Supporting Information

Rhodium-Catalyzed Tunable Oxidative Cyclization toward the Selective Synthesis of α-Pyrones and Furans

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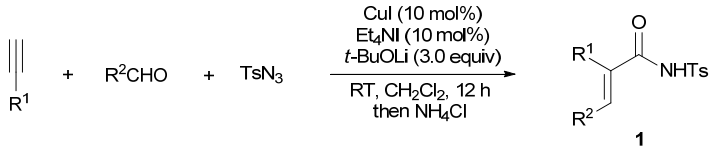
Experimental section

General information

All reactions were carried out under oxygen atmosphere, with dry, freshly distilled solvents in anhydrous conditions. DCM was distilled from CaH_2 immediately prior to use. All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F–254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400 MHz or 600 MHz for ^{1}H NMR, 100 MHz or 150 MHz for ^{13}C NMR) spectra were recorded in $CDCl_3$ with TMS as the internal standard unless otherwise noted. High resolution mass spectral (HRMS) analyses were measured using ESI techniques.

Diazo compound **2**[1] was prepared according to the literature procedure.

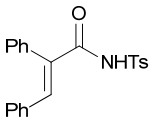
General procedure A for the synthesis of 1



1

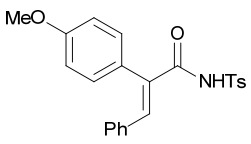
To a mixture of 4-methylbenzenesulfonyl azide (0.45 mmol), CuI (5.7 mg, 0.03 mmol), and Et_4NI (7.7 mg, 0.03 mmol) in CH_2Cl_2 (3 mL) under nitrogen atmosphere at room temperature, aldehyde (0.3 mmol), terminal alkyne (0.45 mmol) and *t*-BuOLi (72.0 mg, 0.9 mmol) were added sequentially. The reaction was monitored by TLC and quenched with saturated aqueous ammonium chloride (3 mL) at the desired time. The reaction mixture was extracted with DCM (5 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v) to give the product **1**.

(*E*)-2,3-Diphenyl-*N*-tosylacrylamide (1a)



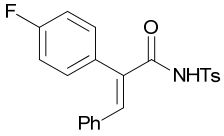
The product **1a** was isolated as a white solid in 90% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H), 7.82 (s, 1H), 7.49-7.48 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22-7.189 (m, 3H), 7.14-7.10 (m, 2H), 6.93-6.91 (d, *J* = 7.2 Hz, 2H), 2.44 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.1, 145.2, 141.4, 135.5, 134.2, 133.8, 131.7, 130.8, 130.3, 129.8, 129.7, 129.6, 128.7, 128.4, 21.7 ppm; **HRMS** calc for $C_{22}H_{19}NO_3S$ $[M]^+$ 377.1086, found 377.1092.

(*E*)-2-(4-Methoxyphenyl)-3-phenyl-*N*-tosylacrylamide (1b)



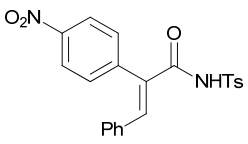
The product **1b** was isolated as an off-white solid in 82% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.98-7.96 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H), 7.78 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.11-7.10 (m, 4H), 7.00-6.95 (m, 4H), 3.88 (s, 3H), 2.44 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.5, 160.4, 145.1, 141.2, 135.5, 134.0, 131.3, 131.1, 130.8, 129.7, 129.6, 128.7, 128.4, 125.8, 115.8, 55.4, 21.7 ppm; **HRMS** calc for $C_{23}H_{21}NO_4S$ $[M]^+$ 407.1191, found 407.1205.

(*E*)-2-(4-Fluorophenyl)-3-phenyl-*N*-tosylacrylamide (1c)



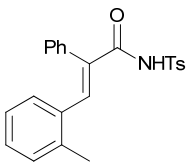
The product **1c** was isolated as a white solid in 87% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.98-7.96 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H), 7.81 (s, 1H), 7.37-7.35 (d, *J* = 8.4 Hz, 2H), 7.25-7.13 (m, 7H), 6.93-6.91 (d, *J* = 8.4 Hz, 2H), 2.45 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.5, 164.0 ($J_{C\text{-}F}$ = 203 Hz), 145.3, 141.9, 135.4, 133.7, 131.9 ($J_{C\text{-}F}$ = 8.2 Hz), 130.7, 130.0, 129.7, 129.6, 128.7 ($J_{C\text{-}F}$ = 24.6 Hz), 117.6 ($J_{C\text{-}F}$ = 21.0 Hz), 21.8 ppm; **HRMS** calc for $C_{22}H_{18}FNO_3S$ $[M]^+$ 395.0991, found 395.0995.

(*E*)-2-(4-Nitrophenyl)-3-phenyl-*N*-tosylacrylamide (1d)



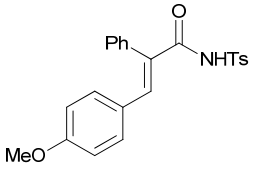
The product **1d** was isolated as a white solid in 87% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.04 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.41-7.32 (m, 6H), 7.15-7.09 (m, 3H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 2.46 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.7, 145.2, 137.7, 135.4, 135.2, 134.3, 133.3, 132.7, 130.6, 130.1, 129.9, 129.8, 129.5, 129.4, 128.8, 128.6, 126.1, 126.0, 21.6 ppm; **HRMS** calc for $C_{22}H_{18}N_2O_5S$ $[M]^+$ 422.0936, found 422.0933.

(*E*)-2-Phenyl-3-(o-tolyl)-*N*-tosylacrylamide (1e)



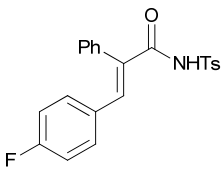
The product **1e** was isolated as a white solid in 71% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.00 (s, 1H), 8.00-7.98 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 1H), 7.39-7.36 (m, 5H), 7.12-7.05 (m, 4H), 6.79-6.76 (t, *J* = 7.2 Hz, 1H), 6.56-6.54 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 2.33 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.1, 145.1, 139.9, 138.4, 135.4, 133.8, 133.1, 132.8, 130.2, 130.0, 129.7, 129.5, 129.2, 129.1, 129.0, 128.6, 125.3, 21.6, 20.0 ppm; **HRMS** calc for $C_{23}H_{21}NO_3S$ $[M]^+$ 391.1242, found 391.1245.

(*E*)-3-(4-Methoxyphenyl)-2-phenyl-*N*-tosylacrylamide (1f)



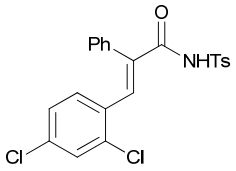
The product **1f** was isolated as a white solid in 85% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.97-7.95 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.78 (s, 1H), 7.52-7.49 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.23-7.21 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.72 (s, 3H), 2.44 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.2, 160.8, 145.0, 141.1, 135.5, 134.5, 132.7, 130.3, 129.8, 129.4, 129.4, 128.8, 128.6, 126.4, 113.8, 55.2, 21.6 ppm; **HRMS** calc for $C_{23}H_{21}NO_4S$ $[M]^+$ 407.1191, found 407.1205.

(*E*)-3-(4-Fluorophenyl)-2-phenyl-*N*-tosylacrylamide (1g)



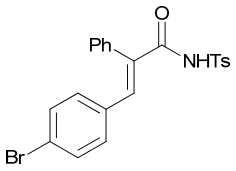
The product **1g** was isolated as a light yellow solid in 88% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.73 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (m, 7H), 6.84 (d, *J* = 7.6 Hz, 2H), 2.37 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.0 ($J_{C\text{-}F}$ = 249.0 Hz), 163.5, 144.8, 141.4, 134.9, 133.2, 131.4 ($J_{C\text{-}F}$ = 8.3 Hz), 130.2, 129.5 ($J_{C\text{-}F}$ = 3.6 Hz), 129.4, 129.1, 128.2, 128.0, 117.1 ($J_{C\text{-}F}$ = 28.8 Hz), 21.3 ppm; **HRMS** calc for $C_{22}H_{18}FNO_3S$ $[M]^+$ 395.0991, found 395.0993.

(*E*)-3-(2,4-Dichlorophenyl)-2-phenyl-*N*-tosylacrylamide (1h)



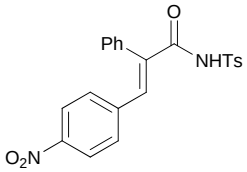
The product **1h** was isolated as a light yellow solid in 87% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.92-7.89 (m, 4H), 7.36-7.35 (m, 3H), 7.31-7.28 (m, 3H), 7.07-7.05 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 2H), 2.39 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.5, 145.4, 136.6, 136.3, 135.5, 135.3, 134.9, 133.1, 131.4, 131.3, 130.1, 129.8, 129.8, 129.7, 129.6, 128.8, 126.7, 21.8 ppm; **HRMS** calc for $C_{22}H_{17}Cl_2NO_3S$ $[M]^+$ 445.0306, found 445.0304.

(*E*)-3-(4-Bromophenyl)-2-phenyl-*N*-tosylacrylamide (1i)



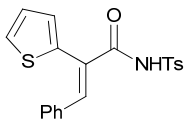
The product **1i** was isolated as a light yellow solid in 83% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.74 (s, 1H), 7.67 (s, 1H), 7.44-7.42 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.19–7.17 (m, 2H), 7.13-7.11 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 2.38 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.9, 145.3, 140.0, 135.4, 133.8, 132.7, 132.3, 132.1, 131.7, 130.4, 129.8, 129.6, 129.6, 128.7, 124.2, 21.8 ppm; **HRMS** calc for $C_{22}H_{18}BrNO_3S$ $[M]^+$ 455.0191, found 455.0191.

(*E*)-3-(4-Nitrophenyl)-2-phenyl-*N*-tosylacrylamide (1j)



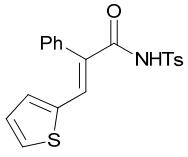
The product **1j** was isolated as a light yellow solid in 84% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.90-7.88 (m, 5H), 7.74 (s, 1H), 7.44-7.42 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12-7.10 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.38 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.4, 147.6, 145.5, 140.2, 138.3, 135.2,132.9, 131.1, 130.5, 130.2, 129.7, 129.5, 129.4, 128.8, 123.5, 21.8 ppm; **HRMS** calc for $C_{22}H_{18}N_2O_5S$ $[M]^+$ 422.0936, found 422.4538.

(*Z*)-3-Phenyl-2-(thiophen-2-yl)-*N*-tosylacrylamide (1k)



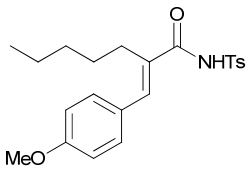
The product **1k** was isolated as a brown solid in 75% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.13 (s, 1H), 8.00-7.97 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 7.54-7.42 (d, *J* =5.2 Hz, 1H), 7.37-7.35 (d, *J* = 8.4 Hz, 2H), 7.29-7.25 (m, 1H), 7.21-7.17 (m, 3H), 7.03-7.01 (m, 3H), 2.45 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.4, 145.2, 144.7, 135.4, 134.2, 133.5, 130.9, 130.4, 129.6, 129.5, 129.4, 128.8, 128.7, 128.5, 123.9, 21.8 ppm; **HRMS** calc for $C_{20}H_{17}NO_3S_2$ $[M]^+$ 383.0650, found 383.0653.

(*E*)-2-Phenyl-3-(thiophen-2-yl)-*N*-tosylacrylamide (1l)



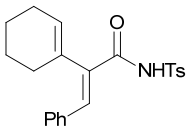
The product **1l** was isolated as a brown solid in 82% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.97 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H), 7.49-7.47 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.18-7.16 (m, 3H), 7.04-7.03 (m, 1H), 6.84-6.82 (m, 1H), 5.21 (s, 1H), 2.36 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.6, 145.1, 138.0, 135.5, 134.8, 134.7, 133.2, 131.7, 130.7, 130.2, 129.6, 128.7, 128.3, 127.0, 53.5, 21.8 ppm; **HRMS** calc for $C_{23}H_{21}NO_3S$ $[M]^+$ 383.0650, found 383.0651.

(*E*)-2-(4-Methoxybenzylidene)-*N*-tosylheptanamide (1m)



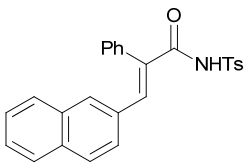
The product **1m** was isolated as a yellow solid in 86% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.70 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.20-7.13 (m, 3H), 6.83-6.81 (m, 2H), 3.75 (s, 3H), 2.40-2.37 (m, 5H), 1.34-1.31 (m, 2H), 1.18-1.17 (m, 4H), 0.75 ppm (t, *J* = 4.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 166.8, 160.1, 145.0, 136.8, 135.7, 133.7, 131.1, 129.6, 128.5, 127.3, 114.1, 55.3, 31.8, 28.5, 27.4, 22.4, 21.7, 14.0 ppm; **HRMS** calc for $C_{22}H_{27}NO_4S$ $[M]^+$ 401.1661, found 401.1659.

(*E*)-2-(Cyclohex-1-en-1-yl)-3-phenyl-*N*-tosylacrylamide (1n)



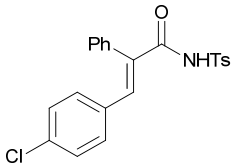
The product **1n** was isolated as an white solid in 88% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.54 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 7.41-7.39 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.24-7.22 (m, 3H), 5.79 (s, 1H), 2.36 (s, 3H), 2.15-2.14 (m, 2H), 1.94-1.94 (m, 2H), 1.67-1.63 ppm (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.0, 145.1, 139.0, 135.6, 134.3, 133.9, 133.6, 132.2, 130.2, 129.7, 129.6, 128.7, 128.5, 28.0, 25.5, 22.7, 21.7, 21.4 ppm; **HRMS** calc for $C_{22}H_{23}NO_3S$ $[M]^+$ 381.1399, found 381.1401.

(*E*)-3-(Naphthalen-2-yl)-2-phenyl-*N*-tosylacrylamide (1o)



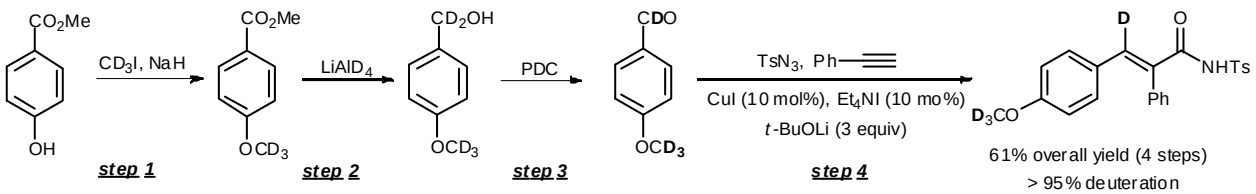
The product **1o** was isolated as a brown solid in 76% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.44 (s, 1H), 7.98-7.87 (m, 4H), 7.75-7.73 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.48-7.43 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H),7.28-7.24 (m, 3H), 7.06-7.00 (m, 3H), 6.75 (d, *J* = 7.2 Hz, 1H), 2.41 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.0, 145.3, 139.6, 135.5, 134.4, 133.9, 133.3, 132.1, 131.3, 130.1, 129.7, 129.7, 129.5, 129.2, 128.8, 128.7, 128.0, 126.8, 126.2, 124.9, 124.0, 21.8 ppm; **HRMS** calc for$C_{26}H_{21}NO_3S$ $[M]^+$ 427.1242, found 427.1242.

(*E*)-3-(4-Chlorophenyl)-2-phenyl-*N*-tosylacrylamide (1p)



The product **1p** was isolated as a yellow solid in 79% yield following general procedure A. The purification was performed by flash column chromatography on silica gel (*n*-hexane/EtOAc = 3:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.96 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H), 7.75 (s, 1H), 7.50-7.47 (m, 3H), 7.36-7.34 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 2H), 7.10-7.07 (m, 2H), 6.84-6.82 (d, *J* = 8.4 Hz, 2H), 2.44 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.8, 145.1, 139.8, 135.6, 135.3, 133.7, 132.2, 132.1, 131.8, 130.3, 129.6, 129.5, 129.5, 128.6, 21.6 ppm; **HRMS** calc for $C_{22}H_{18}ClNO_3S$ $[M]^+$ 411.0696, found 411.0691.

Synthesis of 1f-d_4



Step 1:

Methyl 4-hydroxybenzoate (500 mg, 3.30 mmol) was dissolved in dry DMF (6 mL) under N_2. The solution was cooled to 0°C and NaH (60% in mineral oil, 158 mg, 3.94 mmol) was added. The mixture was stirred at room temperature for 0.5 h, then CD_3I (0.5 mL) was added at 0°C. Stirring was continued at room temperature for 30 min and then Et_2O (20 mL) was added to the reaction mixture. The mixture was washed three times with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the desired methyl 4-methoxybenzoate-d_3.

Step 2:

To a solution of methyl 4-methoxybenzoate-d_3 obtained in step 1(about 520 mg, 3.04 mmol) in dry THF (20 mL) under N_2 at room temperature, lithium aluminum deuteride ($LiAlD_4$, 65 mg, 1.54 mmol) was carefully added. The reaction mixture was then heated to reflux at 70 ^oC and stirred for 1.5 h. After the completion of reaction, the mixture was cooled to 0 ^oC and treated with H_2O and aqueous NaOH (10%), and extracted twice with Et_2O (20 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford the desired 4-methoxybenzyl alcohol-d_5.

Step 3:

4-Methoxybenzyl alcohol-d_5 obtained in step 2 (about 391 mg, 2.74 mmol) was treated with PDC (2.10 g, 5.50 mmol) in dry CH_2Cl_2 (15 mL) at room temperature under N_2 for 24 h. The reaction mixture was filtered through a pad of Celite and the filter cake was washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to give crude 4-methoxybenzaldehyde-d_4.

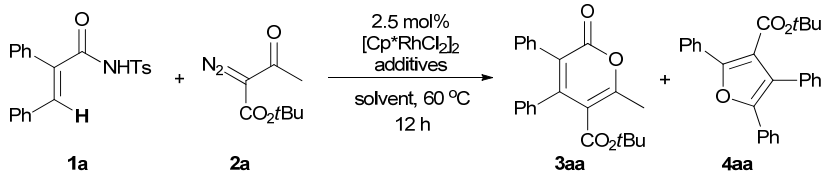
Step 4:

To a mixture of 4-methylbenzenesulfonyl azide (729 mg, 3.70 mmol), CuI (47.5 mg, 0.25 mmol), and Et_4NI (64.3 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) under N_2 at room temperature, 4-methoxybenzaldehyde-d_4 (obtained in step 3, about 345mg, 2.5 mmol), ethynylbenzene (0.41 ml, 3.70 mmol) and *t*-BuOLi (600 mg, 7.50 mmol) were added sequentially. After 12 h, the reaction was quenched with saturated aqueous ammonium chloride (10 mL) and extracted with DCM (20 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography silica gel (*n*-hexane/EtOAc = 3:1, v/v) to give the product **1f-d$_4$** (822mg, 61% yield over four steps). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.88 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.44-7.43 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.16-7.14 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 2.37 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ =164.3, 160.9, 145.1, 135.6, 134.6, 132.8, 130.4, 129.9, 129.6, 129.5, 128.8, 128.7, 126.4, 113.9, 31.6, 22.7, 21.8, 14.2 ppm; **HRMS** calc for $C_{23}H_{17}D_4NO_4S$ $[M]^+$ 411.1442, found 411.1438.

Optimization of reaction conditions (Table S1)

To a schlenk tube (10 mL) were added N-tosylacrylamides **1** (0.20 mmol), diazo compounds **2** (0.4 mmol), catalyst, additive, and solvent (2.0 mL) under nitrogen atmosphere. After stirring the reaction mixture at the indicated temperature for 12 h, it was cooled to room temperature and diluted with dichloromethane (10 mL). The mixture was filtered through a Celite pad and washed with dichloromethane (3 x 20 mL). The filtrate was concentrated, and the product was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to afford pure products.

Table S1. Optimization of reaction conditions[a]

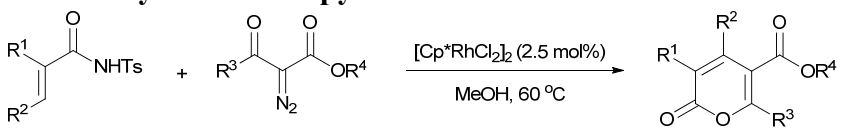


1a 2a 3aa 4aa

Entry	Additives (equiv)	Solvent	Yield (%)[b]	
			3aa	**4aa**
1	–	MeOH	98	–
2	NaOAc (2.0)	MeOH	93	
3[c]	–	MeOH	–	–
4	–	EtOH	92	–
5	–	*t*BuOH	90	–
6	–	DCE	56	–
7	–	MeCN	17	–
8	–	THF	23	–
9	–	1,4-dioxane	30	–
10	–	toluene	34	–
11	–	DMF	26	–
12[d]	–	MeOH	56	–
13	AgOAc (1.0)	MeOH	64	30
14	AgOAc (2.0)	MeOH	33	61
15	Ag_2O (2.0)	MeOH	35	60
16	Ag_2CO_3 (2.0)	MeOH	40	45
17	$Cu(OAc)_2$ (2.0)	MeOH	78	15
18	AgOAc (2.0)/$AgSbF_6$ (0.1)	MeOH	13	78
19	AgOAc (2.0)/$AgSbF_6$ (0.1)	t-AmOH	21	70
20	AgOAc (2.0)/$AgSbF_6$ (0.1)	DCE	40	–
21	AgOAc (2.0)/CsOAc (0.1)	MeOH	42	52
22	AgOAc (2.0)/NaOPiv (0.1)	MeOH	40	55
23	AgOAc (2.0)/$AgBF_4$ (0.1)	MeOH	53	40
24	AgOAc (2.0)/$AgSbF_6$ (0.1)/TEMPO(2.0)	MeOH	93	–
25[c]	AgOAc (2.0)/$AgSbF_6$ (0.1)	MeOH	<5	–

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%) , and additives in solvent (2.0 mL) at 60 °C, 12 h, under N_2. [b] Isolated yields. [c] Without $[Cp^*RhCl_2]_2$. [e] 1.0 equiv of **2a** was used.

General procedure B for the synthesis of α-pyrones 3

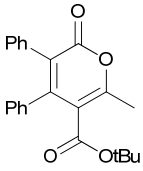


1 2 3

A Schlenk tube (10 mL) was charged with N-tosylacrylamides **1** (0.2 mmol), diazo compound **2** (0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) under N_2, MeOH (2.0 mL) was added by syringe. After stirring the reaction mixture at 60 °C for 12 h, it was cooled to room temperature and diluted with dichloromethane (10 mL). The mixture was filtered through a Celite pad and washed with dichloromethane (3 x 20 mL). The filtrate was

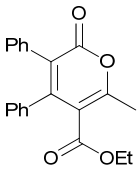
concentrated, and the residue was purified by column chromatography on silica gel to afford the product **3.**

Tert-butyl 6-methyl-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3aa)



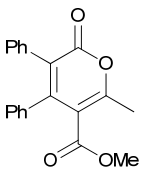
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a**, 75.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3aa** as a white solid (71.0 mg, 98%); **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.13-7.10 (m, 3H), 7.08-7.06 (m, 3H), 6.97-6.93 (m, 4H), 2.36 (s, 3H), 1.06 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.8, 161.6, 160.8, 151.5, 136.2, 133.1, 130.6, 128.4, 128.2, 128.0, 127.8, 127.6, 123.9, 116.1, 82.7, 27.4, 18.6 ppm; HRMS calc for $C_{23}H_{22}O_4$ $[M]^+$ 362.1518, found 362.1521.

Ethyl 6-methyl-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3ab)



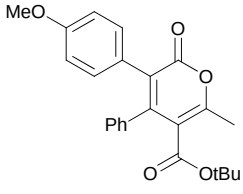
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a**, 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxobutanoate (**2b**, 62.4 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ab** as a white solid (63.5 mg, 95%); **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.19-7.07 (m, 6H), 6.99-6.96 (m, 2H), 6.93-6.90 (m, 2H), 3.80 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 0.72 ppm (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.9, 161.7, 161.5, 151.4, 136.3, 133.0, 130.6, 128.2, 128.1, 128.0, 127.8, 127.7, 123.8, 114.8, 61.6, 18.8, 13.4 ppm; **HRMS** calc for $C_{21}H_{18}O_4$ $[M]^+$ 334.1205, found 334.1207.

Methyl 6-methyl-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3ac)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a**, 75.4 mg, 0.2 mmol), methyl 2-diazo-3-oxobutanoate (**2c**, 56.8 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ac** as a white solid (59.5 mg, 93%); **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.20-7.16 (m, 6H), 7.06-7.04 (m, 2H), 6.98-6.96 (m, 2H), 3.40 (s, 3H), 2.45 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 166.4, 161.7, 161.5, 151.3, 136.2, 133.0, 130.6, 128.3, 128.1, 128.0, 127.8, 127.7, 123.8, 114.6, 52.3, 18.9 ppm; **HRMS** calc for $C_{20}H_{16}O_4$ $[M]^+$ 320.1049, found 320.1049.

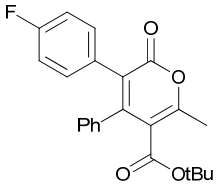
Tert-butyl 3-(4-methoxyphenyl)-6-methyl-2-oxo-4-phenyl-*2H*-pyran-5-carboxylate (3ba)



To a mixture of (*E*)-2-(4-methoxyphenyl)-3-phenyl-N-tosylacrylamide (**1b**, 81.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ba** as a white solid (70.6 mg, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.24-7.22 (m, 3H), 7.05-7.04 (m, 2H), 6.98 (d, *J* = 8.8 Hz , 2H), 6.70 (d, *J* = 9.2 Hz , 2H), 3.73 (s, 3H), 2.44 (s, 3H), 1.15 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.4, 161.5, 159.8, 158.3, 150.5, 136.0, 131.4, 127.9, 127.6, 127.6, 124.7, 123.0, 115.6, 112.8, 82.1, 54.6, 26.9,

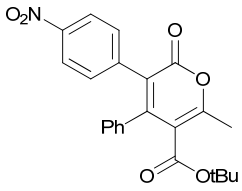
18.0 ppm; **HRMS** calc for $C_{24}H_{24}O_5$ $[M]^+$ 392.1624, found 392.1625.

Tert-butyl 3-(4-fluorophenyl)-6-methyl-2-oxo-4-phenyl-*2H*-pyran-5-carboxylate (3ca)



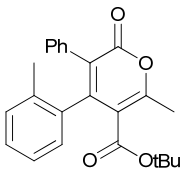
To a mixture of (*E*)-2-(4-fluorophenyl)-3-phenyl-N-tosylacrylamide (**1c**, 79.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ca** as a white solid (71.4 mg, 94%); **^{1}H NMR** (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.22-7.20 (m, 3H), 7.02-6.99 (m, 4H), 6.86-6.82 (m, 2H), 2.43 (s, 3H), 1.12 ppm (s, 9H); **^{13}C NMR** (100 MHz, CDCl3, 25°C, TMS) δ = 164.7 ($J_{C\text{-}F}$ = 372.6 Hz), 163.2, 161.6, 160.7, 151.8, 136.1, 132.5 ($J_{C\text{-}F}$ = 8.0 Hz), 129.0 ($J_{C\text{-}F}$ = 3.3 Hz), 128.3, 128.2, 122.8, 116.1, 115.0, 114.8, 82.8, 27.4, 18.6 ppm; **HRMS** calc for $C_{23}H_{21}FO_4$ $[M]^+$ 380.1424, found 380.1427.

Tert-butyl 6-methyl-3-(4-nitrophenyl)-2-oxo-4-phenyl-*2H*-pyran-5-carboxylate (3da)



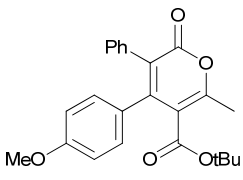
To a mixture of (*E*)-2-(4-nitrophenyl)-3-phenyl-N-tosylacrylamide (**1d**, 84.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate **2a** (73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3da** as a white solid (73.3 mg, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.12-7.10 (m, 3H), 6.94-6.92 (m, 2H), 2.41 (s, 3H), 1.10ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.1, 162.2, 160.9, 149.1, 147.3, 143.1, 132.2, 130.4, 129.6, 128.3, 128.2, 124.7, 123.2, 114.8, 83.3, 27.6, 18.9 ppm; **HRMS** calc for $C_{23}H_{21}NO_6$ $[M]^+$ 407.1369, found 407.1367.

Tert-butyl 6-methyl-2-oxo-3-phenyl-4-(o-tolyl)-*2H*-pyran-5-carboxylate (3ea)



To a mixture of (*E*)-2-phenyl-3-(o-tolyl)-N-tosylacrylamide (**1e**, 78.2 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syring, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ea** as an off white solid (67.8 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.07-7.05 (m, 3H), 7.00-6.92 (m, 4H), 6.78 (s, 1H), 6.69 (d, *J* = 7.2 Hz , 1H), 2.36 (s, 3H), 2.14 (m, 3H), 1.07 ppm (s, 9H); **^{13}C NMR** (100 MHz, CDCl3, 25 °C, TMS) δ = 164.9, 161.7, 160.7, 151.7, 137.6, 136.1, 133.2, 130.5, 128.9, 128.8, 127.9, 127.7, 127.5, 125.6, 123.7, 116.1, 82.6, 27.4, 21.3, 18.6 ppm; **HRMS** calc for $C_{24}H_{24}O_4$ [M]+ 376.1675, found 376.1677.

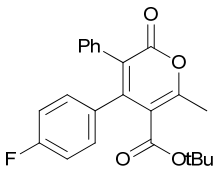
Tert-butyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3-phenyl-*2H*-pyran-5-carboxylate (3fa)



To a mixture of (*E*)-3-(4-methoxyphenyl)-2-phenyl-N-tosylacrylamide (**1f**, 81.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3fa** as a white solid (72.9 mg, 93%).

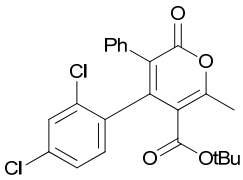
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.19-7.16 (m, 3H), 7.07-7.04 (m, 2H), 6.95 (d, *J* = 8.2 Hz , 2H), 6.73 (d, *J* = 8.8 Hz , 2H), 3.73 (s, 3H), 2.43 (s, 3H), 1.21 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.5, 161.2, 159.8, 159.0, 150.8, 132.9, 130.1, 129.3, 127.9, 127.3, 127.0, 123.2, 115.9, 113.0, 82.1, 54.7, 27.1, 18.1 ppm; **HRMS** calc for $C_{24}H_{24}O_5$ [M]+ 392.1624, found 392.1621.

Tert-butyl 4-(4-fluorophenyl)-6-methyl-2-oxo-3-phenyl-*2H*-pyran-5-carboxylate (3ga)



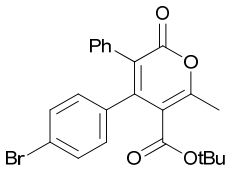
To a mixture of (*E*)-3-(4-fluorophenyl)-2-phenyl-N-tosylacrylamide (**1g**, 79.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 6:1, v/v) to give the product **3ga** as a white solid (64.6 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.24-7.23 (m, 3H), 7.05-7.00 (m, 4H), 6.88-6.83 (m, 2H), 2.45 (s, 3H), 1.14 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.2 ($J_{C\text{-}F}$ = 371.0 Hz), 162.7, 161.1, 160.2, 151.3, 135.6, 132.0, 128.5 ($J_{C\text{-}F}$ = 3.6 Hz), 127.8 ($J_{C\text{-}F}$ = 3.1 Hz),, 127.7, 122.3, 115.6, 114.5 ($J_{C\text{-}F}$ = 21.2 Hz), 82.3, 26.9, 18.1 ppm; **HRMS** calc for $C_{23}H_{21}FO_4$ [M]+ 380.1424, found 380.1426.

Tert-butyl 4-(2,4-dichlorophenyl)-6-methyl-2-oxo-3-phenyl-*2H*-pyran-5-carboxylate (3ha)



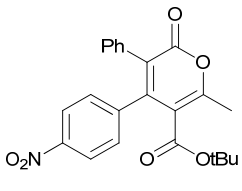
To a mixture of (*E*)-3-(2,4-dichlorophenyl)-2-phenyl-N-tosylacrylamide (**1h**, 89.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ha** as a white solid (77.4 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.31 (s, 1H), 7.21-7.20 (m, 3H), 7.11-7.08 (m, 3H), 6.96 (d, *J* = 8.4 Hz , 1H), 2.51 (s, 3H), 1.22 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.4, 162.2, 160.6, 147.7, 134.3, 133.7, 132.7, 132.1, 130.7, 129.3, 128.5, 127.7, 127.4, 126.3, 124.9, 114.3, 82.2, 27.0, 17.8 ppm; **HRMS** calc for $C_{23}H_{24}Cl_2O_4$ $[M]^+$ 430.0739, found 430.0740.

Tert-butyl 4-(4-bromophenyl)-6-methyl-2-oxo-3-phenyl-*2H*-pyran-5-carboxylate (3ia)



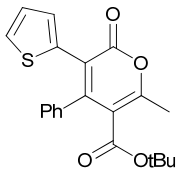
To a mixture of (*E*)-3-(4-bromophenyl)-2-phenyl-N-tosylacrylamide (**1i**, 91.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ia** as a yellow solid (75.7 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.36 (d, *J* = 8.4 Hz , 2H), 7.21-7.19 (m, 3H), 7.05-7.03 (m, 2H), 6.92 (d, *J* = 8.4 Hz , 2H), 2.46 (s, 3H), 1.20 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.1, 160.8, 160.7, 149.7, 134.7, 132.2, 130.8, 130.0, 129.6, 127.5, 127.4, 123.6, 121.9, 115.1, 82.4, 27.0, 18.2 ppm; **HRMS** calc for $C_{23}H_{21}BrO_4$ $[M]^+$ 440.0623, found 440.0624.

Tert-butyl 6-methyl-4-(4-nitrophenyl)-2-oxo-3-phenyl-*2H*-pyran-5-carboxylate (3ja)



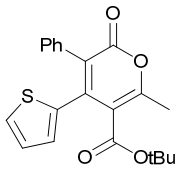
To a mixture of (*E*)-3-(4-nitrophenyl)-2-phenyl-N-tosylacrylamide (**1j**, 84.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ja** as a white solid (75.7 mg, 93%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.00 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.11-7.09 (m, 3H), 6.94-6.93 (m, 2H), 7.10-7.09 (m, 2H), 2.40 (s, 3H), 1.10 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.6, 161.7, 160.4, 148.6, 146.8, 142.6, 131.7, 129.9, 129.1, 127.7, 127.7, 124.1, 122.7, 114.3, 82.8, 27.1, 18.4 ppm; **HRMS** calc for $C_{23}H_{21}NO_6$ $[M]^+$ 407.1369, found 407.1367.

Tert-butyl 6-methyl-2-oxo-4-phenyl-3-(thiophen-2-yl)-*2H*-pyran-5-carboxylate (3ka)



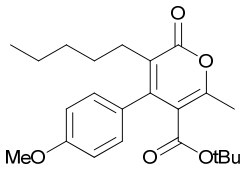
To a mixture of (*Z*)-3-phenyl-2-(thiophen-2-yl)-N-tosylacrylamide (**1k,** 76.6 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ka** as a white solid (69.9 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.36-7.34 (m, 3H), 7.23-7.22 (m, 1H), 7.18-7.16 (m, 2H), 6.85-6.81 (m, 2H), 2.43 (s, 3H), 1.15 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.5, 160.8, 159.6, 150.5, 136.4, 133.8, 130.4, 128.7, 128.6, 128.3, 127.4, 126.1, 117.3, 116.6, 82.8, 27.4, 18.5 ppm; **HRMS** calc for $C_{21}H_{20}O_4S$ $[M]^+$ 368.1082, found 368.1082.

Tert-butyl 6-methyl-2-oxo-3-phenyl-4-(thiophen-2-yl)-*2H*-pyran-5-carboxylate (3la)



To a mixture of (*E*)-2-phenyl-3-(thiophen-2-yl)-N-tosylacrylamide (**1l**, 76.6 mg, 0.2 mmol), *tert*-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3la** as a white solid (71.4 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.19-7.15 (m, 4H), 7.07-7.05 (m, 2H), 6.83-6.82 (m, 2H), 2.35 (s, 3H), 1.19 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.3, 160.7, 159.8, 144.1, 135.8, 132.7, 129.8, 128.3, 127.5, 127.5, 126.2, 124.5, 115.8, 82.5, 27.1, 18.1 ppm; **HRMS** calc for $C_{21}H_{20}O_4S$ $[M]^+$ 368.1082, found 368.1084.

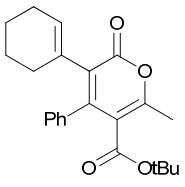
Tert-butyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3-pentyl-*2H*-pyran-5-carboxyate (3ma)



To a mixture of (*E*)-2-(4-methoxybenzylidene)-N-tosylheptanamide (**1m**, 80.2 mg, 0.2 mmol), *tert*-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ma** as a white solid (73.3 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.11-7.09 (m, 2H), 6.96-6.94 (m, 2H), 3.85 (s, 3H), 2.34 (s, 3H), 2.28-2.24 (m, 2H), 1.43-1.40 (m, 2H), 1.16-1.13 (m, 13H), 0.80 ppm (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.1, 162.4, 129.6, 158.2, 150.4, 128.9, 128.6, 124.8, 116.1, 113.7, 82.3, 55.4, 31.7, 28.2,

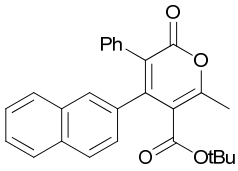
27.7, 27.5, 22.2, 18.3, 13.4 ppm; **HRMS** calc for $C_{23}H_{30}O_5$ $[M]^+$ 386.2093, found 386.2095.

Tert-butyl 3-(cyclohex-1-en-1-yl)-6-methyl-2-oxo-4-phenyl-*2H*-pyran-5-carboxylate (3na)



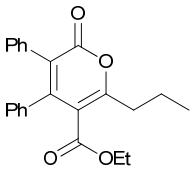
To a mixture of (*E*)-2-(cyclohex-1-en-1-yl)-3-phenyl-N-tosylacrylamide (**1n**, 76.2 mg, 0.2 mmol), *tert*-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3na** as a white solid (60.8 mg, 83%).**^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.35-7.32 (m, 3H), 7.17-7.14 (m, 2H), 5.38 (m, 1H), 2.38 (s, 3H), 1.95-1.94 (m, 2H), 1.86-1.85 (m, 2H), 1.50-1.47 (m, 2H), 1.43-1.40 (m, 2H), 1.13 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.5, 160.9, 159.3, 150.1, 136.3, 130.6, 130.5, 127.6, 127.3, 127.2, 126.2, 115.2, 82.0, 27.8, 26.9, 24.7, 21.9, 21.0, 18.0 ppm; **HRMS** calc for $C_{23}H_{26}O_4$ $[M]^+$ 366.1831, found 366.1833.

Tert-butyl 6-methyl-4-(naphthalen-2-yl)-2-oxo-3-phenyl-*2H*-pyran-5-carboxylate (3oa)



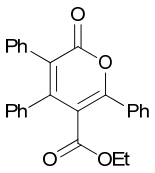
To a mixture of (*E*)-3-(naphthalen-2-yl)-2-phenyl-N-tosylacrylamide (**1o,** 85.4 mg, 0.2 mmol), *tert*-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3oa** as a white solid (71.7 mg, 87%).**^{1}H NMR** (400 MHz, $CDCl_3$, 25^{o}C, TMS) δ = 7.78-7.73 (m, 3H), 7.48-7.44 (m, 2H), 7.33-7.30 (m, 1H), 7.15-7.13 (m, 1H), 7.03-7.01 (m, 5H), 2.52 (s, 3H), 0.72 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25^{o}C, TMS) δ = 164.4, 161.3, 150.8, 133.9, 133.2, 133.0, 130.7, 129.7, 128.6, 128.2, 127.6, 127.6, 126.7, 126.5, 126.2, 125.5, 125.2, 124.9, 116.6, 82.3, 26.9, 18.9 ppm; **HRMS** calc for $C_{27}H_{24}O_4$ $[M]^+$ 412.1675, found 412.1674.

Ethyl 2-oxo-3,4-diphenyl-6-propyl-*2H*-pyran-5-carboxylate (3ad)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxohexanoate (**2d,** 73.6 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ad** as a white solid (69.5 mg, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.1.2-7.08 (m, 6H), 6.99-6.94 (m, 2H), 6.93-6.91 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 3.8 Hz, 2H), 1.79-1.73 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.73 ppm (t, *J* = 3.8 Hz,3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.9, 164.6, 161.6, 151.3, 136.2, 133.1, 130.6, 128.2, 128.1, 128.0, 127.8, 127.6, 123.8, 114.8, 61.6, 34.3, 21.2, 13.8, 13.4 ppm; **HRMS** calc for $C_{23}H_{22}O_4$ $[M]^+$ 362.1518, found 362.1519.

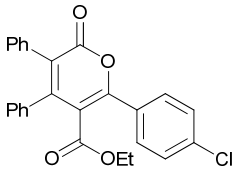
Ethyl 2-oxo-3,4,6-triphenyl-*2H*-pyran-5-carboxylate (3ae)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2e,** 87.2 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ae** as a white solid (68.1 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =

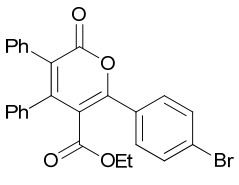
7.19-7.07 (m, 6H), 6.99-6.93 (m, 2H), 6.92-6.90 (m, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 0.72 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.9, 161.7, 161.5, 151.4, 136.3, 133.0, 130.6, 128.2, 128.1, 128.0, 127.8, 127.7, 123.8, 114.8, 61.6, 18.8, 13.4 ppm; **HRMS** calc for $C_{26}H_{20}O_4$ [M]+ 396.1362, found 396.1364.

Ethyl 6-(4-chlorophenyl)-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3af)



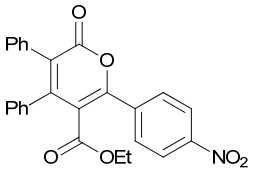
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 3-(4-chlorophenyl)-2-diazo-3-oxopropanoate (**2f**, 100.8 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ae** as a white solid (71.4 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.63-7.61 (m, 2H), 7.42-7.37 (m, 3H), 7.14-7.11 (m, 5H), 7.03-7.01 (m, 2H), 6.96-6.94 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 0.78 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.8, 161.0, 158.8, 150.3, 134.6, 133.9, 132.7, 131.5, 131.2, 130.5, 129.9, 128.7, 128.4, 128.1, 128.1, 128.0, 125.2, 114.8, 62.0 13.4 ppm; **HRMS** calc for $C_{26}H_{19}ClO_4$ [M]+ 430.0972, found 430.0973.

Ethyl 6-(4-bromophenyl)-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3ag)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 3-(4-bromophenyl)-2-diazo-3-oxopropanoate (**2g,** 118.4 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ae** as a white solid (73.0 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.63-7.61 (m, 2H), 7.43-7.38 (m, 3H), 7.29-7.27 (m, 2H), 7.14 (m, 3H), 7.03-7.01 (m,2H), 6.90-6.88 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 0.79 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.8, 161.0, 158.8, 150.3, 134.4, 132.7, 131.5, 131.4, 131.2, 130.5, 130.1, 128.7, 128.1, 125.2, 122.9, 114.7, 62.0, 13.4 ppm; **HRMS** calc for $C_{26}H_{19}BrO_4$ [M]+ 474.0467, found 474.0467.

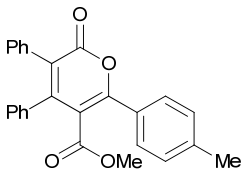
Ethyl 6-(4-nitrophenyl)-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3ah)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-(4-nitrophenyl)-3-oxopropanoate (**2h**, 105.2 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4:1, v/v) to give the product **3ah** as a white solid (75.0 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.25 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.19-7.12 (m, 6H), 7.06-6.99 (m, 4H), 3.77 (q, *J* = 7.2 Hz, 2H), 0.75 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.3, 160.5, 155.4, 151.1, 149.0, 137.3, 135.0, 132.5, 130.5, 129.3, 128.7, 128.3, 128.2, 128.2, 128.0, 126.5, 123.9, 116.8, 62.3, 13.3 ppm; **HRMS** calc for $C_{26}H_{19}NO_6$ $[M]^+$ 441.1212, found 441.1210.

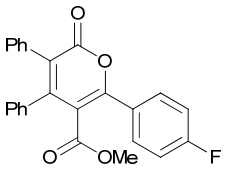
Methyl 2-oxo-3,4-diphenyl-6-(*p*-tolyl)-*2H*-pyran-5-carboxylate (3ai)

To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-oxo-3- phenyl-propanoate **2i** (81.6 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The



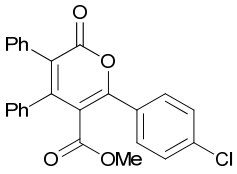
solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ai** as a white solid (67.3 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25-7.19 (m, 6H), 7.15-7.13 (m, 2H), 7.10-7.09 (m, 2H), 3.40 (s, 3H), 2.44 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 166.7, 161.4, 158.6, 151.7, 141.7, 135.5, 133.1, 130.6, 129.5, 128.7, 128.4, 128.2, 128.1, 127.9, 127.9, 127.8, 124.6, 114.5, 52.5, 21.6 ppm; **HRMS** calc for $C_{26}H_{20}O_4$ $[M]^+$ 396.1362, found 396.1361.

Methyl 6-(4-fluorophenyl)-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3aj)



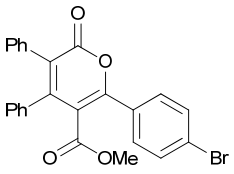
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-(4-fluorophenyl)-3-oxopropanoate (**2j,** 88.8 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3aj** as a white solid (68.8 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.76-7.73 (m, 2H), 7.25-7.24 (m, 3H), 7.22-7.13 (m, 7H), 7.10-7.09 (m, 2H), 3.39 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 166.4, 165.6, 163.0, 161.1 ($J_{C\text{-}F}$ = 378.8 Hz), 151.5, 135.4, 132.9, 130.6, 130.4 ($J_{C\text{-}F}$ = 9.5 Hz), 128.5, 128.2, 127.9, 127.8 ($J_{C\text{-}F}$ = 4.1 Hz), 125.0, 116.1 ($J_{C\text{-}F}$ = 21.4 Hz), 114.9, 52.6 ppm; **HRMS** calc for $C_{25}H_{17}FO_4$ $[M]^+$ 400.1111, found 400.1110.

Methyl 6-(4-chlorophenyl)-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3ak)



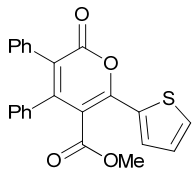
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 3-(4-chlorophenyl)-2-diazo-3-oxopropanoate (**2k**, 95.2 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3ak** as a white solid (67.4 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.52 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.09-7.04 (m, 6H), 6.98-6.96 (m, 2H), 6.93-6.92 (m, 2H), 3.23 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 166.3, 161.0, 157.1, 151.4, 137.5, 135.3, 132.8, 130.5, 129.9, 129.3, 129.1, 128.6, 128.2, 128.2, 127.9, 127.9, 125.3, 115.1, 52.7 ppm; **HRMS** calc for $C_{25}H_{17}ClO_4$ $[M]^+$ 416.0895, found 416.0898.

Methyl 6-(4-bromophenyl)-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3al)



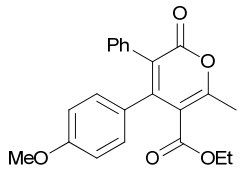
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 3-(4-bromophenyl)-2-diazo-3-oxopropanoate (**2l**, 112.4 mg, 0.4 mmol), and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3al** as a white solid (70.8 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.64-7.59 (m, 4H), 7.25-7.23 (m, 3H), 7.22-7.20 (m, 3H), 7.14-7.12 (m, 2H), 7.09-7.07 (m, 2H) 3.39 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.8, 160.5, 156.6, 150.9, 134.8, 132.3, 131.6, 130.0, 129.9, 129.0, 128.1, 127.7, 127.7, 127.4, 127.4, 125.4, 124.8, 114.7, 52.2 ppm; **HRMS** calc for $C_{25}H_{17}BrO_4$ $[M]^+$ 460.0310, found 460.0311.

Methyl 2-oxo-3,4-diphenyl-6-(thiophen-2-yl)-*2H*-pyran-5-carboxylate (3am)



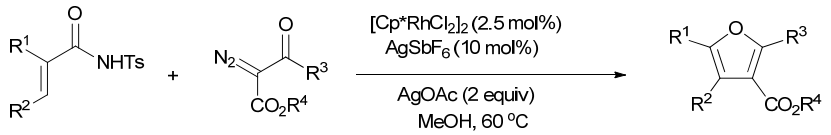
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-oxo-3-(thiophen-2-yl)propanoate (**2m**, 84.0 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3am** as a white solid (66.0 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.65 (d, *J* = 4.4 Hz, 1H), 7.59 (d, *J* = 4.8 Hz, 1H), 7.25-7.23 (m, 3H), 7.21-7.19 (m, 3H), 7.16-7.09 (m, 5H), 3.49 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 165.8, 160.0, 151.5, 151.0, 134.8, 132.6, 132.5, 130.3, 130.1, 129.6, 128.0, 127.9, 127.6, 127.3, 127.3, 123.9, 112.4, 52.3 ppm; **HRMS** calc for $C_{23}H_{16}O_4S$ $[M]^+$ 388.0769, found 388.0771.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3-phenyl-2*H*-pyran-5-carboxylate (3fb)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1f**, 81.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxobutanoate (**2b**, 62.4 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) under N_2, MeOH (2.0 mL) was added via syringe, and then stirred at 60 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 5:1, v/v) to give the product **3fb** as a white solid (69.9 mg, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.12-7.10 (m, 3H), 7.00-6.97 (m, 2H), 6.83 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 2H), 6.63 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 2H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.66 (s, 3H), 2.36 (s, 3H), 0.82 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 166.1, 161.6, 161.2, 159.5, 151.1, 133.3, 130.7, 129.6, 128.4, 127.9, 127.5, 123.6, 115.1, 113.5, 61.6, 55.2, 18.8, 13.6 ppm; **HRMS** calc for $C_{22}H_{20}O_5$ $[M]^+$ 364.1311, found 364.1312.

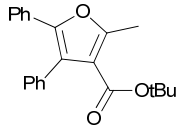
General procedure C for the synthesis of furans 4



1 **2** **4**

A Schlenk tube (10 mL) was charged with the N-tosylacrylamides **1** (0.2 mmol), diazo compound **2** (0.4 mmol) $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added by syringe. After stirring the reaction mixture at 60 °C for 12 h, the reaction mixture was cooled to room temperature and diluted with dichloromethane (10 mL). The resulting mixture was filtered through a Celite pad and washed with dichloromethane (3 x 20 mL). The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to afford **4** as a pure product.

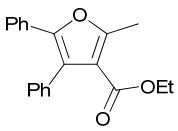
Tert-butyl 2-methyl-4,5-diphenylfuran-3-carboxylate (4aa)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), *tert*-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4aa** as a colorless syrup (48.7 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.30-7.27 (m, 3H), 7.24-7.19 (m, 4H), 7.11- 7.08 (m, 3H), 2.58 (s, 3H), 1.16 ppm (s, 9H);

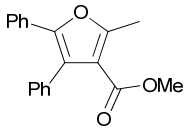
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.4, 156.7, 146.0, 133.2, 129.4, 129.0, 127.2, 127.1, 126.1, 126.1, 124.3, 121.2, 116.0, 79.3, 26.9, 13.0 ppm; **HRMS** calc for $C_{22}H_{22}O_3$ $[M]^+$ 334.1569, found 334.1570.

Ethyl 2,4,5-triphenylfuran-3-carboxylate (4ab)



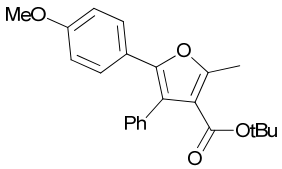
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxobutanoate (**2b**, 62.4 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ab** as a colorless syrup (36.7 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =7.30-7.21 (m, 7H), 7.13-7.07(m, 3H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 0.95 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.0, 157.2, 146.3, 132.7, 129.3, 129.1, 127.2, 127.1, 126.3, 126.2, 124.4, 121.3, 114.6, 58.8, 13.2, 12.8 ppm; **HRMS** calc for $C_{20}H_{18}O_3$ $[M]^+$ 306.1256, found 306.1256.

Methyl 2,4,5-triphenylfuran-3-carboxylate (4ac)



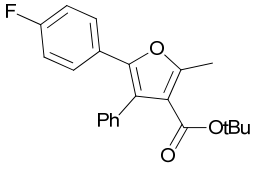
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-oxobutanoate **2c** (56.8 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ac** as a colorless syrup (38.5 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.30-7.27 (m, 3H), 7.23-7.20 (m, 4H), 7.10-7.08 (m, 3H), 3.54 (s, 3H), 2.59 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.4, 157.3, 146.5, 132.4, 129.2, 129.1, 127.2, 127.1, 126.4, 126.3, 124.5, 121.3, 114.3, 50.0, 13.3 ppm; **HRMS** calc for $C_{19}H_{16}O_3$ $[M]^+$ 292.1099, found 292.1101.

Tert-butyl 5-(4-methoxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (4ba)



To a mixture of (*E*)-2-(4-methoxyphenyl)-3-phenyl-N-tosylacrylamide (**1b,** 81.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ba** as an off white solid (49.5 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =δ = 7.29-7.26 (m, 3H), 7.21-7.18 (m, 3H), 7.17-7.15 (m, 1H), 6.66 (d, *J* = 9.2 Hz, 2H), 3.67 (s, 3H), 2.57 (s, 3H), 1.16 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.5, 157.7, 156.2, 146.1, 133.4, 129.2, 127.1, 126.0, 125.8, 122.3, 119.6, 115.8, 112.7, 79.3, 54.2, 26.9, 12.9 ppm; **HRMS** calc for $C_{23}H_{24}O_4$ $[M]^+$ 364.1675, found 364.1677.

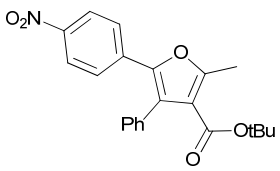
Tert-butyl 5-(4-fluorophenyl)-2-methyl-4-phenylfuran-3-carboxylate (4ca)



To a mixture of (*E*)-2-(4-fluorophenyl)-3-phenyl-N-tosylacrylamide (**1c,** 79.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%) and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the

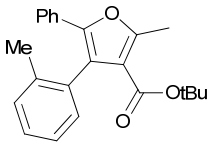
product **4ca** as a white solid (42.9 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.30-7.27 (m, 3H), 7.20-7.17 (m, 4H), 6.80 (t, *J* = 8.8 Hz, 2H), 2.57 (s, 3H), 1.16 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.4, 163.1 ($J_{C\text{-}F}$ = 246.7 Hz), 157.7, 146.3, 134.1, 130.1, 128.3, 127.3 ($J_{C\text{-}F}$ = 9.0 Hz), 127.1, 126.7 ($J_{C\text{-}F}$ = 2.7 Hz), 121.9, 117.1, 115.4 ($J_{C\text{-}F}$ = 20.9 Hz), 80.5, 27.9, 14.0 ppm; **HRMS** calc for $C_{22}H_{21}FO_3$ $[M]^+$ 352.1475, found 352.1476.

Tert-butyl 2-methyl-5-(4-nitrophenyl)-4-phenylfuran-3-carboxylate (4da)



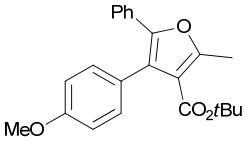
To a mixture of (*E*)-2-(4-nitrophenyl)-3-phenyl-N-tosylacrylamide (**1d,** 84.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol) and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4da** as an off white solid (53.1 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.33-7.29 (m, 3H), 7.18-7.12 (m, 4H), 7.00-6.98 (m, 1H), 6.89-6.88 (m, 1H), 2.57 (s, 3H), 1.24 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.1, 158.9, 147.8, 133.4, 128.9, 127.3, 126.8, 126.6, 126.0, 125.1, 124.4, 116.6, 113.3, 79.5, 26.9, 13.0 ppm; **HRMS** calc for $C_{22}H_{21}NO_5$ $[M]^+$ 379.1420, found 379.1421.

Tert-butyl 2-methyl-5-phenyl-4-(*o*-tolyl)furan-3-carboxylate (4ea)



To a mixture of (*E*)-2-phenyl-3-(o-tolyl)-N-tosylacrylamide (**1e,** 78.2 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ea** as an off white solid (44.5 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.27-7.24 (m, 2H), 7.18-7.16 (m, 1H), 7.13-7.06 (m, 4H), 7.02-7.00 (m, 2H), 2.58 (s, 3H), 2.27 (s, 3H), 1.18 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.5, 156.6, 145.8, 136.5, 133.0, 129.7, 129.5, 127.2, 127.1, 126.8, 126.1, 126.0, 124.2, 121.3, 116.1, 79.2, 26.8, 20.4, 12.9 ppm; **HRMS** calc for $C_{23}H_{24}O_3$ $[M]^+$ 348.1725, found 348.1725.

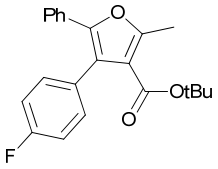
Tert-butyl 4-(4-methoxyphenyl)-2-methyl-5-phenylfuran-3-carboxylate (4fa)



To a mixture of (*E*)-3-(4-methoxyphenyl)-2-phenyl-N-tosylacrylamide (**1f**, 81.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 30:1, v/v) to give the product **4fa** as an off white solid (36.5 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ= 7.27-7.24 (m, 2H), 7.14-7.10 (m, 5H), 8.85 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.59 (s, 3H), 1.23 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.5, 157.8, 156.6, 146.1, 130.1, 129.5, 127.2, 126.1, 125.2, 124.3, 120.9, 116.1, 112.7, 79.3, 54.2, 27.0, 13.1 ppm; **HRMS** calc for $C_{23}H_{24}O_4$ $[M]^+$ 364.1675, found 364.1678.

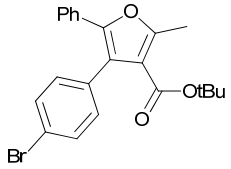
Tert-butyl 4-(4-fluorophenyl)-2-methyl-5-phenylfuran-3-carboxylate (4ga)

To a mixture of (*E*)-3-(4-fluorophenyl)-2-phenyl-N-tosylacrylamide (**1g,** 79.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol),



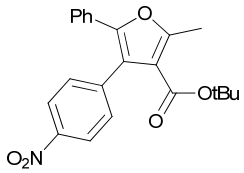
and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ga** as an off white solid (48.6 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.30-7.27 (m, 3H), 7.20-7.17 (m, 4H), 6.80 (t, *J* = 8.8 Hz, 2H), 2.57 (s, 3H), 1.16 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.3, 162.0 ($J_{C\text{-}F}$ = 245.9 Hz), 156.7, 145.3, 133.0, 129.0, 127.3, 126.3, 126.2 ($J_{C\text{-}F}$ = 7.0 Hz), 125.7 ($J_{C\text{-}F}$ = 4.3 Hz), 120.8, 116.0, 114.4 ($J_{C\text{-}F}$ = 21.5 Hz), 79.4, 26.9, 12.9 ppm; **HRMS** calc for $C_{22}H_{21}FO_3$ $[M]^+$ 352.1475, found 352.1476.

Tert-butyl 4-(4-bromophenyl)-2-methyl-5-phenylfuran-3-carboxylate (4ia)



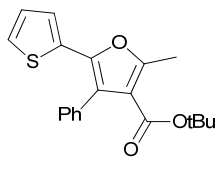
To a mixture of (*E*)-3-(4-bromophenyl)-2-phenyl-N-tosylacrylamide (**1i,** 91.0 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ia** as an off white solid (44.5 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =7.44 (d, *J* = 8.4 Hz, 2H), 7.21-7.15 (m, 2H), 7.13-7.09 (m, 5H), 2.58 (s, 3H), 1.22 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.1, 157.0, 146.2, 132.2, 130.9, 130.4, 129.1, 127.3, 126.4, 124.4, 120.3, 120.0, 115.7, 79.7, 27.0, 13.1 ppm; **HRMS** calc for $C_{22}H_{21}BrO_3$ $[M]^+$ 412.0674, found 412.0673.

Tert-butyl 2-methyl-4-(4-nitrophenyl)-5-phenylfuran-3-carboxylate (4ja)



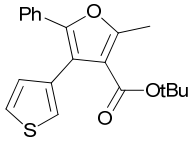
To a mixture of (*E*)-3-(4-nitrophenyl)-2-phenyl-N-tosylacrylamide (**1j,** 84.4 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a**, 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ja** as an off white solid (45.5 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =8.00 (d , *J* = 8.4 Hz, 2H), 7.15(d, *J* = 8.4 Hz, 2H), 7.11-7.09 (m, 3H), 6.94-6.92 (m, 2H), 2.40 (s, 3H), 1.10 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25°C, TMS) δ = 162.0, 156.9, 147.8, 133.4, 128.9, 127.3, 126.8, 126.6, 126.0, 125.1, 124.4, 116.6, 113.3, 79.5, 26.9, 13.0 ppm; **HRMS** calc for $C_{22}H_{21}NO_5$ $[M]^+$ 379.1420, found 379.1422.

Tert-butyl 2-methyl-4-phenyl-5-(thiophen-2-yl)furan-3-carboxylate (4ka)



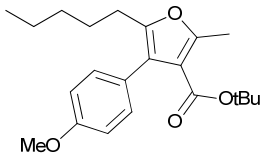
To a mixture of (*Z*)-3-phenyl-2-(thiophen-2-yl)-N-tosylacrylamide (**1k,** 76.6 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ka** as an off white solid (38.1 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.33-7.30 (m, 3H), 7.24-7.22 (m, 2H), 7.02-7.00 (m, 1H), 6.85-6.84 (m, 1H), 6.81-6.79 (m, 1H), 2.60 (s, 3H), 1.16 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.2, 156.6, 142.8, 132.4, 131.4, 129.2, 127.2, 126.5, 126.0, 123.4, 122.4, 120.3, 115.8, 79.4, 26.8, 13.0 ppm; **HRMS** calc for $C_{20}H_{20}O_3S$ $[M]^+$ 340.1133, found 340.1133.

Tert-butyl 2-methyl-5-phenyl-4-(thiophen-3-yl)furan-3-carboxylate (4la)



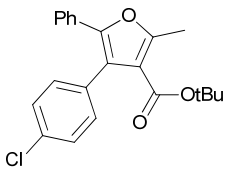
To a mixture of (*E*)-2-phenyl-3-(thiophen-2-yl)-N-tosylacrylamide (**1l,** 76.6 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4la** as an off white solid (48.3 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =7.34-7.30 (m , 3H), 7.18-7.12 (m, 3H), 7.01-6.89 (m, 1H), 6.89-6.88 (m, 1H), 2.58 (s, 3H), 1.25 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.1, 157.9, 148.8, 134.5, 130.0, 128.3, 127.9, 127.6, 127.1, 126.2, 125.5, 117.7, 114.4, 80.6, 28.0, 14.1 ppm; **HRMS** calc for $C_{20}H_{20}O_3S$ $[M]^+$ 340.1133, found 340.1131.

Ethyl 4-(4-methoxyphenyl)-2-methyl-5-pentylfuran-3-carboxylate (4ma)



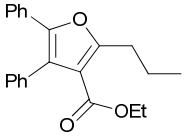
To a mixture of (*E*)-2-(4-methoxybenzylidene)-N-tosylheptanamide (**1m,** 80.2 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ma** as a colorless syrup (35.6 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.08-7.04 (m, 2H), 6.83-6.81 (m, 2H), 3.75 (s, 3H), 2.47 (s, 3H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.49 (q, *J* = 7.6 Hz, 2H), 1.24 (s, 9H), 1.18-1.12 (m, 9H), 0.77 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.8, 157.3, 155.6, 149.9, 130.0, 125.1, 119.7, 113.9, 112.1, 79.1, 54.2, 30.2, 27.2, 27.0, 24.8, 21.3, 13.0, 12.9 ppm; **HRMS** calc for $C_{20}H_{26}O_4$ $[M]^+$ 330.1831, found 330.1830.

Tert-butyl 4-(4-chlorophenyl)-2-methyl-5-phenylfuran-3-carboxylate (4pa)



To a mixture of (*E*)-3-(4-chlorophenyl)-2-phenyl-N-tosylacrylamide (**1p,** 80.2 mg, 0.2 mmol), tert-butyl 2-diazo-3-oxobutanoate (**2a,** 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4pa** as a white solid (37.5 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =7.30-7.28 (m , 2H), 7.23-7.20 (m, 2H), 7.16-7.12 (m, 5H), 2.58 (s, 3H), 1.22 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 162.2, 157.0, 146.2, 132.1, 131.7, 130.5, 129.1, 127.4, 126.4, 124.4, 119.9, 120.0, 115.7, 79.6, 26.9, 13.1 ppm; **HRMS** calc for $C_{22}H_{21}ClO_3$ $[M]^+$ 368.1179, found 368.1180.

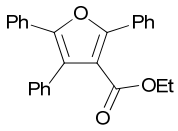
Ethyl 4,5-diphenyl-2-propylfuran-3-carboxylate (4ad)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxohexanoate (**2d**, 73.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ad** as a colorless syrup (50.8 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.32-7.22 (m, 7H), 7.14-7.06 (m, 3H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H),

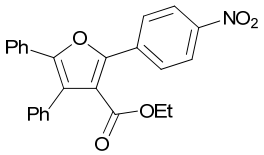
1.80-1.70 (m, 3H), 0.97 (t, J = 7.2 Hz, 3H) , 0.94 ppm (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.0, 160.9, 146.3, 132.8, 129.4, 129.1, 127.2, 127.1, 126.3, 126.2, 124.4, 121.2, 114.3, 58.8, 28.9, 20.6, 12.9, 12.7 ppm; **HRMS** calc for $C_{22}H_{22}O_3$ $[M]^+$ 334.1569, found 334.1568.

Ethyl 2,4,5-triphenylfuran-3-carboxylate (4ae)



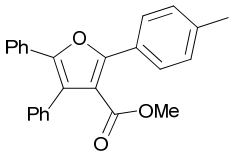
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate **2e** (87.2 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ae** as an off white solid (50.1 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.85 (d, J = 8.4 Hz, 2H), 7.40-7.28 (m, 10H), 7.18- 7.12 (m, 3H), 3.98 (q, J = 7.2 Hz, 2H), 0.85 ppm (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.3, 153.2, 147.2, 132.2, 129.1, 129.0, 128.8, 128.1, 127.4, 127.3, 127.2, 126.7, 126.6, 126.5, 124.7, 122.6, 115.9, 59.5, 12.5 ppm; **HRMS** calc for $C_{25}H_{20}O_3$ $[M]^+$ 368.1412, found 368.1410.

Ethyl 2-(4-nitrophenyl)-4,5-diphenylfuran-3-carboxylate (4ah)



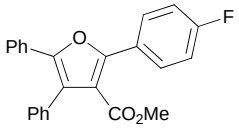
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), ethyl 2-diazo-3-(4-nitrophenyl)-3-oxopropanoate (**2h,** 105.2 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ah** as an off white solid (39.9 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ =8.24 (d , J = 9.2 Hz, 2H), 8.08 (d, J = 9.2 Hz, 2H), 7.39-7.33 (m, 5H), 7.30-7.27 (m, 2H), 7.22-7.18 (m, 3H), 4.02 (q, J = 7.2 Hz, 2H), 0.89 ppm (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.0, 150.9, 150.0, 147.4, 135.6, 132.6, 129.9, 129.5, 128.6, 128.5, 128.0,127.9, 126.0, 124.3, 123.8, 119.9, 61.1, 13.5 ppm; **HRMS** calc for $C_{24}H_{17}NO_5$ $[M]^+$ 399.1107, found 399.1109.

Methyl 4,5-diphenyl-2-(*p*-tolyl)furan-3-carboxylate (4ai)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol) methyl 2-diazo-3-oxo-3-phenylpropanoate (**2i,** 81.6 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ai** as an off white solid (47.8 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.70 (d, J = 8.4 Hz, 2H), 7.35-7.30 (m, 7H), 7.20 -7.14 (m, 5H), 3.51 (s, 3H), 2.34 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.8, 154.9, 148.2, 139.3, 133.2, 130.2, 130.0, 129.1, 128.4, 128.4, 127.8, 127.7, 127.7, 127.1, 125.8, 123.6, 116.0, 51.5, 21.5 ppm; **HRMS** calc for $C_{25}H_{20}O_3$ $[M]^+$ 368.1412, found 368.1413.

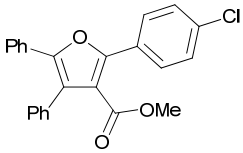
Methyl 2-(4-fluorophenyl)-4,5-diphenylfuran-3-carboxylate (4aj)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-(4-fluorophenyl)-3-oxopropanoate (**2j**, 88.8 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2,

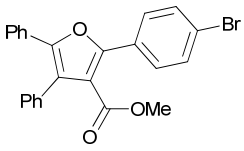
MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4aj** as an off white solid (46.1 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.85-7.82 (m, 2H), 7.34-7.27 (m, 7H), 7.17-7.15(m, 3H), 7.10-7.05 (m, 2H), 3.50 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.1, 164.0 (J_{C-F} = 248.5 Hz), 153.3, 148.0, 132.5, 129.5, 129.4, 129.4, 128.0, 127.9, 127.4 (J_{C-F} = 14.4 Hz), 125.6 (J_{C-F} = 2.1 Hz), 125.4, 123.1, 115.9, 115.1 (J_{C-F} = 21.7 Hz), 51.1 ppm; **HRMS** calc for $C_{24}H_{17}FO_3$ $[M]^+$ 372.1162, found 372.1165.

Methyl 2-(4-chlorophenyl)-4,5-diphenylfuran-3-carboxylate (4ak)



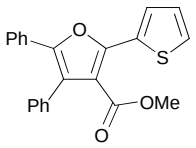
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 3-(4-chlorophenyl)-2-diazo-3-oxopropanoate (**2k,** 95.2 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4ak** as an off white solid (51.2 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.77 (d, *J* = 8.8 Hz, 2H), 7.36-7.31 (m, 7H), 7.28- 7.26 (m, 2H), 7.16-7.14 (m, 2H), 3.50 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 163.5, 152.2, 147.6, 134.1, 131.8, 128.8, 128.7, 128.0, 127.6, 127.4, 127.3, 127.2, 126.9, 126.7, 124.8, 122.7, 115.8, 50.5 ppm; **HRMS** calc for $C_{24}H_{17}ClO_3$ $[M]^+$ 388.0866, found 388.0867.

Methyl 2-(4-bromophenyl)-4,5-diphenylfuran-3-carboxylate (4al)



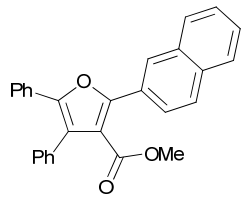
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 3-(4-bromophenyl)-2-diazo-3-oxopropanoate (**2l,** 112.4 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4al** as an off white solid (65.7 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.34-7.26 (m, 7H), 7.16-7.15 (m, 3H), 3.51 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.6, 153.3, 148.8, 132.9, 131.6, 129.9, 129.8, 129.3, 128.8, 128.5, 128.4, 128.0, 127.8, 125.9, 123.8, 123.5, 117.0, 51.6 ppm; **HRMS** calc for $C_{24}H_{17}BrO_3$ $[M]^+$ 432.0361, found 432.0362.

Methyl 4,5-diphenyl-2-(thiophen-2-yl)furan-3-carboxylate (4am)



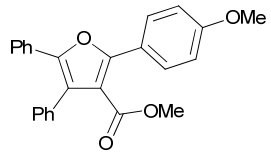
To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-oxo-3-(thiophen-2-yl)propanoate (**2m,** 84.0 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4am** as an off white solid (46.8 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ =δ = 7.89-7.87 (m, 1H), 7.38-7.36 (m, 1H), 7.35-7.29 (m, 5H), 7.27-7.25 (m, 2H), 7.18-7.13 (m, 3H), 7.07-7.05 (m, 1H), 3.55 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ = 164.2, 151.0, 147.9, 133.2, 131.7, 130.0, 129.8, 128.5, 128.4, 128.4, 127.9, 127.9, 127.7, 127.5, 125.8, 123.6, 114.7, 51.3 ppm; **HRMS** calc for $C_{22}H_{16}O_3S$ $[M]^+$ 360.0820, found 360.0820.

Methyl 2-(naphthalen-2-yl)-4,5-diphenylfuran-3-carboxylate (4an)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-(naphthalen-2-yl)-3-oxopropanoate (**2n,** 101.6mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4an** as an off white solid (57.4 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.33 (s, 1H), 7.86-7.77 (m, 4H), 7.45-7.43 (m, 2H), 7.40-7.38 (m, 2H), 7.34-7.31(m, 5H), 7.18-7.15 (m, 3H), 3.54 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.9, 154.4, 148.7, 133.5, 133.1, 133.0, 130.1, 130.0, 128.7, 128.5, 128.5, 127.9, 127.9, 127.8, 127.8, 127.5, 127.3, 126.9, 126.5, 126.0, 125.0, 123.8, 116.9, 51.6 ppm; **HRMS** calc for $C_{28}H_{20}O_3$ $[M]^+$ 404.1412, found 404.1411.

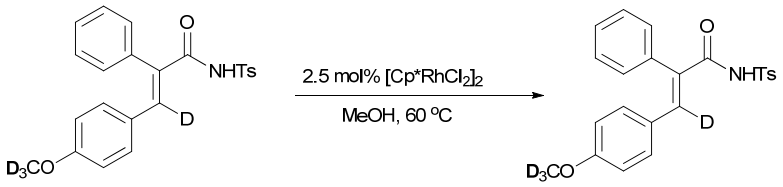
Methyl 2-(4-methoxyphenyl)-4,5-diphenylfuran-3-carboxylate (4ao)



To a mixture of (*E*)-2,3-diphenyl-N-tosylacrylamide (**1a,** 75.4 mg, 0.2 mmol), methyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate (**2o,** 93.6mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) $AgSbF_6$ (6.9 mg, 0.02 mmol), and AgOAc (66.8 mg, 0.4 mmol) under N_2, MeOH (2.0 mL) was added via syringe. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10:1, v/v) to give the product **4an** as an off white solid (38.4 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.79 (d, *J* = 9.2 Hz, 2H), 7.34-7.27 (m, 7H), 7.17-7.11 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.49 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 164.4, 159.9, 154.6, 147.4, 132.8, 129.7, 129.5, 129.0, 127.9, 127.9, 127.2, 127.1, 125.3, 123.1, 122.1, 114.8, 113.3, 54.9, 50.9 ppm; **HRMS** calc for $C_{25}H_{20}O_4$ $[M]^+$ 384.1362, found 384.1365.

Mechanistic studies

- **Olefin deuteration experiment**

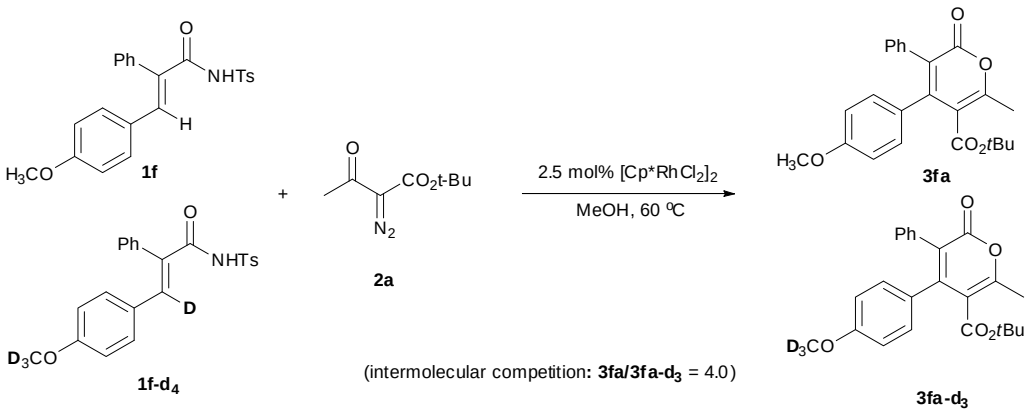


1f-d_4 96% recovery, < 5% H

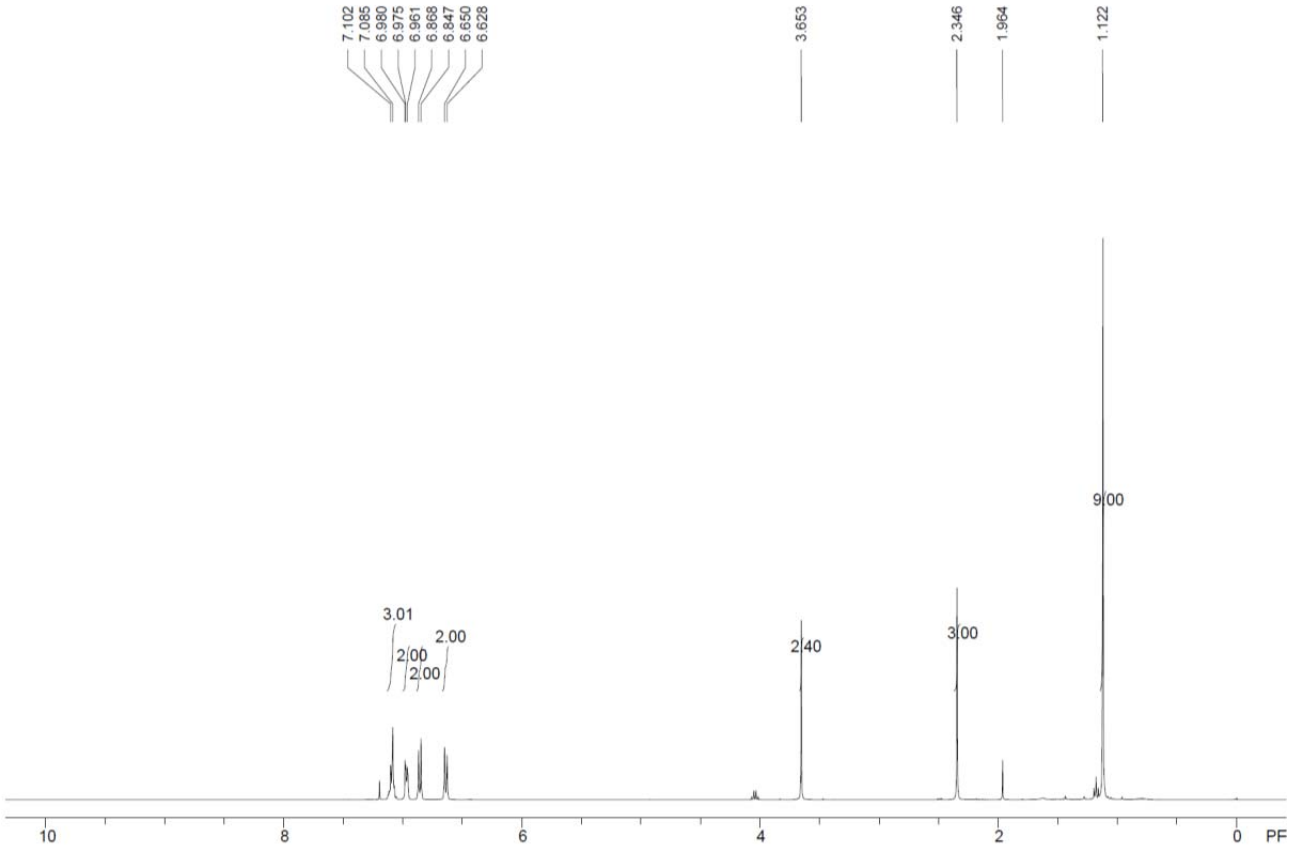
$[RhCp^*Cl_2]_2$ (1.6 mg, 0.0025 mmol, 1.5 mol %) and **1f-d_4** (41.1 mg, 0.1 mmol, 1.0 equiv) were added to a 10 mL vial equipped with a stir bar. MeOH (1.0 mL) was added using a syringe. The reaction was stirred at 60 ºC under nitrogen atmosphere for 4 h, then the reaction mixture was quckli cooled and filtered through a pad of Celite and the filter cake is washed with CH_2Cl_2. The filtrate was concentrated in vacuo to leave a crude mixture, which was purified by silica gel column chromatography to afford **1f-d_4** in 96% yield with no hydrogen incorporation at the olefin position according to ^{1}H NMR.

