Electronic Supplementary Information

Intermolecular Chemo- and Regioselective Aromatic C-H Amination of Alkoxyarenes Promoted by Rhodium Nitrenoids

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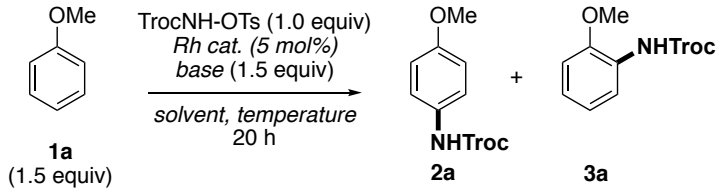
General

^{1}H NMR spectra were recorded on BRUKER Ultrasield Plus (400 MHz), and are reported in ppm using solvent resonance as the internal standard (acetone-d_6 at 2.05 ppm, $CDCl_3$ at 7.26 ppm, CD_3CN at 1.94 ppm). Chemical shifts are reported in ppm. When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet; quint, quintet; sept, septet; m, multiplet; br, broadened. ^{13}C NMR spectra were recorded on Ultrasield Plus (100 MHz), BRUKER Ascend (125 MHz) and are reported in ppm using solvent resonance as the internal standard (acetone-d_6 at 29.84 ppm, $CDCl_3$ at 77.16 ppm, CD_3CN at 118.26 ppm). Infrared (IR) spectra were recorded using HORIBA FT-720. High-resolution mass spectra (HRMS) were obtained using WATERS H-class/Xevo G2-XS for ESI. Melting points were measured using METTLER TOLEDO MP70. Column chromatography was performed on silica gel 60N (spherical, neutral, KANTO). Preparative TLC was performed on precoated plates (0.50 mm, Merck). TrocNHOTs[1], $Rh_2(tpa)_4$[2] and $Rh_2(piv)_4$[3] were prepared according to literature procedure. $Rh_2(oct)_4$ was purchased from TCI. $Rh_2(n\text{-}C_3F_7CO_2)_4$ and $Rh_2(esp)_2$ were purchased from Sigma-Aldrich. K_2CO_3, Na_2CO_3, Cs_2CO_3, $CaCO_3$, and MgO were purchased from Wako Chemical. Li_2CO_3 was purchased from TCI. Anhydrous chlorobenzene, trifluoromethylbenzene and *o*-dichlorobenzene were purchased from Sigma-Aldrich. Anhydrous dichloromethane, THF, Et_2O and AcOEt were purchased from Kanto Kagaku. Fluorobenzene was purchased from TCI and dried over activated molecular sieves. Anhydrous DMF and acetonitrile were purchased from Nacalai tesque.

List of Abbreviation

Ac	acetyl
Bz	benzoyl
CDI	carbonyldiimidazole
DMF	*N*,*N*-dimethylformamide
Ns	2-nitrobenzenesulfonyl
$Rh_2(esp)_4$	bis[rhodium(α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid)]
$Rh_2(oct)_4$	rhodium(Ⅱ) octanoate dimer
$Rh_2(piv)_4$	rhodium(Ⅱ) pivalate dimer
$Rh_2(tpa)_4$	rhodium(Ⅱ) triphenylacetate dimer
TBS	*tert*-butyldimethylsilyl
THF	tetrahydrofuran
Troc	2,2,2-trichloroethoxycarbonyl
Ts	*p*-toluenesulfonyl

Table S1. Optimization of conditions for dirhodium-catalyzed intermolecular C-H amination



entry	catalyst	solvent	base	Temp. (°C)	yield of (**2a**+**3a**)	**2a**:**3a**
1	$Rh_2(oct)_4$	PhCl	K_2CO_3	20	trace	-
2	$Rh_2(piv)_4$	PhCl	K_2CO_3	20	trace	-
3	$Rh_2(n\text{-}C_3F_7CO_2)_4$	PhCl	K_2CO_3	20	0%	-
4	$Rh_2(esp)_2$	PhCl	K_2CO_3	20	12%	7.8:1
5	$Rh_2(tpa)_4$	PhCl	K_2CO_3	20	50%	6.6:1
6	$Rh_2(tpa)_4$	PhCl	K_2CO_3	0	60%	11:1
7	$Rh_2(tpa)_4$	PhCl	K_2CO_3	–20	26%	12:1
8[a]	$Rh_2(tpa)_4$	PhCl	K_2CO_3	0	37%	9.5:1
9[b]	$Rh_2(tpa)_4$	PhCl	K_2CO_3	0	42%	11:1
10[c]	$Rh_2(tpa)_4$	PhCl	K_2CO_3	0	58%	12:1
11[d]	$Rh_2(tpa)_4$	PhCl	K_2CO_3	0	60%	13:1
12	$Rh_2(tpa)_4$	CH_2Cl_2	K_2CO_3	0	9%	8.0:1
13	$Rh_2(tpa)_4$	AcOEt	K_2CO_3	0	trace	-
14	$Rh_2(tpa)_4$	CH_3CN	K_2CO_3	0	trace	-
15	$Rh_2(tpa)_4$	$PhCF_3$	K_2CO_3	0	30%	10:1
16	$Rh_2(tpa)_4$	PhF	K_2CO_3	0	39%	10:1
17	$Rh_2(tpa)_4$	$o\text{-}Cl_2C_6H_4$	K_2CO_3	0	44%	14:1
18	$Rh_2(tpa)_4$	PhCl	Li_2CO_3	0	trace	-
19	$Rh_2(tpa)_4$	PhCl	Na_2CO_3	0	9%	7.8:1
20	$Rh_2(tpa)_4$	PhCl	MgO	0	28%	14:1
21	$Rh_2(tpa)_4$	PhCl	$CaCO_3$	0	trace	-
22	$Rh_2(tpa)_4$	PhCl	Cs_2CO_3	0	55%	11:1
23	$Rh_2(tpa)_4$	PhCl	KOAc	0	51%	13:1
24	$Rh_2(tpa)_4$	PhCl	K_3PO_4	0	42%	11:1

[a]**1a** (1.0 equiv) and TrocNH-OTs (1.5 equiv) were employed. [b]**1a** (1.0 equiv) was employed. [c]**1a** (3.0 equiv) was employed. [d]**1a** (5.0 equiv) was employed.

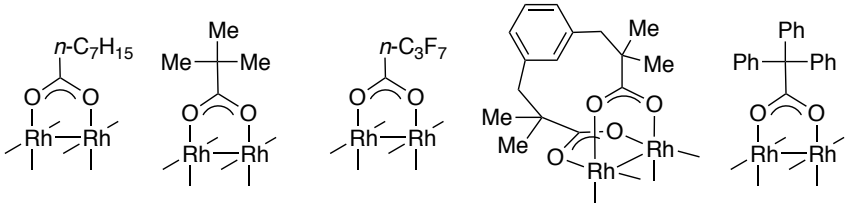
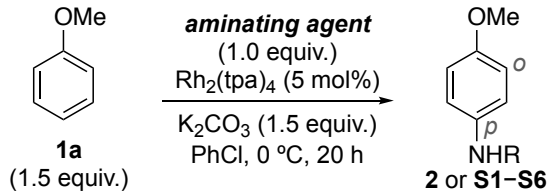
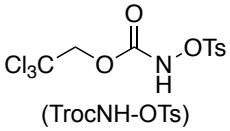
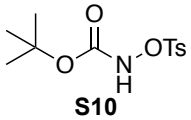
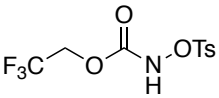
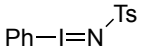
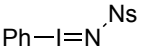
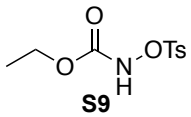


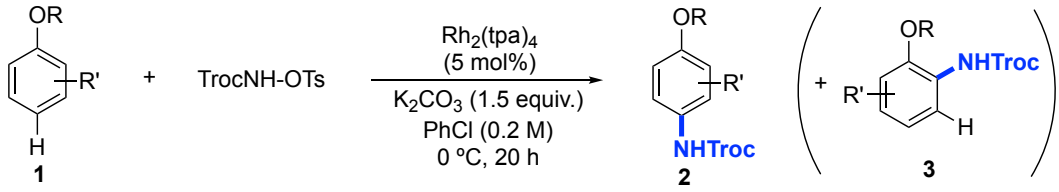
Table S2. Effects of aminating agents on dirhodium-catalyzed intermolecular C-H amination



entry	aminating agents	results	entry	aminating agents	results
1	 (TrocNH-OTs)	60% yield (*p*:*o* = 11:1)[a] **2**: R = Troc	5	 **S10**	0% yield[a] **S4**: R = CO_2t-Bu
2	 **S7**	41% yield (*p*:*o* = 6.5:1)[a] **S1**: R = $CO_2CH_2CF_3$	6[b]	 **S11**	0% yield[a] **S5**: R = Ts
3	 **S8**	25% yield (*p*:*o* = 1.9:1)[a] **S2**: R = $CO_2CH(CF_3)_2$	7[b]	 **S12**	0% yield[a] **S6**: R = Ns
4	 **S9**	0% yield[a] **S3**: R = CO_2Et			

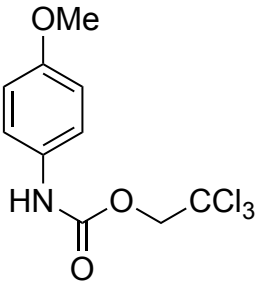
[a] Determined by ^{1}H NMR using 1,3-dinitrobenzene as an internal standard. [b] These reactions were performed without K_2CO_3.

General Procedure for Dirhodium-Catalyzed Intermolecular C-H Amination

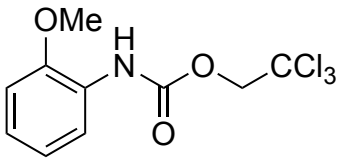


To a suspension of alkoxyarenes **1** (0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.) and K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.) in PhCl (1.0 mL) were added $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) at 0 °C. After being stirred for 20 h at 0 °C, the reaction was quenched by addition of water and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified by preparative TLC purification to afford the aminated product(s) **2** (and **3**).

Specific Procedures and Characterization Data of 2,2,2-Trichloroethyl-*N*-arylcarbamate in Table 1 and Scheme 4b



2a



3a

Following the general procedure for intermolecular amination, anisole (32.6 μL, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a mixture of **2a** and **3a** (32.0 mg, 60%, **2a**/**3a**=12/1) as a white solid. **2a** and **3a** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

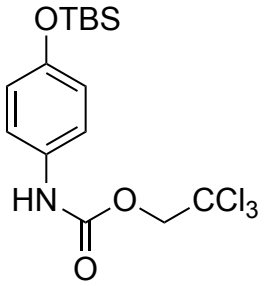
2,2,2-trichloroethyl-*N*-4-methoxyphenylcarbamate (2a)

White solid: **m.p.** 92 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.00 (br s, 1H), 7.50 (br d, J = 8.6 Hz, 2H), 6.93–6.89 (m, J = 9.1 Hz, 2H), 4.89 (s, 2H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 156.9, 152.9 132.4, 121.2, 114.9, 96.9, 74.7, 55.7; **IR** (neat, cm^{-1}): 3297, 1729, 1538, 1508, 1413, 1209, 1180, 1106, 1054, 1022, 833, 738; **HRMS-ESI$^+$** (*m/z*): Calcd. for $C_{10}H_{10}Cl_3NO_3$ $[M+Na]^+$ 319.9624; found, 319.9623.

2,2,2-trichloroethyl-*N*-2-methoxyphenylcarbamate (3a)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.19 (br s, 1H), 7.98 (br d, J = 7.6 Hz, 1H), 7.10–7.03 (m, 2H), 6.95 (td, J = 7.9 Hz, 1.9 Hz, 1H), 4.92 (s, 2H), 3.89 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 152.5, 149.8, 127.9, 124.8, 121.4, 120.1, 111.6, 96.7, 74.8, 56.2; **IR** (neat, cm^{-1}): 3359, 2948, 1754, 1598, 1540, 1461, 1251, 1199, 1095, 1025, 954, 806; **HRMS-ESI$^+$** (*m/z*): Calcd. for $C_{10}H_{10}Cl_3NO_3$ $[M+Na]^+$ 319.9624;

found, 319.9627.

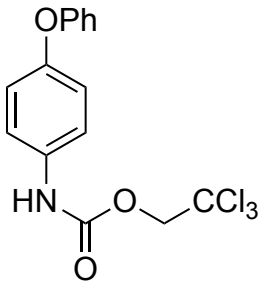


2b

2,2,2-trichloroethyl-*N*-4-(*tert*-butyldimethylsilyloxy)phenylcarbamate (2b)

Following the general procedure for intermolecular amination, *tert*-butyldimethyl(phenoxy)silane (42.6 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (27.2 mg, 0.020 mmol, 0.10 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 48 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford **2b** (31.7 mg, 40%) as a white solid.

Analytical data: **m.p.** 120 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.03 (br s, 1H), 7.47 (br d, J = 8.6 Hz, 2H), 6.87–6.83 (m, 2H), 4.89 (s, 2H), 0.99 (s, 9H), 0.21 (s, 6H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 152.8, 152.5, 133.2, 121.0, 96.9, 74.7, 26.1, 18.8, -4.3; **IR** (neat, cm^{-1}): 3282, 2958, 2360, 1706, 1544, 1508, 1261, 1218, 1116, 833, 738, 682; **HRMS-ESI$^+$** (*m/z*): Calcd. for $C_{15}H_{22}Cl_3NO_3Si$ $[M+Na]^+$ 420.0332; found, 420.0327

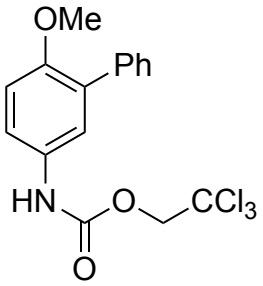


2c

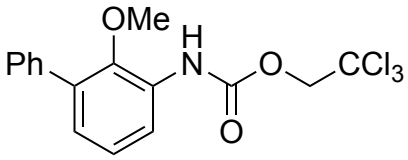
2,2,2-trichloroethyl-*N*-4-phenoxyphenylcarbamate (2c)

Following the general procedure for intermolecular amination, diphenylether (47.4 μL, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (21.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (27.2 mg, 0.020 mmol, 0.1 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 48 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford **2c** (28.4 mg, 39%) as a white solid.

Analytical data: **m.p.** 118 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.22 (br s, 1H), 7.62 (br d, J = 8.8 Hz, 2H), 7.39–7.34 (m, 2H), 7.12–7.08 (m, 1H), 7.04–6.96 (m, 4H), 4.91 (s, 2H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 158.8, 153.6, 152.9, 135.2, 130.7, 123.8, 121.2, 120.6, 118.9, 96.8, 74.8; **IR** (neat, cm^{-1}): 3291, 2360, 1708, 1540, 1488, 1409, 1218, 1101, 1049, 852, 809; **HRMS-ESI$^+$** (*m/z*): Calcd. for $C_{15}H_{12}Cl_3NO_3$ $[M+Na]^+$ 381.9780; found, 382.9776.



2d



3d

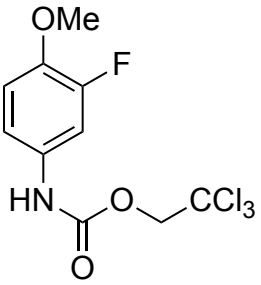
Following the general procedure for intermolecular amination, 2-methoxybiphenyl (55.3 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a mixture of **2d** and **3d** (37.9 mg, 51%, **2d**/**3d** =11/1) as a white solid. **2d** and **3d** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

2,2,2-trichloroethyl-*N*-(4-methoxy-3-phenyl)phenylcarbamate (2d)

White solid: **m.p.** 108 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.07 (br s, 1H), 7.59–7.51 (m, 4H), 7.42–7.38 (m, 2H), 7.34–7.30 (m, 1H), 7.09 (d, J = 9.2 Hz, 1H), 4.90 (s, 2H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 153.7, 152.9, 139.3, 132.7, 131.7, 130.3, 128.8, 127.8, 122.4, 120.0, 113.0, 96.8, 74.7, 56.2; **IR** (neat, cm^{-1}): 3386, 2362, 1738, 1571, 1506, 1434, 1207, 1145, 1110, 1045, 871, 825; **HRMS-ESI$^+$** (*m/z*): Calcd. for $C_{16}H_{14}Cl_3NO_3$ $[M+Na]^+$ 395.9937; found, 395.9931.

2,2,2-trichloroethyl-*N*-(2-methoxy-3-phenyl)phenylcarbamate (3d)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.61 (br s, 1H), 8.04 (br d, J = 8.0 Hz, 1H), 7.60–7.57 (m, 2H), 7.49–7.45 (m, 2H), 7.37-7.41 (m, 1H), 7.21 (t, J = 7.9 Hz, 1H), 7.11 (dd, J = 7.7, 1.6 Hz, 1H), 4.95 (s, 2H), 3.38 (s, 3H); **^{13}C NMR** (125 MHz, acetone-d_6) δ: 153.0, 148.2, 139.0, 135.5, 132.6, 129.7, 129.3, 128.3, 126.6, 125.2, 120.4, 96.7, 74.9, 60.9; **IR** (neat, cm^{-1}): 3388, 1731, 1540, 1506, 1434, 1263, 1207, 1110, 1045, 871, 823; **HRMS-ESI$^+$** (*m/z*): Calcd. for $C_{16}H_{14}Cl_3NO_3$ $[M+Na]^+$ 395.9937; found, 395.9938.



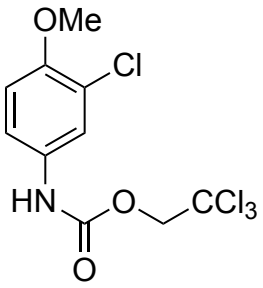
2e

2,2,2-trichloroethyl-*N*-(3-fluoro-4-methoxy)phenylcarbamate (2e)

Following the general procedure for intermolecular amination, 2-fluoroanisole (37.8 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude

material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2e** (18.7 mg, 30%) as a white amorphous.

Analytical data: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.19 (br s, 1H), 7.50 (br d, J = 12.8 Hz, 1H), 7.29 (br d, J = 8.7 Hz, 1H), 7.10 (t, J = 9.2 Hz, 1H), 4.90 (s, 2H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 152.84 (d, J = 241.5 Hz), 152.77, 144.6 (d, J = 10.2 Hz), 132.9 (d, J = 10.9 Hz), 115.3, 115.1 (d, J = 2.4 Hz), 108.2 (d, J = 23.4 Hz),, 96.7, 74.7, 56.8; **IR** (neat, cm^{-1}): 3303, 2360, 1706, 1604, 1521, 1419, 1272, 1222, 1101, 1018, 948, 862, 821; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{10}H_9Cl_3FNO_3$ $[M+Na]^+$ 337.9530; found, 337.9528.

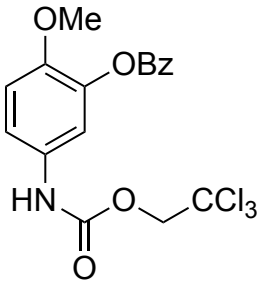


2f

2,2,2-trichloroethyl-*N*-(3-chloro-4-methoxy)phenylcarbamate (2f)

Following the general procedure for intermolecular amination, 2-chloroanisole (42.8 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford **2f** (20.9 mg, 31%) as a white amorphous.

Analytical data: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.16 (br s, 1H), 7.72 (br s, 1H), 7.47 (br d, J = 8.8 Hz, 1H), 7.10 (d, J = 8.9 Hz, 1H), 4.90 (s, 2H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 152.8, 152.2, 133.1, 122.8, 121.5, 119.3, 113.7, 96.7, 74.8, 56.7; **IR** (neat, cm^{-1}): 3320, 2360, 1702, 1589, 1525, 1284, 1228, 1105, 1056, 1016, 865, 804; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{10}H_9Cl_4NO_3$ $[M+Na]^+$ 353.9234; found, 353.9231.



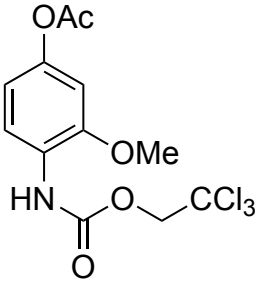
2g

2,2,2-trichloroethyl-*N*-(3-benzoyloxy-4-methoxy)phenylcarbamate (2g)

Following the general procedure for intermolecular amination, 2-methoxyphenyl benzoate (68.5 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude

material was purified by preparative TLC purification ($CHCl_3$/hexane = 4/1) to afford **2g** (35.0 mg, 42%) as a white amorphous.

Analytical data: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.19 (br s, 1H), 8.20–8.17 (m, 2H), 7.76–7.71 (m, 1H), 7.63–7.59 (m, 2H), 7.56 (br s, 1H), 7.45 (dd, J = 8.8, 2.2 Hz, 1H), 7.14 (d, J = 8.9 Hz, 1H), 4.90 (s, 2H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 163.9, 151.8, 147.6, 140.0, 133.6, 131.8, 129.8, 129.4, 128.7, 116.9, 114.2, 112.9, 95.8, 73.8, 55.6; **IR** (neat, cm^{-1}): 3357, 2360, 1739, 1533, 1438, 1365, 1263, 1207, 1024, 889, 815; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{17}H_{14}Cl_3NO_5$ $[M+Na]^+$ 439.9835; found, 439.9833.

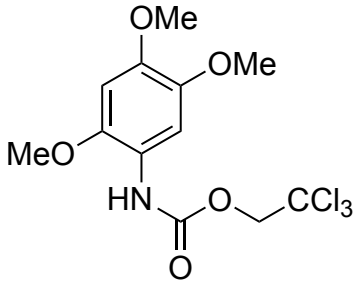


3h

2,2,2-trichloroethyl-*N*-(4-acetoxy-2-methoxy)phenylcarbamate (3h)

Following the general procedure for intermolecular amination, 2-methoxyphenyl acetate (49.9 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **3h** (27.8 mg, 39%) as a white solid.

Analytical data: **m.p.** 120 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.25 (br s, 1H), 7.93 (br d, J = 7.8 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.72 (dd, J = 8.8, 2.5 Hz, 1H), 4.92 (s, 2H), 3.88 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 169.7, 152.8, 150.6, 148.3, 125.5, 120.6, 114.3, 106.3, 96.7, 74.9, 56.5, 20.9; **IR** (neat, cm^{-1}): 3380, 2360, 1747, 1540, 1463, 1413, 1367, 1205, 1033, 964, 896, 808; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{12}H_{12}Cl_3NO_5$ $[M+Na]^+$ 377.9679; found, 377.9675.

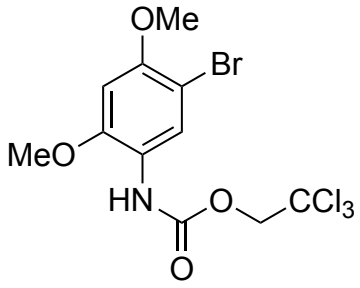


2i

2,2,2-trichloroethyl-*N*-2,4,5-trimethoxyphenylcarbamate (2i)

Following the general procedure for intermolecular amination, 1,2,4-trimethoxybenzene (50.5 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification (AcOEt/hexane = 1/4) to afford **2i** (58.0 mg, 81%) as a white solid.

Analytical data: **m.p.** 78 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.08 (br s, 1H), 7.63 (br s, 1H), 6.78 (s, 1H), 4.90 (s, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 152.8, 147.2, 144.7, 144.0, 120.5, 107.8, 99.9, 96.8, 74.9, 57.1, 57.0, 56.8; **IR** (neat, cm^{-1}): 3243, 2950, 2360, 1735, 1536, 1444, 1351, 1205, 1147, 1029, 854; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{12}H_{14}Cl_3NO_5$ $[M+Na]^+$ 379.9835; found, 379.9829.

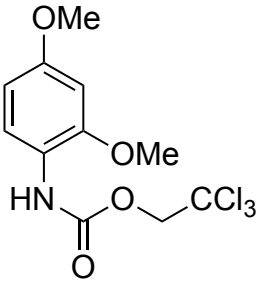


2j

2,2,2-trichloroethyl-*N*-5-bromo-2,4-dimethoxyphenylcarbamate (2j)

Following the general procedure for intermolecular amination, 1-bromo-2,4-dimethoxybenzene (54.7 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2j** (55.2 mg, 68%) as a white solid.

Analytical data: **m.p.** 125 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.24 (brs, 1H), 8.09 (brs, 1H), 6.86 (s, 1H), 4.90 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 153.8, 152.9, 151.1, 125.0, 121.8, 101.4, 98.4, 96.7, 74.9, 57.0, 56.7; **IR** (neat, cm^{-1}): 3417, 2946, 2360, 1739, 1525, 1455, 1392, 1201, 1101, 1025, 966, 809; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_{11}BrCl_3NO_4$ $[M+Na]^+$ 427.8835; found, 427.8830.



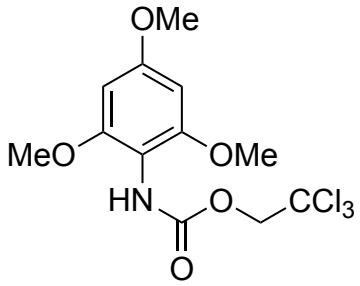
2k

2,2,2-trichloroethyl-*N*-2,4-dimethoxyphenylcarbamate (2k)

Following the general procedure for intermolecular amination, 1,3-dimethoxybenzene (41.4 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2k** (40.4 mg, 61%) as a white amorphous.

Analytical data: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.02 (br s, 1H), 7.77 (br d, J = 6.3 Hz, 1H), 6.62 (d, J = 2.6 Hz, 1H), 6.52 (dd, J = 9.8, 2.7 Hz, 1H), 4.89 (s, 2H), 3.86 (s, 3H) , 3.79 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 158.1, 152.9, 151.7, 122.0, 121.0, 105.0, 99.6, 96.8, 74.9, 56.2, 55.8; **IR** (neat, cm^{-1}): 3349,

2360, 1739, 1602, 1547, 1533, 1365, 1207, 1031, 811; **HRMS-ESI**$^+$ (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_4$ $[M+Na]^+$ 349.9730; found, 349.9724.

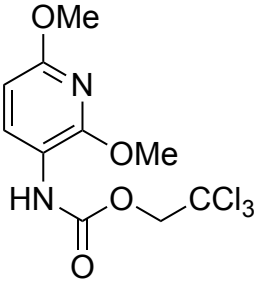


2l

2,2,2-trichloroethyl-*N*-2,4,6-trimethoxyphenylcarbamate (2l)

Following the general procedure for intermolecular amination, 1,3,5-trimethoxybenzene (50.5 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification (AcOEt/hexane = 1/4) to afford **2l** (35.8 mg, 50%) as a white solid.

Analytical data: **m.p.** 151 °C; **^{1}H NMR** (400 MHz, CD_3CN, 333 K) δ: 6.59 (br s, 1H), 6.25 (s, 2H), 4.78 (s, 2H), 3.82 (s, 3H), 3.80 (s, 6H); **^{13}C NMR** (100 MHz, CD_3CN) δ: 161.4, 158.2, 154.5, 107.6, 96.9, 91.9, 75.2, 56.7, 56.2; **IR** (neat, cm^{-1}): 3357, 2942, 2360, 1725, 1592, 1521, 1469, 1365, 1226, 1106, 1043, 813; **HRMS-ESI**$^+$ (m/z): Calcd. for $C_{12}H_{14}Cl_3NO_5$ $[M+Na]^+$ 379.9835; found, 379.9832.

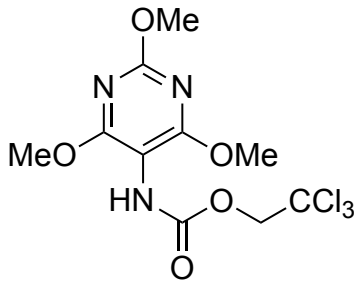


2m

2,2,2-trichloroethyl-*N*-2,6-dimethoxypyridin-3-ylcarbamate (2m)

Following the general procedure for intermolecular amination, 2,6-dimethoxypyridine (41.7 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford **2m** (35.0 mg, 53%) as colorless oil.

Analytical data: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.22 (br s, 1H), 8.03 (br d, J = 6.8 Hz, 1H), 6.35 (d, J = 8.4 Hz, 1H), 4.89 (s, 2H), 3.96 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 159.1, 153.6, 152.4, 133.1, 114.0, 100.4, 95.8, 74.1, 53.0, 52.9; **IR** (neat, cm^{-1}): 3421, 2948, 2360, 1743, 1547, 1517, 1390, 1205, 1114, 1018, 813; **HRMS-ESI**$^+$ (m/z): Calcd. for $C_{10}H_{11}Cl_3N_2O_4$ $[M+Na]^+$ 350.9682; found, 350.9681.

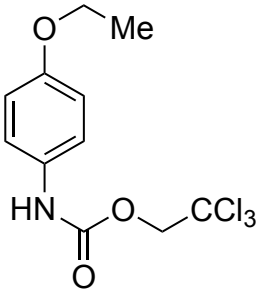


2n

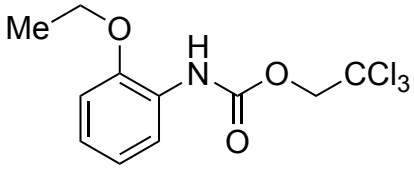
2,2,2-trichloroethyl-*N*-2,4,6-trimethoxypyrimidin-5-ylcarbamate (2n)

Following the general procedure for intermolecular amination, 2,4,6-trimethoxypyrimidine (51.0 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 4/1) to afford **2n** (43.6 mg, 60%) as a white amorphous.

Analytical data: **^{1}H NMR** (400 MHz, CD_3CN, 333 K) δ: 6.65 (br s, 1H), 4.79 (s, 2H), 3.96 (s, 3H), 3.95 (s, 6H); **^{13}C NMR** (100 MHz, CD_3CN) δ: 168.6, 163.5, 154.2, 97.0, 96.6, 75.3, 55.6, 55.2; **IR** (neat, cm^{-1}): 3321, 2969, 2360, 1757, 1739, 1521, 1455, 1365, 1228, 1135, 1016; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{10}H_{12}Cl_3N_3O_5$ $[M+Na]^+$ 381.9740; found, 381.9748.



2o



3o

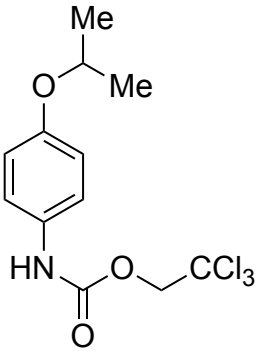
Following the general procedure for intermolecular amination, phenetol (36.7 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a mixture of **2o** and **3o** (28.7 mg, 46%, **2o**/**3o**=17/1) as a white solid. **2o** and **3o** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

2,2,2-trichloroethyl-*N*-4-ethoxyphenylcarbamate (2o)

White solid: **m.p.** 111 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.99 (br s, 1H), 7.49 (br d, J = 8.6 Hz, 2H), 6.91–6.87 (m, 2H), 4.89 (s, 2H), 4.02 (q, J = 7.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 156.2, 152.9, 132.4, 121.2, 115.5, 96.9, 74.7, 64.2, 15.1; **IR** (neat, cm^{-1}): 3343, 2969, 2362, 1716, 1529, 1419, 1365, 1216, 1105, 1043, 919, 827; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_3$ $[M+Na]^+$ 333.9780; found, 333.9778.

2,2,2-trichloroethyl-*N*-2-ethoxyphenylcarbamate (3o)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.18 (br s, 1H), 7.99 (br d, J = 7.6 Hz, 1H), 7.09–7.01 (m, 2H), 6.96–6.92 (m, 1H), 4.93 (s, 2H), 4.15 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 152.5, 149.1, 128.0, 124.8, 121.3, 120.2, 112.4, 96.7, 74.8, 64.9, 15.0; **IR** (neat, cm^{-1}): 3423, 2983, 2364, 1743, 1602, 1525, 1454, 1365, 1160, 1095, 1043, 817; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_3$ $[M+Na]^+$ 333.9780; found, 333.9790.

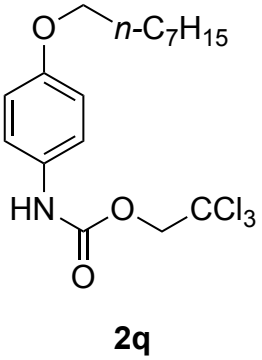


2p

2,2,2-trichloroethyl-*N*-4-isopropoxyphenylcarbamate (2p)

Following the general procedure for intermolecular amination, isopropoxybenzene (40.9 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2p** (36.2 mg, 55%) as white solid.

Analytical data: **m.p.** 109 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.99 (br s, 1H), 7.48 (br d, J = 8.6 Hz, 2H), 6.91–6.87 (m, 2H), 4.89 (s, 2H), 4.56 (sep, J = 6.0 Hz, 1H), 1.28 (d, J = 6.0 Hz, 6H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 155.1, 152.9, 132.3, 121.2, 117.1, 96.9, 74.7, 70.6, 22.3; **IR** (neat, cm^{-1}): 3286, 2969, 2360, 1739, 1540, 1435, 1373, 1226, 1099, 1052, 946, 821; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{12}H_{14}Cl_3NO_3$ $[M+Na]^+$ 347.9937; found, 347.9936.



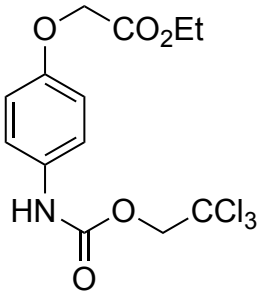
2q

2,2,2-trichloroethyl-*N*-4-octyloxyphenylcarbamate (2q)

Following the general procedure for intermolecular amination, *n*-octyloxybenzene (61.9 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude

material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2q** (44.5 mg, 56%) as a white amorphous.

Analytical data: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.99 (br s, 1H), 7.49 (br d, J = 8.6 Hz, 2H), 6.92–6.88 (m, 2H), 4.88 (s, 2H), 3.96 (t, J = 6.5 Hz, 2H), 1.79–1.72 (m, 2H), 1.50–1.43 (m, 2H), 1.41–1.25 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 156.4, 152.9, 132.3, 121.1, 115.5, 96.9, 74.7, 68.8, 32.6, 30.09, 30.06, 30.01, 26.8, 23.3, 14.4; **IR** (neat, cm^{-1}): 3357, 2921, 2362, 1716, 1525, 1473, 1417, 1363, 1216, 1106, 1043, 995, 833; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{17}H_{24}Cl_3NO_3$ $[M+Na]^+$ 418.0719; found, 418.0714.

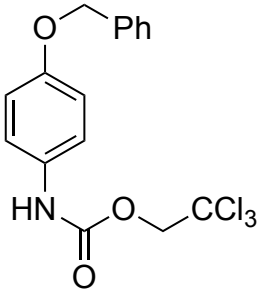


2r

2,2,2-trichloroethyl-*N*-4-ethoxycarbonylmethoxyphenylcarbamate (2r)

Following the general procedure for intermolecular amination, ethyl 2-phenoxyacetate (54.1 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification (AcOEt/hexane = 1/2) to afford **2r** (29.3 mg, 40%) as a white solid.

Analytical data: **m.p.** 95 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.05 (br s, 1H), 7.51 (br d, J = 8.7 Hz, 2H), 6.95–6.91 (m, 2H), 4.89 (s, 2H), 4.69 (s, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 169.4, 155.3, 152.9, 133.2, 121.0, 115.9, 96.8, 74.7, 66.1, 61.4, 14.5; **IR** (neat, cm^{-1}): 3297, 2989, 2360, 1718, 1540, 1448, 1378, 1201, 1106, 1054, 815; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{13}H_{14}Cl_3NO_5$ $[M+Na]^+$ 391.9835; found, 391.9836.



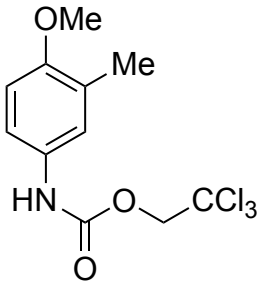
2s

2,2,2-trichloroethyl-*N*-4-benzyloxyphenylcarbamate (2s)

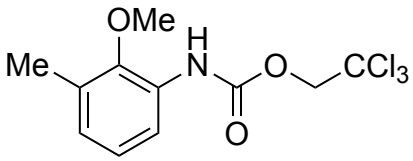
Following the general procedure for intermolecular amination, benzyloxybenzene (55.3 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude

material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2s** (33.4 mg, 45%) as a white solid.

Analytical data: **m.p.** 108 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.03 (br s, 1H), 7.51 (br d, J = 8.6 Hz, 2H), 7.49–7.46 (m, 2H), 7.41–7.36 (m, 2H), 7.34–7.30 (m, 1H), 7.02–6.98 (m, 2H), 5.10 (s, 2H), 4.89 (s, 2H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 156.0, 152.9, 138.5, 132.7, 129.3, 128.6, 128.4, 121.1, 116.0, 96.9, 74.7, 70.7; IR (neat, cm^{-1}): 3342, 2360, 1716, 1598, 1527, 1378, 1295, 1216, 1105, 1039, 821; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{16}H_{14}Cl_3NO_3$ $[M+Na]^+$ 395.9937; found, 395.9932.



2t



3t

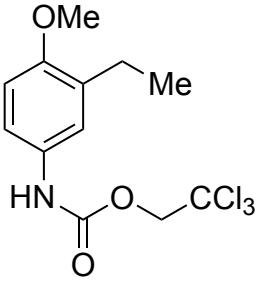
Following the general procedure for intermolecular amination, 2-methylanisole (36.7 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a mixture of **2t** and **3t** (31.4 mg, 50%, **2t**/**3t**=14/1) as a white solid. **2t** and **3t** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

2,2,2-trichloroethyl-*N*-(4-methoxy-3-methyl)phenylcarbamate (2t)

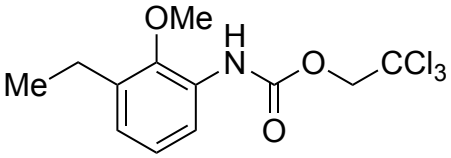
White solid: **m.p.** 92 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.91 (br s, 1H), 7.38–7.36 (m, 2H), 6.88 (d, J = 8.5 Hz, 1H), 4.88 (s, 2H), 3.80 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 155.0, 152.9, 132.0, 127.3, 122.5, 118.3, 111.1, 96.9, 74.7, 55.8, 16.4; **IR** (neat, cm^{-1}): 3278, 2360, 1704, 1544, 1508, 1440, 1228, 1132, 1105, 1035, 890, 806; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_3$ $[M+Na]^+$ 333.9780; found, 333.9780.

2,2,2-trichloroethyl-*N*-(2-methoxy-3-methyl)phenylcarbamate (3t)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.43 (br s, 1H), 7.82 (br d, J = 7.8 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.95 (dd, J = 7.6, 0.8 Hz, 1H), 4.93 (s, 2H), 3.76 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (125 MHz, acetone-d_6) δ: 152.9, 149.4, 132.0, 131.7, 127.0, 124.8, 119.2, 96.7, 74.9, 60.7, 16.0; **IR** (neat, cm^{-1}): 3280, 2952, 1704, 1546, 1508, 1440, 1365, 1226, 1105, 1035, 890, 806; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_3$ $[M+Na]^+$ 333.9780; found, 333.9773.



2u



3u

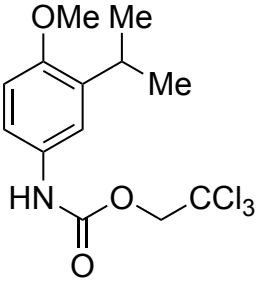
Following the general procedure for intermolecular amination, 2-ethylanisole (40.9 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a mixture of **2u** and **3u** (32.3 mg, 49%, **2u**/**3u**=16/1) as a white amorphous. **2u** and **3u** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

2,2,2-trichloroethyl-*N*-(3-ethyl-4-methoxy)phenylcarbamate (2u)

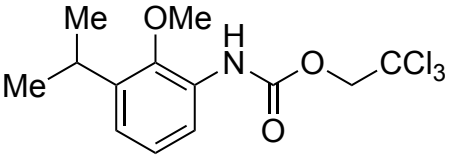
White amorphous: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.92 (br s, 1H), 7.40–7.37 (m, 2H), 6.90 (d, J = 8.6 Hz, 1H), 4.89 (s, 2H), 3.81 (s, 3H), 2.60 (q, J = 7.5 Hz, 2H), 1.15 (t, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 154.6, 152.8, 133.4, 132.3, 121.0, 111.5, 96.9, 74.7, 55.9, 23.9, 14.5; **IR** (neat, cm^{-1}): 3284, 2954, 1706, 1550, 1498, 1365, 1226, 1105, 1027, 970, 896, 819; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{12}H_{14}Cl_3NO_3$ $[M+Na]^+$ 347.9937; found, 347.9932.

2,2,2-trichloroethyl-*N*-(3-ethyl-2-methoxy)phenylcarbamate (3u)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.41 (br s, 1H), 7.81 (br d, J = 8.0 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 7.00 (dd, J = 7.7, 1.6 Hz, 1H), 4.93 (s, 2H), 3.77 (s, 3H), 2.68 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 1H); **^{13}C NMR** (125 MHz, acetone-d_6) δ: 153.0, 149.1, 137.9, 132.0, 125.4, 125.1, 119.5, 96.8, 74.9, 61.4, 23.2, 15.2; **IR** (neat, cm^{-1}): 3284, 2954, 1706, 1550, 1511, 1365, 1228, 1105, 1060, 1027, 970, 896, 819; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{12}H_{14}Cl_3NO_3$ $[M+Na]^+$ 347.9937; found, 347.9926.



2v



3v

Following the general procedure for intermolecular amination, 2-isopropylanisole (45.1 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a miture of **2v** and **3v** (29.0 mg, 43%, **2v**/**3v**=15/1) as colorless oil. **2v** and **3v** were isolated by further preparative TLC purification

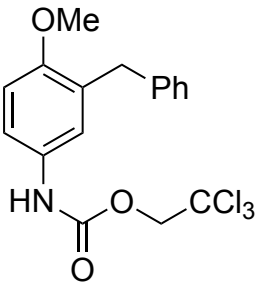
(AcOEt/hexane = 1/9).

2,2,2-trichloroethyl-*N*-(4-methoxy-3-isopropyl)phenylcarbamate (2v)

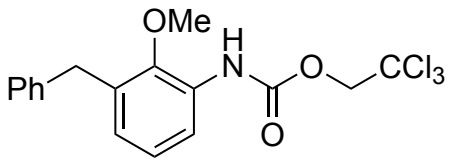
Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.93 (br s, 1H), 7.43–7.40 (m, 2H), 6.91 (d, J = 8.7 Hz, 1H), 4.89 (s, 2H), 3.82 (s, 3H), 3.29 (sep, J = 6.9 Hz, 1H), 1.18 (d, J = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 154.0, 152.8, 137.8, 132.5, 118.1, 118.0, 111.7, 96.9, 74.7, 56.0, 27.5, 22.9; **IR** (neat, cm^{-1}): 3290, 2969, 2360, 1739, 1540, 1363, 1216, 1108, 1031, 811; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{13}H_{16}Cl_3NO_3$ $[M+Na]^+$ 362.0093; found, 362.0090.

2,2,2-trichloroethyl-*N*-(2-methoxy-3-isopropyl)phenylcarbamate (3v)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.41 (br s, 1H), 7.79 (br d, J = 7.5 Hz, 1H), 7.11 (t, J = 7.9 Hz, 1H), 7.07 (dd, J = 7.8, 1.9 Hz, 1H), 4.94 (s, 2H), 3.76 (s, 3H), 3.33 (sep, J = 6.9 Hz, 1H), 1.22 (d, J = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, acetone-d_6) δ: 153.0, 148.4, 142.6, 131.9, 125.3, 122.6, 119.4, 96.8, 74.9, 61.9, 27.1, 24.0; **IR** (neat, cm^{-1}): 3290, 2969, 2362, 1785, 1540, 1506, 1365, 1216, 1108, 1033, 815; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{13}H_{16}Cl_3NO_3$ $[M+Na]^+$ 362.0093; found, 362.0084.



2w



3w

Following the general procedure for intermolecular amination, 2-methoxydiphenylmethane (59.5 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford a mixture of **2w** and **3w** (38.6 mg, 50%, **2w**/**3w**=13/1) as colorless oil. **2w** and **3w** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

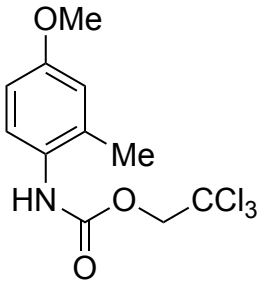
2,2,2-trichloroethyl-*N*-(3-benzyl-4-methoxy)phenylcarbamate (2w)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.95 (br s, 1H), 7.45 (br d, J = 8.1 Hz, 1H), 7.31 (br d, J = 1.7 Hz, 1H), 7.27–7.21 (m, 4H), 7.18–7.13 (m, 1H), 6.95 (d, J = 8.8 Hz, 1H), 4.86 (s, 2H), 3.94 (s, 2H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 154.5, 152.8, 141.8, 132.3, 130.9, 129.7, 129.1, 126.6, 122.3, 118.9, 111.8, 96.9, 74.7, 56.0, 36.4; **IR** (neat, cm^{-1}): 3315, 2969, 2360, 1739, 1540, 1506, 1436, 1365, 1216, 1118, 1029, 823; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{17}H_{16}Cl_3NO_3$ $[M+Na]^+$ 410.0093; found, 410.0092.

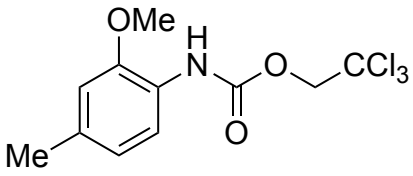
2,2,2-trichloroethyl-*N*-(3-benzyl-2-methoxy)phenylcarbamate (3w)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.48 (br s, 1H), 7.84 (br d, J = 8.0 Hz, 1H), 7.30–7.16 (m, 5H), 7.07 (t, J = 7.9 Hz, 1H), 6.92 (dd, J = 7.7, 1.4 Hz, 1H), 4.94 (s, 2H), 4.03 (s, 2H), 3.73 (s, 3H); **^{13}C NMR** (125 MHz, acetone-d_6) δ: 153.1, 149.5, 141.8, 135.4, 132.3, 129.7, 129.2, 127.0, 126.9, 125.0, 120.3,

111.6, 96.7, 74.9, 61.3, 36.2; **IR** (neat, cm^{-1}): 3315, 3025, 2358, 1735, 1535, 1504, 1454, 1365, 1216, 1118, 1029, 823; **HRMS-ESI**$^+$ (m/z): Calcd. for $C_{17}H_{16}Cl_3NO_3$ $[M+Na]^+$ 410.0093; found, 410.0096.



2x



3x

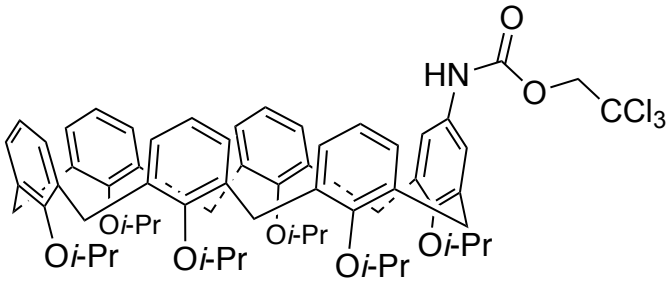
Following the general procedure for intermolecular amination, 3-methylanisole (36.7 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.), K_2CO_3 (21.6 mg, 0.30 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford a mixture of **2x** and **3x** (29.3 mg, 47%, **2x**/**3x**=4.0/1) as a white solid. **2x** and **3x** were isolated by further preparative TLC purification (AcOEt/hexane = 1/9).

2,2,2-trichloroethyl-*N*-(4-methoxy-2-methyl)phenylcarbamate (2x)

White solid: **m.p.** 83 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.37 (br s, 1H), 7.31 (br d, J = 8.4 Hz, 1H), 6.81 (d, J = 2.9 Hz, 1H), 6.76 (dd, J = 8.6, 2.9 Hz, 1H), 4.88 (s, 2H), 3.77 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 158.6, 154.0, 135.2, 129.5, 127.4, 116.4, 112.3, 97.1, 74.8, 55.6, 18.3; **IR** (neat, cm^{-1}): 3264, 3008, 2360, 1735, 1525, 1434, 1365, 1226, 1112, 1035, 846, 802; **HRMS-ESI**$^+$ (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_3$ $[M+Na]^+$ 333.9780; found, 333.9778.

2,2,2-trichloroethyl-*N*-(2-methoxy-4-methyl)phenylcarbamate (3x)

Colorless oil: **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.07 (br s, 1H), 7.81 (br d, J = 7.2 Hz, 1H), 6.88 (d, J = 1.2 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 4.90 (s, 2H), 3.87 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (125 MHz, acetone-d_6) δ: 152.6, 149.9, 134.7, 125.3, 121.7, 120.2, 112.5, 96.7, 74.8, 56.1, 21.2; **IR** (neat, cm^{-1}): 3272, 3006, 2360, 1739, 1525, 1455, 1365, 1226, 1112, 1035, 802; **HRMS-ESI**$^+$ (m/z): Calcd. for $C_{11}H_{12}Cl_3NO_3$ $[M+Na]^+$ 333.9780; found, 333.9775.

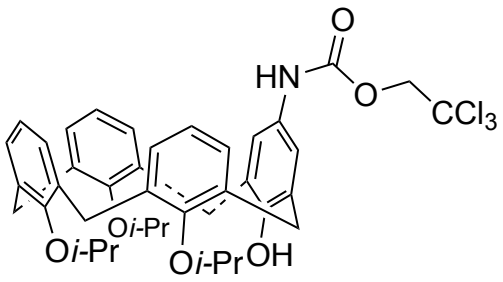


2y

2,2,2-trichloroethyl-*N*-(1^2,3^2,5^2,7^2,9^2,11^2-hexaisopropoxy-1,3,5,7,9,11(1,3)-hexabenzenacyclododecaphane-1^5-yl)carbamate (2y)

Following the general procedure for intermolecular amination, **1y** (88.9 mg, 0.10 mmol, 1.0 equiv.), TrocNHOTs (36.2 mg, 0.10 mmol, 1.0 equiv.), K_2CO_3 (21.6 mg, 0.15 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (6.8 mg, 5.0 μmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 2/1) to afford **2y** (42.9 mg, 40%) as a white solid.

Analytical data: **m.p.** 113 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.59 (br s, 1H), 7.12 (br s, 2H), 6.91–6.88 (m, 10H), 6.75–6.70 (m, 5H), 4.81 (s, 2H), 4.14–4.05 (m, 6H), 3.97 (br s, 12H), 1.09–1.05 (m, 36H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 154.4, 154.2, 152.4, 150.4, 136.0, 135.7, 135.6, 135.5, 135.3, 133.9, 129.7, 129.6, 129.5, 123.6, 120.4, 96.9, 75.4, 74.6, 32.5, 32.4, 22.71, 22.67; **IR** (neat, cm^{-1}): 2969, 2360, 1739, 1540, 1448, 1365, 1205, 1105, 939; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{63}H_{74}Cl_3NO_8$ $[M+Na]^+$ 1100.4378; found, 1100.4351.

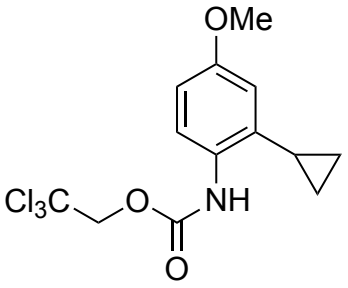


2z

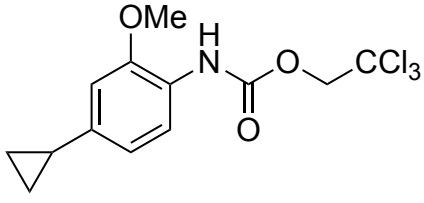
2,2,2-trichloroethyl-*N*-(1^2-hydroxy-3^2,5^2,7^2-triisopropoxy-1,3,5,7(1,3)-tetrabenzenacycloocataphane-1^5-yl)carbamate (2z)

Following the general procedure for intermolecular amination, **1z** (55.1 mg, 0.10 mmol, 1.0 equiv.), TrocNHOTs (36.2 mg, 0.10 mmol, 1.0 equiv.), K_2CO_3 (21.6 mg, 0.15 mmol, 1.5 equiv.), and $Rh_2(tpa)_4$ (6.8 mg, 5.0 μmol, 0.05 equiv.) were stirred at 0 °C in PhCl (1.0 mL) for 20 h. The crude material was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford **2z** (31.0 mg, 42%) as a white solid.

Analytical data: **m.p.** 177 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.92 (br s, 1H), 7.37 (br s, 2H), 7.21 (d, J = 7.5 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.40–6.33 (m, 6H), 4.91 (s, 2H), 4.57 (d, J = 13.0 Hz, 2H), 4.54–4.47 (m, 2H), 4.31 (d, J = 13.6 Hz, 2H), 3.97-4.06 (m, 2H), 3.27 (d, J = 13.7 Hz, 2H), 3.20 (d, J = 13.1 Hz, 2H), 1.48 (d, J = 6.1 Hz, 6H), 1.42 (d, J = 6.1 Hz, 6H), 1.30 (d, J = 6.1 Hz, 6H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 155.4, 153.7, 152.9, 150.5, 138.8, 135.0, 133.8, 132.3, 131.0, 128.6, 128.4, 123.5, 123.4, 120.1, 97.0, 78.1, 75.7, 74.7, 32.4, 32.0, 22.8, 22.2; **IR** (neat, cm^{-1}): 2969, 2360, 1739, 1540, 1455, 1365, 1205, 1153, 1106, 1052, 939; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{40}H_{44}Cl_3NO_6$ $[M+Na]^+$ 762.2132; found, 762.2128.



7



8

To a suspension of 3-cyclopropylanisole (**6**; 44.5 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.) and K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.) in PhCl (1.0 mL) were added $Rh_2(tpa)_4$ (13.6

mg, 0.010 mmol, 0.05 equiv.) at 0 °C. After being stirred for 20 h at 0 °C, the reaction was quenched by addition of water and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified by preparative TLC purification ($CHCl_3$/hexane = 1/1) to afford **7** (colorless oil; 20.9 mg, 31%) and **8** (colorless oil; 12.0 mg, 18%).

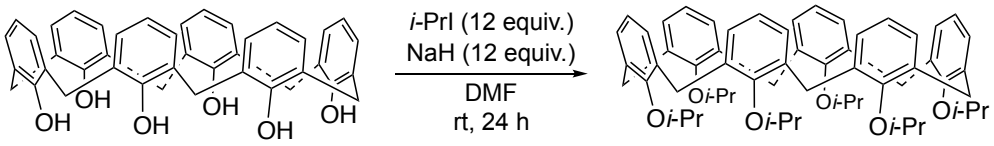
2,2,2-trichloroethyl-*N*-(4-methoxy-2-cyclopropyl)phenylcarbamate (7)

Analytical data: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.71 (br d, J = 7.8 Hz, 1H), 7.04 (br s, 1H), 6.77 (dd, J = 8.8, 2.7 Hz, 1H), 6.66 (s, 1H), 4.84 (s, 2H), 3.79 (s, 3H), 1.86–1.80 (m, 1H), 1.06–0.94 (m, 2H), 0.72–0.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 156.7, 152.3, 134.5, 129.8, 122.4, 114.0, 111.7, 95.6, 74.7, 55.6, 11.6, 6.3; **IR** (neat, cm^{-1}): 3423, 3004, 2358, 1739, 1521, 1365, 1203, 1099, 1033, 804; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{13}H_{14}Cl_3NO_3$ $[M+Na]^+$ 359.9937; found, 359.9938.

2,2,2-trichloroethyl-*N*-(2-methoxy-4-cyclopropyl)phenylcarbamate (8)

Analytical data: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.93 (br d, J = 7.9 Hz, 1H), 7.37 (br s, 1H), 6.68 (dd, J = 8.3, 1.8 Hz, 1H), 6.64 (d, J = 1.8 Hz, 1H), 4.82 (s, 2H), 3.88 (s, 3H), 1.91–1.84 (m, 1H), 1.00–0.88 (m, 2H), 0.72–0.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 151.5, 148.0, 139.8, 124.4, 118.5, 118.1, 108.3, 95.5, 74.4, 55.8, 15.5, 9.0; **IR** (neat, cm^{-1}): 3421, 3004, 2360, 1739, 1531, 1373, 1203, 1097, 1035, 808; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{13}H_{14}Cl_3NO_3$ $[M+Na]^+$ 359.9937; found, 359.9936.

Synthesis of substrates and characterization data of new compounds

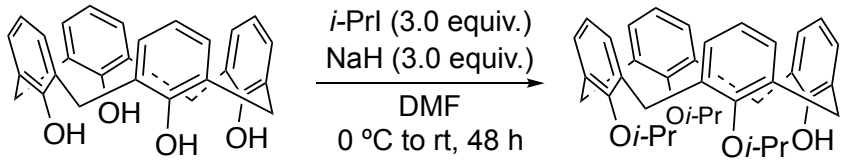


1y

1^2,3^2,5^2,7^2,9^2,11^2-hexaisopropoxy-1,3,5,7,9,11(1,3)-hexabenzenacyclododecaphane (1y)

To a solusion of calix[6]arene (200 mg, 0.31 mmol, 1.0 equiv.) in DMF (5.0 mL) were added NaH (150 mg, 3.8 mmol, 12 equiv.) and 2-iodopropane (0.38 ml, 3.8 mmol, 12 equiv.). After being stirred for 24 h at rt, the reaction was quenched by addition of water and extracted with AcOEt. The organic layer was washed with water, and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was chromatographed on silica gel (AcOEt/hexane = 1/19) to afford **1y** (216 mg, 64% yield) as a white solid.

