic data and structure determinations details are compiled in Table **S3**. The crystals were obtained by slow evaporation of **1** in DCM at r.t. The crystals were coated with silicon oil on a glass slide and a suitable single crystal was mounted on a glass fibre. Crystal data were collected with a Rigaku Oxford diffractometer and with an INCOATEC micro source (Cu-Kα radiation, λ = 1.54184 Å, multilayer optics) at 100 K and 293 K respectively. The structure was determined using direct methods employed in ShelXT,[5] OleX,[6] and refinement was carried out using least-square minimization implemented in ShelXL.[7] All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model. CCDC 2383450 (for **C₁**) contains the supplementary crystallographic data for this paper.

Table S3. Crystallographic Data and Refinement Parameters for complex **1**.

	1
Empirical formula	$C_{15}H_{23}Cl_2FeN_3O_2$
CCDC	2383450
Formula weight (g mol^{-1})	404.11
Temperature	293(2)
Wavelength	1.54184
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.2505(3)
b (Å)	14.1312(4)
c (Å)	12.6158(3)
α (deg)	90
β (deg)	92.263(3)
γ (deg)	90
volume (Å^3)	1826.00(9)
Z	4
ρ_{calc} (g/cm^3)	1.470
μ (mm^{-1})	9.413
F(000)	840.0
Crystal Size /mm^3	0.2 × 0.2 × 0.1
2θ Range (deg)	9.402 to 157.25
Index Ranges	$-12 \le h \le 10$, $-16 \le k \le 17$, $-16 \le l \le 15$
Reflections collected	14189
Independent reflections (R_{int})	3803 (0.0541)
Completeness to theta = 25.07^0	99.9
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/parameters	3803/0/209
Goodness-of-fit on $F2$	1.077
Final R indices [I>2σ(I)]	R_1 = 0.0422, wR_2 = 0.1195
R indices (all data)	R_1 = 0.0448, wR_2 = 0.1216
Largest diff. peak/hole (e Å^{-3})	0.69/-0.72

Table S4. Bond lengths and bond angles of **C_1.**

	Bond Lengths (Å)
Fe1– Cl1	2.2845(6)
Fe1– Cl2	2.3005(6)
Fe1– N1	2.4437(19)
Fe1– N2	2.0943(18)
Fe1– N3	2.3931(18)
	Bond Angles (deg)
Cl1–Fe1– Cl2	112.75(3)
Cl1–Fe1– N1	103.97(5)
Cl1–Fe1– N2	132.43(6)
Cl1–Fe1– N3	95.53(5)
Cl2–Fe1– N1	91.17(5)
Cl2–Fe1– N2	114.75(6)
Cl2–Fe1– N3	105.25(5)
N1–Fe1– N2	73.06(7)
N1–Fe1– N3	147.34(6)
N2–Fe1– N3	74.43(7)

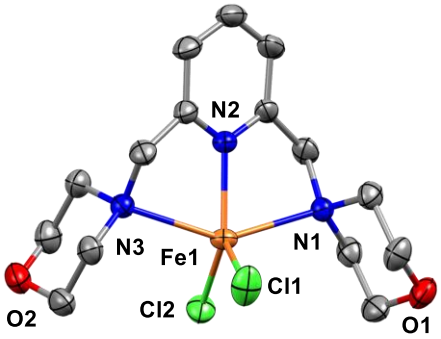


Figure S53. Molecular Structure of complex **1** showing 50% Ellipsoids.

Cyclic voltammetry study of complex 1

The measurements were conducted with an Ag/AgCl reference electrode, a platinum working electrode and a platinum wire auxiliary electrode. Before the measurement, 1 mM solutions of complex **1** were freshly prepared in dry MeCN with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. The scan rate for the CVs reported was 100 mV/s.

The resulting cyclic voltammogram, shown in Figure S54, displays characteristic redox peaks corresponding to the Fe^{II}/Fe^{III} redox couple. The Fe^{II}/Fe^{III} transition exhibits significant peak separation (0.91 V) with distinct anodic and cathodic peaks at 0.87 V and −0.04 V, respectively. This represnts a one-electron redox process. These electrochemical results confirm that the Fe^{II} complex can be oxidized to Fe^{III} oxidation state in solution, further supporting its role in the proposed catalytic cycle.

