Supporting Information for:

Using Rh(III)-Catalyzed C−H activation as a Tool for the Selective Functionalization of Ketone-Containing Molecules

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1. General remarks

All catalysis reactions were carried out in flame-dried reaction vessels with Teflon screw caps under argon. Reaction temperature are reported as the temperature of the oil bath surrounding the vessel Unless otherwise noted, all reactions were carried out in oven-dried glassware and without protective gas atmosphere. Reaction temperatures are reported as the temperature of the oil bath surrounding the vessel.

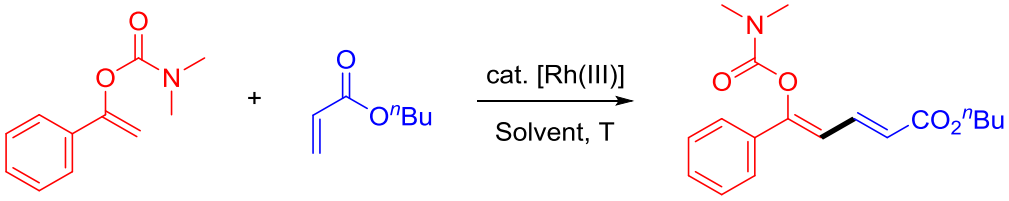
The following solvents were purified by distillation over the drying agents indicated in parentheses: THF (Na/benzophenone), toluene (CaH_2). Additional anhydrous solvents (<50 ppm H_2O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere. Commercially available chemicals were obtained from Acros Organics, Sigma-Aldrich, Alfa Aesar, ABCR, TCI Europe, Combi-Blocks, and used as received unless otherwise stated. $[Cp^*RhCl_2]_2$, $AgSbF_6$ and self-dried $Cu(OAc)_2$ were stored in a glove box.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash column chromatography was performed on Merck silica gel (40-63 mesh). Preparative HPLC was carried out on an Agilent Technologies 1260 infinity system equipped with preparative G1361A pumps, a G2260A autosampler, a G1316A column oven, a G1364B fraction collector and a DAD G1315D detector (λ_1 = 210 nm and λ_2 = 254 nm), using a Zorbax SB-C18 column (9.4 mm × 100 mm, particle size: 5 µm). Data evaluation was performed using CHEMSTATION for LC 3D Systems version Rev. B. 04.03[16] (Agilent Technologies). ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded at room temperature on a Bruker AV 300 or AV 400 and Agilent 600 (DD2). Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 53.84 ppm). ^{19}F-NMR spectra are not calibrated and δ (ppm) is given relative to CCl_3F. Coupling constants (J) are quoted in Hz. GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975

inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, film: 0.25 µm). The major signals are quoted in *m*/*z* with the relative intensity in parentheses. The methods used start with the injection temperature T_0. After holding this temperature for 3 min, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t (method 50_40: T_0 = 50 °C, T_1 = 290 °C, ramp = 40 °C/min, t = 4 min). Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTof. High resolution ESI mass spectra were recorded on a Thermo-Fisher Scientific Orbitrap LTQ XL. Exact EI mass spectra were recorded on a Waters-Micromass GC-Tof. Major signals are quoted in *m*/*z*. Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur. The wave numbers (ν) of recorded IR-signals are quoted in cm^{-1}.

2. Reaction optimisation

Table 1. Reaction optimisation.



1a **2a** **3aa**

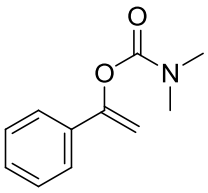
Entry	Solvent	T (°C)	Yield[b] (%)
1	1,4-dioxane	120	47[c]
2	DMF	120	50
3	*t*-AmylOH	120	55
4	DCE	120	50
5	MeCN	60	18
6	THF	60	50
7	EtOH	60	70
8	**MeOH**	**60**	**85**
9[d]	MeOH	60	0
10[e]	MeOH	60	30
11[f]	MeOH	60	0

Standard conditions: **1** (0.20 mmol), **2a** (0.30 mmol), 2.5 mol% [(Cp*RhCl$_2$)$_2$], 10 mol% AgSbF$_6$, 2.1 equiv Cu(OAc)$_2$, solvent (1.0 mL), 16 h, under Ar; [b] NMR yield using CH_2Br_2 as standard; [c] Isolated yield; [d] without Cu(OAc)$_2$; [e] without AgSbF$_6$; [f] without [(Cp*RhCl$_2$)$_2$]. See general procedure.

3. Enol carbamate formation

*General procedure A (described for the formation of **1a**):*[1] Sodium hydride (720 mg, 18.0 mmol, 1.2 equiv, 60 % suspension in oil) was added in portions to dry DMSO (33 mL). After stirring for 2 h at 50 °C the mixture was cooled to room temperature. To the grey solution acetophenone (1.80 g, 15.0 mmol, 1.0 equiv) in 3.6 mL DMSO was added dropwise in 15 min, the addition being slightly exothermic and changing the color of the solution to yellow. This solution was left stirring for 15 min before dimethylcarbamoyl chloride (1.66 mL, 18.0 mmol, 1.2 equiv) in 3.6 mL DMSO was added dropwise in 15 min, while maintaining room temperature. After stirring overnight, water (30 mL) was carefully added to the orange solution. The mixture was extracted with Et_2O (3 × 30 mL) and the combined extracts were washed with brine and dried over magnesium sulfate. Purification by flash chromatography (pentane/ethyl acetate 5:1 to 4:1) afforded the desired enol carbamate **1a** as a colorless oil (1.48 g, 7.75 mmol, 52%).

1-Phenylvinyl dimethylcarbamate (1a)



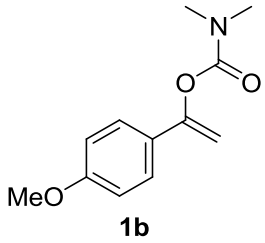
1a

R_f (pentane/ethyl acetate 2:1): 0.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46−7.51 (m, 2H, ArH), 7.27−7.38 (m, 3H, ArH), 5.43 (d, *J* = 2.0 Hz, 1H, CH*H*), 5.04 (d, *J* = 2.0 Hz, 1H, C*H*H), 3.12 (s, 3H, CH_3), 2.98 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.6, 153.5, 135.1, 128.8, 128.5, 125.0, 101.7, 36.8, 36.5. GC-MS t_R (50_40): 8.0 min. EI-MS *m/z* (%): 191 (28), 103 (9), 91 (8), 77 (12), 72 (100), 51 (7).

1-(*p*-Methoxyphenyl)vinyl dimethylcarbamate (1b)

Prepared from *p*-methoxyacetophenone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1 to 1:1) afforded **1b** as a colorless solid (185 mg, 0.84 mmol, 17%).

[1] Panella, L.; Feringa, B. L.; de Vries, J. G.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 4177-4180.

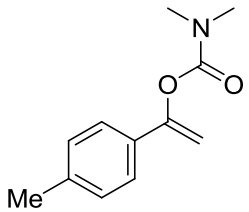


1b

R_f (pentane/ethyl acetate 4:1): 0.16. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.41 (d, *J* = 8.9 Hz, 2H, ArH), 6.86 (d, *J* = 8.9 Hz, 2H, ArH), 5.30 (d, *J* = 2.0 Hz, 1H, CH*H*), 4.92 (d, *J* = 2.0 Hz, 1H, C*H*H), 3.79 (s, 3H, CH_3), 3.10 (s, 3H, CH_3), 2.96 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.0, 154.6, 153.2, 127.7, 126.3, 113.9, 99.8, 55.3, 36.7, 36.4. ATR-FTIR ν (cm^{-1}): 2933, 2827, 1715, 1643, 1609, 1576, 1510, 1456, 1445, 1389, 1302, 1248, 1157, 1096, 1063, 1028, 926, 853, 831, 810, 760. GC-MS t_R (50_40)**:** 8.7 min. EI-MS *m/z* (%): 221 (13), 135 (7), 133 (7), 132 (8), 89 (5), 77 (8), 72 (100). HR-MS (ESI) m/z calculated for $C_{12}H_{15}NO_3Na$ $(M + Na)^+$ 244.0944, found 244.0950.

1-(*p*-Tolyl)vinyl dimethylcarbamate (1c)

Prepared from *p*-methylacetophenone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **1c** as a colorless oil (313 mg, 1.52 mmol, 30%).

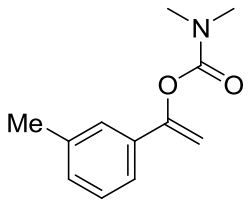


1c

R_f (pentane/ethyl acetate 4:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37 (d, *J* = 8.3 Hz, 2H, ArH), 7.14 (d, *J* = 8.3 Hz, 2H, ArH), 5.37 (d, *J* = 2.0 Hz, 1H, CH*H*), 4.97 (d, *J* = 2.0 Hz, 1H, C*H*H), 3.12 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.34 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 154.7, 153.6, 138.8, 132.4, 129.3, 124.9, 100.8, 36.8, 36.6, 21.4. ATR-FTIR ν (cm^{-1}): 2926, 2849, 1717, 1645, 1512, 1489, 1447, 1387, 1312, 1288, 1260, 1159, 1094, 1063, 1030, 1018, 926, 872, 854, 820, 758, 725. GC-MS t_R (50_40): 8.3 min. EI-MS *m/z* (%): 205 (31), 117 (10), 115 (12), 105 (5), 91 (7), 77 (7), 72 (100), 65 (5). HR-MS (ESI) m/z calculated for $C_{12}H_{15}NO_2Na$ $(M + Na)^+$ 228.0995, found 228.0998.

1-(*m*-Tolyl)vinyl dimethylcarbamate (1d)

Prepared from *m*-methylacetophenone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **1d** as a colorless oil (361 mg, 1.76 mmol, 35%).

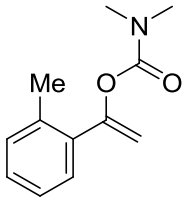


1d

R_f (pentane/ethyl acetate 5:1): 0.19. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.20−7.32 (m, 3H, ArH), 7.13 (m, 1H, ArH), 5.41 (d, *J* = 2.0 Hz, 1H, CH*H*), 5.02 (d, *J* = 2.0 Hz, 1H, C*H*H), 3.12 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.6, 153.6, 138.1, 135.1, 129.6, 128.4, 125.7, 122.1, 101.5, 36.7, 36.5, 21.6. ATR-FTIR ν (cm^{-1}): 2924, 1717, 1640, 1603, 1584, 1487, 1447, 1389, 1265, 1157, 1105, 1084, 1063, 1030, 932, 872, 856, 789, 758, 712. GC-MS t_R (50_40): 8.2 min. EI-MS *m/z* (%): 206 (5), 205 (36), 115 (12), 105 (5), 91 (7), 77 (5), 72 (100), 65 (6), 63 (5), 44 (5), 42 (5), 40 (6). HR-MS (ESI) m/z calculated for $C_{12}H_{15}NO_2Na$ $(M + Na)^+$ 228.0995, found 228.0998.

1-(*o*-Tolyl)vinyl dimethylcarbamate (1e)

Prepared from *o*-methylacetophenone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 10:1) afforded **1e** as a colorless oil (501 mg, 2.44 mmol, 49%).

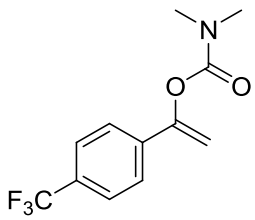


1e

R_f (pentane/ethyl acetate 10:1)**:** 0.20. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm) 7.46 (m, 1H, ArH), 7.19−7.31 (m, 3H, ArH), 5.24 (d, *J* = 1.4 Hz, 1H, CH*H*), 5.02 (d, *J* = 1.4 Hz, 1H, C*H*H), 3.06 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 2.50 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.1, 154.0, 135.8, 135.6, 130.3, 128.9, 128.4, 125.5, 104.8, 36.3, 36.2, 20.2. ATR-FTIR ν (cm^{-1}): 2930, 1717, 1659, 1489, 1456, 1389, 1292, 1252, 1159, 1125, 1076, 1030, 926, 880, 860, 758, 729. GC-MS t_R (50_40): 7.9 min. EI-MS *m/z* (%): 162 (8), 160 (6), 117 (6), 116 (16), 115 (10) 115 (19), 91 (6), 89 (5), 72 (100), 65 (5). HR-MS (ESI) m/z calculated for $C_{12}H_{15}NO_2Na$ $(M + Na)^+$ 228.0995, found 228.0999.

1-(4-(Trifluoromethyl)phenyl)vinyl dimethylcarbamate (1f)

Prepared from *p*-(trifluoromethyl)acetophenone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **1f** as a colorless oil (636 mg, 2.45 mmol, 49%).



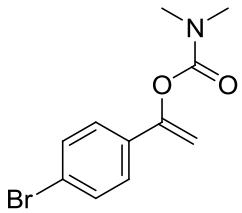
1f

R_f (pentane/ethyl acetate 4:1): 0.23. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.58 (br s, 4H, ArH), 5.50 (d, *J* = 2.3 Hz, 1H, CH*H*), 5.14 (d,

J = 2.3 Hz, 1H, C*H*H), 3.11 (s, 3H, CH_3), 2.96 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.3, 152.3, 138.7, 130.5 (q, *J* = 33 Hz), 125.5 (q, *J* = 4 Hz), 125.2, 124.1 (q, *J* = 272 Hz), 103.8, 36.7, 36.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) −62.7. ATR-FTIR ν (cm^{-1}): 2942, 1721, 1645, 1618, 1578, 1489, 1447, 1393, 1323, 1300, 1263, 1159, 1115, 1096, 1065, 1030, 1015, 930, 883, 860, 841, 762, 750. GC-MS t_R (50_40): 7.8 min. EI-MS *m/z* (%): 259 (16), 240 (11), 171 (10), 151 (15), 125 (5), 75 (6), 73 (8), 72 (100), 44 (8), 42 (6), 40 (13). HR-MS (ESI) m/z calculated for $C_{12}H_{12}F_3NO_2Na$ $(M + Na)^+$ 282.0712, found 282.0710.

1-(*p*-Bromophenyl)vinyl dimethylcarbamate (1g)

Prepared from *p*-bromoacetophenone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **1g** as a colorless oil (534 mg, 1.98 mmol, 40%).

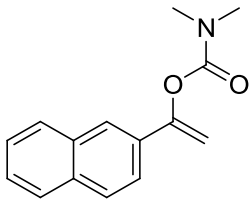


1g

R_f (pentane/ethyl acetate 5:1): 0.17. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46 (d, *J* = 8.7 Hz, 2H, ArH), 7.34 (d, *J* = 8.7 Hz, 2H, ArH), 5.41 (d, *J* = 2.2 Hz, 1H, CH*H*), 5.05 (d, *J* = 2.2 Hz, 1H, C*H*H), 3.11 (s, 3H, CH_3), 2.97 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.5, 152.6, 134.3, 131.7, 126.7, 122.9, 102.4, 36.9, 36.6. ATR-FTIR ν (cm^{-1}): 2932, 1717, 1641, 1589, 1485, 1447, 1387, 1287, 1258, 1159, 1092, 1071, 1028, 1007, 928, 878, 858, 826, 770, 758. GC-MS t_R (50_40): 8.8 min. EI-MS *m/z* (%): 271 (15), 269 (10), 183 (5), 171 (5), 169 (6), 102 (11), 90 (7), 89 (7), 76 (8), 75 (7), 74 (8), 73 (5), 72 (100), 50 (5), 42 (7). HR-MS (ESI) m/z calculated for $C_{11}H_{12}BrNO_2Na$ $(M + Na)^+$ 291.9944, found 291.9942.

1-(Naphthalen-2-yl)vinyl dimethylcarbamate (1h)

Prepared from 2-acetylnaphthalene on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **1h** as a colorless oil (750 mg, 3.11 mmol, 62%).



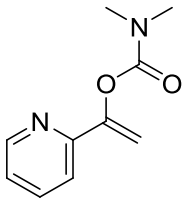
1h

R_f (pentane/ethyl acetate 2:1): 0.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.92 – 7.89 (m, 1H, ArH), 7.87 – 7.78 (m, 3H, ArH), 7.63 (dd, *J* = 8.7, 1.9 Hz, 1H, ArH), 7.52 – 7.43 (m, 2H, ArH), 5.57 (d, *J*

= 2.1 Hz, 1H, CH*H*), 5.14 (d, *J* = 2.1 Hz, 1H, C*H*H), 3.19 (s, 3H, CH_3), 3.01 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.7, 153.5, 133.5, 133.2, 132.5, 128.6, 128.3, 127.7, 126.5, 126.4, 124.1, 123.0, 102.3, 36.9, 36.6. ATR-FTIR ν (cm^{-1}): 1715, 1641, 1506, 1489, 1445, 1391, 1263, 1229, 1159, 1130, 1080, 1030, 928, 860, 818, 733, 700. GC-MS t_R (50_40): 9.5 min. EI-MS *m/z* (%): 242 (8), 241 (55), 153 (11), 152 (27), 151 (9), 141 (25), 127 (20), 126 (8), 115 (16), 72 (100), 42 (9). HR-MS (ESI) m/z calculated for $C_{15}H_{15}NO_2Na$ $(M + Na)^+$ 264.0995, found 264.0998.

1-(Pyridin-2-yl)vinyl dimethylcarbamate (1i)

Prepared from 2-acetylpyridine on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 15:1) afforded **1i** as a colorless oil (930 mg, 4.84 mmol, 97%).

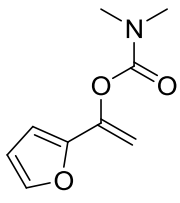


1i

R_f (pentane/ethyl acetate 2:1): 0.24. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.58 (d, *J* = 3.9 Hz, 1H, ArH), 7.68 (td, *J* = 7.9, 1.8 Hz, 1H, ArH), 7.41 (d, *J* = 7.9 Hz, 1H, ArH), 7.20 (dd, *J* = 7.0, 5.0 Hz, 1H, ArH), 6.01 (d, *J* = 1.5 Hz, 1H, CH*H*), 5.21 (d, *J* = 1.5 Hz, 1H, C*H*H), 3.14 (s, 3H, CH_3), 2.99 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.7, 152.5, 152.5, 149.4, 136.8, 123.3, 119.3, 104.7, 36.9, 36.7. ATR-FTIR ν (cm^{-1}): 1713, 1645, 1586, 1566, 1470, 1433, 1391, 1306, 1265, 1244, 1165, 1125, 1090, 1030, 991, 928, 793, 746, 625. GC-MS t_R (50_40): 8.0 min. EI-MS *m/z* (%): 148 (21), 136 (8), 104 (7), 93 (10), 78 (13), 72 (100), 65 (9), 51 (13), 50 (8), 42 (7). HR-MS (ESI) m/z calculated for $C_{10}H_{12}N_2O_2Na$ $(M + Na)^+$ 215.0791, found 215.0799.

1-(Furan-2-yl)vinyl dimethylcarbamate (1j)

Prepared from 2-acetylfurane on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 5.5:1) afforded **1j** as a colorless oil (363 mg, 2.00 mmol, 40%).



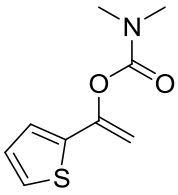
1j

R_f (pentane/ethyl acetate 2:1): 0.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.37 (dd, *J* = 1.9, 0.8 Hz, 1H, ArH), 6.38 (dd, *J* = 3.4, 1.8 Hz, 1H, ArH), 6.33 (dd, *J* = 3.4, 0.8 Hz, 1H, ArH), 5.43 (d, *J* = 2.0 Hz, 1H, CH*H*), 4.97 (d, *J* = 2.0 Hz, 1H, C*H*H), 3.08 (s, 3H, CH_3), 2.99 (s, 3H, CH_3). ^{13}C NMR

(75 MHz, $CDCl_3$) δ (ppm) 154.3, 149.5, 144.9, 142.9, 111.4, 107.3, 100.2, 36.9, 36.6. ATR-FTIR ν (cm^{-1}): 1717, 1653, 1489, 1447, 1383, 1296, 1267, 1225, 1159, 1105, 1028, 1009, 937, 914, 883, 866, 854, 812, 739. GC-MS t_R (50_40): 7.3 min. EI-MS *m/z* (%): 181 (20), 72 (100), 65 (8), 63 (7), 53 (9), 42 (14), 39 (12). HR-MS (ESI) m/z calculated for $C_9H_{11}NO_3Na$ $(M + Na)^+$ 204.0631, found 204.0638.

1-(Thiophen-2-yl)vinyl dimethylcarbamate (1k)

Prepared from 2-acetylthiophene on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **1k** as a colorless oil (366 mg, 1.86 mmol, 37%).

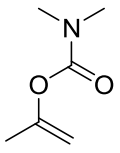


1k

R_f (pentane/ethyl acetate 2:1): 0.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.21 (dd, *J* = 5.0, 1.2 Hz, 1H, ArH), 7.11 (dd, *J* = 3.7, 1.2 Hz, 1H, ArH), 6.96 (dd, *J* = 5.0, 3.7 Hz, 1H, ArH), 5.34 (d, *J* = 2.3 Hz, 1H, CH*H*), 4.96 (d, *J* = 2.3 Hz, 1H, C*H*H), 3.08 (s, 3H, CH_3), 2.98 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.2, 148.2, 139.1, 127.5, 125.6, 124.5, 100.7, 36.8, 36.5. ATR-FTIR ν (cm^{-1}): 1717, 1636, 1518, 1487, 1447, 1435, 1389, 1352, 1256, 1227, 1213, 1157, 1086, 1061, 1036, 924, 851, 756, 700. GC-MS t_R (50_40): 7.9 min. EI-MS *m/z* (%): 197 (28), 109 (11), 97 (11), 72 (100), 65 (7), 45 (11), 42 (12). HR-MS (ESI) m/z calculated for $C_9H_{11}NO_2SNa$ $(M + Na)^+$ 220.0403, found 220.0398.

Prop-1-en-2-yl dimethylcarbamate (4a)

Prepared from acetone on a 5.00 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **4a** as a colorless oil (100 mg, 0.77 mmol, 15%).[2]



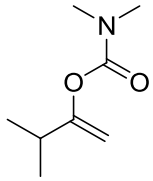
4a

R_f (pentane/ethyl acetate 2:1): 0.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.68 – 4.62 (m, 2H, CH_2), 2.95 (d, *J* = 3.0 Hz, 6H, 2 × CH_3), 1.94 (d, *J* = 0.7 Hz, 3H, CH_3). GC-MS t_R (50_40): 5.3 min. EI-MS *m/z* (%): 282 (8), 281 (31), 208 (32), 207 (69), 193 (8), 191 (20), 177 (10), 129 (9), 72 (100), 56 (10), 44 (7), 43 (8), 42 (25), 41 (8), 39 (23).

[2] Due to the very high volatility of this compound, no other analysis could be measured for full characterisation. However, the ^{1}H NMR and the fully characterised product **5aa** formed after reaction with *n*-butyl acrylate **2a** reveal the formation of this precise enol carbamate.

3-Methylbut-1-en-2-yl dimethylcarbamate (4b)

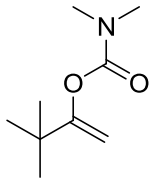
To a solution of KHMDS (3.00 mmol, 600 mg, 1.0 equiv) in dry THF (5 mL) and dry toluene (6 mL) at –78 °C was added dropwise 3-methyl-2-butanone (3.00 mmol, 323 µL, 1.0 equiv) in THF (5 mL) during 5 min. Then the mixture was stirred at –78 °C for 1 h to complete the formation of the potassium enolate and dimethylcarbamoyl chloride in THF (5 mL) was added dropwise. After stirring overnight while reaching very slowly room temperature (acetonitrile/dry ice bath, water (10 mL) was carefully added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined extracts were washed with brine and dried over magnesium sulfate. Purification by flash chromatography (pentane/ethyl acetate 5:1 to 2:1) afforded the desired enol carbamate **4b** as a colorless oil (65 mg, 0.41 mmol, 14%).[3]


4b

R_f (pentane/ethyl acetate 2:1): 0.58. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.69 (s, 2H, CH_2), 2.97 (s, 3H, CH_3), 2.95 (s, 3H, CH_3), 2.45 (hept, *J* = 6.9 Hz, 1H, CH), 1.08 (d, *J* = 6.9 Hz, 6H, 2 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 161.9, 154.8, 98.3, 36.7, 36.4, 32.5, 20.4. ATR-FTIR ν (cm^{-1}): 1650, 1608, 1488, 1427, 1372, 1337, 1306, 1247, 1143, 1089, 1010, 995, 939, 870, 828, 743, 700, 645. GC-MS was not informative for this compound. HR-MS (ESI) m/z calculated for $C_8H_{15}NO_2Na$ $(M + Na)^+$ 180.0995, found 180.0977.

3,3-Dimethylbut-1-en-2-yl dimethylcarbamate (4c)

Prepared from pinacolone on a 25.0 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 8:1 to 6:1) afforded **4c** as a colorless oil (1.1 g, 6.42 mmol, 26%).


4c

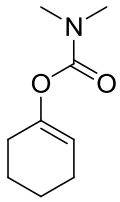
R_f (pentane/ethyl acetate 10:1): 0.29. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 4.79 (d, *J* = 1.9 Hz, 1H, CH*H*), 4.66 (d, *J* = 1.9 Hz, 1H, C*H*H), 2.97 (d, *J* = 14.0 Hz, 6H, 2 × CH_3), 1.11 (s, 9H, 3 × CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 163.1, 154.9, 97.7, 36.8, 36.4, 28.0. ATR-FTIR ν (cm^{-1}): 2969, 1719, 1659, 1481, 1462, 1381, 1362, 1271, 1221, 1142, 1063, 1036, 1022, 928, 872, 860,

[3] Procedure inspired by: Suero, M. G.; De la Campa, R.; Torre-Fernández, L.; García-Granda, S.; Flórez, J. *Chem. Eur. J.* **2012**, *18*, 7287-7285.

756. GC-MS t_R (50_40): 6.5 min. EI-MS *m/z* (%): 171 (10), 72 (100), 41 (7), 40 (14). HR-MS (ESI) m/z calculated for $C_9H_{17}NO_2Na$ $(M + Na)^+$ 194.1151, found 194.1157.

Cyclohexenyl dimethylcarbamate (4d)

Prepared from cyclohexanone on a 51.0 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **4d** as a colorless oil (2.47 g, 14.6 mmol, 29%).

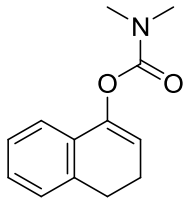


4d

R_f (pentane/ethyl acetate 2:1): 0.62. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.39 – 5.28 (m, 1H, C=CH), 2.92 (s, 3H, CH_3), 2.90 (s, 3H, CH_3), 2.16 – 2.04 (m, 4H, 2 × CH_2), 1.75 – 1.66 (m, 2H, CH_2), 1.60 – 1.52 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 155.1, 148.8, 113.6, 36.5, 36.3, 27.3, 23.8, 22.8, 21.8. ATR-FTIR ν (cm^{-1}): 2930, 1713, 1489, 1447, 1389, 1362, 1273, 1265, 1167, 1130, 1065, 1044, 1013, 916, 874, 862, 797, 760, 621. GC-MS t_R (50_40): 7.3 min. EI-MS *m/z* (%): 169 (20), 72 (100). HR-MS (ESI) m/z calculated for $C_9H_{15}NO_2Na$ $(M + Na)^+$ 192.0995, found 192.1005.

3,4-Dihydronaphthalen-1-yl dimethylcarbamate (4e)

Prepared from α-tetralone on a 25.0 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **4e** as an orange solid (4.00 g, 18.4 mmol, 74%).



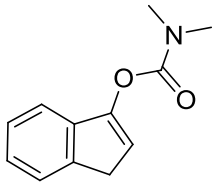
4e

R_f (pentane/ethyl acetate 2:1): 0.48. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.23 – 7.04 (m, 4H, ArH), 5.71 (t, *J* = 4.7 Hz, 1H, C=CH), 3.13 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 2.86 (t, *J* = 8.1 Hz, 2H, $CHCH_2CH_2$), 2.44 (ddd, *J* = 9.0, 7.5, 4.7 Hz, 2H, $CHCH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.9, 146.1, 136.6, 131.3, 127.8, 127.6, 126.5, 120.8, 115.2, 36.8, 36.5, 27.7, 22.2. ATR-FTIR ν (cm^{-1}): 2936, 1717, 1657, 1487, 1449, 1389, 1358, 1335, 1275, 1229, 1182, 1155, 1130, 1082, 1036, 997, 916, 868, 804, 791, 758, 737, 677. GC-MS t_R (50_40): 8.8 min. EI-MS *m/z* (%): 429 (7), 217 (42), 207 (15), 129 (7), 128 (10), 127 (14), 117 (12), 115 (50), 102 (8), 91 (25), 72 (100), 63 (7), 44 (8), 42 (11). HR-MS (ESI) m/z calculated for $C_{13}H_{15}NO_2Na$ $(M + Na)^+$ 240.0995, found 240.1000.

1*H*-inden-3-yl dimethylcarbamate (4f)

Prepared from 1-indanone on a 4.10 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 7:1) afforded **4f** as an orange oil (334 mg, 1.64 mmol, 40%).

Second procedure:[4] A stirred mixture of 1-indanone (2.00 mmol, 264 mg, 1.0 equiv), *N*,*N*- dimethylcarbamoyl chloride (4.00 mmol, 368 µL, 2.0 equiv) and 2,4,6-collidine (121 mg, 1.5 mmol) was irradiated with microwaves in a Biotage® initiator oven (40-45 W and temperature control set at 160 °C) for 12 h. The conversion was evaluated by TLC and the reaction was put under the same heating conditions after addition of *N*,*N*-dimethylcarbamoyl chloride (2.00 mmol, 184 µL, 1.0 equiv) for an additional 4 h. The crude was dissolved in CH_2Cl_2 (60 mL) and washed with 10% aq HCl (2 × 50 mL), dried ($MgSO_4$). Purification by column chromatography (eluent: pentane/ethyl acetate 7:1) afforded **4f** as an orange oil (330 mg, 1.62 mmol, 82%).



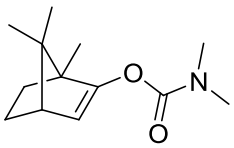
4f

R_f (pentane/ethyl acetate 2:1): 0.58. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43 (dt, *J* = 7.1, 1.0 Hz, 1H, ArH), 7.36 – 7.28 (m, 2H, ArH), 7.26 – 7.20 (m, 1H, ArH), 6.27 (t, *J* = 2.4 Hz, 1H, C=CH), 3.40 (d, *J* = 2.4 Hz, 2H, CH_2), 3.15 (s, 3H, CH_3), 3.04 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.8, 149.6, 142.1, 139.8, 126.3, 125.6, 124.2, 118.0, 114.0, 36.9, 36.7, 35.0. ATR-FTIR ν (cm^{-1}): 1722, 1614, 1603, 1578, 1487, 1464, 1393, 1354, 1308, 1288, 1271, 1233, 1204, 1171, 1157, 1115, 1072, 1017, 995, 970, 914, 847, 758, 716, 640. GC-MS t_R (50_40): 8.6 min. EI-MS *m/z* (%): 203 (25), 103 (17), 102 (15), 77 (21), 76 (7), 72 (100), 42 (8). HR-MS (ESI) m/z calculated for $C_{12}H_{13}NO_2Na$ $(M + Na)^+$ 226.0838, found 226.0843.

(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl dimethylcarbamate (4g)

Prepared from camphor on a 10.0 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 11:1) afforded **4g** as a white amorphous solid (442 mg, 1.98 mmol, 20%).

[4] Procedure inspired by: Seijas, J. A.; Vázquez-Tato, M. P.; Crecente-Campo, J. *Synlett* **2007**, 2420-2424.



4g

R_f (pentane/ethyl acetate 2:1): 0.51. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.48 (d, *J* = 3.6 Hz, 1H, C=CH), 2.97 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 2.31 (t, *J* = 3.6 Hz, 1H, CH), 1.85 (ddt, *J* = 12.0, 8.6, 3.6 Hz, 1H, CH_2CHH), 1.54 (ddd, *J* = 12.0, 8.6, 3.6 Hz, 1H, CH_2CHH), 1.29 (ddd, *J* = 12.0, 9.1, 3.6 Hz, 1H, $CHHCH_2$), 1.14 (ddd, *J* = 12.0, 9.1, 3.6 Hz, 1H, $CHHCH_2$), 0.94 (s, 3H), 0.94 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.1, 154.5, 112.4, 55.8, 53.5, 50.0, 36.6, 36.5, 31.4, 26.3, 20.0, 19.7, 10.2. ATR-FTIR ν (cm^{-1}): 2953, 2872, 1724, 1636, 1622, 1474, 1443, 1385, 1321, 1265, 1209, 1200, 1167, 1136, 1107, 1065, 1015, 993, 862, 835, 802, 756, 623. GC-MS t_R (50_40): 7.8 min. EI-MS *m/z* (%): 223 (11), 72 (100), 41 (7). HR-MS (ESI) m/z calculated for $C_{13}H_{21}NO_2Na$ $(M + Na)^+$ 246.1465, found 246.1469.

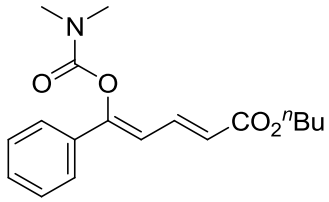
4. Rh(III)-catalysed cross-coupling reactions with activated olefins

General procedure B: A Schlenk tube (8 mL in volume) equipped with a stirring bar was flame-dried under vacuum and back-filled with argon. $[Cp^*RhCl_2]_2$ (2.5-5 mol %), $AgSbF_6$ (10-20 mol %) and $Cu(OAc)_2$ (2.1 equiv) were weighed into the reaction vessel in a glovebox. Enol carbamate (1.0 equiv), olefin (1.5-2.2 equiv) and dry solvent (0.2 M) were added under a stream of argon. The vessel was then sealed and the reaction was allowed to stir at 60 ºC or 100 °C for 16 h.

(2*E*,4*Z*)-Butyl 5-(dimethylcarbamoyloxy)-5-phenylpenta-2,4-dienoate (3aa)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.20 mmol, 38 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv)), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **3aa** as a colorless oil as a mixture of diastereoisomers (49 mg, 0.15 mmol, 77%, (2*E*,4*Z*):(2*Z*,4*Z*) = 88:12). The same reaction performed on a 2.5 mmol scale afforded **3aa** as a colorless oil as a mixture of diastereoisomers (752 mg, 2.37 mmol, 95%, (2*E*,4*Z*):(2*Z*,4*Z*) = 92:8).

Data for major (2*E*,4*Z*) diastereoisomer:



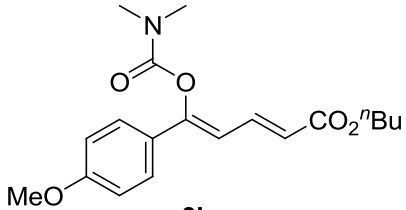
3aa

R_f (pentane/ethyl acetate 2:1): 0.56. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.57 (dd, *J* = 15.4, 11.4 Hz, 1H, CHC*H*=CH), 7.52 – 7.48 (m, 2H, ArH), 7.39 – 7.33 (m, 3H, ArH), 6.53 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.03 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 4.17 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.21 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 1.68 – 1.64 (m, 2H, CH_2), 1.44 – 1.39 (m, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.2, 153.7, 152.8, 137.7, 134.7, 129.7, 128.9, 125.3, 122.1, 115.0, 64.4, 37.0, 36.7, 30.9, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2959, 2928, 2874, 1726, 1713, 1628, 1495, 1447, 1393, 1327, 1316, 1265, 1234, 1138, 1047, 1028, 986, 882, 862, 845, 762, 718, 692. GC-MS t_R (50_40): 10.5 min. EI-MS *m/z* (%): 245 (15), 229 (21), 144 (11), 115 (12), 105 (7), 77 (7), 72 (100). HR-MS (ESI) m/z calculated for $C_{18}H_{23}NO_4Na$ $(M + Na)^+$ 340.1519, found 340.1522.

(2*E*,4*Z*)-butyl 5-(dimethylcarbamoyloxy)-5-(4-methoxyphenyl)penta-2,4-dienoate (3ba)

Prepared by reaction of 1-(*p*-methoxyphenyl)vinyl dimethylcarbamate (**1b**) (0.20 mmol, 44 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ ethyl acetate 3:1) afforded **3ba** as a colorless oil as a mixture of diastereoisomers (59 mg, 0.17 mmol, 85%, (2*E*,4*Z*):(2*Z*,4*Z*):(2*E*,4*E*) = 84:9:7).

Data for major (2*E*,4*Z*) diastereoisomer:



3ba

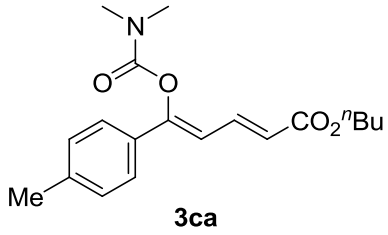
R_f (pentane/ethyl acetate 3:1): 0.28. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 (dd, *J* = 15.4, 11.4 Hz, 1H, CHC*H*=CH), 7.44 (d, *J* = 8.8 Hz, 2H, ArH), 6.88 (d, *J* = 8.8 Hz, 2H, ArH), 6.43 (d, *J* = 11.4 Hz, 1H, C*H*CH=CH), 5.98 (d, *J* = 15.4 Hz, 1H, CHCH=C*H*), 4.15 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.20 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 1.58 – 1.71 (m, 2H, CH_2), 1.33 – 1.47 (m, 2H, CH_2), 0.94 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.3, 160.9, 153.8, 152.7, 138.0, 127.1, 126.8, 121.0, 114.3, 113.2, 64.3, 55.4, 36.9, 36.7, 30.8, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2959, 2934,

2874, 1722, 1707, 1626, 1601, 1574, 1510, 1460, 1390, 1362, 1327, 1304, 1252, 1134, 1080, 1063, 1028, 1045, 988, 889, 841, 826, 754. GC-MS t_R (50_40): 12.1 min. EI-MS *m/z* (%): 347 (16), 275 (7), 259 (19), 246 (5), 203 (5), 174 (5), 159 (6), 135 (8), 72 (100). HR-MS (ESI) m/z calculated for $C_{19}H_{25}NO_5Na$ $(M + Na)^+$ 370.1625, found 370.1623.

(2*E*,4*Z*)-butyl 5-(dimethylcarbamoyloxy)-5-*p*-tolylpenta-2,4-dienoate (3ca)

Prepared by reaction of 1-(*p*-tolyl)vinyl dimethylcarbamate (**1c**) (0.20 mmol, 41 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ca** as a colorless oil as a mixture of diastereoisomers (55 mg, 0.17 mmol, 83%, (2*E*,4*Z*):(2*Z*,4*Z*):(2*E*,4*E*):(2*Z*,4*E*) = 80:10:9:1).

Data for major (2*E*,4*Z*) diastereoisomer:



3ca

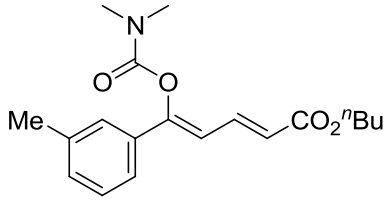
R_f (pentane/ethyl acetate 4:1): 0.22. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56 (dd, *J* = 15.4, 11.4 Hz, 1H, CHC*H*=CH), 7.39 (d, *J* = 8.3 Hz, 2H, ArH), 7.17 (d, *J* = 8.3 Hz, 2H, ArH), 6.48 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.00 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 4.16 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.21 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 1.60 – 1.71 (m, 2H, CH_2), 1.33 – 1.48 (m, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.3, 153.8, 153.0, 140.0, 137.9, 131.8, 129.6, 125.2, 121.6, 114.1, 64.4, 37.0, 36.7, 30.9, 21.5, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2959, 2932, 2872, 1724, 1709, 1628, 1607, 1489, 1454, 1391, 1323, 1263, 1242, 1184, 1136, 1080, 1063, 1044, 1018, 984, 812. GC-MS t_R (50_40): 11.0 min. EI-MS *m/z* (%): 243 (5), 158 (5), 72 (100). HR-MS (ESI) m/z calculated for $C_{19}H_{25}NO_4Na$ $(M + Na)^+$ 354.1676, found 354.1673.

(2*E*,4*Z*)-butyl 5-(dimethylcarbamoyloxy)-5-*m*-tolylpenta-2,4-dienoate (3da)

Prepared by reaction of 1-(*m*-tolyl)vinyl dimethylcarbamate (**1d**) (0.20 mmol, 41 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL)

at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3da** as a colorless oil as a mixture of diastereoisomers (52 mg, 0.16 mmol, 78%, (2*E*,4*Z*):(2*Z*,4*Z*)(2*E*,4*E*) = 88:10:2).

Data for major (2*E*,4*Z*) diastereoisomer:



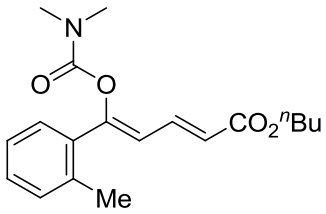
3da

R_f (pentane/ethyl acetate 4:1): 0.23. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56 (dd, *J* = 15.5, 11.4 Hz, 1H, CHC*H*=CH), 7.21 − 7.34 (m, 3H, ArH), 7.14 (m, 1H, ArH), 6.50 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.02 (dd, *J* = 15.5, 0.8 Hz, 1H, CHCH=C*H*), 4.17 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.21 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.59 – 1.74 (m, 2H, CH_2), 1.35 – 1.48 (m, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.2, 153.8, 153.0, 138.5, 137.7, 134.6, 130.6, 128.7, 125.9, 122.4, 121.9, 114.8, 64.4, 36.9, 36.7, 30.9, 21.6, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2959, 2932, 2874, 1722, 1709, 1626, 1487, 1456, 1391, 1319, 1265, 1246, 1198, 1136, 1051, 984, 916, 882, 787. GC-MS t_R (50_40): 11.0 min. EI-MS *m/z* (%): 331 (5), 259 (13), 243 (16), 230 (5), 158 (7), 129 (9), 115 (5), 91 (8), 73 (5), 72 (100), 41 (5). HR-MS (ESI) m/z calculated for $C_{19}H_{25}NO_4Na$ $(M + Na)^+$ 354.1676, found 354.1687.

(2*E*,4*Z*)-butyl 5-(dimethylcarbamoyloxy)-5-*o*-tolylpenta-2,4-dienoate (3ea)

Prepared by reaction of 1-(*o*-tolyl)vinyl dimethylcarbamate (**1e**) (0.20 mmol, 41 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ea** as a colorless oil as a mixture of diastereoisomers (48 mg, 0.14 mmol, 72%, (2*E*,4*Z*):(2*Z*,4*Z*) = 90:10).

Data for major (2*E*,4*Z*) diastereoisomer:



3ea

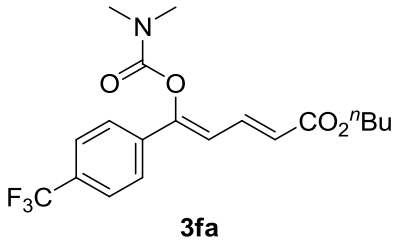
R_f (pentane/ethyl acetate 10:1): 0.20. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.63 (dd, *J* = 15.5, 11.4 Hz, 1H, CHC*H*=CH), 7.37 (m, 1H, ArH), 7.14 − 7.28 (m, 3H, ArH), 6.03 (dd, *J* = 11.4, 0.7 Hz, 1H, C*H*CH=CH), 5.96 (dd, *J* = 15.5, 0.7 Hz, 1H, CHCH=C*H*), 4.17 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.12 (s, 3H,

CH_3), 2.90 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 1.60 – 1.72 (m, 2H, CH_2), 1.34 – 1.48 (m, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.2, 153.8, 153.4, 137.6, 136.0, 135.5, 130.9, 129.2, 128.8, 125.9, 121.6, 118.3, 64.4, 36.8, 36.6, 30.9, 20.6, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2959, 2932, 2874, 1724, 1711, 1636, 1487, 1456, 1391, 1317, 1263, 1229, 1136, 1117, 1053, 1036, 986, 885, 862, 754, 725. GC-MS t_R (50_40): 10.5 min. EI-MS *m/z* (%): 259 (5), 129 (6), 115 (5), 91 (5), 72 (100). HR-MS (ESI) m/z calculated for $C_{19}H_{25}NO_4Na$ $(M + Na)^+$ 354.1676, found 354.1677.

(2*E*,4*Z*)-butyl 5-(dimethylcarbamoyloxy)-5-(4-(trifluoromethyl)phenyl)penta-2,4-dienoate (3fa)

Prepared by reaction of 1-(4-(trifluoromethyl)phenyl)vinyl dimethylcarbamate (**1f**) (0.20 mmol, 52 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3fa** as a colorless oil as a mixture of diastereoisomers (48 mg, 0.12 mmol, 83%, (2*E*,4*Z*):(2*Z*,4*Z*) = 85:15).

Data for major (2*E*,4*Z*) diastereoisomer:



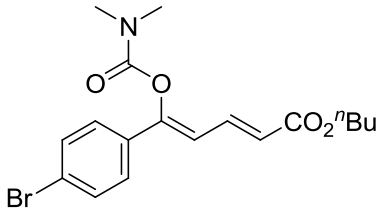
3fa

R_f (pentane/ethyl acetate 4:1): 0.31. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 − 7.69 (m, 5H, ArH and CHC*H*=CH), 6.57 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.08 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 4.17 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.22 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 1.60 – 1.72 (m, 2H, CH_2), 1.34 – 1.48 (m, 2H, CH_2), 0.95 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 166.9, 153.5, 151.2, 137.0, 134.4 (q, *J* = 239 Hz), 131.2 (q, *J* = 33 Hz), 125.9 (q, *J* = 4 Hz), 125.5, 123.5, 116.8, 64.6, 37.0, 36.7, 30.8, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2961, 2936, 2876, 1724, 1713, 1632, 1618, 1456, 1410, 1393, 1323, 1265, 1236, 1157, 1115, 1069, 1044, 1015, 982, 853, 826,752. GC-MS t_R (50_40): 10.4 min. EI-MS *m/z* (%): 212 (8), 183 (5), 173 (5), 145 (5), 73 (5), 72 (100). HR-MS (ESI) m/z calculated for $C_{19}H_{22}F_3NO_4Na$ $(M + Na)^+$ 408.1393, found 408.1394.

(2*E*,4*Z*)-butyl 5-(4-bromophenyl)-5-(dimethylcarbamoyloxy)penta-2,4-dienoate (3ga)

Prepared by reaction of 1-(*p*-bromophenyl)vinyl dimethylcarbamate (**1g**) (0.20 mmol, 54 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **3ga** as an orange solid as a mixture of diastereoisomers (51 mg, 0.13 mmol, 62%, (2*E*,4*Z*):(2*Z*,4*Z*) = 89:11).

Data for major (2*E*,4*Z*) diastereoisomer:



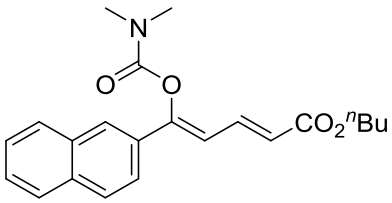
3ga

R_f (pentane/ethyl acetate 5:1): 0.15. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43 – 7.60 (m, 3H, ArH and CHC*H*=CH), 7.29 – 7.40 (m, 2H, ArH), 6.50 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.03 (dd, *J* = 15.5, 0.8 Hz, 1H, CHCH=C*H*), 4.16 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.20 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 1.59 – 1.73 (m, 2H, CH_2), 1.33 – 1.48 (m, 2H, CH_2), 0.95 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.1, 153.6, 151.7, 137.1, 133.7, 132.0, 126.7, 123.9, 122.7, 115.4, 64.5, 37.0, 36.7, 30.8, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2933, 2872, 1724, 1709, 1627, 1586, 1487, 1456, 1389, 1323, 1312, 1261, 1236, 1182, 1138, 1072, 1044, 1007, 982, 816, 754. GC-MS t_R (50_40): 12.2 min. EI-MS *m/z* (%): 224 (6), 185 (5), 115 (7), 72 (100). HR-MS (ESI) m/z calculated for $C_{18}H_{22}BrNO_4Na$ $(M + Na)^+$ 418.0624, found 418.0624.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(naphthalen-2-yl)penta-2,4-dienoate (3ha)

Prepared by reaction of 1-(naphthalen-2-yl)vinyl dimethylcarbamate (**1h**) (0.50 mmol, 121 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.75 mmol, 108 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2$ (1.05 mmol, 191 mg, 2.1 equiv) in MeOH (2.5 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 2.2:1) afforded **3ha** as a colorless oil as a mixture of diastereoisomers (173 mg, 0.47 mmol, 95%, (2*E*,4*Z*):(2*Z*,4*Z*) = 87:13).

Data for major (2*E*,4*Z*) diastereoisomer:



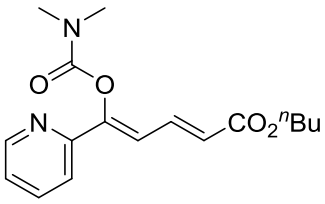
3ha

R_f (pentane/ethyl acetate 2:1): 0.52. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.94 (dd, *J* = 1.9, 0.8 Hz, 1H, ArH), 7.87 – 7.78 (m, 3H, ArH), 7.66 – 7.58 (m, 2H, ArH and CHC*H*=CH), 7.52 – 7.44 (m, 2H, ArH), 6.67 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.08 (dd, *J* = 15.3, 0.8 Hz, 1H, CHCH=C*H*), 4.19 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.28 (s, 3H, CH_3), 3.02 (s, 3H, CH_3), 1.68 (ddt, *J* = 9.0, 7.7, 6.6 Hz, 2H, CH_2), 1.48 – 1.38 (m, 2H, CH_2), 0.97 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 128.8, 128.7, 127.8, 127.1, 126.7, 125.0, 122.6, 115.5, 64.4, 37.1, 36.8, 30.9, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2934, 1707, 1618, 1506, 1487, 1456, 1393, 1356, 1314, 1250, 1219, 1136, 1126, 1045, 982, 882, 854, 814, 750, 735, 675, 631. GC-MS was not informative for this compound. HR-MS (ESI) m/z calculated for $C_{22}H_{25}NO_4Na$ $(M + Na)^+$ 390.1676, found 390.1682.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(pyridin-2-yl)penta-2,4-dienoate (3ia)

Prepared by reaction of 1-(pyridin-2-yl)vinyl dimethylcarbamate (**1i**) (0.50 mmol, 96 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.75 mmol, 108 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2$ (1.05 mmol, 191 mg, 2.1 equiv) in MeOH (2.5 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 2.2:1) afforded **3ia** as a yellow oil as a mixture of diastereoisomers (30 mg, 0.094 mmol, 19%, (2*E*,4*Z*):(2*Z*,4*Z*) = 90:10).

Data for major (2*E*,4*Z*) diastereoisomer:



3ia

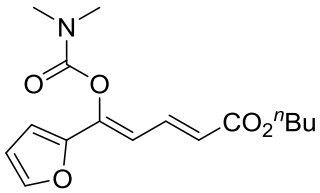
R_f (pentane/ethyl acetate 2:1): 0.21. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.60 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H, ArH), 7.69 (td, *J* = 7.8, 1.8 Hz, 1H, ArH), 7.58 (dd, *J* = 15.4, 11.7 Hz, 1H, CHC*H*=CH), 7.40 (dt, *J* = 7.8, 1.0 Hz, 1H, ArH), 7.22 (ddd, *J* = 7.8, 4.8, 1.0 Hz, 1H, ArH), 7.19 (dd, *J* = 11.7, 0.8 Hz, 1H, C*H*CH=CH), 6.13 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 4.17 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.22 (s, 3H, CH_3), 3.01 (s, 3H, CH_3), 1.66 (m, 2H, CH_2), 1.45 – 1.38 (m, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.0, 153.8, 151.9, 151.0, 149.6, 137.1, 137.0, 124.0, 123.8, 119.9, 117.2, 64.5, 37.0, 36.8, 30.9, 19.3,

13.9. ATR-FTIR ν (cm^{-1}): 2959, 2934, 1726, 1711, 1632, 1616, 1582, 1566, 1468, 1433, 1393, 1321, 1252, 1225, 1190, 1157, 1136, 1059, 1045, 984, 781, 754, 743, 621. GC-MS t_R (50_40): 10.8 min. EI-MS *m/z* (%): 318 (35), 247 (16), 246 (100), 217 (48), 208 (8), 207 (24), 191 (7), 190 (41), 146 (8), 145 (22), 117 (8), 106 (9), 78 (14), 72 (40). HR-MS (ESI) m/z calculated for $C_{17}H_{22}N_2O_4Na$ $(M + Na)^+$ 341.1472, found 341.1476.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(furan-2-yl)penta-2,4-dienoate (3ja)

Prepared by reaction of 1-(furan-2-yl)vinyl dimethylcarbamate (**1j**) (0.50 mmol, 91 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.75 mmol, 108 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2$ (1.05 mmol, 191 mg, 2.1 equiv) in MeOH (2.5 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ja** as a yellow oil as a mixture of diastereoisomers (150 mg, 0.49 mmol, 98%, (2*E*,4*Z*):(2*Z*,4*Z*):(2*E*,4*E*) = 80:12:8).

Data for major (2*E*,4*Z*) diastereoisomer:



3ja

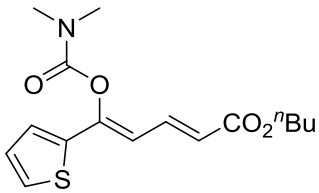
R_f (pentane/ethyl acetate 2:1): 0.22. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.47 (dd, *J* = 15.4, 11.8 Hz, 1H, CHC*H*=CH), 7.42 (dd, *J* = 1.9, 0.6 Hz, 1H, ArH), 6.53 (dt, *J* = 11.8, 0.5 Hz, 1H, C*H*CH=CH), 6.46 (dt, *J* = 3.5, 0.6 Hz, 1H, ArH), 6.42 (dd, *J* = 3.5, 1.9 Hz, 1H, ArH), 6.00 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 4.15 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.14 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 1.66 – 1.62 (m, 2H, CH_2), 1.43 – 1.37 (m, 2H, CH_2), 0.94 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.1, 153.5, 149.3, 144.1, 143.5, 136.8, 122.0, 113.3, 112.1, 110.0, 64.4, 37.0, 36.7, 30.9, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2959, 2934, 1728, 1707, 1618, 1479, 1383, 1314, 1240, 1190, 1152, 1132, 1055, 1017, 984, 883, 858, 748. GC-MS t_R (50_40): 10.0 min. EI-MS *m/z* (%): 307 (16), 219 (8), 134 (9), 95 (9), 72 (100). HR-MS (ESI) m/z calculated for $C_{16}H_{21}NO_5Na$ $(M + Na)^+$ 330.1312, found 330.1317.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-5-(thiophen-2-yl)penta-2,4-dienoate (3ka)

Prepared by reaction of 1-(thiophen-2-yl)vinyl dimethylcarbamate (**1k**) (0.50 mmol, 99 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.75 mmol, 108 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (7.7

mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2$ (1.05 mmol, 191 mg, 2.1 equiv) in MeOH (2.5 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ka** as a yellow oil as a mixture of diastereoisomers (160 mg, 0.49 mmol, 99%, (2*E*,4*Z*):(2*Z*,4*Z*):(2*E*,4*E*) = 78:14:8).

Data for major (2*E*,4*Z*) diastereoisomer:



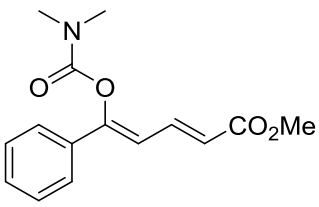
3ka

R_f (pentane/ethyl acetate 2:1): 0.54. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.46 (dd, *J* = 15.4, 11.5 Hz, 1H, CHC*H*=CH), 7.28 (dd, *J* = 5.0, 1.2 Hz, 1H, ArH), 7.18 (dd, *J* = 3.7, 1.2 Hz, 1H, ArH), 6.99 (dd, *J* = 5.0, 3.7 Hz, 1H, ArH), 6.44 (dd, *J* = 11.5, 0.8 Hz, 1H, C*H*CH=CH), 5.98 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 4.14 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.16 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 1.64 (m, 2H, CH_2), 1.43 – 1.37 (m, 2H, CH_2), 0.94 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.1, 153.4, 147.5, 138.9, 137.1, 128.1, 127.2, 125.9, 121.7, 114.1, 64.3, 37.0, 36.6, 30.8, 19.2, 13.8. ATR-FTIR ν (cm^{-1}): 2957, 2934, 1728, 1705, 1618, 1425, 1393, 1356, 1317, 1265, 1236, 1027, 1132, 1055, 1030, 982, 953, 876, 854, 826, 750, 702. GC-MS t_R (50_40): 10.6 min. EI-MS *m/z* (%): 323 (14), 251 (9), 235 (13), 222 (11), 207 (11), 150 (9), 121 (10), 111 (13), 72 (100). HR-MS (ESI) m/z calculated for $C_{16}H_{21}NO_4SNa$ $(M + Na)^+$ 346.1083, found 346.1078.

Methyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-5-phenylpenta-2,4-dienoate (3ab)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.20 mmol, 38 mg, 1.0 equiv), *n*-methyl acrylate (**2b**) (0.30 mmol, 27 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ab** as a colorless oil as a mixture of diastereoisomers (53 mg, 0.19 mmol, 96%, (2*E*,4*Z*):(2*Z*,4*Z*):(2*E*,4*E*) = 88:7:5).

Data for major (2*E*,4*Z*) diastereoisomer:



3ab

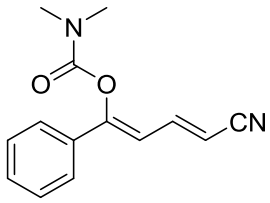
R_f (pentane/ethyl acetate 2:1): 0.39. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.57 (dd, *J* = 15.4, 11.4 Hz, 1H, CHC*H*=CH), 7.51 – 7.49 (m, 2H, ArH), 7.38 – 7.34 (m, 3H, ArH), 6.53 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.03 (dd, *J* = 15.4, 0.8 Hz,

1H, CHCH=C*H*), 3.76 (s, 3H, OCH_3), 3.22 (s, 3H, CH_3), 3.00 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.5, 153.7, 152.9, 138.0, 134.6, 129.8, 128.9, 125.3, 121.6, 115.0. ATR-FTIR ν (cm^{-1}): 2949, 2928, 1713, 1628, 1493, 1445, 1435, 1393, 1327, 1285, 1265, 1234, 1138, 1047, 1028, 984, 882, 860, 754, 721, 691, 650. GC-MS t_R (50_40): 9.7 min. EI-MS *m/z* (%): 275 (9), 203 (7), 187 (10), 115 (19), 77 (11), 72 (100), 51 (8), 42 (7). HR-MS (ESI) m/z calculated for $C_{15}H_{17}NO_4Na$ $(M + Na)^+$ 298.1050, found 298.1050.

(1*Z*,3*E*)-4-cyano-1-phenylbuta-1,3-dien-1-yl dimethylcarbamate (3ac)

The reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), acrylonitrile (**2c**) (1.10 mmol, 73 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h led to a mixture of the two isomers **3ac** (1*Z*,3*E*) and **3ac'** (1*Z*,3*Z*). Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded each of these isomers in a pure form as colorless oils.

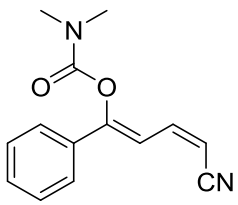
3ac (37 mg, 0.15 mmol, 31%):



3ac

R_f (pentane/ethyl acetate 2:1): 0.38. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.51 – 7.48 (m, 2H, ArH), 7.38 (m, 3H, ArH), 7.28 (dd, *J* = 16.1, 11.3 Hz, 1H, CHC*H*=CH), 6.50 (dd, *J* = 11.3, 0.8 Hz, 1H, C*H*CH=CH), 5.46 (dd, *J* = 16.1, 0.8 Hz, 1H, CHCH=C*H*), 3.22 (s, 3H, CH_3), 3.01 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 153.4, 153.4, 143.9, 134.0, 130.3, 129.0, 125.5, 118.6, 114.4, 98.9, 37.1, 36.8. ATR-FTIR ν (cm^{-1}): 3059, 2932, 2212, 1721, 1626, 1589, 1493, 1447, 1393, 1325, 1285, 1263, 1221, 1148, 1047, 1028, 966, 874, 854, 752, 735, 665. GC-MS t_R (50_40): 9.5 min. EI-MS *m/z* (%): 198 (35), 115 (15), 77 (19), 72 (100), 51 (9), 42 (7). HR-MS (ESI) m/z calculated for $C_{14}H_{14}N_2O_2Na$ $(M + Na)^+$ 265.0947, found 265.0958.

(1*Z*,3*Z*)-4-cyano-1-phenylbuta-1,3-dien-1-yl dimethylcarbamate **(3ac')** (51 mg, 0.21 mmol, 42%):



3ac'

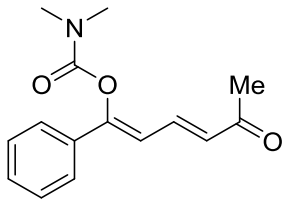
R_f (pentane/ethyl acetate 2:1): 0.29. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.54 (m, 2H, ArH), 7.41 – 7.39 (m, 3H, ArH), 7.13 (dd, *J* = 11.5, 10.9 Hz, 1H, CHC*H*=CH), 6.89 (dd, *J* = 11.5, 0.9 Hz, 1H, C*H*CH=CH), 5.26 (dd, *J* = 10.9, 0.9 Hz, 1H, CHCH=C*H*), 3.20 (s,

3H, CH_3), 3.00 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 154.0, 153.4, 142.5, 134.0, 130.4, 129.0, 125.7, 116.7, 113.2, 97.4, 37.1, 36.8. ATR-FTIR ν (cm^{-1}): 3067, 2934, 2211, 1722, 1626, 1580, 1493, 1447, 1385, 1317, 1306, 1258, 1146, 1047, 1026, 976, 870, 750, 689, 662, 629. GC-MS t_R (50_40): 9.4 min. EI-MS *m/z* (%): 207 (7), 199 (9), 198 (58), 115 (21), 105 (7), 77 (18), 72 (100), 56 (7), 51 (8). HR-MS (ESI) m/z calculated for $C_{14}H_{14}N_2O_2Na$ $(M + Na)^+$ 265.0947, found 265.0952.

(1*Z*,3*E*)-5-oxo-1-phenylhexa-1,3-dien-1-yl dimethylcarbamate (3ad)

The reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), methyl vinyl ketone (**2d**) (1.10 mmol, 89 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in MeOH (2.5 mL) at 60 °C for 16 h led to a mixture of the expected diene **3ad** and the reduced product **3'ad**. Purification by column chromatography (eluent: pentane/ethyl acetate 2:1) afforded a 1.6:1 mixture of **3ad**:**3'ad** as a yellow oil (110 mg, 0.42 mmol, 85%). Each of these products could however be isolated in a pure form by HPLC for characterization (ZORBAX SB-C18, 5 µm, 9.4 × 100 mm; MeOH:H_2O = 40:60 to 30:70; 5 mL/min; approx. 110 bar).[5]

3ad:

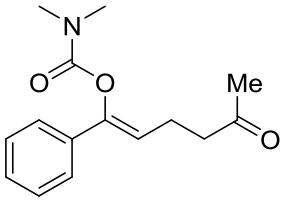


3ad

R_f (pentane/ethyl acetate 2:1): 0.19. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.52 – 7.49 (m, 2H, ArH), 7.45 – 7.40 (m, 2H, ArH and CHC*H*=CH), 7.39 – 7.36 (m, 2H, ArH), 6.53 (dd, *J* = 11.2, 0.8 Hz, 1H, C*H*CH=CH), 6.31 (dd, *J* = 15.6, 0.8 Hz, 1H, CHCH=C*H*), 3.24 (s, 3H, CH_3), 3.01 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 198.3, 153.7, 153.7, 136.2, 134.6, 130.8, 129.9, 128.9, 128.8, 125.3, 115.4, 37.1, 36.8, 28.0. ATR-FTIR ν (cm^{-1}): 2926, 1724, 1686, 1667, 1626, 1587, 1495, 1447, 1393, 1360, 1263, 1254, 1153, 1049, 980, 762, 692. GC-MS t_R (50_40): 9.6 min. EI-MS *m/z* (%): 207 (39), 172 (8), 171 (62), 170 (20), 115 (17), 105 (9), 89 (8), 88 (8), 77 (16), 73 (15), 72 (100), 56 (7), 44 (9), 43 (15), 42 (10). HR-MS (ESI) m/z calculated for $C_{15}H_{17}NO_3Na$ $(M + Na)^+$ 282.1101, found 282.1110.

[5] After separation by HPLC, some traces of a second isomer of the desired diene were observed by NMR. HPLC should be performed carefully in non-acidic conditions to avoid isomerisation.

(*Z*)-5-oxo-1-phenylhex-1-en-1-yl dimethylcarbamate **(3'ad)**:



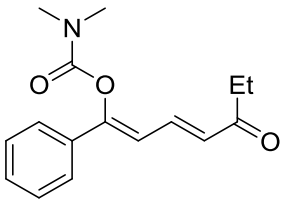
3'ad

R_f (pentane/ethyl acetate 2:1): 0.22. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.40 – 7.38 (m, 2H, ArH), 7.32 – 7.29 (m, 2H, ArH), 7.27 – 7.24 (m, 1H, ArH), 5.78 (t, *J* = 7.5 Hz, 1H, C*H*CH_2CH_2), 3.15 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.62 (t, *J* = 7.5 Hz, 2H, $CHCH_2CH_2$), 2.43 (q, *J* = 7.5 Hz, 2H, $CHCH_2CH_2$), 2.16 (s, 3H, $C(O)CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 208.3, 154.3, 147.3, 135.7, 128.6, 128.2, 124.6, 116.3, 42.9, 36.9, 36.6, 30.1, 20.5. ATR-FTIR ν (cm^{-1}): 2926, 1717, 1495, 1445, 1393, 1263, 1163, 1103, 1049, 760, 694. GC-MS t_R (50_40): 9.2 min. EI-MS *m/z* (%): 356 (8), 281 (7), 207 (25), 173 (12), 172 (45), 171 (13), 157 (43), 147 (20), 129 (8), 105 (18), 77 (32), 76 (8), 72 (100), 63 (10), 44 (18), 43 (21), 42 (10). HR-MS (ESI) m/z calculated for $C_{15}H_{19}NO_3Na$ $(M + Na)^+$ 284.1257, found 284.1265.

(1*Z*,3*E*)-5-oxo-1-phenylhepta-1,3-dien-1-yl dimethylcarbamate (3ae)

The reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), ethyl vinyl ketone (**2e**) (1.10 mmol, 108 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in MeOH (2.5 mL) at 60 °C for 16 h led to a mixture of the expected diene **3ae** and the reduced product **3'ae**. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded a 3:1 mixture of **3ae**:**3'ae** (106 mg, 0.39 mmol, 78%). Each of these products could however be isolated in a pure form by HPLC for characterization (ZORBAX SB-C18, 5 µm, 9.4 × 100 mm; MeOH:H_2O = 45:55; 5 mL/min; approx. 110 bar).[5]

3ae (50 mg, 0.18 mmol, 37%):

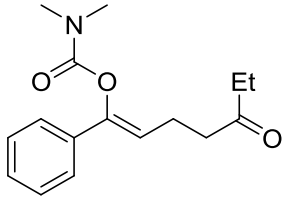


3ae

R_f (pentane/ethyl acetate 2:1): 0.34. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.52 – 7.48 (m, 2H, ArH), 7.45 (dd, *J* = 15.4, 11.4 Hz, 1H, CHC*H*=CH), 7.39 – 7.34 (m, 3H, ArH), 6.52 (dd, *J* = 11.4, 0.8 Hz, 1H, C*H*CH=CH), 6.33 (dd, *J* = 15.4, 0.8 Hz, 1H, CHCH=C*H*), 3.22 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 2.60 (q, *J* = 7.3 Hz, 2H, CH_2CH_3), 1.13 (t, *J* = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 200.9, 153.7, 153.5, 135.1, 135.1, 134.7, 129.8, 129.7, 128.9, 128.7, 128.7, 125.2, 115.5, 37.0, 36.8, 34.5, 8.3. ATR-FTIR ν (cm^{-1}): 2974, 2934, 1722, 1686, 1663, 1624,

1589, 1493, 1447, 1393, 1356, 1325, 1281, 1265, 1152, 1117, 1049, 1028, 984, 883, 856, 762, 692. GC-MS t_R (50_40): 9.9 min. EI-MS *m/z* (%): 207 (8), 186 (13), 185 (81), 184 (18), 144 (8), 115 (12), 105 (7), 77 (13), 72 (100). HR-MS (ESI) m/z calculated for $C_{16}H_{19}NO_3Na$ $(M + Na)^+$ 296.1257, found 296.1259.

(*Z*)-5-oxo-1-phenylhept-1-en-1-yl dimethylcarbamate **(3'ae)** (13 mg, 0.047 mmol, 10%):

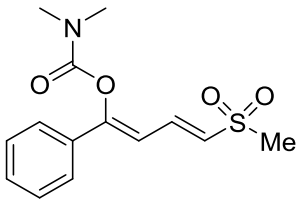


3'ae

R_f (pentane/ethyl acetate 2:1): 0.36. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.40 – 7.37 (m, 2H, ArH), 7.32 – 7.28 (m, 2H, ArH), 7.26 – 7.23 (m, 1H, ArH), 5.78 (t, *J* = 7.5 Hz, 1H, C*H*CH_2CH_2), 3.15 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.61 – 2.57 (m, 2H, $CHCH_2CH_2$), 2.46 – 2.41 (m, 4H, CH_2CH_3 and $CHCH_2CH_2$), 1.06 (t, *J* = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 211.0, 154.3, 147.3, 135.7, 128.6, 128.2, 124.6, 116.5, 41.5, 36.9, 36.6, 36.1, 20.6, 8.0. ATR-FTIR ν (cm^{-1}): 2936, 1713, 1495, 1445, 1391, 1263, 1161, 1117, 1055, 1026, 756, 694. GC-MS t_R (50_40): 9.4 min. EI-MS *m/z* (%): 281 (8), 207 (29), 187 (17), 186 (64), 185 (14), 171 (8), 157 (51), 115 (8), 105 (17), 77 (9), 73 (7), 72 (100), 57 (14), 44 (10), 42 (7). HR-MS (ESI) m/z calculated for $C_{16}H_{21}NO_3Na$ $(M + Na)^+$ 298.1414, found 298.1411.

(1*Z*,3*E*)-4-(methylsulfonyl)-1-phenylbuta-1,3-dien-1-yl dimethylcarbamate (3af)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), methyl vinyl sulfone (**2f**) (1.10 mmol, 96 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 2:1 to 1:1) afforded **3af** as a colorless oil (90 mg, 0.30 mmol, 60%).



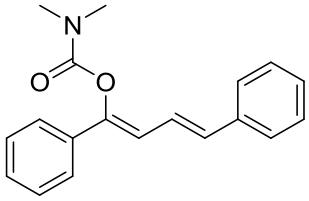
3af

R_f (pentane/ethyl acetate 2:1): 0.06. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.46 (m, 3H, ArH and CHC*H*=CH), 7.37 (m, 3H, ArH), 6.51 (dd, *J* = 14.9, 0.7 Hz, 1H, C*H*CH=CH), 6.46 (dd, *J* = 11.4, 0.7 Hz, 1H, CHCH=C*H*), 3.20 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.96 (s, 3H, SO_2CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 155.3, 153.3, 137.0, 134.1, 130.3, 128.9, 128.9, 125.5, 112.3, 43.4, 37.0, 36.8. ATR-FTIR ν (cm^{-1}): 2932, 1724, 1632, 1493, 1447, 1395, 1306, 1281, 1153, 1128, 1047, 1026, 966, 866, 806, 764, 754, 692. GC-MS t_R (50_40): 10.7 min. EI-MS *m/z* (%): 216

(23), 144 (11), 115 (22), 105 (7), 77 (22), 72 (100). HR-MS (ESI) m/z calculated for $C_{14}H_{17}NO_4SNa$ $(M + Na)^+$ 318.0770, found 318.0771.

(1*Z*,3*E*)-1,4-diphenylbuta-1,3-dien-1-yl dimethylcarbamate (3ag)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), styrene (**2g**) (1.10 mmol, 127 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **3ag** as a colorless oil (37%) as a mixture with some unreacted starting material **1a** (84 mg, **3ag**:**1a** = 1.3:1). **3ag** could be isolated in a pure form by HPLC (ZORBAX SB-C18, 5 µm, 9.4 × 100 mmm; MeOH:H_2O = 70:30; 5 mL/min; approx. 115 bar) (30 mg, 0.10 mmol, 20%).