Analytical data: **m.p.** 246 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.88 (d, J = 7.4 Hz, 12H), 6.70 (t, J = 7.5 Hz, 6H), 4.07–4.01 (m, 6H), 3.93 (br s, 12H), 1.02 (br d, J = 5.2 Hz, 36H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.5, 134.9, 128.9, 122.9, 74.8, 31.8, 22.4; **IR** (neat, cm^{-1}): 2969, 2358, 1739, 1540, 1448, 1367, 1216, 1106, 941; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{60}H_{72}O_6$ $[M+Na]^+$ 911.5227; found, 911.5214.

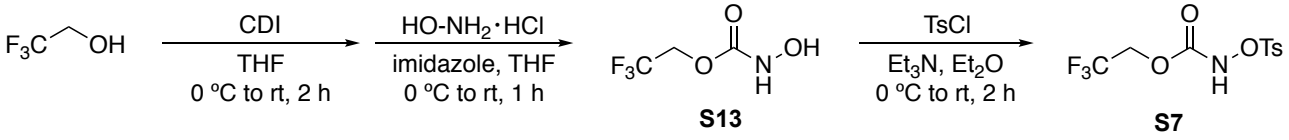


1z

3^2,5^2,7^2-triisopropoxy-1,3,5,7(1,3)-tetrabenzenacycloocataphane-1^2-ol (1z)

To a solusion of calix[4]arene (200 mg, 0.47 mmol, 1.0 equiv.) in DMF (5.0 mL) were added NaH (56 mg, 1.4 mmol, 3.0 equiv.) and 2-iodopropane (0.14 ml, 1.4 mmol, 3.0 equiv.) at 0 °C. After being stirred for 48 h at rt, the reaction was quenched by addition of water and extracted with AcOEt. The organic layer was washed with water, and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was chromatographed on silica gel (AcOEt/hexane = 1/19) to afford **1z** (110 mg, 46% yield) as a white solid.

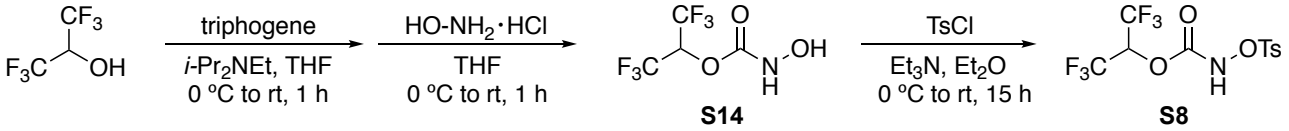
Analytical data: **m.p.** 197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.15 (d, J = 7.4 Hz, 2H), 7.09 (d, J = 7.4 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.4 Hz, 1H), 6.35–6.31 (m, 4H), 6.30–6.26 (m, 2H), 4.54 (d, J = 13.2 Hz, 2H), 4.44 (sep, J = 6.1 Hz, 1H), 4.38 (s, 1H), 4.33 (d, J = 13.8 Hz, 2H), 3.98 (sep, J = 6.1 Hz, 2H), 3.28 (d, J = 13.9 Hz, 2H), 3.15 (d, J = 13.3 Hz, 2H), 1.47 (d, J = 6.1 Hz, 6H), 1.40 (d, J = 6.1 Hz, 6H), 1.29 (d, J = 6.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.9, 153.4, 153.0, 138.3, 134.2, 133.4, 131.5, 129.3, 128.4, 127.8, 127.7, 122.7, 122.6, 119.3, 77.3, 75.3, 32.0, 31.5, 22.7, 22.4, 22.1; **IR** (neat, cm^{-1}): 2969, 2360, 1739, 1540, 1455, 1365, 1205, 1106, 939; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{37}H_{42}O_4$ $[M+Na]^+$ 573.2981; found, 573.2986.



2,2,2-trifluoroethyl-*N*-tosyloxycarbamate (S7)

To a solusion of 2,2,2-trifluoroethanol (0.72 mL, 10 mmol, 1.0 equiv.) in THF (20 mL) was added CDI (1.95 g, 12 mmol, 1.5 equiv.) at 0 °C. After being stirred for 2 h at rt, the solution was cooled to 0 °C. Imidazole (0.82 g, 12 mol, 1.5 equiv.) and hydroxylamine hydrochloride (3.47 g, 50 mol, 5.0 equiv.) were added to the reaction mixture. The reaction mixture was stirred at rt for 1 h and acidified with 1 N HCl. The resulting mixture was extracted with diethylether, the organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. To a solution of the residue in diethylether (20 mL) at 0 °C were added *p*-toluenesulfonyl chloride (1.90 g, 10 mmol, 1.0 equiv.) and triethylamine (1.39 mL, 10 mmol, 1.0 equiv.). The resulting white suspension was stirred at rt for 2 h. The reaction was quenched by addition of water and extracted with diethylether. The organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel ($CHCl_3$) to afford **S7** (0.80 g, 26% yield in 2 steps) as a white solid.

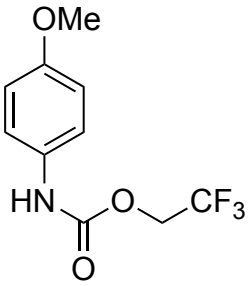
Analytical data: **m.p.** 115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.17 (br s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 4.38 (q, J = 8.2 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.9, 146.8, 130.0, 129.8, 129.7, 122.3 (J = 275.7 Hz), 62.0 (J = 37.2 Hz), 21.9; **IR** (neat, cm^{-1}): 3297, 2969, 2360, 1751, 1540, 1457, 1375, 1295, 1230, 1166, 1089, 997, 958, 844, 813; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{10}H_{10}F_3NO_5S$ $[M+Na]^+$ 336.0129; found, 336.0129.



1,1,1,3,3,3-hexafluoropropan-2-yl-*N*-tosyloxycarbamate (S8)

To a solution of 1,1,1,3,3,3-hexafluoro-2-propanol (1.04 mL, 10 mmol, 1.0 equiv.) and diisopropylethylamine (8.71 mL, 50 mmol, 5.0 equiv.) in THF (20 mL) was added triphosgene (1.04 g, 3.5 mmol, 0.35 equiv) at 0 °C. After being stirred for 1 h at rt, the solution was cooled to 0 °C and hydroxylamine hydrochloride (3.47 g, 50 mmol, 5.0 equiv.) was added to the solution. The reaction mixture was stirred at rt for 1 h and acidified with 1 N HCl. The resulting mixture was extracted with diethylether, the organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. To a solution of the residue in diethylether (20 mL) at 0 °C were added *p*-toluenesulfonyl chloride (1.90 g, 10 mmol, 1.0 equiv.) and triethylamine (1.39 mL, 10 mmol, 1.0 equiv.). The resulting white suspension was stirred at rt for 15 h. The reaction was quenched by addition of water and extracted with diethylether. The organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated *in vauo*. The residue was chromatographed on silica gel ($CHCl_3$) to afford **S8** (0.14 g, 4% yield in 2 steps) as a white solid.

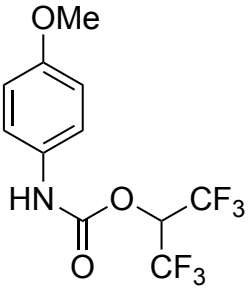
Analytical data: **m.p.** 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.57 (br s, 1H), 7.89–7.86 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 5.45 (sep, J = 5.9 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 151.9, 147.2, 130.2, 129.7, 129.5, 120.0 (J = 280.3 Hz), 68.5 (J = 35.2 Hz), 21.9; **IR** (neat, cm^{-1}): 3291, 2969, 2360, 1739, 1540, 1455, 1363, 1216, 1106, 1039, 998, 887, 813; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_9F_6NO_5S$ $[M+Na]^+$ 404.0003; found, 404.0002.



S1

2,2,2-trifluoroethyl-*N*-4-methoxyphenylcarbamate (S1)

White solid: **m.p.** 85 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 8.91 (br s, 1H), 7.47 (br d, J = 8.6 Hz, 2H), 6.92–6.88 (m, 2H), 4.70 (q, J = 8.9 Hz, 2H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 157.0, 152.8, 132.3, 124.7 (J = 275.2 Hz), 121.2, 114.9, 61.0 (J = 35.6 Hz), 55.7; **IR** (neat, cm^{-1}): 3315, 2969, 2360, 1716, 1533, 1417, 1365, 1292, 1228, 1162, 1097, 1029, 993, 956, 827; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{10}H_{10}F_3NO_3$ $[M+Na]^+$ 272.0510; found, 272.0506.

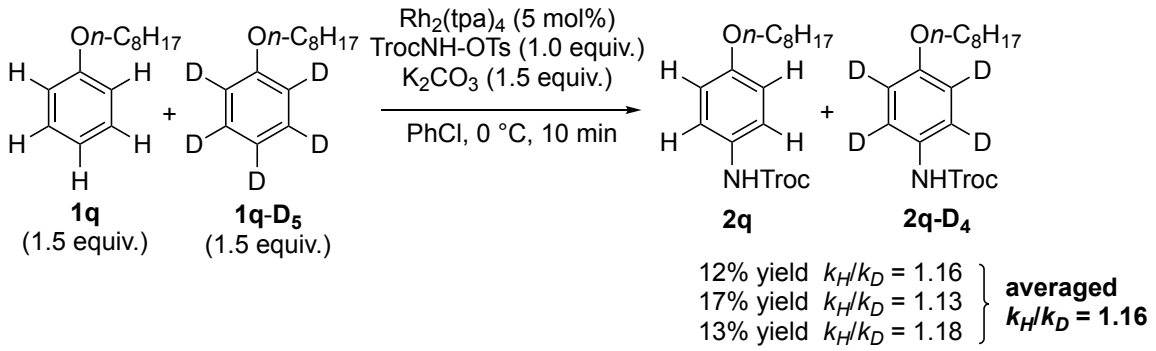


S2

1,1,1,3,3,3-hexafluoropropan-2-yl-*N*-4-methoxyphenylcarbamate (S2)

White solid: **m.p.** 108 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ: 9.39 (br s, 1H), 7.49 (d, J = 9.0 Hz, 2H), 6.96–6.92 (m, 2H), 6.26 (sep, J = 6.4 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ: 157.5, 151.0, 131.4, 122.1 (q, J = 281.0 Hz), 121.6, 115.1, 67.9 (sep, J = 34.0 Hz), 55.7; **IR** (neat, cm^{-1}): 3303, 2969, 2358, 1727, 1540, 1457, 1380, 1216, 1103, 1033, 998, 887, 825; **HRMS-ESI$^+$** (m/z): Calcd. for $C_{11}H_9F_6NO_3$ $[M+Na]^+$ 340.0384; found, 340.0380.

KIE Measurements (Scheme 4a)



To a suspension of *n*-octyloxybenzene (**1q**; 61.9 mg, 0.30 mmol, 1.5 equiv.), *n*-octyloxybenzene-d_5 (**1q-D$_5$**; 61.9 mg, 0.30 mmol, 1.5 equiv.), TrocNHOTs (72.5 mg, 0.20 mmol, 1.0 equiv.) and K_2CO_3 (41.6 mg, 0.30 mmol, 1.5 equiv.) in PhCl (1.0 mL) was added $Rh_2(tpa)_4$ (13.6 mg, 0.010 mmol, 0.05 equiv.) at 0 °C. After being stirred for 10 min at 0 °C, the reaction was quenched by addition of water and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated *in vauo*. ^{1}H NMR of the crude material (acetone-d_6) was measured using 1,1,2,2-tetrachloroethane as internal standard to confirm no decomposition of the starting materials (**1q**,**1q-D$_5$**) and the products (**2q**, **2q-D$_4$**). The residue was purified by preparative TLC purification ($CHCl_3$/hexane =1/1) to afford a mixture of **2q** and **2q-D$_4$**. KIE was calculated from the comparison of the integrals between an aromatic signal (δ 6.92-6.88 ppm, 2H of **2q**) and a trichloroethyl signal (δ 4.88 ppm, 2H of **2q** and **2q-D$_4$**) in ^{1}H NMR of a solution of **2q** and **2q-D$_4$** (acetone-d_6). The experiments were performed three times and the determined KIE was the average of three runs.

X-Ray crystallographic analysis

Single crystal of [**2z**·1/2(C_2H_5OH)] was obtained from recrystallization in C_2H_5OH at room temperature. Intensity data were collected on a RIGAKU Saturn70 CCD (system) with VariMax Mo Optic Using MoKα radiation (λ = 0.71070 Å). Crystal data are summarized in Table S3. The structure was solved by a direct method (SHELXT-2014[4]) and refined by a full-matrix least square method on F^2 for all reflections (SHELXL-2014[4]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC-1581717 (**2z**) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

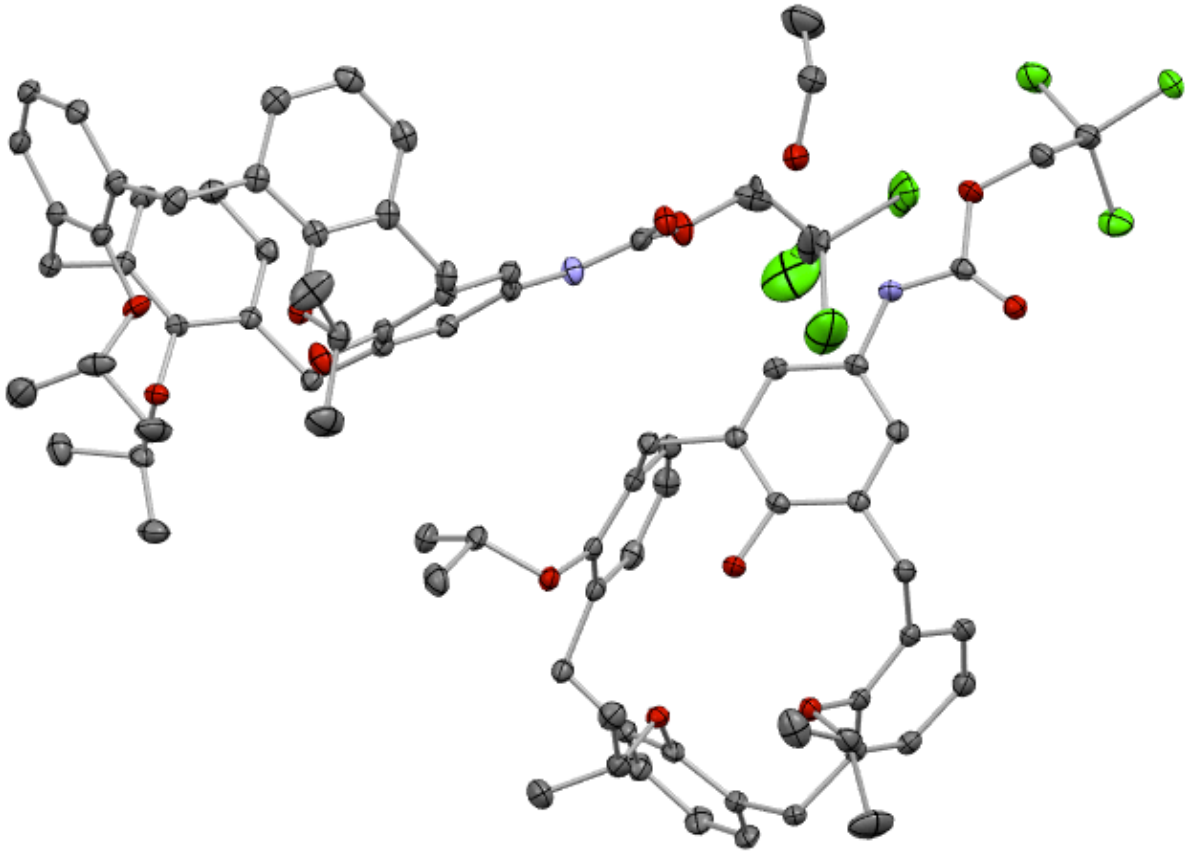


Figure S1 Molecular structure of **2z** (ORTEP drawing; thermal ellipsoids set at 50% probability). Hydrogen atoms were omitted for clarity.

Table S3. Crystal data and structure refinement for [**2z**·1/2(C_2H_5OH)].

CCDC No.	1581717	
Identification code	CD	
Empirical formula	$C_{82}H_{94}Cl_6N_2O_{13}$	
Formula weight	1528.29	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1 (#2)	
Unit cell dimensions	a = 10.6018(2) Å	α= 82.0000(10)°.
	b = 17.0612(3) Å	β= 82.577(2)°.
	c = 21.6709(3) Å	γ = 87.1720(10)°.
Volume	3847.18(11) $Å^3$	
Z	2	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.288 mm^{-1}	
F(000)	1612	
Crystal size	0.230 x 0.150 x 0.070 mm^3	
Theta range for data collection	1.636 to 31.268°	
Index ranges	-14<=h<=15, -24<=k<=24, -31<=l<=31	
Reflections collected	71592	
Independent reflections	22696 [R(int) = 0.0485]	
Completeness to theta = 25.242°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22696 / 0 / 990	
Goodness-of-fit on F2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1132	
R indices (all data)	R1 = 0.0801, wR2 = 0.1267	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.455 and -0.478 e.$Å^{-3}$	

Computational details

All calculation reported in the present study were carried out using density functional theory (DFT) with (U)M06[5] functional, as implemented in the Gaussian 09 (Revision E.01)[6]. For geometry optimizations, the 6-31G(d,p) basis set was used for the H, C, N, O, Cl elements, and the LANL2DZ[7] basis set and pseudopotential for Rh. Based on these optimized geometries, single-point energy calculations were performed using the 6-311++G(2d,2p) basis set for the H, C, N, O, Cl elements, and the SDD[8] basis set and pseudopotential for Rh with solvents effects simulated by SMD[9] solvent model (chlorobenzene). The stationary points were confirmed as minima (no imaginary frequencies) or transition state (only one imaginary frequency) by analytical frequency calculations as the same theory level as the geometry optimizations. Computational time was generously provided by the Supercomputer Laboratory in the Institute for Chemical Research of Kyoto University.

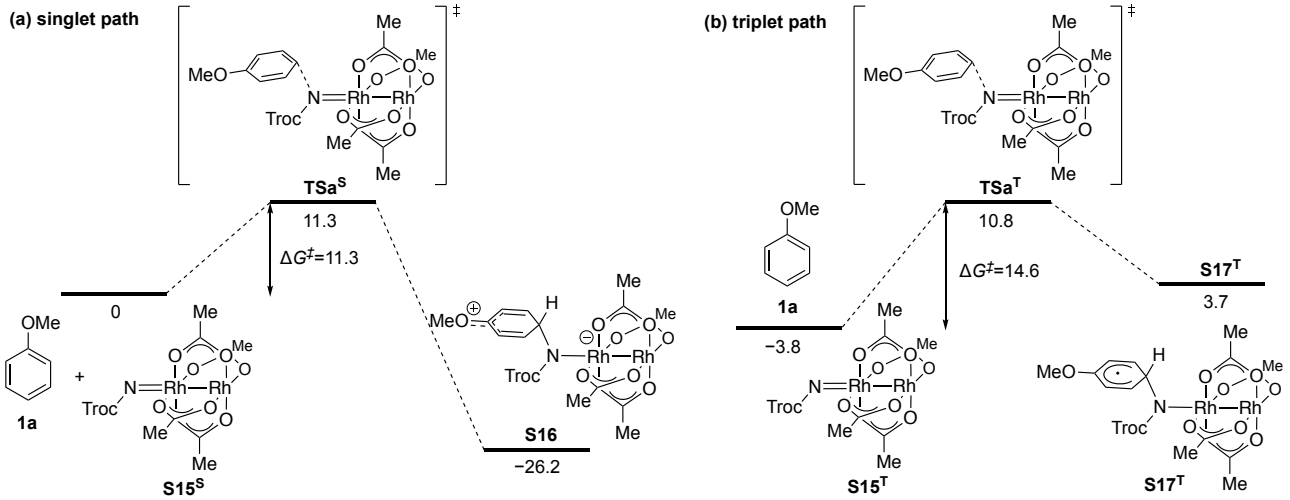
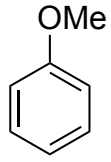


Figure S2. Energy diagram of addition reaction of anisole (**1a**) to rhodium nitrenoid **S15**. (a) singlet path. (b) triplet path. The relative Gibbs free energy differences are shown in kcal/mol.

XYZ coordinates and thermochemical data (energies in Hartree)

Temperature = 273.00 K, Pressure = 1.00 atm

anisole (**1a**)



6-31G(d,p)[LANL2DZ]

Electronic Energy = –346.5299769 Electronic and Zero-Point Energy = –346.3976109

Enthalpy = –346.3907539 Free Energy = –346.4257079

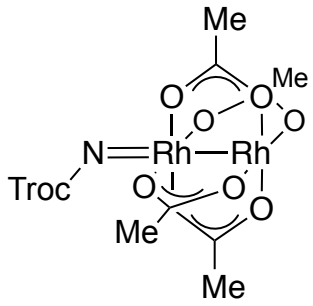
6-311++G(2d,2p)[SDD]

Electronic Energy = –346.6276983

C	-0.000007467	0.000000033	0.000000019
C	-0.000009314	-0.000011134	-0.000000002

C	-0.000001643	-0.000018861	-0.000000002
C	0.000008880	-0.000014949	0.000000005
C	0.000011652	-0.000004516	-0.000000007
C	0.000003033	0.000002679	-0.000000054
H	-0.000013678	0.000005392	0.000000001
H	-0.000017838	-0.000013612	0.000000007
H	-0.000003353	-0.000026981	-0.000000002
H	0.000015430	-0.000021016	-0.000000007
H	0.000019490	-0.000001646	-0.000000004
H	-0.000001259	0.000021308	0.000000006
H	0.000002661	0.000028759	-0.000000018
H	-0.000006506	0.000020711	-0.000000001
H	-0.000006507	0.000020697	-0.000000001
O	0.000006417	0.000013135	0.000000059

Rhodium nitrenoid **S15**[S]



6-31G(d,p)[LANL2DZ]

Electronic Energy = –2833.52349 Electronic and Zero-Point Energy = –2833.255374

Enthalpy = –2833.227067 Free Energy = –2833.314106

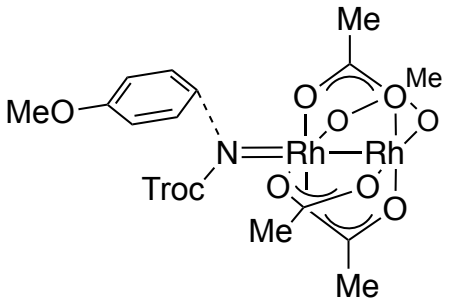
6-311++G(2d,2p)[SDD]

Electronic Energy = –2836.132154

Rh	0.000002686	0.000002787	0.000005616
Rh	-0.000001629	0.000000304	0.000001338
O	0.000001324	-0.000000116	-0.000000784
O	0.000005401	0.000002126	0.000003282
O	-0.000000428	0.000003479	0.000008449
O	-0.000004407	0.000001220	0.000004412
O	0.000001738	-0.000000297	-0.000001301
O	0.000005779	0.000001948	0.000002760
O	-0.000000341	0.000003156	0.000007694
O	-0.000004469	0.000000874	0.000003605
C	0.000004147	0.000000892	0.000000698
C	0.000006266	0.000000462	-0.000000990
H	0.000004421	-0.000000186	-0.000001969
H	0.000007927	-0.000000157	-0.000003078

H	0.000008007	0.000001468	0.000000809
C	-0.000003264	0.000002601	0.000007289
C	-0.000005475	0.000003139	0.000009315
H	-0.000008350	0.000002680	0.000009209
H	-0.000005056	0.000002739	0.000008242
H	-0.000004686	0.000004334	0.000011921
C	-0.000003042	0.000002157	0.000006168
C	-0.000005316	0.000002474	0.000007742
H	-0.000007994	0.000002430	0.000008478
H	-0.000004000	0.000003583	0.000009908
H	-0.000005577	0.000001670	0.000005852
C	0.000004549	0.000000632	-0.000000115
C	0.000006690	0.000000010	-0.000002255
H	0.000005167	-0.000000316	-0.000002454
H	0.000007128	-0.000001001	-0.000004780
H	0.000009294	0.000000826	-0.000001186
N	-0.000004742	-0.000001694	-0.000002345
C	-0.000004070	-0.000002687	-0.000005006
O	-0.000006185	-0.000003063	-0.000005307
O	-0.000001199	-0.000003101	-0.000007007
C	-0.000000222	-0.000004070	-0.000009554
H	-0.000002192	-0.000004304	-0.000009535
H	0.000002459	-0.000003476	-0.000009132
C	-0.000000156	-0.000005420	-0.000012972
Cl	-0.000004464	-0.000006440	-0.000013848
Cl	0.000003061	-0.000005120	-0.000013180
Cl	0.000001220	-0.000006543	-0.000015988

Transition state for addition **TSa**^{S}



6-31G(d,p)[LANL2DZ]

Electronic Energy = –3180.059837 Electronic and Zero-Point Energy = –3179.657275

Enthalpy = –3179.622549 Free Energy = –3179.722223

6-311++G(2d,2p)[SDD]

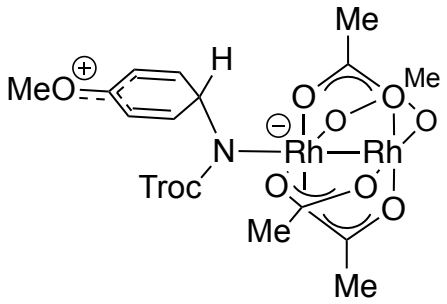
Electronic Energy = –3182.76573

Rh	-0.000000781	-0.000000533	-0.000009624

Rh	0.000000249	0.000001029	-0.000003455
O	0.000003302	0.000009034	-0.000003651
O	0.000002370	0.000007606	-0.000009285
O	-0.000000839	-0.000001932	-0.000002197
O	0.000000088	-0.000000344	0.000003564
O	0.000000177	0.000002131	-0.000010788
O	-0.000000629	0.000001061	-0.000016617
O	-0.000003854	-0.000008603	-0.000009777
O	-0.000002949	-0.000007167	-0.000003749
C	0.000003532	0.000010523	-0.000006475
C	0.000005895	0.000016456	-0.000006344
H	0.000006630	0.000017649	-0.000001876
H	0.000006678	0.000018730	-0.000008039
H	0.000006121	0.000017401	-0.000008870
C	-0.000000419	-0.000001469	0.000002656
C	-0.000000399	-0.000002252	0.000007875
H	0.000001212	0.000001708	0.000009541
H	-0.000001267	-0.000004369	0.000006774
H	-0.000001040	-0.000004452	0.000011244
C	-0.000004284	-0.000010138	-0.000006795
C	-0.000006488	-0.000016016	-0.000006906
H	-0.000007520	-0.000018233	-0.000009441
H	-0.000006771	-0.000016441	-0.000008724
H	-0.000006873	-0.000017629	-0.000002493
C	-0.000000148	0.000001876	-0.000015698
C	-0.000000206	0.000002652	-0.000020839
H	0.000000940	0.000005541	-0.000019906
H	0.000000089	0.000004008	-0.000024568
H	-0.000001741	-0.000001205	-0.000021813
N	0.000001058	0.000002571	0.000001948
C	0.000001310	0.000003680	-0.000001014
O	0.000003036	0.000008288	-0.000002402
O	-0.000000387	-0.000000664	-0.000002576
C	-0.000000155	0.000000546	-0.000006299
H	0.000001417	0.000004861	-0.000007421
H	-0.000001265	-0.000001791	-0.000010197
C	-0.000000580	-0.000000992	-0.000003518
Cl	0.000001213	0.000002773	0.000002820
Cl	-0.000003174	-0.000008050	-0.000001751
Cl	-0.000000332	0.000000486	-0.000008702
C	0.000001189	0.000000611	0.000016171
C	0.000000311	-0.000001038	0.000012728
C	-0.000002195	-0.000006834	0.000007508

C	-0.000001348	-0.000005234	0.000010923
C	0.000000341	-0.000001451	0.000015224
H	0.000002479	0.000003516	0.000019517
H	0.000001026	0.000000618	0.000013230
H	-0.000003467	-0.000009719	0.000004094
H	-0.000001956	-0.000006730	0.000010349
C	-0.000001272	-0.000004589	0.000008228
H	-0.000002038	-0.000006268	0.000005862
O	0.000001095	0.000000019	0.000018201
C	0.000002807	0.000003915	0.000022494
H	0.000003159	0.000004559	0.000024253
H	0.000004174	0.000007749	0.000020650
H	0.000002481	0.000002543	0.000025957

Adduct **S16**^{S}



6-31G(d,p)[LANL2DZ]

Electronic Energy = –3180.108683 Electronic and Zero-Point Energy = –3179.705076

Enthalpy = –3179.669879 Free Energy = –3179.77216

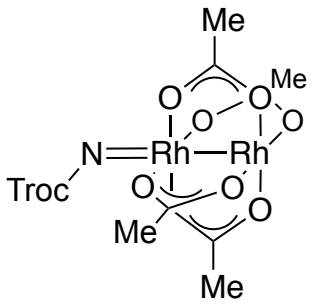
6-311++G(2d,2p)[SDD]

Electronic Energy = –3182.824452

Rh	-0.000001709	0.000012123	-0.000005816
Rh	-0.000001261	0.000004762	-0.000002013
O	-0.000000878	0.000003668	-0.000001569
O	-0.000001337	0.000010595	-0.000005174
O	0.000005052	0.000011012	-0.000008217
O	0.000005597	0.000004020	-0.000004665
O	-0.000007940	0.000005857	0.000000417
O	-0.000008453	0.000012676	-0.000003159
O	-0.000002329	0.000013045	-0.000006192
O	-0.000001716	0.000006211	-0.000002620
C	-0.000001290	0.000006797	-0.000003180
C	-0.000001025	0.000005816	-0.000002699
H	0.000001254	0.000002880	-0.000002132
H	-0.000004258	0.000005423	-0.000001058
H	-0.000000103	0.000008379	-0.000004509

C	0.000006760	0.000007353	-0.000007098
C	0.000011963	0.000006764	-0.000009037
H	0.000013393	0.000004174	-0.000008234
H	0.000013190	0.000006037	-0.000009173
H	0.000012935	0.000009662	-0.000011035
C	-0.000001912	0.000010033	-0.000004499
C	-0.000002590	0.000010985	-0.000004855
H	-0.000001391	0.000013843	-0.000006925
H	-0.000006045	0.000011481	-0.000003573
H	-0.000000848	0.000008351	-0.000004171
C	-0.000010257	0.000009443	-0.000000633
C	-0.000014972	0.000009943	0.000001252
H	-0.000016115	0.000008251	0.000002704
H	-0.000015780	0.000008492	0.000002399
H	-0.000016524	0.000013246	0.000000156
N	-0.000000413	-0.000001834	0.000001187
C	-0.000002309	-0.000004313	0.000003631
O	-0.000005710	-0.000004127	0.000004623
O	-0.000001478	-0.000008639	0.000005299
C	-0.000004055	-0.000011351	0.000008019
H	-0.000002039	-0.000014381	0.000008729
H	-0.000006560	-0.000010160	0.000008439
C	-0.000006090	-0.000012547	0.000009595
Cl	-0.000001998	-0.000015073	0.000009109
Cl	-0.000009202	-0.000007984	0.000008436
Cl	-0.000009551	-0.000016164	0.000013071
C	0.000007831	-0.000009763	0.000001873
C	0.000006194	-0.000006833	0.000000973
C	0.000000916	-0.000003155	0.000001385
C	0.000002400	-0.000006175	0.000002253
C	0.000005917	-0.000009536	0.000002655
H	0.000010385	-0.000012420	0.000002121
H	0.000007408	-0.000006989	0.000000439
H	-0.000001846	-0.000000610	0.000001136
H	0.000001028	-0.000006249	0.000002922
C	0.000002772	-0.000003189	0.000000515
H	0.000004689	-0.000000624	-0.000001767
O	0.000006954	-0.000012373	0.000003563
C	0.000010228	-0.000016009	0.000004178
H	0.000010553	-0.000017816	0.000004996
H	0.000009181	-0.000017834	0.000005629
H	0.000013381	-0.000015173	0.000002300

Rhodium nitrenoid S15^{T}



6-31G(d,p)[LANL2DZ]

Electronic Energy = –2833.530333 Electronic and Zero-Point Energy = –2833.262826

Enthalpy = –2833.235075 Free Energy = –2833.321382

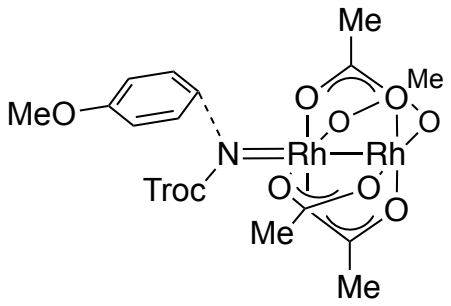
6-311++G(2d,2p)[SDD]

Electronic Energy = –2836.137797

Rh	-0.000000573	0.000000686	-0.000002045
Rh	0.000000673	0.000001570	-0.000000674
O	-0.000002057	-0.000001884	-0.000001686
O	-0.000003253	-0.000002421	-0.000003412
O	-0.000000934	0.000003107	-0.000005858
O	-0.000000070	0.000003567	-0.000004708
O	0.000001339	-0.000000473	0.000003290
O	-0.000000164	-0.000001712	0.000001854
O	0.000002152	0.000003819	-0.000000625
O	0.000003217	0.000004891	0.000000201
C	-0.000003416	-0.000003032	-0.000002902
C	-0.000005340	-0.000005346	-0.000003813
H	-0.000005726	-0.000004685	-0.000005413
H	-0.000005329	-0.000006680	-0.000002077
H	-0.000006378	-0.000006336	-0.000004619
C	-0.000000697	0.000003951	-0.000006359
C	-0.000001079	0.000005552	-0.000009226
H	0.000000110	0.000007316	-0.000009109
H	-0.000002308	0.000004434	-0.000010256
H	-0.000001381	0.000006003	-0.000010417
C	0.000003434	0.000005267	0.000000136
C	0.000005385	0.000007620	0.000000991
H	0.000005832	0.000009360	-0.000000326
H	0.000005417	0.000007787	0.000000842
H	0.000006378	0.000007518	0.000003106
C	0.000000740	-0.000001709	0.000003653
C	0.000001184	-0.000003283	0.000006529
H	0.000002698	-0.000001942	0.000007854
H	0.000000897	-0.000004372	0.000007353

H	0.000000371	-0.000004574	0.000006581
N	0.000001276	0.000001674	0.000000442
C	0.000000195	-0.000000320	0.000000786
O	-0.000000650	-0.000000403	-0.000000813
O	0.000000193	-0.000002155	0.000003141
C	-0.000000958	-0.000004370	0.000003693
H	-0.000001818	-0.000004358	0.000001929
H	-0.000001833	-0.000006102	0.000004129
C	0.000000298	-0.000004414	0.000006236
Cl	0.000001741	-0.000001691	0.000005620
Cl	0.000001727	-0.000004497	0.000009159
Cl	-0.000001294	-0.000007363	0.000006816

Transition state for addition TSa^{T}



6-31G(d,p)[LANL2DZ]

Electronic Energy = –3180.060809 Electronic and Zero-Point Energy = –3179.658762

Enthalpy = –3179.624076 Free Energy = –3179.723915

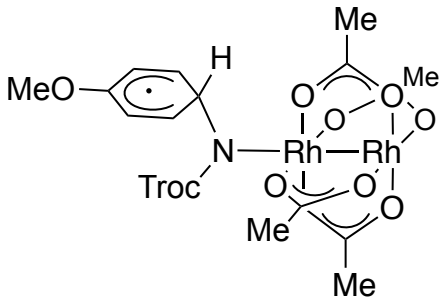
6-311++G(2d,2p)[SDD]

Electronic Energy = –3182.76591

Rh	-0.000000966	-0.000002429	0.000000313
Rh	-0.000000055	-0.000001339	-0.000000077
O	-0.000001455	-0.000001406	0.000000800
O	-0.000002320	-0.000002640	0.000001116
O	-0.000001489	-0.000000774	0.000000847
O	-0.000000431	0.000000287	0.000000271
O	0.000000231	-0.000003047	-0.000000485
O	-0.000000467	-0.000004047	-0.000000193
O	0.000000413	-0.000002148	-0.000000513
O	0.000001254	-0.000001366	-0.000001050
C	-0.000002297	-0.000002028	0.000001239
C	-0.000003272	-0.000002086	0.000001809
H	-0.000003445	-0.000001143	0.000002011
H	-0.000003090	-0.000002730	0.000001730
H	-0.000003881	-0.000002593	0.000002192

C	-0.000000954	0.000000135	0.000000686
C	-0.000001405	0.000001380	0.000000912
H	-0.000000629	0.000001771	0.000000665
H	-0.000001335	0.000002098	0.000001145
H	-0.000002057	0.000001315	0.000001419
C	0.000001351	-0.000001842	-0.000000928
C	0.000002262	-0.000001671	-0.000001607
H	0.000002547	-0.000000691	-0.000001691
H	0.000002134	-0.000002020	-0.000001572
H	0.000002855	-0.000002176	-0.000002058
C	0.000000054	-0.000004071	-0.000000374
C	0.000000298	-0.000005192	-0.000000788
H	0.000001162	-0.000005203	-0.000001357
H	0.000000092	-0.000005290	-0.000000639
H	0.000000027	-0.000005967	-0.000000650
N	0.000000676	-0.000000385	-0.000000358
C	-0.000000113	0.000000256	-0.000000164
O	0.000000095	0.000000049	0.000000028
O	-0.000000673	0.000000998	0.000000591
C	-0.000001426	0.000001522	0.000001026
H	-0.000001877	0.000000771	0.000001291
H	-0.000000983	0.000002086	0.000000880
C	-0.000002113	0.000002287	0.000001568
Cl	-0.000002813	0.000001340	0.000001941
Cl	-0.000001379	0.000003505	0.000001262
Cl	-0.000003037	0.000002911	0.000002247
C	0.000001490	0.000002880	-0.000000689
C	0.000001457	0.000001839	-0.000000817
C	0.000002401	0.000000704	-0.000001467
C	0.000002269	0.000001665	-0.000001279
C	0.000001895	0.000002813	-0.000000928
H	0.000001163	0.000003703	-0.000000333
H	0.000001211	0.000001877	-0.000000537
H	0.000002829	-0.000000098	-0.000001804
H	0.000002754	0.000001708	-0.000001525
C	0.000001820	0.000000785	-0.000001018
H	0.000002198	0.000000033	-0.000001346
O	0.000002010	0.000003690	-0.000000753
C	0.000001353	0.000004778	-0.000000338
H	0.000001404	0.000005360	-0.000000279
H	0.000000518	0.000004566	0.000000162
H	0.000001740	0.000005270	-0.000000534

Adduct S17^{T}



6-31G(d,p)[LANL2DZ]

Electronic Energy = –3180.073154 Electronic and Zero-Point Energy = –3179.669694

Enthalpy = –3179.635022 Free Energy = –3179.735237

6-311++G(2d,2p)[SDD]

Electronic Energy = –3182.778225

Rh	0.000004910	0.000018536	-0.000000237
Rh	0.000001919	0.000007490	-0.000000123
O	0.000009850	0.000003170	0.000002729
O	0.000012624	0.000013490	0.000002631
O	0.000011045	0.000020756	0.000001430
O	0.000008448	0.000010316	0.000001621
O	-0.000004241	0.000005488	-0.000001809
O	-0.000001520	0.000015809	-0.000001958
O	-0.000003140	0.000022748	-0.000003145
O	-0.000005789	0.000012398	-0.000002933
C	0.000013338	0.000007091	0.000003451
C	0.000019101	0.000003652	0.000005542
H	0.000023055	0.000002689	0.000006852
H	0.000017423	-0.000001429	0.000005505
H	0.000021128	0.000006974	0.000005857
C	0.000011472	0.000016281	0.000002036
C	0.000016310	0.000017848	0.000003355
H	0.000013973	0.000016480	0.000002750
H	0.000020715	0.000014591	0.000005018
H	0.000017911	0.000023335	0.000003325
C	-0.000006717	0.000018907	-0.000003801
C	-0.000012187	0.000022181	-0.000005850
H	-0.000010676	0.000022887	-0.000005432
H	-0.000013328	0.000027281	-0.000006660
H	-0.000016677	0.000018754	-0.000006908
C	-0.000004627	0.000009985	-0.000002348
C	-0.000009306	0.000008119	-0.000003609
H	-0.000014465	0.000008211	-0.000005238
H	-0.000008397	0.000002770	-0.000002845

H	-0.000008636	0.000011779	-0.000003772
H	-0.000000904	-0.000001940	-0.000000090
C	0.000002236	-0.000007782	0.000001440
O	-0.000000034	-0.000011376	0.000001090
O	0.000008312	-0.000008503	0.000003334
C	0.000012560	-0.000013412	0.000005114
H	0.000017479	-0.000010897	0.000006411
H	0.000010511	-0.000015289	0.000004676
C	0.000013328	-0.000019681	0.000005960
Cl	0.000016650	-0.000016939	0.000006710
Cl	0.000005493	-0.000024195	0.000003960
Cl	0.000019121	-0.000025367	0.000008269
C	-0.000009765	-0.000015219	-0.000001584
C	-0.000006098	-0.000009068	-0.000001017
C	-0.000012831	-0.000004390	-0.000003541
C	-0.000016405	-0.000010515	-0.000004063
C	-0.000014937	-0.000016078	-0.000003085
H	-0.000008724	-0.000019343	-0.000000878
H	-0.000002050	-0.000008439	0.000000148
H	-0.000013893	-0.000000203	-0.000004247
H	-0.000020584	-0.000011354	-0.000005277
C	-0.000006980	-0.000003213	-0.000001870
H	-0.000007603	0.000001833	-0.000002522
O	-0.000018898	-0.000021870	-0.000003746
C	-0.000017576	-0.000027666	-0.000002852
H	-0.000021148	-0.000031812	-0.000003537
H	-0.000012443	-0.000029479	-0.000001076
H	-0.000018333	-0.000026392	-0.000003160

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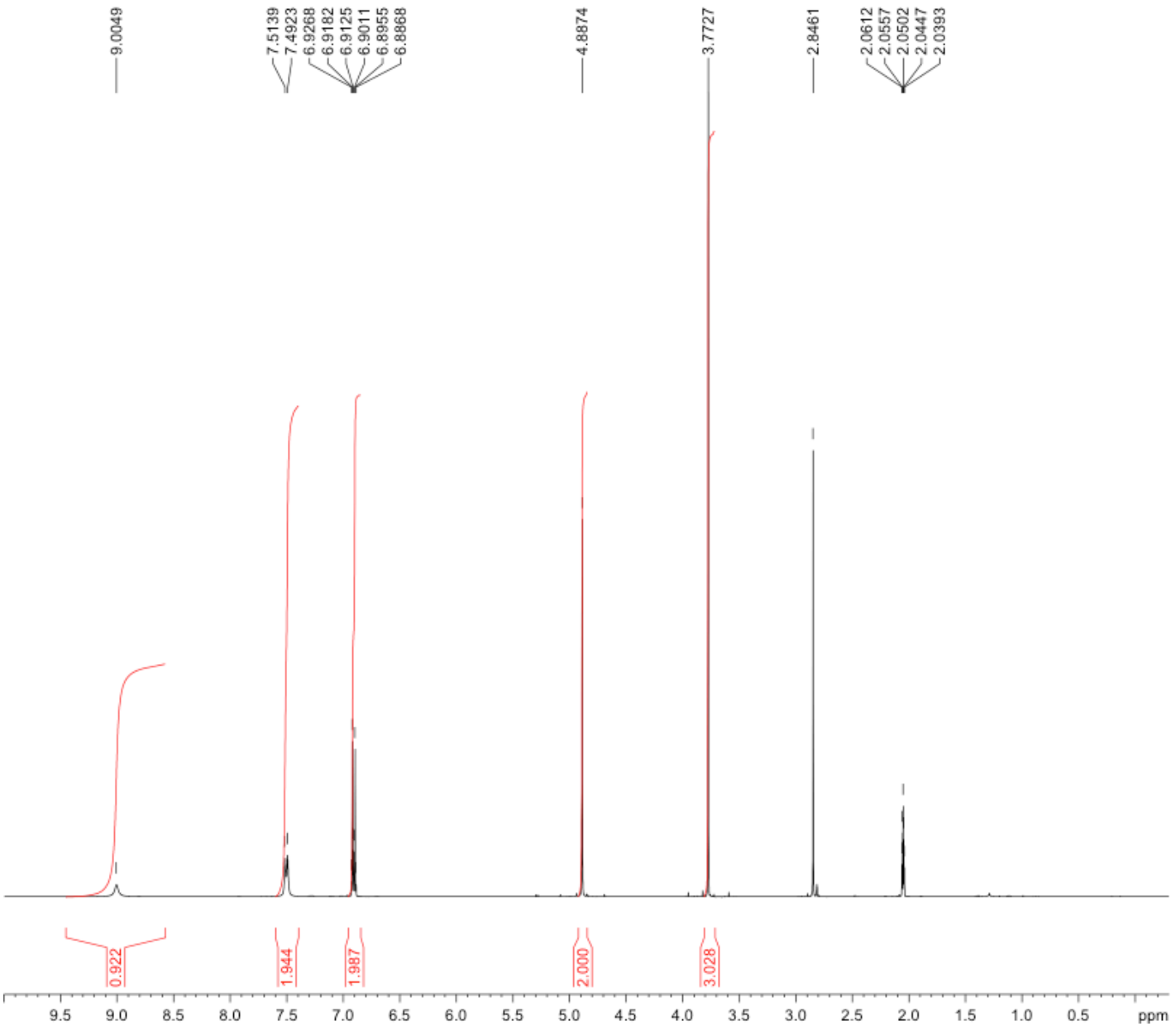
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2.0612
2.0557
2.0502
2.0447
2.0393
0.922
1.944
1.987
2.000
3.028
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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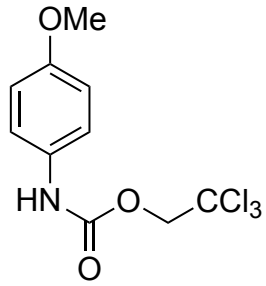
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O
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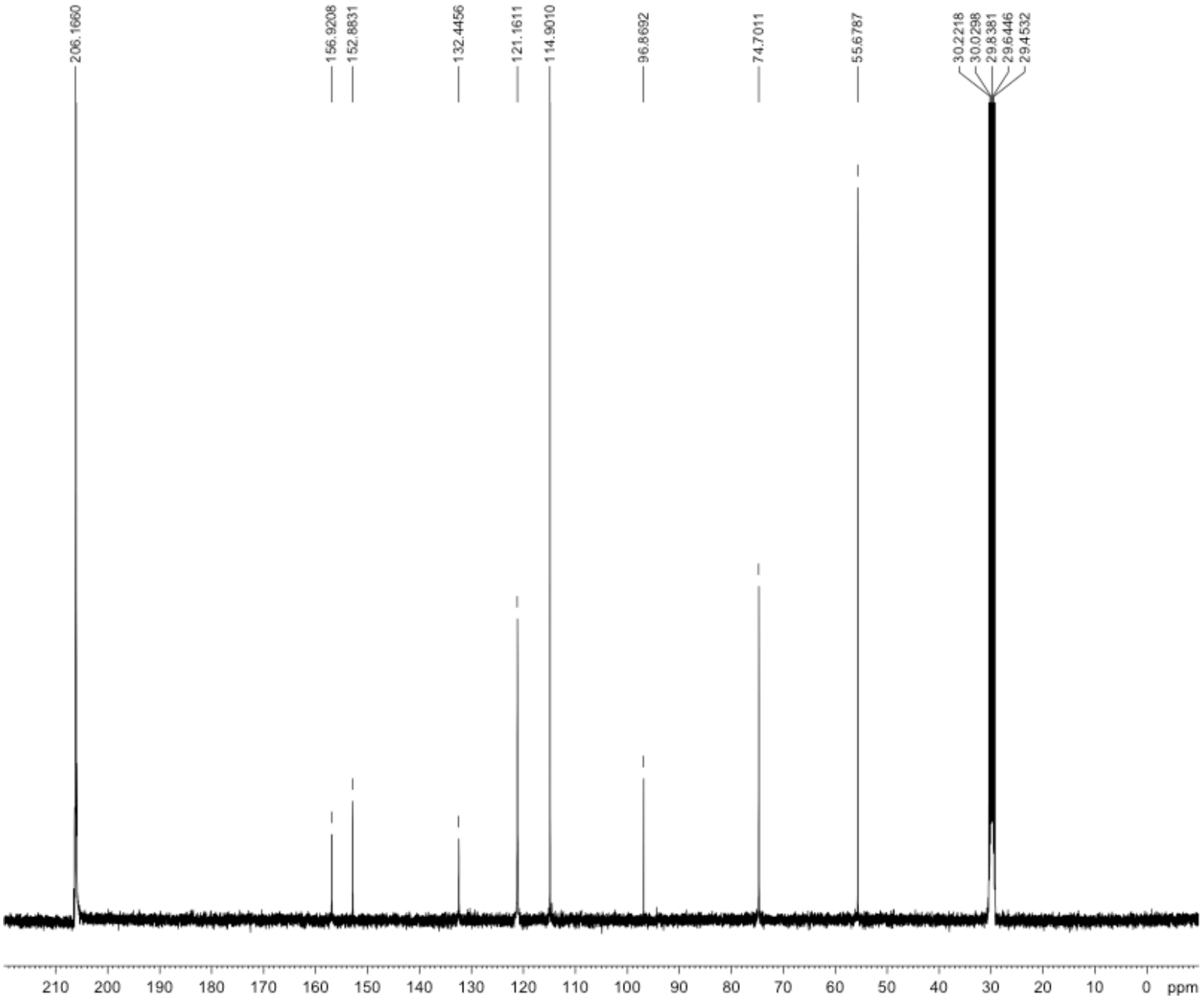
2a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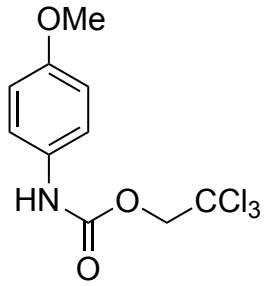
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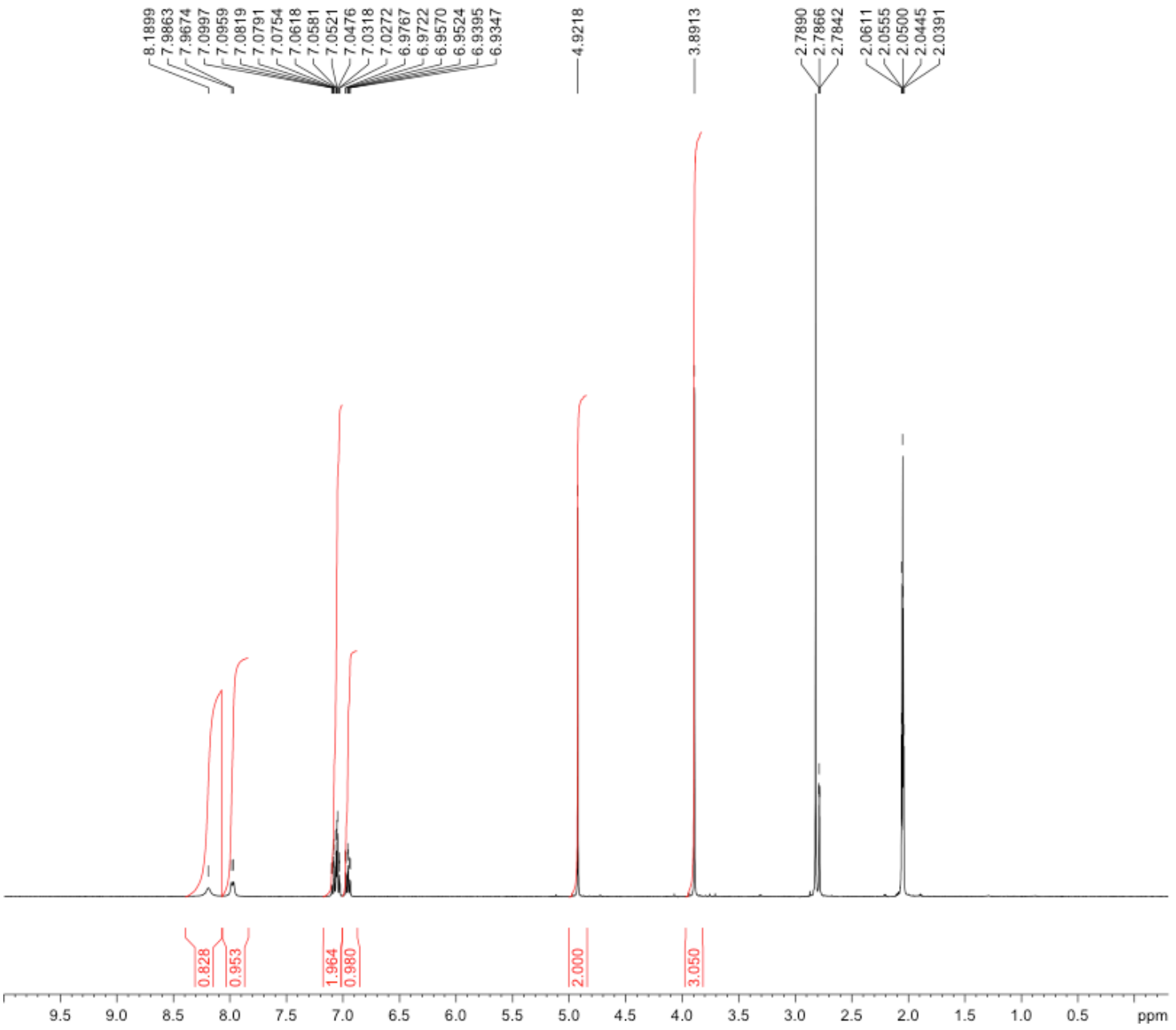
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7.0272
6.9767
6.9722
6.9570
6.9524
6.9395
6.9347
4.9218
3.8913
2.7890
2.7866
2.7842
2.0611
2.0555
2.0500
2.0445
2.0391
0.828
0.953
1.964
0.980
2.000
3.050
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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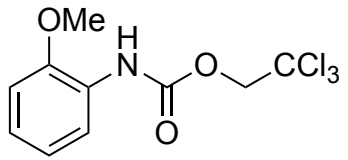
0.5
ppm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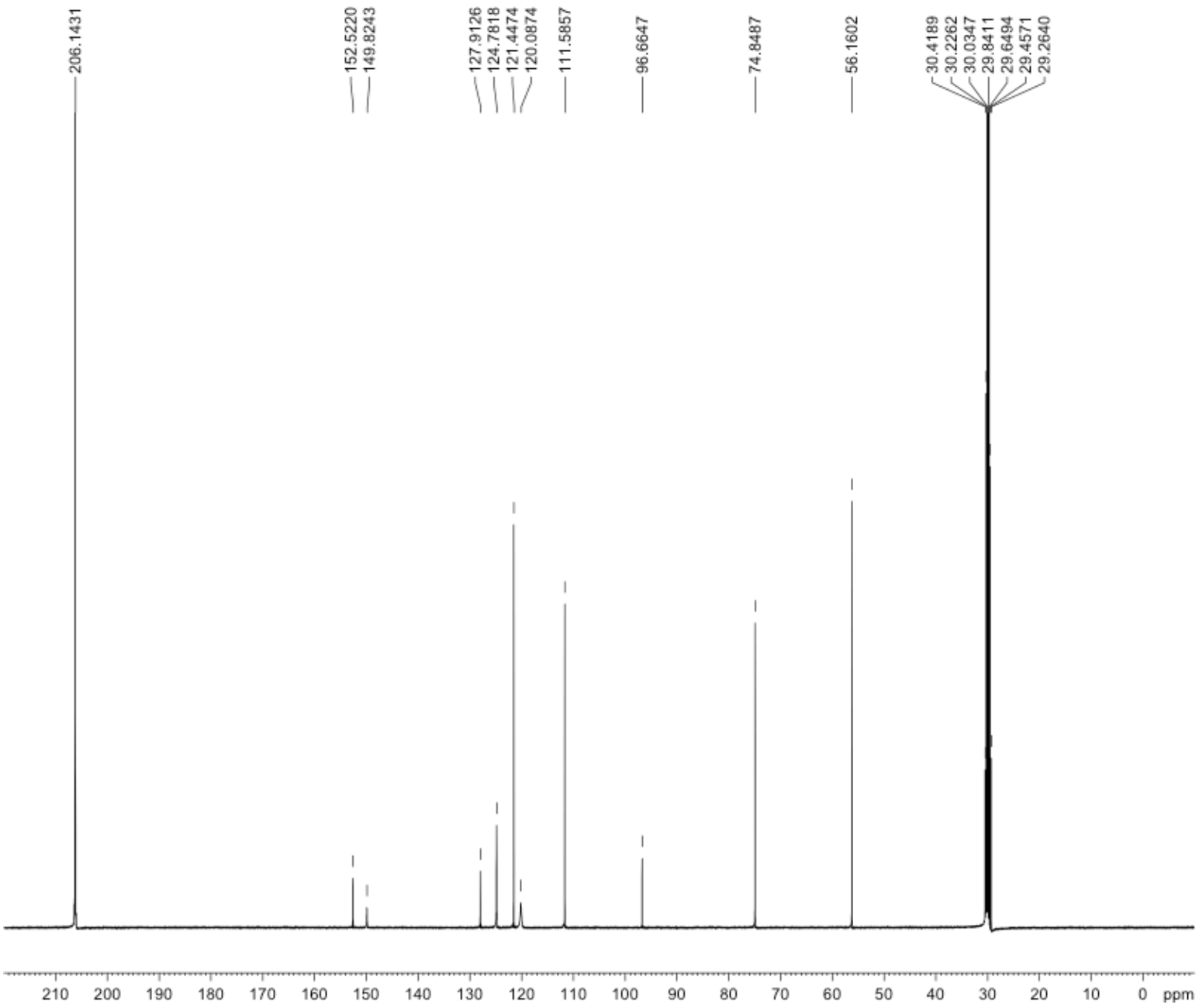
O
CCl3

