Supporting Information

Palladium-catalyzed intermolecular 1,3-dienylation of propargyl esters with alcohols for constructing polysubstituted 1,3-dienes

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I. General remarks

NMR spectra were obtained on Bruker AV-400 MHz and AV-600 MHz spectrometers. The ^{1}H NMR chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI).

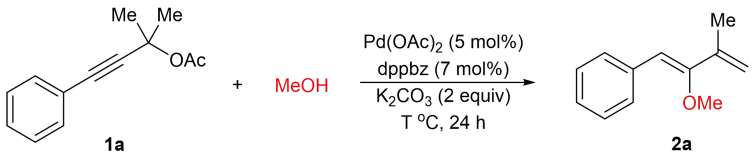
Unless noted otherwise, commercially available chemicals were used as received without purification. The propargyl esters were prepared according to the literatures.[1] All catalytic experiments were carried out using ultra dry solvents purchased from J&K Scientific. The GC internal standard, *n*-$C_{12}H_{26}$ was degassed with nitrogen and dried over activated 4 Å molecular sieve beads before use. Gas chromatography (GC) analysis was performed on a Agilent8890B GC System with Agilent J & W GC column DB-5MS-UI.

II. General procedure for optimization of conditions

(1) MeOH as both substrate and solvent:

A Schlenk tube with a magnetic stir bar was charged with Pd catalyst (5 mol%), diphosphine ligand (7 mol%), base (2 equiv), propargyl acetate **1a** (20.2 mg, 0.2 mmol, 1 equiv), CH_3OH (1 mL) and GC standard *n*-$C_{12}H_{26}$ (10 μL) under an N_2 atmosphere. The reaction mixture was stirred at 110 °C for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. Aliquots were taken from the organic phase and passed through a short plug of silica gel with EtOAc washing (about 2 mL). The filtrate was subjected to GC analysis to determine the GC yield of the product **2a**.

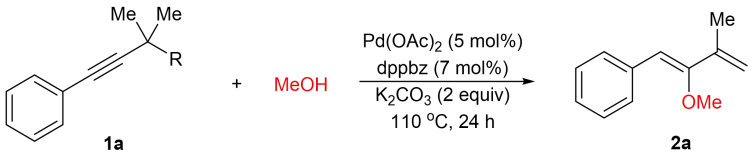
Table S1. The effect of temperature



Entry	T (°C)	Yield (**2a**)
1	70	trace

2	80	40
3	90	68
4	**110**	**85**
5	120	85
6	130	83

Table S2. The effect of leaving group

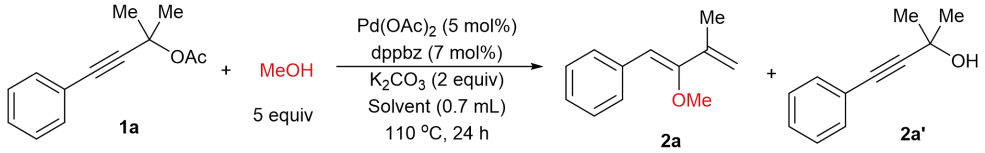


Entry	R	Yield (**3a**)
1	**OAc**	**85**
2	Br	trace
3	OH	10
4	OBoc	72
5	OBz	50
6	OPiv	84

(2) 5 equiv of MeOH as substrate:

A Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 5 mol%), dppbz (6.3 mg, 7 mol%), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), propargyl acetate **1a** (40.4 mg, 0.2 mmol, 1 equiv), MeOH (81 μL, 1 mmol, 5 equiv), solvent (0.7 mL) and GC standard *n*-$C_{12}H_{26}$ (10 μL) under an N_2 atmosphere. The reaction mixture was stirred at 110 ℃ for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. Aliquots were taken from the organic phase and passed through a short plug of silica gel with EtOAc washing (about 2 mL). The filtrate was subjected to GC analysis to determine the GC yield of the product **2a**.

Table S3. optimization of conditions using 5 equiv of MeOH as substrate



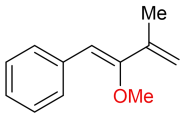
Entry	Solvent	Conv. (**1a**)	Yield (**2a**)	Yield (**2a'**)
1	acetonitrile	15%	<5%	<5%
2	toluene	20%	0	8%
3	THF	17%	0	10%

4	DMSO	<5%	0	0
5	DMF	<5%	0	0
6	cyclohexane	12%	0	<5%
7	isopropanol	32%	21%	<5%
8[a]	isopropanol	42%	32%	<5%

[a] 7 equiv of MeOH was used.

III. General procedure for 1,3-dienylation of propargyl acetates with alcohols

A Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 5 mol%), dppbz (6.3 mg, 7 mol%), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), propargyl acetate **1** (0.2 mmol, 1 equiv) and alcohol (1 mL). The reaction mixture was stirred at 110 ℃ for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. The solution was filtered through a celite pad and washed with 10-20 mL of EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc as eluent to give the desired product **2** or **3**.



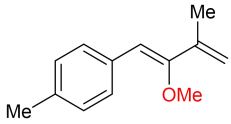
(*Z*)-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)benzene (2a)[2]

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (28.6 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.67 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 5.99 (s, 1H), 5.44 (s, 1H), 5.11 (s, 1H), 3.61 (s, 3H), 1.99 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.4, 138.7, 135.7, 129.0, 128.5, 126.9, 114.3, 113.8, 58.7, 20.2 ppm.

HRMS (ESI): calcd for $C_{12}H_{15}O$ $[M+H]^+$ 175.1123, found 175.1125.



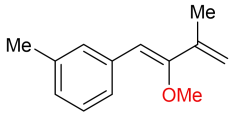
(*Z*)-1-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)-4-methylbenzene (2b)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (30.5 mg, 81% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 5.96 (s, 1H), 5.41 (d, J = 2.4 Hz, 1H), 5.07 (s, 1H), 3.59 (s, 3H), 2.35 (s, 3H), 1.97 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.7, 138.7, 136.8, 132.8, 129.3, 129.0, 113.9, 113.8, 58.7, 21.4, 20.2 ppm.

HRMS (ESI): calcd for $C_{13}H_{17}O$ $(M+H)^+$ 189.1279, found 189.1274.



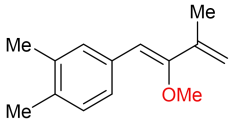
(*Z*)-1-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)-3-methylbenzene (2c)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (29 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.45 (m, 2H), 7.23 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 5.95 (s, 1H), 5.42 (d, J = 2.0 Hz, 1H), 5.09 (s, 1H), 3.60 (s, 3H), 2.35 (s, 3H), 1.97 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.3, 138.8, 138.0, 135.6, 129.8, 128.4, 127.8, 126.2, 114.2, 114.0, 58.8, 21.7, 20.2 ppm.

HRMS (ESI): calcd for $C_{13}H_{17}O$ $(M+H)^+$ 189.1279, found 189.1276.



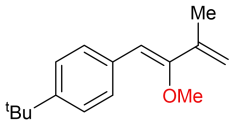
(*Z*)-4-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)-1,2-dimethylbenzene (2d)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (32.4 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.42 (m, 2H), 7.10 (d, J = 7.6 Hz, 1H), 5.94 (s, 1H), 5.40 (d, J = 2.0 Hz, 1H), 5.06 (s, 1H), 3.59 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 1.97 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.6, 138.8, 136.5, 135.6, 133.3, 130.4, 129.9, 126.6, 114.0, 113.7, 58.7, 20.2, 20.0, 19.7 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O$ $(M+H)^+$ 203.1436, found 203.1431.



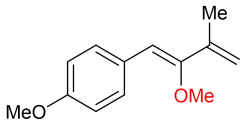
(*Z*)-1-(*tert*-Butyl)-4-(2-methoxy-3-methylbuta-1,3-dien-1-yl)benzene (2e)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (36 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.58 (m, 2H), 7.38-7.34 (m, 2H), 5.96 (s, 1H), 5.41 (d, J = 2.0 Hz, 1H), 5.07 (s, 1H), 3.61 (s, 3H), 1.97 (s, 3H), 1.33 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.9, 150.0, 138.8, 132.9, 128.8, 125.5, 113.9, 113.8, 58.7, 34.7, 31.4, 20.2 ppm.

HRMS (ESI): calcd for $C_{16}H_{23}O$ $[M+H]^+$ 231.1749, found 231.1745.



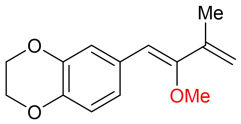
(*Z*)-1-Methoxy-4-(2-methoxy-3-methylbuta-1,3-dien-1-yl)benzene (2f)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 50/1, v/v) as faint yellow oil (28.6 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.93 (s, 1H), 5.38 (d, J = 2.0 Hz, 1H), 5.05 (s, 1H), 3.82 (s, 3H), 3.58 (s, 3H), 1.96 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.6, 155.8, 138.6, 130.4, 128.4, 114.0, 113.6, 113.4, 58.6, 55.4, 20.2 ppm.

HRMS (ESI): calcd for $C_{13}H_{17}O_2$ $[M+H]^+$ 205.1229, found 205.1226.



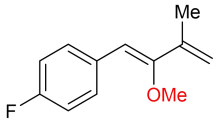
(*Z*)-6-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine (2g)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 40/1, v/v) as faint yellow oil (34.8 mg, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (d, J = 1.6 Hz, 1H), 7.10 (dd, J = 5.6, 1.2 Hz, 1H), 6.82 (d, J = 5.6 Hz, 1H), 5.86 (s, 1H), 5.37 (d, J = 1.8 Hz, 1H), 5.05 (s, 1H), 4.28-4.26 (m, 4H), 3.59 (s, 3H), 1.95 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.2, 143.4, 142.7, 138.6, 129.4, 122.8, 117.6, 117.1, 113.7, 113.4, 64.6, 64.5, 58.6, 20.2 ppm.

HRMS (ESI): calcd for $C_{14}H_{17}O_3(M+H)^+$ 233.1178, found 233.1166.



(*Z*)-1-Fluoro-4-(2-methoxy-3-methylbuta-1,3-dien-1-yl)benzene (2h)

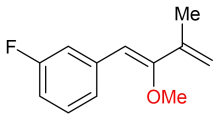
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as a faint yellow oil (28.5 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.60 (m, 2H), 7.05-6.99 (m, 2H), 5.93 (s, 1H), 5.41 (d, J = 2.0 Hz, 1H), 5.10 (s, 1H), 3.58 (s, 3H), 1.97 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.6 (d, $J_{C\text{-}F}$ = 247.8 Hz), 157.0 (d, $J_{C\text{-}F}$ = 2.1 Hz), 138.5, 131.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 130.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.4, 112.7, 58.6, 20.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -114.8 ppm.

HRMS (ESI): calcd for $C_{12}H_{14}FO$ $(M+H)^+$ 193.1029, found 193.1031.



(*Z*)-1-Fluoro-3-(2-methoxy-3-methylbuta-1,3-dien-1-yl)benzene (2i)

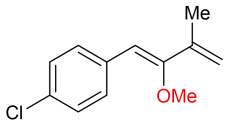
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as a faint yellow oil (27.7 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.46 (m, 1H), 7.33-7.24 (m, 2H), 6.93-6.90 (m, 1H), 5.93 (s, 1H), 5.44 (d, J = 1.6 Hz, 1H), 5.13 (s, 1H), 3.61 (s, 3H), 1.97 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.1 (d, $J_{C\text{-}F}$ = 240.4 Hz), 158.4, 138.5, 137.9 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.7 Hz), 124.9 (d, $J_{C\text{-}F}$ = 2.6 Hz), 115.5, 115.3, 113.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 112.7 (d, $J_{C\text{-}F}$ = 2.7 Hz), 58.8, 20.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -113.7 ppm.

HRMS (ESI): calcd for $C_{12}H_{14}FO$ $(M+H)^+$ 193.1029, found 193.1025.



(*Z*)-1-Chloro-4-(2-methoxy-3-methylbuta-1,3-dien-1-yl)benzene (2j)

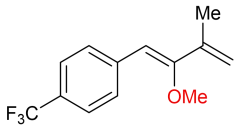
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as faint yellow oil (27 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.57 (m, 2H), 7.31-7.27 (m, 2H), 5.92 (s, 1H), 5.42 (d, J = 1.6 Hz, 1H), 5.12 (s, 1H), 3.58 (s, 3H), 1.96 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.9, 138.5, 134.2, 132.3, 130.2 128.7, 114.9, 112.6, 58.7, 20.1 ppm.

HRMS (ESI): calcd for $C_{12}H_{14}ClO$ $(M+H)^+$ 209.0733, found 209.0735.

The structure of **2j** was further confirmed by 1D NOESY spectrum.



(*Z*)-1-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (2k)

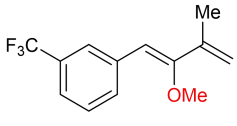
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as faint yellow oil (34.8 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.0 Hz, 2H),7.56 (d, J = 8.0 Hz, 2H), 5.98 (s, 1H), 5.47 (d, J = 1.6 Hz, 1H), 5.17 (s, 1H), 3.60 (s, 3H), 1.98 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.3, 139.3, 138.5, 129.0, 125.4 (q, $J_{C\text{-}F}$ = 4.1 Hz), 124.4 (q, $J_{C\text{-}F}$ = 273.1 Hz), 115.8, 112.3, 58.9, 20.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -113.7 ppm.

HRMS (ESI): calcd for $C_{13}H_{14}F_3O$ $[M+H]^+$ 243.0997, found 243.0982.



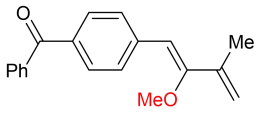
(*Z*)-1-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)-3-(trifluoromethyl)benzene (2l)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as faint yellow oil (31 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.81-7.80 (m, 1H), 7.46-7.41 (m, 2H), 5.98 (s, 1H), 5.46 (d, J = 1.6 Hz, 1H), 5.16 (s, 1H), 3.60 (s, 3H), 1.98 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.9, 138.5, 136.5, 132.0, 128.9, 125.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.4 (q, $J_{C\text{-}F}$ = 273.4 Hz), 123.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 115.6, 112.2, 58.8, 20.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -62.7 ppm.

HRMS (ESI): calcd for $C_{13}H_{14}F_3O$ $[M+H]^+$ 243.0997, found 243.0991.



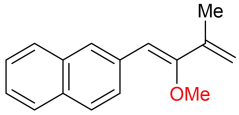
(*Z*)-(4-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)phenyl)(phenyl)methanone (2m)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 40/1, v/v) as colorless oil (40 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.79 (m, 4H), 7.76-7.74 (m, 2H), 7.61-7.56 (m, 1H), 7.50-7.47 (m, 2H), 6.02 (s, 1H), 5.48 (d, J = 2.0 Hz, 1H), 5.18 (s, 1H), 3.64 (s, 3H), 2.00 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.4, 159.6, 140.2, 138.6, 138.1, 135.4, 132.3, 130.6, 130.1, 128.7, 128.4, 115.9, 112.7, 58.9, 20.2 ppm.

HRMS (ESI): calcd for $C_{19}H_{19}O_2$ $(M+H)^+$ 279.1385, found 279.1379.



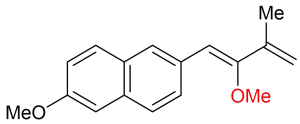
(*Z*)-2-(2-Methoxy-3-methylbuta-1,3-dien-1-yl)naphthalene (2n)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (26.9 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.85-7.79 (m, 4H), 7.46-7.43 (m, 2H), 6.16 (s, 1H), 5.49 (d, J = 1.6 Hz, 1H), 5.14 (s, 1H), 3.65 (s, 3H), 2.03 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.8, 138.7, 133.7, 133.3, 132.5, 128.2, 128.0, 127.9, 127.6, 127.3, 126.1, 125.9, 114.5, 114.0, 59.0, 20.2 ppm.

HRMS (ESI): calcd for $C_{16}H_{17}O$ $(M+H)^+$ 225.1279, found 225.1271.



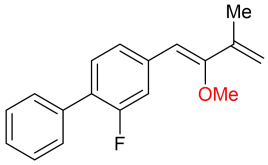
(*Z*)-2-Methoxy-6-(2-methoxy-3-methylbuta-1,3-dien-1-yl)naphthalene (2o)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 50/1, v/v) as faint yellow oil (33 mg, 65% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01, (s, 1H), 7.83-7.82 (m, 1H), 7.72-7.69 (m, 2H), 7.14-7.11 (m, 2H), 6.13 (s, 1H), 5.46 (d, J = 1.8 Hz, 1H), 5.11 (s, 1H), 3.93 (s, 3H), 3.64 (s, 3H), 2.02 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.9, 157.1, 138.7, 133.7, 131.2, 129.8, 129.2, 127.9, 127.8, 126.8, 118.9, 114.1, 114.0, 105.7, 58.9, 55.5, 20.2 ppm.

HRMS (ESI): calcd for $C_{17}H_{19}O_2$ $[M+H]^+$ 255.1385, found 255.1387.



(*Z*)-2-Fluoro-4-(2-methoxy-3-methylbuta-1,3-dien-1-yl)-1,1'-biphenyl (2p)

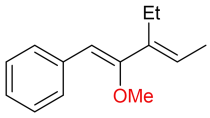
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as colorless oil (45.6 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 3H), 7.47-7.42 (m, 2H), 7.41-7.34 (m, 3H), 5.96 (s, 1H), 5.46 (d, J = 1.2 Hz, 1H), 5.15 (s, 1H), 3.65 (s, 3H), 1.99 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.9 (d, $J_{C\text{-}F}$ = 247.2 Hz), 158.6, 138.5, 137.0 (d, $J_{C\text{-}F}$ = 8.8 Hz), 135.9, 130.4 (d, $J_{C\text{-}F}$ = 4.6 Hz), 129.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 128.6, 127.7, 127.2 (d, $J_{C\text{-}F}$ = 13.8 Hz), 125.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 24.6 Hz), 115.3, 112.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 58.8, 20.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -118.5 ppm.

HRMS (ESI): calcd for $C_{18}H_{18}FO$ $(M+H)^+$ 269.1342, found 269.1338.



((1*Z*,3*E*)-3-Ethyl-2-methoxypenta-1,3-dien-1-yl)benzene (2q)

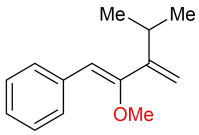
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (34.8 mg, 86% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 3.0 Hz, 1H), 5.94 (q, J = 6.6 Hz, 1H), 5.80 (s, 1H), 3.55 (s, 3H), 2.28 (q, J = 7.2 Hz, 2H), 1.78 (d, J = 6.6 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.0, 138.1, 136.5, 128.7, 128.4, 126.2, 124.1,

111.1, 57.9, 20.8, 13.7, 13.3 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O$ $(M+H)^+$ 203.1436, found 203.1432.



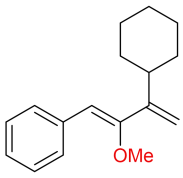
(*Z*)-(2-Methoxy-4-methyl-3-methylenepent-1-en-1-yl)benzene (2r)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (30 mg, 74% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.2 Hz, 2H),7.32 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.8 Hz, 1H), 5.87 (s, 1H), 5.38 (d, J = 1.8 Hz, 1H), 5.12 (s, 1H), 3.58 (s, 3H), 2.63-2.56 (m, 1H), 1.15 (d, J = 7.2 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.5, 151.1, 136.1, 128.8, 128.4, 126.5, 112.0, 111.9, 57.6, 30.0, 22.3 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O$ $(M+H)^+$ 203.1436, found 203.1430.



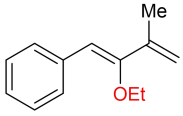
(*Z*)-(3-Cyclohexyl-2-methoxybuta-1,3-dien-1-yl)benzene (2s)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (36.8 mg, 76% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.18 (t, J = 7.2 Hz, 1H), 5.83 (s, 1H), 5.34 (d, J = 1.2 Hz, 1H), 5.08 (s, 1H), 3.57 (s, 3H), 2.19-2.15 (m, 1H), 1.93-1.90 (m, 2H), 1.82-1.80 (m, 2H), 1.74-1.71 (m, 1H), 1.37-1.31 (m, 3H), 1.24-1.18 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.6, 150.4, 136.1, 128.8, 128.4, 126.5, 112.5, 111.8, 57.6, 40.4, 33.0, 27.1, 26.6 ppm.

HRMS (ESI): calcd for $C_{17}H_{23}O$ $(M+H)^+$ 243.1749, found 243.1751.



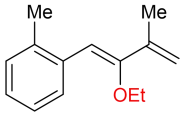
(*Z*)-(2-Ethoxy-3-methylbuta-1,3-dien-1-yl)benzene (3a)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (27.1 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 5.99 (s, 1H), 5.44 (d, J = 1.8 Hz, 1H), 5.07 (s, 1H), 3.76 (q, J = 7.2 Hz, 2H), 1.98 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.3, 139.3, 136.0, 129.0, 128.4, 126.8, 114.1, 114.0, 66.7, 20.2, 15.7 ppm.

HRMS (ESI): calcd for $C_{13}H_{16}NaO$ $(M+Na)^+$ 211.1099, found 211.1092.



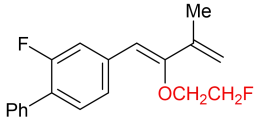
(*Z*)-1-(2-Ethoxy-3-methylbuta-1,3-dien-1-yl)-2-methylbenzene (3b)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (24.7 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.8 Hz, 1H), 7.18-7.15 (m, 2H), 7.13-7.11 (m, 1H), 6.08 (s, 1H), 5.47 (d, J = 1.8 Hz, 1H), 5.06 (s, 1H), 3.62 (q, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.99 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.2, 139.7, 136.1, 134.8, 129.9, 129.2, 126.8, 125.8, 114.0, 111.0, 67.2, 29.9, 20.2, 15.6 ppm.

HRMS (ESI): calcd for $C_{14}H_{18}NaO$ $(M+Na)^+$ 225.1255, found 225.1250.



(*Z*)-2-Fluoro-4-(2-(2-fluoroethoxy)-3-methylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3c)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as faint yellow oil (39.6 mg, 66% yield).

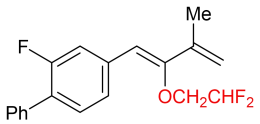
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 3H), 7.46-7.40 (m, 4H), 7.38-7.34 (m, 1H), 6.03 (s, 1H), 5.53 (s, 1H), 5.16 (s, 1H), 4.74-4.72 (m, 1H), 4.62-4.60 (m, 1H), 4.03-4.01 (m, 1H), 3.96-3.94 (m, 1H), 2.00 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8 (d, $J_{C\text{-}F}$ = 247.7 Hz), 156.6, 138.3, 136.6 (d, $J_{C\text{-}F}$ = 8.5 Hz), 135.8, 130.5 (d, $J_{C\text{-}F}$ = 4.2 Hz), 129.0 (d, $J_{C\text{-}F}$ = 3.1 Hz), 128.6, 127.7, 127.5 (d, $J_{C\text{-}F}$ = 13.7 Hz), 125.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 116.3 (d, $J_{C\text{-}F}$ = 24.3 Hz), 115.6,

113.3 (d, $J_{C\text{-}F}$ = 2.4 Hz), 82.7 (d, $J_{C\text{-}F}$ = 171.5 Hz), 70.0 (d, $J_{C\text{-}F}$ = 19.6 Hz), 20.2 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -118.3, -118.4 (m) ppm.

HRMS (ESI): calcd for $C_{19}H_{19}F_2O$ $(M+H)^+$ 301.1404, found 301.1401.



(*Z*)-4-(2-(2,2-Difluoroethoxy)-3-methylbuta-1,3-dien-1-yl)-2-fluoro-1,1'-biphenyl (3d)

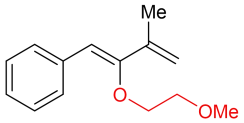
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as faint yellow oil (41.4 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.58 (m, 2H), 7.52-7.49 (m, 1H), 7.48-7.42(m, 4H), 7.39-7.35 (m, 1H), 6.05 (s, 1H), 6.00 (tt, J = 40.4, 4.0 Hz, 1H), 5.50 (s, 1H), 5.19 (s, 1H), 3.93 (td, J = 13.6, 4.0 Hz, 2H), 2.00 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8 (d, $J_{C\text{-}F}$ = 248.2 Hz), 156.0, 137.8, 136.0 (d, $J_{C\text{-}F}$ = 8.7 Hz), 135.7 (d, $J_{C\text{-}F}$ = 1.3 Hz), 130.6 (d, $J_{C\text{-}F}$ = 4.1 Hz), 129.0 (d, $J_{C\text{-}F}$ = 3.1 Hz), 128.6, 127.8 (t, $J_{C\text{-}F}$ = 7.1 Hz), 125.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 116.4 (d, $J_{C\text{-}F}$ = 24.8 Hz), 115.8, 113.8, 113.5 (d, $J_{C\text{-}F}$ = 2.3 Hz), 111.4, 69.6 (t, $J_{C\text{-}F}$ = 28.4 Hz), 29.9, 20.2 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -118.1, -125.3 ppm.

HRMS (ESI): calcd for $C_{19}H_{18}F_3O$ $(M+H)^+$ 319.1310, found 319.1301.



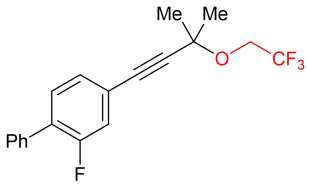
(*Z*)-(2-(2-Methoxyethoxy)-3-methylbuta-1,3-dien-1-yl)benzene (3e)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 75/1, v/v) as faint yellow oil (32.3 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.67 (m, 2H), 7.34-7.30 (m, 2H), 7.22-7.18 (m, 1H), 6.01 (s, 1H), 5.52 (d, J = 2.0 Hz, 1H), 5.10 (s, 1H), 3.85-3.82 (m, 2H), 3.64-3.62 (m, 2H), 3.39 (s, 3H), 1.98 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.0, 138.8, 135.7, 129.2, 128.5, 126.9, 114.6, 114.3, 72.0, 69.9, 59.1, 20.2 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1385, found 219.1389.



2-Fluoro-4-(3-methyl-3-(2,2,2-trifluoroethoxy)but-1-yn-1-yl)-1,1'-biphenyl (3f)

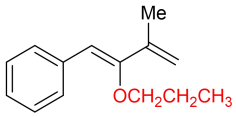
Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 150/1, v/v) as colorless oil (55.2 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55-7.54 (m, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.41-7.38 (m, 2H), 7.28-7.27 (m, 1H), 7.23-7.21 (m, 1H), 4.01 (q, J = 8.4 Hz, 2H), 1.61 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.3 (d, $J_{C\text{-}F}$ = 249.0 Hz), 135.1, 130.8 (d, $J_{C\text{-}F}$ = 4.2 Hz), 129.9 (d, $J_{C\text{-}F}$ = 13.4 Hz), 129.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.7, 128.2, 128.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 124.2 (q, $J_{C\text{-}F}$ = 277.7 Hz), 122.9 (d, $J_{C\text{-}F}$ = 9.7 Hz), 119.4 (d, $J_{C\text{-}F}$ = 24.8 Hz), 100.1, 90.8, 84.3, 72.5, 62.8 (q, $J_{C\text{-}F}$ = 34.7 Hz), 28.6 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = -74.1, -117.6--117.7 (m) ppm.

HRMS (ESI): calcd for $C_{19}H_{16}F_4NaO$ $(M+Na)^+$ 359.1035, found 359.1027.



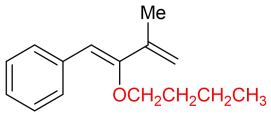
(*Z*)-(3-Methyl-2-propoxybuta-1,3-dien-1-yl)benzene (3g)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (18.6 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.21-7.17 (m, 1H), 5.98 (s, 1H), 5.43 (d, J = 2.0 Hz, 1H), 5.06 (s, 1H), 3.63 (t, J = 6.8 Hz, 2H), 1.98 (s, 3H), 1.74 (q, J = 7.2 Hz, 2H), 0.99 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.5, 139.3, 136.0, 129.0, 128.4, 126.8, 114.2, 113.9, 72.6, 23.6, 20.3, 10.7 ppm.

HRMS (ESI): calcd for $C_{14}H_{18}NaO$ $(M+Na)^+$ 225.1250, found 225.1253.



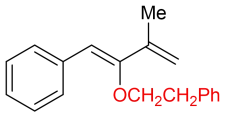
(*Z*)-(2-Butoxy-3-methylbuta-1,3-dien-1-yl)benzene (3h)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (24.2 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.21-7.17 (m, 1H), 5.98 (s, 1H), 5.43 (d, J = 2.0 Hz, 1H), 5.07 (s, 1H), 3.67 (t, J = 6.8 Hz, 2H), 1.98 (s, 3H), 1.74-1.67 (m, 2H), 1.50-1.40 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.5, 139.3, 136.0, 129.0, 128.4, 126.8, 114.2, 113.8, 70.8, 32.5, 20.3, 19.4, 14.1 ppm.

HRMS (ESI): calcd for $C_{15}H_{24}NO$ $(M+NH_4)^+$ 234.1852, found 234.1857.



(*Z*)-(2-((3-Methyl-1-phenylbuta-1,3-dien-2-yl)oxy)ethyl)benzene (3i)

Following the general procedure, product was isolated by flash chromatography (petroleum ether/EtOAc = 100/1, v/v) as faint yellow oil (32.8 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.26-7.21 (m, 5H), 7.18-7.14 (m, 1H), 5.97 (s, 1H), 5.29 (s, 1H), 5.01 (s, 1H), 3.87 (t, J = 7.2 Hz, 2H), 3.01 (t, J = 7.2 Hz, 2H), 1.94 (s, 3H) ppm.

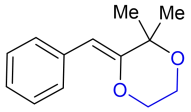
^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.1, 139.0, 138.6, 135.7, 129.3, 129.0, 128.5, 128.4, 126.8, 126.5, 114.3, 114.2, 71.5, 36.9, 20.2 ppm.

HRMS (ESI): calcd for $C_{19}H_{20}NaO$ $(M+Na)^+$ 287.1406, found 287.1402.

IV. General procedure for alkenylation of propargyl acetates with ethylene glycol

Procedure A *(ethylene glycol as both substrate and solvent):* A Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 5 mol%), dppbz (6.3 mg, 7 mol%), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), propargyl acetate **1** (0.2 mmol, 1 equiv) and ethylene glycol (1 mL). The reaction mixture was stirred at 110 °C for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. The solution was filtered through a celite pad and washed with 10-20 mL of EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc as eluent to give the desired product **4**.

Procedure B *(isopropanol as solvent):* A Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 5 mol%), dppbz (6.3 mg, 7 mol%), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), propargyl acetate **1** (0.2 mmol, 1 equiv), ethylene glycol (1 mmol, 5 equiv) and isopropanol (0.7 mL). The reaction mixture was stirred at 110 ℃ for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. The solution was filtered through a celite pad and washed with 10-20 mL of EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc as eluent to give the desired product **4**.



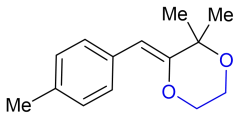
(*Z*)-3-Benzylidene-2,2-dimethyl-1,4-dioxane (4a)[3]

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 25/1, v/v) as faint yellow oil (31 mg, 76% yield). Following the *procedure B*, product was isolated in 64% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.17 (t, J = 6.6 Hz, 1H), 5.61 (s, 1H), 4.10 (t, J = 4.2 Hz, 2H), 3.95 (t, J = 4.8 Hz, 2H), 1.53 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.0, 135.6, 128.7, 128.3, 126.4, 106.5, 73.3, 68.3, 60.4, 26.7 ppm.

HRMS (ESI): calcd for $C_{13}H_{17}O_2$ $(M+H)^+$ 205.1229, found 205.1219.



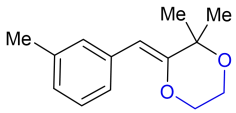
(*Z*)-2,2-Dimethyl-3-(4-methylbenzylidene)-1,4-dioxane (4b)

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 25/1, v/v) as faint yellow oil (34 mg, 78% yield). Following the *procedure B*, product was isolated in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.59 (s, 1H), 4.08 (t, J = 4.8 Hz, 2H), 3.94 (t, J = 4.8 Hz, 2H), 2.32 (s, 3H), 1.52 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.3, 136.1, 132.7, 129.0, 128.6, 106.5, 73.3, 68.3, 60.5, 26.6, 21.3 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1385, found 219.1381.



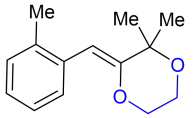
(*Z*)-2,2-Dimethyl-3-(3-methylbenzylidene)-1,4-dioxane (4c)

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 25/1, v/v) as faint yellow oil (32.3 mg, 74% yield). Following the *procedure B*, product was isolated in 60% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (d, J = 7.8 Hz, 1H), 7.38 (s, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 5.58 (s, 1H), 4.09 (t, J = 4.8 Hz, 2H), 3.94 (t, J = 4.8 Hz, 2H), 2.33 (s, 3H), 1.52 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.8, 137.8, 135.4, 129.4, 128.2, 127.2, 125.8, 106.6, 73.3, 68.3, 60.5, 26.7, 21.7 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1385, found 219.1382.



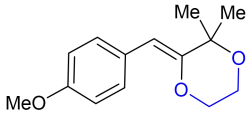
(*Z*)-2,2-Dimethyl-3-(2-methylbenzylidene)-1,4-dioxane (4d)

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 25/1, v/v) as faint yellow oil (28.4 mg, 65% yield). Following the *procedure B*, product was isolated in 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.2 Hz, 1H), 7.17-7.14 (m, 2H), 7.11-7.09 (m, 1H), 5.72 (s, 1H), 4.02 (t, J = 4.8 Hz, 2H), 3.93 (t, J = 4.8 Hz, 2H), 2.29 (s, 3H), 1.55 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.5, 135.9, 133.9, 129.9, 129.3, 126.5, 125.7, 104.3, 73.3, 68.5, 60.5, 26.8, 20.3 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1385, found 219.1388.



(*Z*)-3-(4-Methoxybenzylidene)-2,2-dimethyl-1,4-dioxane (4e)

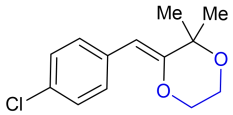
Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 20/1, v/v) as faint yellow oil (36.6 mg, 78% yield). Following the *procedure B*, product was isolated in 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.56 (s, 1H), 4.08-4.06 (m, 2H), 3.95-3.92 (m, 2H), 3.80 (s, 3H), 1.51 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.1, 155.4, 129.9, 128.3, 113.8, 106.1, 73.3, 68.3, 60.5, 55.4, 26.6 ppm.

HRMS (ESI): calcd for $C_{14}H_{19}O_3$ $(M+H)^+$ 235.1334, found 235.1338.

The structure of **4e** was further confirmed by 1D NOESY spectrum.



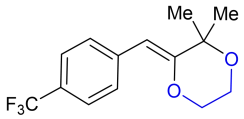
(*Z*)-3-(4-Chlorobenzylidene)-2,2-dimethyl-1,4-dioxane (4f)

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 30/1, v/v) as faint yellow oil (34.4 mg, 72% yield). Following the *procedure B*, product was isolated in 58% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 5.55 (s, 1H), 4.10-4.08 (m, 2H), 3.95-3.93 (m, 2H), 1.51 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.6, 134.1, 131.7, 123.0, 128.4, 105.3, 73.3, 68.3, 60.4, 26.8 ppm.

HRMS (ESI): calcd for $C_{13}H_{15}ClNaO_2$ $(M+Na)^+$ 261.0658, found 261.0653.



(*Z*)-2,2-Dimethyl-3-(4-(trifluoromethyl)benzylidene)-1,4-dioxane (4g)

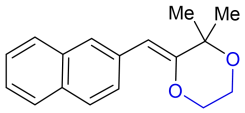
Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 30/1, v/v) as faint yellow oil (39.2 mg, 72% yield). Following the *procedure B*, product was isolated in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.61 (s, 1H), 4.12 (t, J = 4.8 Hz, 2H), 3.95 (t, J = 4.8 Hz, 2H), 1.53 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.2, 139.2, 135.1 (q, $J_{C\text{-}F}$ = 288.8 Hz), 128.7, 127.5 (q, $J_{C\text{-}F}$ = 31.8 Hz), 125.2 (q, $J_{C\text{-}F}$ = 4.0 Hz), 105.1, 73.3, 68.2, 60.3, 26.9 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -62.4 ppm.

HRMS (ESI): calcd for $C_{14}H_{16}F_3O_2$ $(M+H)^+$ 273.1102, found 273.1106.



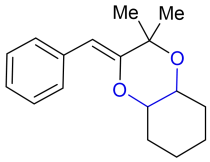
(*Z*)-2,2-Dimethyl-3-(naphthalen-2-ylmethylene)-1,4-dioxane (4h)

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 25/1, v/v) as faint yellow oil (32.6 mg, 64% yield). Following the *procedure B*, product was isolated in 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.80-7.76 (m, 4H), 7.46-7.39 (m, 2H), 5.78 (s, 1H), 4.16 (t, J = 4.8 Hz, 2H), 3.98 (t, J = 4.8 Hz, 2H), 1.58 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.5, 133.7, 133.2, 132.3, 128.1, 127.7, 127.6, 127.3, 127.2, 126.0, 125.5, 106.6, 73.4, 68.4, 60.5, 26.8 ppm.

HRMS (ESI): calcd for $C_{17}H_{19}O_2$ $(M+H)^+$ 255.1385, found 255.1381.



(*Z*)-3-Benzylidene-2,2-dimethyloctahydrobenzo[*b*][1,4]dioxine (4i)

Following the *procedure A*, product was isolated by flash chromatography (petroleum ether/EtOAc = 25/1, v/v) as faint yellow oil (23.8 mg, 46% yield). Following the *procedure B*, product was isolated in 25% yield.

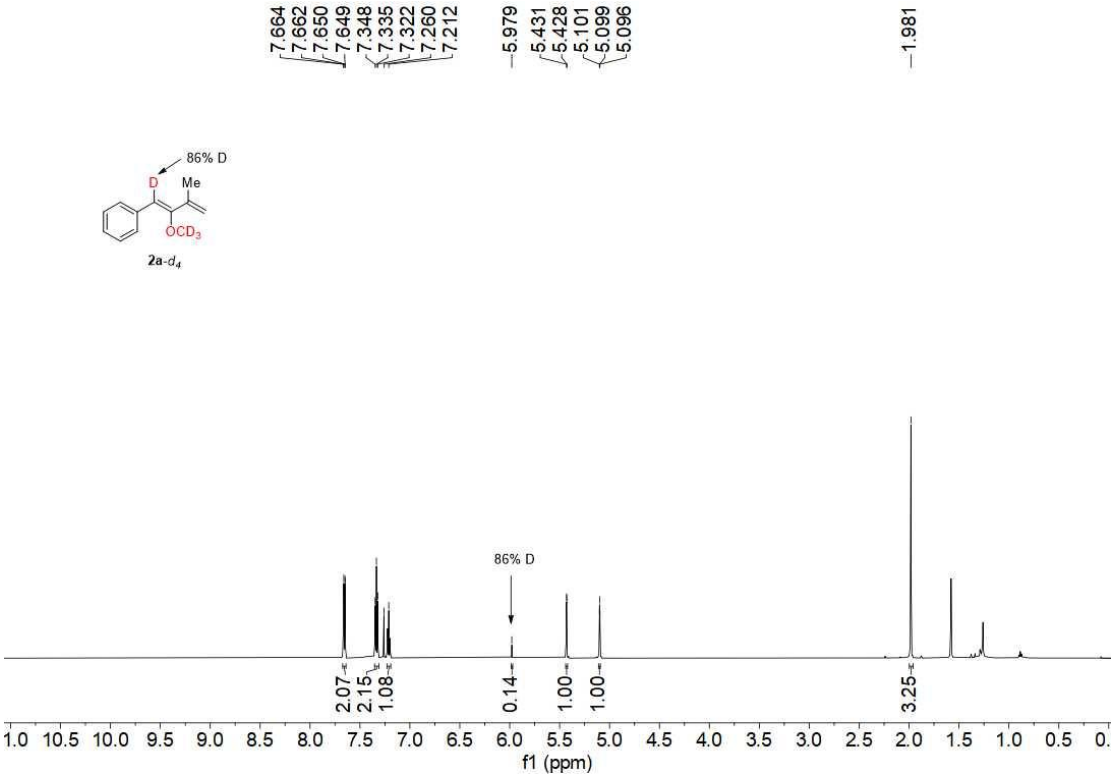
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.6 Hz, 2H), 7.30-7.26 (m, 2H), 7.17-7.13 (m, 1H), 5.58 (s, 1H), 3.72-3.56 (m, 2H), 2.16-2.13 (m, 1H), 1.89-1.86 (m, 1H), 1.80-1.75 (m, 2H), 1.55 (s, 3H), 1.51 (s, 3H), 1.34-1.26 (m, 4H) ppm.

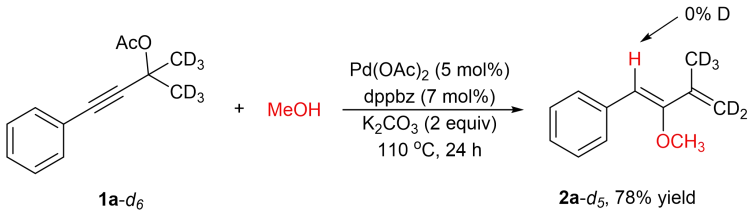
^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.7, 135.9, 128.7, 128.3, 126.2, 105.9, 81.8, 73.9, 73.2, 30.7, 30.5, 28.5, 26.4, 24.3, 24.1 ppm.

HRMS (ESI): calcd for $C_{17}H_{23}O_2$ $(M+H)^+$ 259.1693, found 259.1693.

V. Mechanistic studies

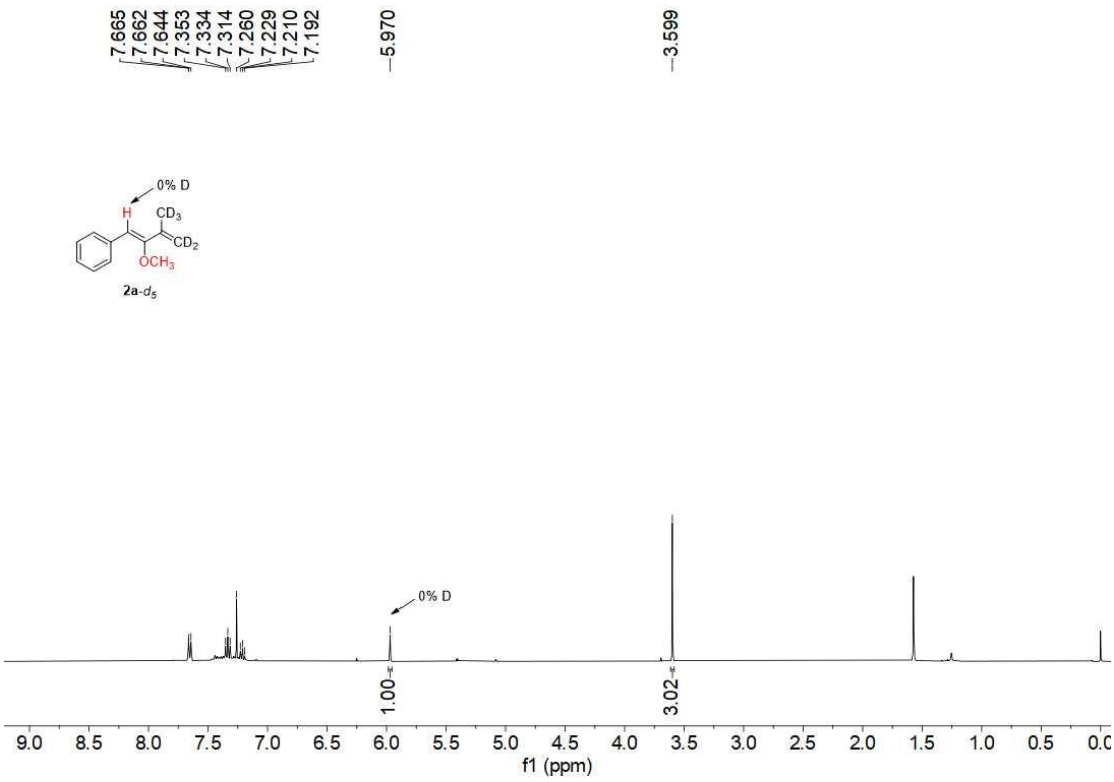
A typical procedure: A Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 5 mol%), dppbz (6.3 mg, 7 mol%), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), **1a** (0.2 mmol, 1 equiv) and CD_3OD (1 mL). The reaction mixture was stirred at 110 ℃ for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. The solution was filtered through a celite pad and washed with 10-20 mL of EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc (100/1, v/v) as eluent to give the desired product **2a**-*d*$_4$ in 80% yield. ^{1}H-NMR showed the deuterium content of the vinyl C-D is 86%.





