Hydroesterification and difunctionalization of olefins with N-hydroxyphthalimide esters

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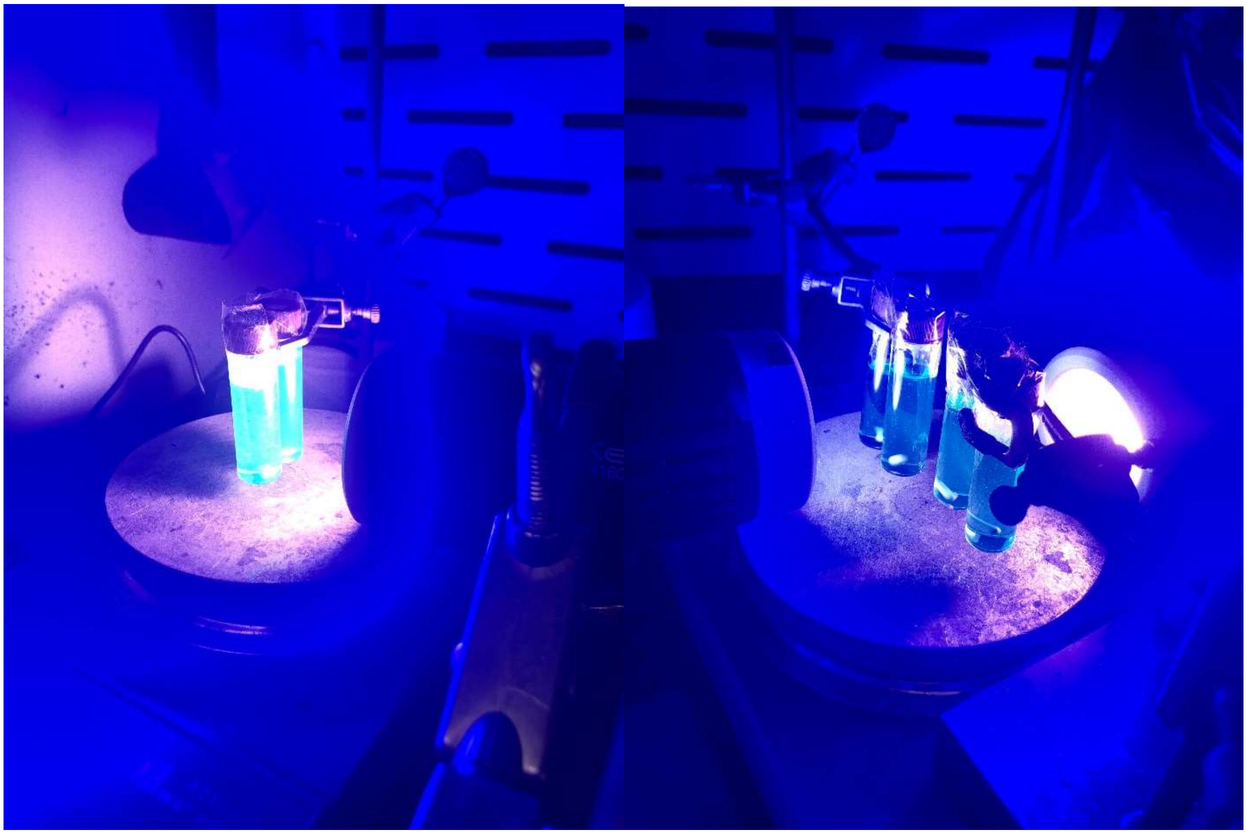
Supporting information

General Information.

Unless otherwise stated, all solvents were commercial anhydrous products and used directly without further purification. DCM was dried from Glass Contour Solvent Drying System and used directly. Photo-catalyst ($Ir(dFppy)_3$) was purchased from STREM CHEMICALS. INC. All reactions were performed under nitrogen atmosphere and irradiated by photo-initiator specially stated in related tables and general procedures.

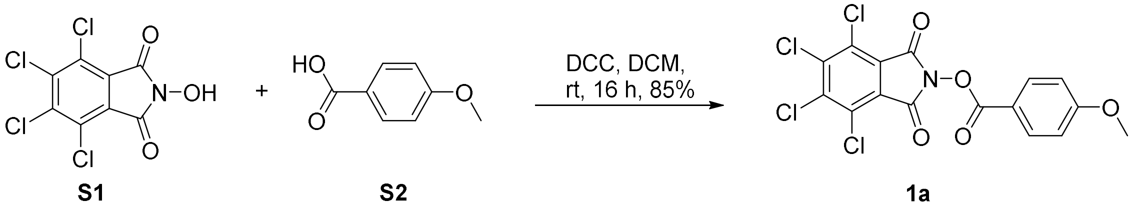
^{1}H NMR spectra were recorded on a Bruker UltraShield Plus 600 MHz or Bruker UltraShield Plus 400 HMz unless otherwise noted and are internally referenced to residual proton solvent signals as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplet, ddd = doublet of doublets of doublets), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus 600 MHz or a Bruker UltraShield Plus 400 HMz and data are reported in terms of chemical shift relative to the solvent signal as noted. Mass spectra were obtained from Agilent technologies 1200 series LC/MS using indicated ionization methods.

Figure S1. The basic reaction setup



Preparation of Substrates and Commercial Unavailable Olefins

Preparation of 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (1a)



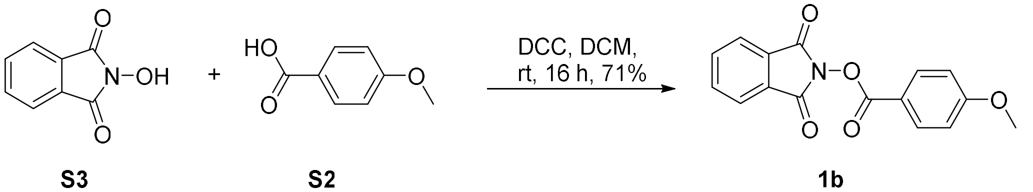
To a suspension of 4,5,6,7-tetrachloro-2-hydroxyisoindoline-1,3-dione (3.00 g, 10.0 mmol, 1 equiv) and 4-methoxybenzoic acid (1.67 g, 11.0 mmol, 1.1 equiv) in dry dichloromethane (80 mL) was added DCC (2.47 g, 12.0 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After reaction, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column directly, eluted with pure dichloromethane to receive the crude product solution. Combined solutions were concentrated to around 30 mL to obtain a yellow suspension. Then hexane (10 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, the desired product was obtained as a colorless solid (3.68 g, 85%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.04 – 6.98 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.11, 161.94, 157.83, 140.94, 133.03, 130.43, 124.82, 116.62, 114.33, 55.66.

ESI MS m/z: 890.7, 892.7 $[2M+Na]^+$.

Preparation of 1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (1b)



To a suspension of 2-hydroxyisoindoline-1,3-dione (2.00 g, 12.26 mmol, 1 equiv) and 4-methoxybenzoic acid (2.05 g, 13.50 mmol, 1.1 equiv) in dry dichloromethane (60 mL) was added DCC (3.04 g, 14.71 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After reaction, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. Combined solutions were concentrated to obtain a yellow residue. Recrystallization of the residue with ethanol provided the target product as a colorless solid (2.60 g, 71%).

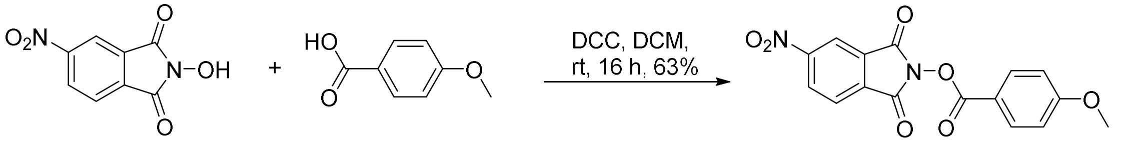
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.12 (m, 2H), 7.91 (dd, J = 5.4, 3.2 Hz, 2H), 7.83 – 7.76 (m, 2H), 7.02 – 6.97 (m, 2H), 3.90 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.85, 162.38, 162.23, 134.71, 132.91, 129.00, 123.94, 117.19, 114.18, 55.59.

ESI MS m/z: 298.0 $[M+H]^+$.

The analytic data is consistent with those reported in the literature.[1]

Preparation of 1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (S6)



S5 **S2** **S6**

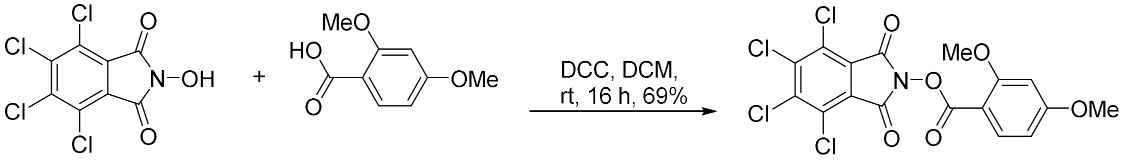
To a suspension of 2-hydroxy-5-nitroisoindoline-1,3-dione (600 mg, 2.88 mmol, 1 equiv) and 4-methoxybenzoic acid (482 mg, 3.17 mmol, 1.1 equiv) in dry dichloromethane (40 mL) was added DCC (714 mg, 3.46 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After reaction, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 15 mL to obtain a yellow suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, the desired product was obtained as a colorless solid (620 mg, 63%).

TLC: (hexane/ethyl acetate = 3/1, v/v) R$_f$ = 0.6.

^{1}H NMR (600 MHz, CDCl$_3$) *δ* 8.77 – 8.73 (m, 1H), 8.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 8.18 – 8.12 (m, 3H), 7.04 – 6.99 (m, 2H), 3.92 (s, 3H).**^{13}C NMR** (150 MHz, CDCl$_3$) *δ* 164.85, 162.38, 162.23, 134.71, 132.91, 129.00, 123.94, 117.19, 114.18, 55.59.

ESI MS m/z: 365.2 [M+Na]$^+$.

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2,4-dimethoxybenzoate (S8)



S1 **S7** **S8**

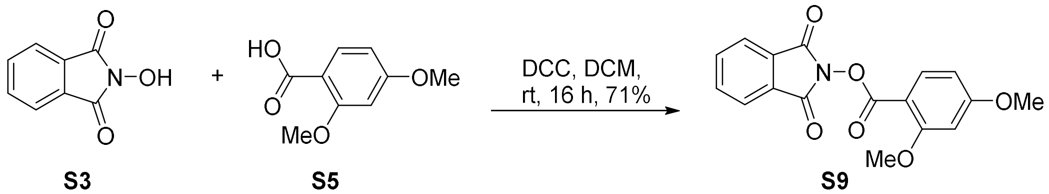
To a suspension of 4,5,6,7-tetrachloro-2-hydroxyisoindoline-1,3-dione (1.00 g, 3.32 mmol, 1.0 equiv) and 2,4-dimethoxybenzoic acid (665 mg, 3.66 mmol, 1.1 equiv) in dry dichloromethane (50 mL) was added DCC (822 mg, 4.00 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a white suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 15 mL to obtain a white suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The recovered solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, the desired product was obtained as a light yellow solid (1.06 g, 69%).

TLC: (hexane/ethyl acetate = 3/1, v/v) R$_f$ = 0.6.

^{1}H NMR (600 MHz, CDCl$_3$) *δ* 8.11 (d, *J* = 8.8 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 3.91 – 3.89 (m, 6H). **^{13}C NMR** (150 MHz, CDCl$_3$) *δ* 166.45, 163.13, 160.17, 158.12, 140.79, 134.91, 130.31, 124.94, 105.77, 105.38, 98.88, 56.06, 55.72.

ESI MS m/z: 950.7, 952.7 [2M+Na]$^+$.

Preparation of 1,3-dioxoisoindolin-2-yl 2,4-dimethoxybenzoate (S9)



To a suspension of 2-hydroxyisoindoline-1,3-dione (1.00 g, 6.13 mmol, 1.0 equiv) and 2,4-dimethoxybenzoic acid (1.23 g, 6.74 mmol, 1.1 equiv) in dry dichloromethane (50 mL) was added DCC (1.52 g, 7.36 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a white suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 15 mL to obtain a white suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, the desired product was obtained as a white solid (1.42 g, 71%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.

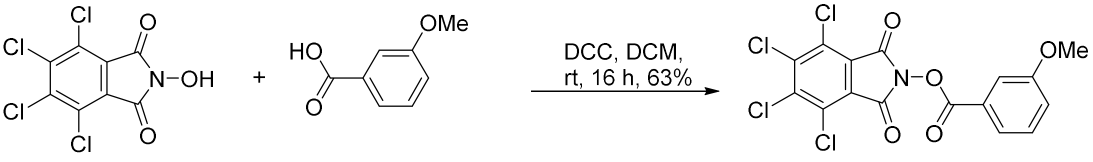
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 1H), 7.91 (dd, J = 5.6, 3.2 Hz, 2H), 7.79 (dd, J = 5.6, 3.2 Hz, 2H), 6.57 (dd, J = 8.8, 2.4 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 3.90 – 3.89 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.22, 163.02, 162.59, 160.66, 134.93, 134.61, 129.23, 123.88, 106.45, 105.26, 98.91, 56.06, 55.71.

ESI MS m/z: 328.1 $[M+H]^+$.

The analytic data is consistent with those reported in the literature.[2]

Preparation of 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 3-methoxybenzoate (S11)



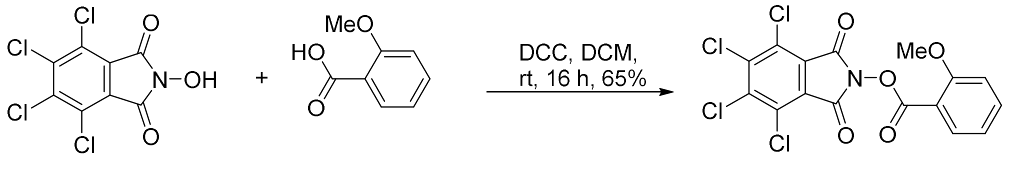
To a suspension of 4,5,6,7-tetrachloro-2-hydroxyisoindoline-1,3-dione (500 mg, 1.66 mmol, 1 equiv) and 3-methoxybenzoic acid (278 mg, 1.83 mmol, 1.1 equiv) in dry dichloromethane (30 mL) was added DCC (411 mg, 2.00 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After reaction, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column directly and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 10 mL to obtain a yellow suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The recovered solid was washed with hexane/dichloromethane (4 mL, 1/1, v/v). After drying on an oil pump, desired product was obtained as a colorless solid (455 mg, 63%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dt, J = 7.6, 1.2 Hz, 1H), 7.65 (dd, J = 2.8, 1.6 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.26 – 7.23 (m, 1H), 3.88 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.29, 159.78, 157.61, 141.04, 130.51, 130.03, 125.80, 124.76, 123.13, 121.95, 114.72, 55.58.

ESI MS m/z: 890.8, 892.8 $[2M+Na]^+$.

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-methoxybenzoate (S13)



S1 **S12** **S13**

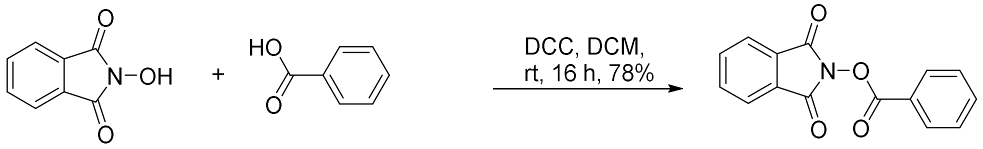
To a suspension of 4,5,6,7-tetrachloro-2-hydroxyisoindoline-1,3-dione (500 mg, 1.66 mmol, 1 equiv) and 2-methoxybenzoic acid (278 mg, 1.83 mmol, 1.1 equiv) in dry dichloromethane (30 mL) was added DCC (411 mg, 2.00 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After reaction, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column directly and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 10 mL to obtain a yellow suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The recovered solid was washed with hexane/dichloromethane (4 mL, 1/1, v/v). After drying on an oil pump, the desired product was obtained as a colorless solid (468 mg, 65%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.64 (ddd, $J = 8.6, 7.4, 1.8$ Hz, 1H), 7.10 – 7.03 (m, 2H), 3.94 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.87, 160.73, 157.85, 140.89, 136.27, 132.75, 130.39, 124.87, 120.36, 113.58, 112.24, 56.10.

ESI MS m/z: 890.8, 892.8 $[2M+Na]^+$.

Preparation of 1,3-dioxoisoindolin-2-yl benzoate (S15)



S3 **S14** **S15**

To a suspension of 2-hydroxyisoindoline-1,3-dione (1.00 g, 6.13 mmol, 1.0 equiv) and benzoic acid (823 mg, 6.74 mmol, 1.1 equiv) in dry dichloromethane (50 mL) was added DCC (1.52 g, 7.36 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a white suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 15 mL to obtain a white suspension. Then hexane (10 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, the desired product was obtained as a white solid (1.28 g, 78%).

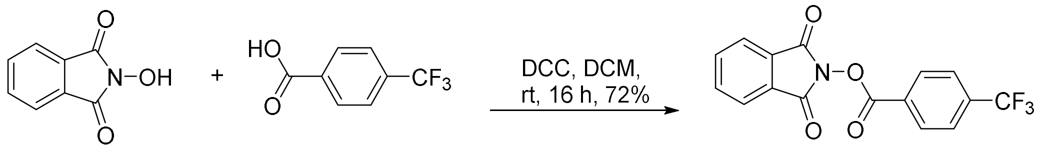
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 2H), 7.93 (dd, $J = 5.5, 3.2$ Hz, 2H), 7.85 – 7.78 (m, 2H), 7.73 – 7.67 (m, 1H), 7.57 – 7.51 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.78, 162.04, 134.88, 134.78, 130.62, 128.97, 128.85, 125.23, 124.00.

ESI MS m/z: 268.1 $[M+H]^+$.

The analytic data was consistent with those reported in the literature [3]

1,3-dioxoisoindolin-2-yl 4-(trifluoromethyl)benzoate (S17)



S3 **S16** **S17**

To a suspension of 2-hydroxyisoindoline-1,3-dione (1.00 g, 6.13 mmol, 1.0 equiv) and 4-(trifluoromethyl)benzoic acid (1.28 g, 6.74 mmol, 1.1 equiv) in dry dichloromethane (50 mL) was added DCC (1.52 g, 7.36 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a white suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 20 mL to obtain a white suspension. Then hexane (10 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (10 mL, 1/1, v/v). After drying on an oil pump, desired product was obtained as a light yellow solid (1.47 g, 72%).

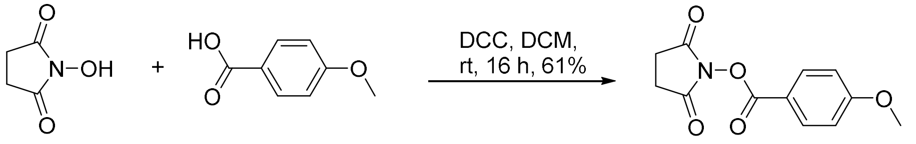
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 2H), 7.95 – 7.92 (m, 2H), 7.86 – 7.79 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.79, 161.76, 136.14 (q, J = 32.9 Hz), 134.93, 131.03, 128.84, 128.60, 125.90 (q, J = 3.8 Hz), 124.12, 123.25 (q, J = 123.25 Hz).

ESI MS m/z: 336.0 $[M+H]^+$.

Preparation of 2,5-dioxopyrrolidin-1-yl 4-methoxybenzoate (S19)



S18 **S2** **S19**

To a suspension of 1-hydroxypyrrolidine-2,5-dione (800 mg, 6.95 mmol, 1 equiv) and 4-methoxybenzoic acid (1.16 g, 7.65 mmol, 1.1 equiv) in dry dichloromethane (40 mL) was added DCC (1.72 g, 8.34 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 10 mL to obtain a white suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, desired product was obtained as a white solid (1.06 g, 61%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

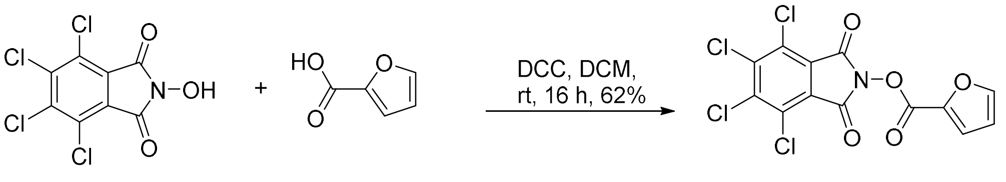
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.00 – 6.95 (m, 2H), 3.89 (s, 3H), 2.90 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.46, 164.89, 161.46, 132.88, 117.06, 114.18, 55.60, 25.65.

ESI MS m/z: 250.1 $[M+H]^+$.

The analytic data was consistent with those reported in the literature [4]

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl furan-2-carboxylate (S21)



S1 **S20** **S21**

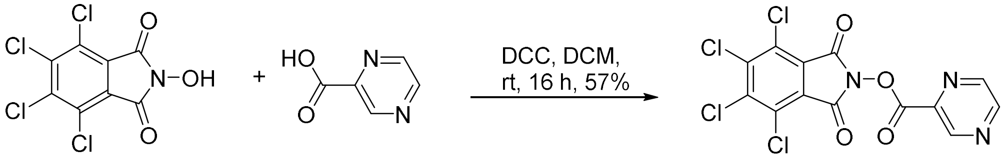
To a suspension of 4,5,6,7-tetrachloro-2-hydroxyisoindoline-1,3-dione (1.00 g, 3.32 mmol, 1.0 equiv) and furan-2-carboxylic acid (410 mg, 3.66 mmol, 1.1 equiv) in dry dichloromethane (50 mL) was added DCC (822 mg, 4.00 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 10 mL to obtain a white suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, desired product was obtained as a light yellow solid (820 mg, 62%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, $J = 1.6, 0.8$ Hz, 1H), 7.56 (dd, $J = 3.6, 0.8$ Hz, 1H), 6.67 (dd, $J = 3.6, 1.6$ Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.43, 153.95, 149.11, 141.13, 139.35, 130.58, 124.66, 122.78, 112.80.

ESI MS m/z: 395.8 $[M+H]^+$.

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl pyrazine-2-carboxylate (S23)



S1 **S22** **S23**

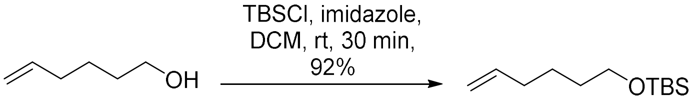
To a suspension of 4,5,6,7-tetrachloro-2-hydroxyisoindoline-1,3-dione (1.00 g, 3.32 mmol, 1.0 equiv) and pyrazine-2-carboxylic acid (453 mg, 3.66 mmol, 1.1 equiv) in dry dichloromethane (50 mL) was added DCC (822 mg, 4.00 mmol, 1.2 equiv). The mixture was stirred overnight under ambient temperature. After the reaction was complete, a yellow suspension was obtained, which was concentrated and then added to the silica-gel column and eluted with pure dichloromethane to receive the crude product solution. The combined solutions were concentrated to around 10 mL to obtain a white suspension. Then hexane (5 mL) was added to the suspension, followed by filtration. The solid was washed with hexane/dichloromethane (5 mL, 1/1, v/v). After drying on an oil pump, desired product was obtained as a light yellow solid (776 mg, 57%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.3$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.44 (d, $J = 1.4$ Hz, 1H), 8.94 (d, $J = 2.4$ Hz, 1H), 8.86 (dd, $J = 2.4, 1.4$ Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.07, 157.06, 149.40, 147.20, 145.07, 141.32, 139.73, 130.73, 124.62.

ESI MS m/z: 407.9 $[M+H]^+$.

Synthesis of S25



S24 **S25**

To a solution of hex-5-en-1-ol (600 mg, 6.00 mmol, 1 equiv) in DCM (30 mL) was added imidazole (611 mg, 9.00 mmol, 1.5 equiv), followed by TBSCl (990 mg, 6.60 mmol, 1.1 equiv). The mixture was stirred for 30 min. Water (30 mL) was added to quench the reaction, the organic layer was collected, and aqueous layer was extracted by DCM (20 mL) once. Combined organic layers were dried by anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (eluting with hexane/ethyl acetate = 40/1, v/v) to obtain the target product (1.18 g, 92%) as a colorless oil.

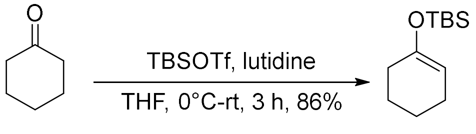
TLC: (hexane/ethyl acetate = 6/1, v/v) $R_f = 0.9$. Visual method: $KMnO_4$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.81 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 5.00 (dq, J = 17.2, 1.8 Hz, 1H), 4.94 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 3.61 (t, J = 6.4 Hz, 2H), 2.10 – 2.03 (m, 2H), 1.56 – 1.49 (m, 2H), 1.47 – 1.39 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.95, 114.34, 63.07, 33.53, 32.28, 25.97, 25.13, 18.37, -5.29.

GC-MS m/z: 157 $[M\text{–}t\text{-Bu}]^+$.

The analytic data was consistent with those reported in the literature.[5]

Synthesis of S27



S26 **S27**

Under cooling of an ice water bath, to a solution of cyclohexanone (600 mg, 6.11 mmol, 1.0 equiv), and 2,6-dimethylpyridine (1.97 g, 18.34 mmol, 3.0 equiv) in dry THF (40 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (2.42 g, 9.17 mmol, 1.5 equiv). The mixture was warmed to room temperature and stirred for 3 h. After the reaction was complete, a saturated NH_4Cl aqueous solution (30 mL) was added to quench the reaction. The organic layer was collected and the aqueous phase was extracted with ethyl acetate once (30 mL). The combined organic phases were dried with anhydrous Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography. It is essential to mix the silica gel with hexane/trimethylamine solution (1000/1, v/v), and then add to the column. Eluting with Hexane/triethylamine = 1000/1, v/v) provided the target product (1.12 g, 86%) as a colorless oil.

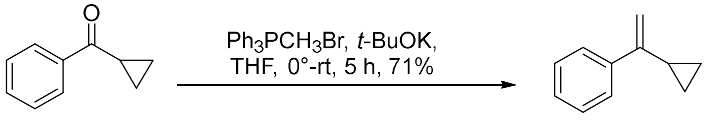
TLC: (hexane/DCM = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, DMSO) δ 4.79 (tt, J = 3.8, 1.2 Hz, 1H), 1.98 – 1.89 (m, 4H), 1.63 – 1.55 (m, 2H), 1.49 – 1.38 (m, 2H), 0.88 (s, 9H), 0.09 (s, 6H). **^{13}C NMR** (150 MHz, DMSO) δ 150.42, 103.93, 29.94, 26.05, 23.76, 23.11, 22.37, 18.19, -3.95.

GC-MS m/z: 212 $[M]^+$.

The analytic data was consistent with those reported in the literature.[6]

Synthesis of S29



S28 **S29**

Under cooling of an ice water bath, to a suspension of methyltriphenylphosphonium bromide (1.76 g, 4.93 mmol, 1.2 equiv) in dry tetrahydrofuran (40 mL) was added *t*-BuOK (552 mg, 4.93 mmol, 1.2 equiv). The mixture was stirred for 60 min at 0 ˚C. **S28** (600 mg, 4.10 mmol, dissolved in 5 mL THF) was added slowly. The mixture was stirred for further 4 h under ambient temperature. After the reaction was complete, a saturated NH_4Cl aqueous solution (30 mL) was added to quench the reaction. The organic layer was collected and the aqueous phase was extracted with ethyl acetate once (30 mL). The combined organic phases were dried with anhydrous Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography (eluting with Hexane/ethyl acetate = 20/1, v/v) to obtain target product (420 mg, 71%) as a colorless oil.

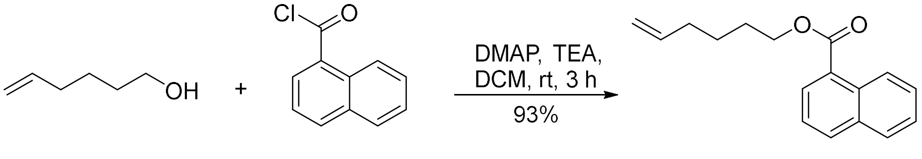
TLC: (hexane/ethyl acetate = 6/1, v/v) $R_f = 0.9$. Visual method: $KMnO_4$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.35 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.32 – 7.27 (m, 1H), 5.28 (d, *J* = 1.0 Hz, 1H), 4.94 (t, *J* = 1.2 Hz, 1H), 1.66 (dddd, *J* = 13.6, 8.4, 5.4, 1.2 Hz, 1H), 0.88 – 0.80 (m, 2H), 0.63 – 0.57 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.31, 141.60, 128.12, 127.43, 126.09, 108.99, 15.60, 6.65.

GC-MS m/z: 144 $[M]^+$.

The analytic data is consistent with those reported in the literature.[7]

Synthesis of S32



S30 **S31** **S32**

Under cooling of an ice water bath, to a solution of hex-5-en-1-ol (500 mg, 5.00 mmol, 1.0 equiv), 4-N,N-dimethylamino pyridine (60 mg, 0.5 mmol, 0.1 equiv), and triethylamine (760 mg, 7.50 mmol, 1.5 equiv) in dry DCM (40 mL) was added 1-naphthoyl chloride (1.05 g, 5.5 mmol, 1.1 equiv). The mixture was warmed to room temperature and stirred for 3 h. After the reaction was complete, a saturated $NaHCO_3$ aqueous solution (30 mL) was added to quench the reaction. The organic layer was collected and the aqueous phase was extracted with DCM once (30 mL). The combined organic phases were dried with anhydrous Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography (eluting with Hexane/DCM = 3/1, v/v) to obtain target product (1.18 g, 93%) as a colorless oil.

TLC: (hexane/DCM = 1/1, v/v) $R_f = 0.8$.

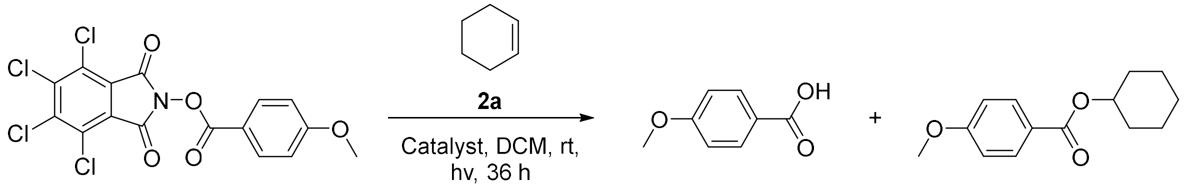
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (dq, *J* = 8.6, 1.0 Hz, 1H), 8.18 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.02 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.62 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.57 – 7.48 (m, 2H), 5.84 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.06 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.99 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 2.20 – 2.13 (m, 2H), 1.89 – 1.82 (m, 2H), 1.65 – 1.59 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.66, 138.34, 133.80, 133.22, 131.31, 130.04, 128.51, 127.68, 127.40, 126.16, 125.79, 124.48, 114.90, 64.99, 33.32, 28.19, 25.38.

ESI MS m/z: 531.2 $[2M+Na]^+$.

The analytic data was consistent with those reported in the literature.[8]

Optimization of Reaction Conditions

Table S1. Optimizing Catalysts

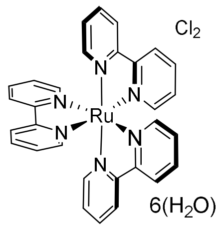


1a **3** **4a**

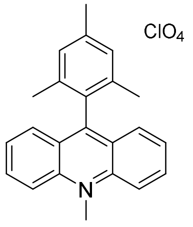
Entry	Catalysts	Light Sources	Yield **3** (%)	Yield **4a** (%)
1 [a]	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	Kessil H150-BLUE	0 [b]	0
2 [a]	$9\text{-Mes-10-Me-Acr}{\cdot}ClO_4$	Kessil H150-BLUE	45	38
3 [a]	$Xanthylium{\cdot}BF_4$	Kessil H150-BLUE	53	13
4 [a]	$Acridinium{\cdot}BF_4$	Kessil H150-BLUE	28	25
5 [a]	4CzIPN	Kessil PR160L-440 nm	22	62
6 [a]	perylene	Kessil PR160L-390 nm	74	14
7 [a]	10-Phenylphenothiazine	Kessil PR160L-390 nm	55	8
8 [a]	Eosin Y	Kessil H150-BLUE	29	43
9	$Ir(ppy)_2(dtbbpy)PF_6$	Kessil PR160L-440 nm	18	73
10	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	Kessil PR160L-440 nm	40	10
11	$Ir(ppy)_3$	Kessil PR160L-440 nm	11	81
12	**$Ir(dFppy)_3$**	**Kessil PR160L-440 nm**	**<5**	**87**

Unless otherwise noted the reactions were conducted with substrate **1a** (44.0 mg, 0.1 mmol, 1.0 equiv), DCM (5.0 mL), catalysts (0.01 equiv, shown in table), cyclohexene (5.0 equiv), carried out under ambient temperature (actual reaction solution temperature: 40 - 45 °C) and nitrogen atmosphere. Reactions were irritated by blue LED (shown in table) for 36 h. Yields were obtained by ^{1}H NMR integrations by using 1,3,5-trimethoxybenzene as internal standard sample. [a] catalyst (0.05 equiv), [b] substrate **1a** recovered.

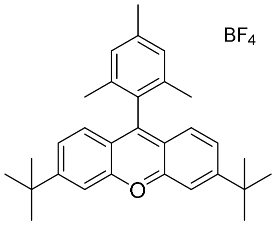
The Chemical Structures of the Catalysts in Figure 1



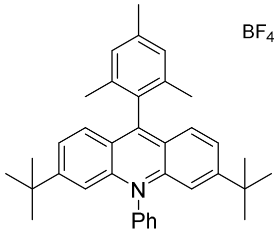
$Ru(bpy)_3Cl_2$



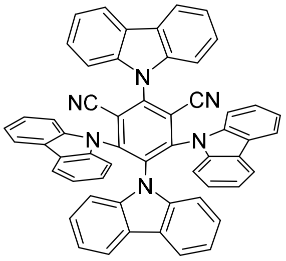
$9\text{-Mes-10-Me-Acr}{\cdot}ClO_4$



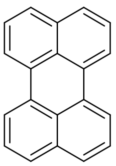
Xanthylium·BF4



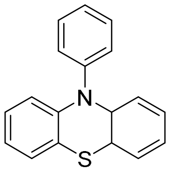
Acridinium·BF4



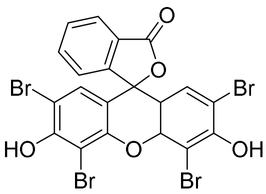
4CzIPN



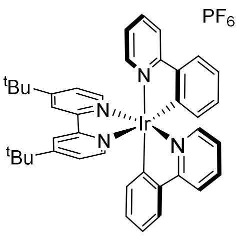
perylene



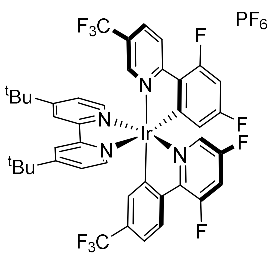
10-Phenylphenothiazine



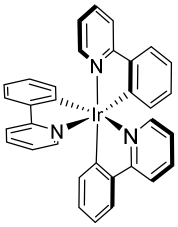
Eosin Y



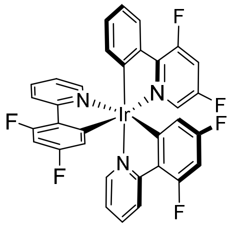
Ir(ppy)$_2$(dtbbpy)PF$_6$



Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$

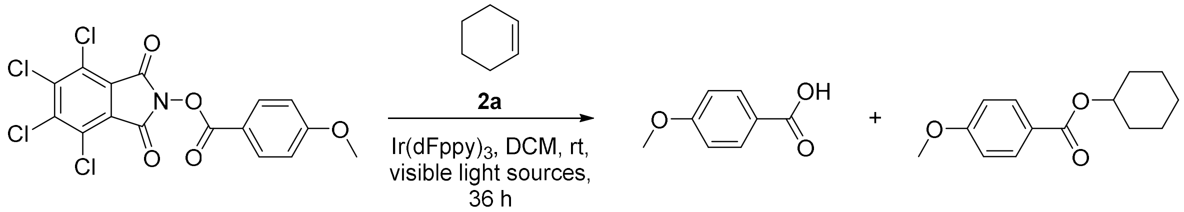


Ir(ppy)$_3$



Ir(dFppy)$_3$

Table S2. Optimizing Light Source

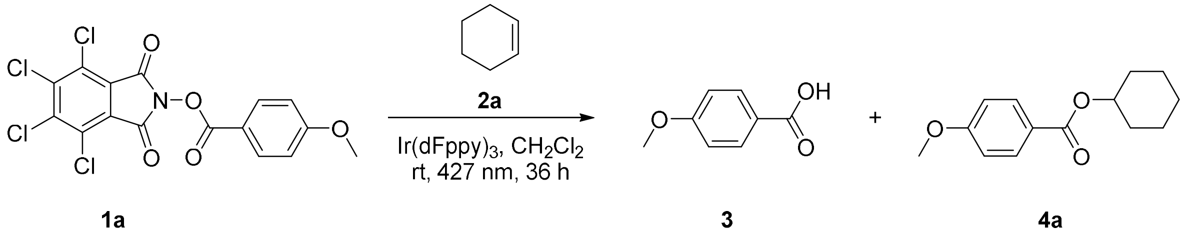


1a **3** **4a**

Entry	Catalysts	Light Sources	Yield **3** (%)	Yield **4a** (%)
1	none	254 nm (Rayonet)	0[a]	0[a]
2	none	PR m2 365 nm	43[b]	8
3	none	Kessil PR160L-440 nm	<5[b]	<5
4	none	Kessil PR160L-427 nm	<5[b]	<5
5	Ir(dFppy)$_3$	PR m2 365 nm	38	50
6	Ir(dFppy)$_3$	Kessil PR160L-390 nm	21	73
7	**Ir(dFppy)$_3$**	**Kessil PR160L-427 nm**	**<5**	**91**
8	Ir(dFppy)$_3$	Kessil PR160L-440 nm	<5	87
9	Ir(dFppy)$_3$	PR m2 450 nm	<5	76
10	Ir(dFppy)$_3$	Kessil H150-BLUE	<5	72
11	Ir(dFppy)$_3$	None (heating to 40 ˚C)	0[b]	0

Unless otherwise noted, the reactions were conducted with substrate **1a** (44.0 mg, 0.1 mmol, 1.0 equiv), DCM (5.0 mL), catalysts (0.01 equiv), cyclohexene (5.0 equiv), carried out under ambient temperature (actual reaction solution temperature: 40 - 45 ˚C) and nitrogen atmosphere. Reactions were irritated by blue LED (shown in table) for 36 h. Yields were obtained by ^{1}H NMR integrations by using 1,3,5-trimethoxybenzene as internal standard sample. [a] substrate decomposed. [b] Substrate **1a** remained.

Table S3. Effect of Additives



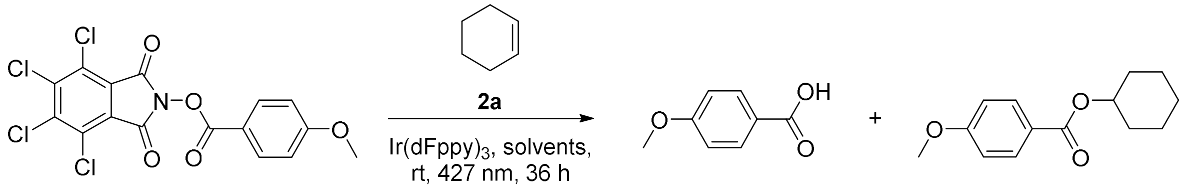
1a **3** **4a**

Entry	Catalysts	Additives (3.0 equiv)	Yield **3** (%)	Yield **4a**
1	**Ir(dFppy)$_3$**	**none**	**<5**	**91**
2 [a]	Ir(dFppy)$_3$	none	39[b]	0
3 [c]	Ir(dFppy)$_3$	none	14[d]	29
4 [c]	Ir(dFppy)$_3$	PhMe	17	26
5 [c]	Ir(dFppy)$_3$	PhCH$_2$Ph	12	33

6 [c]	Ir(dFppy)$_3$	*t*-BuSH	71	8
7 [c]	Ir(dFppy)$_3$	(*n*-Bu)$_3$SnH	71	9
8 [c]	Ir(dFppy)$_3$	(TMS)$_3$SiH	48	24
9	Ir(dFppy)$_3$	DIPEA	87	0
10	Ir(dFppy)$_3$	quinuclidine	42	45
11	Ir(dFppy)$_3$	Hantzsch ester	89	0
12	Ir(dFppy)$_3$	Cu(OAc)$_2$[e]	9[f]	16

Unless otherwise noted, the reactions were conducted with substrate **1a** (44.0 mg, 0.1 mmol, 1.0 equiv), DCM (5.0 mL), catalysts (0.01 equiv), cyclohexene (5.0 equiv), under ambient temperature (actual reaction solution temperature: 40 - 45 ˚C) and nitrogen atmosphere, irritated by blue LED (Kessil PR160L-427 nm) for 36 h. Yields were obtained by ^{1}H NMR integrations by using 1,3,5-trimethoxybenzene as internal sample. [a]Without cyclohexene. [b]40 % starting material **1a** remained. [c]Cyclohexene (1.1 equiv). [d]48 % starting material **1a** remained. [e]Cu(OAc)$_2$ (0.1 equiv). [f]49 % starting material **1a** recovered. DIPEA: N,N-diisopropylethylamine. Hantzsch ester: Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate;

Table S4. Optimizing Solvents

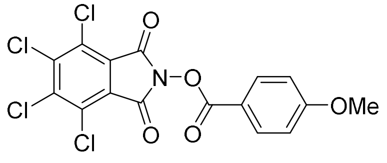


1a **3** **4a**

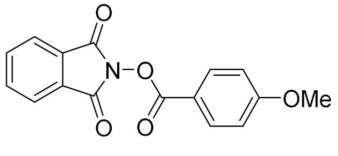
Entry	Solvents	Yield **3** (%)	Yield **4a** (%)
1	**DCM**	**<5**	**91**
2	CHCl$_3$	43	20
3	DCE	10	89
4	CH$_3$CN	10	77
5	acetone	22	72
6	ethyl acetate	10	57
7	MeOH	58	13
8	CF$_3$CH$_2$OH	52	<5
9	(CF$_3$)$_2$CHOH	47	<5
10	PhCF$_3$	19	39
11	PhMe	8	43
12	THF	76	12
13	DME	55	17
14	dioxane	60	13
15	DMF	65	<5
16	DMSO	76	<5

Unless otherwise noted, the reactions were conducted with substrate **1a** (44.0 mg, 0.1 mmol, 1.0 equiv), solvents (5.0 mL), catalysts (Ir(dFppy)$_3$, 0.01 equiv), cyclohexene (5.0 equiv), carried out under ambient temperature and nitrogen atmosphere, irritated by blue LED (Kessil PR160L-427 nm) for 36 h. Yields were obtained by ^{1}H NMR integrations by using 1,3,5-trimethoxybenzene as internal sample. DCE: 1,2-dichloroethane, DME: 1,2-dimethoxyethane.

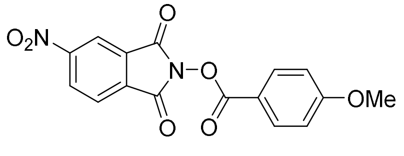
Figure S2. N-Acyloxy imides



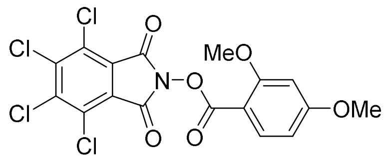
1a, 87%



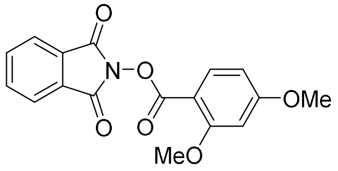
1b, 81%



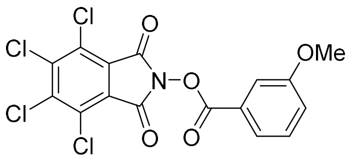
S6, no desired product



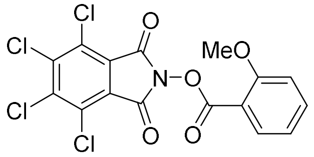
S8, 77%



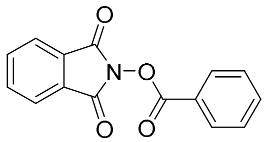
S9, 73%



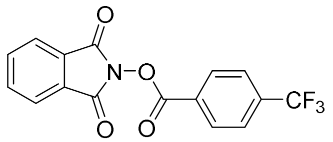
S11, messy



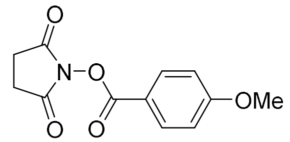
S13, messy



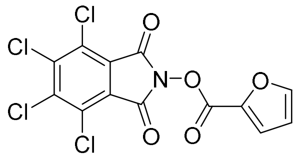
S15, messy



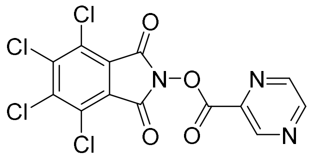
S17, messy



S19, no desired product



S21, messy



S23, messy

The reactions were conducted with substrate (0.1 mmol, 1.0 equiv), solvents (DCM, 5.0 mL), Ir(dFppy)$_3$ (0.01 equiv), cyclohexene (5.0 equiv), carried out under ambient temperature (actual reaction solution temperature: 40 - 45 ˚C) and nitrogen atmosphere, irritated by blue LED (Kessil PR160L-427 nm) for 24 h. isolated yields.

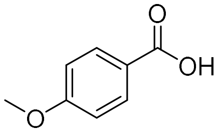
General procedure A for optimization studies (Tables S1 – S4, Figure S2)

An 8 mL dry vial equipped with a magnetic stirring bar was charged with substrate the appropriate N-acyloxy imide (44.0 mg for **1a**, 0.10 mmol, 1.0 equiv), photocatalyst (0.01 equiv or 0.05 equiv), cyclohexene (5.0 equiv or 1.1 equiv) and additive (0.1 equiv or 3 equiv as indicated). Then solvent (5.0 mL) was added sequentially. The mixture was protected by nitrogen, irritated by blue LED for 36 h under ambient temperature. After reaction, 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol, 0.33 equiv) was added to reaction solution. The reaction mixture was stirred for 5 min, filtered by Celite and washed with DCM (2 mL). The filtrate was concentrated under vacuum. The residue was further dried under oil pump, and yields were obtained by 1H NMR relative to the internal standard.

Purification of **3**, **4a**, **S33**:

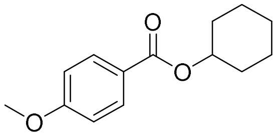
After the reaction, the solution was filtered and washed by DCM (2 mL), the white solid was collected and further dried by oil pump to recover 4,5,6,7-tetrachloroisoindoline-1,3-dione **S33** as a white solid. The filtrate was concentrated and the residue was purified by silica-gel column chromatography to get target product **4a** as a colorless oil and 4-methoxybenzoic acid **3** as a white solid.

3



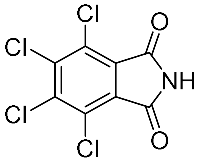
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.1$.
Purification: eluting with hexane/ ethyl acetate = 1/1, v/v.
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.21 (m, 1H), 8.10 – 8.05 (m, 2H), 6.98 – 6.93 (m, 2H), 3.88 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.57, 164.03, 132.35, 121.58, 113.73, 55.48.
ESI MS m/z: 151.0 $[M–H]^-$.

4a



TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
Purification: eluting with hexane/ ethyl acetate = 15/1, v/v.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 6.94 – 6.88 (m, 2H), 5.00 (tt, *J* = 8.6, 3.8 Hz, 1H), 3.86 (s, 3H), 1.97 – 1.90 (m, 2H), 1.78 (ddt, *J* = 14.2, 9.8, 4.2 Hz, 2H), 1.62 – 1.53 (m, 3H), 1.44 (dtt, *J* = 13.6, 10.0, 3.6 Hz, 2H), 1.34 (tdd, *J* = 13.2, 8.4, 4.8 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.76, 163.12, 131.50, 123.44, 113.46, 72.63, 55.40, 31.68, 25.49, 23.67.
ESI MS m/z: 235.1 $[M+H]^+$.
The analytic data was consistent with those reported in the literature.[9]

S33

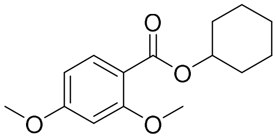


TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.3$.
Purification: direct filtration.
^{1}H NMR (600 MHz, DMSO) δ 11.94 (s, 1H).
^{13}C NMR (150 MHz, DMSO) δ 165.05, 138.40, 129.66, 128.36.
ESI MS m/z: 285.8 $[M+H]^+$.
The analytic data is consistent with those reported in the literature [10]

For the substrate S8 and S9 in Figure S2, the procedure and data is following.

Substrate S8

An 8 mL dry vial equipped with a magnetic stirring bar was charged with **S8** (46.5 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 μmol, 0.01 equiv), and dry DCM (5.0 mL). Then cyclohexene (41.5 mg, 0.5 mmol, 5.0 equiv) was added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 24 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The filtrate was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography to obtain products **S34** (20.3 mg, 77%) as an oil.



S34

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
Purification: eluting with hexane/ ethyl acetate = 8/1, v/v.
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.84 (d, J = 8.4 Hz, 1H), 6.51 – 6.46 (m, 2H), 4.99 (tt, J = 8.4, 3.8 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 1.95 – 1.87 (m, 2H), 1.77 (ddp, J = 13.2, 6.4, 3.6 Hz, 2H), 1.61 – 1.50 (m, 3H), 1.43 (dtt, J = 13.3, 9.8, 3.6 Hz, 2H), 1.34 (ddt, J = 16.2, 9.8, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 165.00, 163.99, 161.37, 133.59, 113.22, 104.40, 98.98, 72.27, 55.96, 55.49, 31.64, 25.59, 23.63.
ESI MS m/z: 265.1 [M+H]$^+$.

For substrate S9

Following the procedure described for **S8**, substrate **S9** (33.0 mg, 0.10 mmol, 1.0 equiv) was added to the reaction solution. After reaction and work up, product **S34** (19.5 mg, 73%) was obtained (characterization data provided above).

Fluorescence Quenching Experiments

Experimental Details: all fluorescence data was acquired on an ISS PC1 photon counting spectrofluorimeter with a 300 W high-pressure xenon arc lamp. Stock solution of Ir(dFppy)$_3$ (1 mmol/L, 5mL); 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (**1a**, 10 mmol/L, 10 mL), and cyclohexane (100 mmol/L, 10 mL) were prepared in HPLC-grade degassed 1,2-dichloroethane (DCE). Stock solutions were combined by volume (v) to give 2 mL samples which each contained 0.05 mmol/L Ir(dFppy)$_3$ as well as the concentration of reagents indicated in the "concentration" column of each table. After preparing these stock solutions in separate vials, the volume was transferred to a nitrogen protected 1 cm path cuvette. Samples were excited at 378 nm, then collected from 430-520 nm. Intensities were recorded at 474 nm (λ_{max} emissions of Ir(dFppy)$_3$).

Table S5. Design and results of Stern-Volmer quenching studies.

Experiment	Ir(dFppy)$_3$ mmol/L(v)	**1a** mmol/L(v)	Cyclohexene mmol/L(v)	DCE (v)	Emission height	F$_0$/F
1	0.05 (100 µL)	0 (0 µL)	0	1.90 mL	85.56	1
2	0.05 (100 µL)	0.125 (25 µL)	0	1.88 mL	44.34	1.92
3	0.05 (100 µL)	0.250 (50 µL)	0	1.85 mL	29.86	2.86
4	0.05 (100 µL)	0.375 (75 µL)	0	1.83 mL	22.69	3.77
5	0.05 (100 µL)	0.50 (100 µL)	0	1.80 mL	18.47	4.6
6	0.05 (100 µL)	0	25 (500 µL)	1.40 mL	80.35	1.06
7	0.05 (100 µL)	0	50 (1.00 mL)	0.90 mL	81.30	1.05

Figure S3. Stern-Volmer quenching of Ir(dFppy)$_3$ by 1a.

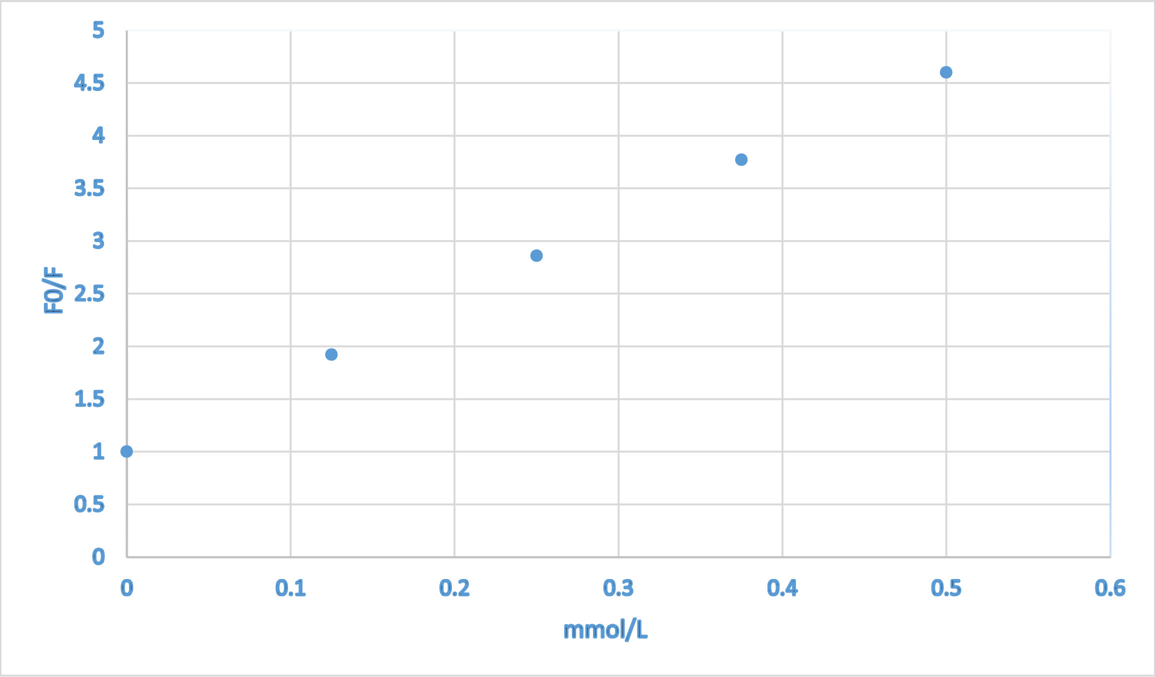
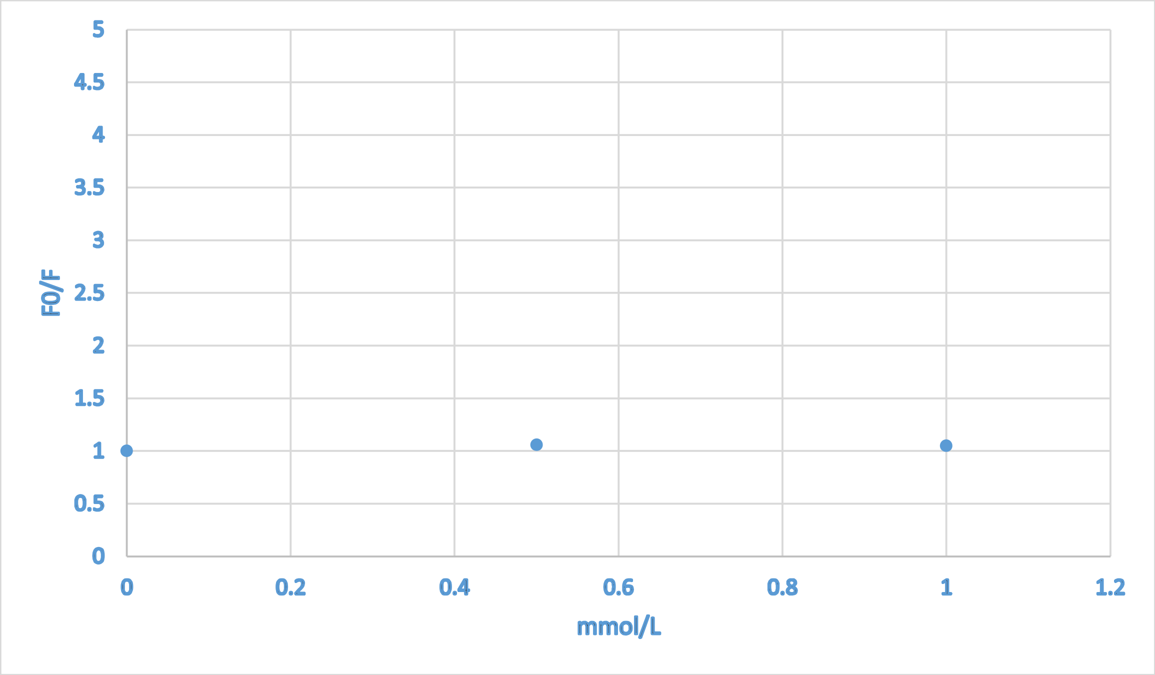
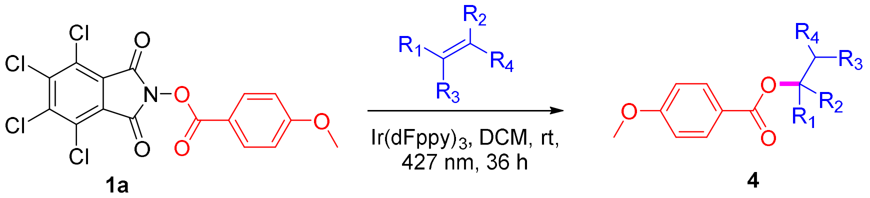


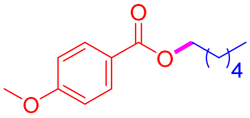
Figure S4. Stern-Volmer quenching of Ir(dFppy)$_3$ by cyclohexene.



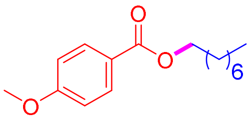
Scope of Hydroesterification (terminal olefins)



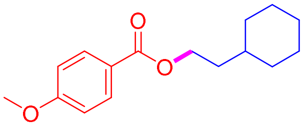
Terminal olefins



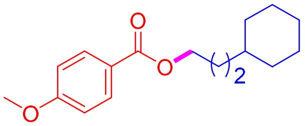
4b: 46%, rr = 4.5/1



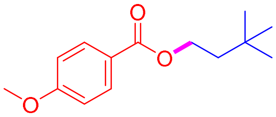
4c: 55%, rr = 3.8/1



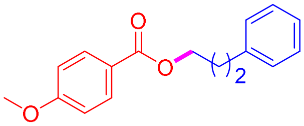
4d: 61%, rr > 10/1



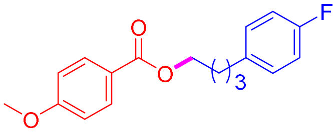
4e: 65%, rr = 6.2/1



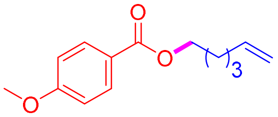
4f: 7%, rr = 2.0/1



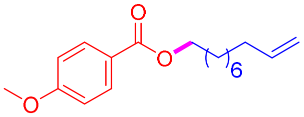
4g: 52%, rr = 4.7/1



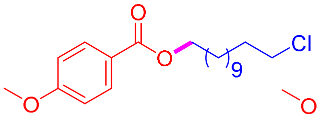
4h: 67%, rr > 10/1



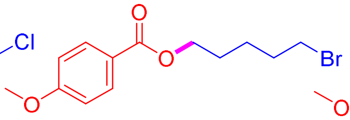
4i: 53%, rr = 4.0/1



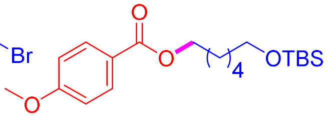
4j: 53%, , rr =5.5/1



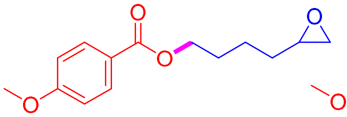
4k: 50%, rr = 3.9/1



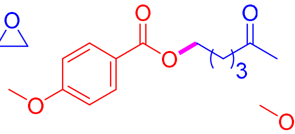
4l: 54%, rr = 5.4/1



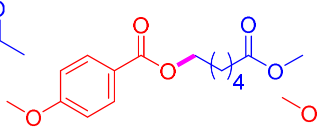
4m: 44%, rr = 3.6/1



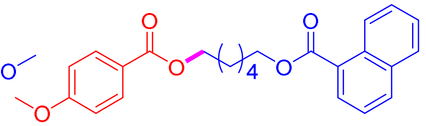
4n: 61% , rr = 3.6/1



4o: 57%, rr = 10/1

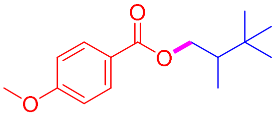


4p: 65%, rr > 10/1

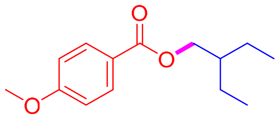


4q: 50%, rr = 3.9/1

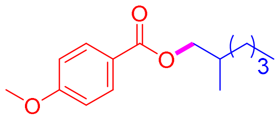
2,2-disubstituted olefins



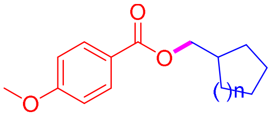
4r: 43%, rr > 10/1



4s: 58%, rr > 10/1



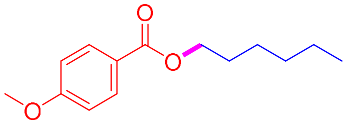
4t: 47%, rr > 10/1



4u (n = 1): 53%, rr > 10/1
4v (n = 2): 66%, rr > 10/1

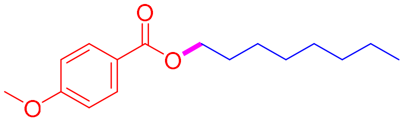
General procedure B.

A dry 8 mL vial equipped with a magnetic stirring bar was charged with 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate **1a** (44.0 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and dry DCM (5.0 mL). Then olefins (5.0 equiv) were added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 24 h or 36 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography to obtain products.



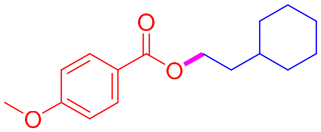
4b

According to the general procedure B, hex-1-ene (42.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (11.0 mg, 46%, rr = 4.5/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 6.94 – 6.89 (m, 2H), 4.28 (t, $J = 6.8$ Hz, 2H), 3.86 (s, 3H), 1.79 – 1.69 (m, 2H), 1.43 (q, $J = 7.4$ Hz, 2H), 1.39 – 1.29 (m, 4H), 0.90 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.46, 163.20, 131.52, 122.96, 113.53, 64.84, 55.41, 31.47, 28.72, 25.72, 22.55, 14.02.
ESI MS m/z: 259.1 $[M+Na]^+$.
The analytic data is consistent with those reported in the literature.[11]



4c

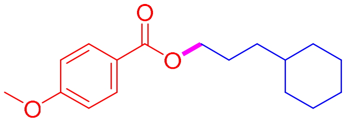
According to the general procedure B, oct-1-ene (56.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (14.7mg, 55%, rr = 3.8/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, $J = 9.0$, 2.2 Hz, 2H), 6.95 – 6.89 (m, 2H), 4.28 (t, $J = 6.8$ Hz, 2H), 3.86 (s, 3H), 1.78 – 1.69 (m, 2H), 1.47 – 1.21 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.51, 163.24, 131.60, 122.99, 113.59, 71.38, 64.88, 55.40, 31.82, 29.23, 28.79, 26.08, 22.67, 14.10.
ESI MS m/z: 287.1 $[M+Na]^+$.
The analytic data is consistent with those reported in the literature.[12]



4d

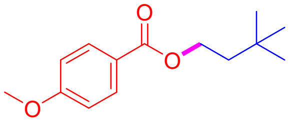
According to the general procedure B, vinylcyclohexane (55.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (16.2 mg, 61%, rr > 10/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 6.96 – 6.89 (m, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 1.80 – 1.74 (m, 2H), 1.71 (dt, *J* = 12.6, 3.6 Hz, 2H), 1.66 – 1.63 (m, 3H), 1.45 (ttt, *J* = 10.6, 7.0, 3.6 Hz, 1H), 1.25 (qt, *J* = 12.4, 3.0 Hz, 2H), 1.16 (qt, *J* = 12.5, 3.1 Hz, 1H), 1.02 – 0.92 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.47, 163.20, 131.52, 122.97, 113.53, 62.99, 55.41, 36.11, 34.72, 33.20, 26.48, 26.21.
ESI MS m/z: 263.1 $[M+H]^+$.



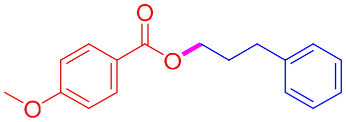
4e

According to the general procedure B, allylcyclohexane (62.8 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (18.3 mg, 65%, rr = 6.2/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 6.96 – 6.89 (m, 2H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 1.81 – 1.61 (m, 7H), 1.34 – 1.09 (m, 6H), 0.96 – 0.85 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.50, 163.24, 131.55, 122.99, 113.56, 65.21, 55.44, 37.36, 33.72, 33.33, 26.66, 26.37, 26.16.
ESI MS m/z: 277.2 $[M+H]^+$.



4f

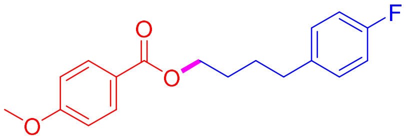
According to the general procedure B, 3,3-dimethylbut-1-ene (42.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (1.6 mg, 7%, rr = 2.0/1) was obtained.
Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.35 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.69 (t, *J* = 7.2 Hz, 2H), 0.99 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.53, 163.24, 131.54, 122.98, 113.57, 62.44, 55.44, 41.95, 40.09, 29.71.
ESI MS m/z: 237.1 $[M+H]^+$.



4g

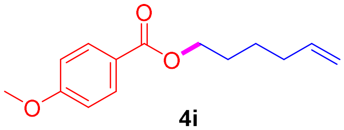
According to the general procedure B, allylbenzene (59.8 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (14.3 mg, 52%, rr = 4.7/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ethyl acetate = 12/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.8Hz, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 6.92 (d, J = 8.8Hz, 2H), 4.31 (t, J = 6.4 Hz, 2H), 3.86 (s, 3H), 2.81 – 2.76 (m, 2H), 2.13 – 2.05 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.40, 163.32, 141.30, 131.59, 128.49, 128.47, 126.02, 122.81, 113.60, 64.00, 55.46, 32.35, 30.39.
ESI MS m/z: 271.1 $[M+H]^+$.
The analytic data is consistent with those reported in the literature.[13]



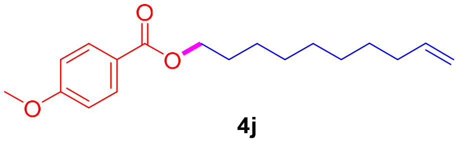
4h

According to the general procedure B, 1-(but-3-en-1-yl)-4-fluorobenzene (76.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (20.6 mg, 67%, rr > 10/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 10/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.16 – 7.11 (m, 2H), 7.00 – 6.94 (m, 2H), 6.94 – 6.89 (m, 2H), 4.30 (t, J = 6.2 Hz, 2H), 3.86 (s, 3H), 2.65 (t, J = 7.2 Hz, 2H), 1.80 – 1.71 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.44, 163.31, 161.27 (d, J = 241.5 Hz), 137.65 (d, J = 3.3 Hz), 131.57, 129.71 (d, J = 7.8 Hz), 122.82, 115.08 (d, J = 20.6 Hz), 113.59, 64.46, 55.45, 34.68, 28.30, 28.00.
ESI MS m/z: 303.1 $[M+H]^+$.



4i

According to the general procedure B, hexa-1,5-diene (41.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (12.5 mg, 53%, rr = 4.0/1) was obtained.
Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 6.96 – 6.88 (m, 2H), 5.82 (ddt, J = 16.9, 10.2, 6.8 Hz, 1H), 5.03 (dq, J = 17.2, 1.6 Hz, 1H), 4.97 (dq, J = 10.2, 1.4 Hz, 1H), 4.29 (t, J = 6.6 Hz, 2H), 3.86 (s, 3H), 2.16 – 2.09 (m, 2H), 1.77 (dt, J = 15.3, 6.7 Hz, 2H), 1.55 – 1.51 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.48, 163.27, 138.44, 131.57, 122.91, 114.86, 113.58, 64.63, 55.45, 33.37, 28.24, 25.35.
ESI MS m/z: 489.9 $[2M+Na]^+$.
The analytic data is consistent with those reported in the literature.[14]



4j

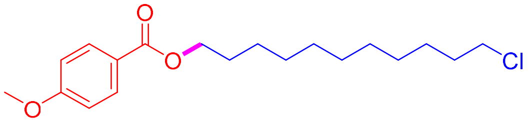
According to the general procedure B, deca-1,9-diene (70.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (15.7 mg, 53%, rr = 5.5/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.94 – 6.89 (m, 2H), 5.86 – 5.71 (m, 1H), 4.99 (dq, J = 17.2, 1.6 Hz, 1H), 4.93 (ddt, J = 10.2, 2.4, 1.2 Hz, 1H), 4.28 (t, J = 6.8 Hz, 2H), 3.86 (s, 3H), 2.07 – 1.99 (m, 2H), 1.78 – 1.67 (m, 2H), 1.47 – 1.27 (m, 10H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.50, 163.25, 139.21, 131.56, 122.98, 114.18, 113.56, 64.86, 55.45, 33.81, 29.39, 29.26, 29.06, 28.91, 28.78, 26.06.

ESI MS m/z: 291.1 $[M+H]^+$.



4k

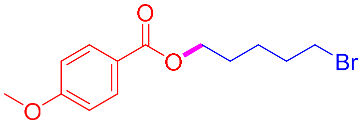
According to the general procedure B, 11-chloroundec-1-ene (95.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (17.2 mg, 50%, rr = 3.9/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 6.96 – 6.89 (m, 2H), 4.28 (t, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.53 (t, J = 6.8 Hz, 2H), 1.80 – 1.69 (m, 4H), 1.46 – 1.37 (m, 4H), 1.37 – 1.24 (m, 10H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.50, 163.25, 131.55, 122.98, 113.56, 71.31, 64.85, 55.45, 45.24, 36.10, 32.66, 29.46, 28.90, 26.89, 26.06, 25.43, 20.17.

ESI MS m/z: 341.1 $[M+H]^+$.



4l

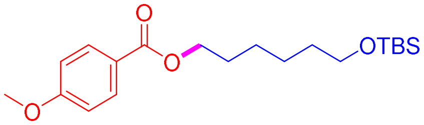
According to the general procedure B, 5-bromopent-1-ene (75.4 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (16.3 mg, 54%, rr = 5.4/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.30 (t, J = 6.4 Hz, 2H), 3.86 (s, 3H), 3.44 (td, J = 6.8, 2.8 Hz, 2H), 1.94 (dt, J = 14.8, 6.8 Hz, 2H), 1.86 – 1.75 (m, 2H), 1.64 – 1.58 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.41, 163.33, 131.58, 122.77, 113.61, 64.35, 55.46, 33.56, 32.35, 27.98, 24.77.

ESI MS m/z: 301.0, 303.1 $[M+H]^+$.



4m

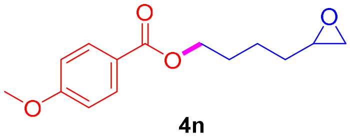
According to the general procedure B, tert-butyl(hex-5-en-1-yloxy)dimethylsilane (108.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (16.3 mg, 44%, rr = 3.6/1) was obtained.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, $J = 8.8$ Hz, 2H), 6.94 – 6.88 (m, 2H), 4.28 (t, $J = 6.8$ Hz, 2H), 3.86 (S, 3H), 3.61 (t, $J = 6.5$ Hz, 2H), 1.75 (dq, $J = 13.6, 6.9$ Hz, 2H), 1.58 – 1.50 (m, 2H), 1.50 – 1.35 (m, 4H), 0.88 (d, $J = 11.2$ Hz, 9H), -0.04 (d, $J = 8.2$ Hz, 6H). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 166.48, 163.25, 131.56, 122.96, 113.56, 64.78, 63.13, 55.44, 32.75, 28.82, 26.00, 25.96, 25.93, 25.56, -5.25.

ESI MS m/z: 367.2 $[M+H]^+$.



4n

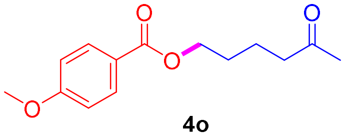
According to the general procedure B, 2-(but-3-en-1-yl)oxirane (49.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (15.5 mg, 61%, rr = 3.6/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ethyl acetate = 10/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 6.94 – 6.89 (m, 2H), 4.30 (t, $J = 6.4$ Hz, 2H), 3.86 (s, 3H), 2.98 – 2.91 (m, 1H), 2.77 (dd, $J = 5.0, 3.8$ Hz, 1H), 2.51 – 2.46 (m, 1H), 1.82 (p, $J = 6.8$ Hz, 2H), 1.70 – 1.54 (m, 4H). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 166.39, 163.28, 131.54, 122.75, 113.56, 64.43, 55.42, 52.13, 47.03, 32.11, 28.58, 22.66.

ESI MS m/z: 251.1 $[M+H]^+$.



4o

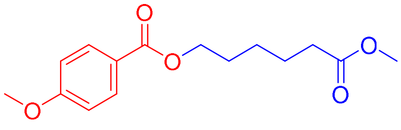
According to the general procedure B, hex-5-en-2-one (50.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (14.5 mg, 57%, rr = 10/1) was obtained.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 6.96 – 6.89 (m, 2H), 4.29 (t, $J = 6.2$ Hz, 2H), 3.86 (s, 3H), 2.51 (t, $J = 6.8$ Hz, 2H), 2.15 (s, 3H), 1.75 (tdt, $J = 10.3, 5.3, 2.4$ Hz, 4H). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 208.59, 166.41, 163.33, 131.59, 122.74, 113.60, 64.24, 55.45, 43.10, 29.99, 28.22, 20.27.

ESI MS m/z: 251.1 $[M+H]^+$.



4p

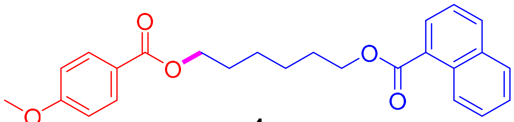
According to the general procedure B, methyl hex-5-enoate (64.8 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (18.3 mg, 65%, rr > 10/1) was obtained as a oil.

Eluting Solvents: hexane/ethyl acetate = 10/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 6.94 – 6.89 (m, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.86 (s, 3H), 3.67 (s, 3H), 2.35 (t, J = 7.6 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.71 (p, J = 7.6 Hz, 2H), 1.52 – 1.42 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.02, 166.39, 163.26, 131.54, 122.80, 113.55, 64.43, 55.42, 51.53, 33.93, 28.46, 25.64, 24.60.

ESI MS m/z: 281.1 $[M+H]^+$.



4q

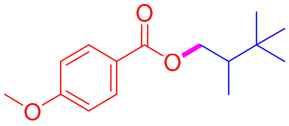
According to the general procedure B, hex-5-en-1-yl 1-naphthoate (128.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (20.5 mg, 50%, rr = 3.9/1) was obtained as a solid.

Eluting Solvents: hexane/DCM = 1/2, v/v.

TLC: (hexane/DCM = 1/1, v/v) $R_f = 0.2$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 – 8.87 (m, 1H), 8.18 – 8.12 (m, 1H), 8.04 – 7.95 (m, 3H), 7.91 – 7.86 (m, 1H), 7.65 – 7.56 (m, 1H), 7.56 – 7.42 (m, 2H), 6.92 – 6.84 (m, 2H), 4.42 (td, J = 6.6, 4.8 Hz, 2H), 4.31 (t, J = 6.6 Hz, 2H), 3.84 (s, 3H), 1.91 – 1.77 (m, 4H), 1.62 – 1.53 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.70, 166.47, 163.28, 133.85, 133.28, 131.56, 131.35, 130.09, 128.55, 127.73, 127.41, 126.20, 125.82, 124.53, 122.86, 113.58, 65.06, 64.63, 55.43, 28.74, 28.74, 25.94, 25.88.

ESI MS m/z: 407.1 $[M+H]^+$.



4r

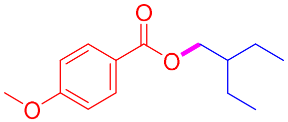
According to the general procedure B, 2,3,3-trimethylbut-1-ene (49.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (11.0 mg, 43%, rr > 10/1) was obtained.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.9$.

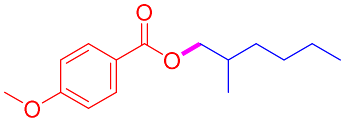
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.95 – 6.89 (m, 2H), 4.44 (dd, J = 10.8, 4.2 Hz, 1H), 4.04 (dd, J = 10.8, 8.4 Hz, 1H), 3.86 (s, 3H), 1.72 (dqd, J = 8.4, 6.8, 4.2 Hz, 1H), 1.01 (d,

J = 6.8 Hz, 3H), 0.96 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 166.62, 163.24, 131.53, 123.04, 113.59, 67.42, 55.45, 42.26, 32.26, 27.70, 12.89.
ESI MS m/z: 251.1 $[M+H]^+$.



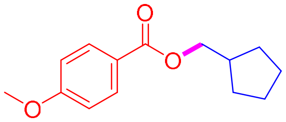
4s

According to the general procedure B, 3-methylenepentane (42.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (14.0 mg, 58%, rr > 10/1) was obtained as a colorless oil.
Eluting Solvents: hexane/DCM = 3/2, v/v.
TLC: (hexane/DCM = 1/1, v/v) R_f = 0.7.
^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.03 – 7.97 (m, 2H), 6.94 – 6.89 (m, 2H), 4.22 (d, *J* = 5.8 Hz, 2H), 3.86 (s, 3H), 1.65 (p, *J* = 6.2 Hz, 1H), 1.45 (pd, *J* = 7.6, 1.6 Hz, 4H), 0.94 (t, *J* = 7.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 166.53, 163.21, 131.51, 122.99, 113.55, 66.64, 55.41, 40.51, 23.51, 11.13.
ESI MS m/z: 237.1 $[M+H]^+$.



4t

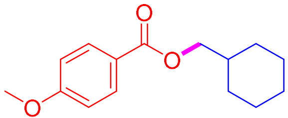
According to the general procedure B, 2-methylhex-1-ene (50.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (12.0 mg, 47%, rr > 10/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 20/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) R_f = 0.9.
^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.04 – 7.97 (m, 2H), 6.97 – 6.89 (m, 2H), 4.17 (dd, *J* = 10.8, 5.8 Hz, 1H), 4.07 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.86 (s, 3H), 1.95 – 1.87 (m, 1H), 1.47 – 1.44 (m, 1H), 1.42 – 1.27 (m, 4H), 1.26 – 1.20 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.95 – 0.87 (m, 3H). **^{13}C NMR** *δ* 166.50, 163.25, 131.54, 123.01, 113.58, 69.62, 55.45, 33.19, 32.73, 29.11, 22.92, 17.09, 14.10.
ESI MS m/z: 251.0 $[M+H]^+$.



4u

According to the general procedure B, methylenecyclopentane (41.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (12.6 mg, 53%, rr > 10/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) R_f = 0.8.

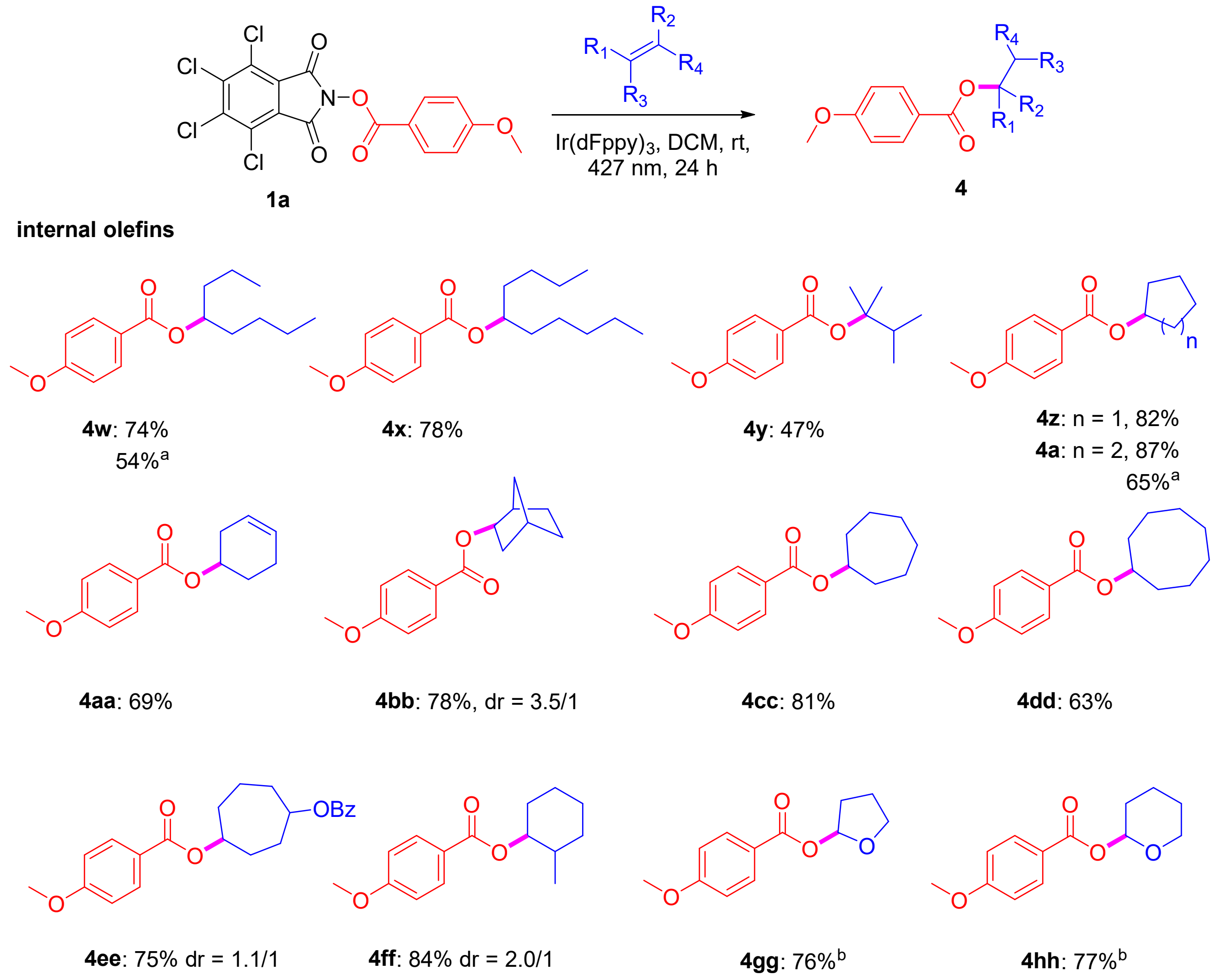
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.12 – 7.80 (m, 2H), 6.96 – 6.87 (m, 2H), 4.18 (d, J = 7.2 Hz, 2H), 3.86 (s, 3H), 2.36 – 2.29 (m, 1H), 1.86 – 1.76 (m, 2H), 1.71 – 1.53 (m, 4H), 1.41 – 1.31 (m, 2H).
^{13}C NMR (150 MHz, CDCl$_3$) δ 166.55, 163.25, 131.57, 123.01, 113.57, 68.62, 55.44, 38.72, 29.43, 25.40.
ESI MS m/z: 235.1 [M+H]$^+$.



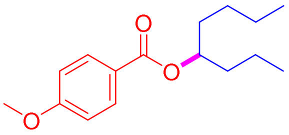
4v

According to the general procedure B, methylenecyclohexane (48.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (16.6 mg, 66%, rr > 10/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) R$_f$ = 0.8.
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.02 – 7.95 (m, 2H), 6.94 – 6.89 (m, 2H), 4.10 (d, J = 6.4 Hz, 2H), 3.86 (s, 3H), 1.83 – 1.67 (m, 6H), 1.32 – 1.13 (m, 3H), 1.07 (td, J = 12.2, 3.6 Hz, 2H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 166.49, 163.24, 131.57, 123.01, 113.57, 69.82, 55.46, 37.33, 29.81, 26.42, 25.76.
ESI MS m/z: 249.1 [M+H]$^+$.

Scope of Hydroesterification (internal olefins)



[a] 1 mmol of **1a**. [b] The phthalimide ester substrate was 1,3-dioxoisoindolin-2-yl 4-methoxybenzoate.

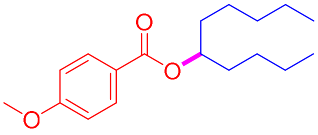


4w

According to the general procedure B, (E)-oct-4-ene (56.8 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (19.8 mg, 74%) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 6.96 – 6.89 (m, 2H), 5.11 (tt, $J = 7.6, 5.0$ Hz, 1H), 3.86 (s, 3H), 1.71 – 1.57 (m, 4H), 1.47 – 1.27 (m, 6H), 0.98 – 0.85 (m, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.19, 163.17, 131.55, 123.33, 113.53, 74.45, 55.45, 36.48, 34.03, 27.55, 22.69, 18.67, 14.09, 14.05.
ESI MS m/z: 265.1 $[M+H]^+$.

1 mmol scale reaction

A 100 mL dry flask equipped with a magnetic stirring bar was charged with 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate **1a** (440 mg, 1.0 mmol, 1.0 equiv), Ir(dFppy)$_3$ (7.8 mg, 1.00 µmol, 0.01 equiv), and dry DCM (80 mL). Then (E)-oct-4-ene (567 mg, 5 mmol, 5.0 equiv) was added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 60 h (the internal temperature of reaction solution was about 40 ˚C). After reaction, the mixture was filtered by Celite and washed with DCM (10 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography (eluting with hexane/ ethyl acetate = 15/1, v/v).) to obtain product (146 mg, 54%) as a yellow oil.



4x

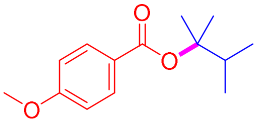
According to the general procedure B, (E)-dec-5-ene (71.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (23.0 mg, 78%) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.

TLC: (hexane/ ethyl acetate = 3/1, v/v) R$_f$ = 0.8.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.03 – 7.97 (m, 2H), 6.96 – 6.89 (m, 2H), 5.09 (tt, J = 7.3, 5.1 Hz, 1H), 3.86 (s, 3H), 1.71 – 1.57 (m, 4H), 1.45 – 1.16 (m, 10H), 0.96 – 0.83 (m, 6H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 166.19, 163.17, 131.54, 123.35, 113.53, 74.70, 55.45, 34.25, 33.99, 31.80, 27.56, 25.05, 22.69, 22.57, 14.05, 14.05.

ESI MS m/z: 293.2 [M+H]$^+$.



4y

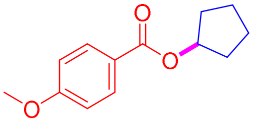
According to the general procedure B, 2,3-dimethylbut-2-ene (42.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (11.3 mg, 47%) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.

TLC: (hexane/ ethyl acetate = 3/1, v/v) R$_f$ = 0.8.

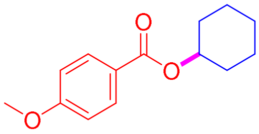
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.98 – 7.90 (m, 2H), 6.94 – 6.87 (m, 2H), 3.85 (s, 3H), 2.37 – 2.27 (m, 1H), 1.54 (s, 6H), 0.98 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 165.54, 162.93, 131.34, 124.66, 113.42, 85.67, 55.42, 36.75, 23.00, 17.45.

ESI MS m/z: 259.2 [M+Na]$^+$.



4z

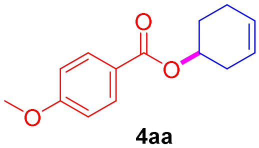
According to the general procedure B, cyclopentene (34.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (18.2 mg, 82%) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) R_f = 0.8.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 6.93 – 6.88 (m, 2H), 5.38 (tt, J = 6.2, 2.8 Hz, 1H), 3.86 (s, 3H), 1.99 – 1.89 (m, 2H), 1.86 – 1.76 (m, 4H), 1.69 – 1.61 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.18, 163.16, 131.50, 123.37, 113.49, 77.33, 55.44, 32.82, 23.85.
ESI MS m/z: 221.1 $[M+H]^+$.
The analytic data is consistent with those reported in the literature.[15]



4a

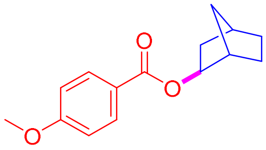
According to the general procedure B, cyclohexene (41.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (20.6 mg, 87%) was obtained as a colorless oil.
TLC: (hexane/ethyl acetate = 3/1, v/v) R_f = 0.8.
Purification: eluting with hexane/ ethyl acetate = 15/1, v/v.
Data refer to former data for this product in the optimization section above.

1 mmol scale reaction
The procedure described for product **4w** was followed. The crude reaction residue was purified directly by silica-gel column chromatography (eluting with hexane/ ethyl acetate = 15/1, v/v).) to obtain product (154 mg, 65%) as a yellow solid.



4aa

According to the general procedure B, cyclohexa-1,4-diene (40.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (16.2 mg, 69%) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) R_f = 0.7.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 6.94 – 6.89 (m, 2H), 5.73 (ddt, J = 9.8, 3.6, 1.6 Hz, 1H), 5.66 – 5.60 (m, 1H), 5.25 (dddd, J = 9.6, 6.8, 5.2, 3.2 Hz, 1H), 3.86 (s, 3H), 2.52 – 2.45 (m, 1H), 2.30 – 2.14 (m, 3H), 2.04 – 1.94 (m, 1H), 1.91 – 1.82 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.93, 163.23, 131.58, 126.81, 123.78, 123.27, 113.53, 69.86, 55.45, 30.87, 27.38, 23.23.
ESI MS m/z: 233.1 $[M+H]^+$.



4bb

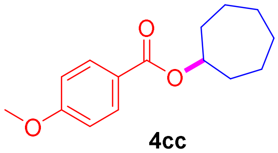
According to the general procedure B, bicyclo[2.2.1]hept-2-ene (47.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (19.4 mg, 78%, dr = 3.5/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 12/1, v/v.

TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 7.88 (m, 2H), 6.99 – 6.79 (m, 2H), 4.82 (ddt, *J* = 7.2, 2.4, 1.2 Hz, 1H), 3.86 (s, 3H), 2.43 (d, *J* = 5.0 Hz, 1H), 2.33 (t, *J* = 4.4 Hz, 1H), 1.82 (ddd, *J* = 13.6, 7.0, 2.5 Hz, 1H), 1.64 (dp, *J* = 9.8, 1.9 Hz, 1H), 1.60 – 1.53 (m, 2H), 1.50 – 1.44 (m, 1H), 1.24 – 1.18 (m, 2H), 1.16 – 1.11 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.01, 163.17, 131.48, 123.34, 113.50, 77.81, 55.44, 41.59, 39.71, 35.45, 35.45, 28.24, 24.32.

ESI MS m/z: 267.1 $[M+Na]^+$.



4cc

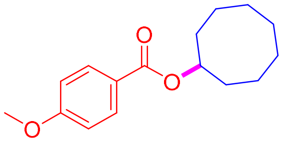
According to the general procedure B, cycloheptene (48.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (20.3 mg, 81%) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.

TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.94 – 6.88 (m, 2H), 5.16 (tt, *J* = 8.4, 4.4 Hz, 1H), 3.86 (s, 3H), 2.04 – 1.95 (m, 2H), 1.83 – 1.78 (m, 2H), 1.76 – 1.68 (m, 2H), 1.64 – 1.58 (m, 4H), 1.55 – 1.48 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.71, 163.10, 131.48, 123.50, 113.46, 75.21, 55.40, 33.86, 28.32, 22.94.

ESI MS m/z: 271.1 $[M+Na]^+$.



4dd

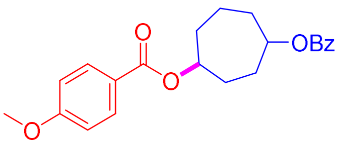
According to the general procedure B, (Z)-cyclooctene (55.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (16.8 mg, 63%) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.

TLC: (hexane/ ethyl acetate = 6/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 6.95 – 6.88 (m, 2H), 5.16 (tt, *J* = 8.2, 4.0 Hz, 1H), 3.86 (s, 3H), 1.96 – 1.82 (m, 4H), 1.82 – 1.72 (m, 2H), 1.69 – 1.48 (m, 8H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.74, 163.12, 131.50, 123.58, 113.49, 75.26, 55.44, 31.56, 27.20, 25.38, 22.96.

ESI MS m/z: 285.2 $[M+Na]^+$.



4ee

According to the general procedure B, cyclohept-4-en-1-yl benzoate (109.4 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target products (isomer A: 14.8 mg, 40%, isomer B: 13.2 mg, 35%, dr = 1.1/1) were obtained as white solid.

Isomer A:

Eluting Solvents: dichloromethane.

TLC: (hexane/ dichloromethane = 10/1, v/v) $R_f = 0.3$.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.08 – 8.02 (m, 2H), 8.02 – 7.98 (m, 2H), 7.60 – 7.53 (m, 1H), 7.48 – 7.42 (m, 2H), 6.95 – 6.90 (m, 2H), 5.33 – 5.24 (m, 2H), 3.87 (s, 3H), 2.22 – 2.13 (m, 2H), 2.13 – 2.05 (m, 2H), 1.90 – 1.82 (m, 4H), 1.80 – 1.69 (m, 2H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 165.88, 165.63, 163.30, 132.87, 131.57, 130.75, 129.56, 128.37, 123.16, 113.59, 74.46, 74.00, 55.47, 34.04, 34.00, 28.04, 28.04, 18.49.

ESI MS m/z: 391.2 $[M+Na]^+$.

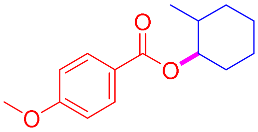
Isomer B:

Eluting Solvents: dichloromethane.

TLC: (hexane/ dichloromethane = 10/1, v/v) $R_f = 0.2$.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.11 – 8.04 (m, 2H), 8.04 – 7.94 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 6.96 – 6.89 (m, 2H), 5.29 – 5.19 (m, 2H), 3.86 (s, 3H), 2.17 – 2.06 (m, 4H), 1.99 – 1.84 (m, 5H), 1.57 (s, 3H), 1.57 – 1.47 (m, 1H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 165.88, 165.63, 163.28, 132.84, 131.57, 130.80, 129.57, 128.35, 123.21, 113.57, 74.40, 73.94, 55.46, 34.12, 34.07, 27.97, 27.94, 18.70.

ESI MS m/z: 391.2 $[M+Na]^+$.



4ff

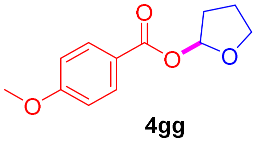
According to the general procedure B, 1-methylcyclohex-1-ene (48.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (21.0 mg, 84%, dr = 2.0/1) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 12/1, v/v.

TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, CDCl$_3$ δ 8.09 – 7.95 (m, 2H), 6.96 – 6.92 (m, 2H), 5.19 – 5.17 (m, 0.34 H), 4.65 (td, J = 10.2, 4.2 Hz, 0.67H), 3.88 (s, 3H), 2.39 – 1.65 (m, 5H), 1.55 – 1.09 (m, 4H), 0.97 – 0.96 (m, 3H). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 166.11, 165.96, 163.18, 163.18, 131.54, 131.51, 123.52, 123.35, 113.57, 113.52, 78.68, 73.96, 55.45, 55.43, 37.48, 36.84, 35.01, 33.54, 31.85, 29.70, 25.47, 25.38, 24.87, 24.78, 22.19, 21.10, 18.55, 17.64.

ESI MS m/z: 519.2 $[2M+Na]^+$.



4gg

According to the general procedure B, 1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (30 mg, 0.1 mmol, 1 equiv), 2,3-dihydrofuran (35.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (17.0 mg, 76%) was obtained as a colorless oil.

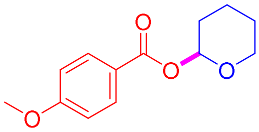
Eluting Solvents: hexane/ ethyl acetate = 10/1, v/v.

TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.6$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 6.93 – 6.89 (m, 2H), 6.52 (d, J = 4.0 Hz, 1H), 4.13 (td, J = 8.0, 5.4 Hz, 1H), 3.99 (q, J = 7.6 Hz, 1H), 3.86 (s, 3H), 2.22 – 2.08 (m, 3H), 2.03 – 1.97 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.71, 163.43, 131.73, 122.77, 113.56, 99.39, 68.99, 55.46, 32.30, 23.02.

ESI MS m/z: 245.1 $[M+Na]^+$.

The analytic data is consistent with those reported in the literature.[16]



4hh

According to the general procedure B, 1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (30 mg, 0.1 mmol, 1 equiv), 3,4-dihydro-2H-pyran (42.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (18.3 mg, 77%) was obtained as a colorless oil.

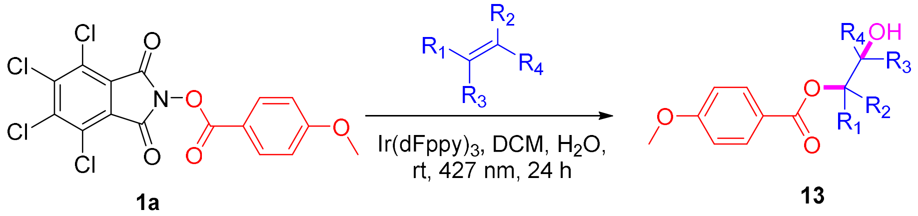
Eluting Solvents: hexane/ ethyl acetate = 10/1, v/v.

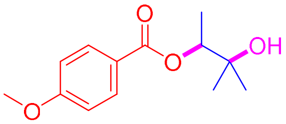
TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.6$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 7.99 (m, 2H), 6.99 – 6.91 (m, 2H), 6.21 (t, J = 3.2 Hz, 1H), 3.99 (ddd, J = 11.6, 10.0, 3.0 Hz, 1H), 3.87 (s, 3H), 3.75 (dtd, J = 11.4, 4.2, 1.6 Hz, 1H), 2.01 – 1.79 (m, 3H), 1.78 – 1.69 (m, 2H), 1.68 – 1.60 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.94, 163.52, 131.84, 122.68, 113.65, 92.83, 63.27, 55.47, 29.37, 25.08, 18.76.

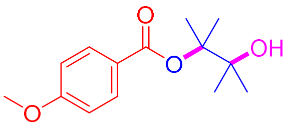
ESI MS m/z: 495.2 $[2M+Na]^+$.

Difunctionalization of olefins

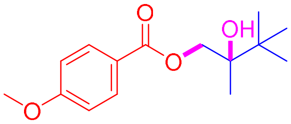




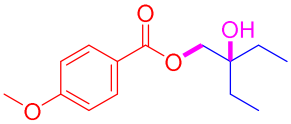
13a: 33%



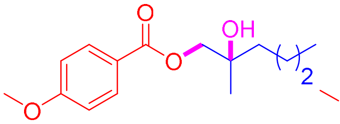
13b: 43%



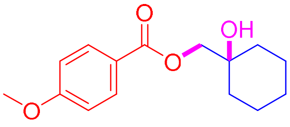
13c: 63%



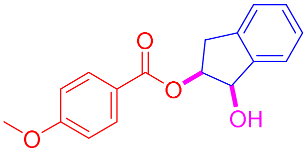
13d: 47%



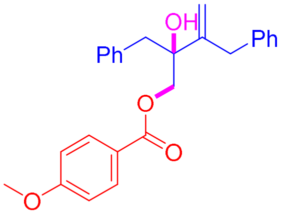
13e: 45%



13f: 50%

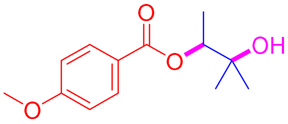


13g: 63%



13g: 64%

General procedure C.
A 8 dry mL vial equipped with a magnetic stirring bar was charged with 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate **1A** (44.0 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 μmol, 0.01 equiv), and DCM (5.0 mL). Then olefins (5.0 equiv) and H_2O (18.0 mg, 1 mmol, 10.0 equiv) were added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 24 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography to obtain products.



13a

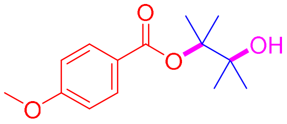
According to the general procedure C, 2-methylbut-2-ene (35.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (8.0 mg, 33%) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 6/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.4$.

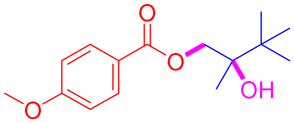
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 6.98 – 6.93 (m, 2H), 5.04 (q, J = 6.4 Hz, 1H), 3.89 (s, 3H), 1.86 (s, 1H), 1.36 (d, J = 6.4 Hz, 3H), 1.31 (d, J = 5.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.85, 163.47, 131.63, 122.75, 113.69, 72.45, 55.50, 26.31, 24.86, 15.09.

ESI MS m/z: 239.1 $[M+H]^+$.



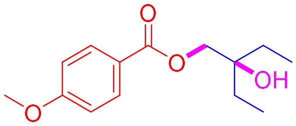
13b

According to the general procedure C, 2,3-dimethylbut-2-ene (42.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (11.0 mg, 43%) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.4$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 6.95 – 6.89 (m, 2H), 3.93 (s, 1H), 3.86 (s, 3H), 1.61 (s, 6H), 1.28 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.58, 163.43, 131.65, 123.58, 113.65, 89.98, 74.83, 55.50, 25.34, 22.22.
ESI MS m/z: 253.1 $[M+H]^+$.



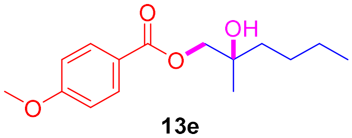
13c

According to the general procedure C, 2,3,3-trimethylbut-1-ene (49.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (17.0 mg, 63%) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 6.96 – 6.88 (m, 2H), 4.42 (d, J = 11.2 Hz, 1H), 4.30 (d, J = 11.2 Hz, 1H), 3.87 (s, 3H), 1.96 (s, 1H), 1.27 (s, 3H), 1.04 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.72, 163.53, 131.68, 122.42, 113.73, 75.73, 69.15, 55.49, 36.90, 25.47, 20.32.
ESI MS m/z: 267.1 $[M+H]^+$.



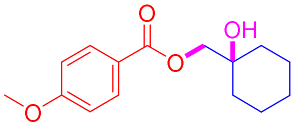
13d

According to the general procedure C, 3-methylenepentane (42.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (12.0 mg, 47%) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 6.96 – 6.91 (m, 2H), 4.23 (s, 2H), 3.87 (s, 3H), 1.86 (s, 1H), 1.62 (q, J = 7.5 Hz, 4H), 0.95 (t, J = 7.5 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.43, 163.53, 131.69, 122.36, 113.72, 74.05, 69.13, 55.49, 28.73, 7.69.
ESI MS m/z: 253.1 $[M+H]^+$.



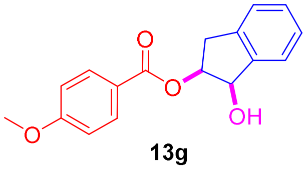
13e

According to the general procedure C, 2-methylhex-1-ene (49.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (12.0 mg, 45%) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.
^{1}**H NMR** (600 MHz, $CDCl_3$) *δ* 8.05 – 7.98 (m, 2H), 6.96 – 6.91 (m, 2H), 4.24 – 4.16 (m, 2H), 3.87 (s, 3H), 1.96 (s, 1H), 1.60 – 1.57 (m, 2H), 1.43 – 1.29 (m, 4H), 1.28 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (150 MHz, $CDCl_3$) *δ* 166.39, 163.54, 131.70, 122.34, 113.72, 72.09, 71.27, 55.49, 39.01, 25.83, 24.02, 23.26, 14.07.
ESI MS m/z: 267.1 $[M+H]^+$.