3a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30.4189
30.2262
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29.8411
29.6494
29.4571
29.2640
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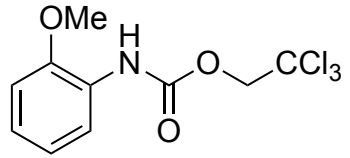
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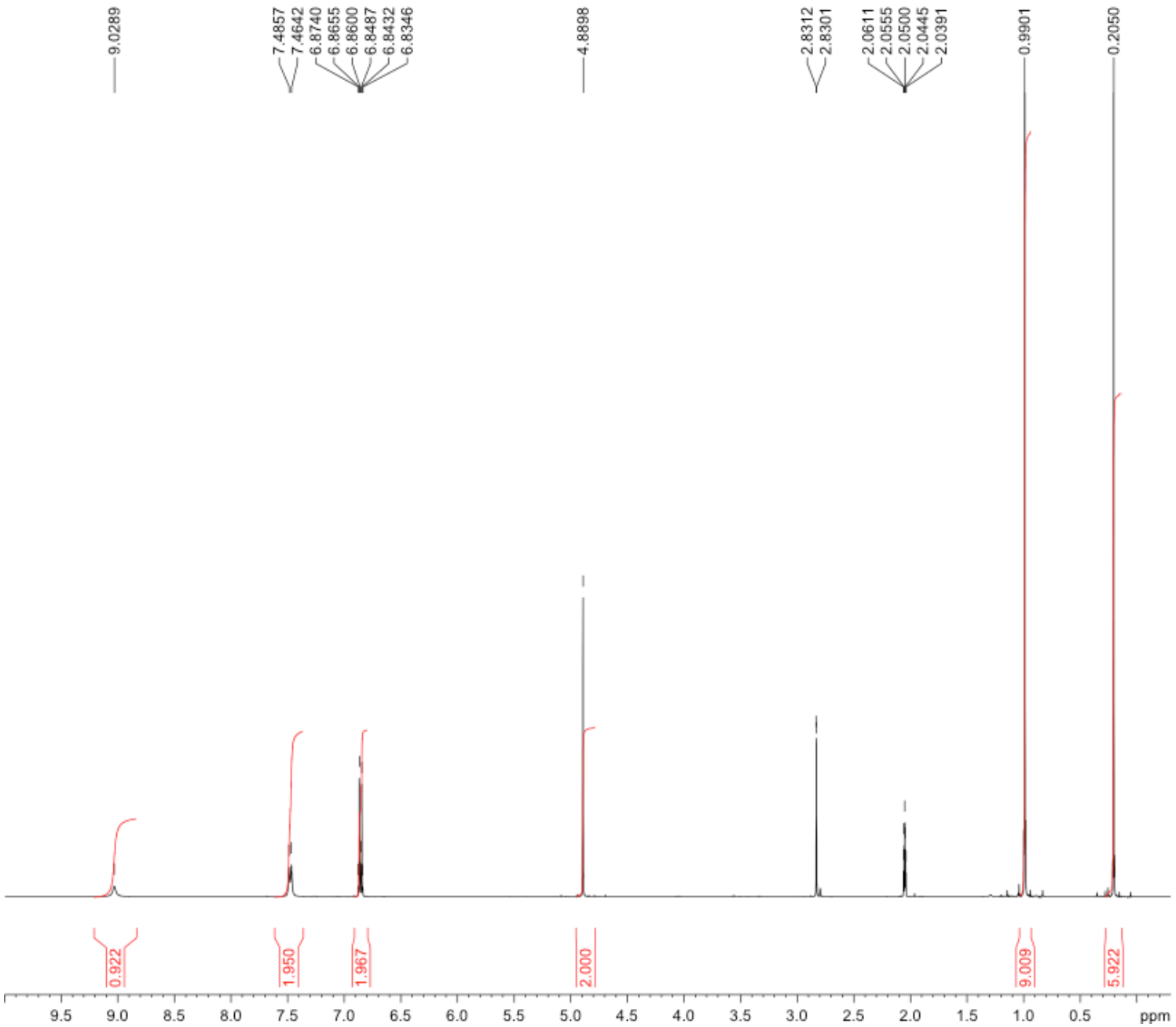
N
O
O
CCl3

3a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2.0611
2.0555
2.0500
2.0445
2.0391
0.9901
0.2050
0.922
1.950
1.967
2.000
9.009
5.922
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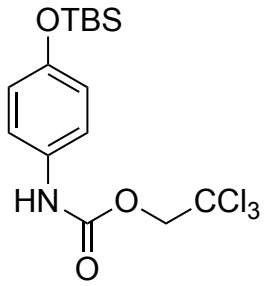
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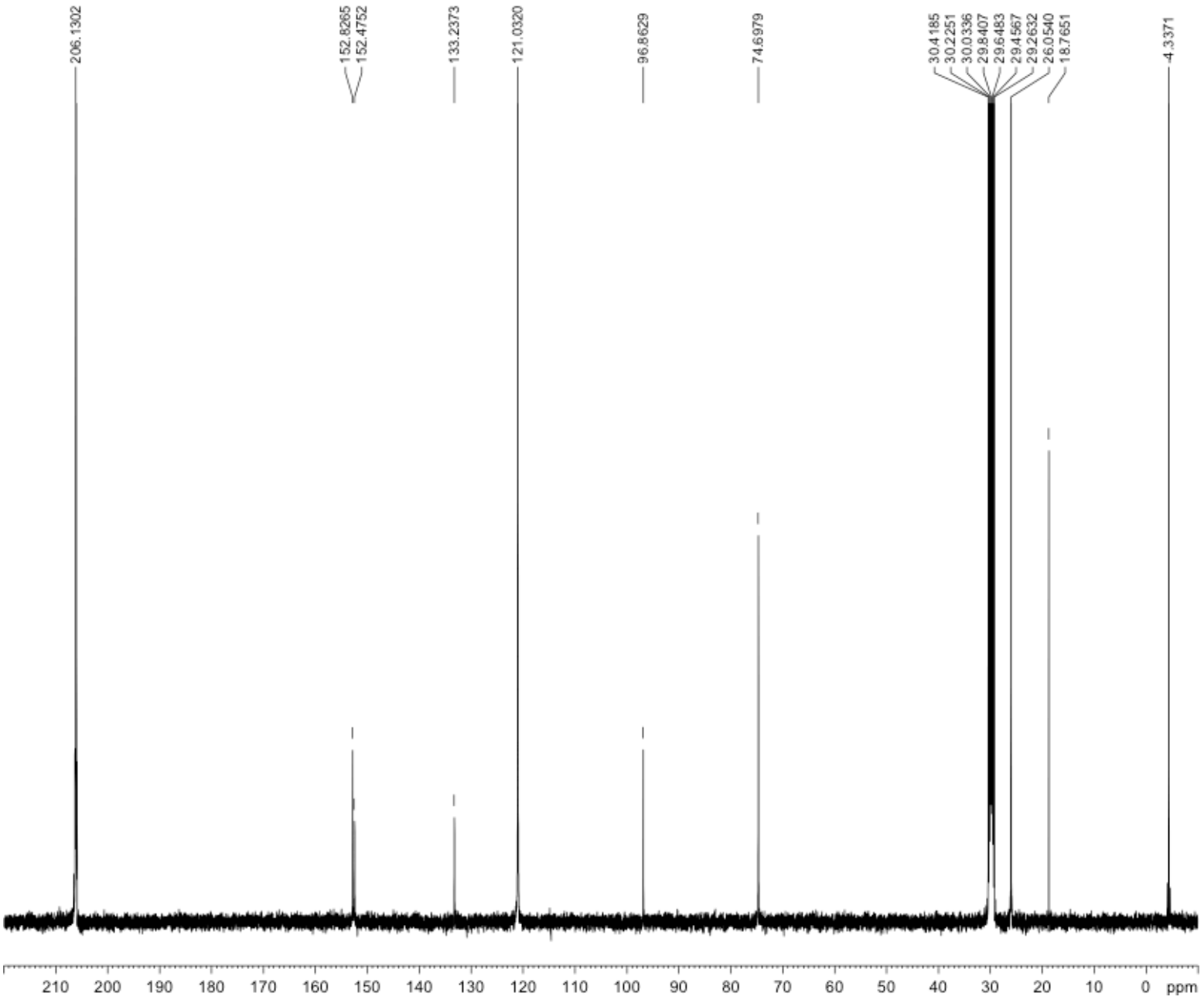
O
O
CCl3

2b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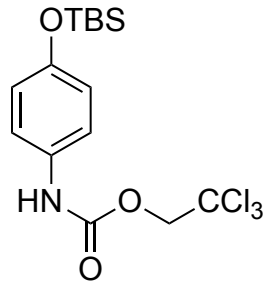
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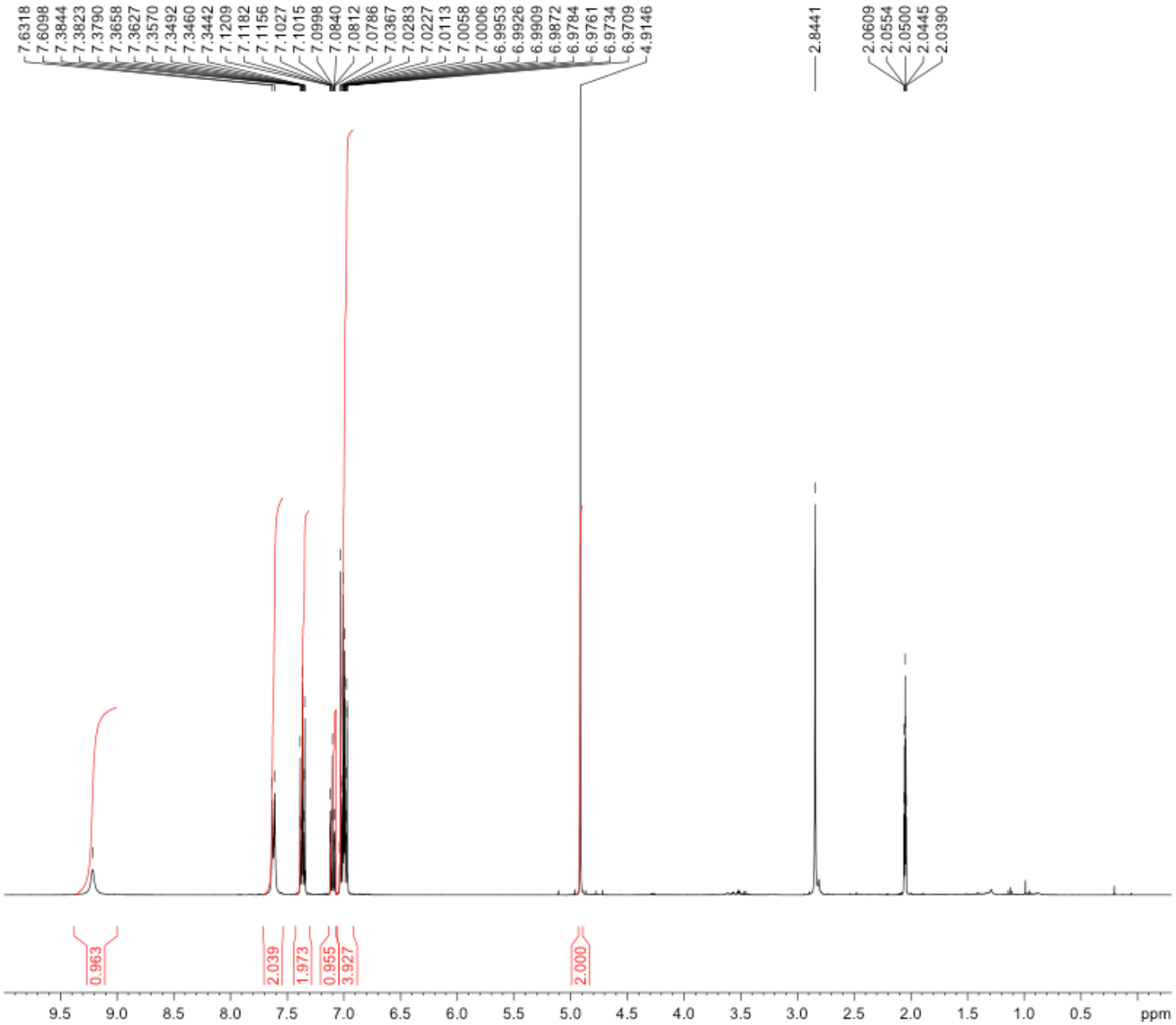
O
CCl3

2b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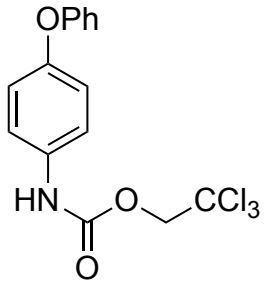
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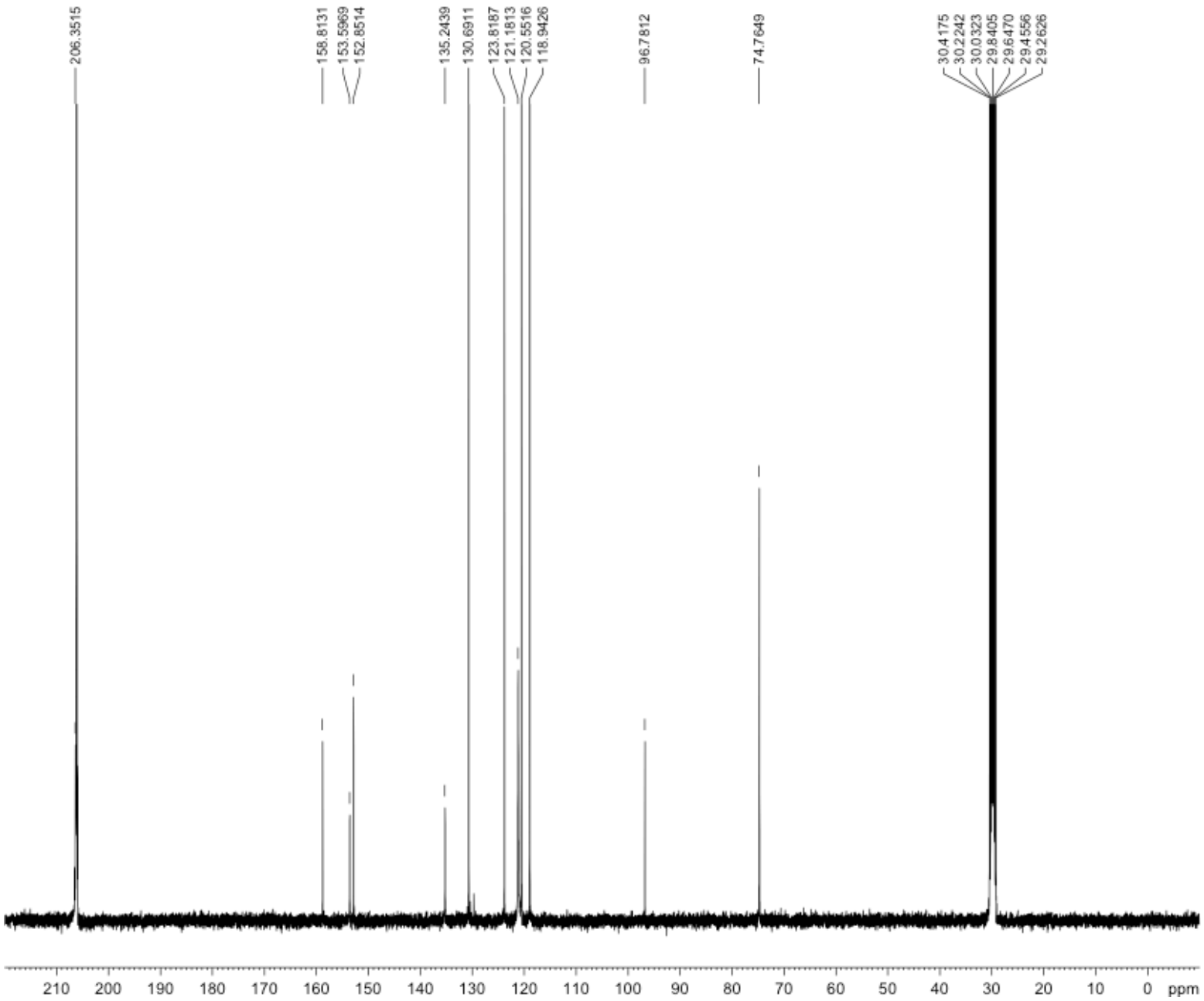
O
O
CCl3

2c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30.4175
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29.2626
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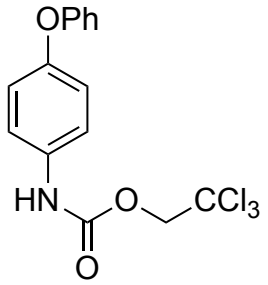
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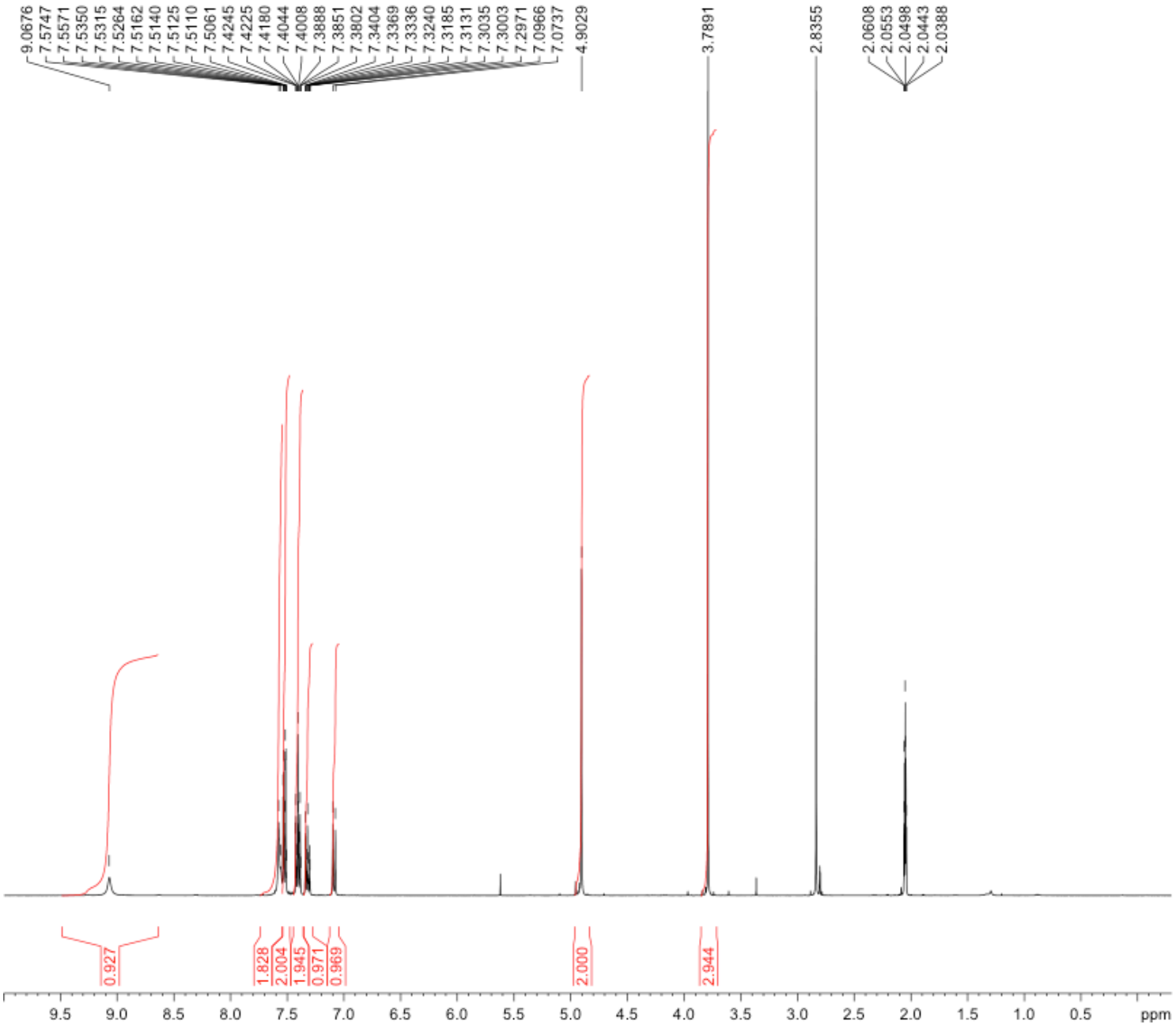
O
O
CCl3

2c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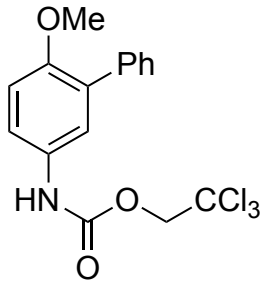
OMe
Ph
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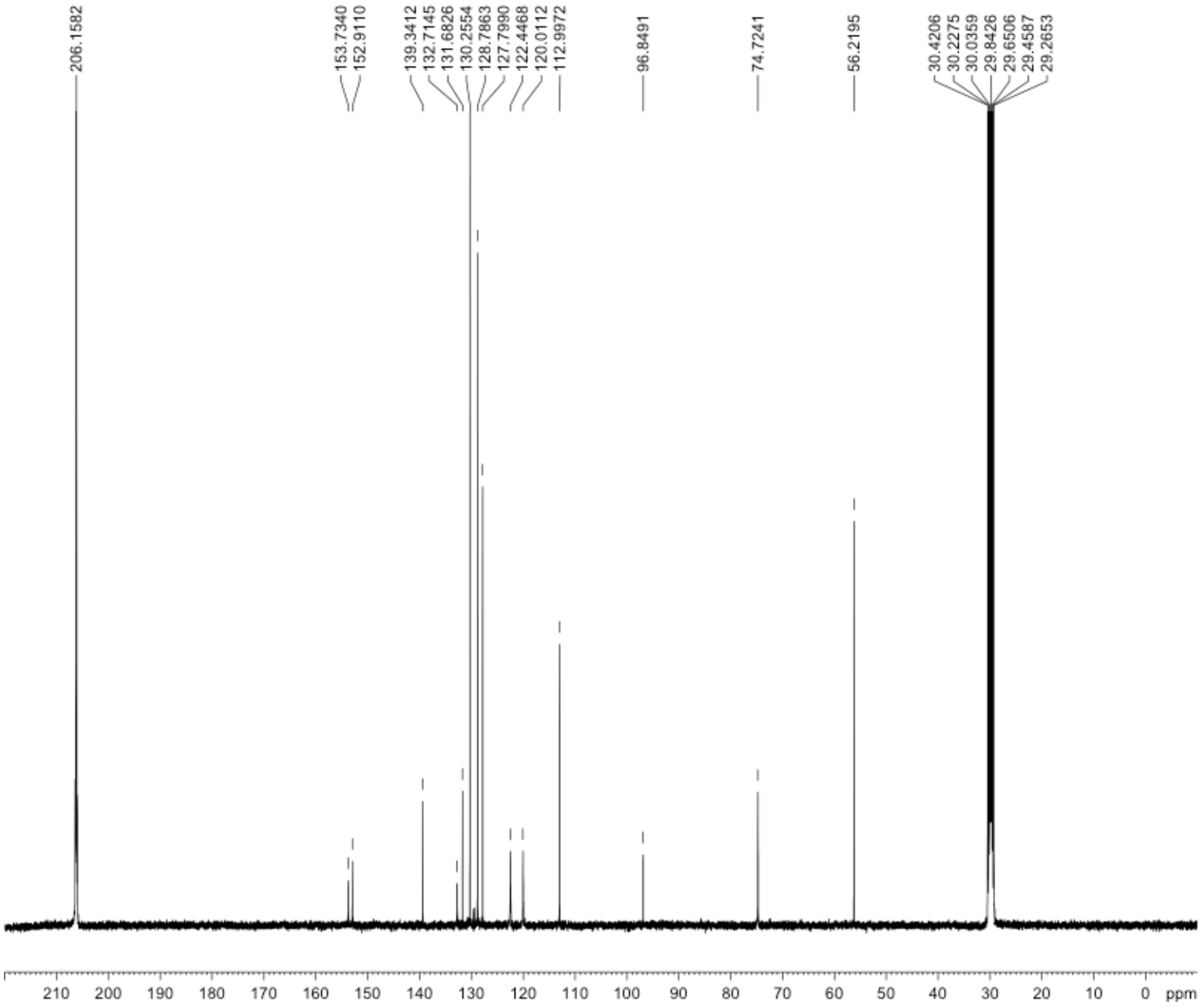
CCl3

2d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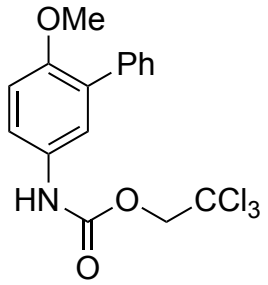
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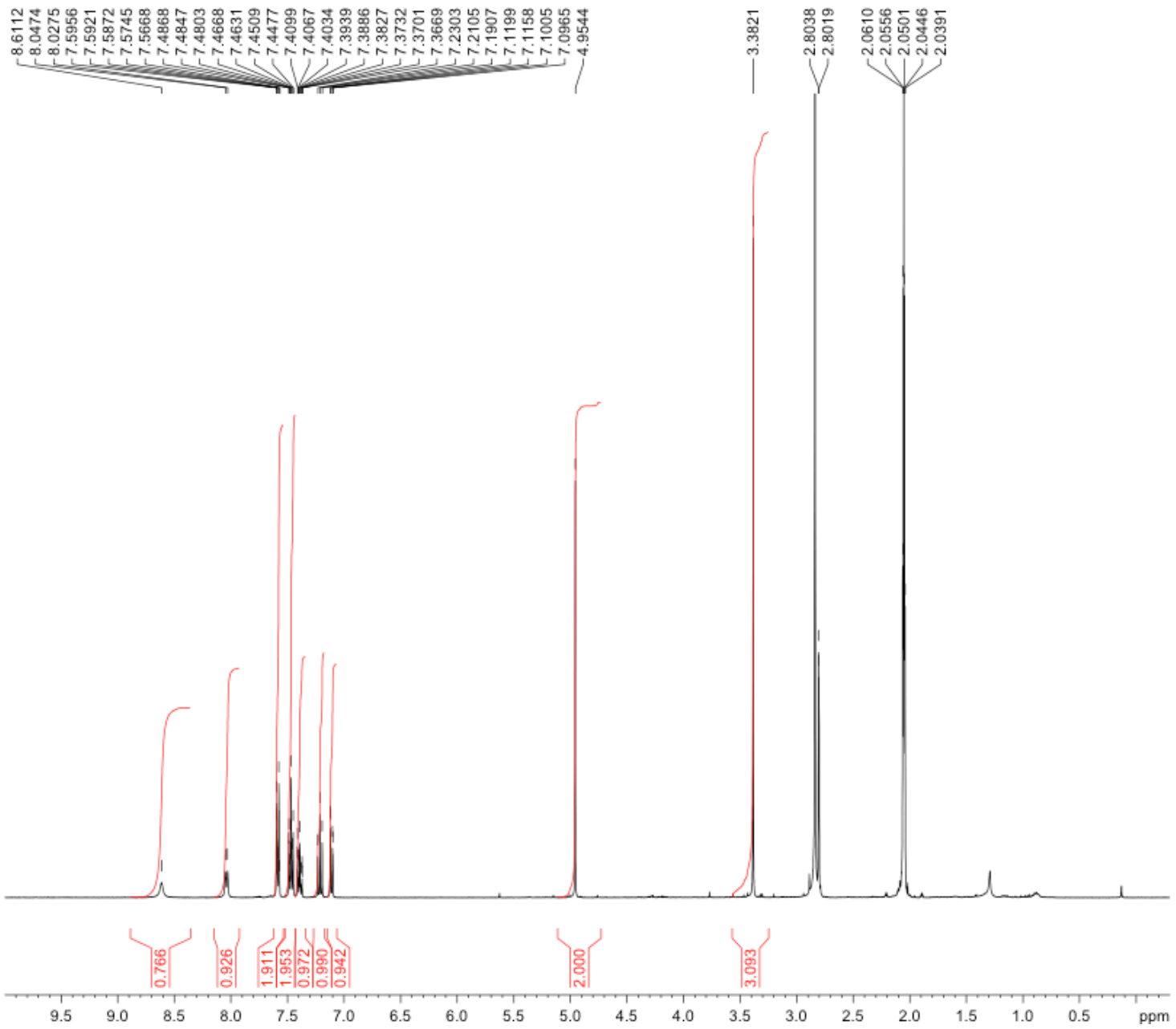
CCl3
O

2d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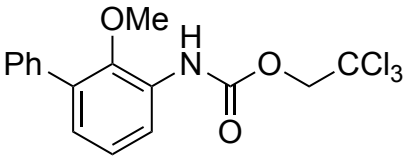
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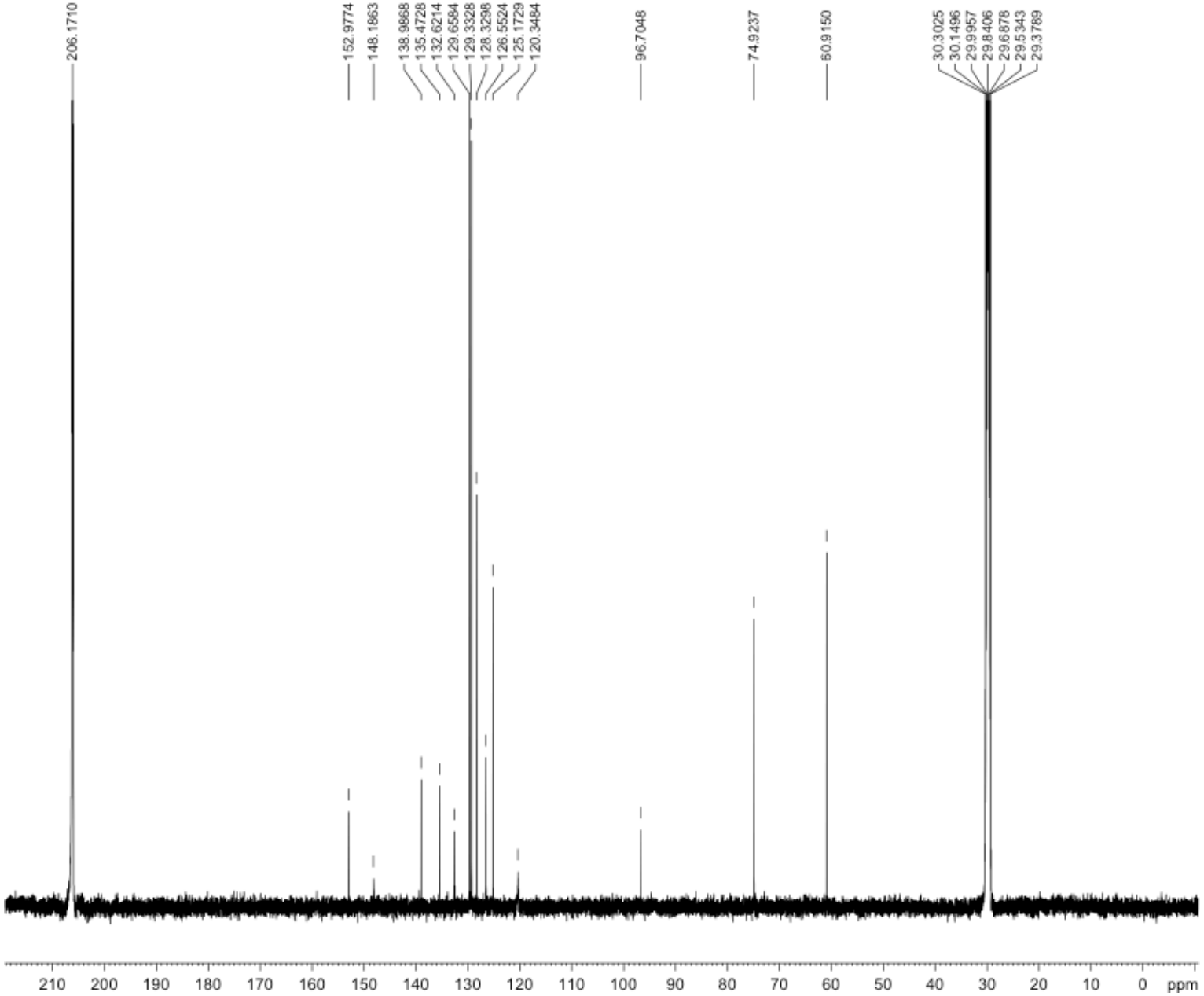
O
O
CCl3

3d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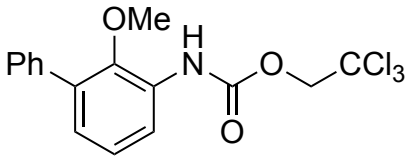
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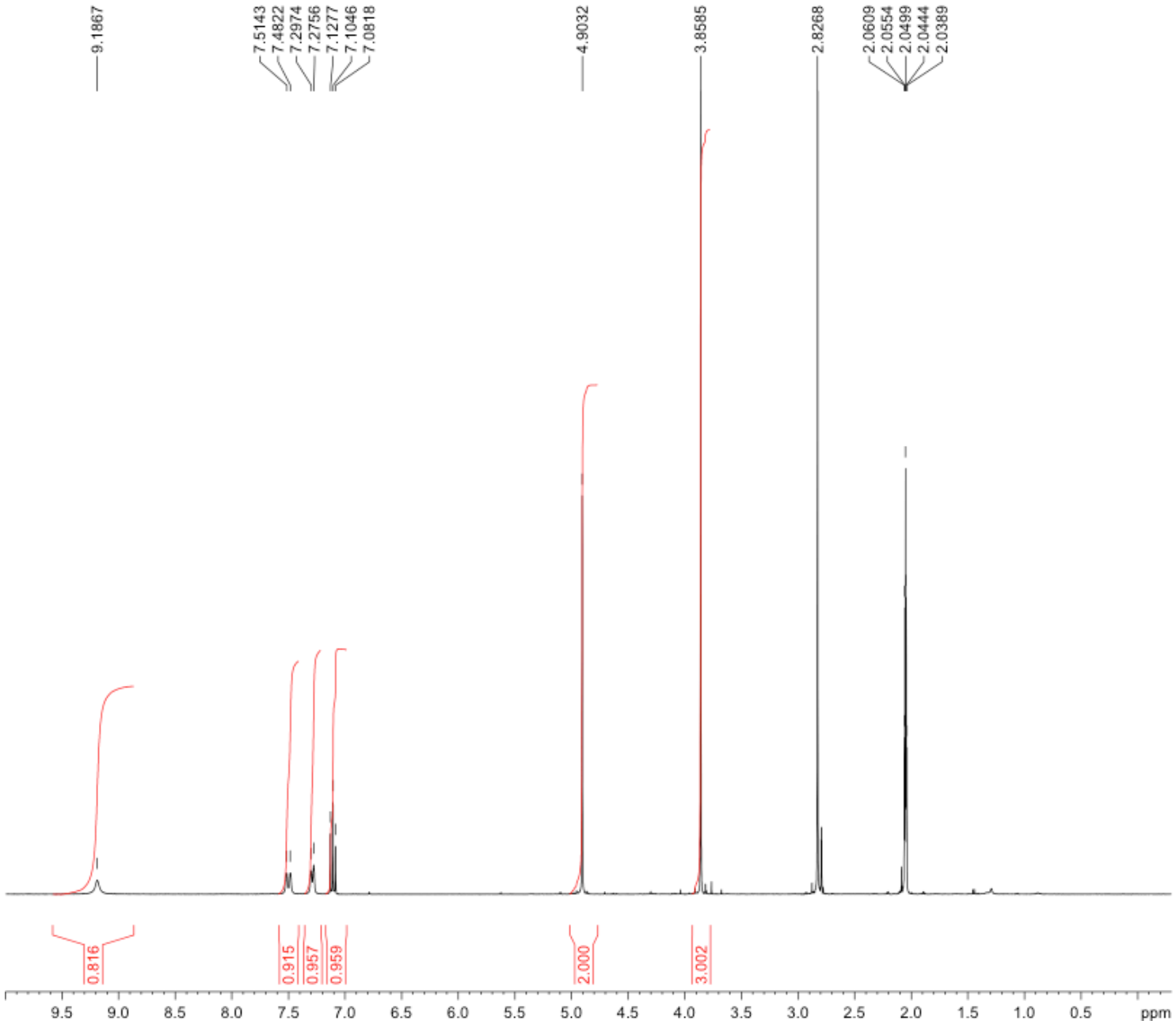
Ph
O
O
CCl3

3d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2.0609
2.0554
2.0499
2.0444
2.0389
0.816
0.915
0.957
0.959
2.000
3.002
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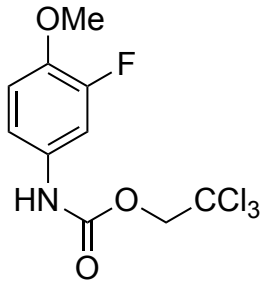
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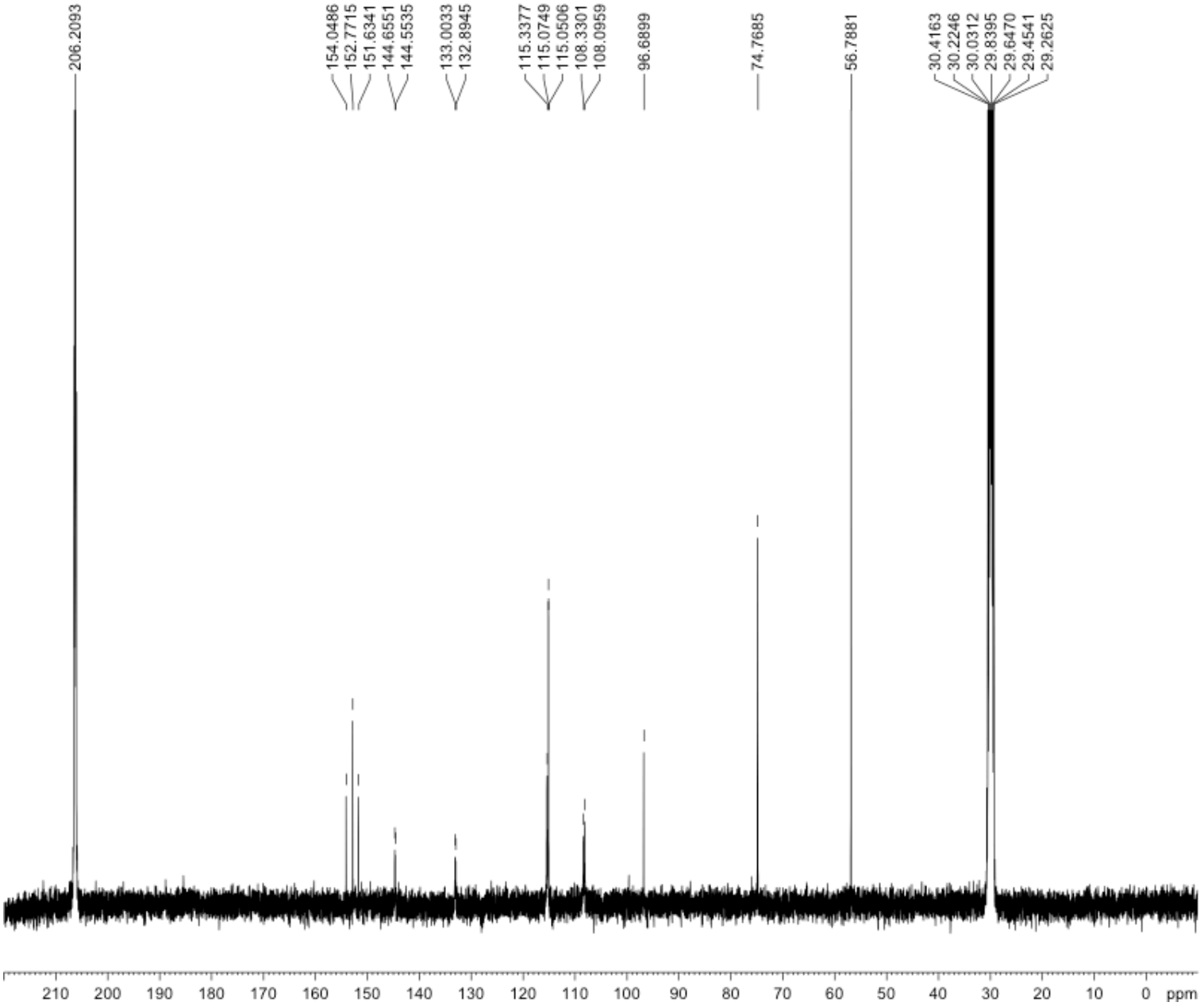
2e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30.2246
30.0312
29.8395
29.6470
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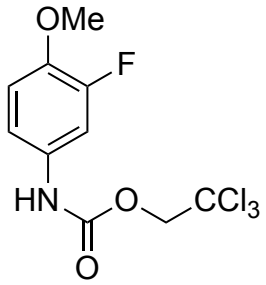
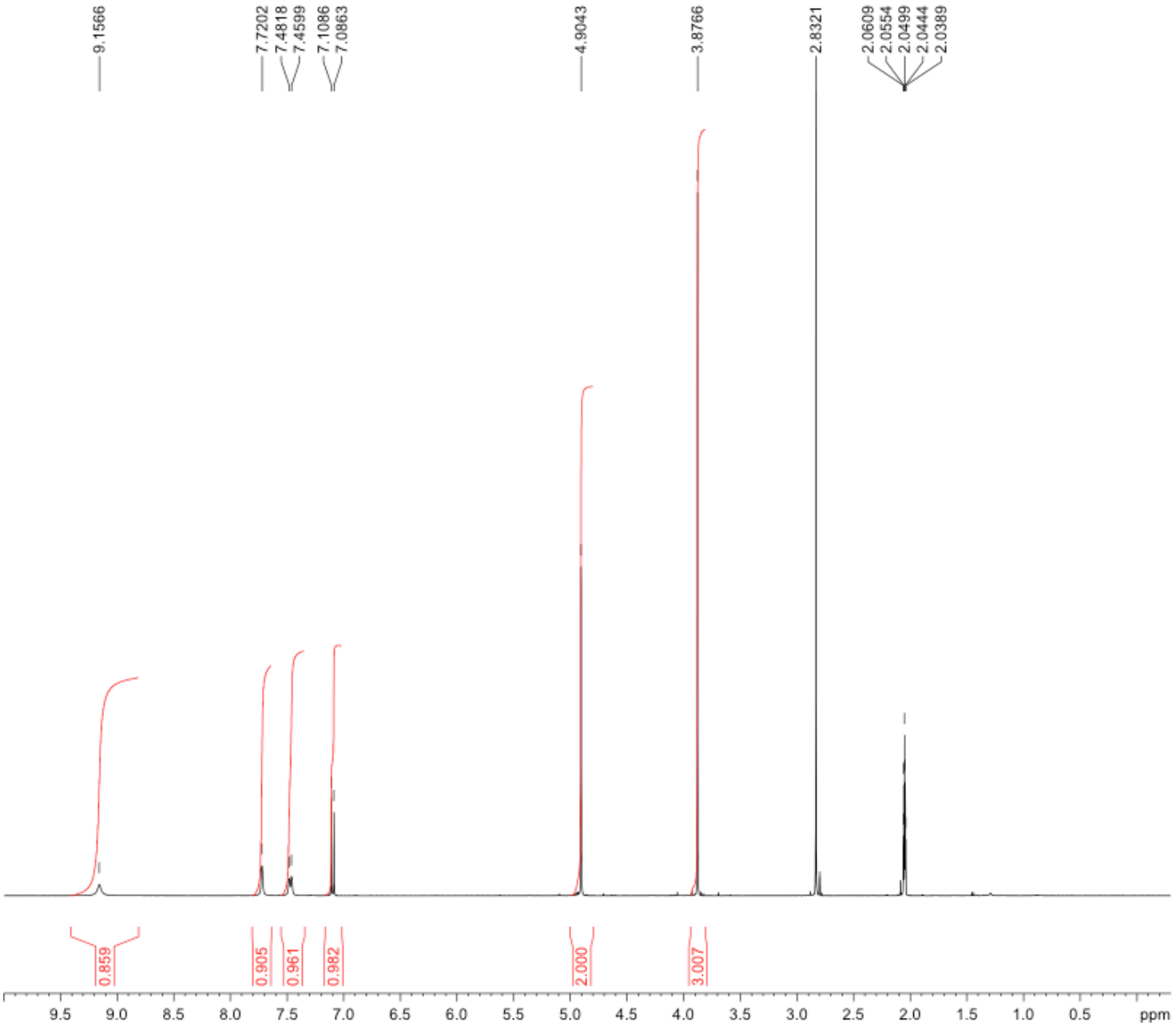
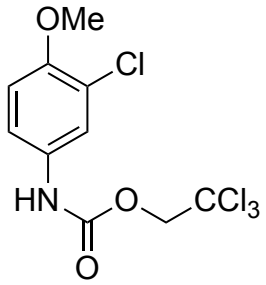
29.2625
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

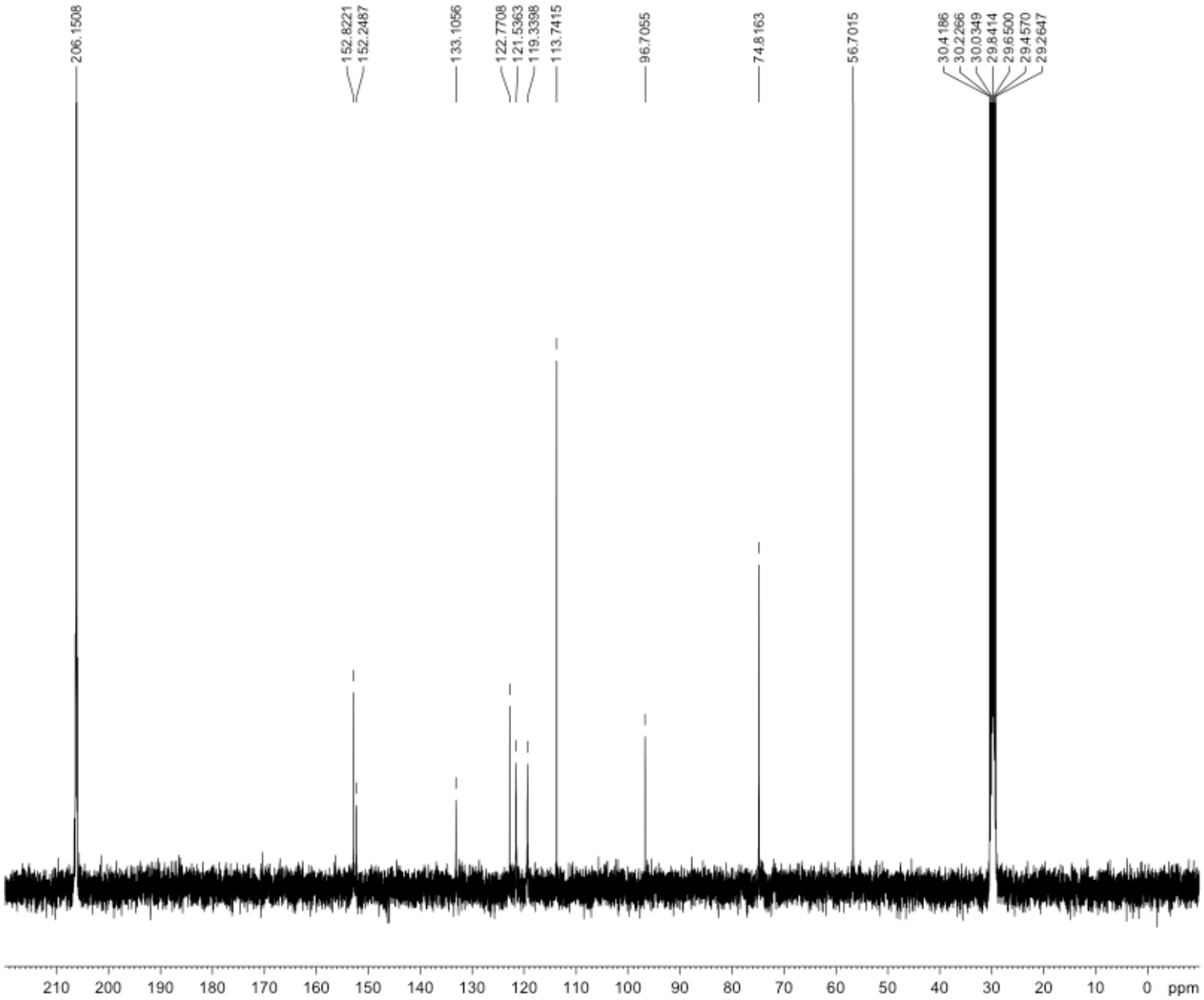

OMe
F
HN
O
O
CCl3

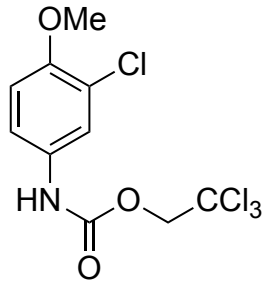
2e


9.1566
7.7202
7.4818
7.4599
7.1086
7.0863
4.9043
3.8766
2.8321
2.0609
2.0554
2.0499
2.0444
2.0389
0.859
0.905
0.961
0.982
2.000
3.007
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

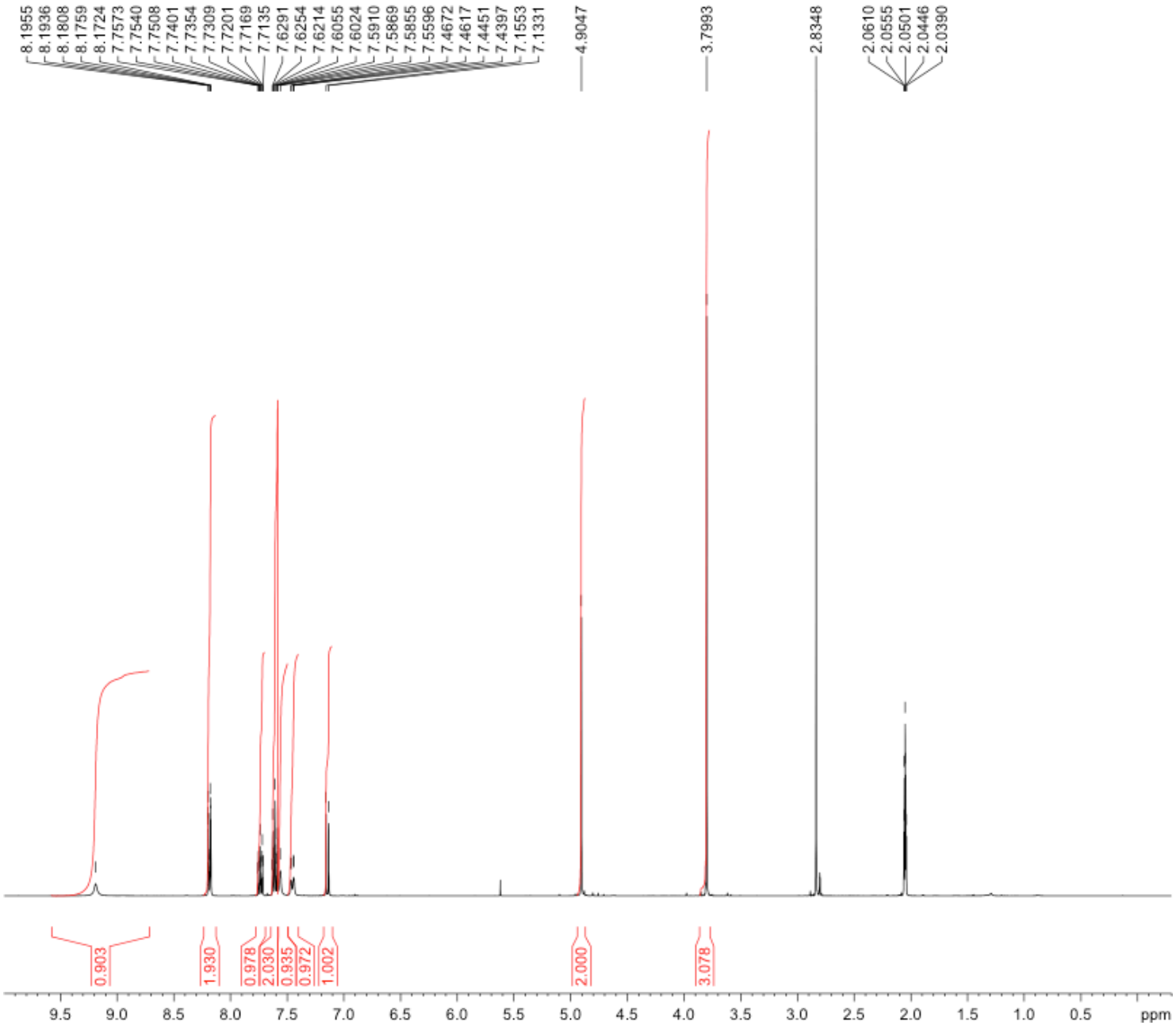

OMe
Cl
HN
O
O
CCl3

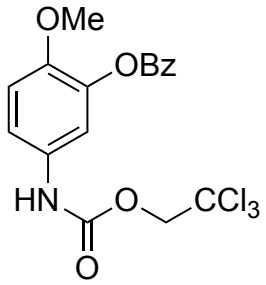
2f


206.1508
152.8221
152.2487
133.1056
122.7708
121.5363
119.3398
113.7415
96.7055
74.8163
56.7015
30.4186
30.2266
30.0349
29.8414
29.6500
29.4570
29.2647
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

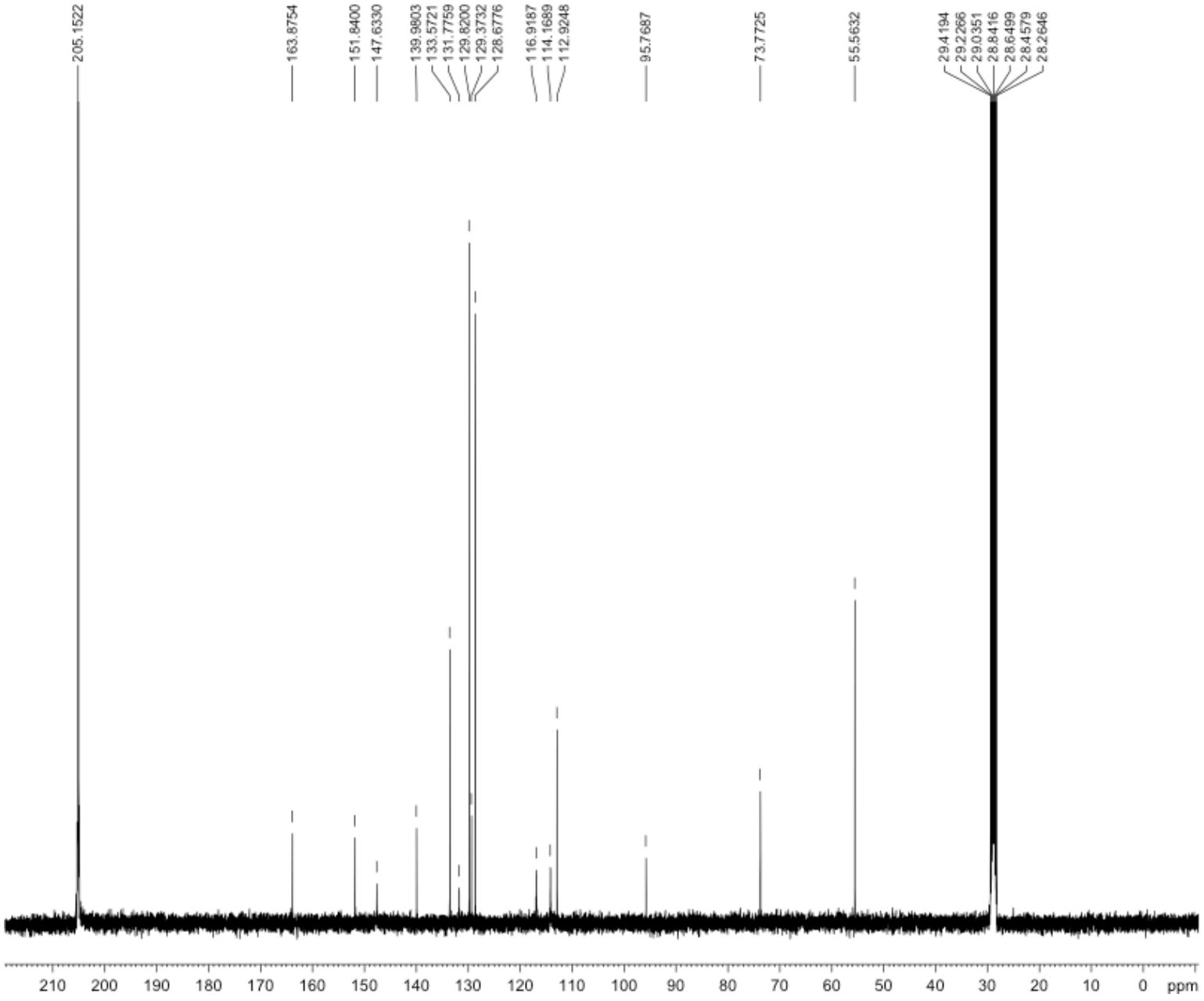

OMe
Cl
HN
O
O
CCl3
O

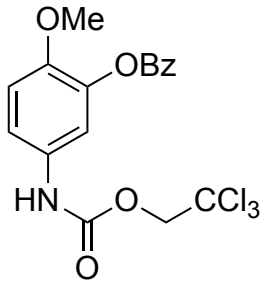
2f


8.1955
8.1936
8.1808
8.1759
8.1724
7.7573
7.7540
7.7508
7.7401
7.7354
7.7309
7.7201
7.7169
7.7135
7.6291
7.6254
7.6214
7.6055
7.6024
7.5910
7.5869
7.5855
7.5596
7.4672
7.4617
7.4451
7.4397
7.1553
7.1331
4.9047
3.7993
2.8348
2.0610
2.0555
2.0501
2.0446
2.0390
0.903
1.930
0.978
2.030
0.935
0.972
1.002
2.000
3.078
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