A typical procedure: A Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 5 mol%), dppbz (6.3 mg, 7 mol%), K_2CO_3 (55.3 mg, 0.4 mmol, 2

equiv), **1a**-d_6 (0.2 mmol, 1 equiv) and CD_3OD (1 mL). The reaction mixture was stirred at 110 ℃ for 24 h by use of module heating. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with 3 mL of EtOAc. The solution was filtered through a celite pad and washed with 10-20 mL of EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc (100/1, v/v) as eluent to give the desired product **2a**-d_5 in 78% yield. ^{1}H-NMR showed the deuterium content is 0%.



1a-d_6 was prepared according to the literature.[1] The experimental data for **1a**-d_6:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.42 (m, 2H), 7.29-7.27 (m, 3H), 2.05 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5, 131.9, 128.4, 128.3, 122.8, 90.3, 84.1, 72.3, 22.2 ppm.

HRMS (ESI): calcd for $C_{13}H_9D_6O_2$ $(M+H)^+$ 209.1449, found 209.1445.

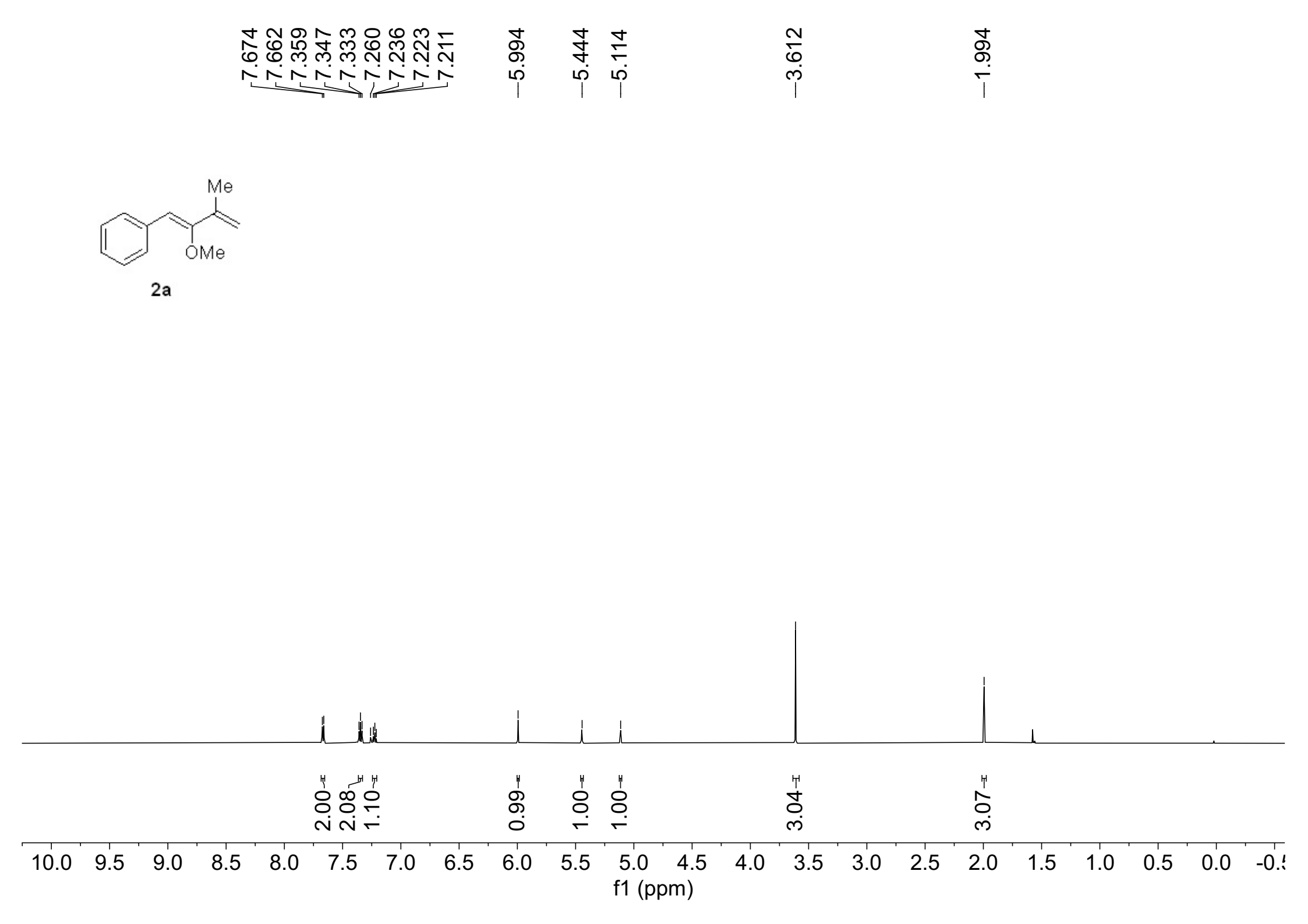
VI. References

(1) Teng, S.; Liang, P.; Hu, L.; Chen, S.; Wang, S.; Huang, W. *Org. Chem. Front.* **2024**, *11*, 4077-4083.

(2) a) Krijnen, E. S.; Zuilhof, H.; Lodder, G. *J. Org. Chem.* **1994**, *59*, 8139-8150. b) Kleijn, H.; Westmijze, H.; Vermeer, P. *Tetrahedron Lett.* **1978**, *19*, 1133-1136.

(3) Wei, H.-X.; Schlosser M. *Chem. Eur. J.* **1998**, *4*, 1738-1743.

VII. Copies of ^{1}H, ^{13}C NMR, ^{19}F NMR and 1D NOESY spectra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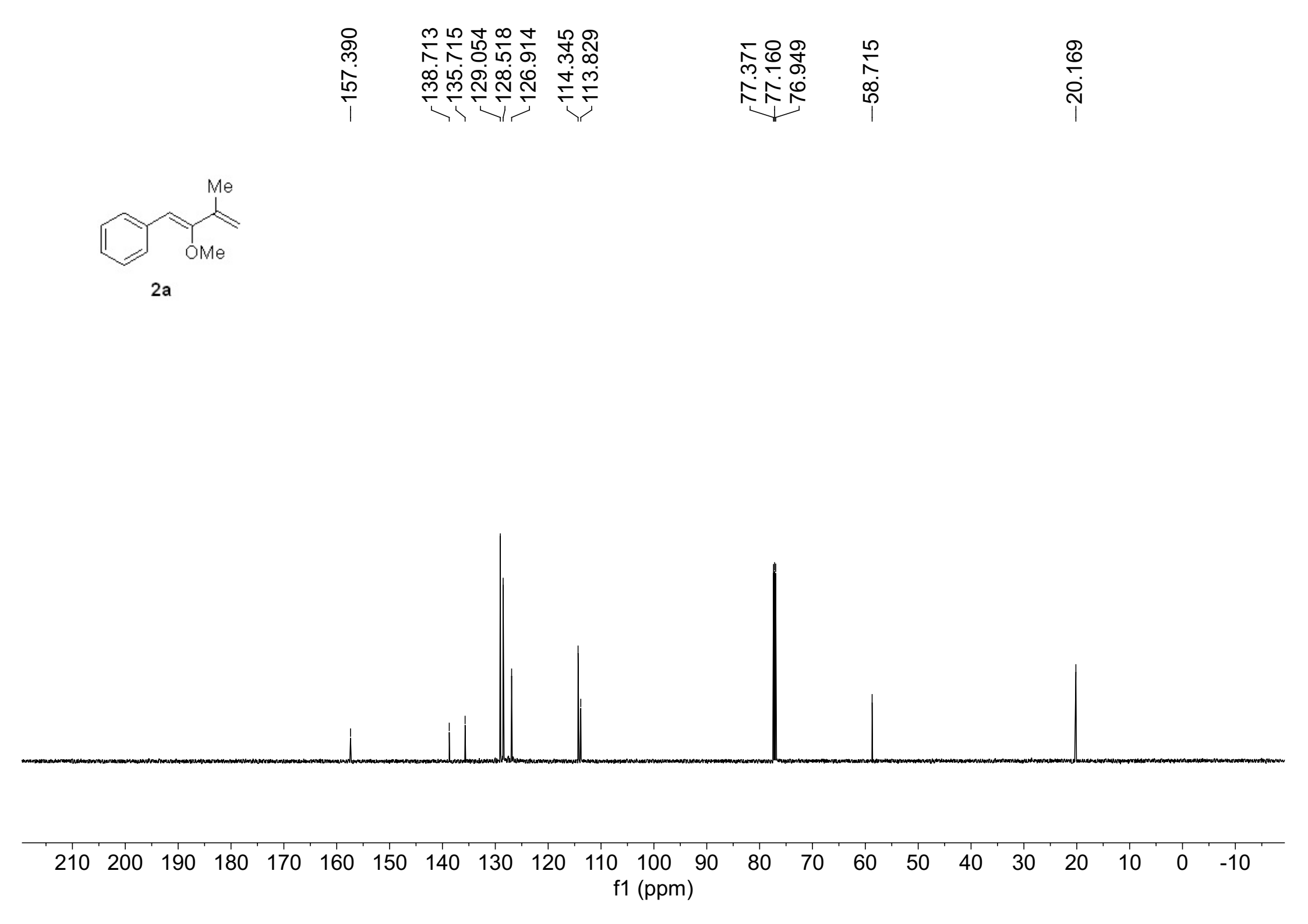
7.662
7.359
7.347
7.333
7.260
7.236
7.223
7.211
5.994
5.444
5.114
3.612
1.994
Me
OMe
2a
2.00
2.08
1.10
0.99
1.00
1.00
3.04
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.371
77.160
76.949
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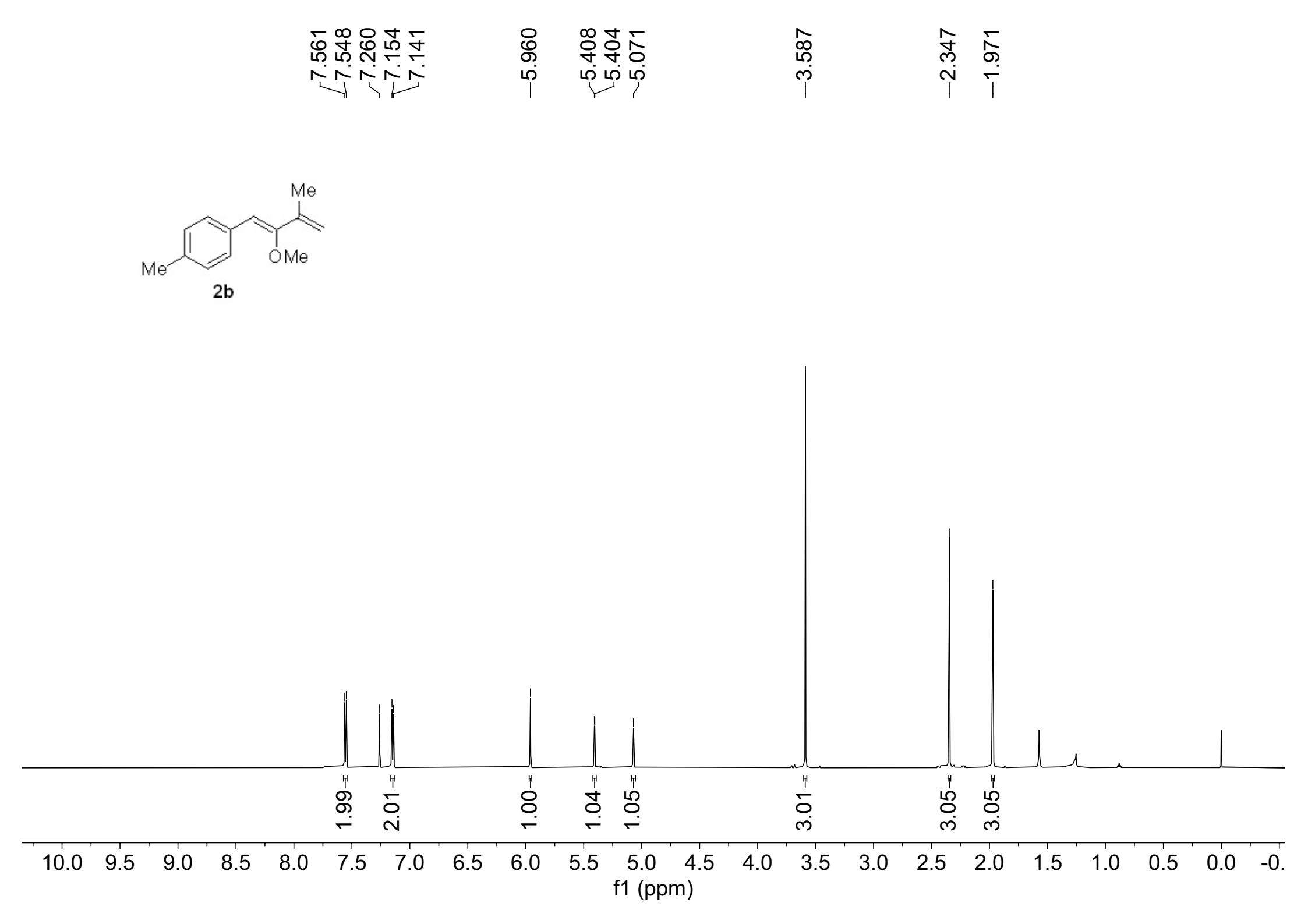
20.169
Me
OMe
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.154
7.141
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5.404
5.071
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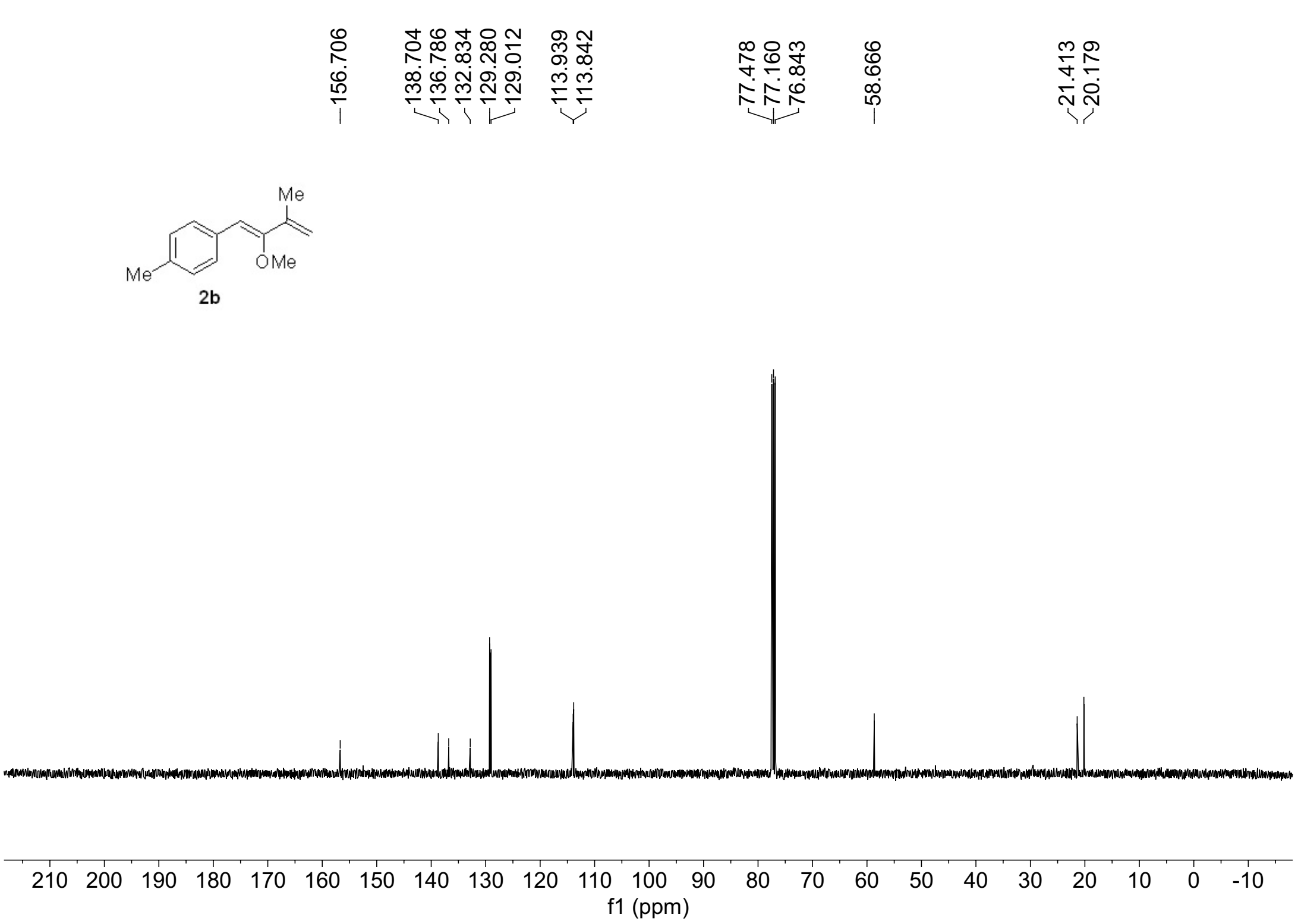
2.347
1.971
Me
OMe
Me
2b
1.99
2.01
1.00
1.04
1.05
3.01
3.05
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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132.834
129.280
129.012
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113.842
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77.160
76.843
58.666
21.413
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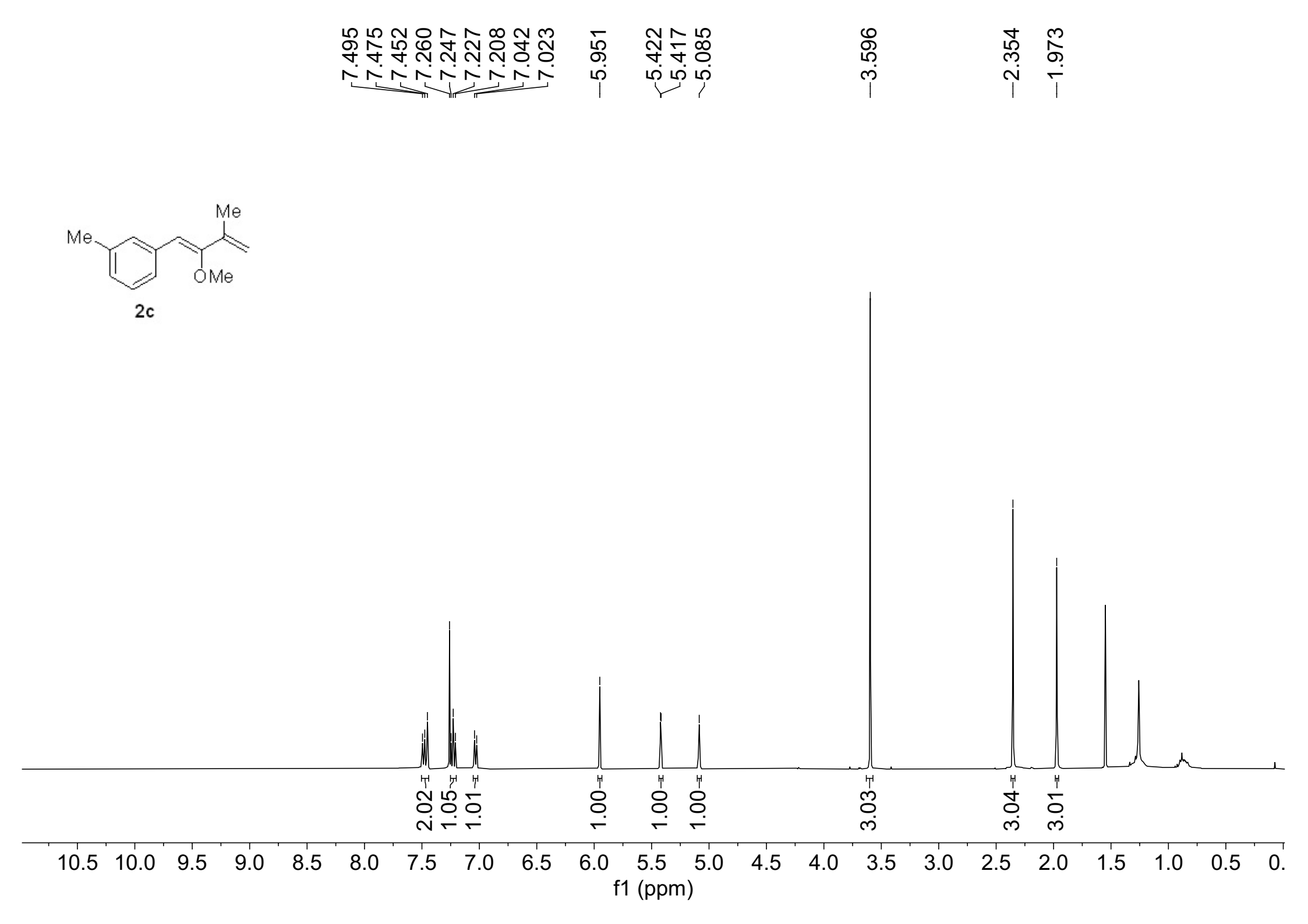
Me
OMe
Me
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.247
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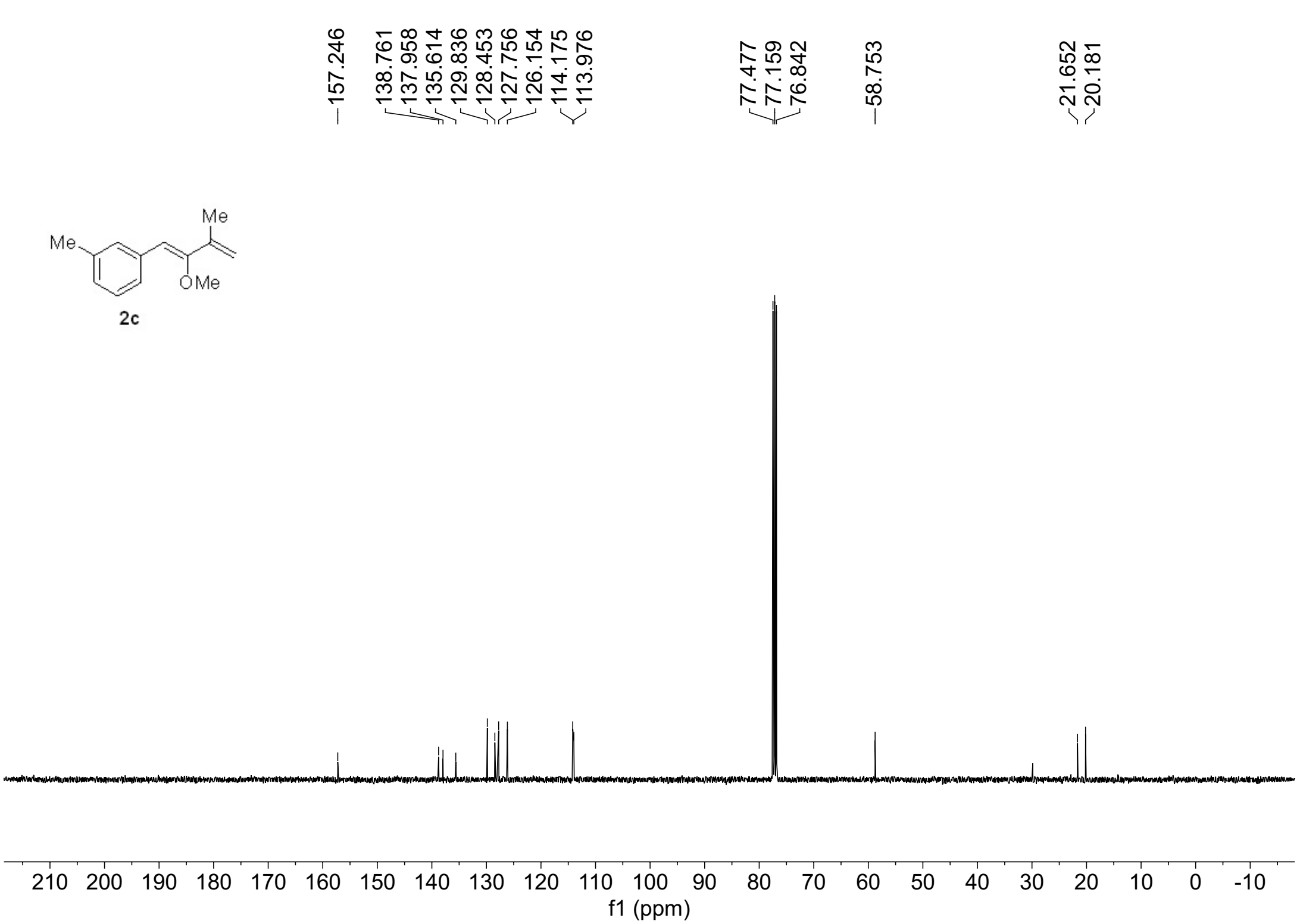
5.417
5.085
3.596
2.354
1.973
Me
Me
OMe
2c
2.02
1.05
1.01
1.00
1.00
1.00
3.03
3.04
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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126.154
114.175
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77.159
76.842
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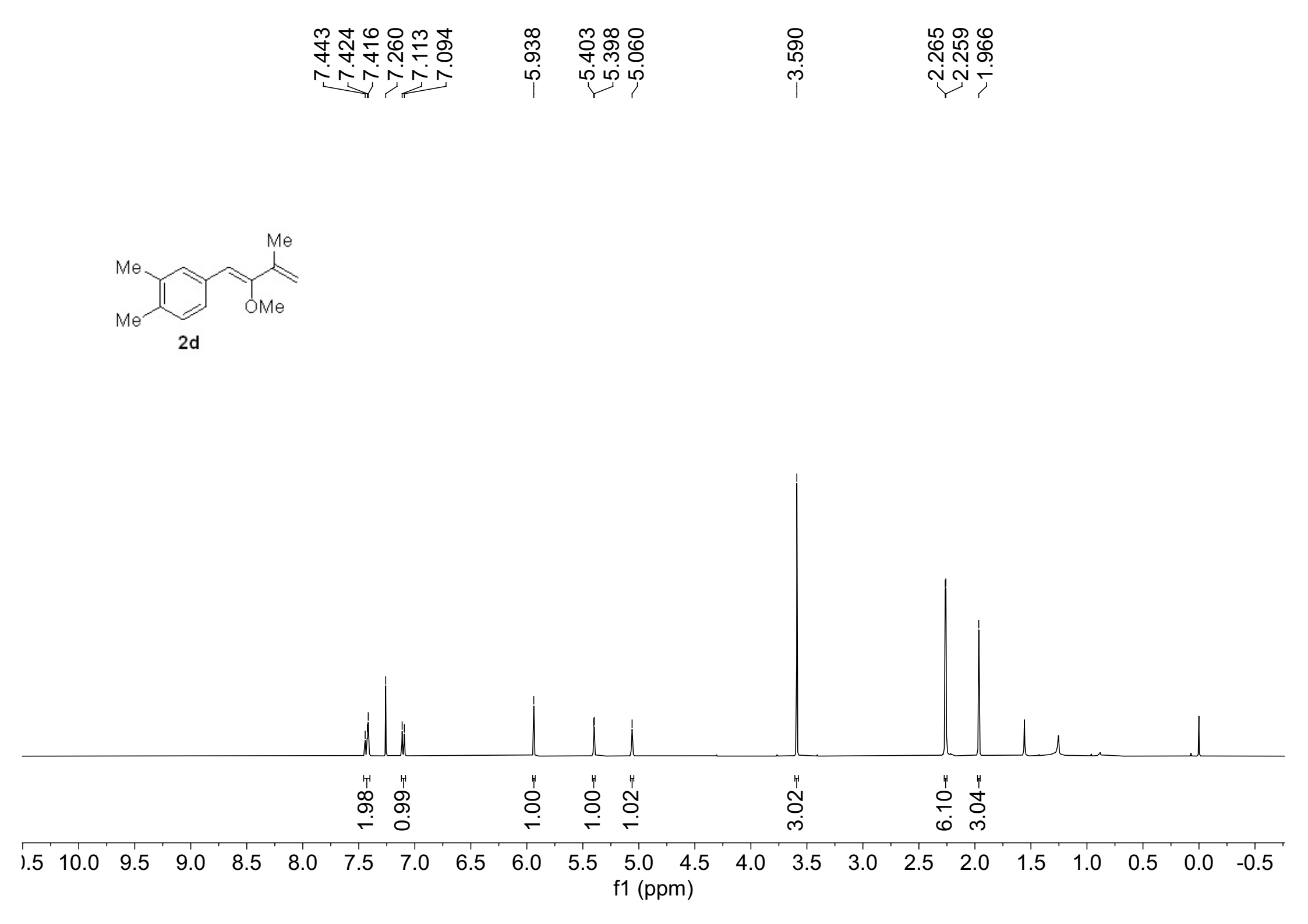
Me
Me
OMe
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.590
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2.259
1.966
Me
Me
Me
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2d
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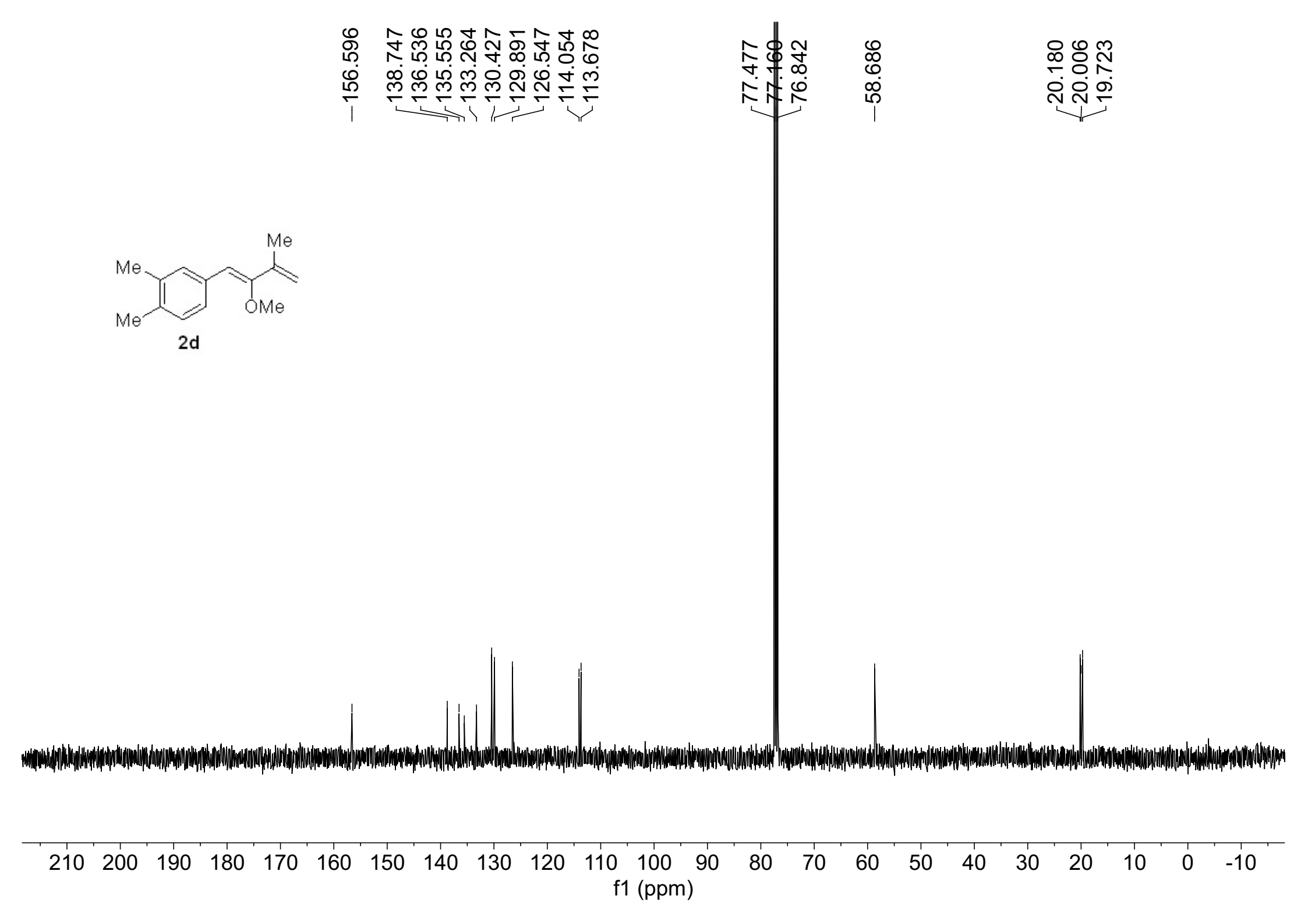
1.00
1.00
1.02
3.02
6.10
3.04
f1 (ppm)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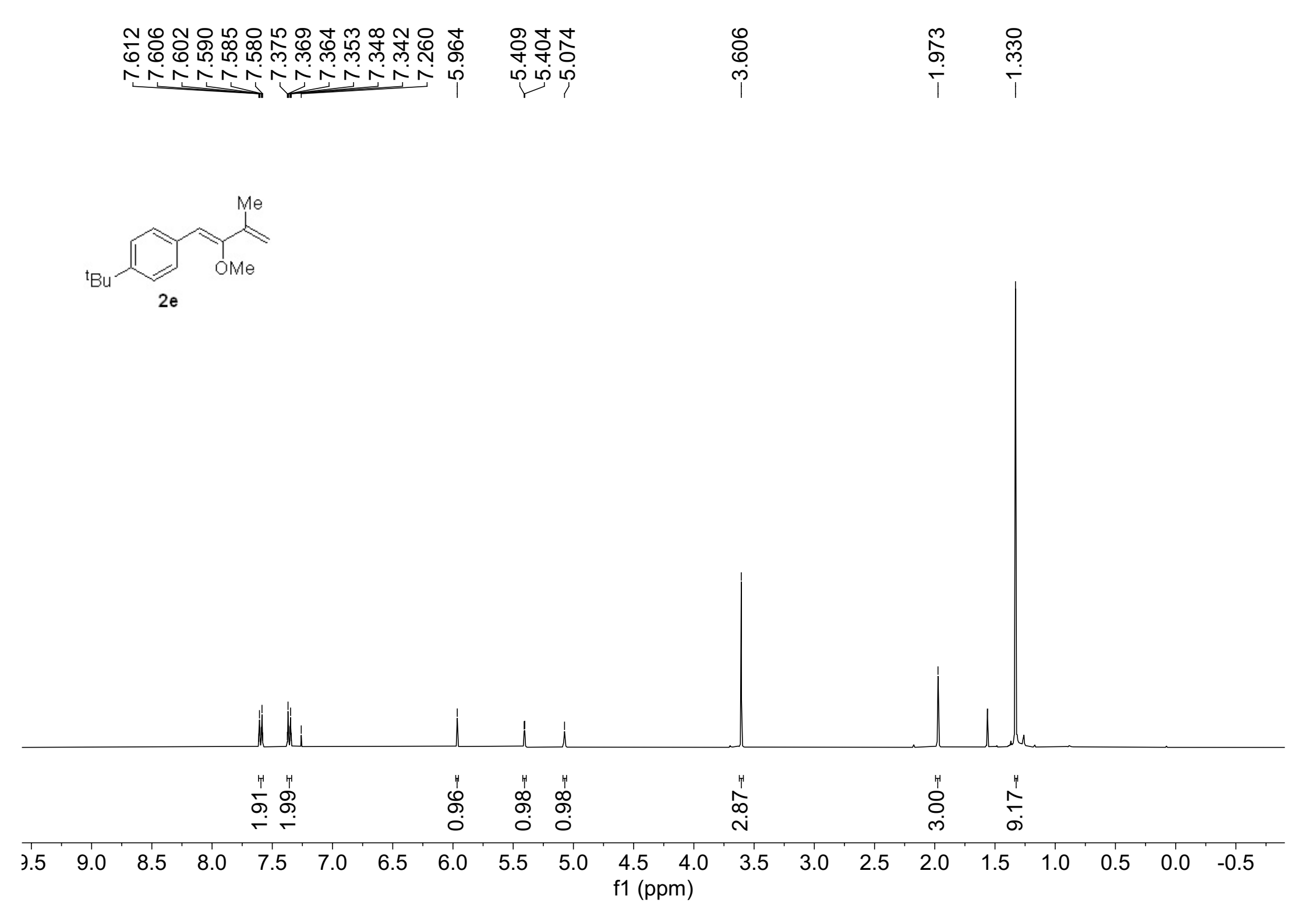
76.842
58.686
20.180
20.006
19.723
Me
Me
Me
OMe
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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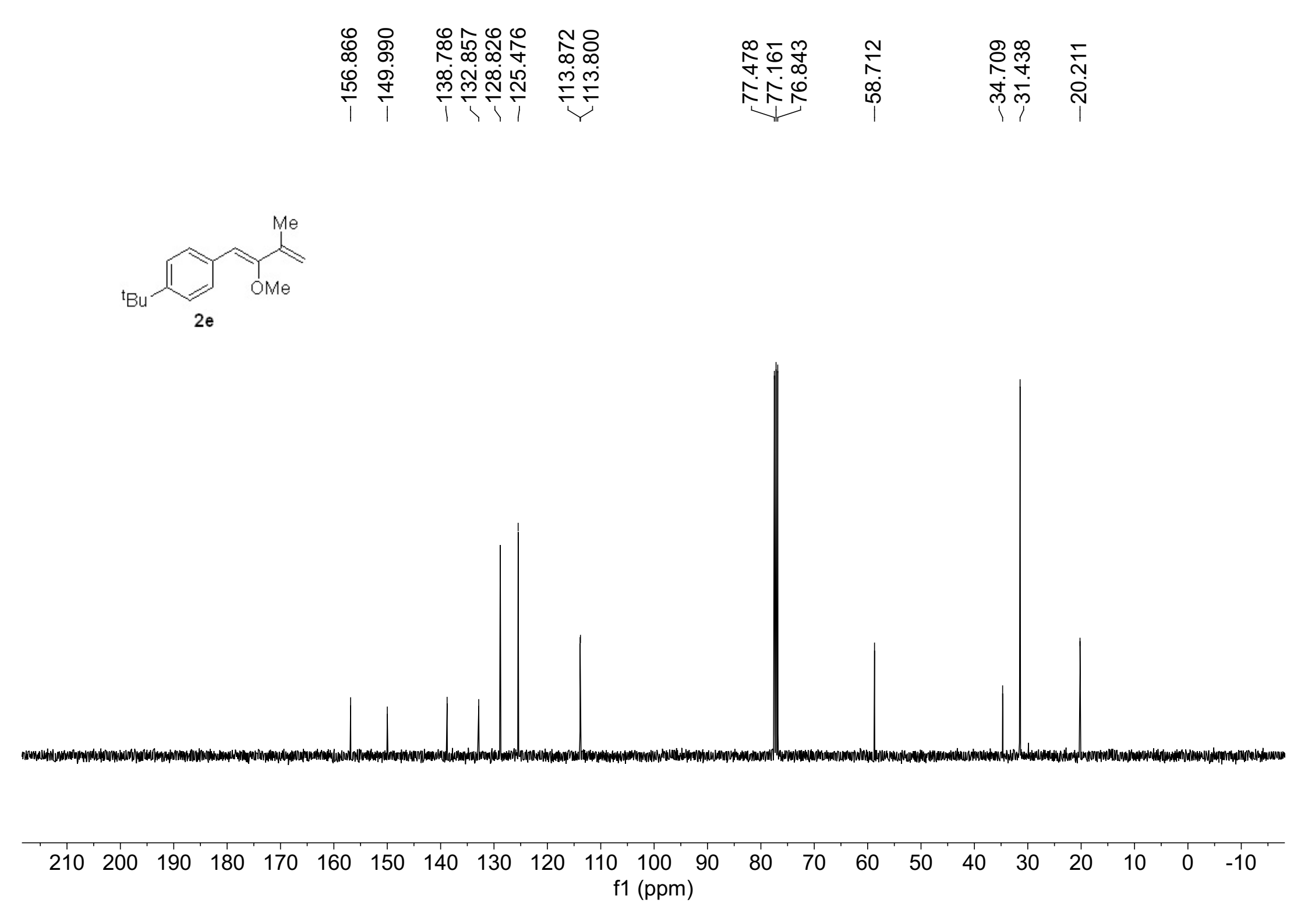
7.606
7.602
7.590
7.585
7.580
7.375
7.369
7.364
7.353
7.348
7.342
7.260
5.964
5.409
5.404
5.074
3.606
1.973
1.330
Me
OMe
tBu
2e
1.91
1.99
0.96
0.98
0.98
2.87
3.00
9.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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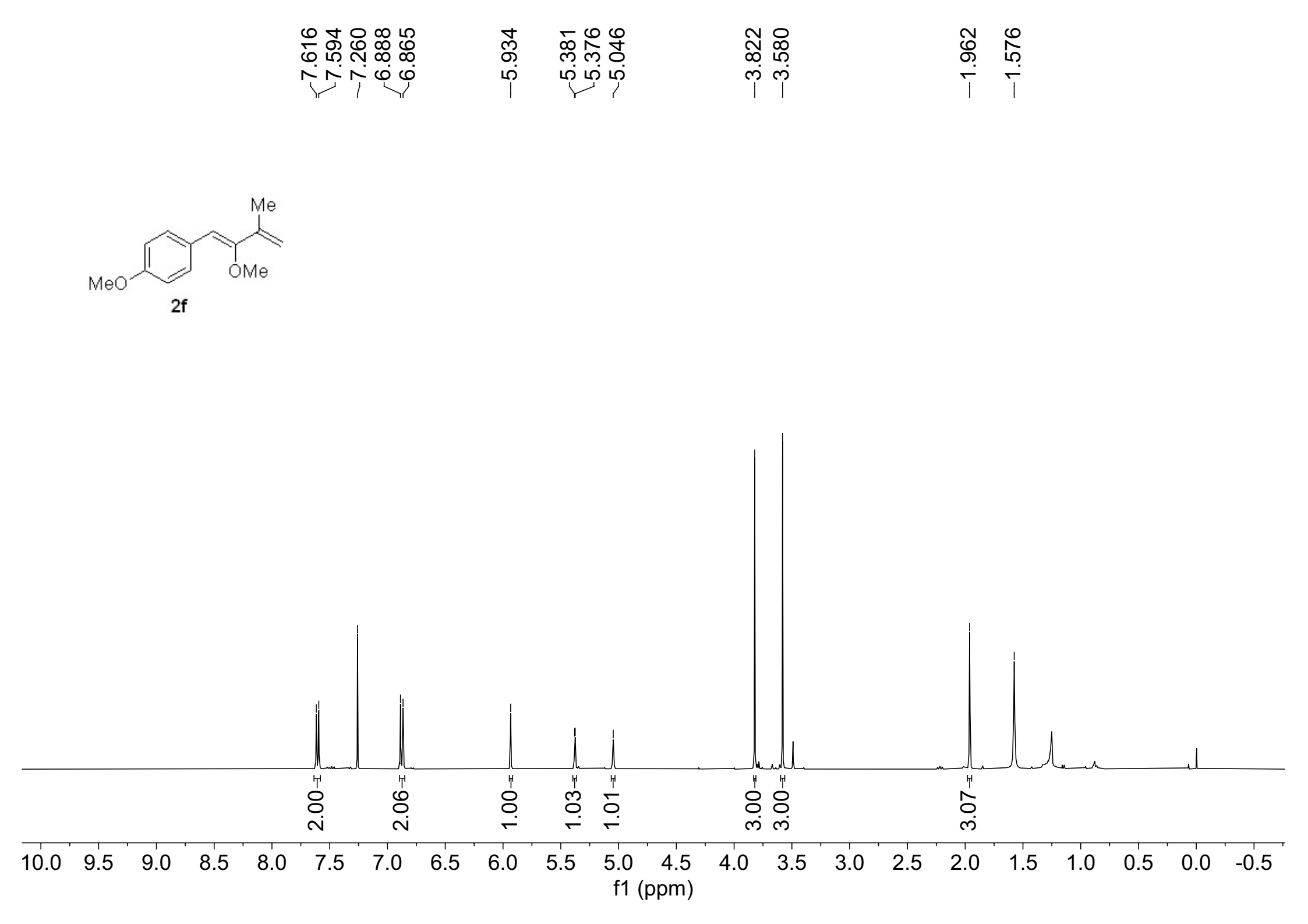
149.990
138.786
132.857
128.826
125.476
113.872
113.800
77.478
77.161
76.843
58.712
34.709
31.438
20.211
Me
OMe
tBu
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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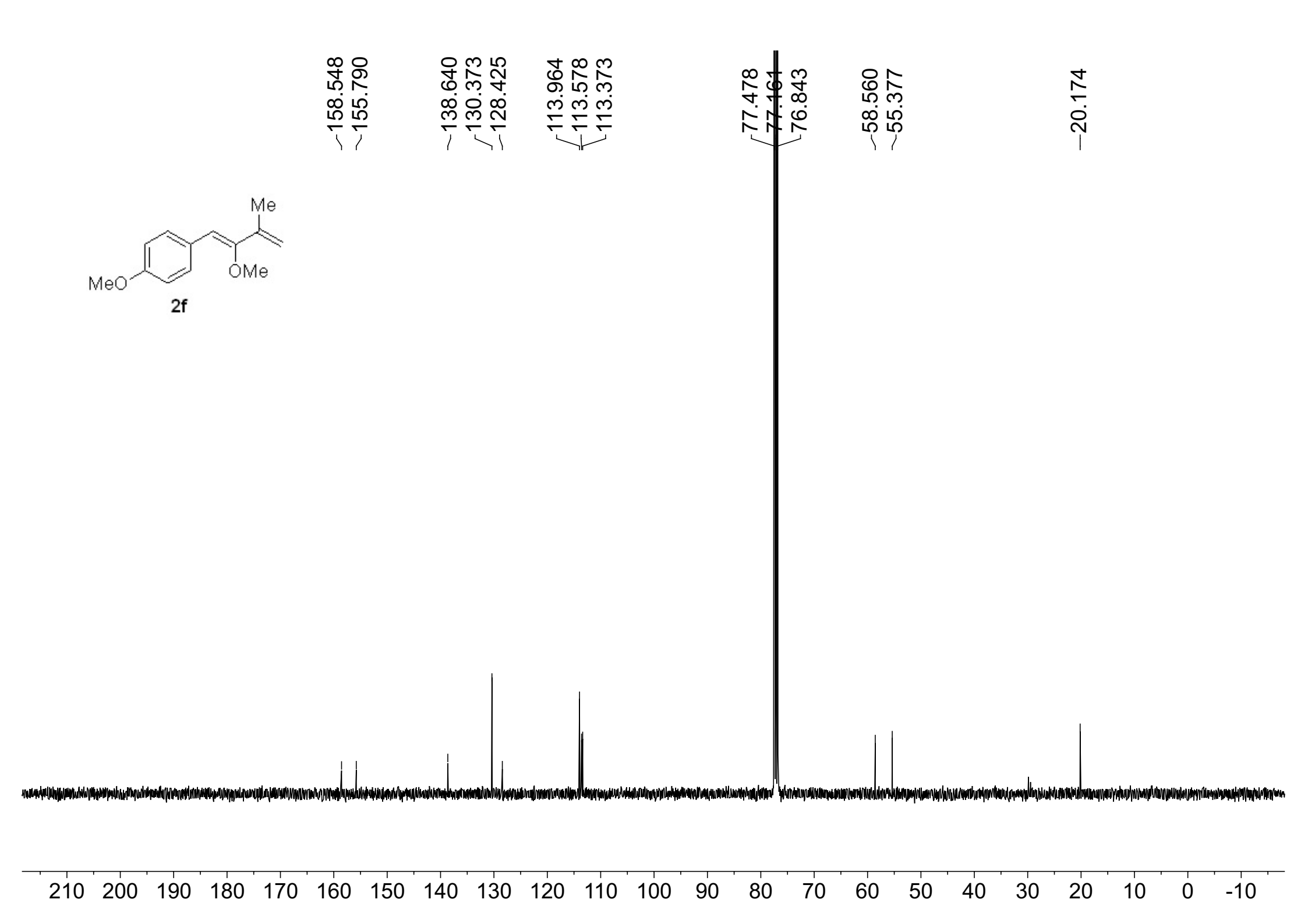
7.594
7.260
6.888
6.865
5.934
5.381
5.376
5.046
3.822
3.580
1.962
1.576
Me
OMe
MeO
2f
2.00
2.06
1.00
1.03
1.01
3.00
3.00
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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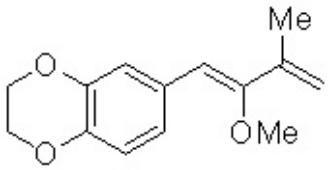
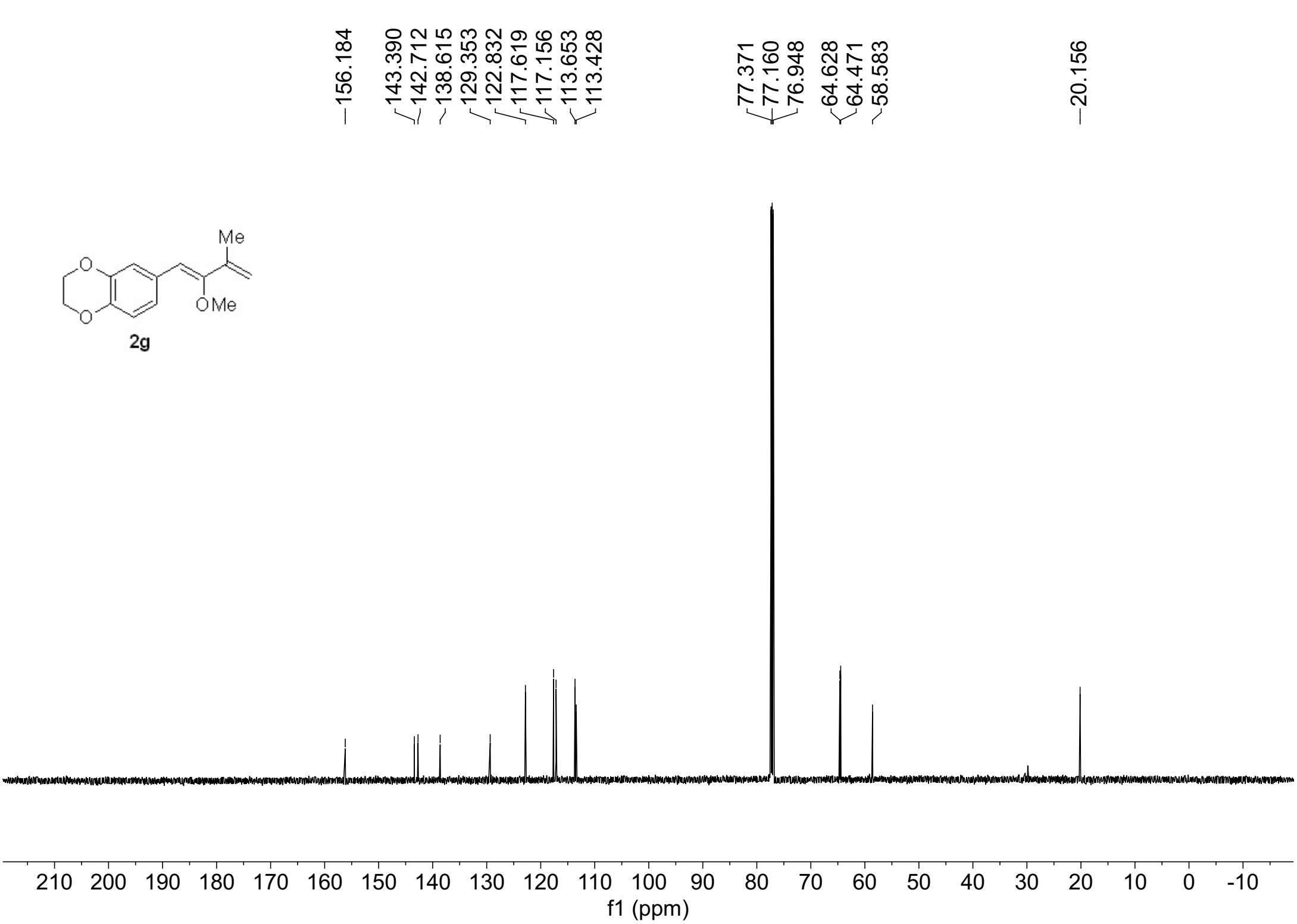
155.790
138.640
130.373
128.425
113.964
113.578
113.373
77.478
77.161
76.843
58.560
55.377
20.174
Me
OMe
MeO
2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Me
O
O
OMe