- **KIE experiments**

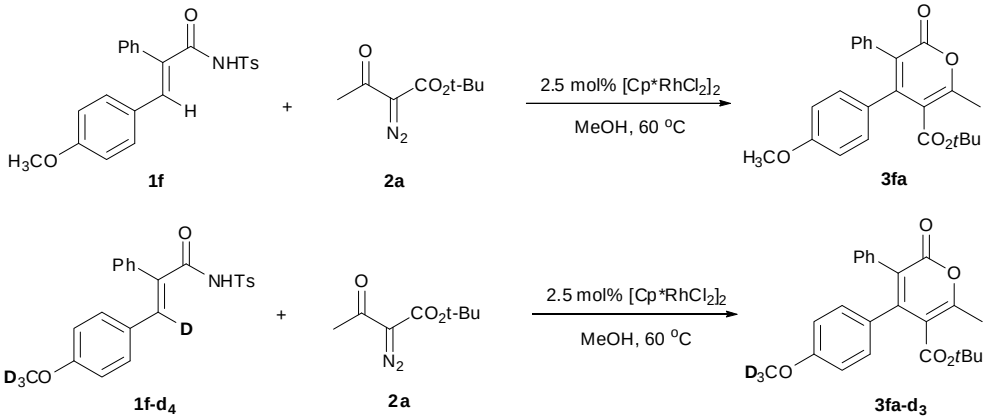
KIE experiments for the synthesis of pyrone 3fa (intermolecular competition)



$[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), **1f** (40.7 mg, 0.1 mmol, 0.05 equiv), **1f-d_4** (41.1 mg, 0.1 mmol, 0.05 equiv) and **2a** (73.6 mg, 0.4 mmol, 2.0 equiv) were successively added to a 10 mL vial equipped with a stir bar. MeOH (2.0 mL) was added using a syringe. The mixture was stirred at 60 ºC for 2 h under N_2, then the reaction mixture was quickly cooled and filtered through a pad of Celite and the filter cake was washed with CH_2Cl_2. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5:1, v/v) to afford **3fa/3fa-d_3**.. The ratio of **3fa**/**3fa-d_3** = 4.0 was determined by ^{1}H NMR.

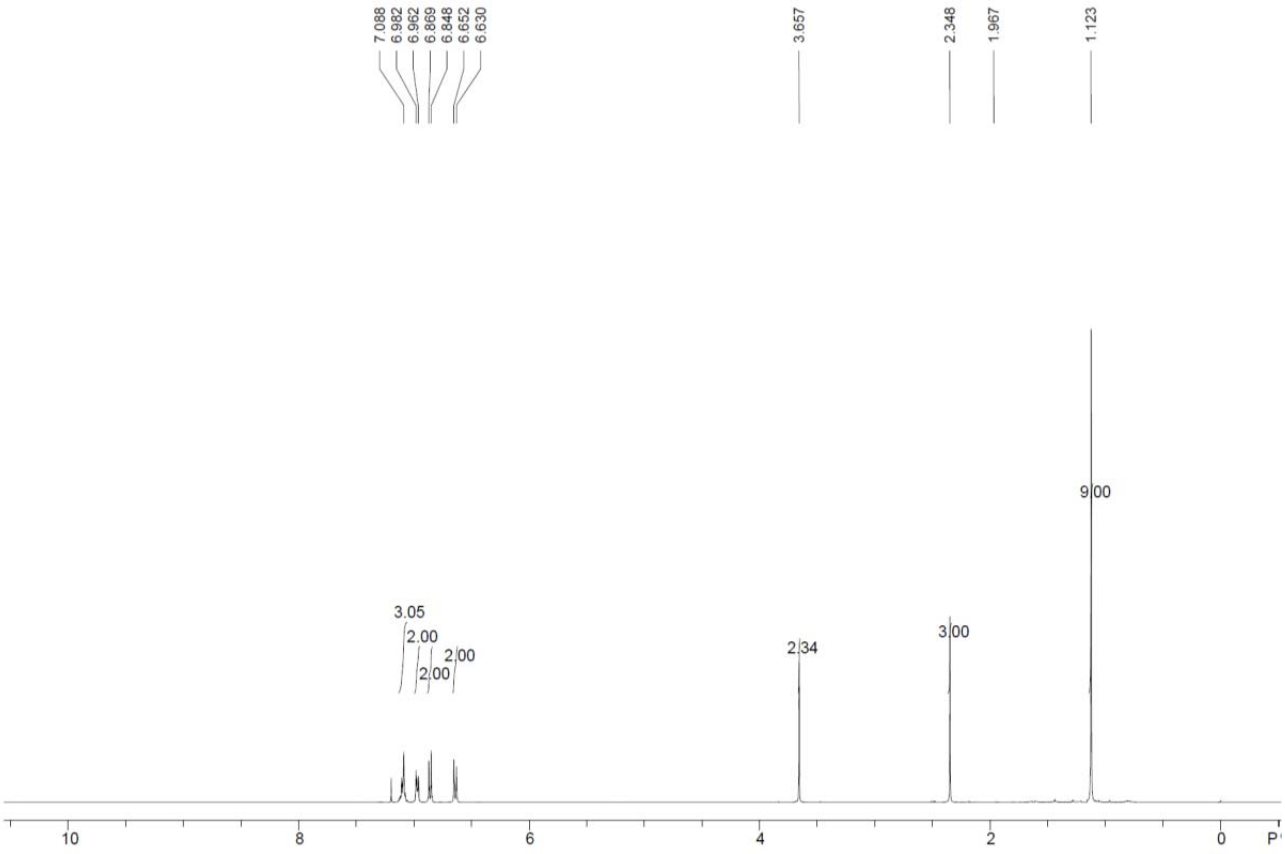


KIE experiments for the synthesis of pyrone 3fa (parallel experiments)

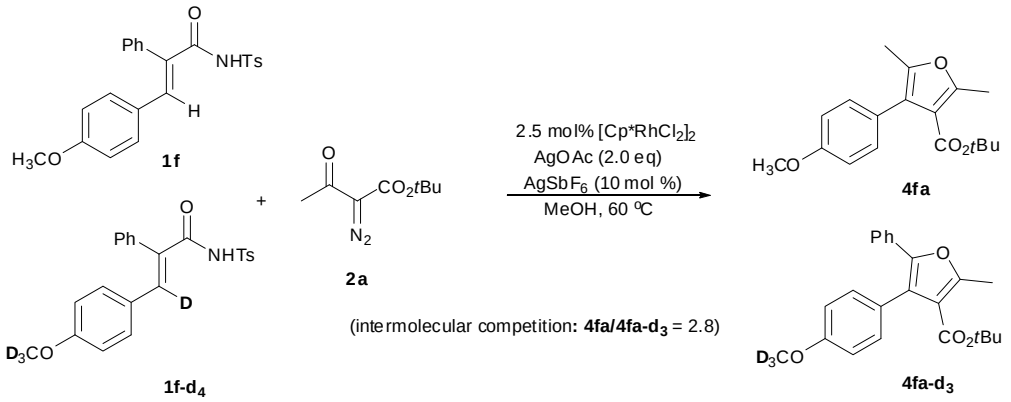


(parallel experiments: **3fa/3fa-d$_3$** = 3.5)

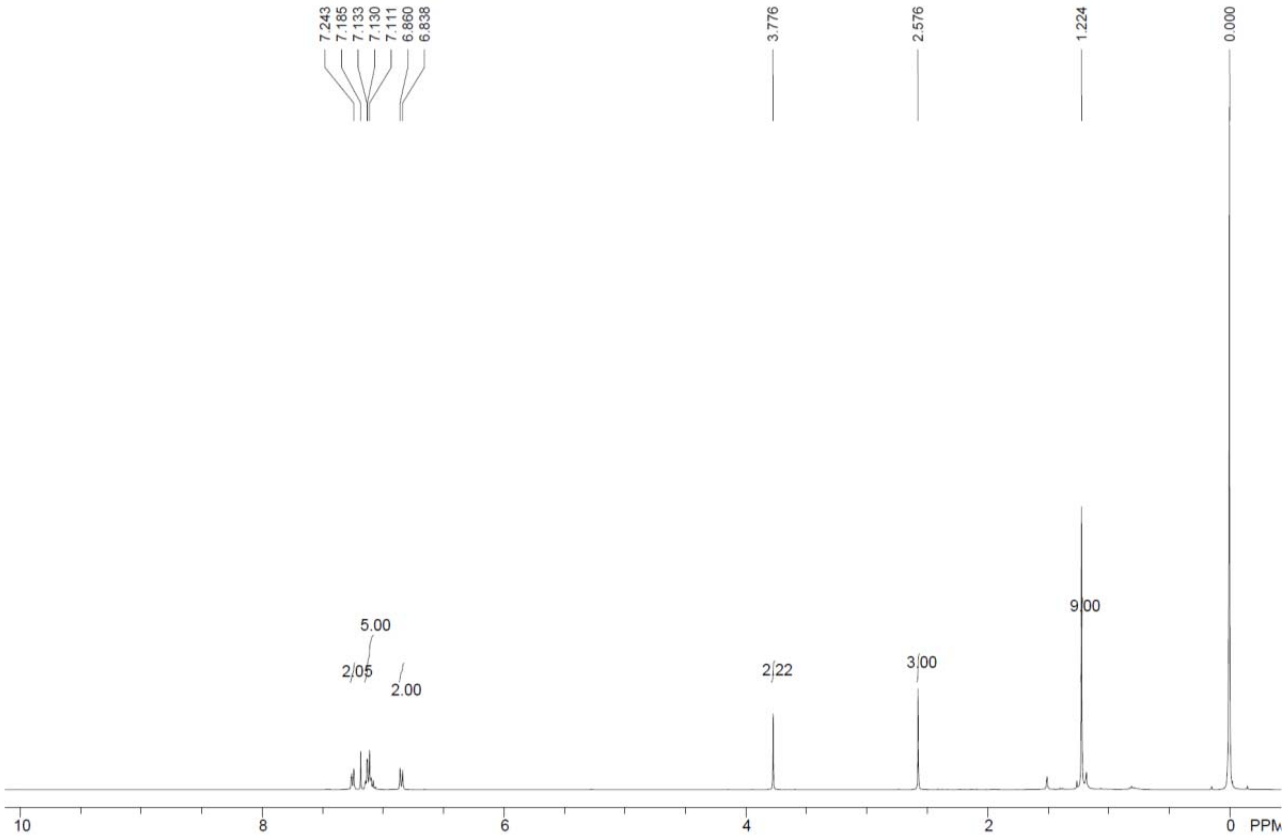
$[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), **1f** (81.4 mg, 0.2 mmol, 1.0 equiv) and **2a** (73.6 mg, 0.4 mmol, 2.0 equiv) were successively added to a 10 mL vial equipped with a stir bar. MeOH (2.0 mL) was added using a syringe. In another reaction vessel, **1f-d$_4$** (82.2mg, 0.2 mmol, 1.0 equiv) was used instead of **1f**. The two reactions were stirred at 60 ºC for 2 h under N_2, then the reaction mixtures were quickly cooled and filtered through a pad of Celite and the filter cake was washed with CH_2Cl_2, respectively. The resulting filtrate was mixed and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5:1, v/v) to afford **3fa/3fa-d$_3$**. The ratio of **3fa**/**3fa-d$_3$ (KIE)** = 3.5 was determined by ^{1}H NMR.



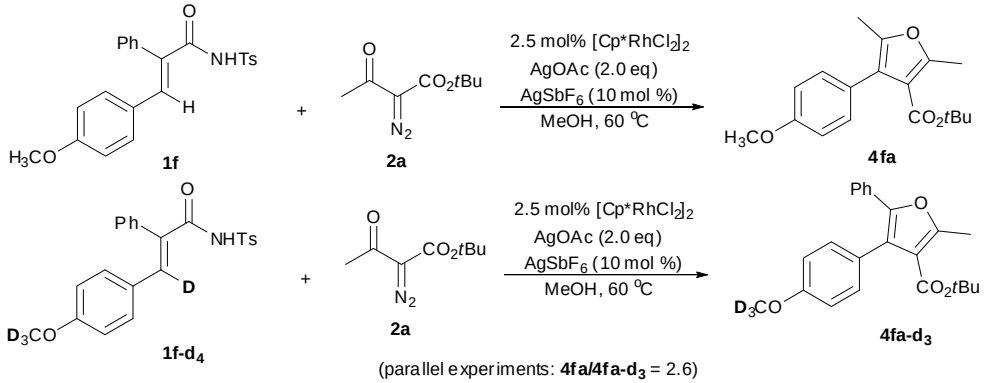
KIE experiments for the synthesis of furan 4fa (intermolecular competition)



$[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgOAc (66.8 mg, 0.4 mmol, 2.0 equiv), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%), **1f** (40.7 mg, 0.1 mmol, 0.05 equiv), **1f-d$_4$** (41.1 mg, 0.1 mmol, 0.05 equiv) and **2a** (73.6 mg, 0.4 mmol, 2.0 equiv) were successively added to a 10 mL vial equipped with a stir bar. MeOH (2.0 mL) was added using a syringe. The mixture was stirred at 60 ºC for 2 h under N_2, then the reaction mixture was filtered through a pad of Celite and the filter cake was washed with CH_2Cl_2. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 30:1, v/v) to afford **4fa/4fa-d$_3$** (about 20% conversion). The ratio of **4fa**/**4fa-d$_3$** = 2.8 was determined by ^{1}H NMR.

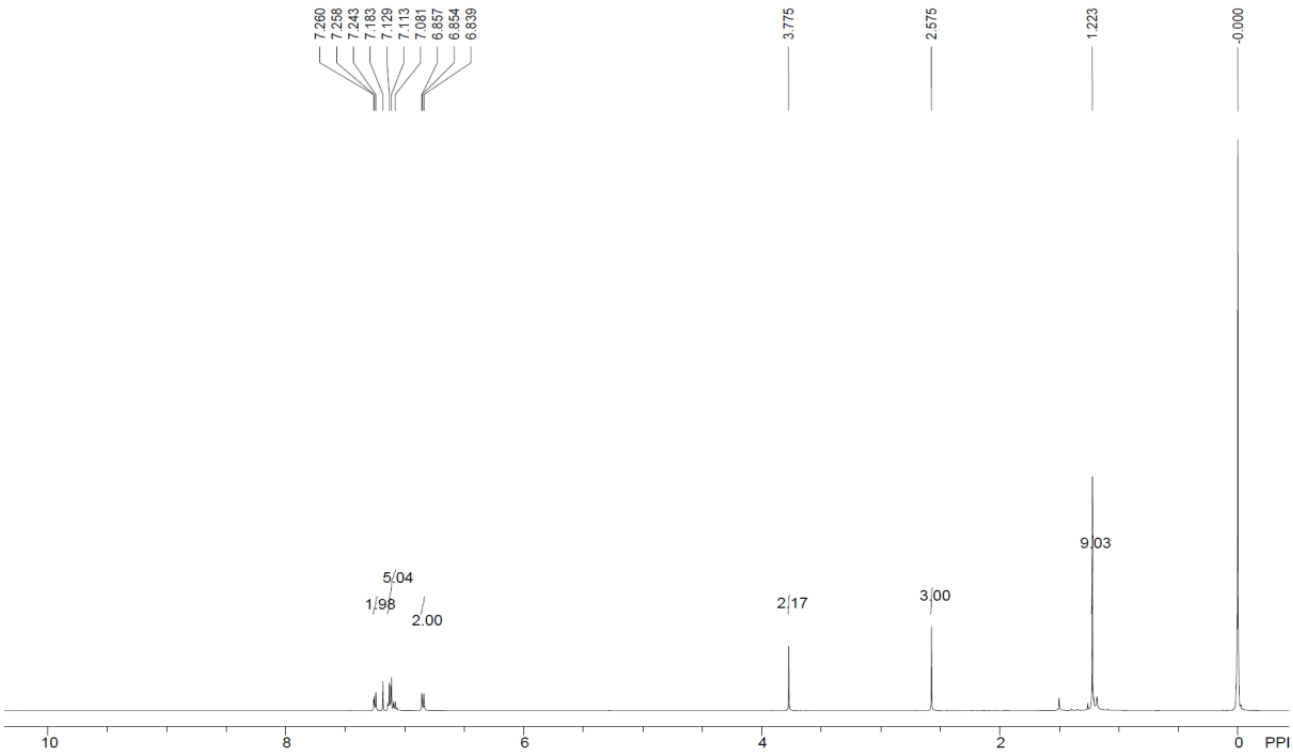


KIE experiments for the synthesis of furan 4fa (parallel experiments)



(parallel experiments: **4fa/4fa-d$_3$** = 2.6)

[RhCp*Cl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgOAc (66.8 mg, 0.4 mmol, 2.0 equiv), AgSbF$_6$ (6.9 mg, 0.02 mmol, 10 mol%), **1f (**81.4 mg, 0.2 mmol, 1.0 equiv) and **2a** (73.6 mg, 0.4 mmol, 2.0 equiv) were successively added to a 10 mL vial equipped with a stir bar. MeOH (2.0 mL) was added using a syringe. In another reaction vessel, **1f-d$_4$** (82.2mg, 0.2 mmol, 1.0 equiv) was used instead of **1f**. The two reactions were stirred at 60 ºC for 2 h under N_2, then the reaction mixtures were quickly cooled and filtered through a pad of Celite and the filter cake was washed with CH_2Cl_2, respectively. The resulting filtrate was mixed and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 30:1) to afford 4**fa/4fa-d$_3$** (about 20% conversion). The ratio of **4fa:[D$_4$]-4fa** (KIE) = 2.6 was determined by ^{1}H NMR.

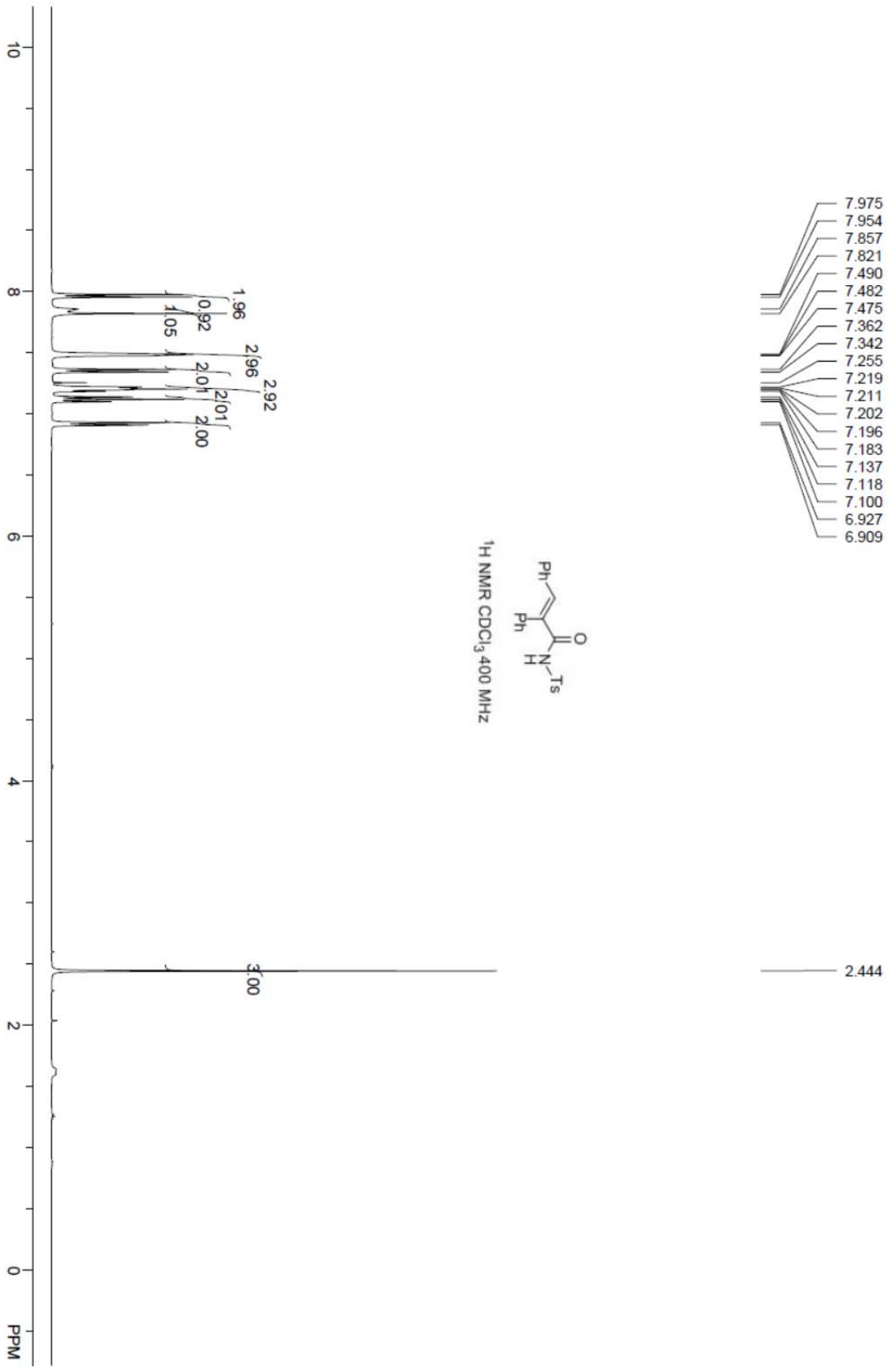


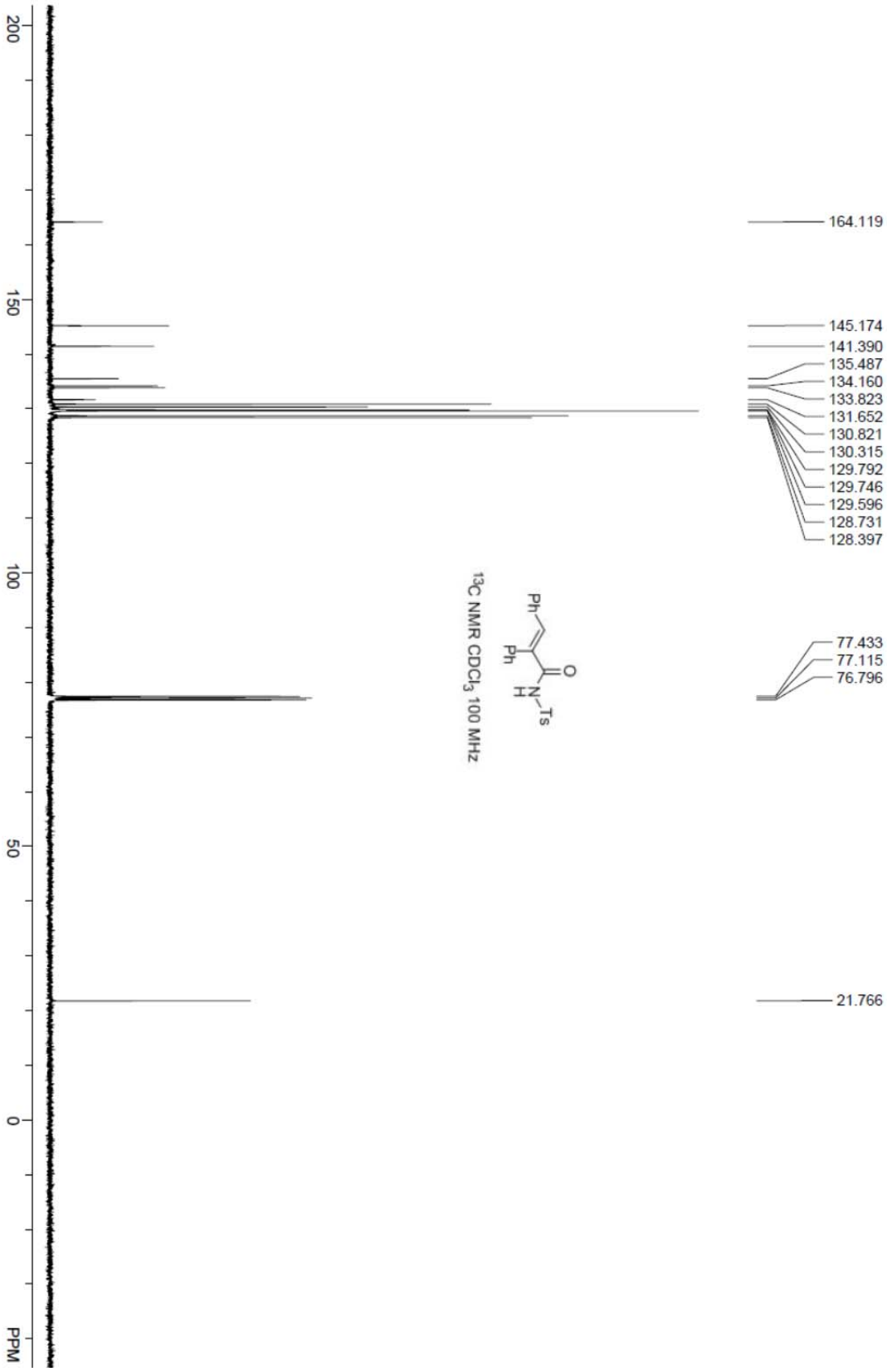
References

[1] a) Y. Jiang, V. Z. Y. Khong, E. Lourdusamy and C.-M. Park, *Chem. Commun.*, 2012, **48,** 3133; b) J. Linder, T. P. Garner, H. E. L. Williams, M. S. Searle and C. J. Moody, *J. Am. Chem. Soc.*, 2011, **133**, 1044; c) B. Shi, A. J. Blake, W. Lewis, I. B. Campbell, B. D. Judkins and C. J. Moody, *J. Org. Chem.*, 2010, **75**, 152; d) J. Pietruszka and A. Witt, *Synthesis* 2006, 4266.

NMR spectra

(*E*)-2,3-Diphenyl-*N*-tosylacrylamide (1a)

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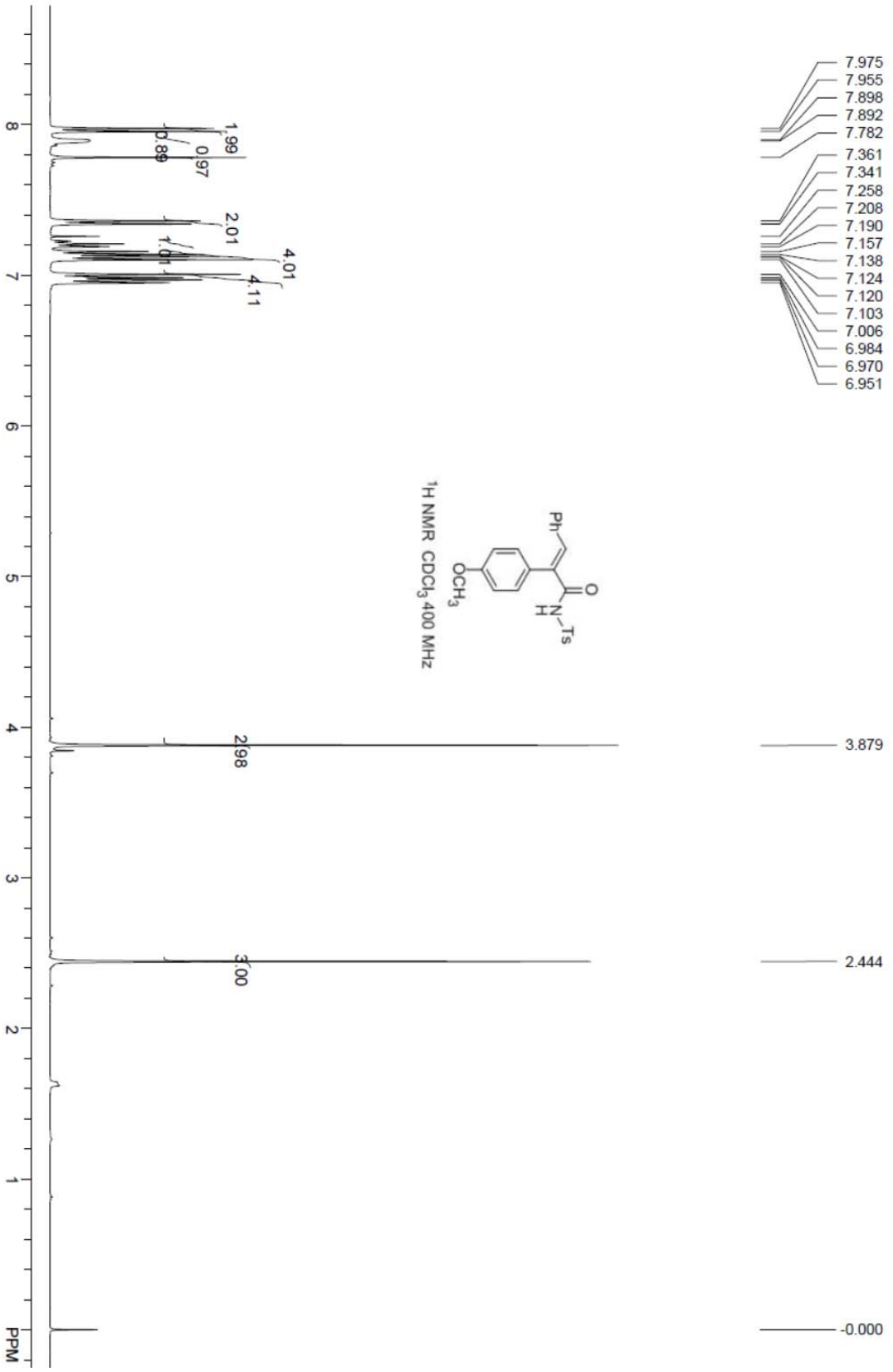
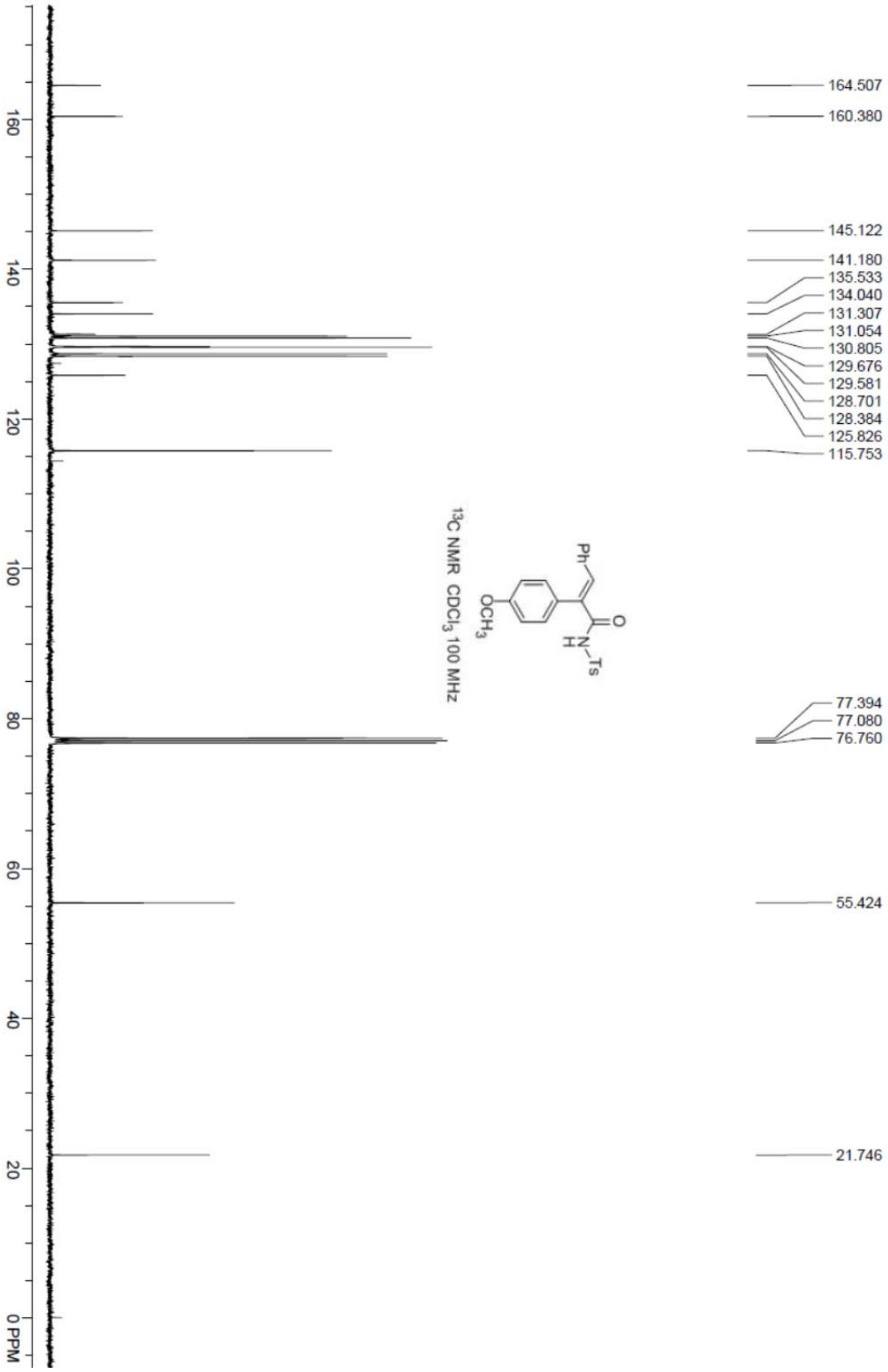
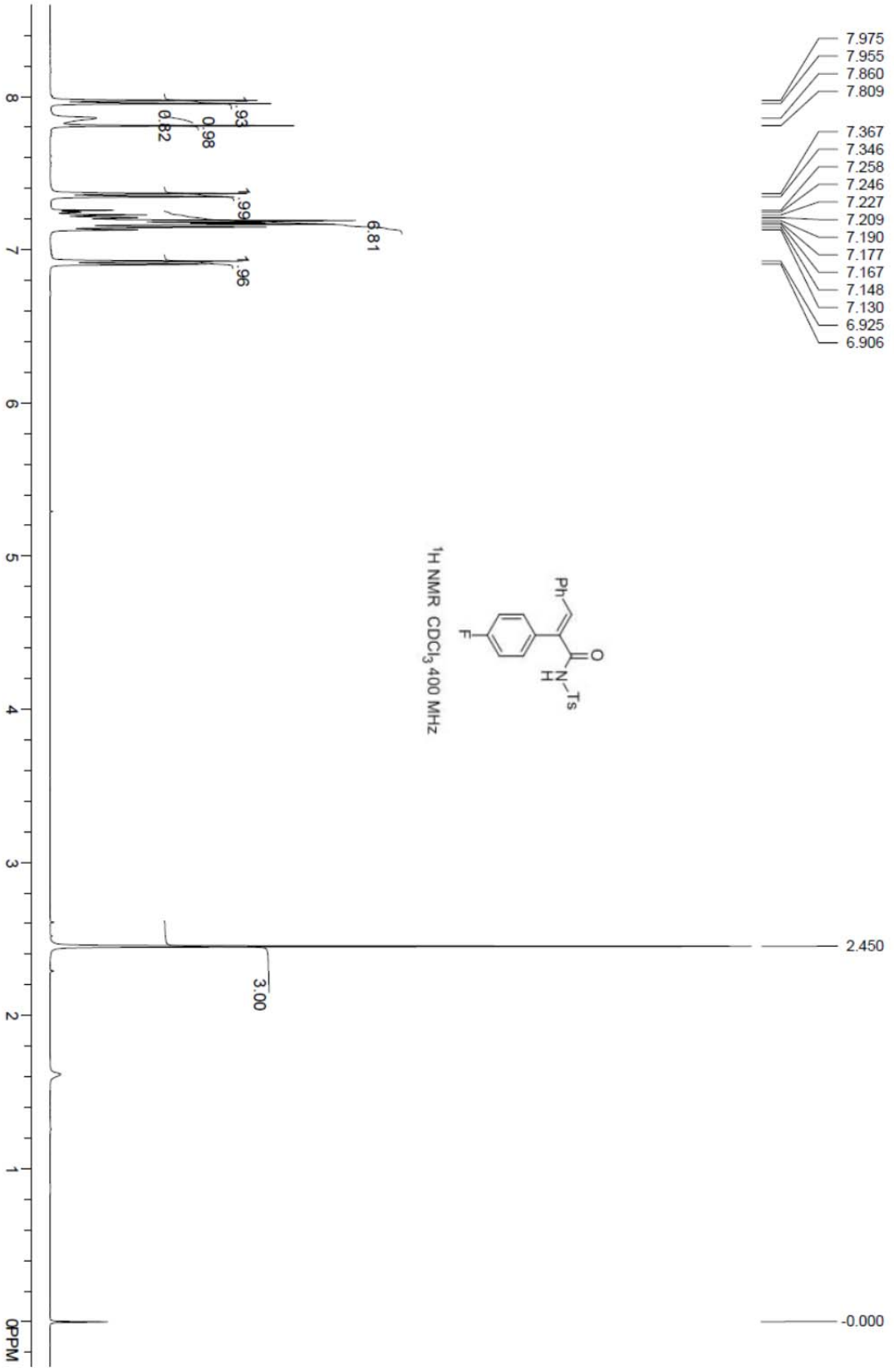
128.731
128.397
77.433
77.115
76.796
21.766
200
150
100
50
0
PPM
^{13}C NMR $CDCl_3$ 100 MHz
Ph
Ph
O
N
H
Ts

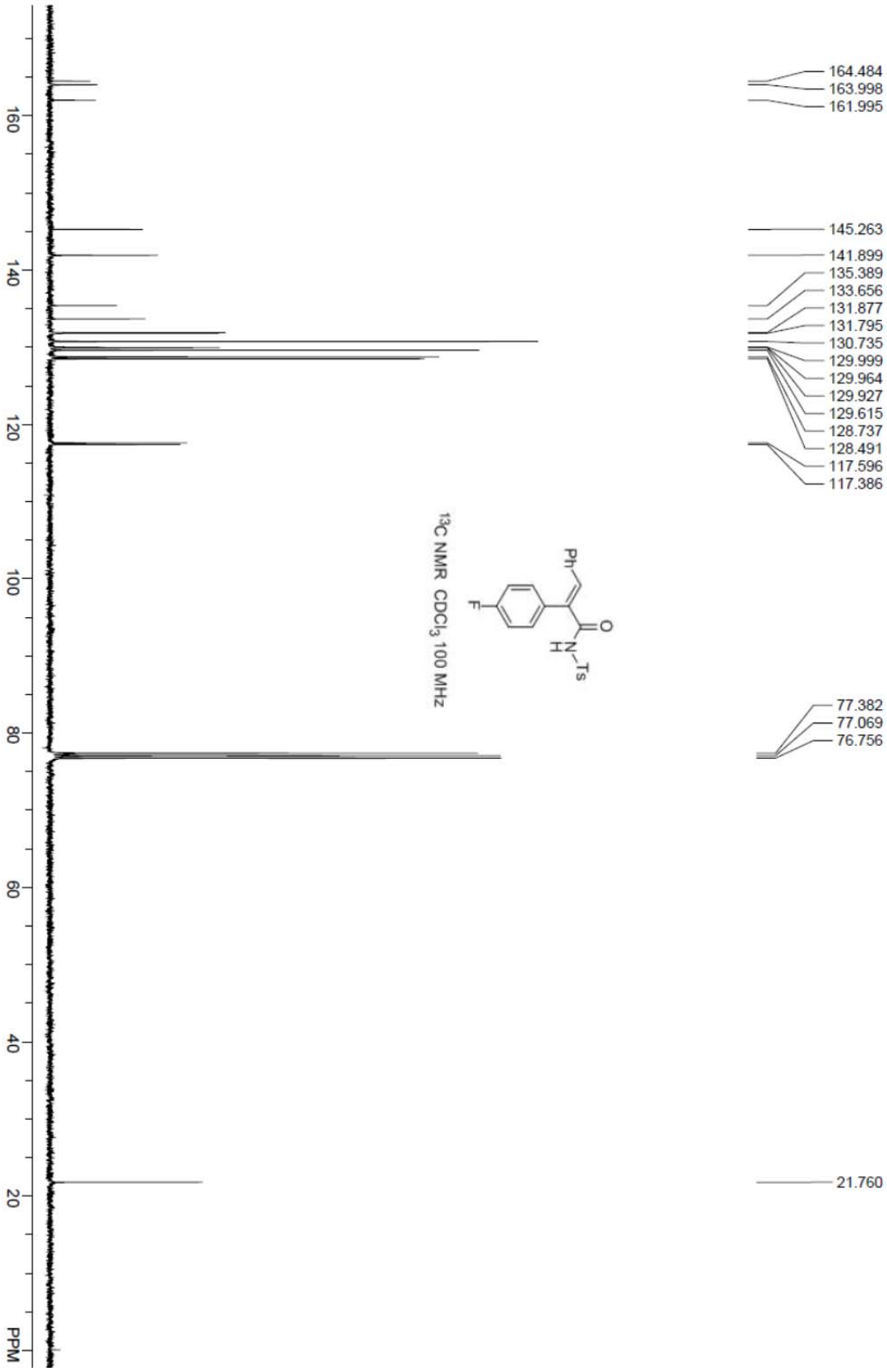
(*E*)-2-(4-Methoxyphenyl)-3-phenyl-*N*-tosylacrylamide (1b)



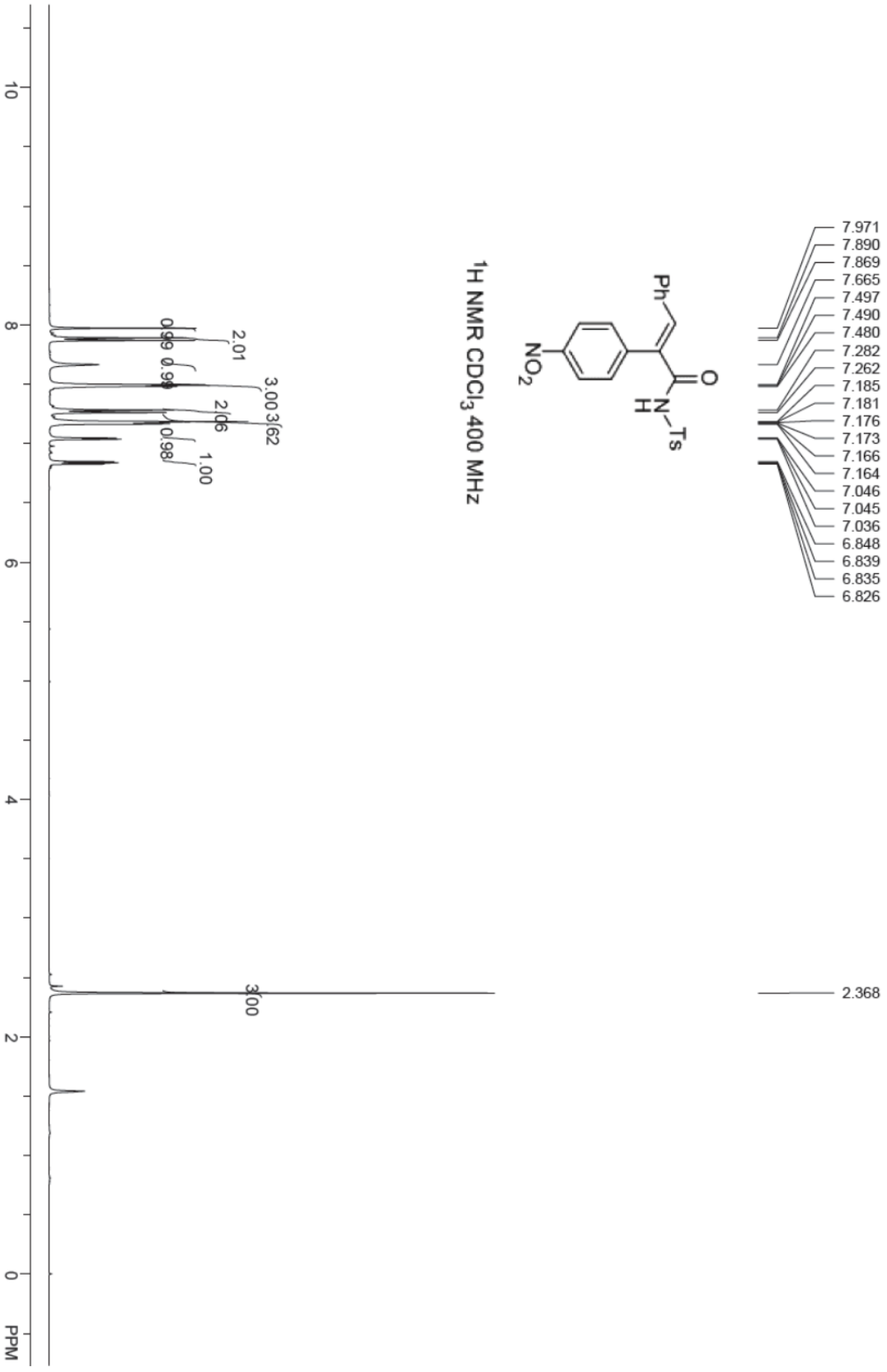

164.507
160.380
145.122
141.180
135.533
134.040
131.307
131.054
130.805
129.676
129.581
128.701
128.384
125.826
115.753
77.394
77.080
76.760
55.424
21.746
160
140
120
100
80
60
40
20
0 PPM
^{13}C NMR CDCl$_3$ 100 MHz
Ph
OCH$_3$
O
N
H
Ts

(*E*)-2-(4-Fluorophenyl)-3-phenyl-*N*-tosylacrylamide (1c)



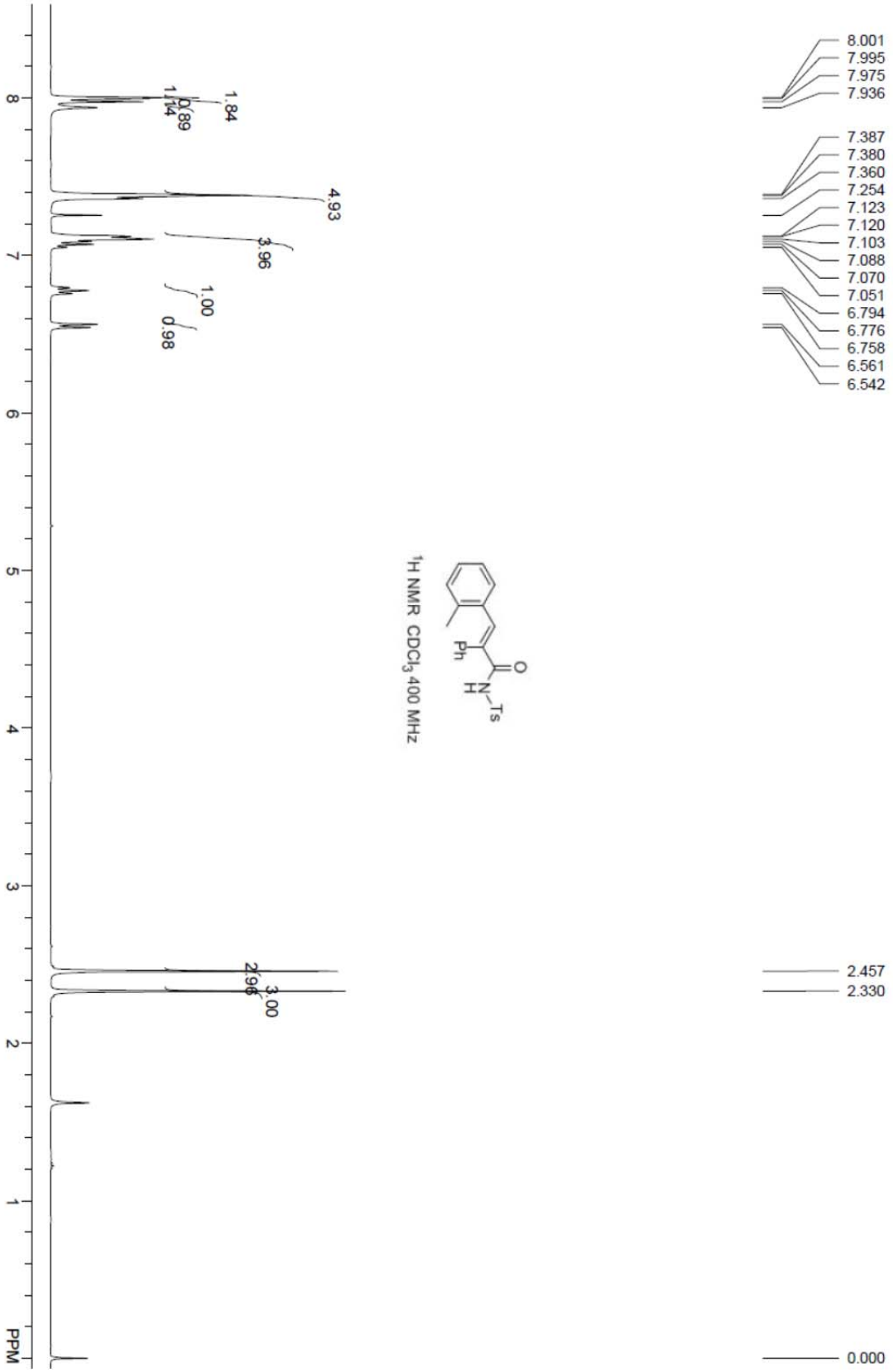

164.484
163.998
161.995
145.263
141.899
135.389
133.656
131.877
131.795
130.735
129.999
129.964
129.927
129.615
128.737
128.491
117.596
117.386
77.382
77.069
76.756
21.760
160
140
120
100
80
60
40
20
PPM
^{13}C NMR CDCl$_3$ 100 MHz
Ph
F
O
N
H
Ts

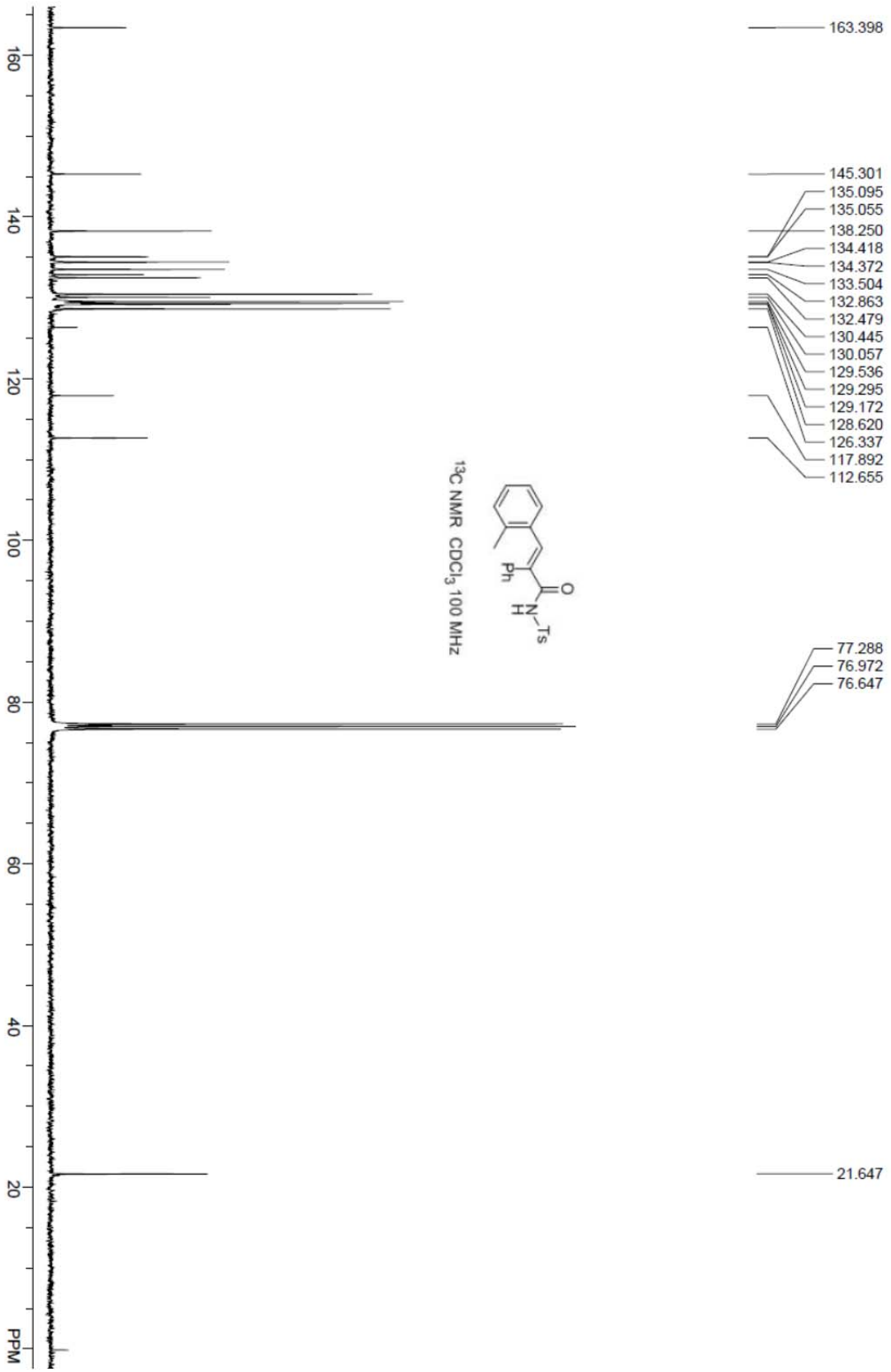
(*E*)-2-(4-Nitrophenyl)-3-phenyl-*N*-tosylacrylamide (1d)



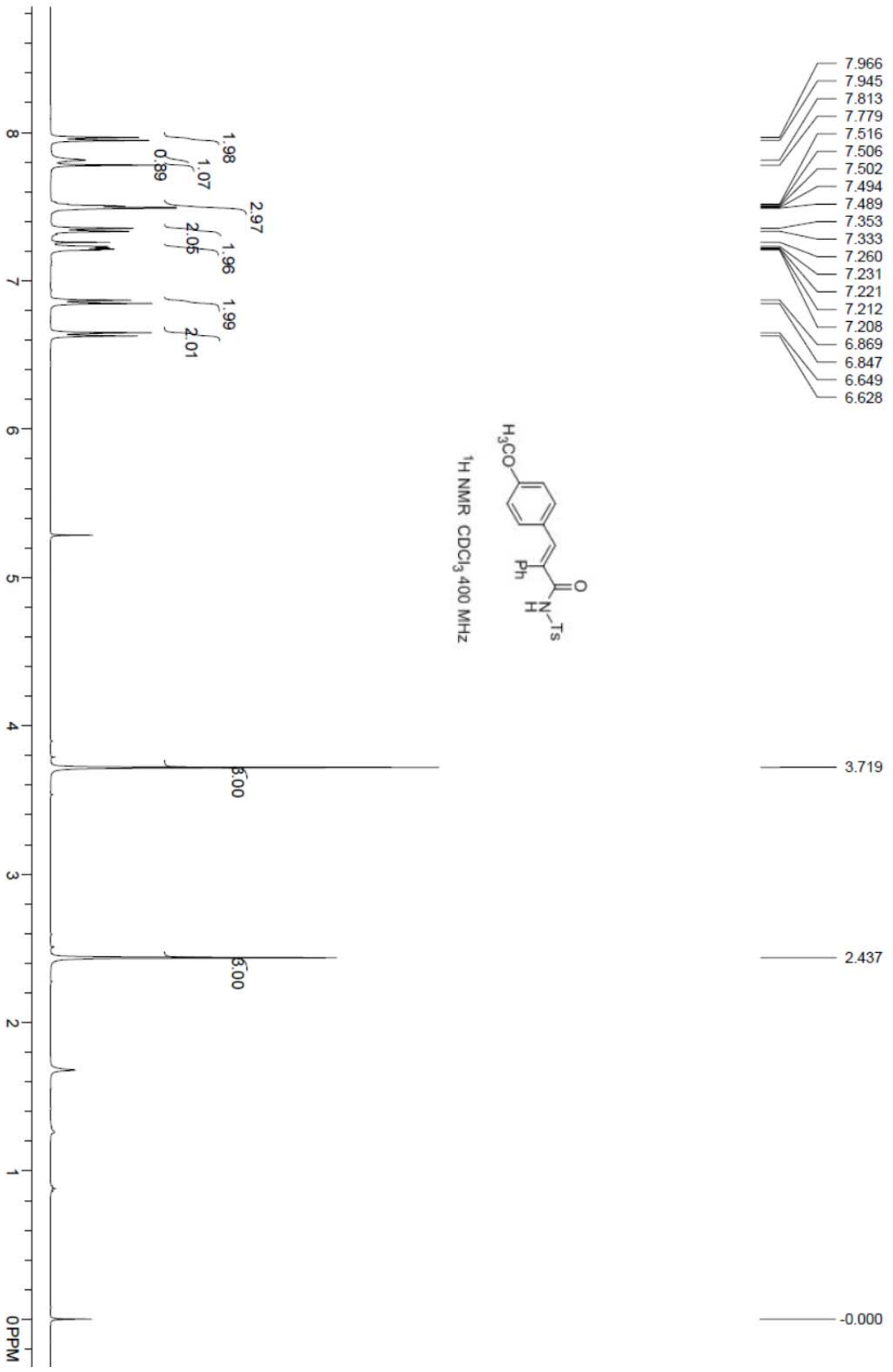

^{13}C NMR CDCl$_3$ 100 MHz
Ph
NO$_2$
O
N
H
Ts
163.564
145.129
138.043
135.511
134.763
134.690
133.244
131.726
130.710
130.218
129.571
128.705
128.237
126.976
77.395
77.081
76.761
21.750
200
150
100
50
0 PPM

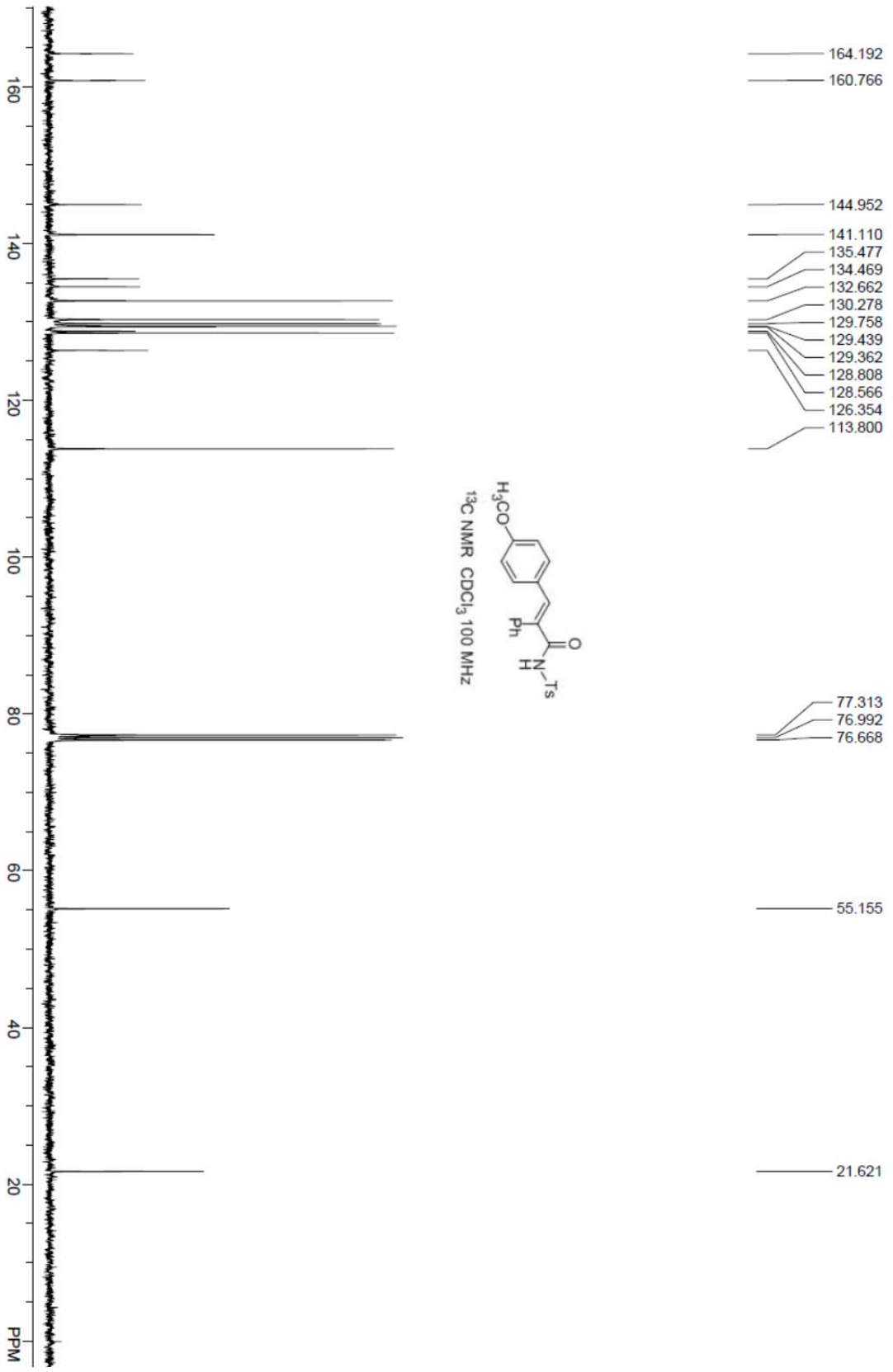
(*E*)-2-Phenyl-3-(o-tolyl)-*N*-tosylacrylamide (1e)



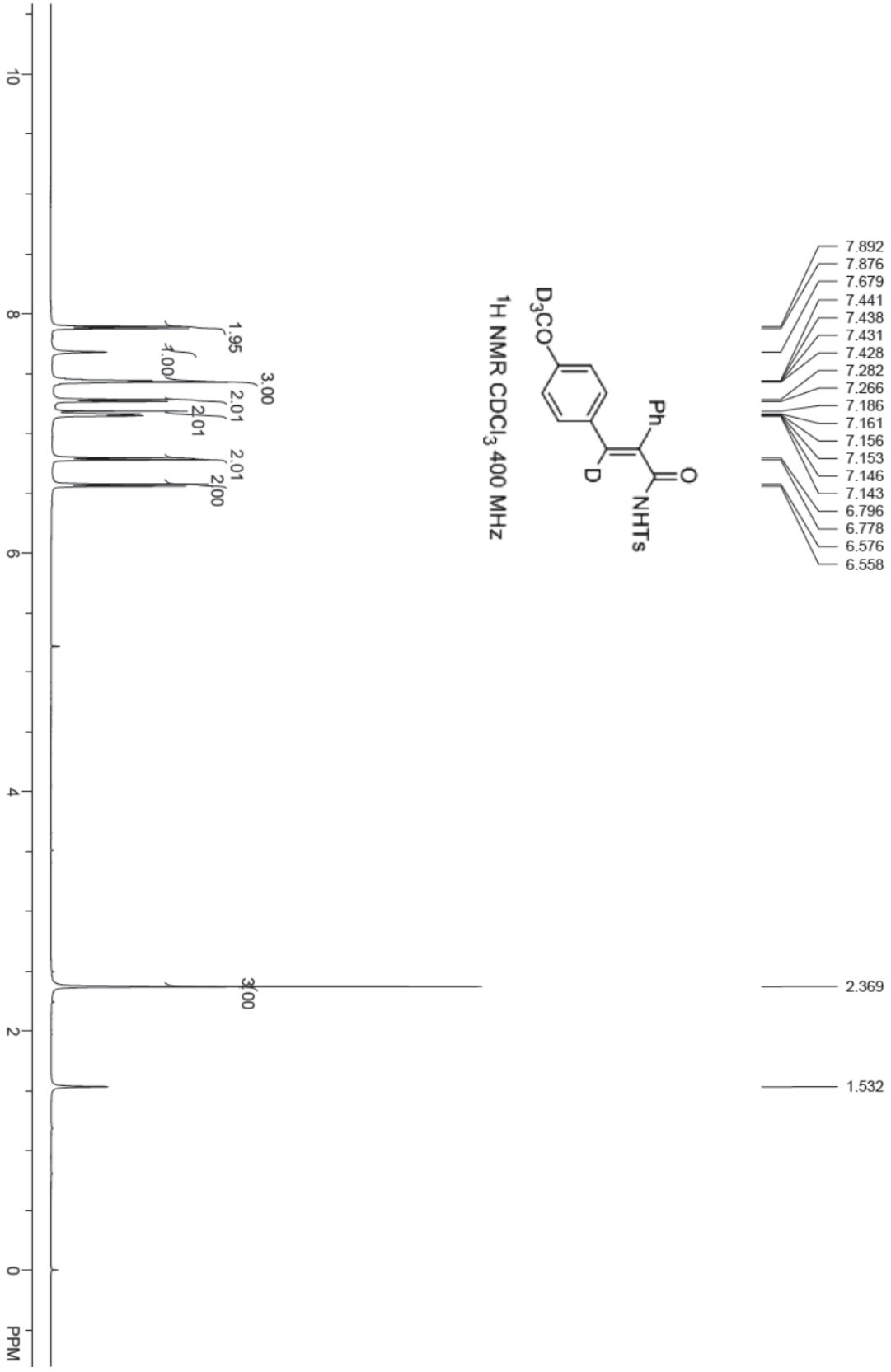

163.398
145.301
135.095
135.055
138.250
134.418
134.372
133.504
132.863
132.479
130.445
130.057
129.536
129.295
129.172
128.620
126.337
117.892
112.655
77.288
76.972
76.647
21.647
160
140
120
100
80
60
40
20
PPM
^{13}C NMR CDCl$_3$ 100 MHz
Ph
O
N
H
Ts

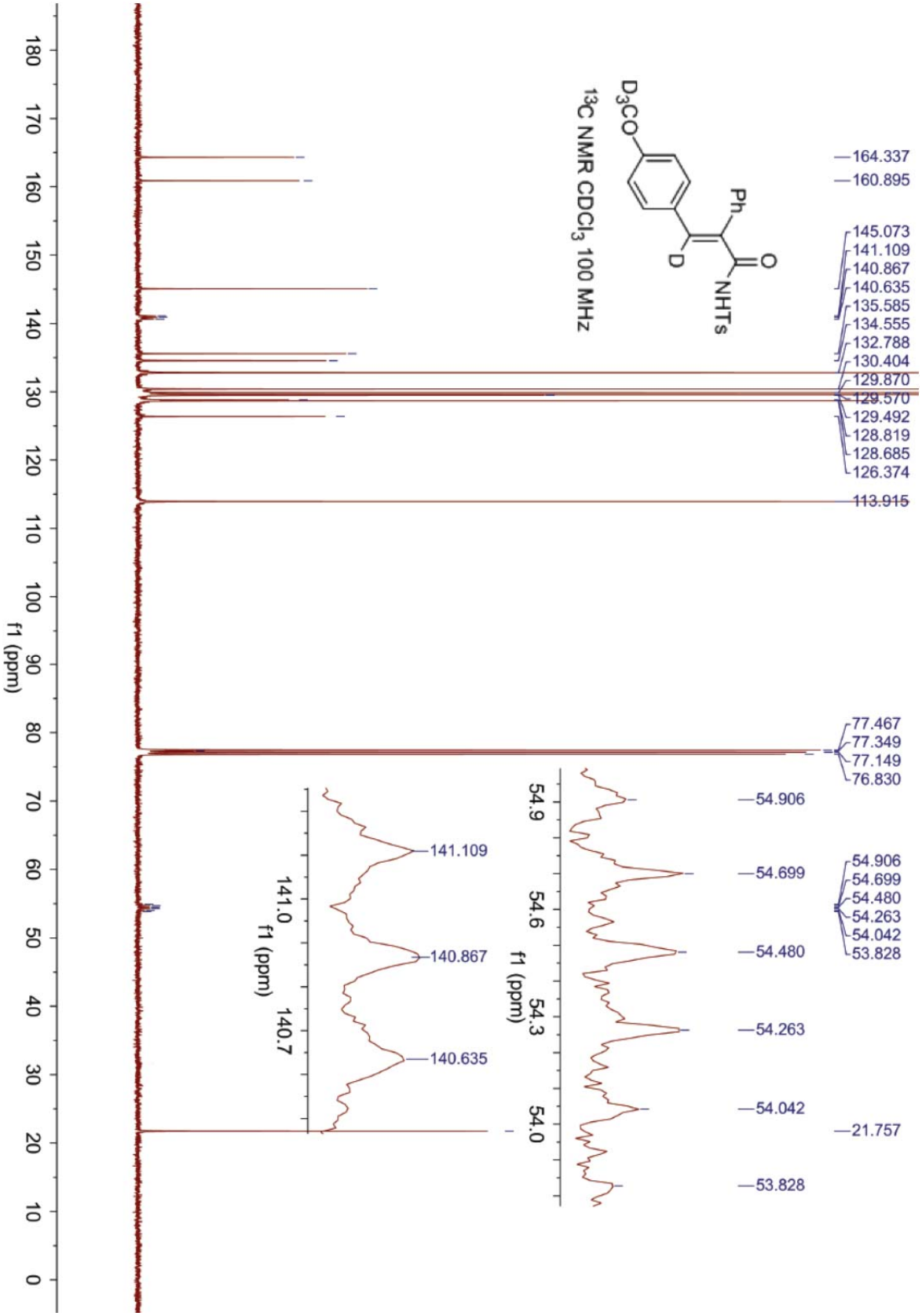
(*E*)-3-(4-Methoxyphenyl)-2-phenyl-*N*-tosylacrylamide (1f)



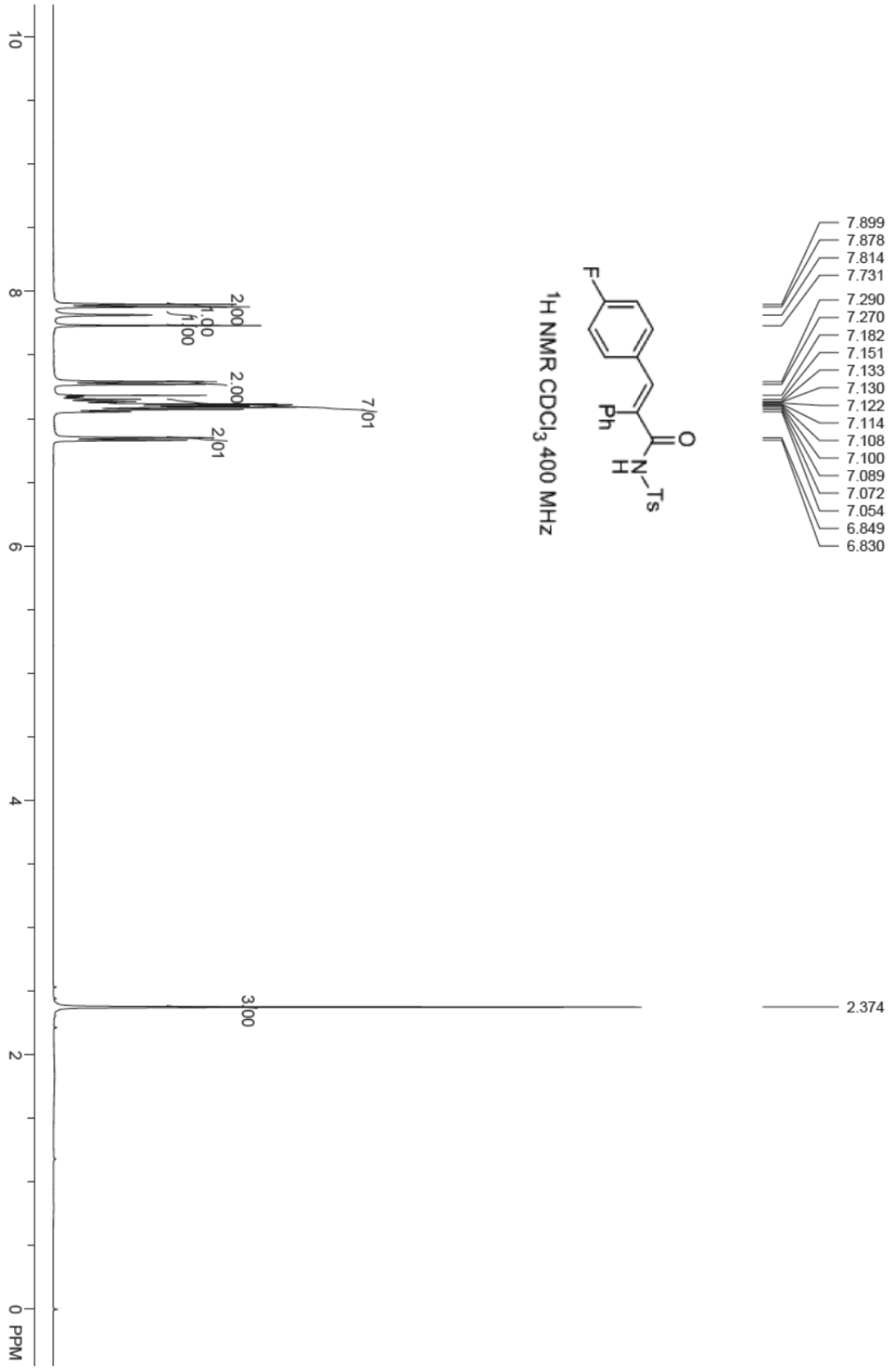

164.192
160.766
144.952
141.110
135.477
134.469
132.662
130.278
129.758
129.439
129.362
128.808
128.566
126.354
113.800
77.313
76.992
76.668
55.155
21.621
160
140
120
100
80
60
40
20
PPM
^{13}C NMR CDCl$_3$ 100 MHz
H$_3$CO
Ph
O
N
H
Ts

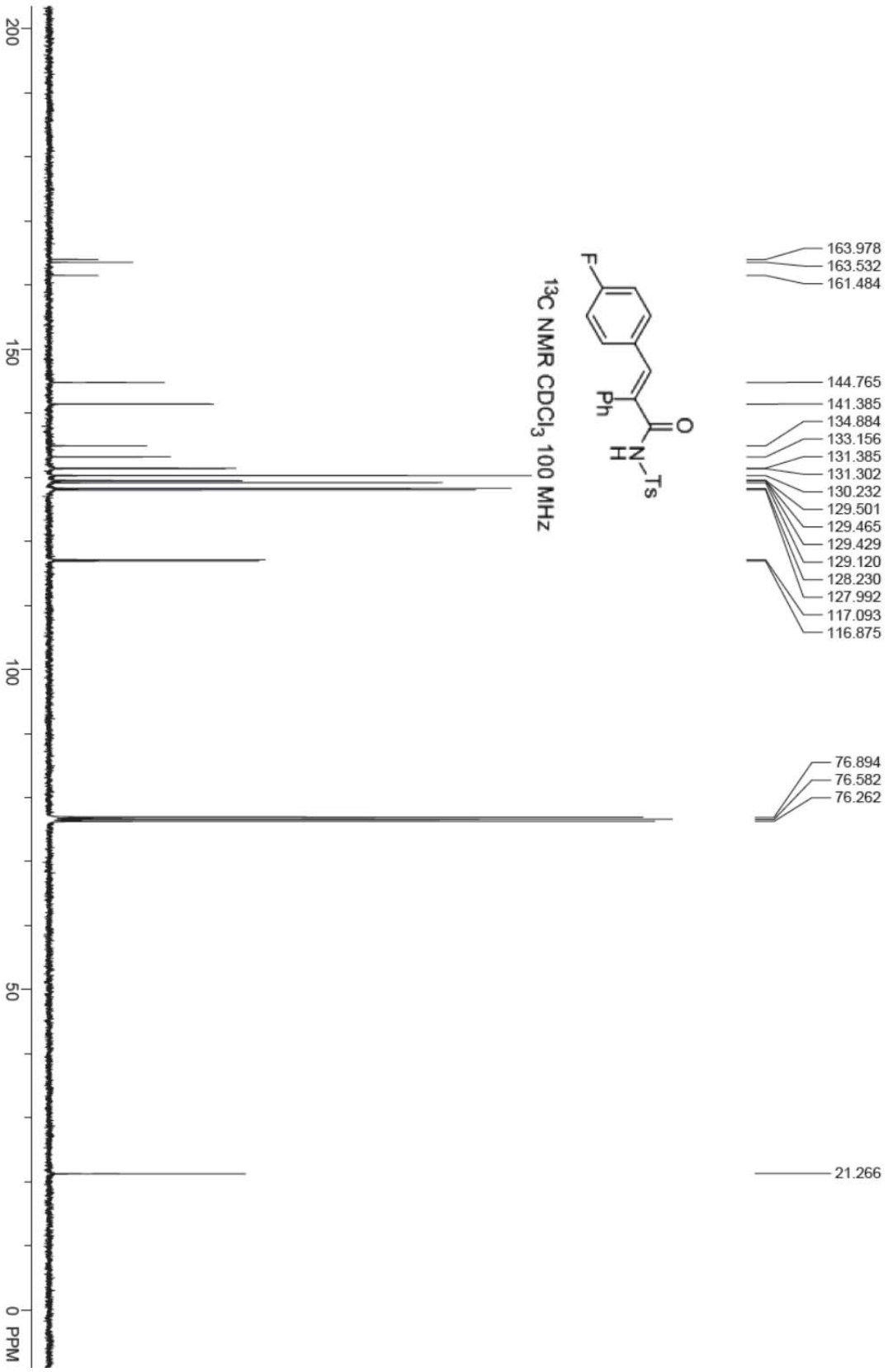
(*E*)-3-(4-Methoxyphenyl)-2-phenyl-*N*-tosylacrylamid-d_4 (1f-d_4)



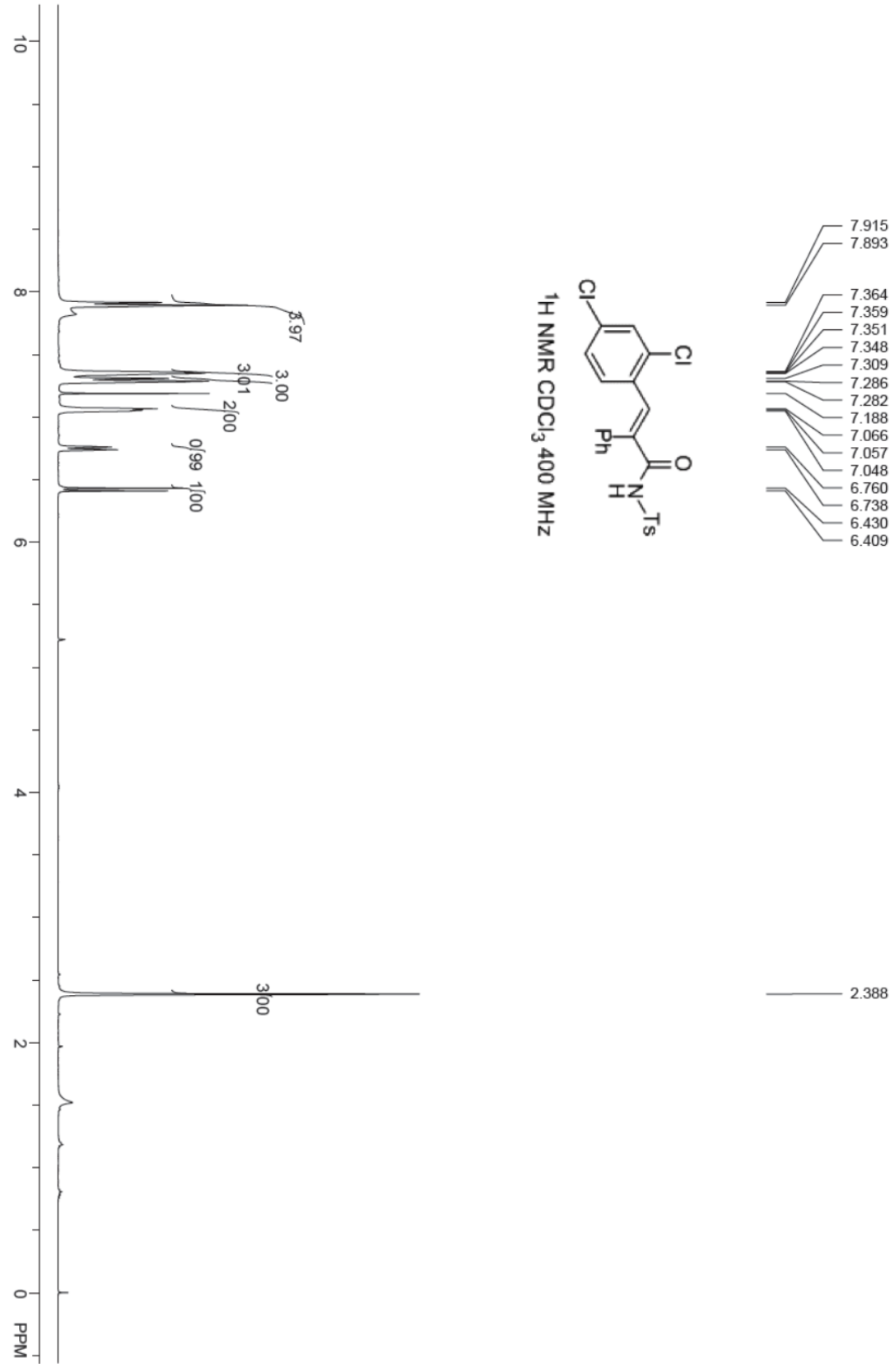

^{13}C NMR CDCl$_3$ 100 MHz
D$_3$CO
Ph
D
O
NHTs
164.337
160.895
145.073
141.109
140.867
140.635
135.585
134.555
132.788
130.404
129.870
129.570
129.492
128.819
128.685
126.374
113.915
77.467
77.349
77.149
76.830
54.906
54.699
54.480
54.263
54.042
53.828
21.757
f1 (ppm)