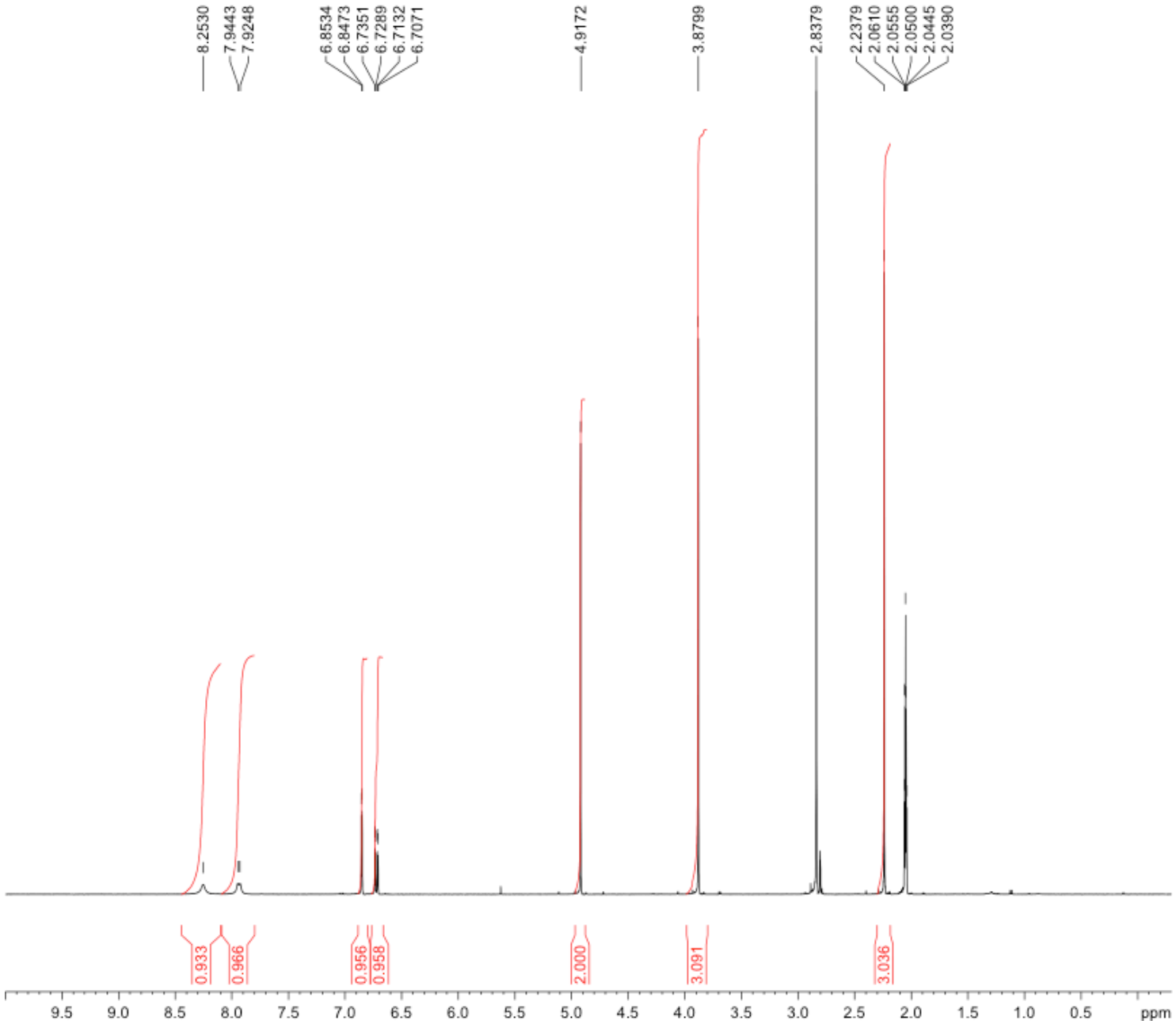

OMe
OBz
HN
O
O
CCl3
O

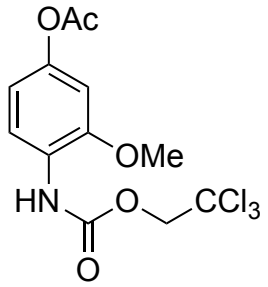
2g


205.1522
163.8754
151.8400
147.6330
139.9803
133.5721
131.7759
129.8200
129.3732
128.6776
116.9187
114.1689
112.9248
95.7687
73.7725
55.5632
29.4194
29.2266
29.0351
28.8416
28.6499
28.4579
28.2646
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

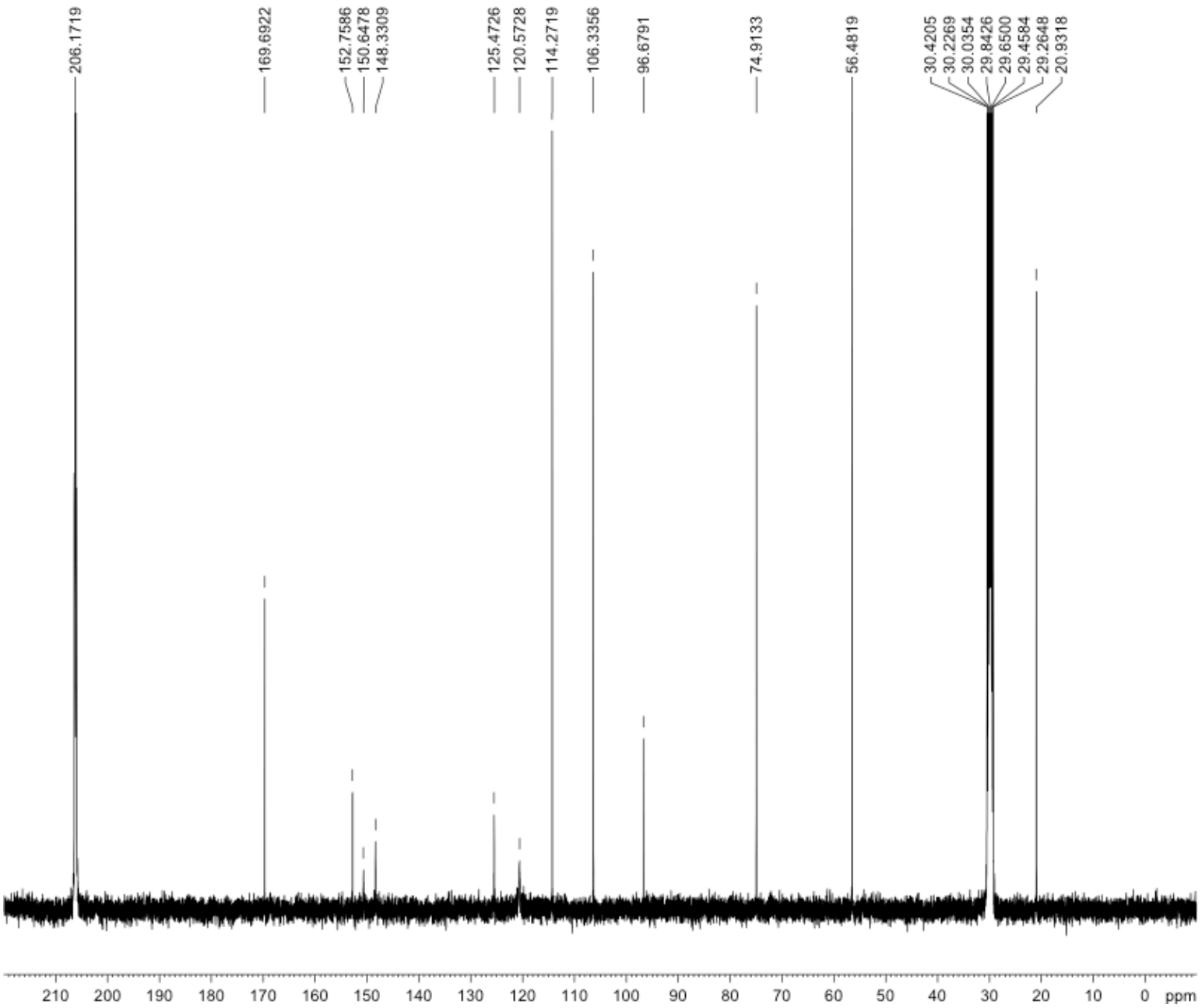

OMe
OBz
HN
O
O
CCl3
O

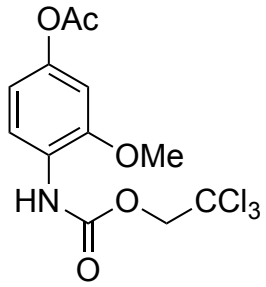
2g


8.2530
7.9443
7.9248
6.8534
6.8473
6.7351
6.7289
6.7132
6.7071
4.9172
3.8799
2.8379
2.2379
2.0610
2.0555
2.0500
2.0445
2.0390
0.933
0.966
0.956
0.958
2.000
3.091
3.036
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

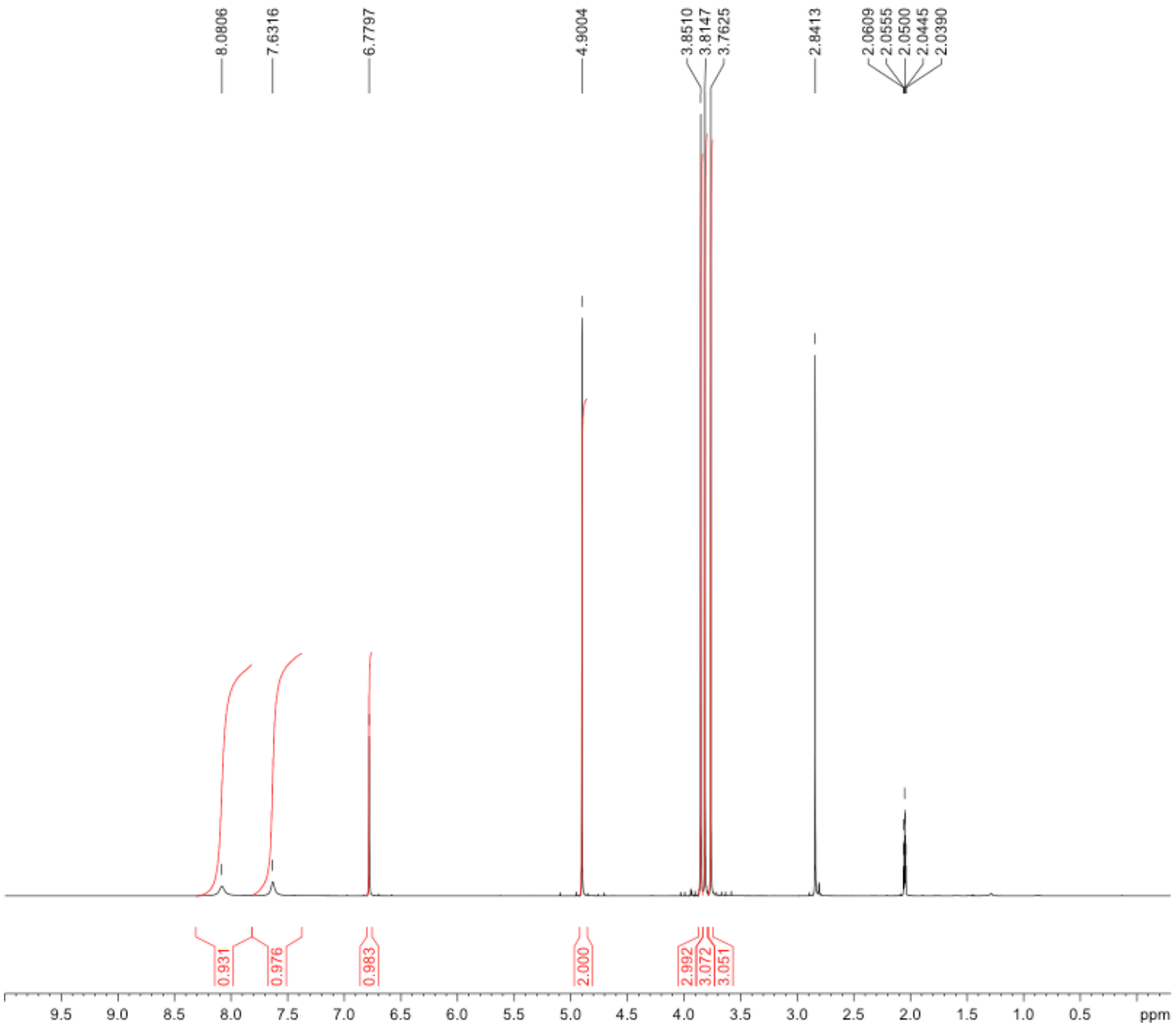

OAc
OMe
HN
O
O
CCl3

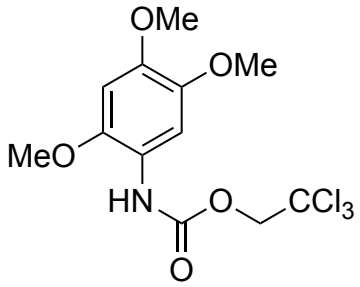
3h


206.1719
169.6922
152.7586
150.6478
148.3309
125.4726
120.5728
114.2719
106.3356
96.6791
74.9133
56.4819
30.4205
30.2269
30.0354
29.8426
29.6500
29.4584
29.2648
20.9318
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

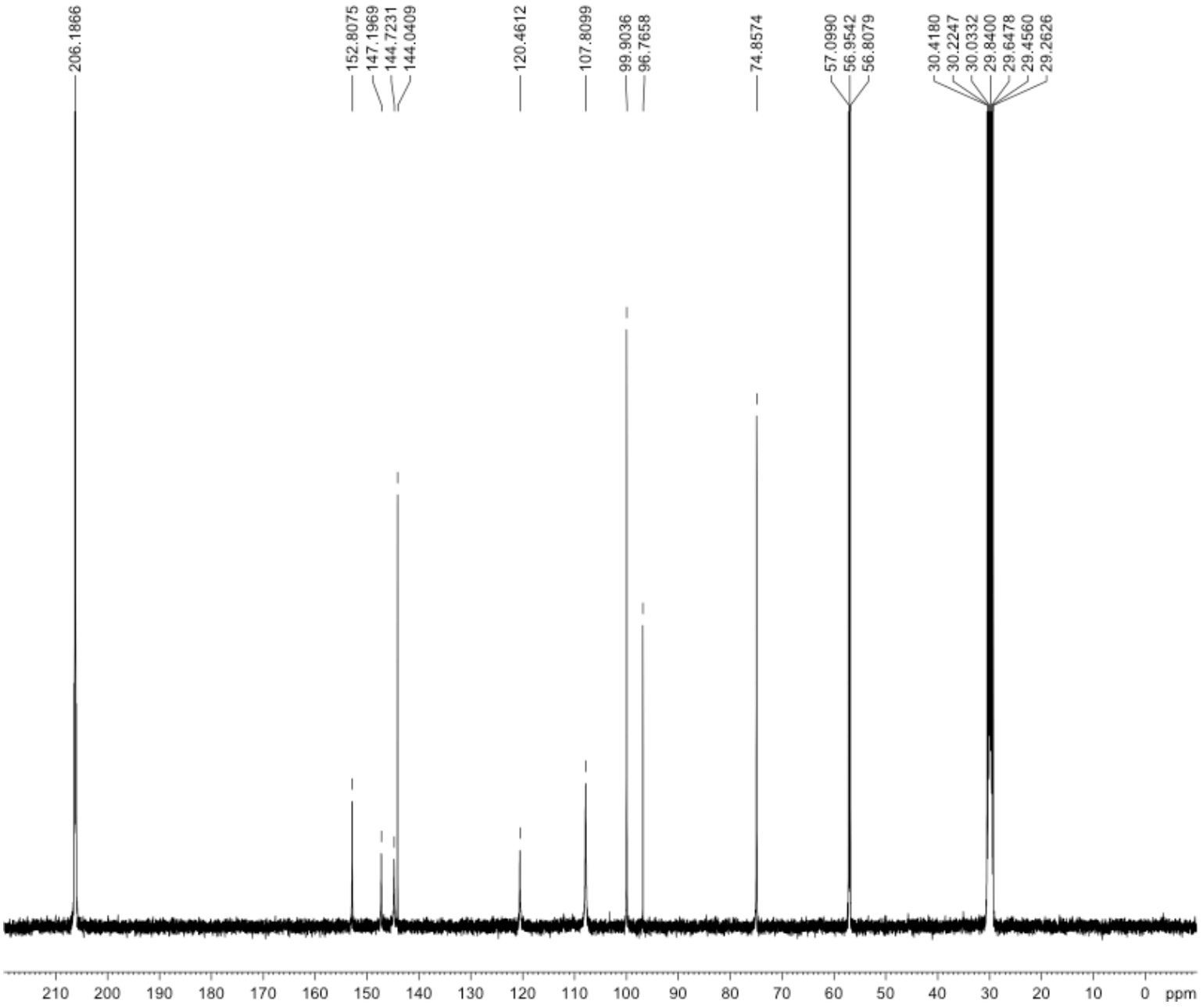

OAc
OMe
HN
O
O
CCl3

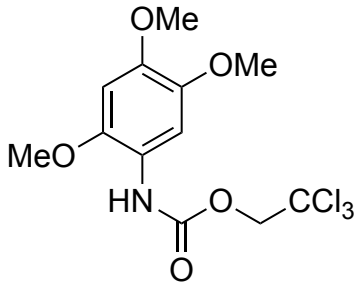
3h


8.0806
7.6316
6.7797
4.9004
3.8510
3.8147
3.7625
2.8413
2.0609
2.0555
2.0500
2.0445
2.0390
0.931
0.976
0.983
2.000
2.992
3.072
3.051
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

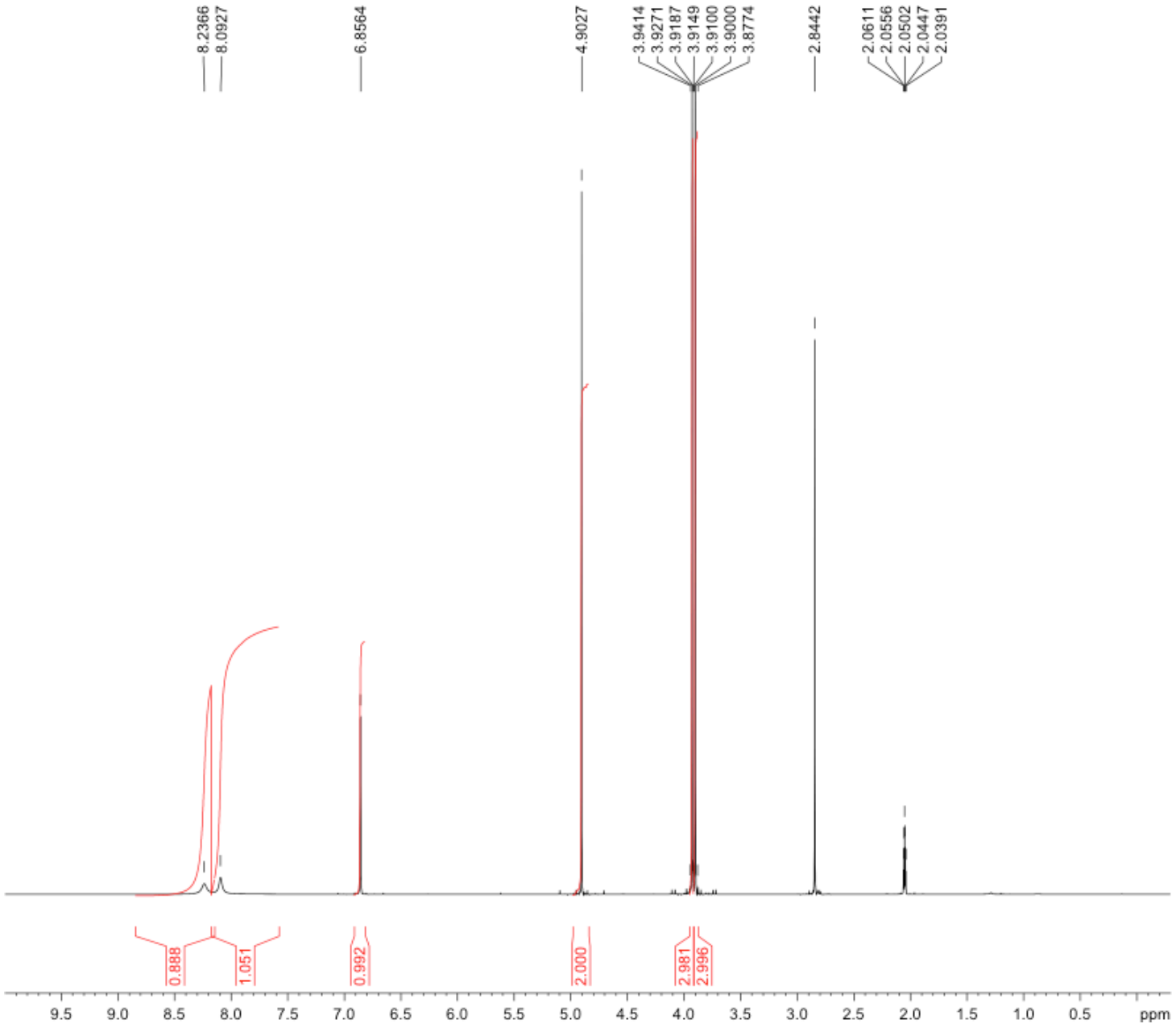

OMe
OMe
MeO
HN
O
O
CCl3

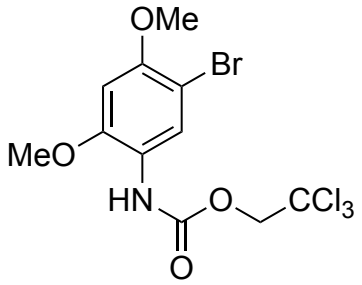
2i


206.1866
152.8075
147.1969
144.7231
144.0409
120.4612
107.8099
99.9036
96.7658
74.8574
57.0990
56.9542
56.8079
30.4180
30.2247
30.0332
29.8400
29.6478
29.4560
29.2626
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

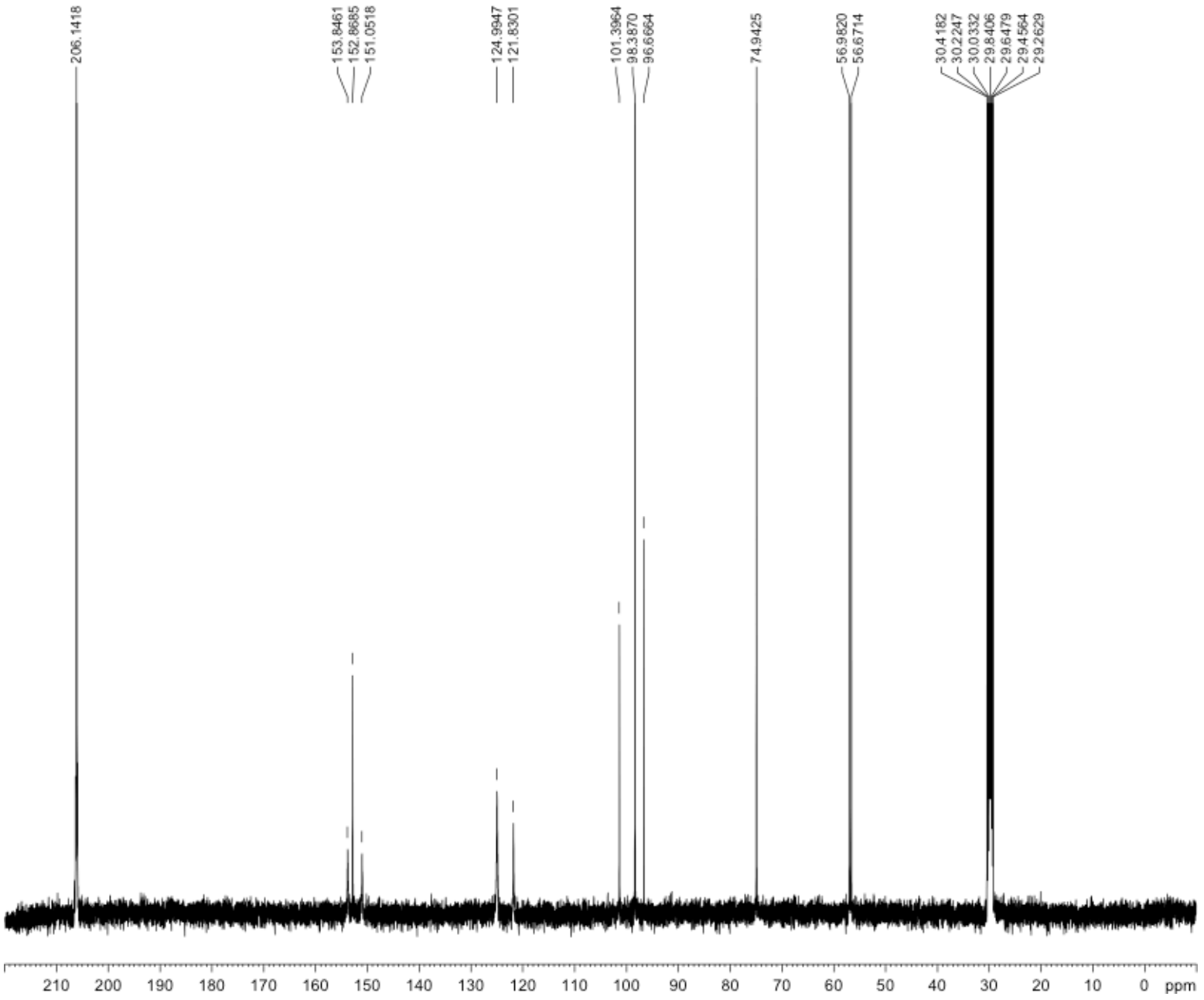

OMe
OMe
MeO
HN
O
O
CCl3
O

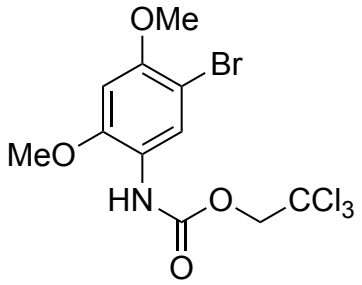
2i


8.2366
8.0927
6.8564
4.9027
3.9414
3.9271
3.9187
3.9149
3.9100
3.9000
3.8774
2.8442
2.0611
2.0556
2.0502
2.0447
2.0391
0.888
1.051
0.992
2.000
2.981
2.996
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

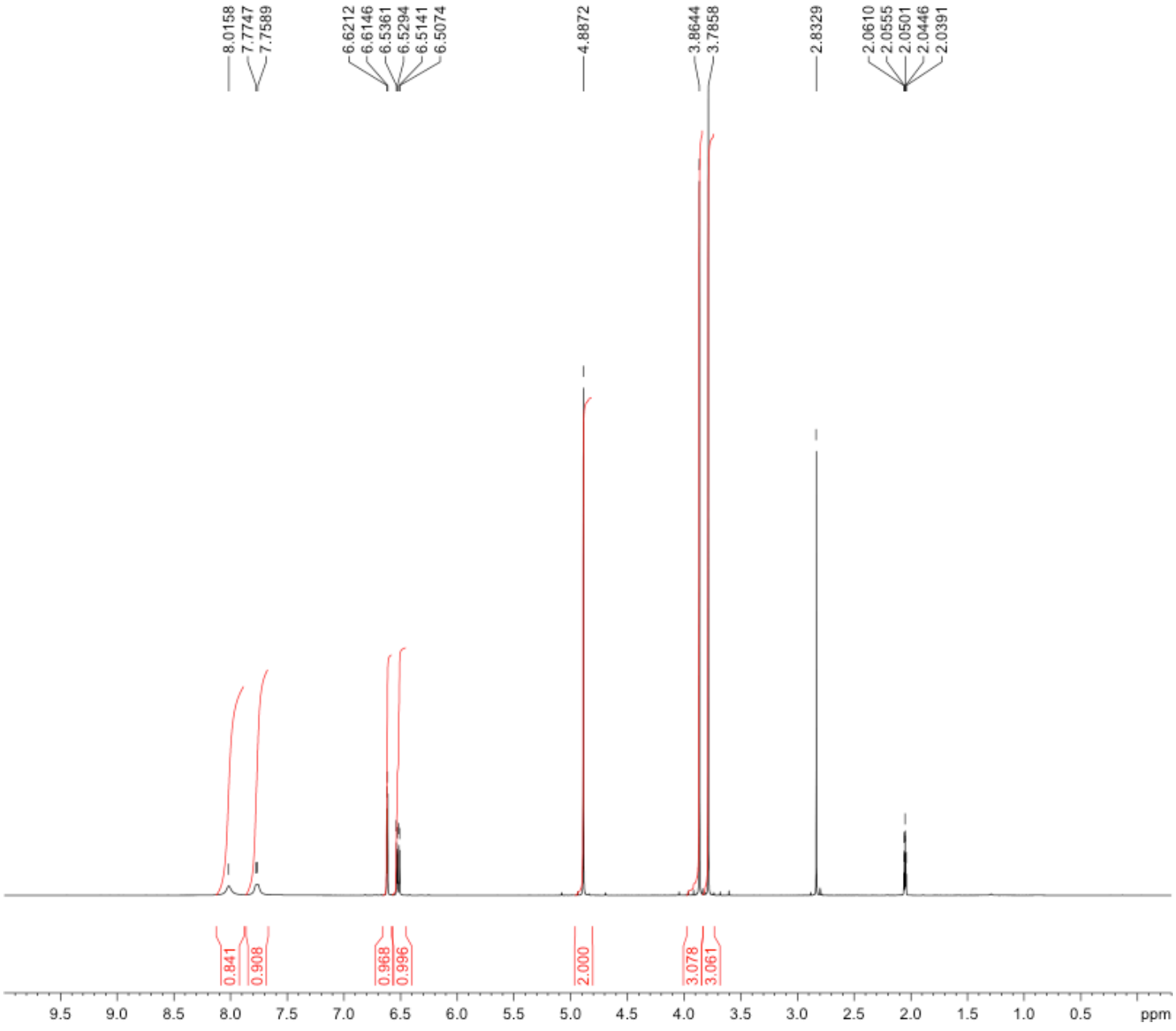

OMe
Br
MeO
HN
O
O
CCl3
O

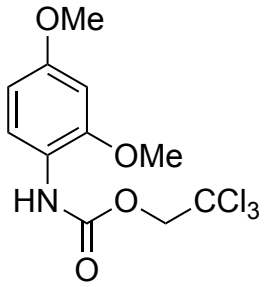
2j


206.1418
153.8461
152.8685
151.0518
124.9947
121.8301
101.3964
98.3870
96.6664
74.9425
56.9820
56.6714
30.4182
30.2247
30.0332
29.8406
29.6479
29.4564
29.2629
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

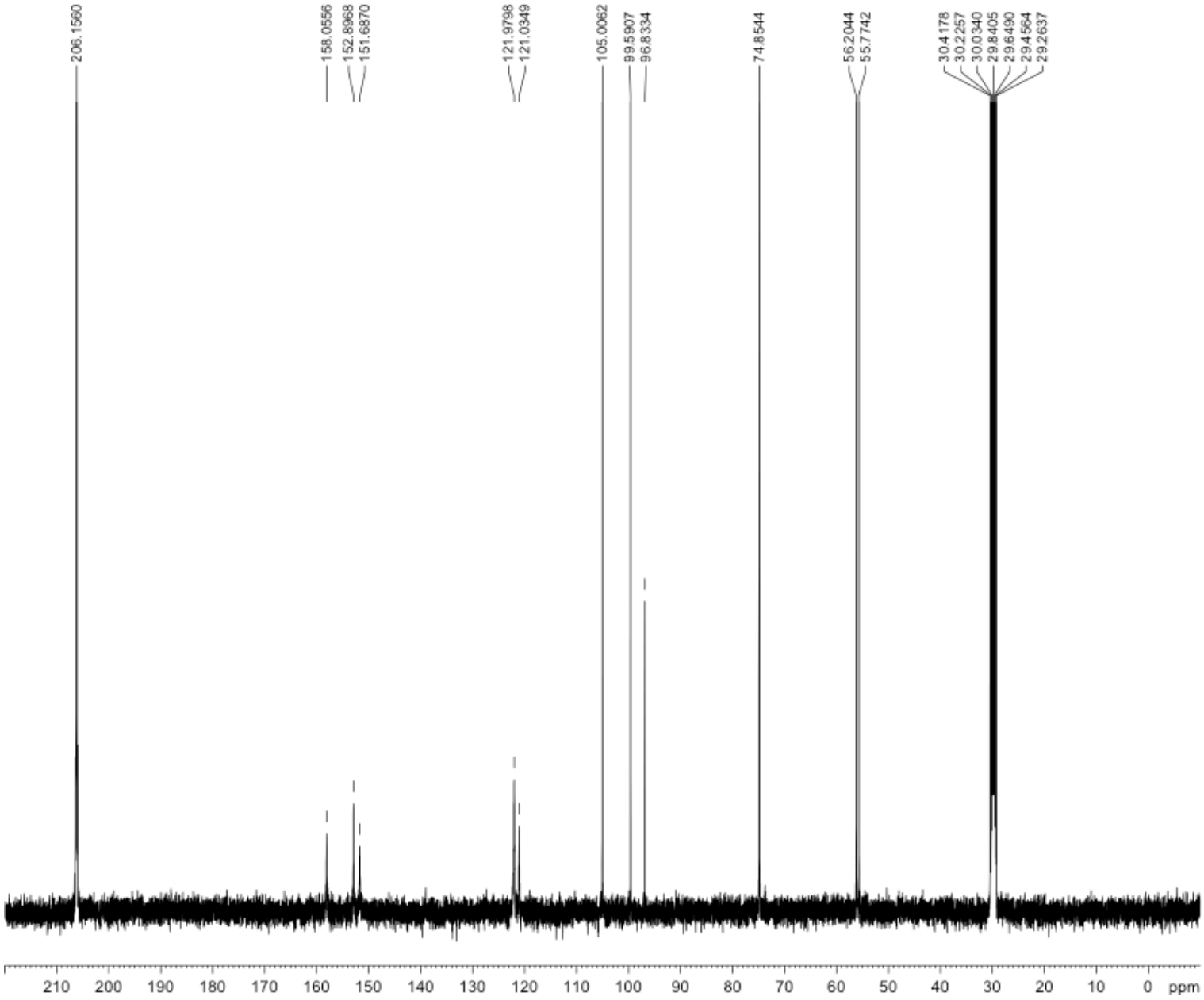

OMe
Br
MeO
HN
O
O
CCl3
O

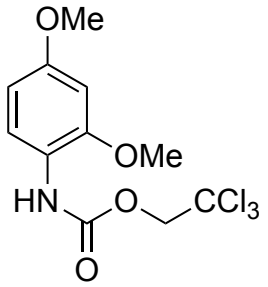
2j


8.0158
7.7747
7.7589
6.6212
6.6146
6.5361
6.5294
6.5141
6.5074
4.8872
3.8644
3.7858
2.8329
2.0610
2.0555
2.0501
2.0446
2.0391
0.841
0.908
0.968
0.996
2.000
3.078
3.061
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

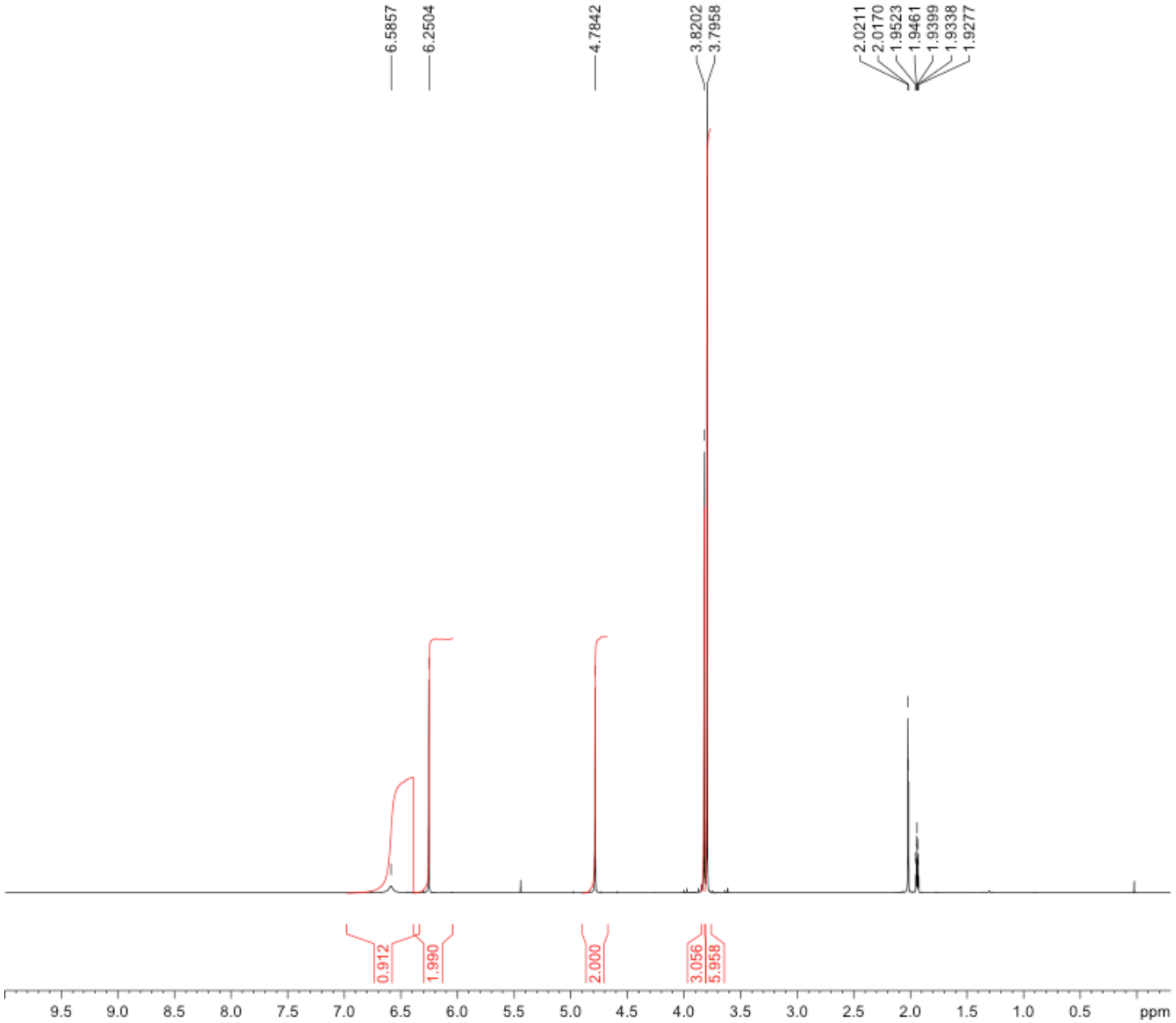

OMe
OMe
HN
O
O
CCl3

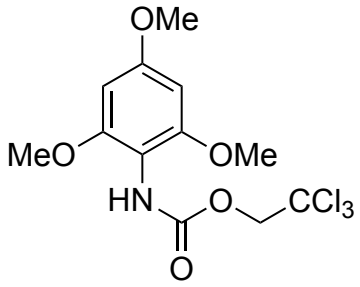
2k


206.1560
158.0556
152.8968
151.6870
121.9798
121.0349
105.0062
99.5907
96.8334
74.8544
56.2044
55.7742
30.4178
30.2257
30.0340
29.8405
29.6490
29.4564
29.2637
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

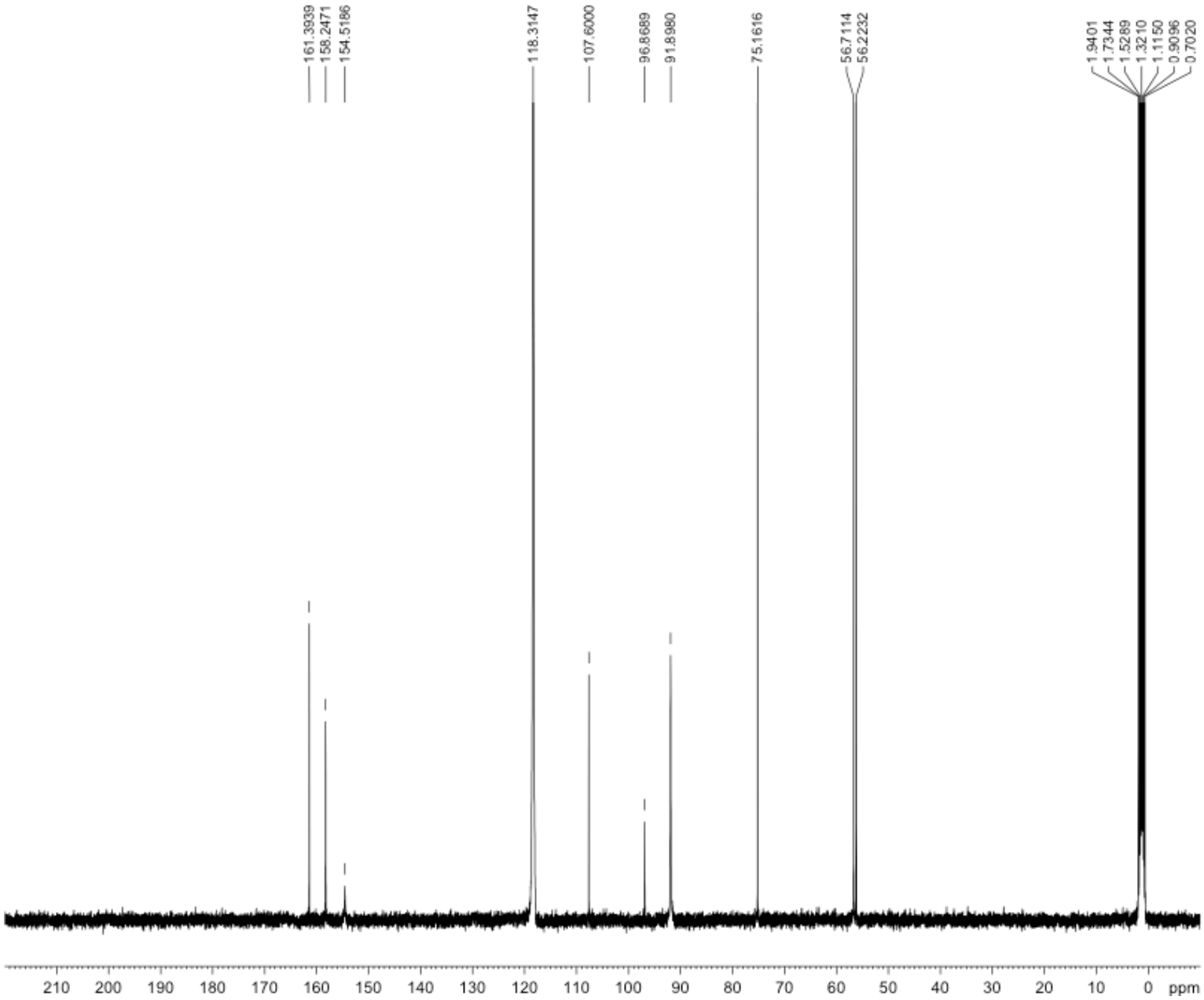

OMe
OMe
HN
O
O
CCl3

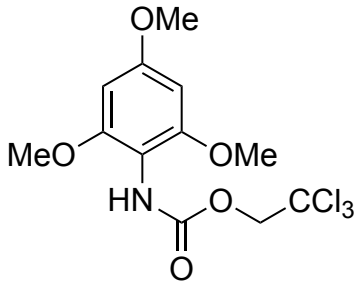
2k


6.5857
6.2504
4.7842
3.8202
3.7958
2.0211
2.0170
1.9523
1.9461
1.9399
1.9338
1.9277
0.912
1.990
2.000
3.056
5.958
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

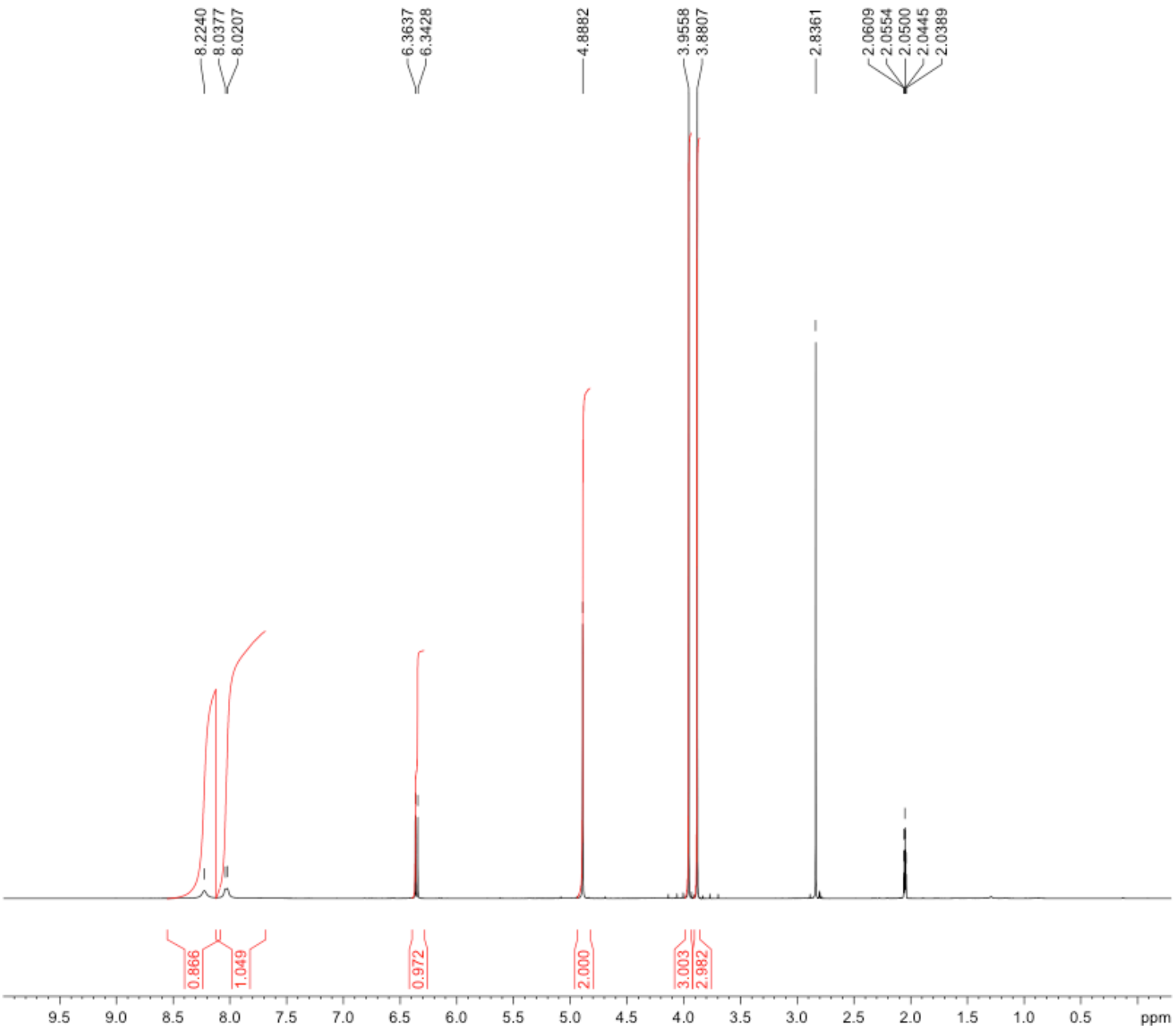

OMe
MeO
OMe
HN
O
O
CCl3

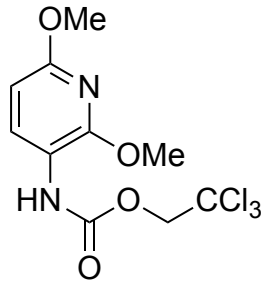
2l


161.3939
158.2471
154.5186
118.3147
107.6000
96.8689
91.8980
75.1616
56.7114
56.2232
1.9401
1.7344
1.5289
1.3210
1.1150
0.9096
0.7020
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

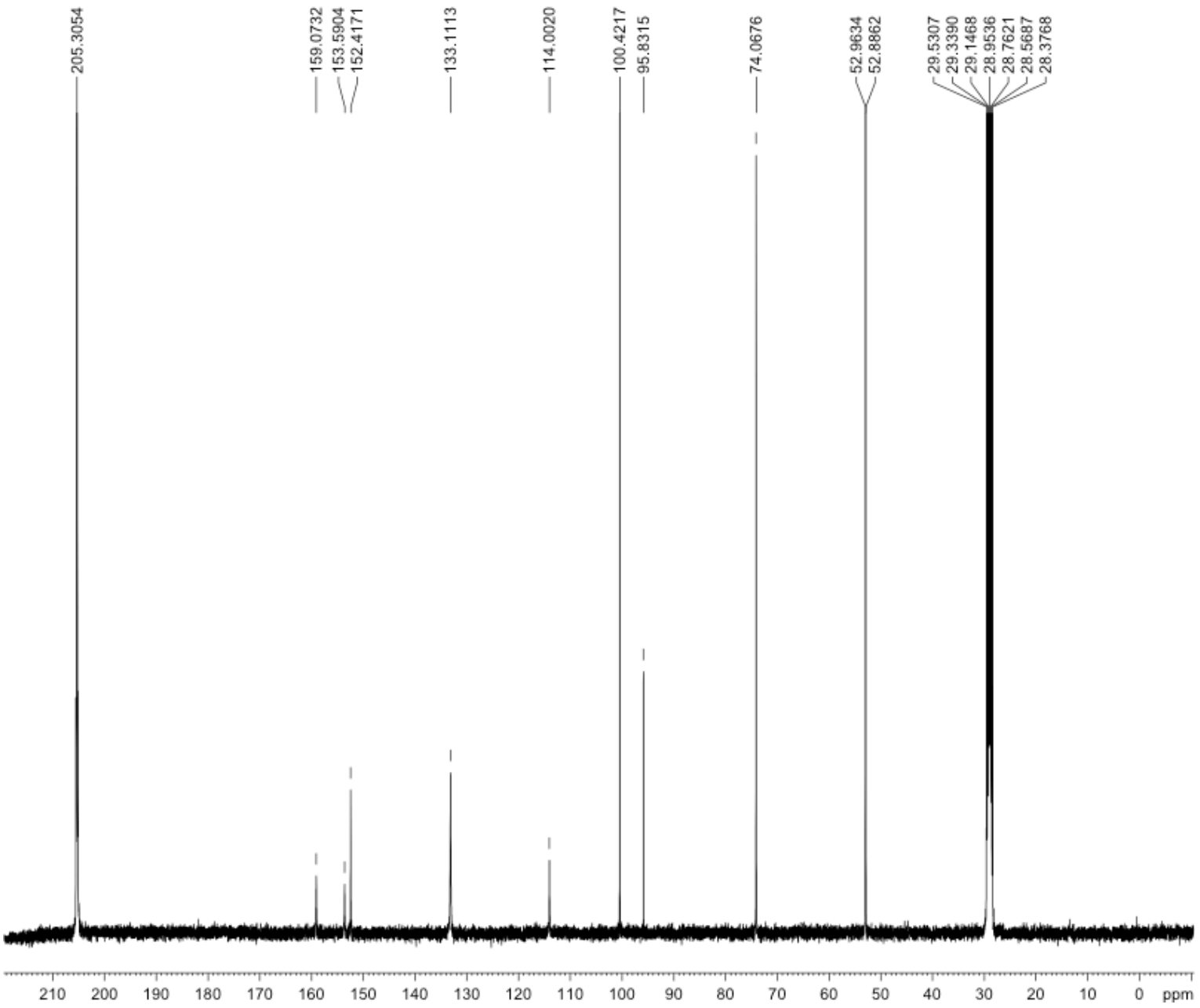

OMe
MeO
OMe
HN
O
O
CCl3

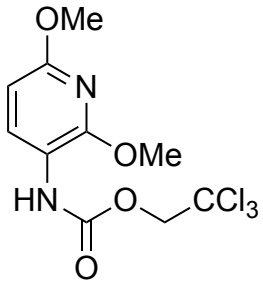
2l


8.2240
8.0377
8.0207
6.3637
6.3428
4.8882
3.9558
3.8807
2.8361
2.0609
2.0554
2.0500
2.0445
2.0389
0.866
1.049
0.972
2.000
3.003
2.982
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

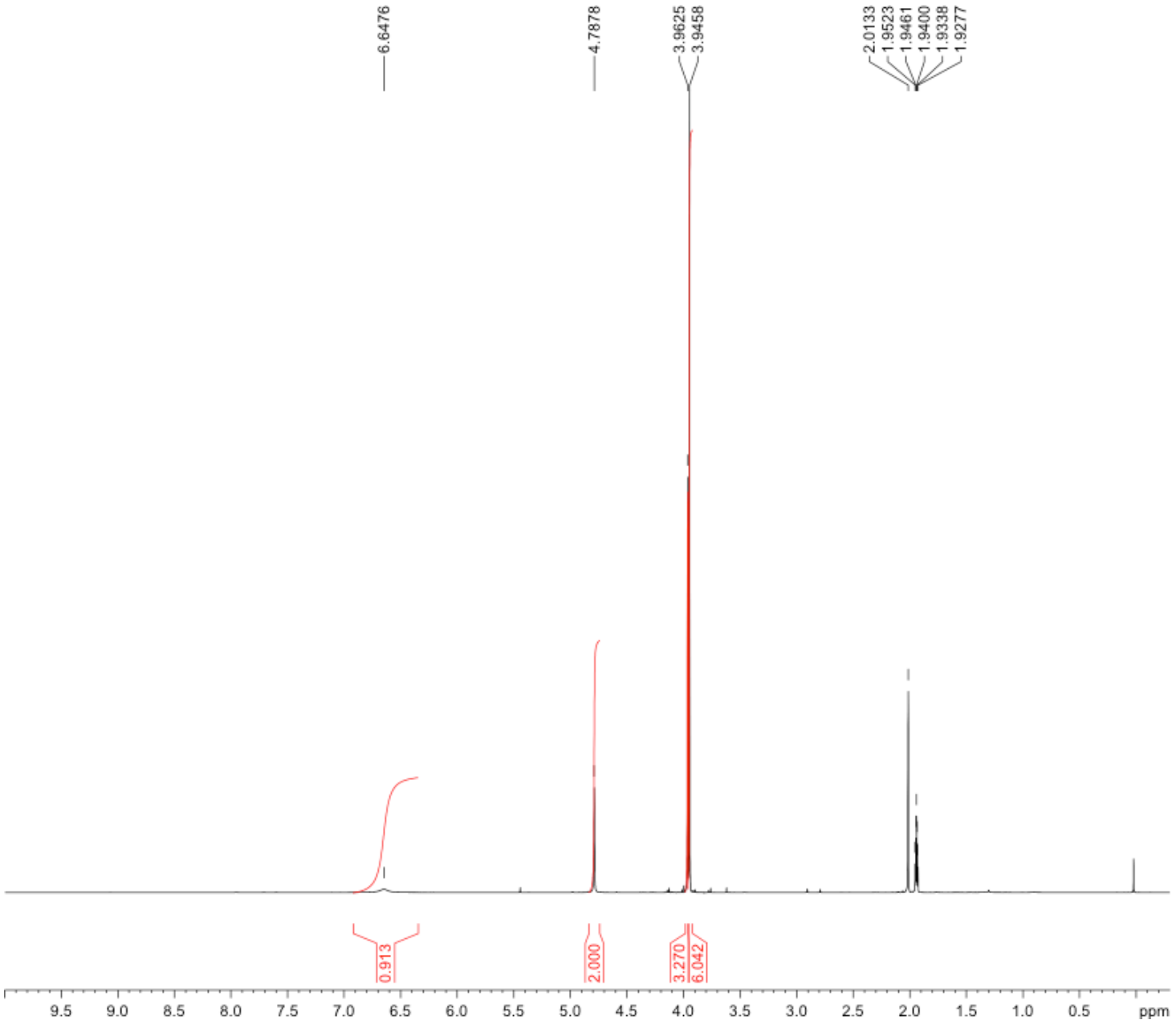

OMe
N
OMe
HN
O
CCl3
O

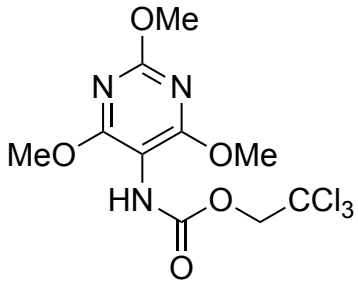
2m


205.3054
159.0732
153.5904
152.4171
133.1113
114.0020
100.4217
95.8315
74.0676
52.9634
52.8862
29.5307
29.3390
29.1468
28.9536
28.7621
28.5687
28.3768
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