2g

7.284
7.280
7.260
7.109
7.106
7.095
7.092
6.823
6.809
5.863
5.376
5.373
5.050
4.275
4.273
4.266
4.259
3.589
1.948
0.99
1.03
1.05
1.00
1.04
1.04
4.01
3.04
3.01
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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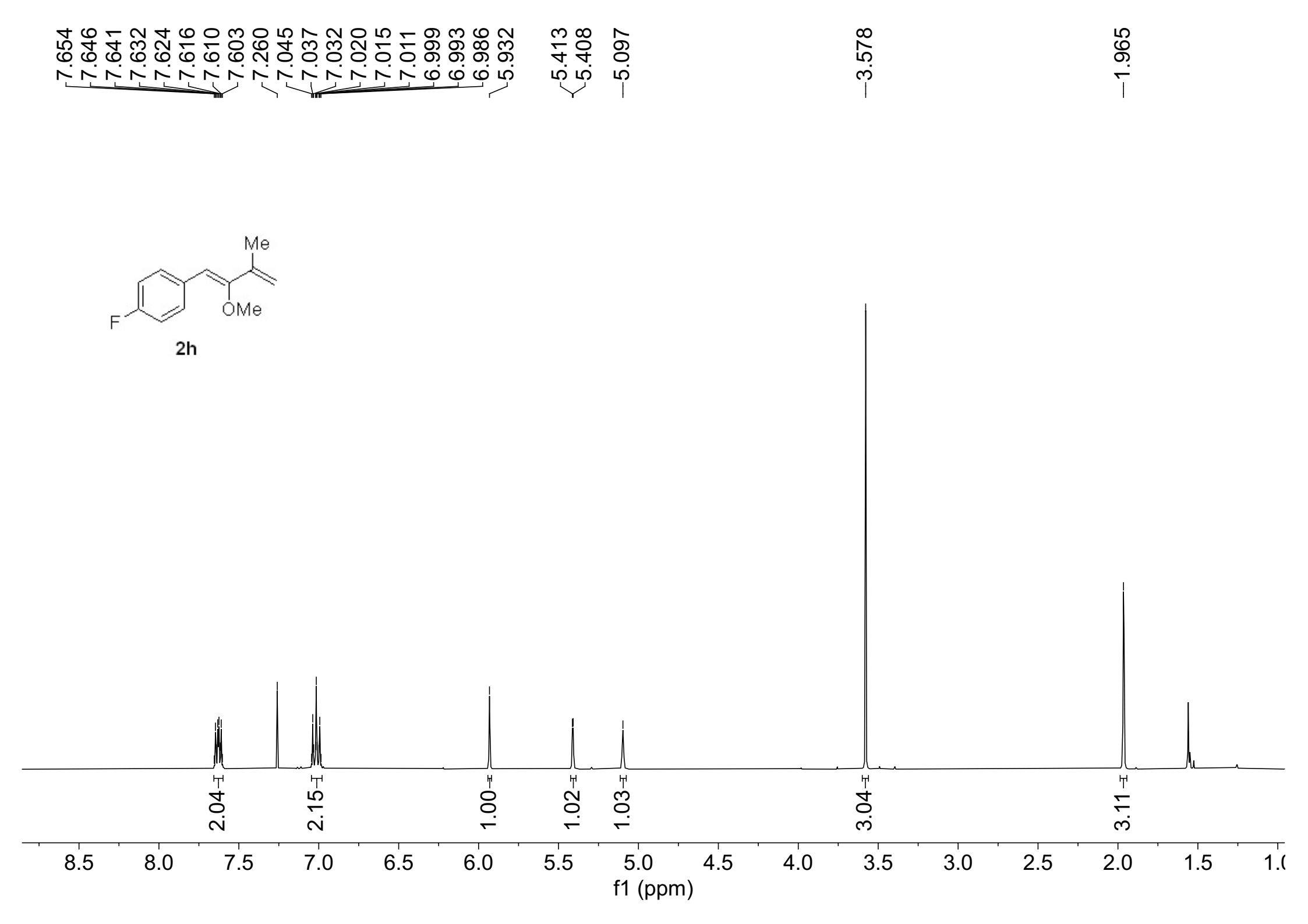
143.390
142.712
138.615
129.353
122.832
117.619
117.156
113.653
113.428
77.371
77.160
76.948
64.628
64.471
58.583
20.156
Me
O
O
O
Me
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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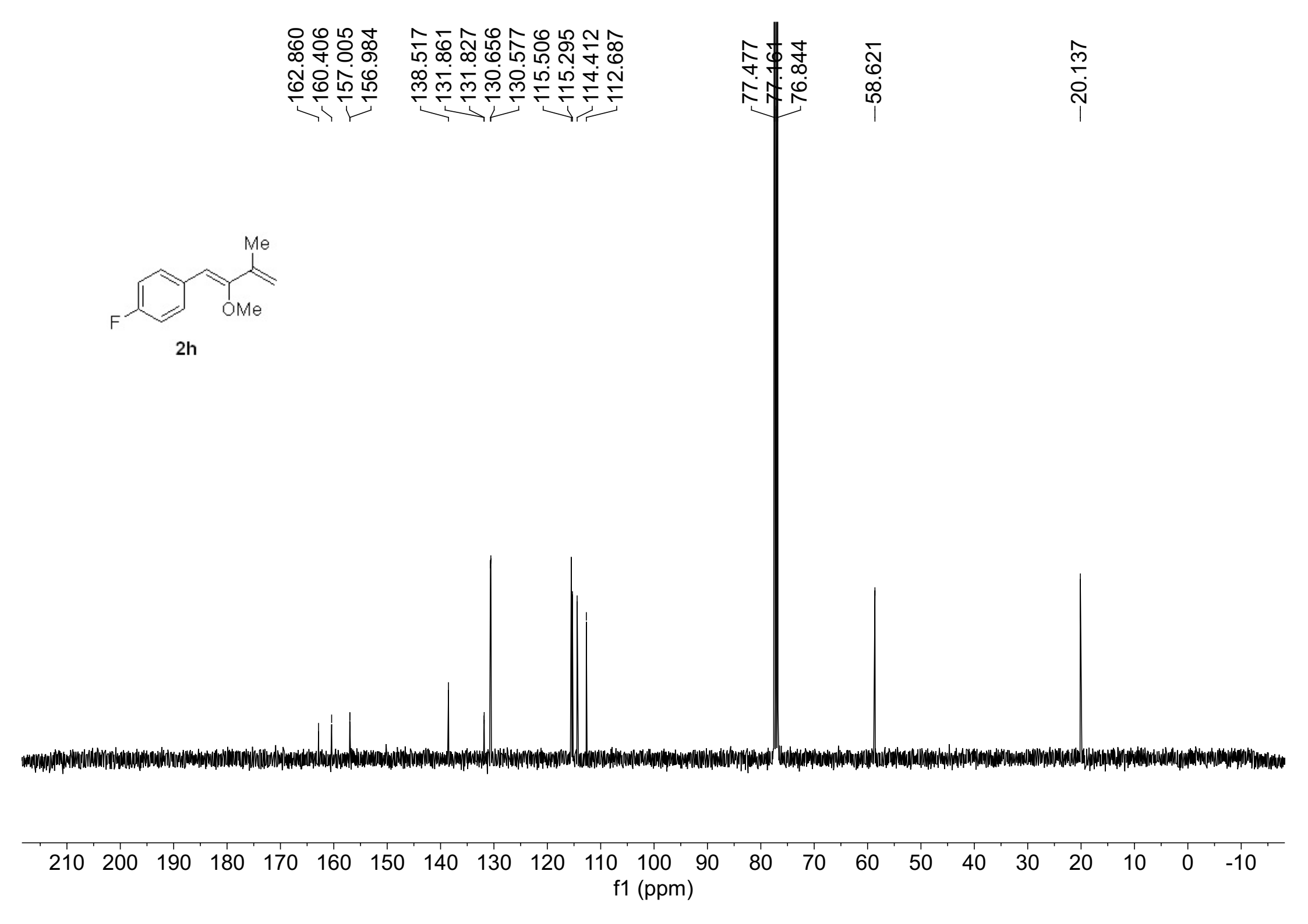
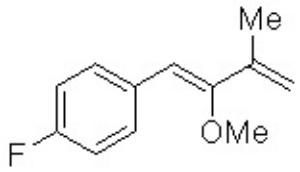
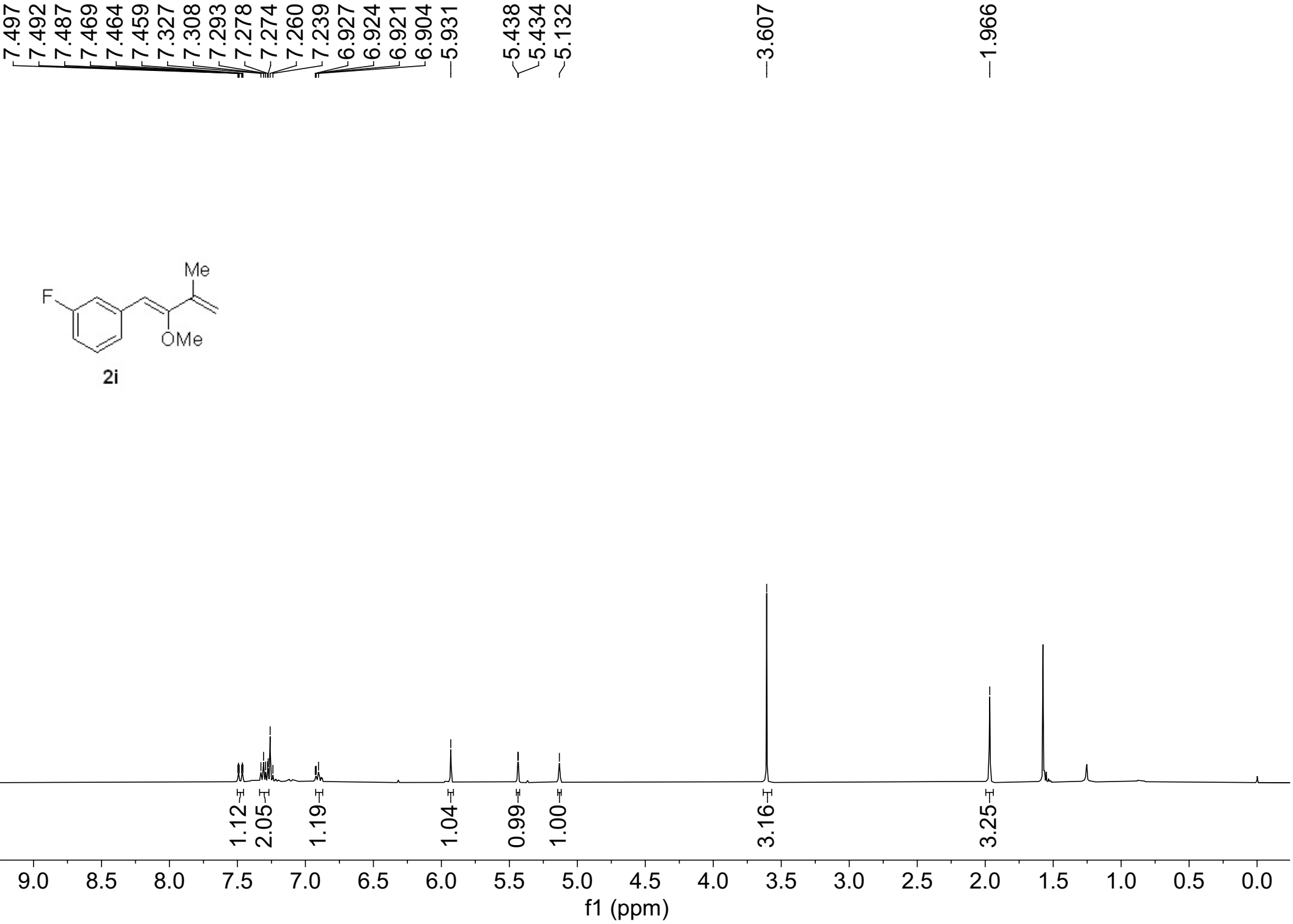
7.646
7.641
7.632
7.624
7.616
7.610
7.603
7.260
7.045
7.037
7.032
7.020
7.015
7.011
6.999
6.993
6.986
5.932
5.413
5.408
5.097
3.578
1.965
Me
OMe
F
2h
2.04
2.15
1.00
1.02
1.03
3.04
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


162.860
160.406
157.005
156.984
138.517
131.861
131.827
130.656
130.577
115.506
115.295
114.412
112.687
77.477
77.161
76.844
58.621
20.137
Me
OMe
F
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
OMe
F

2h

-114.754
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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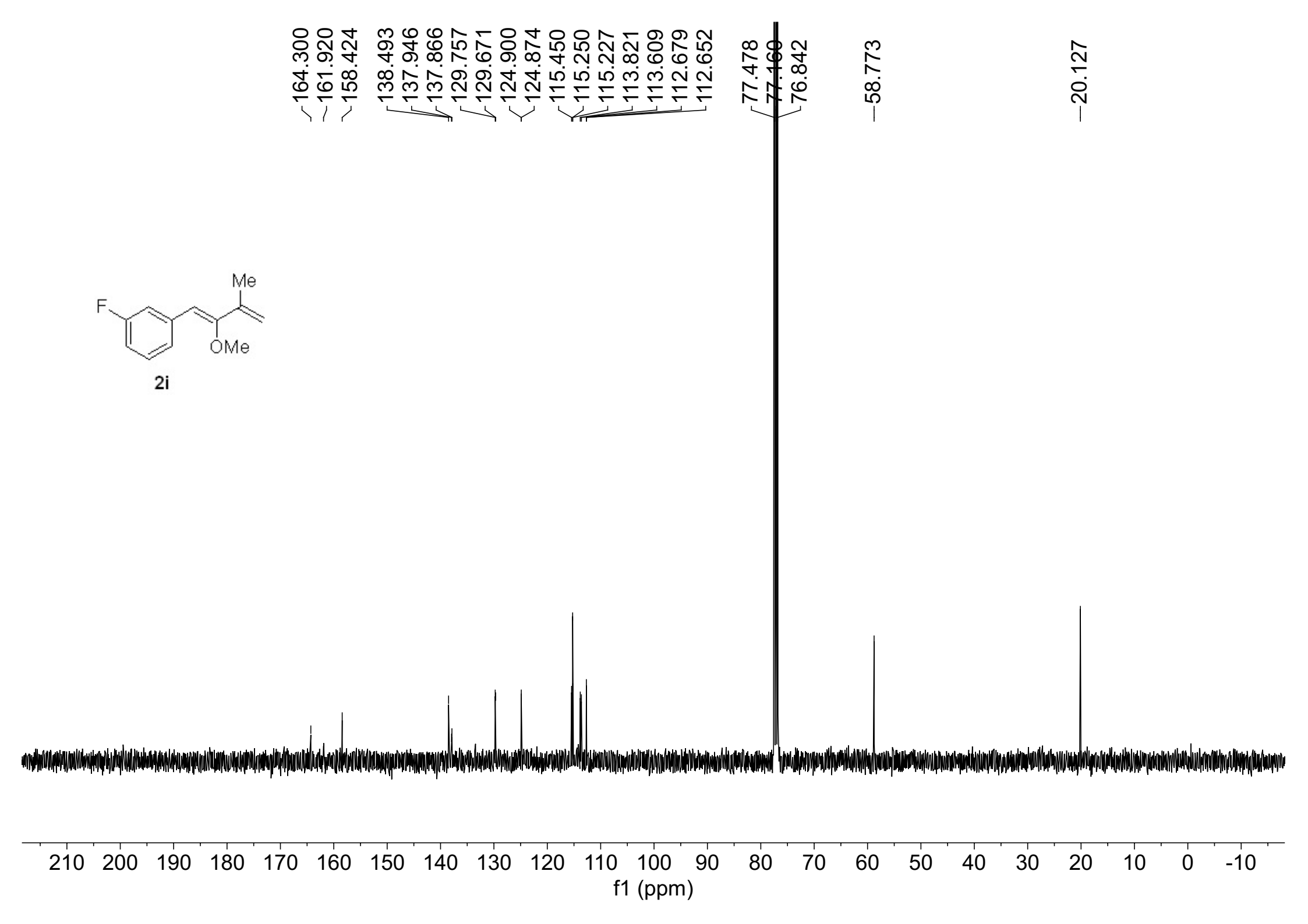
7.492
7.487
7.469
7.464
7.459
7.327
7.308
7.293
7.278
7.274
7.260
7.239
6.927
6.924
6.921
6.904
5.931
5.438
5.434
5.132
3.607
1.966
F
Me
OMe
2i
1.12
2.05
1.19
1.04
0.99
1.00
3.16
3.25
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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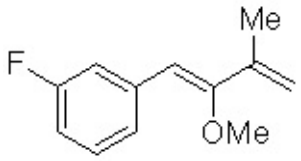
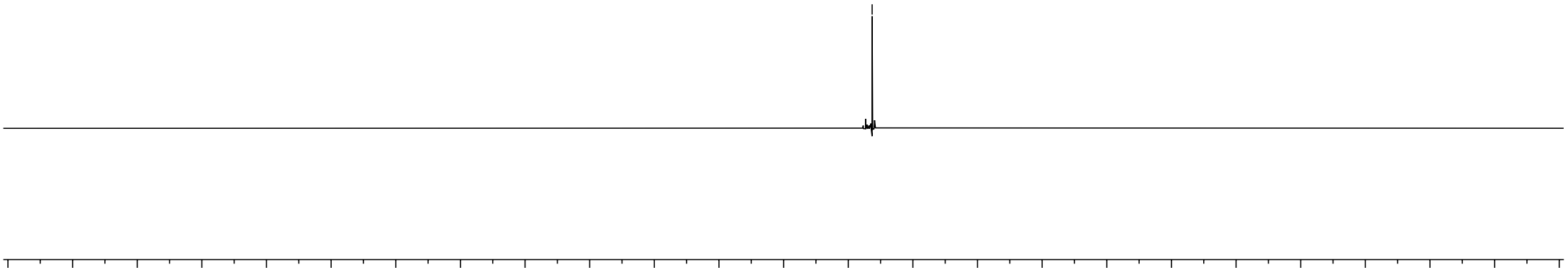
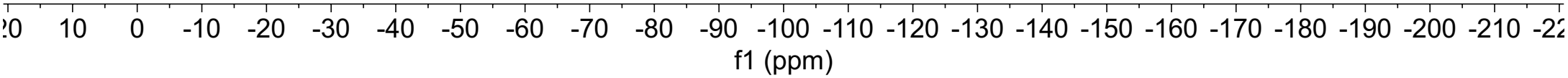
161.920
158.424
138.493
137.946
137.866
129.757
129.671
124.900
124.874
115.450
115.250
115.227
113.821
113.609
112.679
112.652
77.478
77.160
76.842
58.773
20.127
F
Me
OMe
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

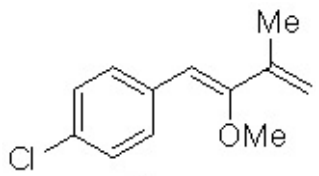

Me
F
OMe

2i

-113.697

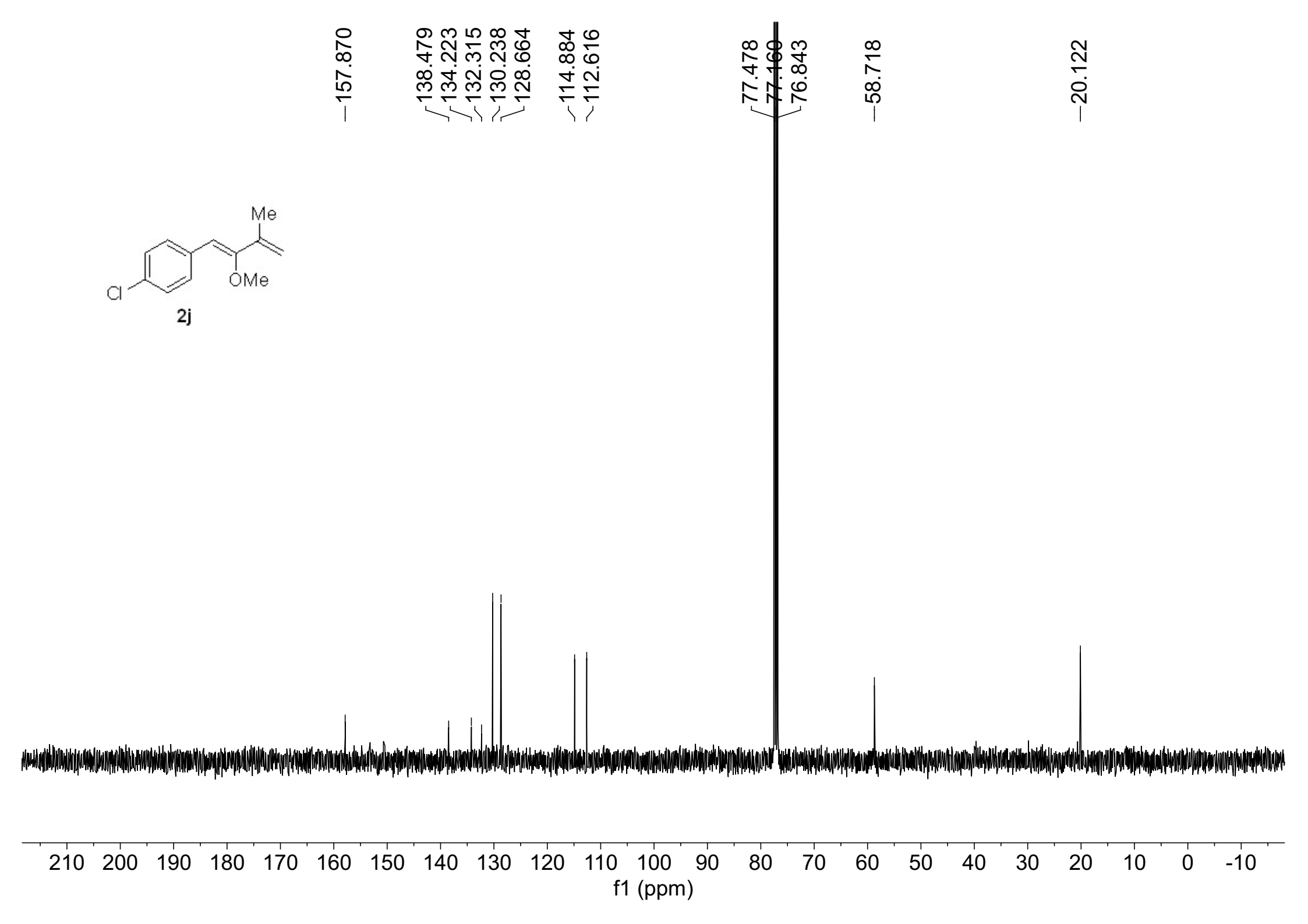



:0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


Me
OMe
Cl

2j

7.600
7.594
7.590
7.577
7.573
7.567
7.305
7.299
7.294
7.282
7.277
7.271
7.260
5.917
5.426
5.422
5.115
3.580
1.964
1.98
2.01
1.00
1.00
1.01
3.00
3.15
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)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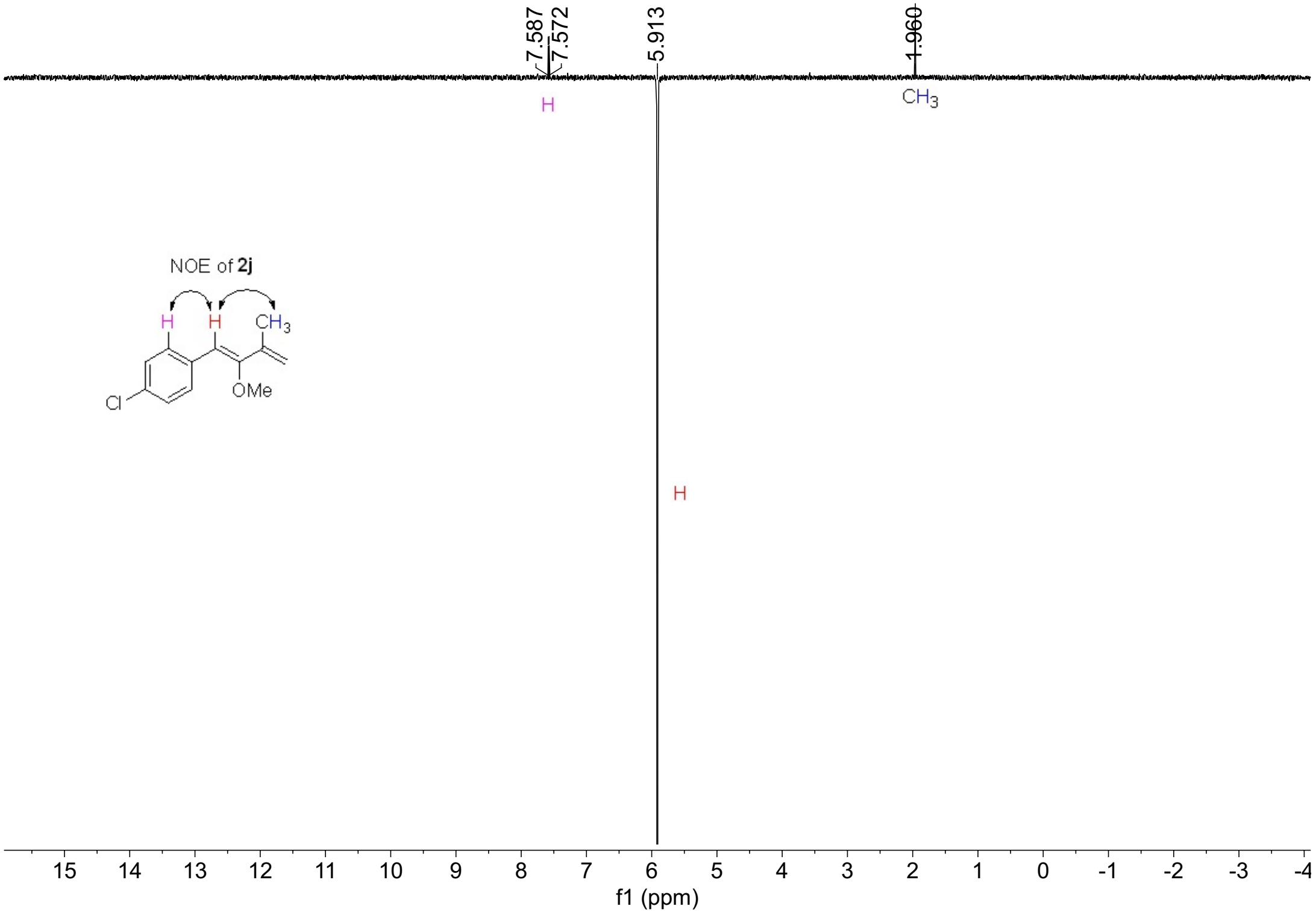
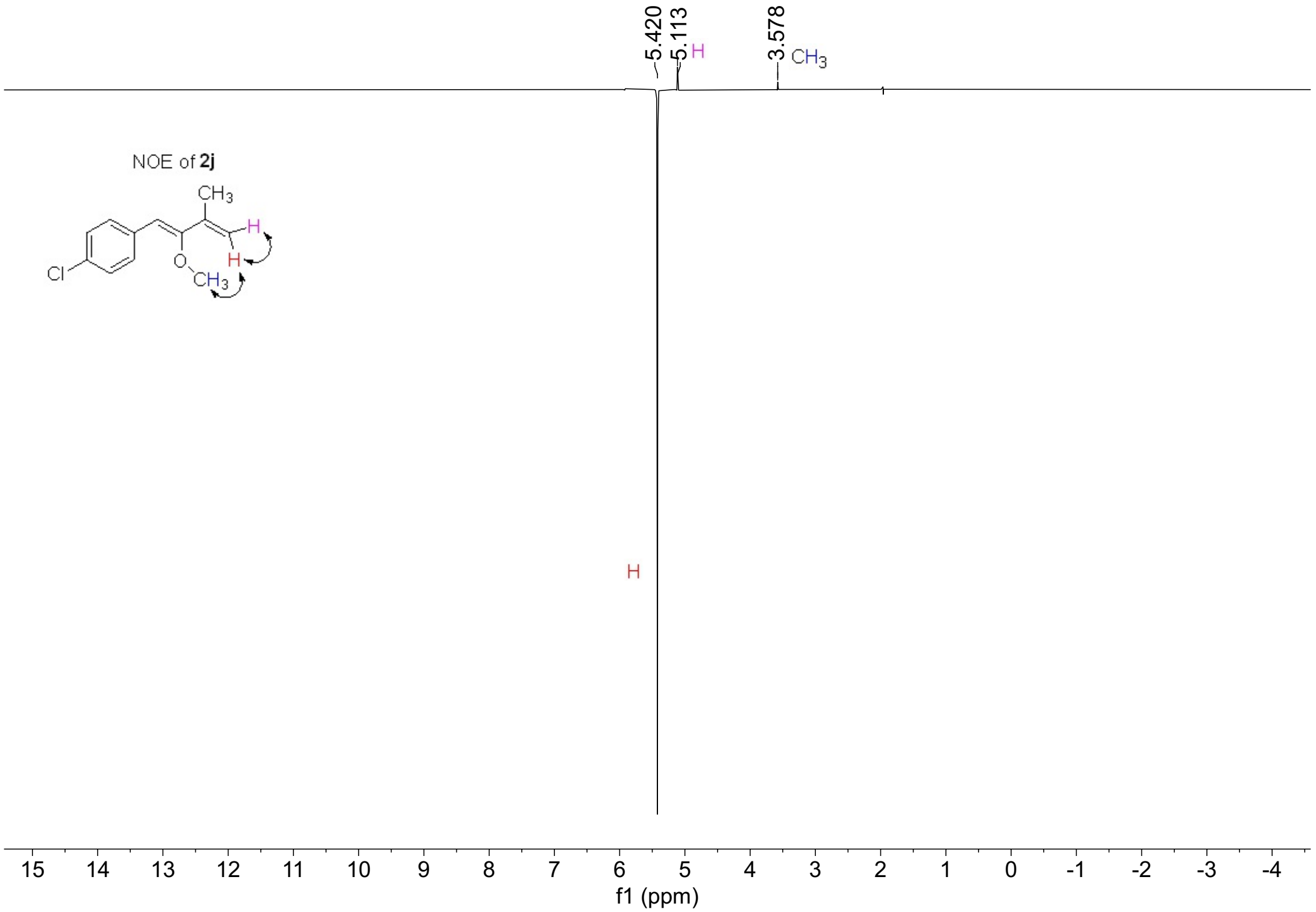
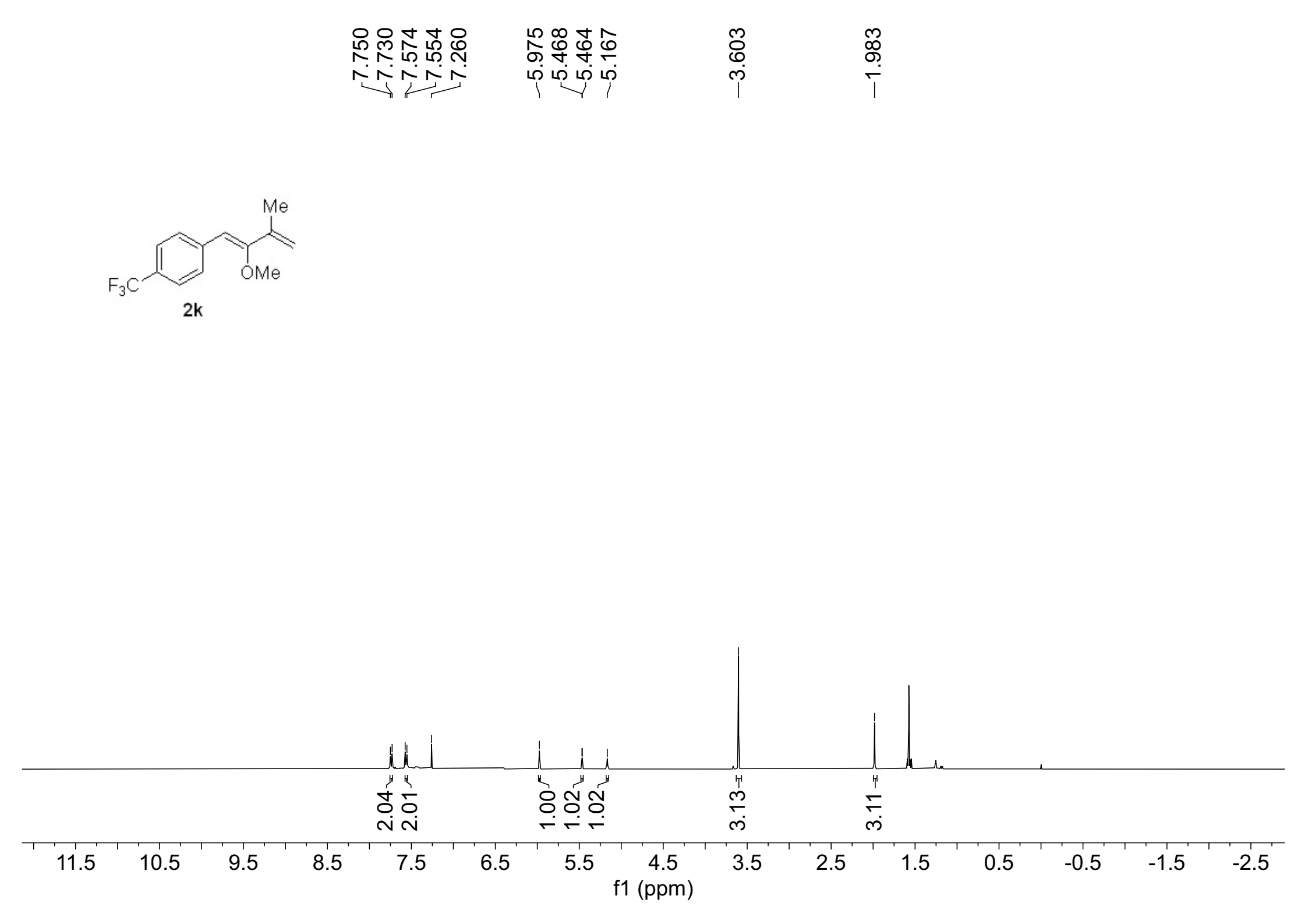
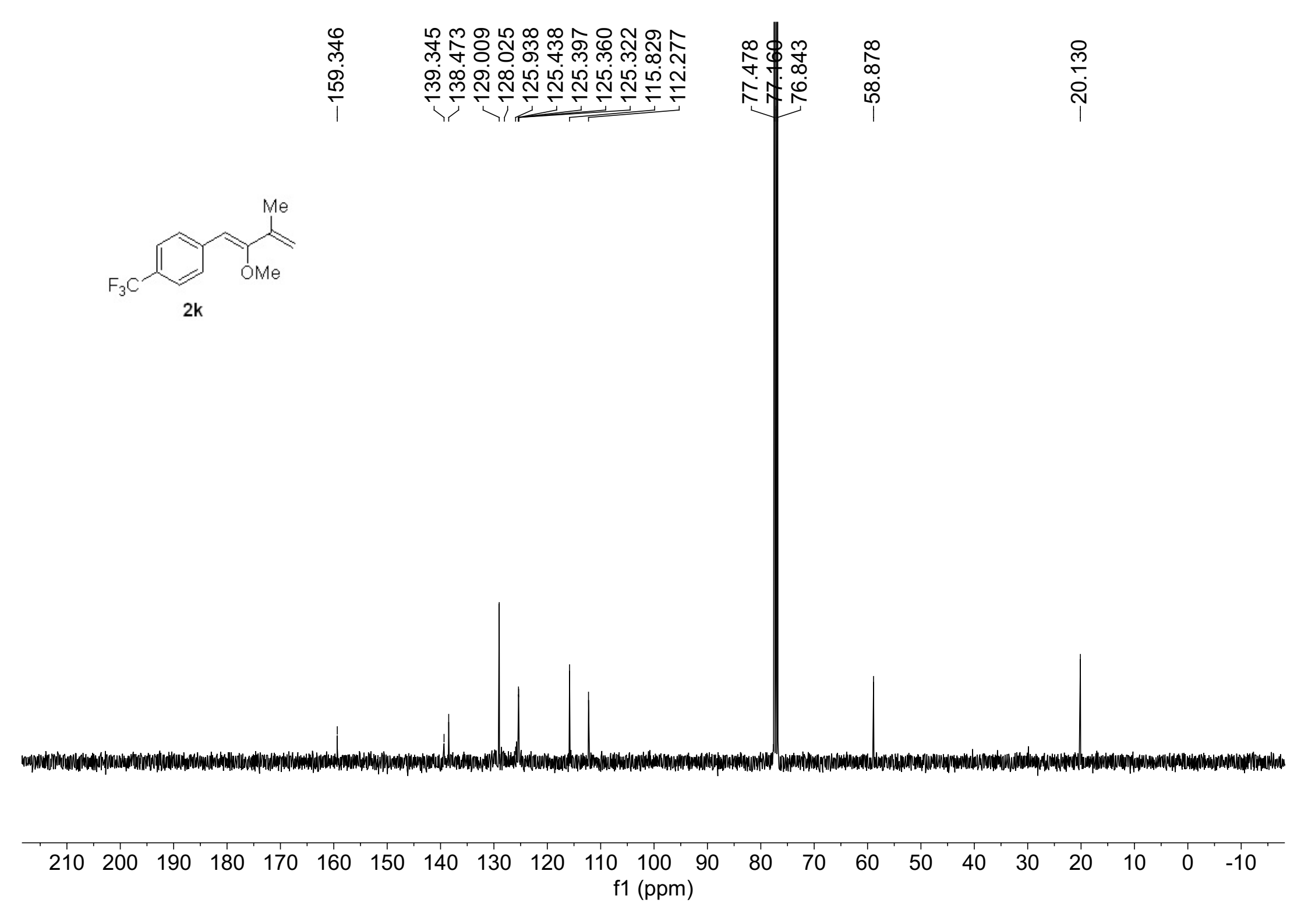
134.223
132.315
130.238
128.664
114.884
112.616
77.478
77.160
76.843
58.718
20.122
Me
OMe
Cl
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.587
7.572
5.913
1.960
H
CH3
H
NOE of 2j
H
H
CH3
Cl
OMe
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


