Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting information

Scope and limitations of the Heck-Matsuda-coupling of phenol diazonium salts and styrenes: a protecting-group economic synthesis of phenolic stilbenes

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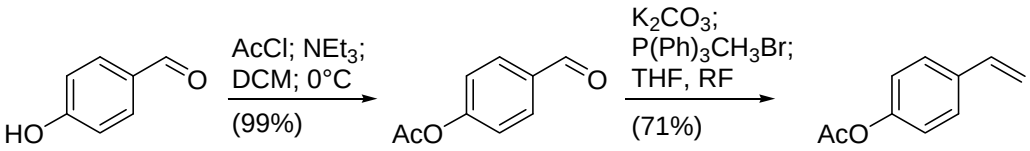
A General Remarks

All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ ($CHCl_3$ (δ = 7.24 ppm) used for calibration), in DMSO-d_6 (DMSO-d_5 (δ = 2.50 ppm) used for calibration), in acetone-d_6 (acetone-d_5 (δ = 2.05 ppm) used for calibration), or in methanol-d_4 (CHD_2OD (δ = 3.31 ppm used for calibration). Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ ($CDCl_3$ (δ = 77.0 ppm) used for calibration), in DMSO-d_6 (DMSO-d_6 (δ = 39.5 ppm) used for calibration), in acetone-d_6 (acetone-d_6 (δ = 29.9 ppm) used for calibration), or in methanol-d_4 (methanol-d_4 (δ = 49.9 ppm) used for calibration). The number of coupled protons was analyzed by APT-experiments and is denoted by a number in parantheses following the chemical shift value. IR spectra were recorded neat on NaCl or KBr plates, or as KBr-discs. Wavenumbers (ν) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV.

B Experimental procedures for styrenes 4e, 4g, 4h-j

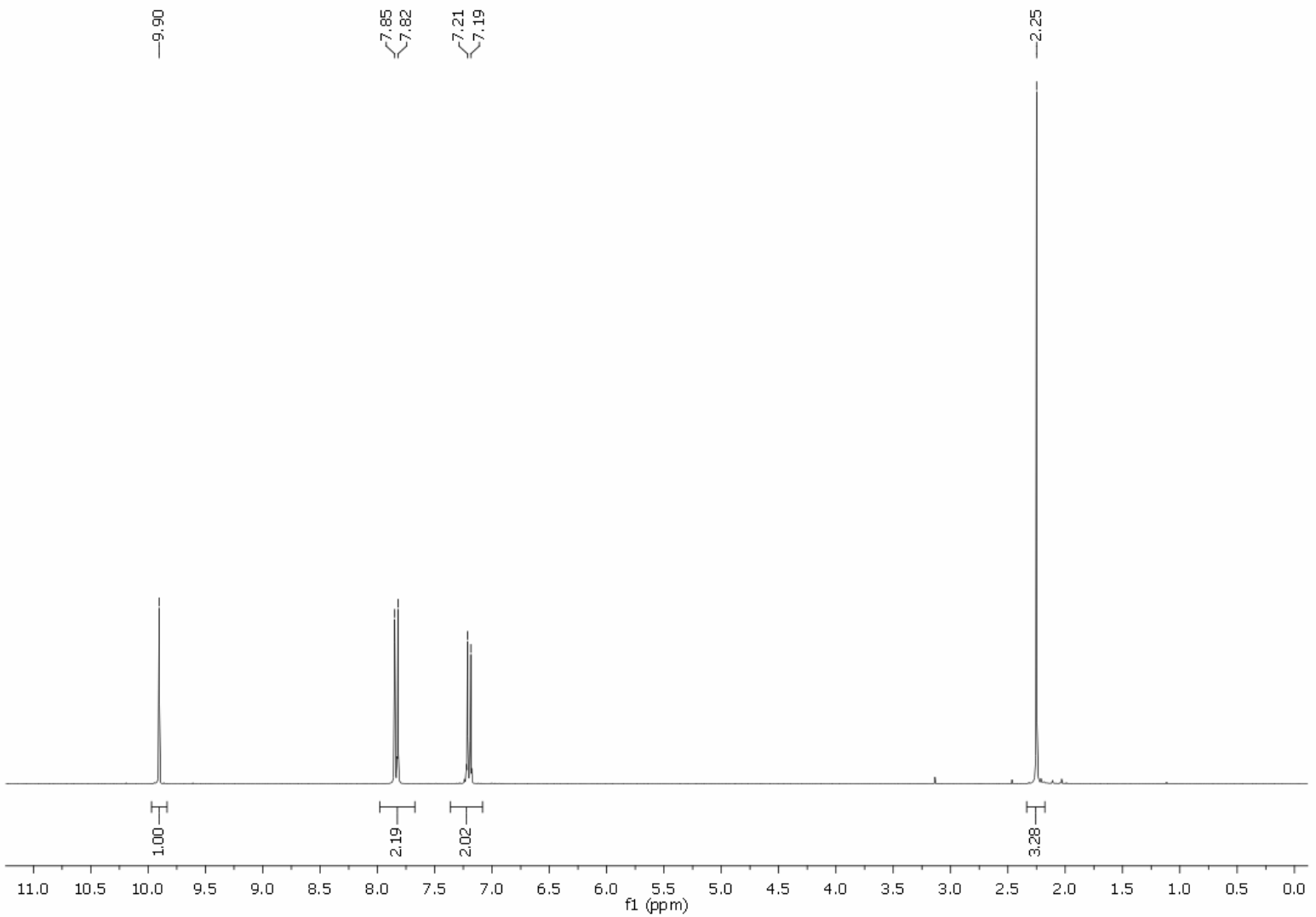
*B1 4-Acetyloxystyrene (**4e**)*



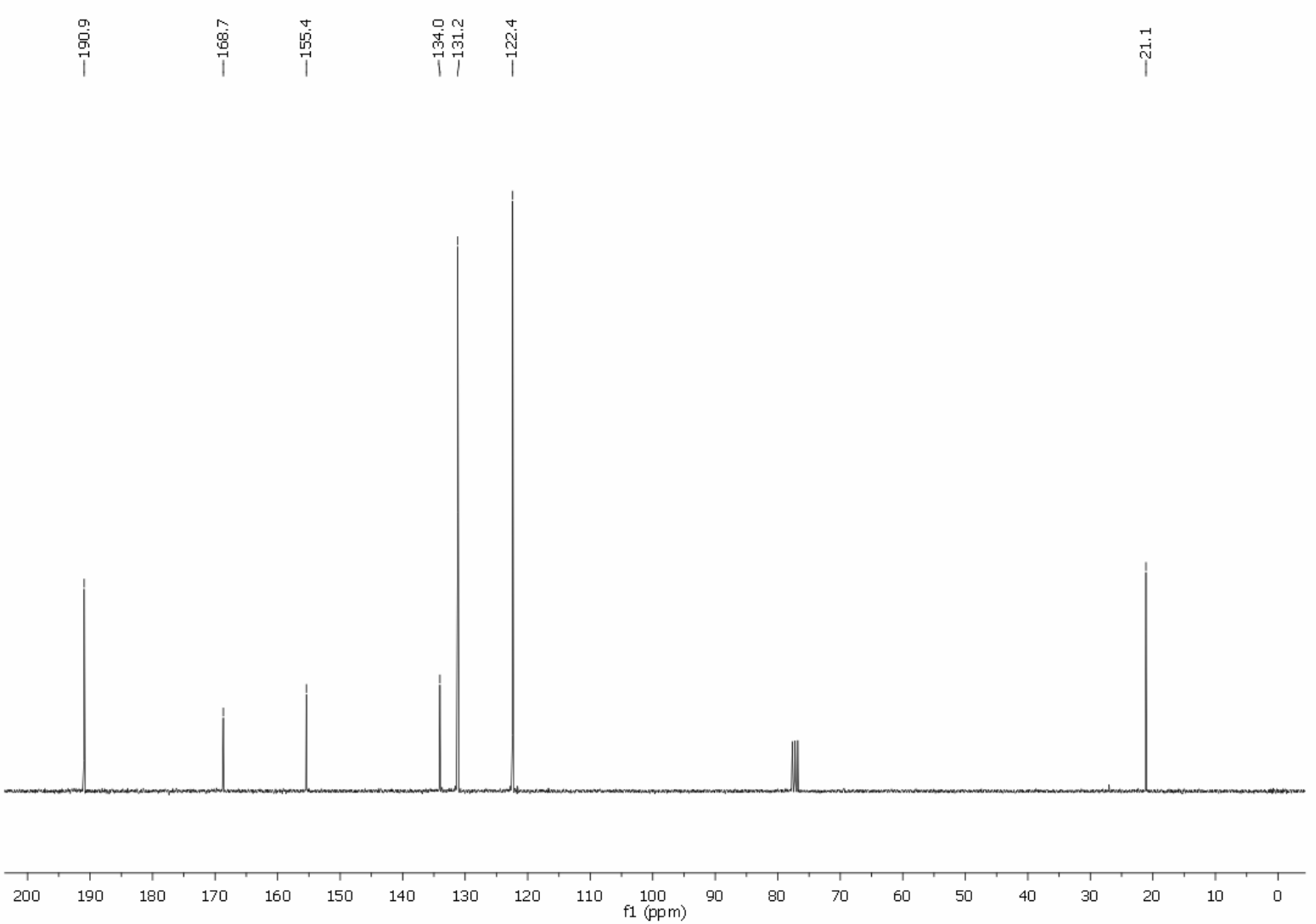
4-Acetyloxybenzaldehyde: To a solution of 4-hydroxybenzaldehyde (1.00 g, 8.2 mmol) and Et_3N (1.20 mL, 8.2 mmol) in anhydrous DCM (25 mL) was added dropwise acetyl chloride (0.60 mL, 8.2 mmol) at 0°C. The solution was stirred for 30 min. The reaction was concentrated under reduced pressure and the residue was dissolved in MTBE and aqueous $NaHCO_3$-solution. The aqueous layer was extracted with MTBE (60 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane : MTBE 2 : 1) to afford 4-acetyloxybenzaldehyde (1.30 g, 8.2 mmol, 99 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.83 (d, J = 8.7, 2H), 7.20 (d, J = 8.6, 2H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9 (0), 168.7 (0), 155.4 (0), 134.0 (0), 131.2 (1), 122.4 (1), 21.1 (3); IR (neat) ν 3072 (m), 1758 (s), 1698 (s), 1595 (s); MS (ESI) *m/z* 99 (24%), 123 (80%), 165 ($[M+H]^+$, 100%); HRMS (ESI) calcd for $C_9H_9O_3$ $[M+H]^+$: 165.0553, found: 165.0552.

*4-Acetyloxystyrene (**4e**)*: To a suspension of 4-acetyloxybenzaldehyde (2.60 g, 15.8 mmol) and K_2CO_3 (2.63 g, 19.0 mmol) in anhydrous THF (50 mL) was added $[PPh_3CH_3]Br$ (6.79 g, 19.0 mmol). The suspension was heated to reflux for 6 hours. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in MTBE and water. The aqueous layer was extracted with MTBE (90 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane : MTBE 10 : 1) to afford **4e** (1.82 g, 11.2 mmol, 71 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6, 2H), 7.06 (d, J = 8.7, 2H), 6.71 (dd, J = 17.6, 10.9, 1H), 5.71 (dd, J = 17.6, 0.7, 1H), 5.25 (dd, J = 10.9, 0.7, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 (0), 150.4 0), 136.1 (1), 135.5 (0), 127.3 (1), 121.8 (1), 114.2 (1), 21.3 (3); IR (neat) ν 3040 (w), 1757 (s), 1504 (s), 1186 (s); MS (ESI) *m/z* 121 (100%), 163 ($[M+H]^+$, 4%), 185 ($[M+Na]^+$, 4%); HRMS (ESI) calcd for $C_{10}H_{11}O_2$ $[M+H]^+$: 163.0759, found: 163.0767; Anal. calcd for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2. Found: C, 74.2; H, 6.2.

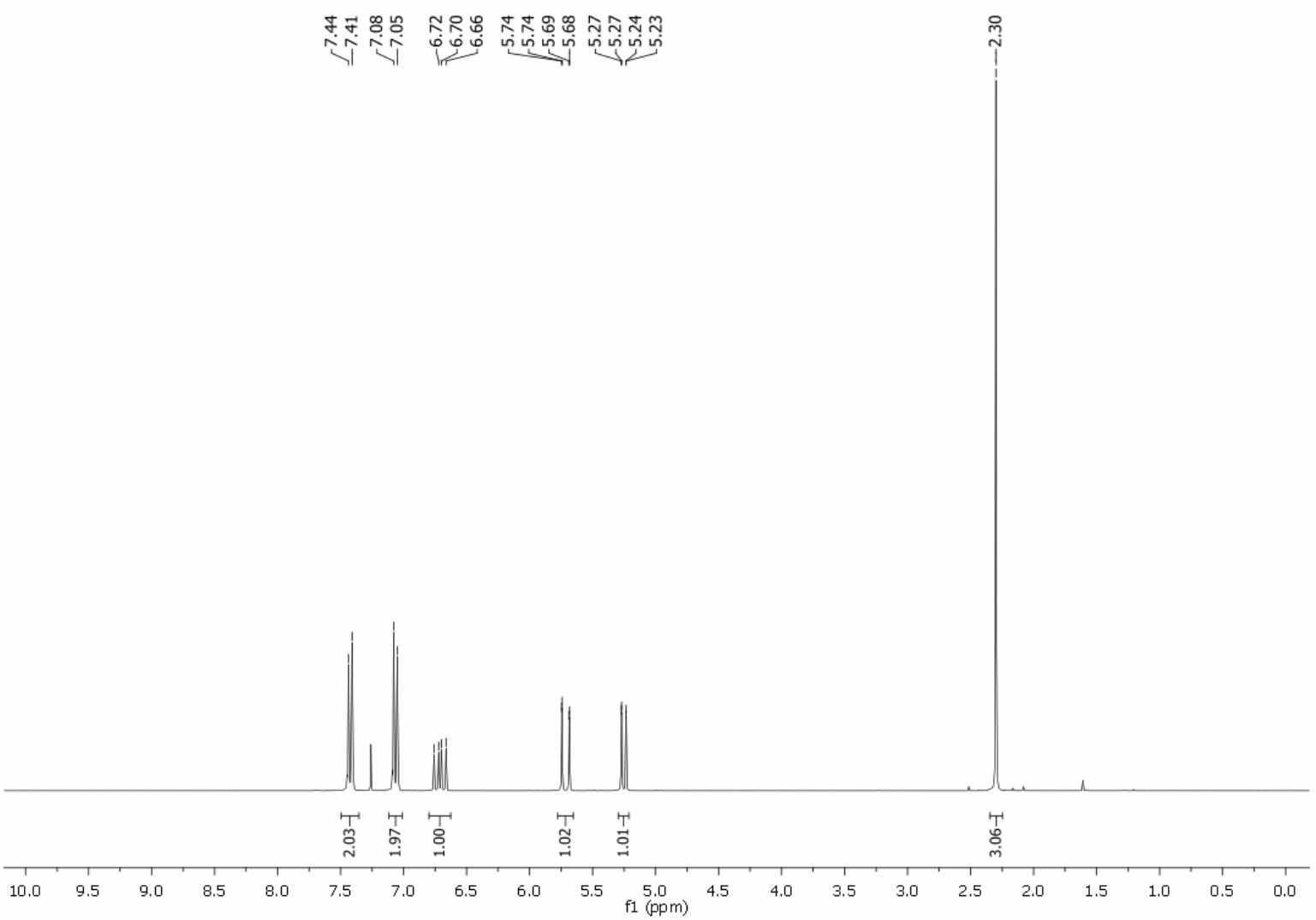
^{1}H NMR (300 MHz, $CDCl_3$) of 4-acetyloxybenzaldehyde



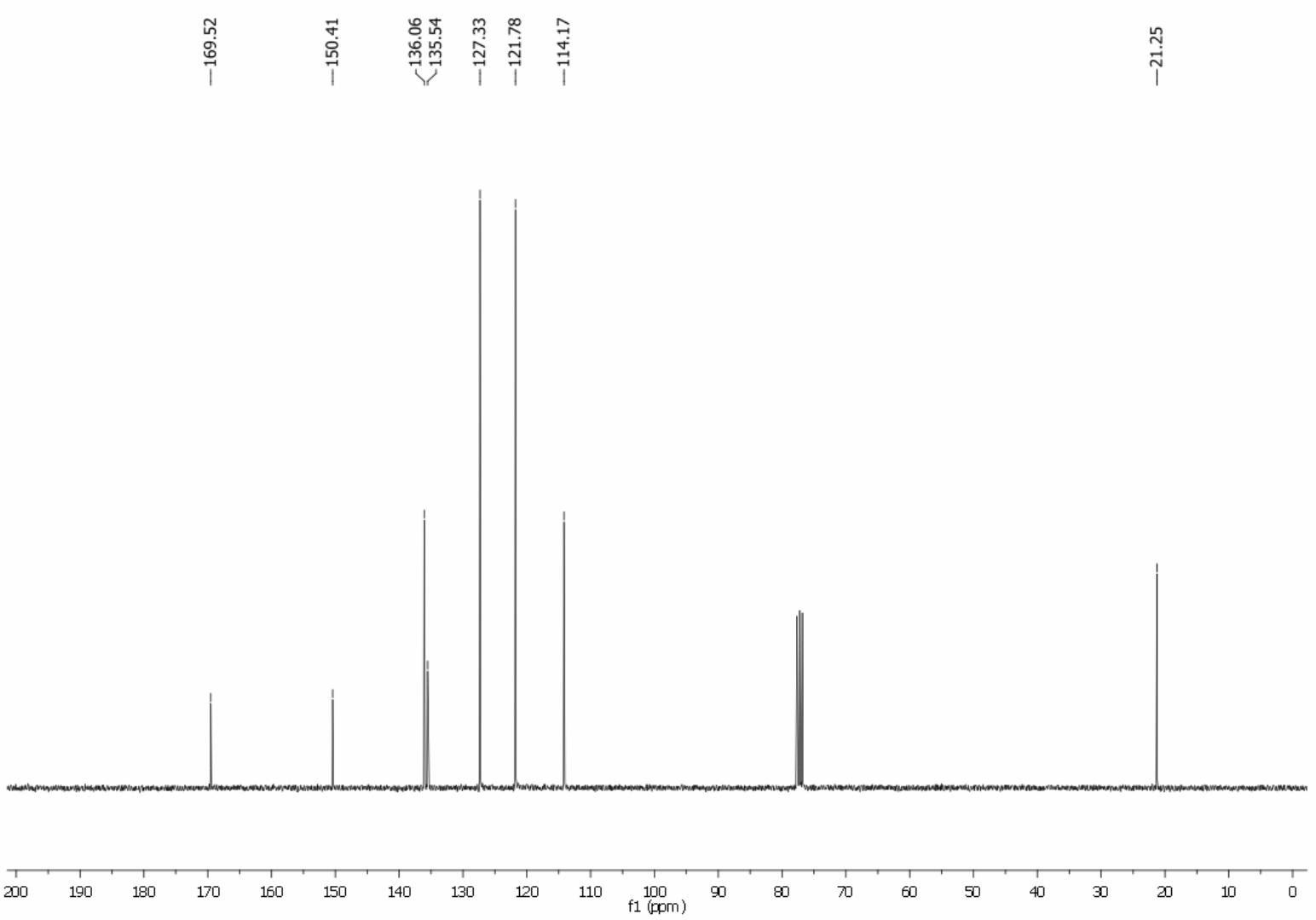
^{13}C NMR (75 MHz, $CDCl_3$) of 4-acetyloxybenzaldehyde



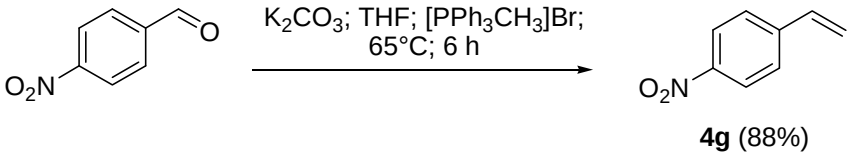
^{1}H NMR (300 MHz, $CDCl_3$) of **4e**



^{13}C NMR (75 MHz, $CDCl_3$) of **4e**



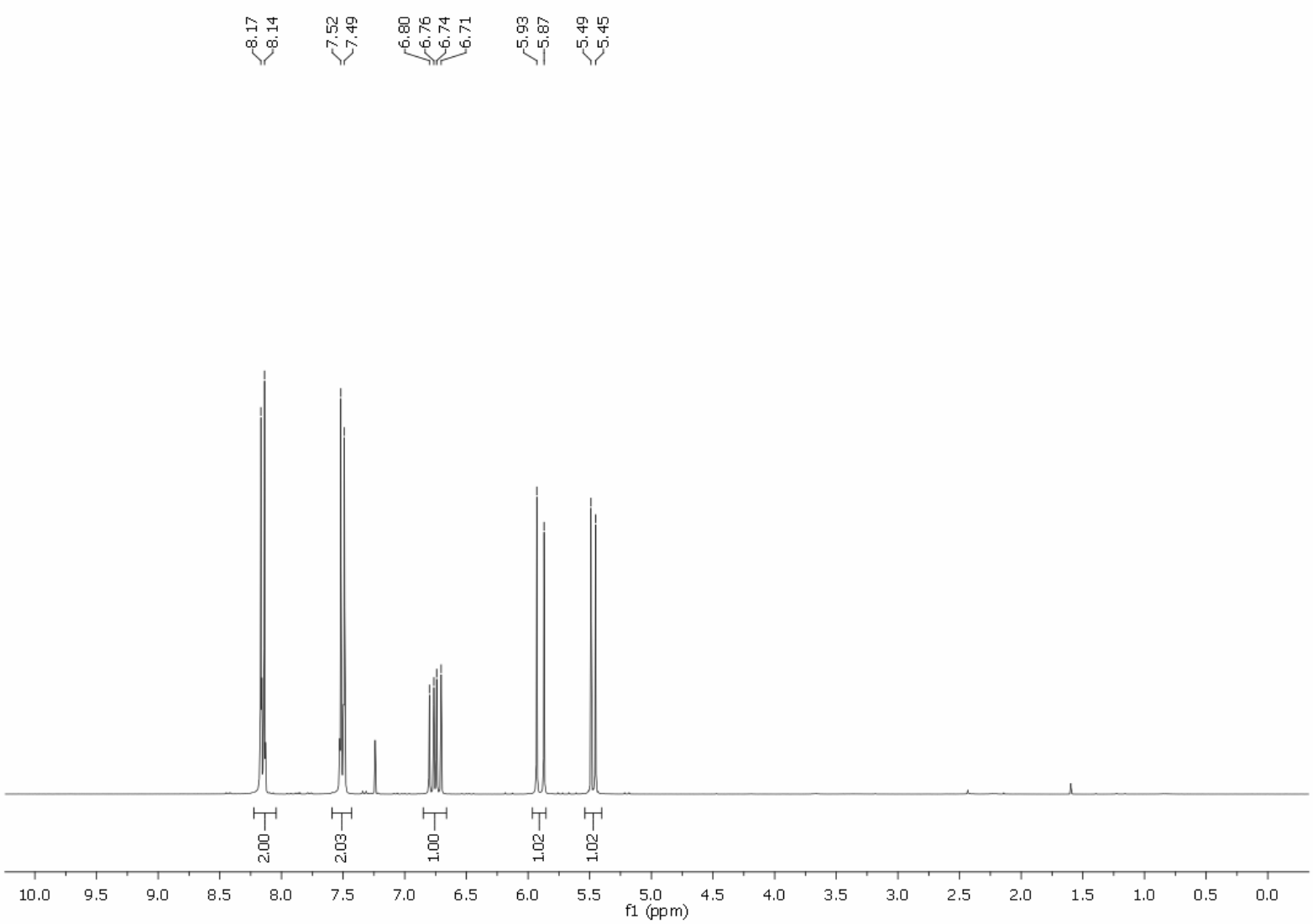
B2 *4-Nitro styrene (**4g**)*



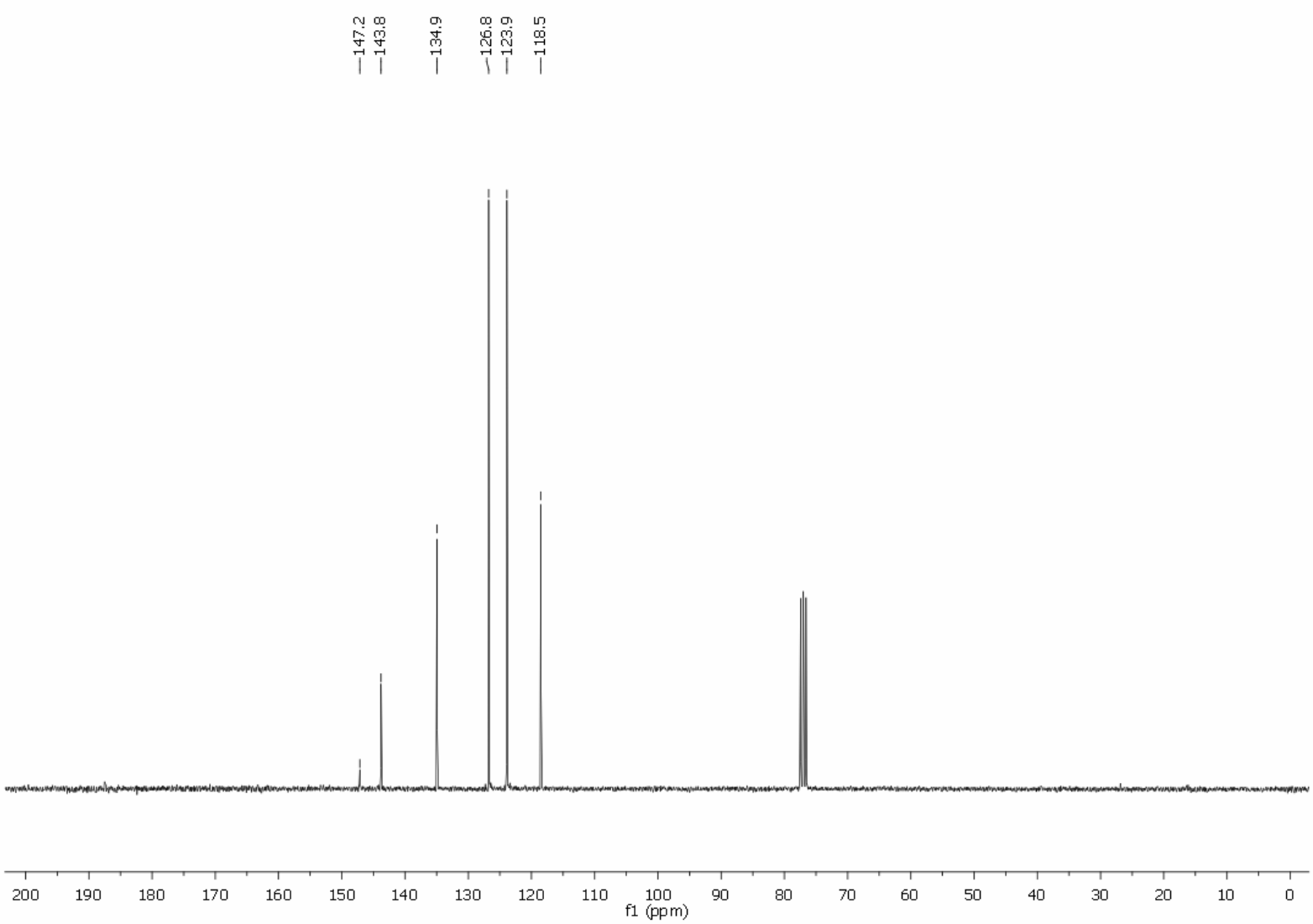
4g (88%)

To a suspension of 4-nitrobenzaldehyde (2.50 g, 16.5 mmol) and K_2CO_3 (2.70 g, 19.8 mmol) in anyhdrous THF (50 mL) was added $[PPh_3CH_3]Br$ (7.00 g, 19.8 mmol) and heated to reflux for 6 hours. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in MTBE and water. The water layer was extracted with MTBE (90 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 10 : 1) to afford **4g** (2.15 g, 14.5 mmol, 88 %) as yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8, 2H), 7.50 (d, J = 8.6, 2H), 6.75 (dd, J = 17.6, 10.9, 1H), 5.90 (d, J = 17.6, 1H), 5.47 (d, J = 11.0, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1 (0), 143.8 (0), 134.9 (1), 126.7 (1), 123.9 (1), 118.5 (1); MS (ESI) *m/z* 104 (22%), 133 (46%), 150 ($[M+H]^+$, 100%); HRMS (ESI) calcd for $C_8H_8NO_2$ $[M+H]^+$: 150.0555, found: 150.0541; IR (neat) ν 3077 (m), 1594 (s), 1509 (s), 1338 (s); Anal. calcd for $C_8H_7NO_2$: C, 64.4; H, 4.7; N, 9.4. Found: C, 63.9; H, 4.7; N, 9.9.

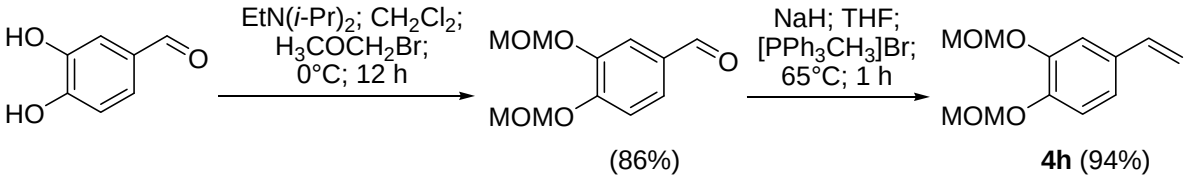
^{1}H NMR (300 MHz, $CDCl_3$) of **4g**



^{13}C NMR (75 MHz, $CDCl_3$) of **4g**



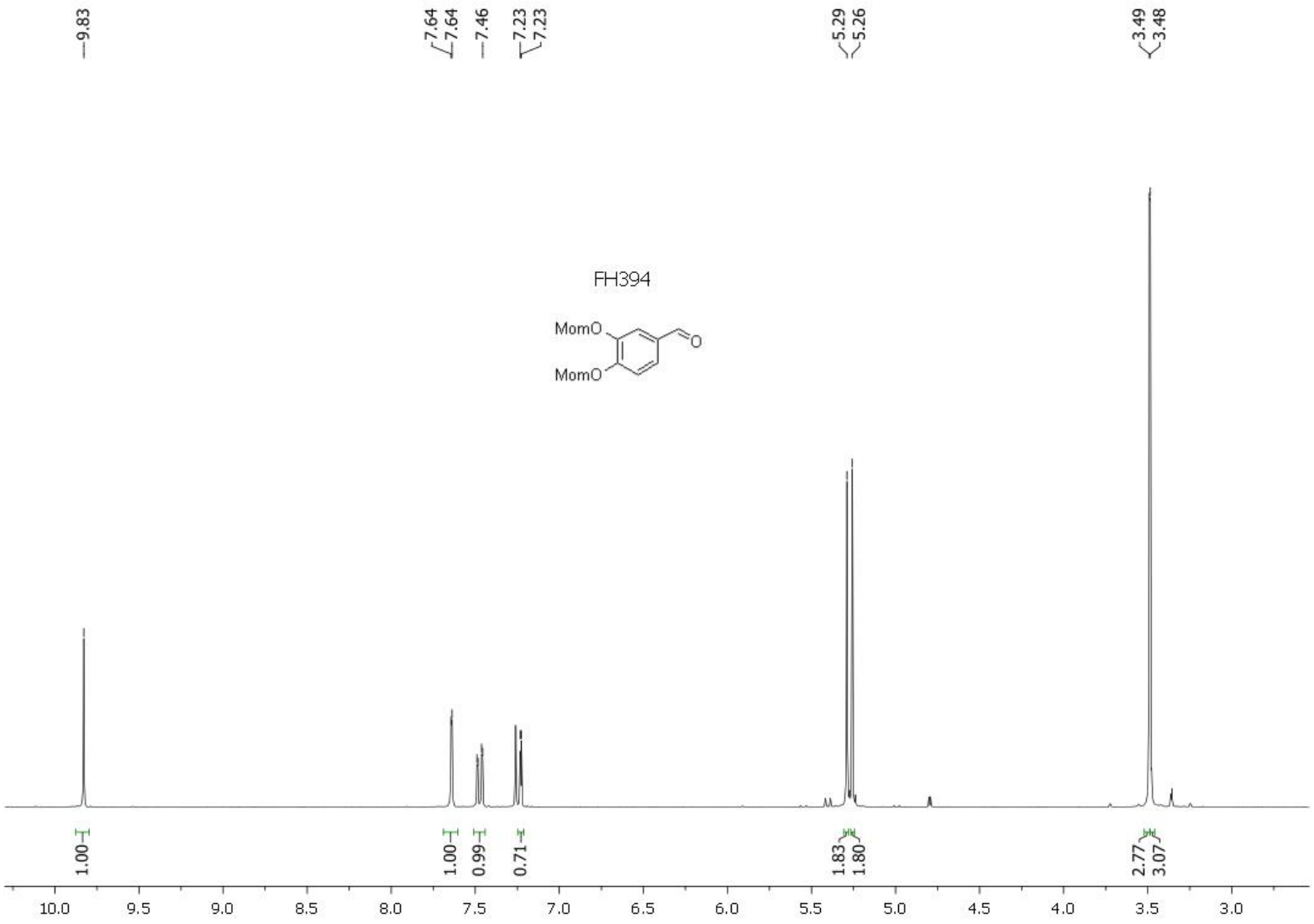
*B3 1,2-Bis(methoxymethoxy)-4-vinylbenzene (**4h**)*



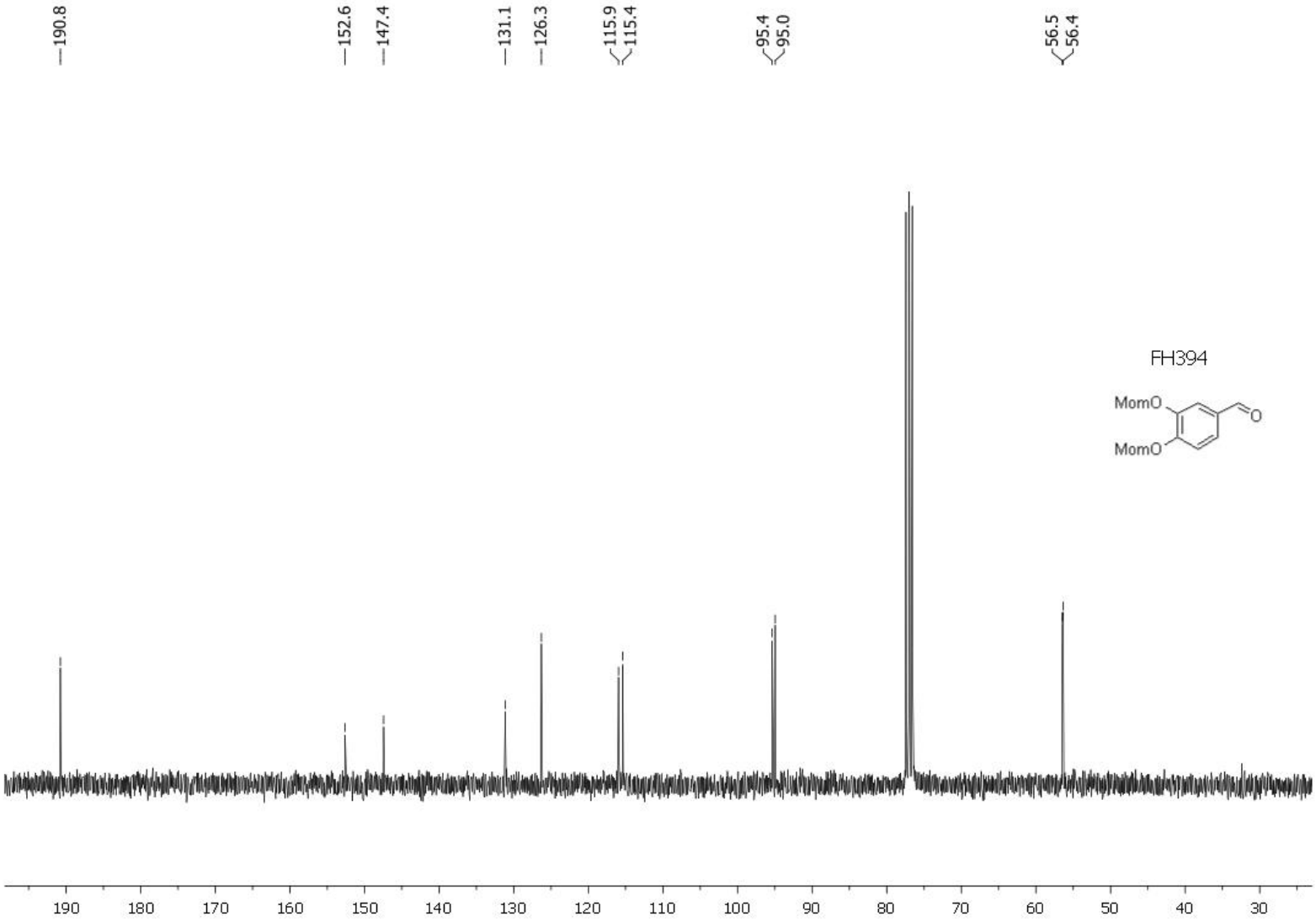
3,4-Bis(methoxy-methoxy)benzaldehyde: To a solution of 3,4-dihydroxybenzaldehyde (1.00 g, 7.2 mmol) and *N*,*N*-diisopropylethylamine (2.50 mL, 15.0 mmol) in anhydrous DCM (50 mL) was added dropwise bromomethyl methyl ether (1.30 mL, 15.0 mmol) at 0°C. The solution was warmed to ambient temperature and stirred at this temperature for 12 h. The solution was washed with water (25 mL) and saturated aqueous Na_2CO_3 solution (25 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 2 : 1) to afford *3,4-bis(methoxy-methoxy)benzaldehyde* (1.40 g, 6.2 mmol, 86 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.64 (d, J = 1.9, 1H), 7.47 (dd, J = 8.4, 1.9, 1H), 7.23 (d, J = 8.4, 1H), 5.29 (s, 2H), 5.26 (s, 2H), 3.49 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8 (1), 152.6 (0), 147.4 (0), 131.1 (0), 126.3 (1), 116.0 (1), 115.4 (1), 95.4 (2), 95.0 (2), 56.5 (3), 56.4 (3).

*1,2-Bis(methoxymethoxy)-4-vinylbenzene (**4h**)*: To a suspension of $[PPh_3CH_3]Br$ (2.50 g, 7.0 mmol) in anhydrous THF (50 mL) was added slowly NaH (60 % dispersion in mineral oil, 0.30 g, 7.0 mmol). The suspension was heated to reflux for 1 h. The mixture was then cooled to ambient temperature, and the aldehyde from the previous step (1.4 g, 6.2 mmol) was added. The solution was heated to reflux for 2 h. The reaction mixture was then washed with saturated aqueous Na_2CO_3 solution (20 mL) and the aqueous layer was extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 2 : 1) to afford **4h** (1.30 g, 5.8 mmol, 94 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 2.0, 1H), 7.11 (d, J = 8.4, 1H), 7.00 (dd, J = 8.4, 2.0, 1H), 6.63 (dd, J = 17.6, 10.9, 1H), 5.63 (dd, J = 17.6, 0.8, 1H), 5.25 (s, 2H), 5.23 (s, 2H), 5.16 (dd, J = 10.9, 0.8, 1H), 3.53 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4 (0), 147.1 (0), 136.2 (1), 132.5 (0), 120.7 (2), 116.6 (1), 114.4 (1), 112.7 (1), 95.5 (2), 95.4 (2), 56.2 (3), 56.2 (3); MS (ESI) *m/z* 181 (100%), 225 ($[M+H]^+$, 52%); HRMS (ESI) calcd for $C_{12}H_{17}O_4$ $[M+H]^+$: 225.1127, found: 225.1138; IR (neat) ν 2924 (m), 2852 (w), 1602 (w), 1578 (w), 1508 (s), 1439 (w), 1393 (w), 1257 (s), 1226 (m), 1202 (m), 1152 (s), 1126 (m), 1072 (s); Anal. calcd for $C_{12}H_{16}O_4$: C, 64.3; H, 7.2. Found: C, 64.2; H, 7.2.

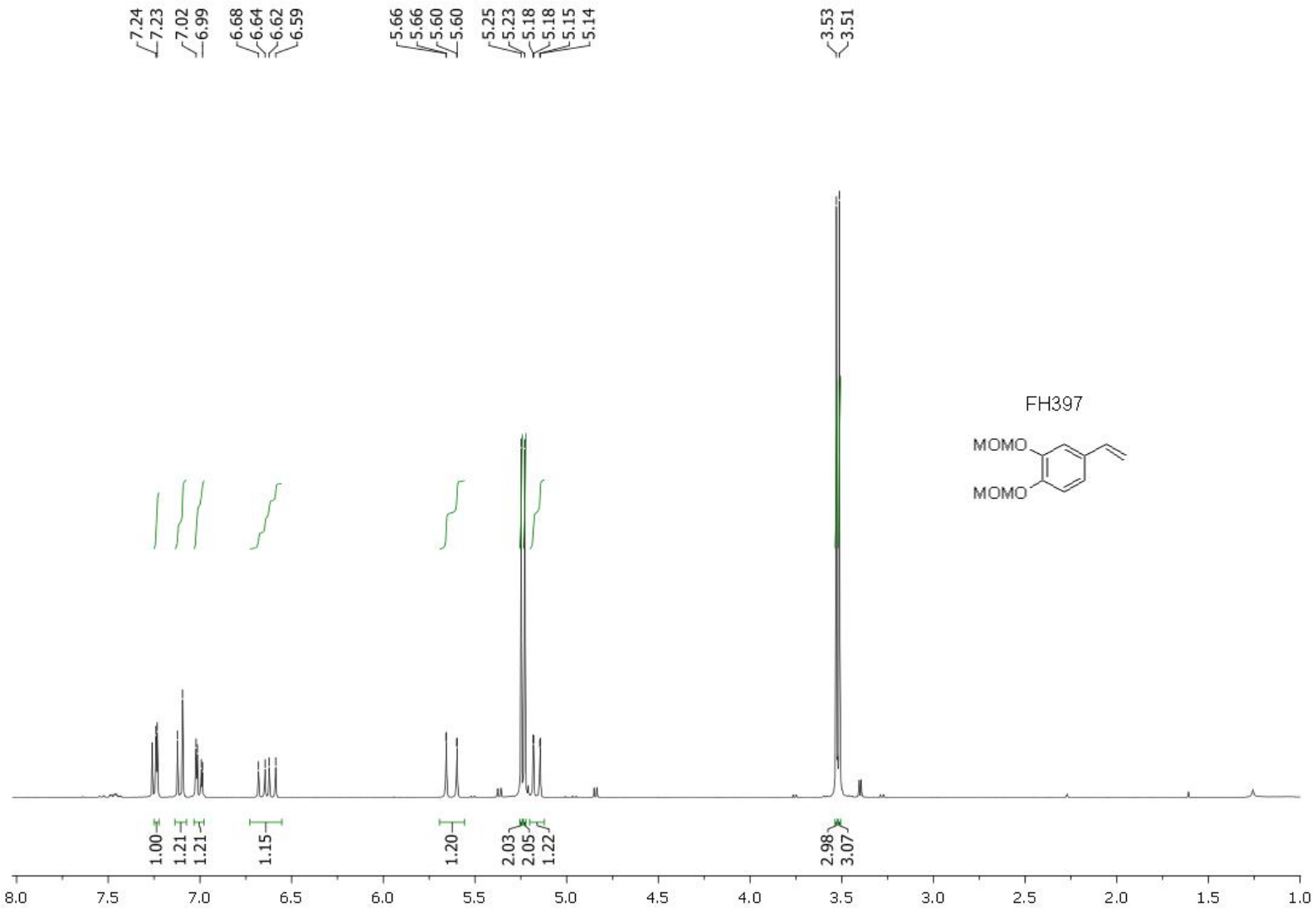
^{1}H NMR (300 MHz, $CDCl_3$) of 3,4-Bis(methoxy-methoxy)benzaldehyde



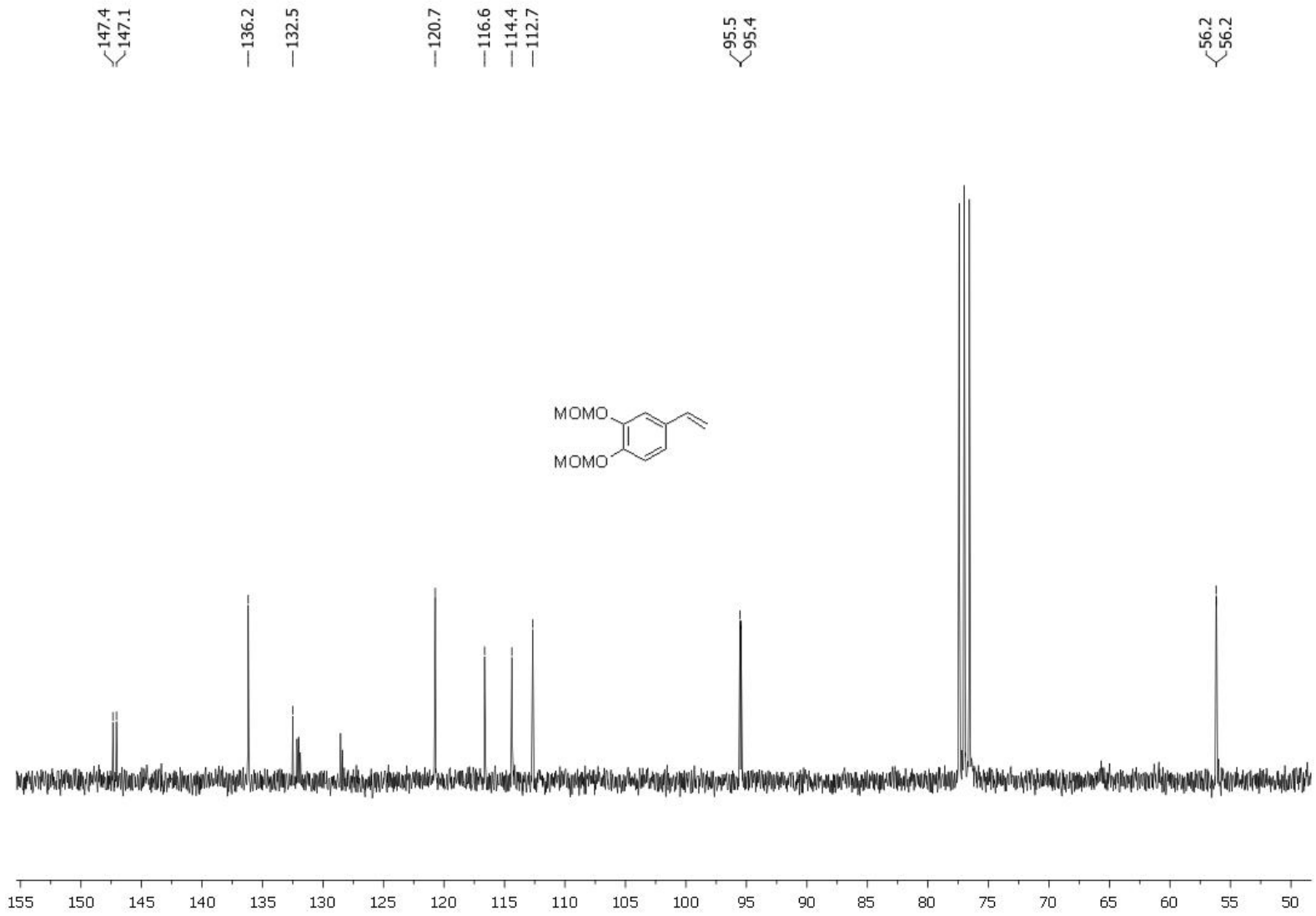
^{13}C NMR (75 MHz, $CDCl_3$) of 3,4-Bis(methoxy-methoxy)benzaldehyde



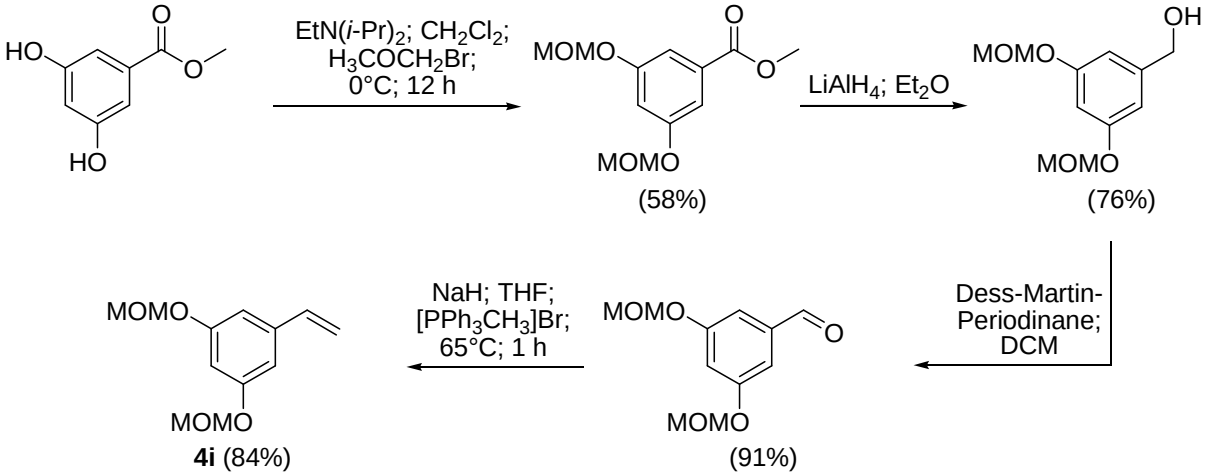
^{1}H NMR (300 MHz, $CDCl_3$) of **4h**



^{13}C NMR (75 MHz, $CDCl_3$) of **4h**



*B4 1,3-Bis(methoxymethoxy)-5-vinylbenzene (**4i**)*



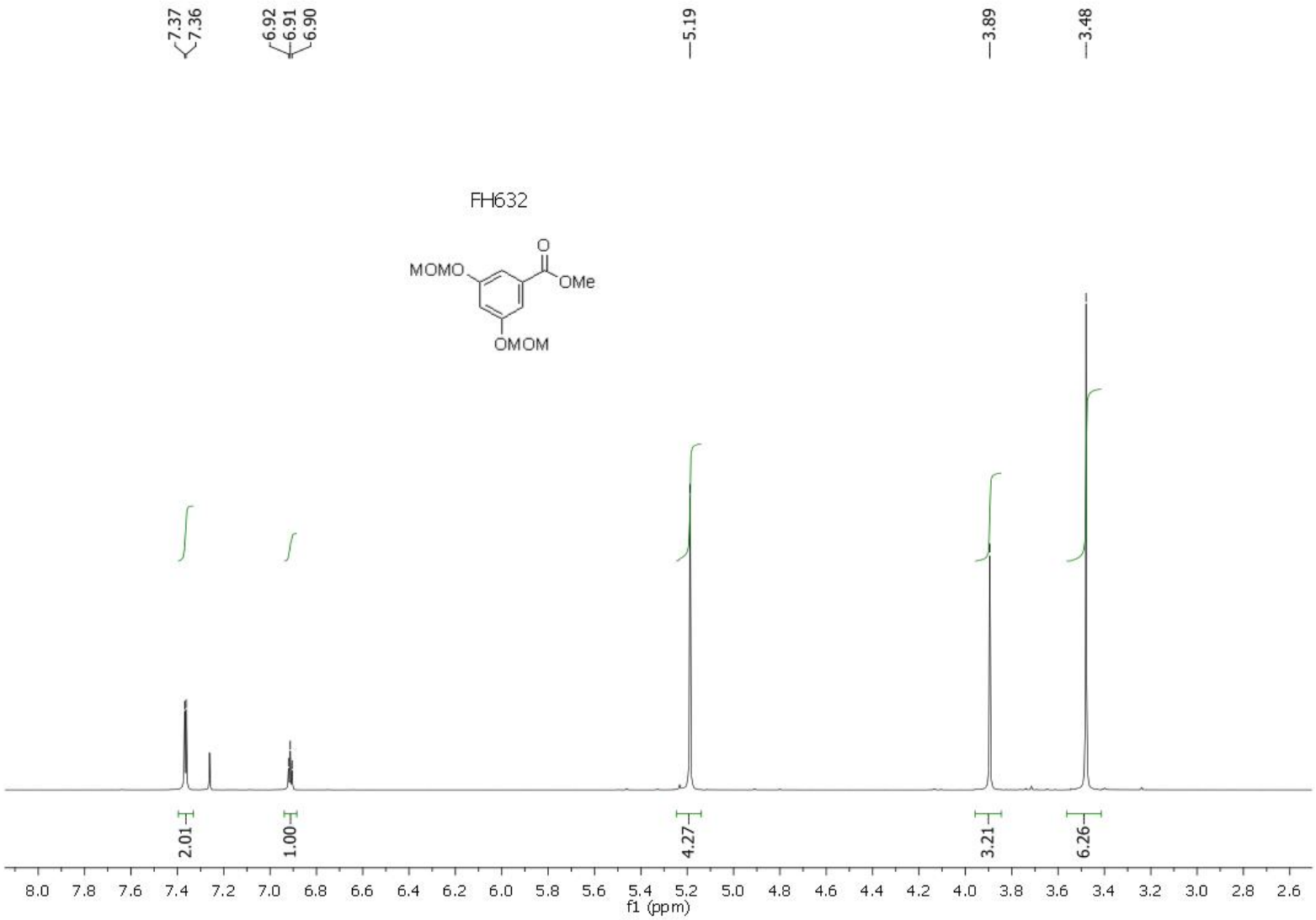
Methyl 3,5-bis(methoxymethoxy)benzoate: To a solution of methyl 3,5-dihydroxybenzoate (2.00 g, 12.0 mmol) and N,N-diisopropylethylamine (4.0 mL, 24.0 mmol) in anhydrous DCM (50 mL) was added dropwise bromomethyl methyl ether (2.00 mL, 24.0 mmol) at 0°C. The solution was warmed to ambient temperature and stirred for 12 h. The solution was washed with water (25 mL) and saturated aqueous Na_2CO_3 solution (25 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 2 : 1) to afford *methyl 3,5-bis(methoxymethoxy)benzoate* (1.80 g, 7.0 mmol, 58 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 2.3, 2H), 6.91 (t, J = 2.3, 1H), 5.19 (s, 4H), 3.89 (s, 3H), 3.48 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 (0), 158.1 (0), 132.2 (0), 110.7 (1), 109.7 (1), 94.5 (2), 56.2 (3), 52.2 (3).

3,5-Bis(methoxymethoxy)phenyl)methanol: A solution of methyl 3,5-bis(methoxymethoxy)benzoate (1.50 g, 5.8 mmol) in anhydrous diethylether (25 mL) was added over 1 h to a stirred slurry of $LiAlH_4$ (220 mg, 5.79 mmol) in anhydrous diethylether (25 mL) under nitrogen. After complete addition, the mixture was stirred for 5 h at ambient temperature and then decomposed by addition of saturated NH_4Cl solution (20 mL). The organic layer was separated and the aqueous layer extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 2 : 1) to afford *(3,5-bis(methoxymethoxy)phenyl)methanol* (1.00 g, 4.4 mmol, 76 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (d, J = 2.3, 2H), 6.63 (t, J = 2.3, 1H), 5.14 (s, 4H), 4.60 (d, J = 5.5, 2H), 3.46 (s, 6H), 2.16 (t, J = 5.9, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4 (0), 143.6 (0), 107.9 (1), 104.0 (1), 94.4 (2), 65.0 (2), 56.0 (3).

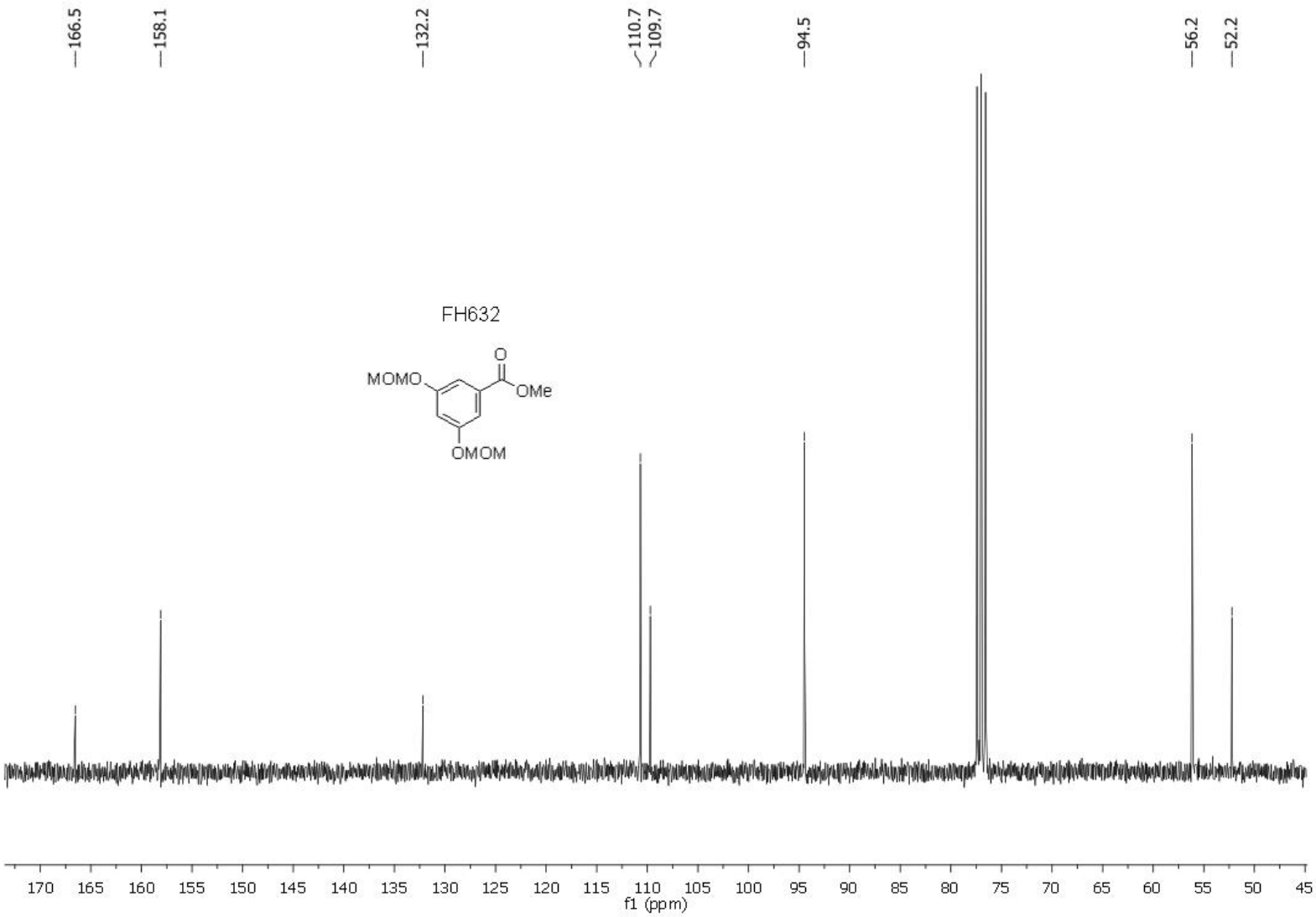
3,5-Bis(methoxymethoxy)benzaldehyde: To a solution of (3,5-bis(methoxymethoxy)-phenyl)methanol (1.00 g, 4.4 mmol) in anhydrous DCM (20 mL) was slowly added Dess-Martin periodinane (2.10 g, 5.0 mmol) at 0°C. The reaction mixture was filtered through celite and washed with a saturated aqueous solution of $NaHCO_3$ (10 mL) containing NaS_2O_3 (2.50 g). The organic layer was separated and the aqueous layer extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 1 : 1) to afford *3,5-Bis(methoxymethoxy)benzaldehyde* (0.9 g, 4.0 mmol, 91 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.21 (d, J = 2.3, 2H), 6.98 (t, J = 2.3, 1H), 5.21 (s, 4H), 3.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6 (1), 158.8 (0), 138.5 (0), 111.2 (1), 110.5 (1), 94.5 (2), 56.2 (3); MS (ESI) *m/z* 163 (100%), 195 (95%), 227 ($[M+H]^+$, 80%); HRMS (ESI) calcd for $C_{11}H_{15}O_5$ $[M+H]^+$: 227.0919, found: 227.0928.

1,3-Bis(methoxymethoxy)-5-vinylbenzene ***(4i):*** To a suspension of $[PPh_3CH_3]Br$ (2.60 g, 7.4 mmol) in anhydrous THF (50 mL) was added slowly NaH (60% dispersion in mineral oil, 0.30 g, 7.4 mmol). The suspension was heated to reflux for 1 h and then cooled to ambient temperature, followed by addition of the aldehyde from the previous step (1.50 g, 6.6 mmol). The solution was then heated to reflux for 2 h. The reaction mixture was washed with saturated aqueous solution of Na_2CO_3 (20 mL) and the aqueous layer was extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 1 : 1) to afford **4i** (1.25 g, 5.6 mmol, 84 %) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (d, J = 2.2, 2H), 6.66 (t, J = 2.2, 1H), 6.64 (dd, J = 17.6, 10.8, 1H), 5.73 (dd, J = 17.5, 0.6, 1H), 5.25 (d, J = 10.8, 1H), 5.17 (s, 4H), 3.48 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4 (0), 139.8 (0), 136.5 (1), 114.6 (2), 107.7 (1), 104.4 (1), 94.5 (2), 56.0 (3); IR (neat) ν 2950 (w), 2890 (w), 1589 (m), 1397 (w), 1287 (m), 1441 (s), 1082 (m), 1023 (s); MS (EI) *m/z* 131 (100%), 224 ($[M]^+$, 72%); HRMS (EI) calcd for $C_{12}H_{16}O_4$ $[M]^+$: 224.1049, found: 224.1051; Anal. calcd for $C_{12}H_{16}O_4$: C, 64.3; H, 7.2. Found: C, 64.0; H, 7.2.

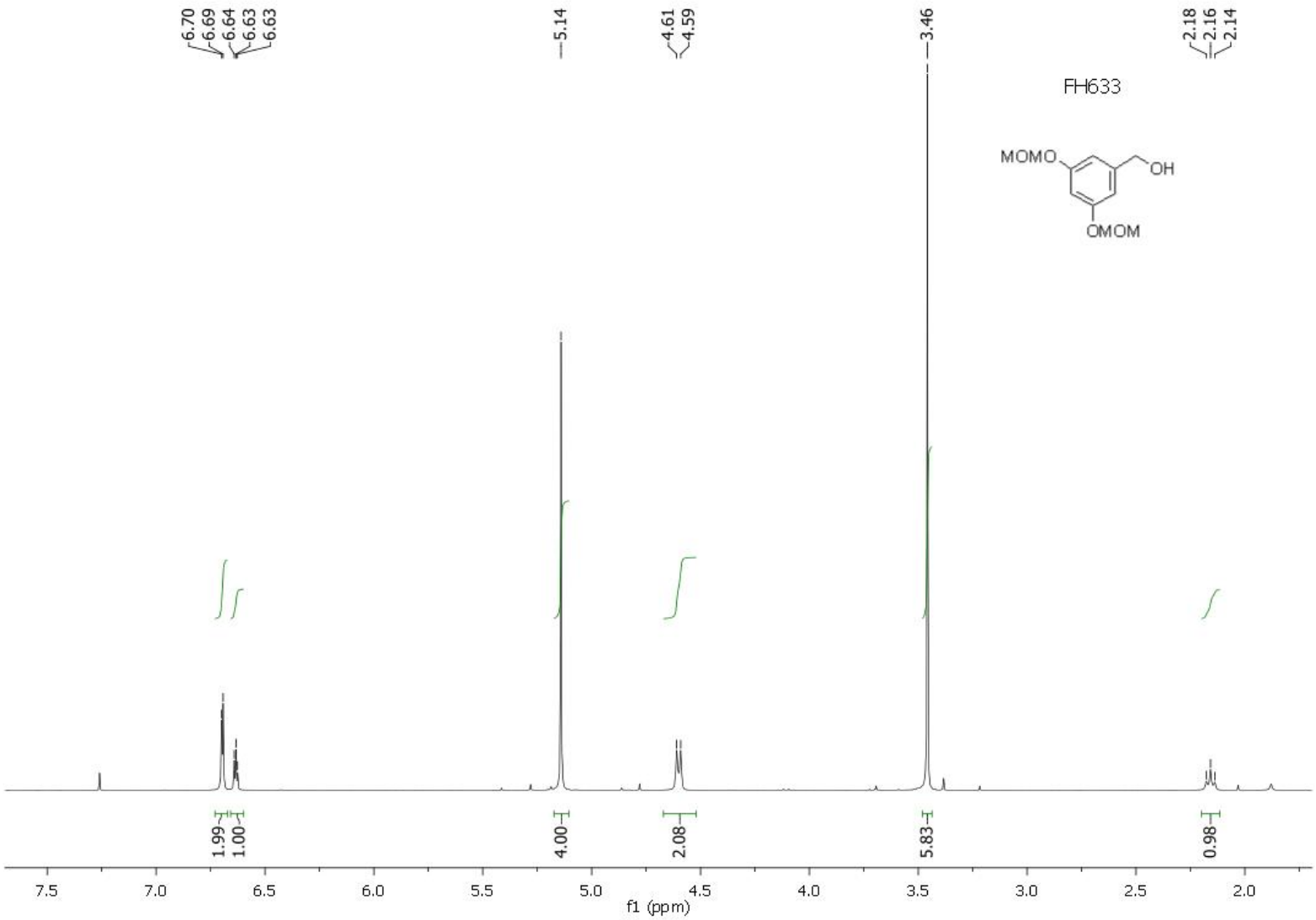
^{1}H NMR (300 MHz, $CDCl_3$) of methyl 3,5-bis(methoxymethoxy)benzoate



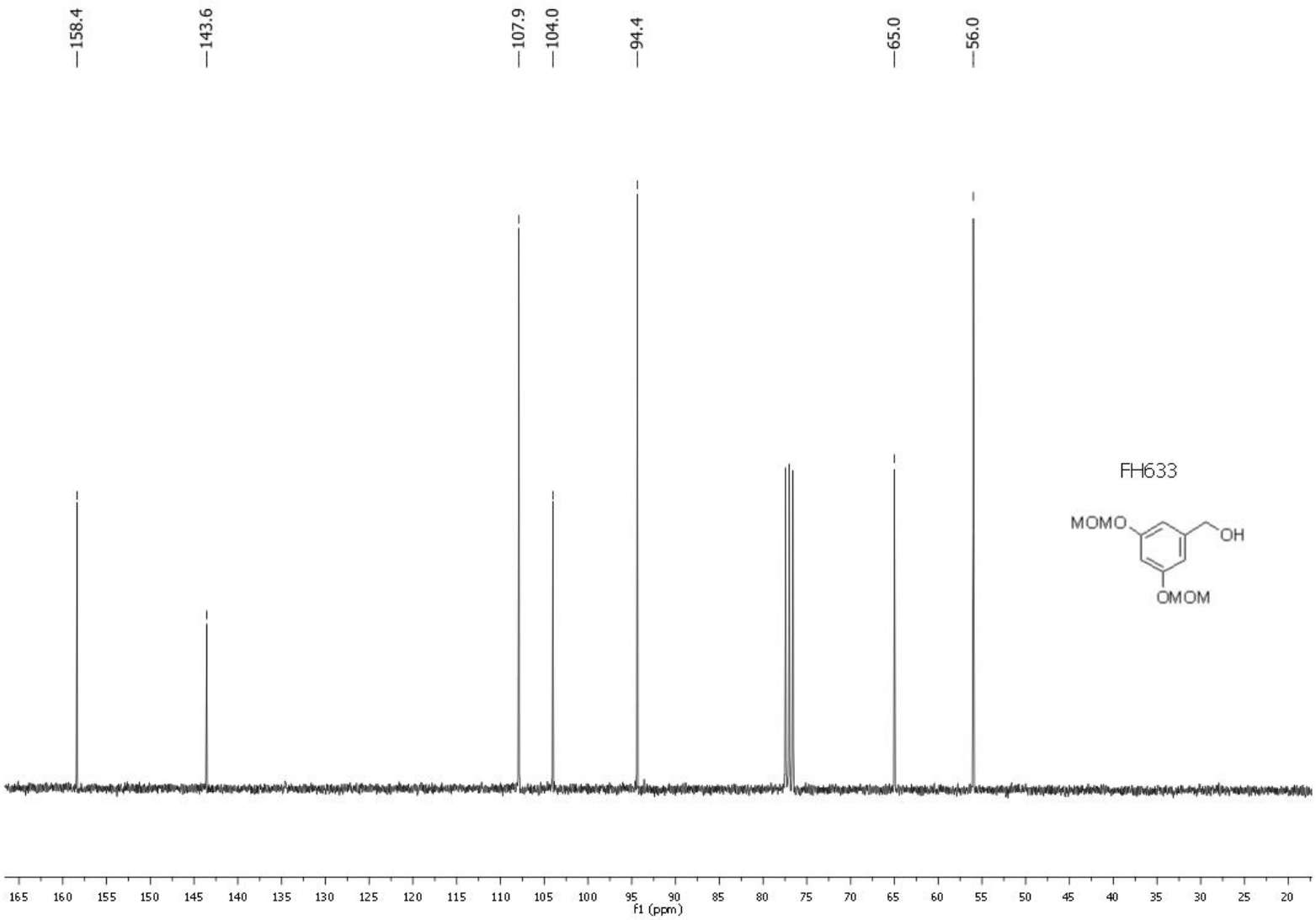
^{13}C NMR (75 MHz, $CDCl_3$) of methyl 3,5-bis(methoxymethoxy)benzoate



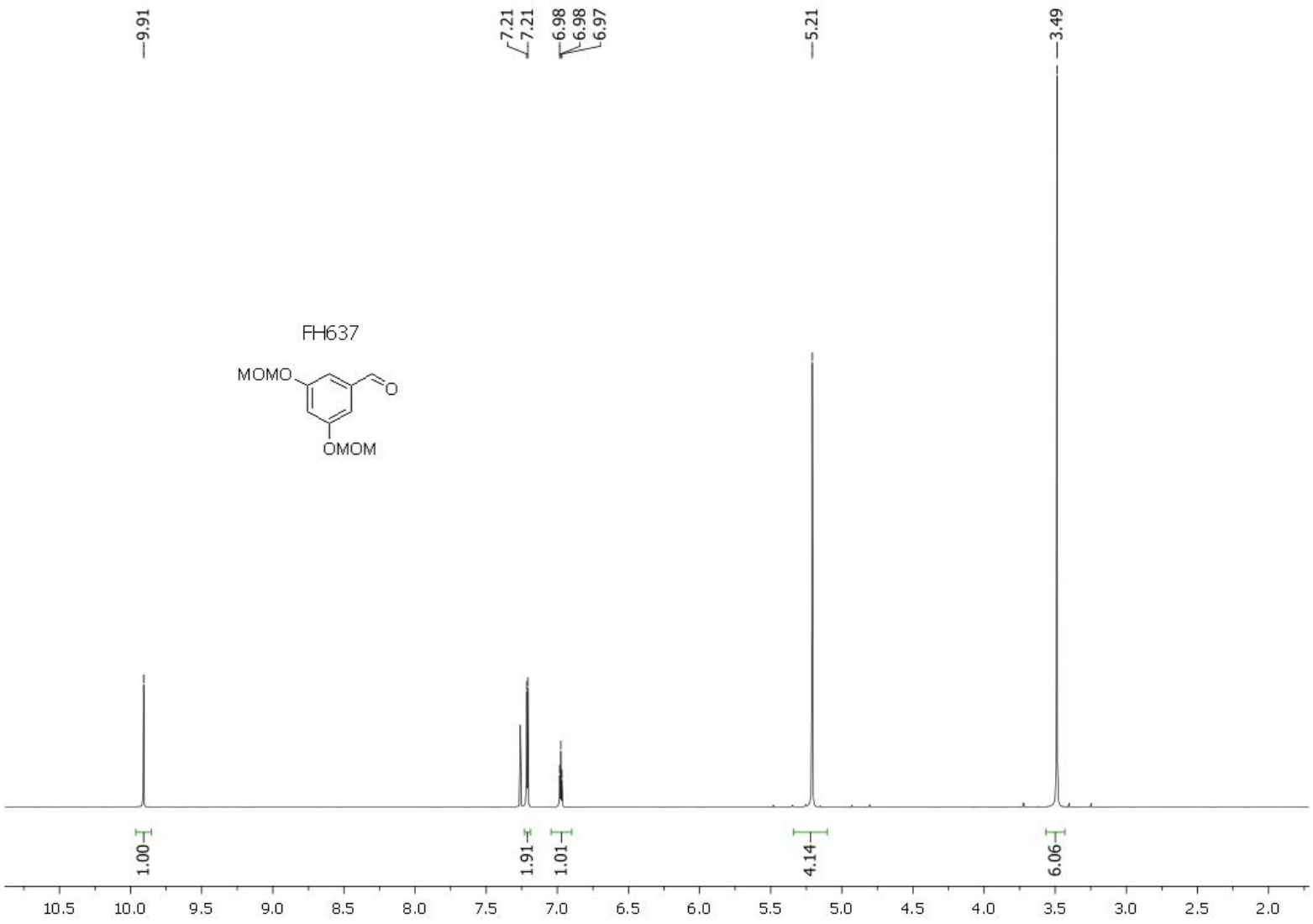
^{1}H NMR (300 MHz, $CDCl_3$) of 3,5-bis(methoxymethoxy)phenyl)methanol