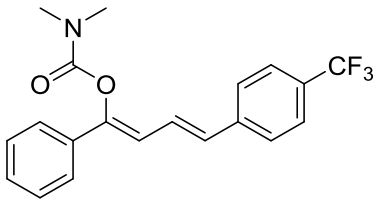
3ag

R_f (pentane/ethyl acetate 2:1): 0.64. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.51 – 7.48 (m, 2H, ArH), 7.45 – 7.43 (m, 2H, ArH), 7.37 – 7.32 (m, 4H, ArH), 7.30 – 7.27 (m, 1H, ArH), 7.26 – 7.23 (m, 1H, ArH), 7.00 (dd, *J* = 15.7, 10.9 Hz, 1H, CHC*H*=CH), 6.73 (d, *J* = 15.7 Hz, 1H, C*H*CH=CH), 6.62 (dd, *J* = 10.9, 0.8 Hz, 1H, CHCH=C*H*), 3.26 (s, 3H, CH_3), 3.04 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 154.3, 147.1, 137.5, 135.5, 133.9, 128.7, 128.7, 128.5, 127.9, 126.7, 124.6, 122.5, 117.6, 37.0, 36.7. ATR-FTIR ν (cm^{-1}): 3055, 3036, 2928, 1722, 1634, 1595, 1491, 1445, 1393, 1265, 1157, 1047, 1028, 966, 750, 691. GC-MS t_R (50_40): 10.9 min. EI-MS *m/z* (%): 294 (17), 293 (57), 281 (7), 221 (9), 209 (7), 207 (18), 205 (7), 204 (24), 202 (25), 191 (11), 115 (38), 105 (23), 91 (7), 77 (16), 72 (100), 63 (10). HR-MS (ESI) m/z calculated for $C_{19}H_{19}NO_2Na$ $(M + Na)^+$ 316.1308, found 316.1306.

(1*Z*,3*E*)-1-phenyl-4-(4-(trifluoromethyl)phenyl)buta-1,3-dien-1-yl dimethylcarbamate (3ah)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), 4-(trifluoromethyl)styrene (**2h**) (1.10 mmol, 163 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in

1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ah** as a colorless oil (34%) as a mixture with some unreacted starting material **1a** (85 mg, **3ah**:**1a** = 2:1). **3ag** could be isolated in a pure form by HPLC (ZORBAX SB-C18, 5 µm, 9.4 × 100 mm; MeOH:H_2O = 75:25; 5 mL/min; approx. 90 bar) (60 mg, 0.17 mmol, 33%).

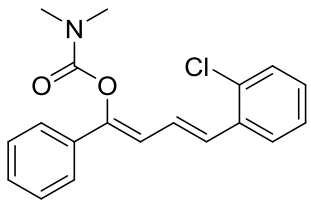


3ah

R_f (pentane/ethyl acetate 2:1): 0.68. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.60 – 7.54 (m, 2H, ArH), 7.54 – 7.47 (m, 4H, ArH), 7.40 – 7.34 (m, 2H, ArH), 7.33 – 7.29 (m, 1H, ArH), 7.08 (dd, *J* = 15.7, 10.9 Hz, 1H, CHC*H*=CH), 6.73 (d, *J* = 15.7 Hz, 1H, C*H*CH=CH), 6.62 (dd, *J* = 10.9, 0.8 Hz, 1H, CHCH=C*H*), 3.26 (s, 3H, CH_3), 3.04 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 154.2, 148.4, 140.9 (q, *J* = 1.5 Hz), 135.2, 132.0, 129.4 (q, *J* = 32.5 Hz), 128.9, 128.8, 126.7, 125.6 (q, *J* = 3.8 Hz), 124.9, 124.7, 124.3 (q, *J* = 271.8 Hz), 117.1, 37.0, 36.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) −62.5. ATR-FTIR ν (cm^{-1}): 2890, 1724, 1609, 1495, 1447, 1414, 1393, 1323, 1265, 1159, 1119, 1067, 1047, 1015, 968, 816, 760, 691. GC-MS t_R (50_40): 10.6 min. EI-MS *m/z* (%): 361 (32), 281 (10), 209 (9), 207 (20), 202 (11), 191 (8), 183 (9), 115 (12), 105 (15), 73 (9), 72 (100), 44 (9). HR-MS (ESI) m/z calculated for $C_{20}H_{18}F_3NO_2Na$ $(M + Na)^+$ 384.1182, found 384.1182.

(1*Z*,3*E*)-4-(2-chlorophenyl)-1-phenylbuta-1,3-dien-1-yl dimethylcarbamate (3ai)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), 2-chlorostyrene (**2i**) (1.10 mmol, 141 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ai** as a colorless oil (26%) as a mixture with some unreacted starting material **1a** (60 mg, **3ai**:**1a** = 1.3:1). **3ai** could be isolated in a pure form by HPLC (ZORBAX SB-C18, 5 µm, 9.4 × 100 mm; MeOH:H_2O = 75:25; 5 mL/min; approx. 90 bar) (21 mg, 0.067 mmol, 13%).



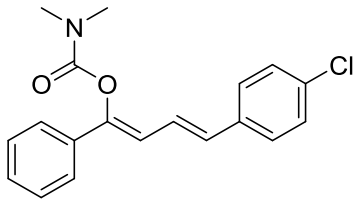
3ai

R_f (pentane/ethyl acetate 2:1): 0.65. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.62 (dd, *J* = 7.9, 1.6 Hz, 1H, ArH), 7.53 – 7.46 (m, 2H, ArH), 7.42 – 7.33 (m, 3H, ArH), 7.32 – 7.29 (m,

1H, ArH), 7.26 – 7.22 (m, 1H, ArH), 7.17 (td, *J* = 7.6, 1.6 Hz, 1H, ArH), 7.12 (d, *J* = 15.6 Hz, 1H, C*H*CH=CH), 6.99 (dd, *J* = 15.6, 10.7 Hz, 1H, CHC*H*=CH), 6.68 (dd, *J* = 10.7, 0.8 Hz, 1H, CHCH=C*H*), 3.25 (s, 3H, CH_3), 3.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 154.2, 147.9, 135.5, 135.3, 133.5, 130.0, 129.5, 128.8, 128.7, 128.7, 126.9, 126.7, 124.8, 124.7, 117.6, 37.0, 36.7. ATR-FTIR ν (cm^{-1}): 2928, 1722, 1632, 1493, 1468, 1443, 1393, 1335, 1265, 1155, 1123, 1047, 1034, 966, 754, 692. GC-MS t_R (50_40): 11.9 min. EI-MS *m/z* (%): 329 (13), 328 (7), 327 (42), 281 (8), 207 (10), 202 (14), 191 (9), 115 (14), 105 (11), 77 (12), 73 (7), 72 (100), 44 (12). HR-MS (ESI) m/z calculated for $C_{19}H_{18}ClNO_2Na$ $(M + Na)^+$ 350.0918, found 350.0914.

(1*Z*,3*E*)-4-(4-chlorophenyl)-1-phenylbuta-1,3-dien-1-yl dimethylcarbamate (3aj)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), 4-chlorostyrene (**2j**) (1.10 mmol, 139 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 3:1) afforded **3aj** as a colorless oil (22 mg, 0.07 mmol, 13%).

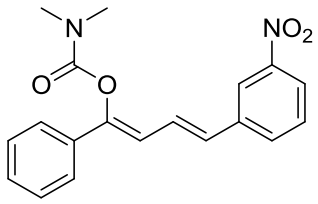


3aj

R_f (pentane/ethyl acetate 2:1): 0.65. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.51 – 7.46 (m, 2H, ArH), 7.38 – 7.32 (m, 4H, ArH), 7.32 – 7.26 (m, 3H, ArH), 6.96 (dd, *J* = 15.7, 10.9 Hz, 1H, CHC*H*=CH), 6.66 (d, *J* = 15.7 Hz, 1H, C*H*CH=CH), 6.59 (dd, *J* = 10.9, 0.9 Hz, 1H, CHCH=C*H*), 3.26 (s, 3H, CH_3), 3.03 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 154.3, 147.5, 136.0, 135.4, 133.4, 132.4, 128.9, 128.8, 128.6, 127.9, 124.6, 123.0, 117.4, 37.0, 36.8. ATR-FTIR ν (cm^{-1}): 3046, 2930, 1719, 1634, 1489, 1445, 1391, 1331, 1316, 1263, 1223, 1153, 1088, 1045, 1026, 1011, 966, 874, 860, 845, 806, 756, 735, 689. GC-MS t_R (50_40): 12.0 min. EI-MS *m/z* (%): 341 (7), 327 (15), 281 (14), 207 (27), 115 (12), 105 (7), 77 (8), 73 (12), 72 (100). HR-MS (ESI) m/z calculated for $C_{19}H_{18}ClNO_2Na$ $(M + Na)^+$ 350.0918, found 350.0912.

(1*Z*,3*E*)-4-(3-nitrophenyl)-1-phenylbuta-1,3-dien-1-yl dimethylcarbamate (3ak)

Prepared by reaction of 1-phenylvinyl dimethylcarbamate (**1a**) (0.50 mmol, 96 mg, 1.0 equiv), 3-nitrostyrene (**2k**) (1.10 mmol, 153 µL, 2.2 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **3ak** as a colorless oil (65 mg, 0.19 mmol, 38%).

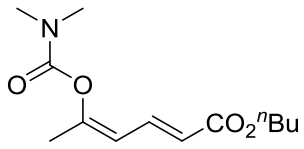


3ak

R_f (pentane/ethyl acetate 2:1): 0.42. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.29 (t, *J* = 2.1 Hz, 1H, ArH), 8.07 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H, ArH), 7.70 (dt, *J* = 8.0, 1.4 Hz, 1H, ArH), 7.55 – 7.44 (m, 3H, ArH), 7.40 – 7.35 (m, 2H, ArH), 7.34 – 7.30 (m, 1H, ArH), 7.12 (dd, *J* = 15.7, 10.9 Hz, 1H, CHC*H*=CH), 6.74 (d, *J* = 15.7 Hz, 1H, C*H*CH=CH), 6.62 (dd, *J* = 10.9, 0.9 Hz, 1H, CHCH=C*H*), 3.29 (s, 3H, CH_3), 3.05 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 154.2, 148.9, 148.8, 139.3, 135.1, 132.6, 130.9, 129.6, 129.0, 128.9, 125.4, 124.8, 122.2, 120.9, 116.9, 37.1, 36.8. ATR-FTIR ν (cm^{-1}): 3055, 2930, 1717, 1632, 1609, 1574, 1526, 1495, 1445, 1393, 1348, 1317, 1265, 1225, 1152, 1047, 964, 899, 845, 758, 733, 691, 673. GC-MS was not informative for this compound. HR-MS (ESI) m/z calculated for $C_{19}H_{18}N_2O_4Na$ $(M + Na)^+$ 361.1159, found 361.1154.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)hexa-2,4-dienoate (5aa)

Prepared by reaction of prop-1-en-2-yl dimethylcarbamate (**4a**) (0.24 mmol, 31 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.75 mmol, 108 µL, 3.1 equiv), $[Cp^*RhCl_2]_2$ (7.7 mg, 5.2 mol %), $AgSbF_6$ (17.2 mg, 21 mol %) and $Cu(OAc)_2$ (191 mg, 4.4 equiv) in MeOH (2.5 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 5:1) afforded **5aa** as a colorless oil (34 mg, 0.13 mmol, 56%).



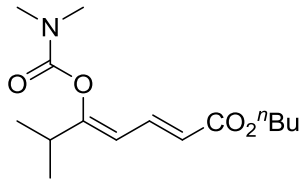
5aa

R_f (pentane/ethyl acetate 2:1): 0.65. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42 (dd, *J* = 15.5, 11.3 Hz, 1H, CHC*H*=CH), 5.81 – 5.74 (m, 2H, C*H*CH=C*H*), 4.12 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.03 (s, 3H, CH_3), 2.96 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.65 – 1.60 (m, 2H, CH_2), 1.41 – 1.35 (m, 2H, CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.4, 154.1, 153.5, 137.7, 119.8, 115.3, 64.3, 36.7, 36.6, 30.9, 20.8, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2956, 2934, 1713, 1657,

1620, 1456, 1395, 1375, 1321, 1261, 1202, 1152, 1128, 1065, 1040, 1022, 988, 880, 754. GC-MS t_R (50_40): 8.8 min. EI-MS *m/z* (%): 72 (100), 39 (7). HR-MS (ESI) m/z calculated for $C_{13}H_{21}NO_4Na$ $(M + Na)^+$ 278.1373, found 278.1368.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-6-methylhepta-2,4-dienoate (5ba)

Prepared by reaction of 3-methylbut-1-en-2-yl dimethylcarbamate (**4b**) (0.35 mmol, 55 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.70 mmol, 101 µL, 2.0 equiv), $[Cp^*RhCl_2]_2$ (5.4 mg, 2.5 mol %), $AgSbF_6$ (12 mg, 10 mol %) and $Cu(OAc)_2$ (134 mg, 2.1 equiv) in MeOH (1.75 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **5ba** as a colorless oil (43 mg, 0.15 mmol, 43%).

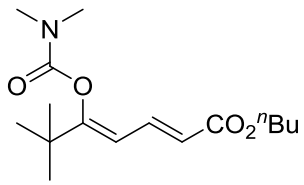


5ba

R_f (pentane/ethyl acetate 2:1): 0.74. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.36 (dd, *J* = 15.4, 11.3 Hz, 1H, CHC*H*=CH), 5.87 – 5.80 (m, 2H, C*H*CH=C*H*), 4.12 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.05 (s, 3H, CH_3), 2.96 (s, 3H, CH_3), 2.63 (p, *J* = 6.9 Hz, 1H, $(CH_3)_2CH$), 1.65 – 1.59 (m, 2H, CH_2), 1.42 – 1.35 (m, 2H, CH_2), 1.11 (d, *J* = 6.9 Hz, 6H, $(CH_3)_2CH$), 0.92 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.3, 162.5, 153.8, 138.0, 120.4, 112.6, 64.2, 36.8, 36.5, 32.8, 30.9, 20.2, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2963, 2934, 2874, 1713, 1651, 1618, 1464, 1393, 1317, 1254, 1200, 1140, 1123, 1059, 986, 901, 880, 860, 756. GC-MS t_R (50_40): 9.0 min. EI-MS *m/z* (%): 209 (14), 95 (13), 72 (100). HR-MS (ESI) m/z calculated for $C_{15}H_{25}NO_4Na$ $(M + Na)^+$ 306.1676, found 306.1672.

Butyl (2*E*,4*Z*)-5-((dimethylcarbamoyl)oxy)-6,6-dimethylhepta-2,4-dienoate (5ca)

Prepared by reaction of 3,3-dimethylbut-1-en-2-yl dimethylcarbamate (**4c**) (0.20 mmol, 34 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in MeOH (1 mL) at 60 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **5ca** as a colorless oil (53 mg, 0.18 mmol, 90%).



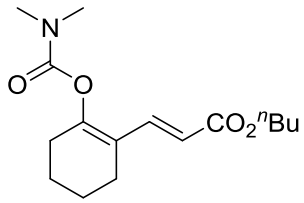
5ca

R_f (pentane/ethyl acetate 2:1): 0.74. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.19 (dd, *J* = 15.4, 11.3 Hz, 1H, CHC*H*=CH), 5.94 (dd, *J* = 11.3, 0.7 Hz, 1H, C*H*CH=CH), 5.85 (dd, *J* = 15.4, 0.7 Hz,

1H, CHCH=C*H*), 4.11 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.06 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 1.64 – 1.59 (m, 2H, CH_2), 1.41 – 1.35 (m, 2H, CH_2), 1.13 (s, 9H, $(CH_3)_3$), 0.92 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.2, 163.5, 153.9, 138.4, 120.8, 112.4, 64.2, 37.2, 37.0, 36.5, 30.9, 28.0, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2961, 2934, 2874, 1713, 1645, 1618, 1479, 1462, 1389, 1317, 1246, 1225, 1188, 1138, 1069, 1028, 982, 878, 858, 752, 721. GC-MS t_R (50_40): 9.2 min. EI-MS *m/z* (%): 209 (8), 95 (8), 72 (100). HR-MS (ESI) m/z calculated for $C_{16}H_{27}NO_4Na$ $(M + Na)^+$ 320.1832, found 320.1833.

Butyl (*E*)-3-(2-((dimethylcarbamoyl)oxy)cyclohex-1-en-1-yl)acrylate (5da)

Prepared by reaction of cyclohexenyl dimethylcarbamate (**4d**) (0.50 mmol, 85 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (1.00 mmol, 144 µL, 2.0 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **5da** as a colorless oil (67 mg, 0.23 mmol, 46%).



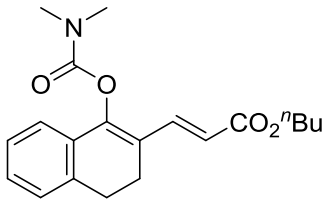
5da

R_f (pentane/ethyl acetate 2:1): 0.61. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.67 (d, *J* = 15.9 Hz, 1H, C*H*=CH), 5.78 (dt, *J* = 15.9, 0.9 Hz, 1H, CH=C*H*), 4.12 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.02 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 2.35 – 2.32 (m, 2H, CH_2), 2.24 – 2.21 (m, 2H, CH_2), 1.75 – 1.66 (m, 4H, 2 × CH_2), 1.64 – 1.60 (m, 2H, CH_2), 1.42 – 1.36 (m, 2H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.7, 154.0, 153.0, 139.3, 121.0, 116.4, 64.2, 36.7, 36.5, 30.9, 28.9, 24.1, 22.5, 21.9, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2934, 2872, 1713, 1645, 1618, 1449, 1393, 1360, 1292, 1271, 1258, 1159, 1134, 1088, 1067, 1024, 1007, 984, 862, 756, 733, 629. GC-MS t_R (50_40): 9.8 min. EI-MS *m/z* (%): 221 (18), 207 (16), 122 (8), 72 (100). HR-MS (ESI) m/z calculated for $C_{16}H_{25}NO_4Na$ $(M + Na)^+$ 318.1676, found 318.1673.

Butyl (*E*)-3-(1-((dimethylcarbamoyl)oxy)-3,4-dihydronaphthalen-2-yl)acrylate (5ea)

Prepared by reaction of 3,4-dihydronaphthalen-1-yl dimethylcarbamate (**4e**) (0.20 mmol, 44 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 44 µL, 1.5 equiv), $[Cp^*RhCl_2]_2$ (6.2

mg, 5 mol %), $AgSbF_6$ (13.8 mg, 20 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in 1,4-dioxane (1 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **5ea** as an orange oil (37 mg, 0.11 mmol, 55%). The same reaction performed on a 10.0 mmol scale afforded **5ea** as an orange oil in a similar yield (1.98 g, 5.77 mmol, 58%).

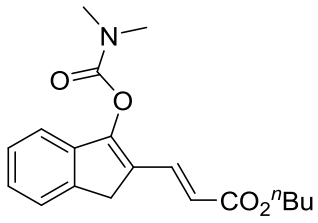


5ea

R_f (pentane/ethyl acetate 2:1): 0.56. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.76 (d, *J* = 15.9 Hz, 1H, C*H*=CH), 7.22 – 7.15 (m, 4H, ArH), 6.01 (d, *J* = 15.9 Hz, 1H, CH=C*H*), 4.17 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.23 (s, 3H, CH_3), 3.02 (s, 3H, CH_3), 2.94 (t, *J* = 8.0 Hz, 2H, CH_2), 2.60 (t, *J* = 8.0 Hz, 2H, CH_2), 1.66 (p, *J* = 6.6 Hz, 2H, CH_2), 1.43 (h, *J* = 7.4 Hz, 2H, CH_2), 0.96 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.5, 154.0, 148.1, 138.7, 137.5, 131.1, 129.1, 127.6, 126.8, 122.6, 122.5, 118.2, 64.4, 37.0, 36.7, 30.9, 27.3, 22.9, 19.4, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2934, 2893, 2874, 1724, 1709, 1614, 1485, 1452, 1393, 1368, 1312, 1273, 1246, 1152, 1132, 1078, 1065, 1028, 980, 860, 764, 733. GC-MS t_R (50_40): 11.9 min. EI-MS *m/z* (%): 343 (14), 271 (11), 256 (9), 255 (49), 207 (7), 199 (8), 198 (7), 170 (19), 169 (13), 141 (21), 115 (11), 72 (100). HR-MS (ESI) m/z calculated for $C_{20}H_{25}NO_4Na$ $(M + Na)^+$ 366.1676, found 366.1672.

Butyl (*E*)-3-(3-((dimethylcarbamoyl)oxy)-1*H*-inden-2-yl)acrylate (5fa)

Prepared by reaction of 1*H*-inden-3-yl dimethylcarbamate (**4f**) (0.50 mmol, 102 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (1.00 mmol, 144 µL, 2.0 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **5fa** as an orange oil (80 mg, 0.24 mmol, 48%).



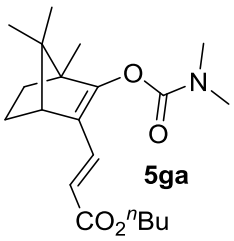
5fa

R_f (pentane/ethyl acetate 2:1): 0.43. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.70 (dt, *J* = 15.7, 0.8 Hz, 1H, C*H*=CH), 7.42 – 7.40 (m, 1H, ArH), 7.31 – 7.25 (m, 3H, ArH), 6.04 (d, *J* = 15.7 Hz, 1H, CH=C*H*), 4.19 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.56 (s, 2H, CH_2), 3.20 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 1.70 – 1.66 (m, 2H, CH_2), 1.46 – 1.40 (m, 2H, CH_2), 0.96 (t, *J* = 7.4 Hz, 3H,

CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.5, 153.1, 152.7, 141.2, 139.3, 135.3, 127.5, 127.1, 126.9, 124.4, 119.8, 117.8, 64.4, 37.1, 36.9, 34.0, 30.9, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2934, 2874, 1732, 1705, 1618, 1462, 1393, 1360, 1298, 1273, 1252, 1146, 1121, 1090, 1063, 1024, 978, 843, 760, 712. GC-MS t_R (50_40): 11.6 min. EI-MS *m/z* (%): 329 (7), 207 (10), 128 (10), 73 (8), 72 (100). HR-MS (ESI) m/z calculated for $C_{19}H_{23}NO_4Na$ $(M + Na)^+$ 352.1519, found 352.1524.

Butyl (*E*)-3-((1*R*,4*S*)-3-((dimethylcarbamoyl)oxy)-4,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)acrylate (5ga)

Prepared by reaction of (1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl dimethylcarbamate (**4g**) (0.50 mmol, 112 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (1.00 mmol, 144 µL, 2.0 equiv), $[Cp^*RhCl_2]_2$ (15.4 mg, 5 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2$ (191 mg, 2.1 equiv) in 1,4-dioxane (2.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 6:1) afforded **5ga** as a colorless oil (122 mg, 0.35 mmol, 70%).

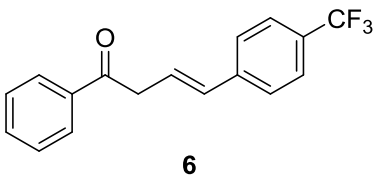


R_f (pentane/ethyl acetate 2:1): 0.74. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.31 (d, *J* = 15.7 Hz, 1H, C*H*=CH), 5.72 (dd, *J* = 15.7, 0.7 Hz, 1H, CH=C*H*), 4.10 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.00 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 2.52 (d, *J* = 3.7 Hz, 1H, CH), 1.88 – 1.83 (m, 1H, C_aHH), 1.66 (ddd, *J* = 12.5, 8.9, 3.9 Hz, 1H, C_bHH), 1.62 – 1.55 (m, 3H, CH_2 and C_bHH), 1.39 – 1.33 (m, 2H, CH_2), 1.10 (ddd, *J* = 12.5, 8.9, 3.9 Hz, 1H, C_aHH), 0.93 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.90 (dd, *J* = 8.2, 7.4 Hz, 3H, CH_3), 0.78 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.7, 161.2, 153.8, 134.9, 127.5, 115.6, 64.1, 56.0, 55.6, 49.9, 36.8, 36.7, 33.3, 30.9, 25.3, 19.6, 19.4, 19.2, 13.8, 9.9. ATR-FTIR ν (cm^{-1}): 2955, 2936, 2874, 1728, 1709, 1628, 1609, 1456, 1387, 1339, 1294, 1267, 1248, 1234, 1198, 1146, 1136, 1063, 1015, 980, 997, 858, 752, 737. GC-MS t_R (50_40): 10.1 min. EI-MS *m/z* (%): 204 (13), 72 (100). HR-MS (ESI) m/z calculated for $C_{20}H_{31}NO_4Na$ $(M + Na)^+$ 372.2145, found 372.2147.

5. Derivatisation of the alkenylated enol carbamates

(*E*)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-one (6)

To a suspension of $Cp_2Zr(H)Cl$ (0.40 mmol, 102 mg, 4.0 equiv) in dry THF (0.75 mL) at room temperature was added a solution of enol carbamate **3ah** (0.10 mmol, 37 mg, 1.0 equiv) in THF (1.25 mL). The resulting mixture was stirred at room temperature and the reaction was monitored by TLC. After 20 h, the reaction was quenched by addition of HCl 1N (2 mL) and extracted with Et_2O (3 × 4 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. Purification by column chromatography (eluent: pentane/ethyl acetate 12:1) afforded **6** as a white solid (10 mg, 34 µmol, 34%).[6]



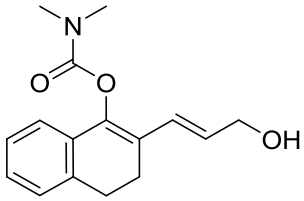
6

R_f (pentane/ethyl acetate 2:1): 0.72. ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 8.04 – 7.96 (m, 2H, ArH), 7.63 – 7.48 (m, 7H, ArH), 6.68 – 6.55 (m, 2H, CH=CH), 3.97 (d, *J* = 5.3 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2) δ (ppm) 197.9, 141.2, 137.1, 133.8, 132.4, 129.3, 128.7, 127.0, 126.5, 126.0 (q, *J* = 3.9 Hz), 43.0. ATR-FTIR ν (cm^{-1}): 2984, 1736, 1692, 1466, 1449, 1393, 1373, 1327, 1236, 1167, 1126, 1111, 1099, 1045, 939, 847, 702, 692. GC-MS was not informative for this compound. HR-MS (ESI) m/z calculated for $C_{17}H_{13}F_3ONa$ $(M + Na)^+$ 313.0811, found 313.0822.

(*E*)-3-(1-hydroxy-3,4-dihydronaphthalen-2-yl)allyl dimethylcarbamate (7)

To a suspension of $Cp_2Zr(H)Cl$ (0.60 mmol, 155 mg, 3.0 equiv) in dry THF (1.5 mL) at room temperature was added a solution of enol carbamate **5ea** (0.20 mmol, 69 mg, 1.0 equiv) in THF (2.5 mL). The resulting mixture was stirred at room temperature and the reaction was monitored by TLC. After 15 min, the reaction mixture turned to a clear yellow solution. After 30 min at room temperature, the reaction was quenched by addition of HCl 1N (4 mL) and extracted with Et_2O (3 × 5 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. Purification by column chromatography (eluent: dichloromethane/ethyl acetate 2:1) afforded **7** as a light yellow oil (55 mg, 0.20 mmol, 100%).[6]

[6] Procedure from: Morin, J.; Zhao, Y.; Snieckus, V. *Org. Lett.* **2013**, *15*, 4102-4105.

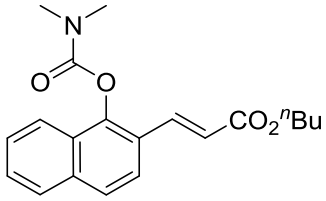


7

R_f (pentane/ethyl acetate 1:1): 0.16. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 4H, ArH), 6.66 (d, *J* = 15.8 Hz, 1H, C*H*=CHCH$_2$), 6.01 (dt, *J* = 15.8, 6.0 Hz, 1H, CH=C*H*CH$_2$), 4.29 (dd, *J* = 6.0, 1.5 Hz, 2H, CH=CHC*H*$_2$), 3.21 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 2.95 – 2.86 (m, 3H, CH_2 and OH), 2.59 (t, *J* = 8.0 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 142.9, 136.5, 131.7, 129.5, 127.8, 127.4, 126.6, 125.7, 123.5, 121.4, 64.1, 37.0, 36.6, 27.5, 23.2. ATR-FTIR ν (cm^{-1}): 3422, 2934, 2888, 2837, 1705, 1487, 1452, 1395, 1306, 1246, 1167, 1132, 1074, 966, 762, 735. GC-MS t_R (50_40): 10.4 min. EI-MS *m/z* (%): 431 (13), 429 (8), 406 (7), 355 (11), 341 (16), 327 (10), 281 (36), 273 (21), 267 (12), 209 (16), 208 (16), 297 (56), 185 (24), 184 (81), 183 (35), 169 (10), 166 (9), 165 (8), 156 (12), 153 (15), 152 (10), 141 (20), 128 (15), 127 (12), 115 (45), 102 (10), 91 (24), 89 (11), 74 (7), 73 (13), 72 (100), 55 (8), 51 (16), 44 (20), 42 (16). HR-MS (ESI) m/z calculated for $C_{16}H_{19}NO_3Na$ $(M + Na)^+$ 296.1257, found 296.1255.

Butyl (*E*)-3-(1-((dimethylcarbamoyl)oxy)naphthalen-2-yl)acrylate (8)

To a solution of enol carbamate **5ea** (0.20 mmol, 69 mg, 1.0 equiv) in dry toluene (2 mL) in a Schlenk tube was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.20 mmol, 46 mg, 1.0 equiv). The reaction vessel was sealed and the reaction was allowed to stir at 110 °C for 7 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo*. Purification by column chromatography (eluent: pentane/ethyl acetate 2.5:1) afforded **8** as a colorless oil (60 mg, 0.18 mmol, 88%).



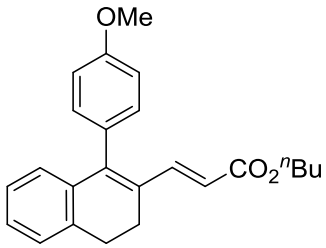
8

R_f (pentane/ethyl acetate 2:1): 0.54. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 16.0 Hz, 1H, C*H*=CH), 7.90 – 7.80 (m, 2H, ArH), 7.70 (d, *J* = 1.5 Hz, 2H, ArH), 7.56 – 7.49 (m, 2H, ArH), 6.55 (d, *J* = 16.0 Hz, 1H, CH=C*H*), 4.23 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.35 (s, 3H, CH_3), 3.09 (s, 3H, CH_3), 1.75 – 1.66 (m, 2H, CH_2), 1.53 – 1.40 (m, 2H, CH_2), 0.98 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.1, 154.4, 146.8, 138.1, 135.4, 128.1, 127.5, 127.2, 126.3, 124.1, 122.9, 122.3, 120.0, 64.5, 37.1, 36.8, 30.9, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2932, 2872, 1722, 1709, 1632, 1464, 1393, 1362, 1294, 1258, 1246, 1171, 1142, 1078,

1063, 1028, 982, 870, 847, 812, 777, 752, 664. GC-MS t_R (50_40): 12.1 min. EI-MS *m/z* (%): 342 (16), 281 (14), 253 (22), 207 (27), 197 (7), 196 (11), 168 (14), 139 (7), 73 (20), 72 (100). HR-MS (ESI) m/z calculated for $C_{20}H_{23}NO_4Na$ $(M + Na)^+$ 364.1519, found 364.1519.

Butyl (*E*)-3-(1-(4-methoxyphenyl)-3,4-dihydronaphthalen-2-yl)acrylate (9)

A flame-dried Schlenk tube (8 mL in volume) equipped with a magnetic stirring bar was charged with anhydrous K_3PO_4 (2.88 mmol, 611 mg, 7.2 equiv) in a glovebox. *p*-Methoxy-phenylboronic acid (1.20 mmol, 243 mg, 4.0 equiv), $NiCl_2(PCy_3)_2$ (27.3 mg, 10 mol %), enol carbamate **5ea** (0.40 mmol, 137 mg, 1.0 equiv) and toluene (1.4 mL) were then added under a stream of argon. The reaction vessel was sealed with a Teflon-lined screw cap and the heterogeneous mixture was allowed to stir at 23 °C for 1 h before heating up to 110 °C for 24 h. After cooling down to room temperature, the reaction mixture was transferred to a round bottom flask and rinsed with dichloromethane. Silica was then added and the solvent was removed under *vacuo*. The obtained powder was dry-loaded onto a silica gel column and purification by column chromatography (eluent: pentane/ethyl acetate 16:1) afforded the desired arylated product **9** as a colorless oil (35 mg, 0.10 mmol, 25%).[7]



9

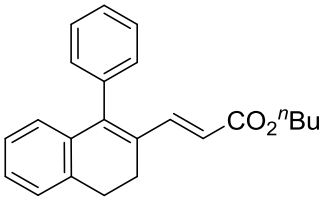
R_f (pentane/ethyl acetate 10:1): 0.34. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.49 (d, *J* = 15.7 Hz, 1H, C*H*=CH), 7.21 – 7.16 (m, 2H, ArH), 7.11 (d, *J* = 8.7 Hz, 1H, ArH), 7.10 – 7.05 (m, 2H, ArH), 6.97 (d, *J* = 8.7 Hz, 1H, ArH), 6.97 – 6.94 (m, 1H, ArH), 6.79 – 6.77 (m, 1H, ArH), 6.02 (d, *J* = 15.7 Hz, 1H, CH=C*H*), 4.10 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.87 (s, 3H, OCH_3), 2.96 – 2.91 (m, 2H, CH_2), 2.63 (dd, *J* = 8.9, 7.0 Hz, 2H, CH_2), 1.62 – 1.57 (m, 2H, CH_2), 1.39 – 1.32 (m, 2H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 167.8, 159.3, 144.5, 144.4, 137.2, 136.5, 131.8, 131.6, 129.9, 128.2, 128.0, 127.4, 126.5, 117.2, 113.9, 64.2, 55.4, 30.9, 28.1, 24.5, 19.3, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2934, 1703, 1607, 1508, 1460, 1452, 1302, 1273, 1244, 1165, 1107, 1065, 1034, 986, 957,

[7] Procedure from: Quasdorf, K. W.; Antoft-Finch, A.; Liu, P.; Silberstein, A. L.; Komaromi, A.; Blackburn, T.; Ramgren, S. D.; Houk, K. N.; Snieckus, V.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, *133*, 6352-6363.

831, 772, 737. GC-MS t_R (50_40): 13.7 min. EI-MS *m/z* (%): 362 (58), 261 (93), 260 (100), 259 (46), 207 (55). HR-MS (ESI) m/z calculated for $C_{24}H_{26}O_3Na$ $(M + Na)^+$ 385.1774, found 385.1775.

Butyl (*E*)-3-(1-phenyl-3,4-dihydronaphthalen-2-yl)acrylate (9')

The procedure used for the formation of **8**[7] was applied with phenylboronic acid on a 0.20 mmol scale. Purification by column chromatography (eluent: toluene/dichloromethane 15:1) afforded the desired arylated product **9'** as a colorless oil (30 mg, 90 µmol, 45%).



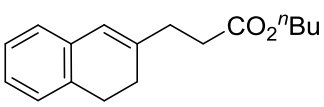
9'

R_f (pentane/ethyl acetate 10:1): 0.46. ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 7.50 – 7.43 (m, 3H, ArH), 7.34 (d, *J* = 15.8 Hz, 1H, C*H*=CH), 7.23 – 7.15 (m, 4H, ArH), 7.05 (td, *J* = 7.4, 1.8 Hz, 1H, ArH), 6.69 (dd, *J* = 7.8, 1.4 Hz, 1H, ArH), 6.03 (d, *J* = 15.8 Hz, 1H, CH=C*H*), 4.06 (t, *J* = 6.5 Hz, 2H, OCH_2), 2.96 (dd, *J* = 9.2, 6.7 Hz, 2H, CH_2), 2.64 (dd, *J* = 9.2, 6.7 Hz, 2H, CH_2), 1.61 – 1.53 (m, 2H, CH_2), 1.39 – 1.27 (m, 2H, CH_2), 0.91 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ (ppm) 167.7, 144.9, 144.2, 138.5, 137.6, 136.6, 132.2, 131.0, 128.8, 128.7, 128.2, 128.1, 127.8, 126.9, 117.9, 64.5, 31.3, 28.4, 24.7, 19.7, 14.1. ATR-FTIR ν (cm^{-1}): 2957, 2934, 2891, 2872, 1703, 1611, 1595, 1452, 1443, 1381, 1302, 1271, 1252, 1165, 1065, 1036, 1028, 984, 856, 772, 729, 702, 669. GC-MS t_R (50_40): 11.9 min. EI-MS *m/z* (%): 333 (11), 332 (31), 259 (9), 258 (9), 257 (12), 232 (13), 231 (94), 230 (100), 229 (88), 228 (36), 227 (10), 226 (13), 217 (7), 216 (36), 215 (82), 207 (7), 204 (8), 203 (9), 202 (32), 191 (7). HR-MS (ESI) m/z calculated for $C_{23}H_{24}O_2Na$ $(M + Na)^+$ 355.1669, found 355.1670.

Butyl 3-(3,4-dihydronaphthalen-2-yl)propanoate (10)

A flame-dried Schlenk tube (8 mL in volume) equipped with a magnetic stirring bar was charged with anhydrous K_3PO_4 (1.80 mmol, 382 mg, 4.5 equiv) in a glovebox. $NiCl_2(PCy_3)_2$ (13.6 mg, 5 mol %), enol carbamate **5ea** (0.40 mmol, 137 mg, 1.0 equiv), toluene (1.5 mL) and TMDSO (1.00 mmol, 178 µL, 2.5 equiv) were then added subsequently under a stream of argon. The reaction vessel was sealed with a Teflon-lined screw cap and the heterogeneous mixture was allowed to stir at 115 °C for 15 h before cooling down to room temperature. The reaction mixture was then transferred to a round bottom flask and rinsed with dichloromethane. Silica was added and the solvent was removed under *vacuo*. The obtained powder was dry-loaded onto a silica gel column and

purification by column chromatography (eluent: pentane/ethyl acetate 13:1) afforded the reduced product **10** as a colorless oil (70 mg, 0.27 mmol, 68%).[8]

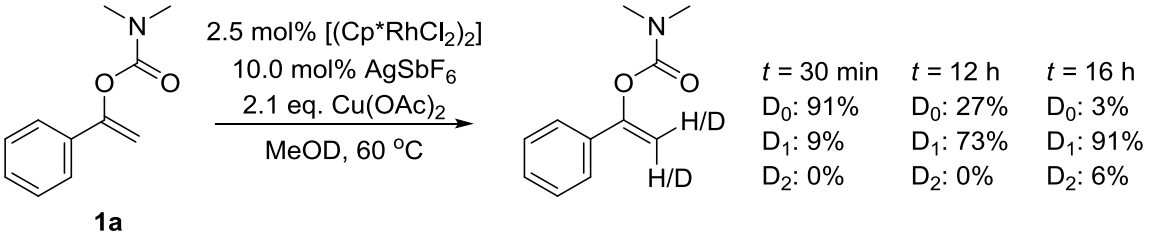


10

R_f (pentane/ethyl acetate 10:1): 0.64. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.15 – 7.11 (m, 1H, ArH), 7.10 – 7.07 (m, 2H, ArH), 6.98 (d, *J* = 7.0 Hz, 1H, ArH), 6.24 (t, *J* = 1.4 Hz, 1H, CH), 4.10 (t, *J* = 6.7 Hz, 2H, OCH_2), 2.83 – 2.80 (m, 2H, CH_2), 2.56 – 2.52 (m, 4H, 2 × CH_2), 2.26 (td, *J* = 8.5, 1.3 Hz, 2H, CH_2), 1.63 – 1.59 (m, 2H, CH_2), 1.42 – 1.35 (m, 2H, CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 173.3, 140.1, 134.7, 134.5, 127.3, 126.5, 126.5, 125.7, 122.8, 64.5, 32.8, 32.6, 30.8, 28.2, 27.4, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2959, 2932, 1732, 1485, 1454, 1435, 1358, 1290, 1258, 1244, 1169, 1065, 1030, 937, 880, 851, 754, 746, 727. GC-MS t_R (50_40): 9.3 min. EI-MS *m/z* (%): 259 (8), 258 (37), 185 (10), 184 (48), 183 (23), 159 (13), 157 (9), 156 (47), 155 (16), 154 (9), 143 (44), 142 (68), 141 (100), 129 (46), 128 (68), 127 (14), 116 (7), 115 (26), 41 (15). HR-MS (ESI) m/z calculated for $C_{17}H_{22}O_2Na$ $(M + Na)^+$ 281.1512, found 281.1519.

6. Mechanistic investigation: Deuterium labelling and KIE

Deuteration experiments



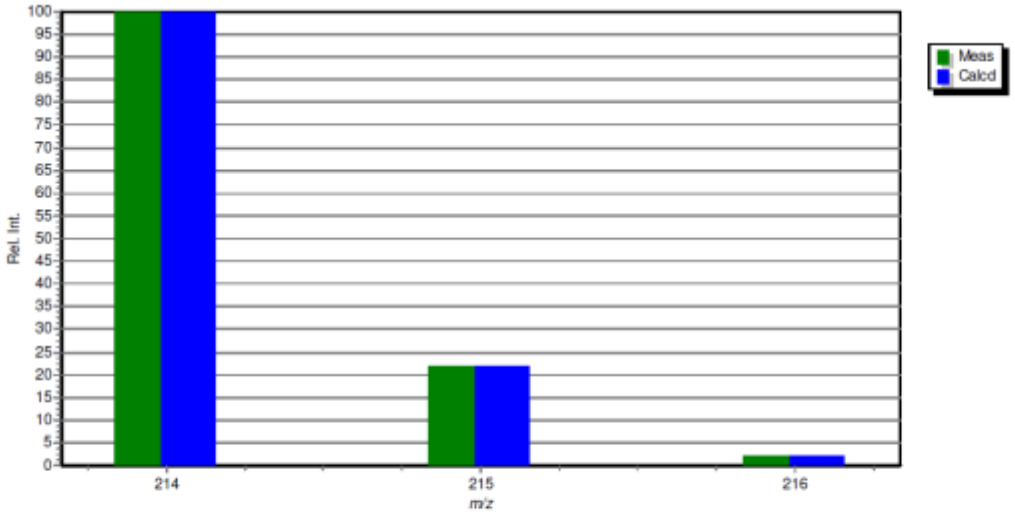
1a

Three Schlenk tubes (8 mL in volume) equipped with a stirring bar were flame-dried and cooled under vacuum, and back-filled with argon. $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %), $AgSbF_6$ (3.5 mg, 10 mol %) and $Cu(OAc)_2$ (38.2 mg, 2.1 equiv) were weighed into each reaction vessels in a glovebox. Enol carbamate **1a** (0.10 mmol, 19 mg, 1.0 equiv) and dry MeOD (0.5 mL) were added under a stream of argon. The vessels were then sealed and the reactions were allowed to stir at 60 ºC for 30 min, 12 h and 16 h. After the given time,

[8] Procedure from: Mesganaw, T.; Fine Nathel, N. F.; Garg, N. K. *Org. Lett.* **2012**, *14*, 2918-2921.

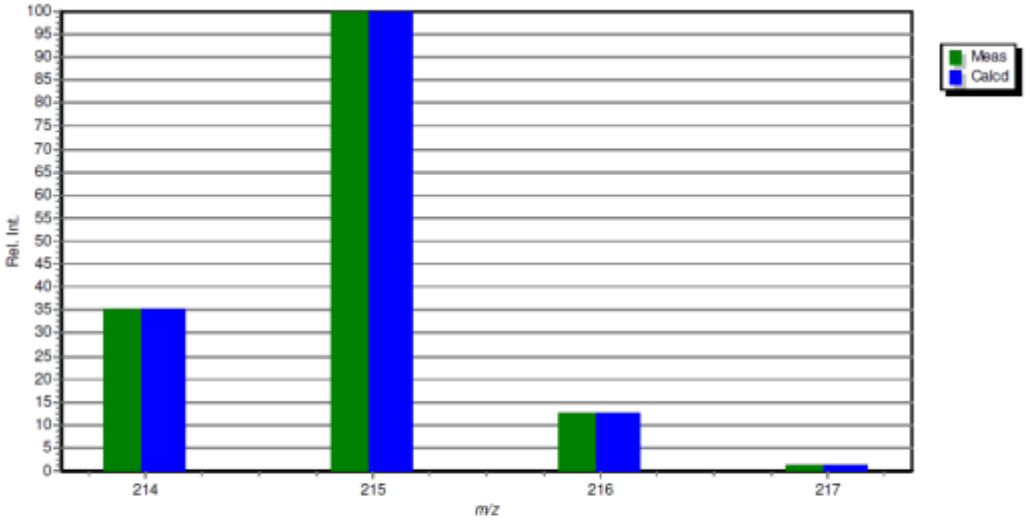
each reaction mixture was filtered through a small pad of silica gel and washed with ethyl acetate. The samples were concentrated *in vacuo* and submitted to ESI-MS analysis for determination of deuterium incorporation.

t = 30 min



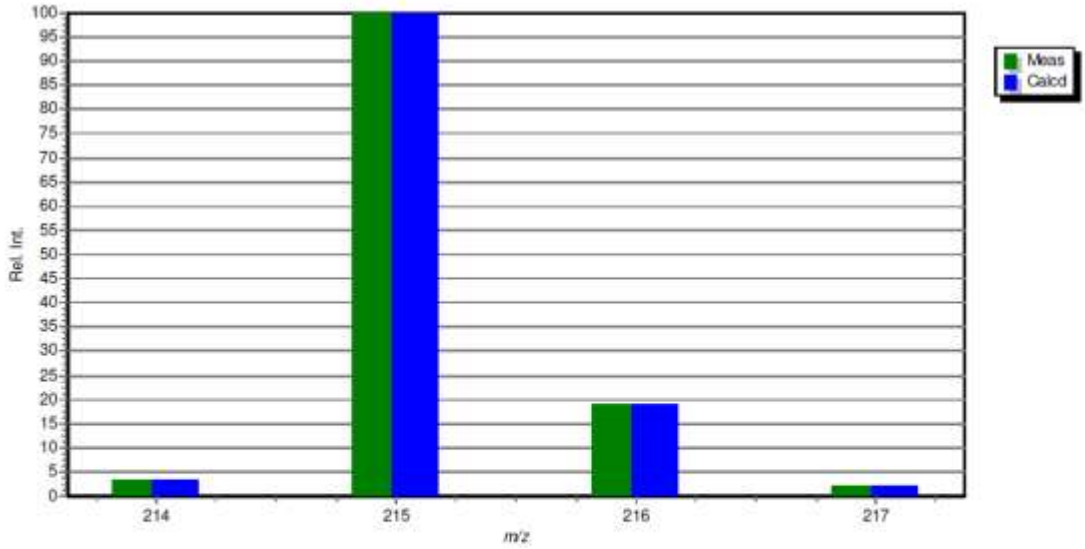
Deuteration 0-fold (%):	100.00	91.22
Deuteration 1-fold (%):	9.62	8.77
Deuteration 2-fold (%):	0.00	0.00
Deuteration 3-fold (%):	0.00	0.00
Deuteration 4-fold (%):	0.00	0.00

t = 12 h



Deuteration 0-fold (%):	37.12	26.97
Deuteration 1-fold (%):	100.00	72.65
Deuteration 2-fold (%):	0.53	0.39
Deuteration 3-fold (%):	0.00	0.00
Deuteration 4-fold (%):	0.00	0.00

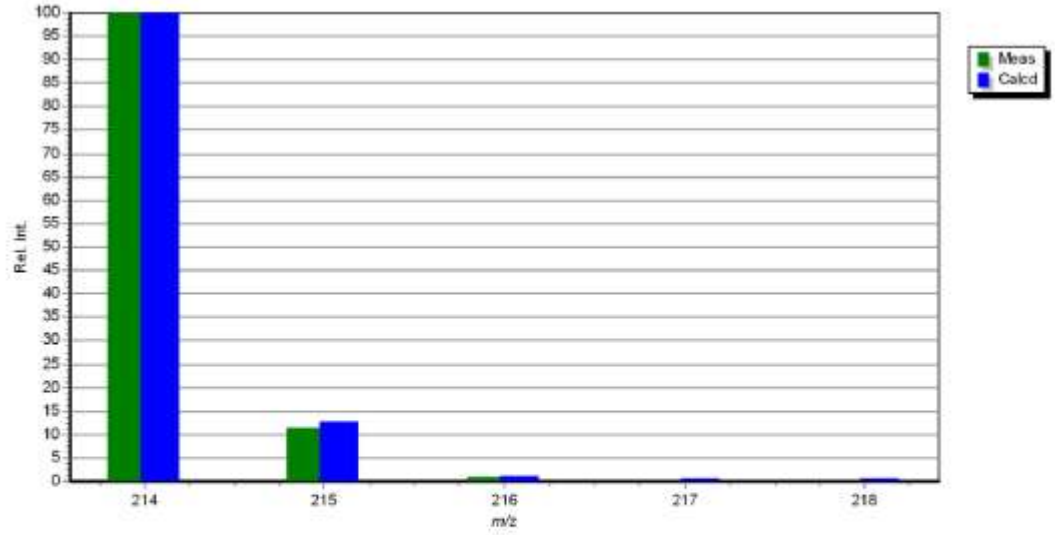
t = 16 h



Deuteration 0-fold (%):	3.50	3.17
Deuteration 1-fold (%):	100.00	90.71
Deuteration 2-fold (%):	6.54	5.94
Deuteration 3-fold (%):	0.20	0.18
Deuteration 4-fold (%):	0.00	0.00
Deuteration 5-fold (%):	0.00	0.00

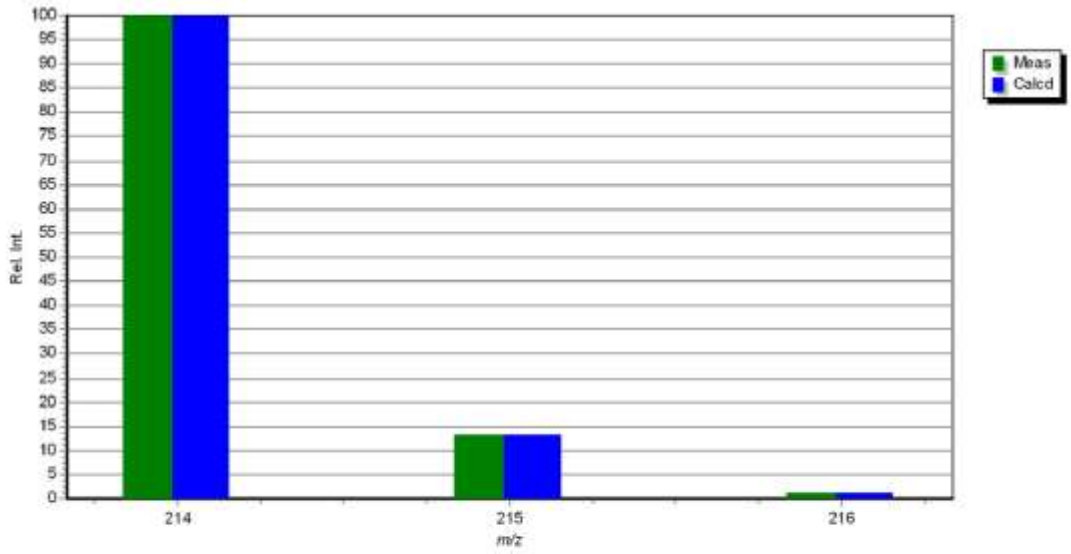
Control reactions, performed in the absence of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$ revealed that the observed scrambling was caused by the catalyst.

Reaction without $[Cp^*RhCl_2]_2$



Deuteration 0-fold (%):	100,00	98,73
Deuteration 1-fold (%):	0,37	0,37
Deuteration 2-fold (%):	0,00	0,00
Deuteration 3-fold (%):	0,44	0,43
Deuteration 4-fold (%):	0,45	0,45
Deuteration 5-fold (%):	0,02	0,02

Reaction without $Cu(OAc)_2$



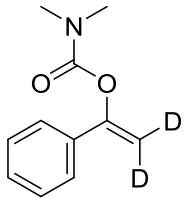
Deuteration 0-fold (%):	100,00	99,24
Deuteration 1-fold (%):	0,73	0,72
Deuteration 2-fold (%):	0,05	0,05
Deuteration 3-fold (%):	0,00	0,00
Deuteration 4-fold (%):	0,00	0,00
Deuteration 5-fold (%):	0,00	0,00

Kinetic isotope effect study

Deuterated enol carbamate formation

1-Phenylvinyl-2,2-*d*$_2$ dimethylcarbamate (*D*$_2$-1a)

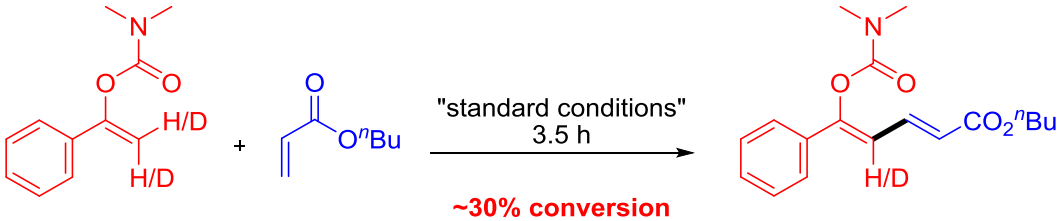
Prepared from acetophenone-d_3 (D = 97%, prepared from acetophenone according to the procedure of Wang)[9] on a 3.12 mmol scale according to general procedure **A** using DMSO-d_6 as solvent and quenching with D_2O. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded D_2-**1a** as a colorless oil (219 mg, 1.12 mmol, 36%). ^{1}H NMR analysis indicated a mixture of three products in the following ratio: *D*$_2$-**1a**:(*E*)-*D*$_1$-**1a**:(*Z*)-*D*$_1$-**1a** = 84:8:8. The deuteration incorporation was enriched upon treating the mixture under the standard catalysis reaction conditions on a 0.20 mmol scale according to general procedure **B** in MeOH-D_4 in the absence of an alkene coupling partner. Purification by column chromatography (eluent: pentane/ethyl acetate 4:1) afforded **1a** as a colorless oil (31 mg, 0.16 mmol, 80%). ^{1}H NMR analysis indicated a mixture of three products in the following ratio: *D*$_2$-**1a**:(*E*)-*D*$_1$-**1a**:(*Z*)-*D*$_1$-**1a** = 96:3:1.



D$_2$-**1a**

R_f (pentane/ethyl acetate 2:1): 0.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46−7.51 (m, 2H, ArH), 7.27−7.38 (m, 3H, ArH), 3.12 (s, 3H, CH_3), 2.98 (s, 3H, CH_3).

KIE measurements



D$_2$-**1a/1a** **2a** D$_1$-**3a/3a**

Due to the scrambling observed in the reaction conditions in MeOD, the competition experiment starting from a 1:1 mixture *D*$_2$-**1a**:**1a** couldn't be carried out. Thus, two parallel experiments were undertaken in separate vials.

[9] Zhao, X.; Jing, J.; Lu, K.; Zhang, Y.; Wang, J. *Chem. Commun.* **2010**, *46*, 1724-1726.

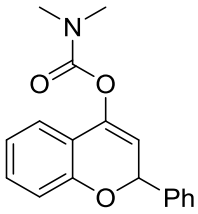
Following general procedure B, two Schlenk tubes (8 mL in volume) equipped with a stirring bar were flame-dried under vacuum and back-filled with argon. $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) were weighed into the reaction vessels in a glovebox. Enol carbamate **1a** (0.20 mmol, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 1.5 equiv) and dry MeOH (1.0 mL) were added under a stream of argon in one of the vessels. In the second one, deuterated enol carbamate D_2-**1a** (0.20 mmol, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.30 mmol, 1.5 equiv), and MeOD (1.0 mL) were added under a stream of argon. The vessels were then sealed and the two reactions were allowed to stir at 60 ºC for 3.5 h, reaching around 30% conversion. After cooling down to room temperature, the solvent was removed under reduced pressure. The obtained crude products were dissolved in $CDCl_3$ to determine the ^1H NMR yield and thus the value of k_H/k_D using CH_2Br_2 as an internal standard. The NMR yields gave a KIE value of 5, suggesting that C–H activation is the rate-limiting step.

7. Application of the strategy to natural products

Enol carbamate formation

2-Phenyl-2*H*-chromen-4-yl dimethylcarbamate (11)

Prepared from 2-phenylchroman-4-one on a 0.736 mmol scale according to general procedure A. Purification by column chromatography (eluent: pentane/ethyl acetate 3:1 to 2:1) afforded **11** as a colorless oil (80 mg, 0.27 mmol, 37%).



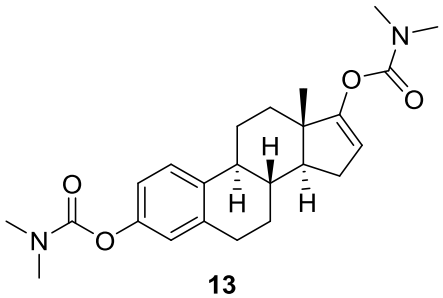
11

R_f (pentane/ethyl acetate 2:1): 0.37. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.65 (dt, *J* = 7.6, 1.1 Hz, 1H, ArH), 7.61 – 7.53 (m, 3H, ArH and C=C*H*CHPh), 7.54 – 7.50 (m, 1H, ArH), 7.46 – 7.33 (m, 3H, ArH), 7.31 (tt, *J* = 7.6, 1.1 Hz, 1H, ArH), 7.23 (dt, *J* = 8.1, 1.1 Hz, 1H, ArH), 7.15 – 7.11 (m, 1H, C=CHC*H*Ph), 2.97 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 192.6, 154.3, 149.6, 145.0, 134.8, 132.9, 132.4, 130.7, 129.7, 129.1, 128.5, 126.1, 125.6, 123.9, 36.8, 36.5. ATR-FTIR ν (cm^{-1}): 2926, 1721, 1667, 1643, 1605, 1574, 1495, 1478, 1449, 1385, 1331, 1302, 1287, 1265, 1202, 1153, 1103, 1065, 1053, 1018, 999, 980, 883, 845, 777, 752, 737, 698, 681, 654, 635. GC-MS t_R (50_40): 10.6 min. EI-MS *m/z* (%): 295 (10), 223 (17), 208 (7), 207 (52), 206 (38), 166

(9), 165 (18), 103 (7), 102 (9), 77 (10), 72 (100). HR-MS (ESI) m/z calculated for $C_{18}H_{17}NO_3Na$ $(M + Na)^+$ 318.1101, found 318.1099.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[a]phenanthrene-3,17-diyl bis(dimethylcarbamate) (13)

Prepared from estrone on a 1.66 mmol scale according to general procedure A with the use of 3 equiv of NaH and dimethylcarbamoyl chloride. Purification by column chromatography (eluent: pentane/ethyl acetate 2:1) afforded **13** as a colorless oil as a mixture with phenol-carbamate **15** (460 mg, **13**:**15** 1:4). This residue was then dissolved in MeOH (9 mL) and $NaBH_4$ (1.98 mmol, 75 mg) was added at 0 °C. The reaction mixture was allowed to stir at 0 °C for 3 h and quenched with a saturated acqueous solution of NH_4Cl. After extraction with dichloromethane (3 × 10 mL), the organic layer was dried over magnesium sulfate and concentrated *in vacuo*. Purification by column chromatography (eluent: pentane:ethyl acetate 1:1) afforded the desired bis-protected steroid **13** as a white amorphous solid (165 mg, 0.40 mmol, 24%).

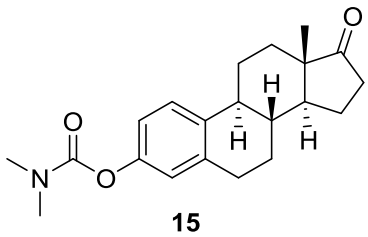


13

R_f (pentane/ethyl acetate 2:1): 0.30. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.3 Hz, 1H, ArH), 6.89 – 6.81 (m, 2H, ArH), 5.45 (dd, *J* = 3.3, 1.6 Hz, 1H, C=C*H*CH_2), 3.08 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.96 – 2.85 (m, 1H), 2.38 – 2.19 (m, 3H), 2.07 – 1.97 (m, 1H), 1.96 – 1.88 (m, 1H), 1.83 – 1.67 (m, 2H), 1.66 – 1.55 (m, 4H), 1.50 – 1.37 (m, 1H), 0.93 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 160.1, 155.4, 154.4, 149.4, 138.1, 137.6, 126.0, 121.9, 118.9, 108.6, 53.5, 45.1, 44.7, 36.8, 36.7, 36.6, 36.5, 33.7, 29.5, 28.8, 27.0, 26.1, 15.8. ATR-FTIR ν (cm^{-1}): 2930, 2857, 1717, 1487, 1452, 1385, 1341, 1308, 1290, 1267, 1248, 1227, 1202, 1161, 1103, 1063, 1017, 910, 889, 839, 810, 758, 733, 700, 644. HR-MS (ESI) m/z calculated for $C_{24}H_{32}N_2O_4Na$ $(M + Na)^+$ 435.2254, found 435.2255.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclo-

Penta[a]phenanthren-3-yl dimethylcarbamate **15**



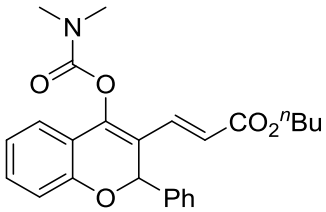
15

Not characterised.

Rh(III)-catalysed cross-coupling reactions

Butyl (*E*)-3-(4-((dimethylcarbamoyl)oxy)-2-phenyl-2*H*-chromen-3-yl)acrylate (12)

Prepared by reaction of 2-phenyl-2*H*-chromen-4-yl dimethylcarbamate (**11**) (0.10 mmol, 30 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.20 mmol, 29 µL, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and $Cu(OAc)_2$ (76.3 mg, 4.2 equiv) in 1,4-dioxane (0.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 3:1) afforded **12** as a colorless oil (30 mg, 0.07 mmol, 71%).

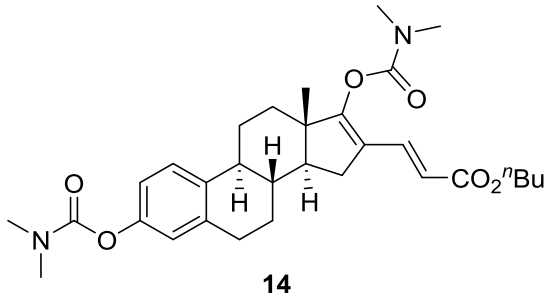


12

R_f (pentane/ethyl acetate 2:1): 0.38. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.61 (d, *J* = 15.8 Hz, 1H, CH=C*H*C(O)), 7.55 (d, *J* = 7.8 Hz, 1H, ArH), 7.51 (dd, *J* = 7.8, 1.9 Hz, 2H, ArH), 7.47 (t, *J* = 8.0 Hz, 1H, ArH), 7.40 – 7.30 (m, 5H, ArH and OCHPh), 6.97 (d, *J* = 16.3 Hz, 1H, ArH), 6.40 (d, *J* = 15.8 Hz, 1H, C*H*=CHC(O)), 4.14 (t, *J* = 6.7 Hz, OCH_2), 2.89 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 1.65 – 1.58 (m, 2H, CH_2), 1.37 (h, *J* = 7.4 Hz, 2H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 195.0, 166.4, 153.9, 148.8, 147.9, 140.6, 134.3, 134.1, 133.6, 131.1, 130.3, 129.1, 128.7, 127.8, 124.9, 123.8, 121.7, 64.7, 36.7, 36.4, 30.8, 19.3, 13.8. ATR-FTIR ν (cm^{-1}): 2957, 2932, 2874, 1717, 1674, 1643, 1626, 1597, 1574, 1464, 1451, 1385, 1314, 1273, 1225, 1204, 1155, 1103, 1063, 1053, 1022, 980, 847, 789, 772, 752, 698. GC-MS was not informative for this compound. HR-MS (ESI) m/z calculated for $C_{25}H_{27}NO_5Na$ $(M + Na)^+$ 444.1781, found 444.1788.

Butyl (*E*)-3-((8*R*,9*S*,13*S*,14*S*)-3,17-bis((dimethylcarbamoyl)oxy)-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[a]phenanthren-16-yl)acrylate (14)

Prepared by reaction of (8*R*,9*S*,13*S*,14*S*)-13-Methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[a]phen-anthrene-3,17-diyl bis(dimethylcarbamate) (**13**) (0.10 mmol, 41 mg, 1.0 equiv), *n*-butyl acrylate (**2a**) (0.12 mmol, 17.5 µL, 1.2 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and $Cu(OAc)_2$ (38.1 mg, 2.1 equiv) in 1,4-dioxane (0.5 mL) at 100 °C for 16 h. Purification by column chromatography (eluent: pentane/ethyl acetate 2:1) afforded **14** as a pale yellow oil (27 mg, 0.05 mmol, 51%).



14

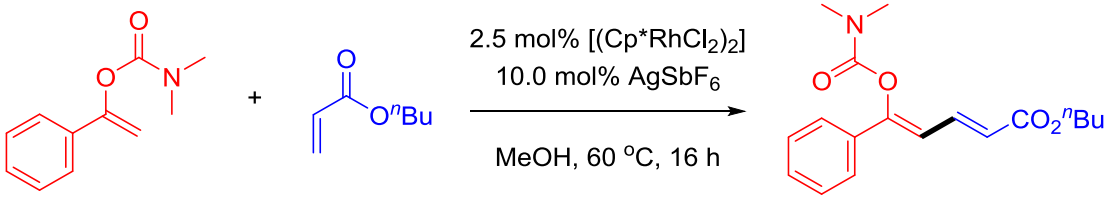
R_f (pentane/ethyl acetate 2:1): 0.23. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.43 (d, *J* = 15.7 Hz, 1H, CH=C*H*C(O)), 7.22 (d, *J* = 8.5 Hz, 1H, ArH), 6.87 – 6.82 (m, 2H, ArH), 5.77 (d, *J* = 15.7 Hz, 1H, C*H*=CHC(O)), 4.15 (td, *J* = 6.7, 1.1 Hz, 2H, OCH_2), 3.08 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 2.92 – 2.88 (m, 2H), 2.46 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.37 – 2.32 (m, 2H), 2.16 – 2.11 (m, 1H), 1.97 – 1.88 (m, 2H), 1.82 (td, *J* = 12.9, 4.1 Hz, 1H), 1.75 (ddd, *J* = 12.9, 4.6, 2.2 Hz, 1H), 1.67 – 1.53 (m, 4H), 1.51 – 1.35 (m, 3H), 0.96 (s, 3H), 0.94 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR ((151 MHz, $CDCl_3$) δ (ppm) 167.6, 164.2, 155.4, 153.9, 149.5, 137.9, 137.2, 136.6, 126.0, 124.2, 121.9, 119.0, 118.0, 64.3, 51.7, 47.2, 44.4, 37.0, 36.8, 36.8, 36.7, 36.6, 33.4, 30.9, 29.4, 28.5, 26.9, 26.0, 19.3, 16.0, 13.9. ATR-FTIR ν (cm^{-1}): 2957, 2932, 2872, 1717, 1628, 1489, 1456, 1387, 1335, 1304, 1277, 1256, 1240, 1225, 1152, 1101, 1065, 1018, 980, 756, 735. HR-MS (ESI) m/z calculated for $C_{31}H_{42}N_2O_6Na$ $(M + Na)^+$ 561.2935, found 561.2922.

8. Robustness Screen

A simplified robustness screen as recently reported[10,11] has been undertaken to evaluate the tolerance of this reaction to the given functionalities and chemical motifs, as well as the stability of these 'additives' to the reaction conditions. This procedure requires the undertaking of a standard reaction in the presence of one molar equivalent of a given additive (functional group or heterocycle). After the pre-determined reaction time, the yield of the product, the starting material remaining, and the additive remaining is determined by GC analysis.

The calibration of the additives, starting materials and the product of the reaction was undertaken using the single point calibration technique for gas chromatography (GC) analysis as previously described. Evaluation of two groups of additives, 'functional groups' (Group A) and 'heterocycles' (Group B) as previously reported was undertaken.

Excluding reaction time and GC running time, the whole screen was undertaken in approximately 8 h including control experiments and analysis.



1a **2a** **3aa**

Scheme 1. The standard reaction evaluated.

Sample procedure:

1) To 11 flame-dried Schlenk flasks under argon was added $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.9 mg, 10 mol %) and $Cu(OAc)_2$ (76.3 mg, 2.1 equiv) in a glovebox. Enol carbamate (1.0 equiv), olefin (1.5-2.2 equiv) and dry solvent (0.2

[10] Collins, K. D.; Glorius, F. *Nature Chem.* **2013**, *5*, 597.
[11] Collins, K. D.; Glorius, F. *Tetrahedron* **2013**, *69*, 7817.

M) were added under a stream of argon. The vessel was then sealed and the reaction was allowed to stir at 60 ºC or 100 °C for 16 h.

2) Batch preparation of a stock solution of the standard reaction was undertaken (12 × 0.20 mmol = 2.4 mmol scale): To 1-phenylvinyl dimethylcarbamate (**1a**) (2.40 mmol, 410 mg, 1.0 equiv.) in dry MeOH (12.0 mL) was added *n*-butyl acrylate **2a** (18.0 mmol, 528 µL, 1.5 equiv) and the mixture was stirred under argon until complete dissolution of reagents.
3) A portion of the stock reaction mixture (1.0 mL, ~0.20 mmol) was then added *via* syringe (1 mL) to a Schlenk flask containing the catalytic system. Immediately, the corresponding additive (0.20 mmol) was added to the reaction vessel, and the vessel sealed. This was repeated for all additional additives and the control reaction.
4) The reactions were heated for 16 h at 60 °C in an oil bath. Once cooled, mesitylene (28 μL, 0.200 mmol, 1.0 equiv) was added to each reaction, and analysis by GC was undertaken.

Note:

- Change in volume of stock solution due to addition of starting materials was not accounted for, hence a control reaction (no additive) is undertaken to determine the maximum yield of reaction in the screen.
- ***N*-methylimidazole** and **dodecylamine** should be filtered through Celite and not silica when preparing samples for GC analysis.
- Following the original screen 5 reactions were repeated to ensure consistency and reproducibility of the data.

Table 2. Investigation of the tolerance of some common functional groups.

Group A - Functional Groups

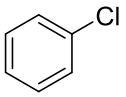
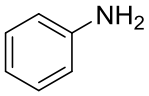
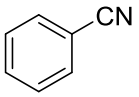
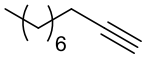
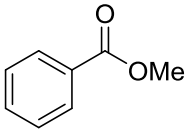
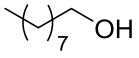
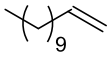
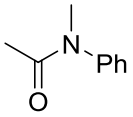
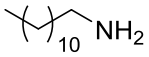
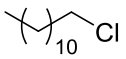
Entry		Amount (0.20 mmol)	Yield of **3aa** %		Additive remaining %		SM remaining % **1a**
A1		21 μL	✓	>95 (>95)	✓	>95 (>95)	0 (0)
A2		19 μL	X	11	-	54	89
A3		21 μL	✓	91	✓	93	<5
A4		32 μL	X	0 (0)	X	0 (0)	>95 (>95)
A5		26 μL	✓	>95	✓	>95	0
A6		32 μL	✓	93	X	0	<5
A7		45 μL	✓	86	-	62	10
A8		30 mg	✓	>95	✓	>95	0
A9		37 mg	X	<5 (<5)	X	16 (14)	>95 (>95)
A10		48 μL	✓	>95	✓	93	<5
A11	none	-	✓	>95	-		0

Table shows the affect of a given additive on the standard reaction. The yield of **3aa**, and the additive and starting material **1a** remaining after reaction are given. Color-coding

should help the ready assessment of the data: green (above 66%), yellow (34-66%), red (below 34%). All yields are GC yields. SM is starting material. Yields in parenthesis are of the control group; selected experiments were repeated to ensure consistency and reproducibility of the data.

Table 3. Investigation of the tolerance of some common heterocycles.