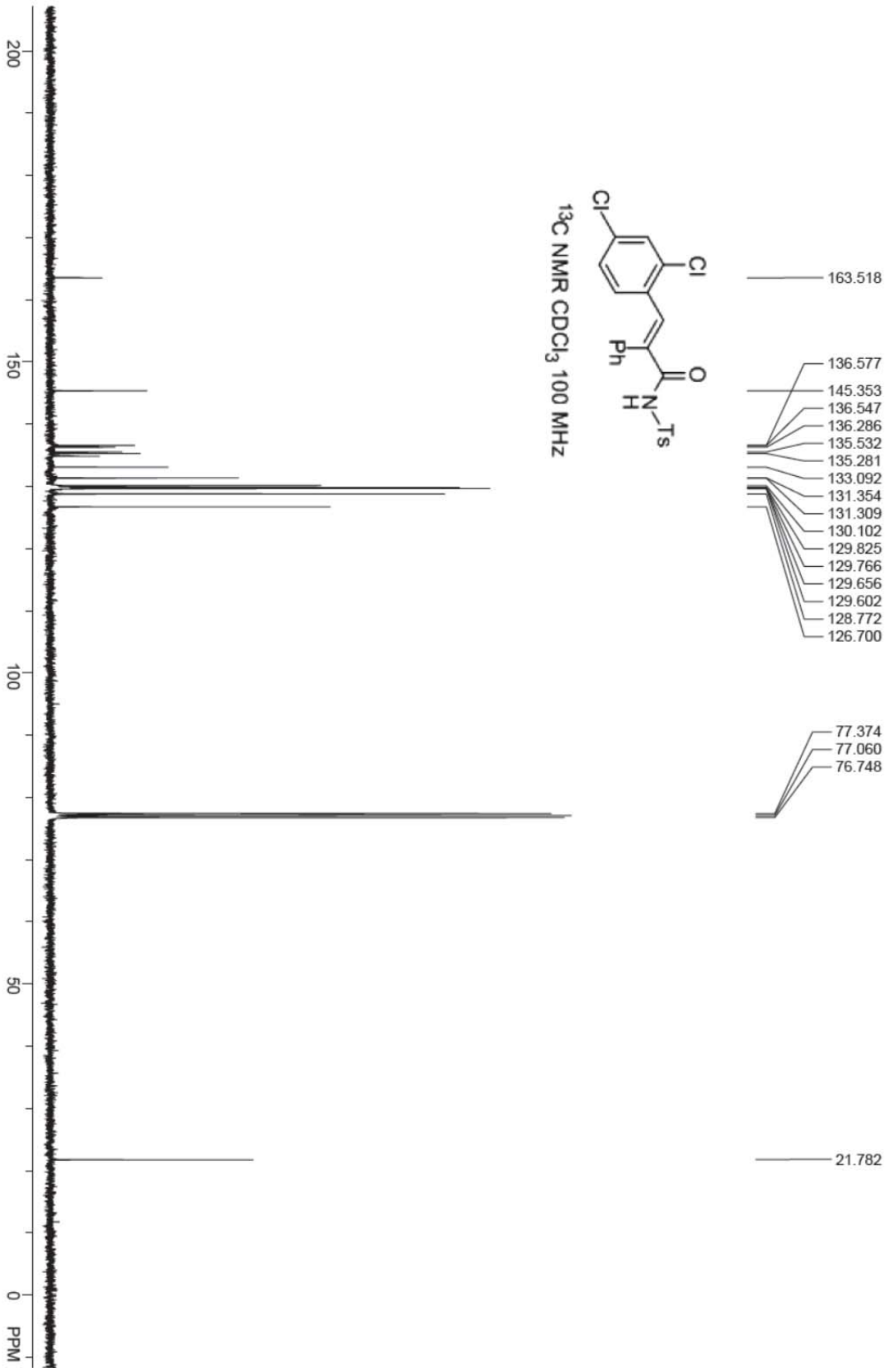
(*E*)-3-(4-Fluorophenyl)-2-phenyl-*N*-tosylacrylamide (1g)



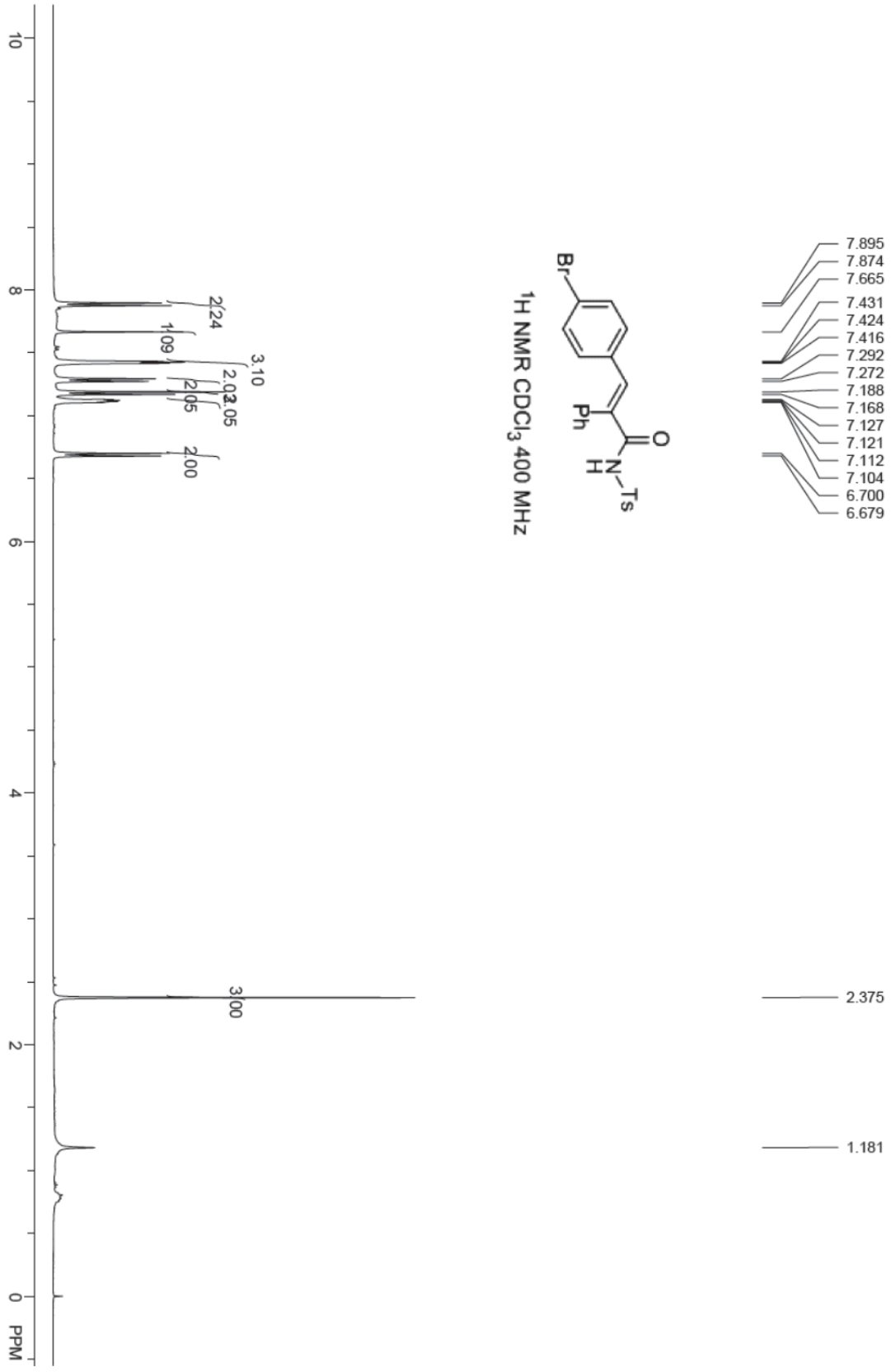

^{13}C NMR CDCl$_3$ 100 MHz
F
Ph
O
N
H
Ts
163.978
163.532
161.484
144.765
141.385
134.884
133.156
131.385
131.302
130.232
129.501
129.465
129.429
129.120
128.230
127.992
117.093
116.875
76.894
76.582
76.262
21.266
200
150
100
50
0 PPM

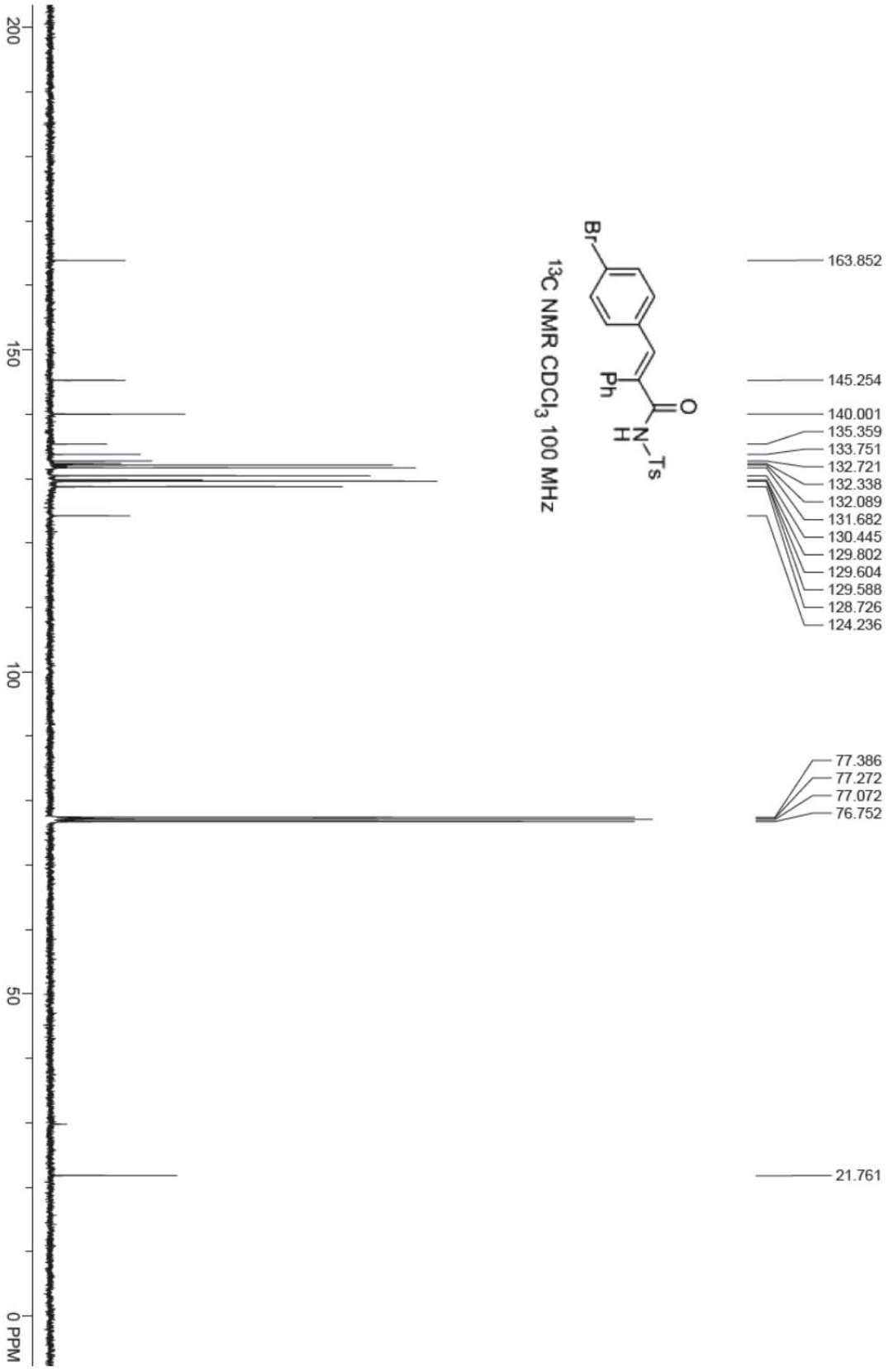
(*E*)-3-(2,4-Dichlorophenyl)-2-phenyl-*N*-tosylacrylamide (1h)



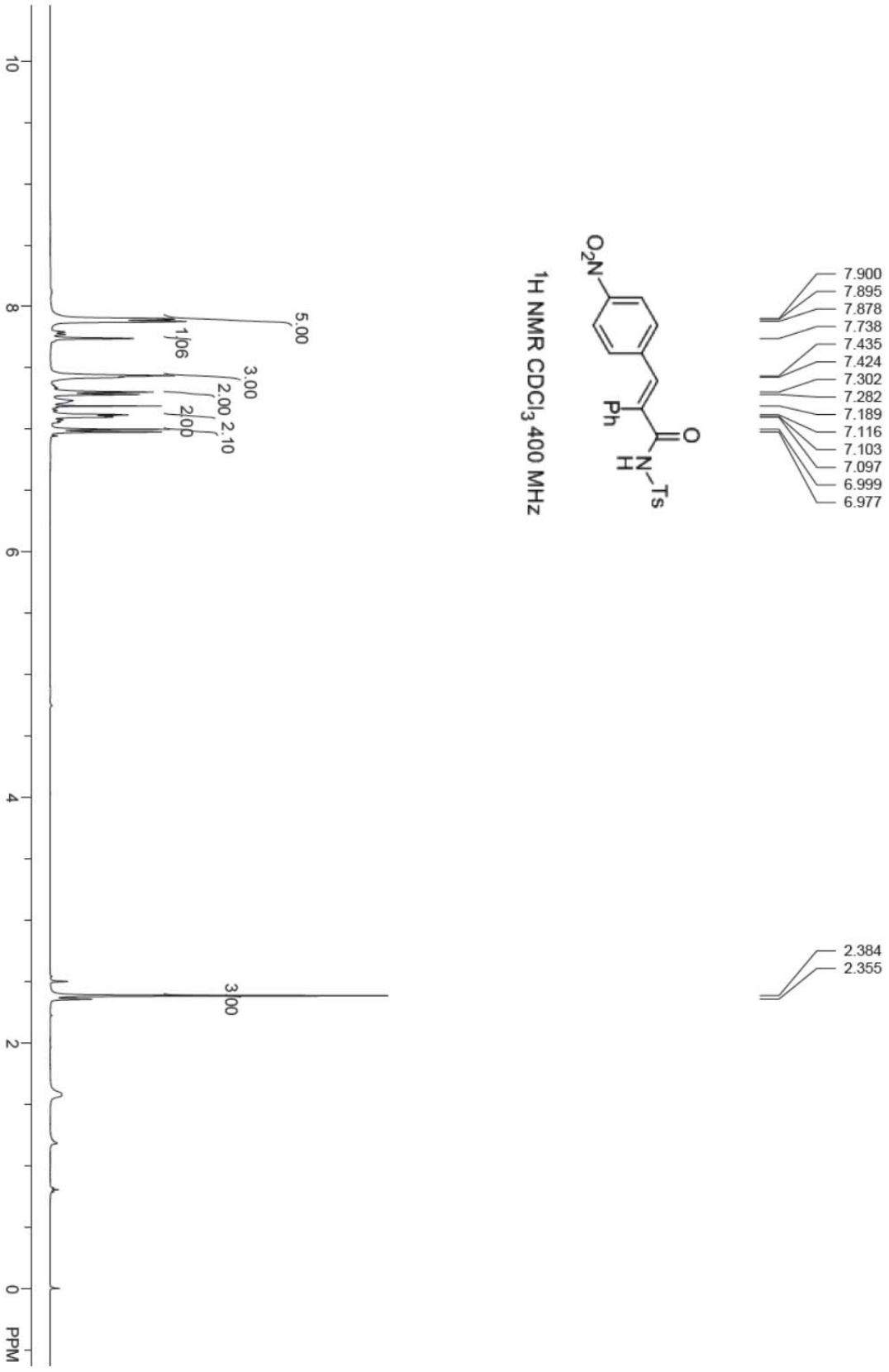

^{13}C NMR $CDCl_3$ 100 MHz
Cl
Cl
Ph
O
N
H
Ts
163.518
136.577
145.353
136.547
136.286
135.532
135.281
133.092
131.354
131.309
130.102
129.825
129.766
129.656
129.602
128.772
126.700
77.374
77.060
76.748
21.782
200
150
100
50
0
PPM

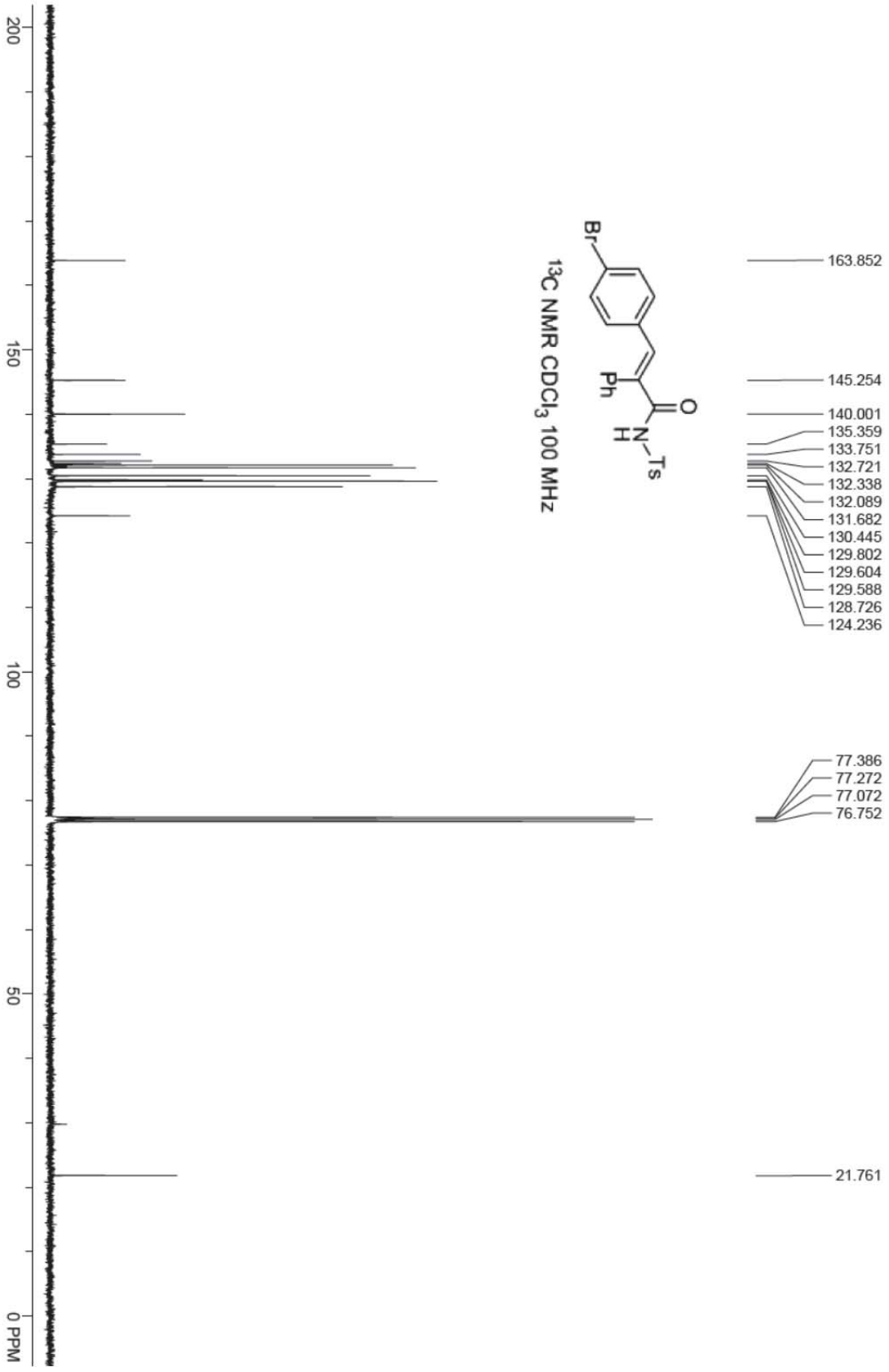
(*E*)-3-(4-Bromophenyl)-2-phenyl-*N*-tosylacrylamide (1i)



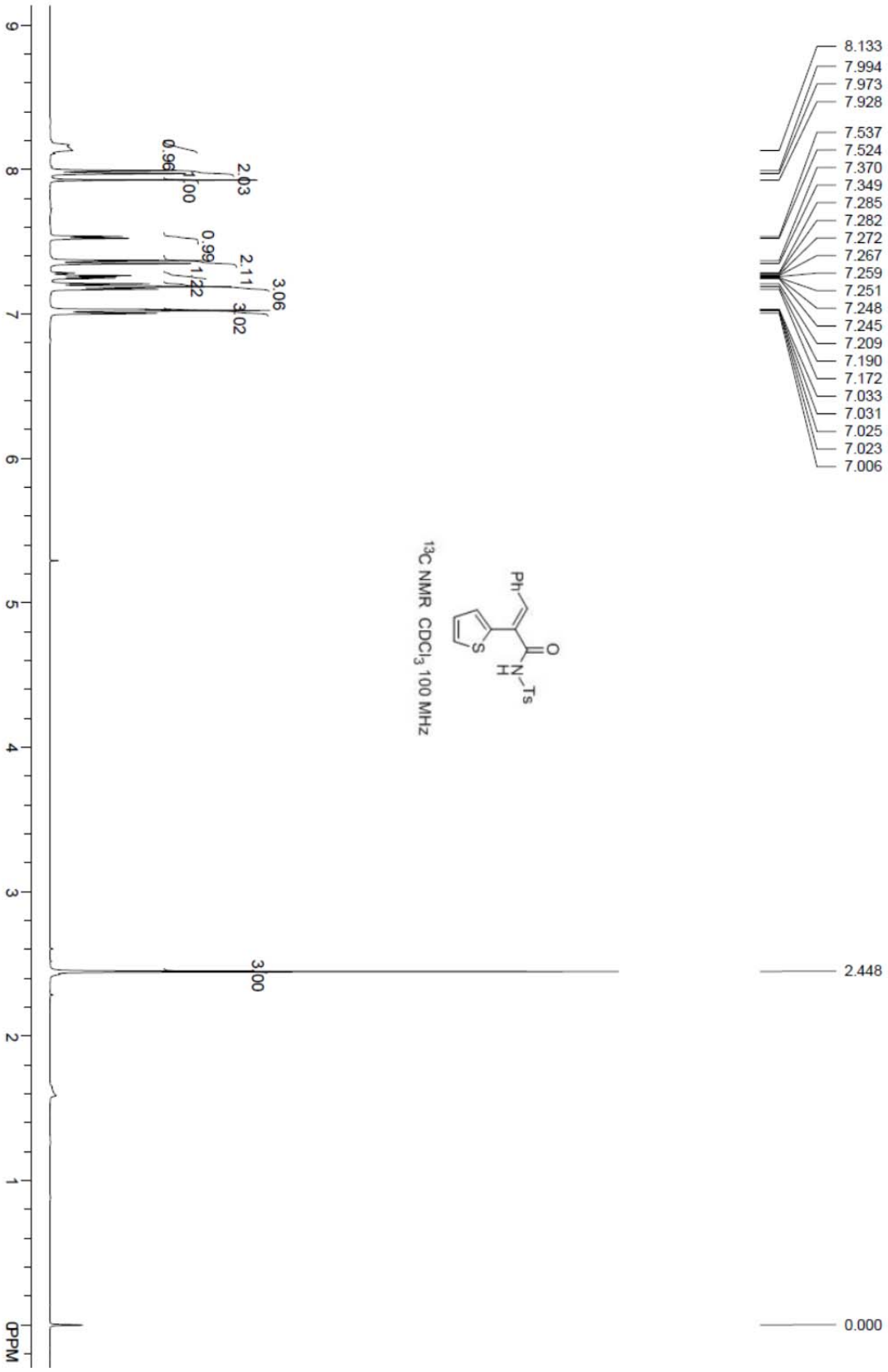

^{13}C NMR CDCl$_3$ 100 MHz
Br
Ph
O
N
H
Ts
163.852
145.254
140.001
135.359
133.751
132.721
132.338
132.089
131.682
130.445
129.802
129.604
129.588
128.726
124.236
77.386
77.272
77.072
76.752
21.761
200
150
100
50
0 PPM

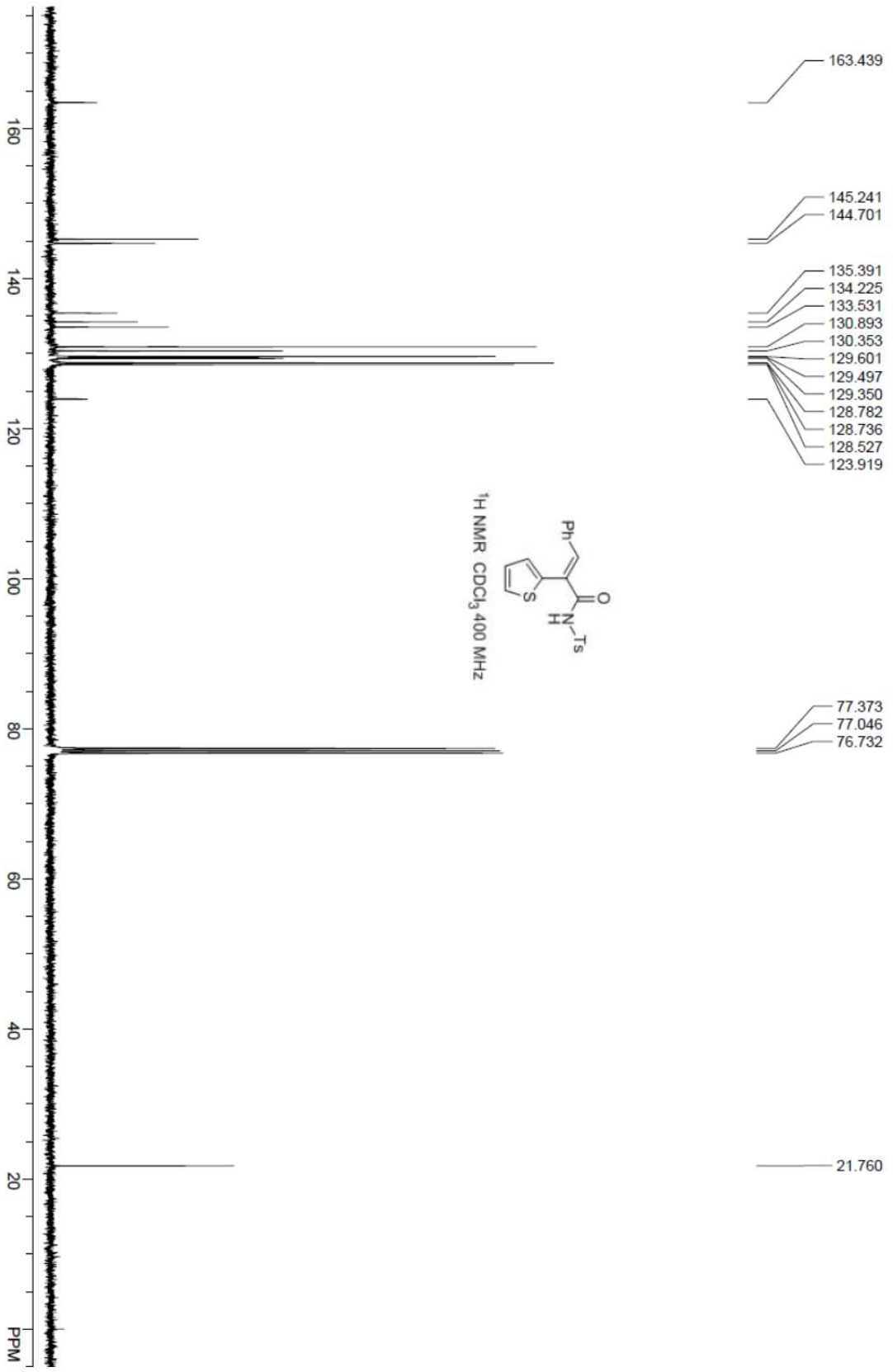
(*E*)-3-(4-Nitrophenyl)-2-phenyl-*N*-tosylacrylamide (1j)



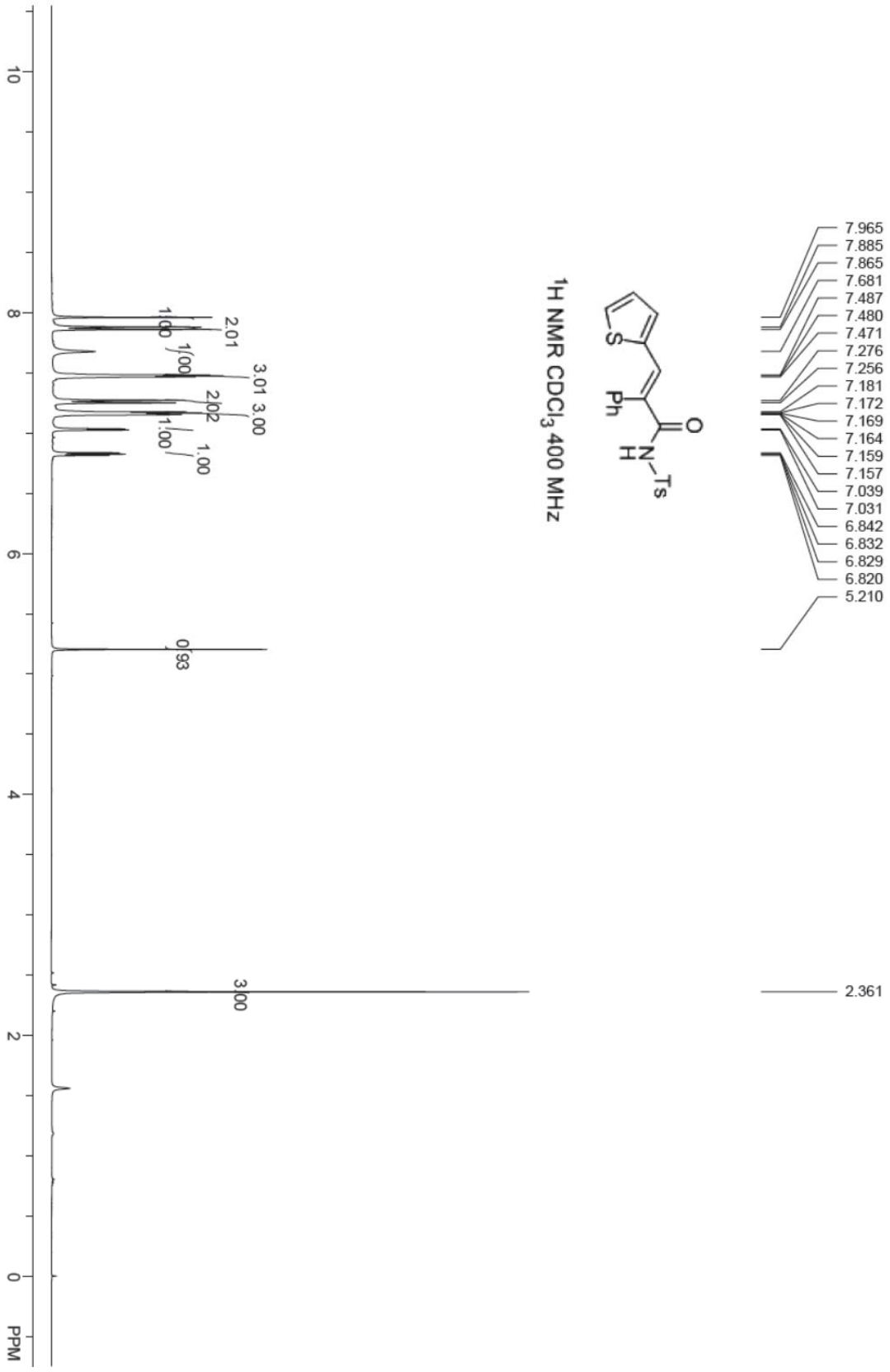

^{13}C NMR CDCl$_3$ 100 MHz
Br
Ph
O
N
H
Ts
163.852
145.254
140.001
135.359
133.751
132.721
132.338
132.089
131.682
130.445
129.802
129.604
129.588
128.726
124.236
77.386
77.272
77.072
76.752
21.761
200
150
100
50
0 PPM

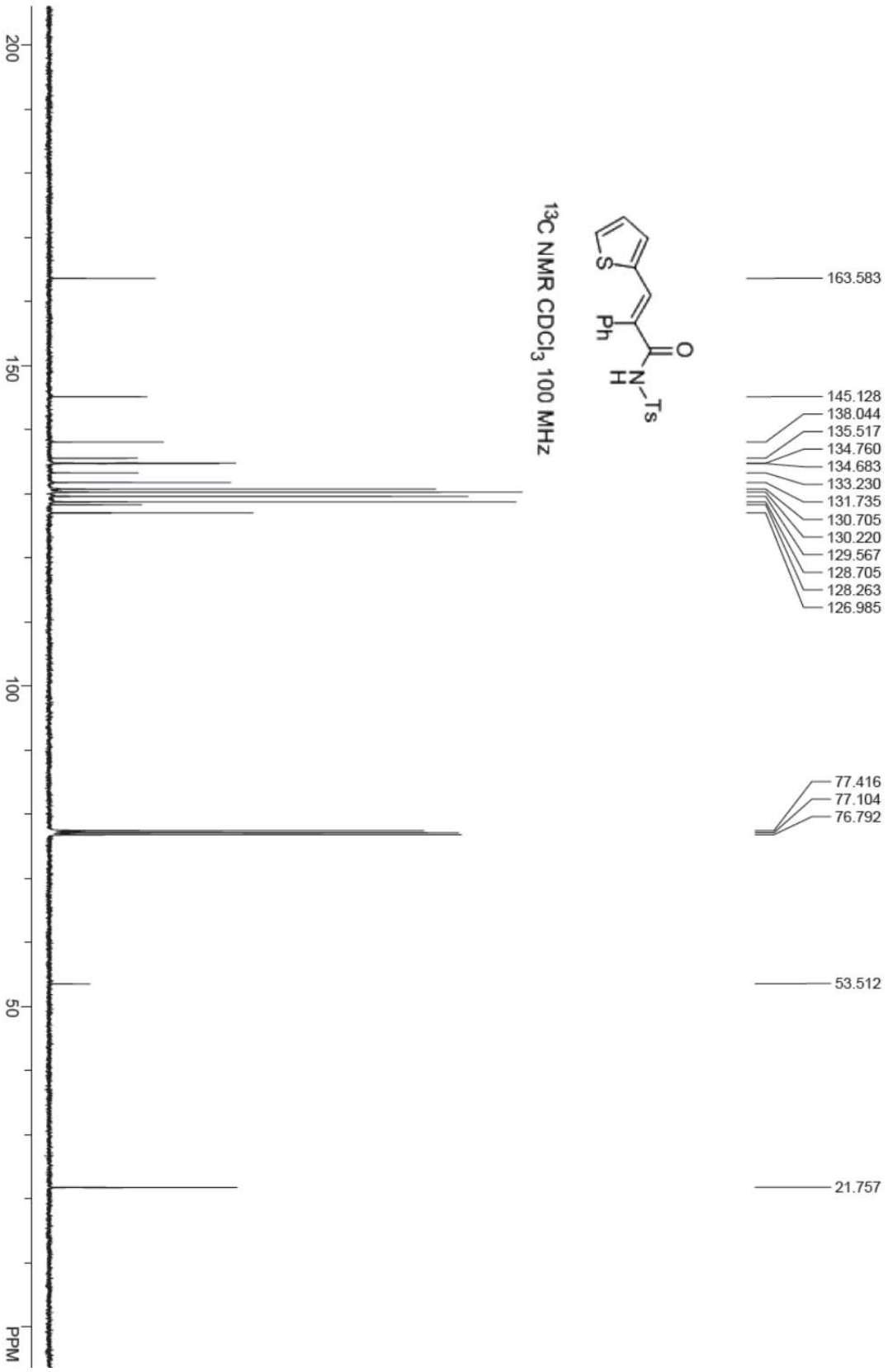
(*Z*)-3-Phenyl-2-(thiophen-2-yl)-*N*-tosylacrylamide (1k)



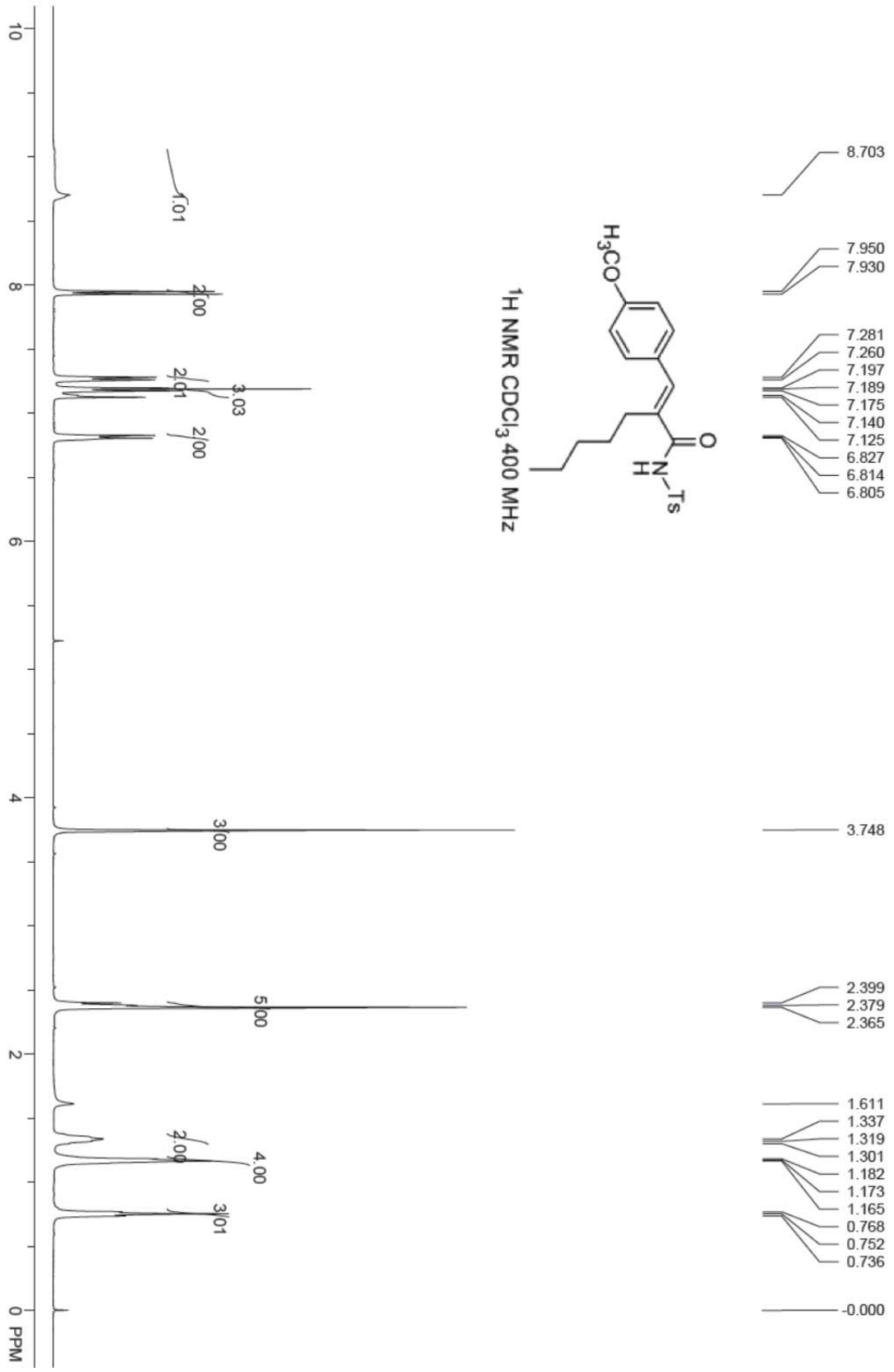

163.439
145.241
144.701
135.391
134.225
133.531
130.893
130.353
129.601
129.497
129.350
128.782
128.736
128.527
123.919
77.373
77.046
76.732
21.760
160
140
120
100
80
60
40
20
PPM
^{1}H NMR CDCl$_3$ 400 MHz
Ph
S
O
N
H
Ts

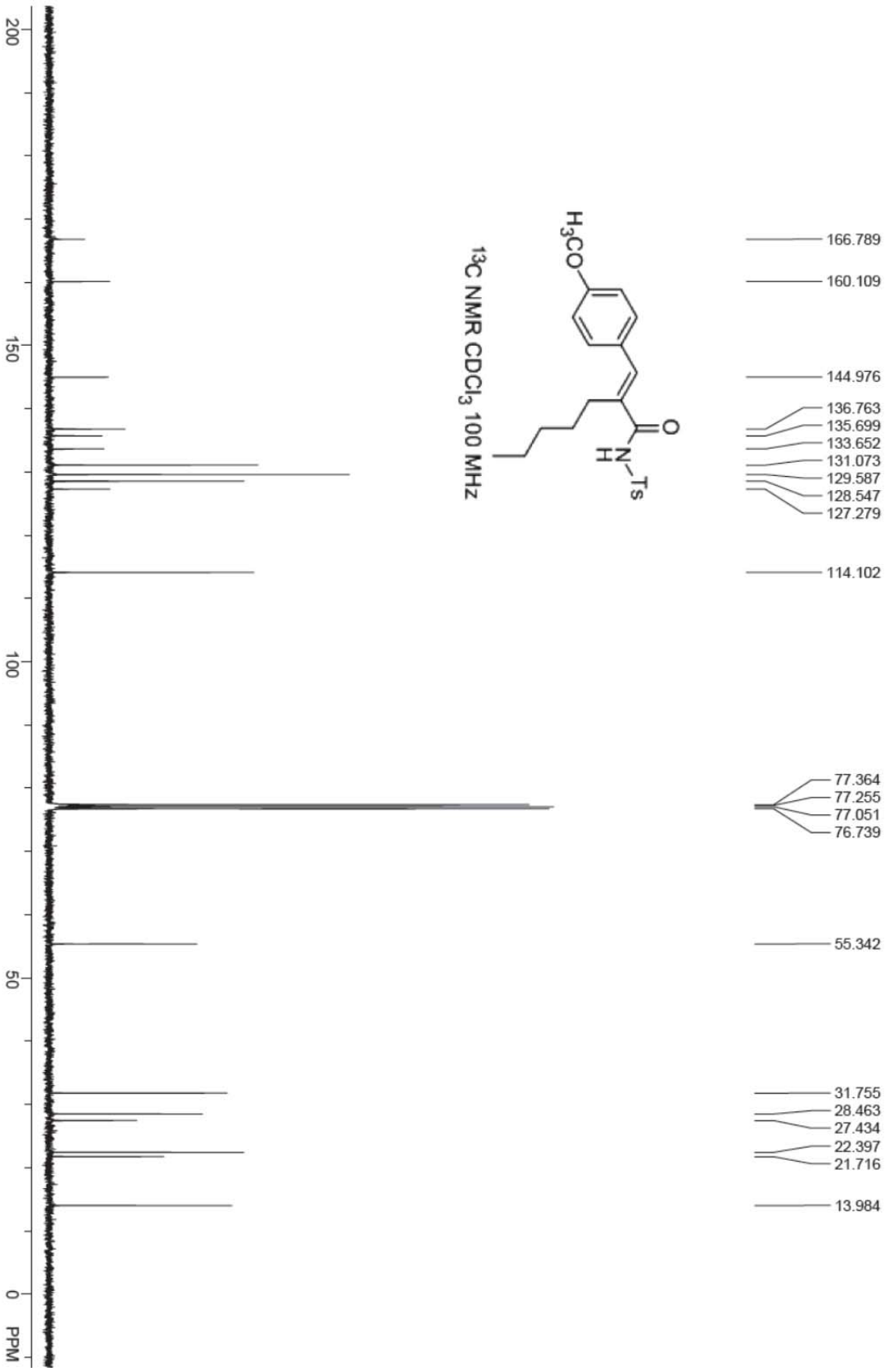
(*E*)-2-Phenyl-3-(thiophen-2-yl)-*N*-tosylacrylamide (1l)



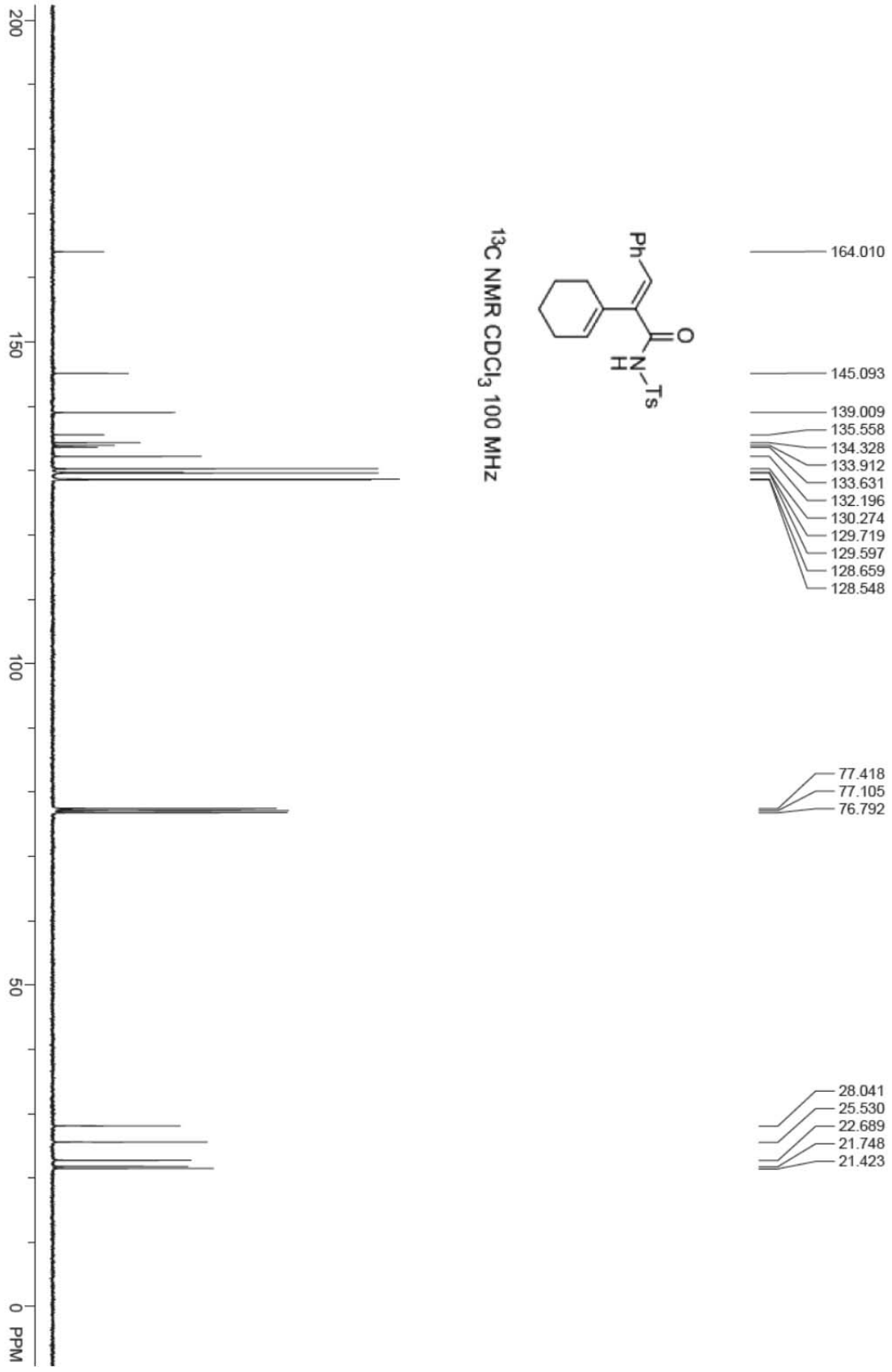

^{13}C NMR CDCl$_3$ 100 MHz
163.583
145.128
138.044
135.517
134.760
134.683
133.230
131.735
130.705
130.220
129.567
128.705
128.263
126.985
77.416
77.104
76.792
53.512
21.757
200
150
100
50
PPM

(*E*)-2-(4-Methoxybenzylidene)-*N*-tosylheptanamide (1m)

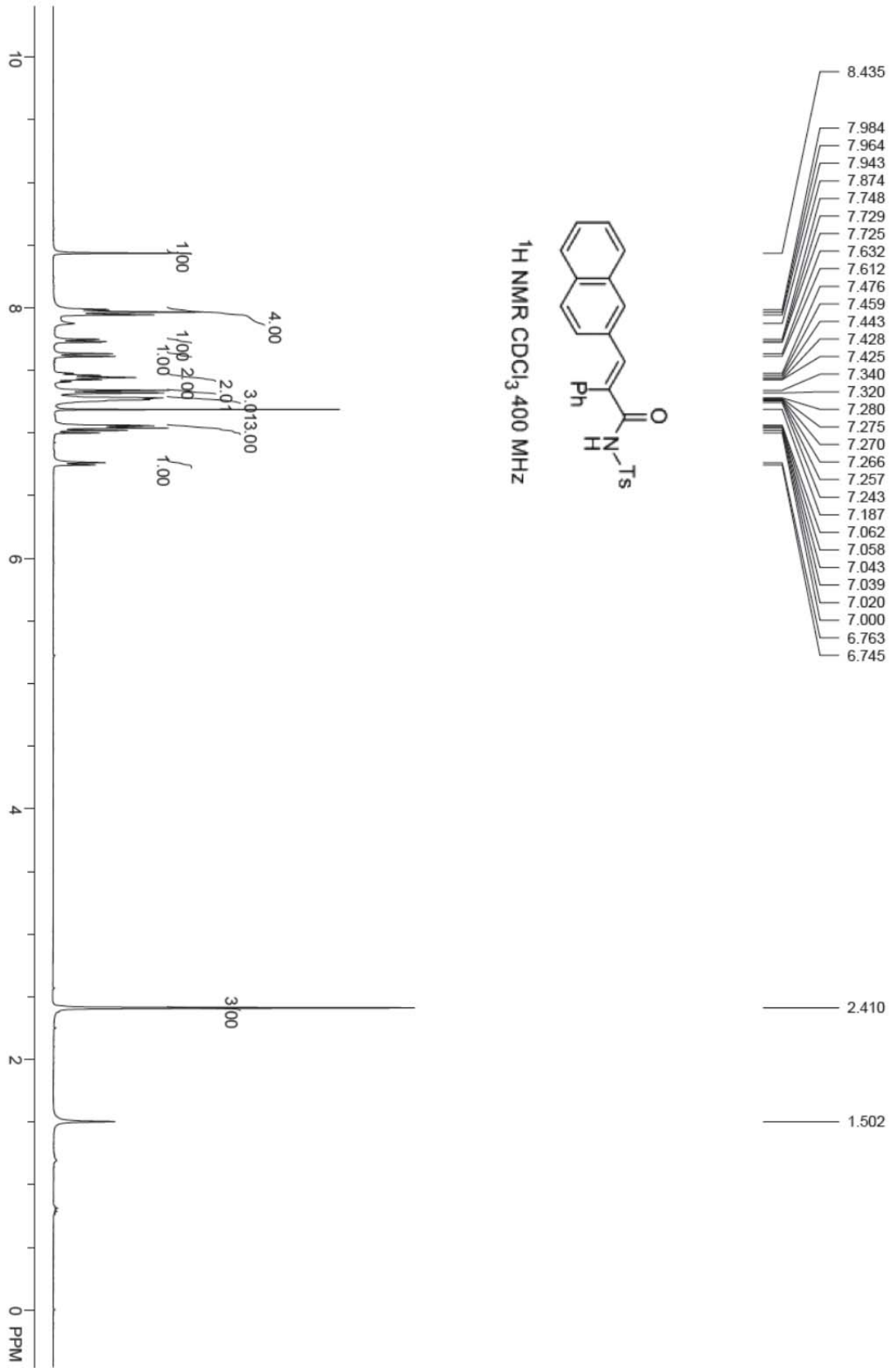


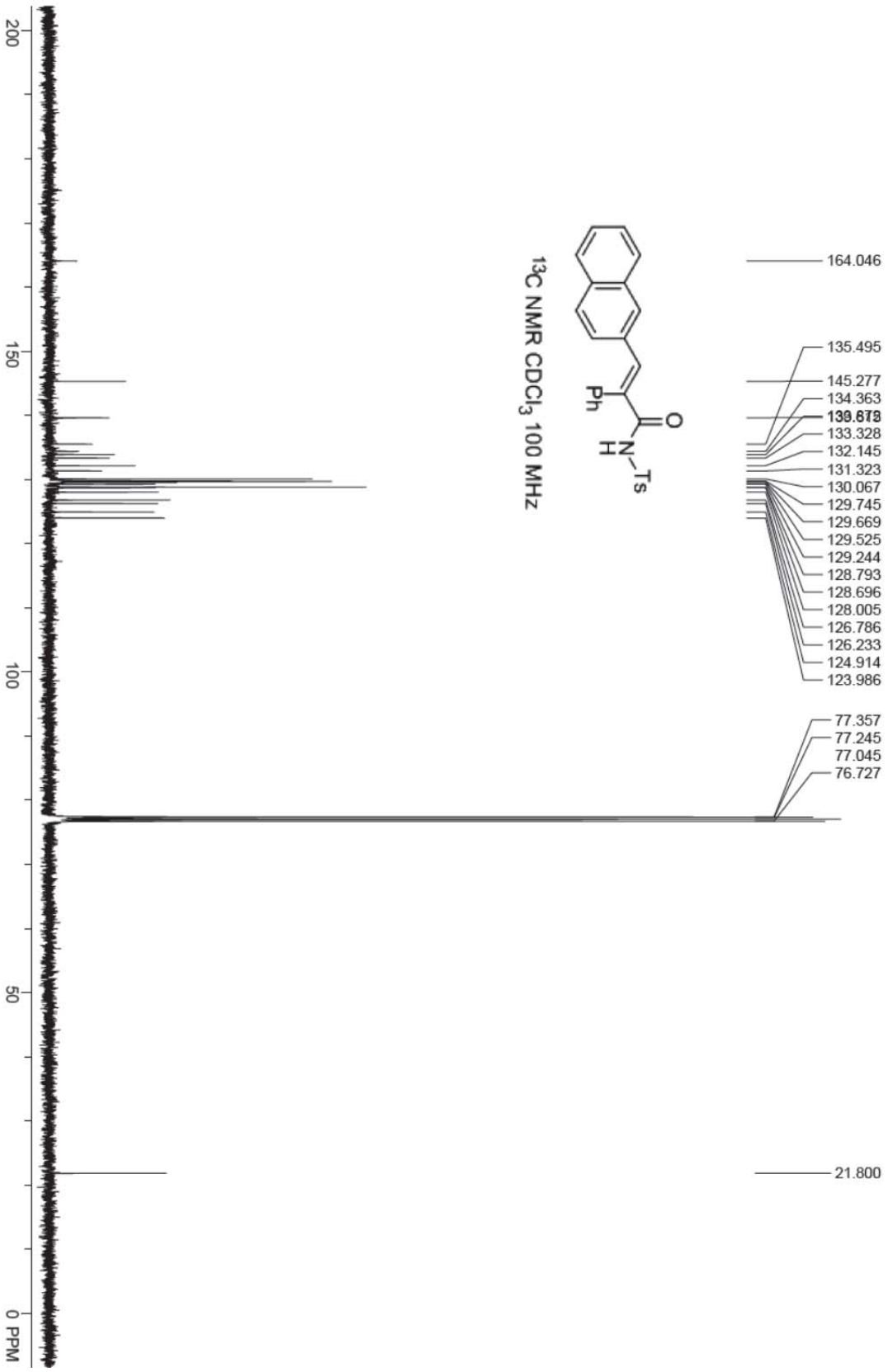

^{13}C NMR CDCl$_3$ 100 MHz
H$_3$CO
O
N
H
Ts
166.789
160.109
144.976
136.763
135.699
133.652
131.073
129.587
128.547
127.279
114.102
77.364
77.255
77.051
76.739
55.342
31.755
28.463
27.434
22.397
21.716
13.984
200
150
100
50
0
PPM

(*E*)-2-(Cyclohex-1-en-1-yl)-3-phenyl-*N*-tosylacrylamide (1n)

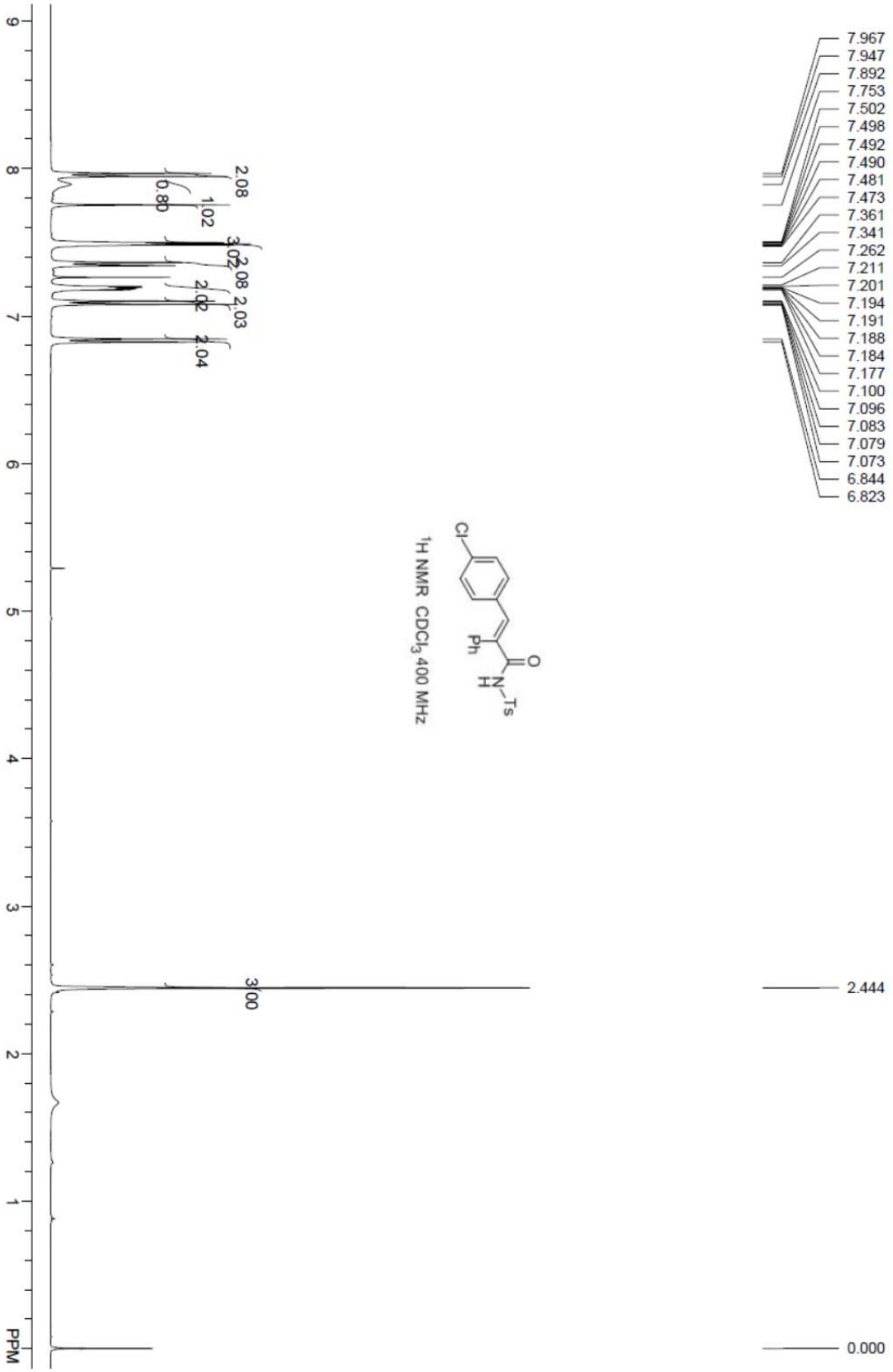

200
150
100
50
0 PPM
^{13}C NMR $CDCl_3$ 100 MHz
Ph
O
N
H
Ts
164.010
145.093
139.009
135.558
134.328
133.912
133.631
132.196
130.274
129.719
129.597
128.659
128.548
77.418
77.105
76.792
28.041
25.530
22.689
21.748
21.423

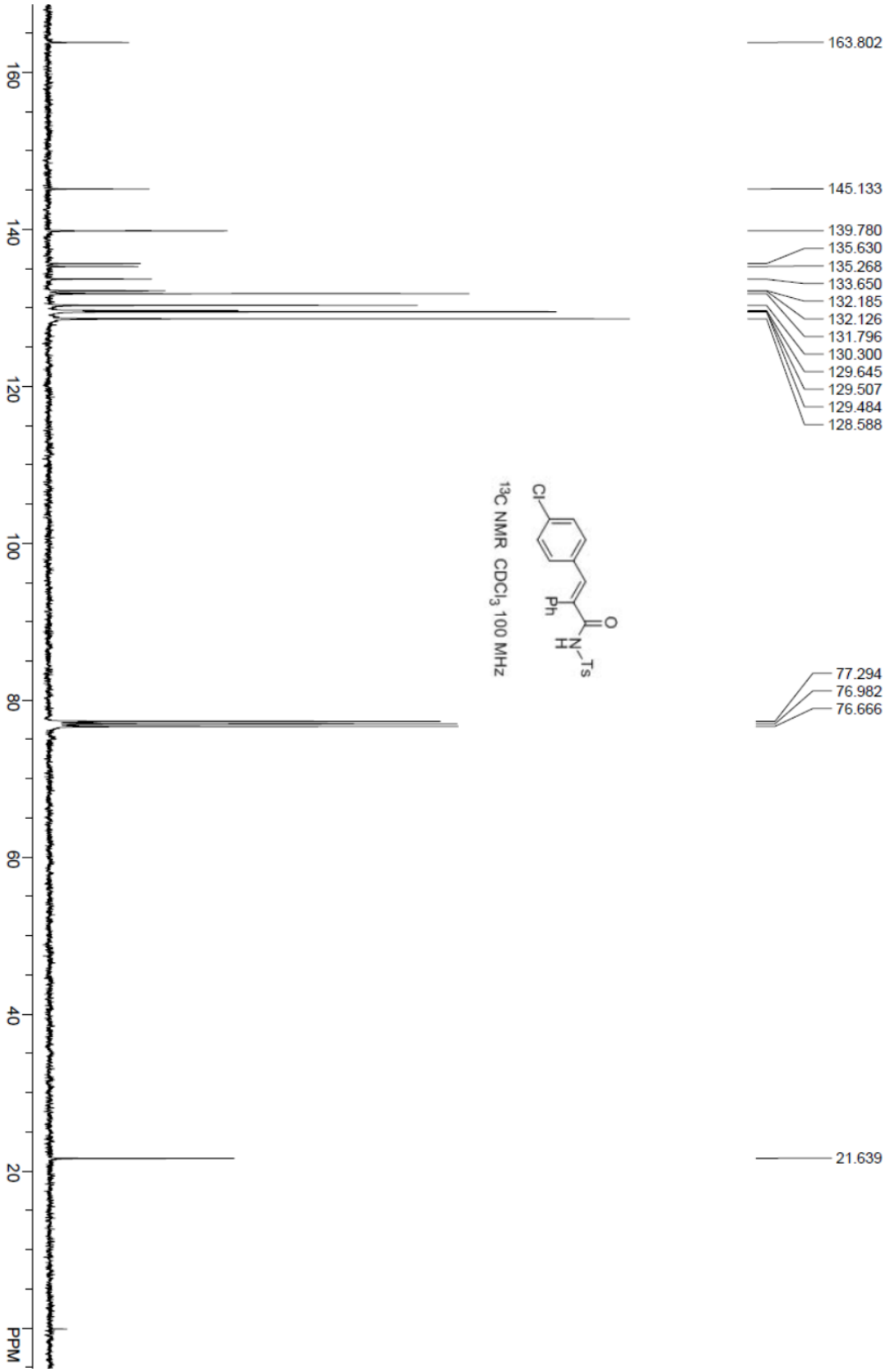
(*E*)-3-(Naphthalen-2-yl)-2-phenyl-*N*-tosylacrylamide (1o)



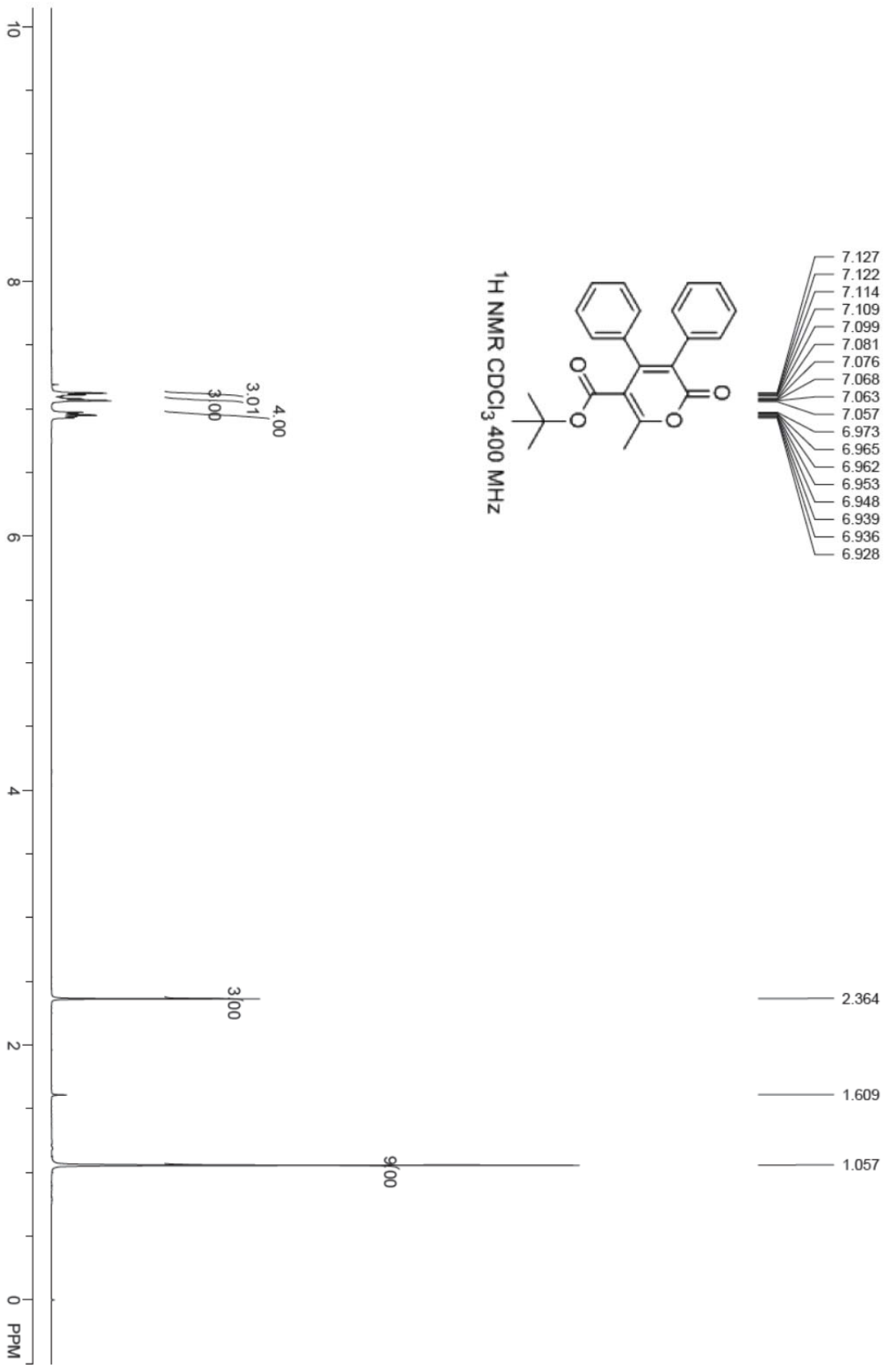

^{13}C NMR CDCl$_3$ 100 MHz
Ph
O
N
H
Ts
164.046
135.495
145.277
134.363
133.328
132.145
131.323
130.067
129.745
129.669
129.525
129.244
128.793
128.696
128.005
126.786
126.233
124.914
123.986
77.357
77.245
77.045
76.727
21.800
200
150
100
50
0 PPM

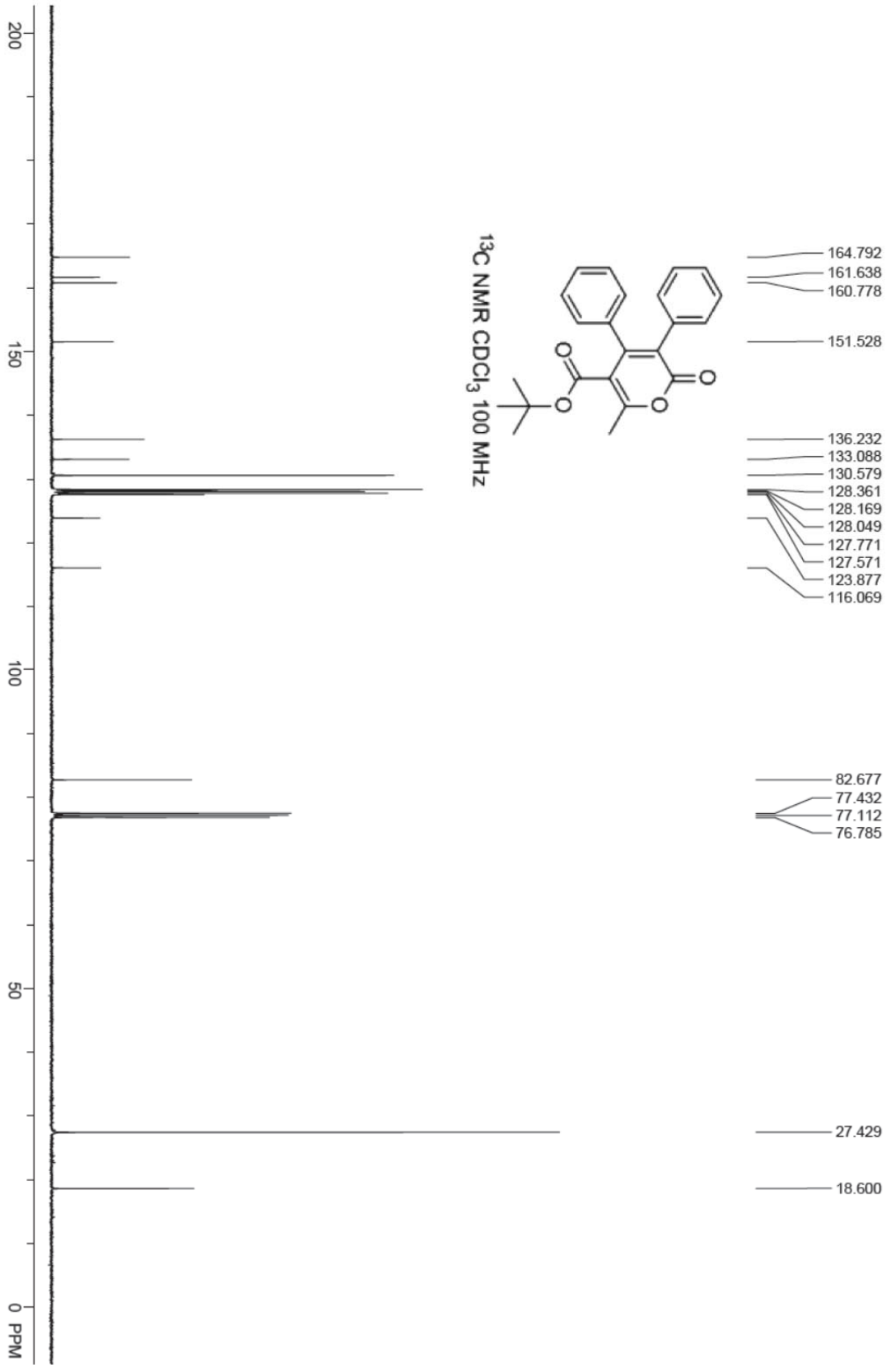
(*E*)-3-(4-Chlorophenyl)-2-phenyl-*N*-tosylacrylamide (1p)



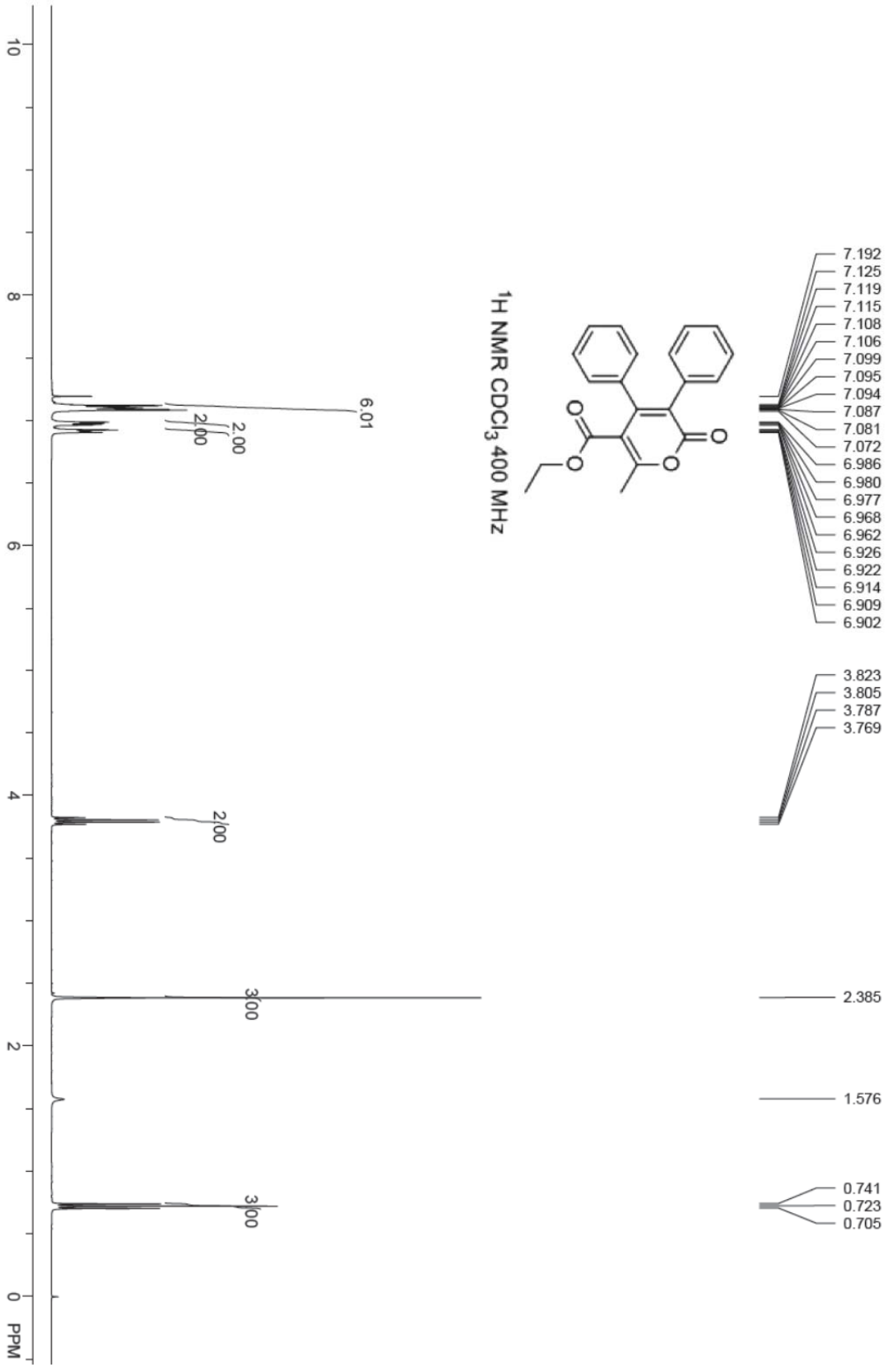

163.802
145.133
139.780
135.630
135.268
133.650
132.185
132.126
131.796
130.300
129.645
129.507
129.484
128.588
77.294
76.982
76.666
21.639
160
140
120
100
80
60
40
20
PPM
^{13}C NMR CDCl$_3$ 100 MHz
Cl
Ph
O
N
H
Ts

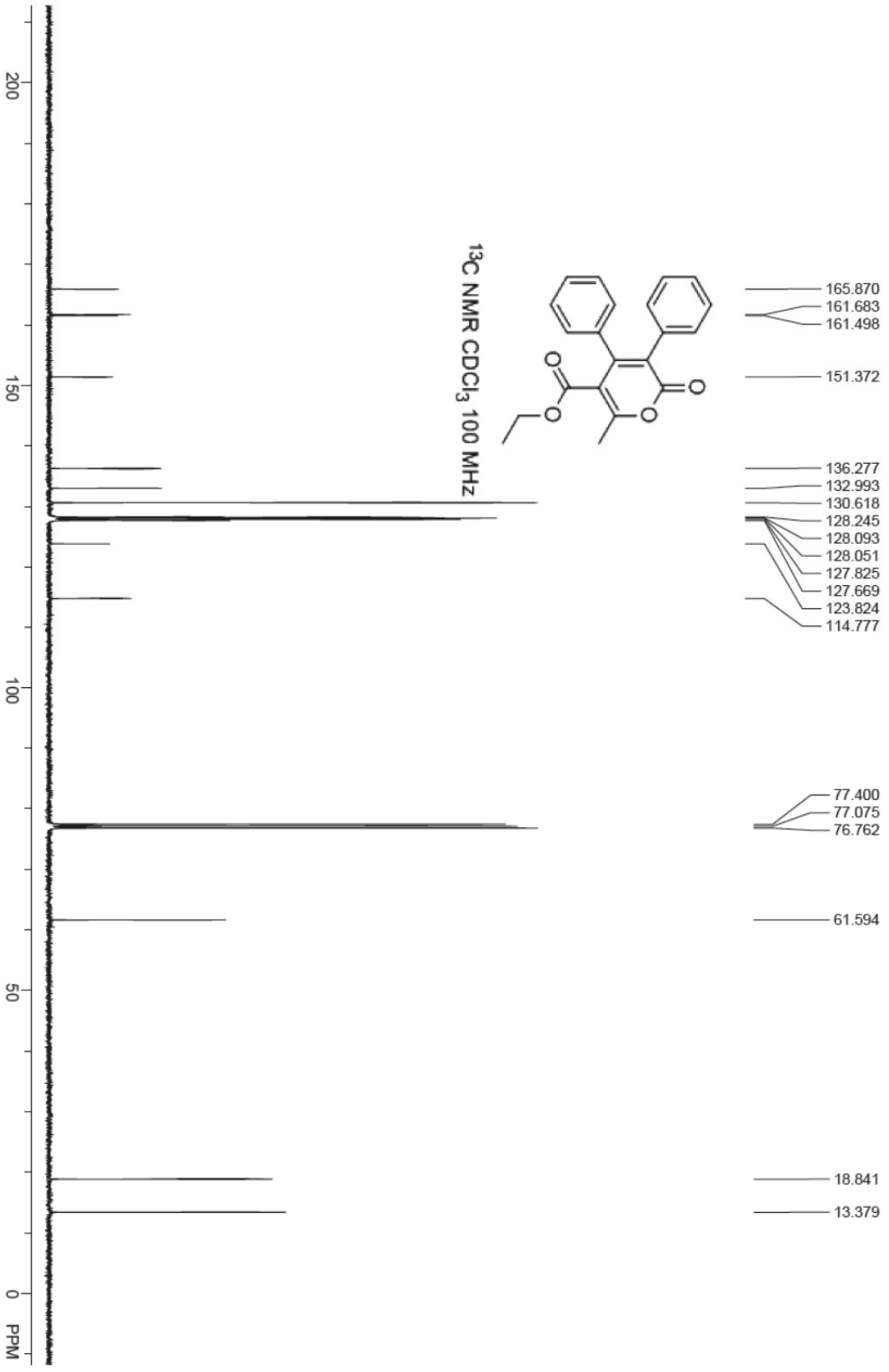
Tert-butyl 6-methyl-2-oxo-3,4-diphenyl-*2H*-pyran-5-carboxylate (3aa)



