Supporting Information

Metal Catalyst-Free Photo-Induced Alkyl C–O Bond Borylation

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I. Experimental Section

Part 1. General Information

1. Chemical and Reagents

Unless otherwise mentioned, all reactions were performed under an atmosphere of nitrogen or argon using anhydrous solvents in flame-dried tube. B_2cat_2 was purchased from TCI, Fluorochem, Bidepharm and purified by recrystallization in toluene. All alcohols were either obtained from commercial suppliers or prepared according to the literature procedures.

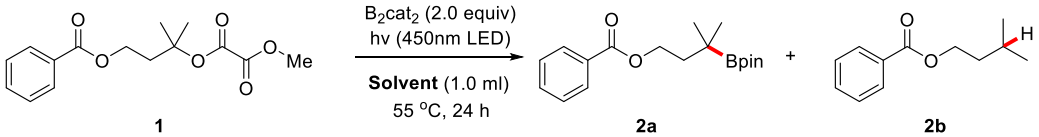
2. Physical Method

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 600 MHz spectrometer at STP. NMR spectra are internally referenced to residual proton solvent signals (note: $CDCl_3$ referenced at 7.26 for ^1H NMR and 77.0 ppm for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded at 151 MHz (the carbon attached to B was not observed). ^{11}B spectra were recorded at 193 MHz. Coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); br (broad). High-resolution mass spectra (HRMS) were recorded using Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Optimization Experiments

General procedure for optimization experiments: A flame-dried tube with a stir bar was charged with B_2cat_2 (3.0 equiv). The tube was capped with a rubber septum. After evacuation and backfilled nitrogen for 5 times, DMF (1.0 mL) was added to the tube. The reaction mixture was stirred for 15 min at 40 °C, at which point, tertiary alkyl oxalate **1** (1.0 equiv, 0.3 mmol) was added via a syringe. The resultant reaction mixture was stirred under Blue LED (30 W, 450 nm) irradiation for 24 - 48 h. The internal temperature of the reaction tube was determined to be 55 °C during the course of photo irradiation. After the reaction was complete, the photo irradiation was stopped. Pinacol (2.0 equiv. based on B_2cat_2) dissolved in Et_3N (1.0 mL) was added via a syringe, and the mixture was stirred for additional 2 h at room temperature. The reaction mixture was subjected to a quick flash column chromatograph to give a mixture containing the products and other impurities. The yield of the target compound was determined using 2,5-dimethylfuran as standard by ^1H NMR spectroscopic analysis.

Table S1. Screening of Solvents.

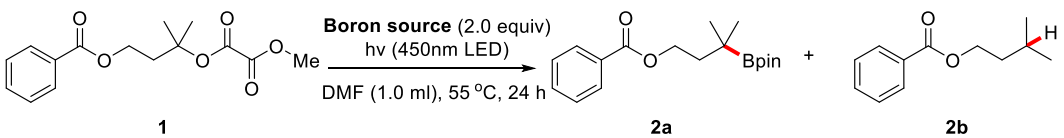


1 0.30 mmol, 1.0 equiv — **2a** — **2b**

entry	solvent (ml)	**2a** (%)[a]	**2b** (%)[a]	recovered **1** (%)[a]
1	DMF	51	9	29
2	DMA	30	15	48
3	NMP	43	4	42
4	DMPU	17	5	65
5	DMI	22	3	50
6	DMSO	trace	trace	28
7	CH_3CN	trace	2	96
8	DCE	trace	15	46
9	Dioxane	2	5	85
10	Hexane	trace	15	53

[a] NMR yield using 2,5-dimethylfuran as the internal standard.

Table S2. Screening of Boron Sources.



1 0.30 mmol, 1.0 equiv — **2a** — **2b**

entry	boron source	**2a** (%)[a]	**2b** (%)[a]	recovered **1** (%)[a]
1	B_2cat_2	51	9	29
2	**B1**	trace	2	93
3	**B2**	33	50	17
4	**B3**	trace	trace	98
5	**B4**	trace	trace	100%
6	**B5**	trace	trace	100%
7	B_2pin_2	trace	trace	100%

[a] NMR yield using 2,5-dimethylfuran as the internal standard.

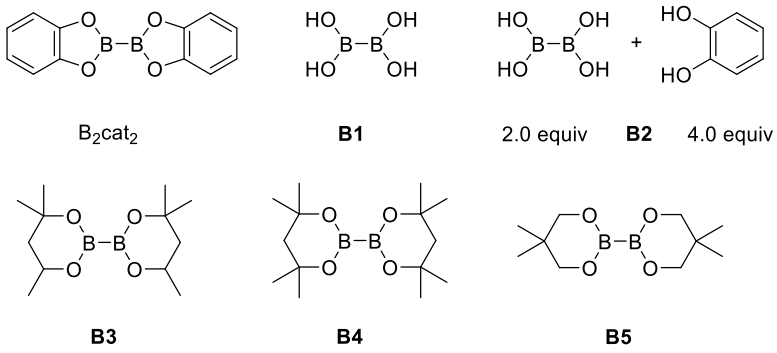
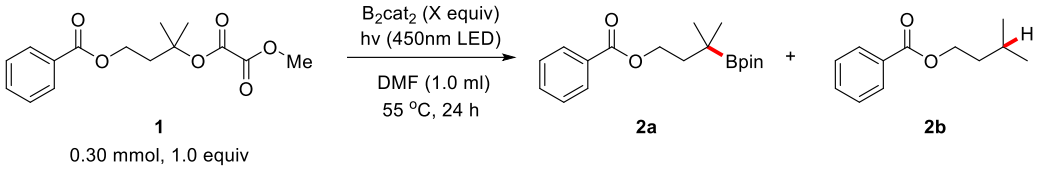


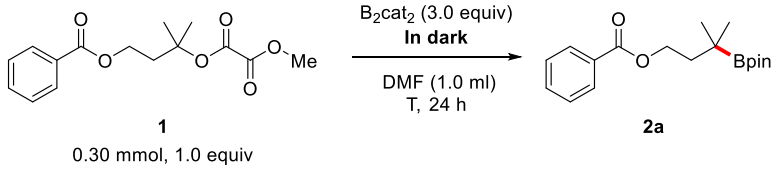
Table S3. Screening of the amount of B_2cat_2.



entry	B_2cat_2 (x equiv)	**2a** (%)[a]	**2b** (%)[a]	recovered **1** (%)[a]
1	1.5	42	4.5	41
2	2.0	51	9	29
3	2.5	67	2	27
4	3.0	75	5	12
5[c]	3.0	91 (87[b])	3	7

[a] NMR yield using 2,5-dimethylfuran as the standard. [b] Isolated yield. [c] The reaction was run for 48 h

Table S4. Control Experiments.

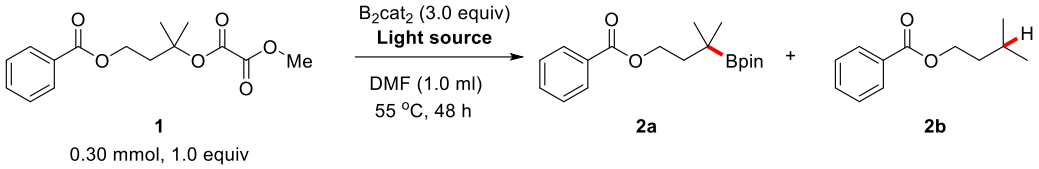


entry	Temp. (°C)	**2a** (%)[a]	B_2cat_2 recovered (%)[a]	recovered **1** (%)[a]
1	25	trace	100	100
2	40	trace	100	93
3	60	trace	52	85

4	80	trace	23	80
5	100	8	11	15

[a] NMR yield using 2,5-dimethylfuran as the internal standard.