Group B - Heterocycles

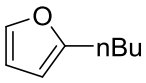
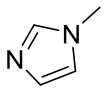
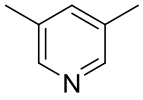
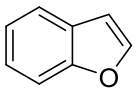
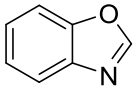
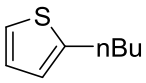
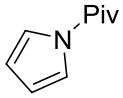
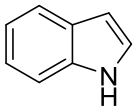
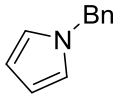
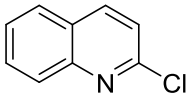
Entry		Amount (0.20 mmol)	Yield of **3aa** %		Additive remaining %		SM remaining % **1a**
B1		30 μL	✓	>95 (>95)	✓	84 (80)	<5 (<5)
B2		16 μL	X	<5	✓	>95	>95
B3		22 μL	X	7	X	16	89
B4		22 μL	✓	>95	✓	>95	0
B5		24 mg	X	<5	-	65	93
B6		29 μL	✓	94	✓	>95	0
B7		30 μL	X	4	-	61	91
B8		24 mg	✓	89	✓	>95	<5
B9		30 μL	X	14	✓	89	0
B10		34 mg	✓	85 (80)	✓	89 (83)	17 (24)
B11	none	-	✓	97	-		0

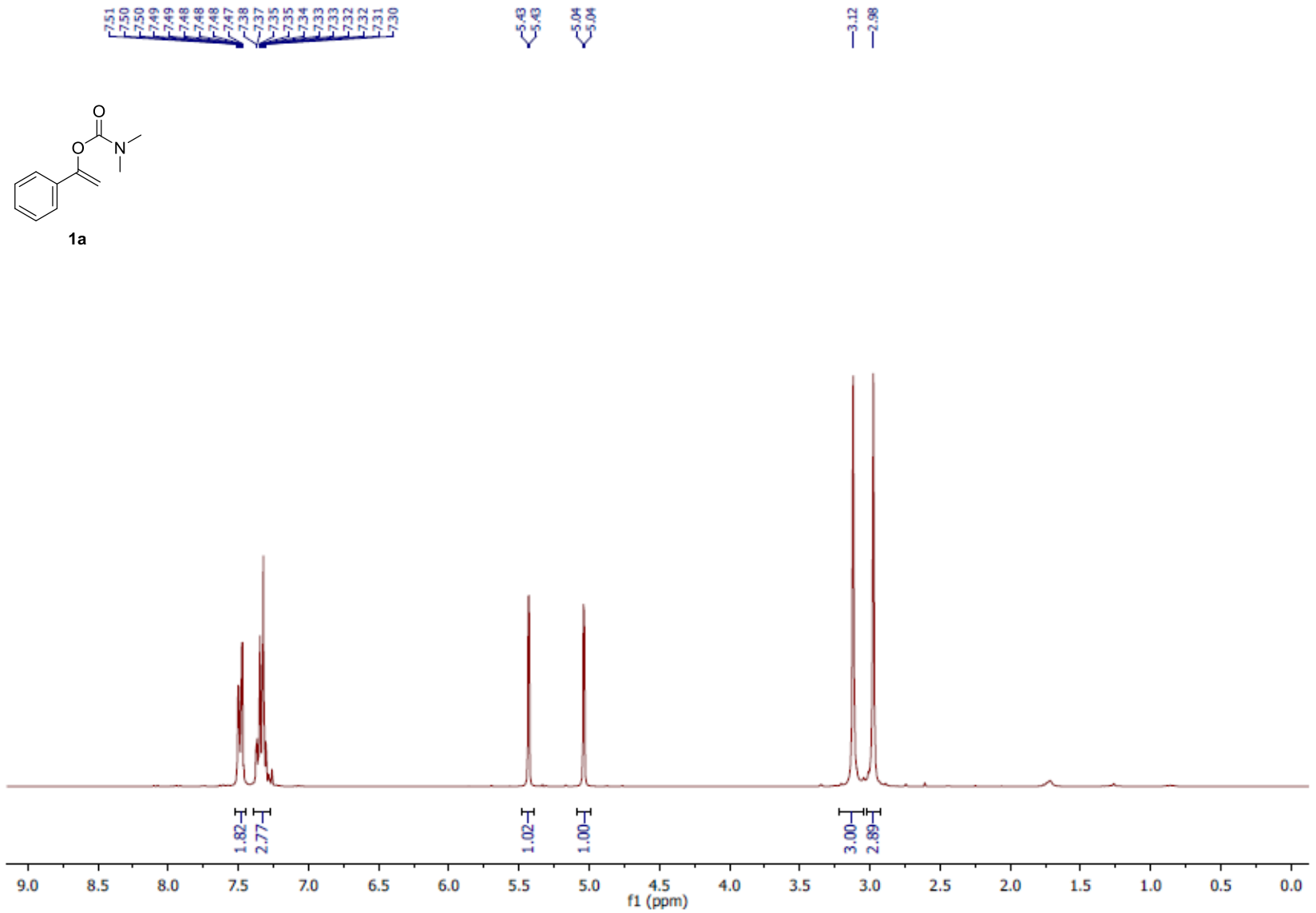
Table shows the affect of a given additive on the standard reaction. The yield of **3aa**, and the additive and starting material **1a** remaining after reaction are given. Color-coding should help the ready assessment of the data: green (above 66%), yellow (34-66%), red

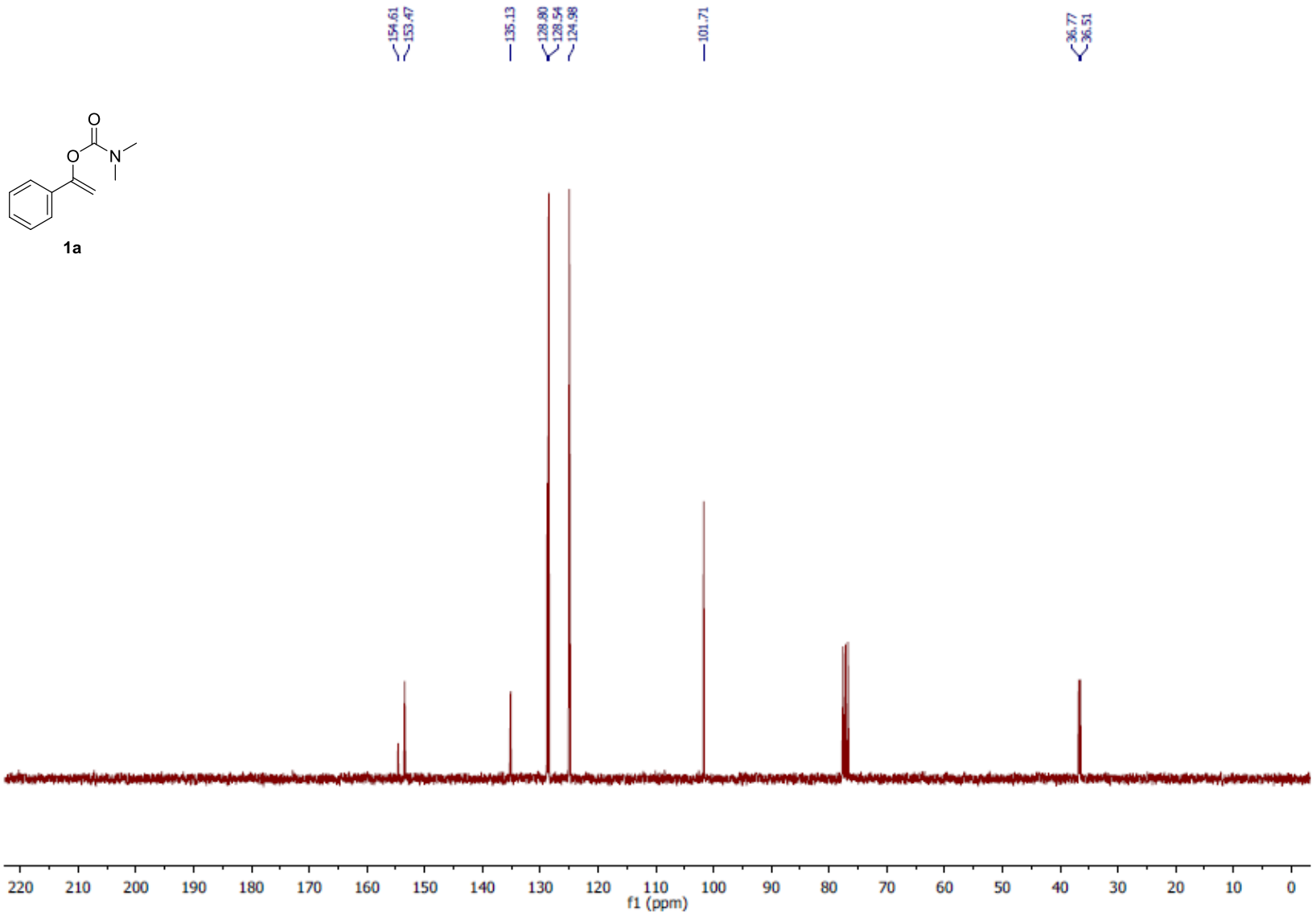
(below 34%). All yields are GC yields. SM is starting material. Yields in parenthesis are of the control group; selected experiments were repeated to ensure consistency and reproducibility of the data.

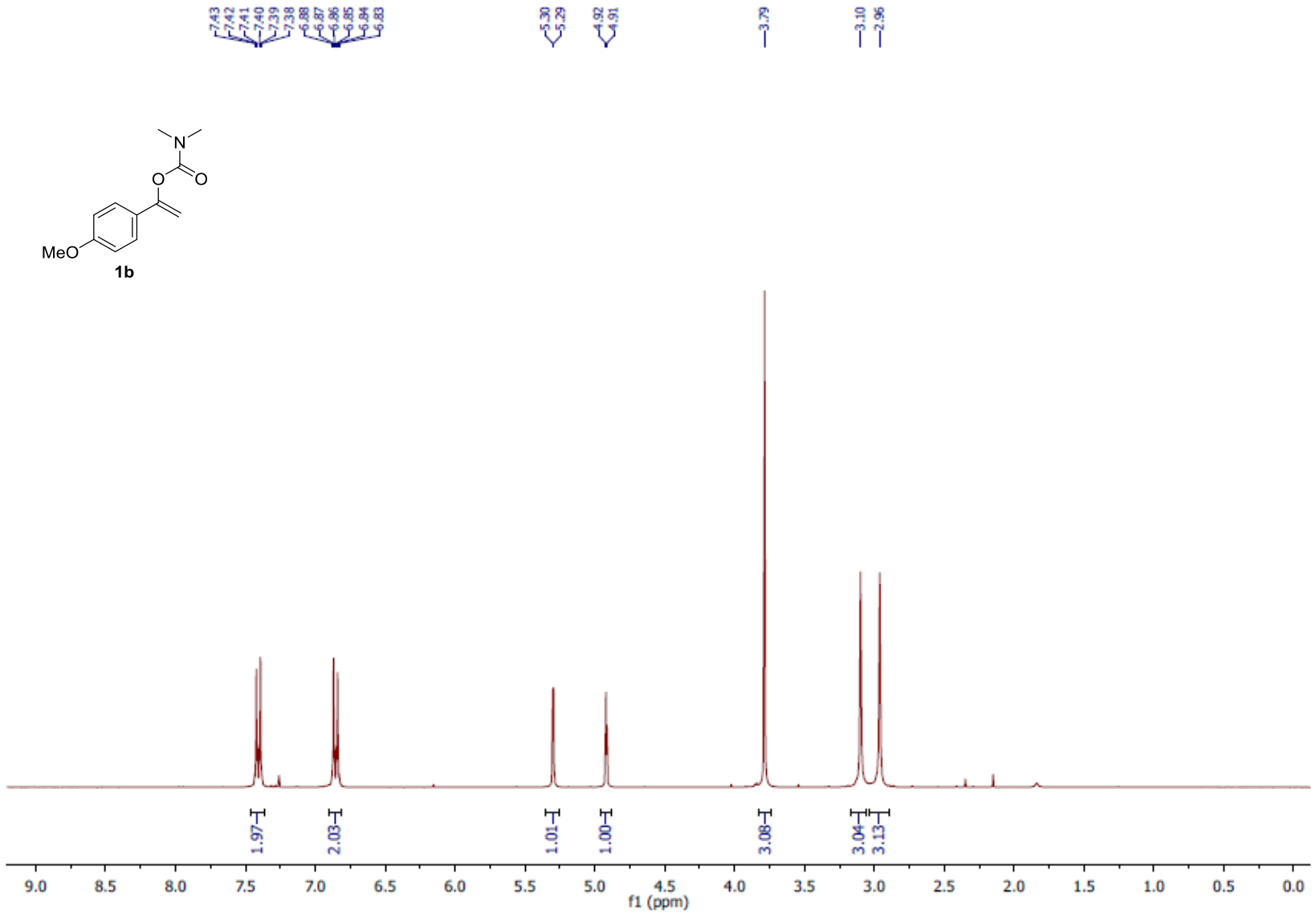
Group A suggests that aryl and alkyl chlorides, aromatic esters, tertiary amides, alcohols, terminal alkenes (partially decomposed) and aromatic nitriles are tolerated by the reaction and are stable to the conditions. Aniline and the primary amine both inhibit the reaction, though unlike aniline the primary amine is unstable to the reaction conditions. The terminal alkyne inhibits product formation and is unstable to the reaction conditions. The primary alcohol does not inhibit product formation but displays very low stability.

Group B demonstrates that the reaction is tolerant of many of the heterocycles assessed. However, most of the nitrogen-containing heterocycles appear to inhibit the reaction.

9. ^{1}H, ^{13}C and ^{19}F NMR of substrates and products


7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.48
7.47
7.38
7.37
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
5.43
5.43
5.04
5.04
3.12
2.98
O
O
N
1a
1.82
2.77
1.02
1.00
3.00
2.89
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)


154.61
153.47
135.13
128.80
128.54
124.98
101.71
36.77
36.51
O
O
N
1a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.43
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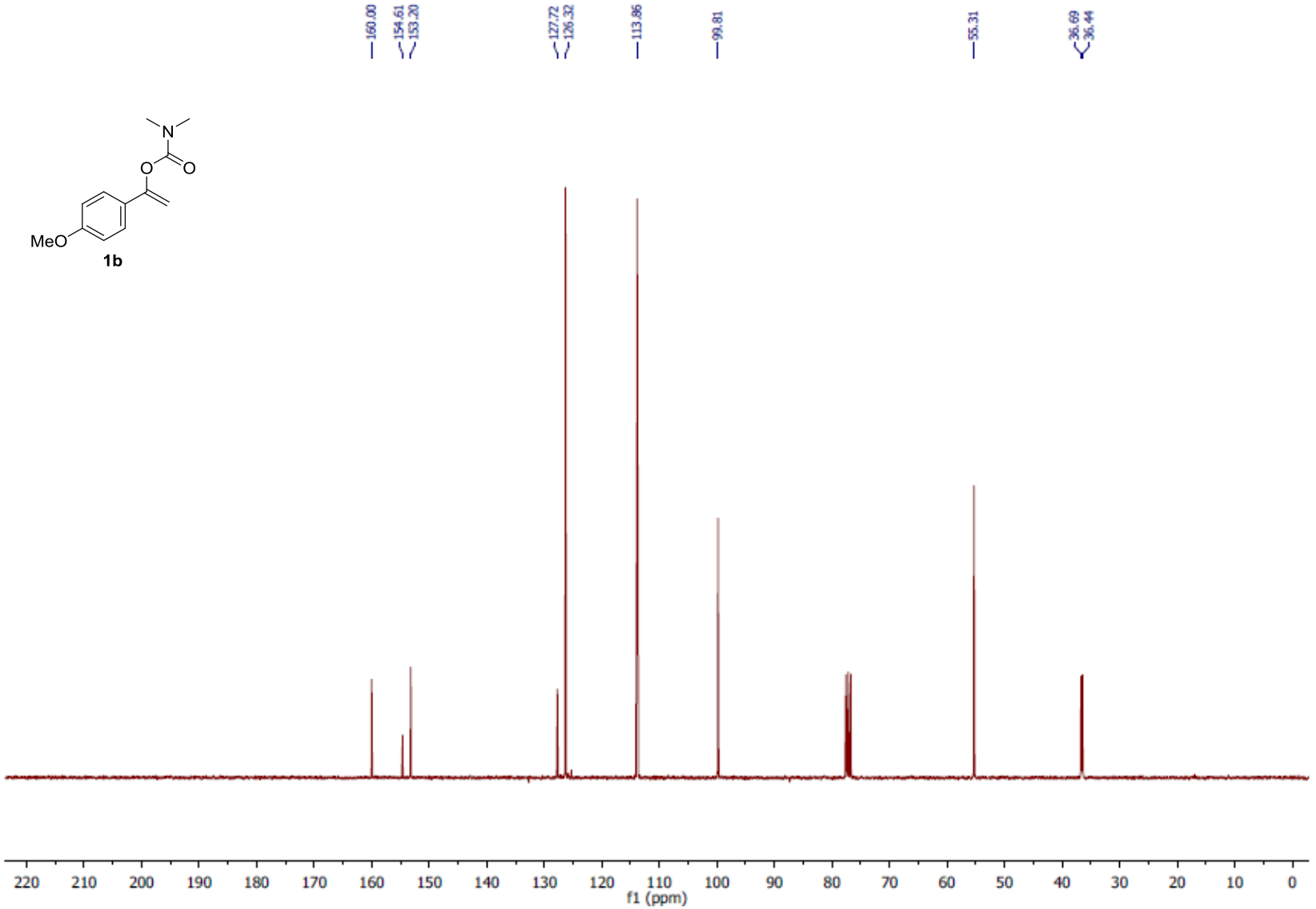
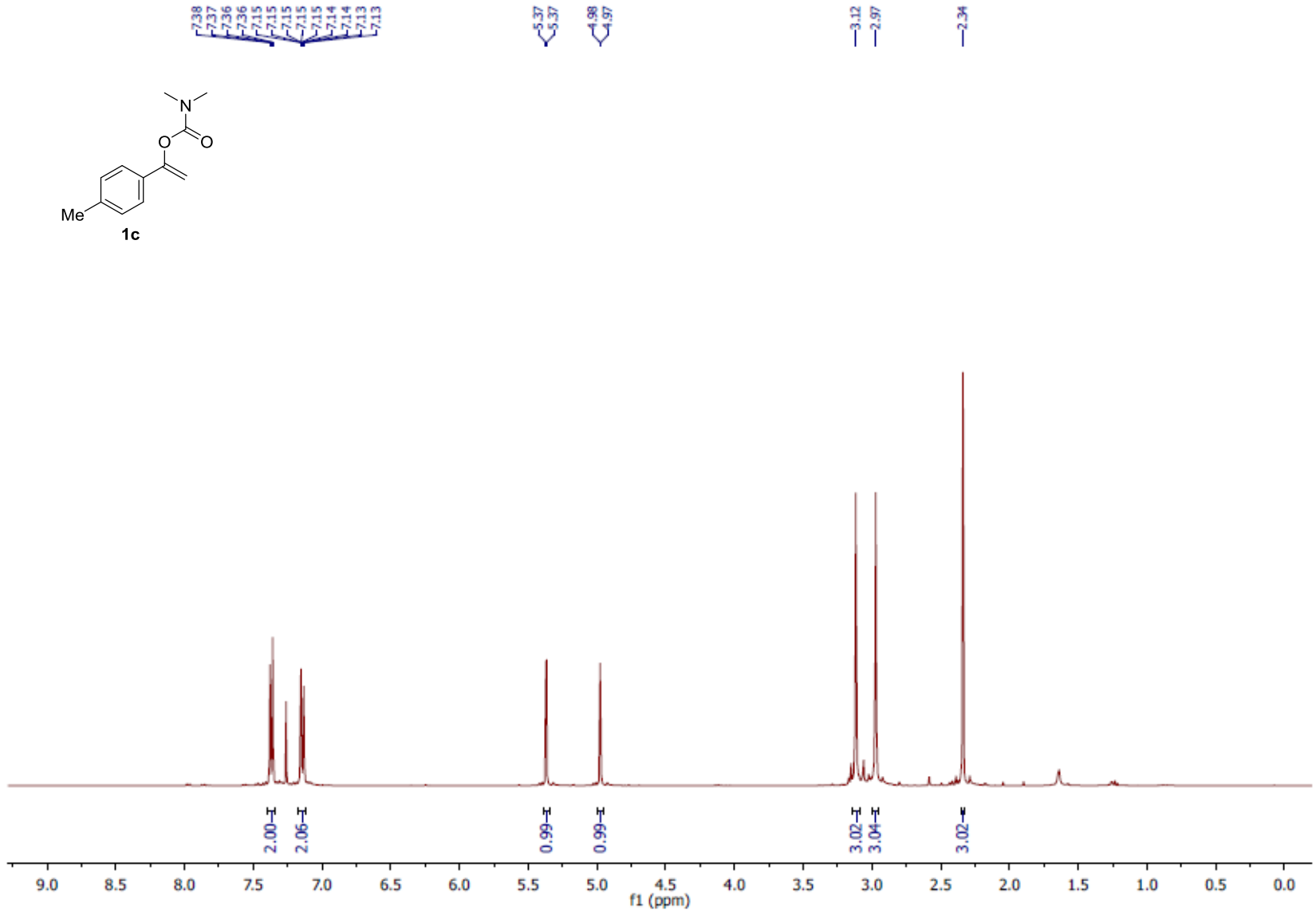
7.38
6.88
6.87
6.86
6.85
6.84
6.83
5.30
5.29
4.92
4.91
3.79
3.10
2.96
N
O
O
MeO
1b
1.97
2.03
1.01
1.00
3.08
3.04
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.00
154.61
153.20
127.72
126.32
113.86
99.81
55.31
36.69
36.44
MeO
1b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.15
7.15
7.15
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7.14
7.14
7.13
7.13
5.37
5.37
4.98
4.97
3.12
2.97
2.34
N
O
O
Me
1c
2.00
2.06
0.99
0.99
3.02
3.04
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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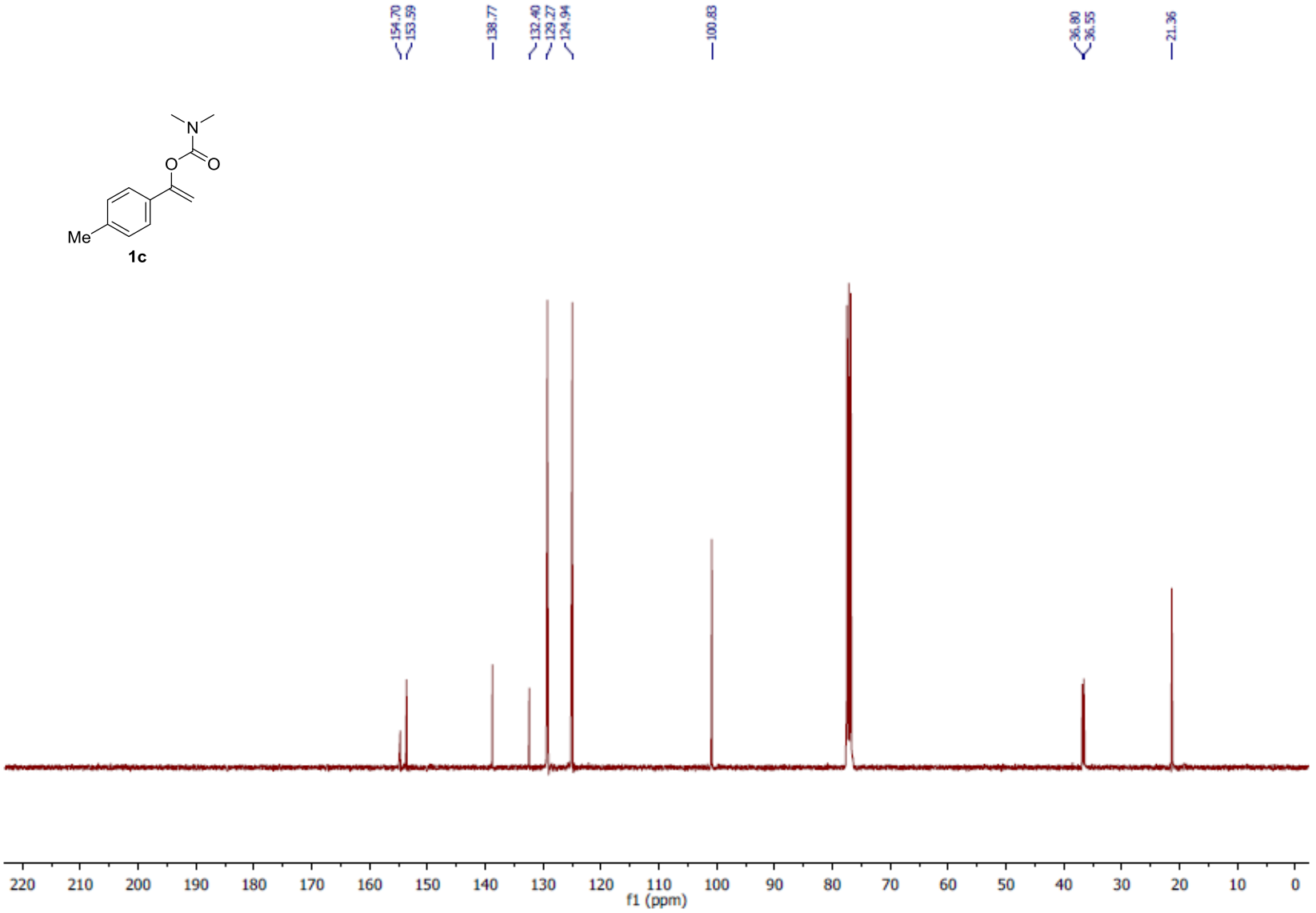
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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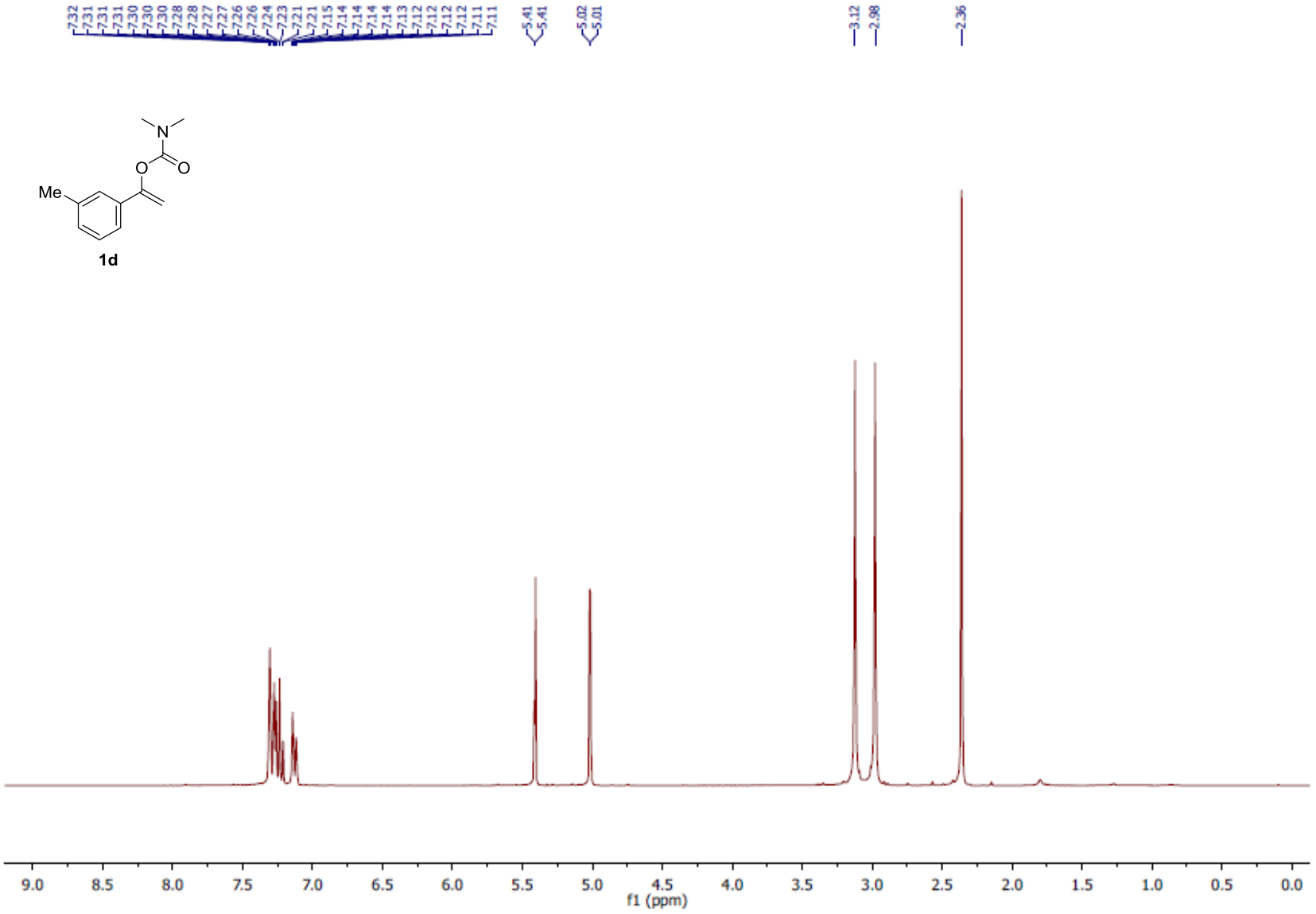
153.59
138.77
132.40
129.27
124.94
100.83
36.80
36.55
21.36
N
O
O
Me
1c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
7.26
7.24
7.23
7.21
7.21
7.15
7.14
7.14
7.14
7.14
7.13
7.12
7.12
7.12
7.12
7.11
7.11
5.41
5.41
5.02
5.01
3.12
2.98
2.36
N
O
O
Me
1d
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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1.0
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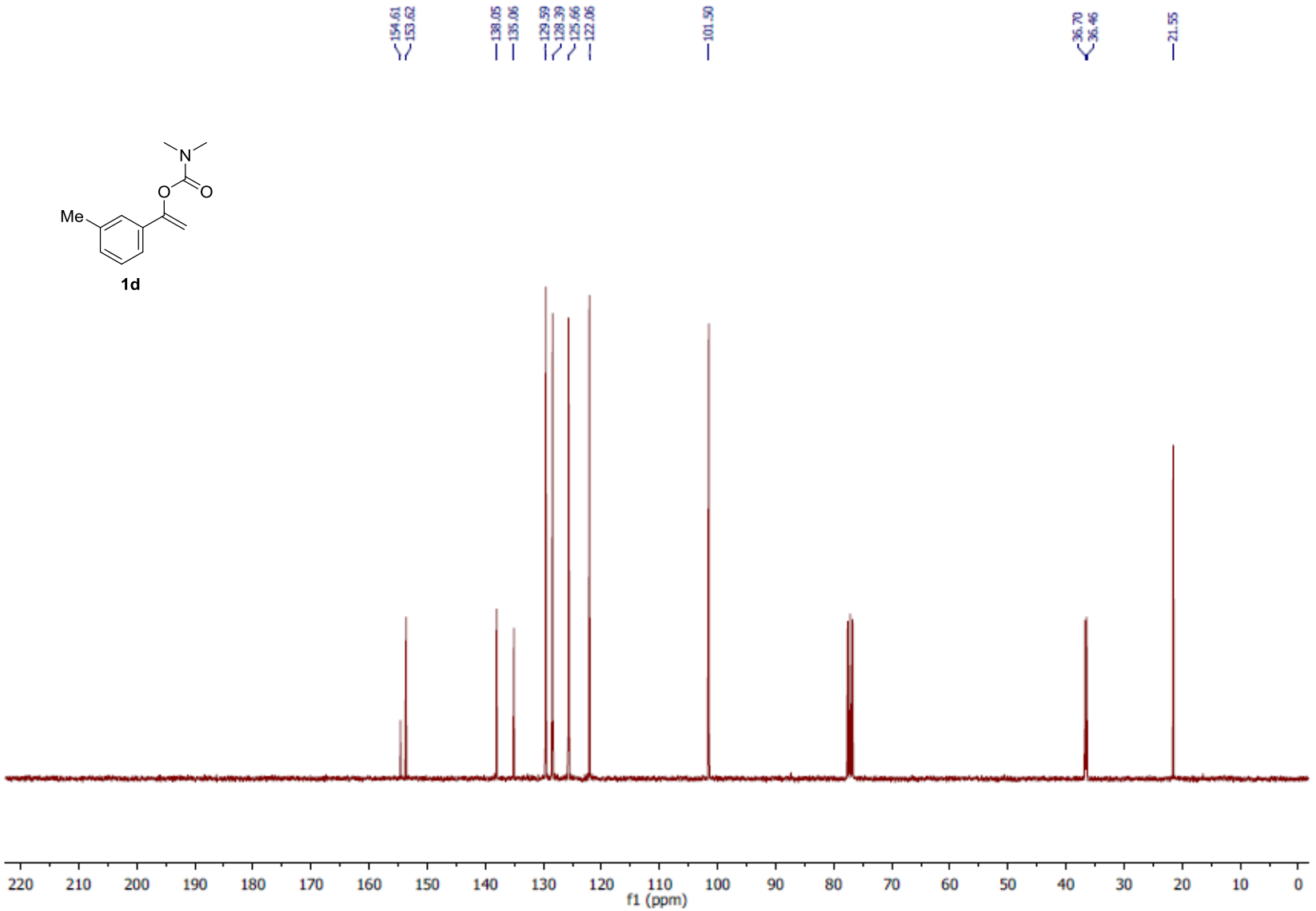
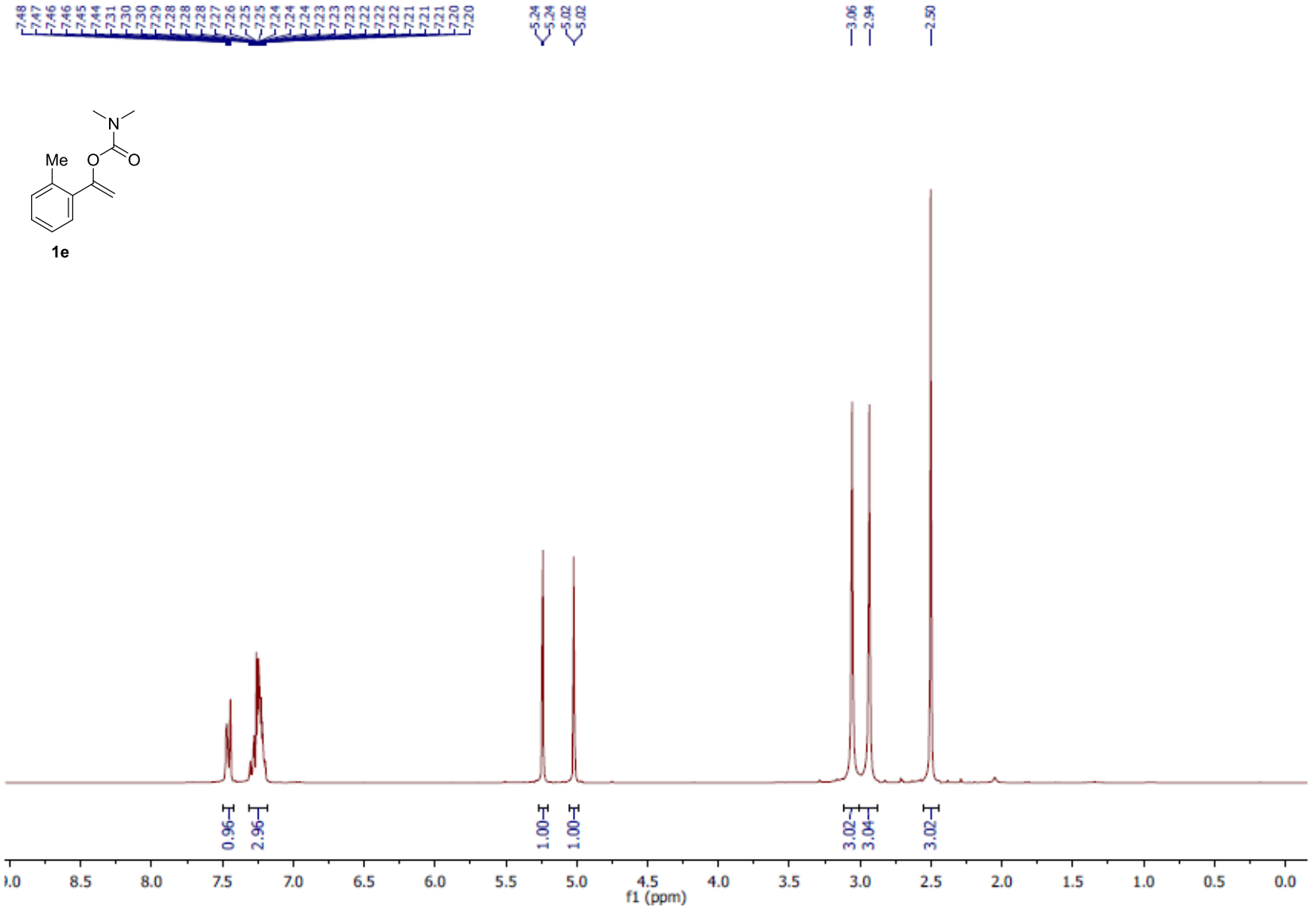
0.0
f1 (ppm)


154.61
153.62
138.05
135.06
129.59
128.39
125.66
122.06
101.50
36.70
36.46
21.55
Me
1d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.29
7.28
7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.21
7.20
7.20
5.24
5.24
5.02
5.02
3.06
2.94
2.50
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Me
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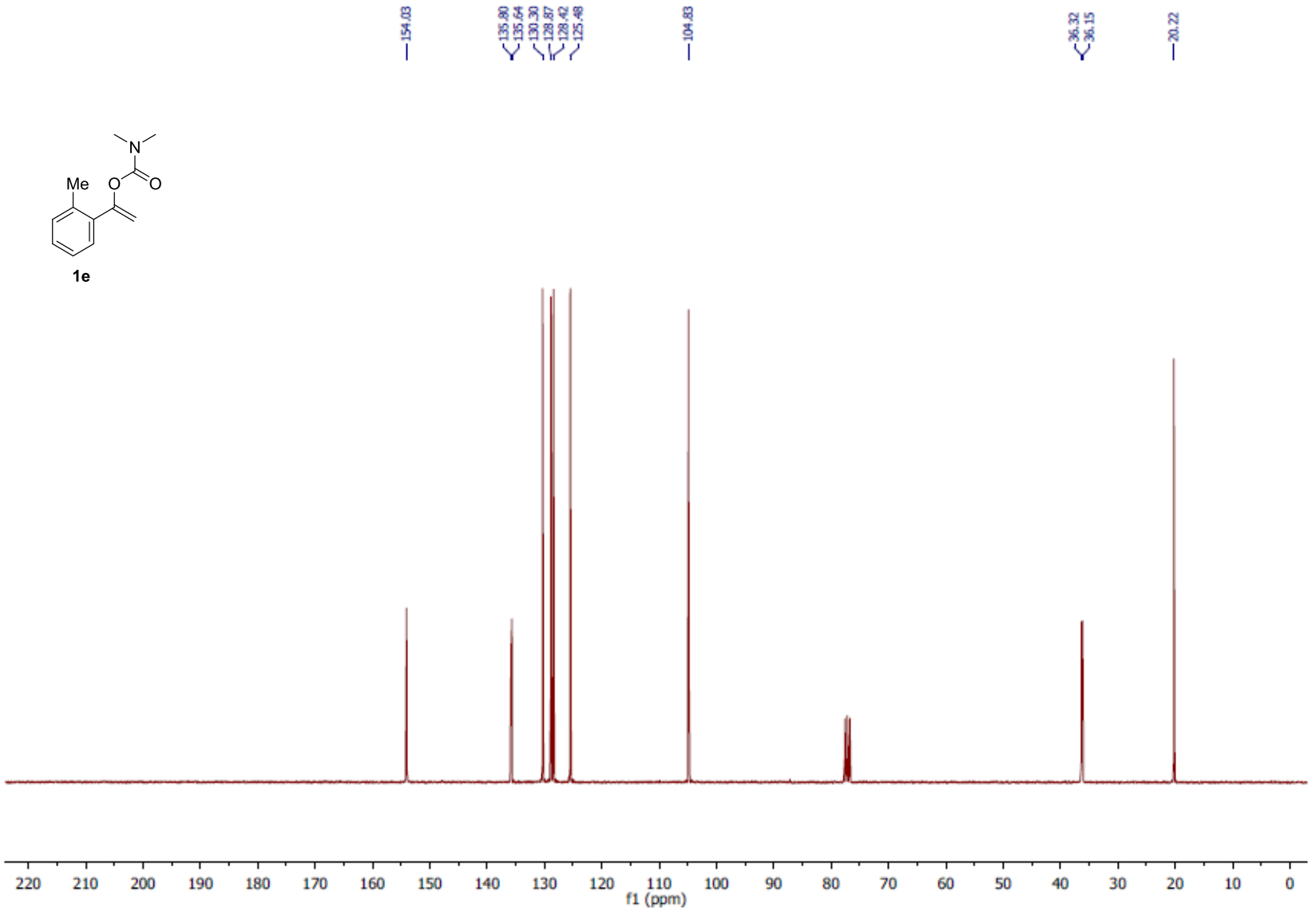
O
1e
0.96
2.96
1.00
1.00
3.02
3.04
3.02
f1 (ppm)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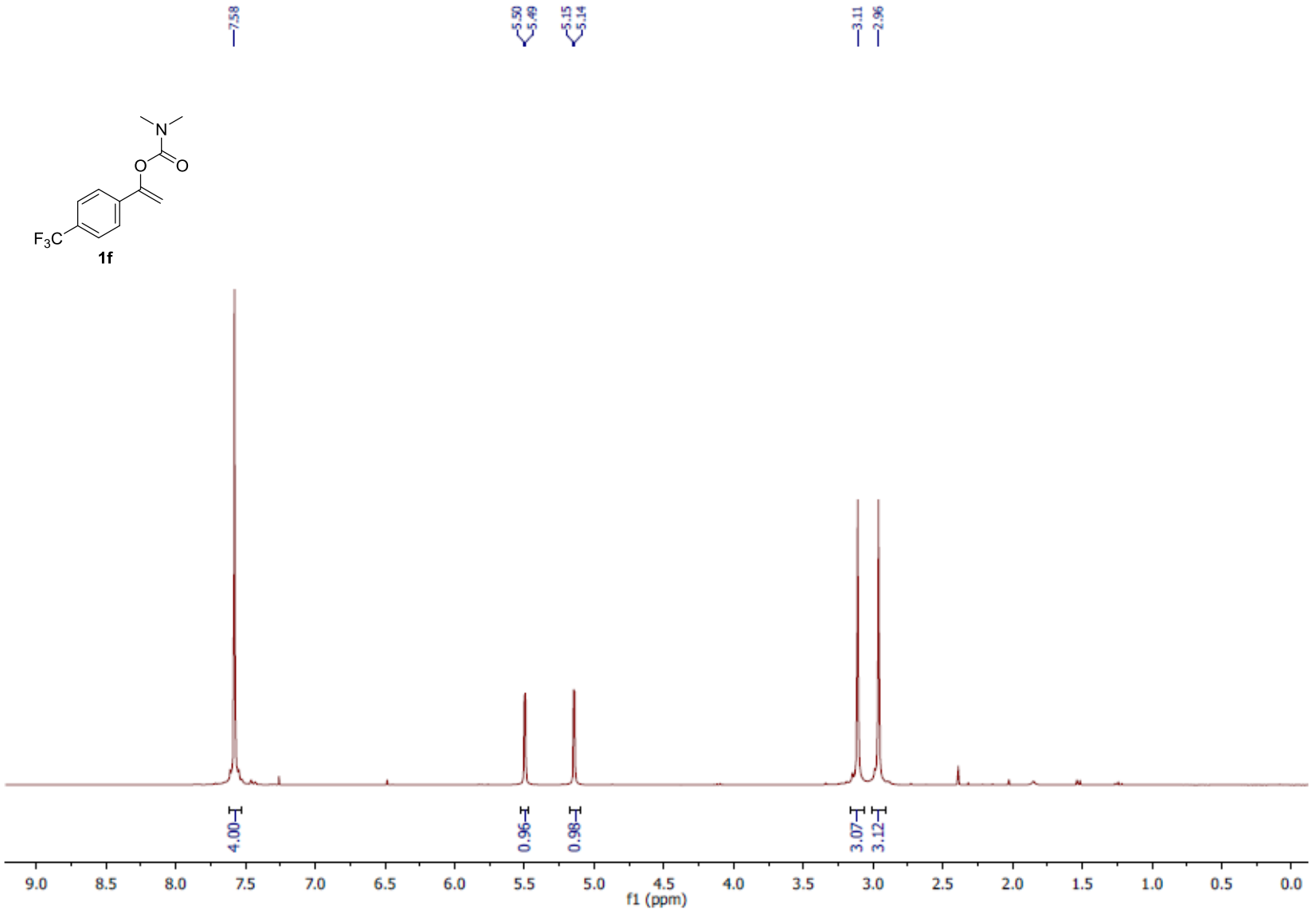
135.80
135.64
130.30
128.87
128.42
125.48
104.83
36.32
36.15
20.22
Me
O
O
N
1e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.58
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3.11
2.96
N
O
O
F3C
1f
4.00
0.96
0.98
3.07
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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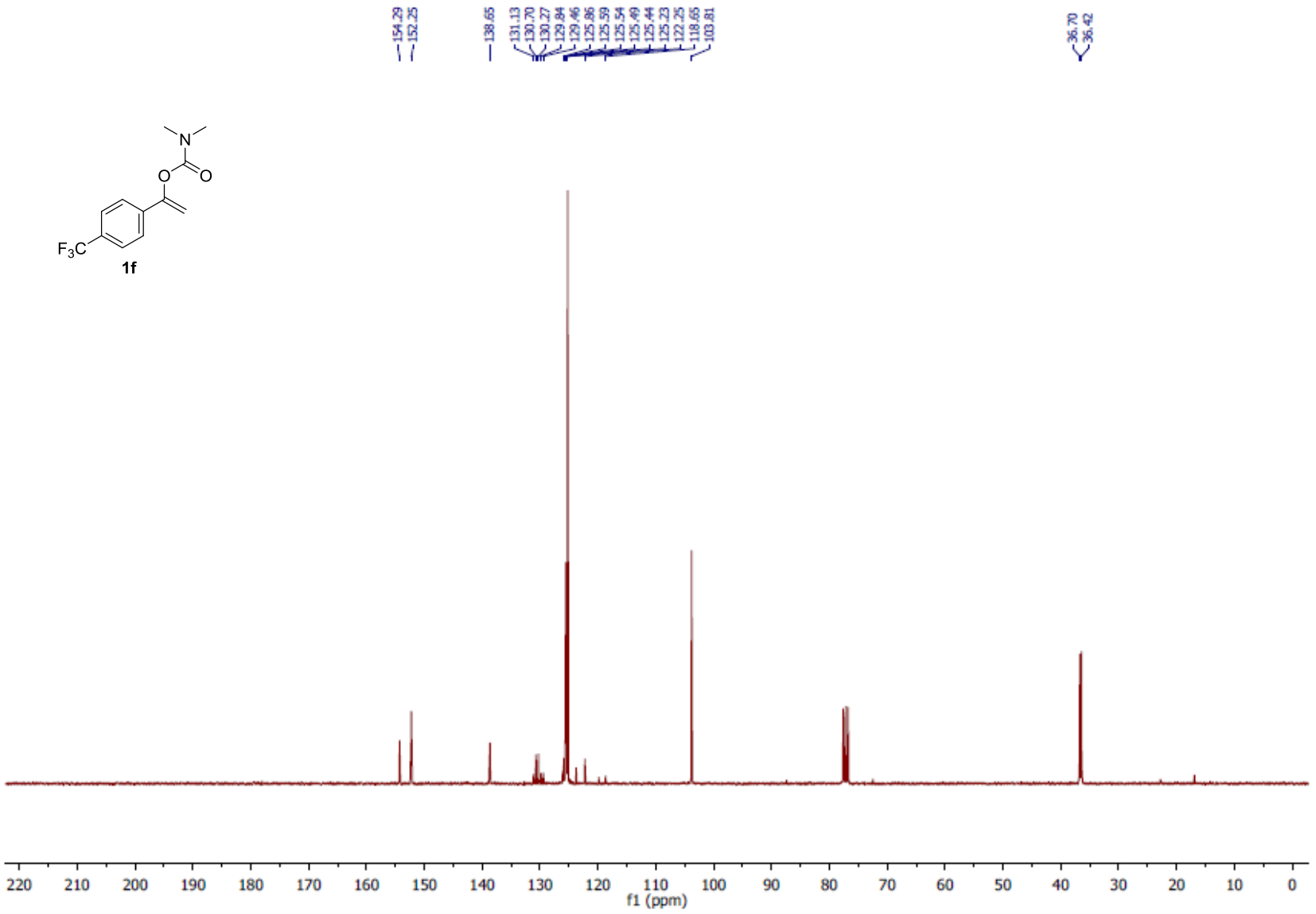
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.13
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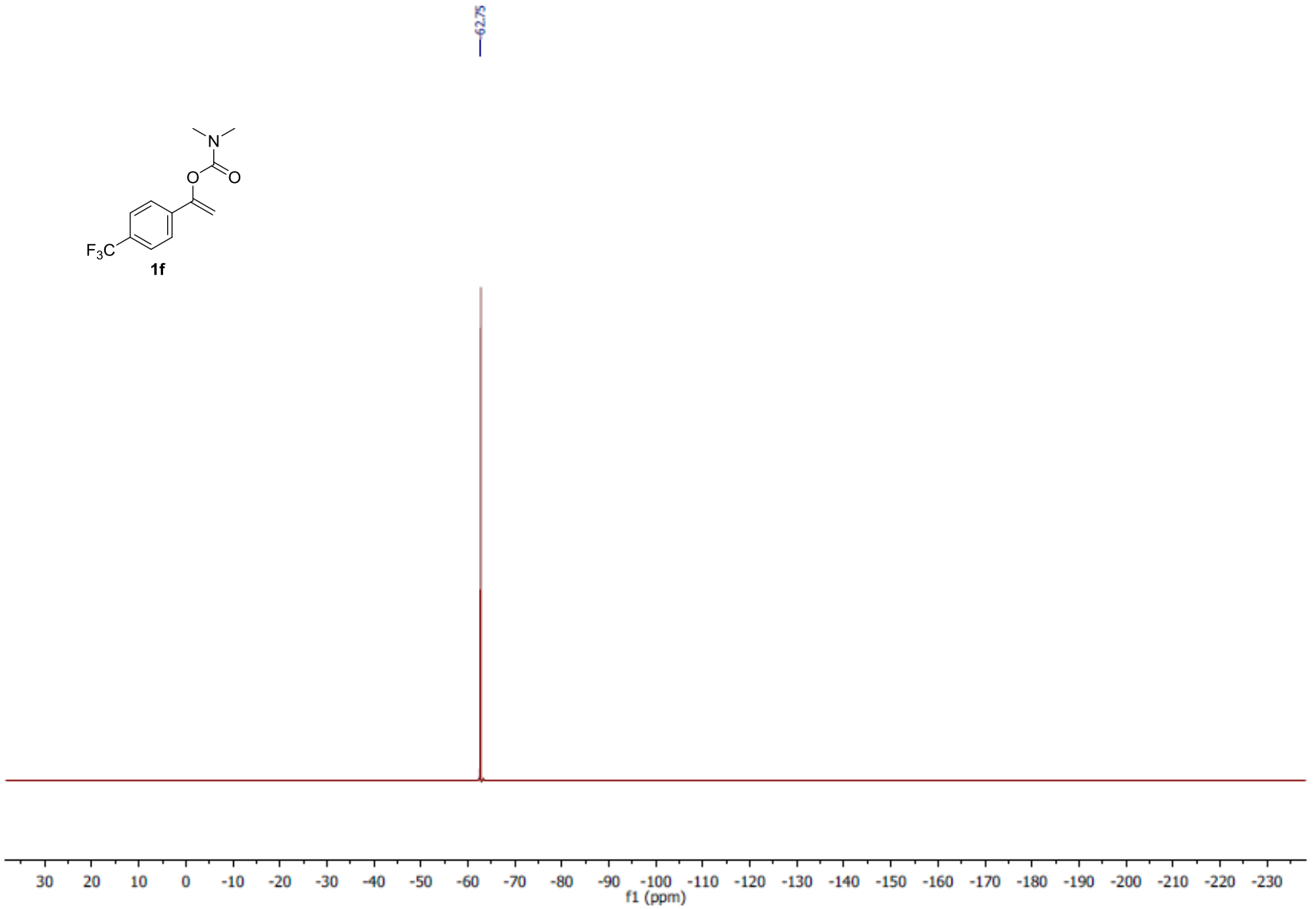
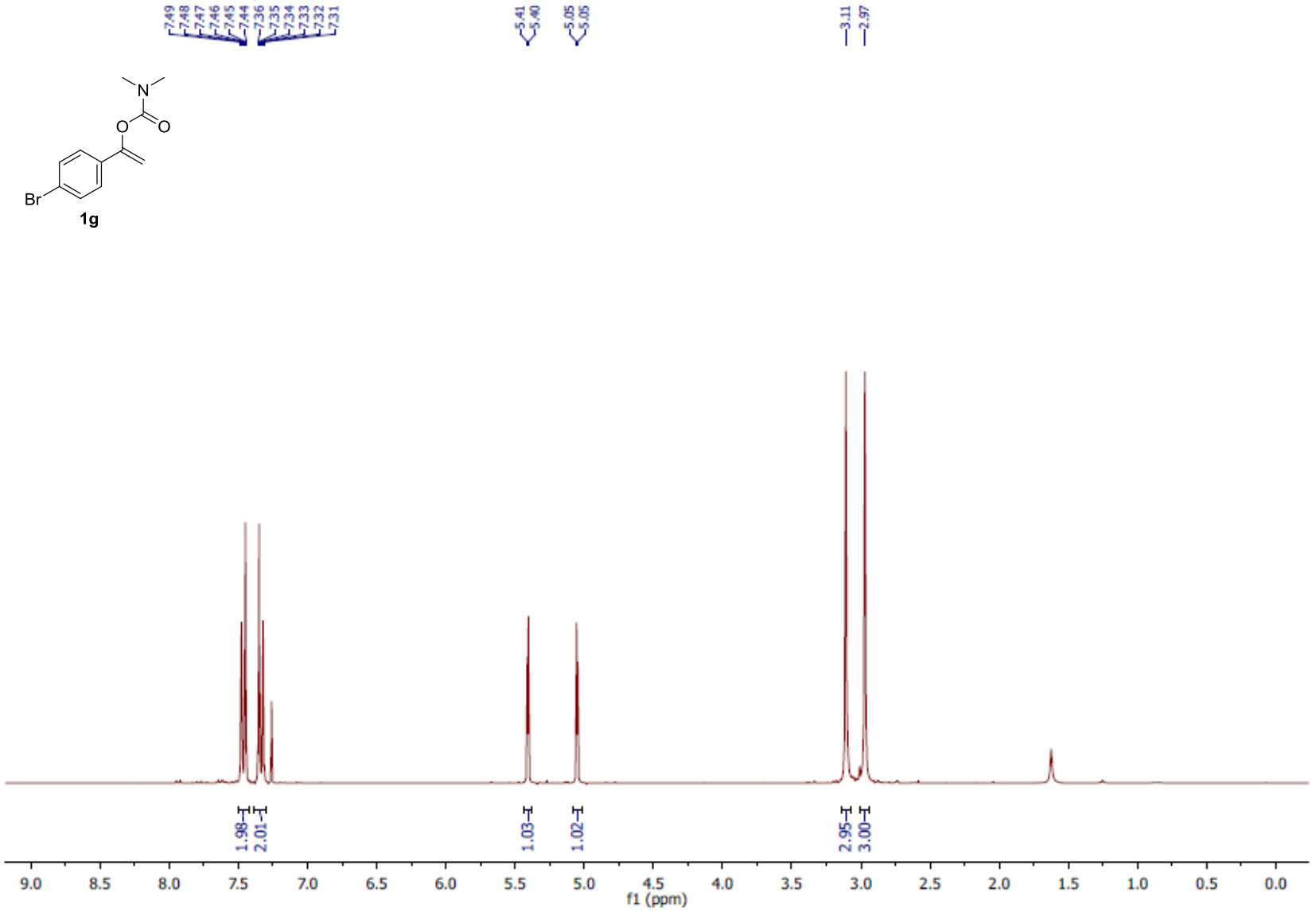
125.54
125.49
125.44
125.23
122.25
118.65
103.81
36.70
36.42
N
O
O
F3C
1f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


62.75
N
O
O
F3C
1f
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


7.49
7.48
7.47
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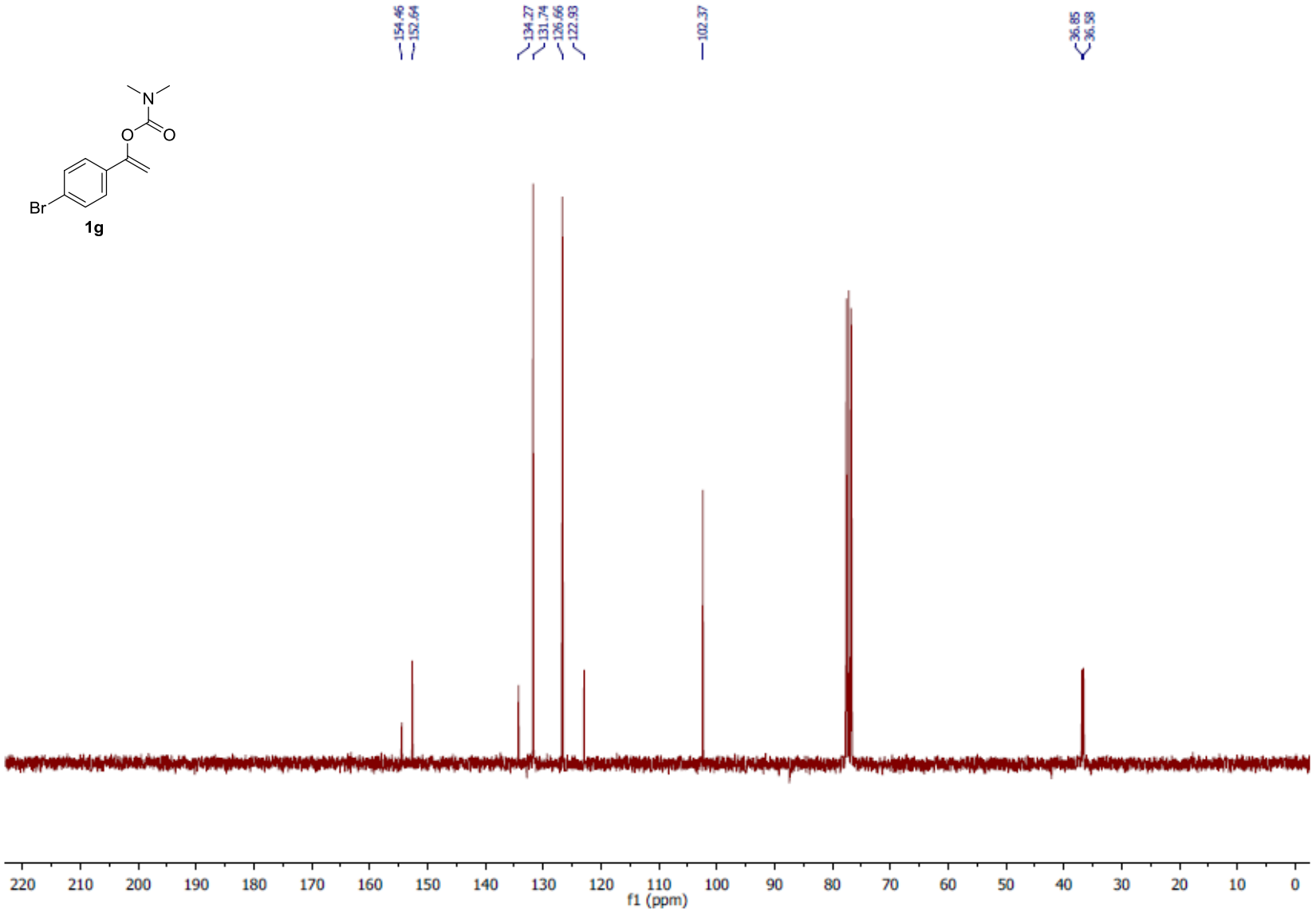
7.45
7.44
7.36
7.35
7.34
7.33
7.32
7.31
5.41
5.40
5.05
5.05
3.11
2.97
N
O
O
Br
1g
1.98
2.01
1.03
1.02
2.95
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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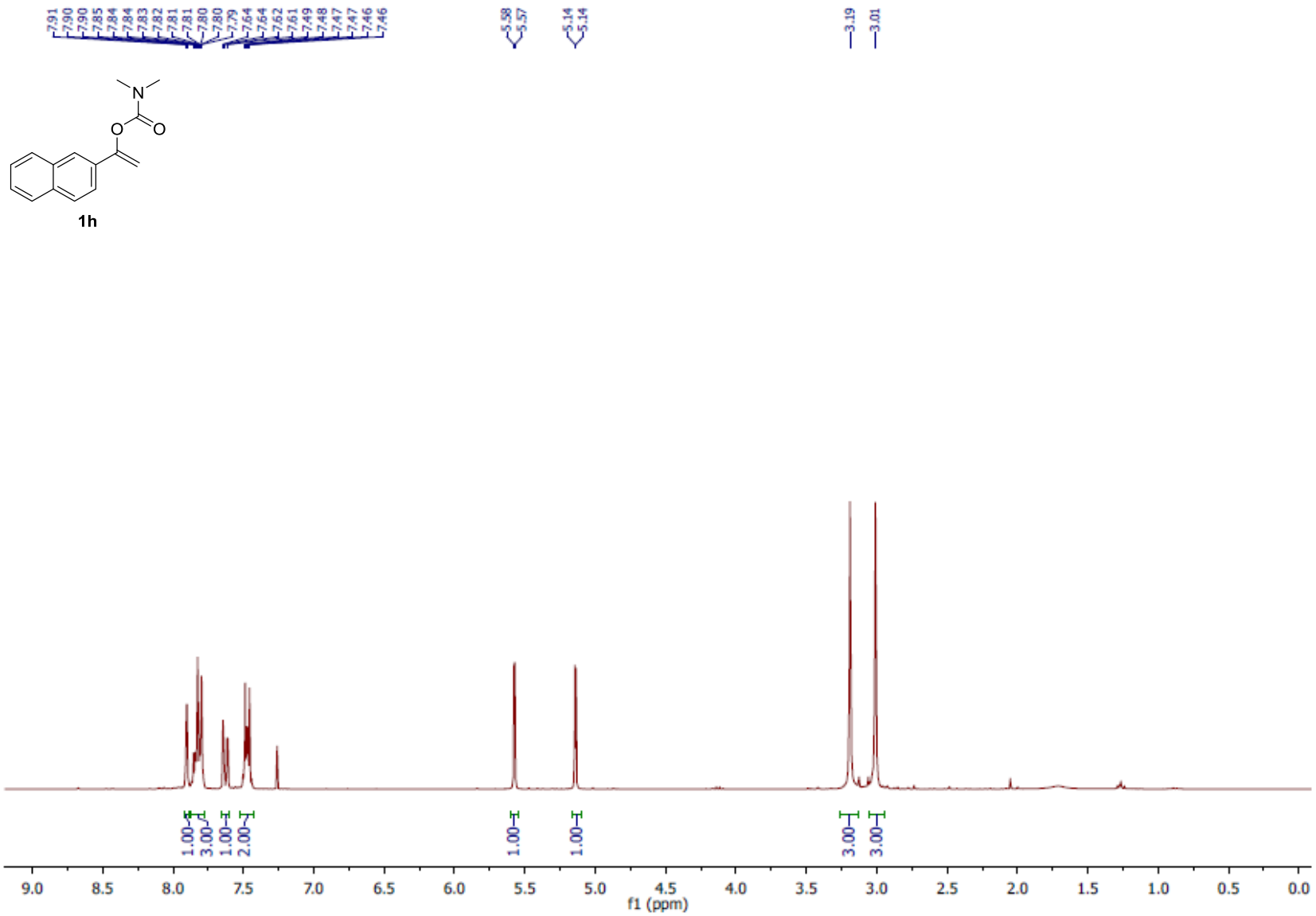
134.27
131.74
126.66
122.93
102.37
36.85
36.58
Br
1g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.91
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7.90
7.85
7.84
7.84
7.83
7.82
7.81
7.81
7.80
7.80
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7.62
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3.01
N
O
O
1h
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3.00
1.00
2.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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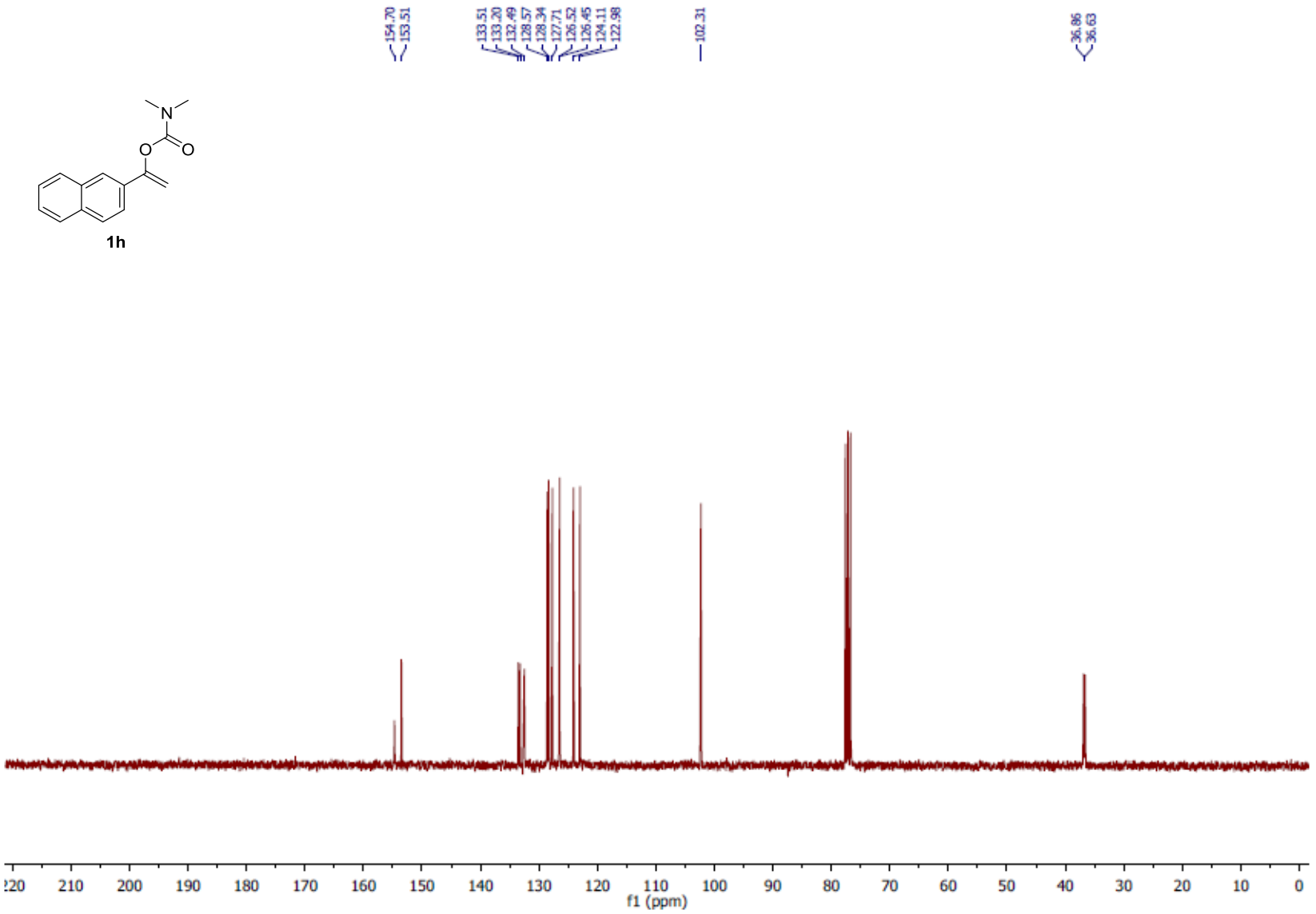
0.0
f1 (ppm)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133.51
133.20
132.49
128.57
128.34
127.71
126.52
126.45
124.11
122.98
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36.86
36.63
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O
O
1h
220
210
200
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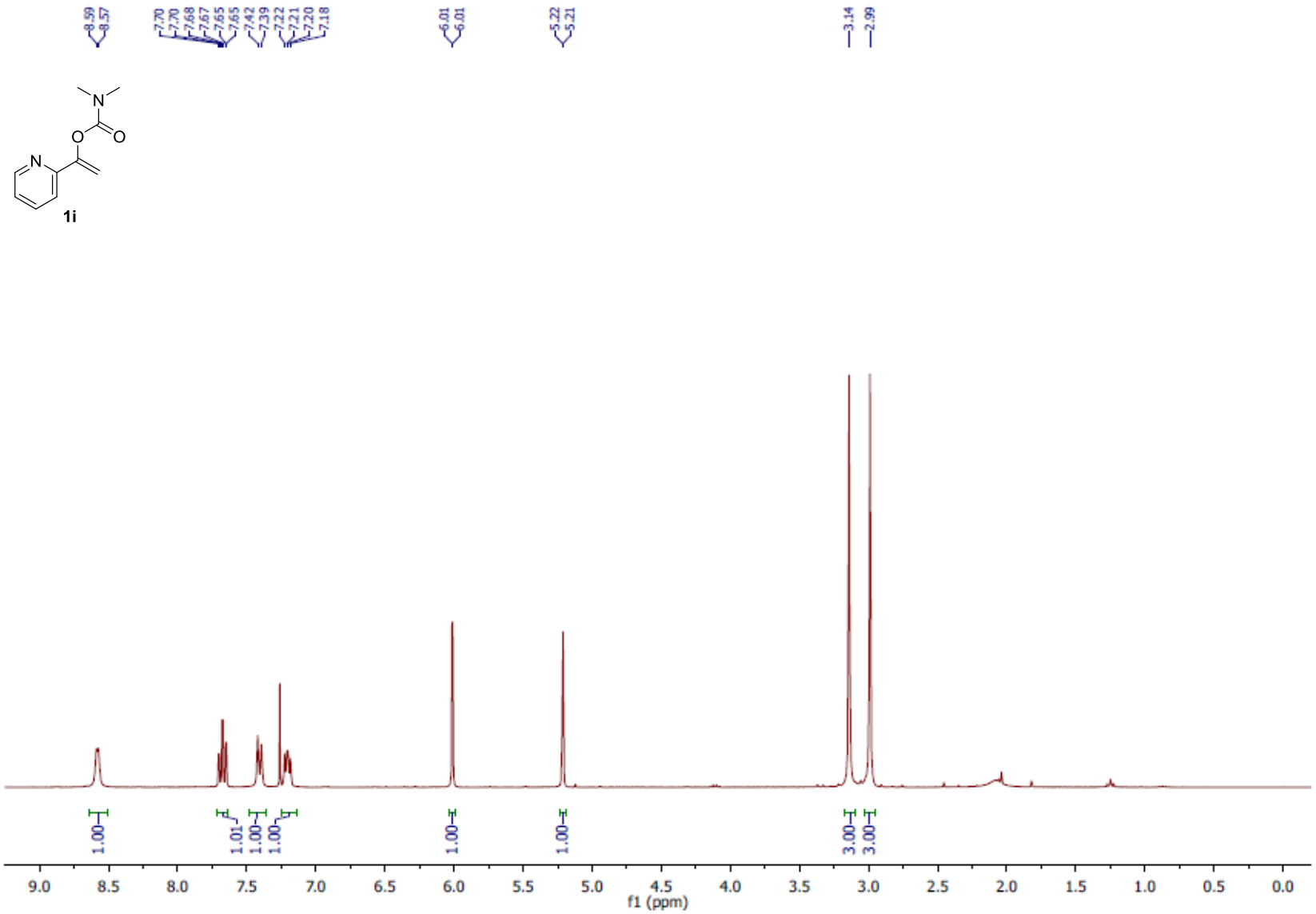
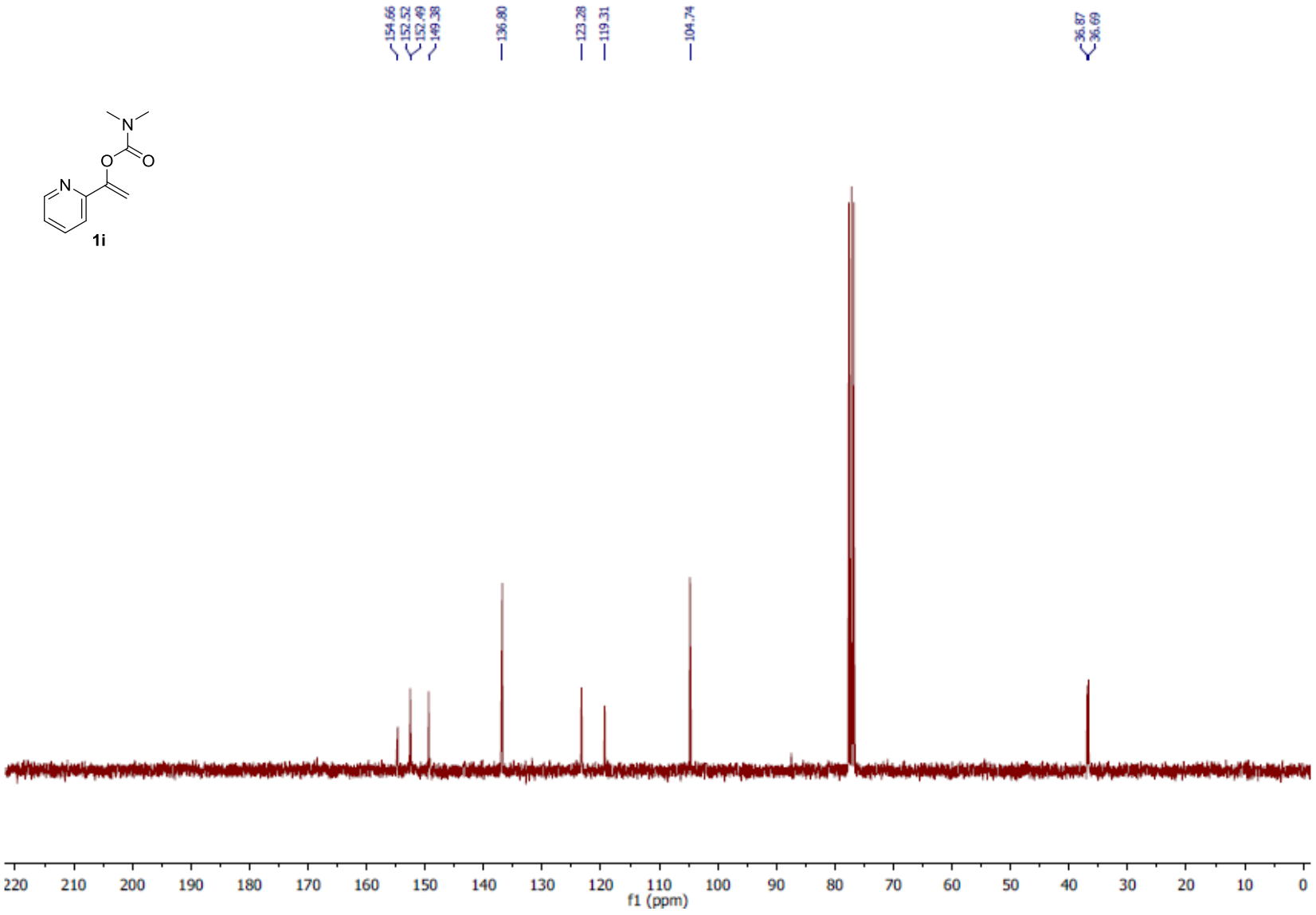
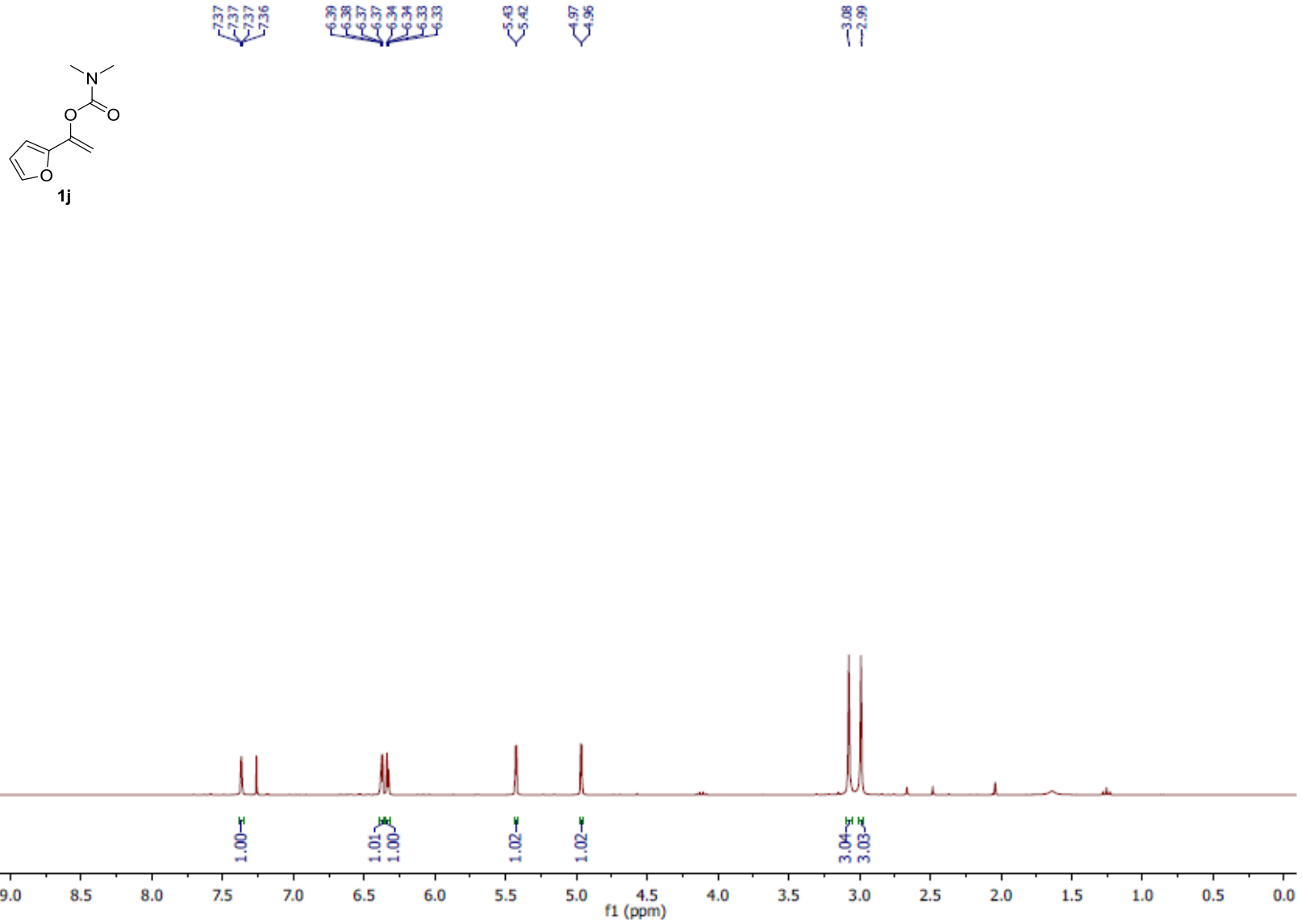
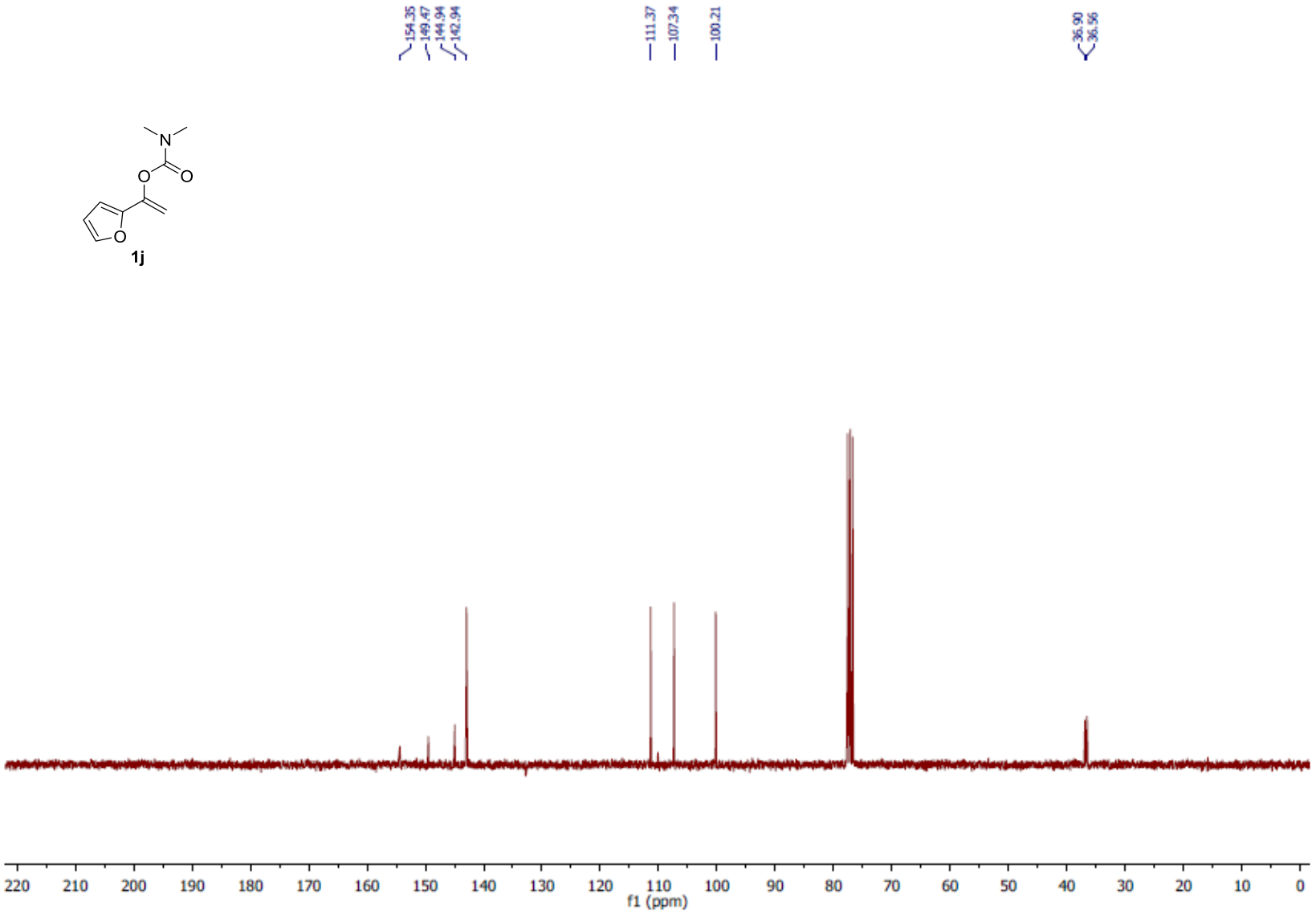
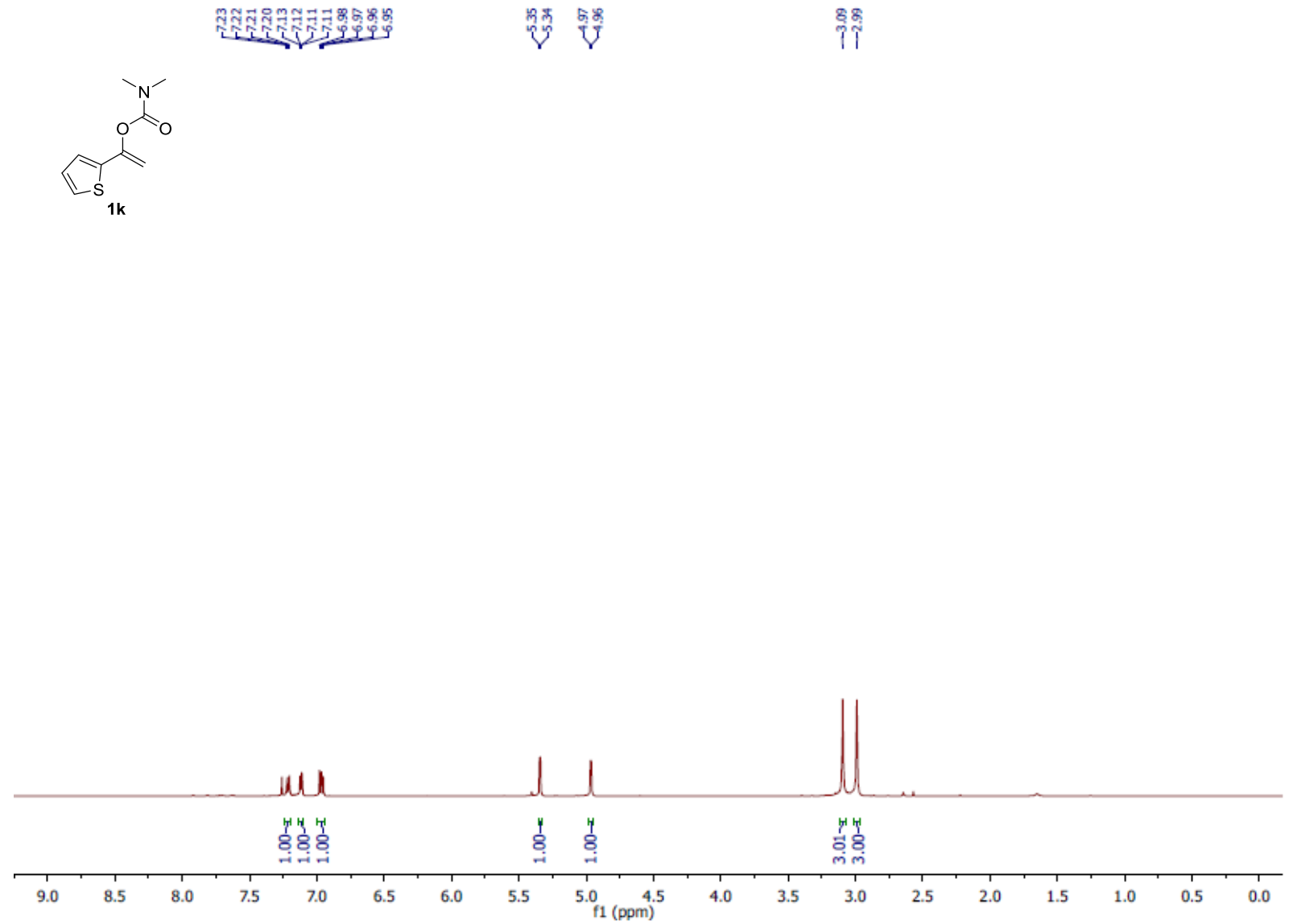
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