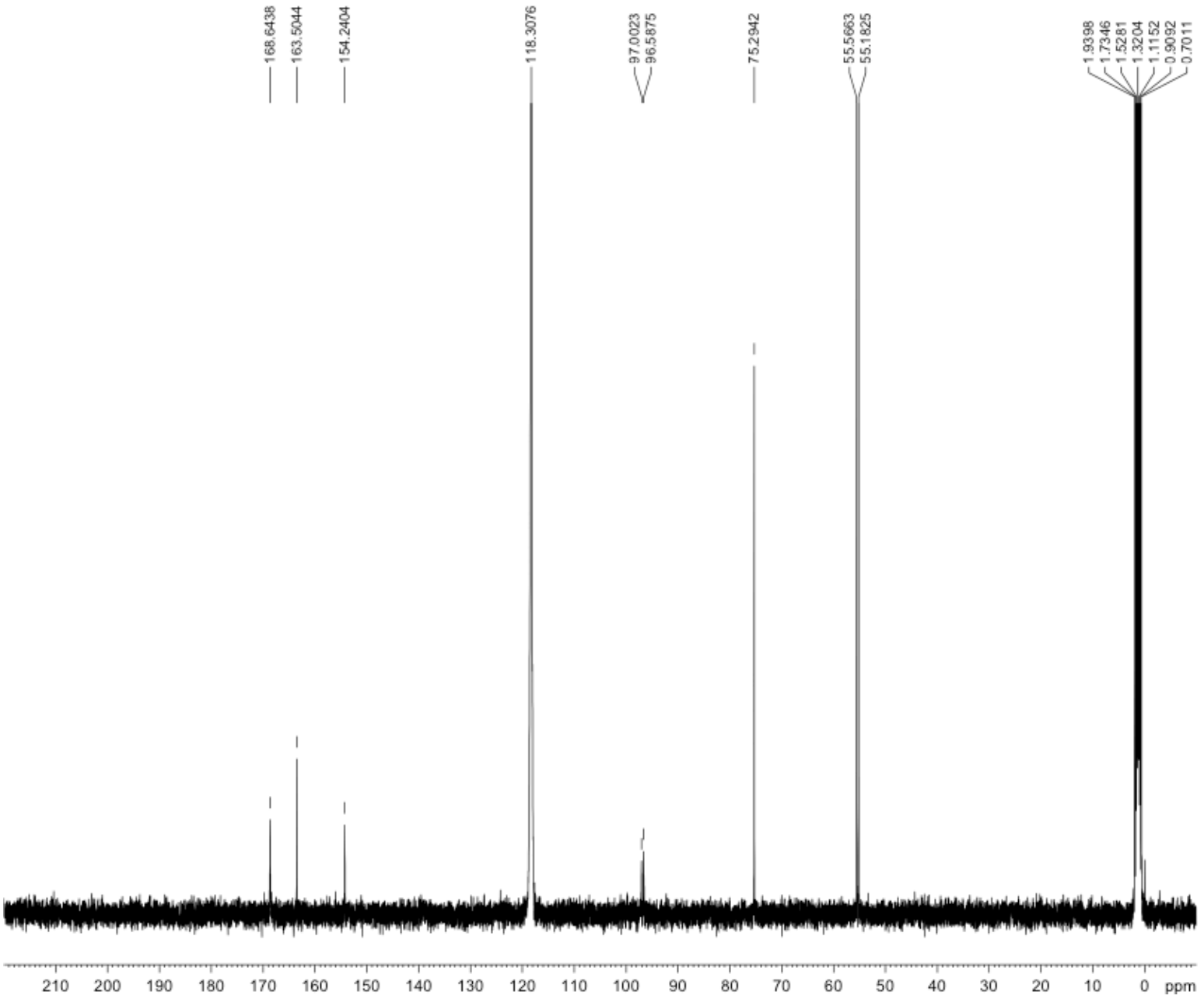

OMe
N
OMe
HN
O
CCl3
O

2m


6.6476
4.7878
3.9625
3.9458
2.0133
1.9523
1.9461
1.9400
1.9338
1.9277
0.913
2.000
3.270
6.042
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


OMe
N
N
MeO
OMe
HN
O
CCl3
O

2n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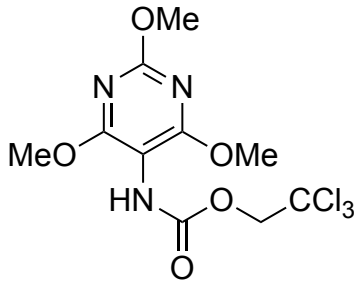
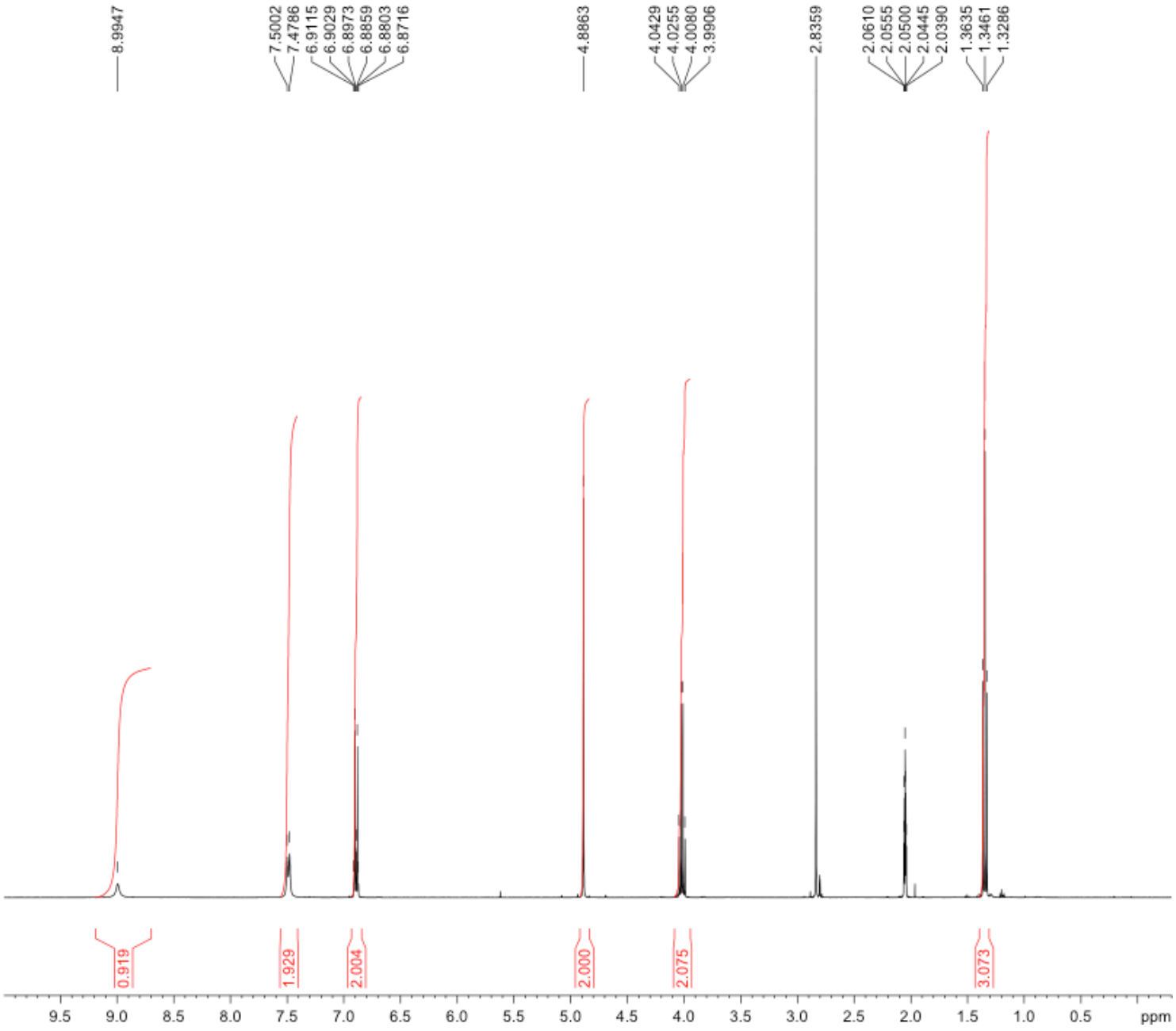
163.5044
154.2404
118.3076
97.0023
96.5875
75.2942
55.5663
55.1825
1.9398
1.7346
1.5281
1.3204
1.1152
0.9092
0.7011
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
N
N
MeO
OMe
HN
O
O
CCl3

2n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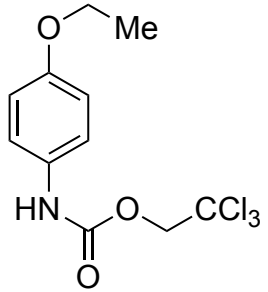
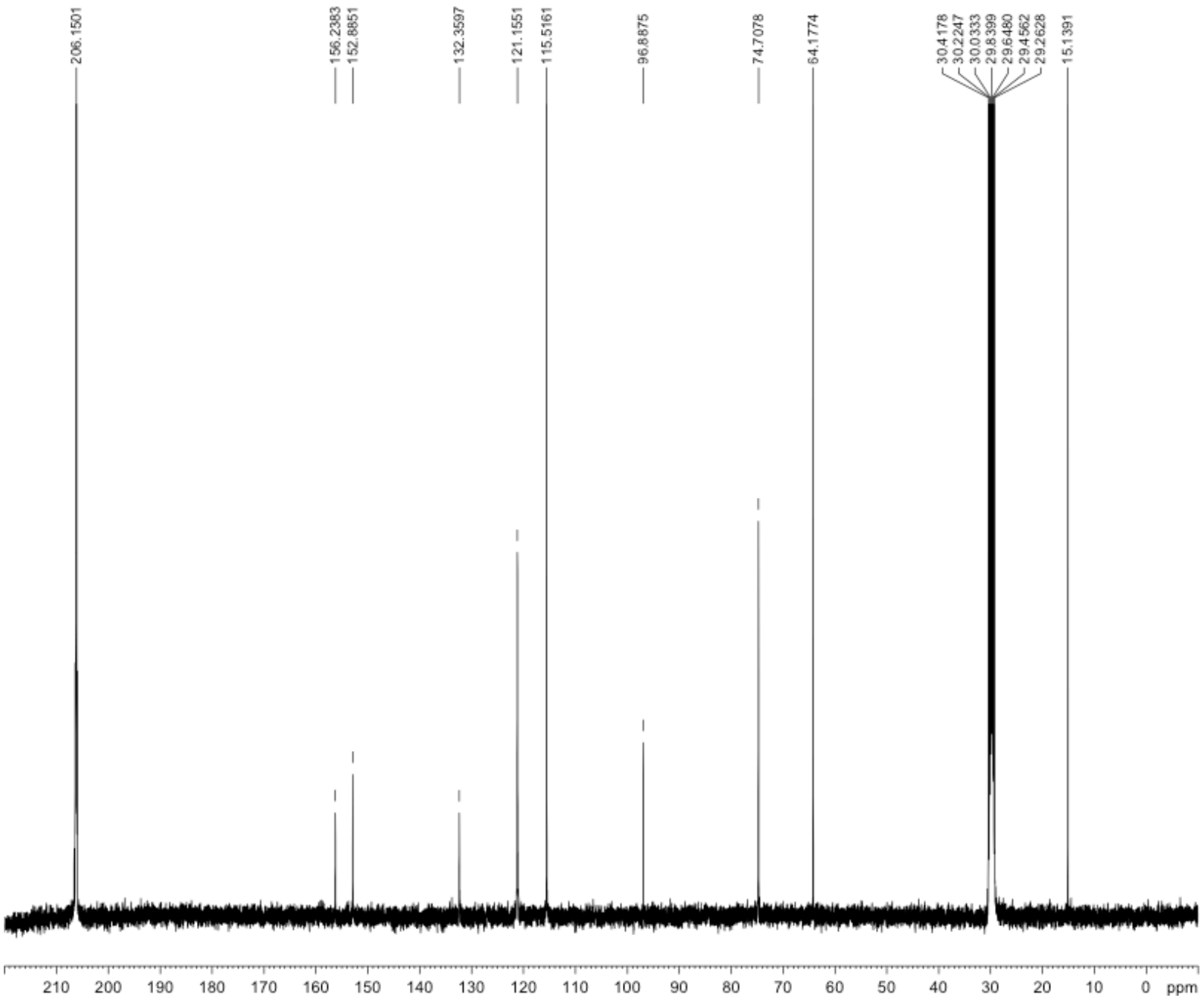
7.5002
7.4786
6.9115
6.9029
6.8973
6.8859
6.8803
6.8716
4.8863
4.0429
4.0255
4.0080
3.9906
2.8359
2.0610
2.0555
2.0500
2.0445
2.0390
1.3635
1.3461
1.3286
0.919
1.929
2.004
2.000
2.075
3.073
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


O
Me
HN
O
O
CCl3

2o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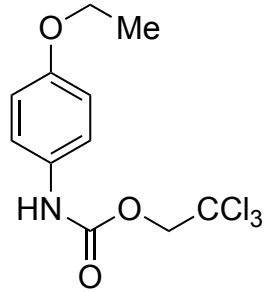
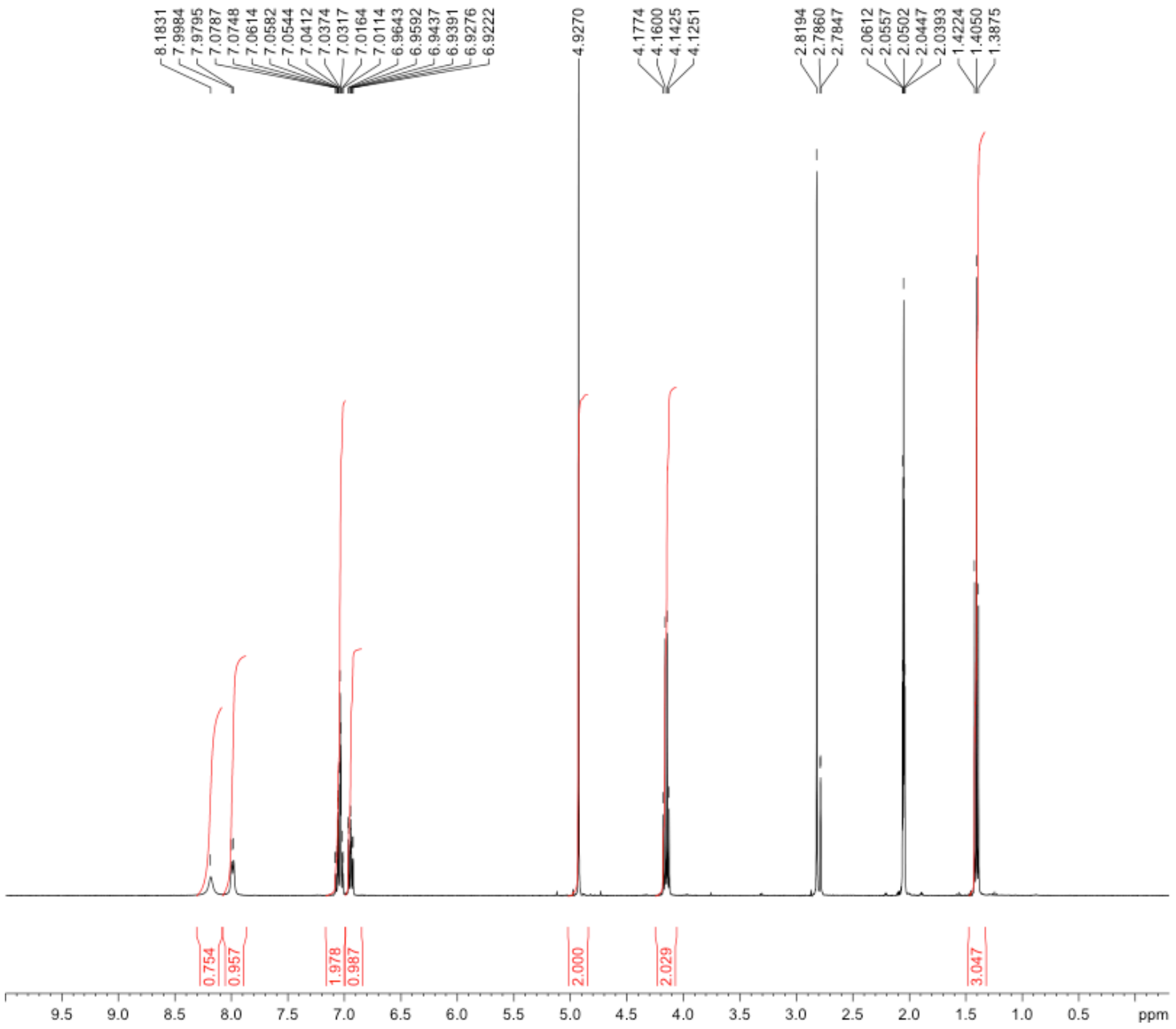
156.2383
152.8851
132.3597
121.1551
115.5161
96.8875
74.7078
64.1774
30.4178
30.2247
30.0333
29.8399
29.6480
29.4562
29.2628
15.1391
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
Me
HN
O
O
CCl3

2o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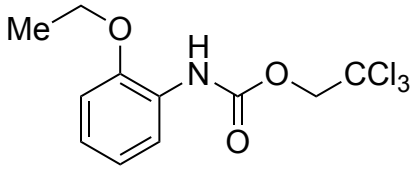
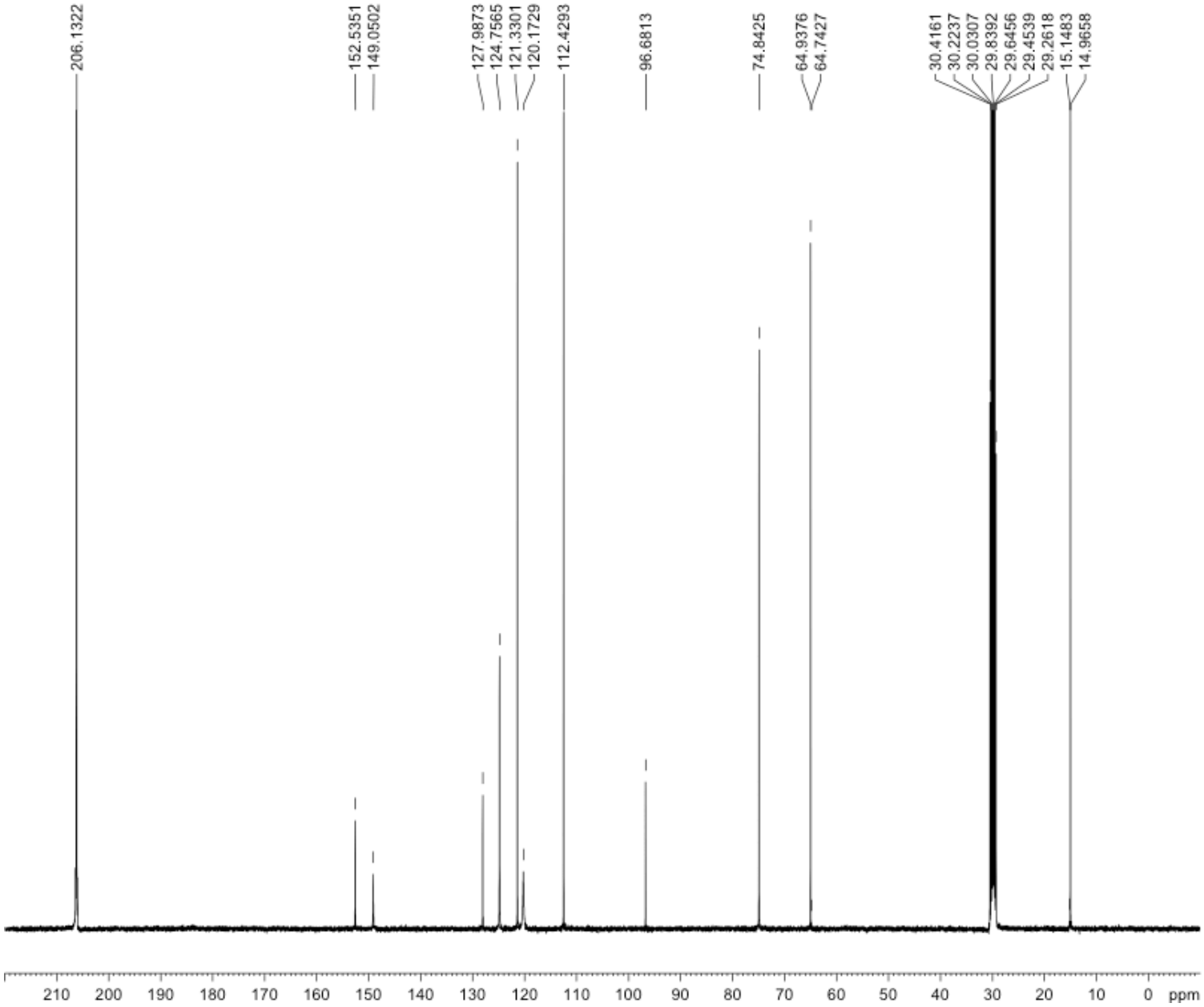
7.9984
7.9795
7.0787
7.0748
7.0614
7.0582
7.0544
7.0412
7.0374
7.0317
7.0164
7.0114
6.9643
6.9592
6.9437
6.9391
6.9276
6.9222
4.9270
4.1774
4.1600
4.1425
4.1251
2.8194
2.7860
2.7847
2.0612
2.0557
2.0502
2.0447
2.0393
1.4224
1.4050
1.3875
0.754
0.957
1.978
0.987
2.000
2.029
3.047
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Me
O
H
N
O
O
CCl3

3o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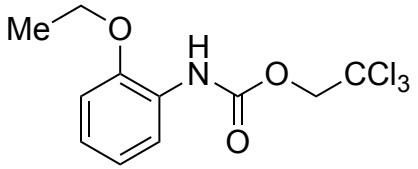
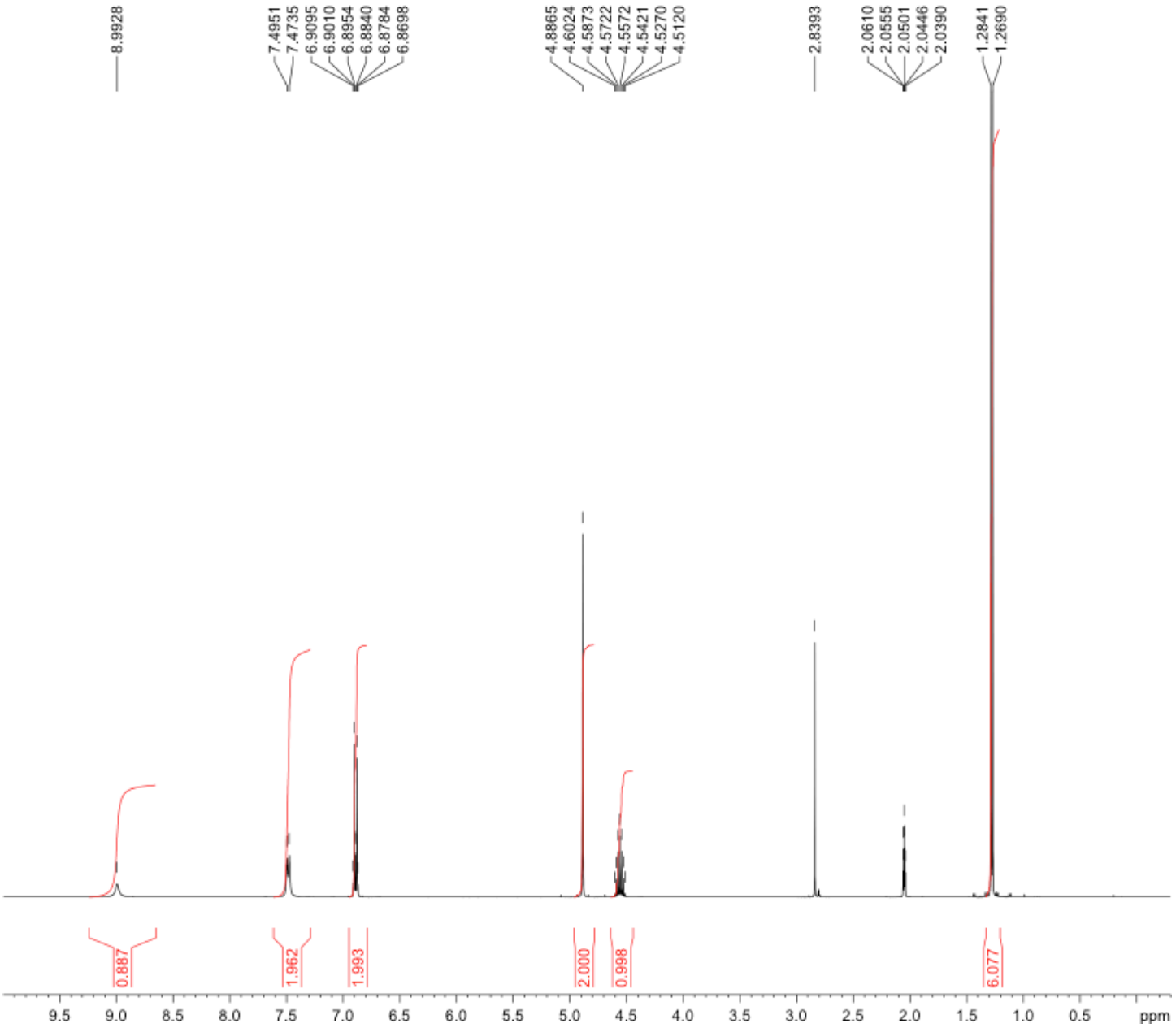
152.5351
149.0502
127.9873
124.7565
121.3301
120.1729
112.4293
96.6813
74.8425
64.9376
64.7427
30.4161
30.2237
30.0307
29.8392
29.6456
29.4539
29.2618
15.1483
14.9658
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
O
H
N
O
O
CCl3

3o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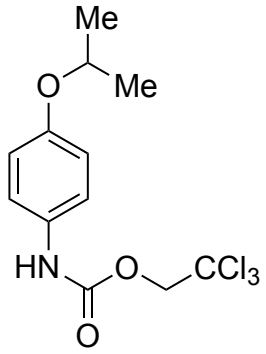
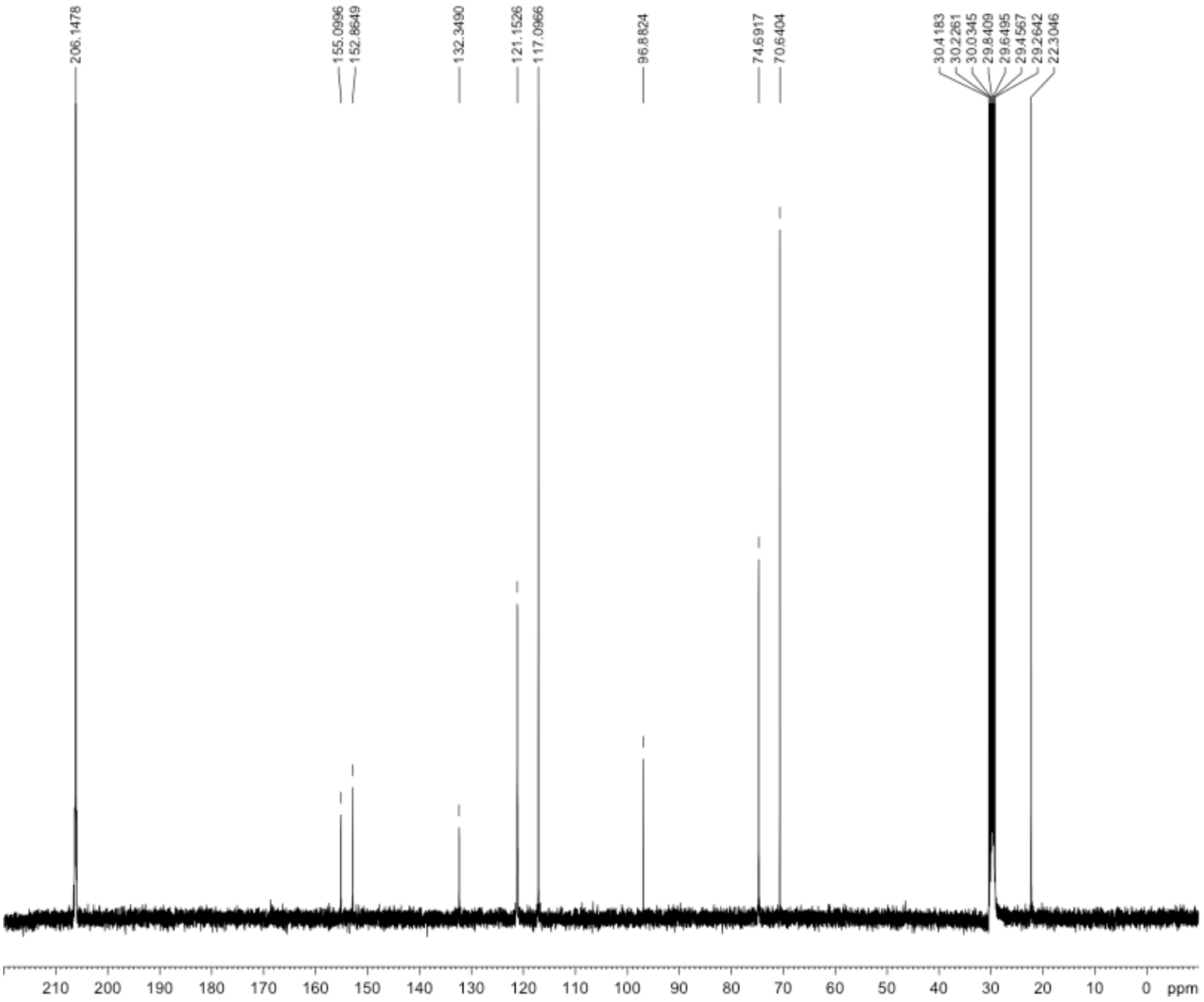
7.4735
6.9095
6.9010
6.8954
6.8840
6.8784
6.8698
4.8865
4.6024
4.5873
4.5722
4.5572
4.5421
4.5270
4.5120
2.8393
2.0610
2.0555
2.0501
2.0446
2.0390
1.2841
1.2690
0.887
1.962
1.993
2.000
0.998
6.077
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Me
O
Me
HN
O
CCl3
O

2p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152.8649
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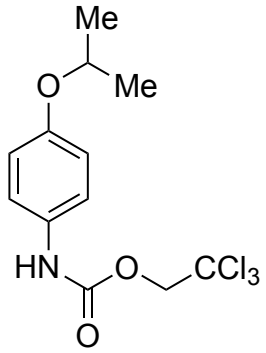
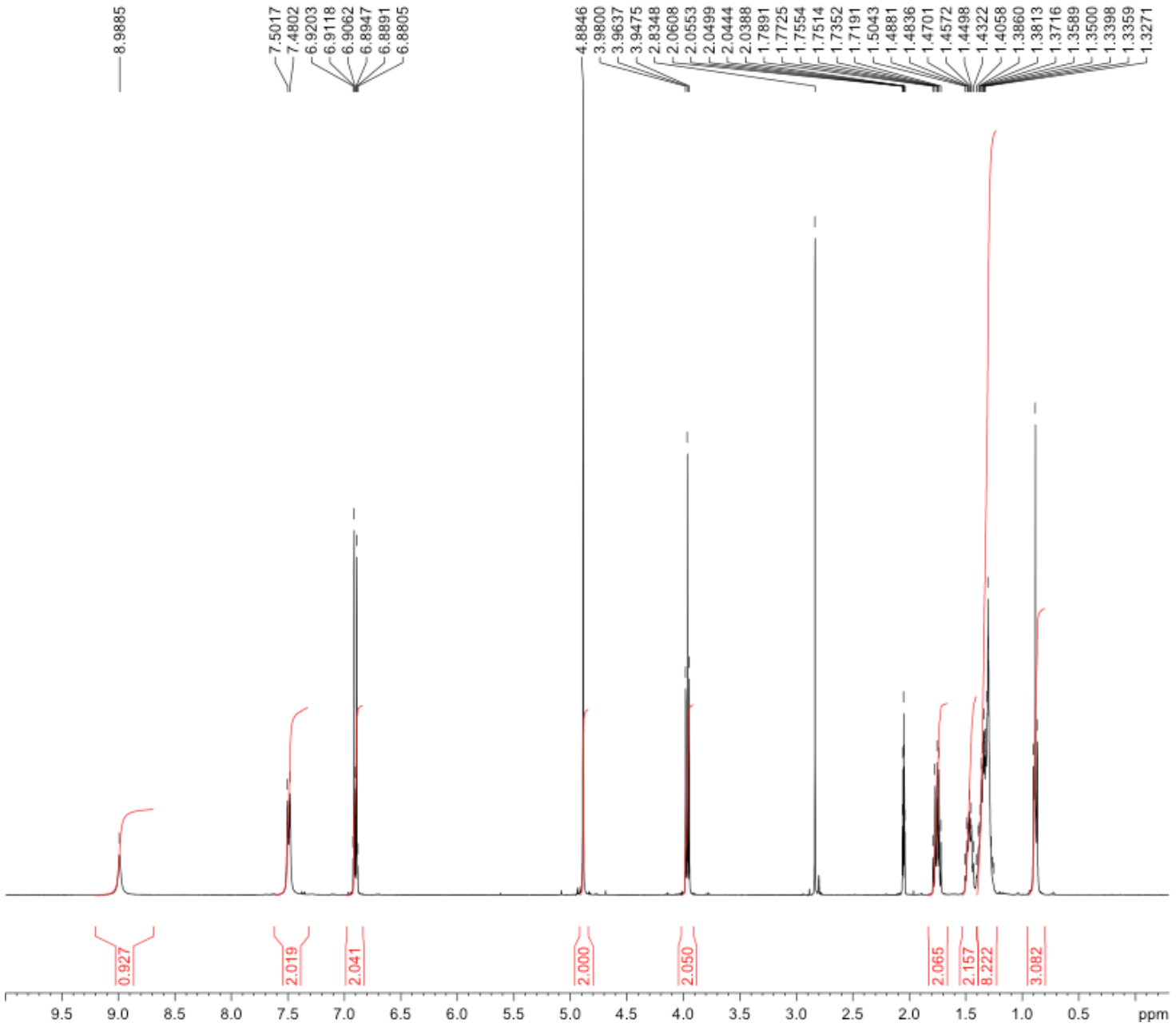
121.1526
117.0966
96.8824
74.6917
70.6404
30.4183
30.2261
30.0345
29.8409
29.6495
29.4567
29.2642
22.3046
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
O
Me
HN
O
CCl3
O

2p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7.4802
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6.9118
6.9062
6.8947
6.8891
6.8805
4.8846
3.9800
3.9637
3.9475
2.8348
2.0608
2.0553
2.0499
2.0444
2.0388
1.7891
1.7725
1.7554
1.7514
1.7352
1.7191
1.5043
1.4881
1.4836
1.4701
1.4572
1.4498
1.4322
1.4058
1.3860
1.3813
1.3716
1.3589
1.3500
1.3398
1.3359
1.3271
0.927
2.019
2.041
2.000
2.050
2.065
2.157
8.222
3.082
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
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2.0
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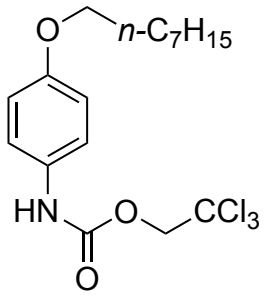
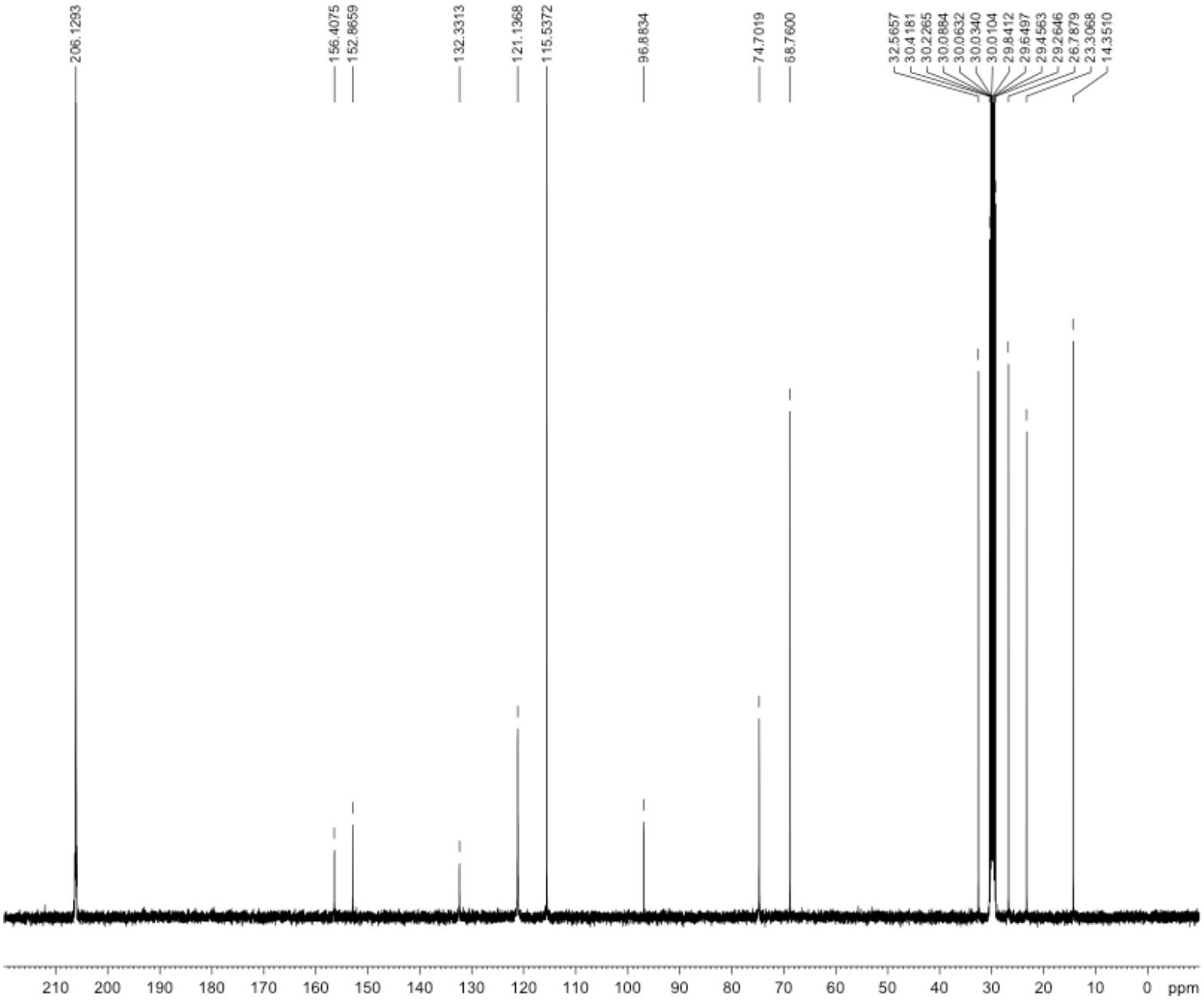
1.0
0.5
ppm


O
n-C7H15
HN
O
O
CCl3
O

2q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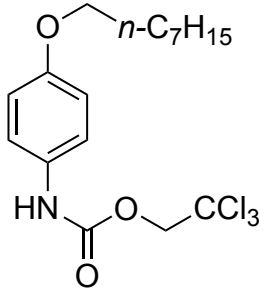
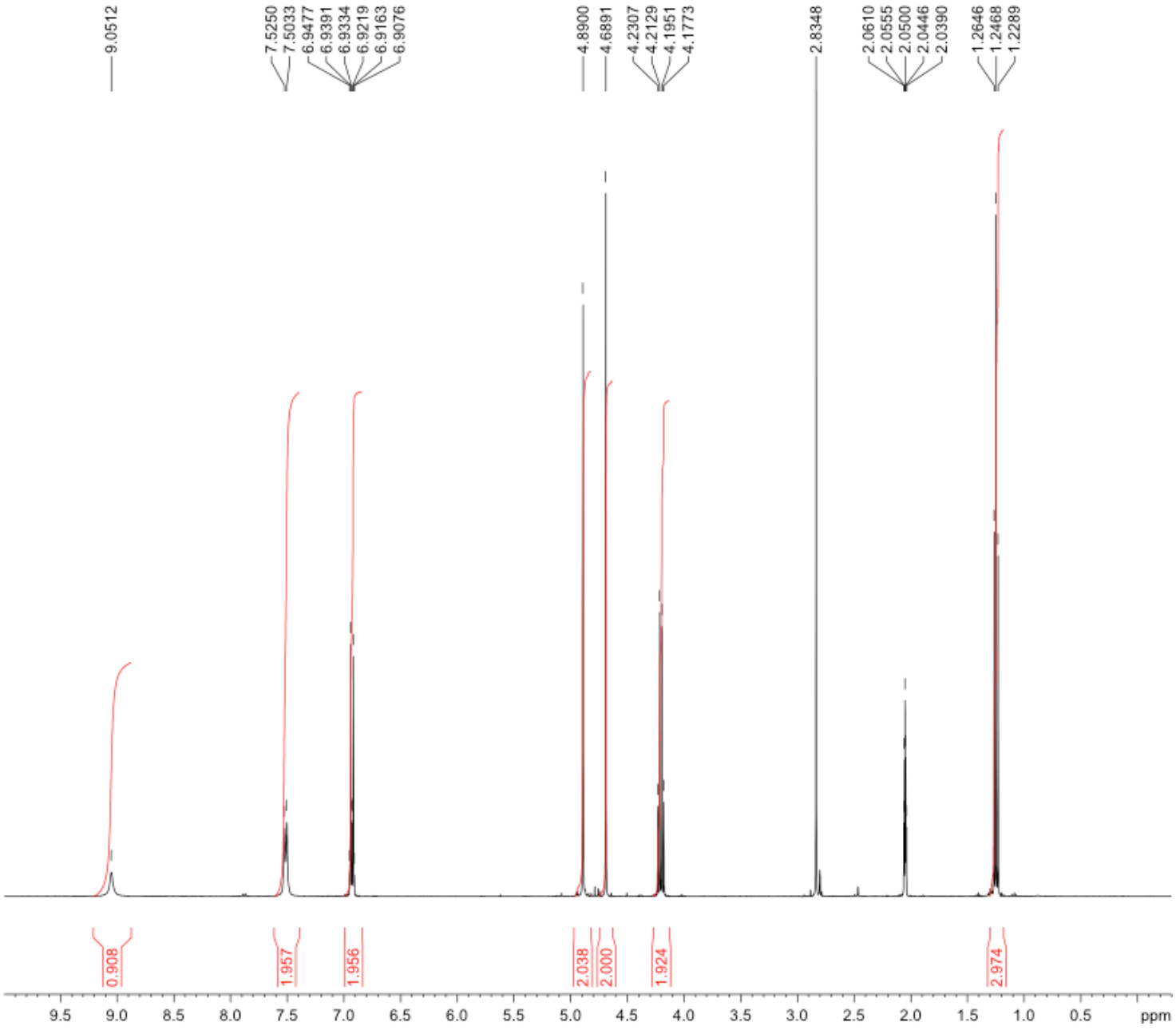
96.8834
74.7019
68.7600
32.5657
30.4181
30.2265
30.0884
30.0632
30.0340
30.0104
29.8412
29.6497
29.4563
29.2646
26.7879
23.3068
14.3510
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
n-C7H15
HN
O
O
CCl3
O

2q


9.0512
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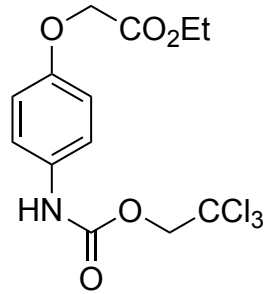
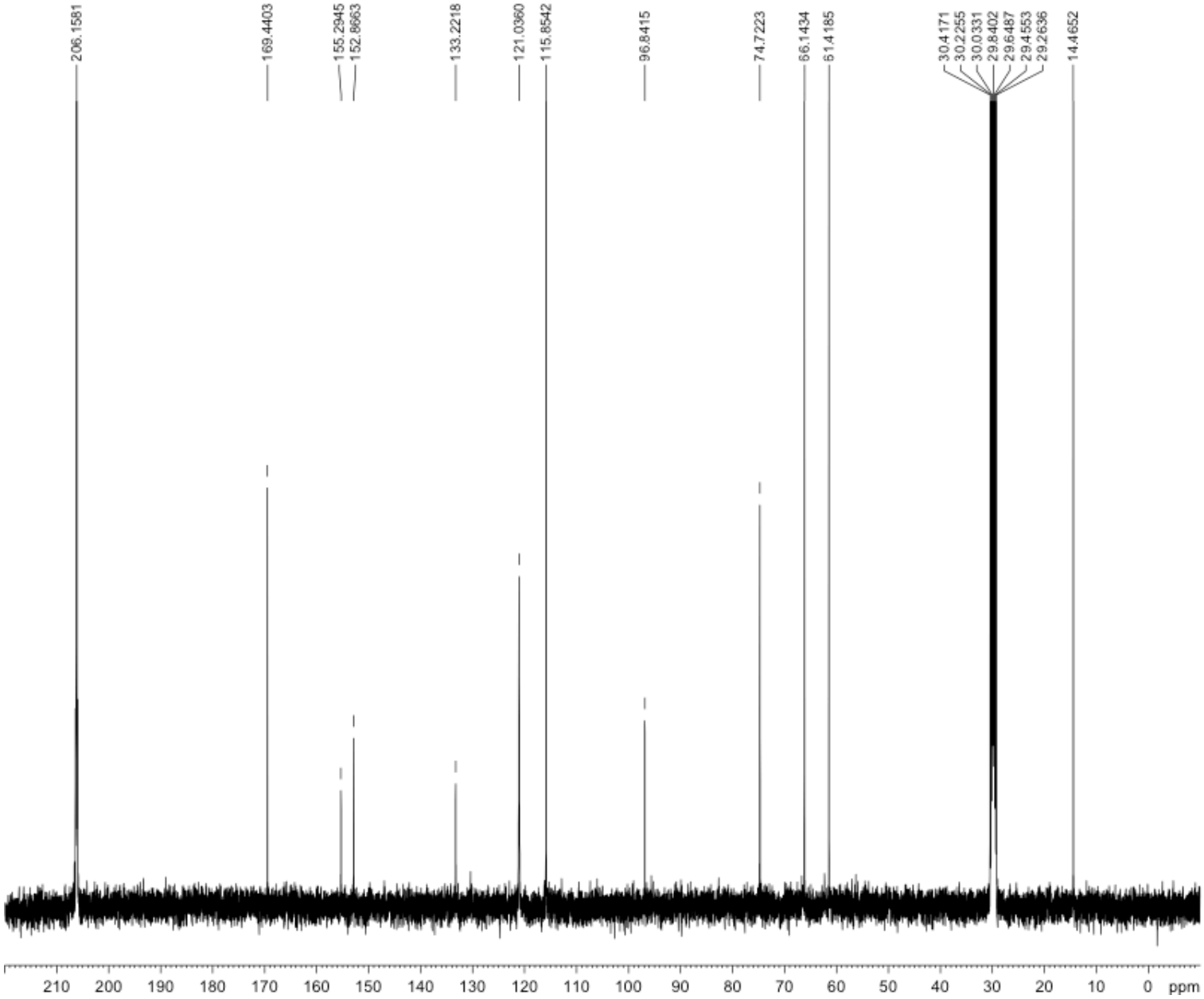
7.5033
6.9477
6.9391
6.9334
6.9219
6.9163
6.9076
4.8900
4.6891
4.2307
4.2129
4.1951
4.1773
2.8348
2.0610
2.0555
2.0500
2.0446
2.0390
1.2646
1.2468
1.2289
0.908
1.957
1.956
2.038
2.000
1.924
2.974
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


O
CO2Et
HN
O
O
CCl3

2r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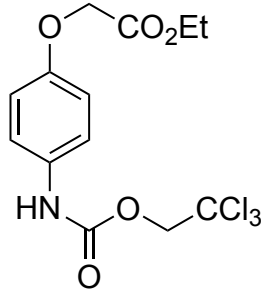
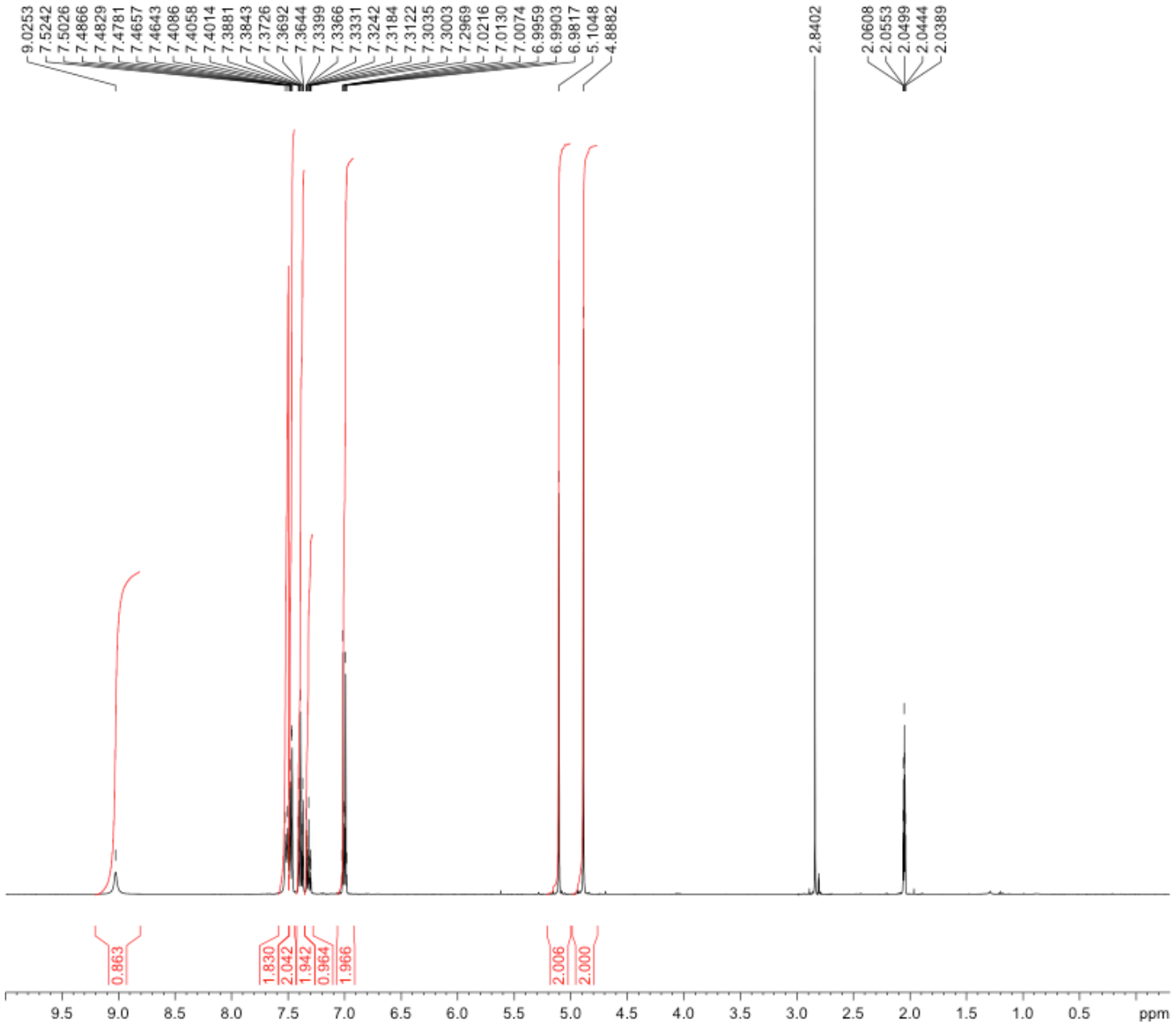
155.2945
152.8663
133.2218
121.0360
115.8542
96.8415
74.7223
66.1434
61.4185
30.4171
30.2255
30.0331
29.8402
29.6487
29.4553
29.2636
14.4652
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
CO2Et
HN
O
O
CCl3
O

2r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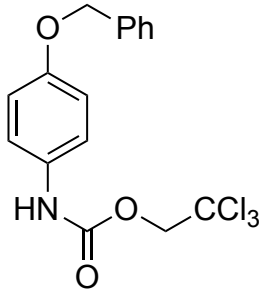
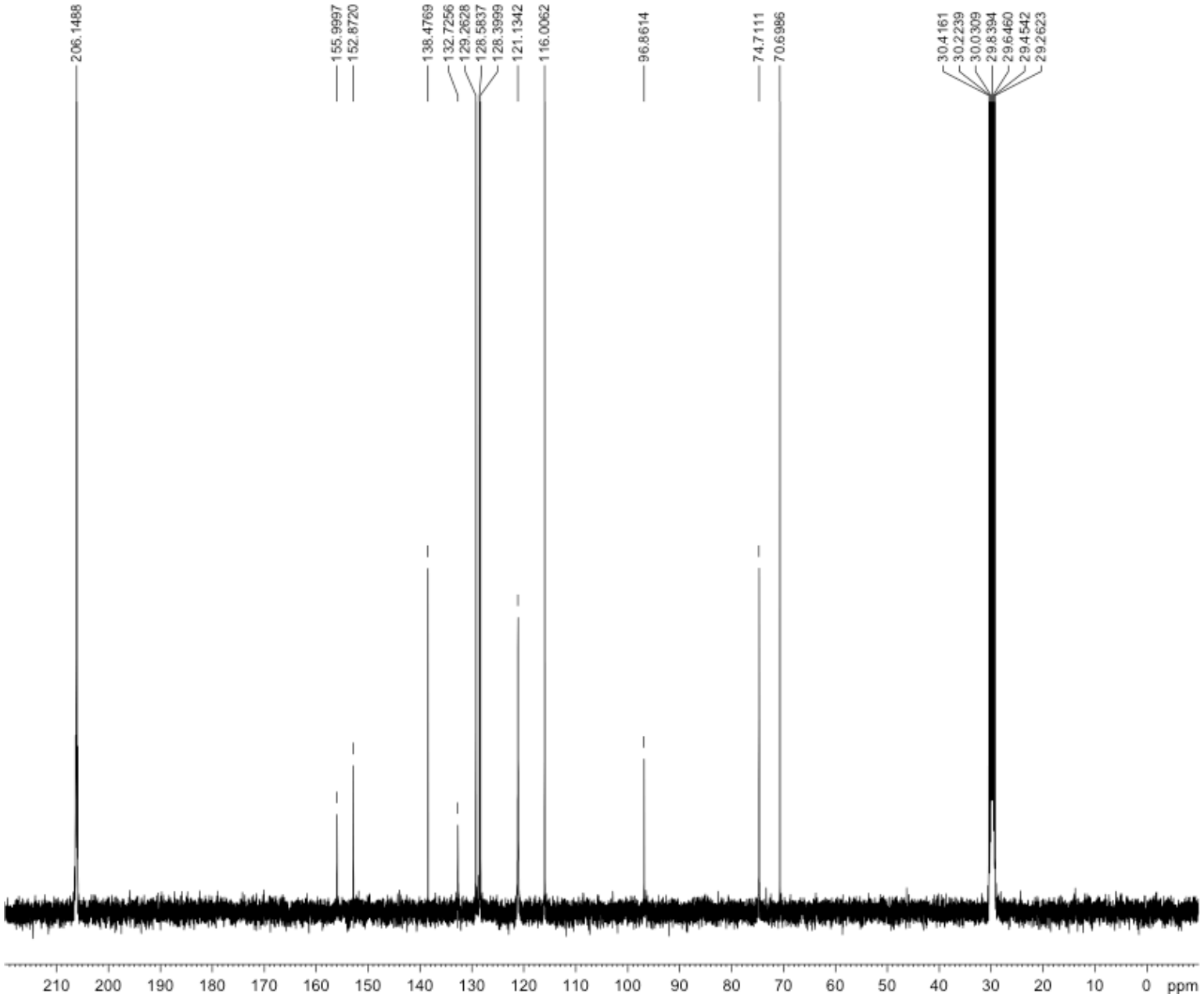
7.5026
7.4866
7.4829
7.4781
7.4657
7.4643
7.4086
7.4058
7.4014
7.3881
7.3843
7.3726
7.3692
7.3644
7.3399
7.3366
7.3331
7.3242
7.3184
7.3122
7.3035
7.3003
7.2969
7.0216
7.0130
7.0074
6.9959
6.9903
6.9817
5.1048
4.8882
2.8402
2.0608
2.0553
2.0499
2.0444
2.0389
0.863
1.830
2.042
1.942
0.964
1.966
2.006
2.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