5.420
5.113
H
3.578
CH3
NOE of 2j
CH3
H
H
O
CH3
Cl
H
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


7.750
7.730
7.574
7.554
7.260
5.975
5.468
5.464
5.167
3.603
1.983
Me
OMe
F3C
2k
2.04
2.01
1.00
1.02
1.02
3.13
3.11
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
-2.5
f1 (ppm)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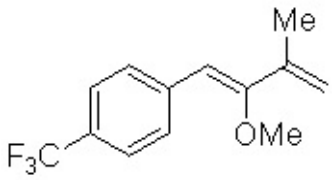
139.345
138.473
129.009
128.025
125.938
125.438
125.397
125.360
125.322
115.829
112.277
77.478
77.160
76.843
58.878
20.130
Me
OMe
F3C
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
OMe
F3C

2k

-62.558
10
0
-10
-20
-30
-40
-50
-60
-70
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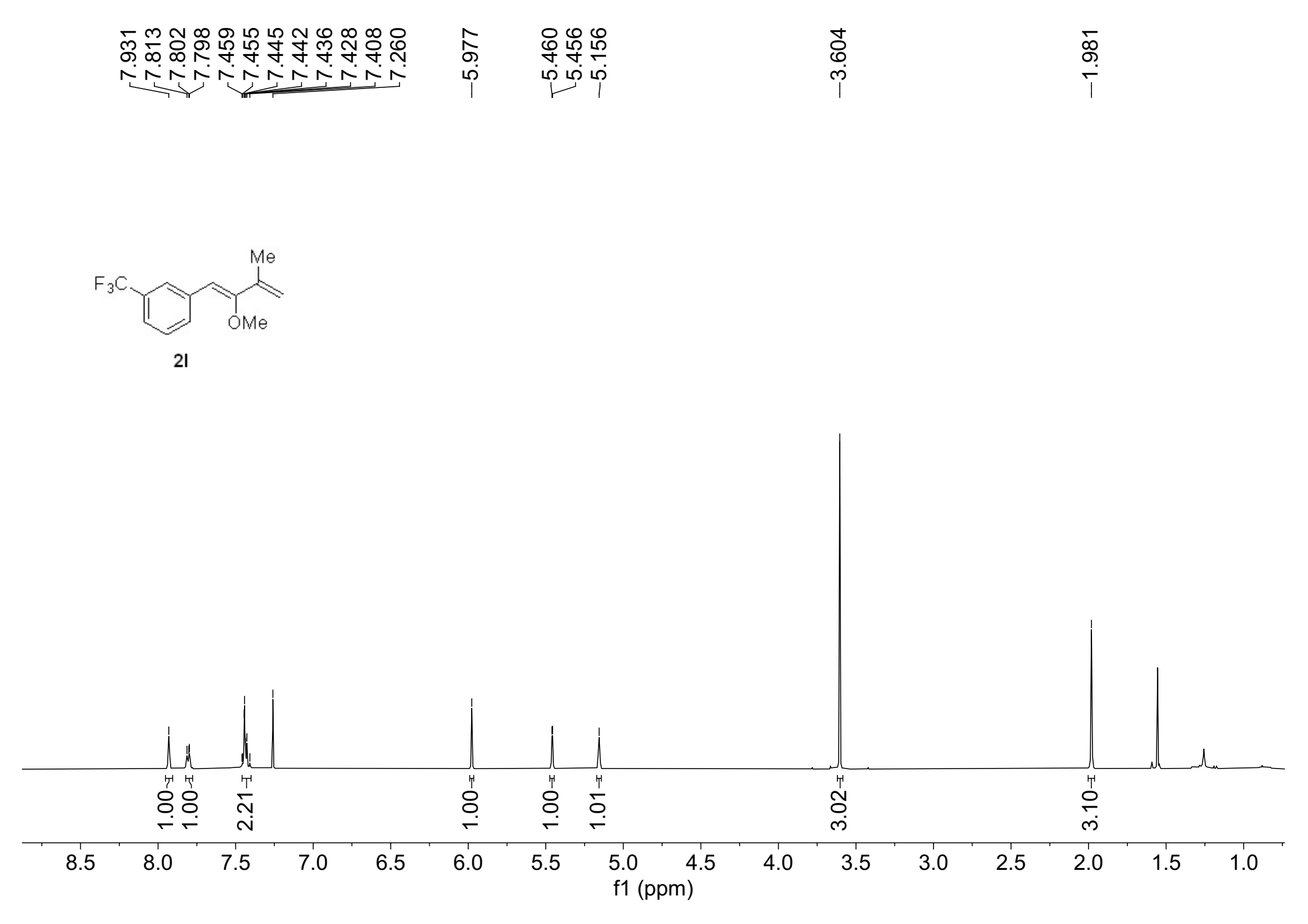
-170
-180
-190
-200
-210
f1 (ppm)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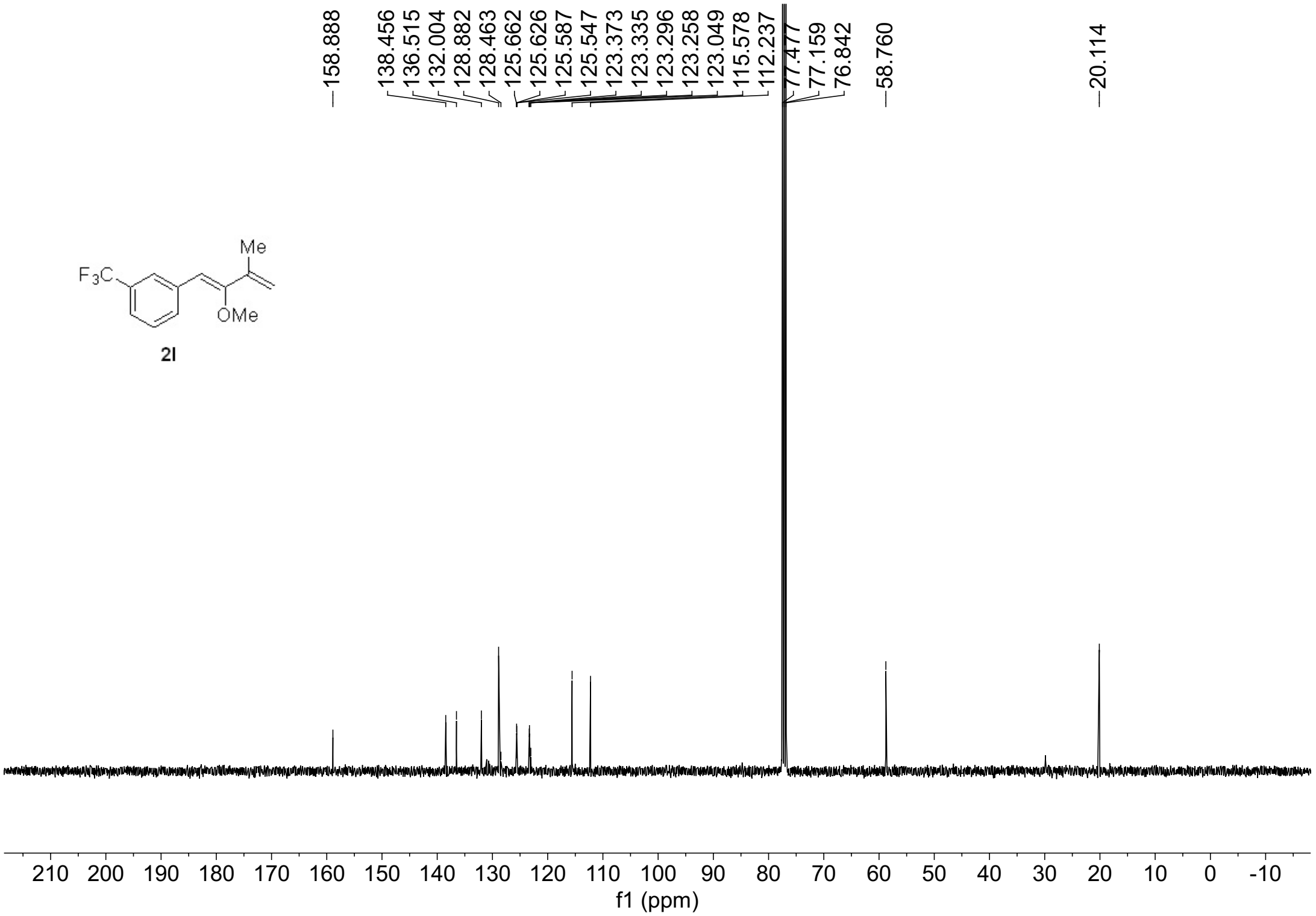
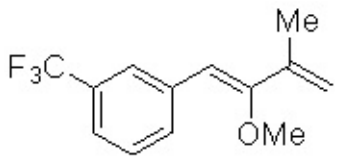
7.459
7.455
7.445
7.442
7.436
7.428
7.408
7.260
5.977
5.460
5.456
5.156
3.604
1.981
Me
F3C
OMe
2l
1.00
1.00
2.21
1.00
1.00
1.01
3.02
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


158.888
138.456
136.515
132.004
128.882
128.463
125.662
125.626
125.587
125.547
123.373
123.335
123.296
123.258
123.049
115.578
112.237
77.477
77.159
76.842
58.760
20.114
Me
F3C
OMe
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
F3C
OMe

2l

-62.741
10
0
-10
-20
-30
-40
-50
-60
-70
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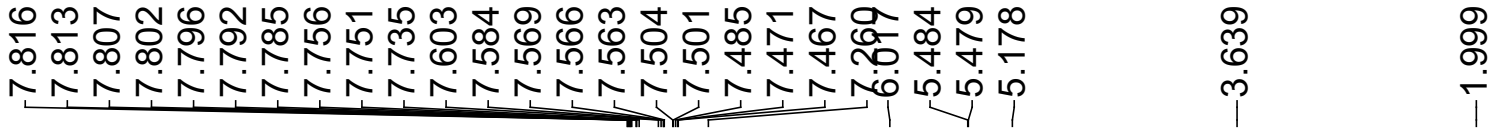
-170
-180
-190
-200
-210
f1 (ppm)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7.792
7.785
7.756
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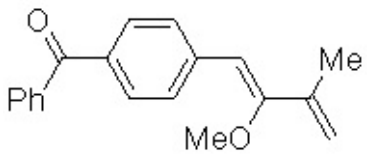
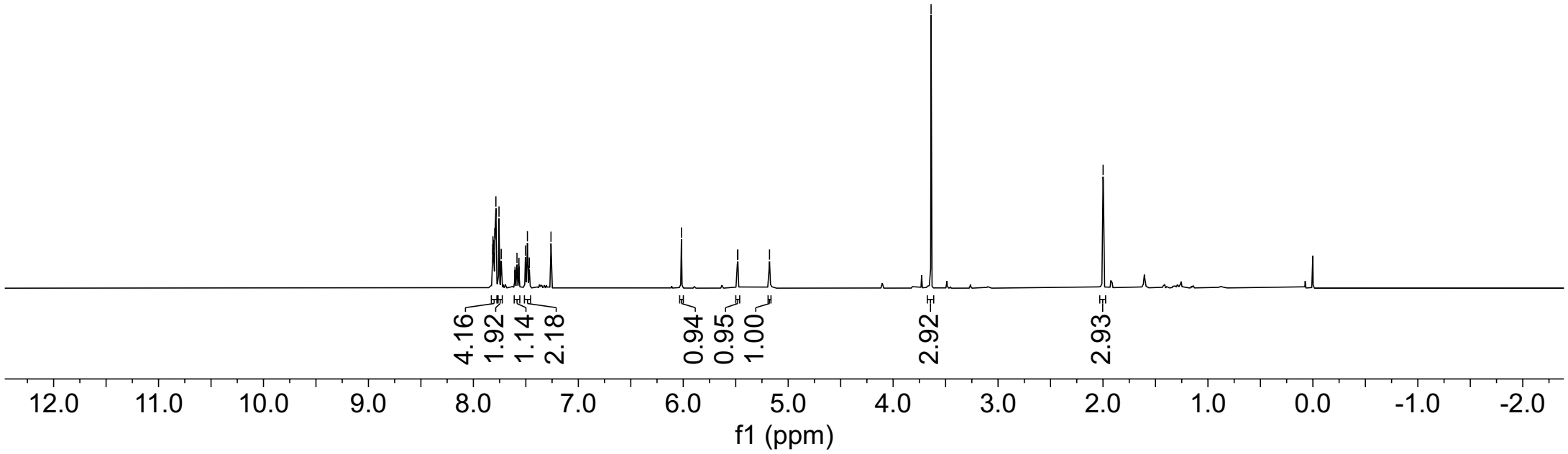
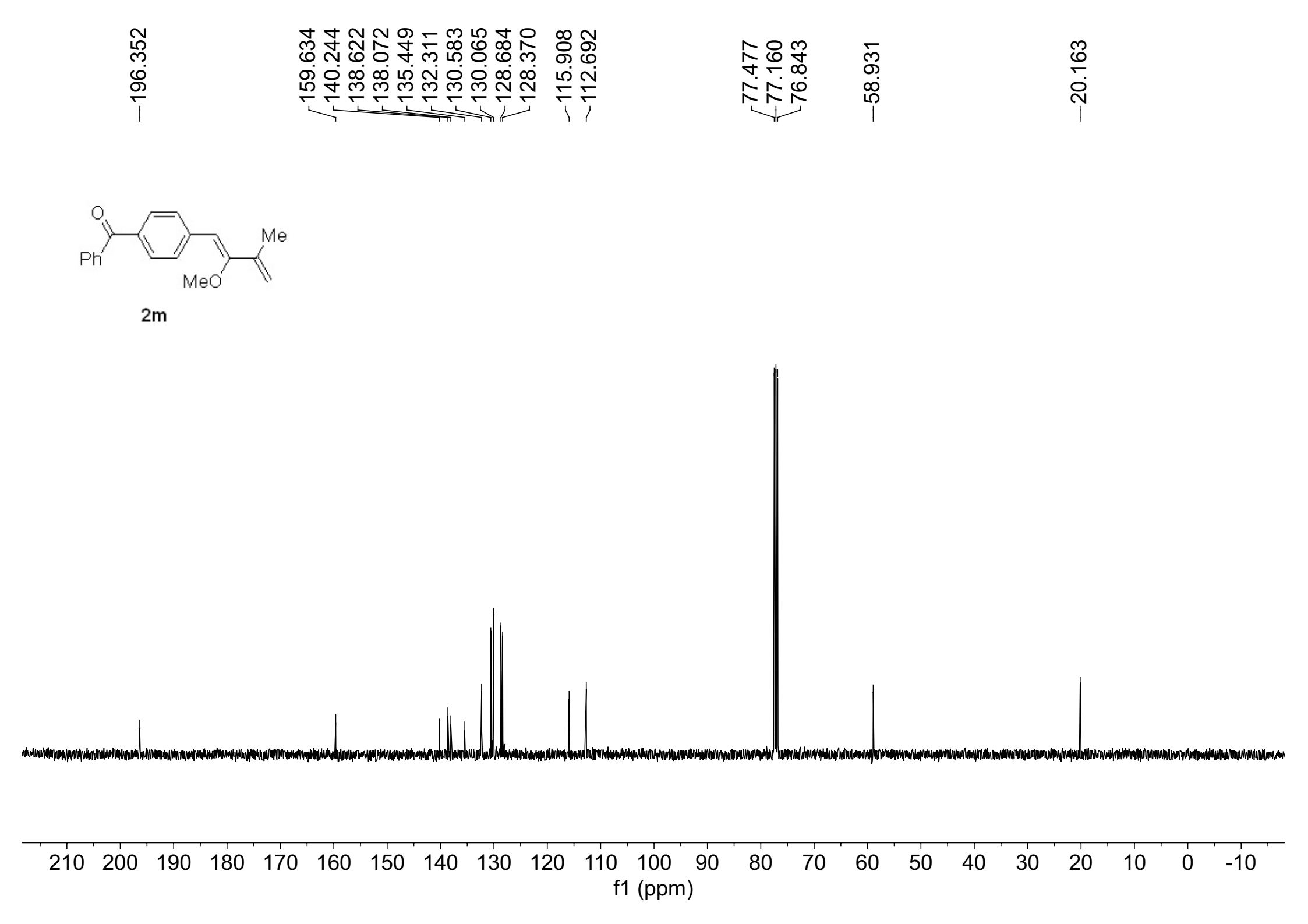
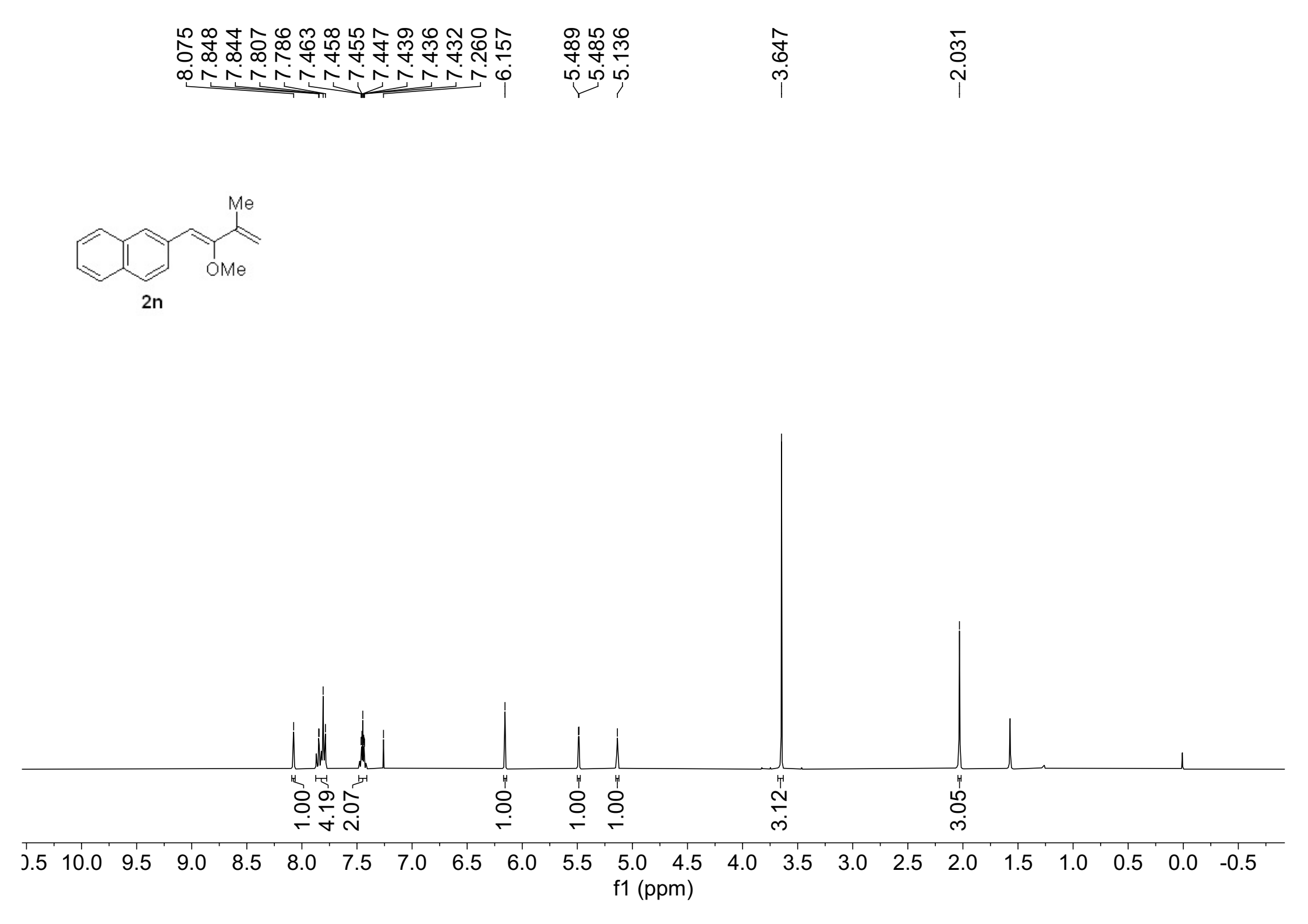
7.735
7.603
7.584
7.569
7.566
7.563
7.504
7.501
7.485
7.471
7.467
7.260
6.017
5.484
5.479
5.178
3.639
1.999

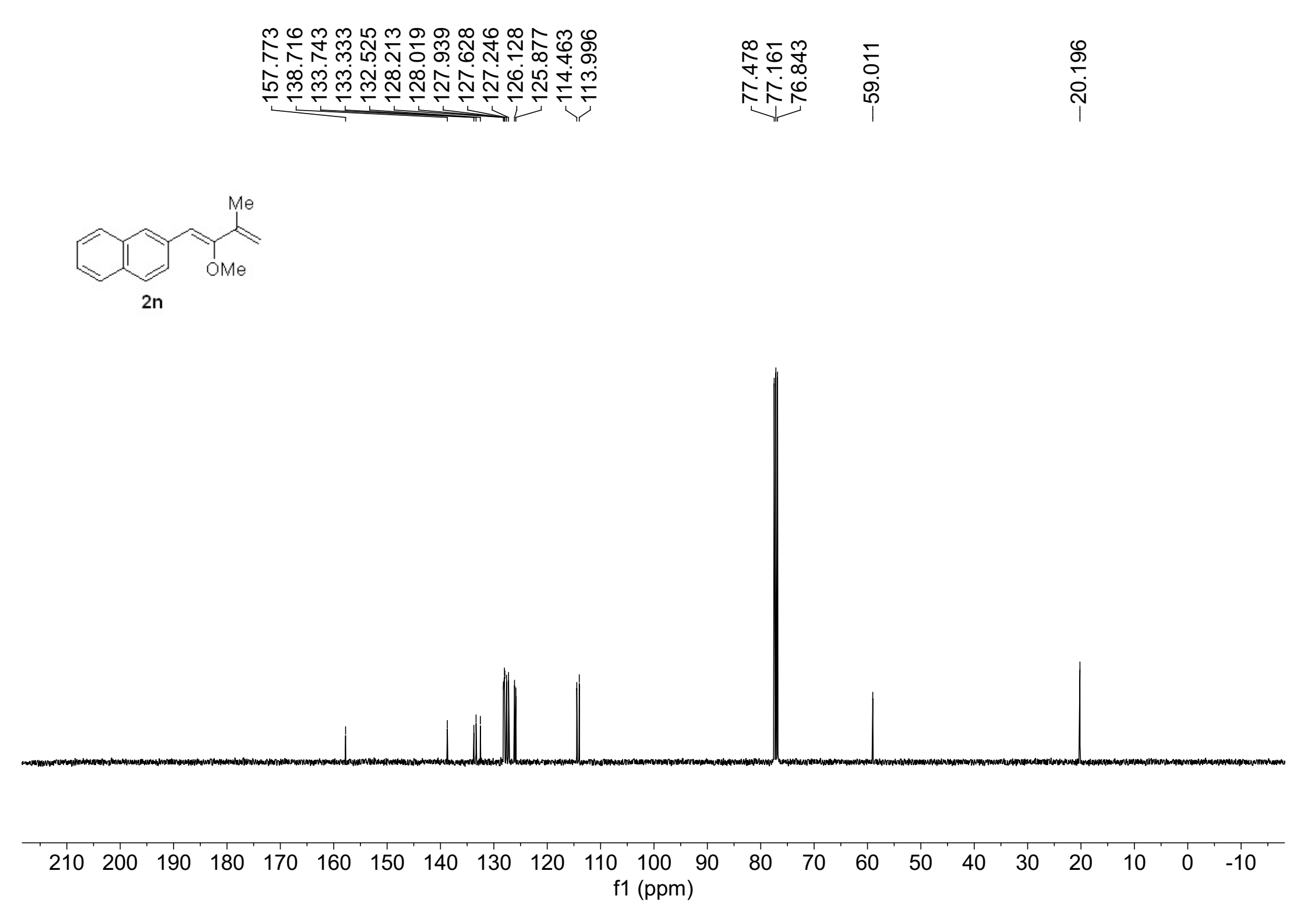

O
Ph
Me
MeO

2m


4.16
1.92
1.14
2.18
0.94
0.95
1.00
2.92
2.93
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


196.352
159.634
140.244
138.622
138.072
135.449
132.311
130.583
130.065
128.684
128.370
115.908
112.692
77.477
77.160
76.843
58.931
20.163
O
Ph
Me
MeO
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.075
7.848
7.844
7.807
7.786
7.463
7.458
7.455
7.447
7.439
7.436
7.432
7.260
6.157
5.489
5.485
5.136
3.647
2.031
Me
OMe
2n
1.00
4.19
2.07
1.00
1.00
1.00
3.12
3.05
f1 (ppm)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133.743
133.333
132.525
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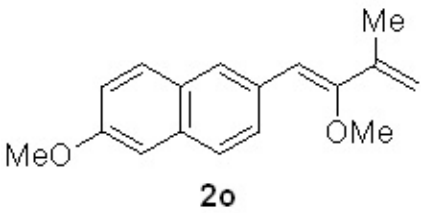
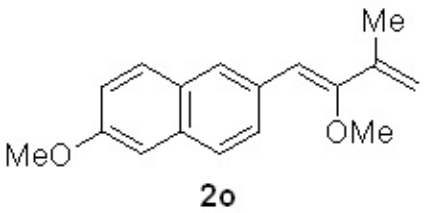
128.019
127.939
127.628
127.246
126.128
125.877
114.463
113.996
77.478
77.161
76.843
59.011
20.196
Me
OMe
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
OMe
MeO

2o

8.011
7.832
7.829
7.817
7.815
7.723
7.708
7.702
7.687
7.260
7.137
7.133
7.123
7.119
7.110
7.106
6.125
5.462
5.459
5.109
3.925
3.639
2.019
1.00
1.06
2.22
2.18
1.08
1.06
1.05
3.06
3.05
3.18
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
-0.5
f1 (ppm)



2o

157.854
157.071
138.718
133.650
131.160
129.771
129.194
127.941
127.793
126.804
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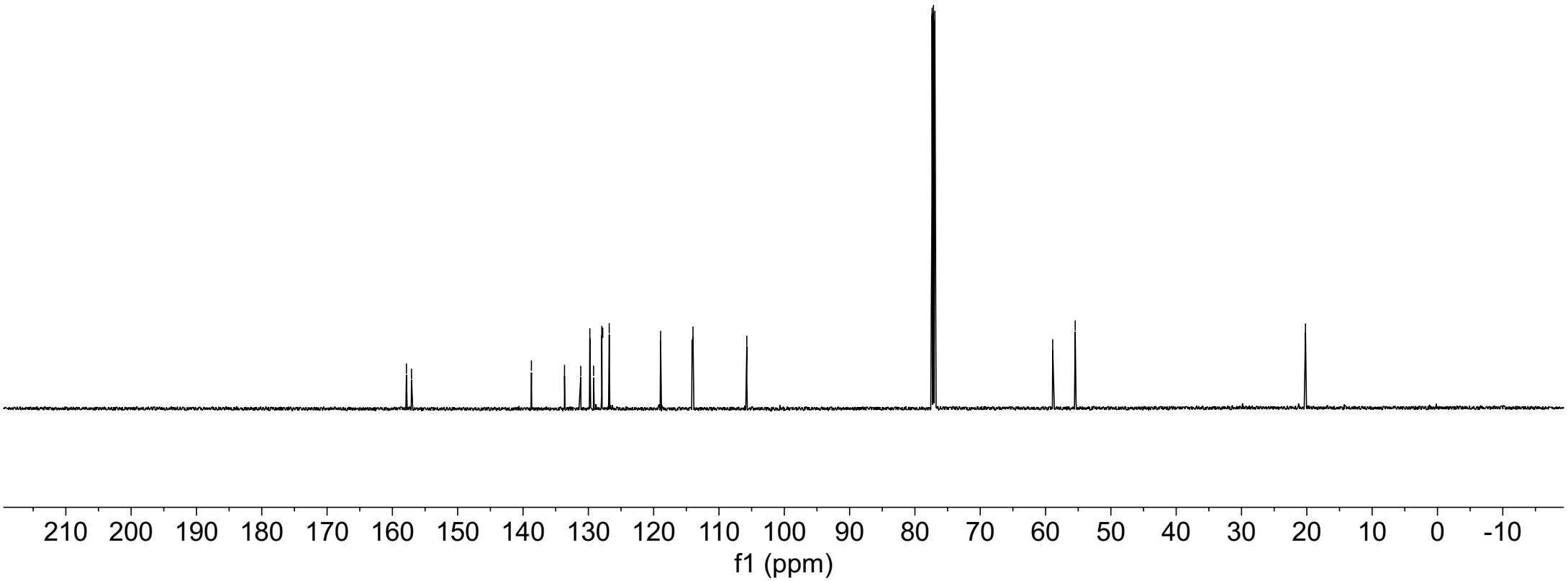
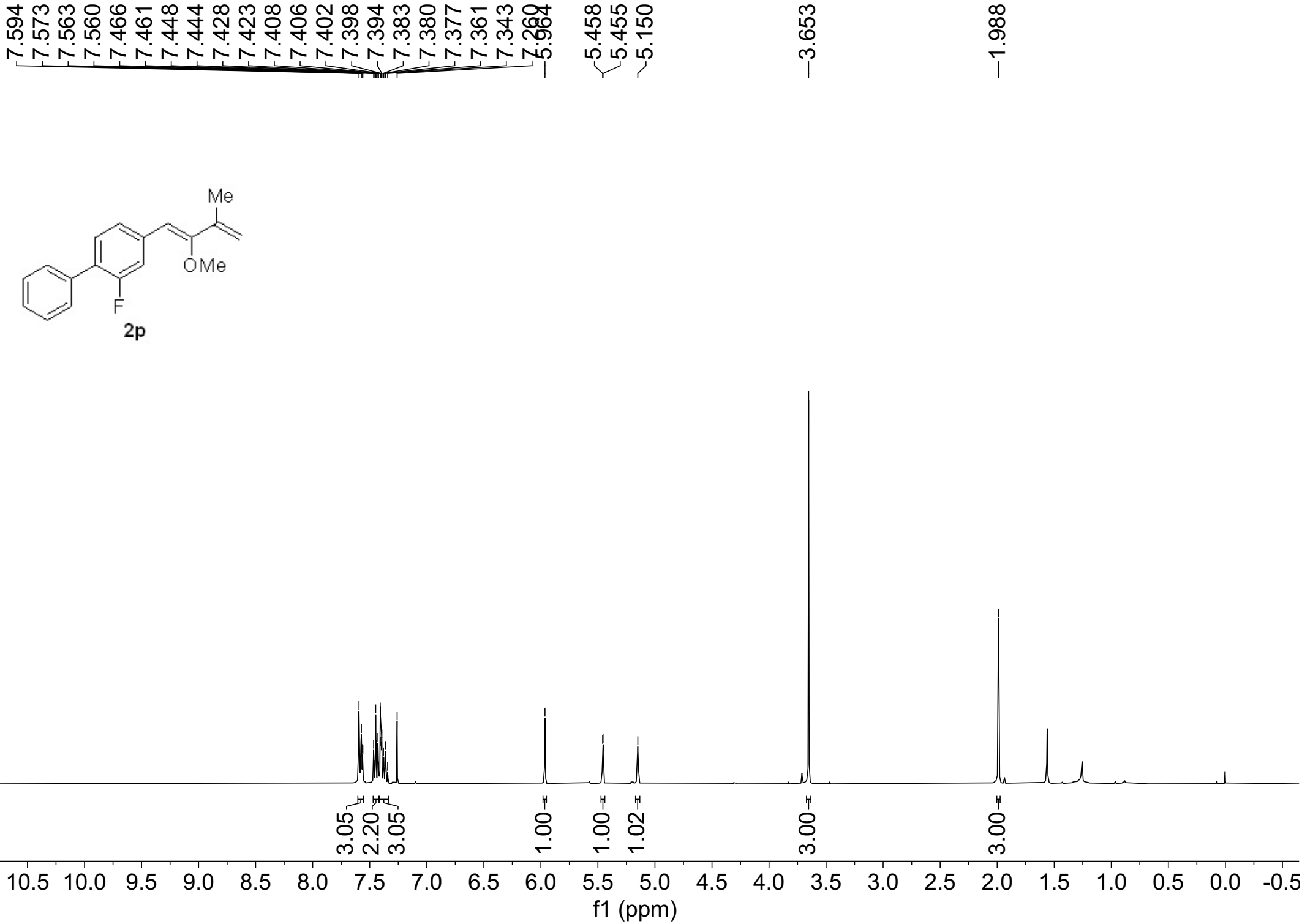
114.126
113.983
105.740
77.372
77.160
76.949
58.905
55.461
20.206

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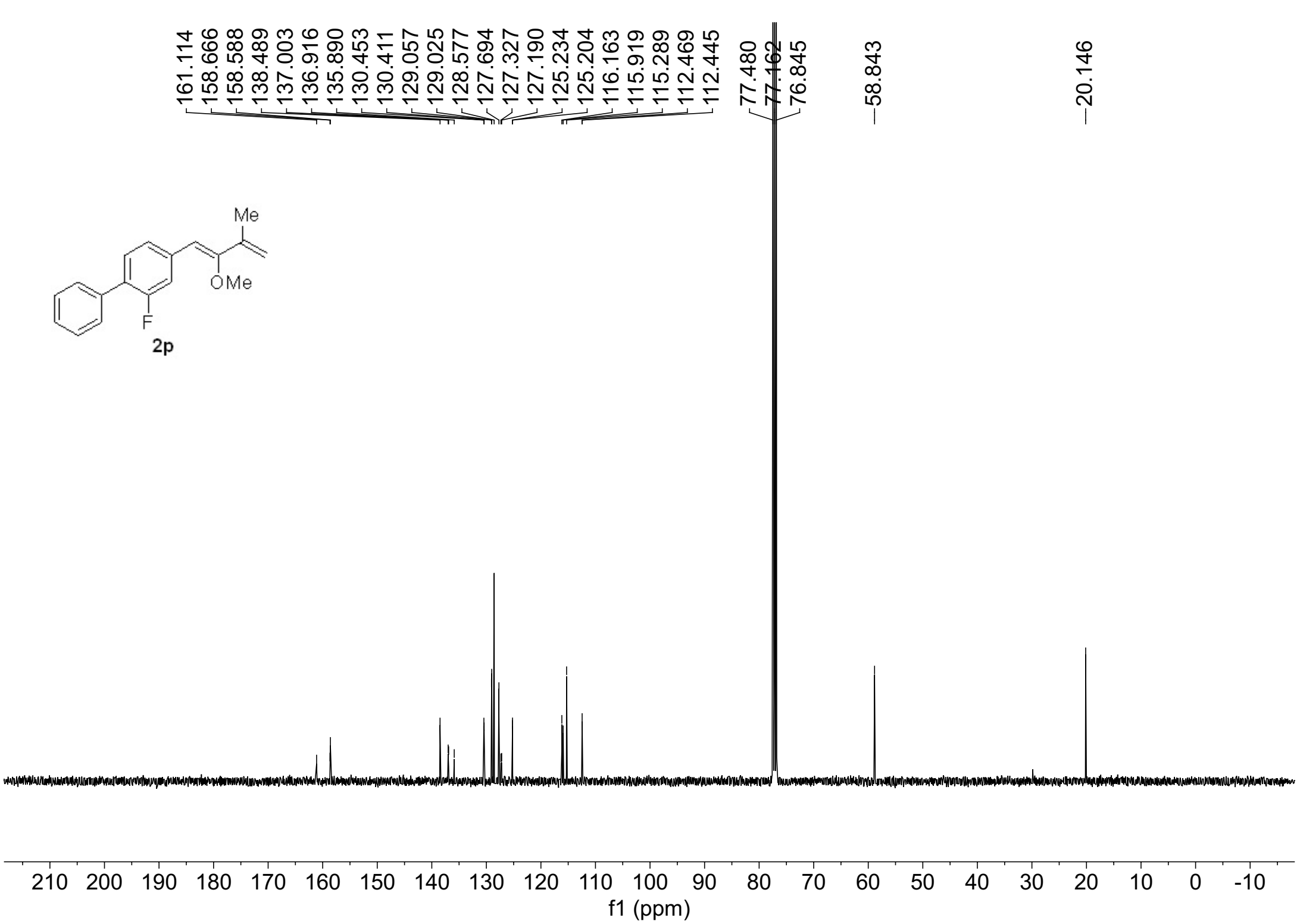
7.573
7.563
7.560
7.466
7.461
7.448
7.444
7.428
7.423
7.408
7.406
7.402
7.398
7.394
7.383
7.380
7.377
7.361
7.343
7.260
5.964
5.458
5.455
5.150
3.653
1.988
Me
OMe
F
2p
3.05
2.20
3.05
1.00
1.00
1.02
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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158.666
158.588
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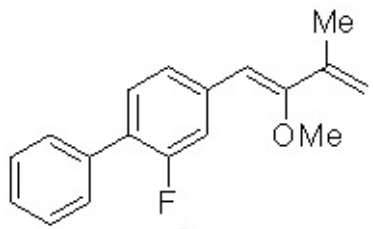
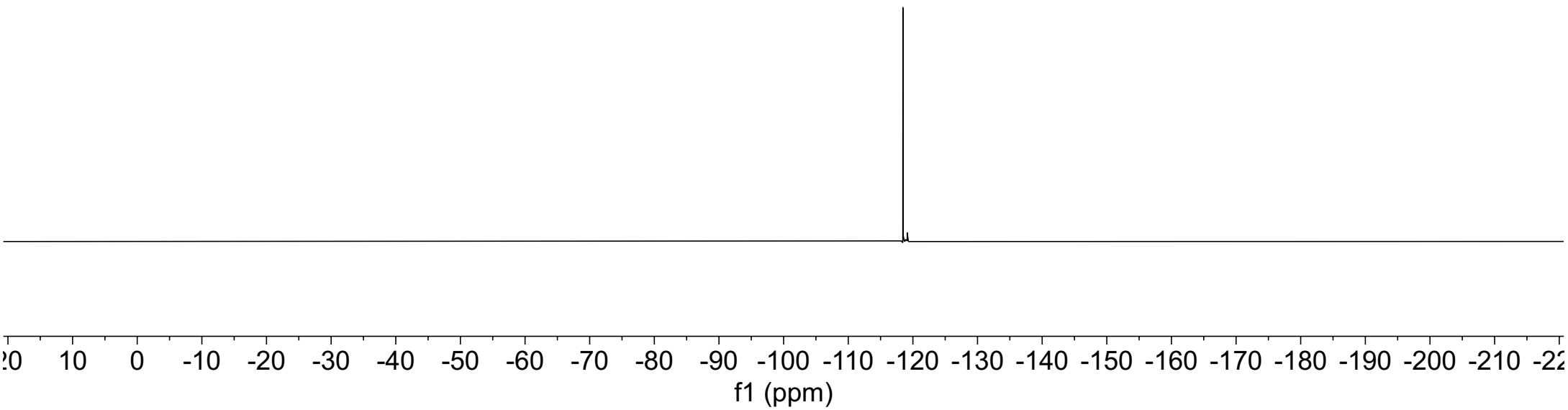
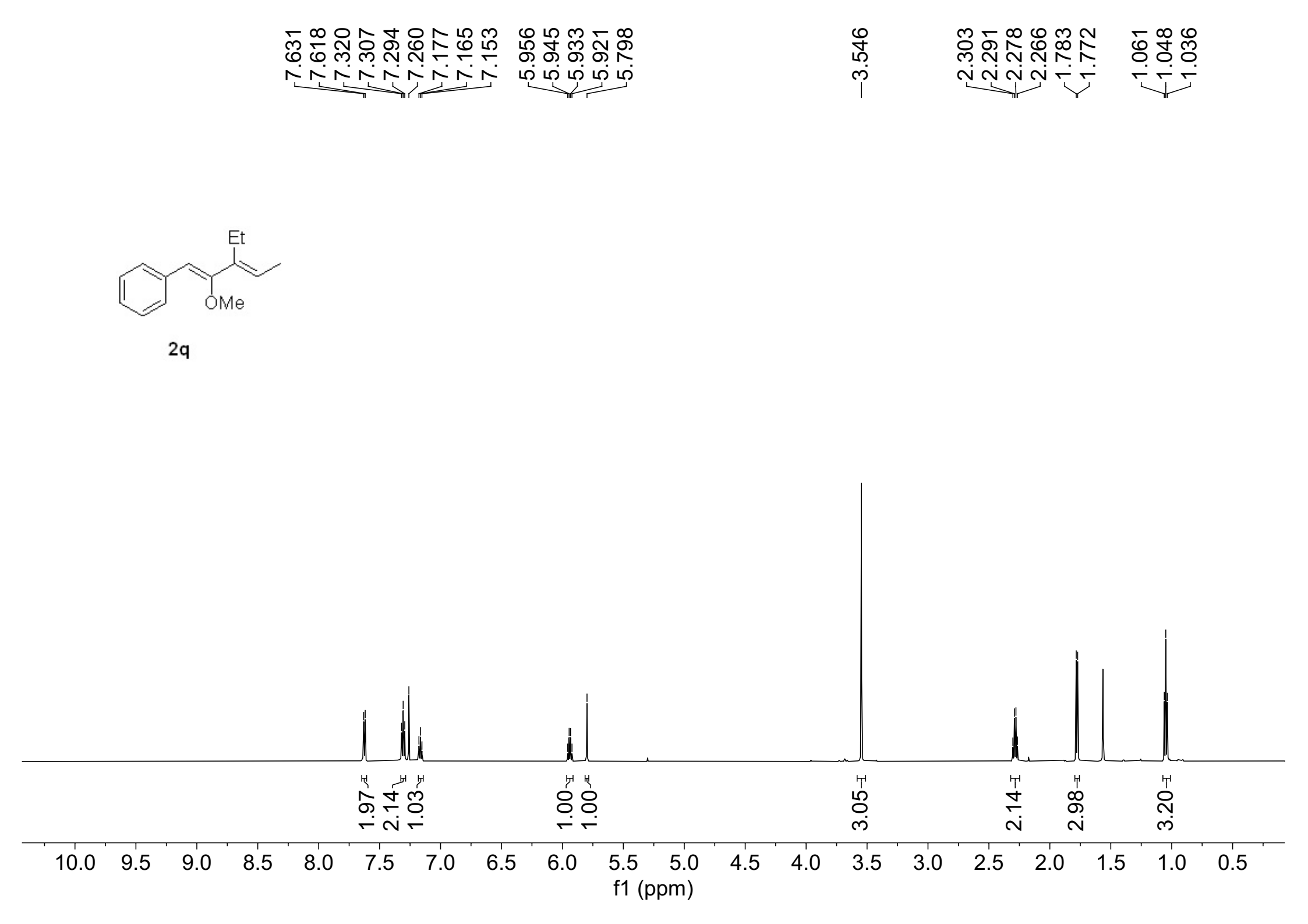
135.890
130.453
130.411
129.057
129.025
128.577
127.694
127.327
127.190
125.234
125.204
116.163
115.919
115.289
112.469
112.445
77.480
77.162
76.845
58.843
20.146
Me
OMe
F
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