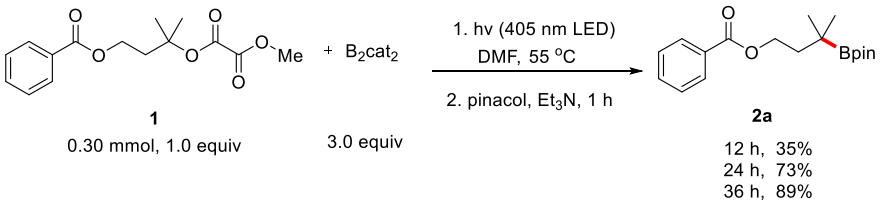
Table S5. Screening of Light Source.



entry	light (30 W)	**2a** (%)[a]	**2b** (%)[a]	1 recovered (%)[a]
1	White LED	47	15	33
2	Green LED (520 nm)	6	2	90
3	Blue LED (450 nm)	91	3	7
4	Purple LED (405 nm)	97	trace	trace
5	UV (365 nm)	78	2	19

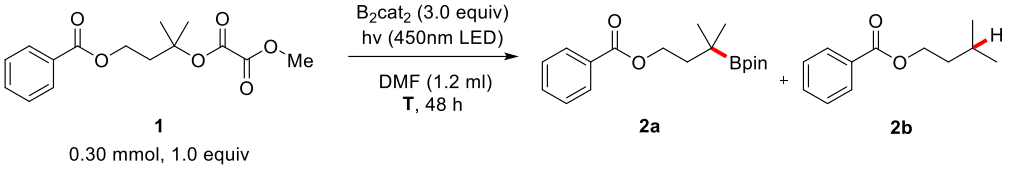
[a] NMR yield using 2,5-dimethylfuran as the internal standard.

A flame-dried tube with a stir bar was charged with B_2cat_2 (3.0 equiv). The tube was capped with a rubber septum. After evacuation and backfilled nitrogen for 5 times, DMF (1.20 mL) was added to the tube. The reaction mixture was stirred for 15 min at 40 ℃, at which point, tertiary alkyl oxalate 1 (1.0 equiv., 0.3 mmol) was added via a syringe. The resultant reaction mixture was stirred under Blue LED (30 W, 405 nm) irradiation for 24 - 48 h. The internal temperature of the reaction tube was determined to be 55 °C during the course of photo irradiation. After the reaction was complete, the photo irradiation was stopped. Pinacol (2.0 equiv. based on B_2cat_2) dissolved in Et_3N (1.0 mL) was added via a syringe, and the mixture was stirred for additional 2 h at room temperature. The reaction mixture was subjected to a quick flash column chromatograph to give a mixture containing the products and other impurities. The yield of the target compound was determined using 2,5-dimethylfuran as standard by ^1H NMR spectroscopic analysis.



Scheme S1. Tracking the reaction of **1** with B_2cat_2 using 405 nm Purple LED as the light source.

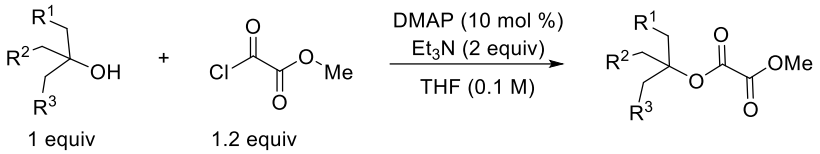
Table S6. Screening of Temperature.



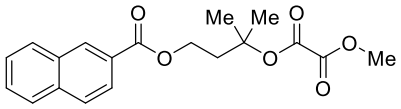
entry	Temp.	**2a** (%)[a]	**2b** (%)[a]	1 recovered (%)[a]
1	25	17	trace	76
2	55	91	3	7

[a] NMR yield using 2,5-dimethylfuran as the internal standard.

Part 3. Preparation of tertiary Alkyl Oxalates



General Procedure for the Preparation of tertiary Alkyl Oxalates **(GP-A)**. The tertiary alkyl oxalates were prepared according to a literature procedure.[1] A round-bottom flask equipped with a stirring bar was charged with tertiary alkyl alcohol (1.0 equiv), Et_3N (2.0 equiv), DMAP (10 mol %), and THF (0.1 M) followed by addition of methyl chlorooxoacetate (1.2 equiv) dropwise at 0 °C. The reaction mixture was warmed to 25 °C and stirred for 5 hours. It was quenched with sat. NH_4Cl (aq). The aqueous phase was extracted with DCM. The organic phase were collected, dried over $MgSO_4$, concentrated under reduced pressure. The crude material was purified by flash column chromatograph to give the target tertiary alkyl oxalate.



4-((2-Naphthoyl)oxy)-2-methylbutan-2-yl methyl oxalate

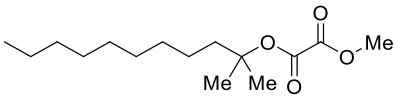
The compound was prepared according to the general procedure using 3-hydroxy-3-methylbutyl 2-naphthoate (5.17 g，20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (ethyl acetate: petroleum ether, namely EA : PE = 1 : 25), the title compound (6.62 g, 19.2 mmol) was obtained in in 96 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.57 (*J* = 7.2 Hz, 1H), 7.54 (*J* = 7.2 Hz, 1H), 4.54 (t, *J* = 6.5 Hz, 2H), 3.73 (s, 3H), 2.42 (t, *J* = 6.5 Hz, 2H), 1.67 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 158.6, 156.6, 135.5, 132.4, 131.0, 129.4, 128.3, 128.2, 127.7, 127.2, 126.7, 125.1, 85.4, 60.9, 53.2, 38.9, 26.1.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{19}H_{20}NaO_6$: 367.1152. Found: 367.1155.

M.P. 57-58 ℃.



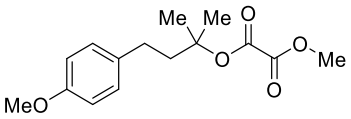
Methyl (2-methylundecan-2-yl) oxalate

The compound was prepared according to the general procedure using 2-methylundecan-2-ol (5.59 g, 30.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 100), the title compound (7.12 g, 26.2 mmol) was obtained in in 87 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 3H), 1.80 (m, 2H), 1.51 (s, 6H), 1.27 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.7, 87.5, 53.2, 40.4, 31.8, 29.8, 29.5, 29.5, 29.3, 25.6, 23.8, 22.6, 14.1.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{15}H_{28}NaO_4$: 295.1880. Found: 295.1885.



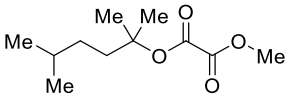
4-(4-Methoxyphenyl)-2-methylbutan-2-yl methyl oxalate

The compound was prepared according to the general procedure using 4-(4-methoxyphenyl)-2-methylbutan-2-ol (5.82 g, 30.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 20), the title compound (6.83 g, 24.4 mmol) was obtained in 81% yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 3.86 (s, 3H), 3.77 (s, 3H), 2.62 (m, 2H), 2.12 (m, 2H), 1.59 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 157.8, 156.6, 133.4, 129.1, 113.7, 86.7, 55.1, 53.1, 42.4, 29.2, 25.6.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{15}H_{20}NaO_5$: 303.1203. Found: 303.1205.