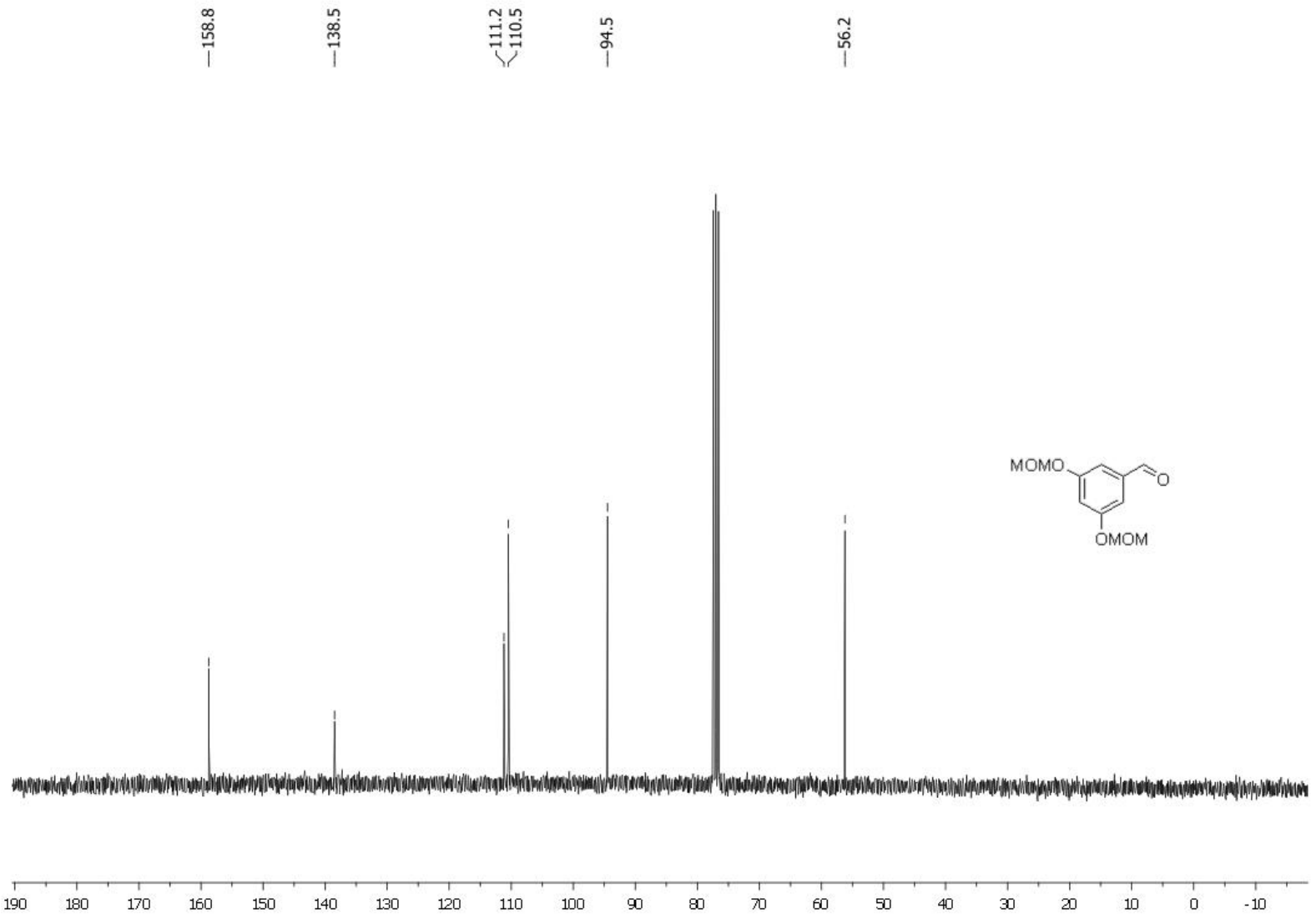
^{13}C NMR (75 MHz, $CDCl_3$) of 3,5-bis(methoxymethoxy)phenyl)methanol



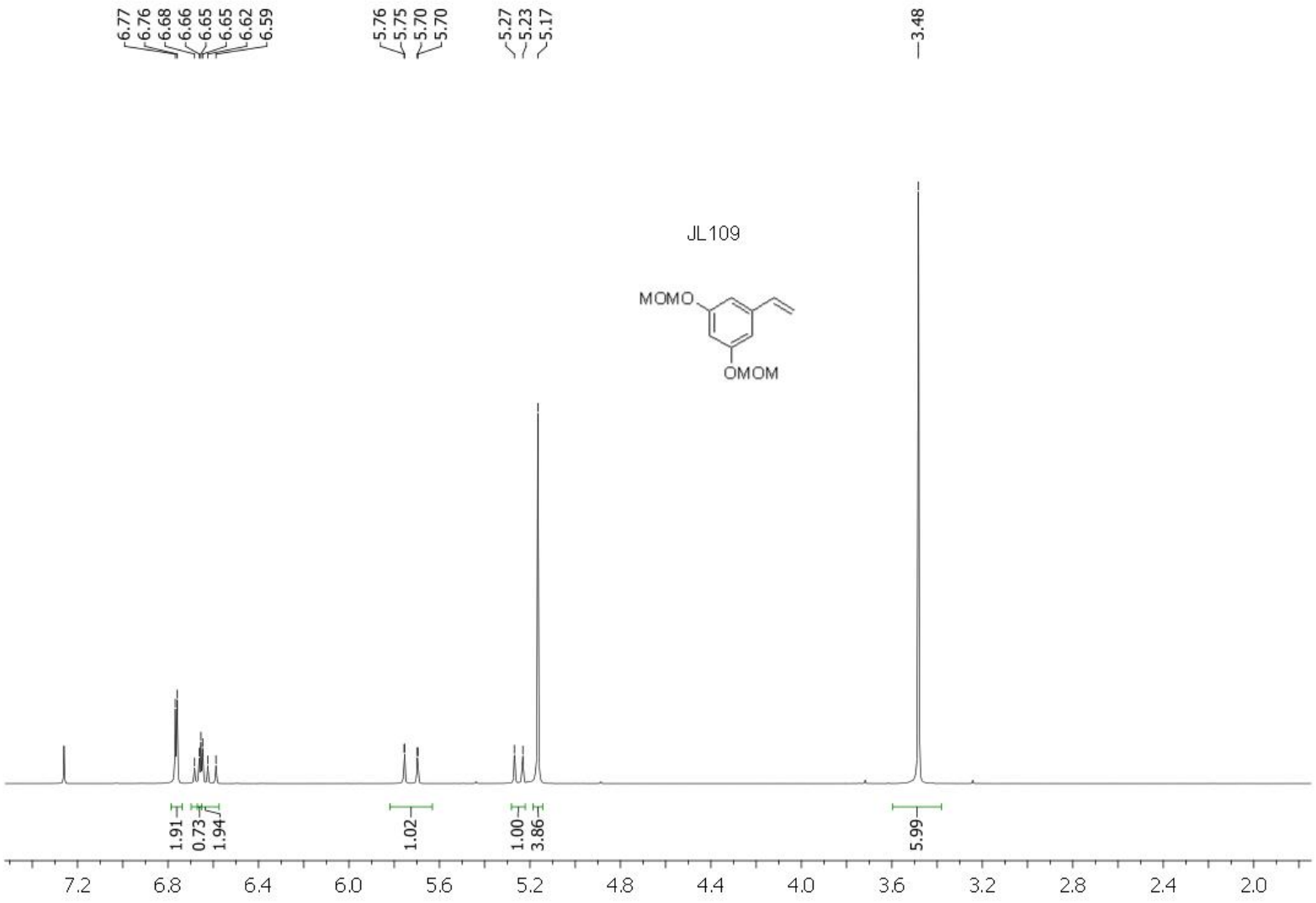
^{1}H NMR (300 MHz, $CDCl_3$) of 3,5-bis(methoxymethoxy)benzaldehyde



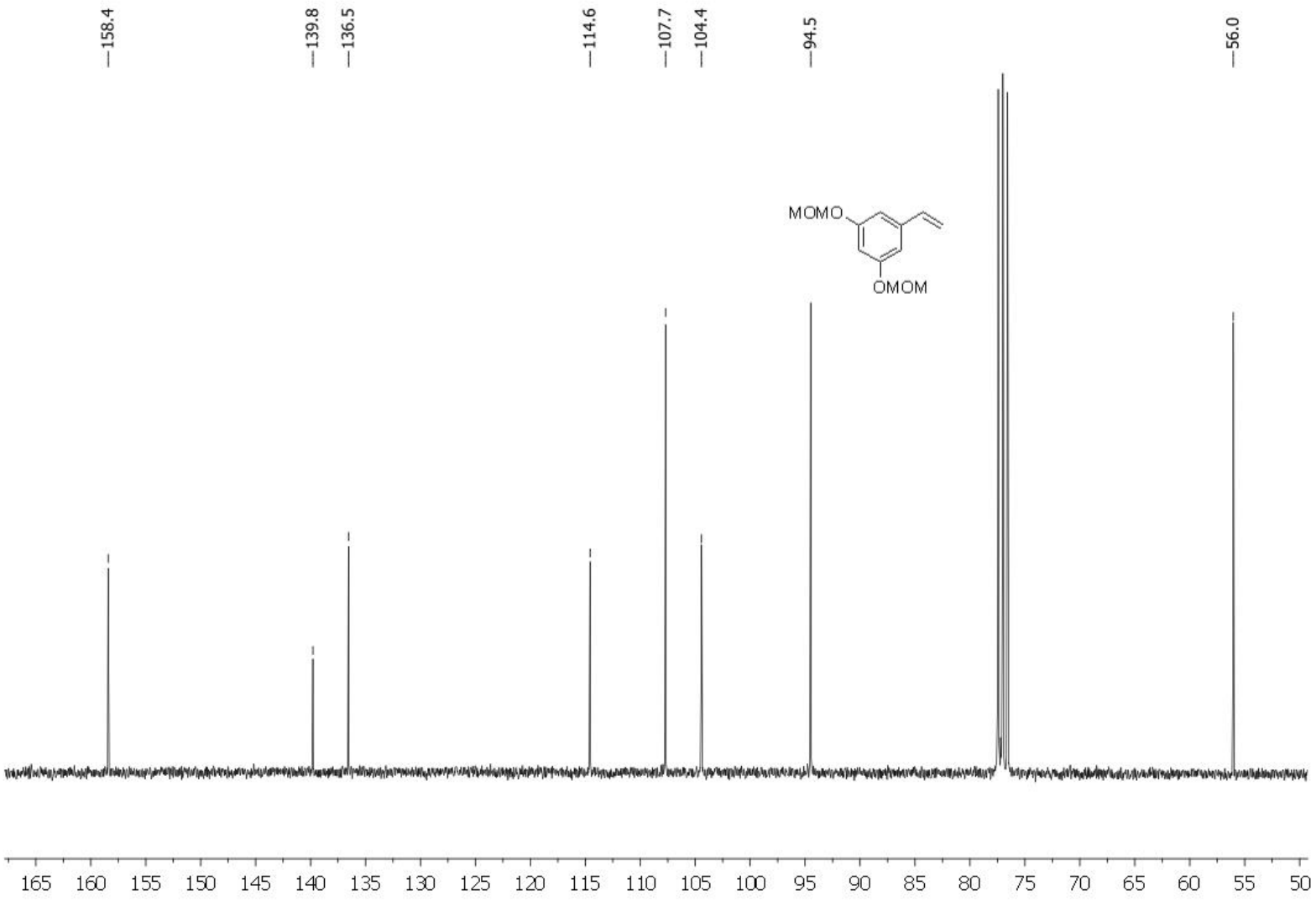
^{13}C NMR (75 MHz, $CDCl_3$) of 3,5-bis(methoxymethoxy)benzaldehyde



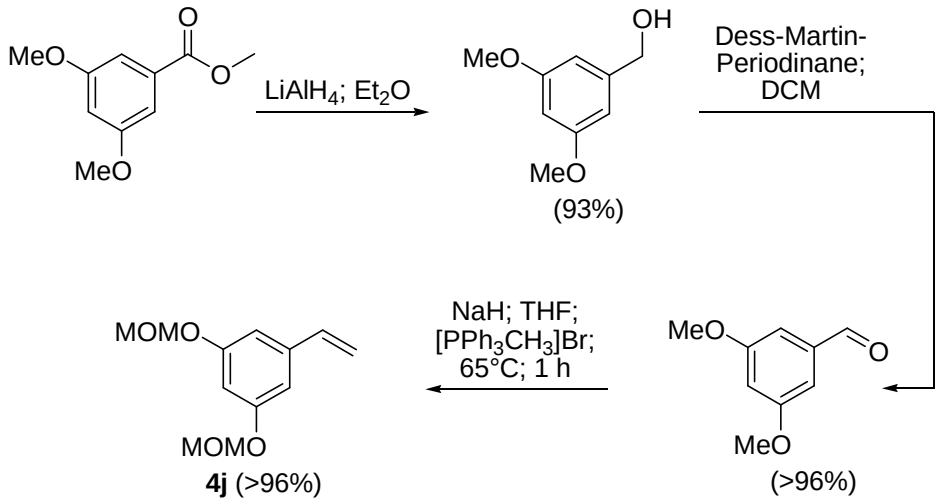
^{1}H NMR (300 MHz, $CDCl_3$) of **4i**



^{13}C NMR (75 MHz, $CDCl_3$) of **4i**



*B5 1,3-dimethoxy-5-vinylbenzene (**4j**)*



(3,5-Dimethoxyphenyl)methanol: A solution of methyl 3,5-dimethoxybenzoate (2.00 g, 10.2 mmol) in anhydrous diethylether (25 mL) was added during 1 h to a stirred slurry of $LiAlH_4$ (380 mg, 10.2 mmol) in anhydrous diethylether (25 mL) under nitrogen. After completed addition, the mixture was stirred for 5 h at ambient temperature and then decomposed by addition of saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated and the aqueous layer extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 2 : 1) to afford *(3,5-dimethoxyphenyl)methanol* (1.56 g, 9.5 mmol, 93 %) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (d, J = 2.3, 2H), 6.37 (t, J = 2.3, 1H), 4.62 (s, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 1.63 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 143.6, 104.8, 99.9, 65.6, 55.6; MS (EI) *m/z* 168 ([M]$^+$, 100%), 139 (59%), 109 (39%); HRMS (EI) calcd for $C_9H_{12}O_3$ [M]$^+$: 168.0786, found: 168.0775.

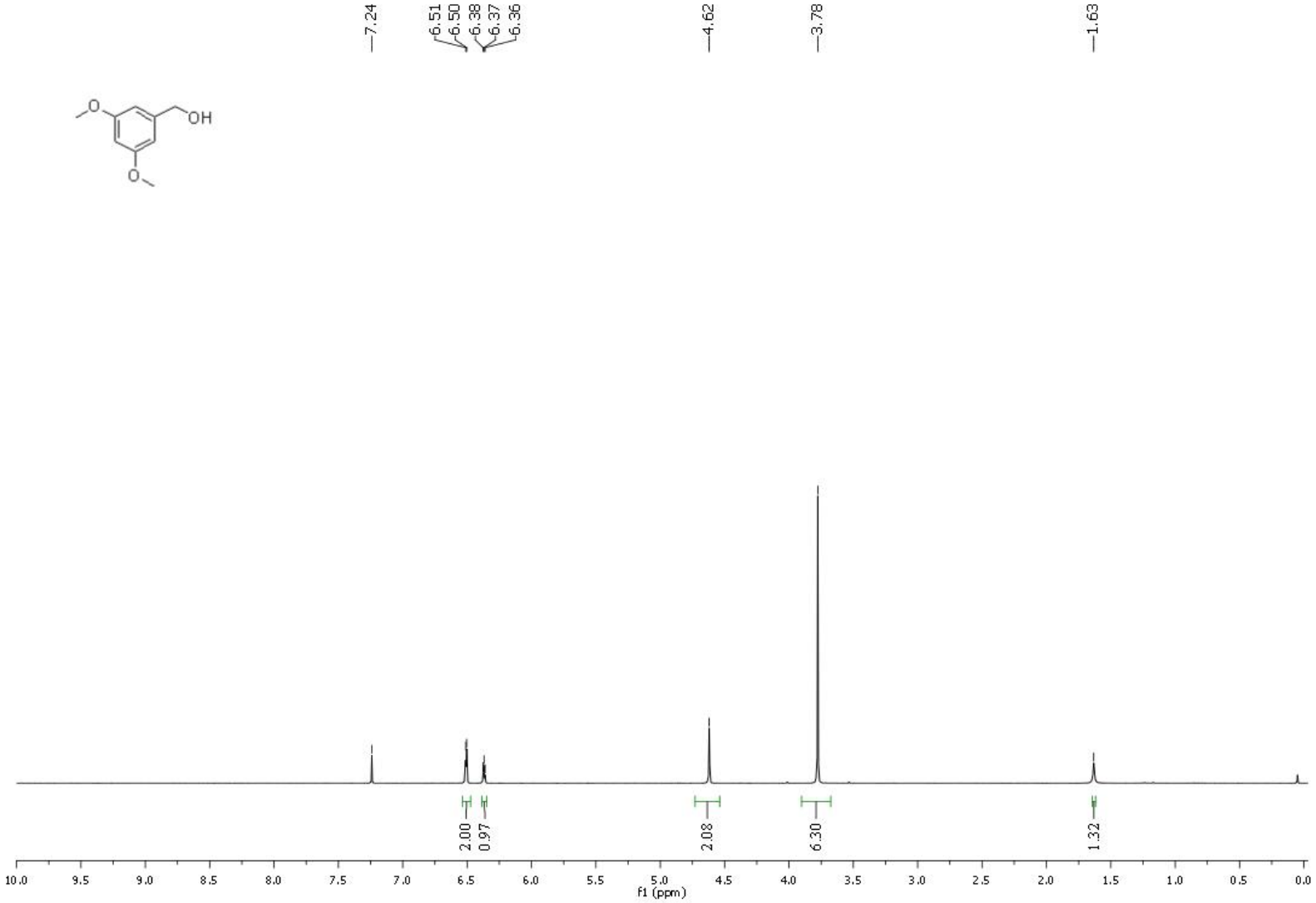
3,5-dimethoxybenzaldehyde: To a solution of (3,5-dimethoxyphenyl)methanol (1.00 g, 5.9 mmol) in anhydrous DCM (30 mL) was slowly added Dess-Martin periodinane (3.00 g, 7.1 mmol) at 0°C. The reaction mixture was filtered through celite and washed with a saturated aqueous solution of $NaHCO_3$ (20 mL) containing NaS_2O_3 (2.5 g). The organic layer was separated, and the aqueous layer extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 9 : 1) to afford *3,5-dimethoxybenzaldehyde* (974 mg, 5.9 mmol, >96 %) as a colourless solid. Mp 45-48°C (47-

47.5°C[1]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (s, 1H), 6.96 (d, J = 2.3, 2H), 6.66 (t, J = 2.3, 1H), 3.80 (s, 6H), 3.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 161.4, 138.6, 107.3, 107.3, 55.8; MS (EI) *m/z* 166 ([M]$^+$, 100%), 149 (46%), 135 (37%); HRMS (EI) calcd for $C_9H_{10}O_3$ [M]$^+$: 166.0630, found: 168.0623.

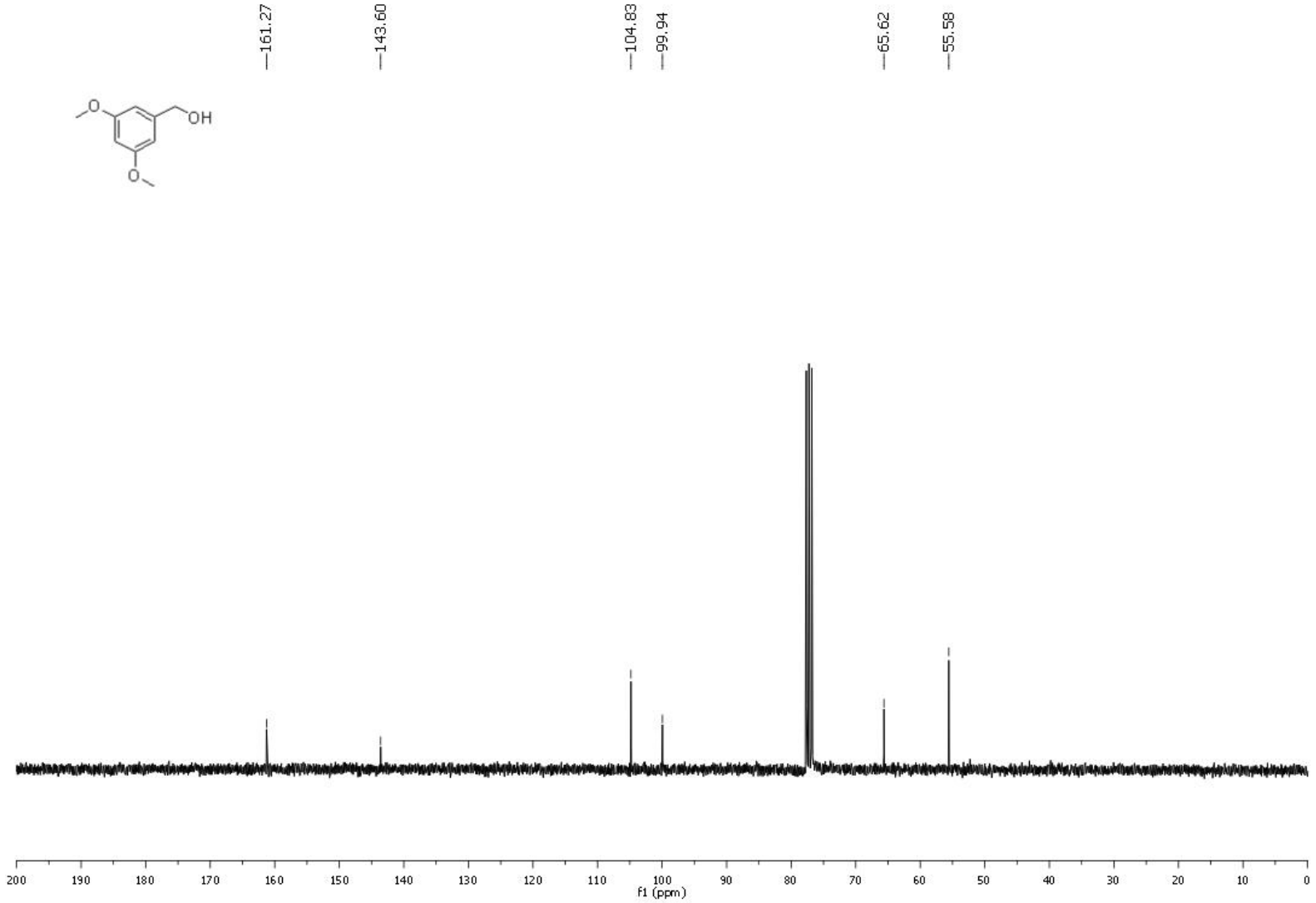
1,3-Dimethoxy-5-vinylbenzene ***(4j)***: To a suspension of $[PPh_3CH_3]Br$ (2.32 g, 6.5 mmol) in anhydrous THF (30 mL) was added slowly NaH (60% dispersion in mineral oil) (0.26 g, 6.5 mmol). The suspension was heated to reflux for 1 h, and then cooled to ambient temperature, followed by addition of 3,5-dimethoxybenzaldehyde (0.90 g, 5.4 mmol) from the previous step. The solution was heated tor reflux for 2 h. The reaction mixture was washed with saturated aqueous Na_2CO_3 solution (20 mL), and the aqueous layer was extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane / MTBE 3 : 1) to afford **4j** (869 g, 5.3 mmol, >96 %) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, J = 17.5, 10.8 1H), 6.57 (d, J = 2.3, 2H), 6.39 (t, J = 2.3, 1H), 5.73 (dd, J = 17.5, 0.8, 1H), 5.25 (d, J = 10.8, 0.7, 1H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 139.6, 136.9, 114.3, 104.4, 100.11, 55.3; MS (EI) *m/z* 164 (27%), 57 (63%), 43 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{10}H_{12}O_2$ [M]$^+$: 164.0837, found: 168.0841.

[1] N. Jana and S. Nanda, *Eur. J. Org. Chem.*, 2012, 4313–4320.

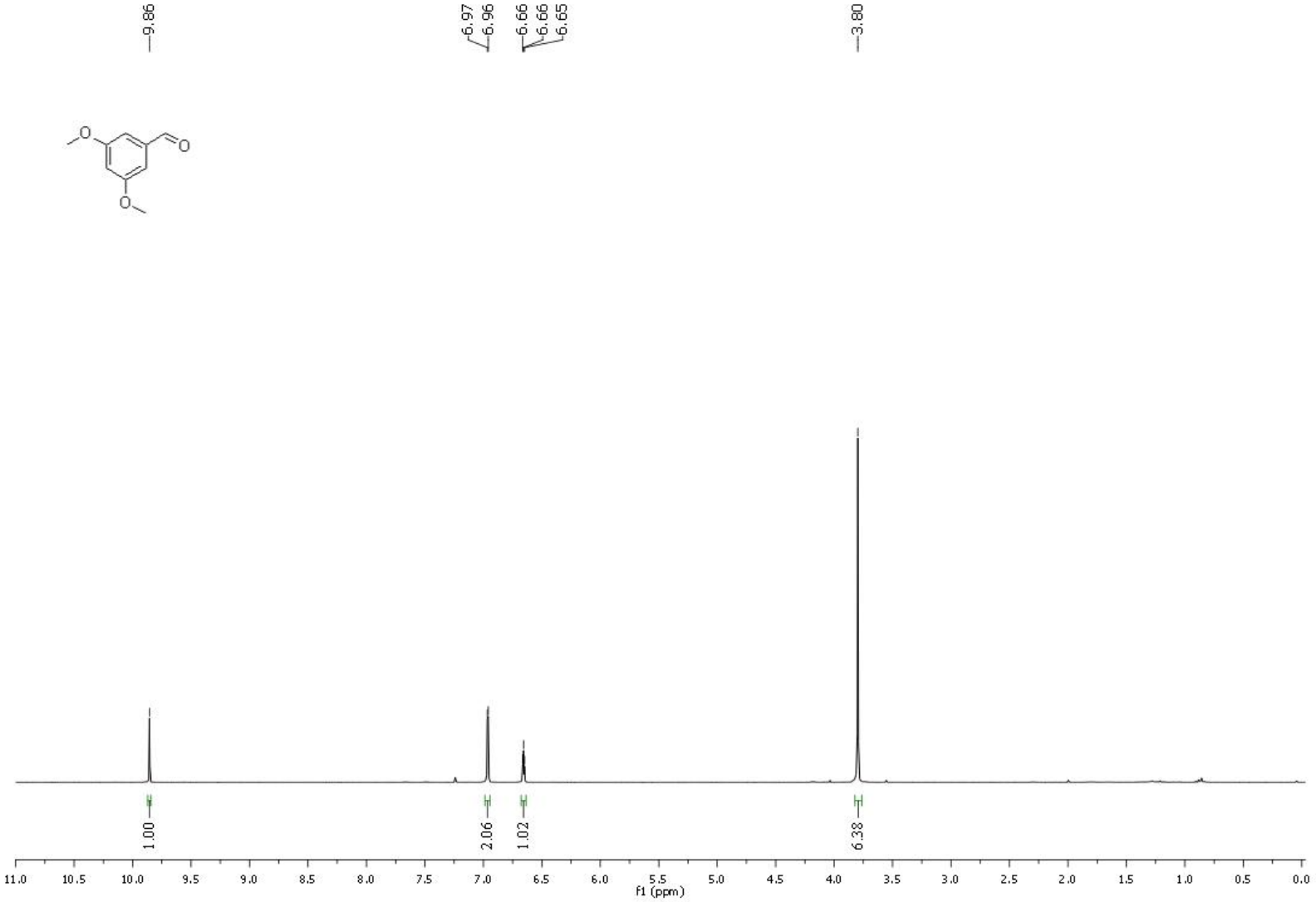
^{1}H NMR (300 MHz, $CDCl_3$) of (3,5-dimethoxyphenyl)methanol



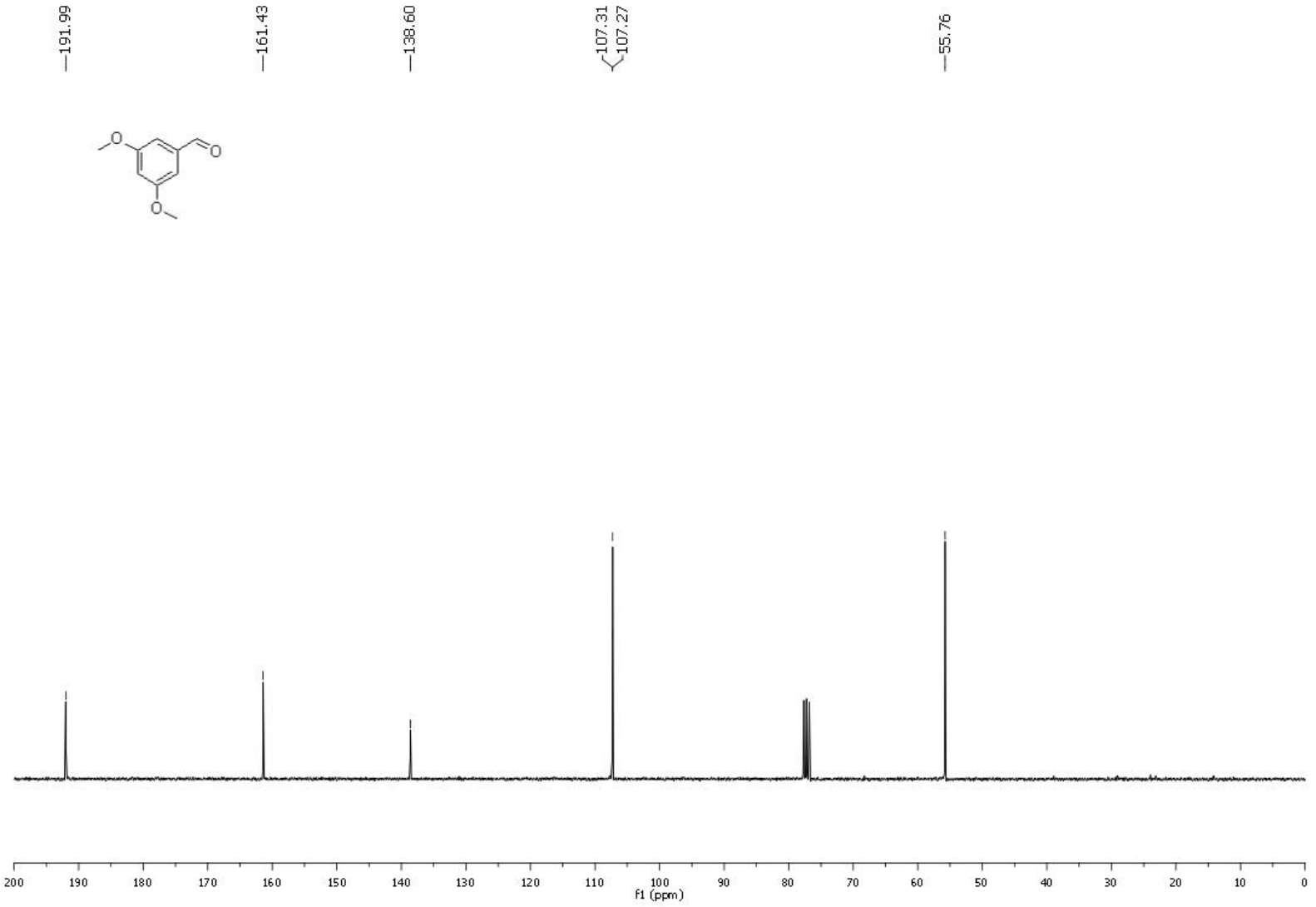
^{13}C NMR (75 MHz, $CDCl_3$) of (3,5-dimethoxyphenyl)methanol



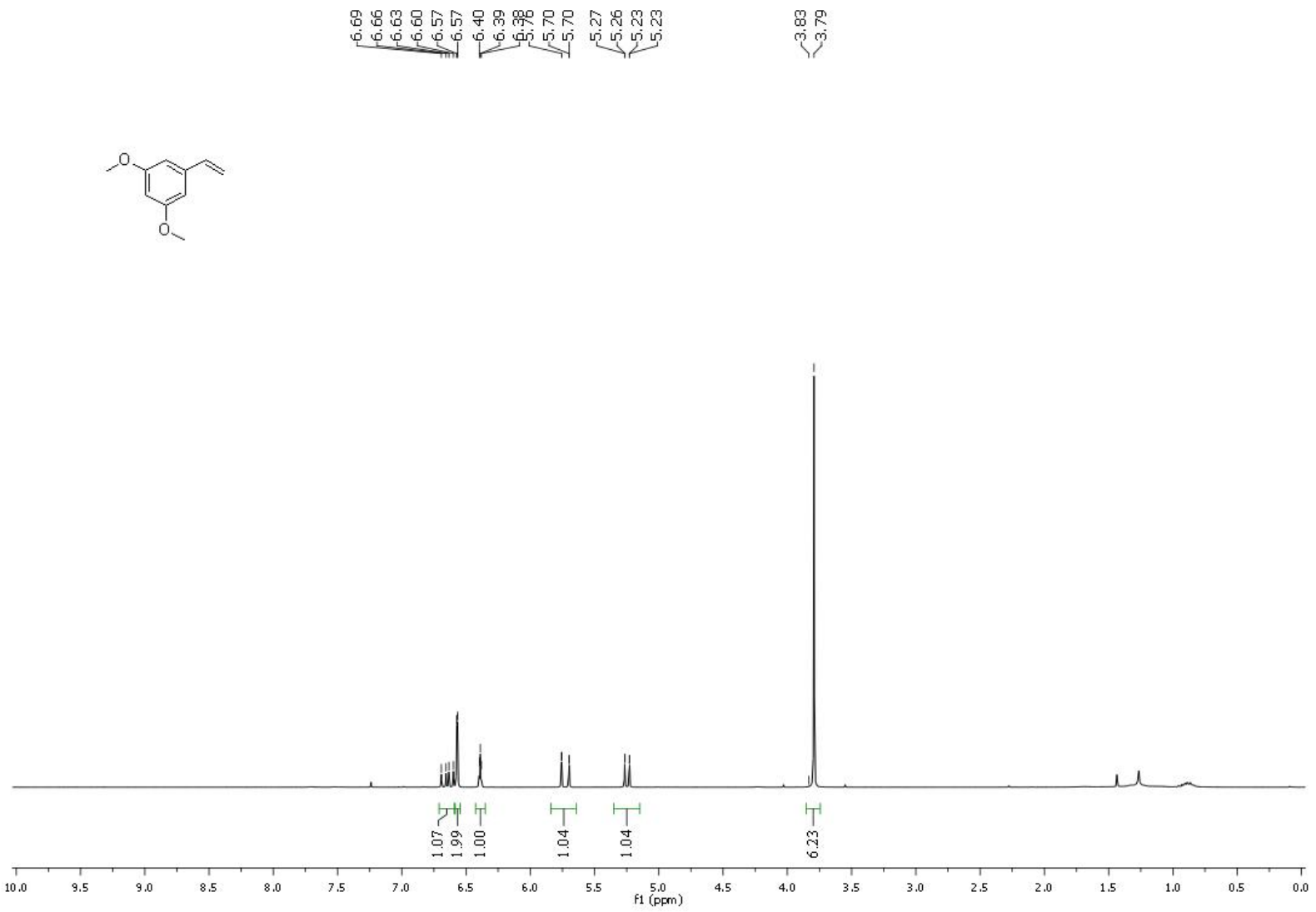
^{1}H NMR (300 MHz, $CDCl_3$) of 3,5-dimethoxybenzaldehyde



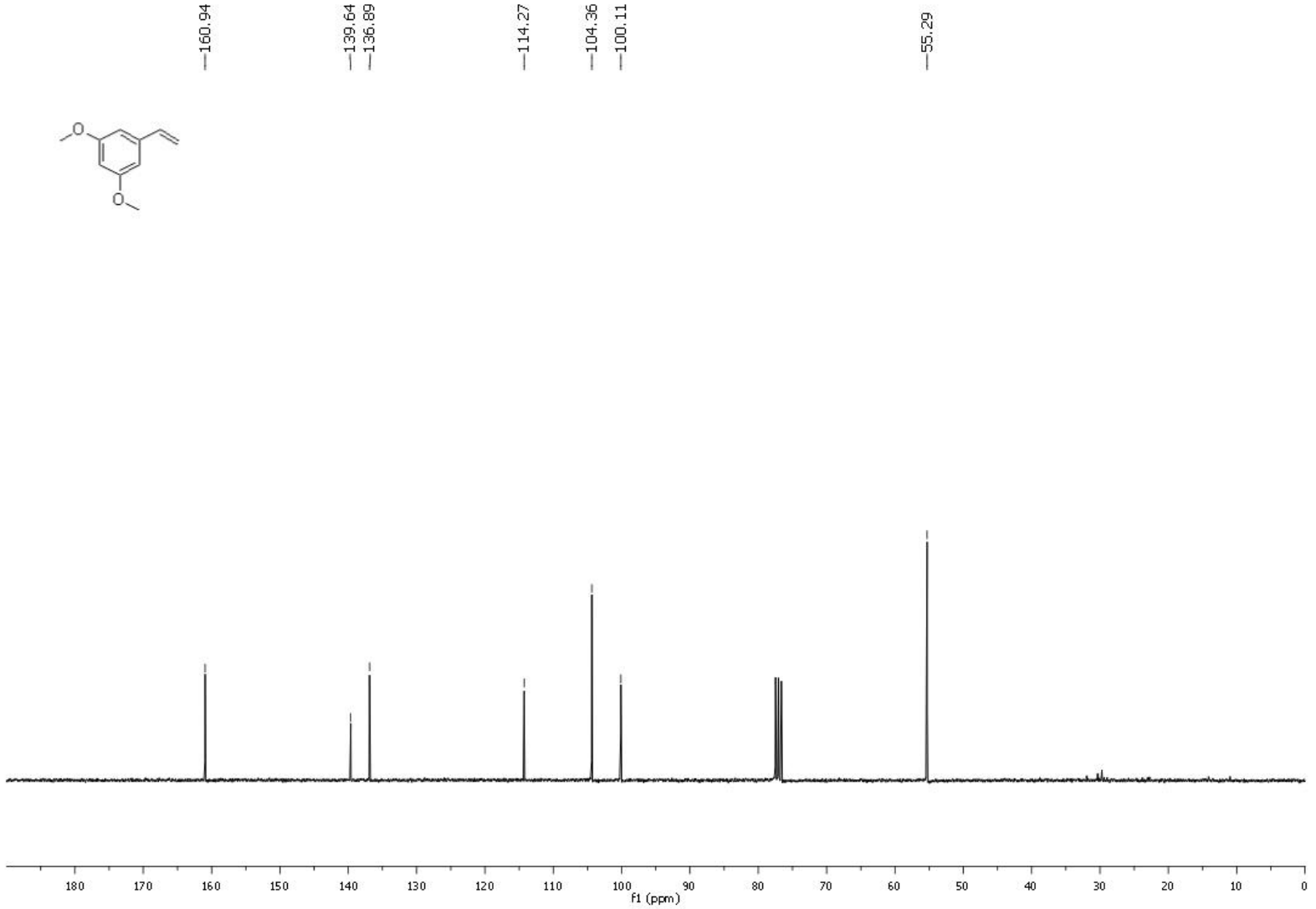
^{13}C NMR (75 MHz, $CDCl_3$) of 3,5-dimethoxybenzaldehyde



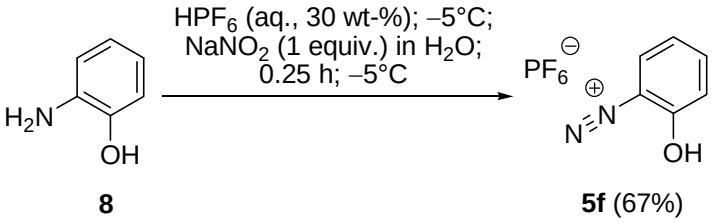
^{1}H NMR (300 MHz, $CDCl_3$) of **4j**



^{13}C NMR (75 MHz, $CDCl_3$) of **4j**



C Synthesis, characterization data and spectra for 5f[2]

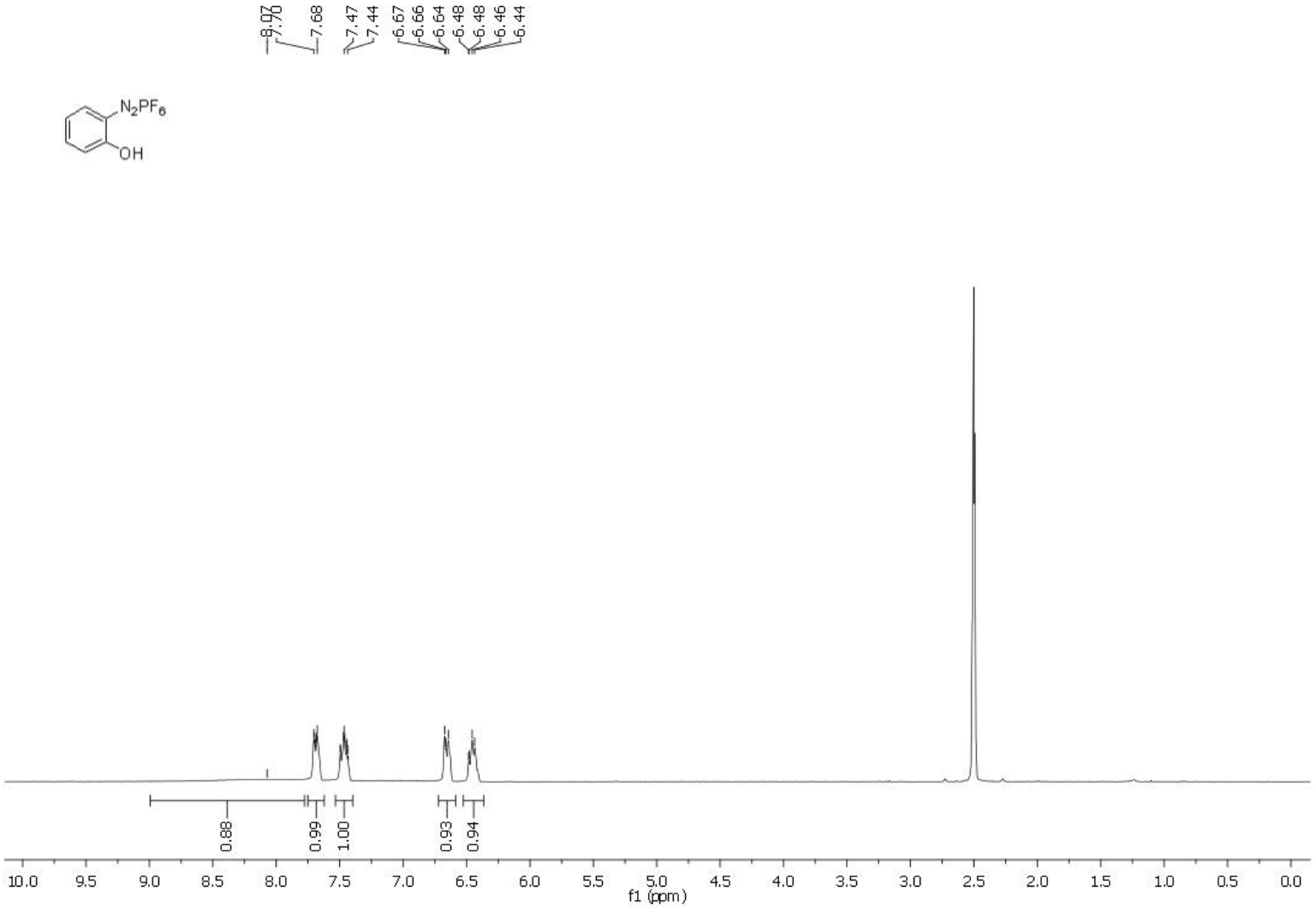


8 **5f** (67%)

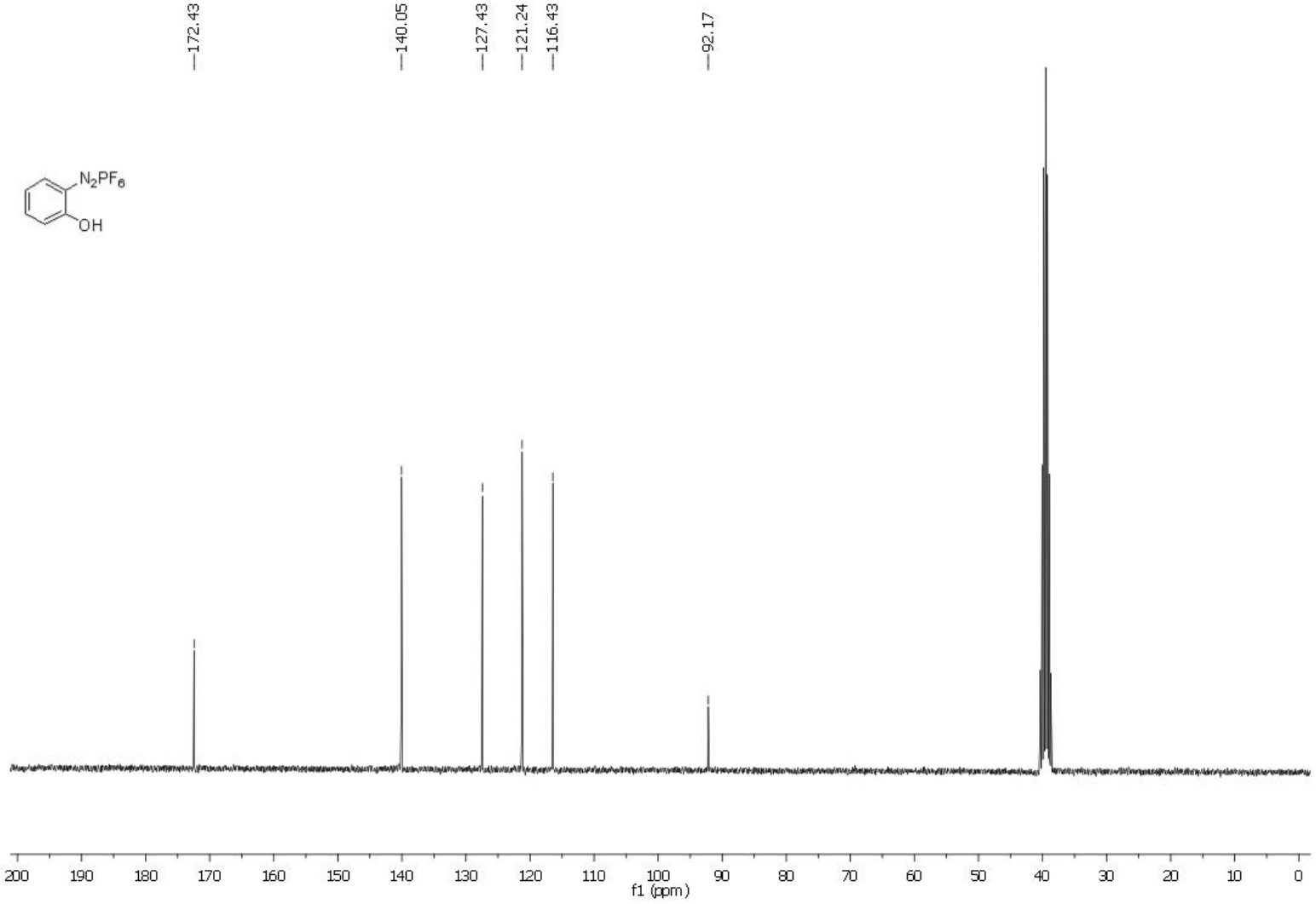
Ortho-aminophenol (2.73 g, 25.0 mmol) was dissolved in aqueous HPF6 (30 wt-%, 11.0 mL) and cooled to -5°C. A solution of NaNO2 (1.73 g, 25.0 mmol) in water (4 mL) was added slowly added at this temperature, and the resulting suspension was stirred for 15 min., filtered through a Büchner-funnel and dried under air. The solid was washed with methanol/MTBE mixture (1 : 4) and dried to furnish 5f (4.46 g, 16.7 mmol, 67%) as a yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.69 (m, 1H), 7.46 (m, 1H), 6.66 (m, 1H), 6.46 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.4 (1), 140.0 (0), 127.4 (0), 121.2 (0), 116.4 (0), 92.1 (1); MS (ESI) *m*/*z* 63 (91%), 92 (37%), 107 (100%), 120 ([M]+, 23%); HRMS (ESI) calcd for $C_6H_5N_2O$ $[M]^+$: 121.0402, found: 121.0404; IR (KBr-disc) ν 3102 (m), 2196 (s), 1609 (s), 1514 (s).

[2] E. D. Coy B, L. Jovanovic and M. Sefkow, *Org. Lett.*, 2010, **12**, 1976-1979.

^{1}H NMR (300 MHz, DMSO-d_6) of **5f**



^{13}C NMR (75 MHz, DMSO-d_6) of **5f**



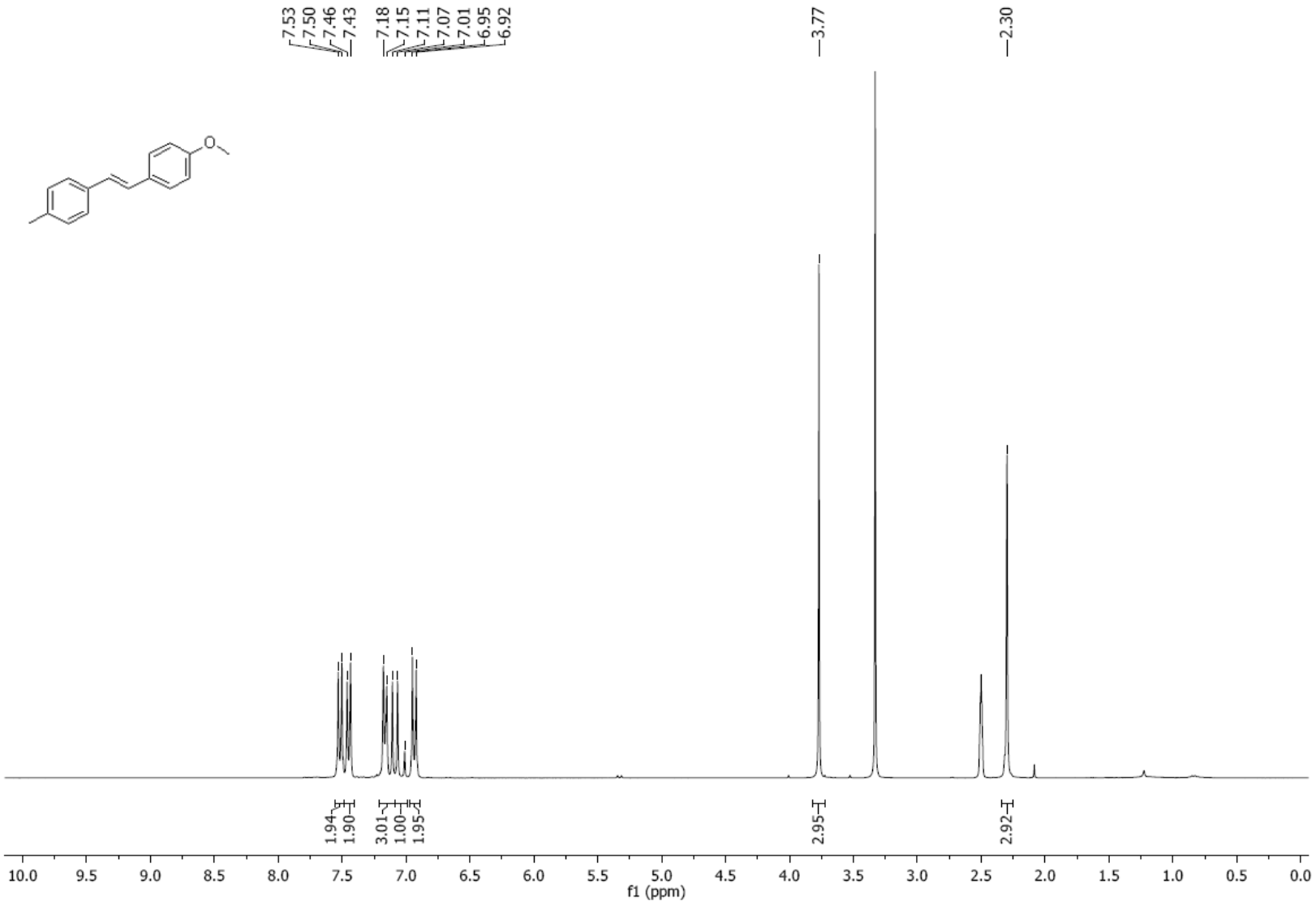
D References for known stilbenes 6 and NMR-Spectra for stilbenes 6

No.	Known?	Reference	Location in paper
6aa	Yes	S. S. Siewert and L. H. Spangler, *J.Phys. Chem*, 1995, **99**, 9316-9324.	Table 1
6ab	Yes	J.-E. Dubois and M.-F. Ruasse, *J. Org. Chem*, 1973, **38**, 493-499.	Table 1
6ba	Yes	D. L. Vander Jagt, L. M. Deck, US2007/249647 A1, **2007**.	Table 1
6bb	Yes	T. P. Schulz, T. F. Hubbard, L. H. Jin, T. H. Fisher, D. D. Nicholas, *Phytochemistry*, 1990, **29**, 1501–1507.	Table 1
6ca	Yes	R. Quelet, J. Hoch, C. Borgel, M. Mansouri, R. Pineau, E. Tchiroukine, N. Vinot, *Bull. Soc. Chim. Fr.*, 1956, 26-29.	Table 1
6cb	Yes	T. Narender, K. Papi Reddy, G. Madhur *Synthesis*, 2009, 3791–3796.	Table 1
6da	Yes	D. L. Vander Jagt, L. M. Deck, US2007/249647 A1, **2007**.	Table 1
6db	Yes	J.-E. Dubois and M.-F. Ruasse, *J. Org. Chem*, 1973, **38**, 493-499.	Table 1
6ea	Yes	J. Velder, S. Ritter, J. Lex and H.-G. Schmalz, *Synthesis*, 2006, 273-278.	Table 1
6eb	Yes	S. Chang, Y. Na, H. J. Shin, E. Choi and L. S. Jeong, *Tetrahedron Lett.*, 2002, **43**, 7445-7448	Table 1
6fa	Yes	J. F. Civicos, D. A. Alonso, and C. Najera, *Adv. Synth. Catal.*, 2011, **353**, 1683-1687.	Table 1
6fb	Yes	J. F. Civicos, D. A. Alonso, and C. Najera, *Adv. Synth. Catal.*, 2011, **353**, 1683-1687.	Table 1
6ga	Yes	P. Colbon, J. H. Barnard, I. Kozhevnikov, J. Xiao, M. Purdie and K. Mulholland, *Adv. Synth. Catal.*, 2012, **354**, 1395-1400.	Table 1
6gb	Yes	V. Diemer, H. Chaumeil, A. Defoin and C. Carre, *Synthesis*, 2007, 3333-3338.	Table 1
6ha	No	--	Table 1
6hb	No	--	Table 1
6ia	No	--	Table 1
6ib	No	--	Table 1
6ja	Yes	G. A. Molander and D. L. Sandrock, *Org. Lett.*, 2009, **11**, 2369-2372.	Table 1
6jb	Yes	F. Orsini, L. Verotta, M. Lecchi, R. Restano, G. Curia, E. Radaelli and E. Wanke, *J. Nat. Prod.*, 2004, **67**, 421-426.	Table 1
1	Yes	J. A. Morales-Serna, A. Zuniga-Martinez, M. Salmon, R. Gavino and J. Cardenas, *Synthesis*, 2012, *44*, 446-452.	Scheme 1

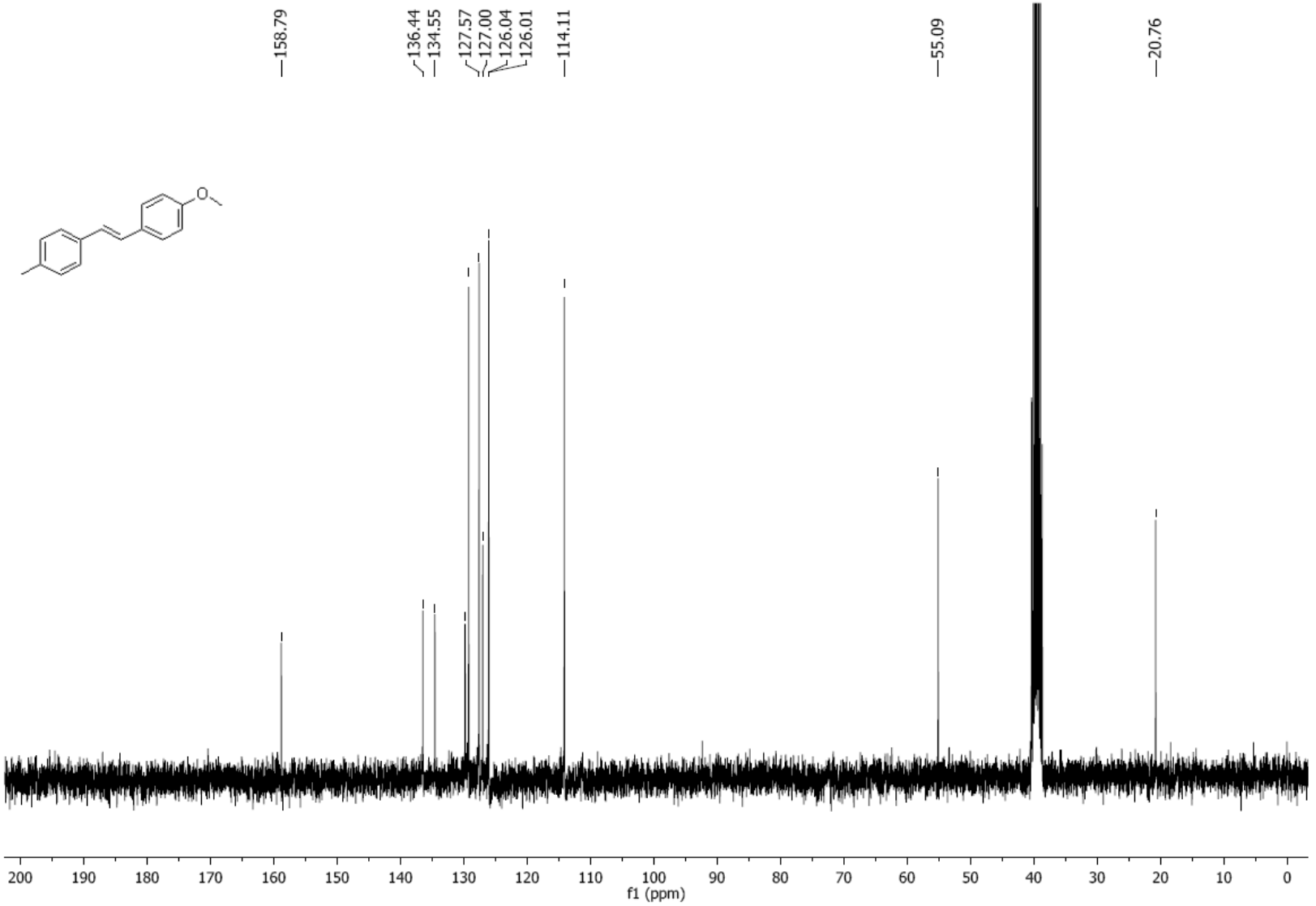
6ac	Yes	B. R. Buckley and S. P. Neary, *Tetrahedron*, 2010, **66**, 7988-7994.	Table 2
6cc	Yes	P. Colbon, J. H. Barnard, I. Kozhevnikov, J. Xiao, M. Purdie and K. Mulholland, *Adv. Synth. Catal.*, 2012, **354**, 1395-1400.	Table 2
6dc	No	--	Table 2
6gc	Yes	K. Motoshima, T. Noguchi-Yachide, K. Sugita, Y. Hashimoto, and M. Ishikawa, *Bioorg. Med. Chem.*, 2009, **17**, 5001–5014.	Table 2
6ae	Yes	P. Srinivas, K. Srinivas, P. R. Likhar, M. L. Kantam, B. Sridhar, K. V. Mohan and S. Bhargava, J. Organomet. Chem., 2011, **696**, 795-801.	Table 3
6be	No	--	Table 3
6ce	Yes	M. Chalal, D. Vervandier-Fasseur, P. Meunier, H. Cattey and J.-C. Hierso, *Tetrahedron*, 2012, **68**, 3899-3907.	Table 3
6de	No	--	Table 3
6fe	Yes	P. Srinivas, K. Srinivas, P. R. Likhar, M. L. Kantam, B. Sridhar, K. V. Mohan and S. Bhargava, J. Organomet. Chem., 2011, **696**, 795-801.	Table 3
6ge	Yes	P. S. Kendurkar and R. S. Tewari, *J. Organomet. Chem.*, 1973, **60**, 247-254.	Table 3
6ff	Yes	F. V. Singh and T. Wirth, *Synthesis*, 2012, **44**, 1171-1177.	Scheme 4
9	No	--	Scheme 6
6ah	No	--	Table 4
6bg	No	--	Table 4
6bh	No	--	Table 4
6ch	No	--	Table 4
6dg	No	--	Table 4
6dh	No	--	Table 4
6fg	Yes	R. F. Heck, *J. Am. Chem. Soc*, 1968, **90**, 5518-5526.	Table 4
6fh	Yes	R. B. Chhor, K. A. Singh, B. Nosse and V. K. Tandon, *Synth. Commun.*, 2003, **33**, 2519-2530.	Table 4
6gg	Yes	J. Colonge and P. von Arx, *Bull. Soc. Chim. Fr.*, 1965, 1486-1489	Table 4
6gh	Yes	A. C. Bishop, D. Moore, T. S. Scanlan and K. M. Shokat, *Tetrahedron*, 1997, **53**, 11995-12004.	Table 4
6ai	No	--	Table 5
6aj	No	--	Table 5
6bi	No	--	Table 5
6bj	No	--	Table 5
6ci	No	--	Table 5

6cj	No	--	Table 5
6di	No	--	Table 5
6dj	No	--	Table 5
6fi	No	--	Table 5
6fj	No	--	Table 5
6gi	No	--	Table 5
6gj	No	--	Table 5
6ak	No	--	Table 6
6bk	No	--	Table 6
6ck	No	--	Table 6
6dk	No	--	Table 6
6fk	No	--	Table 6
6gk	No	--	Table 6
6fm	Yes	S. Shrestha, B. R. Bhattarai, B. Kafle, K.-H. Lee and H. Cho, *Bioorg. Med. Chem*., 2008, **16**, 8643-8652.	Scheme 9

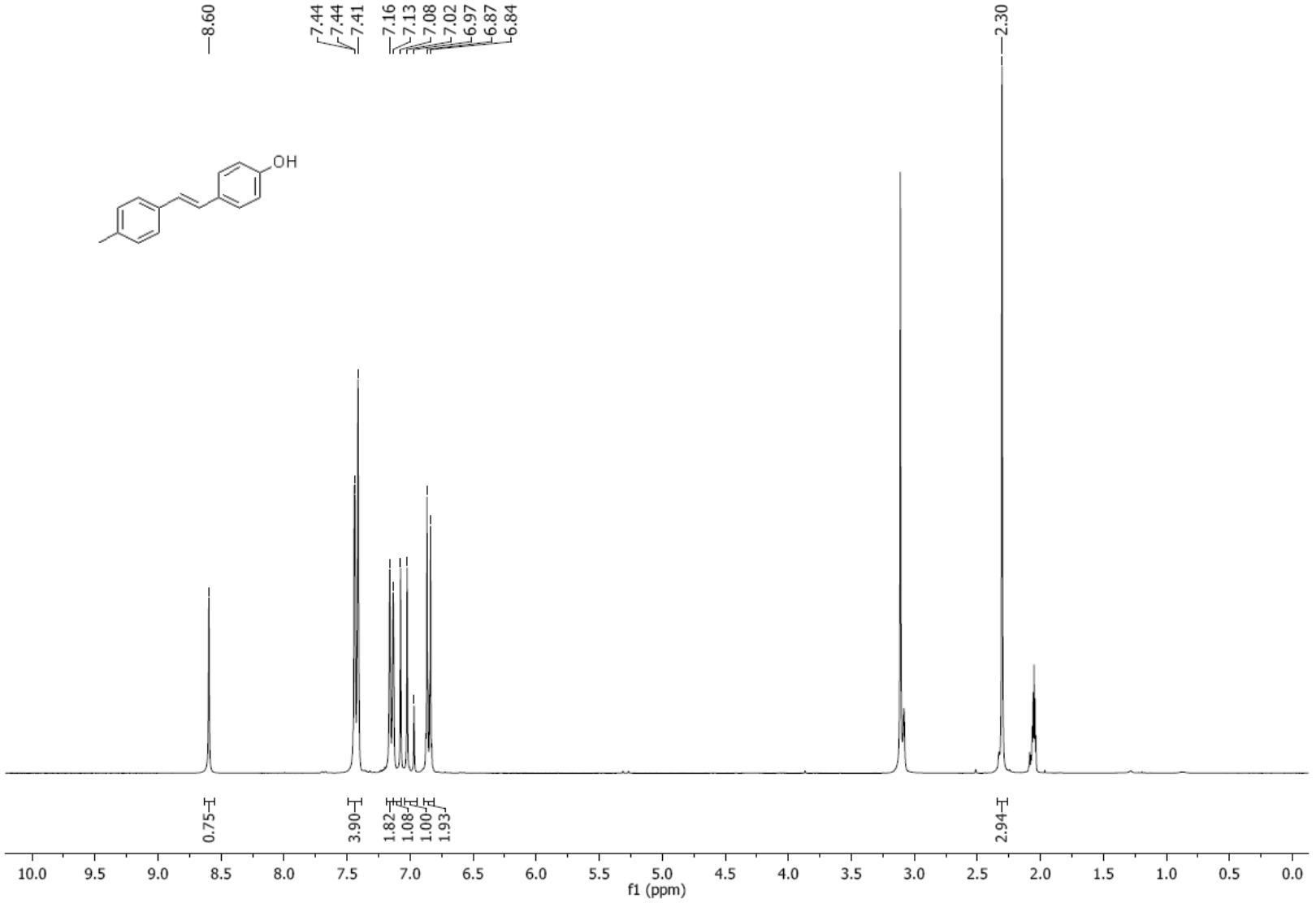
^{1}H NMR (300 MHz, DMSO-d_6) of **6aa**



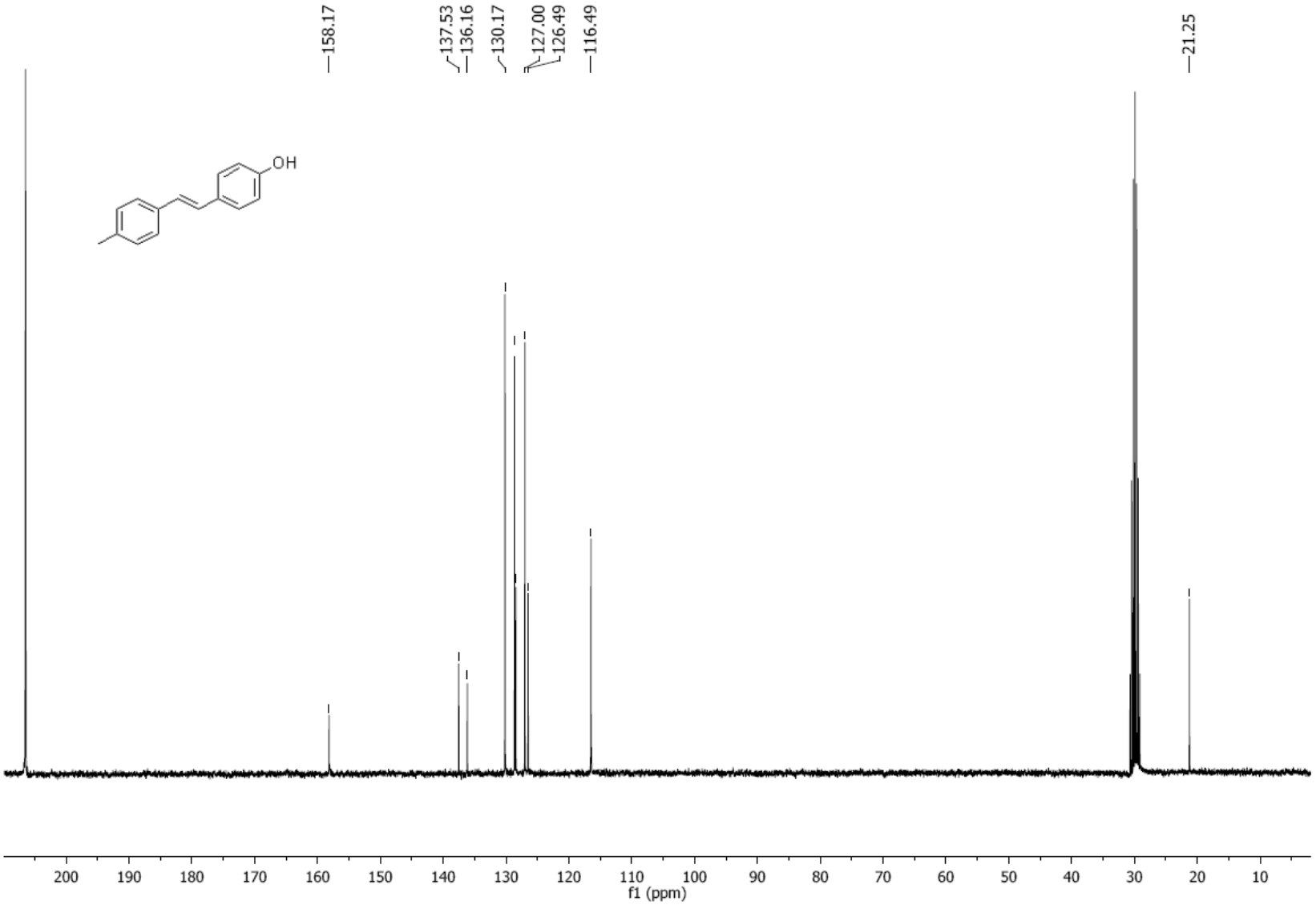
^{13}C NMR (75 MHz, DMSO-d_6) of **6aa**



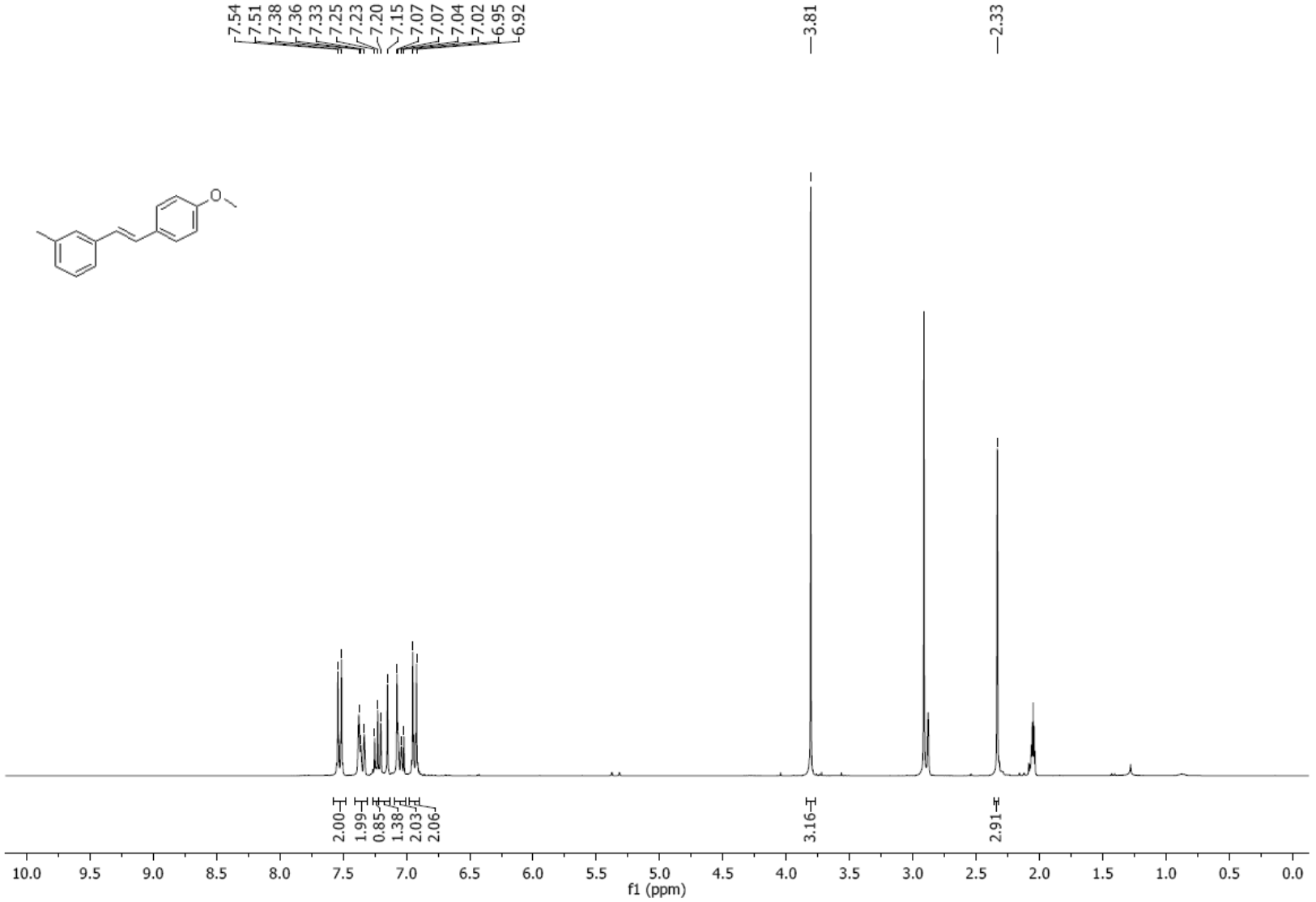
^{1}H NMR (300 MHz, acetone-d_6) of **6ab**



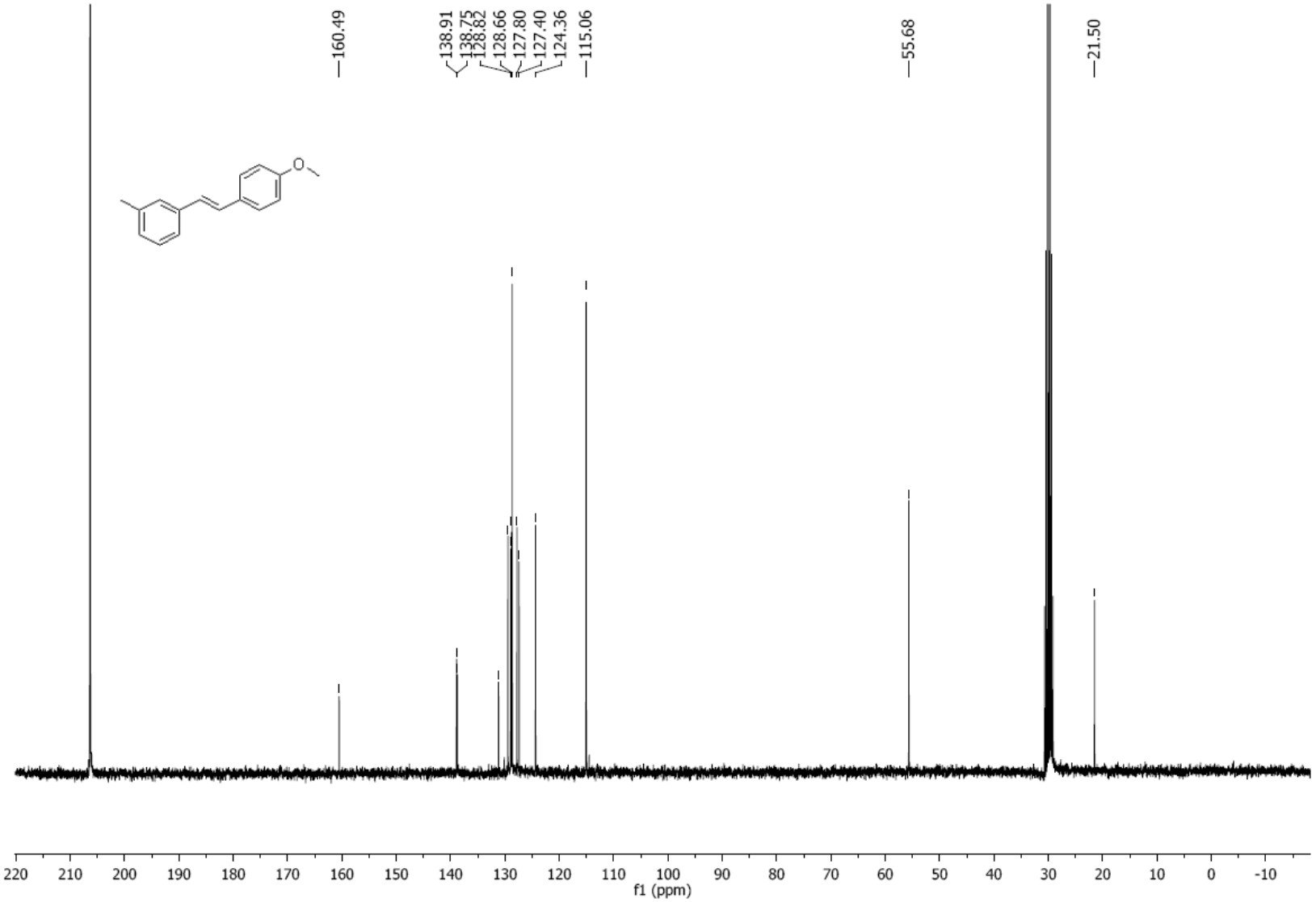
^{13}C NMR (75 MHz, acetone-d_6) of **6ab**