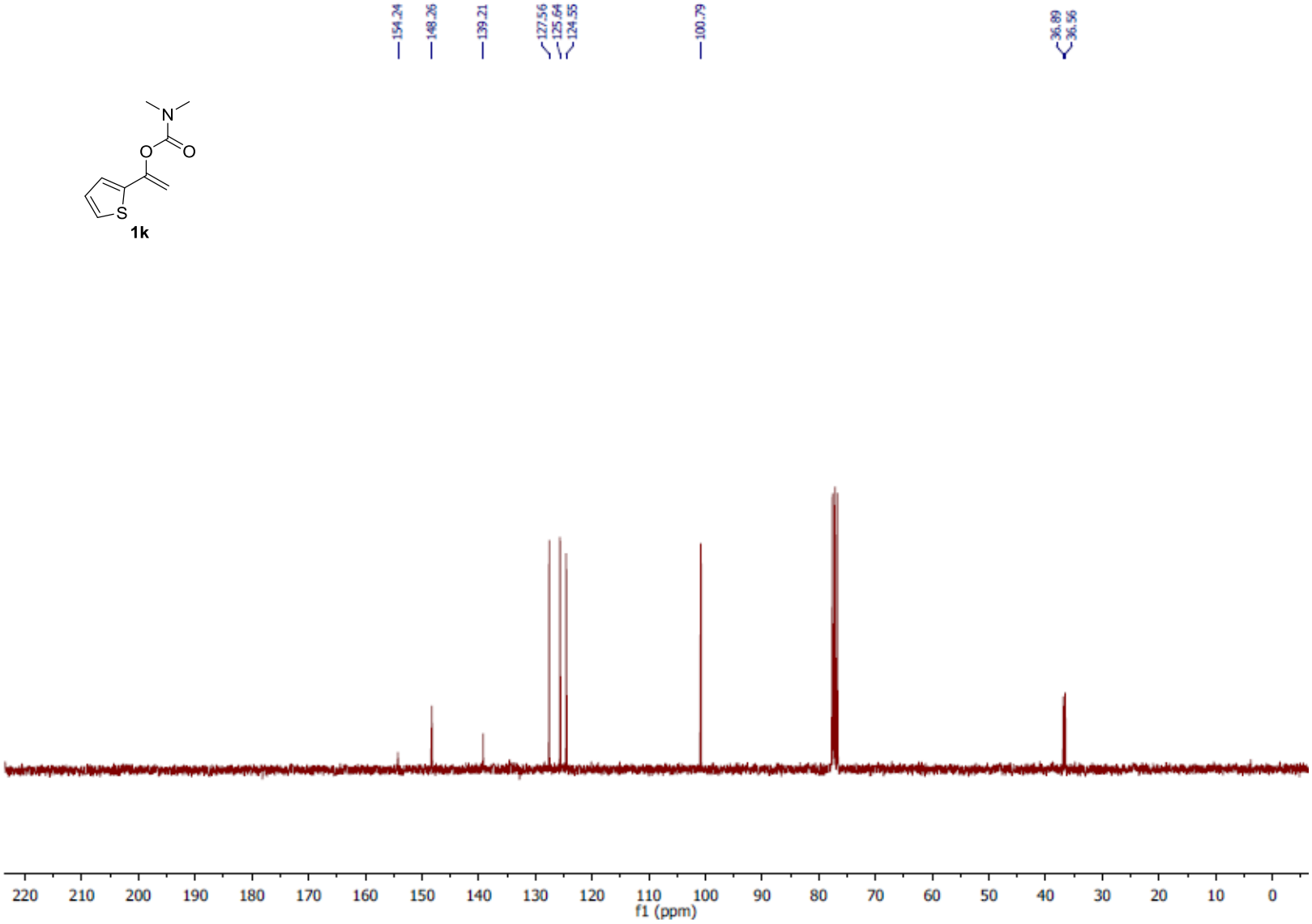

8.59
8.57
7.70
7.70
7.68
7.67
7.65
7.65
7.42
7.39
7.22
7.21
7.20
7.18
6.01
6.01
5.22
5.21
3.14
2.99
N
O
O
N
1i
1.00
1.01
1.00
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

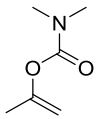

154.66
152.52
152.49
149.38
136.80
123.28
119.31
104.74
36.87
36.69
1i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37
7.37
7.37
7.36
6.39
6.38
6.37
6.37
6.34
6.34
6.33
6.33
5.43
5.42
4.97
4.96
3.08
2.99
N
O
O
O
1j
1.00
1.01
1.00
1.02
1.02
3.04
3.03
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)


154.35
149.47
144.94
142.94
111.37
107.34
100.21
36.90
36.56
N
O
O
O
1j
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

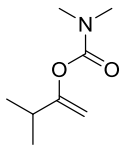

7.23
7.22
7.21
7.20
7.13
7.12
7.11
7.11
6.98
6.97
6.96
6.95
5.35
5.34
4.97
4.96
3.09
2.99
1k
1.00
1.00
1.00
1.00
1.00
3.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.24
148.26
139.21
127.56
125.64
124.55
100.79
36.89
36.56
N
O
O
S
1k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



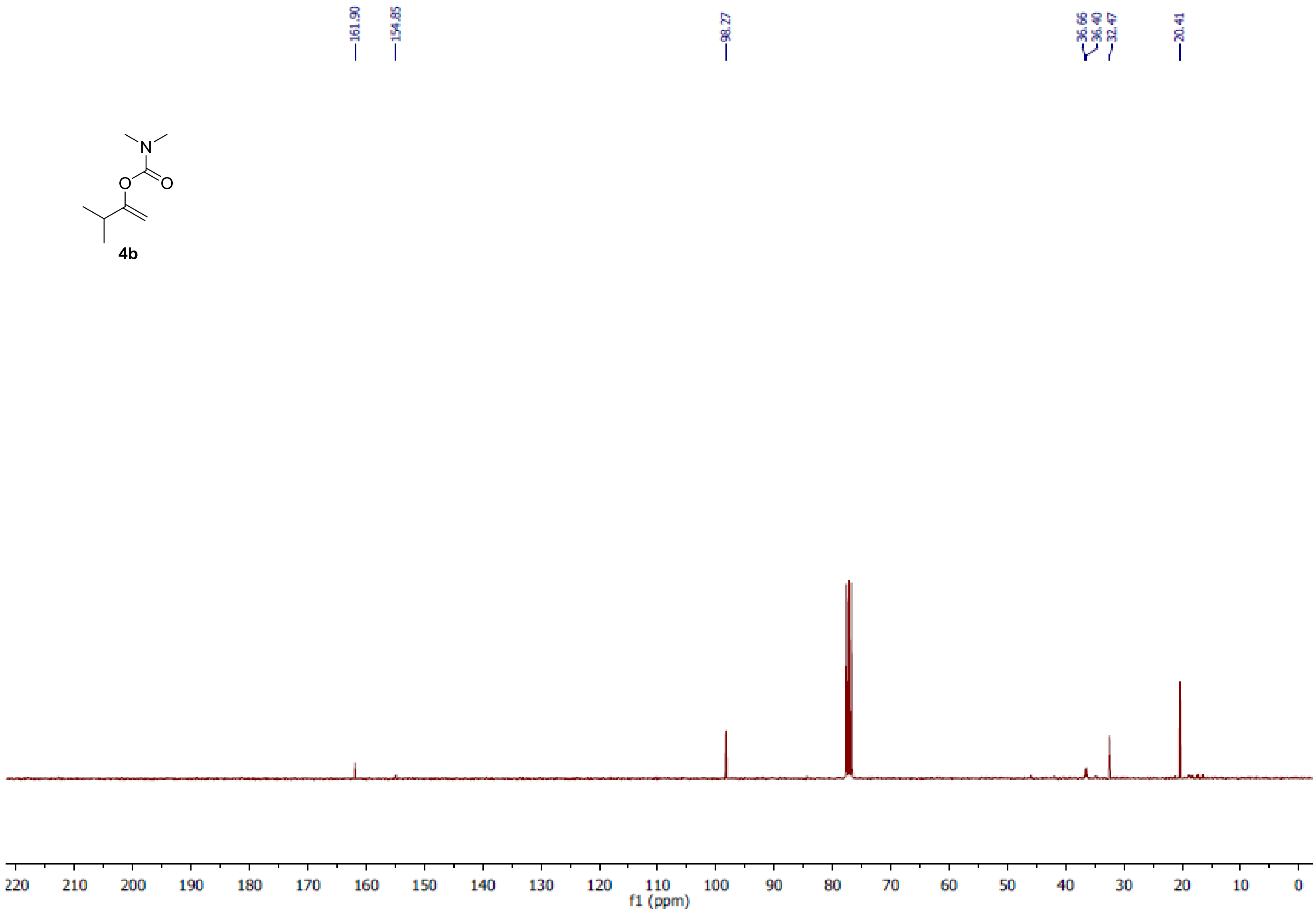
4a

1.67
1.67
1.66
1.65
1.64
1.64
2.95
2.94
1.94
1.94
2.00
6.03
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



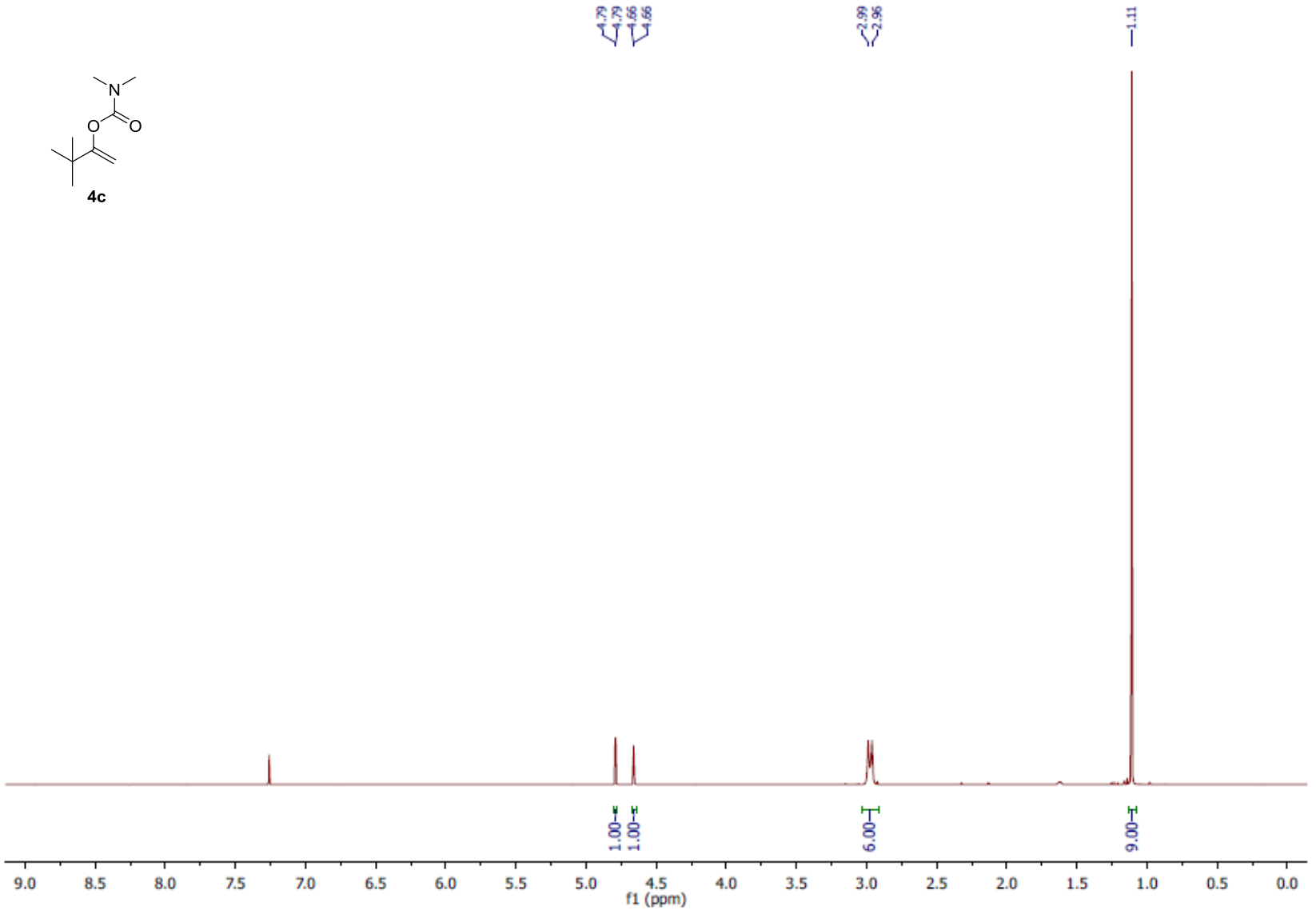
4b

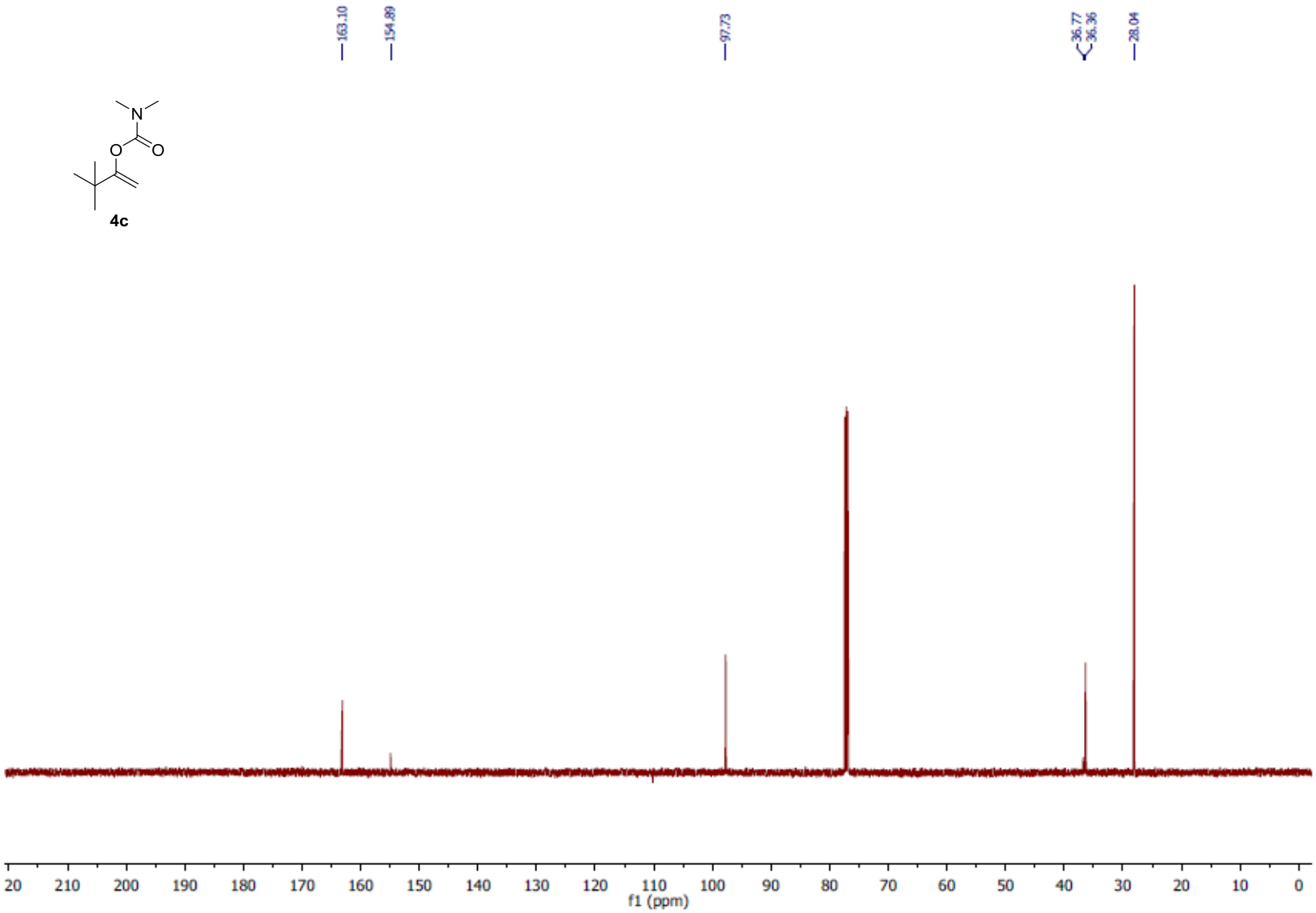
4.69
3.06
2.97
2.95
2.86
2.53
2.51
2.49
2.47
2.44
2.42
2.40
1.10
1.07
1.84
6.05
0.97
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

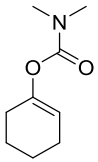


4b

161.90
154.85
98.27
36.66
36.40
32.47
20.41
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

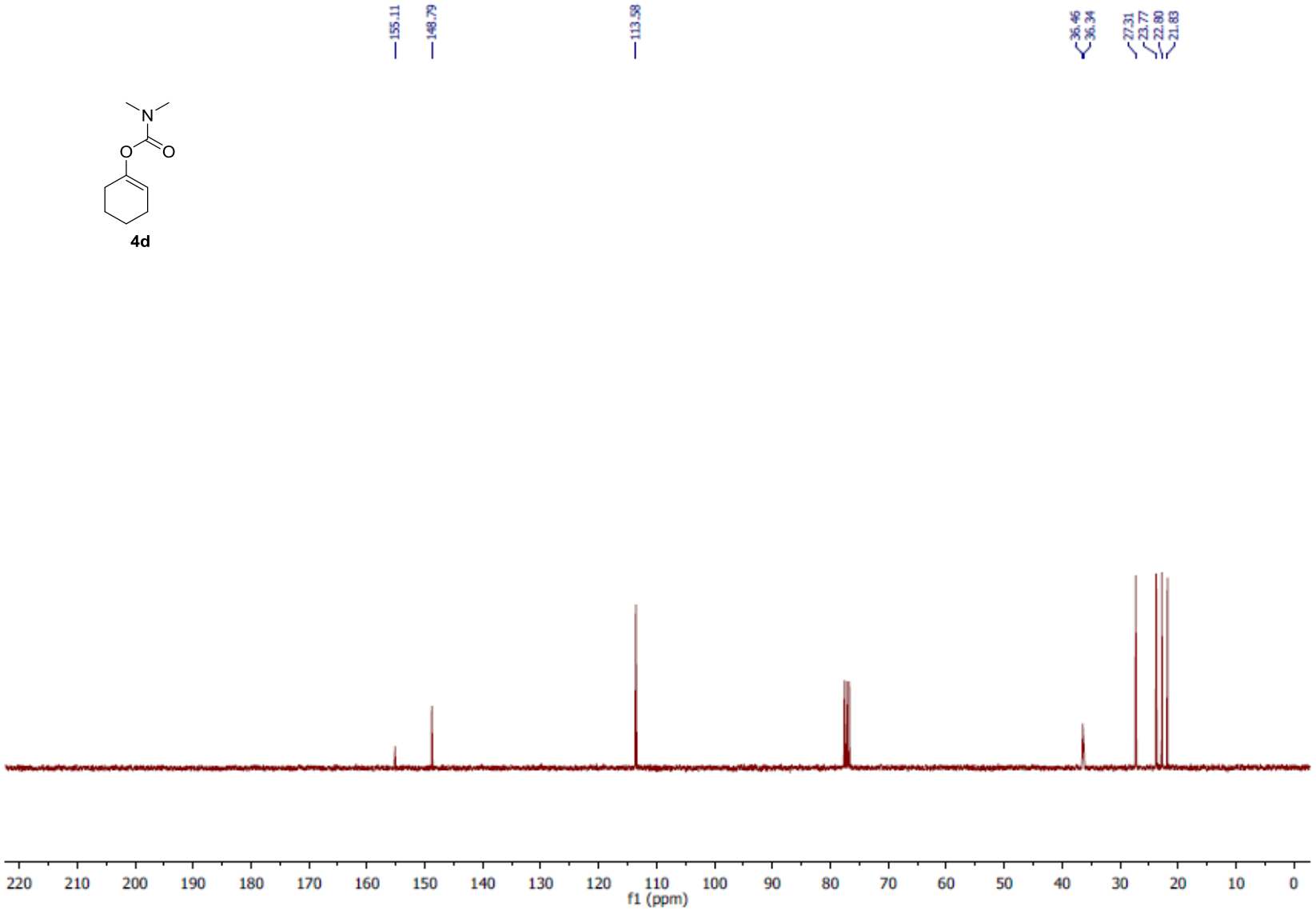

4.79
4.79
4.66
4.66
2.99
2.96
1.11
4c
1.00
1.00
6.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.10
154.89
97.73
36.77
36.36
28.04
N
O
O
4c
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



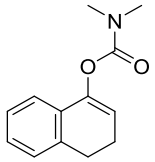
4d

5.34
5.34
5.33
5.33
5.32
5.32
5.31
5.31
2.92
2.90
2.15
2.15
2.14
2.13
2.13
2.12
2.11
2.11
2.10
2.09
2.09
2.08
2.07
2.07
2.06
2.05
2.04
1.74
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.60
1.59
1.58
1.57
1.56
1.55
1.54
1.53
0.97
6.02
4.07
2.05
2.00
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)

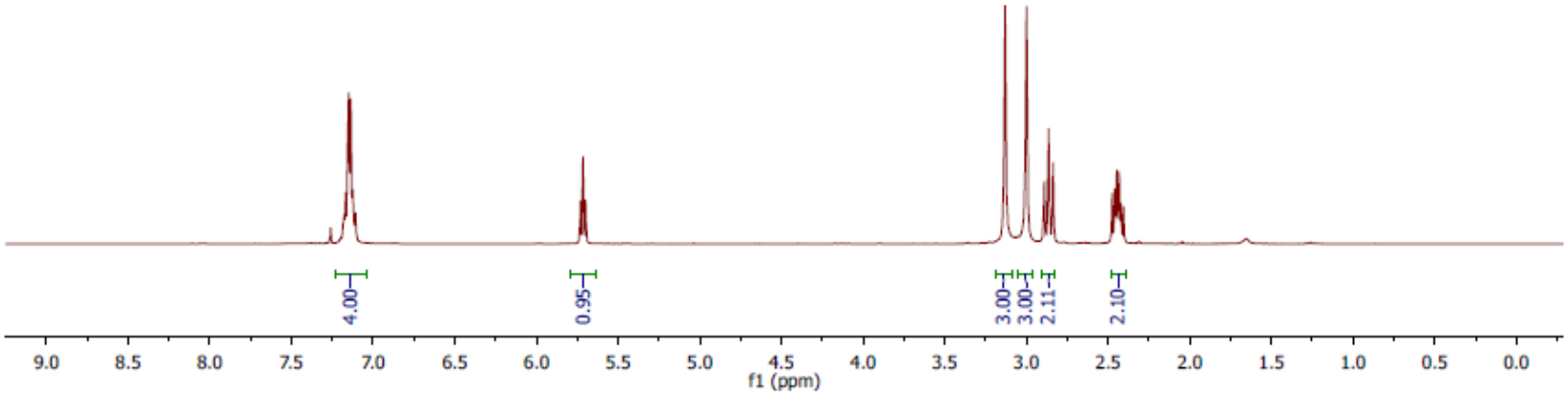

155.11
148.79
113.58
36.46
36.34
27.31
23.77
22.80
21.83
N
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

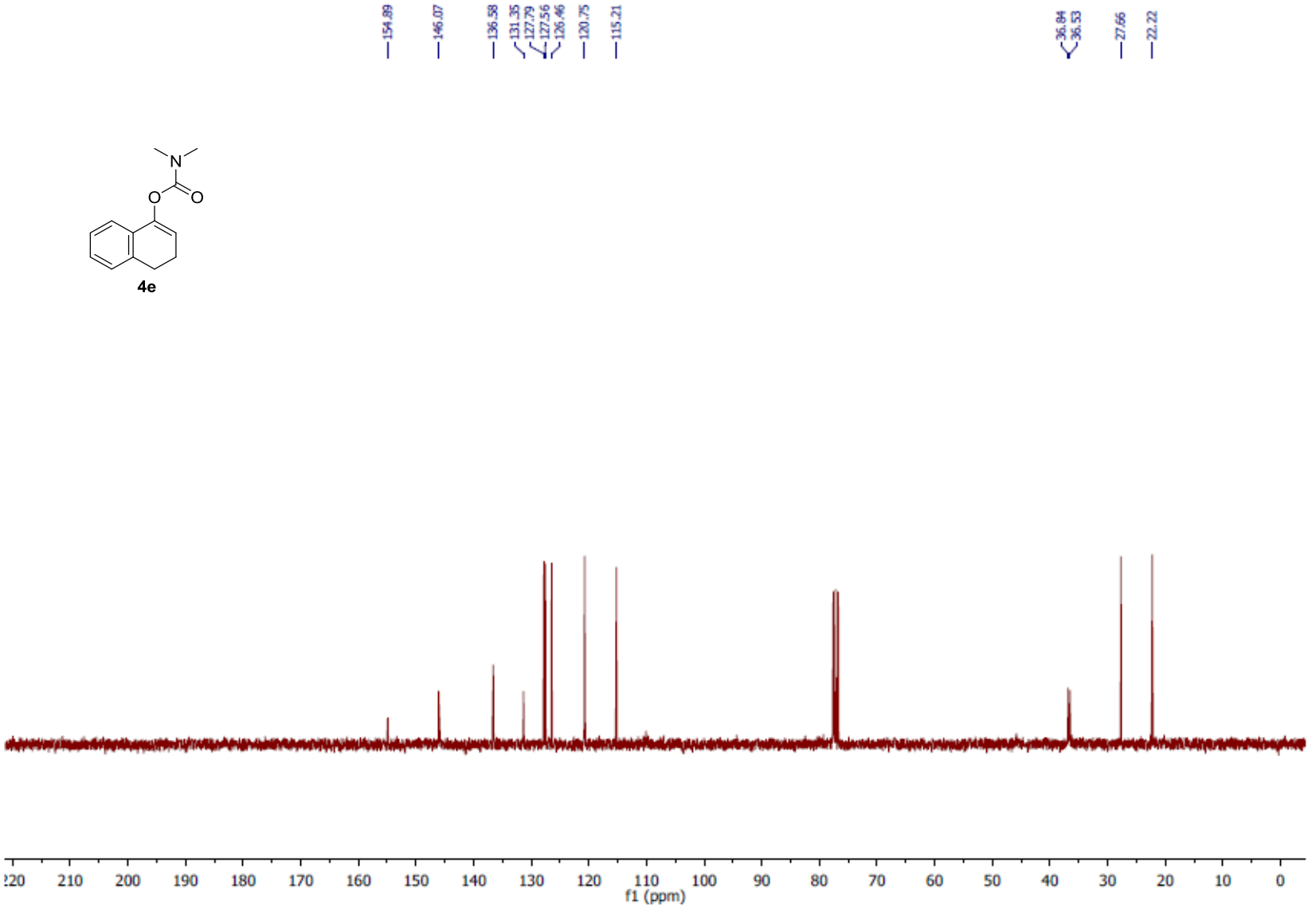
4d


7.18
7.18
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.11
7.11
5.73
5.71
5.70
3.13
3.00
2.89
2.86
2.84
2.47
2.46
2.45
2.45
2.44
2.43
2.42
2.41

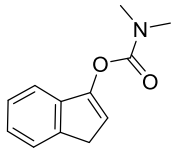

N
O
O

4e

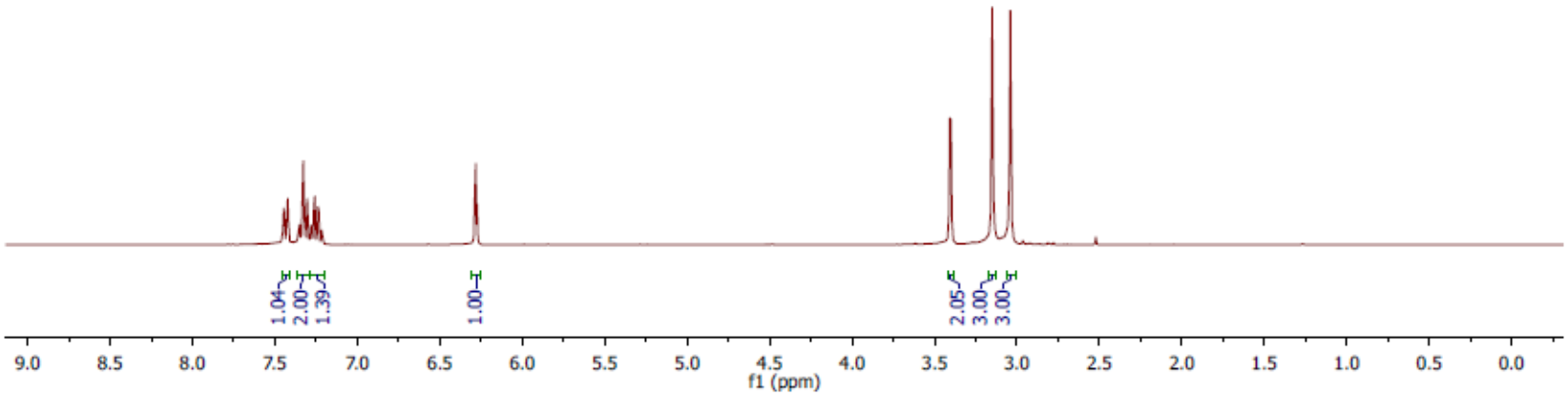

4.00
0.95
3.00
3.00
2.11
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

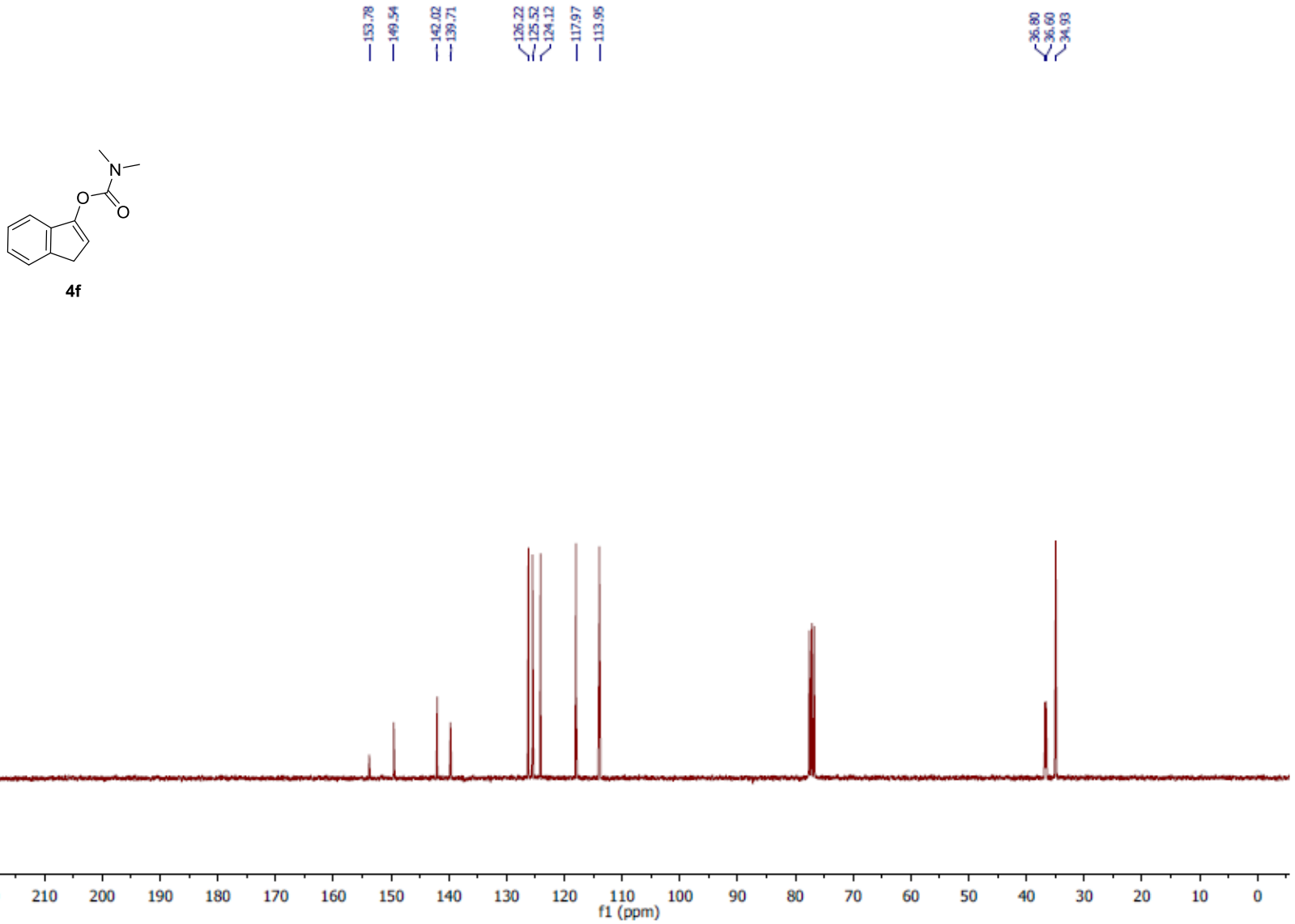

154.89
146.07
136.58
131.35
127.79
127.56
126.46
120.75
115.21
36.84
36.53
27.66
22.22
4e
f1 (ppm)

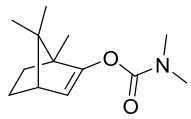

7.45
7.45
7.44
7.43
7.42
7.42
7.36
7.36
7.35
7.35
7.33
7.33
7.33
7.32
7.30
7.30
7.28
7.28
7.26
7.26
7.24
7.23
7.22
7.21
6.29
6.28
6.27
3.41
3.40
3.15
3.04


N
O
O

4f

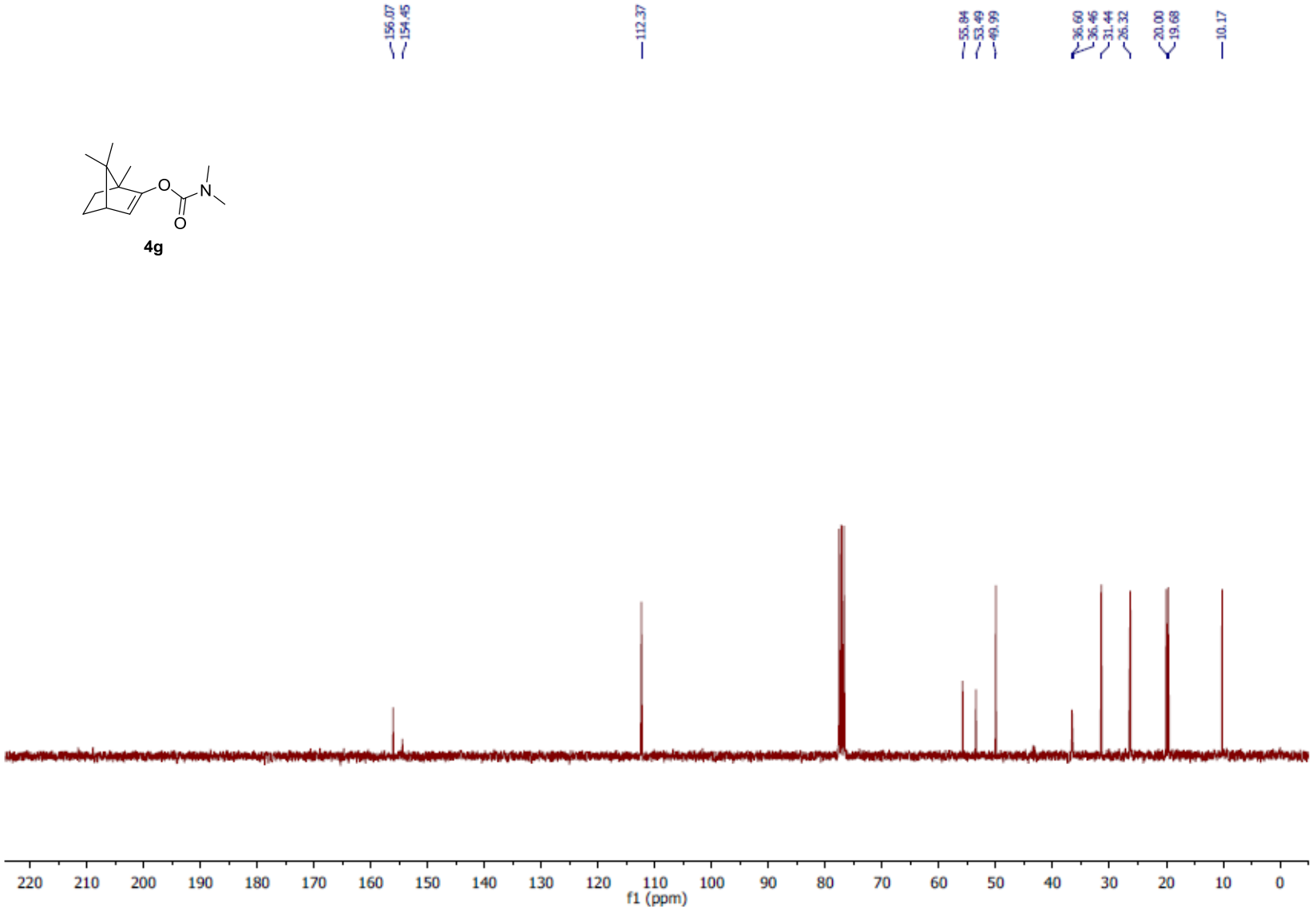

1.04
2.00
1.39
1.00
2.05
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

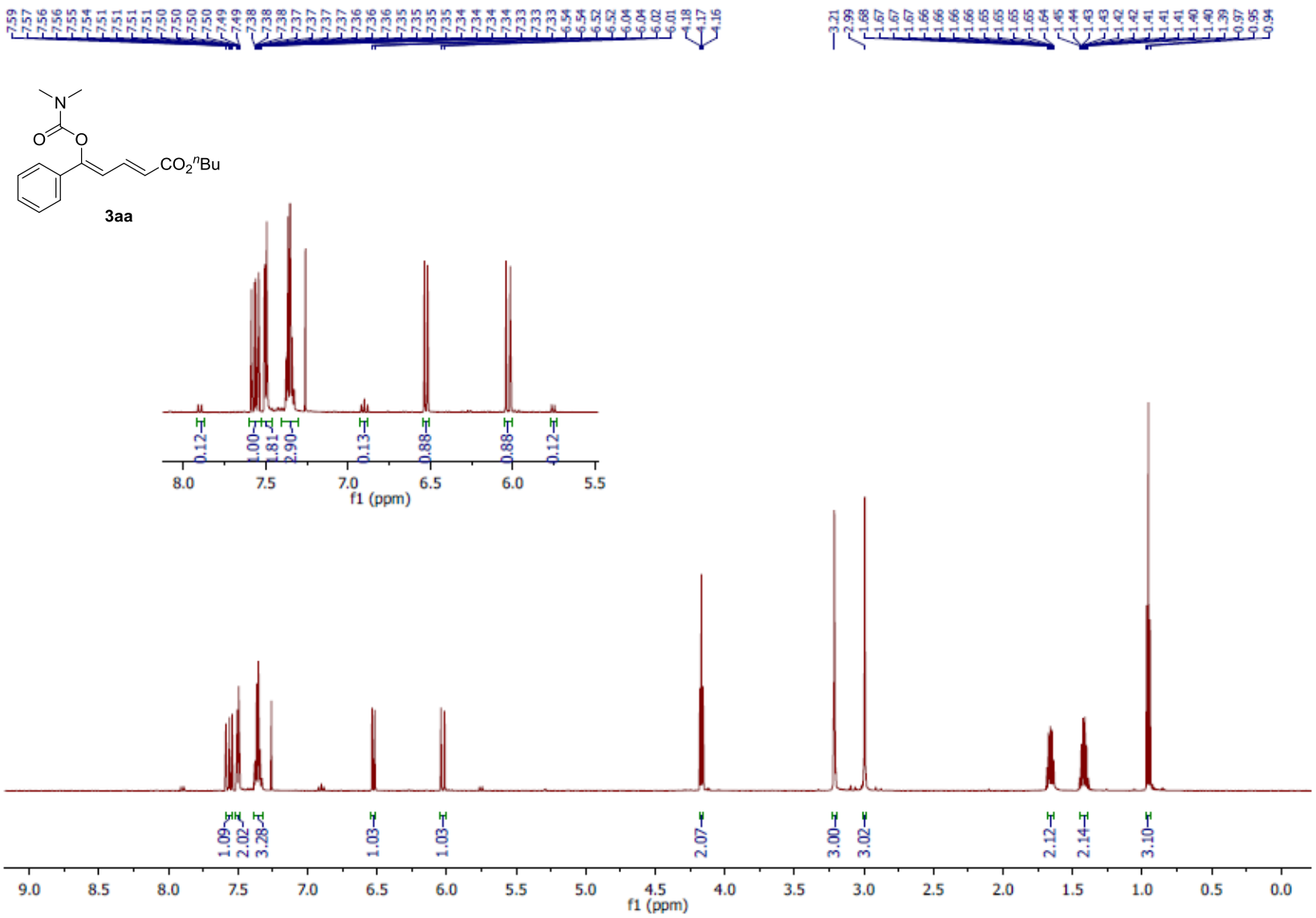

153.78
149.54
142.02
139.71
126.22
125.52
124.12
117.97
113.95
36.80
36.60
34.93
N
O
O
4f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

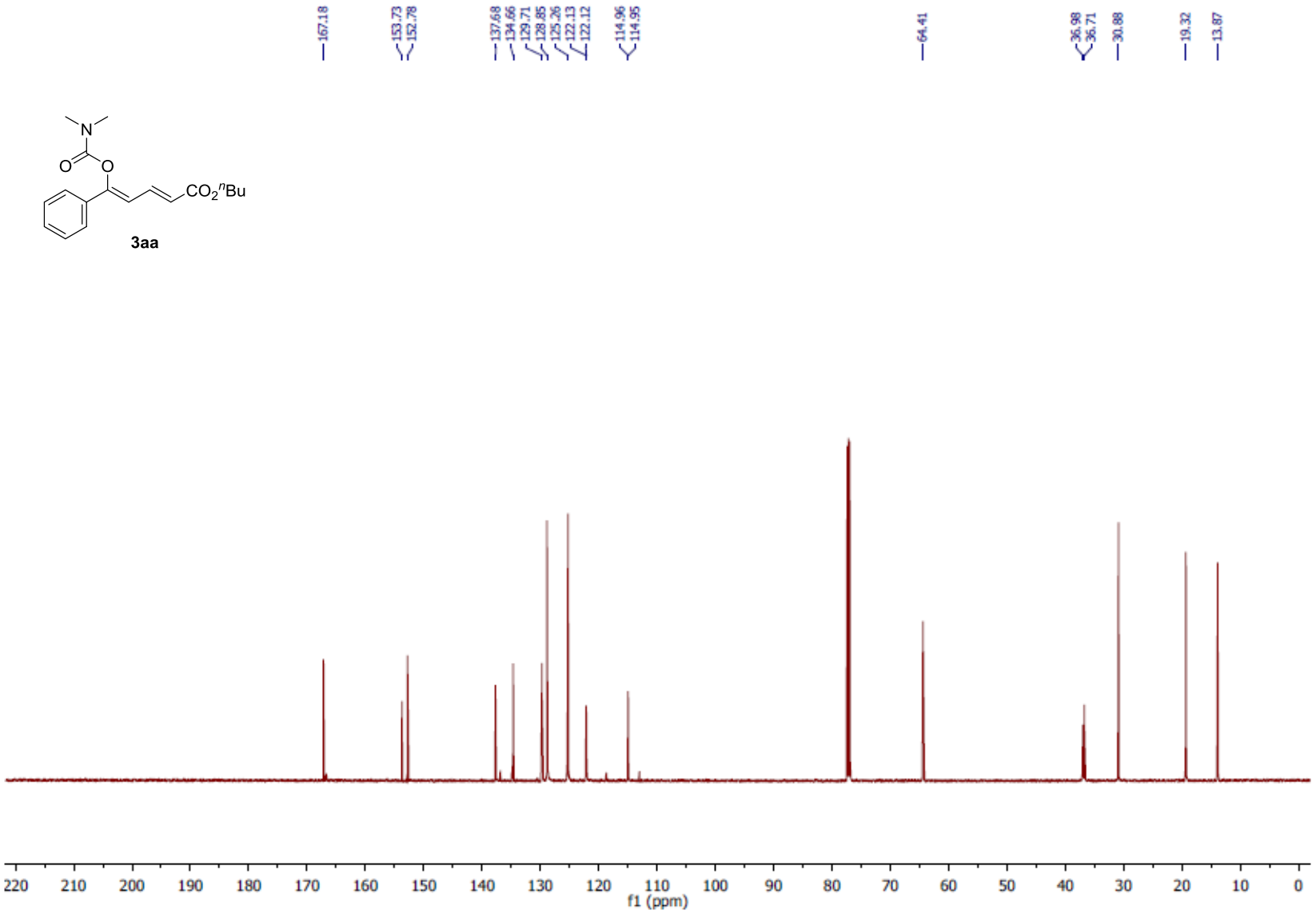

O
N
O

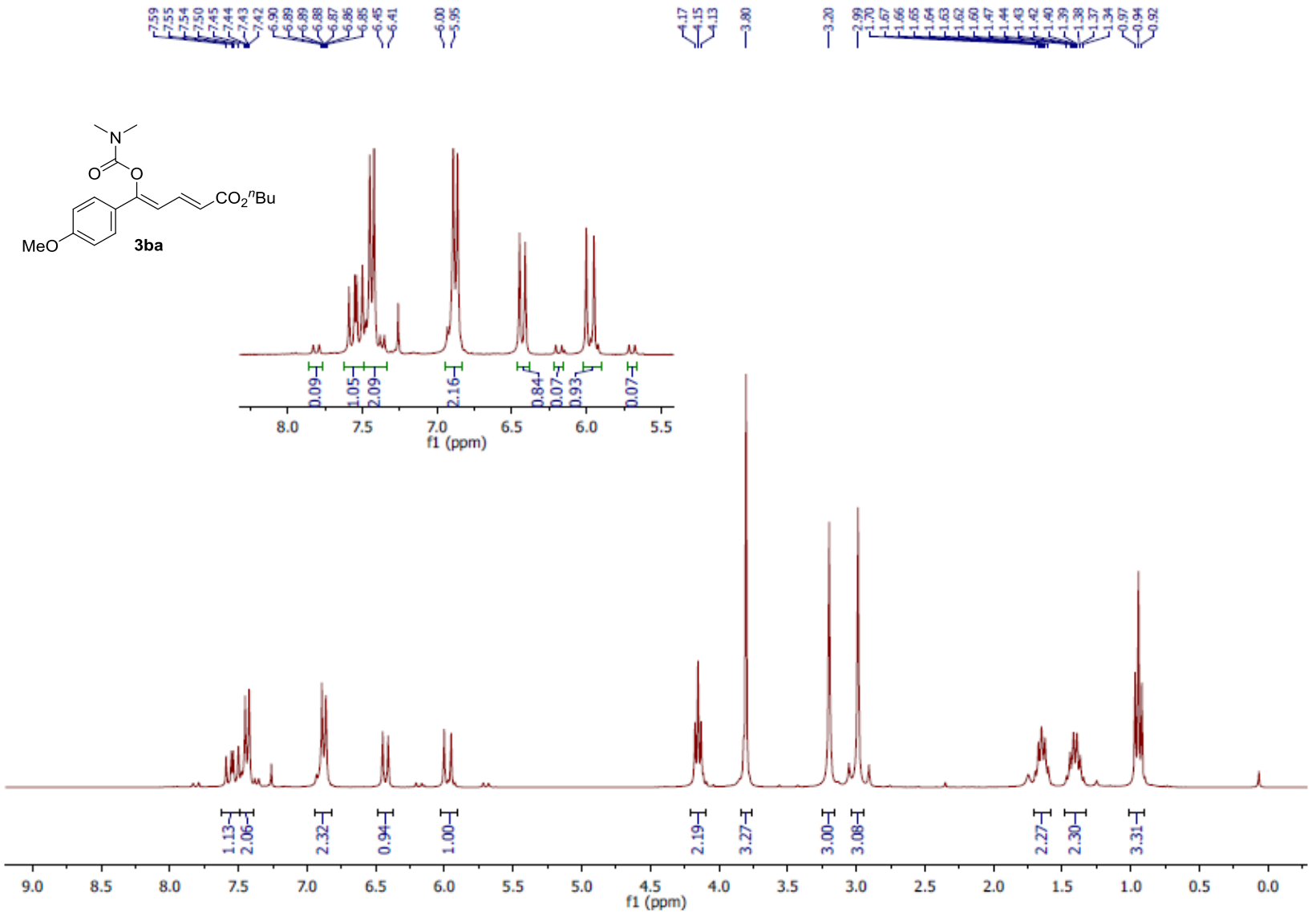
4g

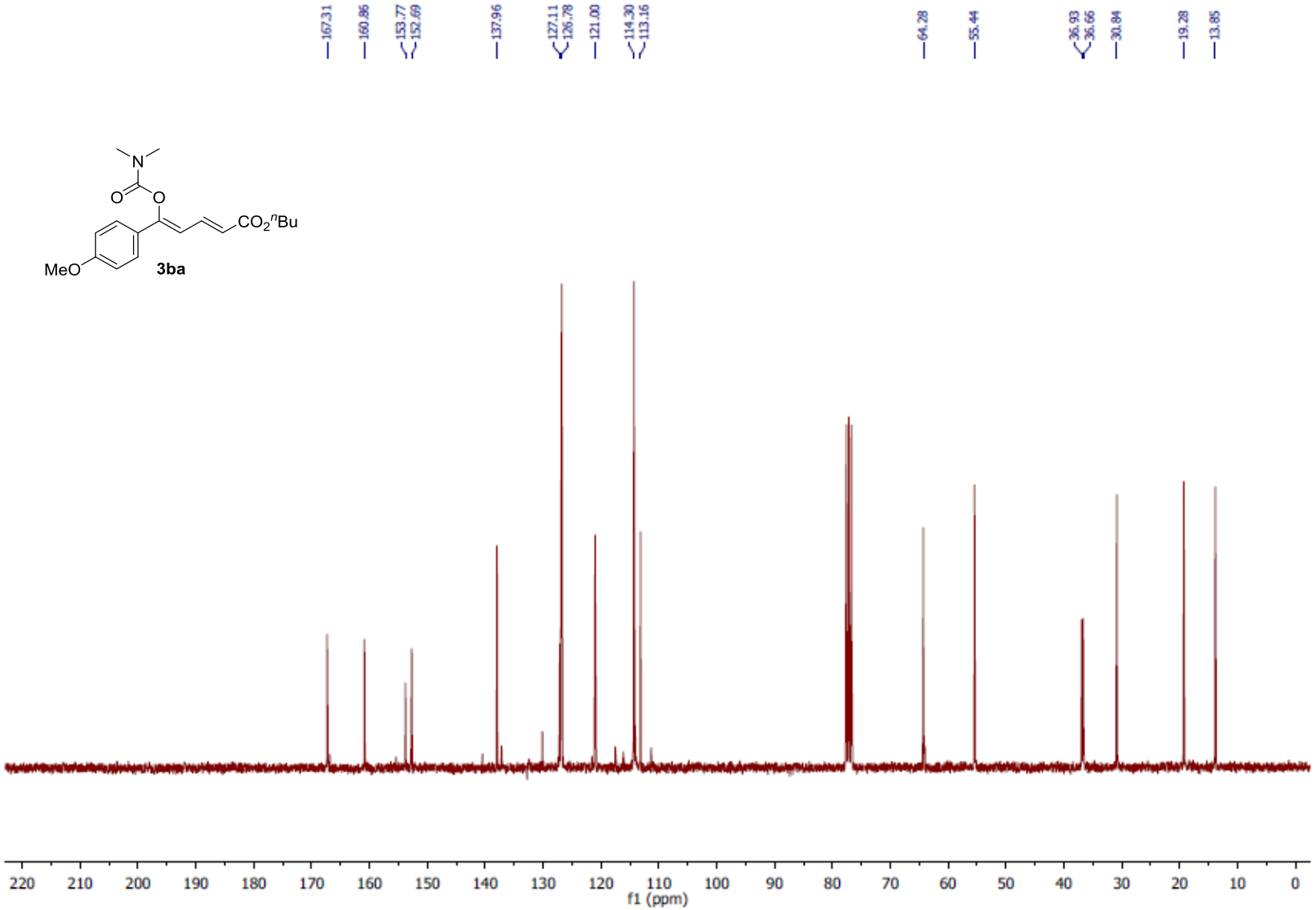
5.49
5.48
2.97
2.93
2.32
2.31
2.30
1.89
1.88
1.87
1.87
1.85
1.84
1.83
1.83
1.82
1.80
1.58
1.57
1.55
1.54
1.53
1.51
1.50
1.33
1.32
1.30
1.29
1.28
1.26
1.25
1.17
1.16
1.14
1.14
1.13
1.11
1.09
0.94
0.94
0.74
0.97
6.00
1.00
1.03
1.03
1.03
1.09
6.07
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

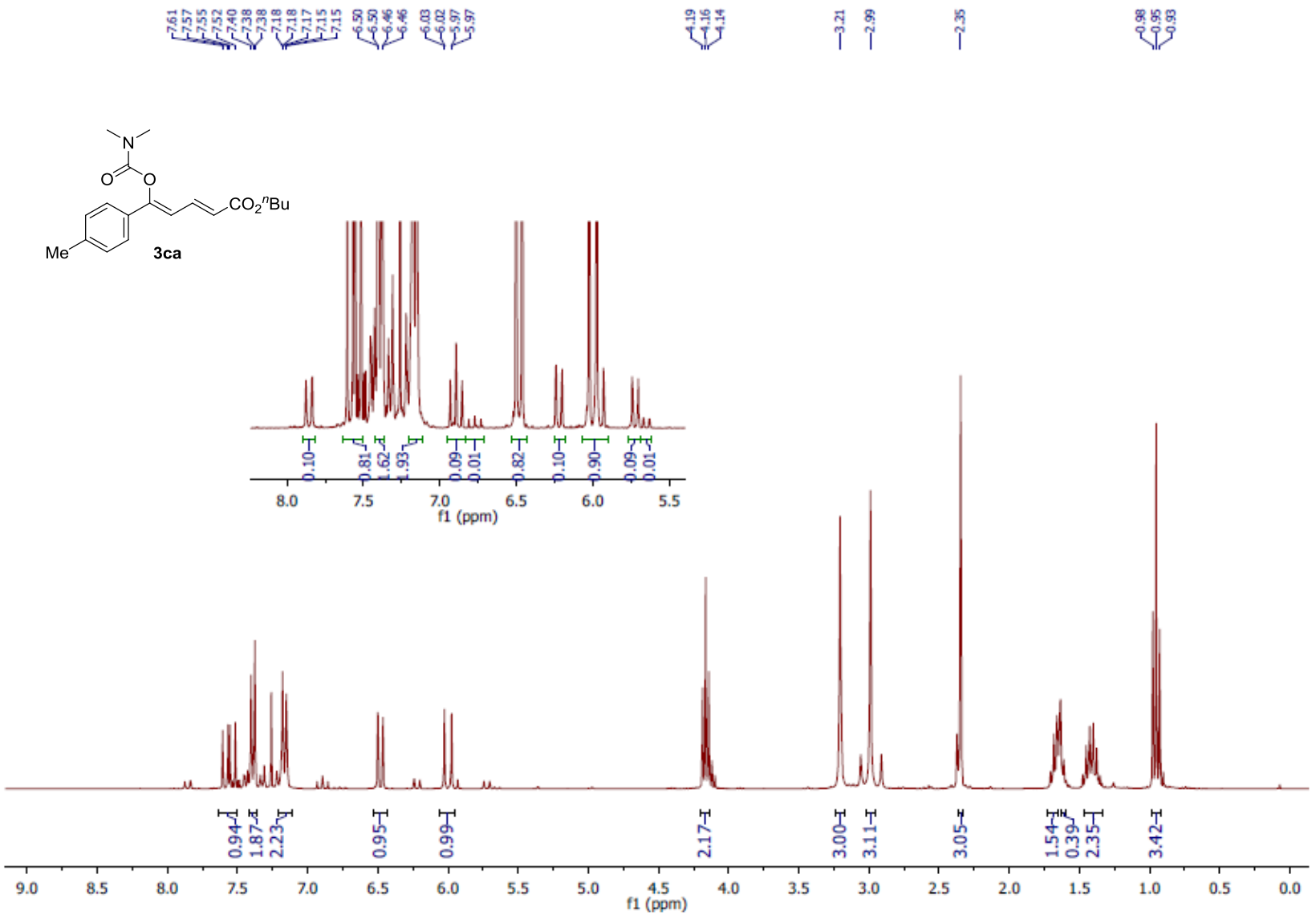

156.07
154.45
112.37
55.84
53.49
49.99
36.60
36.46
31.44
26.32
20.00
19.68
10.17
O
N
O
4g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

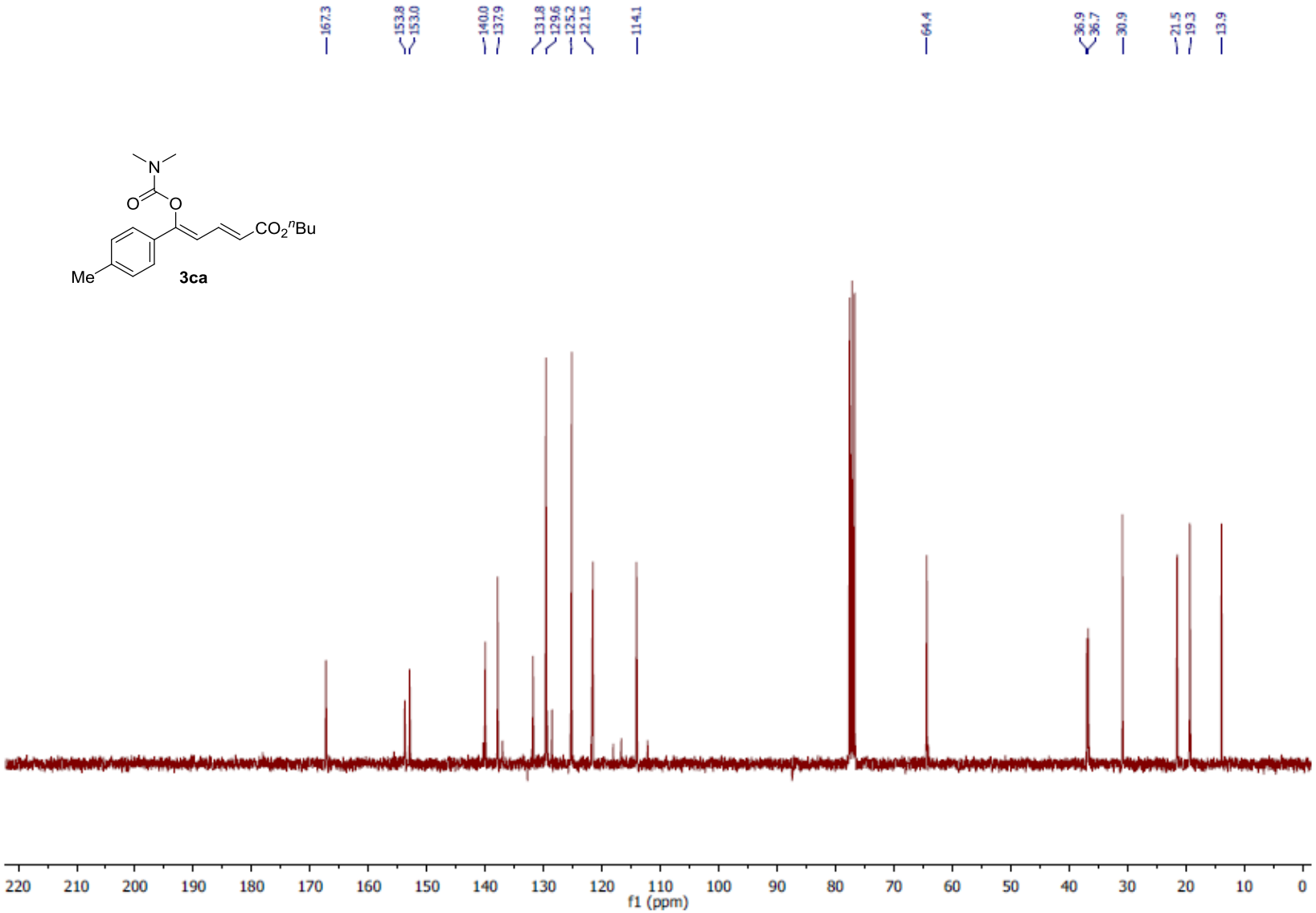

3aa
f1 (ppm)
f1 (ppm)