2,5-Dimethylhexan-2-yl methyl oxalate

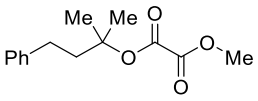
The compound was prepared according to the general procedure using 2,5-dimethylhexan-2-ol (3.93 g,

30.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 100), the title compound (5.08 g, 23.5 mmol) was obtained in 78% yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (s, 3H), 1.80 (m, 2H), 1.50 (m, 7H), 1.20 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.7, 87.5, 53.2, 38.2, 32.6, 28.2, 25.6, 22.5.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{11}H_{20}NaO_4$: 239.1254. Found: 239.1257.



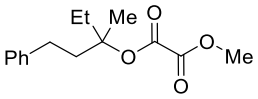
Methyl (2-methyl-4-phenylbutan-2-yl) oxalate

The compound was prepared according to the general procedure using 2-methyl-4-phenylbutan-2-ol (4.93 g, 30.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (7.16 g, 28.6 mmol) was obtained in 95% yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (m, 3H), 3.87 (s, 3H), 2.69 (m, 2H), 2.16 (m, 2H), 1.61 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 156.7, 141.4, 128.4, 128.3, 125.9, 86.7, 53.2, 42.3, 30.2, 25.7.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{14}H_{18}NaO_4$: 273.1097. Found: 273.1101.



Methyl (3-methyl-1-phenylpentan-3-yl) oxalate

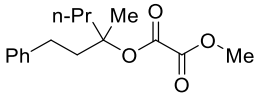
The compound was prepared according to the general procedure using 3-methyl-1-phenylpentan-3-ol (3.57 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (4.81 g, 18.2 mmol) was obtained in 91 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (m, 3H), 3.87 (s, 3H), 2.65 (m, 2H), 2.25 (m, 1H), 2.12 (m, 1H), 2.05 (m, 1H), 1.92 (m, 1H), 1.58 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 156.7, 141.5, 128.4, 128.3, 125.9, 89.6, 53.2, 39.5, 30.7, 29.9,

23.0, 8.0.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{15}H_{20}NaO_4$: 287.1254. Found: 287.1258.



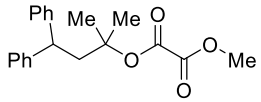
Methyl (3-methyl-1-phenylhexan-3-yl) oxalate

The compound was prepared according to the general procedure using 3-methyl-1-phenylhexan-3-ol (3.08 g, 16.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (3.92 g, , 14.1 mmol) was obtained in 88% yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (m, 3H), 3.87 (s, 3H), 2.65 (m, 2H), 2.23 (m, 1H), 2.12 (m, 1H), 1.96 (m, 1H), 1.85 (m, 1H), 1.58 (s, 3H), 1.38 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.7, 141.5, 128.4, 128.3, 125.9, 89.4, 53.2, 40.3, 40.0, 30.0, 23.5, 17.0, 14.3.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{16}H_{22}NaO_4$: 301.1410. Found: 301.1421.



Methyl (2-methyl-4,4-diphenylbutan-2-yl) oxalate

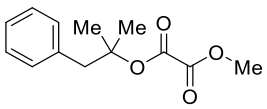
The compound was prepared according to the general procedure using 2-methyl-4,4-diphenylbutan-2-ol (4.81 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (5.79 g, 17.7 mmol) was obtained in 89 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (m, 8H), 7.15 (t, *J* = 7.0 Hz, 2H), 4.19 (t, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 2.74 (d, *J* = 6.9 Hz, 2H), 1.50 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 156.2, 144.9, 128.5, 127.7, 126.1, 86.7, 53.0, 47.2, 44.9, 26.6.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{20}H_{22}NaO_4$: 349.1410. Found: 349.1413.

M.P. 80-81 ℃.



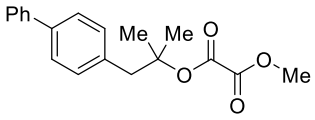
Methyl (2-methyl-1-phenylpropan-2-yl) oxalate

The compound was prepared according to the general procedure using 2-methyl-1-phenylpropan-2-ol (6.01 g, 40.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 100), the title compound (8.81 g, 37.3 mmol) was obtained in 93 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.26 (m, 1H), 7.23 (d, *J* = 7.3 Hz, 2H), 3.88 (s, 3H), 3.12 (s, 2H), 1.55 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 156.7, 136.3, 130.6, 128.1, 126.8, 86.7, 53.3, 46.6, 25.4.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{13}H_{16}NaO_4$: 259.0941. Found: 259.0945.



1-([1,1'-Biphenyl]-4-yl)-2-methylpropan-2-yl methyl oxalate

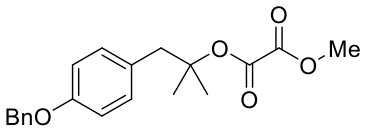
The compound was prepared according to the general procedure using 1-([1,1'-biphenyl] -4-yl)-2-methylpropan-2-ol (3.40 g, 15.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and DCM (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (4.55 g, 14.6 mmol) was obtained in 97 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 3.16 (s, 2H), 1.59 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 156.7, 140.8, 139.7, 135.3, 131.0, 128.7, 127.2, 127.0, 126.8, 86.7, 53.3, 46.3, 25.4.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{19}H_{20}NaO_4$: 335.1254. Found: 335.1253.

M.P. 89-90 ℃.



1-(4-(Benzyloxy)phenyl)-2-methylpropan-2-yl methyl oxalate

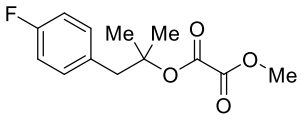
The compound was prepared according to the general procedure using 1-(4-(benzyloxy)phenyl)-2-methylpropan-2-ol (5.13 g, 20 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph on silica gel (EA : PE = 1 : 20), the compound (5.48 g, 16.0 mmol) was obtained 80 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.05 (s, 2H), 3.87 (s, 3H), 3.05 (s, 2H), 1.53 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 157.8, 156.7, 137.1, 131.6, 128.6, 128.6, 127.9, 127.5, 114.5, 86.9, 70.0, 53.3, 45.8, 25.3.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{20}H_{22}NaO_5$: 365.1359. Found: 365.1361.

M.P. 65-67 ℃.



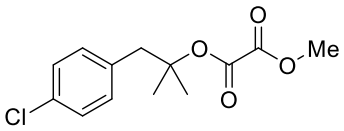
1-(4-Fluorophenyl)-2-methylpropan-2-yl methyl oxalate

The compound was prepared according to the general procedure using 1-(4-fluorophenyl)-2-methylpropan-2-ol (3.36 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (4.36 g, 17.0 mmol) was obtained in 85 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.1 Hz, *J* = 5.7 Hz, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 3.86 (s, 3H), 3.06 (s, 2H), 1.52 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7(d, *J* =245.1 Hz), 158.7, 156.6, 132.1(d, *J* =7.7 Hz), 131.9(d, *J* =3.5 Hz), 115.0(d, *J* =21.1 Hz), 114.8, 86.4, 53.3, 45.9, 25.2.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{13}H_{15}FNaO_4$: 277.0847. Found: 277.0851.



1-(4-Chlorophenyl)-2-methylpropan-2-yl methyl oxalate

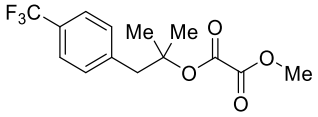
The compound was prepared according to the general procedure using 1-(4-chlorophenyl)-2-methylpropan-2-ol (3.70 g, 20 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph on silica gel (EA : PE = 1 : 50), the compound (4.53 g, 16.7 mmol) was obtained 84 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 3H), 3.06 (s, 2H), 1.53 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.6, 134.6, 132.7, 131.9, 128.2, 86.2, 53.3, 46.0, 25.2.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{13}H_{15}ClNaO_4$: 293.0551. Found: 293.0555.