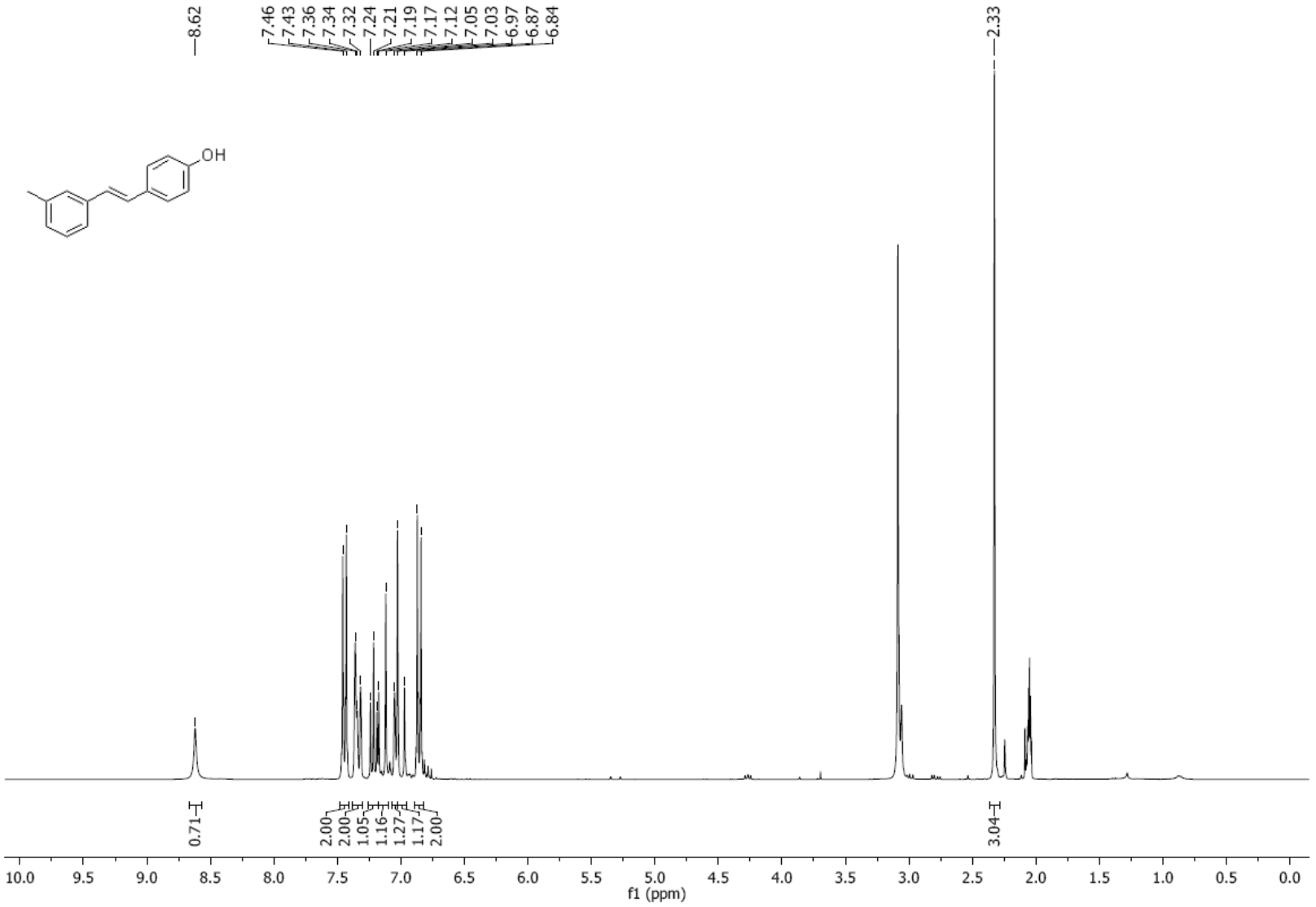
^{1}H NMR (300 MHz, acetone-d_6) of **6ba**



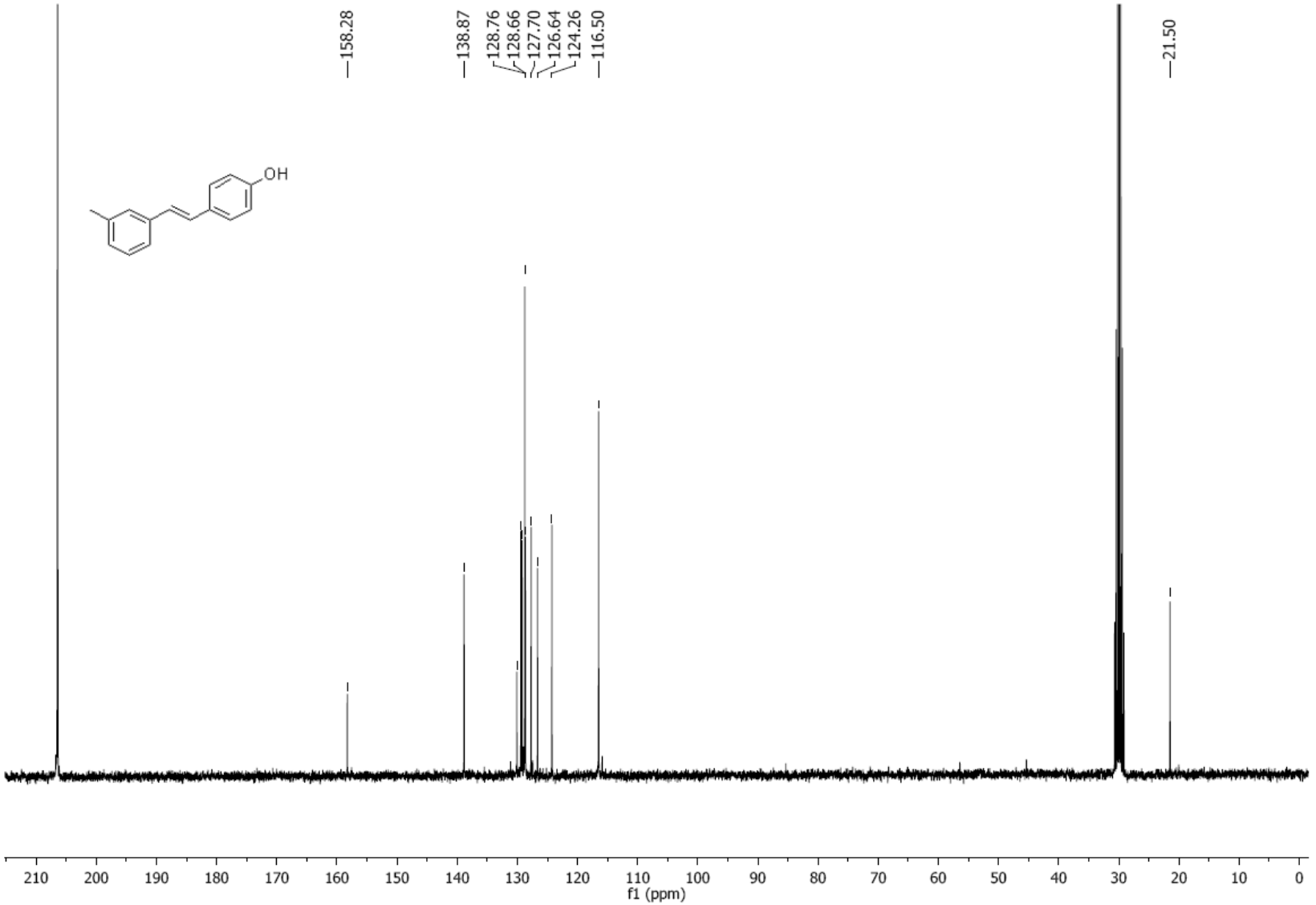
^{13}C NMR (75 MHz, acetone-d_6) of **6ba**



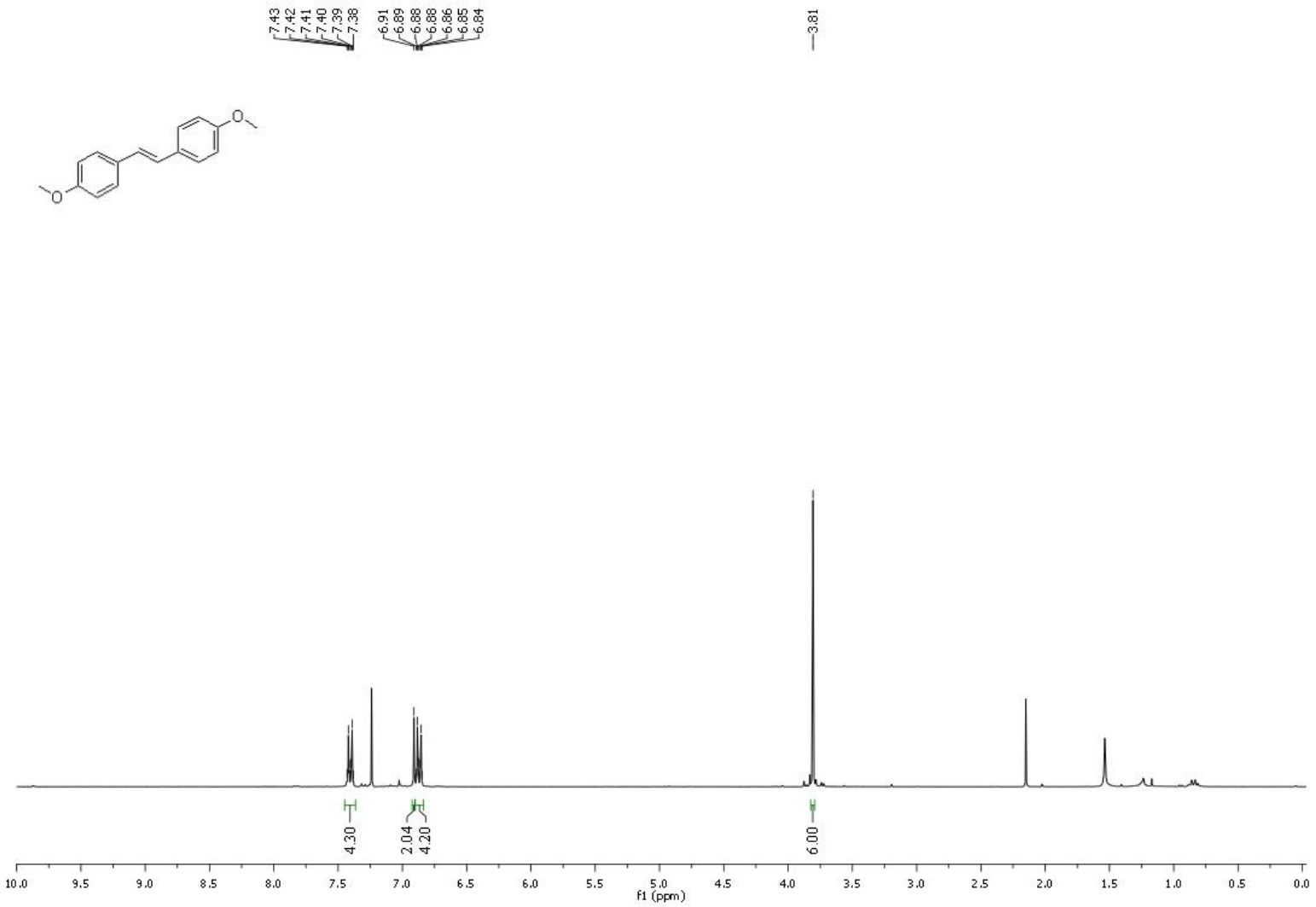
^{1}H NMR (300 MHz, acetone-d_6) of **6bb**



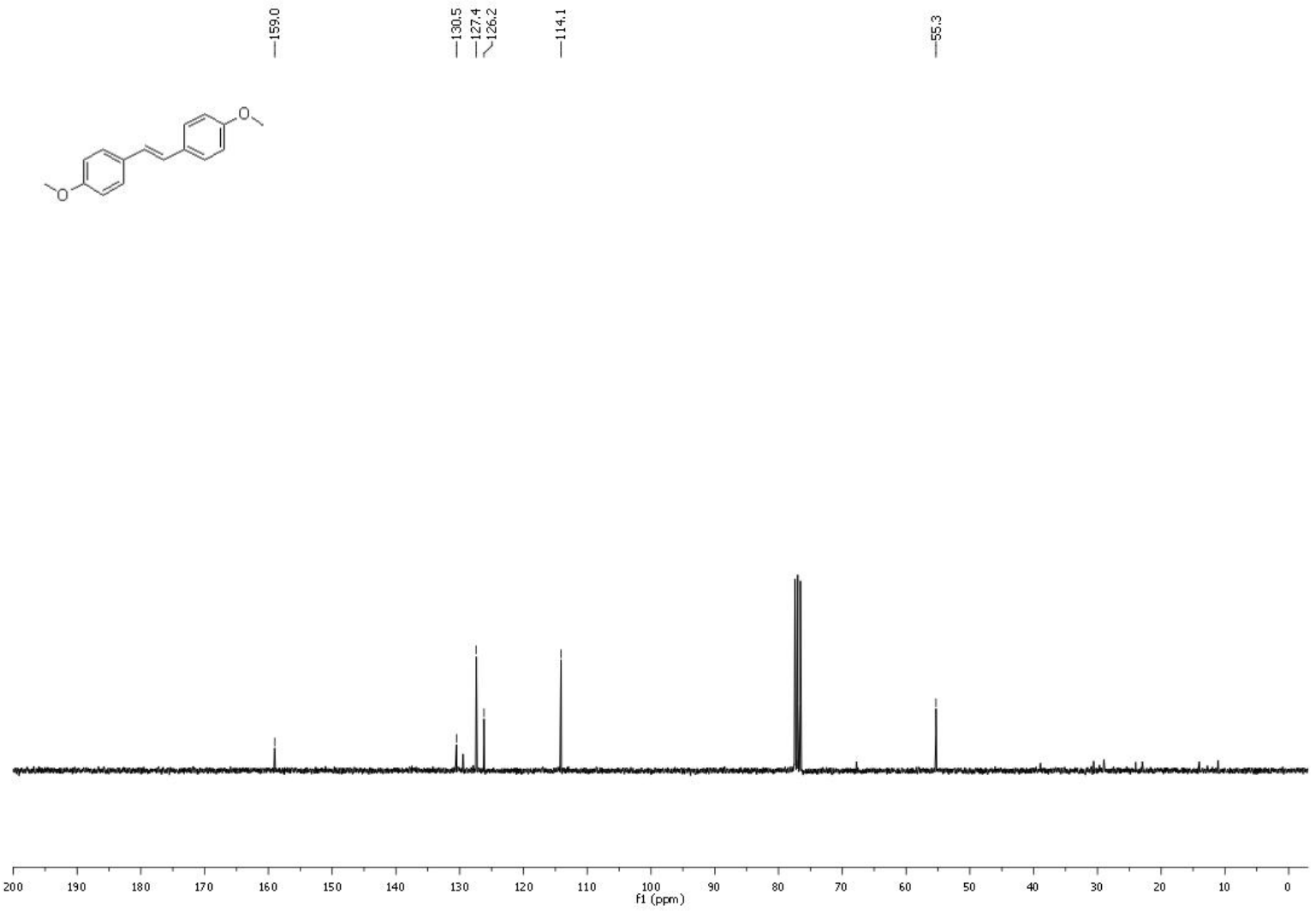
^{13}C NMR (75 MHz, acetone-d_6) of **6bb**



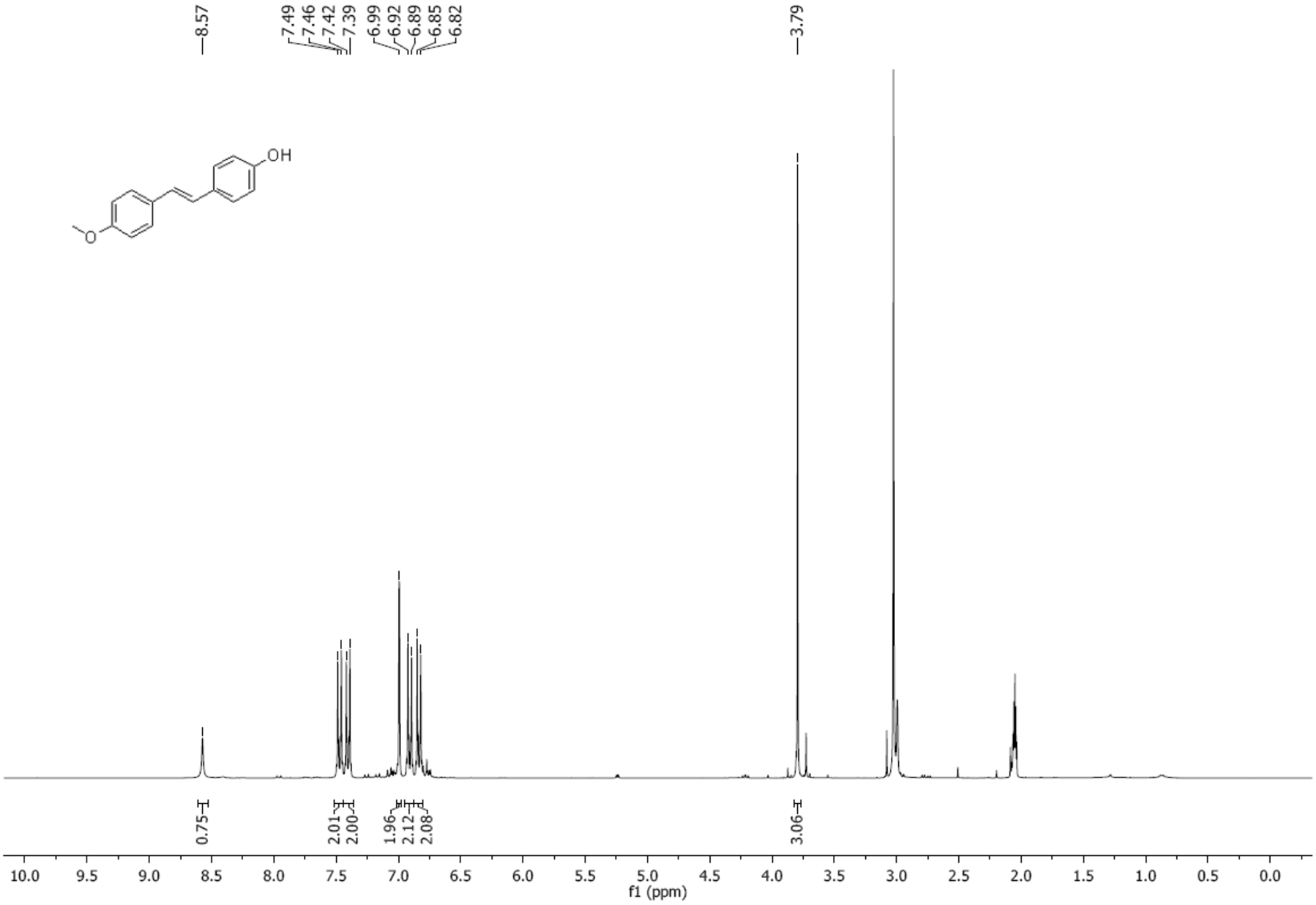
^{1}H NMR (300 MHz, $CDCl_3$) of **6ca**



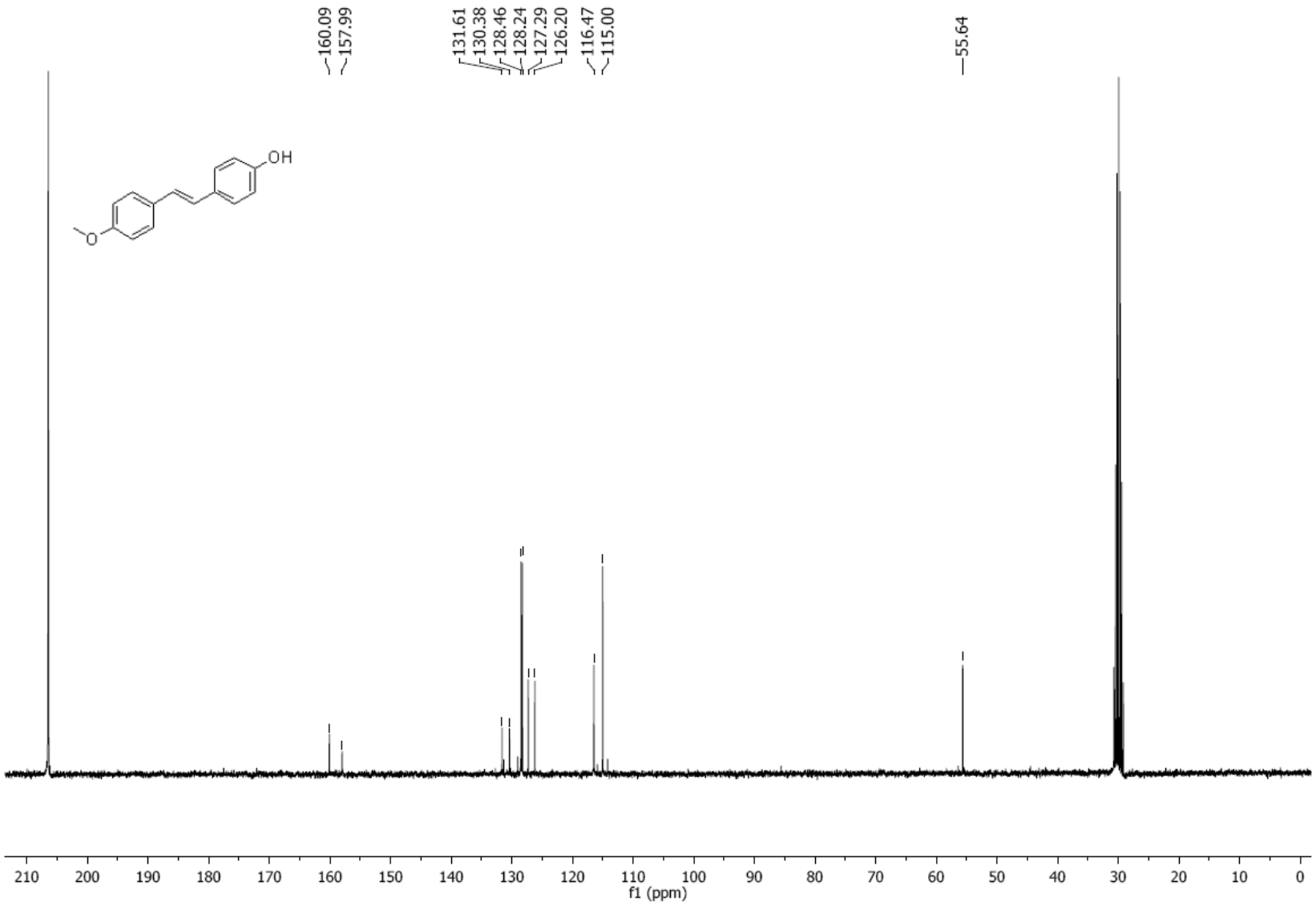
^{13}C NMR (75 MHz, $CDCl_3$) of **6ca**



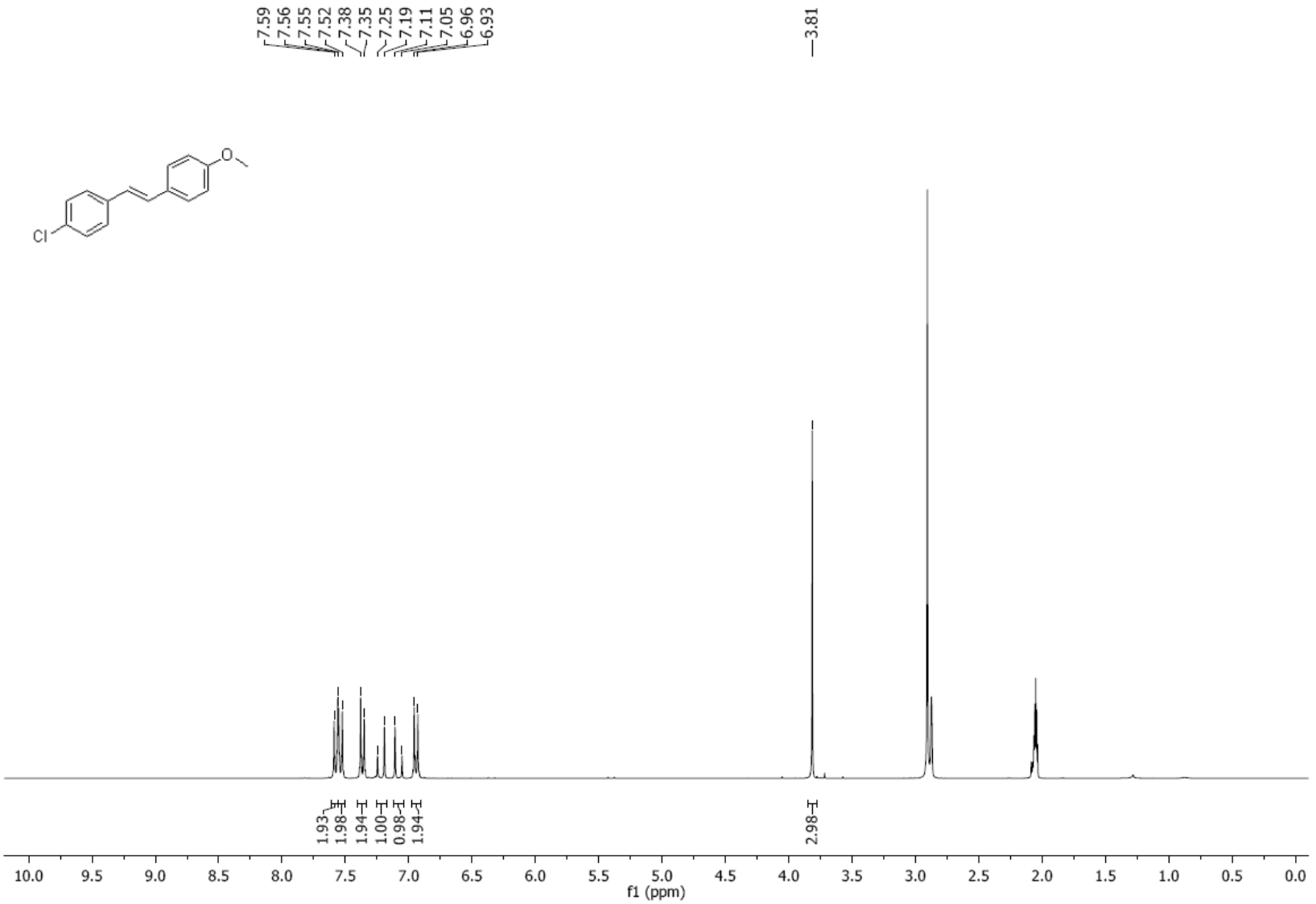
^{1}H NMR (300 MHz, acetone-d_6) of **6cb**



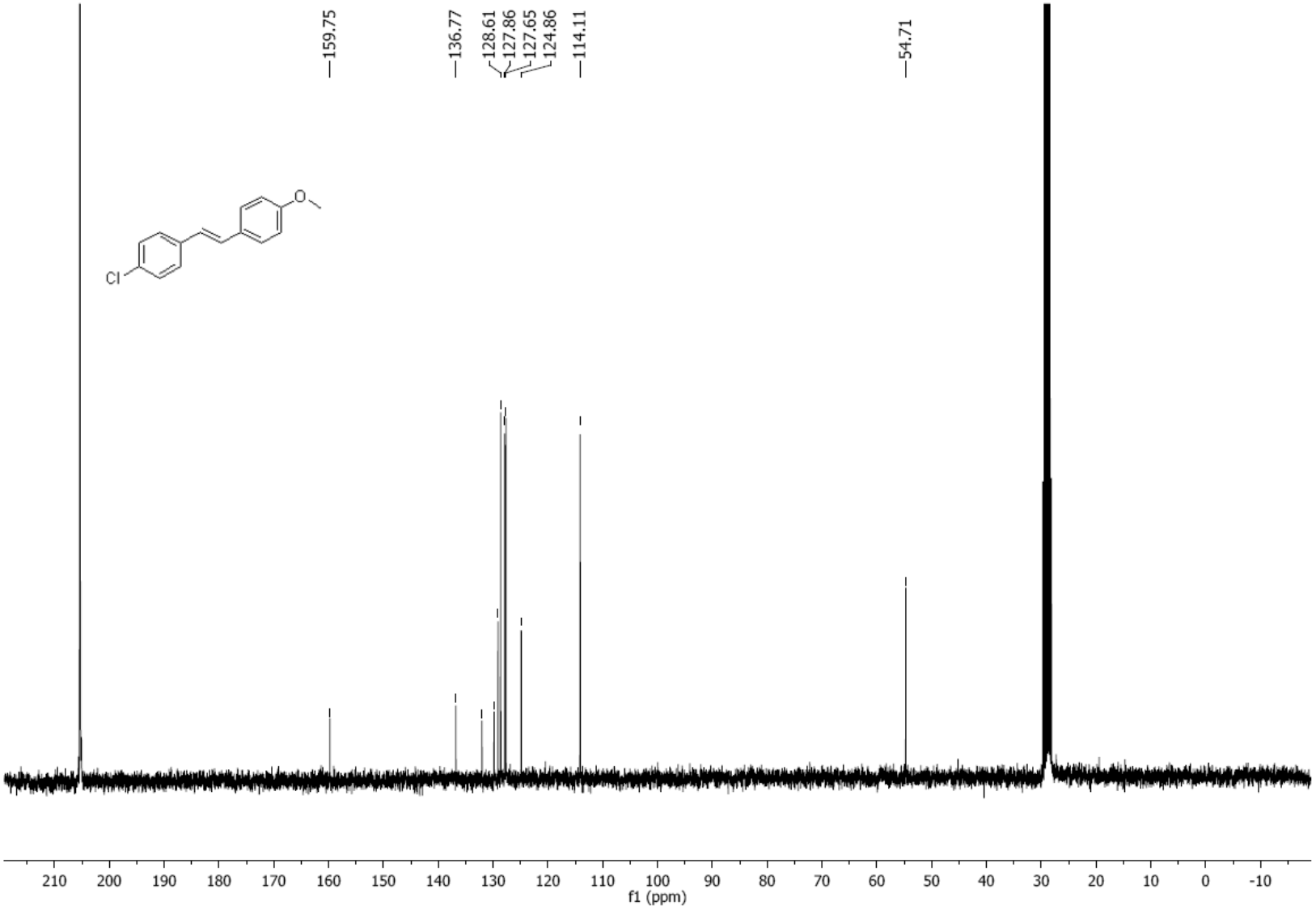
^{13}C NMR (75 MHz, acetone-d_6) of **6cb**



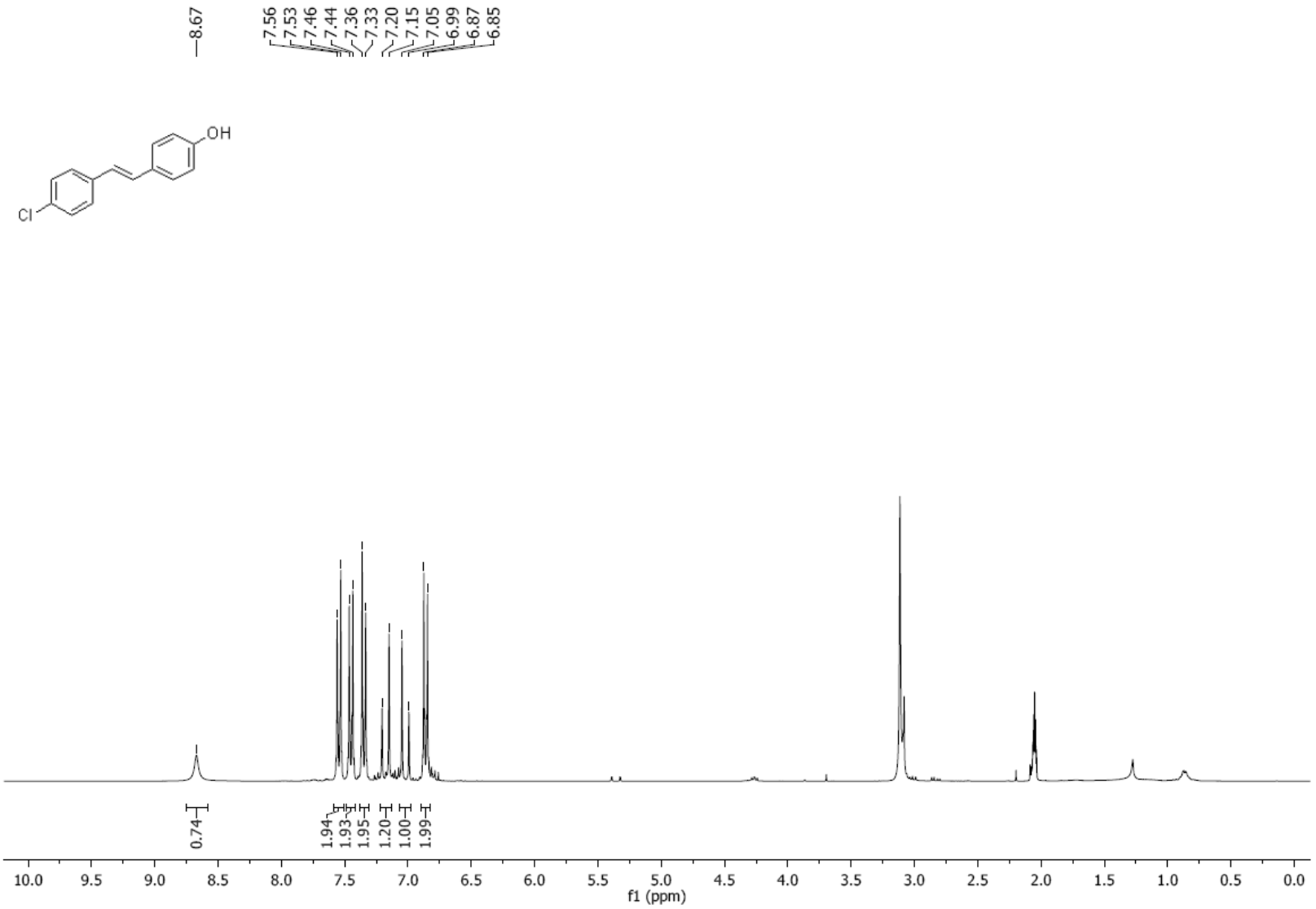
^{1}H NMR (300 MHz, acetone-d_6) of **6da**



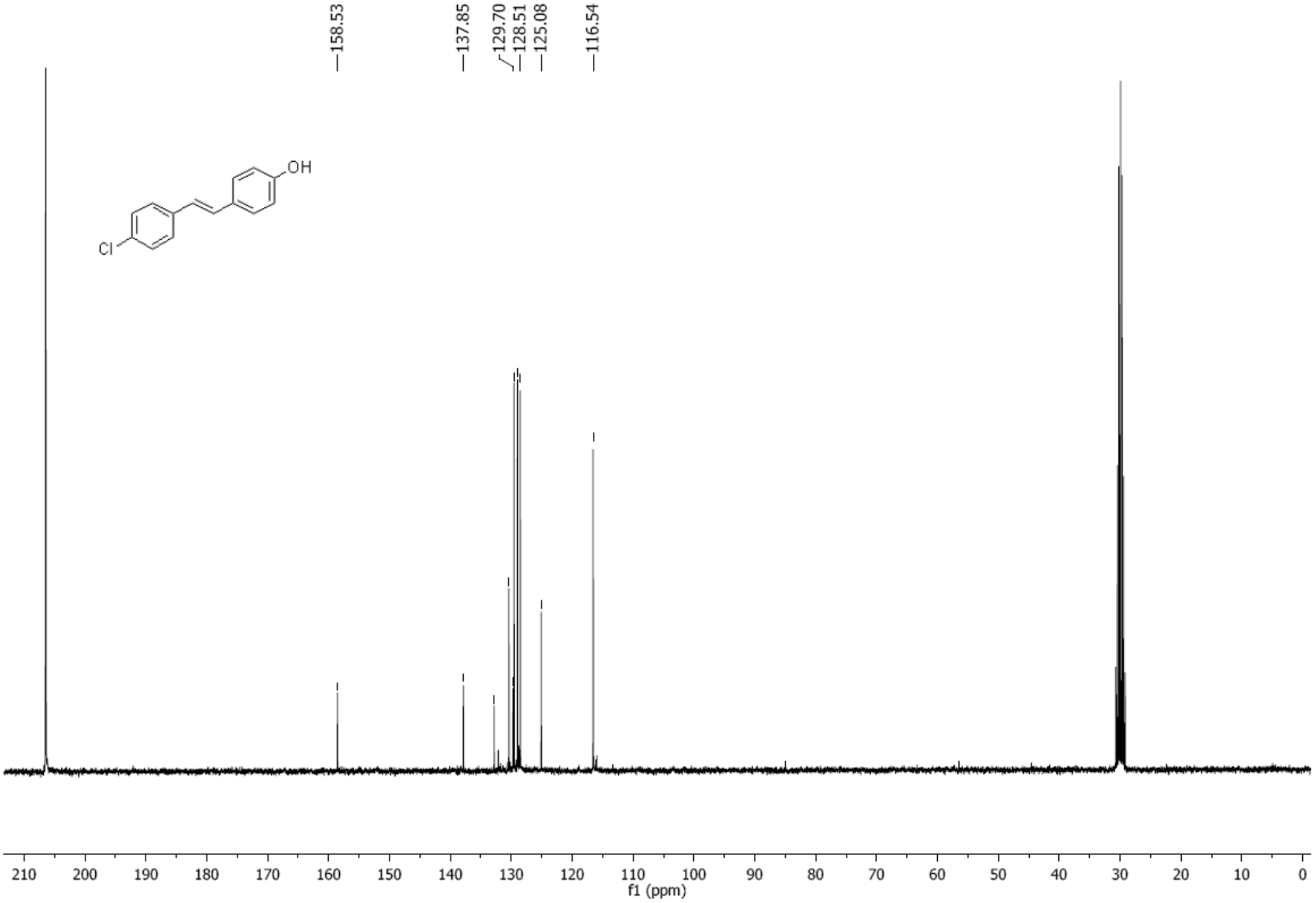
^{13}C NMR (75 MHz, acetone-d_6) of **6da**



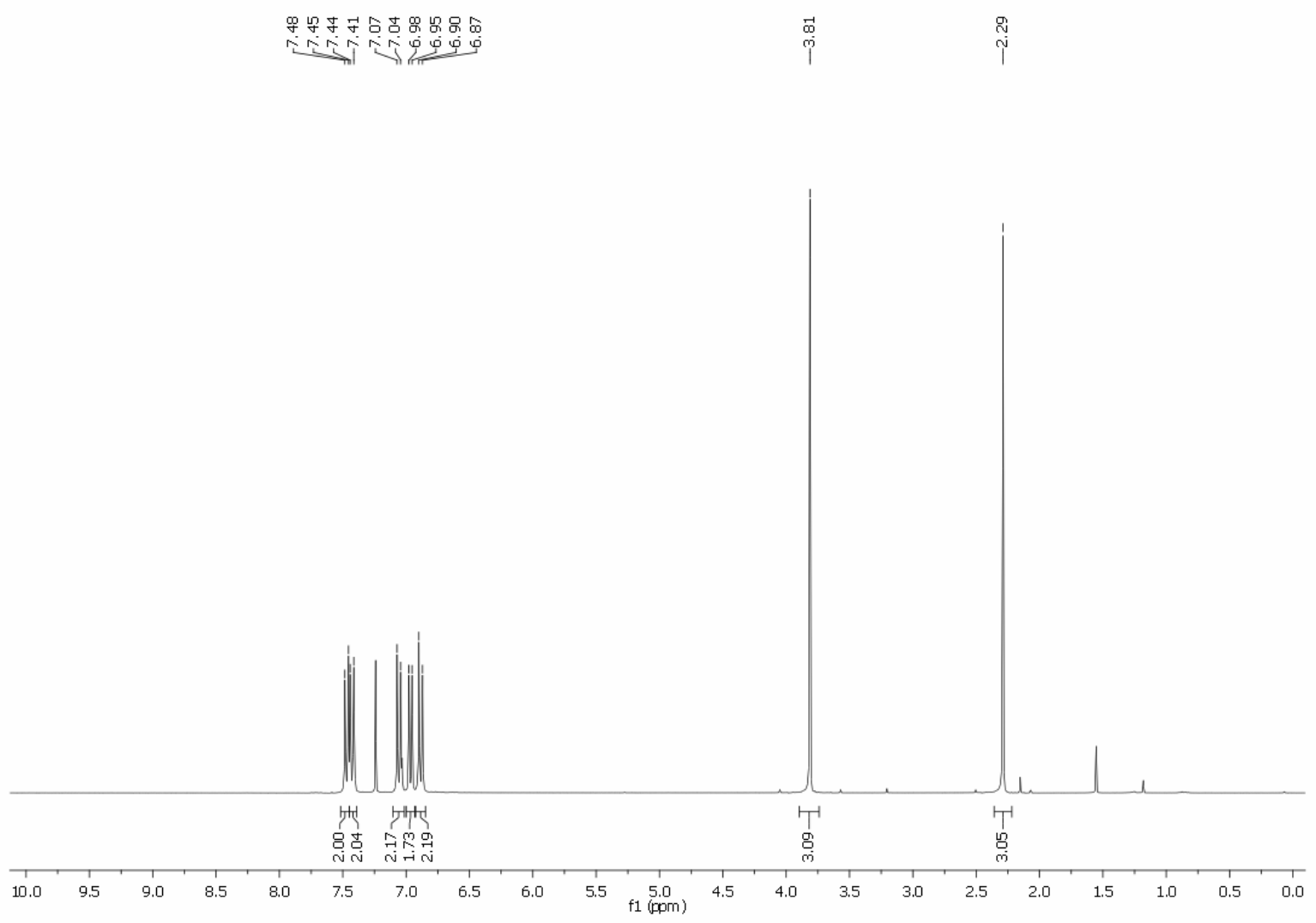
^{1}H NMR (300 MHz, acetone-d_6) of **6db**



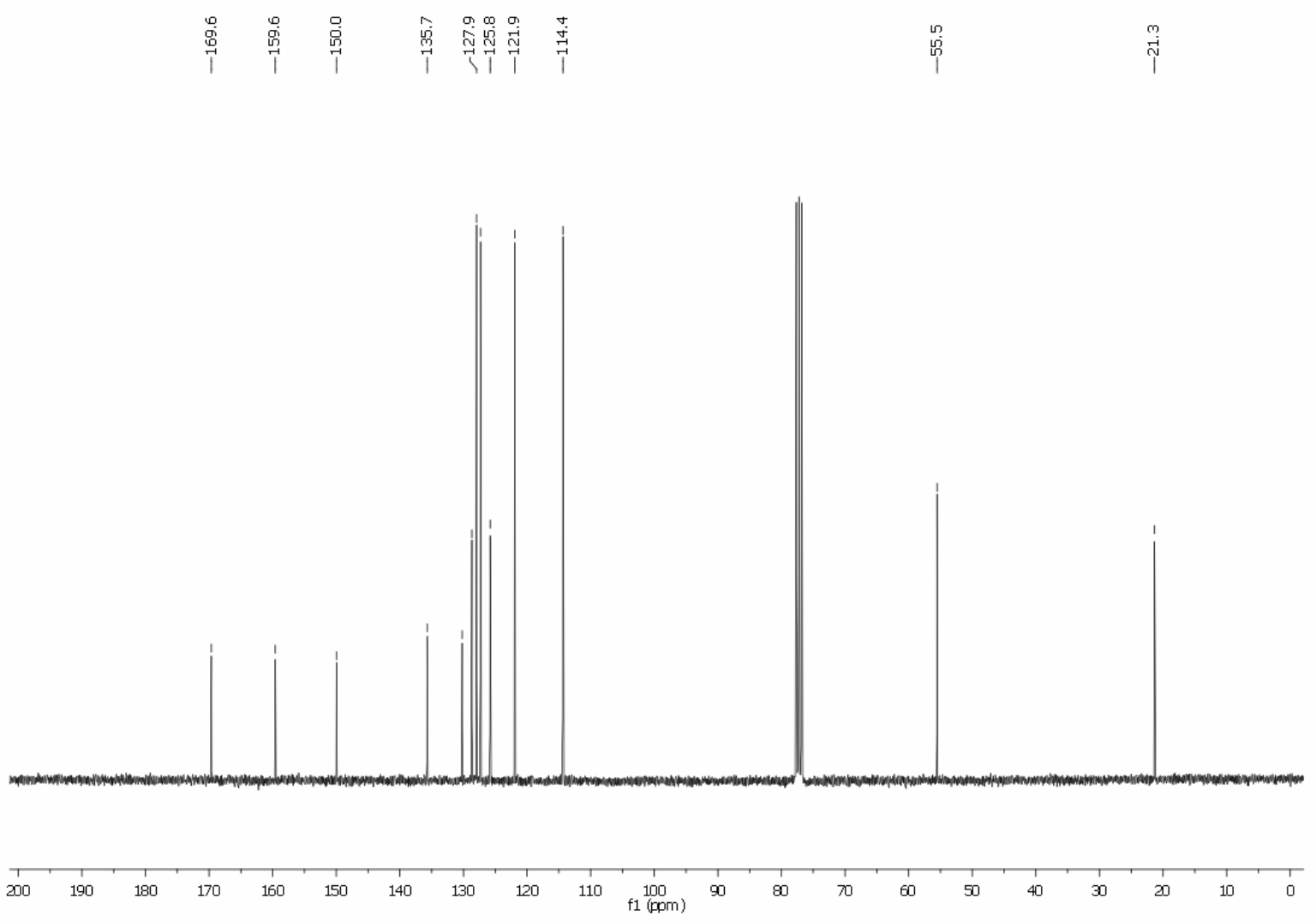
^{13}C NMR (75 MHz, acetone-d_6) of **6db**



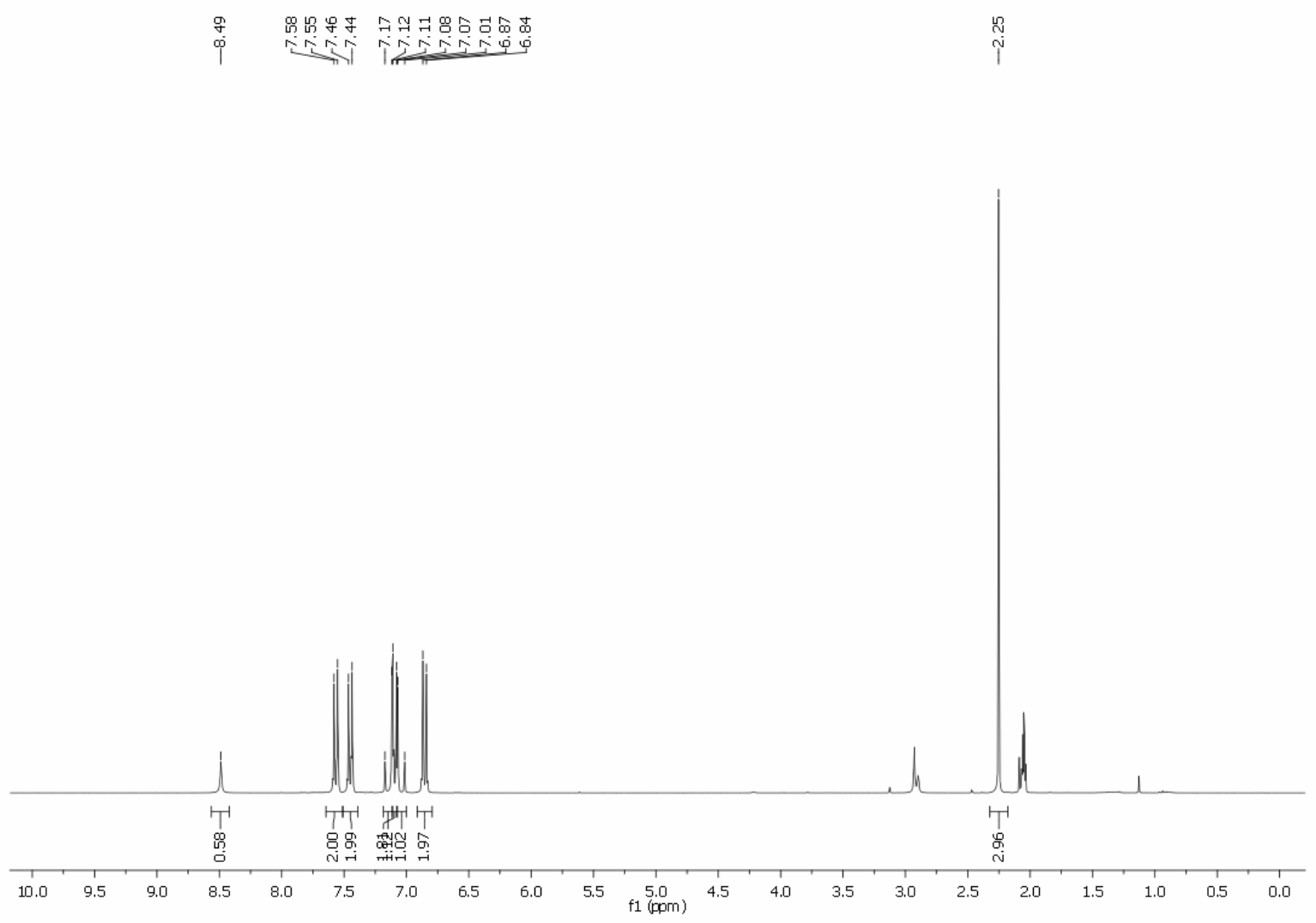
^{1}H NMR (300 MHz, $CDCl_3$) of **6ea**



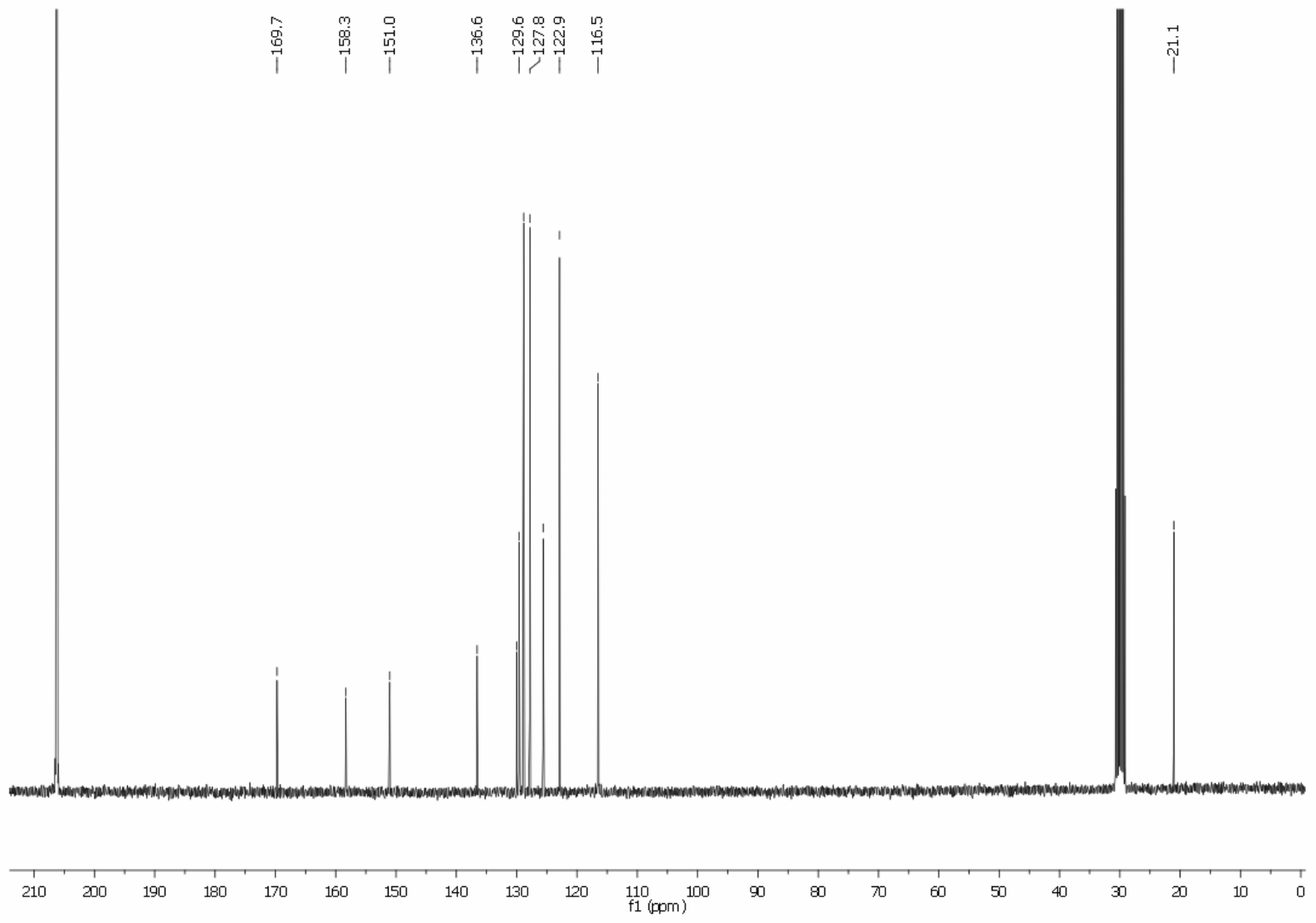
^{13}C NMR (75 MHz, $CDCl_3$) of **6ea**



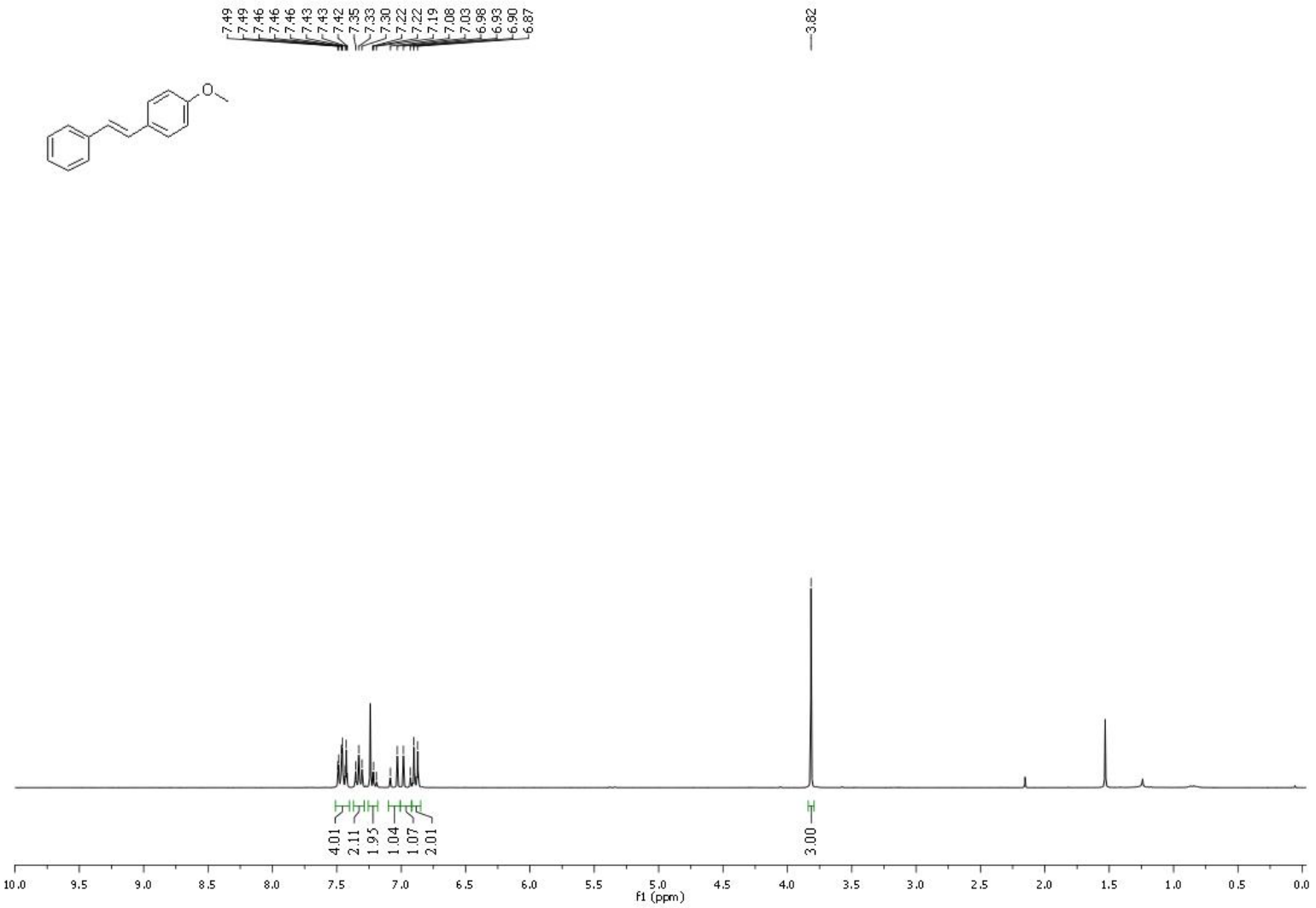
^{1}H NMR (300 MHz, acetone-d_6) of **6eb**



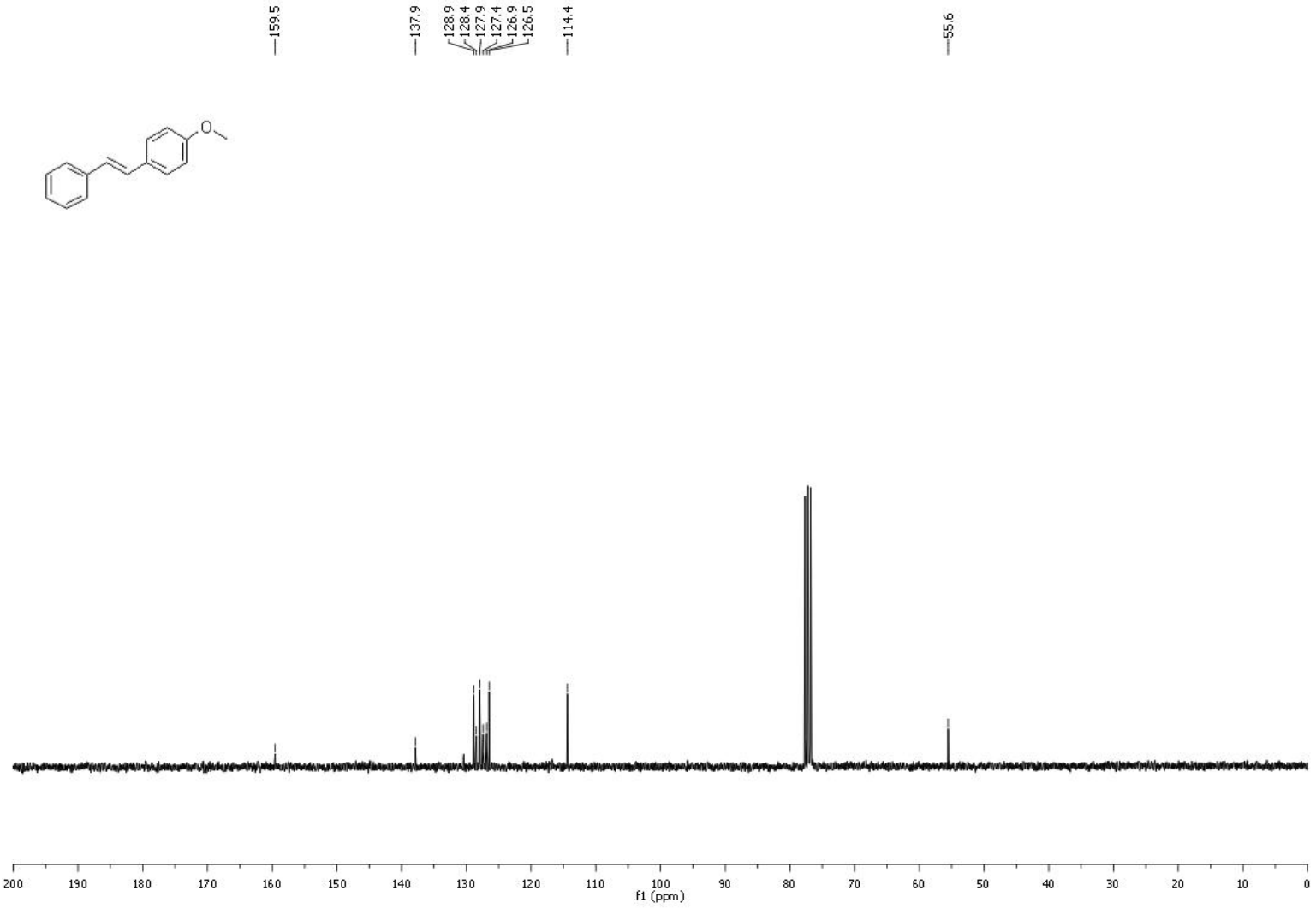
^{13}C NMR (75 MHz, acetone-d_6) of **6eb**



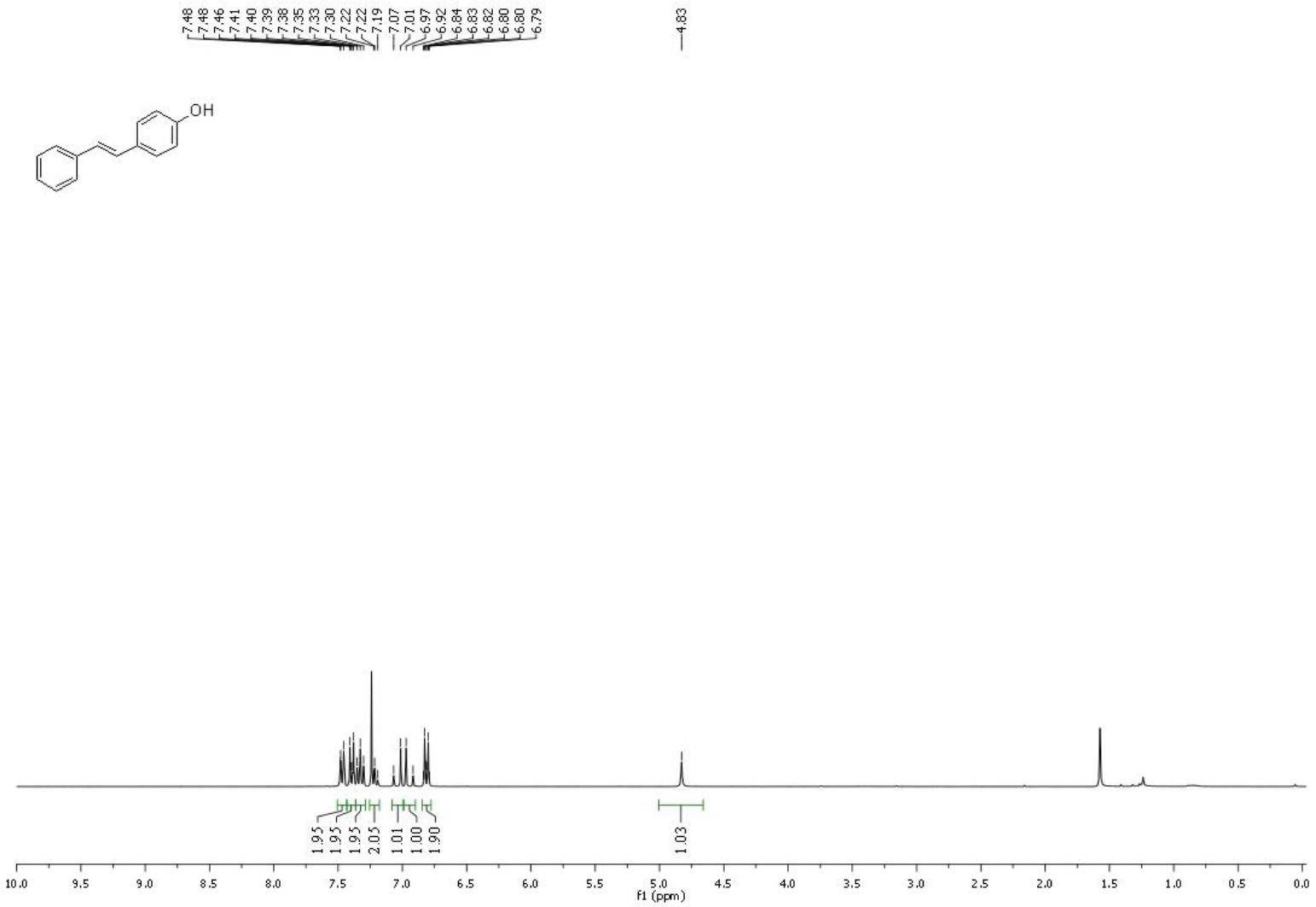
^{1}H NMR (300 MHz, $CDCl_3$) of **6fa**



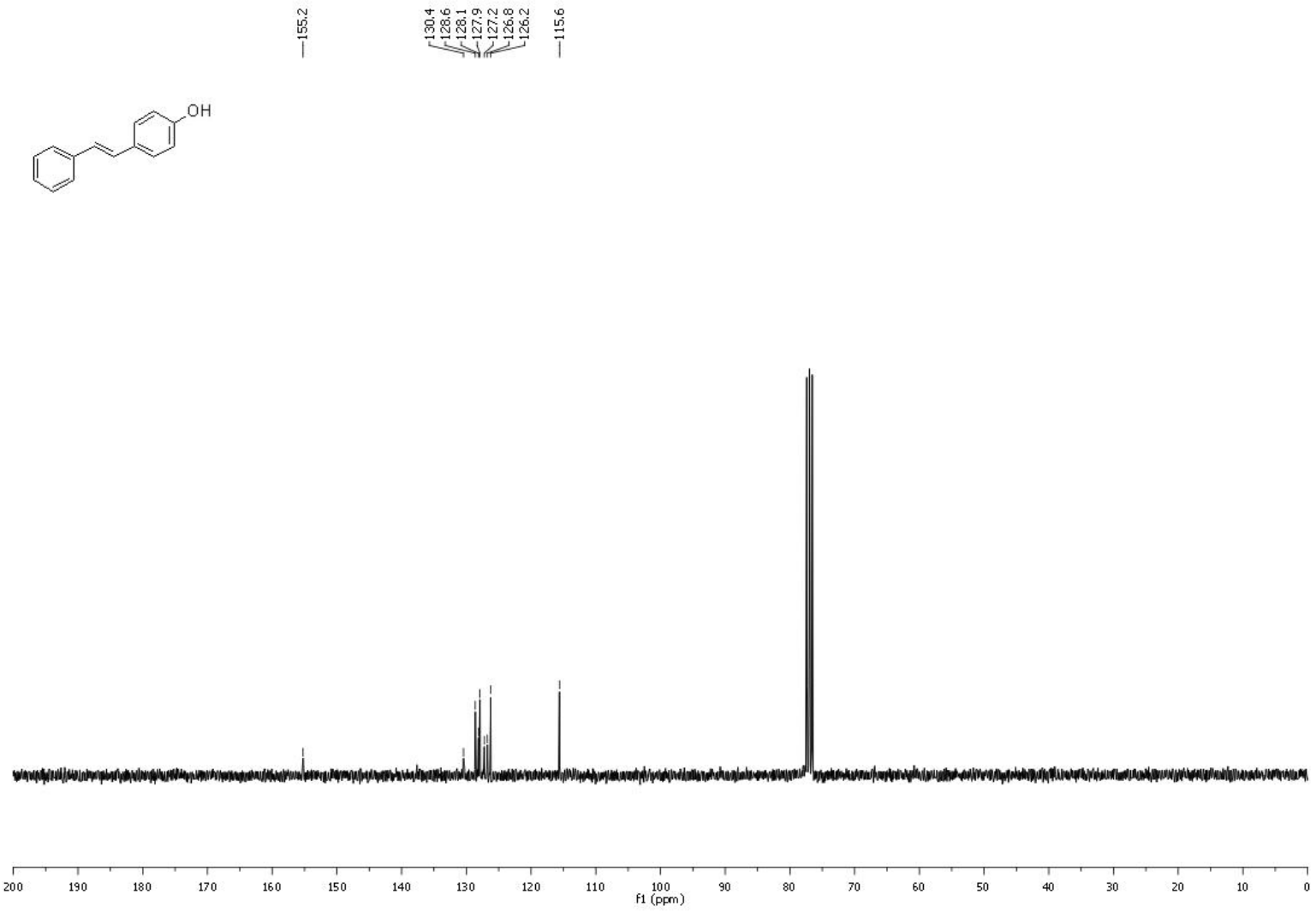
^{13}C NMR (75 MHz, $CDCl_3$) of **6fa**



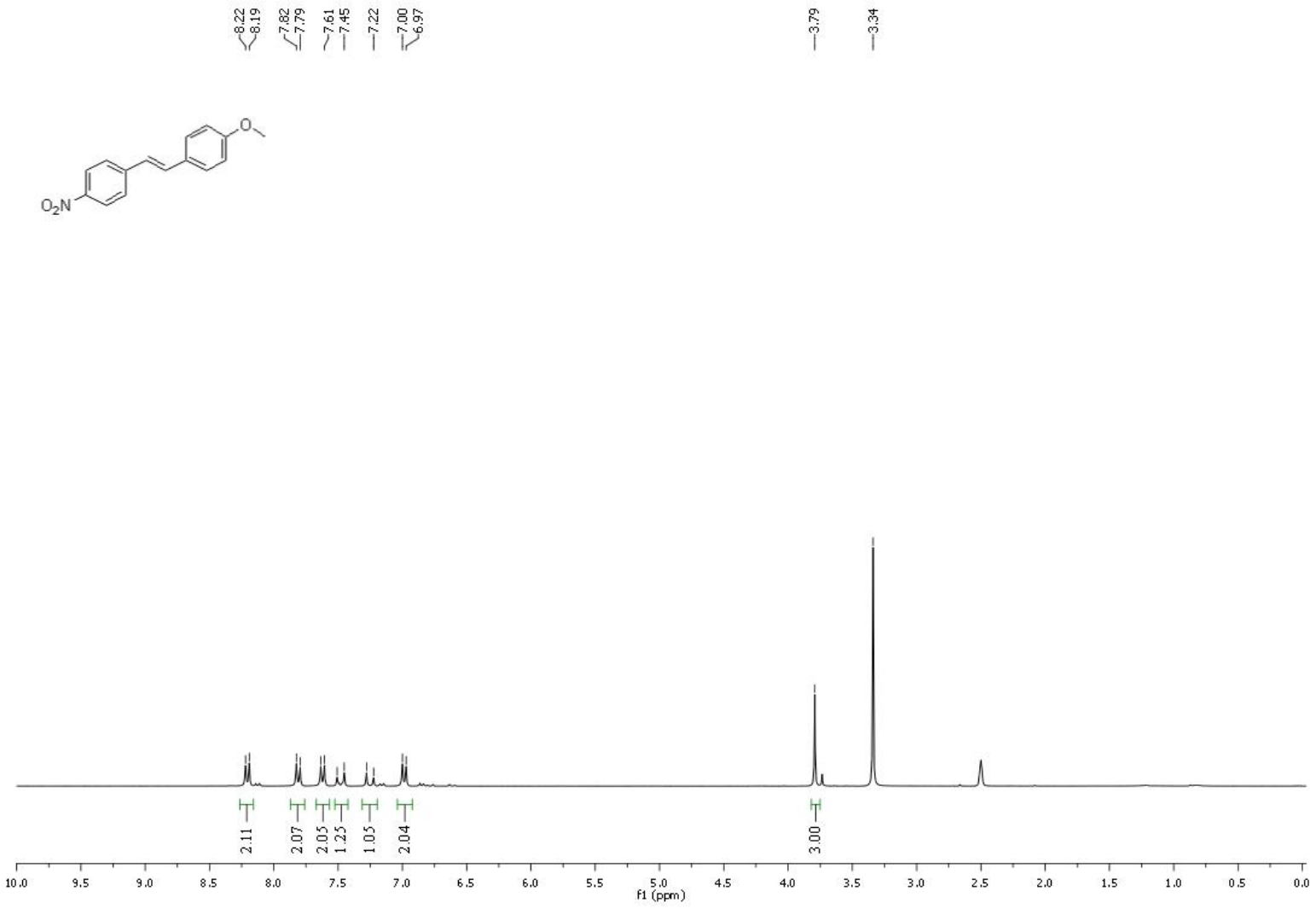
^{1}H NMR (300 MHz, $CDCl_3$) of **6fb**



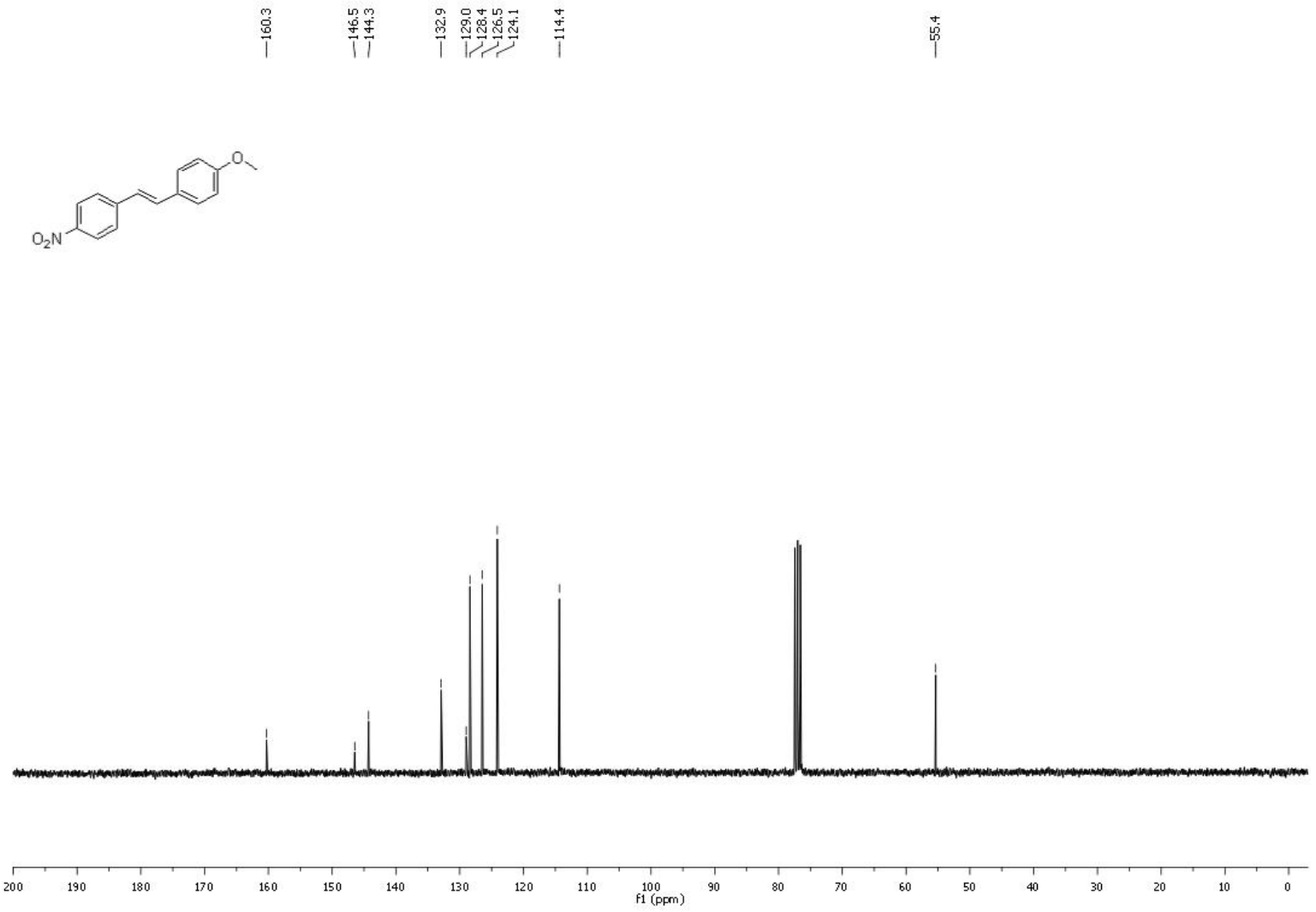
^{13}C NMR (75 MHz, $CDCl_3$) of **6fb**