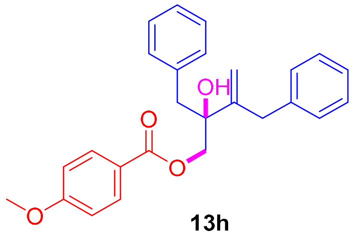
13f

According to the general procedure C, methylenecyclohexane (48.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (13.3 mg, 50%) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
^{1}**H NMR** (600 MHz, $CDCl_3$) *δ* 8.04 – 7.98 (m, 2H), 6.96 – 6.90 (m, 2H), 4.21 (s, 2H), 3.87 (s, 3H), 1.91 (s, 1H), 1.70 – 1.64 (m, 4H), 1.62 – 1.49 (m, 5H), 1.35 – 1.28 (m, 1H). ^{13}**C NMR** (150 MHz, $CDCl_3$) *δ* 166.42, 163.52, 131.71, 122.36, 113.70, 71.77, 70.93, 55.49, 34.44, 25.73, 21.67.
ESI MS m/z: 265.1 $[M+H]^+$.



13g

According to the general procedure C, 1H-indene (58.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (18.0 mg, 63%) was obtained as a colorless oil.
Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.
^{1}**H NMR** (600 MHz, $CDCl_3$) *δ* 7.98 – 7.93 (m, 2H), 7.49 – 7.43 (m, 1H), 7.39 – 7.27 (m, 3H), 6.93 – 6.87 (m, 2H), 5.73 (dt, *J* = 6.6, 3.2 Hz, 1H), 5.42 (d, *J* = 3.2 Hz, 1H), 3.85 (s, 3H), 3.68 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.06 (dd, *J* = 16.8, 3.6 Hz, 1H). ^{13}**C NMR** (150 MHz, $CDCl_3$) *δ* 165.74, 163.63, 140.19, 140.07, 131.85, 129.52, 127.73, 125.44, 125.11, 121.99, 113.66, 81.96, 64.41, 55.48, 37.03.
ESI MS m/z: 267.1 $[M–H_2O+H]^+$.



13h

According to the general procedure C, (2,3-dimethylenebutane-1,4-diyl)dibenzene (118.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (26.0 mg, 64%) was obtained as a white solid.

Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.

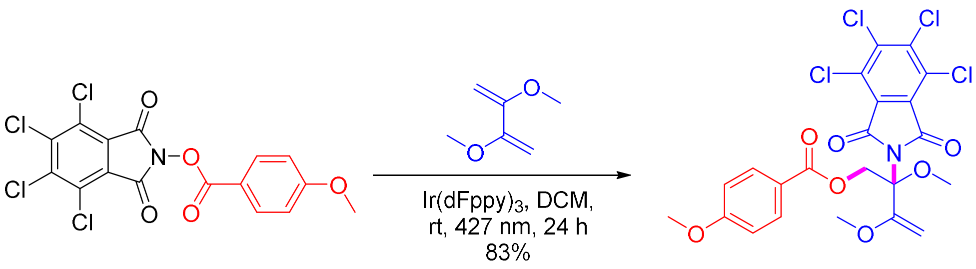
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.33 – 7.22 (m, 7H), 7.21 – 7.15 (m, 1H), 7.15 – 7.12 (m, 2H), 6.94 – 6.89 (m, 2H), 5.17 (s, 1H), 4.77 (d, *J* = 1.6 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.28 (d, *J* = 11.4 Hz, 1H), 3.87 (s, 3H), 3.45 (d, *J* = 15.8 Hz, 1H), 3.39 (d, *J* = 15.8 Hz, 1H), 3.09 – 3.00 (m, 2H), 2.31 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.18, 163.57, 150.17, 139.27, 135.79, 131.73, 130.69, 129.45, 128.39, 128.23, 126.86, 126.20, 122.13, 114.37, 113.70, 77.0, 69.26, 55.49, 43.76, 38.97.

ESI MS m/z: 403.2 $[M+H]^+$.

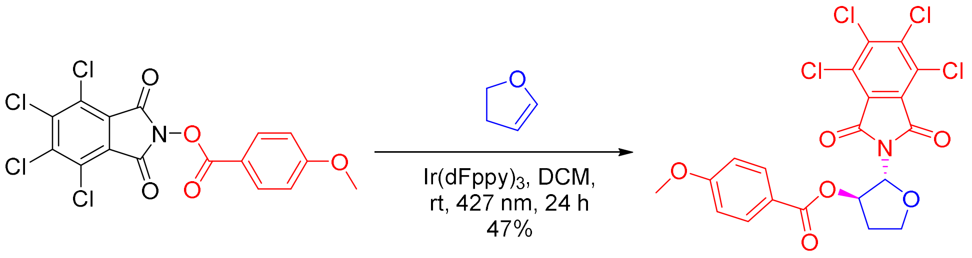
Unexpected Oxidations with 1a

General procedure B.
A dry 8 mL vial equipped with a magnetic stirring bar was charged with 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate **1a** (44.0 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and dry DCM (5.0 mL). Then olefins (5.0 equiv) were added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 24 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography to obtain products.



1a **14a**

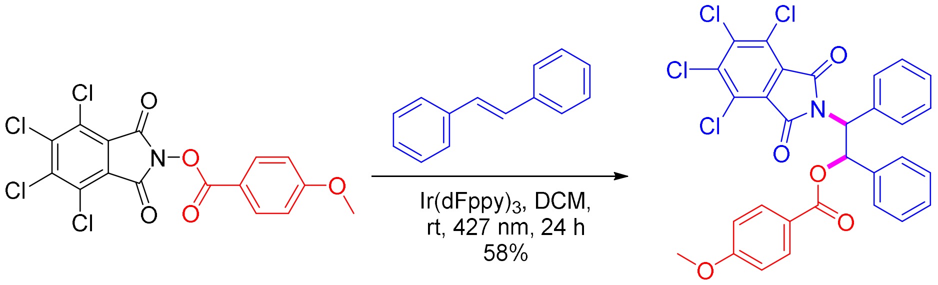
According to the general procedure B, 2,3-dimethoxybuta-1,3-diene (57.8 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, the target product (46.3 mg, 83%) was obtained as a white solid.
Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
^{1}**H NMR** (600 MHz, CDCl$_3$) δ 8.00 – 7.95 (m, 2H), 6.94 – 6.89 (m, 2H), 5.50 (dd, *J* = 12.0, 1.6 Hz, 1H), 4.99 (dd, *J* = 12.0, 1.6 Hz, 1H), 4.74 (t, *J* = 2.2 Hz, 1H), 4.36 (t, *J* = 2.2 Hz, 1H), 3.86 (s, 3H), 3.53 (s, 3H), 3.46 (s, 3H). ^{13}**C NMR** (150 MHz, CDCl$_3$) δ 165.25, 163.49, 163.23, 156.54, 140.62, 131.86, 129.96, 126.81, 122.29, 113.65, 90.73, 85.24, 60.58, 55.60, 55.46, 51.64.
ESI MS m/z: 549.9, 548.0 $[M+H]^+$.



1a **14b**

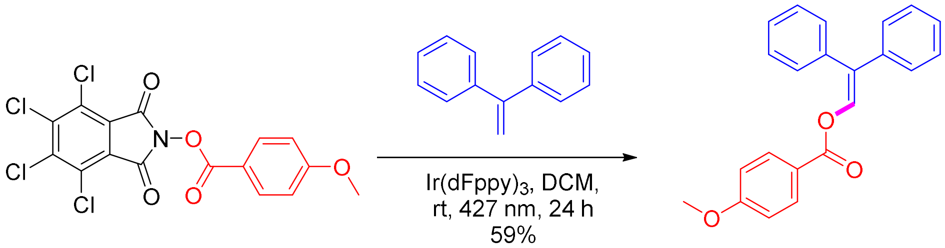
According to the general procedure B, 2,3-dihydrofuran (35.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (24.3 mg, 47%) was obtained as a white solid. Relative stereochemistry was established by x-ray crystallography (see p S48). A single crystal was grown from slow evaporation from EtOAc.
Eluting Solvents: hexane/ethyl acetate = 6/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.5$.
^{1}**H NMR** (600 MHz, CDCl$_3$) δ 7.98 – 7.89 (m, 2H), 7.09 – 7.02 (m, 2H), 5.83 (ddd, *J* = 7.2, 3.2, 2.4 Hz, 1H), 5.79 (d, *J* = 2.2 Hz, 1H), 4.23 (td, *J* = 8.0, 5.6 Hz, 1H), 4.12 (dt, *J* = 8.4, 7.2 Hz, 1H),

3.84 (s, 3H), 2.76 (dq, J = 13.6, 7.6 Hz, 1H), 2.19 (dddd, J = 13.2, 7.2, 5.6, 3.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.40, 163.94, 163.20, 139.09, 132.03, 128.97, 128.46, 121.68, 114.58, 85.69, 77.53, 69.31, 56.06, 32.83.
ESI MS m/z: 506.0, 504.0 $[M+H]^+$.



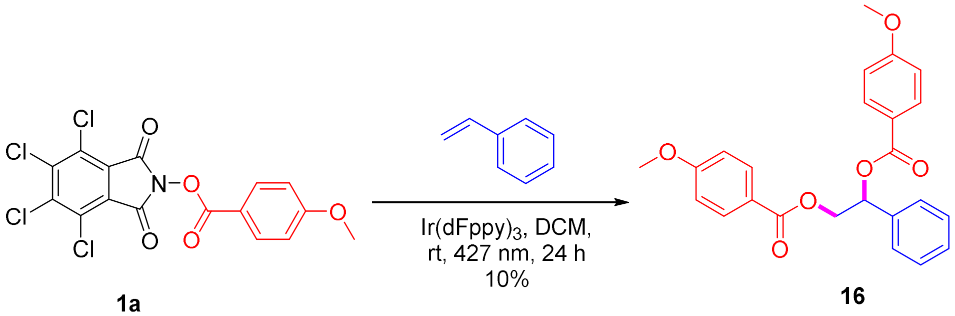
1a **14c**

According to the general procedure B, (E)-1,2-diphenylethene (91.1 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (36.0 mg, 58%) was obtained as a white solid.
Eluting Solvents: hexane/ethyl acetate = 10/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.73 (dd, J = 7.2, 1.8 Hz, 2H), 7.58 (dd, J = 7.2, 1.8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.23 (t, J = 7.4 Hz, 1H), 6.83 – 6.78 (m, 2H), 5.94 (d, J = 11.1 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.66, 163.43, 162.81, 140.26, 136.98, 135.95, 131.64, 129.69, 129.09, 128.91, 128.89, 128.76, 128.76, 127.63, 126.82, 122.07, 113.55, 73.06, 58.49, 55.42.
ESI MS m/z: 638.0, 636.0 $[M+Na]^+$.



1a **15**

According to the general procedure B, ethene-1,1-diyldibenzene (91.1 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (19.8 mg, 59%) was obtained as a white solid.
Eluting Solvents: hexane/ethyl acetate = 12/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.91 (s, 1H), 7.42 (d, J = 4.4 Hz, 4H), 7.39 – 7.29 (m, 6H), 6.94 – 6.88 (m, 2H), 3.86 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.91, 163.19, 139.07, 136.99, 132.59, 132.25, 130.22, 128.43, 128.38, 128.09, 127.60, 127.56, 127.38, 121.15, 113.92, 55.52.
ESI MS m/z: 353.1 $[M+Na]^+$.



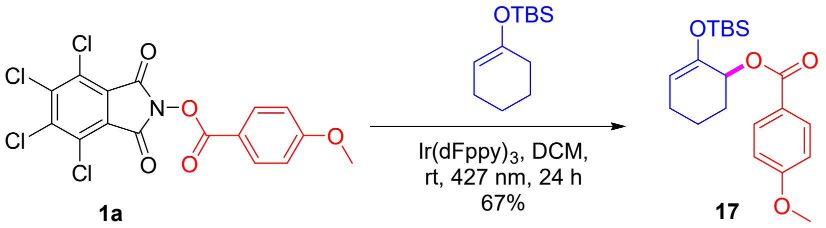
According to the general procedure B, styrene (56.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (4.3 mg, 10%) was obtained as a colorless oil.

Eluting Solvents: hexane/ethyl acetate = 12/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.97 – 7.92 (m, 2H), 7.53 – 7.48 (m, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 6.95 – 6.90 (m, 2H), 6.90 – 6.85 (m, 2H), 6.37 (dd, *J* = 8.2, 3.7 Hz, 1H), 4.70 (dd, *J* = 11.9, 8.2 Hz, 1H), 4.61 (dd, *J* = 11.9, 3.8 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 165.99, 165.40, 163.56, 163.48, 136.94, 131.86, 131.76, 128.73, 128.62, 126.71, 122.35, 122.16, 113.70, 113.67, 73.76, 66.53, 55.48, 55.45.

ESI MS m/z: 835.2 $[2M+Na]^+$.



According to the general procedure B, tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (107.2 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. After reaction and work up, target product (24.6 mg, 67%) was obtained as a colorless oil.

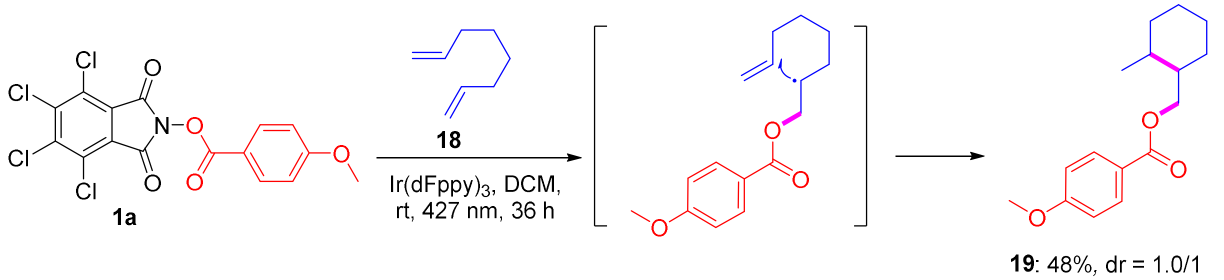
Eluting Solvents: hexane/ethyl acetate = 12/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.13 – 7.93 (m, 2H), 6.98 – 6.76 (m, 2H), 5.51 – 5.39 (m, 1H), 5.16 (dd, *J* = 5.0, 3.2 Hz, 1H), 3.86 (s, 3H), 2.21 – 2.12 (m, 1H), 2.10 – 2.02 (m, 1H), 2.02 – 1.93 (m, 1H), 1.87 – 1.80 (m, 1H), 1.70 – 1.59 (m, 2H), 0.81 (s, 9H), 0.14 (s, 3H), 0.07 (s, 3H). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 168.04, 165.29, 149.77, 133.77, 125.28, 115.57, 111.57, 71.91, 57.51, 31.68, 27.62, 26.07, 20.34, 20.00, -2.14, -2.65.

ESI MS m/z: 363.1 $[M+H]^+$.

Evidence for Radical Intermediates



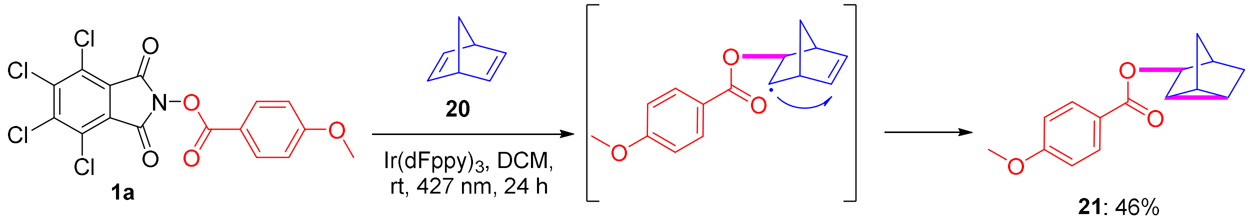
According to the general procedure B, octa-1,7-diene (55.7 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, two cyclized products (12.8 mg, 48%, dr = 1/1) were obtained as two main isomers.

Eluting Solvents: hexane/ethyl acetate = 15/1, v/v.

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.92 – 6.90 (m, 2H), 4.46 – 4.12 (m, 2H), 3.86 (s, 3H), 2.09 – 1.60 (m, 4H), 1.56 – 1.13 (m, 6H), 0.98 (d, *J* = 6.0 Hz, 1.5H), 0.94 (d, *J* = 6.9 Hz, 1.5H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.55, 166.51, 163.24, 131.55, 123.04, 123.03, 113.59, 113.57, 67.83, 55.44, 43.80, 39.20, 35.66, 34.37, 32.39, 30.16, 26.37, 26.35, 26.14, 24.86, 20.28.

ESI MS m/z: 285.1 $[M+Na]^+$.



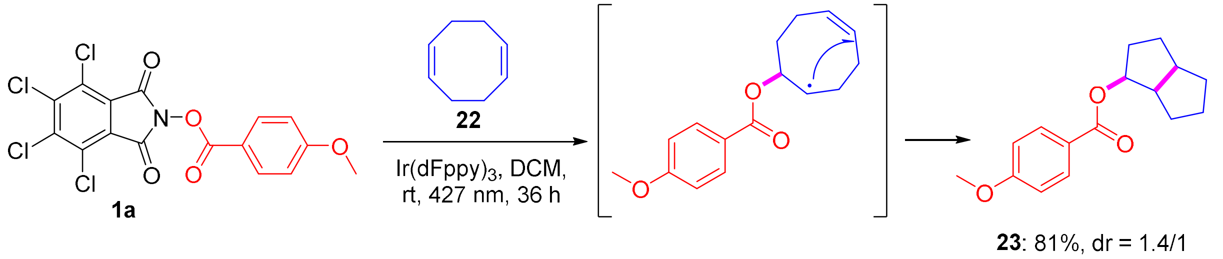
According to the general procedure B, 2,5-Norbornadiene (46.6 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (11.3 mg, 46%) was obtained as a colorless oil.

Eluting Solvents: hexane/ ethyl acetate = 15/1, v/v.

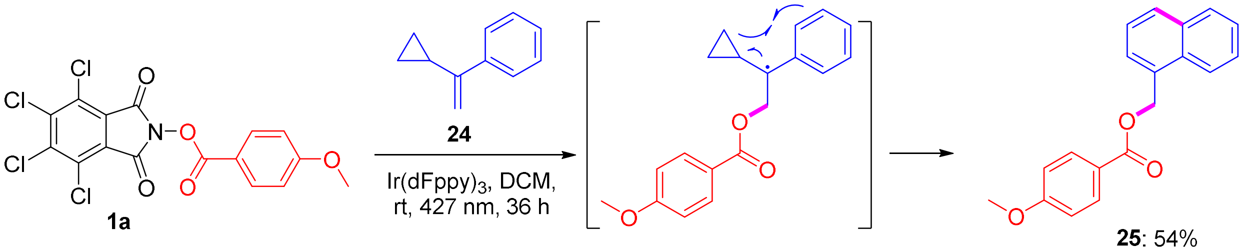
TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.7$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 6.94 – 6.87 (m, 2H), 4.88 (t, *J* = 1.8 Hz, 1H), 3.86 (s, 3H), 2.15 (p, *J* = 1.5 Hz, 1H), 1.92 (dt, *J* = 10.4, 1.4 Hz, 1H), 1.57 – 1.52 (m, 1H), 1.39 – 1.28 (m, 5H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.36, 163.18, 131.51, 123.15, 113.49, 80.10, 55.41, 33.55, 30.48, 30.47, 13.90, 13.05, 11.29.

ESI MS m/z: 245.1 $[M+H]^+$.

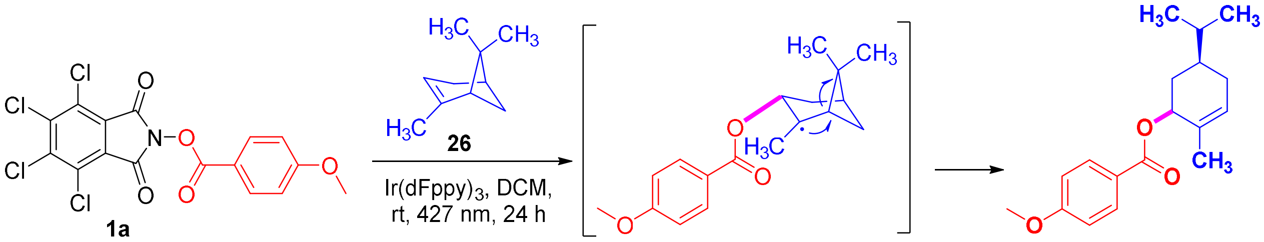


According to the general procedure B, (1Z,5Z)-cycloocta-1,5-diene (54.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (21.3 mg, 81%, dr = 1.4/1) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 12/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.7$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 6.94 – 6.88 (m, 2H), 5.31 – 5.28 (m, 0.4 H) 5.03 (td, *J* = 4.8, 4.3, 2.6 Hz, 0.53H), 3.86 (d, *J* = 2.3 Hz, 3H), 2.77 – 2.47 (m, 2H), 2.05 – 1.74 (m, 4H), 1.70 – 1.18 (m, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.16, 163.20, 163.15, 131.51, 123.42, 123.25, 113.57, 113.49, 82.82, 77.98, 55.44, 49.96, 45.99, 42.69, 41.94, 34.53, 34.18, 31.90, 31.70, 31.40, 30.68, 29.58, 27.64, 27.49, 26.81.
ESI MS m/z: 543.2 $[2M+Na]^+$.



25: 54%

According to the general procedure B, (1-cyclopropylvinyl)benzene (73.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction and work up, target product (16.0 mg, 54%) was obtained as a solid.
Eluting Solvents: hexane/ethyl acetate = 10/1, v/v.
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.6$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 1H), 8.04 – 7.98 (m, 2H), 7.93 – 7.85 (m, 2H), 7.63 (dd, *J* = 6.9, 1.2 Hz, 1H), 7.58 – 7.51(m, 2H), 7.48 (dd, *J* = 8.3, 7.0 Hz, 1H), 6.91 – 6.86 (m, 2H), 5.79 (s, 2H), 3.84 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.28, 163.45, 133.75, 131.81, 131.78, 131.75, 129.27, 128.74, 127.42, 126.61, 125.96, 125.34, 123.71, 122.50, 113.63, 64.90, 55.45.
ESI MS m/z: 607.2 $[2M+Na]^+$.
The analytic data is consistent with those reported in the literature.[17]



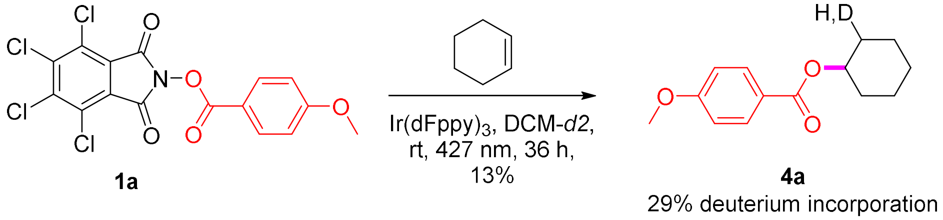
27, 55%

According to the general procedure B, alpha-Pinene (69.0 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture. The mixture was irritated by blue LED (Kessil PR160L-427 nm) for 24 h. After reaction and work up, target product (16.0 mg, 55%) was obtained as a colorless oil.
Eluting Solvents: hexane/ ethyl acetate = 12/1, v/v.
TLC: (hexane/ ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 7.93 (m, 2H), 6.99 – 6.84 (m, 2H), 5.76 (dq, *J* = 5.4, 1.6 Hz, 1H), 5.45 (dd, *J* = 4.2, 2.2 Hz, 1H), 3.86 (s, 3H), 2.21 – 2.09 (m, 1H), 2.00 (dq, *J* = 13.9, 2.1 Hz,

1H), 1.78 – 1.64 (m, 4H), 1.53 – 1.44 (m, 2H), 0.88 – 0.86 (m, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.28, 163.25, 131.65, 131.25, 128.33, 123.28, 113.55, 71.27, 55.46, 34.97, 32.75, 31.79, 28.89, 20.78, 19.99, 19.43.
ESI MS m/z: 289.2 $[M+H]^+$.

Mechanism Exploration

Conduct the reaction in DCM-d_2



A dry 8 mL vial equipped with a magnetic stirring bar was charged with substrate **1a** (44.0 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and DCM-*d2* (4.0 mL). Then olefins (41.5 mg, 0.5 mmol, 5.0 equiv) were added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 36 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, TLC showed only a little product and most of SM remained, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography (Eluting Solvents: hexane/ethyl acetate = 12/1, v/v) to obtain product as a colorless oil (3.0 mg, 13%).

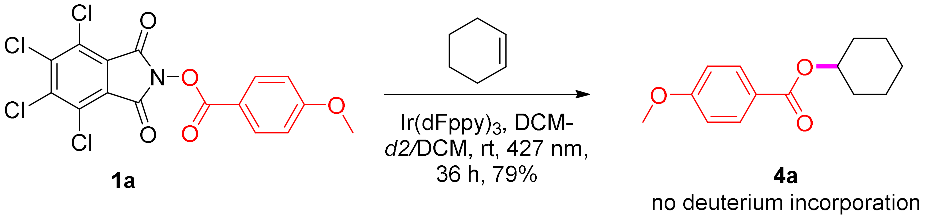
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (400 MHz, DMSO, ***exact integration for C2/6 hydrogens***) δ 7.96 – 7.87 (m, 2H), 7.09 – 7.01 (m, 2H), 4.90 (tt, *J* = 8.4, 3.8 Hz, 1H), 3.83 (s, 3H), ***1.91 – 1.81(dd, J = 7.9, 4.0 Hz, 1.93H)***, 1.77 – 1.66 (m, 2 H), ***1.59 – 1.47 (m, 2.91H)***, 1.47 – 1.26 (m, 3 H).

ESI MS m/z: 235.1 $[M+H]^+$.

Original for reference ^{1}H NMR (600 MHz, DMSO, ***exact integration C2/6 hydrogens***) δ 7.96 – 7.91 (m, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 4.91 (tt, *J* = 8.5, 3.8 Hz, 1H), 3.85 (s, 3H), ***1.92– 1.85 (m, 2.04H)***, 1.78 – 1.70 (m, 2 H), ***1.59 – 1.49(m, 3.09H),*** 1.47 – 1.29 (m, 3 H).

Control reaction to test for potential poisons in CD2Cl2: Reaction in DCM-d_2/DCM (1/1, v/v)



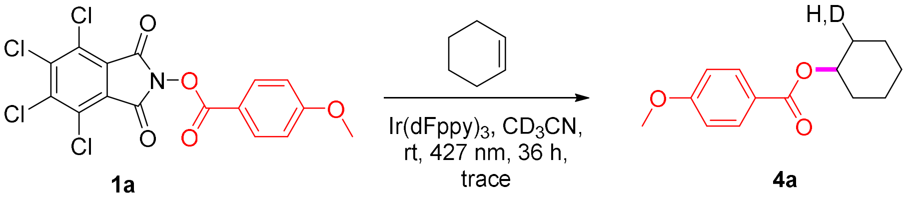
A dry 8 mL vial equipped with a magnetic stirring bar was charged with substrate **1A** (44.0 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and DCM-d_2/DCM(4.0 mL, 1/1, v/v). Next, olefin (41.5 mg, 0.5 mmol, 5.0 equiv) was added. The reaction mixture was protected by nitrogen and irritated by blue LED (Kessil PR160L-427 nm) for 24 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography (Eluting Solvents: hexane/ethyl acetate = 15/1, v/v) to obtain product as a colorless oil (18.7 mg, 79%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}H NMR (400 MHz, DMSO, ***exact integration for C2/6 hydrogens***) 1H NMR (600 MHz, DMSO) δ 7.93 – 7.88 (m, 2H), 7.07 – 7.01 (m, 2H), 4.89 (tt, *J* = 8.4, 3.8 Hz, 1H), 3.83 (s, 3H), ***1.90 – 1.81***

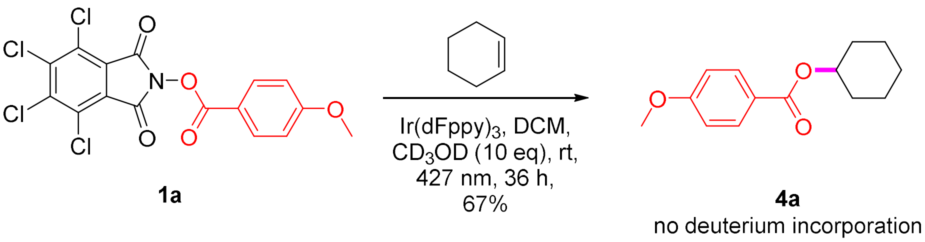
(m, 2.06 H), 1.71 (dtt, *J* = 13.1, 6.4, 3.6 Hz, 2 H), ***1.52 (dtd, J = 12.7, 9.3, 3.5 Hz, 3.01 H)***, 1.45 – 1.35 (m, 2H), 1.32 (ddd, *J* = 12.9, 8.3, 3.3 Hz, 1H).
ESI MS m/z: 235.1 $[M+H]^+$.

Reaction in CD_3CN



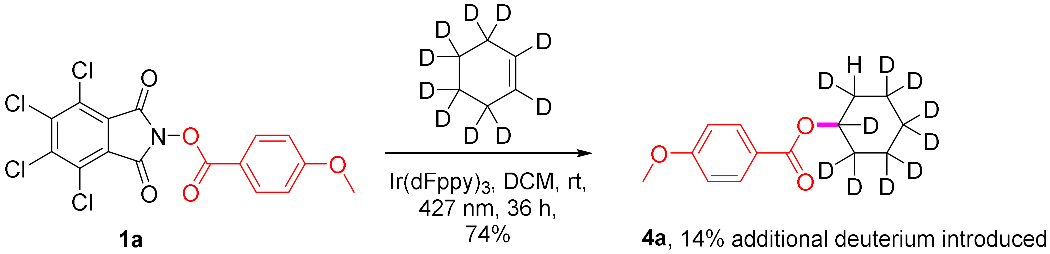
A dry 8 mL vial equipped with a magnetic stirring bar was charged with substrate **1A** (44.0 mg, 0.10 mmol, 1.0 equiv), $Ir(dFppy)_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and CD_3CN (4.0 mL). Then olefins (41.5 mg, 0.5 mmol, 5.0 equiv) were added. The suspension was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 36 h. After reaction, TLC showed only trace product and most of SM remained. The reaction mixture wasn't purified.

MeOD-*d4* as additive



A dry 8 mL vial equipped with a magnetic stirring bar was charged with substrate **1A** (44.0 mg, 0.10 mmol, 1.0 equiv), $Ir(dFppy)_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and DCM (5.0 mL). Then olefins (41.5 mg, 0.5 mmol, 5.0 equiv) and MeOD-*d4* (36.5 mg, 1 mmol, 10 equiv) were added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 36 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). Combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography (Eluting Solvents: hexane/ethyl acetate = 12/1, v/v) to obtain products as a colorless oil (15.8 mg, 67%).
TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.
^{1}H NMR (400 MHz, DMSO, ***exact integration for C2/6 hydrogens***) δ 7.95 – 7.87 (m, 2H), 7.10 – 7.00 (m, 2H), 4.89 (tt, *J* = 8.4, 3.8 Hz, 1H), 3.83 (s, 3H), ***1.90 – 1.80 (m, 2.04 H)***, 1.77 – 1.66 (m, 2 H), ***1.59 – 1.46 (m, 3.08H)***, 1.36 – 1.24 (m, 3 H).
ESI MS m/z: 235.1 $[M+H]^+$.

Deuterium cyclohexene-d_{10} as reagent

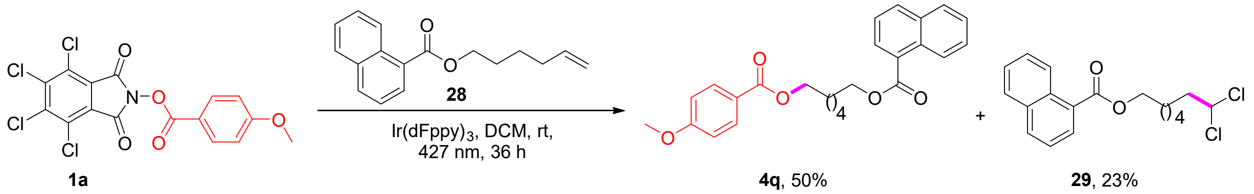


A dry 8 mL vial equipped with a magnetic stirring bar was charged with substrate **1A** (44.0 mg, 0.10 mmol, 1.0 equiv), Ir(dFppy)$_3$ (0.8 mg, 1.00 µmol, 0.01 equiv), and DCM (5.0 mL). Then cyclohex-1-ene-d_{10} (46.6 mg, 0.5 mmol, 5.0 equiv) was added. The reaction mixture was protected by nitrogen, irritated by blue LED (Kessil PR160L-427 nm) for 36 h (the internal temperature of reaction solution is 40 – 45 ˚C). After reaction, the reaction mixture was filtered by Celite and washed with DCM (2 mL). The combined solution was concentrated under vacuum. The residue was purified directly by silica-gel column chromatography (Eluting Solvents: hexane/ethyl acetate = 12/1, v/v) to obtain products as colorless oil (18.2 mg, 74%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.8$.

^{1}**H NMR** (400 MHz, DMSO, ***exact integration for C2/6 hydrogens***) δ 7.95 – 7.87 (m, 2H), 7.08 – 7.00 (m, 2H), 3.83 (s, 3H), ***1.81 (s, 0.42H)***, ***1.48 (s, 0.44H)***, ^{13}**C NMR** (150 MHz, DMSO) δ 164.76, 163.05, 131.17, 122.51, 113.98, 71.46, 55.51, 30.31, 23.76, 22.11.

ESI MS m/z: 245.1 [M+H]$^+$.



Refer to former procedure for preparing compound **4q**. The dichloro byproduct was received by silica-gel column chromatography (Eluting Solvents: hexane/dichloromethane = 3/1, v/v) to obtain products **29** as colorless oil (8.0 mg, 23%).

TLC: (hexane/ethyl acetate = 3/1, v/v) $R_f = 0.9$.

^{1}**H NMR** (600 MHz, CDCl$_3$) δ 8.90 (dq, J = 8.8, 1.0 Hz, 1H), 8.17 (dd, J = 7.2, 1.2 Hz, 1H), 8.03 (dt, J = 8.2, 1.2 Hz, 1H), 7.89 (dt, J = 8.2, 0.8 Hz, 1H), 7.62 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.57 – 7.48 (m, 2H), 5.75 (t, J = 6.0 Hz, 1H), 4.42 (t, J = 6.6 Hz, 2H), 2.25 – 2.18 (m, 2H), 1.91 – 1.81 (m, 2H), 1.64 – 1.58 (m, 2H), 1.53 (dtd, J = 9.2, 7.2, 5.5 Hz, 2H), 1.49 – 1.41 (m, 2H). ^{13}**C NMR** (150 MHz, CDCl$_3$) δ 167.70, 133.86, 133.31, 131.34, 130.07, 128.58, 127.75, 127.40, 126.23, 125.80, 124.53, 73.56, 65.00, 43.49, 28.62, 28.25, 25.96, 25.84.

ESI MS m/z: 339.0 [M+H]$^+$.

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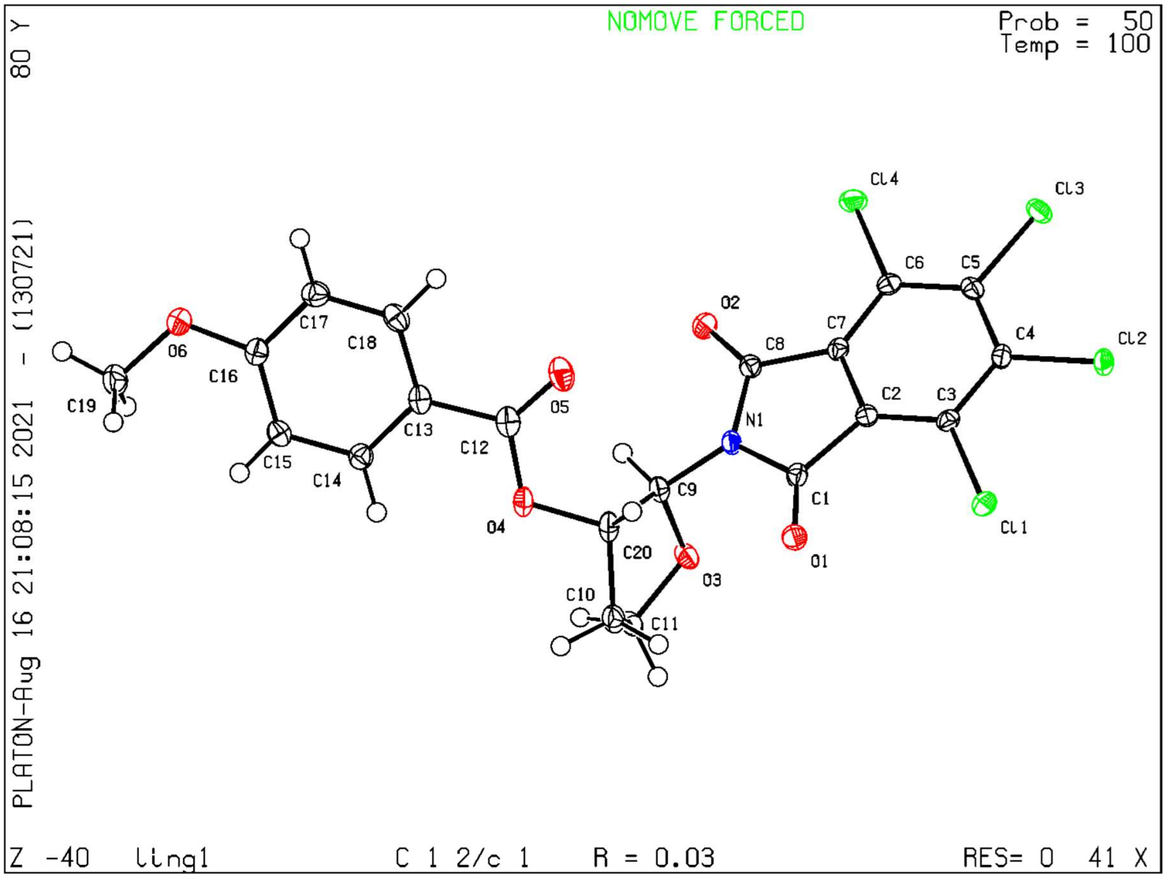
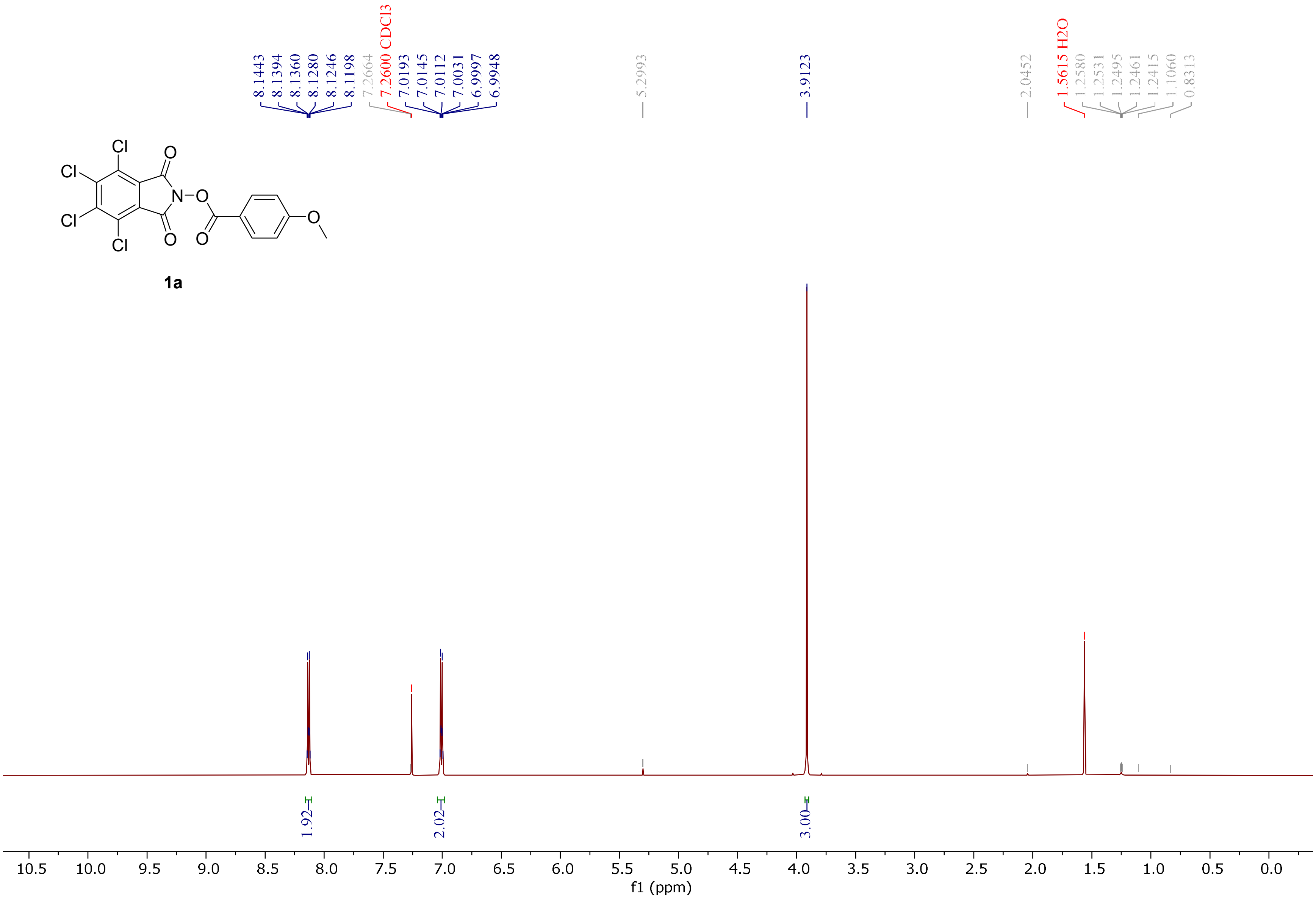
Crystal data for product 14b

CCDC Deposition Number 2103778



NMR Spectra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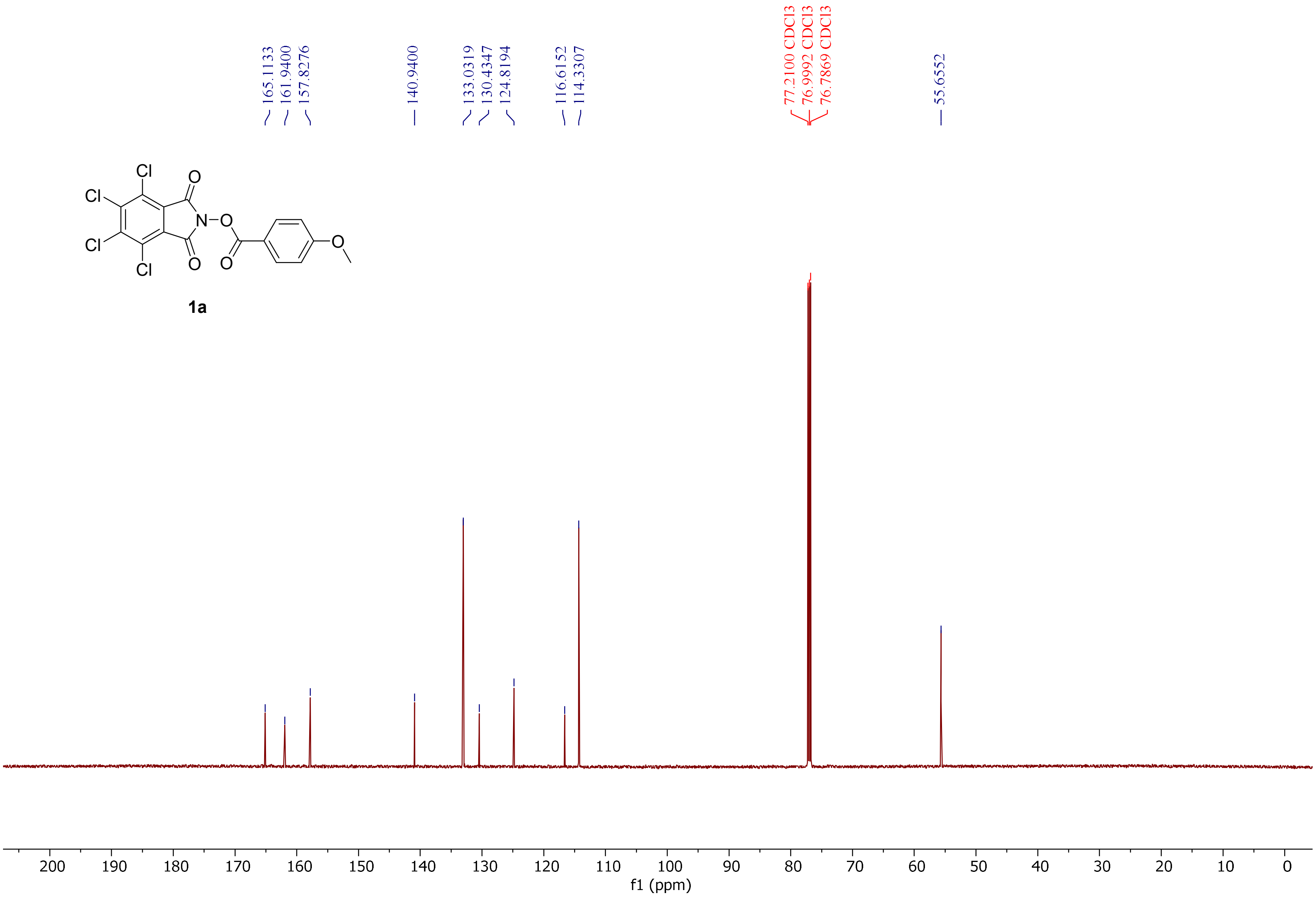
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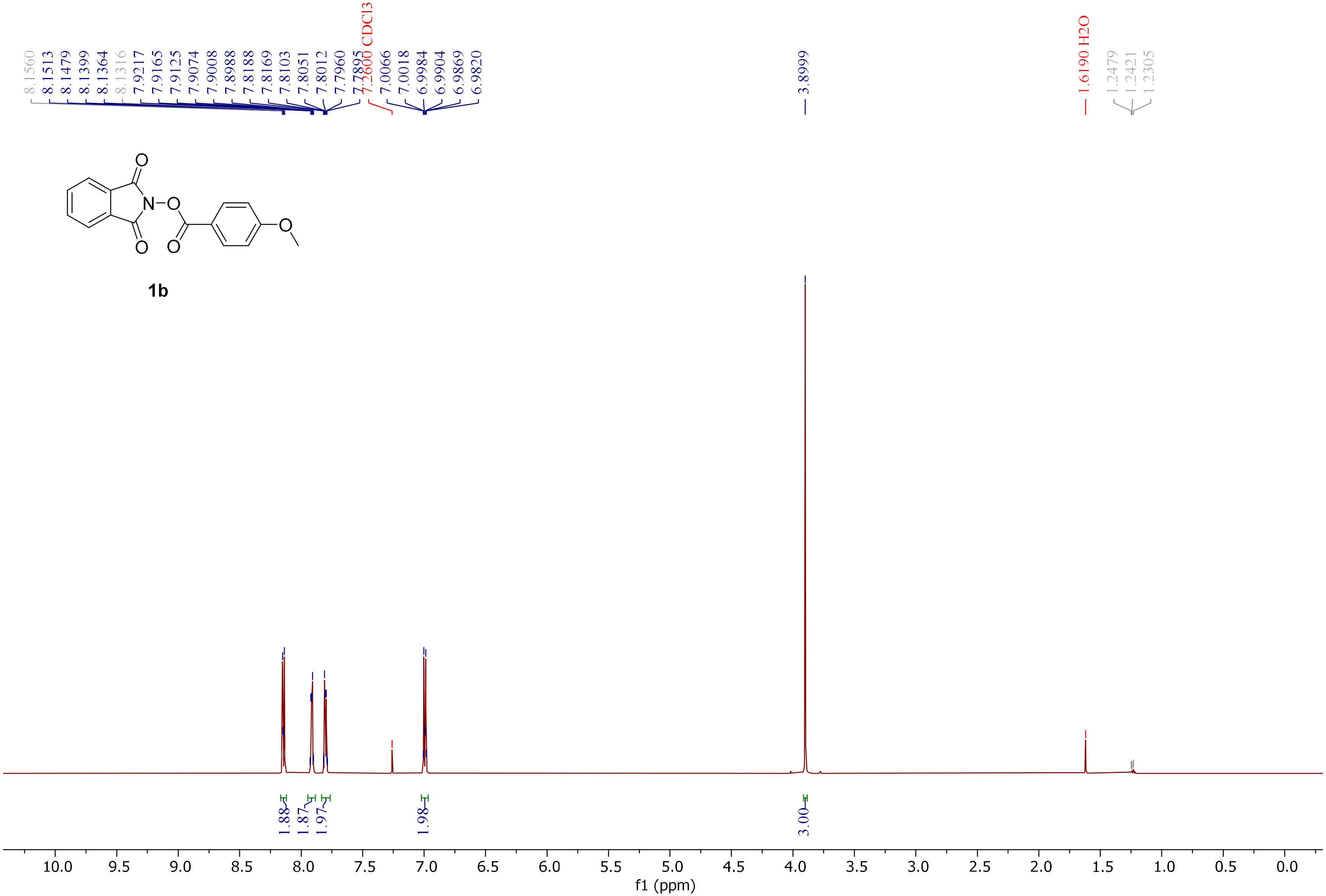
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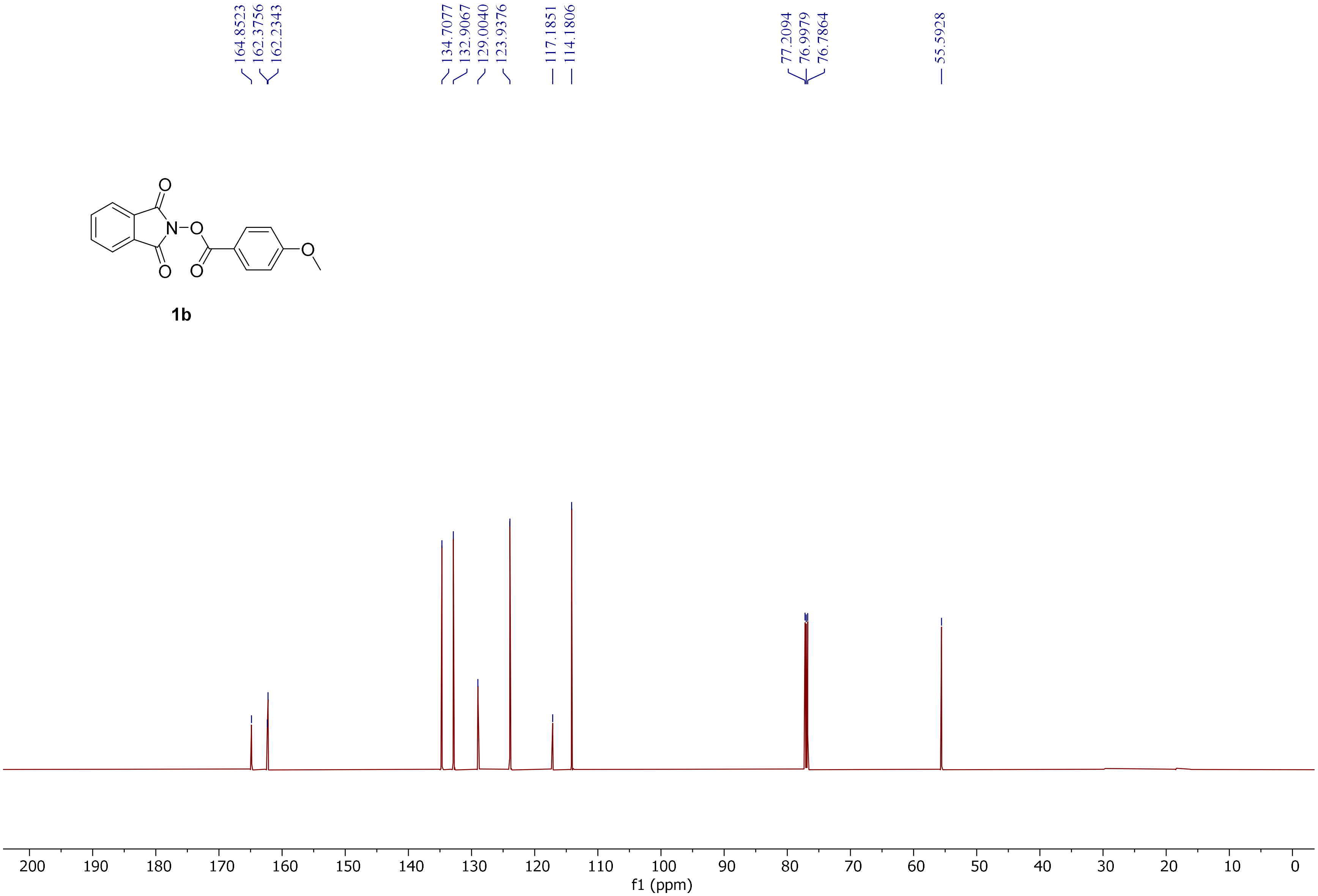

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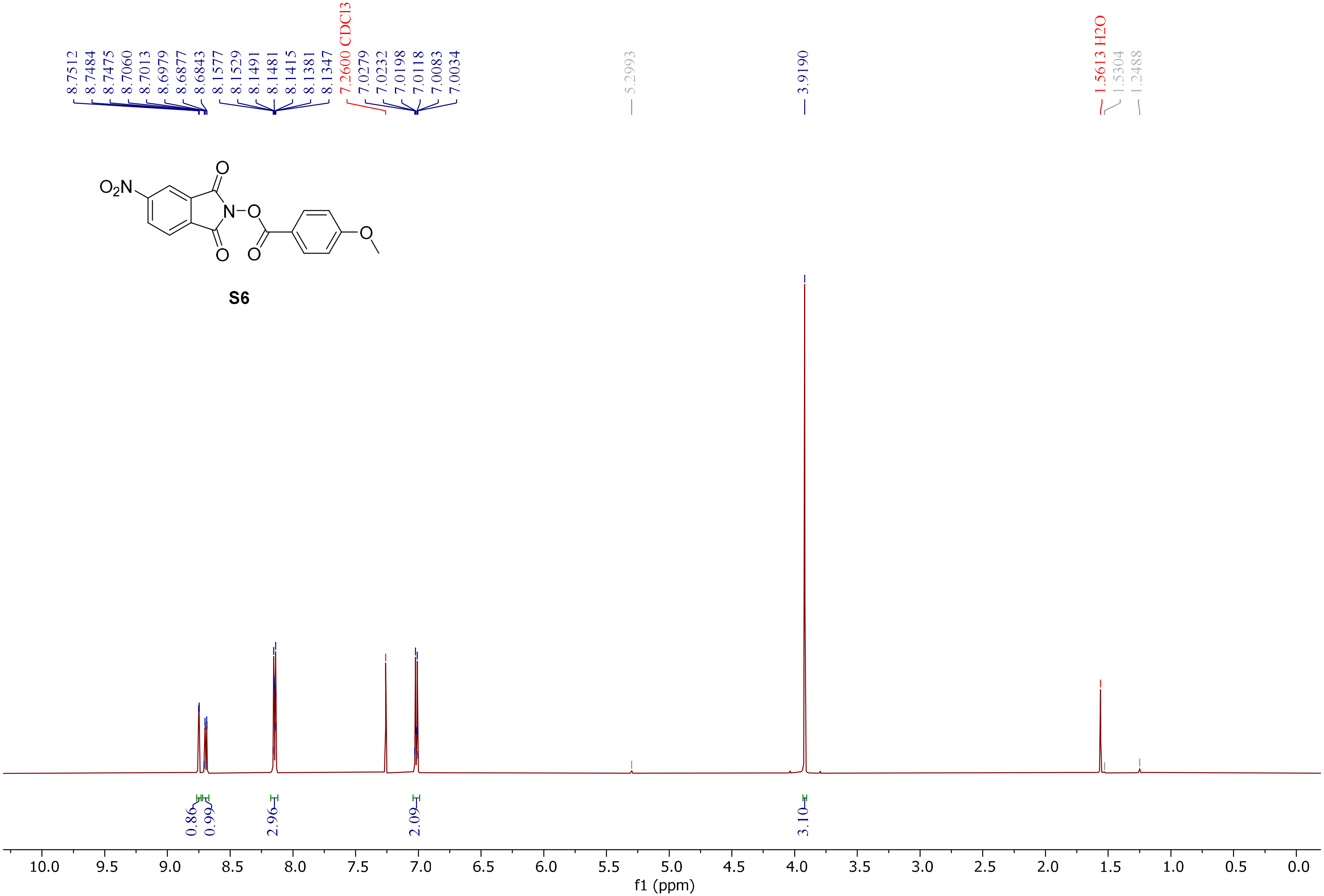
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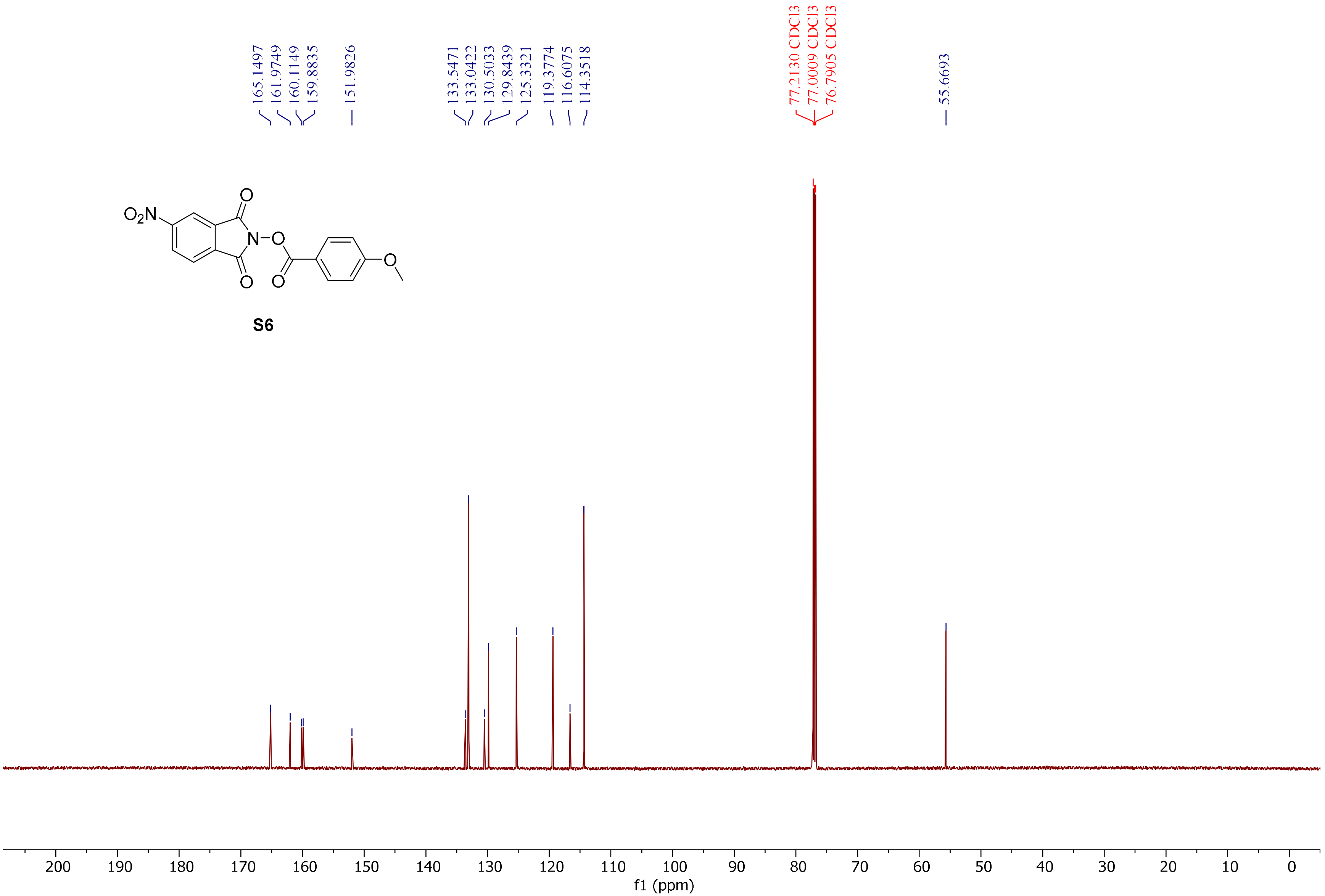
S6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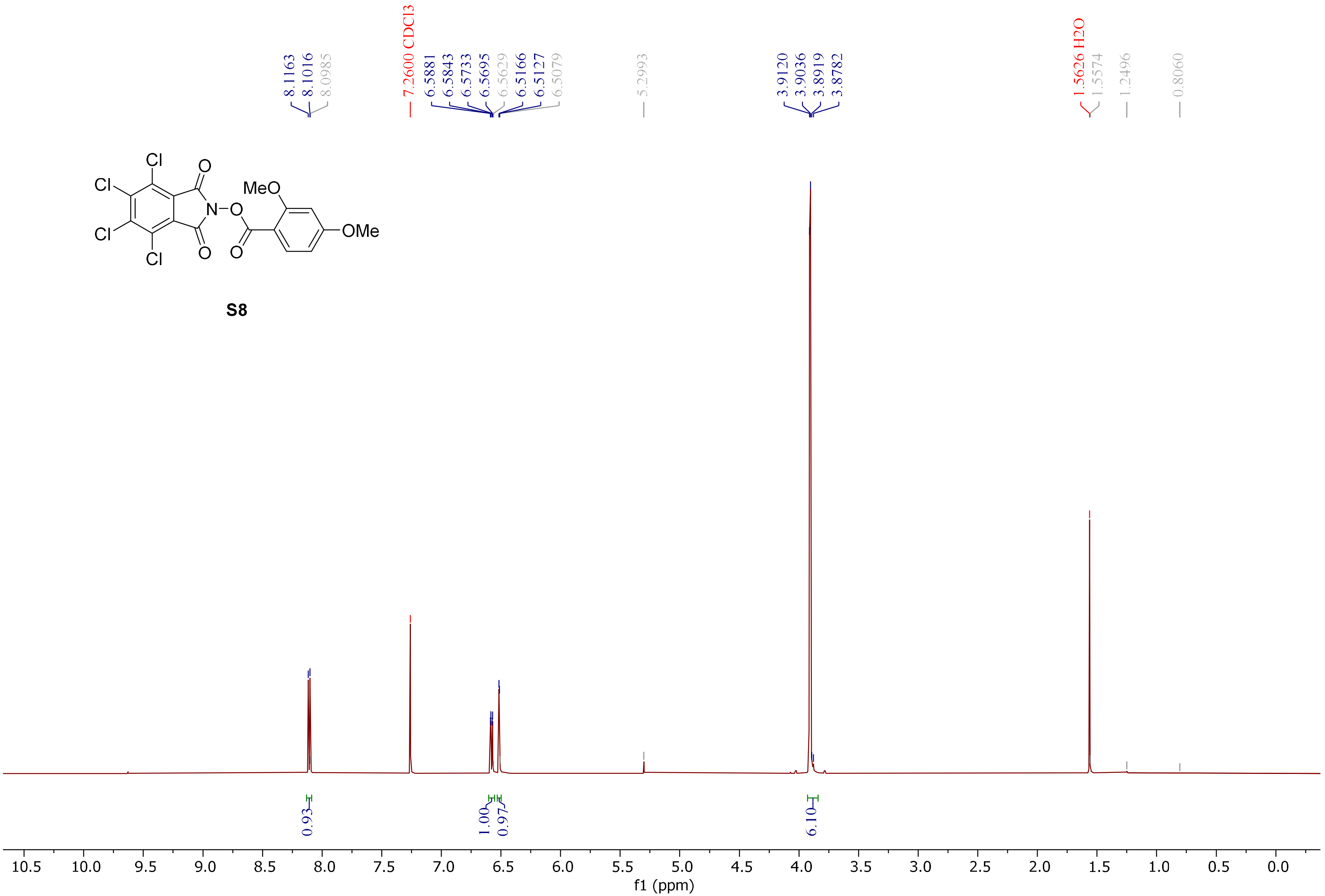
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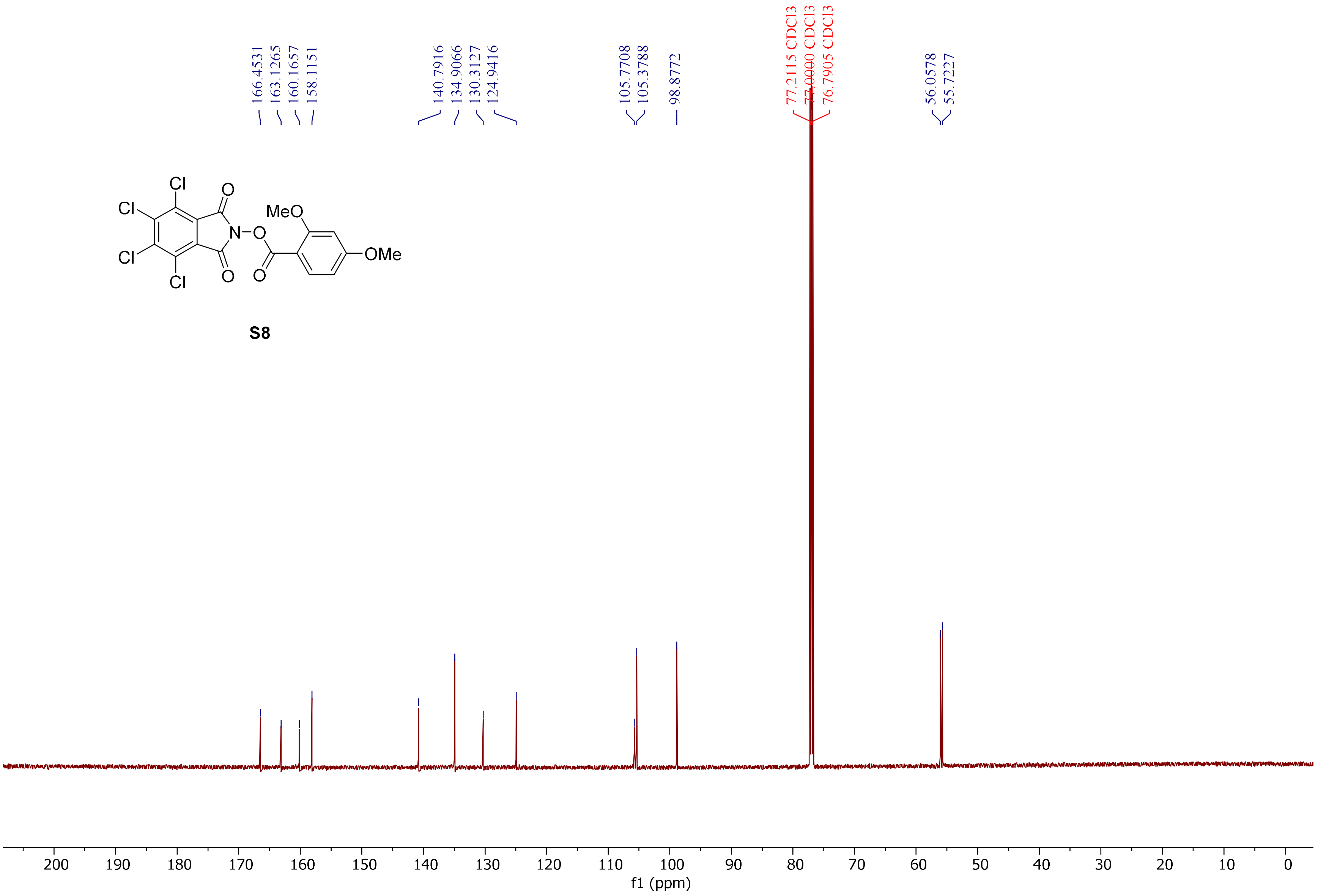
f1 (ppm)

S8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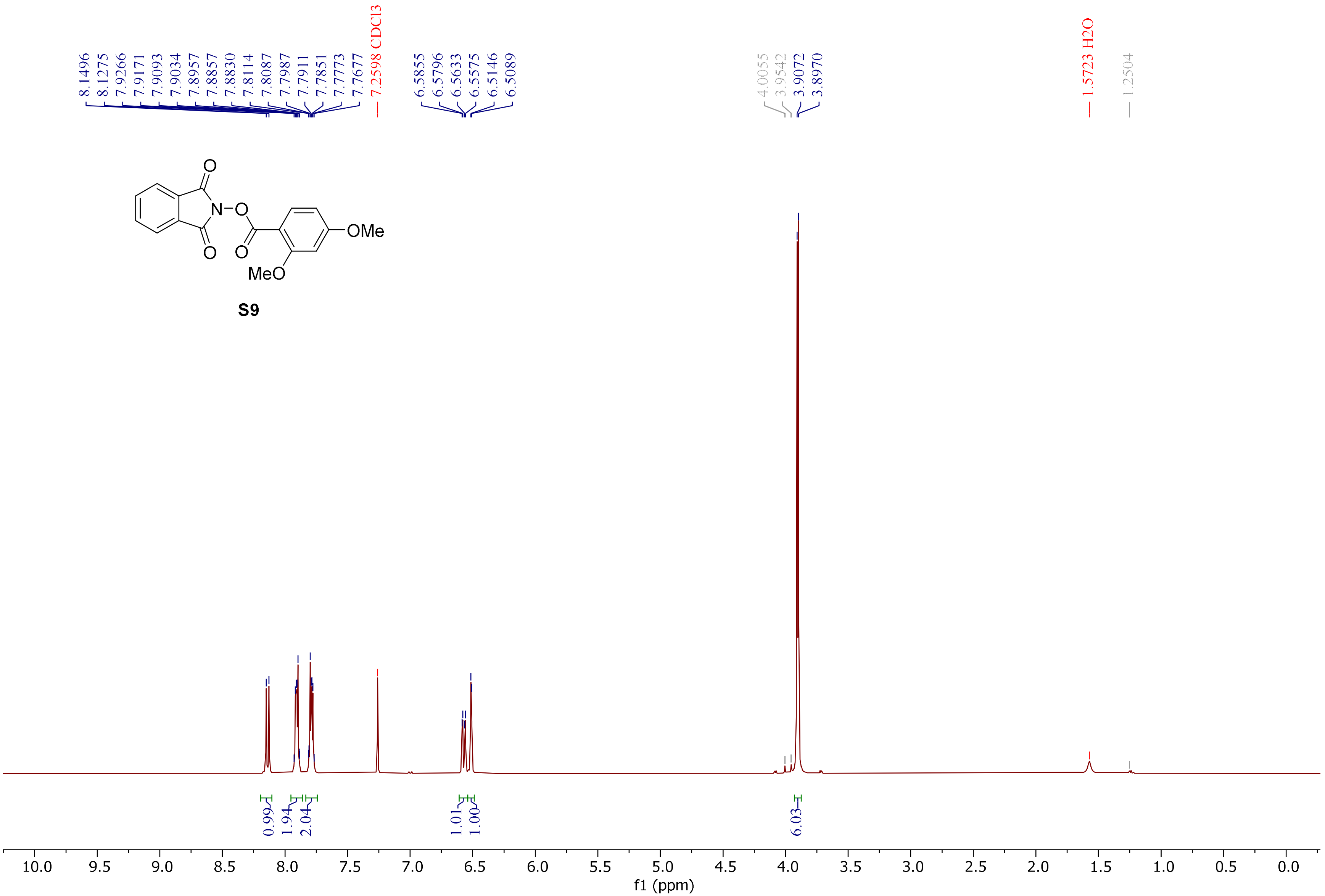

S9

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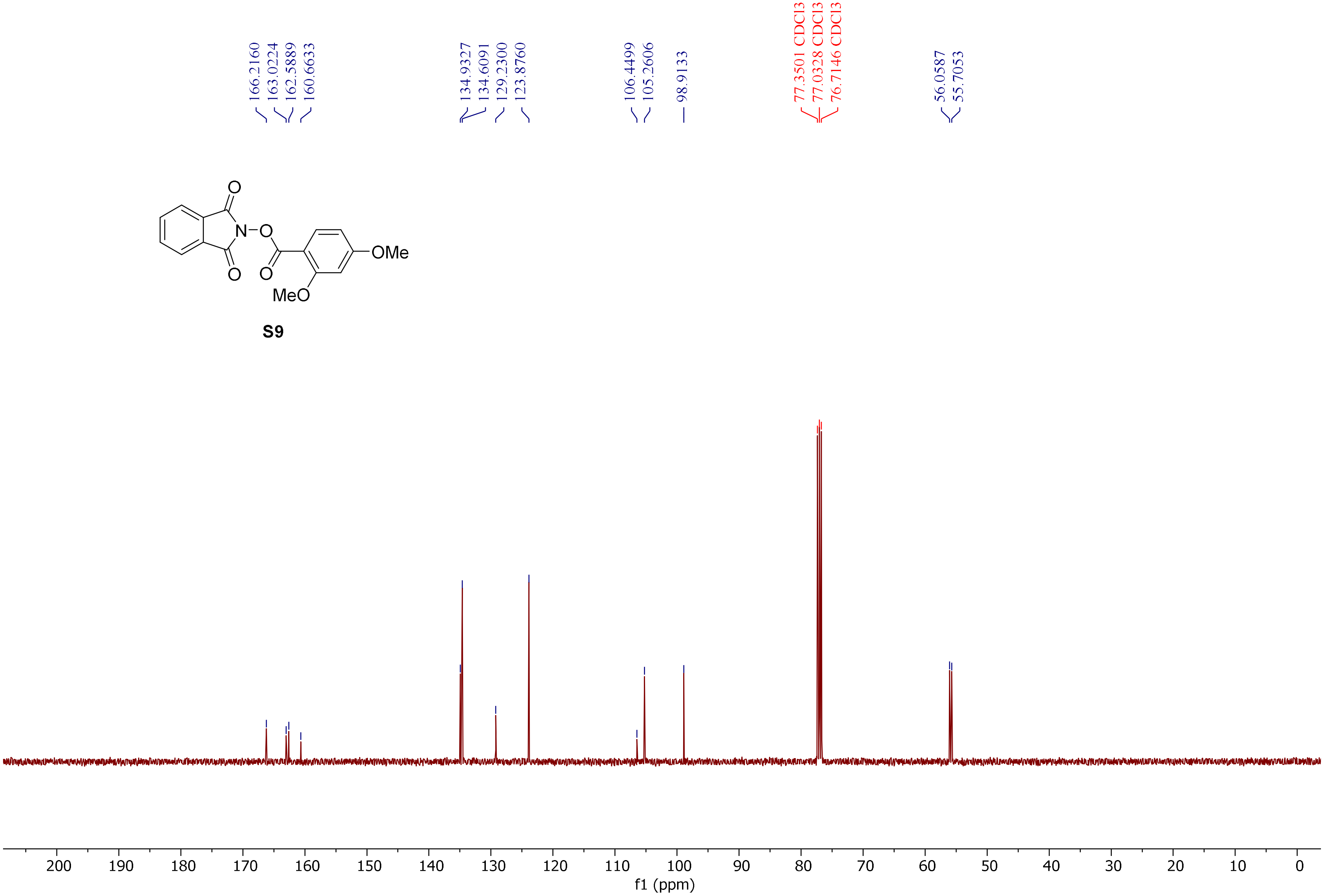
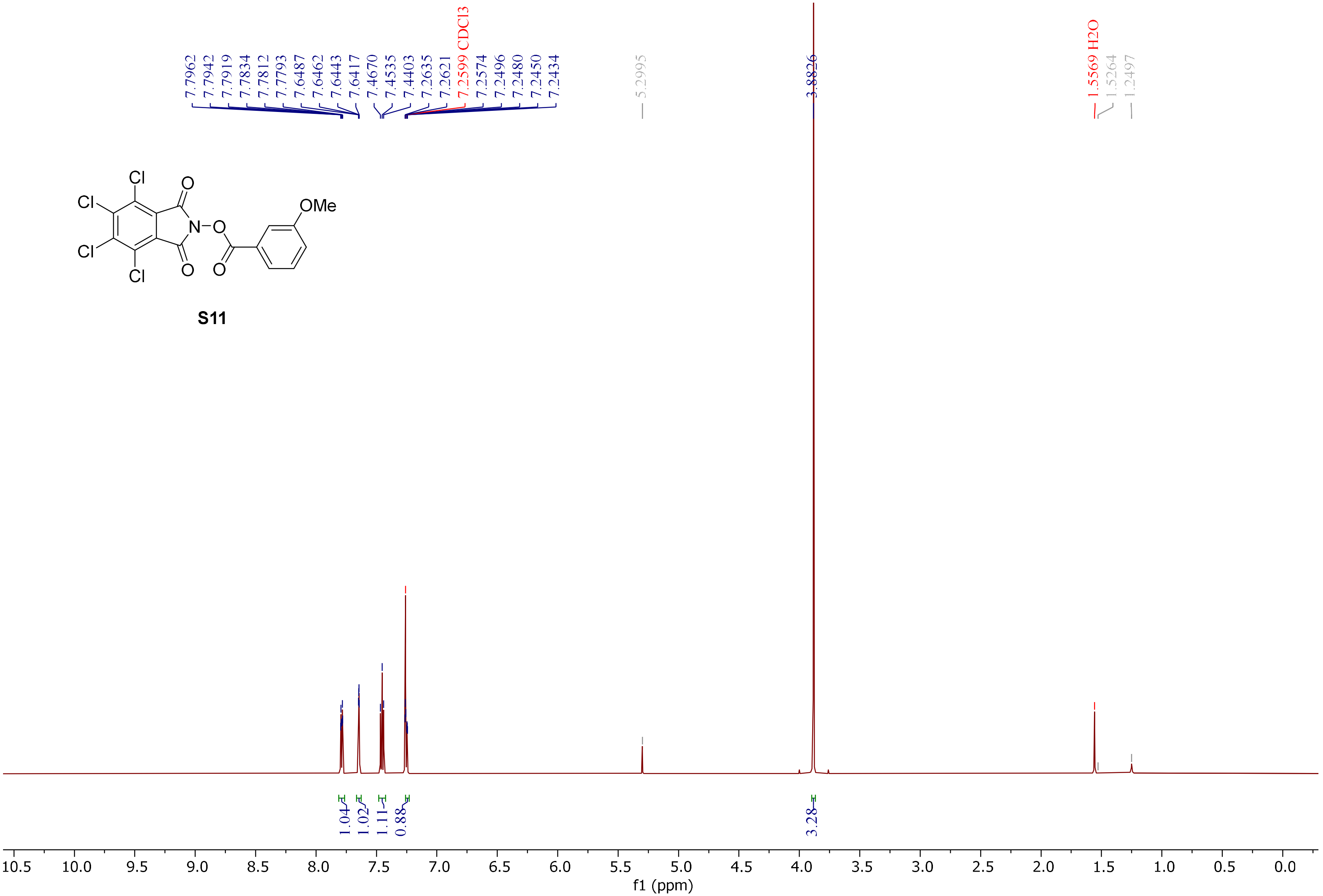
7.8830
7.8114
7.8087
7.7987
7.7911
7.7851
7.7773
7.7677
7.2598 CDCl3
6.5855
6.5796
6.5633
6.5575
6.5146
6.5089
4.0055
3.9542
3.9072
3.8970
1.5723 H2O
1.2504
N
O
O
O
O
OMe
MeO
0.99
1.94
2.04
1.01
1.00
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

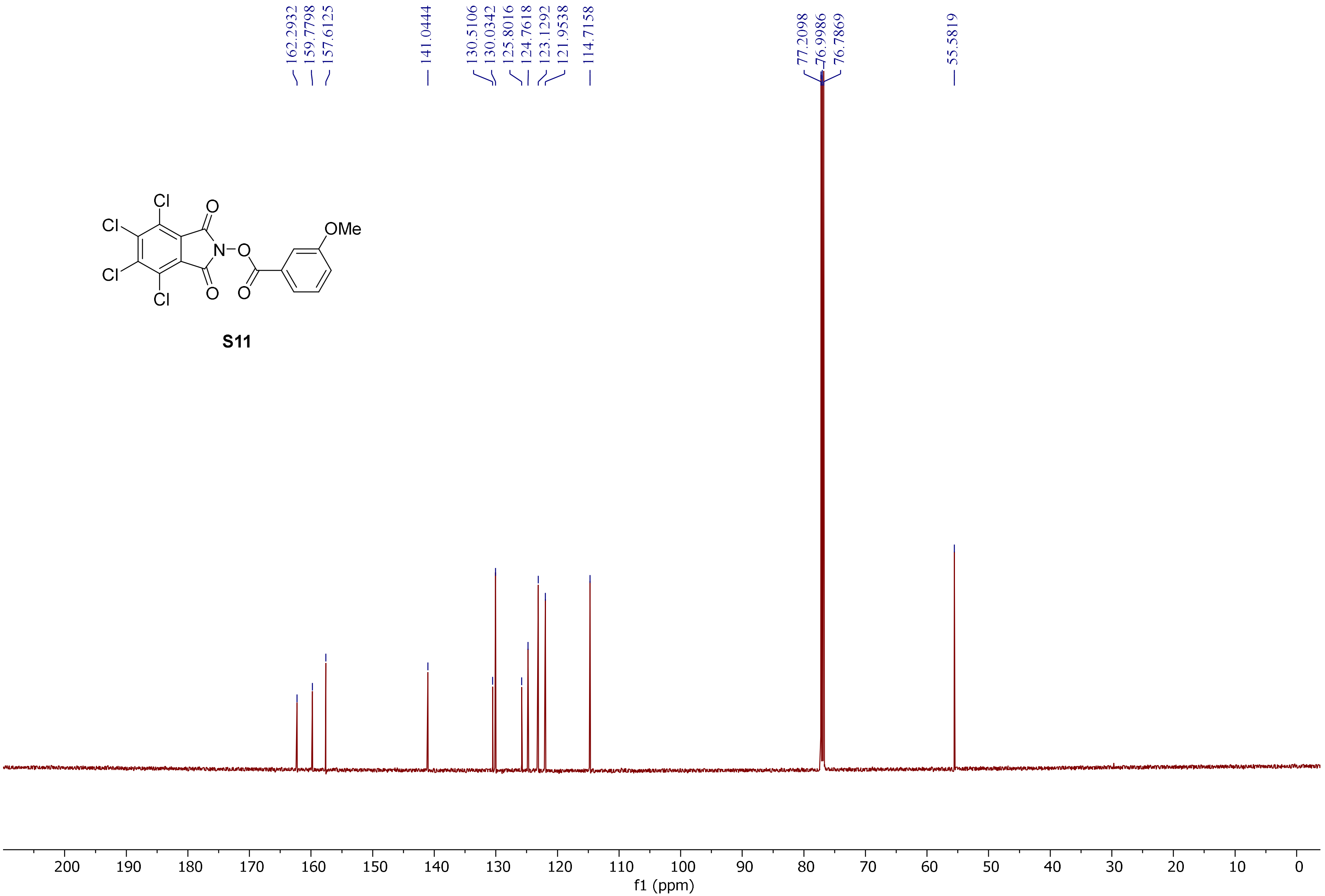


S9

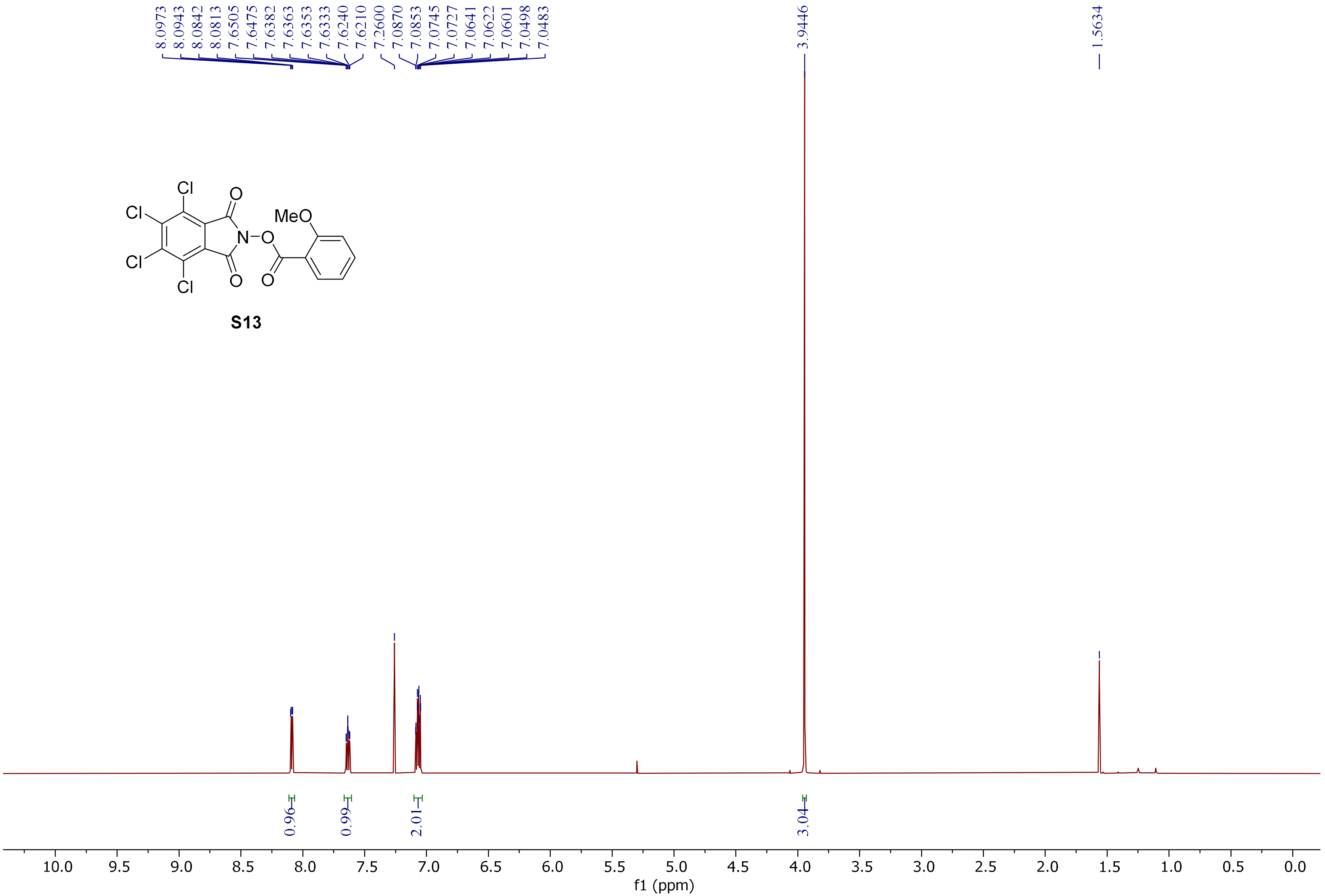
166.2160
163.0224
162.5889
160.6633
134.9327
134.6091
129.2300
123.8760
106.4499
105.2606
98.9133
77.3501 CDCl3
77.0328 CDCl3
76.7146 CDCl3
56.0587
55.7053
O
N
O
O
O
OMe
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7962
7.7942
7.7919
7.7834
7.7812
7.7793
7.6487
7.6462
7.6443
7.6417
7.4670
7.4535
7.4403
7.2635
7.2621
7.2599 CDCl3
7.2574
7.2496
7.2480
7.2450
7.2434
5.2995
3.8826
1.5569 H2O
1.5264
1.2497
Cl
Cl
Cl
Cl
O
O
N
O
O
OMe
1.04
1.02
1.11
0.88
3.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

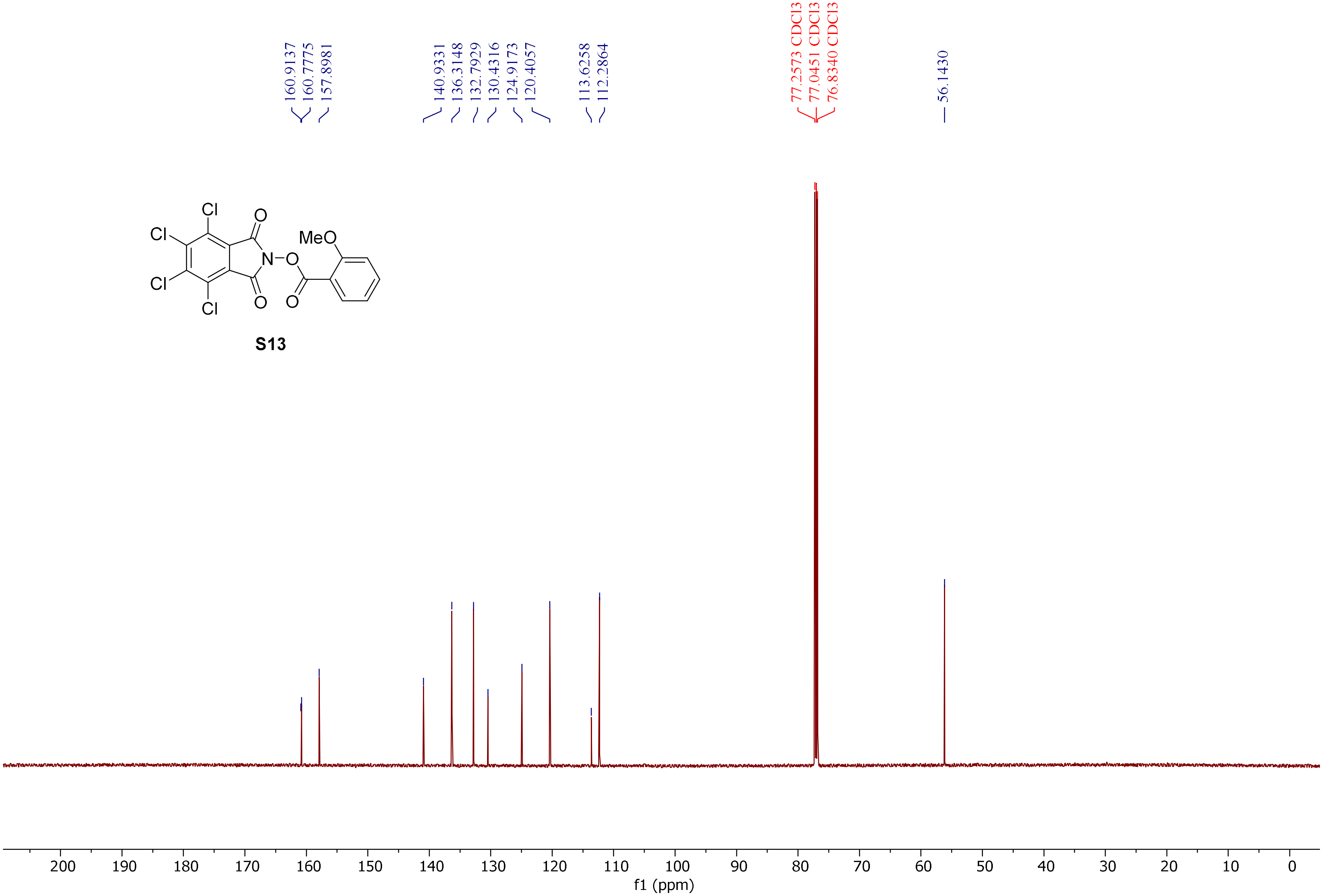
S11


162.2932
159.7798
157.6125
141.0444
130.5106
130.0342
125.8016
124.7618
123.1292
121.9538
114.7158
77.2098
76.9986
76.7869
55.5819
Cl
Cl
Cl
Cl
O
O
N
O
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

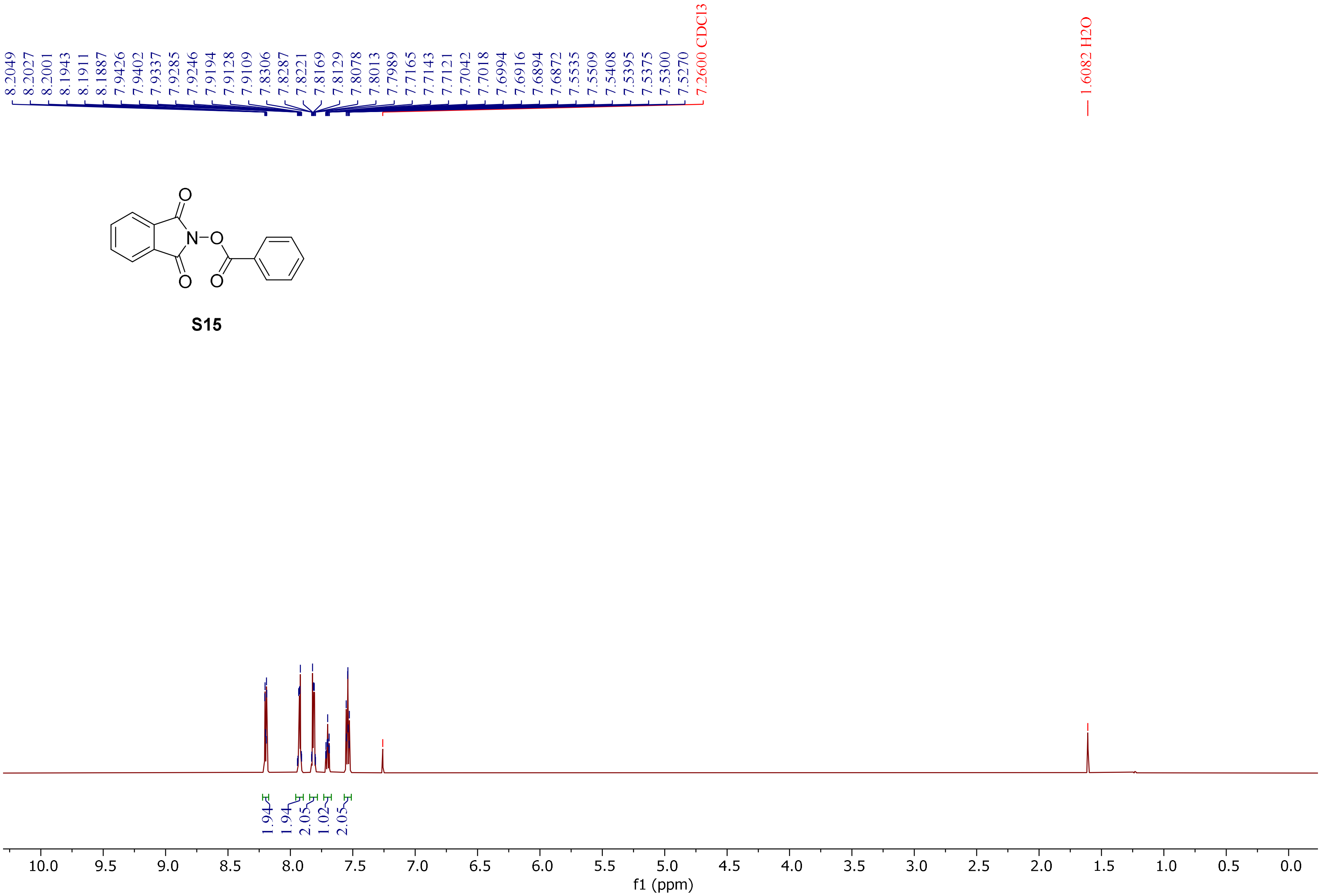
S11


8.0973
8.0943
8.0842
8.0813
7.6505
7.6475
7.6382
7.6363
7.6353
7.6333
7.6240
7.6210
7.2600
7.0870
7.0853
7.0745
7.0727
7.0641
7.0622
7.0601
7.0498
7.0483
3.9446
1.5634
Cl
Cl
Cl
Cl
O
O
N
O
O
MeO
0.96
0.99
2.01
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

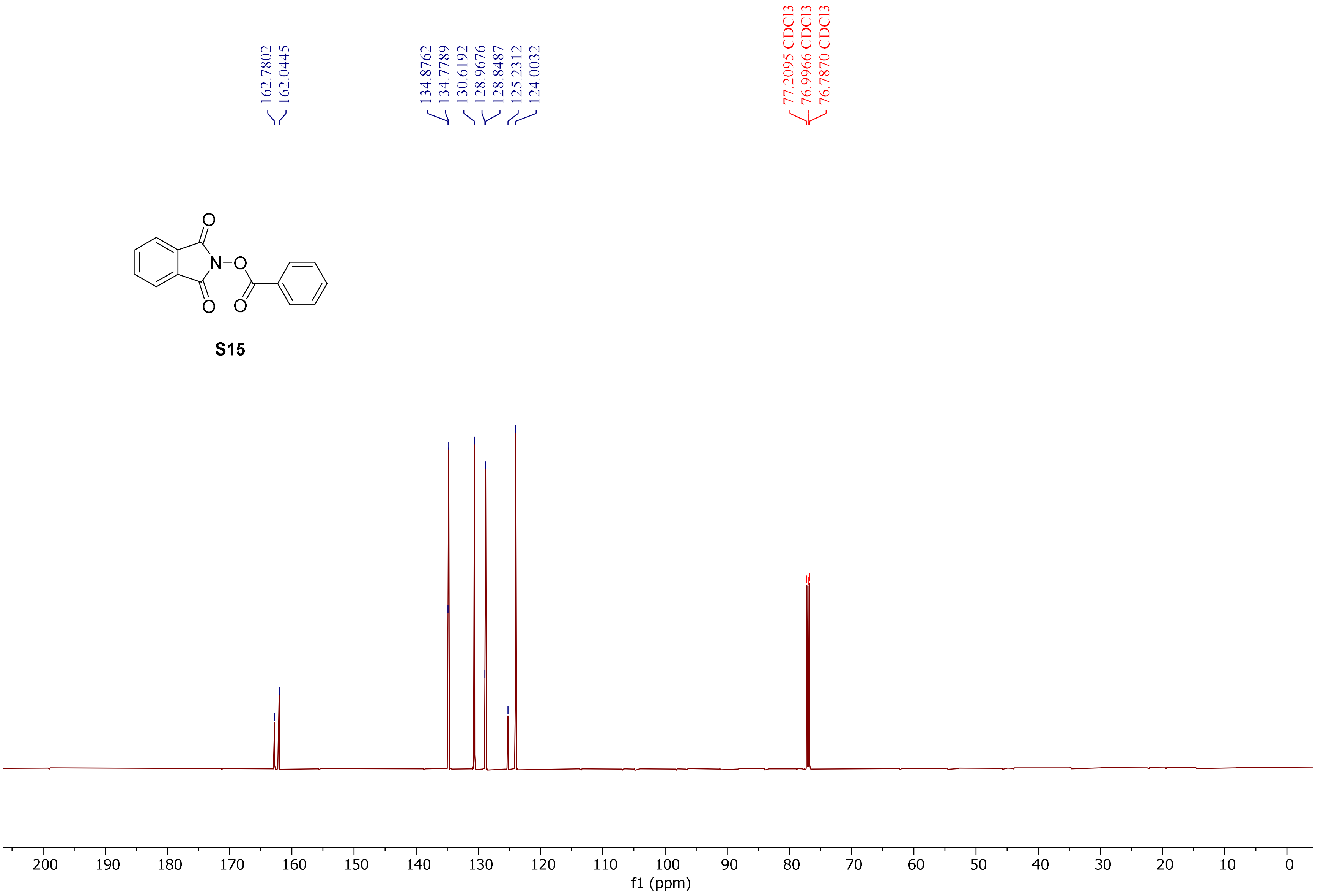
S13


160.9137
160.7775
157.8981
140.9331
136.3148
132.7929
130.4316
124.9173
120.4057
113.6258
112.2864
77.2573 CDCl3
77.0451 CDCl3
76.8340 CDCl3
56.1430
Cl
Cl
Cl
Cl
O
O
N
O
O
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

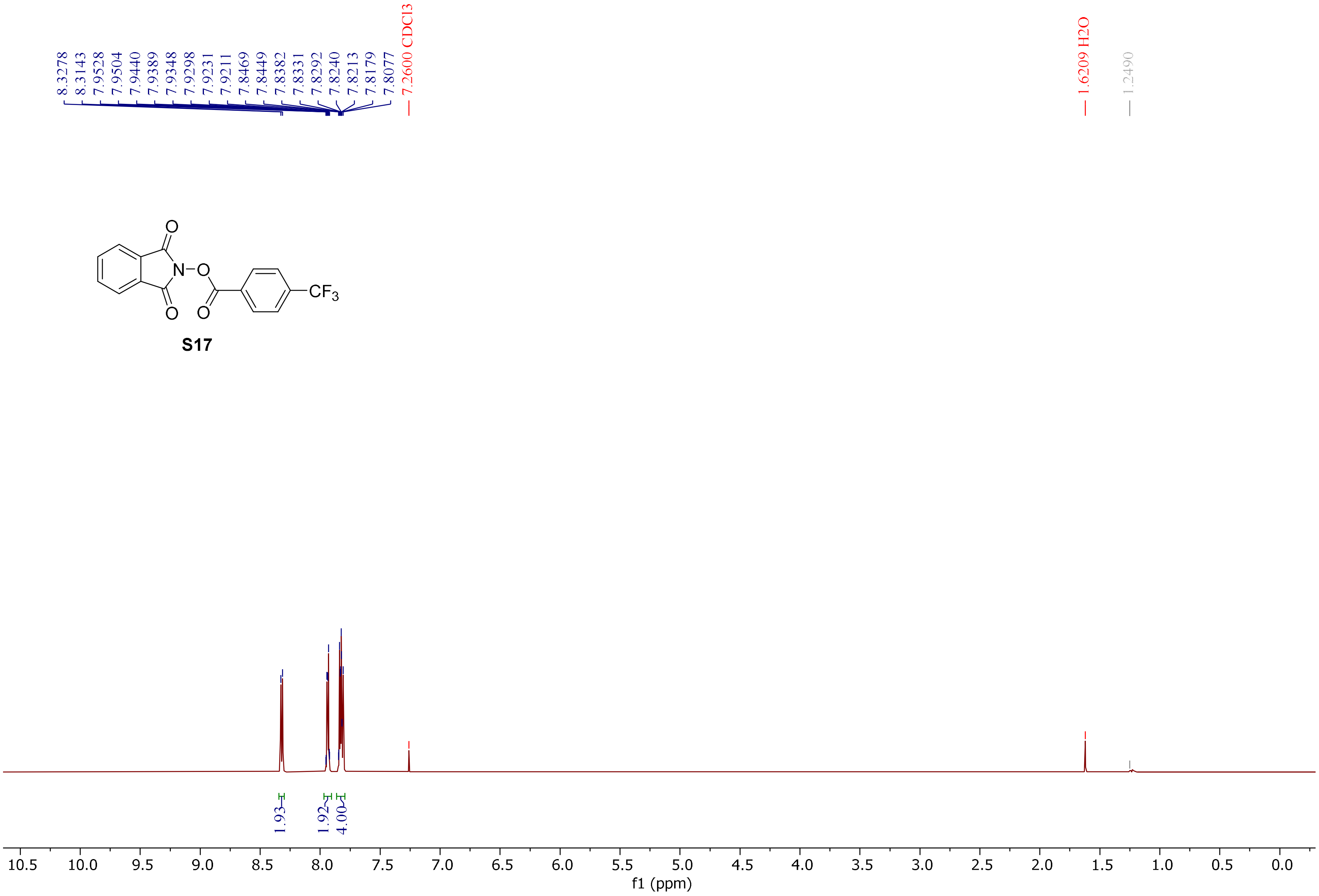
S13


8.2049
8.2027
8.2001
8.1943
8.1911
8.1887
7.9426
7.9402
7.9337
7.9285
7.9246
7.9194
7.9128
7.9109
7.8306
7.8287
7.8221
7.8169
7.8129
7.8078
7.8013
7.7989
7.7165
7.7143
7.7121
7.7042
7.7018
7.6994
7.6916
7.6894
7.6872
7.5535
7.5509
7.5408
7.5395
7.5375
7.5300
7.5270
7.2600 CDCl3
1.6082 H2O
O
N
O
O
O
1.94
1.94
2.05
1.02
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