M.P. 22-24 ℃.



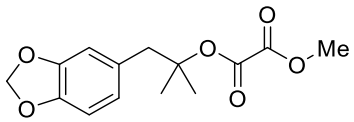
Methyl (2-methyl-1-(4-(trifluoromethyl)phenyl)propan-2-yl) oxalate

The compound was prepared according to the general procedure using 2-methyl-1-(4-(trifluoromethyl)-phenyl)propan-2-ol (3.30 g, 15.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (3.71 g, 12.2 mmol) was obtained in 81 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 3.86 (s, 3H), 3.14 (s, 2H), 1.54 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.5, 140.3, 130.9, 129.2 (q, *J* = 32.5 Hz), 125.1 (q, *J* = 271.6 Hz), 125.0 (q, *J* = 3.7 Hz), 85.9, 53.3, 46.5, 25.3.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{14}H_{15}F_3NaO_4$: 327.0815. Found: 327.0818.



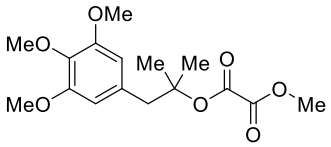
1-(Benzo[d][1,3]dioxol-5-yl)-2-methylpropan-2-yl methyl oxalate

The compound was prepared according to the general procedure using 1-(benzo[d][1,3]dioxol-5-yl)-2-methylpropan-2-ol (3.88 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 10), the title compound (5.12 g, 18.3 mmol) was obtained in 91 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.75 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 2H), 3.86 (s, 3H), 3.00 (s, 2H), 1.52 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 156.6, 147.3, 146.4, 129.8, 123.6, 110.9, 107.8, 100.8, 86.7, 53.2, 46.4, 25.2.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{14}H_{16}NaO_6$: 303.0839. Found: 303.0846.



Methyl (2-methyl-1-(3,4,5-trimethoxyphenyl)propan-2-yl) oxalate

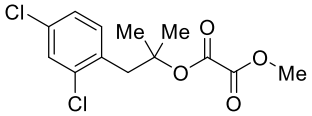
The compound was prepared according to the general procedure using 2-methyl-1-(3,4,5-trimethoxyphenyl)propan-2-ol (4.81 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (6.15 g, 18.8 mmol) was obtained in 94 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.46 (s, 2H), 3.84 (s, 3H), 3.84 (s, 6H), 3.82 (s, 3H), 3.01 (s, 2H), 1.55 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 156.7, 152.7, 136.8, 131.8, 107.6, 86.5, 60.8, 56.0, 53.2, 47.1, 25.4.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{16}H_{22}NaO_7$: 349.1258. Found: 349.1260.

M.P. 69-70 ℃.



1-(2,4-Dichlorophenyl)-2-methylpropan-2-yl methyl oxalate

The compound was prepared according to the general procedure using 1-(2,4-dichlorophenyl)-2-methylpropan-2-ol (4.40 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (5.31 g, 17.4 mmol) was obtained in 87 % yield as a white solid.

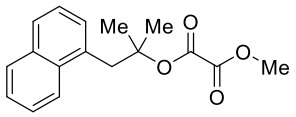
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.19 (dd, *J* = 8.3, 2.1

Hz, 1H), 3.87 (s, 3H), 3.24 (s, 2H), 1.57 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.4, 135.6, 133.5, 133.3, 132.9, 129.2, 126.8, 86.7, 53.3, 42.4, 25.0.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{13}H_{14}Cl_2NaO_4$: 327.0161. Found: 327.0164.

M.P. 30-31 ℃.



Methyl (2-methyl-1-(naphthalen-1-yl)propan-2-yl) oxalate

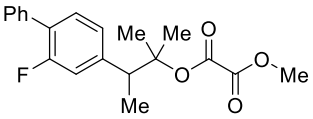
The compound was prepared according to the general procedure using 2-methyl-1-(naphthalen-1-yl)propan-2-ol (4.01 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (5.46 g, 19.1 mmol) was obtained in 95 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (m, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.43 (m, 2H), 3.85 (s, 3H), 3.64 (s, 2H), 1.60 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 156.8, 133.9, 132.9, 132.7, 129.3, 128.7, 127.7, 125.8, 125.4, 125.1, 124.9, 87.7, 53.2, 42.1, 25.8.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{17}H_{18}NaO_4$: 309.1097. Found: 309.1098.

M.P. 48-49 ℃.



3-(2-Fluoro-[1,1'-biphenyl]-4-yl)-2-methylbutan-2-yl methyl oxalate

The compound was prepared according to the general procedure using 3-(2-fluoro-[1,1'-biphenyl]-4-yl)-2-methylbutan-2-ol (4.65 g, 18.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (5.18g, 15.0 mmol) was obtained in 84 % yield as a white solid.

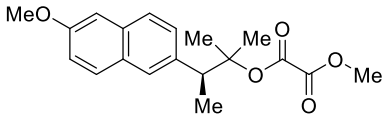
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 (m, 2H), 7.16 (m,

2H), 3.90 (s, 3H), 3.20 (q, *J* = 7.1 Hz, 1H), 1.62 (s, 3H), 1.53 (s, 3H), 1.42 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1 (d, *J* = 247.4 Hz), 158.7, 156.4, 143.7 (d, *J* = 7.2Hz), 135.6, 130.0(d, *J* = 3.7 Hz),128.9(d, *J* = 2.4 Hz), 128.4, 127.5, 127.4(d, *J* = 13.5 Hz), 125.3(d, *J* = 2.7 Hz), 116.8(d, *J* = 23.4 Hz), 88.4, 53.3, 48.5, 23.7, 23.6, 15.6.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{20}H_{21}FNaO_4$: 367.1316. Found: 367.1319.

M.P. 58-59 ℃



(*S*)-3-(6-Methoxynaphthalen-2-yl)-2-methylbutan-2-yl methyl oxalate

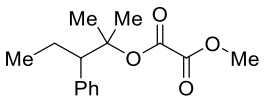
The compound was prepared according to the general procedure using (S)-3-(6-methoxynaphthalen-2-yl)-2-methylbutan-2-ol (2.44 g, 10.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 20), the title compound (2.58 g, 7.81 mmol) was obtained in 78 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (m, 3H), 7.45 (m, 1H), 7.15 (m, 1H), 7.12 (m, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.36 (q, *J* = 7.2 Hz, 1H), 1.60 (s, 3H), 1.52 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 157.6, 156.6, 137.3, 133.6, 129.3, 128.7, 128.1, 127.9, 126.3, 118.8, 105.5, 89.2, 55.3, 53.3, 48.7, 24.0, 23.6, 15.8.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{19}H_{22}NaO_5$: 353.1359. Found: 353.1361.

M.P. 91-92 ℃



Methyl (2-methyl-3-phenylpentan-2-yl) oxalate

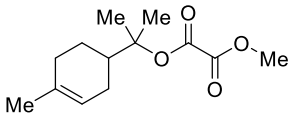
The compound was prepared according to the general procedure using 2-methyl-3-phenylpentan-2-ol (3.57 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (4.72 g, 17.9 mmol) was obtained in 89 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (m, 5H), 3.87 (s, 3H), 2.92 (m, 1H), 1.92 (m, 1H), 1.83 (m, 1H),

1.54 (s, 3H), 1.46 (s, 3H), 0.71 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 156.6, 139.8, 129.8, 128.0, 126.8, 89.2, 57.0, 53.3, 24.5, 23.7, 22.0, 12.5.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{15}H_{20}NaO_4$: 287.1254. Found: 287.1258.