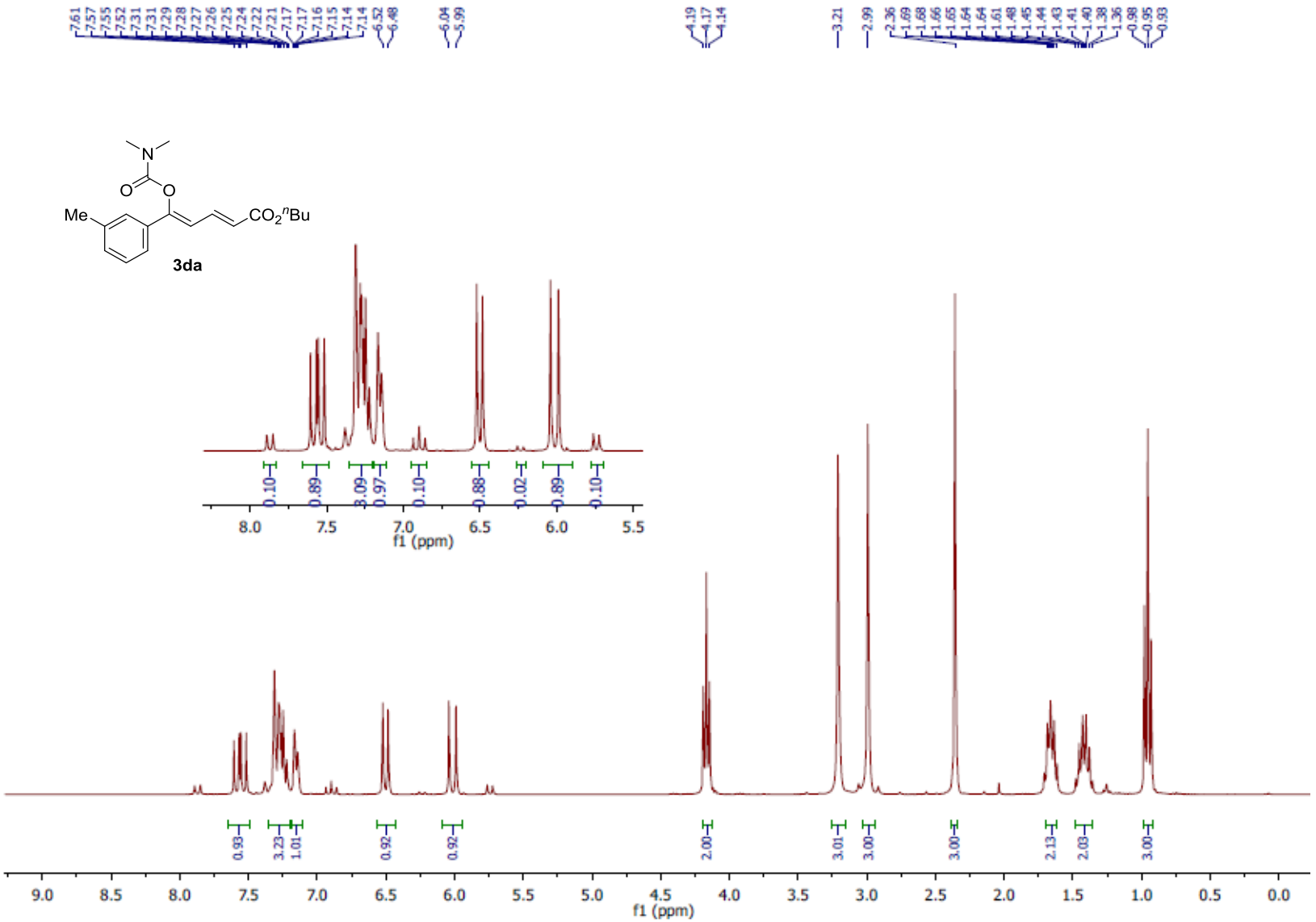

167.18
153.73
152.78
137.68
134.66
129.71
128.85
125.26
122.13
122.12
114.96
114.95
64.41
36.98
36.71
30.88
19.32
13.87
O
O
N
CO2nBu
3aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

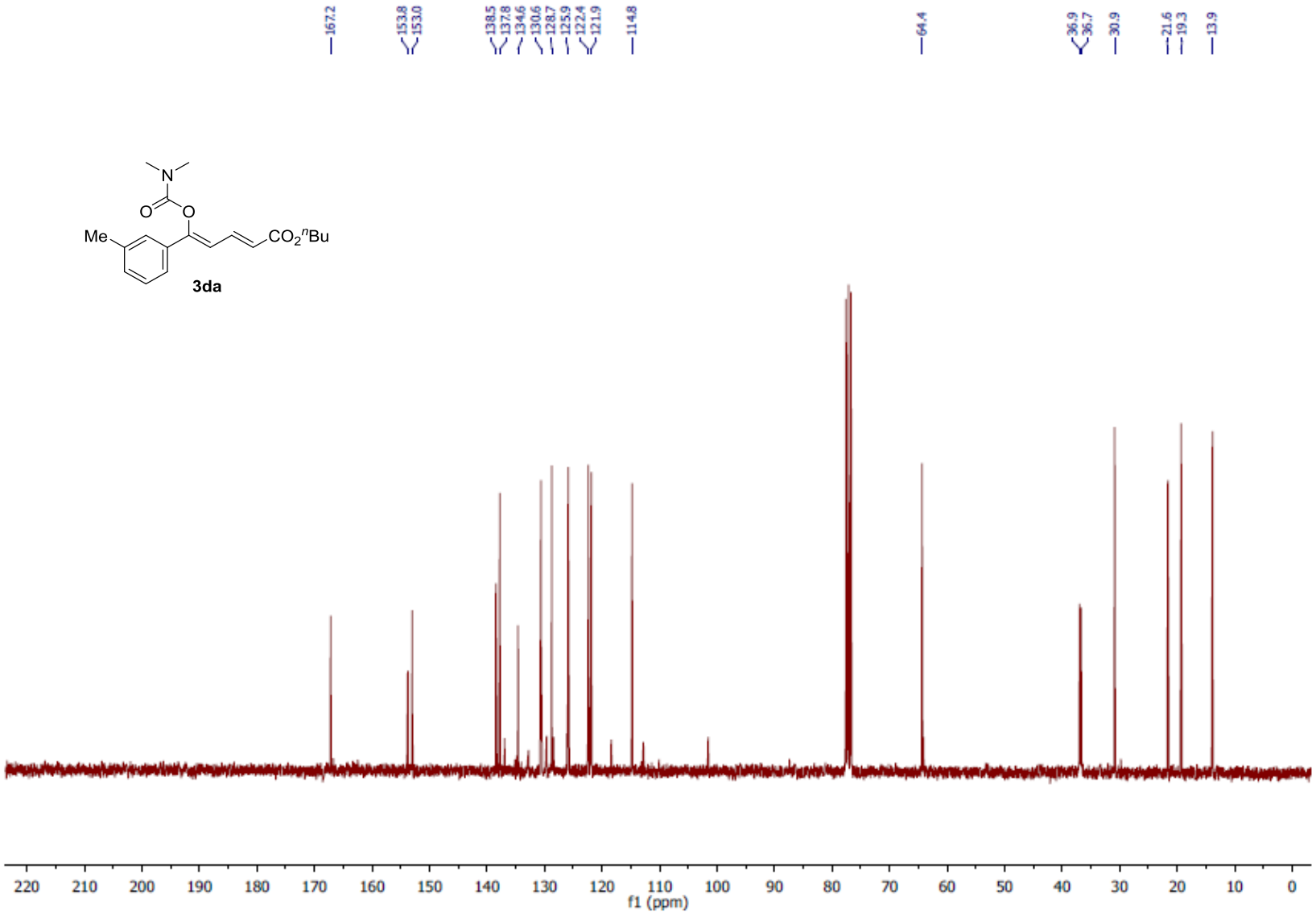

7.59
7.55
7.54
7.50
7.45
7.44
7.43
7.42
6.90
6.89
6.89
6.88
6.87
6.86
6.85
6.45
6.41
6.00
5.95
4.17
4.15
4.13
3.80
3.20
2.99
1.70
1.67
1.66
1.65
1.64
1.63
1.62
1.60
1.47
1.44
1.43
1.42
1.40
1.39
1.38
1.37
1.34
0.97
0.94
0.92
MeO
CO2nBu
3ba
0.09
1.05
2.09
2.16
0.84
0.07
0.93
0.07
8.0
7.5
7.0
6.5
6.0
5.5
f1 (ppm)
1.13
2.06
2.32
0.94
1.00
2.19
3.27
3.00
3.08
2.27
2.30
3.31
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)


167.31
160.86
153.77
152.69
137.96
127.11
126.78
121.00
114.30
113.16
64.28
55.44
36.93
36.66
30.84
19.28
13.85
MeO
CO2nBu
3ba
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.61
7.57
7.55
7.52
7.40
7.38
7.38
7.18
7.18
7.17
7.15
7.15
6.50
6.50
6.46
6.46
6.03
6.02
5.97
5.97
4.19
4.16
4.14
3.21
2.99
2.35
0.98
0.95
0.93
N
O
O
CO2nBu
Me
3ca
0.10
0.81
1.62
1.93
0.09
0.01
0.82
0.10
0.90
0.09
0.01
8.0
7.5
7.0
6.5
6.0
5.5
f1 (ppm)
0.94
1.87
2.23
0.95
0.99
2.17
3.00
3.11
3.05
1.54
0.39
2.35
3.42
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)


167.3
153.8
153.0
140.0
137.9
131.8
129.6
125.2
121.5
114.1
64.4
36.9
36.7
30.9
21.5
19.3
13.9
N
O
O
CO2nBu
Me
3ca
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.61
7.57
7.55
7.52
7.31
7.31
7.29
7.28
7.27
7.26
7.25
7.24
7.22
7.21
7.17
7.17
7.16
7.15
7.14
7.14
6.52
6.48
6.04
5.99
4.19
4.17
4.14
3.21
2.99
2.36
1.69
1.68
1.66
1.65
1.64
1.64
1.61
1.48
1.45
1.44
1.43
1.41
1.40
1.38
1.36
0.98
0.95
0.93
N
O
O
Me
CO2nBu
3da
0.10
0.89
3.09
0.97
0.10
0.88
0.02
0.89
0.10
8.0
7.5
7.0
6.5
6.0
5.5
f1 (ppm)
0.93
3.23
1.01
0.92
0.92
2.00
3.01
3.00
3.00
2.13
2.03
3.00
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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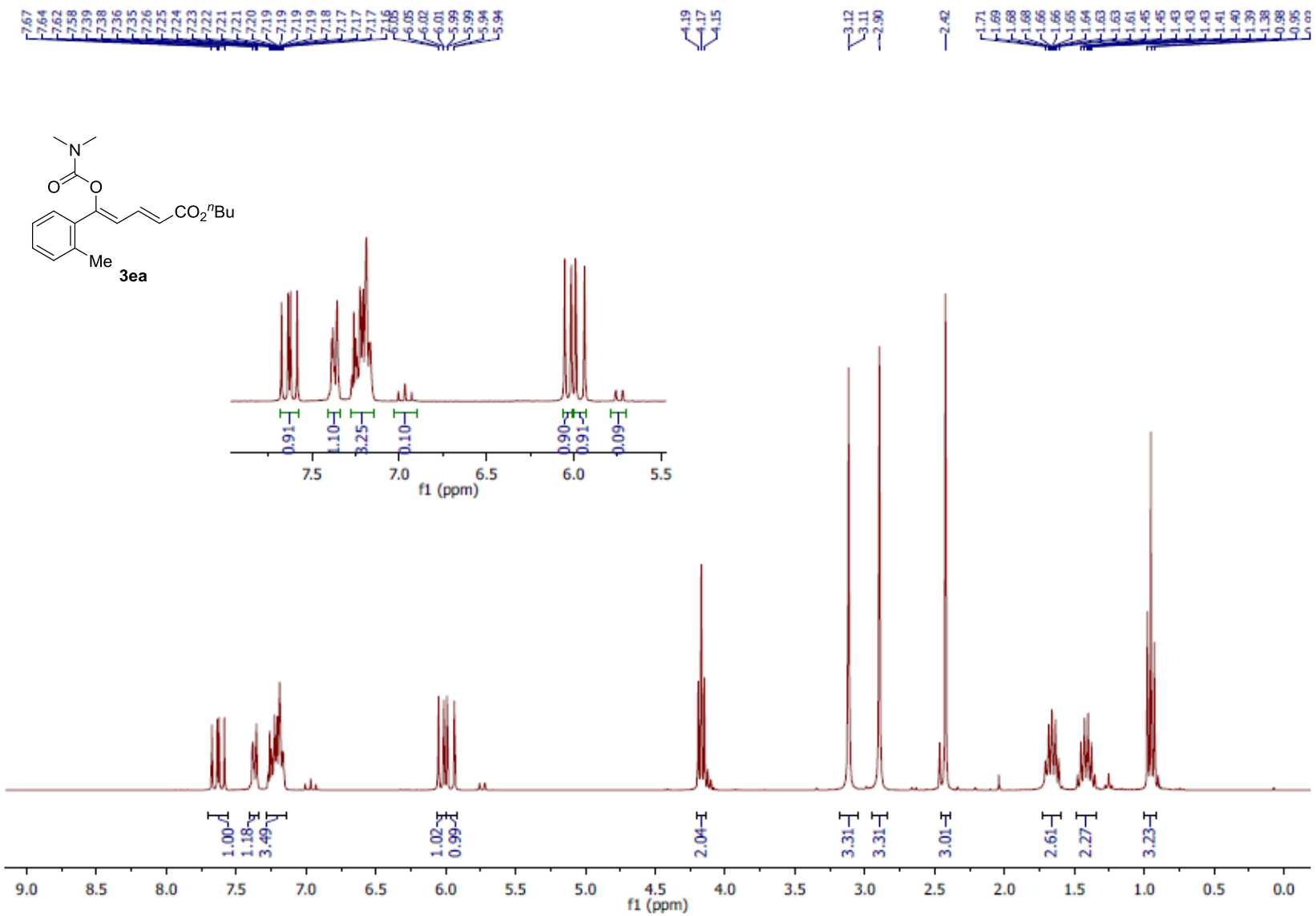
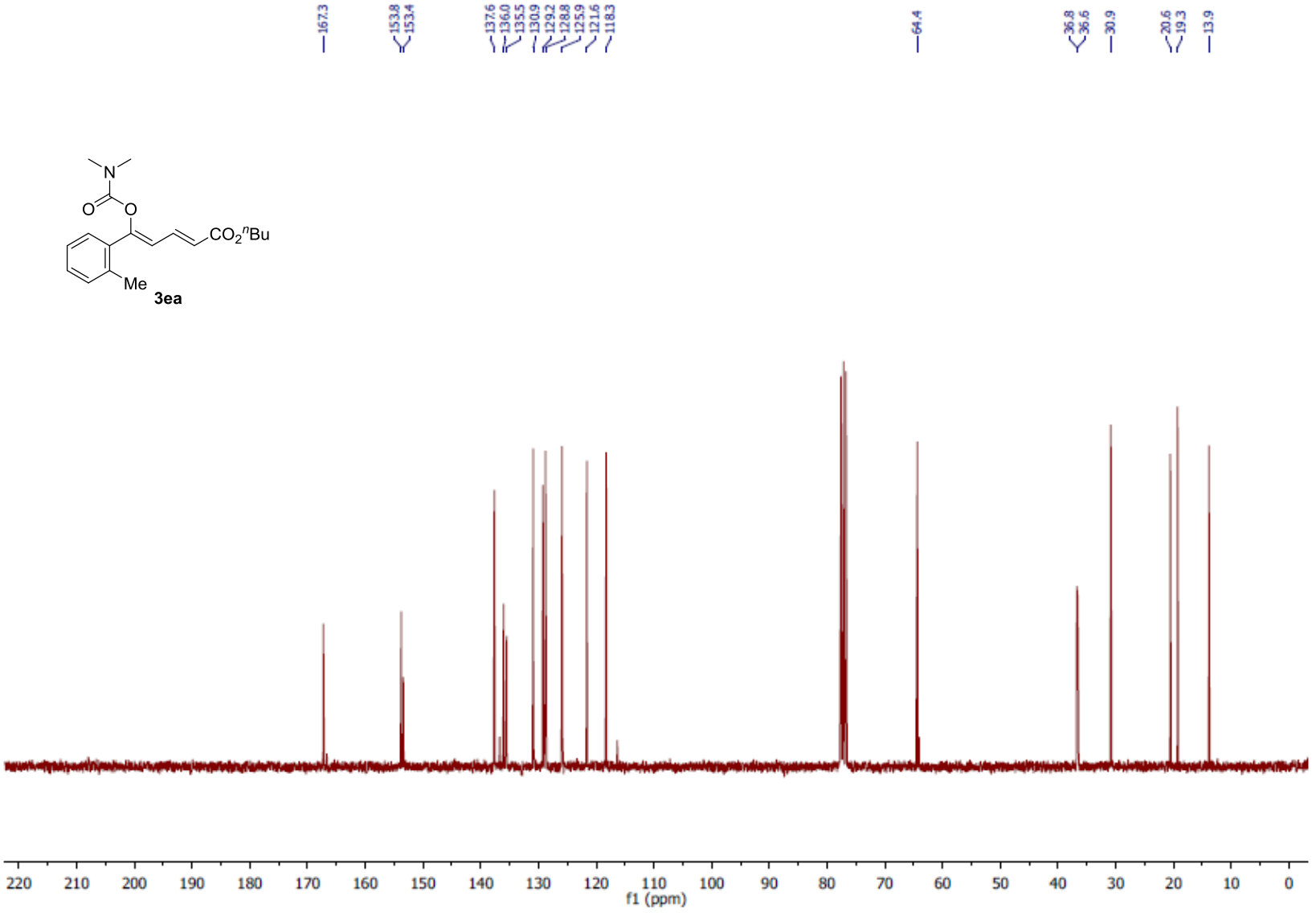
153.0
138.5
137.8
134.6
130.6
128.7
125.9
122.4
121.9
114.8
64.4
36.9
36.7
30.9
21.6
19.3
13.9
Me
CO2nBu
3da
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.67 7.64 7.62 7.58 7.39 7.38 7.36 7.35 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.19 7.19 7.18 7.17 7.17 7.17 6.05 6.02 6.01 5.99 5.99 5.94 5.94
4.19 4.17 4.15
3.12 3.11 2.90
2.42
1.71 1.69 1.68 1.68 1.66 1.66 1.65 1.64 1.63 1.63 1.61 1.45 1.45 1.43 1.43 1.43 1.41 1.40 1.39 1.38 0.98 0.95
N
O
O
CO2nBu
Me
3ea
0.91 1.10 3.25 0.10 0.90 0.91 0.09
7.5 7.0 6.5 6.0 5.5
f1 (ppm)
1.00 1.18 3.49 1.02 0.99 2.04 3.31 3.31 3.01 2.61 2.27 3.23
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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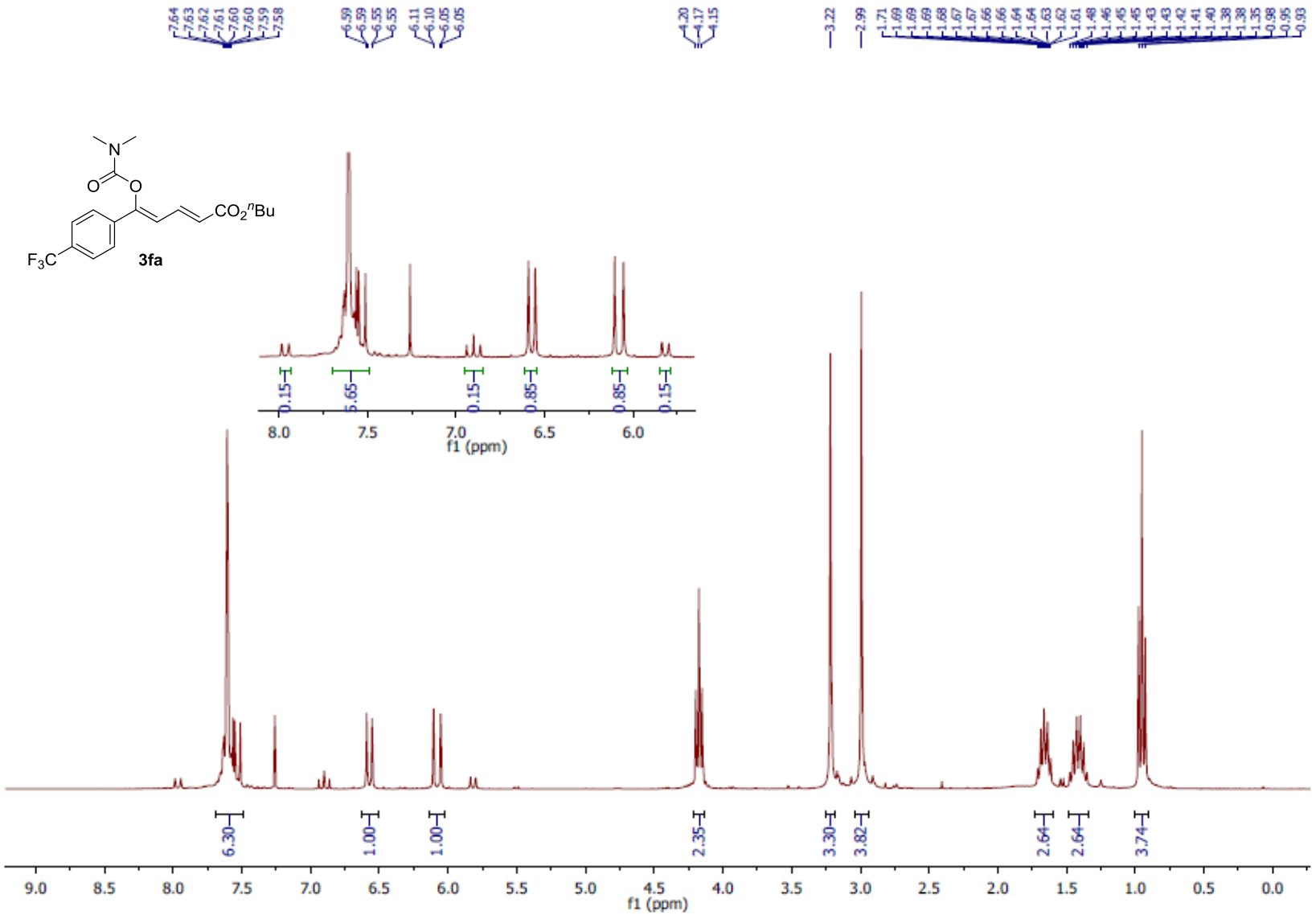
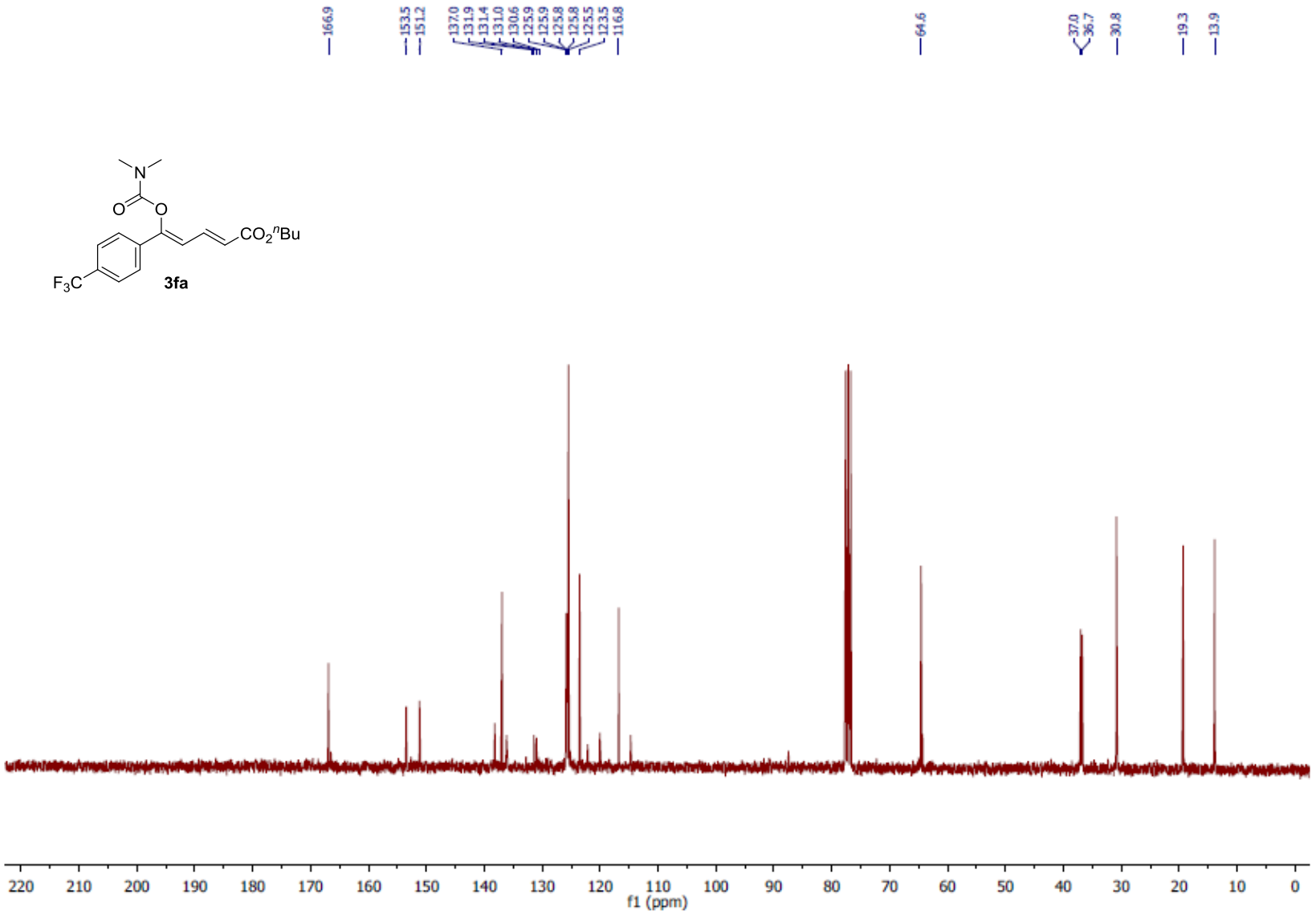
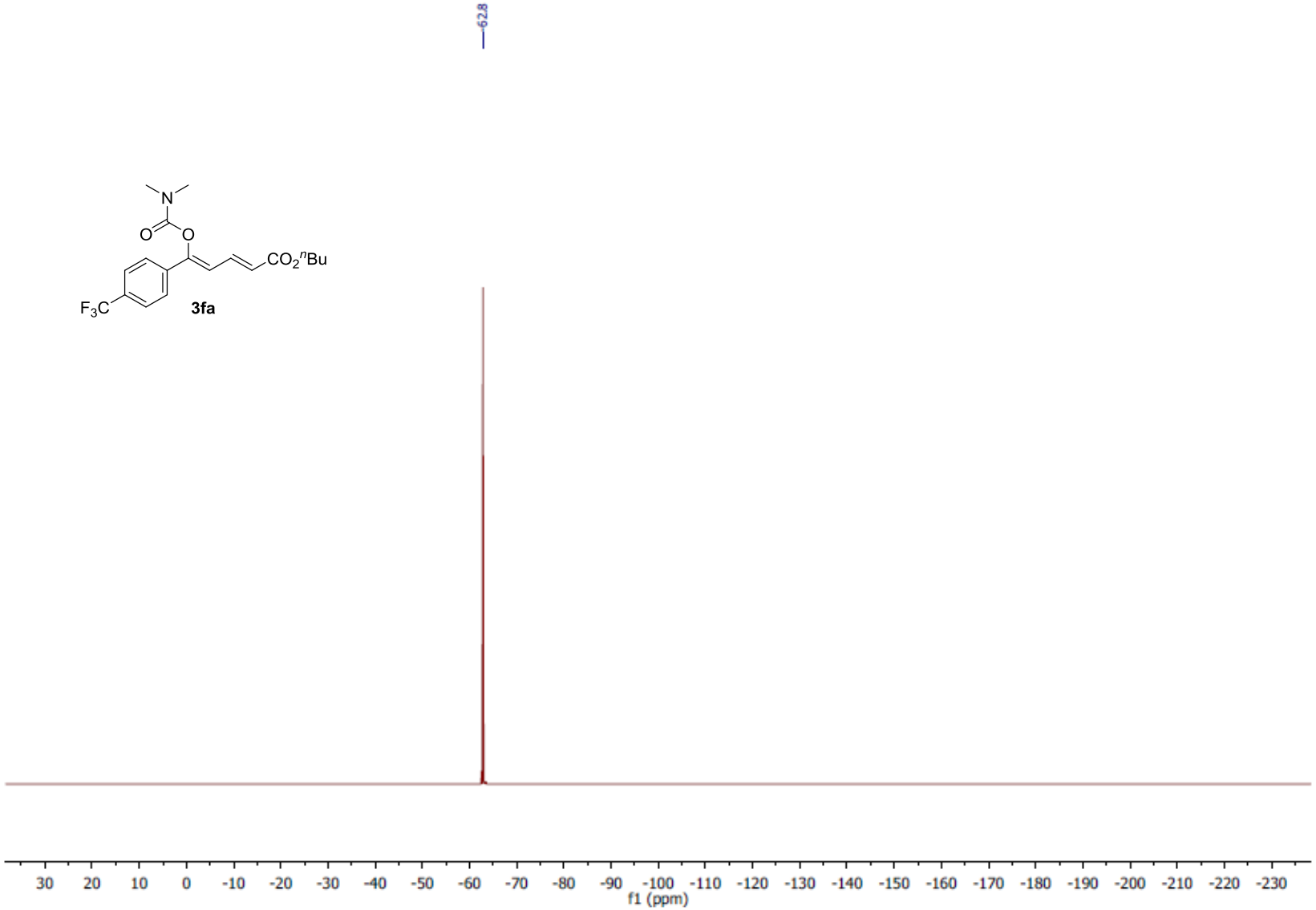
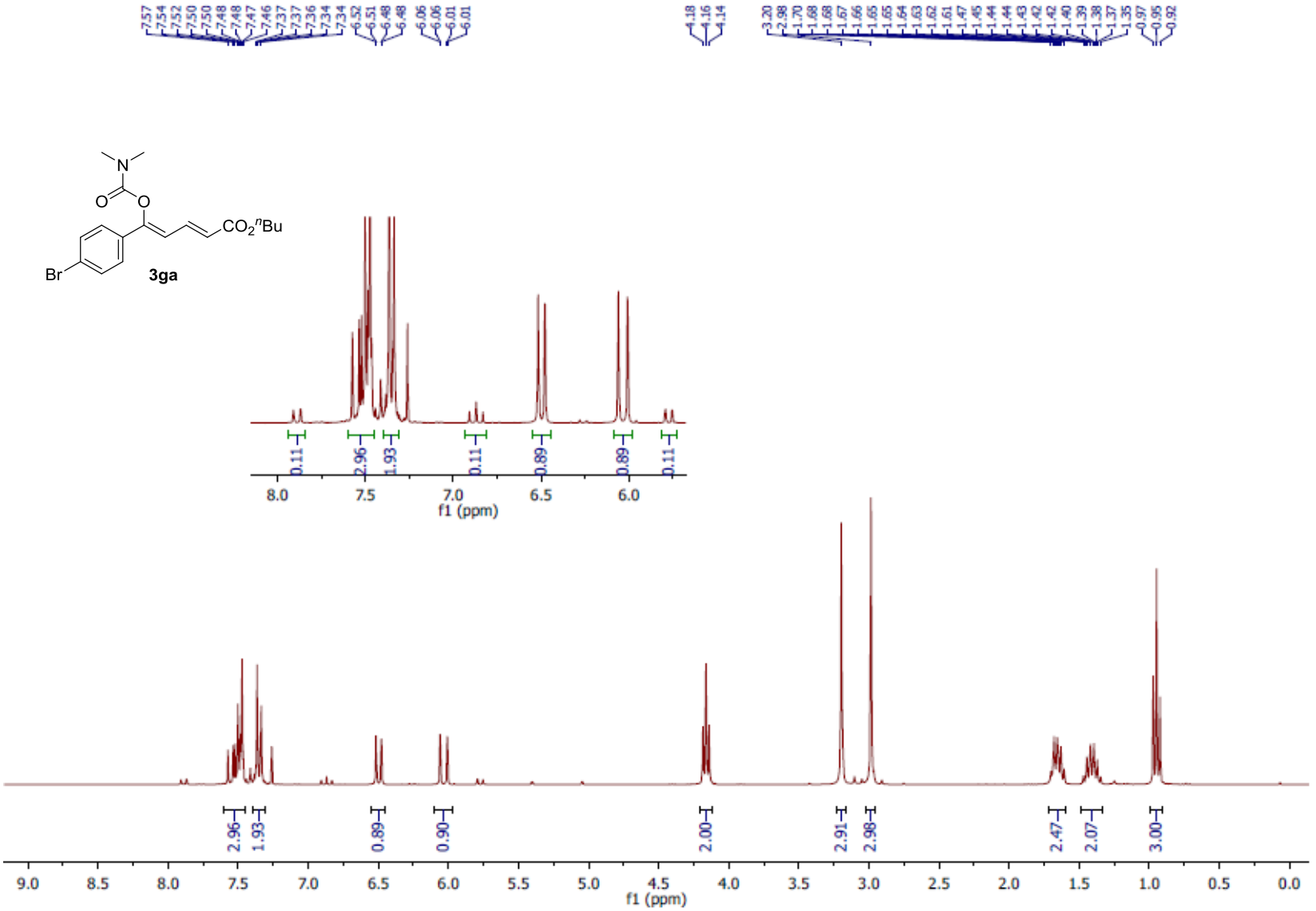
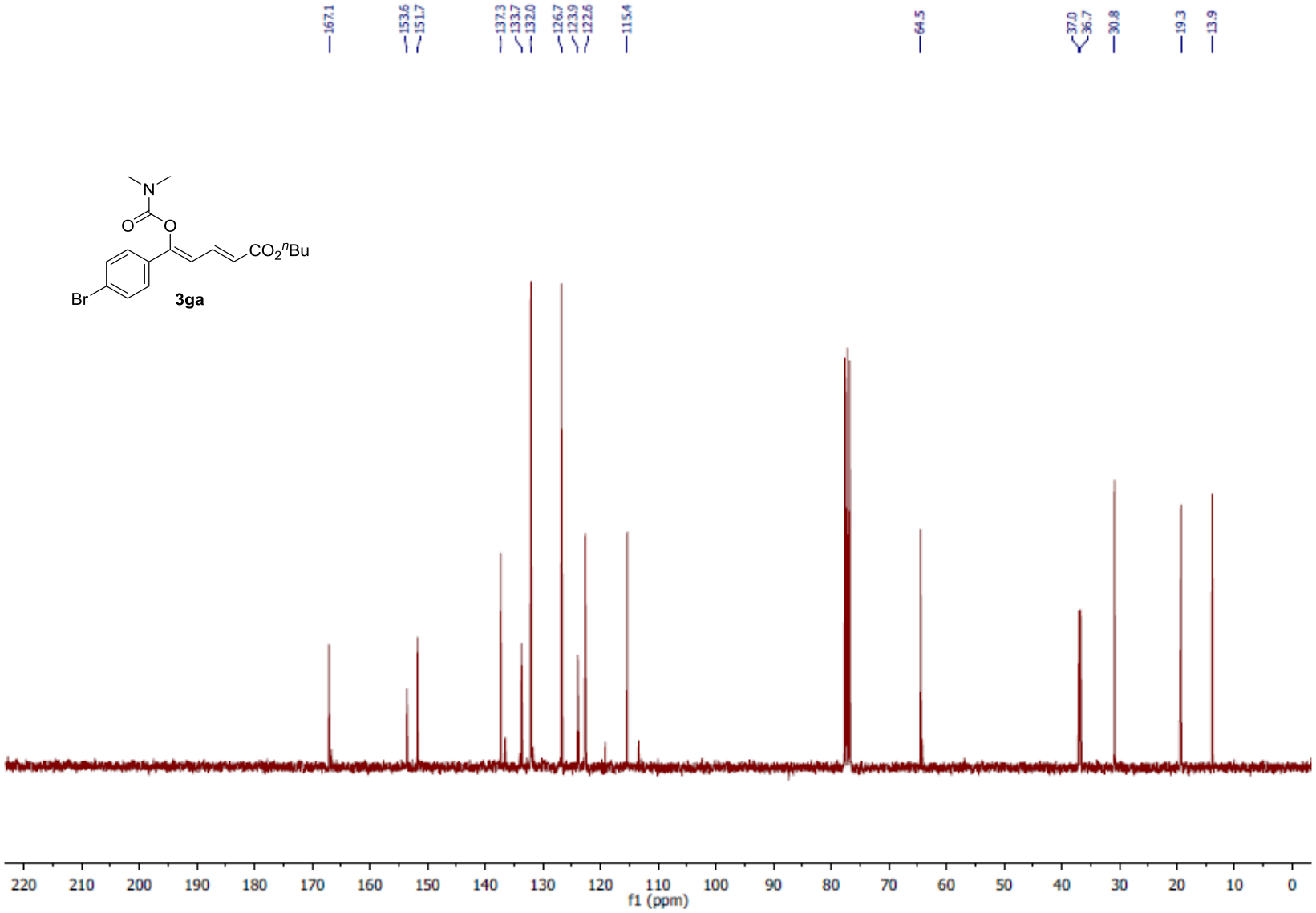
153.8
153.4
137.6
136.0
135.5
130.9
129.2
128.8
125.9
121.6
118.3
64.4
36.8
36.6
30.9
20.6
19.3
13.9
N
O
O
CO2nBu
Me
3ea
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

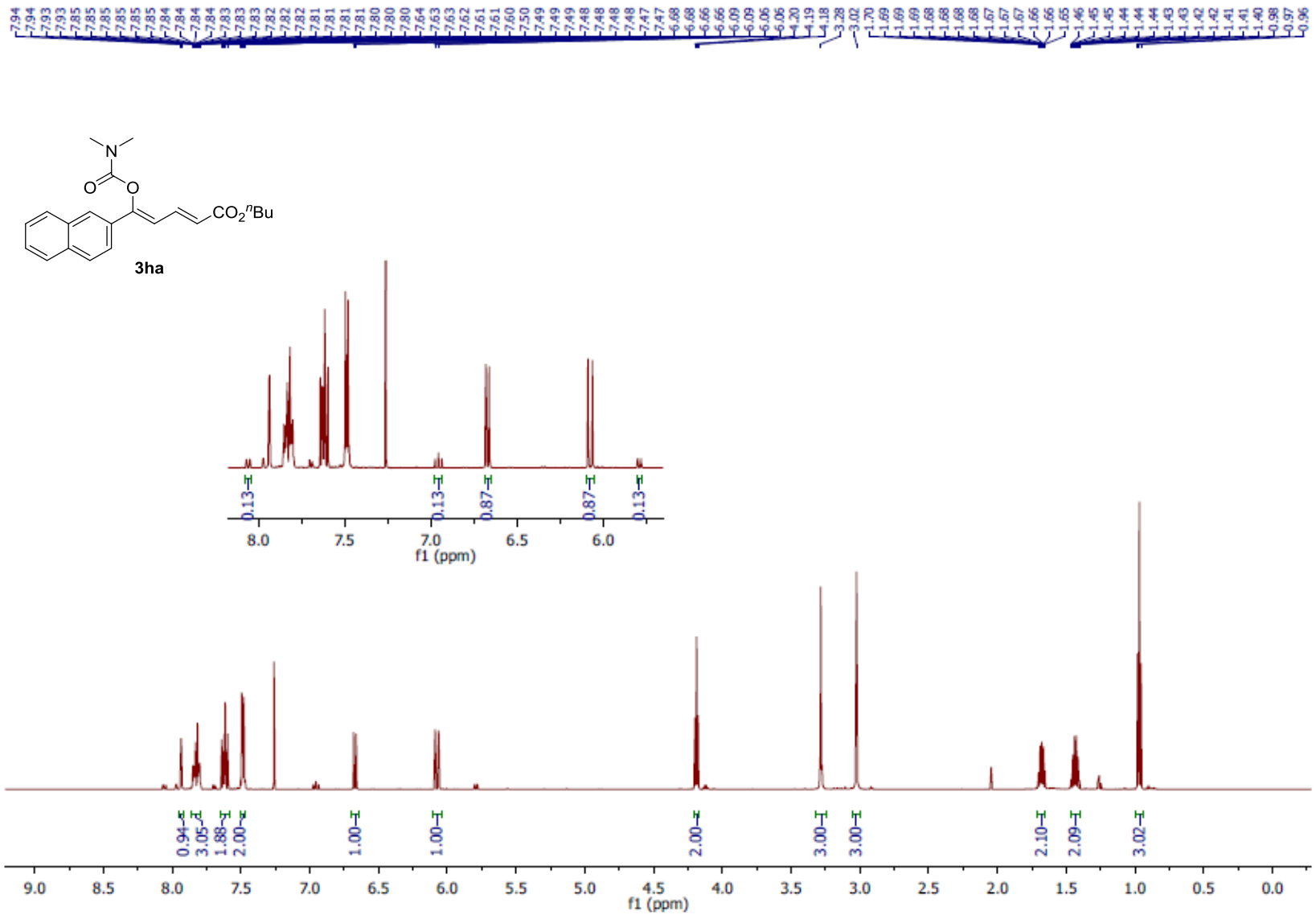

7.64
7.63
7.62
7.61
7.60
7.60
7.59
7.58
6.59
6.59
6.55
6.55
6.11
6.10
6.05
6.05
4.20
4.17
4.15
3.22
2.99
1.71
1.69
1.69
1.69
1.68
1.67
1.67
1.66
1.66
1.64
1.64
1.63
1.62
1.61
1.48
1.46
1.45
1.45
1.43
1.43
1.42
1.41
1.40
1.38
1.38
1.35
0.98
0.95
0.93
N
O
O
CO2nBu
F3C
3fa
0.15
5.65
0.15
0.85
0.85
0.15
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
6.30
1.00
1.00
2.35
3.30
3.82
2.64
2.64
3.74
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

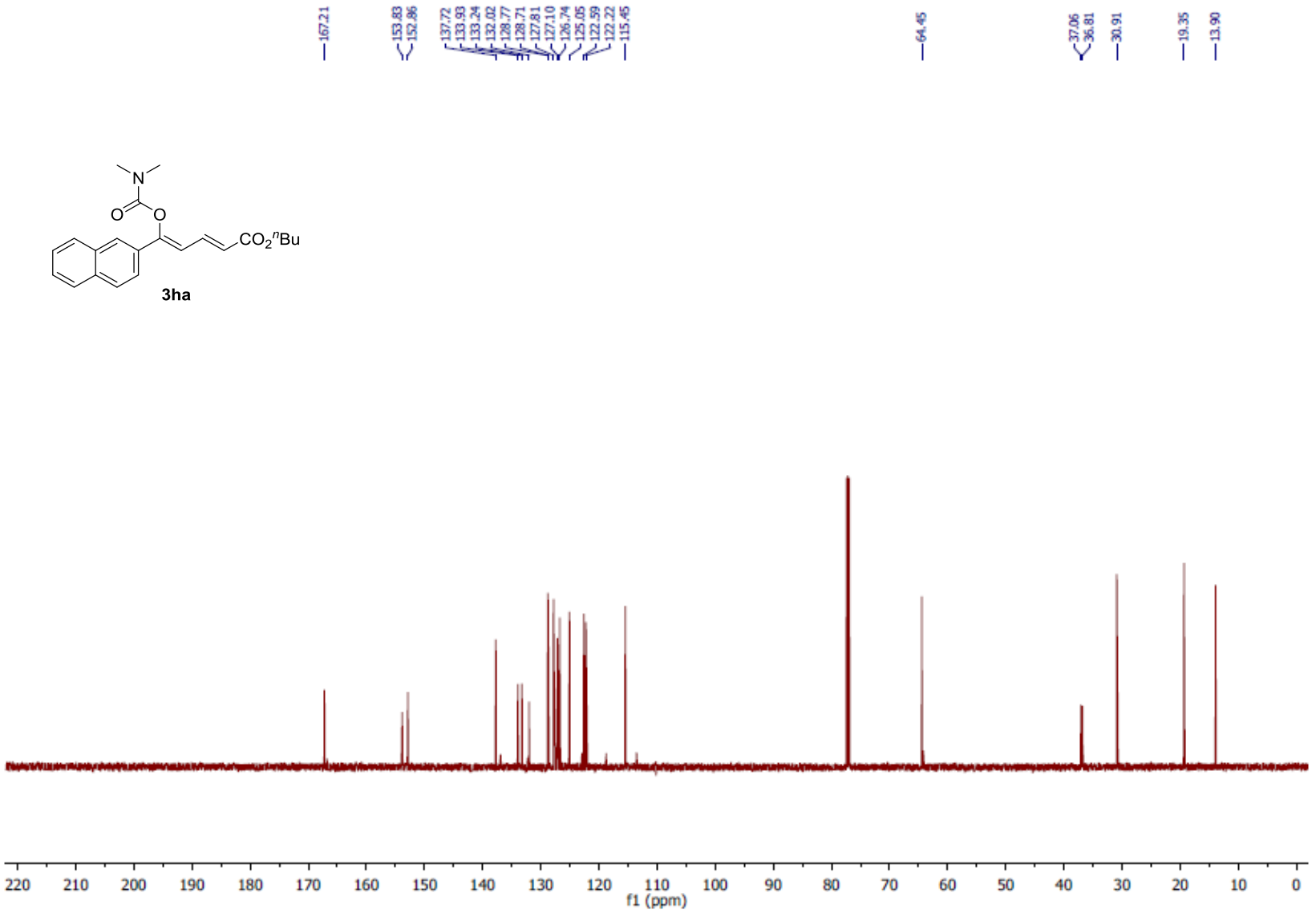

166.9
153.5
151.2
137.0
131.9
131.4
131.0
130.6
125.9
125.9
125.8
125.8
125.5
123.5
116.8
64.6
37.0
36.7
30.8
19.3
13.9
CO2nBu
F3C
3fa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

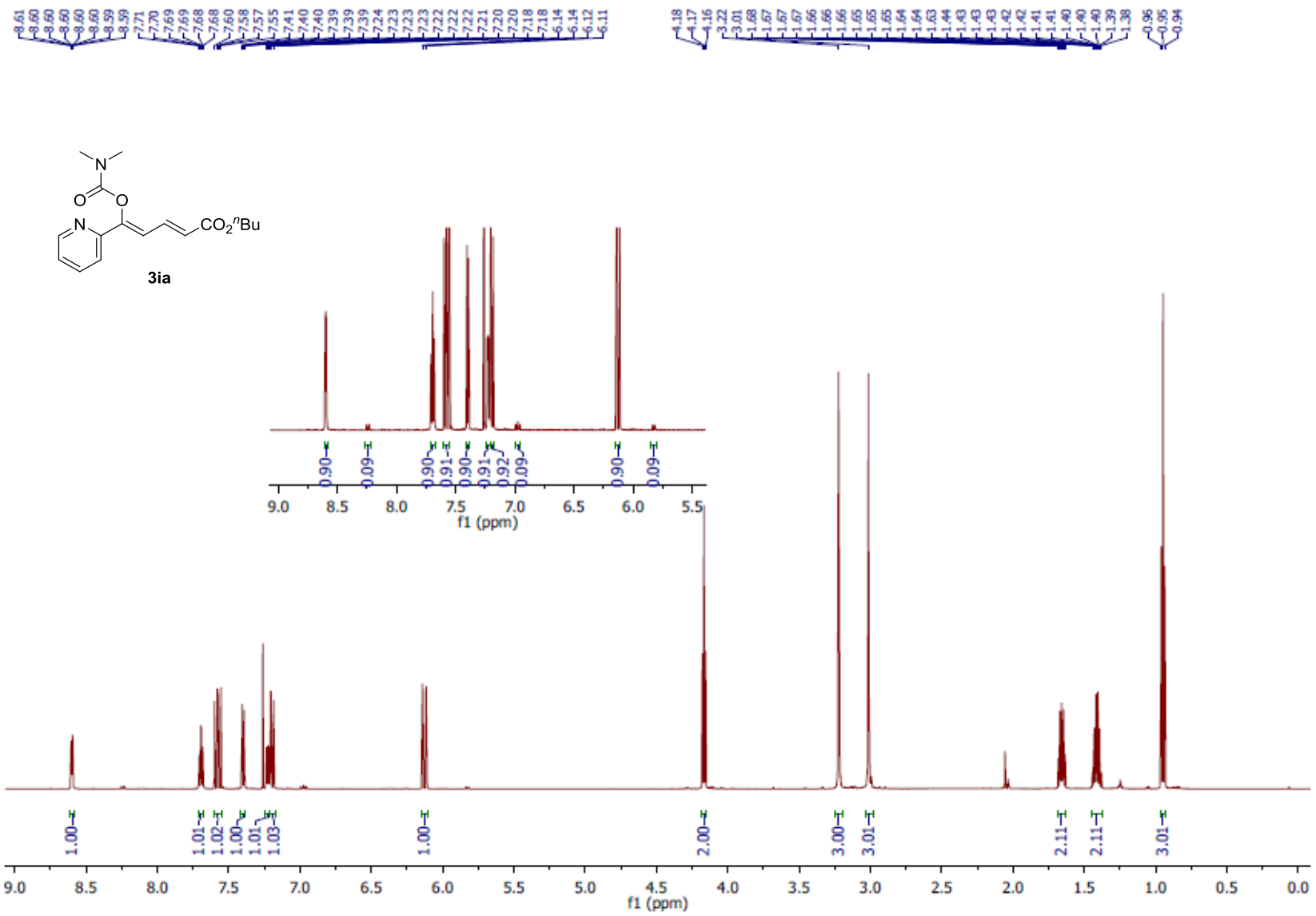

62.8
N
O
O
CO2nBu
F3C
3fa
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

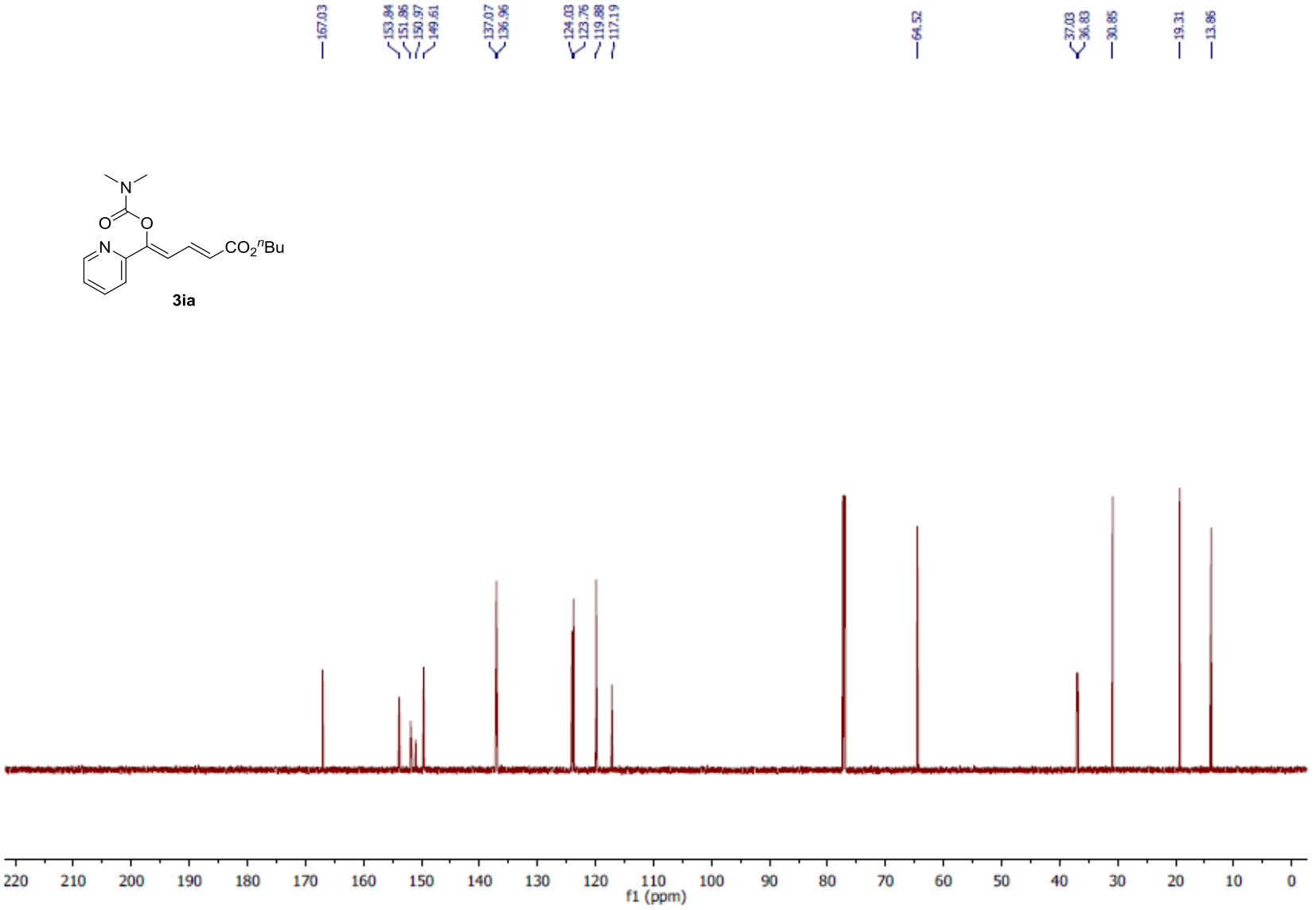

7.57
7.54
7.52
7.50
7.50
7.48
7.48
7.47
7.46
7.37
7.37
7.36
7.34
7.34
6.52
6.51
6.48
6.48
6.06
6.06
6.01
6.01
4.18
4.16
4.14
3.20
2.98
1.70
1.68
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.62
1.61
1.47
1.45
1.44
1.44
1.43
1.42
1.42
1.40
1.39
1.38
1.37
1.35
0.97
0.95
0.92
N
O
O
CO2nBu
Br
3ga
0.11
2.96
1.93
0.11
0.89
0.89
0.11
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
2.96
1.93
0.89
0.90
2.00
2.91
2.98
2.47
2.07
3.00
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)

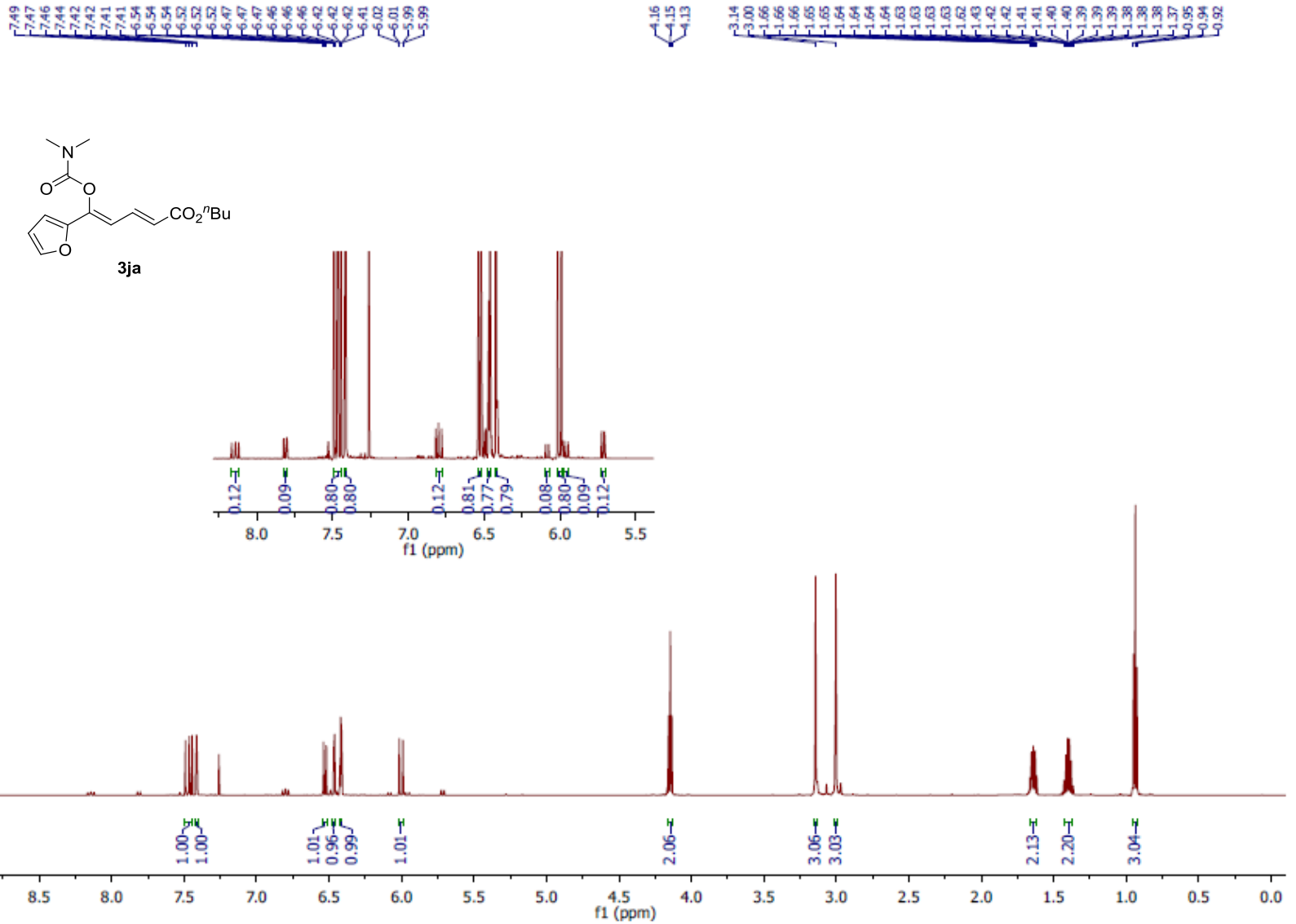

167.1
153.6
151.7
137.3
133.7
132.0
126.7
123.9
122.6
115.4
64.5
37.0
36.7
30.8
19.3
13.9
N
O
O
CO2nBu
Br
3ga
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

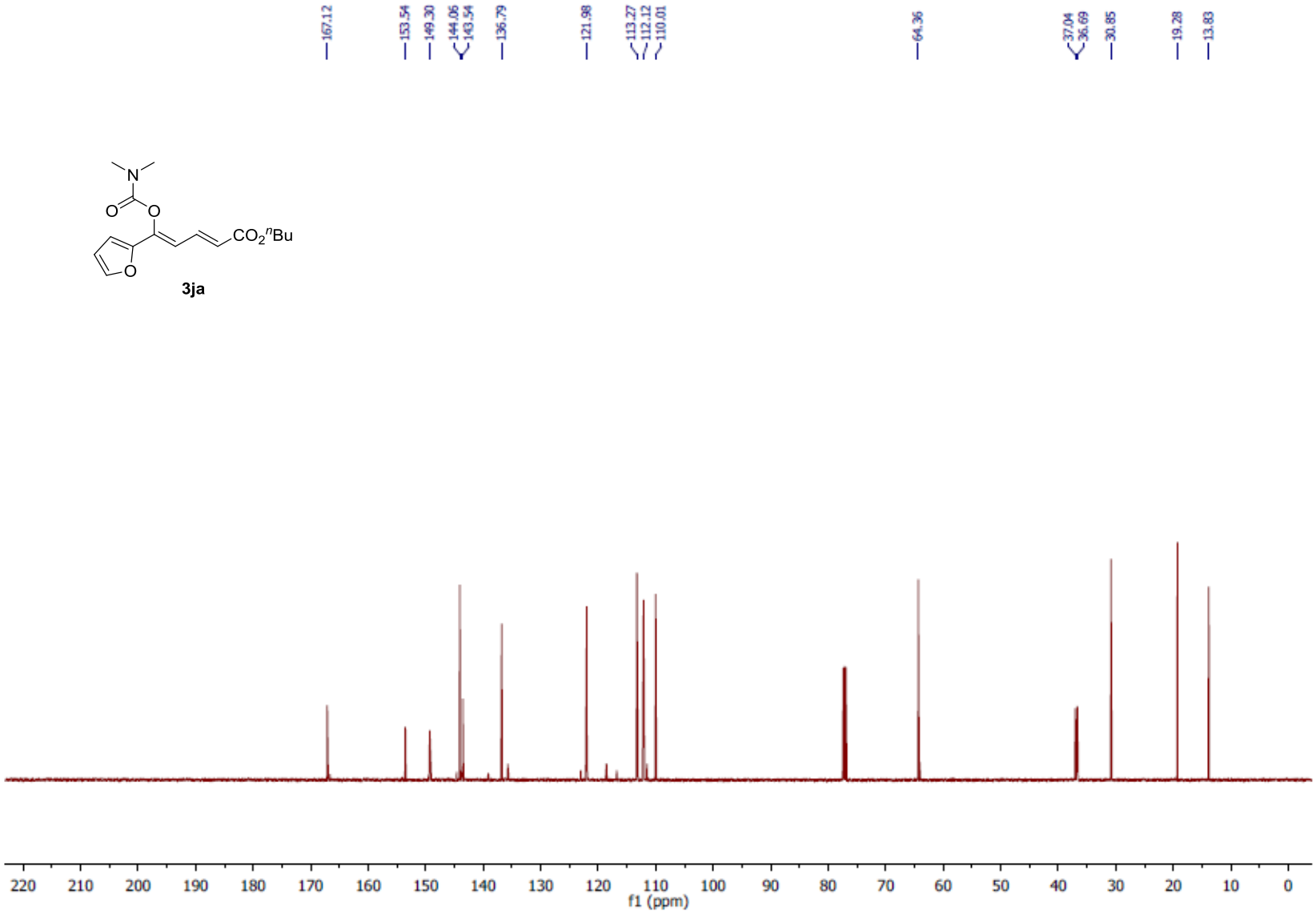

7.94 7.94 7.93 7.93 7.85 7.85 7.85 7.85 7.84 7.84 7.84 7.83 7.83 7.82 7.82 7.82 7.81 7.81 7.81 7.80 7.80 7.80 7.64 7.63 7.62 7.61 7.60 7.50 7.49 7.49 7.49 7.48 7.48 7.48 7.48 7.47 7.47 6.68 6.68 6.66 6.66 6.09 6.06 6.06 4.20 4.19 4.18 3.28 3.02 1.70 1.69 1.69 1.69 1.68 1.68 1.68 1.68 1.67 1.67 1.67 1.66 1.66 1.65 1.46 1.45 1.45 1.44 1.44 1.44 1.43 1.43 1.42 1.42 1.41 1.41 1.40 0.98 0.97 0.96
N
O
O
CO2nBu
3ha
0.13 0.13 0.87 0.87 0.13
8.0 7.5 7.0 6.5 6.0
f1 (ppm)
0.94 3.05 1.88 2.00 1.00 1.00 2.00 3.00 3.00 2.10 2.09 3.02
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)

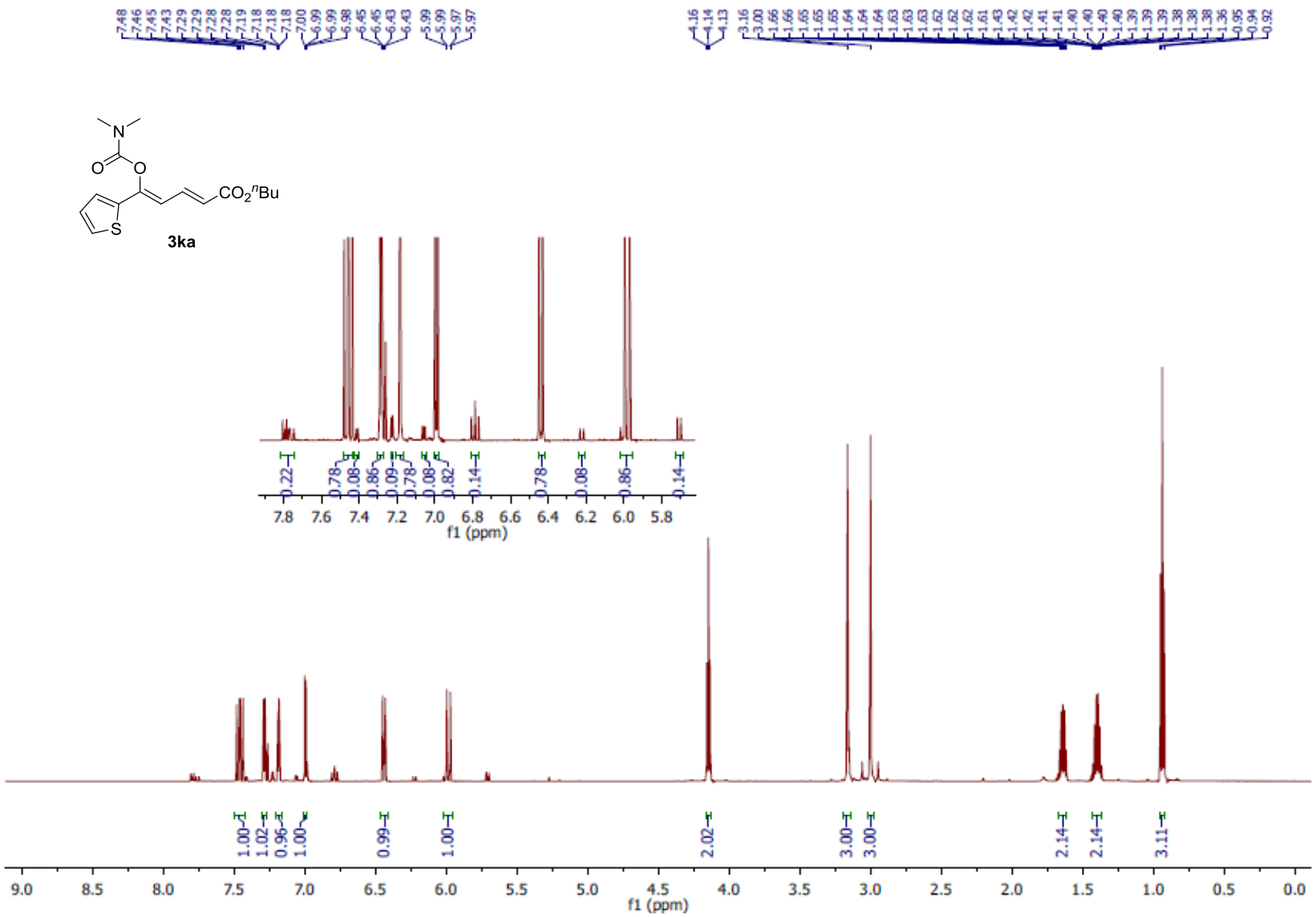

167.21
153.83
152.86
137.72
133.93
133.24
132.02
128.77
128.71
127.81
127.10
126.74
125.05
122.59
122.22
115.45
64.45
37.06
36.81
30.91
19.35
13.90
N
O
O
CO2nBu
3ha
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

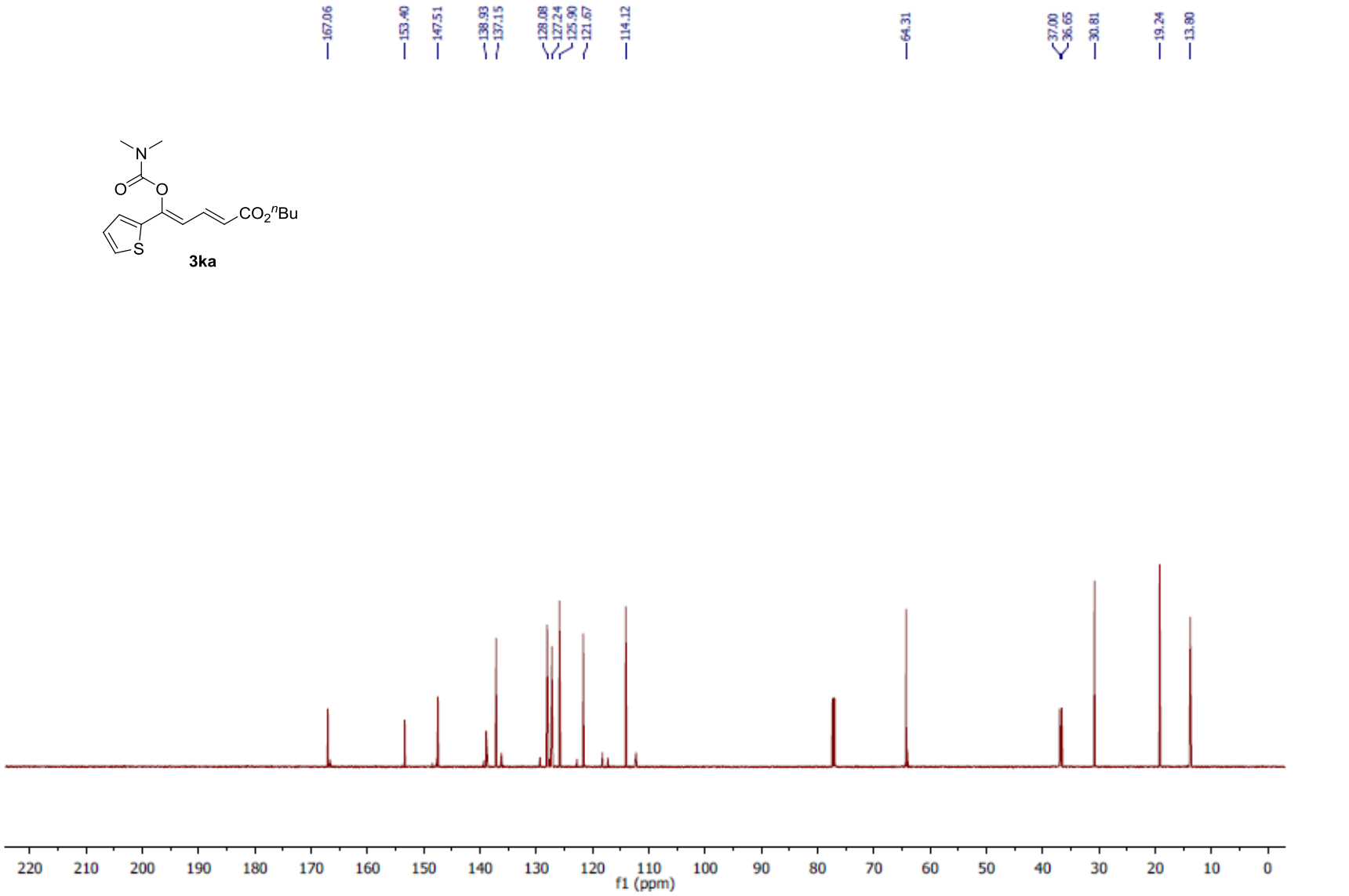

3ia
f1 (ppm)

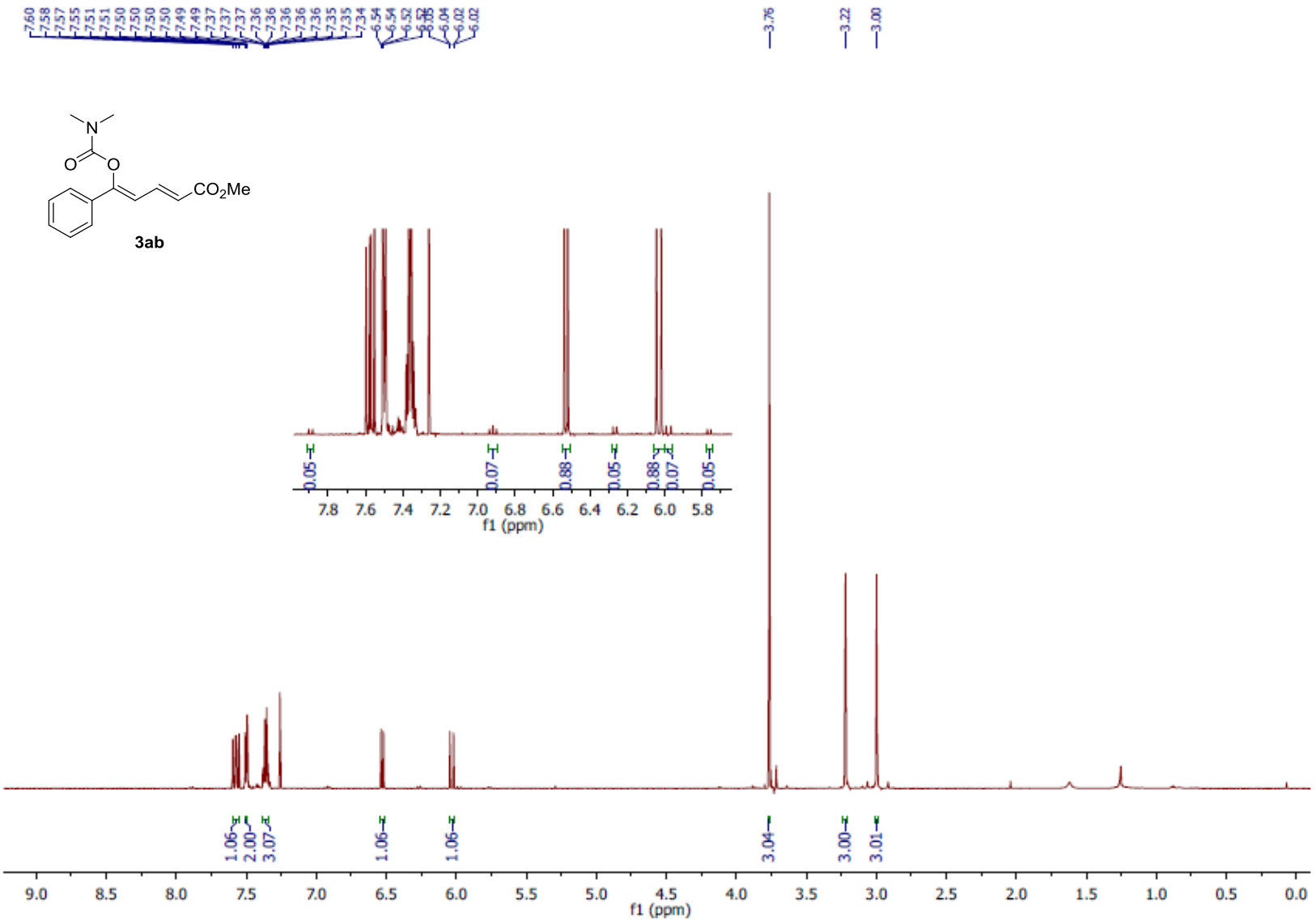

167.03
153.84
151.86
150.97
149.61
137.07
136.96
124.03
123.76
119.88
117.19
64.52
37.03
36.83
30.85
19.31
13.86
N
O
O
N
CO2nBu
3ia
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