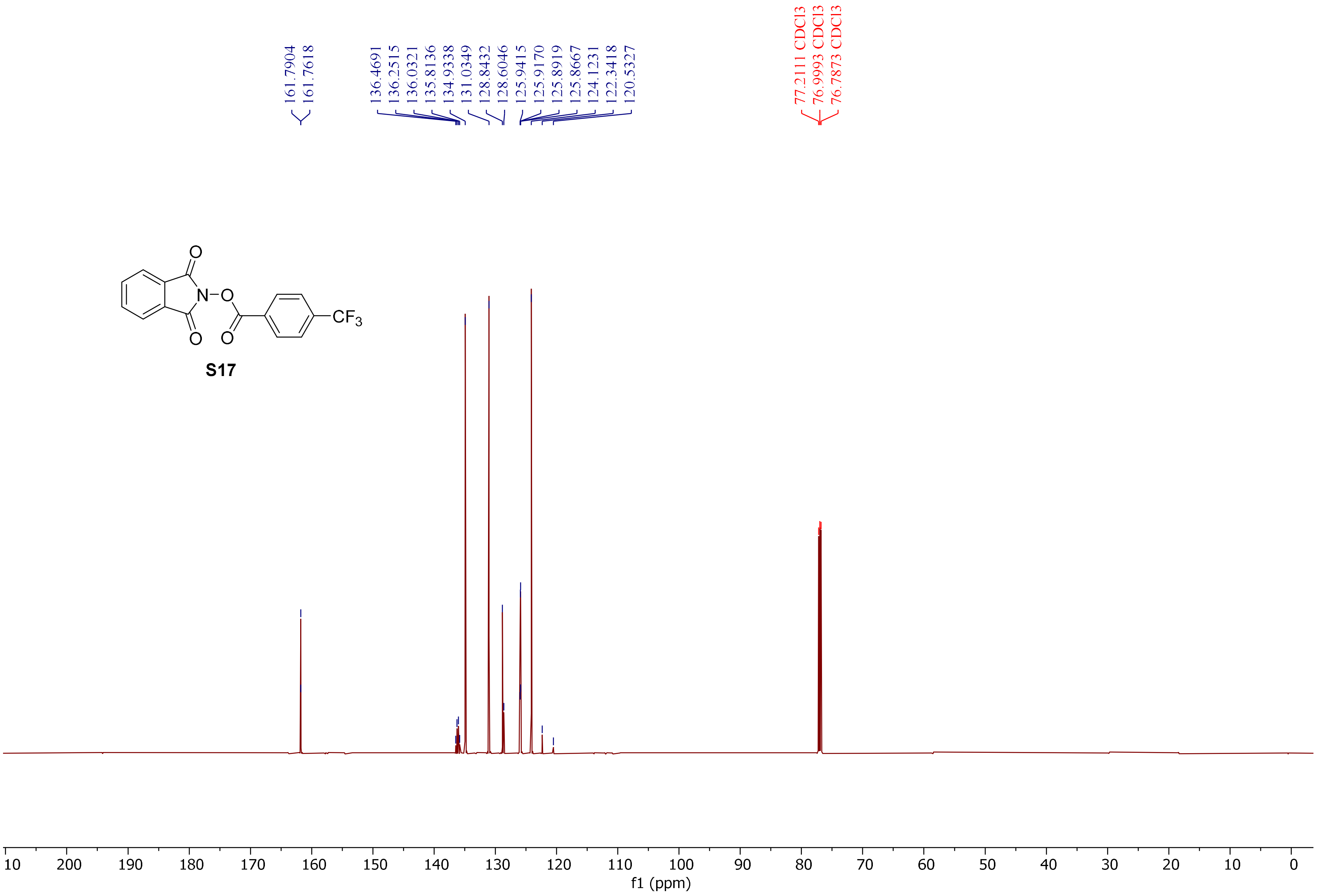
S15


162.7802
162.0445
134.8762
134.7789
130.6192
128.9676
128.8487
125.2312
124.0032
77.2095 CDCl3
76.9966 CDCl3
76.7870 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
N
O
O
O

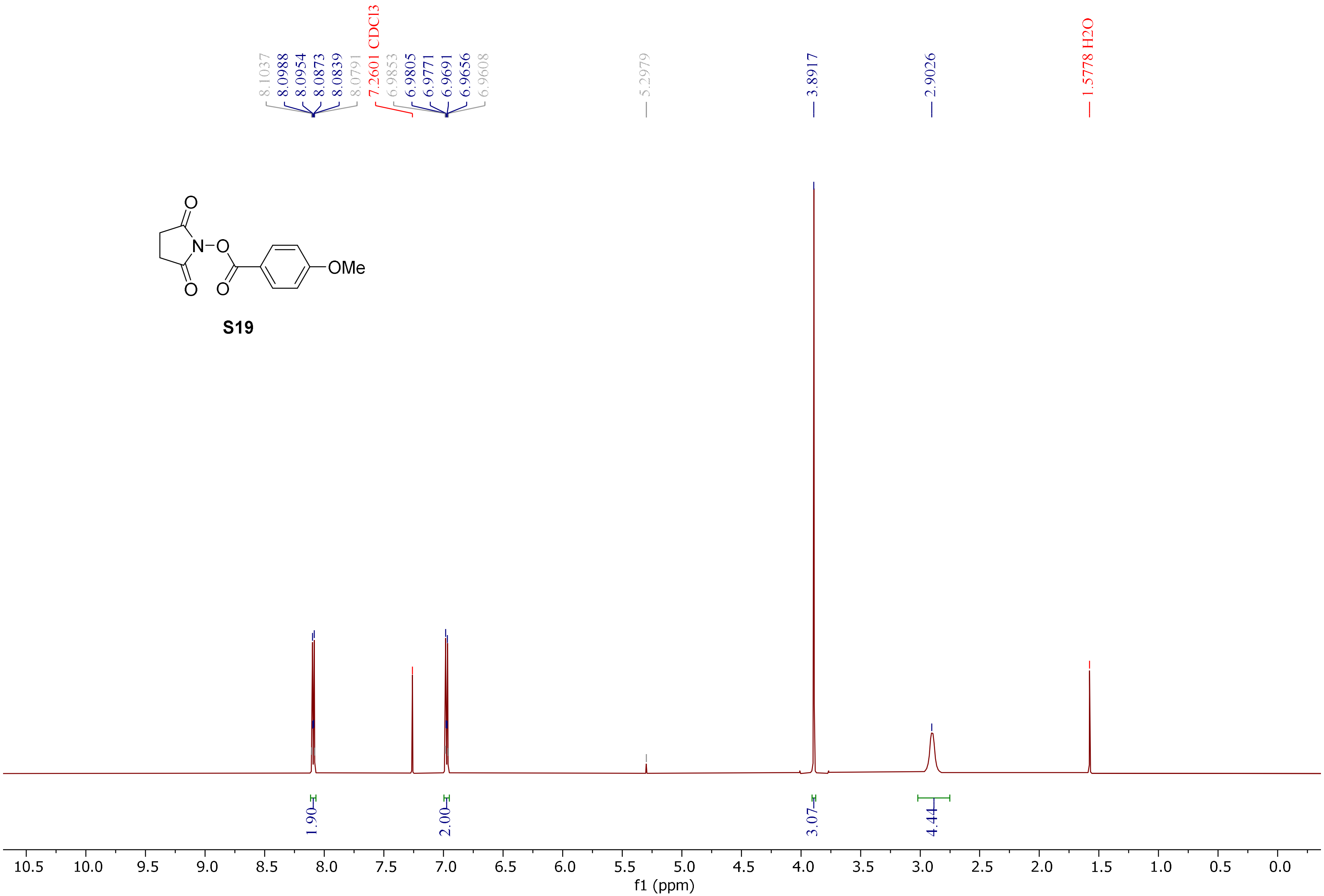
S15


8.3278
8.3143
7.9528
7.9504
7.9440
7.9389
7.9348
7.9298
7.9231
7.9211
7.8469
7.8449
7.8382
7.8331
7.8292
7.8240
7.8213
7.8179
7.8077
7.2600 CDCl3
1.6209 H2O
1.2490
O
N
O
O
O
CF3
1.93
1.92
4.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

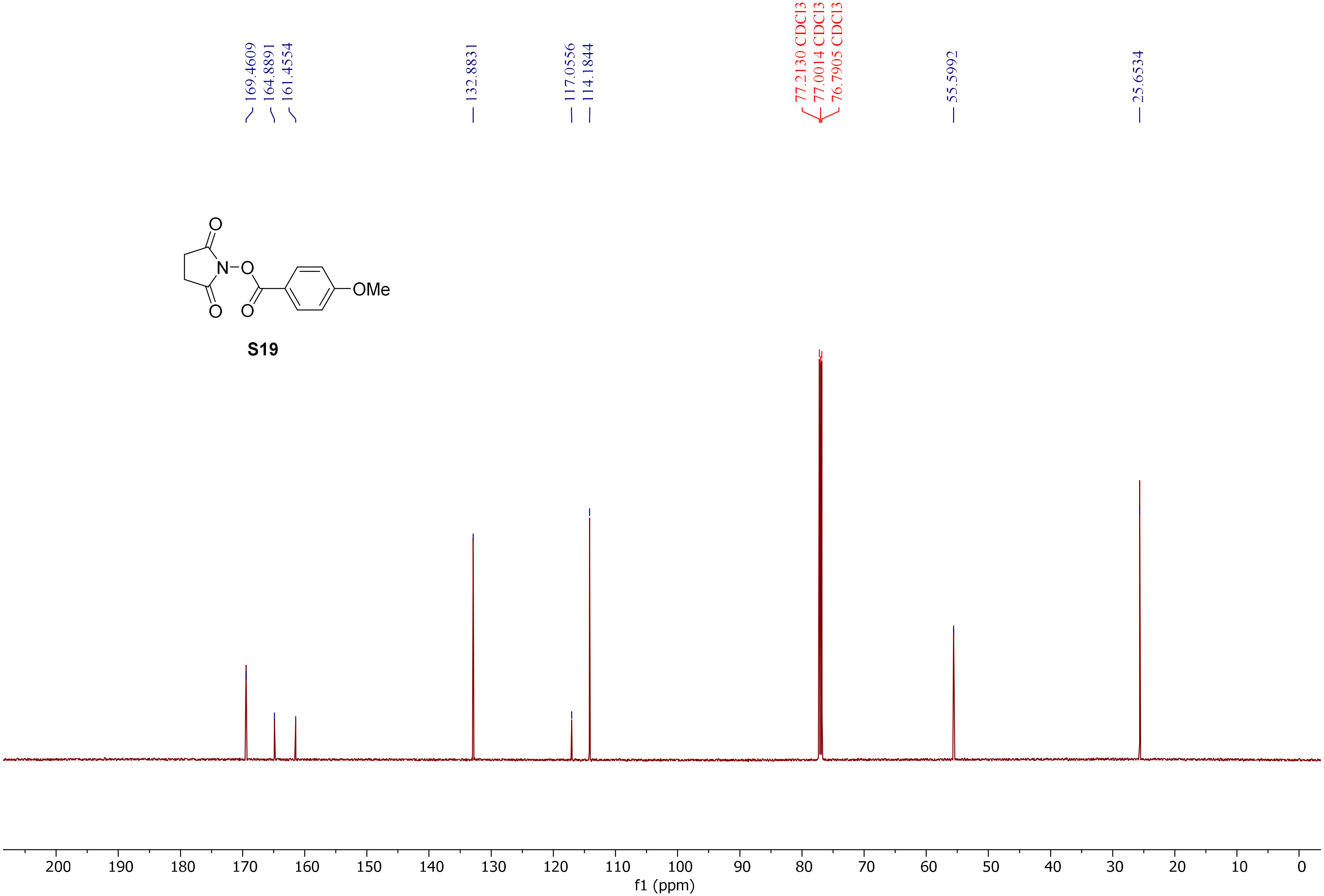
S17

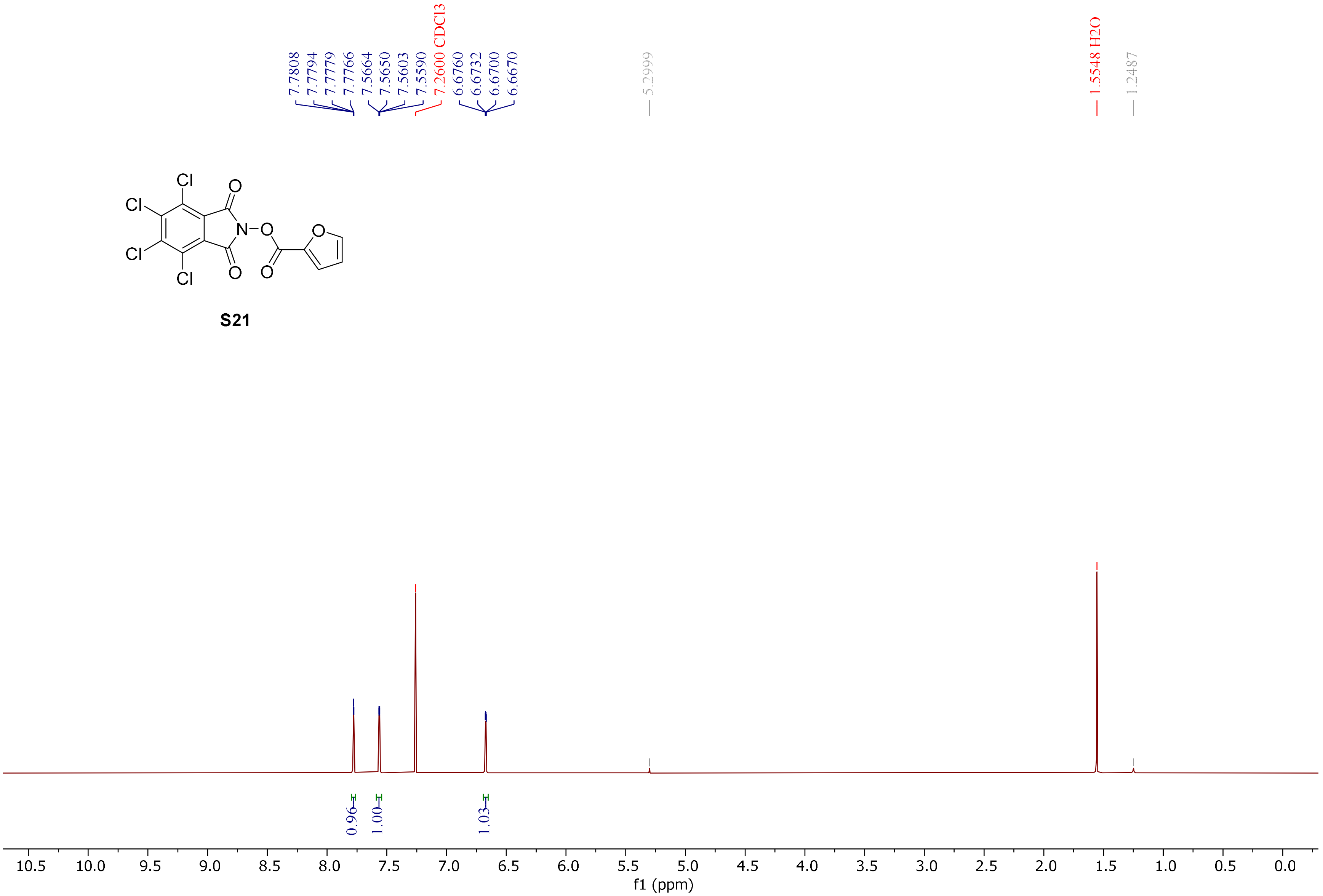

161.7904
161.7618
136.4691
136.2515
136.0321
135.8136
134.9338
131.0349
128.8432
128.6046
125.9415
125.9170
125.8919
125.8667
124.1231
122.3418
120.5327
77.2111 CDCl3
76.9993 CDCl3
76.7873 CDCl3
O
N
O
O
O
CF3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S17

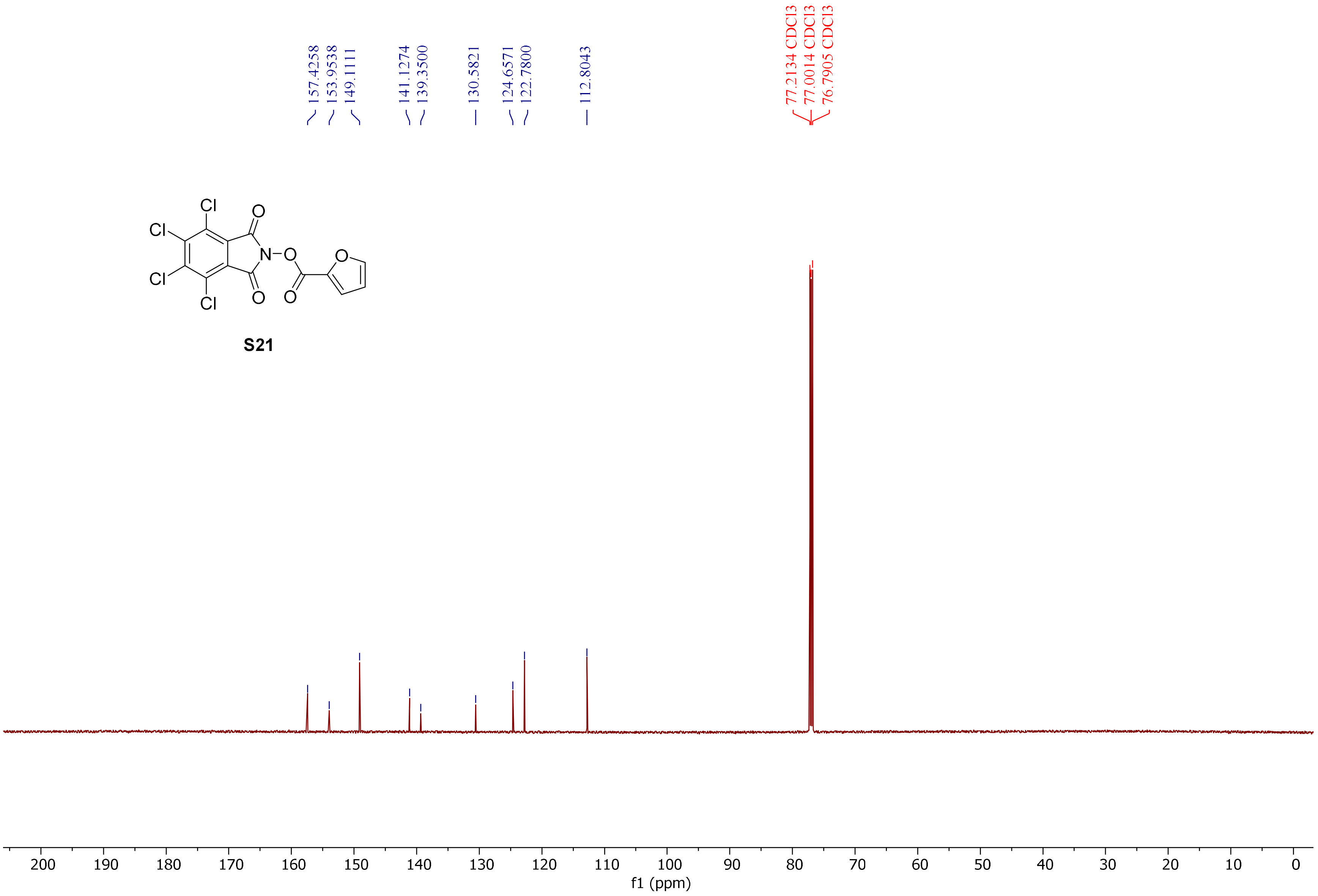

8.1037
8.0988
8.0954
8.0873
8.0839
8.0791
7.2601 CDCl3
6.9853
6.9805
6.9771
6.9691
6.9656
6.9608
5.2979
3.8917
2.9026
1.5778 H2O
N
O
O
O
O
OMe
1.90
2.00
3.07
4.44
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

S19

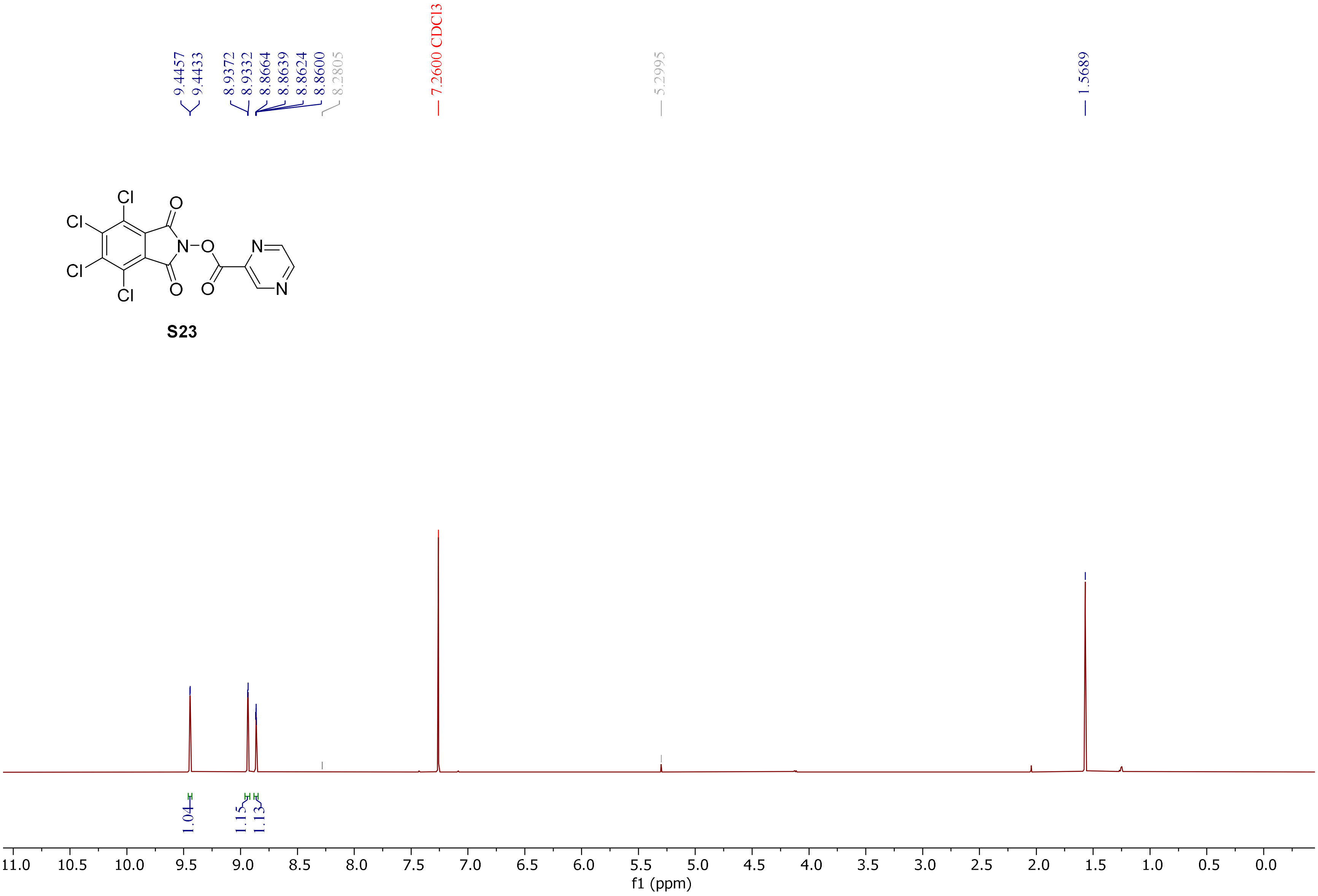

169.4609
164.8891
161.4554
132.8831
117.0556
114.1844
77.2130 CDCl3
77.0014 CDCl3
76.7905 CDCl3
55.5992
25.6534
O
N
O
O
O
OMe
S19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7808
7.7794
7.7779
7.7766
7.5664
7.5650
7.5603
7.5590
7.2600 CDCl3
6.6760
6.6732
6.6700
6.6670
5.2999
1.5548 H2O
1.2487
Cl
Cl
Cl
Cl
O
O
N
O
O
O
0.96
1.00
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

S21

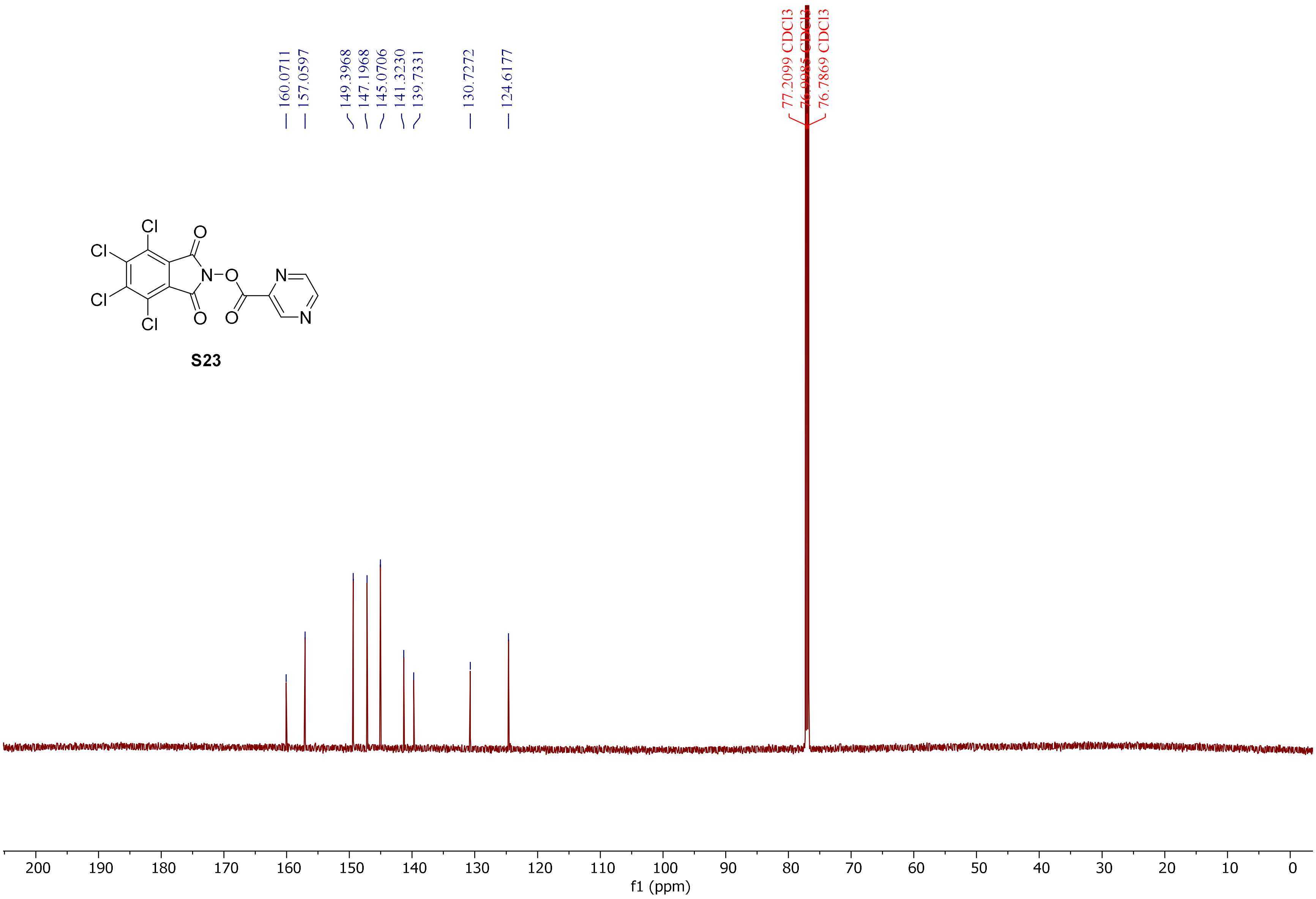

157.4258
153.9538
149.1111
141.1274
139.3500
130.5821
124.6571
122.7800
112.8043
77.2134 CDCl3
77.0014 CDCl3
76.7905 CDCl3
Cl
Cl
Cl
Cl
O
O
N
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S21

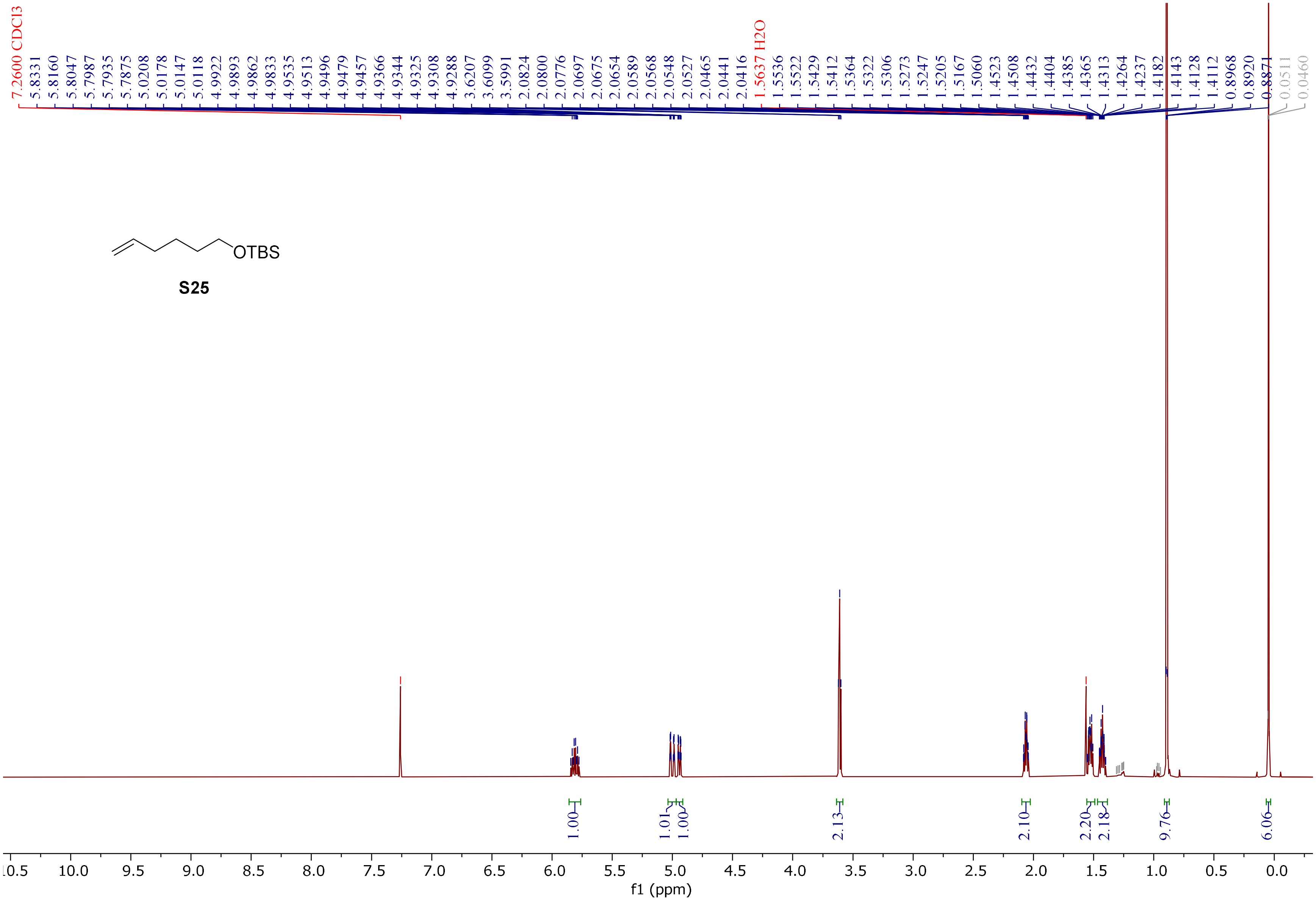


S23

9.4457
9.4433
8.9372
8.9332
8.8664
8.8639
8.8624
8.8600
8.2805
7.2600 CDCl3
5.2995
1.5689
1.04
1.15
1.13
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
Cl
Cl
Cl
Cl
O
O
N
O
O
N
N


160.0711
157.0597
149.3968
147.1968
145.0706
141.3230
139.7331
130.7272
124.6177
77.2099 CDCl3
76.9985 CDCl3
76.7869 CDCl3
Cl
Cl
Cl
Cl
O
O
N
O
O
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

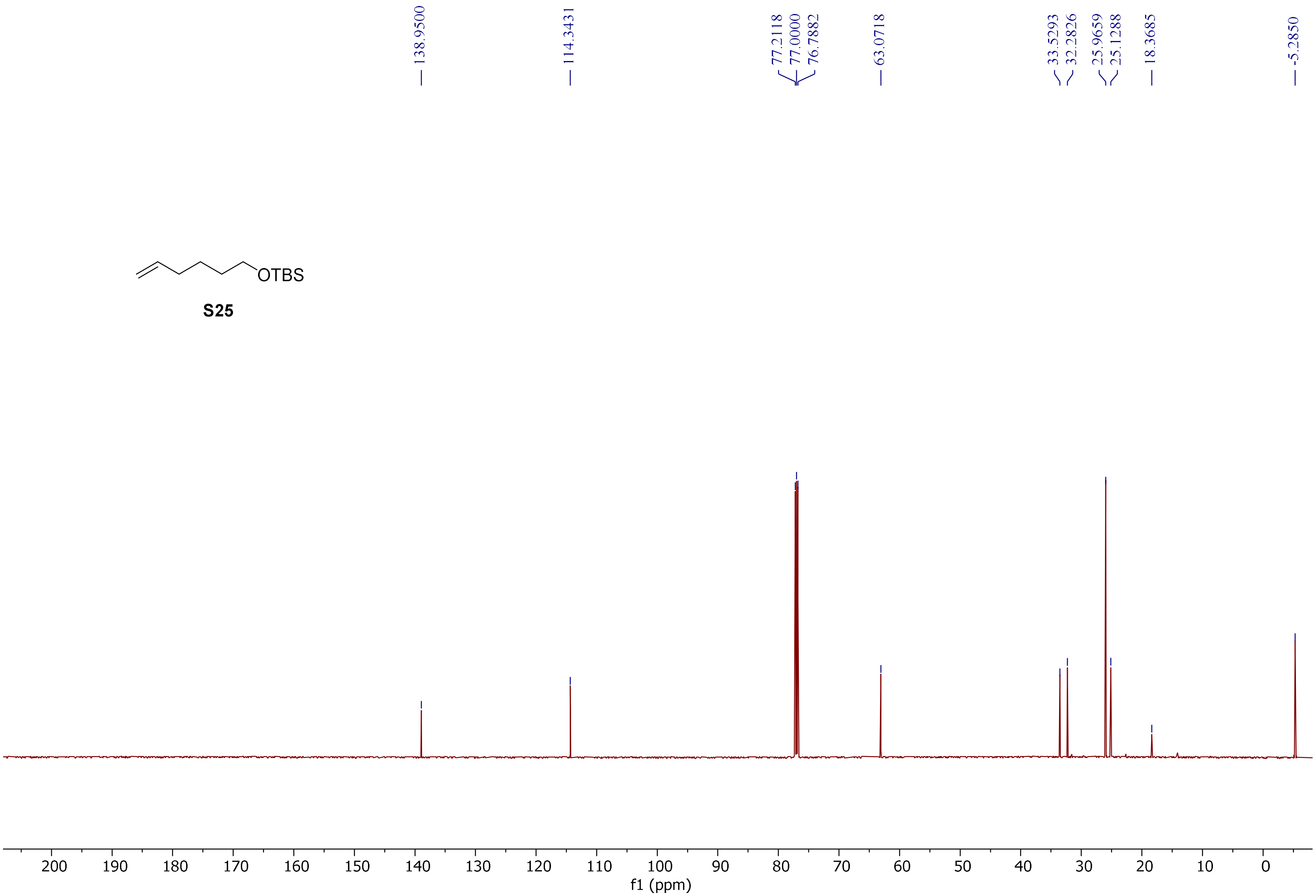
S23

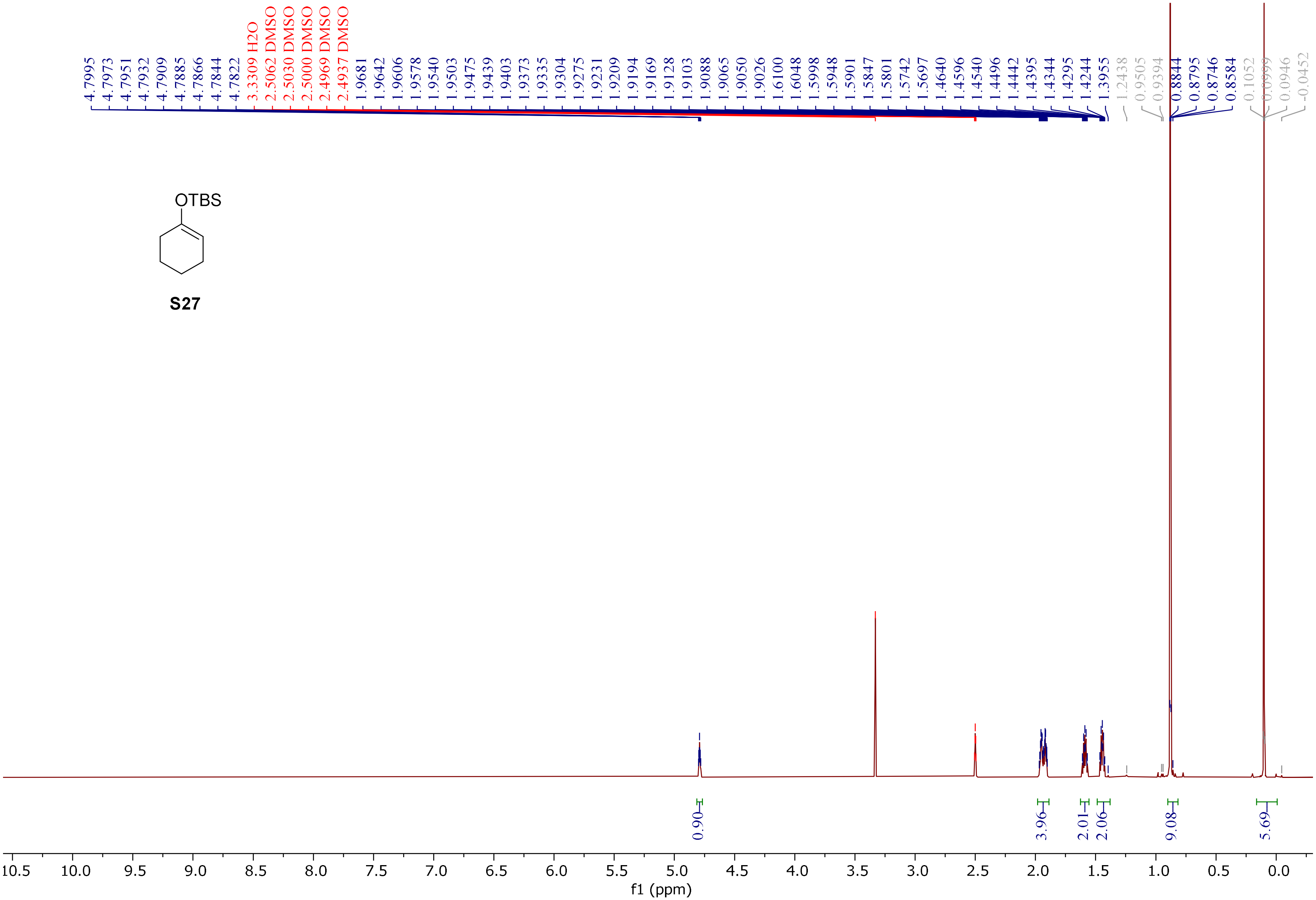

7.2600 CDCl3
5.8331
5.8160
5.8047
5.7987
5.7935
5.7875
5.0208
5.0178
5.0147
5.0118
4.9922
4.9893
4.9862
4.9833
4.9535
4.9513
4.9496
4.9479
4.9457
4.9366
4.9344
4.9325
4.9308
4.9288
3.6207
3.6099
3.5991
2.0824
2.0800
2.0776
2.0697
2.0675
2.0654
2.0589
2.0568
2.0548
2.0527
2.0465
2.0441
2.0416
1.5637 H2O
1.5536
1.5522
1.5429
1.5412
1.5364
1.5322
1.5306
1.5273
1.5247
1.5205
1.5167
1.5060
1.4523
1.4508
1.4432
1.4404
1.4385
1.4365
1.4313
1.4264
1.4237
1.4182
1.4143
1.4128
1.4112
0.8968
0.8920
0.8871
0.0511
0.0460
OTBS
1.00
1.01
1.00
2.13
2.10
2.20
2.18
9.76
6.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

S25

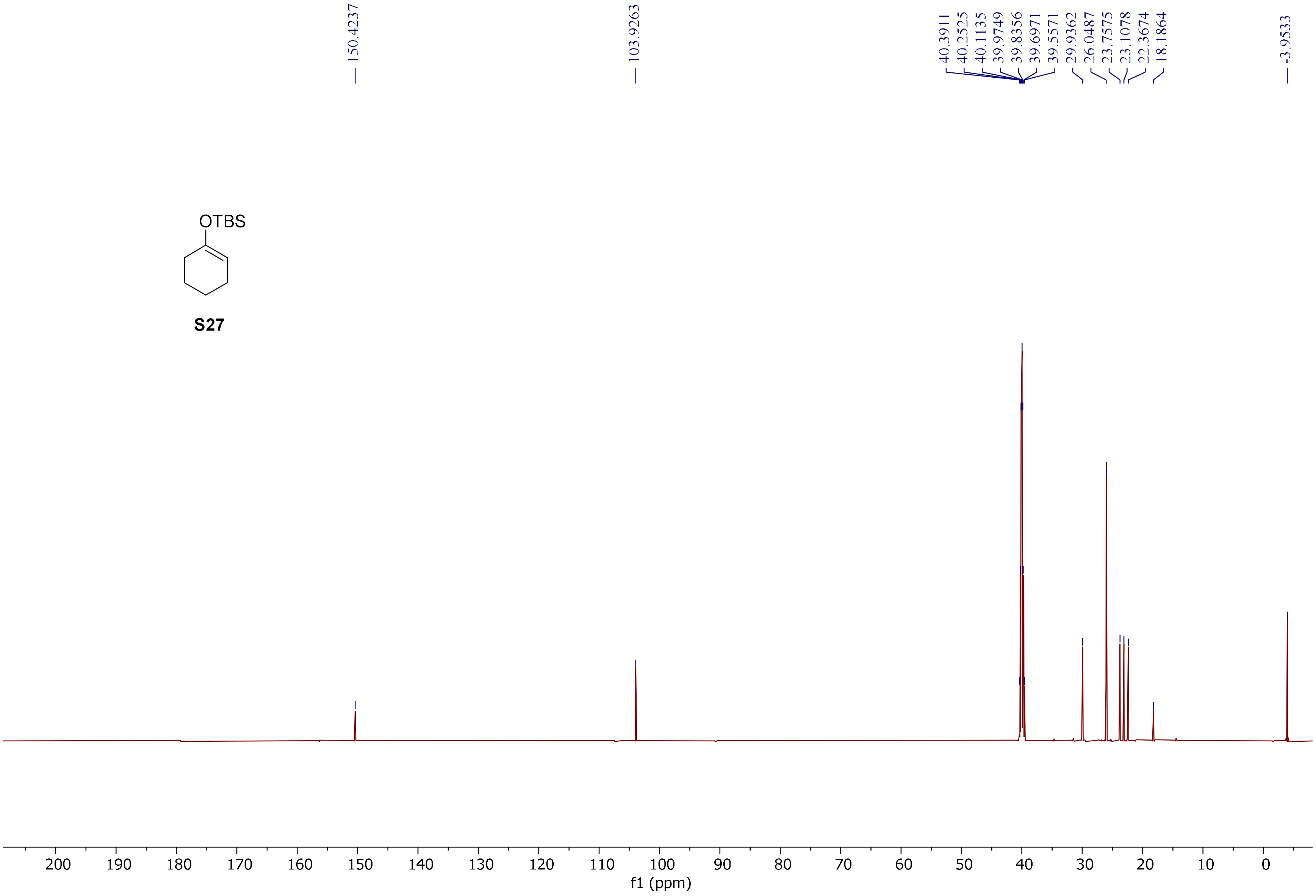
OTBS

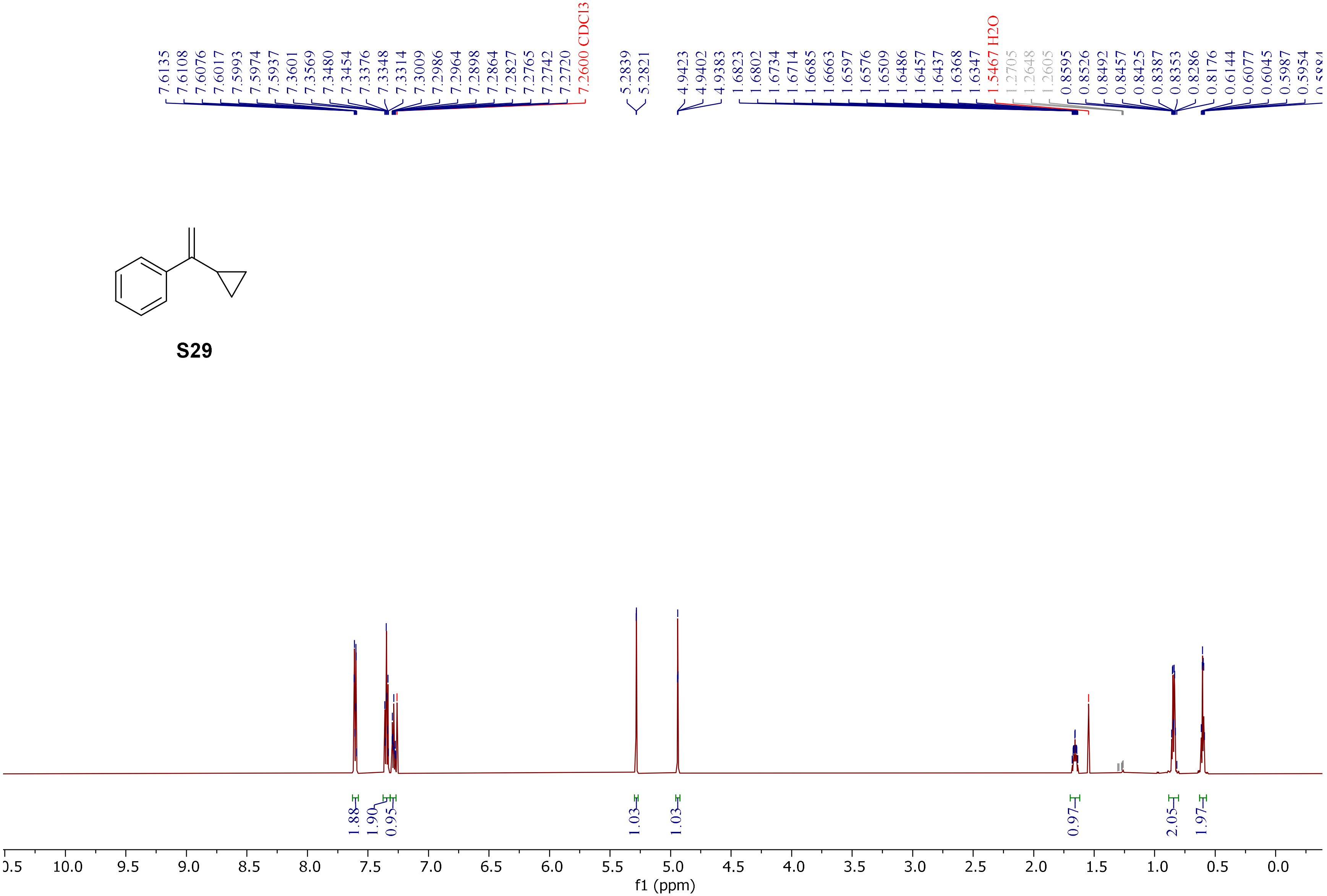
S25


138.9500
114.3431
77.2118
77.0000
76.7882
63.0718
33.5293
32.2826
25.9659
25.1288
18.3685
-5.2850
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4.7995
4.7973
4.7951
4.7932
4.7909
4.7885
4.7866
4.7844
4.7822
3.3309 H2O
2.5062 DMSO
2.5030 DMSO
2.5000 DMSO
2.4969 DMSO
2.4937 DMSO
1.9681
1.9642
1.9606
1.9578
1.9540
1.9503
1.9475
1.9439
1.9403
1.9373
1.9335
1.9304
1.9275
1.9231
1.9209
1.9194
1.9169
1.9128
1.9103
1.9088
1.9065
1.9050
1.9026
1.6100
1.6048
1.5998
1.5948
1.5901
1.5847
1.5801
1.5742
1.5697
1.4640
1.4596
1.4540
1.4496
1.4442
1.4395
1.4344
1.4295
1.4244
1.3955
1.2438
0.9505
0.9394
0.8844
0.8795
0.8746
0.8584
0.1052
0.0999
0.0946
-0.0452
OTBS
0.90
3.96
2.01
2.06
9.08
5.69
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

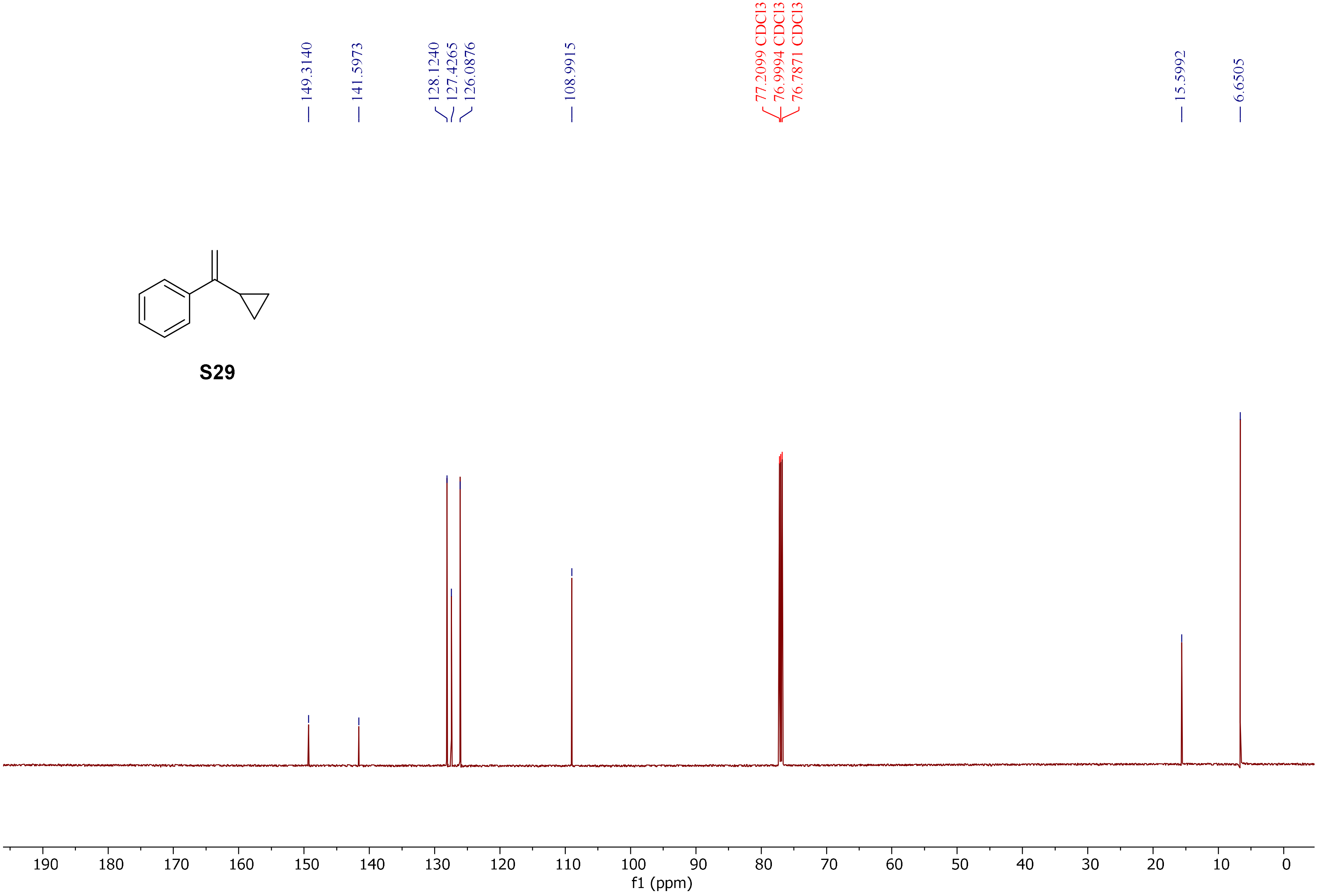
S27

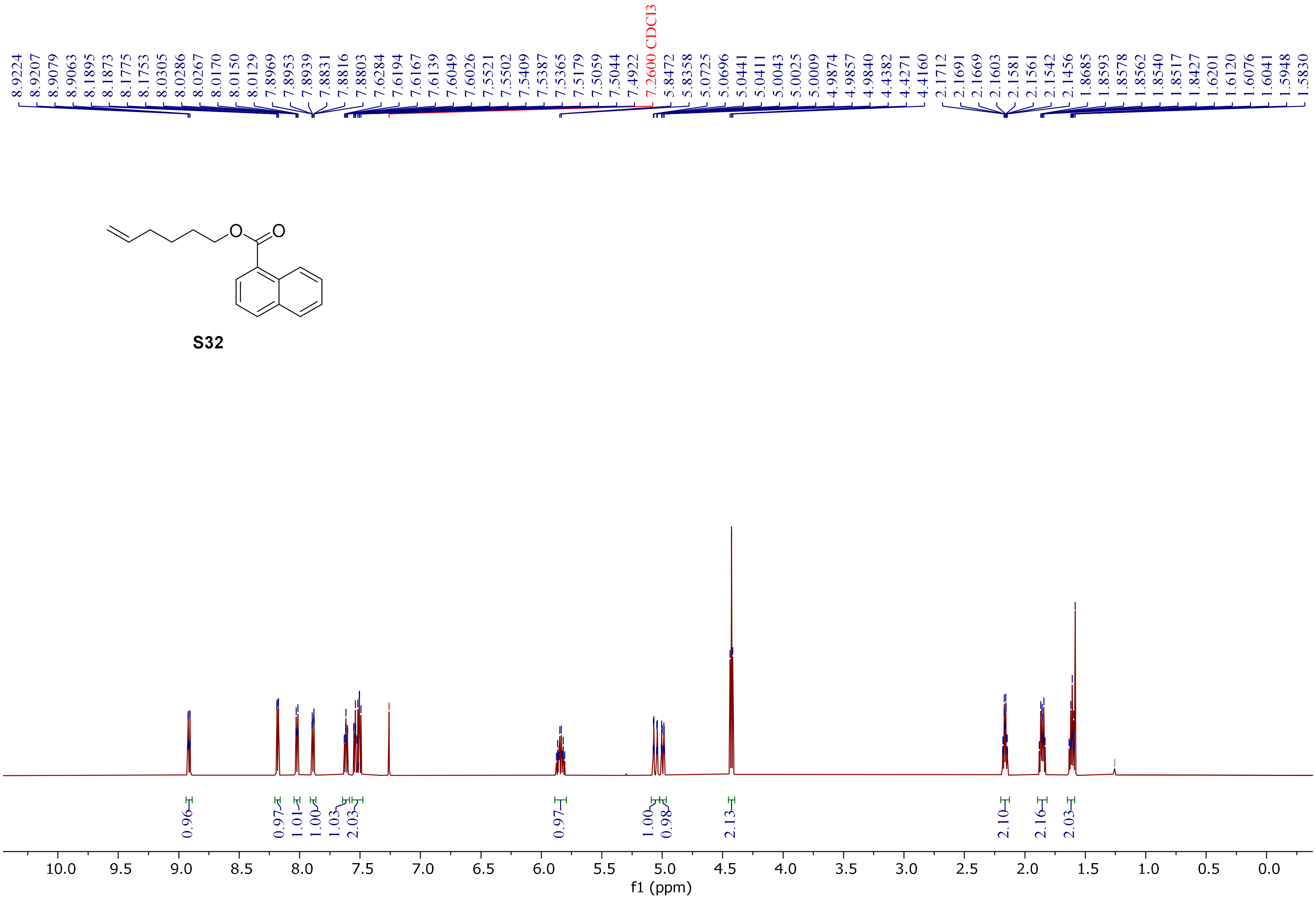

150.4237
103.9263
40.3911
40.2525
40.1135
39.9749
39.8356
39.6971
39.5571
29.9362
26.0487
23.7575
23.1078
22.3674
18.1864
-3.9533
OTBS
S27
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



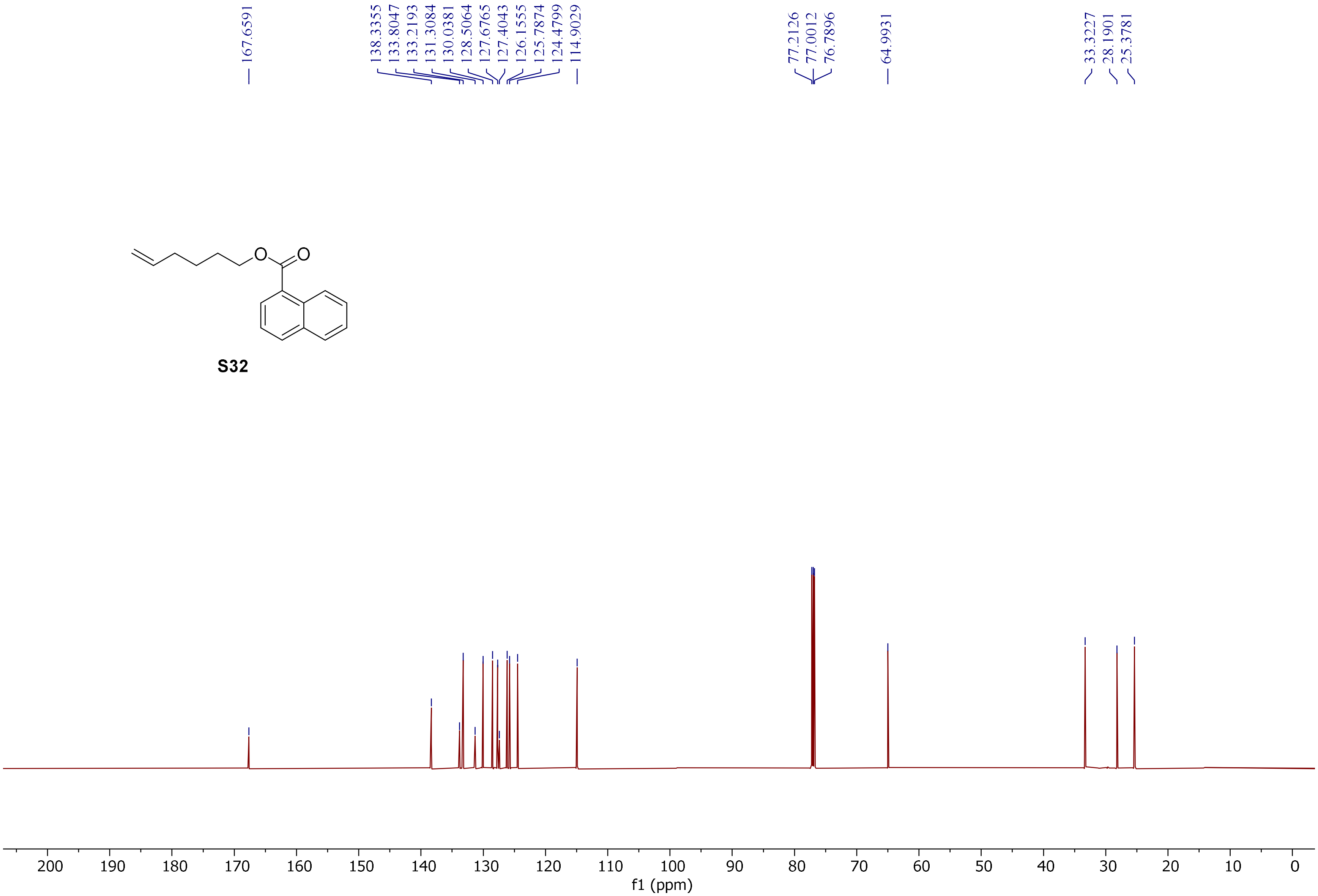
S29

7.6135
7.6108
7.6076
7.6017
7.5993
7.5974
7.5937
7.3601
7.3569
7.3480
7.3454
7.3376
7.3348
7.3314
7.3009
7.2986
7.2964
7.2898
7.2864
7.2827
7.2765
7.2742
7.2720
7.2600 CDCl3
5.2839
5.2821
4.9423
4.9402
4.9383
1.6823
1.6802
1.6734
1.6714
1.6685
1.6663
1.6597
1.6576
1.6509
1.6486
1.6457
1.6437
1.6368
1.6347
1.5467 H2O
1.2705
1.2648
1.2605
0.8595
0.8526
0.8492
0.8457
0.8425
0.8387
0.8353
0.8286
0.8176
0.6144
0.6077
0.6045
0.5987
0.5954
1.88
1.90
0.95
1.03
1.03
0.97
2.05
1.97
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

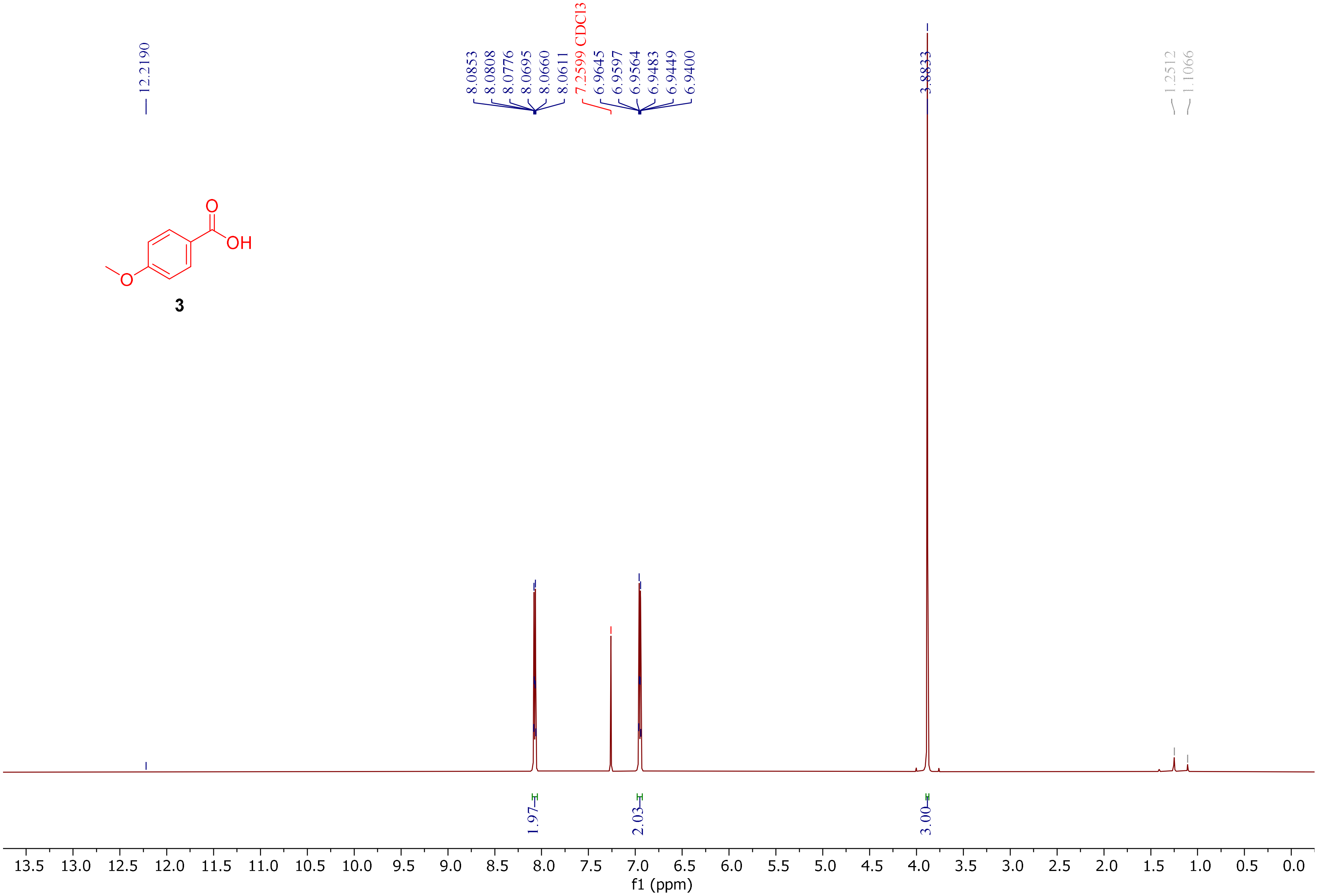

149.3140
141.5973
128.1240
127.4265
126.0876
108.9915
77.2099 CDCl3
76.9994 CDCl3
76.7871 CDCl3
15.5992
6.6505
S29
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

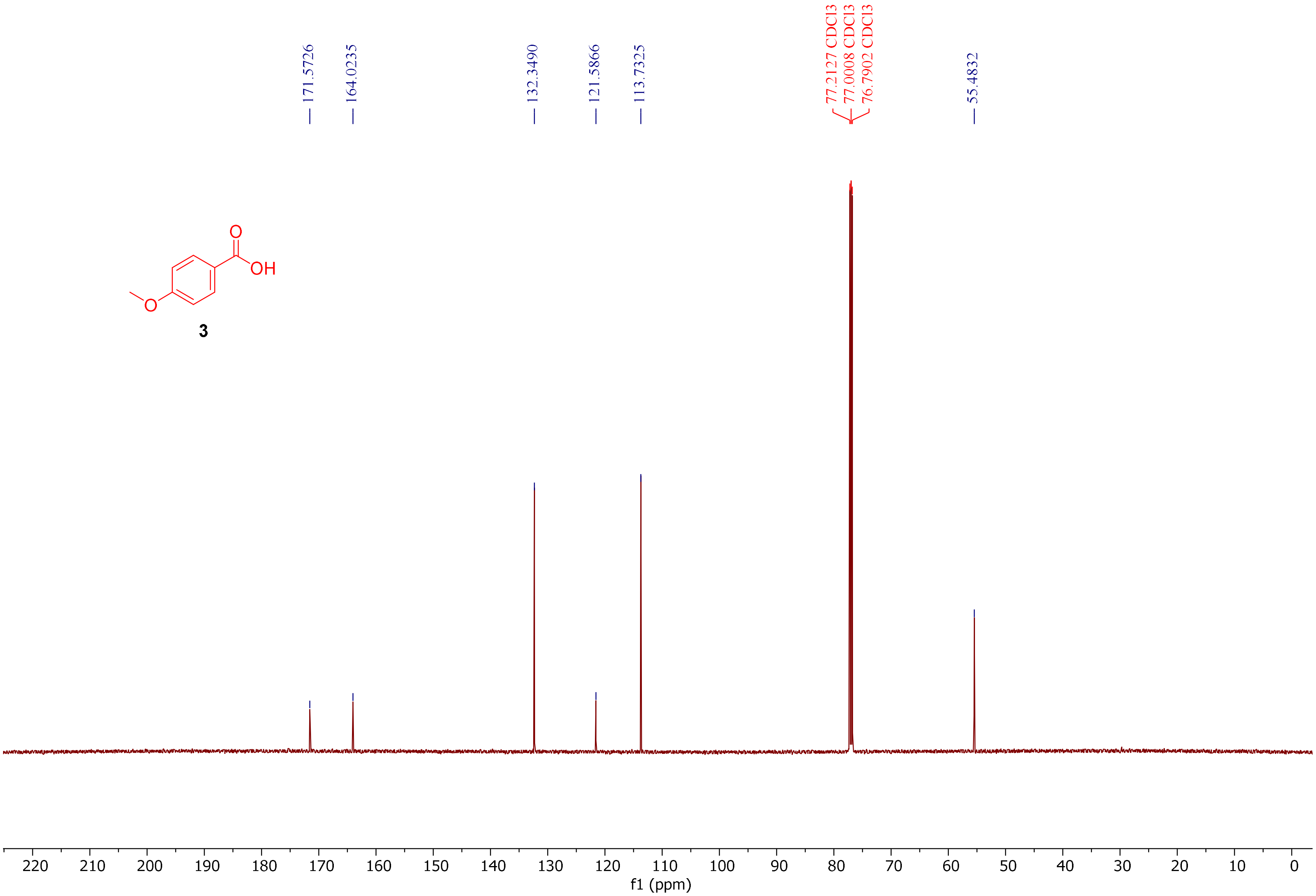

8.9224
8.9207
8.9079
8.9063
8.1895
8.1873
8.1775
8.1753
8.0305
8.0286
8.0267
8.0170
8.0150
8.0129
7.8969
7.8953
7.8939
7.8831
7.8816
7.8803
7.6284
7.6194
7.6167
7.6139
7.6049
7.6026
7.5521
7.5502
7.5409
7.5387
7.5365
7.5179
7.5059
7.5044
7.4922
7.2600 CDCl3
5.8472
5.8358
5.0725
5.0696
5.0441
5.0411
5.0043
5.0025
5.0009
4.9874
4.9857
4.9840
4.4382
4.4271
4.4160
2.1712
2.1691
2.1669
2.1603
2.1581
2.1561
2.1542
2.1456
1.8685
1.8593
1.8578
1.8562
1.8540
1.8517
1.8427
1.6201
1.6120
1.6076
1.6041
1.5948
1.5830
O
O
0.96
0.97
1.01
1.00
1.03
2.03
0.97
1.00
0.98
2.13
2.10
2.16
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

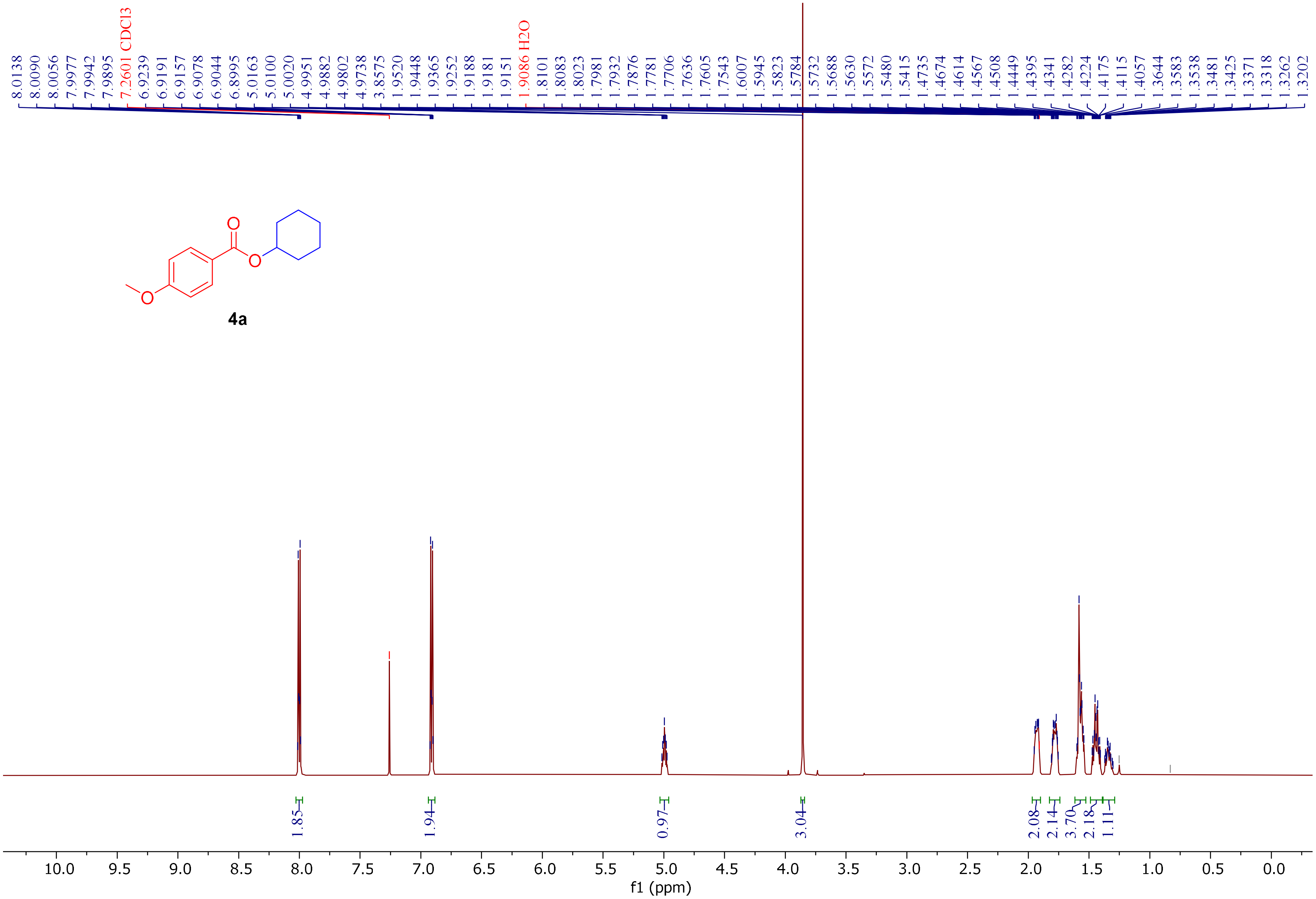
S32

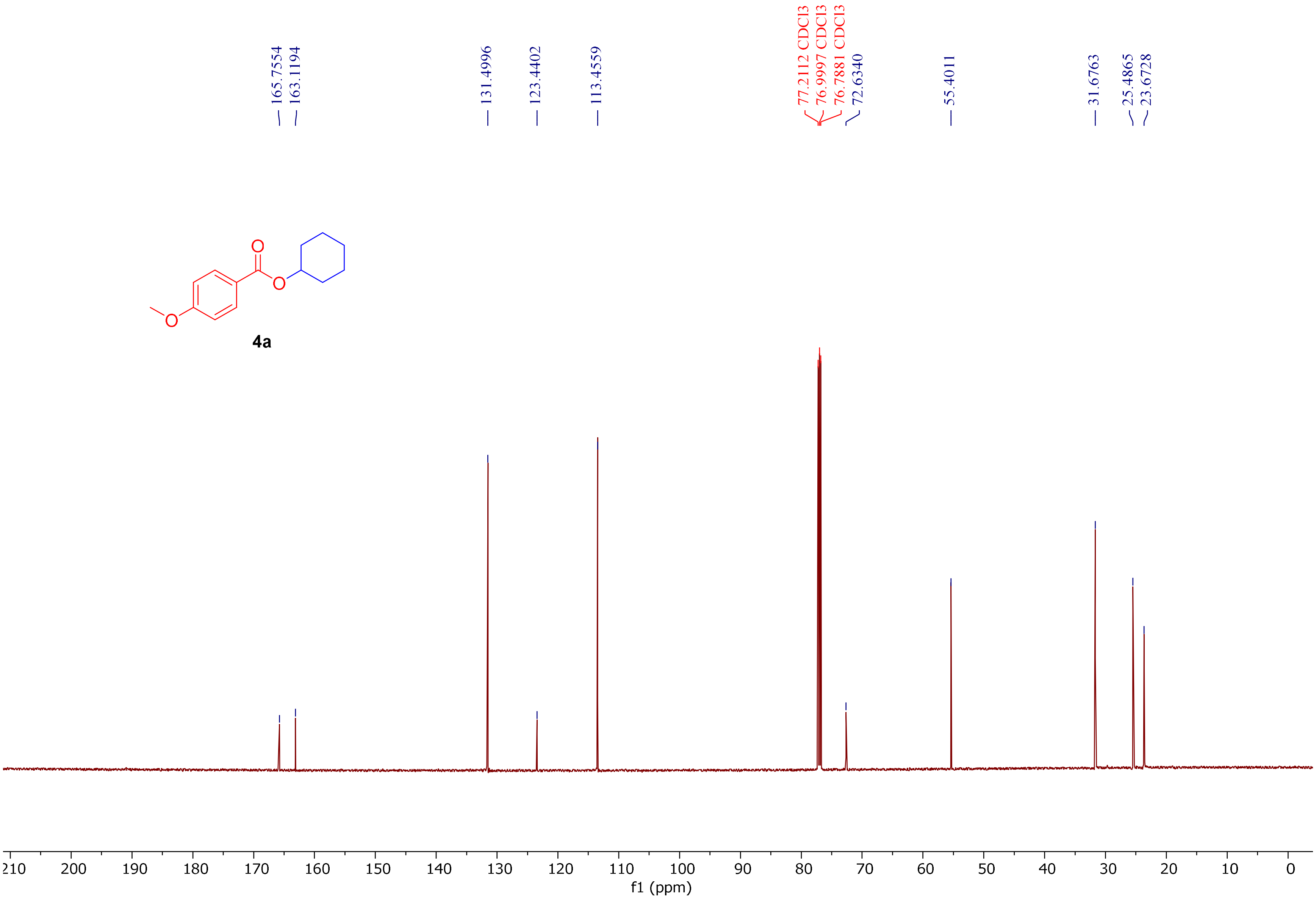

S32

167.6591
138.3355
133.8047
133.2193
131.3084
130.0381
128.5064
127.6765
127.4043
126.1555
125.7874
124.4799
114.9029
77.2126
77.0012
76.7896
64.9931
33.3227
28.1901
25.3781
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.2190
8.0853
8.0808
8.0776
8.0695
8.0660
8.0611
7.2599 CDCl3
6.9645
6.9597
6.9564
6.9483
6.9449
6.9400
3.8833
1.2512
1.1066
O
OH
O
3
1.97
2.03
3.00
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

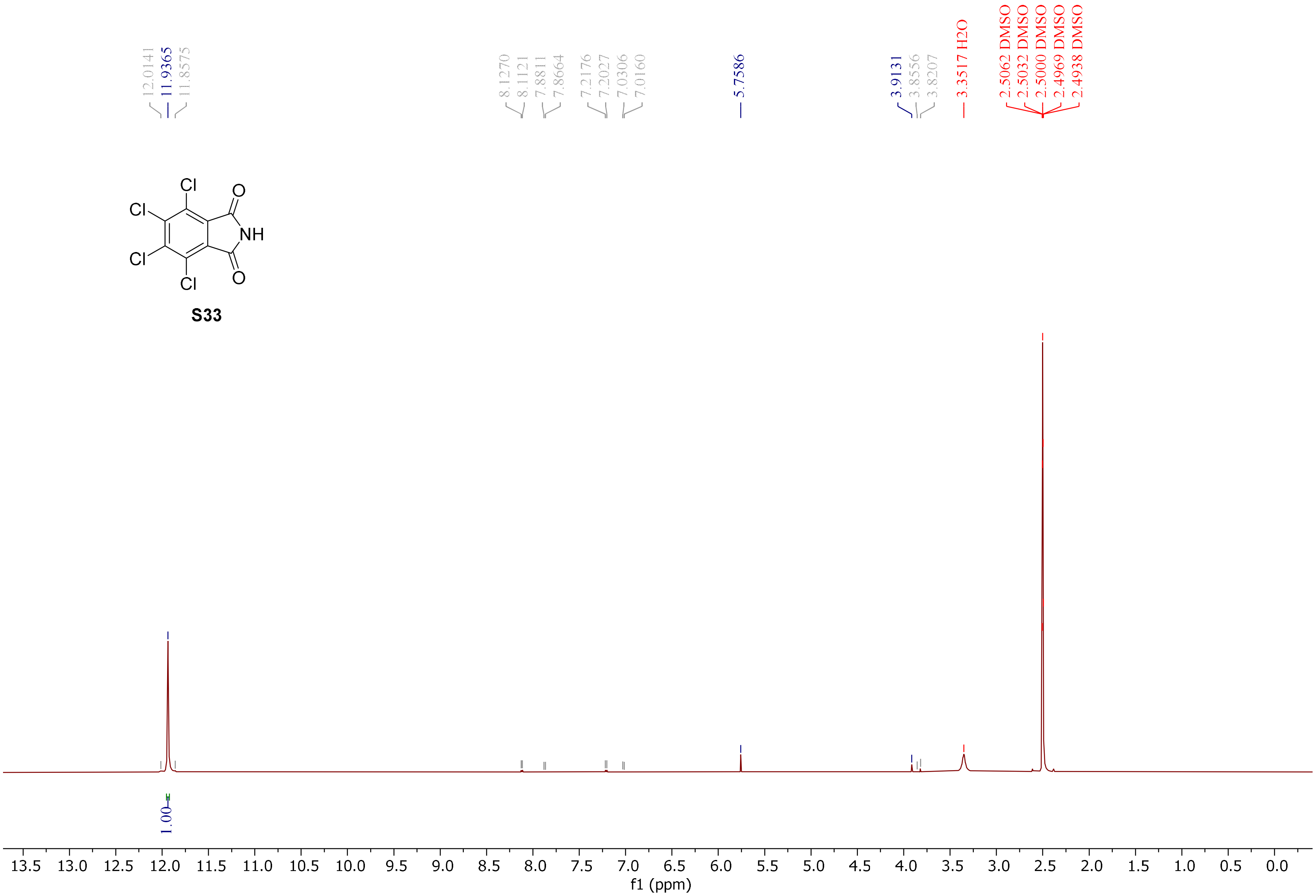

3
171.5726
164.0235
132.3490
121.5866
113.7325
77.2127 CDCl3
77.0008 CDCl3
76.7902 CDCl3
55.4832
O
OH
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0138
8.0090
8.0056
7.9977
7.9942
7.9895
7.2601 CDCl3
6.9239
6.9191
6.9157
6.9078
6.9044
6.8995
5.0163
5.0100
5.0020
4.9951
4.9882
4.9802
4.9738
3.8575
1.9520
1.9448
1.9365
1.9252
1.9188
1.9181
1.9151
1.9086 H2O
1.8101
1.8083
1.8023
1.7981
1.7932
1.7876
1.7781
1.7706
1.7636
1.7605
1.7543
1.6007
1.5945
1.5823
1.5784
1.5732
1.5688
1.5630
1.5572
1.5480
1.5415
1.4735
1.4674
1.4614
1.4567
1.4508
1.4449
1.4395
1.4341
1.4282
1.4224
1.4175
1.4115
1.4057
1.3644
1.3583
1.3538
1.3481
1.3425
1.3371
1.3318
1.3262
1.3202
4a
1.85
1.94
0.97
3.04
2.08
2.14
3.70
2.18
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



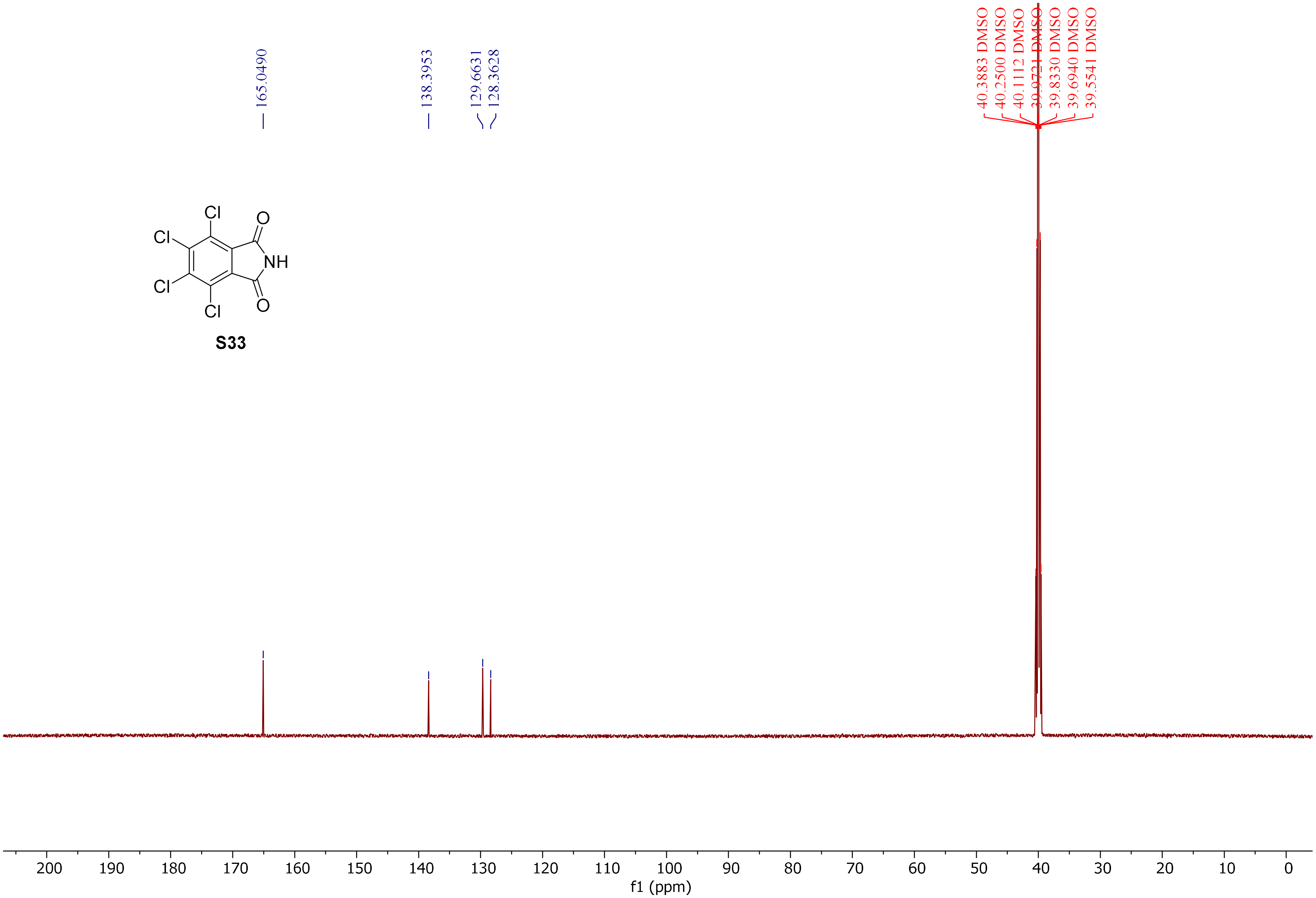
4a

165.7554
163.1194
131.4996
123.4402
113.4559
77.2112 CDCl3
76.9997 CDCl3
76.7881 CDCl3
72.6340
55.4011
31.6763
25.4865
23.6728
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

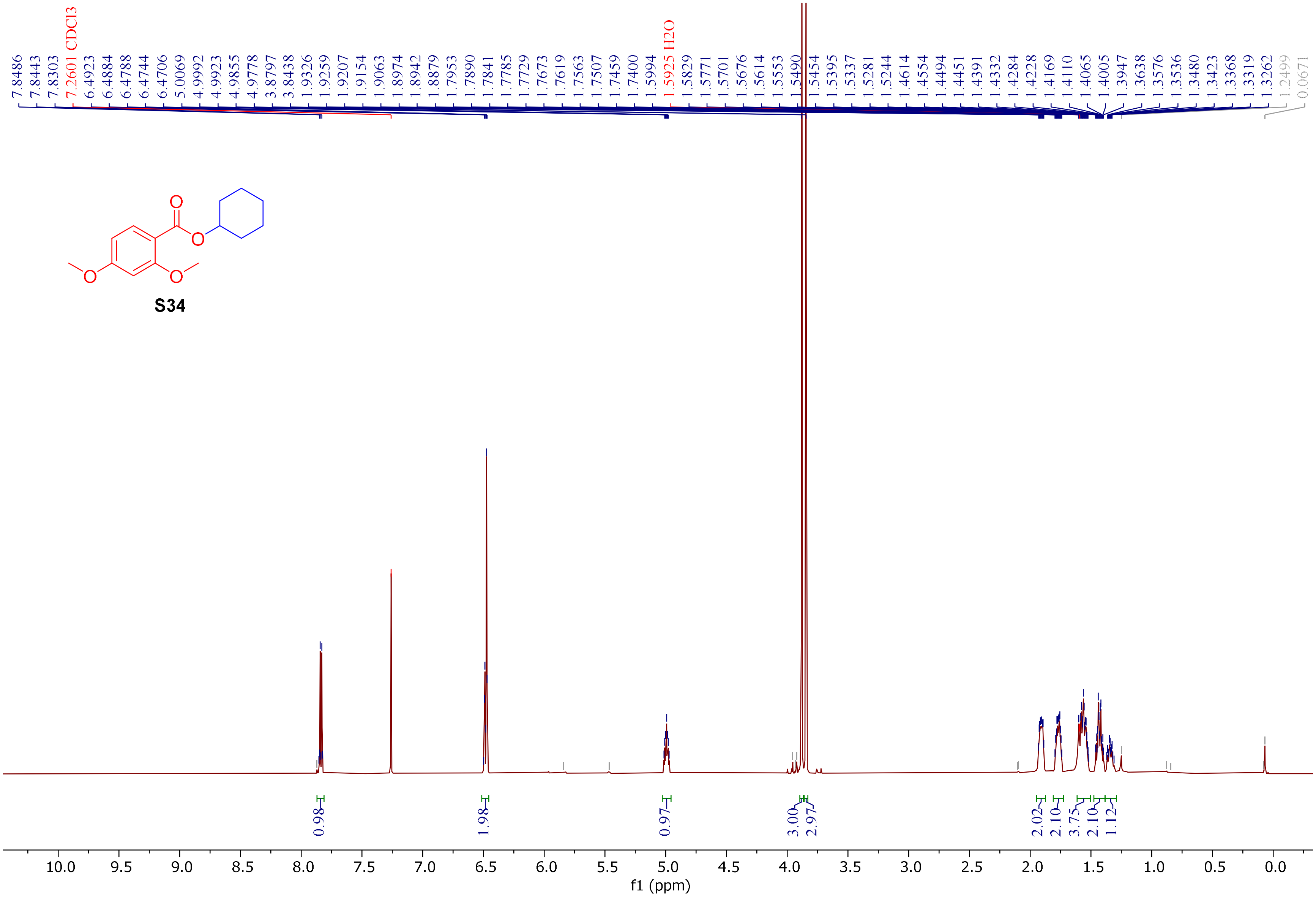


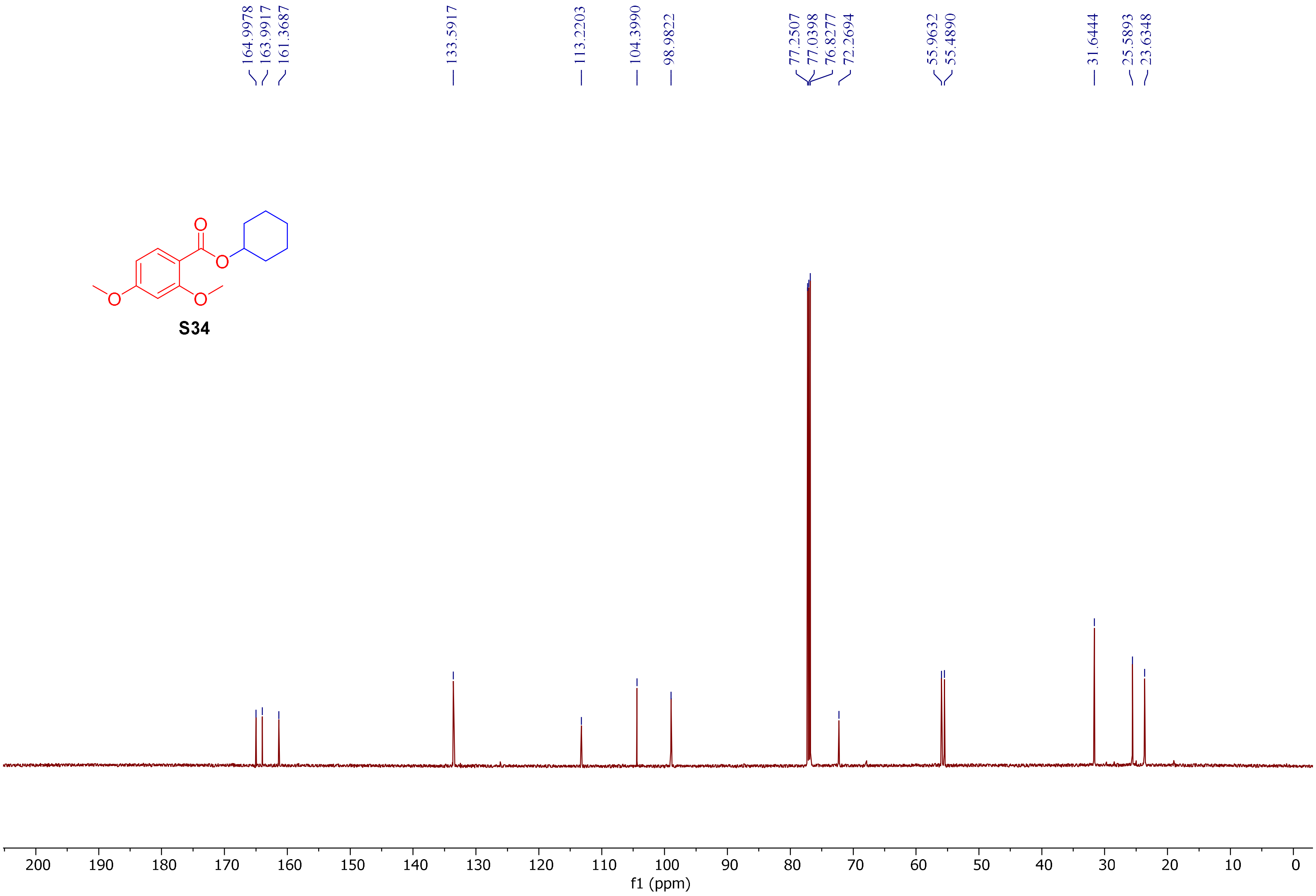
12.0141
11.9365
11.8575
8.1270
8.1121
7.8811
7.8664
7.2176
7.2027
7.0306
7.0160
5.7586
3.9131
3.8556
3.8207
3.3517 H2O
2.5062 DMSO
2.5032 DMSO
2.5000 DMSO
2.4969 DMSO
2.4938 DMSO
Cl
Cl
Cl
Cl
O
O
NH
1.00
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

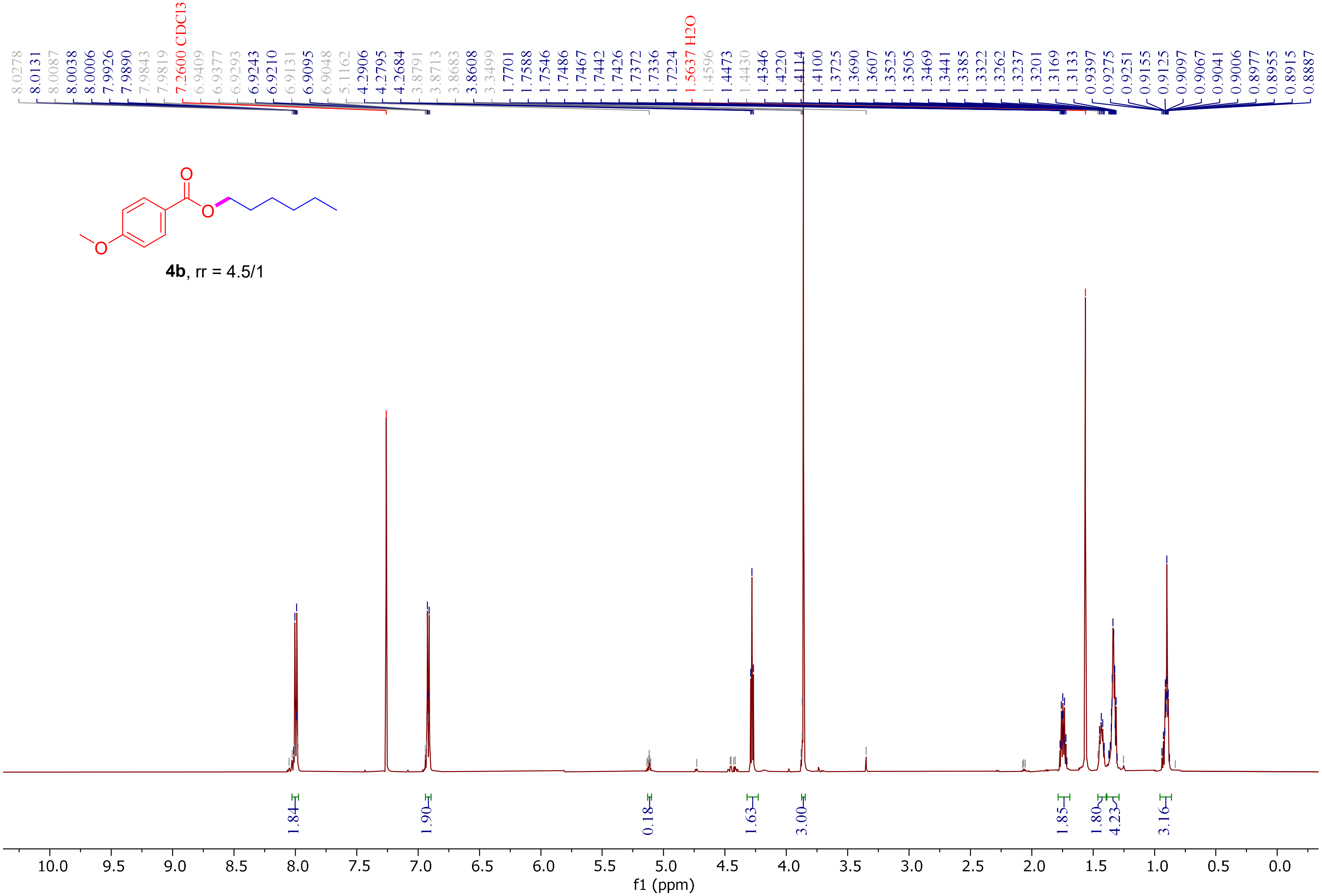
S33

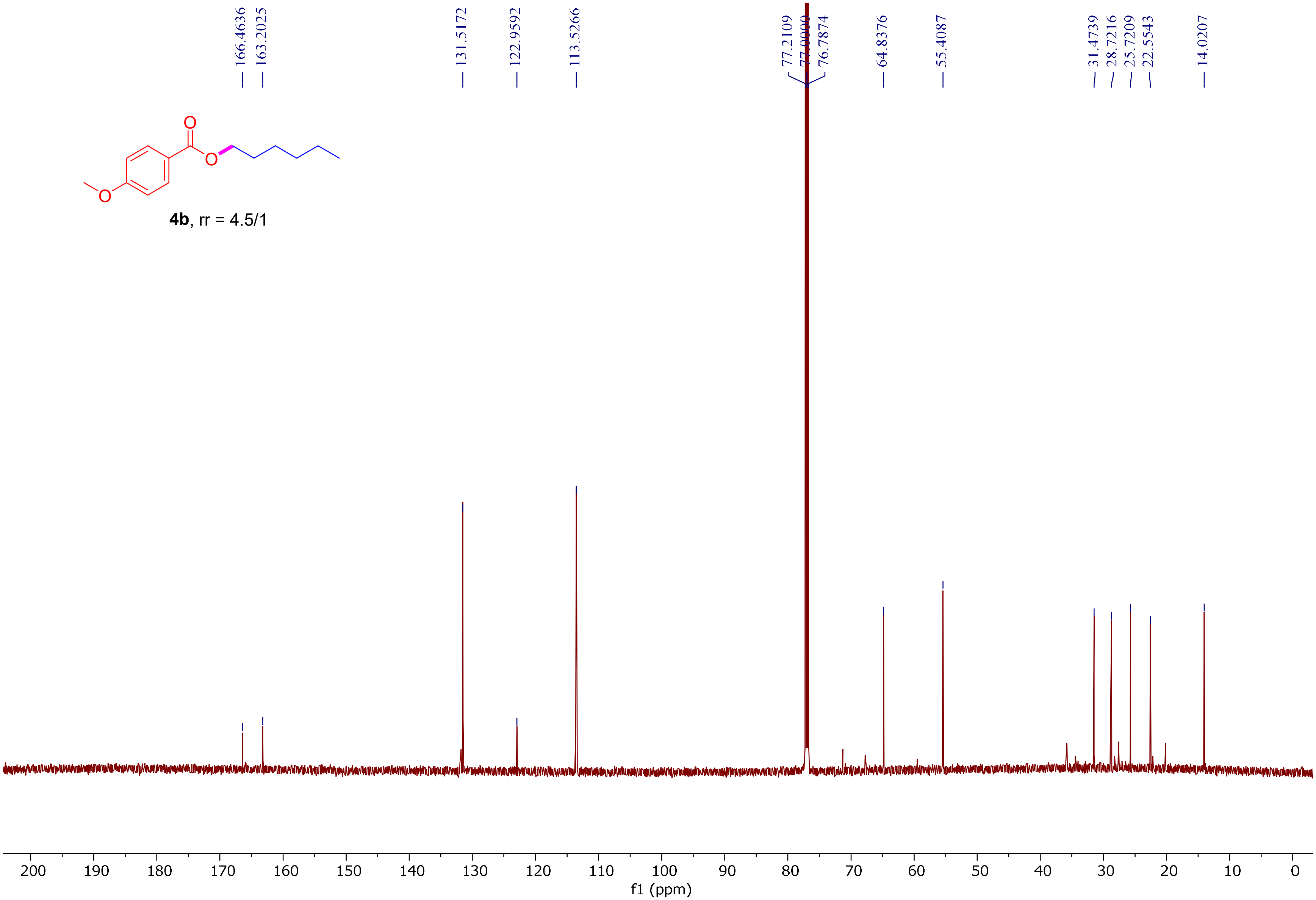

165.0490
138.3953
129.6631
128.3628
40.3883 DMSO
40.2500 DMSO
40.1112 DMSO
39.9721 DMSO
39.8330 DMSO
39.6940 DMSO
39.5541 DMSO
Cl
Cl
Cl
Cl
O
NH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S33


S34
7.8486
7.8443
7.8303
7.2601 CDCl3
6.4923
6.4884
6.4788
6.4744
6.4706
5.0069
4.9992
4.9923
4.9855
4.9778
3.8797
3.8438
1.9326
1.9259
1.9207
1.9154
1.9063
1.8974
1.8942
1.8879
1.7953
1.7890
1.7841
1.7785
1.7729
1.7673
1.7619
1.7563
1.7507
1.7459
1.7400
1.5994
1.5925 H2O
1.5829
1.5771
1.5701
1.5676
1.5614
1.5553
1.5490
1.5454
1.5395
1.5337
1.5281
1.5244
1.4614
1.4554
1.4494
1.4451
1.4391
1.4332
1.4284
1.4228
1.4169
1.4110
1.4065
1.4005
1.3947
1.3638
1.3576
1.3536
1.3480
1.3423
1.3368
1.3319
1.3262
1.2499
0.0671
O
O
O
O
0.98
1.98
0.97
3.00
2.97
2.02
2.10
3.75
2.10
1.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