O
Ph
HN
O
O
CCl3

2s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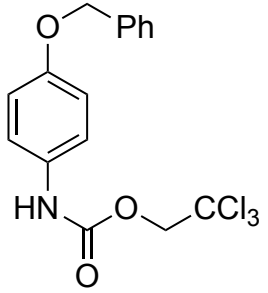
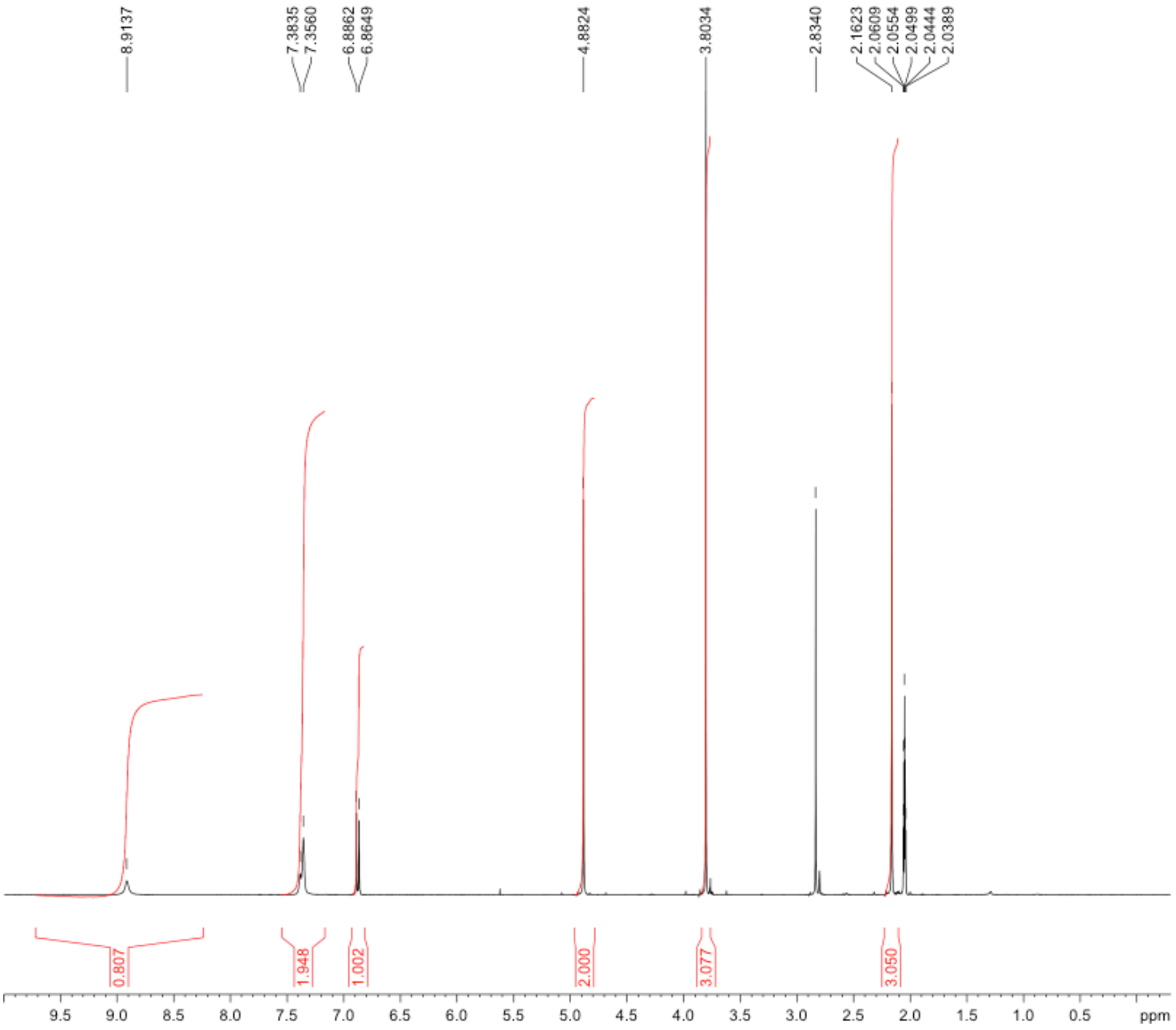
128.5837
128.3999
121.1342
116.0062
96.8614
74.7111
70.6986
30.4161
30.2239
30.0309
29.8394
29.6460
29.4542
29.2623
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
Ph
HN
O
O
CCl3

2s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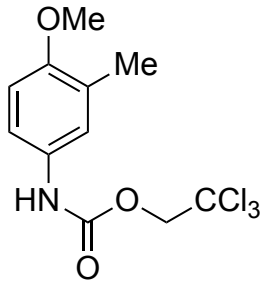
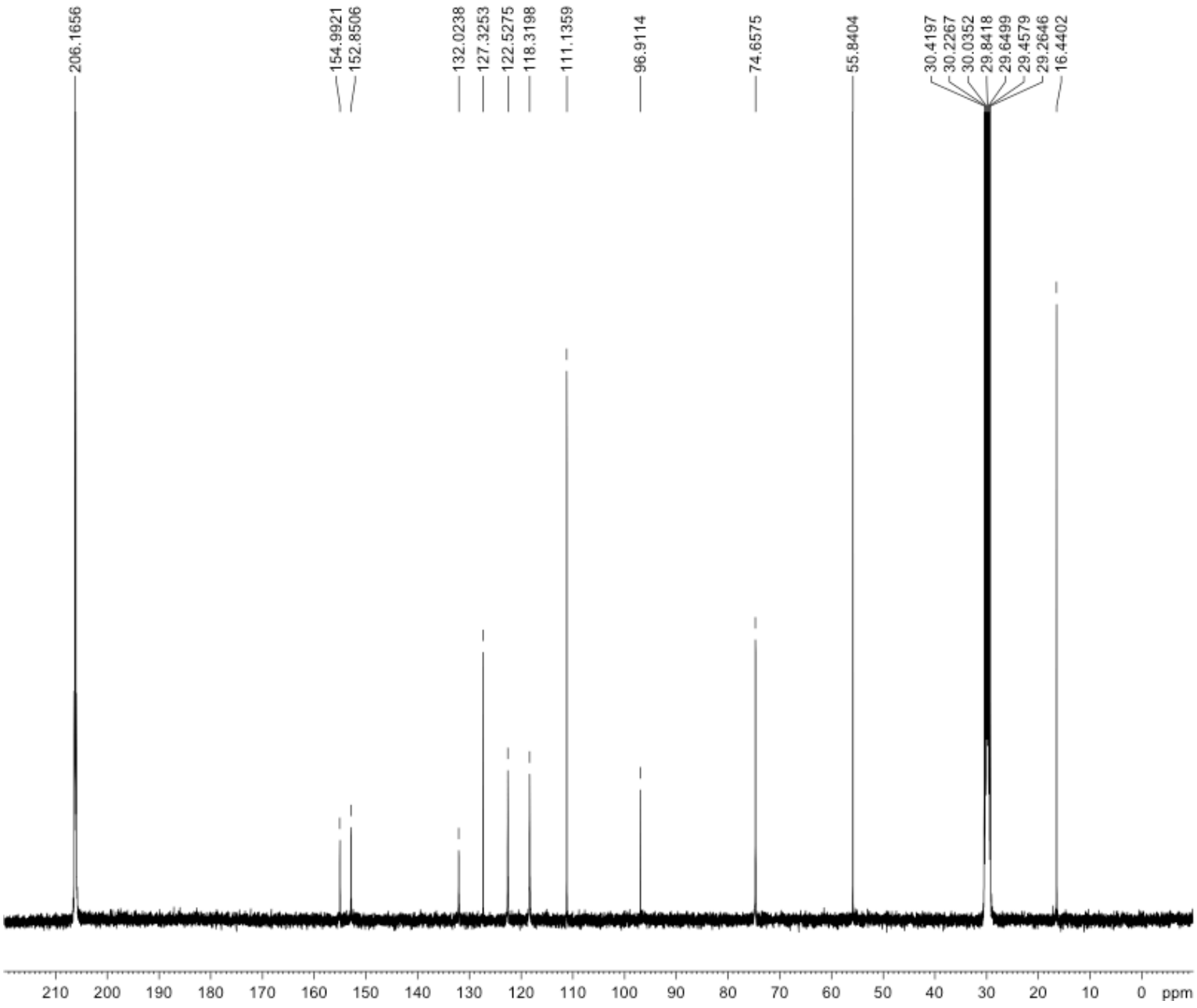
7.3560
6.8862
6.8649
4.8824
3.8034
2.8340
2.1623
2.0609
2.0554
2.0499
2.0444
2.0389
0.807
1.948
1.002
2.000
3.077
3.050
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


OMe
Me
HN
O
O
CCl3

2t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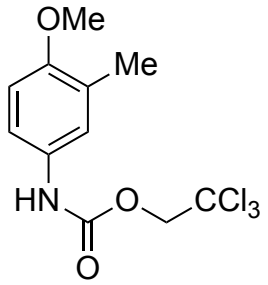
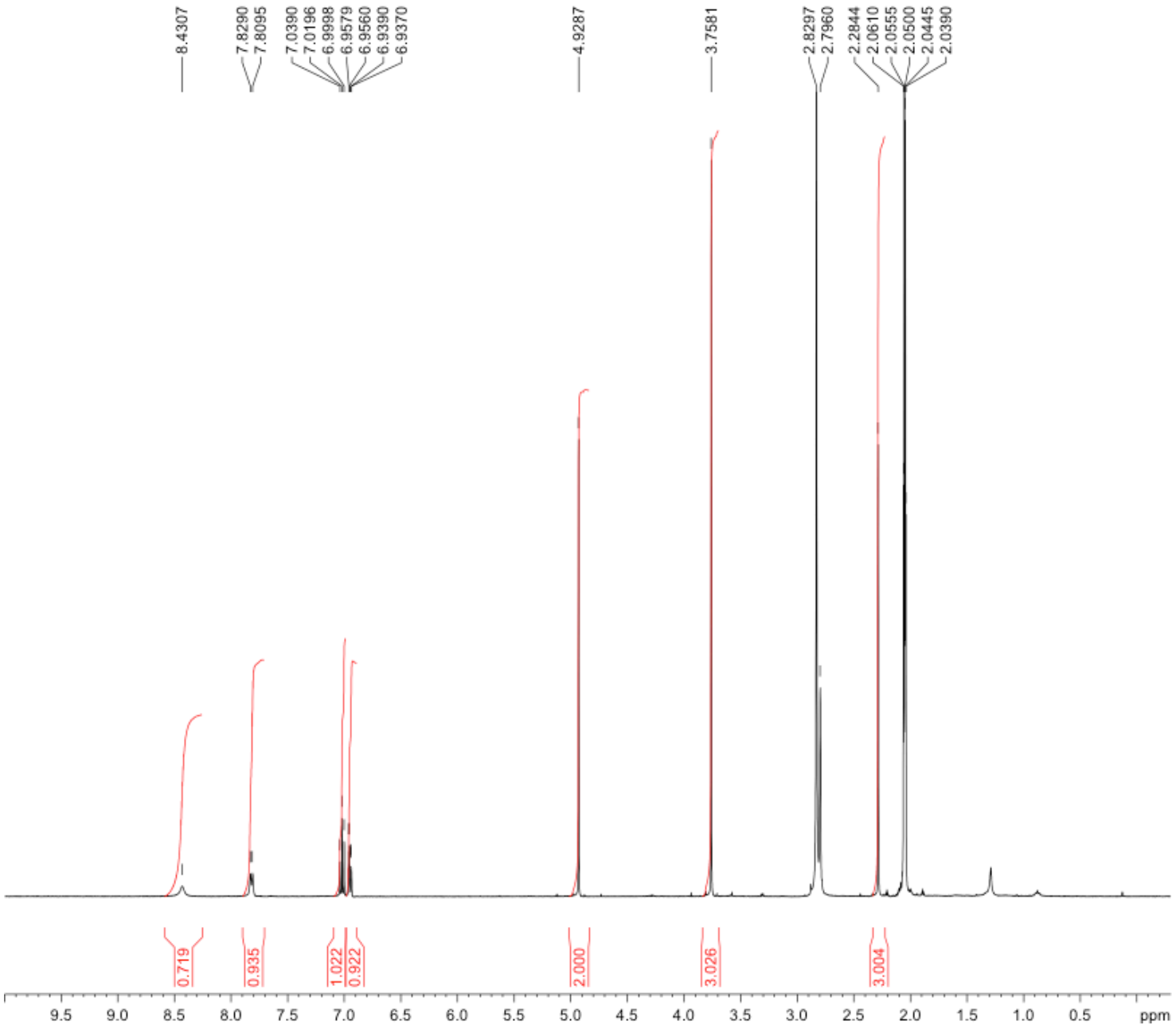
152.8506
132.0238
127.3253
122.5275
118.3198
111.1359
96.9114
74.6575
55.8404
30.4197
30.2267
30.0352
29.8418
29.6499
29.4579
29.2646
16.4402
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
Me
HN
O
O
CCl3

2t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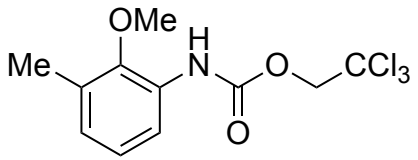
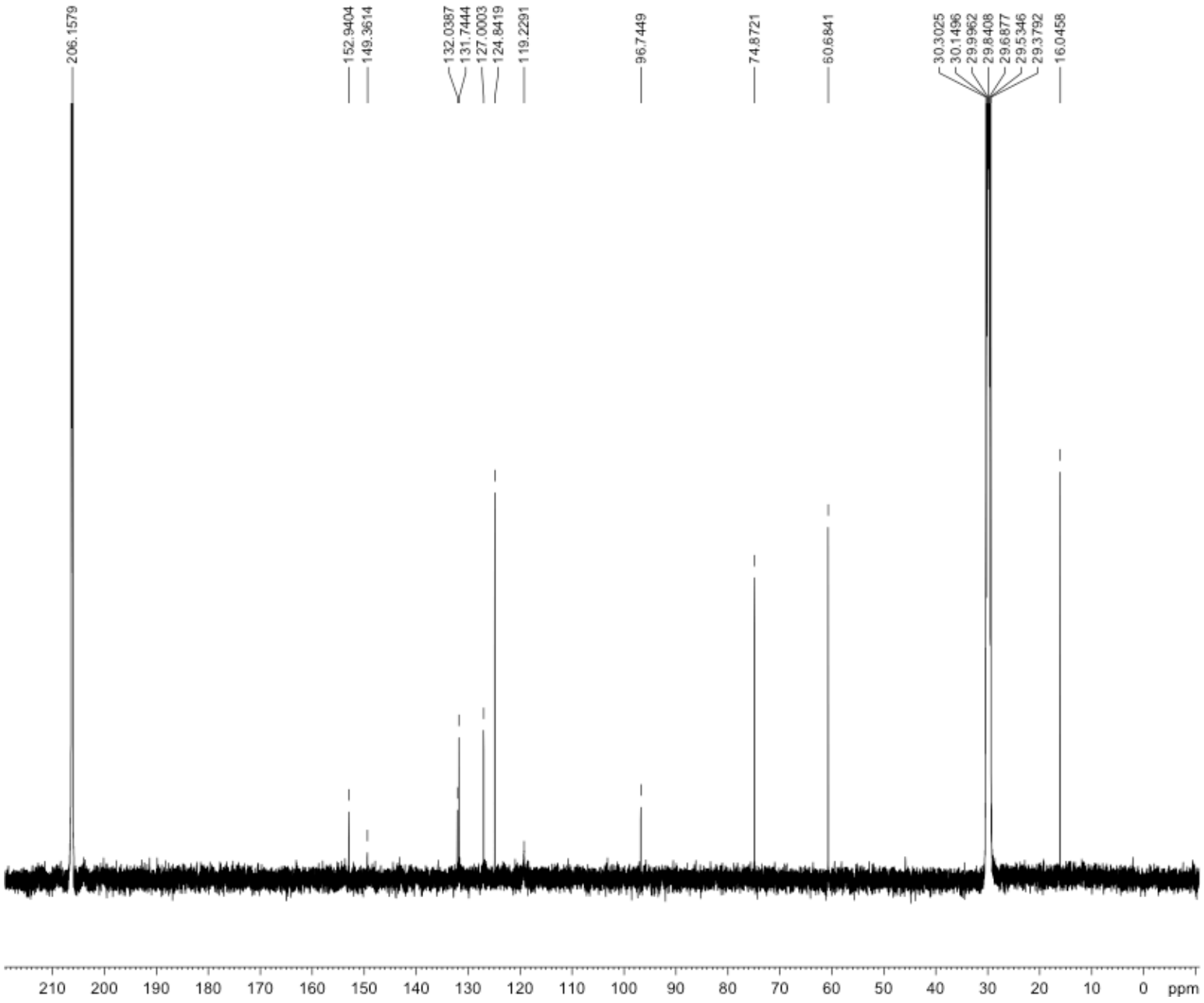
7.8290
7.8095
7.0390
7.0196
6.9998
6.9579
6.9560
6.9390
6.9370
4.9287
3.7581
2.8297
2.7960
2.2844
2.0610
2.0555
2.0500
2.0445
2.0390
0.719
0.935
1.022
0.922
2.000
3.026
3.004
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


OMe
H
N
Me
O
O
CCl3

3t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132.0387
131.7444
127.0003
124.8419
119.2291
96.7449
74.8721
60.6841
30.3025
30.1496
29.9962
29.8408
29.6877
29.5346
29.3792
16.0458
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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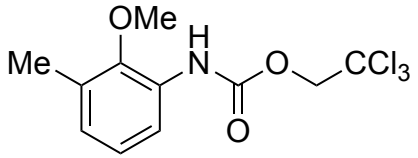
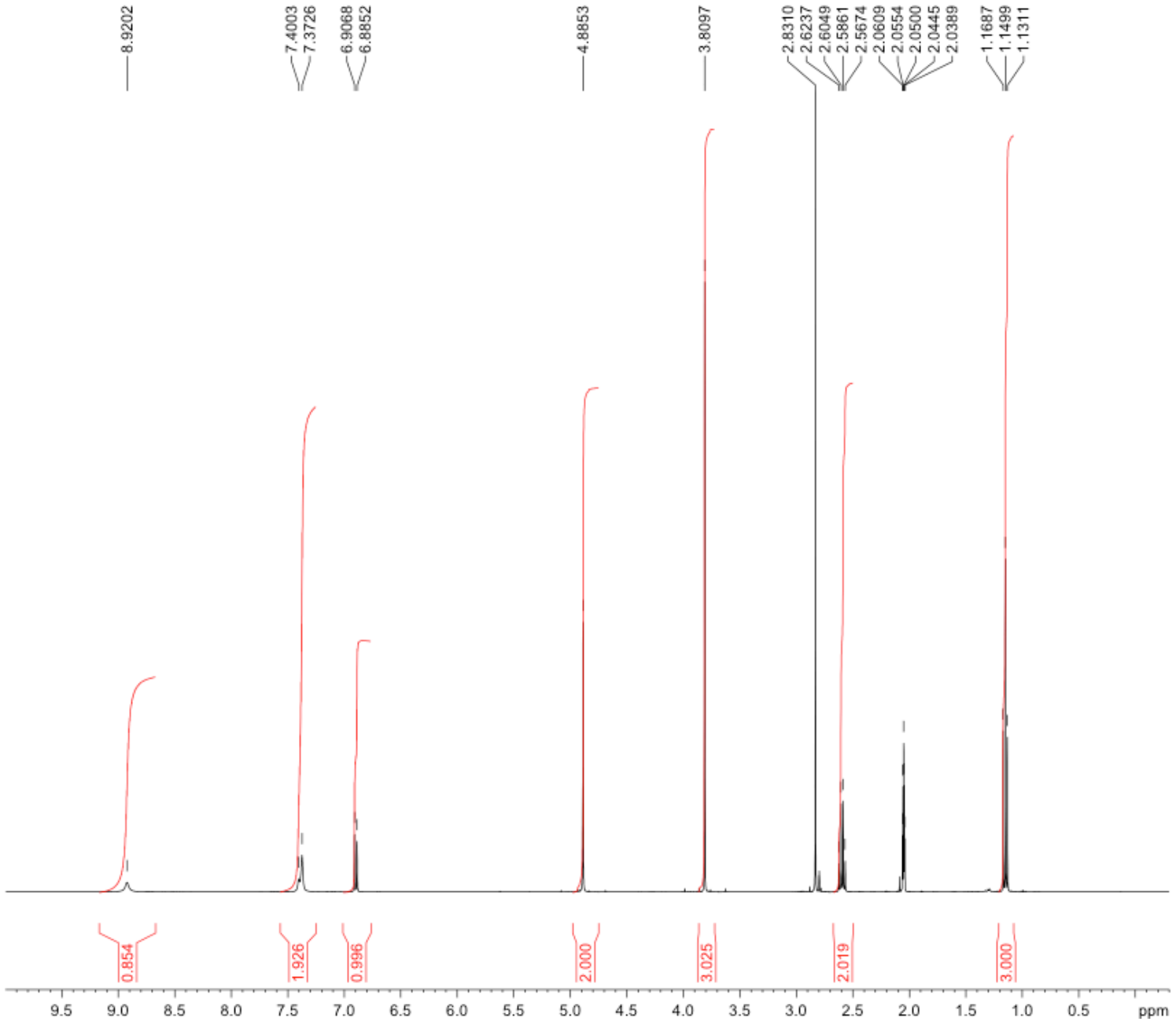
30
20
10
0
ppm


OMe
H
N
Me
O
O
CCl3

3t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7.3726
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6.8852
4.8853
3.8097
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2.6237
2.6049
2.5861
2.5674
2.0609
2.0554
2.0500
2.0445
2.0389
1.1687
1.1499
1.1311
0.854
1.926
0.996
2.000
3.025
2.019
3.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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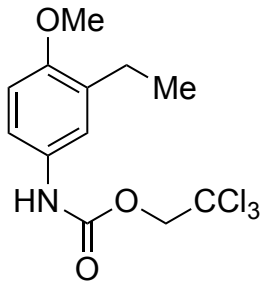
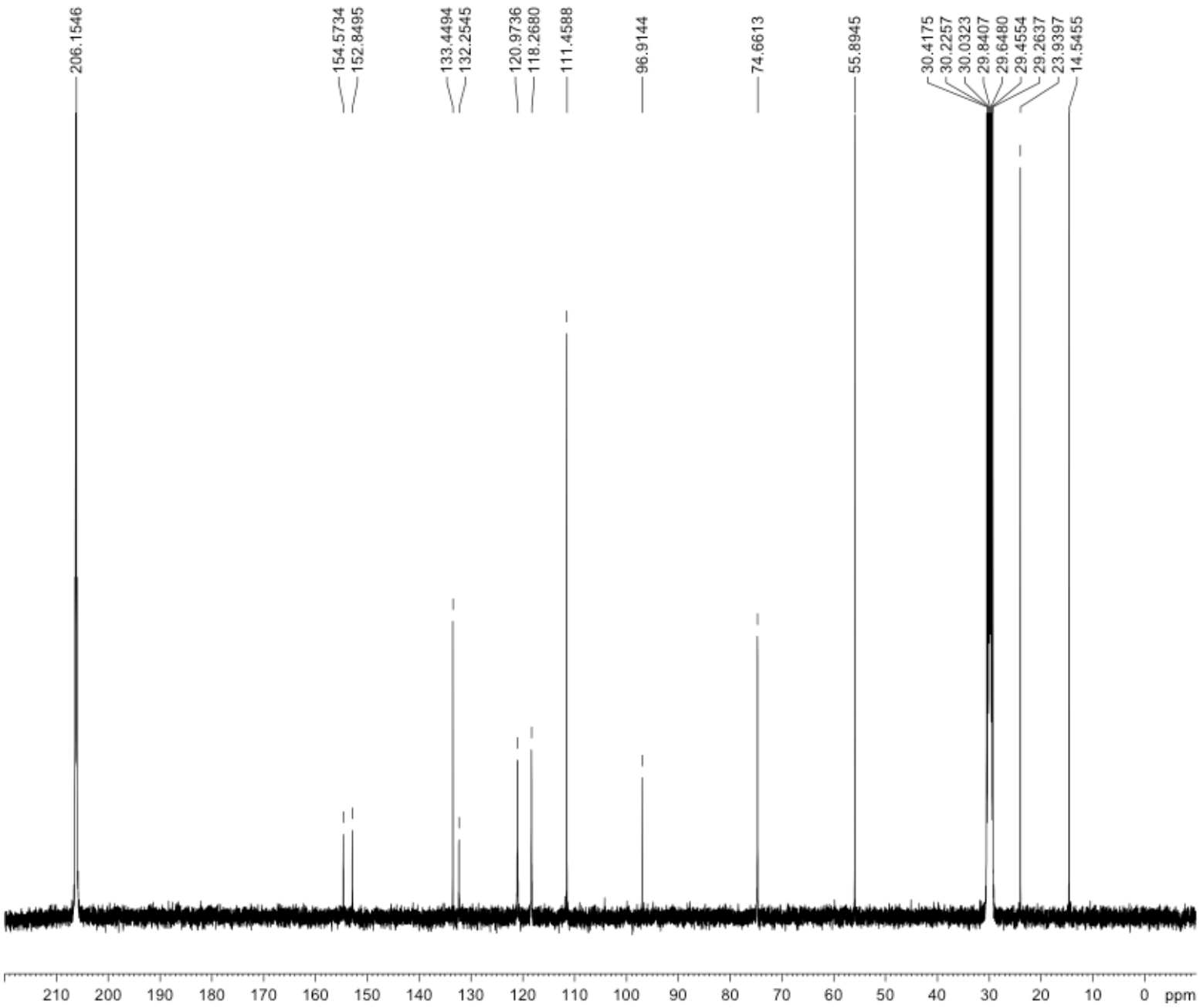
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
Me
HN
O
O
CCl3

2u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152.8495
133.4494
132.2545
120.9736
118.2680
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96.9144
74.6613
55.8945
30.4175
30.2257
30.0323
29.8407
29.6480
29.4554
29.2637
23.9397
14.5455
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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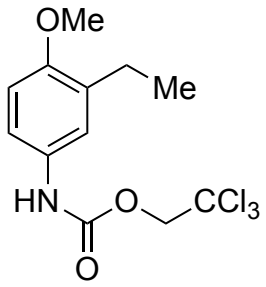
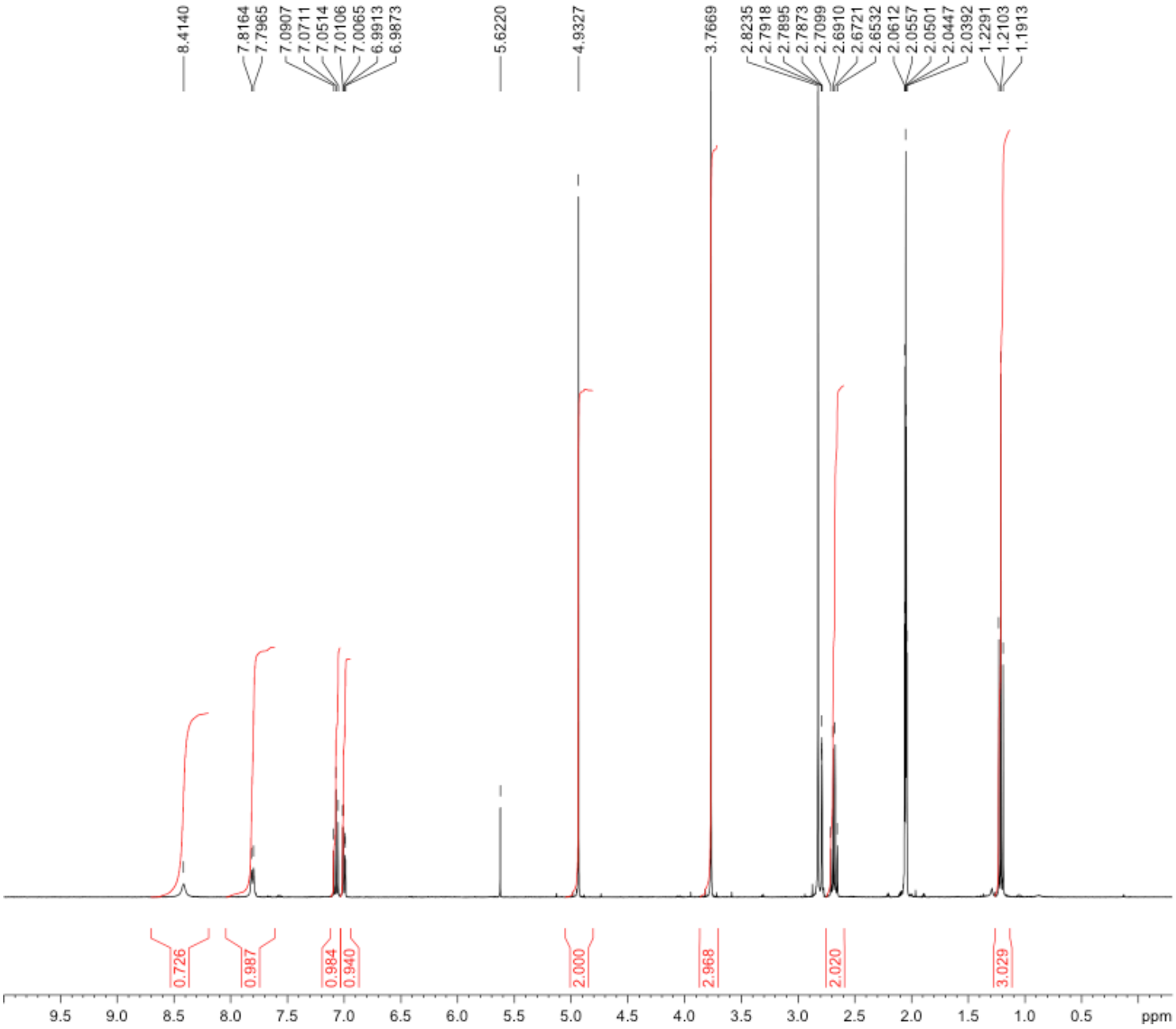
30
20
10
0
ppm


OMe
Me
HN
O
O
CCl3
O

2u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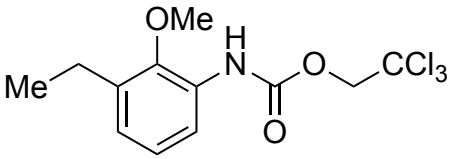
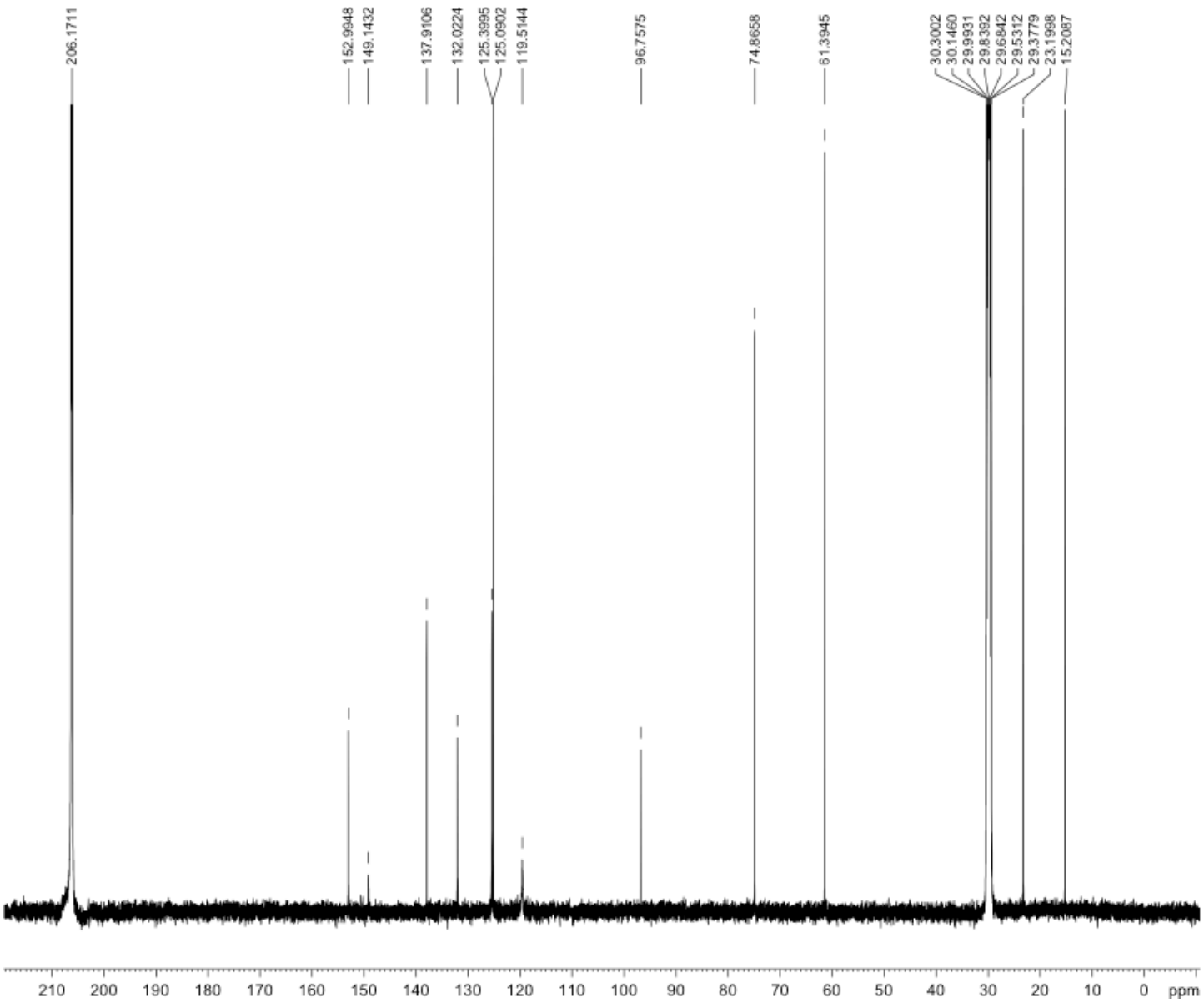
7.8164
7.7965
7.0907
7.0711
7.0514
7.0106
7.0065
6.9913
6.9873
5.6220
4.9327
3.7669
2.8235
2.7918
2.7895
2.7873
2.7099
2.6910
2.6721
2.6532
2.0612
2.0557
2.0501
2.0447
2.0392
1.2291
1.2103
1.1913
0.726
0.987
0.984
0.940
2.000
2.968
2.020
3.029
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
H
N
O
Me
O
CCl3

3u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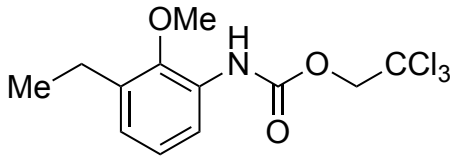
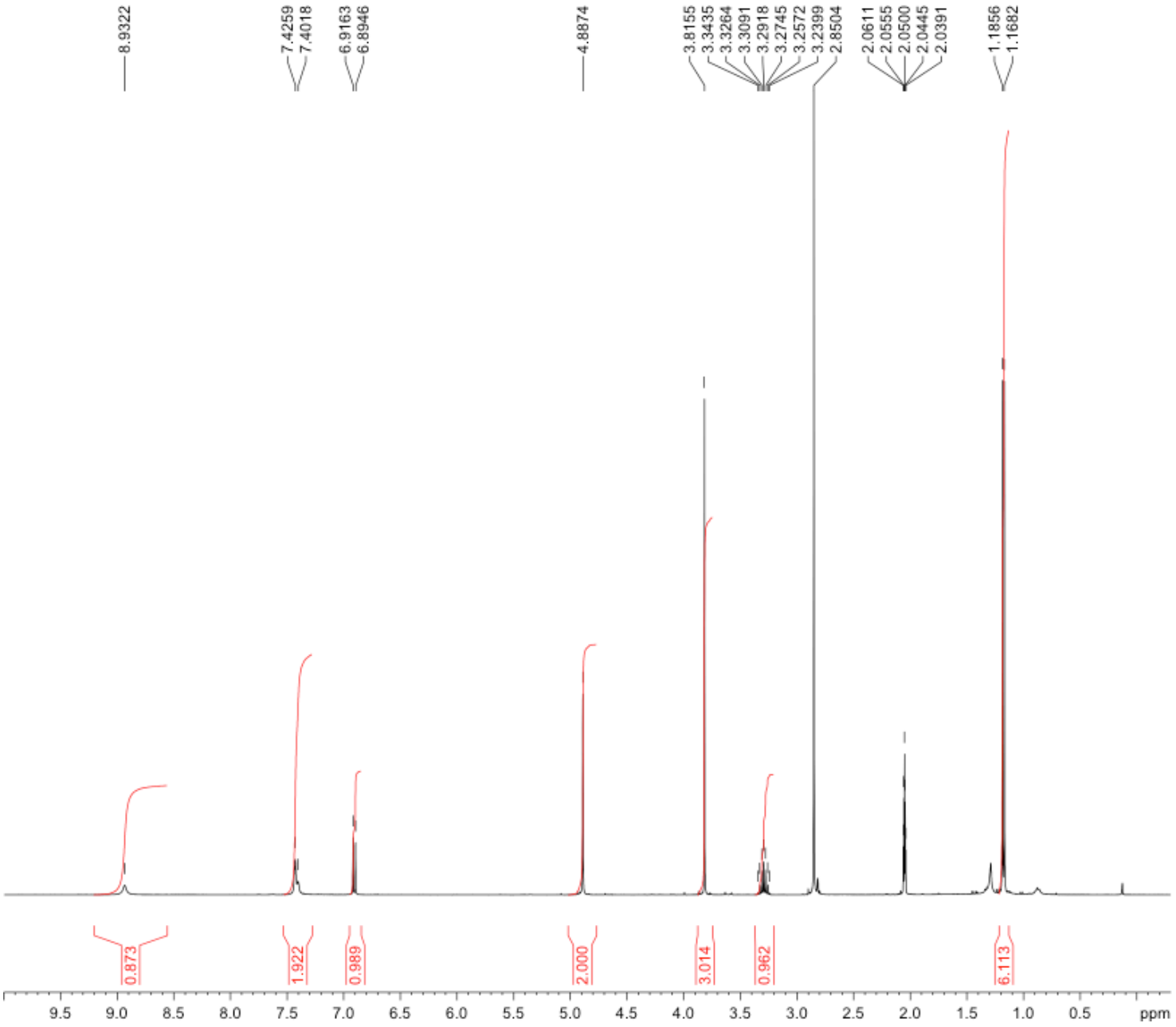
149.1432
137.9106
132.0224
125.3995
125.0902
119.5144
96.7575
74.8658
61.3945
30.3002
30.1460
29.9931
29.8392
29.6842
29.5312
29.3779
23.1998
15.2087
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
H
N
O
CCl3
Me
O

3u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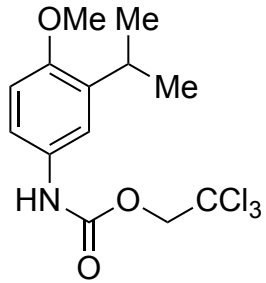
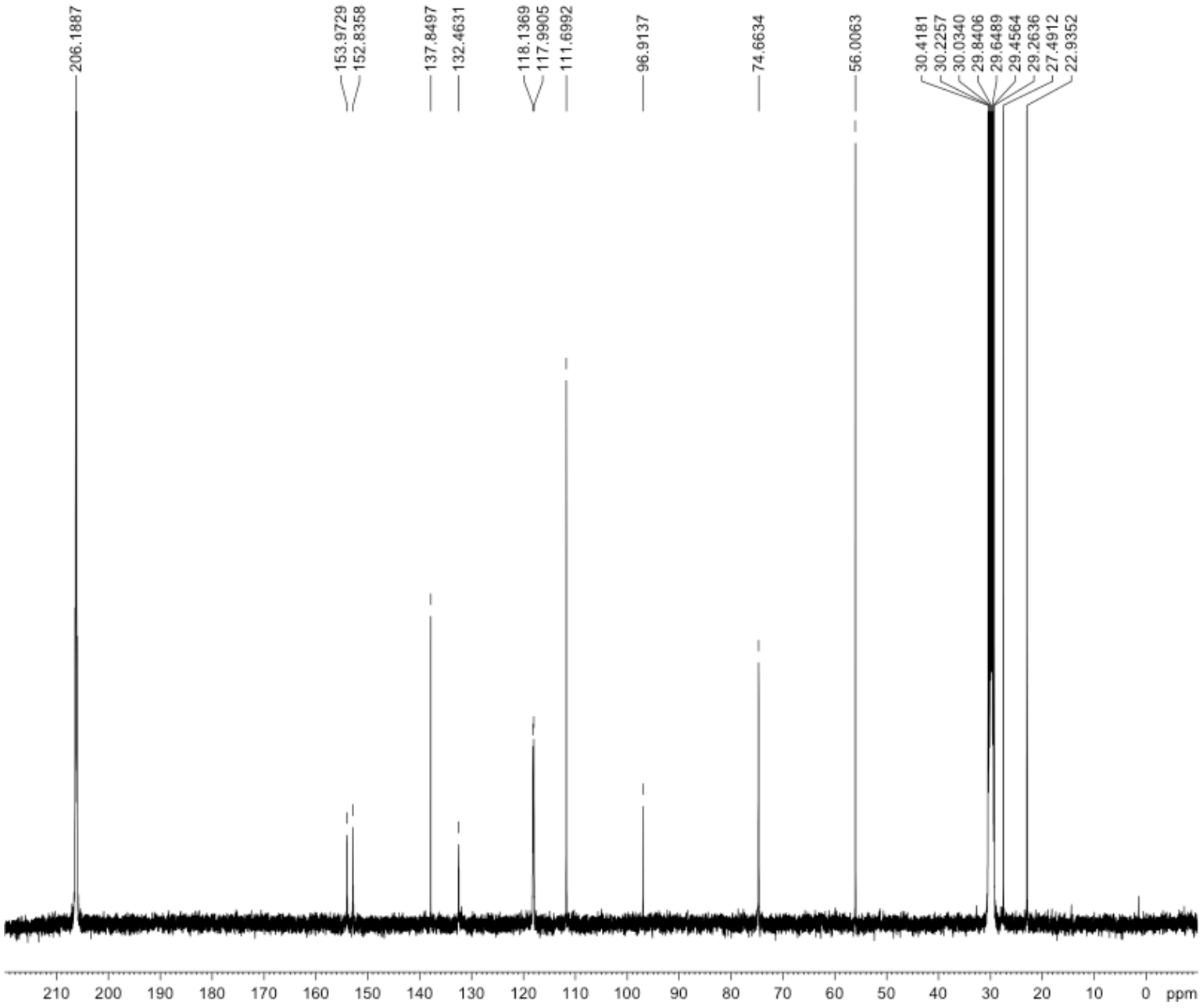
7.4018
6.9163
6.8946
4.8874
3.8155
3.3435
3.3264
3.3091
3.2918
3.2745
3.2572
3.2399
2.8504
2.0611
2.0555
2.0500
2.0445
2.0391
1.1856
1.1682
0.873
1.922
0.989
2.000
3.014
0.962
6.113
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


OMe
Me
Me
HN
O
CCl3
O

2v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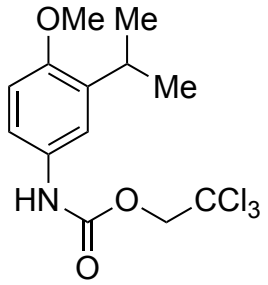
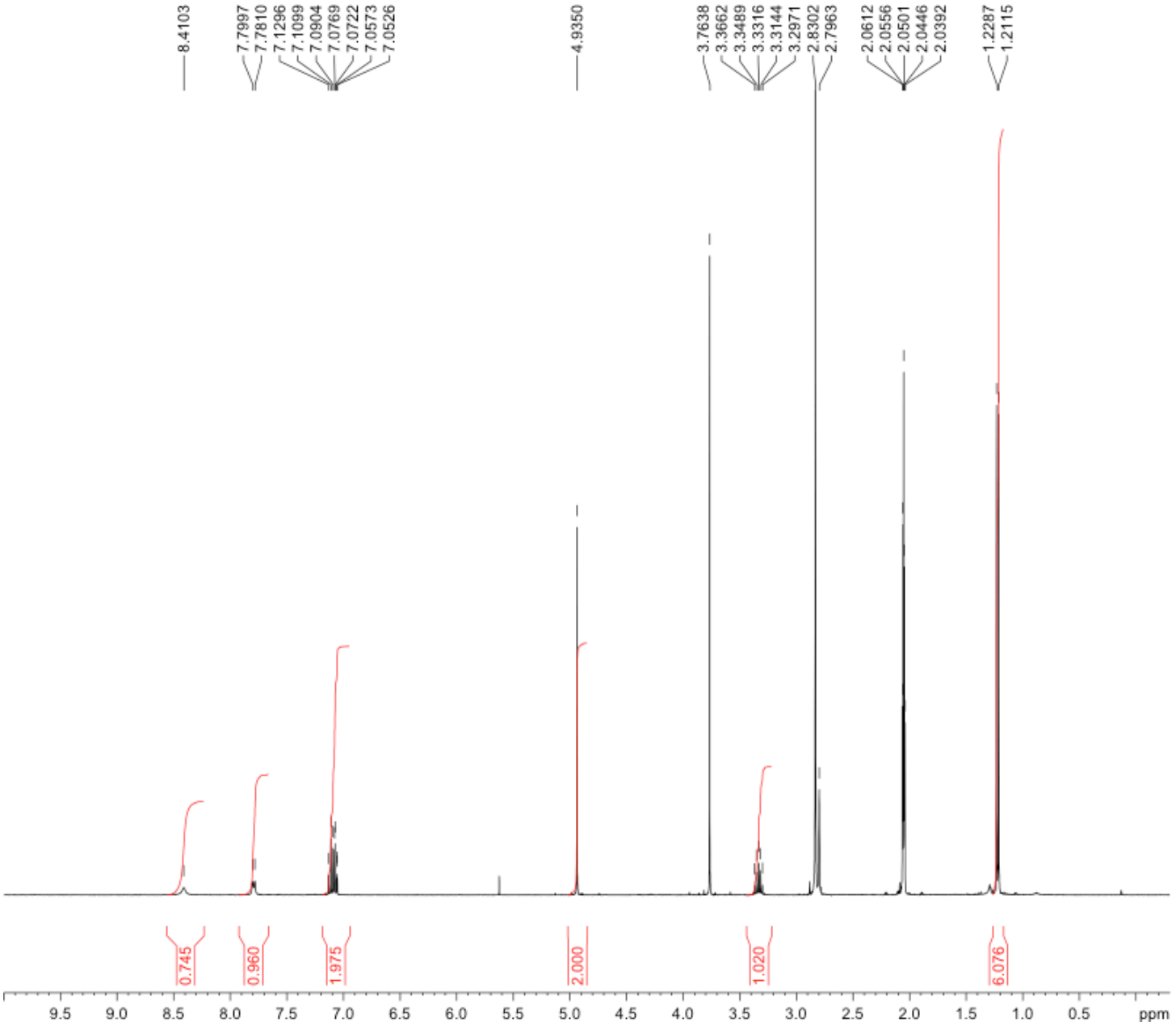
132.4631
118.1369
117.9905
111.6992
96.9137
74.6634
56.0063
30.4181
30.2257
30.0340
29.8406
29.6489
29.4564
29.2636
27.4912
22.9352
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
Me
Me
HN
O
CCl3
O

2v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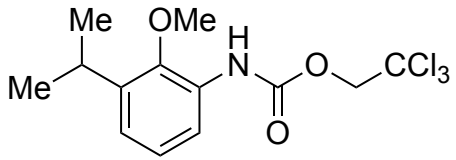
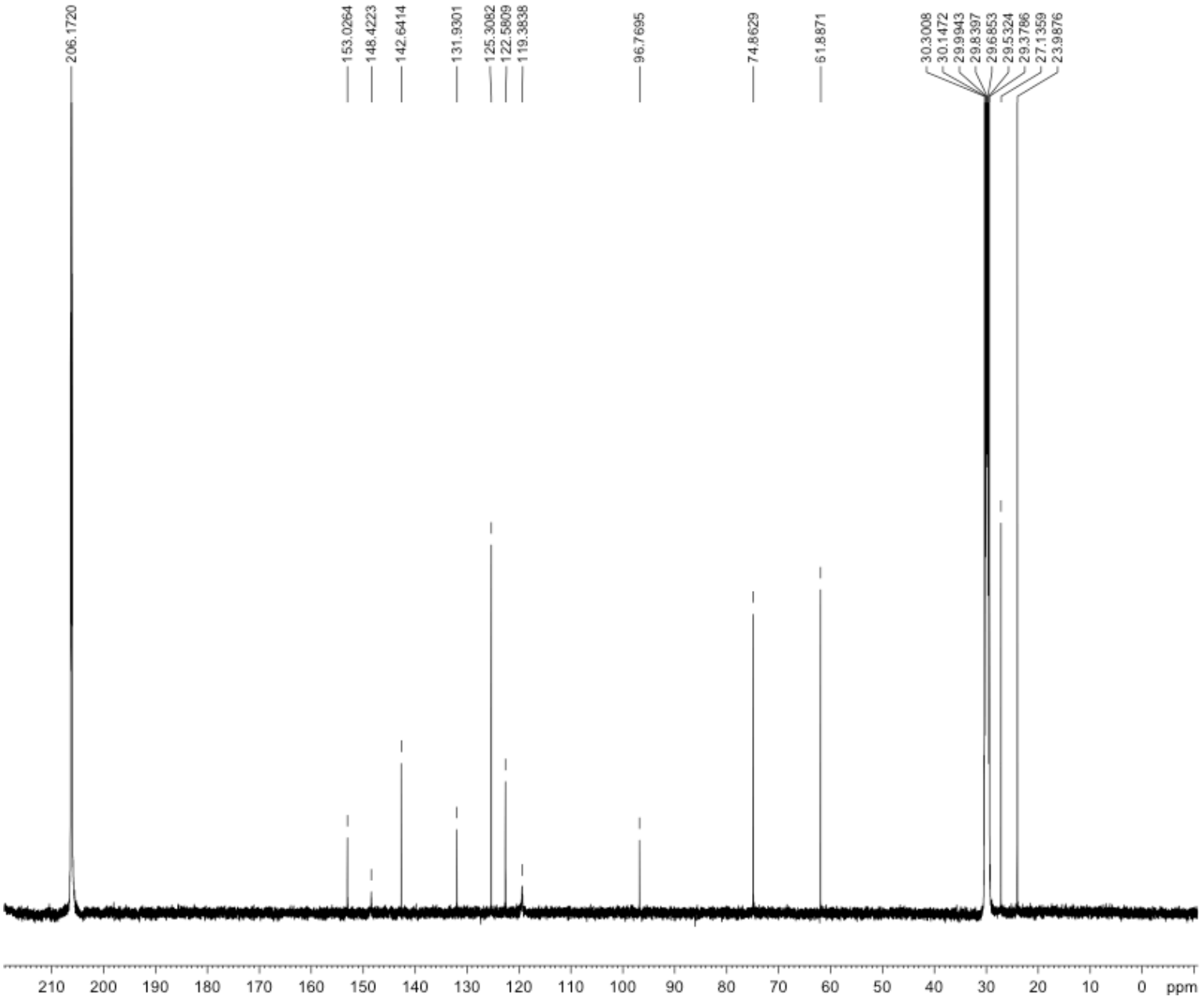
7.7810
7.1296
7.1099
7.0904
7.0769
7.0722
7.0573
7.0526
4.9350
3.7638
3.3662
3.3489
3.3316
3.3144
3.2971
2.8302
2.7963
2.0612
2.0556
2.0501
2.0446
2.0392
1.2287
1.2115
0.745
0.960
1.975
2.000
1.020
6.076
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


Me
OMe
H
N
O
CCl3
Me
O

3v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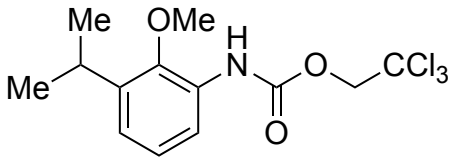
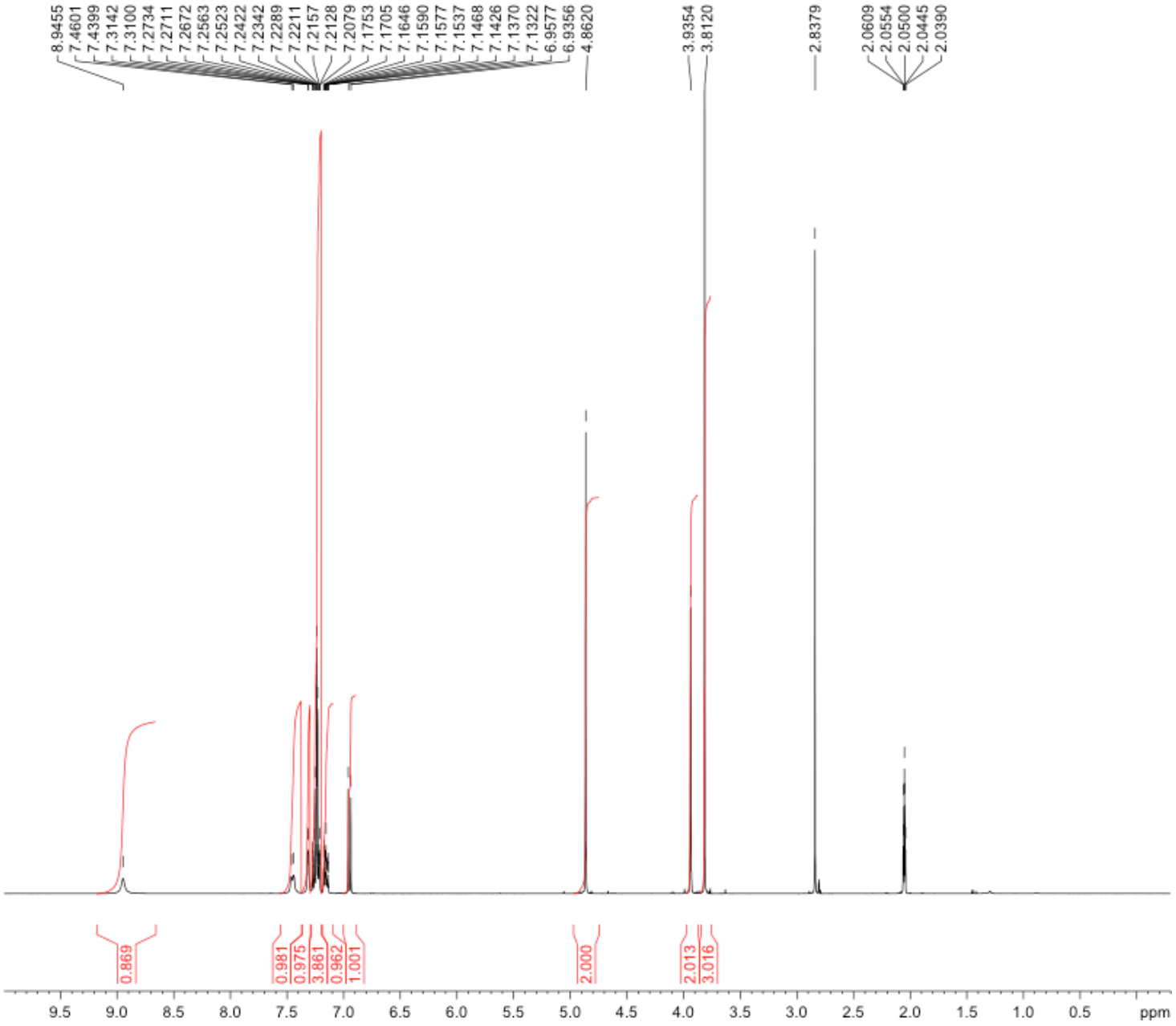
153.0264
148.4223
142.6414
131.9301
125.3082
122.5809
119.3838
96.7695
74.8629
61.8871
30.3008
30.1472
29.9943
29.8397
29.6853
29.5324
29.3786
27.1359
23.9876
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
OMe
H
N
O
CCl3
Me
O

3v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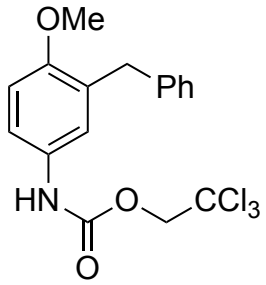
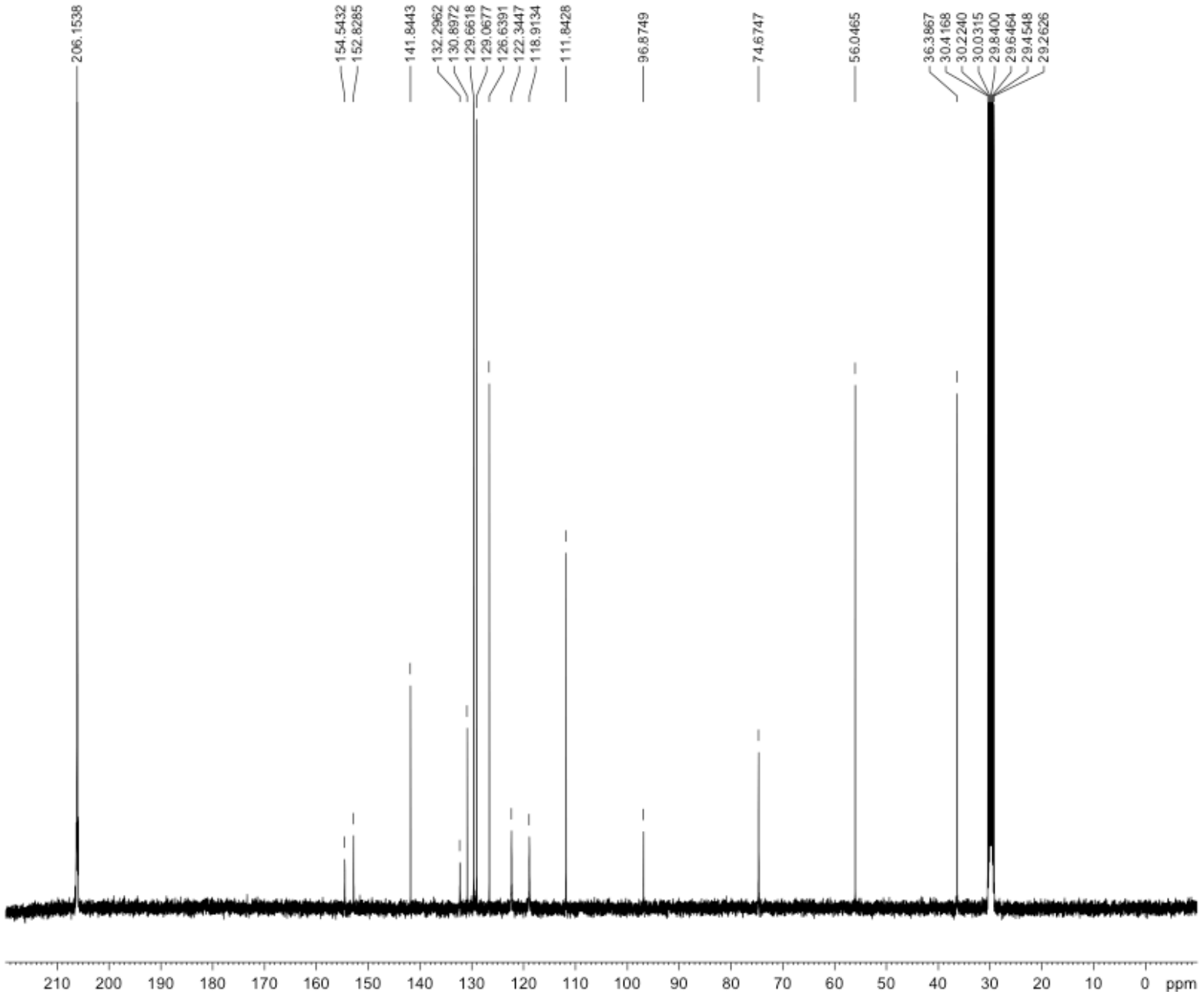
7.4399
7.3142
7.3100
7.2734
7.2711
7.2672
7.2563
7.2523
7.2422
7.2342
7.2289
7.2211
7.2157
7.2128
7.2079
7.1753
7.1705
7.1646
7.1590
7.1577
7.1537
7.1468
7.1426
7.1370
7.1322
6.9577
6.9356
4.8620
3.9354
3.8120
2.8379
2.0609
2.0554
2.0500
2.0445
2.0390
0.869
0.981
0.975
3.861
0.962
1.001
2.000
2.013
3.016
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
Ph
HN
O
O
CCl3