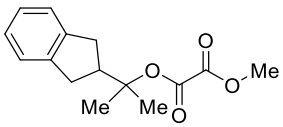
Methyl (2-(4-methylcyclohex-3-en-1-yl)propan-2-yl) oxalate

The compound was prepared according to the general procedure using 2-(4-methylcyclohex-3-en-1-yl)-propan-2-ol (4.63 g，30.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 100), the title compound (6.47 g, 26.9 mmol) was obtained in 90 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.36 (br, 1H), 3.85 (s, 3H), 2.11 (m, 1H), 1.99 (m, 3H), 1.84 (m, 2H), 1.64 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.33 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.7, 134.0, 119.9, 89.9, 53.2, 42.5, 30.7, 26.3, 23.7, 23.2, 23.0, 22.8.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{13}H_{20}NaO_4$: 263.1254. Found: 263.1257.



2-(2,3-Dihydro-1H-inden-2-yl)propan-2-yl methyl oxalate

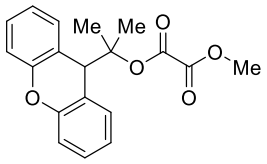
The compound was prepared according to the general procedure using 2-(2,3-dihydro-1H-inden-2-yl)propan-2-ol (3.52 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (4.46 g, 17.0 mmol) was obtained in 85 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (m, 2H), 7.15 (m, 2H), 3.86 (s, 3H), 2.98 (m, 5H), 1.63 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.9, 142.4, 126.3, 124.4, 88.1, 53.2, 49.5, 33.9, 23.7.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{15}H_{18}NaO_4$: 285.1097. Found: 285.1102.

M.P. 80-81 ℃



2-(9H-Xanthen-9-yl)propan-2-yl methyl oxalate

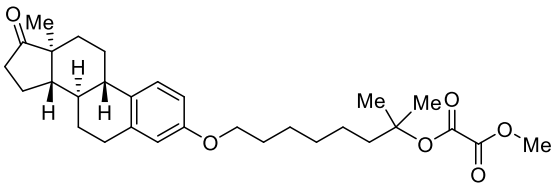
The compound was prepared according to the general procedure using 2-(9H-xanthen-9-yl)propan-2-ol (4.81 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 20), the title compound (5.26 g, 16.1 mmol) was obtained in 81 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 4.56 (s, 1H), 3.90 (s, 3H), 1.43 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.7, 153.6, 130.8, 128.5, 122.9, 121.3, 116.6, 89.9, 53.3, 48.4, 22.2.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{19}H_{18}NaO_5$: 349.1046. Found: 349.1049.

M.P. 68-69 ℃



Methyl (2-methyl-8-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H cyclopenta[a]phenanthren-3-yl)oxy)octan-2-yl) oxalate

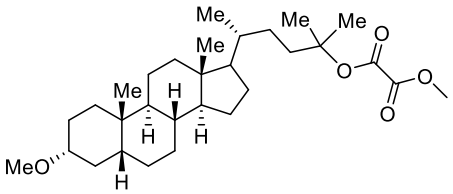
The compound was prepared according to the general procedure using (8R,9S,13S,14S)-3-((7-hydroxy -7-methyloctyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-1 7-one (4.12 g, 10.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (4.23 g, 8.48 mmol) was obtained in in 85 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.5 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.64 (s, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 2.88 (m, 2H), 2.50 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.39 (m, 1H), 2.24 (m, 1H), 2.14 (m, 1H), 2.03 (m, 2H), 1.95 (m, 1H), 1.83 (m, 2H), 1.75 (m, 2H), 1.61 (m, 2H), 1.53 (s, 6H), 1.46 (m, 6H), 1.37 (br, 4H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 220.9, 159.0, 157.1, 156.7, 137.7, 131.8, 126.3, 114.5, 112.1, 87.3, 67.7, 53.2, 50.4, 48.0, 44.0, 40.3, 38.4, 35.8, 31.6, 29.6, 29.5, 29.2, 26.5, 25.9, 25.9, 25.6, 23.7, 21.6, 13.8.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{30}H_{42}NaO_6$: 521.2874. Found: 521.2867.

M.P. 94-95 ℃



(5R)-5-((3R,5R,8R,9S,10S,13R,14S)-3-Methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-methylhexan-2-yl 2-(methylperoxy)-2-oxoacetate

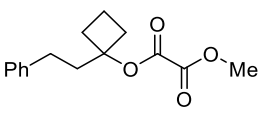
The compound was prepared according to the general procedure using (5R)-5-((3R,5R,8R,9S,10S,13R,14S)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-methylhexan-2-ol (3.24 g, 8.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (3.45 g, 7.03 mmol) was obtained in 88 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.34 (s, 3H), 3.15 (m, 1H), 1.94 m, 1H), 1.84 (m, 4H), 1.71 (m, 3H), 1.57 (m, 2H), 1.51 (s, 3H), 1.51 (s, 3H), 1.37 (m, 7H), 1.23 (m, 4H), 1.10 (m, 4H), 1.02 (m, 2H), 0.92 (m, 7H), 0.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.7, 87.7, 80.4, 56.4, 55.7, 55.5, 53.2, 42.7, 42.0, 40.3, 40.1, 36.6, 35.8, 35.7, 35.3, 34.9, 32.8, 29.5, 28.1, 27.3, 26.8, 26.4, 25.8, 25.6, 24.2, 23.4, 20.8, 18.7, 12.0.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{30}H_{50}NaO_5$: 513.3550. Found: 513.3546.

M.P. 87-88 ℃



Methyl (1-phenethylcyclobutyl) oxalate

The compound was prepared according to the general procedure using 1-phenethylcyclobutan-1-ol (3.53 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and

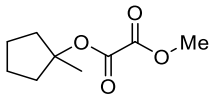
DCM (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (4.73g, 17.8 mmol) was obtained in 89 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (m, 2H), 7.18 (m, 3H), 3.87 (s, 3H), 2.66 (m, 2H), 2.46 (m, 2H), 2.32 (m, 4H), 1.92 (m, 1H), 1.70 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 156.0, 141.3, 128.4, 128.3, 125.9, 85.8, 53.3, 36.5, 33.5, 29.7, 13.8.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{15}H_{18}NaO_4$: 285.1097. Found: 285.1102.

M.P. 28-29 ℃.



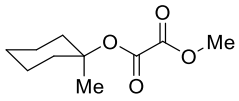
Methyl (1-methylcyclopentyl) oxalate

The compound was prepared according to the general procedure using 1-methylcyclopentan-1-ol (5.01 g, 50.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (7.8 g, 42.2 mmol) was obtained in 84 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.87 (s, 3H), 2.22 (m, 2H), 1.76 (m, 4H), 1.67 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 157.0, 94.2, 53.2, 38.7, 23.8, 23.6.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_9H_{14}NaO_4$: 209.0784. Found: 209.0784.



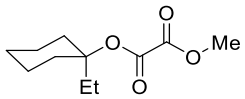
Methyl (1-methylcyclohexyl) oxalate

The compound was prepared according to the general procedure using 1-methylcyclohexan-1-ol (4.56g, 40.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (6.82 g, 34.1 mmol) was obtained in 85 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (s, 3H), 2.20 (m, 2H), 1.52 (m, 10H), 1.29 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.7, 86.7, 53.2, 36.3, 25.1, 25.0, 21.9.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{10}H_{16}NaO_4$: 223.0941. Found: 223.0943.