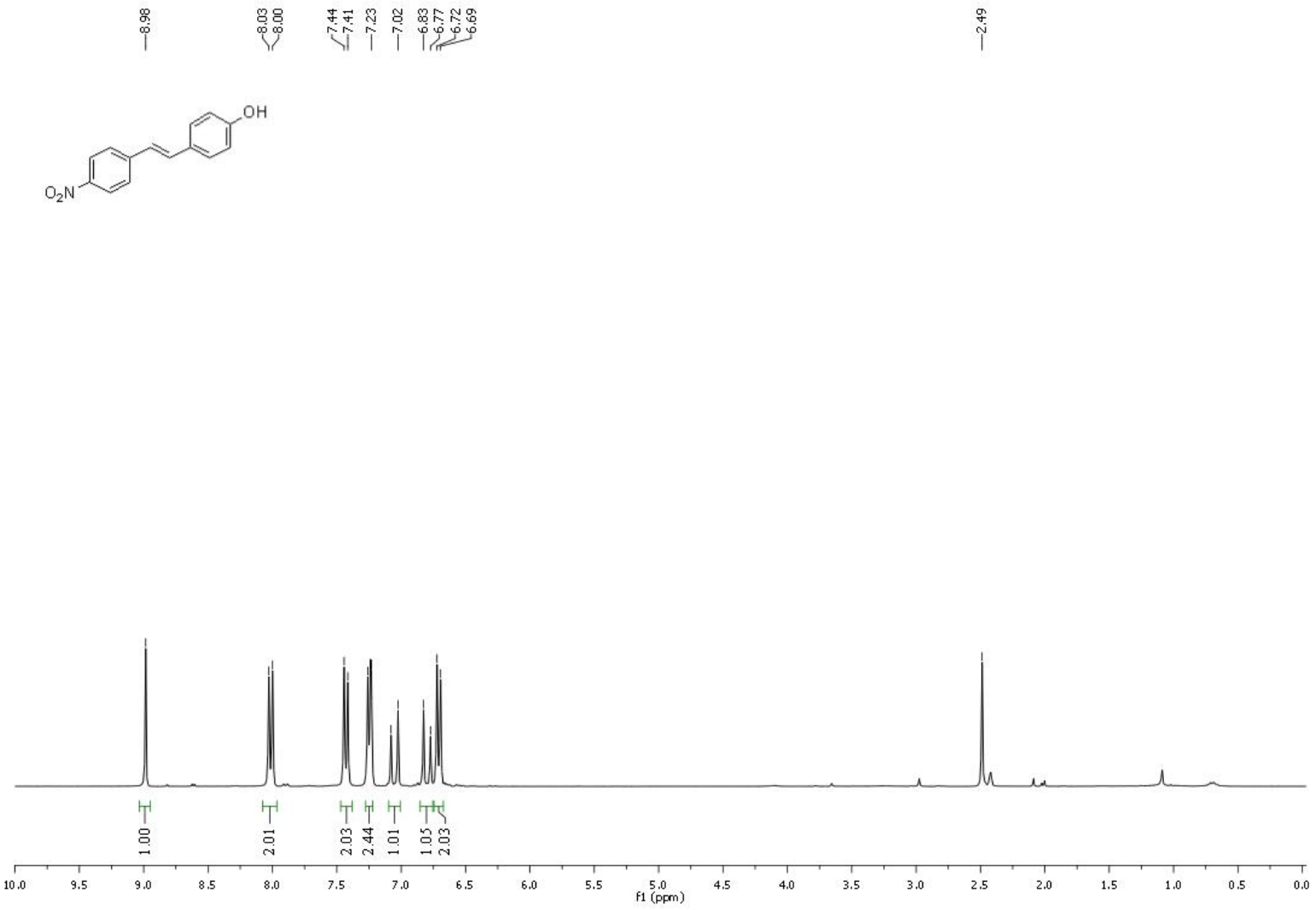
^{1}H NMR (300 MHz, DMSO-d_6) of **6ga**



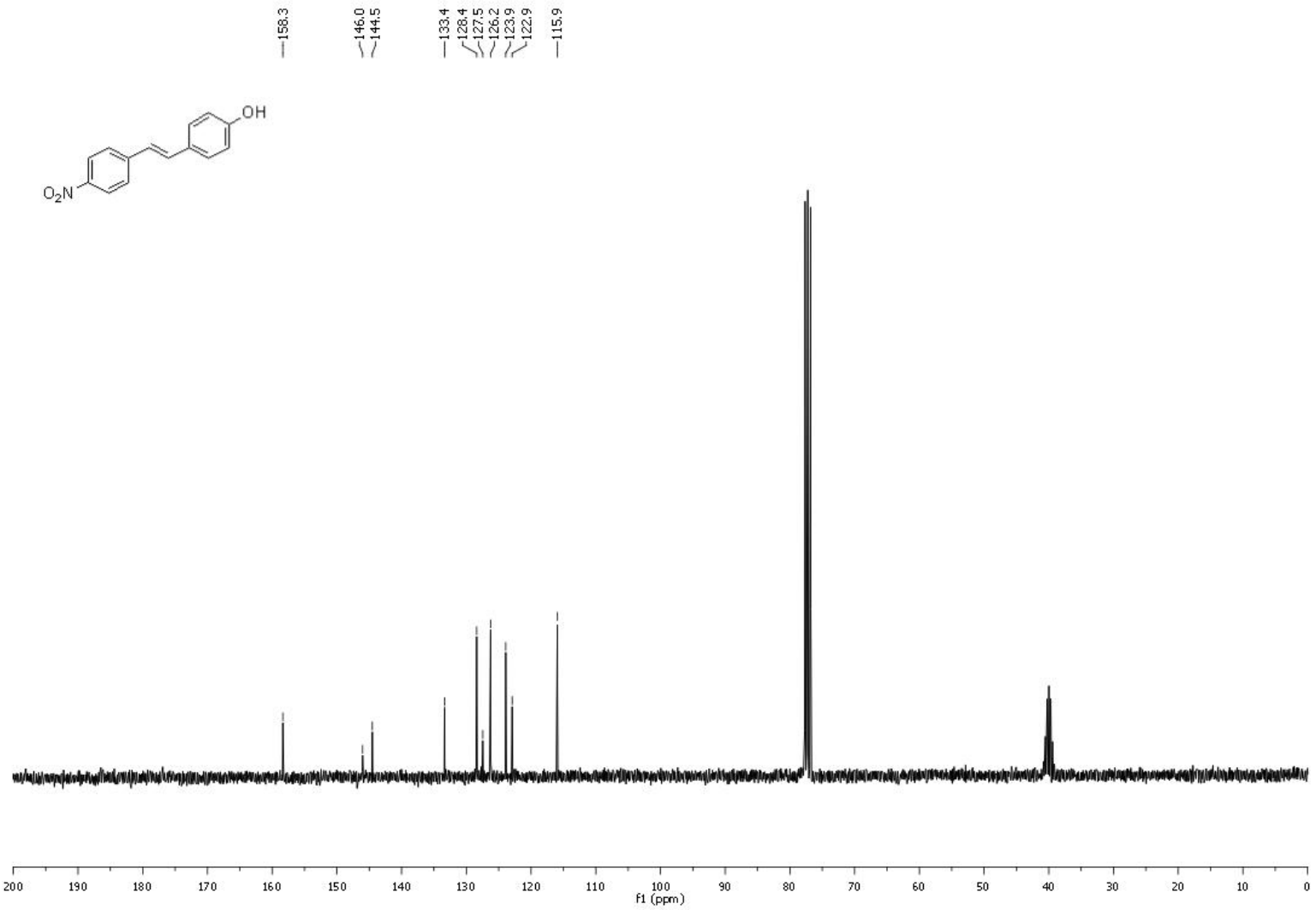
^{13}C NMR (75 MHz, $CDCl_3$) of **6ga**



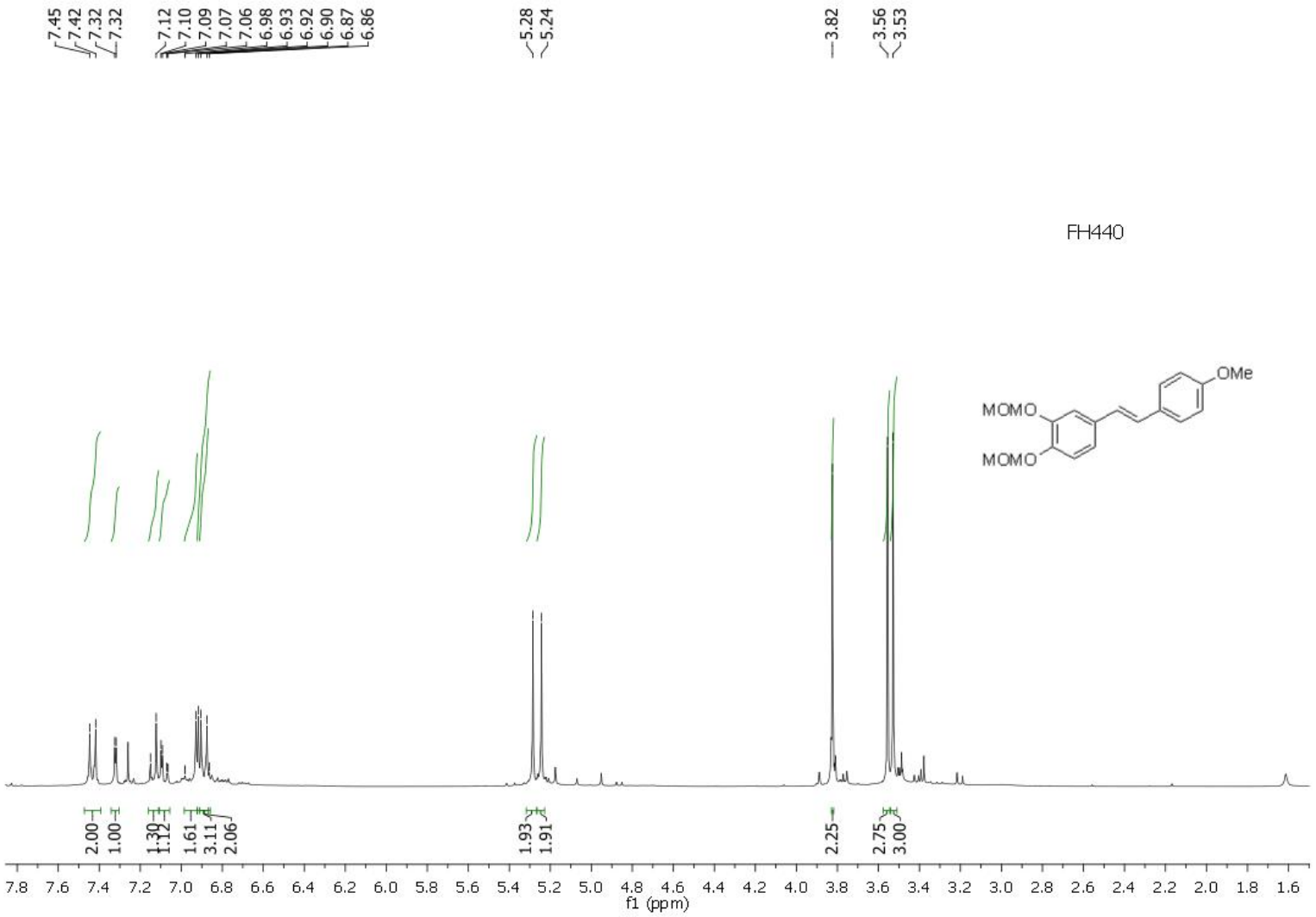
^{1}H NMR (300 MHz, $CDCl_3$/acetone-d_6) of **6gb**



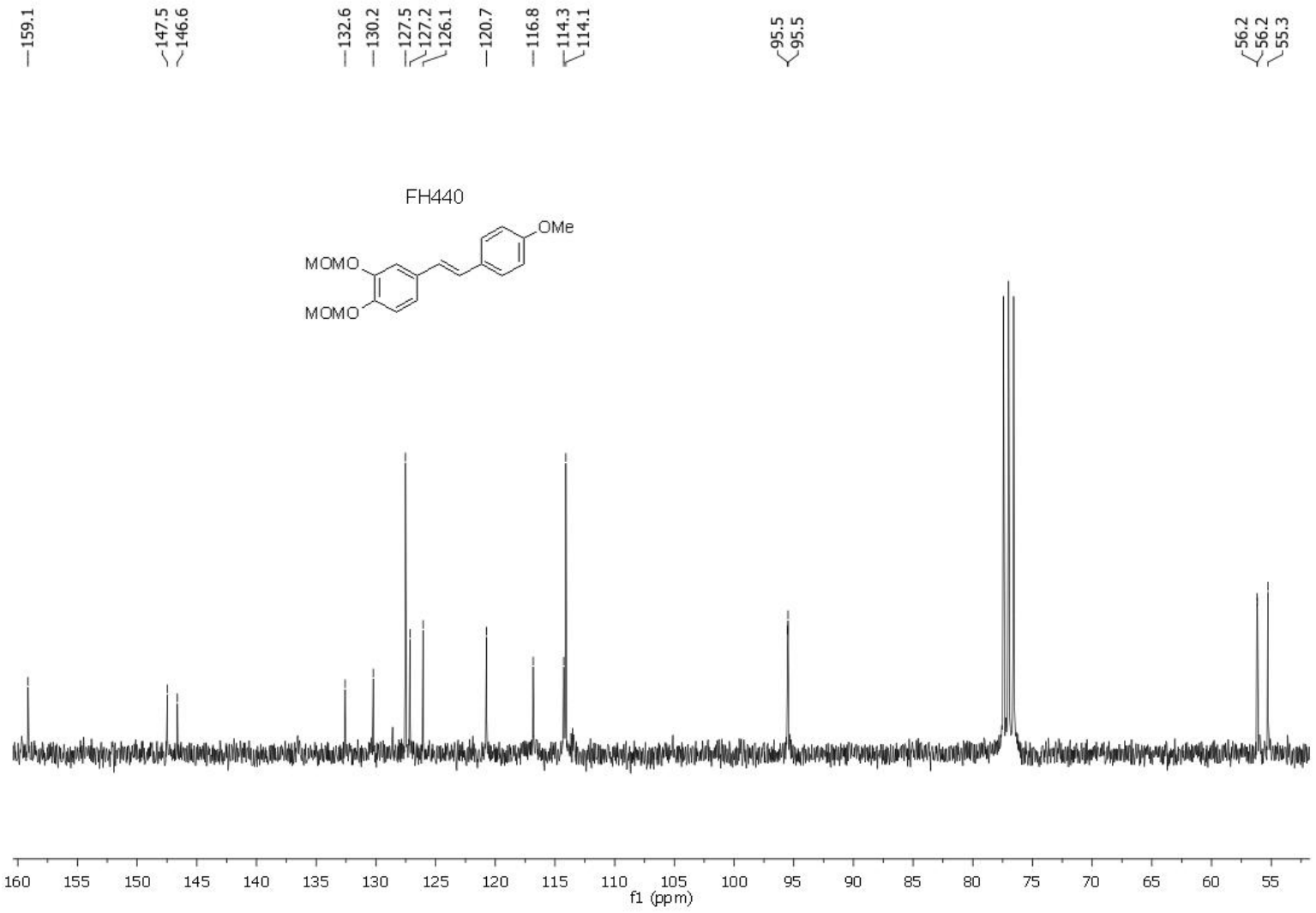
^{13}C NMR (75 MHz, $CDCl_3$/acetone-d_6) of **6gb**



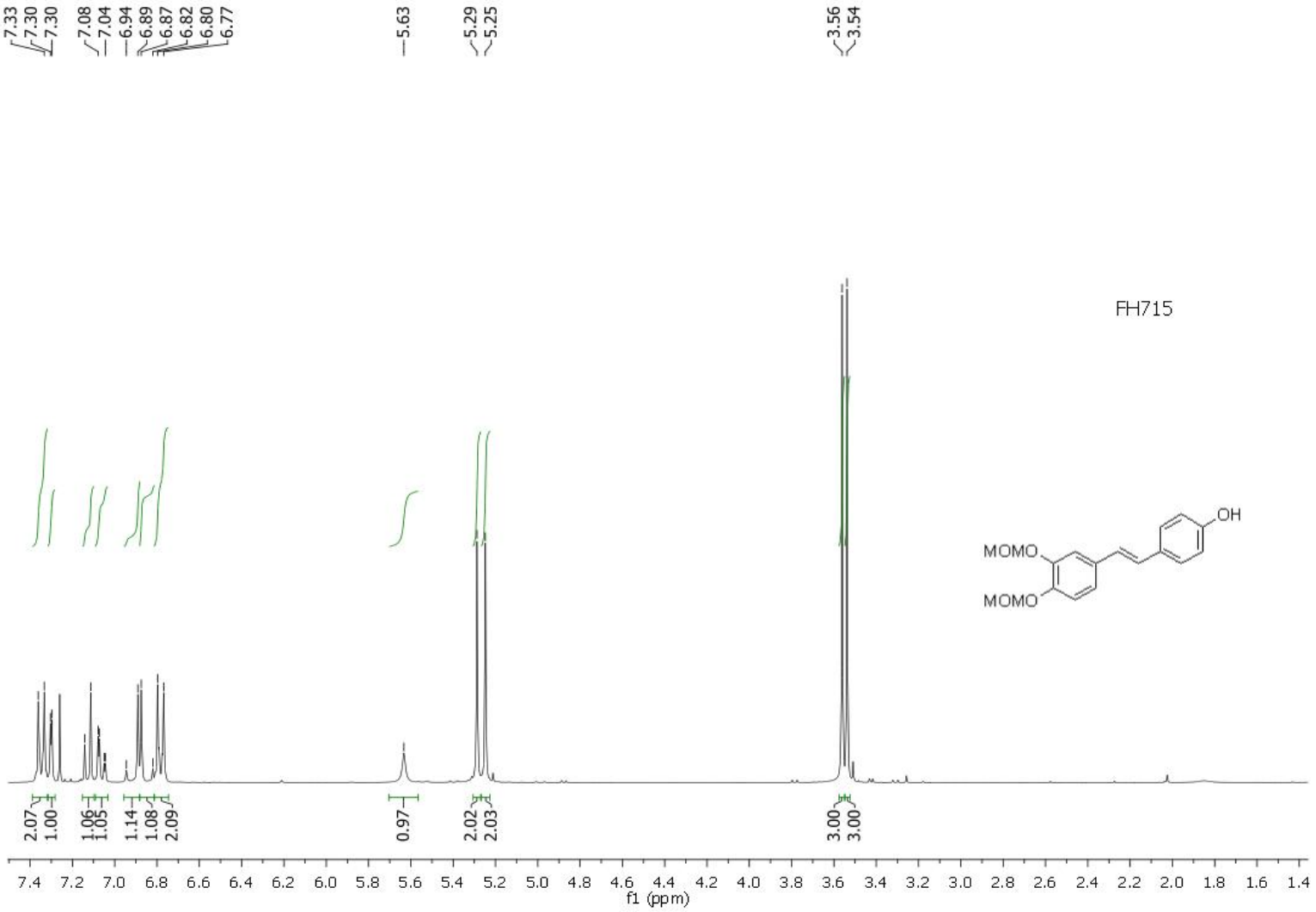
^{1}H NMR (300 MHz, $CDCl_3$) of **6ha**



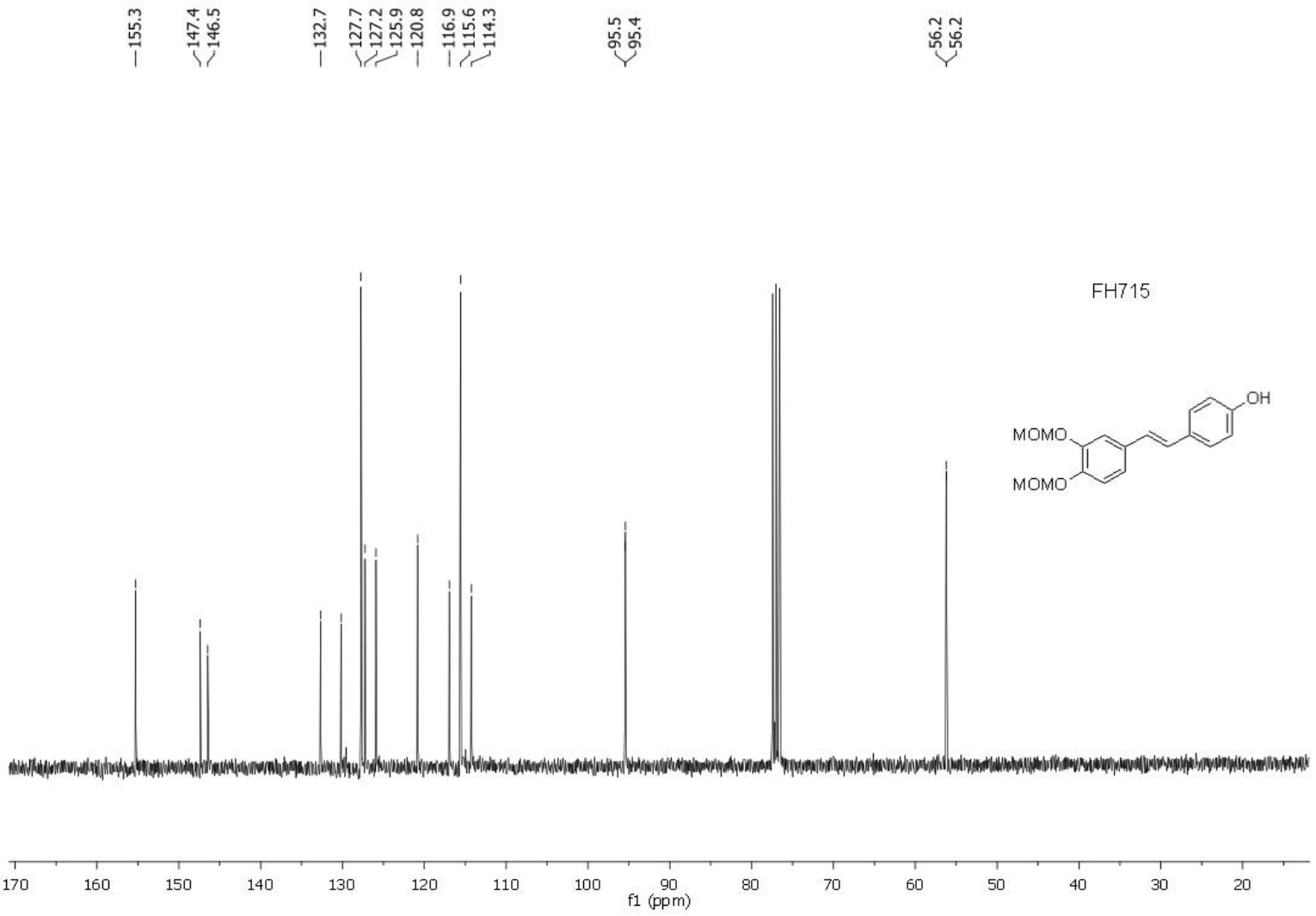
^{13}C NMR (75 MHz, $CDCl_3$) of **6ha**



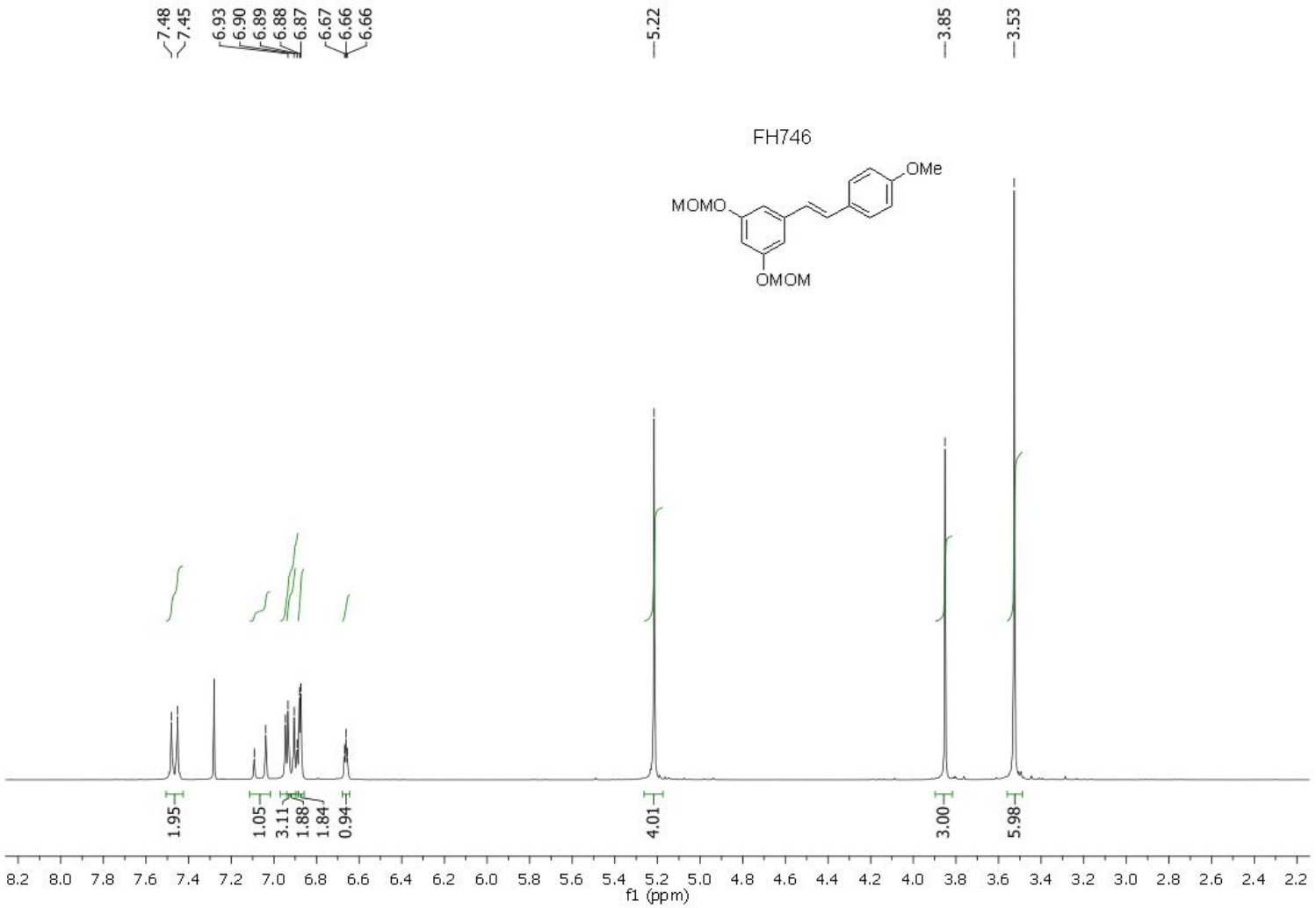
^{1}H NMR (300 MHz, $CDCl_3$) of **6hb**



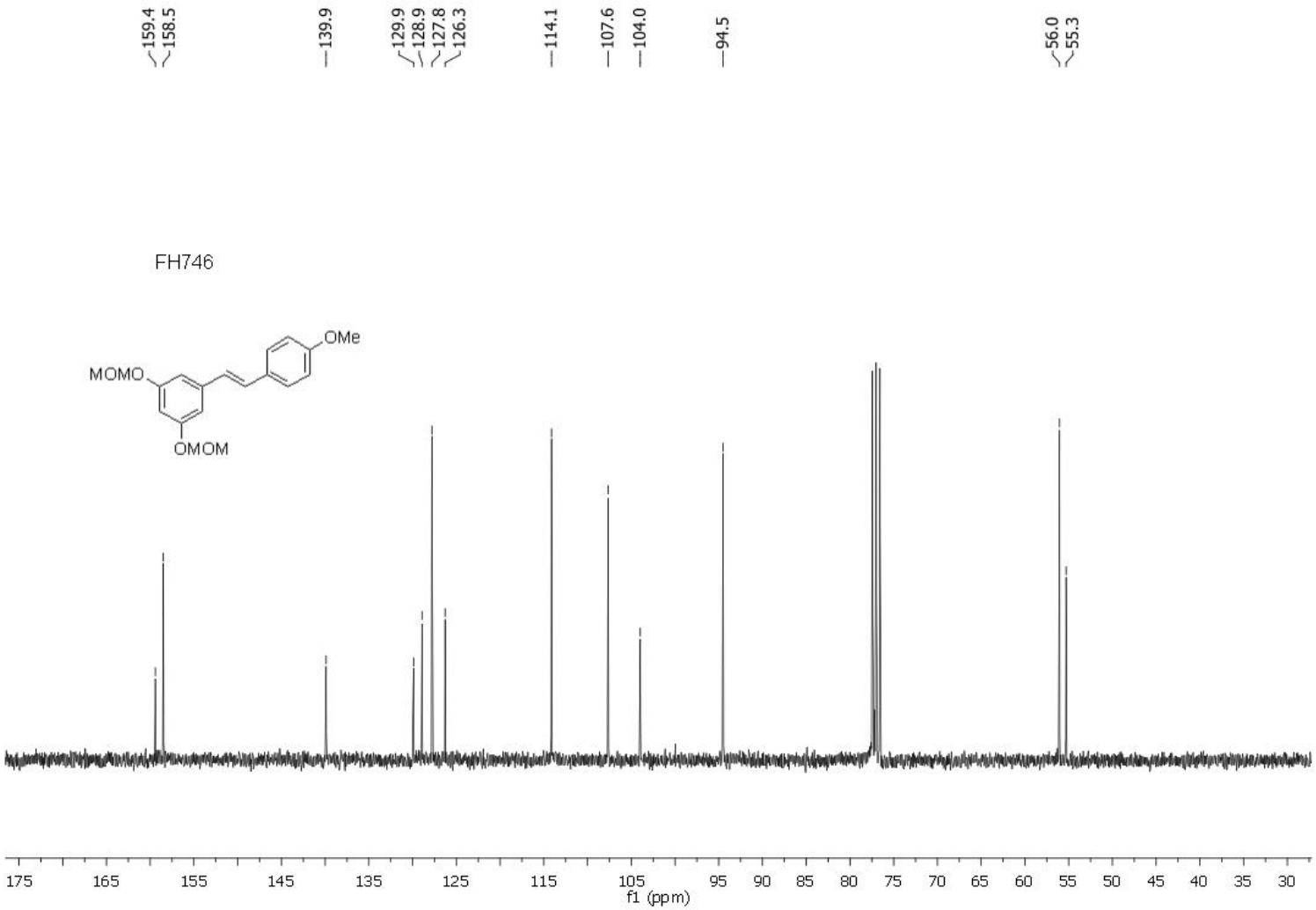
^{13}C NMR (75 MHz, $CDCl_3$) of **6hb**



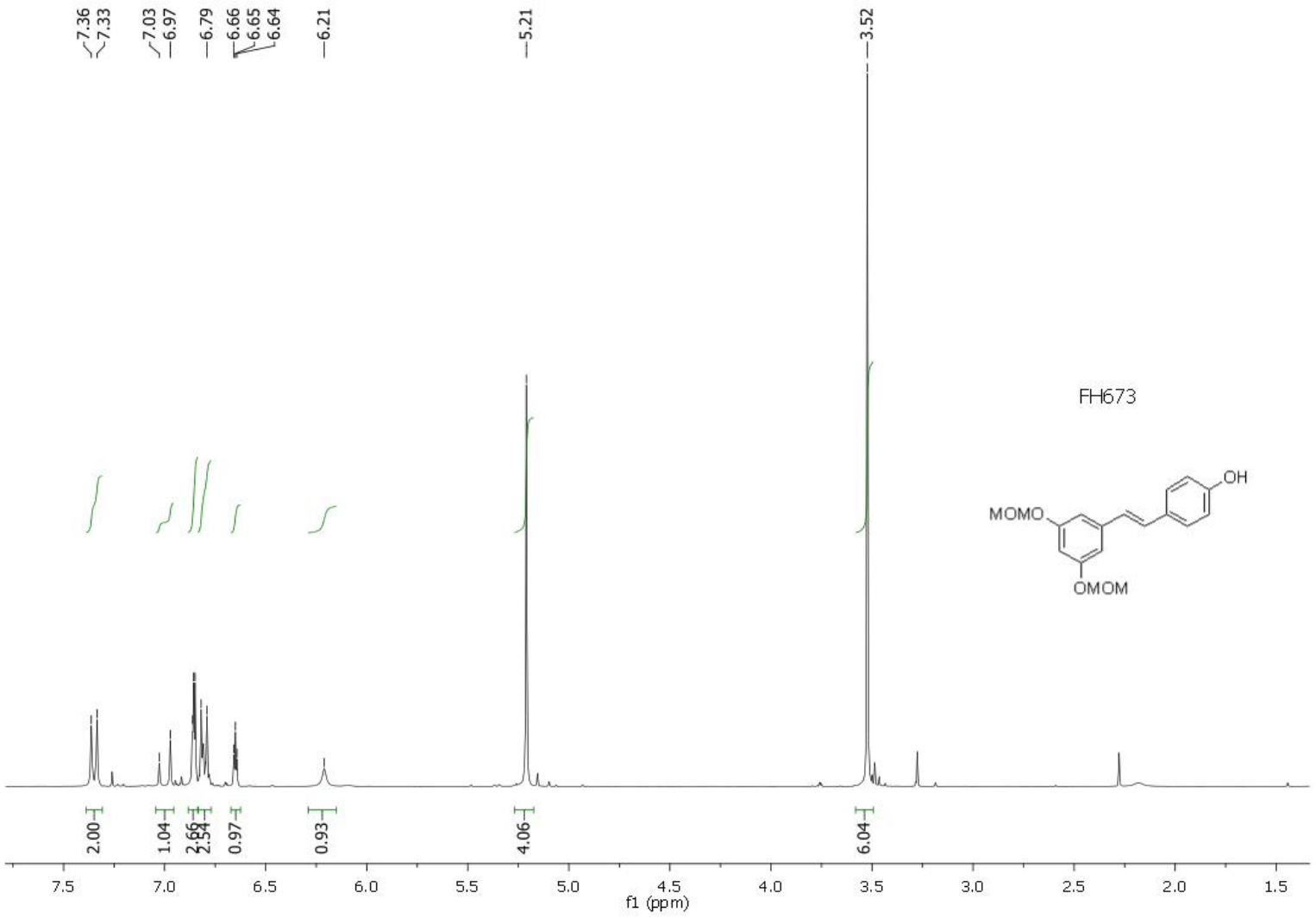
^{1}H NMR (300 MHz, $CDCl_3$) of **6ia**



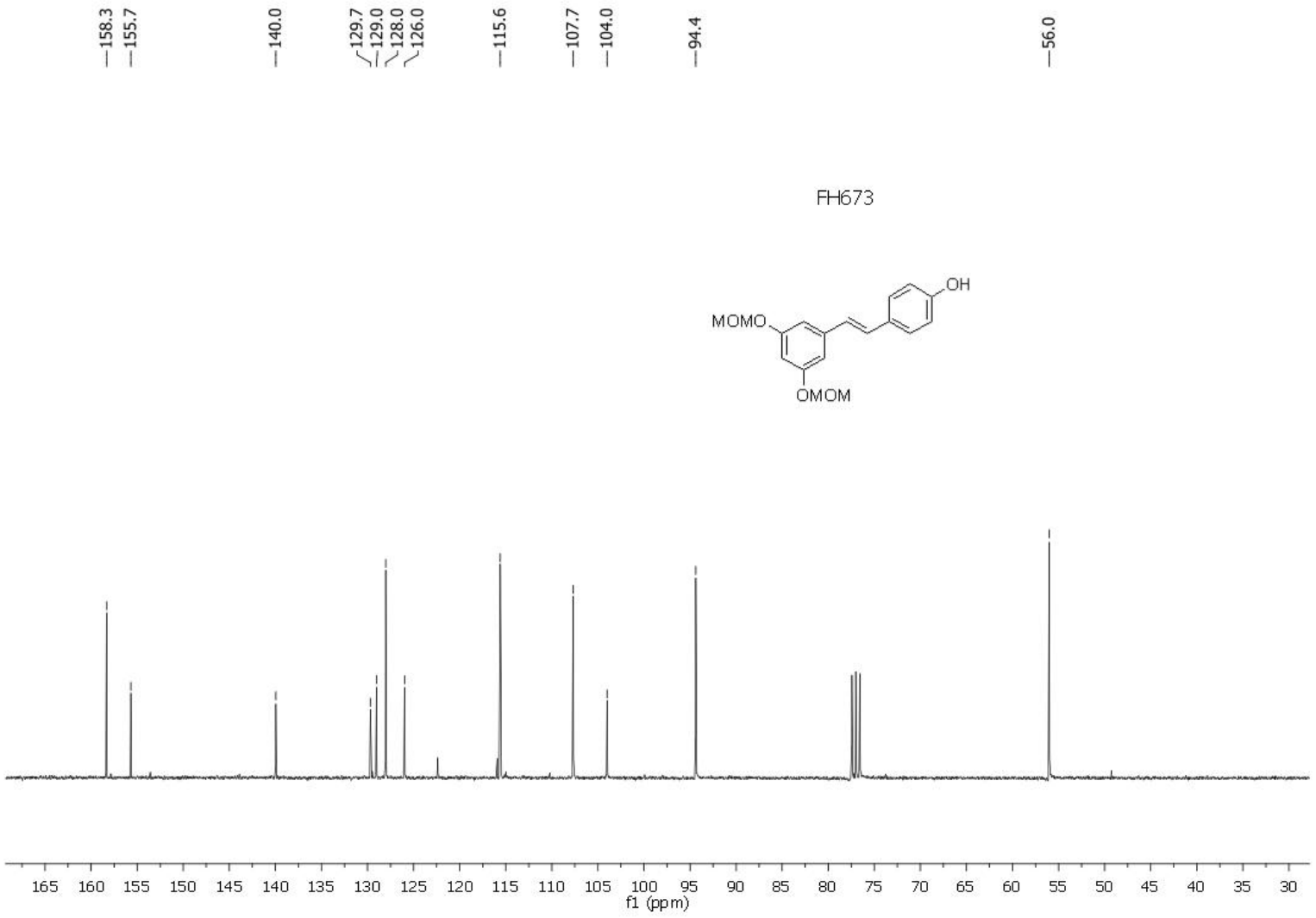
^{13}C NMR (75 MHz, $CDCl_3$) of **6ia**



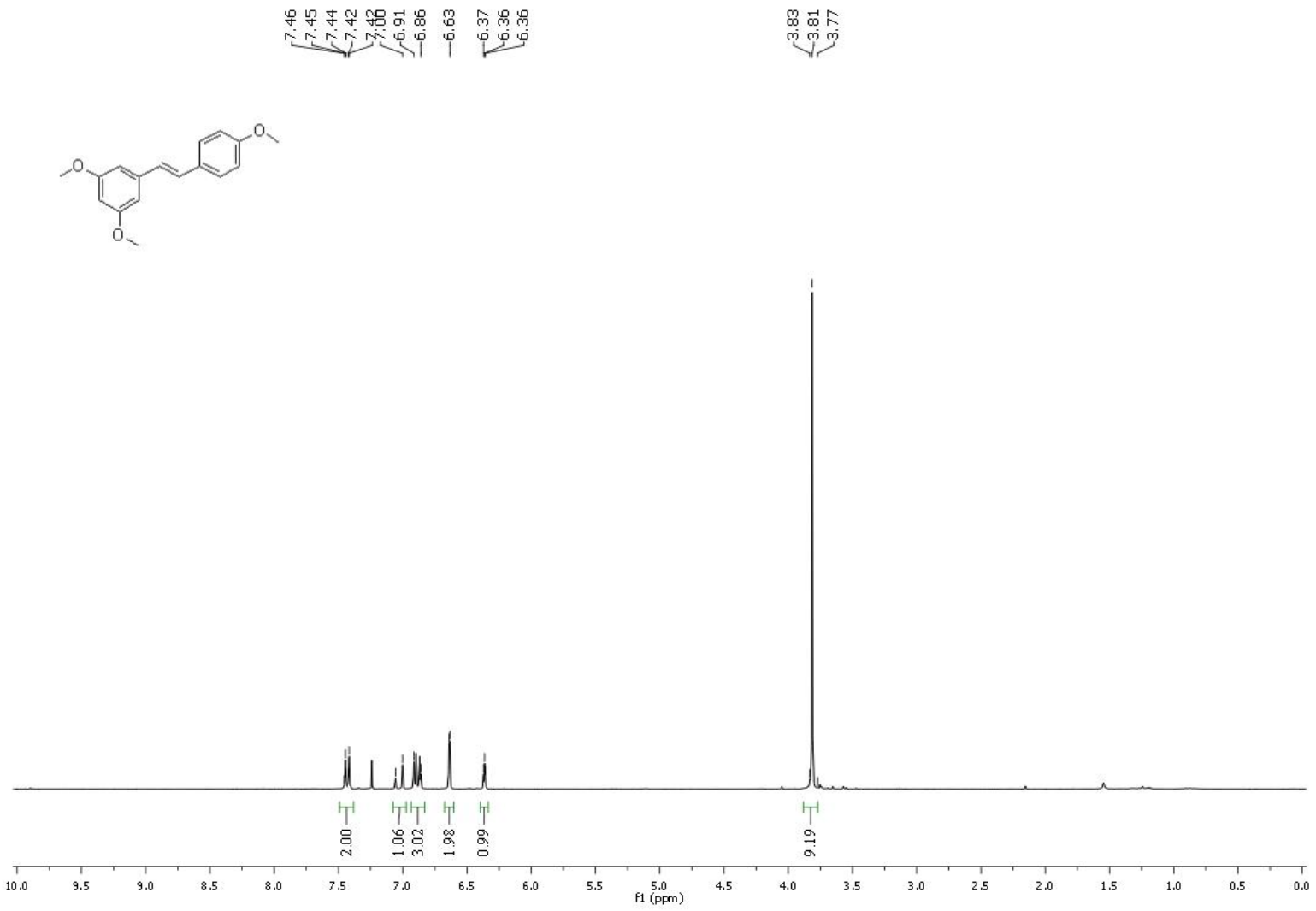
^{1}H NMR (300 MHz, $CDCl_3$) of **6ib**



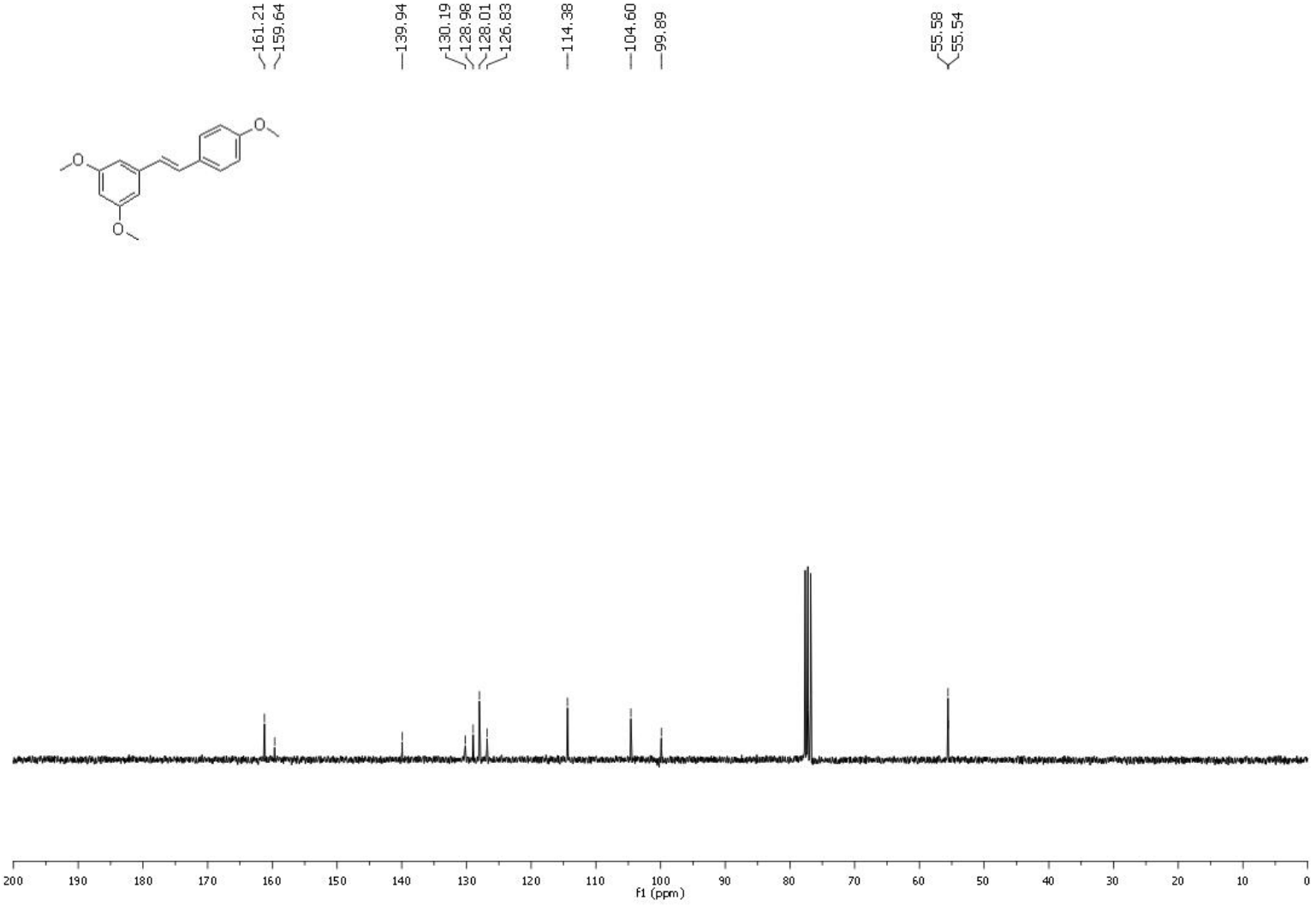
^{13}C NMR (75 MHz, $CDCl_3$) of **6ib**



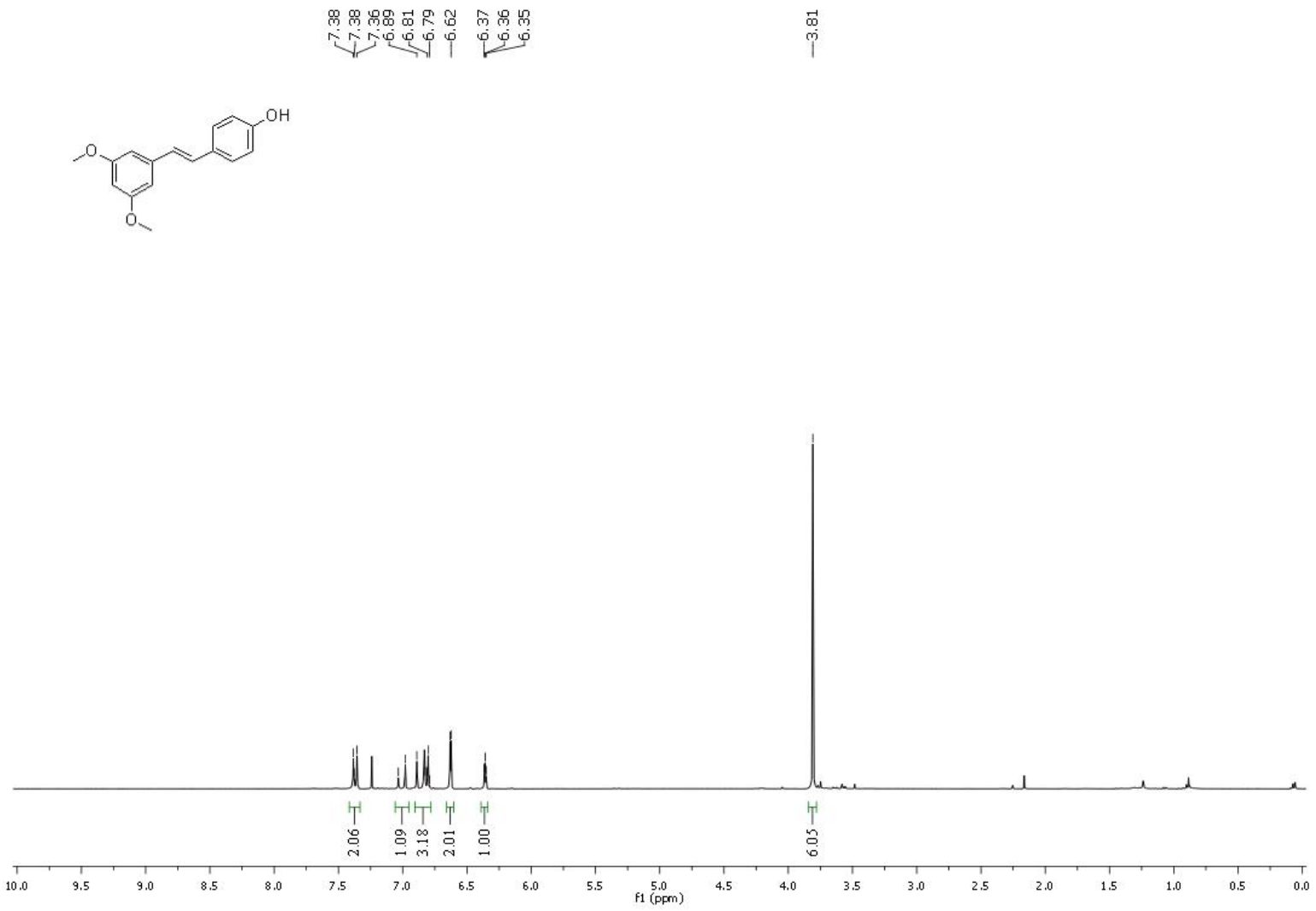
^{1}H NMR (300 MHz, $CDCl_3$) of **6ja**



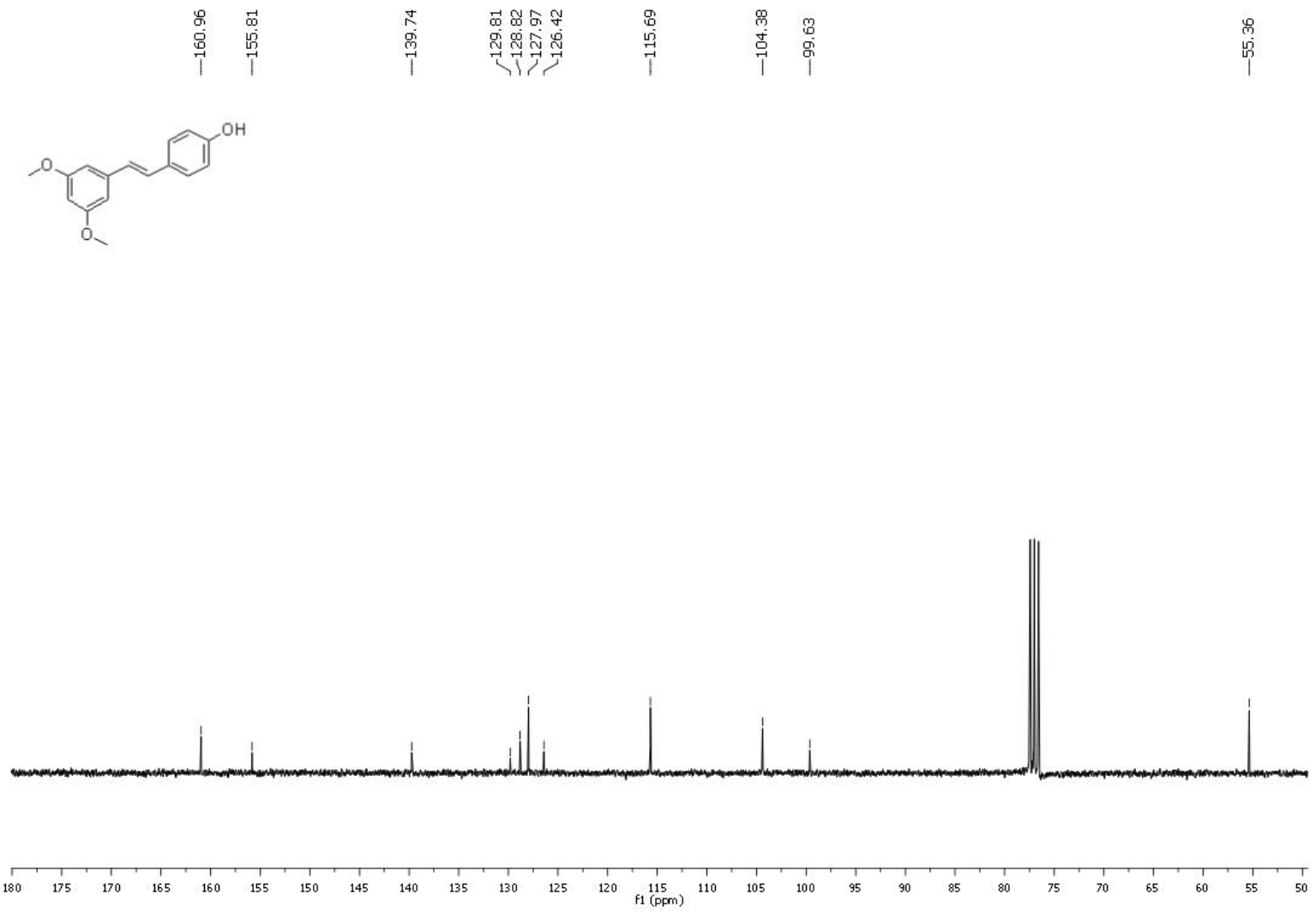
^{13}C NMR (75 MHz, $CDCl_3$) of **6ja**



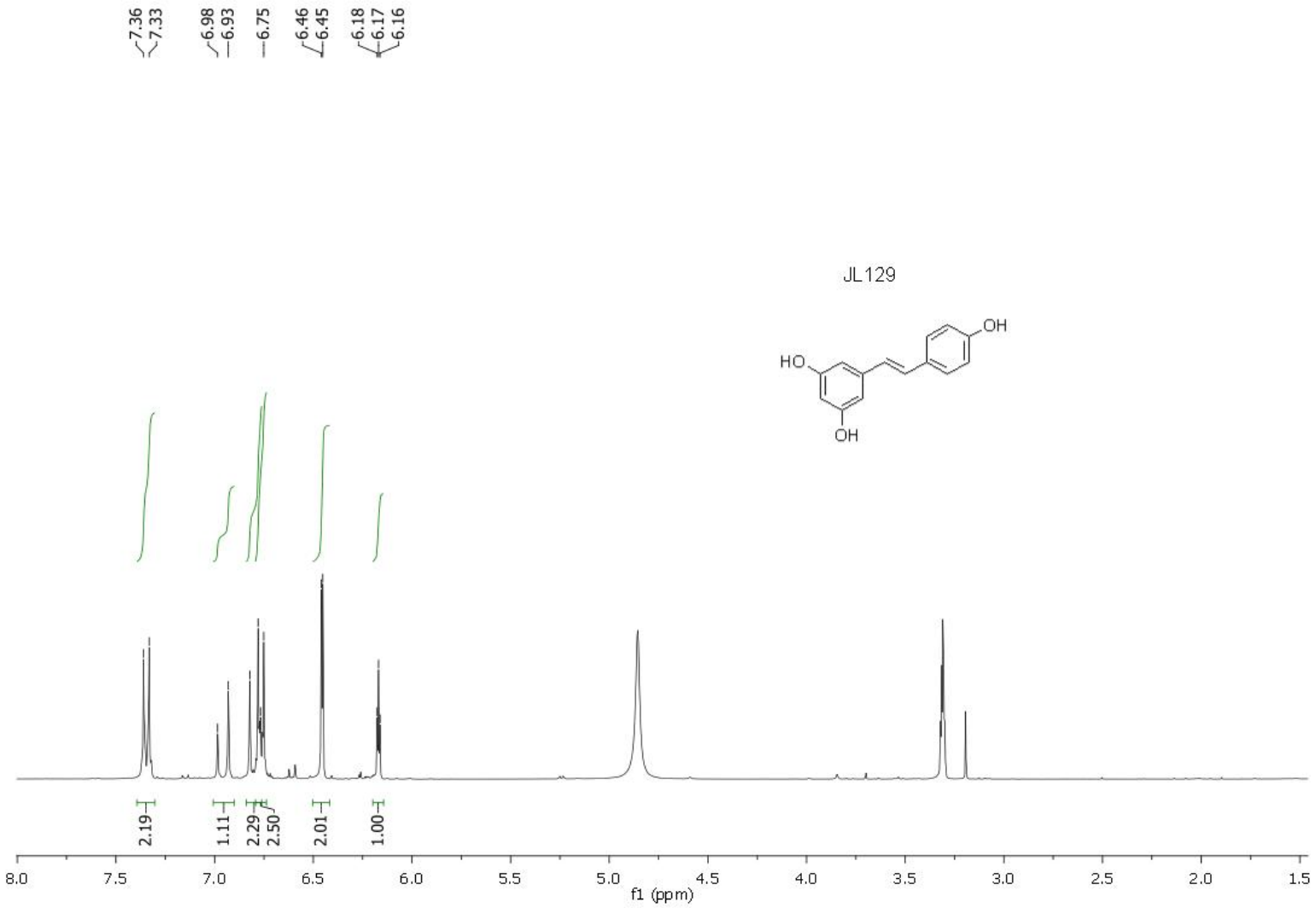
^{1}H NMR (300 MHz, $CDCl_3$) of **6jb**



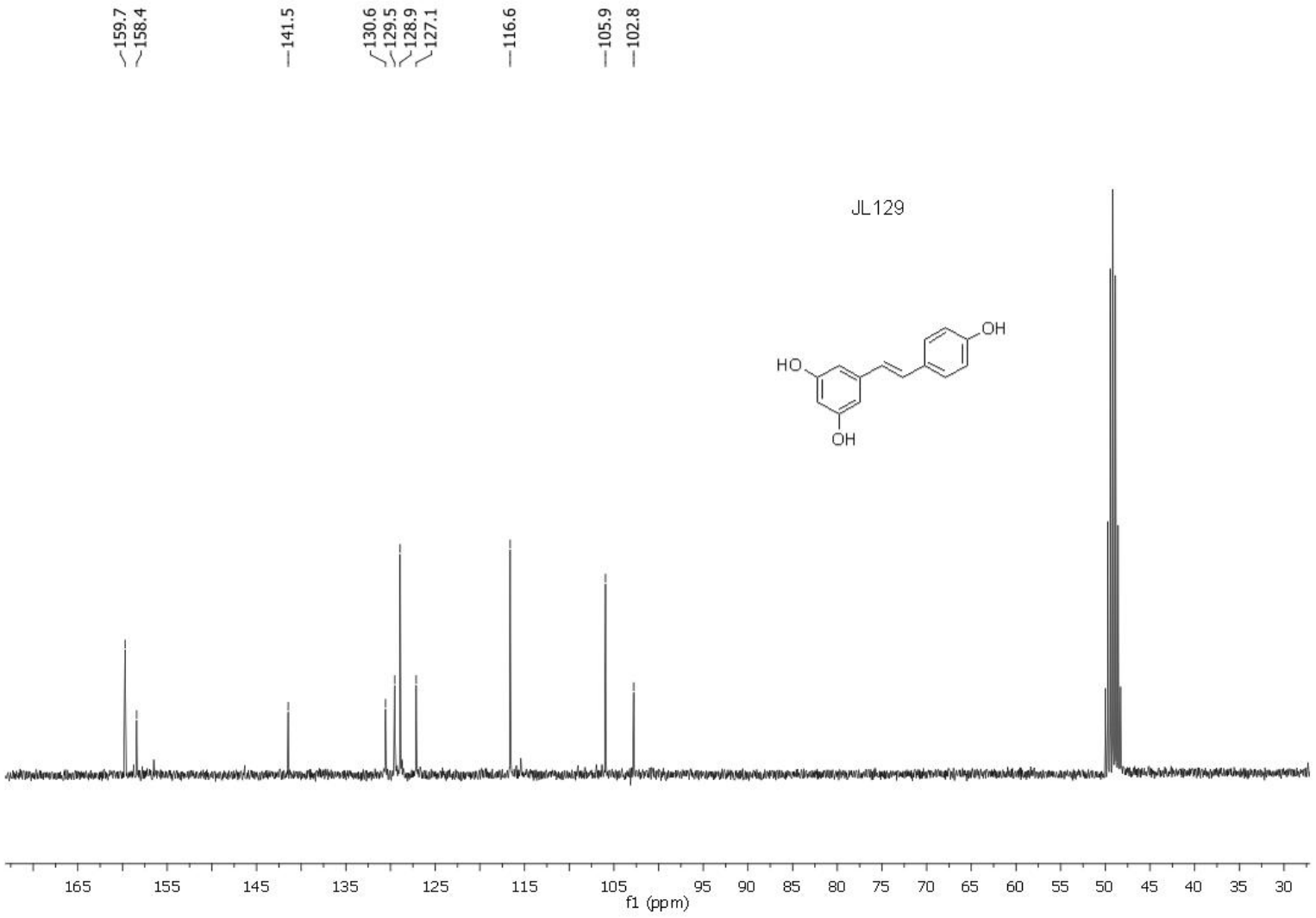
^{13}C NMR (75 MHz, $CDCl_3$) of **6jb**



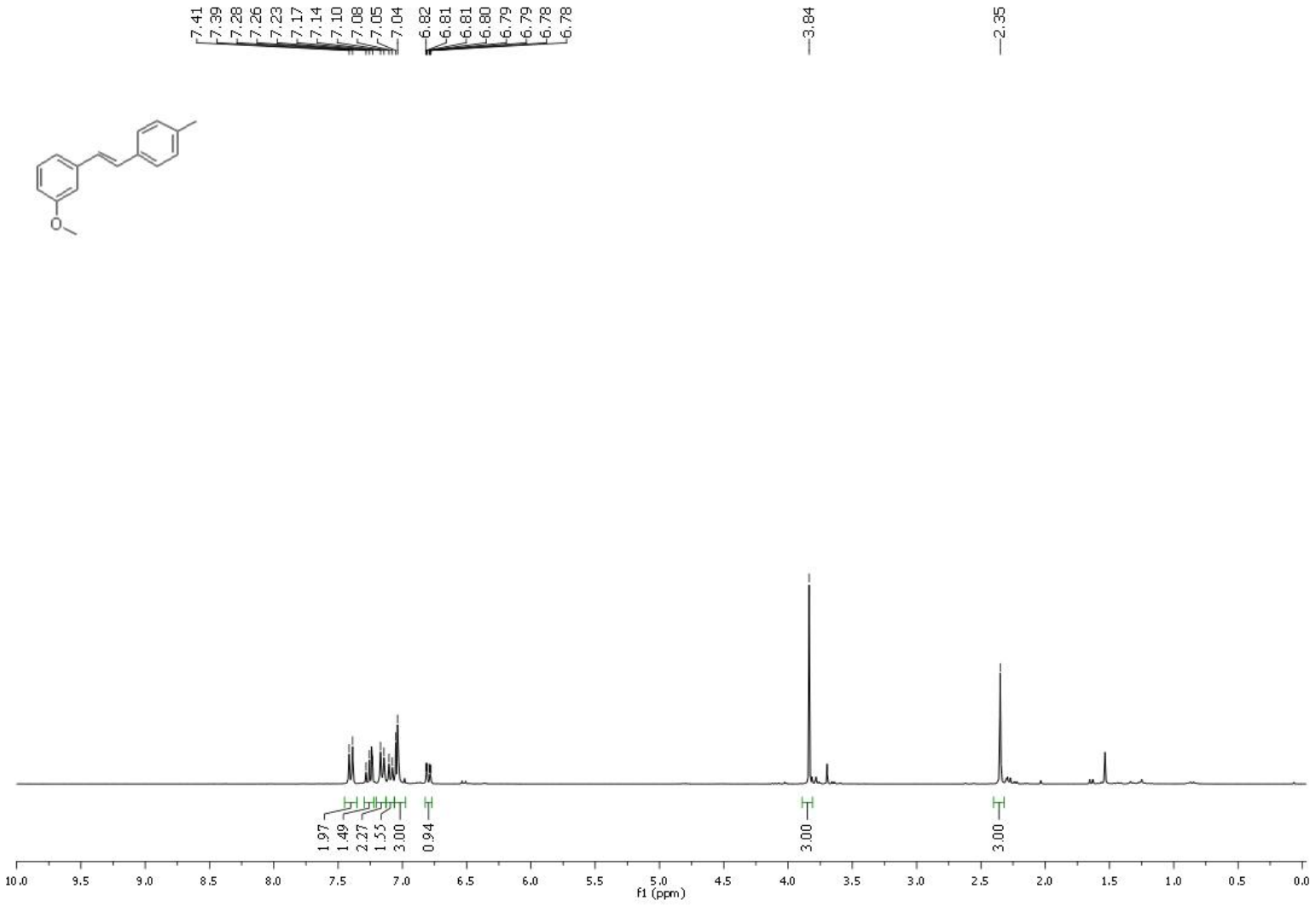
^{1}H NMR (300 MHz, methanol-d_4) of **1**



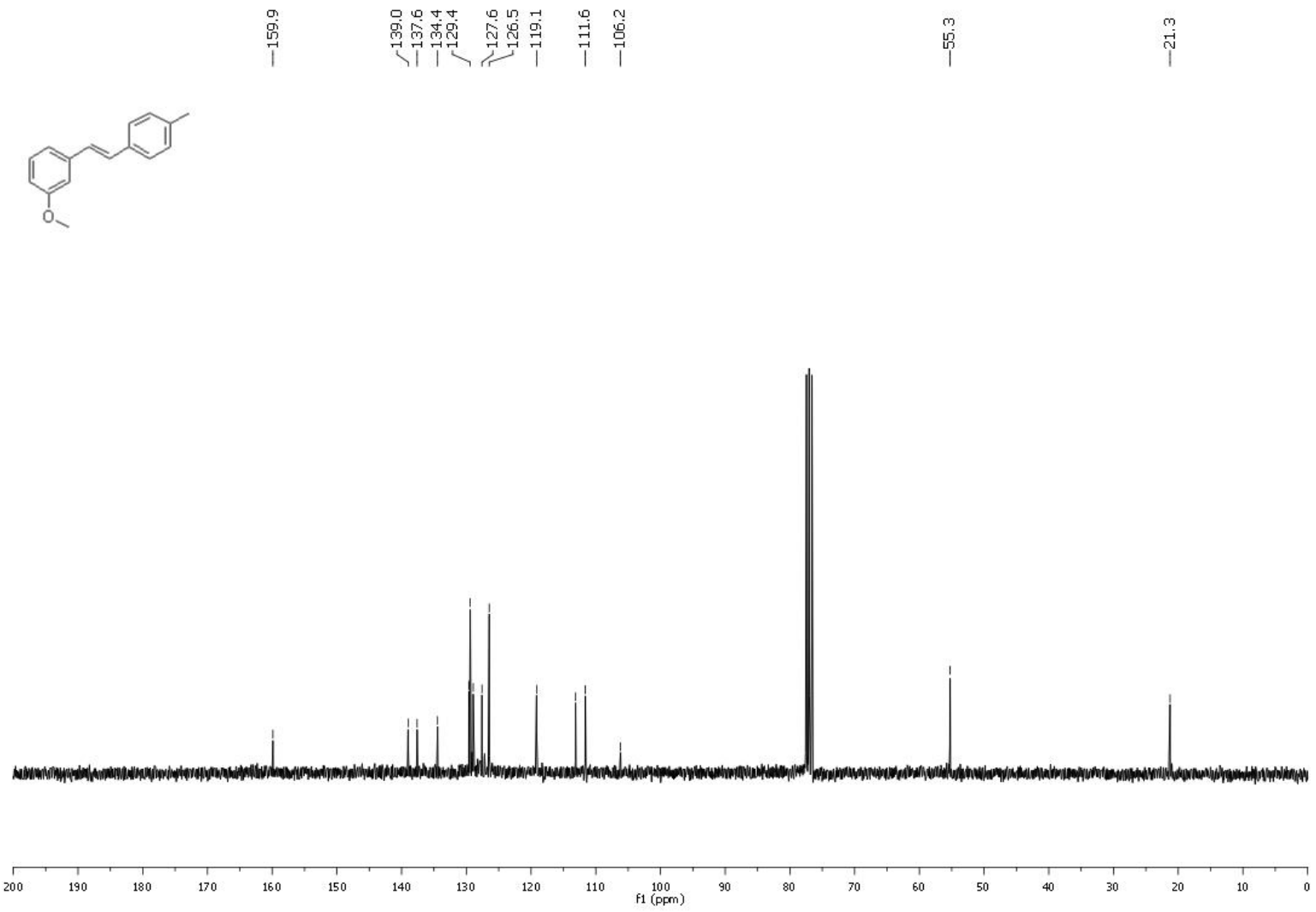
^{13}C NMR (75 MHz, methanol-d_4) of **1**



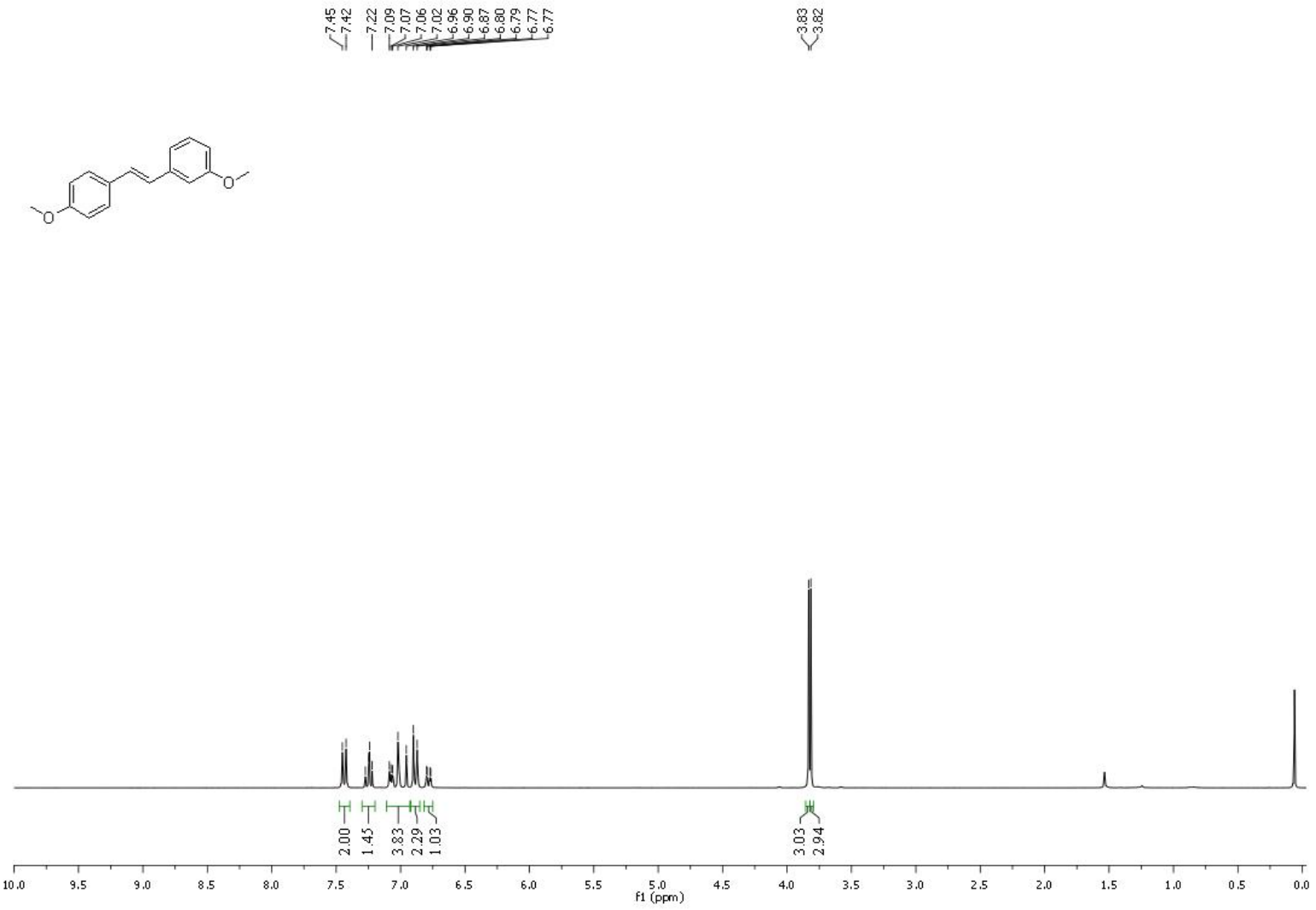
^{1}H NMR (300 MHz, $CDCl_3$) of **6ac**



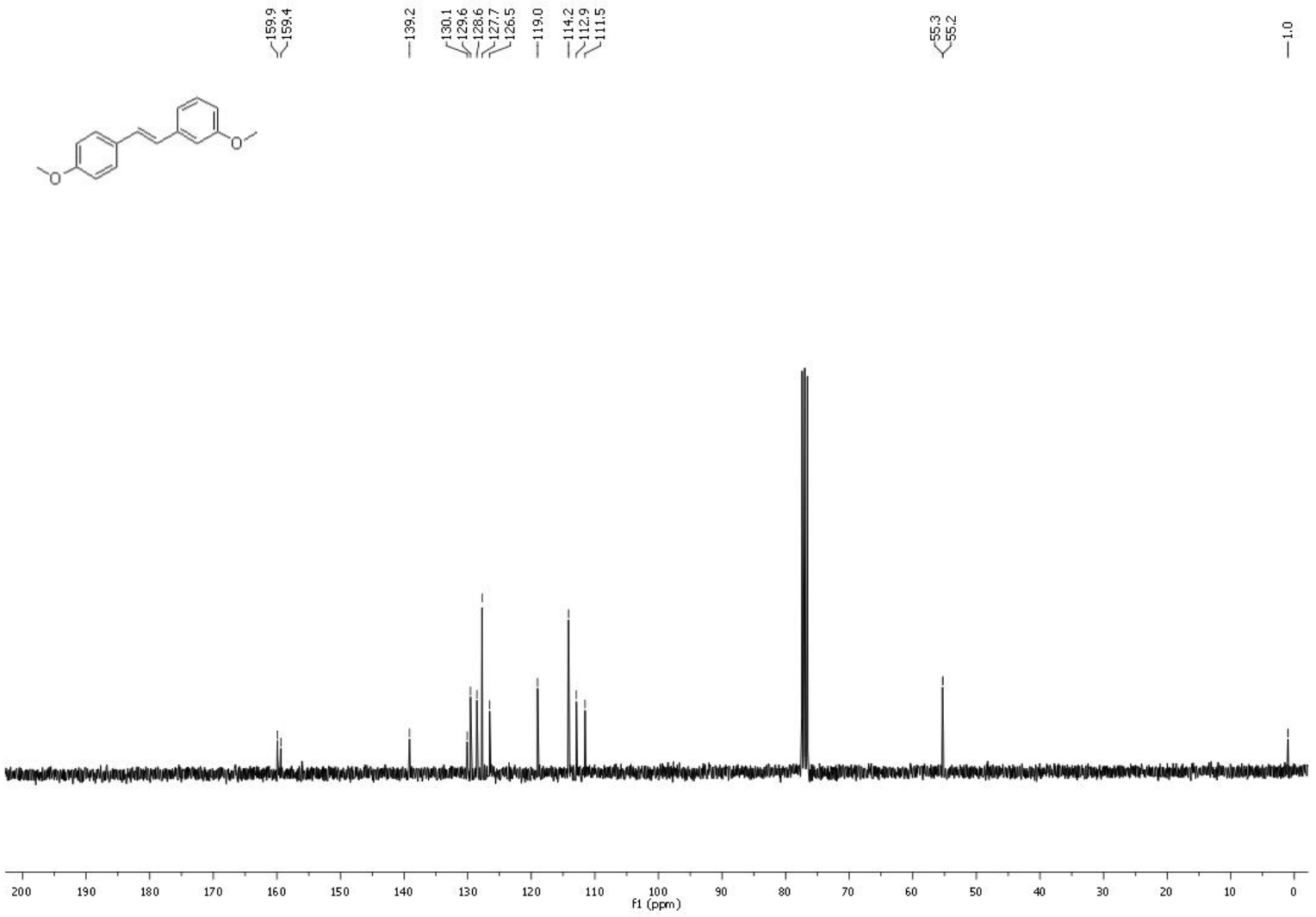
^{13}C NMR (75 MHz, $CDCl_3$) of **6ac**