2w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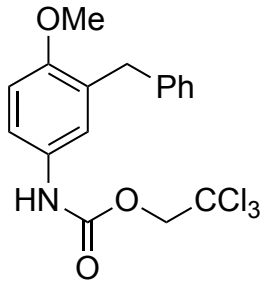
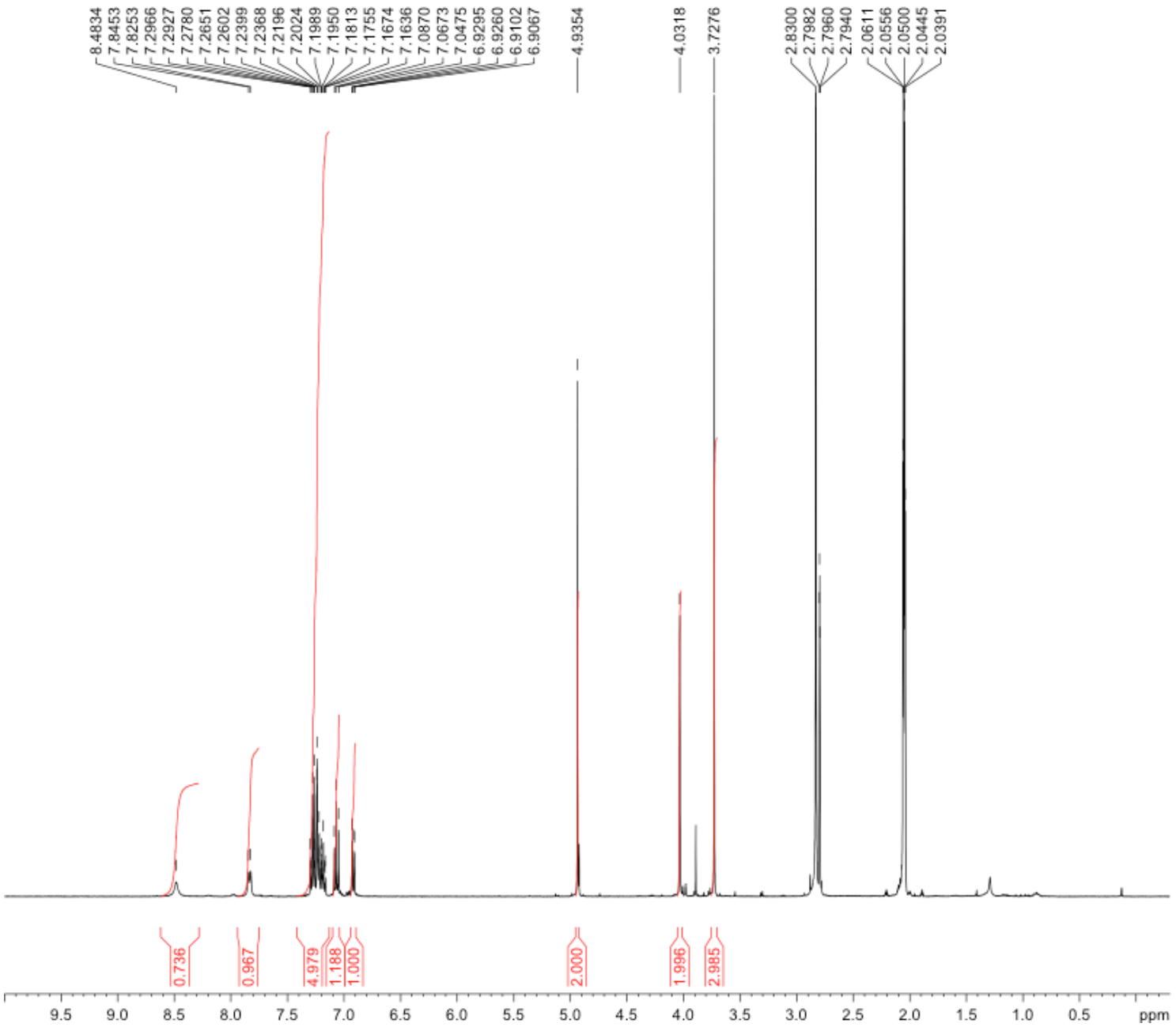
152.8285
141.8443
132.2962
130.8972
129.6618
129.0677
126.6391
122.3447
118.9134
111.8428
96.8749
74.6747
56.0465
36.3867
30.4168
30.2240
30.0315
29.8400
29.6464
29.4548
29.2626
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
Ph
HN
O
O
CCl3

2w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7.8453
7.8253
7.2966
7.2927
7.2780
7.2651
7.2602
7.2399
7.2368
7.2196
7.2024
7.1989
7.1950
7.1813
7.1755
7.1674
7.1636
7.0870
7.0673
7.0475
6.9295
6.9260
6.9102
6.9067
4.9354
4.0318
3.7276
2.8300
2.7982
2.7960
2.7940
2.0611
2.0556
2.0500
2.0445
2.0391
0.736
0.967
4.979
1.188
1.000
2.000
1.996
2.985
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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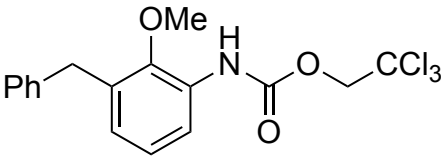
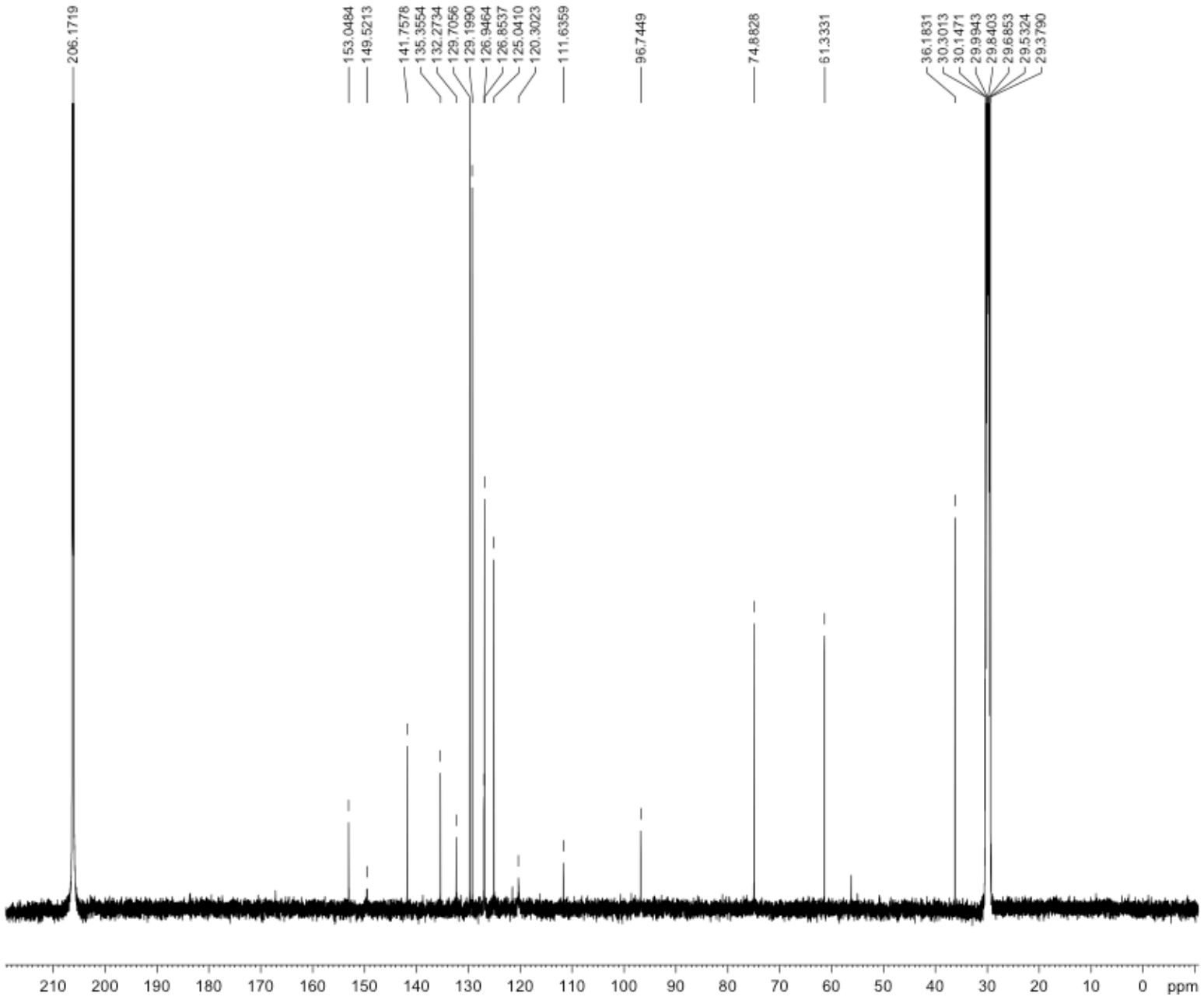
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
H
N
O
O
CCl3
Ph

3w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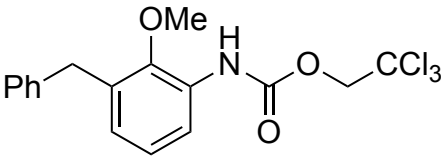
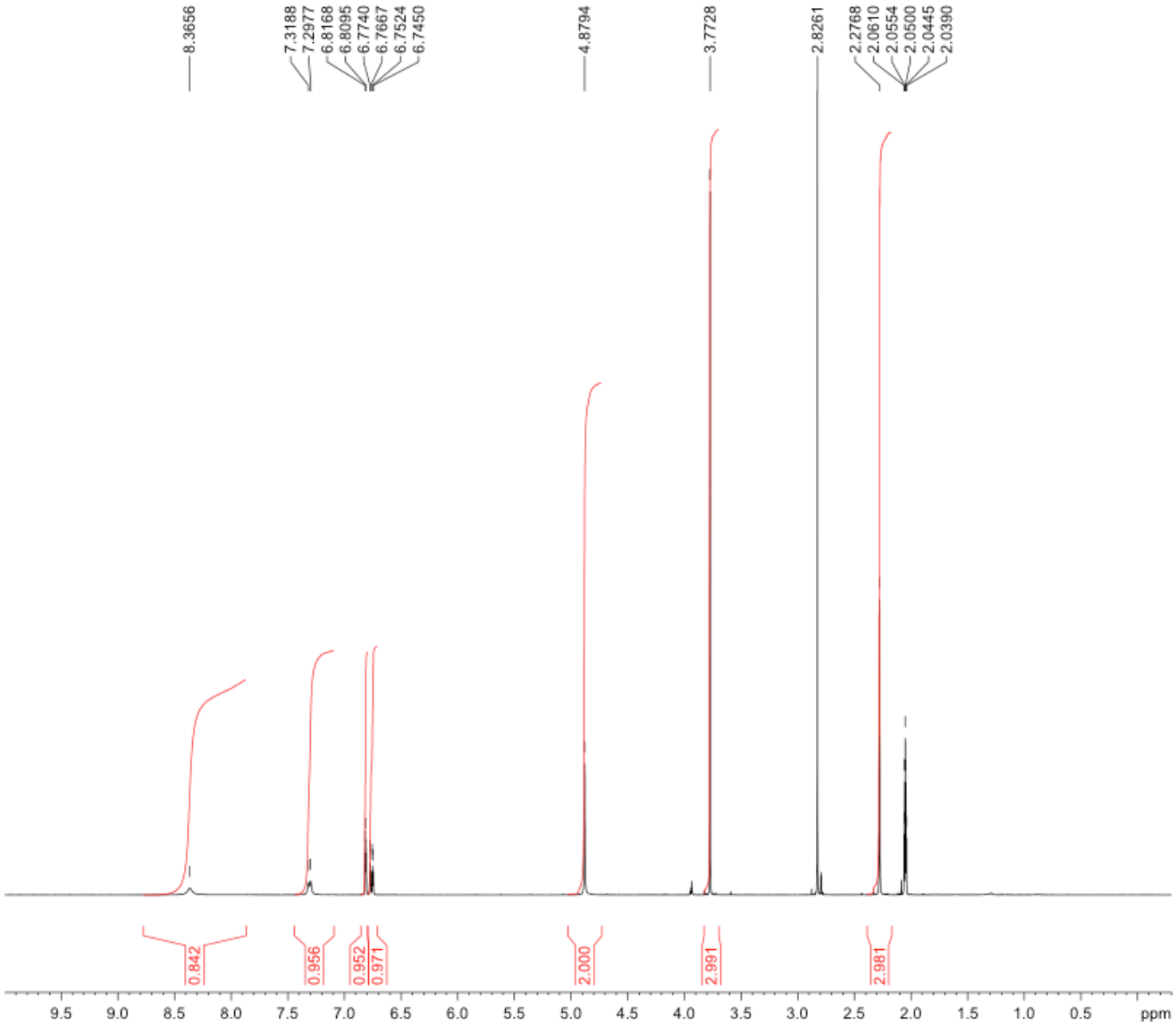
141.7578
135.3554
132.2734
129.7056
129.1990
126.9464
126.8537
125.0410
120.3023
111.6359
96.7449
74.8828
61.3331
36.1831
30.3013
30.1471
29.9943
29.8403
29.6853
29.5324
29.3790
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
H
N
O
O
Ph
CCl3

3w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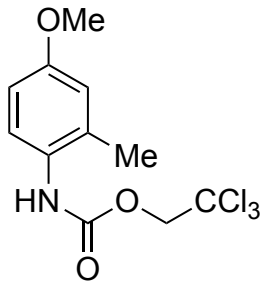
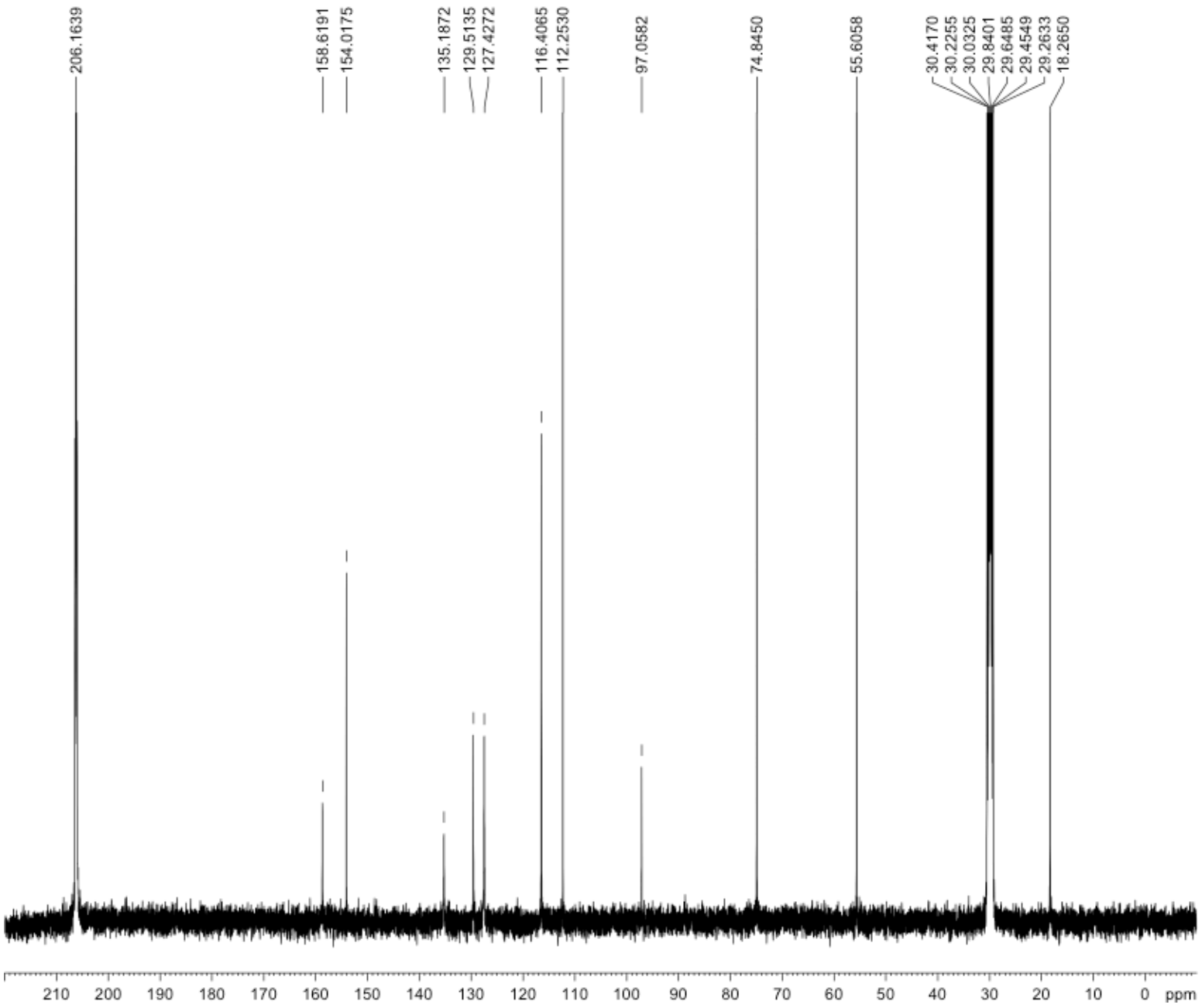
7.2977
6.8168
6.8095
6.7740
6.7667
6.7524
6.7450
4.8794
3.7728
2.8261
2.2768
2.0610
2.0554
2.0500
2.0445
2.0390
0.842
0.956
0.952
0.971
2.000
2.991
2.981
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


OMe
Me
HN
O
O
CCl3

2x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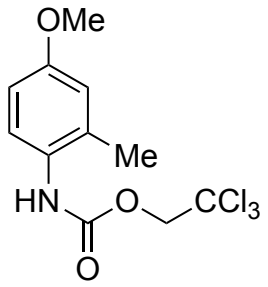
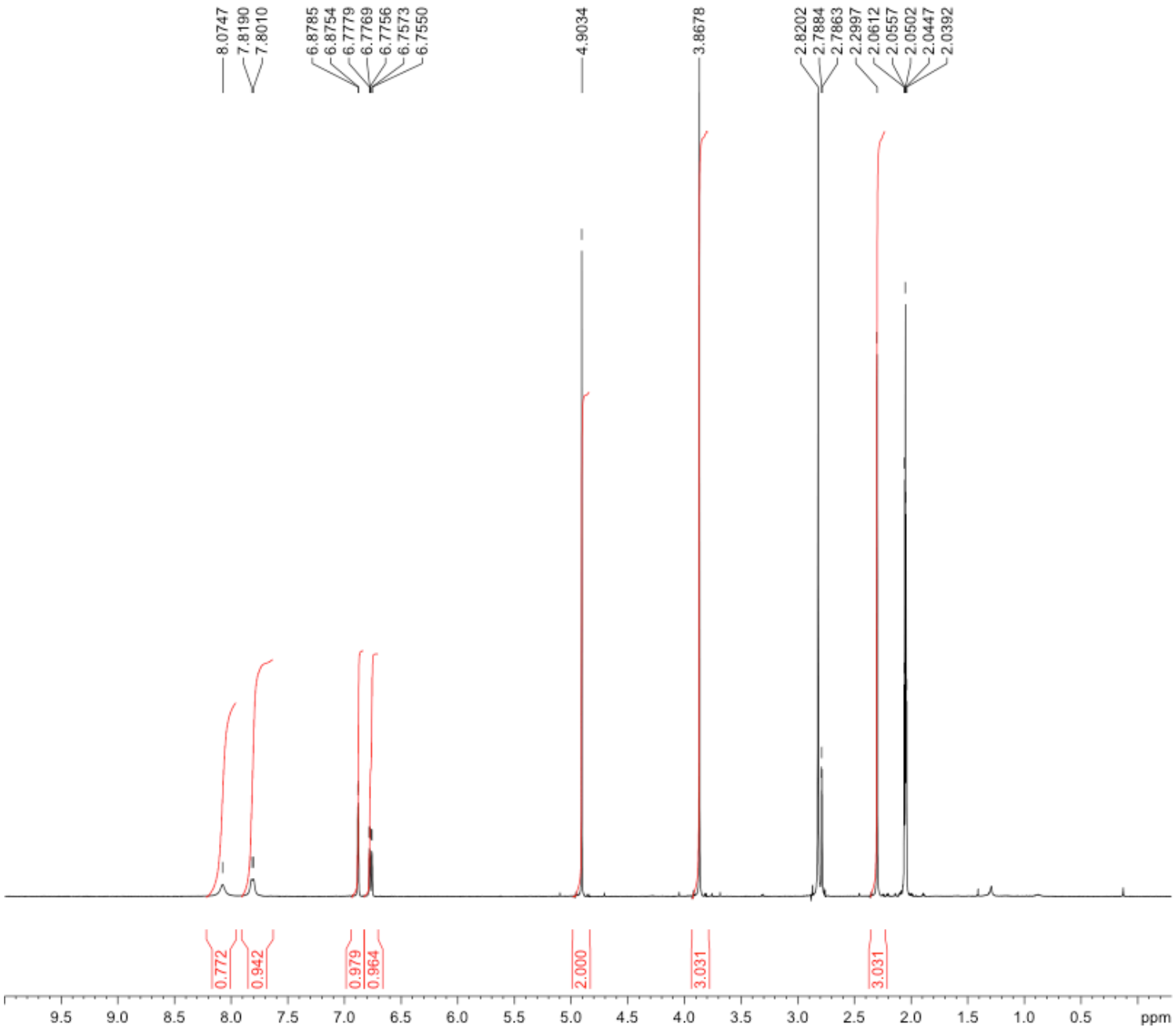
135.1872
129.5135
127.4272
116.4065
112.2530
97.0582
74.8450
55.6058
30.4170
30.2255
30.0325
29.8401
29.6485
29.4549
29.2633
18.2650
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
Me
HN
O
O
CCl3

2x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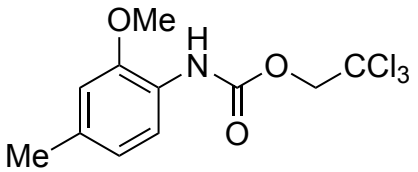
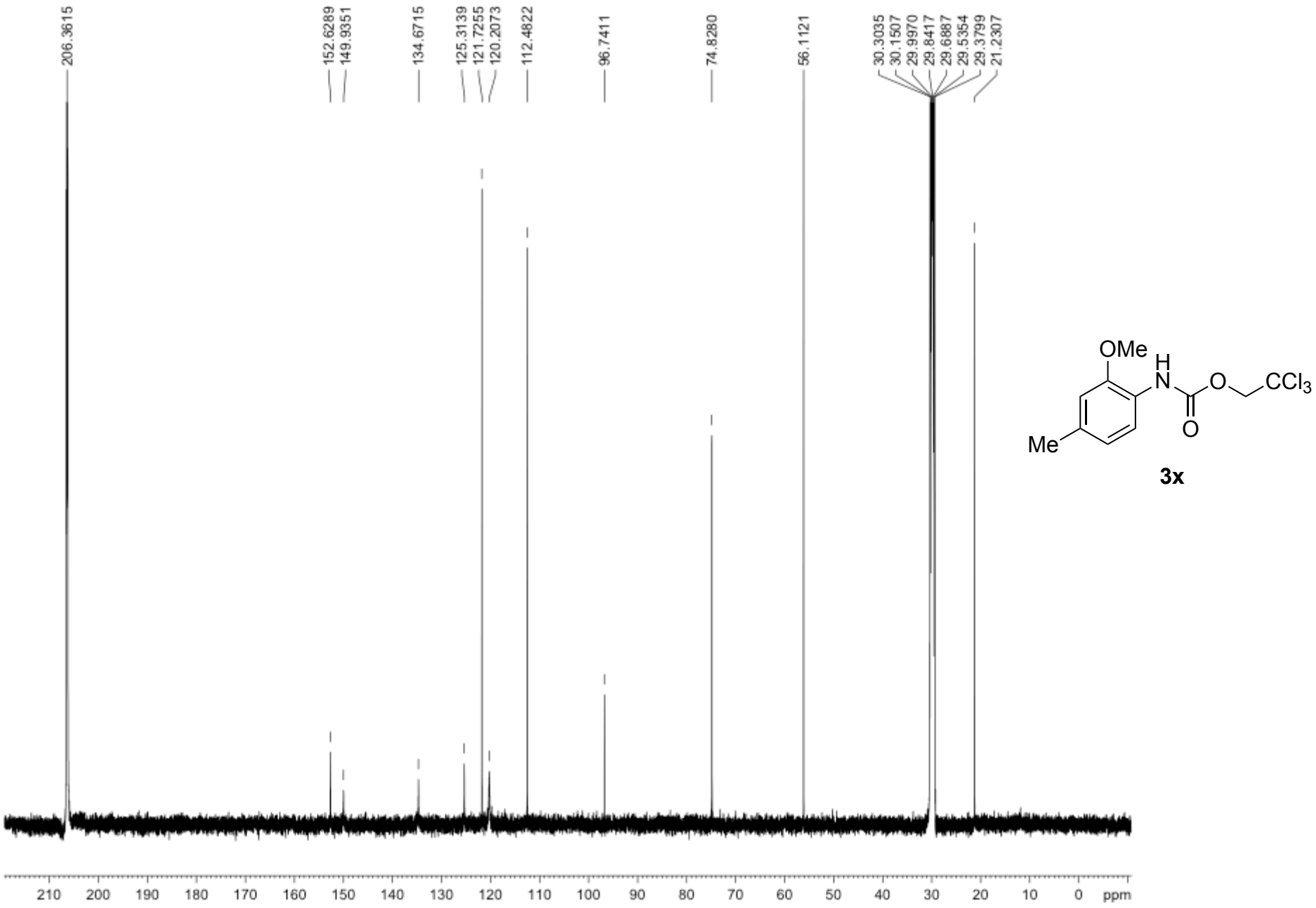
7.8010
6.8785
6.8754
6.7779
6.7769
6.7756
6.7573
6.7550
4.9034
3.8678
2.8202
2.7884
2.7863
2.2997
2.0612
2.0557
2.0502
2.0447
2.0392
0.772
0.942
0.979
0.964
2.000
3.031
3.031
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
H
N
O
O
CCl3
Me

3x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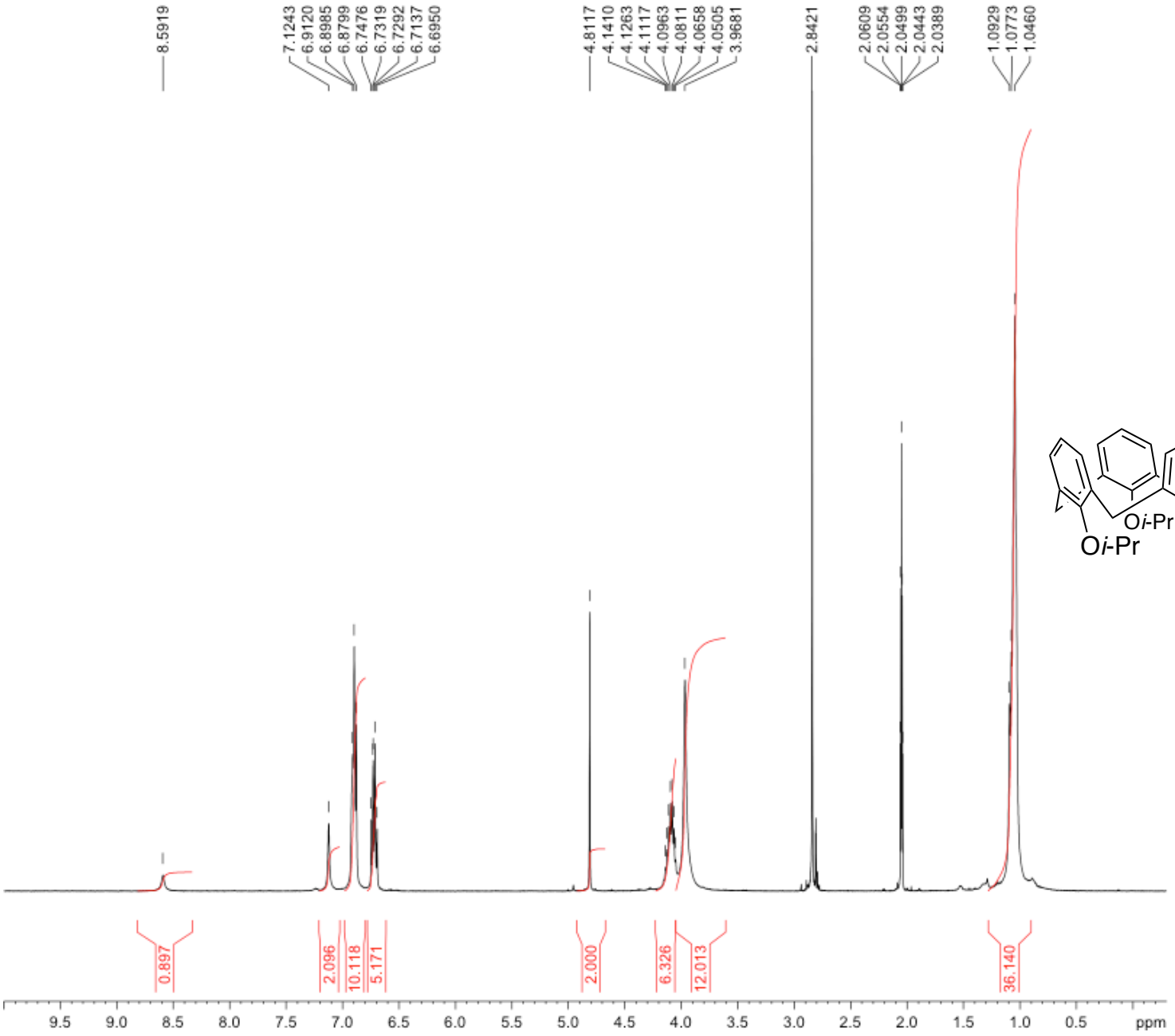
149.9351
134.6715
125.3139
121.7255
120.2073
112.4822
96.7411
74.8280
56.1121
30.3035
30.1507
29.9970
29.8417
29.6887
29.5354
29.3799
21.2307
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

OMe
H
N
O
O
CCl3
Me

3x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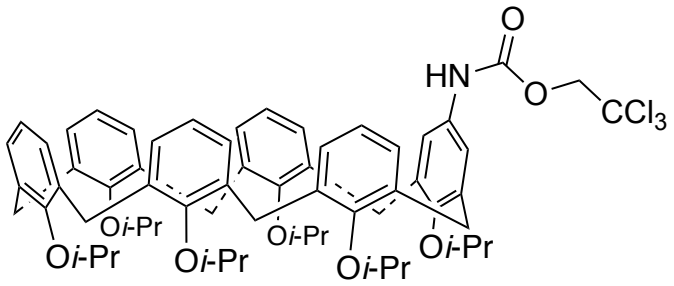
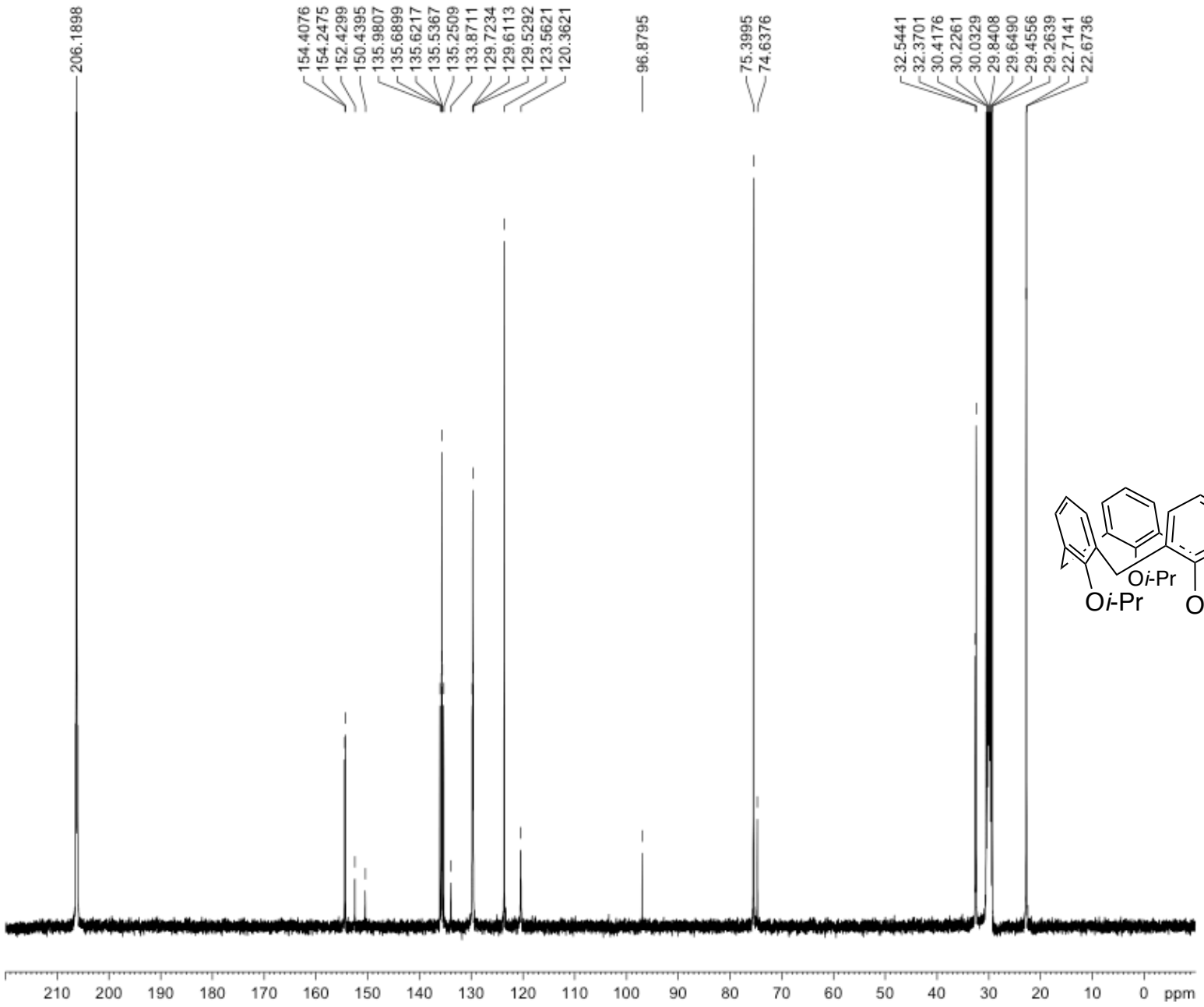
7.1243
6.9120
6.8985
6.8799
6.7476
6.7319
6.7292
6.7137
6.6950
4.8117
4.1410
4.1263
4.1117
4.0963
4.0811
4.0658
4.0505
3.9681
2.8421
2.0609
2.0554
2.0499
2.0443
2.0389
1.0929
1.0773
1.0460
0.897
2.096
10.118
5.171
2.000
6.326
12.013
36.140
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


HN
O
O
CCl3
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr

2y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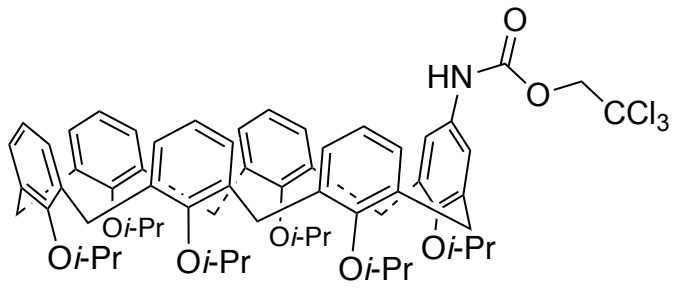
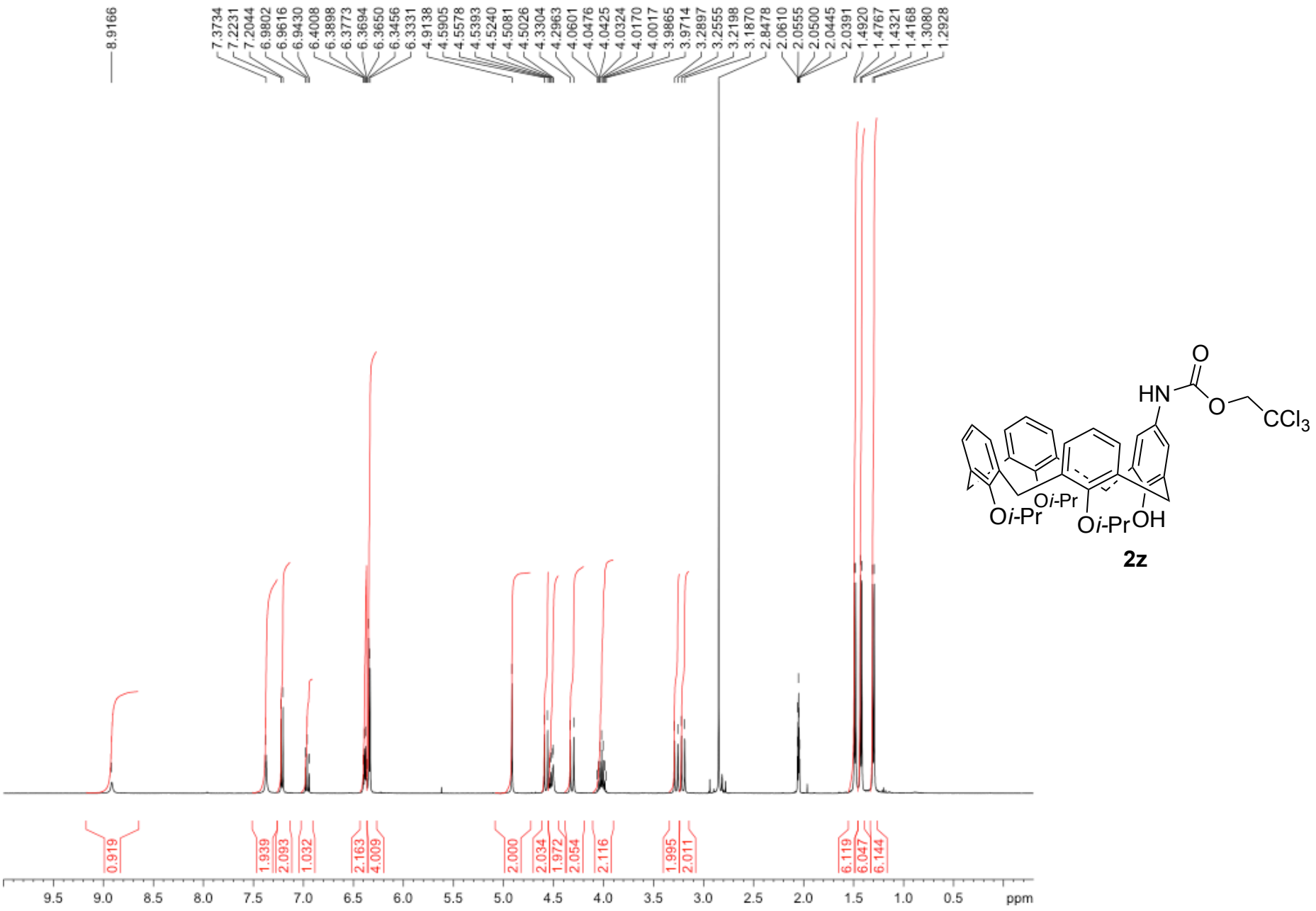
154.4076
154.2475
152.4299
150.4395
135.9807
135.6899
135.6217
135.5367
135.2509
133.8711
129.7234
129.6113
129.5292
123.5621
120.3621
96.8795
75.3995
74.6376
32.5441
32.3701
30.4176
30.2261
30.0329
29.8408
29.6490
29.4556
29.2639
22.7141
22.6736
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


HN
O
O
CCl3
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr

2y


8.9166
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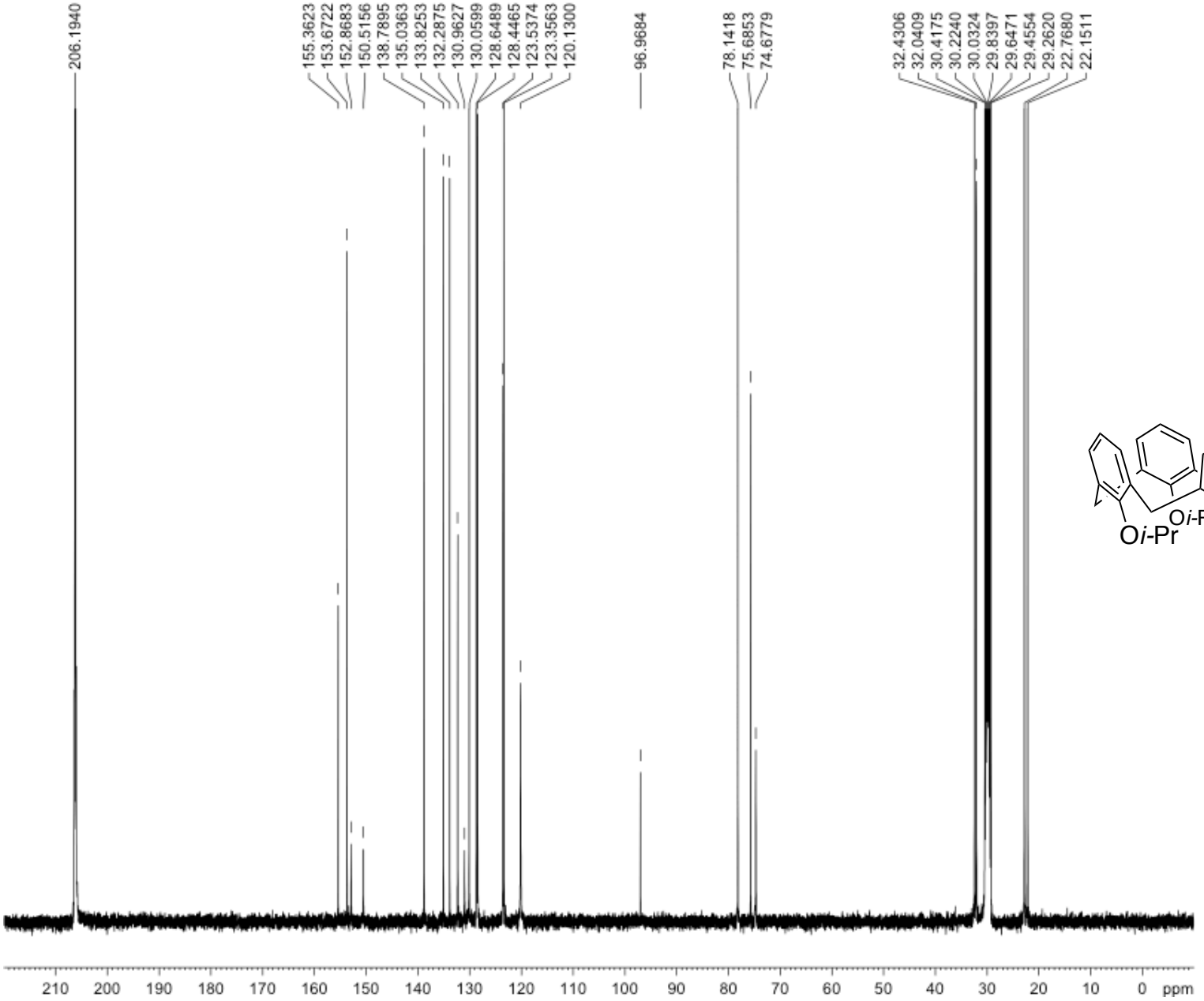
7.2231
7.2044
6.9802
6.9616
6.9430
6.4008
6.3898
6.3773
6.3694
6.3650
6.3456
6.3331
4.9138
4.5905
4.5578
4.5393
4.5240
4.5081
4.5026
4.3304
4.2963
4.0601
4.0476
4.0425
4.0324
4.0170
4.0017
3.9865
3.9714
3.2897
3.2555
3.2198
3.1870
2.8478
2.0610
2.0555
2.0500
2.0445
2.0391
1.4920
1.4767
1.4321
1.4168
1.3080
1.2928
0.919
1.939
2.093
1.032
2.163
4.009
2.000
2.034
1.972
2.054
2.116
1.995
2.011
6.119
6.047
6.144
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

HN
O
O
CCl3
Oi-Pr
Oi-Pr
Oi-Pr
OH

2z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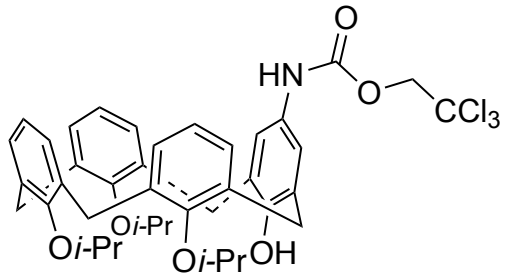
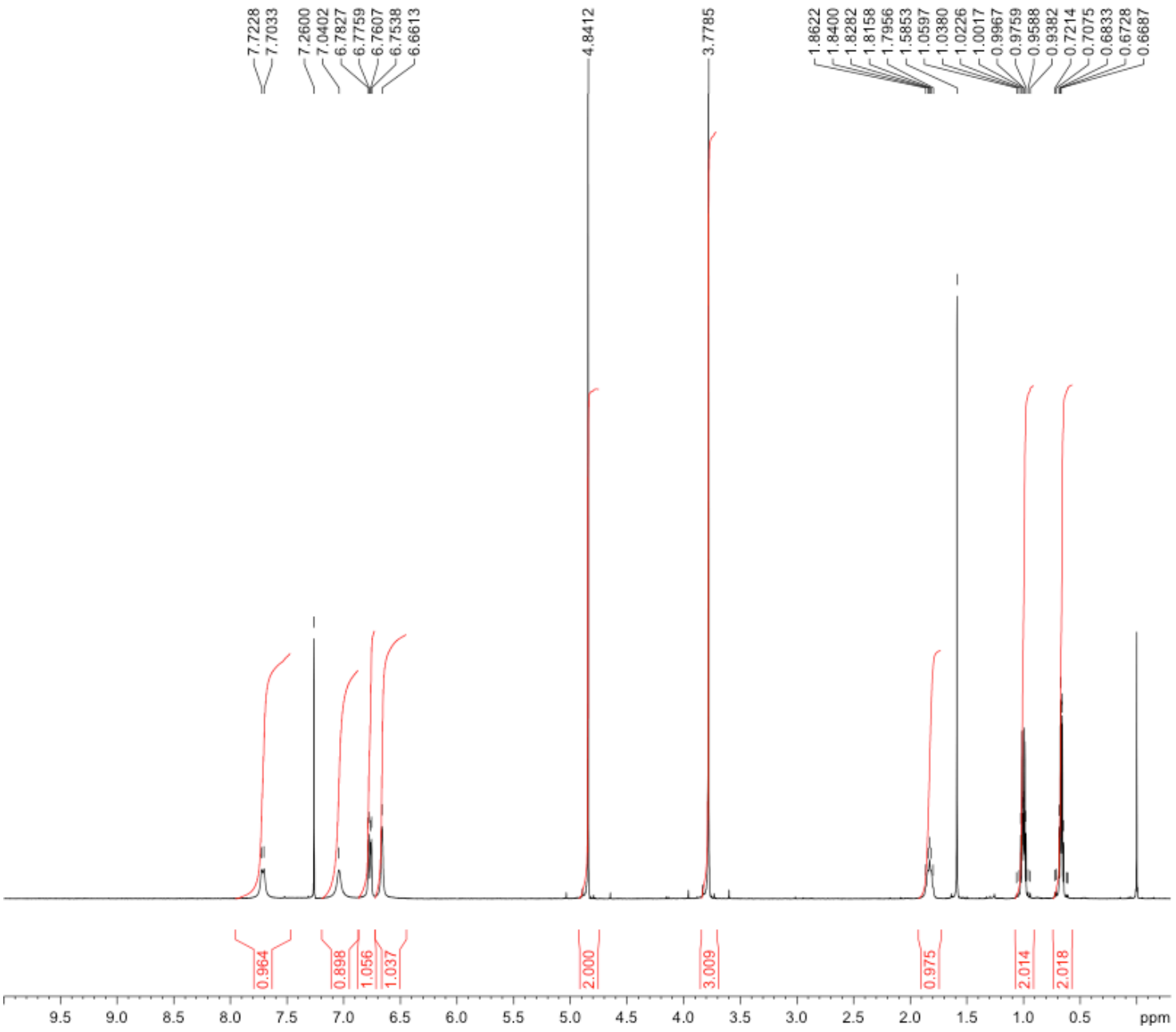
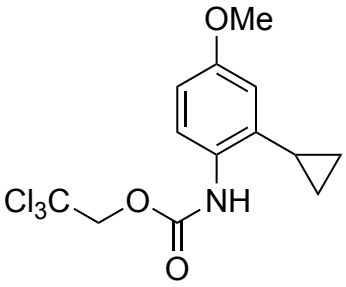
155.3623
153.6722
152.8683
150.5156
138.7895
135.0363
133.8253
132.2875
130.9627
130.0599
128.6489
128.4465
123.5374
123.3563
120.1300
96.9684
78.1418
75.6853
74.6779
32.4306
32.0409
30.4175
30.2240
30.0324
29.8397
29.6471
29.4554
29.2620
22.7680
22.1511
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

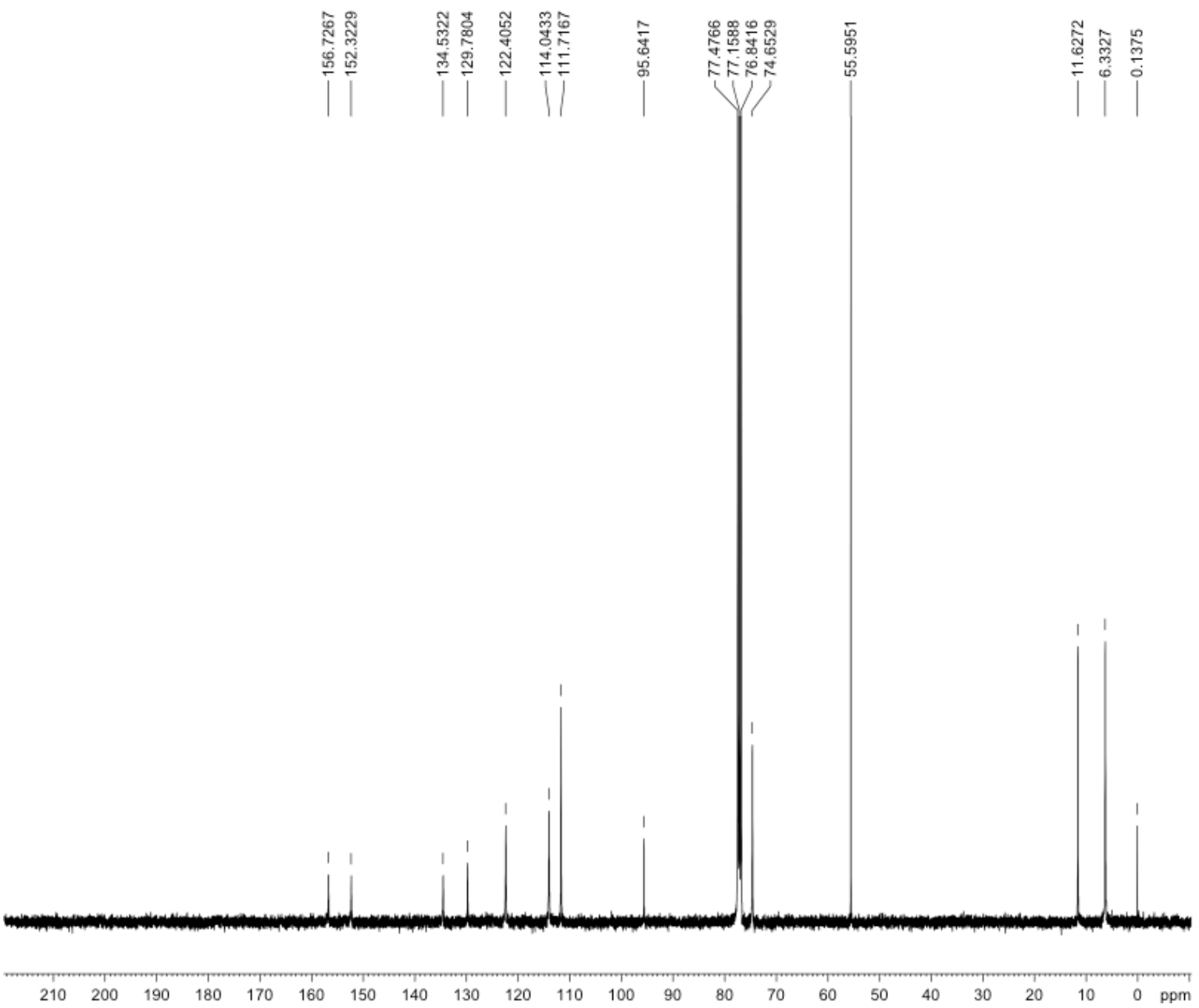

O
HN
O
CCl3
Oi-Pr
Oi-Pr
Oi-Pr
OH

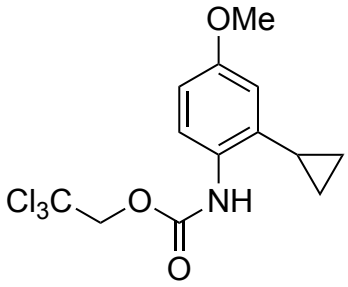
2z


7.7228
7.7033
7.2600
7.0402
6.7827
6.7759
6.7607
6.7538
6.6613
4.8412
3.7785
1.8622
1.8400
1.8282
1.8158
1.7956
1.5853
1.0597
1.0380
1.0226
1.0017
0.9967
0.9759
0.9588
0.9382
0.7214
0.7075
0.6833
0.6728
0.6687
0.964
0.898
1.056
1.037
2.000
3.009
0.975
2.014
2.018
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

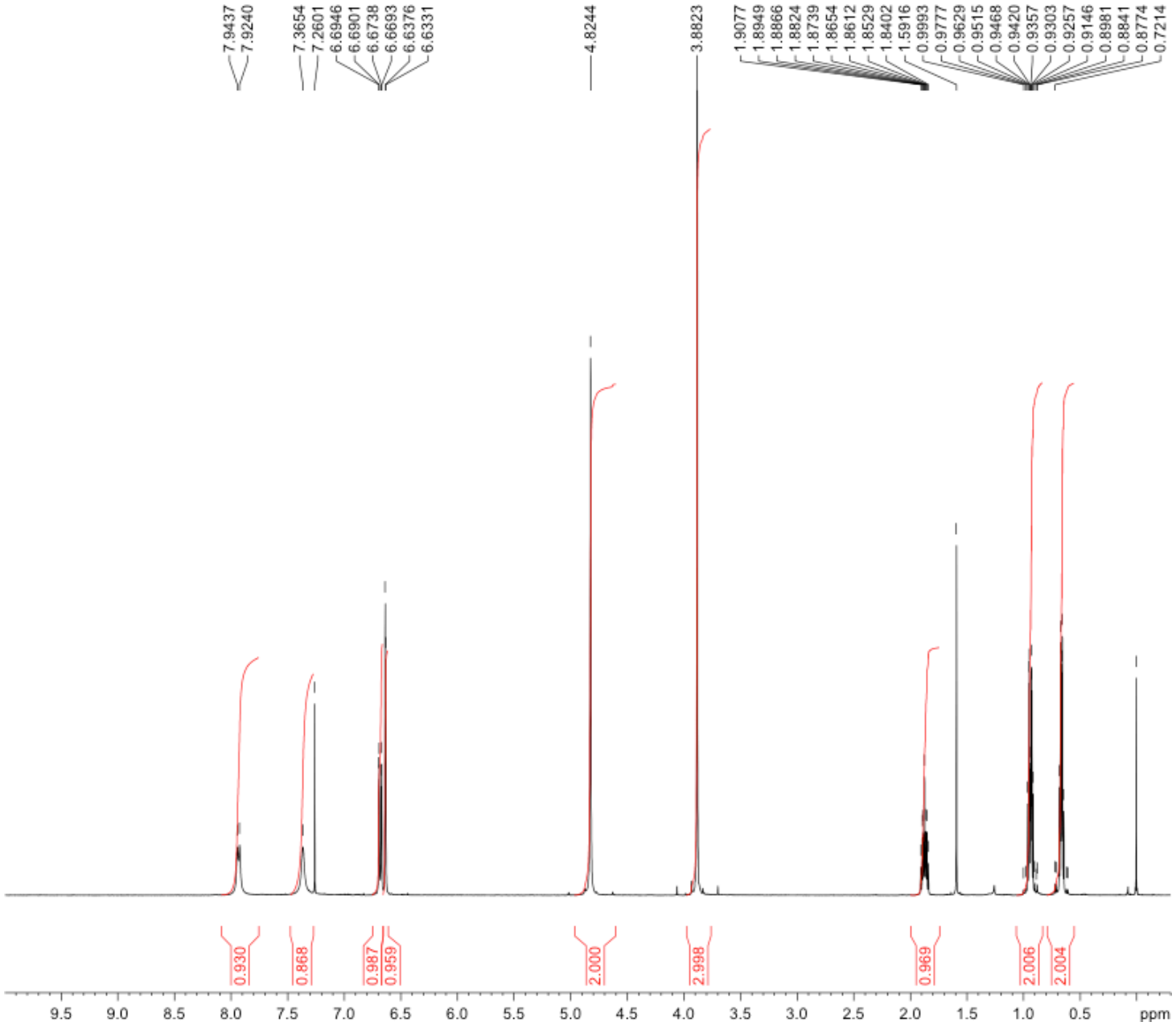

OMe
Cl3C
O
NH
O

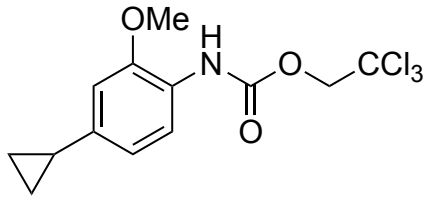
7


156.7267
152.3229
134.5322
129.7804
122.4052
114.0433
111.7167
95.6417
77.4766
77.1588
76.8416
74.6529
55.5951
11.6272
6.3327
0.1375
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