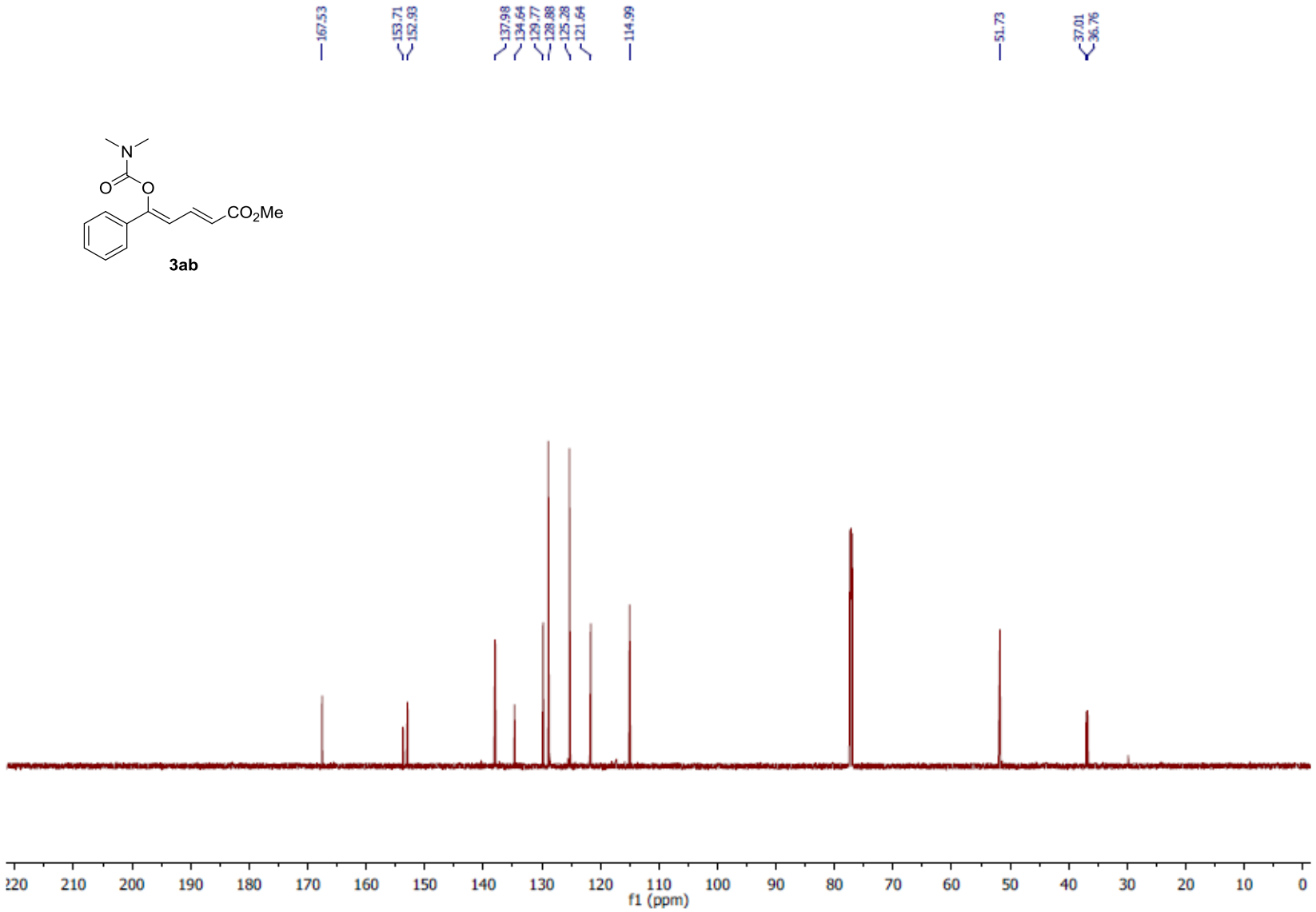

7.49 7.47 7.46 7.44 7.42 7.42 7.41 7.41 6.54 6.54 6.54 6.52 6.52 6.52 6.47 6.47 6.47 6.46 6.46 6.46 6.42 6.42 6.42 6.41 6.02 6.01 5.99 5.99
4.16 4.15 4.13
3.14 3.00 1.66 1.66 1.66 1.65 1.65 1.64 1.64 1.64 1.64 1.63 1.63 1.63 1.63 1.62 1.43 1.42 1.42 1.41 1.41 1.40 1.40 1.39 1.39 1.39 1.38 1.38 1.38 1.37 0.95 0.94 0.92
N
O
O
CO2nBu
O
3ja
0.12 0.09 0.80 0.80 0.12 0.81 0.77 0.79 0.08 0.80 0.09 0.12
8.0 7.5 7.0 6.5 6.0 5.5
f1 (ppm)
1.00 1.00 1.01 0.96 0.99 1.01 2.06 3.06 3.03 2.13 2.20 3.04
.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)


167.12
153.54
149.30
144.06
143.54
136.79
121.98
113.27
112.12
110.01
64.36
37.04
36.69
30.85
19.28
13.83
N
O
O
O
CO2nBu
3ja
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

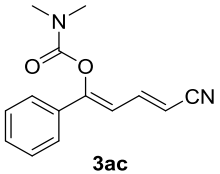

7.48 7.46 7.45 7.43 7.29 7.29 7.28 7.28 7.19 7.18 7.18 7.18 7.00 6.99 6.99 6.98 6.45 6.45 6.43 6.43 5.99 5.99 5.97 5.97
4.16 4.14 4.13 3.16 3.00 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.62 1.61 1.43 1.42 1.42 1.41 1.41 1.40 1.40 1.40 1.40 1.39 1.39 1.38 1.38 1.38 1.36 0.95 0.94 0.92
N
O
O
CO2nBu
S
3ka
0.22 0.78 0.08 0.86 0.09 0.78 0.08 0.82 0.14 0.78 0.08 0.86 0.14
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8
f1 (ppm)
1.00 1.02 0.96 1.00 0.99 1.00 2.02 3.00 3.00 2.14 2.14 3.11
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)


167.06
153.40
147.51
138.93
137.15
128.08
127.24
125.90
121.67
114.12
64.31
37.00
36.65
30.81
19.24
13.80
N
O
O
S
CO2nBu
3ka
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

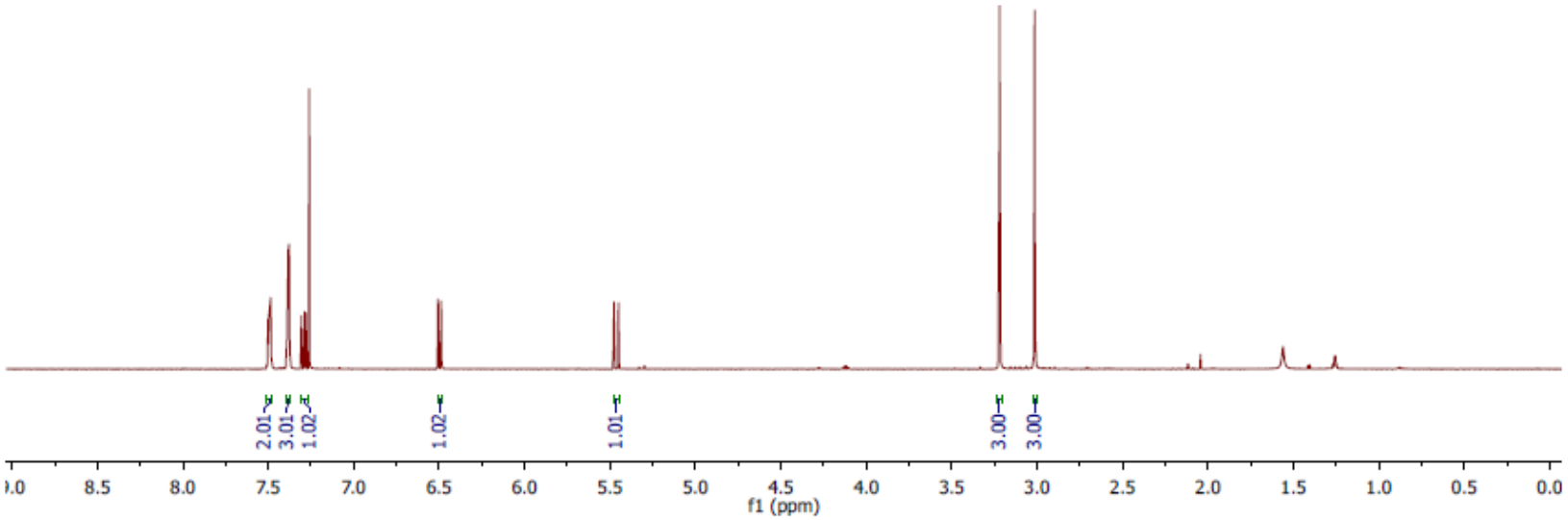

7.60
7.58
7.57
7.55
7.51
7.51
7.50
7.50
7.50
7.50
7.49
7.49
7.37
7.37
7.37
7.36
7.36
7.36
7.36
7.36
7.35
7.35
7.34
6.54
6.54
6.52
6.04
6.02
6.02
3.76
3.22
3.00
N
O
O
CO2Me
3ab
0.05
0.07
0.88
0.05
0.88
0.07
0.05
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8
f1 (ppm)
1.06
2.00
3.07
1.06
1.06
3.04
3.00
3.01
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)

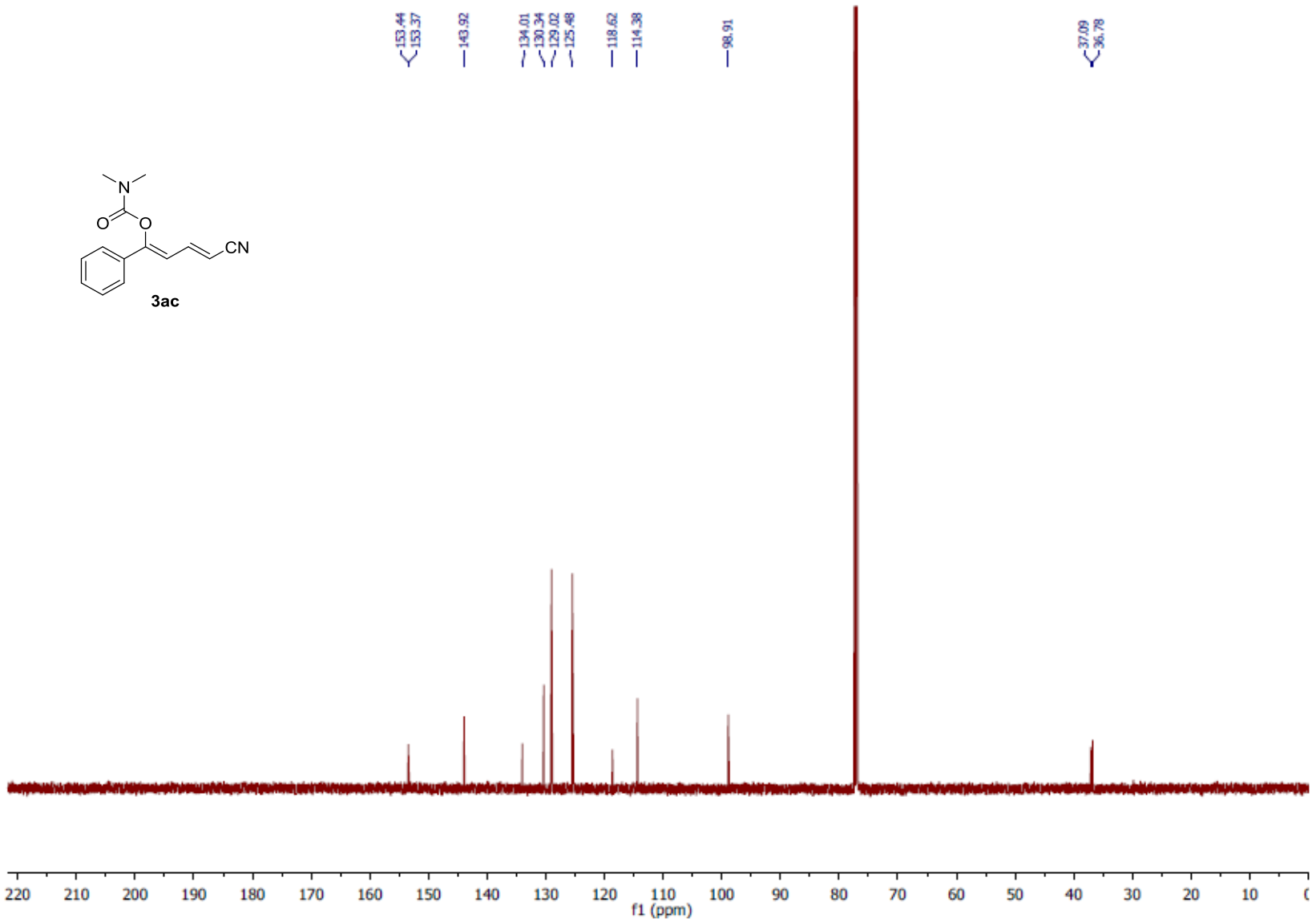

167.53
153.71
152.93
137.98
134.64
129.77
128.88
125.28
121.64
114.99
51.73
37.01
36.76
N
O
O
CO2Me
3ab
f1 (ppm)


7.50
7.50
7.50
7.50
7.49
7.49
7.49
7.48
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.31
7.29
7.28
7.26
6.51
6.51
6.49
6.49
5.48
5.48
5.45
5.45
3.22
3.01

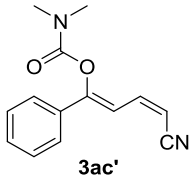

N
O
O
CN

3ac

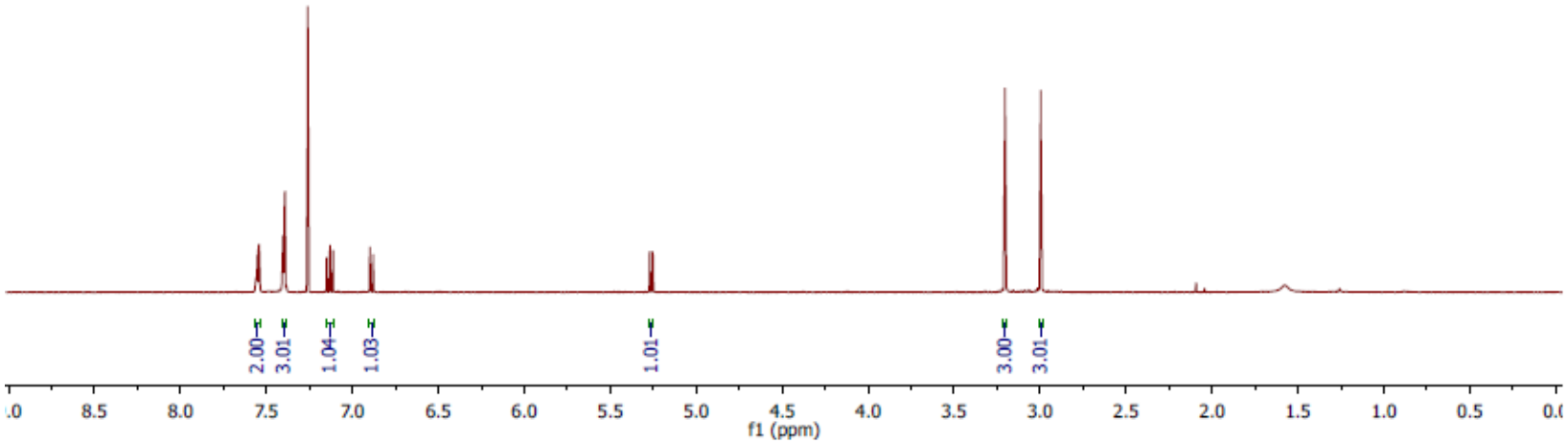

2.01
3.01
1.02
1.02
1.01
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

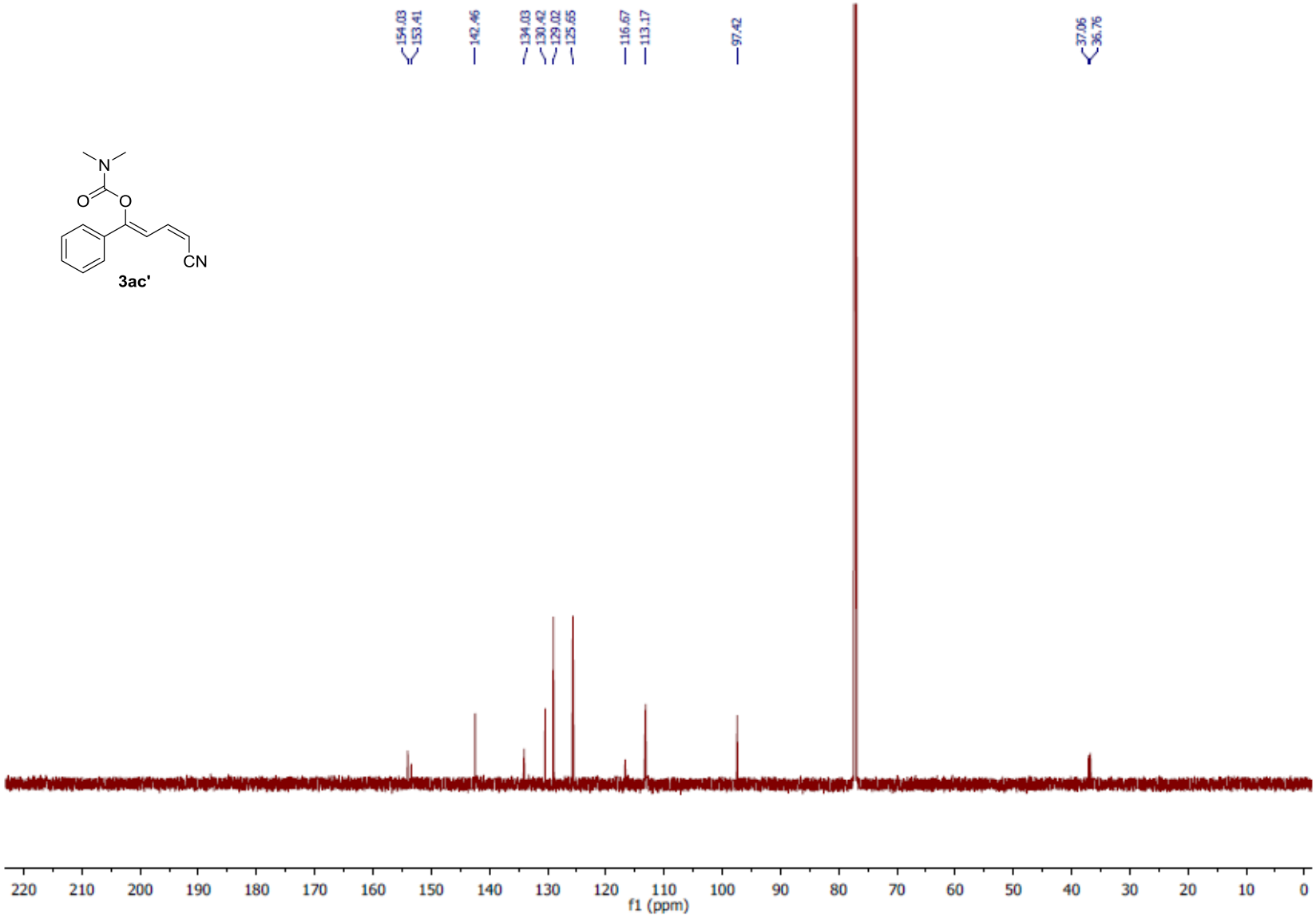

153.44
153.37
143.92
134.01
130.34
129.02
125.48
118.62
114.38
98.91
37.09
36.78
N
O
O
CN
3ac
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.56
7.56
7.56
7.56
7.55
7.55
7.55
7.55
7.54
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.15
7.13
7.13
7.11
6.90
6.90
6.88
6.88
5.27
5.27
5.25
5.25
3.20
3.00

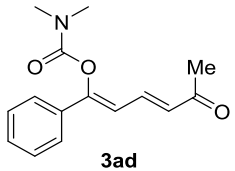

N
O
O
CN

3ac'

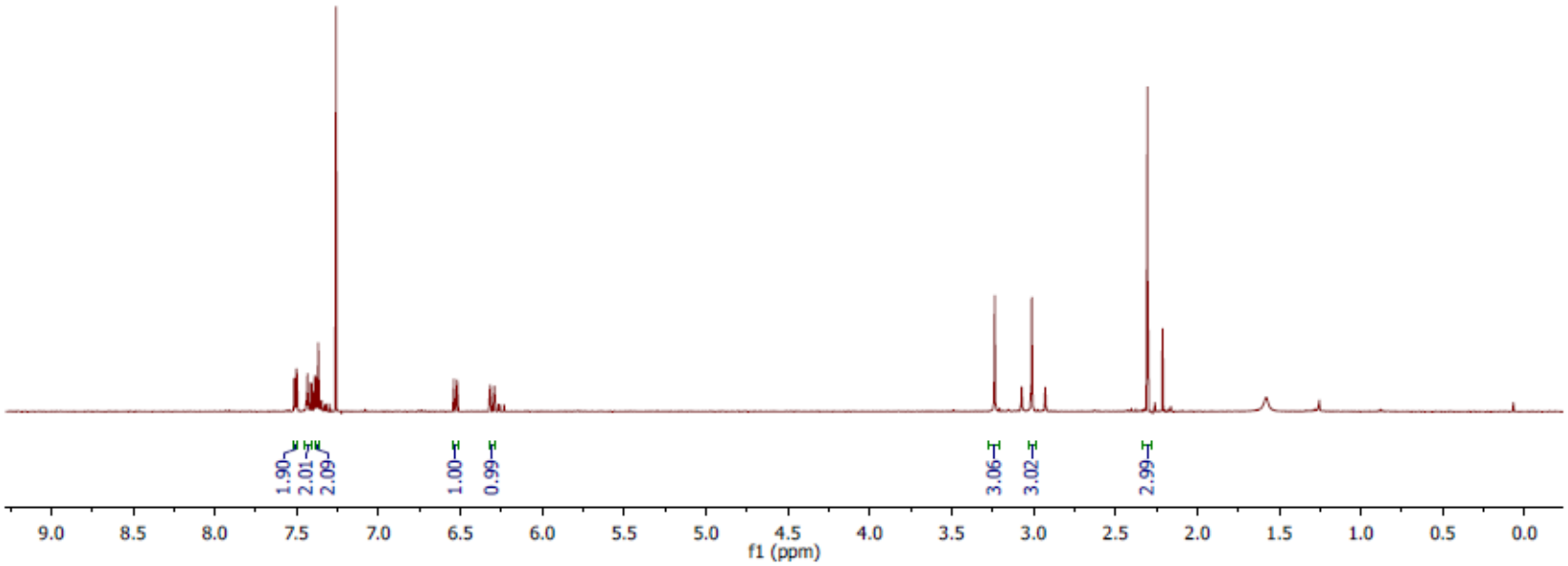

2.00
3.01
1.04
1.03
1.01
3.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

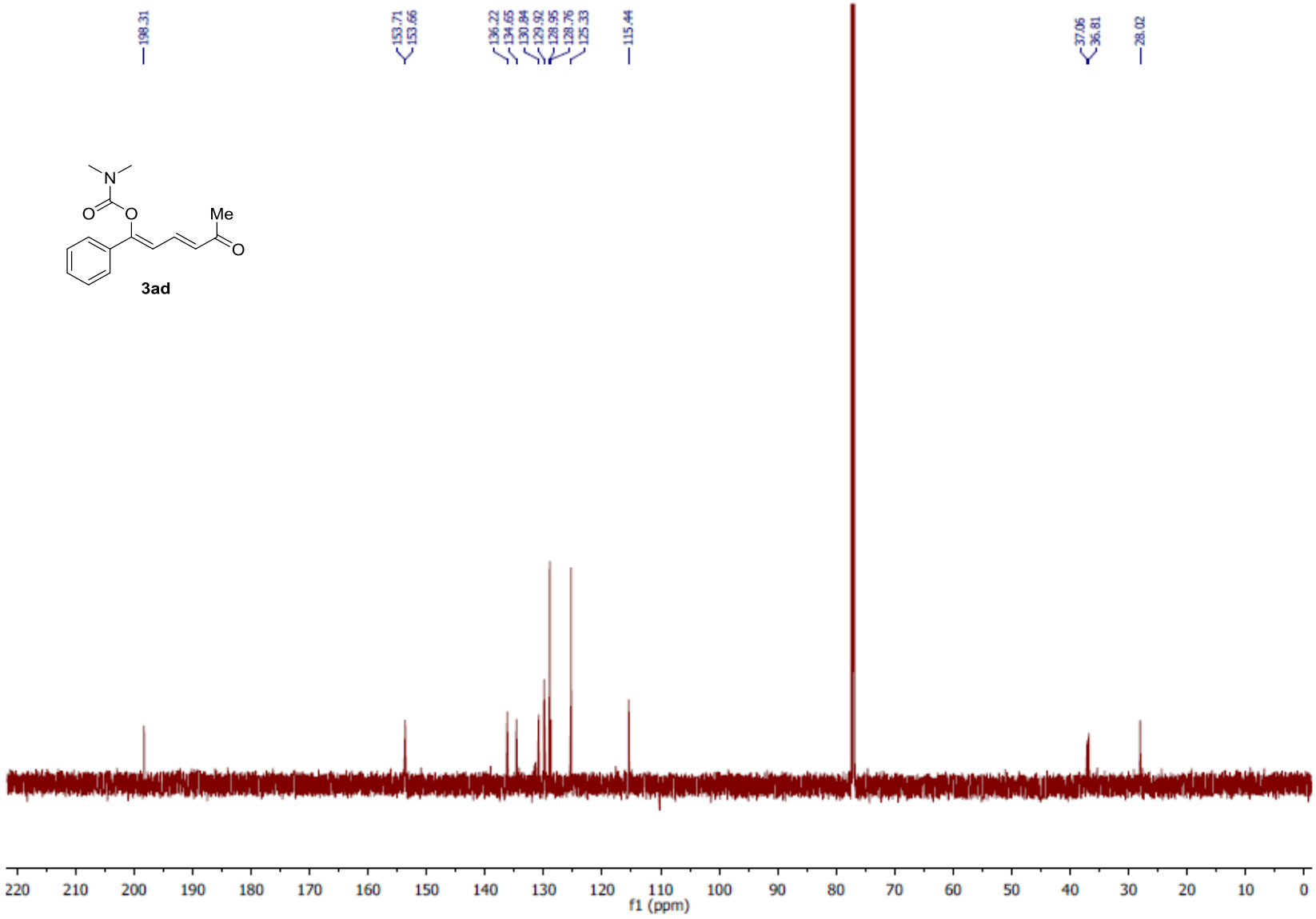

154.03
153.41
142.46
134.03
130.42
129.02
125.65
116.67
113.17
97.42
37.06
36.76
N
O
O
CN
3ac'
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

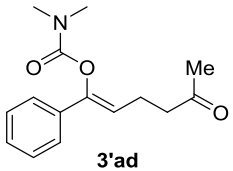

7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.50
7.44
7.44
7.43
7.43
7.42
7.41
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.37
6.54
6.54
6.52
6.52
6.32
6.32
6.29
6.29
3.24
3.01
2.30


N
O
O
Me
O

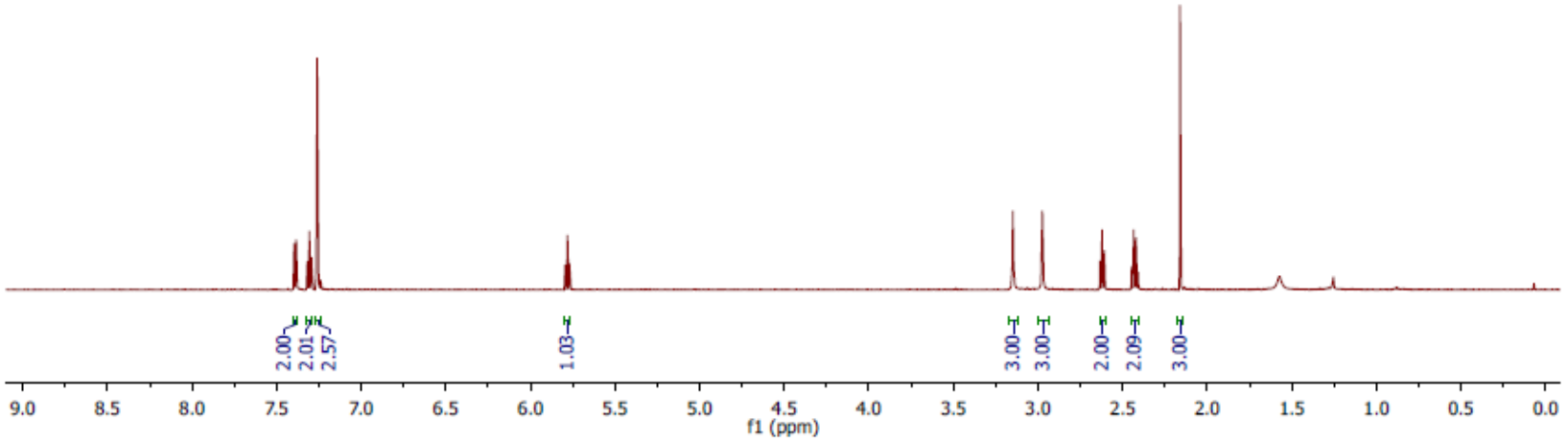
3ad

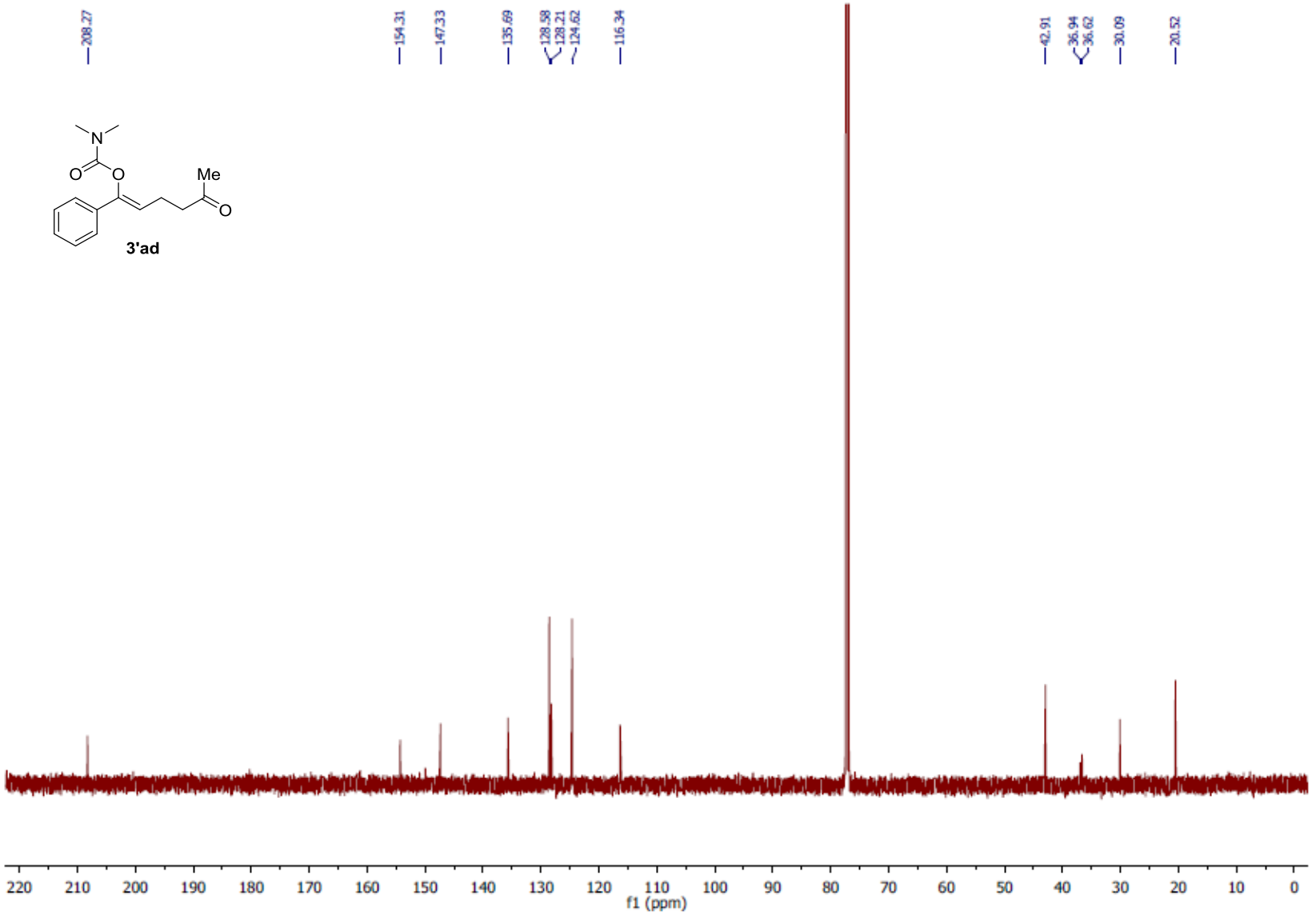

1.90
2.01
2.09
1.00
0.99
3.06
3.02
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.31
153.71
153.66
136.22
134.65
130.84
129.92
128.95
128.76
125.33
115.44
37.06
36.81
28.02
N
O
O
Me
O
3ad
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

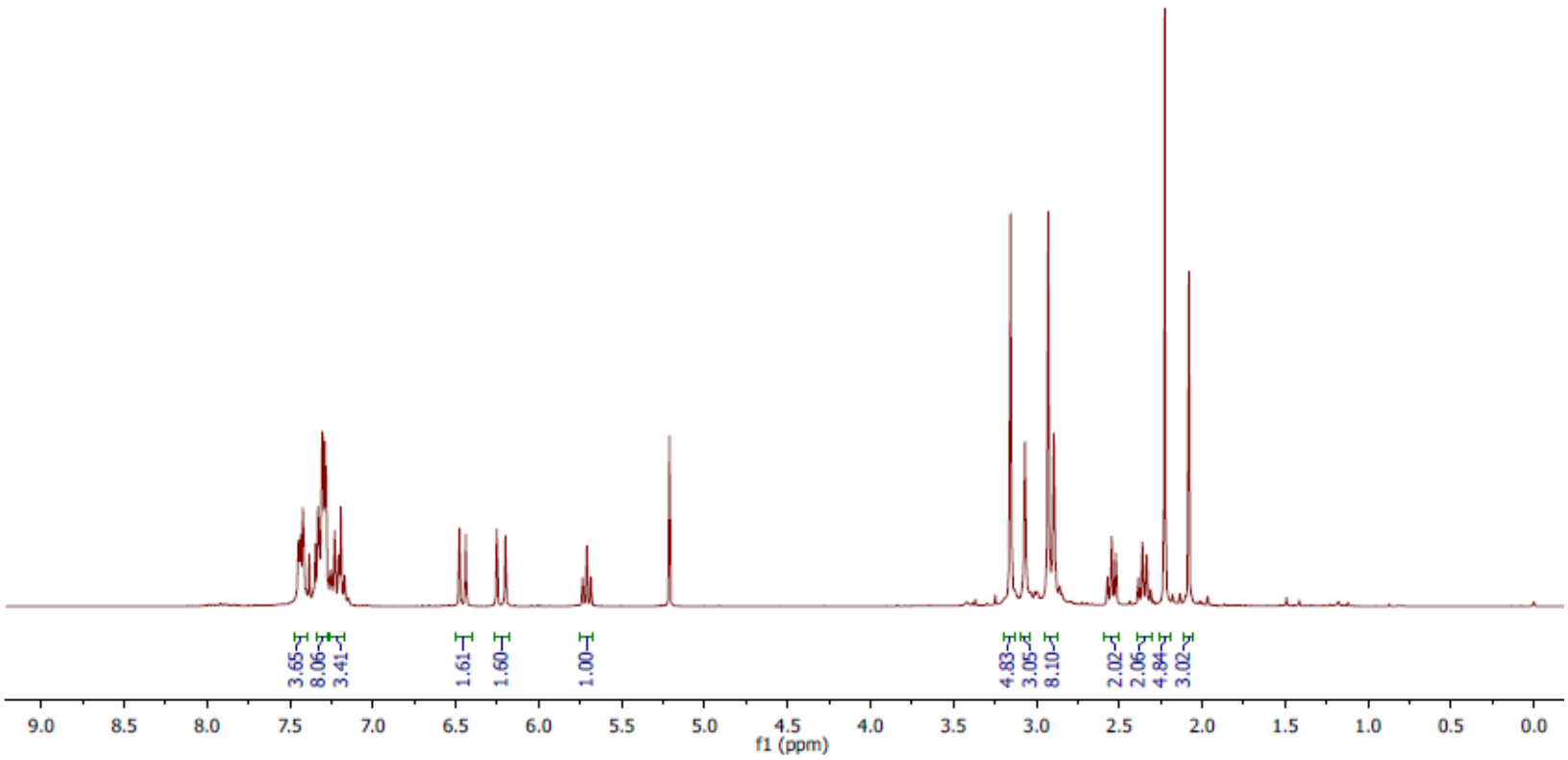

N
O
O
Me
O

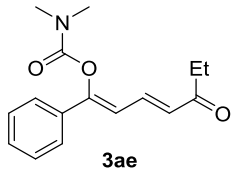
3'ad


2.00
2.01
2.57
1.03
3.00
3.00
2.00
2.09
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

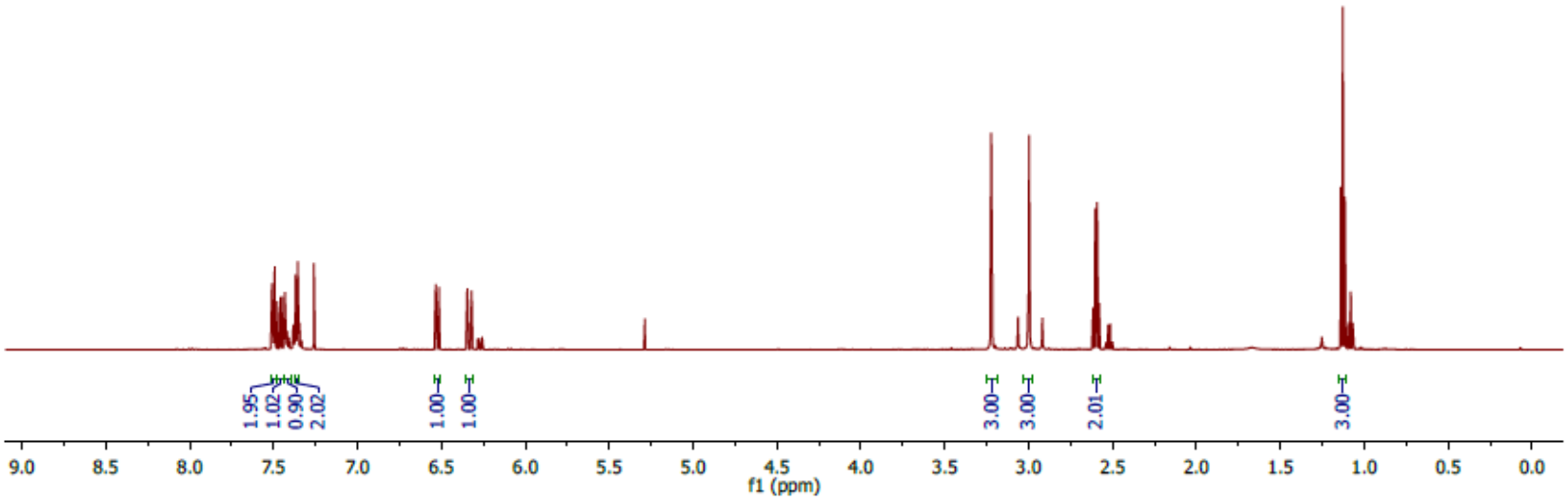

208.27
154.31
147.33
135.69
128.58
128.21
124.62
116.34
42.91
36.94
36.62
30.09
20.52
N
O
O
Me
O
3'ad
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

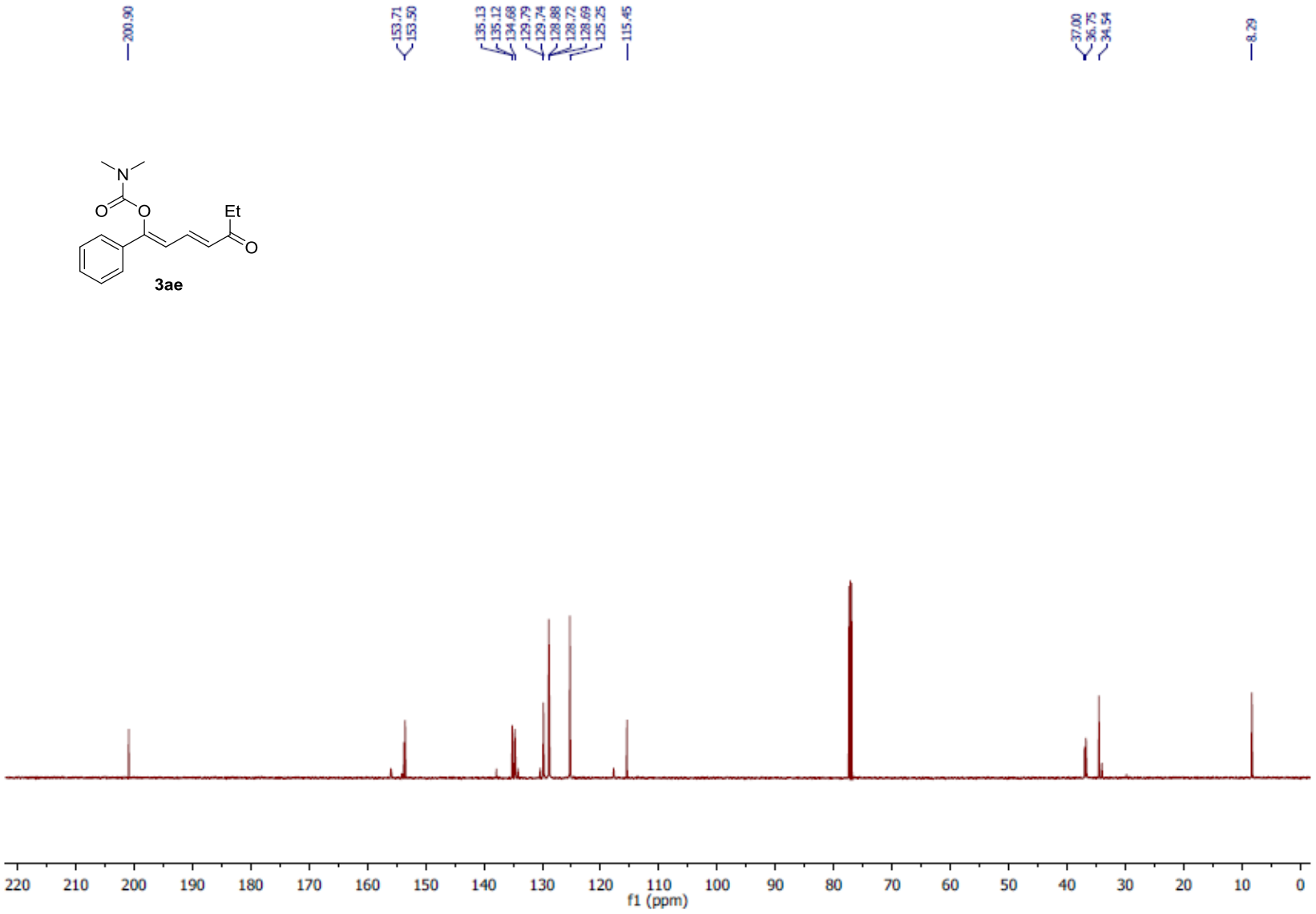
^{1}H NMR of 1.6:1 mixture of **3ad**:**3'ad**

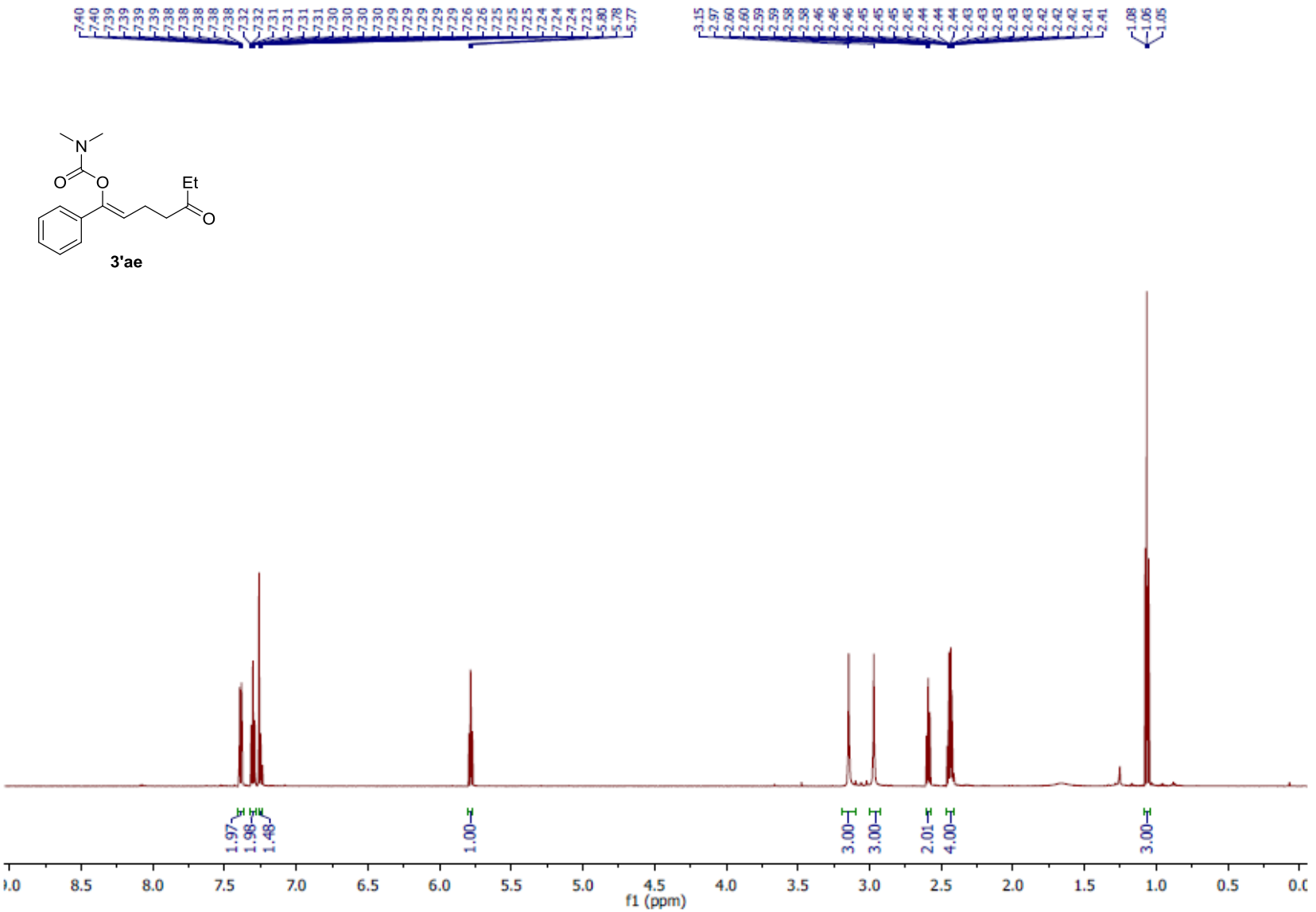


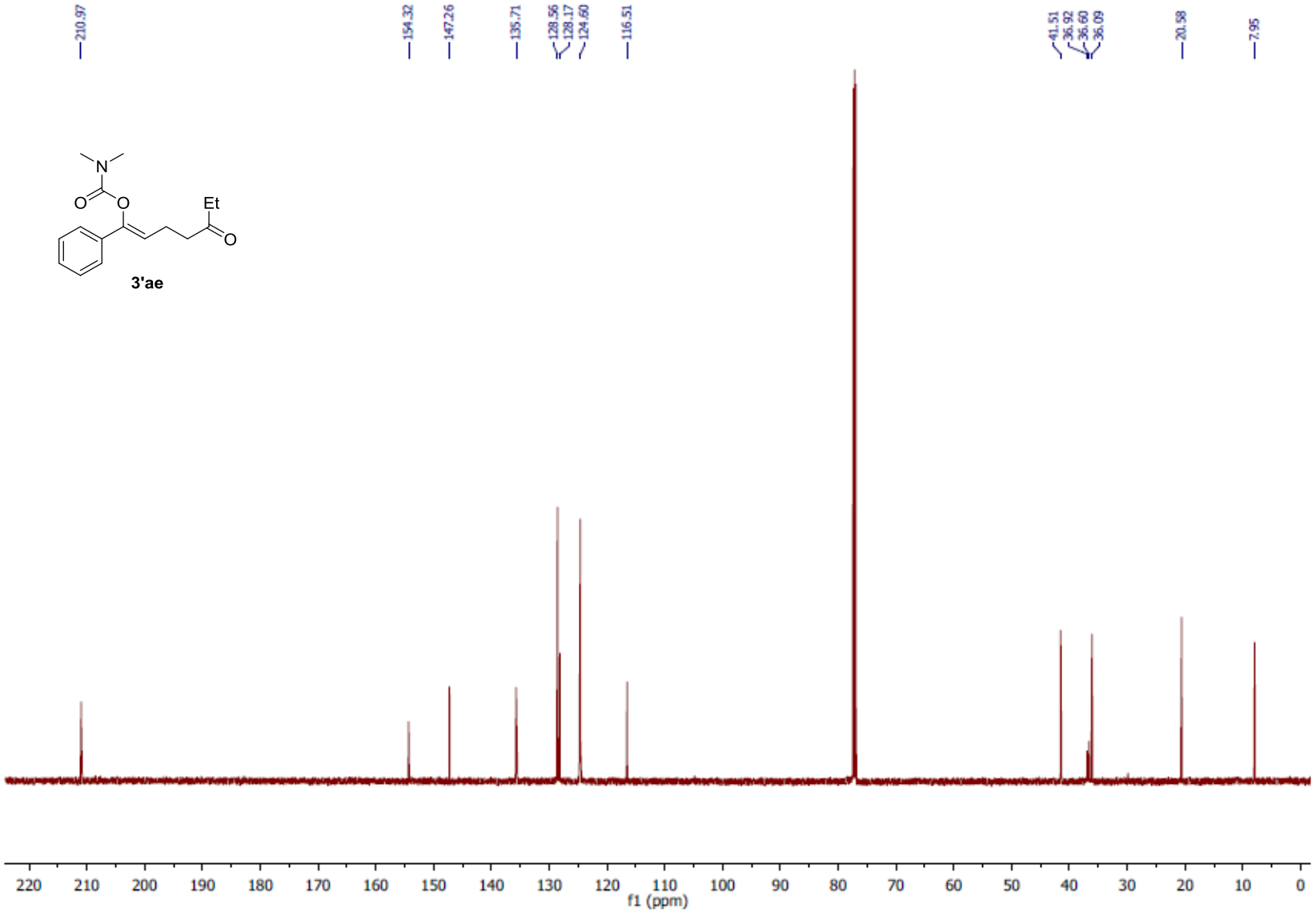


3ae

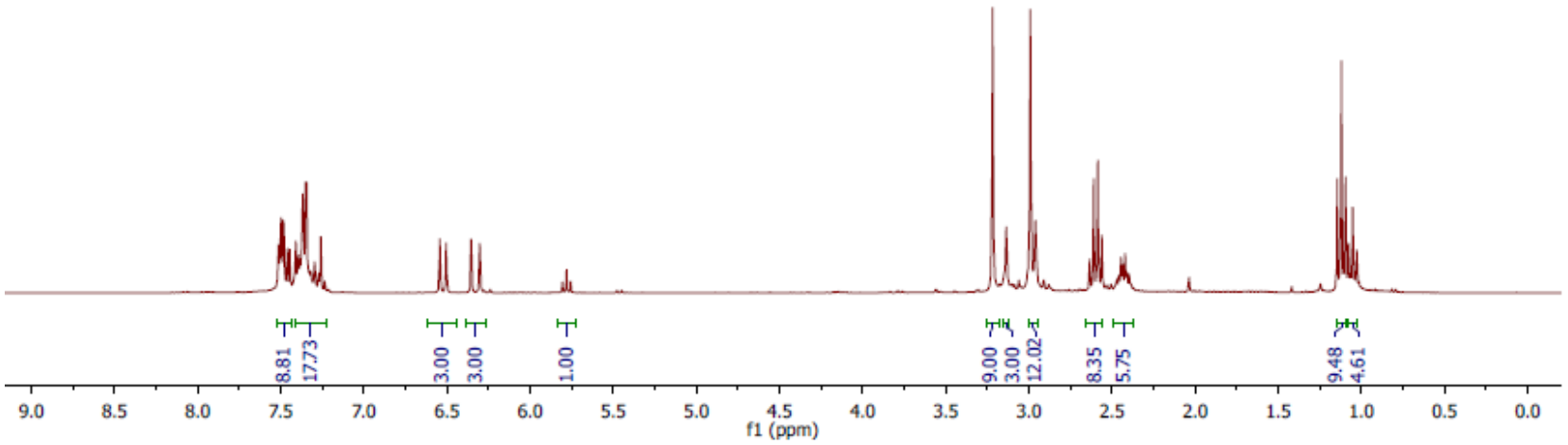

1.95
1.02
0.90
2.02
1.00
1.00
3.00
3.00
2.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

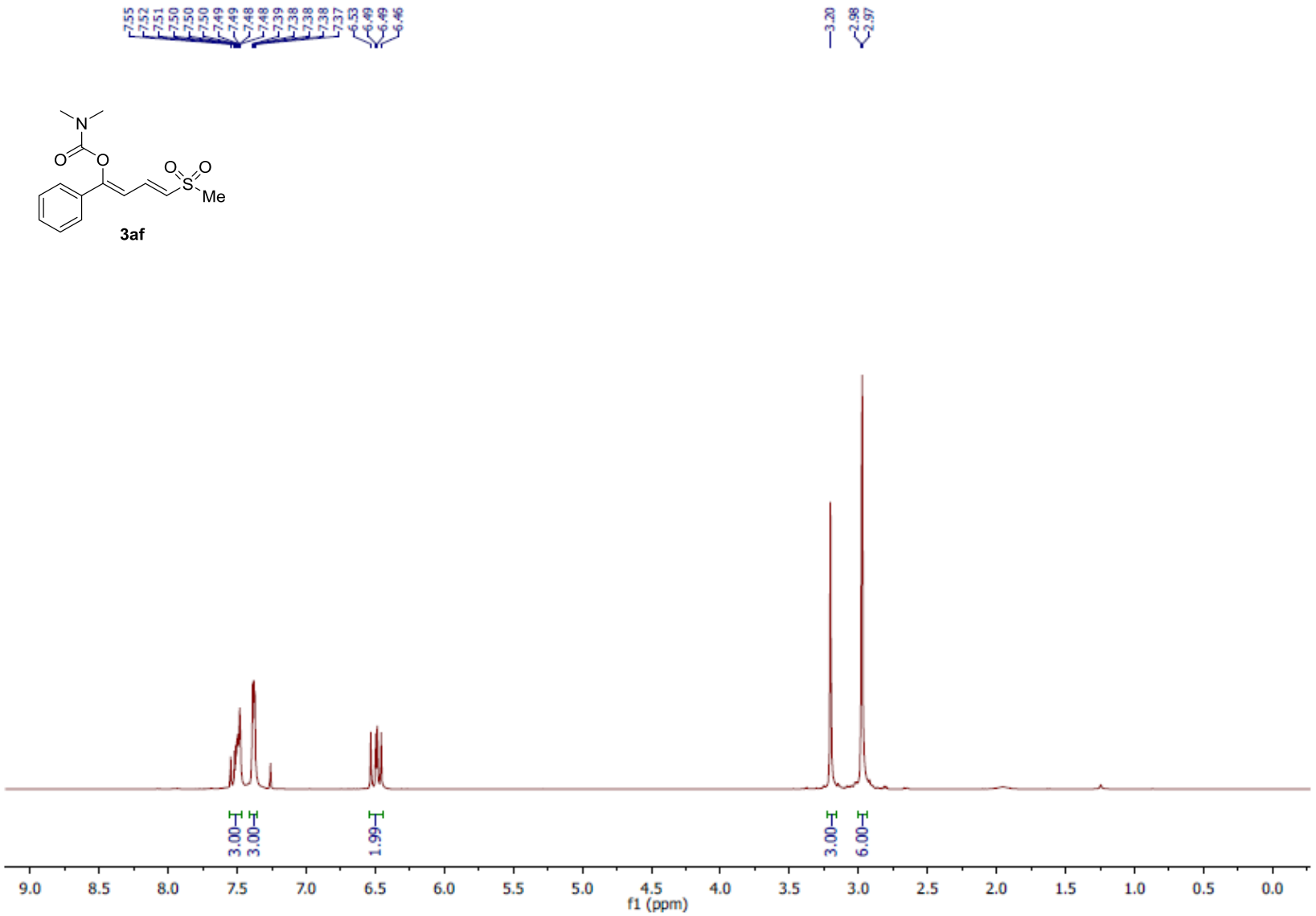

200.90
153.71
153.50
135.13
135.12
134.68
129.79
129.74
128.88
128.72
128.69
125.25
115.45
37.00
36.75
34.54
8.29
N
O
O
Et
O
3ae
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

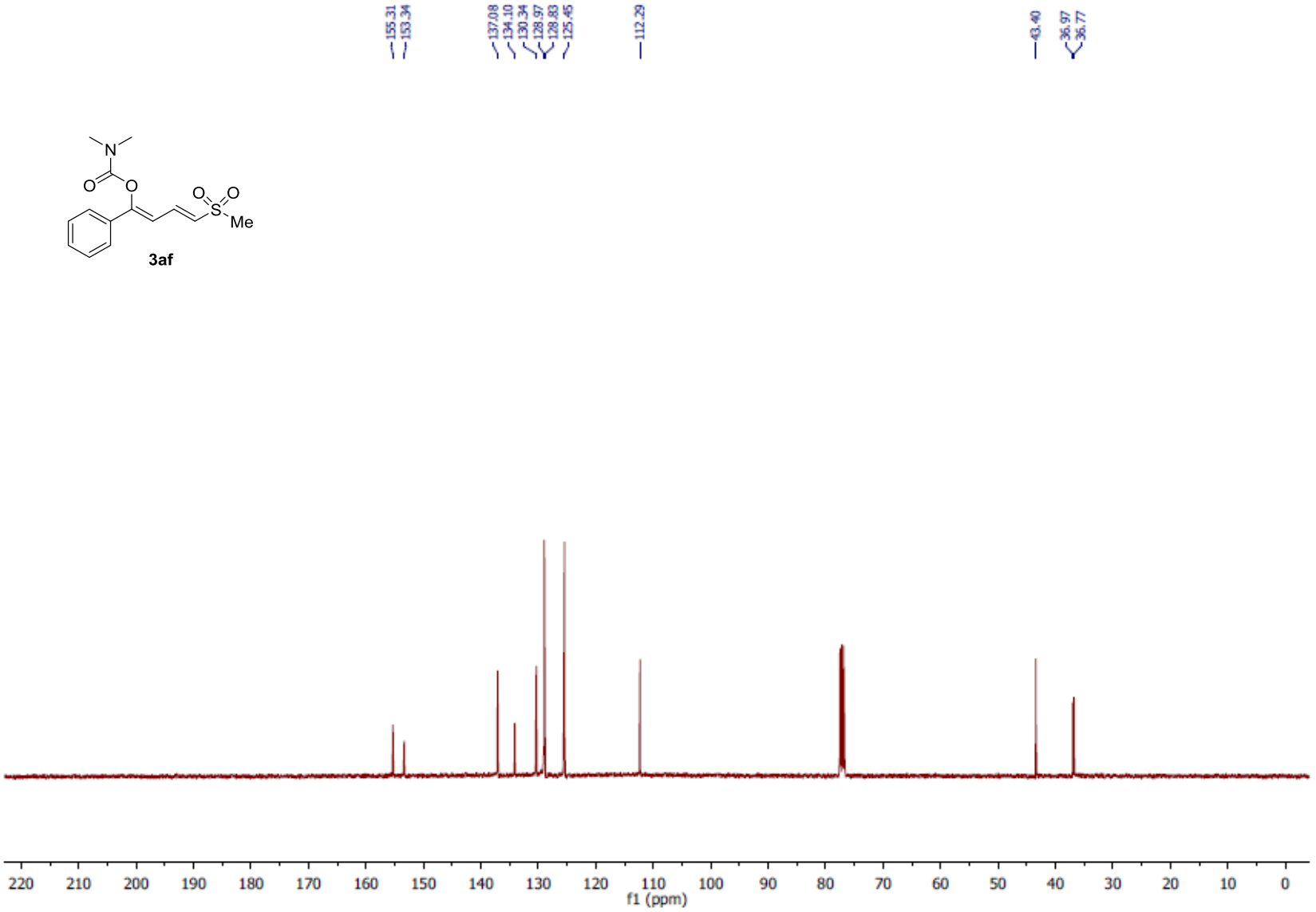

7.40
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.30
7.29
7.29
7.29
7.29
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.23
5.80
5.78
5.77
3.15
2.97
2.60
2.60
2.59
2.59
2.58
2.58
2.46
2.46
2.46
2.45
2.45
2.45
2.45
2.44
2.44
2.44
2.43
2.43
2.43
2.43
2.43
2.42
2.42
2.42
2.41
2.41
1.08
1.06
1.05
N
O
O
Et
O
3'ae
1.97
1.98
1.48
1.00
3.00
3.00
2.01
4.00
3.00
f1 (ppm)

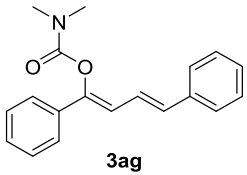

210.97
154.32
147.26
135.71
128.56
128.17
124.60
116.51
41.51
36.92
35.60
36.09
20.98
7.95
N
O
O
Et
O
3'ae
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR of 3:1 mixture of **3ae**:**3'ae**

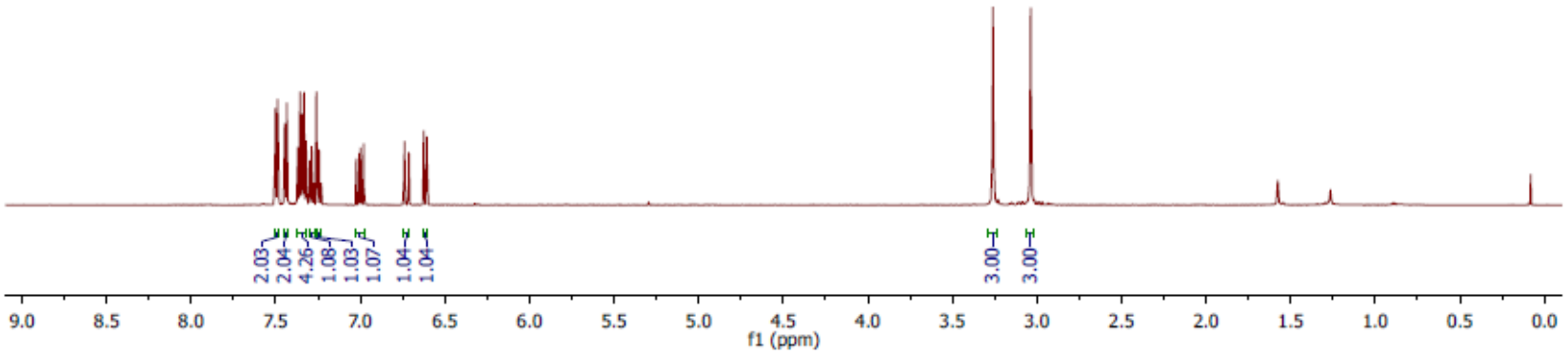


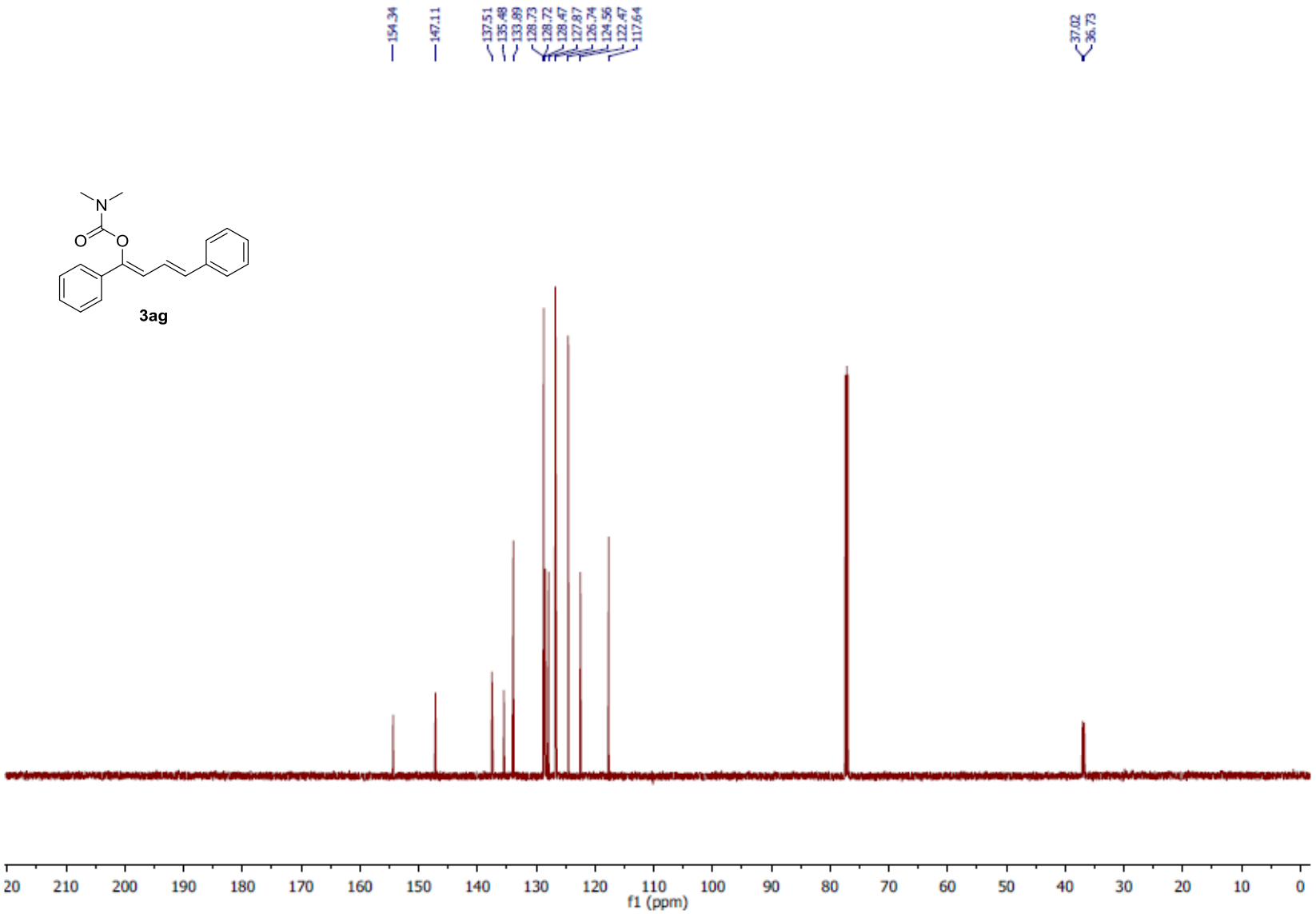

7.55
7.52
7.51
7.50
7.50
7.50
7.49
7.49
7.48
7.48
7.39
7.38
7.38
7.38
7.37
6.53
6.49
6.49
6.46
3.20
2.98
2.97
N
O
O
O
O
S
Me
3af
3.00
3.00
1.99
3.00
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.31
153.34
137.08
134.10
130.34
128.97
128.83
125.45
112.29
63.40
36.97
36.77
N
O
O
O
S
O
Me
3af
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3ag


2.03
2.04
4.26
1.08
1.03
1.07
1.04
1.04
3.00
3.00
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)


154.34
147.11
137.51
135.48
133.89
128.73
128.72
128.47
127.87
126.74
124.56
122.47
117.64
37.02
36.73
3ag
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.58
7.58
7.57
7.57
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.49
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.10
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7.06
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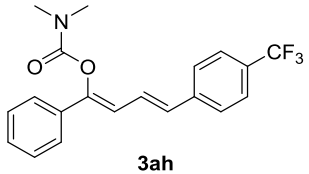
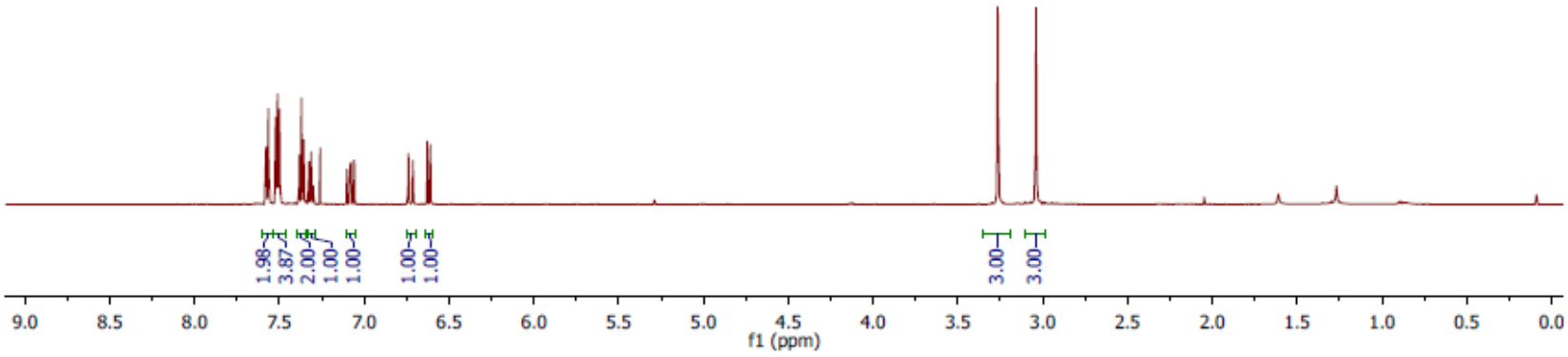
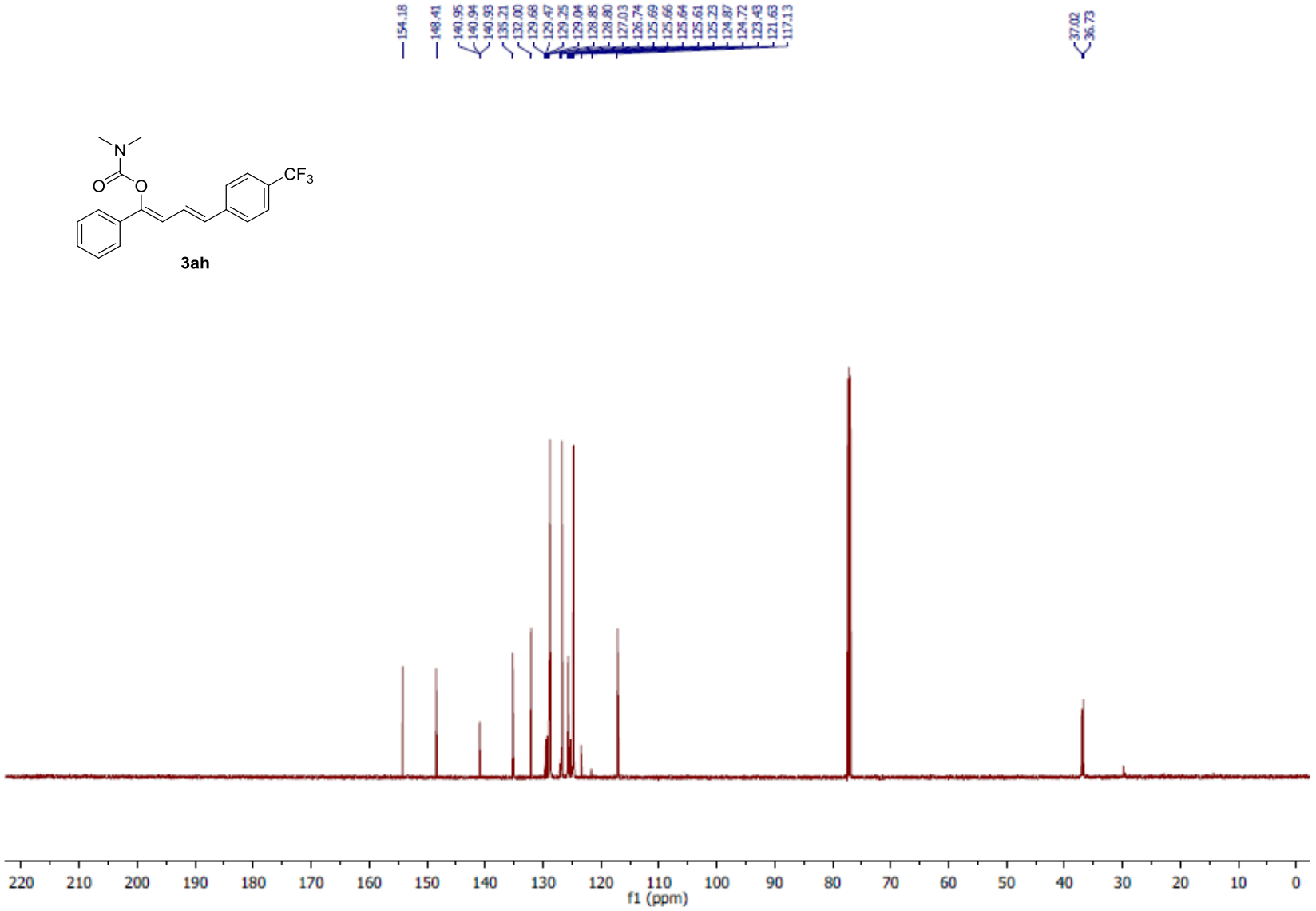
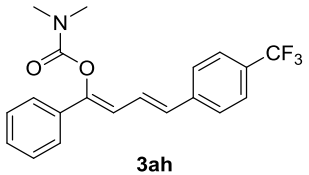
6.63
6.63
6.61
6.61
3.26
3.04