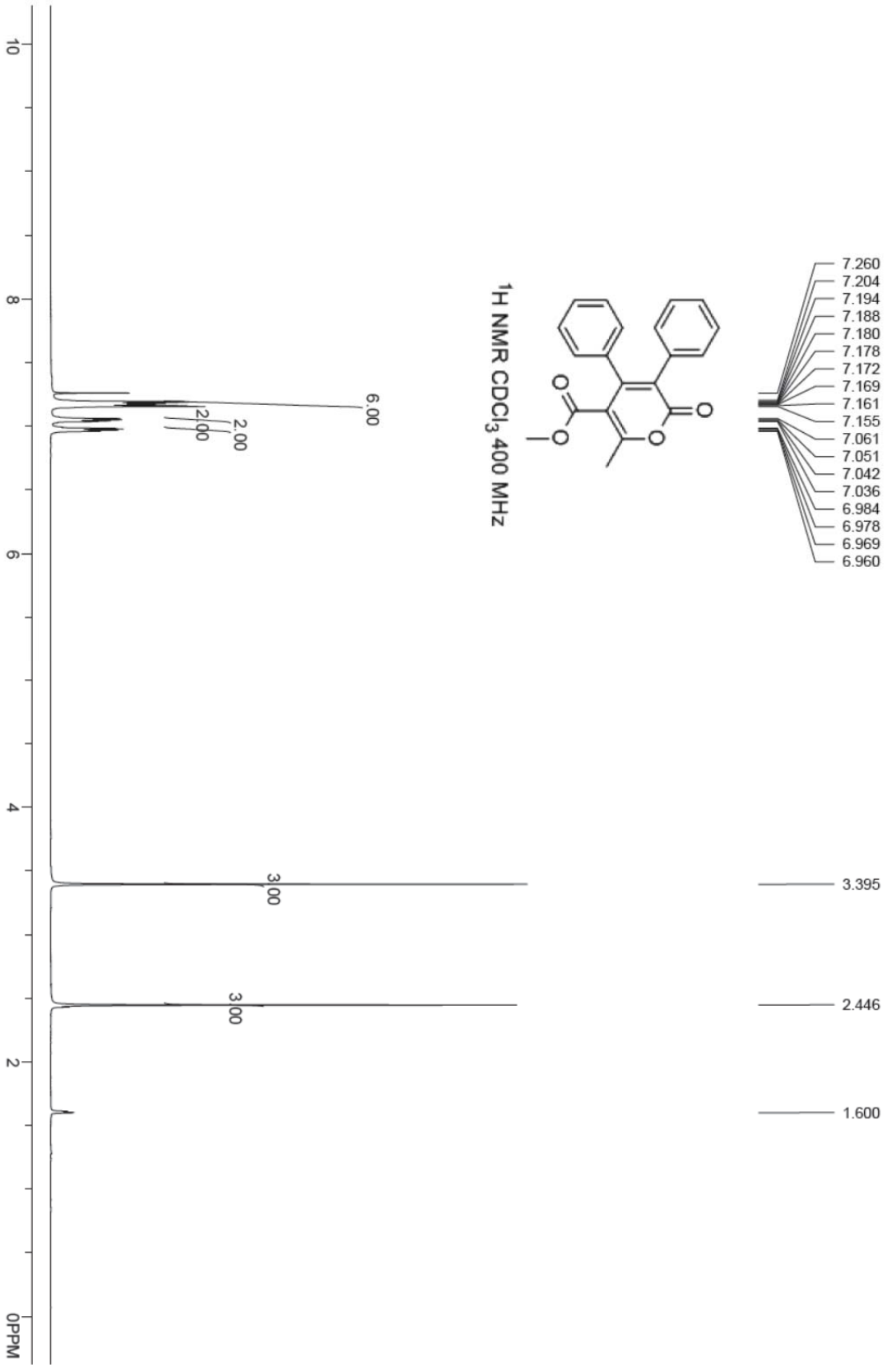

^{13}C NMR CDCl$_3$ 100 MHz
164.792
161.638
160.778
151.528
136.232
133.088
130.579
128.361
128.169
128.049
127.771
127.571
123.877
116.069
82.677
77.432
77.112
76.785
27.429
18.600
200
150
100
50
0 PPM

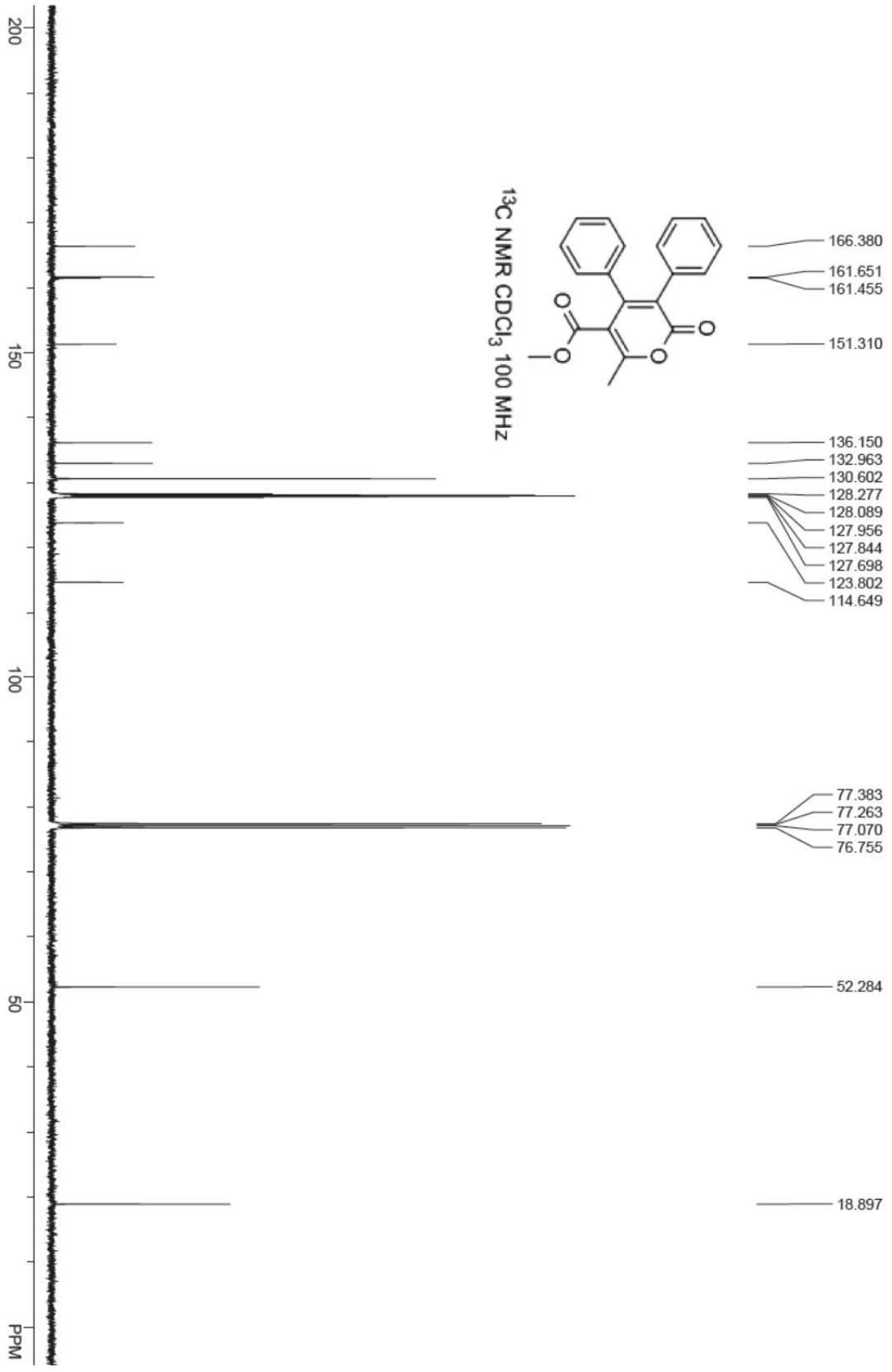
Ethyl 6-methyl-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3ab)



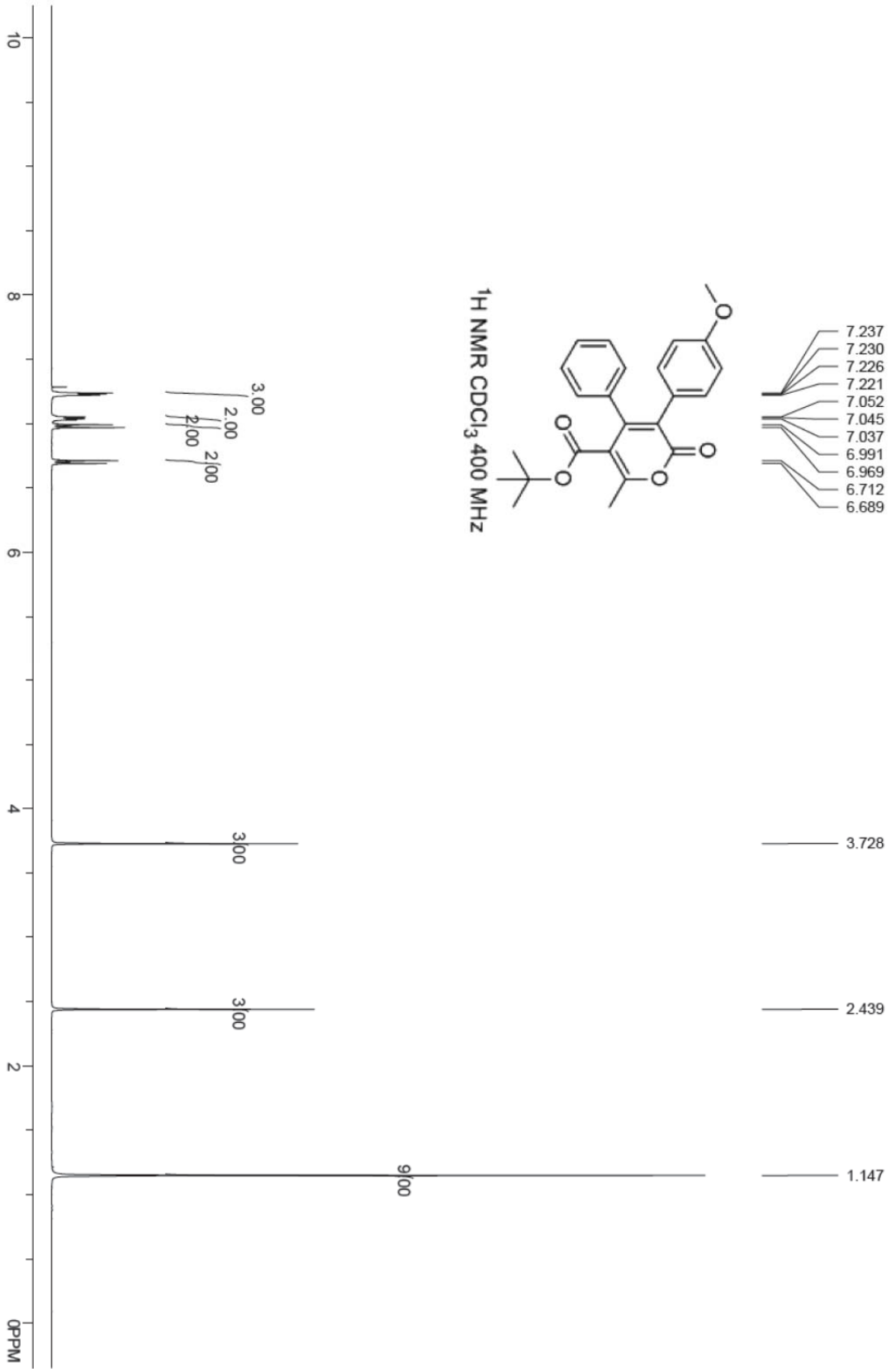

^{13}C NMR CDCl$_3$ 100 MHz
165.870
161.683
161.498
151.372
136.277
132.993
130.618
128.245
128.093
128.051
127.825
127.669
123.824
114.777
77.400
77.075
76.762
61.594
18.841
13.379
200
150
100
50
0
PPM

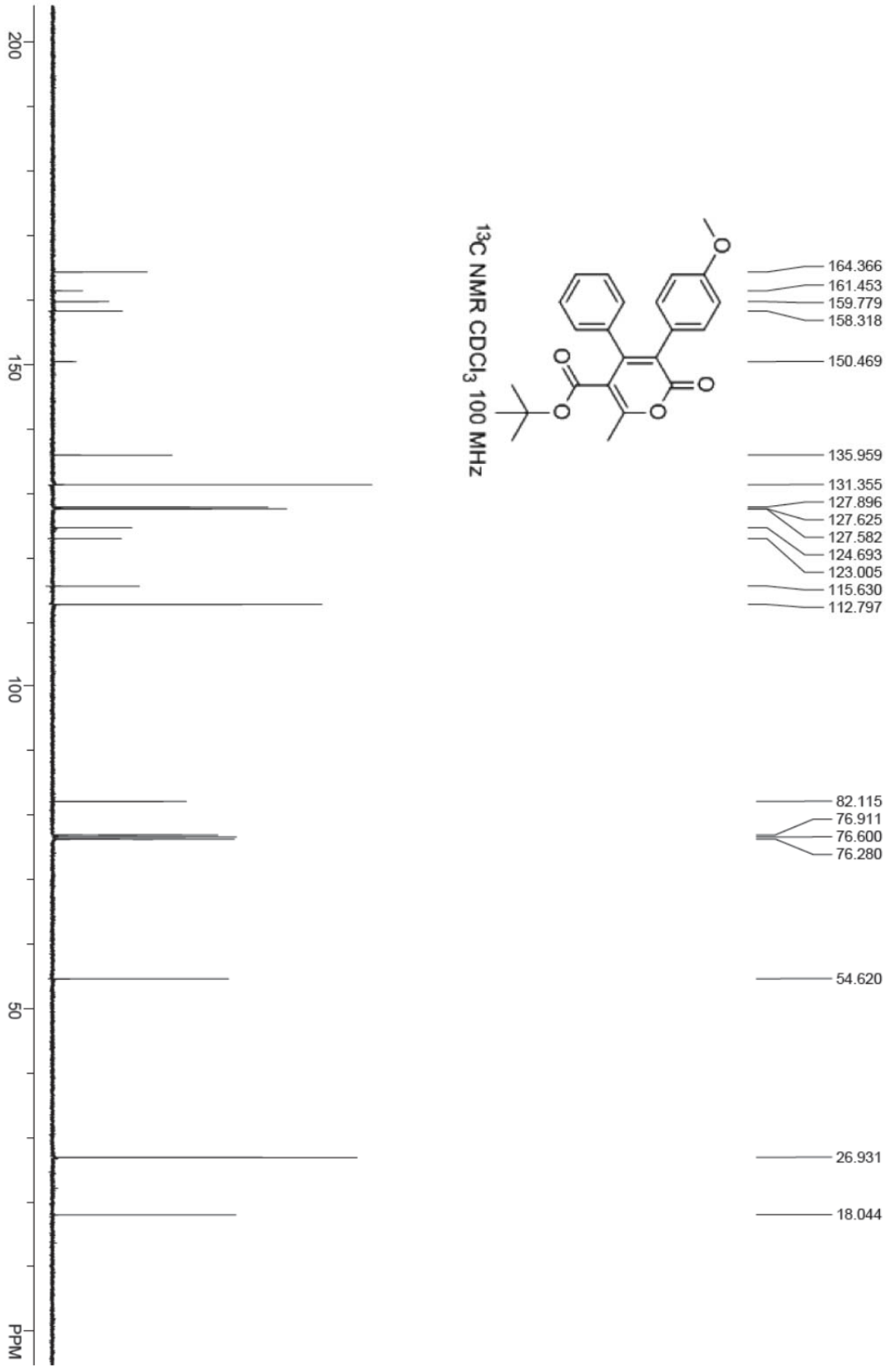
Methyl 6-methyl-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3ac)



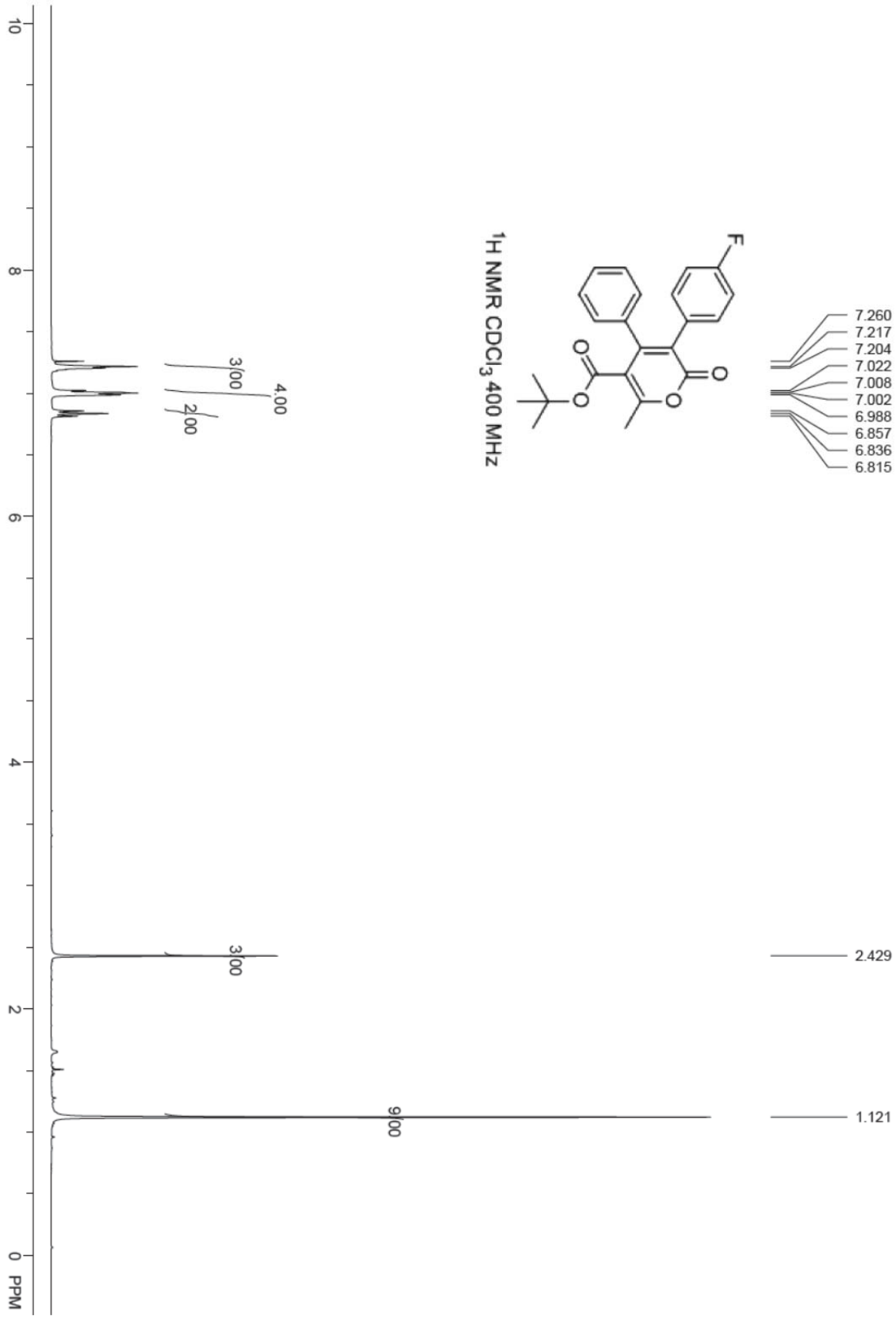

^{13}C NMR CDCl$_3$ 100 MHz
166.380
161.651
161.455
151.310
136.150
132.963
130.602
128.277
128.089
127.956
127.844
127.698
123.802
114.649
77.383
77.263
77.070
76.755
52.284
18.897
200
150
100
50
PPM

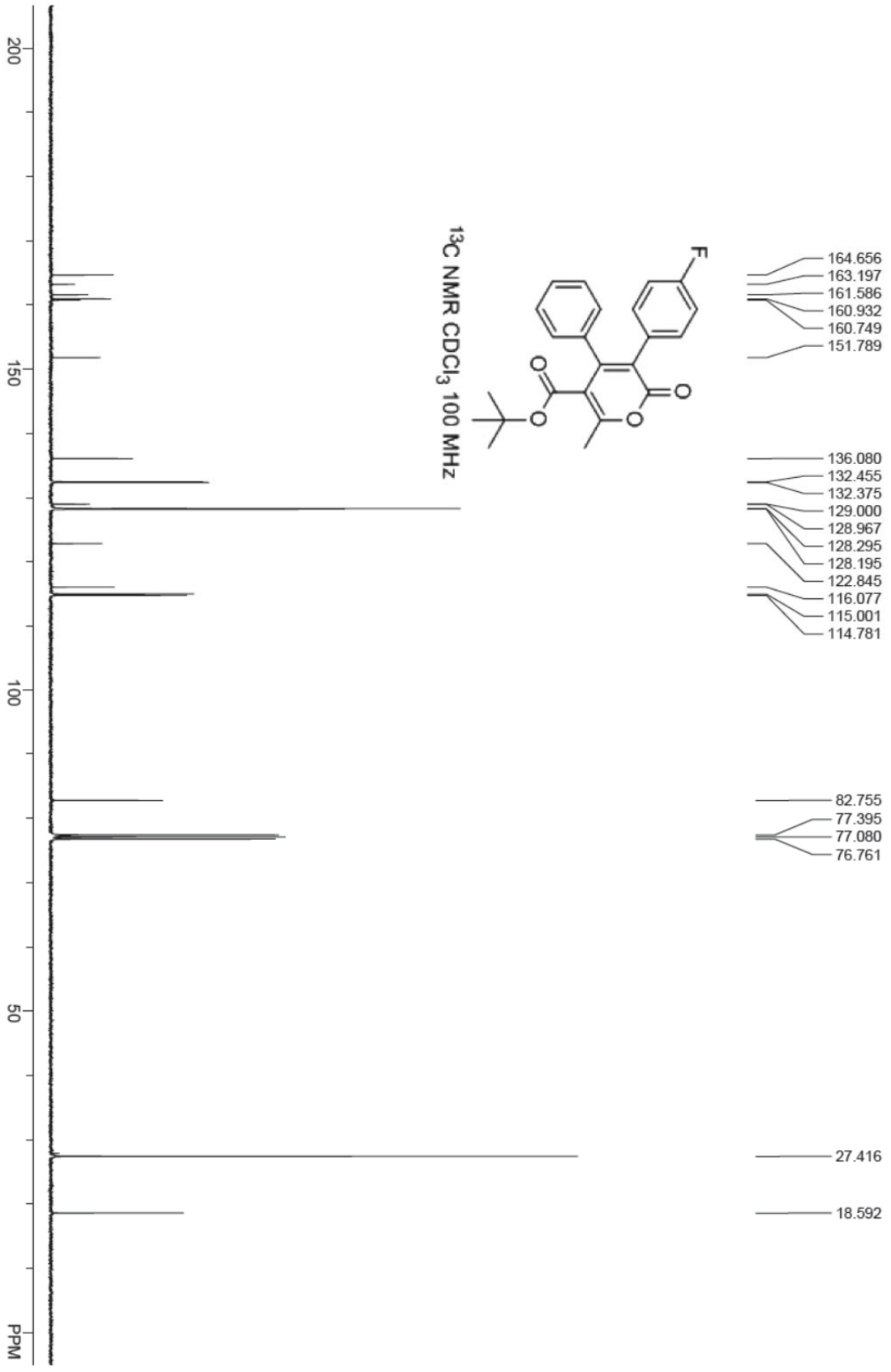
Tert-butyl 3-(4-methoxyphenyl)-6-methyl-2-oxo-4-phenyl-2H-pyran-5-carboxylate (3ba)



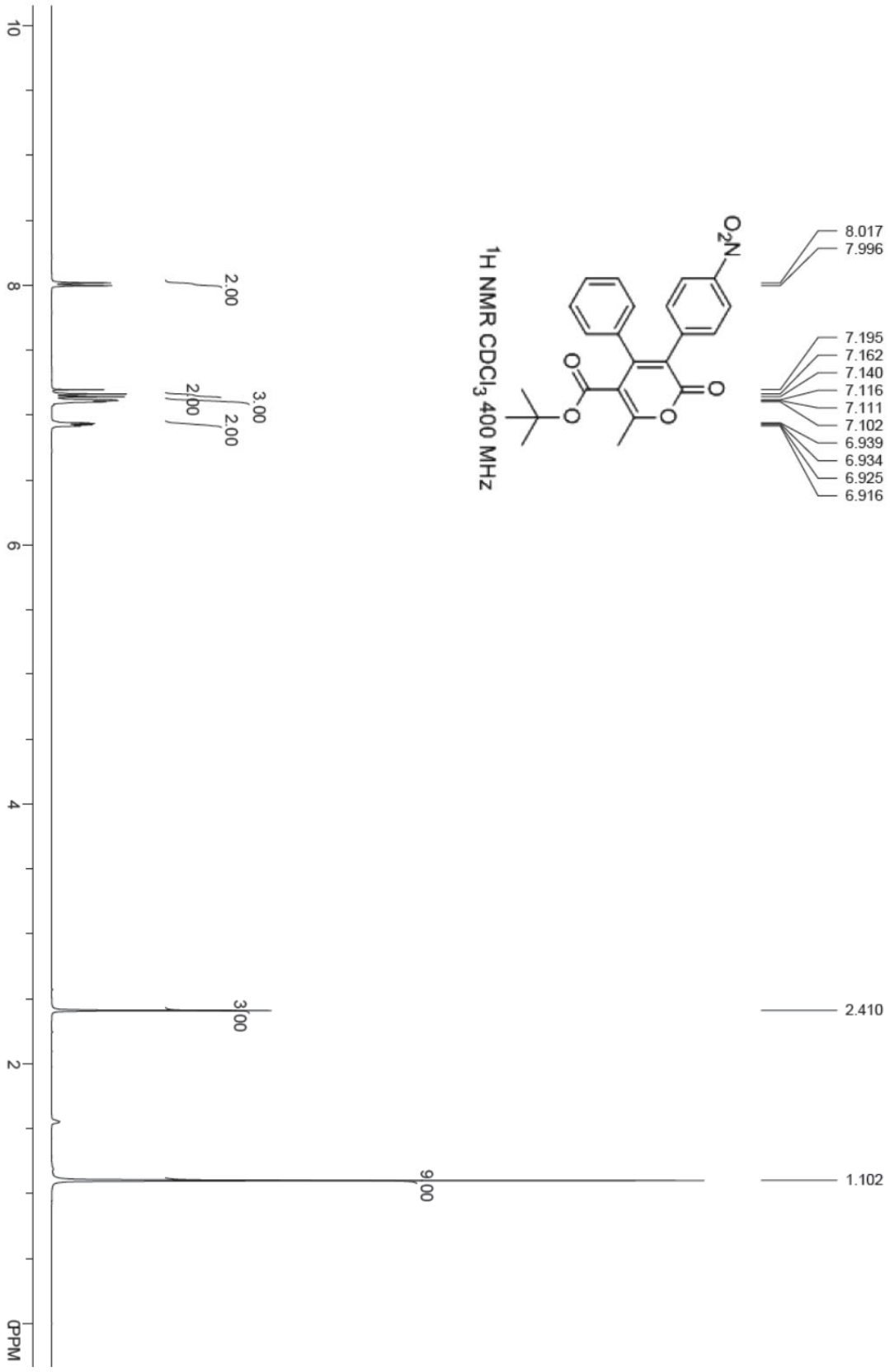

^{13}C NMR CDCl$_3$ 100 MHz
164.366
161.453
159.779
158.318
150.469
135.959
131.355
127.896
127.625
127.582
124.693
123.005
115.630
112.797
82.115
76.911
76.600
76.280
54.620
26.931
18.044
200
150
100
50
PPM

Tert-butyl 3-(4-fluorophenyl)-6-methyl-2-oxo-4-phenyl-2H-pyran-5-carboxylate (3ca)



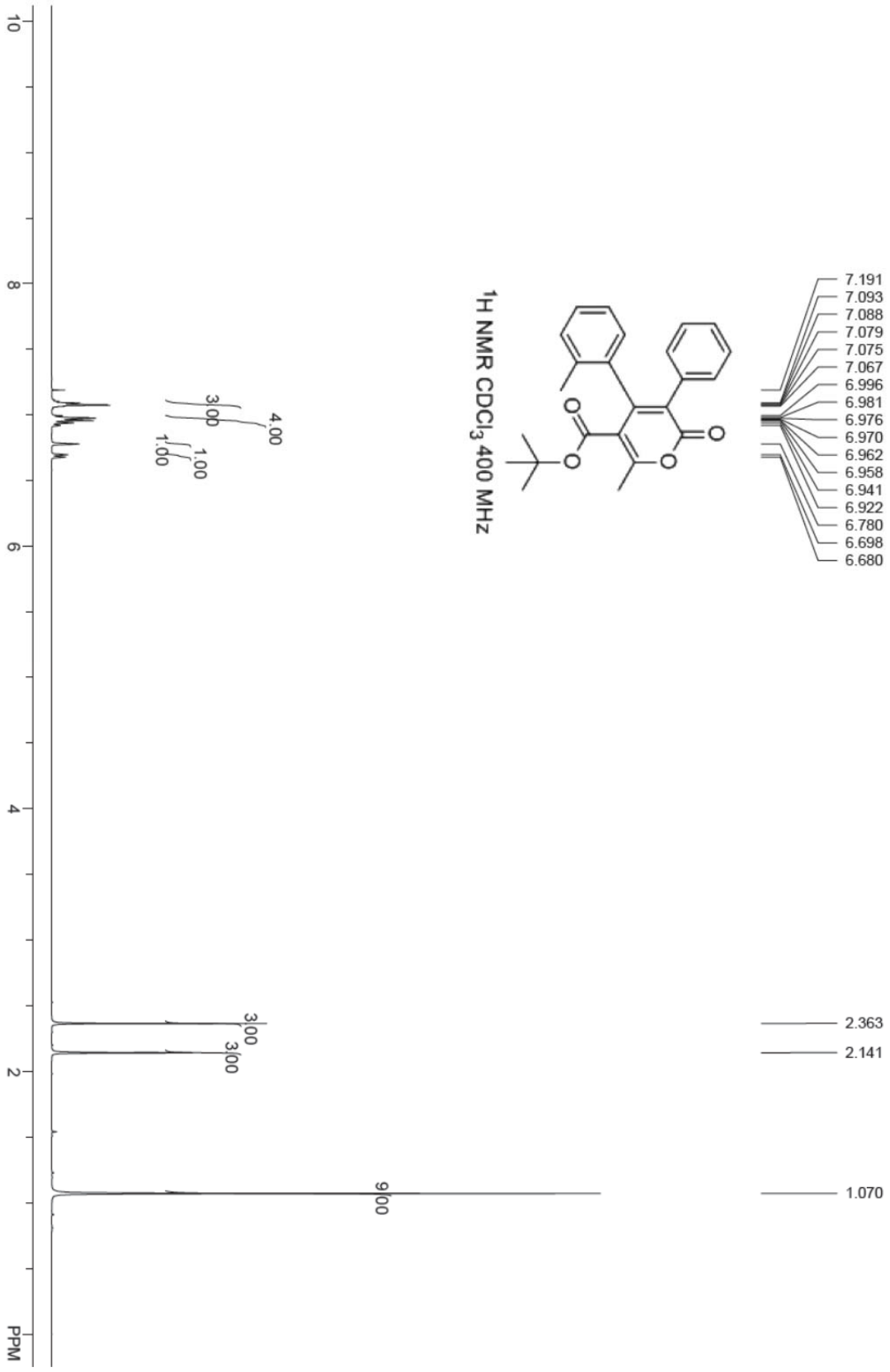

^{13}C NMR CDCl$_3$ 100 MHz
F
O
O
O
O
164.656
163.197
161.586
160.932
160.749
151.789
136.080
132.455
132.375
129.000
128.967
128.295
128.195
122.845
116.077
115.001
114.781
82.755
77.395
77.080
76.761
27.416
18.592
200
150
100
50
PPM

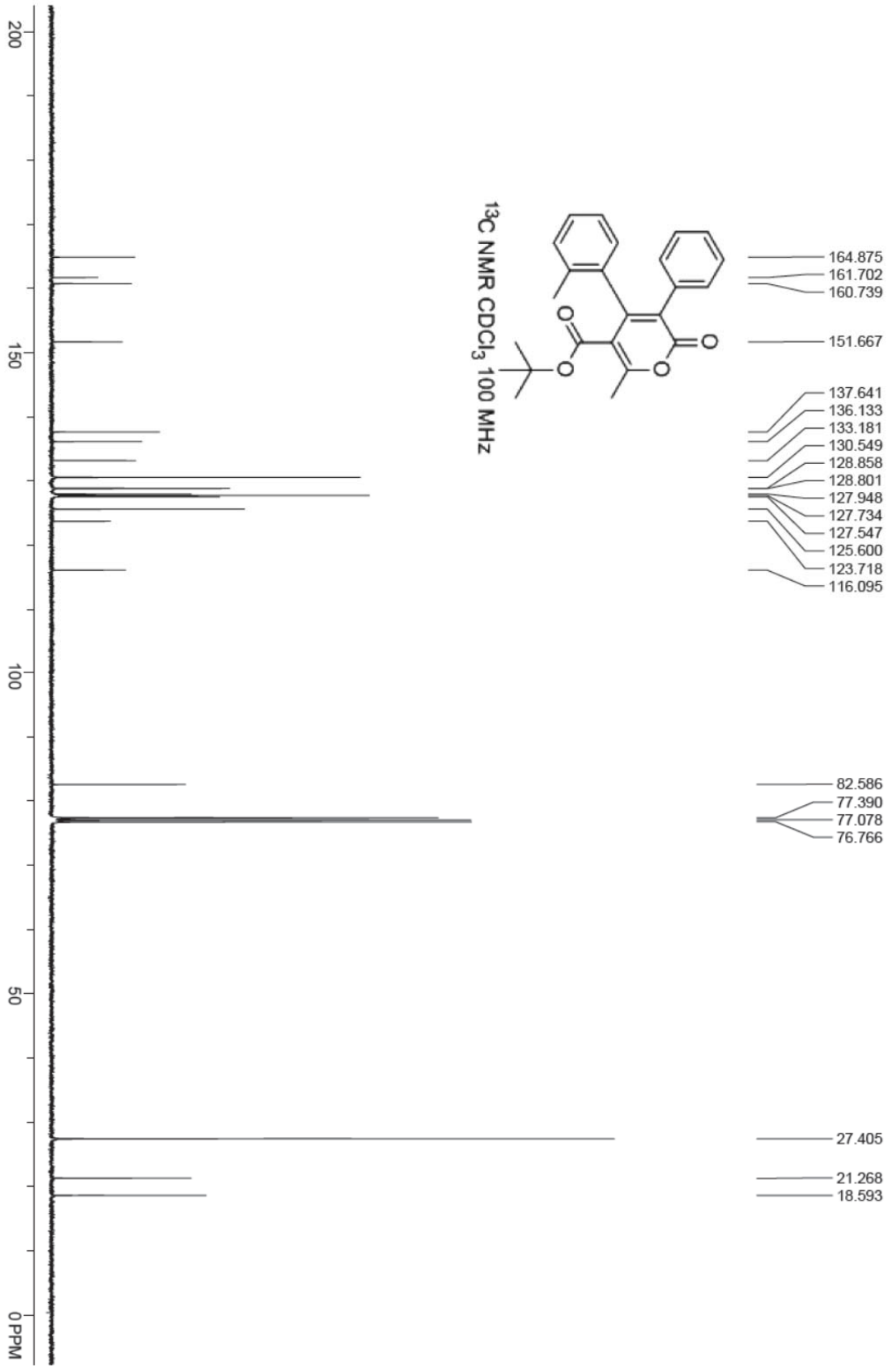
Tert-butyl 6-methyl-3-(4-nitrophenyl)-2-oxo-4-phenyl-2H-pyran-5-carboxylate (3da)



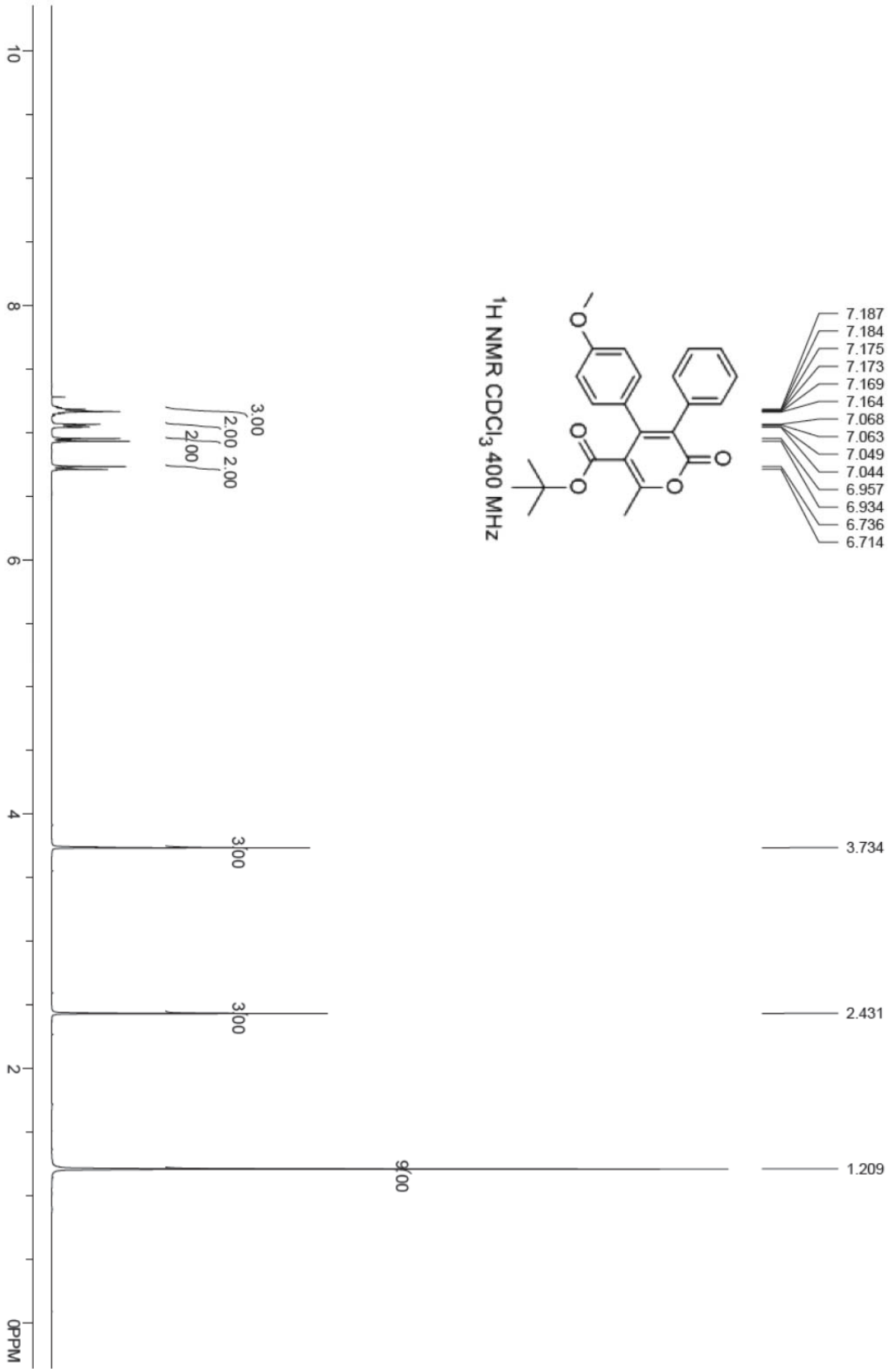

^{13}C NMR CDCl$_3$ 100 MHz
O$_2$N
O
O
O
O
164.130
162.239
160.874
149.102
147.307
143.080
132.183
130.381
129.579
128.268
128.186
124.668
123.233
114.767
83.286
77.397
77.076
76.758
27.597
18.940
200
150
100
50
0 PPM

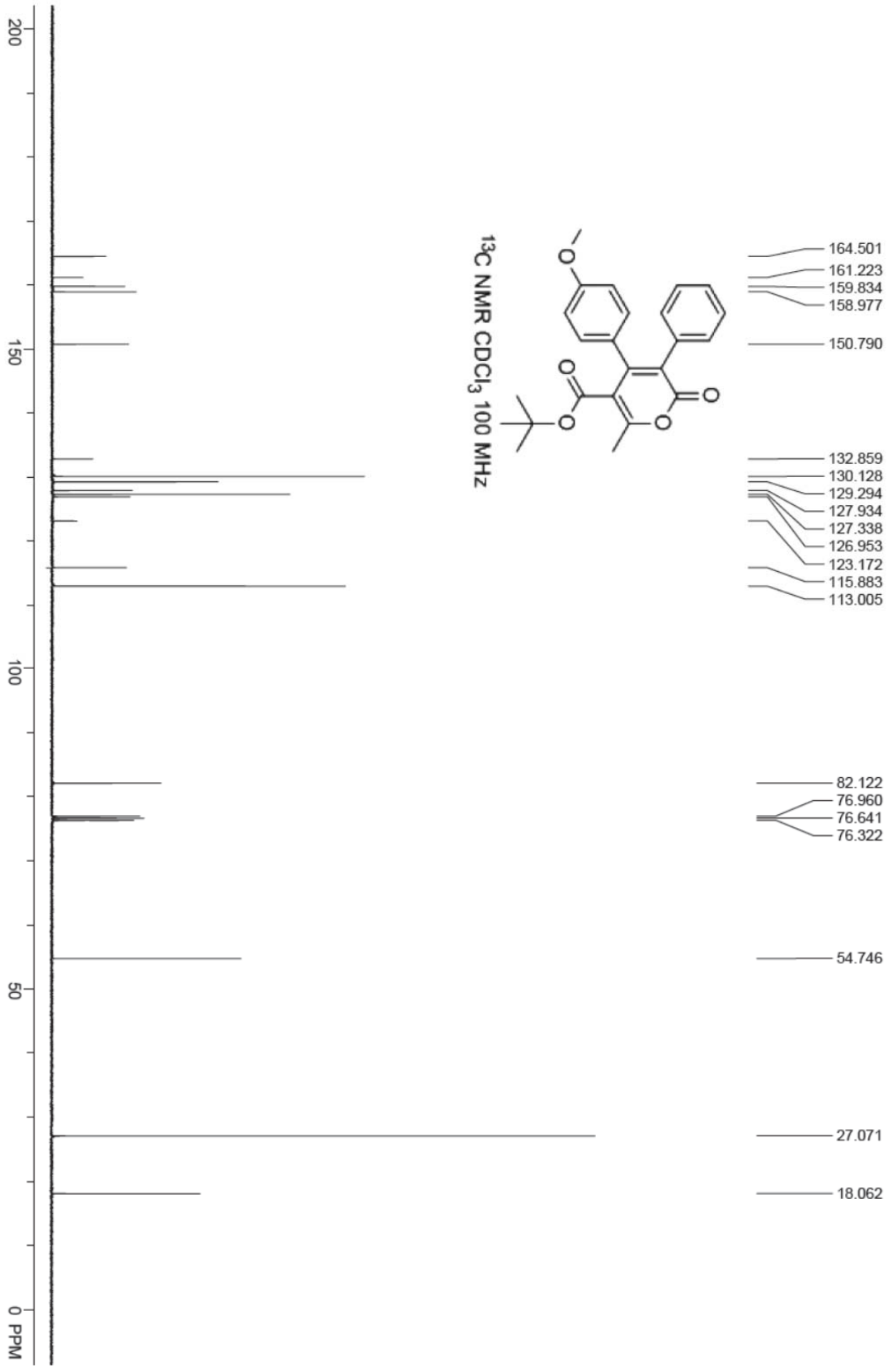
Tert-butyl 6-methyl-2-oxo-3-phenyl-4-(o-tolyl)-2H-pyran-5-carboxylate (3ea)



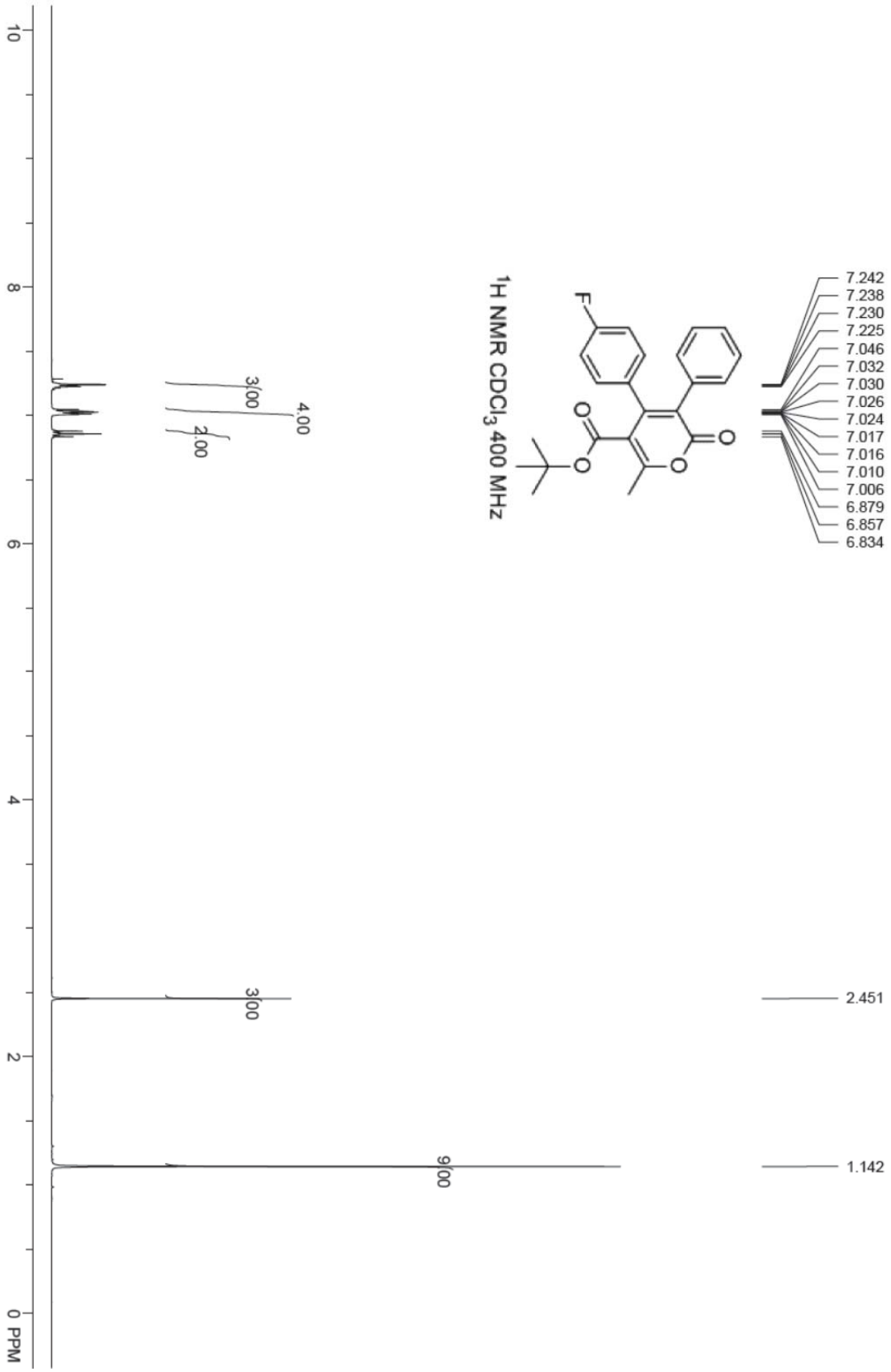

^{13}C NMR CDCl$_3$ 100 MHz
164.875
161.702
160.739
151.667
137.641
136.133
133.181
130.549
128.858
128.801
127.948
127.734
127.547
125.600
123.718
116.095
82.586
77.390
77.078
76.766
27.405
21.268
18.593
200
150
100
50
0 PPM

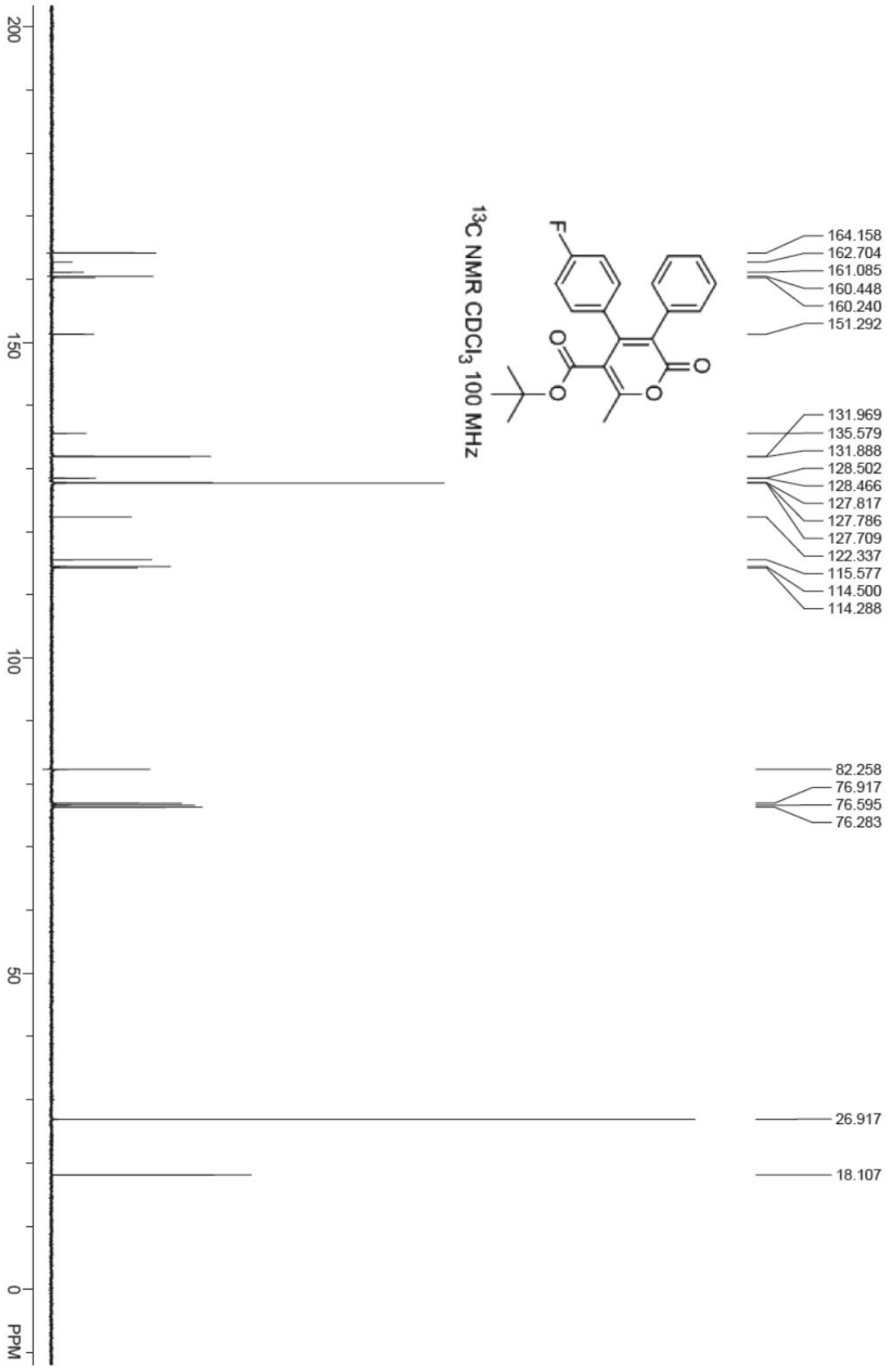
Tert-butyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3-phenyl-2H-pyran-5-carboxylate (3fa)



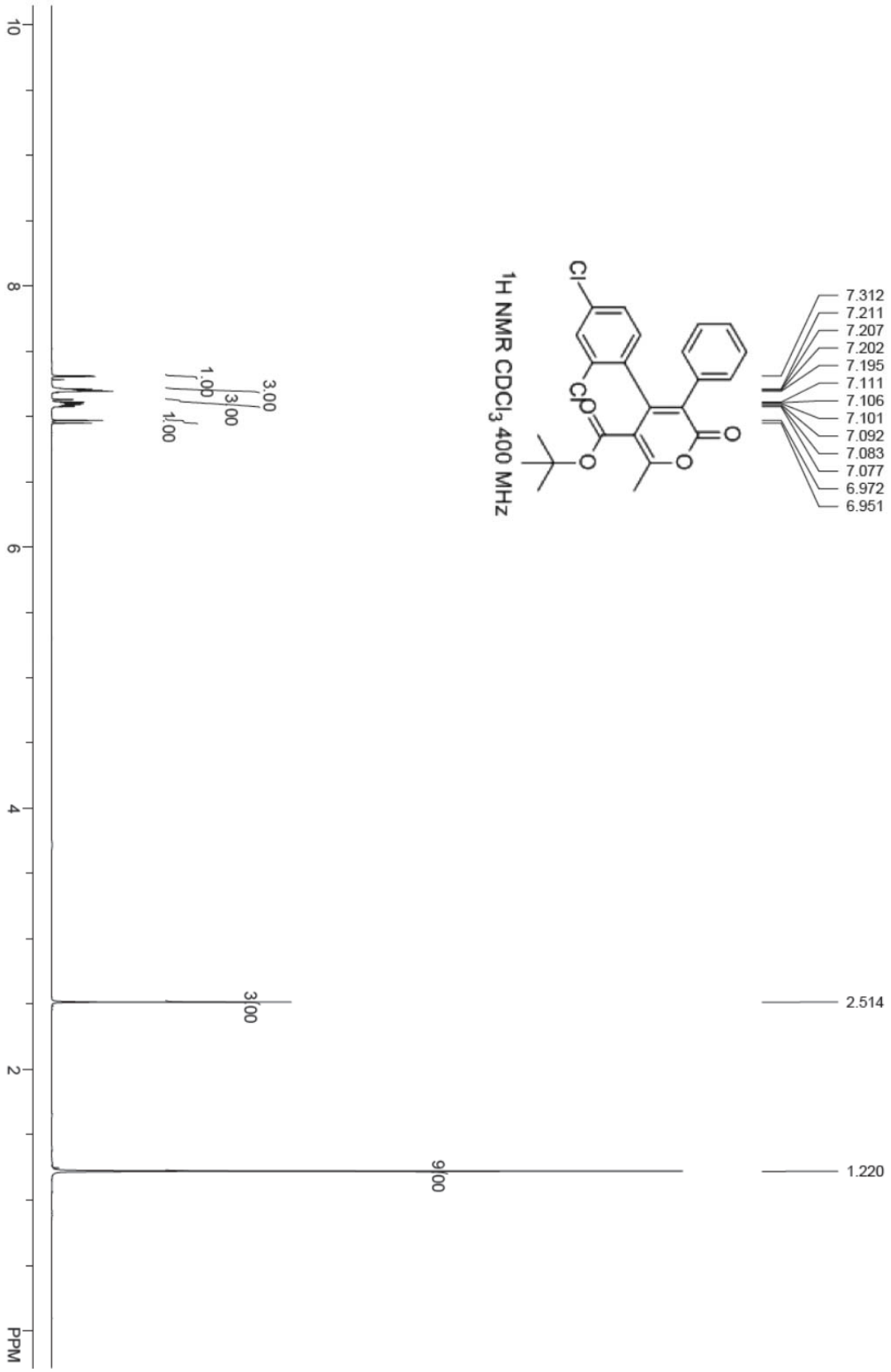

^{13}C NMR CDCl$_3$ 100 MHz
164.501
161.223
159.834
158.977
150.790
132.859
130.128
129.294
127.934
127.338
126.953
123.172
115.883
113.005
82.122
76.960
76.641
76.322
54.746
27.071
18.062
200
150
100
50
0 PPM

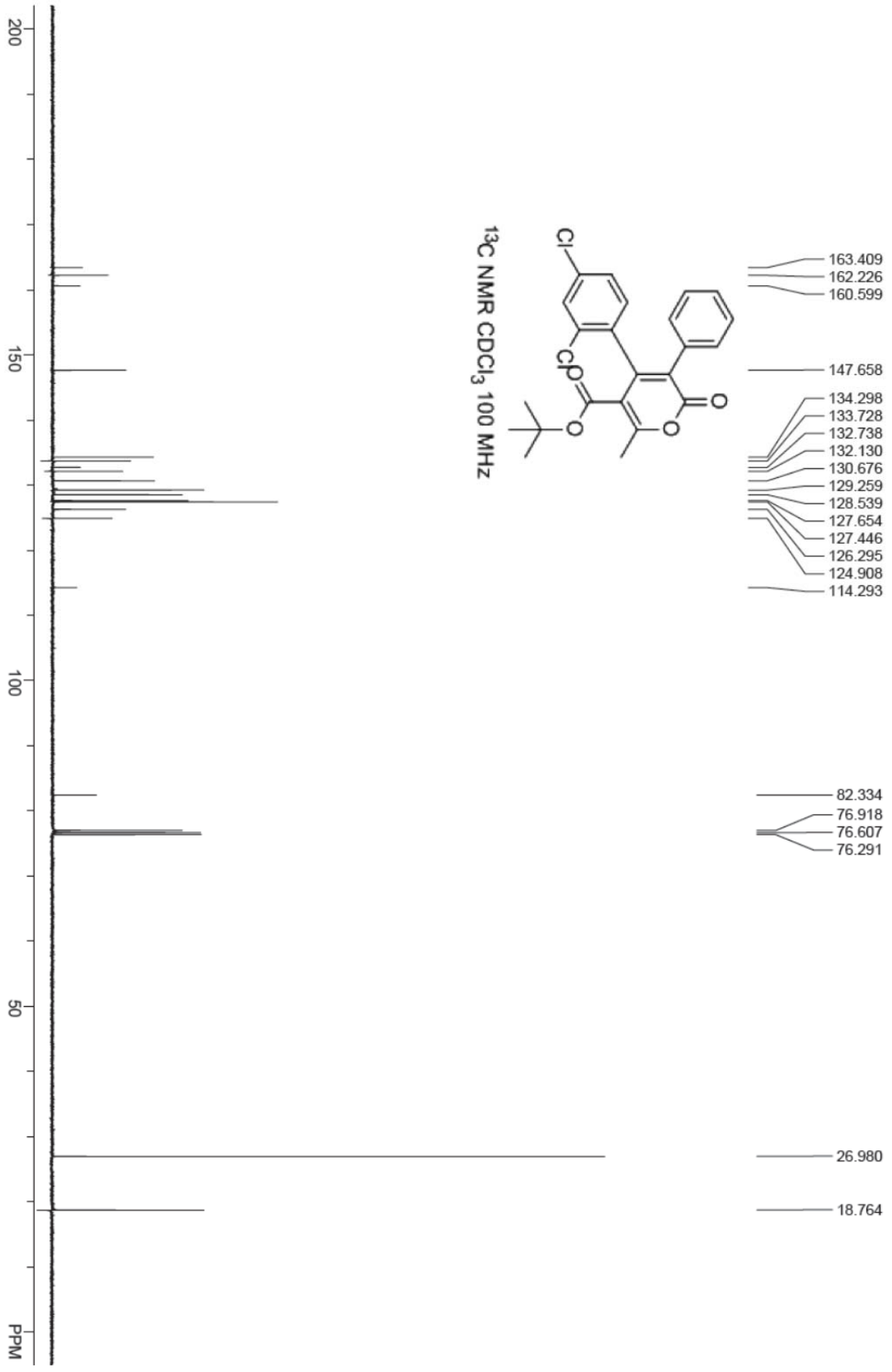
Tert-butyl 4-(4-fluorophenyl)-6-methyl-2-oxo-3-phenyl-2H-pyran-5-carboxylate (3ga)



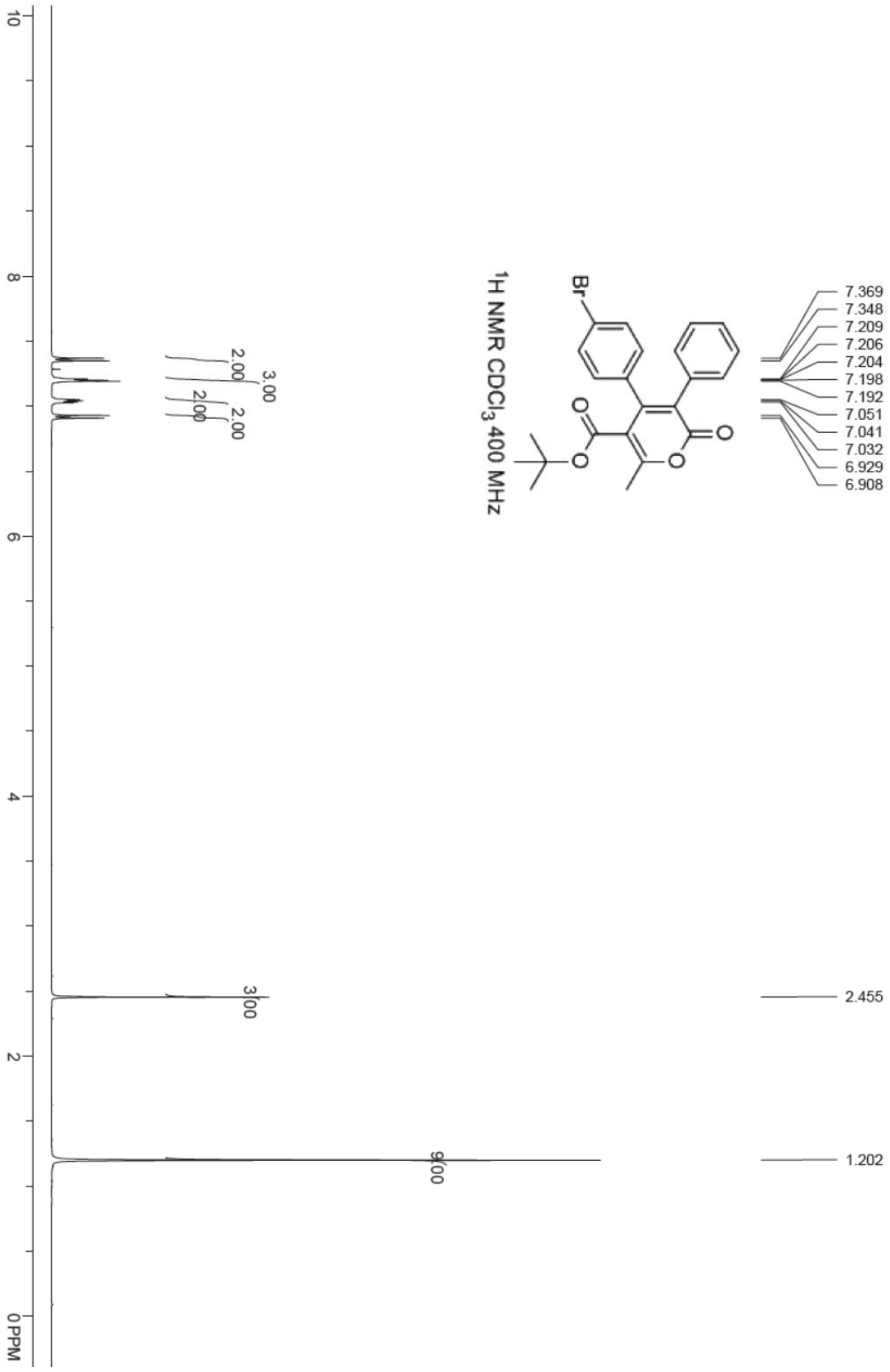

^{13}C NMR CDCl$_3$ 100 MHz
F
O
O
O
O
164.158
162.704
161.085
160.448
160.240
151.292
131.969
135.579
131.888
128.502
128.466
127.817
127.786
127.709
122.337
115.577
114.500
114.288
82.258
76.917
76.595
76.283
26.917
18.107
200
150
100
50
0
PPM

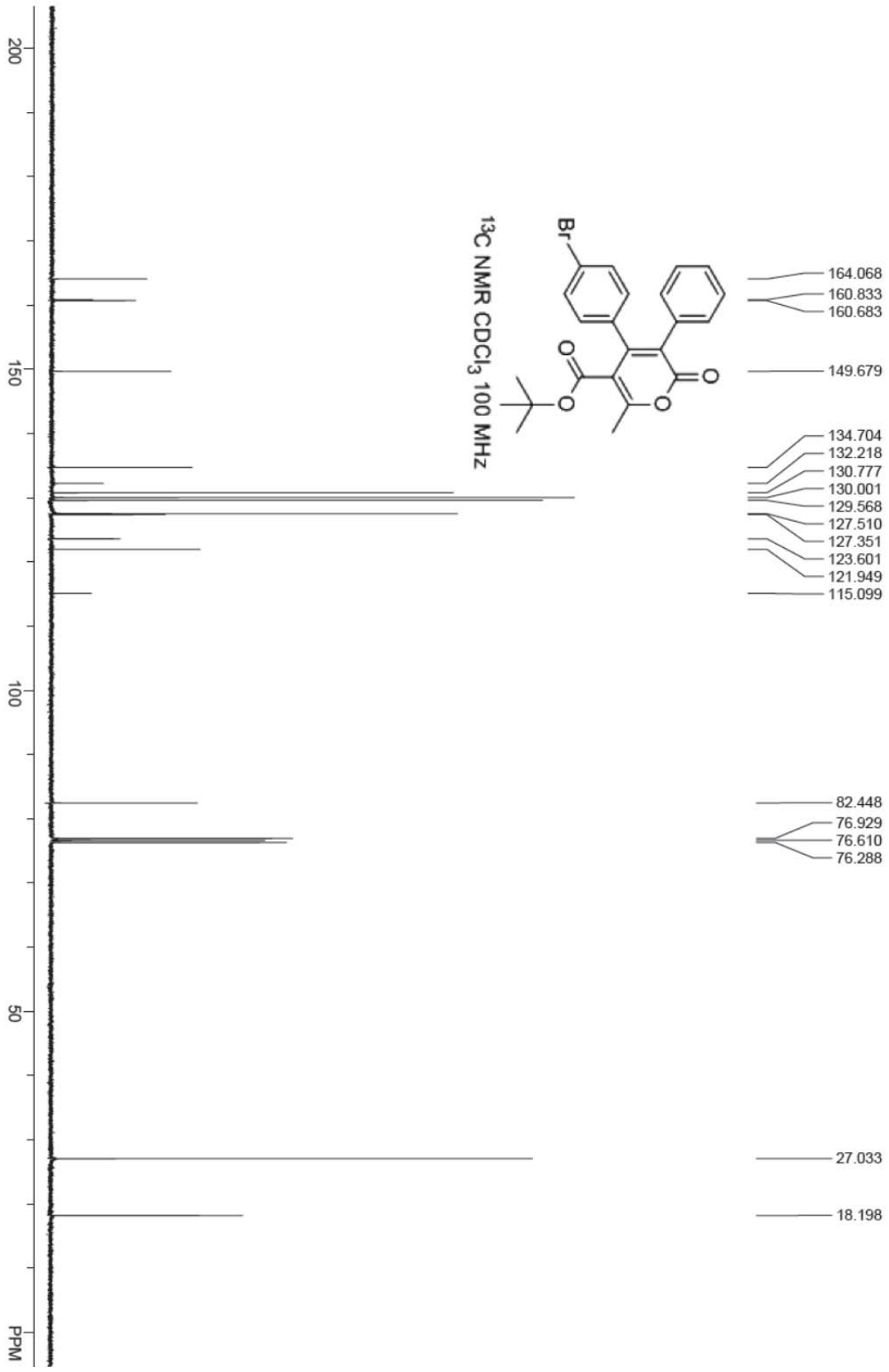
Tert-butyl 4-(2,4-dichlorophenyl)-6-methyl-2-oxo-3-phenyl-2H-pyran-5-carboxylate (3ha)



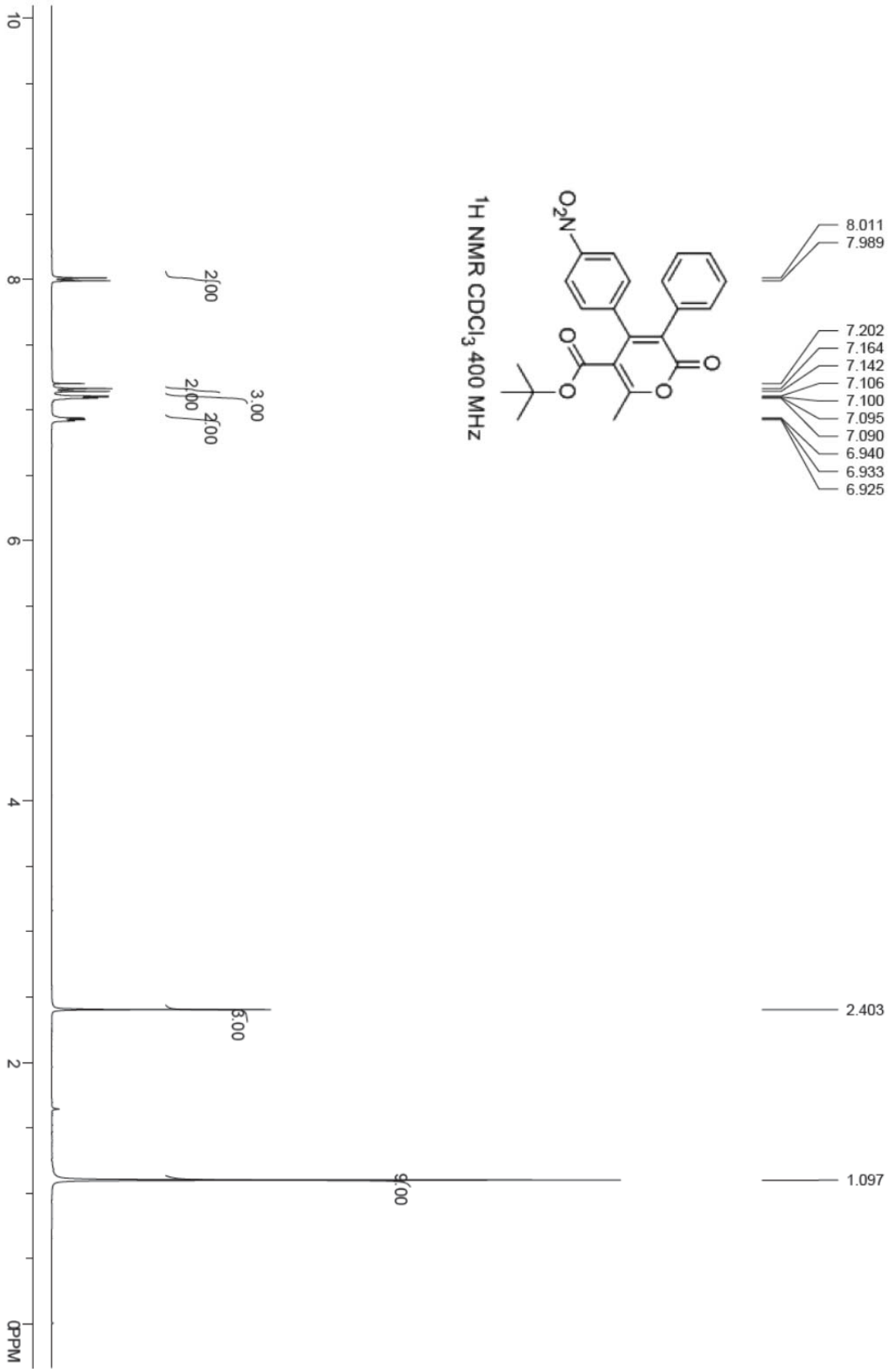

^{13}C NMR CDCl$_3$ 100 MHz
Cl
O
O
O
O
163.409
162.226
160.599
147.658
134.298
133.728
132.738
132.130
130.676
129.259
128.539
127.654
127.446
126.295
124.908
114.293
82.334
76.918
76.607
76.291
26.980
18.764
200
150
100
50
PPM

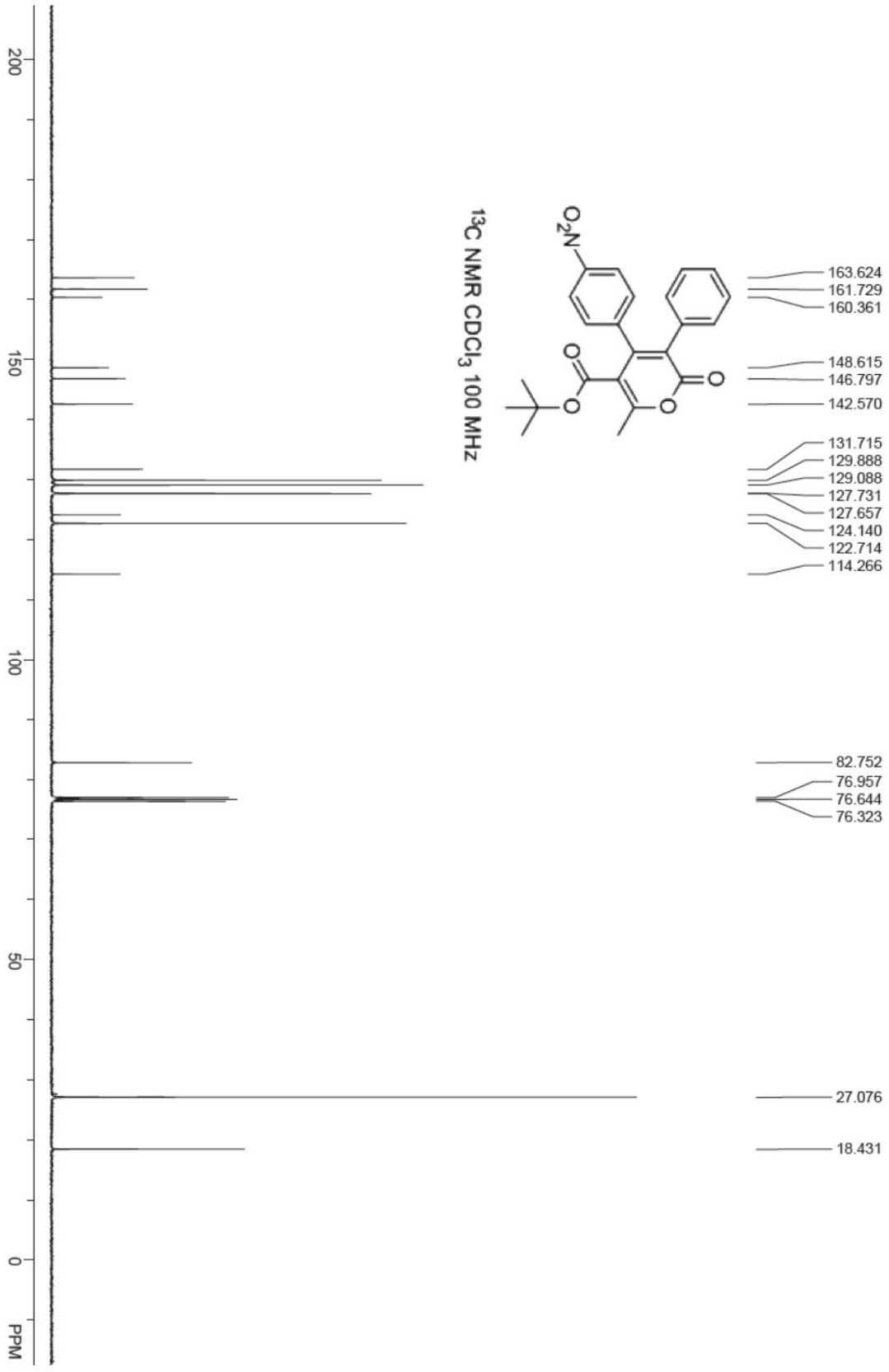
Tert-butyl 4-(4-bromophenyl)-6-methyl-2-oxo-3-phenyl-2H-pyran-5-carboxylate (3ia)



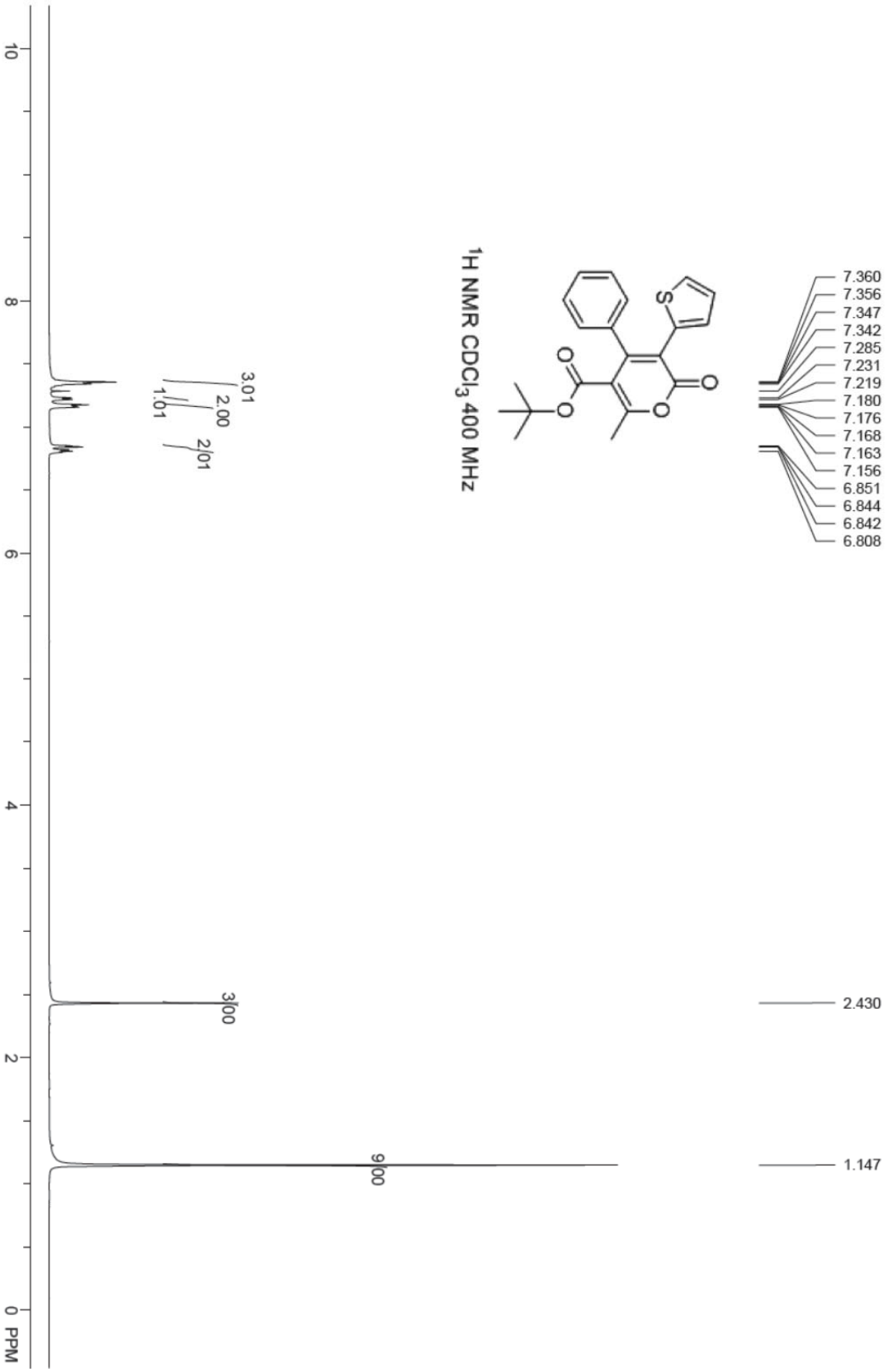

^{13}C NMR CDCl$_3$ 100 MHz
Br
O
O
O
O
200
150
100
50
PPM
164.068
160.833
160.683
149.679
134.704
132.218
130.777
130.001
129.568
127.510
127.351
123.601
121.949
115.099
82.448
76.929
76.610
76.288
27.033
18.198