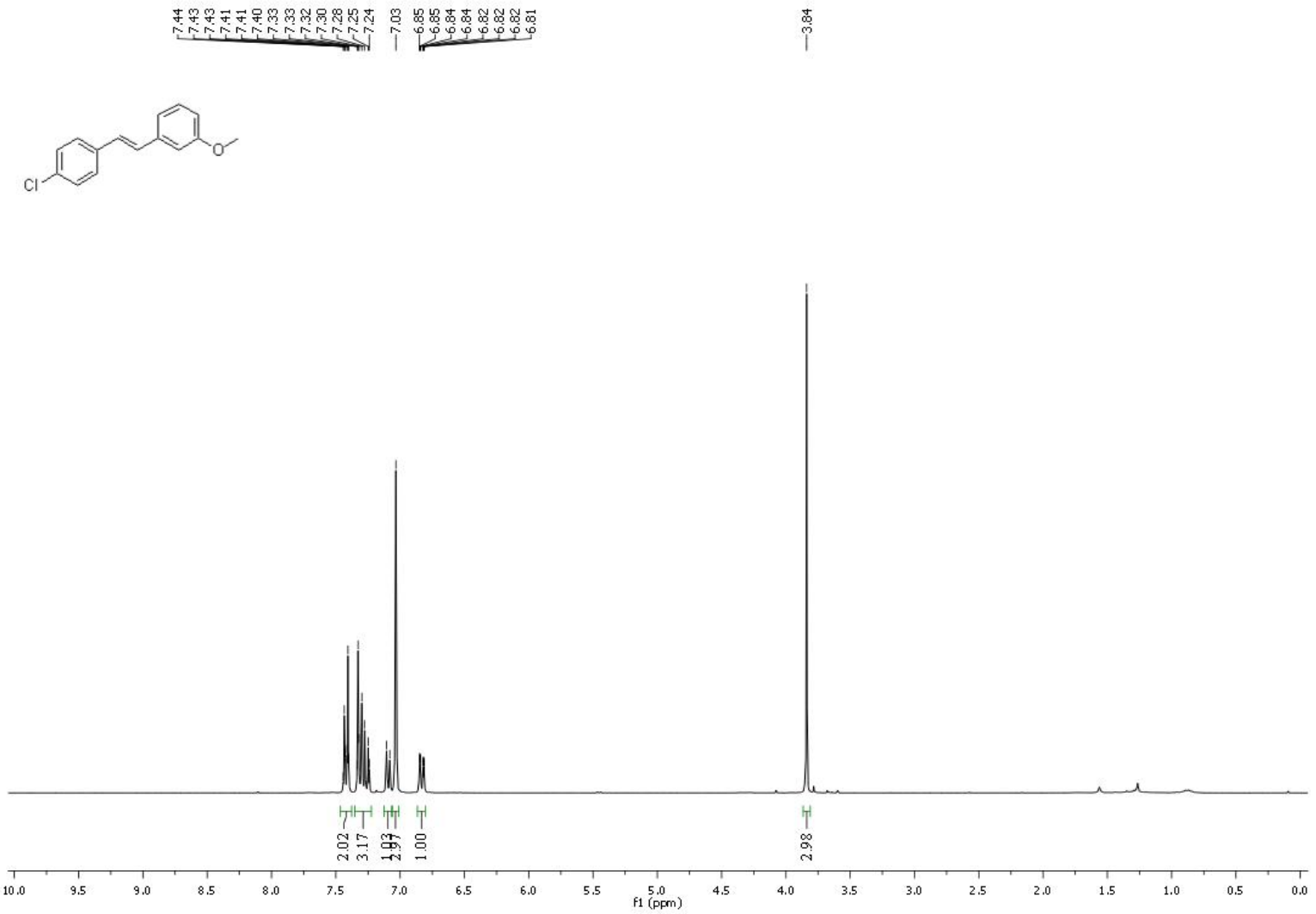
^{1}H NMR (300 MHz, $CDCl_3$) of **6cc**



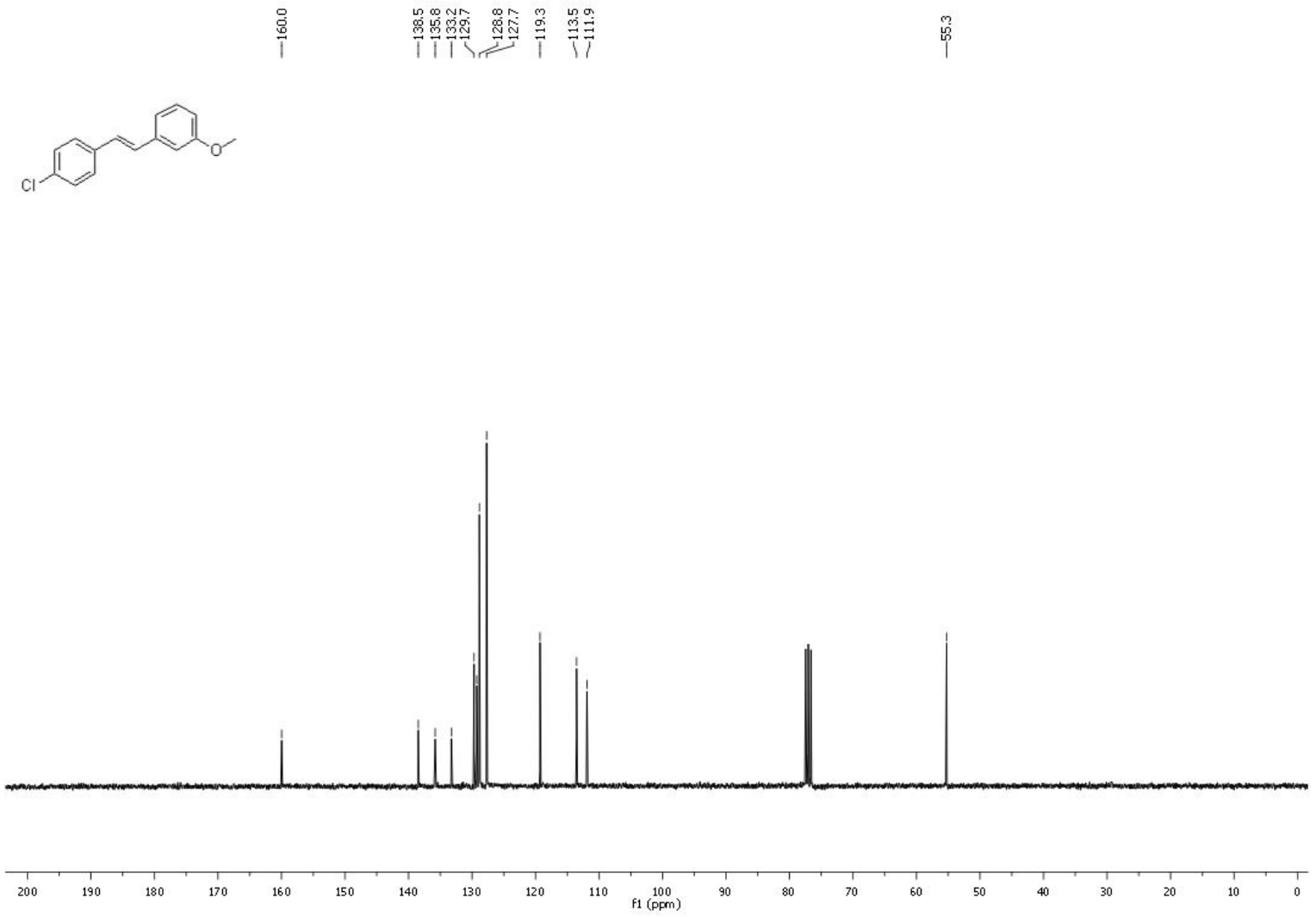
^{13}C NMR (75 MHz, $CDCl_3$) of **6cc**



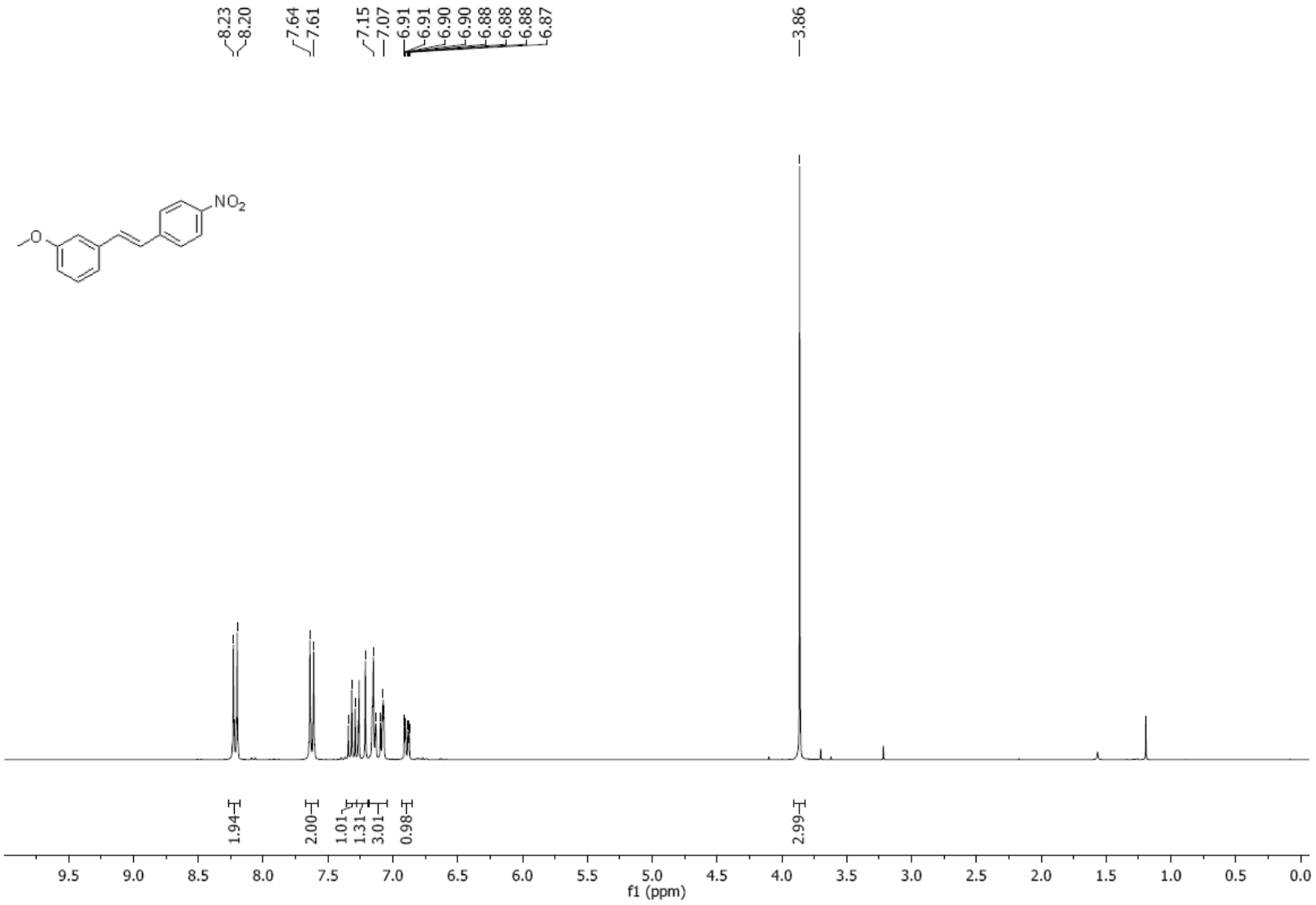
^{1}H NMR (300 MHz, $CDCl_3$) of **6dc**



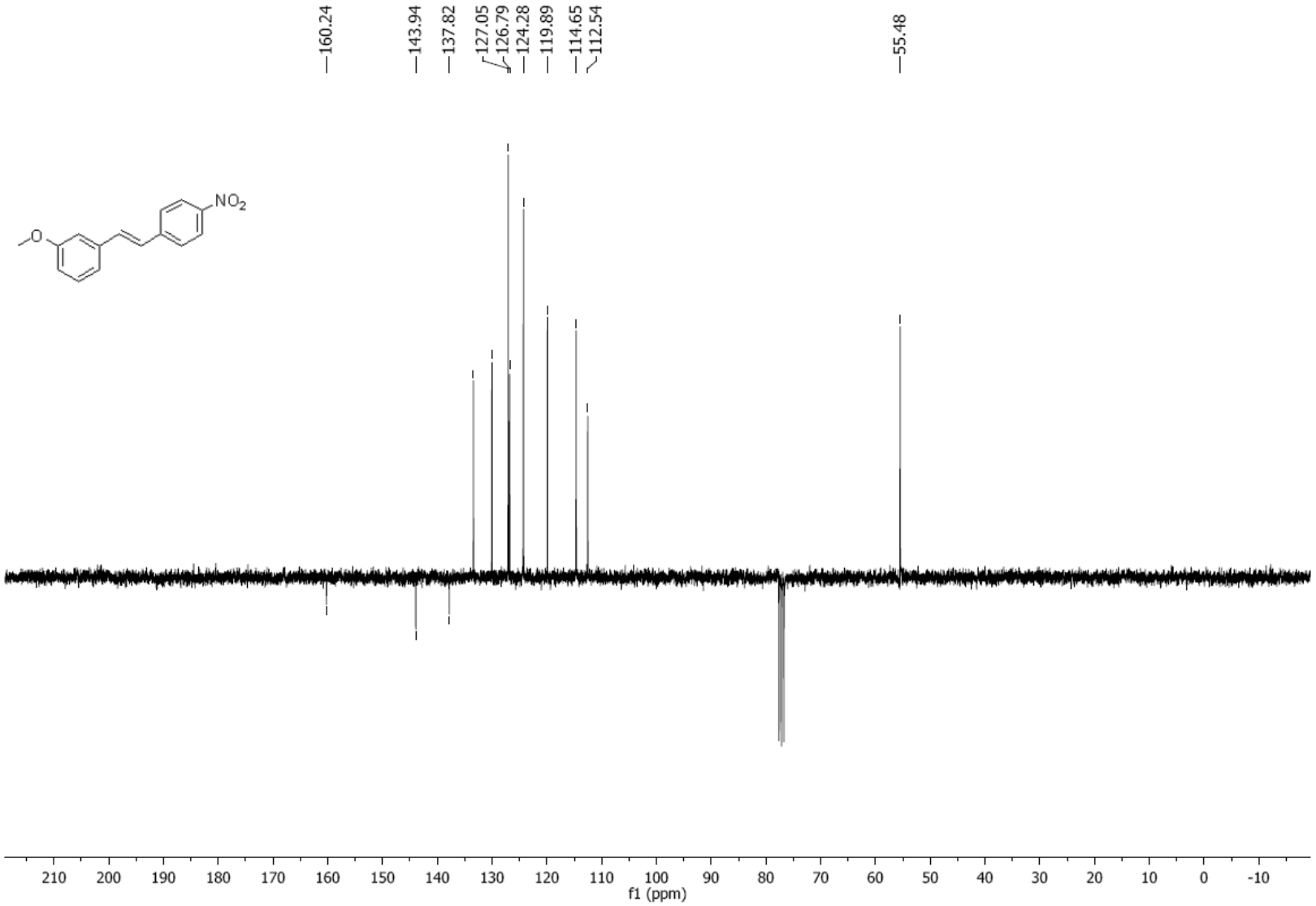
^{13}C NMR (75 MHz, $CDCl_3$) of **6dc**



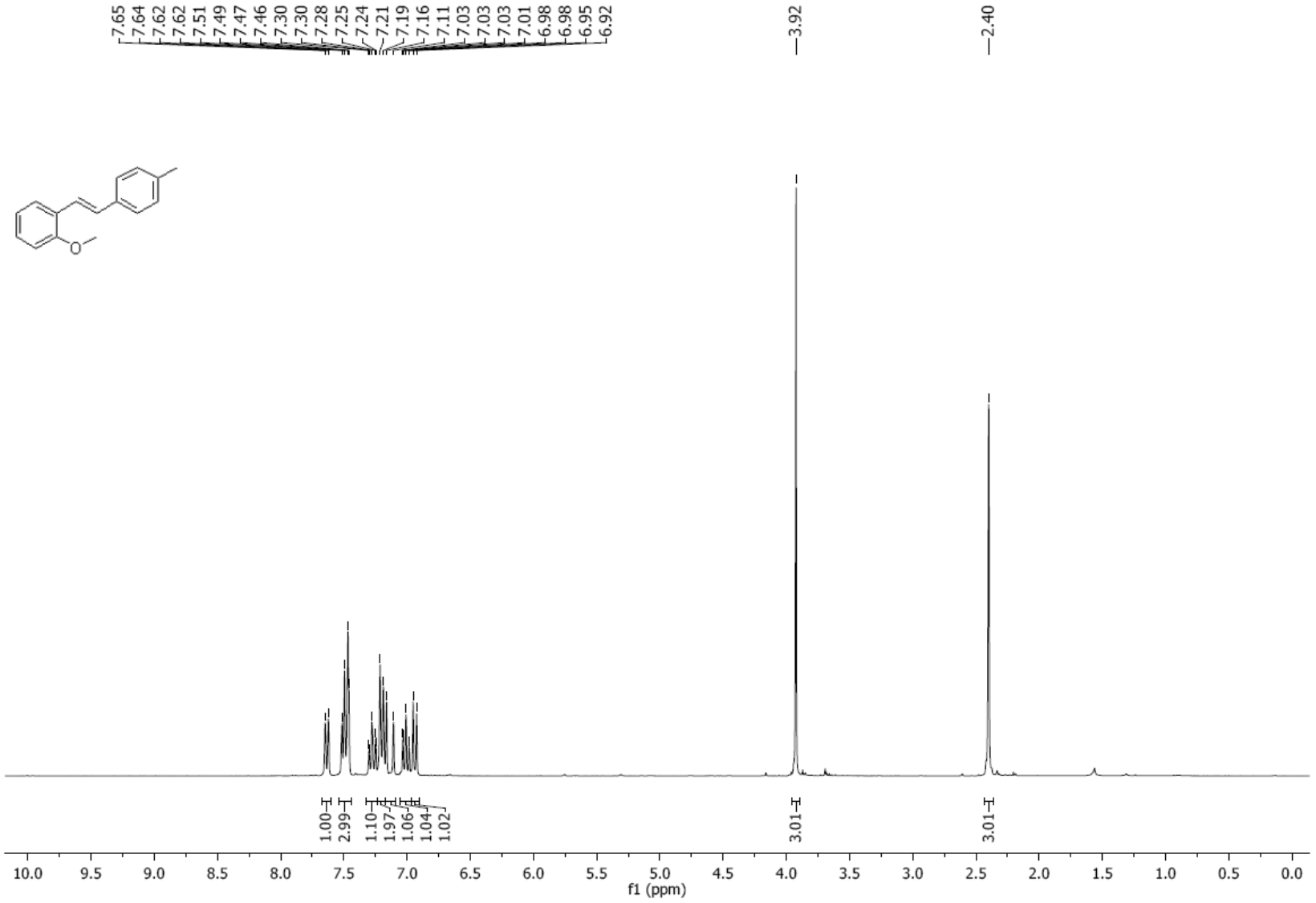
^{1}H NMR (300 MHz, $CDCl_3$) of **6gc**



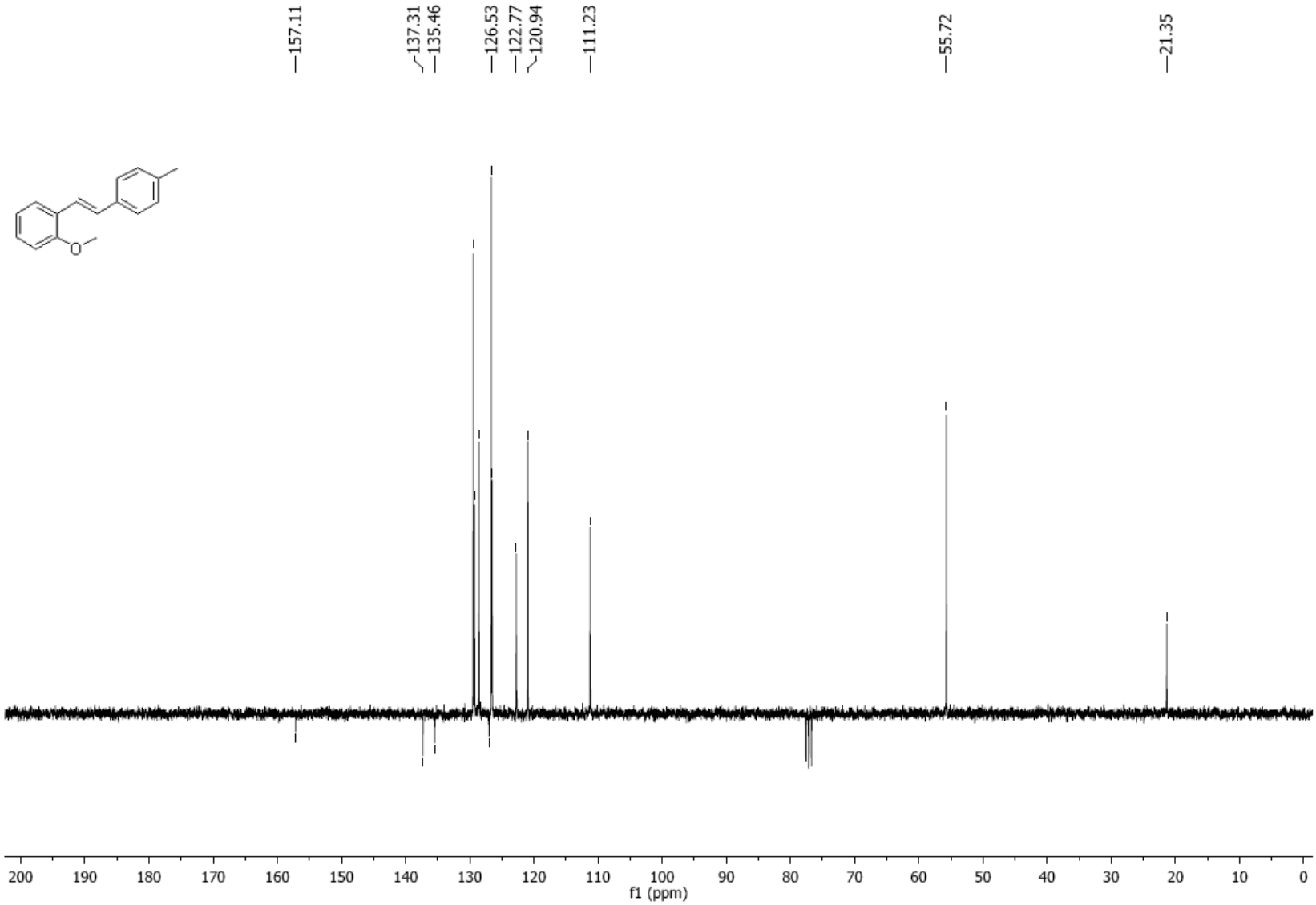
^{13}C NMR (75 MHz, $CDCl_3$) of **6gc**



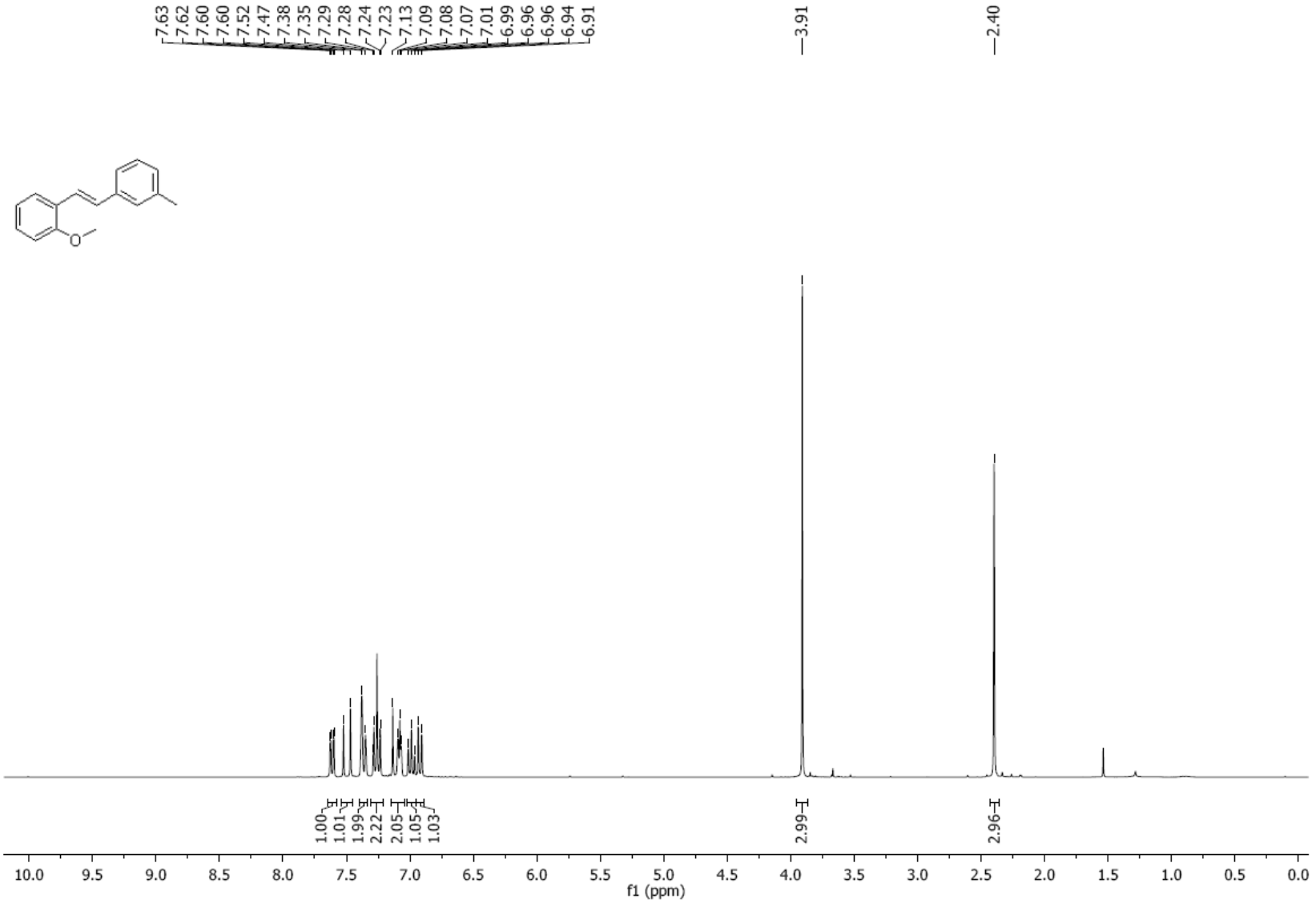
^{1}H NMR (300 MHz, $CDCl_3$) of **6ae**



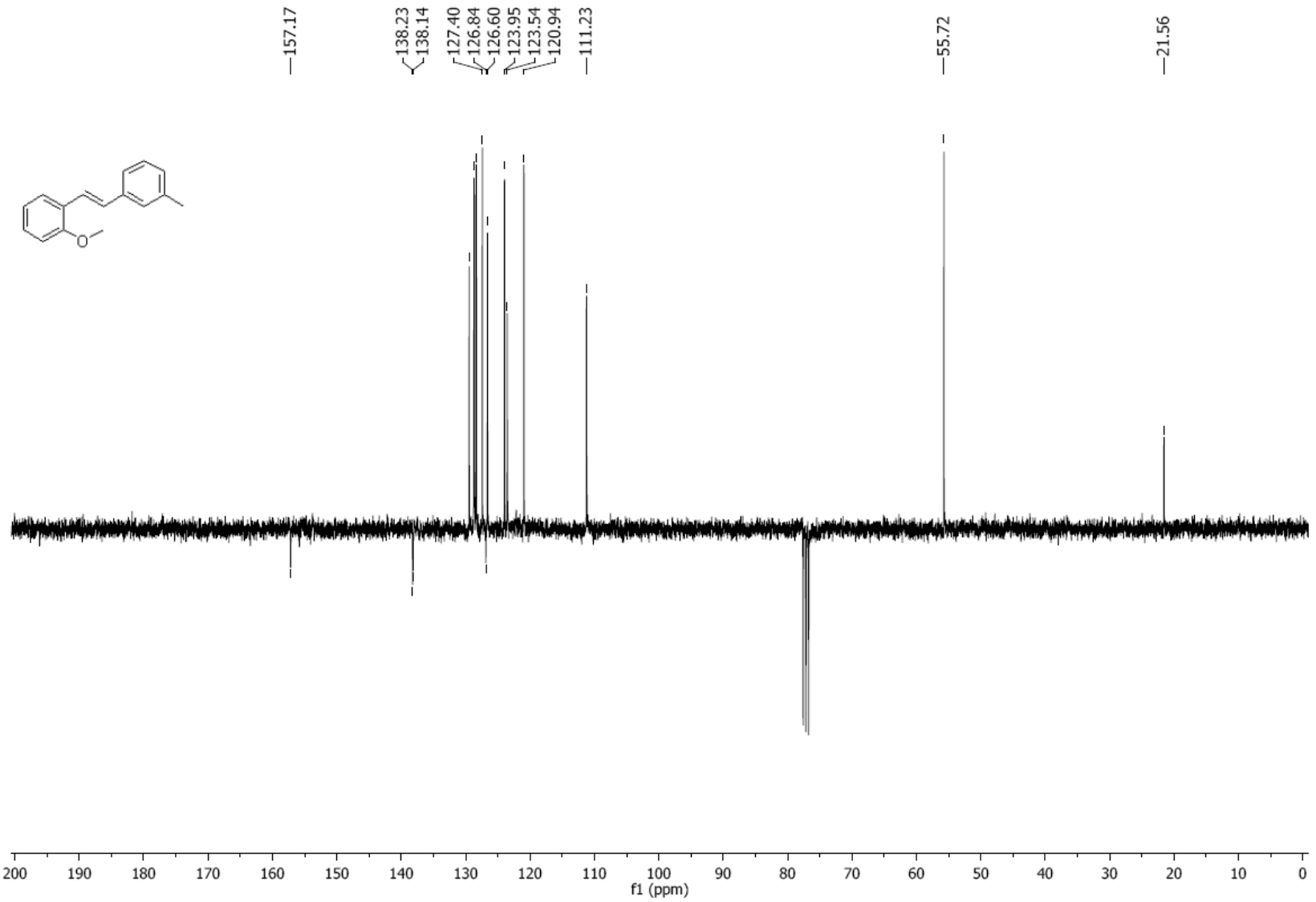
^{13}C NMR (75 MHz, $CDCl_3$) of **6ae**



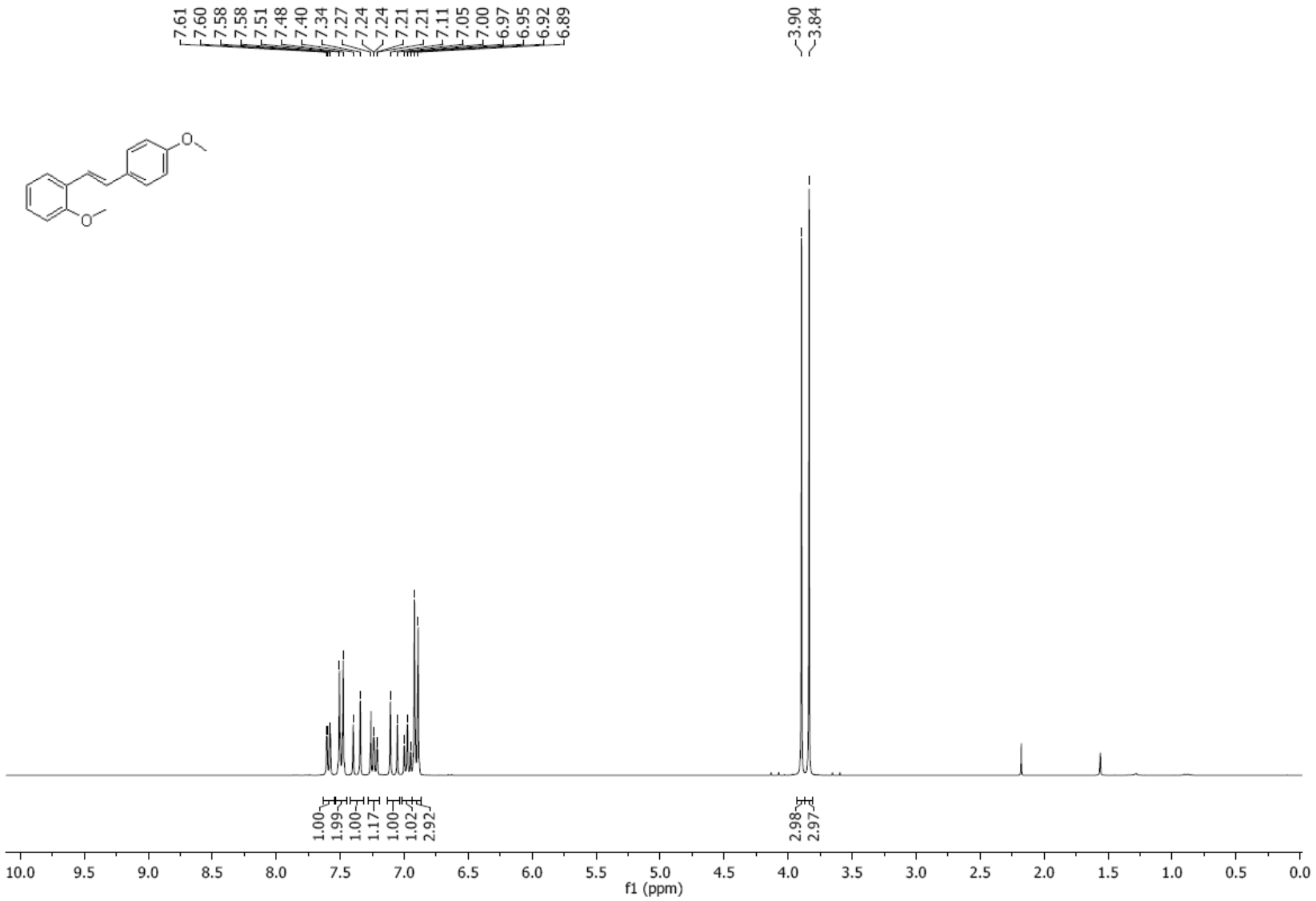
^{1}H NMR (300 MHz, $CDCl_3$) of **6be**



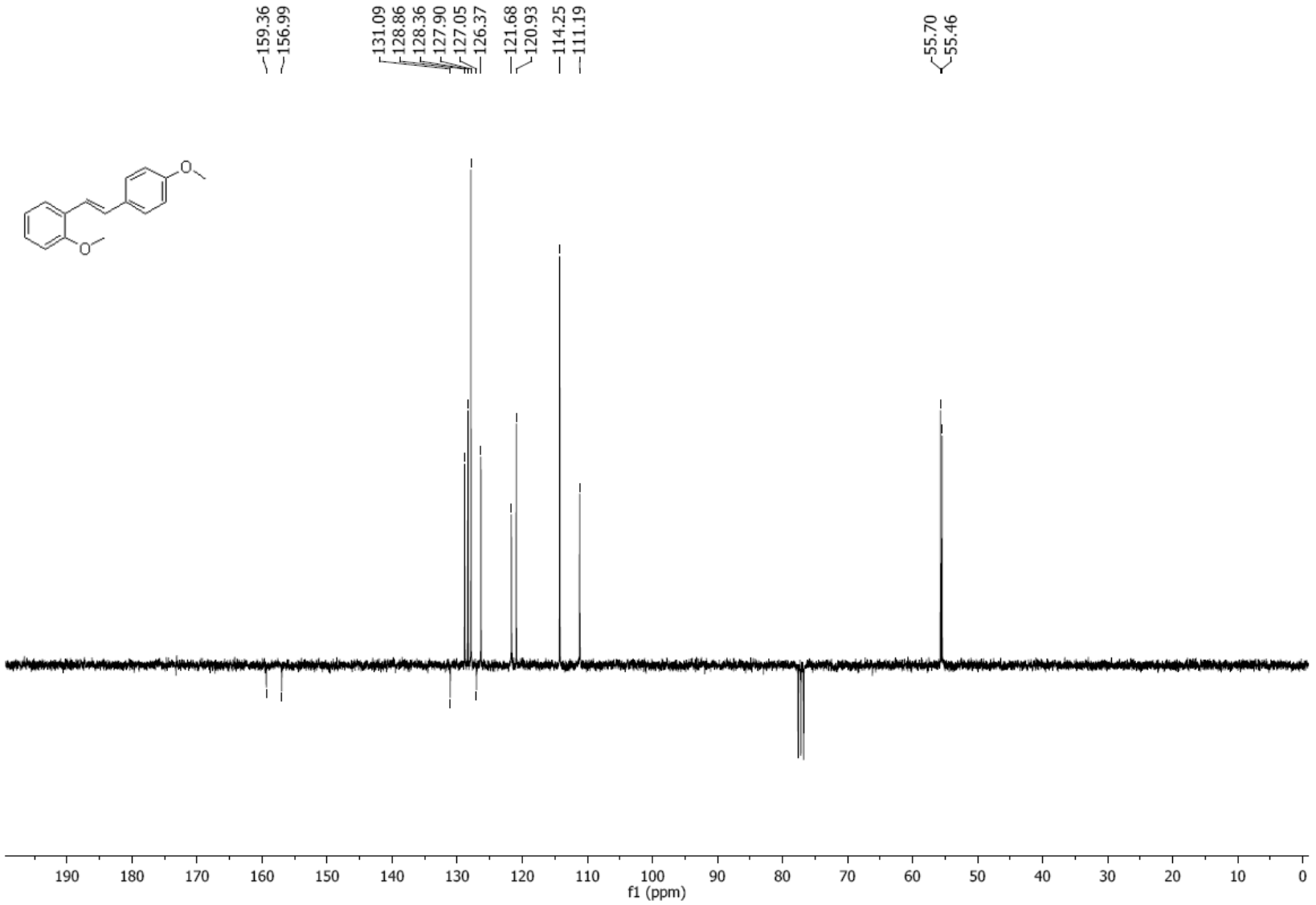
^{13}C NMR (75 MHz, $CDCl_3$) of **6be**



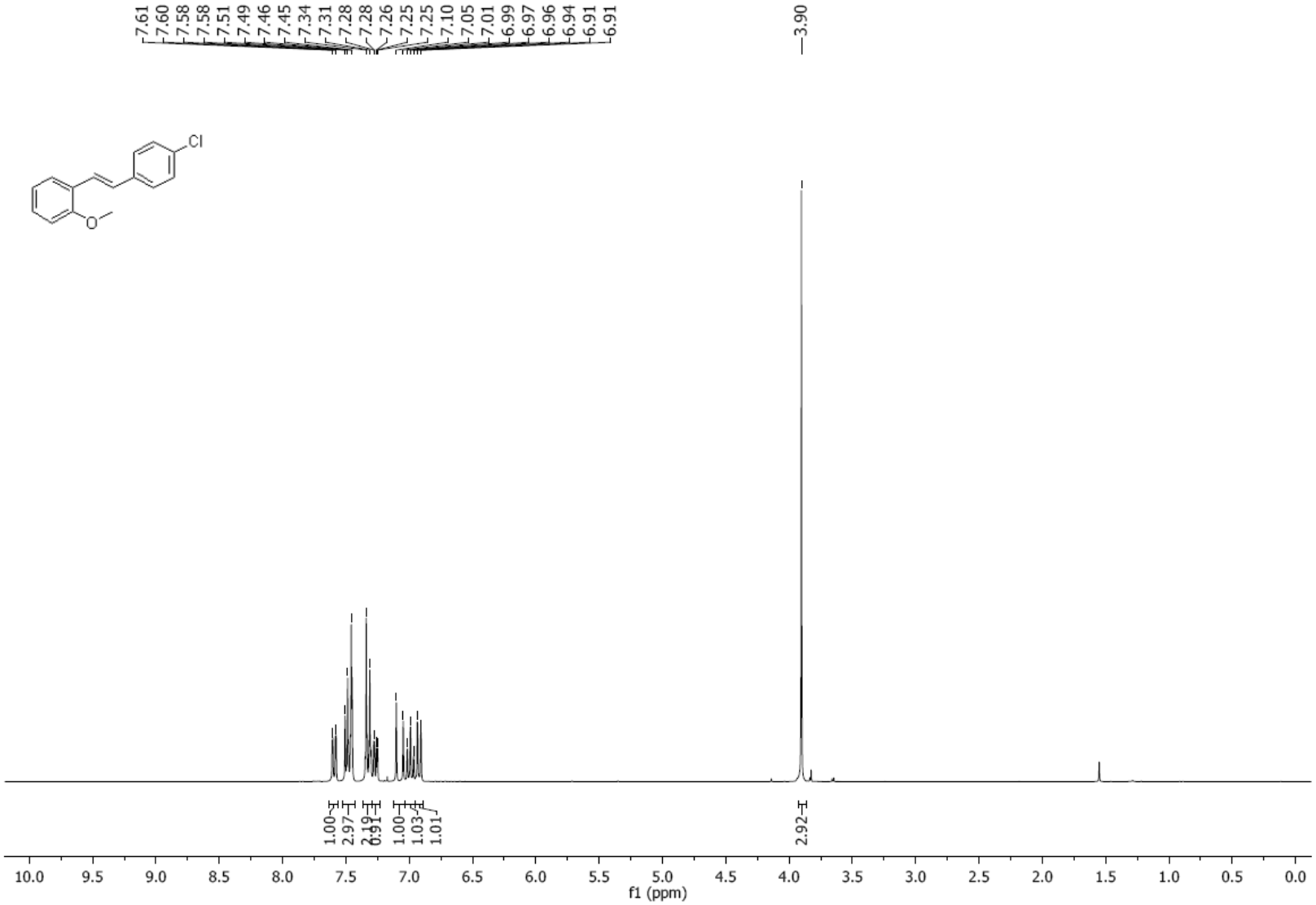
^{1}H NMR (300 MHz, $CDCl_3$) of **6ce**



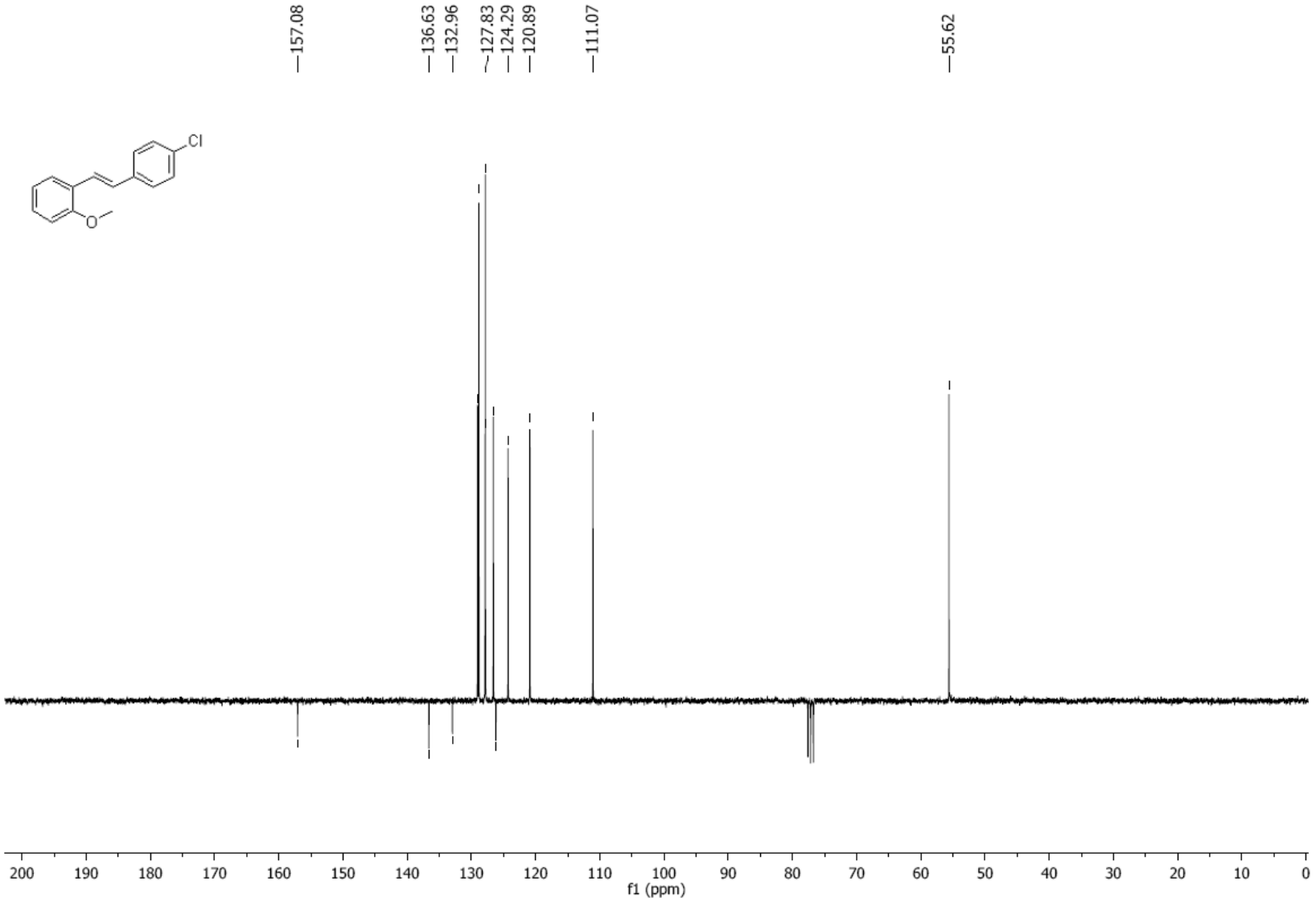
^{13}C NMR (75 MHz, $CDCl_3$) of **6ce**



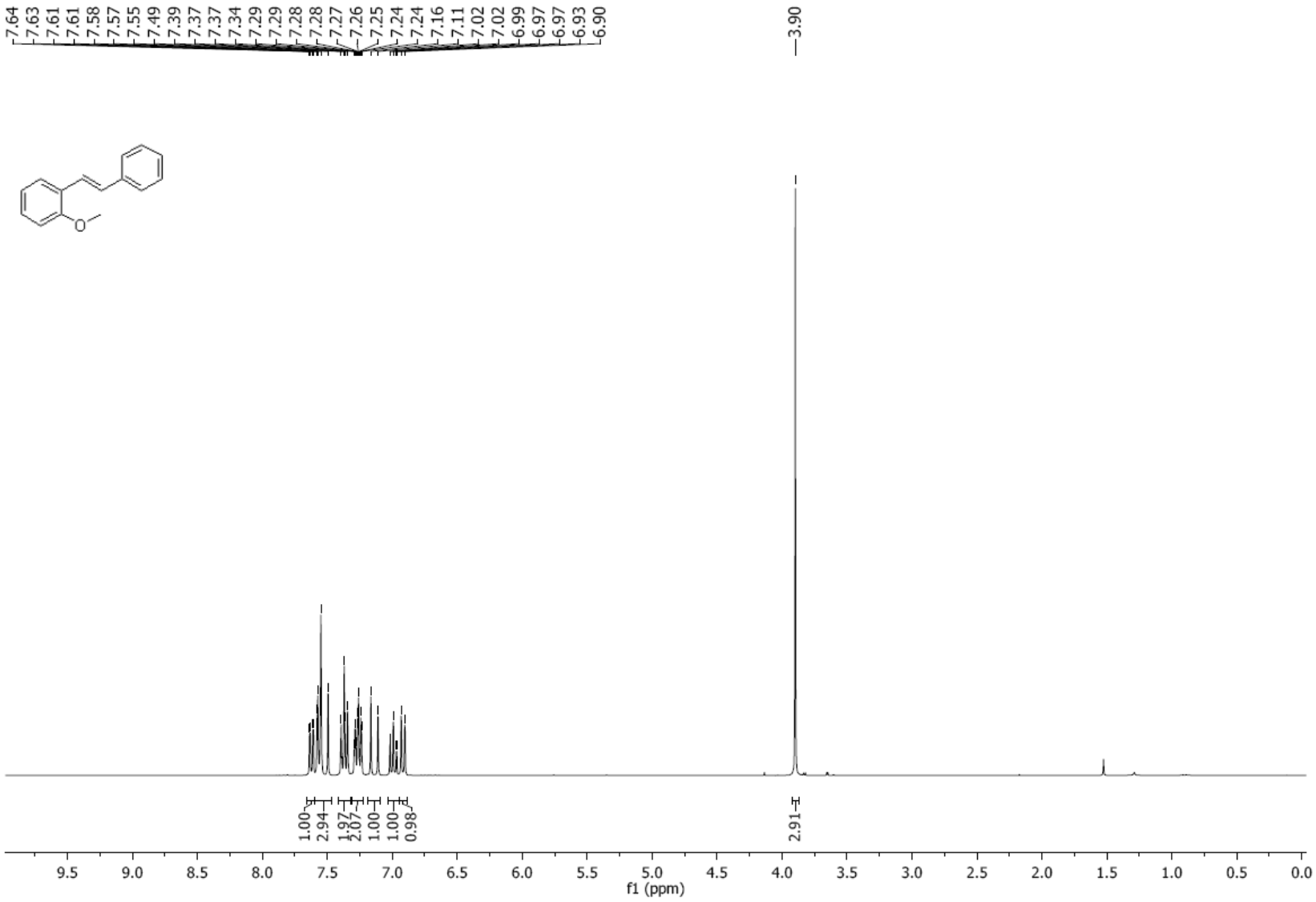
^{1}H NMR (300 MHz, $CDCl_3$) of **6de**



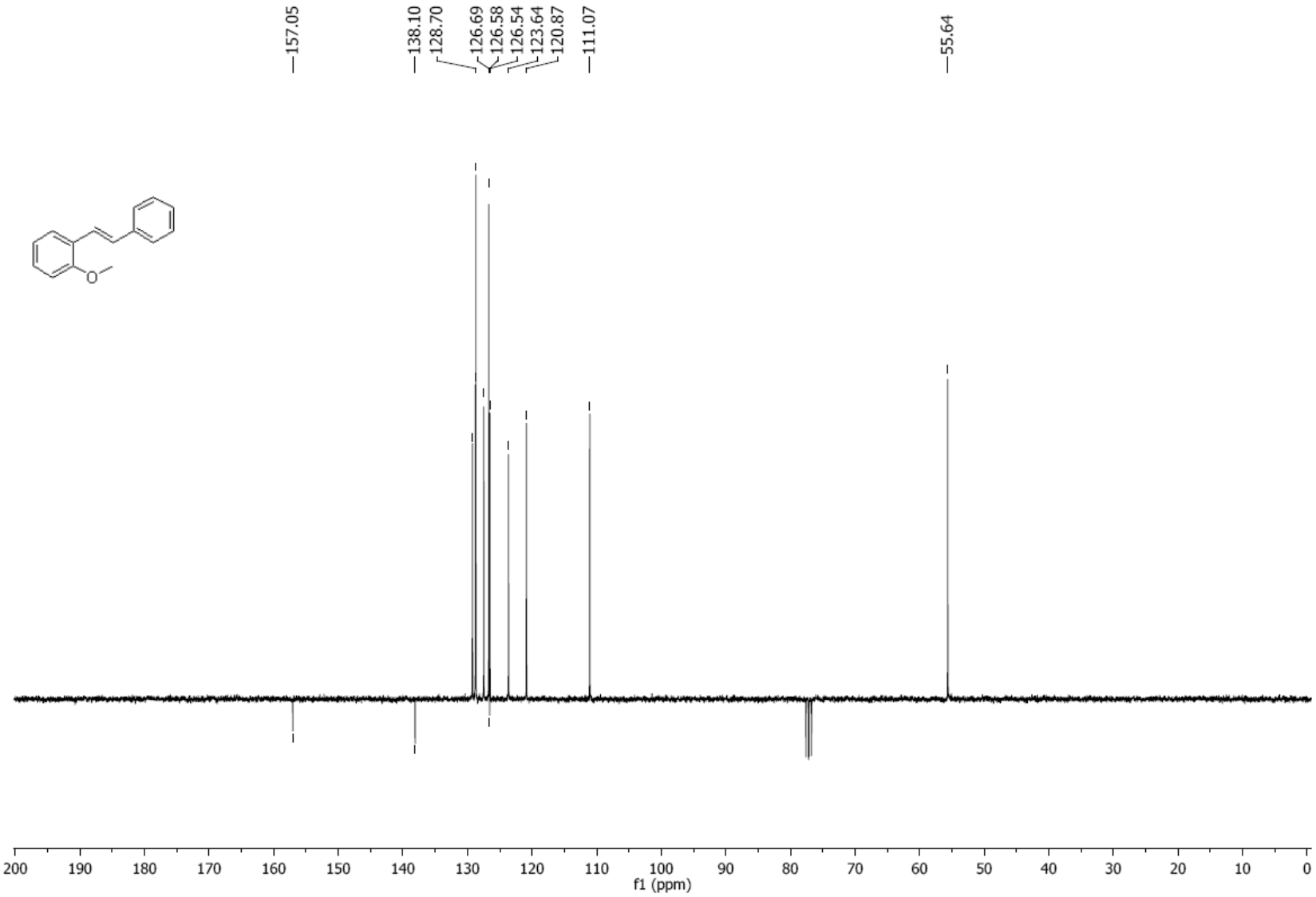
^{13}C NMR (75 MHz, $CDCl_3$) of **6de**



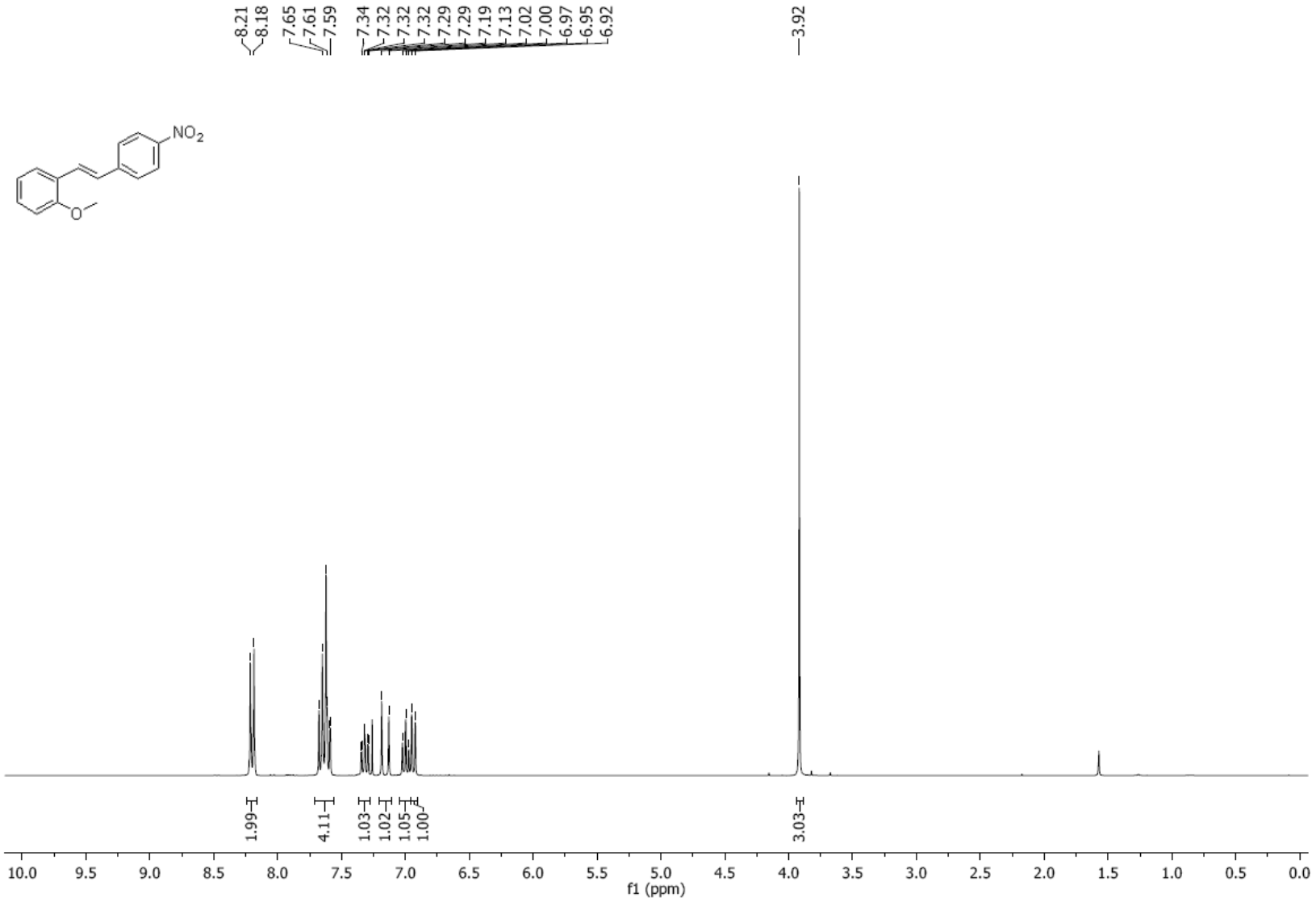
^{1}H NMR (300 MHz, $CDCl_3$) of **6fe**



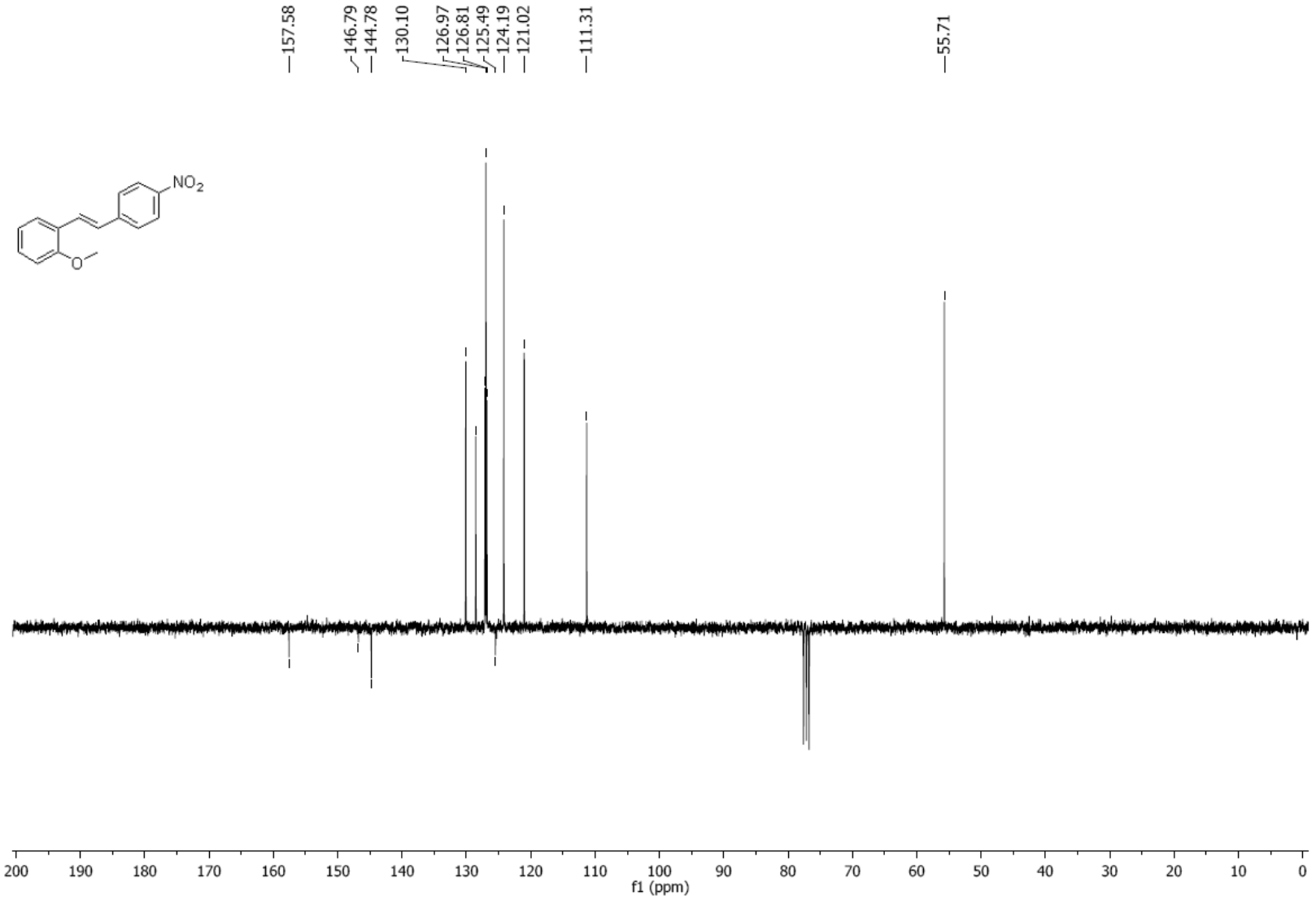
^{13}C NMR (75 MHz, $CDCl_3$) of **6fe**



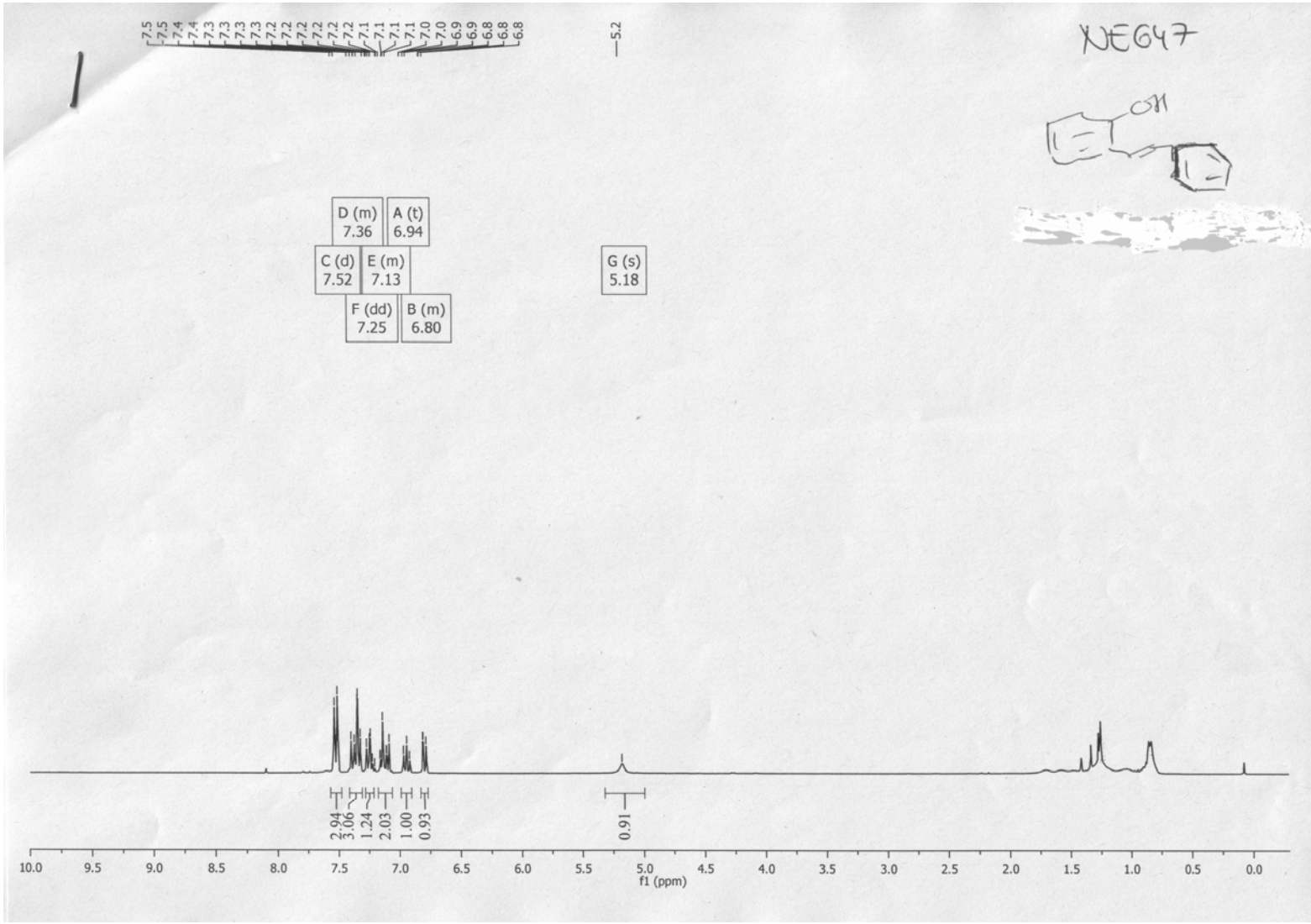
^{1}H NMR (300 MHz, $CDCl_3$) of **6ge**



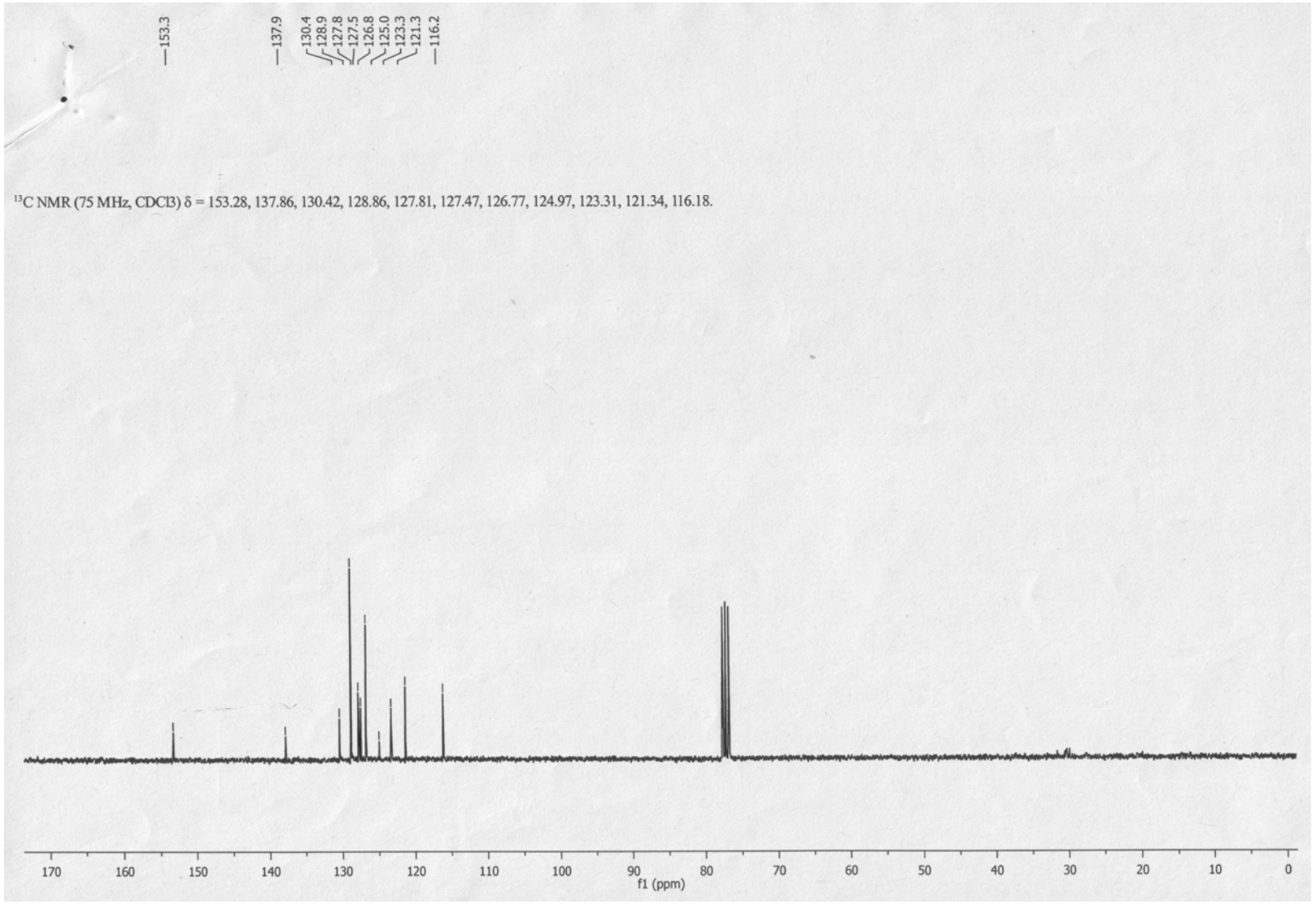
^{13}C NMR (75 MHz, $CDCl_3$) of **6ge**



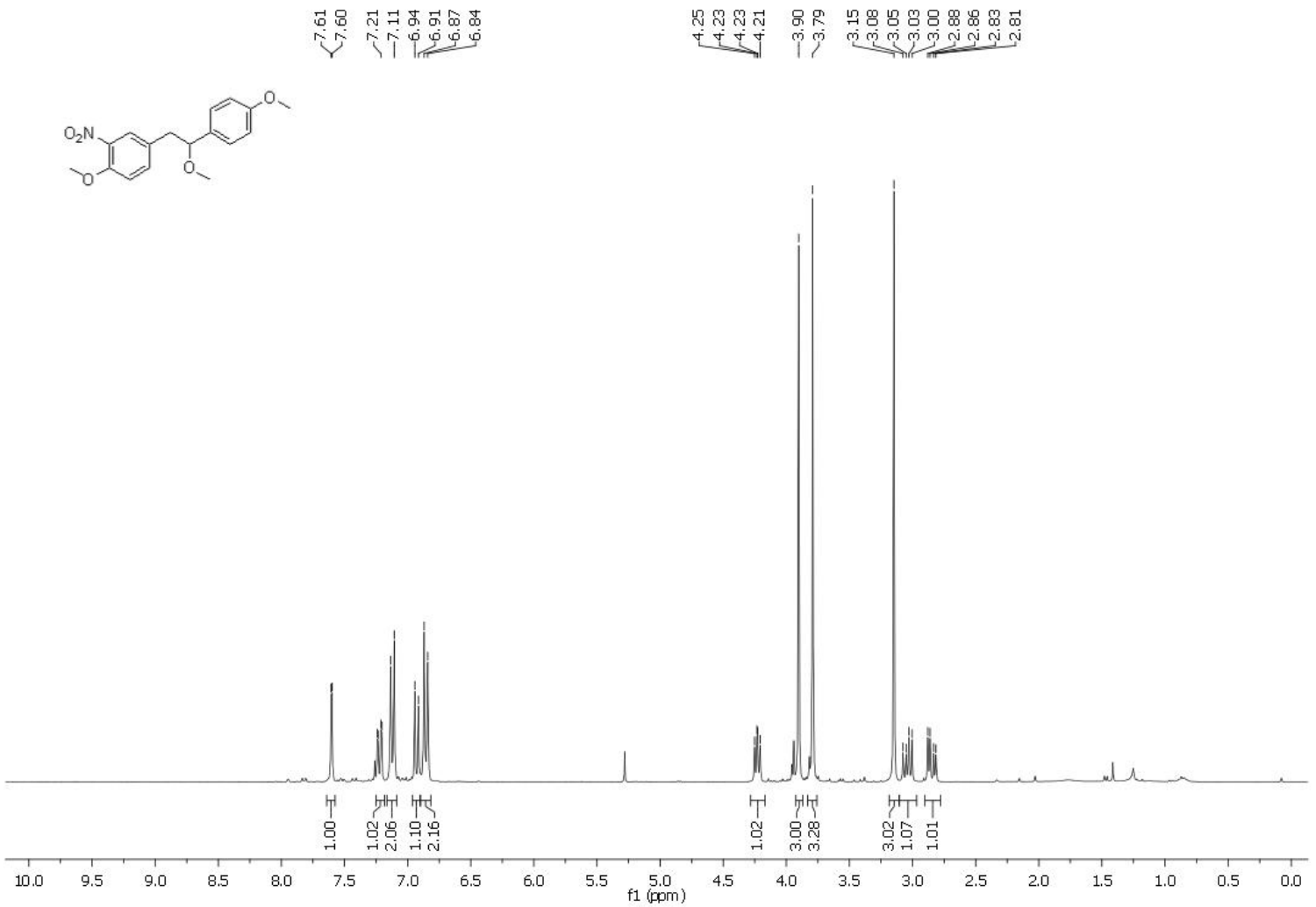
^{1}H NMR (300 MHz, $CDCl_3$) of **6ff**