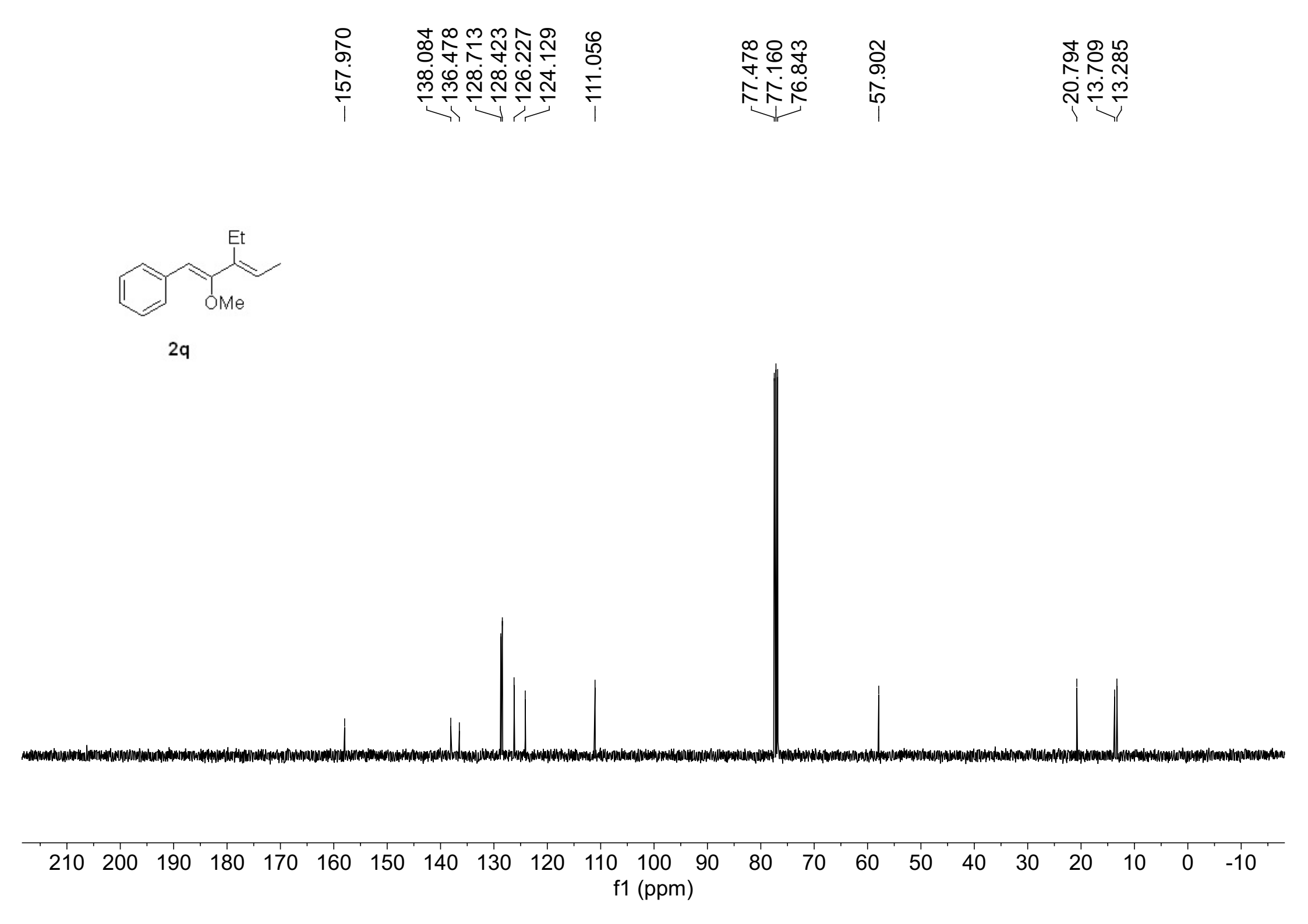

Me
OMe
F

2p

-118.460


10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.631
7.618
7.320
7.307
7.294
7.260
7.177
7.165
7.153
5.956
5.945
5.933
5.921
5.798
3.546
2.303
2.291
2.278
2.266
1.783
1.772
1.061
1.048
1.036
Et
OMe
2q
1.97
2.14
1.03
1.00
1.00
3.05
2.14
2.98
3.20
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
f1 (ppm)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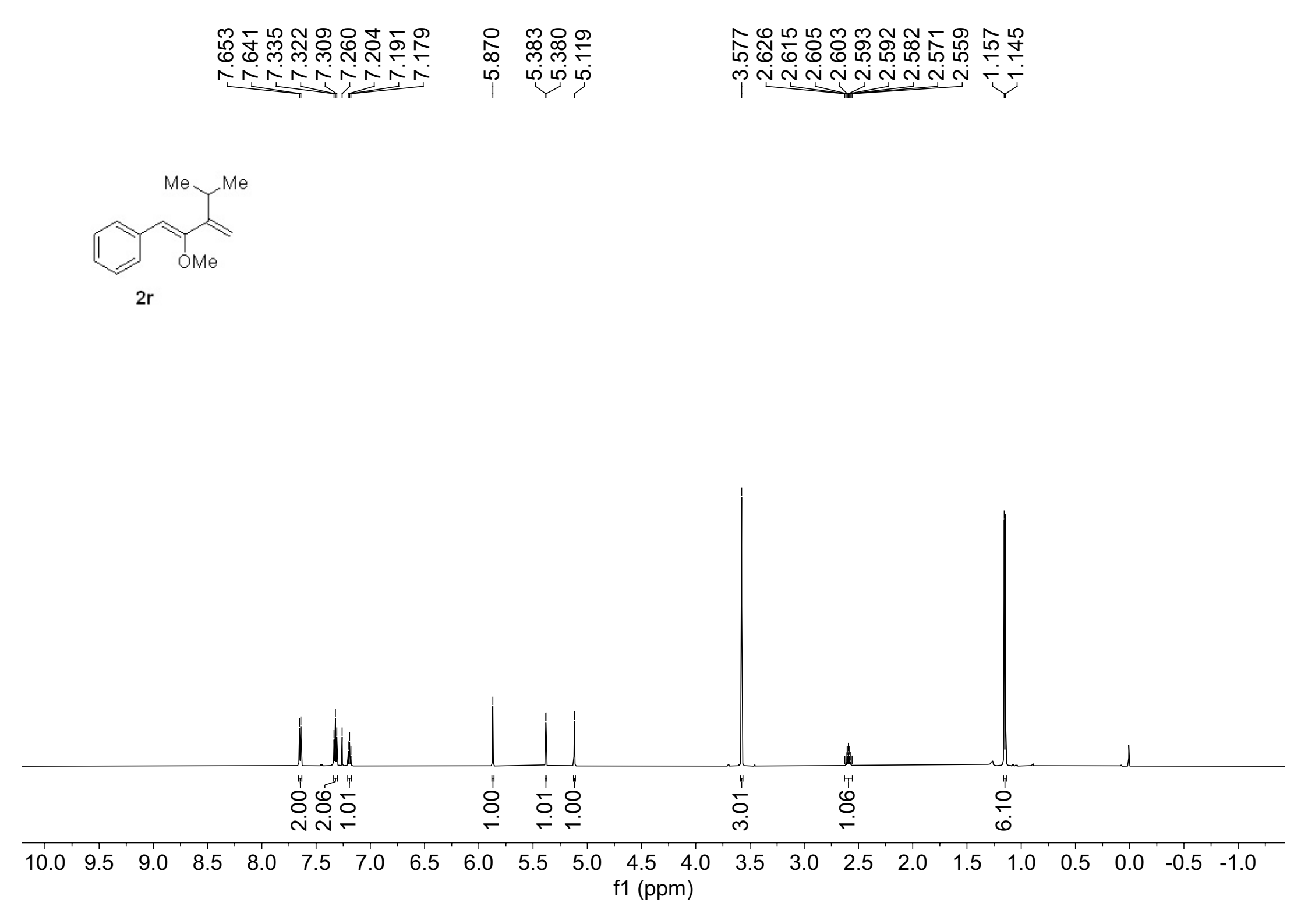
138.084
136.478
128.713
128.423
126.227
124.129
111.056
77.478
77.160
76.843
57.902
20.794
13.709
13.285
Et
OMe
2q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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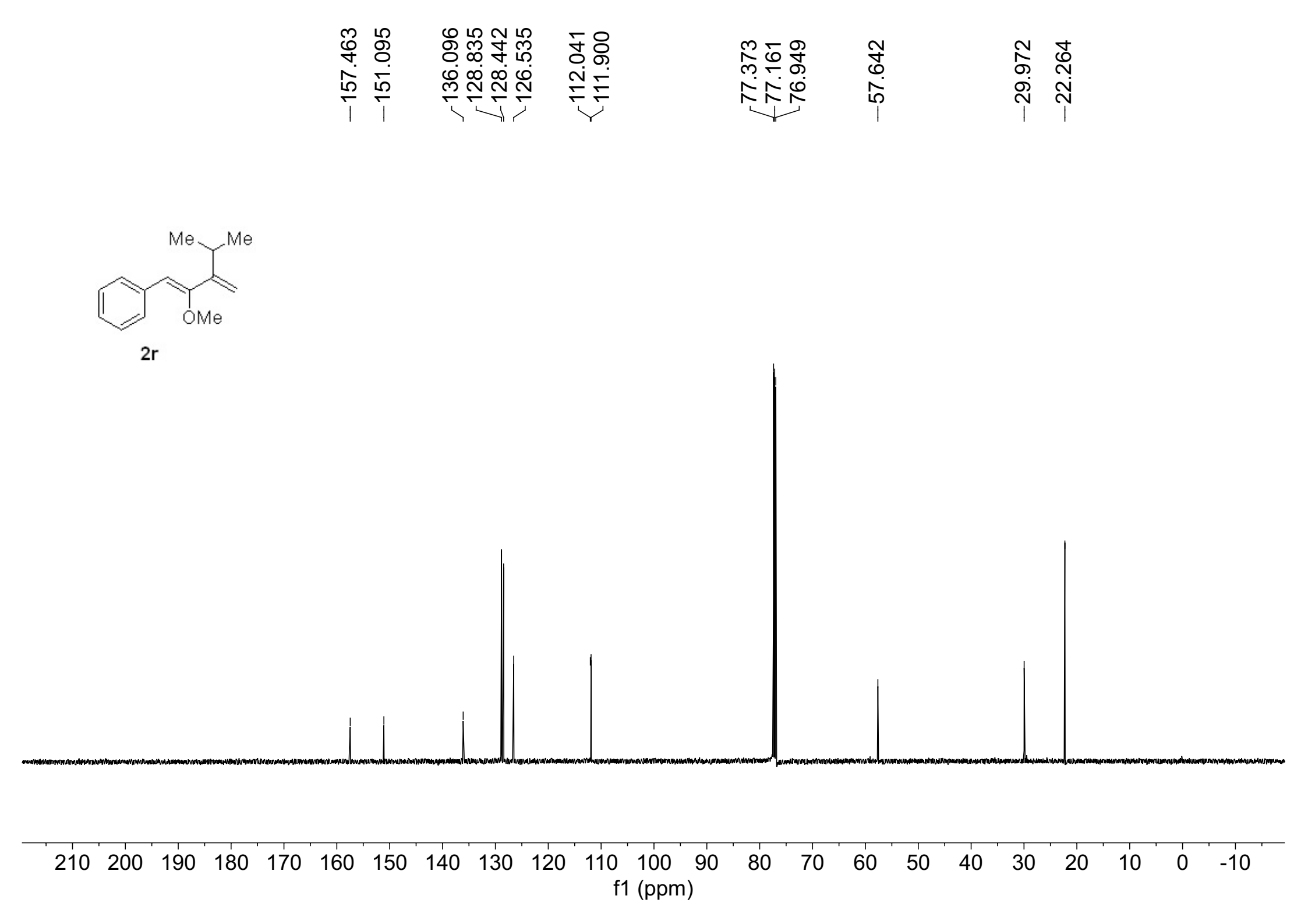
7.641
7.335
7.322
7.309
7.260
7.204
7.191
7.179
5.870
5.383
5.380
5.119
3.577
2.626
2.615
2.605
2.603
2.593
2.592
2.582
2.571
2.559
1.157
1.145
Me
Me
OMe
2r
2.00
2.06
1.01
1.00
1.01
1.00
3.01
1.06
6.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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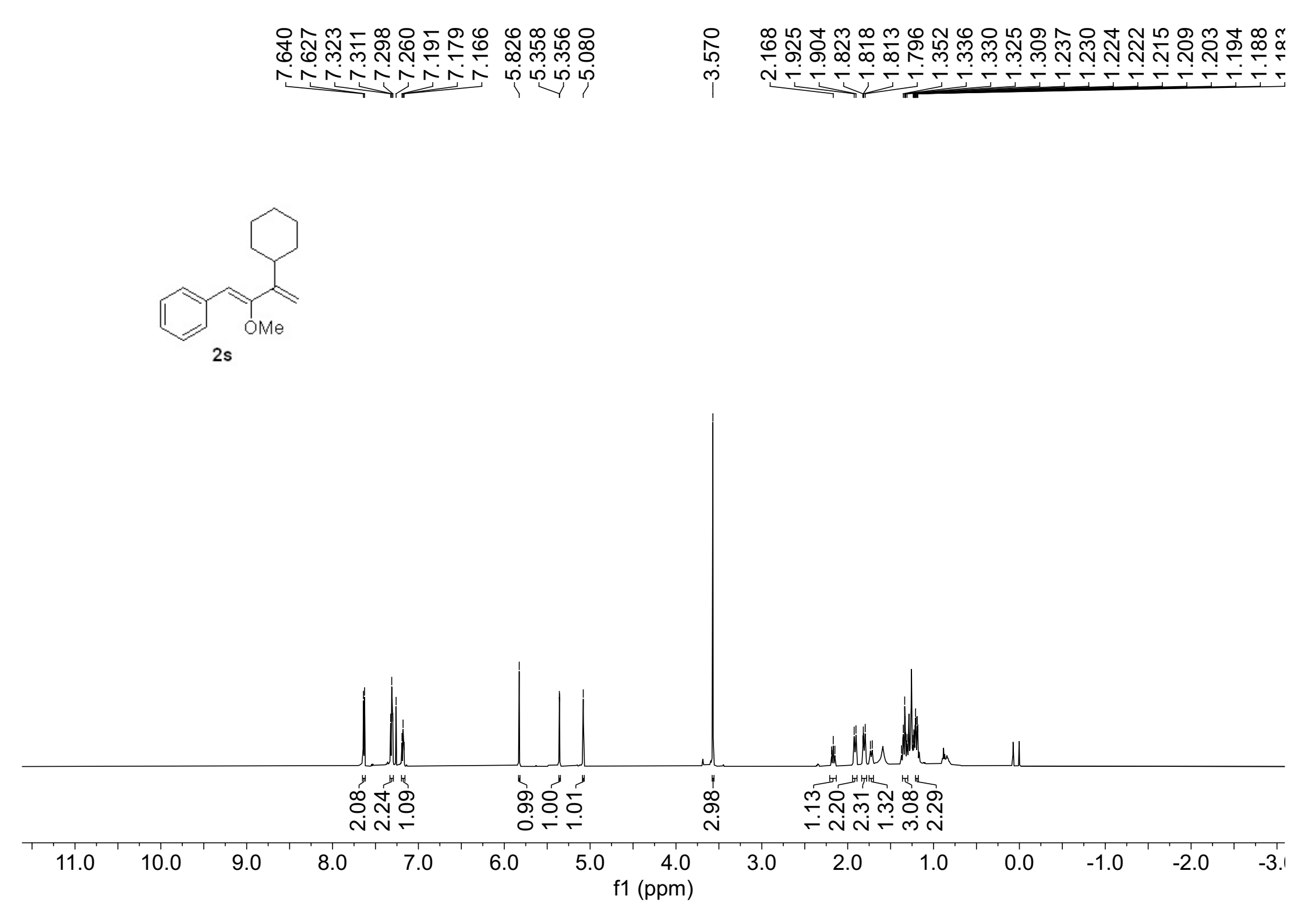
136.096
128.835
128.442
126.535
112.041
111.900
77.373
77.161
76.949
57.642
29.972
22.264
Me
Me
OMe
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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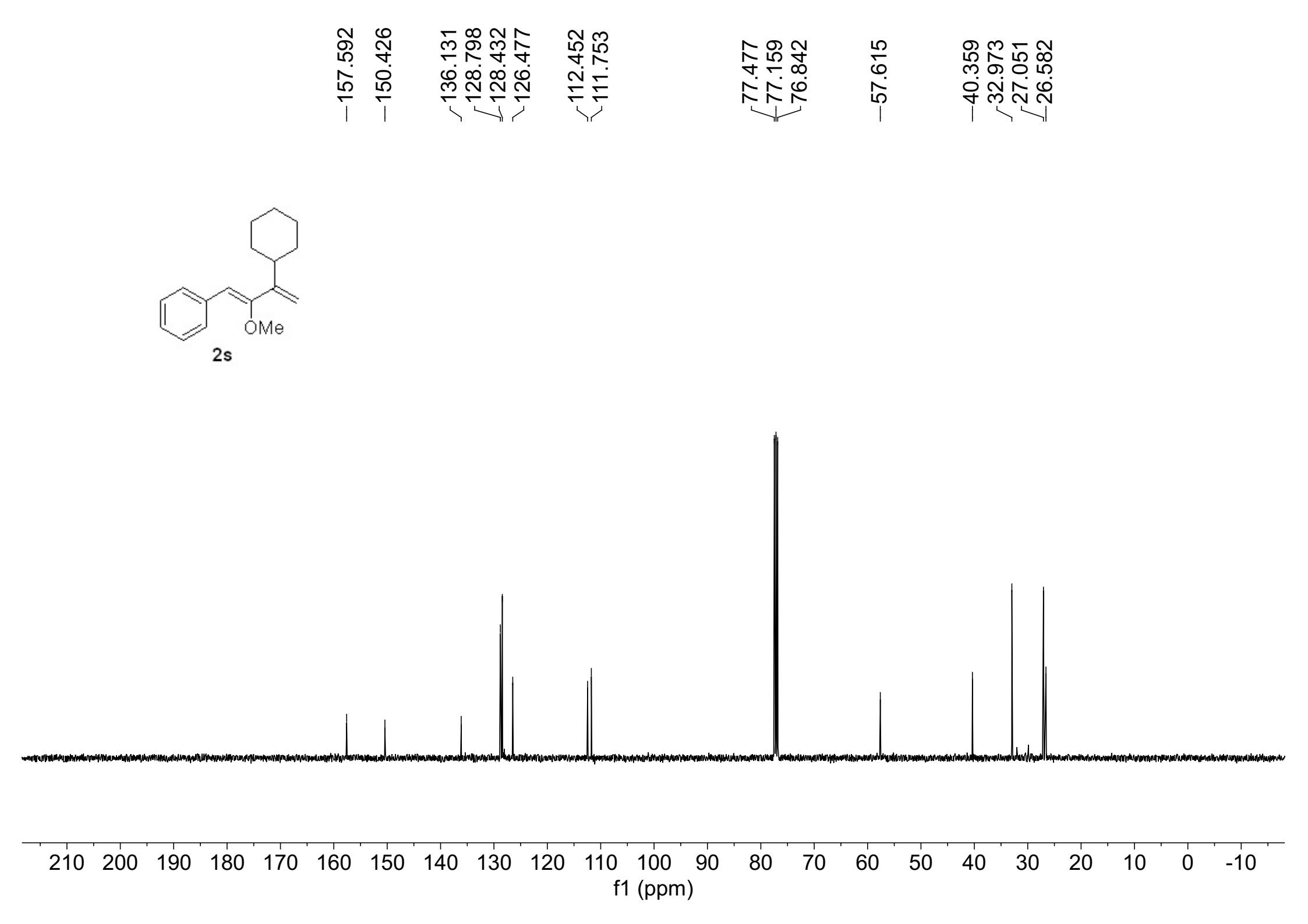
7.627
7.323
7.311
7.298
7.260
7.191
7.179
7.166
5.826
5.358
5.356
5.080
3.570
2.168
1.925
1.904
1.823
1.818
1.813
1.796
1.352
1.336
1.330
1.325
1.309
1.237
1.230
1.224
1.222
1.215
1.209
1.203
1.194
1.188
OMe
2s
2.08
2.24
1.09
0.99
1.00
1.01
2.98
1.13
2.20
2.31
1.32
3.08
2.29
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)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136.131
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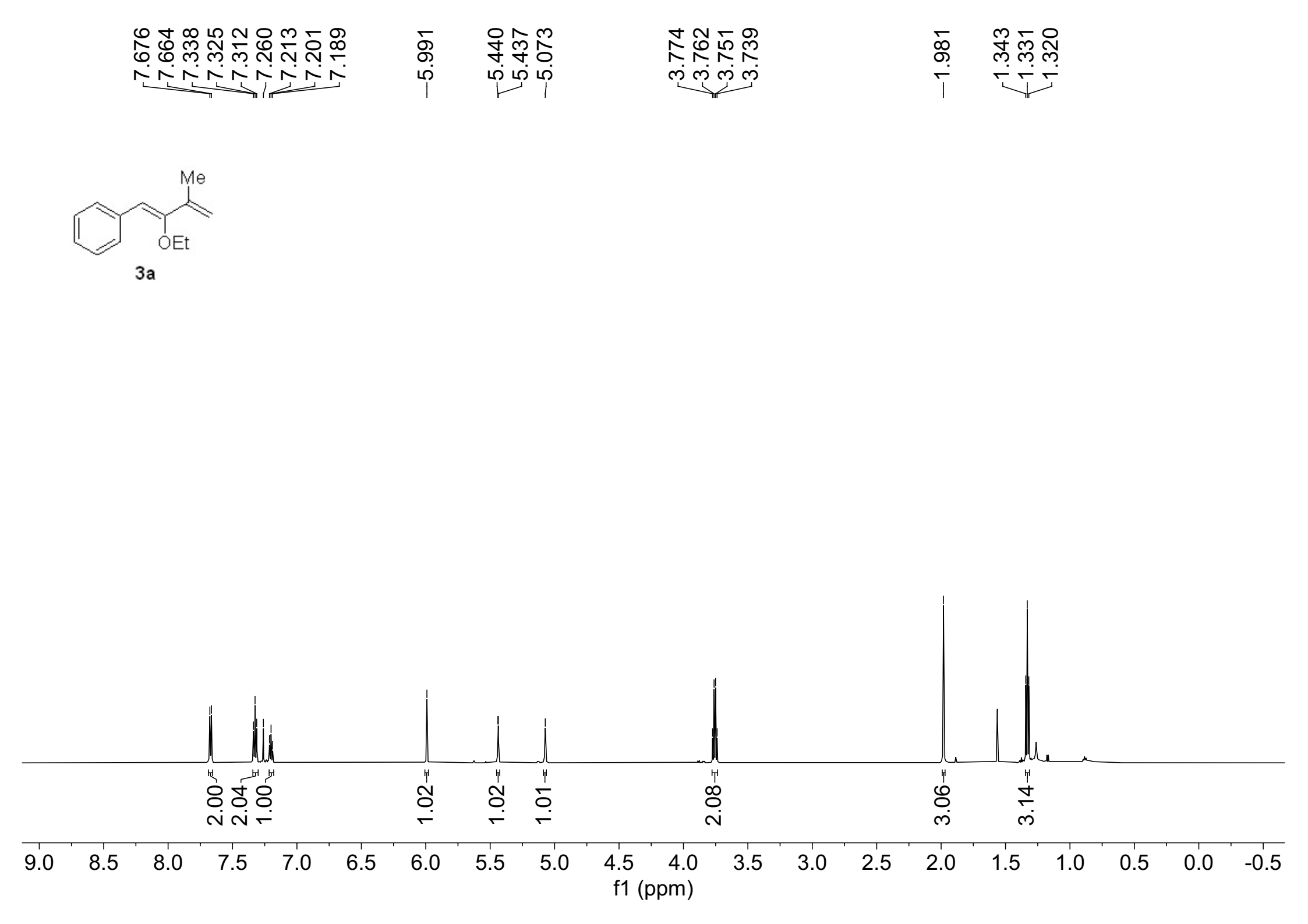
128.432
126.477
112.452
111.753
77.477
77.159
76.842
57.615
40.359
32.973
27.051
26.582
OMe
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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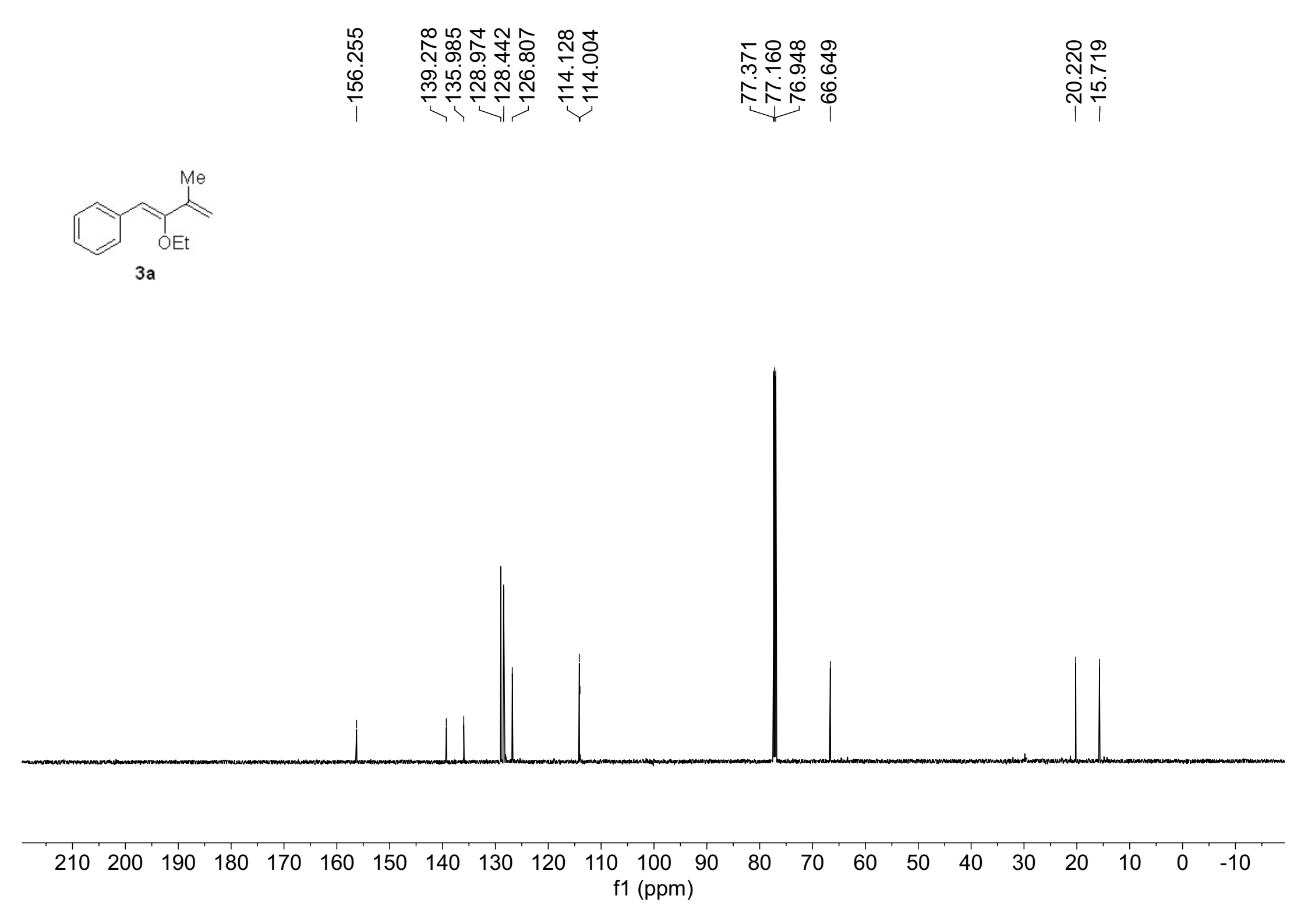
7.325
7.312
7.260
7.213
7.201
7.189
5.991
5.440
5.437
5.073
3.774
3.762
3.751
3.739
1.981
1.343
1.331
1.320
Me
OEt
3a
2.00
2.04
1.00
1.02
1.02
1.01
2.08
3.06
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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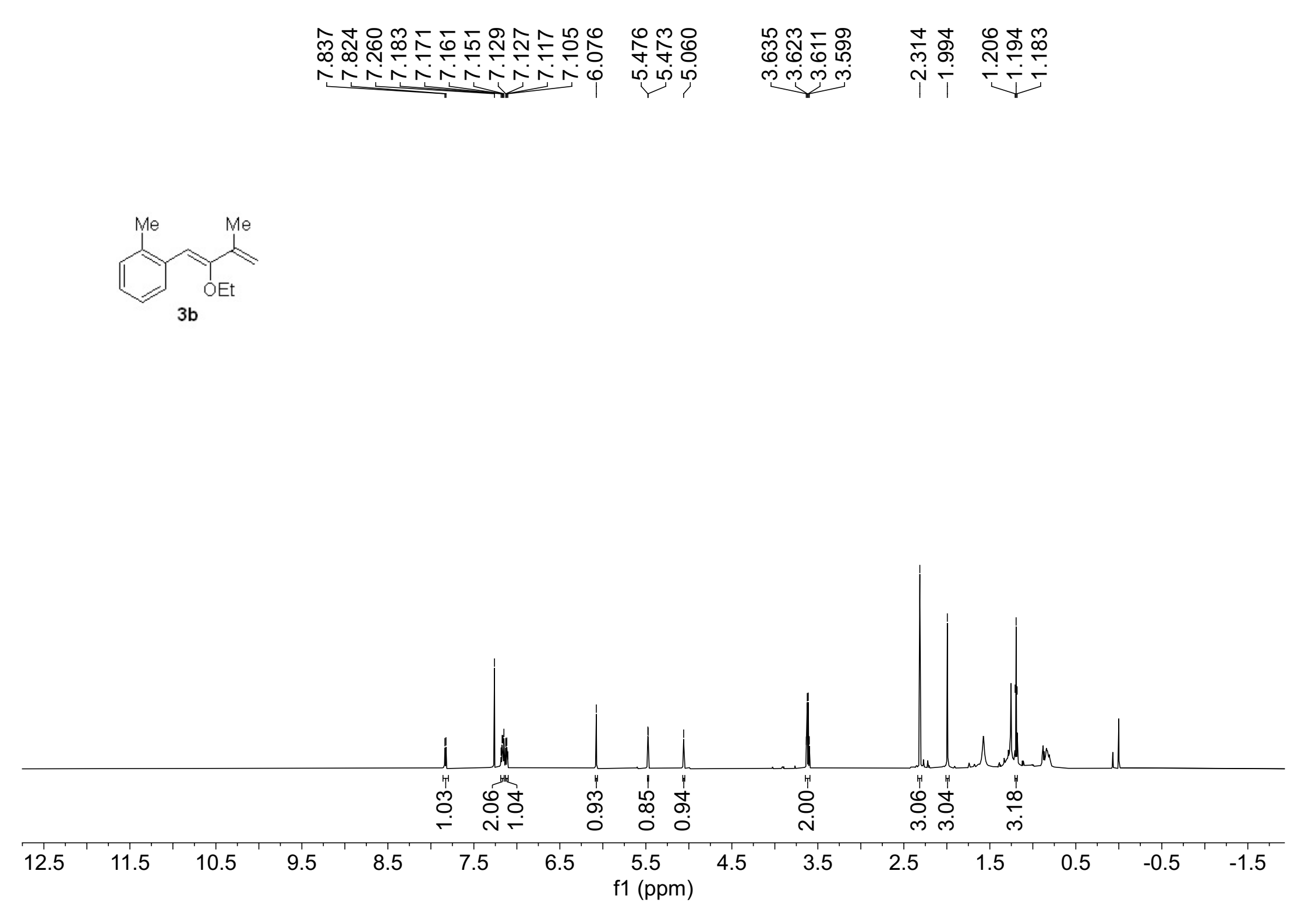
128.974
128.442
126.807
114.128
114.004
77.371
77.160
76.948
66.649
20.220
15.719
Me
OEt
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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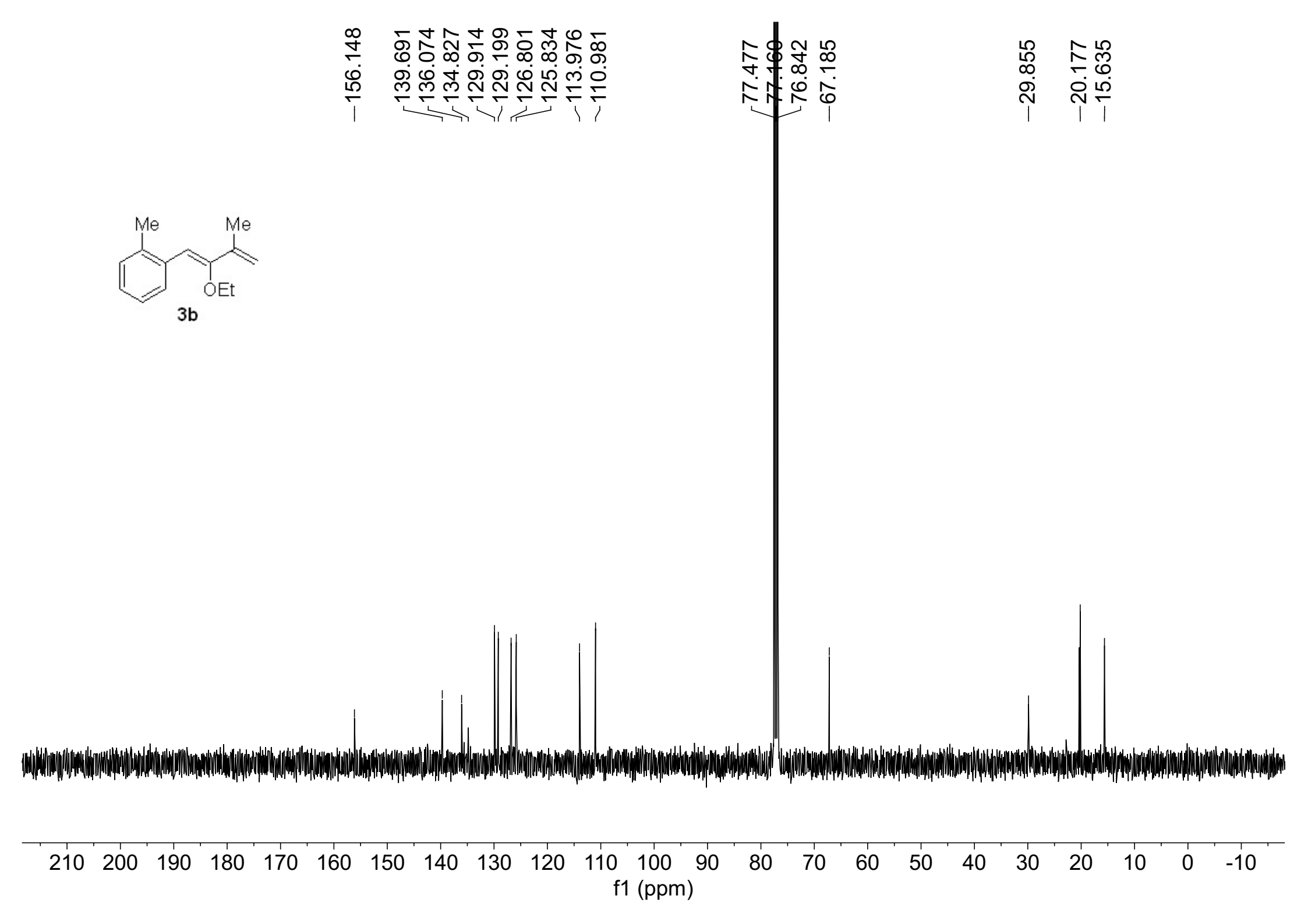
7.171
7.161
7.151
7.129
7.127
7.117
7.105
6.076
5.476
5.473
5.060
3.635
3.623
3.611
3.599
2.314
1.994
1.206
1.194
1.183
Me
Me
OEt
3b
1.03
2.06
1.04
0.93
0.85
0.94
2.00
3.06
3.04
3.18
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)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129.914
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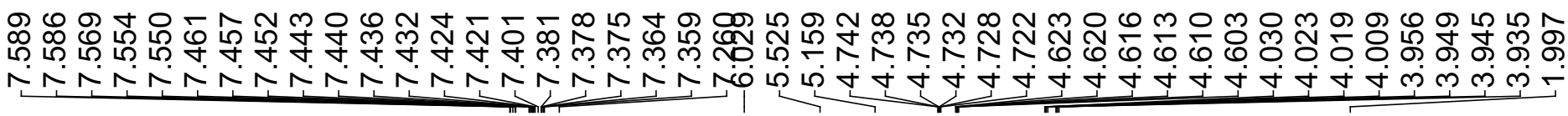
126.801
125.834
113.976
110.981
77.477
77.160
76.842
67.185
29.855
20.177
15.635
Me
Me
OEt
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.457
7.452
7.443
7.440
7.436
7.432
7.424
7.421
7.401
7.381
7.378
7.375
7.364
7.359
7.260
6.029
5.525
5.159
4.742
4.738
4.735
4.732
4.728
4.722
4.623
4.620
4.616
4.613
4.610
4.603
4.030
4.023
4.019
4.009
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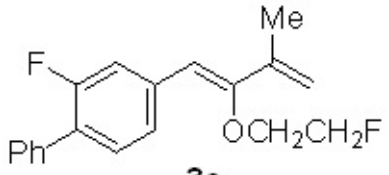
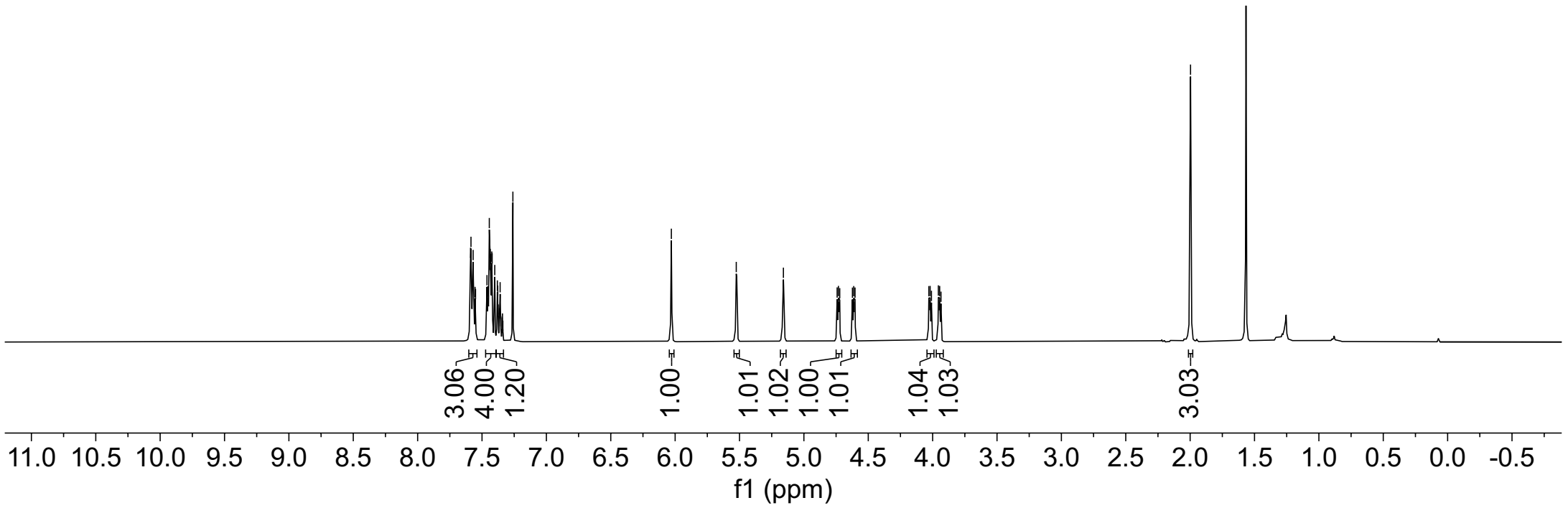
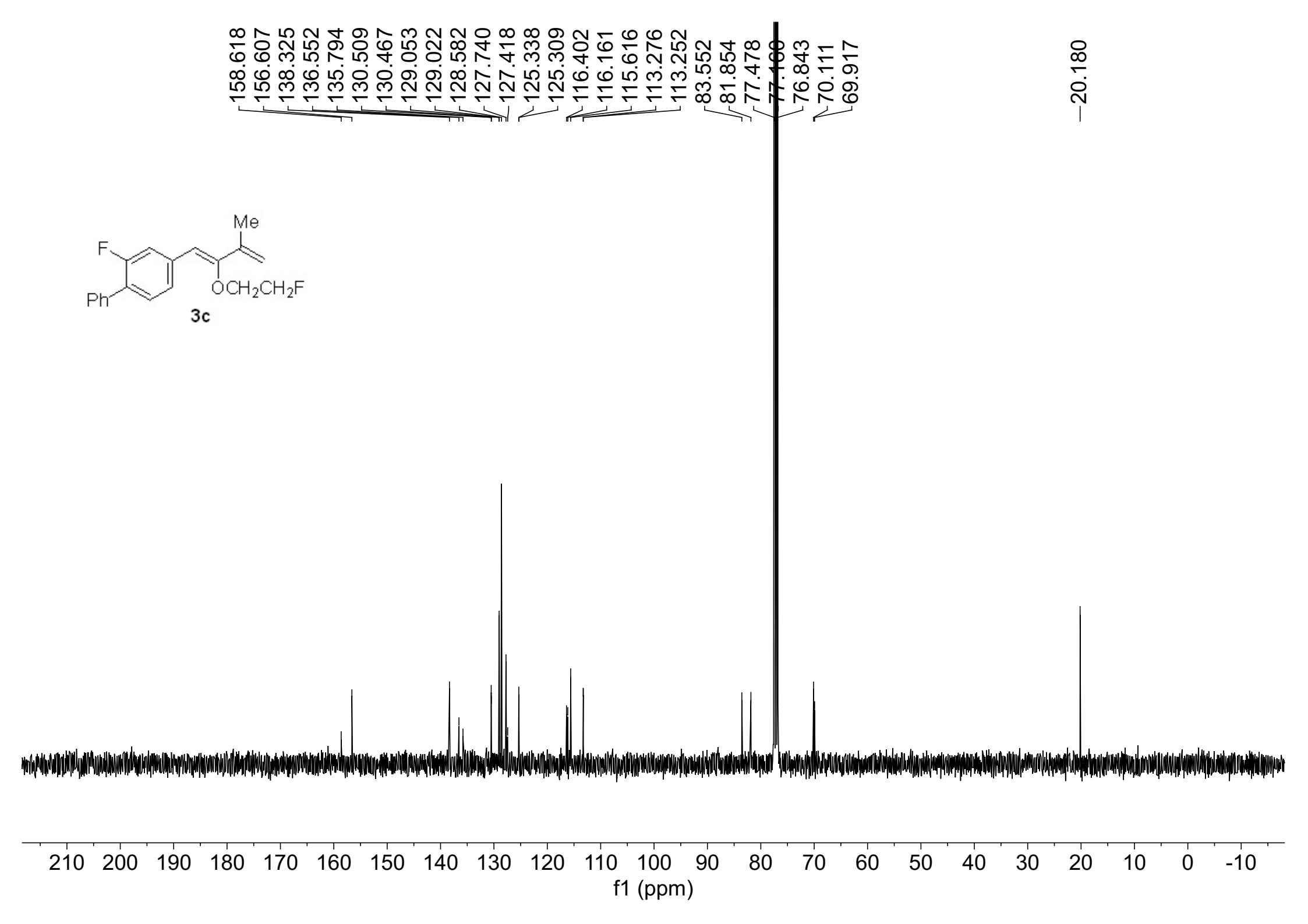
3.949
3.945
3.935
1.997


Me
F
Ph
OCH2CH2F

3c


3.06
4.00
1.20
1.00
1.01
1.02
1.00
1.01
1.04
1.03
3.03
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 -0.5
f1 (ppm)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130.467
129.053
129.022
128.582
127.740
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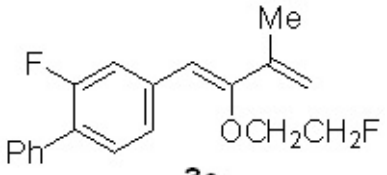
125.309
116.402
116.161
115.616
113.276
113.252
83.552
81.854
77.478
77.100
76.843
70.111
69.917
20.180
Me
F
Ph
OCH2CH2F
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3c

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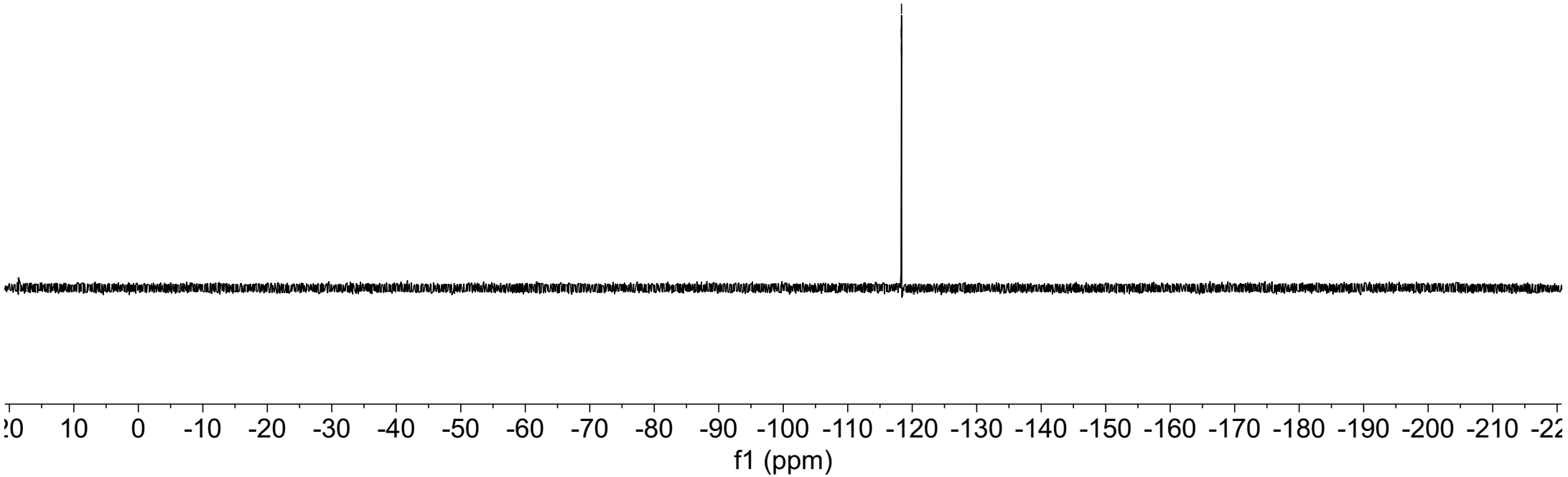
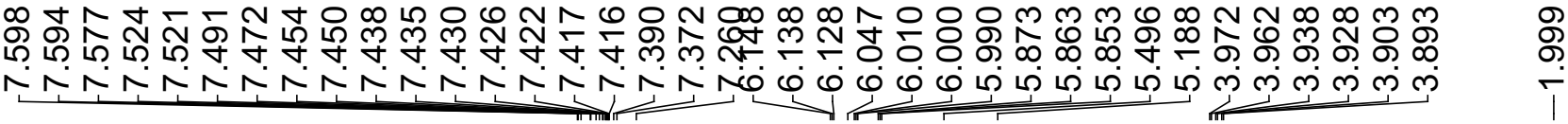
118.325
118.339
118.360