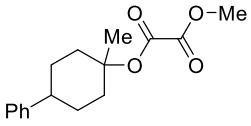
1-Ethylcyclohexyl methyl oxalate

The compound was prepared according to the general procedure using 1-ethylcyclohexan-1-ol (2.56 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (3.52 g, 16.4mmol) was obtained in 82 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (s, 3H), 2.25 (m, 2H), 1.96 (q, *J* = 7.5 Hz, 2H), 1.61 (m, 1H), 1.53 (m, 4H), 1.42 (m, 2H), 1.27 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.6, 89.5, 53.2, 33.8, 29.8, 25.3, 21.7, 7.3.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{11}H_{18}NaO_4$: 237.1097. Found: 237.1102.



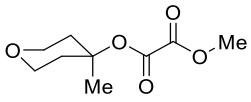
Methyl (1-methyl-4-phenylcyclohexyl) oxalate

The compound was prepared according to the general procedure using 1-methyl-4-phenylcyclohexan-1-ol (3.81 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (4.25 g, 15.4 mmol) was obtained in 77 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.7 Hz, 2H), 7.22 (m, 3H), 3.91 (s, 3H), 2.54 (m, 3H), 1.77 (m, 4H), 1.63 (s, 3H), 1.52 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.7, 146.4, 128.3, 126.7, 126.1, 85.2, 53.2, 43.0, 36.3, 28.9, 25.7.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{11}H_{18}NaO_3$: 221.1148. Found: 221.1173.



Methyl (4-methyltetrahydro-2H-pyran-4-yl) oxalate

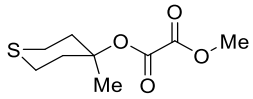
The compound was prepared according to the general procedure using 4-methyltetrahydro-2H-pyran-4-ol (2.32 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl

chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 20), the title compound (3.16 g, 15.6 mmol) was obtained in 78 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.71 (m, 2H), 3.66 (m, 2H), 2.19 (m, 2H), 1.76 (m, 2H), 1.59 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.5, 83.2, 63.5, 53.3, 36.4, 24.7.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_9H_{14}NaO_5$: 225.0733. Found: 225.0735.



Methyl (4-methyltetrahydro-2H-thiopyran-4-yl) oxalate

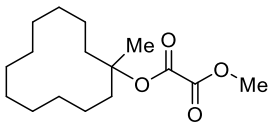
The compound was prepared according to the general procedure using 4-methyltetrahydro-2H-thiopyran-4-ol (2.65 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (3.54 g, 16.2 mmol) was obtained in 81 % yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.88 (s, 3H), 2.88 (t, *J* = 13.0 Hz, 2H), 2.59 (d, *J* = 14.0 Hz, 2H), 2.45 (d, *J* = 14.0 Hz, 2H), 1.78 (t, *J* = 13.0 Hz, 2H), 1.57 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.4, 84.4, 53.4, 37.1, 25.9, 23.9.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_9H_{14}NaO_4S$: 241.0505. Found: 241.0508.

M.P. 41-42 ℃.



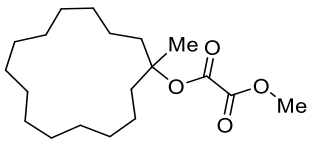
Methyl (1-methylcyclododecyl) oxalate

The compound was prepared according to the general procedure using 1-methylcyclododecan-1-ol (3.97 g, 20.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 50), the title compound (4.59 g, 16.2 mmol) was obtained in 81 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 3H), 2.03 (m, 2H), 1.67 (m, 2H), 1.54 (s, 3H), 1.44 (m, 2H), 1.35 (m, 14H), 1.25 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.6, 90.8, 53.2, 32.8, 26.0, 26.0, 23.8, 22.3, 21.9, 19.3.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{16}H_{28}NaO_4$: 307.1880. Found: 307.1881.



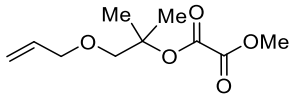
Methyl (1-methylcyclopentadecyl) oxalate

The compound was prepared according to the general procedure using 1-methylcyclopentadecan-1-ol (2.88 g, 12.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and THF (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 25), the title compound (2.9 g, 8.76 mmol) was obtained in 73 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (s, 3H), 1.95 (m, 2H), 1.70 (m, 2H), 1.54 (s, 3H), 1.30 (m, 24H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 156.6, 90.4, 53.1, 36.5, 27.4, 26.9, 26.6, 26.6, 26.2, 24.2, 21.7.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{19}H_{34}NaO_4$: 349.2349. Found: 349.2358.



1-(Allyloxy)-2-methylpropan-2-yl methyl oxalate

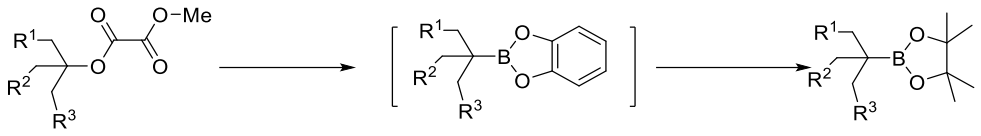
The compound was prepared according to the general procedure using 1-(allyloxy)-2-methylpropan-2-ol (3.90 g, 30.0 mmol), Et_3N (2.0 equiv), DMAP (10 mol %), methyl chlorooxoacetate (1.2 equiv) and DCM (0.1 M). After purification by flash column chromatograph (EA : PE = 1 : 10), the title compound (4.47 g, 20.7 mmol) was obtained in 69 % yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (m, 1H), 5.24 (d, J = 17.2 Hz, 1H), 5.14 (d, J = 10.4 Hz, 1H), 4.00 (d, J = 5.2 Hz, 2H), 3.82 (s, 3H), 3.58 (s, 2H), 1.51 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.5, 134.4, 117.0, 85.5, 74.7, 72.3, 53.2, 23.0.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{10}H_{17}O_5$: 217.1071. Found: 217.1076.

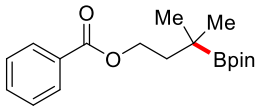
Part 4. Photo-induced Borylation



(1) Photo-induced Borylation of tertiary Alkyl Oxalates.

General Procedure: To a flame-dried tube equipped with a stir bar was charged with tertiary alkyl oxalate (1.0 equiv, 0.3 mmol, if it is a solid), B_2cat_2 (3.0 equiv). The tube was capped with a rubber septum. After being evacuated and backfilled nitrogen for 5 times, DMF (1.2 mL) was added to the tube via a syringe. The reaction mixture was stirred for 15 min at 40 °C followed by addition of alkyl oxalate (1.0 equiv, 0.3 mmol, if it is a liquid) via a syringe. The reaction mixture was stirred under hν 450 nm LED (Blue light) irradiation at 55 °C for 48 h ~72 h **(Note: the internal temperature of the reaction vessel was determined to be 55 °C during the course of photo-irradiation)**. After the reaction was completed, pinacol (4.0 equiv) dissolved in Et_3N (1.0 mL) was added via a syringe. The resultant mixture was stirred for additional 1 h, after which point, the reaction mixture was partitioned between EtOAc and water. The organic layer was collected and washed with an aqueous solution of NH_4Cl, which was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatograph to give the target compound.

Note: The reaction is highly sensitive to moisture and residual O_2. Super dry and air free conditions are crucial for reproducibility.