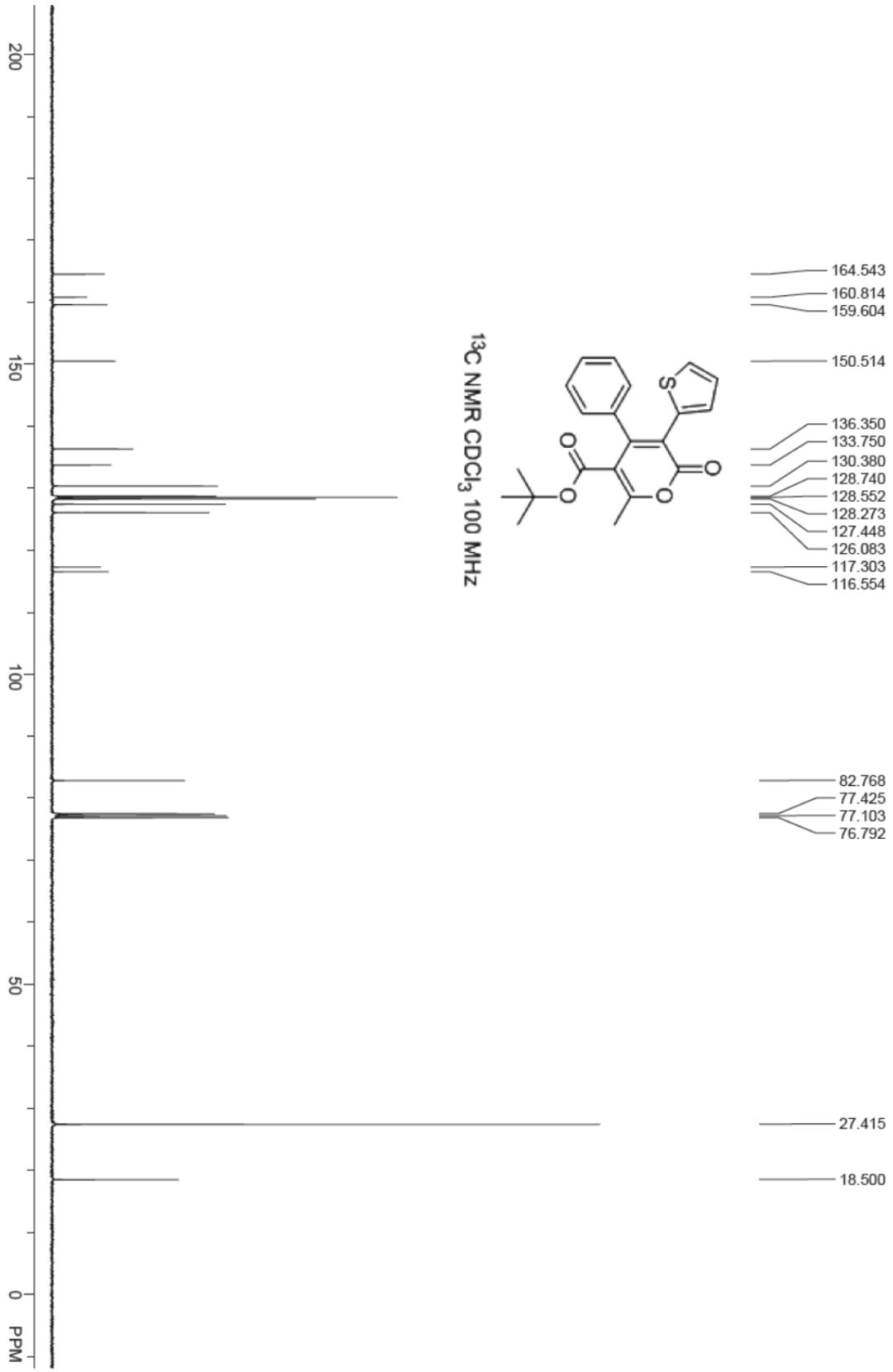
Tert-butyl 6-methyl-4-(4-nitrophenyl)-2-oxo-3-phenyl-2H-pyran-5-carboxylate (3ja)



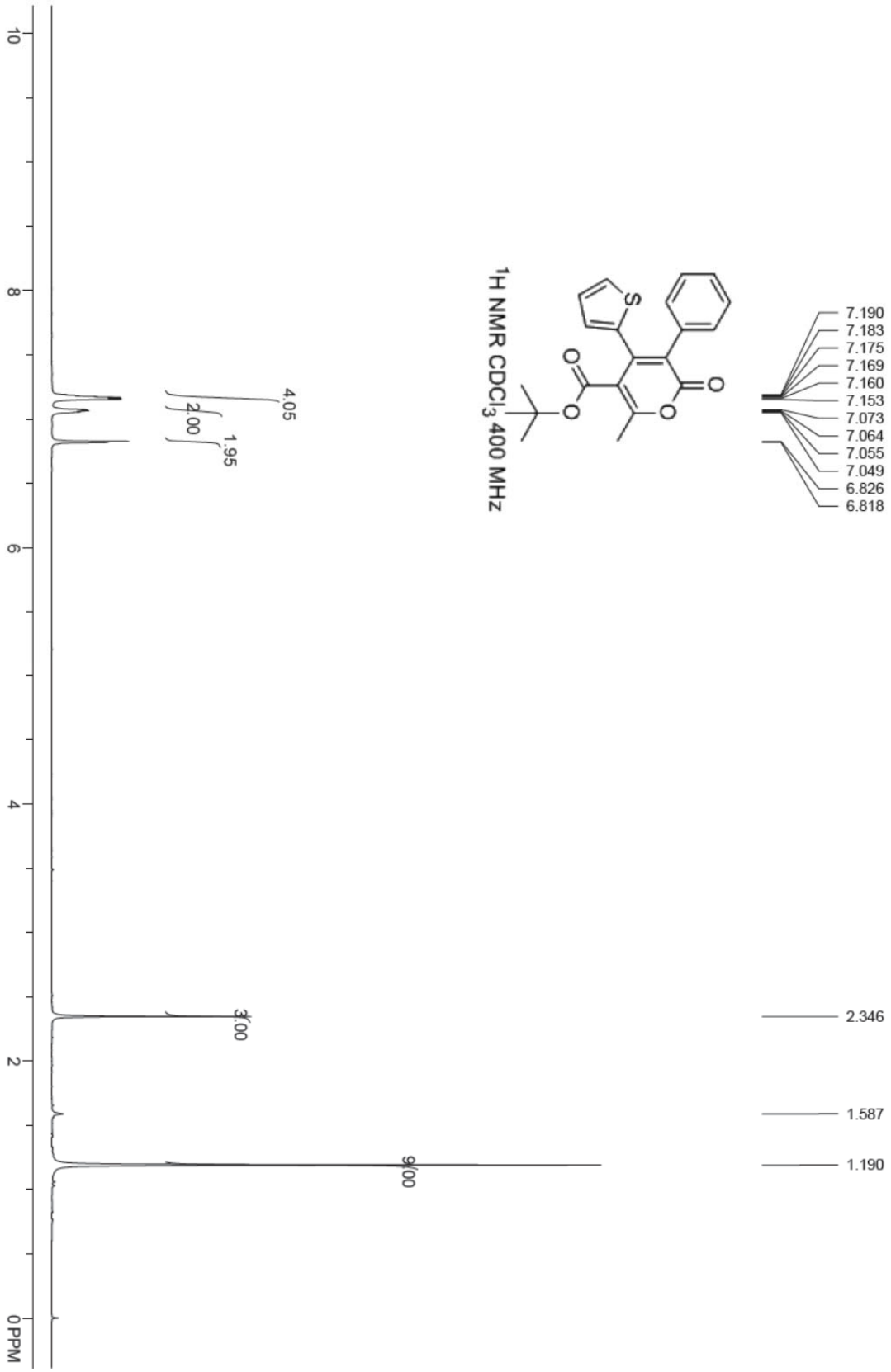

^{13}C NMR CDCl$_3$ 100 MHz
O_2N
O
O
O
O
163.624
161.729
160.361
148.615
146.797
142.570
131.715
129.888
129.088
127.731
127.657
124.140
122.714
114.266
82.752
76.957
76.644
76.323
27.076
18.431
200
150
100
50
0
PPM

Tert-butyl 6-methyl-2-oxo-4-phenyl-3-(thiophen-2-yl)-2H-pyran-5-carboxylate (3ka)



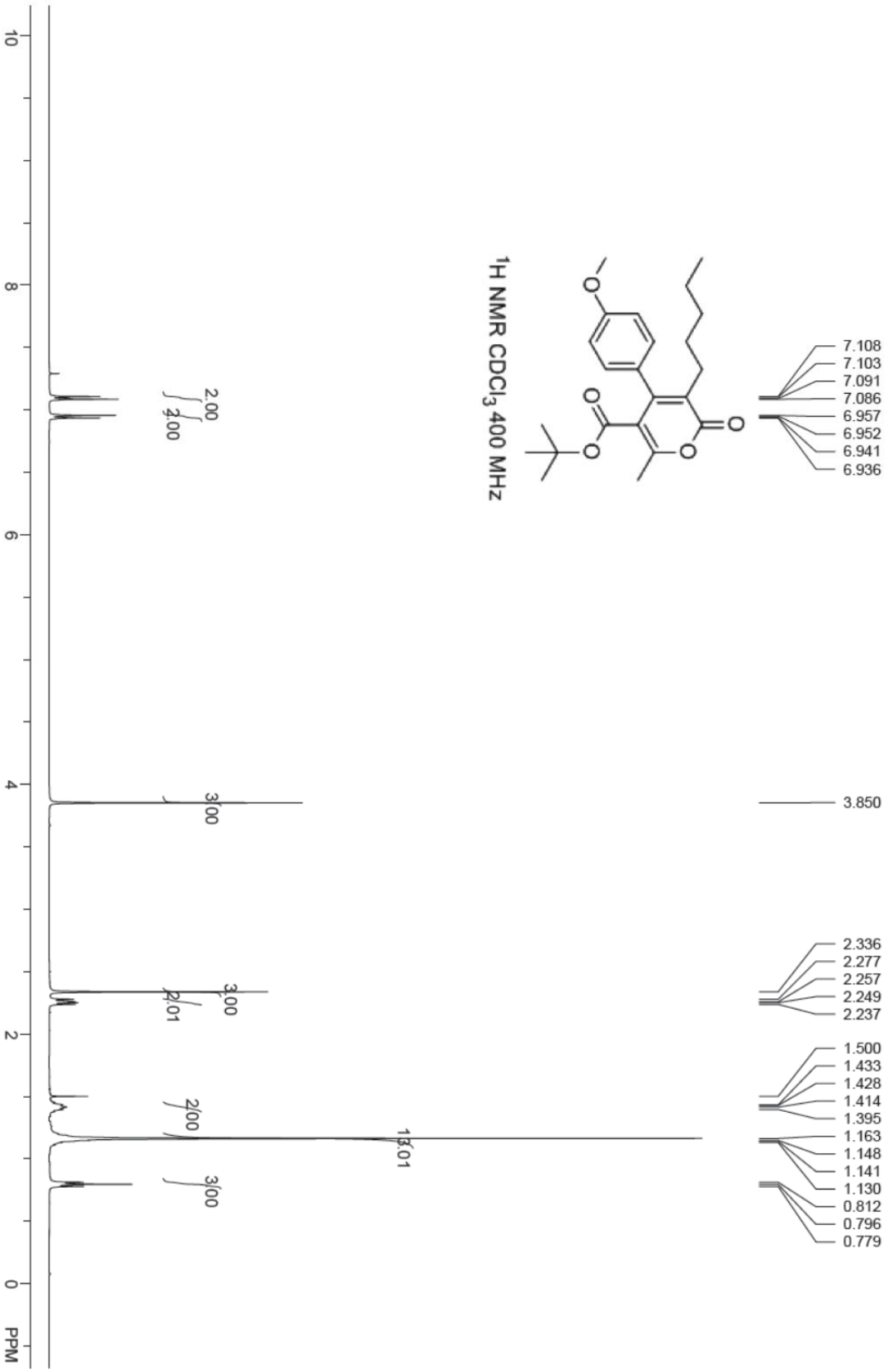

200
150
100
50
0
PPM
^{13}C NMR CDCl$_3$ 100 MHz
S
O
O
O
O
164.543
160.814
159.604
150.514
136.350
133.750
130.380
128.740
128.552
128.273
127.448
126.083
117.303
116.554
82.768
77.425
77.103
76.792
27.415
18.500

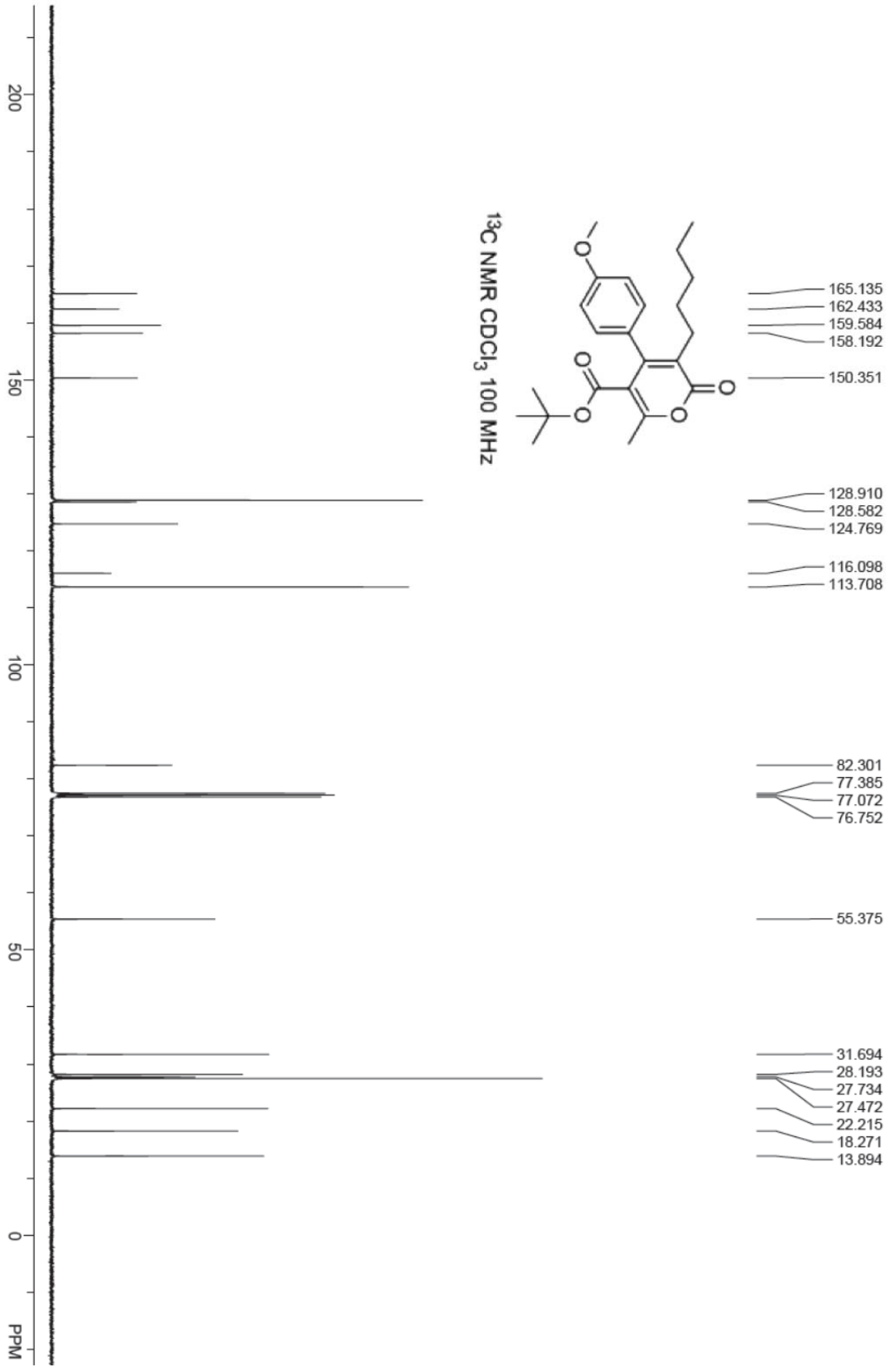
Tert-butyl 6-methyl-2-oxo-3-phenyl-4-(thiophen-2-yl)-2H-pyran-5-carboxylate (3la)



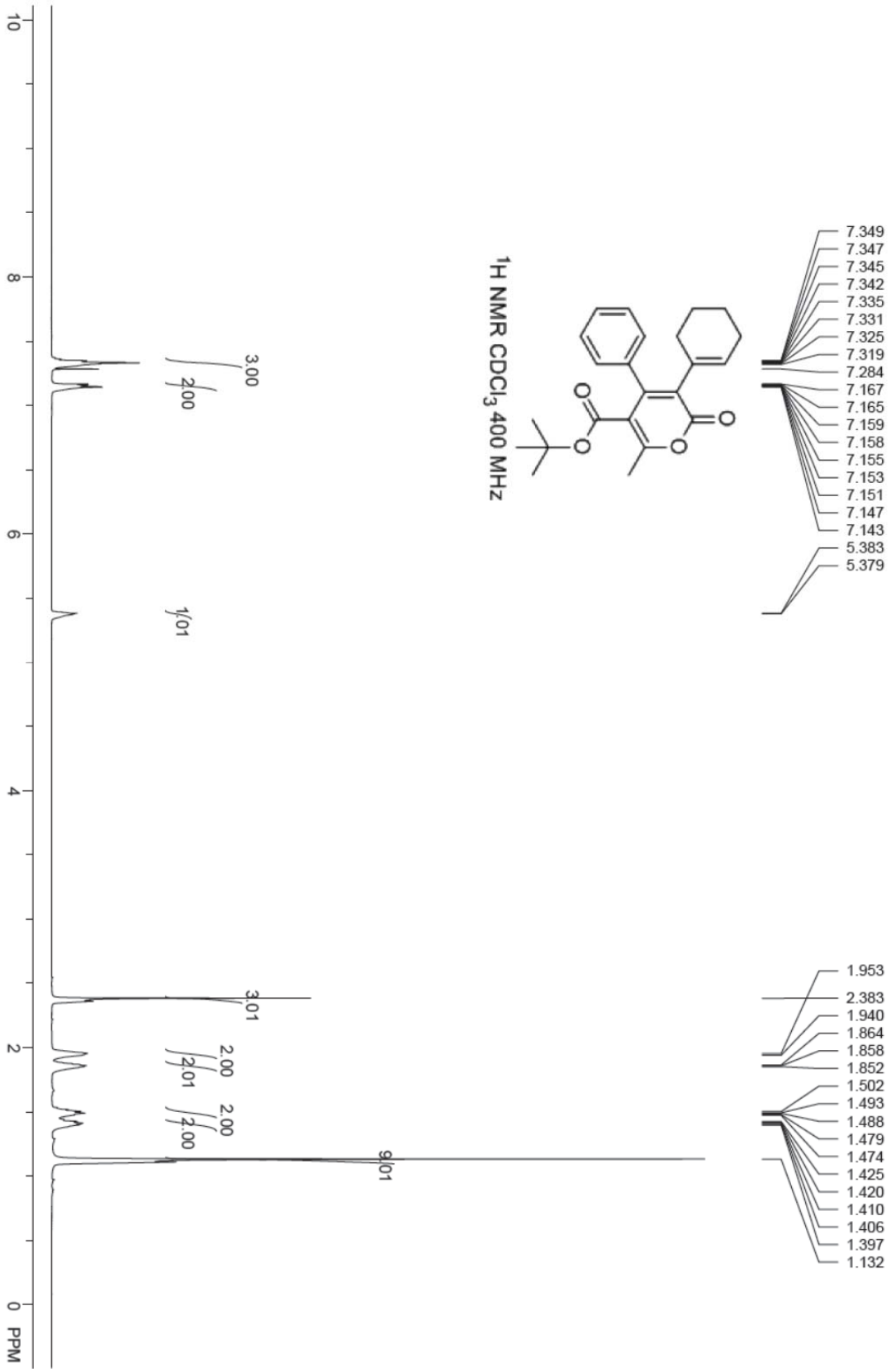

^{13}C NMR CDCl$_3$ 100 MHz
164.253
160.716
159.752
144.070
135.762
132.685
129.796
128.328
127.534
127.477
126.219
124.538
115.841
82.456
76.912
76.600
76.279
27.077
18.078
150
100
50
0 PPM

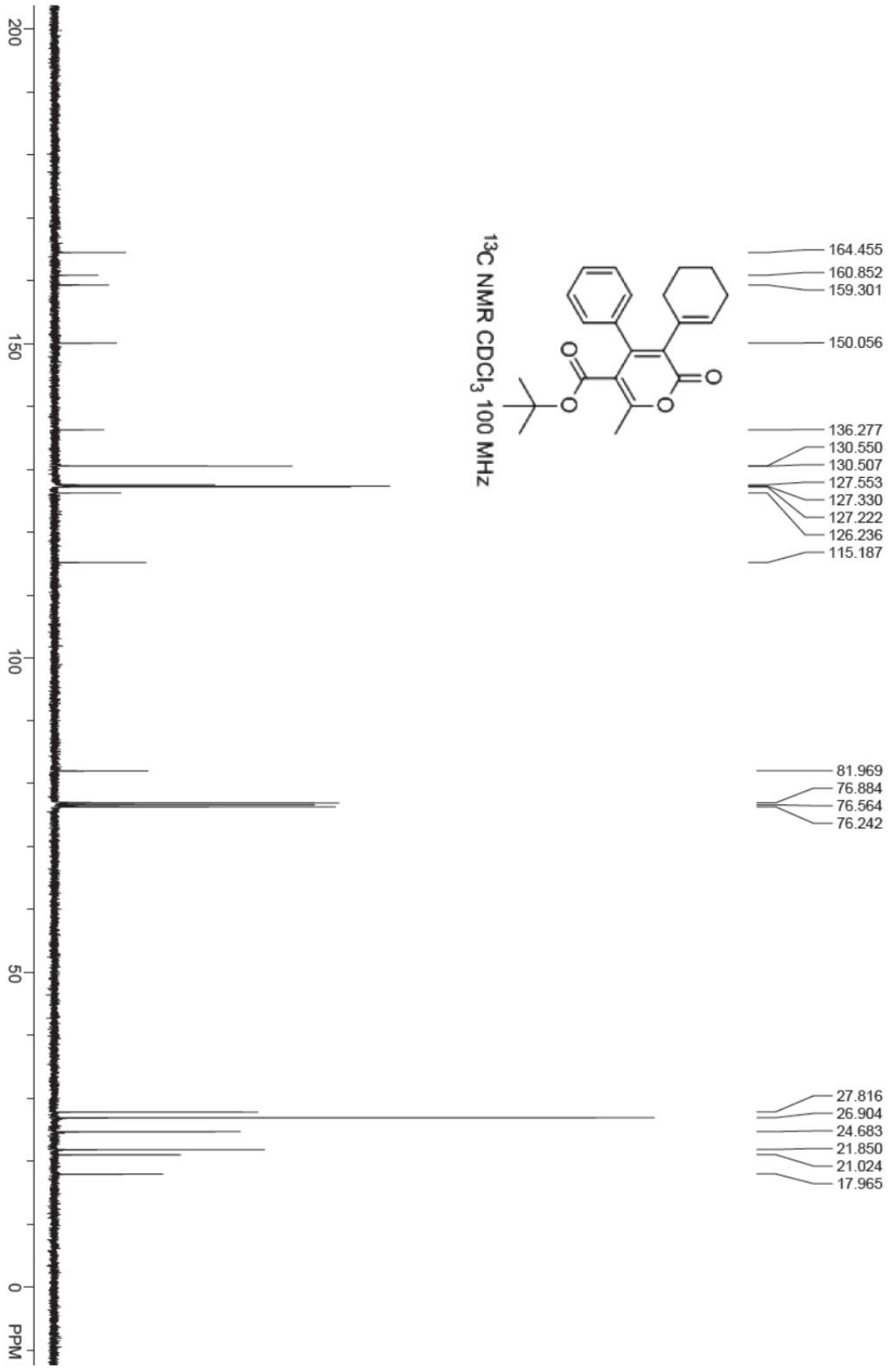
Tert-butyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3-pentyl-2H-pyran-5-carboxyate (3ma)



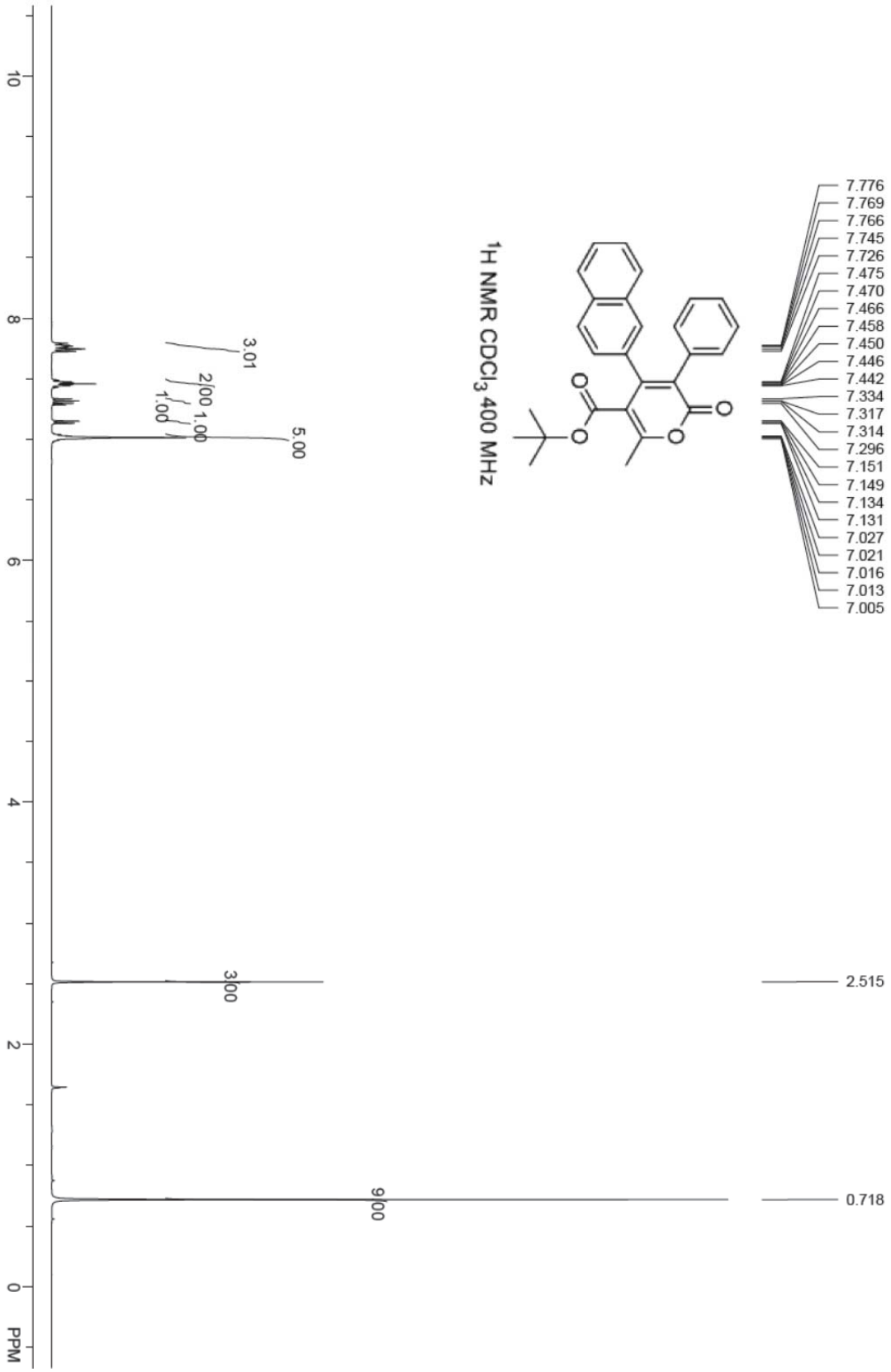

^{13}C NMR CDCl$_3$ 100 MHz
165.135
162.433
159.584
158.192
150.351
128.910
128.582
124.769
116.098
113.708
82.301
77.385
77.072
76.752
55.375
31.694
28.193
27.734
27.472
22.215
18.271
13.894
200
150
100
50
0
PPM

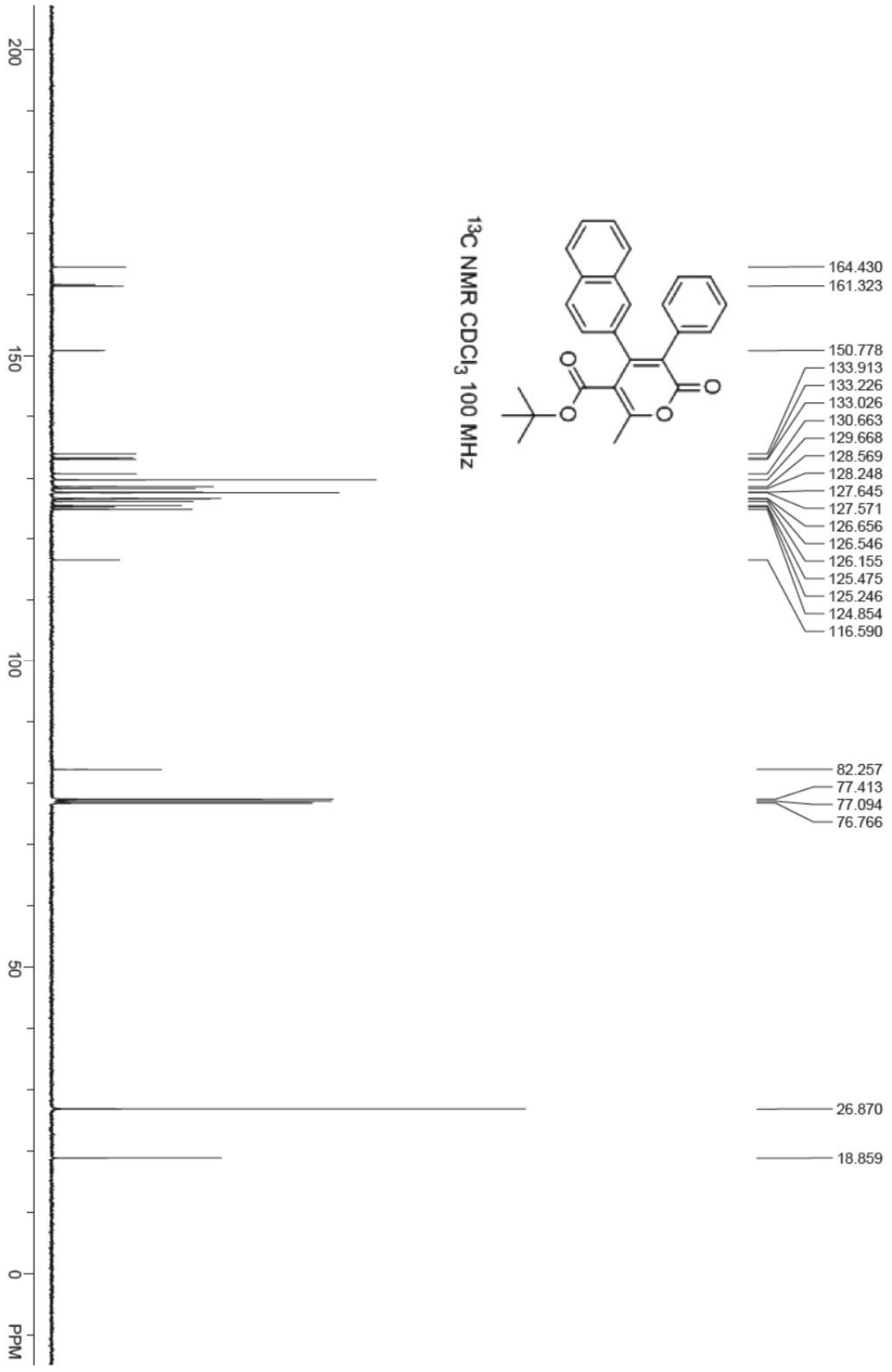
Tert-butyl-3-(cyclohex-1-en-1-yl)-6-methyl-2-oxo-4-phenyl-2H-pyran-5-carboxylate (3na)



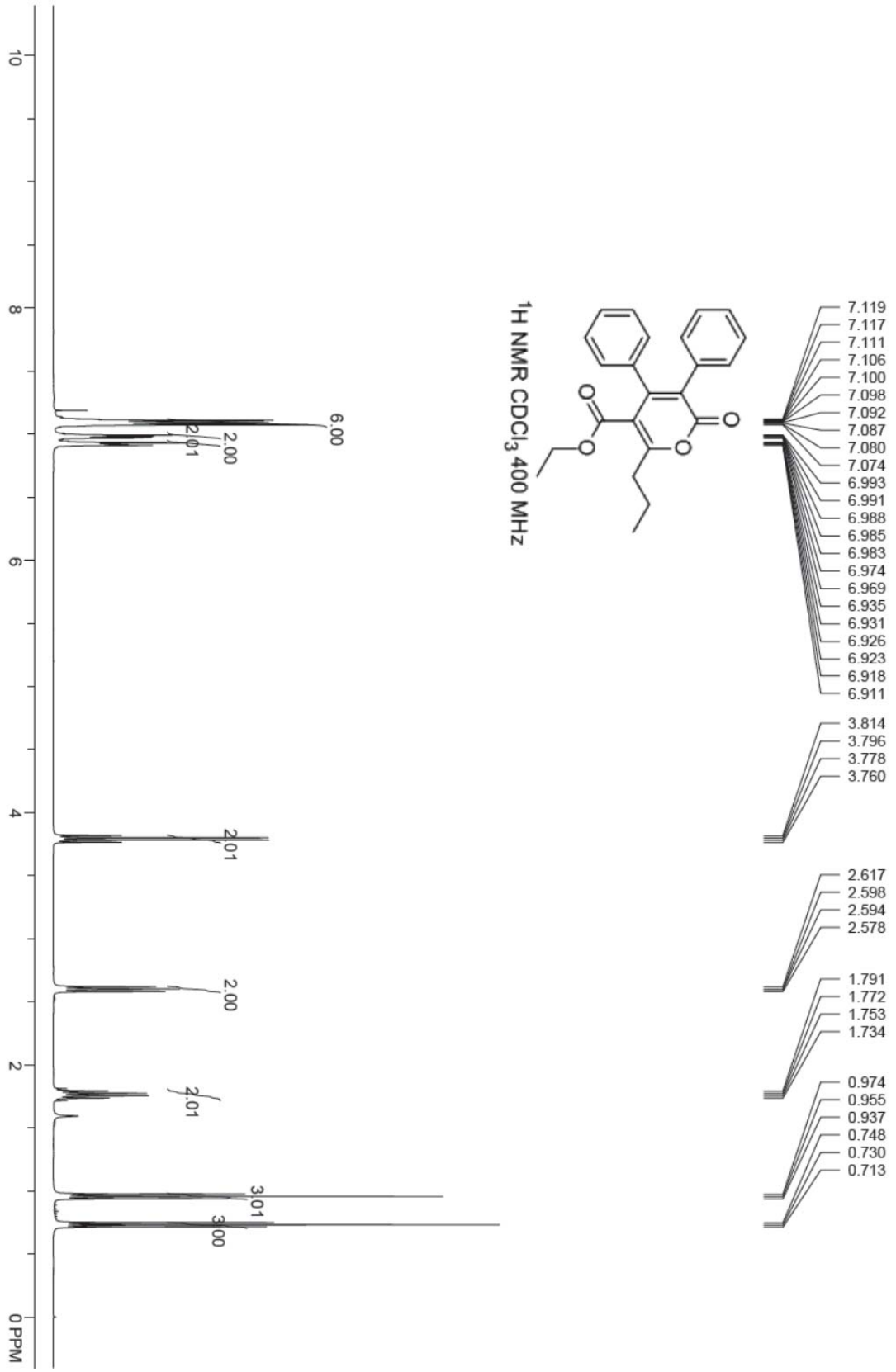

^{13}C NMR CDCl$_3$ 100 MHz
164.455
160.852
159.301
150.056
136.277
130.550
130.507
127.553
127.330
127.222
126.236
115.187
81.969
76.884
76.564
76.242
27.816
26.904
24.683
21.850
21.024
17.965
200
150
100
50
0
PPM

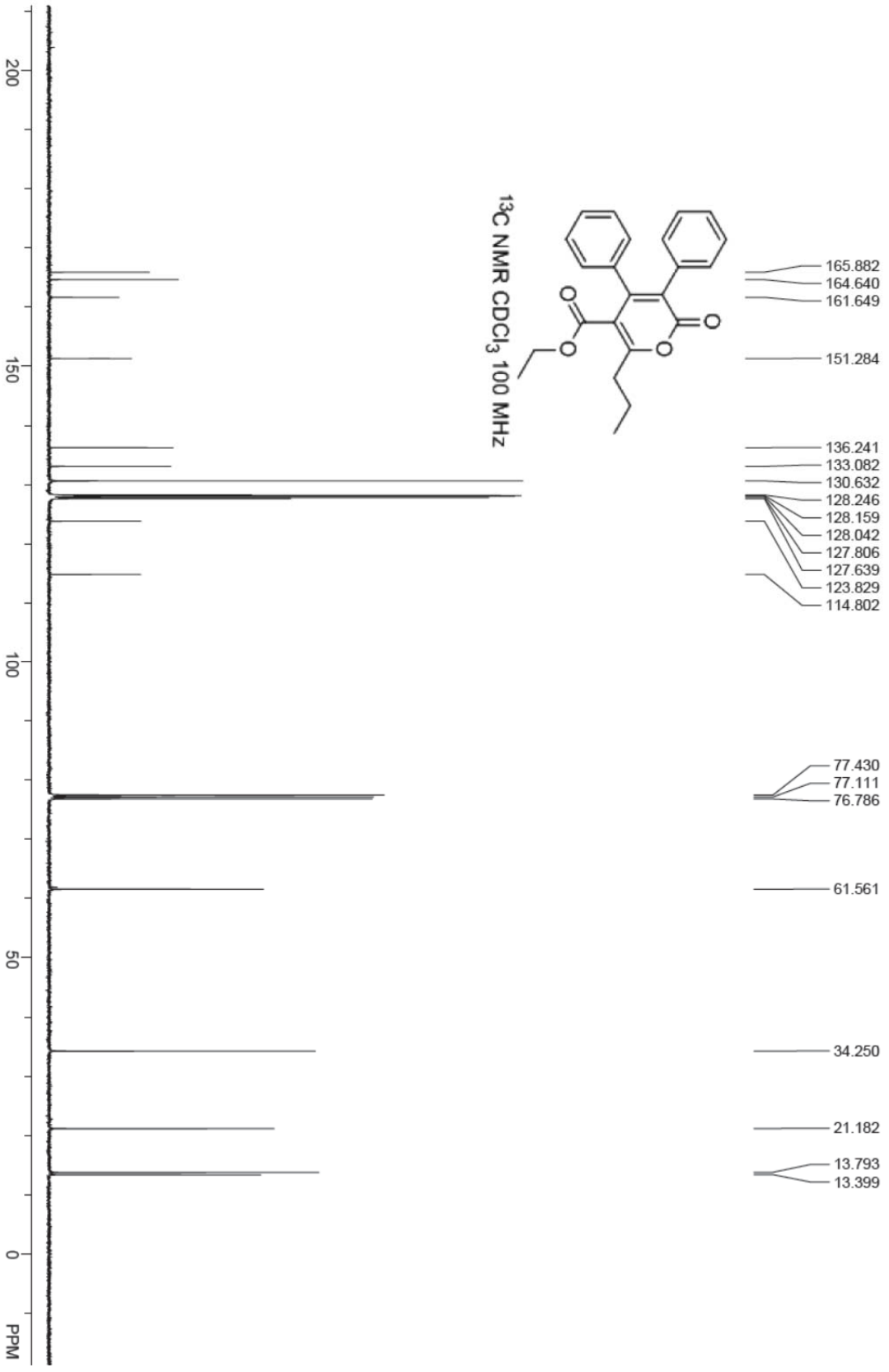
Tert-butyl 6-methyl-4-(naphthalen-2-yl)-2-oxo-3-phenyl-2H-pyran-5-carboxylate (3oa)



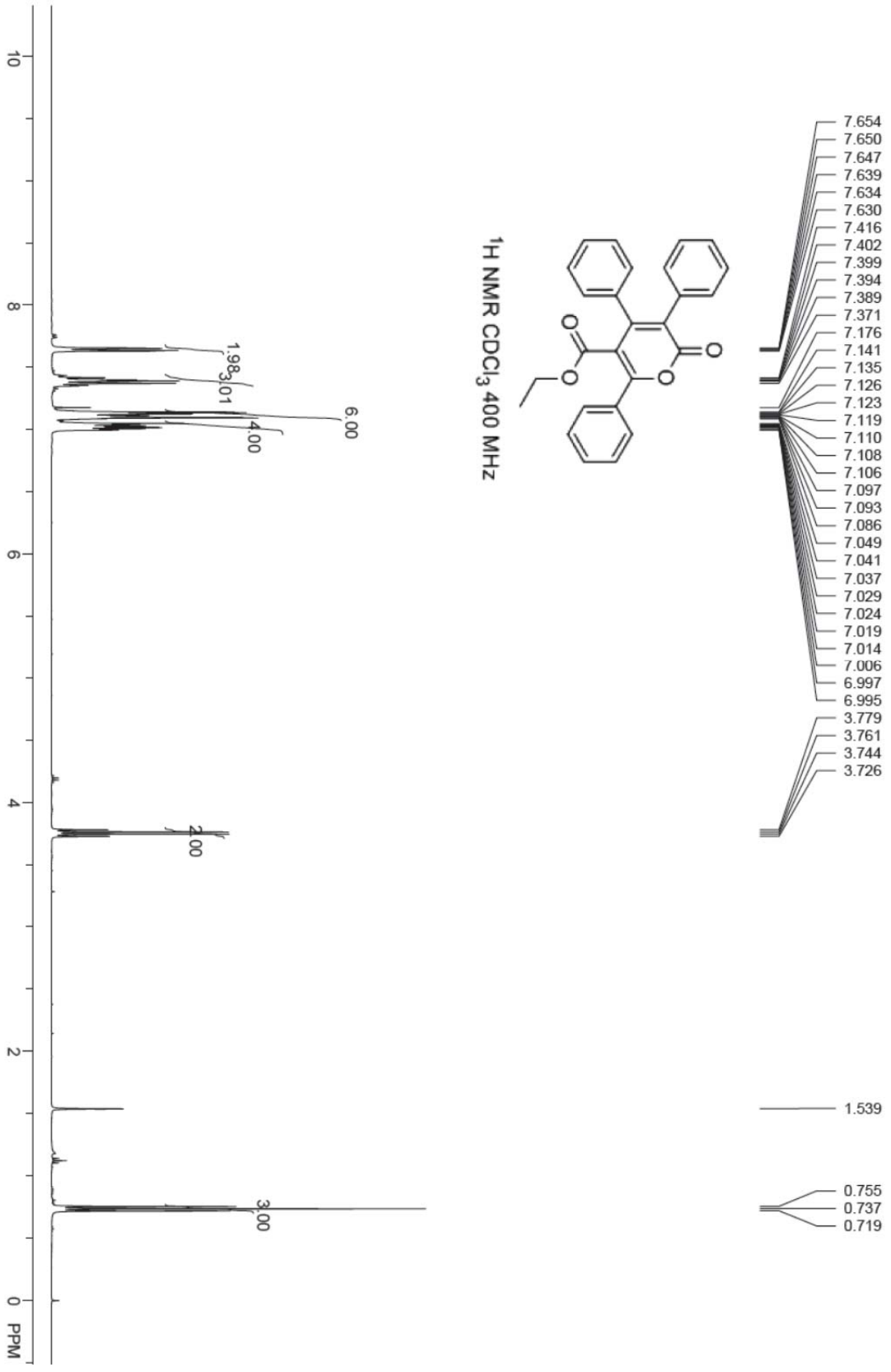

^{13}C NMR $CDCl_3$ 100 MHz
164.430
161.323
150.778
133.913
133.226
133.026
130.663
129.668
128.569
128.248
127.645
127.571
126.656
126.546
126.155
125.475
125.246
124.854
116.590
82.257
77.413
77.094
76.766
26.870
18.859
200
150
100
50
0
PPM

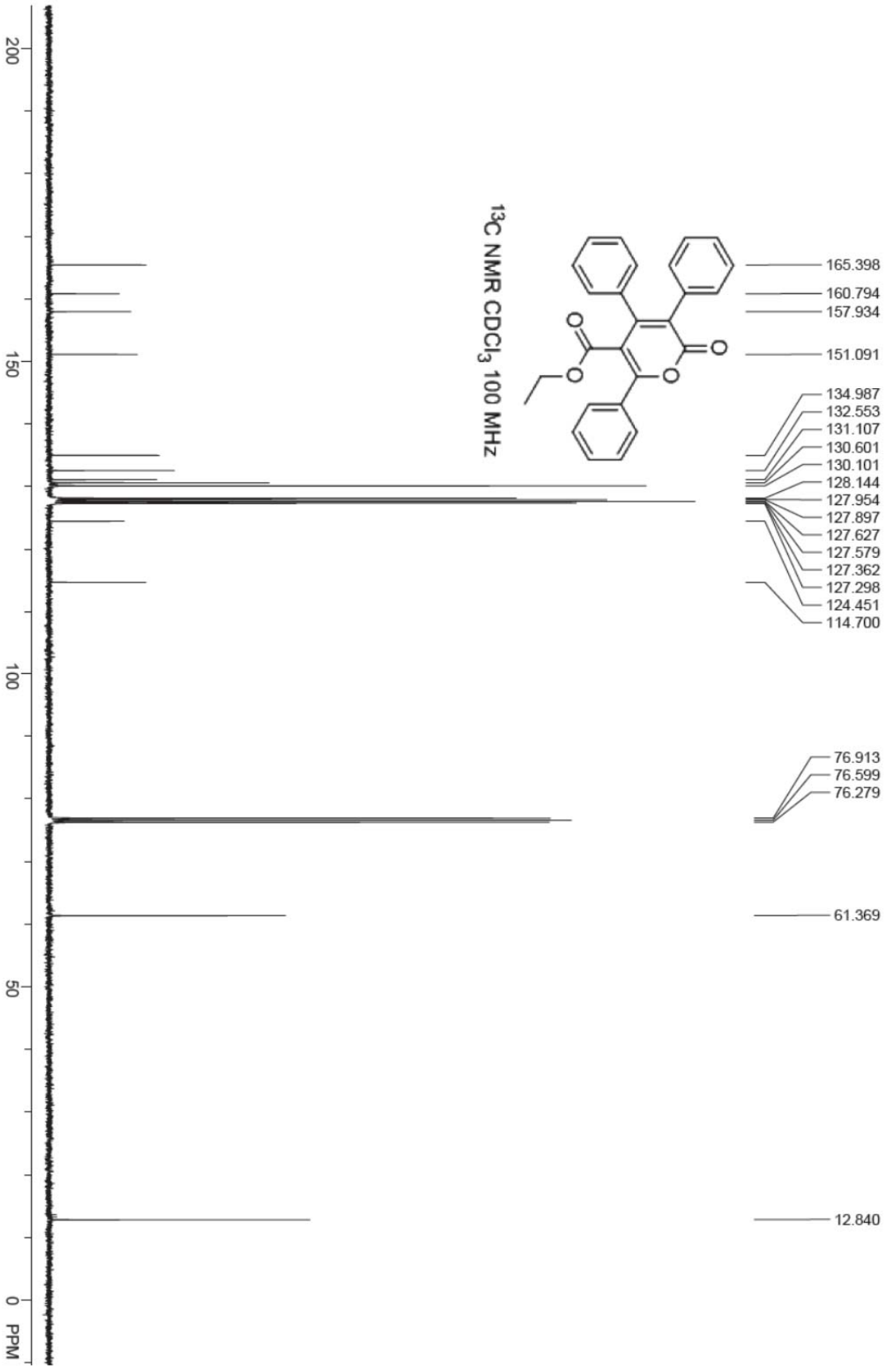
Ethyl 2-oxo-3,4-diphenyl-6-propyl-2H-pyran-5-carboxylate (3ad)



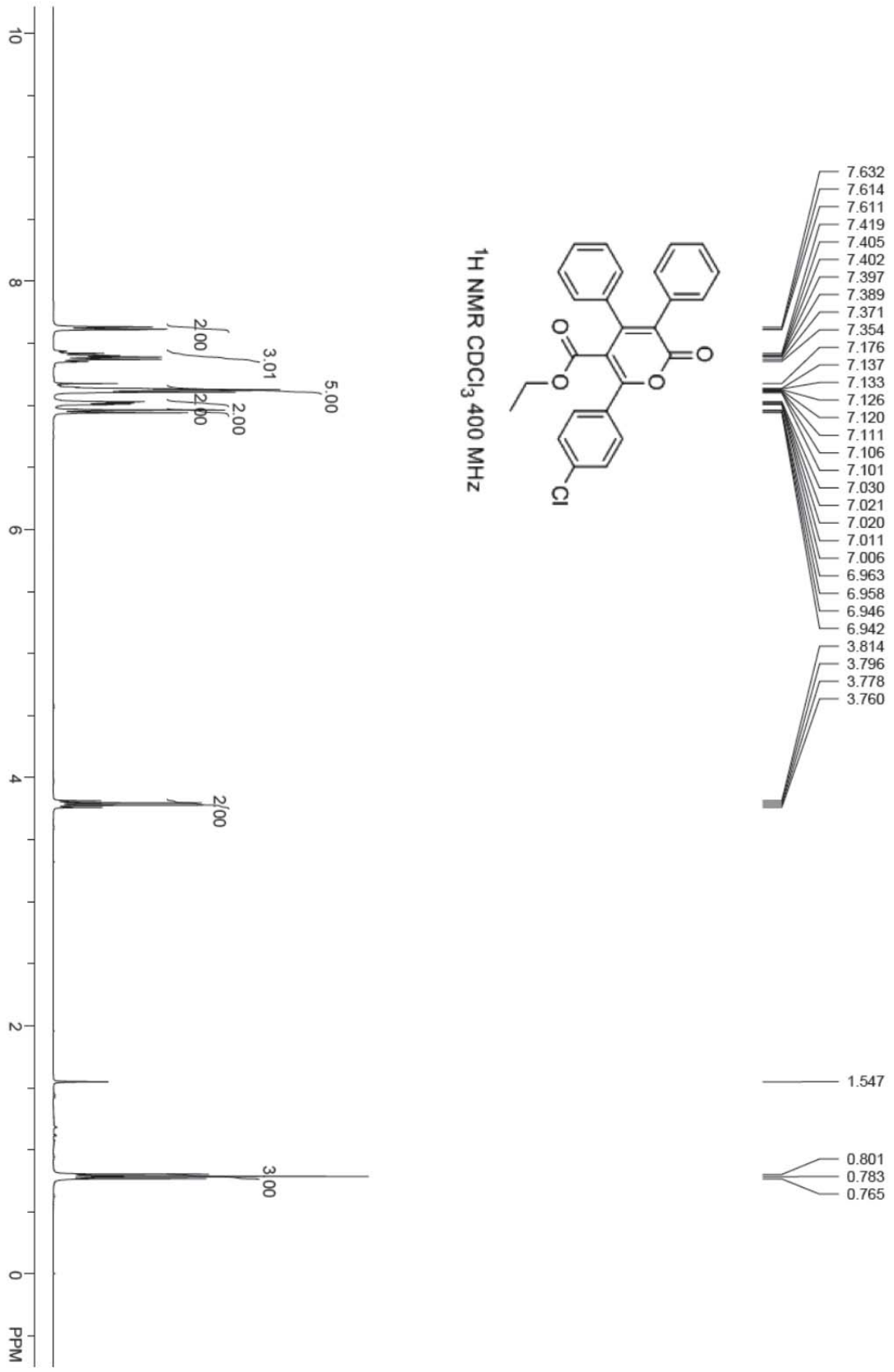

^{13}C NMR $CDCl_3$ 100 MHz
165.882
164.640
161.649
151.284
136.241
133.082
130.632
128.246
128.159
128.042
127.806
127.639
123.829
114.802
77.430
77.111
76.786
61.561
34.250
21.182
13.793
13.399
200
150
100
50
0
PPM

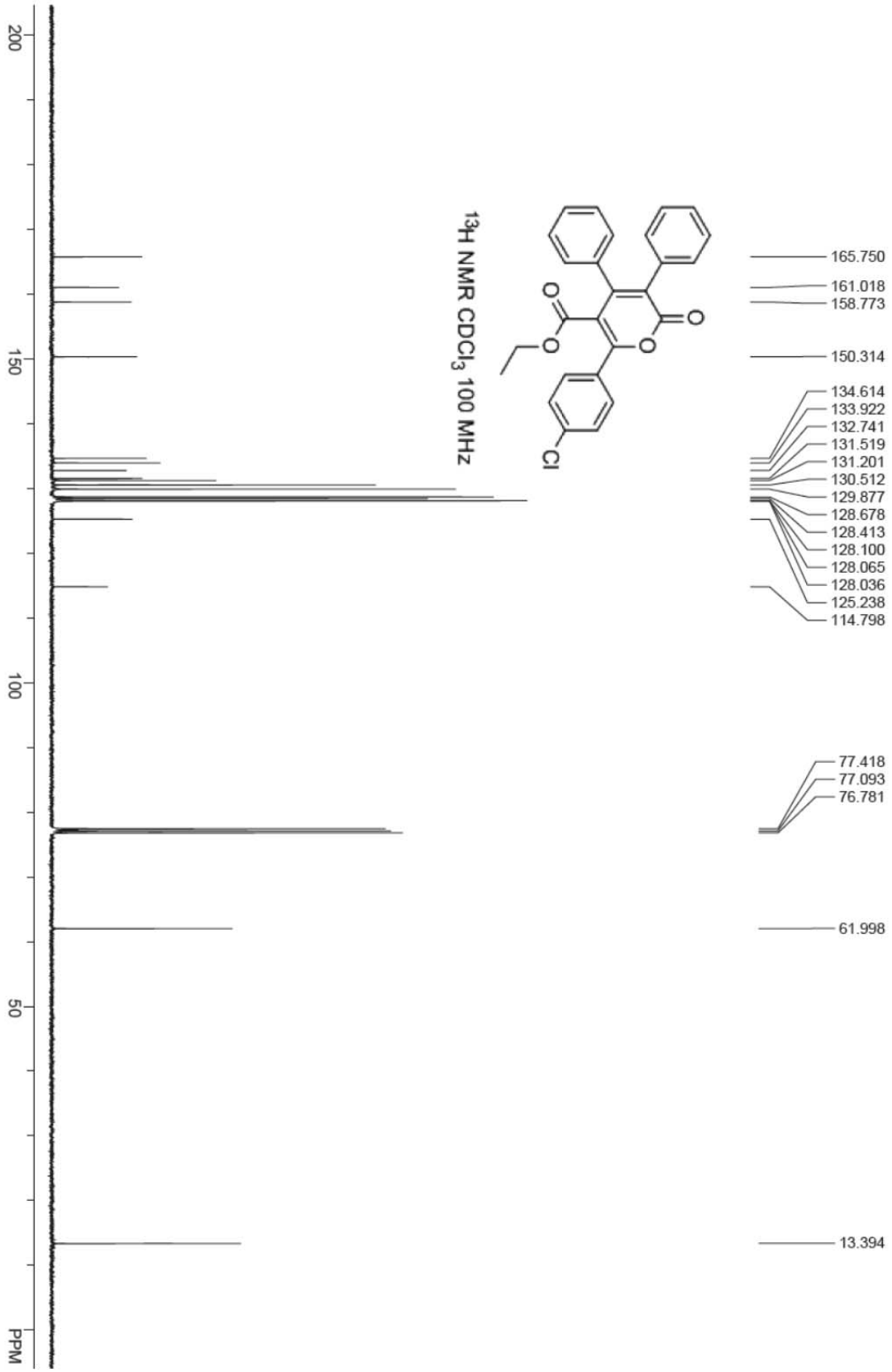
Ethyl 2-oxo-3,4,6-triphenyl-2H-pyran-5-carboxylate (3ae)



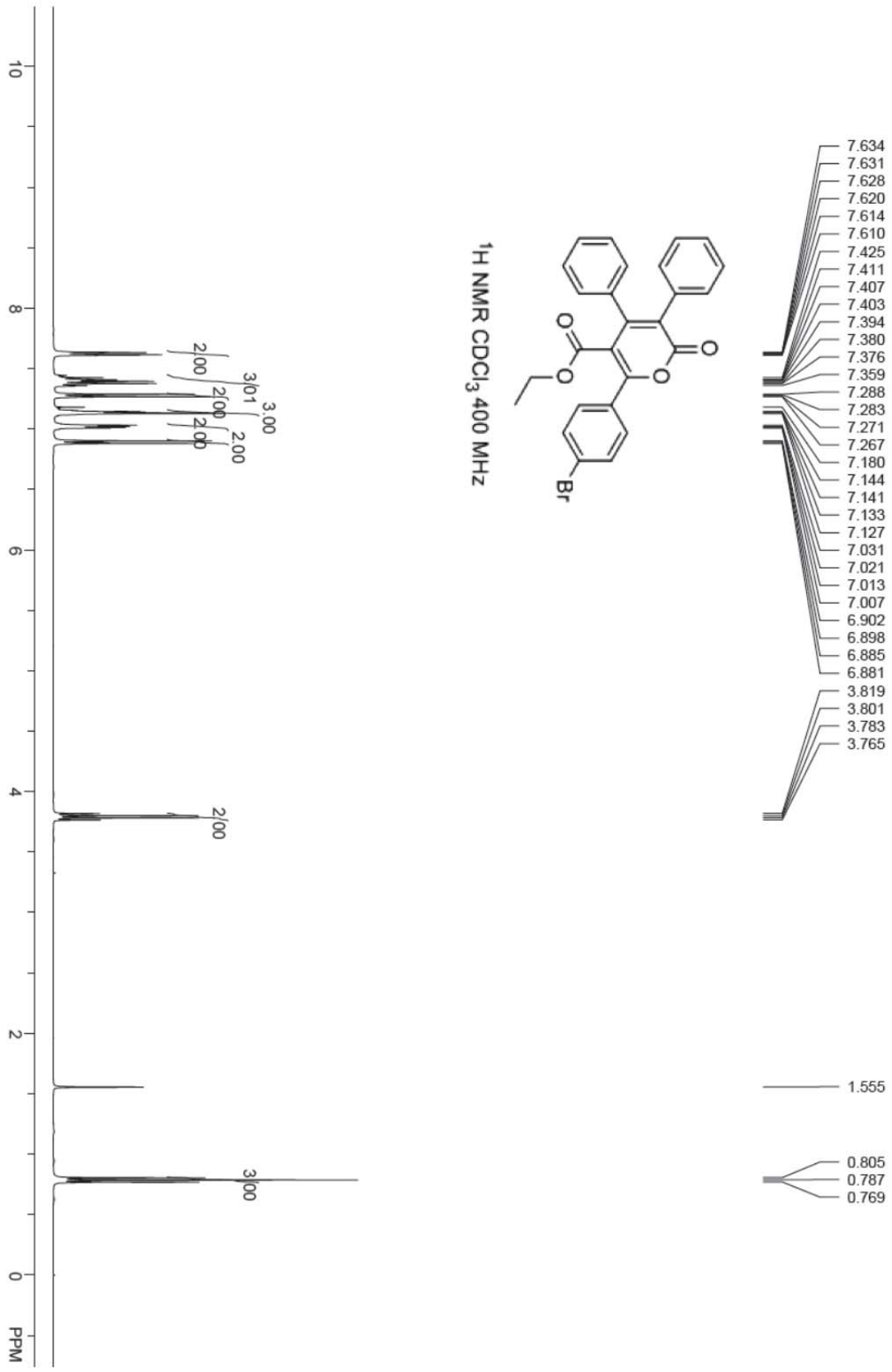

^{13}C NMR CDCl$_3$ 100 MHz
165.398
160.794
157.934
151.091
134.987
132.553
131.107
130.601
130.101
128.144
127.954
127.897
127.627
127.579
127.362
127.298
124.451
114.700
76.913
76.599
76.279
61.369
12.840
200
150
100
50
0
PPM

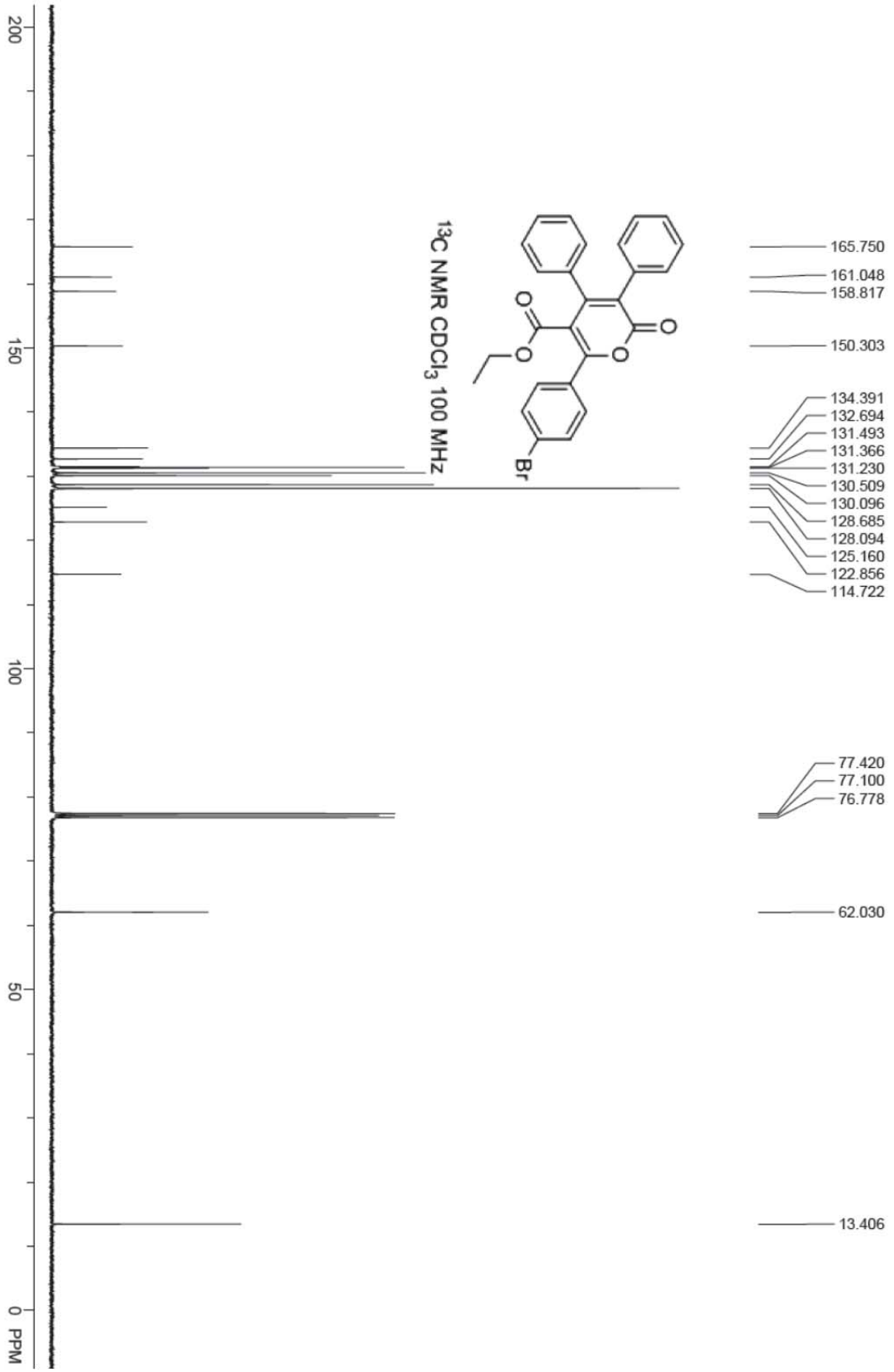
Ethyl 6-(4-chlorophenyl)-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3af)



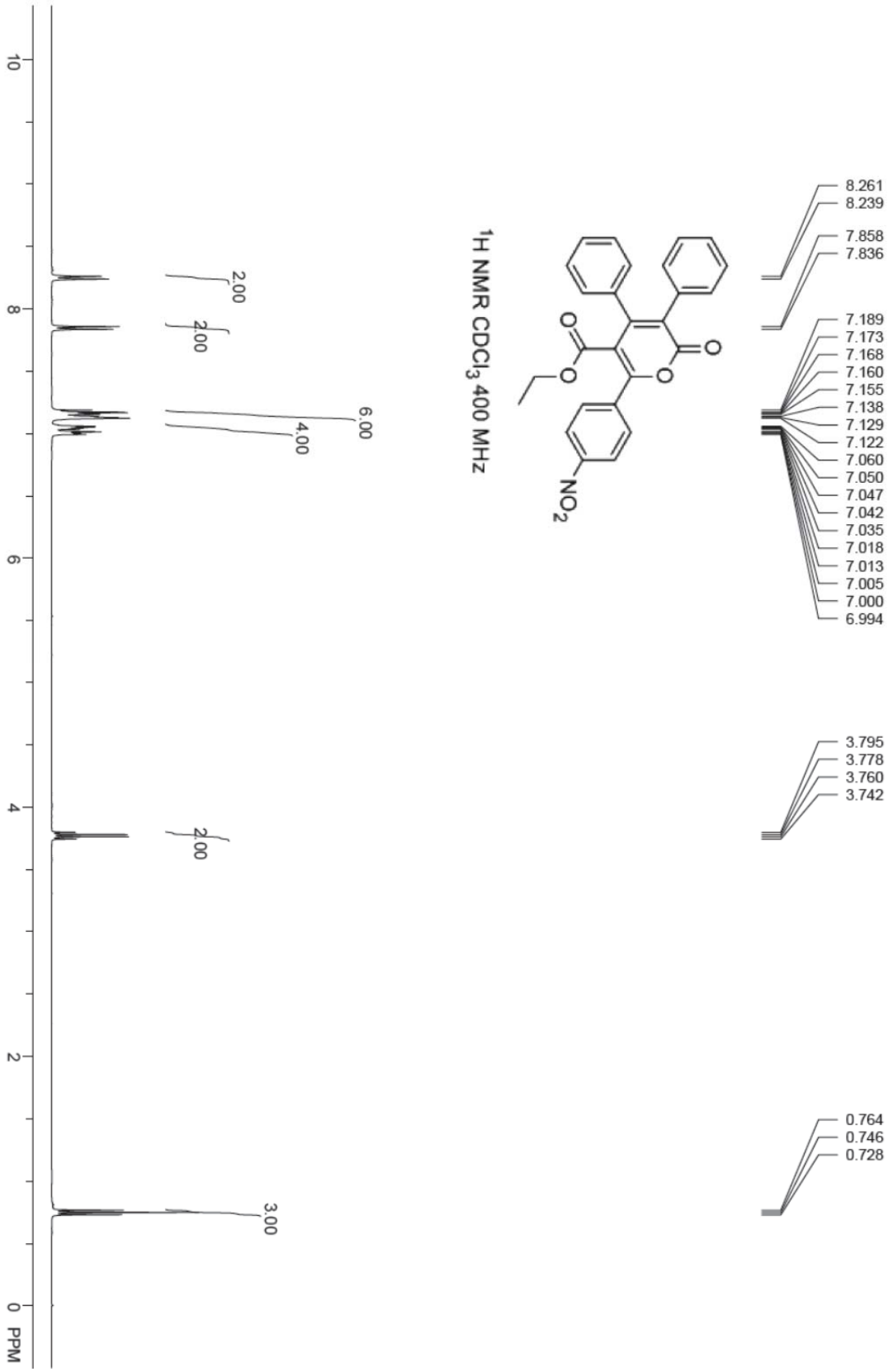

^{13}H NMR CDCl$_3$ 100 MHz
Cl
165.750
161.018
158.773
150.314
134.614
133.922
132.741
131.519
131.201
130.512
129.877
128.678
128.413
128.100
128.065
128.036
125.238
114.798
77.418
77.093
76.781
61.998
13.394
200
150
100
50
PPM

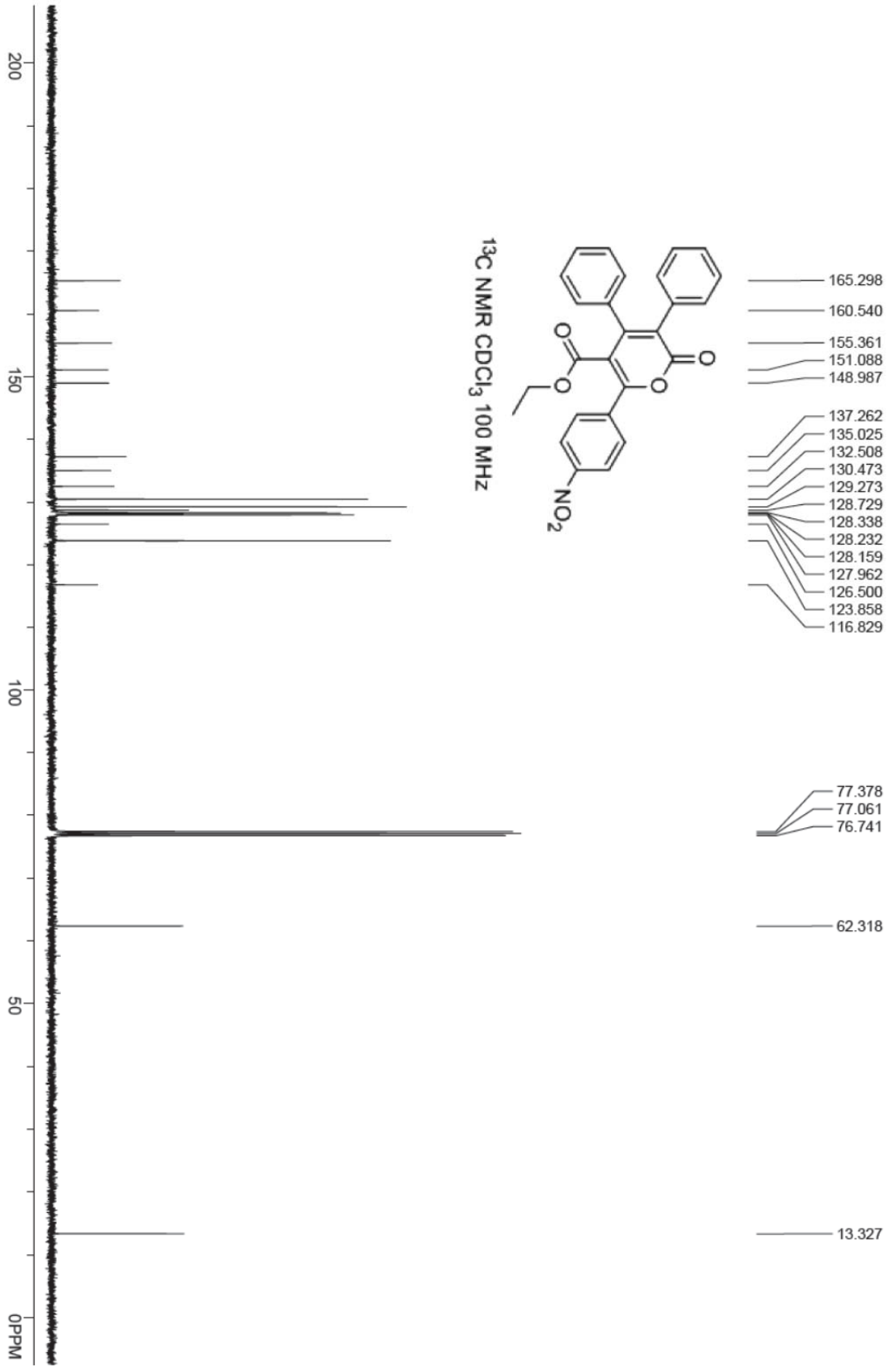
Ethyl 6-(4-bromophenyl)-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3ag)



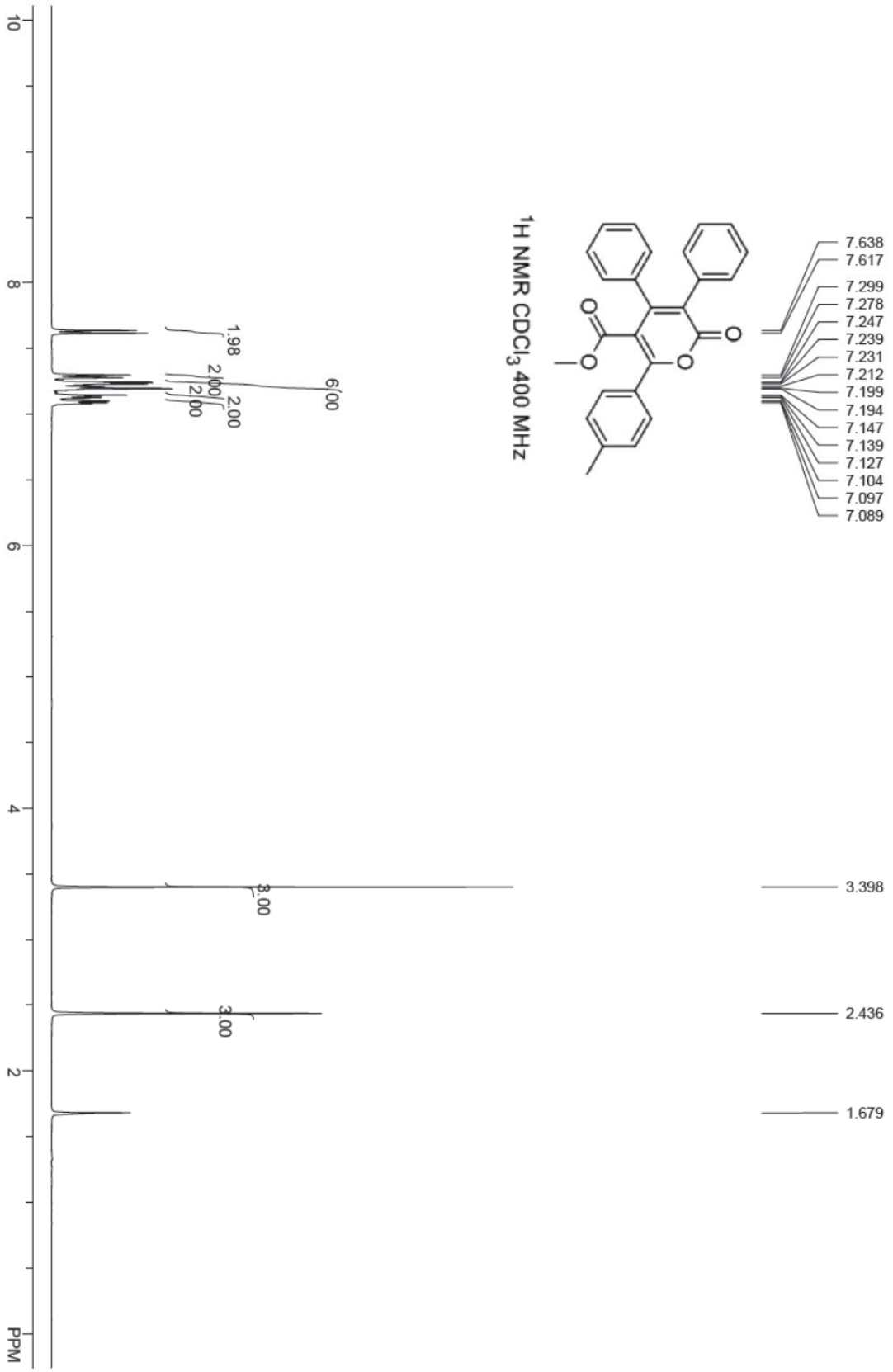

^{13}C NMR $CDCl_3$ 100 MHz
Br
165.750
161.048
158.817
150.303
134.391
132.694
131.493
131.366
131.230
130.509
130.096
128.685
128.094
125.160
122.856
114.722
77.420
77.100
76.778
62.030
13.406
200
150
100
50
0 PPM

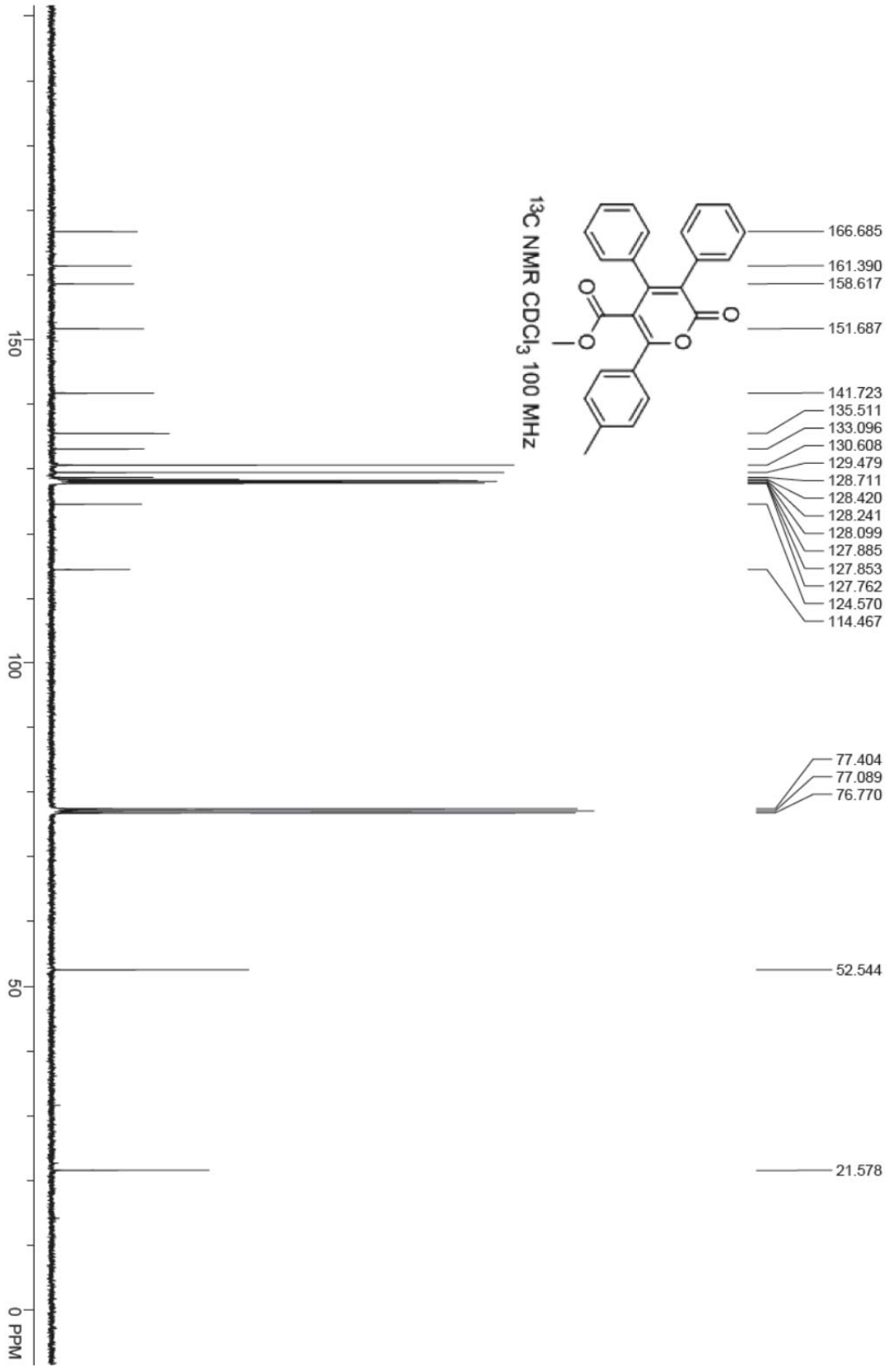
Ethyl 6-(4-nitrophenyl)-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3ah)