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7.450
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7.435
7.430
7.426
7.422
7.417
7.416
7.390
7.372
6.138
6.128
6.047
6.010
6.000
5.990
5.873
5.863
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5.496
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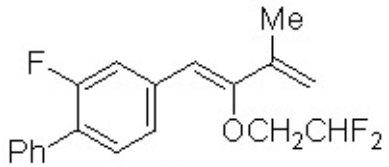
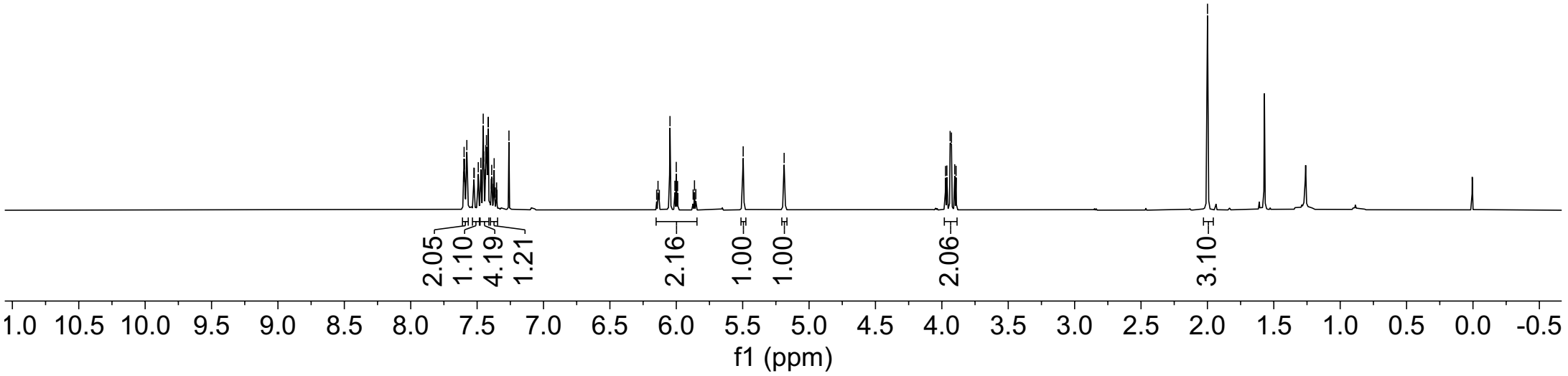
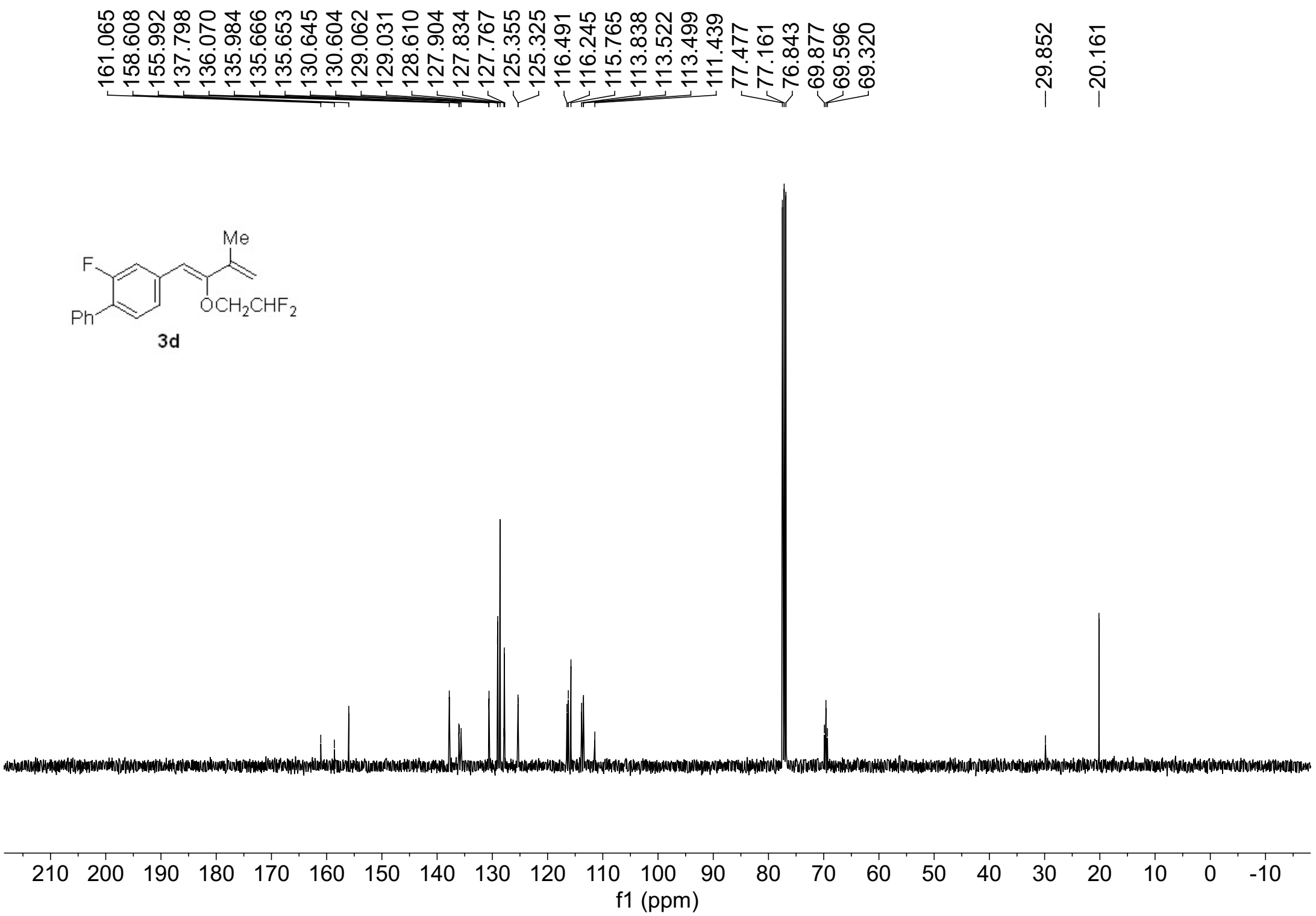
3.962
3.938
3.928
3.903
3.893
1.999


Me
F
Ph
OCH2CHF2

3d


2.05
1.10
4.19
1.21
2.16
1.00
1.00
2.06
3.10
1.0 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 -0.5
f1 (ppm)


161.065
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135.653
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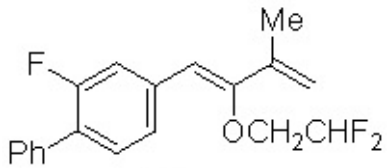
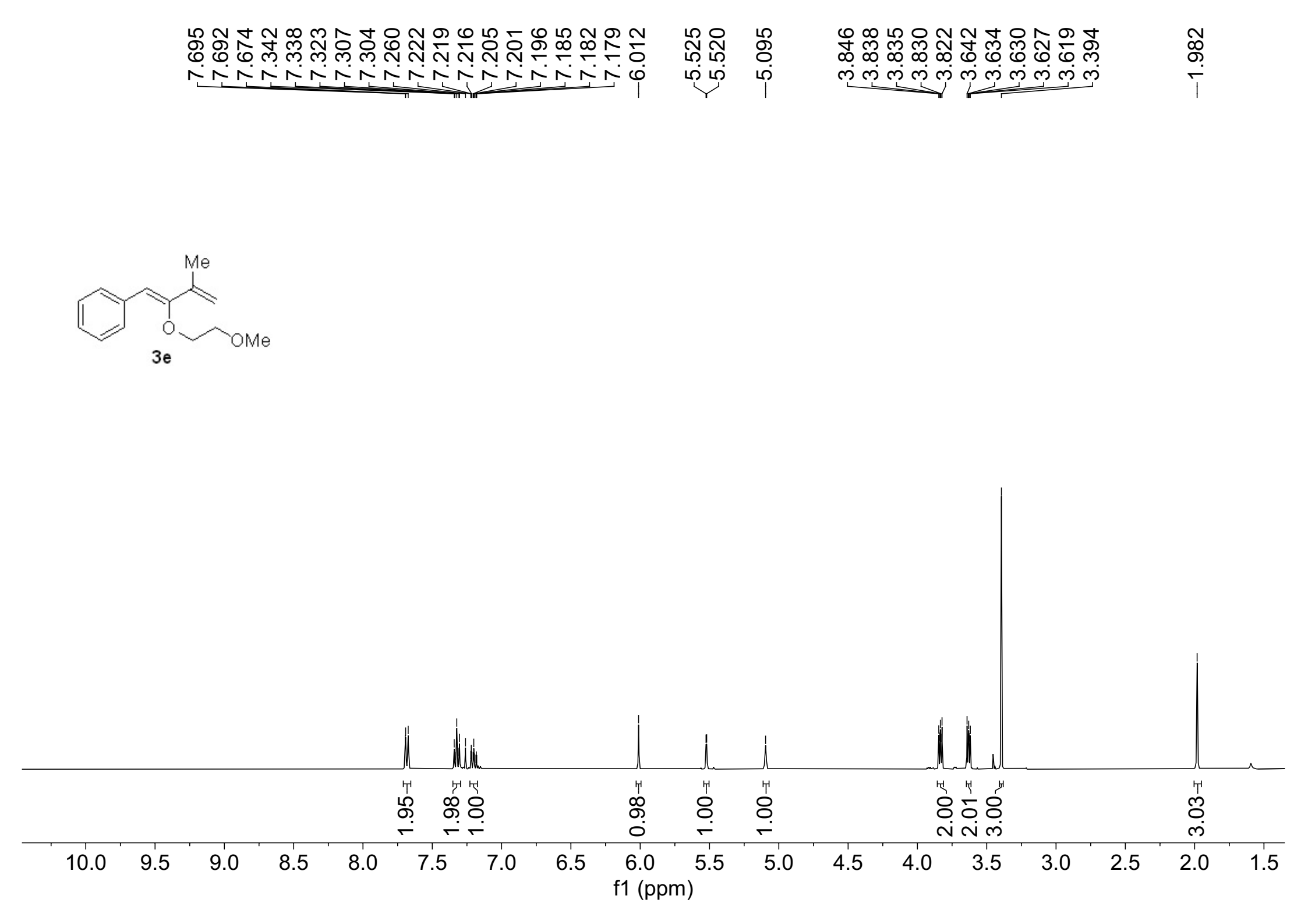
130.604
129.062
129.031
128.610
127.904
127.834
127.767
125.355
125.325
116.491
116.245
115.765
113.838
113.522
113.499
111.439
77.477
77.161
76.843
69.877
69.596
69.320
29.852
20.161
Me
F
Ph
OCH2CHF2
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
F
Ph
OCH2CHF2

3d

-118.077
-125.273
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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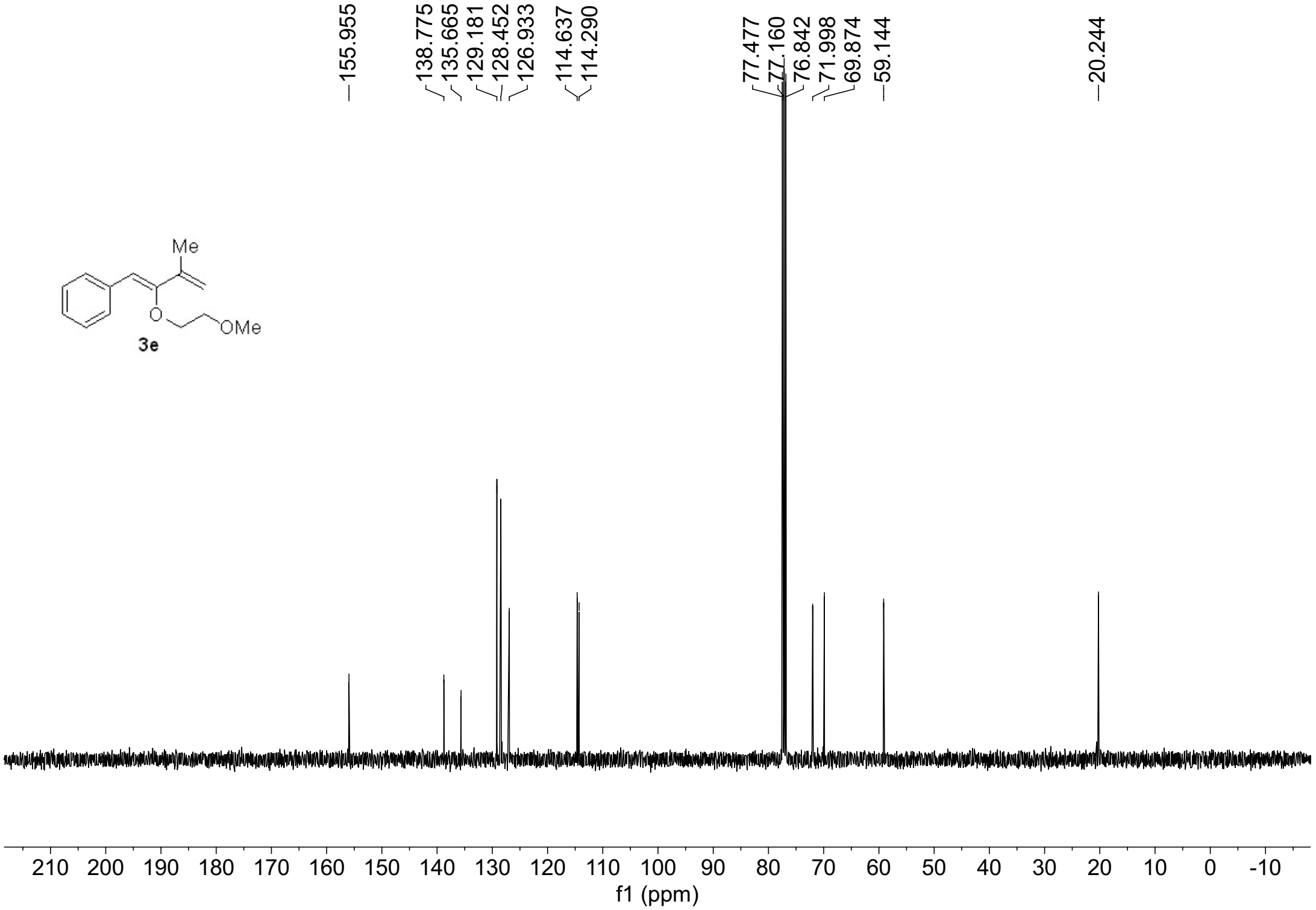
7.323
7.307
7.304
7.260
7.222
7.219
7.216
7.205
7.201
7.196
7.185
7.182
7.179
6.012
5.525
5.520
5.095
3.846
3.838
3.835
3.830
3.822
3.642
3.634
3.630
3.627
3.619
3.394
1.982
Me
O
OMe
3e
1.95
1.98
1.00
0.98
1.00
1.00
2.00
2.01
3.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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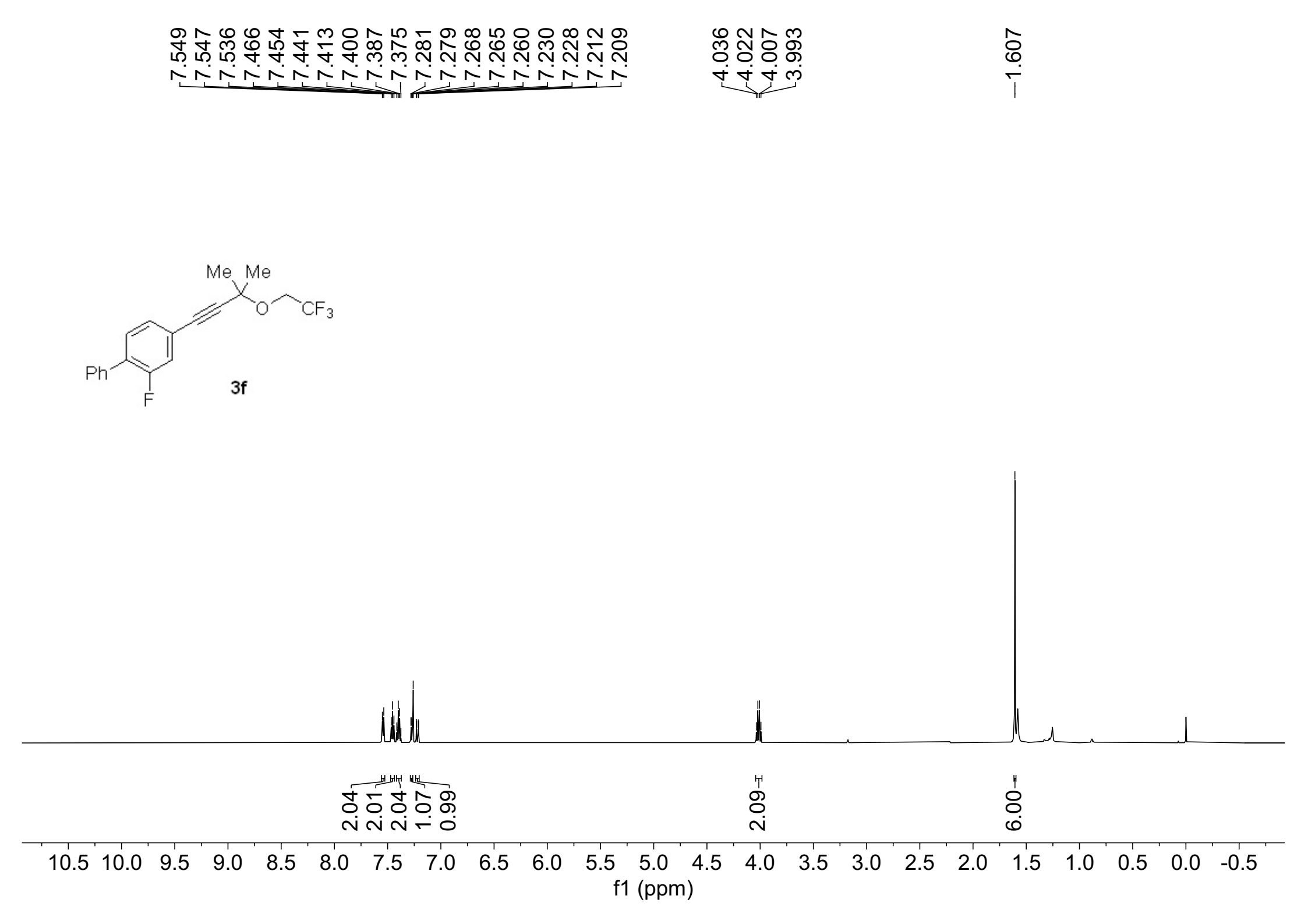
138.775
135.665
129.181
128.452
126.933
114.637
114.290
77.477
77.160
76.842
71.998
69.874
59.144
20.244
Me
O
OMe
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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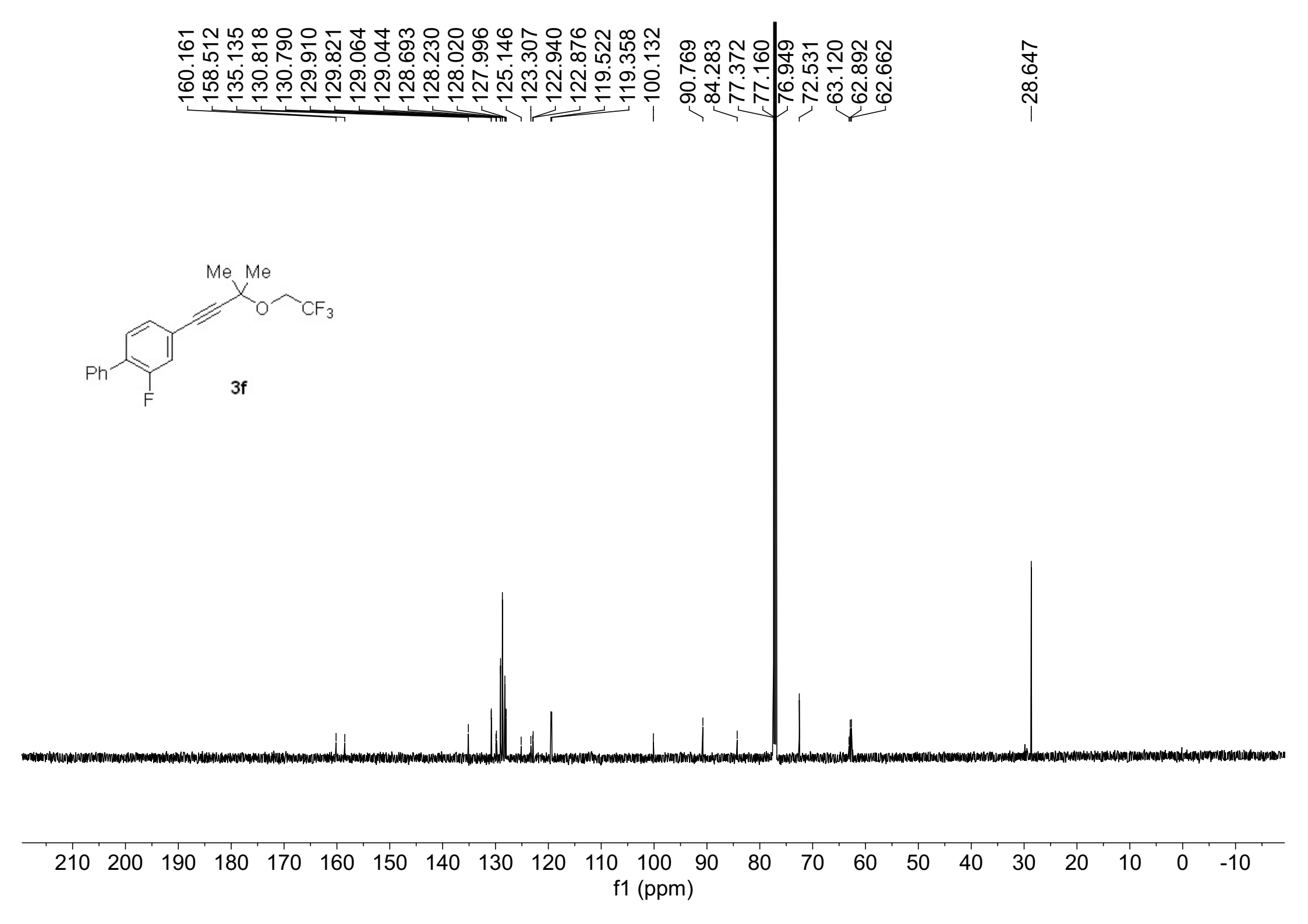
7.536
7.466
7.454
7.441
7.413
7.400
7.387
7.375
7.281
7.279
7.268
7.265
7.260
7.230
7.228
7.212
7.209
4.036
4.022
4.007
3.993
1.607
Me
Me
O
CF3
Ph
F
3f
2.04
2.01
2.04
1.07
0.99
2.09
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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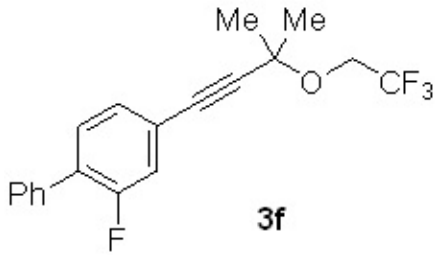
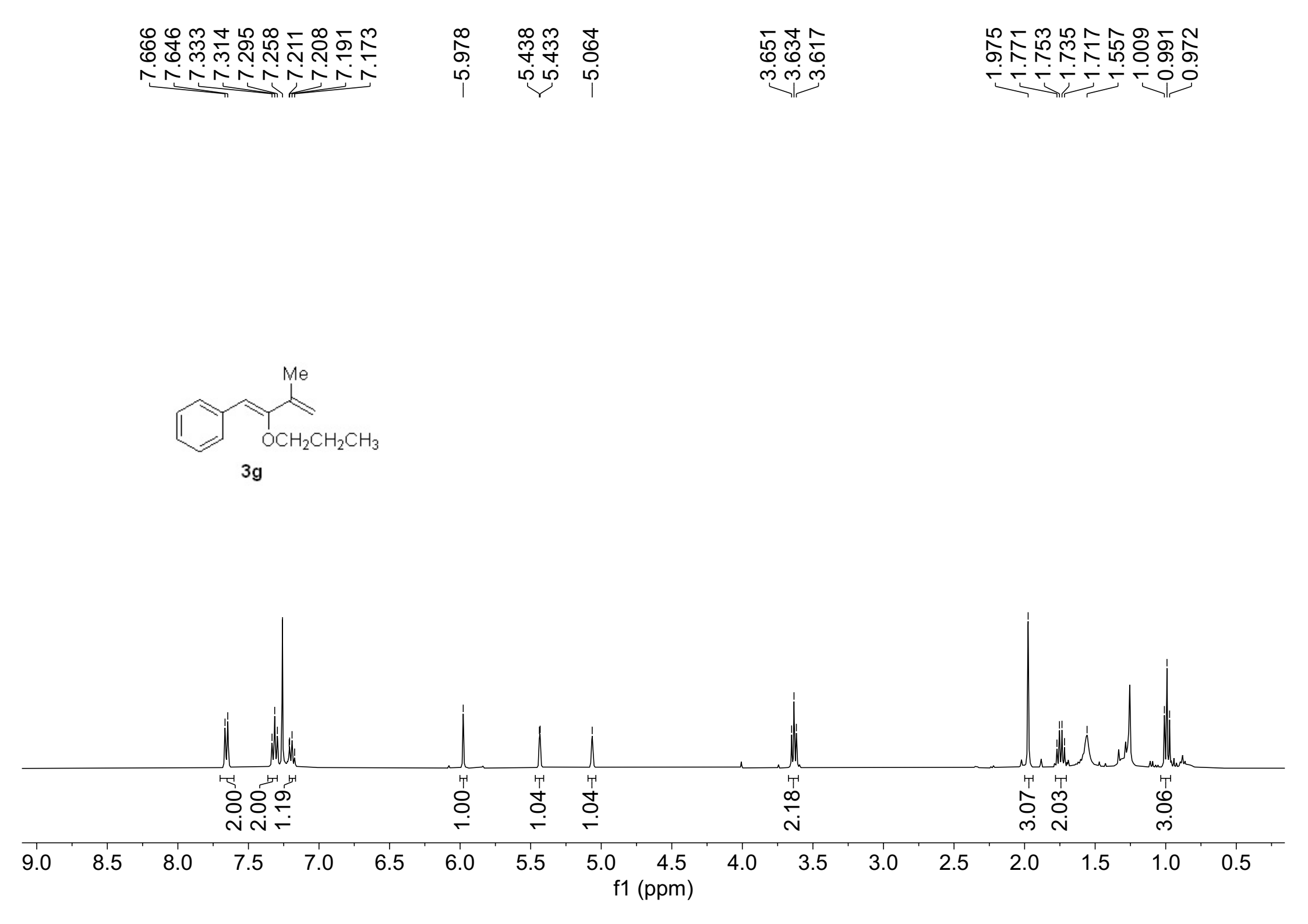
158.512
135.135
130.818
130.790
129.910
129.821
129.064
129.044
128.693
128.230
128.020
127.996
125.146
123.307
122.940
122.876
119.522
119.358
100.132
90.769
84.283
77.372
77.160
76.949
72.531
63.120
62.892
62.662
28.647
Me
Me
O
CF3
Ph
F
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
Me
O
CF3
Ph
F