3-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl benzoate (2).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (89 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1 : 20), the title compound was isolated in 87% yield (83mg, 0.26 mmol) as an off-white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* =8.1, 1.0 Hz, 2H), 7.53 (tt, *J* = 7.5 Hz, 1.2 Hz 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 4.36 (t, *J* = 7.6 Hz, 2H), 1.79 (t, *J* = 7.6 Hz, 2H), 1.22 (s, 12H), 1.03 (s, 6H).

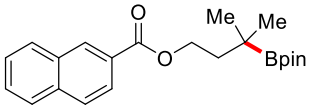
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 132.7, 130.6, 129.5, 128.2, 83.2, 63.6, 39.0, 25.0, 24.6, carbon

attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.65.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{28}BO_4$: 319.2075. Found: 319.2090.

M.P. 63-64.



3-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 2-naphthoate (3).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (104 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1 : 20), the title compound was isolated in 84% yield (92.3 mg, 0.25 mmol) as an off-white solid.

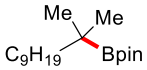
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 4.44 (m, 2H), 1.86 (m, 2H), 1.24 (s, 12H), 1.07 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 135.4, 132.5, 130.9, 129.3, 128.0, 128.0, 127.8, 127.7, 126.5, 125.3, 83.2, 63.8, 39.0, 25.1, 24.6, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.53.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{30}BO_4$: 369.2232. Found: 369.2238.

M.P. 84-85 ℃



4,4,5,5-Tetramethyl-2-(2-methylundecan-2-yl)-1,3,2-dioxaborolane (4).

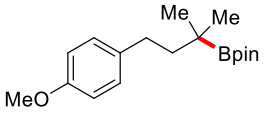
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (82 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 71% yield (62.9 mg, 0.21 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (m, 16H), 1.22 (s, 12H), 0.91 (s, 6H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 41.3, 31.9, 30.5, 29.6, 29.6, 29.3, 26.5, 24.9, 24.7, 22.7, 14.1, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.67.

MS (EI) m/z [M^+]) calcd for $C_{18}H_{38}BO_2$: 297. Found: 297 [M^+], 282 [M-15]$^+$.



2-(4-(4-Methoxyphenyl)-2-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (85 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 60% yield (54.3 mg, 0.18 mmol) as a yellow solid.

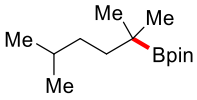
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 2.51 (m, 2H), 1.56 (m, 2H), 1.26 (s, 12H), 1.00 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 135.7, 129.1, 113.7, 83.0, 55.2, 43.8, 32.1, 24.8, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.78.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{30}BO_3$: 305.2283. Found: 305.2279.

M.P. 56-57 ℃.



2-(2,5-Dimethylhexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6).

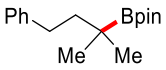
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (65 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 52% yield (37.2 mg, 0.15 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.45 (m, 1H), 1.24 (m, 2H), 1.22 (s, 12H), 1.11 (m, 2H), 0.90 (s, 6H), 0.86 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 39.0, 35.8, 28.8, 24.9, 24.7, 22.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.02.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{14}H_3BO_2$: 241.2333. Found: 241.2208.



4,4,5,5-Tetramethyl-2-(2-methyl-4-phenylbutan-2-yl)-1,3,2-dioxaborolane (7a).

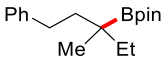
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (75 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 80% yield (66.1 mg, 0.24 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 2.61 (m, 2H), 1.65 (m, 2H), 1.29 (s, 12H), 1.05 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 128.3, 128.2, 125.4, 82.9, 43.5, 33.1, 24.8, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.99.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{17}H_{28}BO_2$: 275.2177. Found: 275.2179.



4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane (7b).

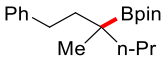
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (80 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 58% yield (49.7 mg, 0.17 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 2.59 (td, *J* = 13.0, 4.7 Hz, 1H), 2.52 (td, *J* = 13.0, 4.7 Hz, 1H), 1.71 (td, *J* = 13.0, 4.7 Hz, 1H), 1.50 (m, 2H), 1.30 (m, 1H), 1.27 (s, 12H), 0.99 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 128.3, 128.2, 125.4, 83.0, 41.4, 32.4, 31.4, 24.9, 24.8, 20.8, 10.0, carbon attached to boron not observed..

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.04.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{30}BO_2$: 289.2333. Found: 289.2335.



4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane (7c).

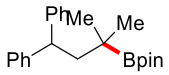
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (84 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 41% yield (39.2 mg, 0.12 mmol) as an off-white oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 2.61 (td, *J* = 13.0, 4.7 Hz, 1H), 2.55 (td, *J* = 13.0, 4.7 Hz, 1H), 1.74 (td, *J* = 13.0, 4.7 Hz, 1H), 1.51 (m, 1H), 1.46 (m, 1H), 1.36 (m, 3H), 1.28 (s, 12H), 1.02 (s, 3H), 0.93 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 128.3, 128.2, 125.4, 83.0, 41.7, 41.6, 32.4, 24.9, 24.8, 21.3, 18.9, 15.1, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.02.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{32}BO_2$: 303.2490. Found: 303.2353.



4,4,5,5-Tetramethyl-2-(2-methyl-4,4-diphenylbutan-2-yl)-1,3,2-dioxaborolane (8).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (98 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 60% yield (63.4 mg, 0.18 mmol) as a yellow solid.

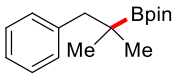
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.5 Hz, 4H), 7.24 (t, *J* = 7.5 Hz, 4H), 7.13 (t, *J* = 7.4 Hz, 2H), 4.06 (t, *J* = 6.7 Hz, 1H), 2.20 (d, *J* = 6.7 Hz, 2H), 1.12 (s, 12H), 0.90 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 128.3, 128.0, 125.8, 82.9, 49.7, 46.6, 25.8, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.72.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{23}H_{32}BO_2$: 351.2490. Found: 351.2494.

M.P. 55-56 ℃



4,4,5,5-Tetramethyl-2-(2-methyl-1-phenylpropan-2-yl)-1,3,2-dioxaborolane (9a).

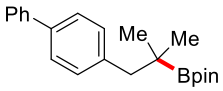
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (71 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 83% yield (64.5 mg, 0.25 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (m, 4H), 7.18 (m, 1H), 2.64 (s, 2H), 1.23 (s, 12H), 0.98 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 130.1, 127.6, 125.6, 83.0, 46.3, 24.7, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.78

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{16}H_{26}BO_2$: 261.2020. Found: 261.2024.



2-(1-([1,1'-Biphenyl]-4-yl)-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (94 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 71% yield (71.9 mg, 0.21 mmol) as a white solid.

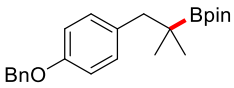
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.68 (s, 2H), 1.24 (s, 12H), 1.00 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 139.7, 138.5, 130.6, 128.6, 126.9, 126.9, 126.3, 83.1, 46.0, 24.8, 24.8, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.05.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{30}BO_2$: 337.2333. Found: 337.2329.

M.P. 102-103 ℃



2-(1-(4-(Benzyloxy)phenyl)-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9c).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (103 mg,0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 15), the title compound was isolated in 75% yield (82.2 mg, 0.22 mmol) as an off-white solid.