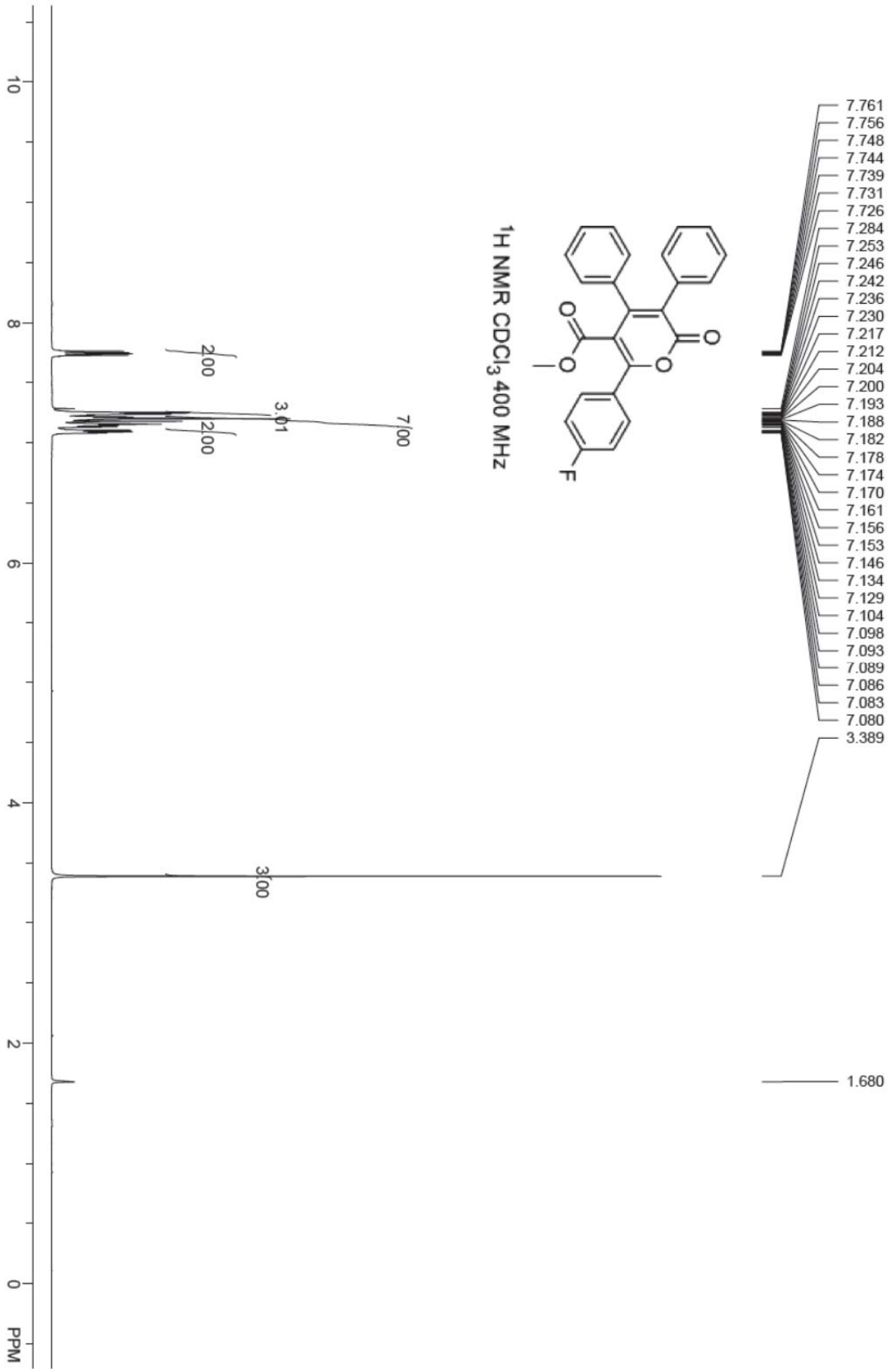

^{13}C NMR CDCl$_3$ 100 MHz
165.298
160.540
155.361
151.088
148.987
137.262
135.025
132.508
130.473
129.273
128.729
128.338
128.232
128.159
127.962
126.500
123.858
116.829
77.378
77.061
76.741
62.318
13.327
200
150
100
50
0PPM

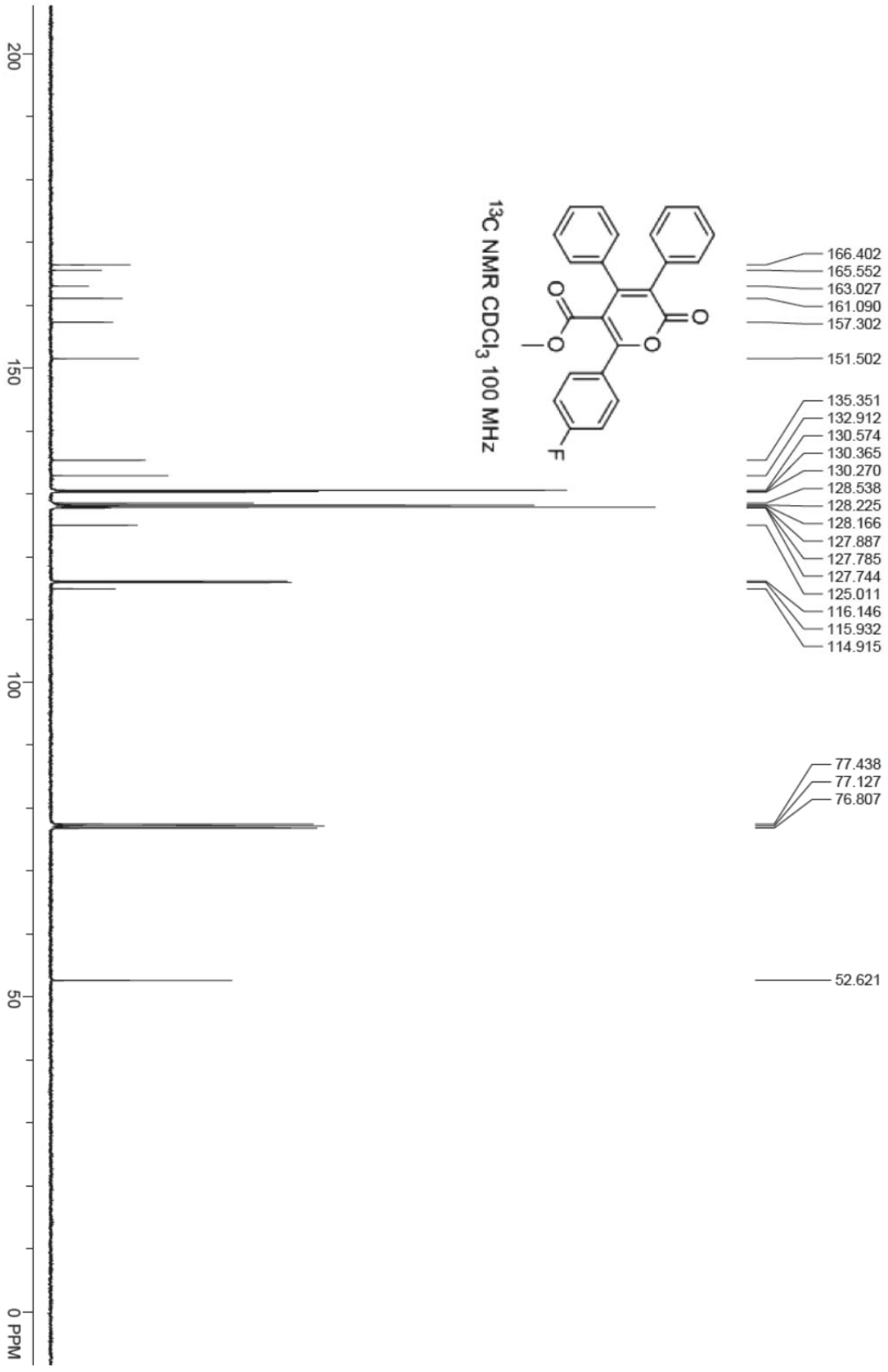
Methyl 2-oxo-3,4-diphenyl-6-(p-tolyl)-2H-pyran-5-carboxylate (3ai)



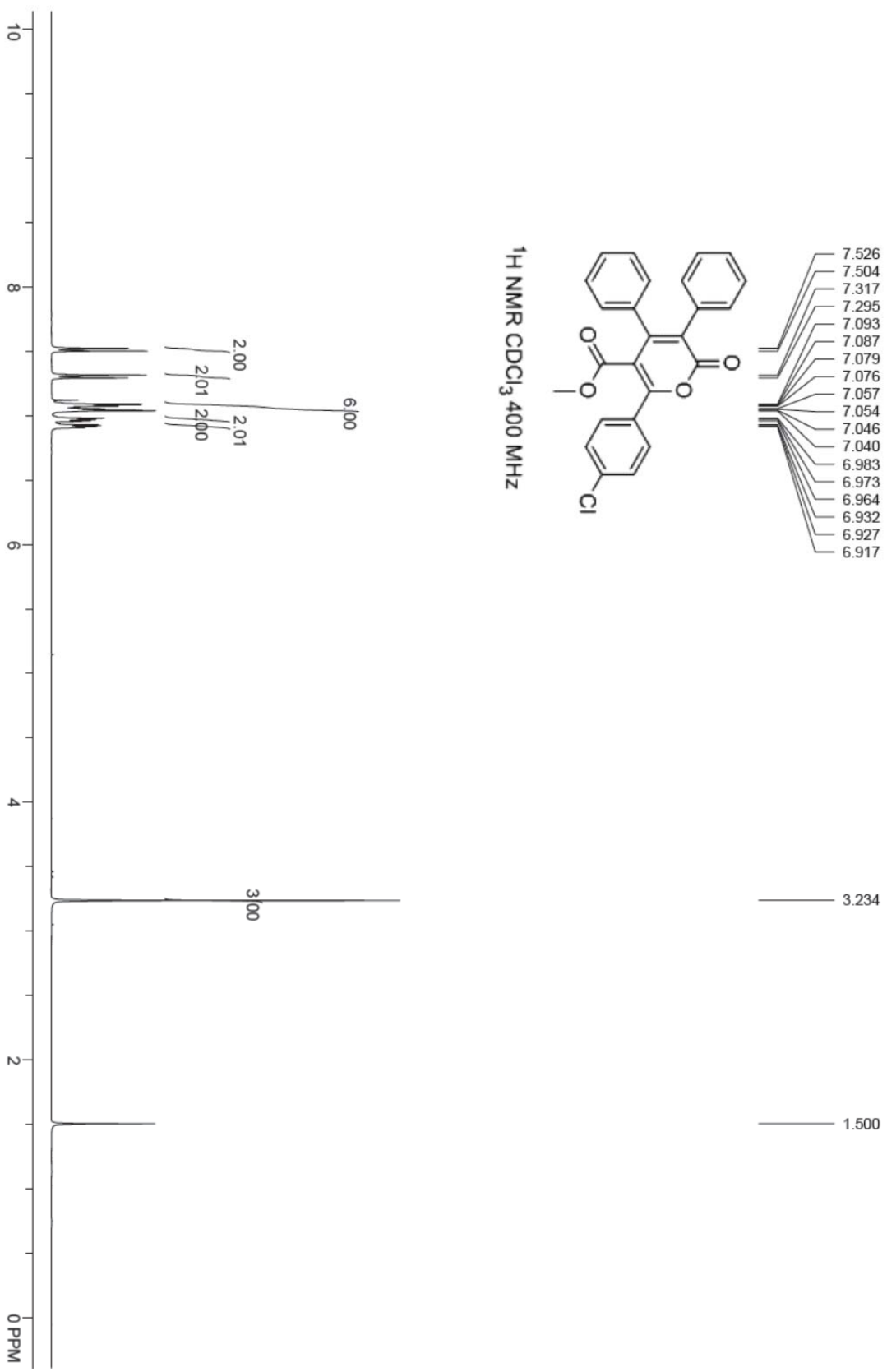

^{13}C NMR CDCl$_3$ 100 MHz
166.685
161.390
158.617
151.687
141.723
135.511
133.096
130.608
129.479
128.711
128.420
128.241
128.099
127.885
127.853
127.762
124.570
114.467
77.404
77.089
76.770
52.544
21.578
150
100
50
0 PPM

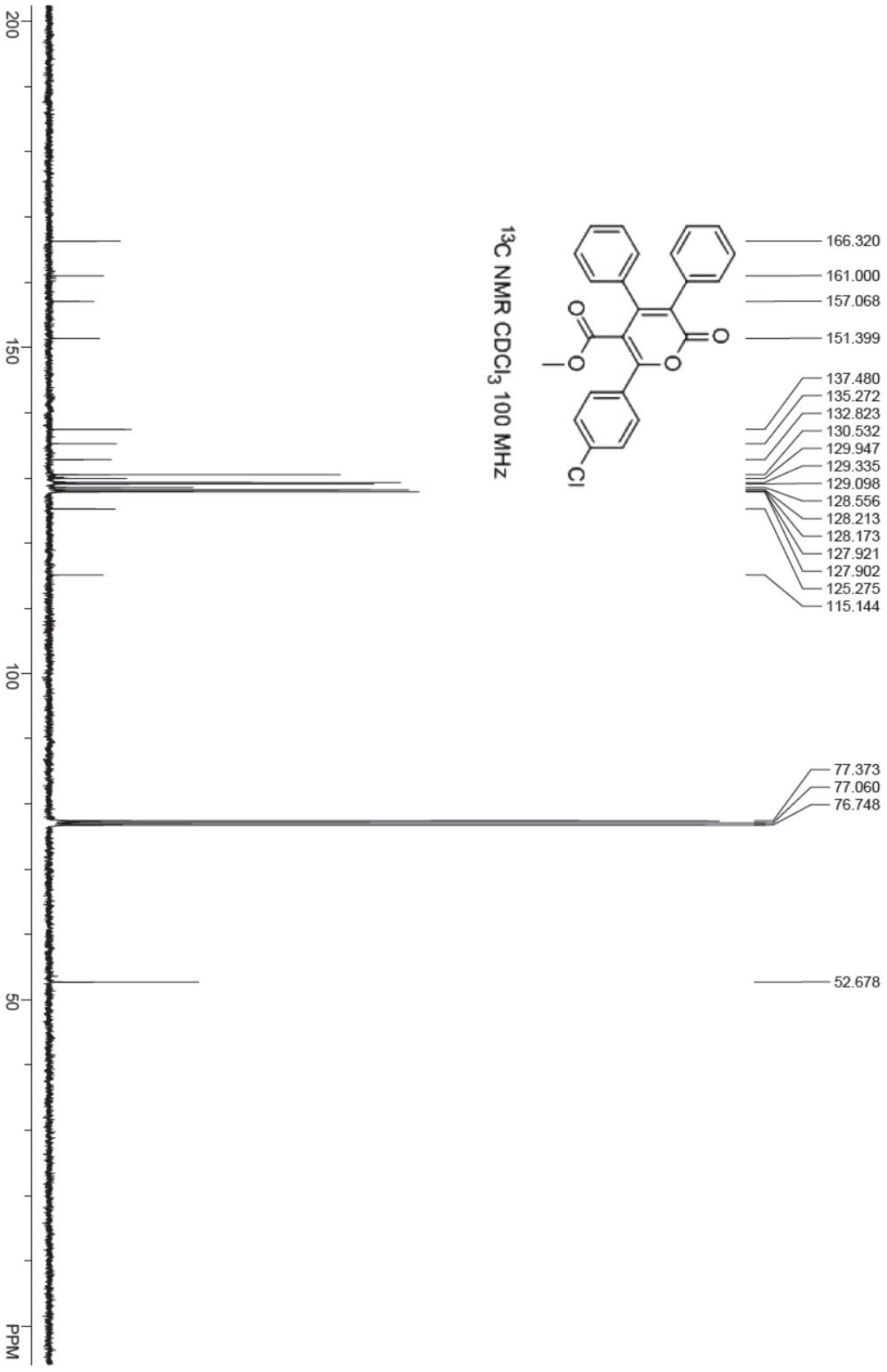
Methyl 6-(4-fluorophenyl)-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3aj)



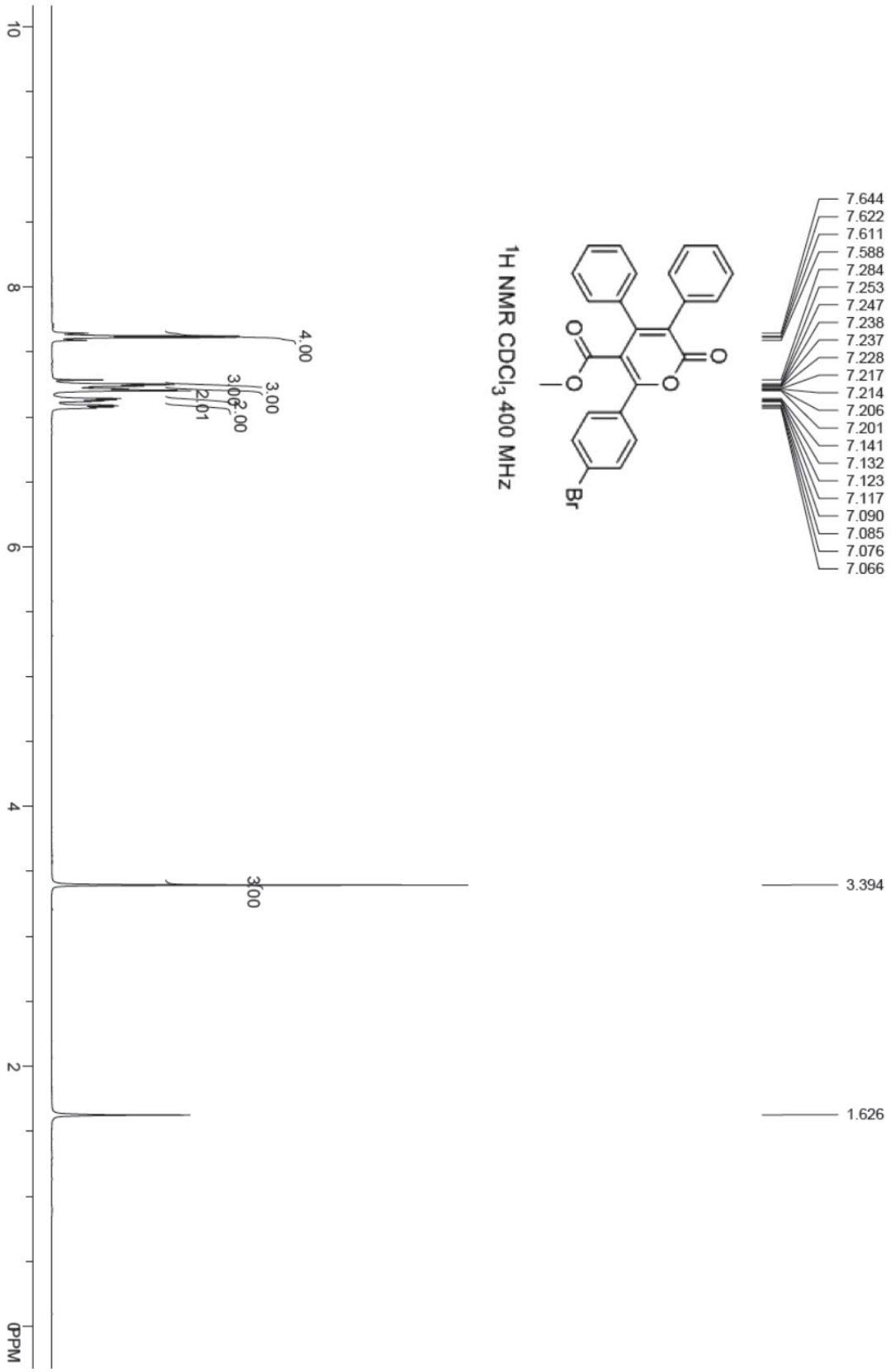

^{13}C NMR CDCl$_3$ 100 MHz
166.402
165.552
163.027
161.090
157.302
151.502
135.351
132.912
130.574
130.365
130.270
128.538
128.225
128.166
127.887
127.785
127.744
125.011
116.146
115.932
114.915
77.438
77.127
76.807
52.621
200
150
100
50
0 PPM

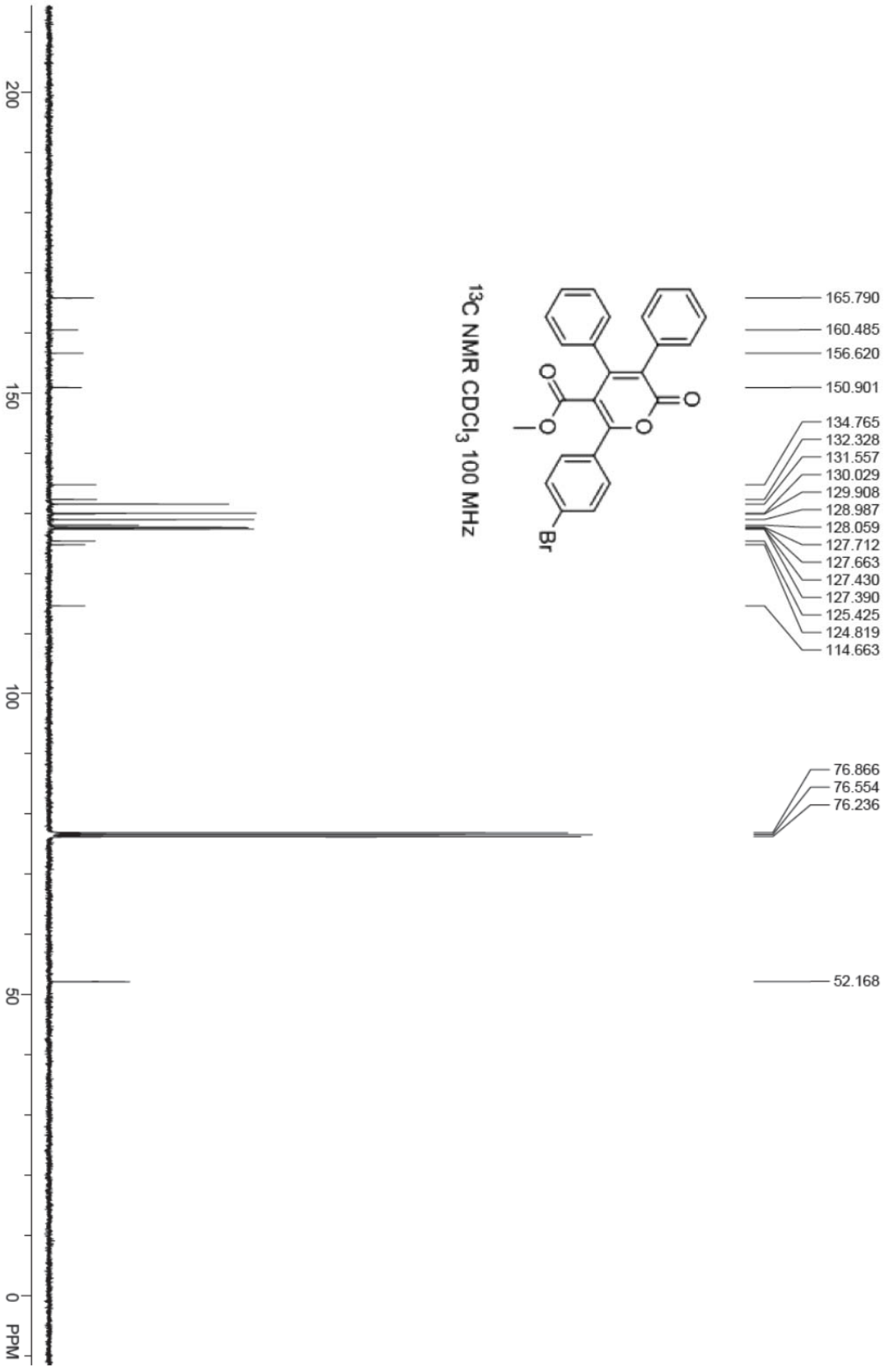
Methyl 6-(4-chlorophenyl)-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3ak)



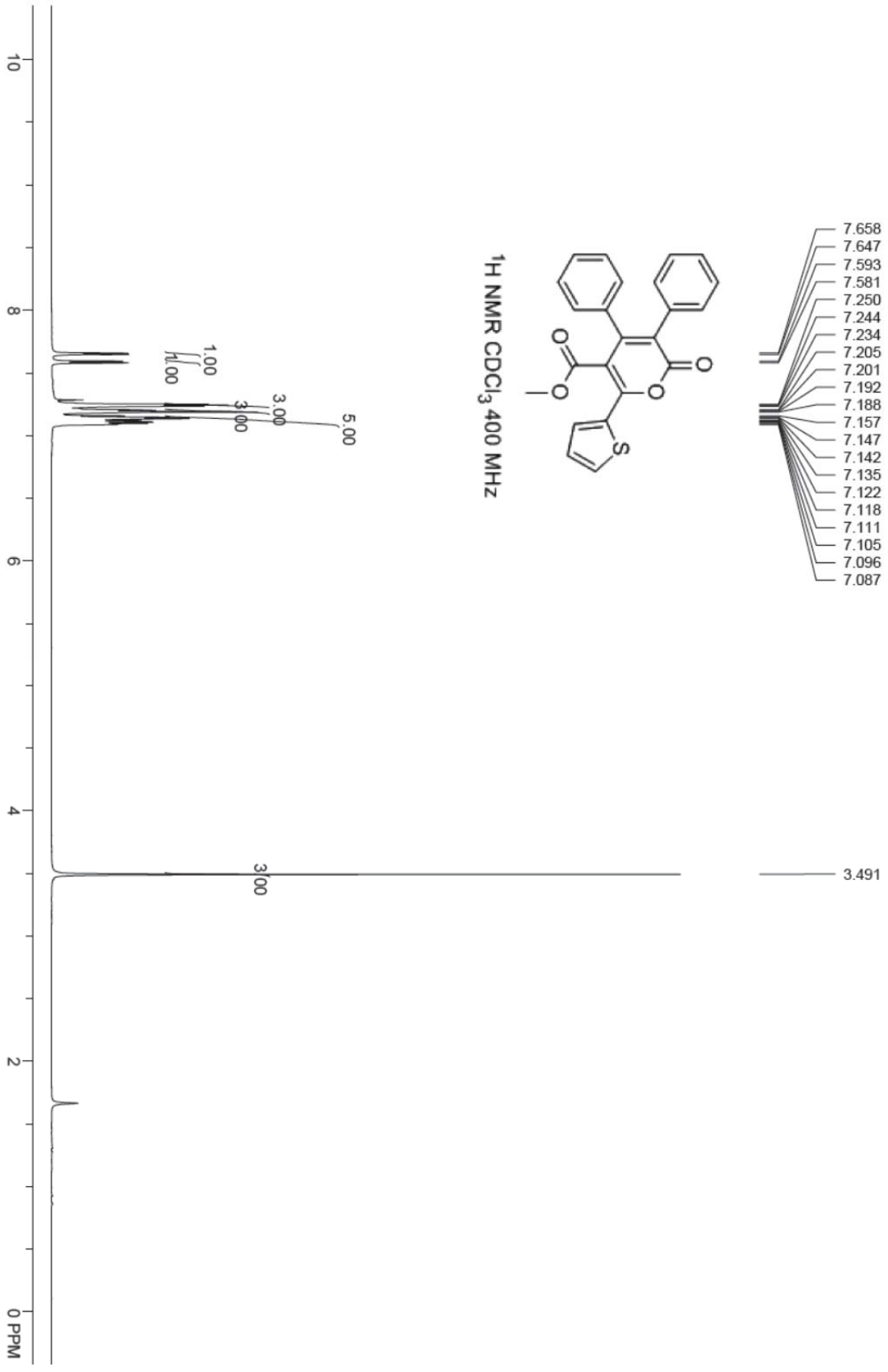

^{13}C NMR $CDCl_3$ 100 MHz
166.320
161.000
157.068
151.399
137.480
135.272
132.823
130.532
129.947
129.335
129.098
128.556
128.213
128.173
127.921
127.902
125.275
115.144
77.373
77.060
76.748
52.678
O
O
O
O
Cl
200
150
100
50
PPM

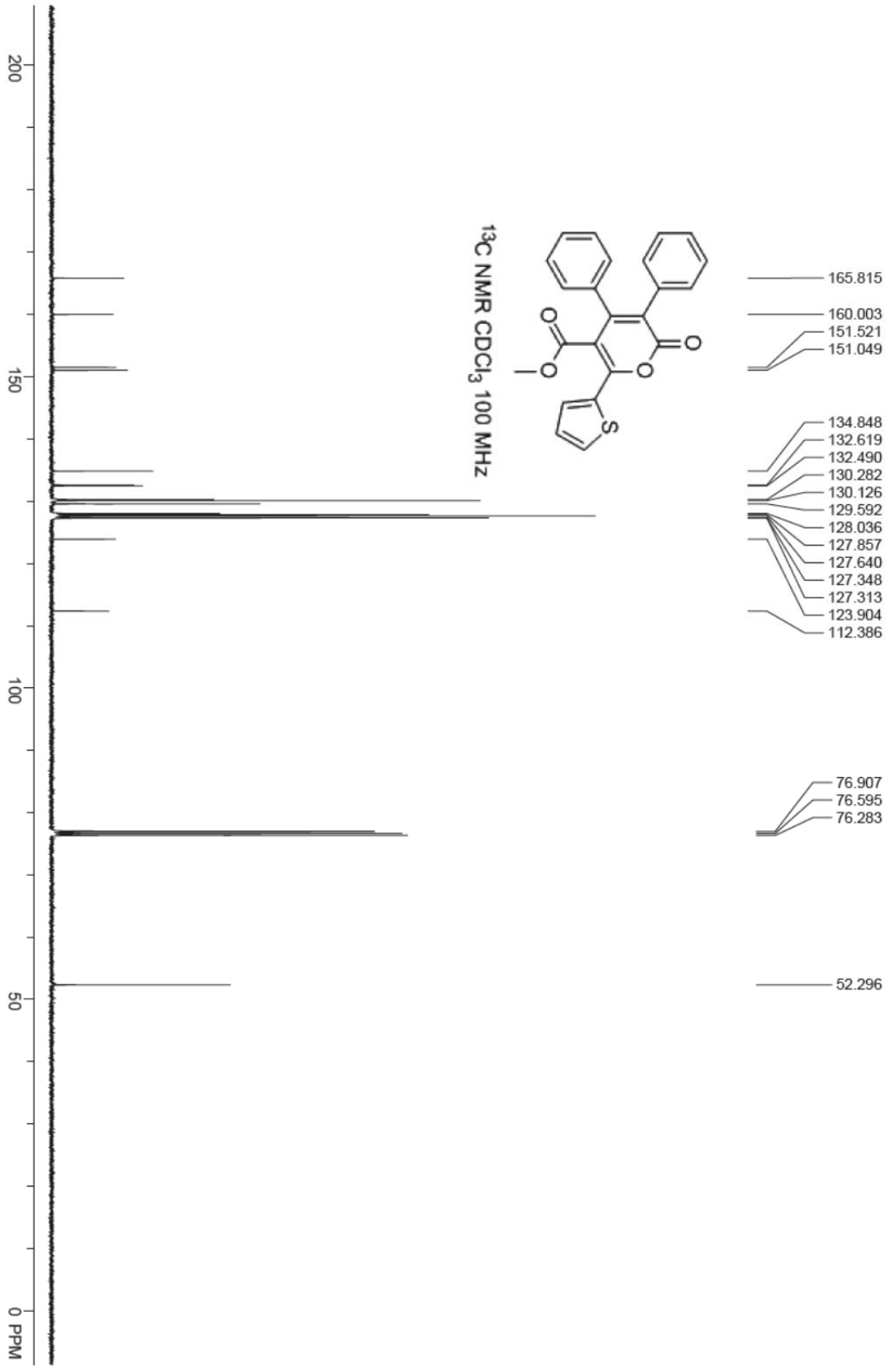
Methyl 6-(4-bromophenyl)-2-oxo-3,4-diphenyl-2H-pyran-5-carboxylate (3al)



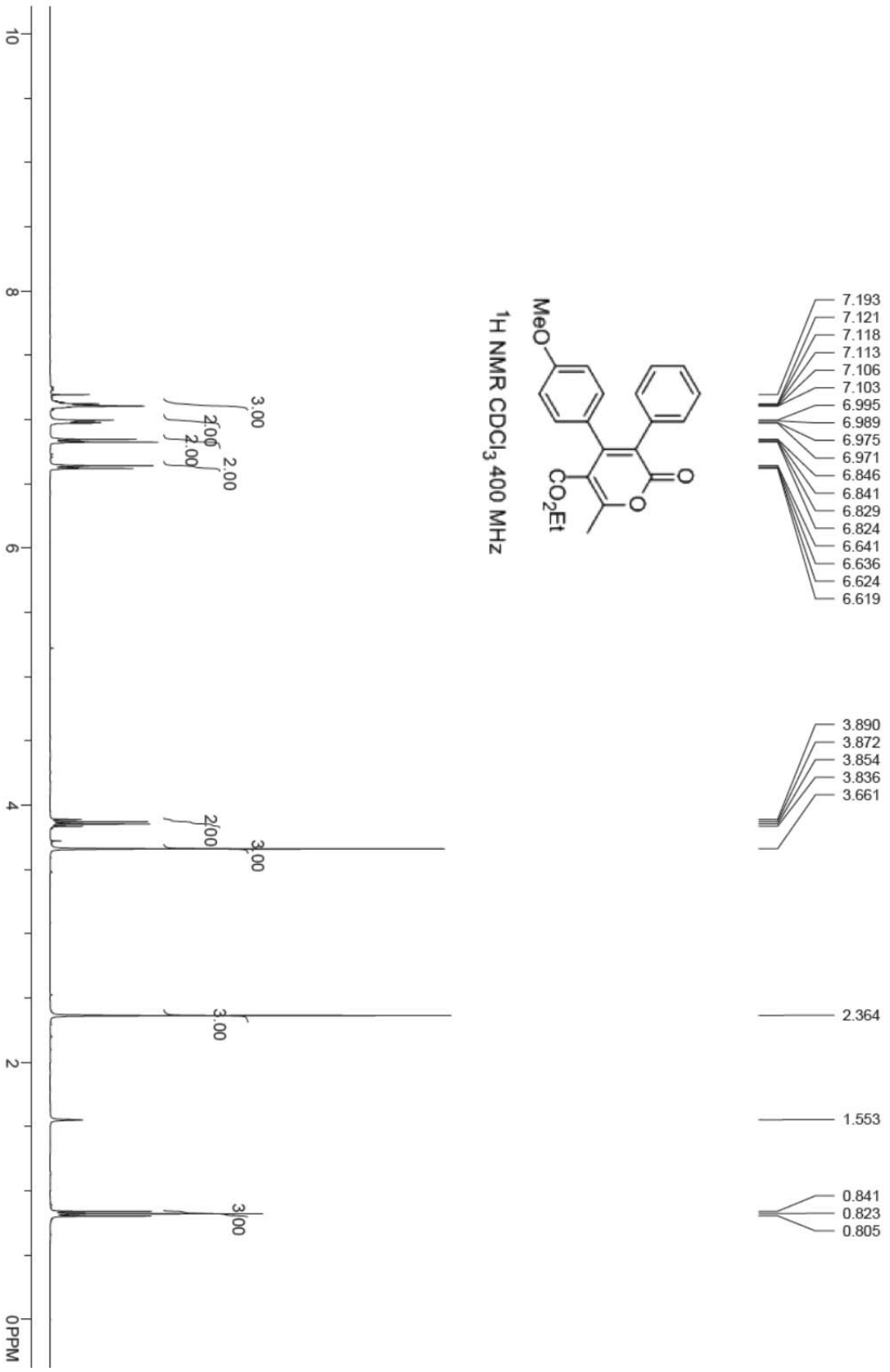

^{13}C NMR $CDCl_3$ 100 MHz
165.790
160.485
156.620
150.901
134.765
132.328
131.557
130.029
129.908
128.987
128.059
127.712
127.663
127.430
127.390
125.425
124.819
114.663
76.866
76.554
76.236
52.168
Br
O
O
O
O
200
150
100
50
0
PPM

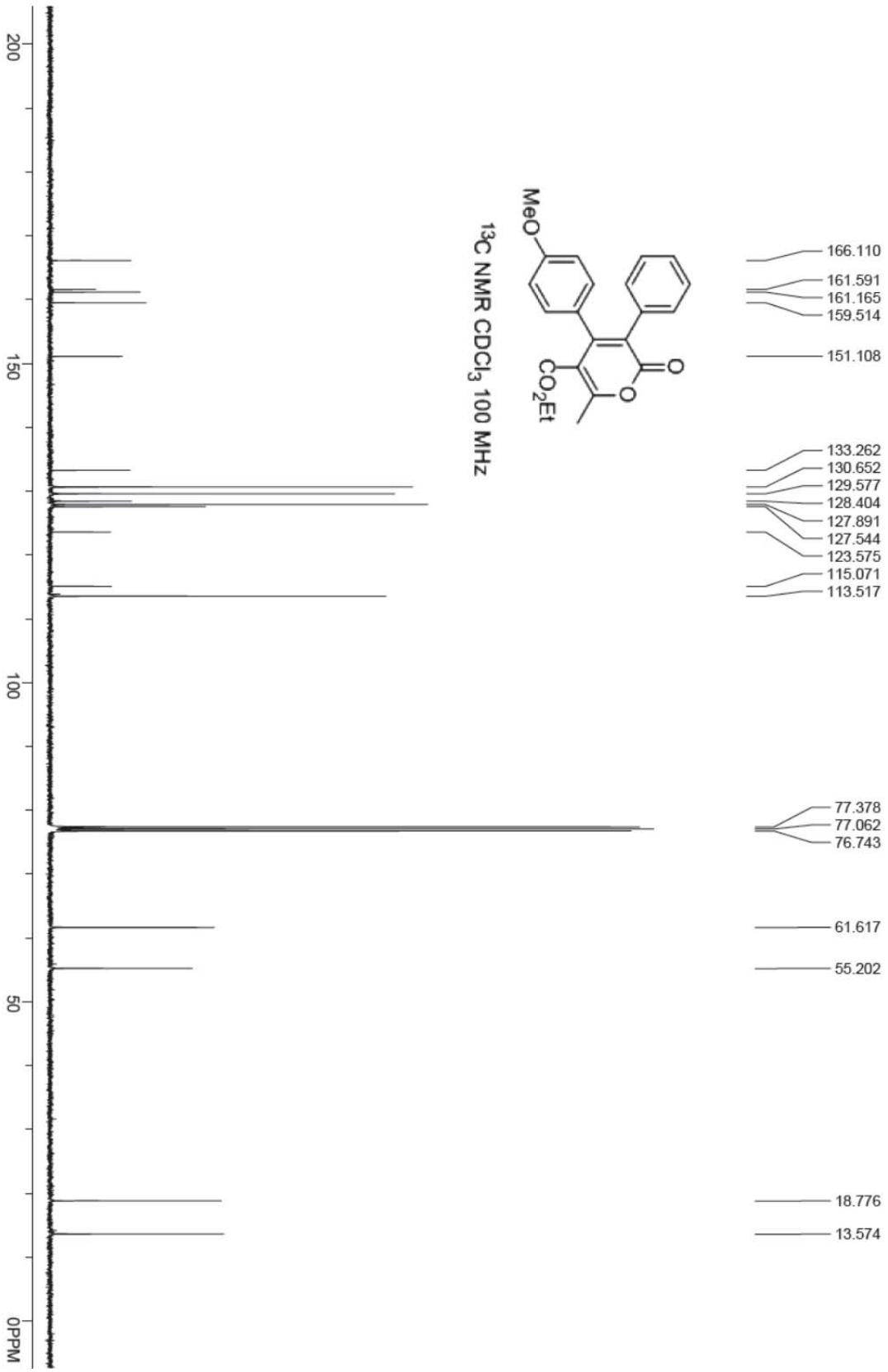
Methyl 2-oxo-3,4-diphenyl-6-(thiophen-2-yl)-2H-pyran-5-carboxylate (3am)



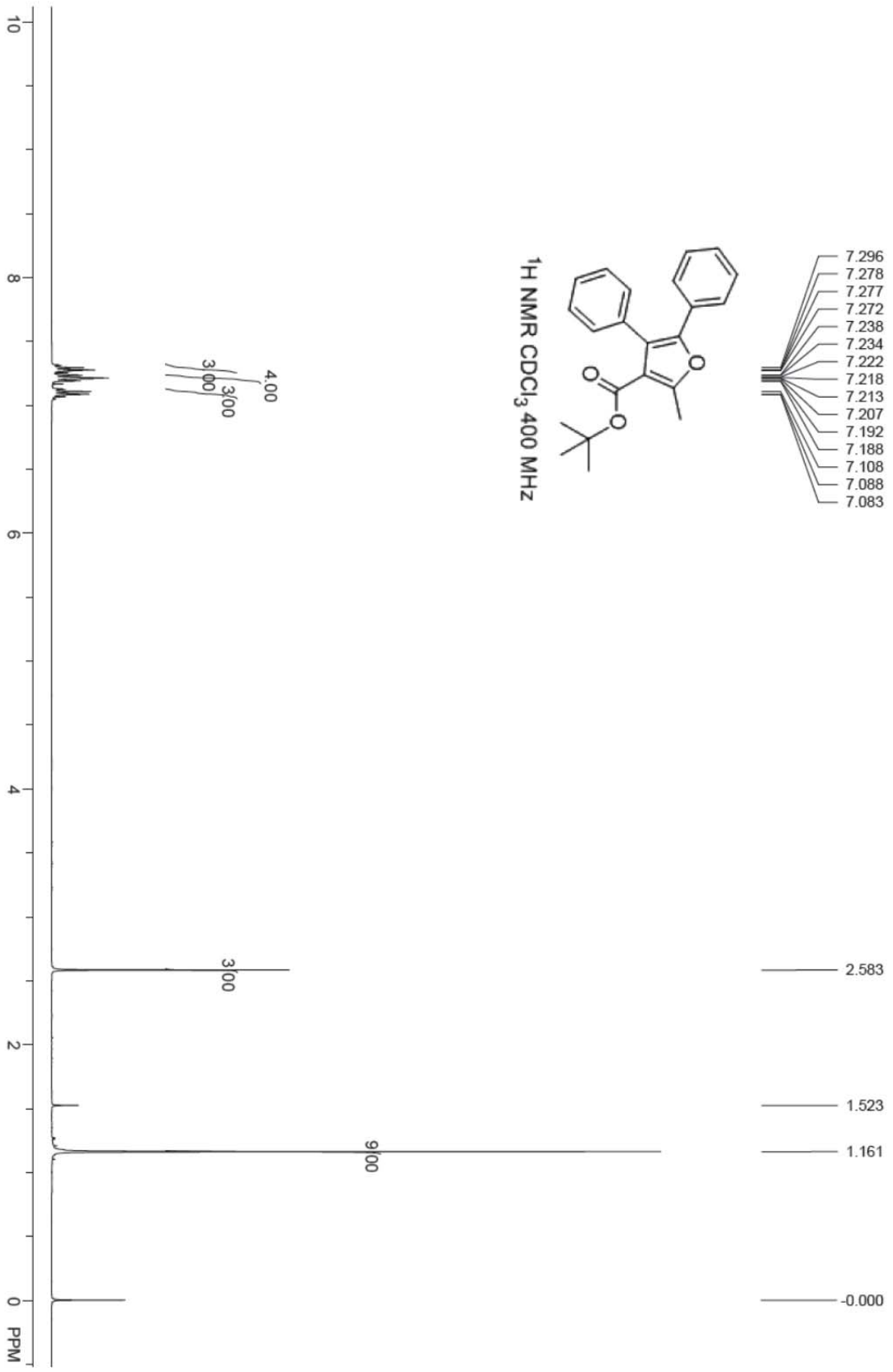

^{13}C NMR $CDCl_3$ 100 MHz
165.815
160.003
151.521
151.049
134.848
132.619
132.490
130.282
130.126
129.592
128.036
127.857
127.640
127.348
127.313
123.904
112.386
76.907
76.595
76.283
52.296
200
150
100
50
0 PPM

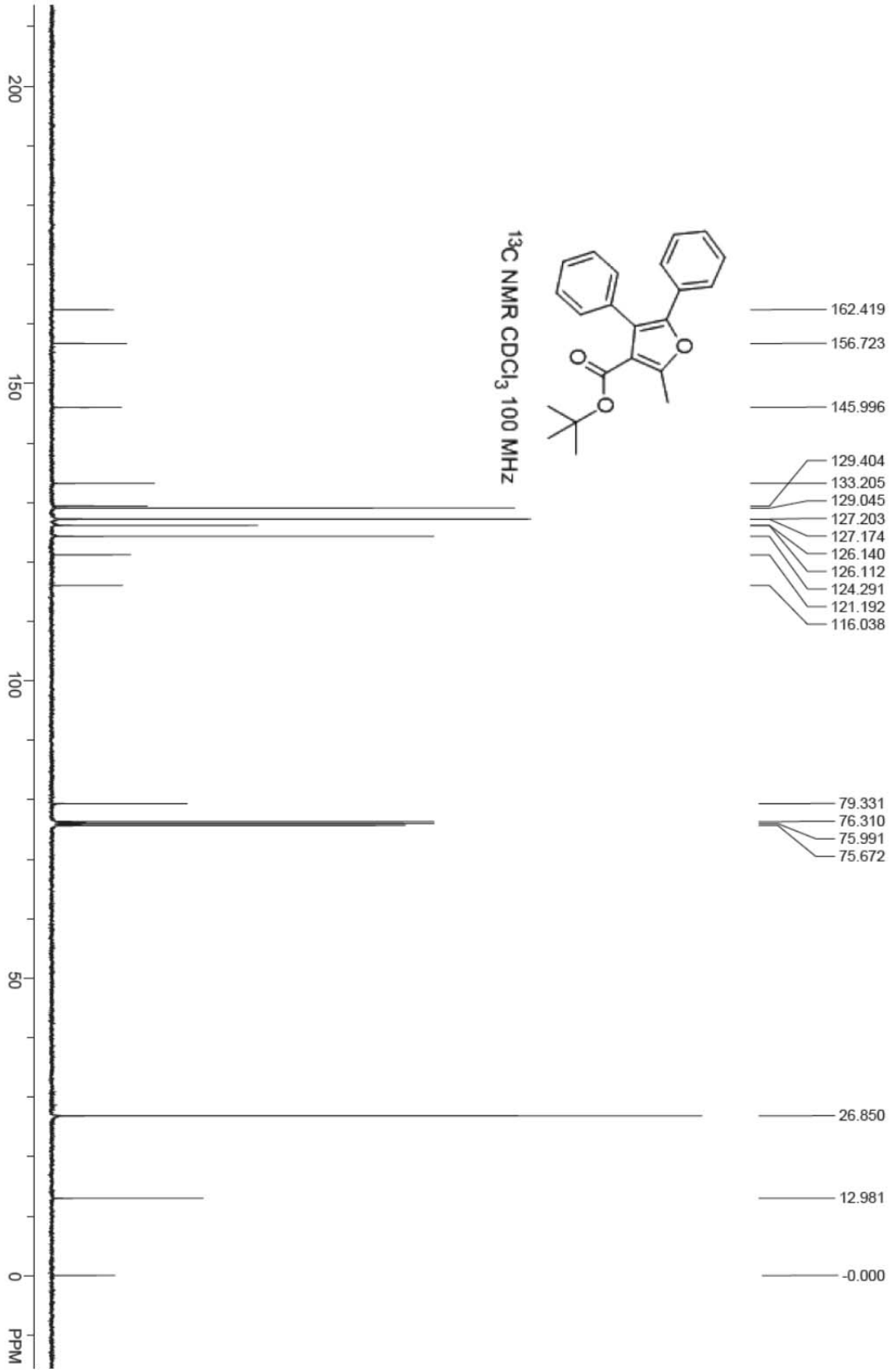
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3-phenyl-2*H*-pyran-5-carboxylate (3fb)



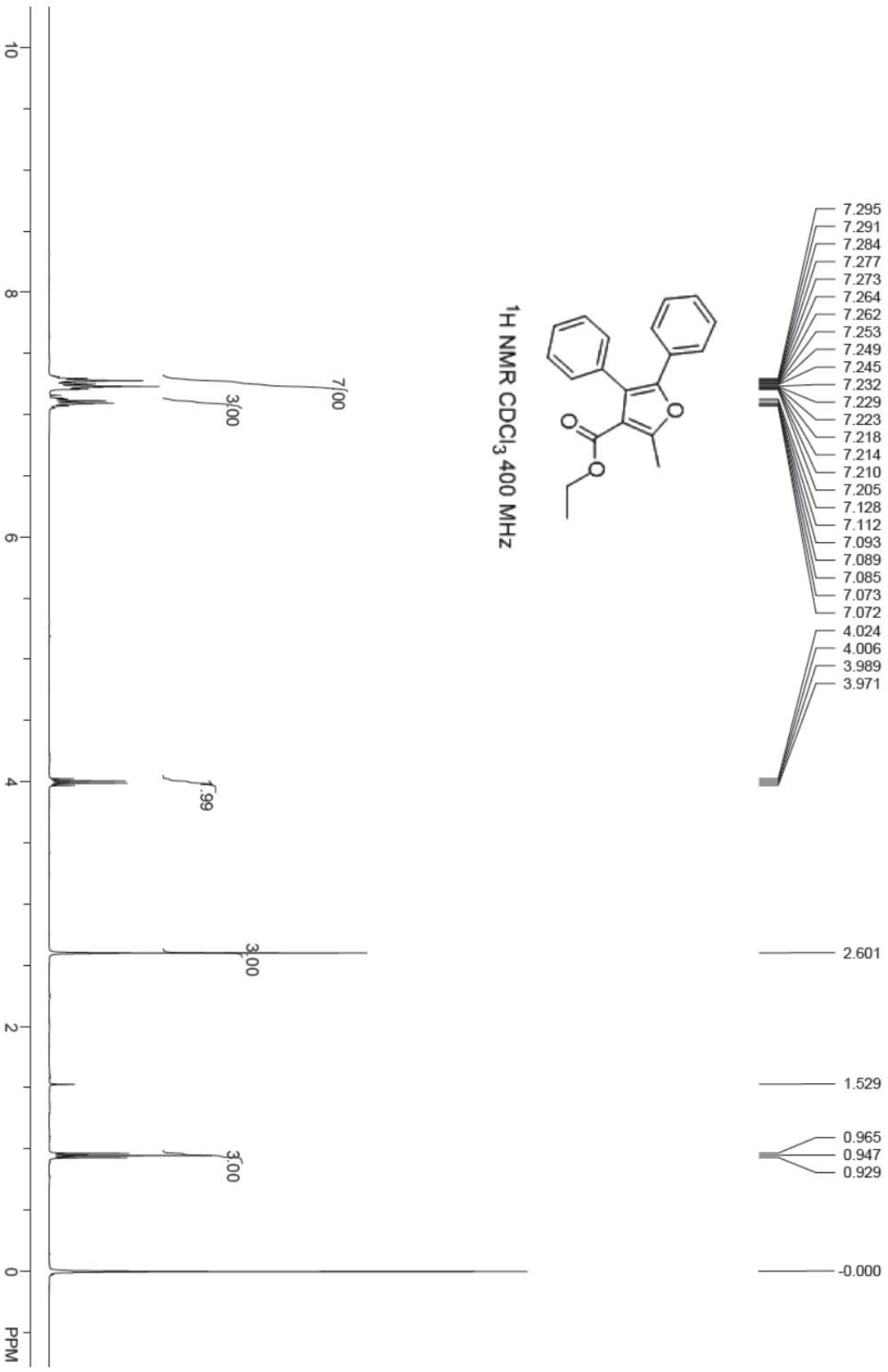

^{13}C NMR CDCl$_3$ 100 MHz
MeO
CO$_2$Et
O
O
166.110
161.591
161.165
159.514
151.108
133.262
130.652
129.577
128.404
127.891
127.544
123.575
115.071
113.517
77.378
77.062
76.743
61.617
55.202
18.776
13.574
200
150
100
50
0PPM

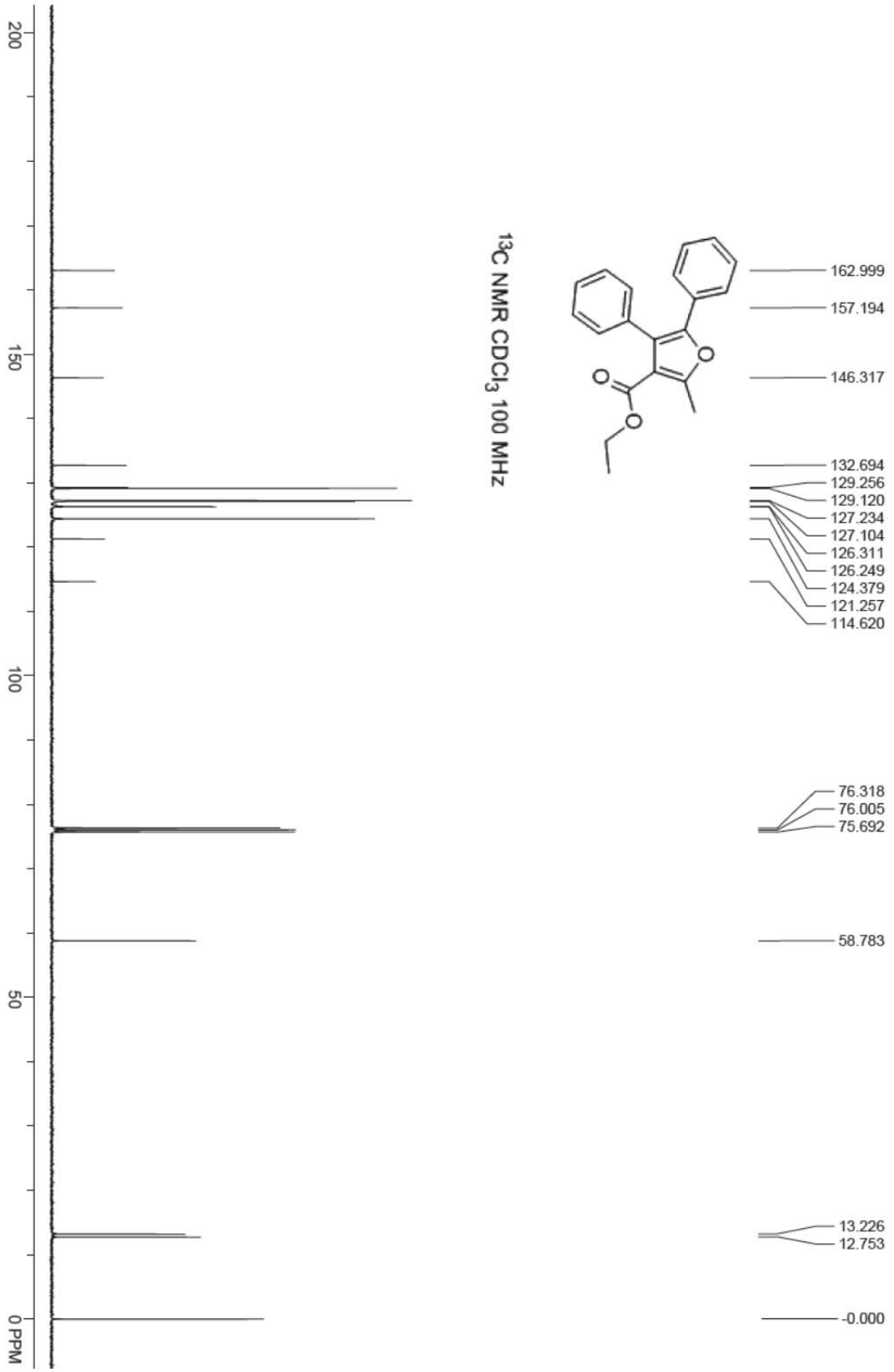
Tert-butyl 2-methyl-4,5-diphenylfuran-3-carboxylate (4aa)



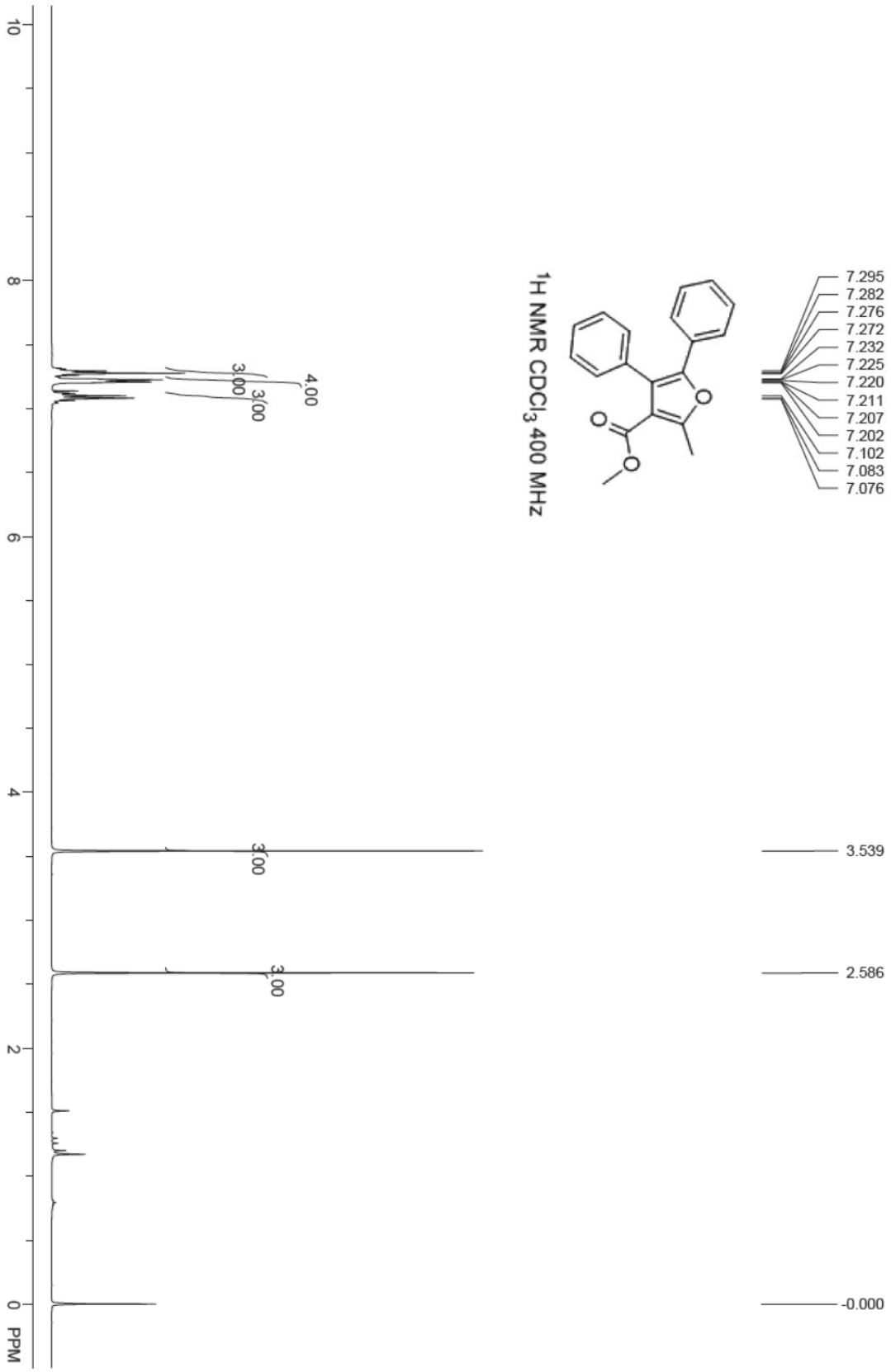

^{13}C NMR CDCl$_3$ 100 MHz
162.419
156.723
145.996
129.404
133.205
129.045
127.203
127.174
126.140
126.112
124.291
121.192
116.038
79.331
76.310
75.991
75.672
26.850
12.981
-0.000
200
150
100
50
0
PPM

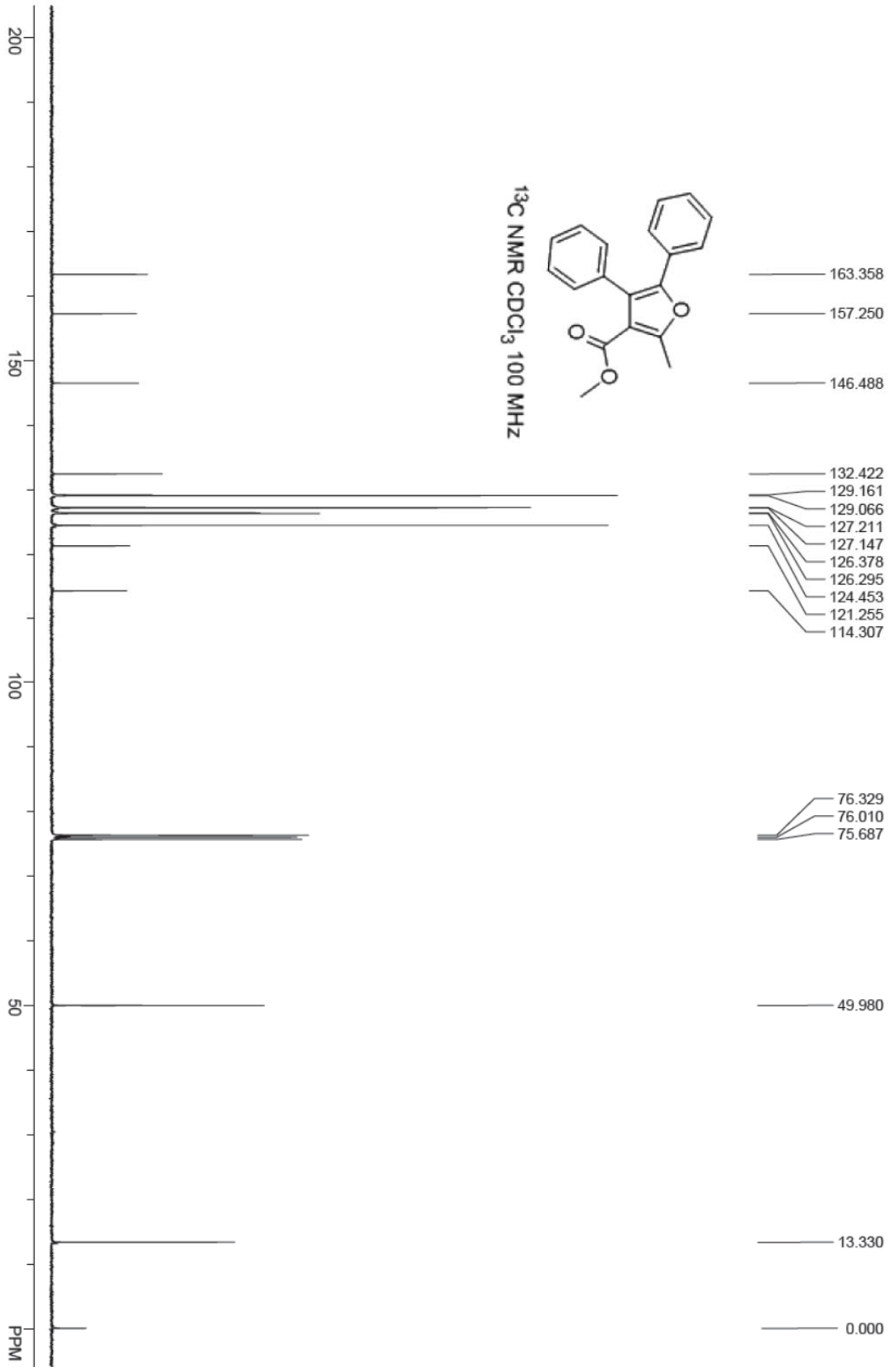
Ethyl 2,4,5-triphenylfuran-3-carboxylate (4ab)



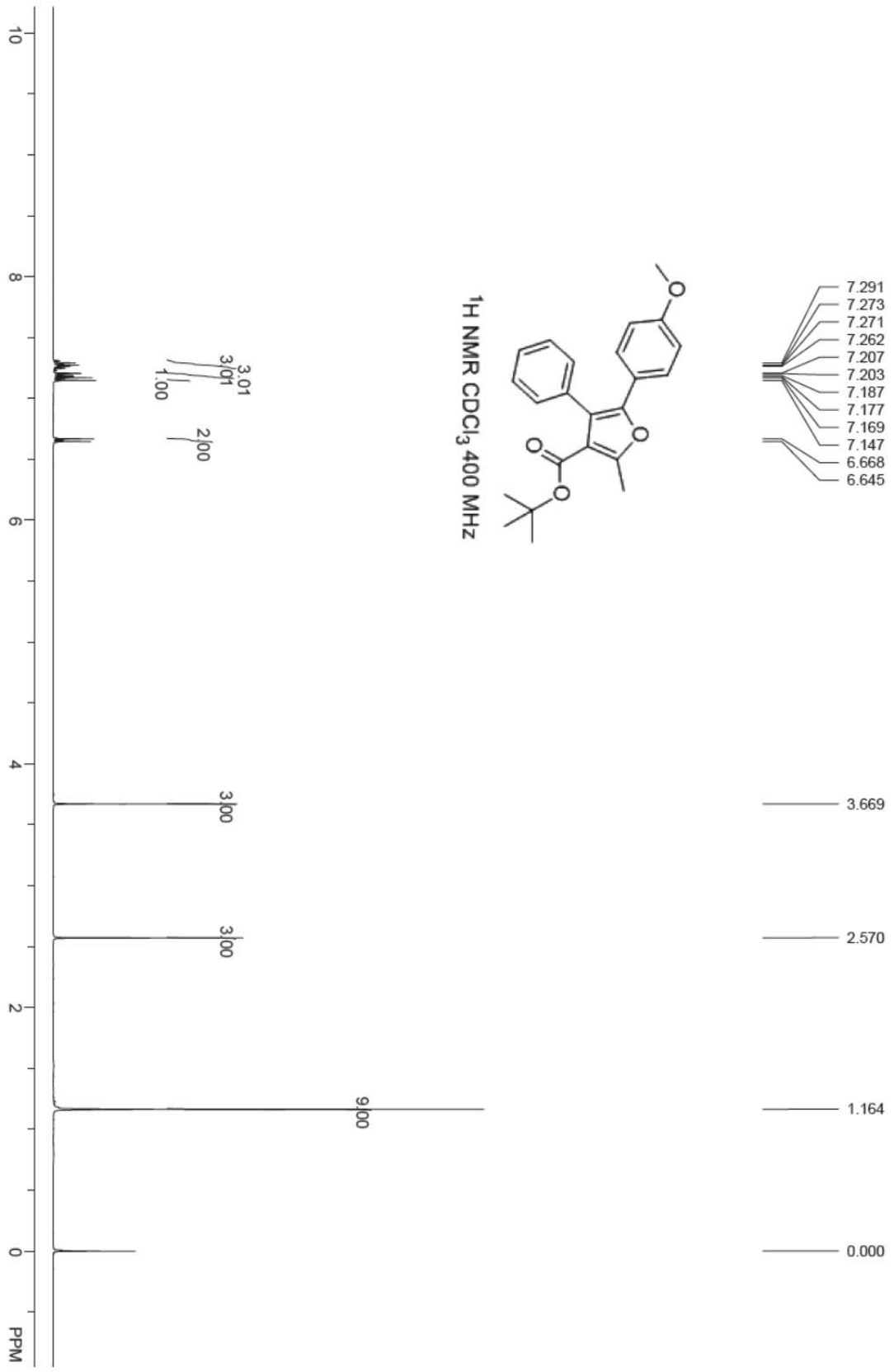

^{13}C NMR CDCl$_3$ 100 MHz
200
150
100
50
0 PPM
162.999
157.194
146.317
132.694
129.256
129.120
127.234
127.104
126.311
126.249
124.379
121.257
114.620
76.318
76.005
75.692
58.783
13.226
12.753
-0.000

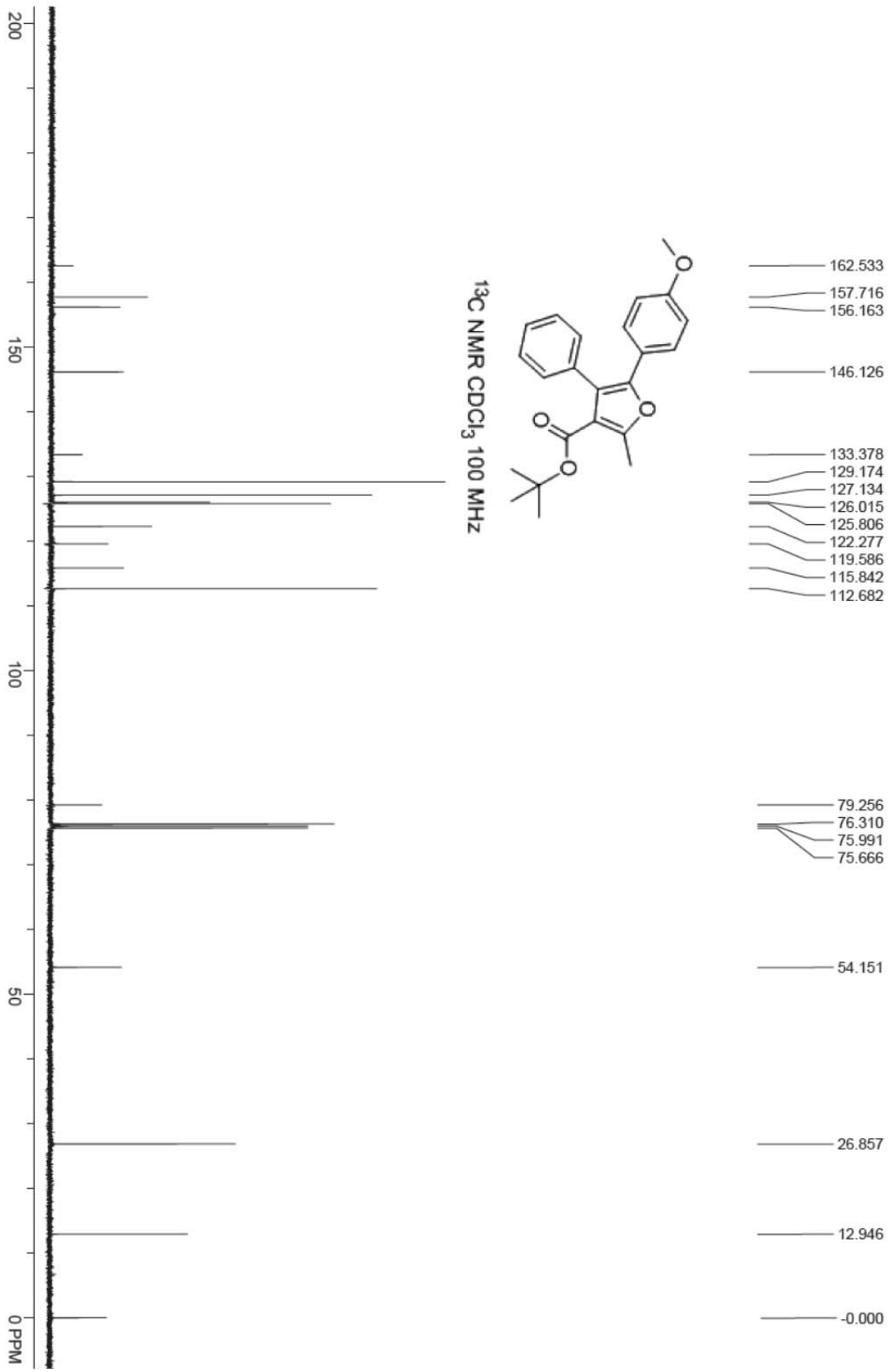
Methyl 2,4,5-triphenylfuran-3-carboxylate (4ac)



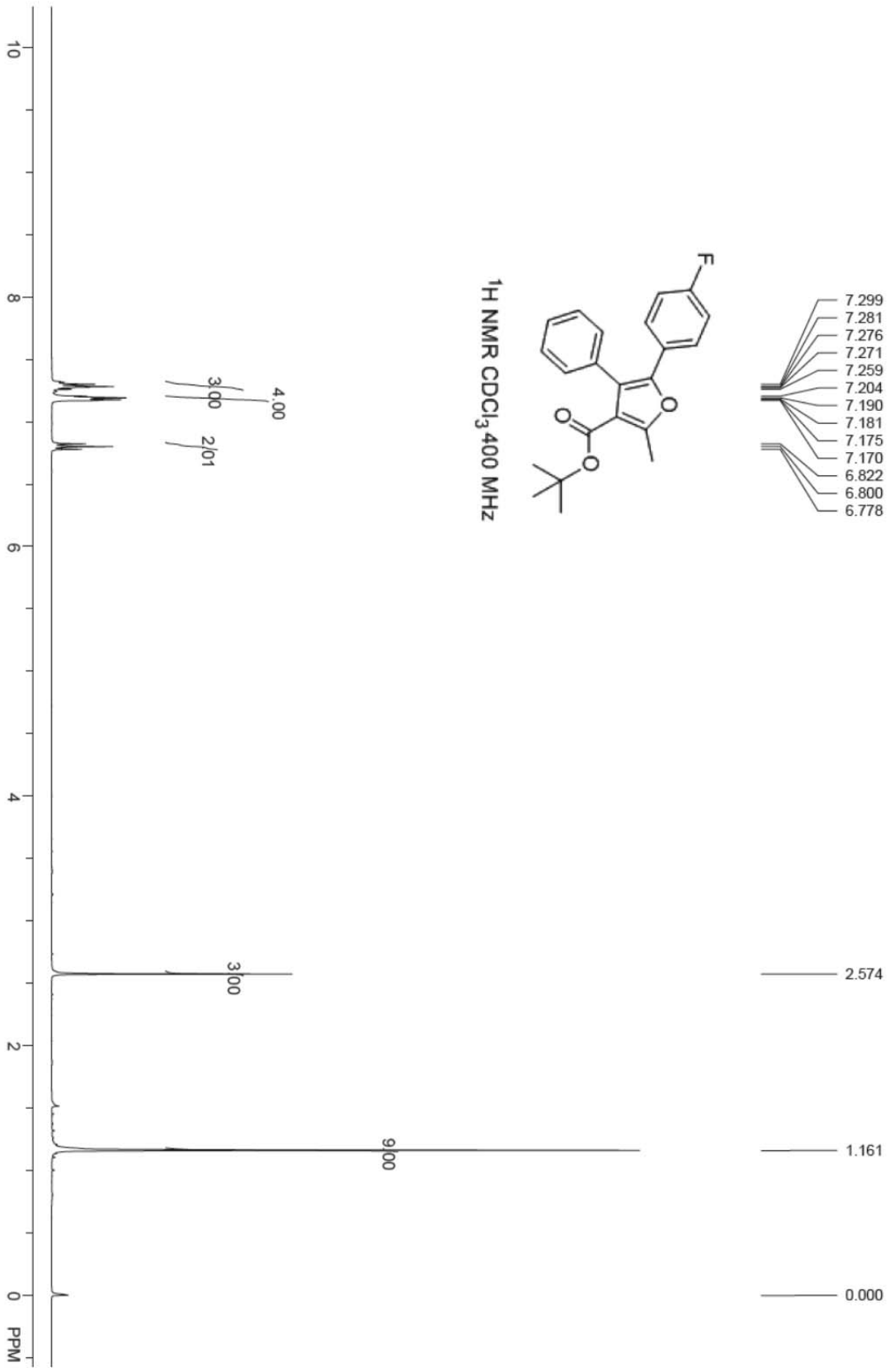

^{13}C NMR $CDCl_3$ 100 MHz
200
150
100
50
PPM
163.358
157.250
146.488
132.422
129.161
129.066
127.211
127.147
126.378
126.295
124.453
121.255
114.307
76.329
76.010
75.687
49.980
13.330
0.000

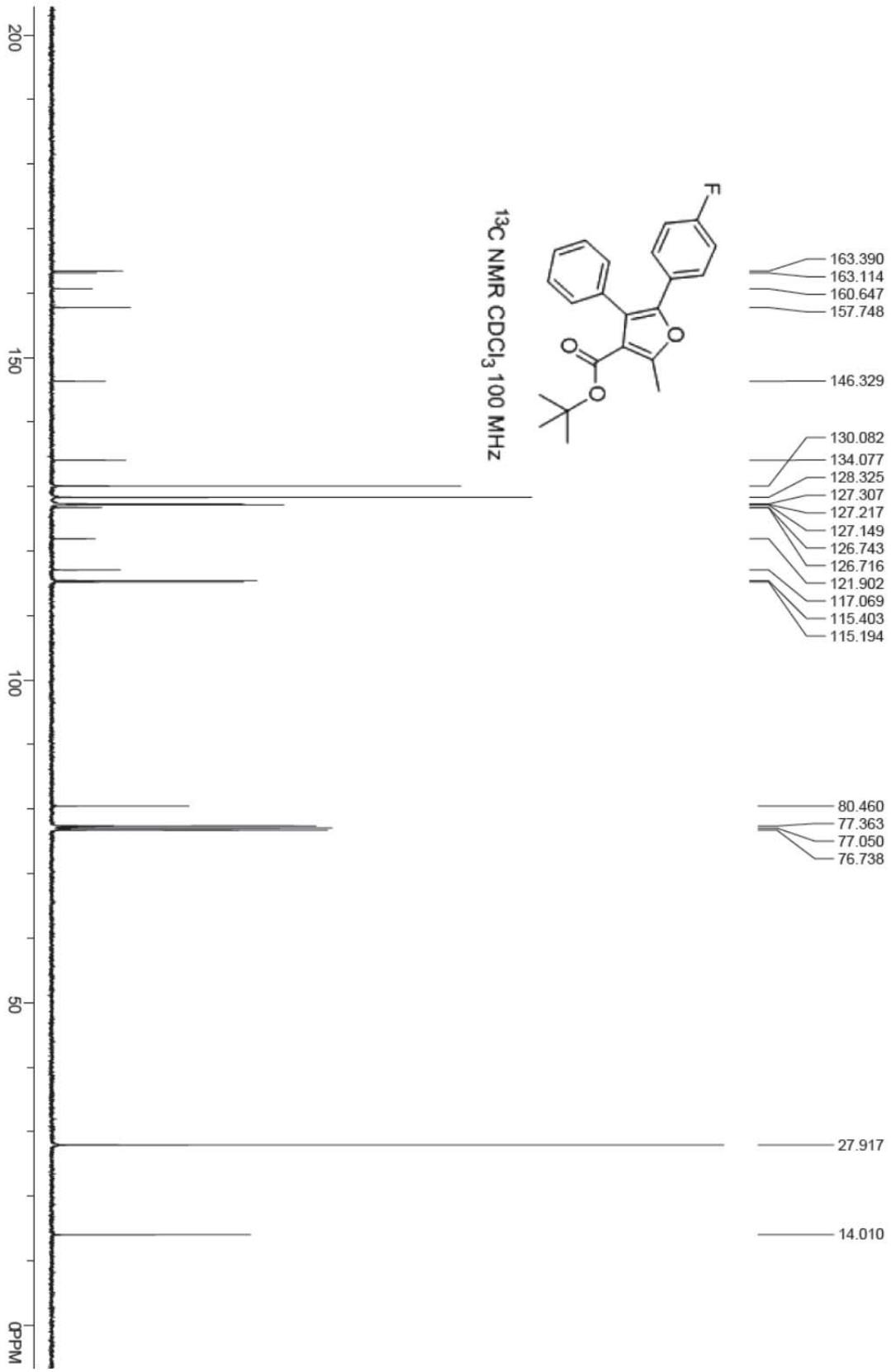
Tert-butyl 5-(4-methoxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (4ba)