3f

-74.141
-117.640
-117.657
-117.674
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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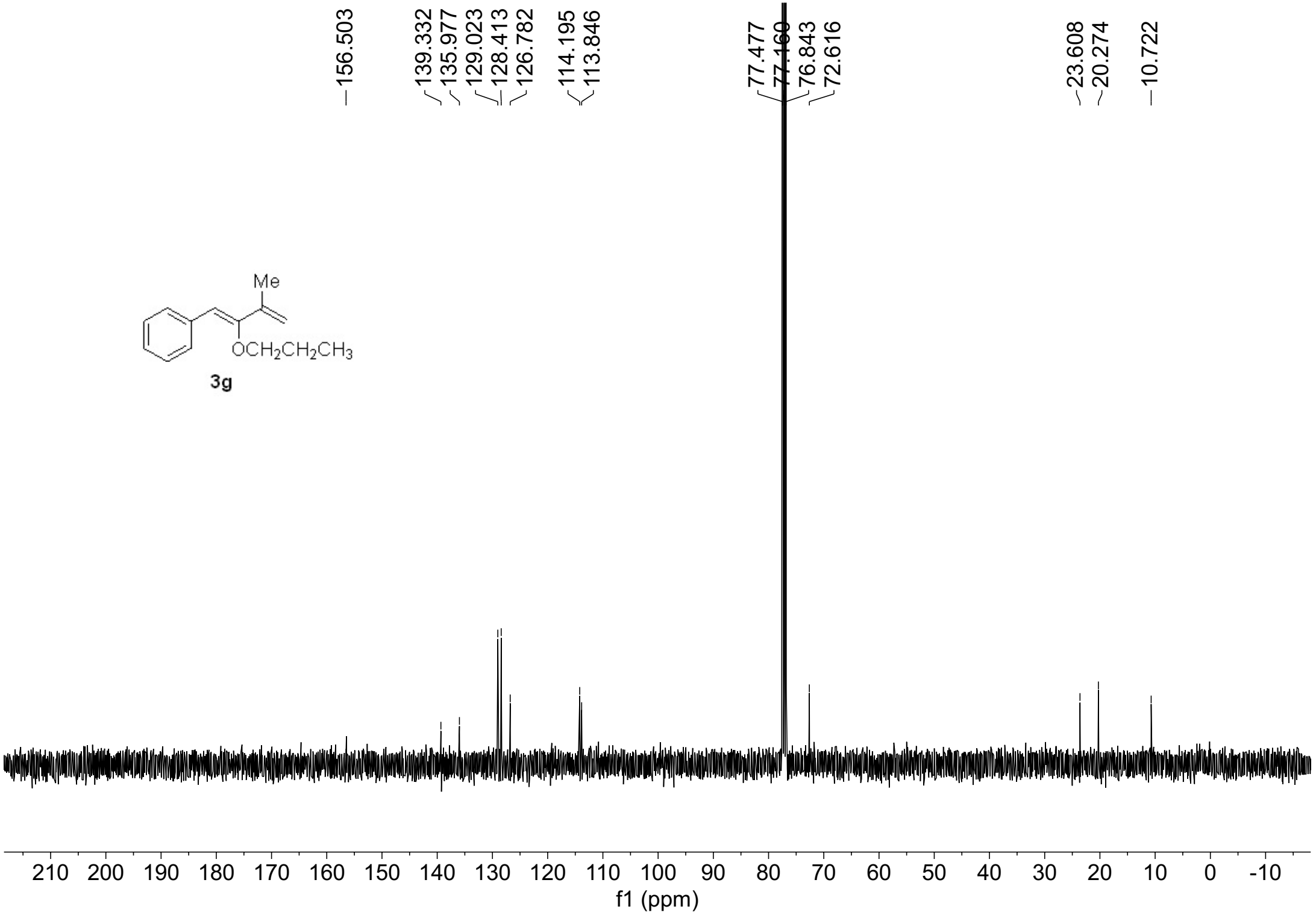
7.333
7.314
7.295
7.258
7.211
7.208
7.191
7.173
5.978
5.438
5.433
5.064
3.651
3.634
3.617
1.975
1.771
1.753
1.735
1.717
1.557
1.009
0.991
0.972
Me
OCH2CH2CH3
3g
2.00
2.00
1.19
1.00
1.04
1.04
2.18
3.07
2.03
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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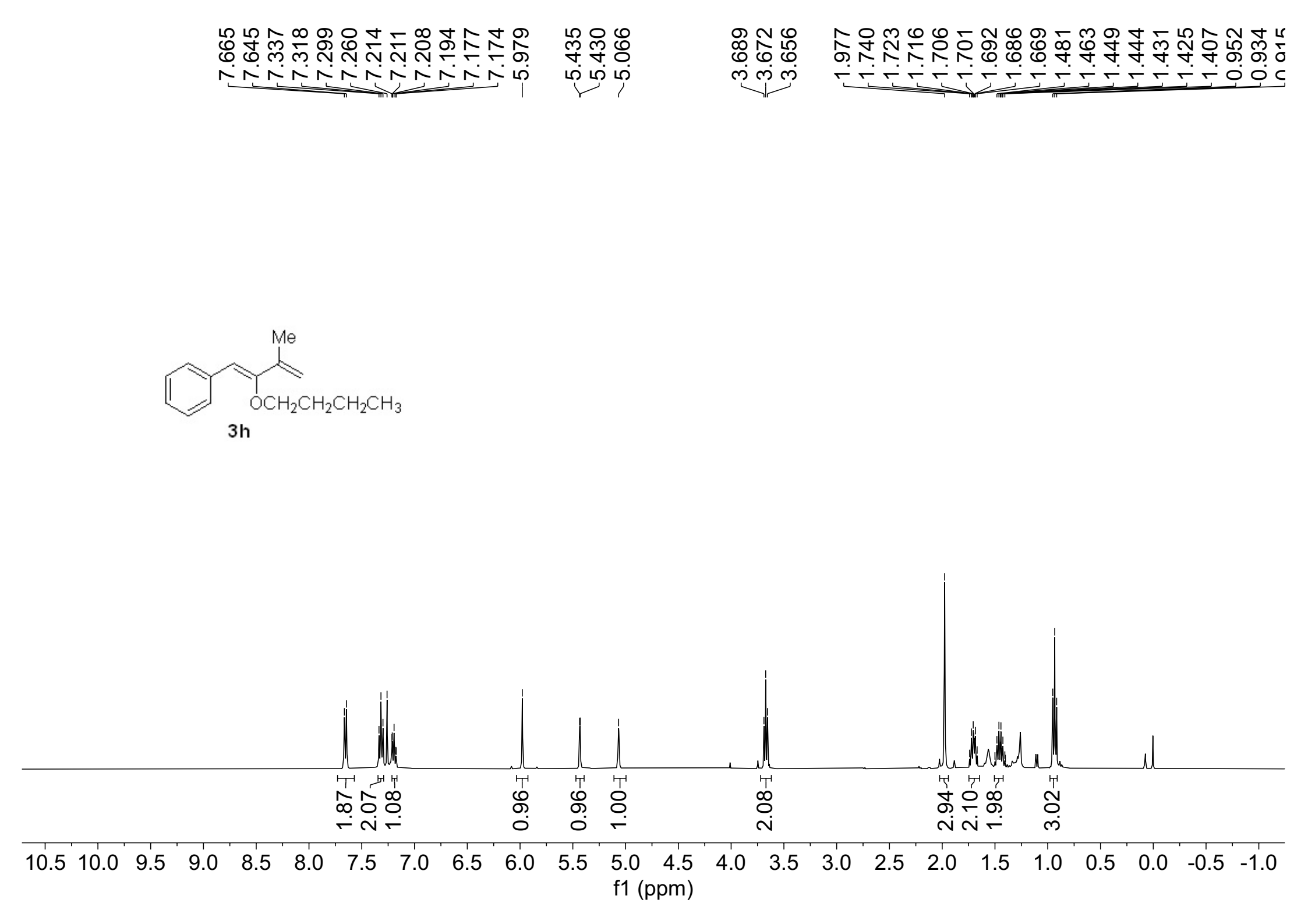
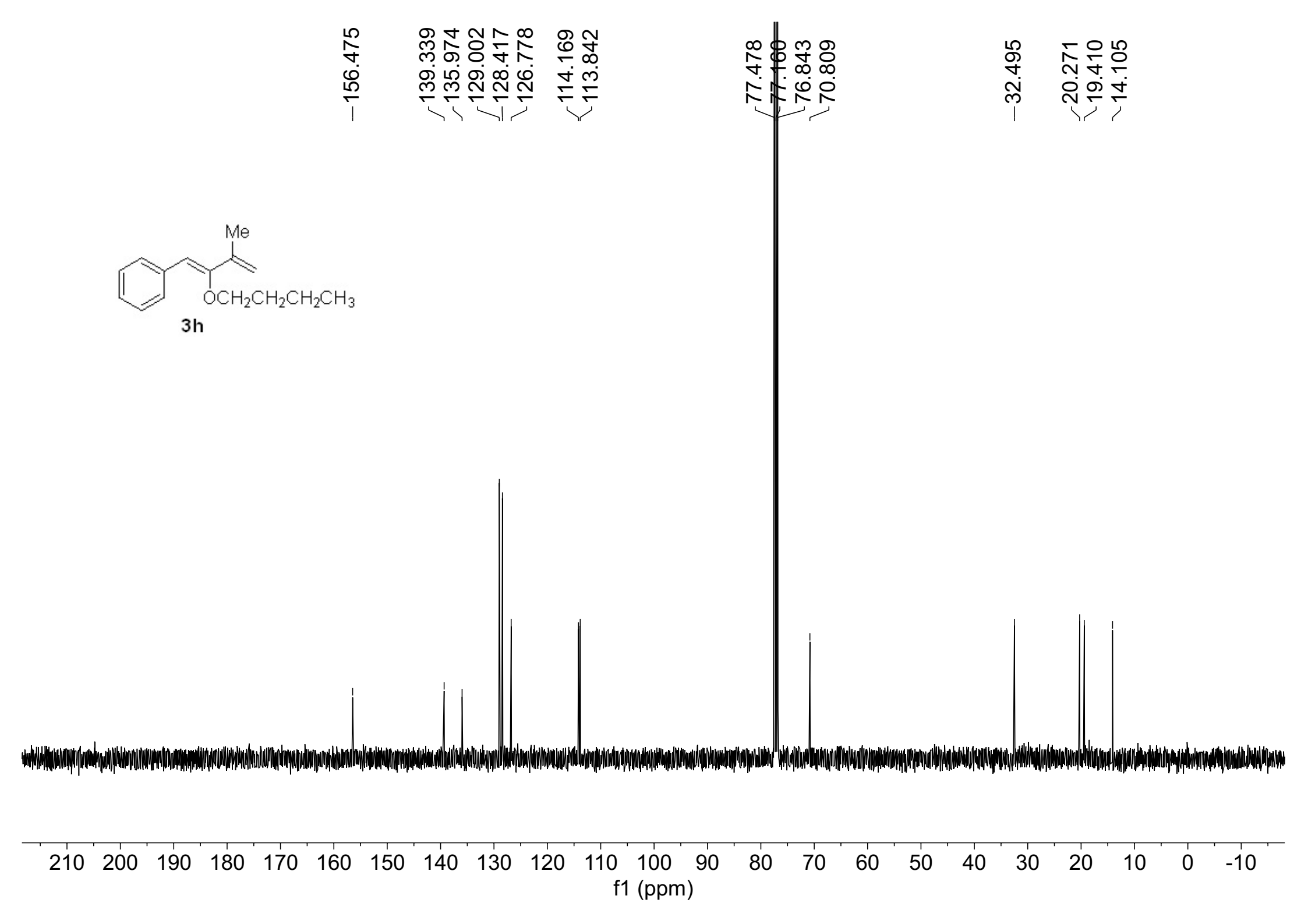
135.977
129.023
128.413
126.782
114.195
113.846
77.477
77.160
76.843
72.616
23.608
20.274
10.722
Me
OCH2CH2CH3
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.665
7.645
7.337
7.318
7.299
7.260
7.214
7.211
7.208
7.194
7.177
7.174
5.979
5.435
5.430
5.066
3.689
3.672
3.656
1.977
1.740
1.723
1.716
1.706
1.701
1.692
1.686
1.669
1.481
1.463
1.449
1.444
1.431
1.425
1.407
0.952
0.934
Me
OCH2CH2CH2CH3
3h
1.87
2.07
1.08
0.96
0.96
1.00
2.08
2.94
2.10
1.98
3.02
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 -0.5 -1.0
f1 (ppm)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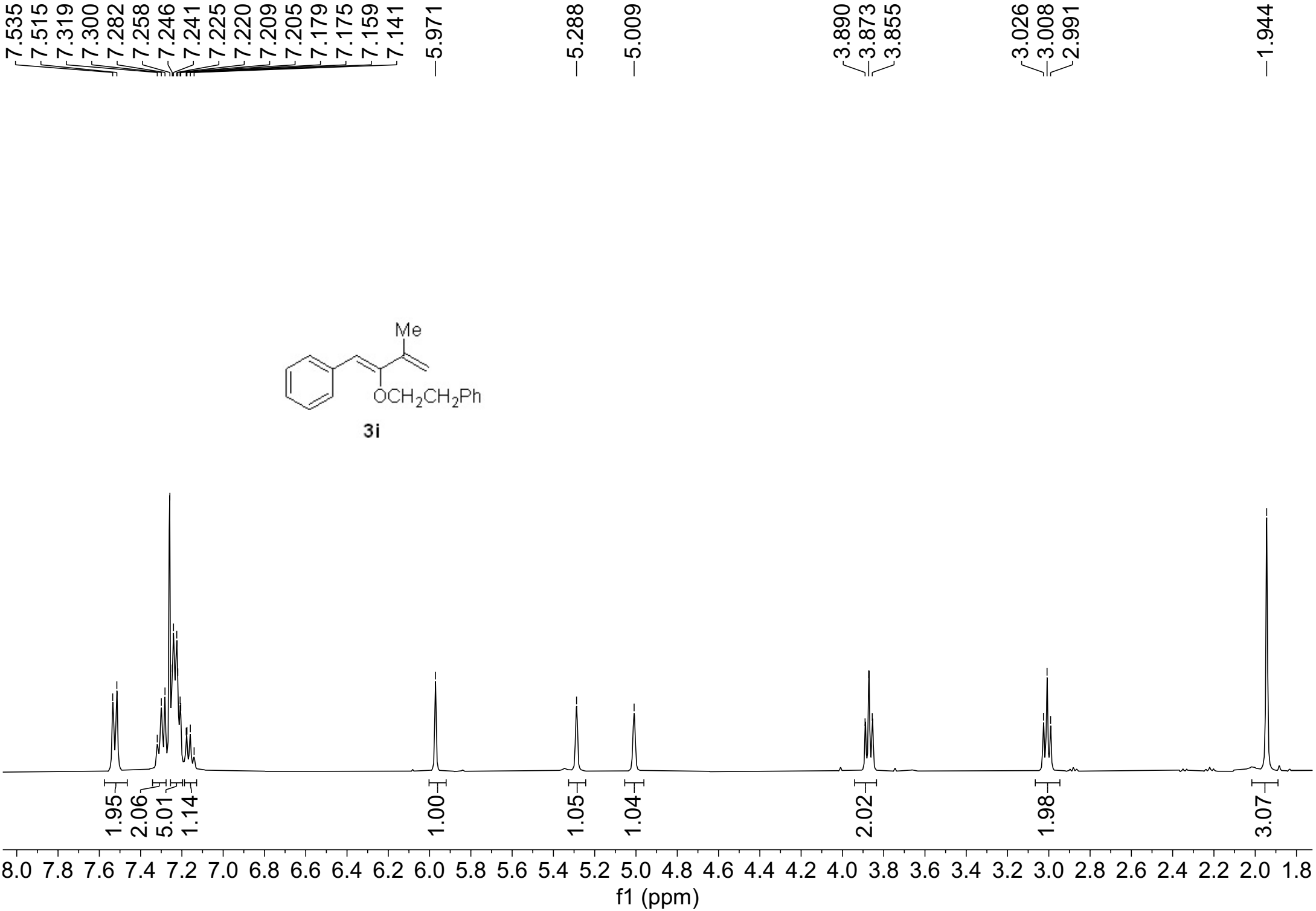
135.974
129.002
128.417
126.778
114.169
113.842
77.478
77.160
76.843
70.809
32.495
20.271
19.410
14.105
Me
OCH2CH2CH2CH3
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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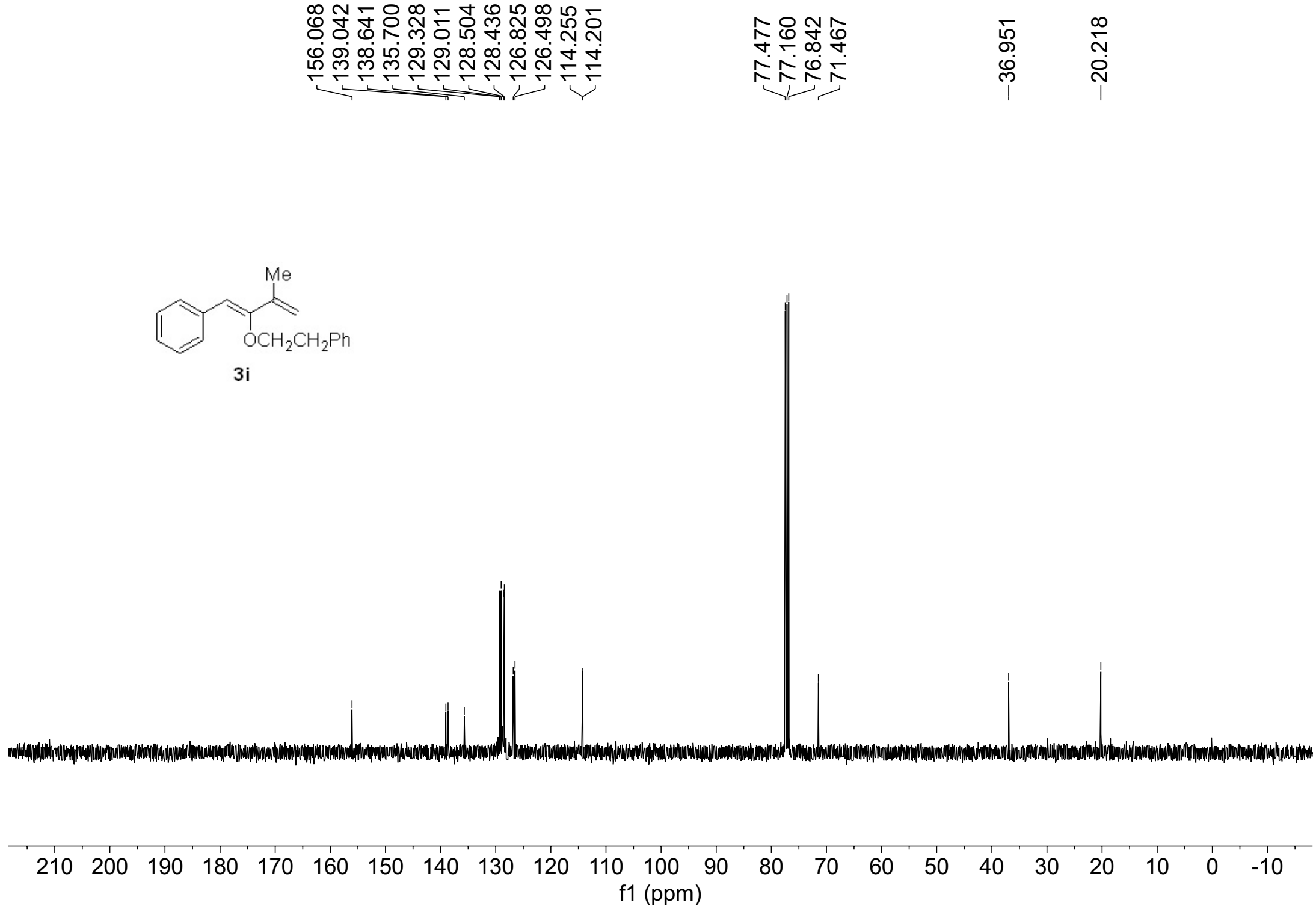
7.515
7.319
7.300
7.282
7.258
7.246
7.241
7.225
7.220
7.209
7.205
7.179
7.175
7.159
7.141
5.971
5.288
5.009
3.890
3.873
3.855
3.026
3.008
2.991
1.944
Me
OCH2CH2Ph
3i
1.95
2.06
5.01
1.14
1.00
1.05
1.04
2.02
1.98
3.07
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)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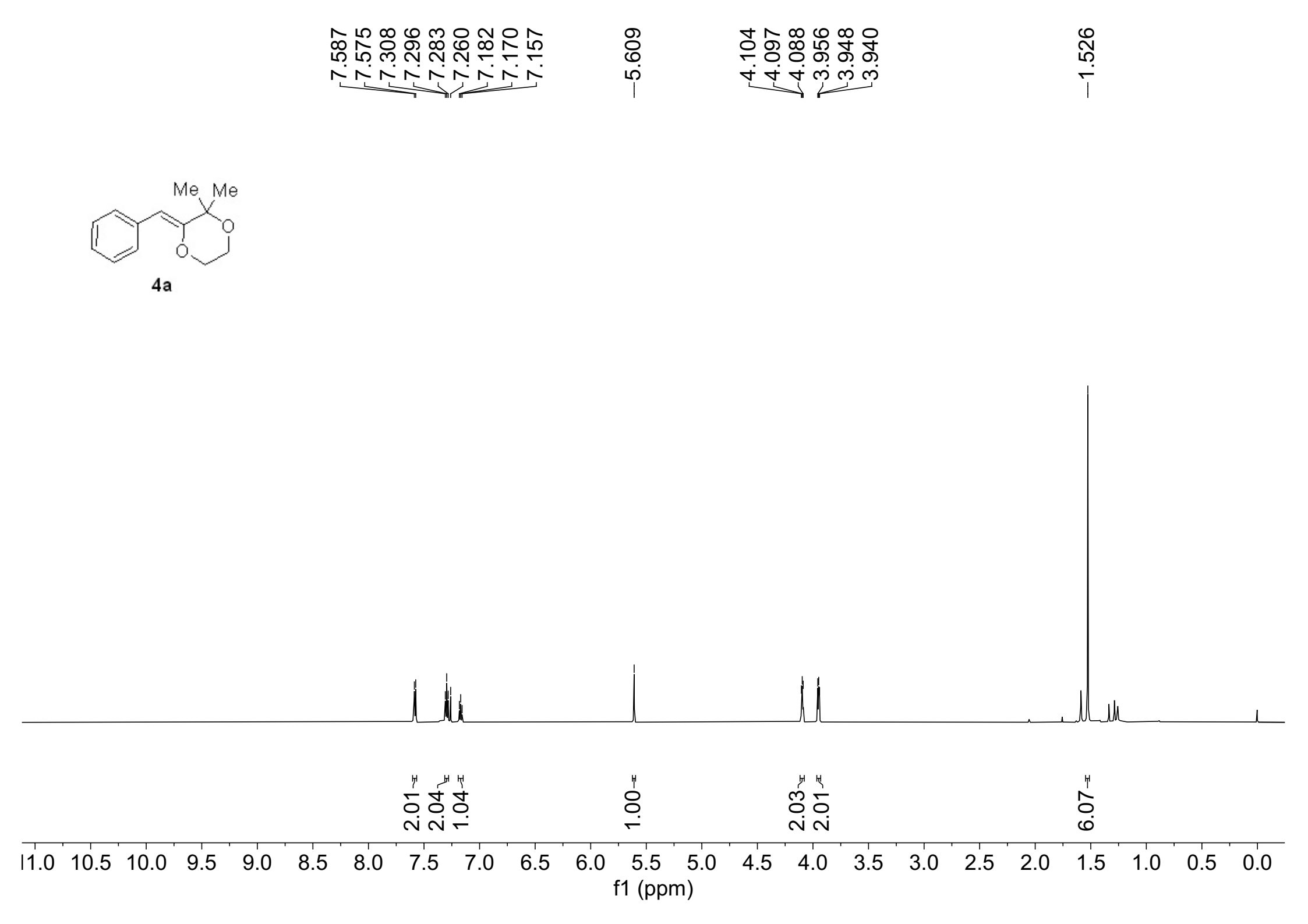
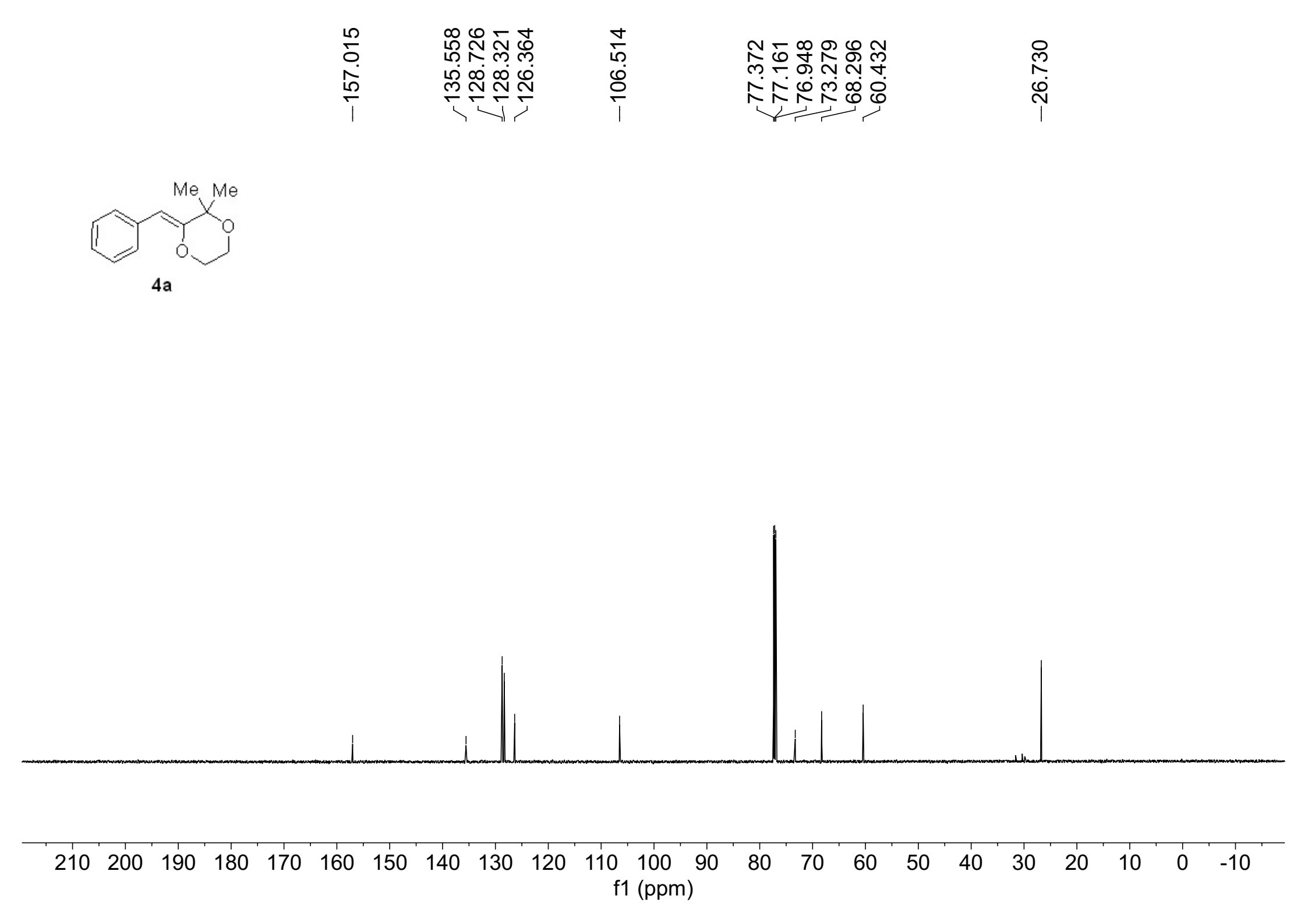
139.042
138.641
135.700
129.328
129.011
128.504
128.436
126.825
126.498
114.255
114.201
77.477
77.160
76.842
71.467
36.951
20.218
Me
OCH2CH2Ph
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.587
7.575
7.308
7.296
7.283
7.260
7.182
7.170
7.157
5.609
4.104
4.097
4.088
3.956
3.948
3.940
1.526
Me
Me
O
O
4a
2.01
2.04
1.04
1.00
2.03
2.01
6.07
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)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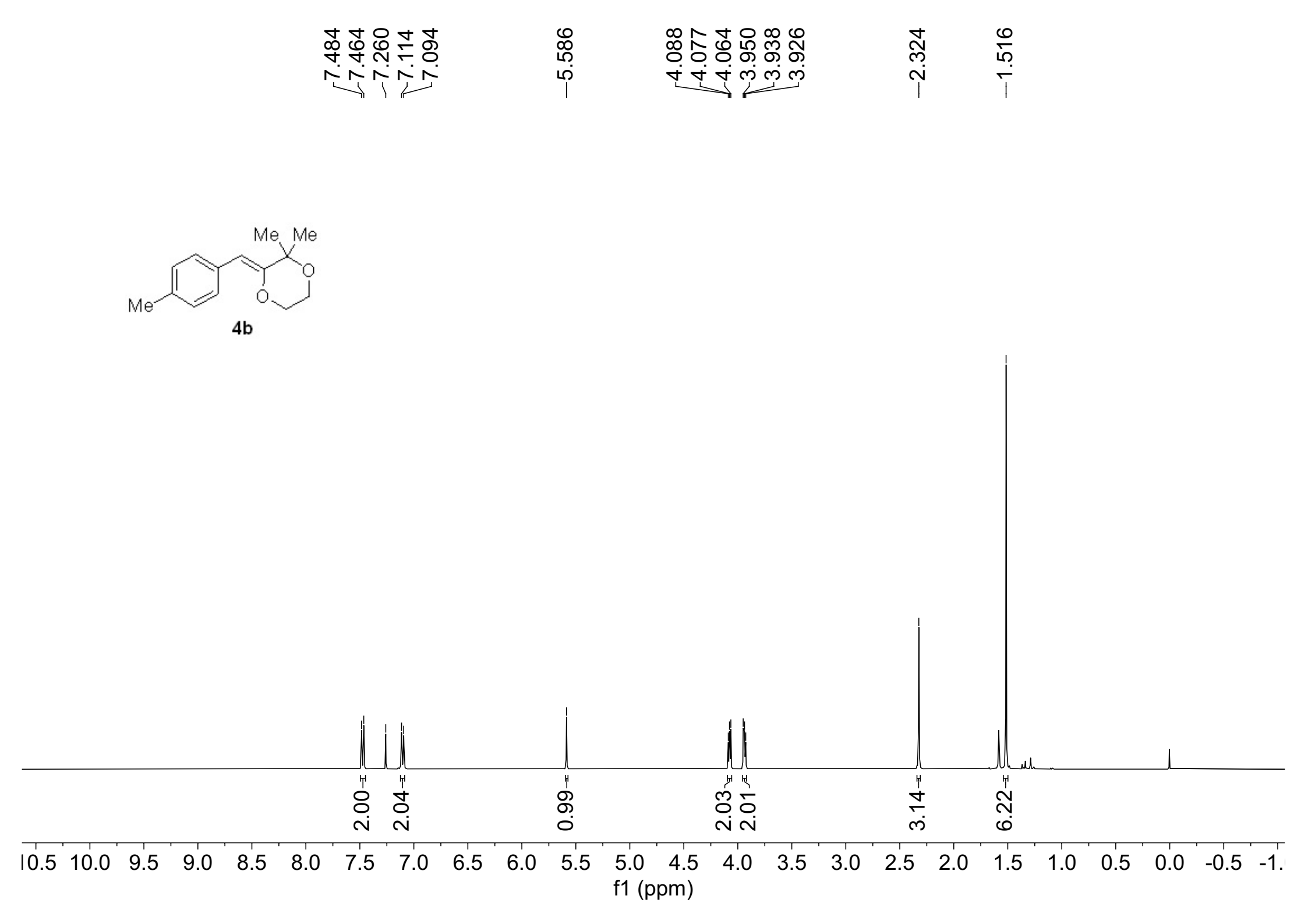
135.558
128.726
128.321
126.364
106.514
77.372
77.161
76.948
73.279
68.296
60.432
26.730
Me
Me
O
O
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.114
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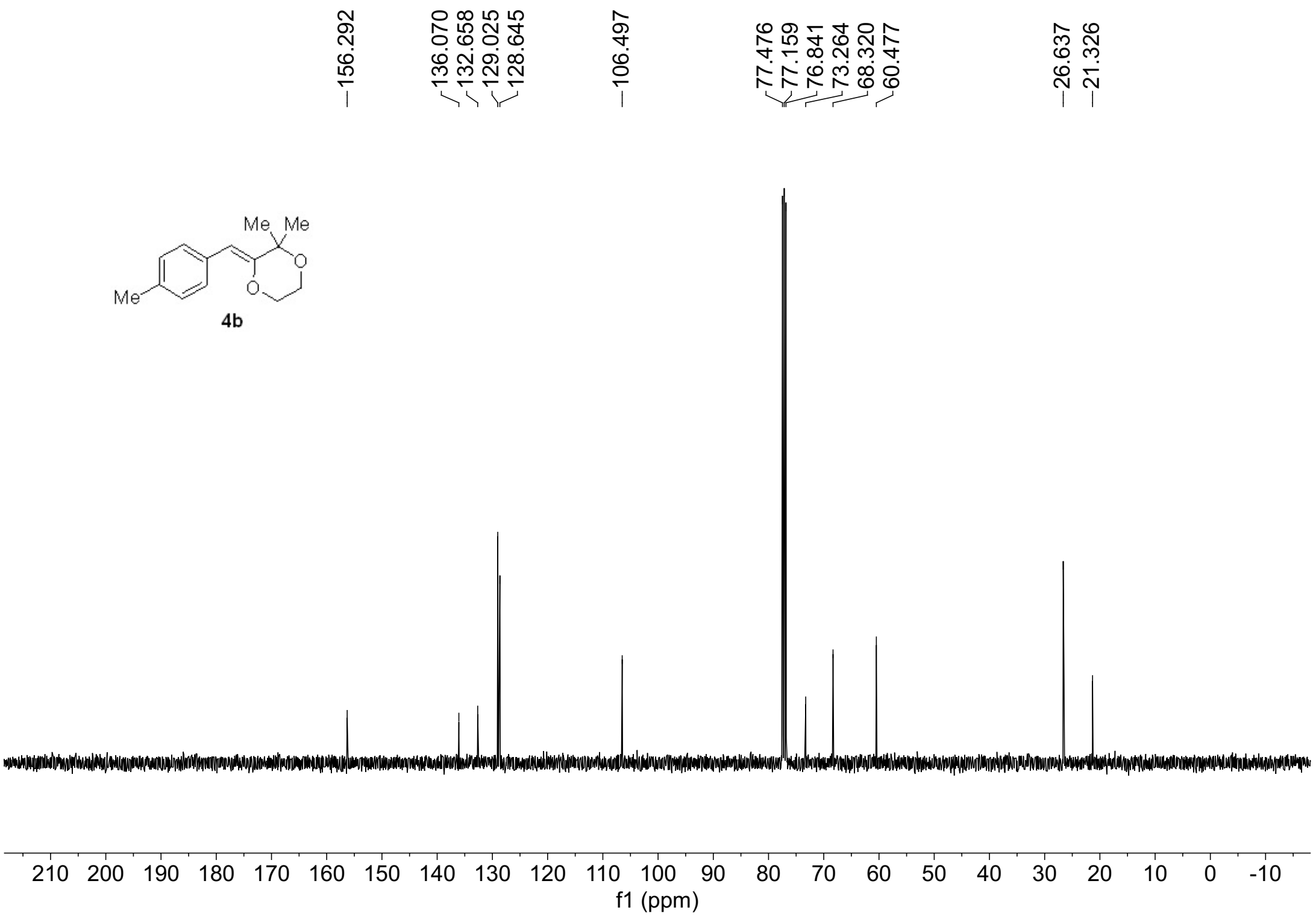
4.088
4.077
4.064
3.950
3.938
3.926
2.324
1.516
Me
Me
Me
O
O
4b
2.00
2.04
0.99
2.03
2.01
3.14
6.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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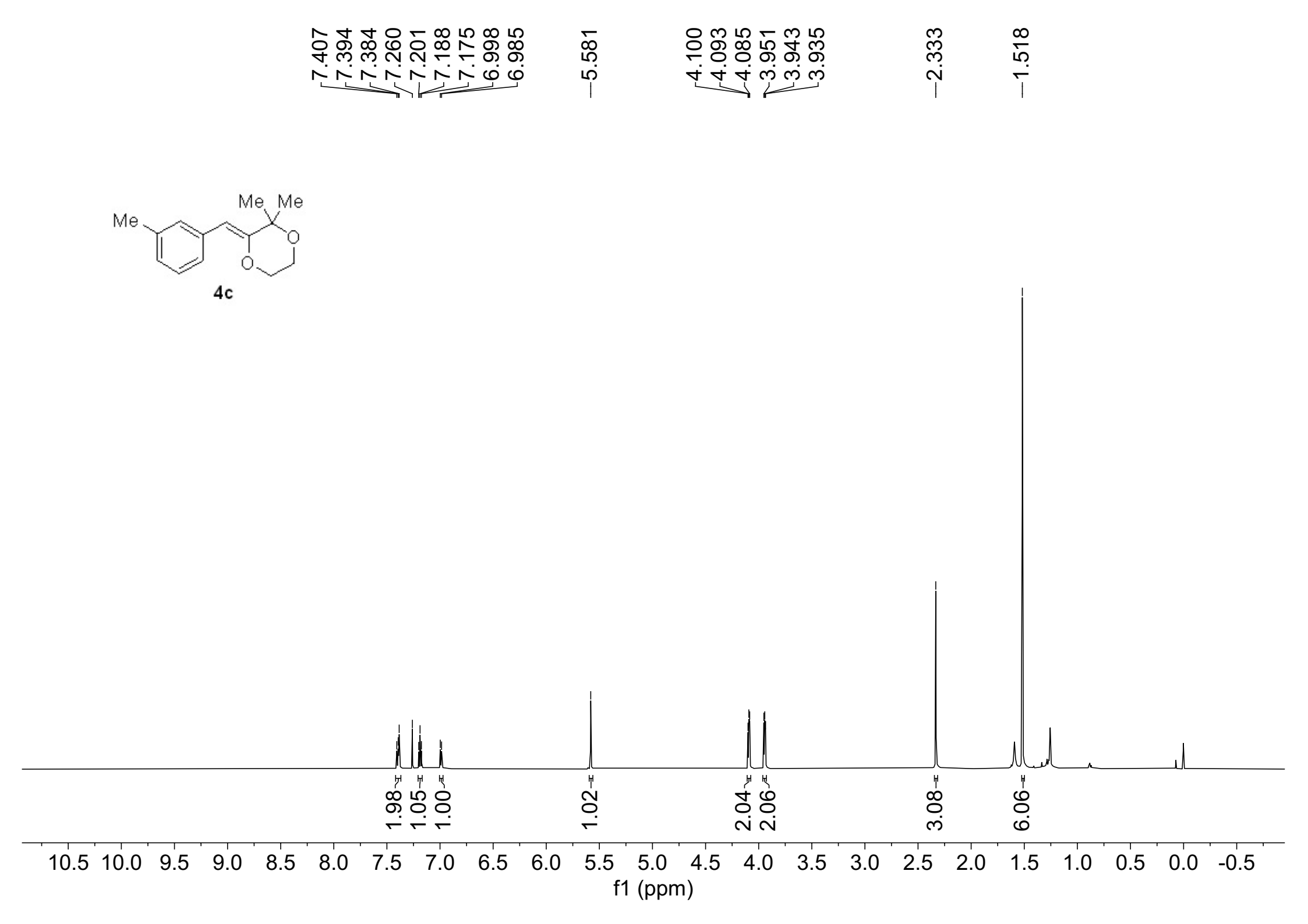
128.645
106.497
77.476
77.159
76.841
73.264
68.320
60.477
26.637
21.326
Me
Me
Me
O
O
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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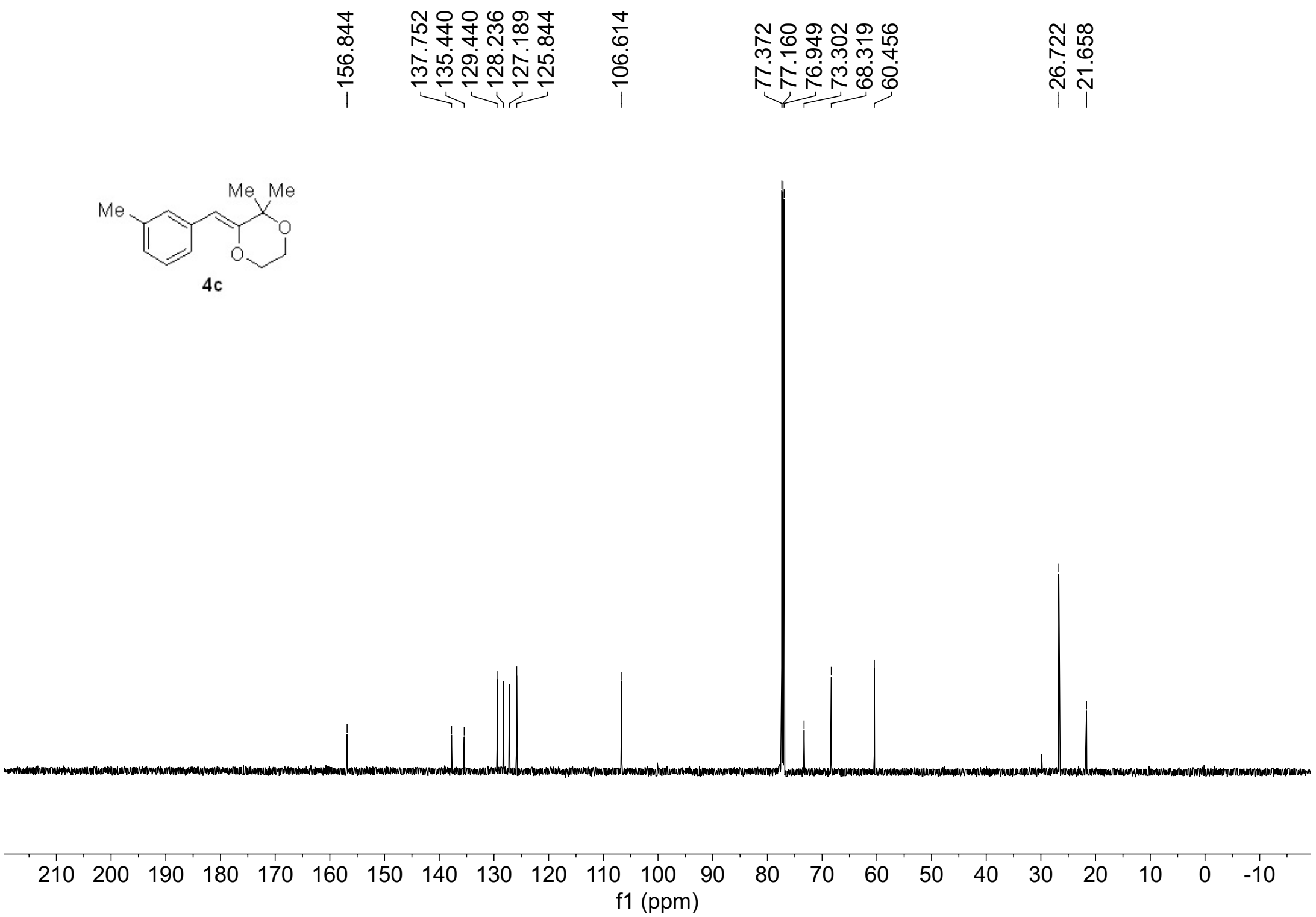
7.201
7.188
7.175
6.998
6.985
5.581
4.100
4.093
4.085
3.951
3.943
3.935
2.333
1.518
Me
Me
Me
O
O
4c
1.98
1.05
1.00
1.02
2.04
2.06
3.08
6.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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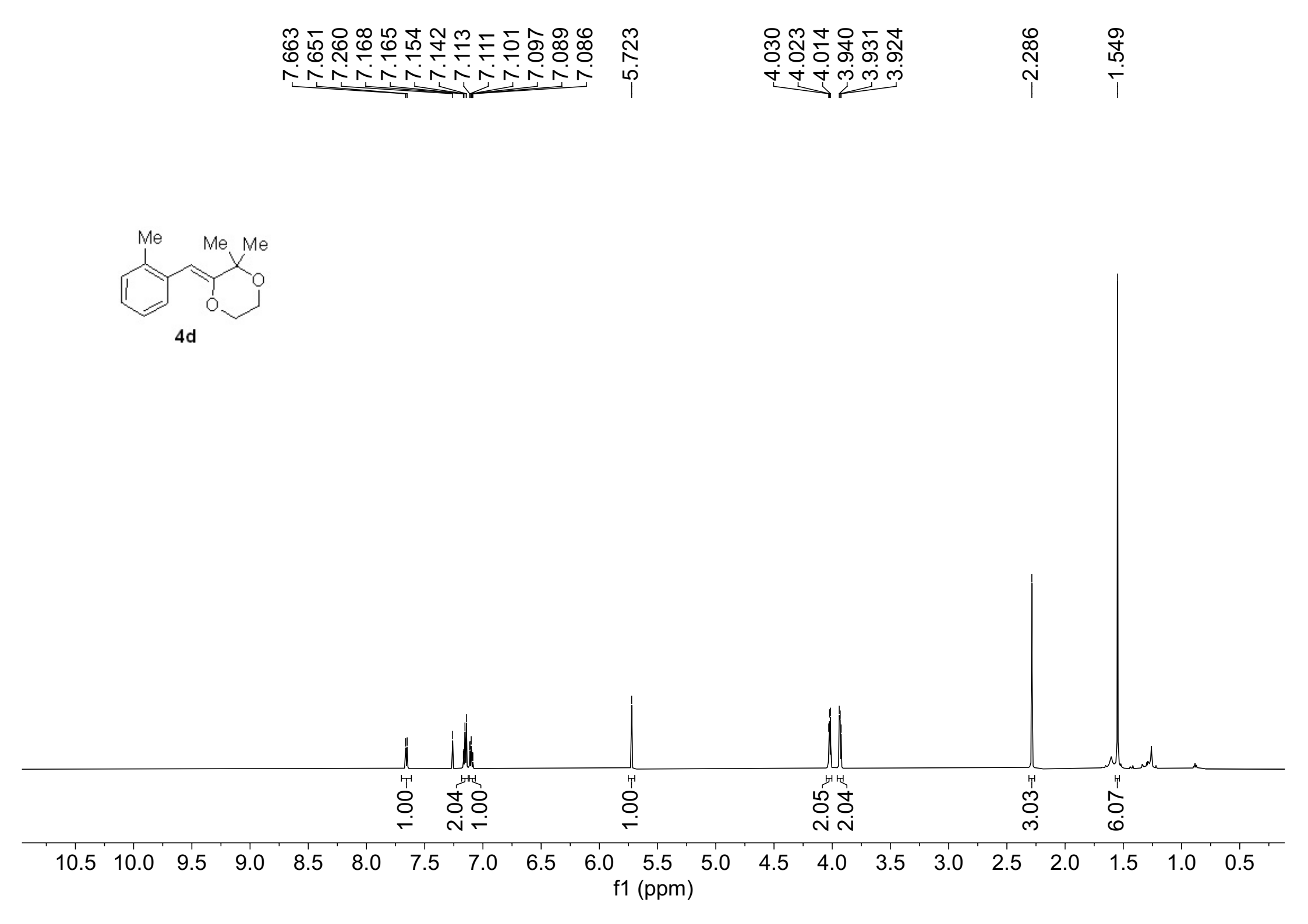
129.440
128.236
127.189
125.844
106.614
77.372
77.160
76.949
73.302
68.319
60.456
26.722
21.658
Me
Me
Me
O
O
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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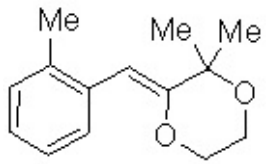
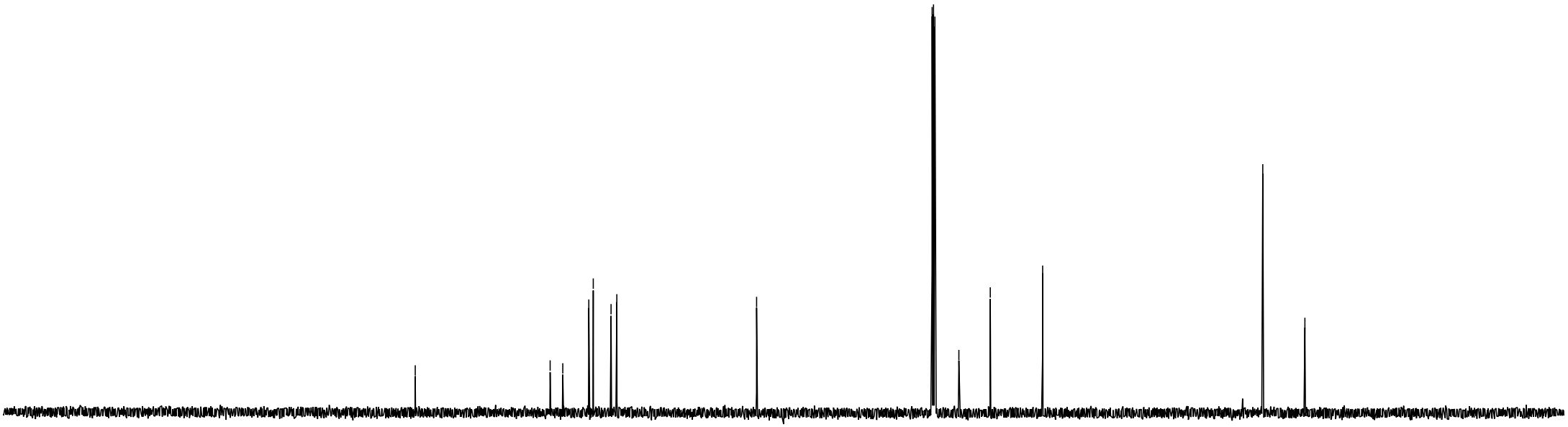
7.168
7.165
7.154
7.142
7.113
7.111
7.101
7.097
7.089
7.086
5.723
4.030
4.023
4.014
3.940
3.931
3.924
2.286
1.549
Me
Me
Me
O
O
4d
1.00
2.04
1.00
1.00
2.05
2.04
3.03
6.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



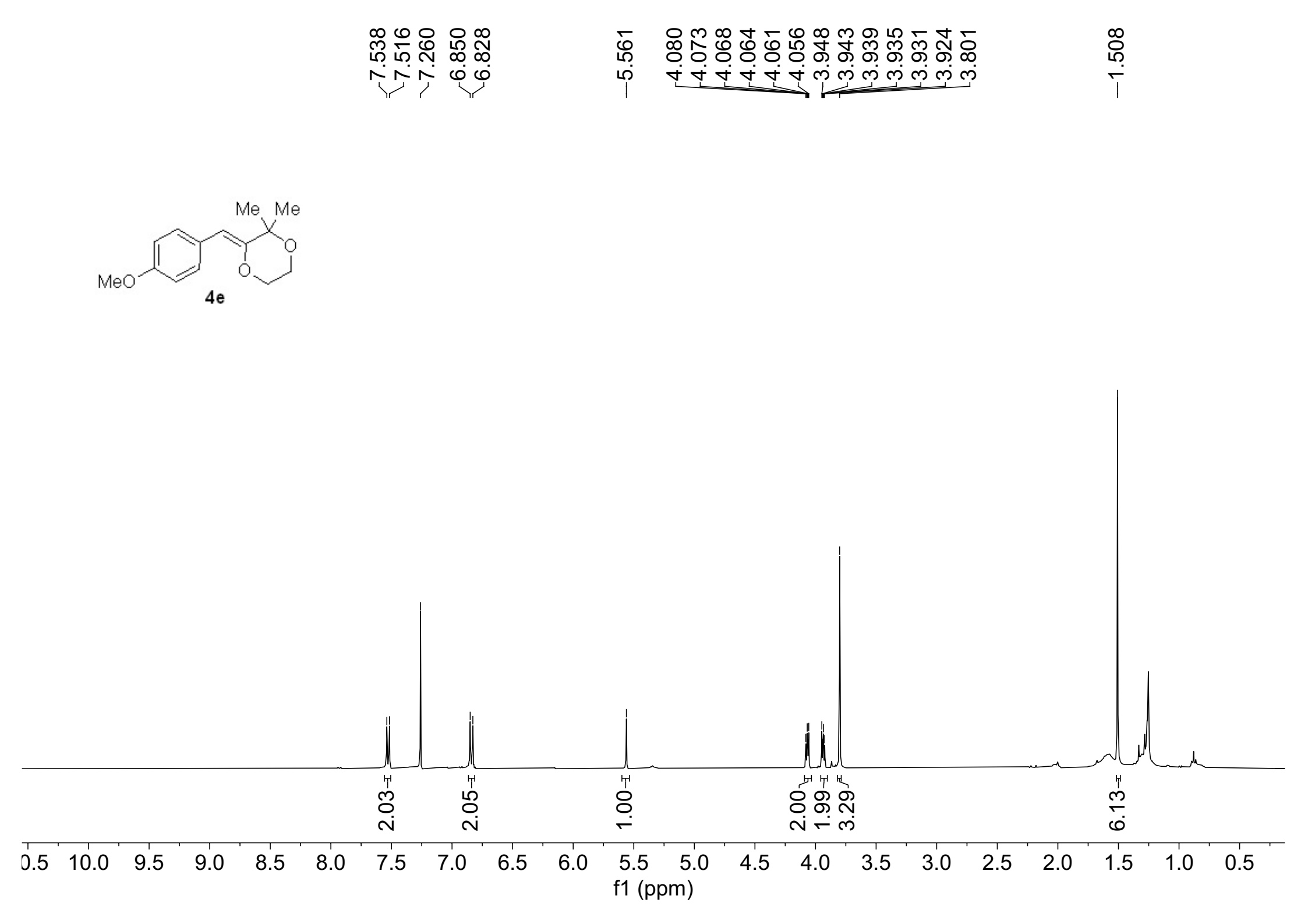
4d

156.510
135.856
133.921
129.937
129.254
126.530
125.646
104.248
77.372
77.161
76.949
73.279
68.473
60.454
26.753
20.304