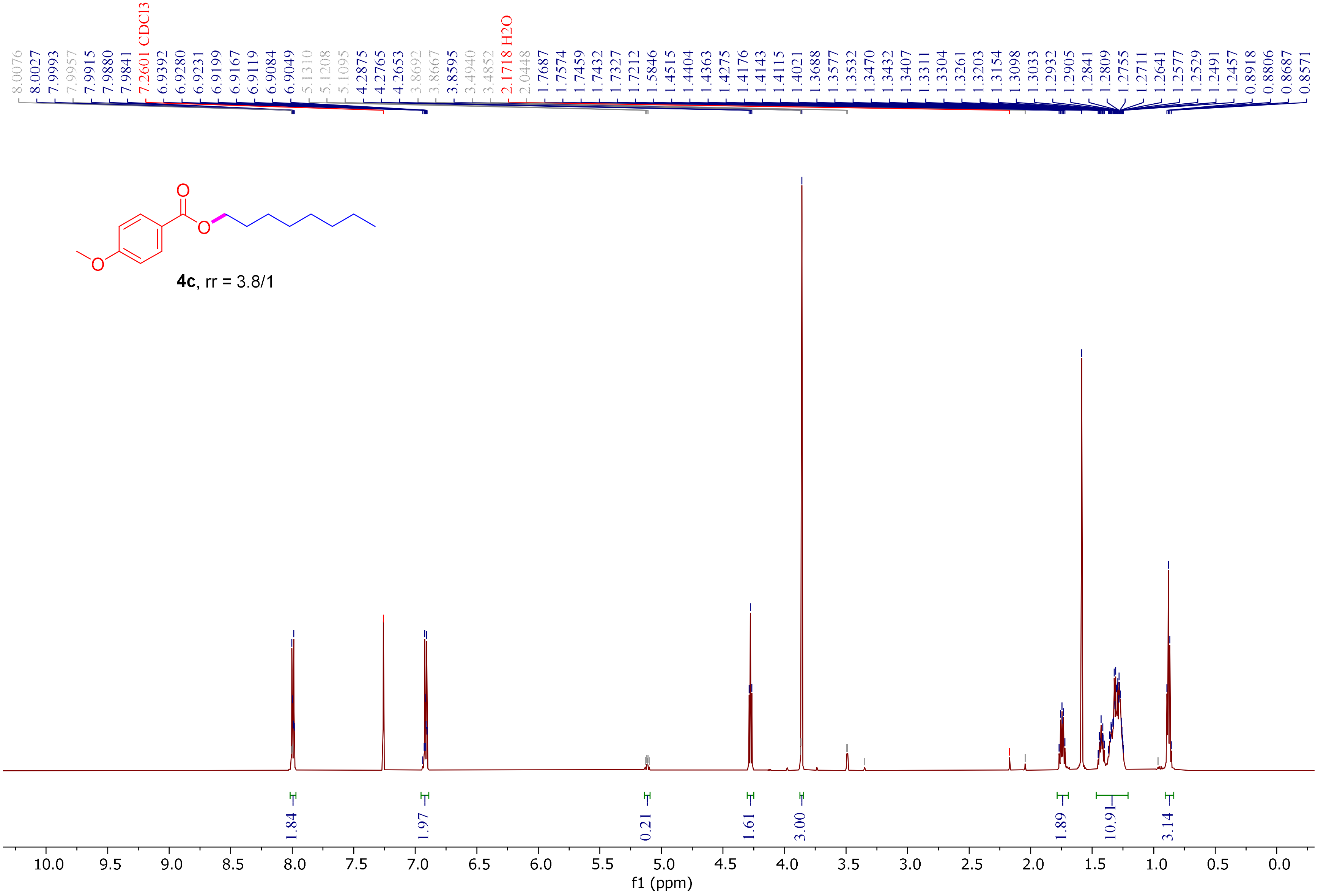

164.9978
163.9917
161.3687
133.5917
113.2203
104.3990
98.9822
77.2507
77.0398
76.8277
72.2694
55.9632
55.4890
31.6444
25.5893
23.6348
O
O
O
O
S34
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0278
8.0131
8.0087
8.0038
8.0006
7.9926
7.9890
7.9843
7.9819
7.2600 CDCl3
6.9409
6.9377
6.9293
6.9243
6.9210
6.9131
6.9095
6.9048
5.1162
4.2906
4.2795
4.2684
3.8791
3.8713
3.8683
3.8608
3.3499
1.7701
1.7588
1.7546
1.7486
1.7467
1.7442
1.7426
1.7372
1.7336
1.7224
1.5637 H2O
1.4596
1.4473
1.4430
1.4346
1.4220
1.4114
1.4100
1.3725
1.3690
1.3607
1.3525
1.3505
1.3469
1.3441
1.3385
1.3322
1.3262
1.3237
1.3201
1.3169
1.3133
0.9397
0.9275
0.9251
0.9155
0.9125
0.9097
0.9067
0.9041
0.9006
0.8977
0.8955
0.8915
0.8887
O
O
O
4b, rr = 4.5/1
1.84
1.90
0.18
1.63
3.00
1.85
1.80
4.23
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

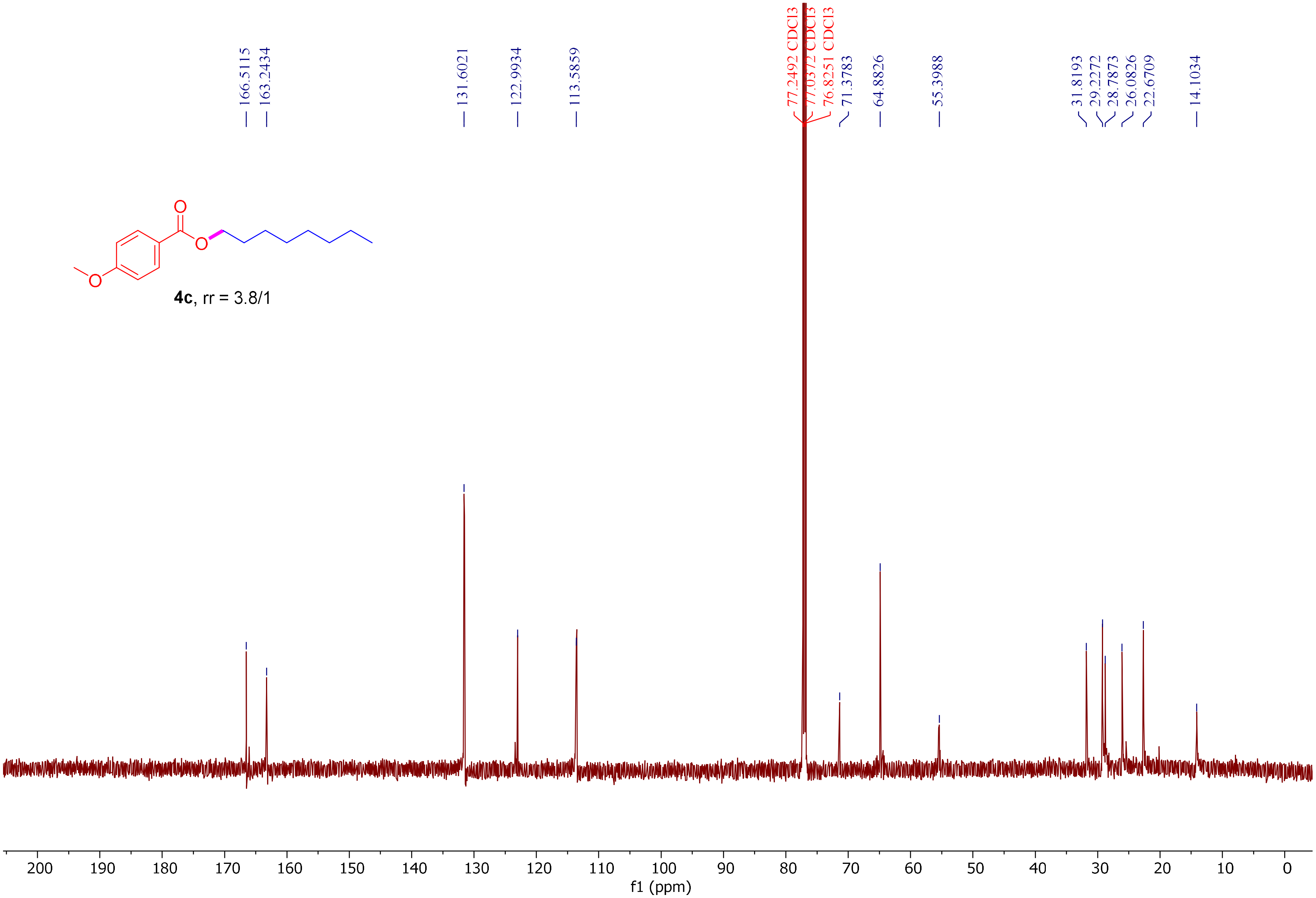


4b, rr = 4.5/1

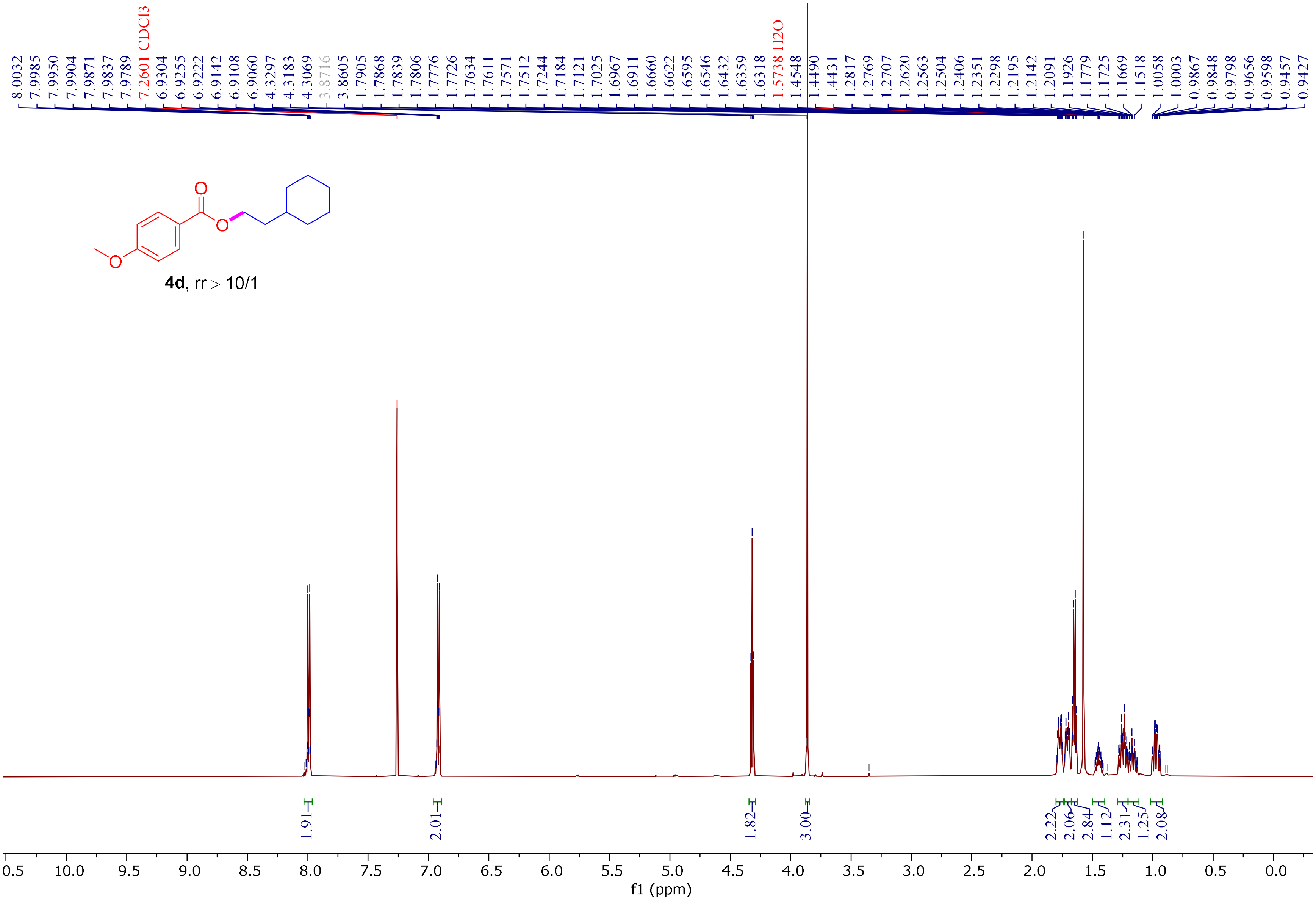
166.4636
163.2025
131.5172
122.9592
113.5266
77.2109
77.0000
76.7874
64.8376
55.4087
31.4739
28.7216
25.7209
22.5543
14.0207
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4c, rr = 3.8/1

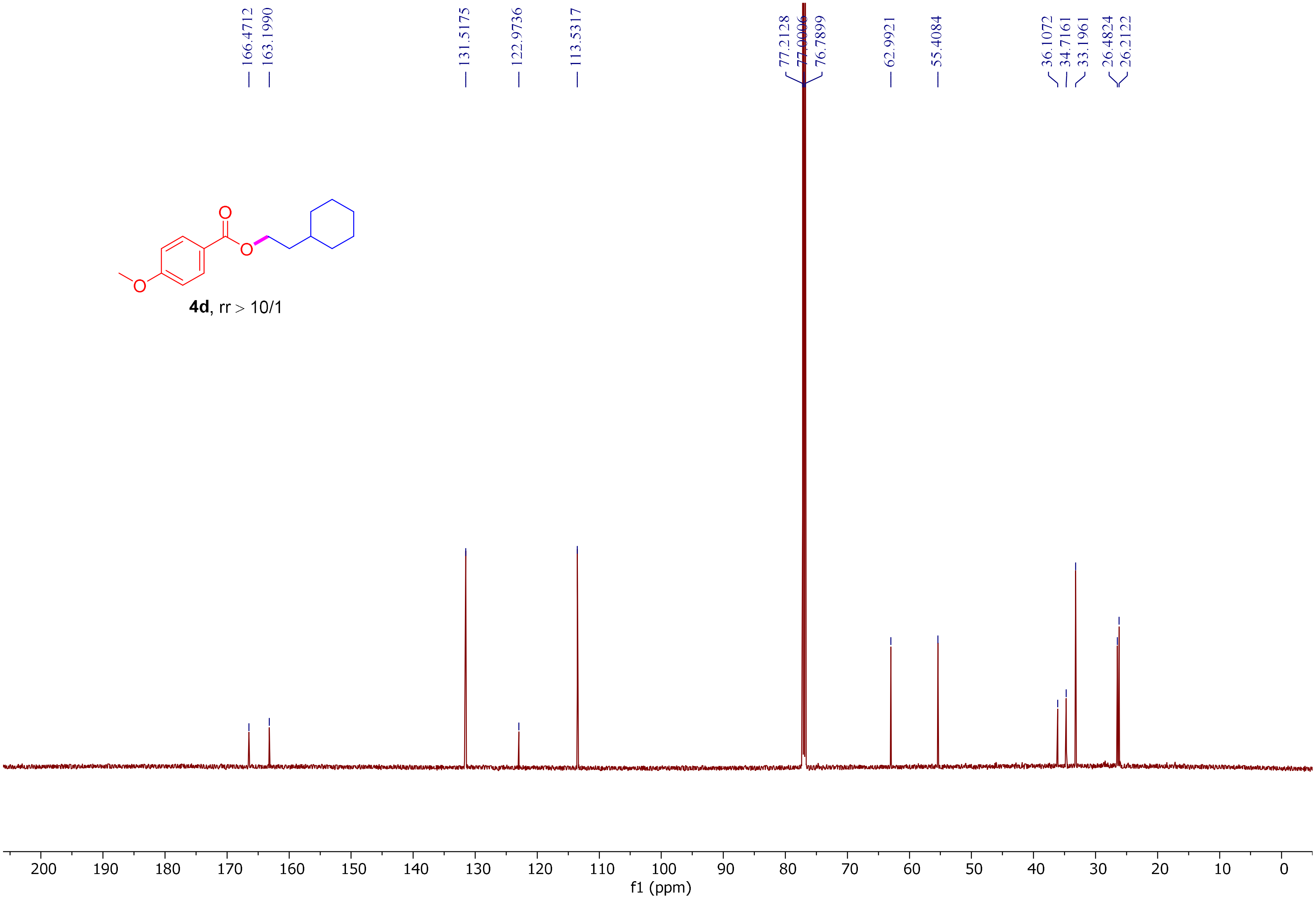
8.0076
8.0027
7.9993
7.9957
7.9915
7.9880
7.9841
7.2601 CDCl3
6.9392
6.9280
6.9231
6.9199
6.9167
6.9119
6.9084
6.9049
5.1310
5.1208
5.1095
4.2875
4.2765
4.2653
3.8692
3.8667
3.8595
3.4940
3.4852
2.1718 H2O
2.0448
1.7687
1.7574
1.7459
1.7432
1.7327
1.7212
1.5846
1.4515
1.4404
1.4363
1.4275
1.4176
1.4143
1.4115
1.4021
1.3688
1.3577
1.3532
1.3470
1.3432
1.3407
1.3311
1.3304
1.3261
1.3203
1.3154
1.3098
1.3033
1.2932
1.2905
1.2841
1.2809
1.2755
1.2711
1.2641
1.2577
1.2529
1.2491
1.2457
0.8918
0.8806
0.8687
0.8571
O
O
O
1.84
1.97
0.21
1.61
3.00
1.89
10.91
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4c, rr = 3.8/1

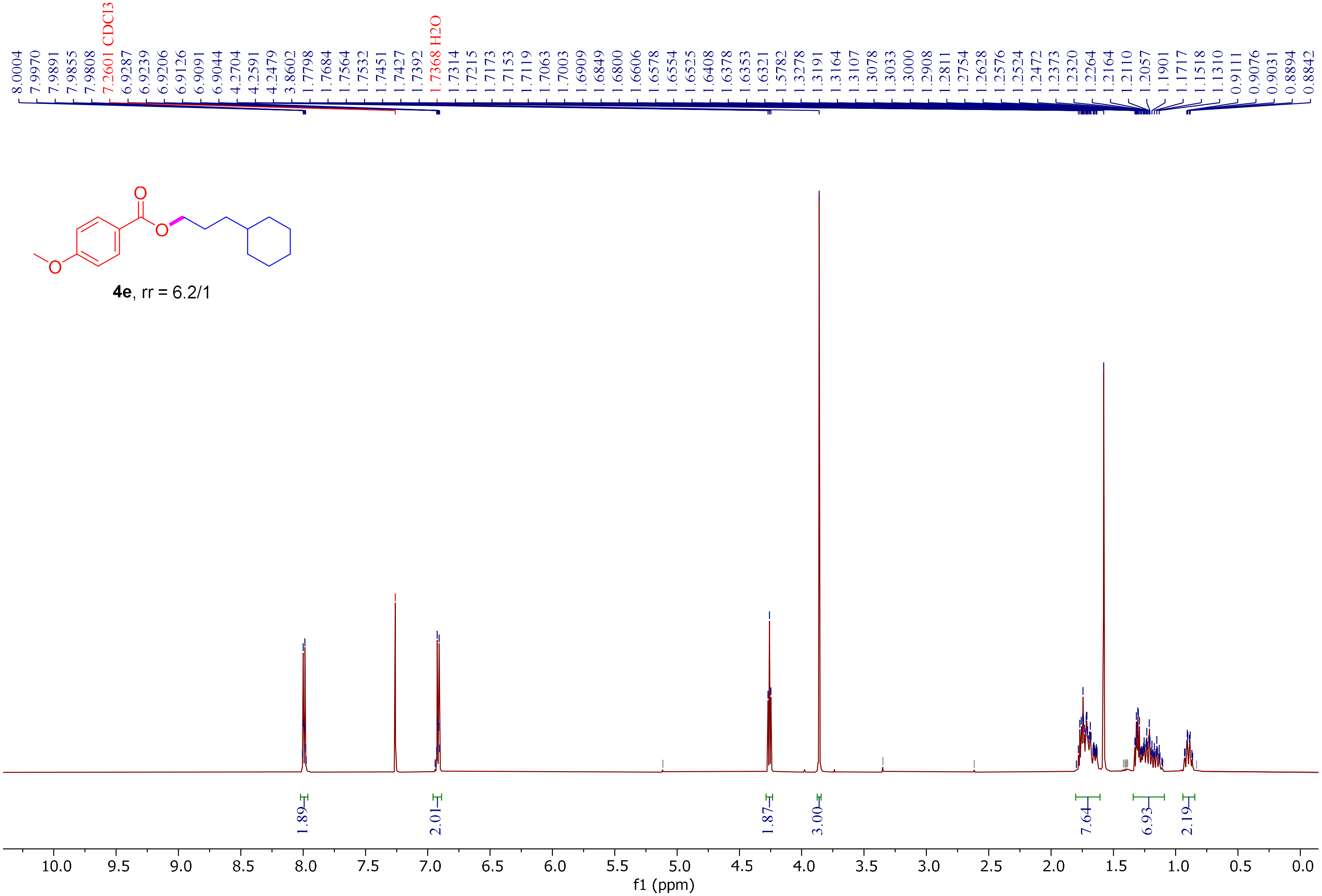
166.5115
163.2434
131.6021
122.9934
113.5859
77.2492 CDCl3
77.0372 CDCl3
76.8251 CDCl3
71.3783
64.8826
55.3988
31.8193
29.2272
28.7873
26.0826
22.6709
14.1034
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0032
7.9985
7.9950
7.9904
7.9871
7.9837
7.9789
7.2601 CDCl3
6.9304
6.9255
6.9222
6.9142
6.9108
6.9060
4.3297
4.3183
4.3069
3.8716
3.8605
1.7905
1.7868
1.7839
1.7806
1.7776
1.7726
1.7634
1.7611
1.7571
1.7512
1.7244
1.7184
1.7121
1.7025
1.6967
1.6911
1.6660
1.6622
1.6595
1.6546
1.6432
1.6359
1.6318
1.5738 H2O
1.4548
1.4490
1.4431
1.2817
1.2769
1.2707
1.2620
1.2563
1.2504
1.2406
1.2351
1.2298
1.2195
1.2142
1.2091
1.1926
1.1779
1.1725
1.1669
1.1518
1.0058
1.0003
0.9867
0.9848
0.9798
0.9656
0.9598
0.9457
0.9427
O
O
O
1.91
2.01
1.82
3.00
2.22
2.06
2.84
1.12
2.31
1.25
2.08
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

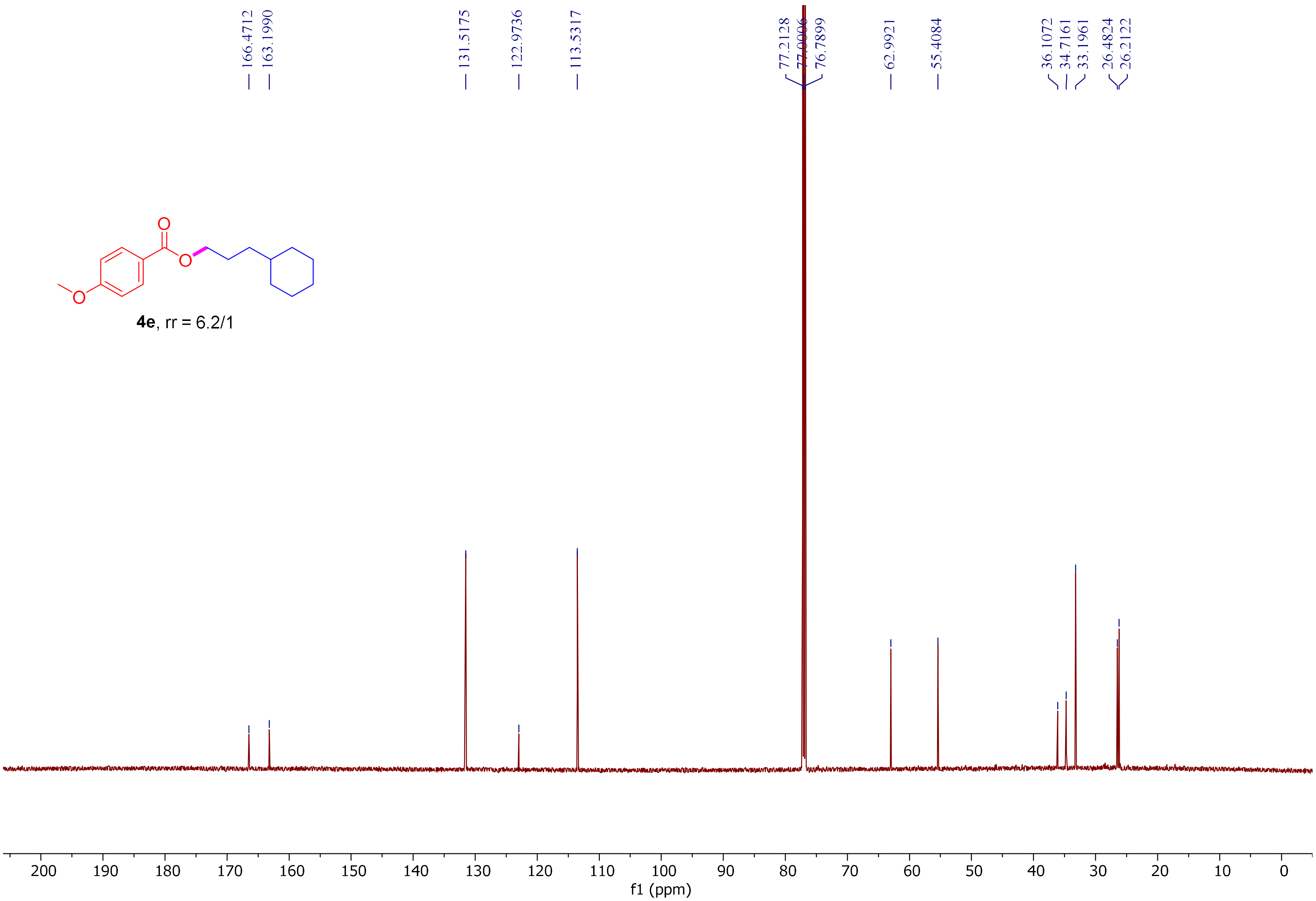
4d, rr > 10/1


4d, rr > 10/1

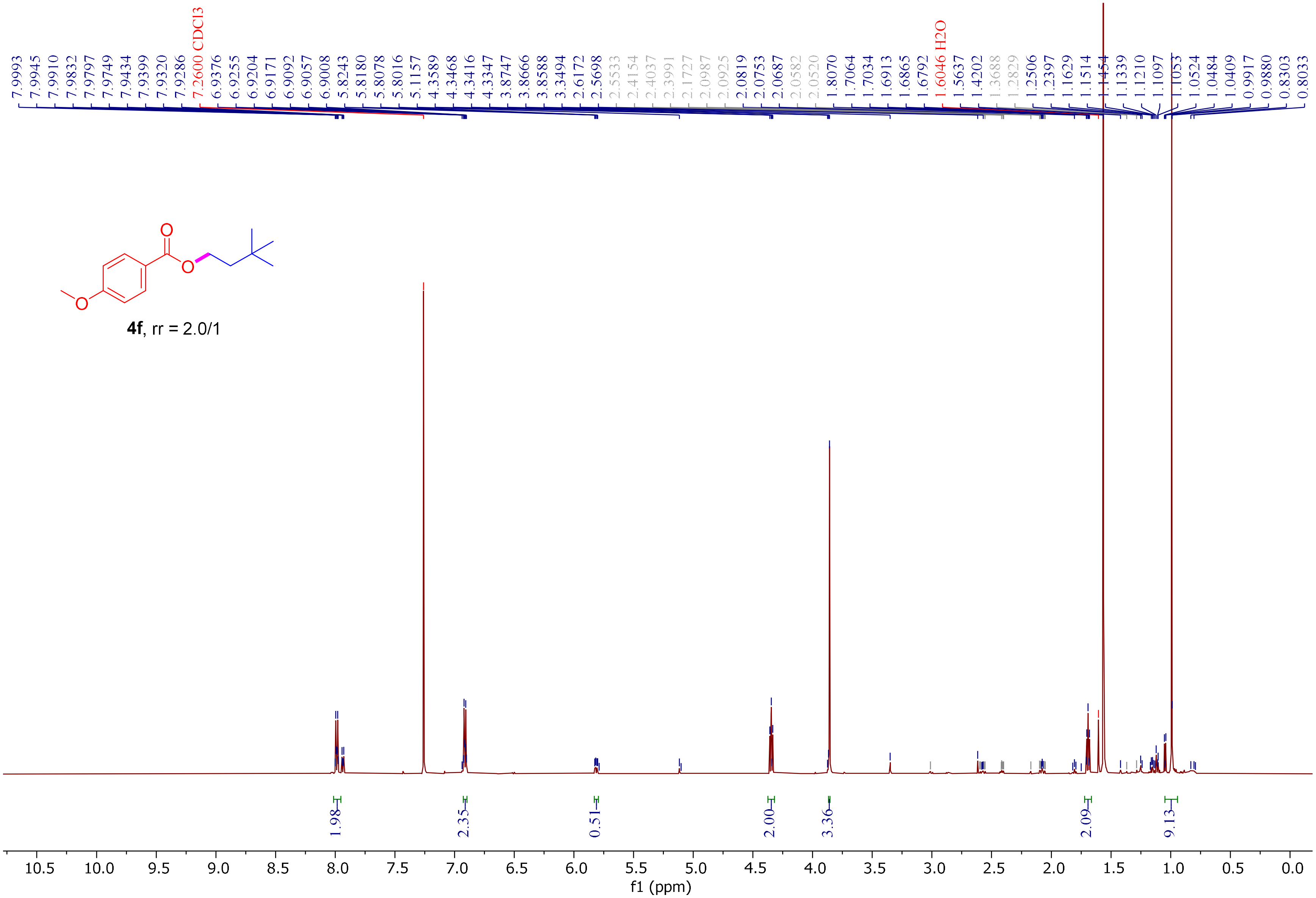
166.4712
163.1990
131.5175
122.9736
113.5317
77.2128
77.0006
76.7899
62.9921
55.4084
36.1072
34.7161
33.1961
26.4824
26.2122
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4e, rr = 6.2/1

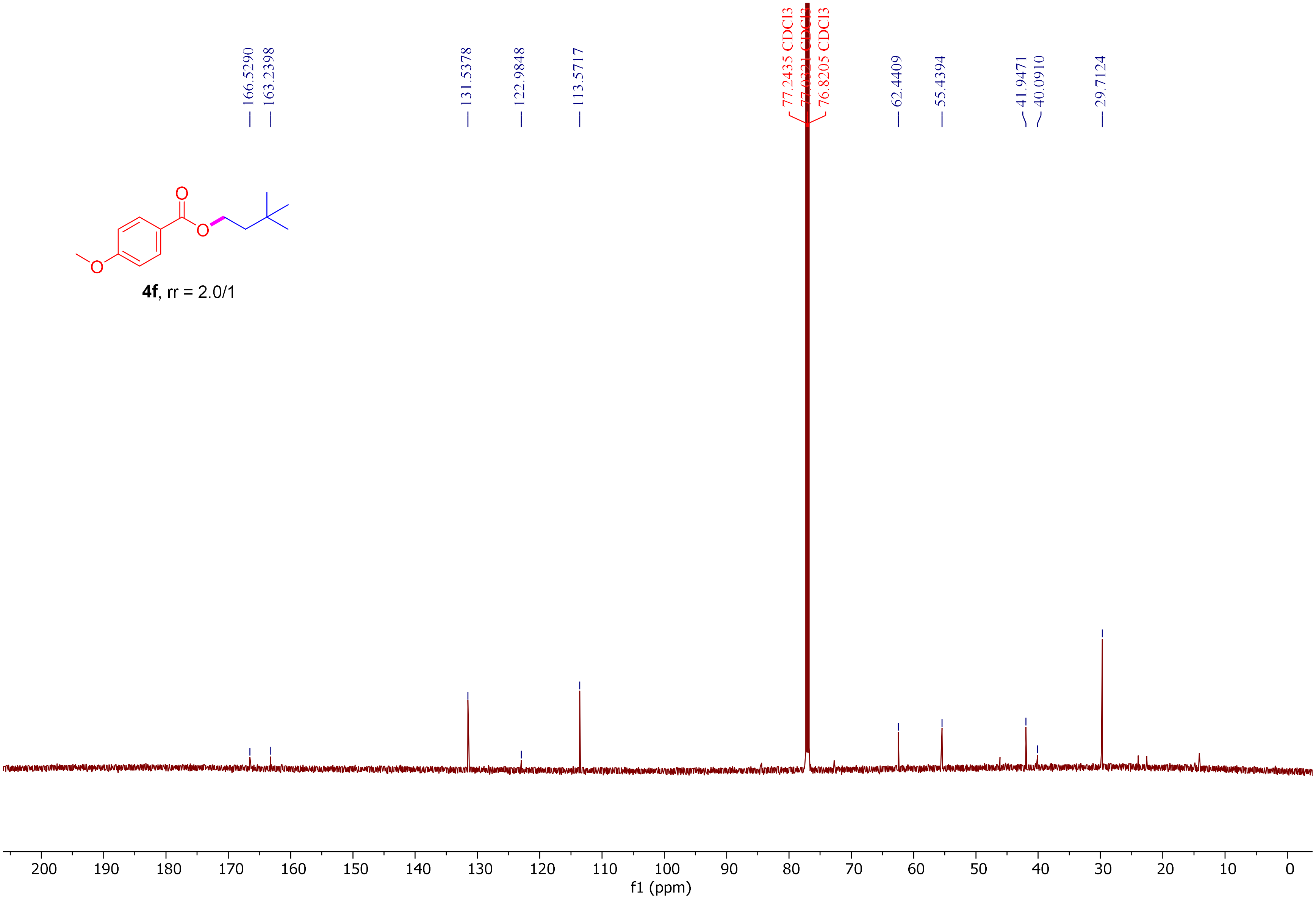
8.0004
7.9970
7.9891
7.9855
7.9808
7.2601 CDCl3
6.9287
6.9239
6.9206
6.9126
6.9091
6.9044
4.2704
4.2591
4.2479
3.8602
1.7798
1.7684
1.7564
1.7532
1.7451
1.7427
1.7392
1.7368 H2O
1.7314
1.7215
1.7173
1.7153
1.7119
1.7063
1.7003
1.6909
1.6849
1.6800
1.6606
1.6578
1.6554
1.6525
1.6408
1.6378
1.6353
1.6321
1.5782
1.3278
1.3191
1.3164
1.3107
1.3078
1.3033
1.3000
1.2908
1.2811
1.2754
1.2628
1.2576
1.2524
1.2472
1.2373
1.2320
1.2264
1.2164
1.2110
1.2057
1.1901
1.1717
1.1518
1.1310
0.9111
0.9076
0.9031
0.8894
0.8842
O
O
O
1.89
2.01
1.87
3.00
7.64
6.93
2.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.4712
163.1990
131.5175
122.9736
113.5317
77.2128
77.0006
76.7899
62.9921
55.4084
36.1072
34.7161
33.1961
26.4824
26.2122
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

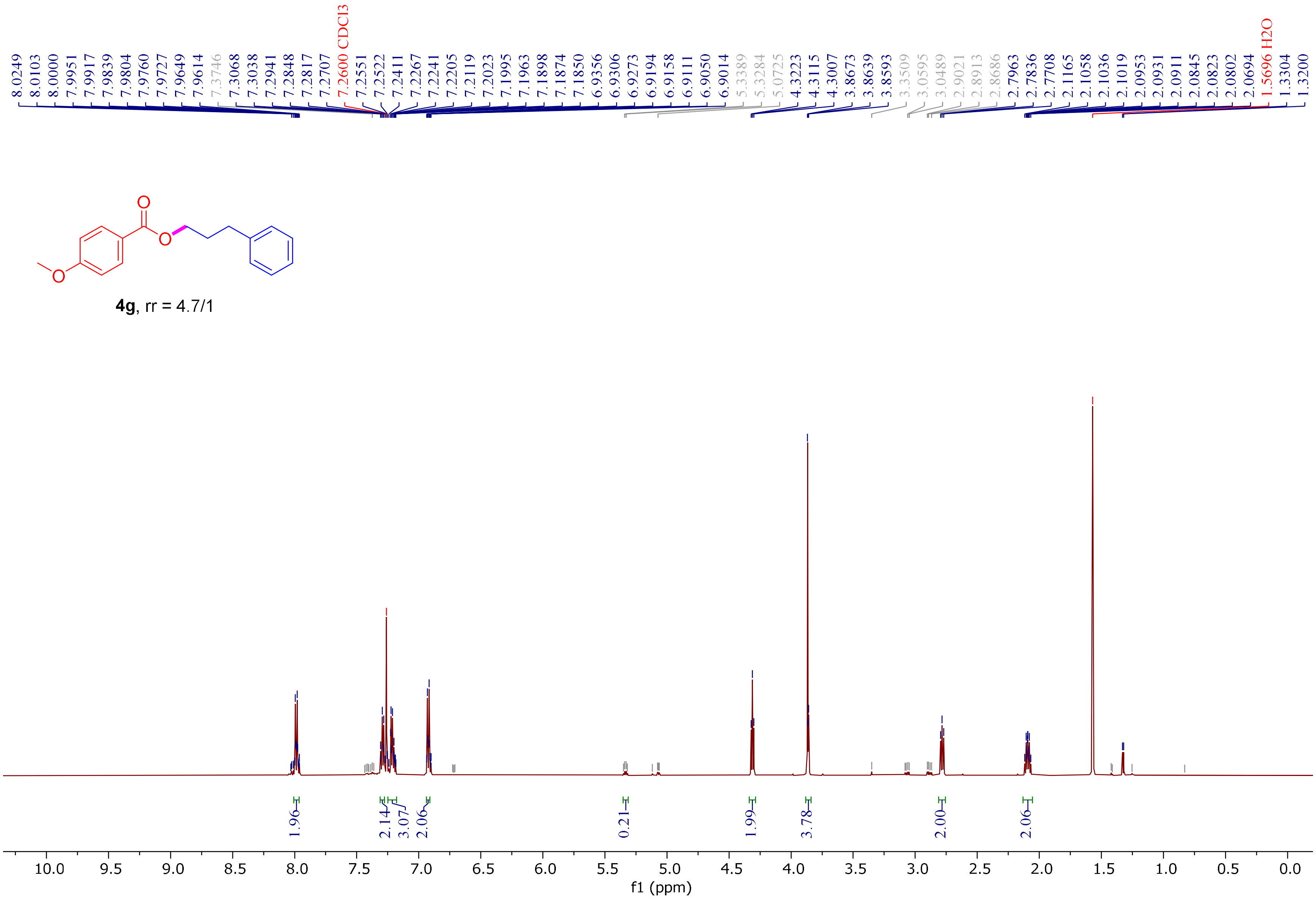
4e, rr = 6.2/1


4f, rr = 2.0/1

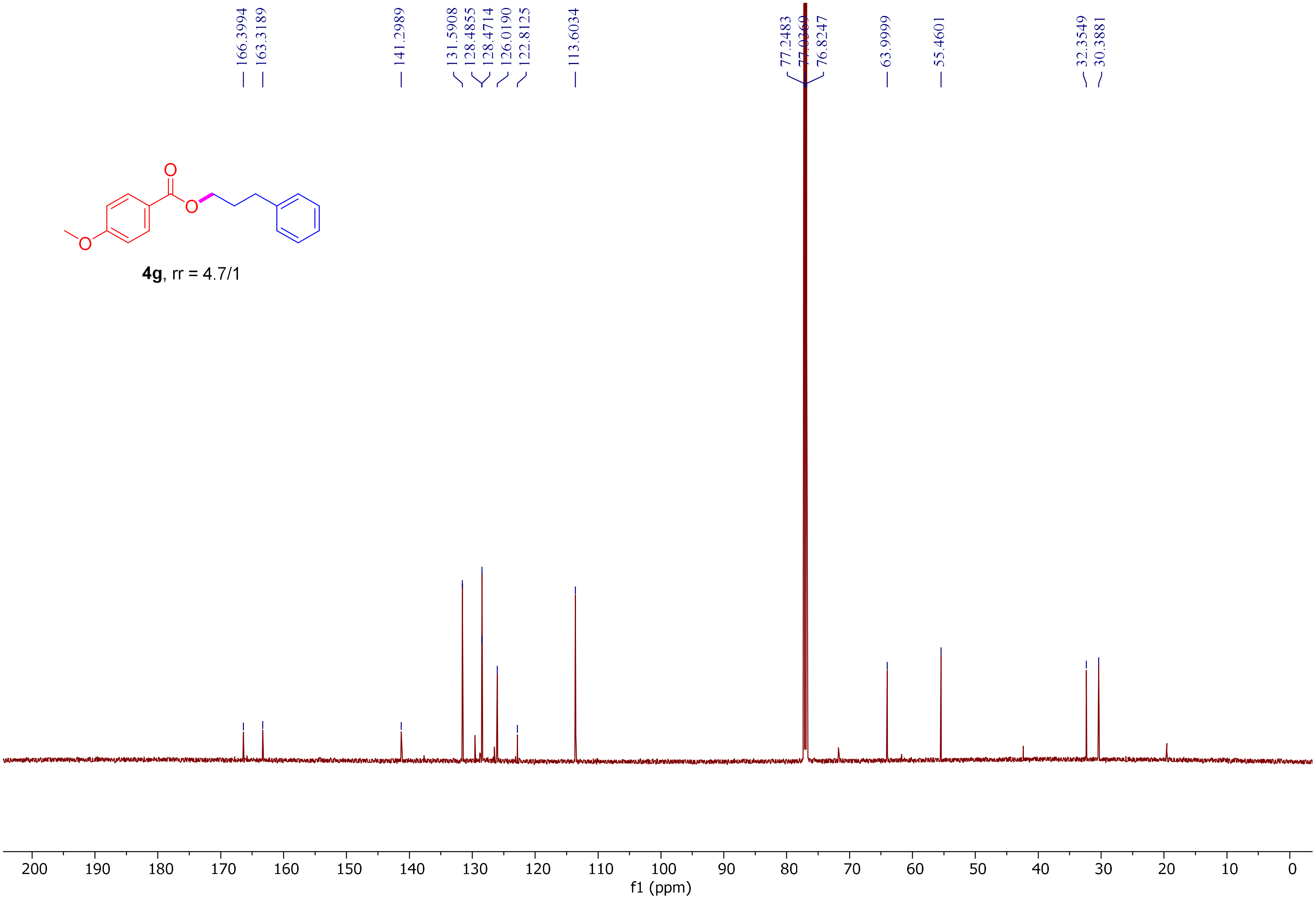
7.9993
7.9945
7.9910
7.9832
7.9797
7.9749
7.9434
7.9399
7.9320
7.9286
7.2600 CDCl3
6.9376
6.9255
6.9204
6.9171
6.9092
6.9057
6.9008
5.8243
5.8180
5.8078
5.8016
5.1157
4.3589
4.3468
4.3416
4.3347
3.8747
3.8666
3.8588
3.3494
2.6172
2.5698
2.5533
2.4154
2.4037
2.3991
2.1727
2.0987
2.0925
2.0819
2.0753
2.0687
2.0582
2.0520
1.8070
1.7064
1.7034
1.6913
1.6865
1.6792
1.6046 H2O
1.5637
1.4202
1.3688
1.2829
1.2506
1.2397
1.1629
1.1514
1.1454
1.1339
1.1210
1.1097
1.1053
1.0524
1.0484
1.0409
0.9917
0.9880
0.8303
0.8033
O
O
O
1.98
2.35
0.51
2.00
3.36
2.09
9.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.5290
163.2398
131.5378
122.9848
113.5717
77.2435 CDCl3
77.0321 CDCl3
76.8205 CDCl3
62.4409
55.4394
41.9471
40.0910
29.7124
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

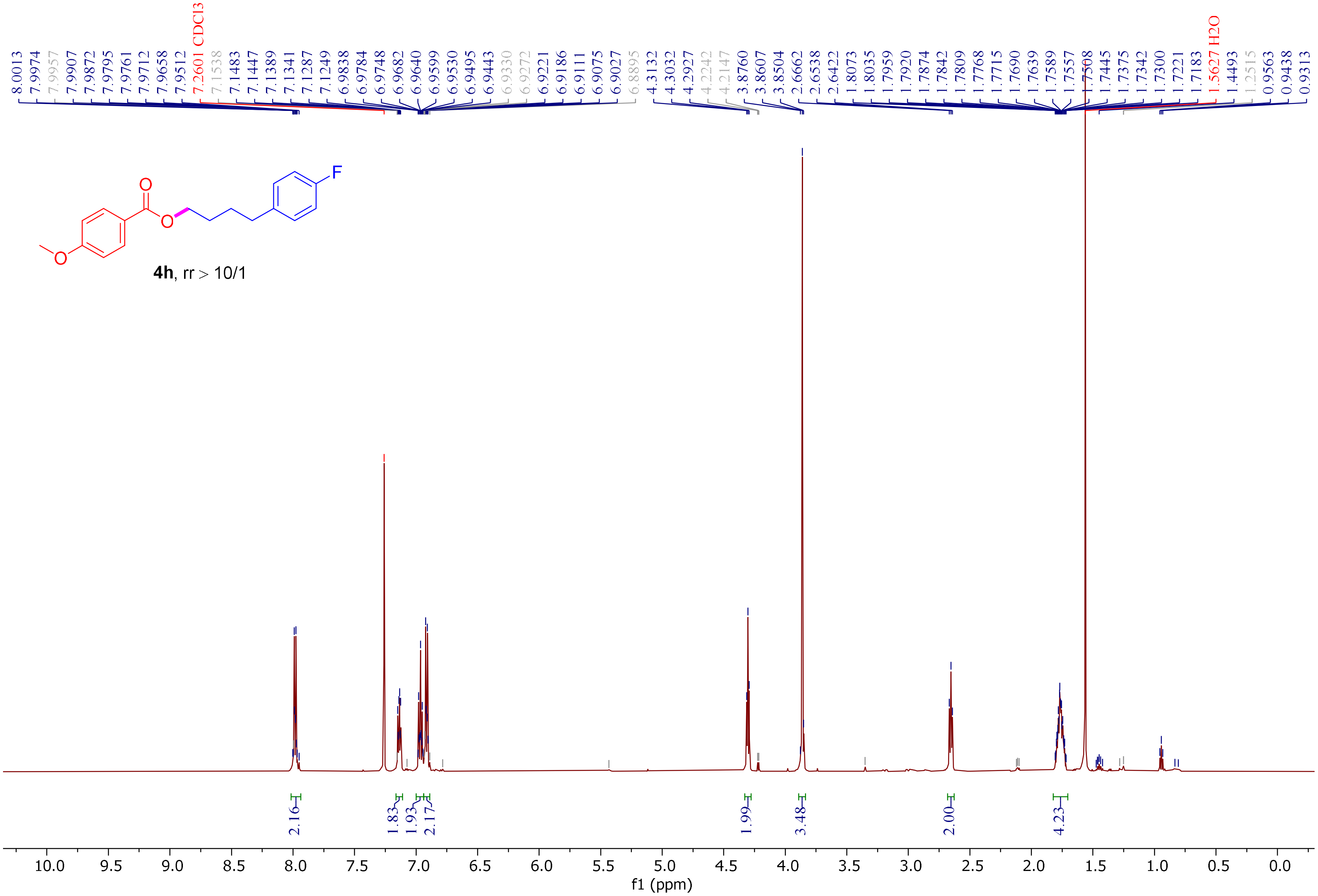
4f, rr = 2.0/1


8.0249
8.0103
8.0000
7.9951
7.9917
7.9839
7.9804
7.9760
7.9727
7.9649
7.9614
7.3746
7.3068
7.3038
7.2941
7.2848
7.2817
7.2707
7.2600 CDCl3
7.2551
7.2522
7.2411
7.2267
7.2241
7.2205
7.2119
7.2023
7.1995
7.1963
7.1898
7.1874
7.1850
6.9356
6.9306
6.9273
6.9194
6.9158
6.9111
6.9050
6.9014
5.3389
5.3284
5.0725
4.3223
4.3115
4.3007
3.8673
3.8639
3.8593
3.3509
3.0595
3.0489
2.9021
2.8913
2.8686
2.7963
2.7836
2.7708
2.1165
2.1058
2.1036
2.1019
2.0953
2.0931
2.0911
2.0845
2.0823
2.0802
2.0694
1.5696 H2O
1.3304
1.3200
1.96
2.14
3.07
2.06
0.21
1.99
3.78
2.00
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

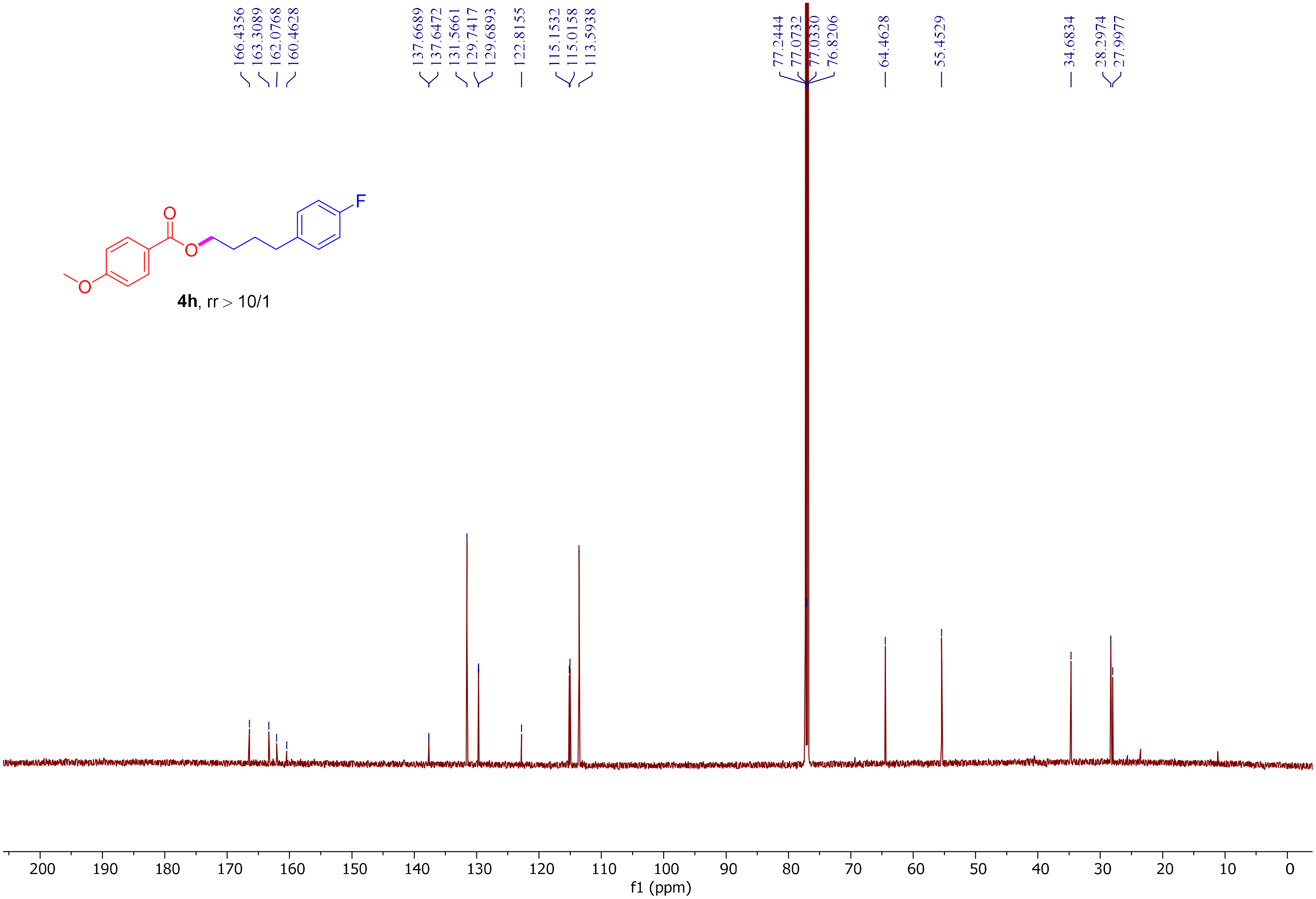
4g, rr = 4.7/1


4g, rr = 4.7/1

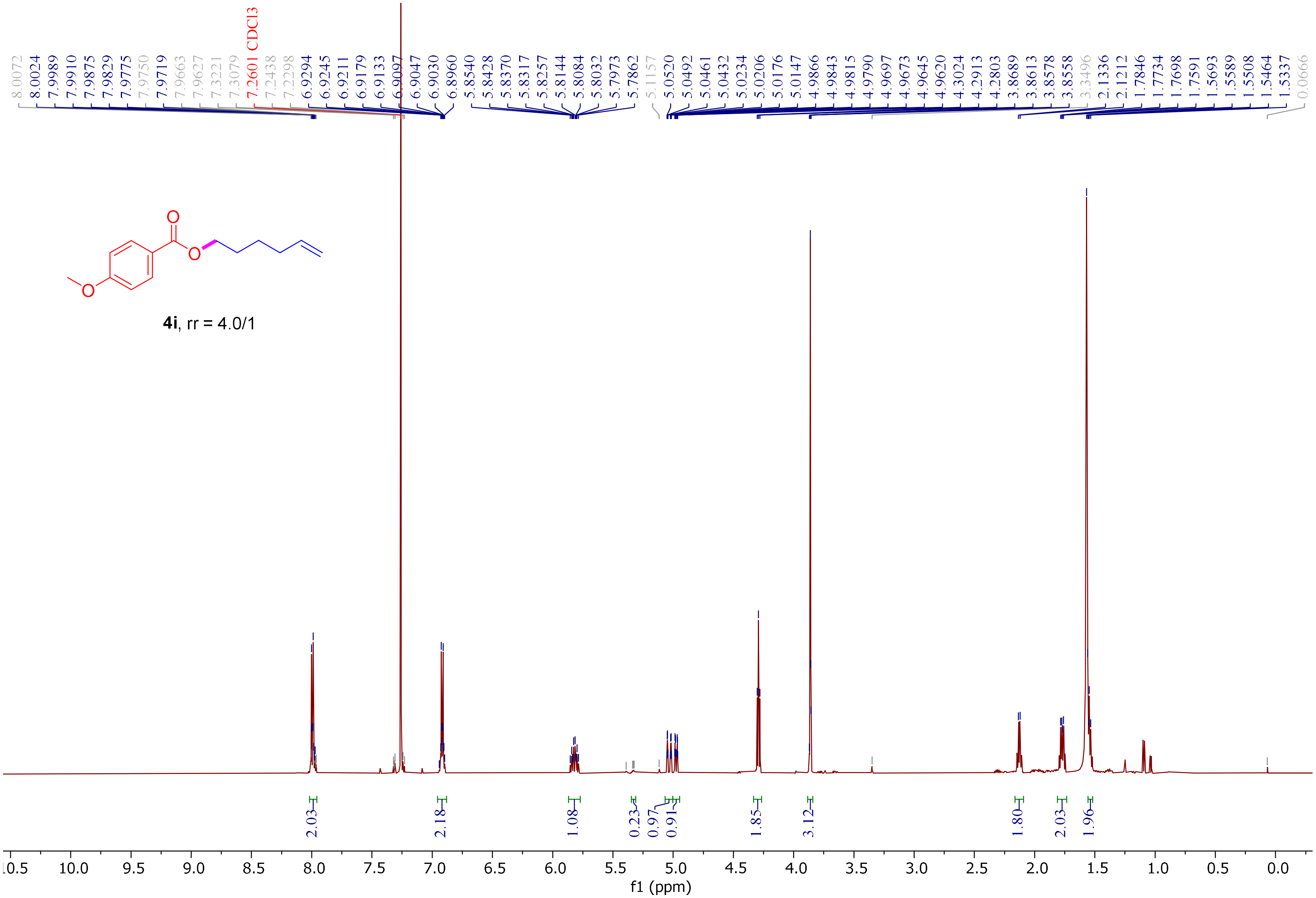
166.3994
163.3189
141.2989
131.5908
128.4855
128.4714
126.0190
122.8125
113.6034
77.2483
77.0369
76.8247
63.9999
55.4601
32.3549
30.3881
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0013
7.9974
7.9957
7.9907
7.9872
7.9795
7.9761
7.9712
7.9658
7.9512
7.2601 CDCl3
7.1538
7.1483
7.1447
7.1389
7.1341
7.1287
7.1249
6.9838
6.9784
6.9748
6.9682
6.9640
6.9599
6.9530
6.9495
6.9443
6.9330
6.9272
6.9221
6.9186
6.9111
6.9075
6.9027
6.8895
4.3132
4.3032
4.2927
4.2242
4.2147
3.8760
3.8607
3.8504
2.6662
2.6538
2.6422
1.8073
1.8035
1.7959
1.7920
1.7874
1.7842
1.7809
1.7768
1.7715
1.7690
1.7639
1.7589
1.7557
1.7508
1.7445
1.7375
1.7342
1.7300
1.7221
1.7183
1.5627 H2O
1.4493
1.2515
0.9563
0.9438
0.9313
O
O
O
F
2.16
1.83
1.93
2.17
1.99
3.48
2.00
4.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

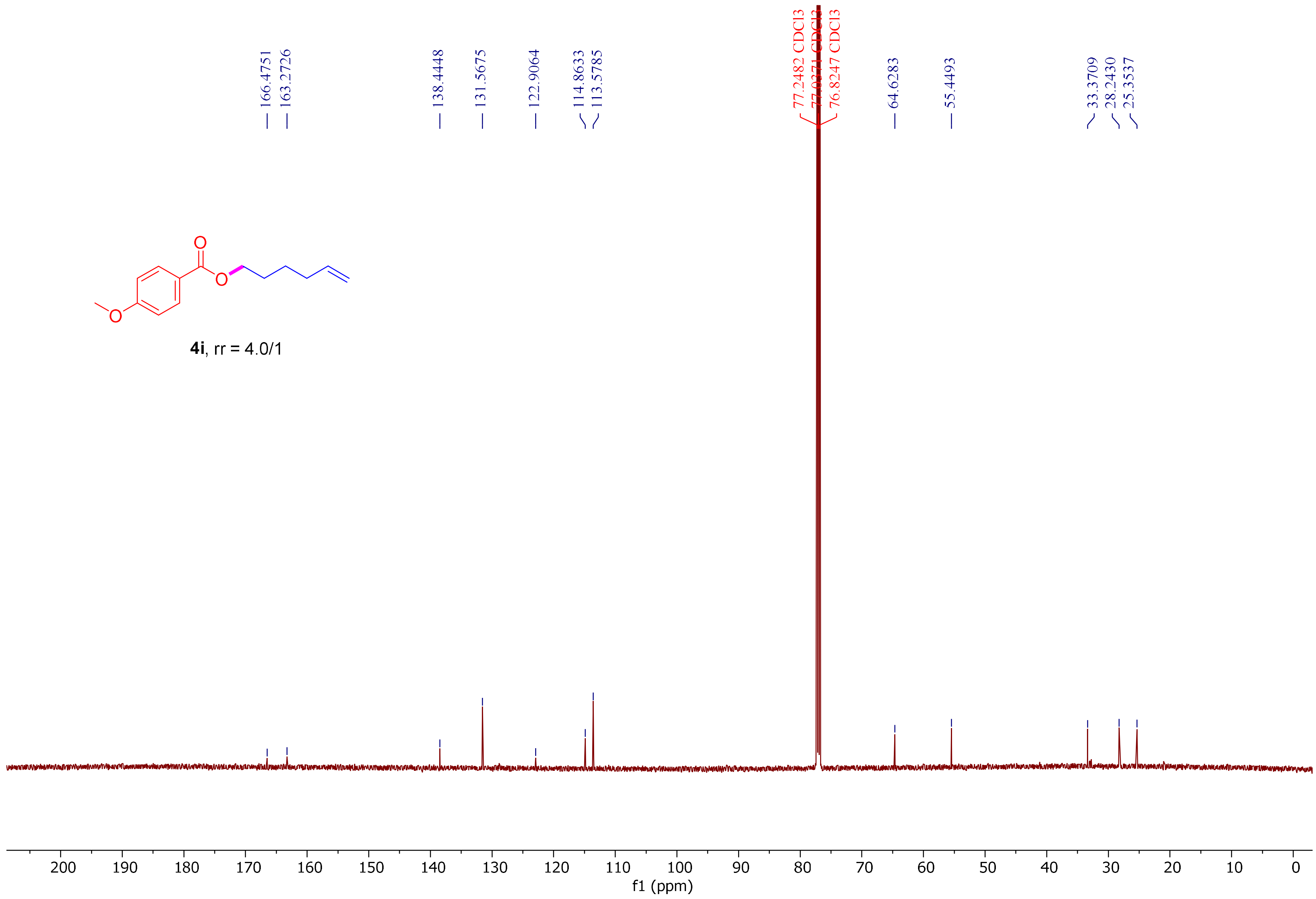
4h, rr > 10/1

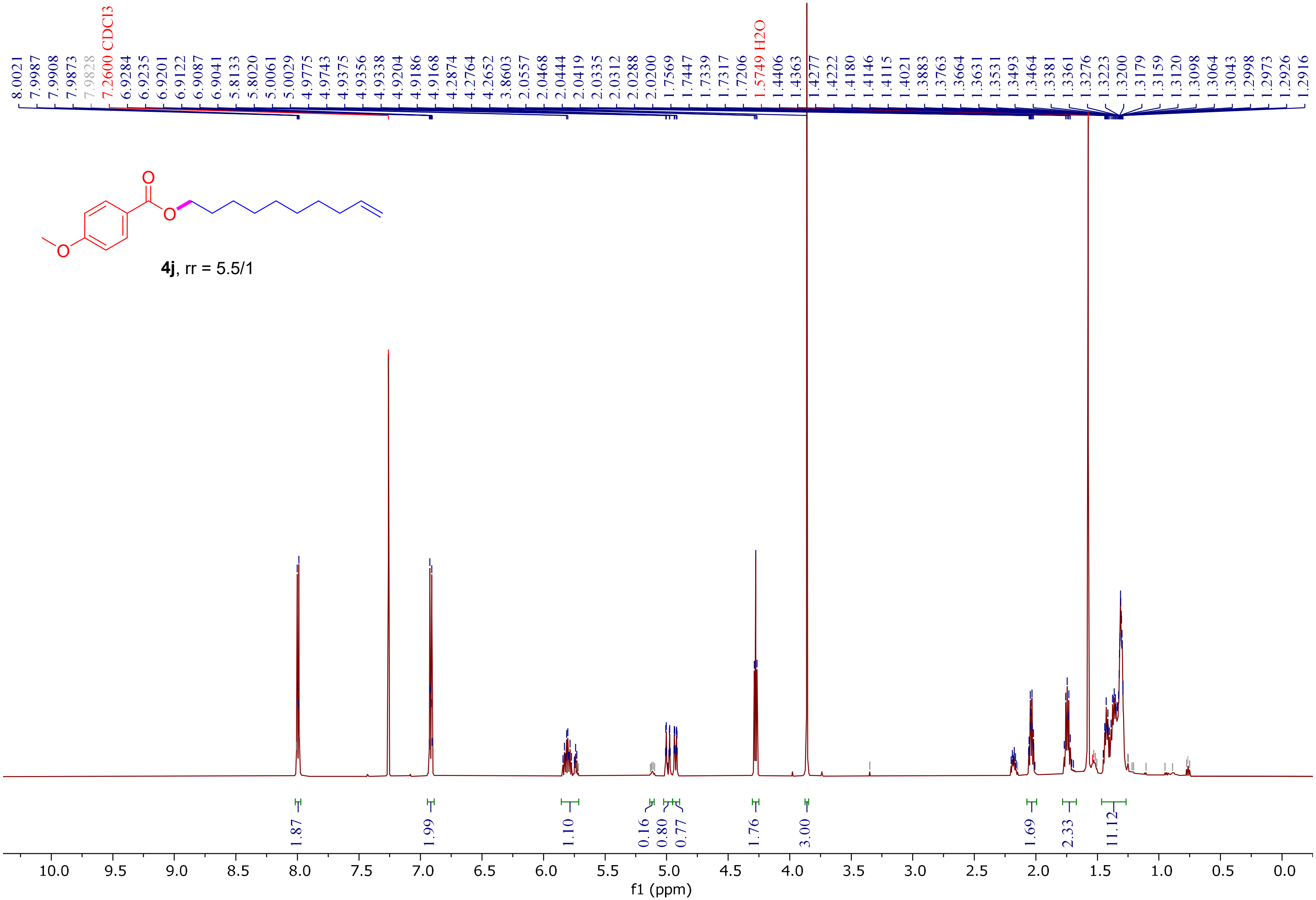

4h, rr > 10/1

166.4356
163.3089
162.0768
160.4628
137.6689
137.6472
131.5661
129.7417
129.6893
122.8155
115.1532
115.0158
113.5938
77.2444
77.0732
77.0330
76.8206
64.4628
55.4529
34.6834
28.2974
27.9977
O
O
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

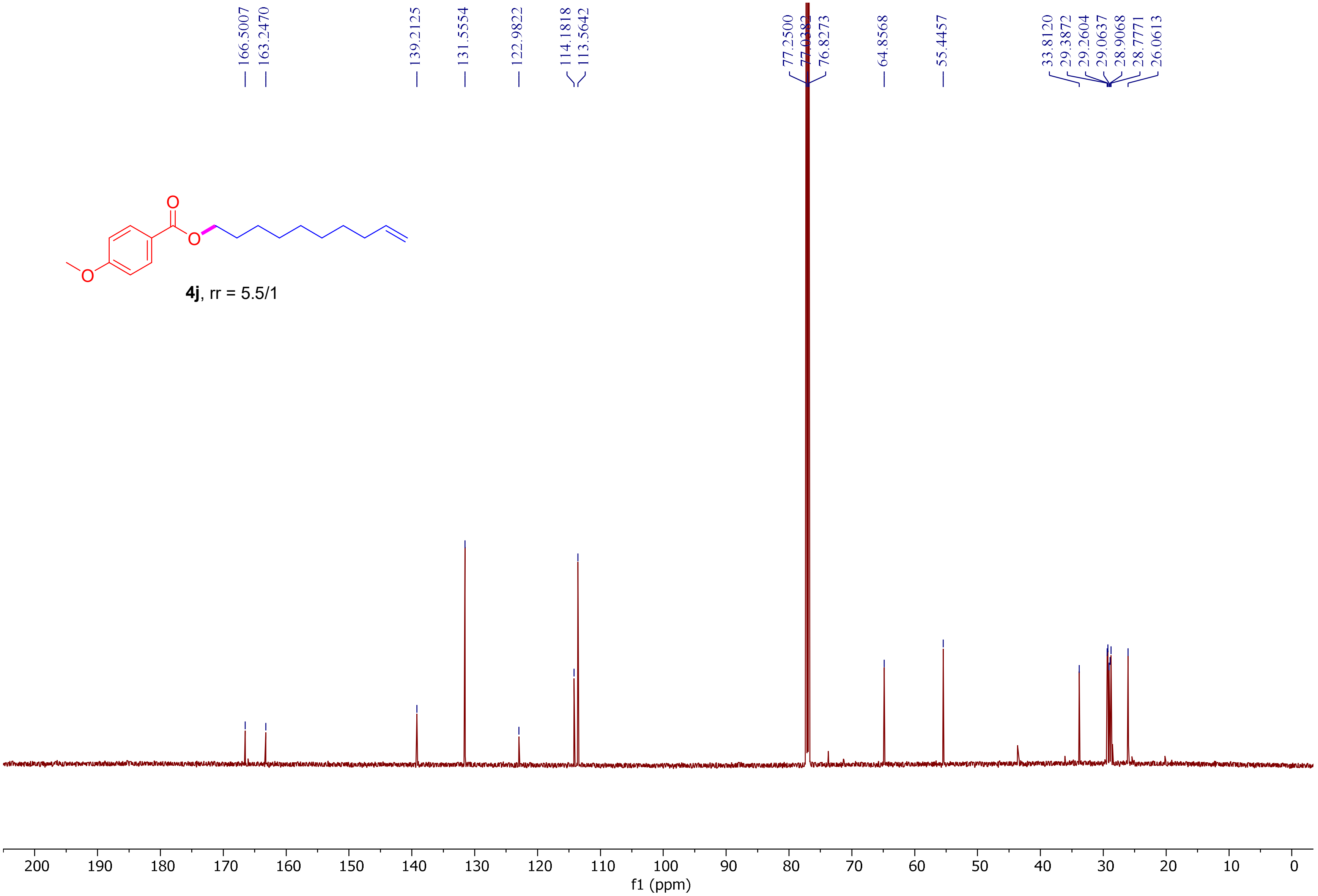

4i, rr = 4.0/1

8.0072
8.0024
7.9989
7.9910
7.9875
7.9829
7.9775
7.9750
7.9719
7.9663
7.9627
7.3221
7.3079
7.2601 CDCl3
7.2438
7.2298
6.9294
6.9245
6.9211
6.9179
6.9133
6.9097
6.9047
6.9030
6.8960
5.8540
5.8428
5.8370
5.8317
5.8257
5.8144
5.8084
5.8032
5.7973
5.7862
5.1157
5.0520
5.0492
5.0461
5.0432
5.0234
5.0206
5.0176
5.0147
4.9866
4.9843
4.9815
4.9790
4.9697
4.9673
4.9645
4.9620
4.3024
4.2913
4.2803
3.8689
3.8613
3.8578
3.8558
3.3496
2.1336
2.1212
1.7846
1.7734
1.7698
1.7591
1.5693
1.5589
1.5508
1.5464
1.5337
0.0666
2.03
2.18
1.08
0.23
0.97
0.91
1.85
3.12
1.80
2.03
1.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

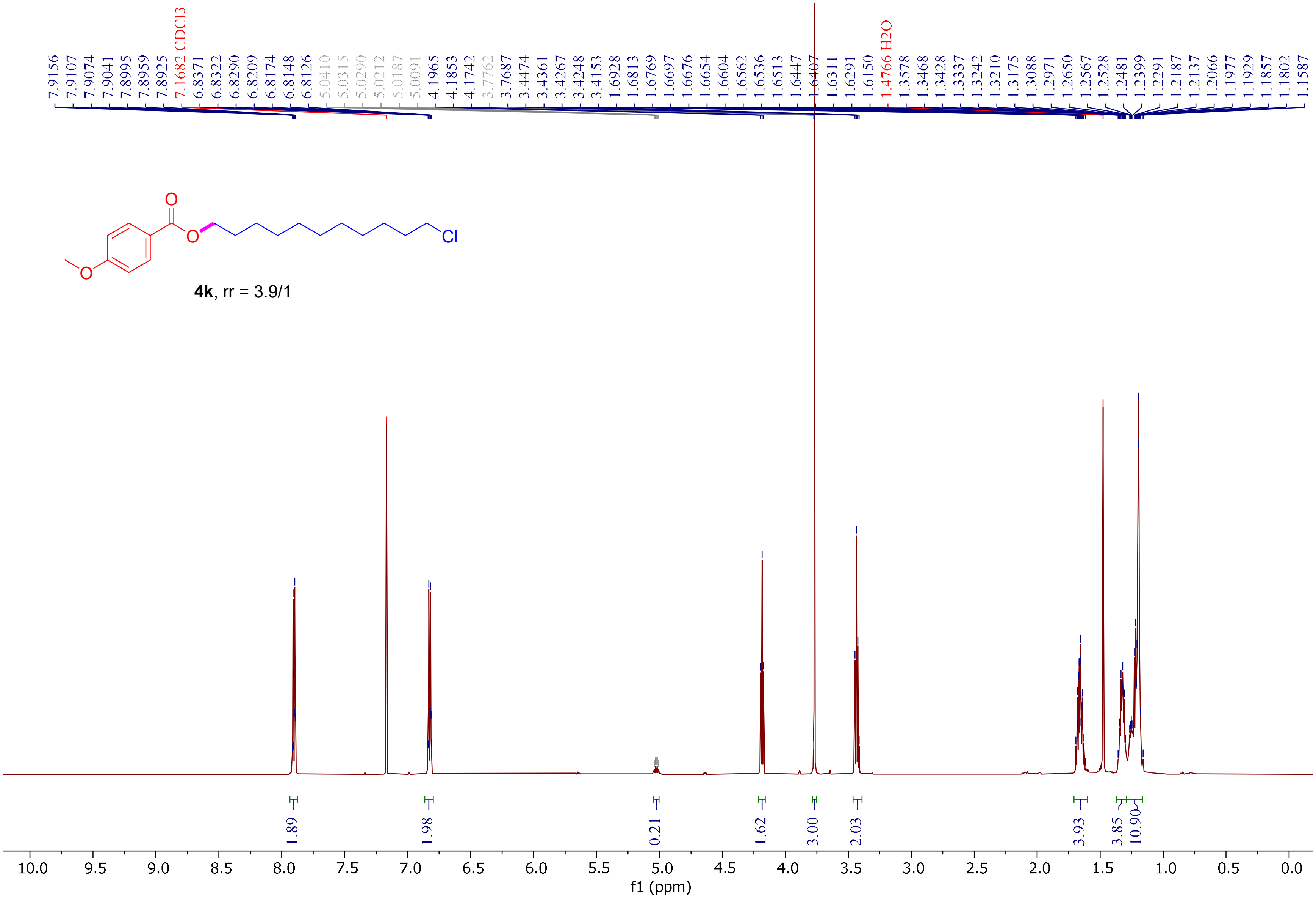

166.4751
163.2726
138.4448
131.5675
122.9064
114.8633
113.5785
77.2482 CDCl3
77.0371 CDCl3
76.8247 CDCl3
64.6283
55.4493
33.3709
28.2430
25.3537
4i, rr = 4.0/1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

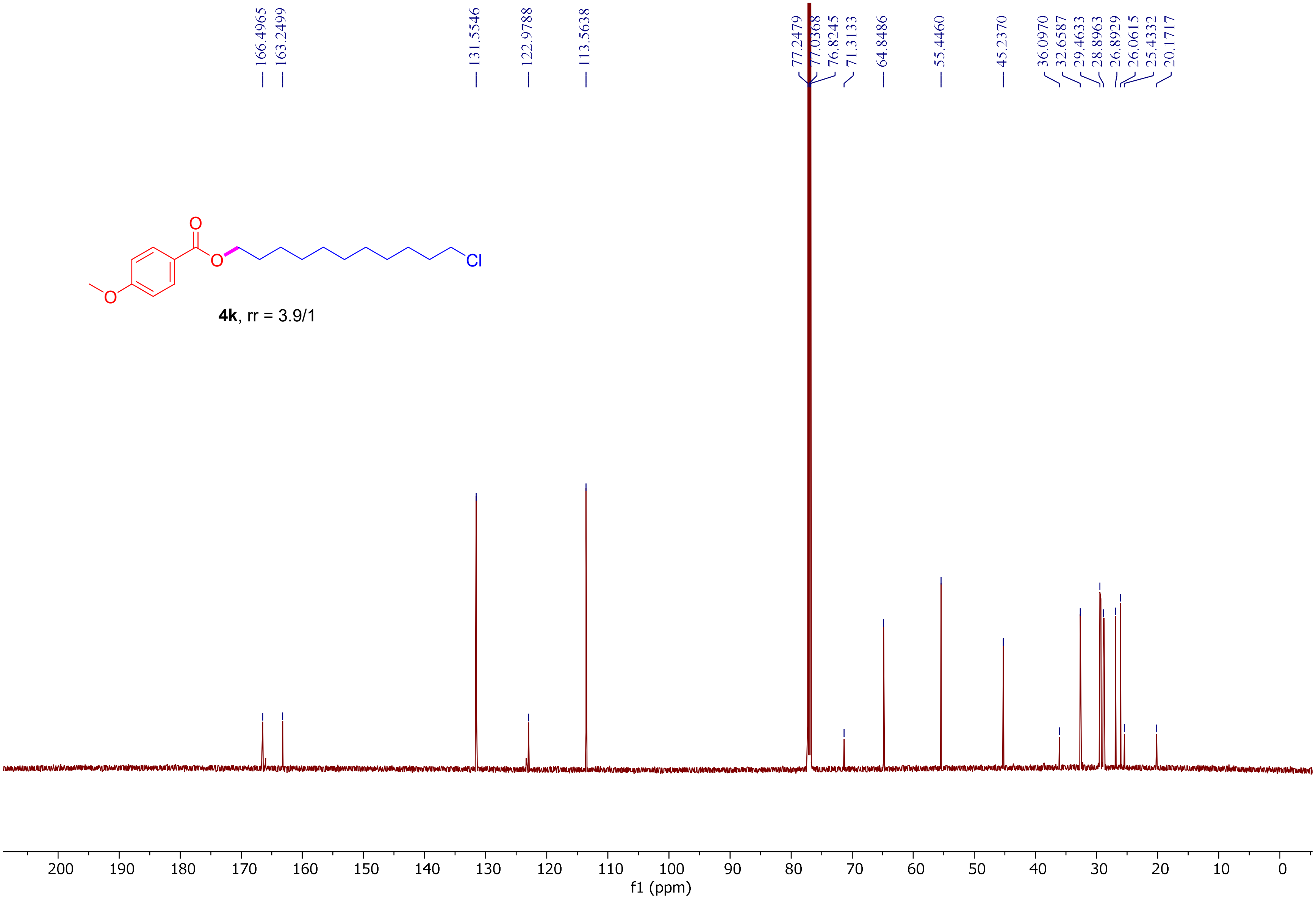

8.0021
7.9987
7.9908
7.9873
7.9828
7.2600 CDCl3
6.9284
6.9235
6.9201
6.9122
6.9087
6.9041
5.8133
5.8020
5.0061
5.0029
4.9775
4.9743
4.9375
4.9356
4.9338
4.9204
4.9186
4.9168
4.2874
4.2764
4.2652
3.8603
2.0557
2.0468
2.0444
2.0419
2.0335
2.0312
2.0288
2.0200
1.7569
1.7447
1.7339
1.7317
1.7206
1.5749 H2O
1.4406
1.4363
1.4277
1.4222
1.4180
1.4146
1.4115
1.4021
1.3883
1.3763
1.3664
1.3631
1.3531
1.3493
1.3464
1.3381
1.3361
1.3276
1.3223
1.3200
1.3179
1.3159
1.3120
1.3098
1.3064
1.3043
1.2998
1.2973
1.2926
1.2916
O
O
O
1.87
1.99
1.10
0.16
0.80
0.77
1.76
3.00
1.69
2.33
11.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4j, rr = 5.5/1

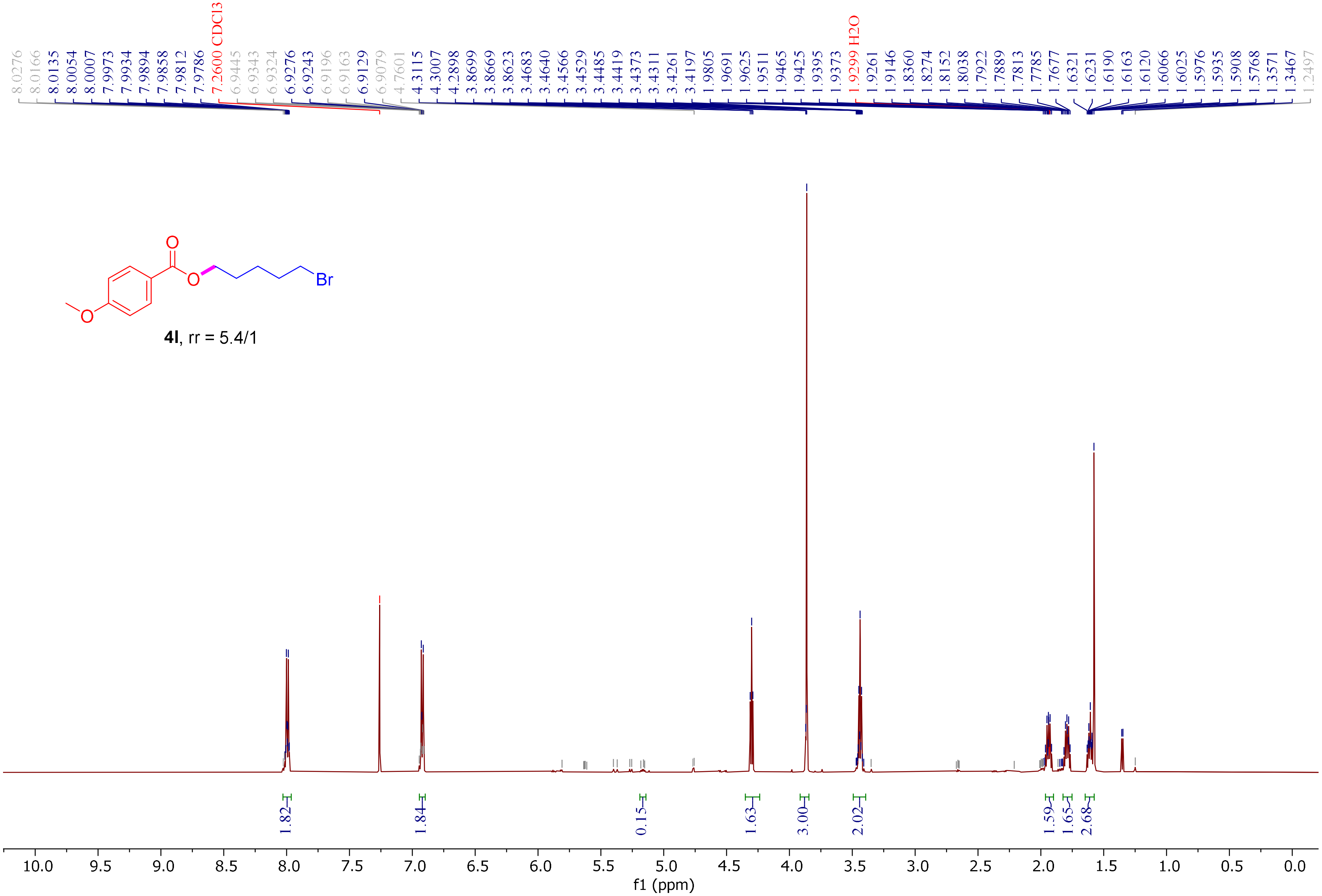

4j, rr = 5.5/1

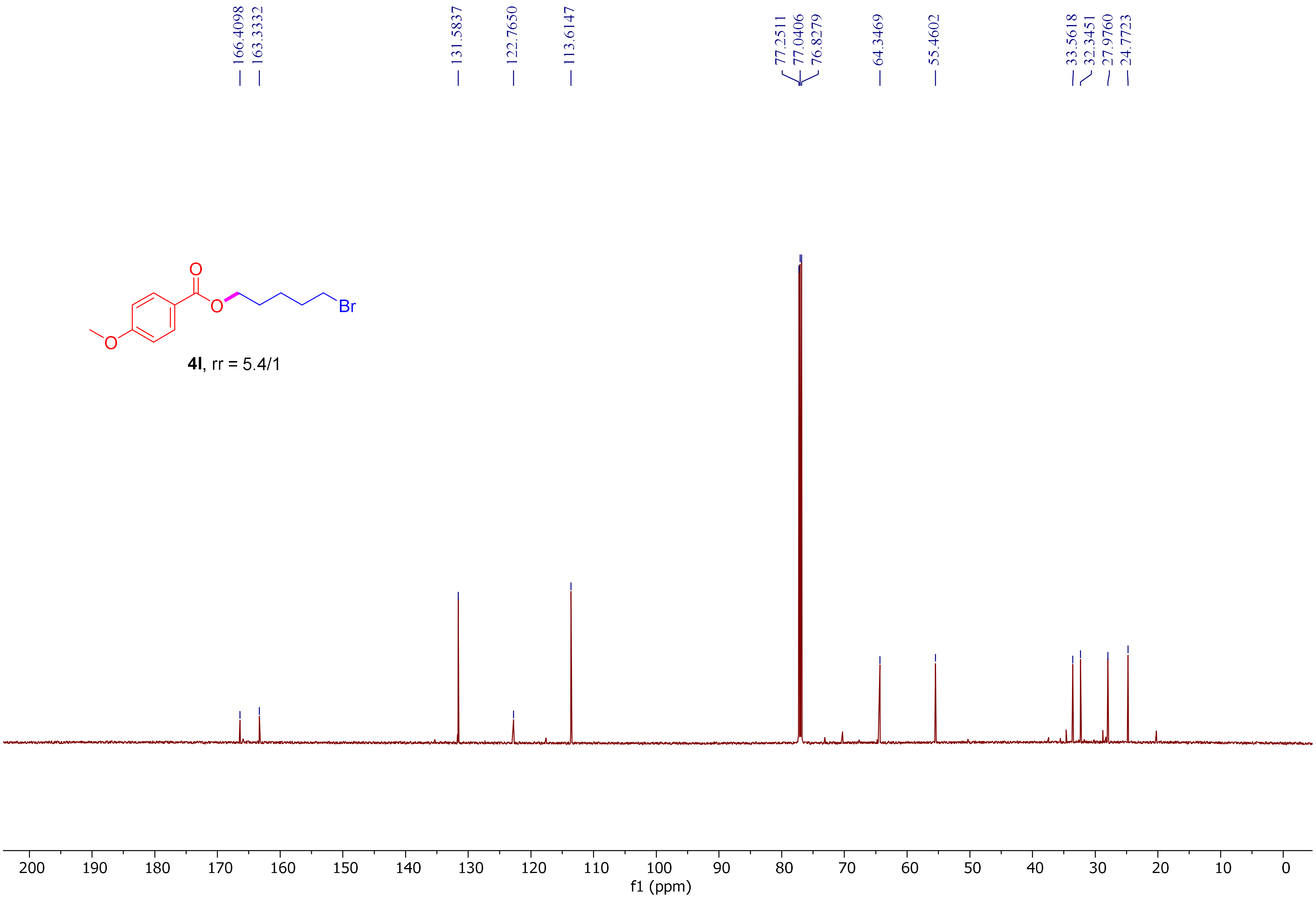
166.5007
163.2470
139.2125
131.5554
122.9822
114.1818
113.5642
77.2500
77.0382
76.8273
64.8568
55.4457
33.8120
29.3872
29.2604
29.0637
28.9068
28.7771
26.0613
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9156
7.9107
7.9074
7.9041
7.8995
7.8959
7.8925
7.1682 CDCl3
6.8371
6.8322
6.8290
6.8209
6.8174
6.8148
6.8126
5.0410
5.0315
5.0290
5.0212
5.0187
5.0091
4.1965
4.1853
4.1742
3.7762
3.7687
3.4474
3.4361
3.4267
3.4248
3.4153
1.6928
1.6813
1.6769
1.6697
1.6676
1.6654
1.6604
1.6562
1.6536
1.6513
1.6447
1.6407
1.6311
1.6291
1.6150
1.4766 H2O
1.3578
1.3468
1.3428
1.3337
1.3242
1.3210
1.3175
1.3088
1.2971
1.2650
1.2567
1.2528
1.2481
1.2399
1.2291
1.2187
1.2137
1.2066
1.1977
1.1929
1.1857
1.1802
1.1587
O
O
O
Cl
4k, rr = 3.9/1
1.89
1.98
0.21
1.62
3.00
2.03
3.93
3.85
10.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

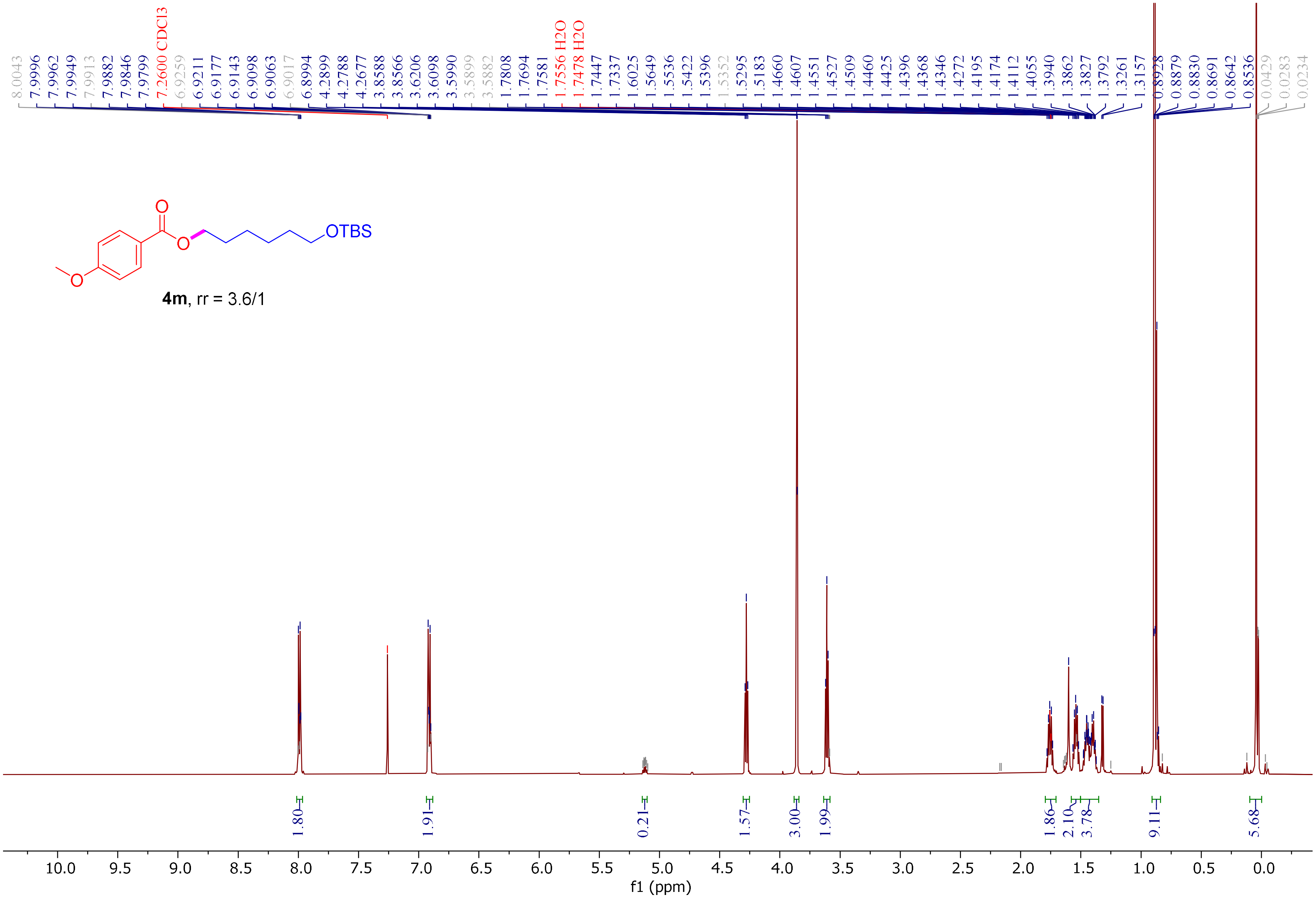

166.4965
163.2499
131.5546
122.9788
113.5638
77.2479
77.0368
76.8245
71.3133
64.8486
55.4460
45.2370
36.0970
32.6587
29.4633
28.8963
26.8929
26.0615
25.4332
20.1717
O
O
O
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

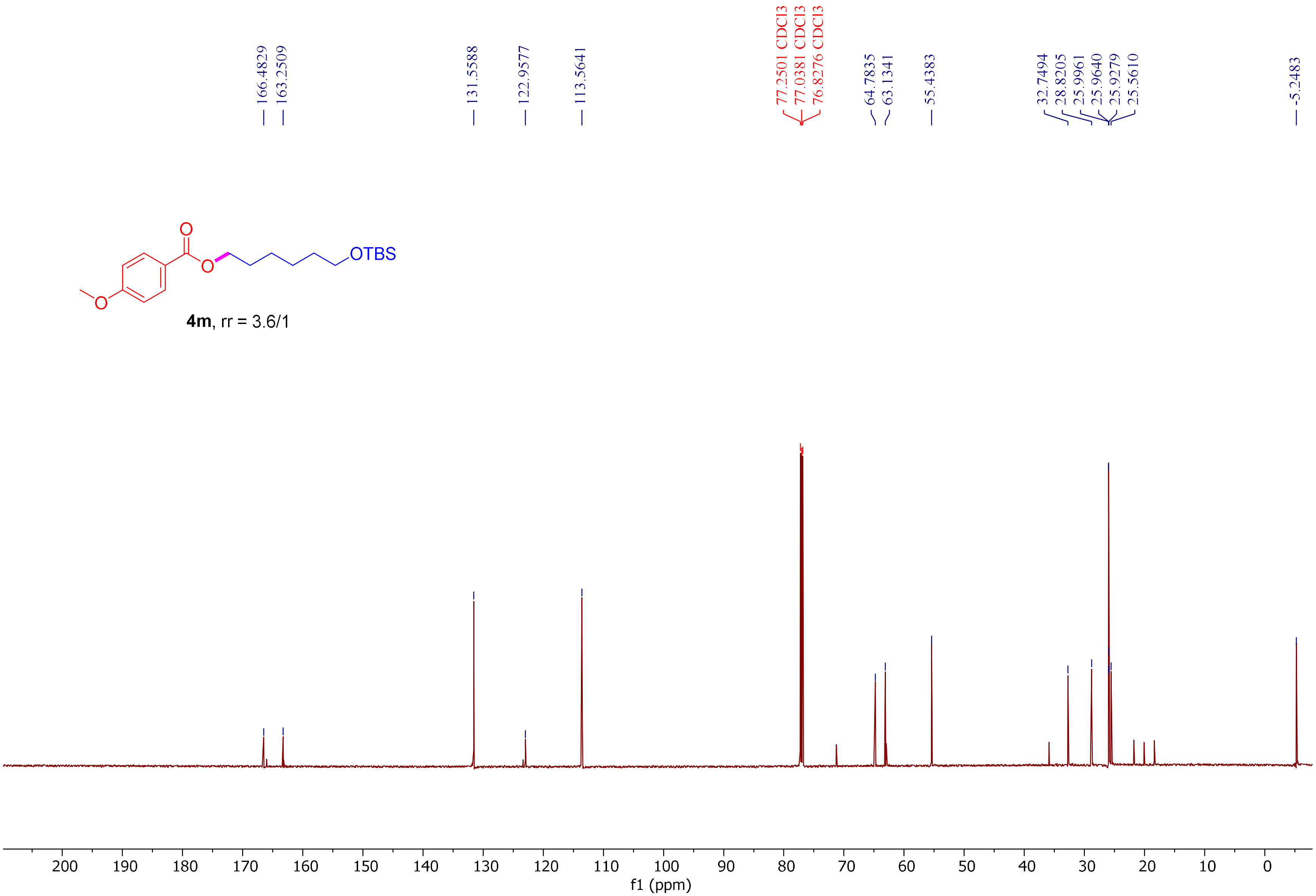
4k, rr = 3.9/1


4l, rr = 5.4/1
8.0276
8.0166
8.0135
8.0054
8.0007
7.9973
7.9934
7.9894
7.9858
7.9812
7.9786
7.2600 CDCl3
6.9445
6.9343
6.9324
6.9276
6.9243
6.9196
6.9163
6.9129
6.9079
4.7601
4.3115
4.3007
4.2898
3.8699
3.8669
3.8623
3.4683
3.4640
3.4566
3.4529
3.4485
3.4419
3.4373
3.4311
3.4261
3.4197
1.9805
1.9691
1.9625
1.9511
1.9465
1.9425
1.9395
1.9373
1.9299 H2O
1.9261
1.9146
1.8360
1.8274
1.8152
1.8038
1.7922
1.7889
1.7813
1.7785
1.7677
1.6321
1.6231
1.6190
1.6163
1.6120
1.6066
1.6025
1.5976
1.5935
1.5908
1.5768
1.3571
1.3467
1.2497
O
O
O
Br
1.82
1.84
0.15
1.63
3.00
2.02
1.59
1.65
2.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

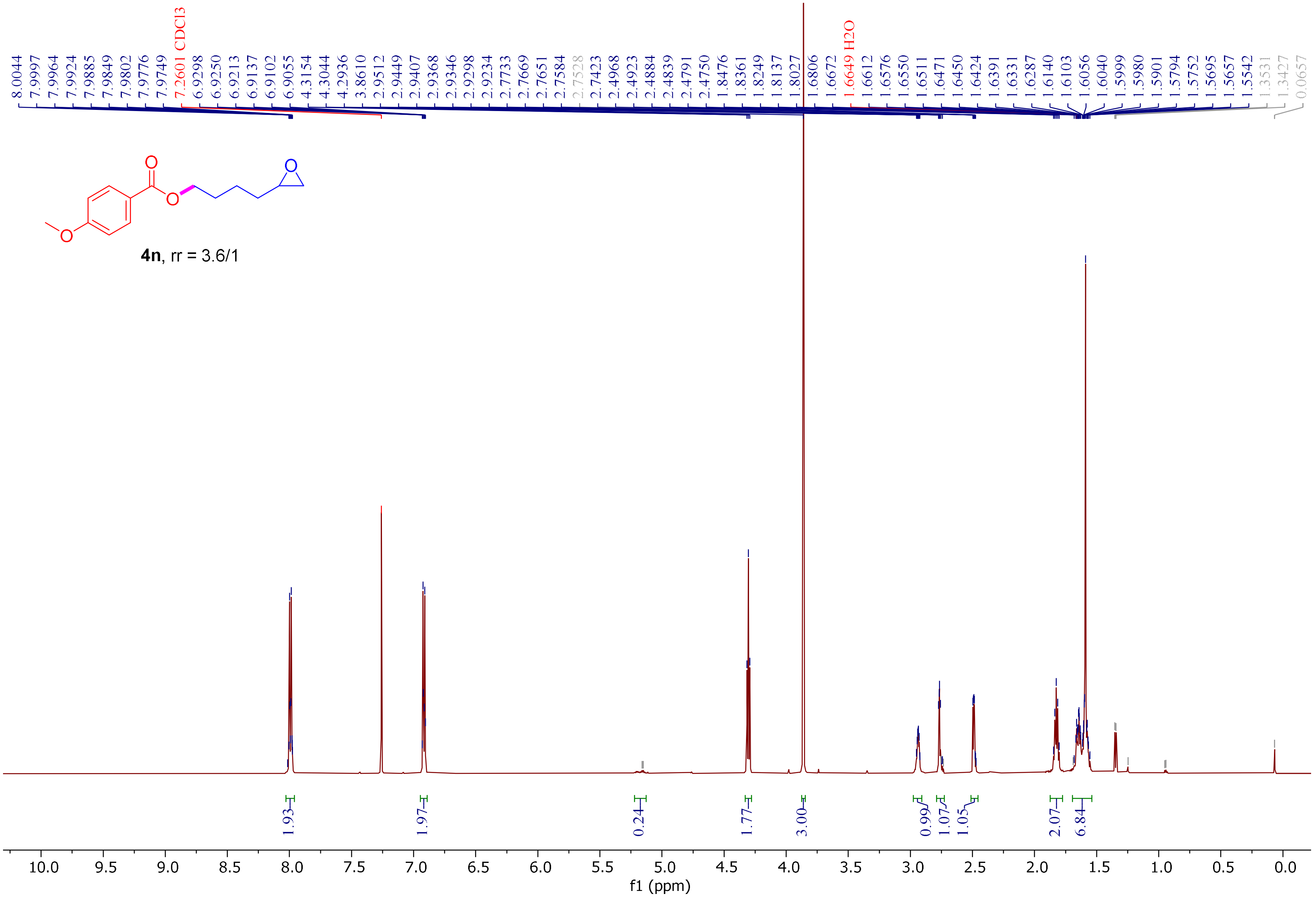

166.4098
163.3332
131.5837
122.7650
113.6147
77.2511
77.0406
76.8279
64.3469
55.4602
33.5618
32.3451
27.9760
24.7723
O
O
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4l, rr = 5.4/1

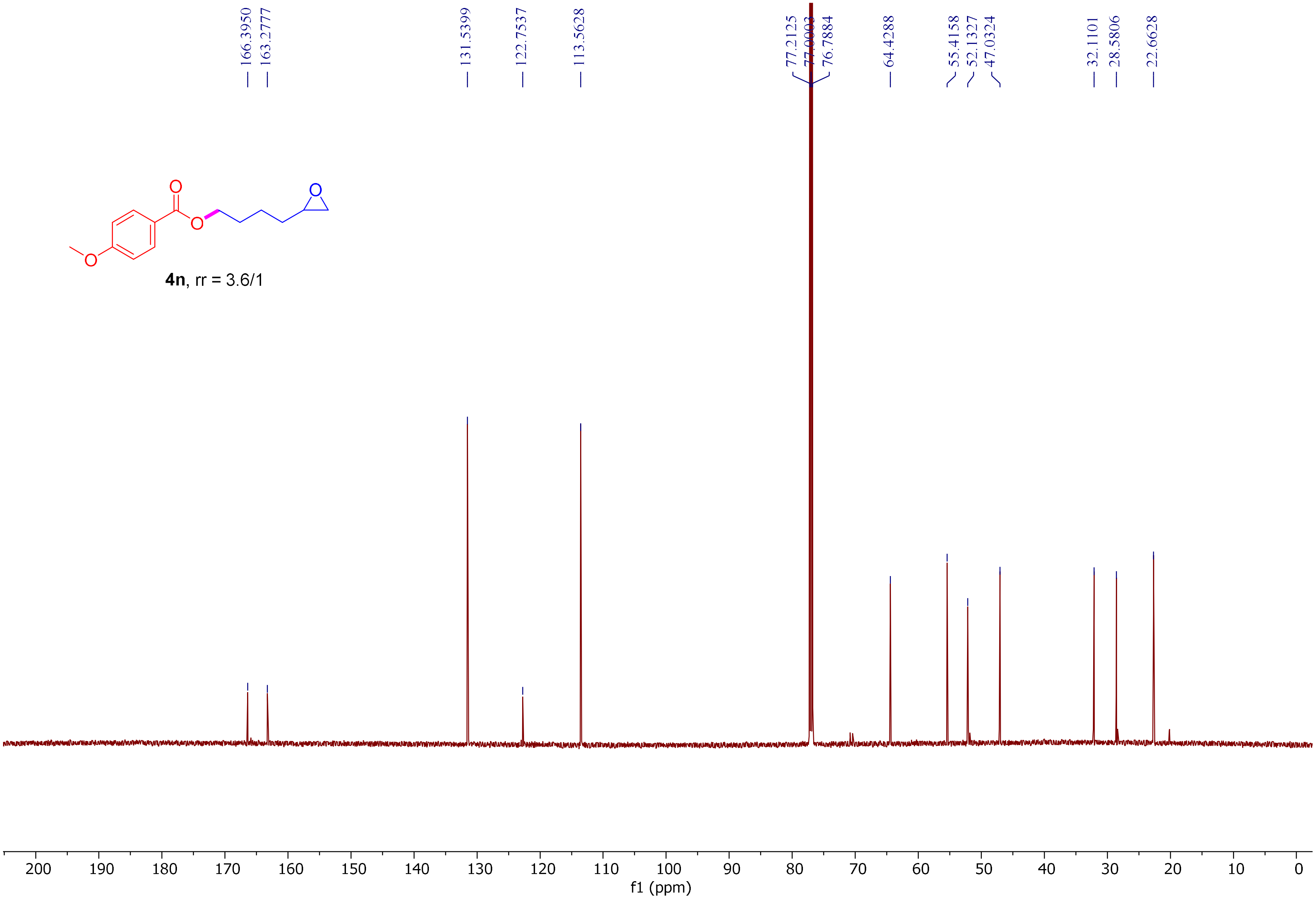

8.0043
7.9996
7.9962
7.9949
7.9913
7.9882
7.9846
7.9799
7.2600 CDCl3
6.9259
6.9211
6.9177
6.9143
6.9098
6.9063
6.9017
6.8994
4.2899
4.2788
4.2677
3.8588
3.8566
3.6206
3.6098
3.5990
3.5899
3.5882
1.7808
1.7694
1.7581
1.7556 H2O
1.7478 H2O
1.7447
1.7337
1.6025
1.5649
1.5536
1.5422
1.5396
1.5352
1.5295
1.5183
1.4660
1.4607
1.4551
1.4527
1.4509
1.4460
1.4425
1.4396
1.4368
1.4346
1.4272
1.4195
1.4174
1.4112
1.4055
1.3940
1.3862
1.3827
1.3792
1.3261
1.3157
0.8928
0.8879
0.8830
0.8691
0.8642
0.8536
0.0429
0.0283
0.0234
O
O
O
OTBS
4m, rr = 3.6/1
1.80
1.91
0.21
1.57
3.00
1.99
1.86
2.10
3.78
9.11
5.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4m, rr = 3.6/1