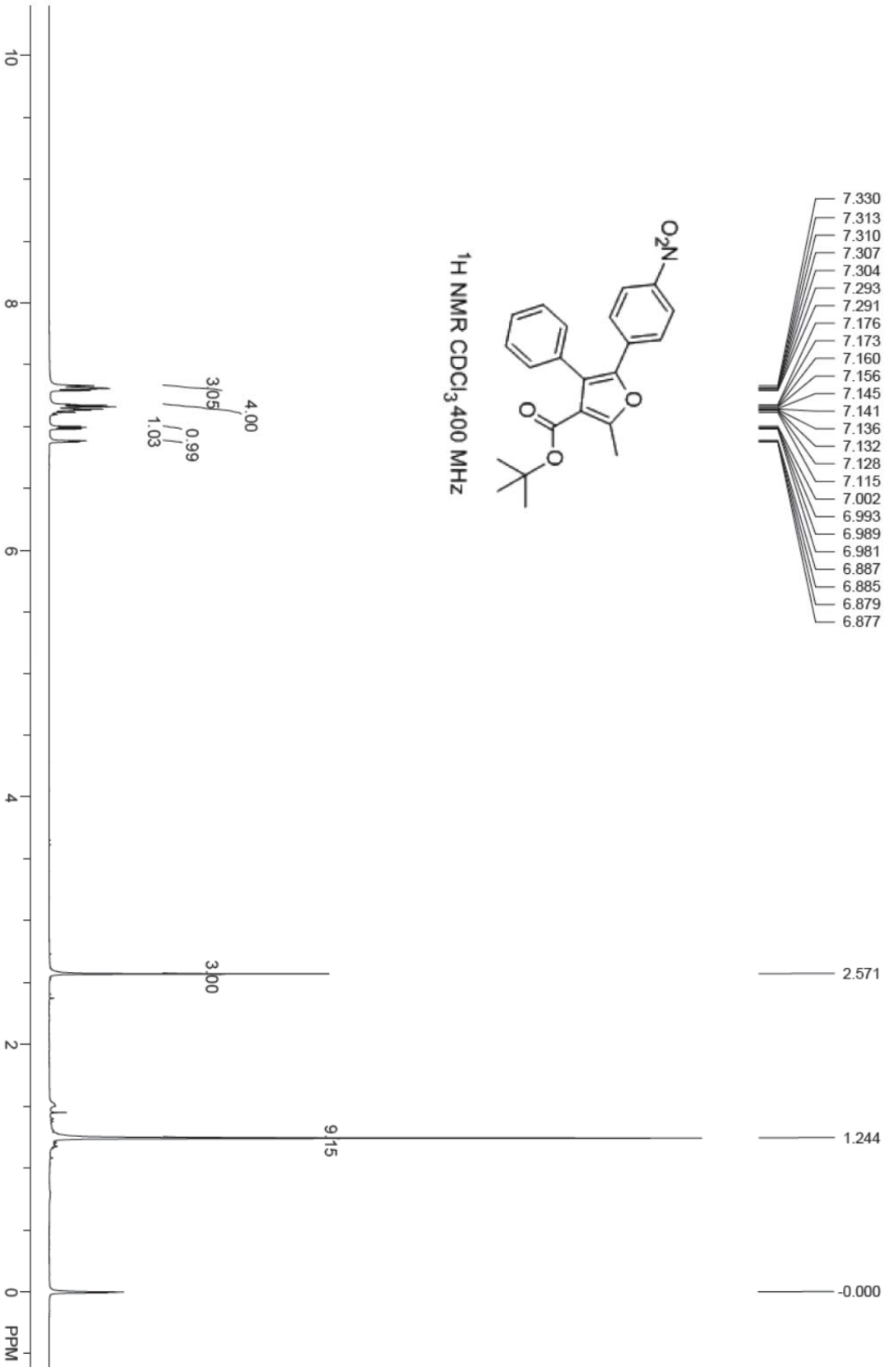

^{13}C NMR CDCl$_3$ 100 MHz
200
150
100
50
0 PPM
162.533
157.716
156.163
146.126
133.378
129.174
127.134
126.015
125.806
122.277
119.586
115.842
112.682
79.256
76.310
75.991
75.666
54.151
26.857
12.946
-0.000

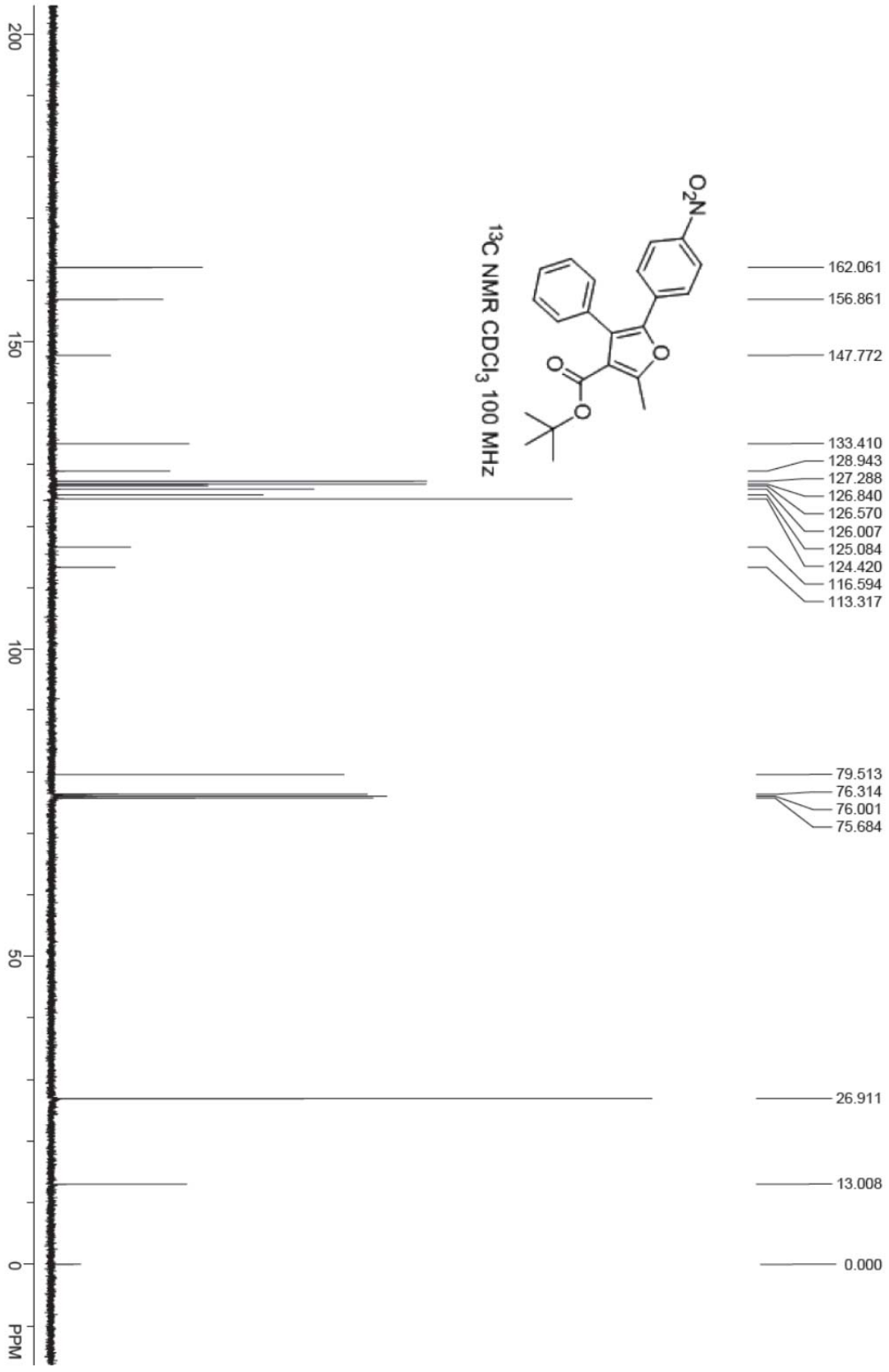
Tert-butyl 5-(4-fluorophenyl)-2-methyl-4-phenylfuran-3-carboxylate (4ca)



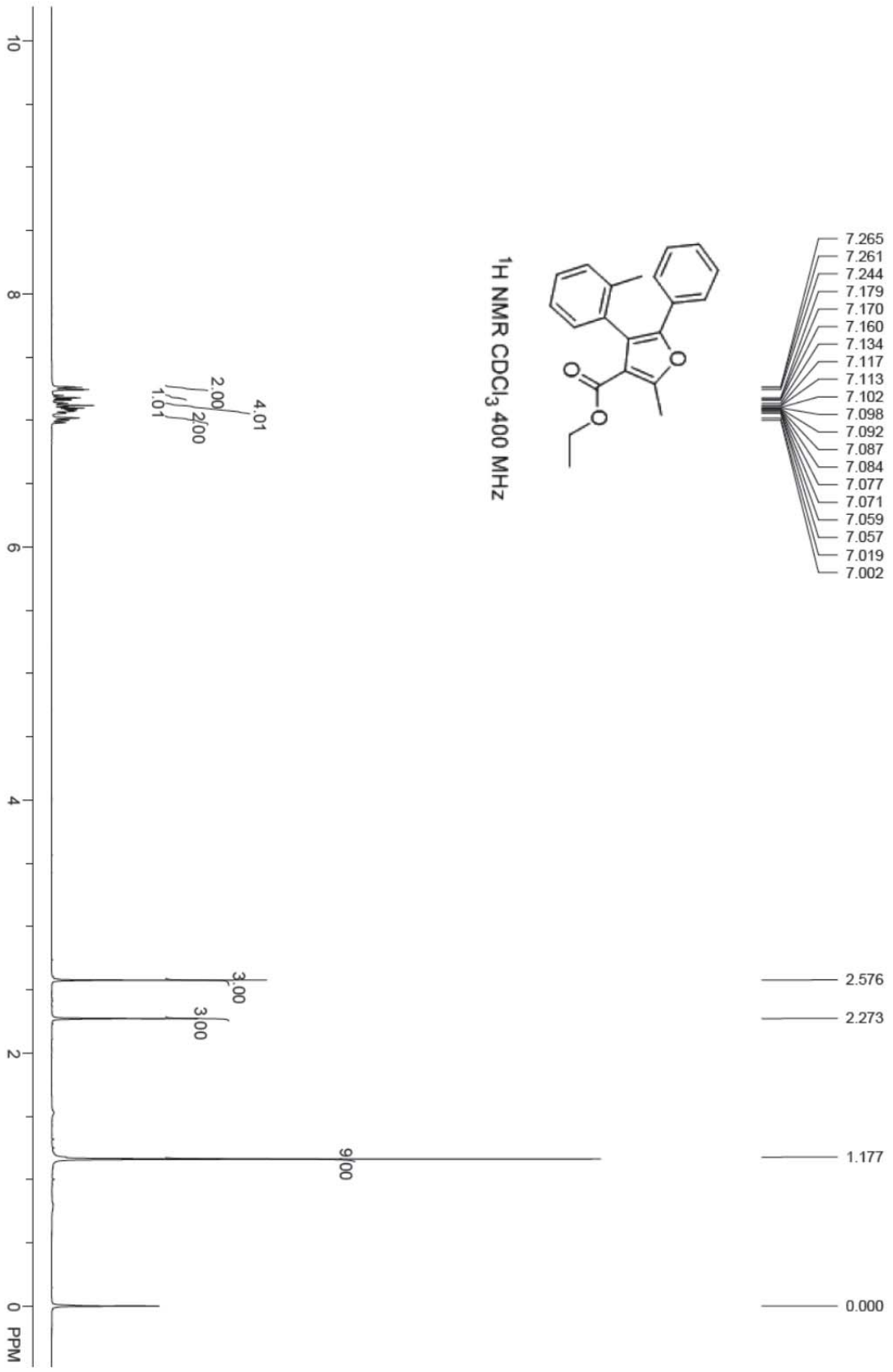

^{13}C NMR CDCl$_3$ 100 MHz
F
O
O
O
163.390
163.114
160.647
157.748
146.329
130.082
134.077
128.325
127.307
127.217
127.149
126.743
126.716
121.902
117.069
115.403
115.194
80.460
77.363
77.050
76.738
27.917
14.010
200
150
100
50
0PPM

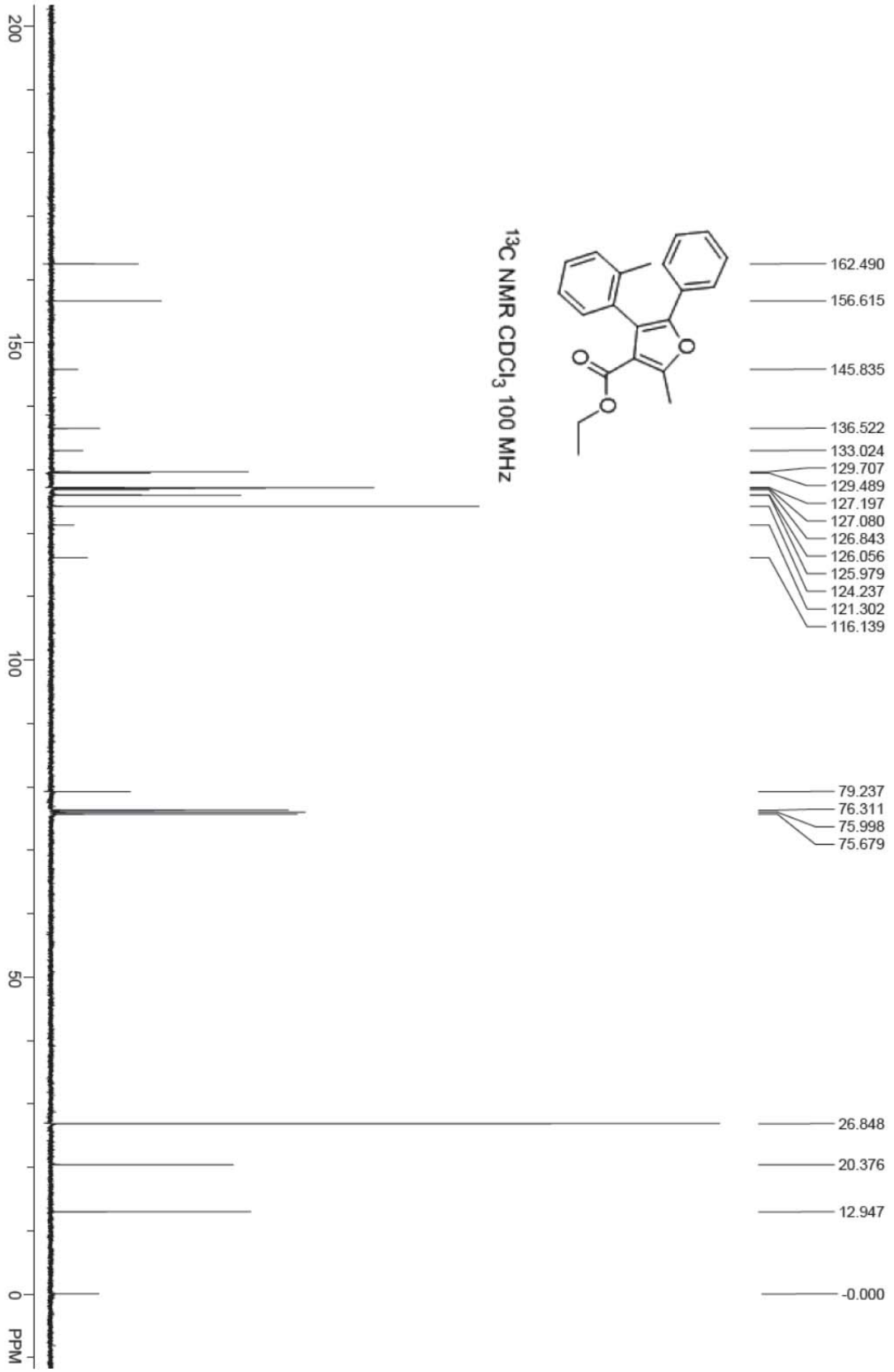
Tert-butyl 2-methyl-5-(4-nitrophenyl)-4-phenylfuran-3-carboxylate (4da)



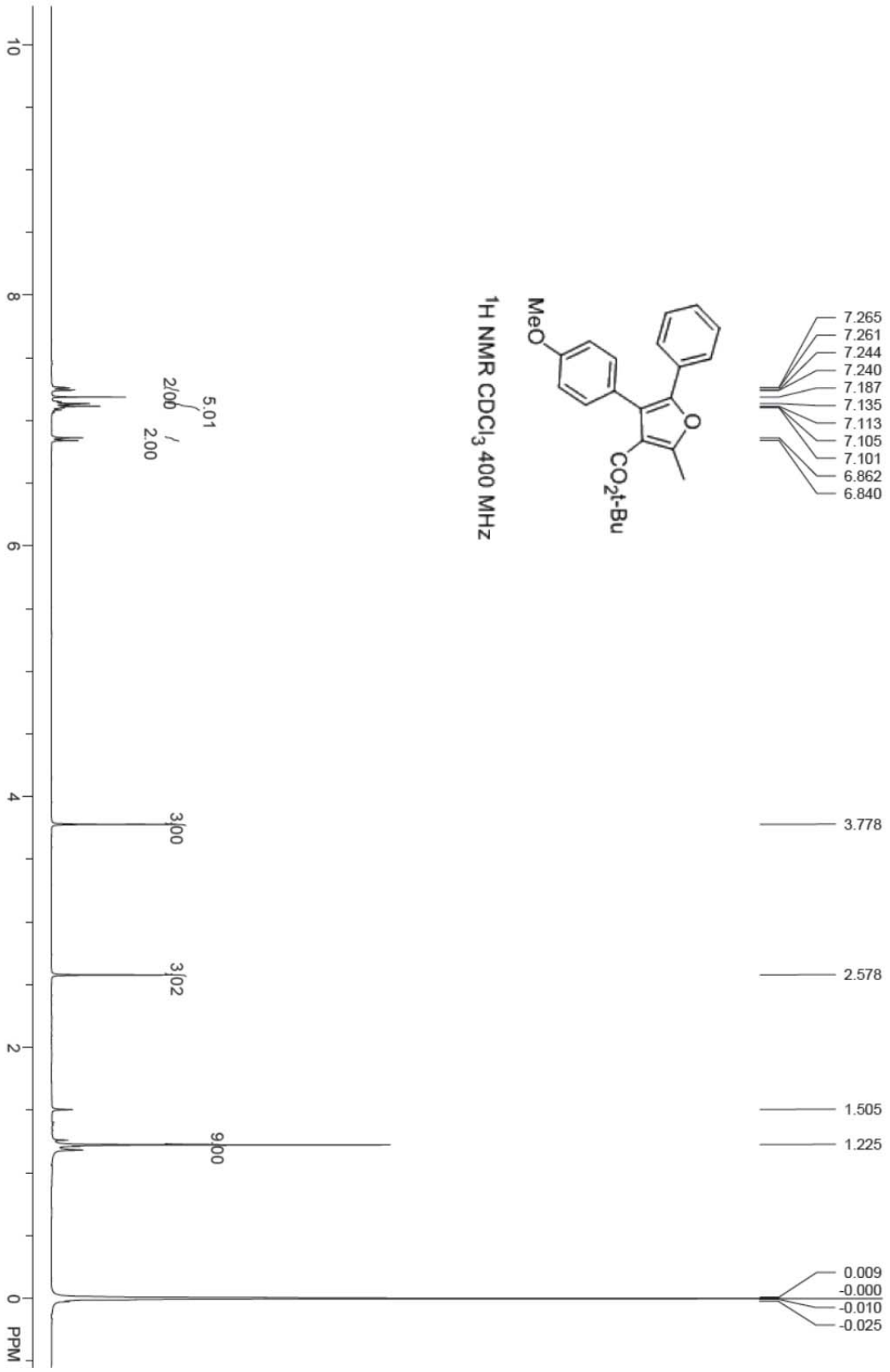

^{13}C NMR CDCl$_3$ 100 MHz
O$_2$N
O
O
O
200
150
100
50
0
PPM
162.061
156.861
147.772
133.410
128.943
127.288
126.840
126.570
126.007
125.084
124.420
116.594
113.317
79.513
76.314
76.001
75.684
26.911
13.008
0.000

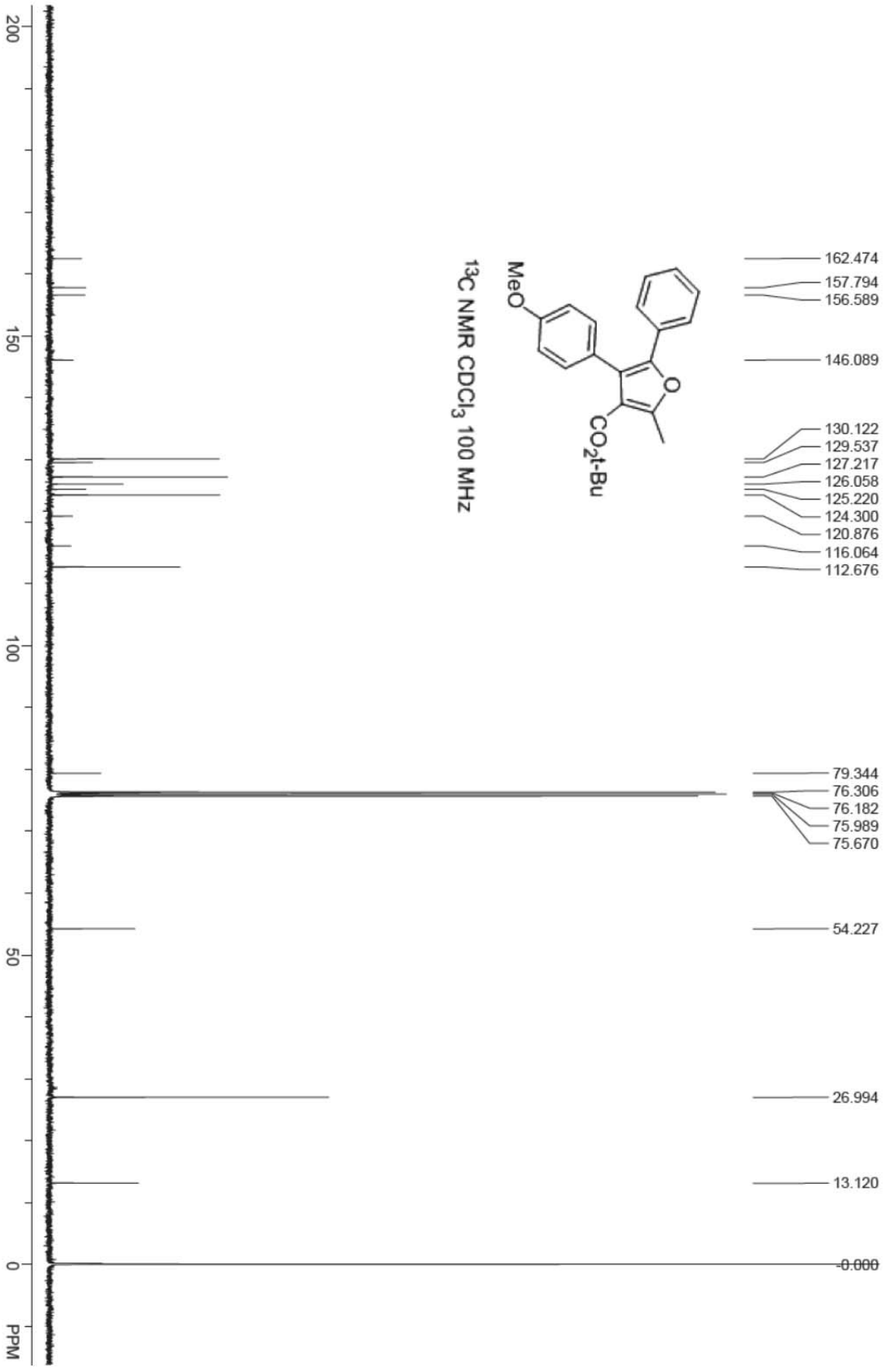
Tert-butyl 2-methyl-5-phenyl-4-(o-tolyl)furan-3-carboxylate (4ea)



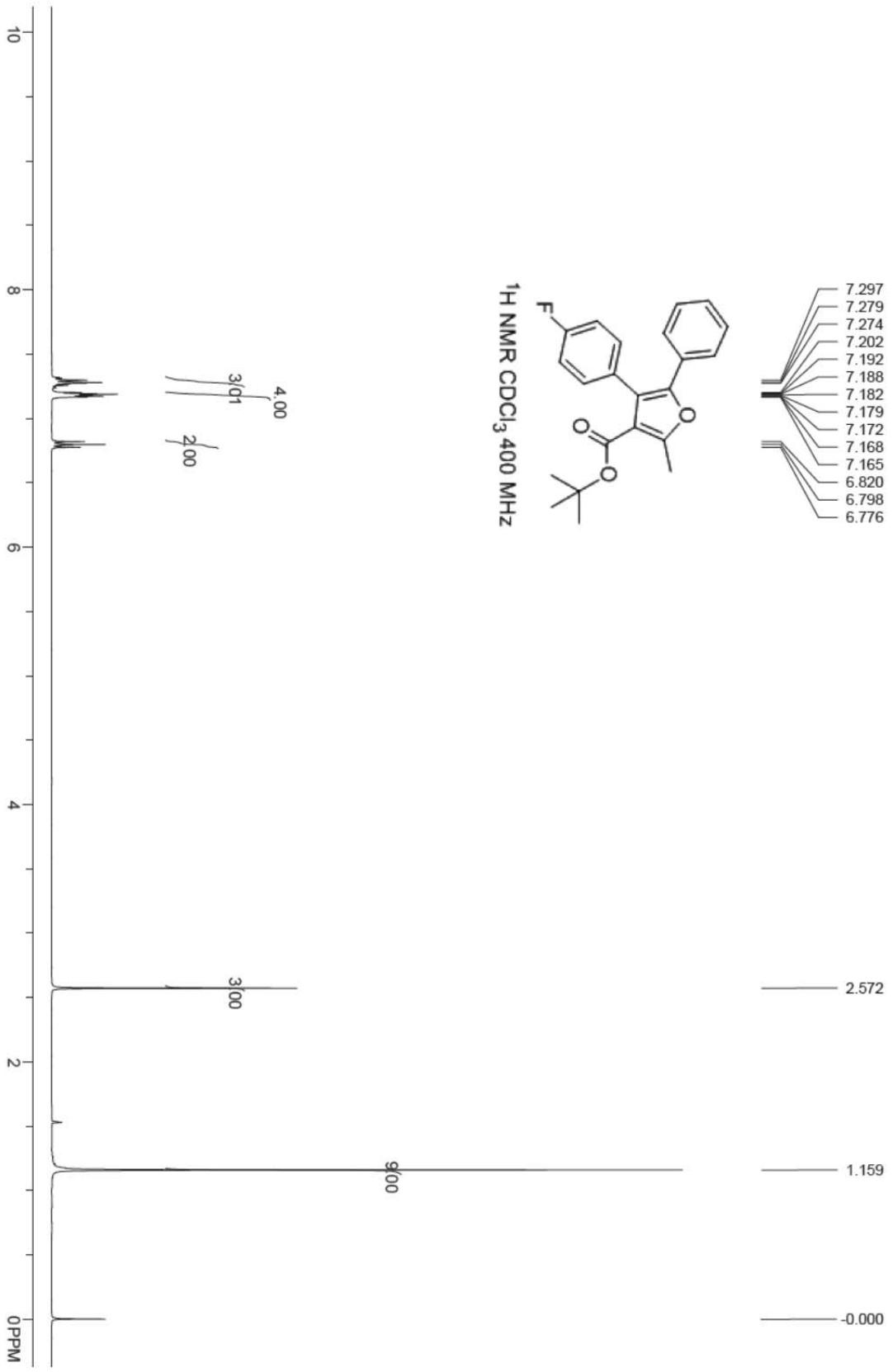

^{13}C NMR CDCl$_3$ 100 MHz
162.490
156.615
145.835
136.522
133.024
129.707
129.489
127.197
127.080
126.843
126.056
125.979
124.237
121.302
116.139
79.237
76.311
75.998
75.679
26.848
20.376
12.947
-0.000
200
150
100
50
0
PPM

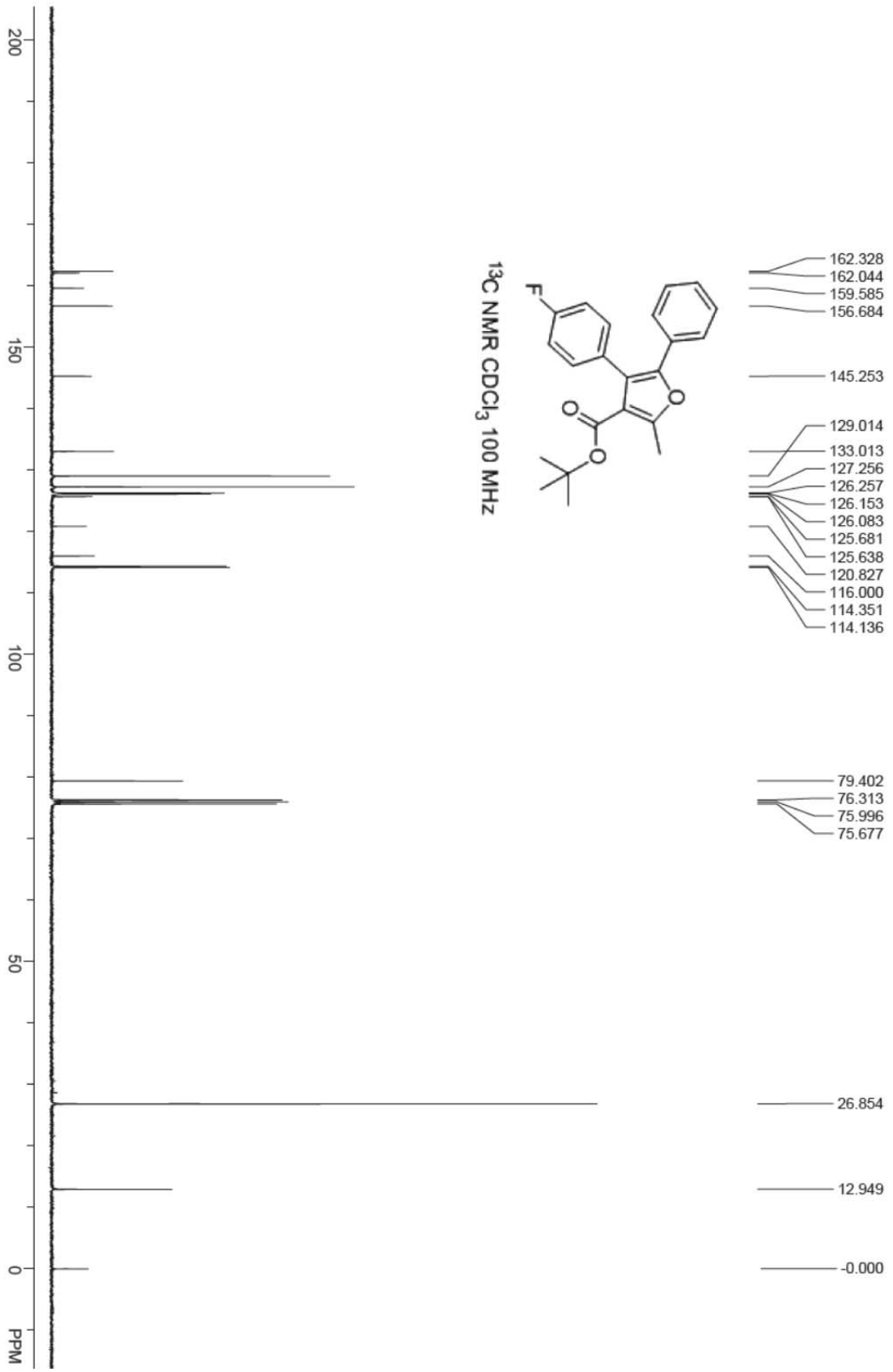
Tert-butyl 4-(4-methoxyphenyl)-2-methyl-5-phenylfuran-3-carboxylate (4fa)



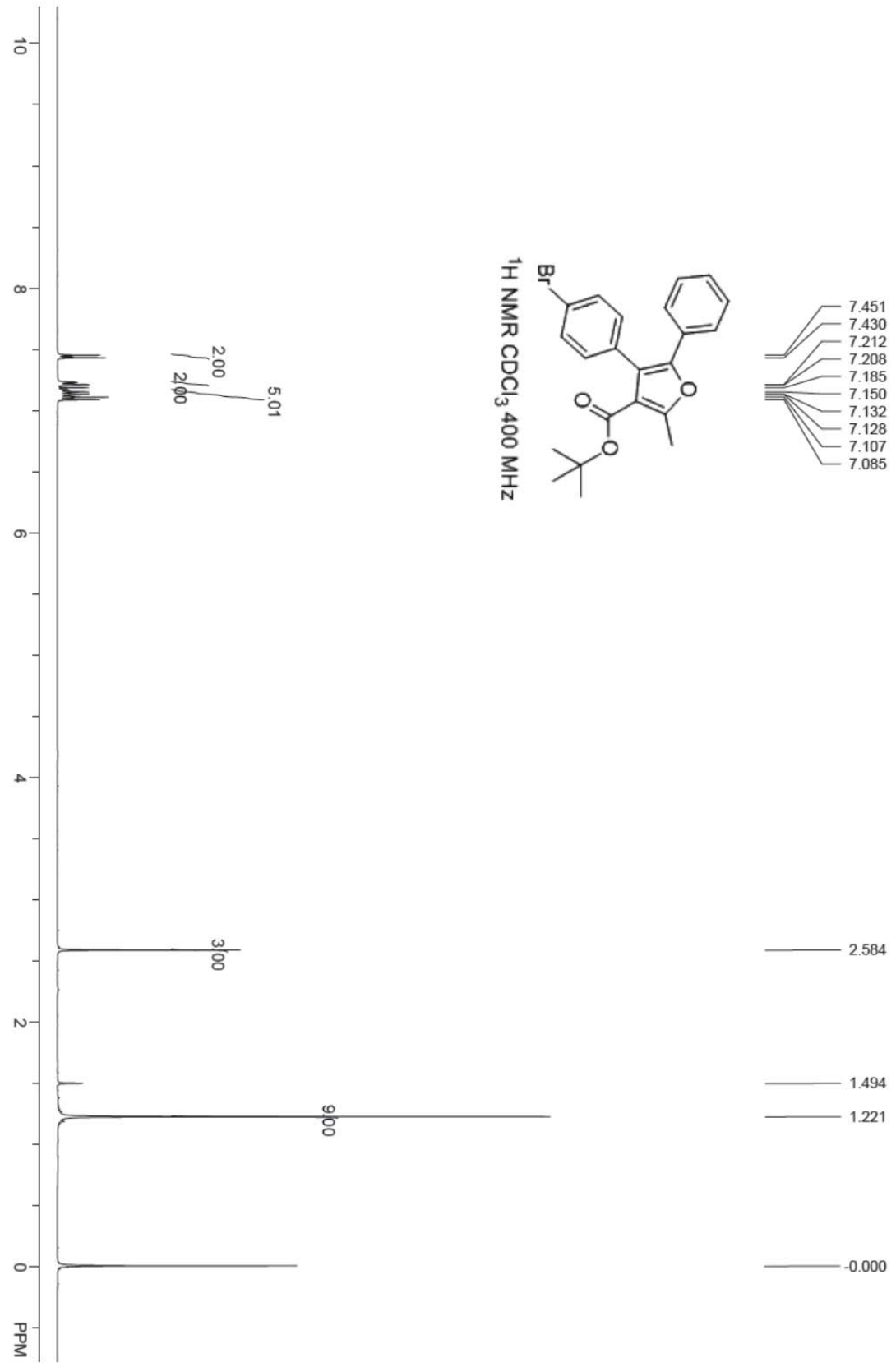

^{13}C NMR $CDCl_3$ 100 MHz
MeO
CO_2t-Bu
O
162.474
157.794
156.589
146.089
130.122
129.537
127.217
126.058
125.220
124.300
120.876
116.064
112.676
79.344
76.306
76.182
75.989
75.670
54.227
26.994
13.120
0.000
200
150
100
50
0
PPM

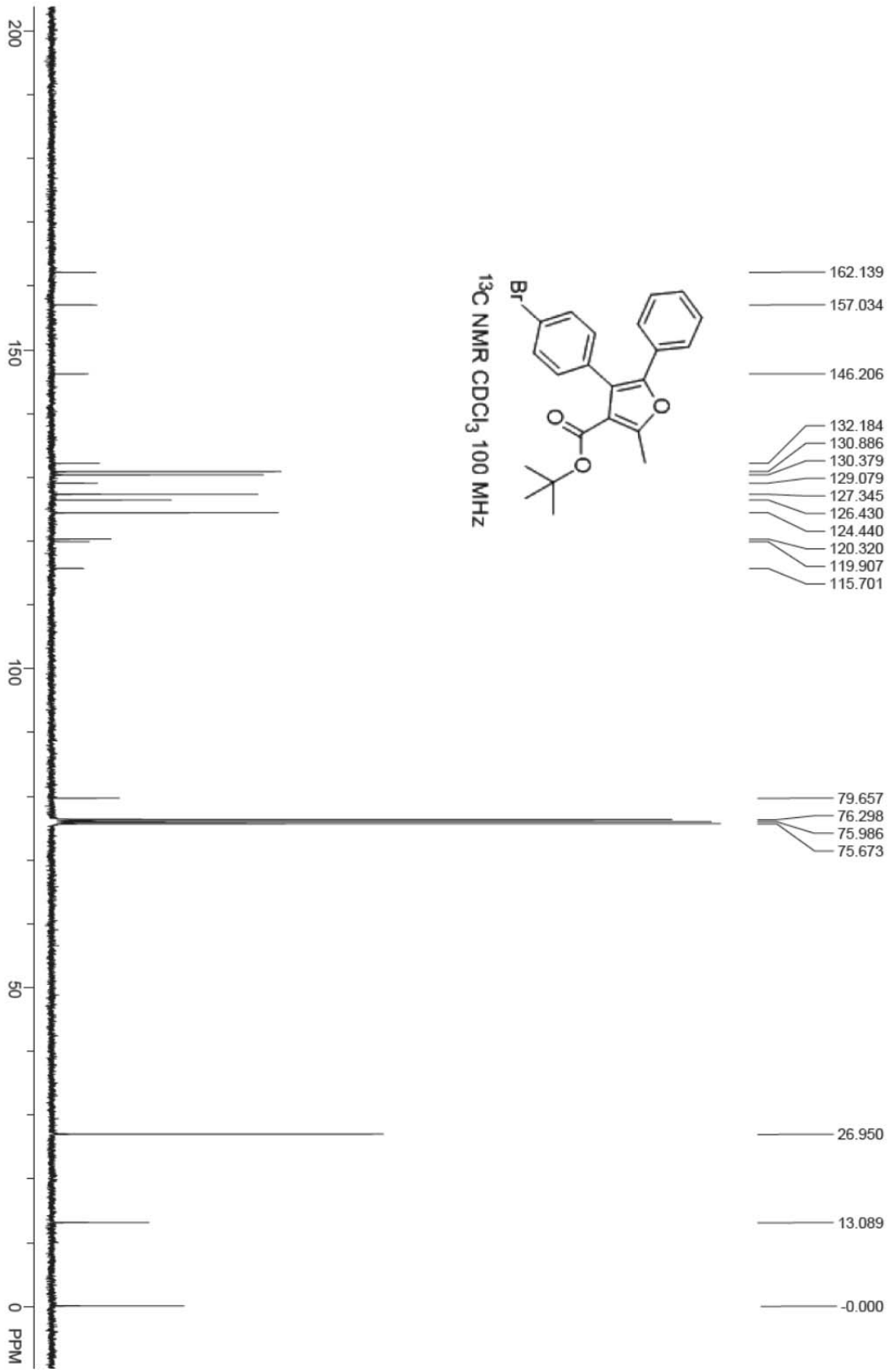
Tert-butyl 4-(4-fluorophenyl)-2-methyl-5-phenylfuran-3-carboxylate (4ga)



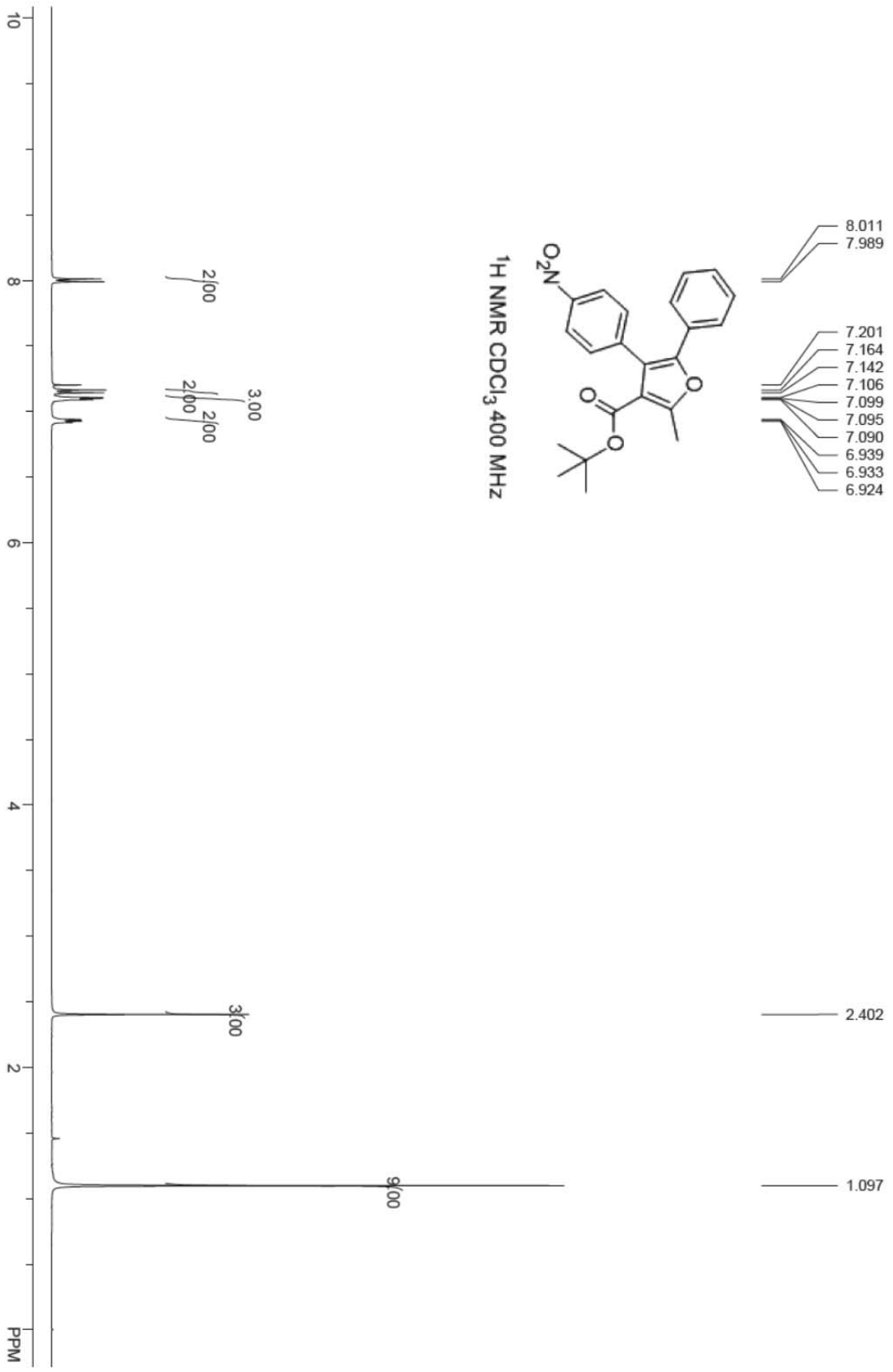

^{13}C NMR $CDCl_3$ 100 MHz
F
O
O
O
162.328
162.044
159.585
156.684
145.253
129.014
133.013
127.256
126.257
126.153
126.083
125.681
125.638
120.827
116.000
114.351
114.136
79.402
76.313
75.996
75.677
26.854
12.949
-0.000
200
150
100
50
0
PPM

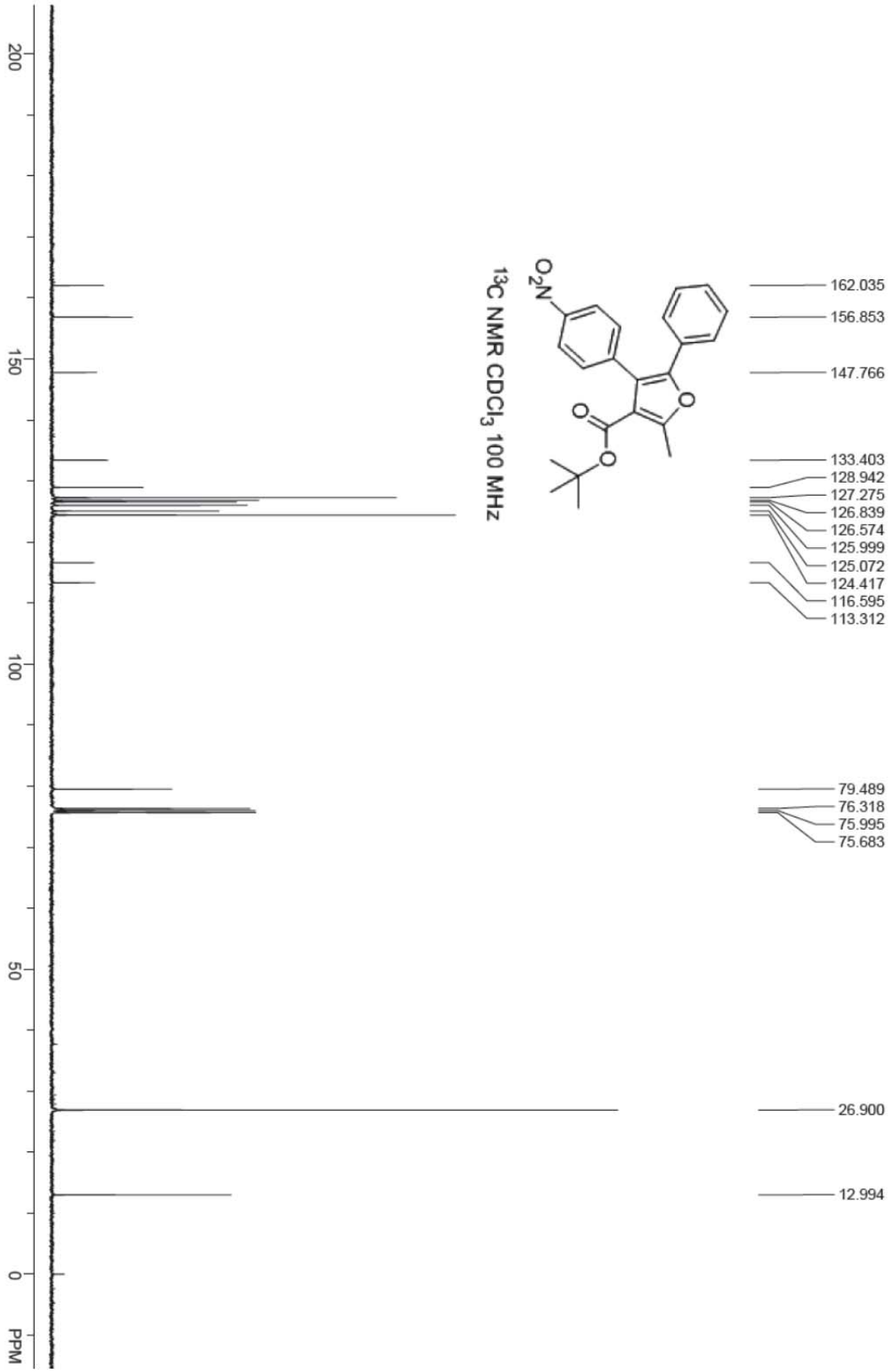
Tert-butyl 4-(4-bromophenyl)-2-methyl-5-phenylfuran-3-carboxylate (4ia)



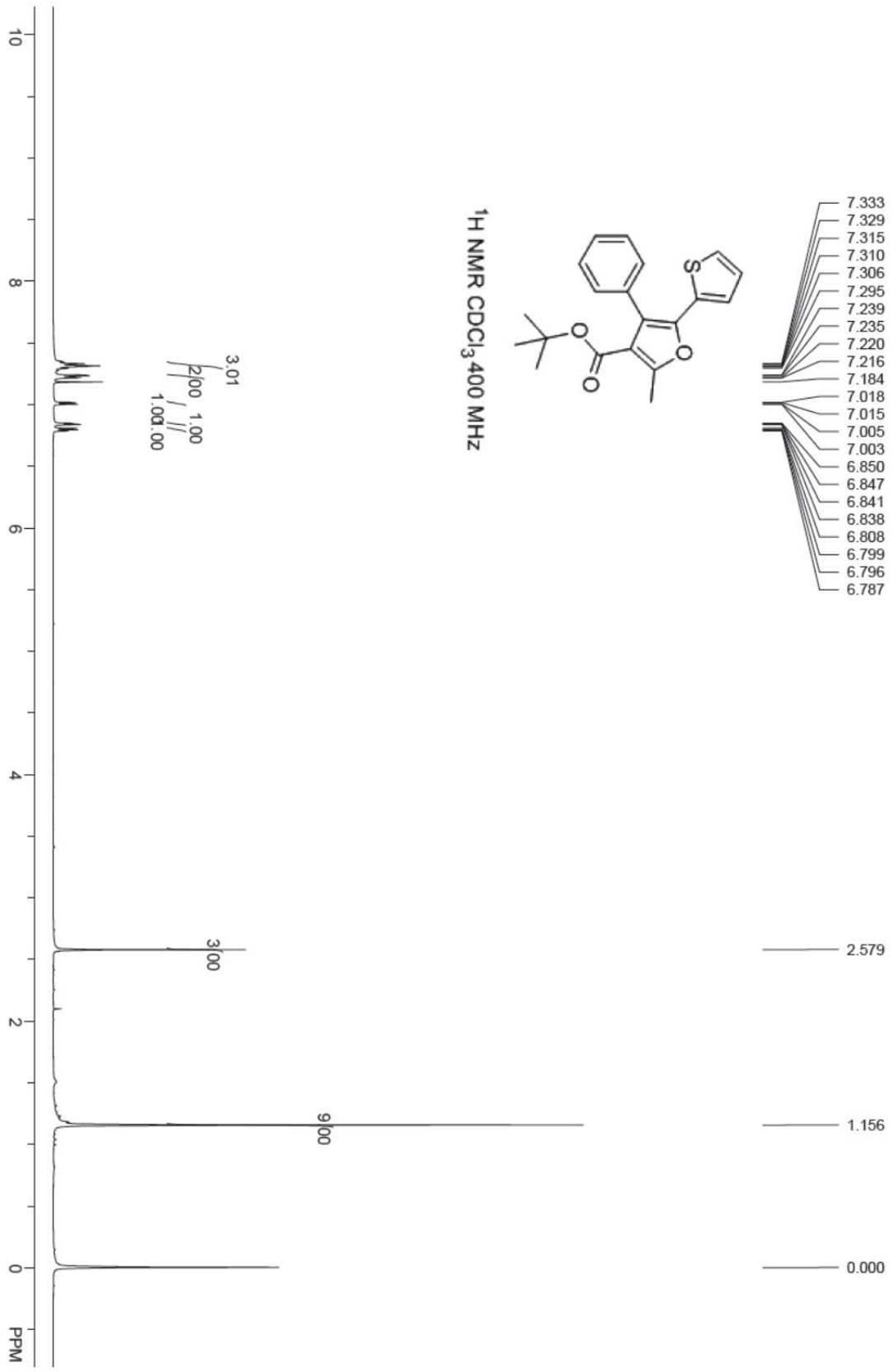

^{13}C NMR CDCl$_3$ 100 MHz
Br
O
O
O
162.139
157.034
146.206
132.184
130.886
130.379
129.079
127.345
126.430
124.440
120.320
119.907
115.701
79.657
76.298
75.986
75.673
26.950
13.089
-0.000
200
150
100
50
0
PPM

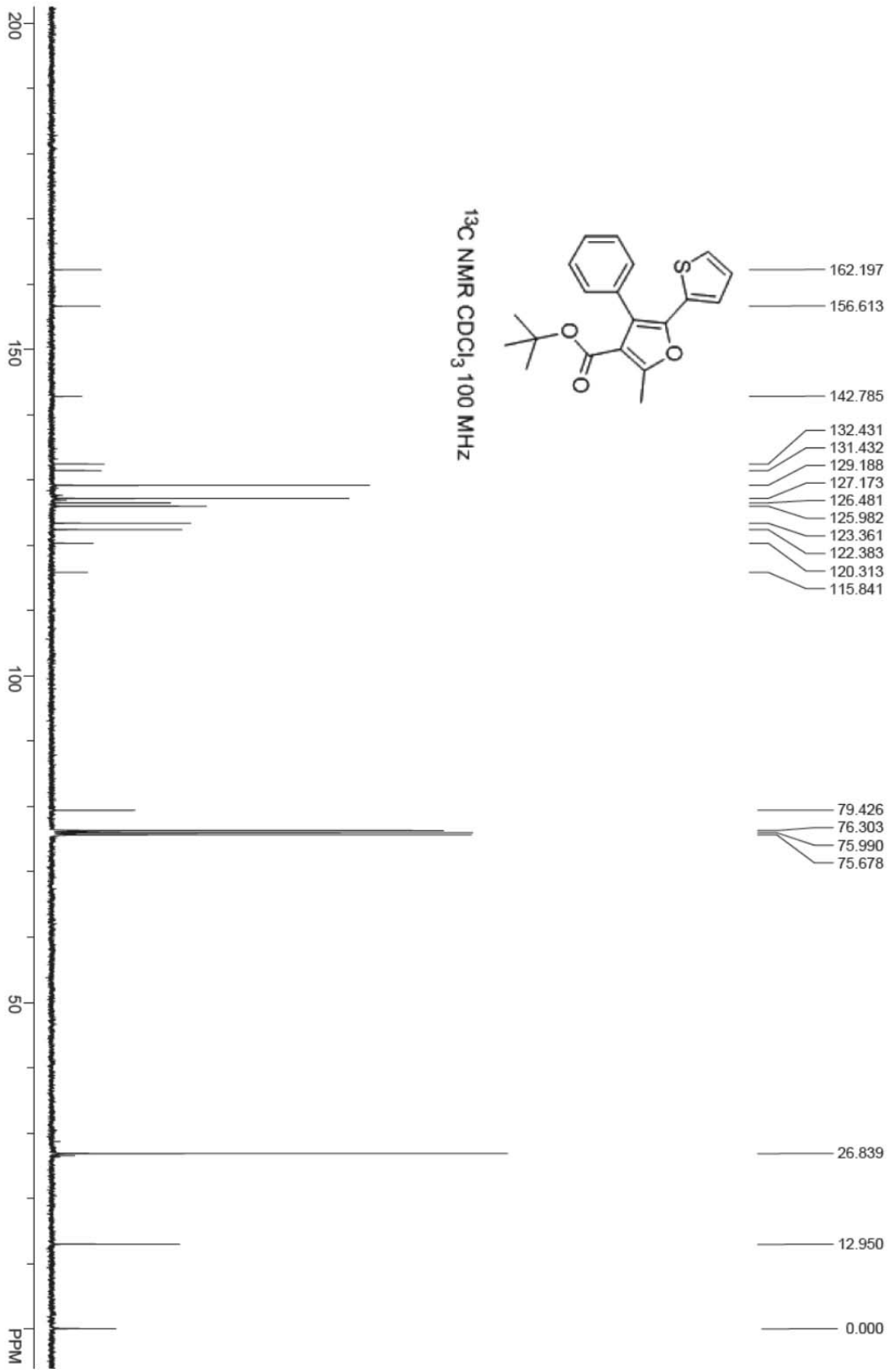
Tert-butyl 2-methyl-4-(4-nitrophenyl)-5-phenylfuran-3-carboxylate (4ja)



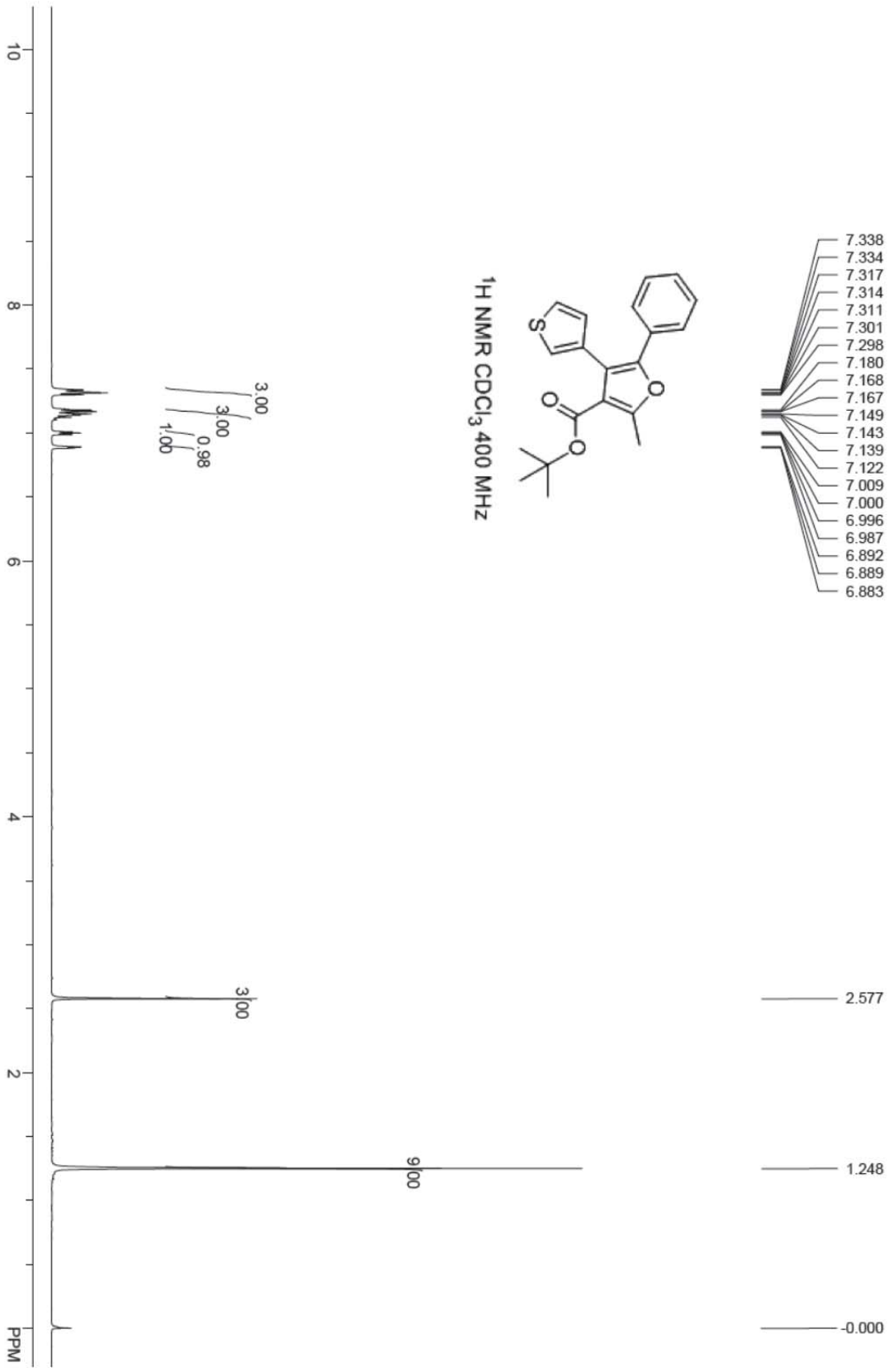

^{13}C NMR CDCl$_3$ 100 MHz
O_2N
O
O
O
162.035
156.853
147.766
133.403
128.942
127.275
126.839
126.574
125.999
125.072
124.417
116.595
113.312
79.489
76.318
75.995
75.683
26.900
12.994
200
150
100
50
0
PPM

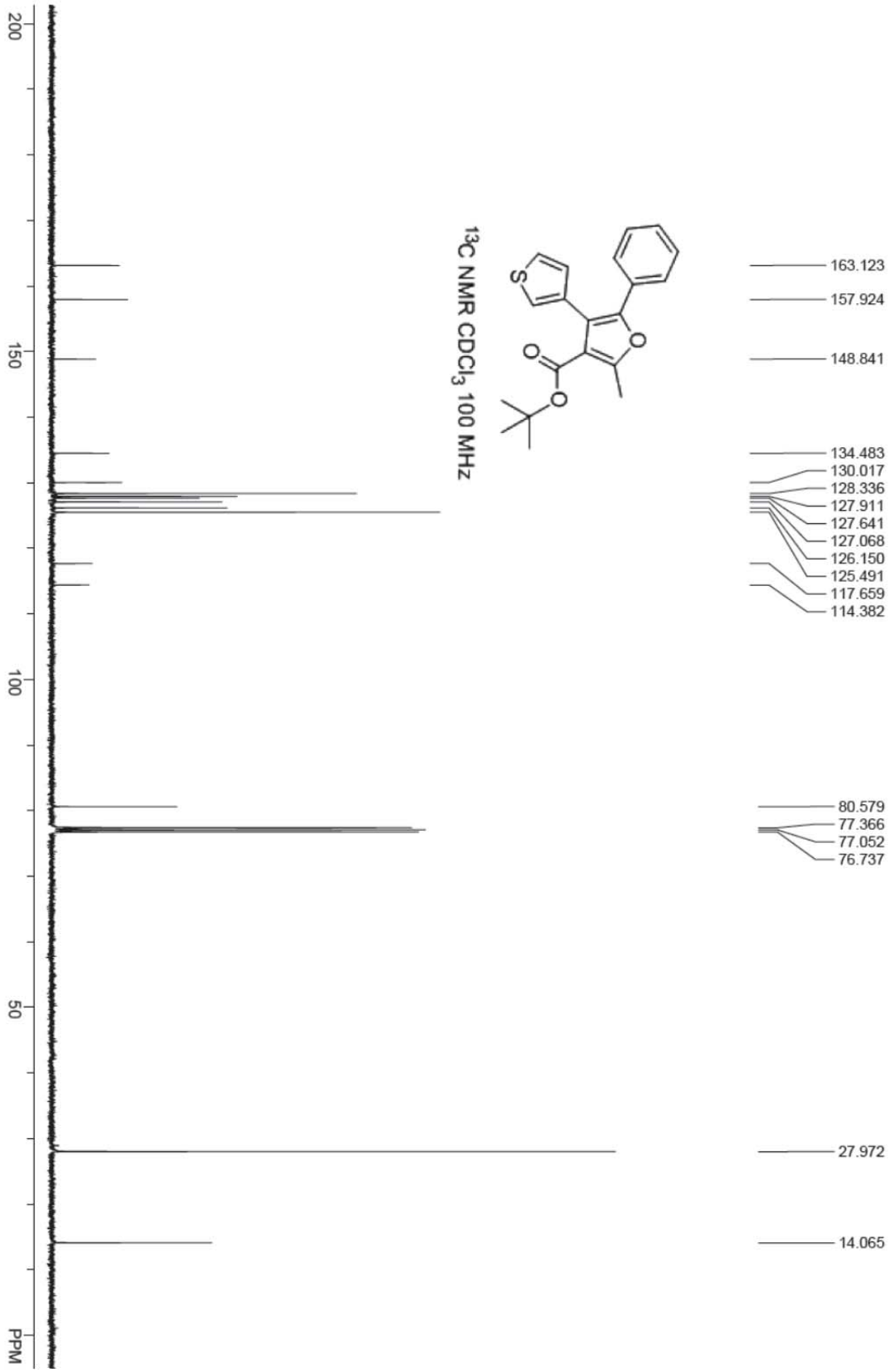
Tert-butyl 2-methyl-4-phenyl-5-(thiophen-2-yl)furan-3-carboxylate (4ka)



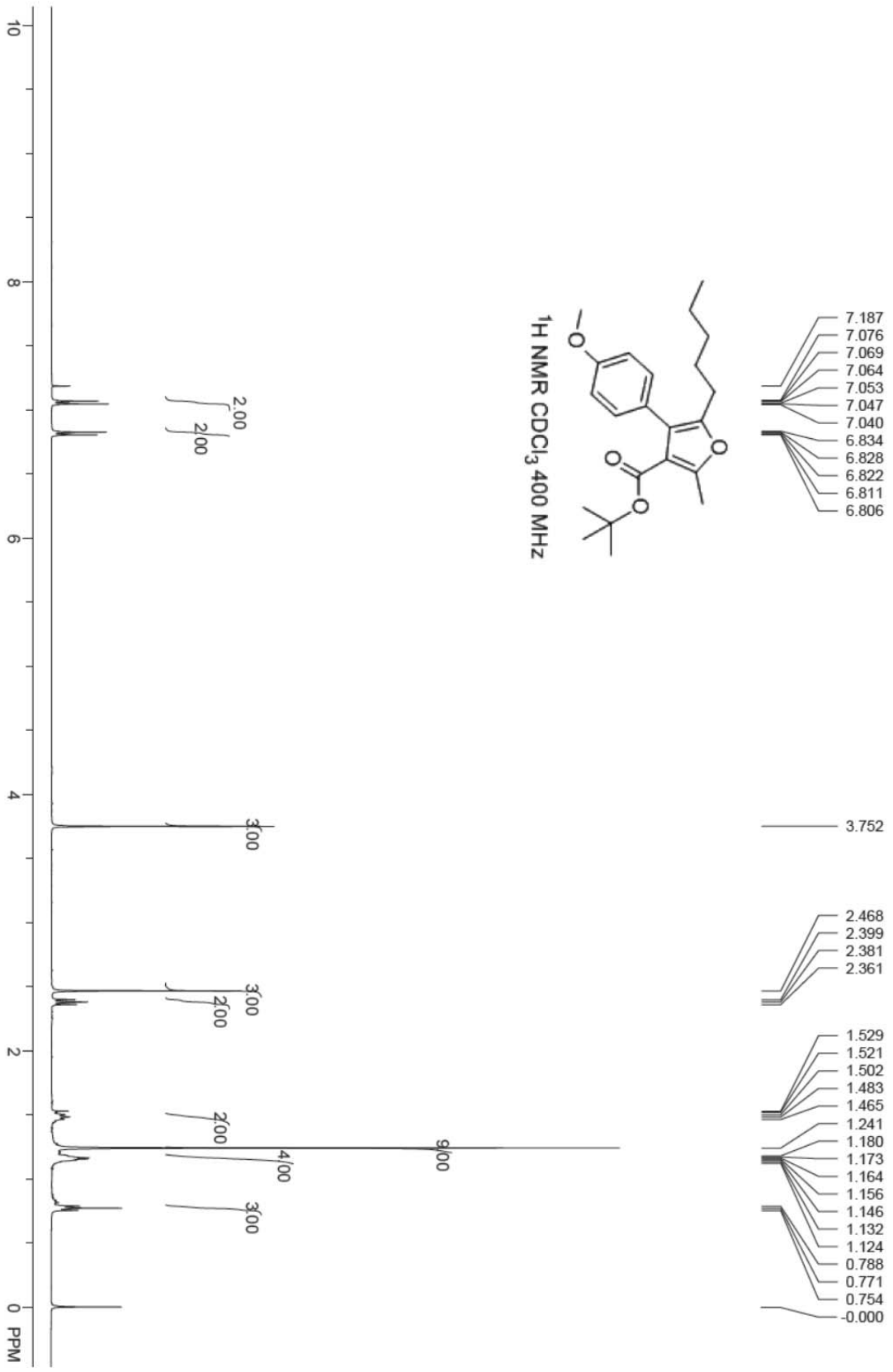

^{13}C NMR $CDCl_3$ 100 MHz
162.197
156.613
142.785
132.431
131.432
129.188
127.173
126.481
125.982
123.361
122.383
120.313
115.841
79.426
76.303
75.990
75.678
26.839
12.950
0.000
200
150
100
50
PPM

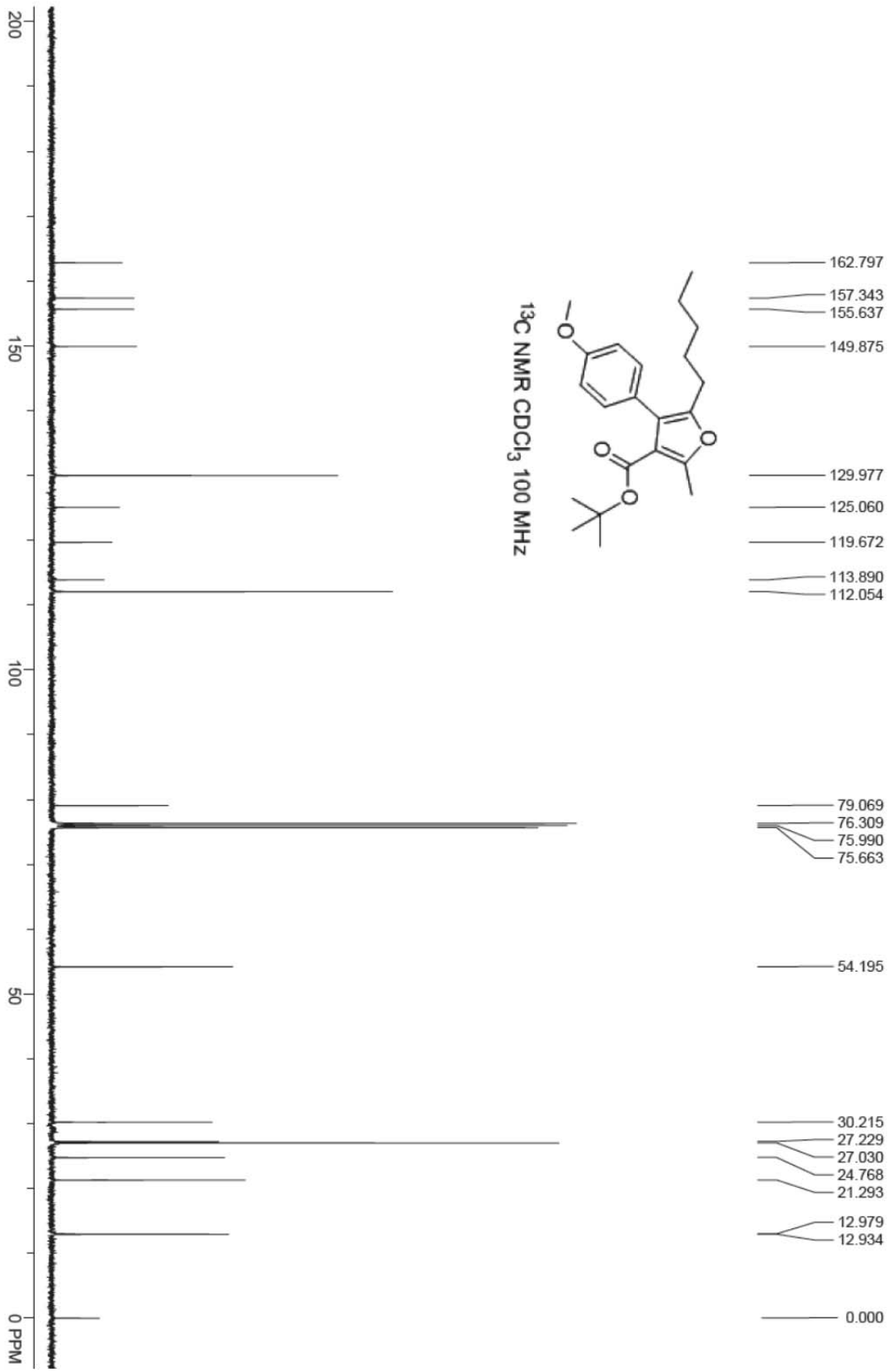
Tert-butyl 2-methyl-5-phenyl-4-(thiophen-3-yl)furan-3-carboxylate (4la)



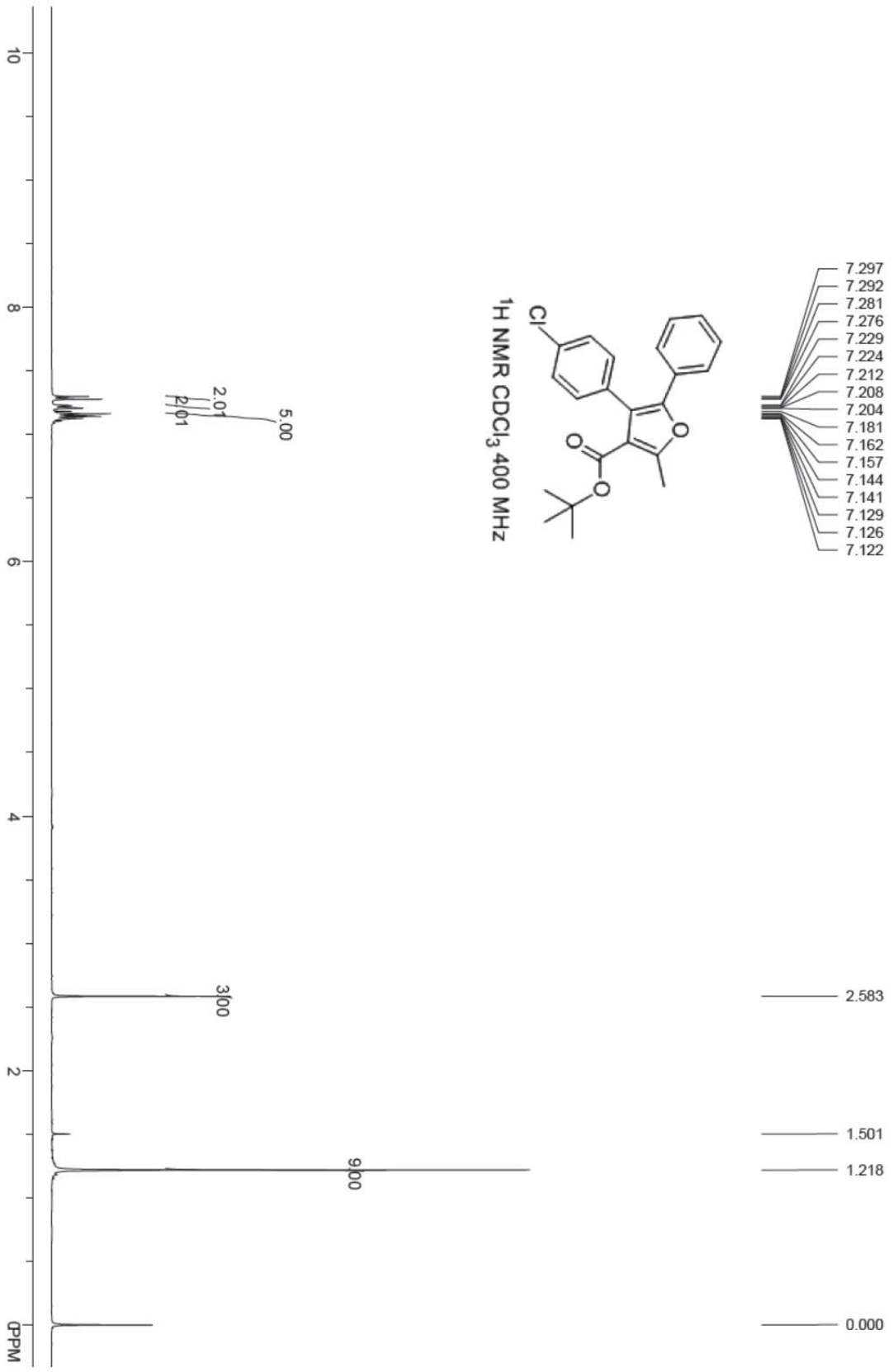

^{13}C NMR CDCl$_3$ 100 MHz
163.123
157.924
148.841
134.483
130.017
128.336
127.911
127.641
127.068
126.150
125.491
117.659
114.382
80.579
77.366
77.052
76.737
27.972
14.065
200
150
100
50
PPM

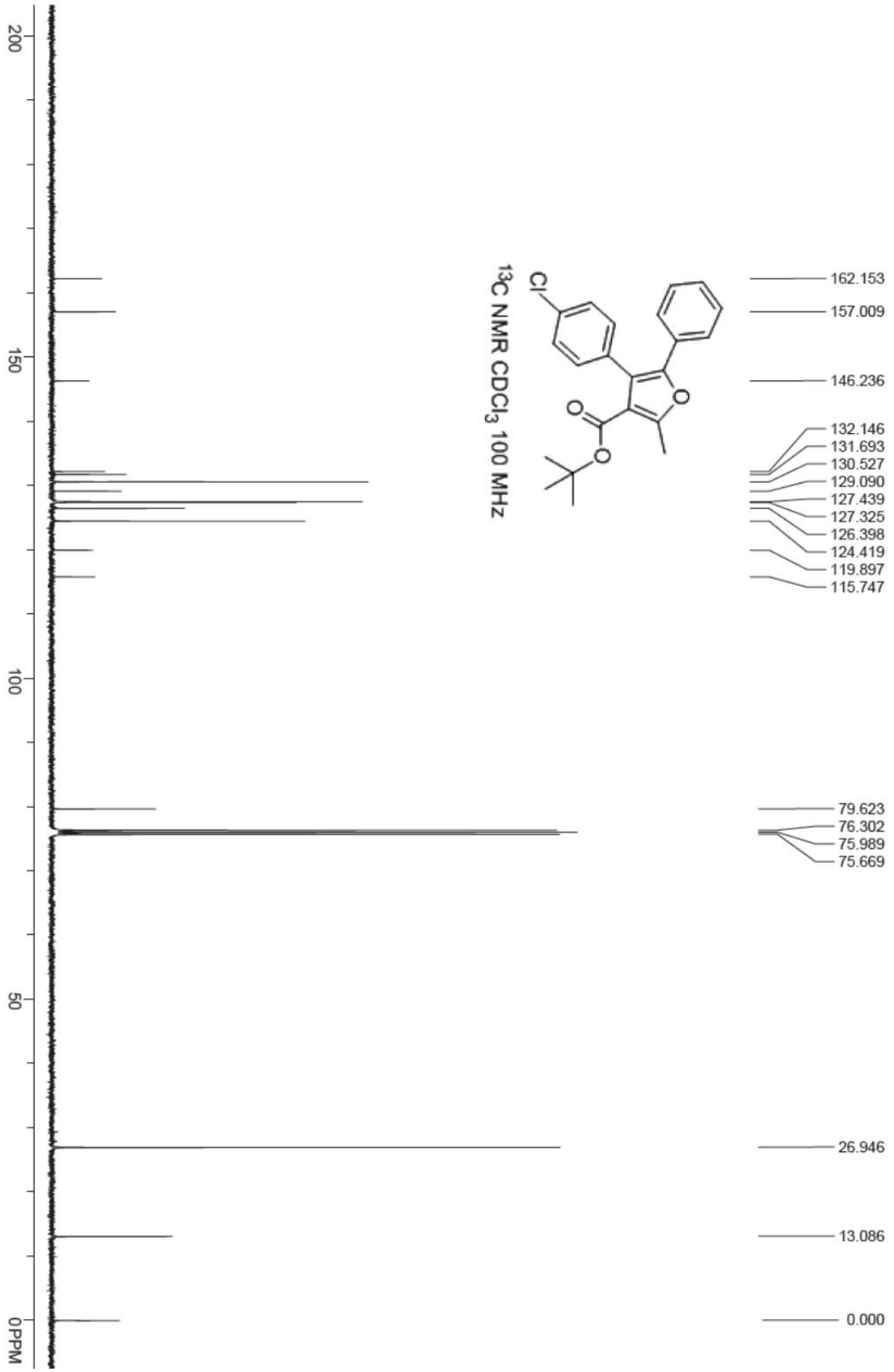
Ethyl 4-(4-methoxyphenyl)-2-methyl-5-pentylfuran-3-carboxylate (4ma)