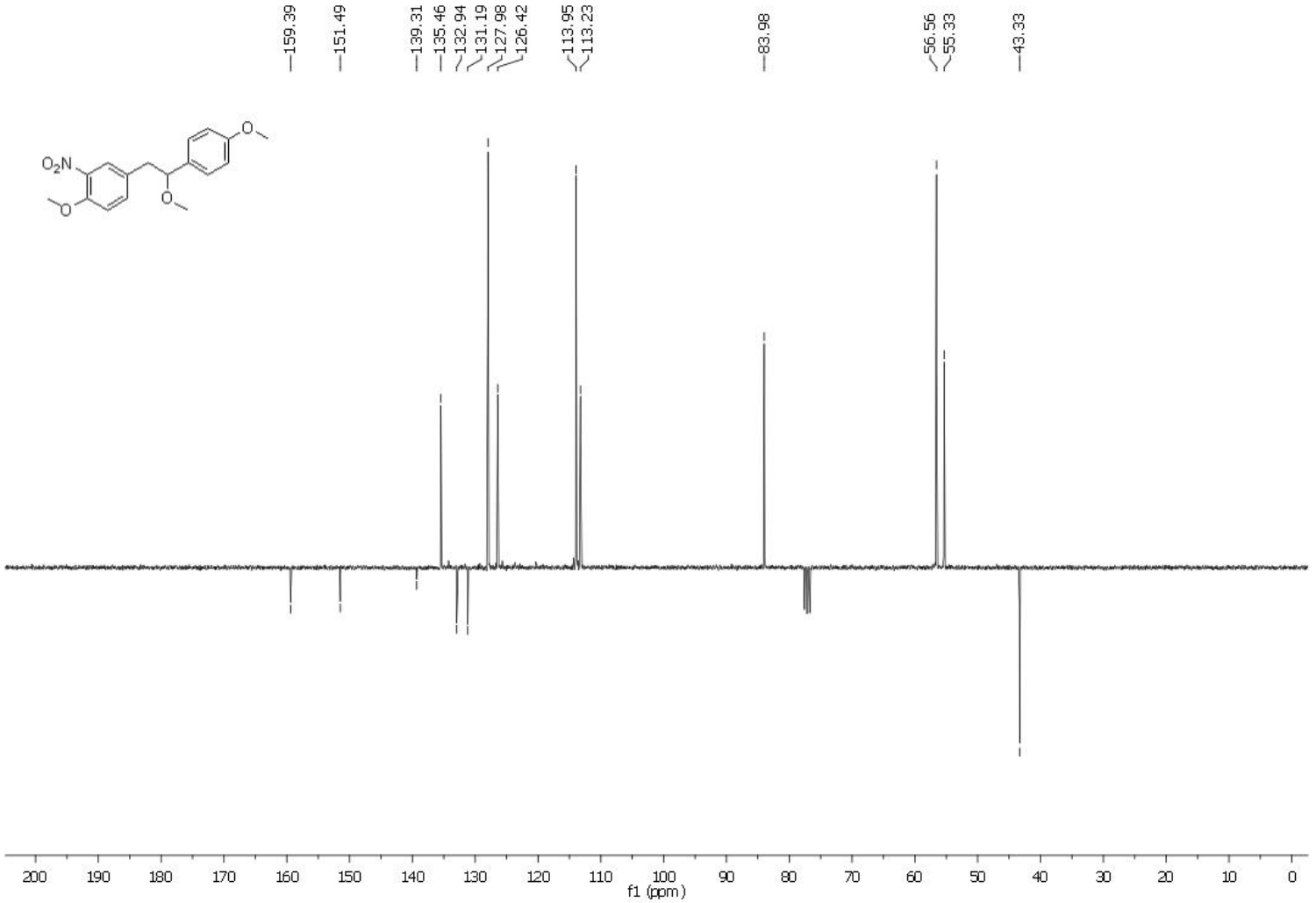
^{13}C NMR (75 MHz, $CDCl_3$) of **6ff**



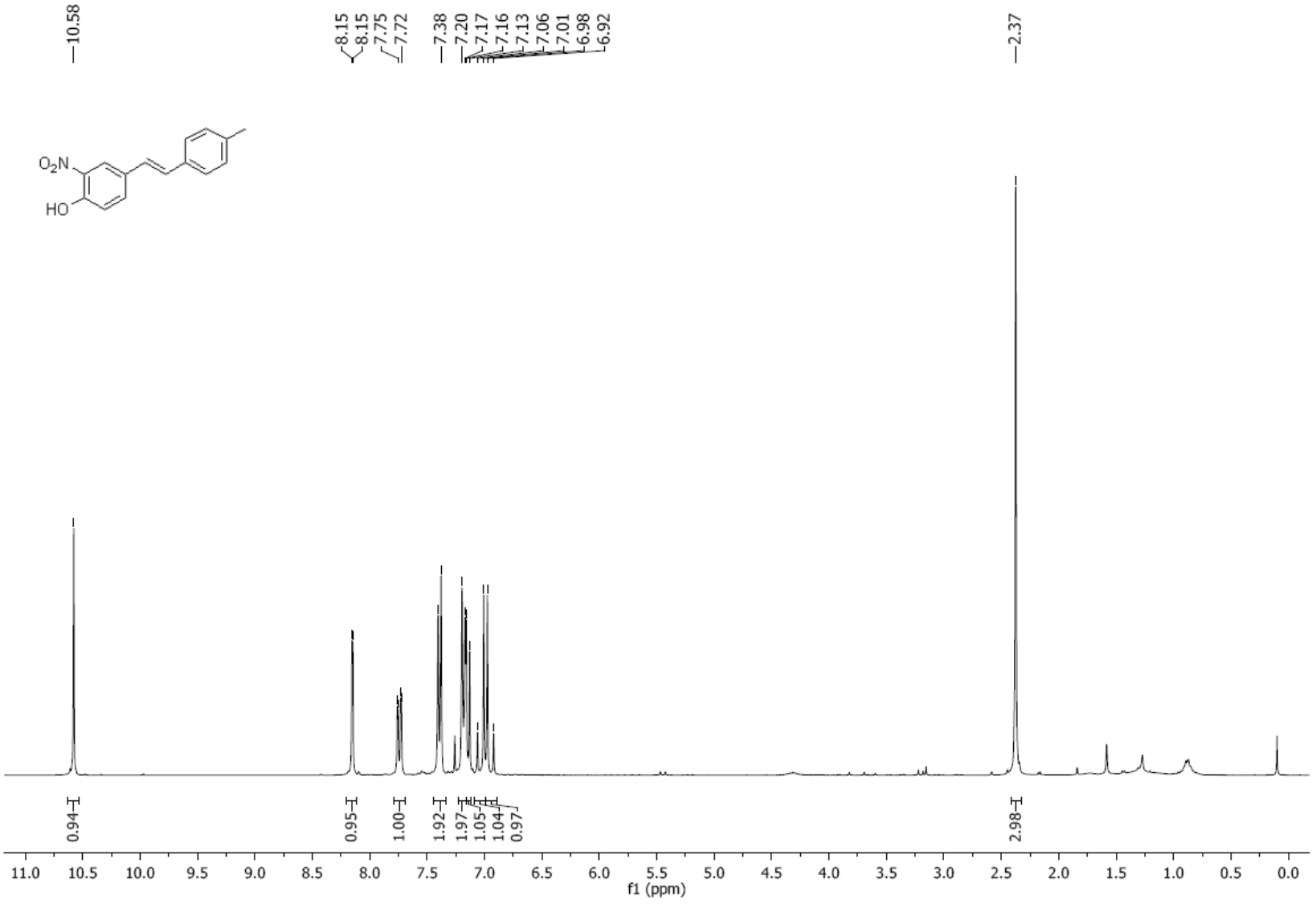
^{1}H NMR (300 MHz, $CDCl_3$) of **9**



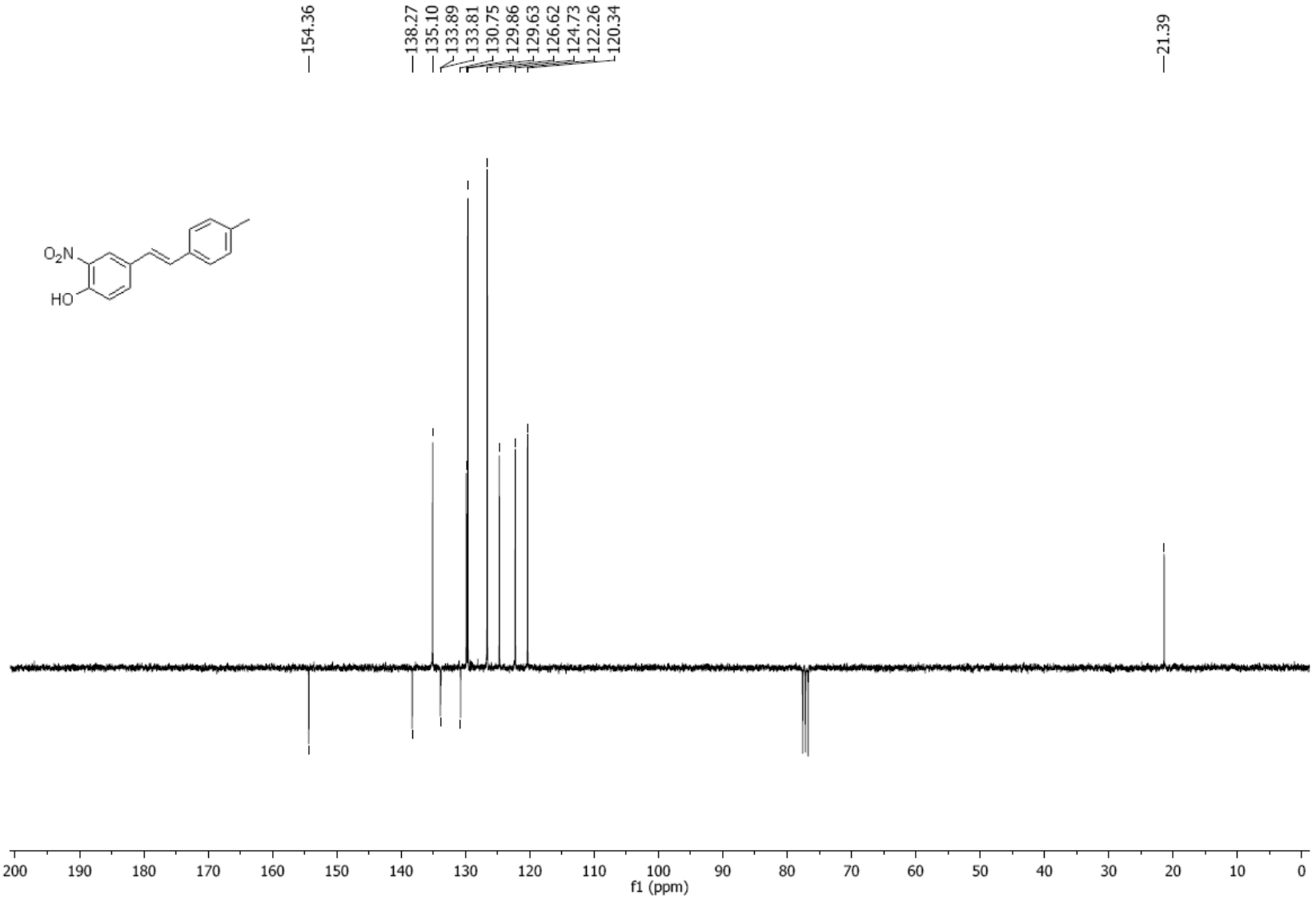
^{13}C NMR (75 MHz, $CDCl_3$) of **9**



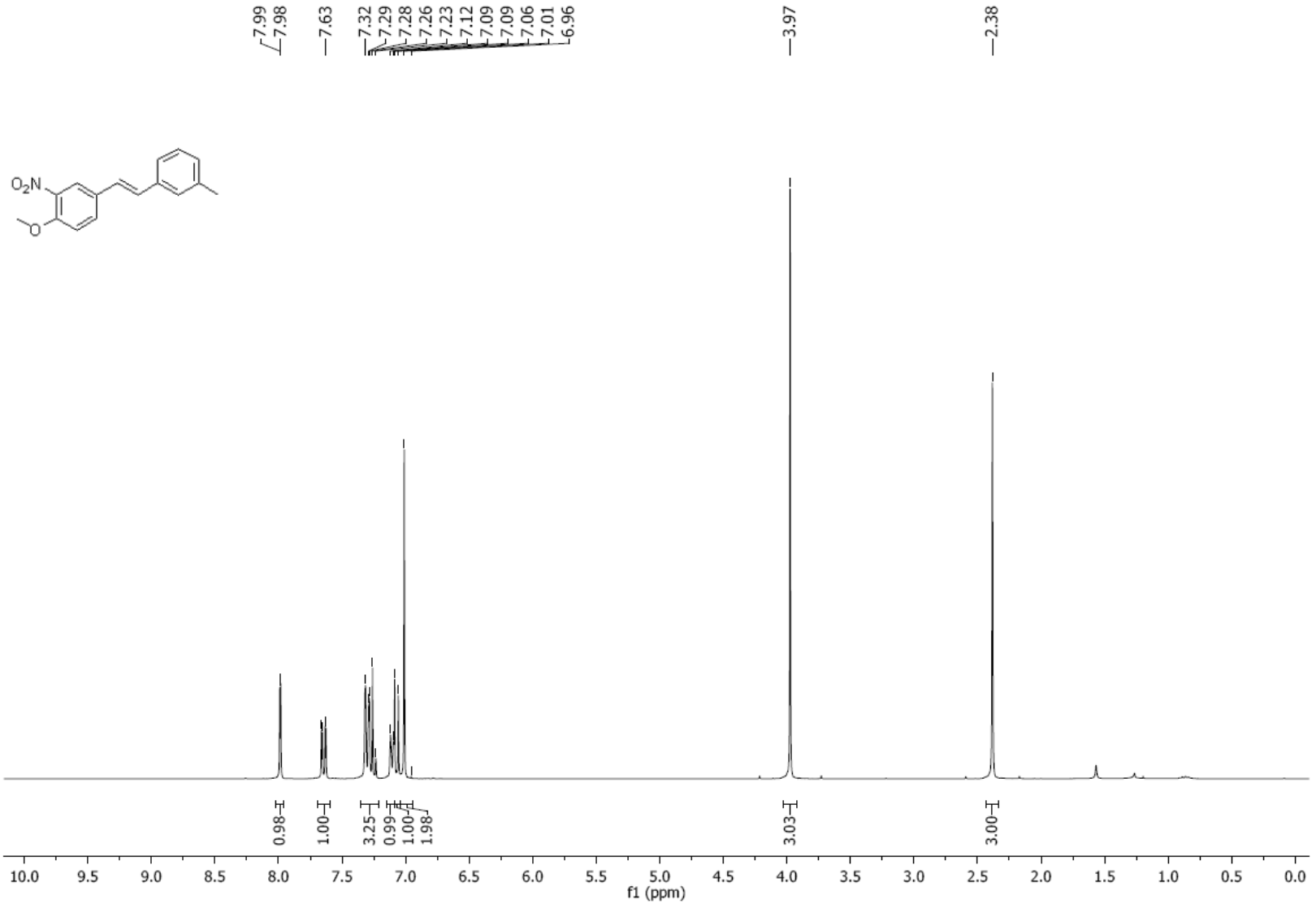
^{1}H NMR (300 MHz, $CDCl_3$) of **6ah**



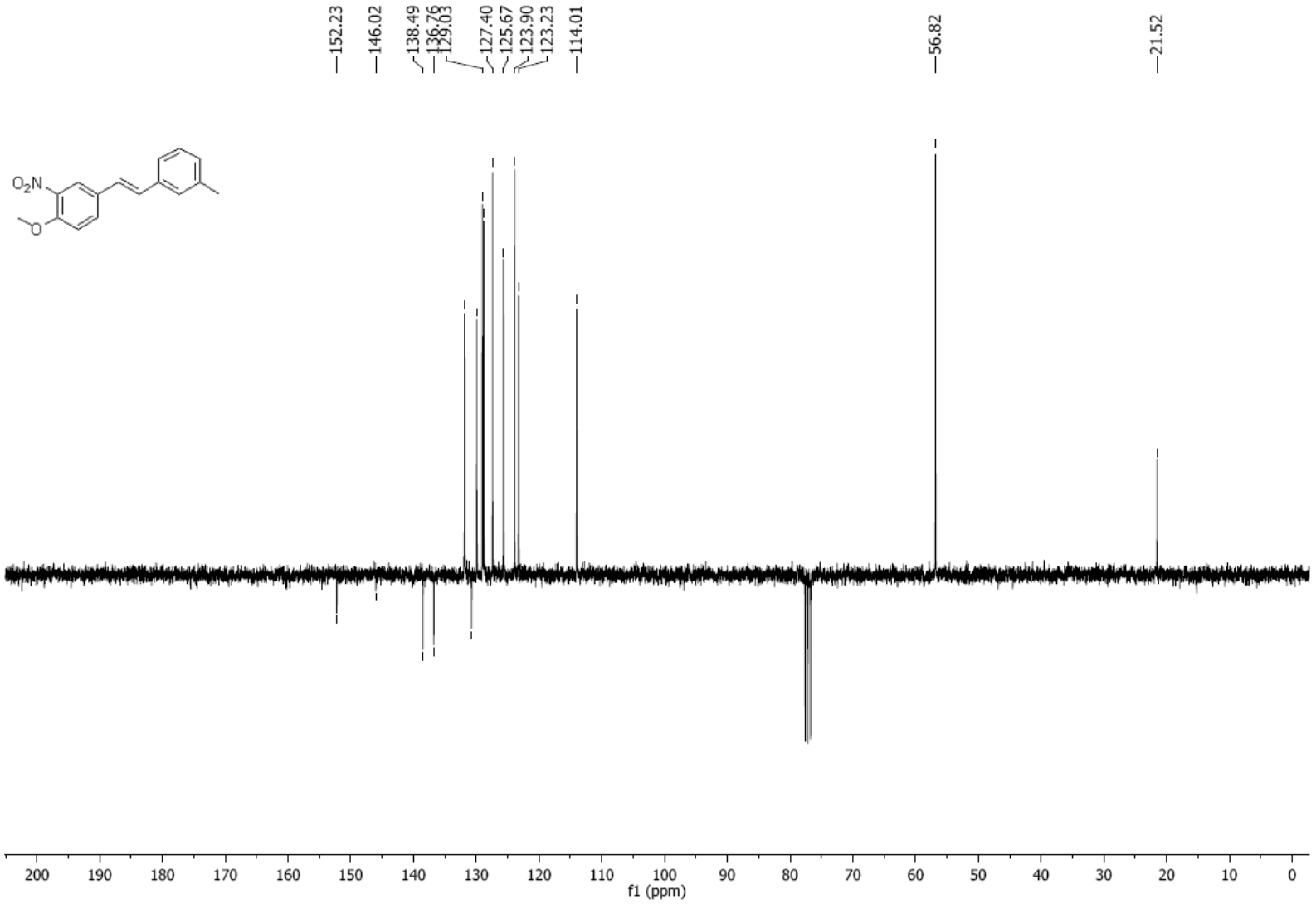
^{13}C NMR (75 MHz, $CDCl_3$) of **6ah**



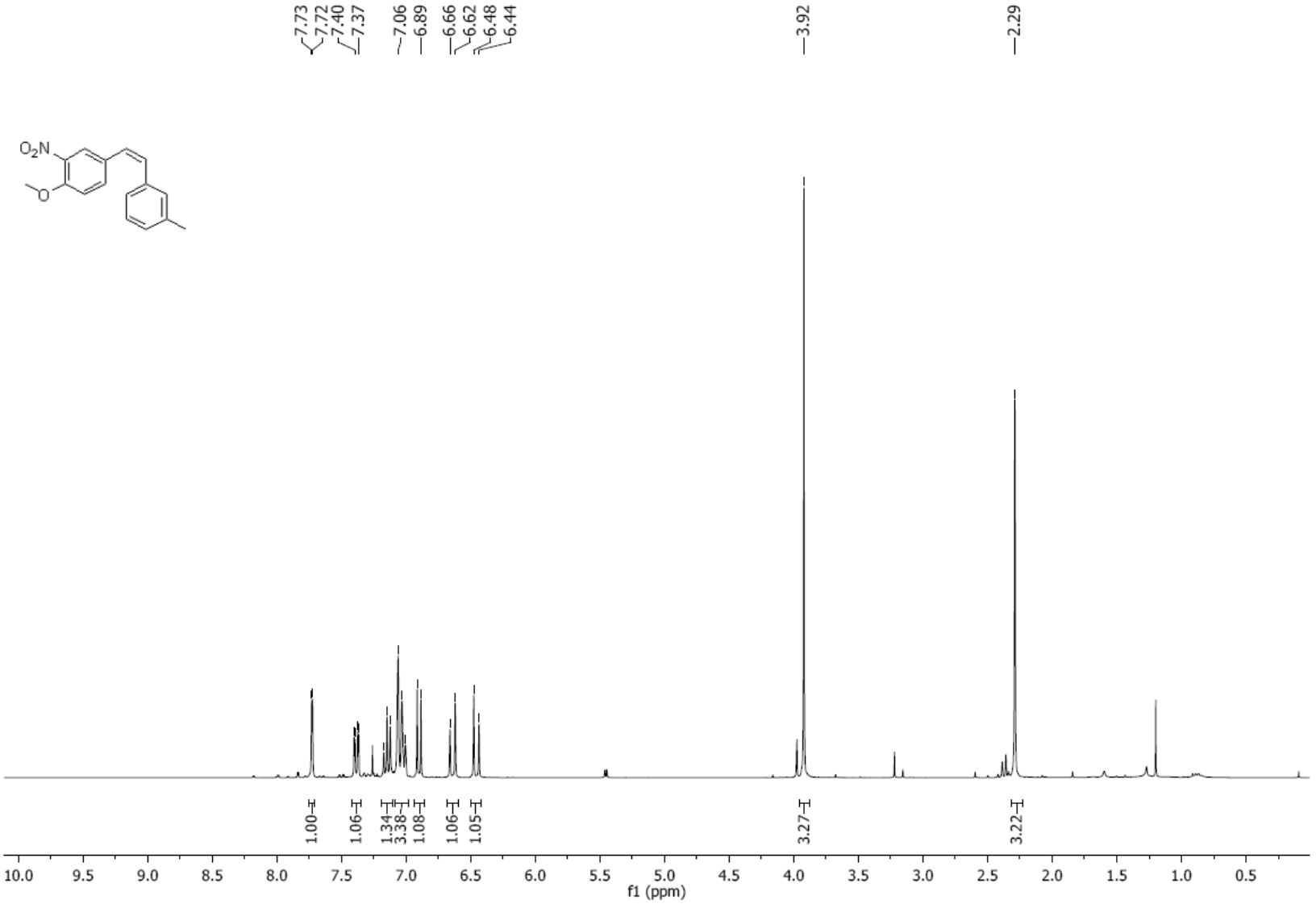
^{1}H NMR (300 MHz, $CDCl_3$) of (*E*)-**6bg**



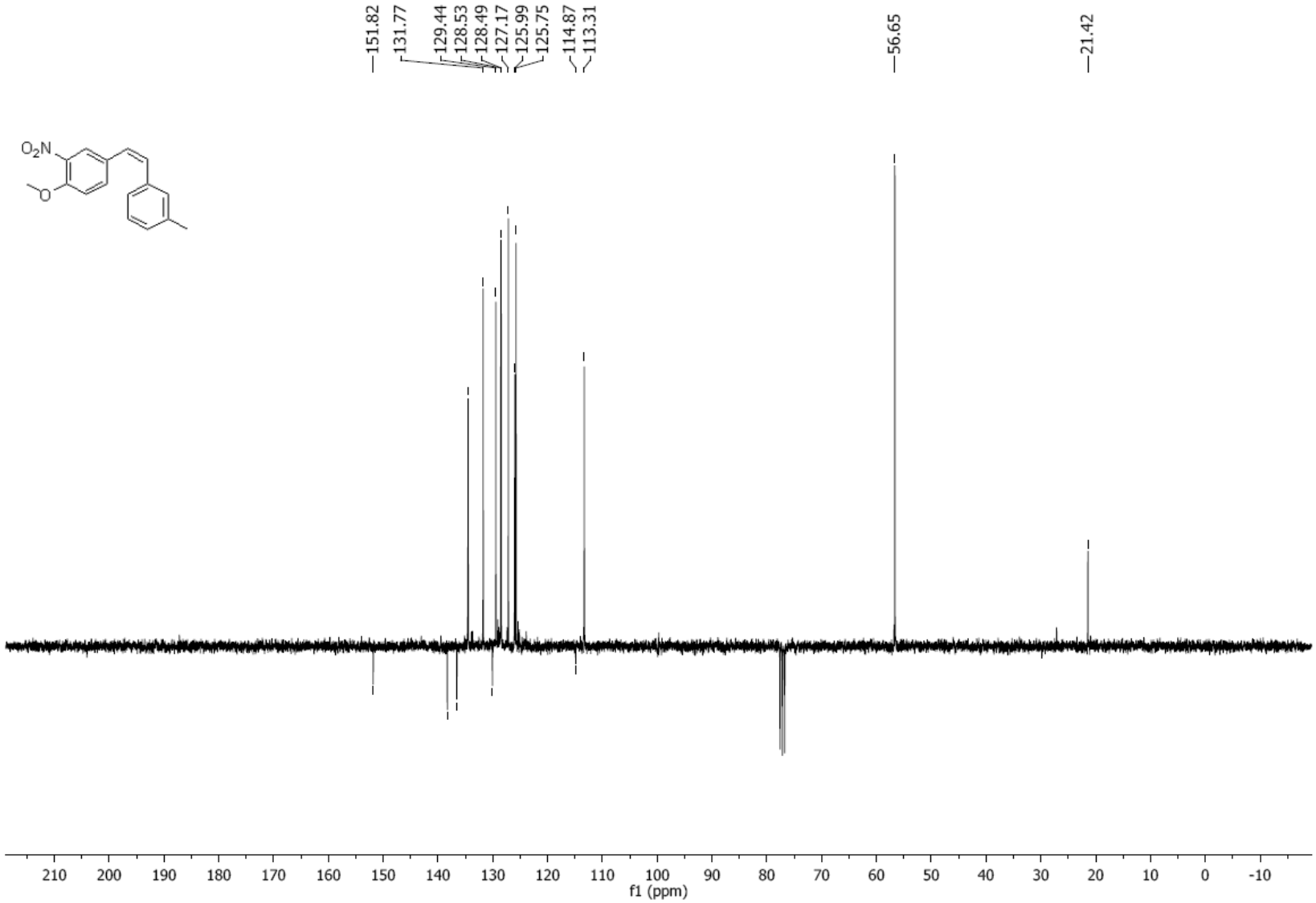
^{13}C NMR (75 MHz, $CDCl_3$) of (*E*)-**6bg**



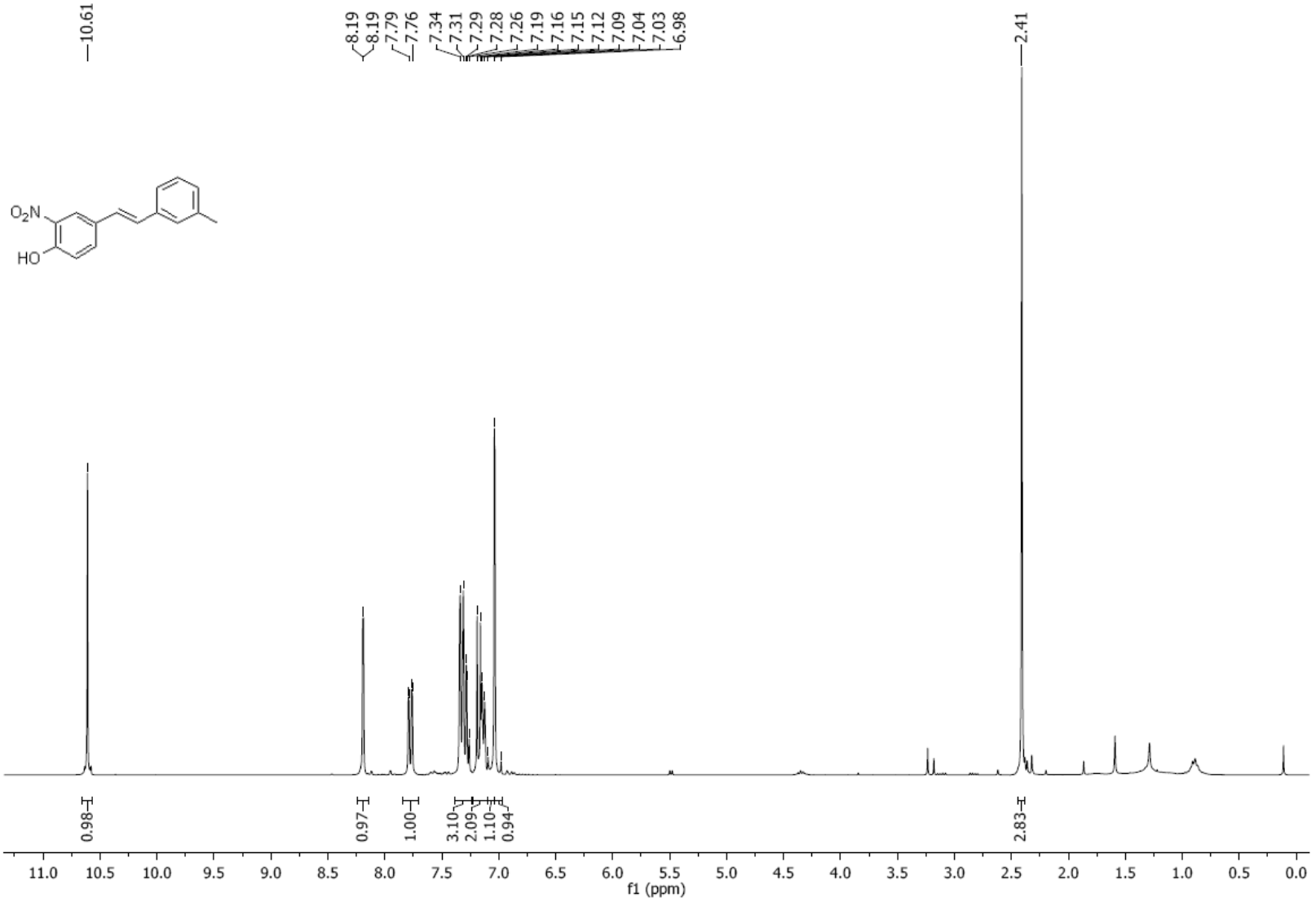
^{1}H NMR (300 MHz, $CDCl_3$) of (*Z*)-**6bg**



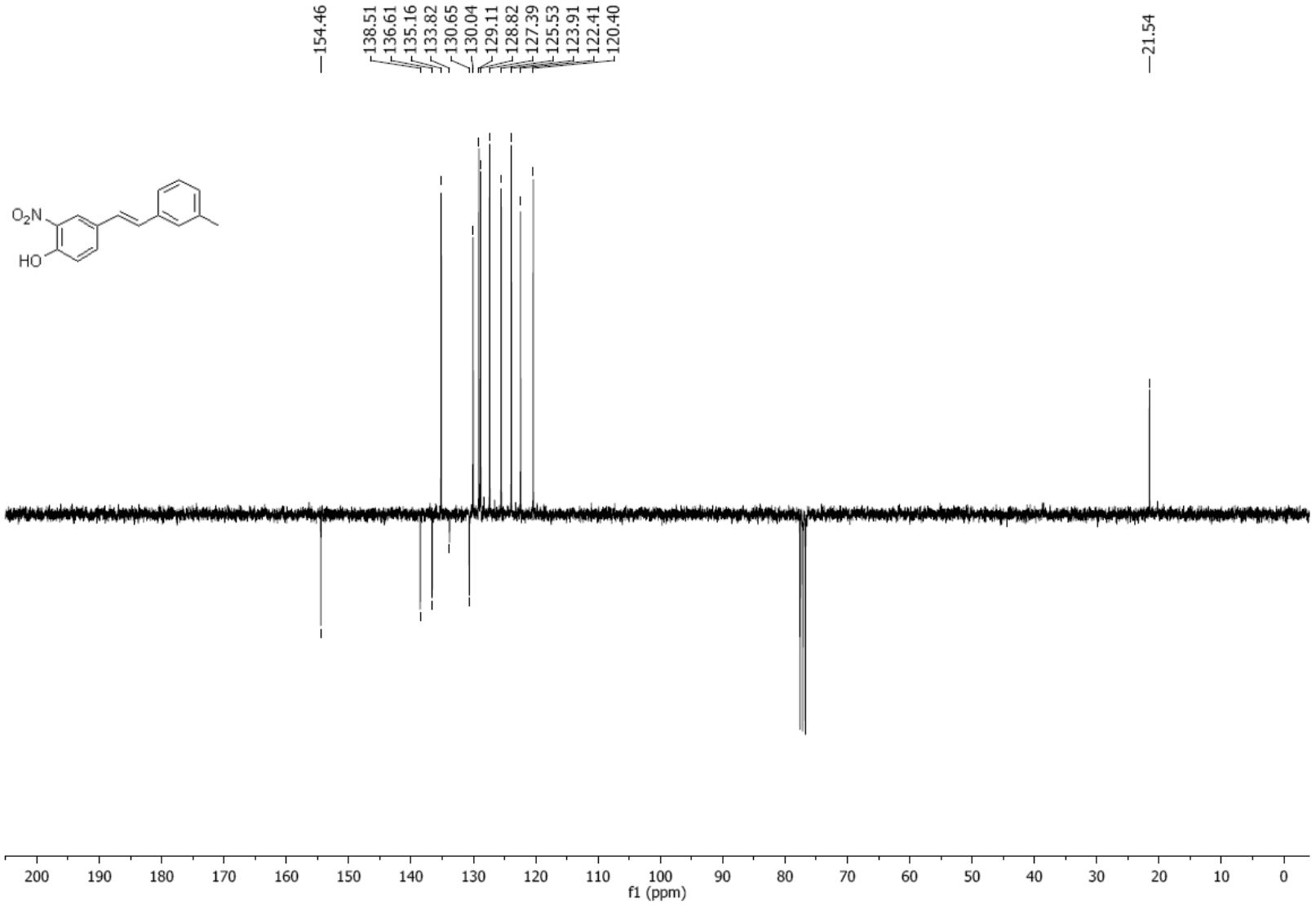
^{13}C NMR (75 MHz, $CDCl_3$) of (*Z*)-**6bg**



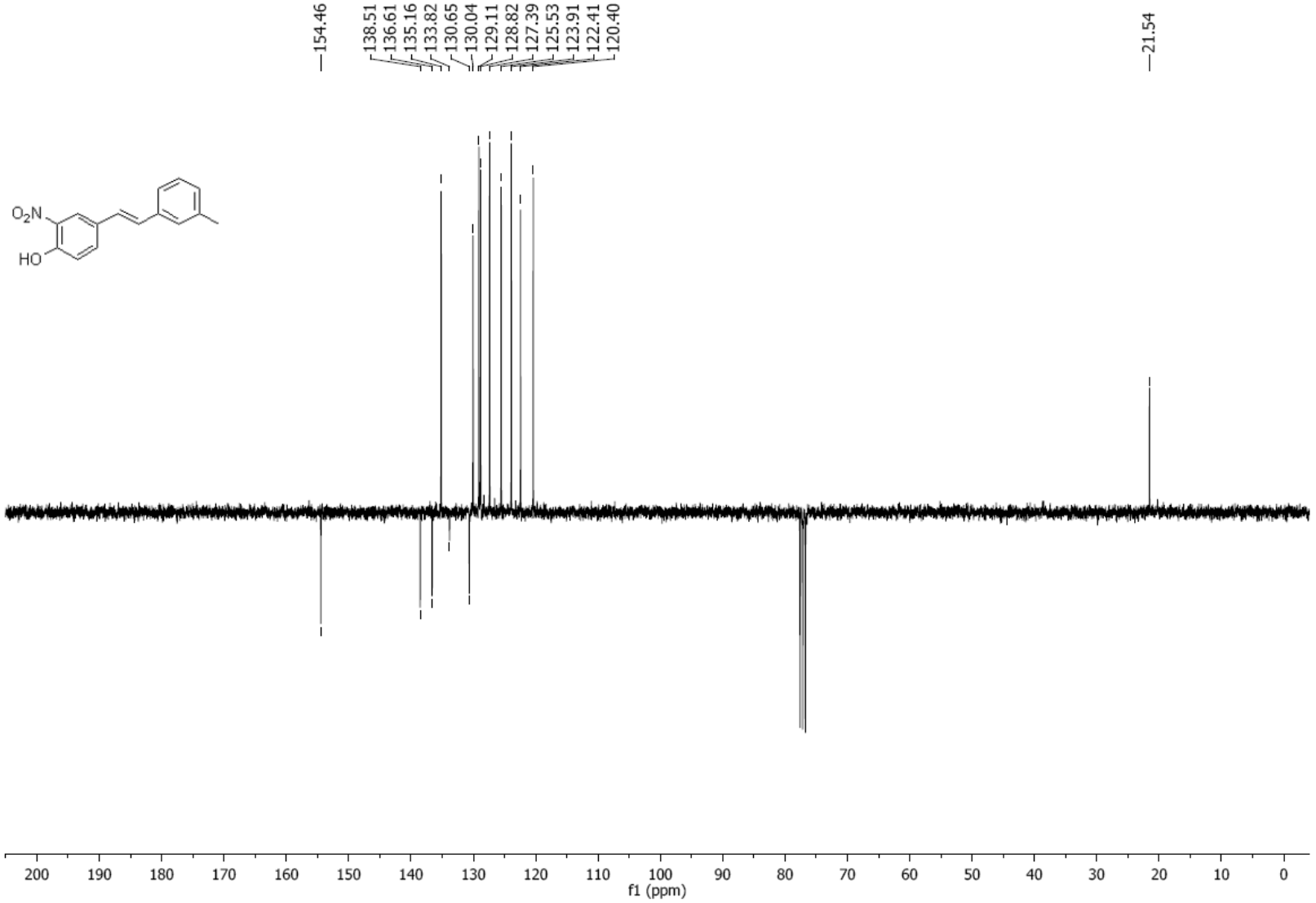
^{1}H NMR (300 MHz, $CDCl_3$) of **6bh**



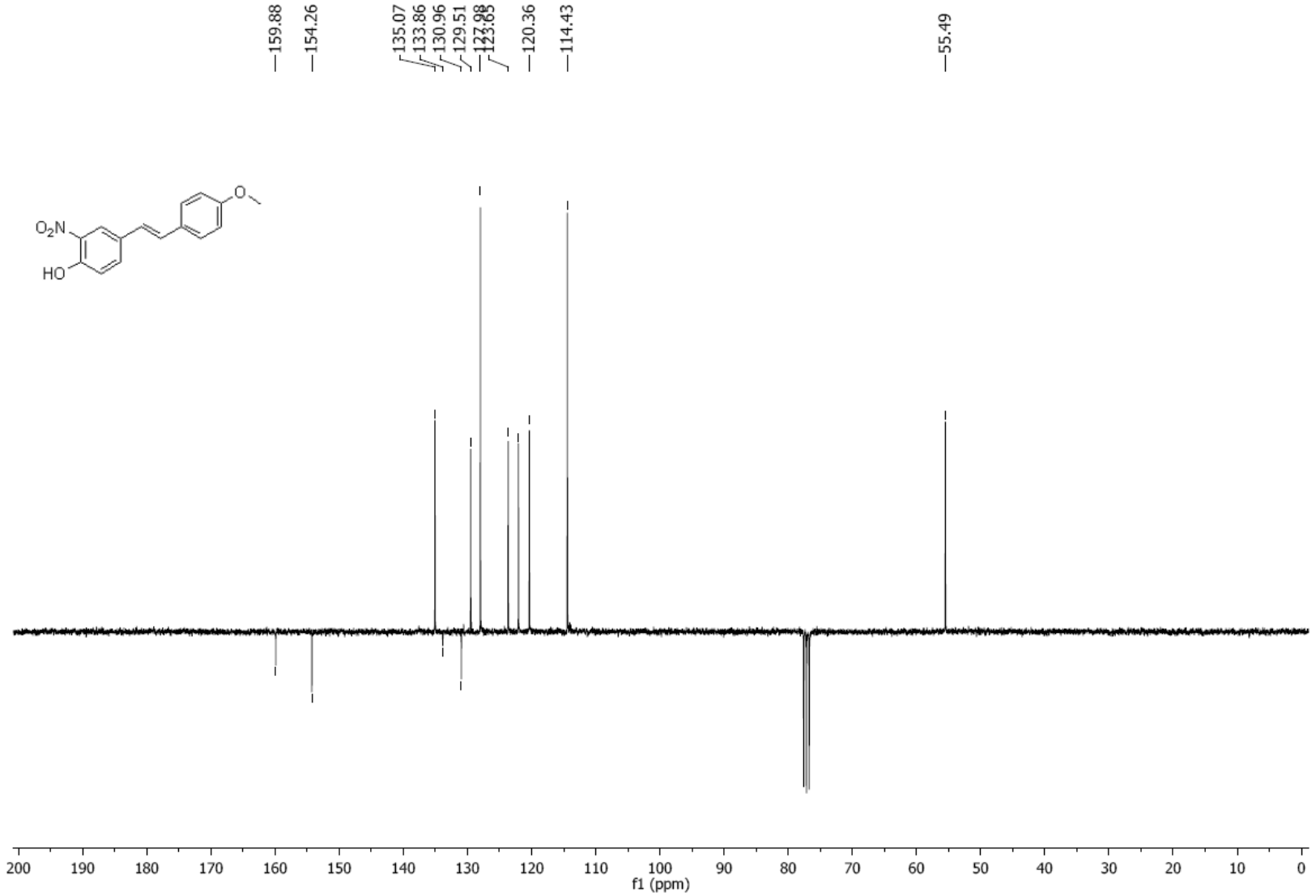
^{13}C NMR (75 MHz, $CDCl_3$) of **6bh**



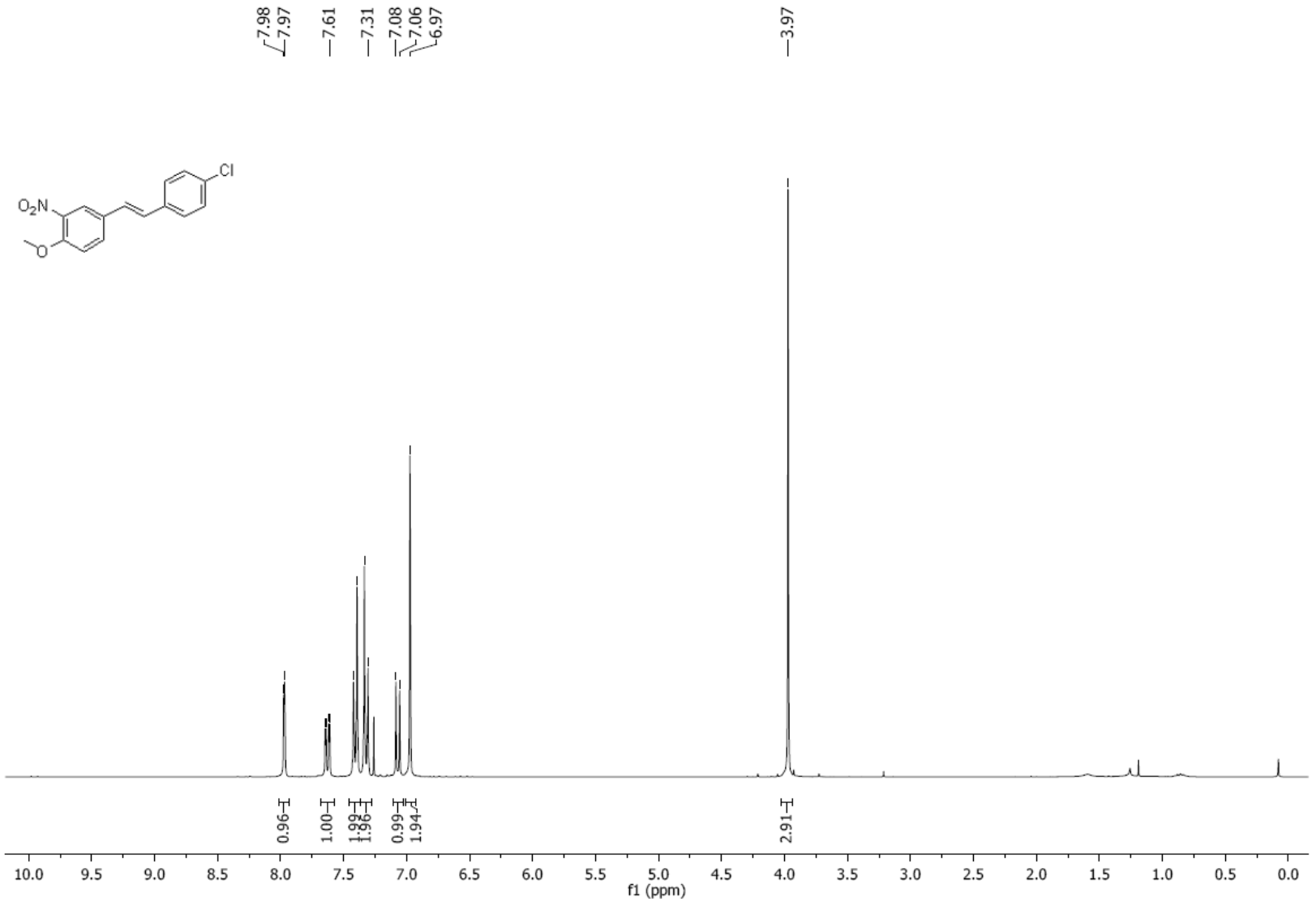
^{1}H NMR (300 MHz, $CDCl_3$) of **6ch**



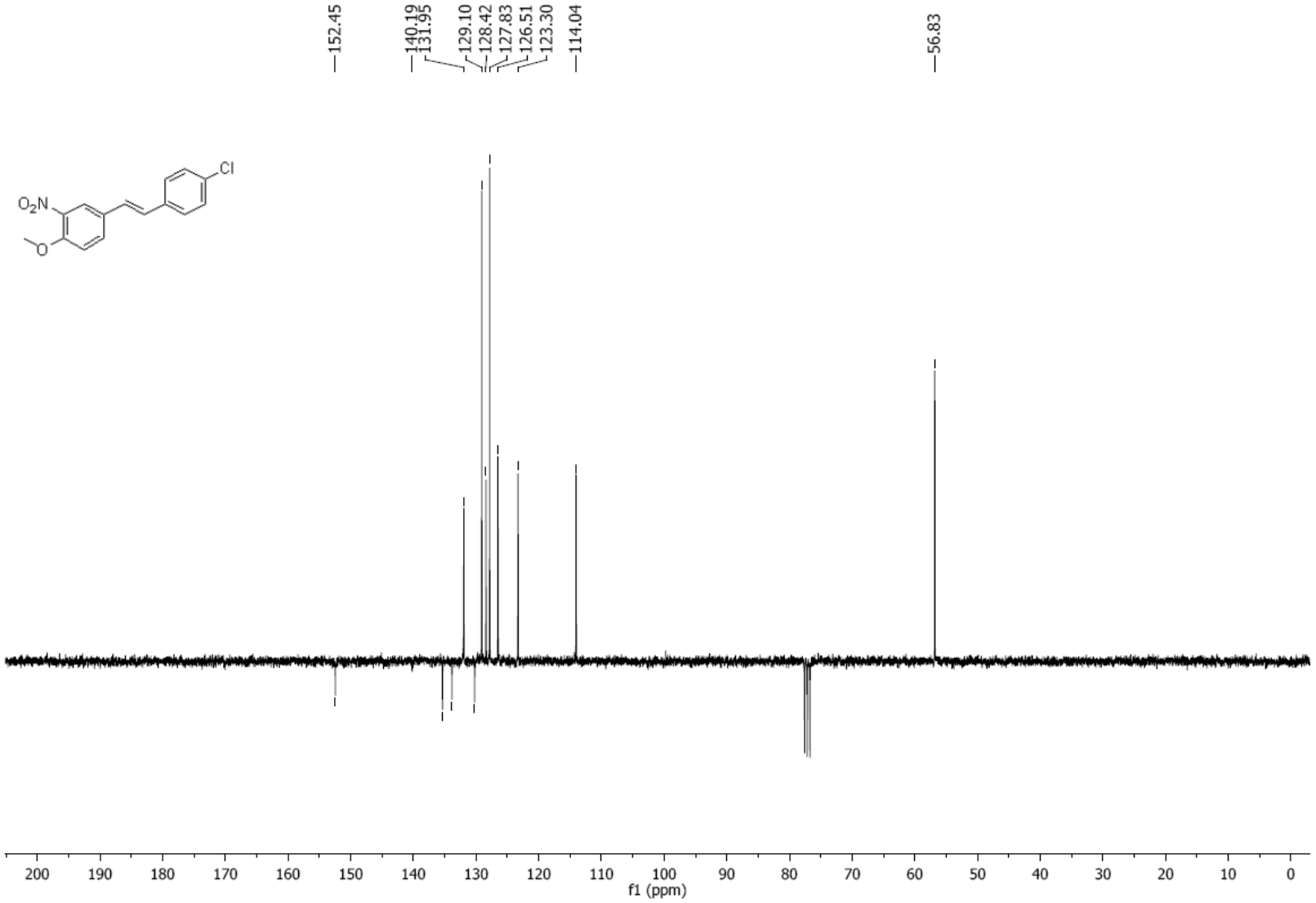
^{13}C NMR (75 MHz, $CDCl_3$) of **6ch**



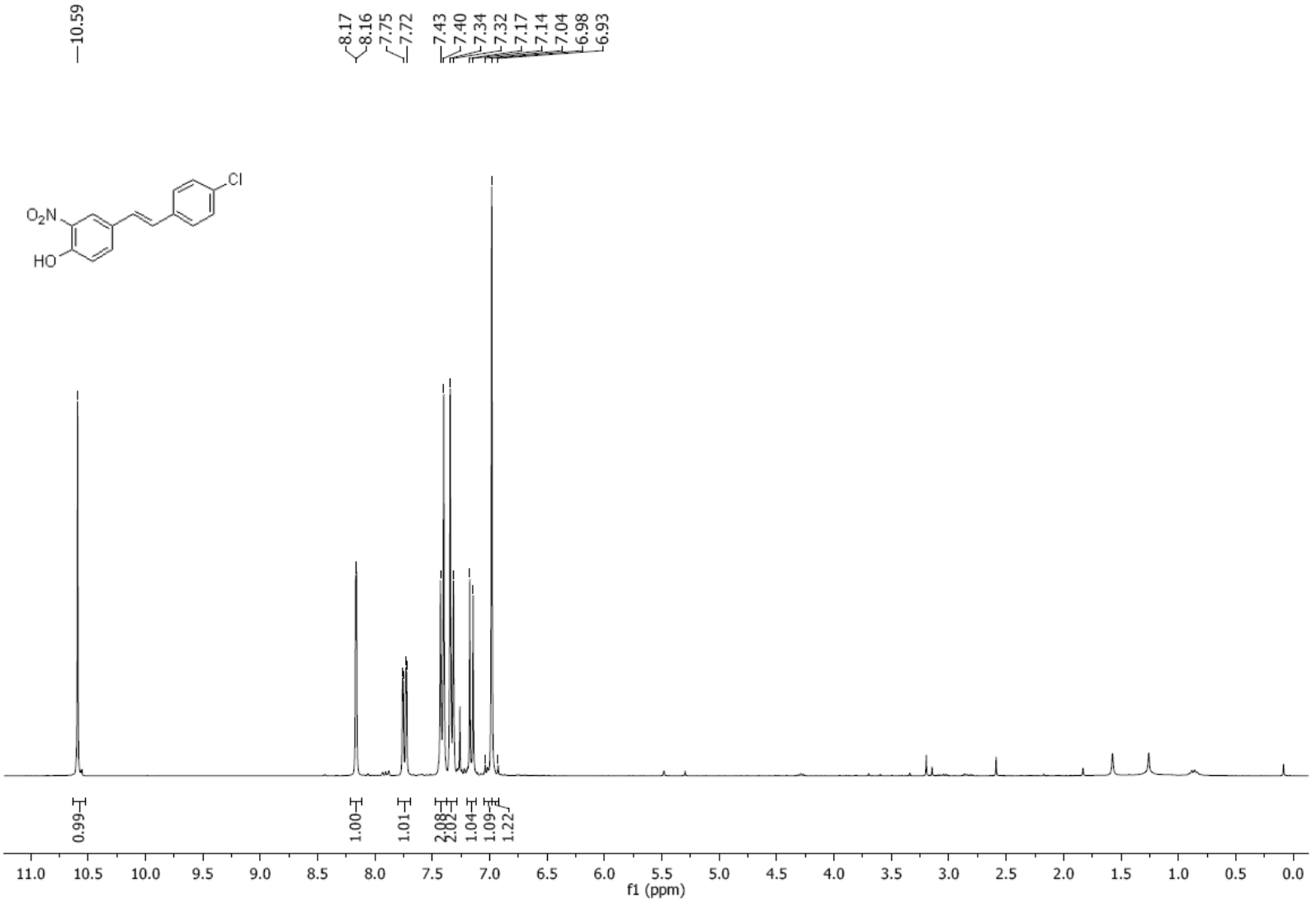
^{1}H NMR (300 MHz, $CDCl_3$) of **6dg**



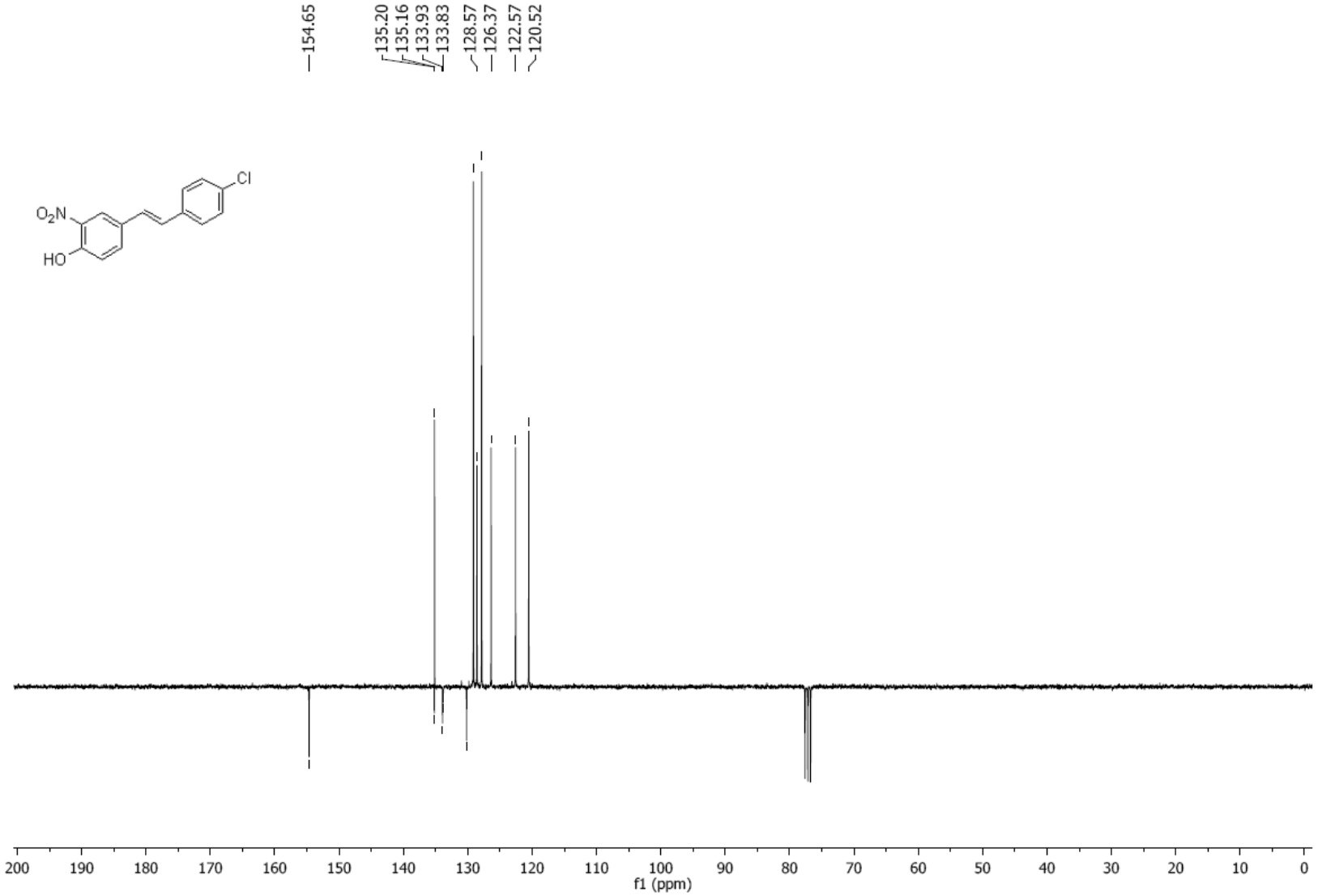
^{13}C NMR (75 MHz, $CDCl_3$) of **6dg**



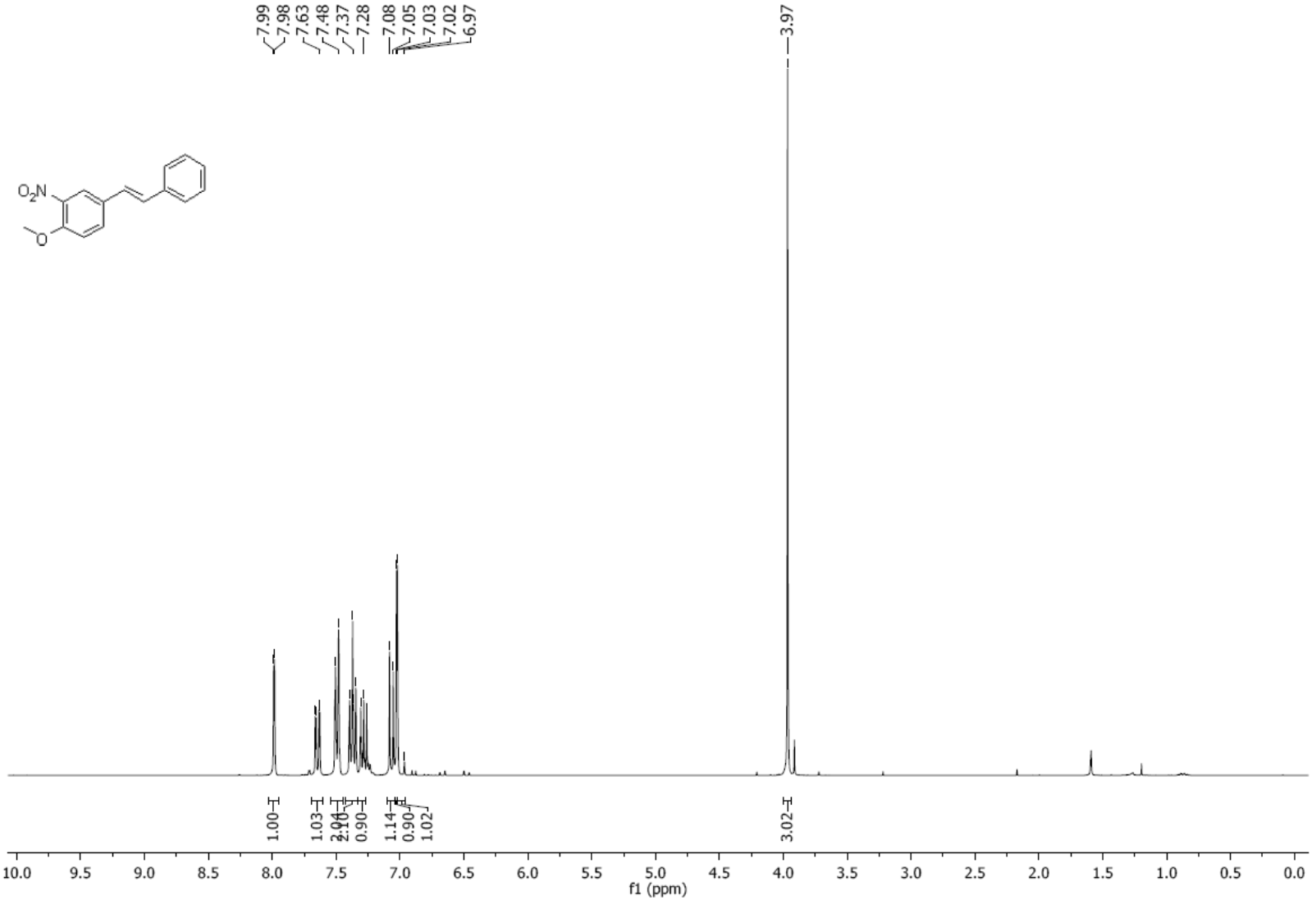
^{1}H NMR (300 MHz, $CDCl_3$) of **6dh**



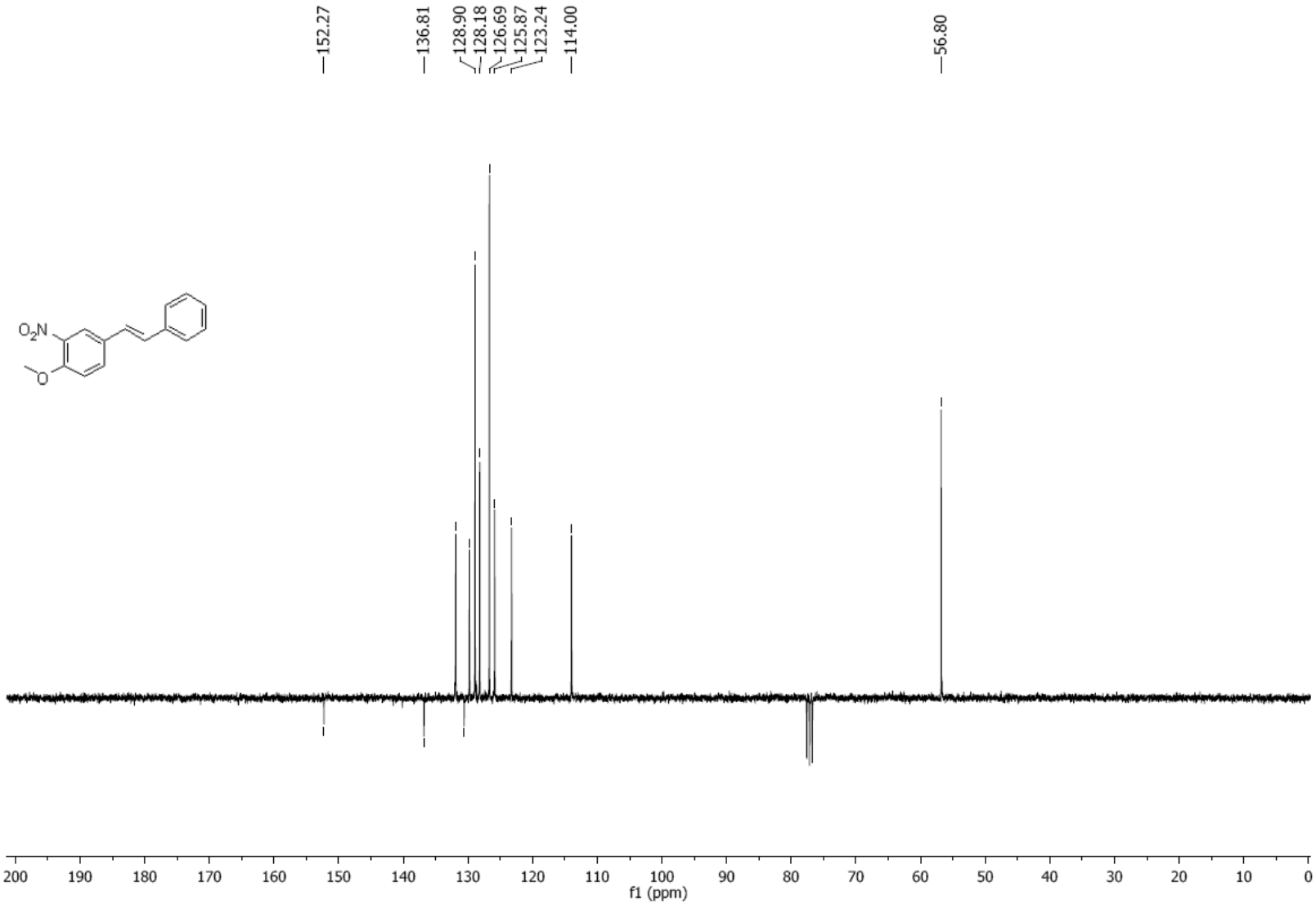
^{13}C NMR (75 MHz, $CDCl_3$) of **6dh**



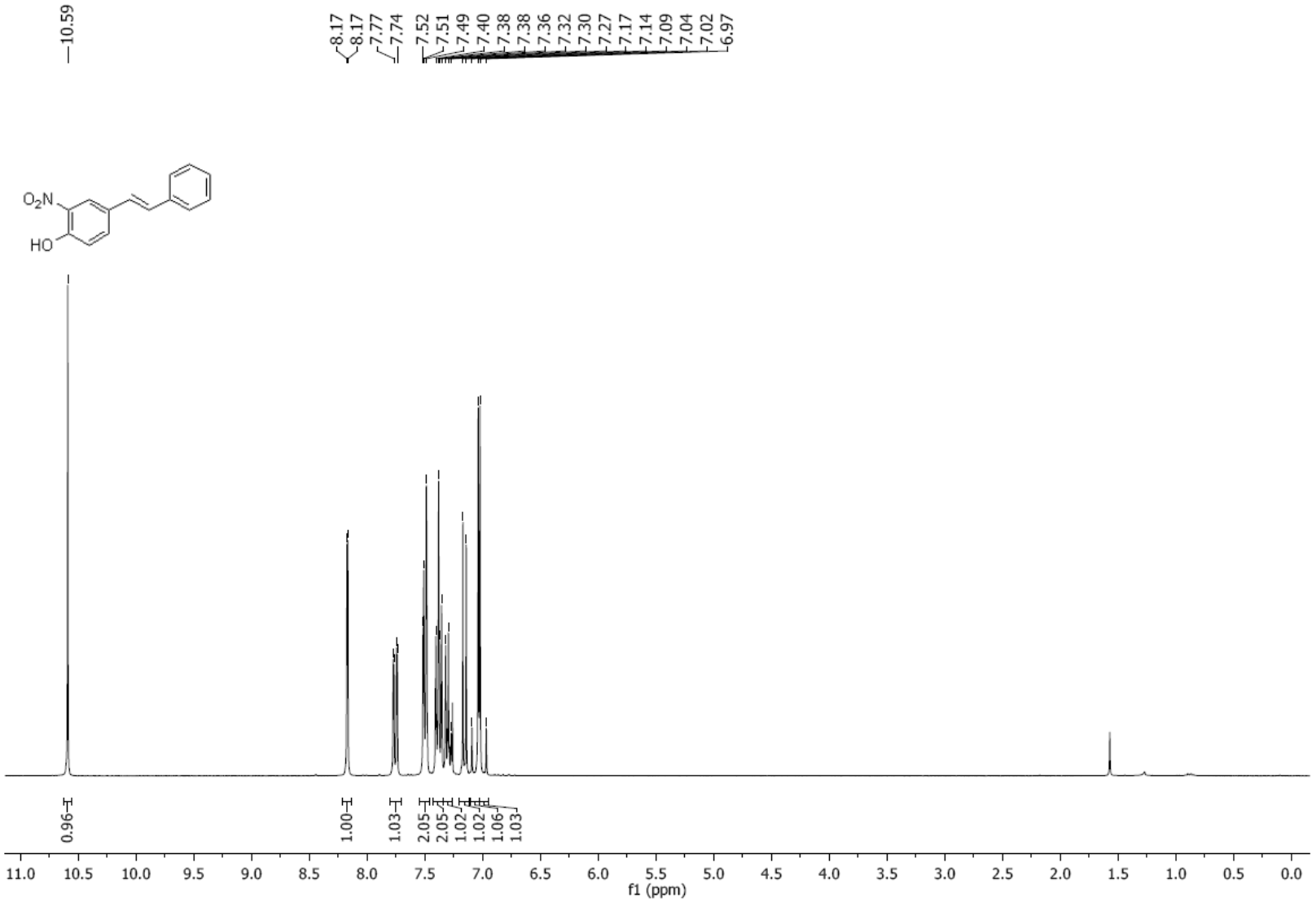
^{1}H NMR (300 MHz, $CDCl_3$) of **6fg**



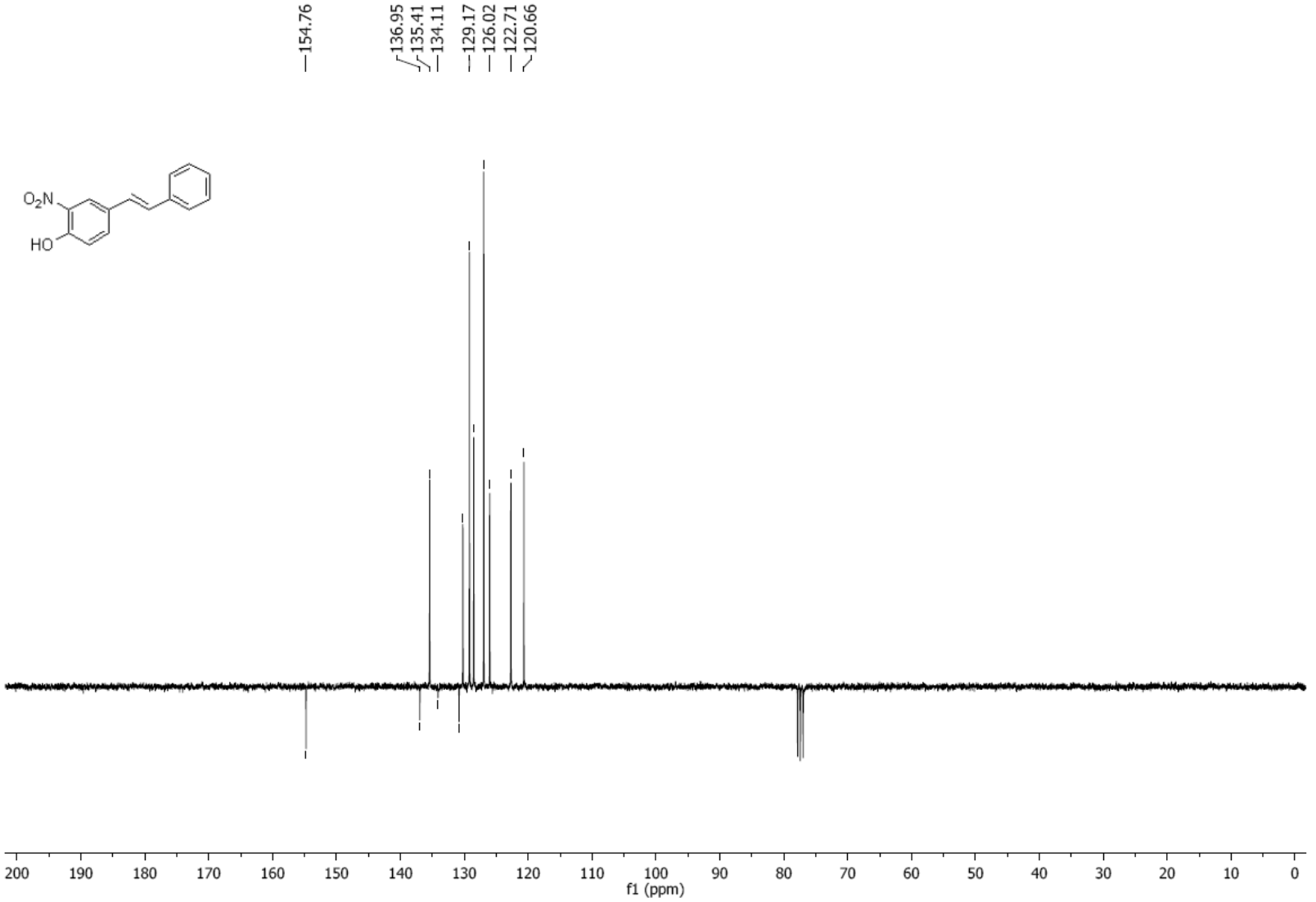
^{13}C NMR (75 MHz, $CDCl_3$) of **6fg**



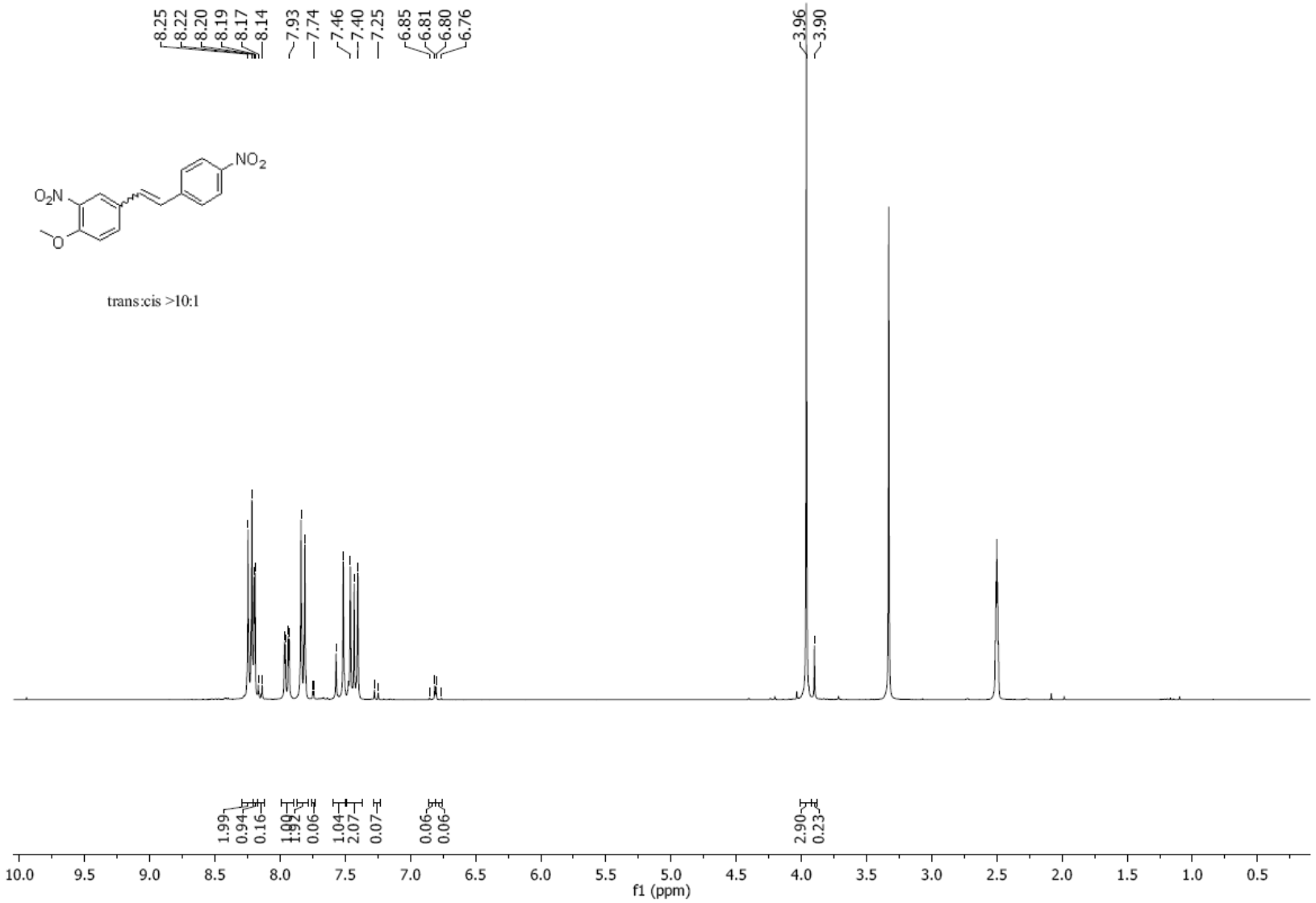
^{1}H NMR (300 MHz, $CDCl_3$) of **6fh**