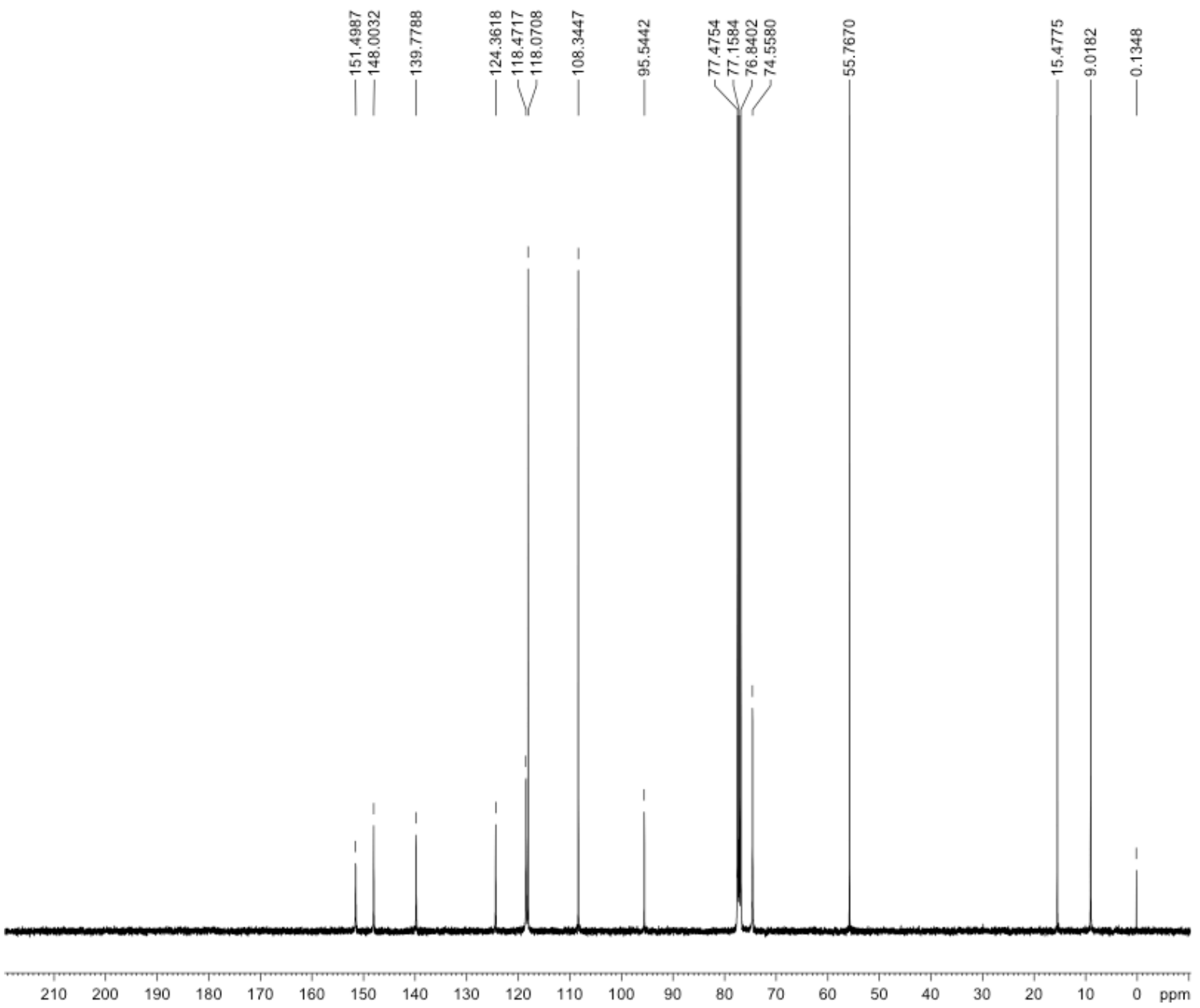

OMe
Cl3C
O
NH
O

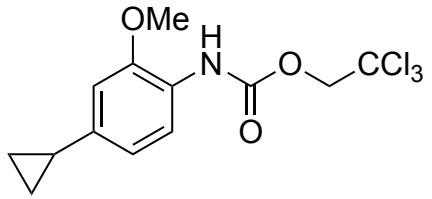
7


7.9437
7.9240
7.3654
7.2601
6.6946
6.6901
6.6738
6.6693
6.6376
6.6331
4.8244
3.8823
1.9077
1.8949
1.8866
1.8824
1.8739
1.8654
1.8612
1.8529
1.8402
1.5916
0.9993
0.9777
0.9629
0.9515
0.9468
0.9420
0.9357
0.9303
0.9257
0.9146
0.8981
0.8841
0.8774
0.7214
0.930
0.868
0.987
0.959
2.000
2.998
0.969
2.006
2.004
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

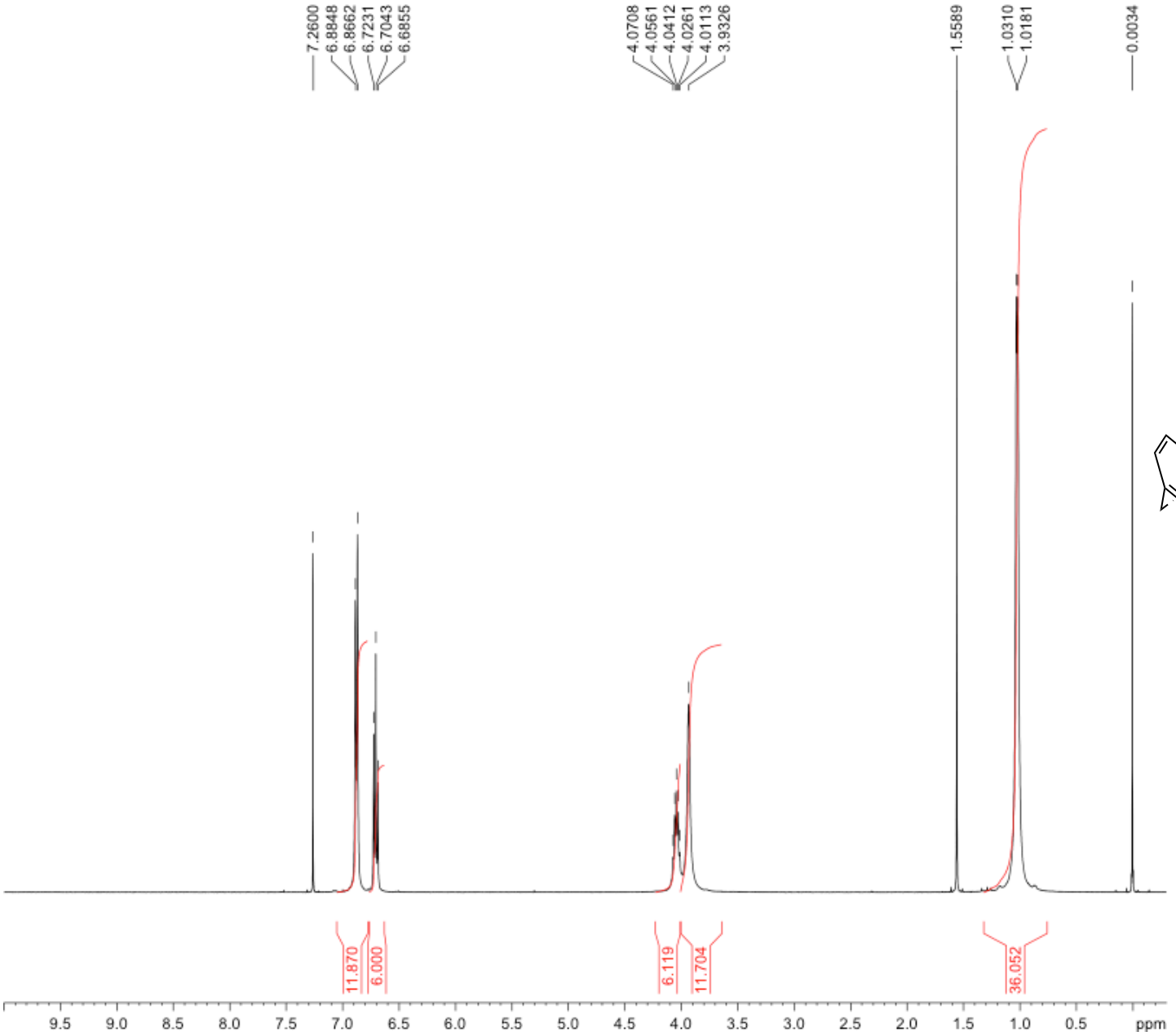

OMe
H
N
O
O
CCl3

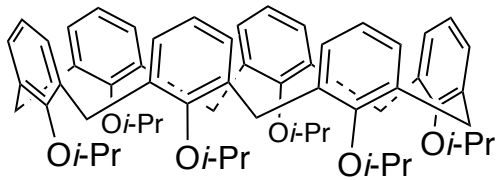
8


151.4987
148.0032
139.7788
124.3618
118.4717
118.0708
108.3447
95.5442
77.4754
77.1584
76.8402
74.5580
55.7670
15.4775
9.0182
0.1348
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

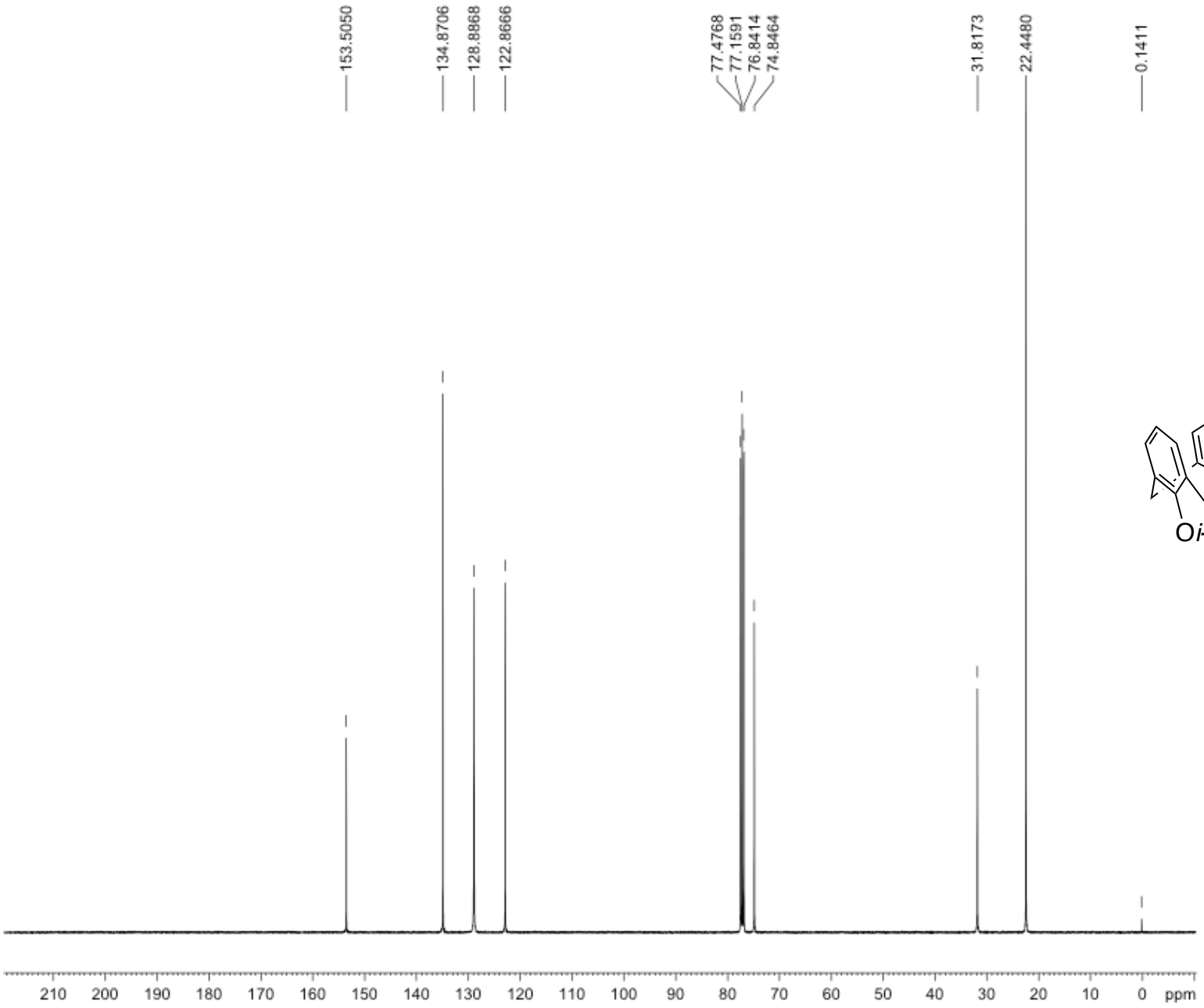

OMe
H
N
O
O
CCl3

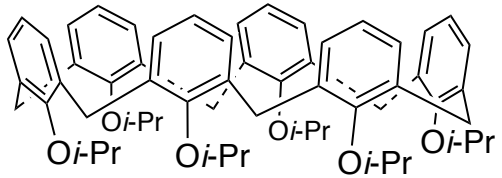
8


7.2600
6.8848
6.8662
6.7231
6.7043
6.6855
4.0708
4.0561
4.0412
4.0261
4.0113
3.9326
1.5589
1.0310
1.0181
0.0034
11.870
6.000
6.119
11.704
36.052
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

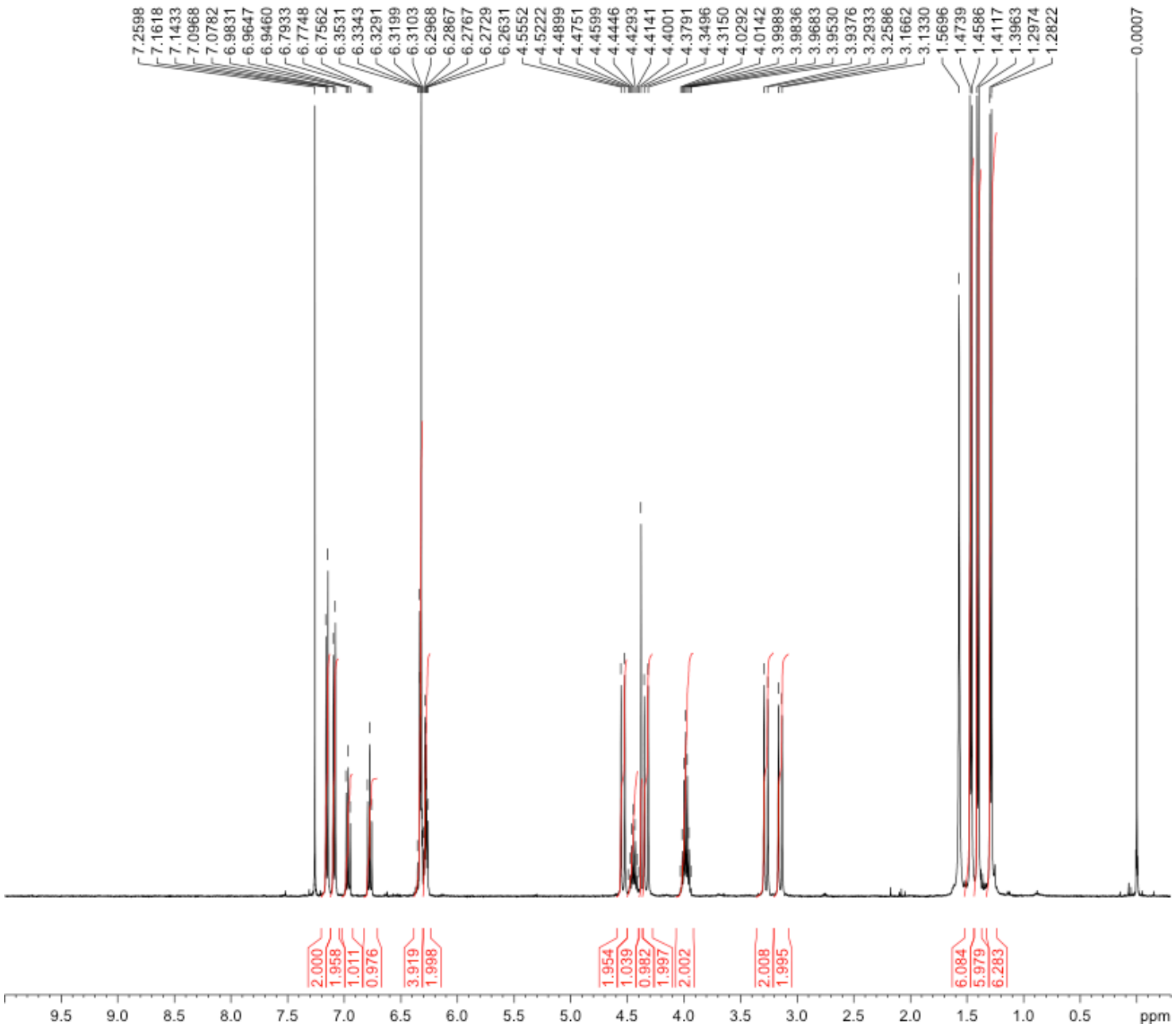

Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr

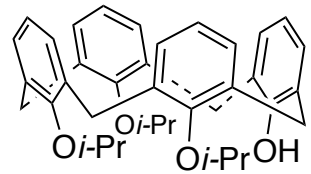
1y


153.5050
134.8706
128.8868
122.8666
77.4768
77.1591
76.8414
74.8464
31.8173
22.4480
0.1411
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

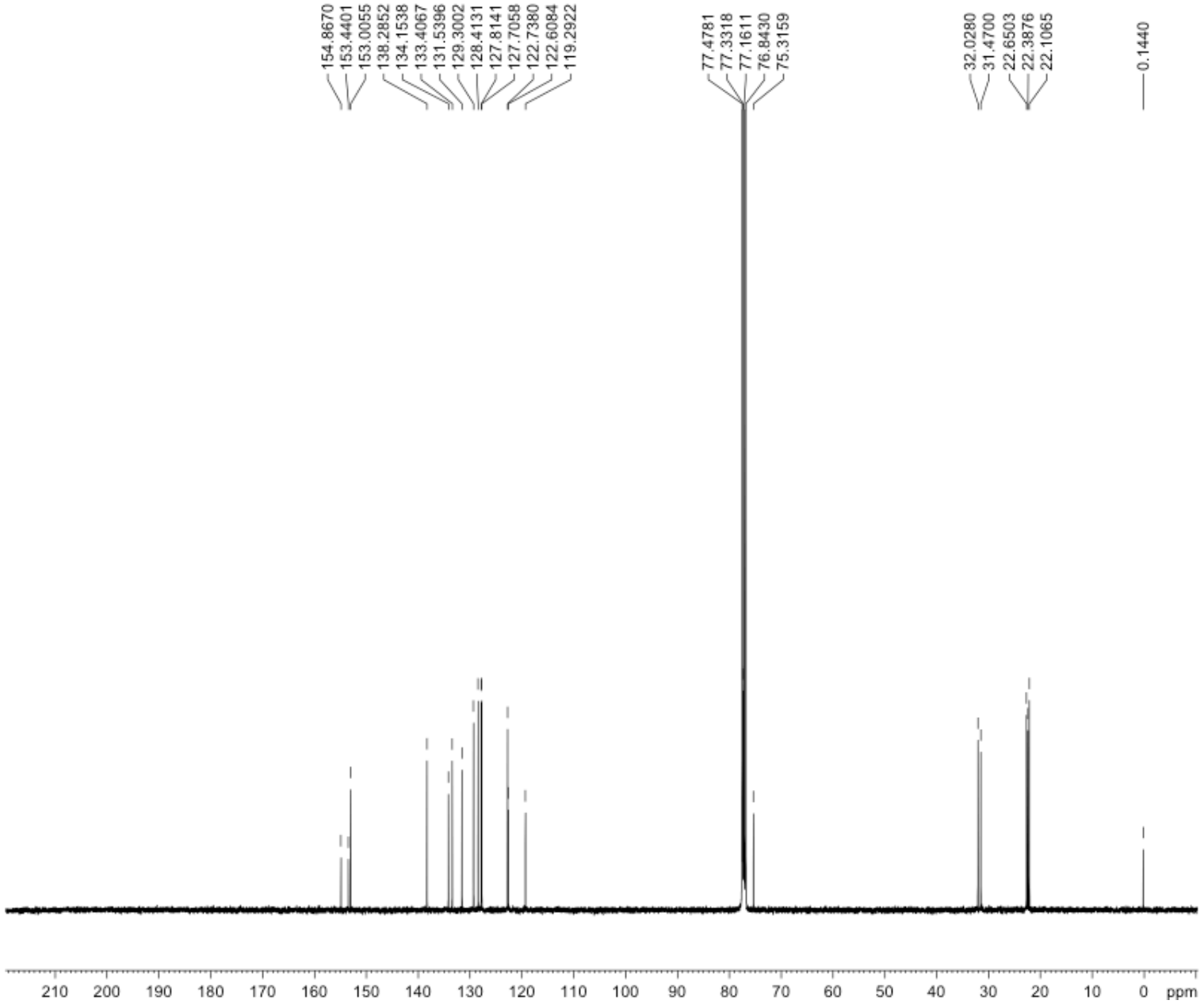

Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr
Oi-Pr

1y


7.2598
7.1618
7.1433
7.0968
7.0782
6.9831
6.9647
6.9460
6.7933
6.7748
6.7562
6.3531
6.3343
6.3291
6.3199
6.3103
6.2968
6.2867
6.2767
6.2729
6.2631
4.5552
4.5222
4.4899
4.4751
4.4599
4.4446
4.4293
4.4141
4.4001
4.3791
4.3496
4.3150
4.0292
4.0142
3.9989
3.9836
3.9683
3.9530
3.9376
3.2933
3.2586
3.1662
3.1330
1.5696
1.4739
1.4586
1.4117
1.3963
1.2974
1.2822
0.0007
2.000
1.958
1.011
0.976
3.919
1.998
1.954
1.039
0.982
1.997
2.002
2.008
1.995
6.084
5.979
6.283
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Oi-Pr
Oi-Pr
Oi-Pr
OH

1z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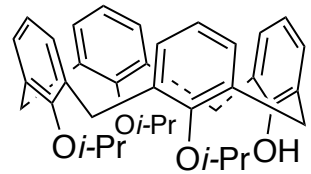
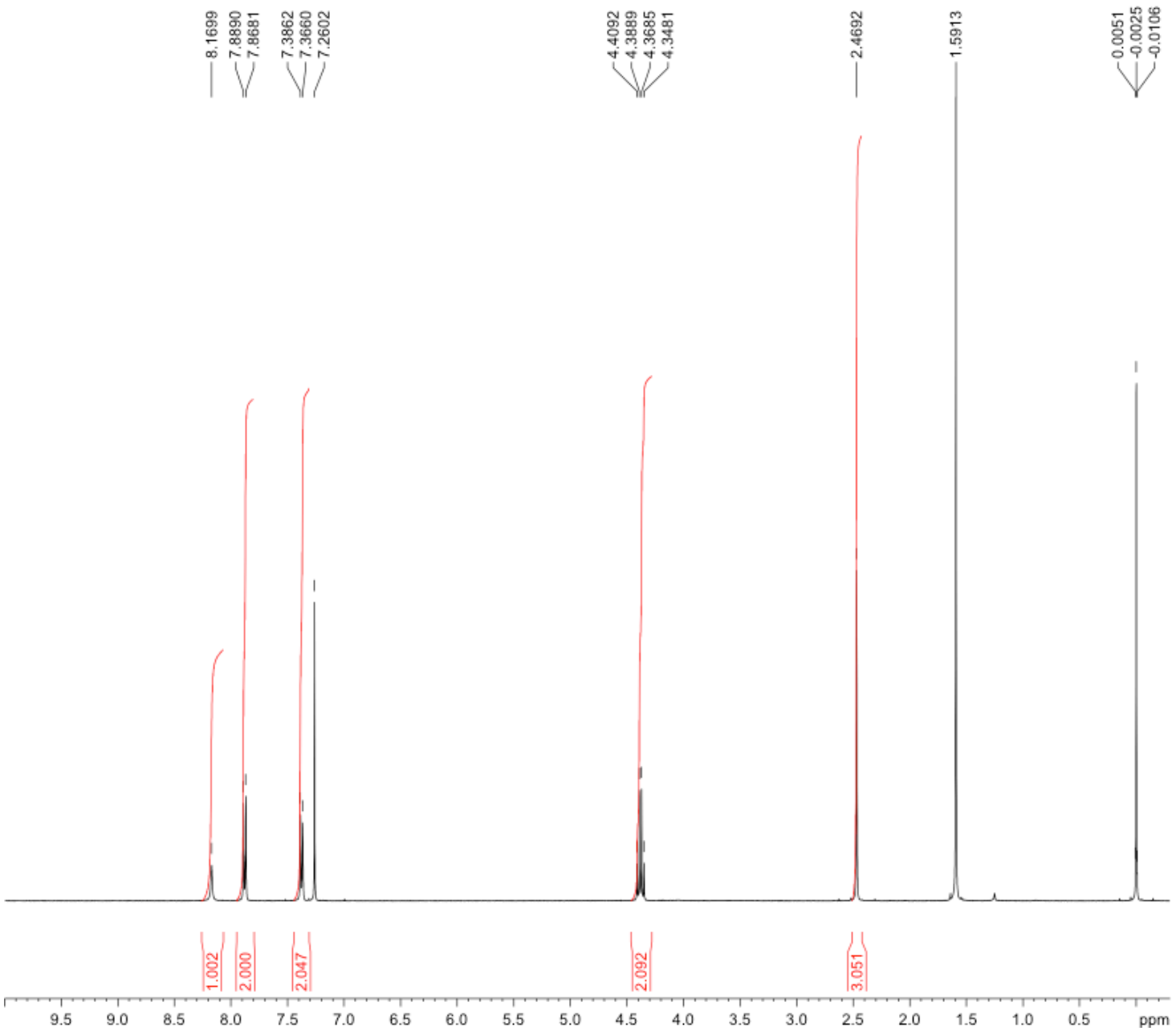
153.4401
153.0055
138.2852
134.1538
133.4067
131.5396
129.3002
128.4131
127.8141
127.7058
122.7380
122.6084
119.2922
77.4781
77.3318
77.1611
76.8430
75.3159
32.0280
31.4700
22.6503
22.3876
22.1065
0.1440
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Oi-Pr
Oi-Pr
Oi-Pr
OH

1z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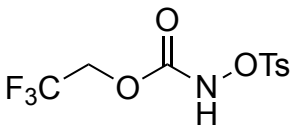
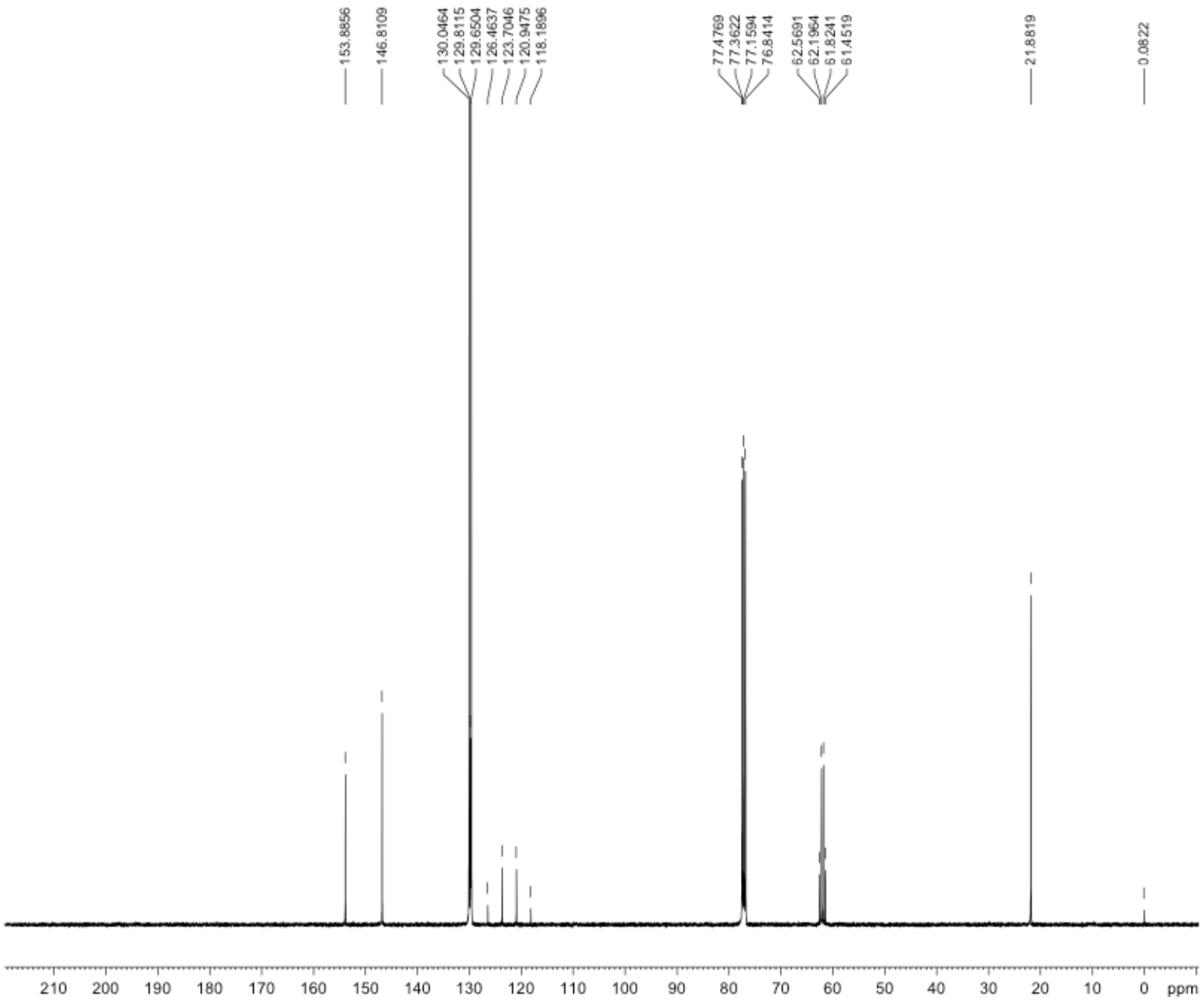
7.8681
7.3862
7.3660
7.2602
4.4092
4.3889
4.3685
4.3481
2.4692
1.5913
0.0051
-0.0025
-0.0106
1.002
2.000
2.047
2.092
3.051
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


O
F3C
O
N
H
OTs

S7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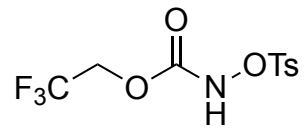
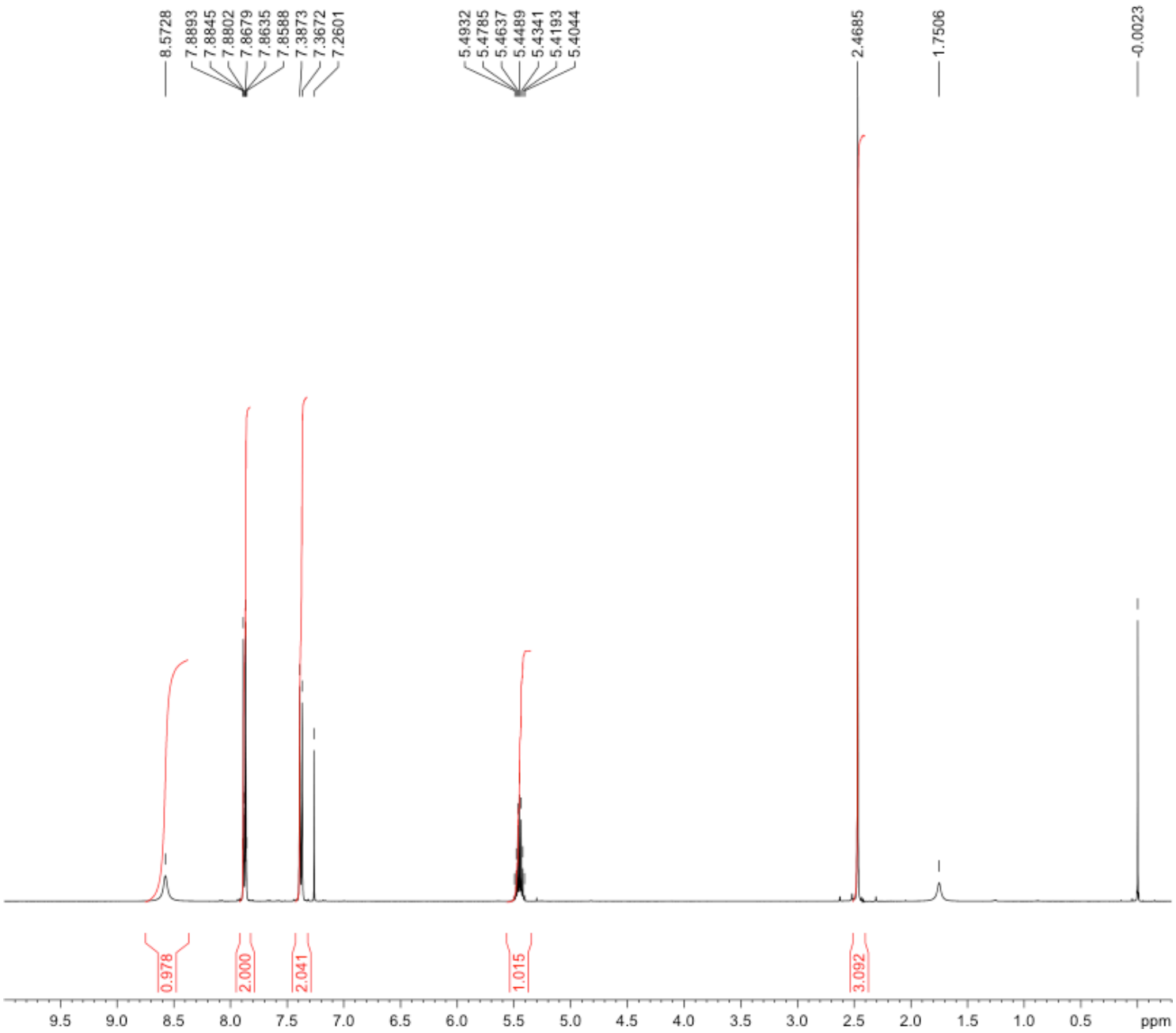
130.0464
129.8115
129.6504
126.4637
123.7046
120.9475
118.1896
77.4769
77.3622
77.1594
76.8414
62.5691
62.1964
61.8241
61.4519
21.8819
0.0822
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
F3C
O
N
H
OTs

S7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7.8893
7.8845
7.8802
7.8679
7.8635
7.8588
7.3873
7.3672
7.2601
5.4932
5.4785
5.4637
5.4489
5.4341
5.4193
5.4044
2.4685
1.7506
-0.0023
0.978
2.000
2.041
1.015
3.092
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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3.5
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2.0
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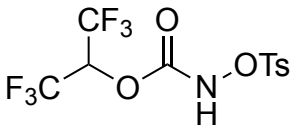
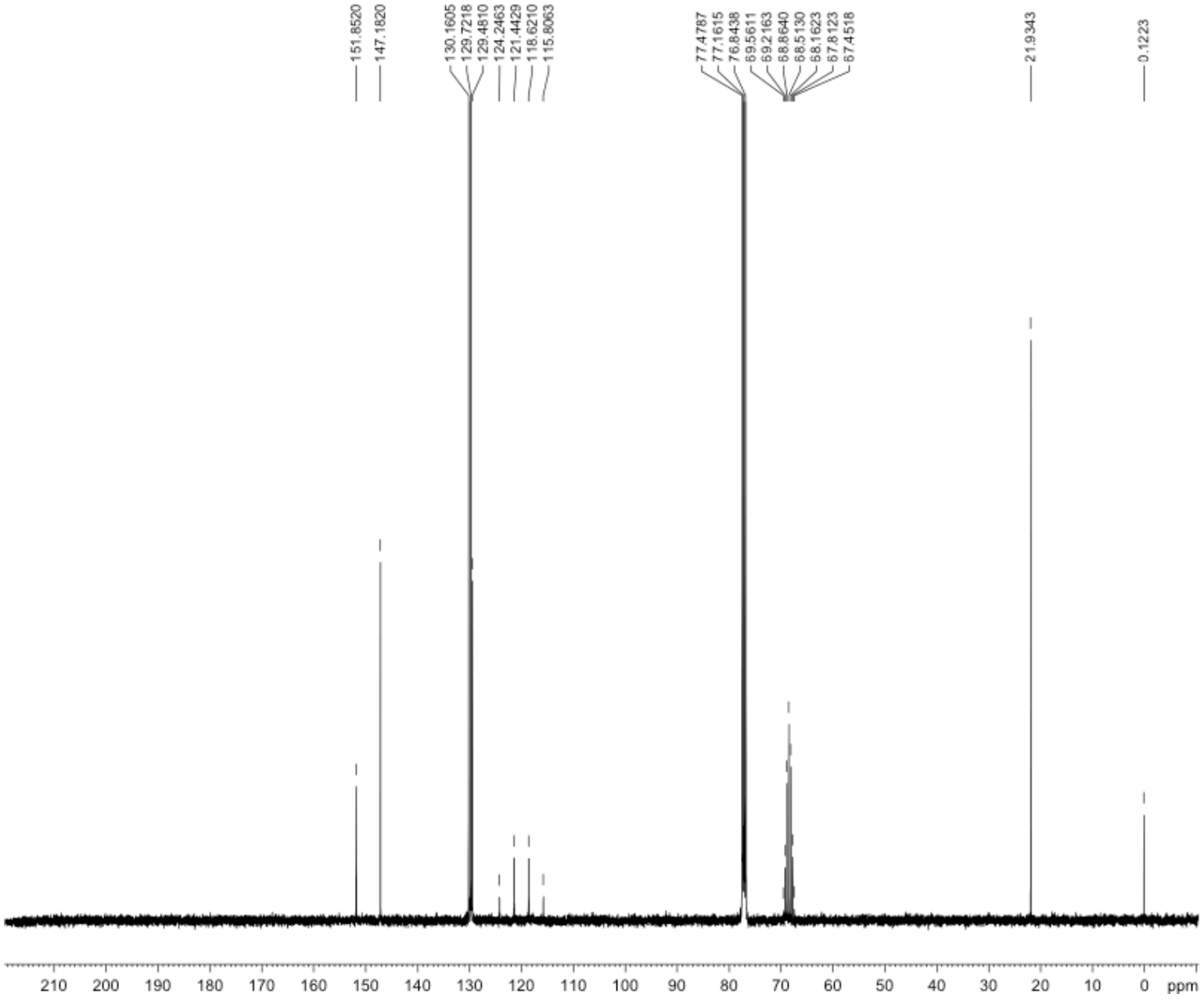
1.0
0.5
ppm


CF3
O
F3C
O
N
H
OTs

S8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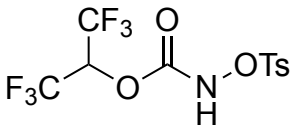
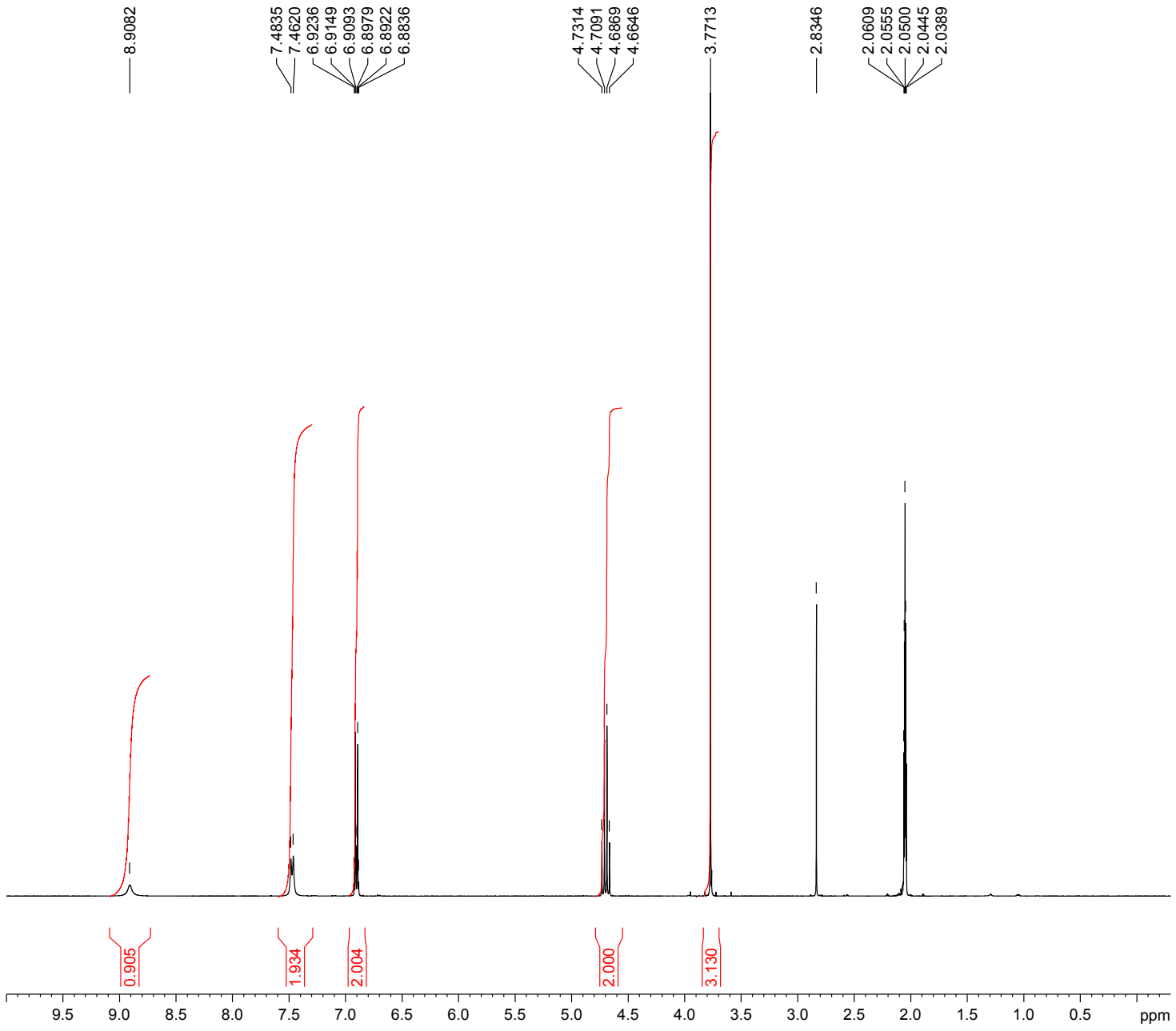
147.1820
130.1605
129.7218
129.4810
124.2463
121.4429
118.6210
115.8063
77.4787
77.1615
76.8438
69.5611
69.2163
68.8640
68.5130
68.1623
67.8123
67.4518
21.9343
0.1223
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


CF3
O
F3C
O
N
H
OTs

S8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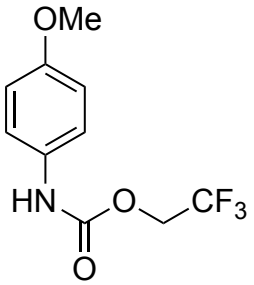
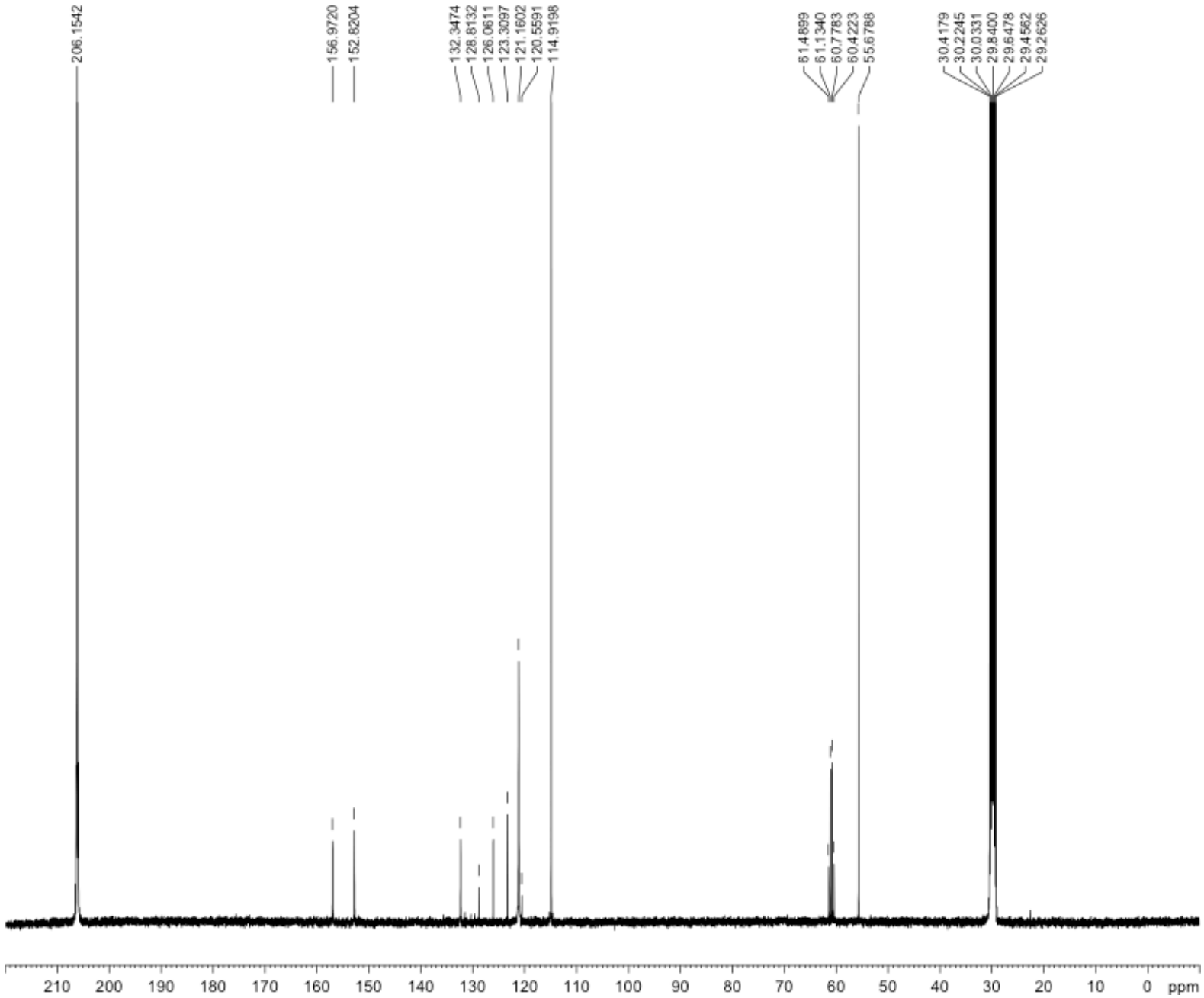
7.4835
7.4620
6.9236
6.9149
6.9093
6.8979
6.8922
6.8836
4.7314
4.7091
4.6869
4.6646
3.7713
2.8346
2.0609
2.0555
2.0500
2.0445
2.0389
0.905
1.934
2.004
2.000
3.130
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
HN
O
O
CF3

S1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156.9720
152.8204
132.3474
128.8132
126.0611
123.3097
121.1602
120.5591
114.9198
61.4899
61.1340
60.7783
60.4223
55.6788
30.4179
30.2245
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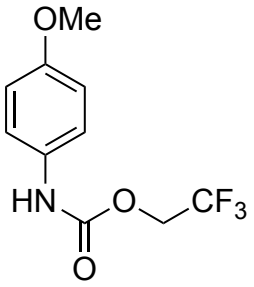
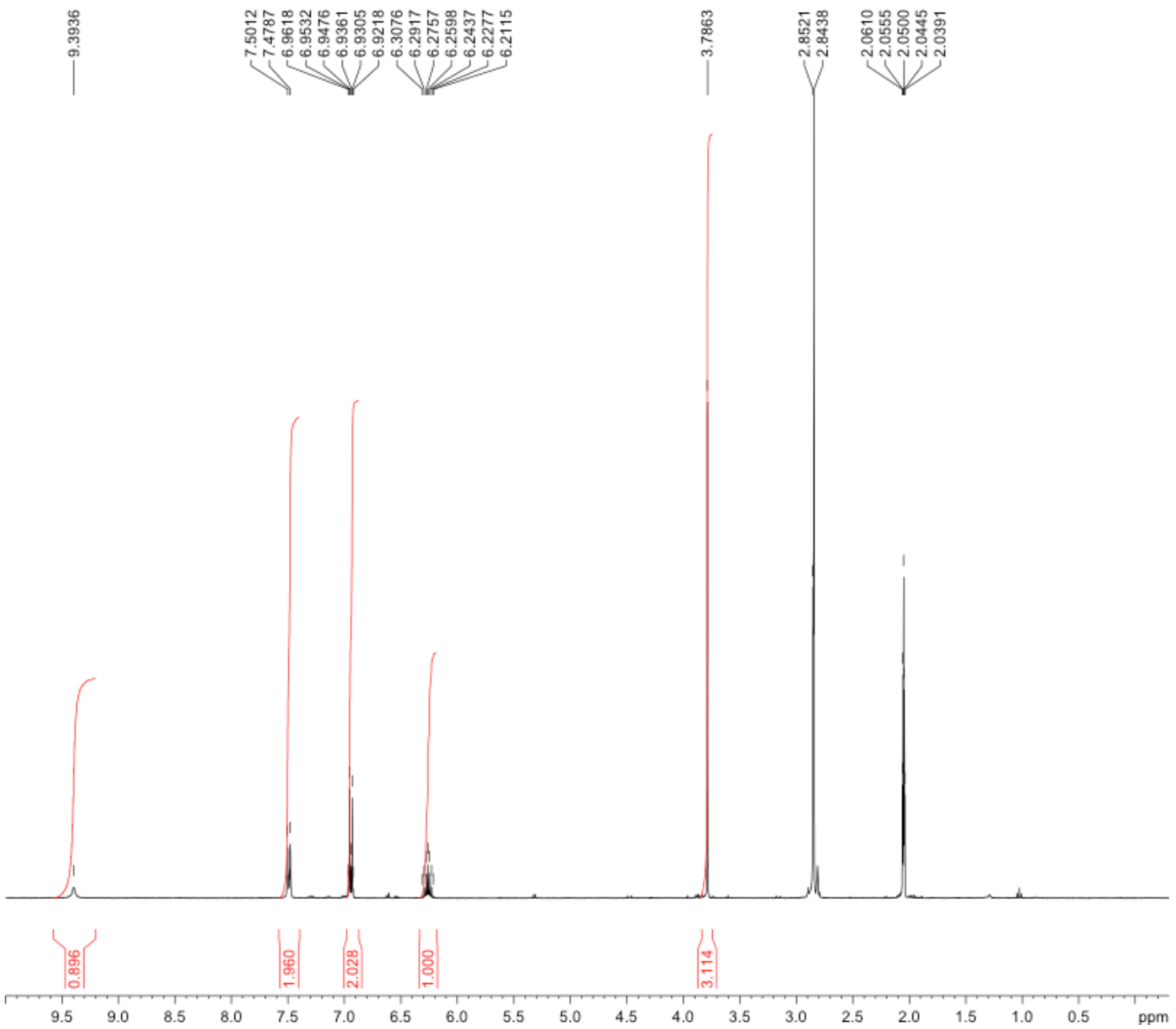
29.8400
29.6478
29.4562
29.2626
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
HN
O
O
CF3

S1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7.4787
6.9618
6.9532
6.9476
6.9361
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6.9218
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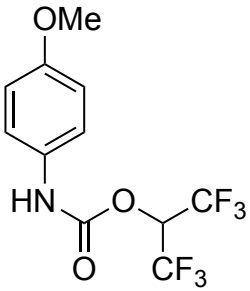
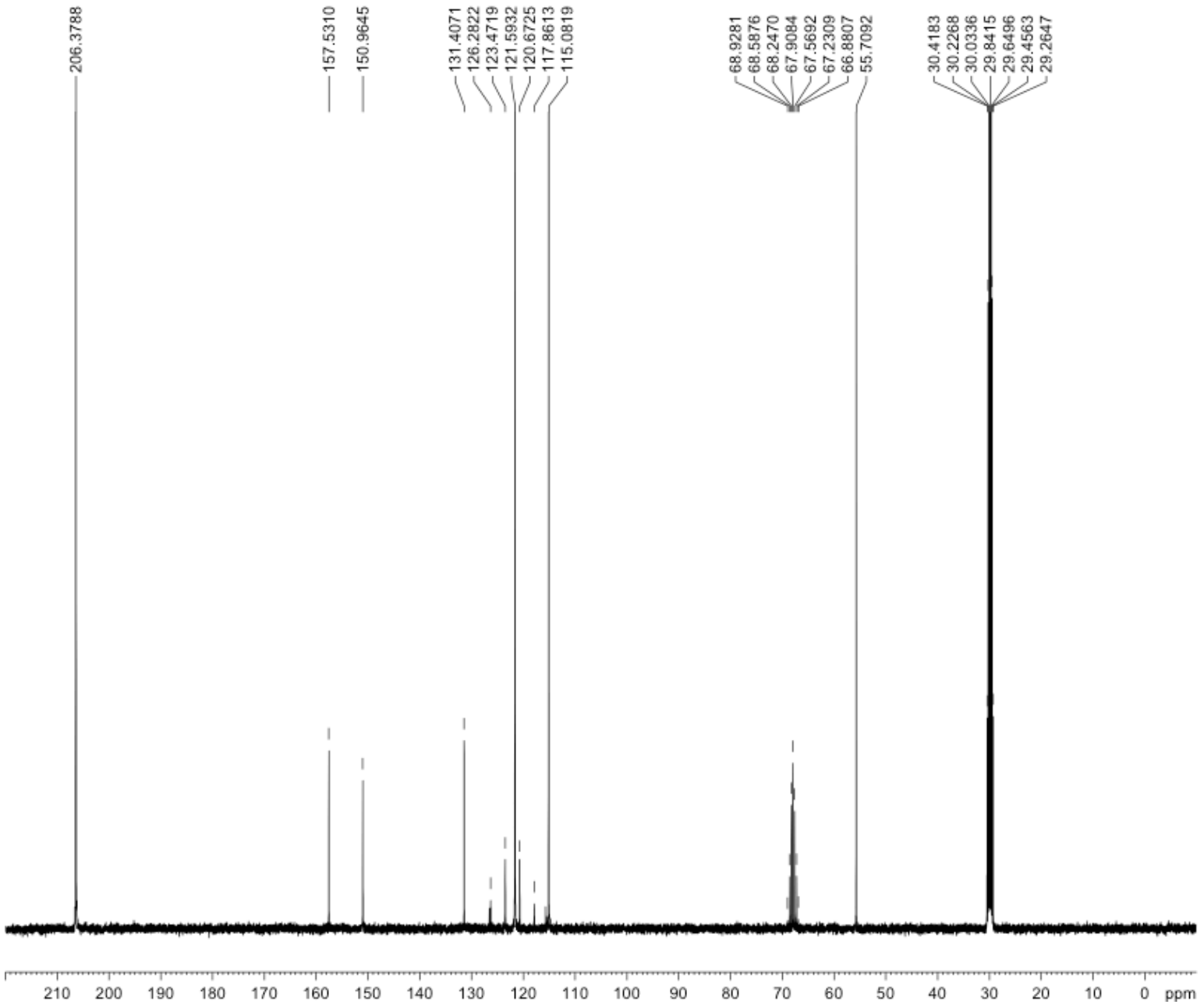
6.2917
6.2757
6.2598
6.2437
6.2277
6.2115
3.7863
2.8521
2.8438
2.0610
2.0555
2.0500
2.0445
2.0391
0.896
1.960
2.028
1.000
3.114
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OMe
HN
O
O
CF3
CF3

S2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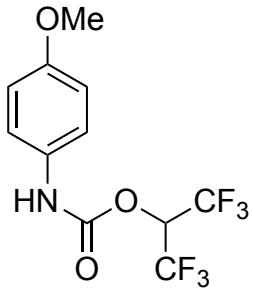
150.9645
131.4071
126.2822
123.4719
121.5932
120.6725
117.8613
115.0819
68.9281
68.5876
68.2470
67.9084
67.5692
67.2309
66.8807
55.7092
30.4183
30.2268
30.0336
29.8415
29.6496
29.4563
29.2647
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
HN
O
O
CF3
CF3

S2