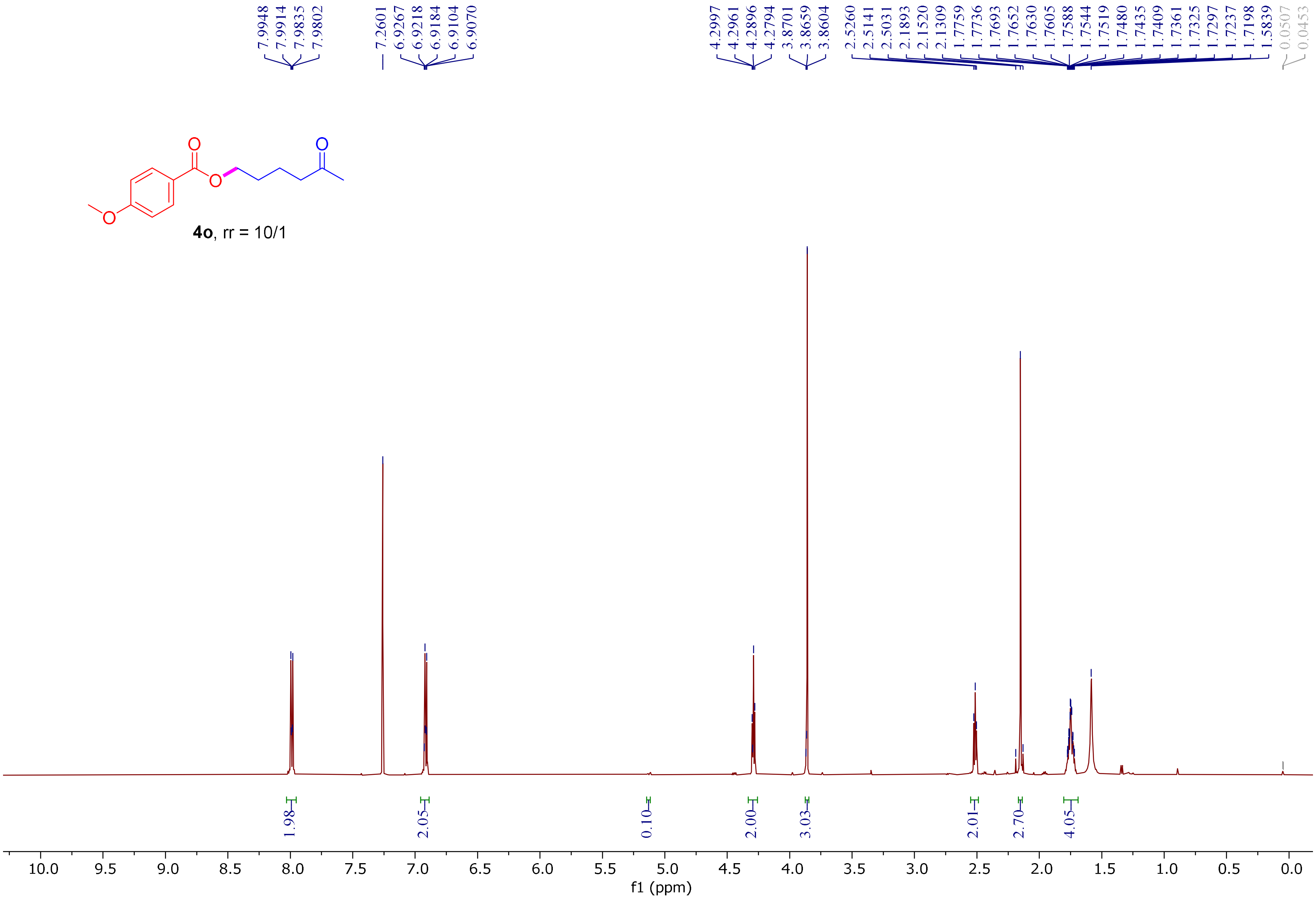
166.4829
163.2509
131.5588
122.9577
113.5641
77.2501 CDCl3
77.0381 CDCl3
76.8276 CDCl3
64.7835
63.1341
55.4383
32.7494
28.8205
25.9961
25.9640
25.9279
25.5610
-5.2483
O
O
O
OTBS
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4n, rr = 3.6/1

8.0044
7.9997
7.9964
7.9924
7.9885
7.9849
7.9802
7.9776
7.9749
7.2601 CDCl3
6.9298
6.9250
6.9213
6.9137
6.9102
6.9055
4.3154
4.3044
4.2936
3.8610
2.9512
2.9449
2.9407
2.9368
2.9346
2.9298
2.9234
2.7733
2.7669
2.7651
2.7584
2.7528
2.7423
2.4968
2.4923
2.4884
2.4839
2.4791
2.4750
1.8476
1.8361
1.8249
1.8137
1.8027
1.6806
1.6672
1.6649 H2O
1.6612
1.6576
1.6550
1.6511
1.6471
1.6450
1.6424
1.6391
1.6331
1.6287
1.6140
1.6103
1.6056
1.6040
1.5999
1.5980
1.5901
1.5794
1.5752
1.5695
1.5657
1.5542
1.3531
1.3427
0.0657
O
O
O
O
1.93
1.97
0.24
1.77
3.00
0.99
1.07
1.05
2.07
6.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

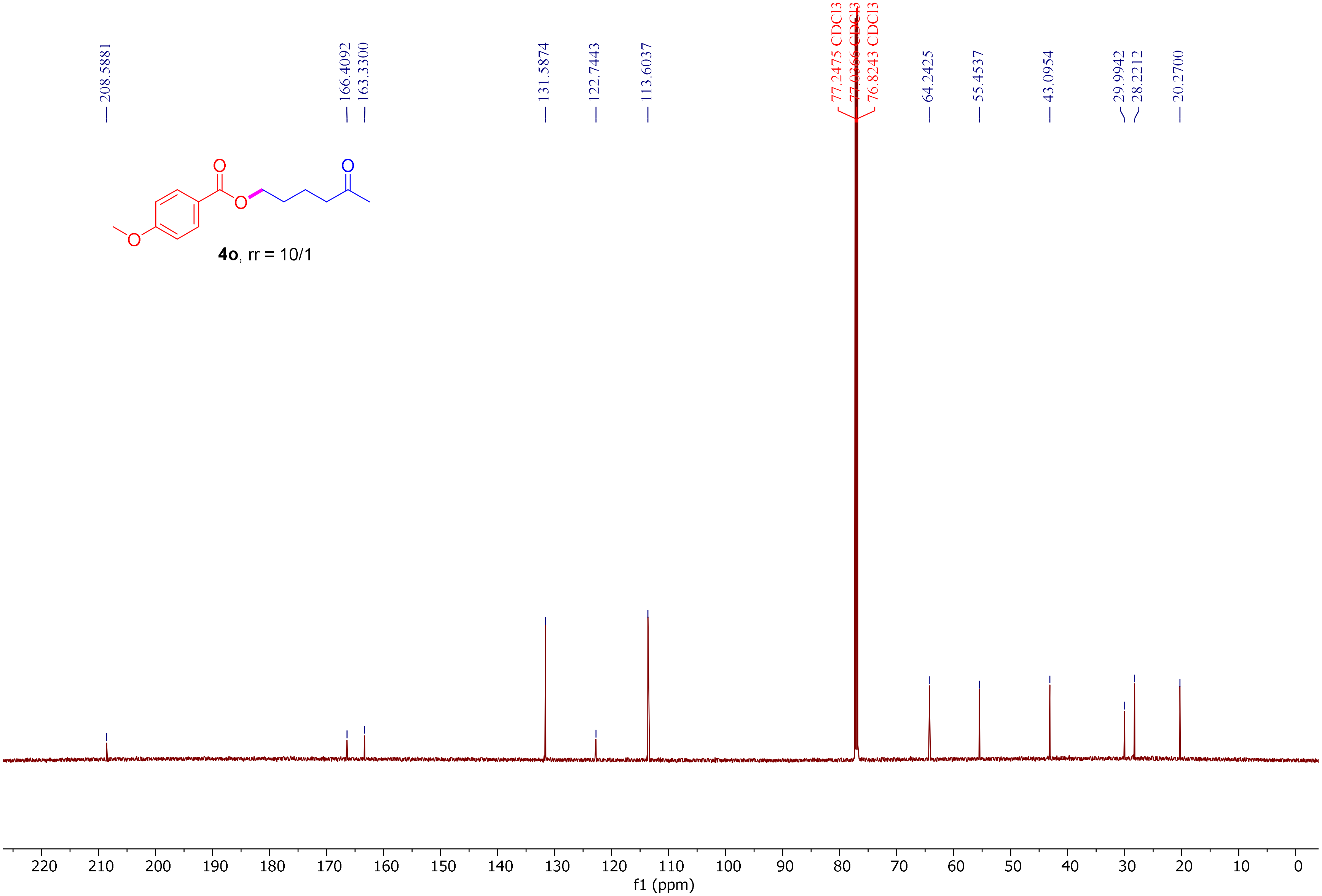

4n, rr = 3.6/1

166.3950
163.2777
131.5399
122.7537
113.5628
77.2125
77.0003
76.7884
64.4288
55.4158
52.1327
47.0324
32.1101
28.5806
22.6628
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

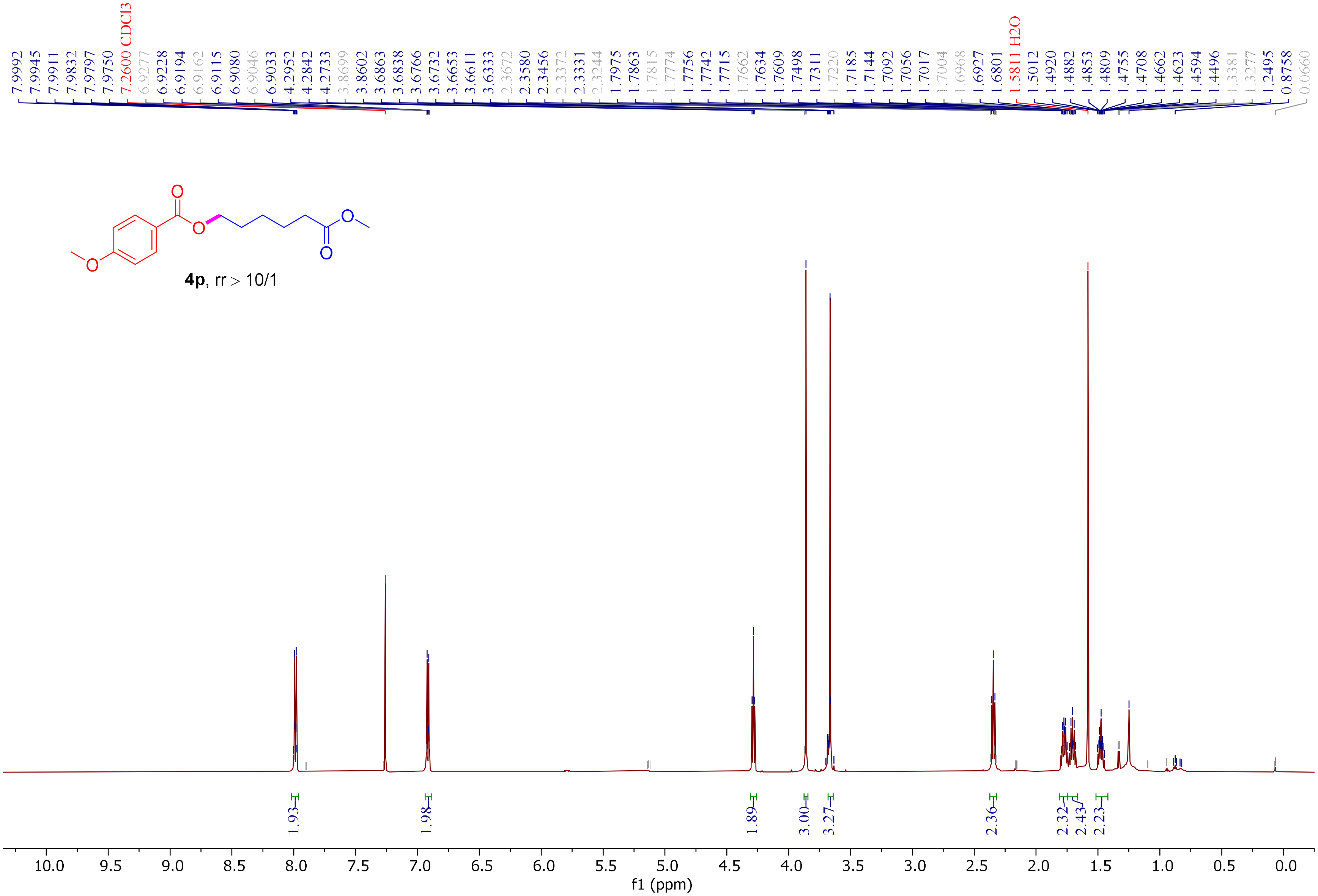


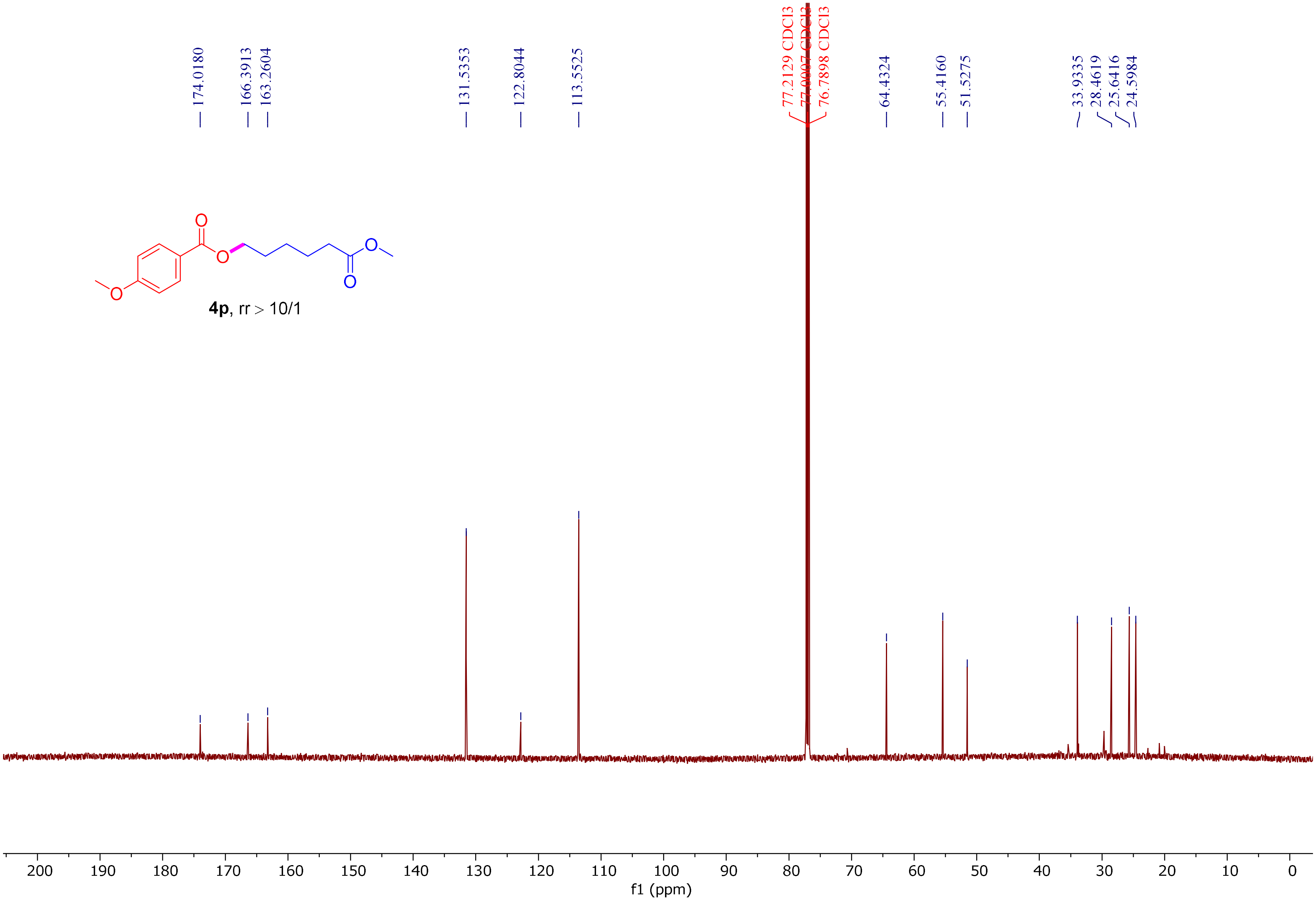
4o, rr = 10/1

7.9948
7.9914
7.9835
7.9802
7.2601
6.9267
6.9218
6.9184
6.9104
6.9070
4.2997
4.2961
4.2896
4.2794
3.8701
3.8659
3.8604
2.5260
2.5141
2.5031
2.1893
2.1520
2.1309
1.7759
1.7736
1.7693
1.7652
1.7630
1.7605
1.7588
1.7544
1.7519
1.7480
1.7435
1.7409
1.7361
1.7325
1.7297
1.7237
1.7198
1.5839
0.0507
0.0453
1.98
2.05
0.10
2.00
3.03
2.01
2.70
4.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

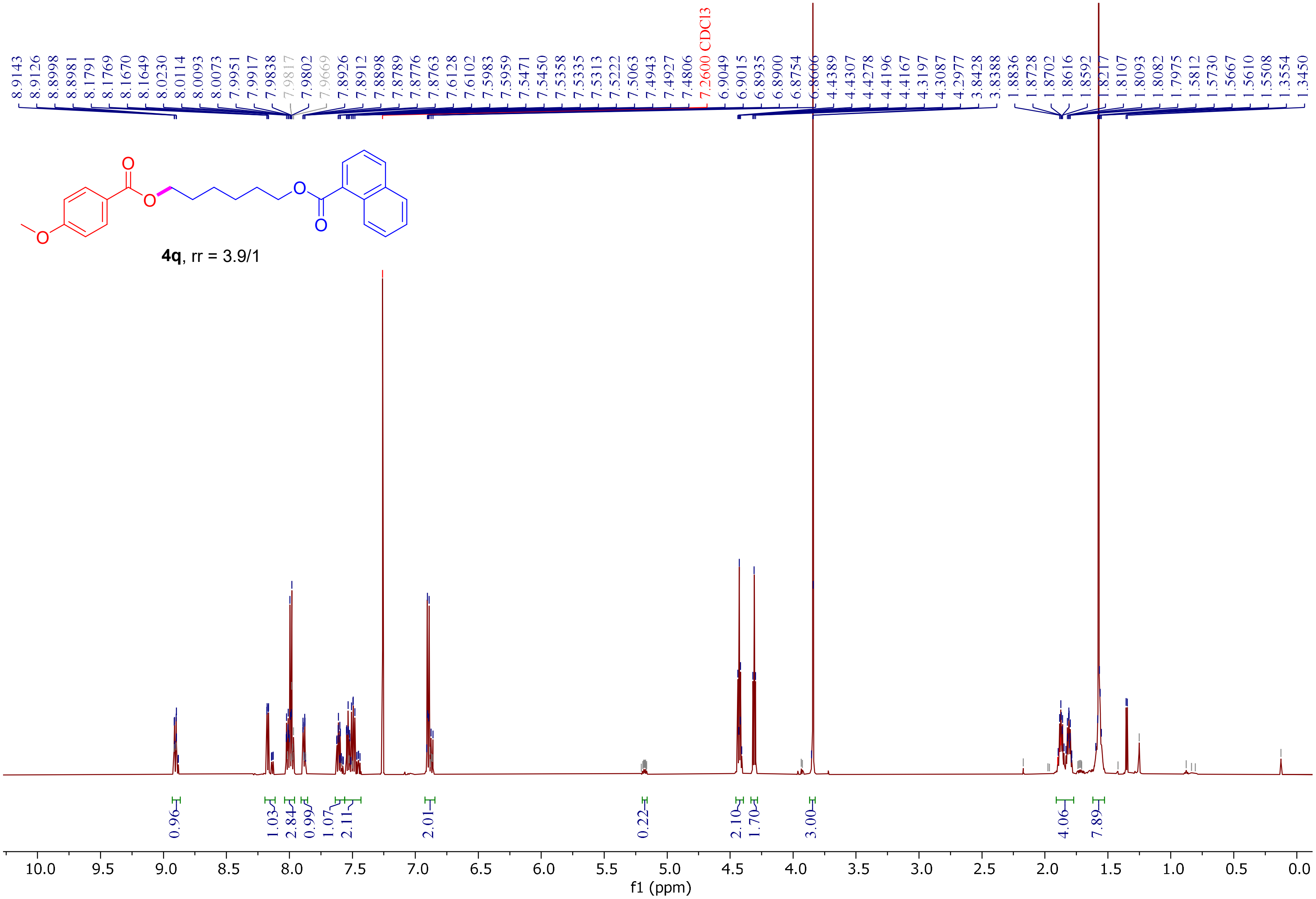

208.5881
166.4092
163.3300
131.5874
122.7443
113.6037
77.2475 CDCl3
77.0366 CDCl3
76.8243 CDCl3
64.2425
55.4537
43.0954
29.9942
28.2212
20.2700
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4o, rr = 10/1

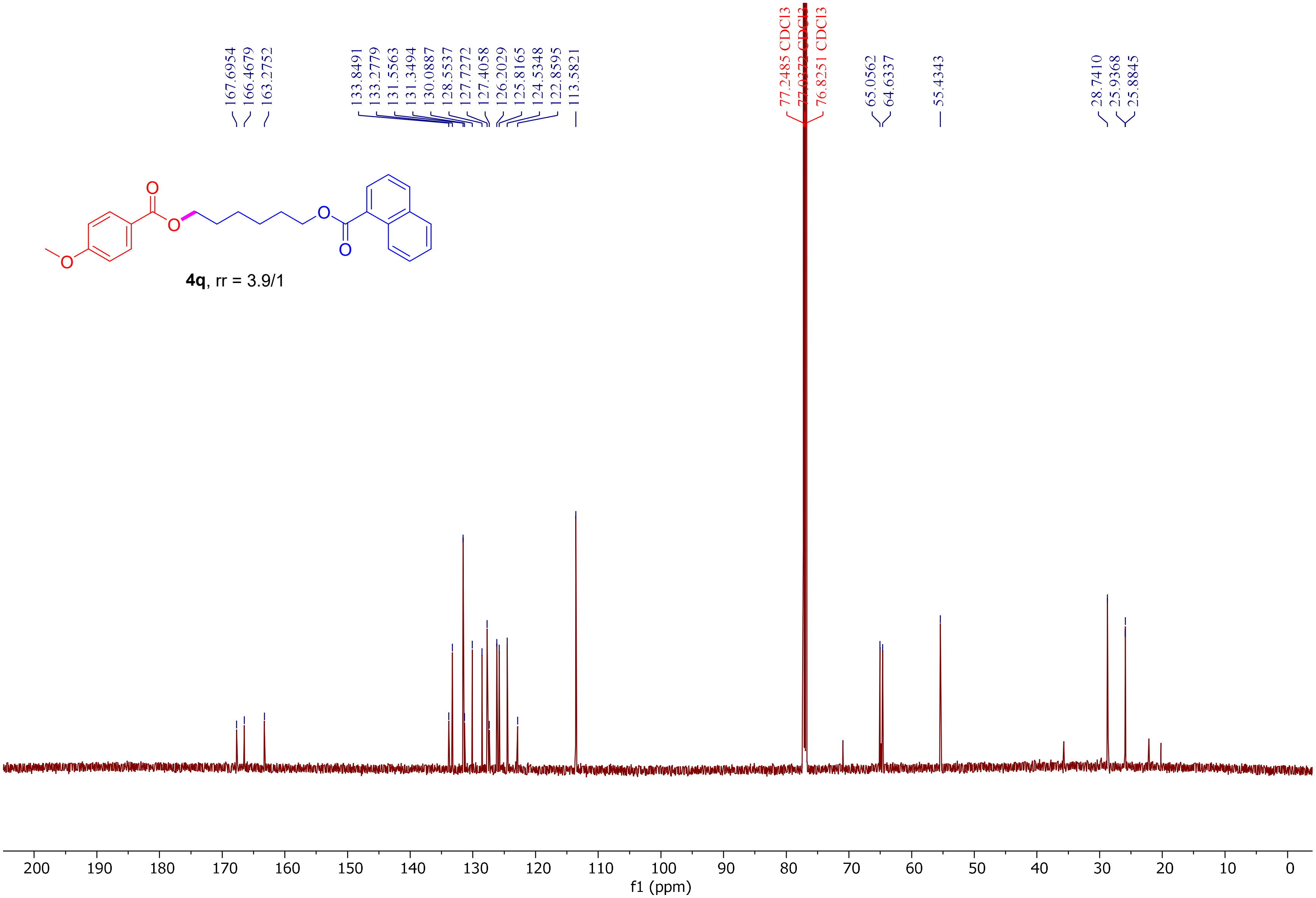

7.9992
7.9945
7.9911
7.9832
7.9797
7.9750
7.2600 CDCl3
6.9277
6.9228
6.9194
6.9162
6.9115
6.9080
6.9046
6.9033
4.2952
4.2842
4.2733
3.8699
3.8602
3.6863
3.6838
3.6766
3.6732
3.6653
3.6611
3.6333
2.3672
2.3580
2.3456
2.3372
2.3331
2.3244
1.7975
1.7863
1.7815
1.7774
1.7756
1.7742
1.7715
1.7662
1.7634
1.7609
1.7498
1.7311
1.7220
1.7185
1.7144
1.7092
1.7056
1.7017
1.7004
1.6968
1.6927
1.6801
1.5811 H2O
1.5012
1.4920
1.4882
1.4853
1.4809
1.4755
1.4708
1.4662
1.4623
1.4594
1.4496
1.3381
1.3277
1.2495
0.8758
0.0660
O
O
O
O
O
4p, rr > 10/1
1.93
1.98
1.89
3.00
3.27
2.36
2.32
2.43
2.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4p, rr > 10/1

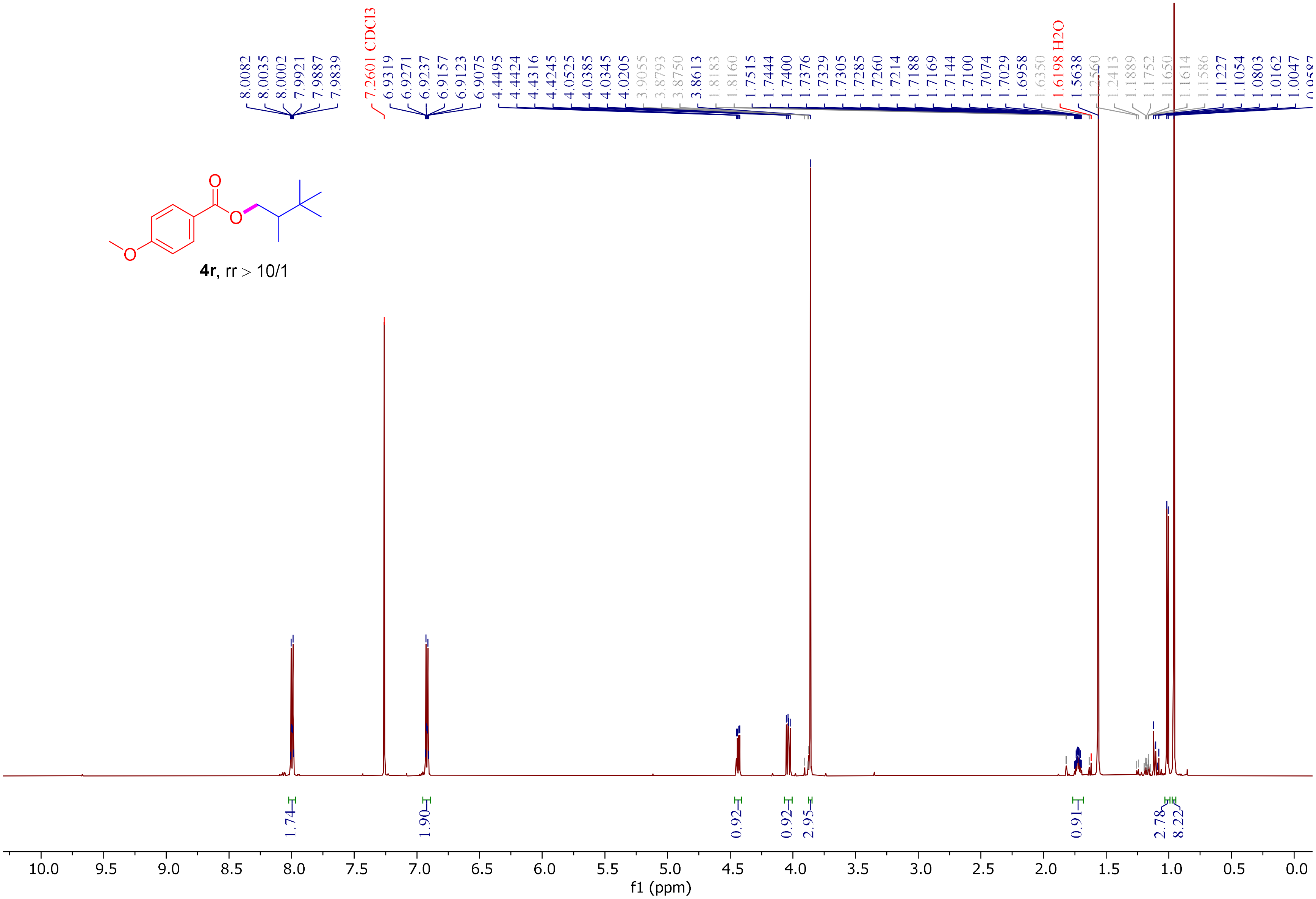
174.0180
166.3913
163.2604
131.5353
122.8044
113.5525
77.2129 CDCl3
77.0007 CDCl3
76.7898 CDCl3
64.4324
55.4160
51.5275
33.9335
28.4619
25.6416
24.5984
O
O
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

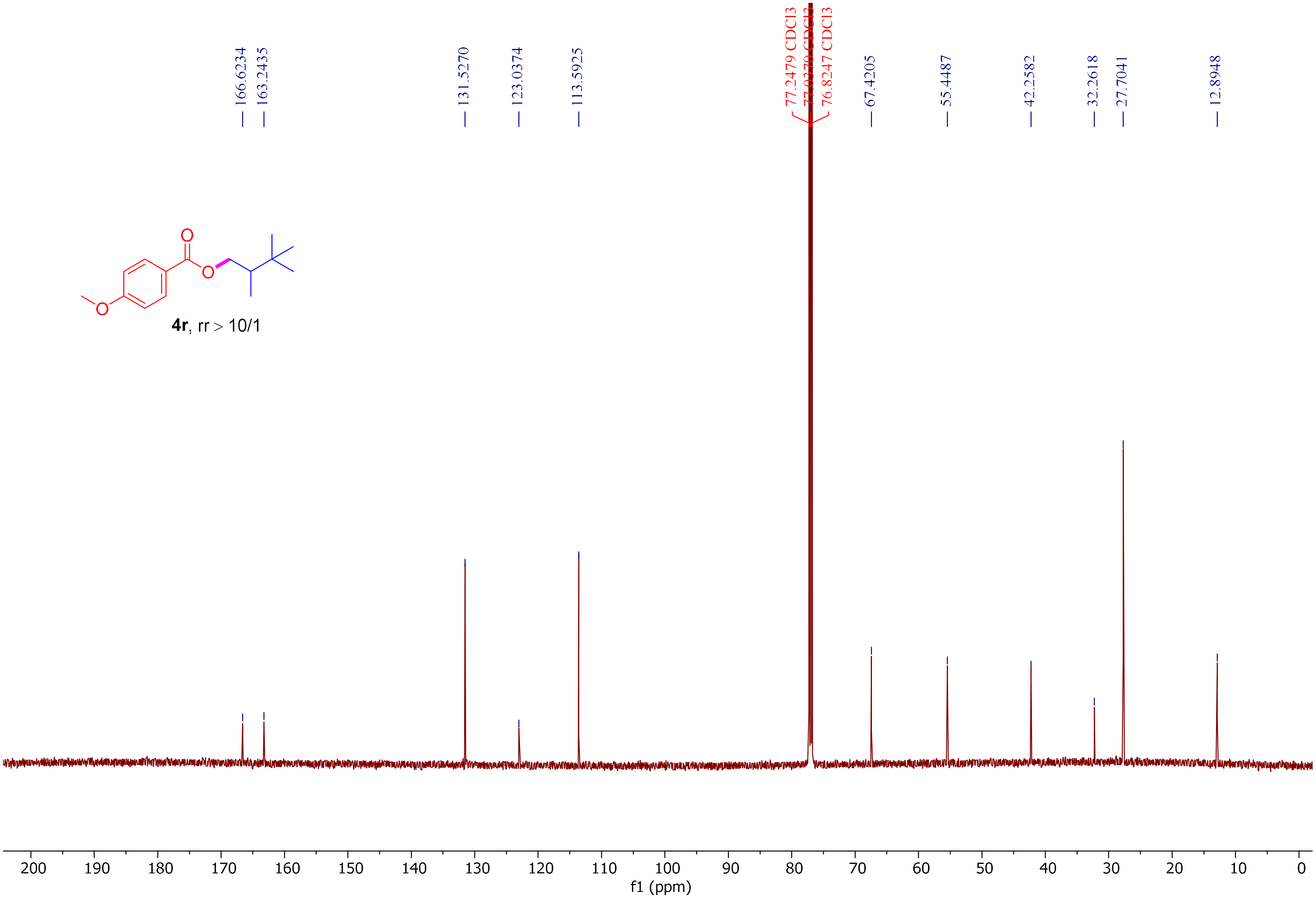

4q, rr = 3.9/1

8.9143
8.9126
8.8998
8.8981
8.1791
8.1769
8.1670
8.1649
8.0230
8.0114
8.0093
8.0073
7.9951
7.9917
7.9838
7.9817
7.9802
7.9669
7.8926
7.8912
7.8898
7.8789
7.8776
7.8763
7.6128
7.6102
7.5983
7.5959
7.5471
7.5450
7.5358
7.5335
7.5313
7.5222
7.5063
7.4943
7.4927
7.4806
7.2600 CDCl3
6.9049
6.9015
6.8935
6.8900
6.8754
6.8606
4.4389
4.4307
4.4278
4.4196
4.4167
4.3197
4.3087
4.2977
3.8428
3.8388
1.8836
1.8728
1.8702
1.8616
1.8592
1.8217
1.8107
1.8093
1.8082
1.7975
1.5812
1.5730
1.5667
1.5610
1.5508
1.3554
1.3450
O
O
O
O
O
O
0.96
1.03
2.84
0.99
1.07
2.11
2.01
0.22
2.10
1.70
3.00
4.06
7.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4q, rr = 3.9/1

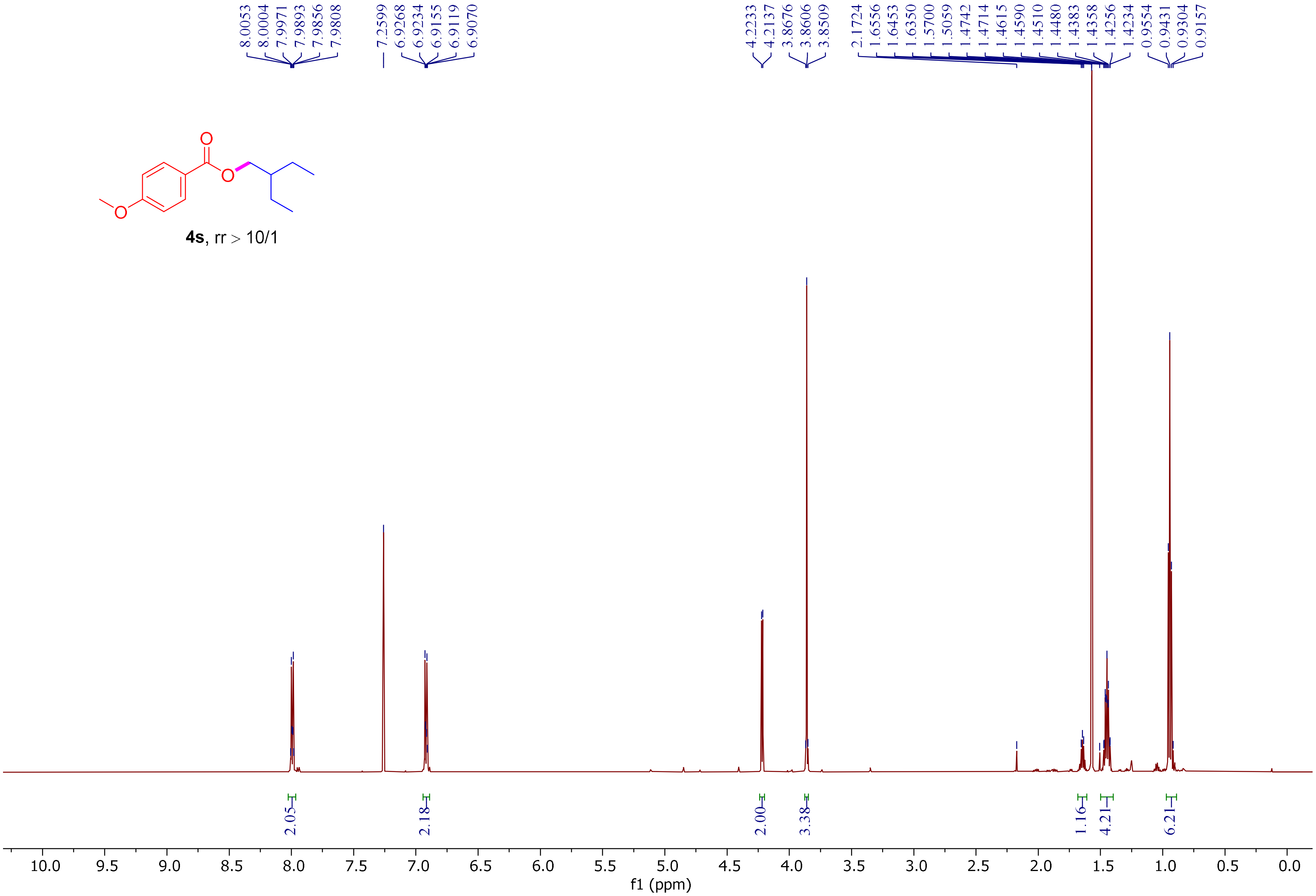
167.6954
166.4679
163.2752
133.8491
133.2779
131.5563
131.3494
130.0887
128.5537
127.7272
127.4058
126.2029
125.8165
124.5348
122.8595
113.5821
77.2485 CDCl3
77.0372 CDCl3
76.8251 CDCl3
65.0562
64.6337
55.4343
28.7410
25.9368
25.8845
O
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0082
8.0035
8.0002
7.9921
7.9887
7.9839
7.2601 CDCl3
6.9319
6.9271
6.9237
6.9157
6.9123
6.9075
4.4495
4.4424
4.4316
4.4245
4.0525
4.0385
4.0345
4.0205
3.9055
3.8793
3.8750
3.8613
1.8183
1.8160
1.7515
1.7444
1.7400
1.7376
1.7329
1.7305
1.7285
1.7260
1.7214
1.7188
1.7169
1.7144
1.7100
1.7074
1.7029
1.6958
1.6350
1.6198 H2O
1.5638
1.2560
1.2413
1.1889
1.1752
1.1650
1.1614
1.1586
1.1227
1.1054
1.0803
1.0162
1.0047
O
O
O
4r, rr > 10/1
1.74
1.90
0.92
0.92
2.95
0.91
2.78
8.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



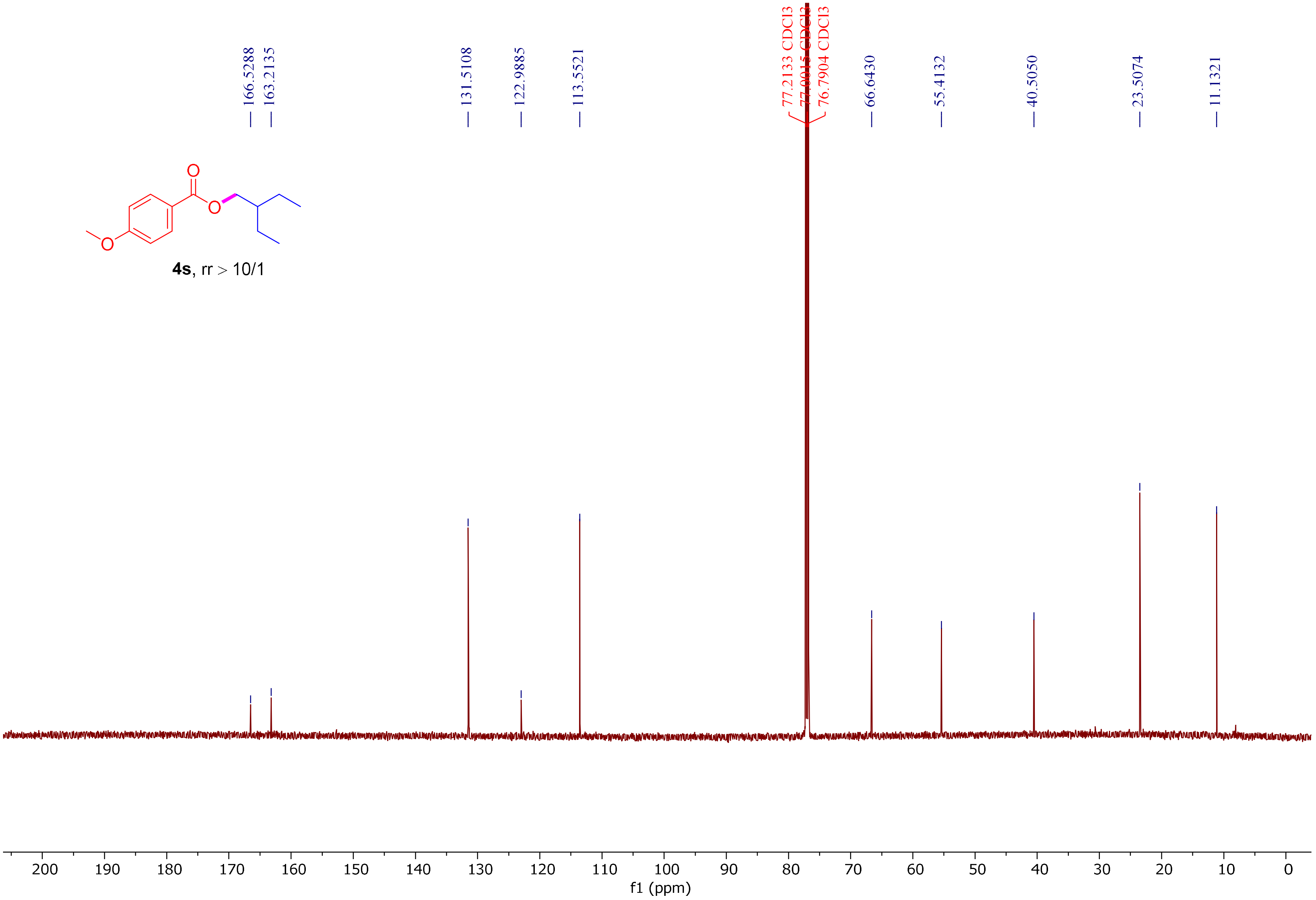
4r, rr > 10/1

166.6234
163.2435
131.5270
123.0374
113.5925
77.2479 CDCl3
77.0370 CDCl3
76.8247 CDCl3
67.4205
55.4487
42.2582
32.2618
27.7041
12.8948
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

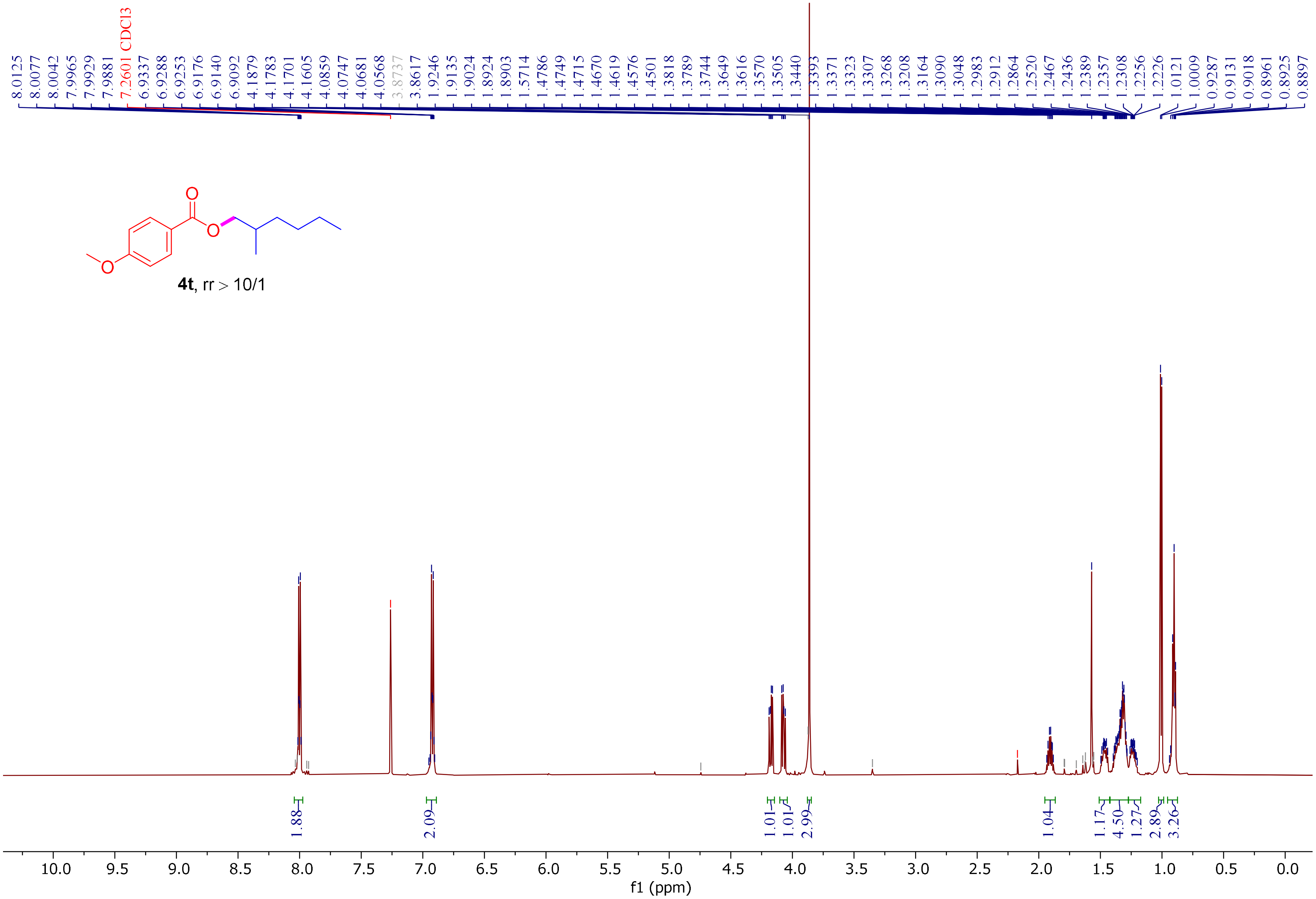


4s, rr > 10/1

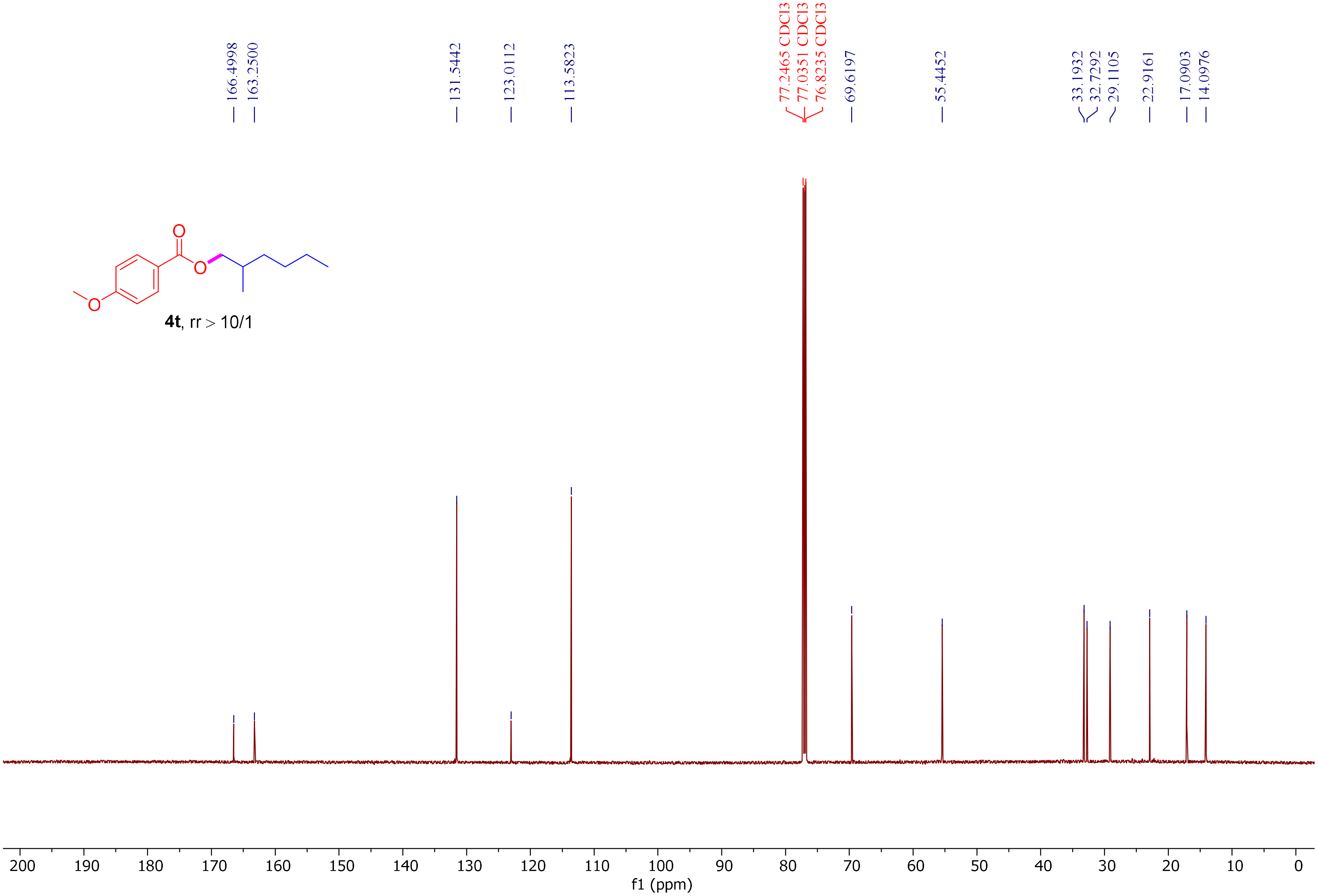
8.0053
8.0004
7.9971
7.9893
7.9856
7.9808
7.2599
6.9268
6.9234
6.9155
6.9119
6.9070
4.2233
4.2137
3.8676
3.8606
3.8509
2.1724
1.6556
1.6453
1.6350
1.5700
1.5059
1.4742
1.4714
1.4615
1.4590
1.4510
1.4480
1.4383
1.4358
1.4256
1.4234
0.9554
0.9431
0.9304
0.9157
2.05
2.18
2.00
3.38
1.16
4.21
6.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4s, rr > 10/1

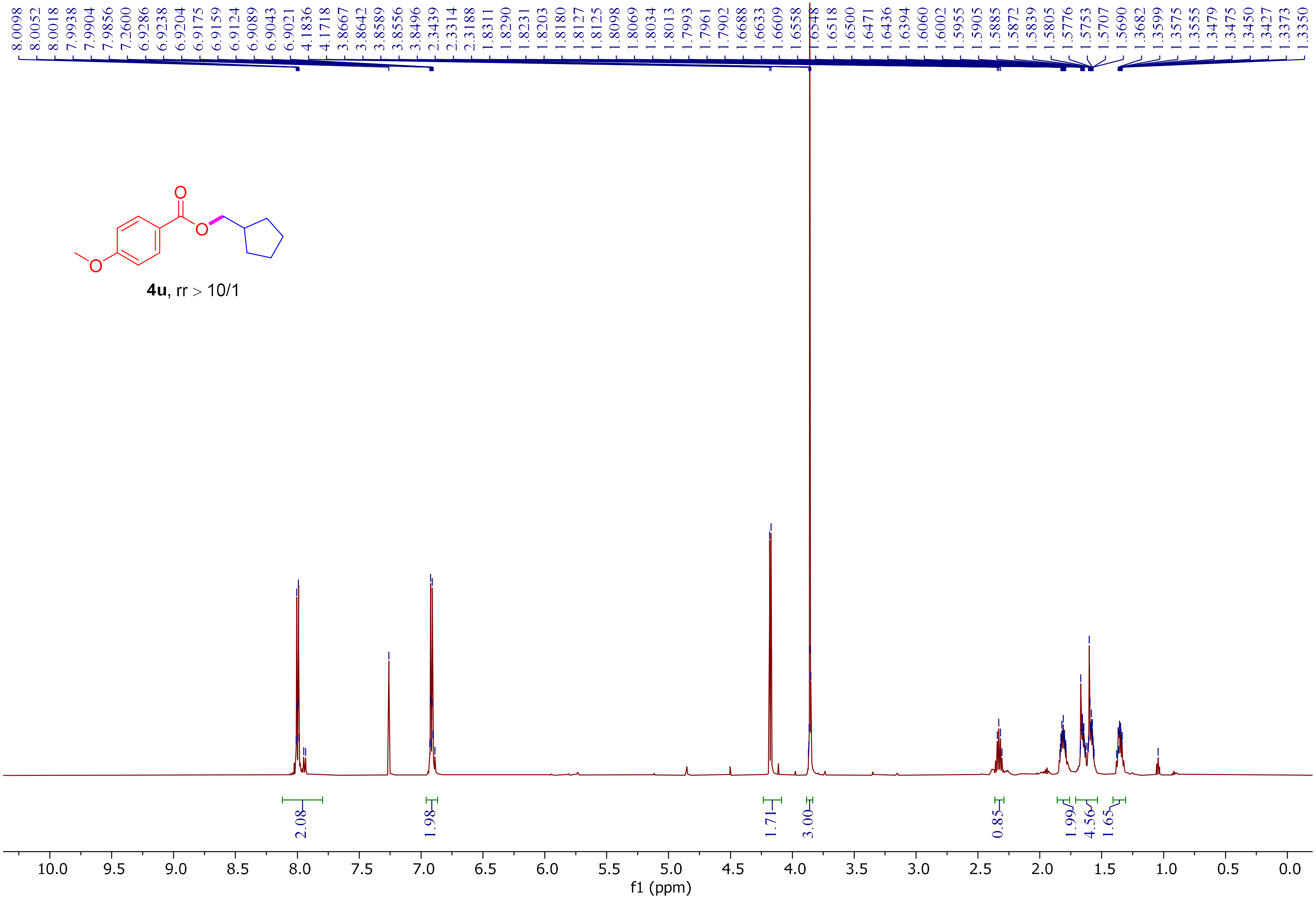
166.5288
163.2135
131.5108
122.9885
113.5521
77.2133 CDCl3
77.0015 CDCl3
76.7904 CDCl3
66.6430
55.4132
40.5050
23.5074
11.1321
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0125
8.0077
8.0042
7.9965
7.9929
7.9881
7.2601 CDCl3
6.9337
6.9288
6.9253
6.9176
6.9140
6.9092
4.1879
4.1783
4.1701
4.1605
4.0859
4.0747
4.0681
4.0568
3.8737
3.8617
1.9246
1.9135
1.9024
1.8924
1.8903
1.5714
1.4786
1.4749
1.4715
1.4670
1.4619
1.4576
1.4501
1.3818
1.3789
1.3744
1.3649
1.3616
1.3570
1.3505
1.3440
1.3393
1.3371
1.3323
1.3307
1.3268
1.3208
1.3164
1.3090
1.3048
1.2983
1.2912
1.2864
1.2520
1.2467
1.2436
1.2389
1.2357
1.2308
1.2256
1.2226
1.0121
1.0009
0.9287
0.9131
0.9018
0.8961
0.8925
0.8897
O
O
O
1.88
2.09
1.01
1.01
2.99
1.04
1.17
4.50
1.27
2.89
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

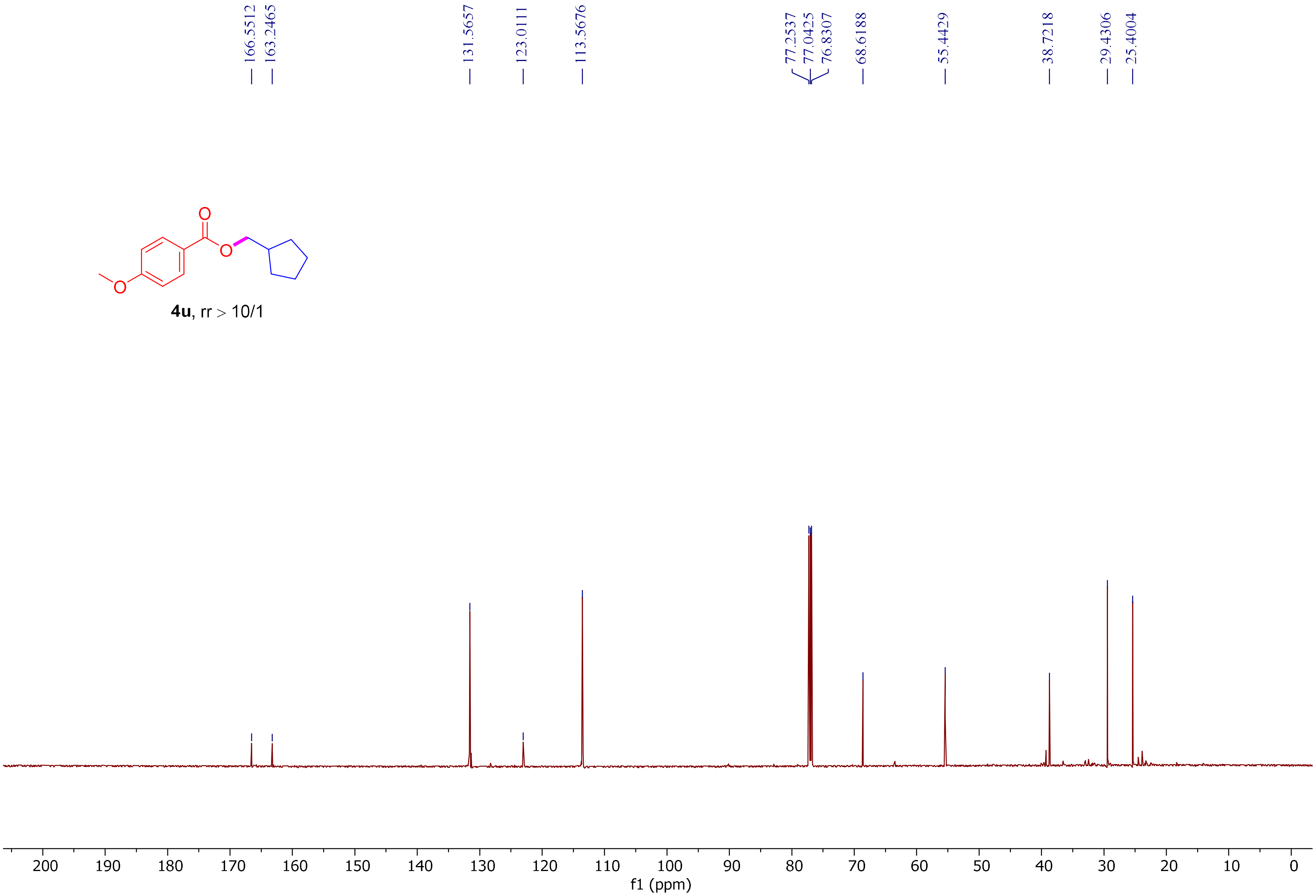
4t, rr > 10/1


4t, rr > 10/1

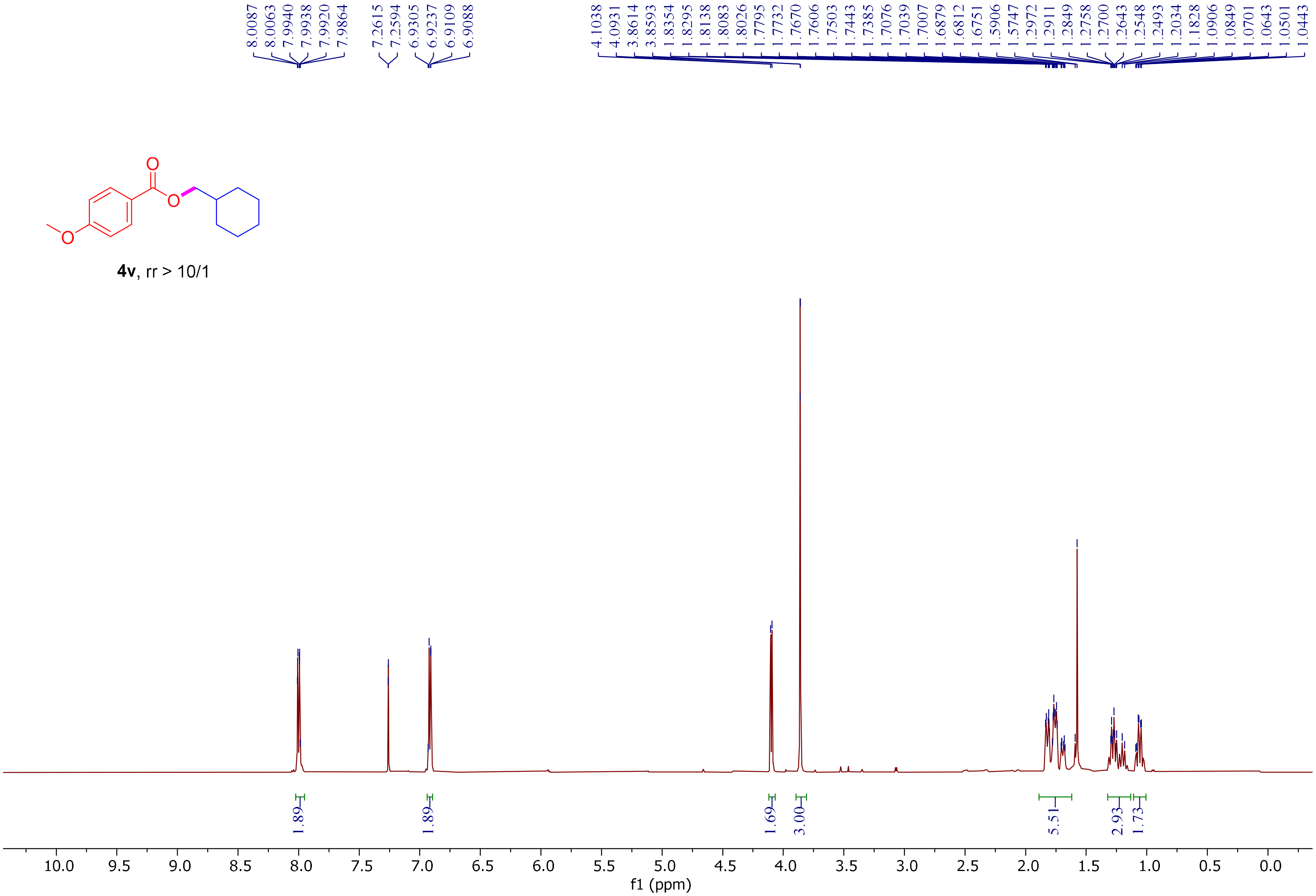
166.4998
163.2500
131.5442
123.0112
113.5823
77.2465 CDCl3
77.0351 CDCl3
76.8235 CDCl3
69.6197
55.4452
33.1932
32.7292
29.1105
22.9161
17.0903
14.0976
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0098
8.0052
8.0018
7.9938
7.9904
7.9856
7.2600
6.9286
6.9238
6.9204
6.9175
6.9159
6.9124
6.9089
6.9043
6.9021
4.1836
4.1718
3.8667
3.8642
3.8589
3.8556
3.8496
2.3439
2.3314
2.3188
1.8311
1.8290
1.8231
1.8203
1.8180
1.8127
1.8125
1.8098
1.8069
1.8034
1.8013
1.7993
1.7961
1.7902
1.6688
1.6633
1.6609
1.6558
1.6548
1.6518
1.6500
1.6471
1.6436
1.6394
1.6060
1.6002
1.5955
1.5905
1.5885
1.5872
1.5839
1.5805
1.5776
1.5753
1.5707
1.5690
1.3682
1.3599
1.3575
1.3555
1.3479
1.3475
1.3450
1.3427
1.3373
1.3350
O
O
O
2.08
1.98
1.71
3.00
0.85
1.99
4.56
1.65
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4u, rr > 10/1


4u, rr > 10/1

166.5512
163.2465
131.5657
123.0111
113.5676
77.2537
77.0425
76.8307
68.6188
55.4429
38.7218
29.4306
25.4004
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O

4v, rr > 10/1

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6.9237
6.9109
6.9088
4.1038
4.0931
3.8614
3.8593
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1.8295
1.8138
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1.8026
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1.7732
1.7670
1.7606
1.7503
1.7443
1.7385
1.7076
1.7039
1.7007
1.6879
1.6812
1.6751
1.5906
1.5747
1.2972
1.2911
1.2849
1.2758
1.2700
1.2643
1.2548
1.2493
1.2034
1.1828
1.0906
1.0849
1.0701
1.0643
1.0501
1.0443
1.89
1.89
1.69
3.00
5.51
2.93
1.73
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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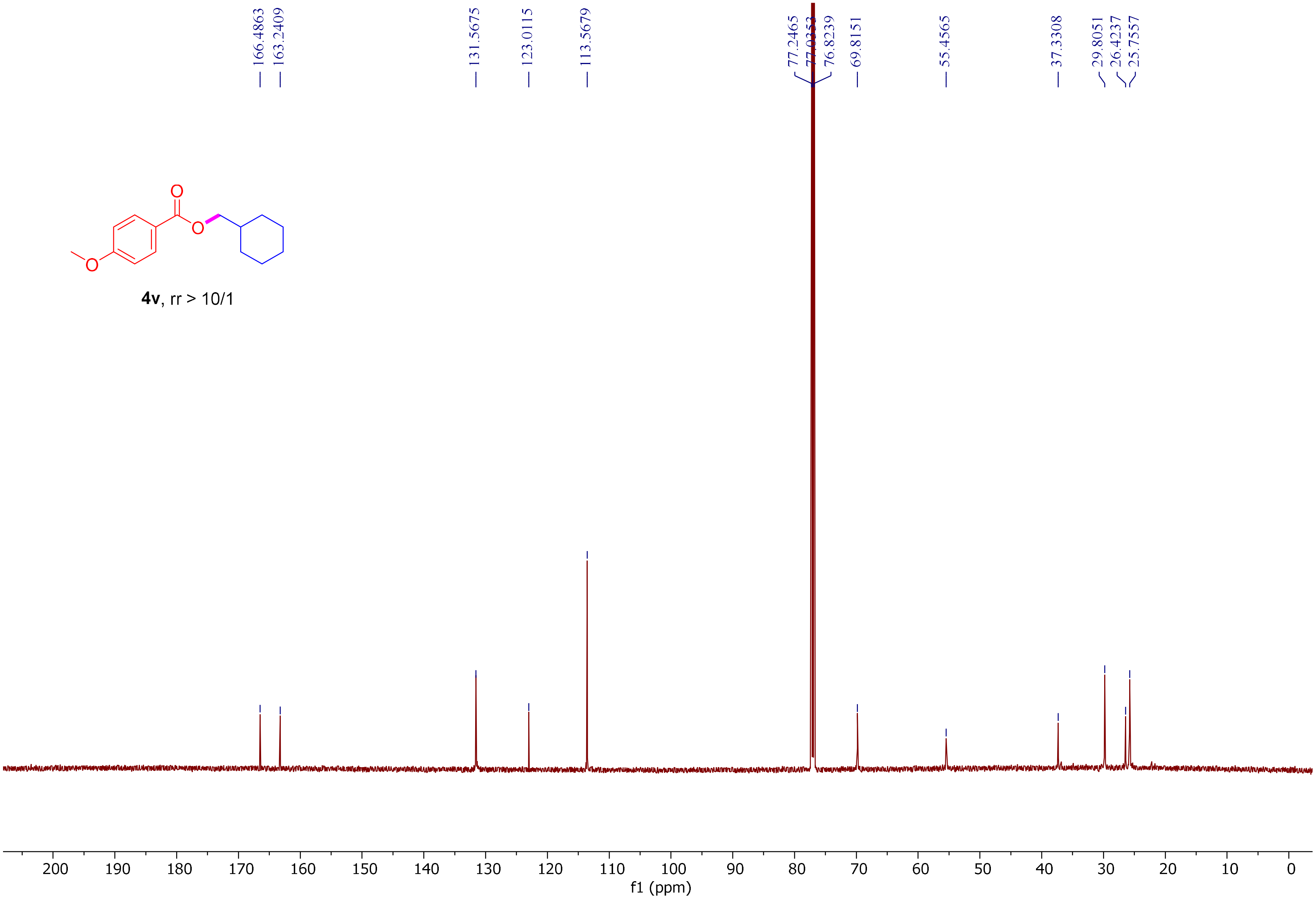
0.0
f1 (ppm)



4v, rr > 10/1

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163.2409
131.5675
123.0115
113.5679
77.2465
77.0353
76.8239
69.8151
55.4565
37.3308
29.8051
26.4237
25.7557
200
190
180
170
160
150
140
130
120
110
100
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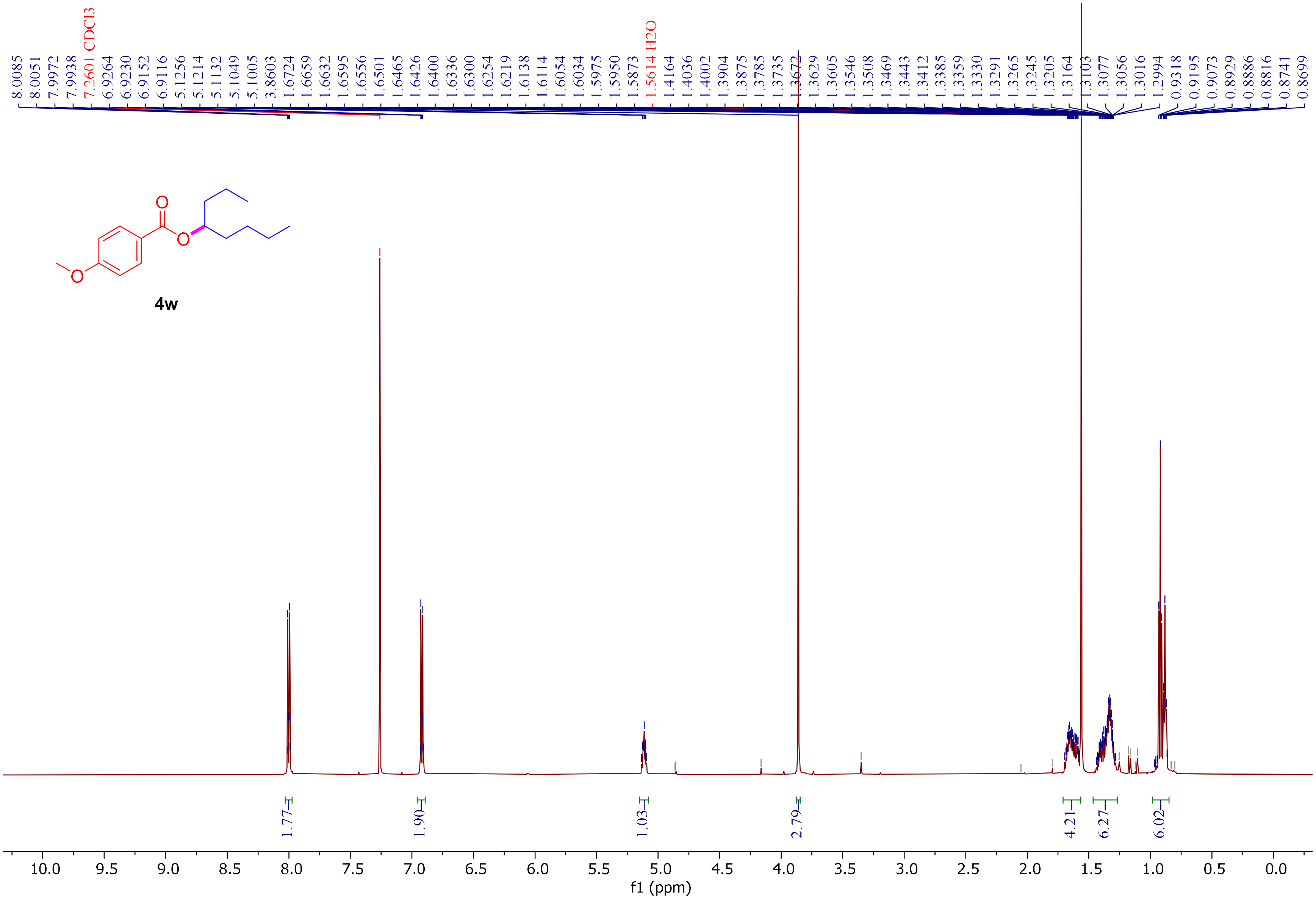
20
10
0
f1 (ppm)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6.9152
6.9116
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5.1214
5.1132
5.1049
5.1005
3.8603
1.6724
1.6659
1.6632
1.6595
1.6556
1.6501
1.6465
1.6426
1.6400
1.6336
1.6300
1.6254
1.6219
1.6138
1.6114
1.6054
1.6034
1.5975
1.5950
1.5873
1.5614 H2O
1.4164
1.4036
1.4002
1.3904
1.3875
1.3785
1.3735
1.3672
1.3629
1.3605
1.3546
1.3508
1.3469
1.3443
1.3412
1.3385
1.3359
1.3330
1.3291
1.3265
1.3245
1.3205
1.3164
1.3103
1.3077
1.3056
1.3016
1.2994
0.9318
0.9195
0.9073
0.8929
0.8886
0.8816
0.8741
0.8699
O
O
O
4w
1.77
1.90
1.03
2.79
4.21
6.27
6.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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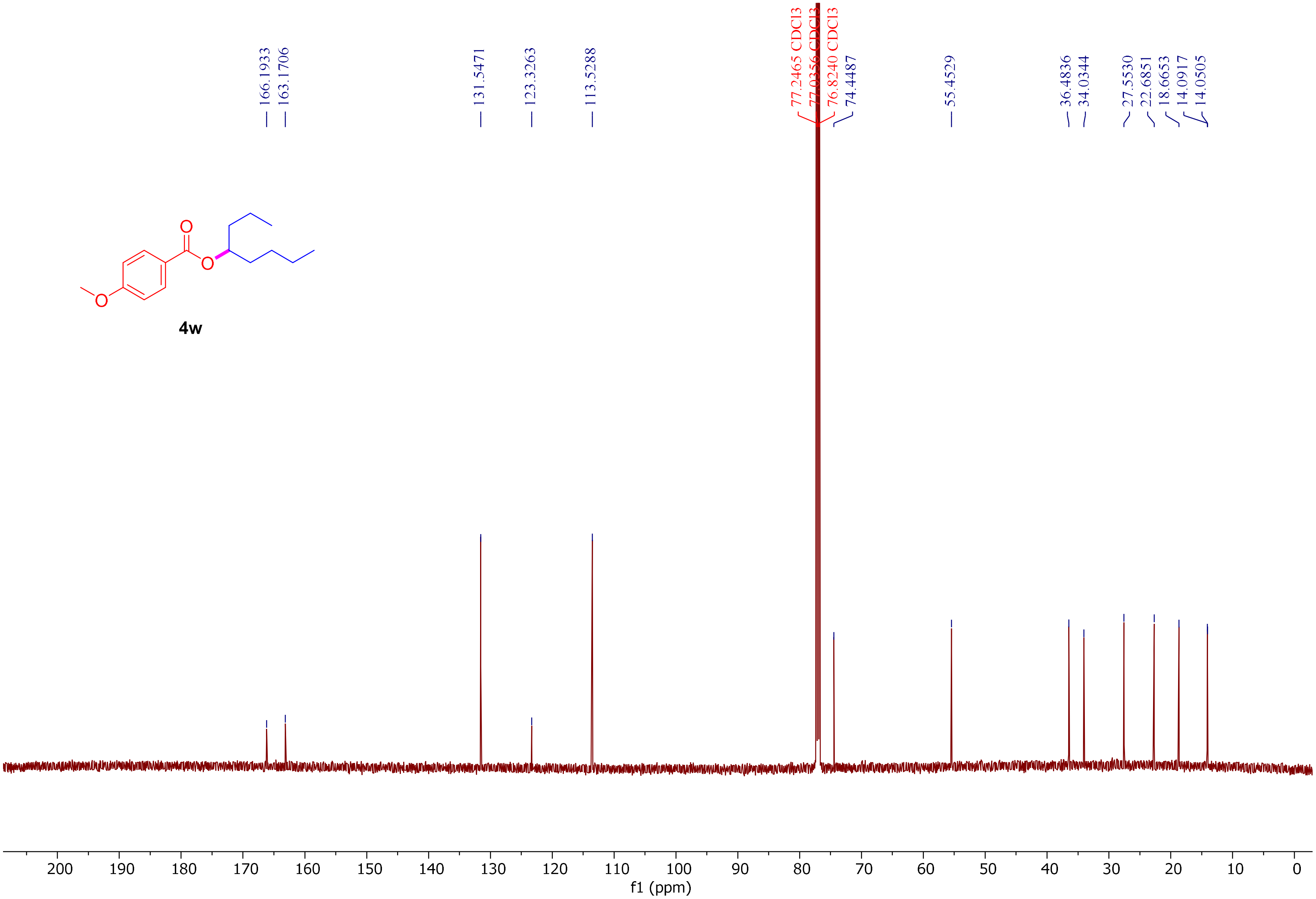
0.0
f1 (ppm)


4w

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163.1706
131.5471
123.3263
113.5288
77.2465 CDCl3
77.0356 CDCl3
76.8240 CDCl3
74.4487
55.4529
36.4836
34.0344
27.5530
22.6851
18.6653
14.0917
14.0505
O
O
O
200
190
180
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130
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110
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90
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50
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30
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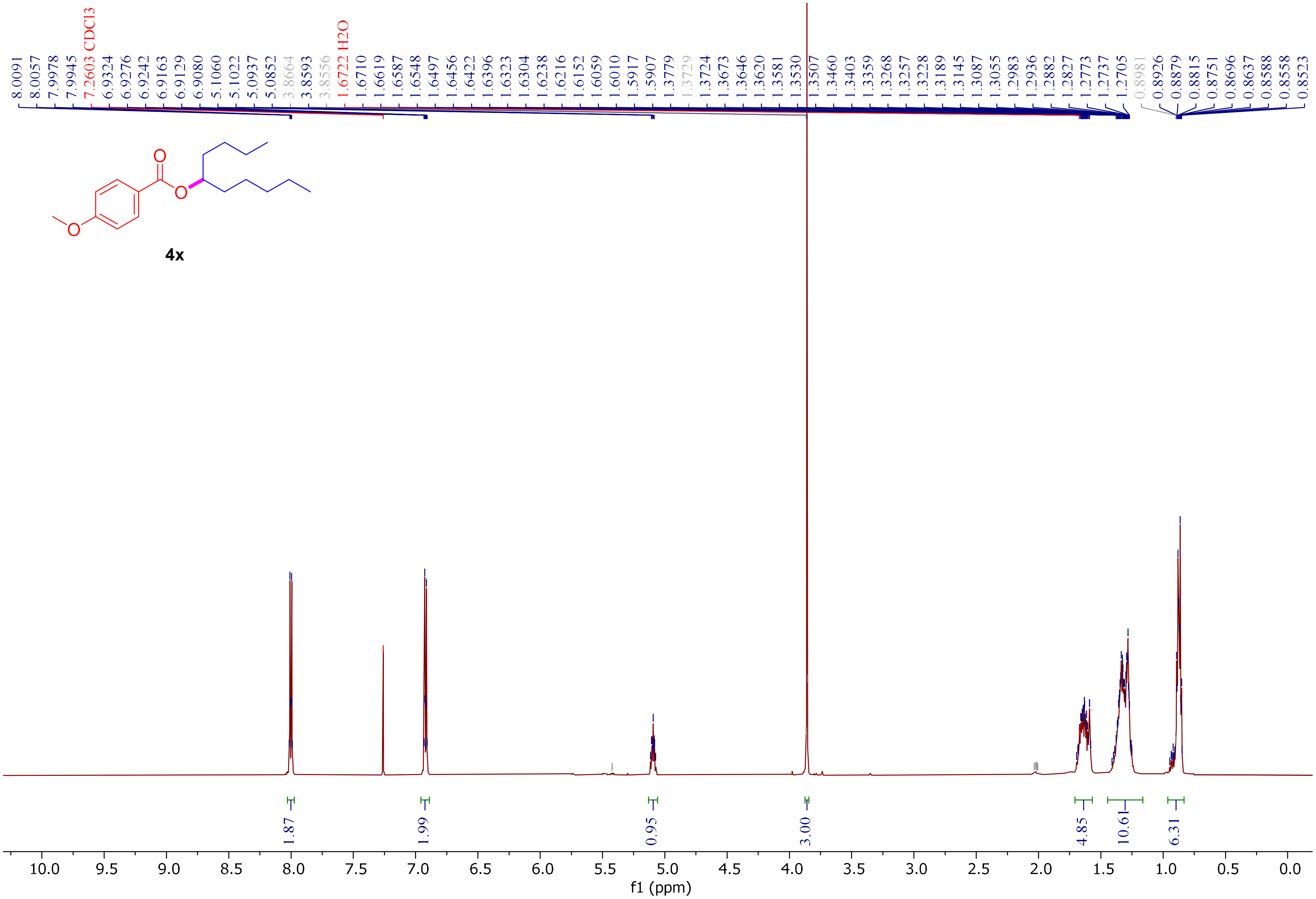
f1 (ppm)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6.9242
6.9163
6.9129
6.9080
5.1060
5.1022
5.0937
5.0852
3.8664
3.8593
3.8556
1.6722 H2O
1.6710
1.6619
1.6587
1.6548
1.6497
1.6456
1.6422
1.6396
1.6323
1.6304
1.6238
1.6216
1.6152
1.6059
1.6010
1.5917
1.5907
1.3779
1.3729
1.3724
1.3673
1.3646
1.3620
1.3581
1.3530
1.3507
1.3460
1.3403
1.3359
1.3268
1.3257
1.3228
1.3189
1.3145
1.3087
1.3055
1.2983
1.2936
1.2882
1.2827
1.2773
1.2737
1.2705
0.8981
0.8926
0.8879
0.8815
0.8751
0.8696
0.8637
0.8588
0.8558
0.8523
O
O
O
4x
1.87
1.99
0.95
3.00
4.85
10.61
6.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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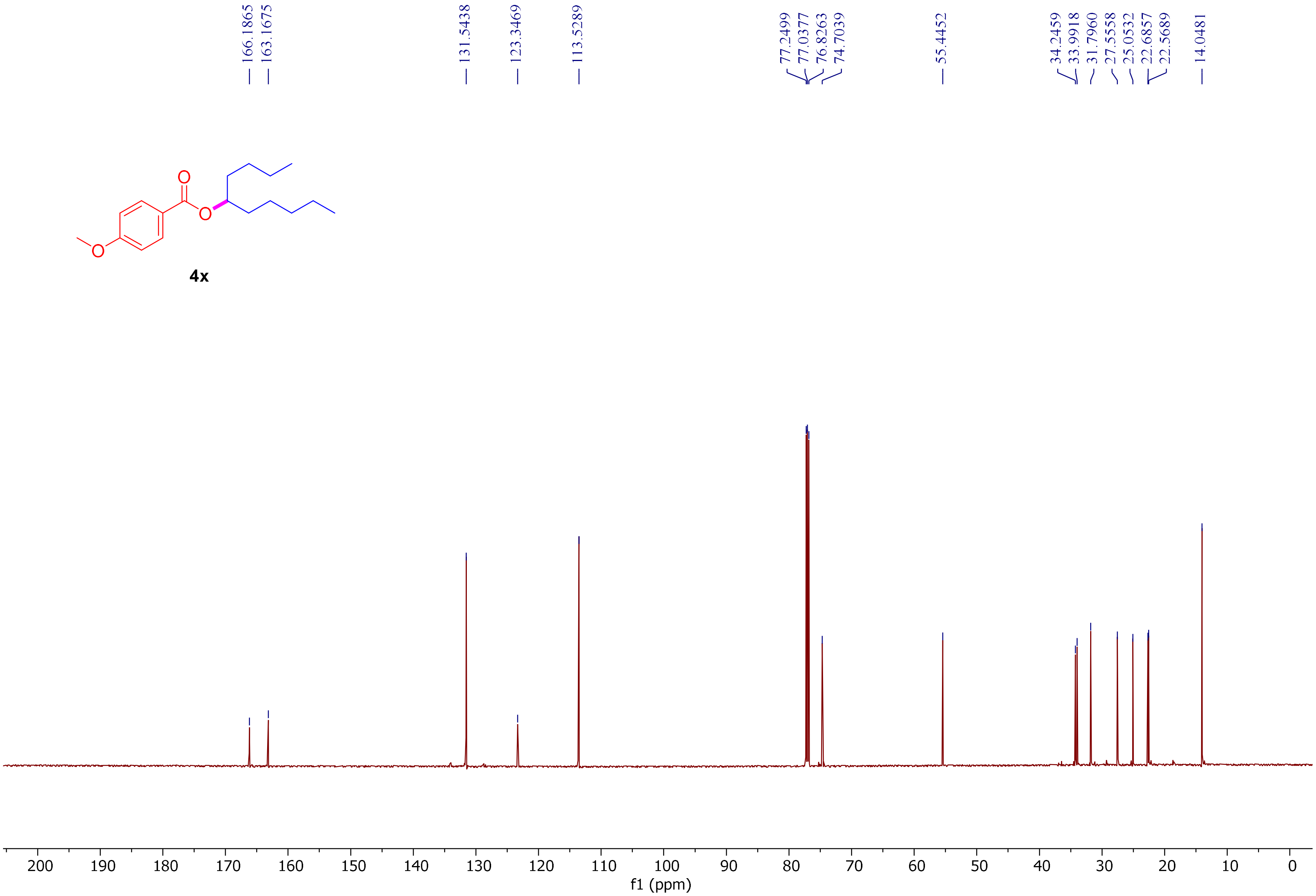
0.0
f1 (ppm)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113.5289
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77.0377
76.8263
74.7039
55.4452
34.2459
33.9918
31.7960
27.5558
25.0532
22.6857
22.5689
14.0481
4x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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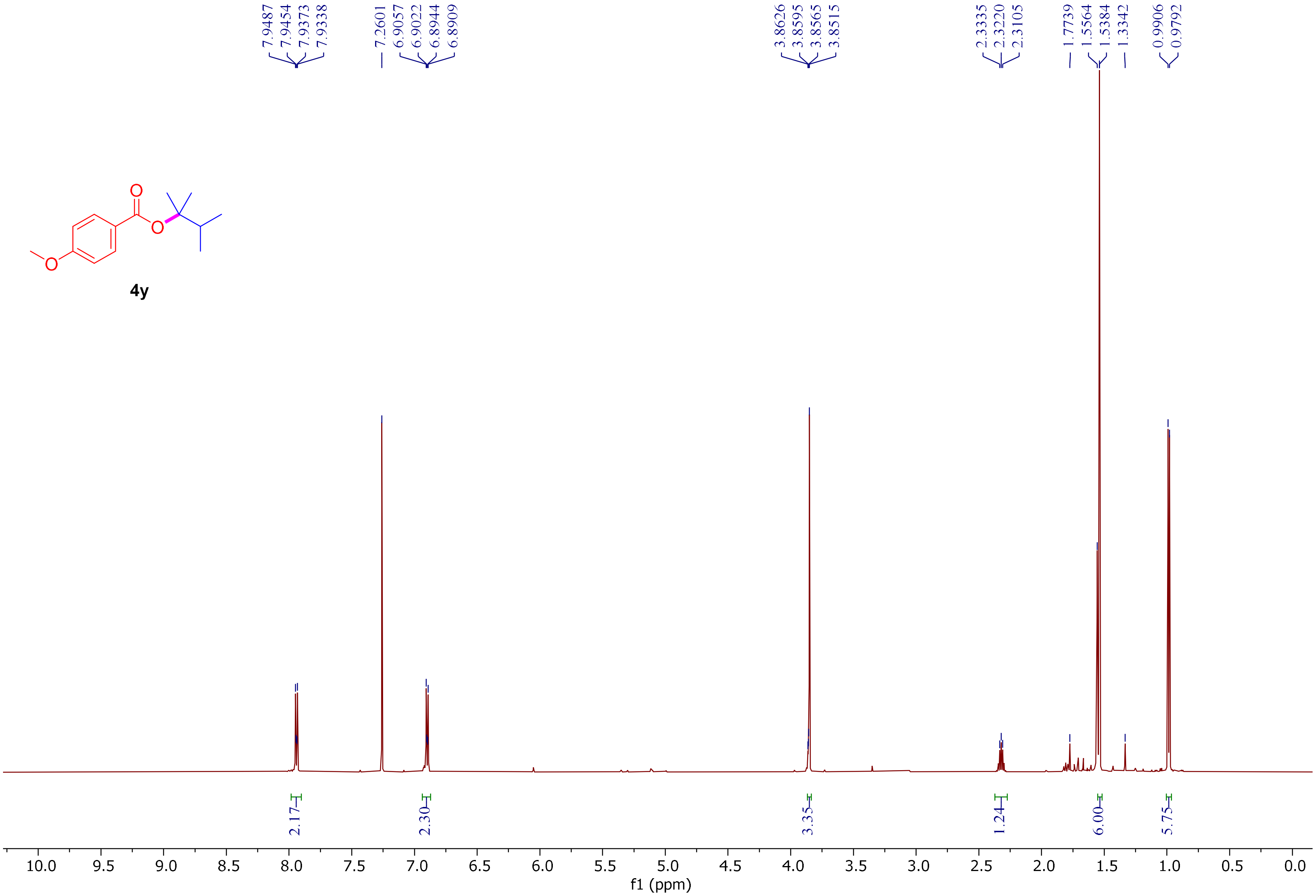
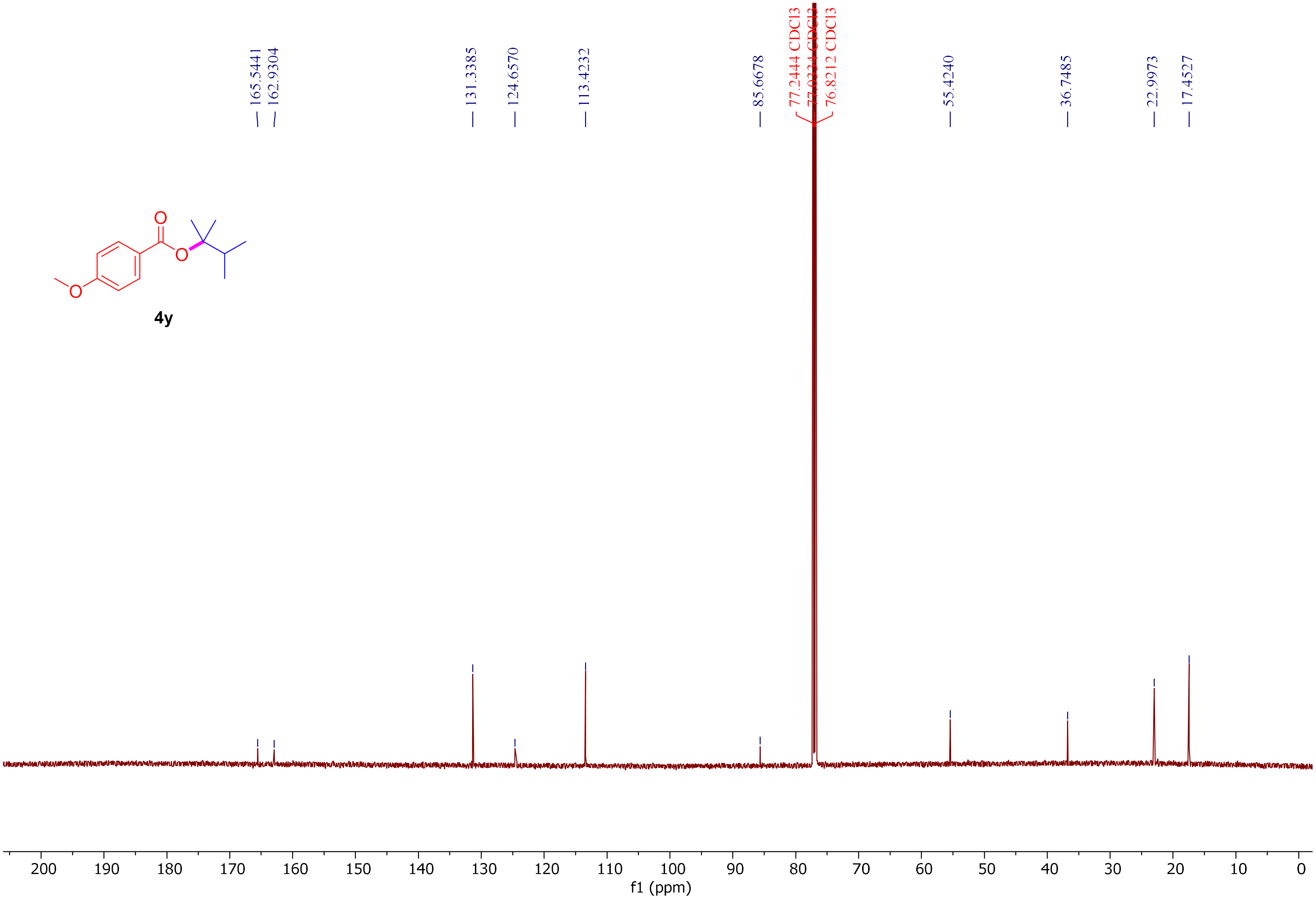
50
40
30
20
10
0
f1 (ppm)



4y

7.9487
7.9454
7.9373
7.9338
7.2601
6.9057
6.9022
6.8944
6.8909
3.8626
3.8595
3.8565
3.8515
2.3335
2.3220
2.3105
1.7739
1.5564
1.5384
1.3342
0.9906
0.9792
2.17
2.30
3.35
1.24
6.00
5.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.3385
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113.4232
85.6678
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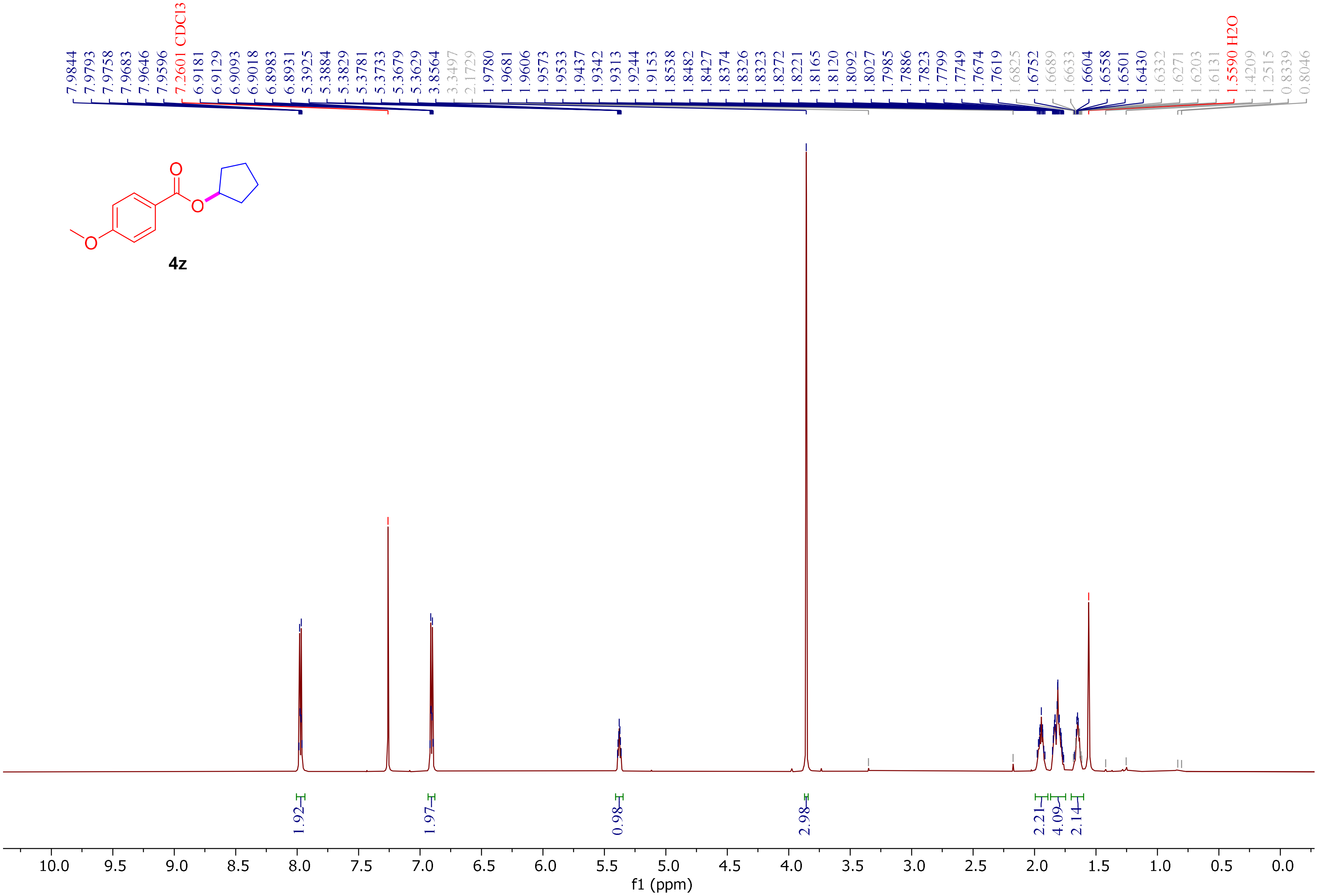
77.0328 CDCl3
76.8212 CDCl3
55.4240
36.7485
22.9973
17.4527
O
O
O
4y
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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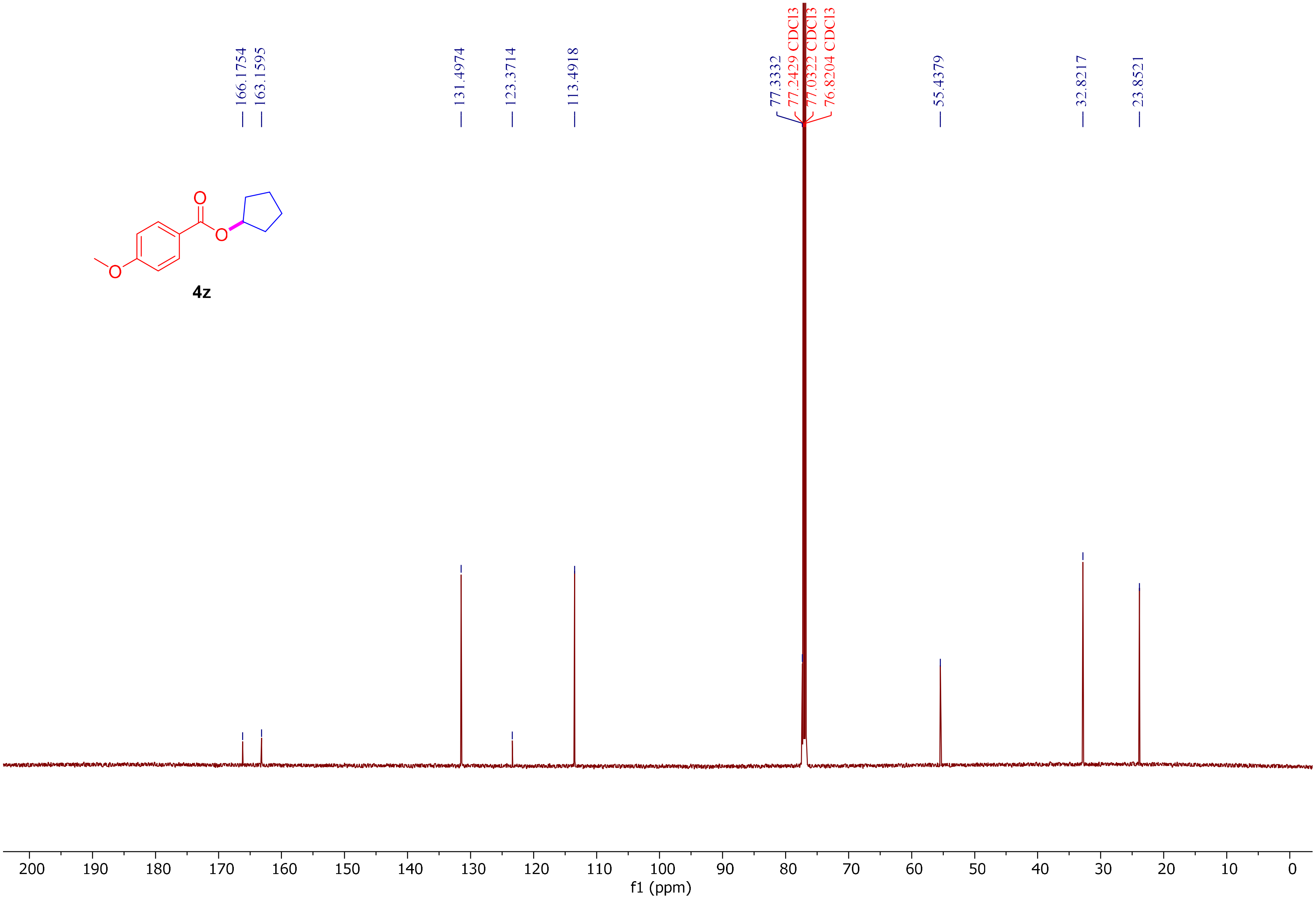
7.9646
7.9596
7.2601 CDCl3
6.9181
6.9129
6.9093
6.9018
6.8983
6.8931
5.3925
5.3884
5.3829
5.3781
5.3733
5.3679
5.3629
3.8564
3.3497
2.1729
1.9780
1.9681
1.9606
1.9573
1.9533
1.9437
1.9342
1.9313
1.9244
1.9153
1.8538
1.8482
1.8427
1.8374
1.8326
1.8323
1.8272
1.8221
1.8165
1.8120
1.8092
1.8027
1.7985
1.7886
1.7823
1.7799
1.7749
1.7674
1.7619
1.6825
1.6752
1.6689
1.6633
1.6604
1.6558
1.6501
1.6430
1.6332
1.6271
1.6203
1.6131
1.5590 H2O
1.4209
1.2515
0.8339
0.8046
O
O
O
1.92
1.97
0.98
2.98
2.21
4.09
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4z