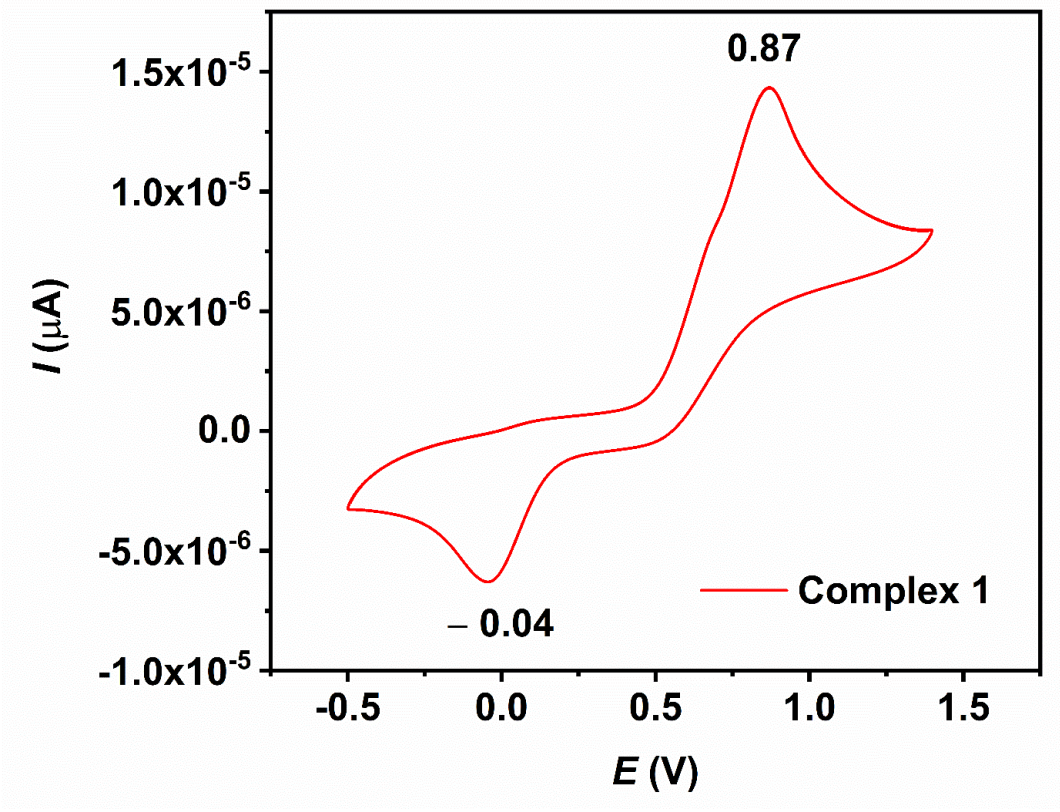


Figure S54. Cyclic voltammogram of complex **1**, measured at room temperature in acetonitrile with TBAP as the supporting electrolyte at a 100 mVs^{-1} scan rate, referenced against an Ag/AgCl electrode.

References:

1. Ubale, A. S.; Chaudhari, M. B.; Shaikh, M. A.; Gnanaprakasam, B. *J. Org. Chem.* **2020**, *85*, 10488– 10503.
2. X. Li, F. Bai, C. Liu, X. Ma, C. Gu and B. Dai, *Org. Lett.*, 2021, **23**, 7445–7449.
3. F. Yang, B. Zhou, P. Chen, D. Zou, Q. Luo, W. Ren, L. Li, L. Fan and J. Li, *Molecules*, 2018, **23**, 1922.
4. M. A. Shaikh, S. G. Agalave, A. S. Ubale and B. Gnanaprakasam, *J. Org. Chem.*, 2020, **85**, 2277–2290.
5. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
7. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112 – 122.