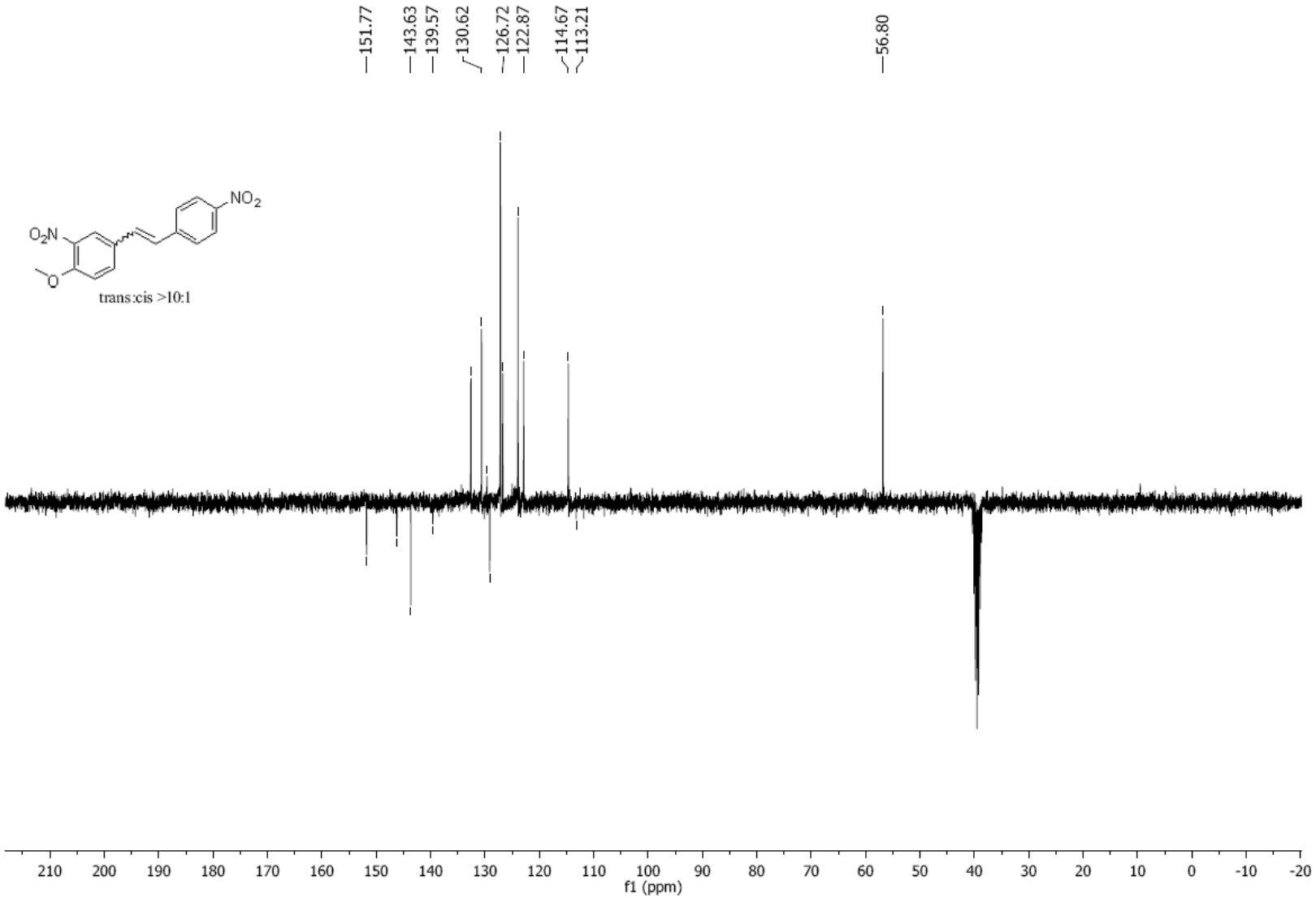
^{13}C NMR (75 MHz, $CDCl_3$) of **6fh**



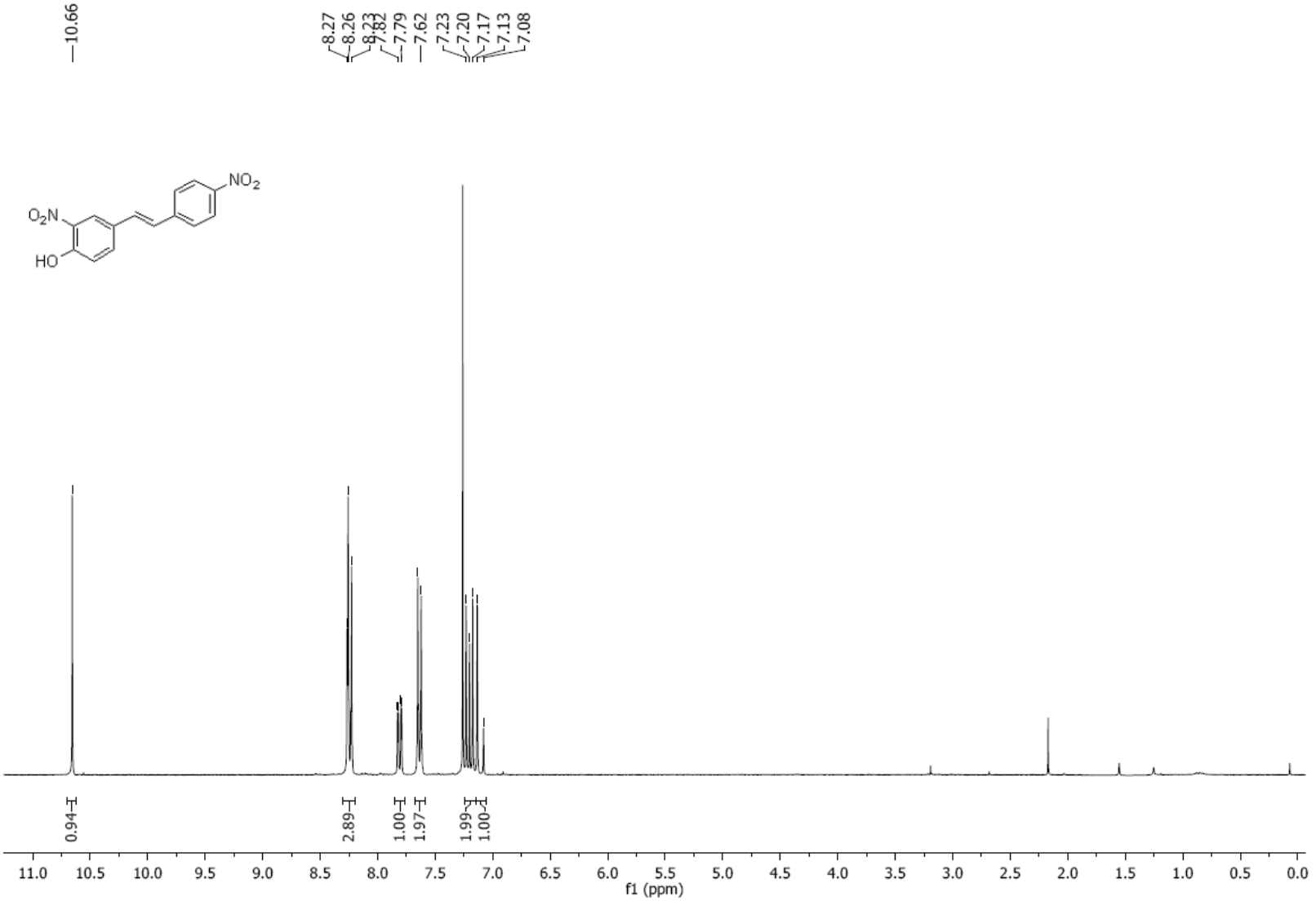
^{1}H NMR (300 MHz, DMSO-d_6) of **6gg**



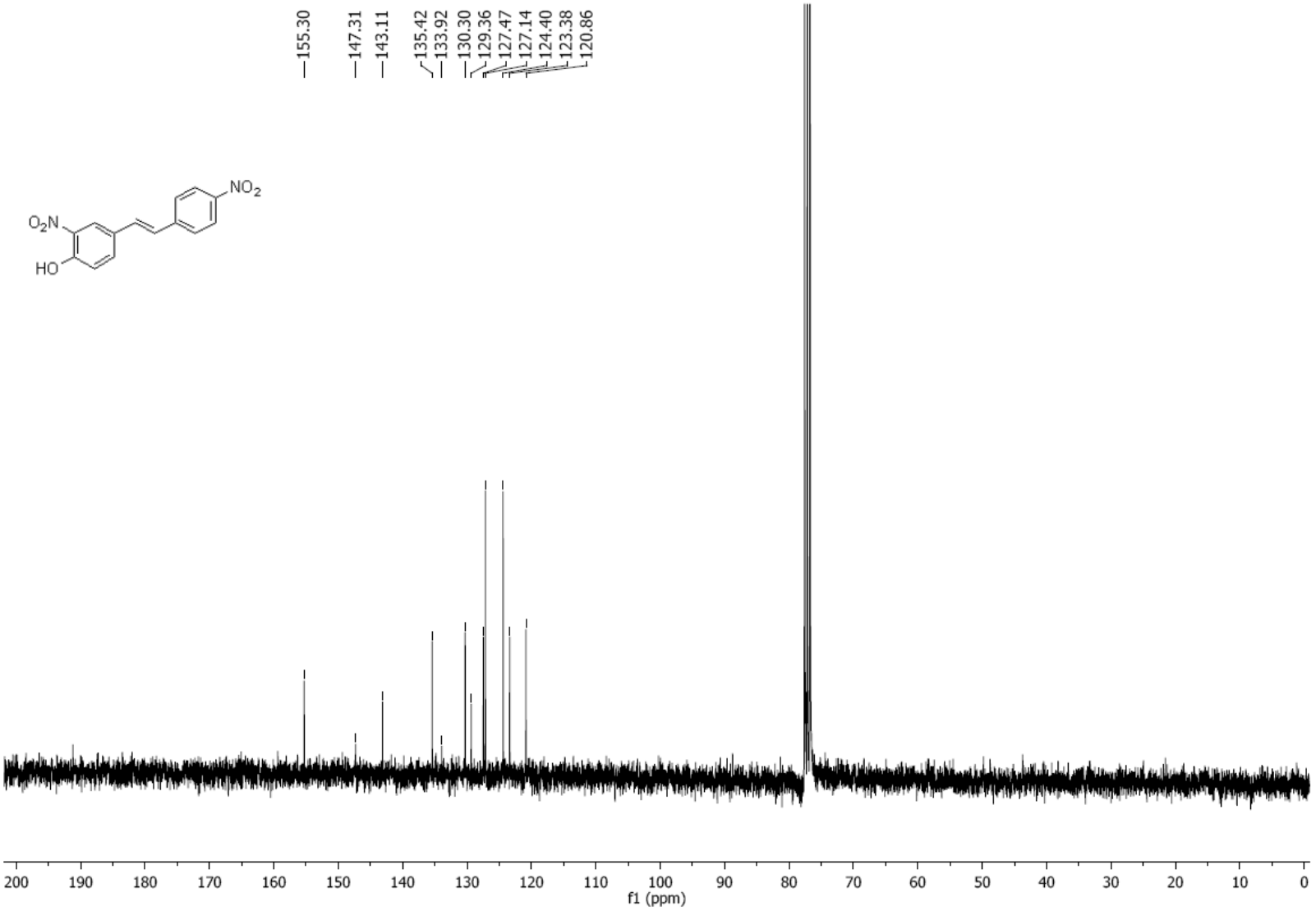
^{13}C NMR (75 MHz, $CDCl_3$) of **6gg**



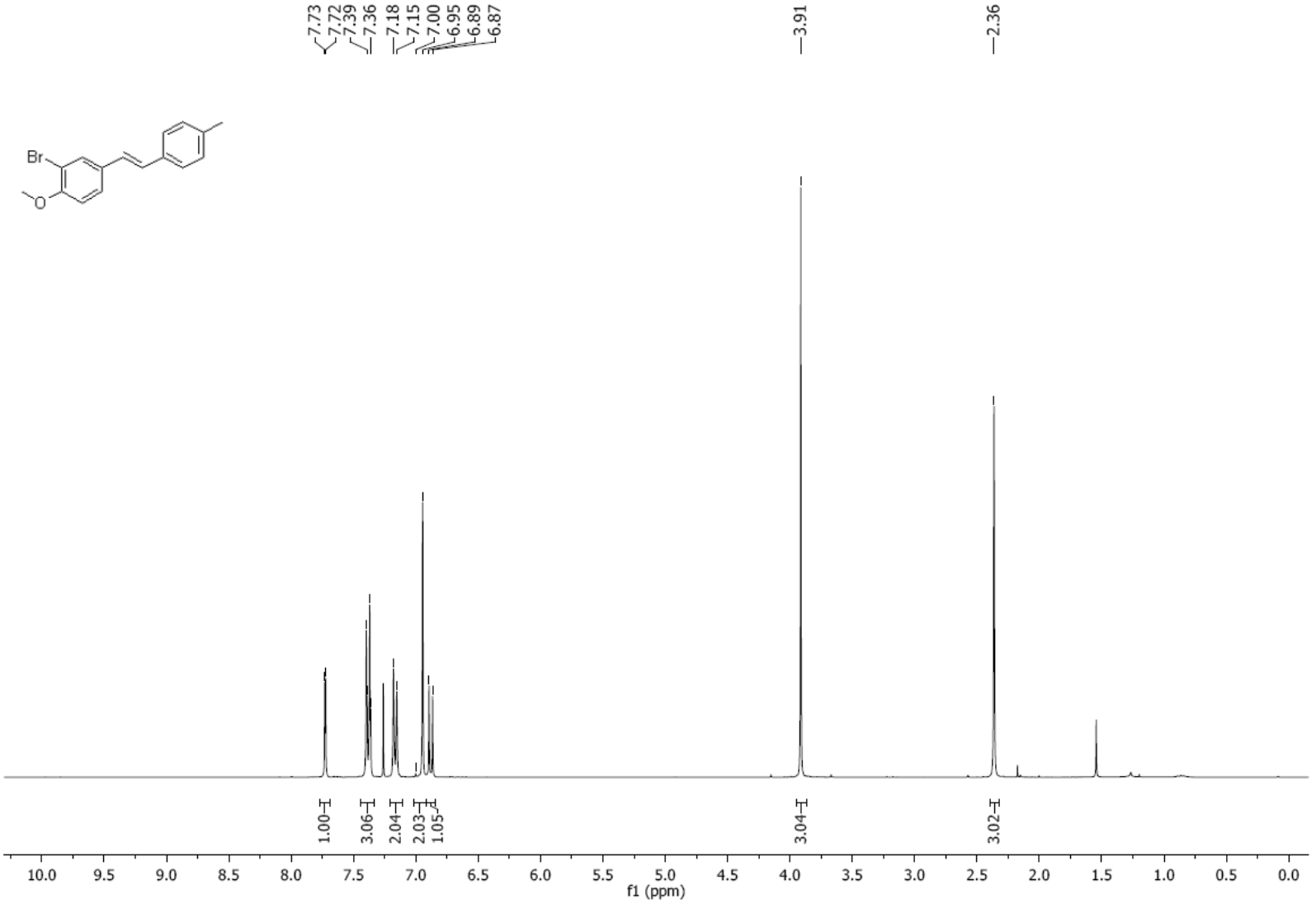
^{1}H NMR (300 MHz, $CDCl_3$) of **6gh**



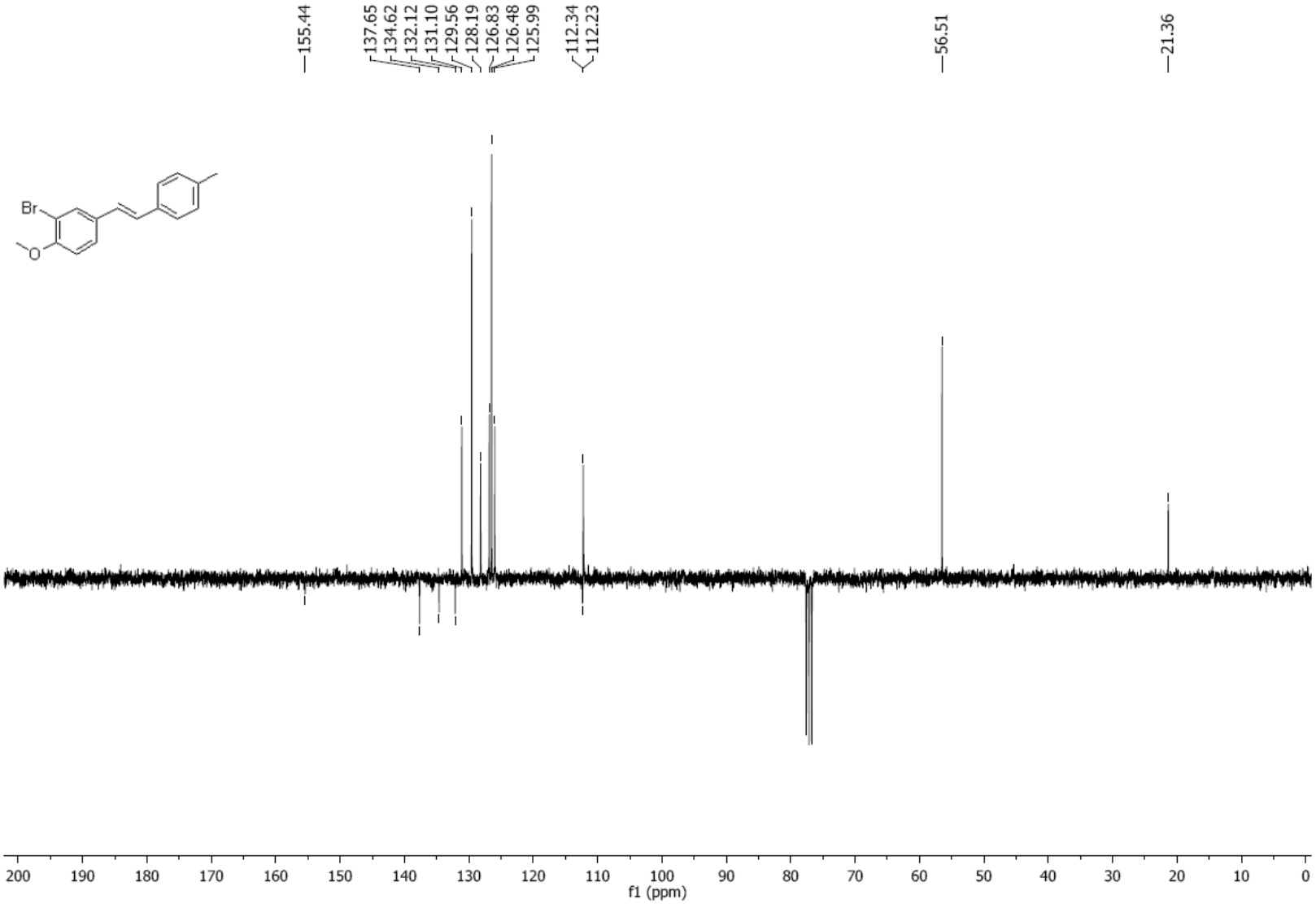
^{13}C NMR (75 MHz, $CDCl_3$) of **6gh**



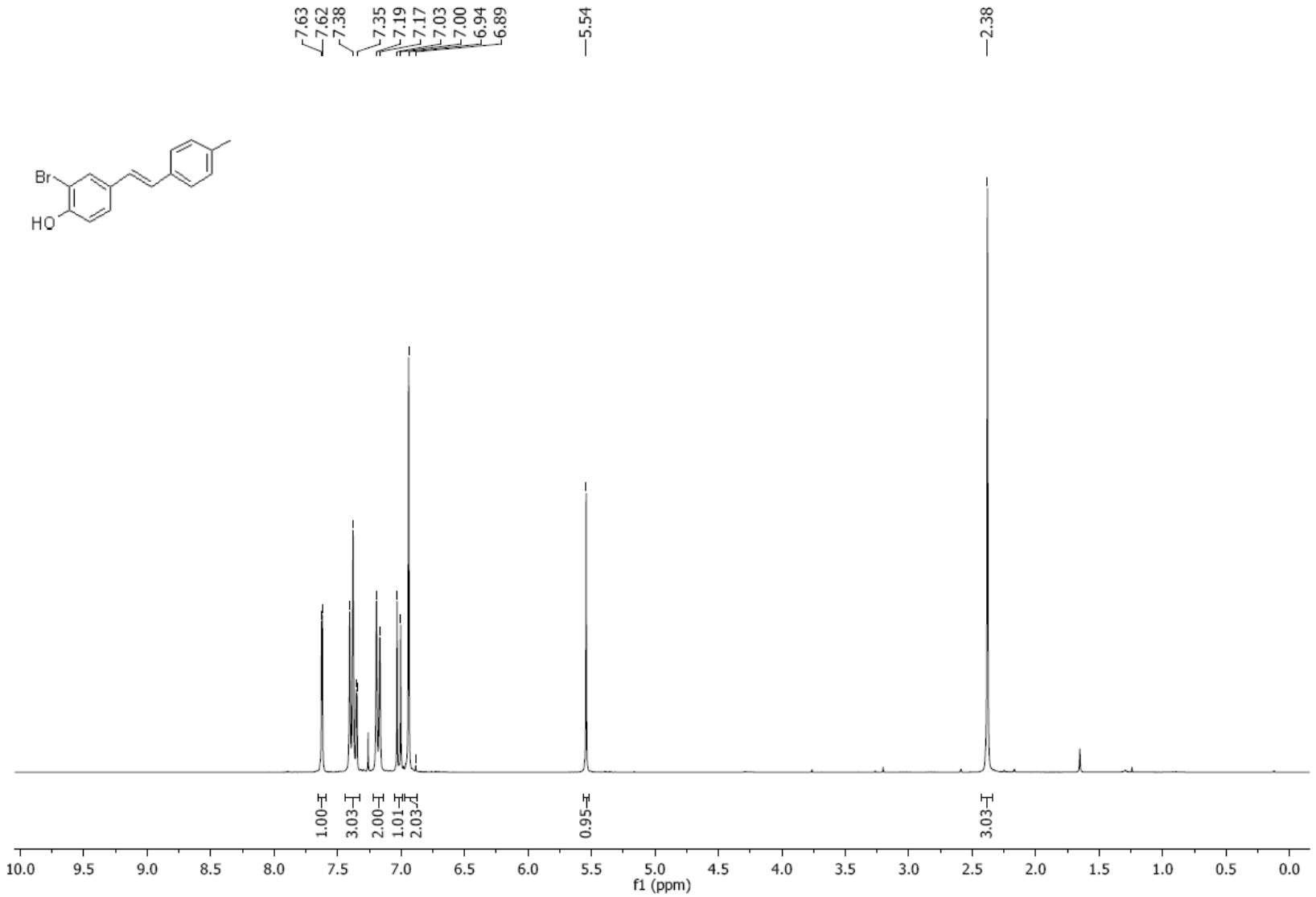
^{1}H NMR (300 MHz, $CDCl_3$) of **6ai**



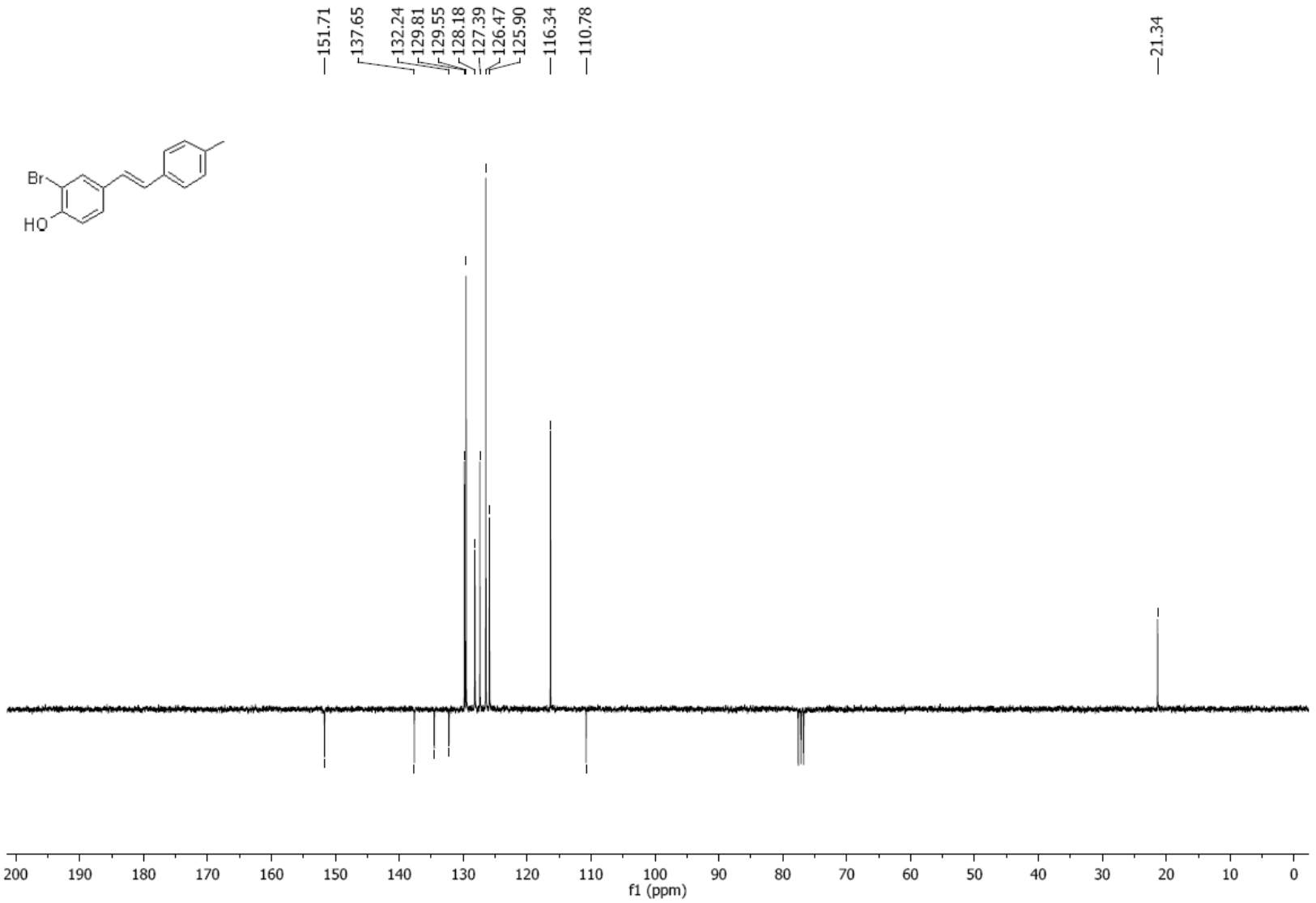
^{13}C NMR (75 MHz, $CDCl_3$) of **6ai**



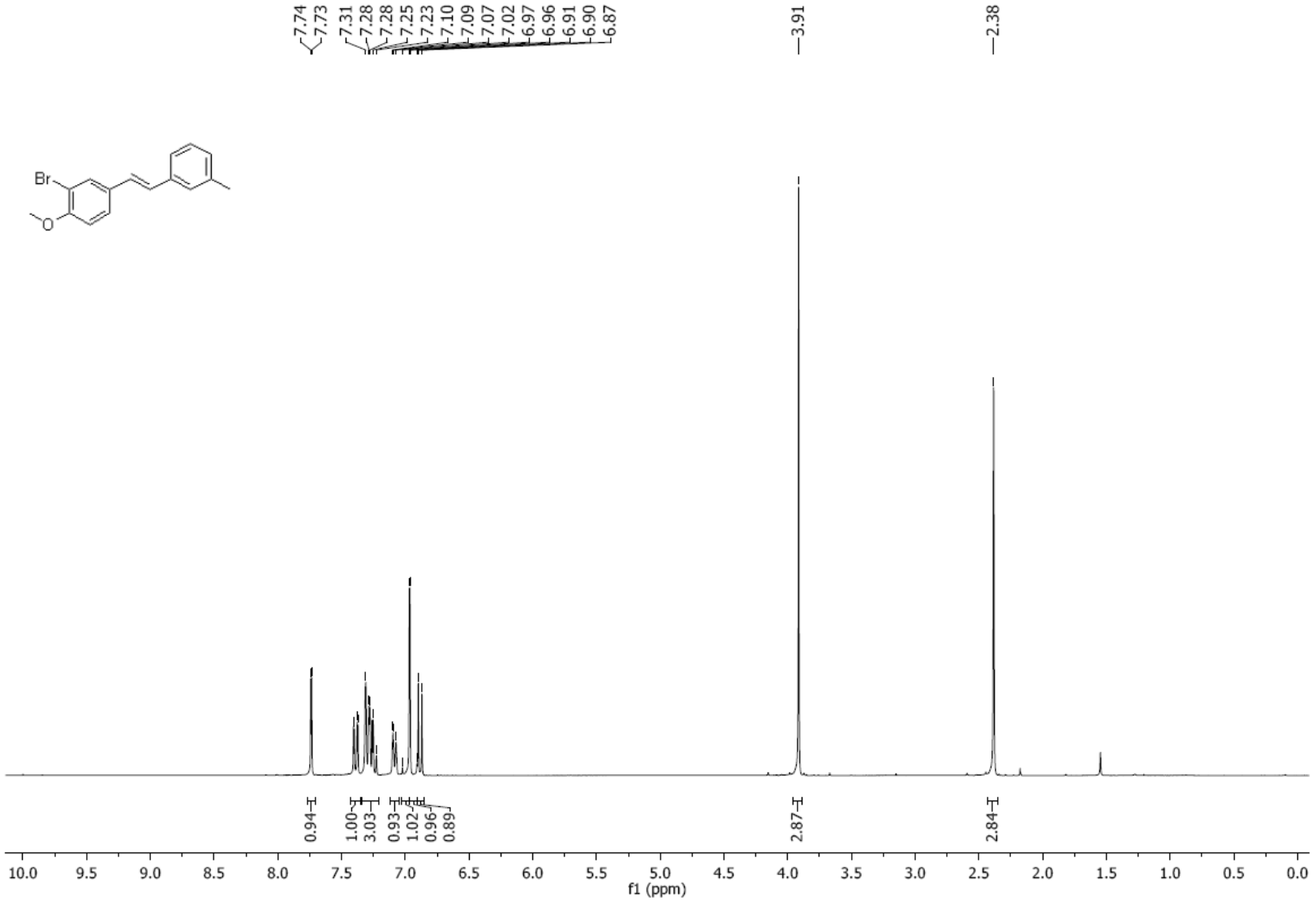
^{1}H NMR (300 MHz, $CDCl_3$) of **6aj**



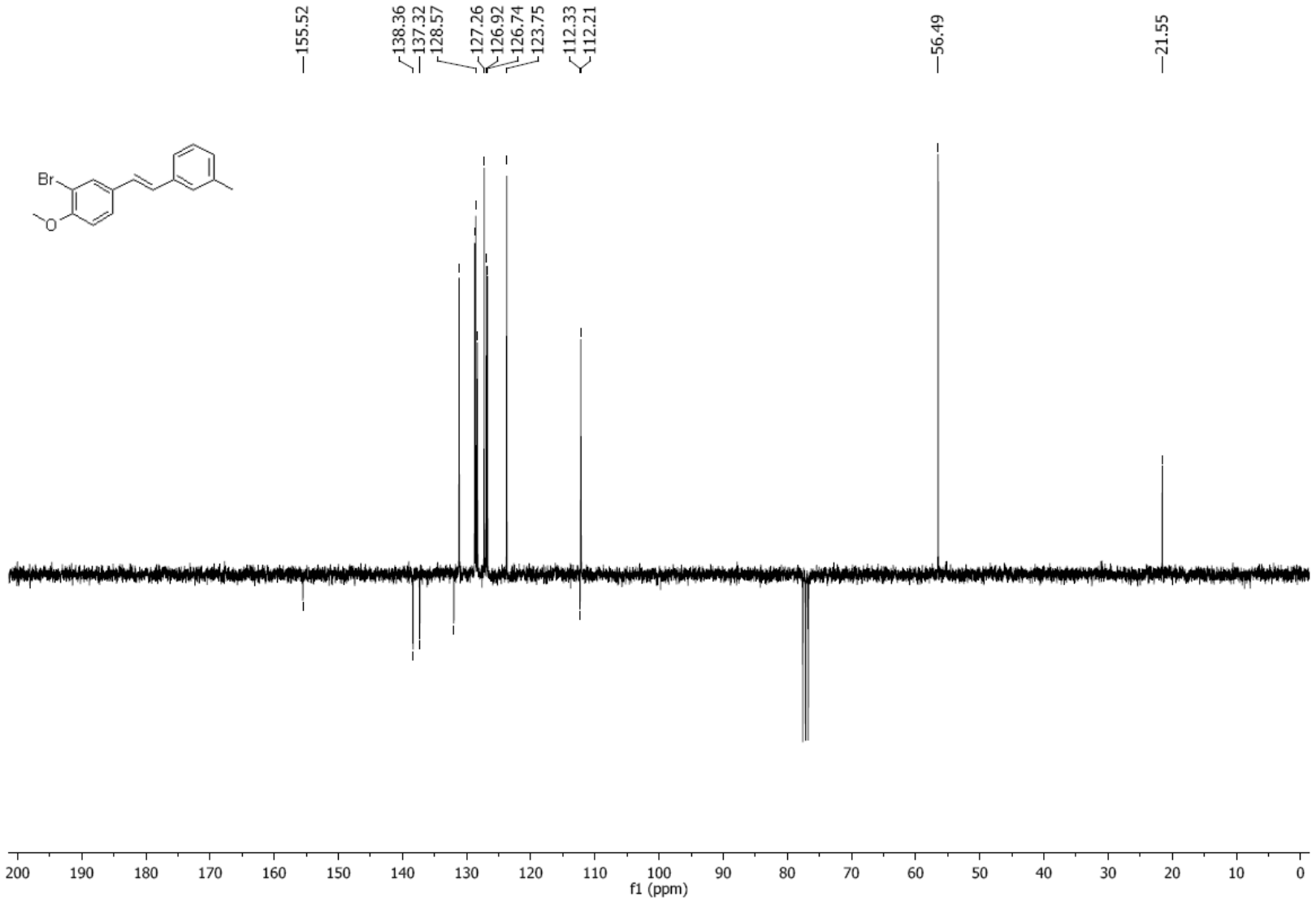
^{13}C NMR (75 MHz, $CDCl_3$) of **6aj**



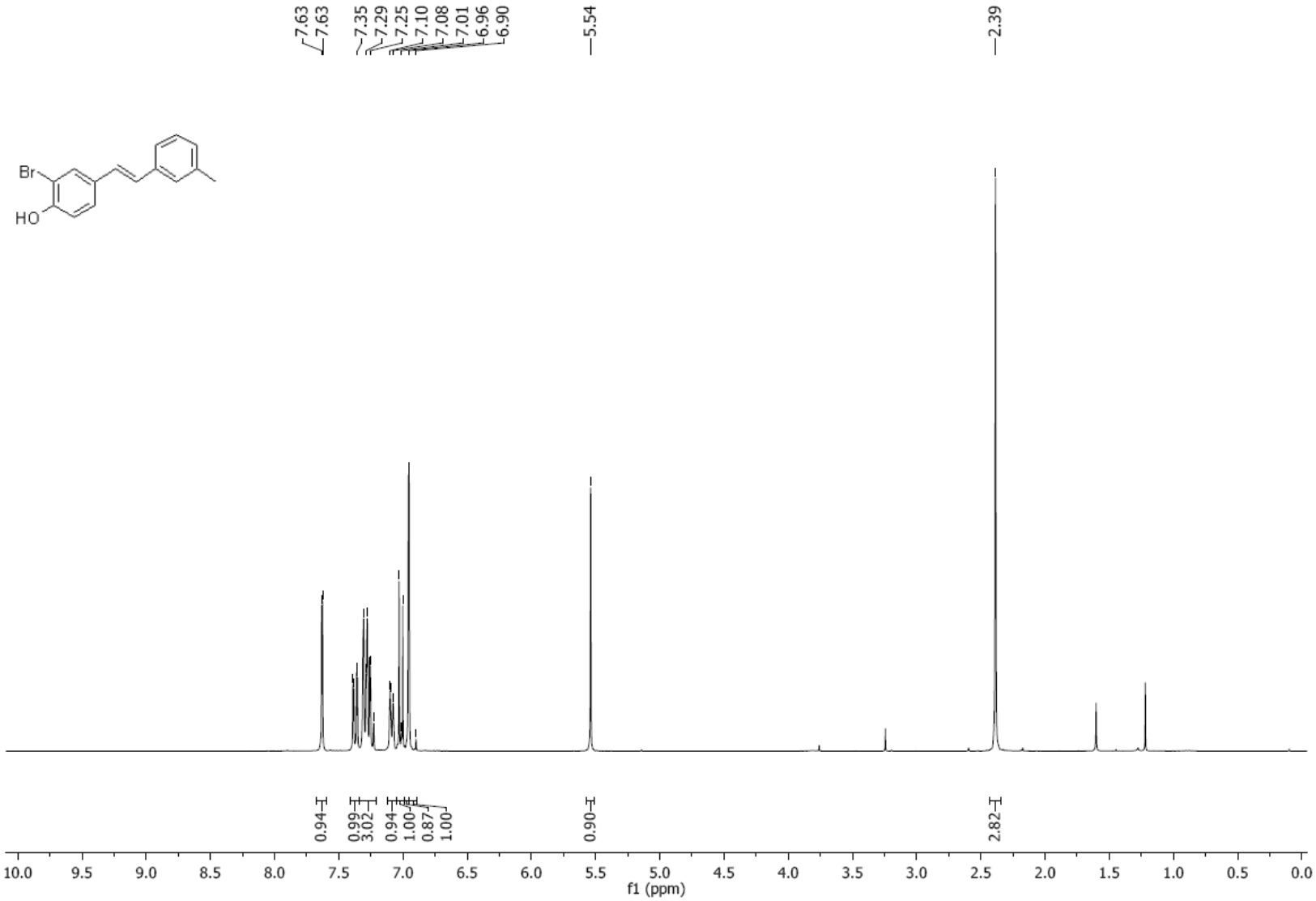
^{1}H NMR (300 MHz, $CDCl_3$) of **6bi**



^{13}C NMR (75 MHz, $CDCl_3$) of **6bi**



^{1}H NMR (300 MHz, $CDCl_3$) of **6bj**



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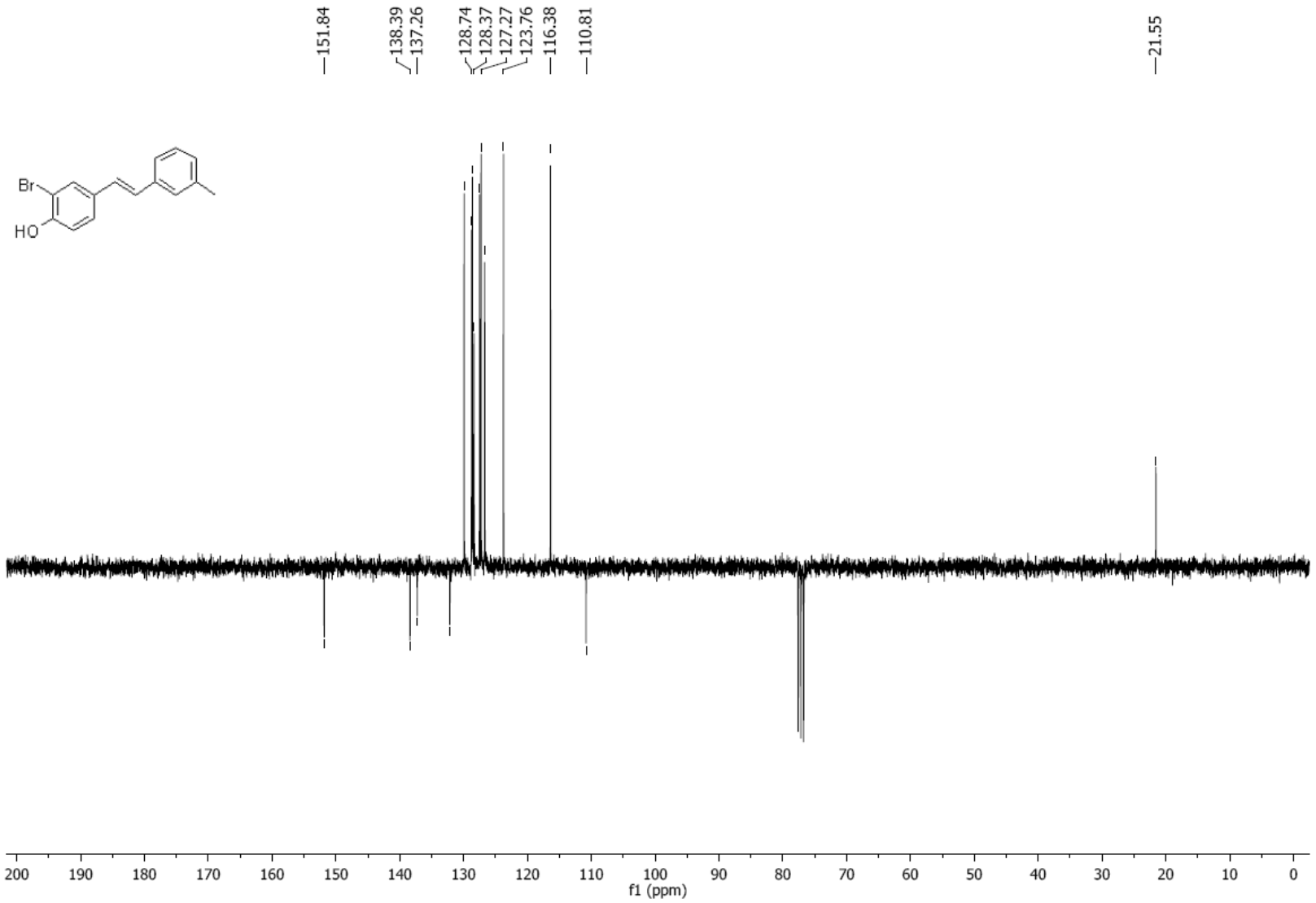

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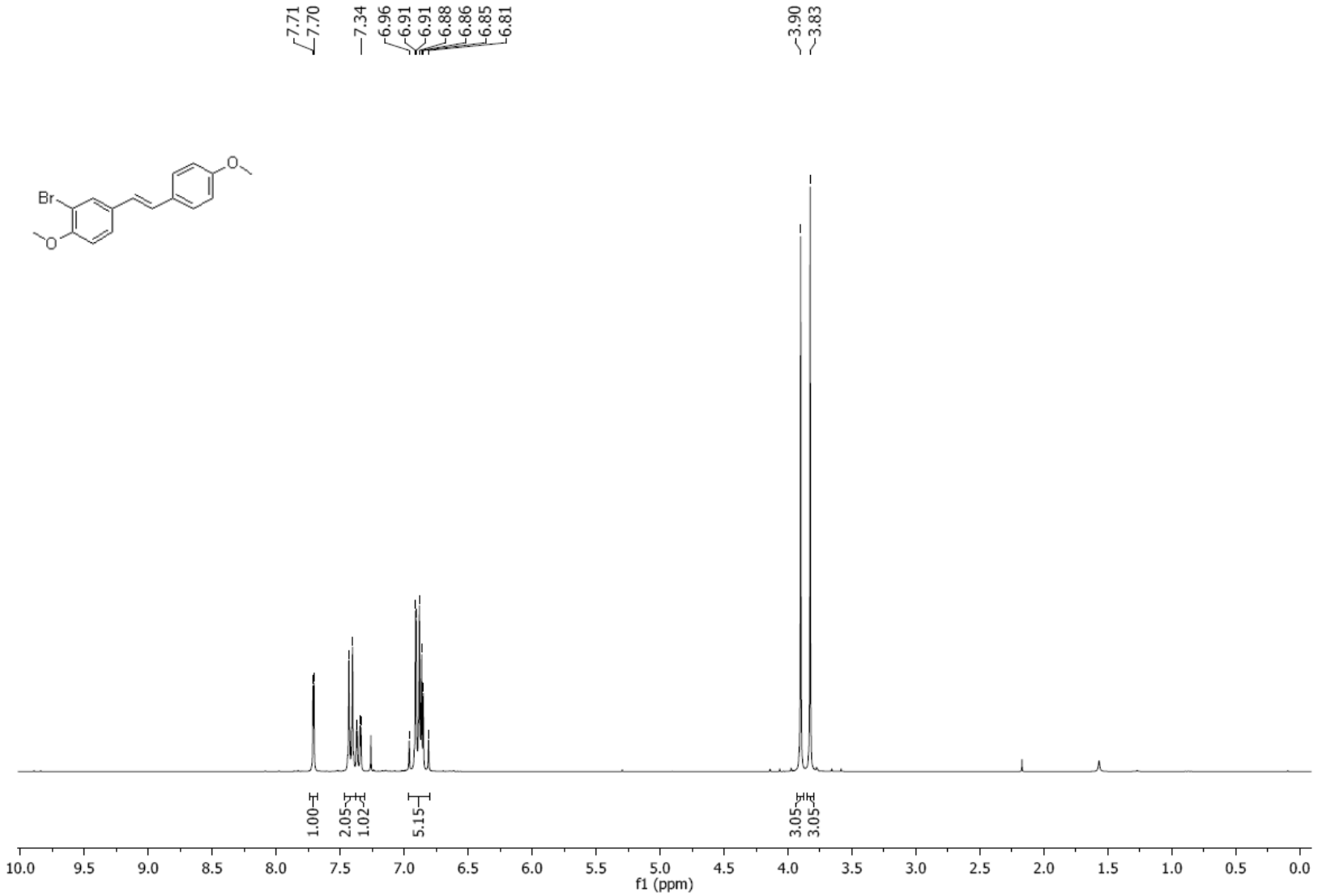
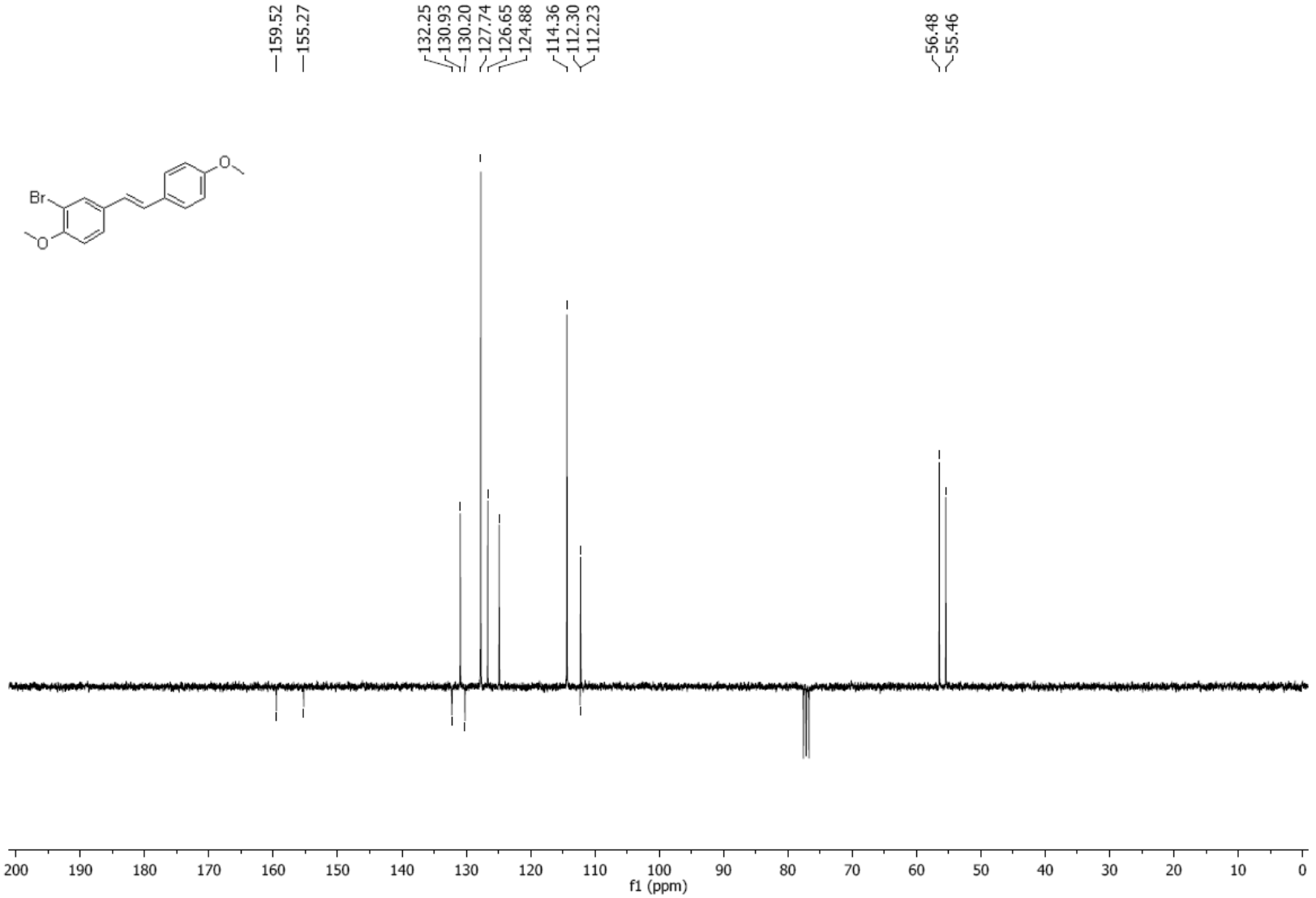
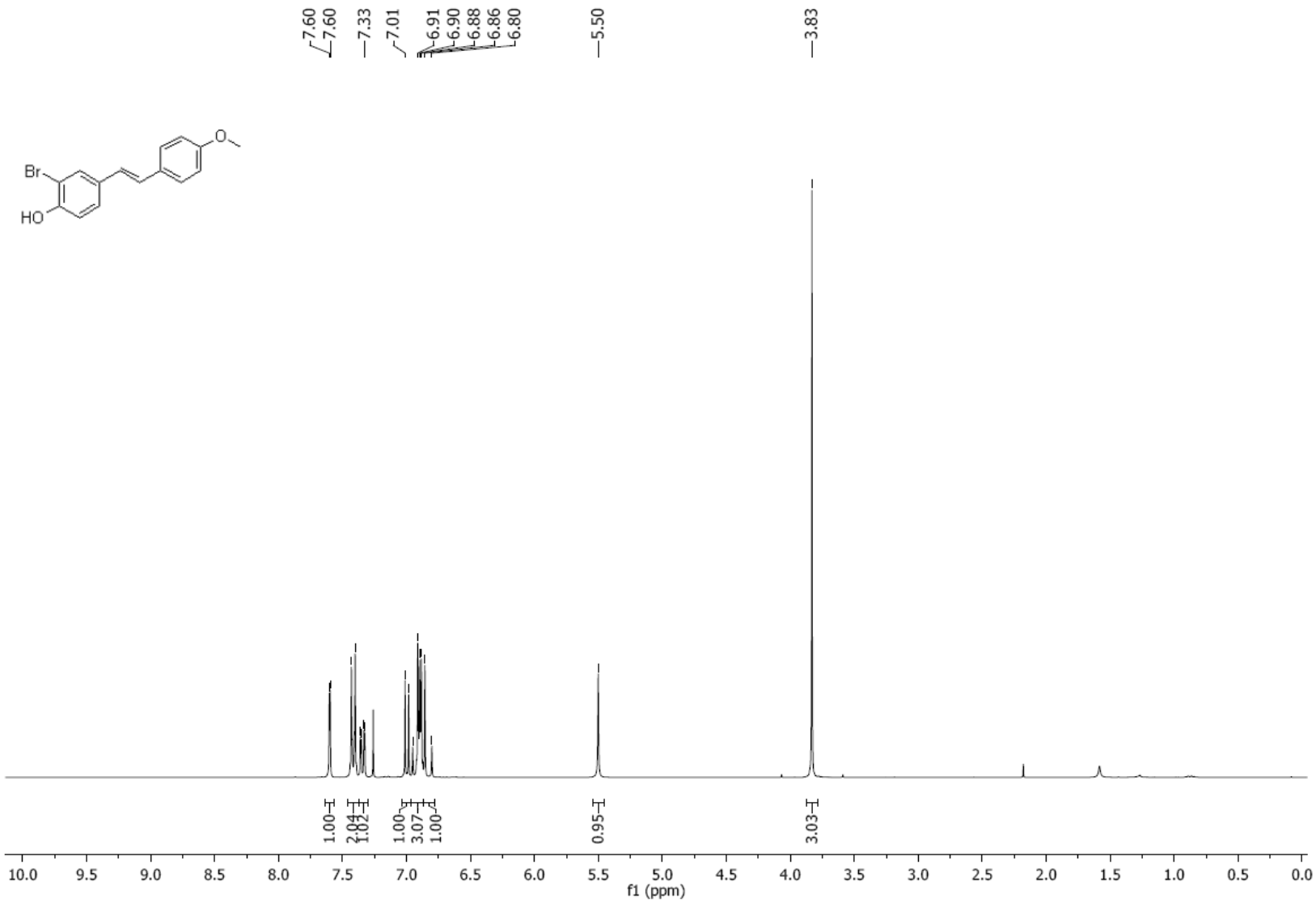


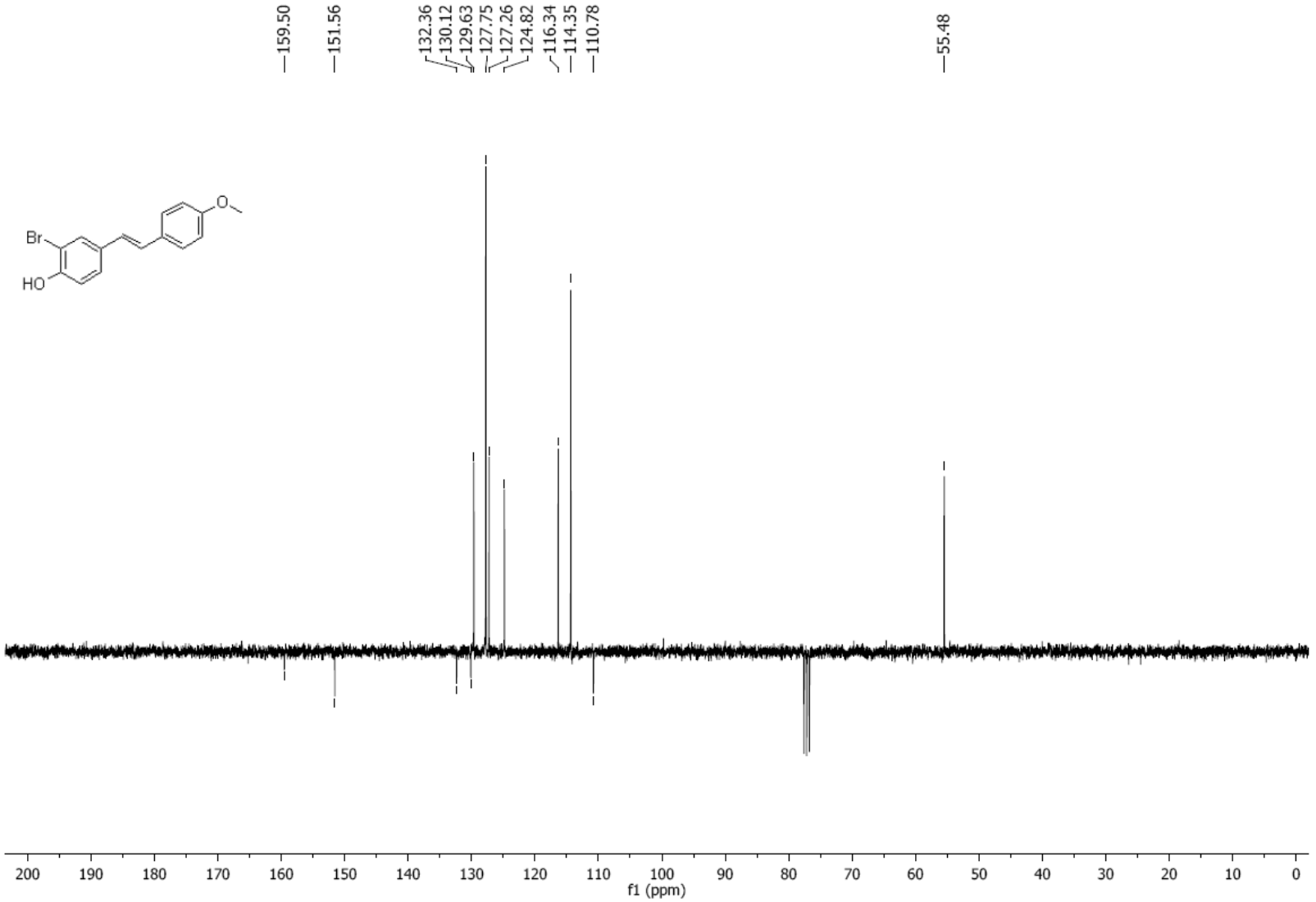
^{13}C NMR (75 MHz, $CDCl_3$) of **6ci**



^{1}H NMR (300 MHz, $CDCl_3$) of **6cj**



^{13}C NMR (75 MHz, $CDCl_3$) of **6cj**



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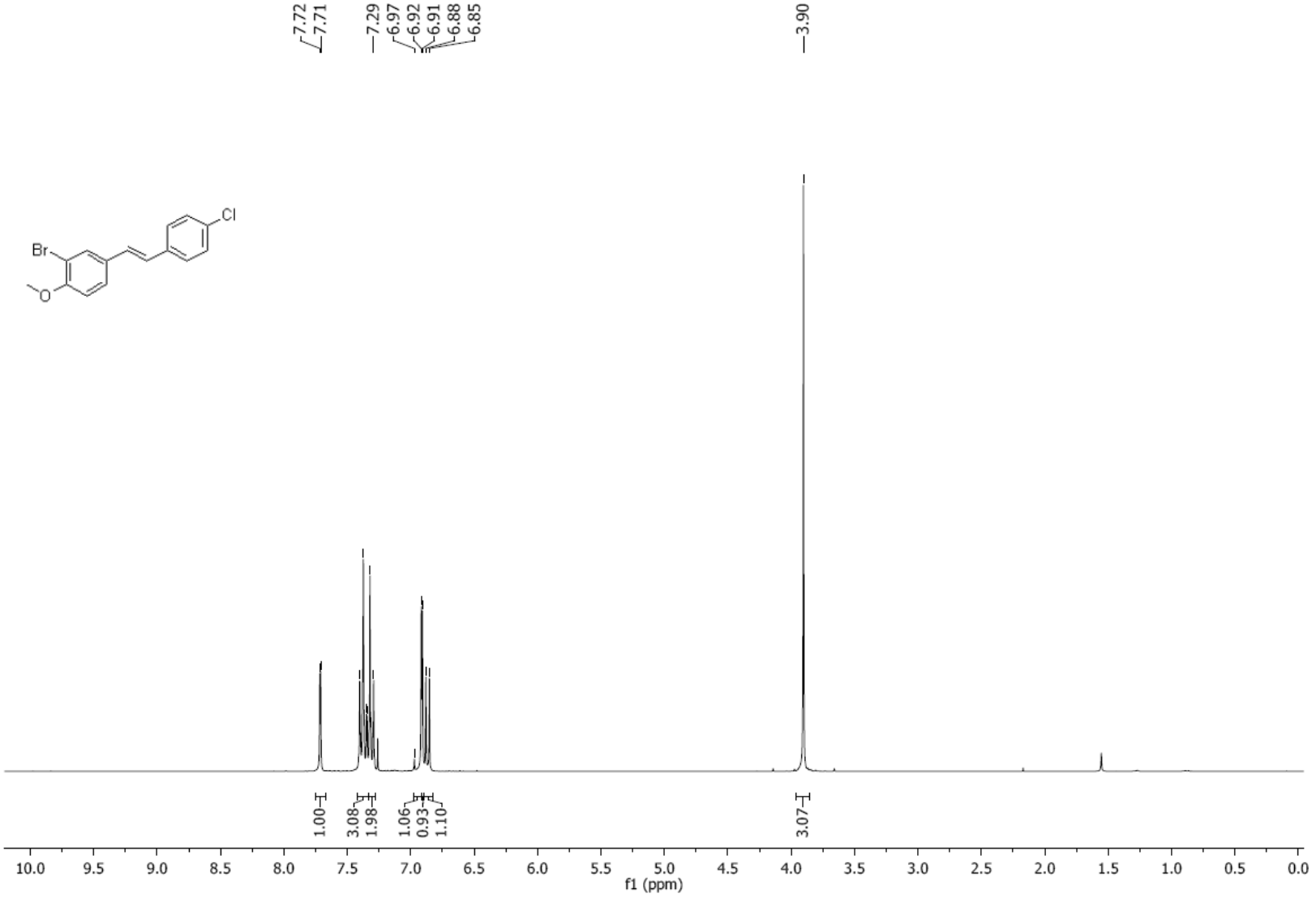

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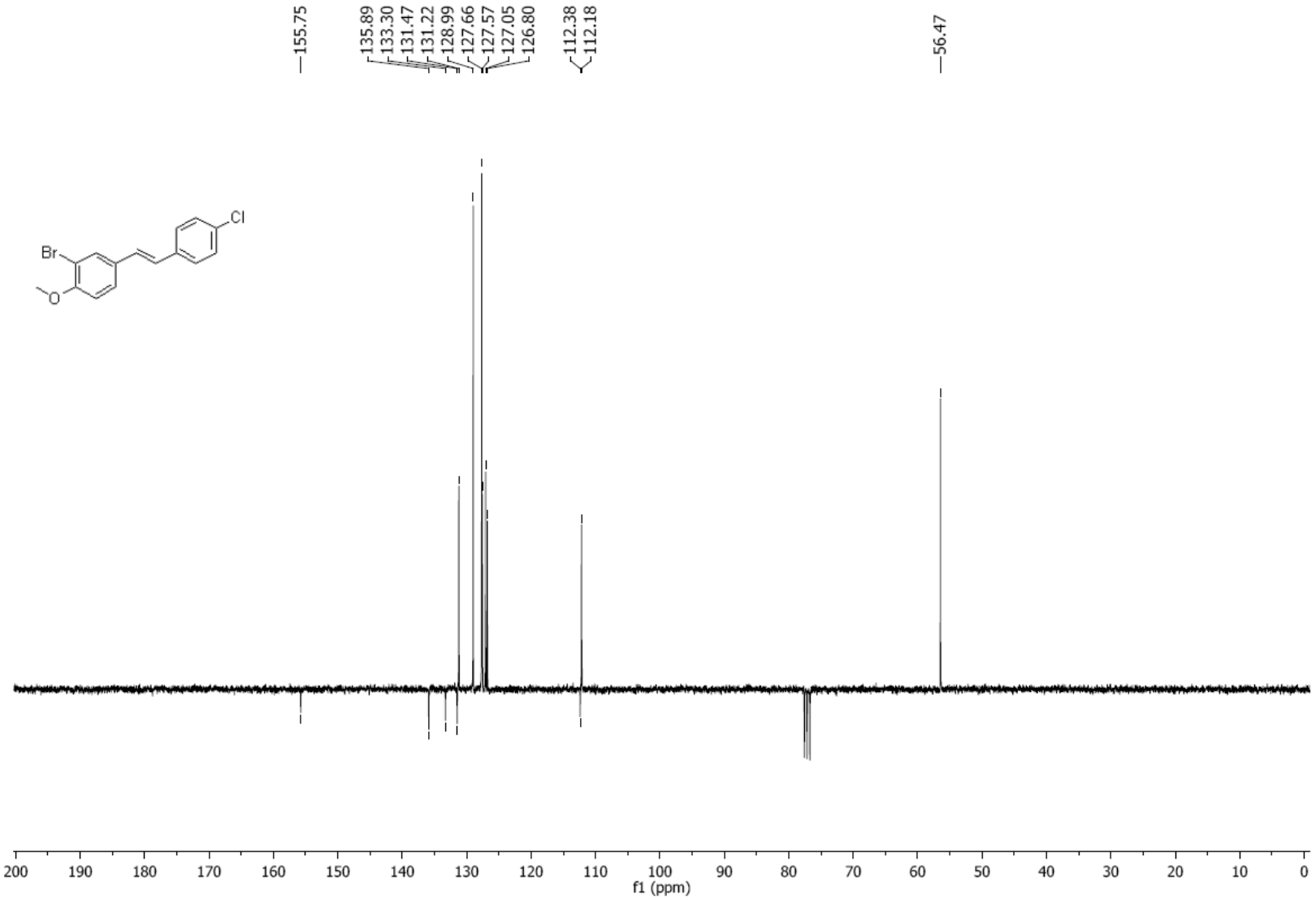
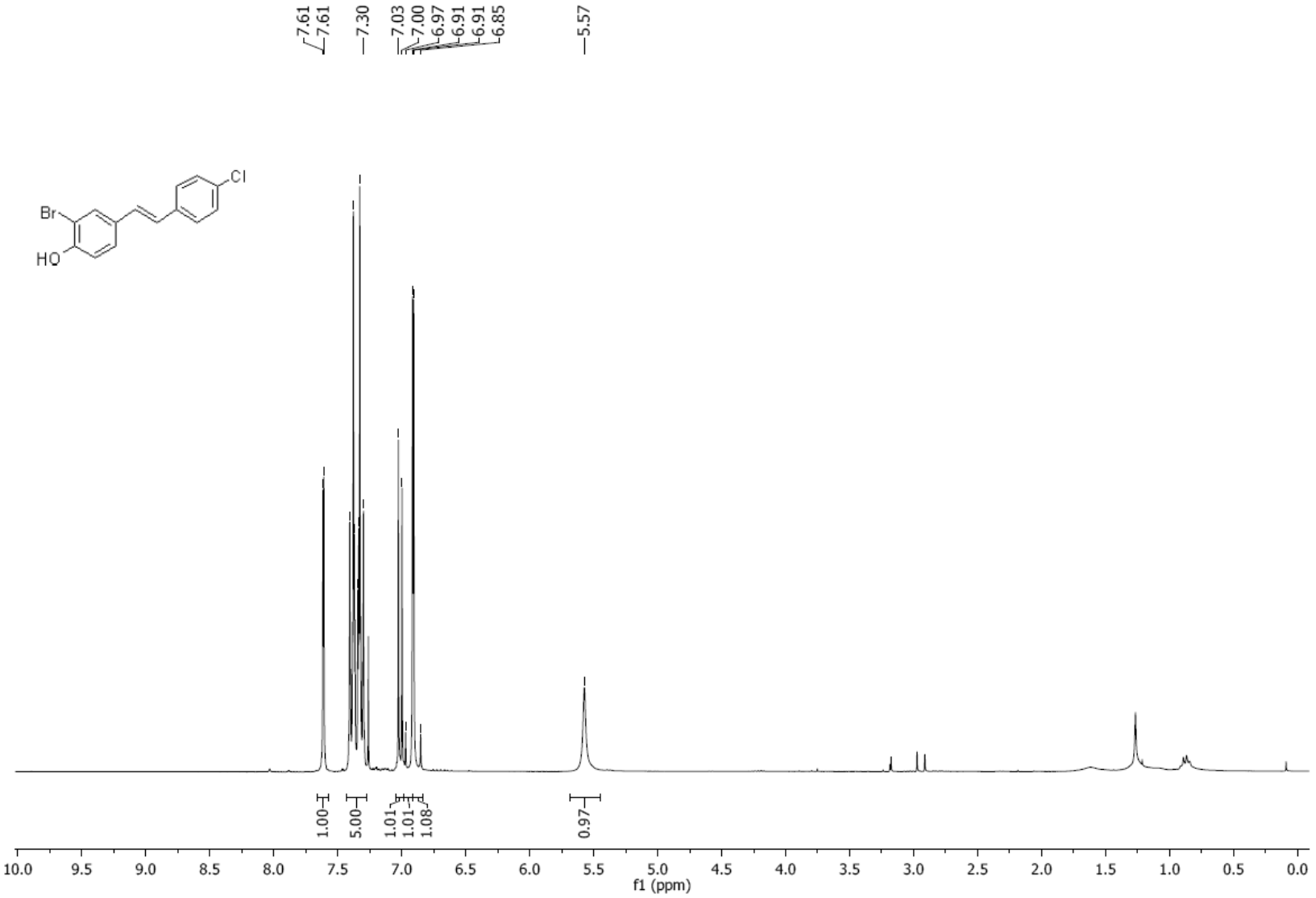


^{1}H NMR (300 MHz, $CDCl_3$) of **6dj**



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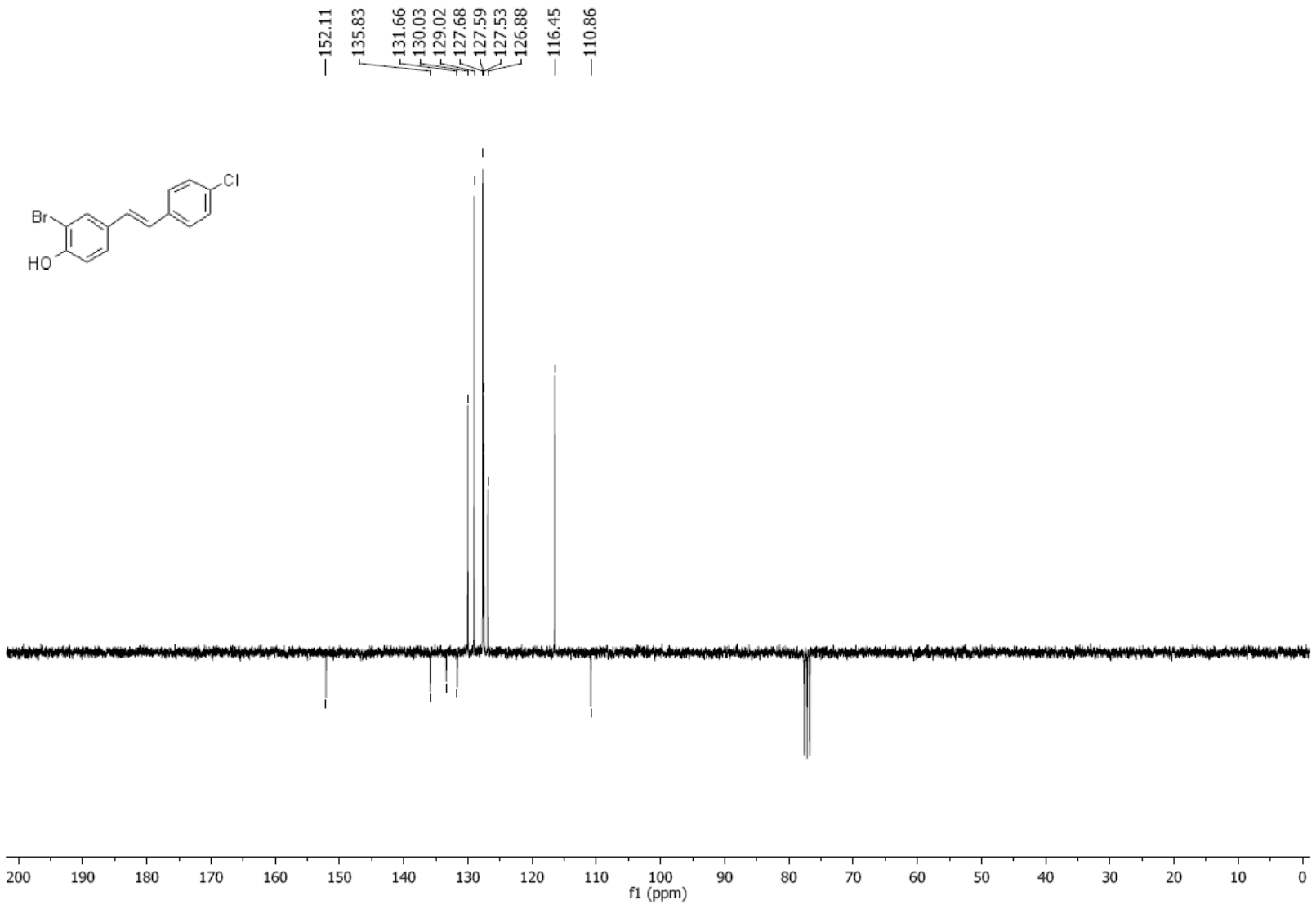

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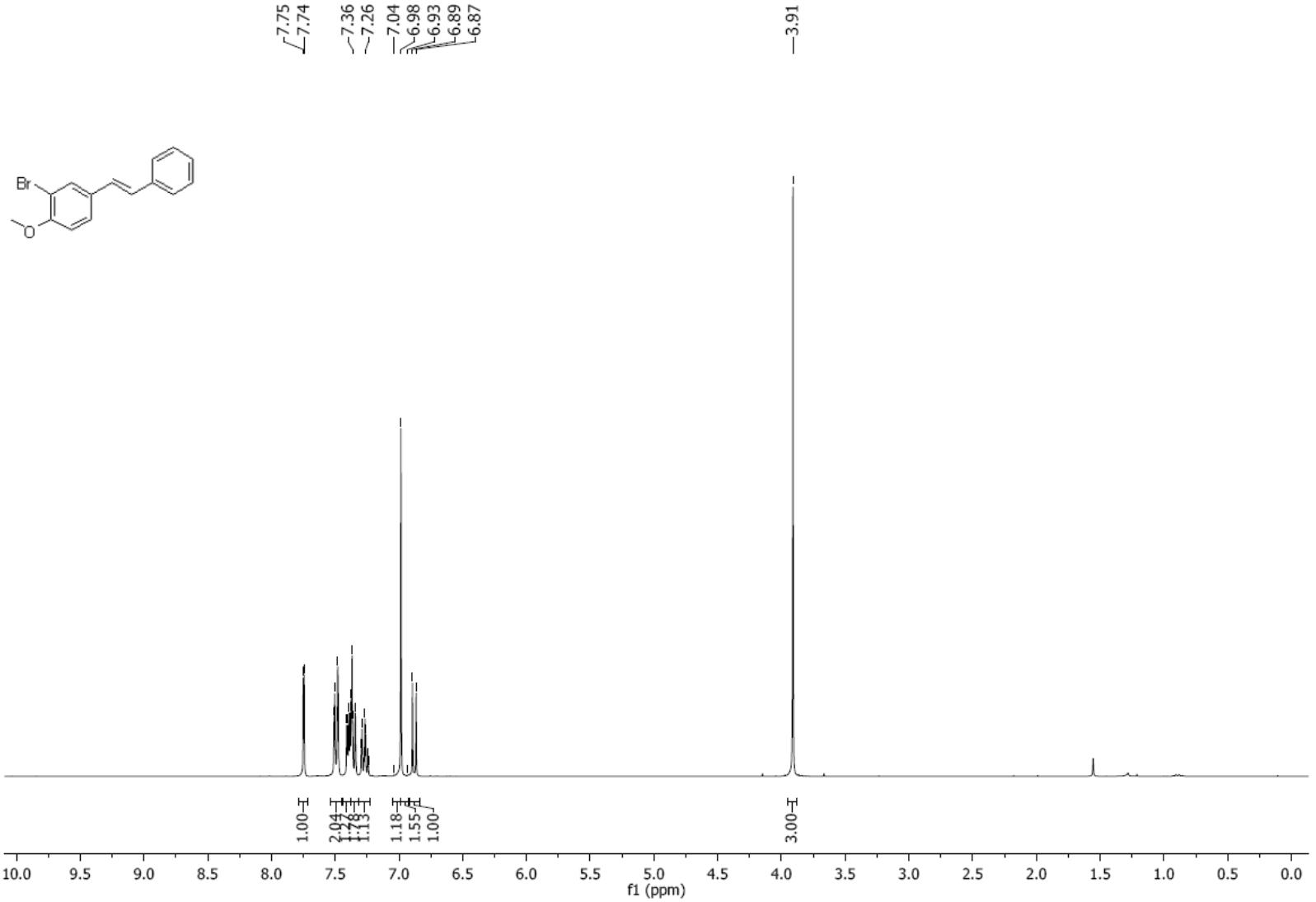