N
O
O
CF3

3ah

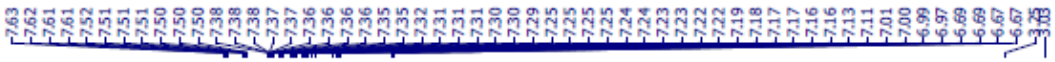

1.98
3.87
2.00
1.00
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

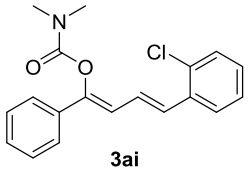

154.18
148.41
140.95
140.94
140.93
135.21
132.00
129.68
129.47
129.25
129.04
128.85
128.80
127.03
126.74
125.69
125.66
125.64
125.61
125.23
124.87
124.72
123.43
121.63
117.13
37.02
36.73
N
O
O
CF3
3ah
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
O
CF3

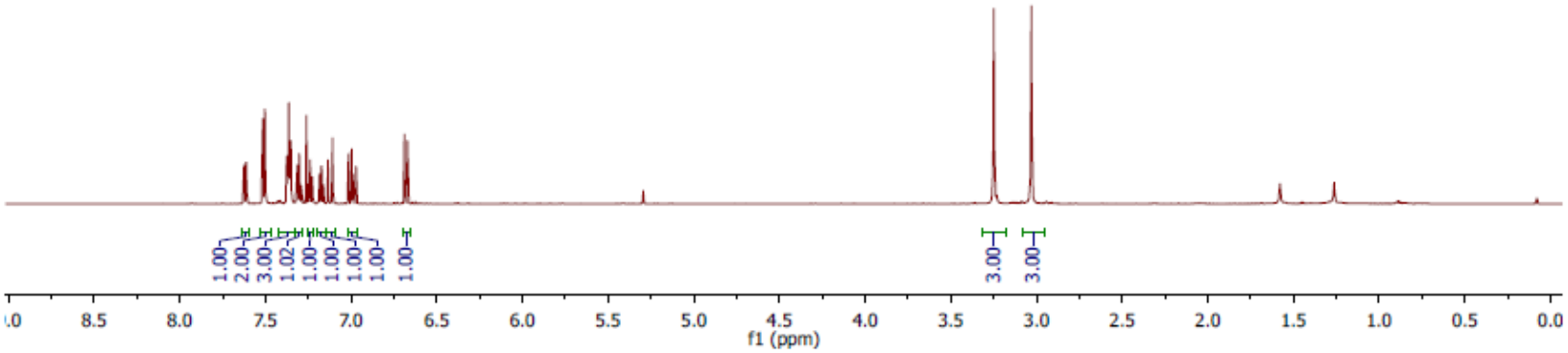
3ah

-62.48
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)




N
O
O
Cl

3ai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2.00
3.00
1.02
1.00
1.00
1.00
1.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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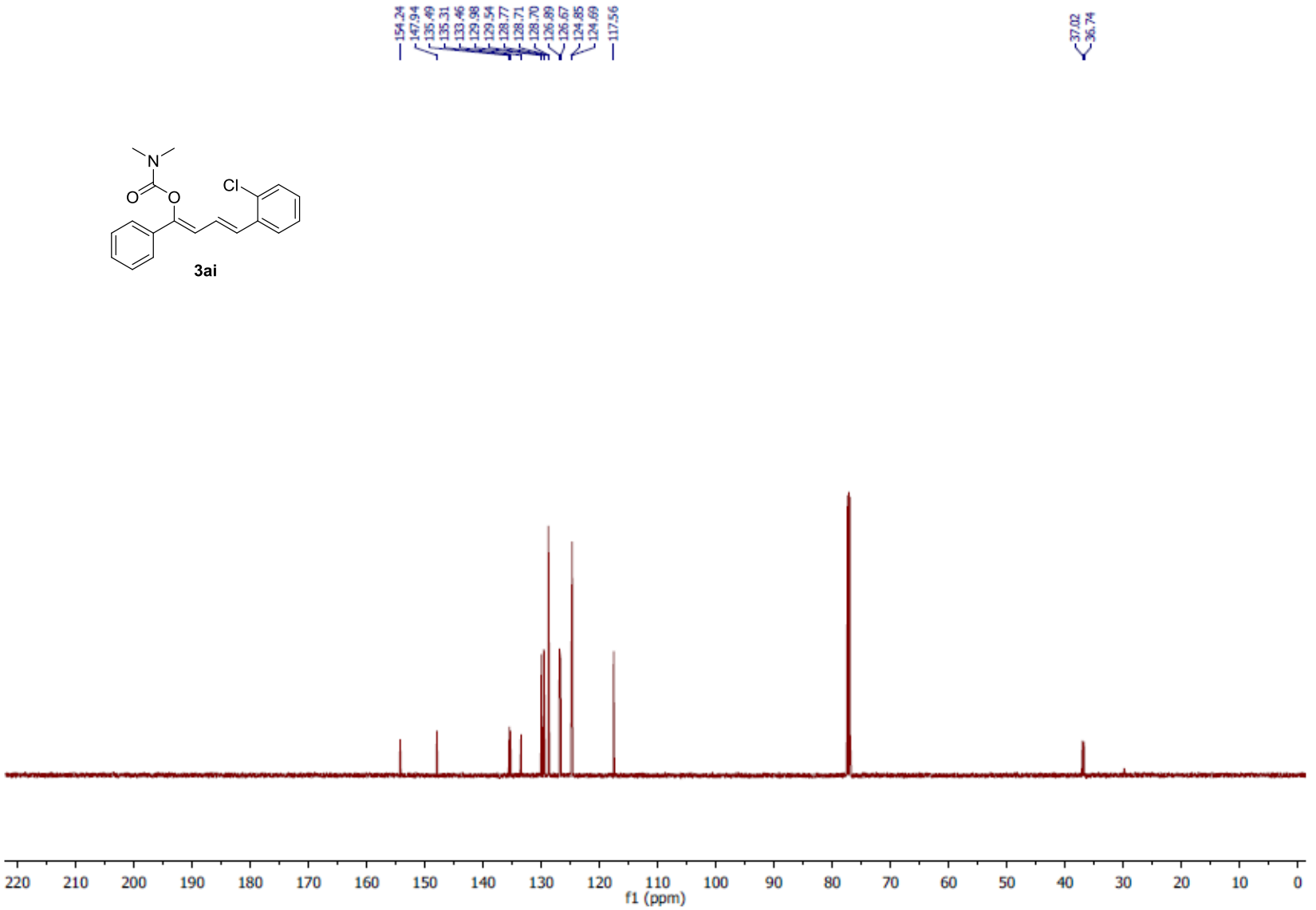
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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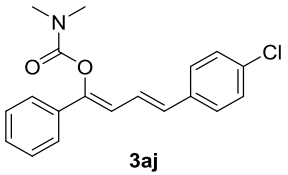
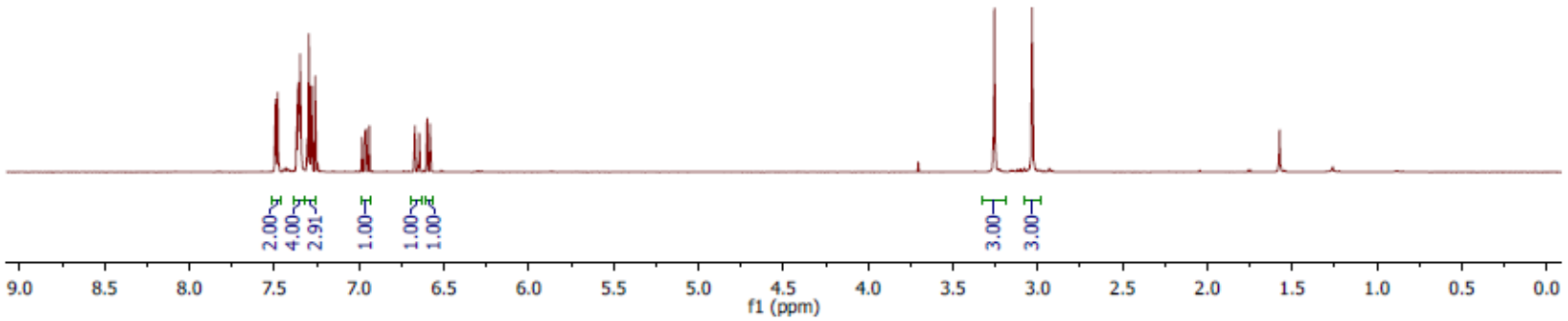
147.94
135.49
135.31
133.46
129.98
129.54
128.77
128.71
128.70
126.89
126.67
124.85
124.69
117.56
37.02
36.74
N
O
O
Cl
3ai
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.49
7.49
7.48
7.48
7.48
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.31
7.30
7.29
6.97
6.96
6.94
6.67
6.65
6.60
6.60
6.58
6.58
3.26
3.03


N
O
O
Cl

3aj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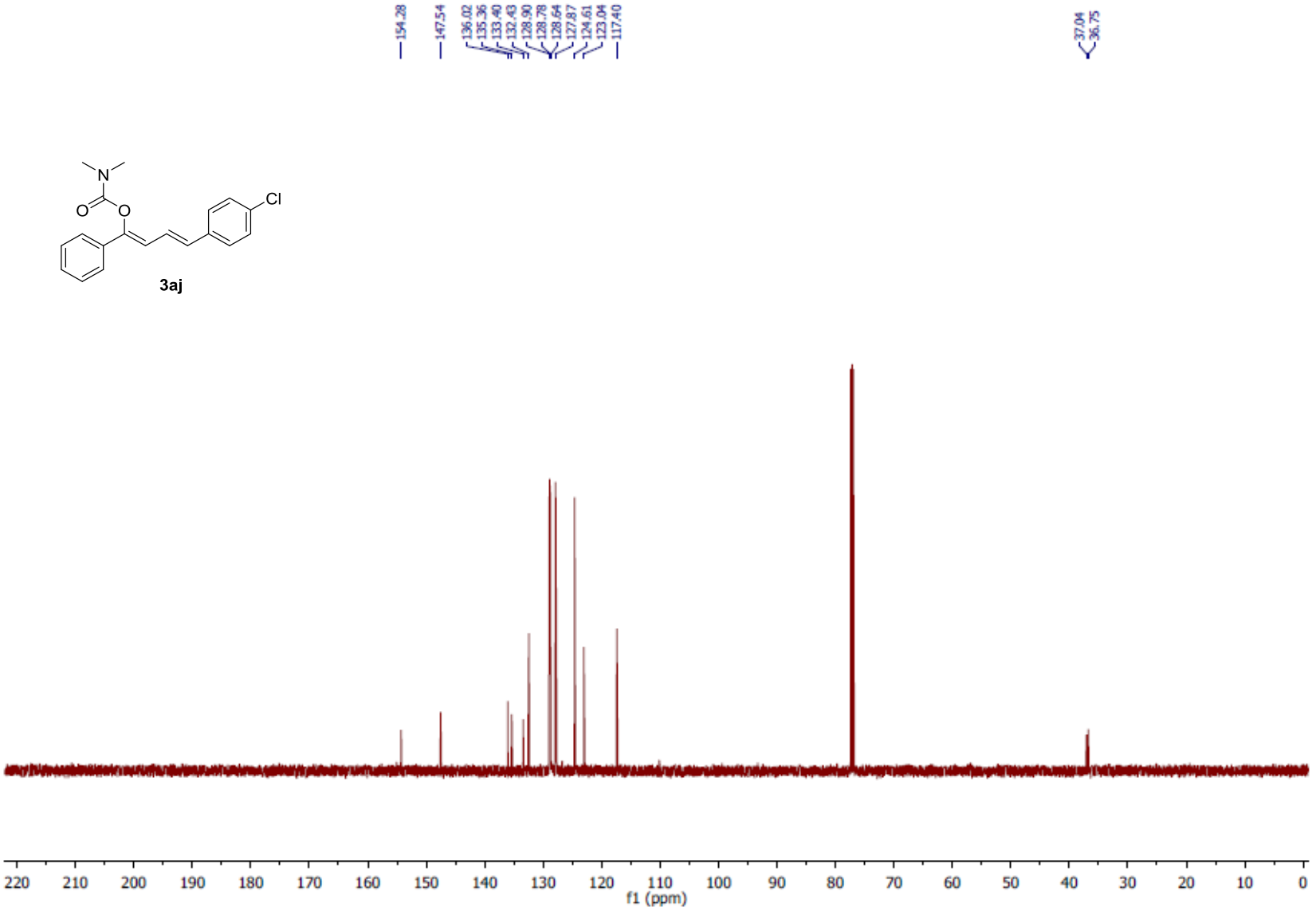
4.00
2.91
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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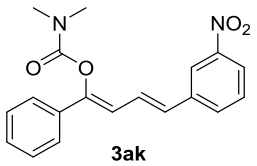
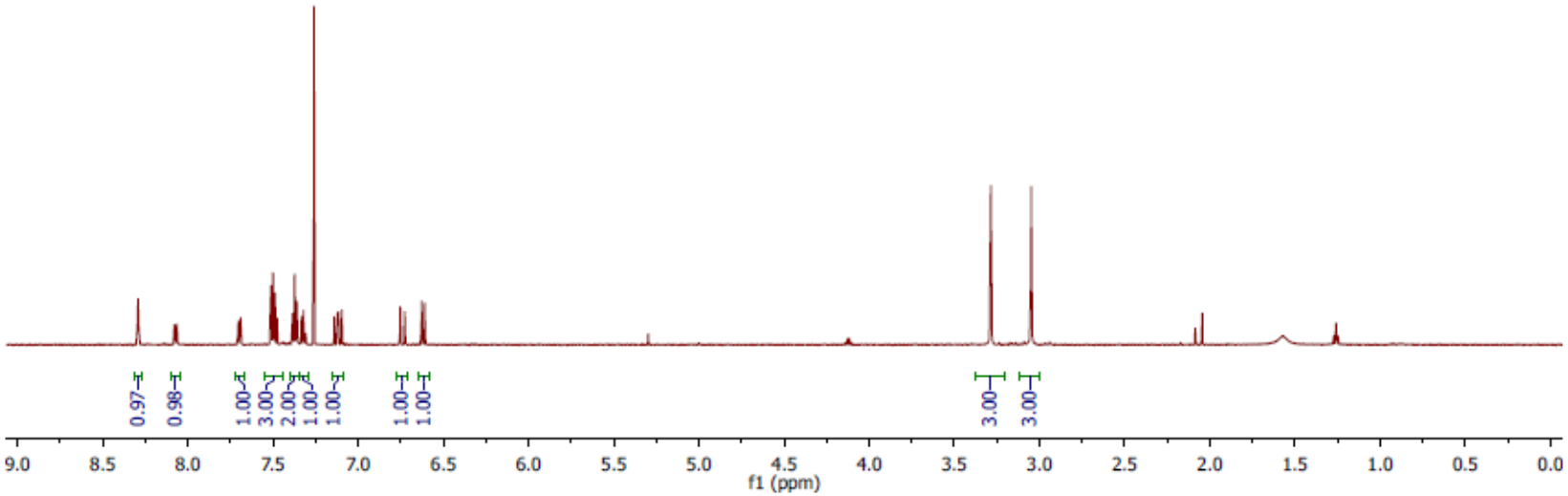
147.54
136.02
135.36
133.40
132.43
128.90
128.78
128.64
127.87
124.61
123.04
117.40
37.04
36.75
N
O
O
Cl
3aj
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
O
NO2

3ak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0.98
1.00
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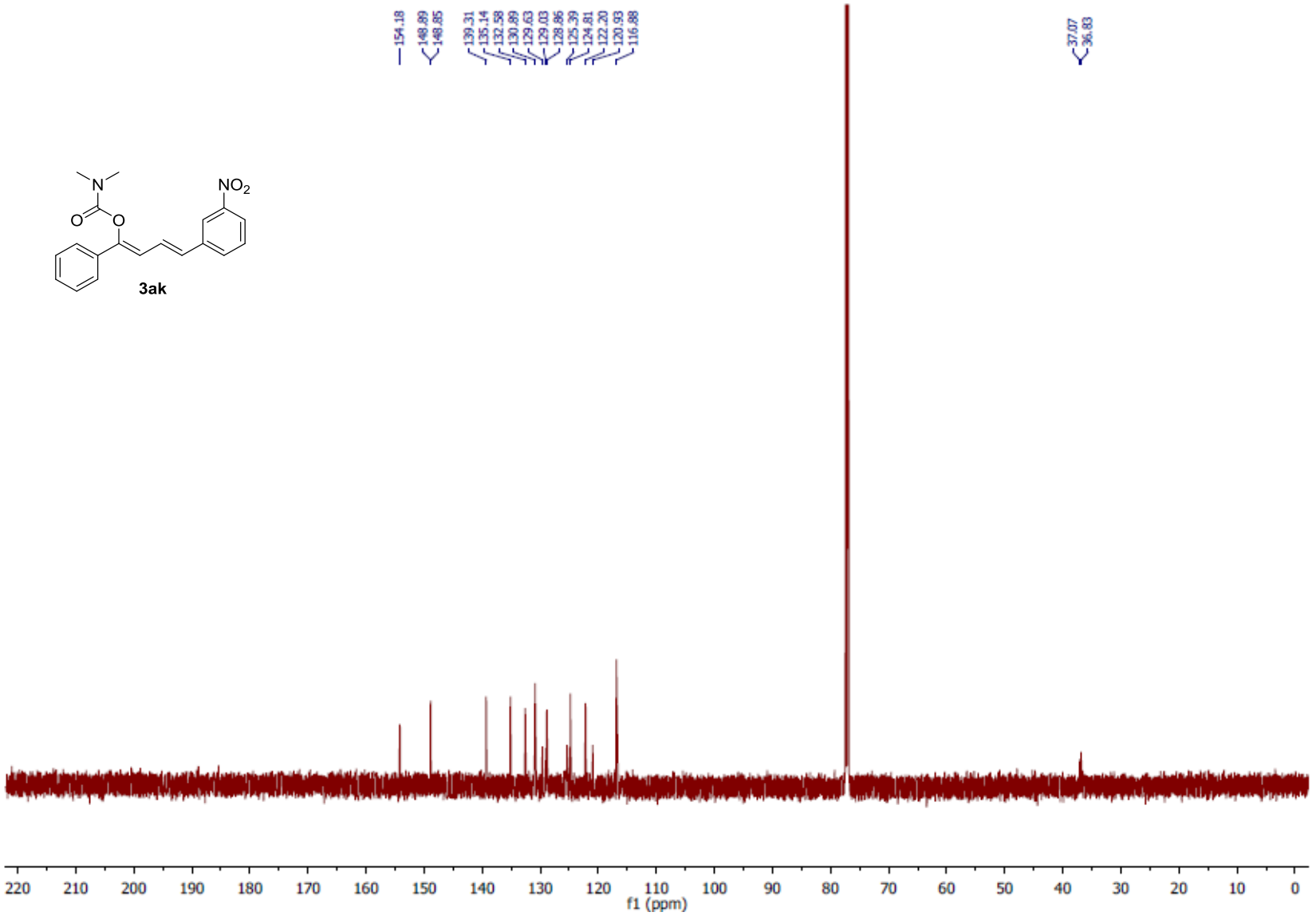
1.00
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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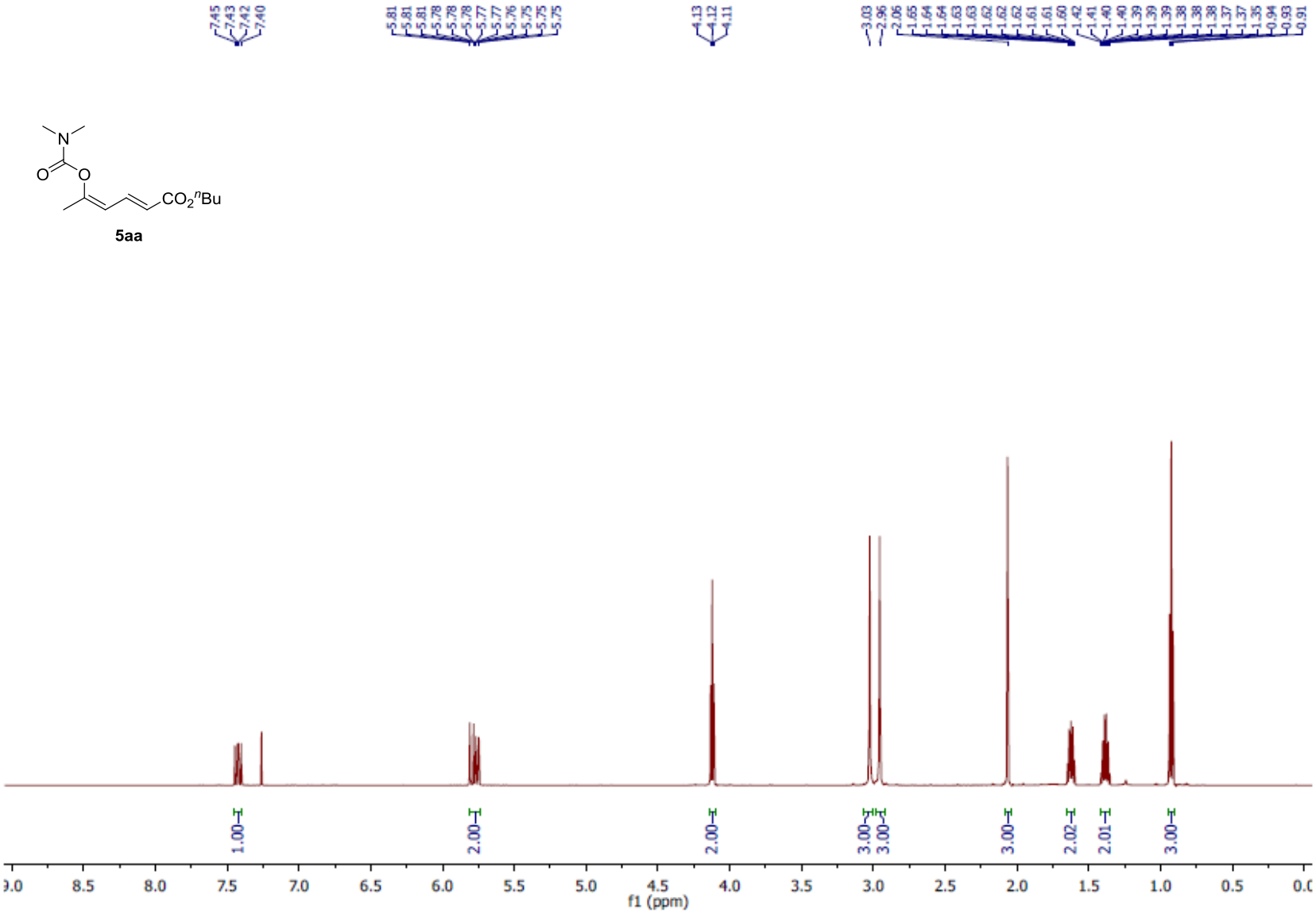
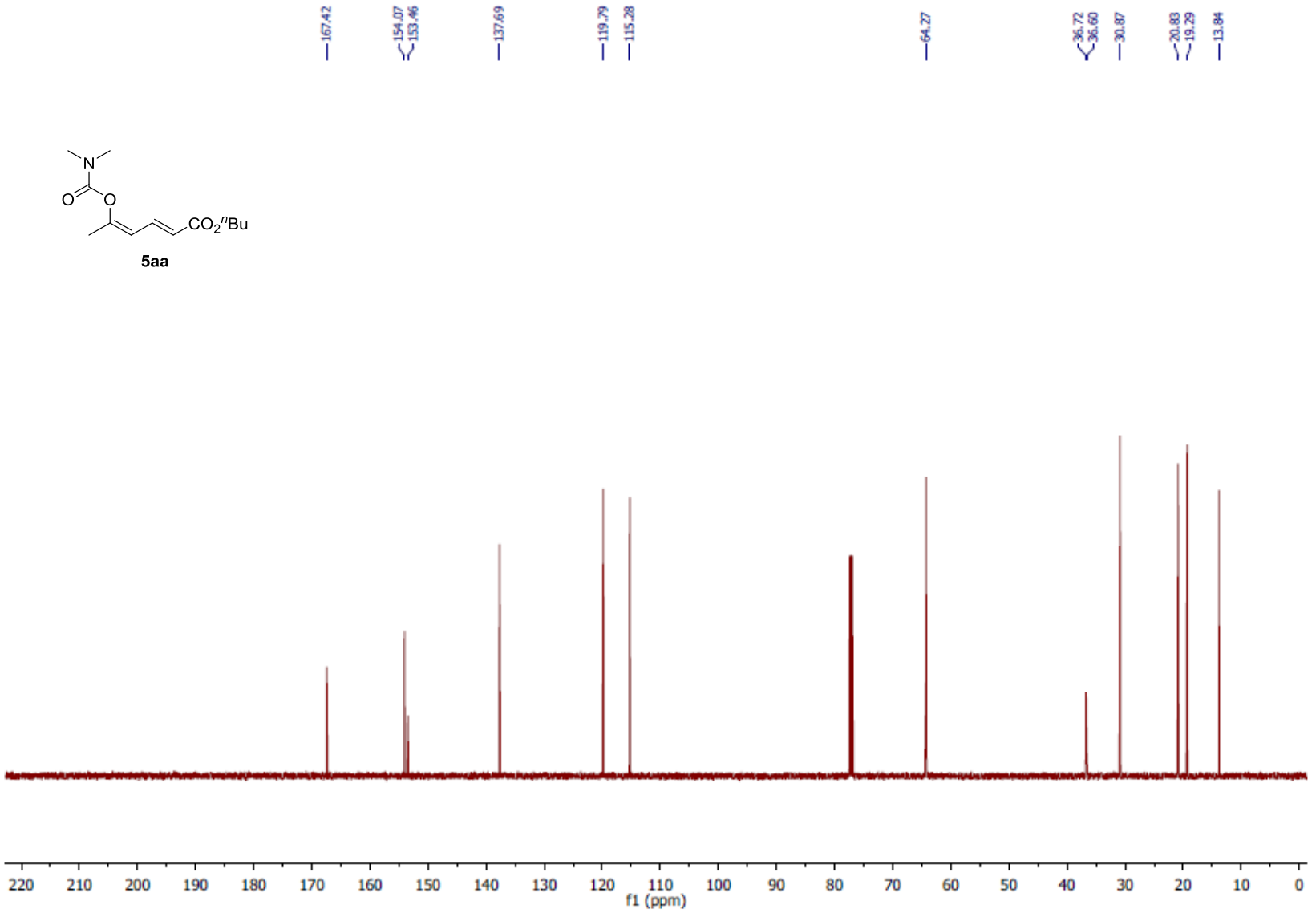
148.89
148.85
139.31
135.14
132.58
130.89
129.63
129.03
128.86
125.39
124.81
122.20
120.93
116.88
37.07
36.83
N
O
O
NO2
3ak
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.45
7.43
7.42
7.40
5.81
5.81
5.81
5.78
5.78
5.78
5.77
5.77
5.76
5.75
5.75
5.75
4.13
4.12
4.11
3.03
2.96
2.06
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.62
1.61
1.61
1.60
1.42
1.41
1.40
1.40
1.39
1.39
1.39
1.38
1.38
1.38
1.37
1.37
1.35
0.94
0.93
0.91
N
O
O
CO2nBu
5aa
1.00
2.00
2.00
3.00
3.00
3.00
2.02
2.01
3.00
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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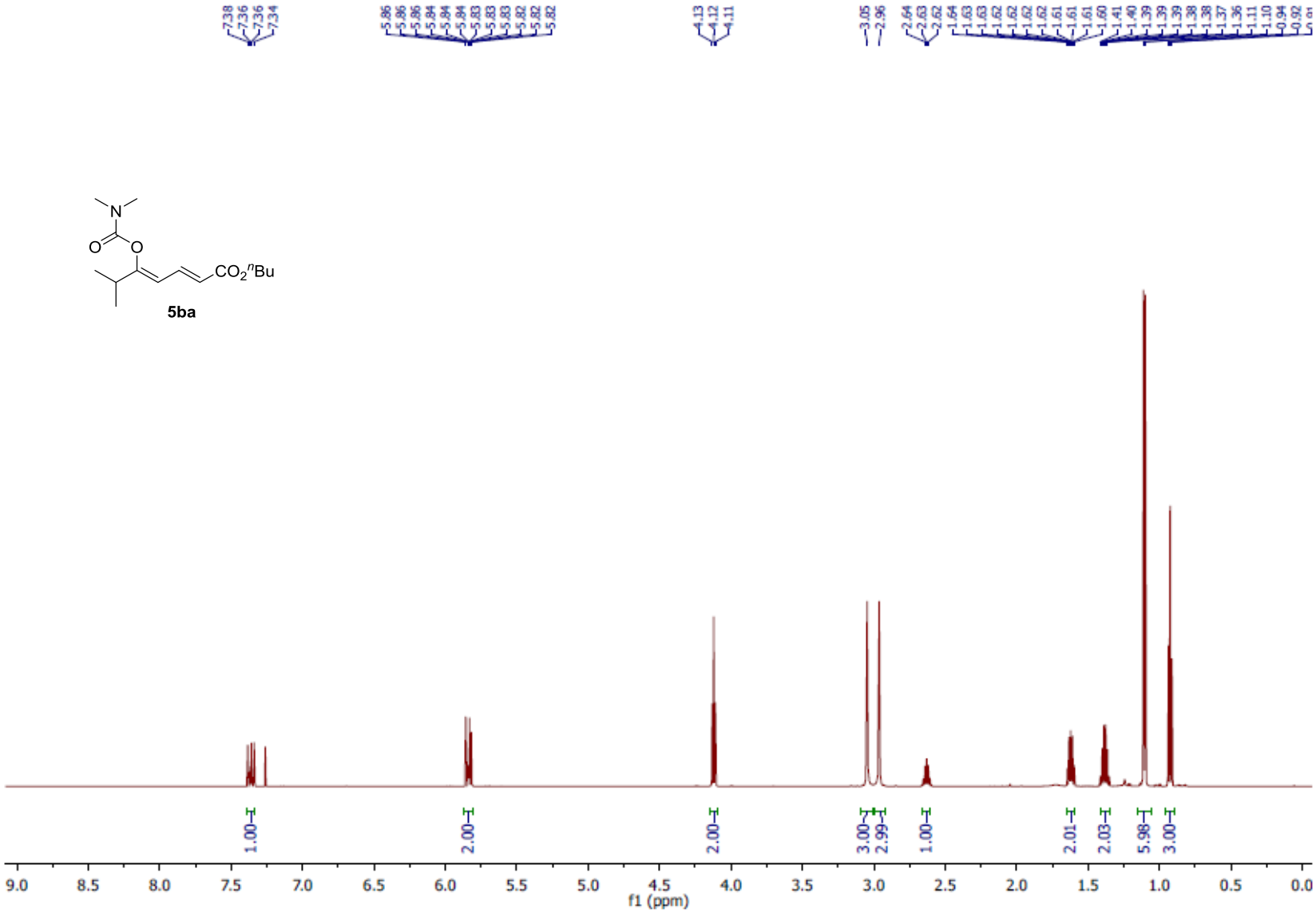
154.07
153.46
137.69
119.79
115.28
64.27
36.72
36.60
30.87
20.83
19.29
13.84
N
O
O
CO2nBu
5aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.36
7.36
7.34
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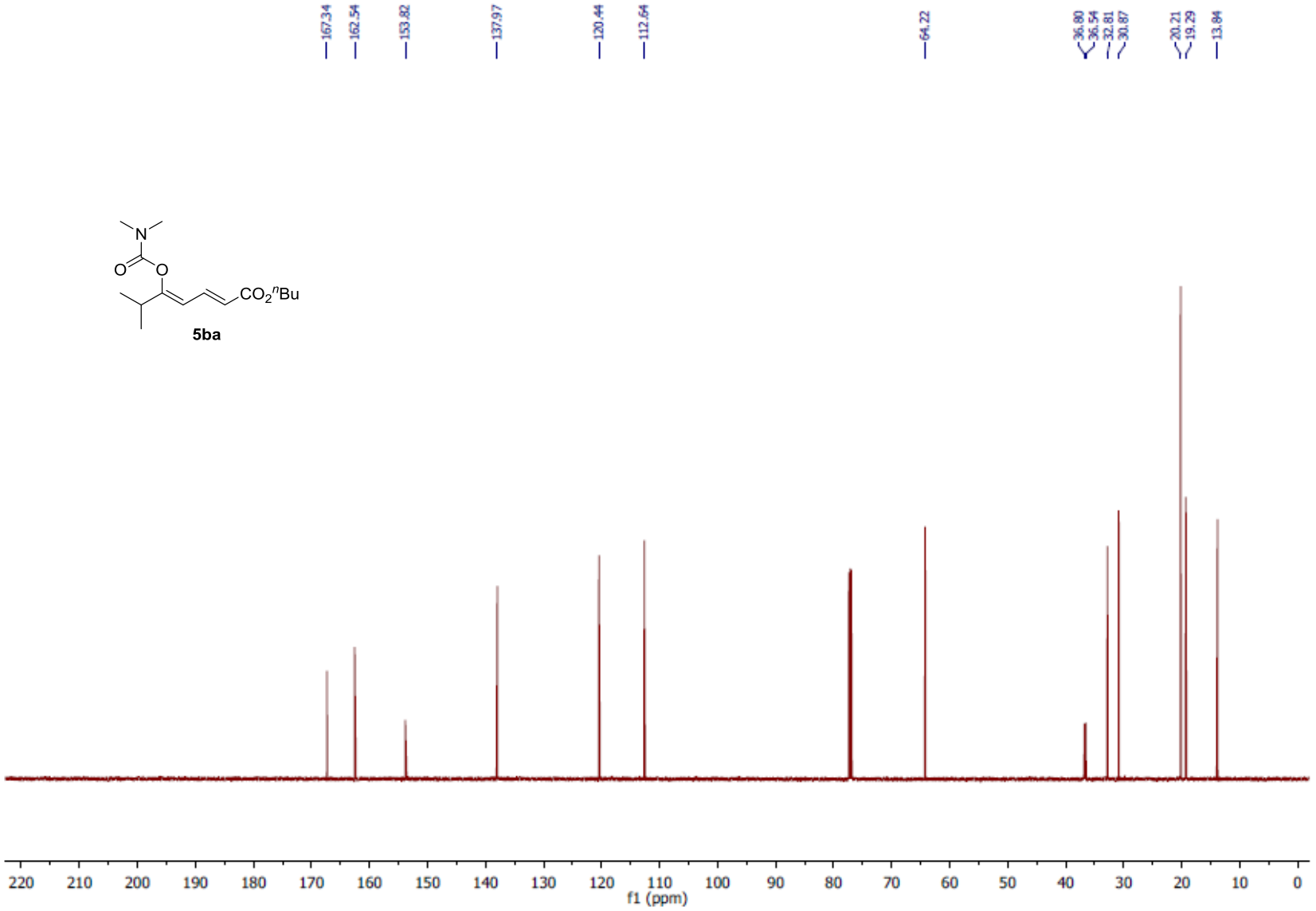
5.86
5.86
5.84
5.84
5.84
5.83
5.83
5.83
5.82
5.82
5.82
4.13
4.12
4.11
3.05
2.96
2.64
2.63
2.62
1.64
1.63
1.63
1.62
1.62
1.62
1.62
1.61
1.61
1.61
1.60
1.41
1.40
1.39
1.39
1.39
1.38
1.38
1.37
1.36
1.11
1.10
0.94
0.92
N
O
O
CO2nBu
5ba
1.00
2.00
2.00
3.00
2.99
1.00
2.01
2.03
5.98
3.00
9.0
8.5
8.0
7.5
7.0
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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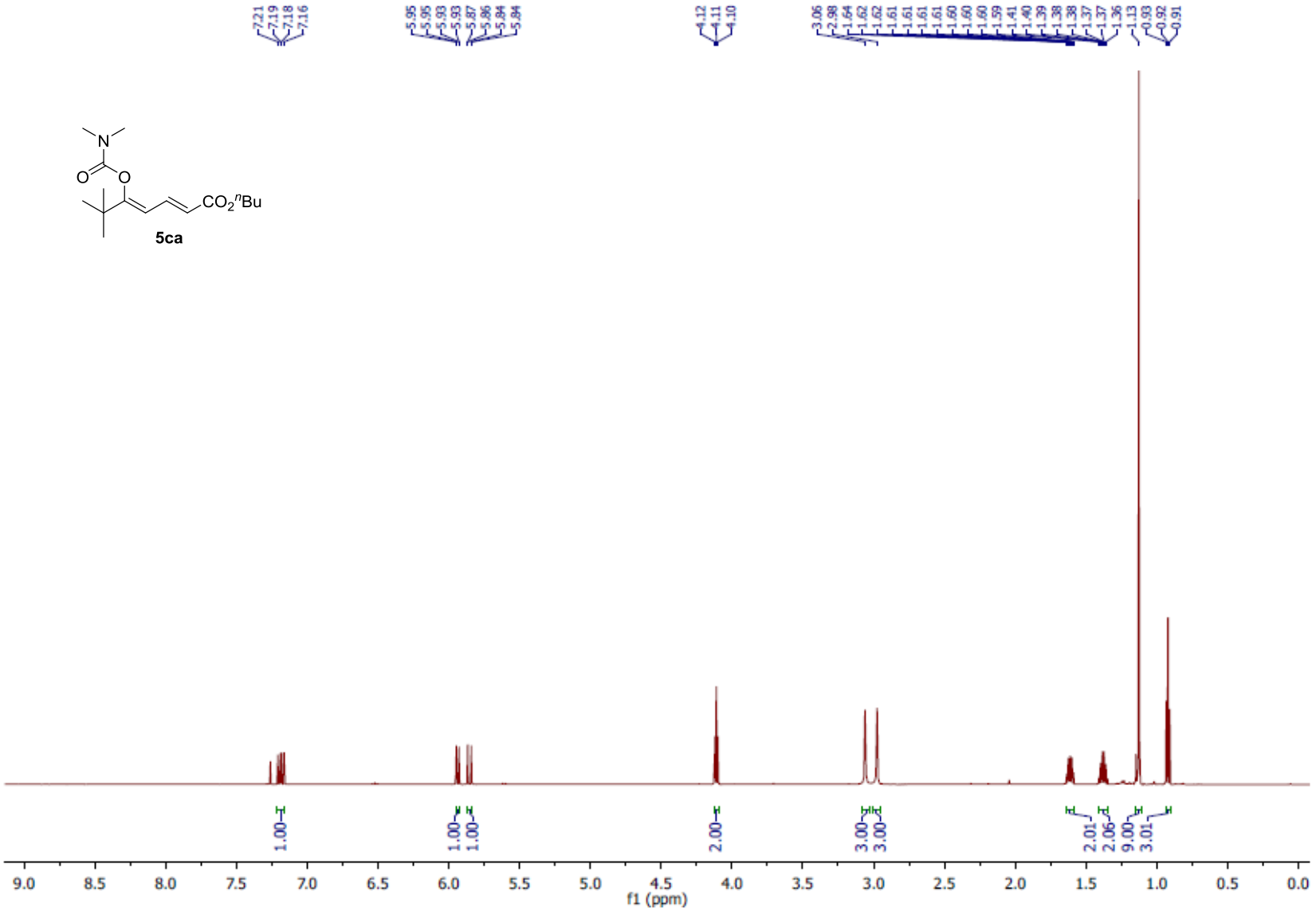
162.54
153.82
137.97
120.44
112.64
64.22
36.80
36.54
32.81
30.87
20.21
19.29
13.84
N
O
O
CO2nBu
5ba
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.19
7.18
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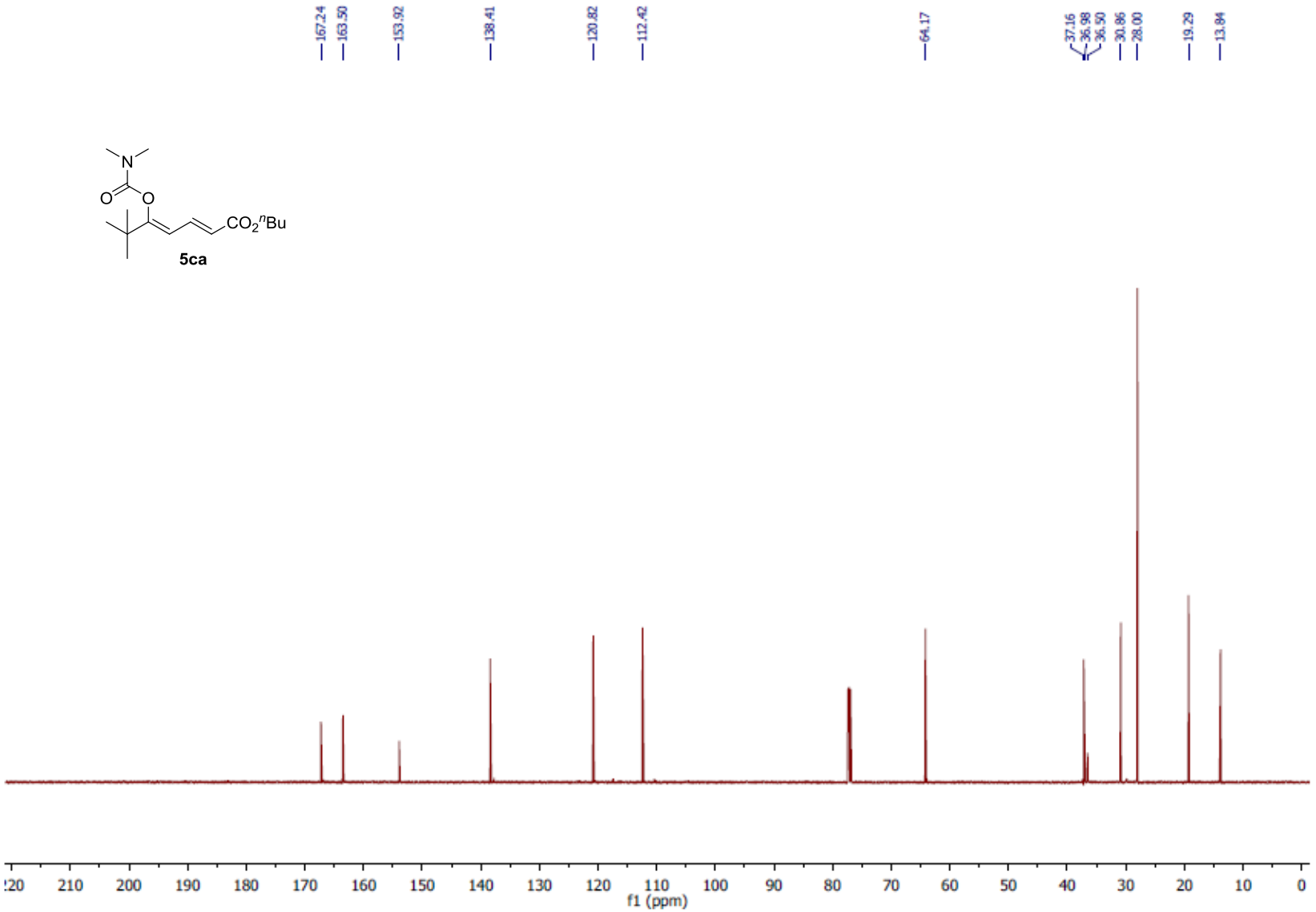
5.95
5.93
5.93
5.87
5.86
5.84
5.84
4.12
4.11
4.10
3.06
2.98
1.64
1.62
1.62
1.61
1.61
1.61
1.61
1.60
1.60
1.60
1.59
1.41
1.40
1.39
1.38
1.38
1.37
1.37
1.36
1.13
0.93
0.92
0.91
N
O
O
CO2nBu
5ca
1.00
1.00
1.00
2.00
3.00
3.00
2.01
2.06
9.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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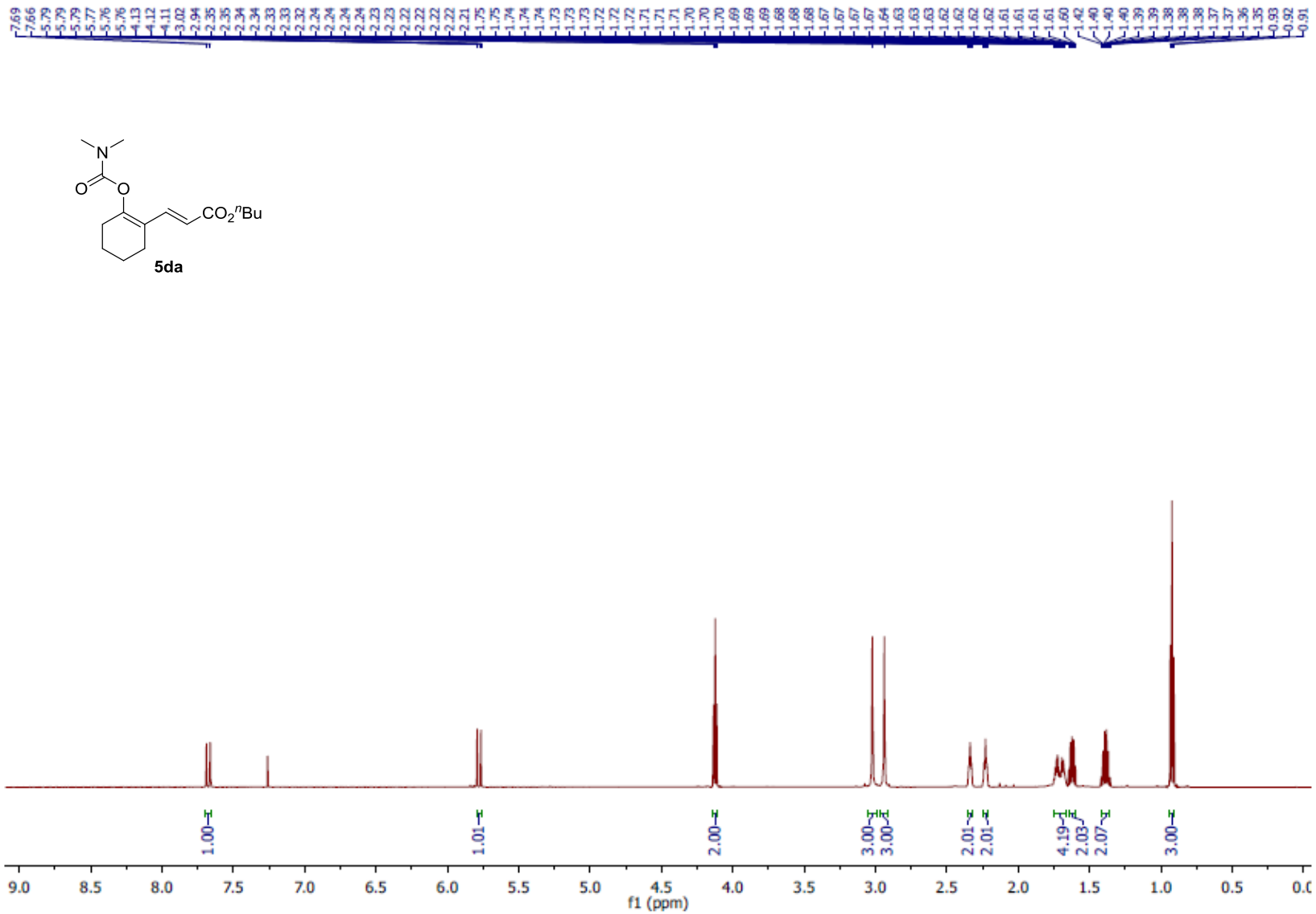
153.92
138.41
120.82
112.42
64.17
37.16
36.98
36.50
30.86
28.00
19.29
13.84
N
O
O
CO2nBu
5ca
f1 (ppm)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5.79
5.77
5.76
5.76
4.13
4.12
4.11
3.02
2.94
2.35
2.35
2.34
2.34
2.33
2.33
2.32
2.24
2.24
2.24
2.24
2.23
2.23
2.22
2.22
2.22
2.22
2.21
1.75
1.75
1.74
1.74
1.74
1.73
1.73
1.73
1.72
1.72
1.72
1.71
1.71
1.71
1.70
1.70
1.70
1.69
1.69
1.69
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1.67
1.67
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1.62
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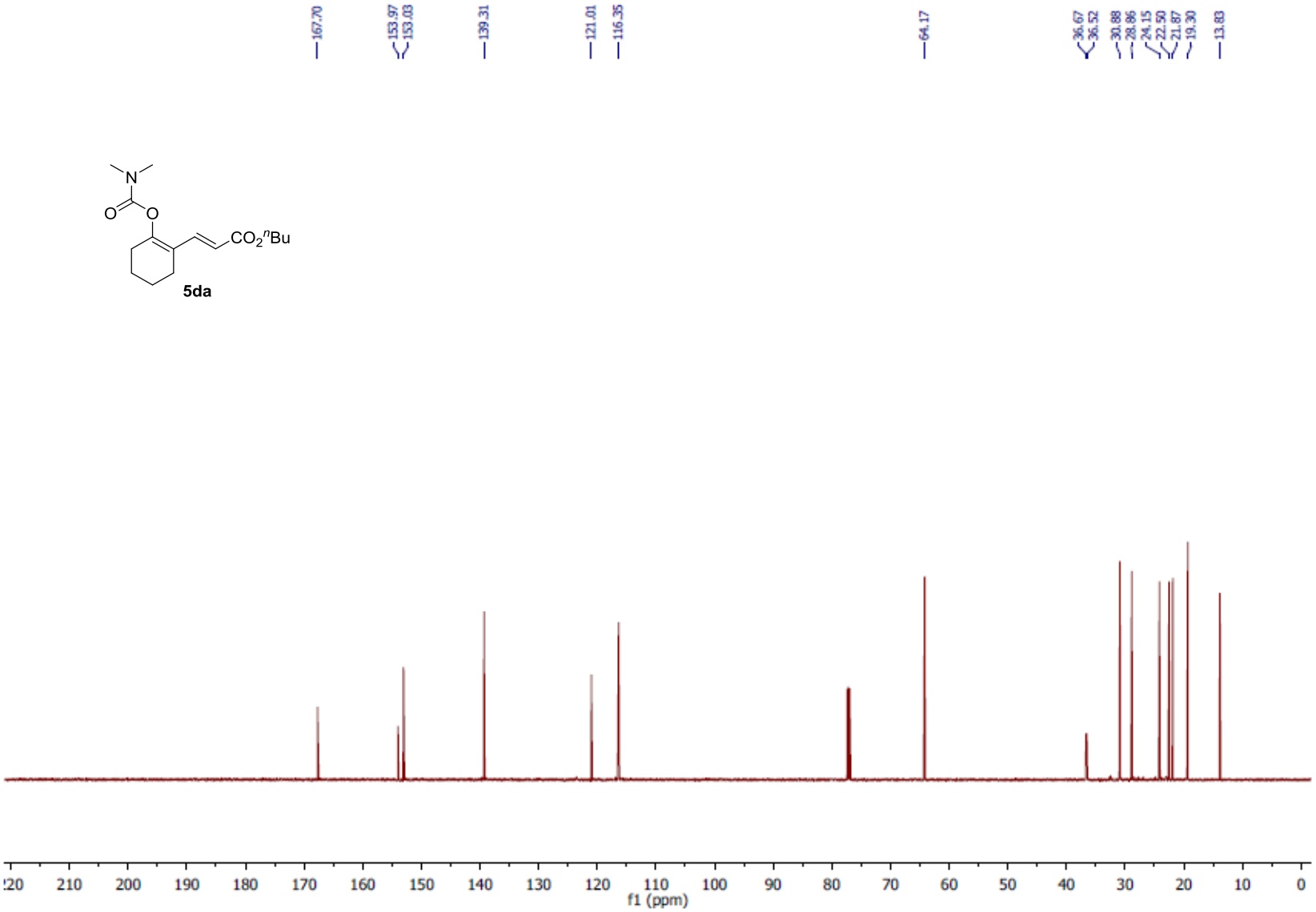
1.61
1.61
1.61
1.60
1.42
1.40
1.40
1.40
1.39
1.39
1.38
1.38
1.38
1.37
1.37
1.36
1.35
0.93
0.92
0.91
N
O
O
CO2nBu
5da
1.00
1.01
2.00
3.00
3.00
2.01
2.01
4.19
2.03
2.07
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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153.03
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121.01
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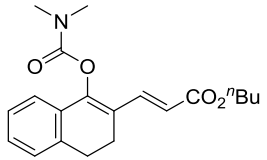
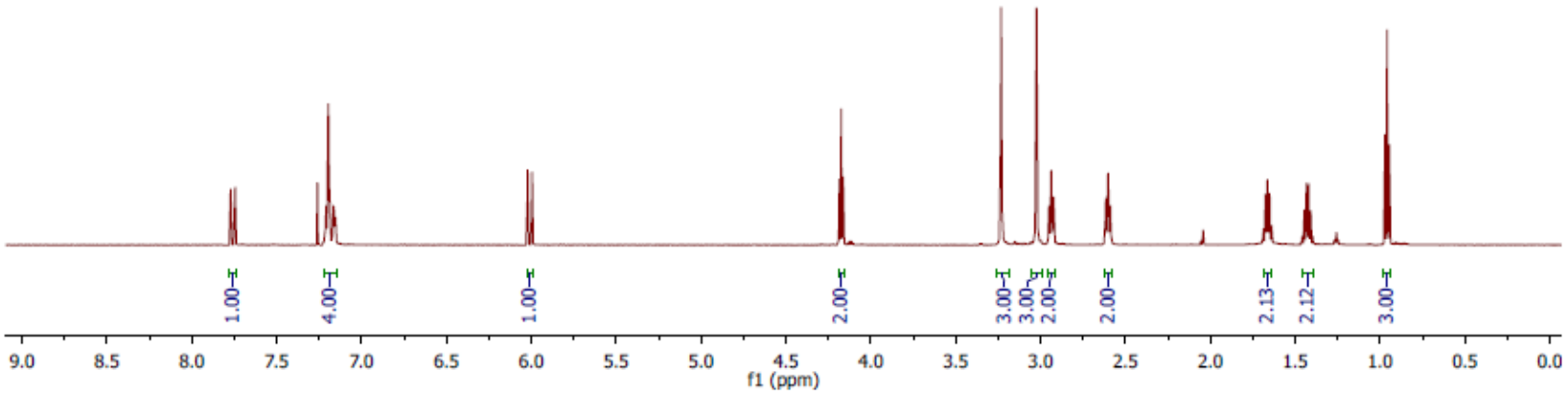
36.67
36.52
30.88
28.86
24.15
22.50
21.87
19.30
13.83
N
O
O
CO2nBu
5da
f1 (ppm)


7.77
7.75
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.15
6.02
6.00
4.19
4.17
4.16
3.23
3.02
2.95
2.94
2.92
2.62
2.60
2.59
1.69
1.68
1.66
1.65
1.64
1.46
1.45
1.43
1.42
1.41
1.40
0.97
0.96
0.95


N
O
O
CO2nBu

5ea


1.00
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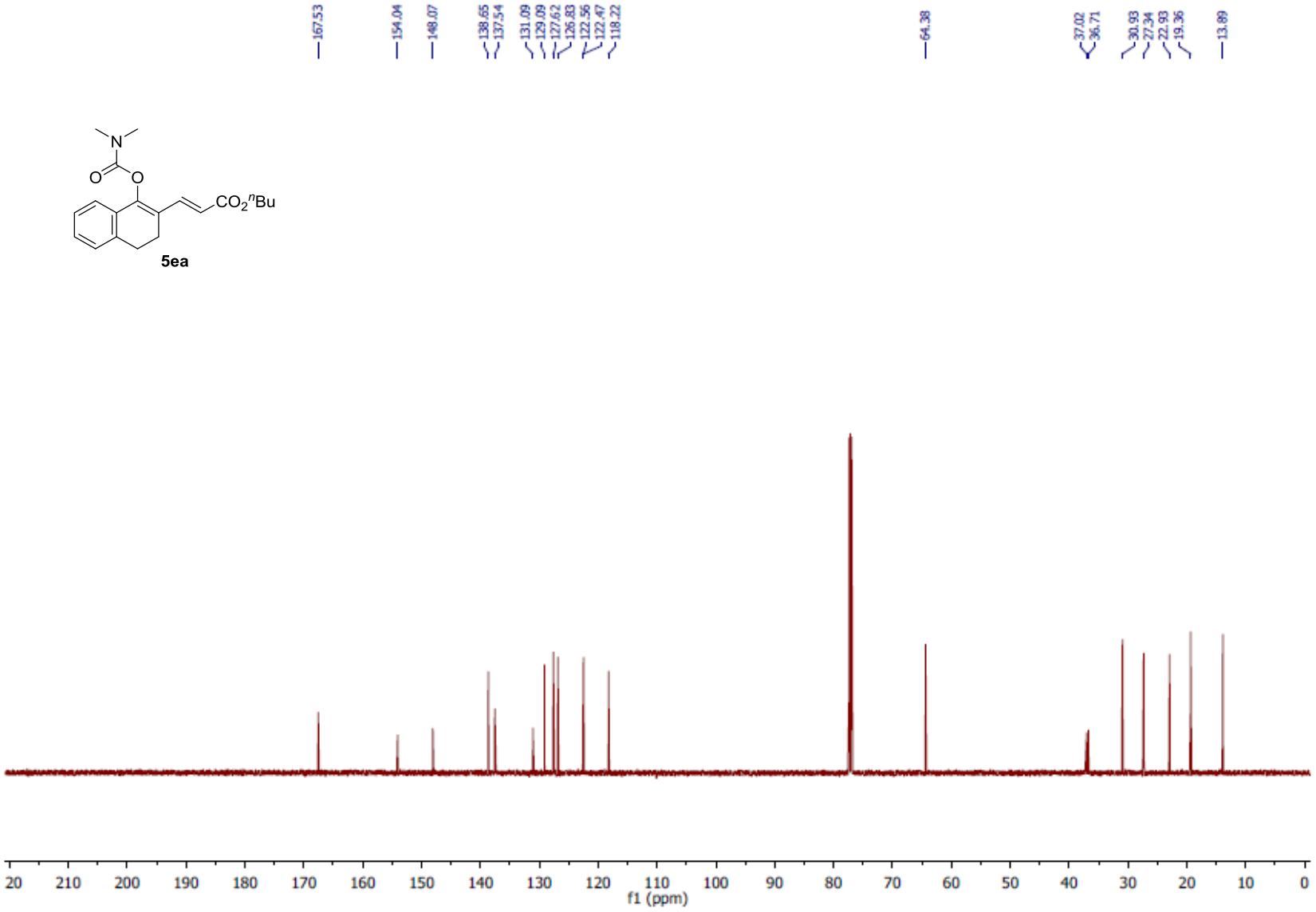
2.00
3.00
3.00
2.00
2.00
2.13
2.12
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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154.04
148.07
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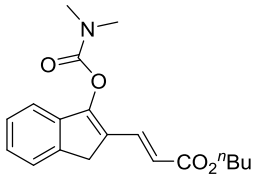
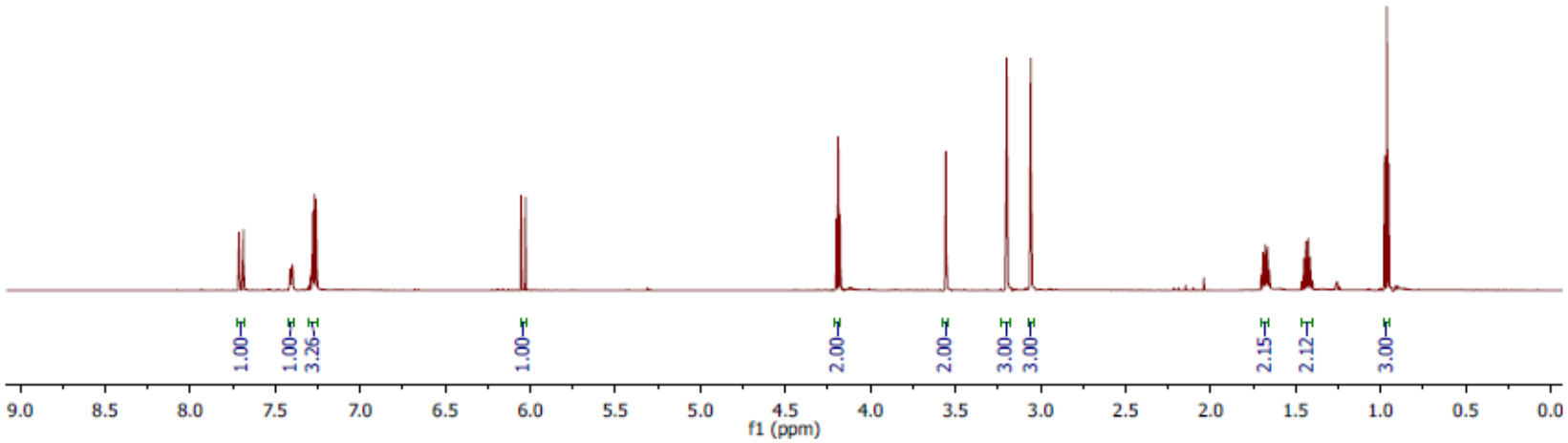
137.54
131.09
129.09
127.62
126.83
122.56
122.47
118.22
64.38
37.02
36.71
30.93
27.34
22.93
19.36
13.89
N
O
O
CO2nBu
5ea
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
O
CO2nBu

5fa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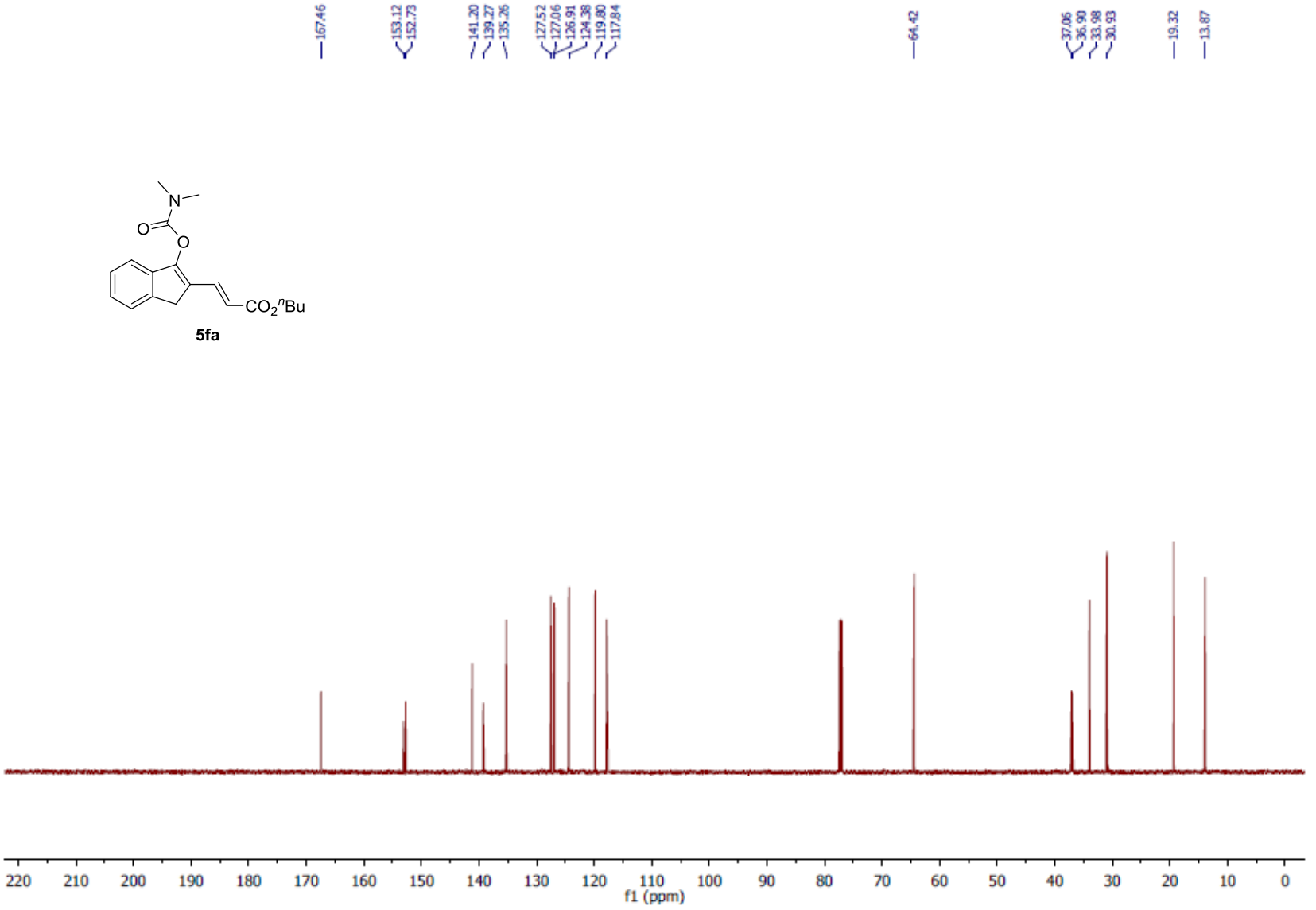
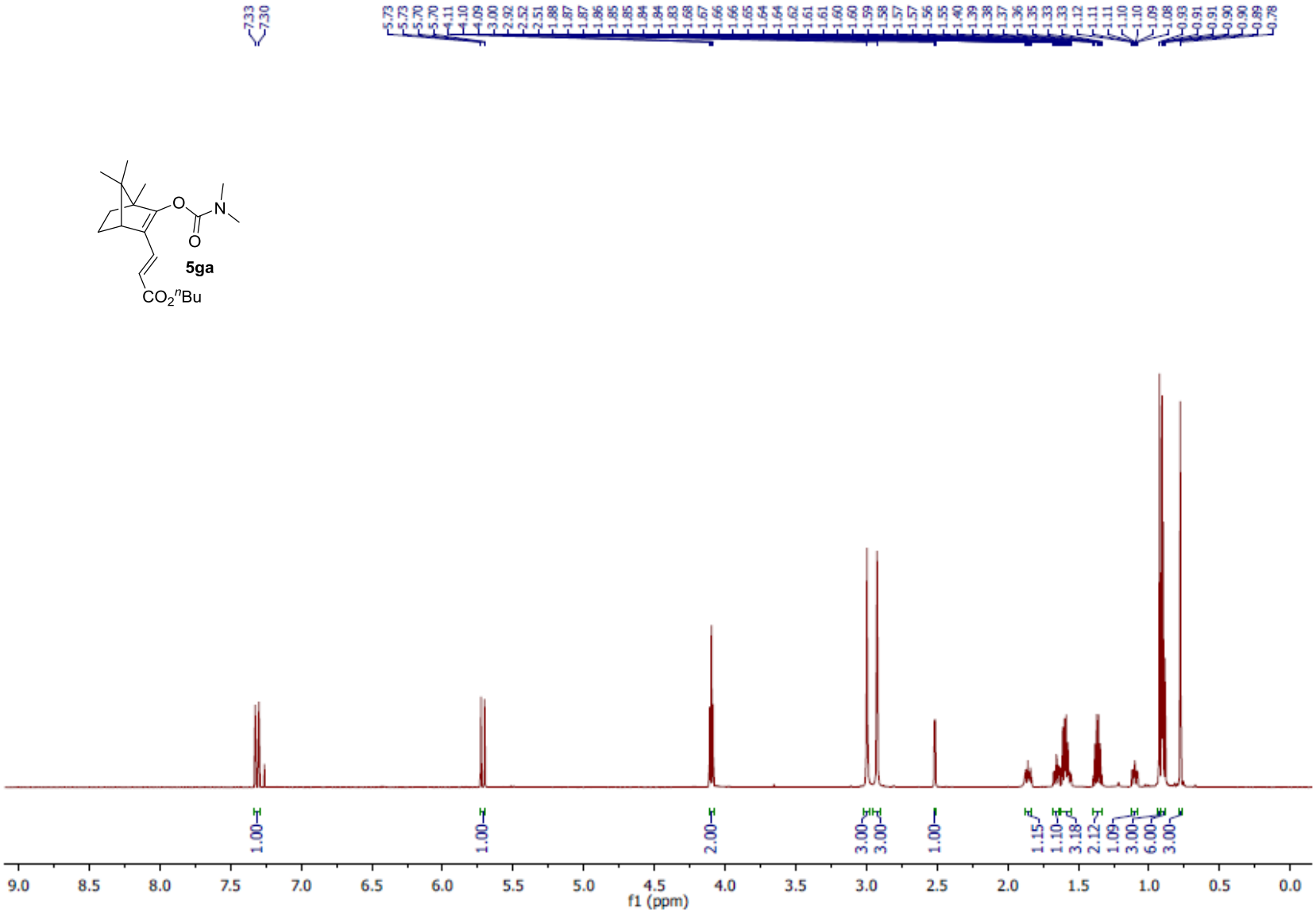
1.00
3.26
1.00
2.00
2.00
3.00
3.00
2.15
2.12
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.46
153.12
152.73
141.20
139.27
135.26
127.52
127.06
126.91
124.38
119.80
117.84
64.42
37.06
36.90
33.98
30.93
19.32
13.87
O
O
N
CO2nBu
5fa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.33
7.30
5.73
5.73
5.70
5.70
4.11
4.10
4.09
3.00
2.92
2.52
2.51
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.68
1.67
1.66
1.66
1.65
1.64
1.64
1.62
1.61
1.61
1.60
1.60
1.59
1.58
1.57
1.57
1.56
1.55
1.40
1.39
1.38
1.37
1.36
1.35
1.33
1.33
1.12
1.11
1.11
1.10
1.10
1.09
1.08
0.93
0.91
0.91
0.90
0.90
0.89
0.78
O
N
O
5ga
CO2nBu
1.00
1.00
2.00
3.00
3.00
1.00
1.15
1.10
3.18
2.12
1.09
3.00
6.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.0
2.5
2.0
1.5
1.0
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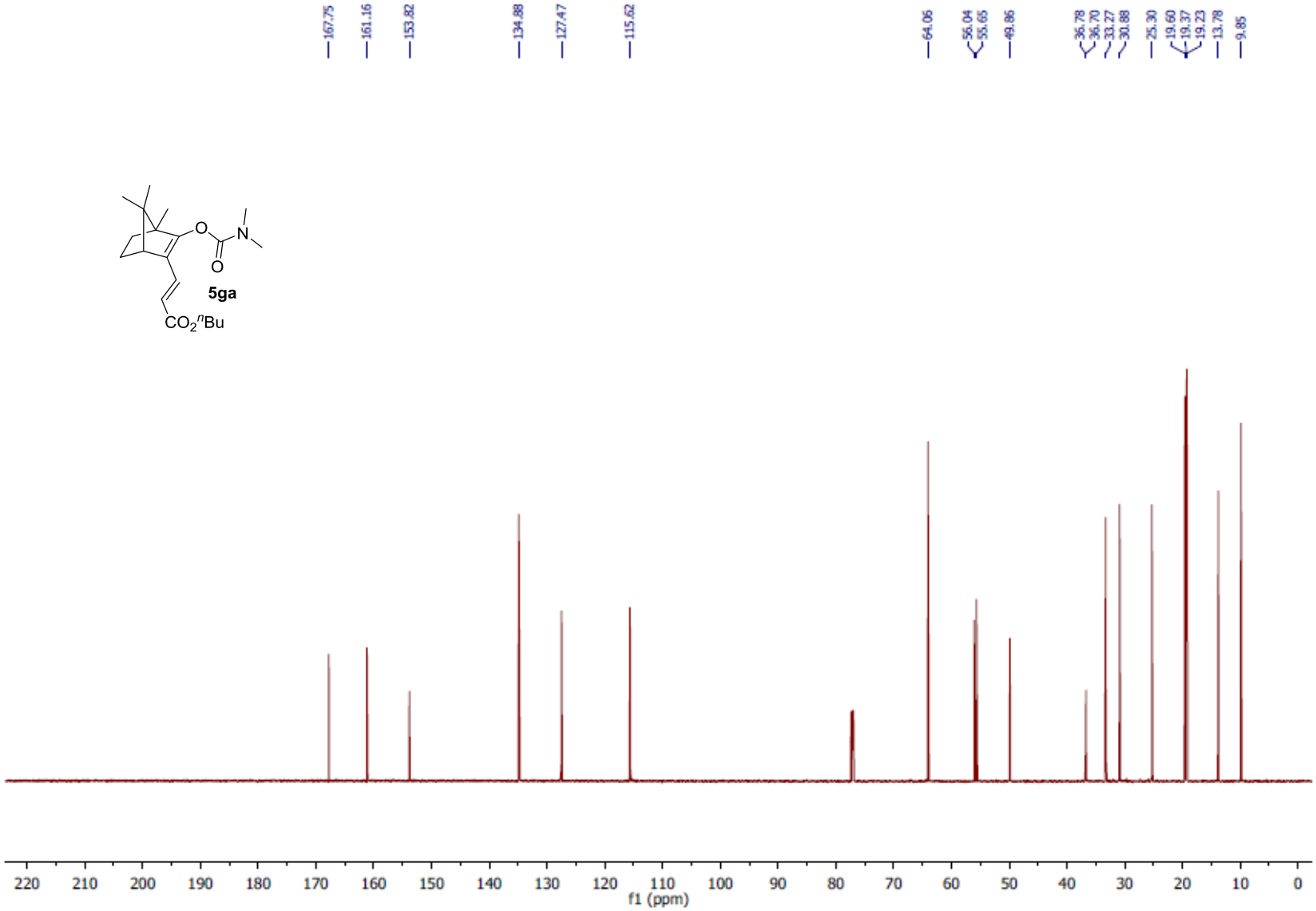
0.0
f1 (ppm)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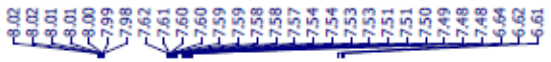
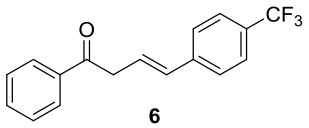
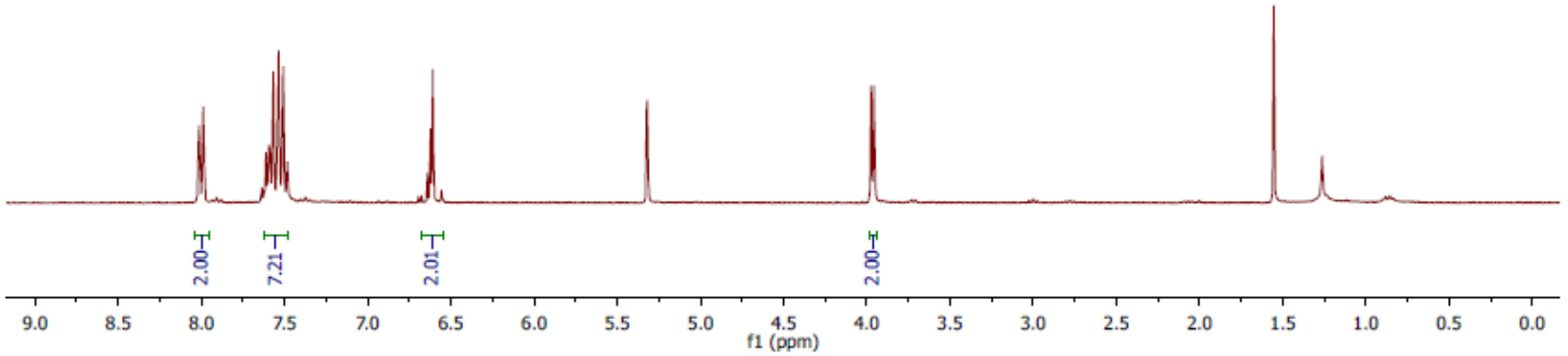
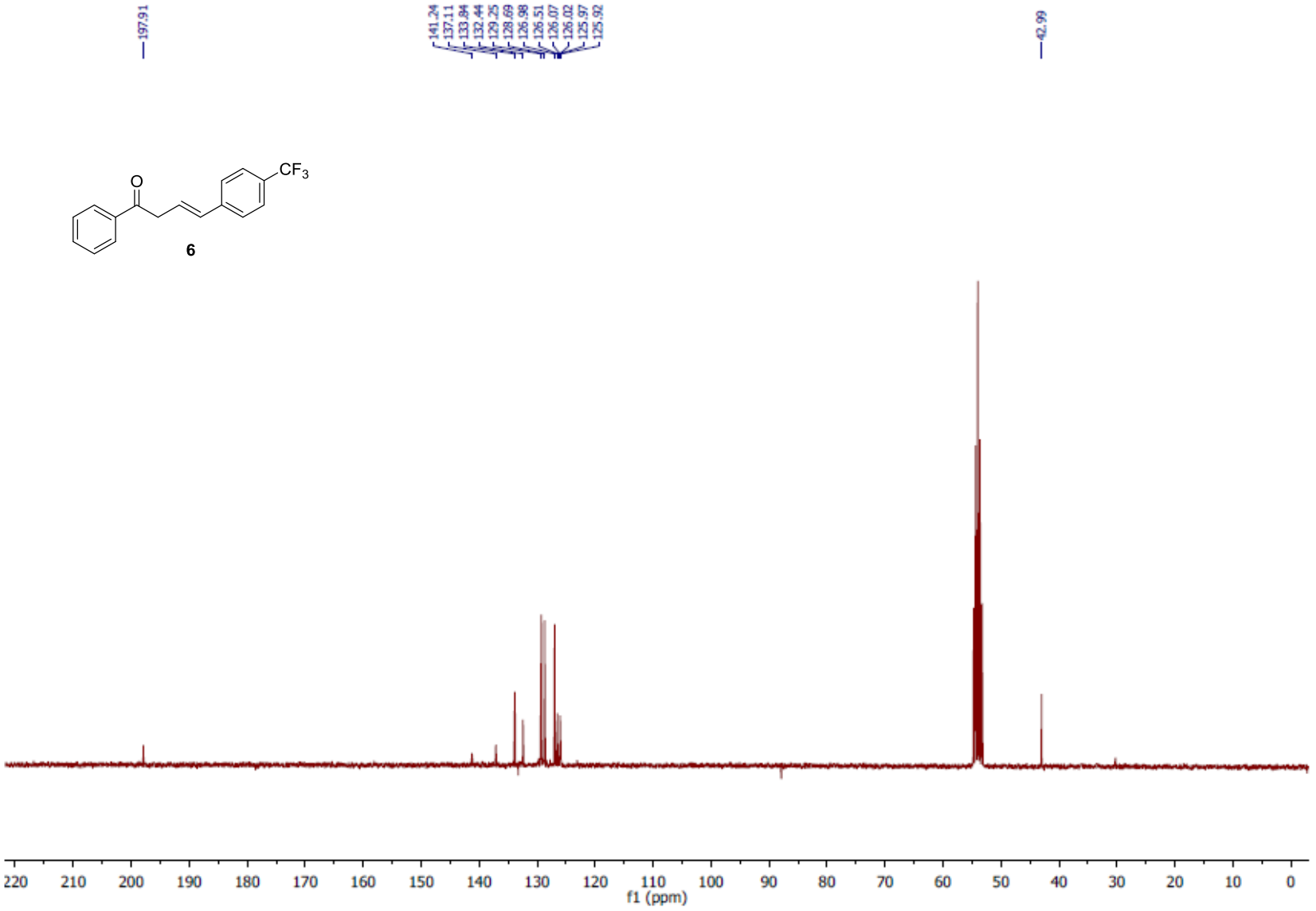
153.82
134.88
127.47
115.62
64.06
56.04
55.65
49.86
36.78
36.70
33.27
30.88
25.30
19.60
19.37
19.23
13.78
9.85
O
N
O
5ga
CO2nBu
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