166.1754
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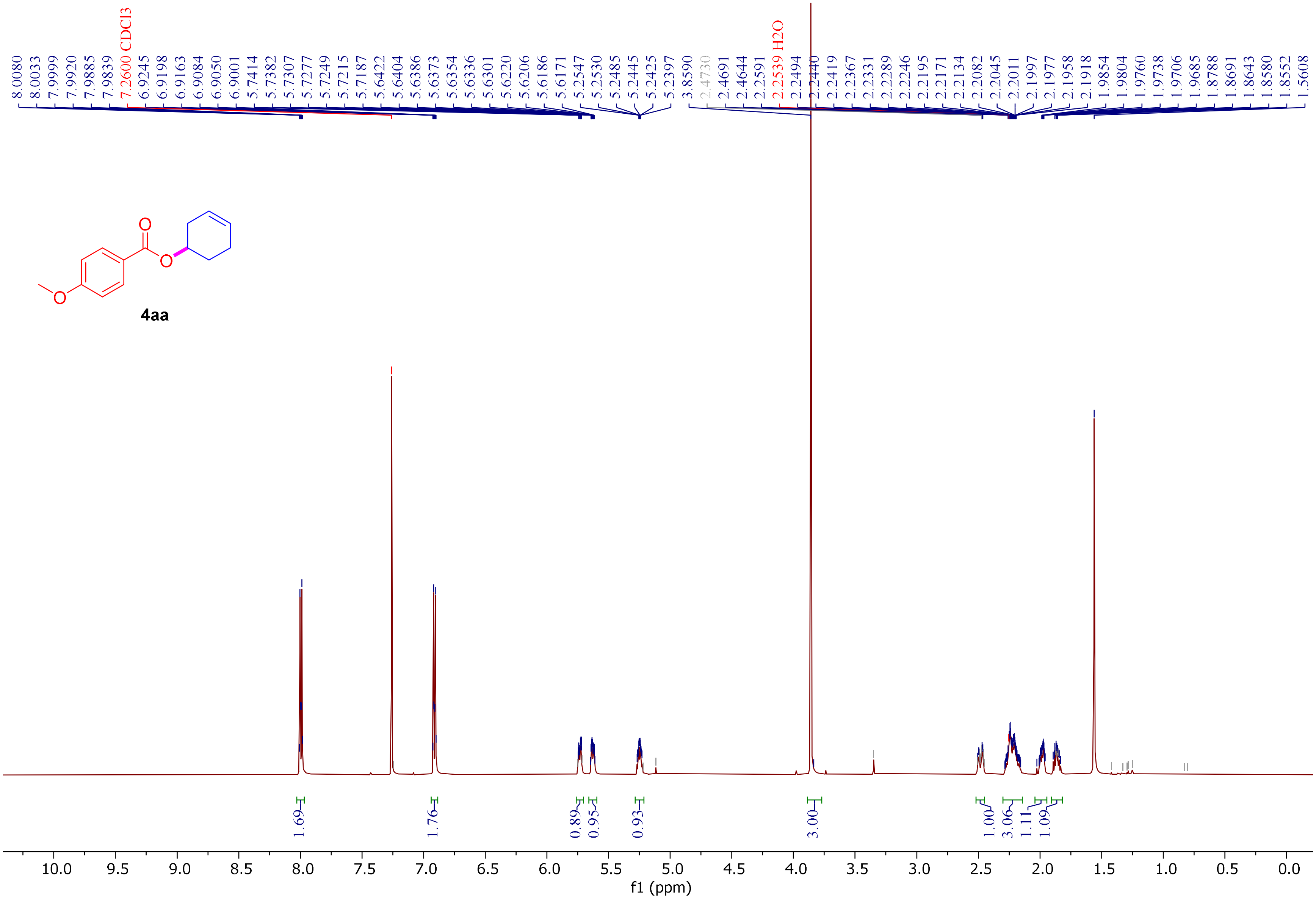
131.4974
123.3714
113.4918
77.3332
77.2429 CDCl3
77.0322 CDCl3
76.8204 CDCl3
55.4379
32.8217
23.8521
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.9885
7.9839
7.2600 CDCl3
6.9245
6.9198
6.9163
6.9084
6.9050
6.9001
5.7414
5.7382
5.7307
5.7277
5.7249
5.7215
5.7187
5.6422
5.6404
5.6386
5.6373
5.6354
5.6336
5.6301
5.6220
5.6206
5.6186
5.6171
5.2547
5.2530
5.2485
5.2445
5.2425
5.2397
3.8590
2.4730
2.4691
2.4644
2.2591
2.2539 H2O
2.2494
2.2440
2.2419
2.2367
2.2331
2.2289
2.2246
2.2195
2.2171
2.2134
2.2082
2.2045
2.2011
2.1997
2.1977
2.1958
2.1918
1.9854
1.9804
1.9760
1.9738
1.9706
1.9685
1.8788
1.8691
1.8643
1.8580
1.8552
1.5608
O
O
O
4aa
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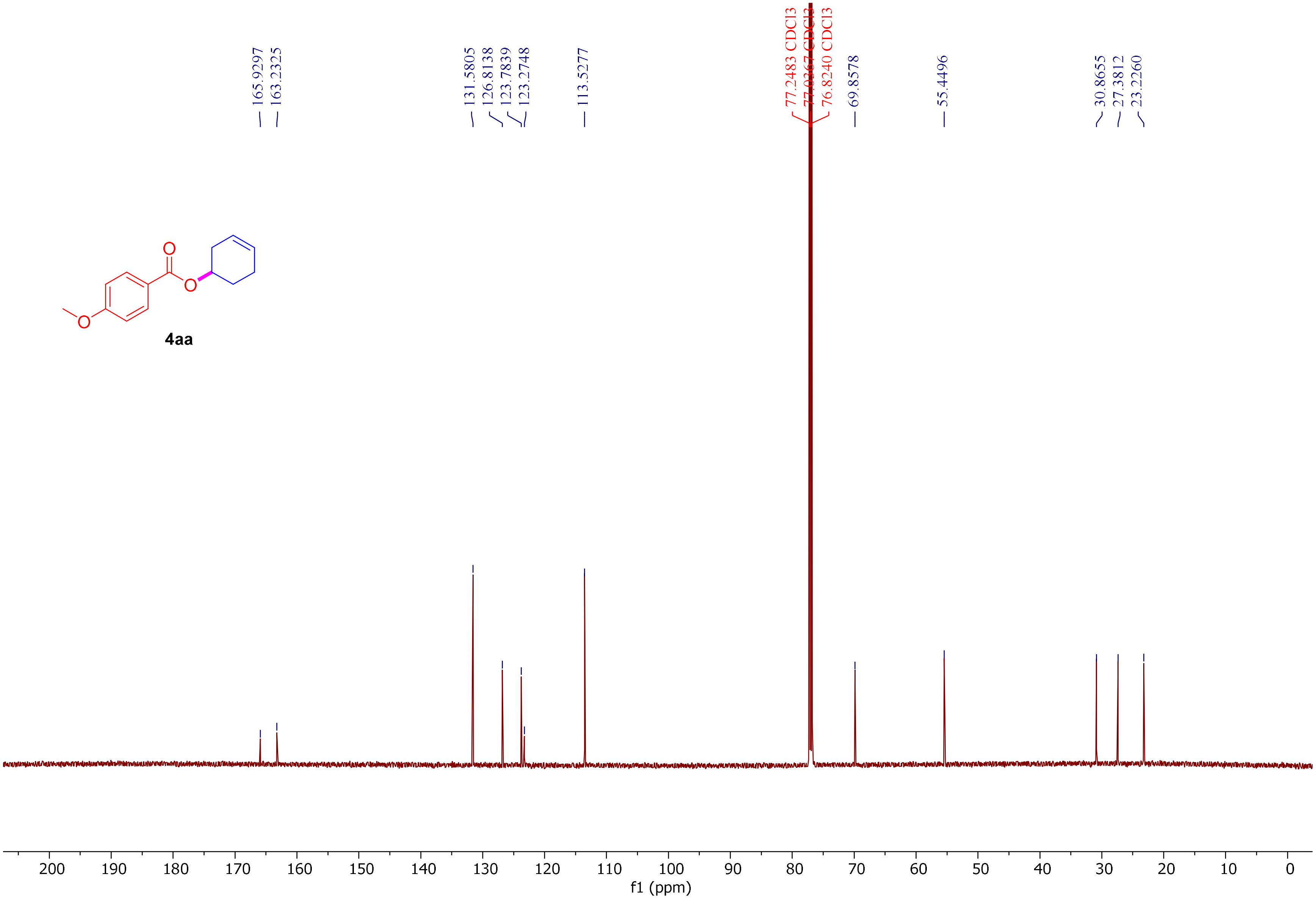
1.76
0.89
0.95
0.93
3.00
1.00
3.06
1.11
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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123.2748
113.5277
77.2483 CDCl3
77.0367 CDCl3
76.8240 CDCl3
69.8578
55.4496
30.8655
27.3812
23.2260
4aa
200
190
180
170
160
150
140
130
120
110
100
90
80
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50
40
30
20
10
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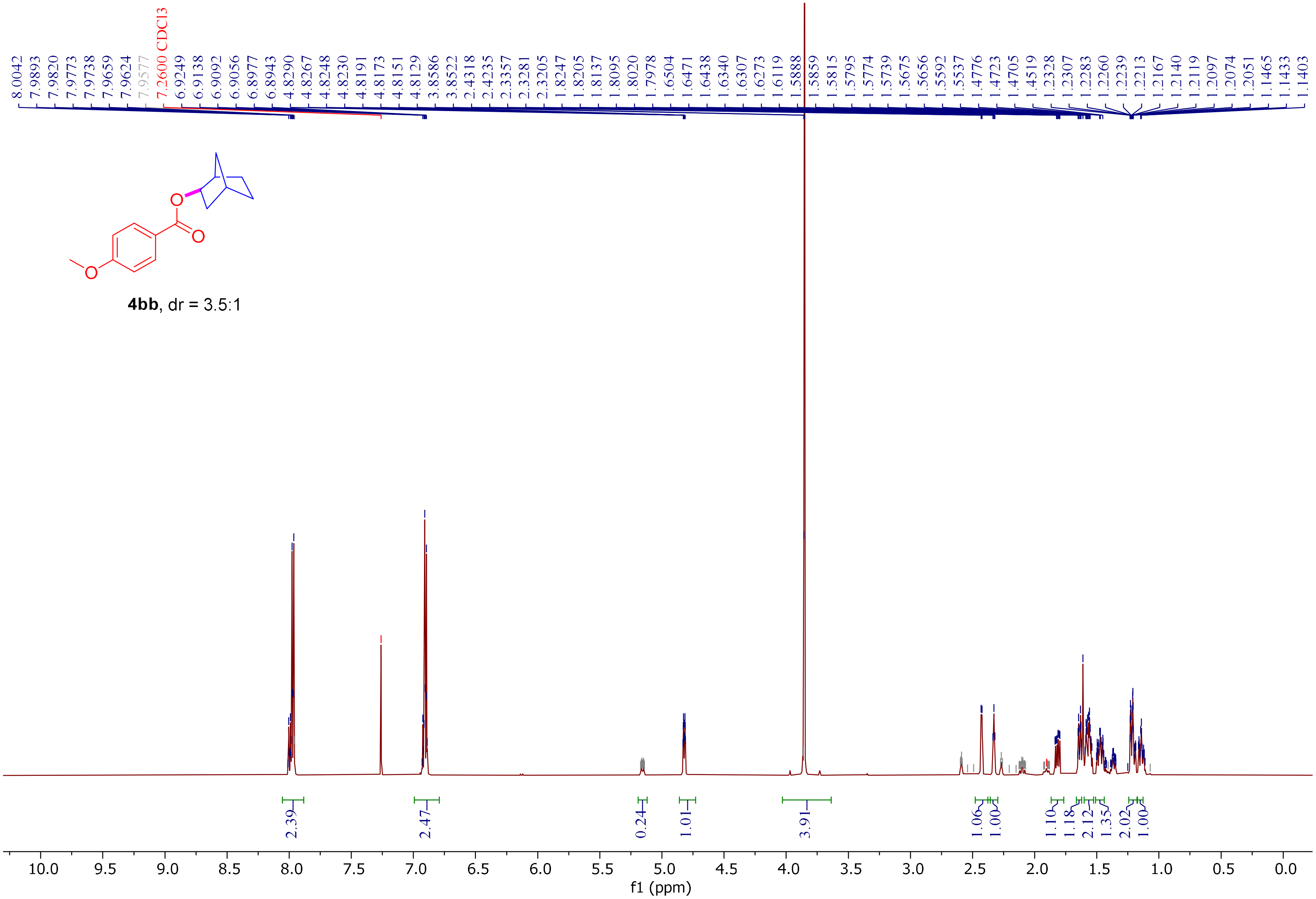
f1 (ppm)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7.9659
7.9624
7.9577
7.2600 CDCl3
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6.9138
6.9092
6.9056
6.8977
6.8943
4.8290
4.8267
4.8248
4.8230
4.8191
4.8173
4.8151
4.8129
3.8586
3.8522
2.4318
2.4235
2.3357
2.3281
2.3205
1.8247
1.8205
1.8137
1.8095
1.8020
1.7978
1.6504
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1.6438
1.6340
1.6307
1.6273
1.6119
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1.5859
1.5815
1.5795
1.5774
1.5739
1.5675
1.5656
1.5592
1.5537
1.4776
1.4723
1.4705
1.4519
1.2328
1.2307
1.2283
1.2260
1.2239
1.2213
1.2167
1.2140
1.2119
1.2097
1.2074
1.2051
1.1465
1.1433
1.1403
O
O
O
2.39
2.47
0.24
1.01
3.91
1.06
1.00
1.10
1.18
2.12
1.35
2.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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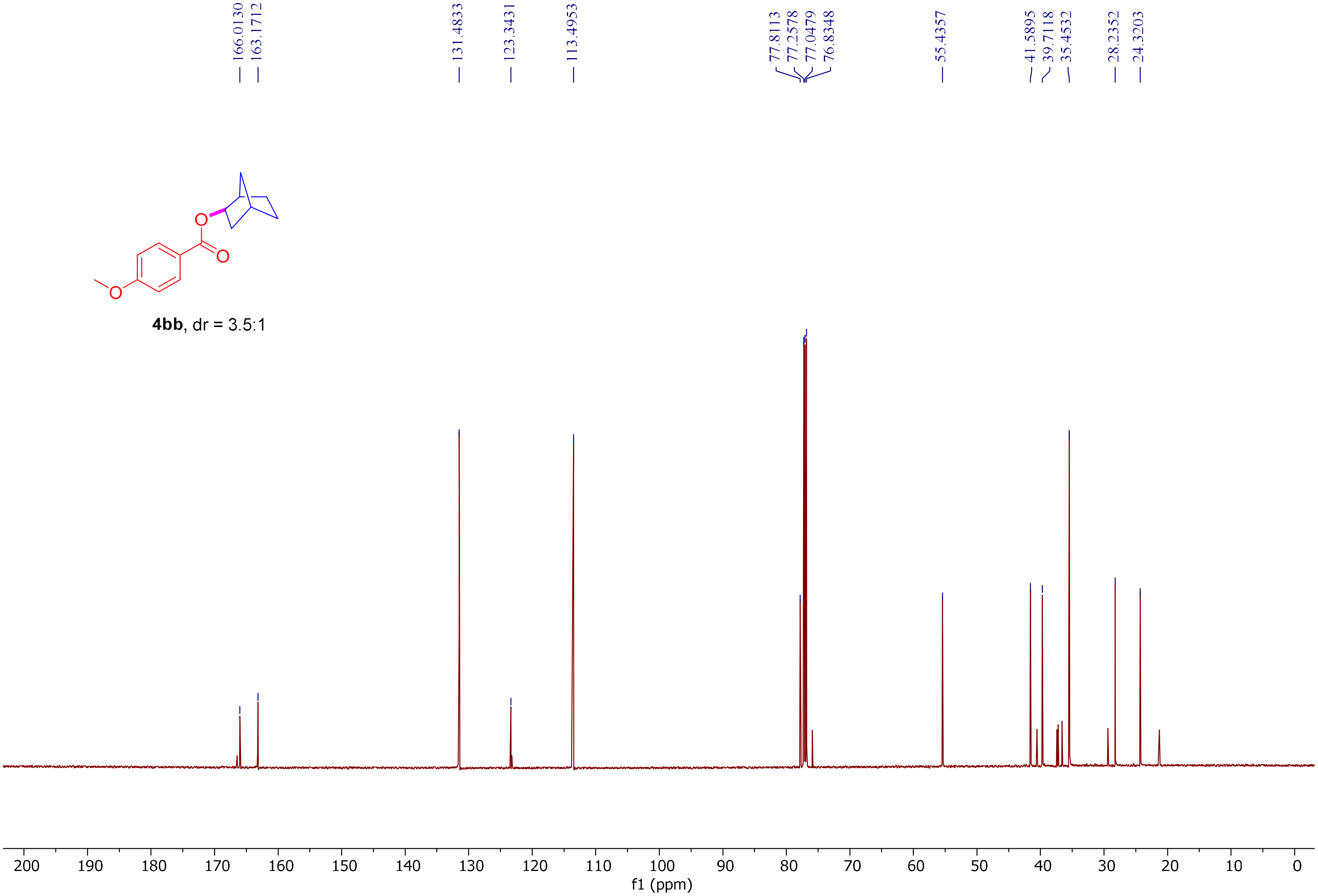
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4bb, dr = 3.5:1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77.0479
76.8348
55.4357
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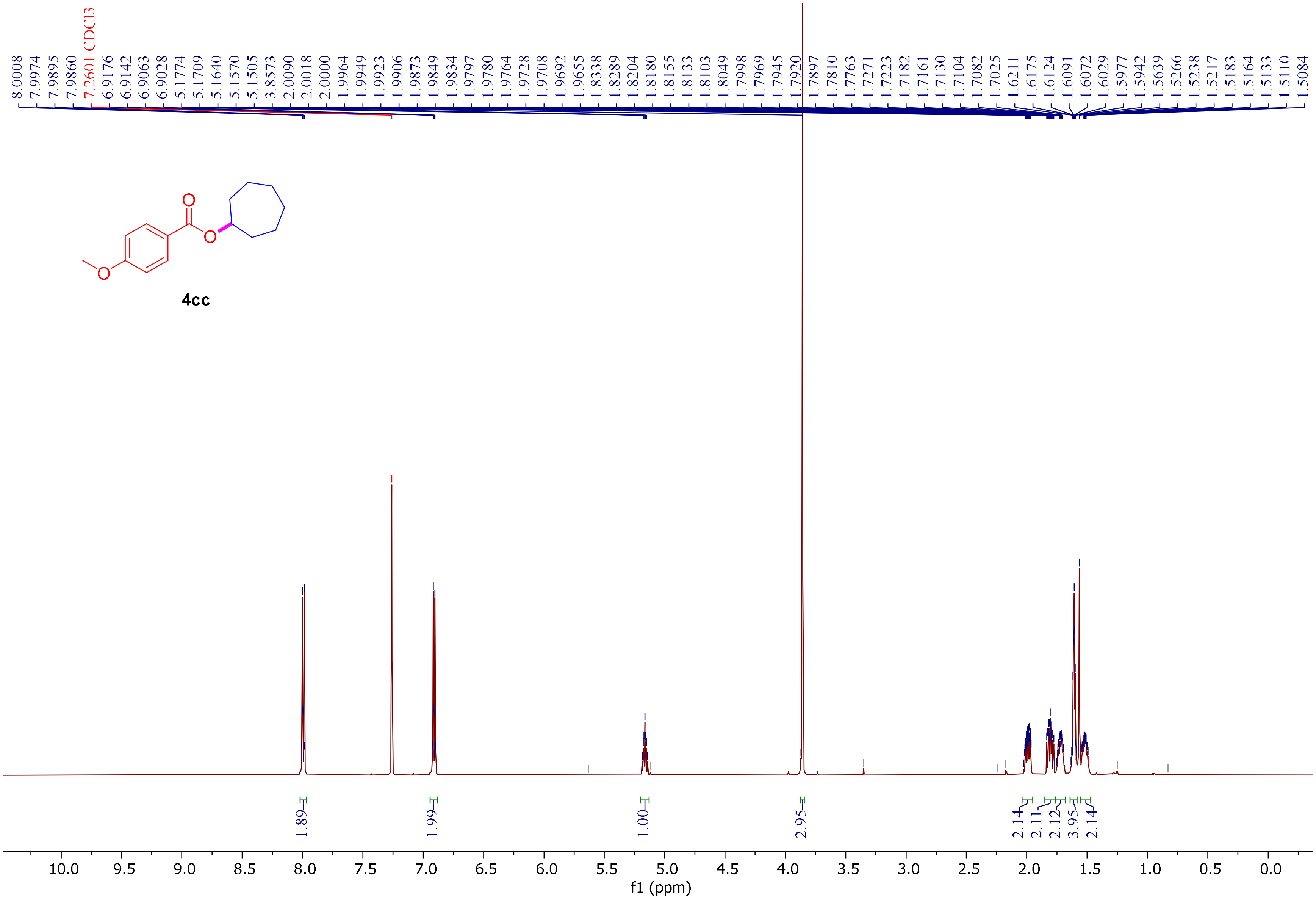
39.7118
35.4532
28.2352
24.3203
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4bb, dr = 3.5:1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6.9028
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5.1709
5.1640
5.1570
5.1505
3.8573
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2.0018
2.0000
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1.9949
1.9923
1.9906
1.9873
1.9849
1.9834
1.9797
1.9780
1.9764
1.9728
1.9708
1.9692
1.9655
1.8338
1.8289
1.8204
1.8180
1.8155
1.8133
1.8103
1.8049
1.7998
1.7969
1.7945
1.7920
1.7897
1.7810
1.7763
1.7271
1.7223
1.7182
1.7161
1.7130
1.7104
1.7082
1.7025
1.6211
1.6175
1.6124
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1.6072
1.6029
1.5977
1.5942
1.5639
1.5266
1.5238
1.5217
1.5183
1.5164
1.5133
1.5110
1.5084
O
O
O
4cc
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1.99
1.00
2.95
2.14
2.11
2.12
3.95
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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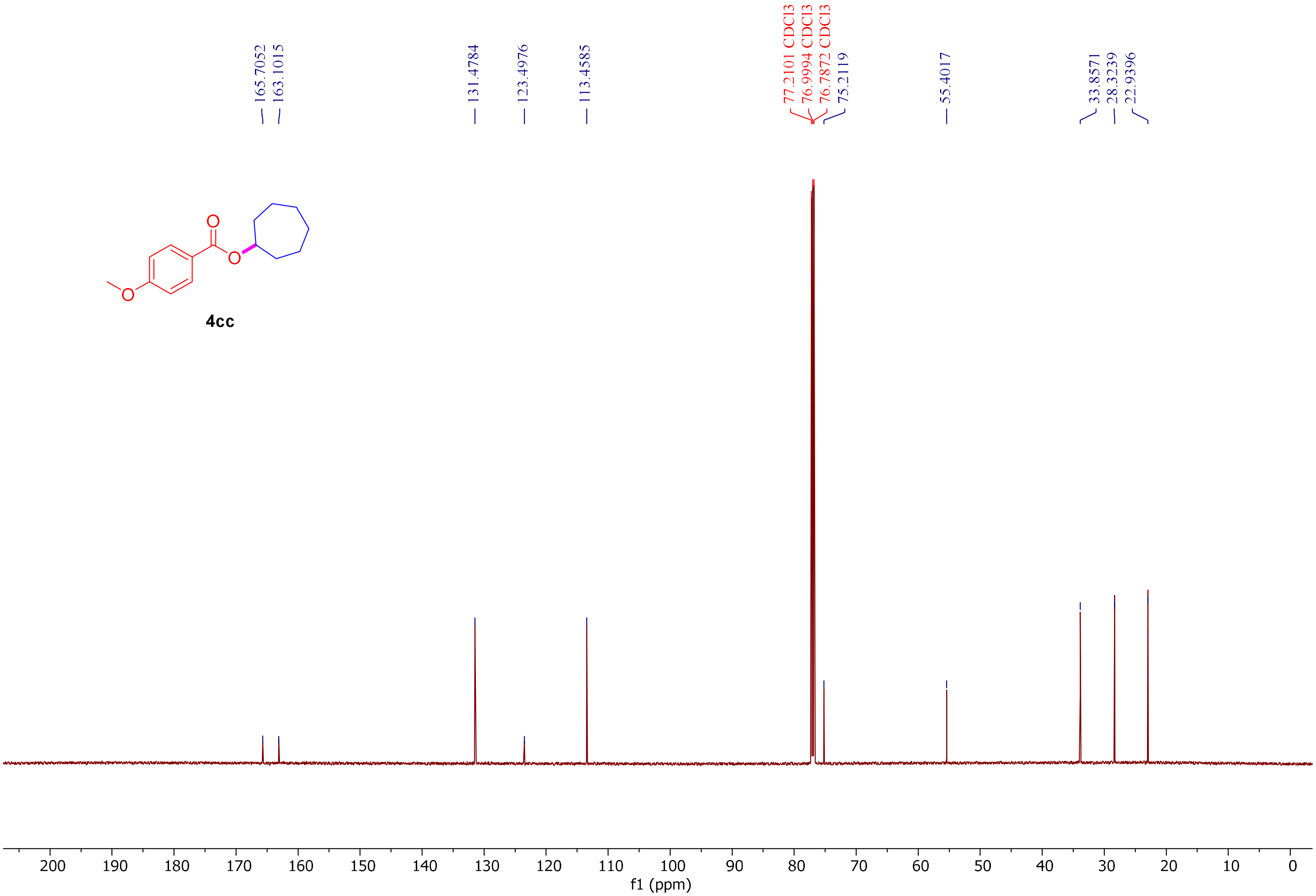
1.0
0.5
0.0
f1 (ppm)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113.4585
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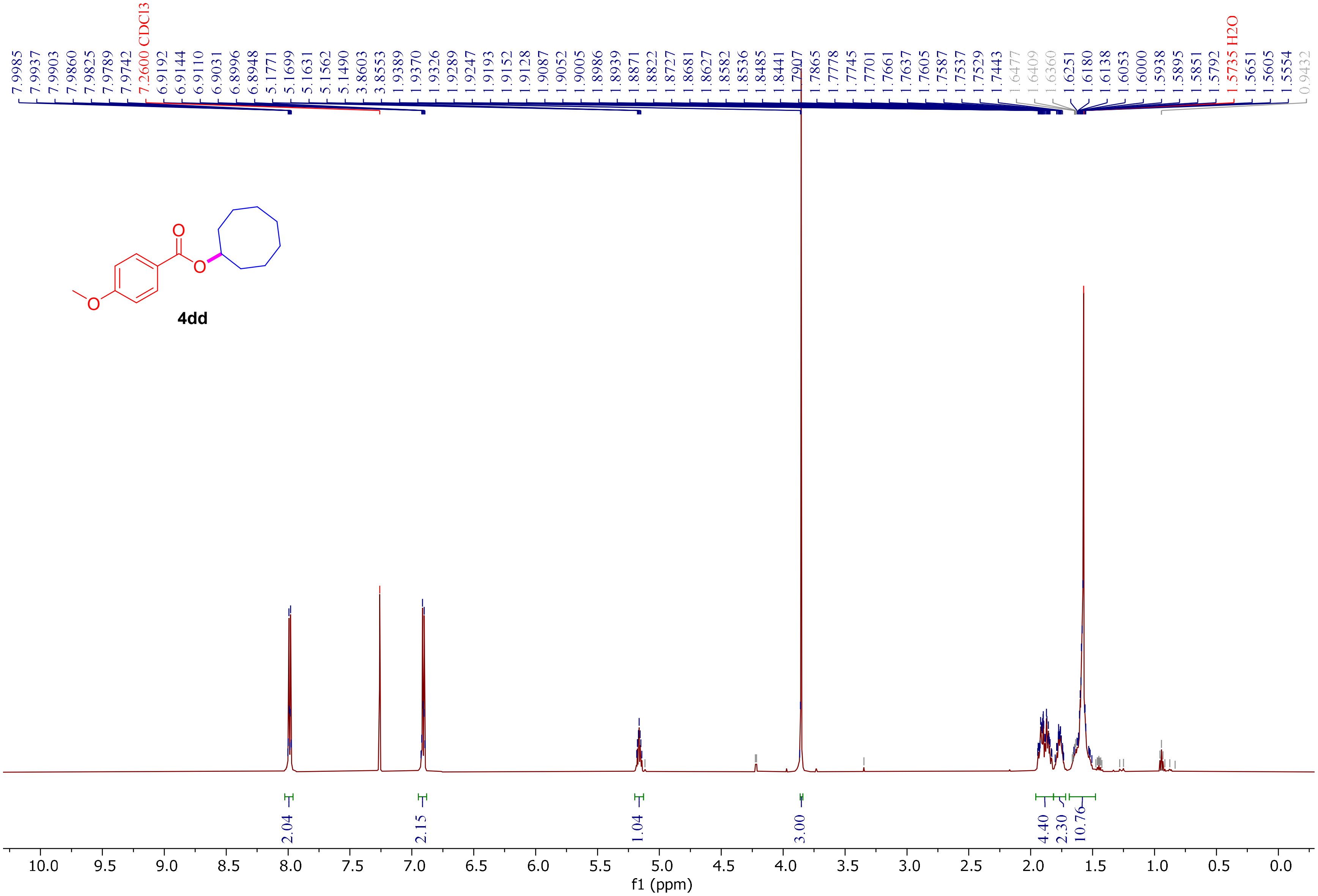
76.9994 CDCl3
76.7872 CDCl3
75.2119
55.4017
33.8571
28.3239
22.9396
4cc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.9937
7.9903
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7.9825
7.9789
7.9742
7.2600 CDCl3
6.9192
6.9144
6.9110
6.9031
6.8996
6.8948
5.1771
5.1699
5.1631
5.1562
5.1490
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3.8553
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1.9370
1.9326
1.9289
1.9247
1.9193
1.9152
1.9128
1.9087
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1.6138
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1.5938
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1.5851
1.5792
1.5735 H2O
1.5651
1.5605
1.5554
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O
O
O
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2.15
1.04
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8.0
7.5
7.0
6.5
6.0
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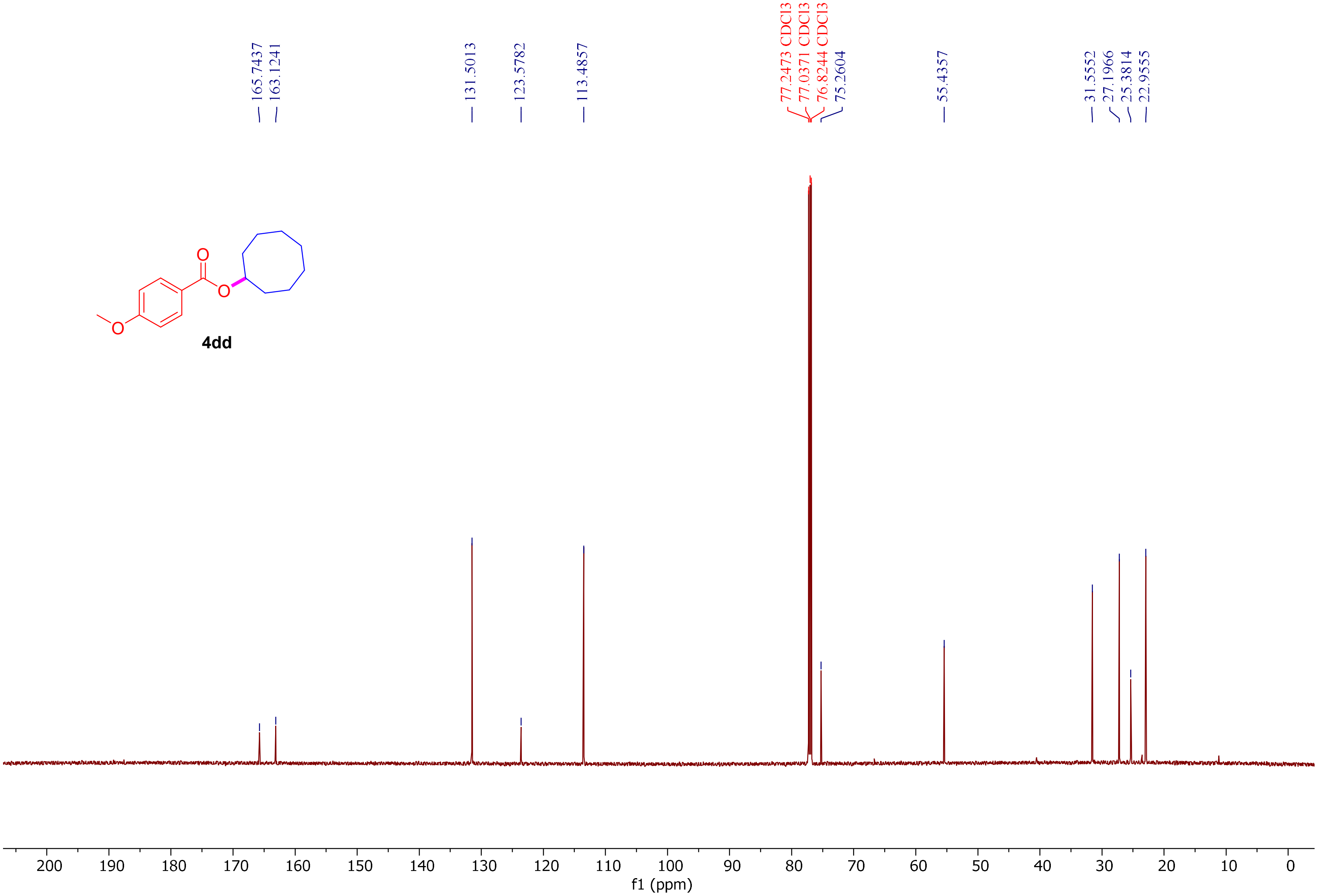
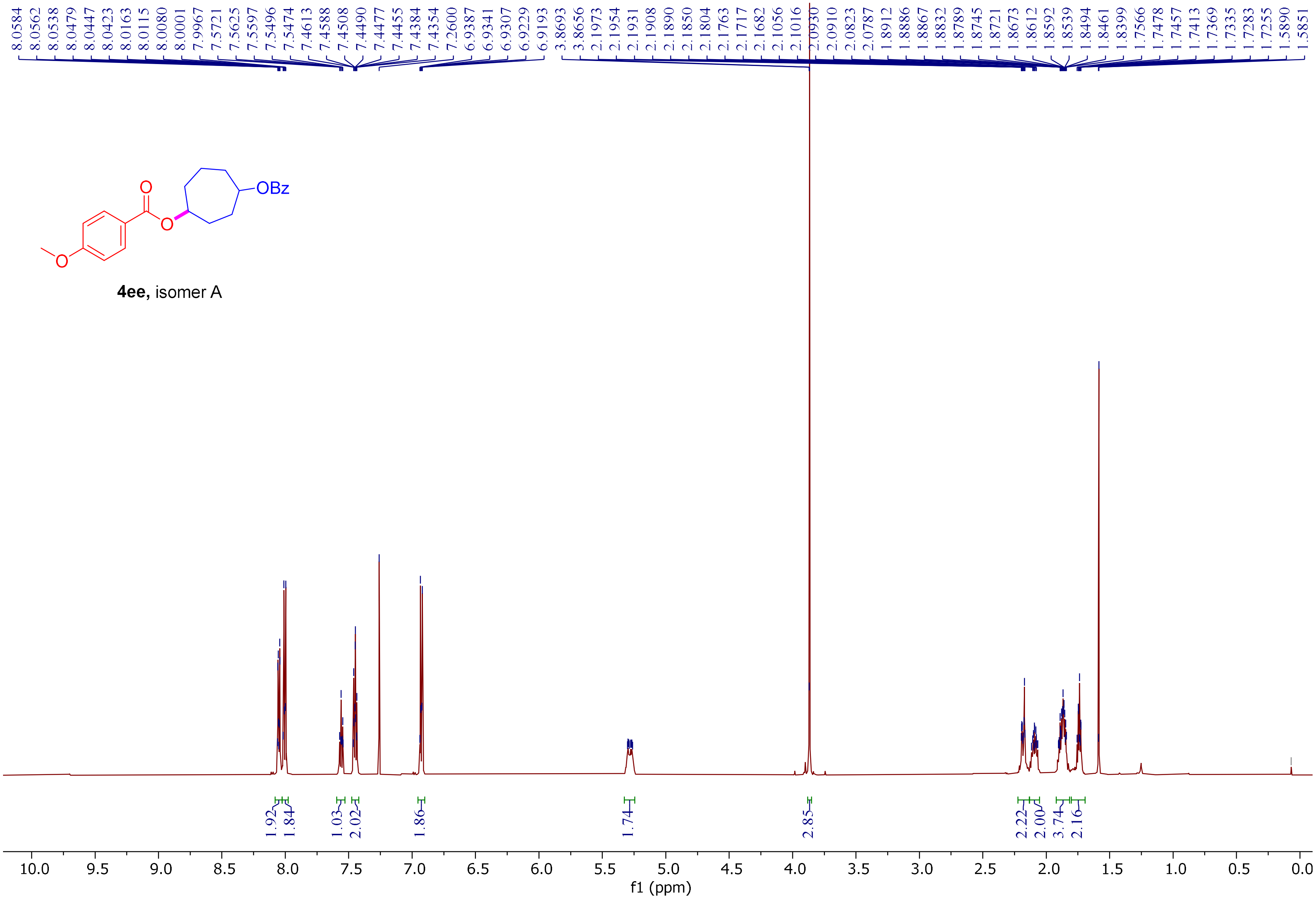
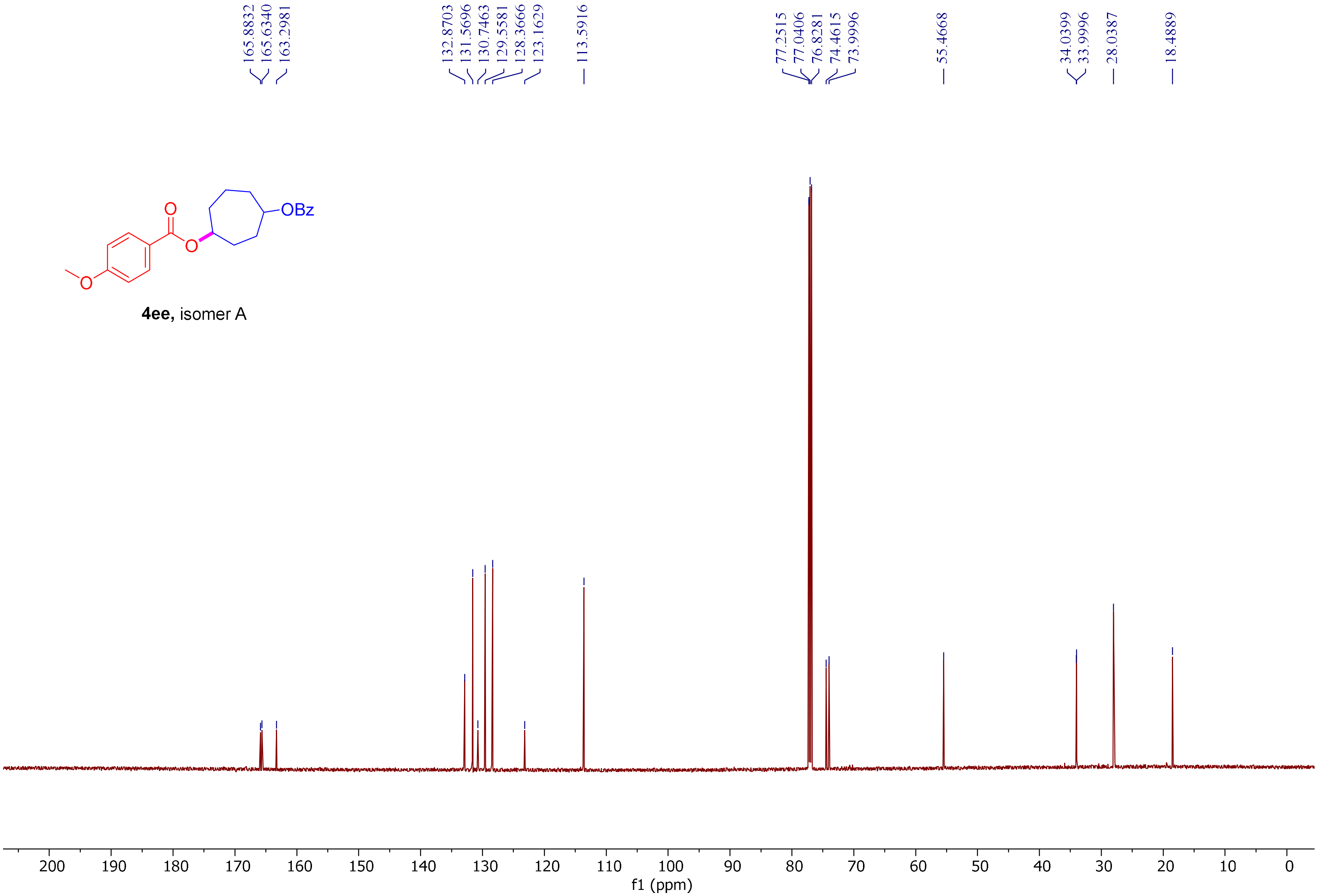
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4dd

165.7437
163.1241
131.5013
123.5782
113.4857
77.2473 CDCl3
77.0371 CDCl3
76.8244 CDCl3
75.2604
55.4357
31.5552
27.1966
25.3814
22.9555
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4ee, isomer A
O
O
O
OBz
8.0584
8.0562
8.0538
8.0479
8.0447
8.0423
8.0163
8.0115
8.0080
8.0001
7.9967
7.5721
7.5625
7.5597
7.5496
7.5474
7.4613
7.4588
7.4508
7.4490
7.4477
7.4455
7.4384
7.4354
7.2600
6.9387
6.9341
6.9307
6.9229
6.9193
3.8693
3.8656
2.1973
2.1954
2.1931
2.1908
2.1890
2.1850
2.1804
2.1763
2.1717
2.1682
2.1056
2.1016
2.0930
2.0910
2.0823
2.0787
1.8912
1.8886
1.8867
1.8832
1.8789
1.8745
1.8721
1.8673
1.8612
1.8592
1.8539
1.8494
1.8461
1.8399
1.7566
1.7478
1.7457
1.7413
1.7369
1.7335
1.7283
1.7255
1.5890
1.5851
1.92
1.84
1.03
2.02
1.86
1.74
2.85
2.22
2.00
3.74
2.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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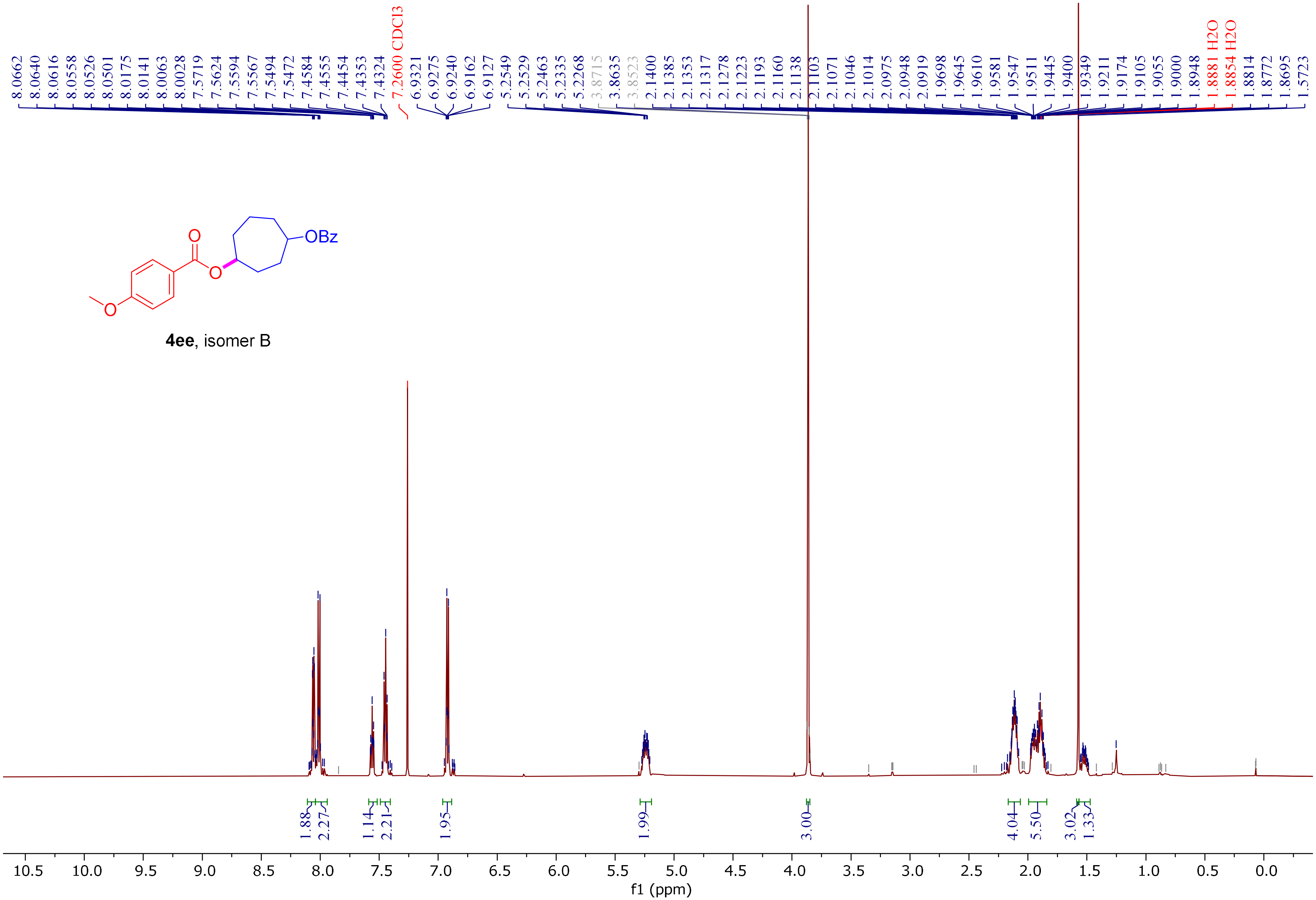
163.2981
132.8703
131.5696
130.7463
129.5581
128.3666
123.1629
113.5916
77.2515
77.0406
76.8281
74.4615
73.9996
55.4668
34.0399
33.9996
28.0387
18.4889
O
O
OBz
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4ee, isomer A

O
O
O
OBz

4ee, isomer B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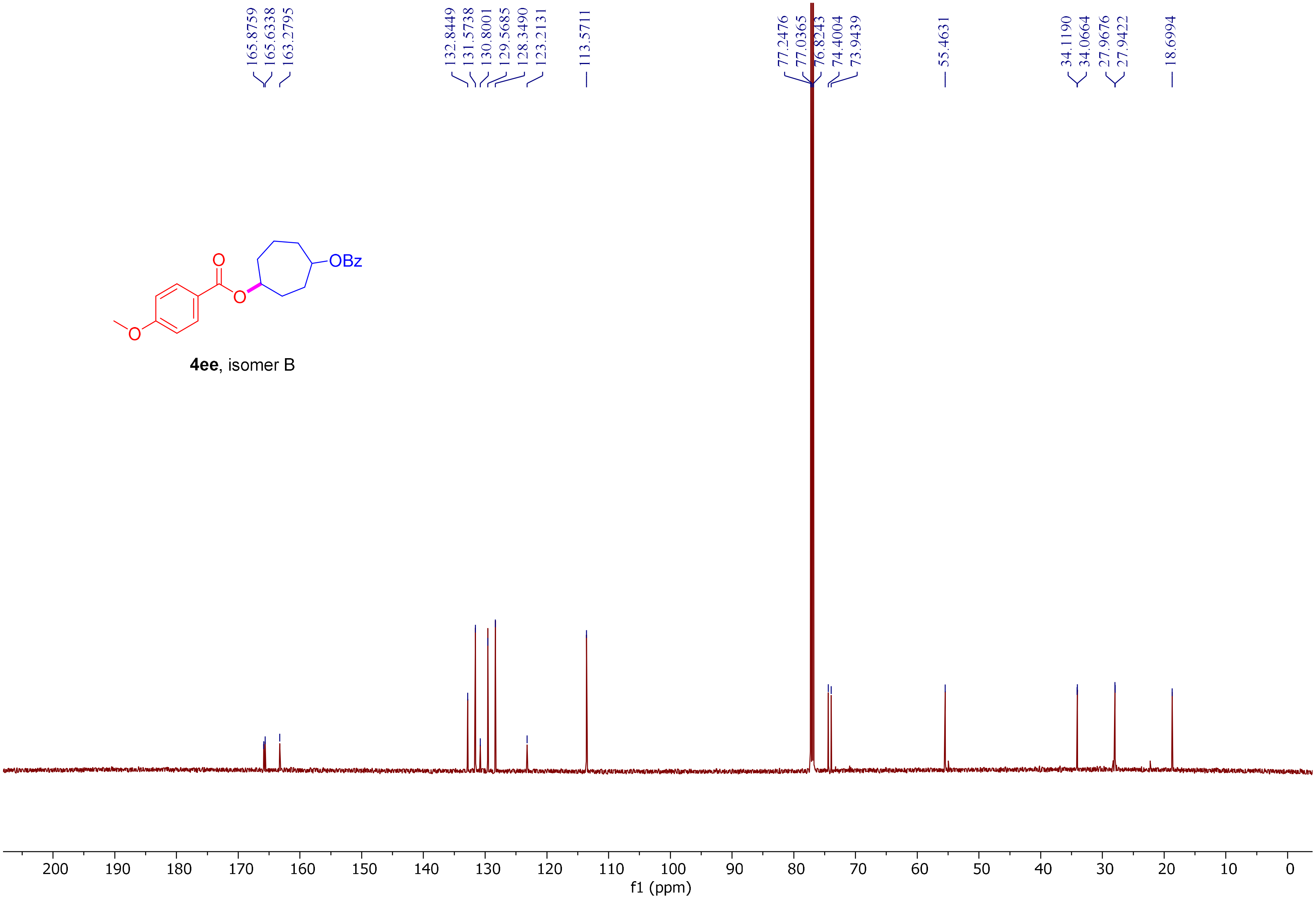
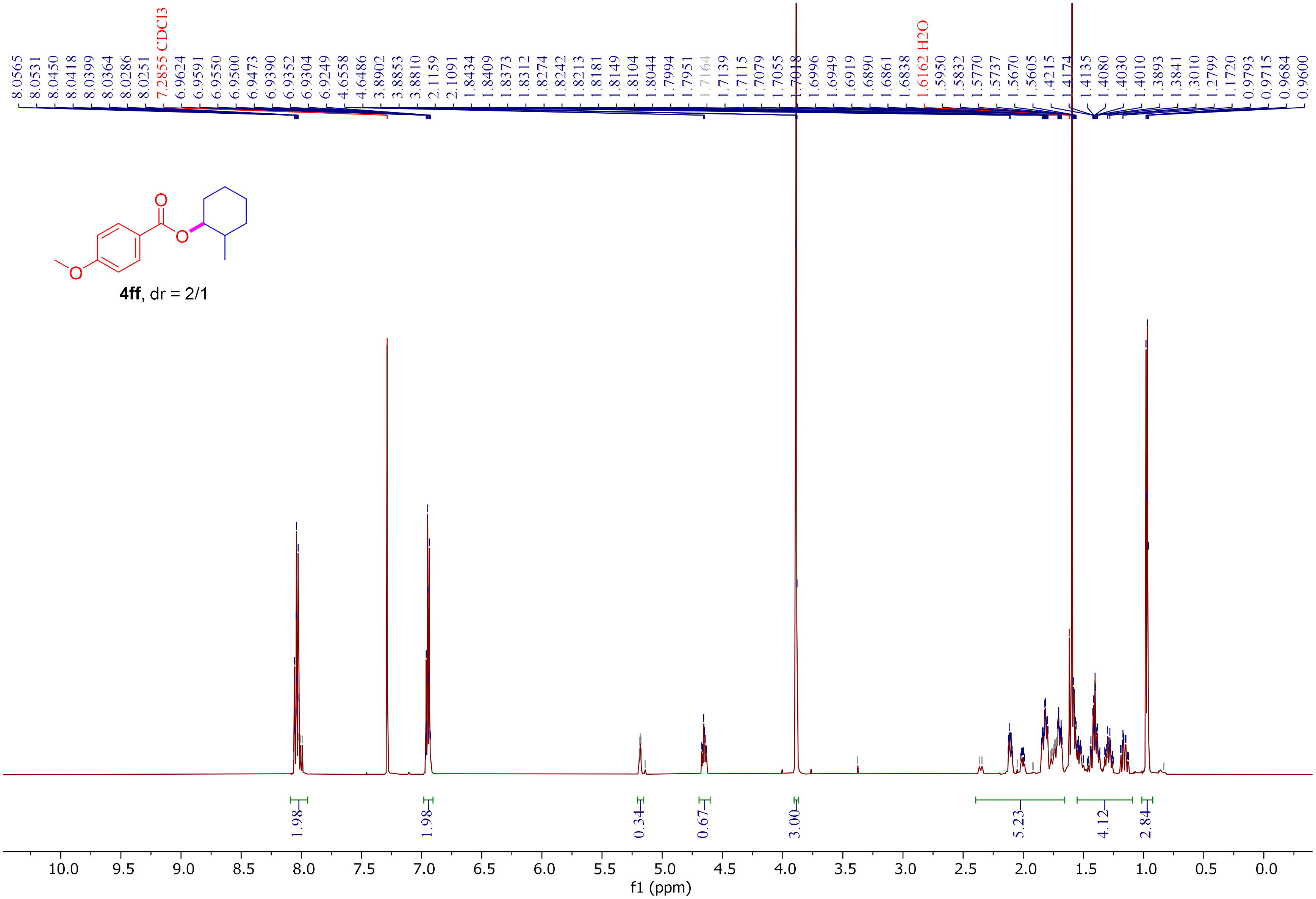
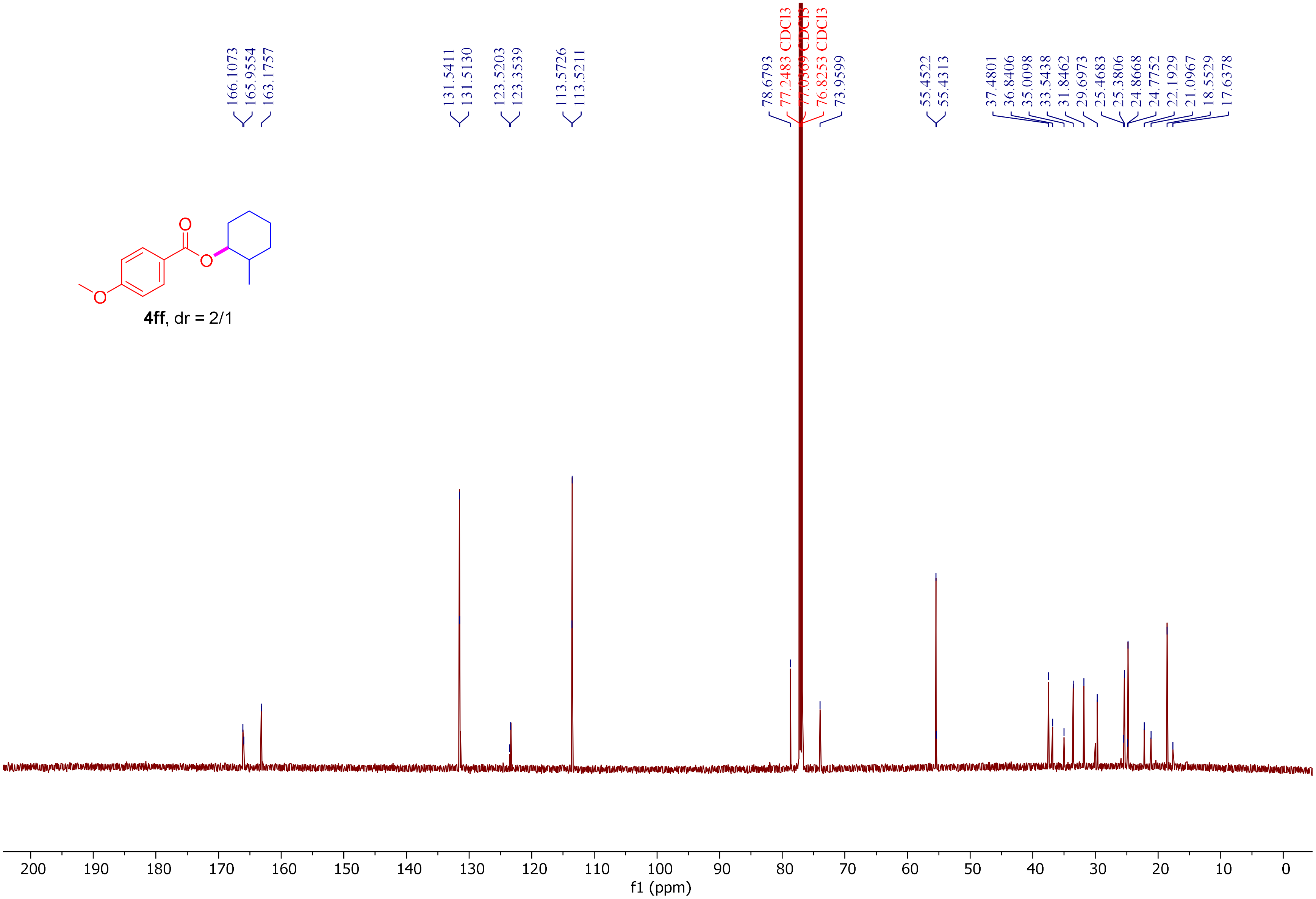
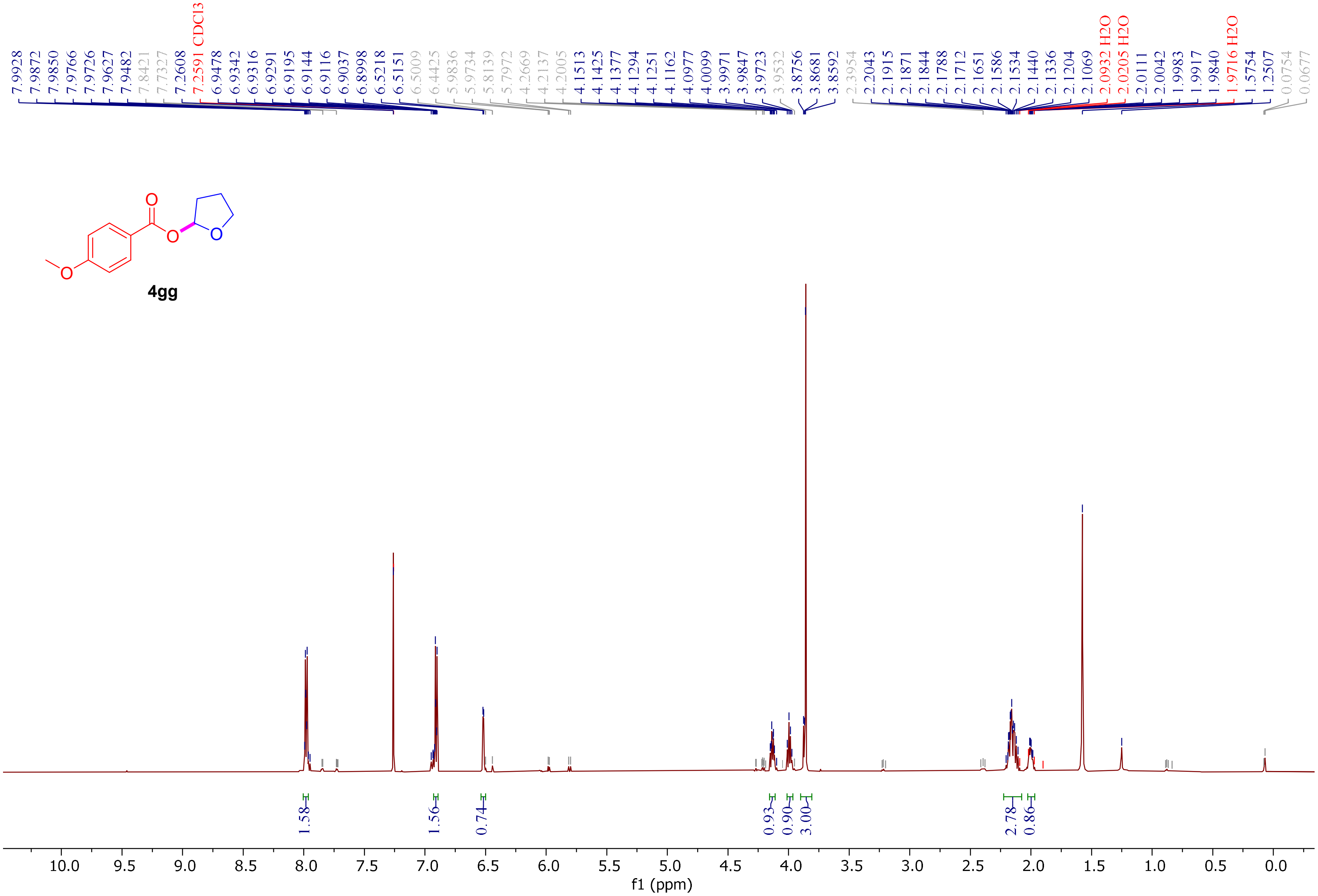
8.0640
8.0616
8.0558
8.0526
8.0501
8.0175
8.0141
8.0063
8.0028
7.5719
7.5624
7.5594
7.5567
7.5494
7.5472
7.4584
7.4555
7.4454
7.4353
7.4324
7.2600 CDCl3
6.9321
6.9275
6.9240
6.9162
6.9127
5.2549
5.2529
5.2463
5.2335
5.2268
3.8715
3.8635
3.8523
2.1400
2.1385
2.1353
2.1317
2.1278
2.1223
2.1193
2.1160
2.1138
2.1103
2.1071
2.1046
2.1014
2.0975
2.0948
2.0919
1.9698
1.9645
1.9610
1.9581
1.9547
1.9511
1.9445
1.9400
1.9349
1.9211
1.9174
1.9105
1.9055
1.9000
1.8948
1.8881 H2O
1.8854 H2O
1.8814
1.8772
1.8695
1.5723
1.88
2.27
1.14
2.21
1.95
1.99
3.00
4.04
5.50
3.02
1.33
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

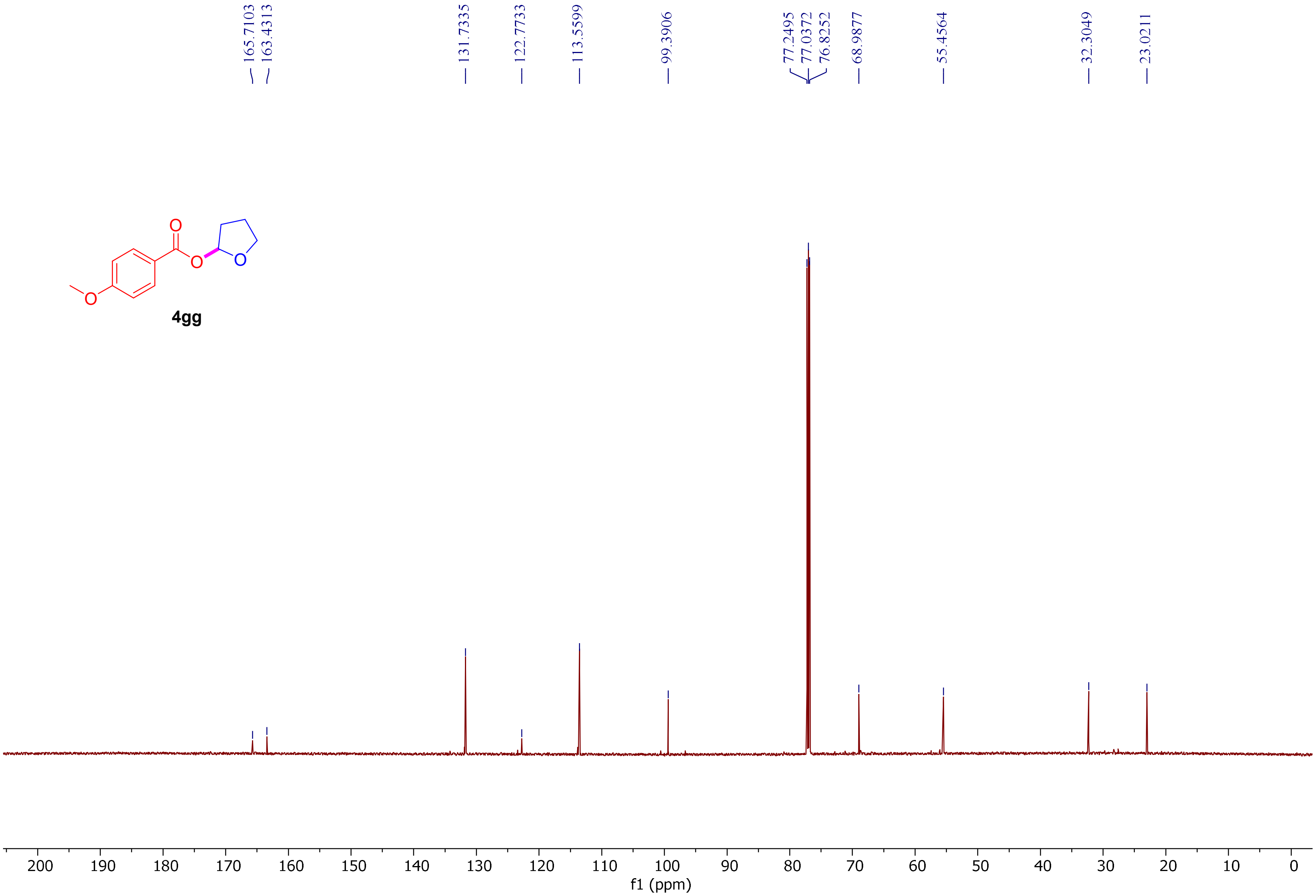

165.8759
165.6338
163.2795
132.8449
131.5738
130.8001
129.5685
128.3490
123.2131
113.5711
77.2476
77.0365
76.8243
74.4004
73.9439
55.4631
34.1190
34.0664
27.9676
27.9422
18.6994
O
O
O
OBz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4ee, isomer B


4ff, dr = 2/1
8.0565
8.0531
8.0450
8.0418
8.0399
8.0364
8.0286
8.0251
7.2855 CDCl3
6.9624
6.9591
6.9550
6.9500
6.9473
6.9390
6.9352
6.9304
6.9249
4.6558
4.6486
3.8902
3.8853
3.8810
2.1159
2.1091
1.8434
1.8409
1.8373
1.8312
1.8274
1.8242
1.8213
1.8181
1.8149
1.8104
1.8044
1.7994
1.7951
1.7164
1.7139
1.7115
1.7079
1.7055
1.7018
1.6996
1.6949
1.6919
1.6890
1.6861
1.6838
1.6162 H2O
1.5950
1.5832
1.5770
1.5737
1.5670
1.5605
1.4215
1.4174
1.4135
1.4080
1.4030
1.4010
1.3893
1.3841
1.3010
1.2799
1.1720
0.9793
0.9715
0.9684
0.9600
1.98
1.98
0.34
0.67
3.00
5.23
4.12
2.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.1073
165.9554
163.1757
131.5411
131.5130
123.5203
123.3539
113.5726
113.5211
78.6793
77.2483 CDCl3
77.0369 CDCl3
76.8253 CDCl3
73.9599
55.4522
55.4313
37.4801
36.8406
35.0098
33.5438
31.8462
29.6973
25.4683
25.3806
24.8668
24.7752
22.1929
21.0967
18.5529
17.6378
O
O
O
4ff, dr = 2/1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9928
7.9872
7.9850
7.9766
7.9726
7.9627
7.9482
7.8421
7.7327
7.2608
7.2591 CDCl3
6.9478
6.9342
6.9316
6.9291
6.9195
6.9144
6.9116
6.9037
6.8998
6.5218
6.5151
6.5009
6.4425
5.9836
5.9734
5.8139
5.7972
4.2669
4.2137
4.2005
4.1513
4.1425
4.1377
4.1294
4.1251
4.1162
4.0977
4.0099
3.9971
3.9847
3.9723
3.9532
3.8756
3.8681
3.8592
2.3954
2.2043
2.1915
2.1871
2.1844
2.1788
2.1712
2.1651
2.1586
2.1534
2.1440
2.1336
2.1204
2.1069
2.0932 H2O
2.0205 H2O
2.0111
2.0042
1.9983
1.9917
1.9840
1.9716 H2O
1.5754
1.2507
0.0754
0.0677
O
O
O
O
4gg
1.58
1.56
0.74
0.93
0.90
3.00
2.78
0.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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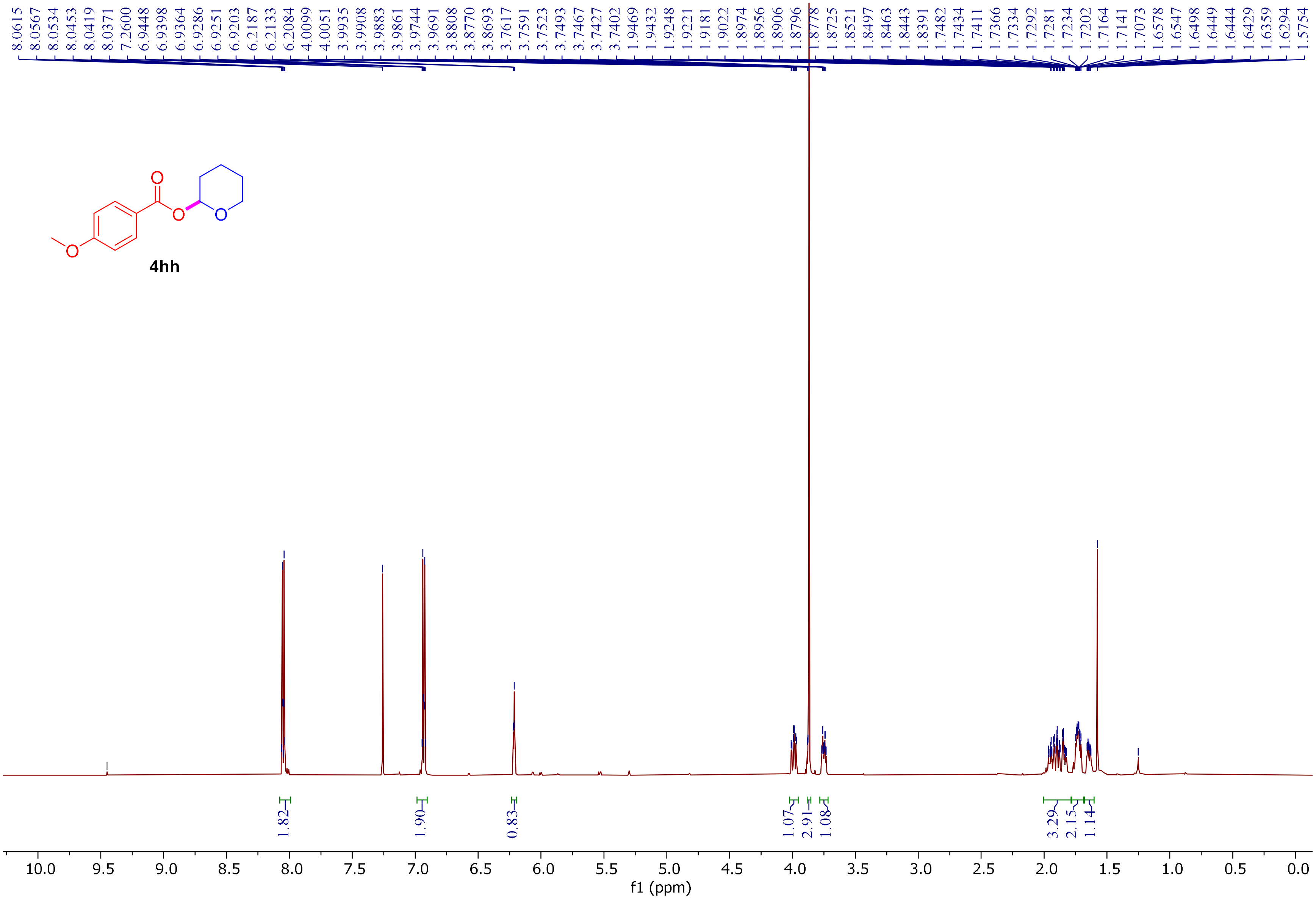
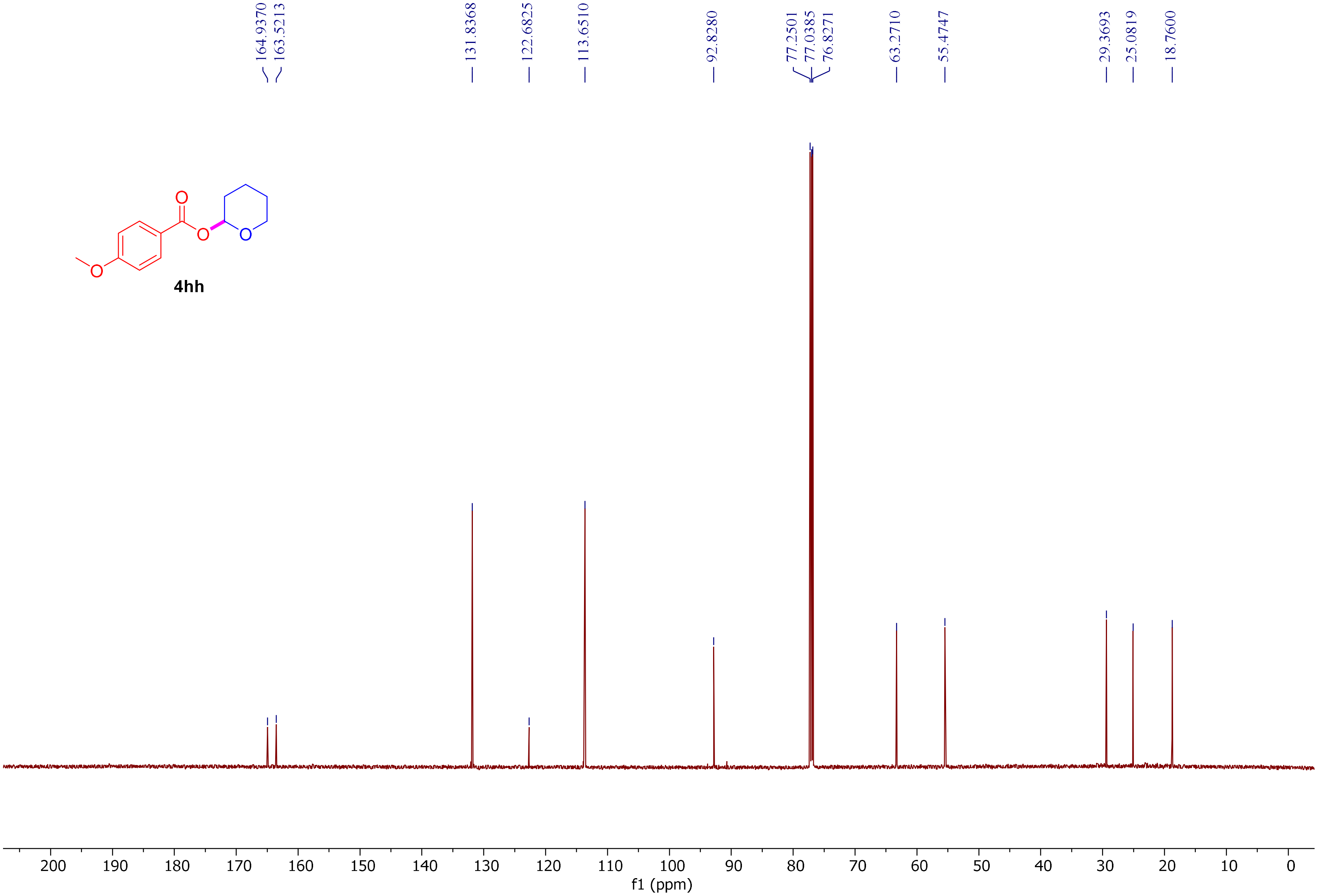
163.4313
131.7335
122.7733
113.5599
99.3906
77.2495
77.0372
76.8252
68.9877
55.4564
32.3049
23.0211
4gg
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0615
8.0567
8.0534
8.0453
8.0419
8.0371
7.2600
6.9448
6.9398
6.9364
6.9286
6.9251
6.9203
6.2187
6.2133
6.2084
4.0099
4.0051
3.9935
3.9908
3.9883
3.9861
3.9744
3.9691
3.8808
3.8770
3.8693
3.7617
3.7591
3.7523
3.7493
3.7467
3.7427
3.7402
1.9469
1.9432
1.9248
1.9221
1.9181
1.9022
1.8974
1.8956
1.8906
1.8796
1.8778
1.8725
1.8521
1.8497
1.8463
1.8443
1.8391
1.7482
1.7434
1.7411
1.7366
1.7334
1.7292
1.7281
1.7234
1.7202
1.7164
1.7141
1.7073
1.6578
1.6547
1.6498
1.6449
1.6444
1.6429
1.6359
1.6294
1.5754
O
O
O
O
1.82
1.90
0.83
1.07
2.91
1.08
3.29
2.15
1.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4hh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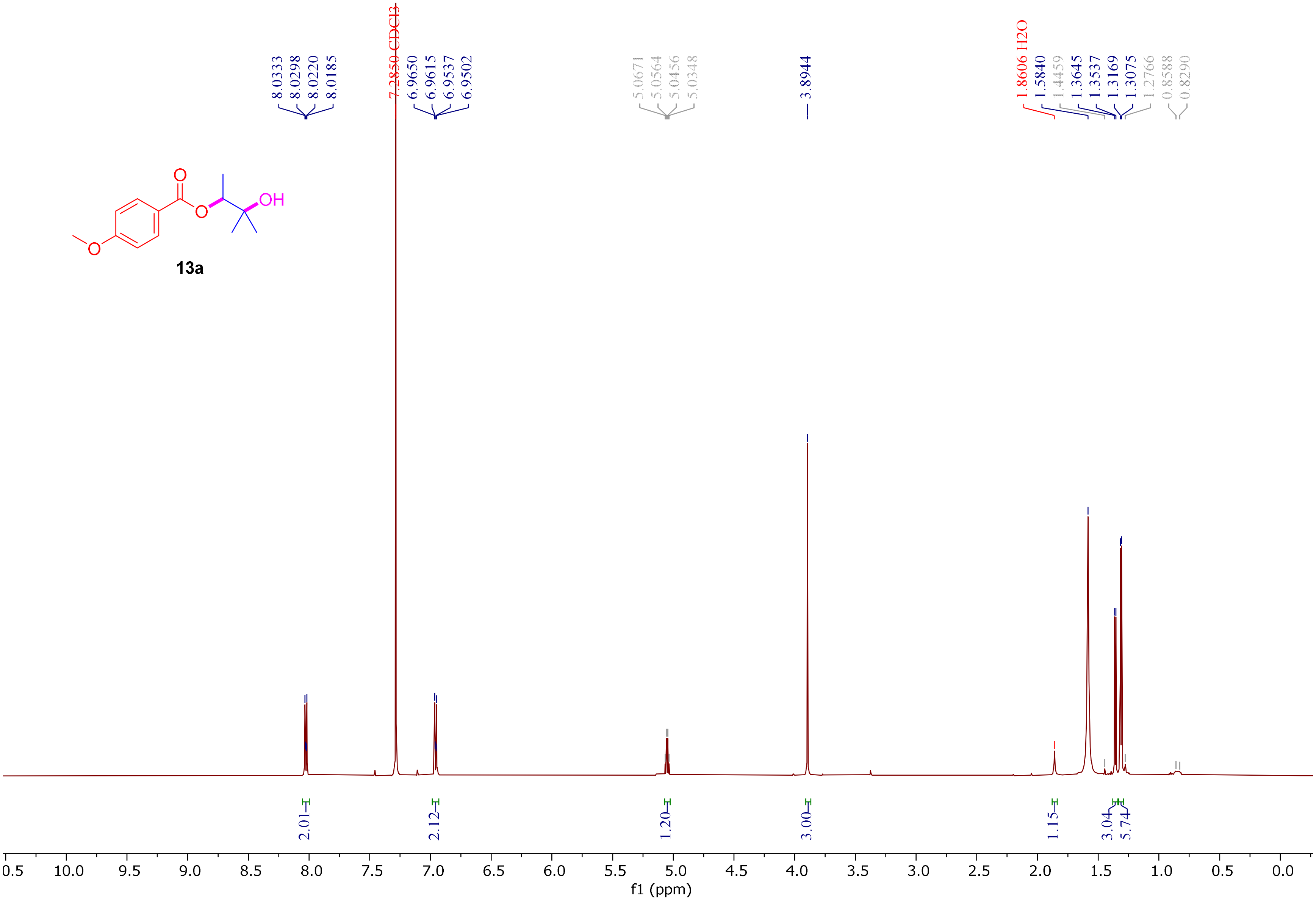
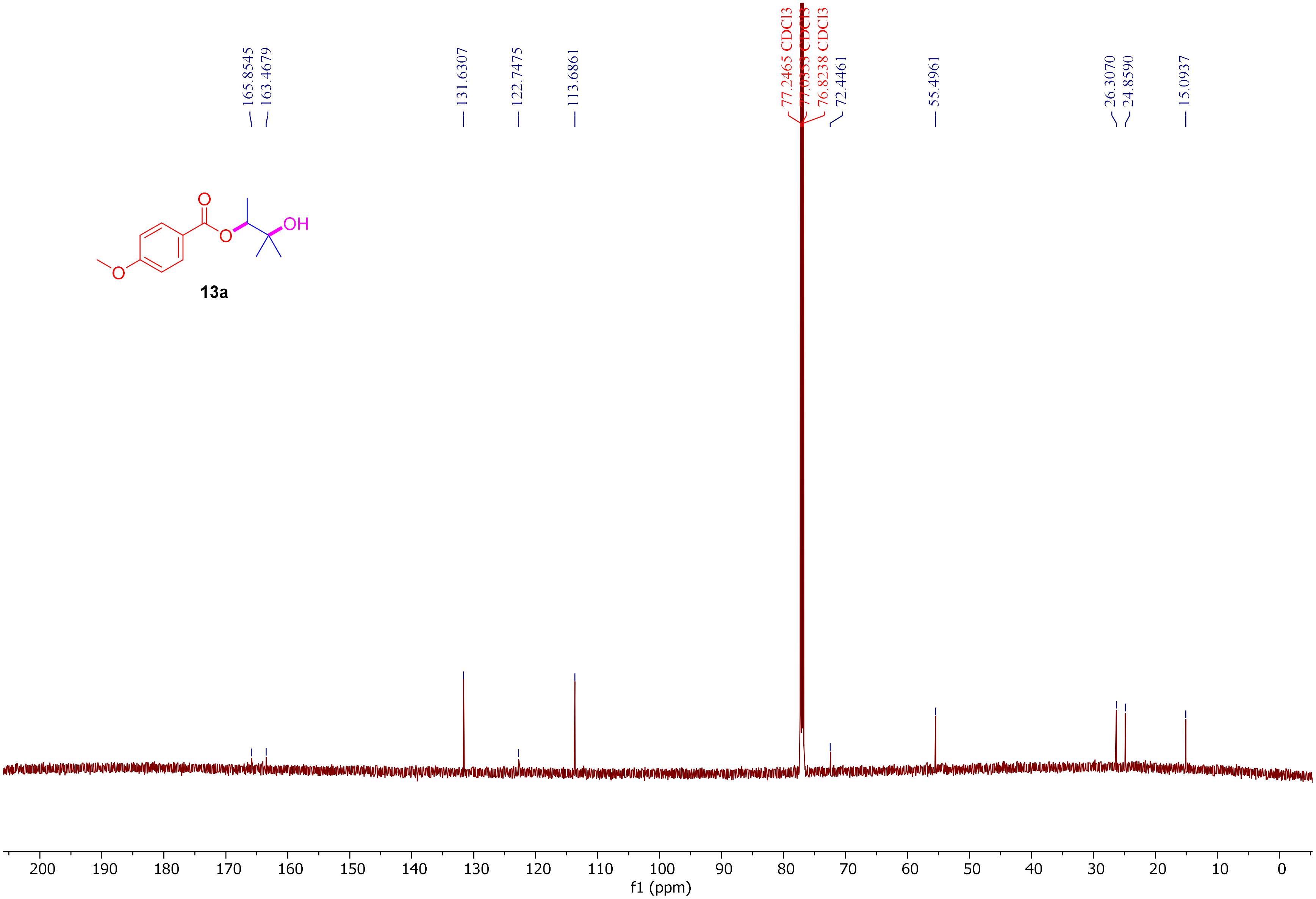
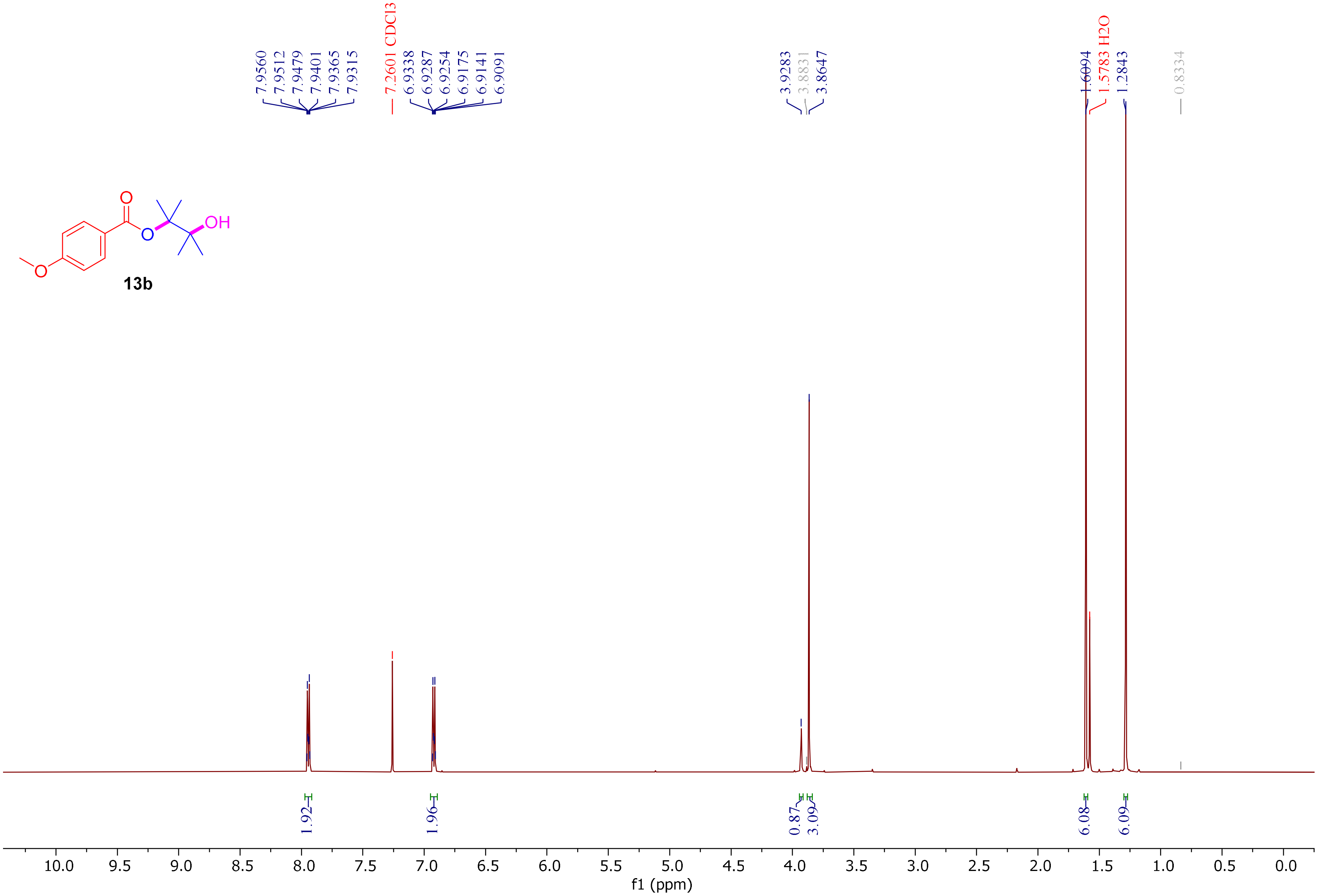
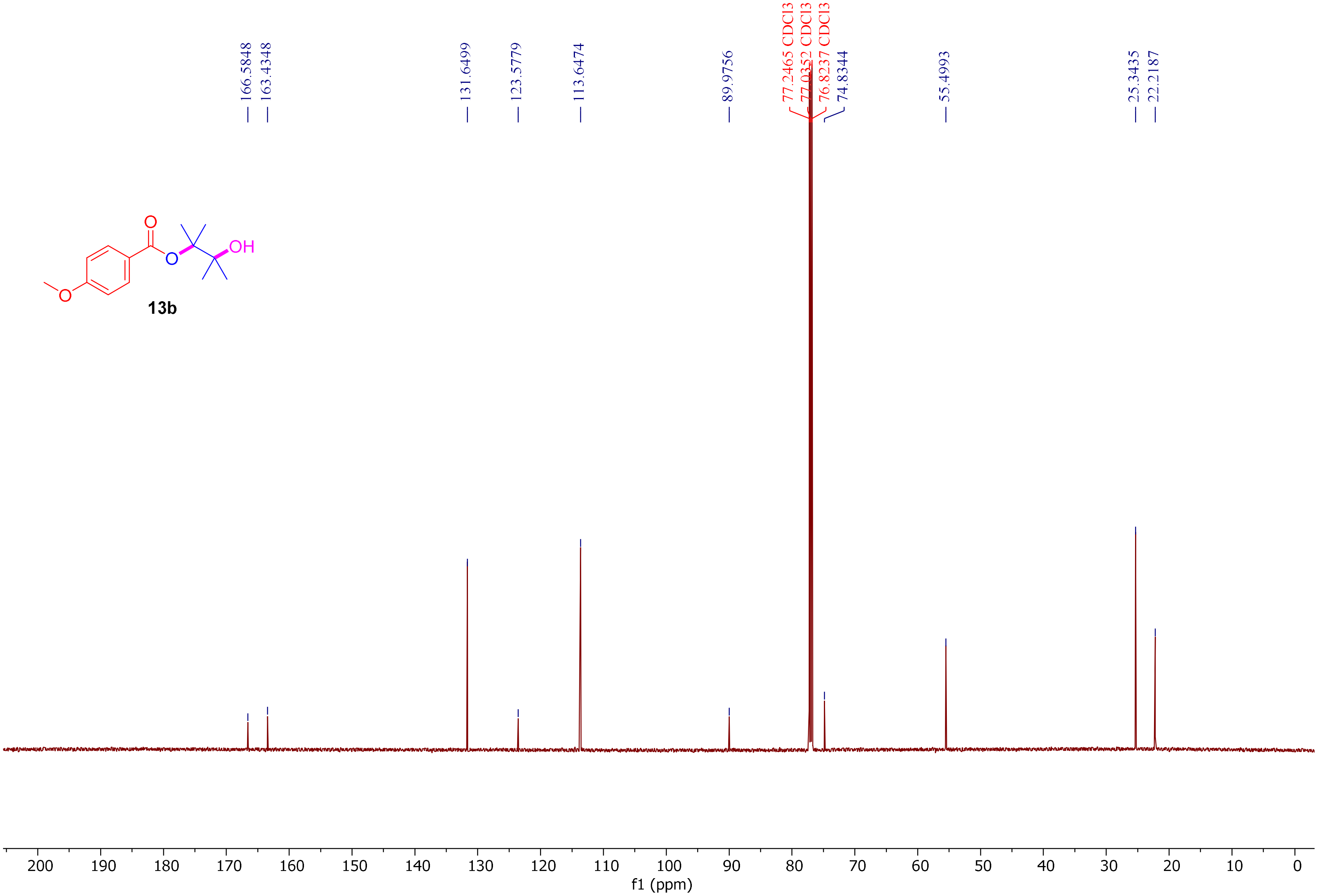
163.5213
131.8368
122.6825
113.6510
92.8280
77.2501
77.0385
76.8271
63.2710
55.4747
29.3693
25.0819
18.7600
4hh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0333
8.0298
8.0220
8.0185
7.2850 CDCl3
6.9650
6.9615
6.9537
6.9502
5.0671
5.0564
5.0456
5.0348
3.8944
1.8606 H2O
1.5840
1.4459
1.3645
1.3537
1.3169
1.3075
1.2766
0.8588
0.8290
O
O
OH
O
13a
2.01
2.12
1.20
3.00
1.15
3.04
5.74
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.8545
163.4679
131.6307
122.7475
113.6861
77.2465 CDCl3
77.0353 CDCl3
76.8238 CDCl3
72.4461
55.4961
26.3070
24.8590
15.0937
O
O
OH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

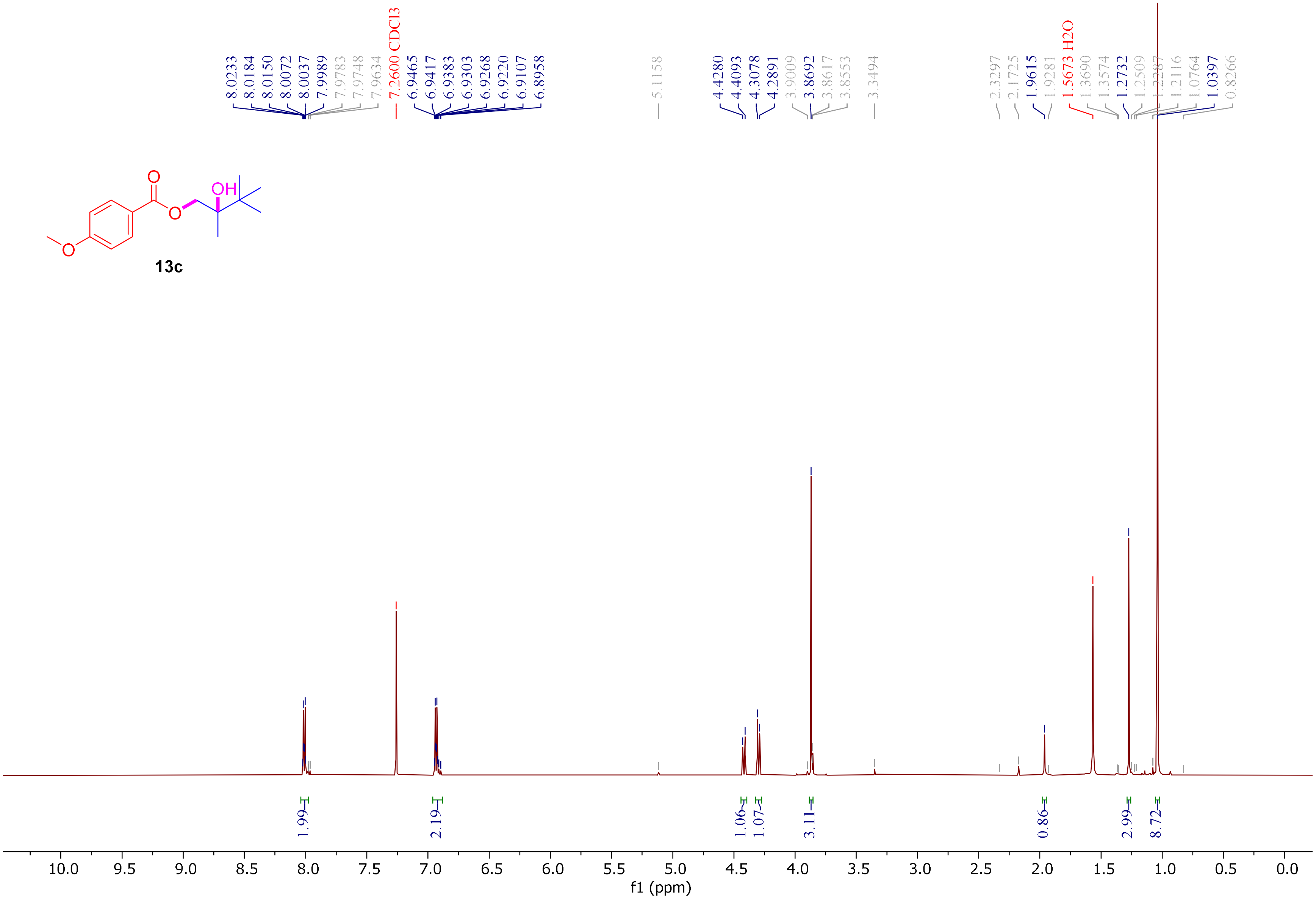
13a


7.9560
7.9512
7.9479
7.9401
7.9365
7.9315
7.2601 CDCl3
6.9338
6.9287
6.9254
6.9175
6.9141
6.9091
3.9283
3.8831
3.8647
1.6094
1.5783 H2O
1.2843
0.8334
O
O
OH
O
13b
1.92
1.96
0.87
3.09
6.08
6.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