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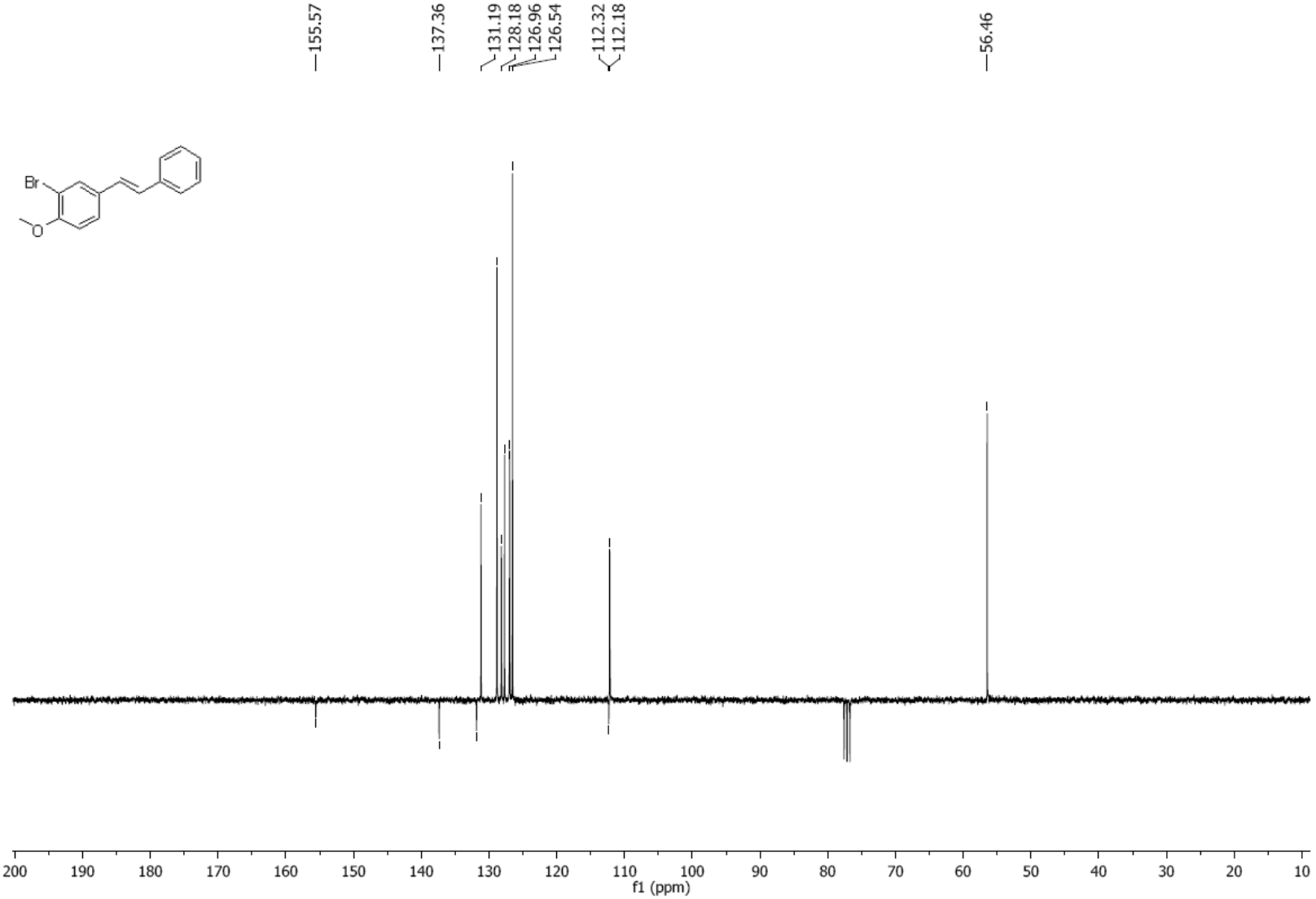

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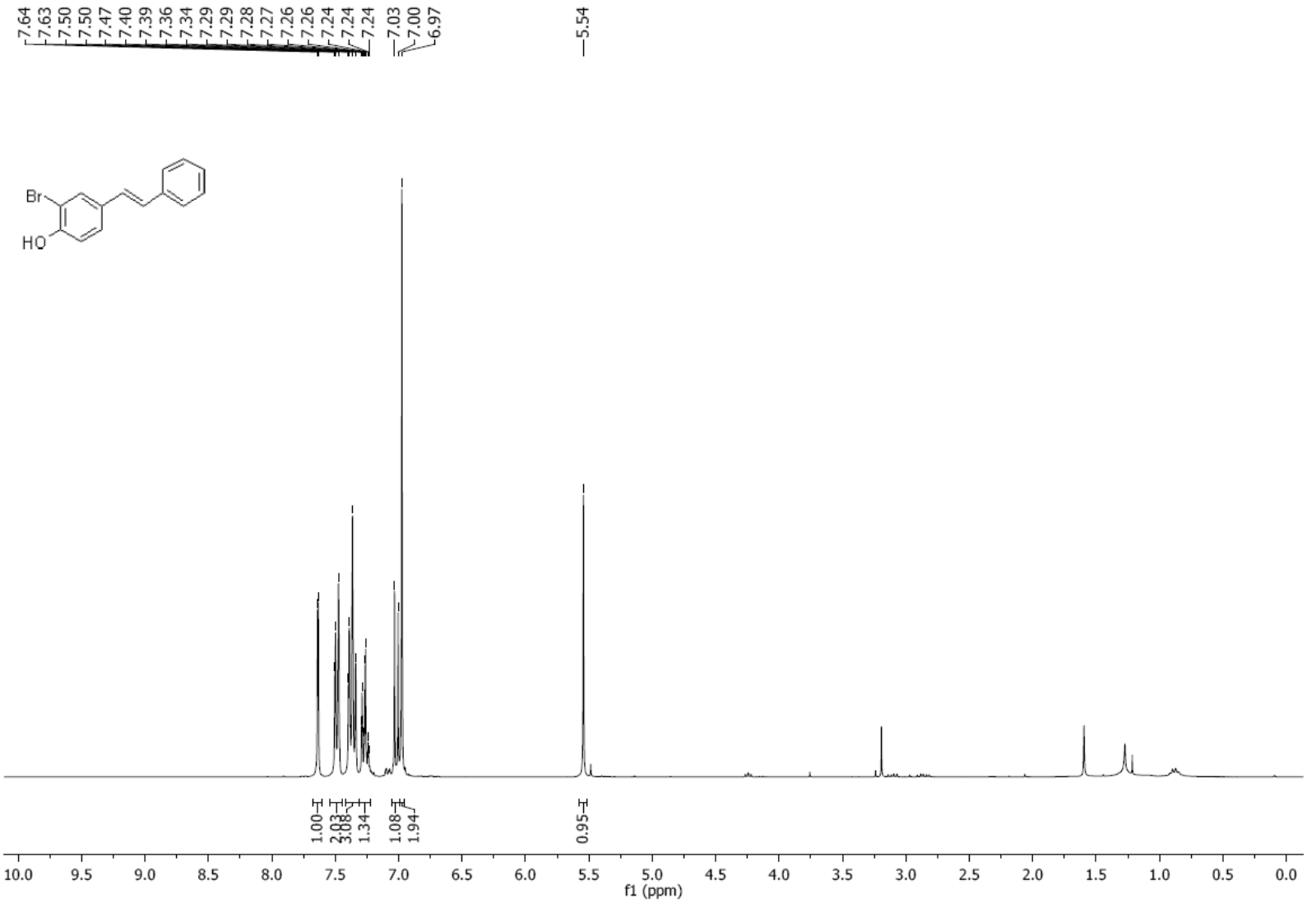
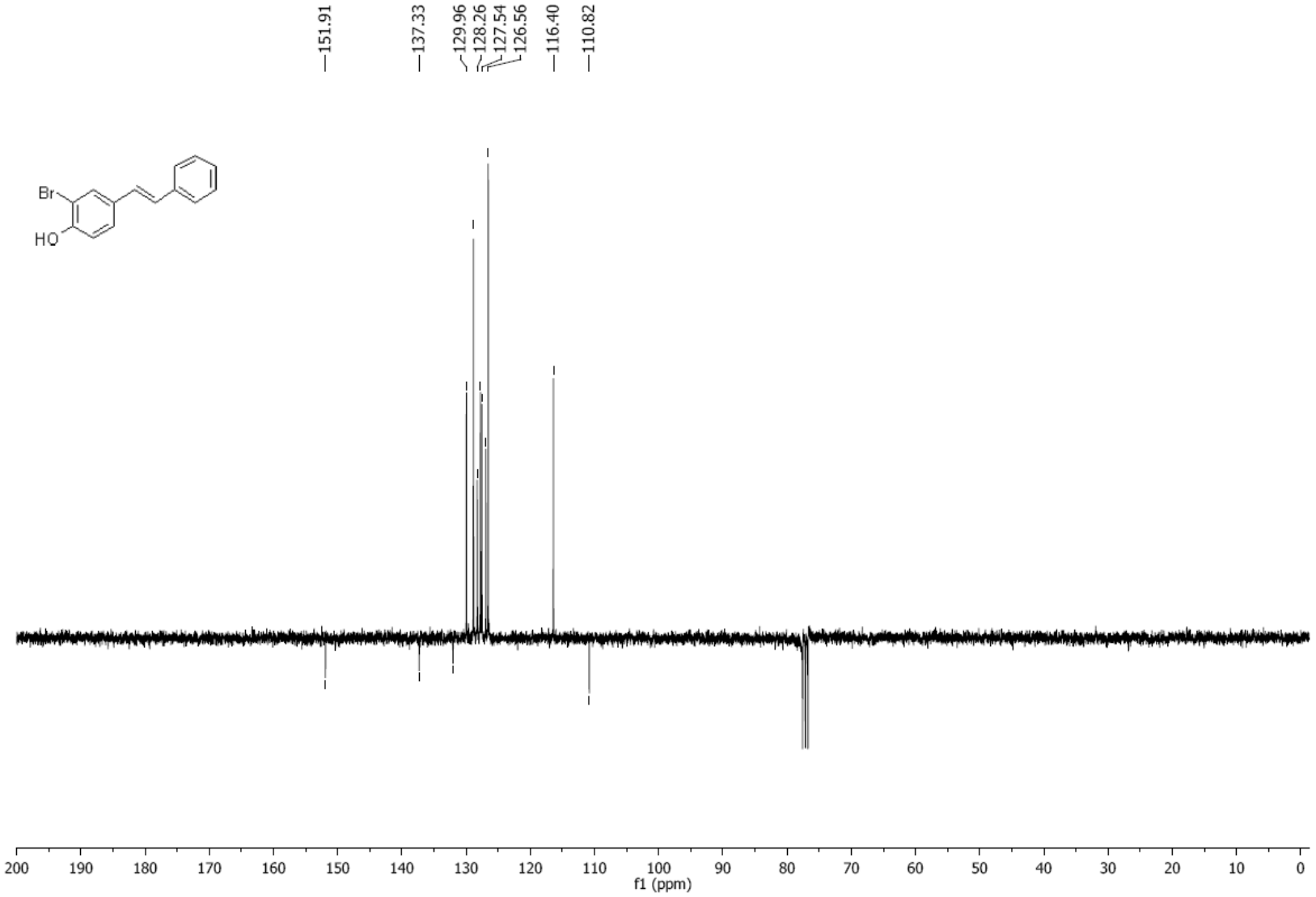
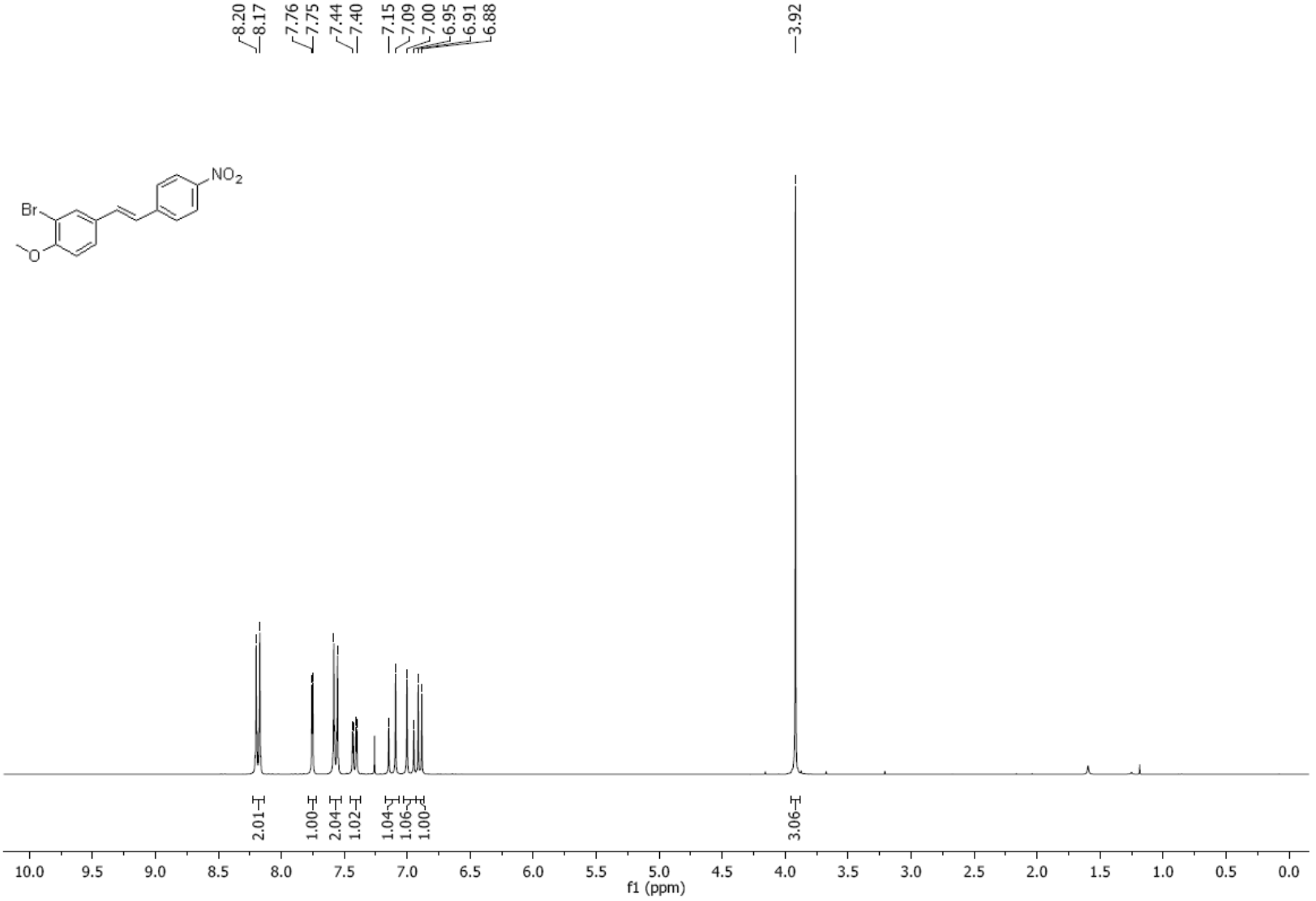


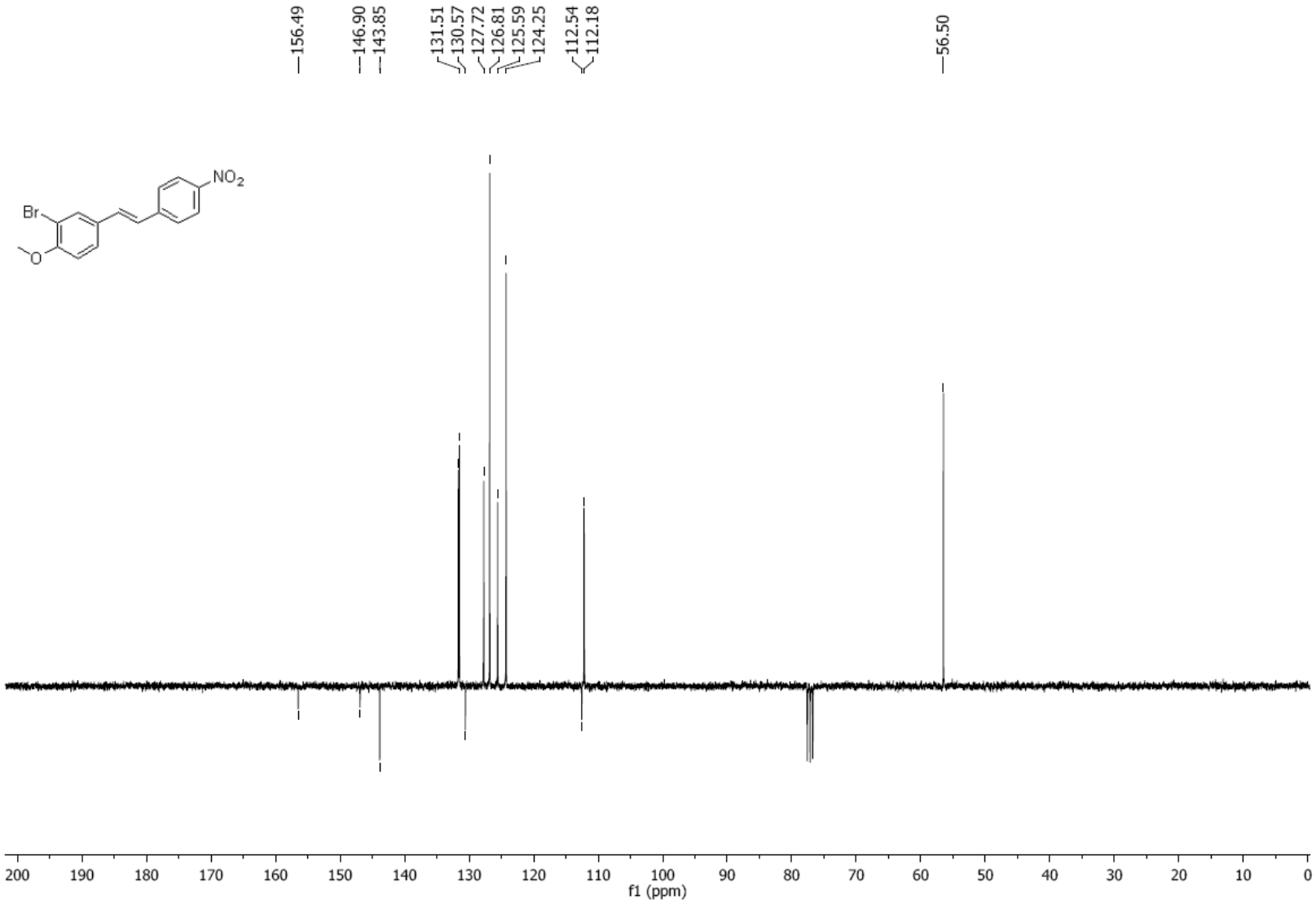
^{13}C NMR (75 MHz, $CDCl_3$) of **6fj**



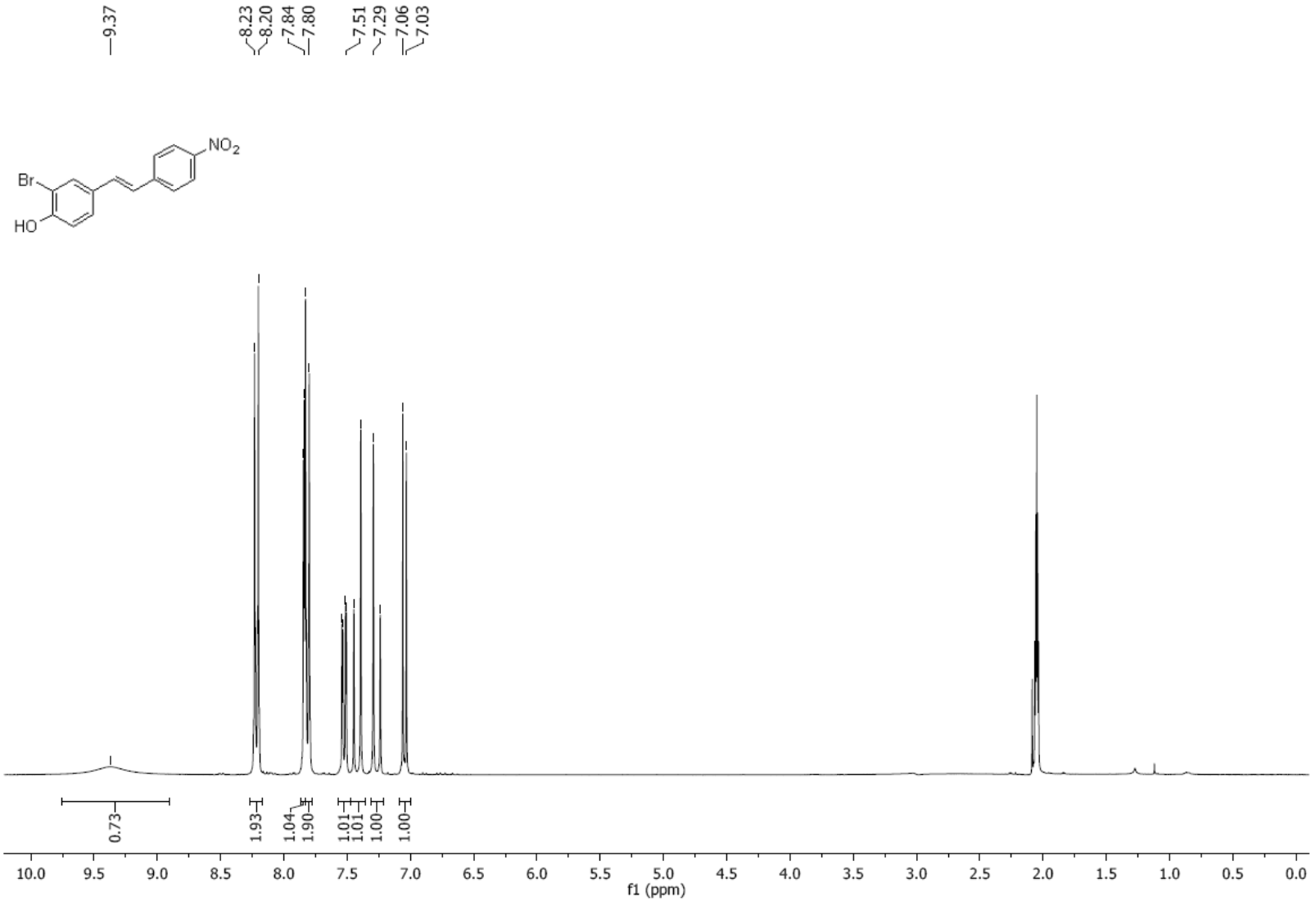
^{1}H NMR (300 MHz, $CDCl_3$) of **6gi**



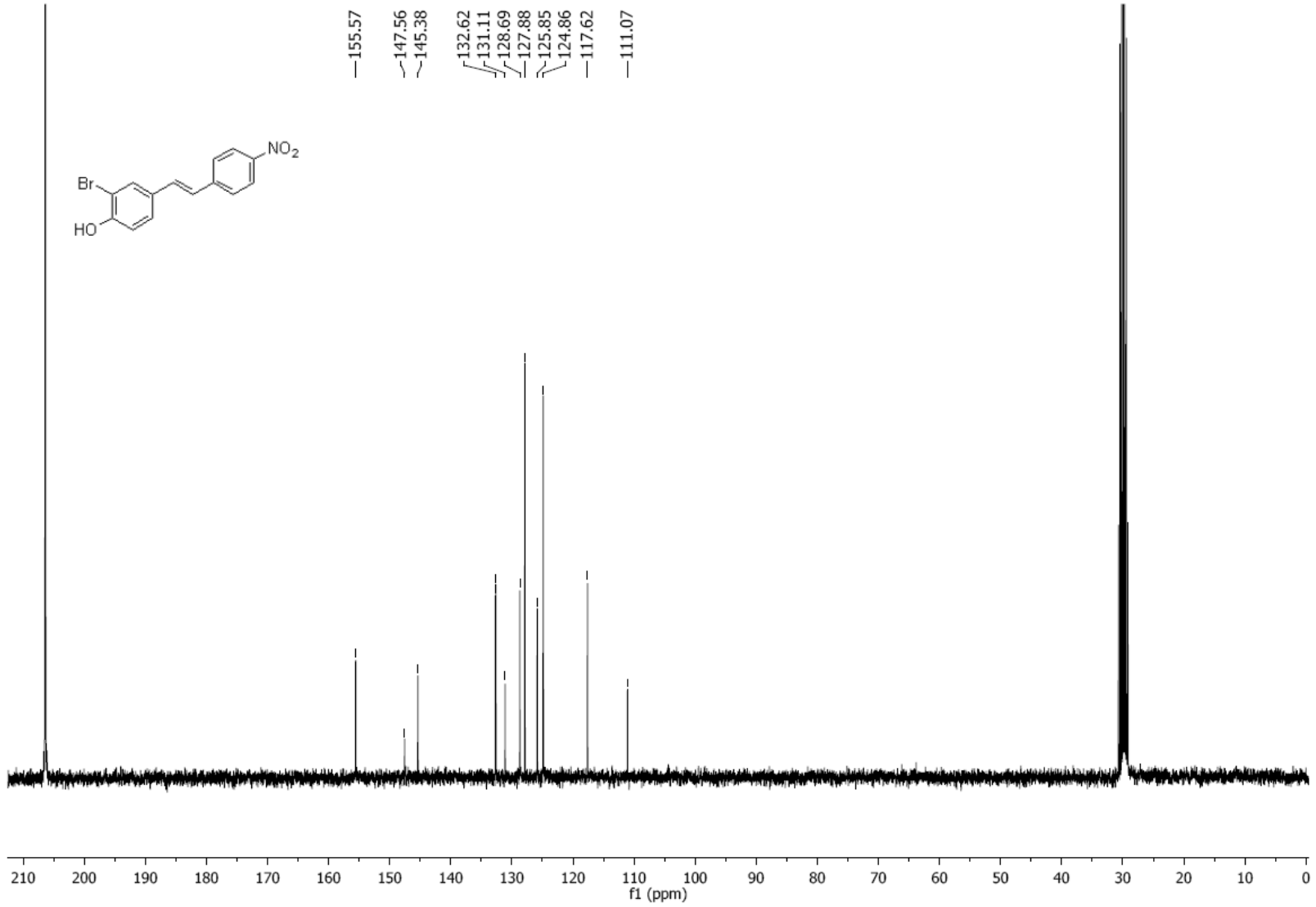
^{13}C NMR (75 MHz, $CDCl_3$) of **6gi**



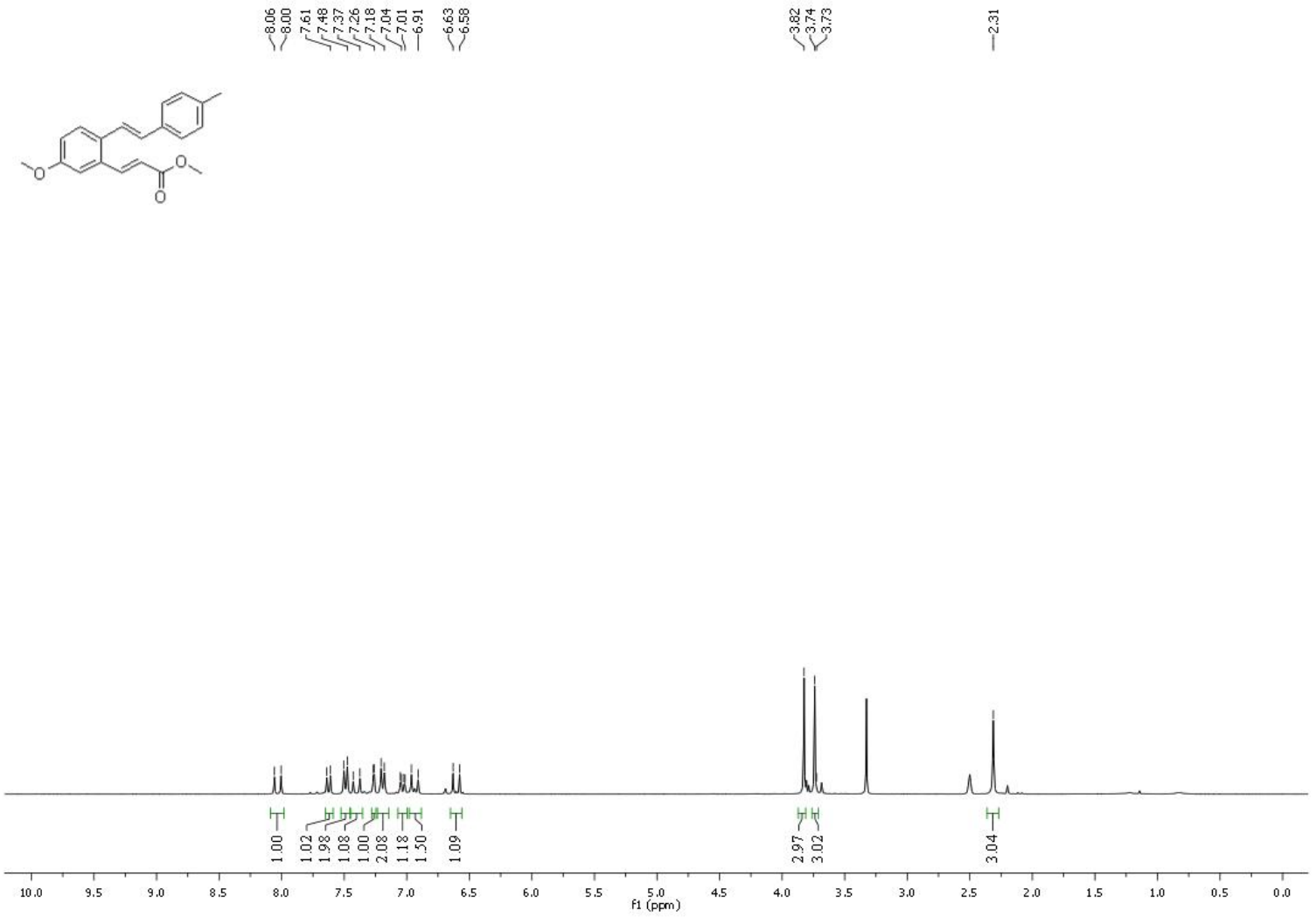
^{1}H NMR (300 MHz, acetone-d_6) of **6gj**



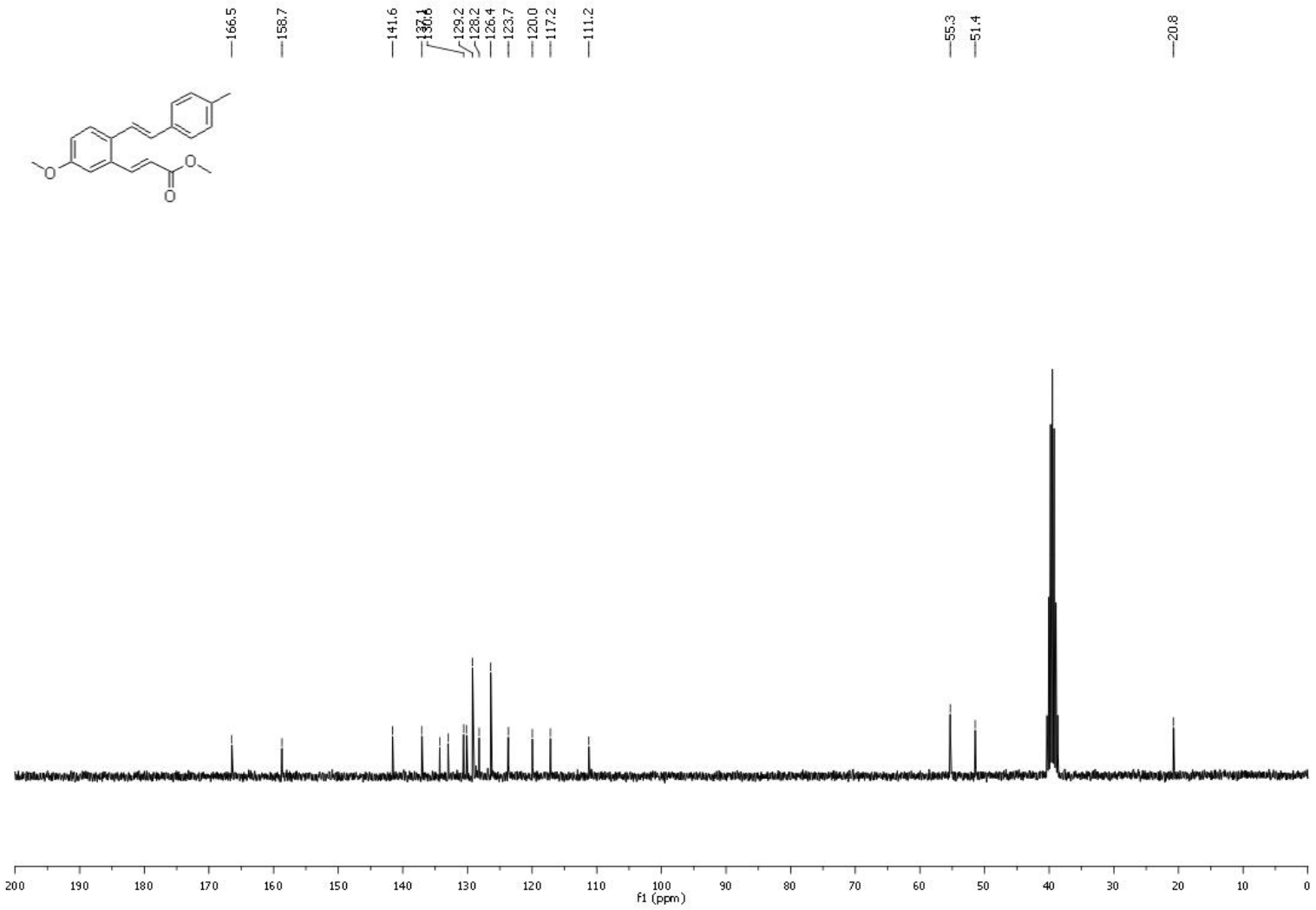
^{13}C NMR (75 MHz, acetone-d_6) of **6gj**



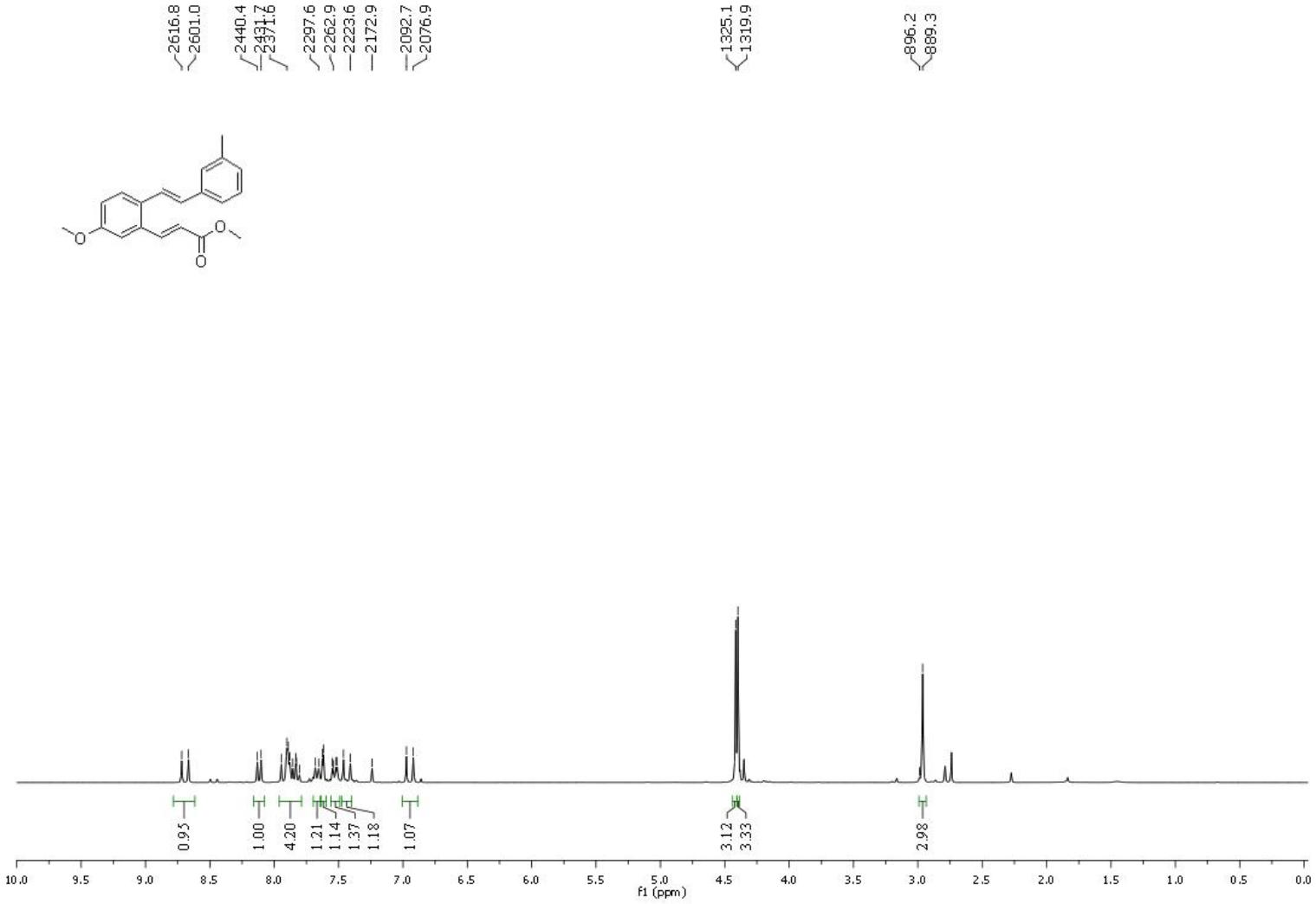
^{1}H NMR (300 MHz, DMSO-d_6) of **6ak**



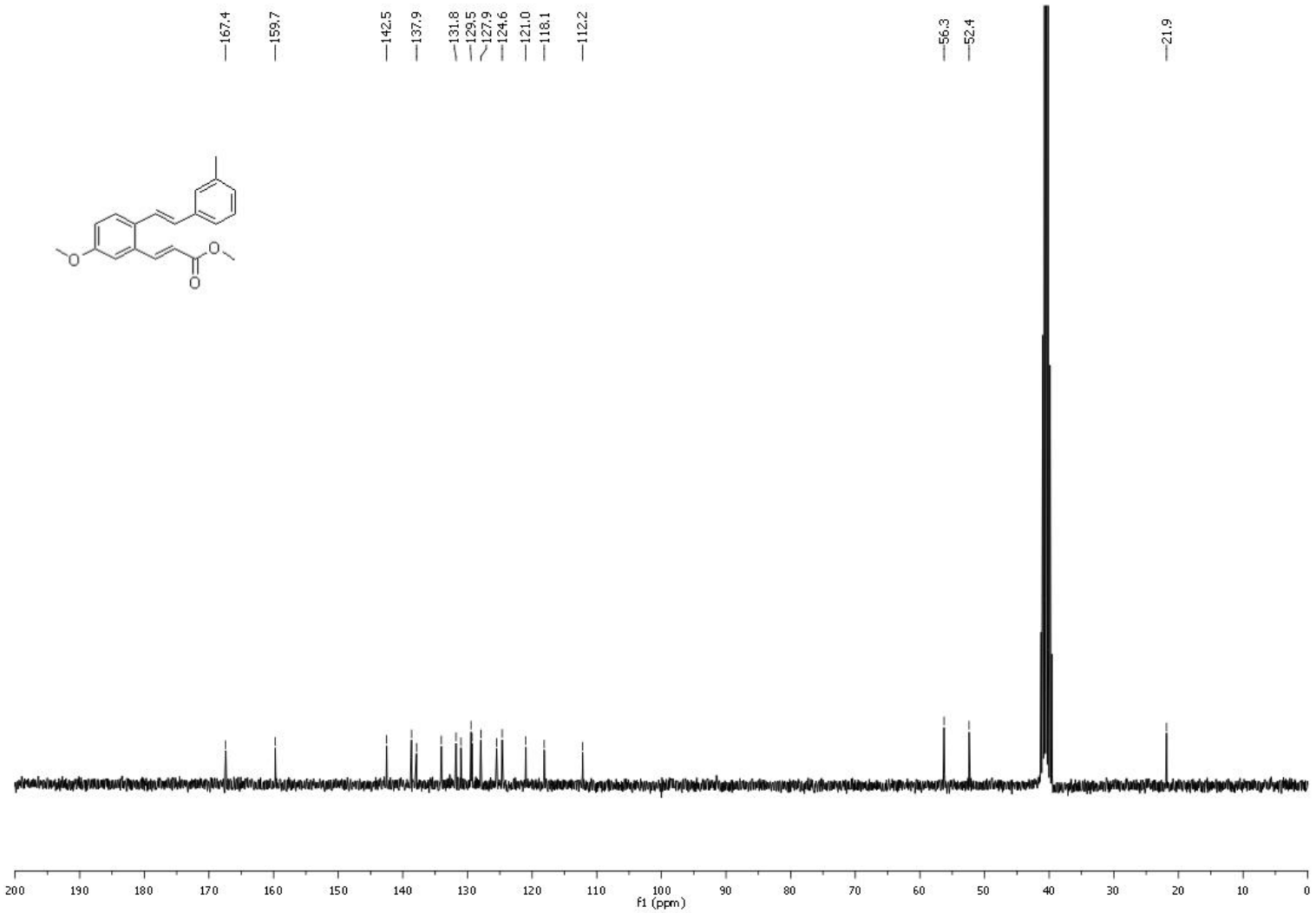
^{13}C NMR (75 MHz, DMSO-d_6) of **6ak**



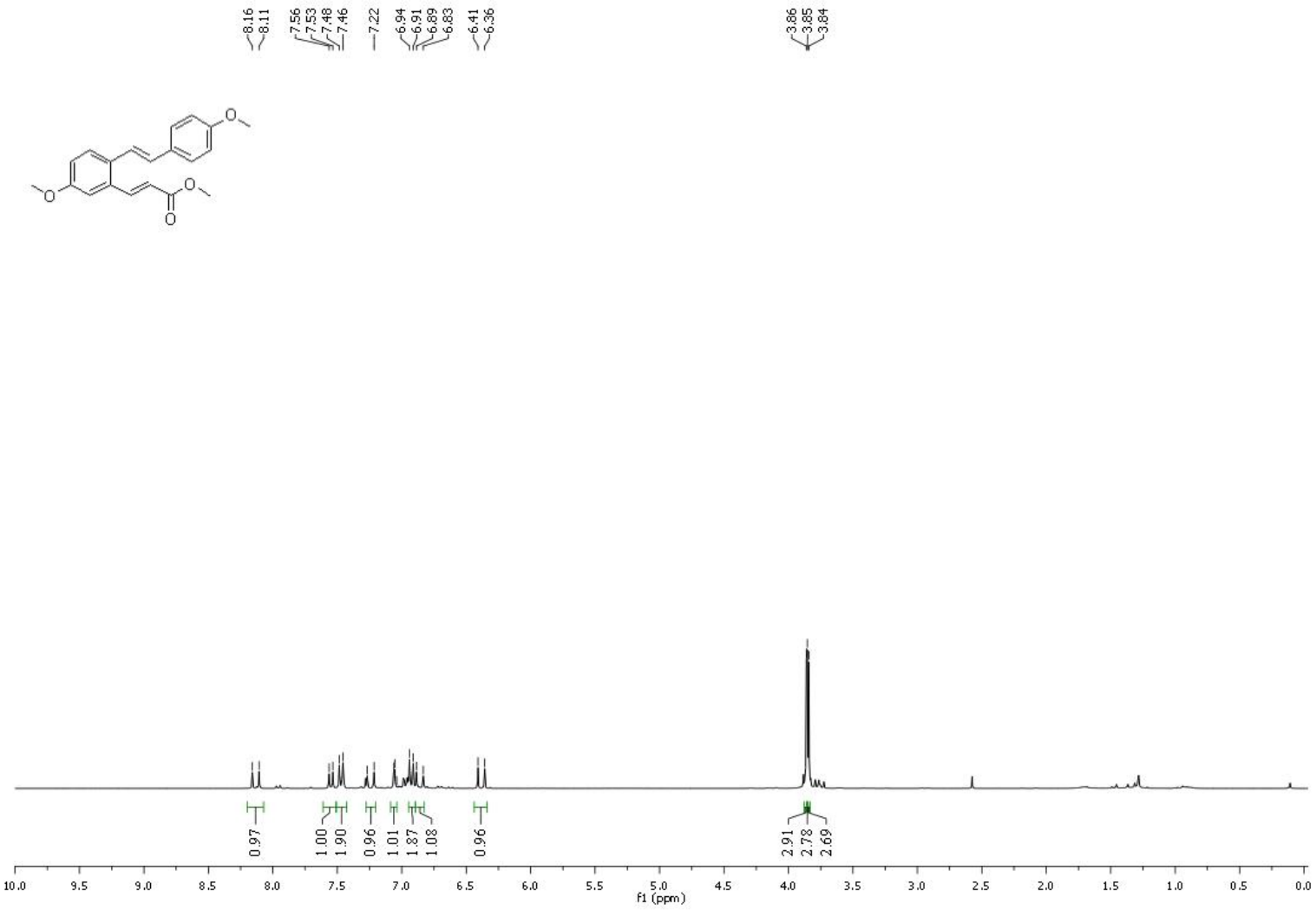
^{1}H NMR (300 MHz, DMSO-d_6) of **6bk**



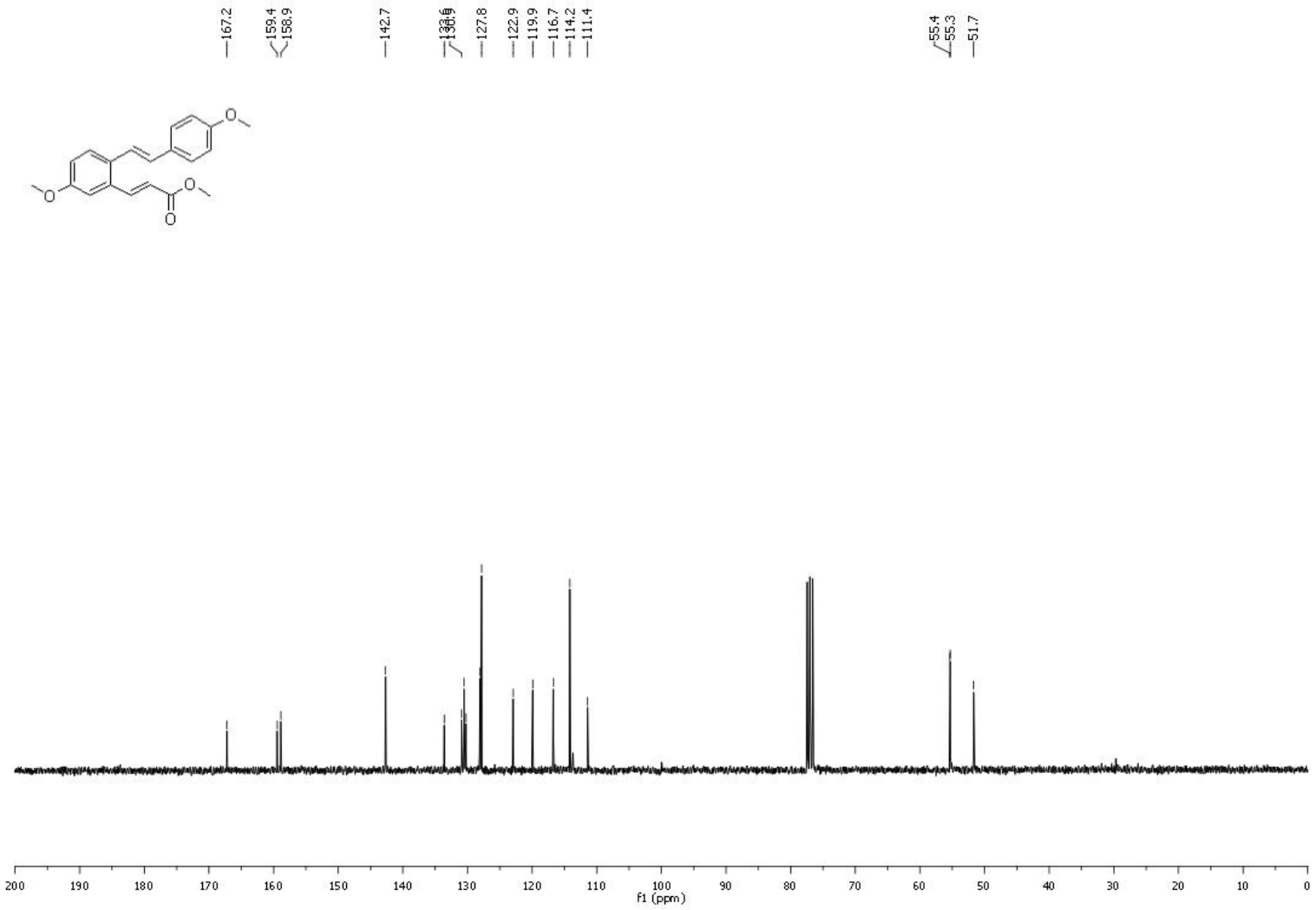
^{13}C NMR (75 MHz, DMSO-d_6) of **6bk**



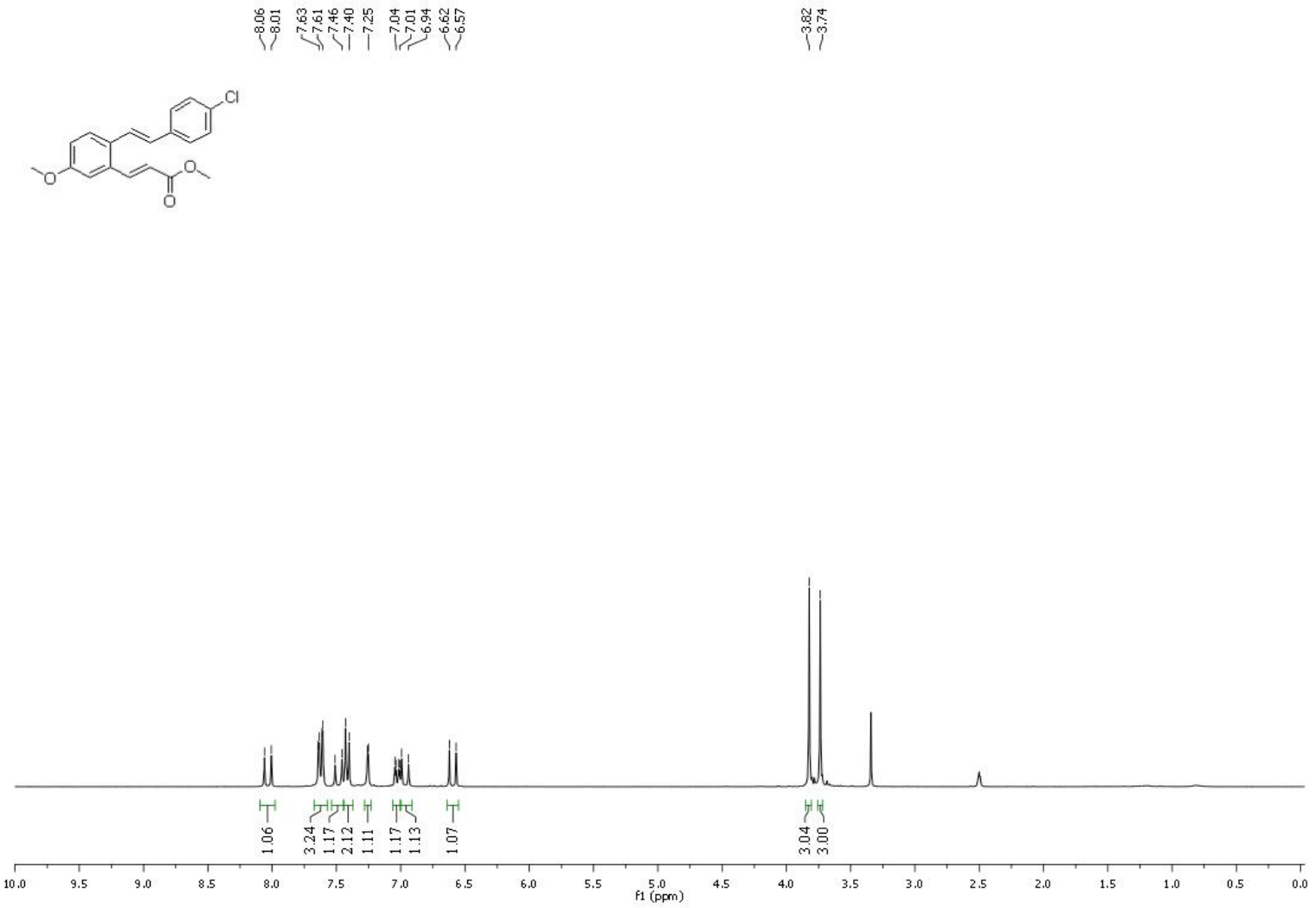
^{1}H NMR (300 MHz, DMSO-d_6) of **6ck**



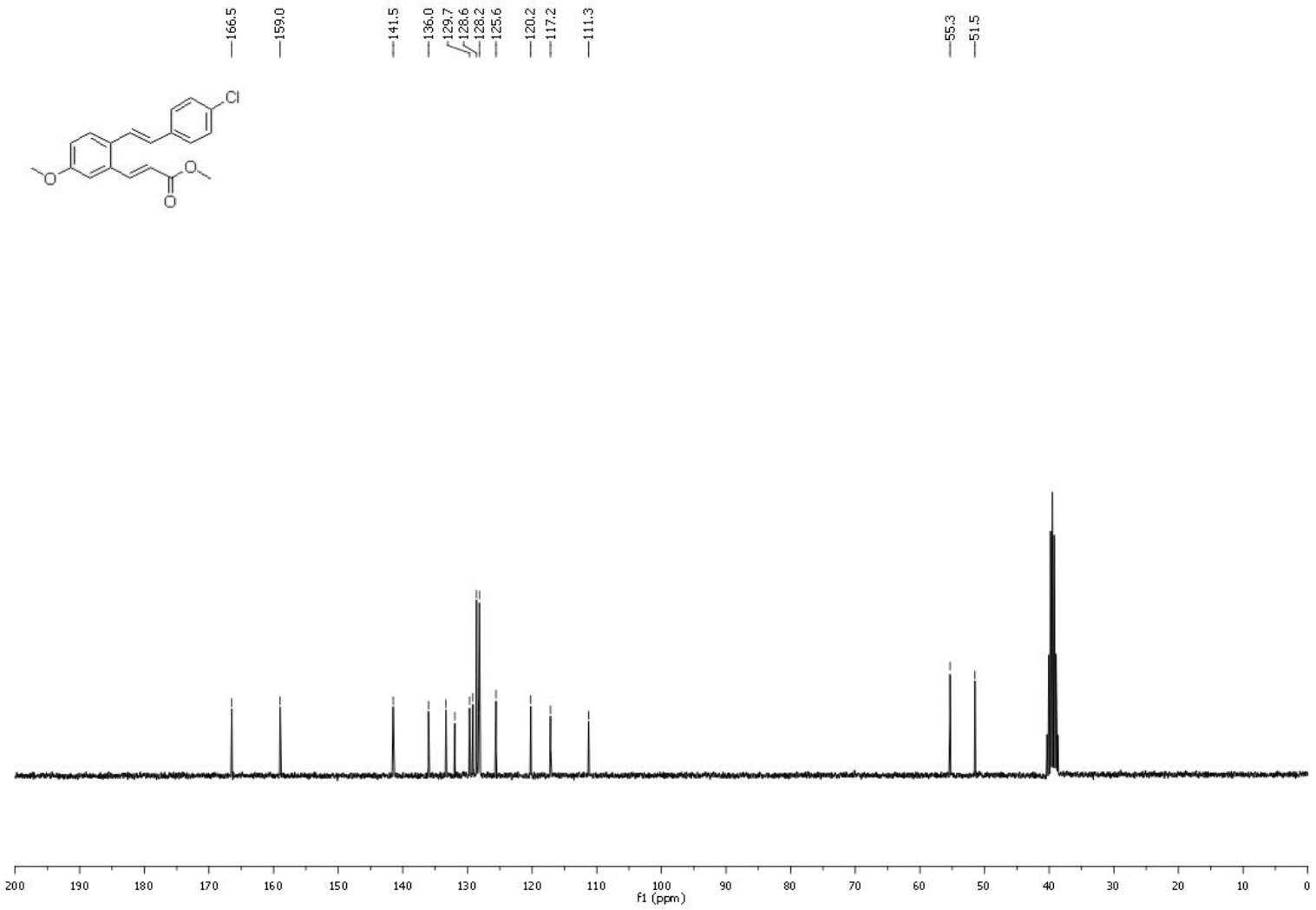
^{13}C NMR (75 MHz, DMSO-d_6) of **6ck**



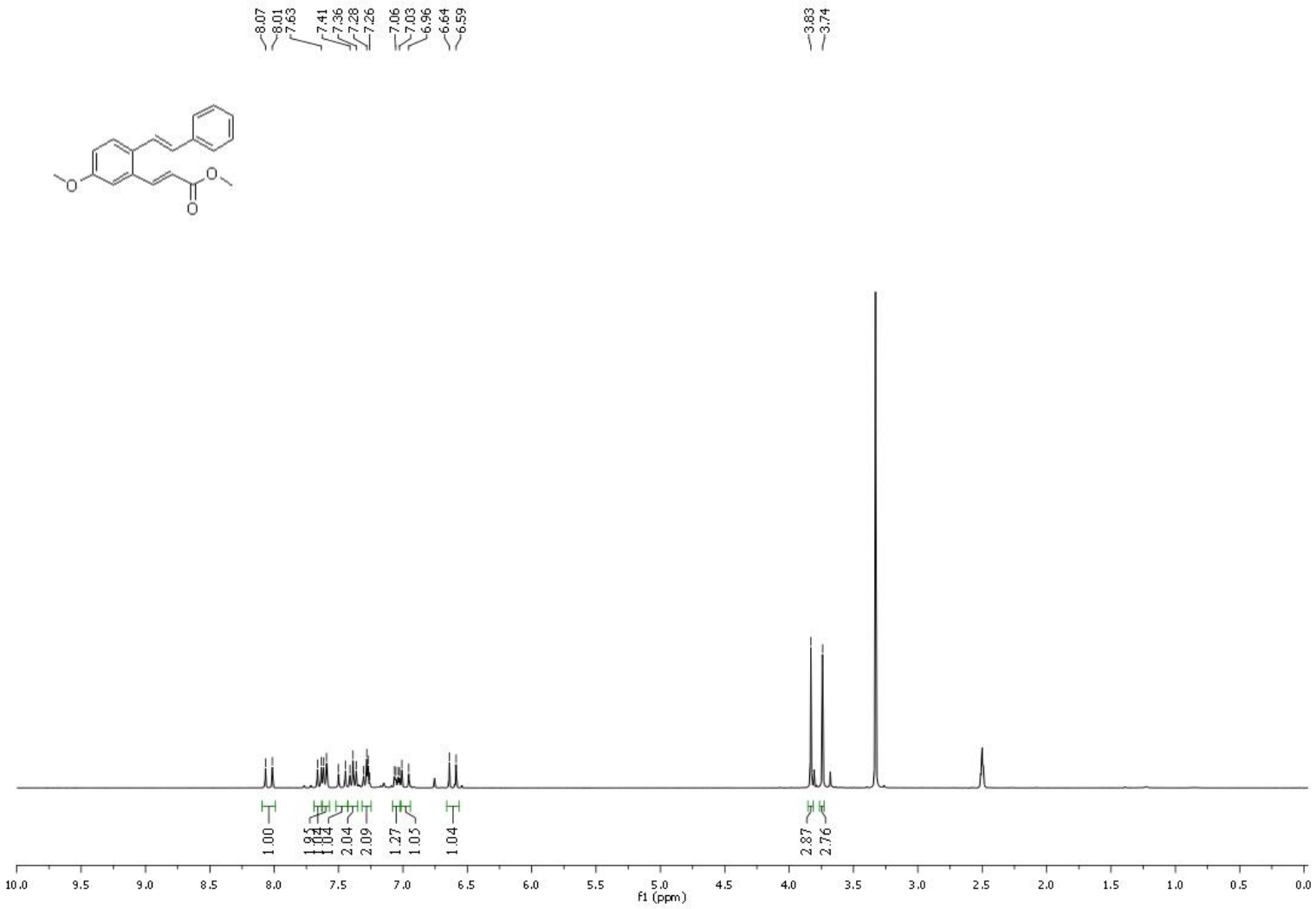
^{1}H NMR (300 MHz, DMSO-d_6) of **6dk**



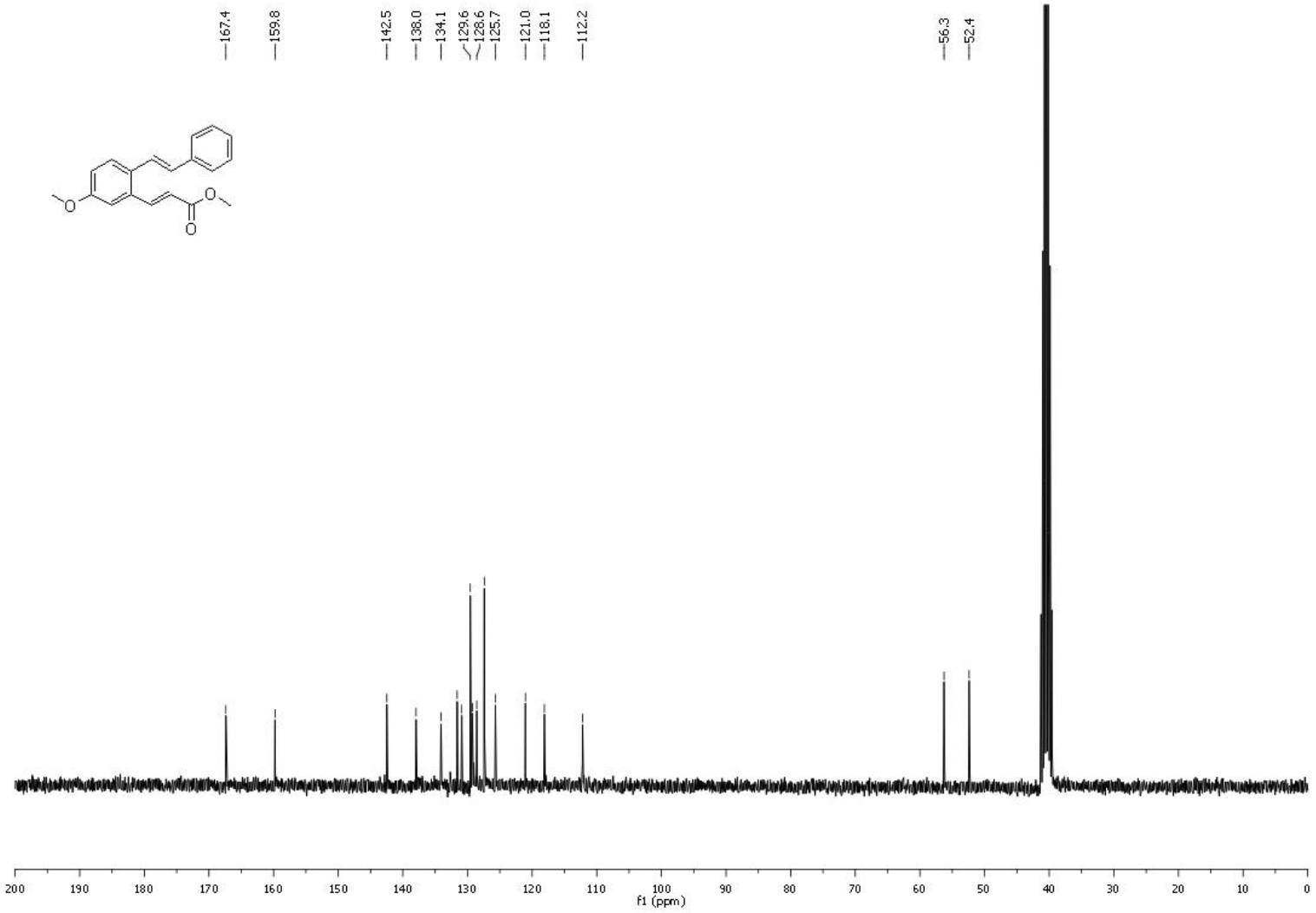
^{13}C NMR (75 MHz, DMSO-d_6) of **6dk**



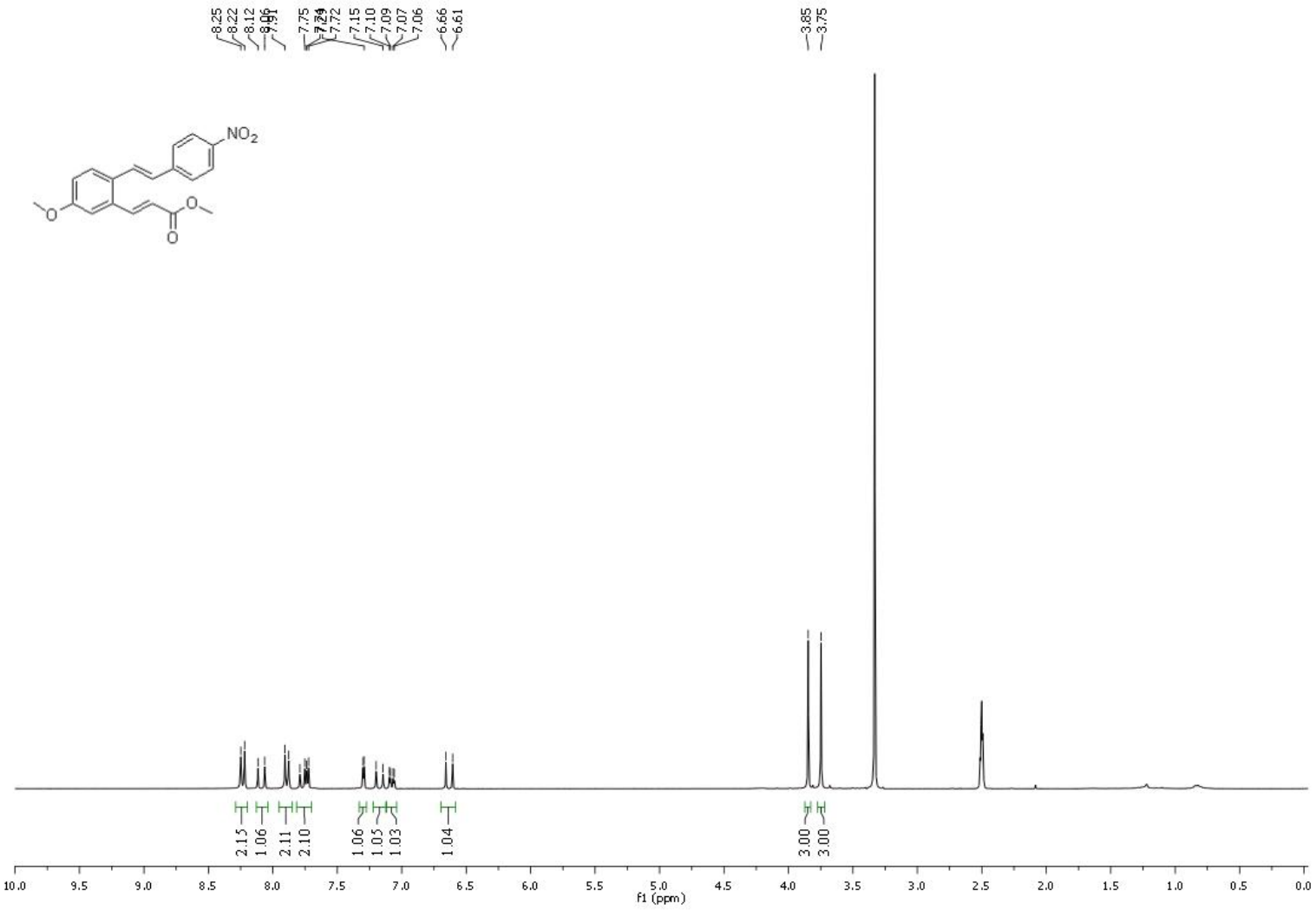
^{1}H NMR (300 MHz, DMSO-d_6) of **6fk**



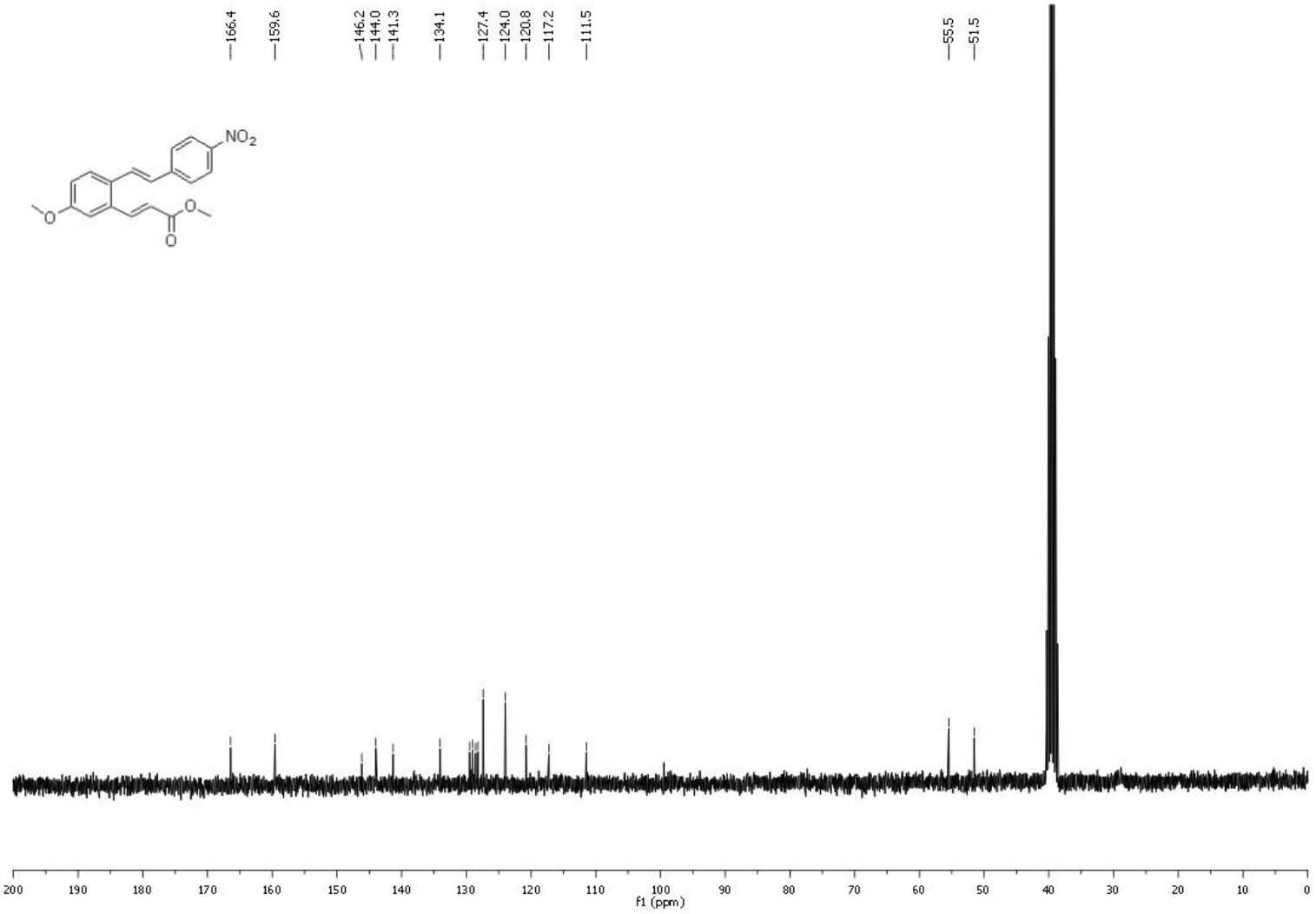
^{13}C NMR (75 MHz, DMSO-d_6) of **6fk**



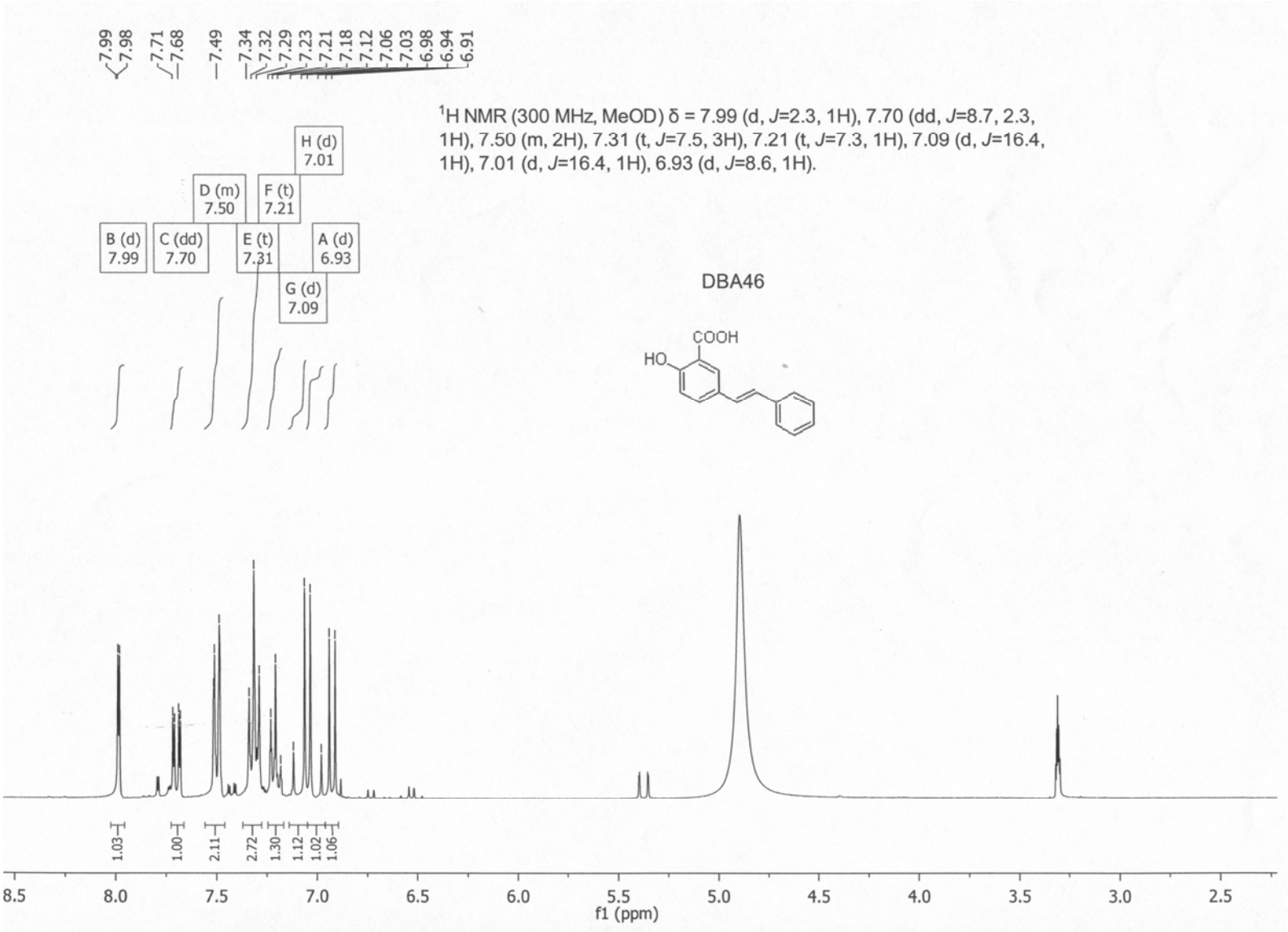
^{1}H NMR (300 MHz, DMSO-d_6) of **6gk**



^{13}C NMR (75 MHz, DMSO-d_6) of **6gk**



^{1}H NMR (300 MHz, methanol-d_4) of **6fm**



^{13}C NMR (75 MHz, methanol-d_4) of **6fm**