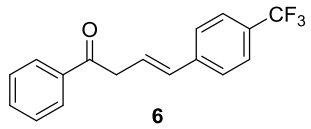

8.02
8.02
8.01
8.01
8.00
7.99
7.98
7.62
7.61
7.60
7.60
7.59
7.59
7.58
7.58
7.57
7.54
7.54
7.53
7.53
7.51
7.51
7.50
7.49
7.48
7.48
6.64
6.62
6.61
3.97
3.96


O
CF3

6


2.00
7.21
2.01
2.00
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)

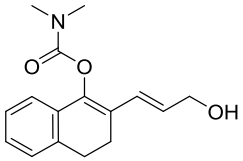

197.91
141.24
137.11
133.84
132.44
129.25
128.69
126.98
126.51
126.07
126.02
125.97
125.92
42.99
O
CF3
6
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
CF3

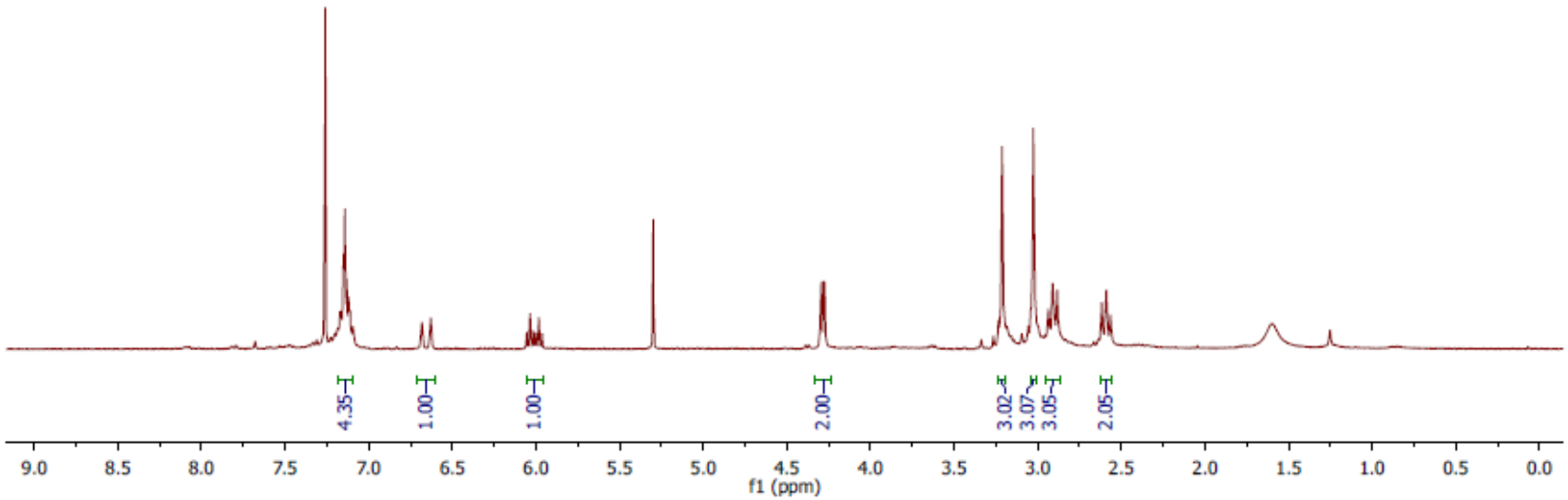
6

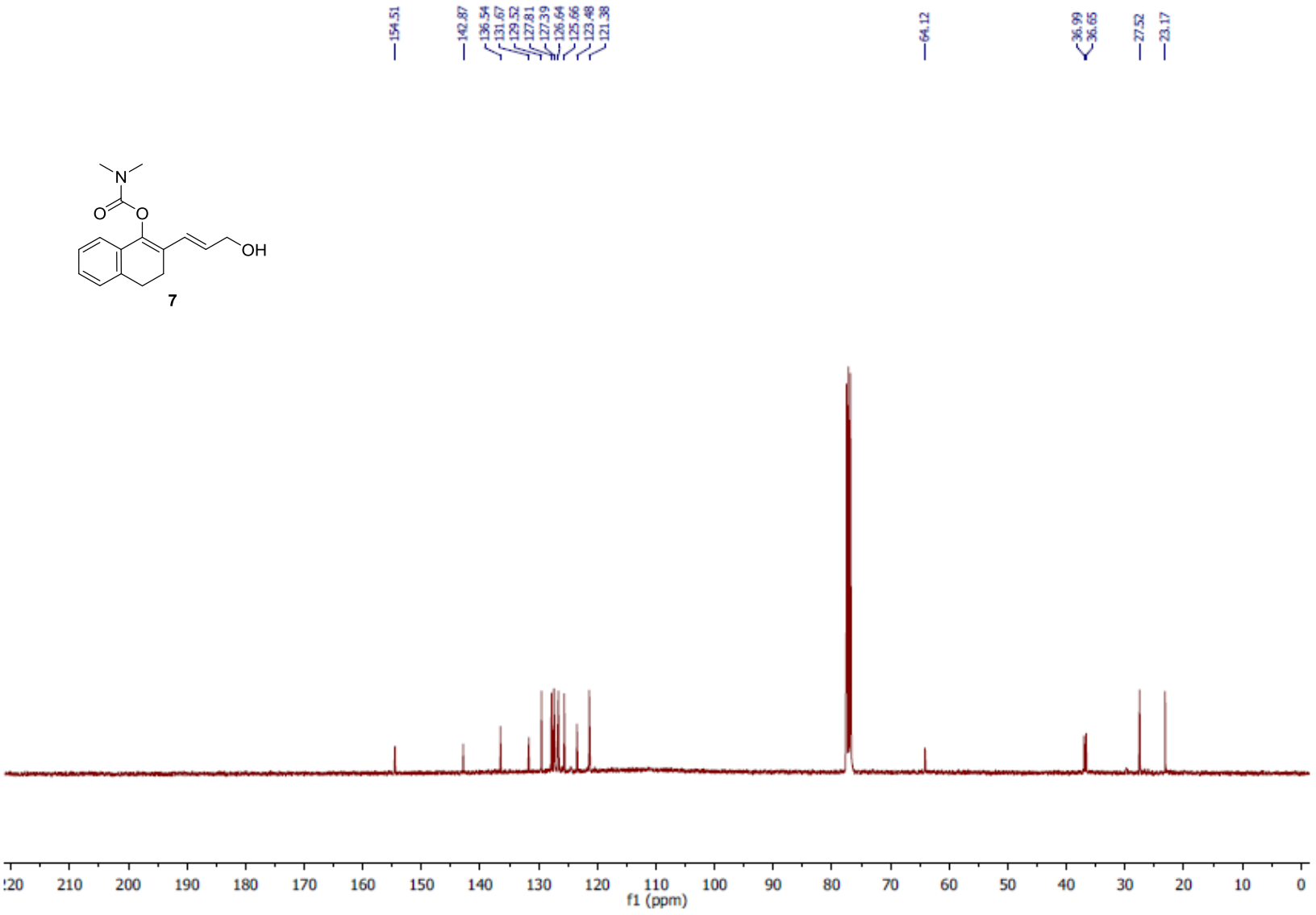
-62.83
0 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

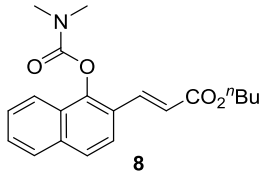

7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.10
7.09
7.09
6.68
6.63
6.06
6.04
6.02
6.00
5.98
5.96
4.30
4.29
4.28
4.27
3.21
3.03
2.94
2.91
2.88
2.62
2.59
2.56


N
O
O
OH

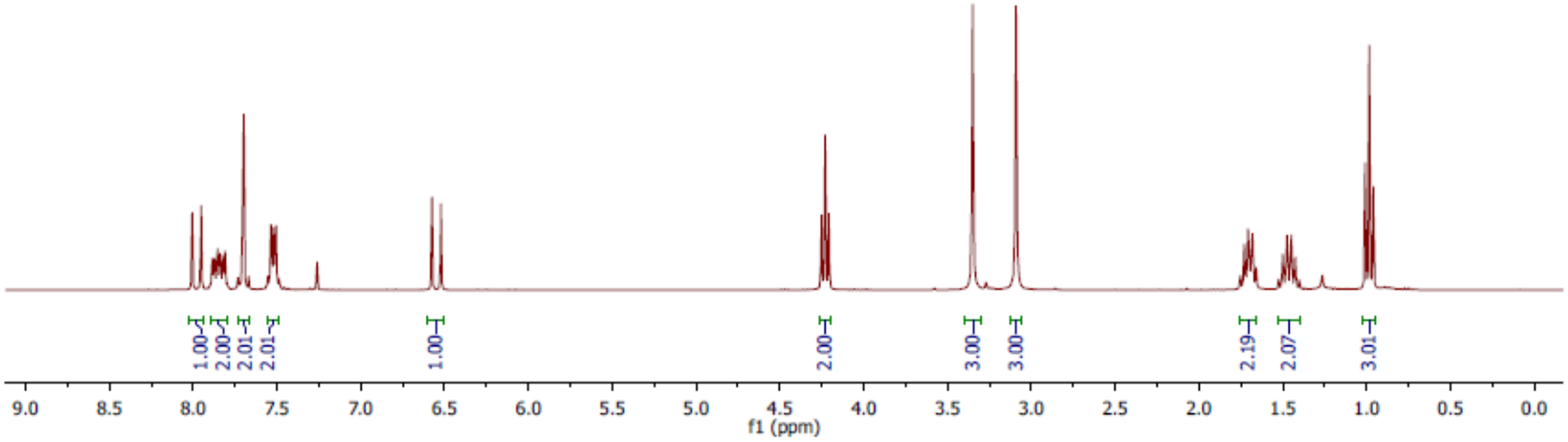
7

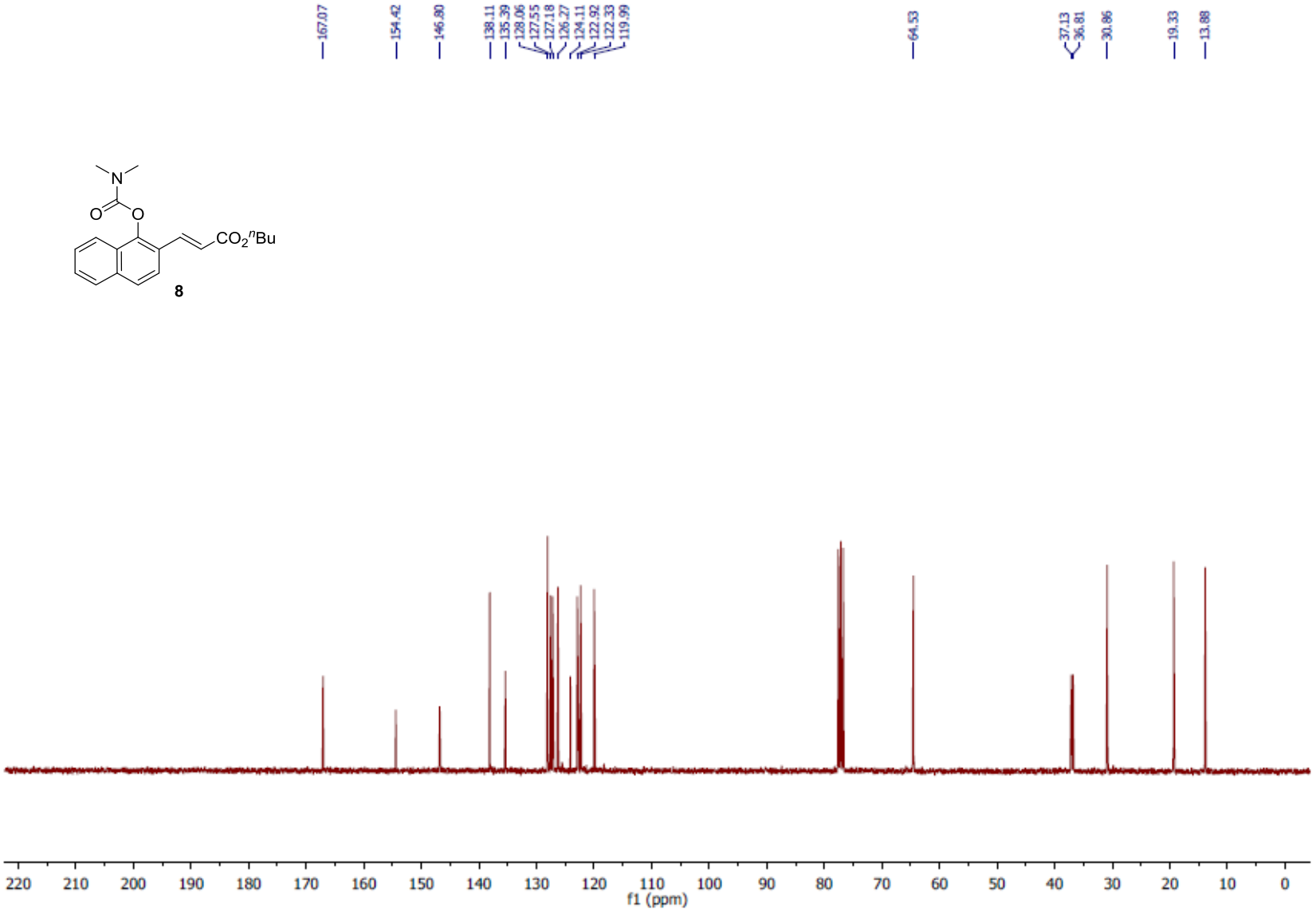

4.35
1.00
1.00
2.00
3.02
3.07
3.05
2.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

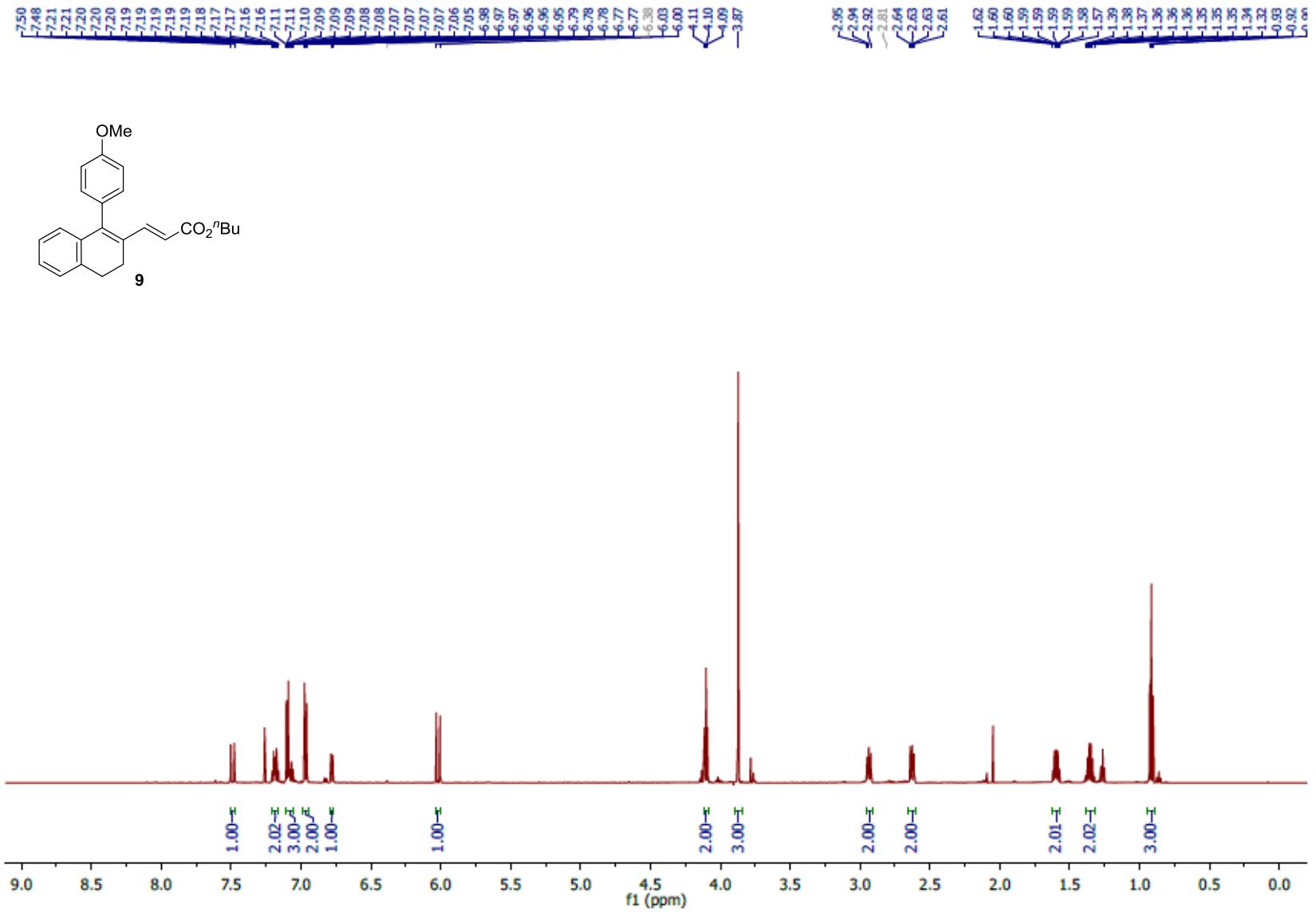

154.51
142.87
136.54
131.67
129.52
127.81
127.39
126.64
125.66
123.48
121.38
64.12
36.99
36.65
27.52
23.17
N
O
O
OH
7
f1 (ppm)

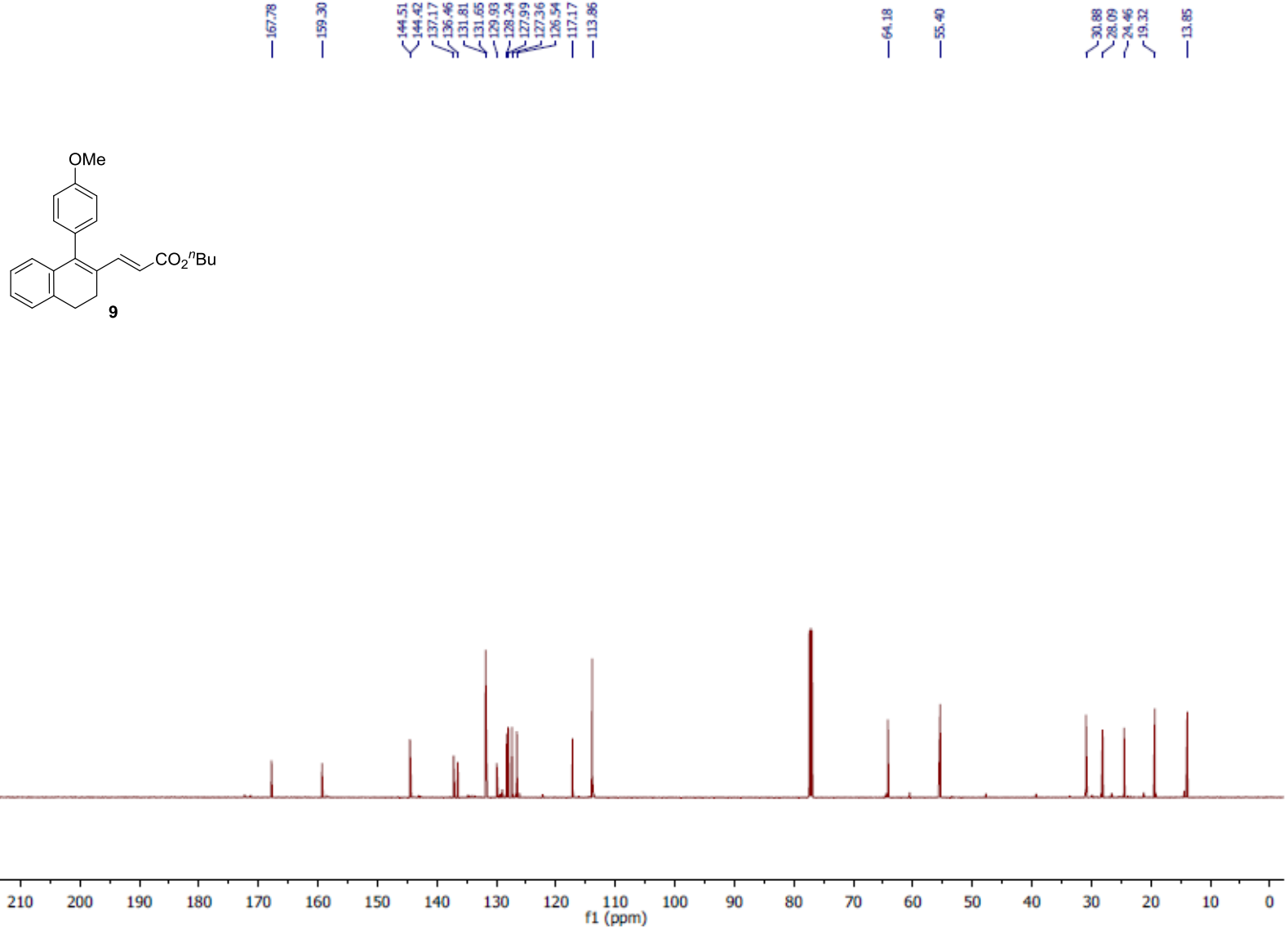

N
O
O
CO2nBu

8

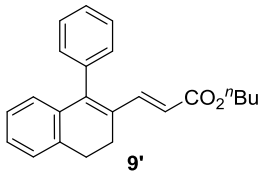

1.00
2.00
2.01
2.01
1.00
2.00
3.00
3.00
2.19
2.07
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.07
154.42
146.80
138.11
135.39
128.06
127.55
127.18
126.27
124.11
122.92
122.33
119.99
64.53
37.13
36.81
30.86
19.33
13.88
N
O
O
CO2nBu
8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

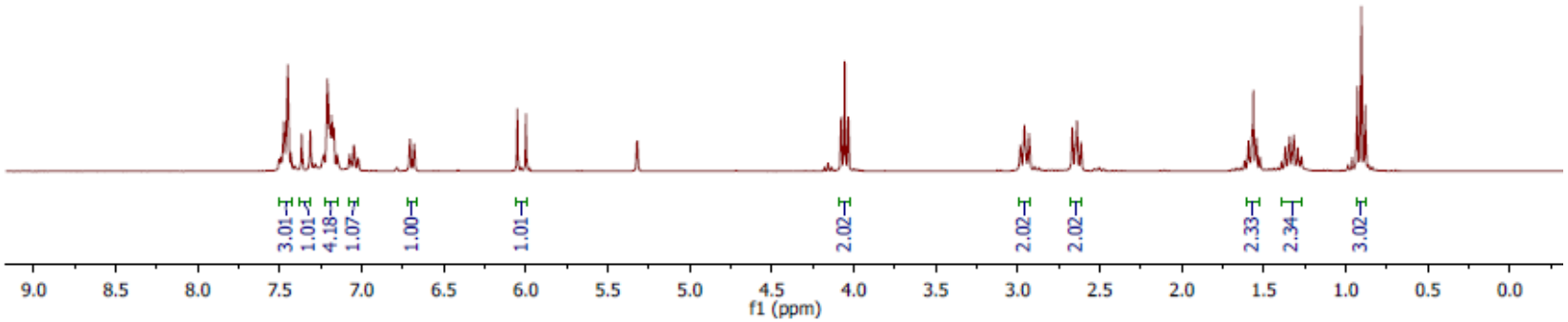

OMe
CO2nBu
9
f1 (ppm)

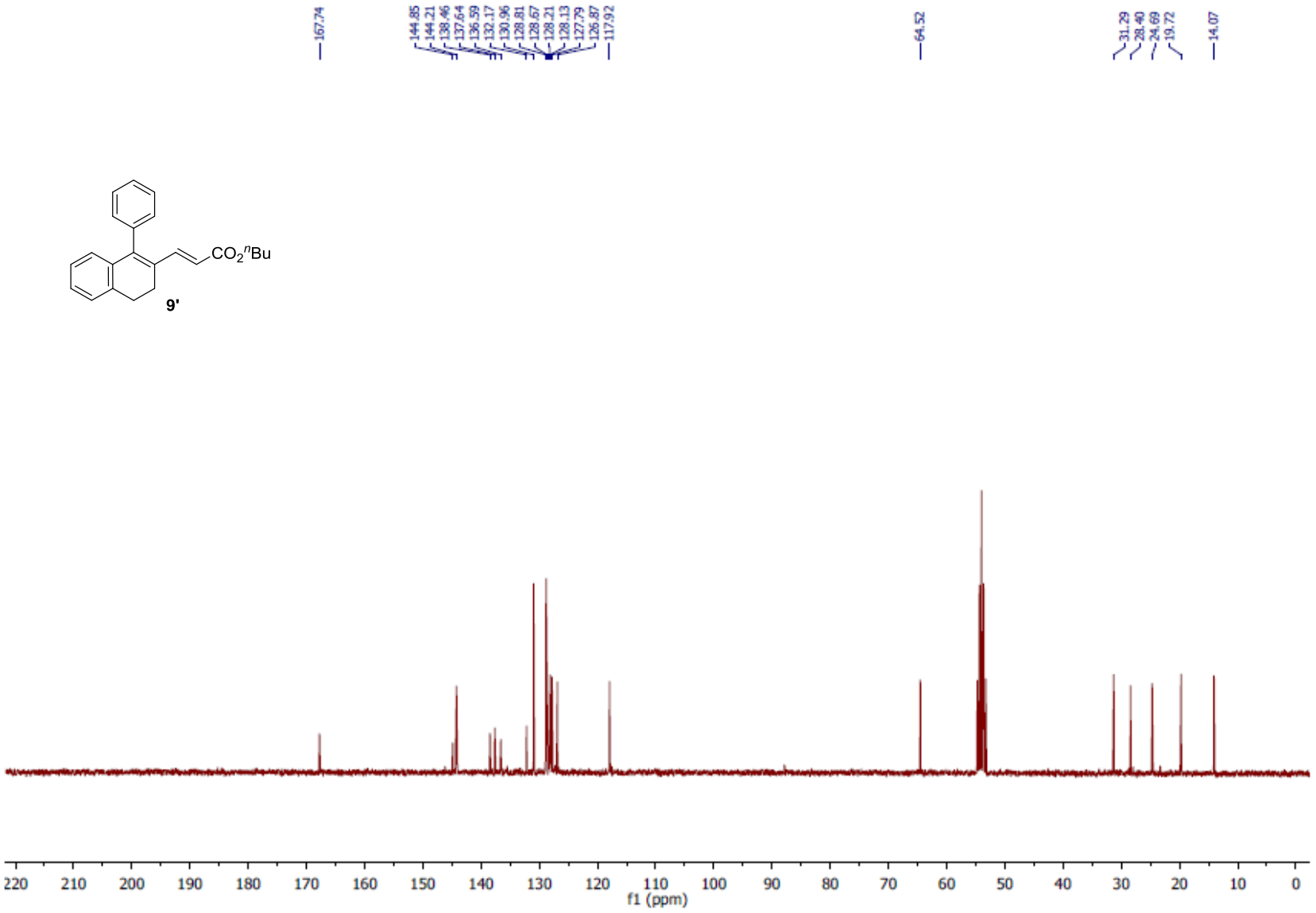

167.78
159.30
144.51
144.42
137.17
136.46
131.81
131.65
129.93
128.24
127.99
127.36
126.54
117.17
113.86
64.18
55.40
30.88
28.09
24.46
19.32
13.85
OMe
CO2nBu
9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

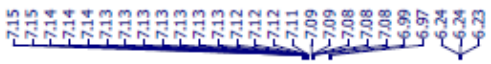

7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.37
7.31
7.24
7.24
7.23
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.15
7.15
7.08
7.07
7.05
7.04
7.03
7.02
6.71
6.70
6.68
6.68
6.05
6.00
4.08
4.06
4.03
2.98
2.96
2.95
2.93
2.67
2.65
2.64
2.62
1.62
1.60
1.59
1.58
1.57
1.57
1.56
1.55
1.54
1.52
1.39
1.37
1.35
1.34
1.32
1.29
1.27
0.93
0.91
0.88

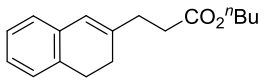

CO2nBu

9'

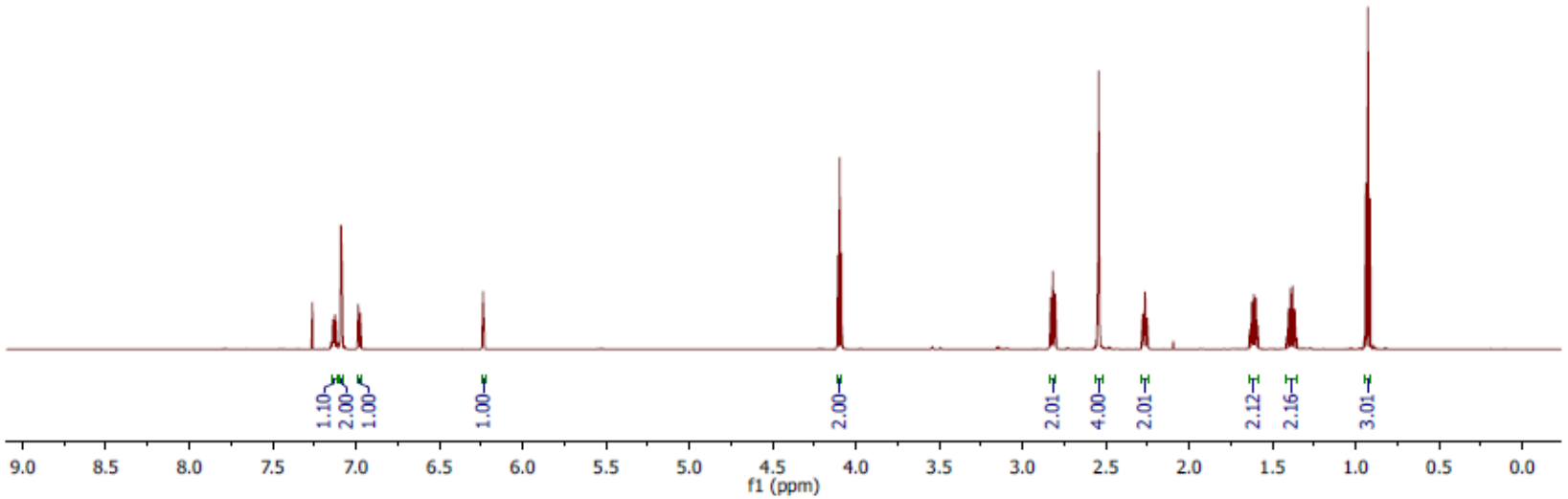

3.01
1.01
4.18
1.07
1.00
1.01
2.02
2.02
2.02
2.33
2.34
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

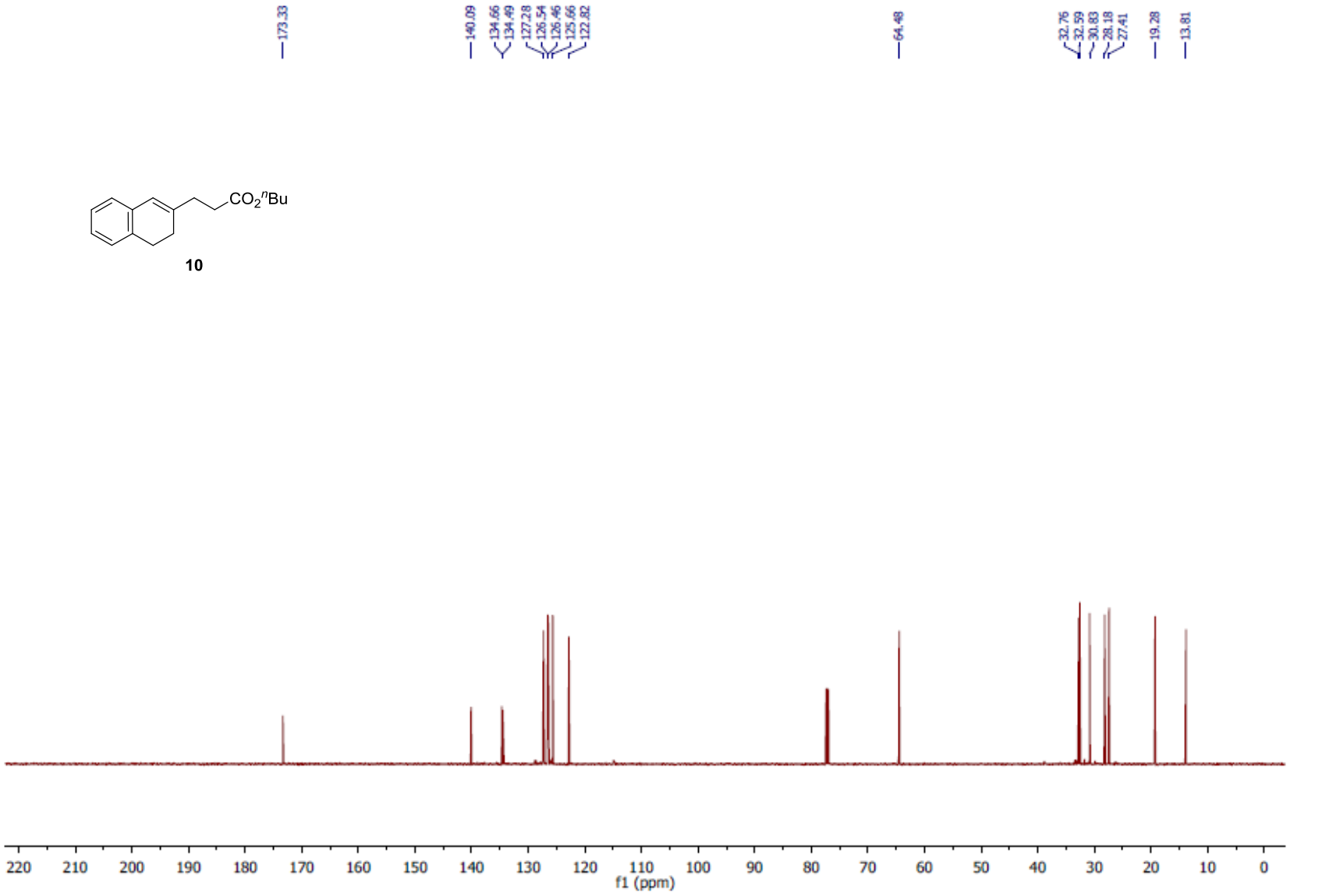

167.74
144.85
144.21
138.46
137.64
136.59
132.17
130.96
128.81
128.67
128.21
128.13
127.79
126.87
117.92
64.52
31.29
28.40
24.69
19.72
14.07
CO2nBu
9'
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

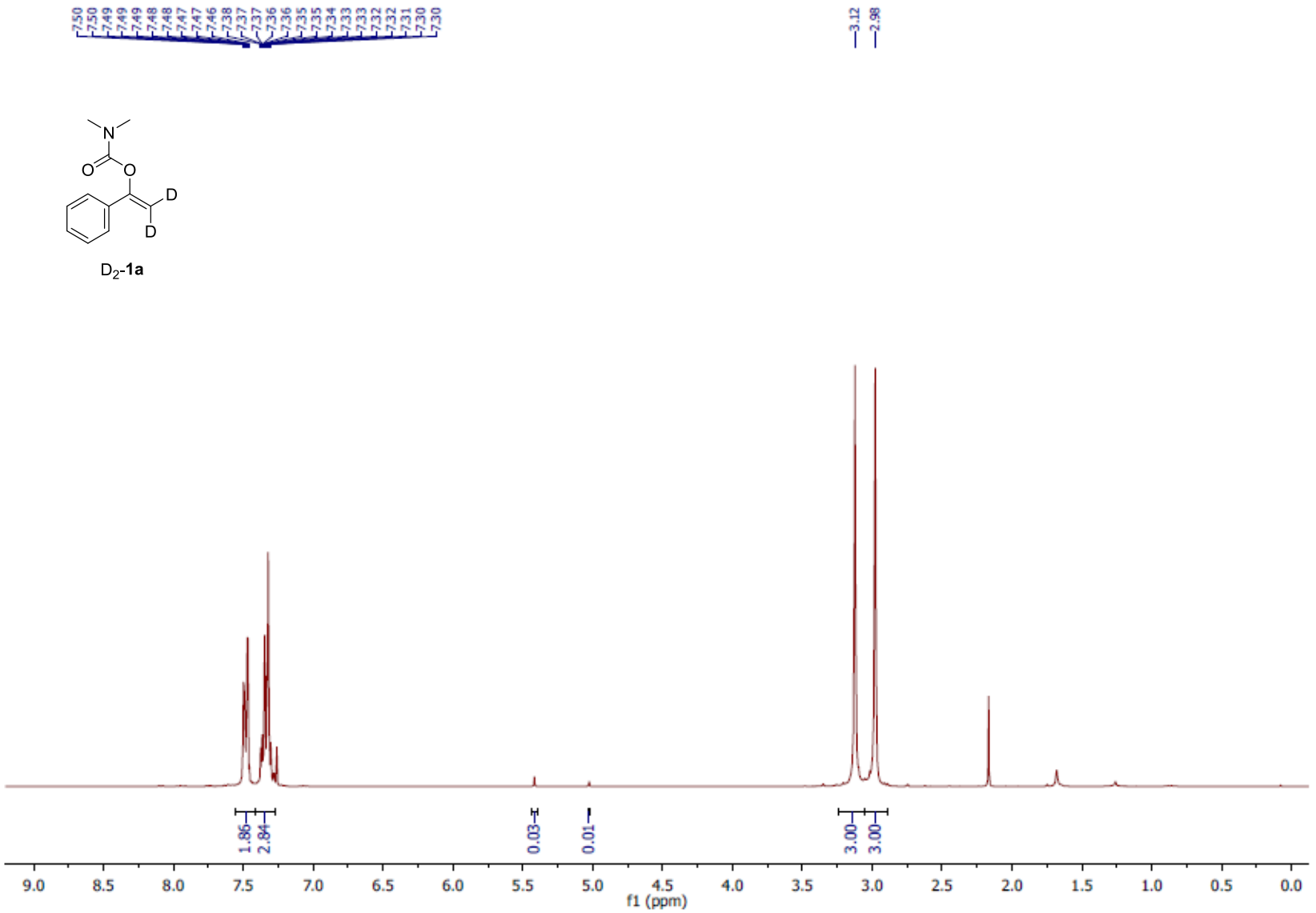



CO2nBu

10

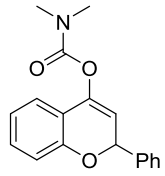

1.10
2.00
1.00
1.00
2.00
2.01
4.00
2.01
2.12
2.16
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.33
140.09
134.66
134.49
127.28
126.54
126.46
125.66
122.82
64.48
32.76
32.59
30.83
28.18
27.41
19.28
13.81
CO2nBu
10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

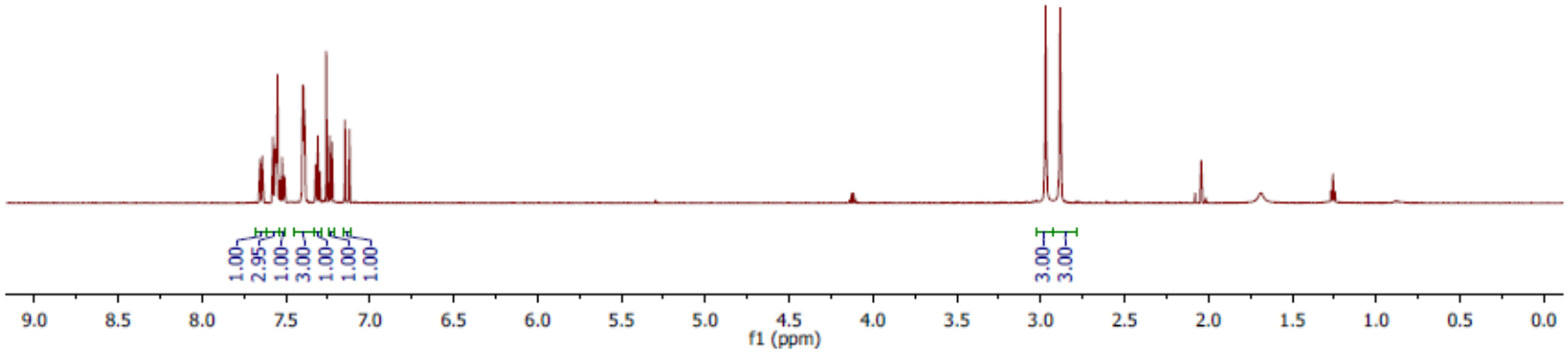

7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
3.12
2.98
N
O
O
D
D
1.86
2.84
0.03
0.01
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

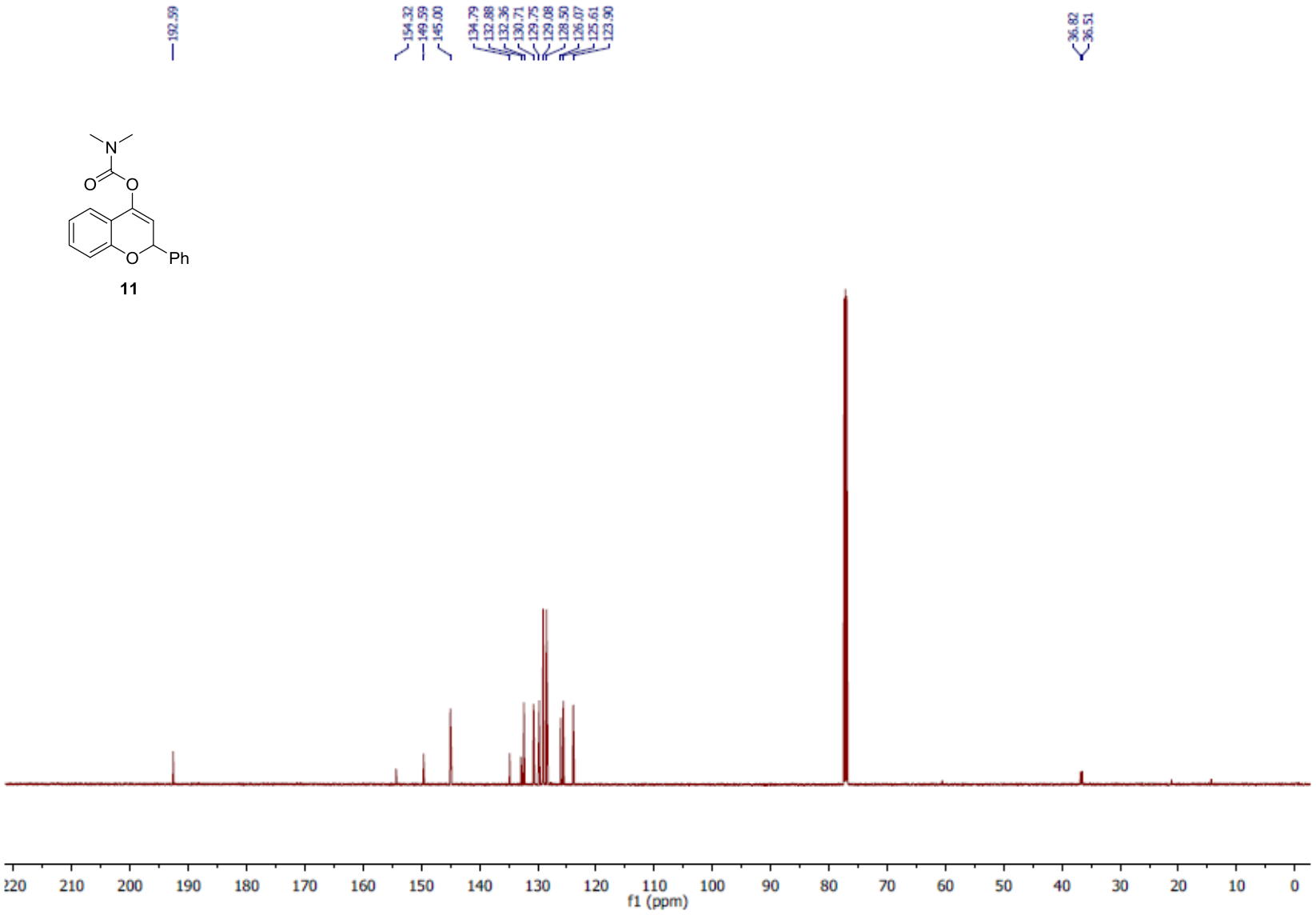
D_2-**1a**

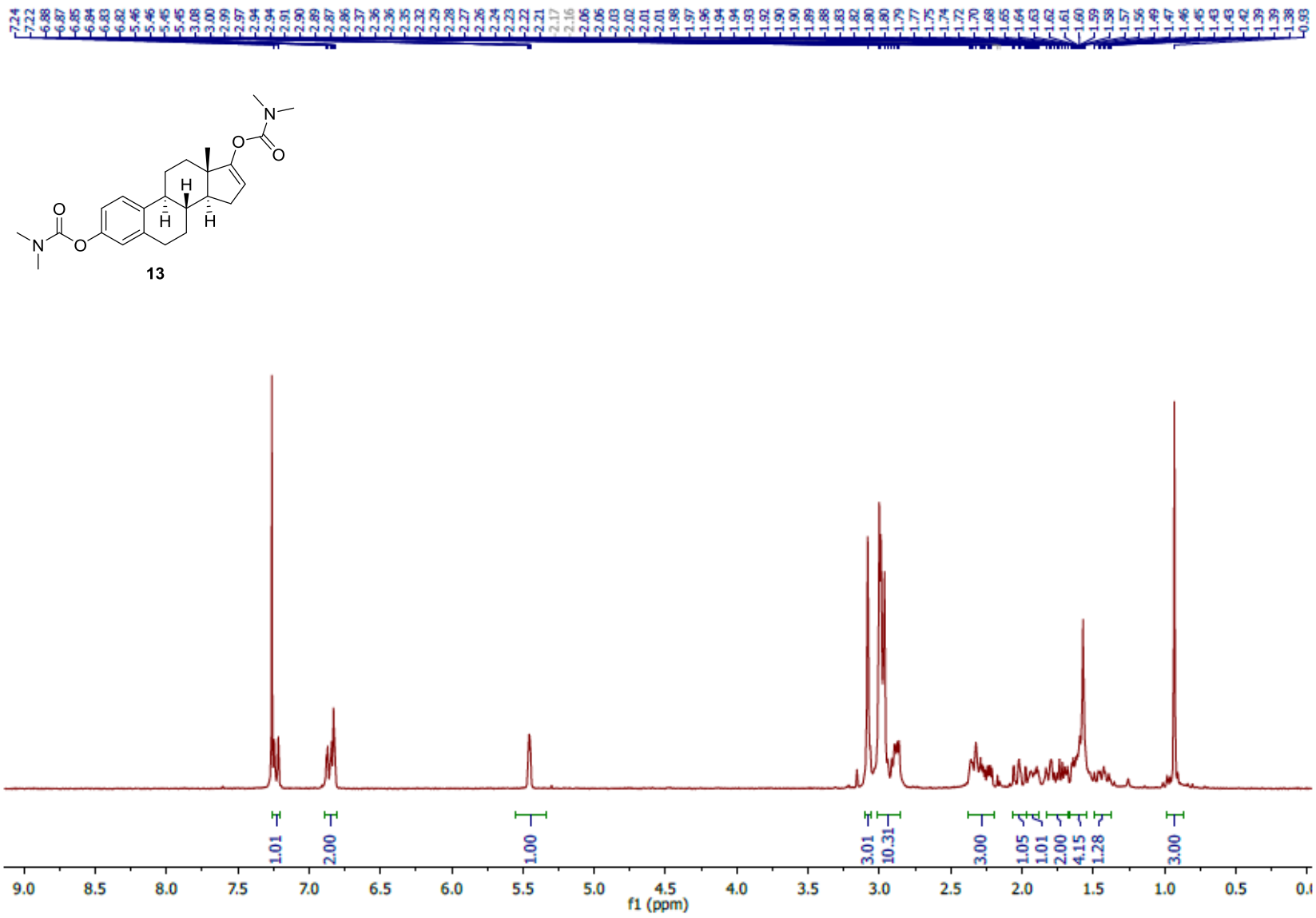

7.66
7.65
7.65
7.64
7.64
7.64
7.58
7.57
7.56
7.56
7.56
7.55
7.54
7.53
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.51
7.40
7.40
7.40
7.39
7.39
7.39
7.32
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.24
7.24
7.24
7.23
7.23
7.22
7.15
7.15
7.15
7.12
7.12
7.12
2.97
2.88

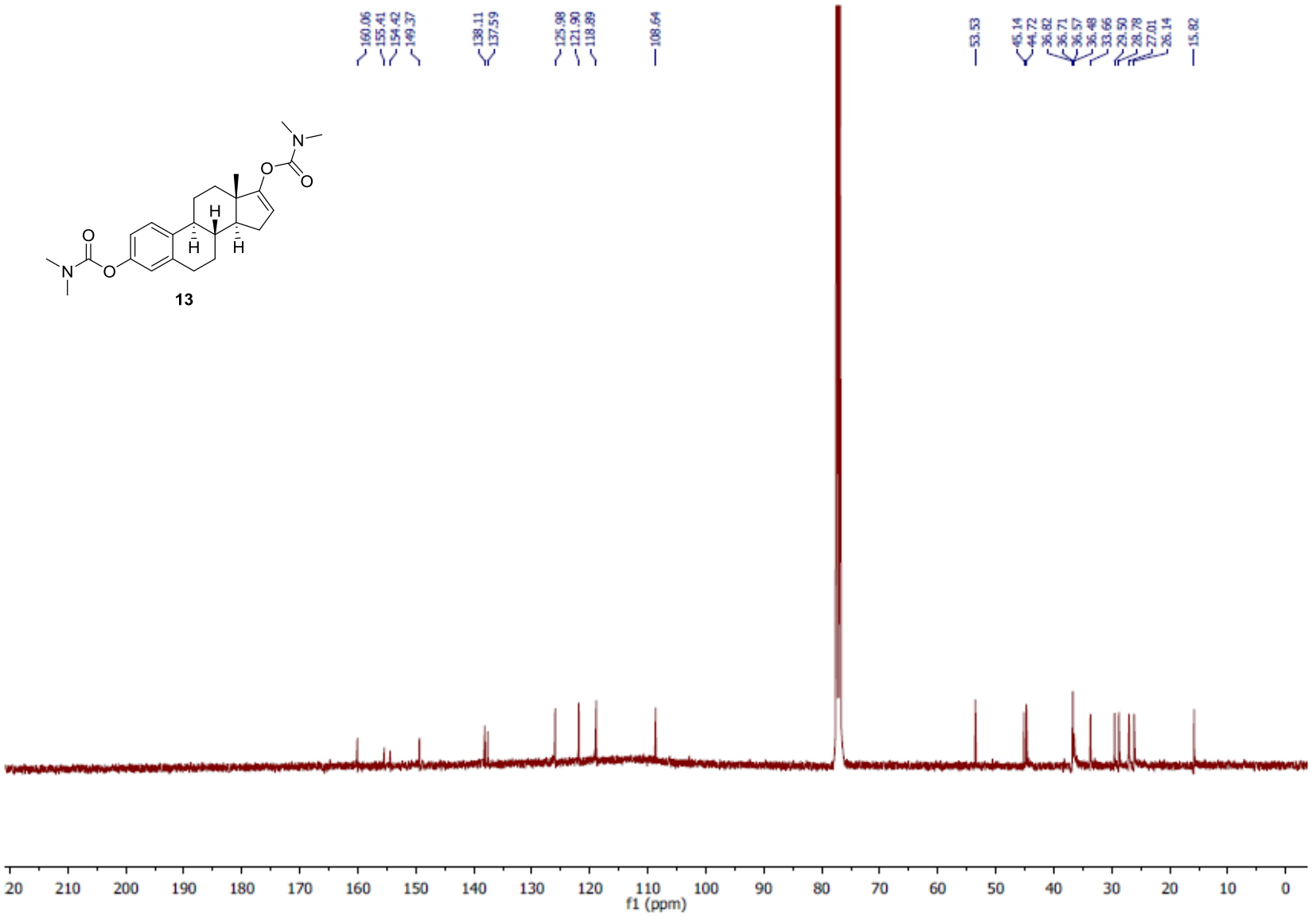

N
O
O
O
Ph

11

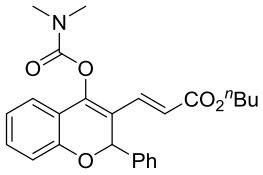

1.00
2.95
1.00
3.00
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.59
154.32
149.59
145.00
134.79
132.88
132.36
130.71
129.75
129.08
128.50
126.07
125.61
123.90
36.82
36.51
N
O
O
O
Ph
11
f1 (ppm)

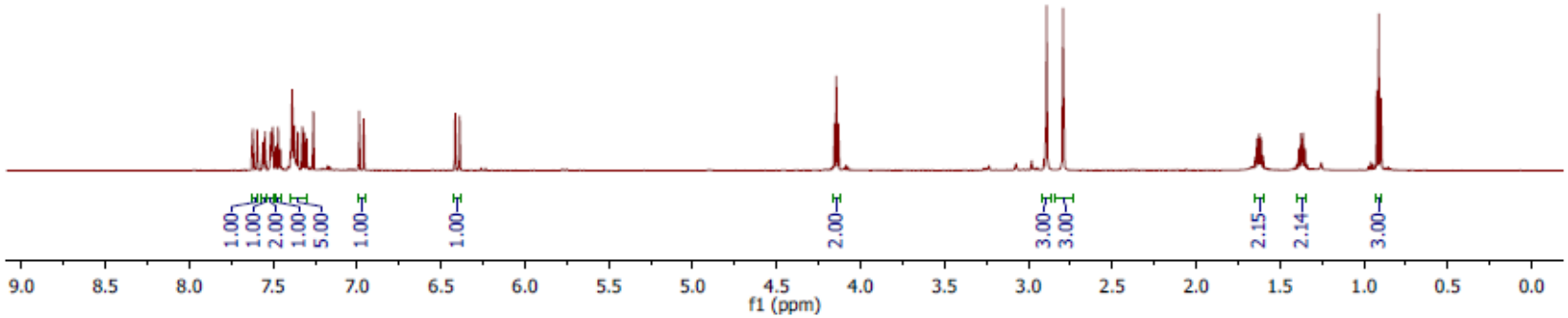

13
1.01
2.00
1.00
3.01
10.31
3.00
1.05
1.01
2.00
4.15
1.28
3.00
f1 (ppm)

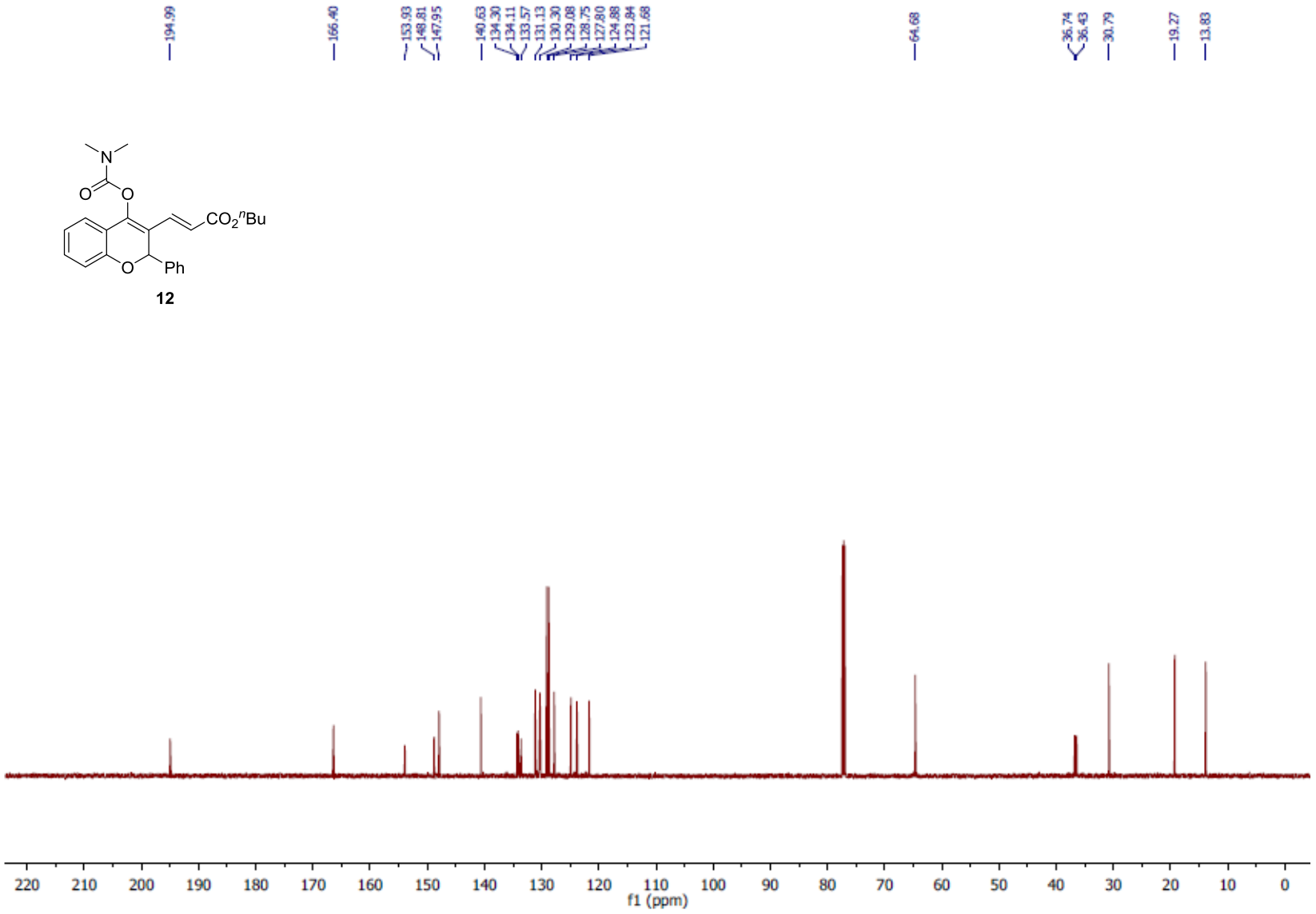

160.06
155.41
154.42
149.37
138.11
137.59
125.98
121.90
118.89
108.64
53.53
45.14
44.72
36.82
36.71
36.57
36.48
33.66
29.50
28.78
27.01
26.14
15.82
13
f1 (ppm)

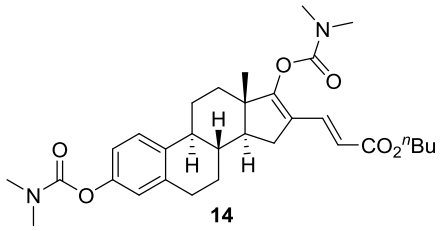

7.62
7.60
7.55
7.52
7.51
7.50
7.50
7.47
7.39
7.39
7.38
7.37
7.35
7.33
7.32
7.31
7.30
7.30
6.99
6.96
6.42
6.39
4.15
4.14
4.13
2.89
2.79
1.65
1.64
1.62
1.61
1.60
1.40
1.39
1.37
1.36
1.35
1.34
0.92
0.91
0.90


N
O
O
O
CO2nBu
O
Ph

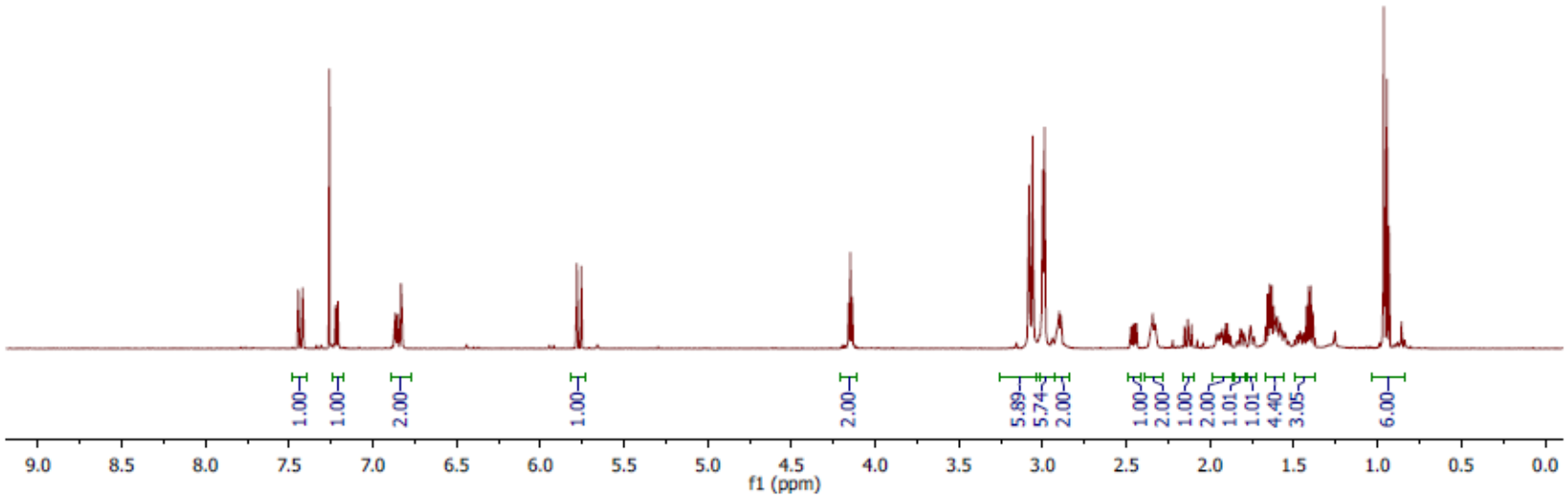
12

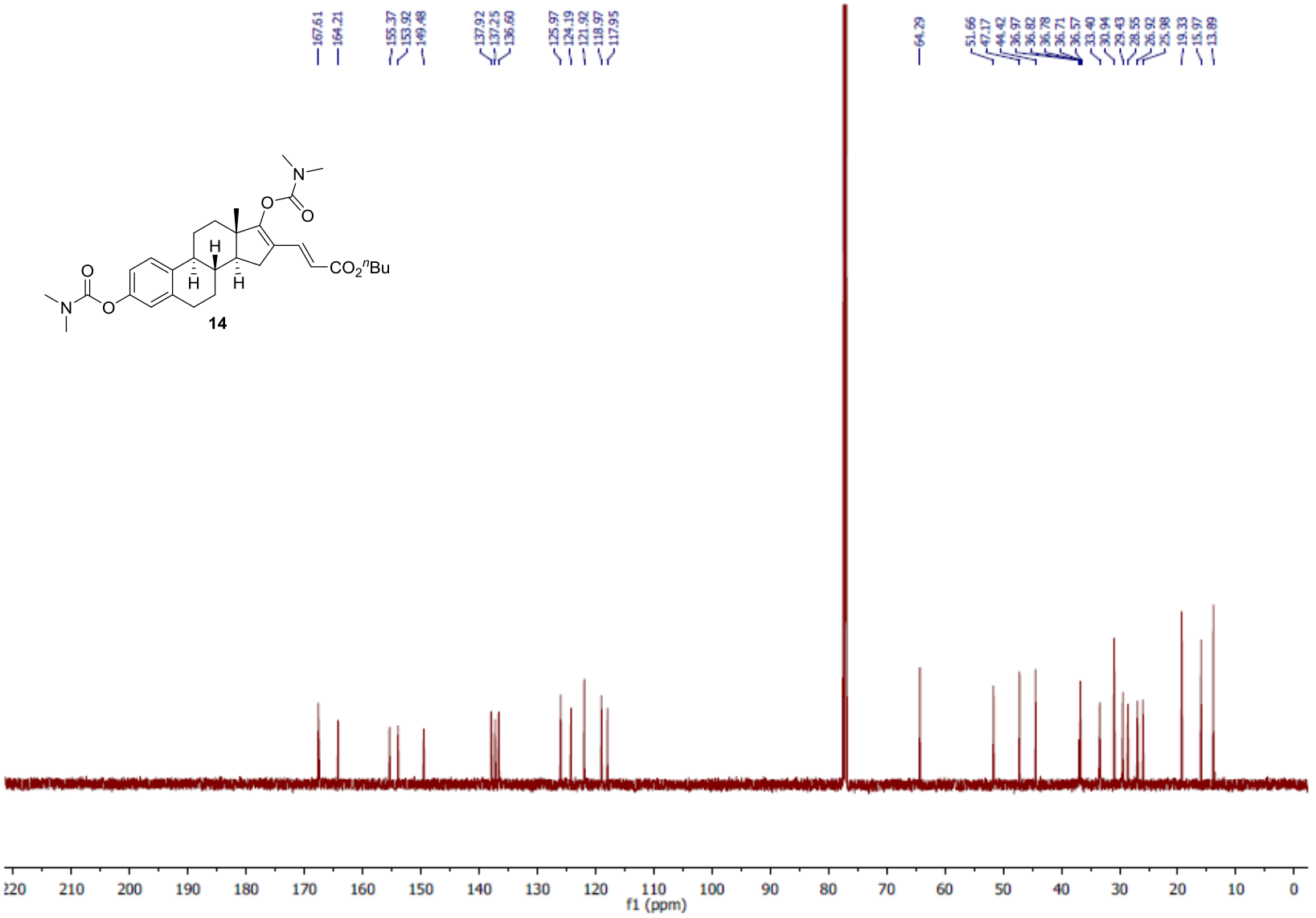

1.00
1.00
2.00
1.00
5.00
1.00
1.00
2.00
3.00
3.00
2.15
2.14
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.99
166.40
153.93
148.81
147.95
140.63
134.30
134.11
133.57
131.13
130.30
129.08
128.75
127.80
124.88
123.84
121.68
64.68
36.74
36.43
30.79
19.27
13.83
N
O
O
O
CO2nBu
O
Ph
12
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
O
H
H
H
O
O
N
CO2nBu

14


1.00
1.00
2.00
1.00
2.00
5.89
5.74
2.00
1.00
2.00
1.00
2.00
1.01
1.01
4.40
3.05
6.00
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)


167.61
164.21
155.37
153.92
149.48
137.92
137.25
136.60
125.97
124.19
121.92
118.97
117.95
64.29
51.66
47.17
44.42
36.97
36.82
36.78
36.71
36.57
33.40
30.94
29.43
28.55
26.92
25.98
19.33
15.97
13.89
O
N
O
O
H
H
H
O
N
O
CO2nBu
14
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)