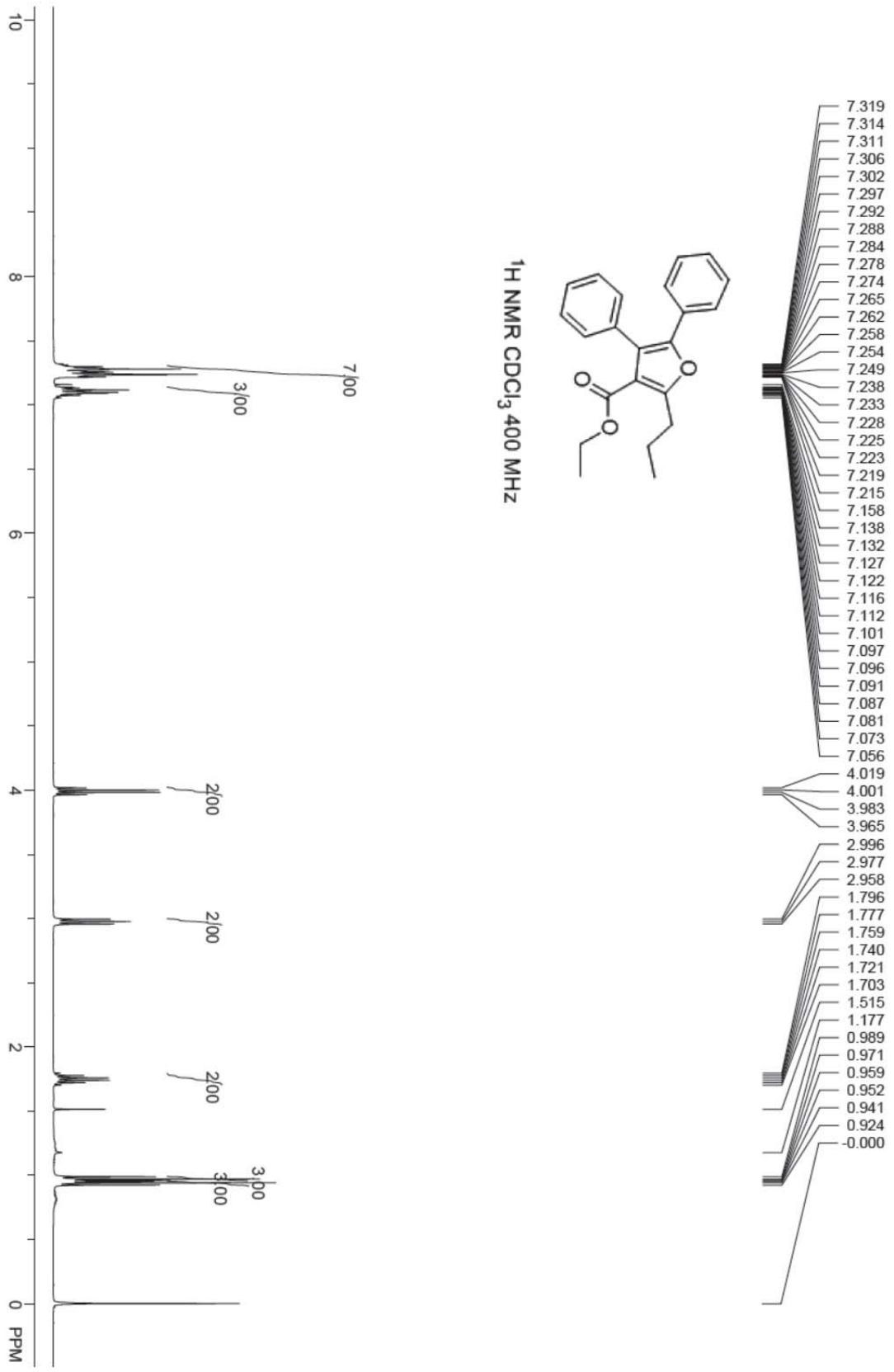

^{13}C NMR CDCl$_3$ 100 MHz
200
150
100
50
0 PPM
162.797
157.343
155.637
149.875
129.977
125.060
119.672
113.890
112.054
79.069
76.309
75.990
75.663
54.195
30.215
27.229
27.030
24.768
21.293
12.979
12.934
0.000

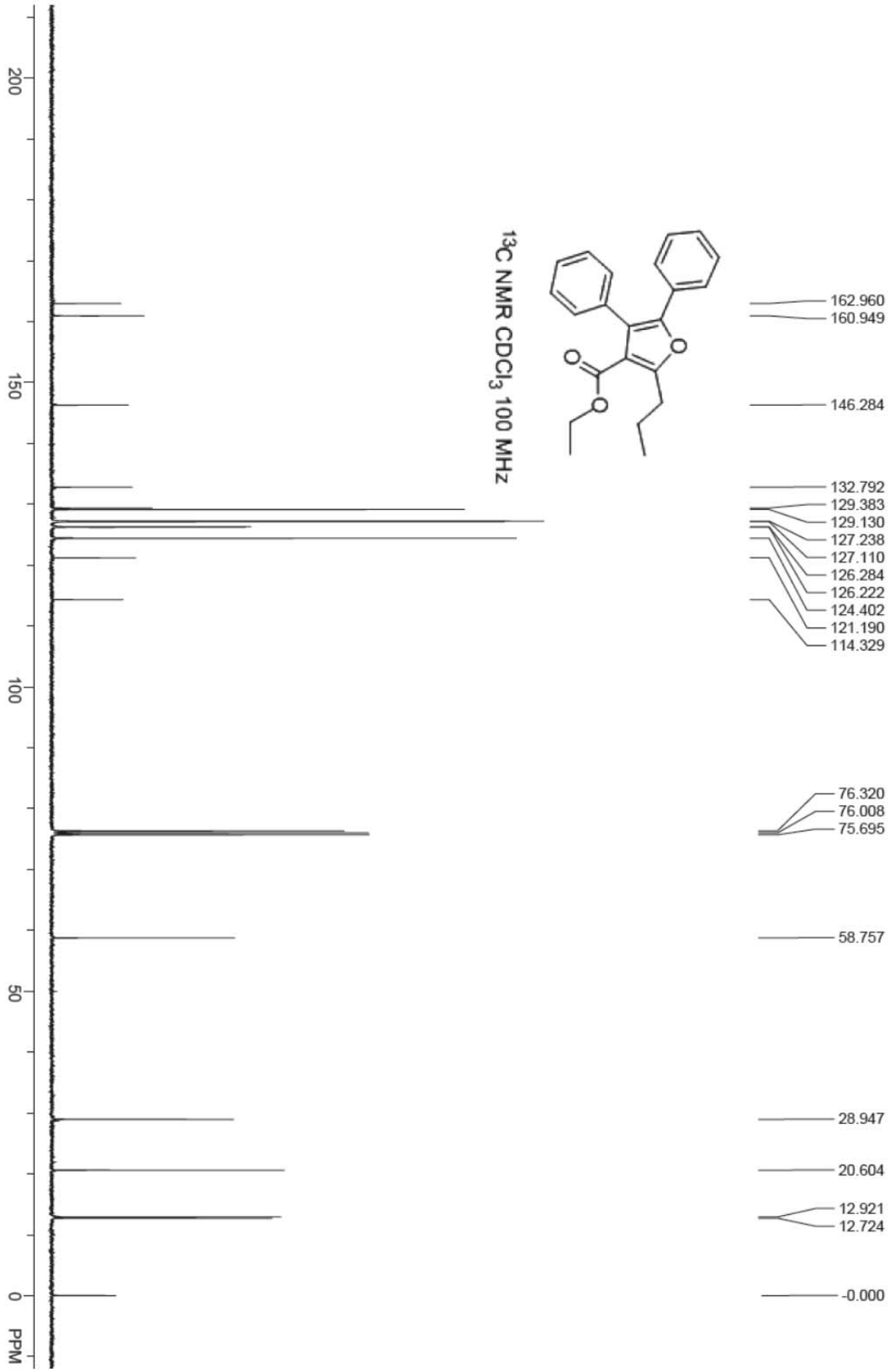
Tert-butyl 4-(4-chlorophenyl)-2-methyl-5-phenylfuran-3-carboxylate (4pa)



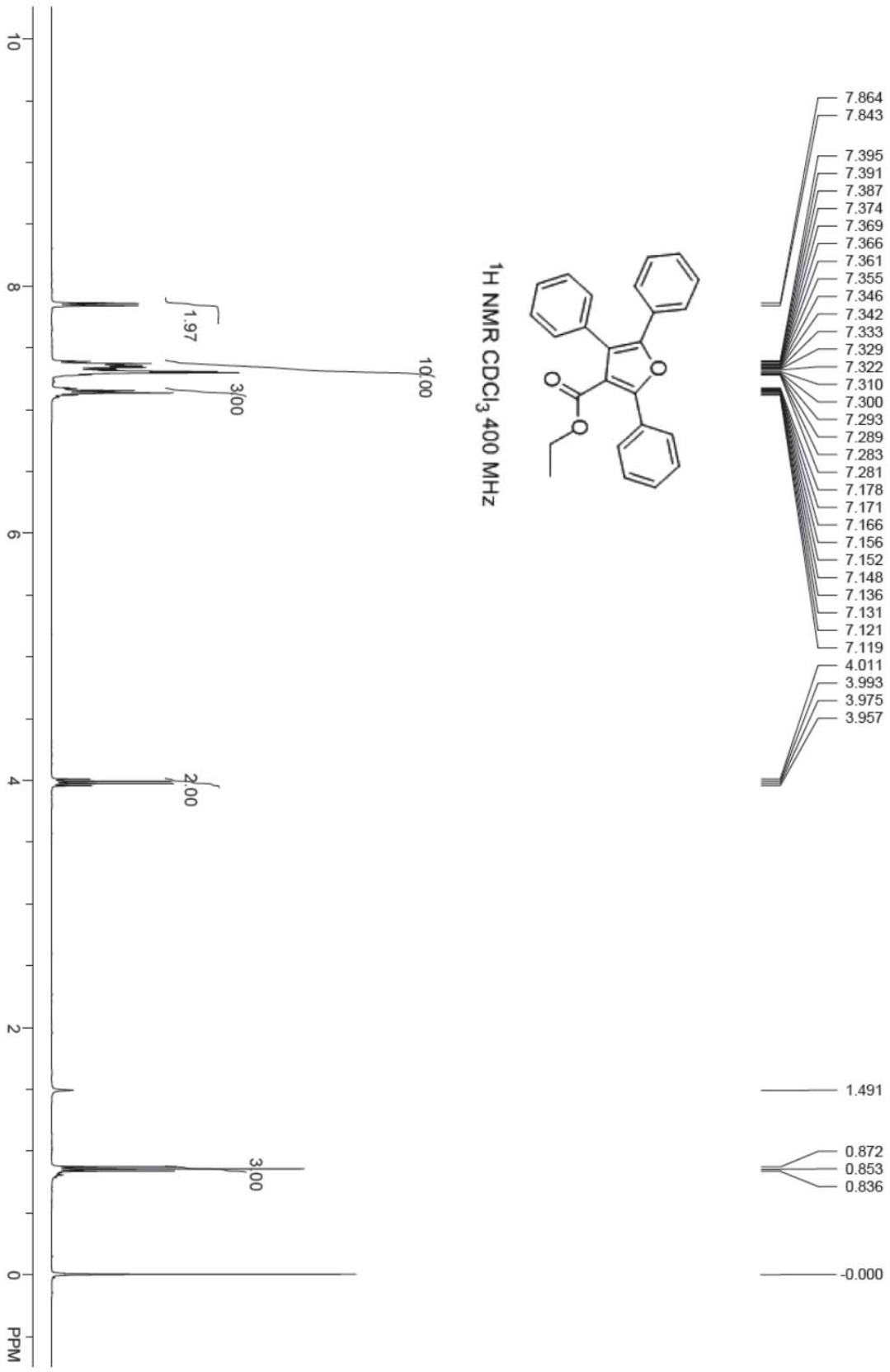

^{13}C NMR CDCl$_3$ 100 MHz
Cl
O
O
O
200
150
100
50
0PPM
162.153
157.009
146.236
132.146
131.693
130.527
129.090
127.439
127.325
126.398
124.419
119.897
115.747
79.623
76.302
75.989
75.669
26.946
13.086
0.000

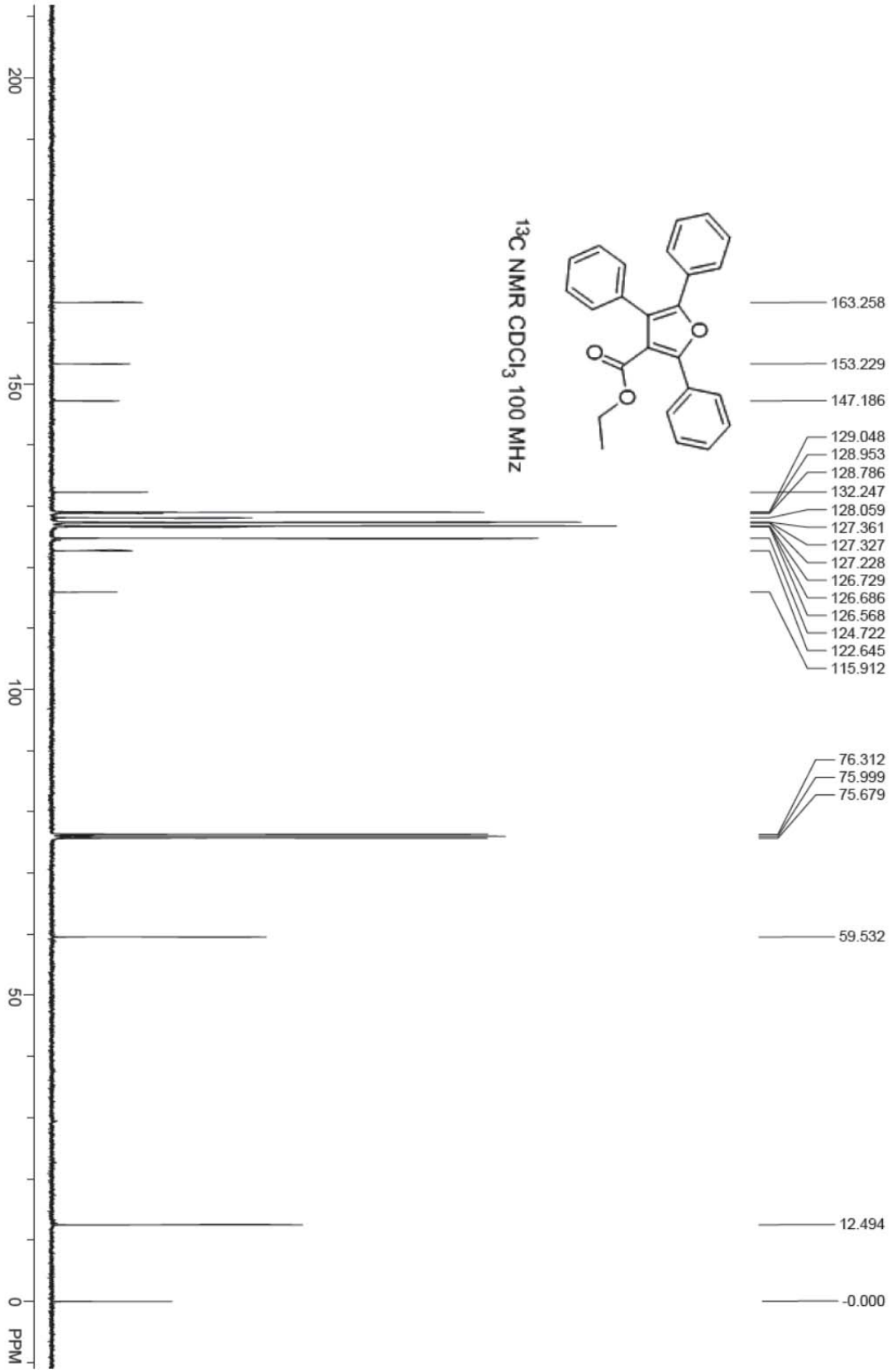
Ethyl 4,5-diphenyl-2-propylfuran-3-carboxylate (4ad)



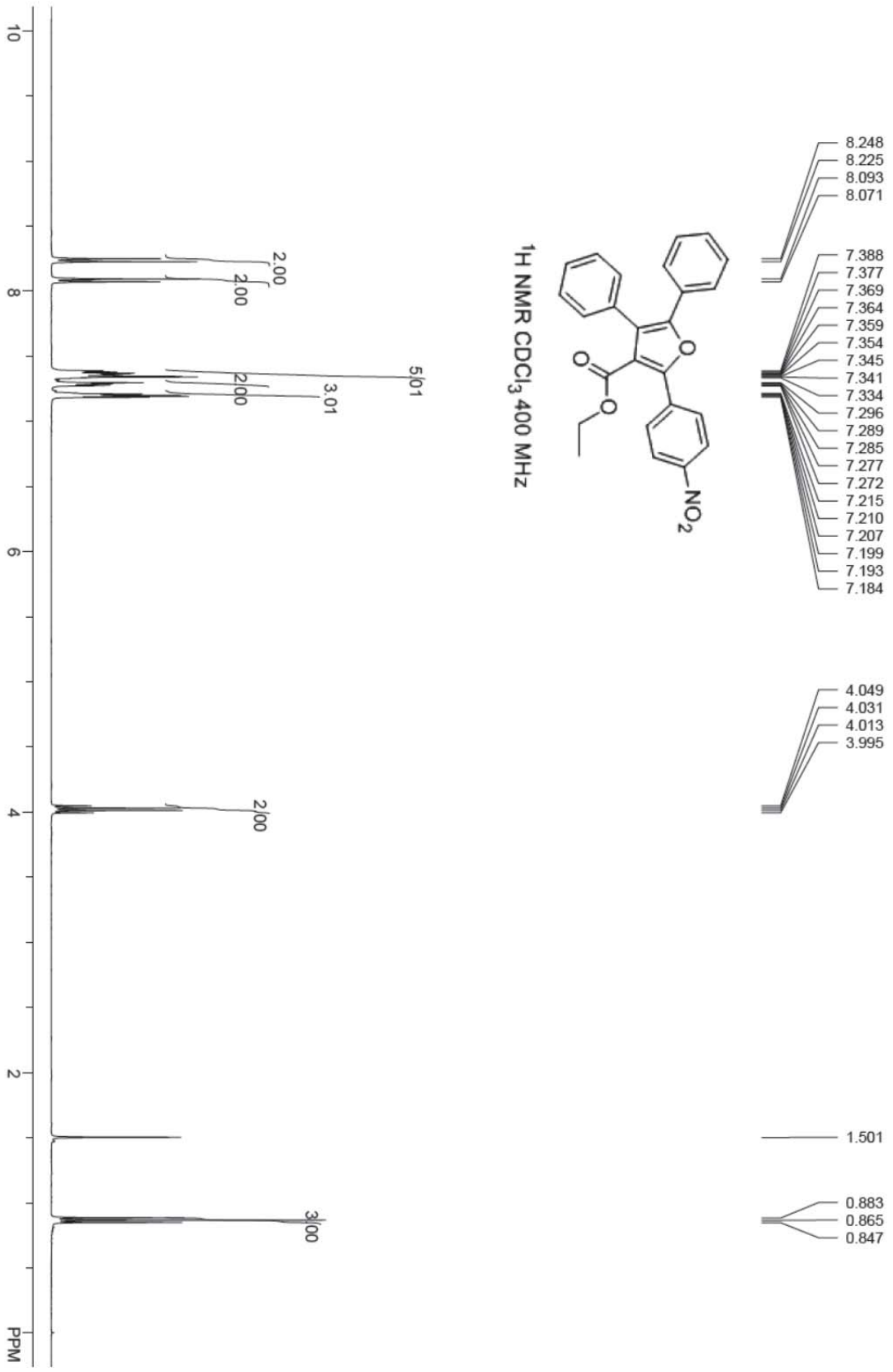

^{13}C NMR CDCl$_3$ 100 MHz
162.960
160.949
146.284
132.792
129.383
129.130
127.238
127.110
126.284
126.222
124.402
121.190
114.329
76.320
76.008
75.695
58.757
28.947
20.604
12.921
12.724
-0.000
200
150
100
50
0
PPM

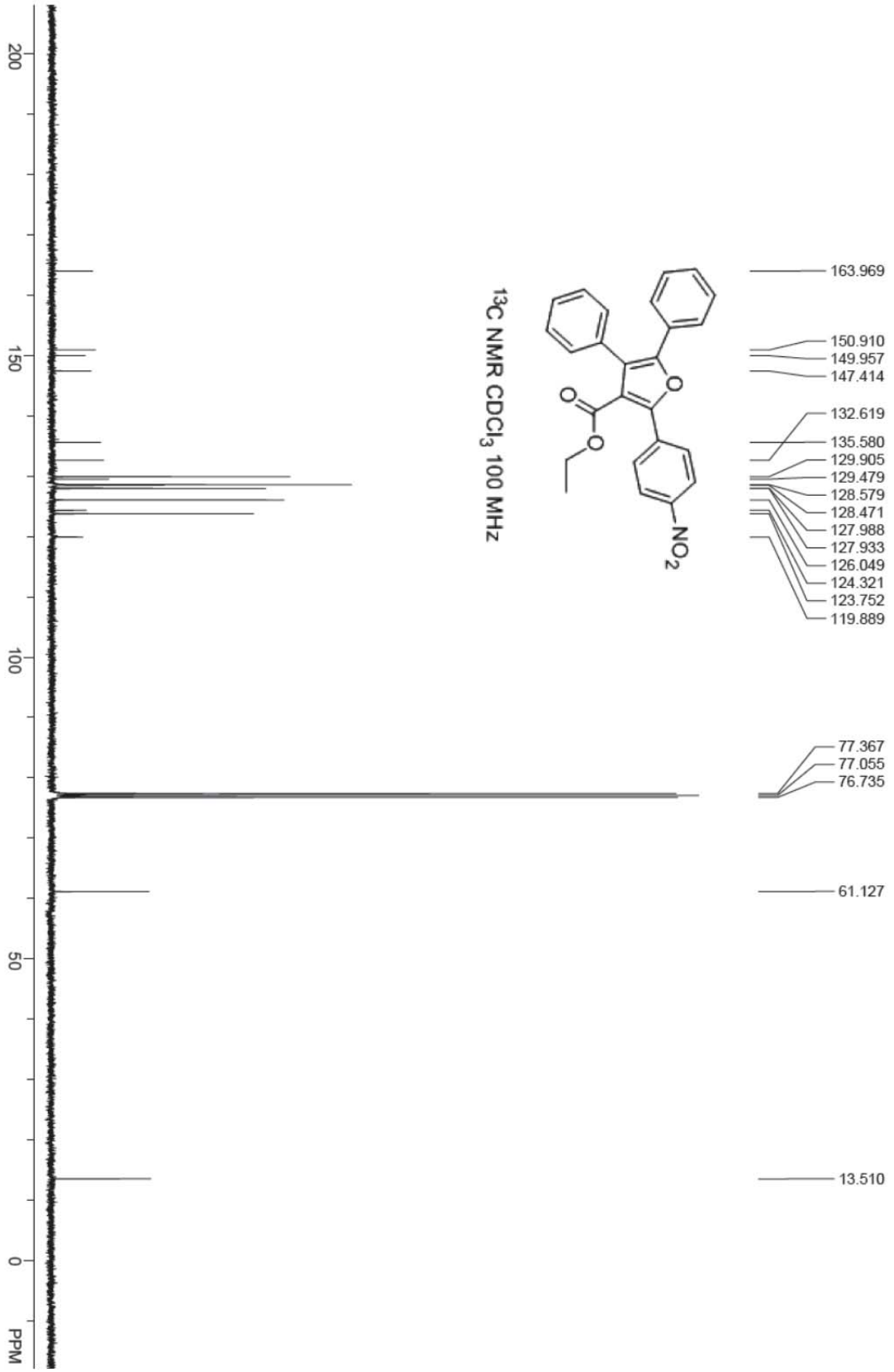
Ethyl 2,4,5-triphenylfuran-3-carboxylate (4ae)



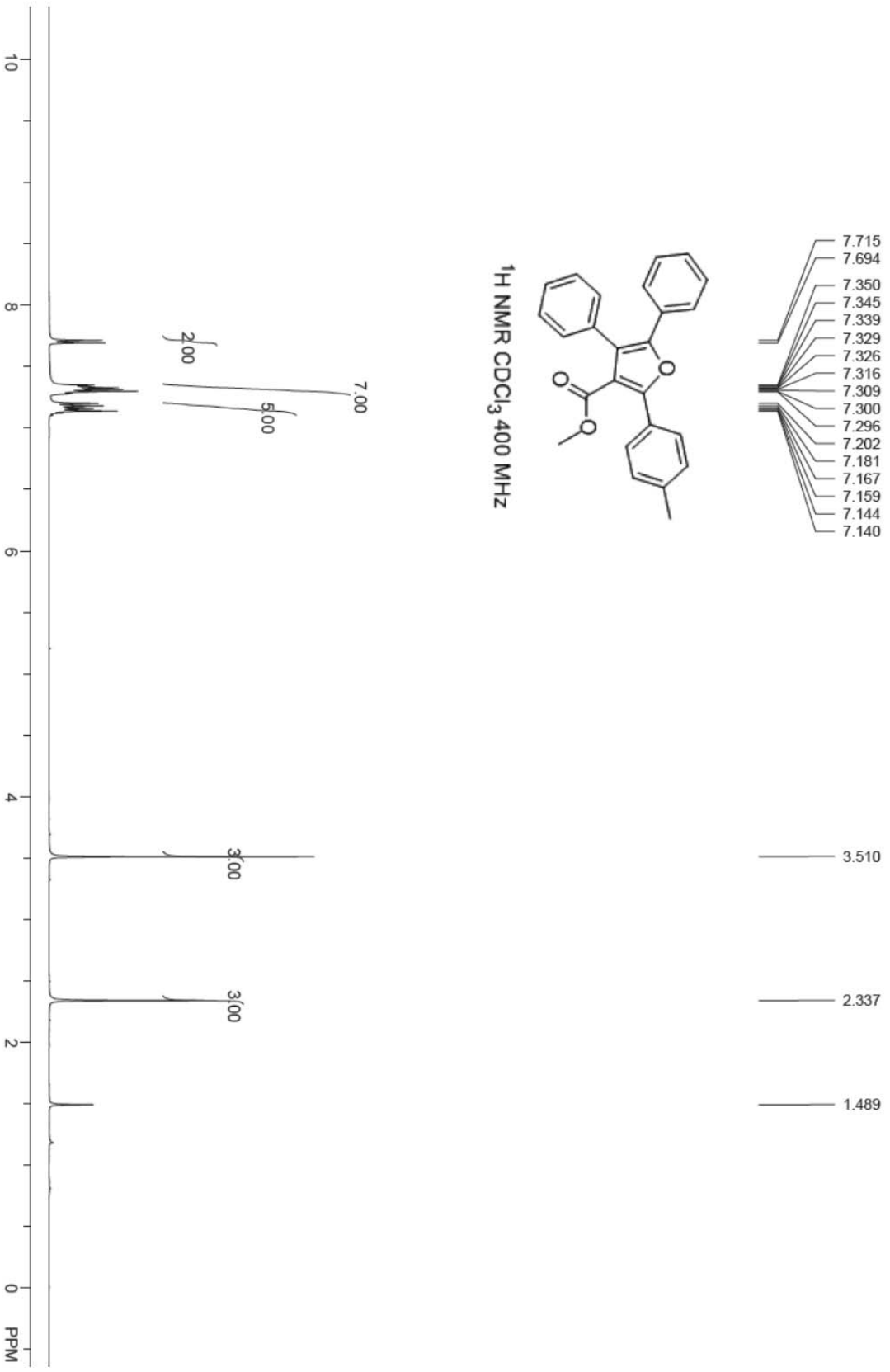

^{13}C NMR CDCl$_3$ 100 MHz
163.258
153.229
147.186
129.048
128.953
128.786
132.247
128.059
127.361
127.327
127.228
126.729
126.686
126.568
124.722
122.645
115.912
76.312
75.999
75.679
59.532
12.494
-0.000
200
150
100
50
0
PPM

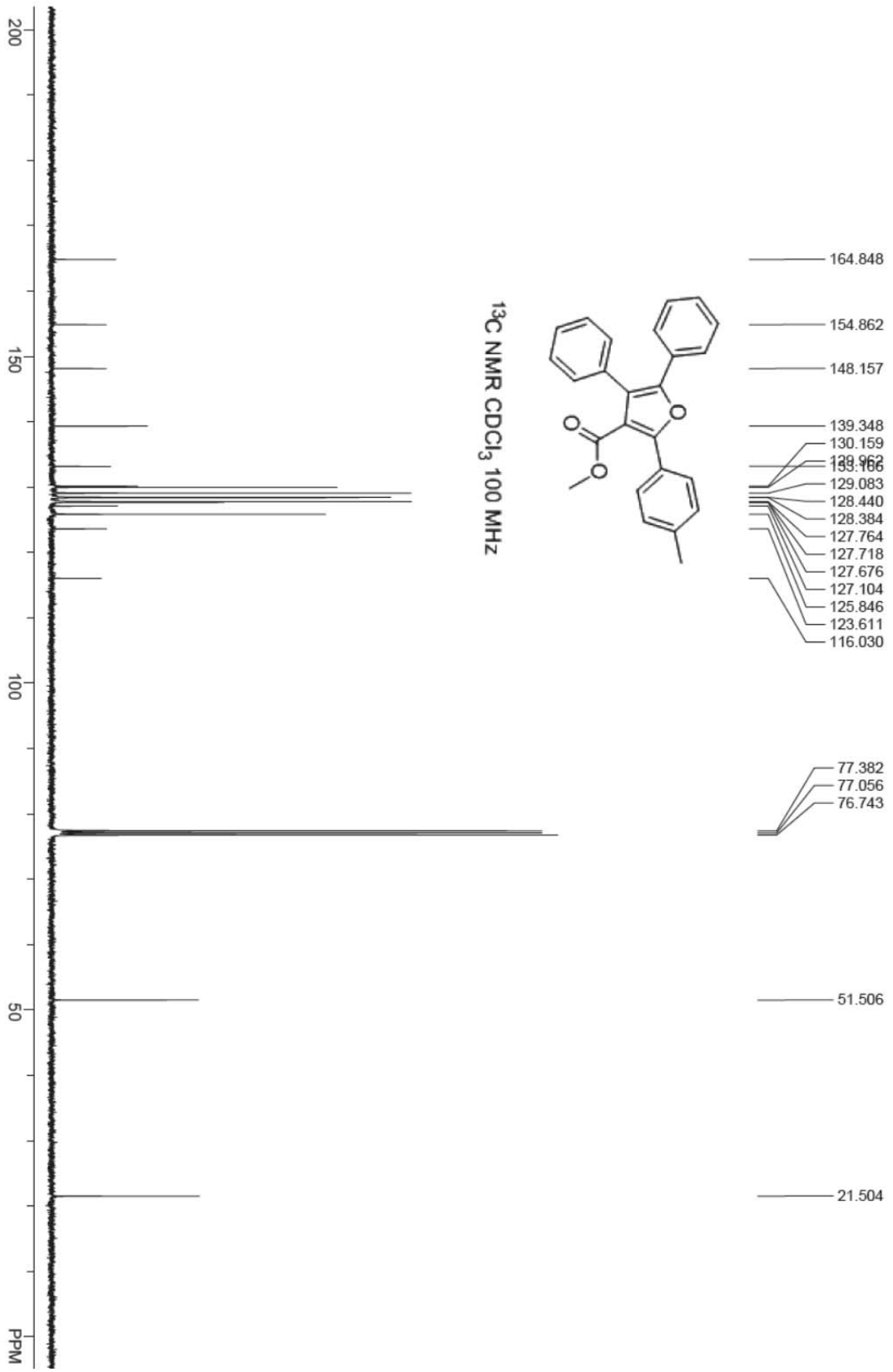
Ethyl 2-(4-nitrophenyl)-4,5-diphenylfuran-3-carboxylate (4ah)



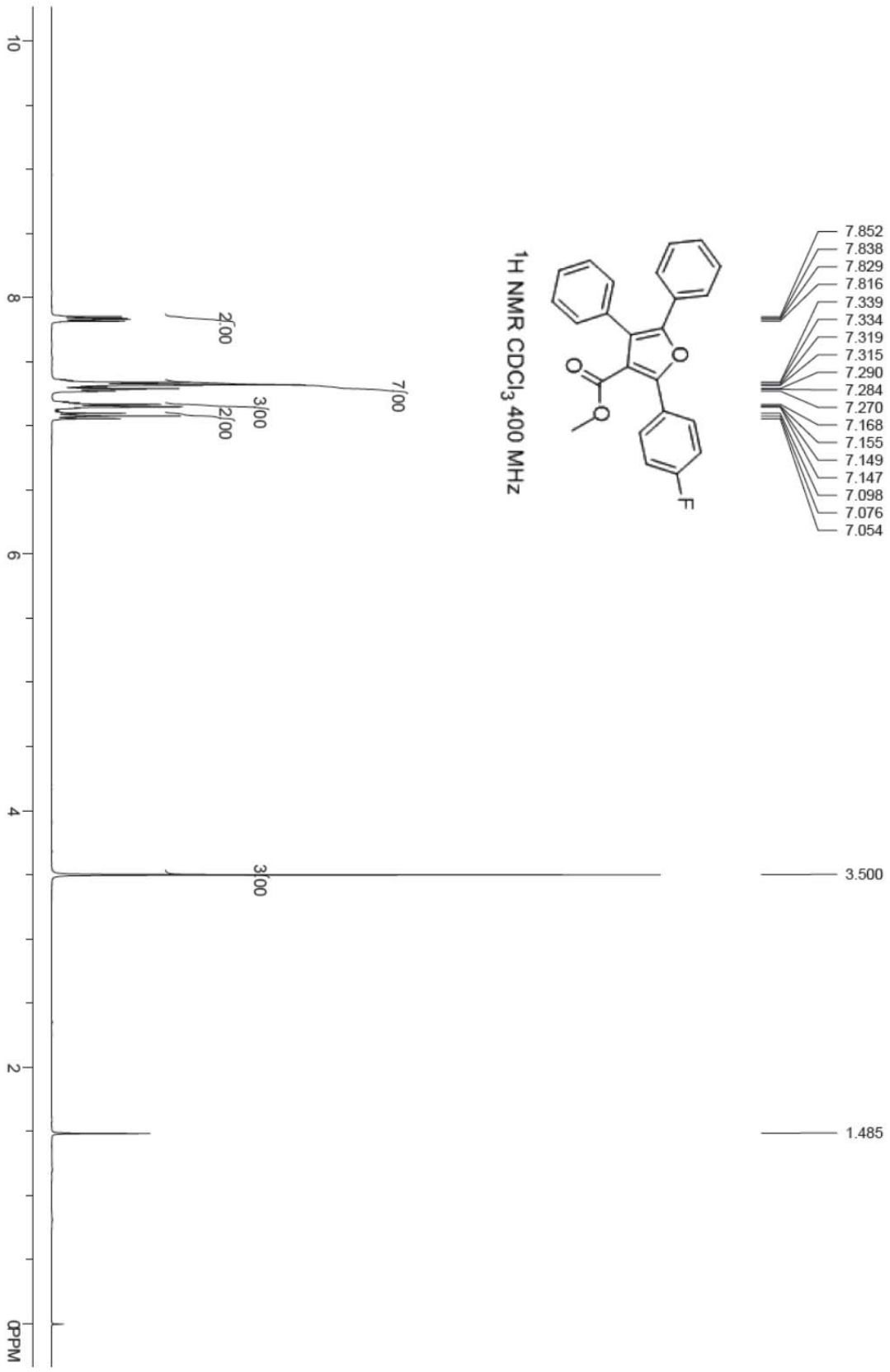

^{13}C NMR $CDCl_3$ 100 MHz
NO_2
163.969
150.910
149.957
147.414
132.619
135.580
129.905
129.479
128.579
128.471
127.988
127.933
126.049
124.321
123.752
119.889
77.367
77.055
76.735
61.127
13.510
200
150
100
50
0
PPM

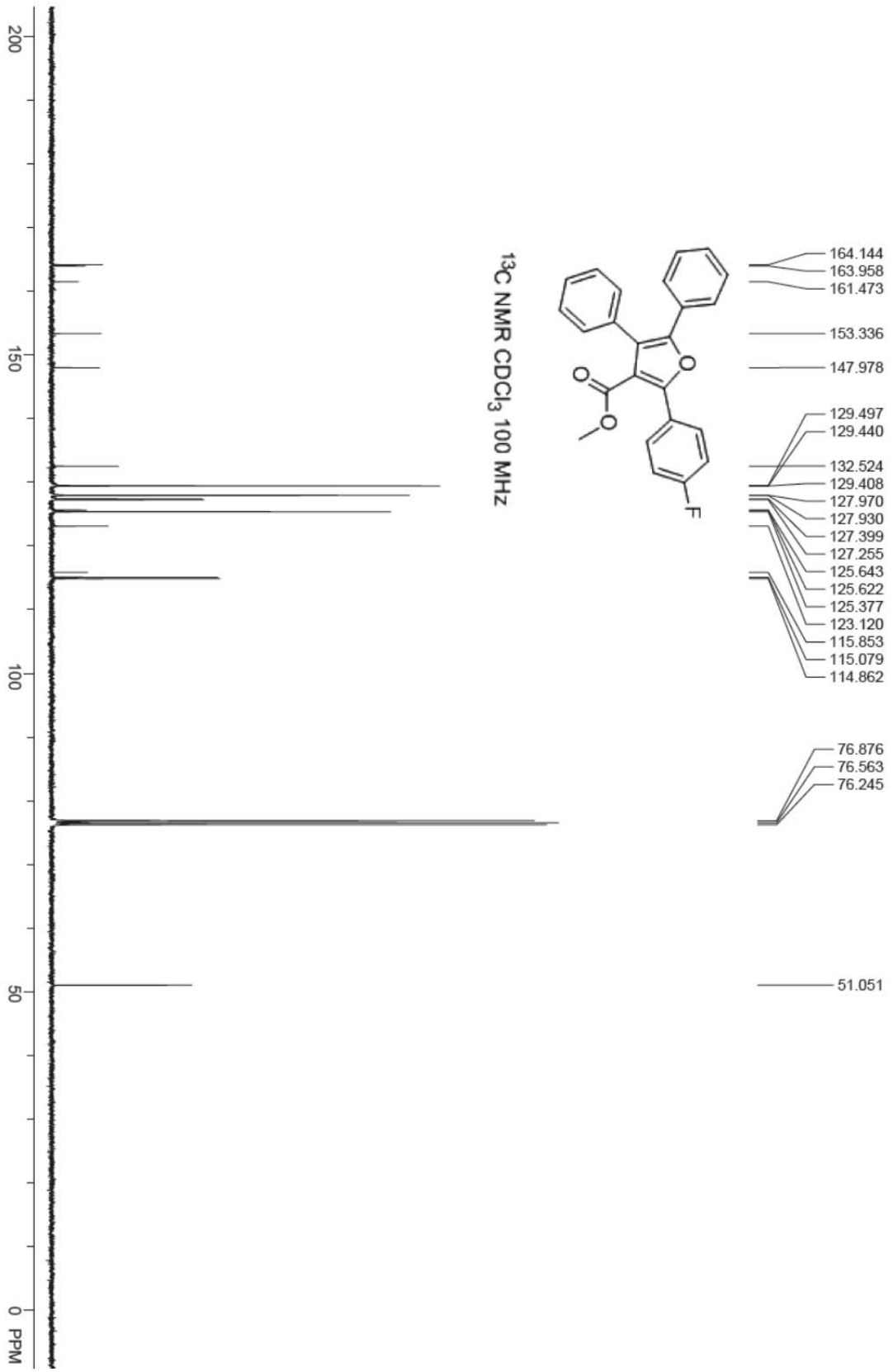
Methyl 4,5-diphenyl-2-(p-tolyl)furan-3-carboxylate (4ai)



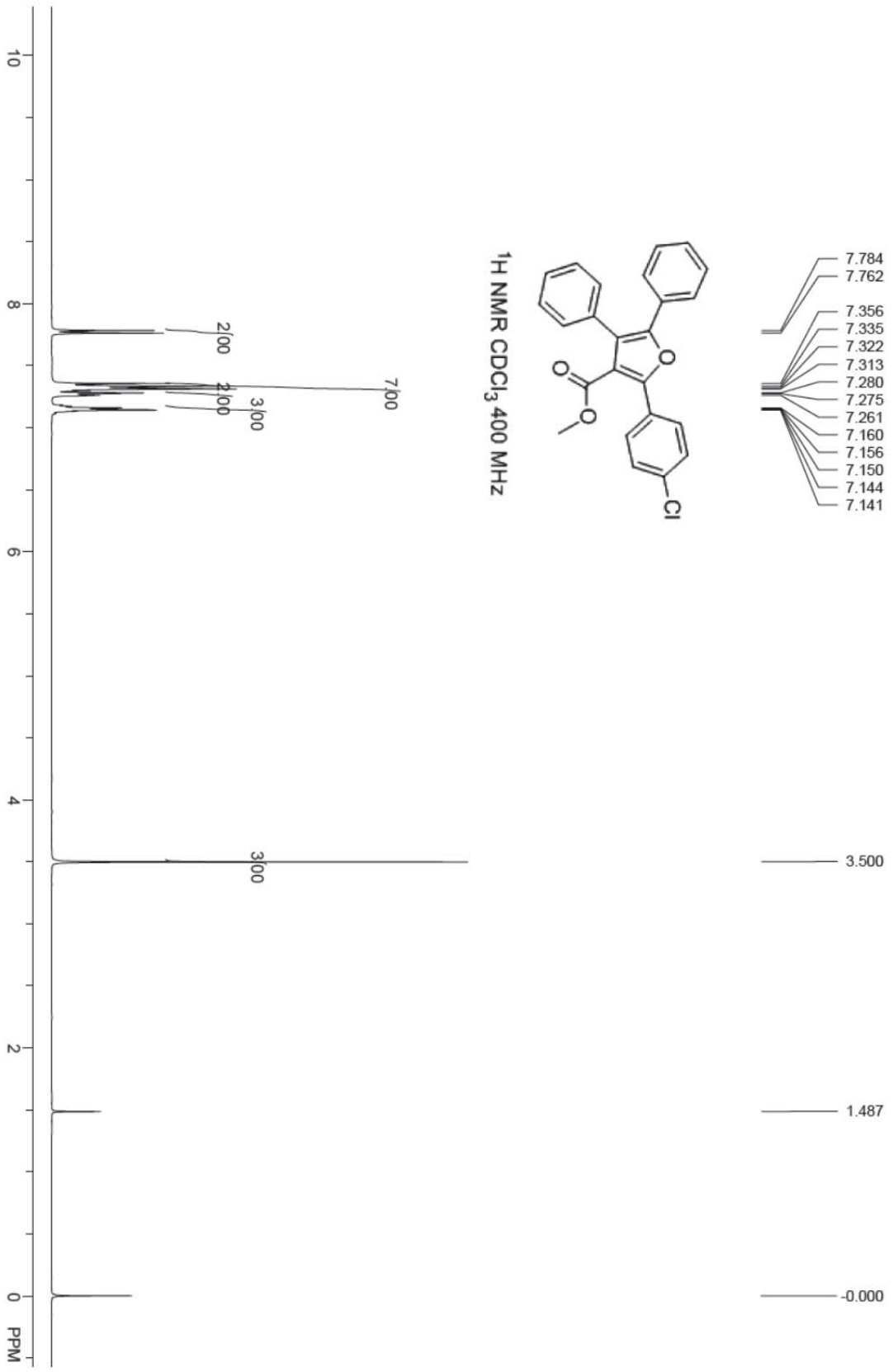

^{13}C NMR $CDCl_3$ 100 MHz
200
150
100
50
PPM
164.848
154.862
148.157
139.348
130.159
129.962
129.083
128.440
128.384
127.764
127.718
127.676
127.104
125.846
123.611
116.030
77.382
77.056
76.743
51.506
21.504

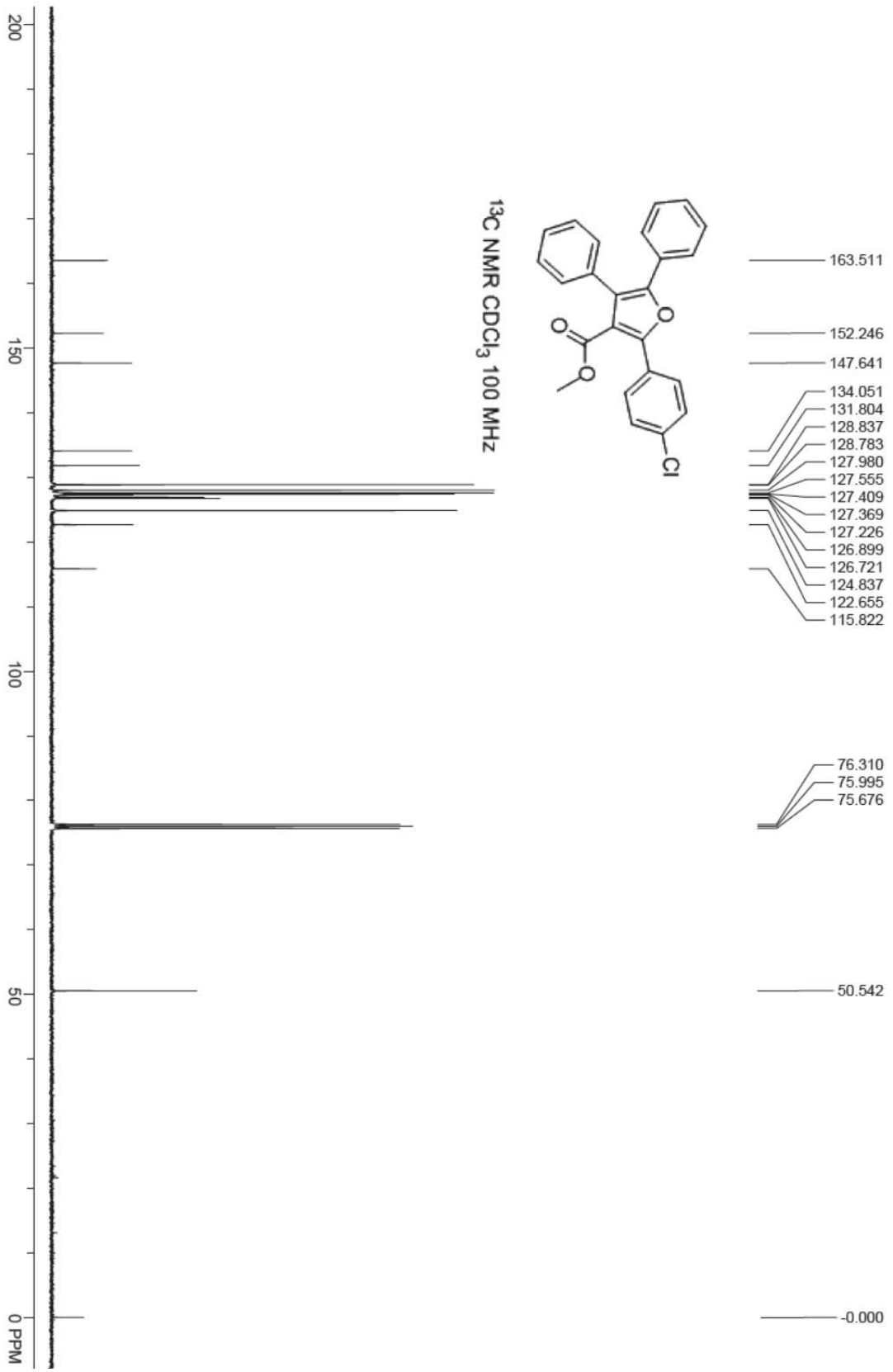
Methyl 2-(4-fluorophenyl)-4,5-diphenylfuran-3-carboxylate (4aj)



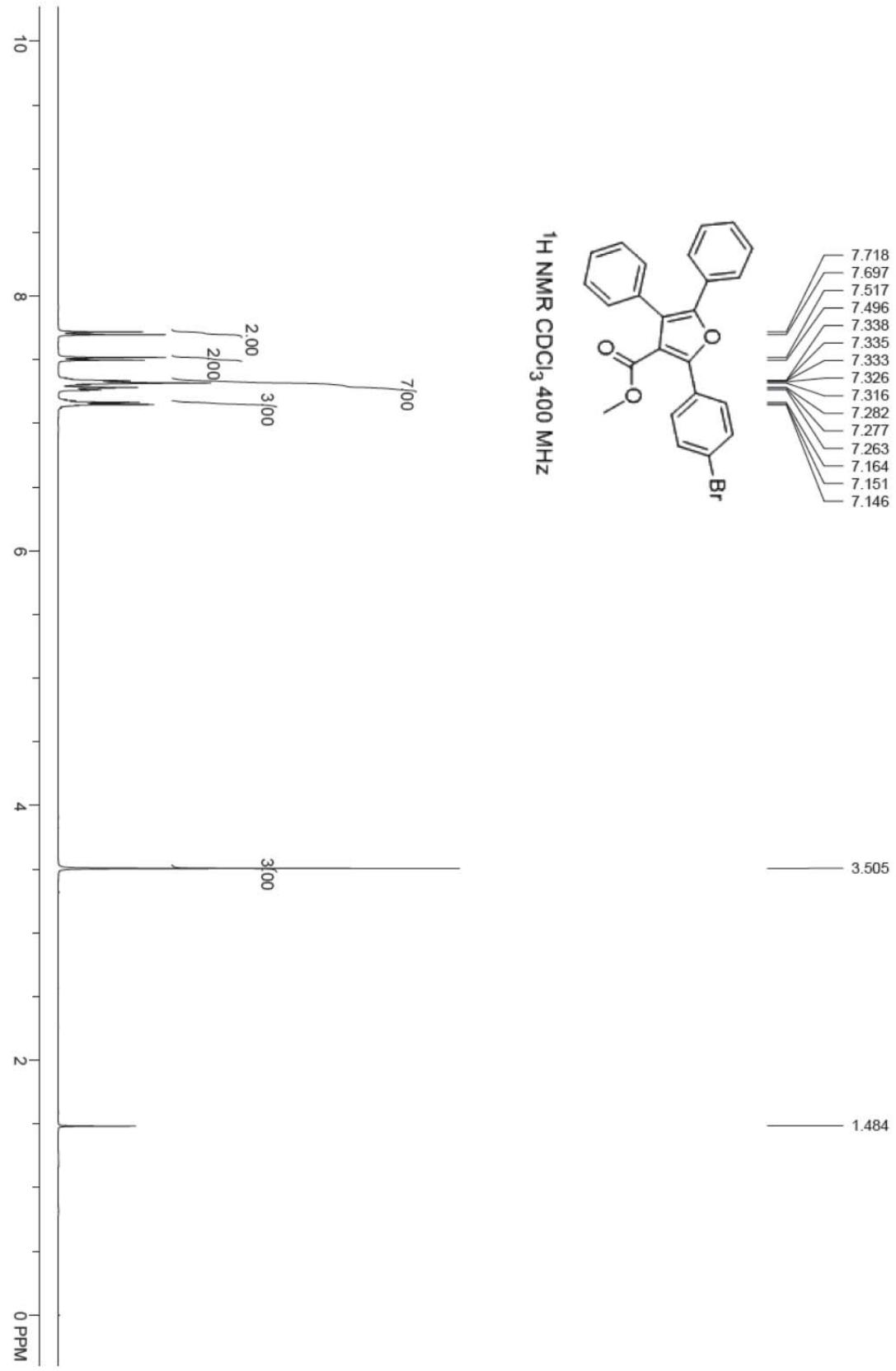

^{13}C NMR CDCl$_3$ 100 MHz
164.144
163.958
161.473
153.336
147.978
129.497
129.440
132.524
129.408
127.970
127.930
127.399
127.255
125.643
125.622
125.377
123.120
115.853
115.079
114.862
76.876
76.563
76.245
51.051
200
150
100
50
0 PPM
O
O
O
F

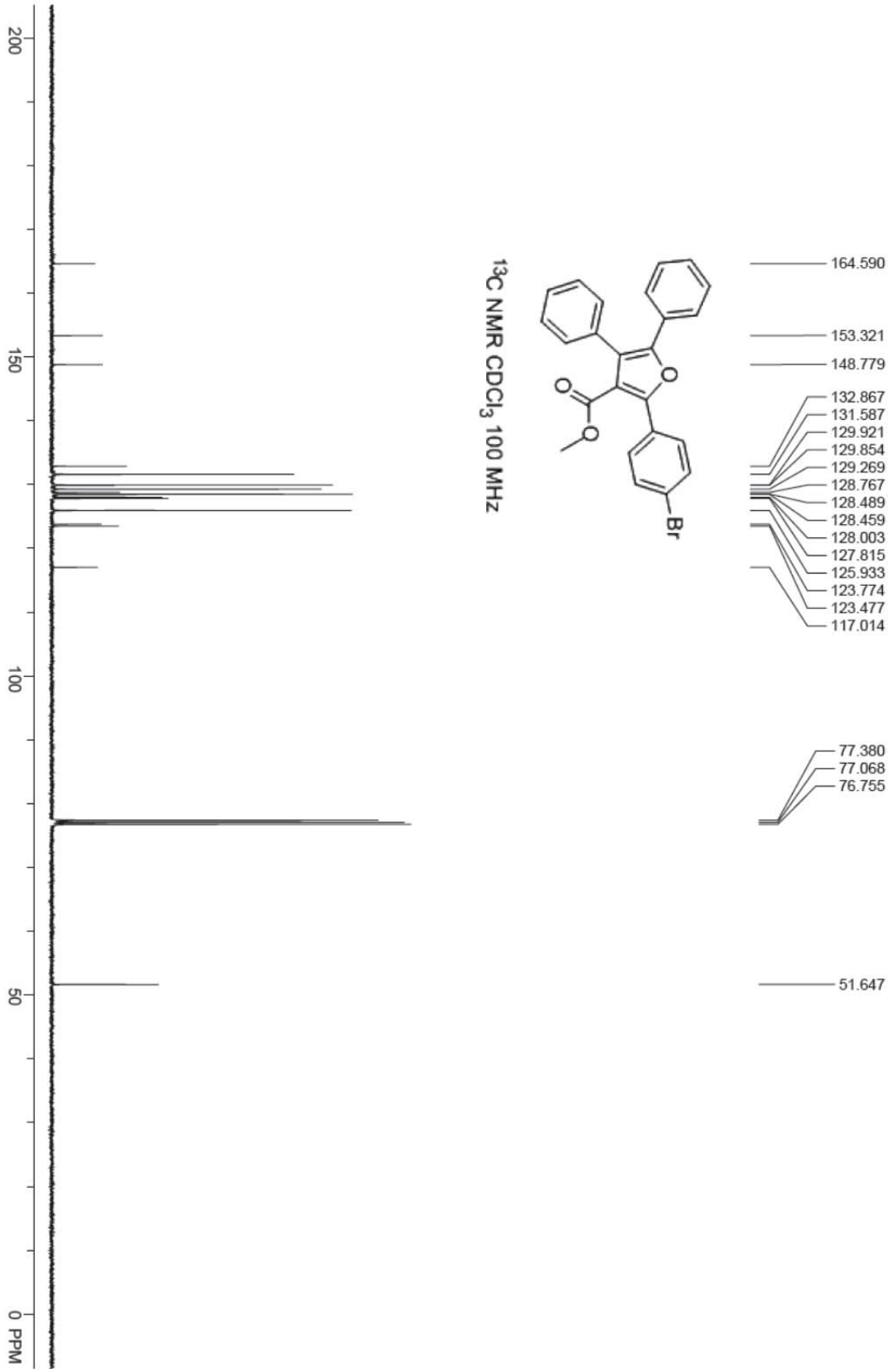
Methyl 2-(4-chlorophenyl)-4,5-diphenylfuran-3-carboxylate (4ak)



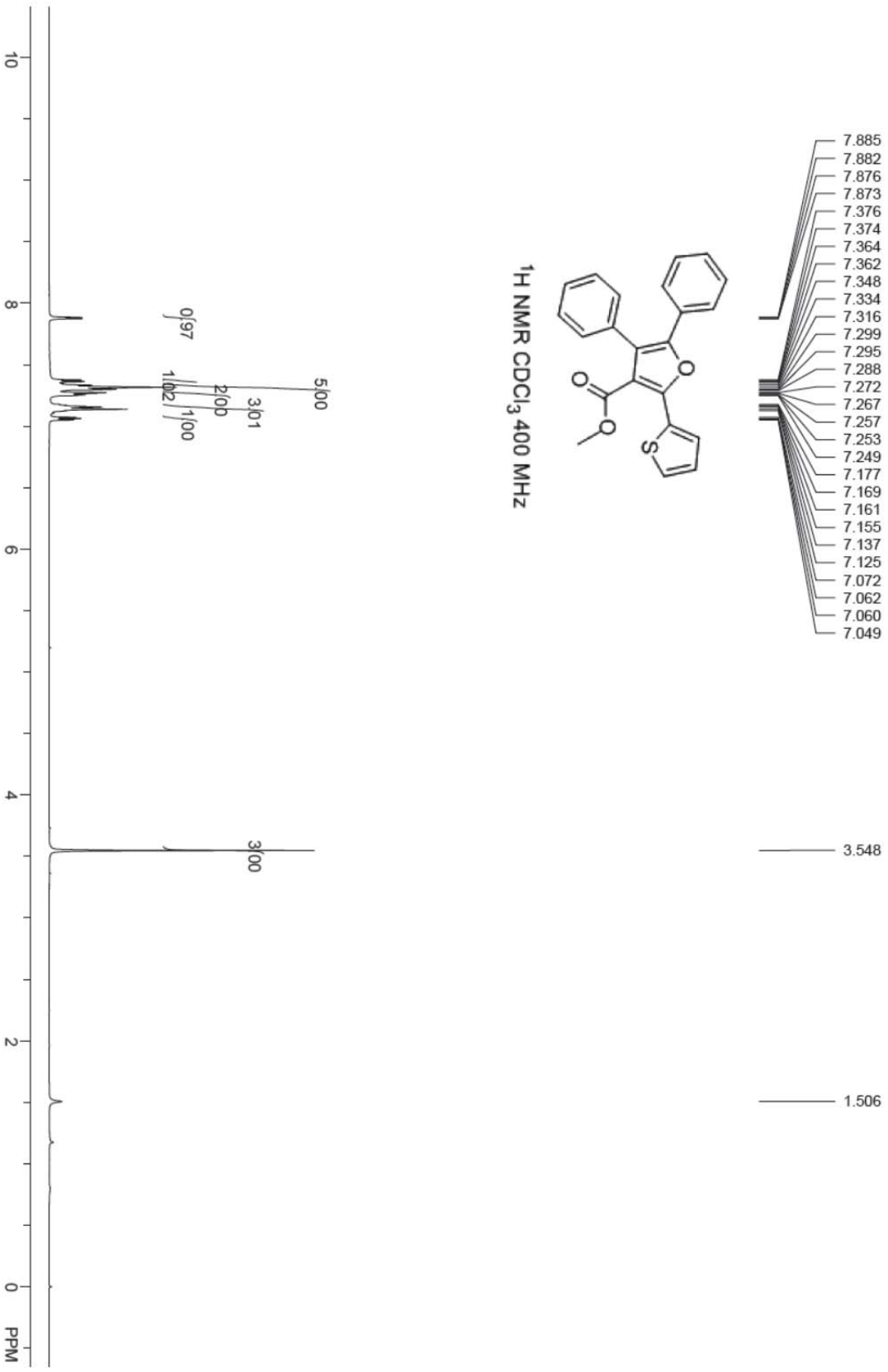

^{13}C NMR CDCl$_3$ 100 MHz
O
O
O
Cl
163.511
152.246
147.641
134.051
131.804
128.837
128.783
127.980
127.555
127.409
127.369
127.226
126.899
126.721
124.837
122.655
115.822
76.310
75.995
75.676
50.542
-0.000
200
150
100
50
0 PPM

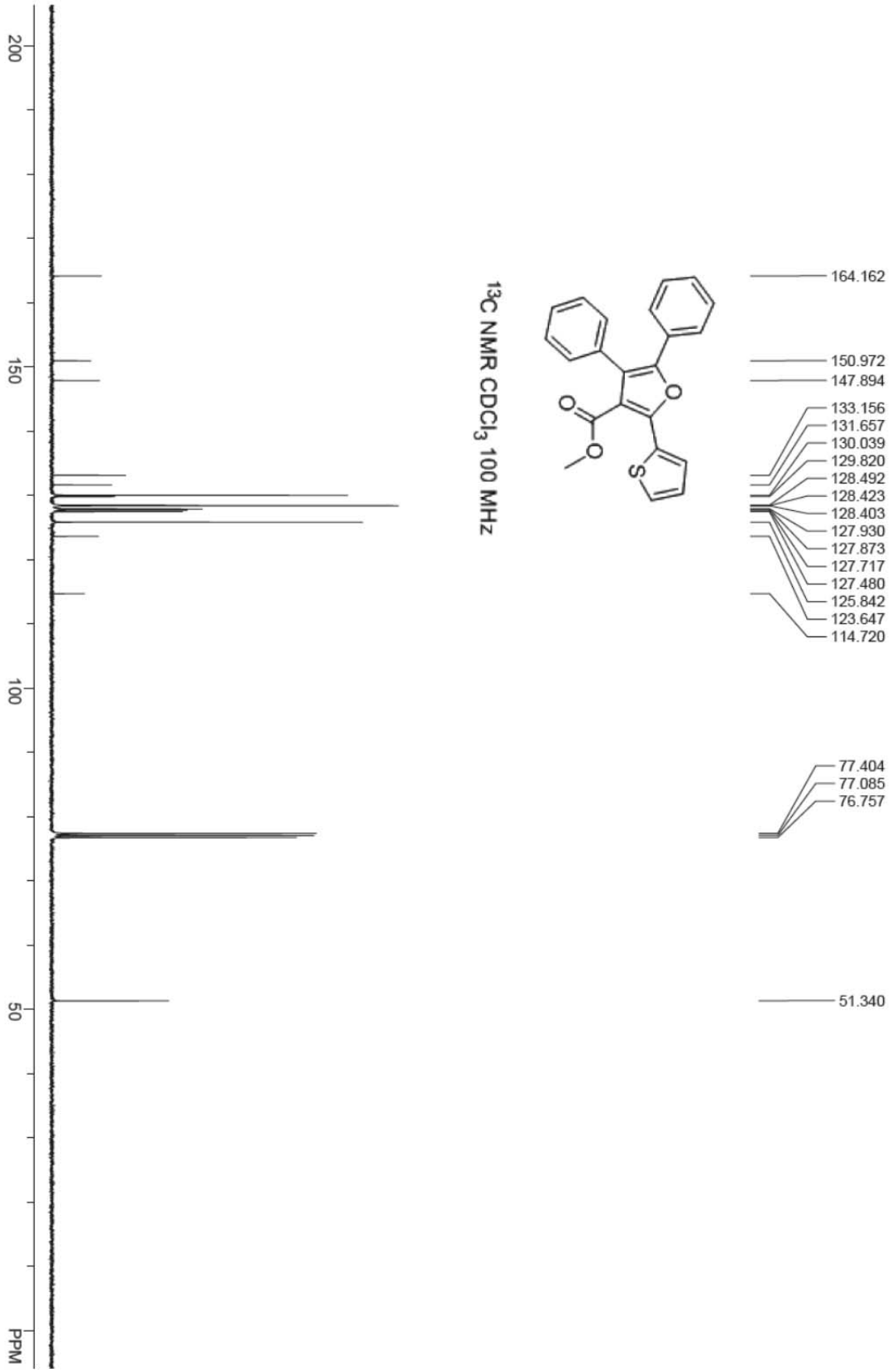
Methyl 2-(4-bromophenyl)-4,5-diphenylfuran-3-carboxylate (4al)



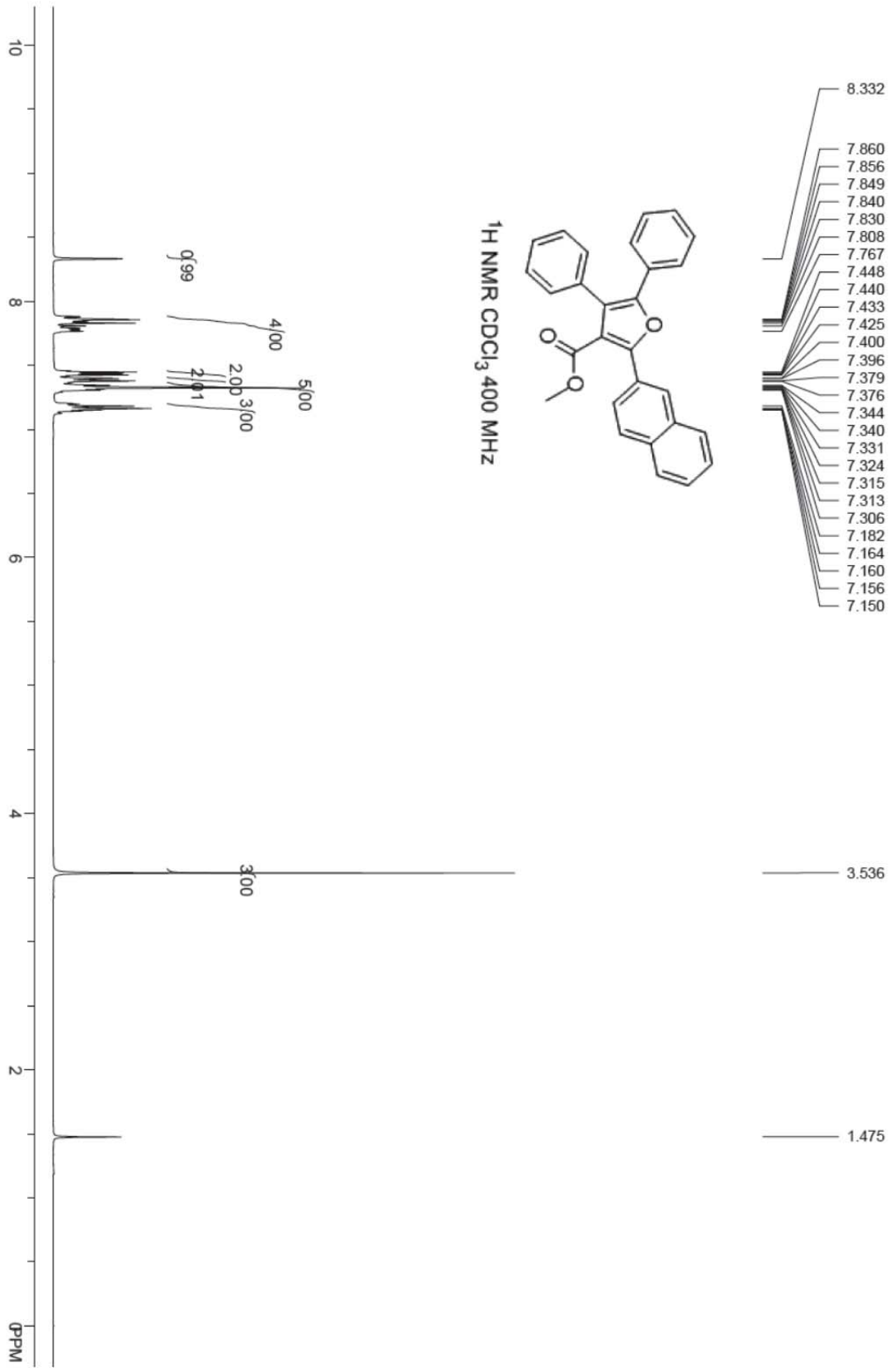

^{13}C NMR CDCl$_3$ 100 MHz
Br
164.590
153.321
148.779
132.867
131.587
129.921
129.854
129.269
128.767
128.489
128.459
128.003
127.815
125.933
123.774
123.477
117.014
77.380
77.068
76.755
51.647
200
150
100
50
0 PPM

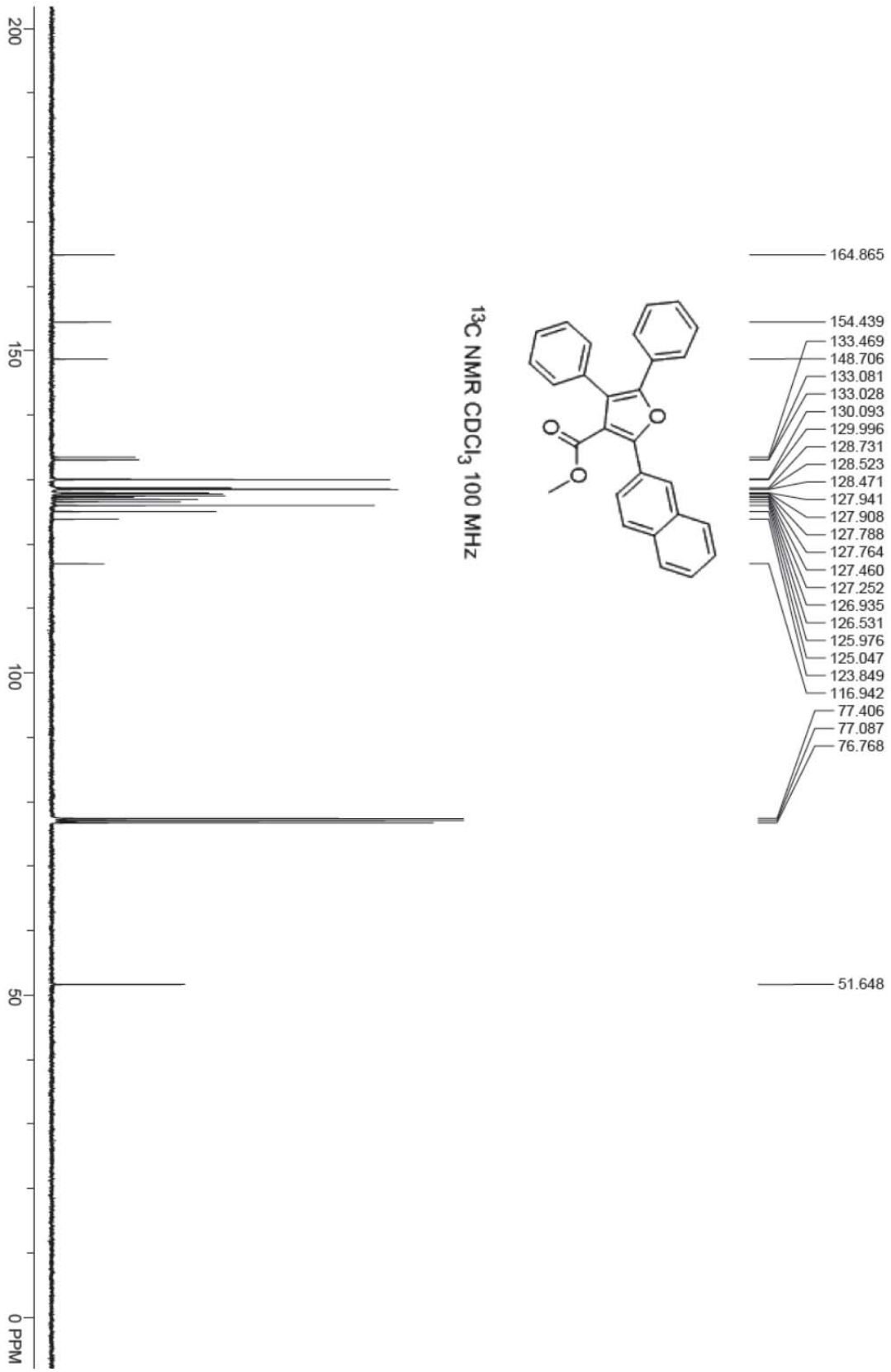
Methyl 4,5-diphenyl-2-(thiophen-2-yl)furan-3-carboxylate (4am)



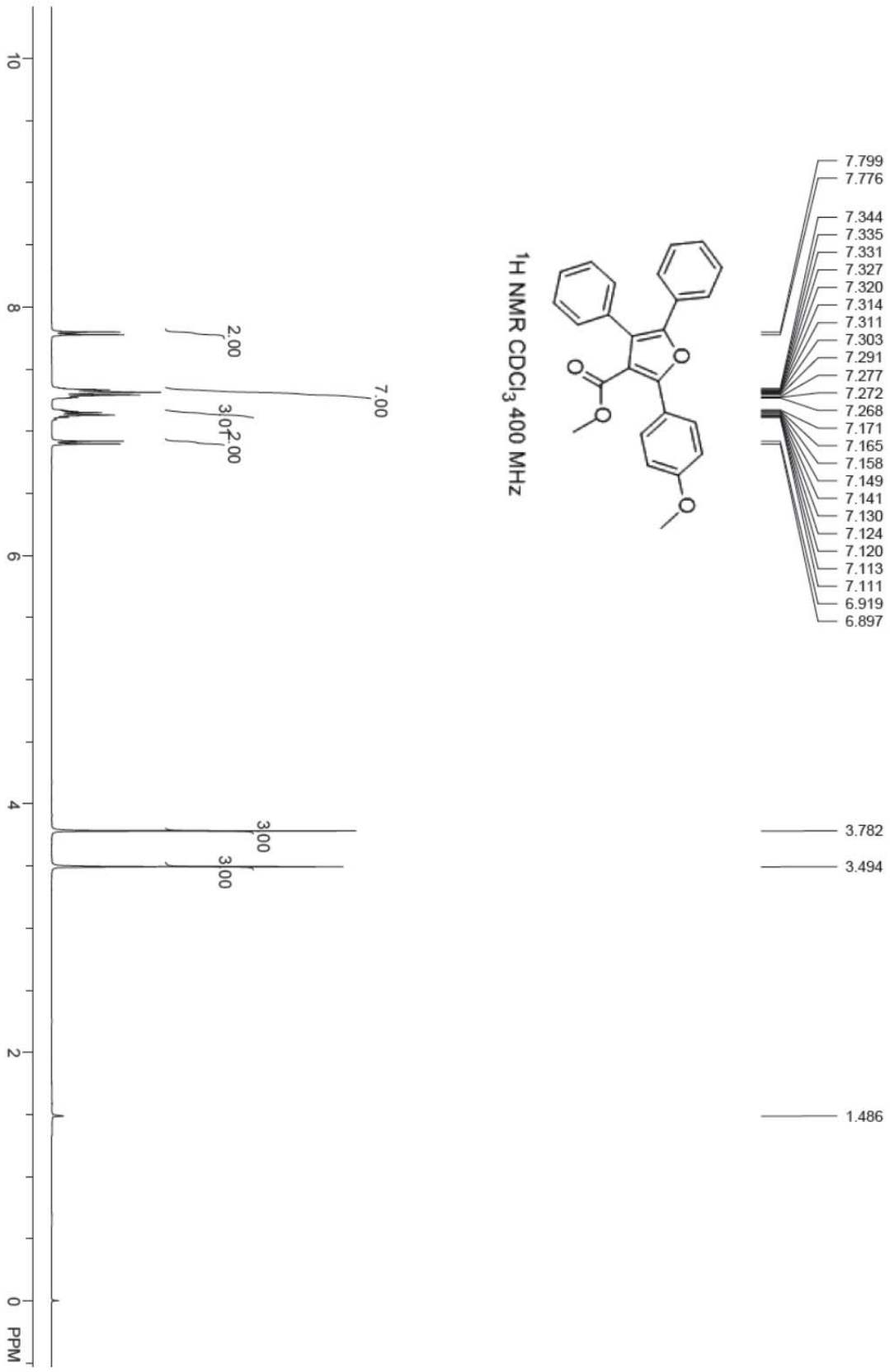

^{13}C NMR CDCl$_3$ 100 MHz
164.162
150.972
147.894
133.156
131.657
130.039
129.820
128.492
128.423
128.403
127.930
127.873
127.717
127.480
125.842
123.647
114.720
77.404
77.085
76.757
51.340
200
150
100
50
PPM

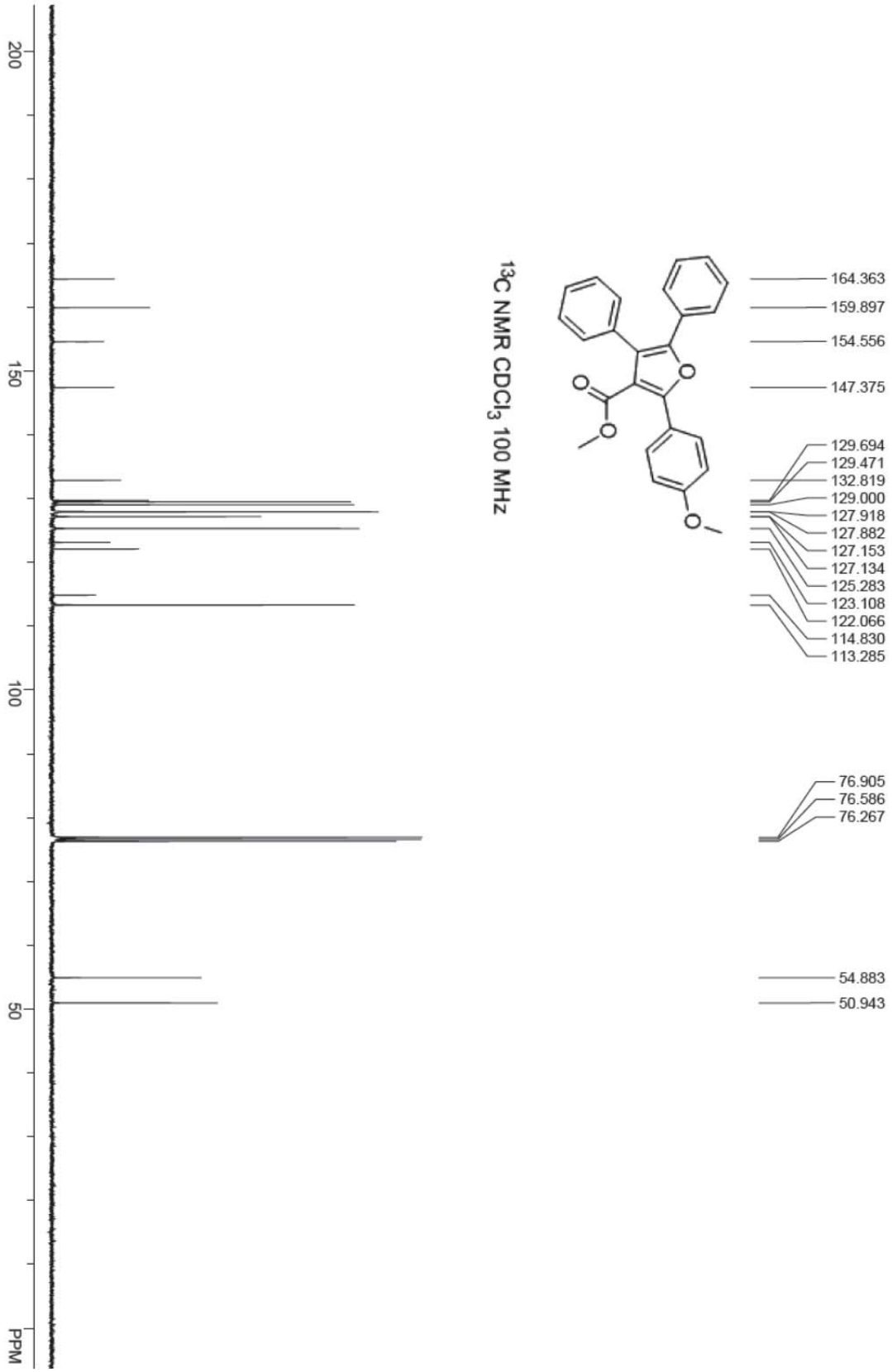
Methyl 2-(naphthalen-2-yl)-4,5-diphenylfuran-3-carboxylate (4an)




200
150
100
50
0 PPM
^{13}C NMR $CDCl_3$ 100 MHz
164.865
154.439
133.469
148.706
133.081
133.028
130.093
129.996
128.731
128.523
128.471
127.941
127.908
127.788
127.764
127.460
127.252
126.935
126.531
125.976
125.047
123.849
116.942
77.406
77.087
76.768
51.648

Methyl 2-(4-methoxyphenyl)-4,5-diphenylfuran-3-carboxylate (4ao)




^{13}C NMR CDCl$_3$ 100 MHz
164.363
159.897
154.556
147.375
129.694
129.471
132.819
129.000
127.918
127.882
127.153
127.134
125.283
123.108
122.066
114.830
113.285
76.905
76.586
76.267
54.883
50.943
200
150
100
50
PPM