13b

166.5848
163.4348
131.6499
123.5779
113.6474
89.9756
77.2465 CDCl3
77.0352 CDCl3
76.8237 CDCl3
74.8344
55.4993
25.3435
22.2187
O
O
O
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0233
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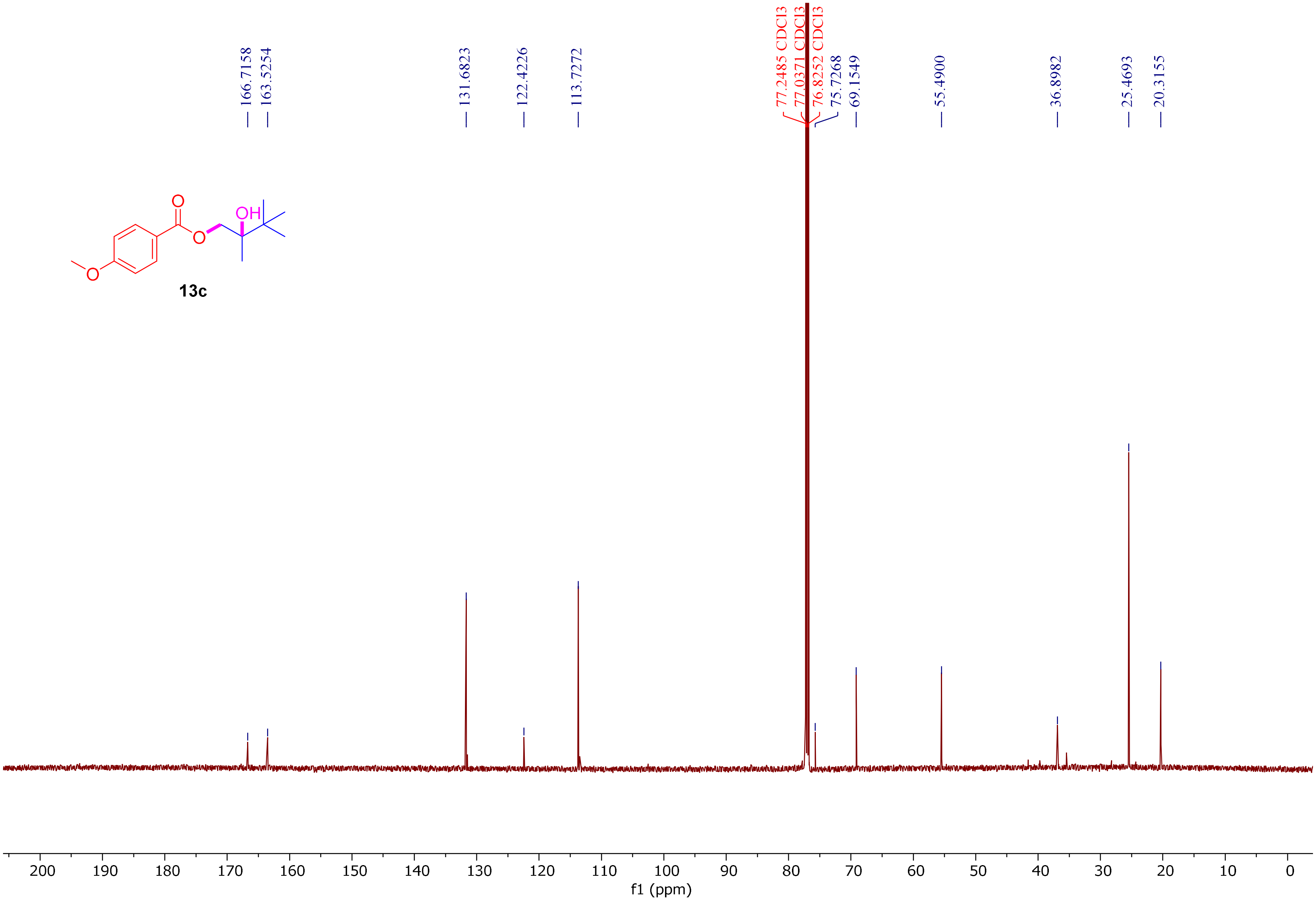
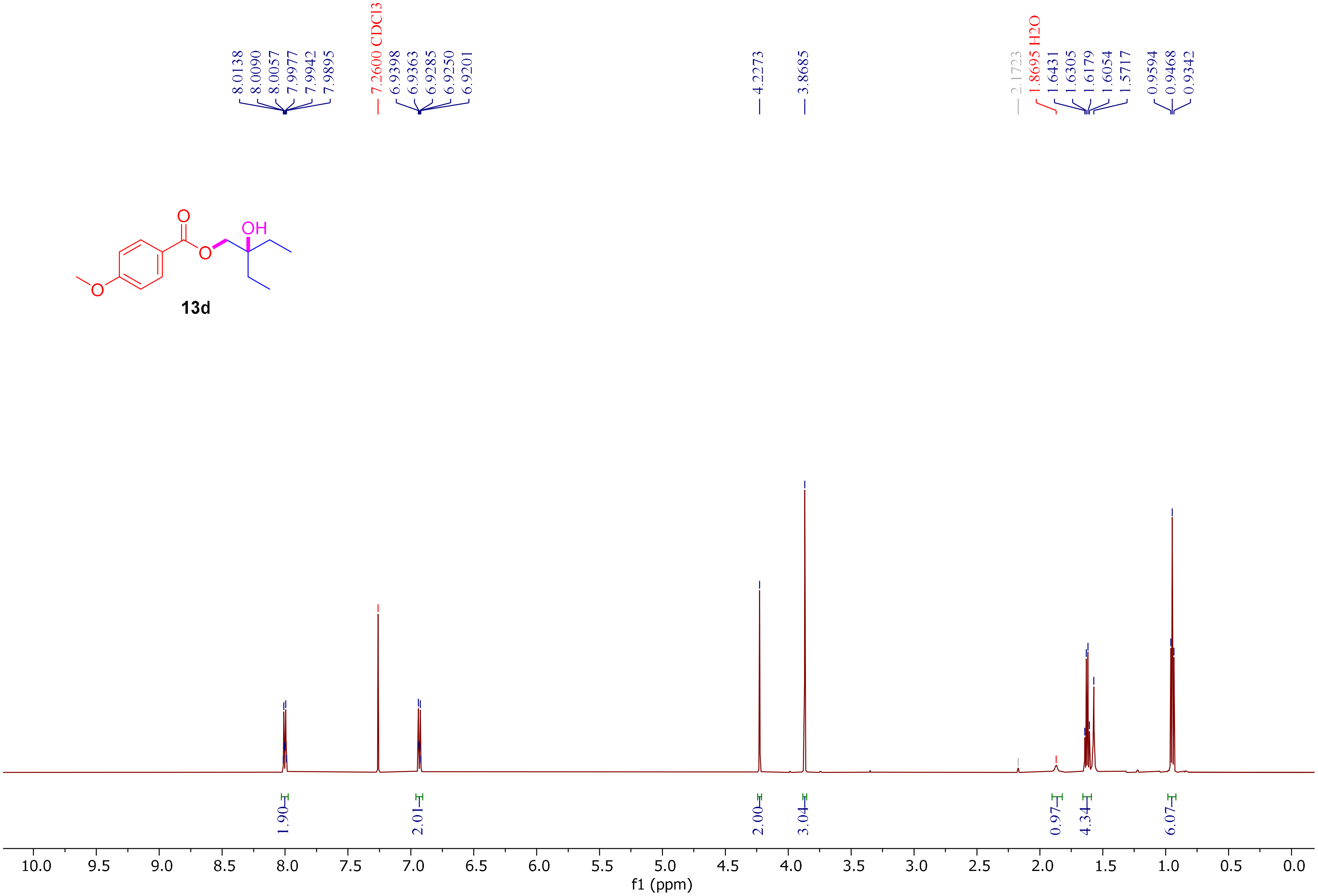
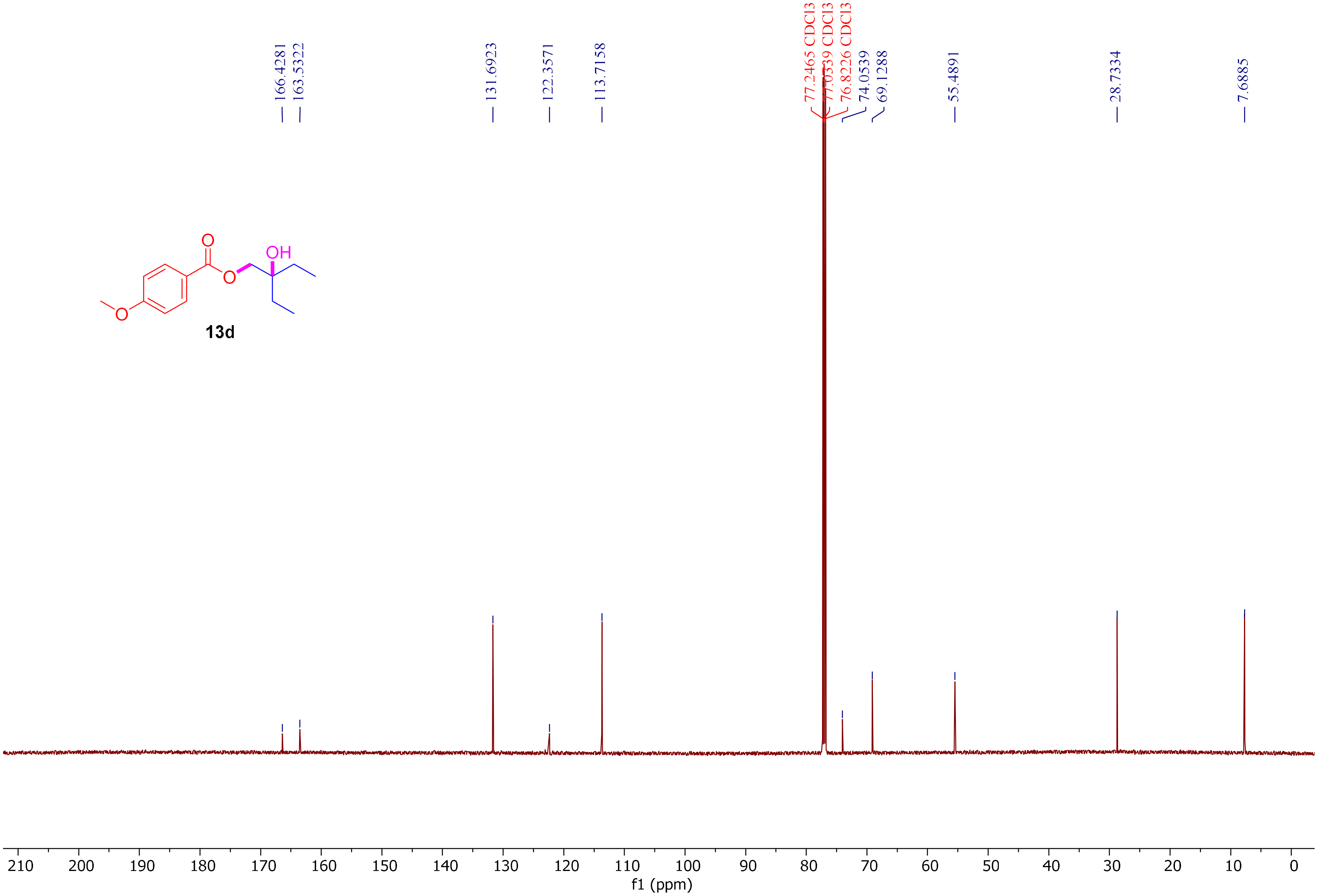
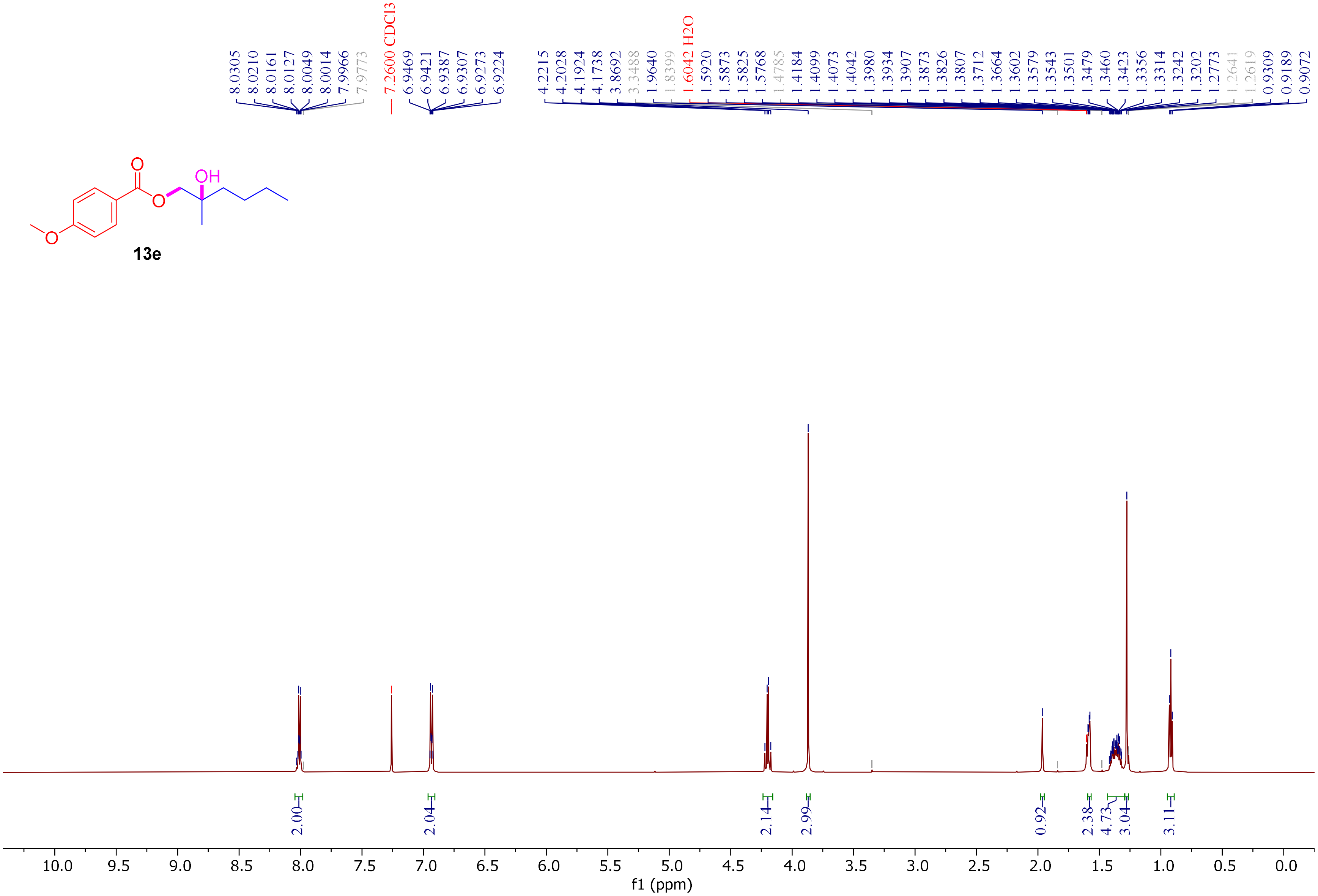
8.0150
8.0072
8.0037
7.9989
7.9783
7.9748
7.9634
7.2600 CDCl3
6.9465
6.9417
6.9383
6.9303
6.9268
6.9220
6.9107
6.8958
5.1158
4.4280
4.4093
4.3078
4.2891
3.9009
3.8692
3.8617
3.8553
3.3494
2.3297
2.1725
1.9615
1.9281
1.5673 H2O
1.3690
1.3574
1.2732
1.2509
1.2287
1.2116
1.0764
1.0397
0.8266
O
OH
O
O
13c
1.99
2.19
1.06
1.07
3.11
0.86
2.99
8.72
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.7158
163.5254
131.6823
122.4226
113.7272
77.2485 CDCl3
77.0371 CDCl3
76.8252 CDCl3
75.7268
69.1549
55.4900
36.8982
25.4693
20.3155
O
OH
O
O
13c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0138
8.0090
8.0057
7.9977
7.9942
7.9895
7.2600 CDCl3
6.9398
6.9363
6.9285
6.9250
6.9201
4.2273
3.8685
2.1723
1.8695 H2O
1.6431
1.6305
1.6179
1.6054
1.5717
0.9594
0.9468
0.9342
O
O
OH
O
13d
1.90
2.01
2.00
3.04
0.97
4.34
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.4281
163.5322
131.6923
122.3571
113.7158
77.2465 CDCl3
77.0339 CDCl3
76.8226 CDCl3
74.0539
69.1288
55.4891
28.7334
7.6885
O
OH
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

13d

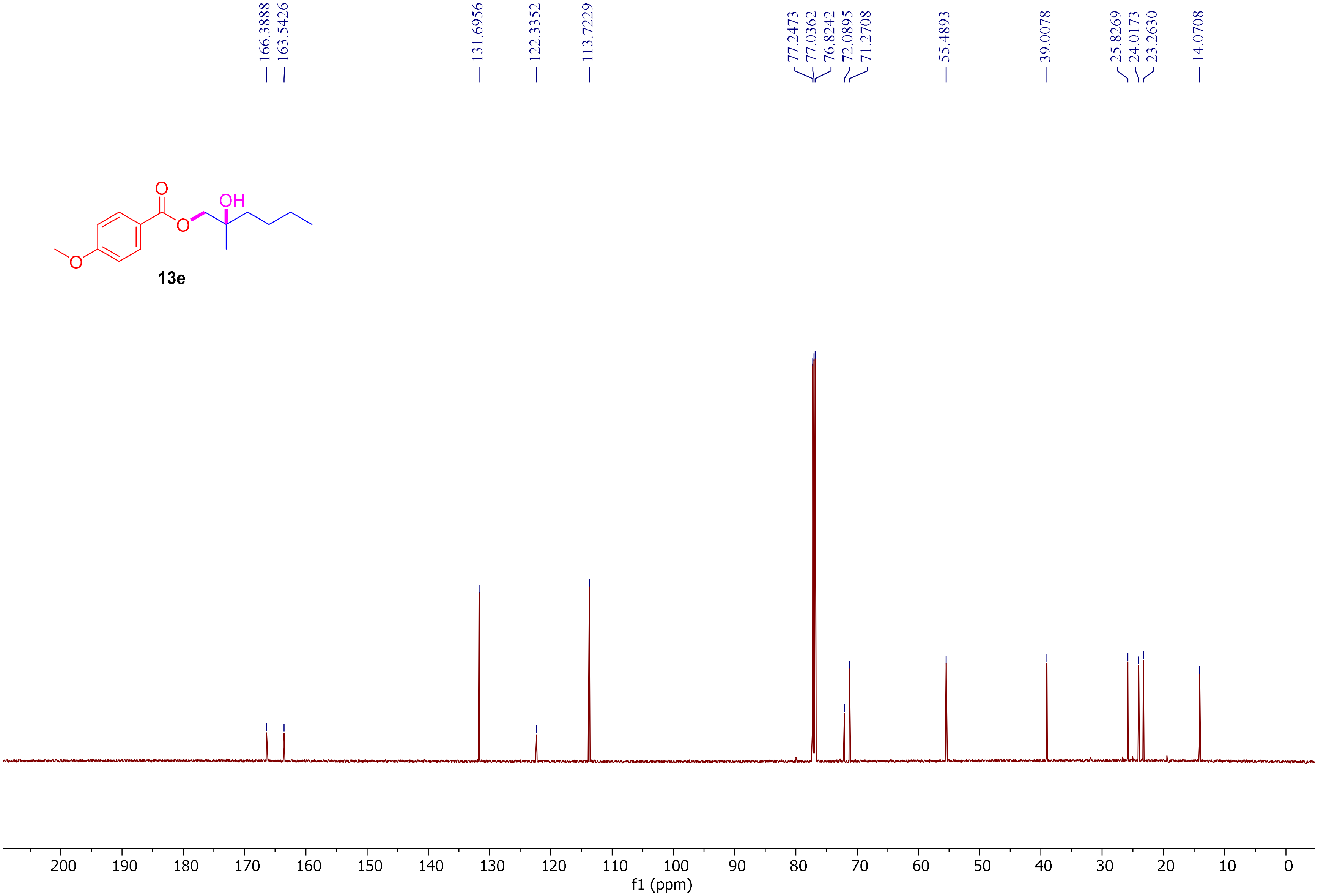


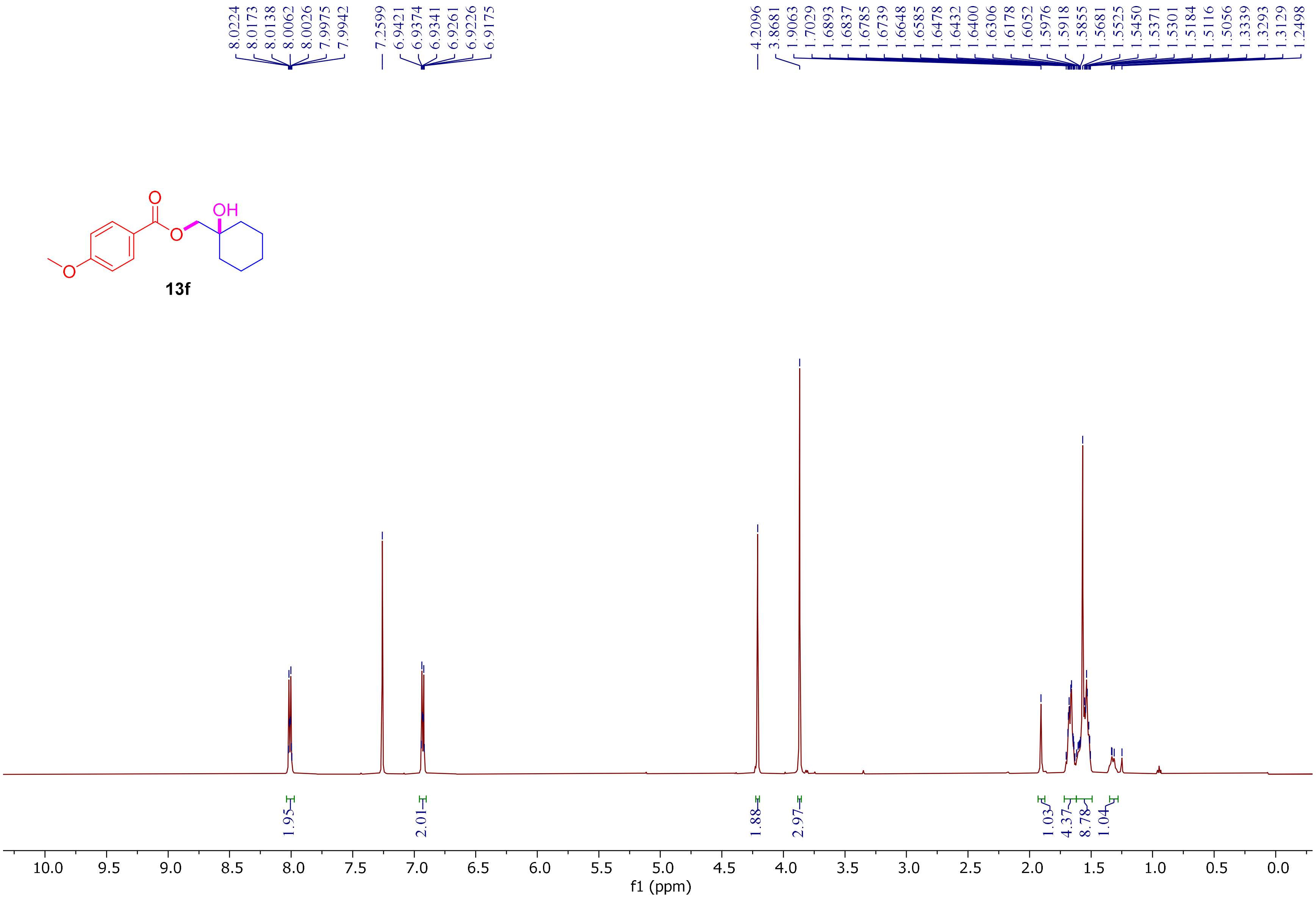
13e

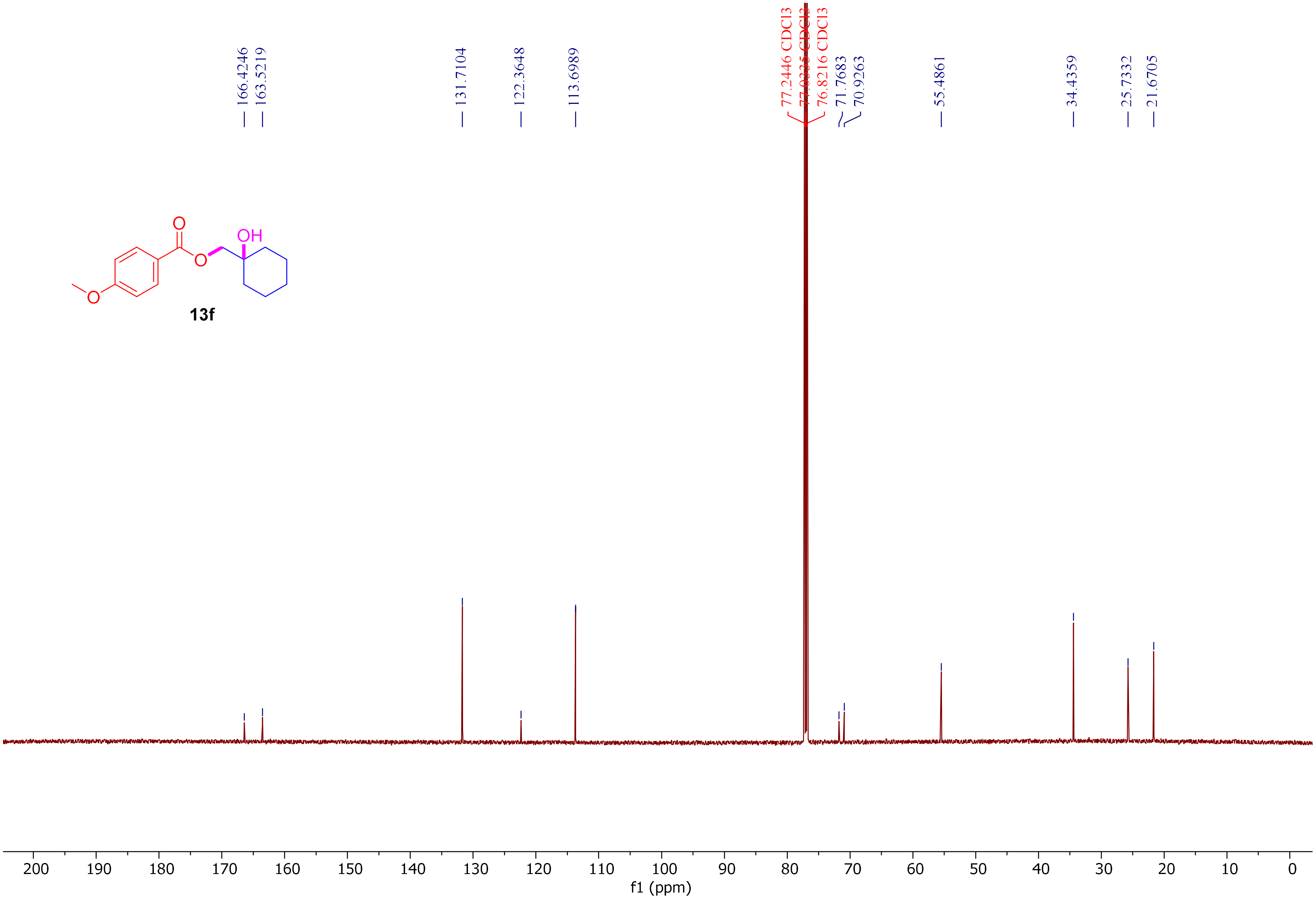
8.0305
8.0210
8.0161
8.0127
8.0049
8.0014
7.9966
7.9773
7.2600 CDCl3
6.9469
6.9421
6.9387
6.9307
6.9273
6.9224
4.2215
4.2028
4.1924
4.1738
3.8692
3.3488
1.9640
1.8399
1.6042 H2O
1.5920
1.5873
1.5825
1.5768
1.4785
1.4184
1.4099
1.4073
1.4042
1.3980
1.3934
1.3907
1.3873
1.3826
1.3807
1.3712
1.3664
1.3602
1.3579
1.3543
1.3501
1.3479
1.3460
1.3423
1.3356
1.3314
1.3242
1.3202
1.2773
1.2641
1.2619
0.9309
0.9189
0.9072
O
O
OH
O
2.00
2.04
2.14
2.99
0.92
2.38
4.73
3.04
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

O
OH
O
O

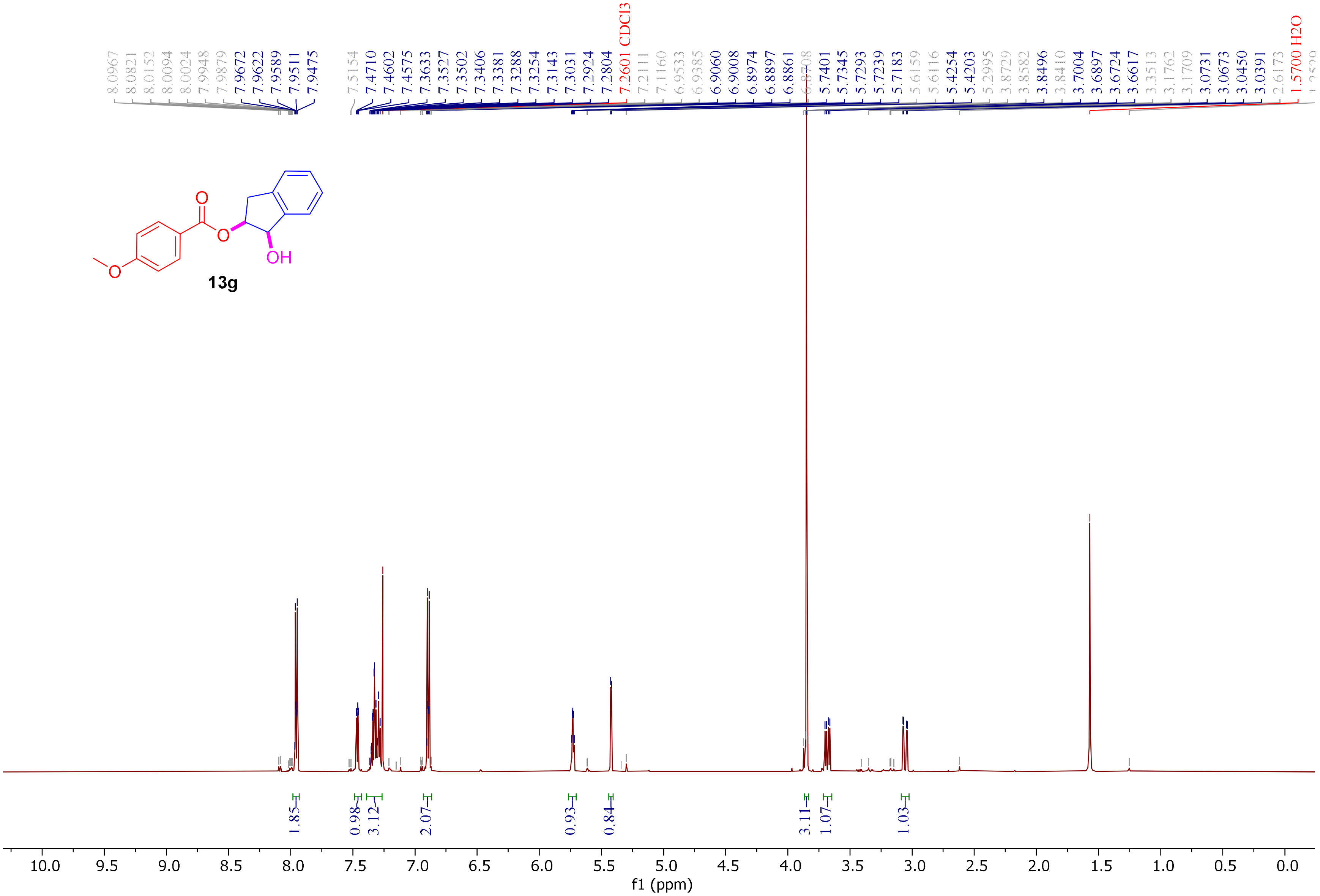
13e

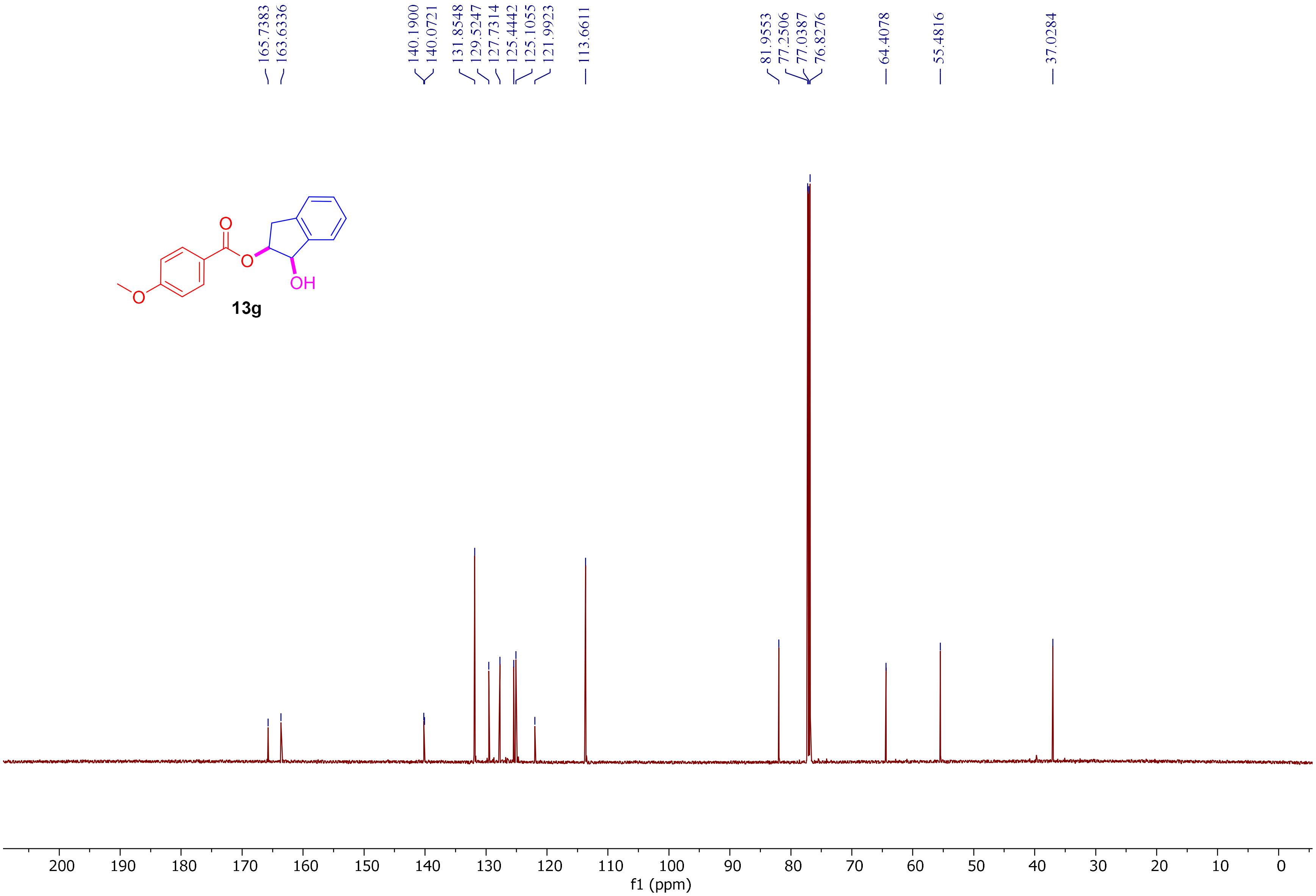

166.3888
163.5426
131.6956
122.3352
113.7229
77.2473
77.0362
76.8242
72.0895
71.2708
55.4893
39.0078
25.8269
24.0173
23.2630
14.0708
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

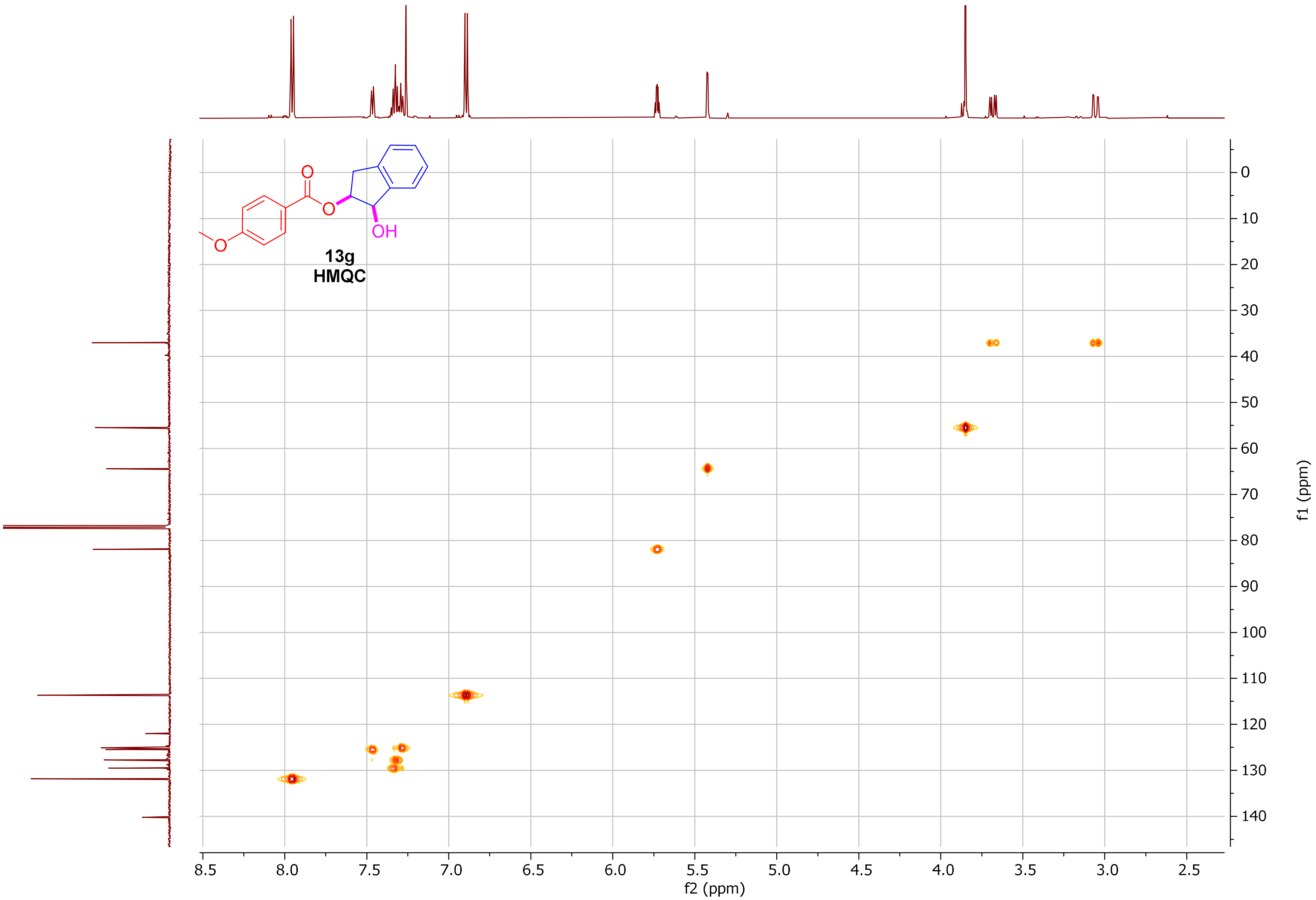

8.0224
8.0173
8.0138
8.0062
8.0026
7.9975
7.9942
7.2599
6.9421
6.9374
6.9341
6.9261
6.9226
6.9175
4.2096
3.8681
1.9063
1.7029
1.6893
1.6837
1.6785
1.6739
1.6648
1.6585
1.6478
1.6432
1.6400
1.6306
1.6178
1.6052
1.5976
1.5918
1.5855
1.5681
1.5525
1.5450
1.5371
1.5301
1.5184
1.5116
1.5056
1.3339
1.3293
1.3129
1.2498
O
OH
O
O
13f
1.95
2.01
1.88
2.97
1.03
4.37
8.78
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



166.4246
163.5219
131.7104
122.3648
113.6989
77.2446 CDCl3
77.0335 CDCl3
76.8216 CDCl3
71.7683
70.9263
55.4861
34.4359
25.7332
21.6705
O
O
OH
O
13f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

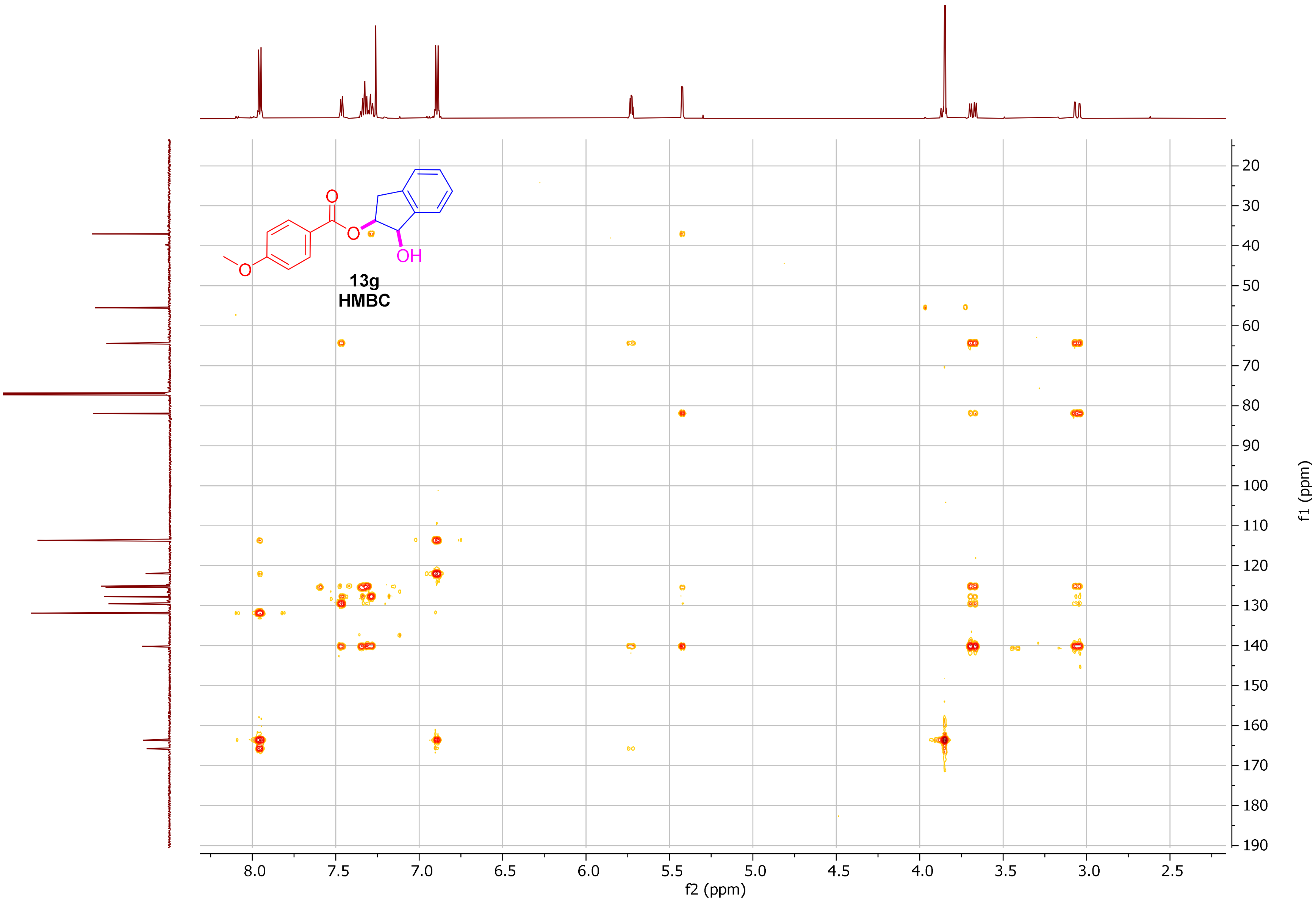

8.0967
8.0821
8.0152
8.0094
8.0024
7.9948
7.9879
7.9672
7.9622
7.9589
7.9511
7.9475
7.5154
7.4710
7.4602
7.4575
7.3633
7.3527
7.3502
7.3406
7.3381
7.3288
7.3254
7.3143
7.3031
7.2924
7.2804
7.2601 CDCl3
7.2111
7.1160
6.9533
6.9385
6.9060
6.9008
6.8974
6.8897
6.8861
6.8708
5.7401
5.7345
5.7293
5.7239
5.7183
5.6159
5.6116
5.4254
5.4203
5.2995
3.8729
3.8582
3.8496
3.8410
3.7004
3.6897
3.6724
3.6617
3.3513
3.1762
3.1709
3.0731
3.0673
3.0450
3.0391
2.6173
1.5700 H2O
O
O
O
OH
13g
1.85
0.98
3.12
2.07
0.93
0.84
3.11
1.07
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

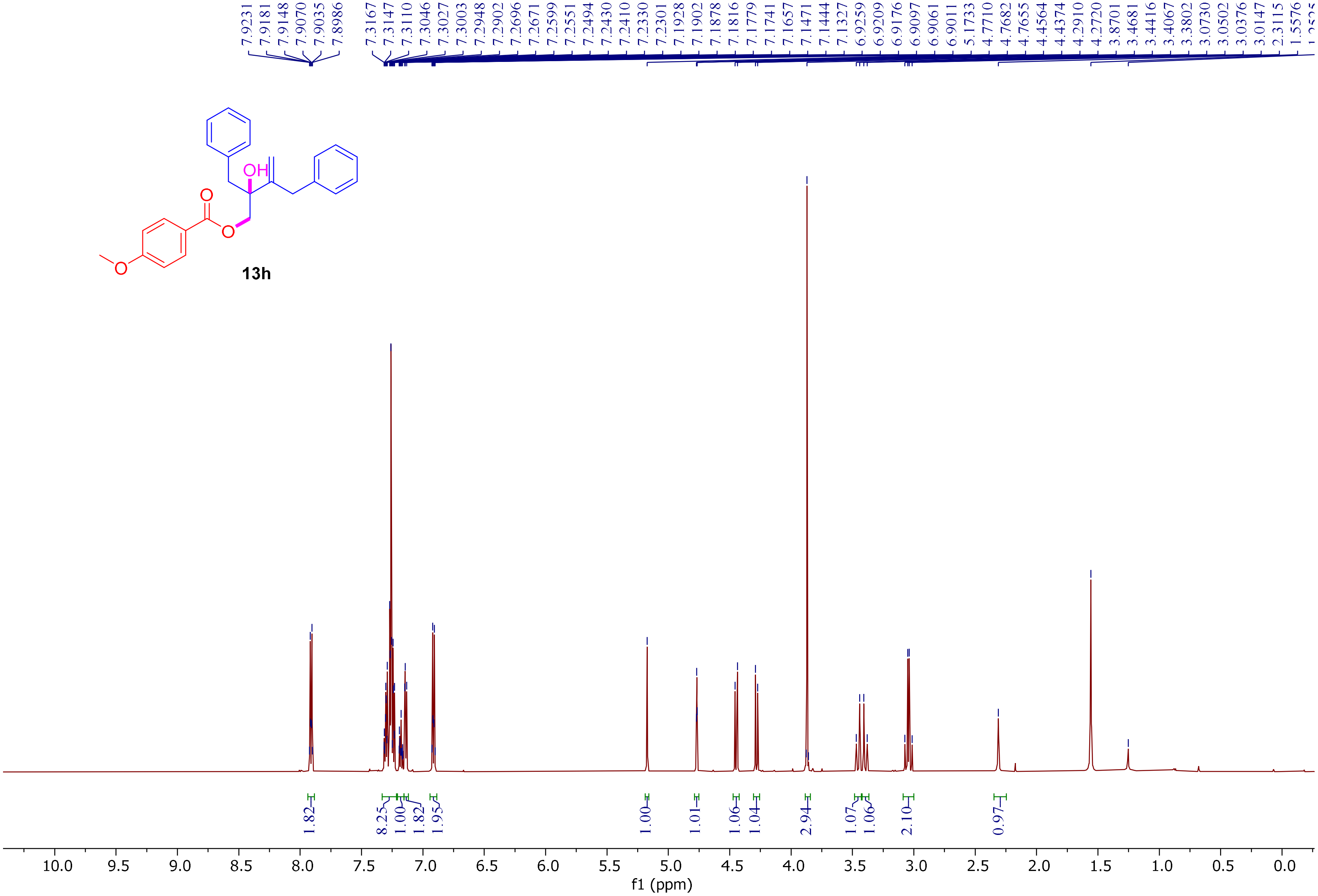

165.7383
163.6336
140.1900
140.0721
131.8548
129.5247
127.7314
125.4442
125.1055
121.9923
113.6611
81.9553
77.2506
77.0387
76.8276
64.4078
55.4816
37.0284
O
O
O
OH
13g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



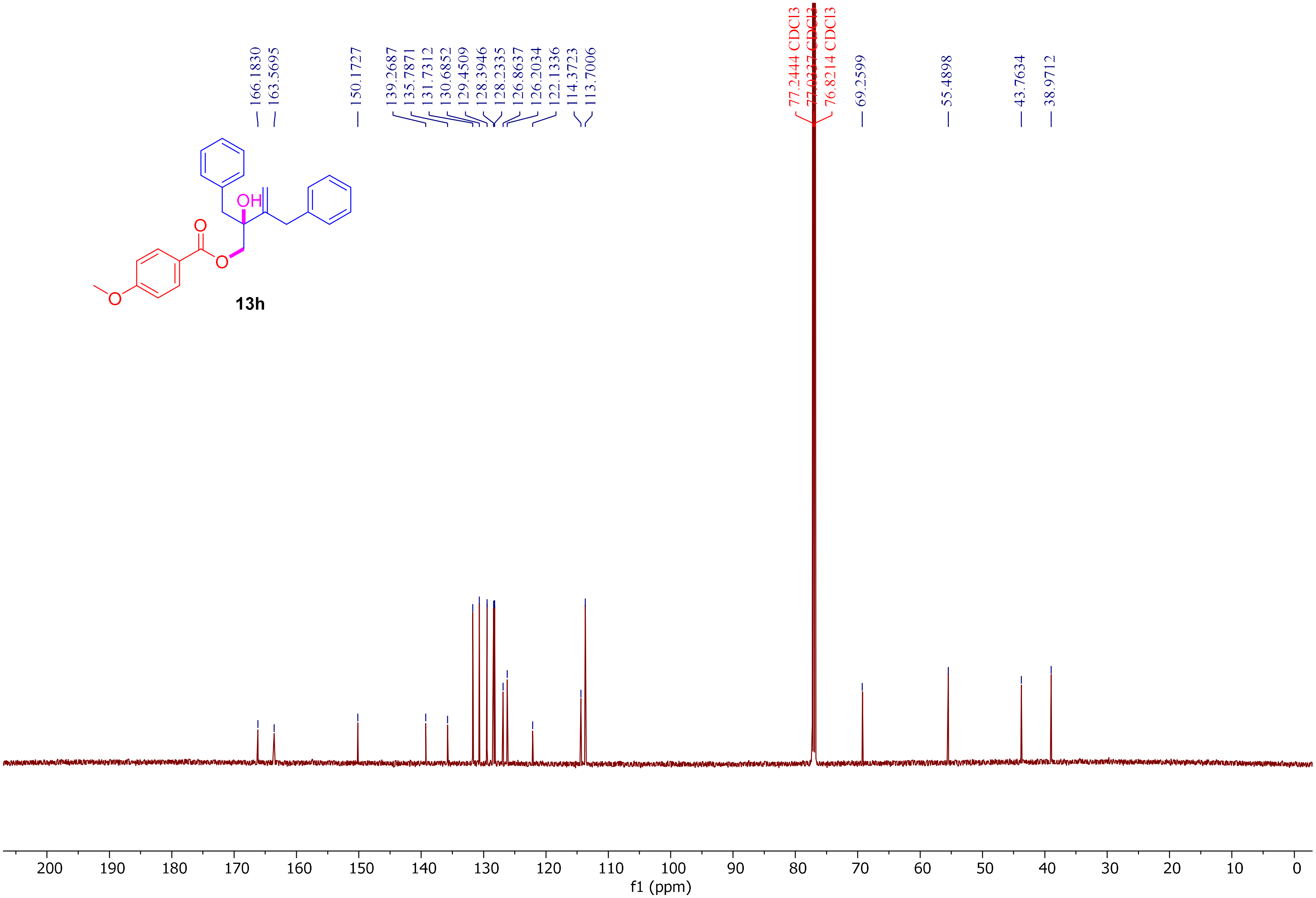
13g
HMQC

O
O
O
OH
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

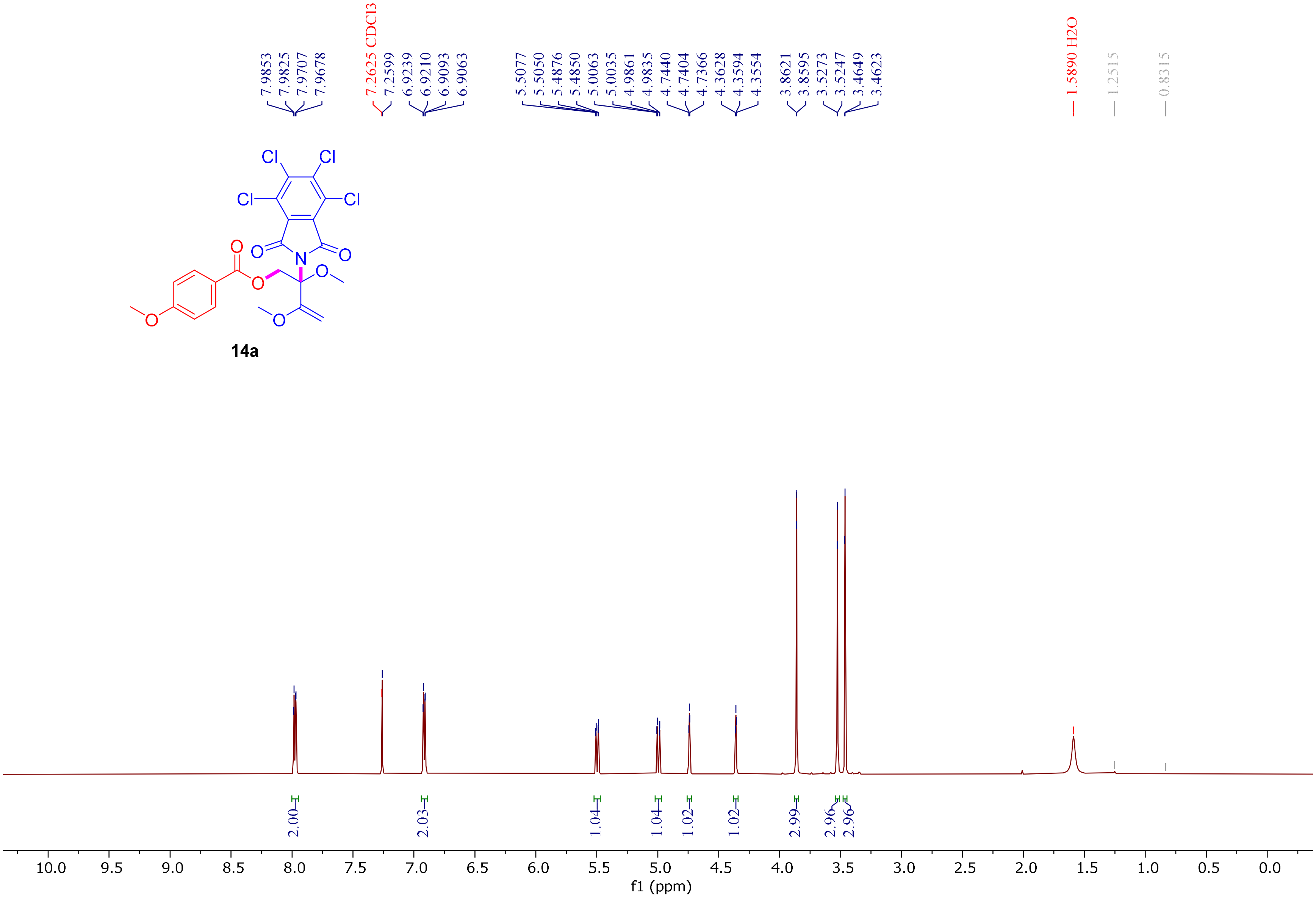

O
O
O
OH
13g
HMBC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)


7.9231
7.9181
7.9148
7.9070
7.9035
7.8986
7.3167
7.3147
7.3110
7.3046
7.3027
7.3003
7.2948
7.2902
7.2696
7.2671
7.2599
7.2551
7.2494
7.2430
7.2410
7.2330
7.2301
7.1928
7.1902
7.1878
7.1816
7.1779
7.1741
7.1657
7.1471
7.1444
7.1327
6.9259
6.9209
6.9176
6.9097
6.9061
6.9011
5.1733
4.7710
4.7682
4.7655
4.4564
4.4374
4.2910
4.2720
3.8701
3.4681
3.4416
3.4067
3.3802
3.0730
3.0502
3.0376
3.0147
2.3115
1.5576
OH
O
O
O
1.82
8.25
1.00
1.82
1.95
1.00
1.01
1.06
1.04
2.94
1.07
1.06
2.10
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

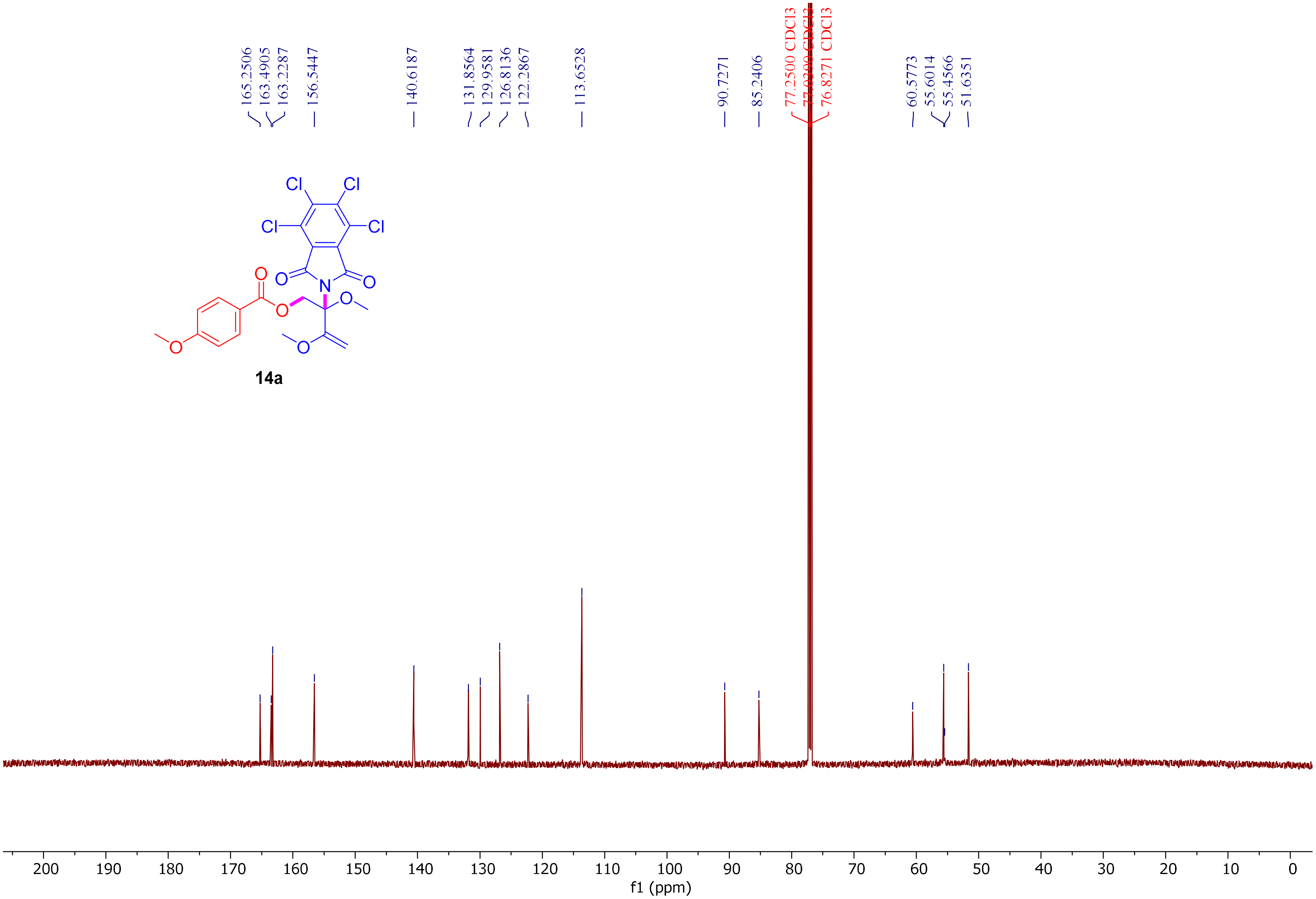
13h

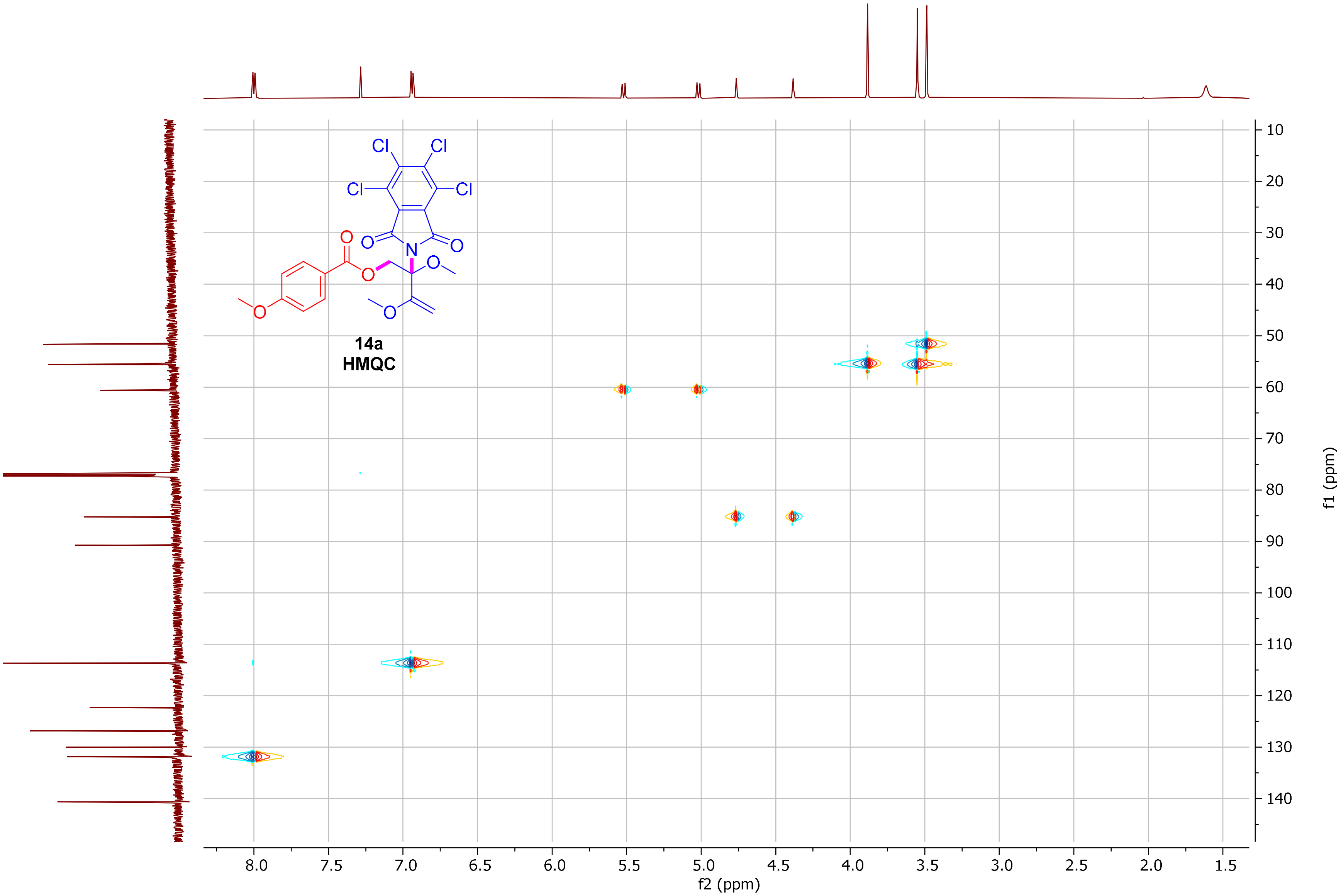

166.1830
163.5695
150.1727
139.2687
135.7871
131.7312
130.6852
129.4509
128.3946
128.2335
126.8637
126.2034
122.1336
114.3723
113.7006
77.2444 CDCl3
77.0337 CDCl3
76.8214 CDCl3
69.2599
55.4898
43.7634
38.9712
OH
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

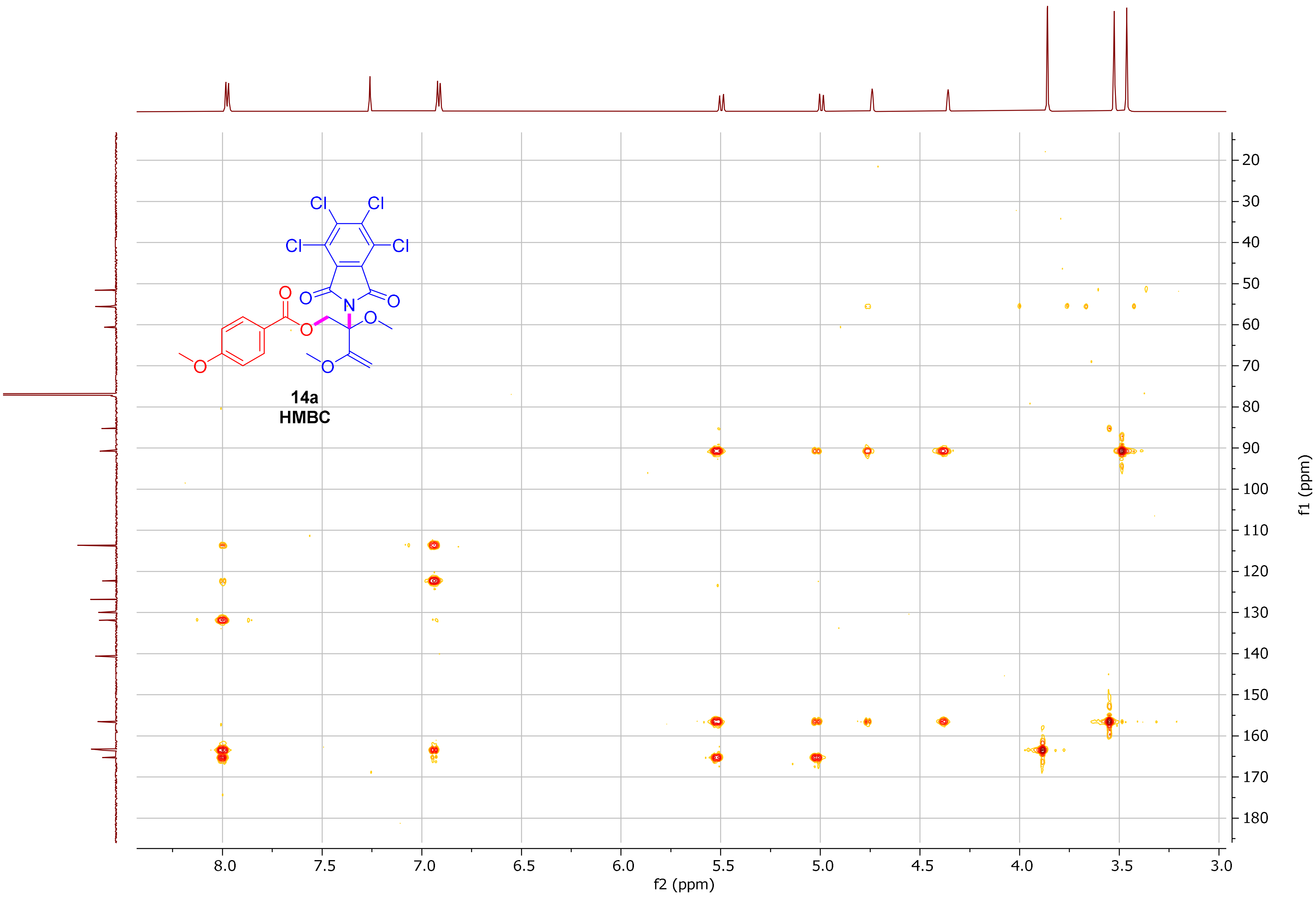
13h

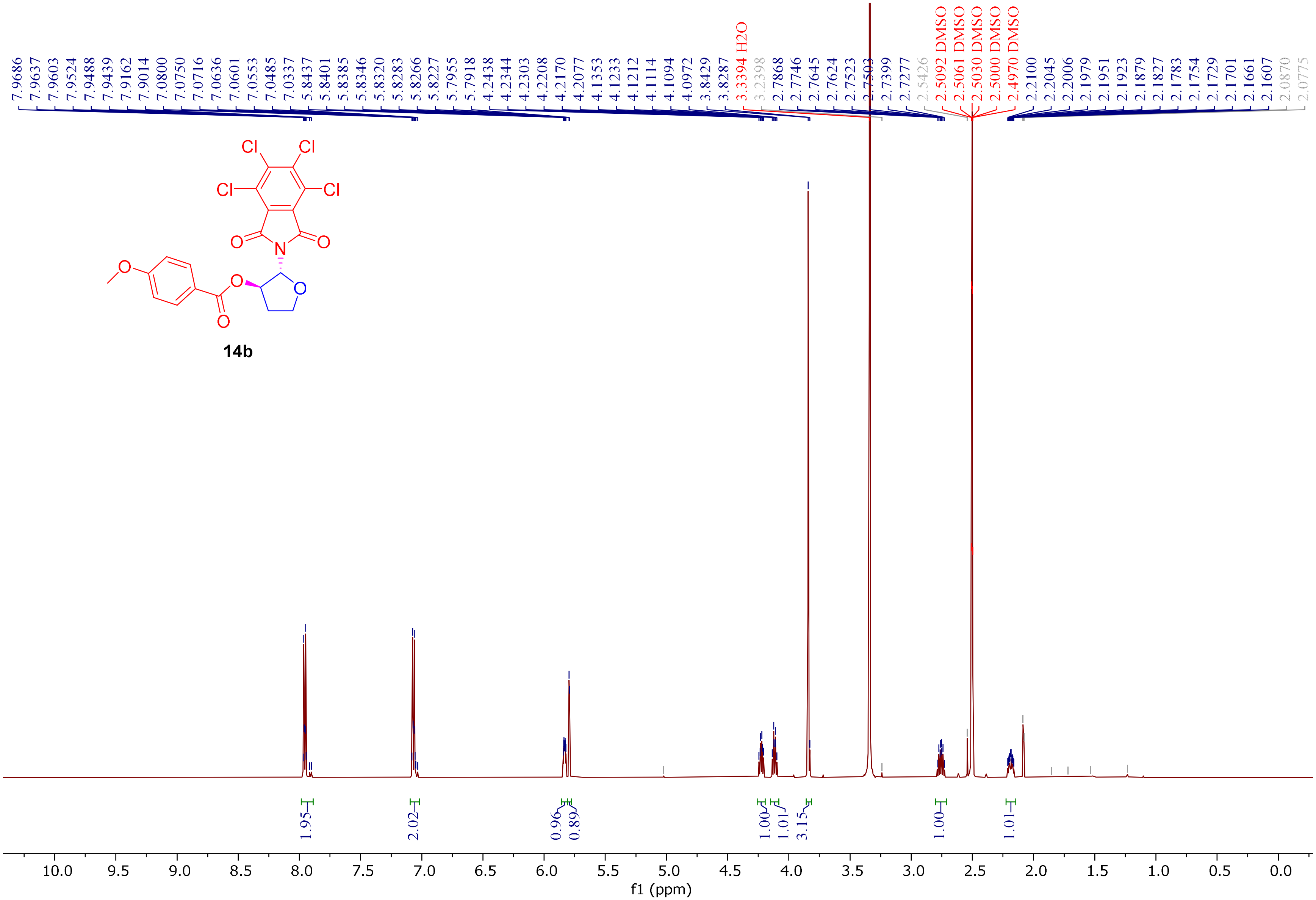

7.9853
7.9825
7.9707
7.9678
7.2625 CDCl3
7.2599
6.9239
6.9210
6.9093
6.9063
5.5077
5.5050
5.4876
5.4850
5.0063
5.0035
4.9861
4.9835
4.7440
4.7404
4.7366
4.3628
4.3594
4.3554
3.8621
3.8595
3.5273
3.5247
3.4649
3.4623
1.5890 H2O
1.2515
0.8315
Cl
Cl
Cl
Cl
O
N
O
O
O
O
O
O
O
2.00
2.03
1.04
1.04
1.02
1.02
2.99
2.96
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

14a


165.2506
163.4905
163.2287
156.5447
140.6187
131.8564
129.9581
126.8136
122.2867
113.6528
90.7271
85.2406
77.2500 CDCl3
77.0300 CDCl3
76.8271 CDCl3
60.5773
55.6014
55.4566
51.6351
Cl
Cl
Cl
Cl
O
O
N
O
O
O
O
O
14a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
Cl
Cl
Cl
O
O
N
O
O
O
O
O
O
14a
HMQC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)


Cl
Cl
Cl
Cl
O
N
O
O
O
O
O
O
14a
HMBC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)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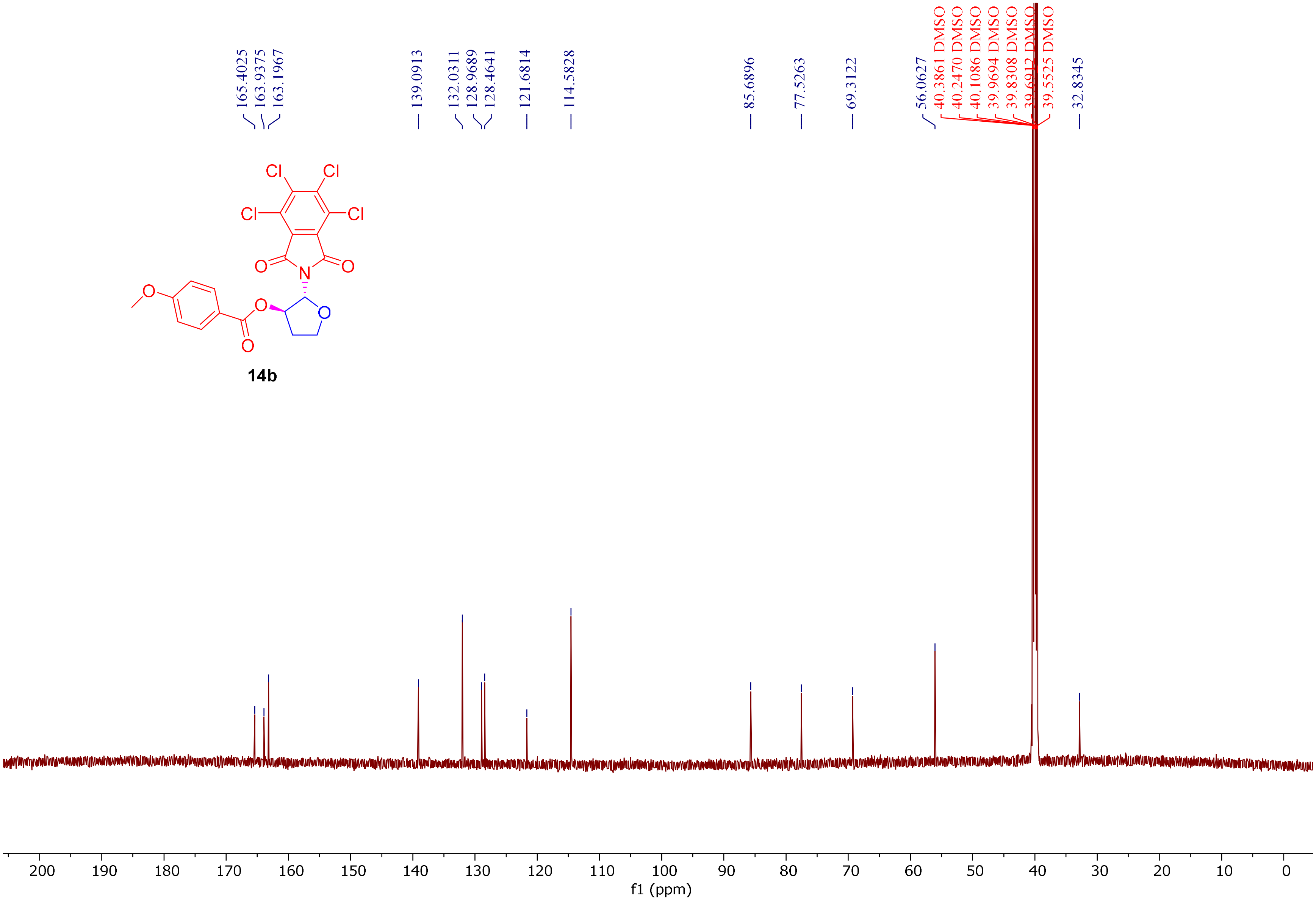
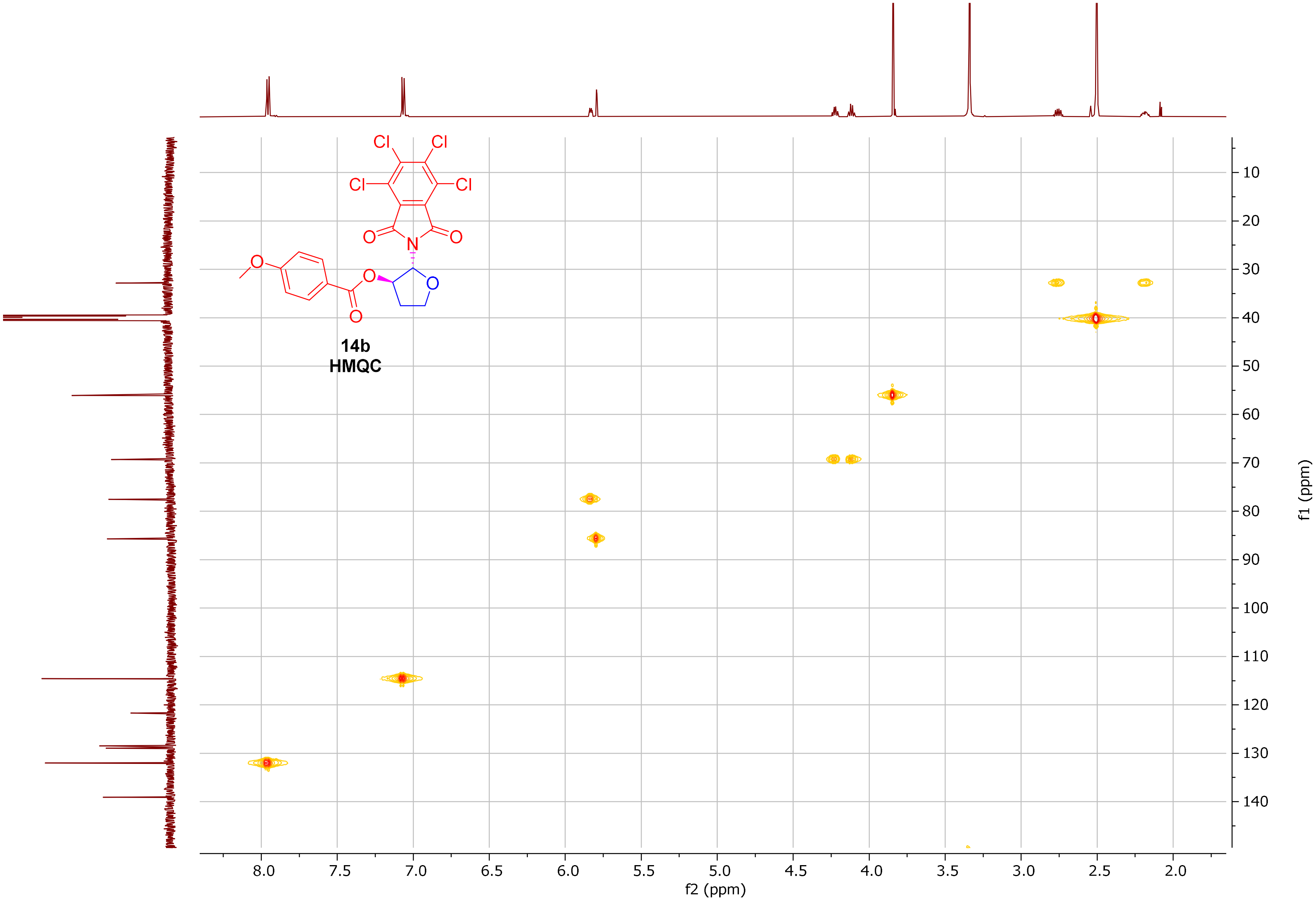
7.9637
7.9603
7.9524
7.9488
7.9439
7.9162
7.9014
7.0800
7.0750
7.0716
7.0636
7.0601
7.0553
7.0485
7.0337
5.8437
5.8401
5.8385
5.8346
5.8320
5.8283
5.8266
5.8227
5.7955
5.7918
4.2438
4.2344
4.2303
4.2208
4.2170
4.2077
4.1353
4.1233
4.1212
4.1114
4.1094
4.0972
3.8429
3.8287
3.3394 H2O
3.2398
2.7868
2.7746
2.7645
2.7624
2.7523
2.7503
2.7399
2.7277
2.5426
2.5092 DMSO
2.5061 DMSO
2.5030 DMSO
2.5000 DMSO
2.4970 DMSO
2.2100
2.2045
2.2006
2.1979
2.1951
2.1923
2.1879
2.1827
2.1783
2.1754
2.1729
2.1701
2.1661
2.1607
2.0870
2.0775
Cl
Cl
Cl
Cl
O
O
N
O
O
O
O
1.95
2.02
0.96
0.89
1.00
1.01
3.15
1.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

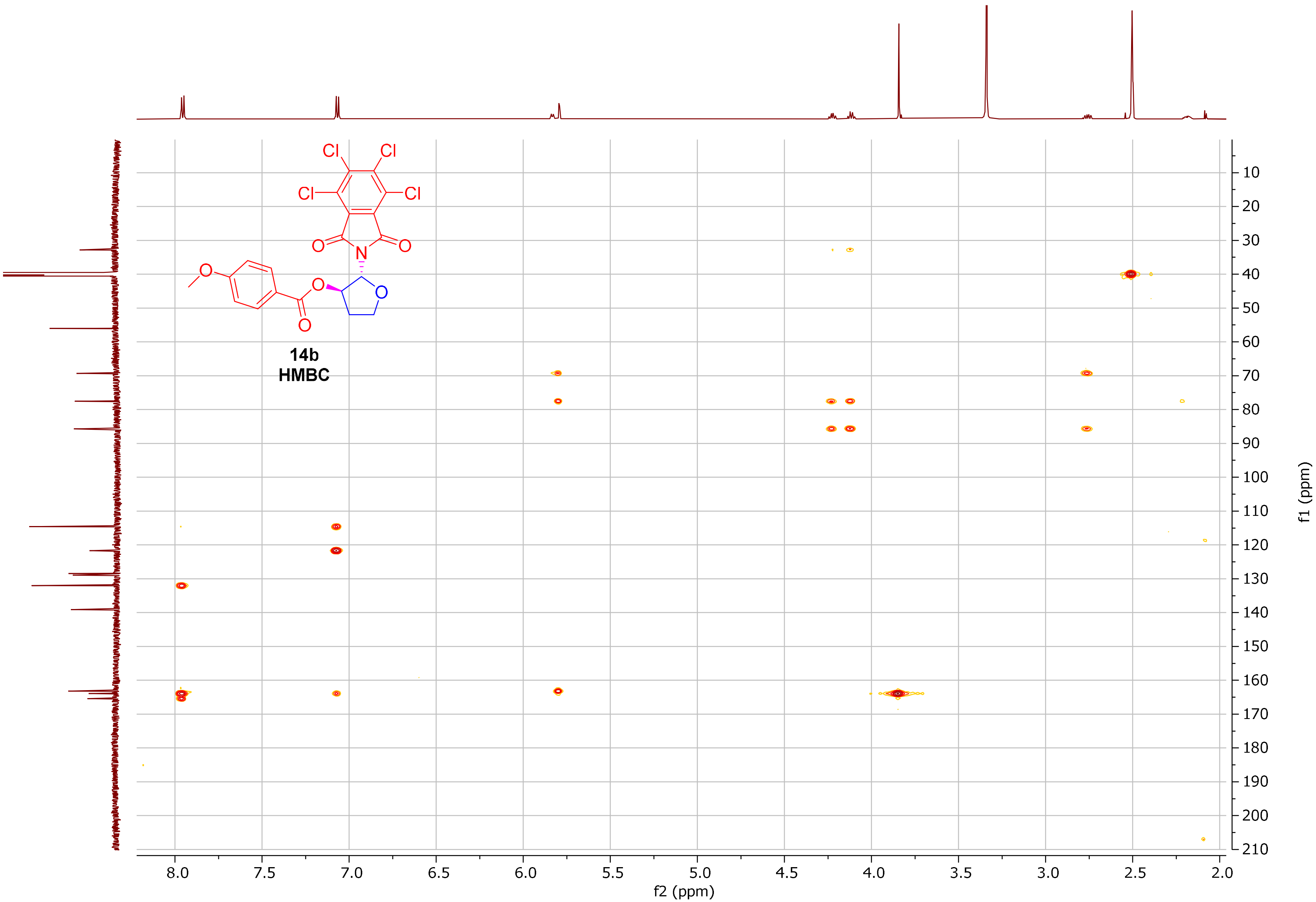
14b


165.4025
163.9375
163.1967
139.0913
132.0311
128.9689
128.4641
121.6814
114.5828
85.6896
77.5263
69.3122
56.0627
40.3861 DMSO
40.2470 DMSO
40.1086 DMSO
39.9694 DMSO
39.8308 DMSO
39.6912 DMSO
39.5525 DMSO
32.8345
Cl
Cl
Cl
Cl
O
N
O
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

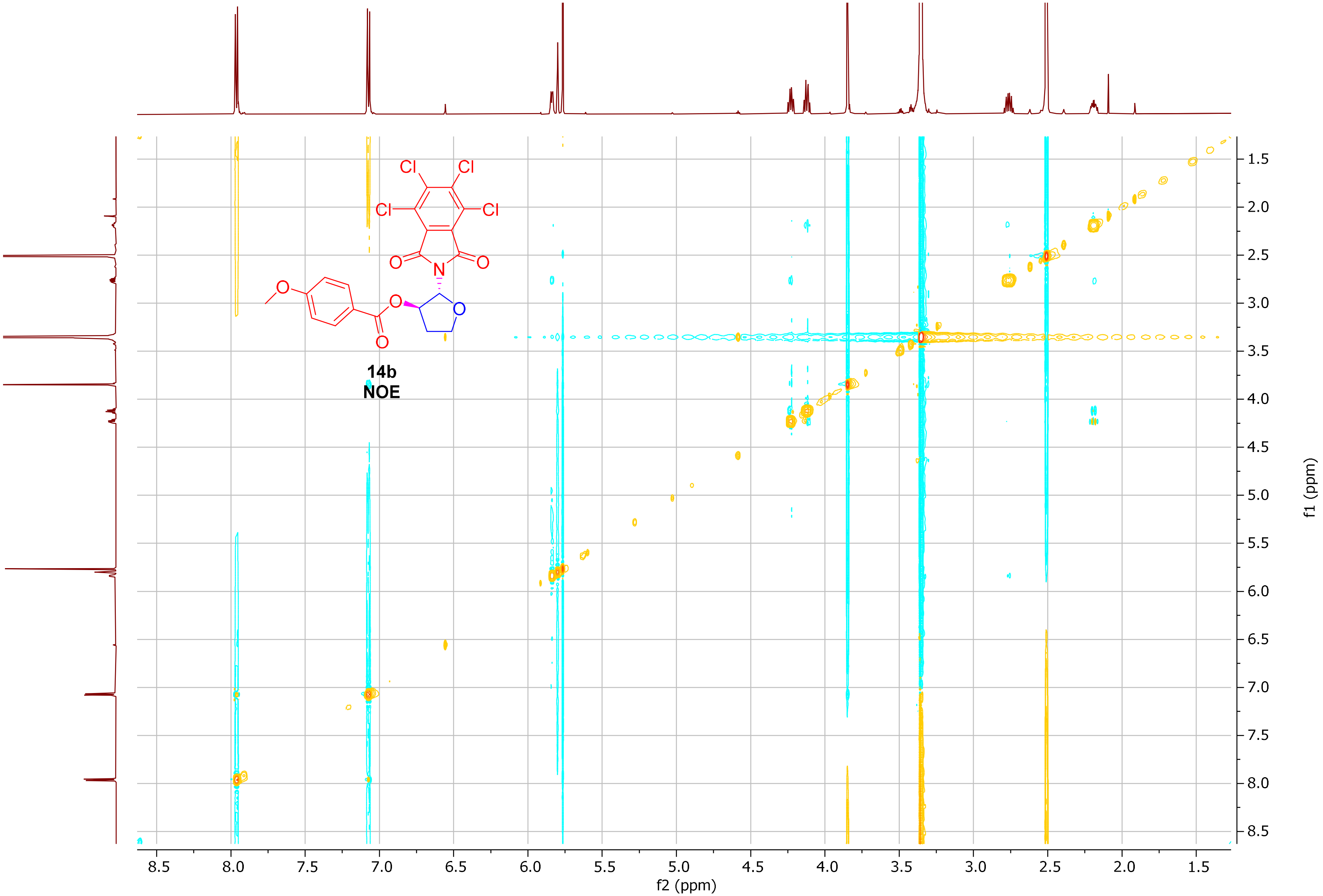
14b



Cl
Cl
Cl
Cl
O
N
O
O
O
O
O
14b
HMQC
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

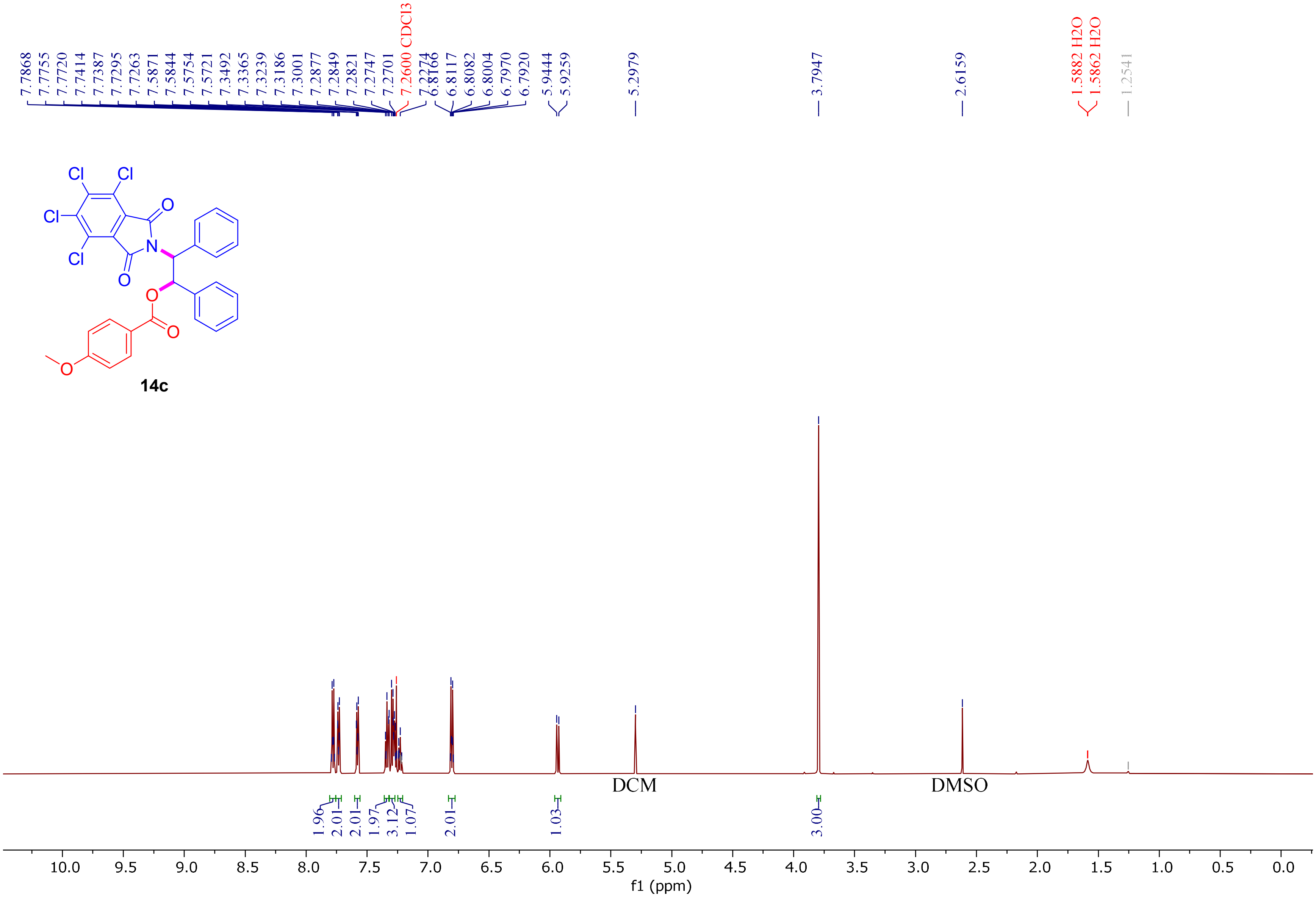


Cl
Cl
Cl
Cl
O
N
O
O
O
O
O
14b
HMBC
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)



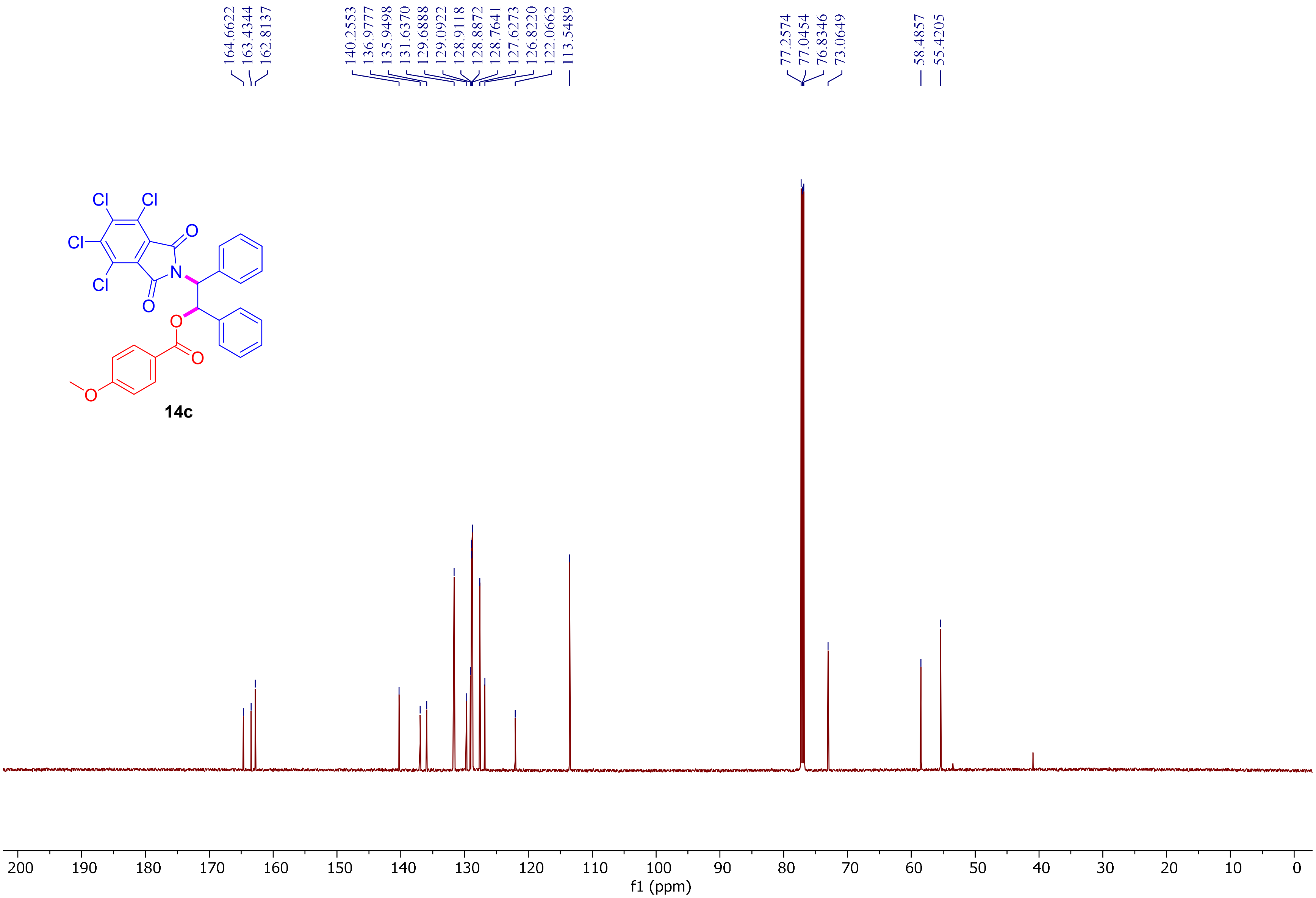
14b
NOE

Cl
Cl
Cl
Cl
O
N
O
O
O
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)

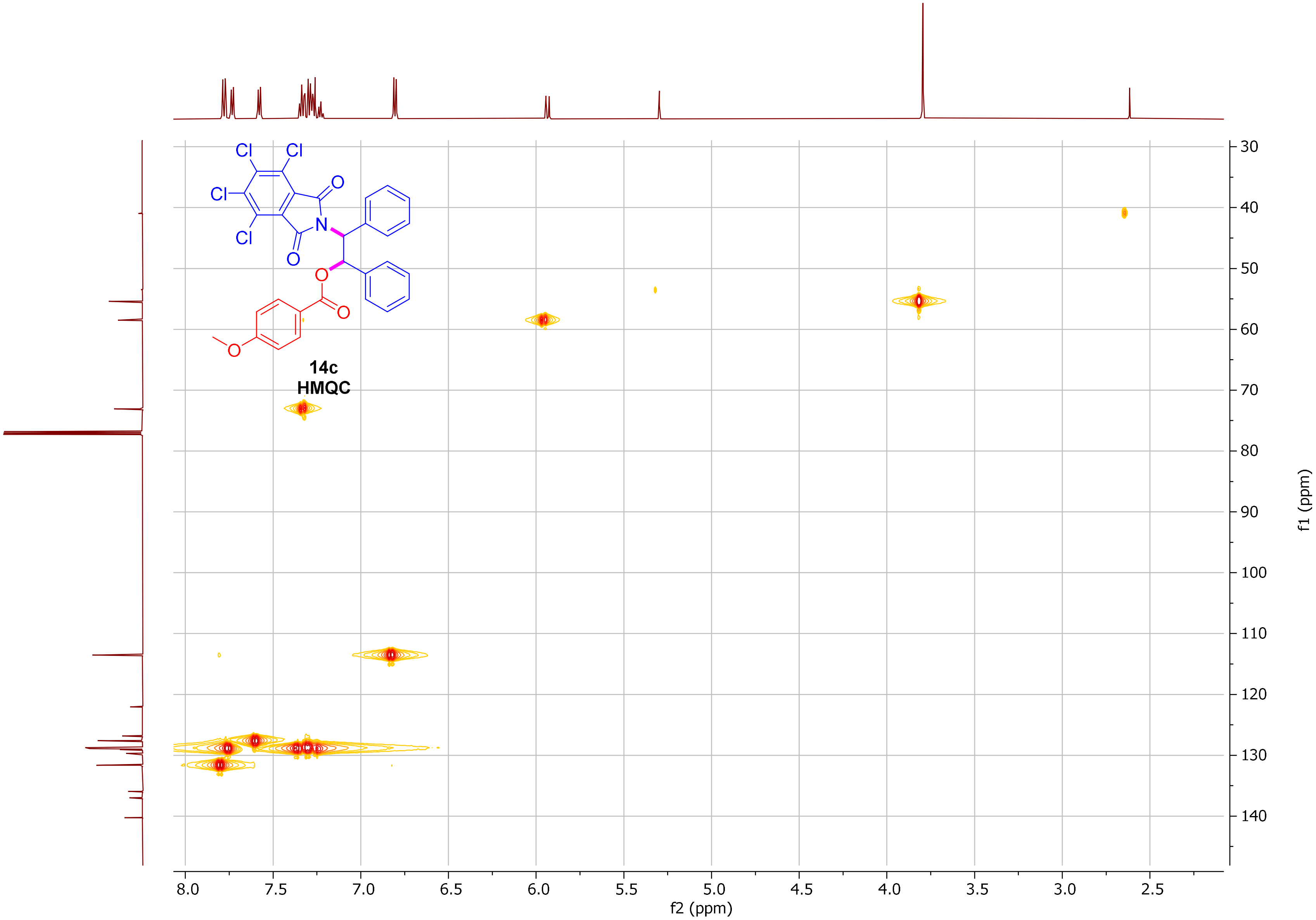


14c

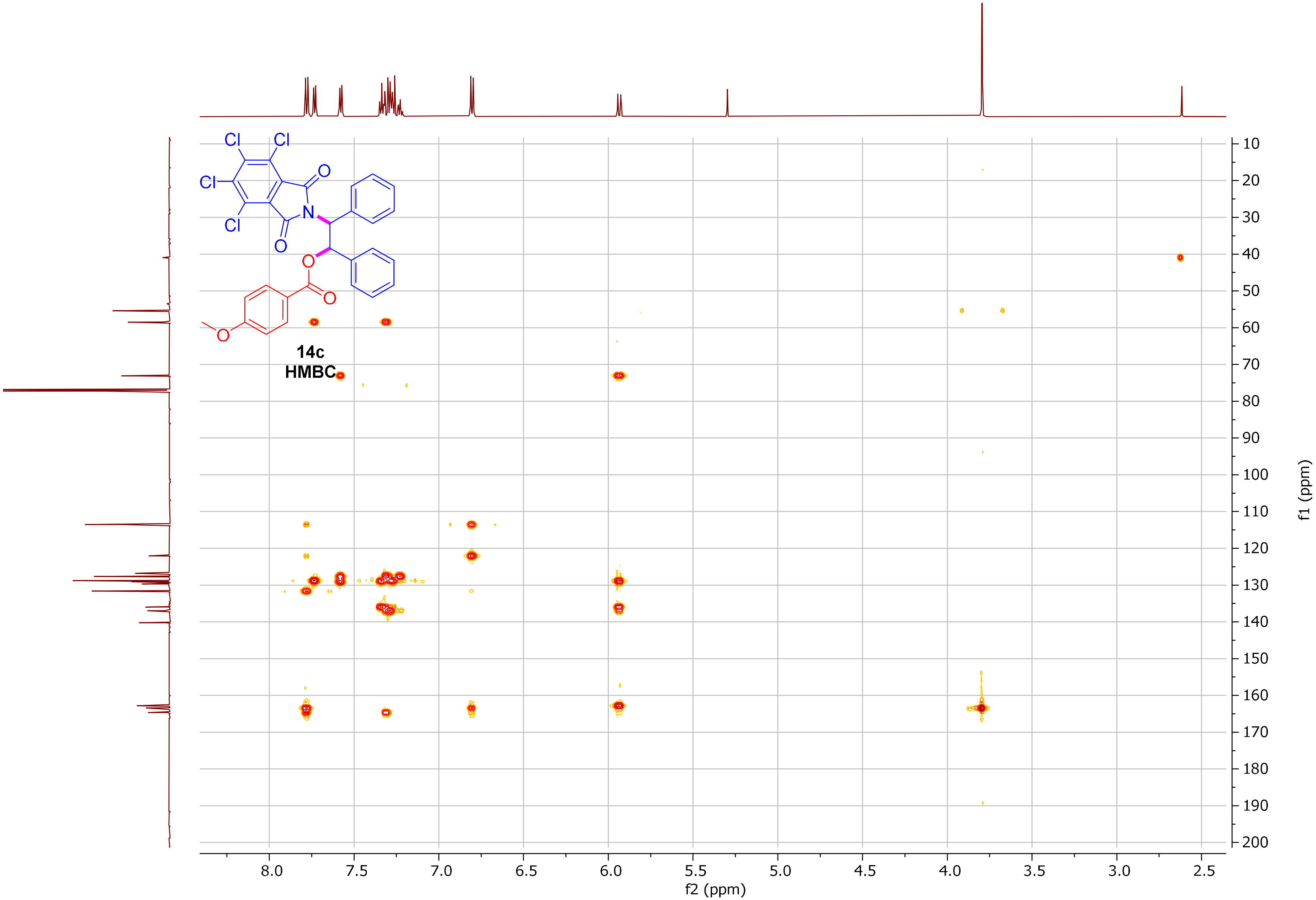
7.7868
7.7755
7.7720
7.7414
7.7387
7.7295
7.7263
7.5871
7.5844
7.5754
7.5721
7.3492
7.3365
7.3239
7.3186
7.3001
7.2877
7.2849
7.2821
7.2747
7.2701
7.2600 CDCl3
7.2274
6.8166
6.8117
6.8082
6.8004
6.7970
6.7920
5.9444
5.9259
5.2979
3.7947
2.6159
1.5882 H2O
1.5862 H2O
1.2541
Cl
Cl
Cl
Cl
O
O
N
O
O
O
DCM
DMSO
1.96
2.01
2.01
1.97
3.12
1.07
2.01
1.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.6622
163.4344
162.8137
140.2553
136.9777
135.9498
131.6370
129.6888
129.0922
128.9118
128.8872
128.7641
127.6273
126.8220
122.0662
113.5489
77.2574
77.0454
76.8346
73.0649
58.4857
55.4205
Cl
Cl
Cl
Cl
O
N
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

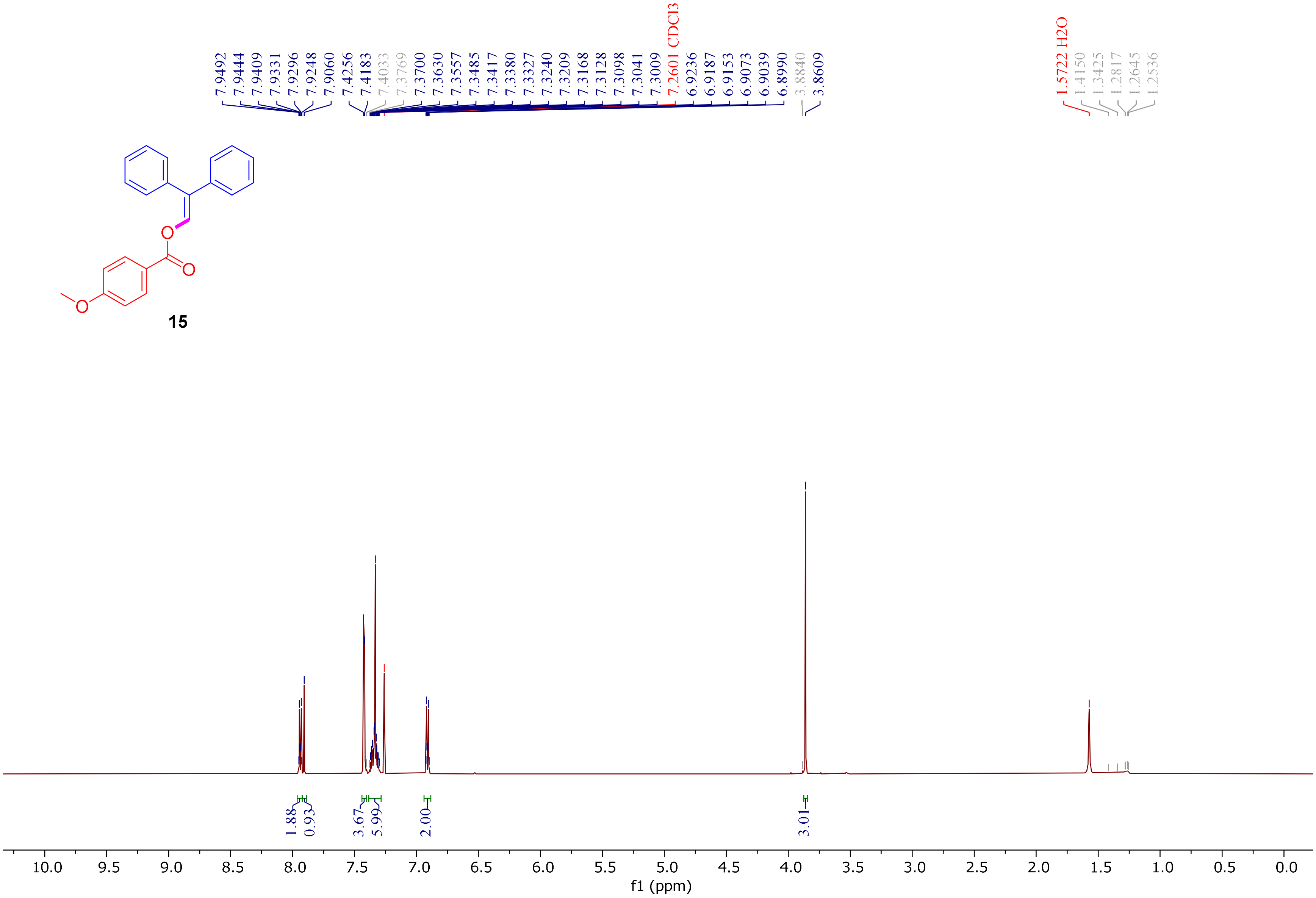
14c



Cl
Cl
Cl
Cl
O
N
O
O
O
O
14c
HMQC
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