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)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4.073
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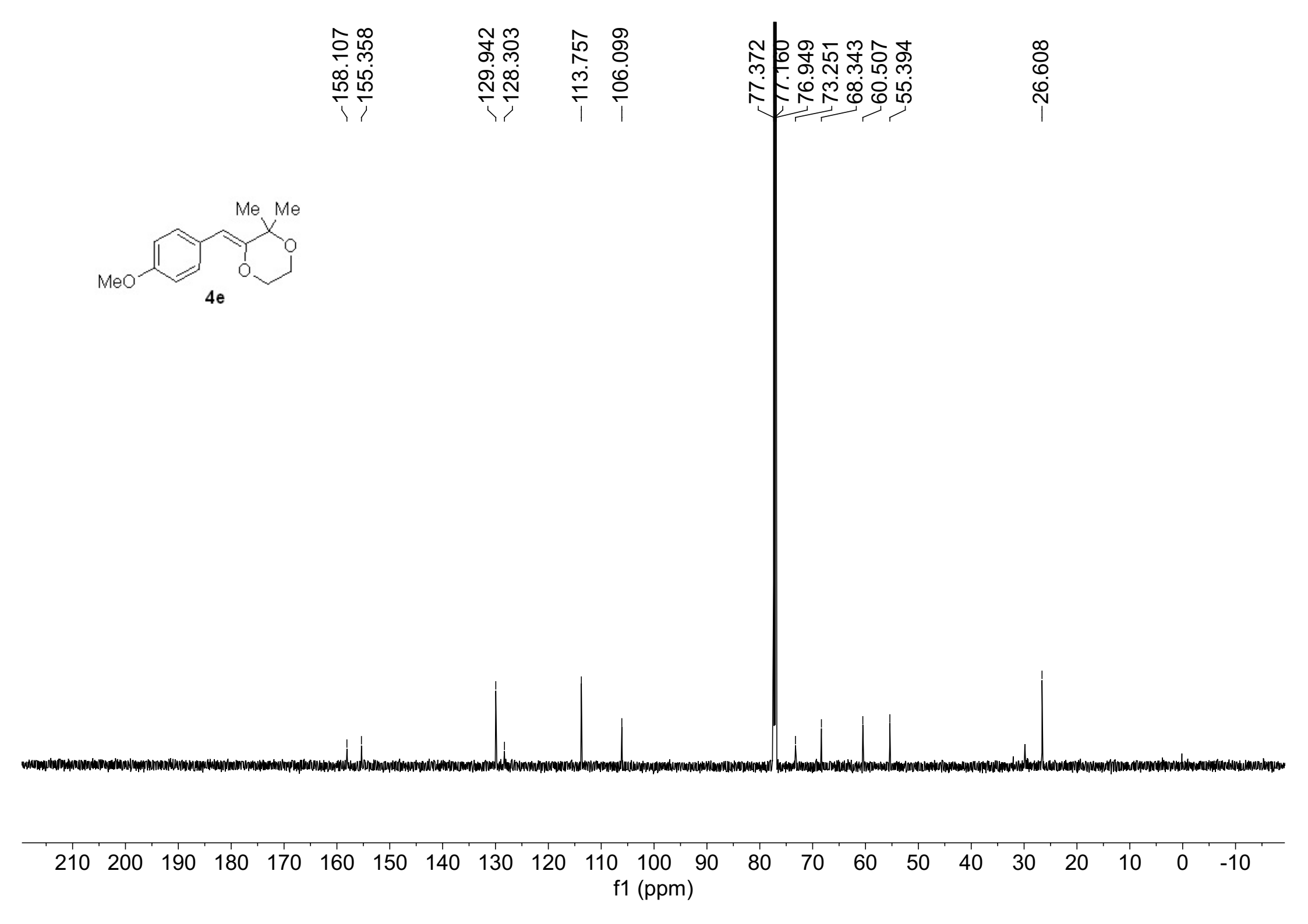
4.064
4.061
4.056
3.948
3.943
3.939
3.935
3.931
3.924
3.801
1.508
Me
Me
O
O
MeO
4e
2.03
2.05
1.00
2.00
1.99
3.29
6.13
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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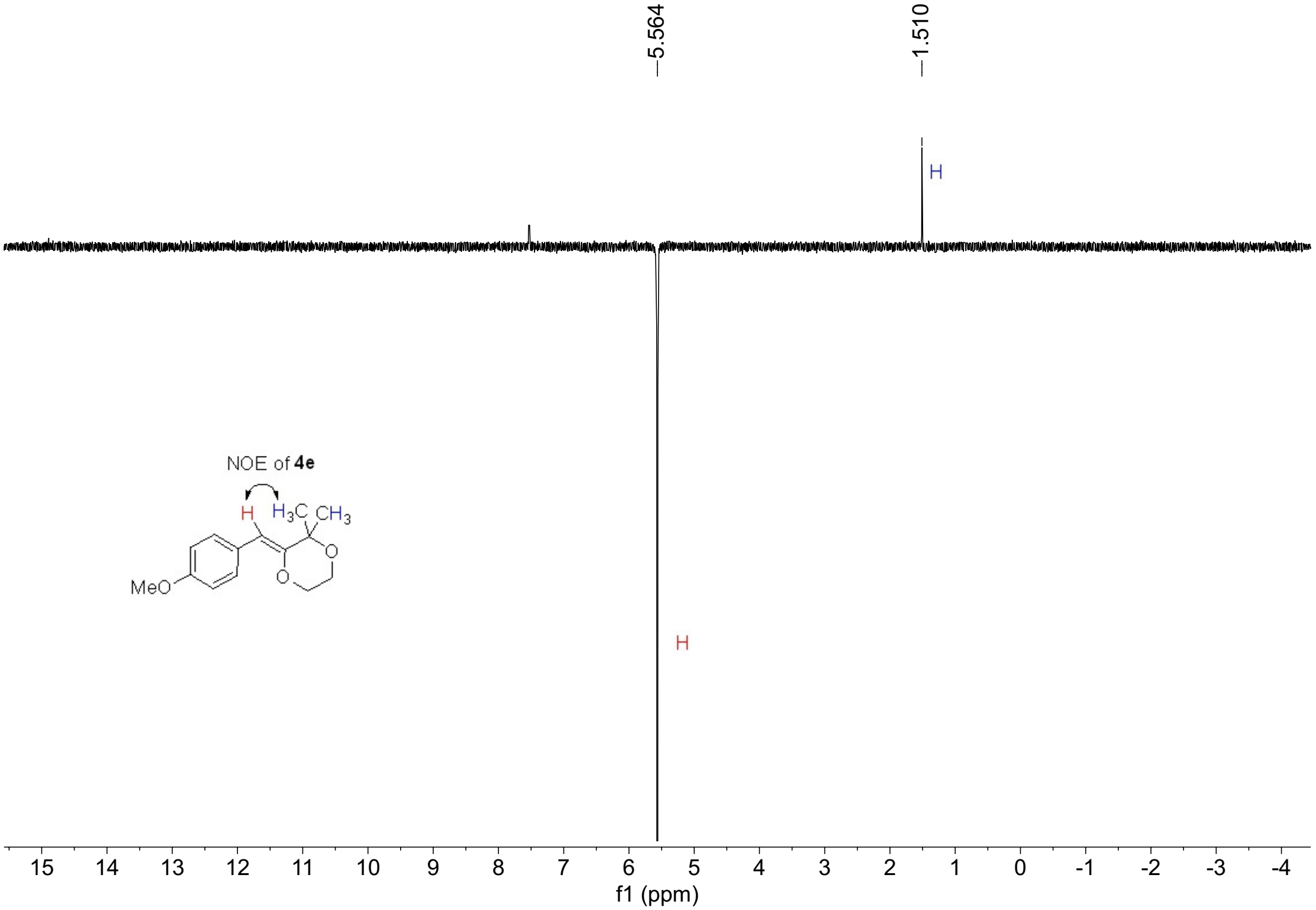
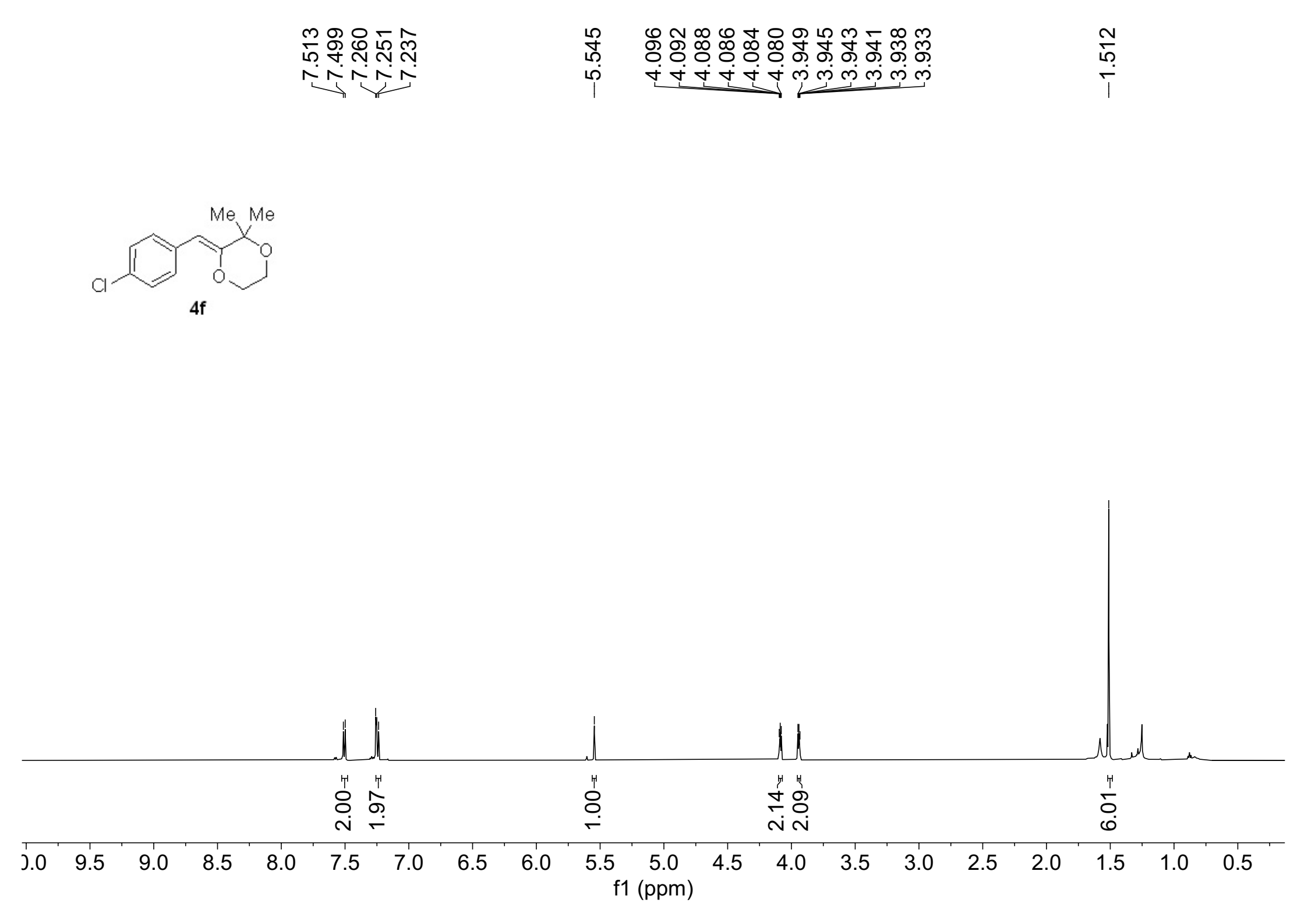
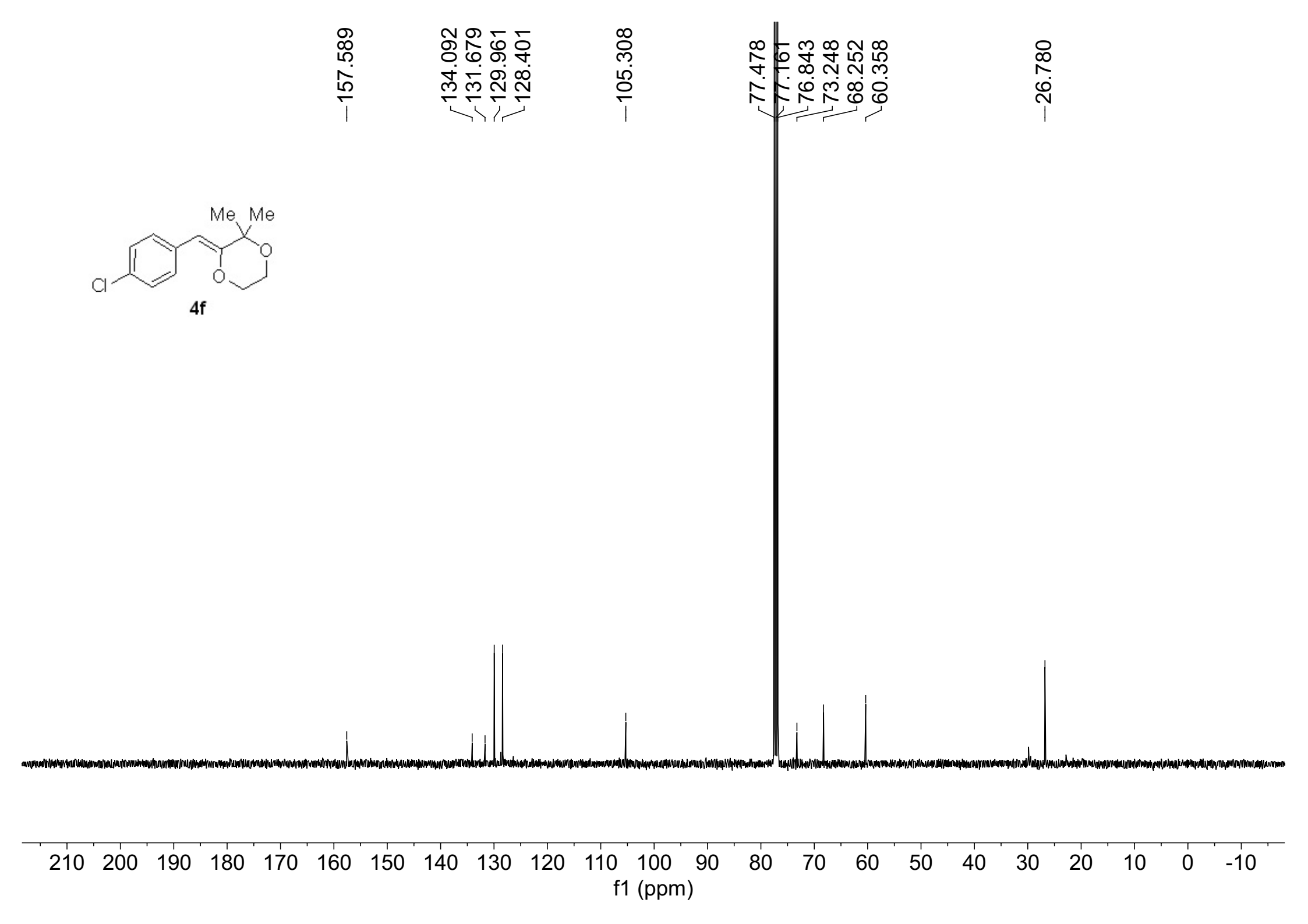
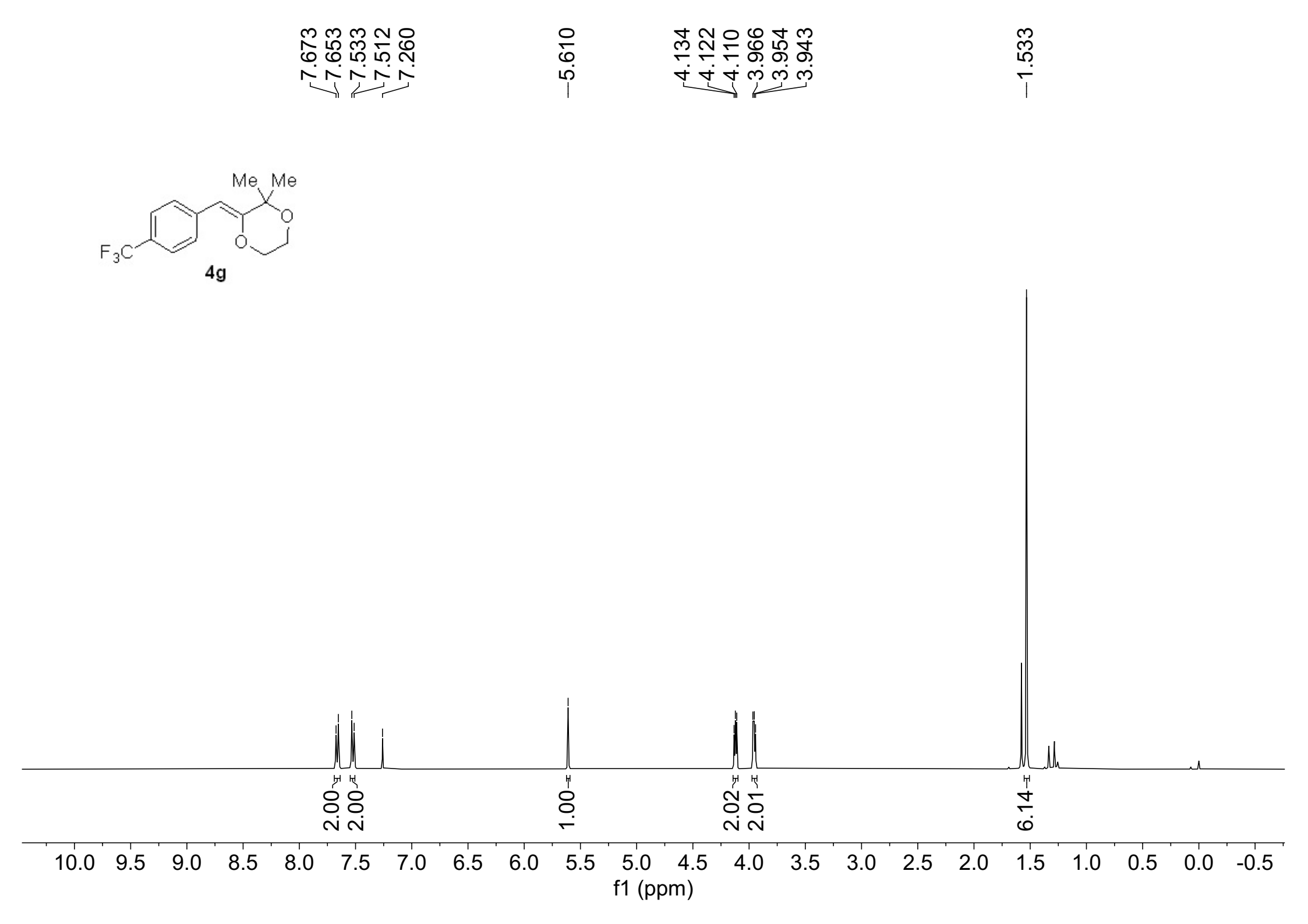
155.358
129.942
128.303
113.757
106.099
77.372
77.160
76.949
73.251
68.343
60.507
55.394
26.608
Me
Me
O
O
MeO
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.564
1.510
H
H
NOE of 4e
H
H3C
CH3
O
O
MeO
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


7.513
7.499
7.260
7.251
7.237
5.545
4.096
4.092
4.088
4.086
4.084
4.080
3.949
3.945
3.943
3.941
3.938
3.933
1.512
Me
Me
O
O
Cl
4f
2.00
1.97
1.00
2.14
2.09
6.01
f1 (ppm)


157.589
134.092
131.679
129.961
128.401
105.308
77.478
77.161
76.843
73.248
68.252
60.358
26.780
Me
Me
O
O
Cl
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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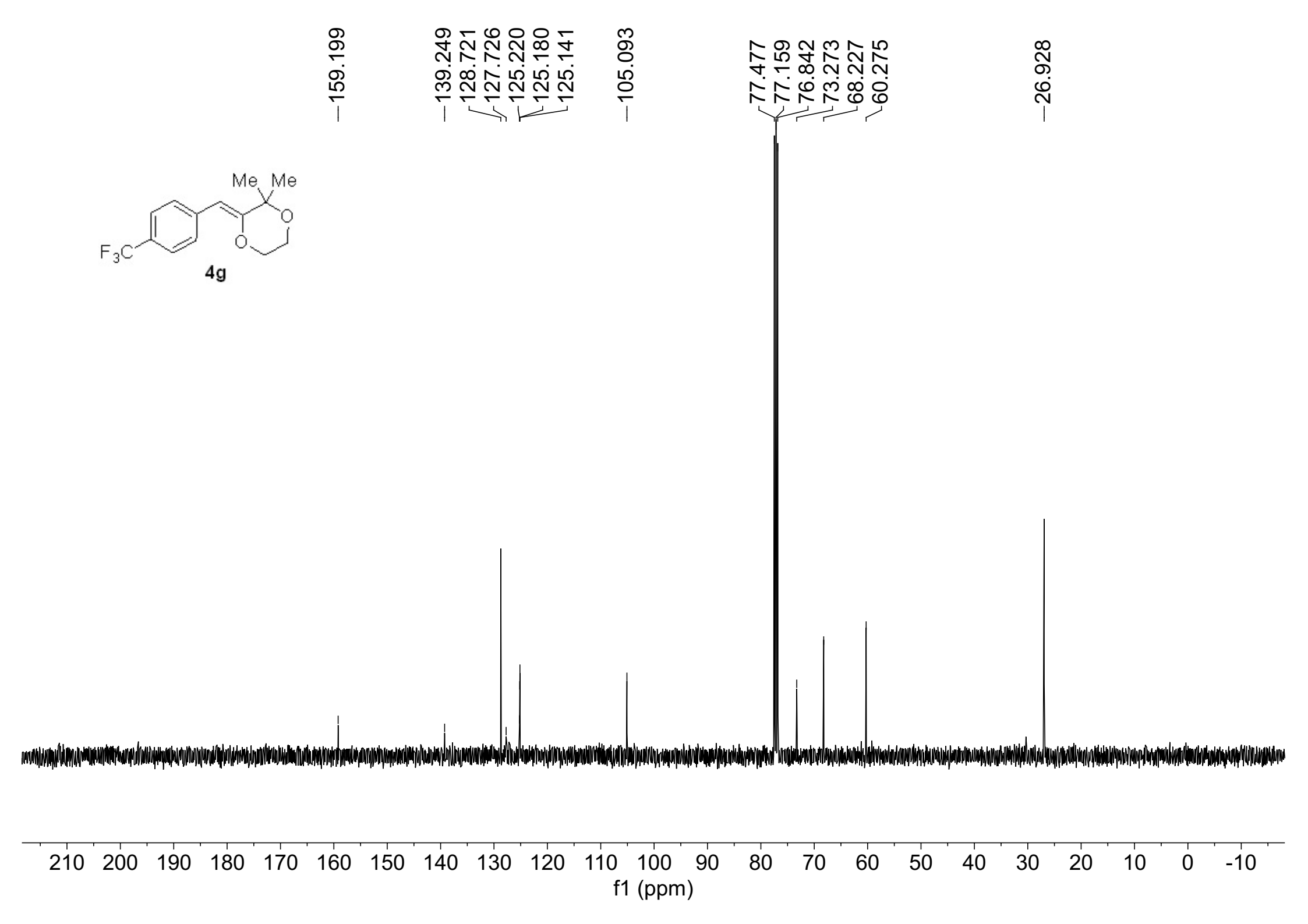
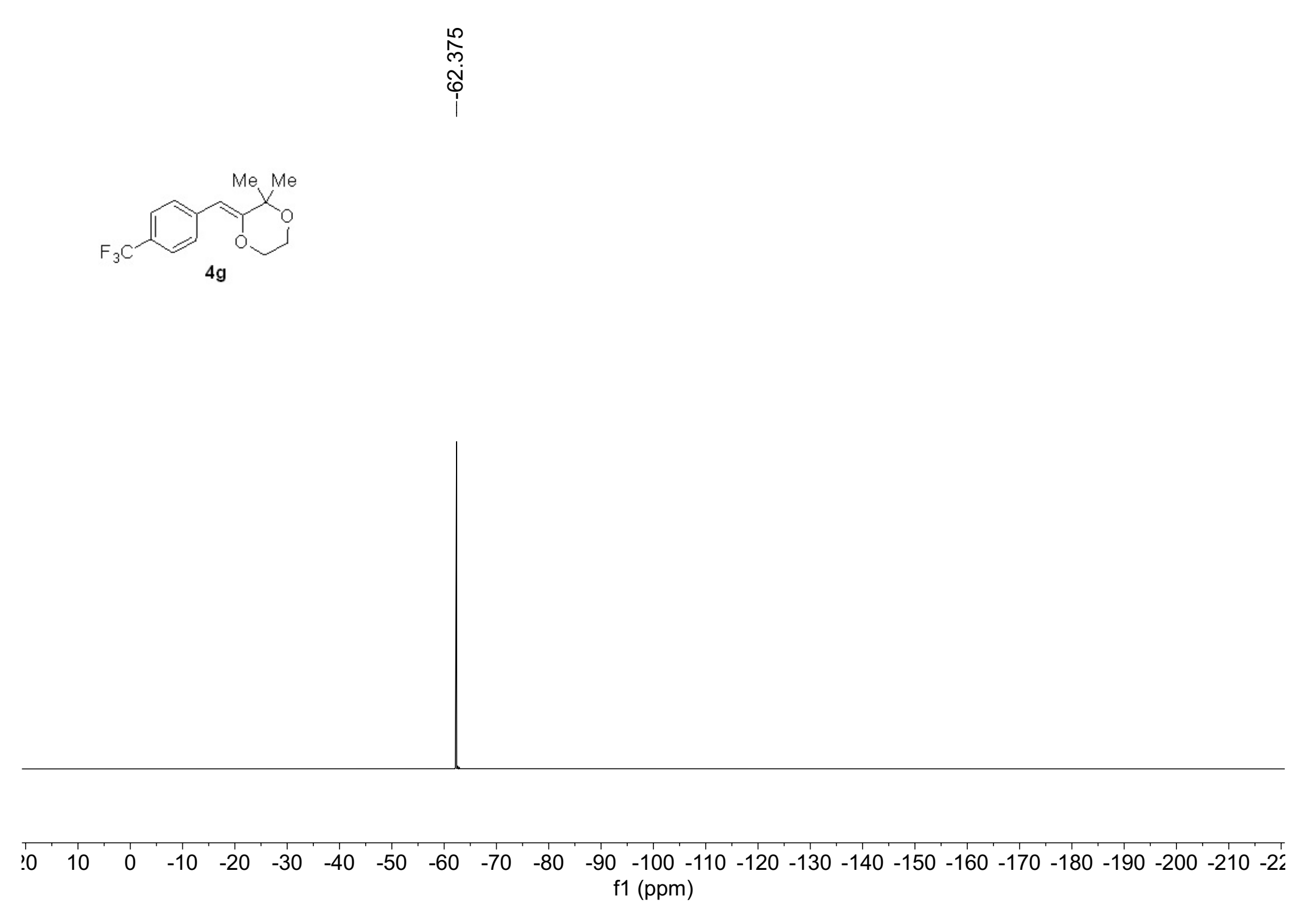
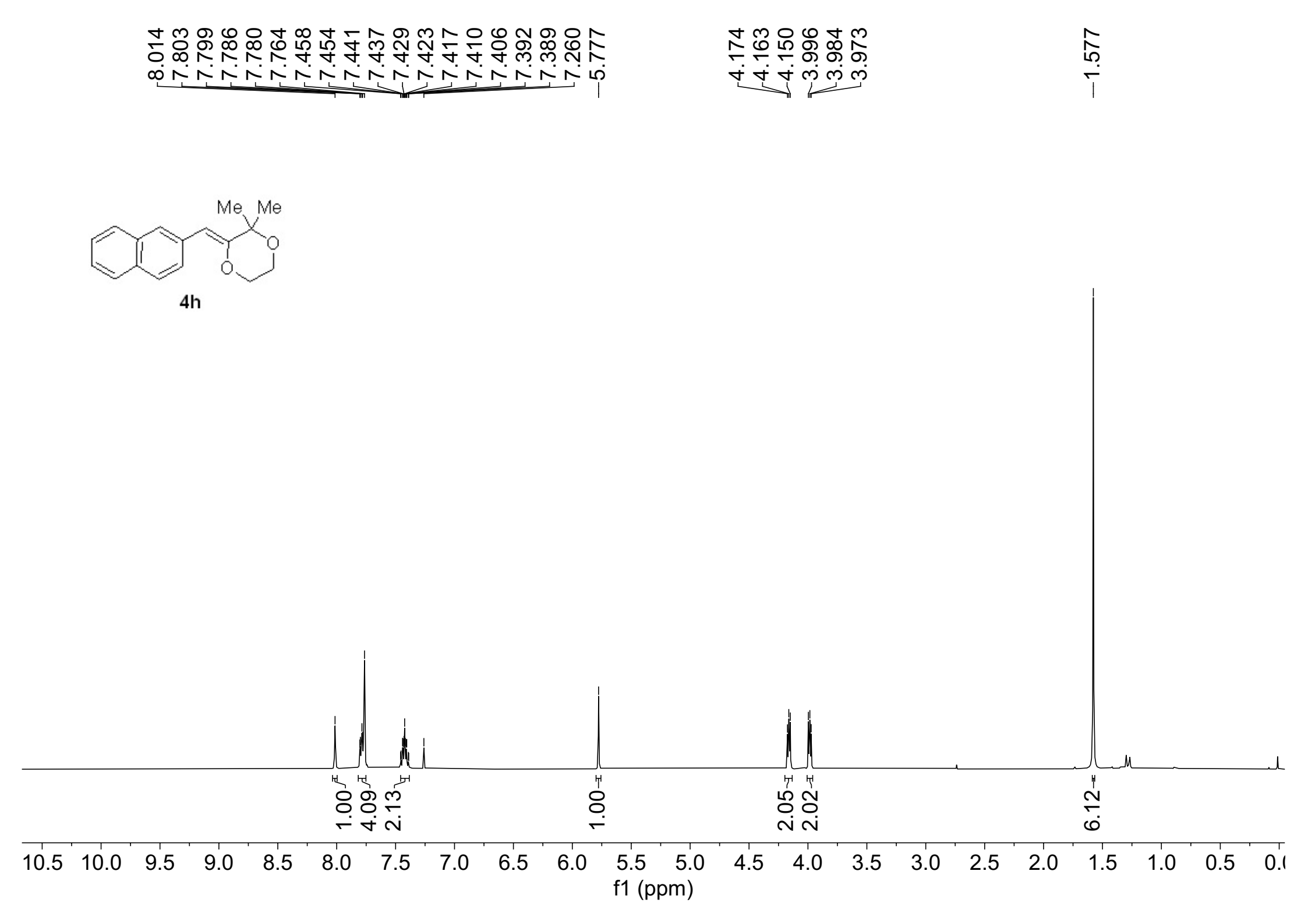
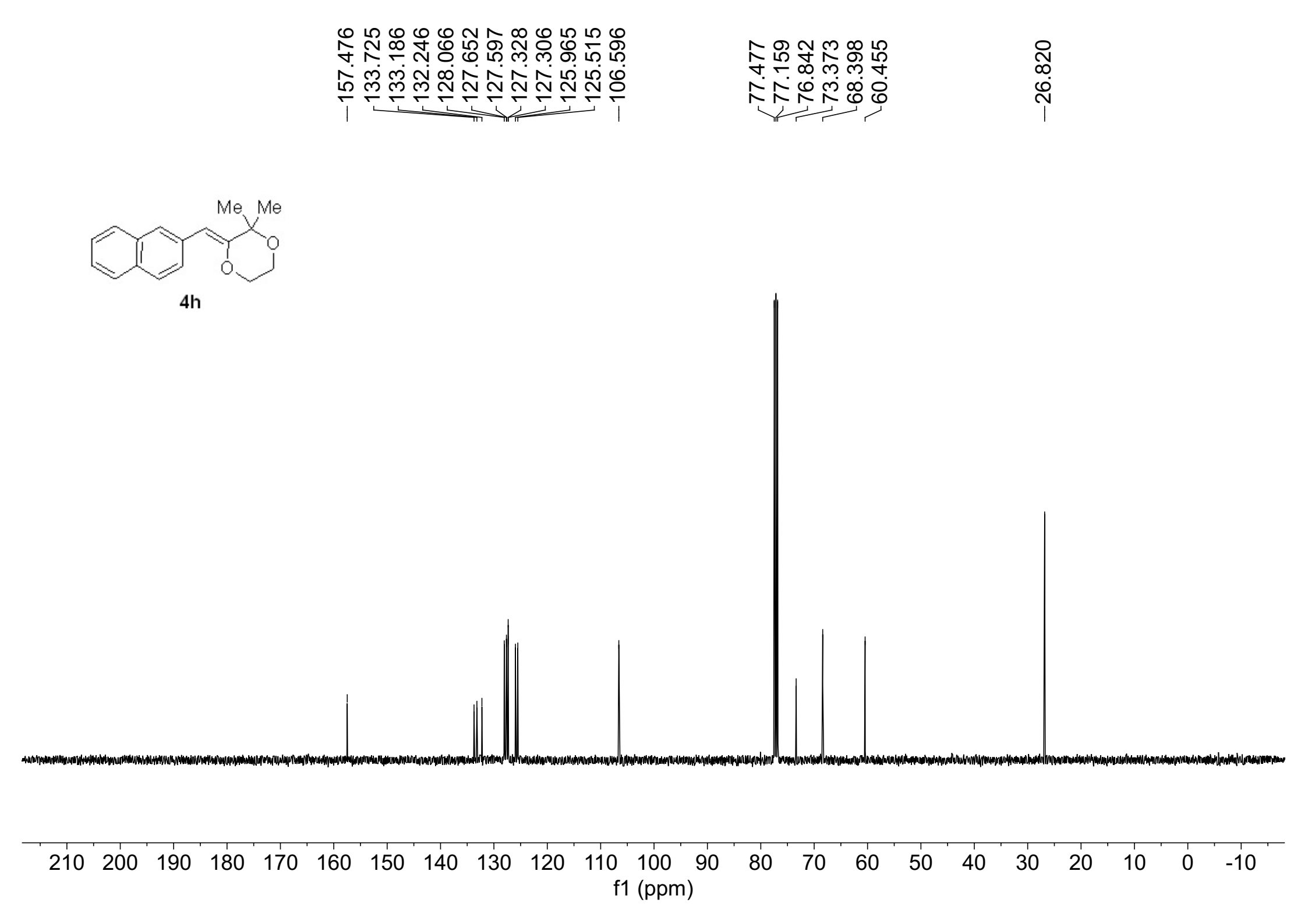
7.653
7.533
7.512
7.260
5.610
4.134
4.122
4.110
3.966
3.954
3.943
1.533
Me
Me
O
O
F3C
4g
2.00
2.00
1.00
2.02
2.01
6.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


159.199
139.249
128.721
127.726
125.220
125.180
125.141
105.093
77.477
77.159
76.842
73.273
68.227
60.275
26.928
Me
Me
O
O
F3C
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.375
Me Me
O
O
F3C
4g
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


8.014
7.803
7.799
7.786
7.780
7.764
7.458
7.454
7.441
7.437
7.429
7.423
7.417
7.410
7.406
7.392
7.389
7.260
5.777
4.174
4.163
4.150
3.996
3.984
3.973
1.577
Me
Me
O
O
4h
1.00
4.09
2.13
1.00
2.05
2.02
6.12
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
f1 (ppm)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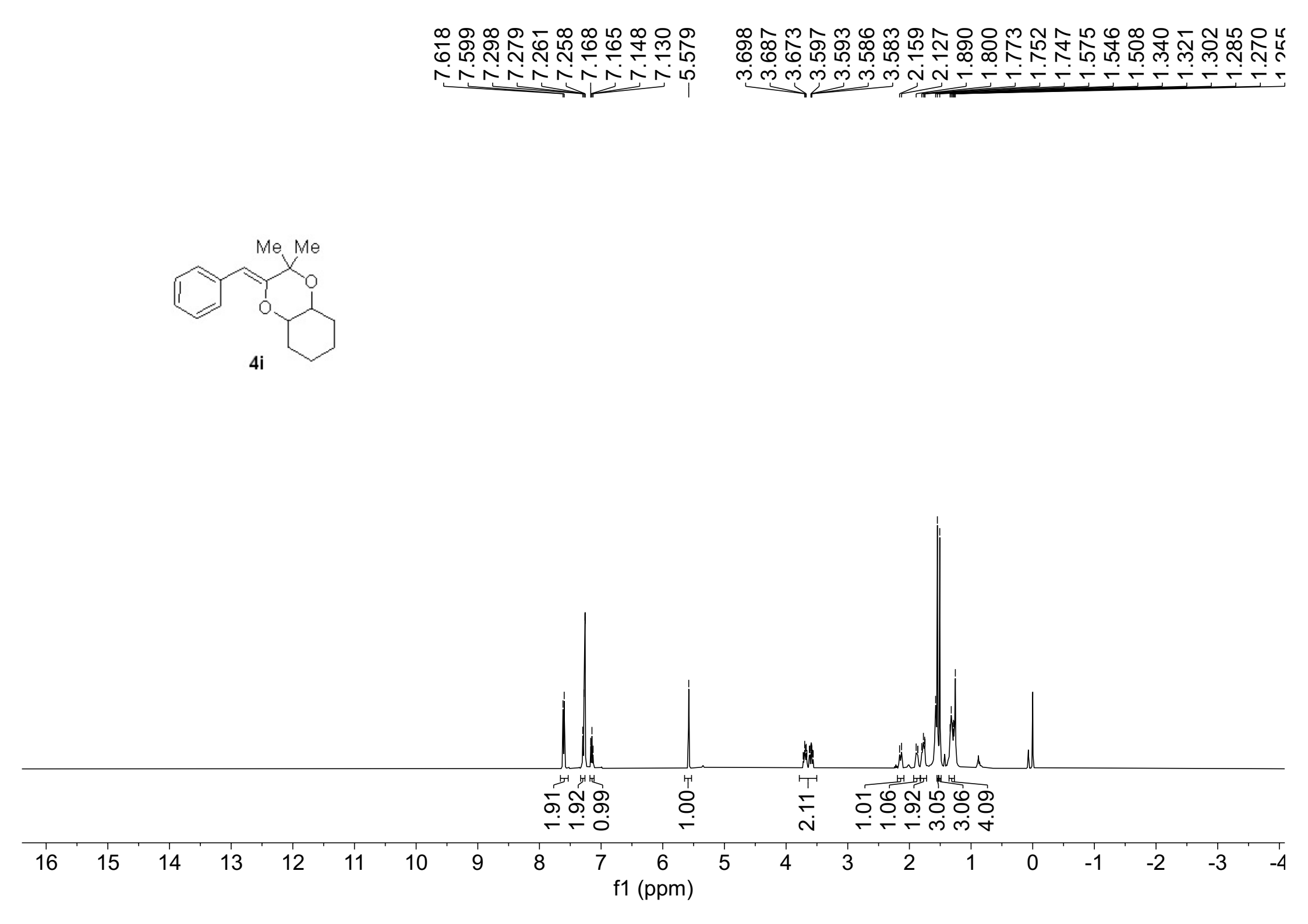
133.725
133.186
132.246
128.066
127.652
127.597
127.328
127.306
125.965
125.515
106.596
77.477
77.159
76.842
73.373
68.398
60.455
26.820
Me
Me
O
O
4h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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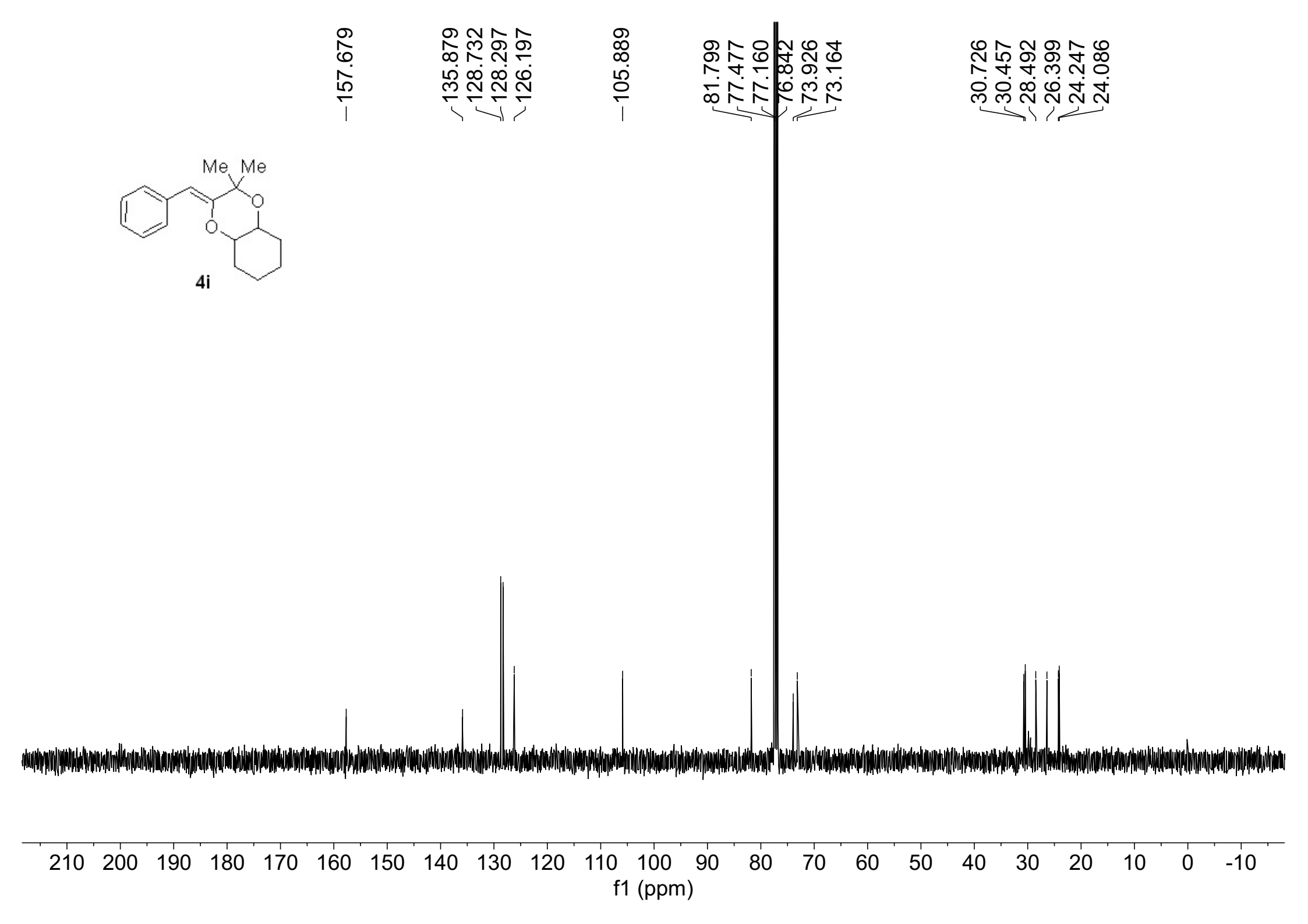
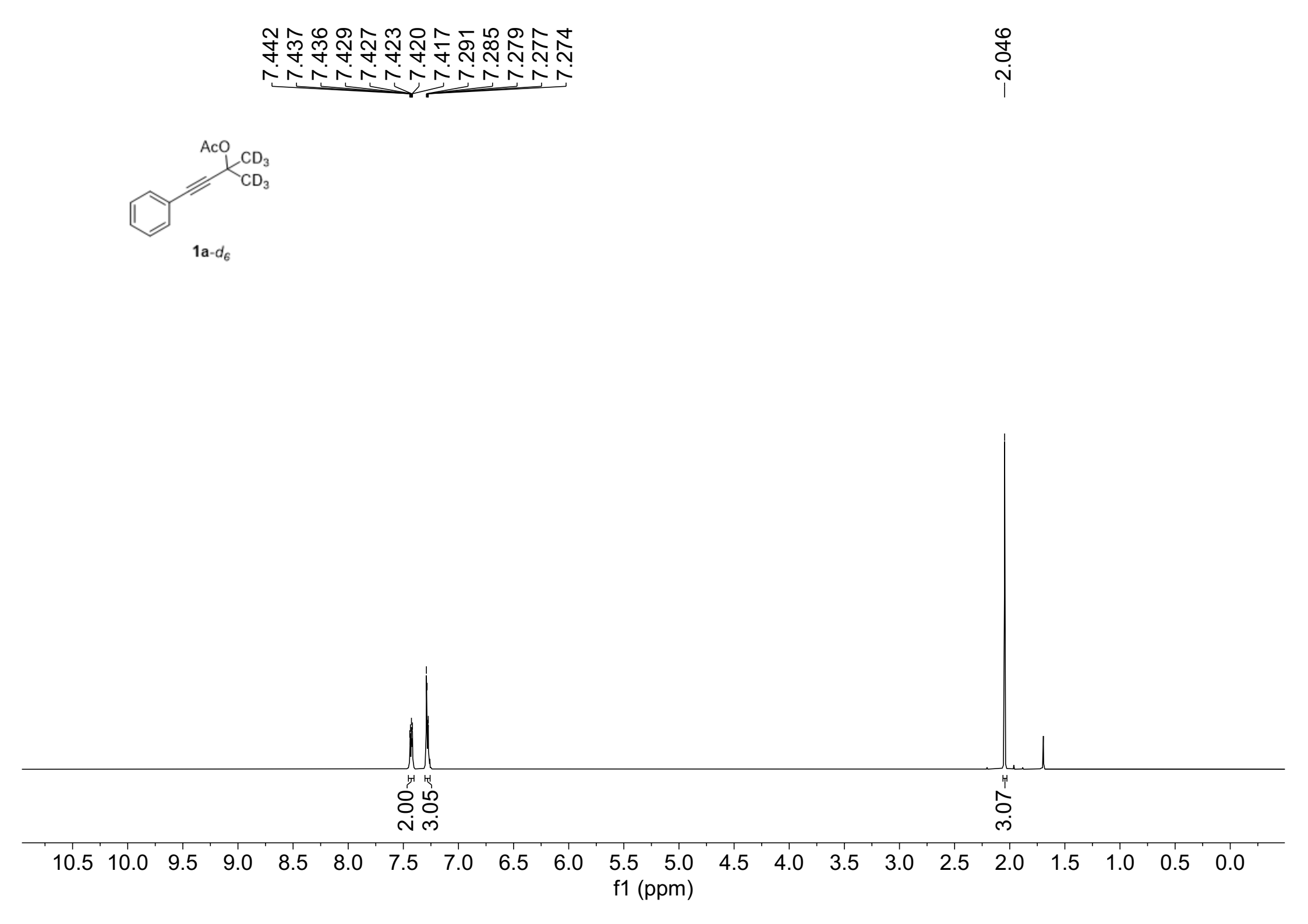
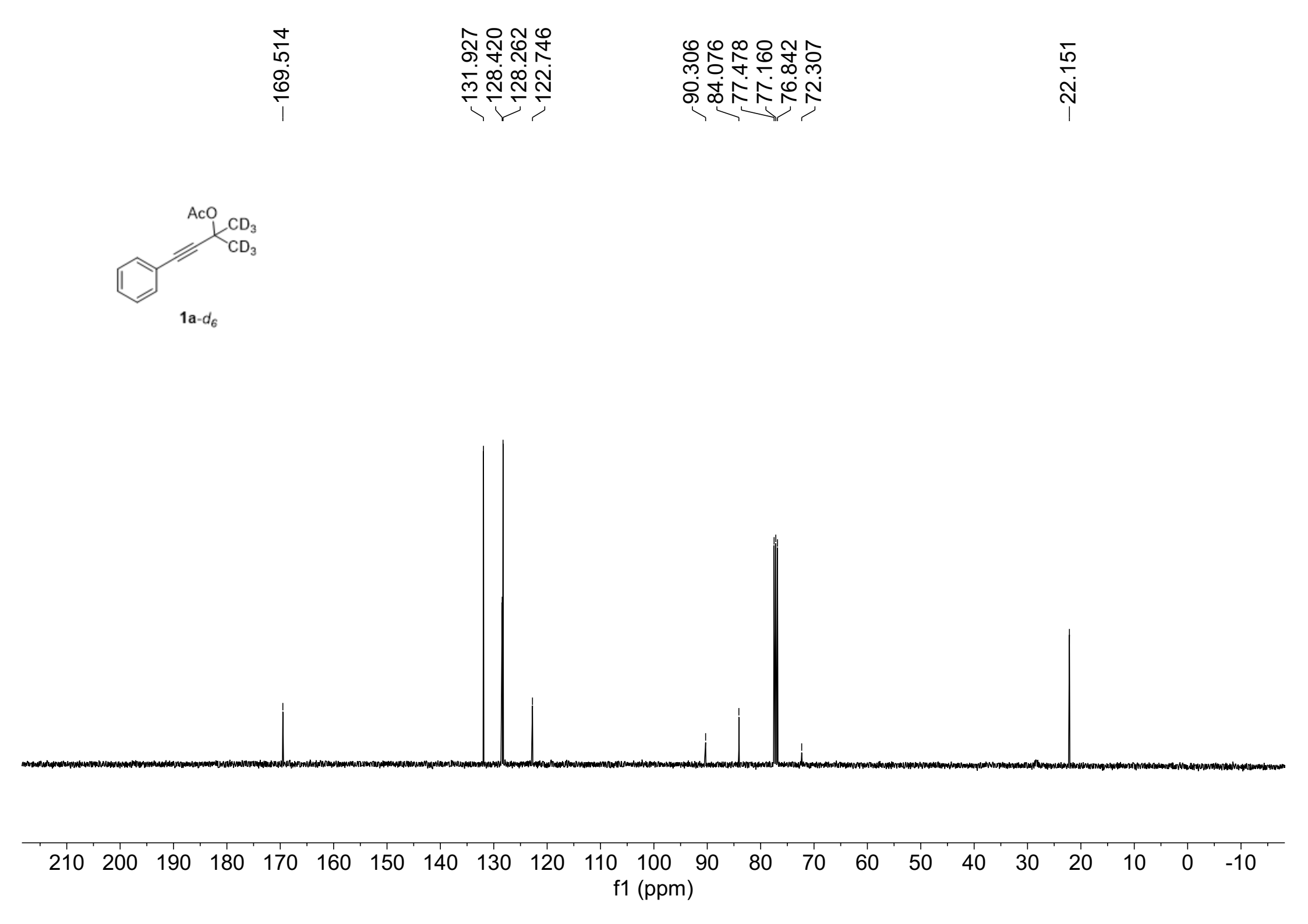
7.599
7.298
7.279
7.261
7.258
7.168
7.165
7.148
7.130
5.579
3.698
3.687
3.673
3.597
3.593
3.586
3.583
2.159
2.127
1.890
1.800
1.773
1.752
1.747
1.575
1.546
1.508
1.340
1.321
1.302
1.285
1.270
Me
Me
O
O
4i
1.91
1.92
0.99
1.00
2.11
1.01
1.06
1.92
3.05
3.06
4.09
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


157.679
135.879
128.732
128.297
126.197
105.889
81.799
77.477
77.160
76.842
73.926
73.164
30.726
30.457
28.492
26.399
24.247
24.086
Me
Me
O
O
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.442
7.437
7.436
7.429
7.427
7.423
7.420
7.417
7.291
7.285
7.279
7.277
7.274
2.046
AcO
CD3
CD3
1a-d6
2.00
3.05
3.07
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)


169.514
131.927
128.420
128.262
122.746
90.306
84.076
77.478
77.160
76.842
72.307
22.151
AcO
CD3
CD3
1a-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)