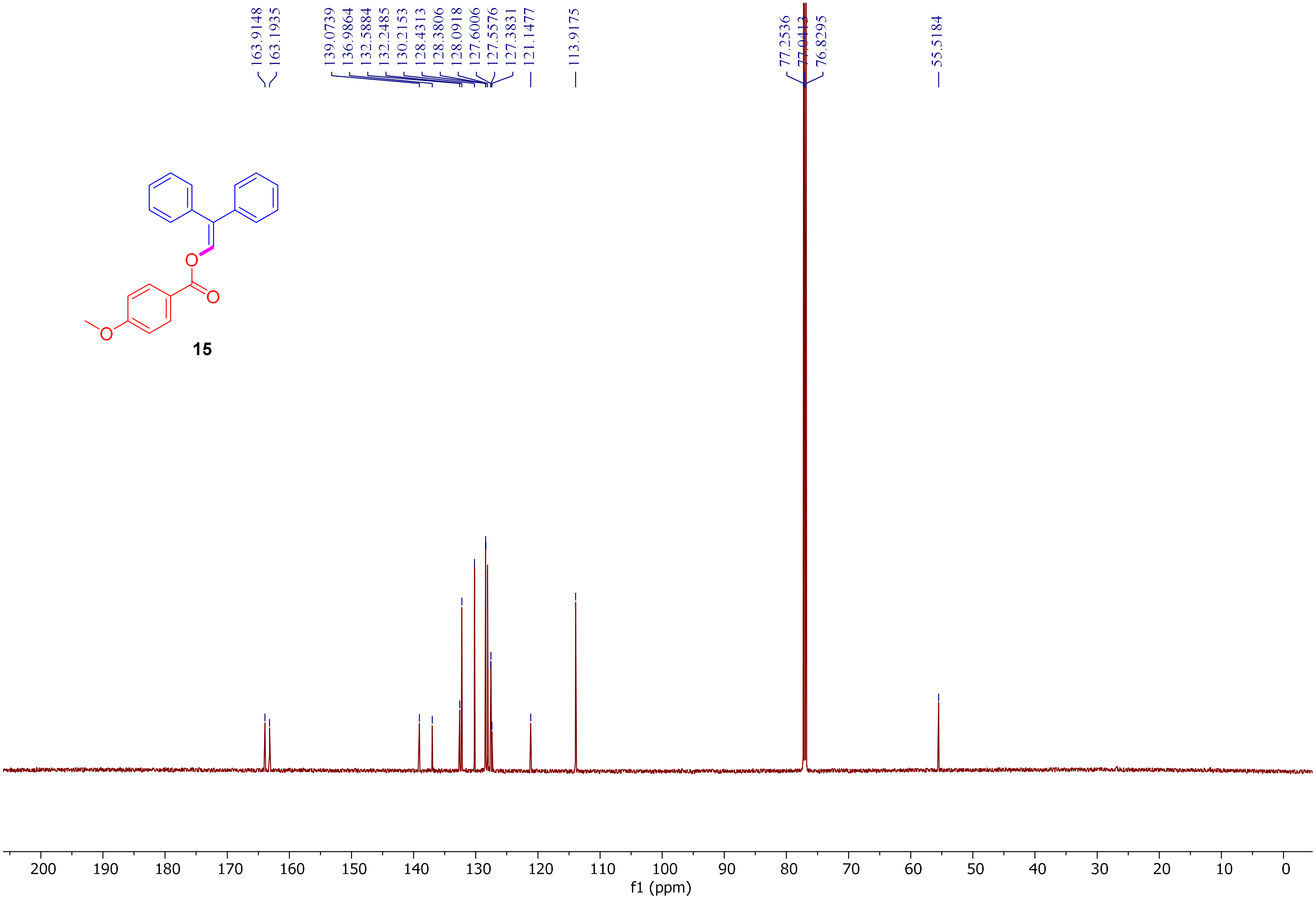


Cl
Cl
Cl
Cl
O
N
O
O
O
O
14c
HMBC
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)

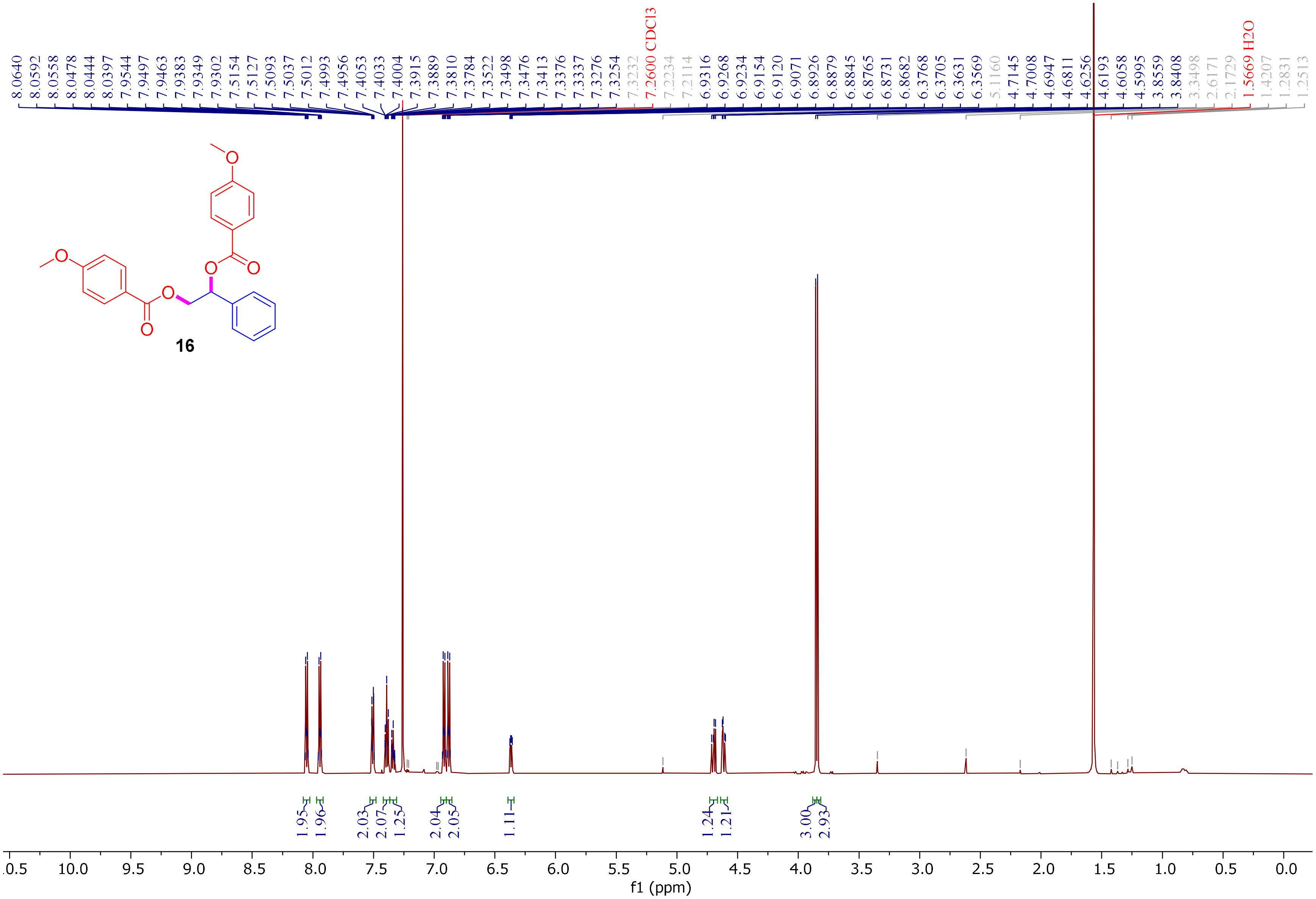


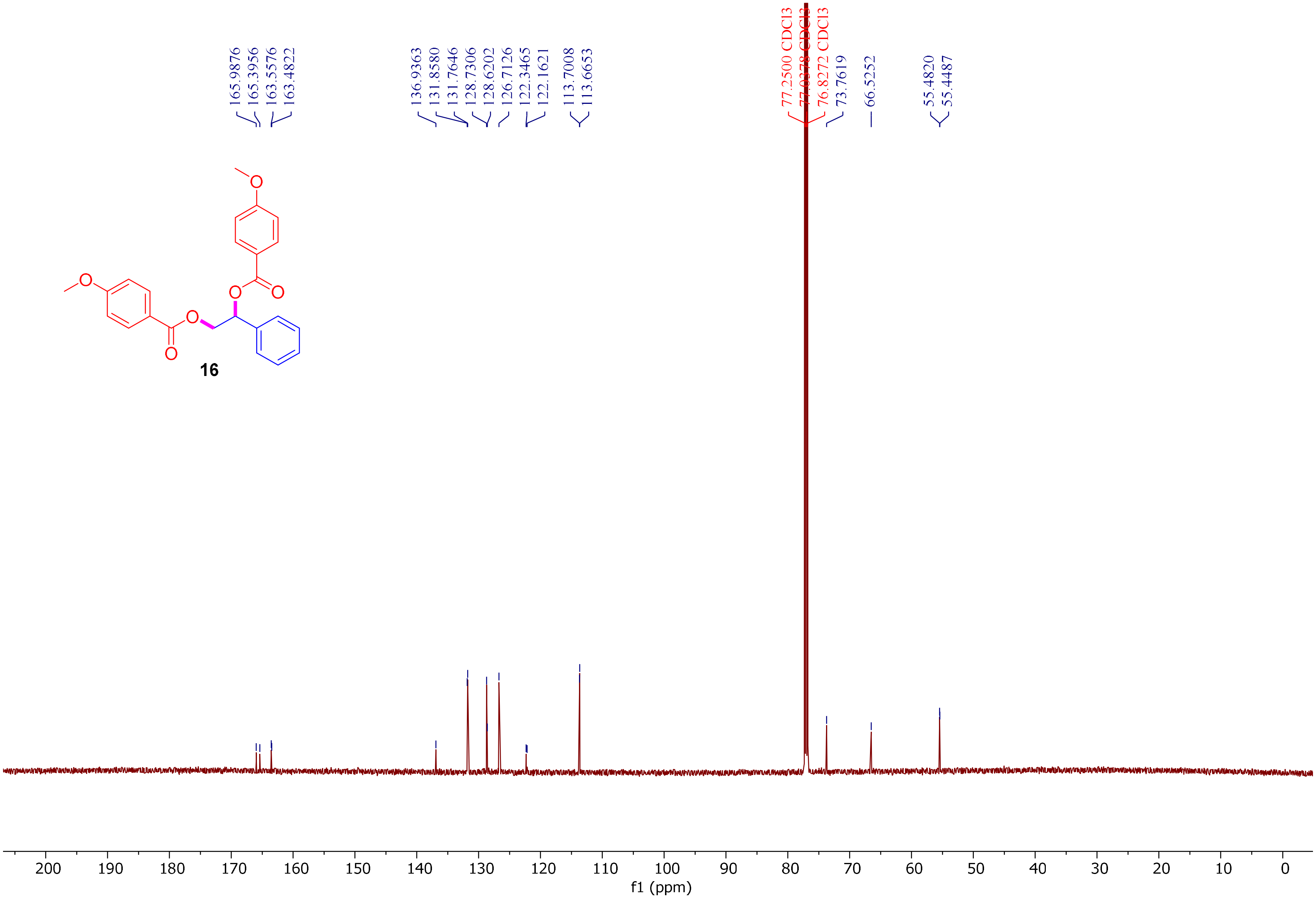
15

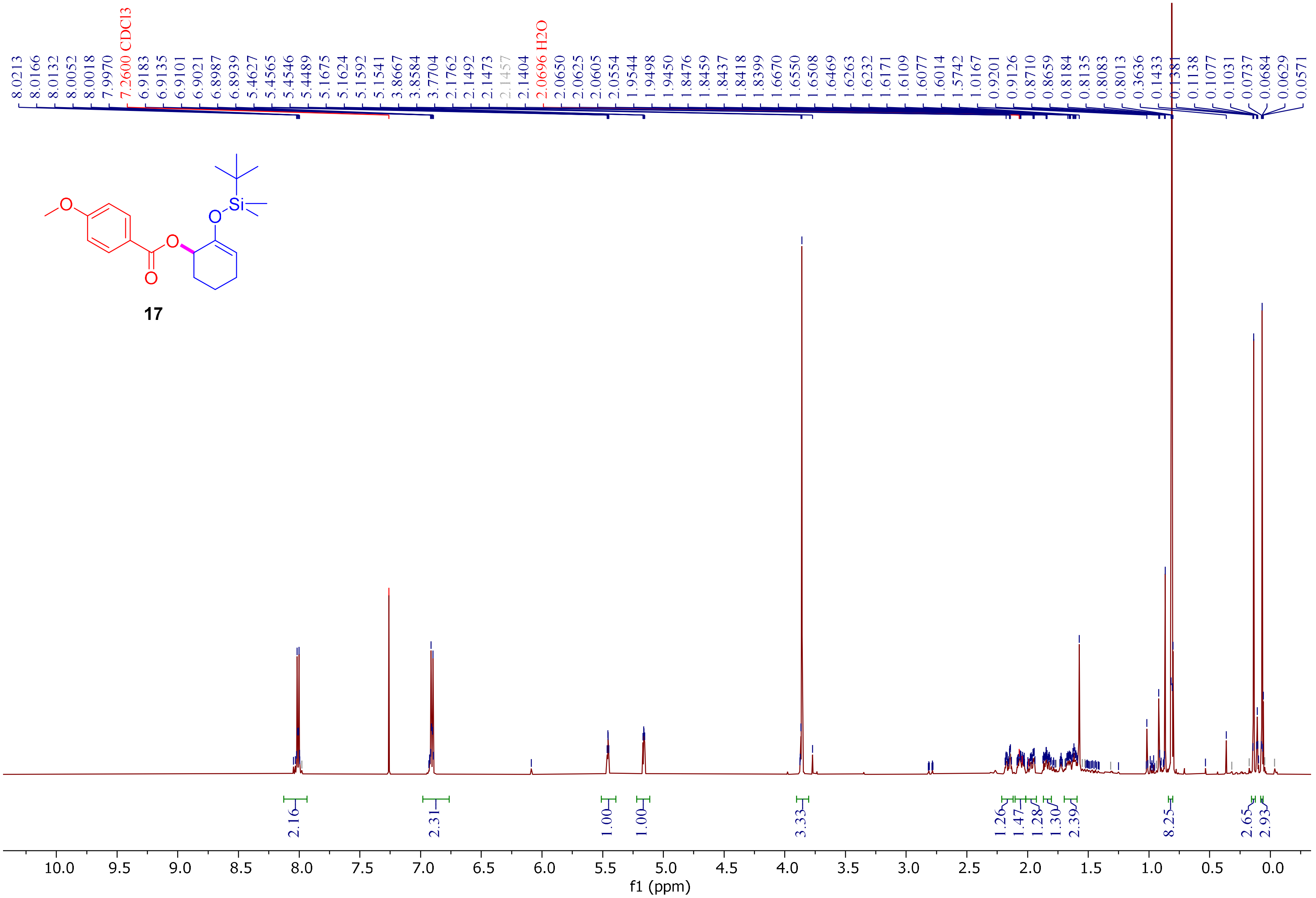
7.9492
7.9444
7.9409
7.9331
7.9296
7.9248
7.9060
7.4256
7.4183
7.4033
7.3769
7.3700
7.3630
7.3557
7.3485
7.3417
7.3380
7.3327
7.3240
7.3209
7.3168
7.3128
7.3098
7.3041
7.3009
7.2601 CDCl3
6.9236
6.9187
6.9153
6.9073
6.9039
6.8990
3.8840
3.8609
1.5722 H2O
1.4150
1.3425
1.2817
1.2645
1.2536
1.88
0.93
3.67
5.99
2.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


15

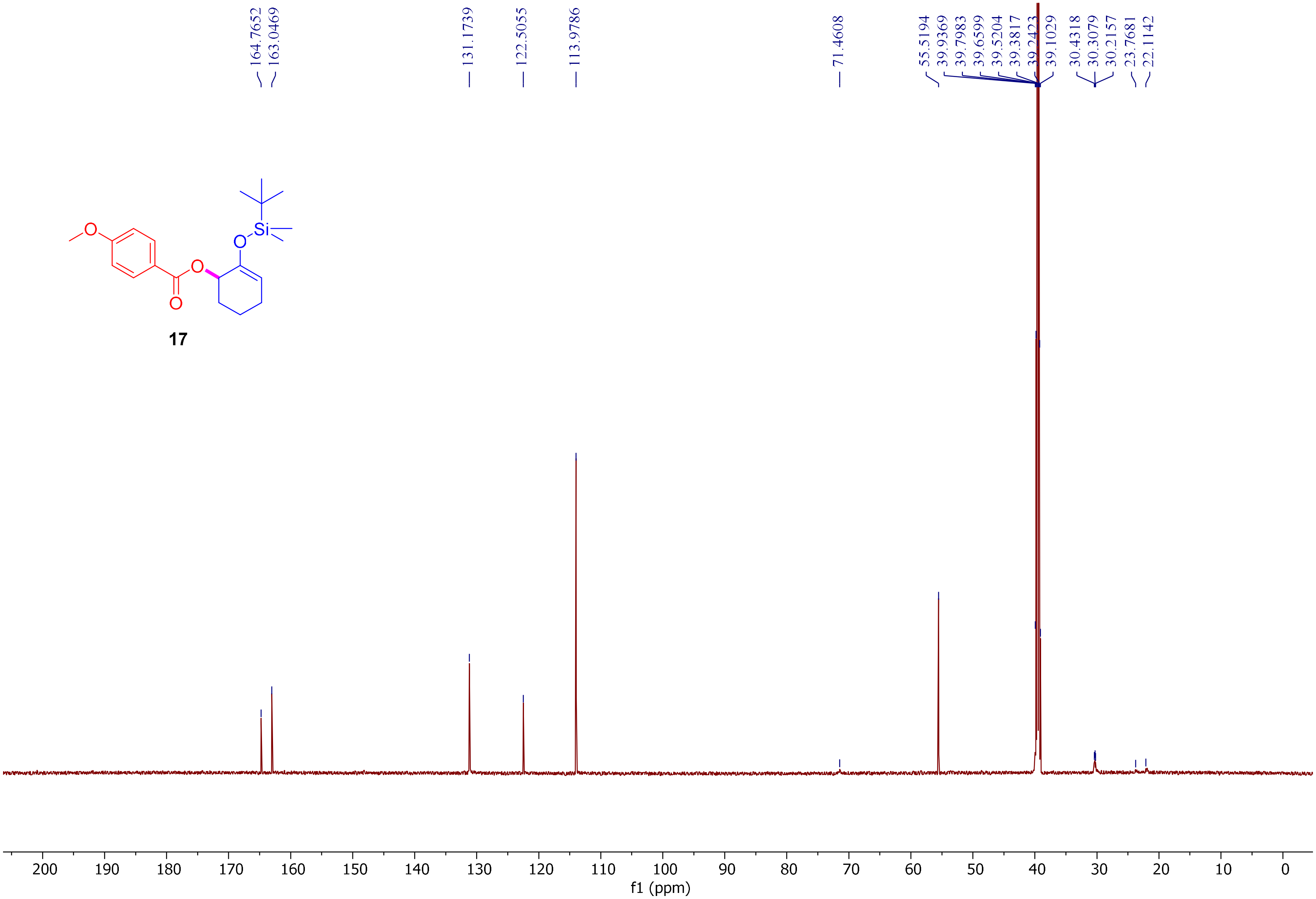
163.9148
163.1935
139.0739
136.9864
132.5884
132.2485
130.2153
128.4313
128.3806
128.0918
127.6006
127.5576
127.3831
121.1477
113.9175
77.2536
77.0413
76.8295
55.5184
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

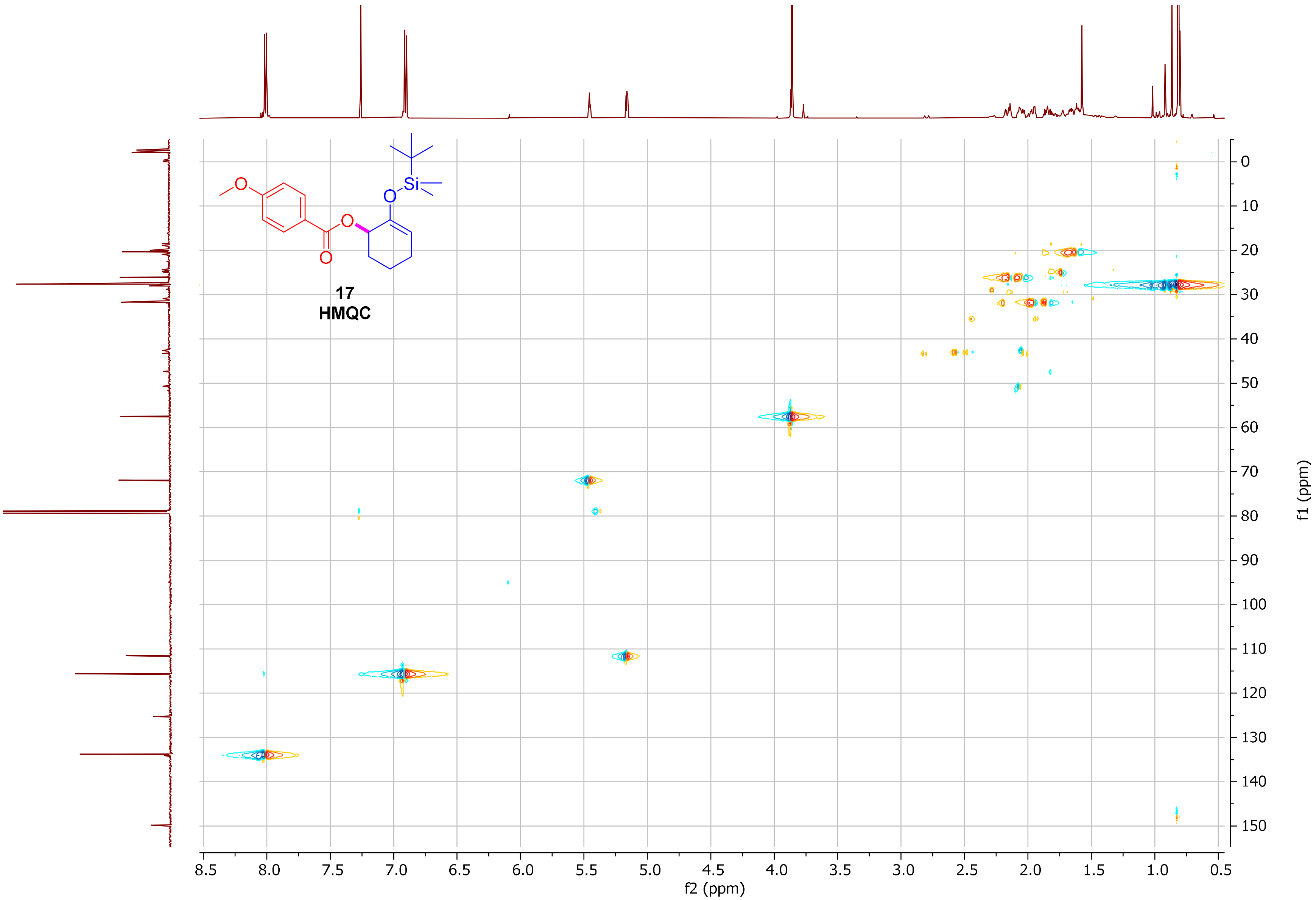

8.0640
8.0592
8.0558
8.0478
8.0444
8.0397
7.9544
7.9497
7.9463
7.9383
7.9349
7.9302
7.5154
7.5127
7.5093
7.5037
7.5012
7.4993
7.4956
7.4053
7.4033
7.4004
7.3915
7.3889
7.3810
7.3784
7.3522
7.3498
7.3476
7.3413
7.3376
7.3337
7.3276
7.3254
7.3232
7.2600 CDCl3
7.2234
7.2114
6.9316
6.9268
6.9234
6.9154
6.9120
6.9071
6.8926
6.8879
6.8845
6.8765
6.8731
6.8682
6.3768
6.3705
6.3631
6.3569
5.1160
4.7145
4.7008
4.6947
4.6811
4.6256
4.6193
4.6058
4.5995
3.8559
3.8408
3.3498
2.6171
2.1729
1.5669 H2O
1.4207
1.2831
1.2513
O
O
O
O
O
O
16
1.95
1.96
2.03
2.07
1.25
2.04
2.05
1.11
1.24
1.21
3.00
2.93
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.9876
165.3956
163.5576
163.4822
136.9363
131.8580
131.7646
128.7306
128.6202
126.7126
122.3465
122.1621
113.7008
113.6653
77.2500 CDCl3
77.0378 CDCl3
76.8272 CDCl3
73.7619
66.5252
55.4820
55.4487
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8.0213
8.0166
8.0132
8.0052
8.0018
7.9970
7.2600 CDCl3
6.9183
6.9135
6.9101
6.9021
6.8987
6.8939
5.4627
5.4565
5.4546
5.4489
5.1675
5.1624
5.1592
5.1541
3.8667
3.8584
3.7704
2.1762
2.1492
2.1473
2.1457
2.1404
2.0696 H2O
2.0650
2.0625
2.0605
2.0554
1.9544
1.9498
1.9450
1.8476
1.8459
1.8437
1.8418
1.8399
1.6670
1.6550
1.6508
1.6469
1.6263
1.6232
1.6171
1.6109
1.6077
1.6014
1.5742
1.0167
0.9201
0.9126
0.8710
0.8659
0.8184
0.8135
0.8083
0.8013
0.3636
0.1433
0.1381
0.1138
0.1077
0.1031
0.0737
0.0684
0.0629
0.0571
O
O
O
O
Si
2.16
2.31
1.00
1.00
3.33
1.26
1.47
1.28
1.30
2.39
8.25
2.65
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

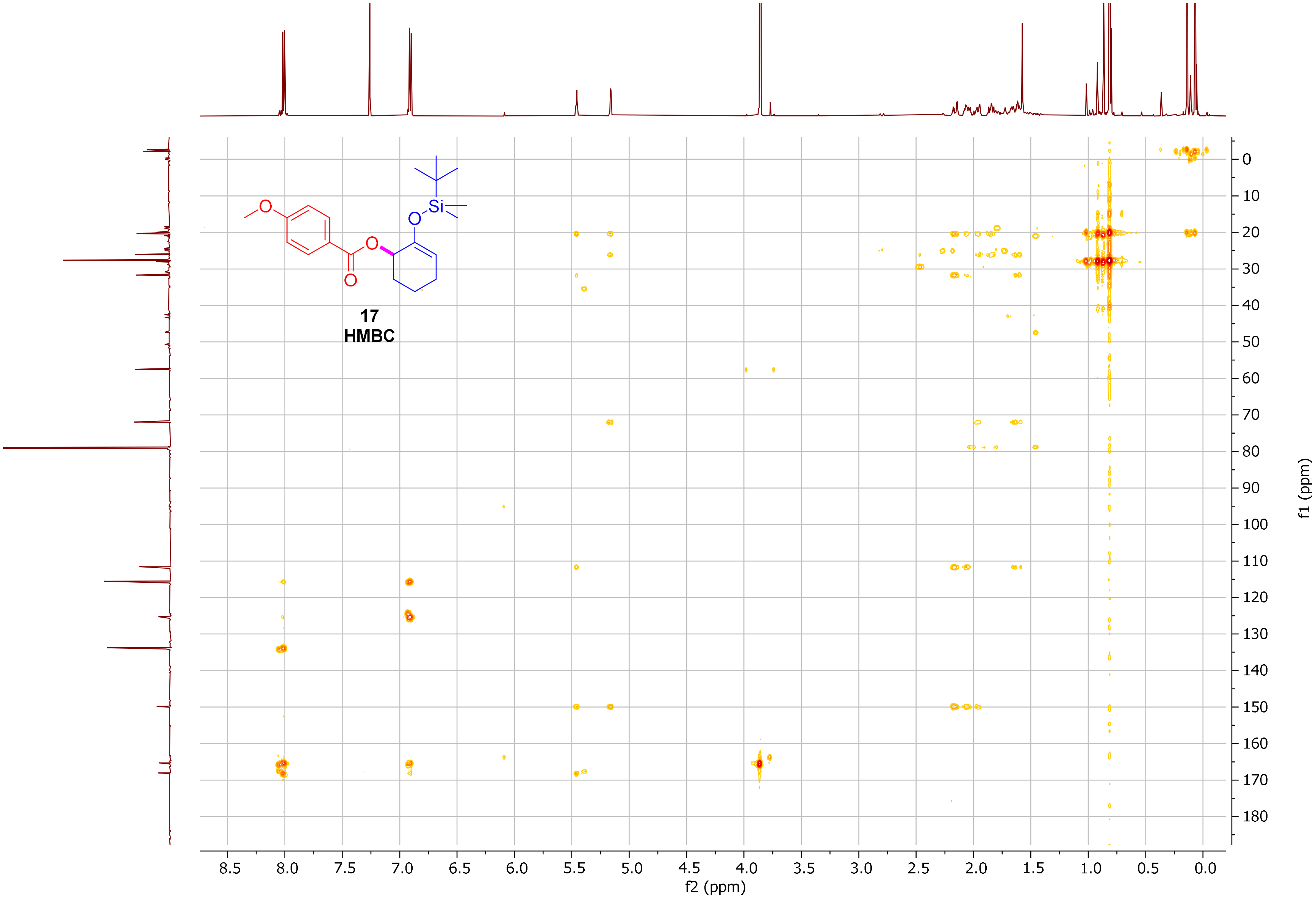
17


17
164.7652
163.0469
131.1739
122.5055
113.9786
71.4608
55.5194
39.9369
39.7983
39.6599
39.5204
39.3817
39.2423
39.1029
30.4318
30.3079
30.2157
23.7681
22.1142
O
O
O
O
Si
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

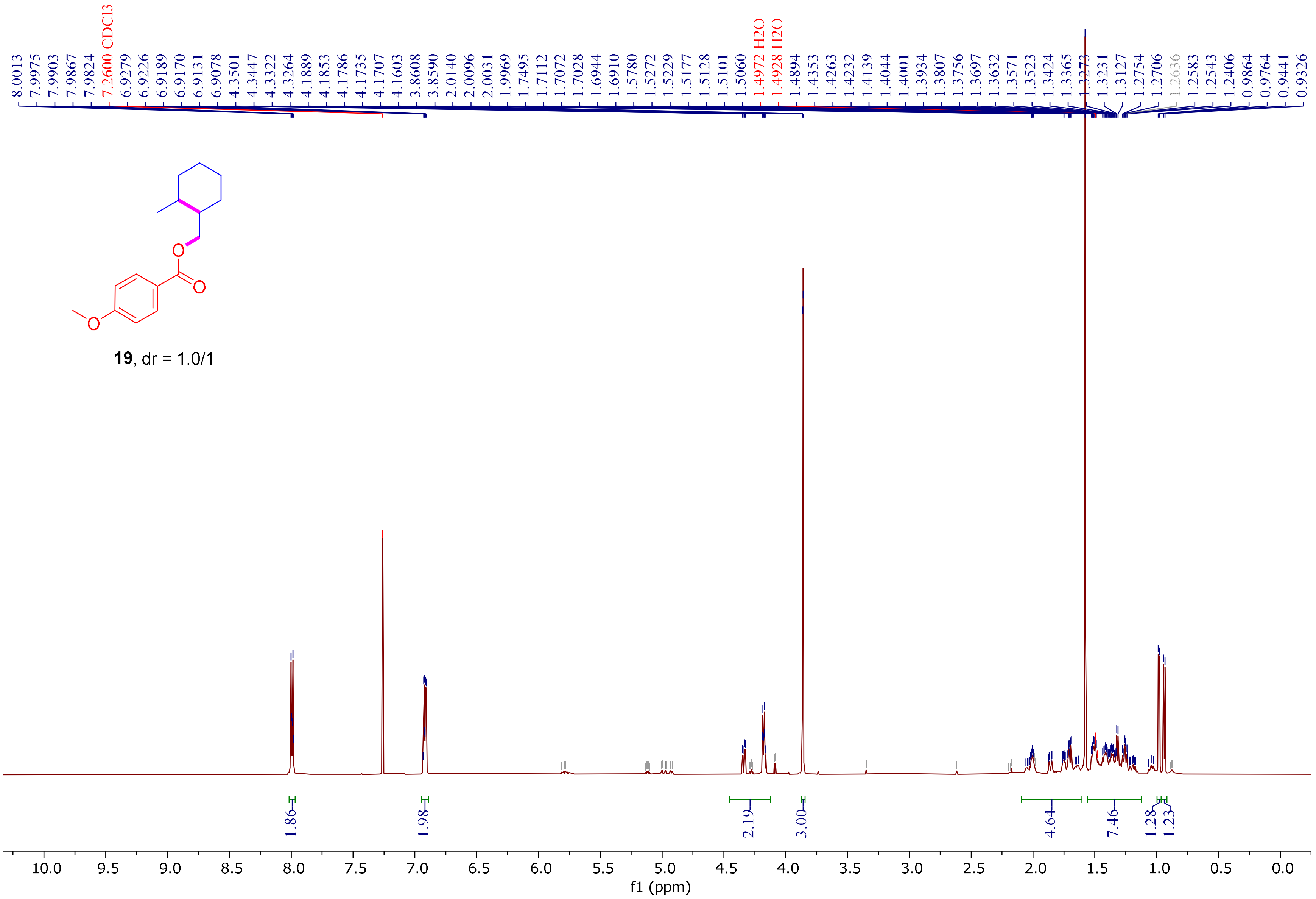


17
HMQC

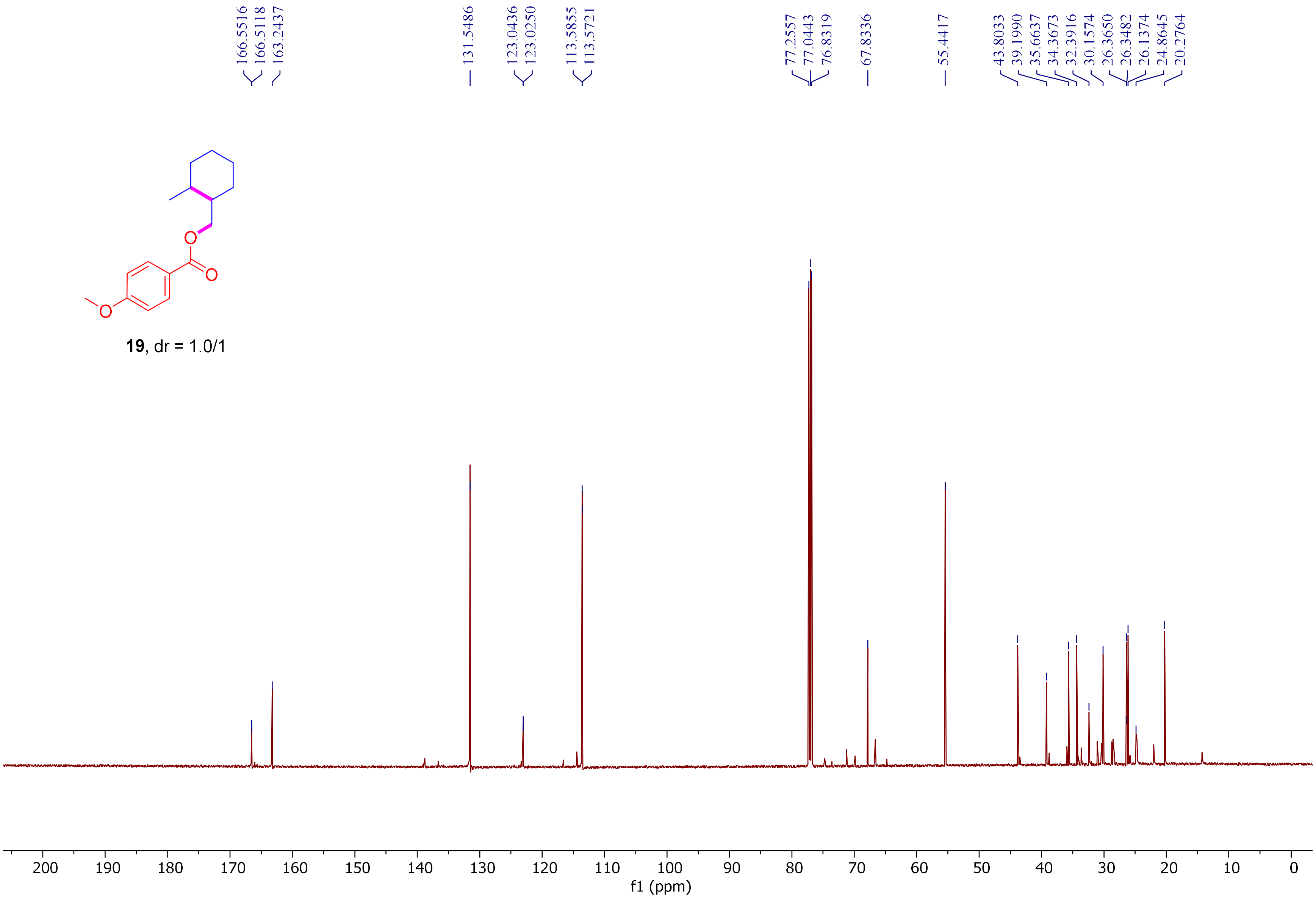
O
O
O
O
Si
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)



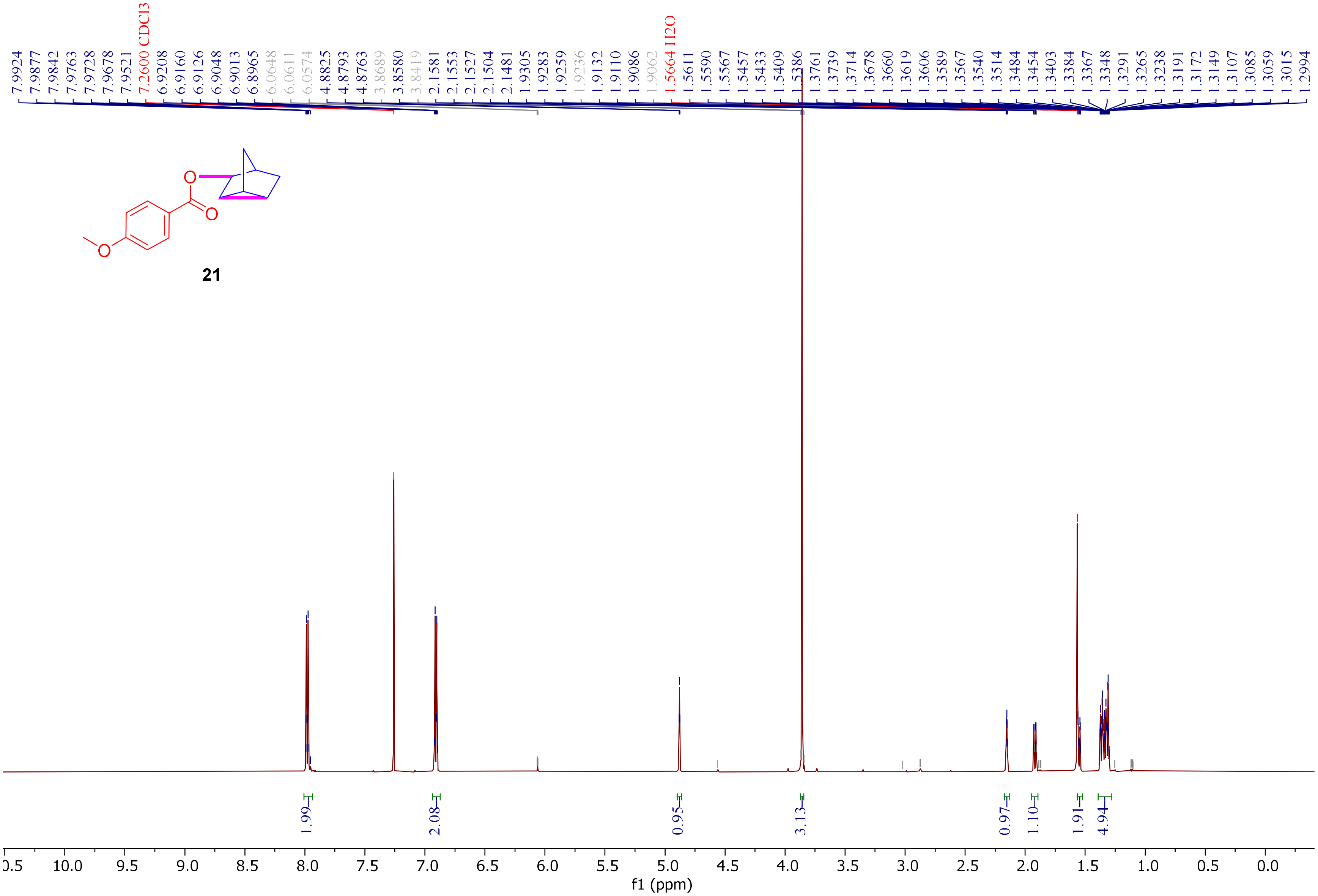
17
HMBC
O
O
O
O
Si
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


8.0013
7.9975
7.9903
7.9867
7.9824
7.2600 CDCl3
6.9279
6.9226
6.9189
6.9170
6.9131
6.9078
4.3501
4.3447
4.3322
4.3264
4.1889
4.1853
4.1786
4.1735
4.1707
4.1603
3.8608
3.8590
2.0140
2.0096
2.0031
1.9969
1.7495
1.7112
1.7072
1.7028
1.6944
1.6910
1.5780
1.5272
1.5229
1.5177
1.5128
1.5101
1.5060
1.4972 H2O
1.4928 H2O
1.4894
1.4353
1.4263
1.4232
1.4139
1.4044
1.4001
1.3934
1.3807
1.3756
1.3697
1.3632
1.3571
1.3523
1.3424
1.3365
1.3273
1.3231
1.3127
1.2754
1.2706
1.2636
1.2583
1.2543
1.2406
0.9864
0.9764
0.9441
0.9326
O
O
O
1.86
1.98
2.19
3.00
4.64
7.46
1.28
1.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

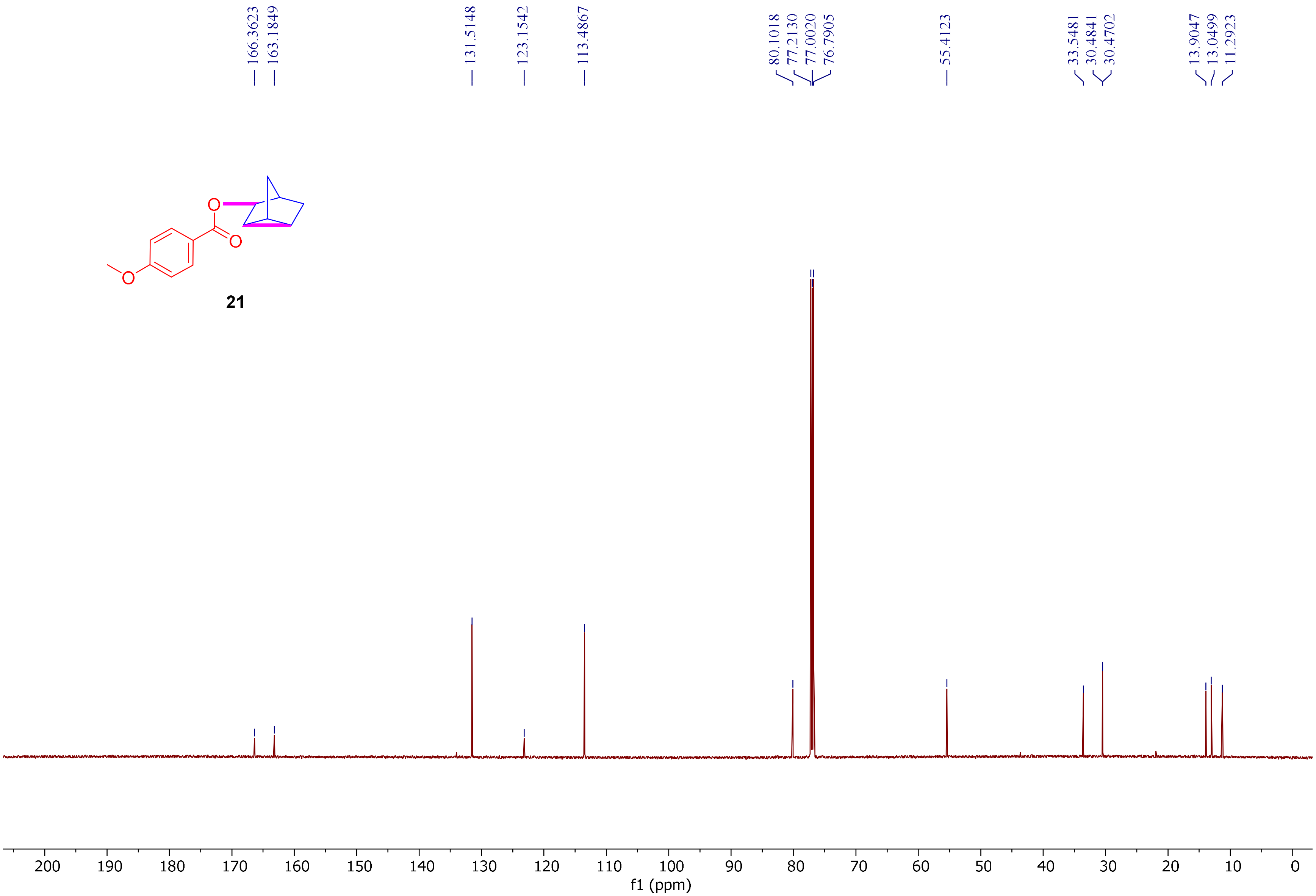
19, dr = 1.0/1

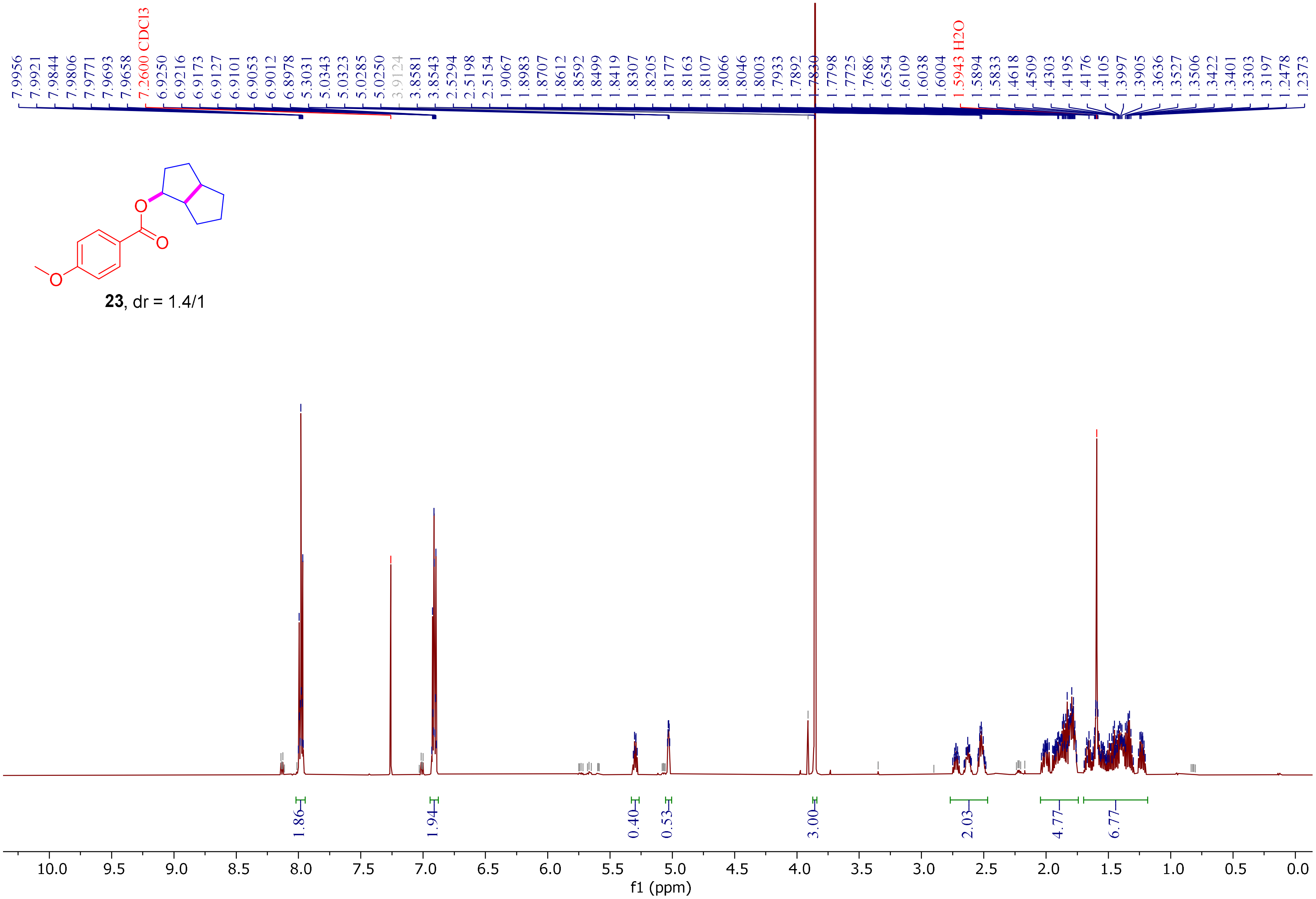

19, dr = 1.0/1

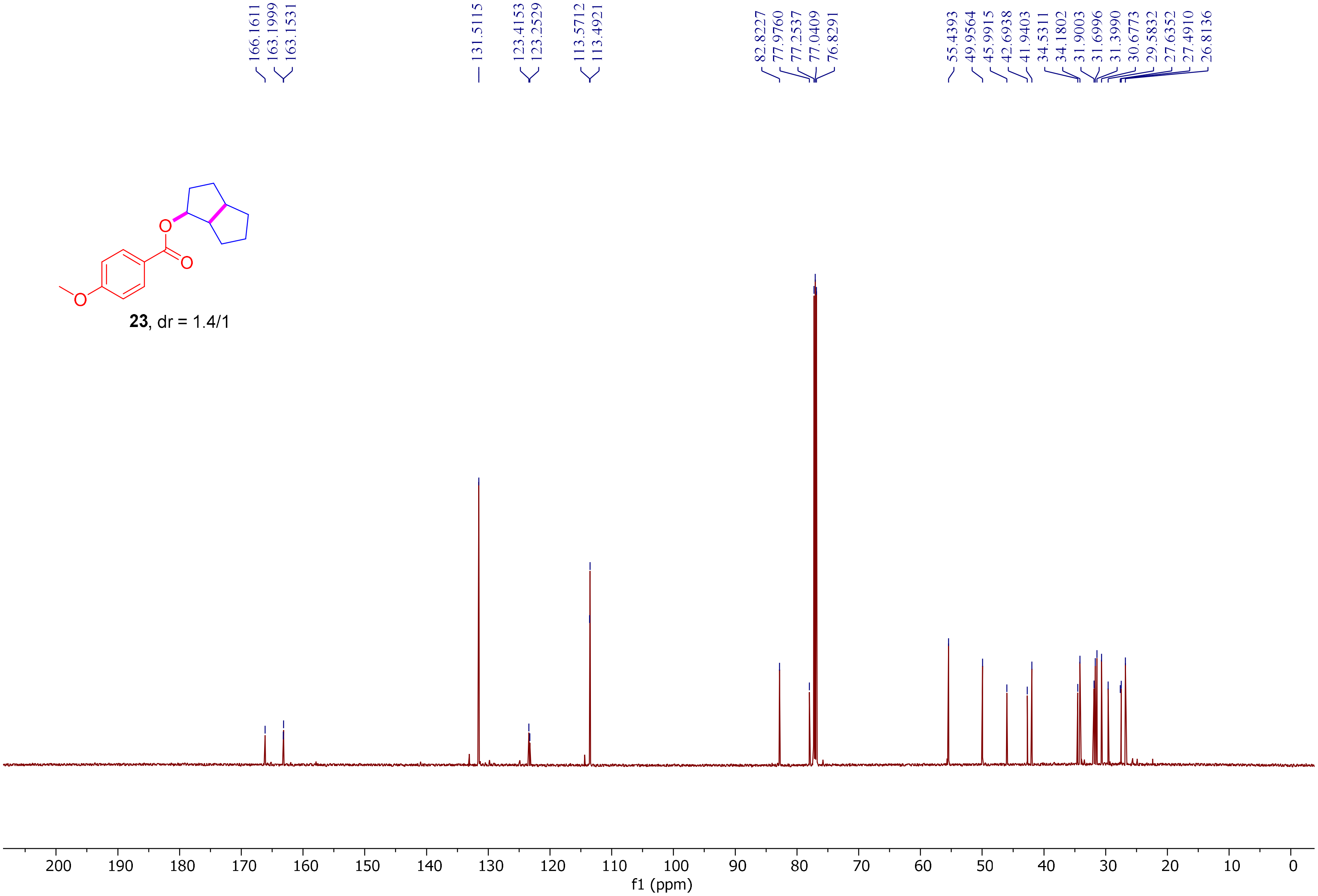
166.5516
166.5118
163.2437
131.5486
123.0436
123.0250
113.5855
113.5721
77.2557
77.0443
76.8319
67.8336
55.4417
43.8033
39.1990
35.6637
34.3673
32.3916
30.1574
26.3650
26.3482
26.1374
24.8645
20.2764
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9924
7.9877
7.9842
7.9763
7.9728
7.9678
7.9521
7.2600 CDCl3
6.9208
6.9160
6.9126
6.9048
6.9013
6.8965
6.0648
6.0611
6.0574
4.8825
4.8793
4.8763
3.8689
3.8580
3.8419
2.1581
2.1553
2.1527
2.1504
2.1481
1.9305
1.9283
1.9259
1.9236
1.9132
1.9110
1.9086
1.9062
1.5664 H2O
1.5611
1.5590
1.5567
1.5457
1.5433
1.5409
1.5386
1.3761
1.3739
1.3714
1.3678
1.3660
1.3619
1.3606
1.3589
1.3567
1.3540
1.3514
1.3484
1.3454
1.3403
1.3384
1.3367
1.3348
1.3291
1.3265
1.3238
1.3191
1.3172
1.3149
1.3107
1.3085
1.3059
1.3015
1.2994
O
O
O
1.99
2.08
0.95
3.13
0.97
1.10
1.91
4.94
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

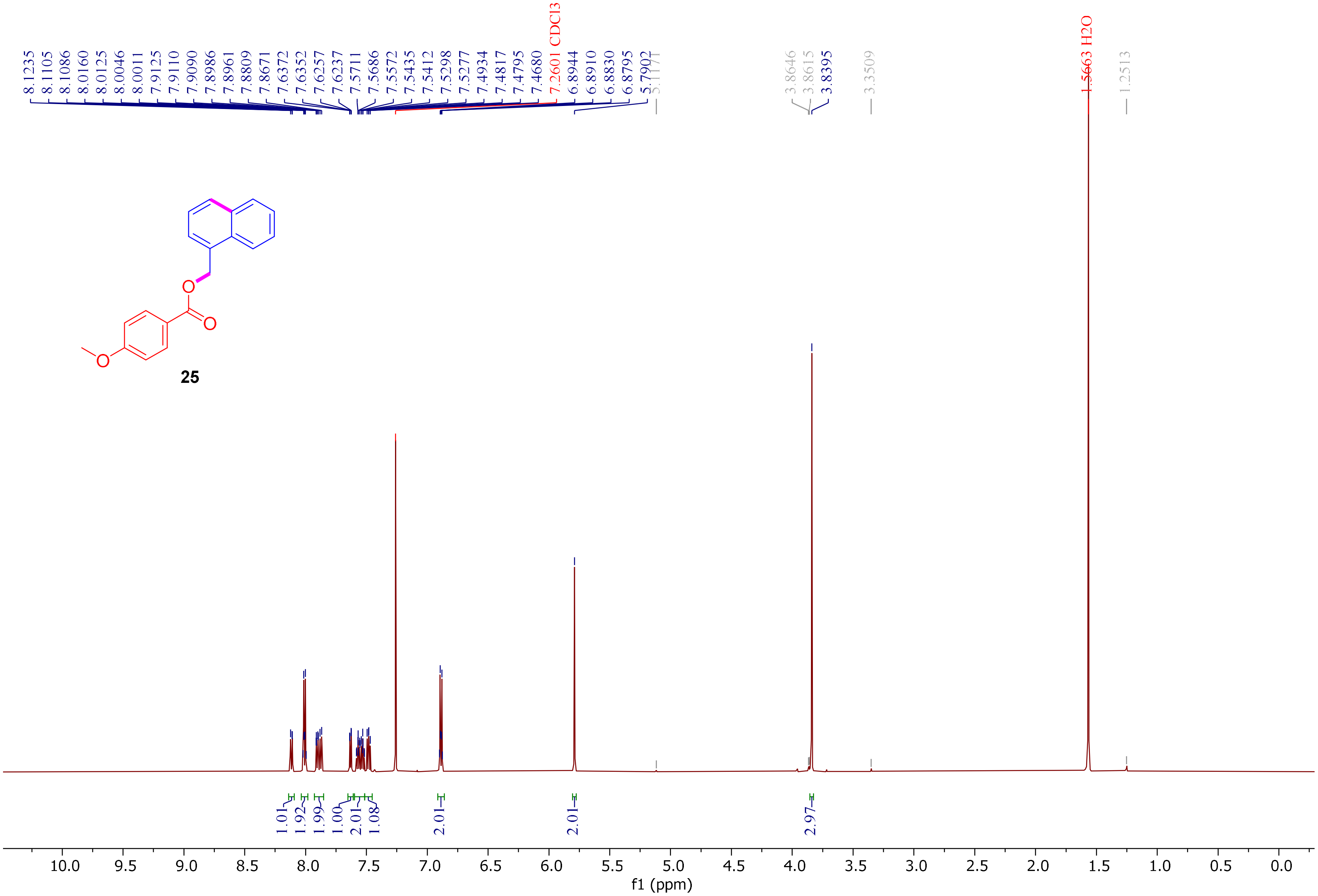
21

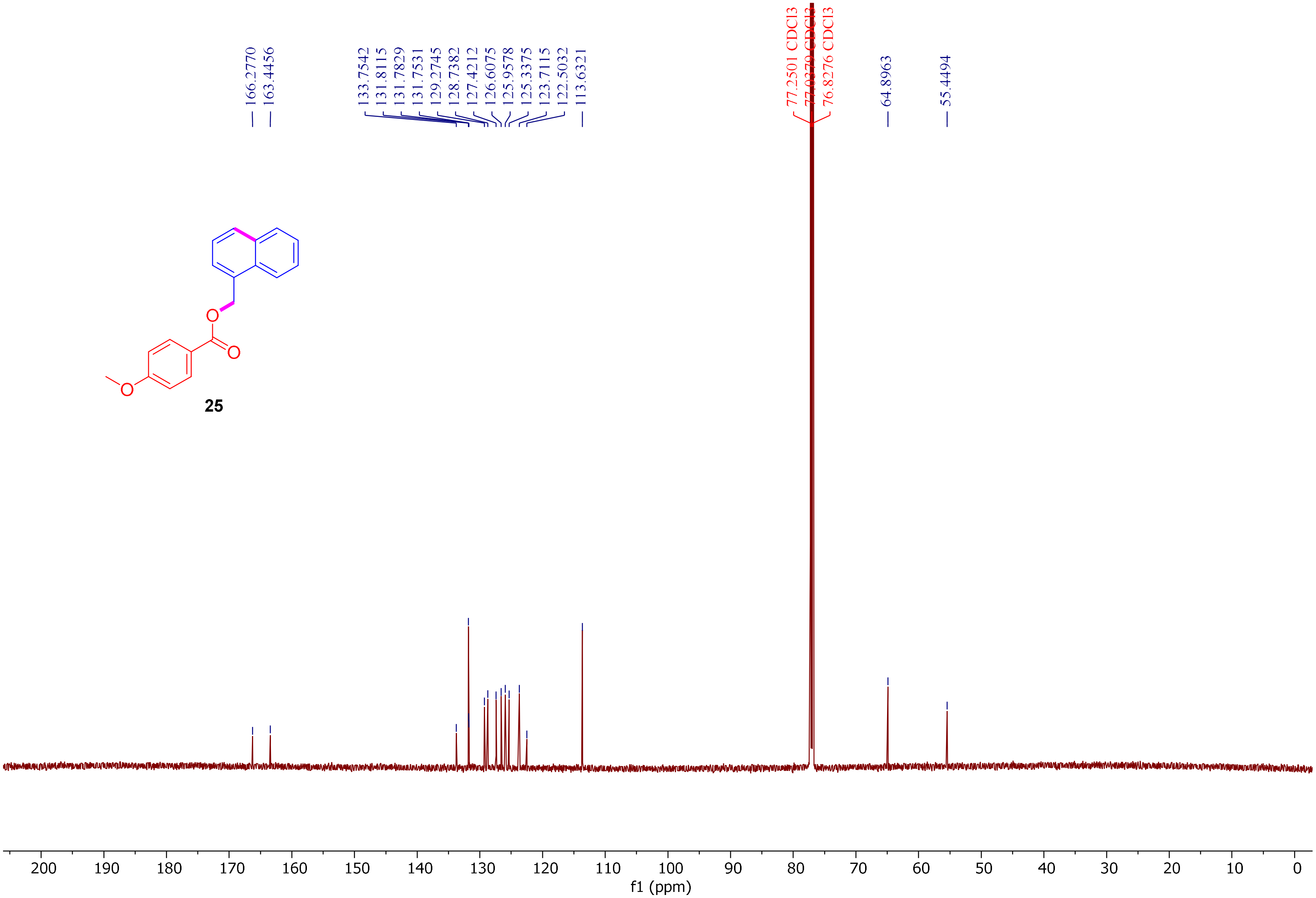

166.3623
163.1849
131.5148
123.1542
113.4867
80.1018
77.2130
77.0020
76.7905
55.4123
33.5481
30.4841
30.4702
13.9047
13.0499
11.2923
21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9956
7.9921
7.9844
7.9806
7.9771
7.9693
7.9658
7.2600 CDCl3
6.9250
6.9216
6.9173
6.9127
6.9101
6.9053
6.9012
6.8978
5.3031
5.0343
5.0323
5.0285
5.0250
3.9124
3.8581
3.8543
2.5294
2.5198
2.5154
1.9067
1.8983
1.8707
1.8612
1.8592
1.8499
1.8419
1.8307
1.8205
1.8177
1.8163
1.8107
1.8066
1.8046
1.8003
1.7933
1.7892
1.7830
1.7798
1.7725
1.7686
1.6554
1.6109
1.6038
1.6004
1.5943 H2O
1.5894
1.5833
1.4618
1.4509
1.4303
1.4195
1.4176
1.4105
1.3997
1.3905
1.3636
1.3527
1.3506
1.3422
1.3401
1.3303
1.3197
1.2478
1.2373
23, dr = 1.4/1
1.86
1.94
0.40
0.53
3.00
2.03
4.77
6.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


23, dr = 1.4/1

166.1611
163.1999
163.1531
131.5115
123.4153
123.2529
113.5712
113.4921
82.8227
77.9760
77.2537
77.0409
76.8291
55.4393
49.9564
45.9915
42.6938
41.9403
34.5311
34.1802
31.9003
31.6996
31.3990
30.6773
29.5832
27.6352
27.4910
26.8136
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.1235
8.1105
8.1086
8.0160
8.0125
8.0046
8.0011
7.9125
7.9110
7.9090
7.8986
7.8961
7.8809
7.8671
7.6372
7.6352
7.6257
7.6237
7.5711
7.5686
7.5572
7.5435
7.5412
7.5298
7.5277
7.4934
7.4817
7.4795
7.4680
7.2601 CDCl3
6.8944
6.8910
6.8830
6.8795
5.7902
5.1171
3.8646
3.8615
3.8395
3.3509
1.5663 H2O
1.2513
25
1.01
1.92
1.99
1.00
2.01
1.08
2.01
2.01
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



25

166.2770
163.4456
133.7542
131.8115
131.7829
131.7531
129.2745
128.7382
127.4212
126.6075
125.9578
125.3375
123.7115
122.5032
113.6321
77.2501 CDCl3
77.0379 CDCl3
76.8276 CDCl3
64.8963
55.4494
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
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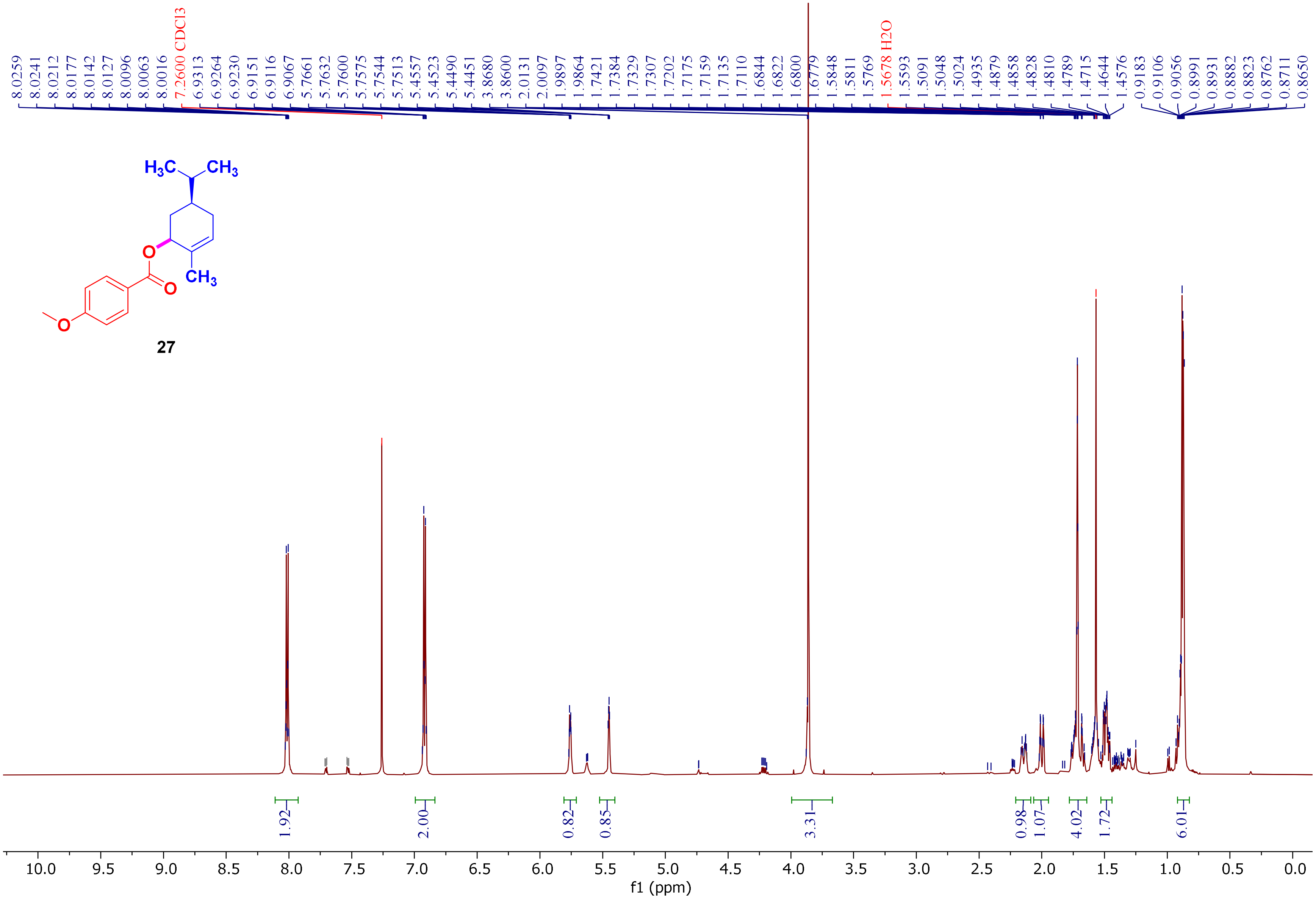
f1 (ppm)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6.9313
6.9264
6.9230
6.9151
6.9116
6.9067
5.7661
5.7632
5.7600
5.7575
5.7544
5.7513
5.4557
5.4523
5.4490
5.4451
3.8680
3.8600
2.0131
2.0097
1.9897
1.9864
1.7421
1.7384
1.7329
1.7307
1.7202
1.7175
1.7159
1.7135
1.7110
1.6844
1.6822
1.6800
1.6779
1.5848
1.5811
1.5769
1.5678 H2O
1.5593
1.5091
1.5048
1.5024
1.4935
1.4879
1.4858
1.4828
1.4810
1.4789
1.4715
1.4644
1.4576
0.9183
0.9106
0.9056
0.8991
0.8931
0.8882
0.8823
0.8762
0.8711
0.8650
H3C
CH3
O
O
CH3
O
27
1.92
2.00
0.82
0.85
3.31
0.98
1.07
4.02
1.72
6.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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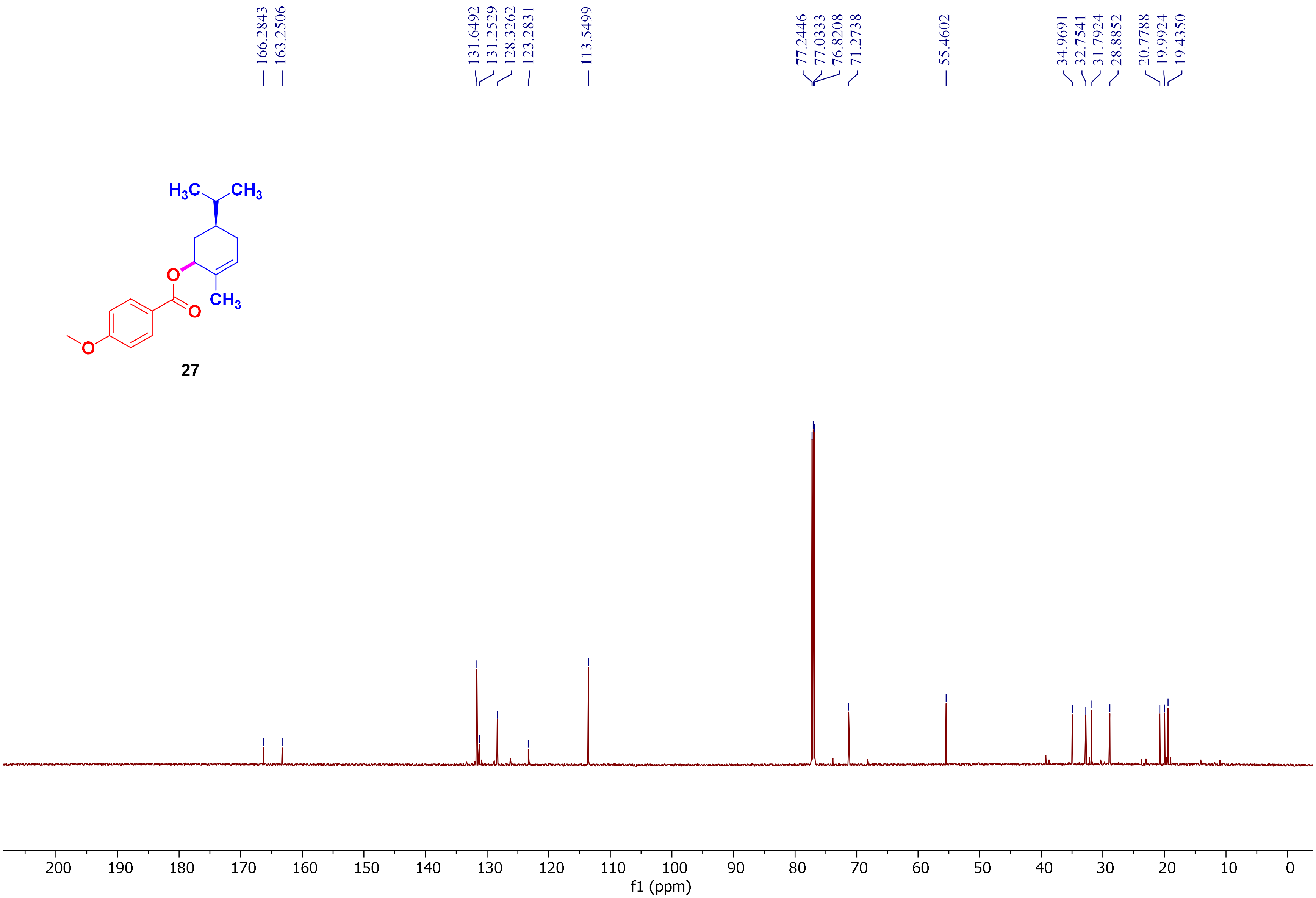
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.6492
131.2529
128.3262
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71.2738
55.4602
34.9691
32.7541
31.7924
28.8852
20.7788
19.9924
19.4350
H_3C
CH_3
CH_3
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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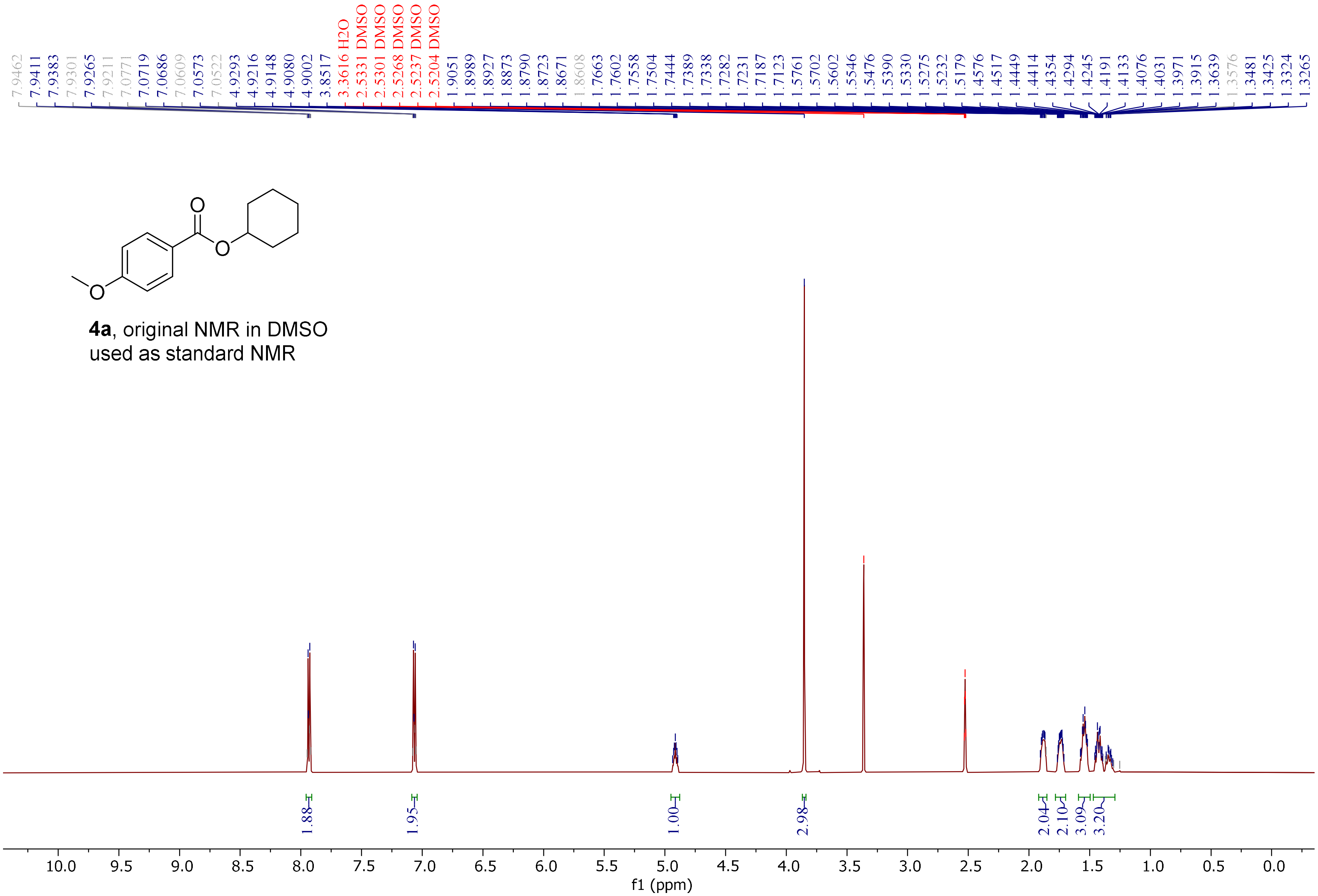
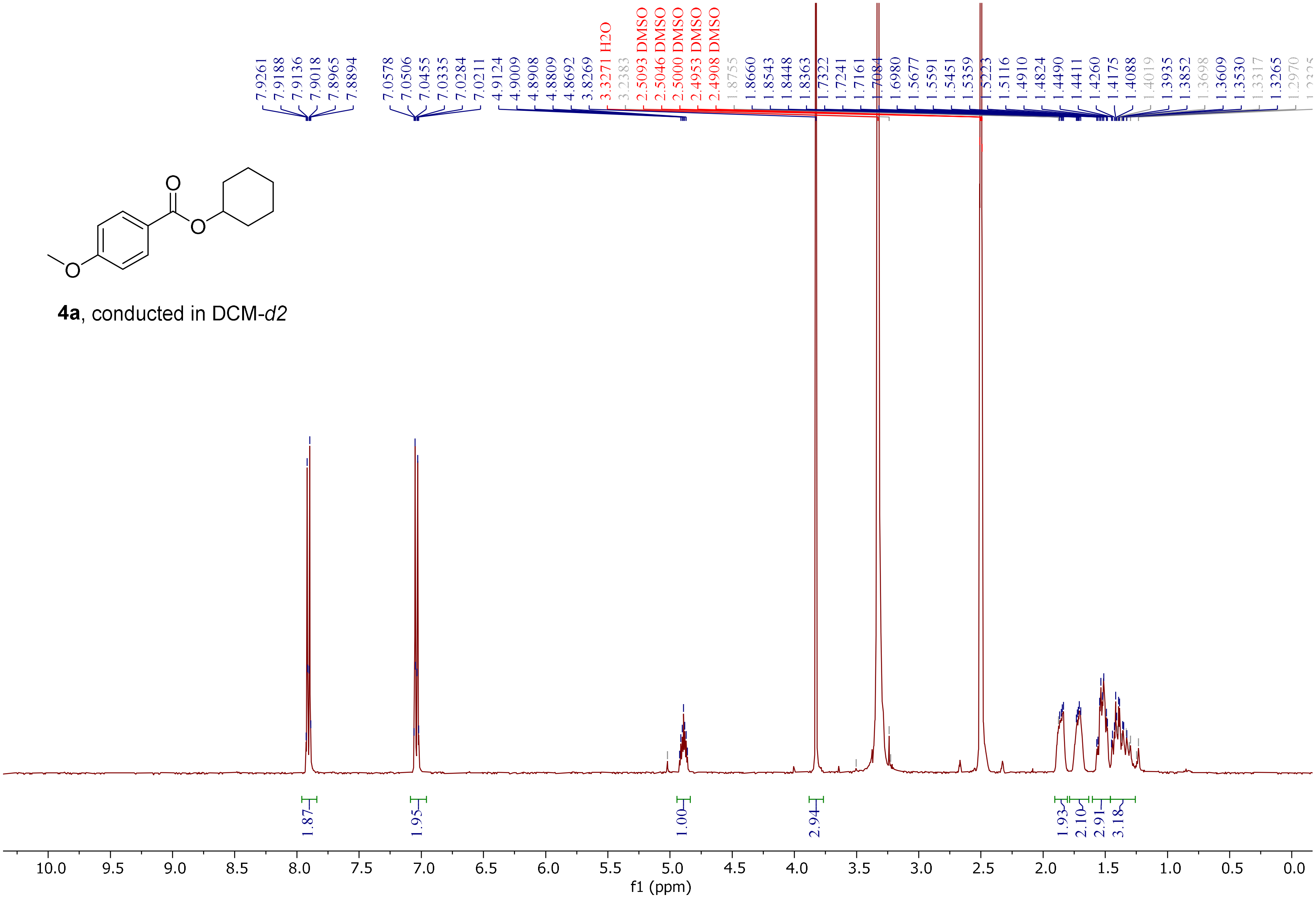
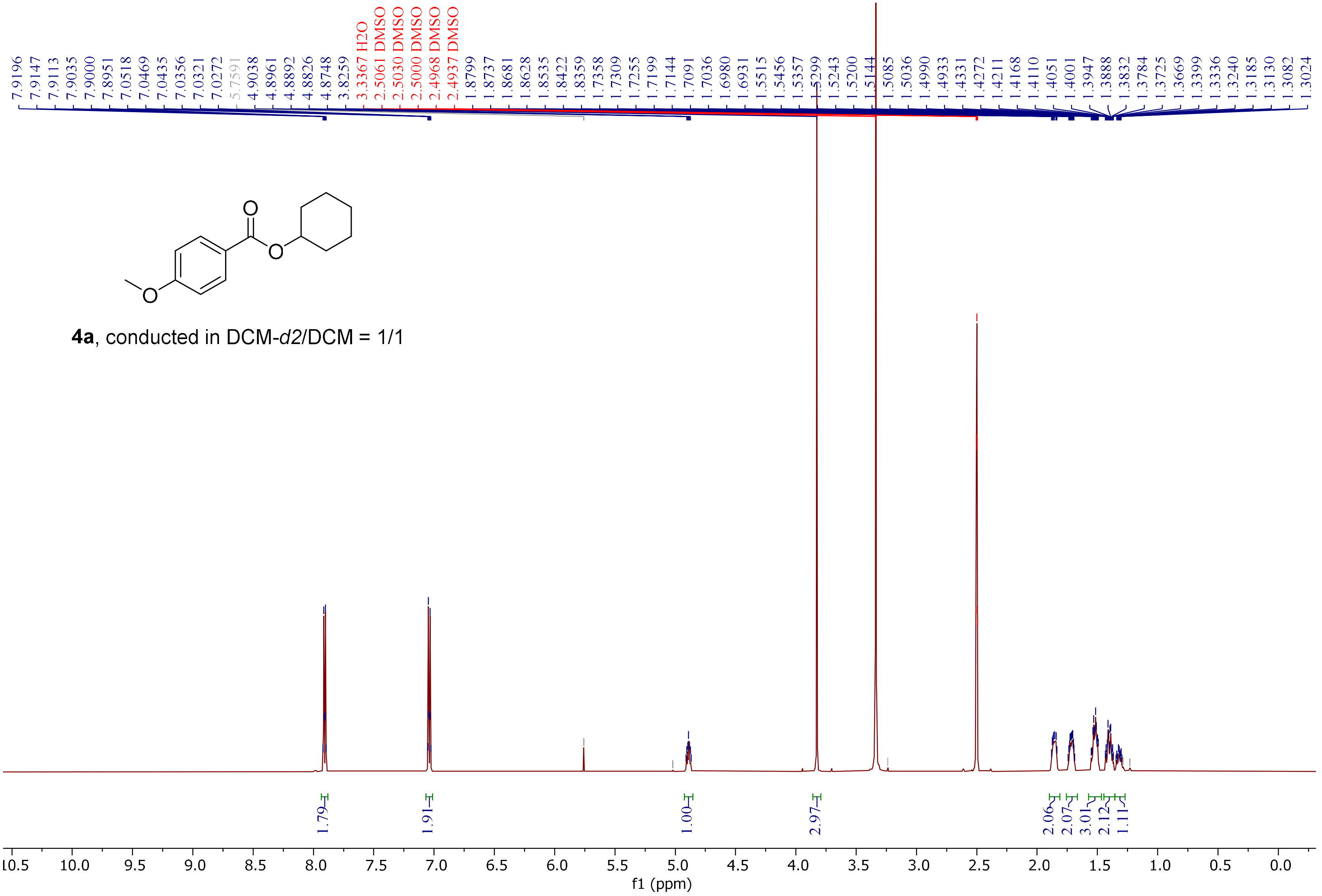
30
20
10
0
f1 (ppm)

27

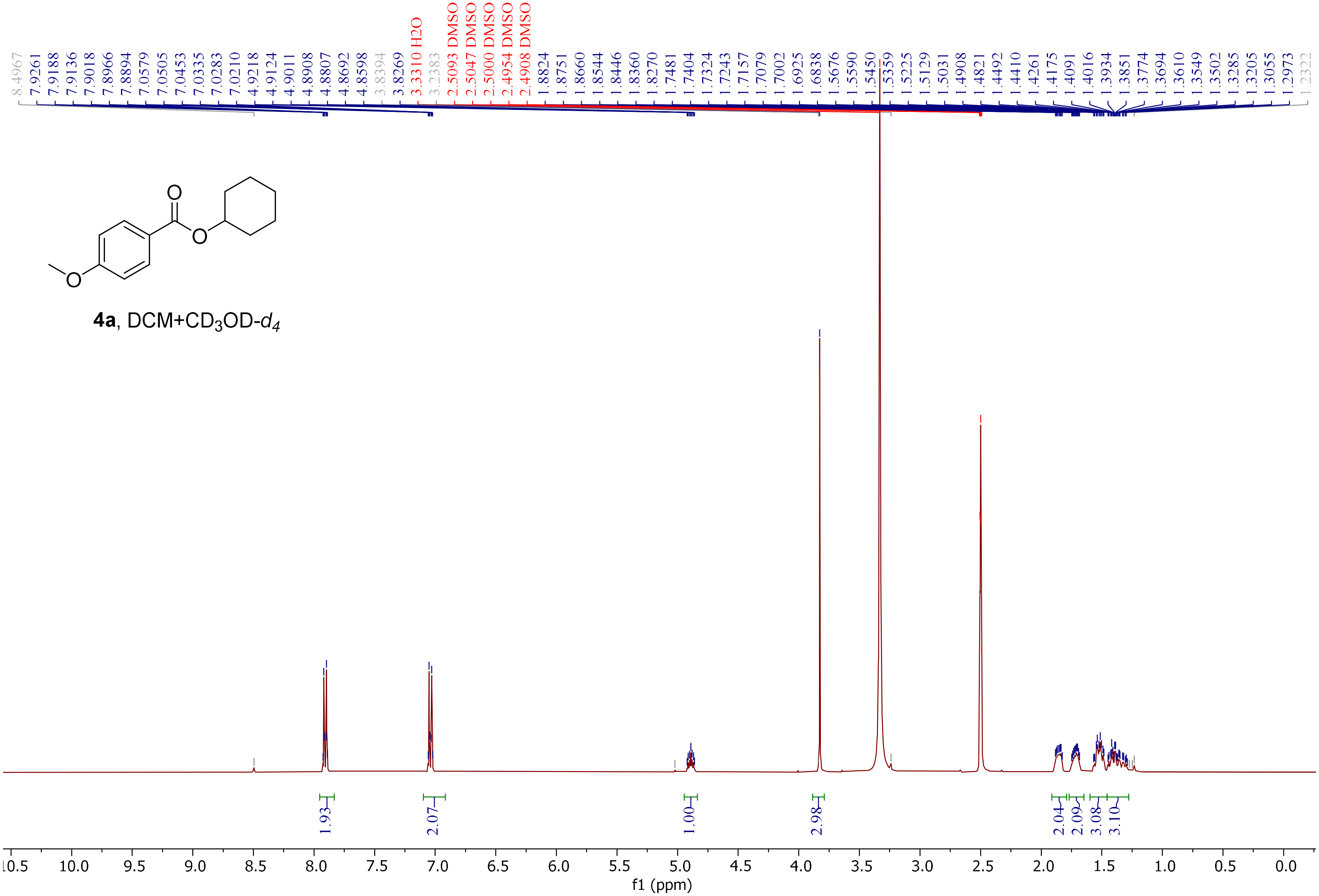


4a, original NMR in DMSO
used as standard NMR

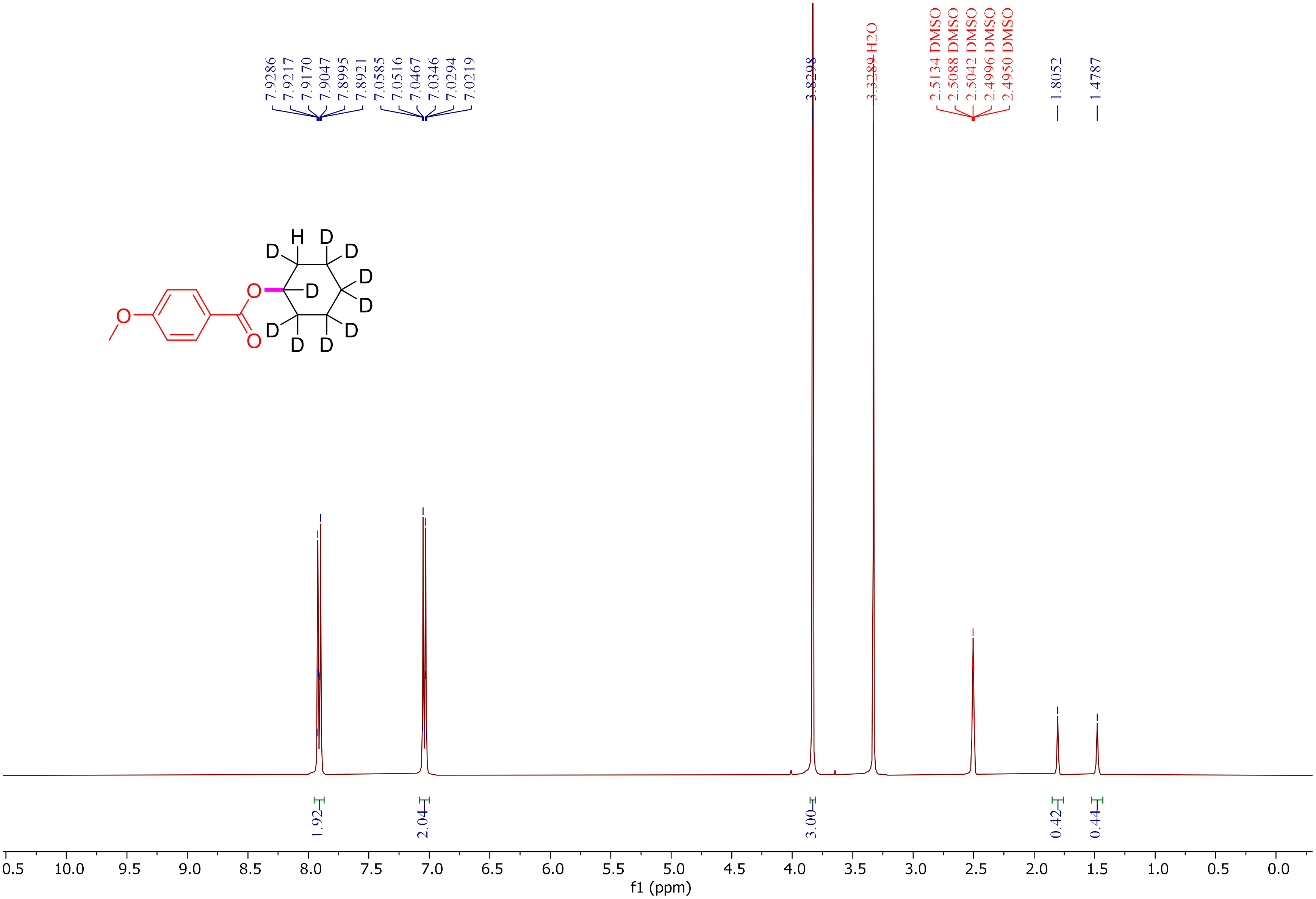

4a, conducted in DCM-*d2*



4a, conducted in DCM-*d2*/DCM = 1/1



4a, DCM+CD_3OD-*d_4*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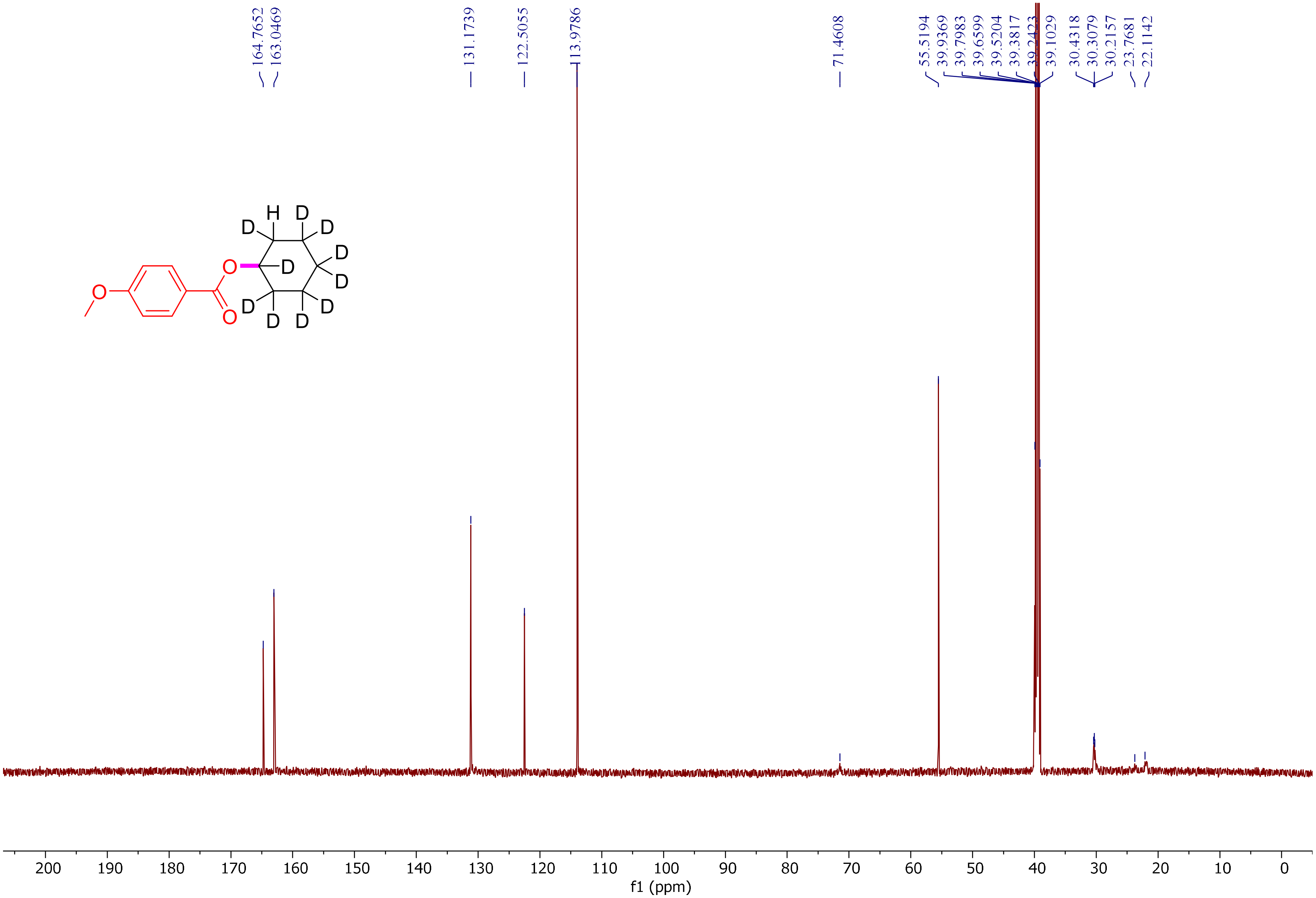
7.9170
7.9047
7.8995
7.8921
7.0585
7.0516
7.0467
7.0346
7.0294
7.0219
3.8298
3.3289 H2O
2.5134 DMSO
2.5088 DMSO
2.5042 DMSO
2.4996 DMSO
2.4950 DMSO
1.8052
1.4787
H
D
O
O
O
1.92
2.04
3.00
0.42
0.44
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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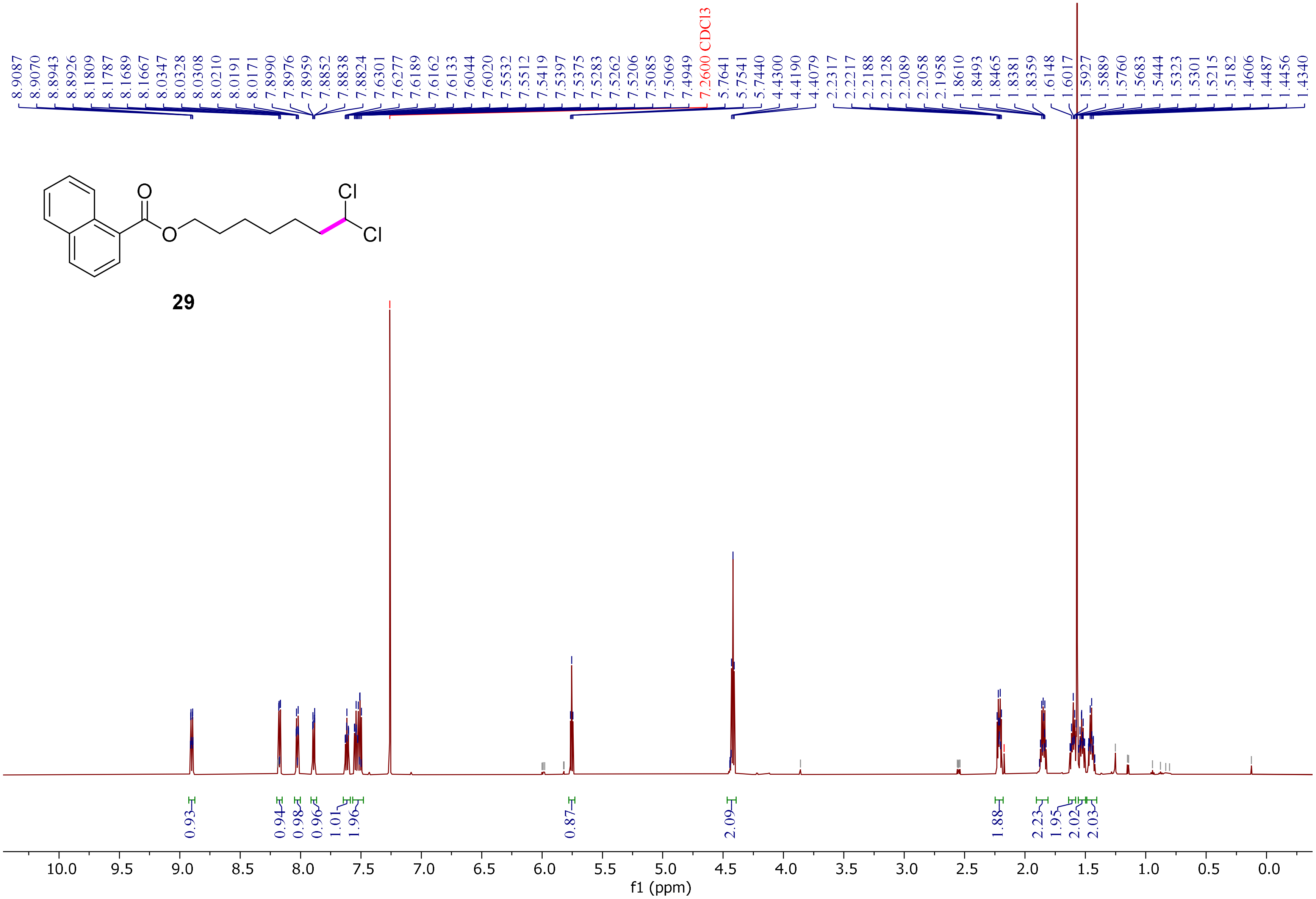
131.1739
122.5055
113.9786
71.4608
55.5194
39.9369
39.7983
39.6599
39.5204
39.3817
39.2423
39.1029
30.4318
30.3079
30.2157
23.7681
22.1142
H
D
O
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.8943
8.8926
8.1809
8.1787
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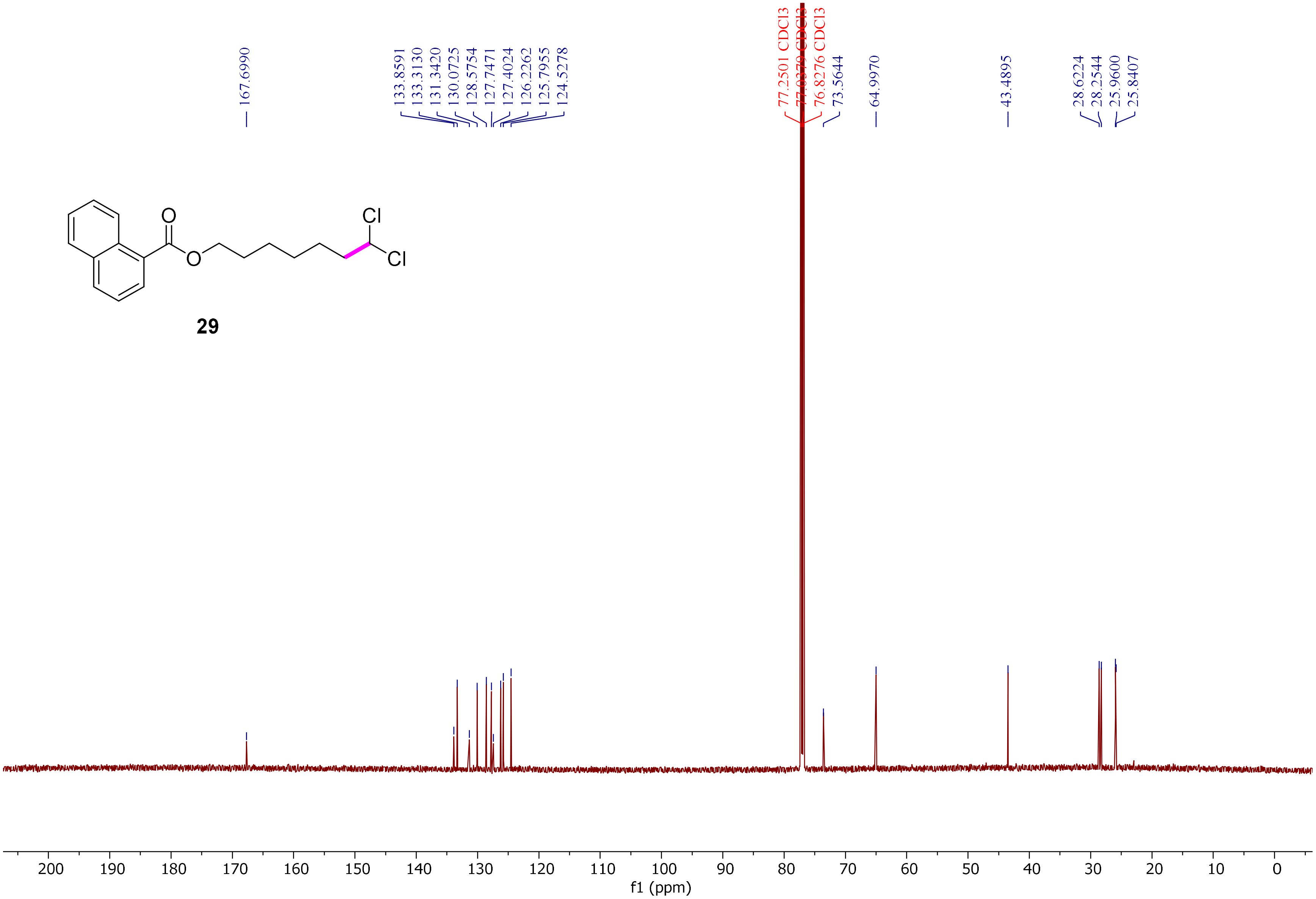
8.0308
8.0210
8.0191
8.0171
7.8990
7.8976
7.8959
7.8852
7.8838
7.8824
7.6301
7.6277
7.6189
7.6162
7.6133
7.6044
7.6020
7.5532
7.5512
7.5419
7.5397
7.5375
7.5283
7.5262
7.5206
7.5085
7.5069
7.4949
7.2600 CDCl3
5.7641
5.7541
5.7440
4.4300
4.4190
4.4079
2.2317
2.2217
2.2188
2.2128
2.2089
2.2058
2.1958
1.8610
1.8493
1.8465
1.8381
1.8359
1.6148
1.6017
1.5927
1.5889
1.5760
1.5683
1.5444
1.5323
1.5301
1.5215
1.5182
1.4606
1.4487
1.4456
1.4340
O
O
Cl
Cl
29
0.93
0.94
0.98
0.96
1.01
1.96
0.87
2.09
1.88
2.23
1.95
2.02
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.3420
130.0725
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127.7471
127.4024
126.2262
125.7955
124.5278
77.2501 CDCl3
77.0379 CDCl3
76.8276 CDCl3
73.5644
64.9970
43.4895
28.6224
28.2544
25.9600
25.8407
O
O
Cl
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

29