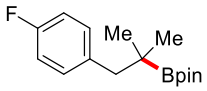
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.05 (s, 2H), 2.58 (s, 2H), 1.23 (s, 12H), 0.96 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 137.3, 132.9, 131.1, 128.5, 127.8, 127.4, 114.0, 83.0, 69.9, 45.5, 24.7, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.73

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{23}H_{32}BO_3$: 367.2443. Found: 367.2448.

M.P. 76-78 ℃



2-(1-(4-Fluorophenyl)-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9d).

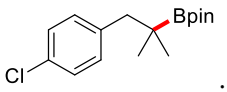
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (77 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 74% yield (62 mg, 0.22 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.4 Hz, 5.7 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 2.58 (s, 2H), 1.20 (s, 12H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1 (d, *J* = 243.2 Hz), 136.1(d, *J* = 3.2 Hz), 131.5(d, *J* = 7.7 Hz), 114.3(d, *J* = 20.8 Hz), 83.1, 45.5, 24.7, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.66.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{16}H_{25}BFO_2$: 279.1926. Found: 279.1925.



2-(1-(4-Chlorophenyl)-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9e).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate

(82 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 66% yield (57.9 mg, 0.20 mmol) as an off-white solid.

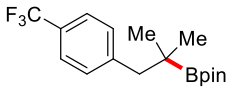
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 2H), 1.21 (s, 12H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 131.5, 131.4, 127.7, 83.2, 45.6, 24.7, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.61

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{16}H_{25}BClO_2$: 295.1631. Found: 295.1634.

M.P. 41-43 ℃.



4,4,5,5-Tetramethyl-2-(2-methyl-1-(4-(trifluoromethyl)phenyl)propan-2-yl)-1,3,2-dioxaborolane (9f).

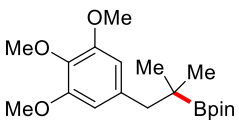
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (92 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 82% yield (80.4 mg, 0.24 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.67 (s, 2H), 1.21 (s, 12H), 0.95 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 130.4, 128.1 (q, *J* = 32.1), 125.4 (q, *J* = 271.5), 124.5 (q, *J* = 3.5), 83.3, 46.1, 24.7, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.65.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{17}H_{25}BF_3O_2$: 329.1894. Found: 329.1901.



4,4,5,5-Tetramethyl-2-(2-methyl-1-(3,4,5-trimethoxyphenyl)propan-2-yl)-1,3,2-dioxaborolane (10).

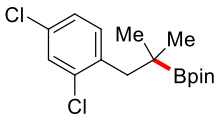
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (99 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 15), the title compound was isolated in 72% yield (76 mg, 0.22 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.43 (s, 2H), 3.83 (s, 6H), 3.80 (s, 3H), 2.55 (s, 2H), 1.19 (s, 12H), 0.96 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 136.1, 107.3, 83.0, 60.8, 56.0, 46.7, 24.9, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.71.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{32}BO_5$: 351.2340. Found: 351.2349



2-(1-(2,4-Dichlorophenyl)-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (92 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 74% yield (72.6 mg, 0.22 mmol) as a white solid.

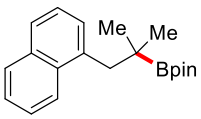
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.1 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.12 (dd, *J* = 8.3, 2.1 Hz, 1H), 2.78 (s, 2H), 1.23 (s, 12H), 0.97 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 135.7, 132.4, 131.8, 129.1, 126.3, 83.3, 41.0, 24.7, 24.4, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.71.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{16}H_{24}BCl_2O_2$: 329.1241. Found: 329.1243.

M.P. 63-64 ℃



4,4,5,5-Tetramethyl-2-(2-methyl-1-(naphthalen-1-yl)propan-2-yl)-1,3,2-dioxaborolane (12).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate

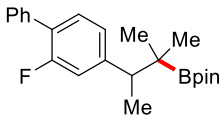
(87 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 52% yield (48.7 mg, 0.16 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.41 (t, *J* = 8.1 Hz, 1H), 3.19 (s, 2H), 1.21 (s, 12H), 1.07 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 133.8, 133.1, 128.5, 127.6, 126.4, 125.1, 125.1, 125.0, 125.0, 83.1, 41.1, 25.4, 24.7, carbon attached to boron not observed..

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.95.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{20}H_{28}BO_2$: 311.2177. Found: 311.2182.



2-(3-(2-Fluoro-[1,1'-biphenyl]-4-yl)-2-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (105 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 285 mg, 4 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 53% yield (59.2 mg, 0.16 mmol) as a white solid.

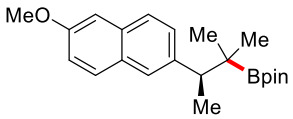
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.05 (m, 2H), 2.88 (q, *J* = 7.2 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.26 (s, 6H), 1.24 (s, 6H), 0.92 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0 (d, *J* = 246.5 Hz), 146.8 (d, *J* = 6.9 Hz), 136.0, 129.4 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 2.4 Hz), 128.3, 127.3, 126.2 (d, *J* = 13.4 Hz), 125.1 (d, *J* = 2.9 Hz), 116.5 (d, *J* = 22.3 Hz), 83.1, 46.0, 24.8, 24.6, 23.4, 20.8, 17.1, carbon attached to boron not observed..

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.35.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{23}H_{31}BFO_2$: 369.2396. Found: 369.2399.

M.P. 58-59 ℃



(R)-2-(3-(6-Methoxynaphthalen-2-yl)-2-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (100 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 4 equiv). After purification by flash column chromatograph (EA : PE = 1: 15), the title compound was isolated in 45% yield (48.0 mg, 0.14 mmol) as a yellow solid.

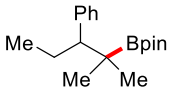
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.11 (m, 2H), 3.91 (s, 3H), 2.99 (q, *J* = 7.1 Hz, 1H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.24 (s, 6H), 1.22 (s, 6H), 0.92 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 140.1, 133.0, 129.1, 128.6, 128.5, 127.1, 125.5, 118.3, 105.4, 82.9, 55.3, 46.2, 24.8, 24.6, 23.5, 20.7, 17.4, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.60

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{32}BO_3$: 355.2439. Found: 355.2444.

M.P. 65-66 ℃



4,4,5,5-Tetramethyl-2-(2-methyl-3-phenylpentan-2-yl)-1,3,2-dioxaborolane (15).

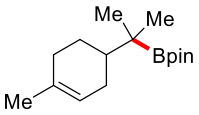
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (80 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 38% yield (33.0 mg, 0.11 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.2 Hz, 2H), 7.17 (m, 3H), 2.53 (dd, *J* = 11.9, 3.0 Hz, 1H), 1.82 (m, 1H), 1.63 (m, 1H), 1.24 (s, 6H), 1.20 (s, 6H), 0.87 (s, 3H), 0.80 (s, 3H), 0.70 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 129.8, 127.4, 125.7, 82.9, 54.9, 24.8, 24.7, 24.5, 23.9, 20.6, 13.1, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.70.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{30}BO_2$: 289.2333. Found: 289.2336.



4,4,5,5-Tetramethyl-2-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)-1,3,2-dioxaborolane (16).

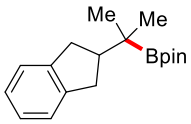
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (73 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4.5 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 43% yield (34.1 mg, 0.13 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.37 (br, 1H), 1.92 (m, 2H), 1.82 (m, 1H), 1.72 (m, 1H), 1.62 (s, 3H), 1.41 (m, 1H), 1.26 (m, 2H), 1.22 (s, 6H), 1.22 (s, 6H), 0.91 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.7, 121.4, 82.7, 41.7, 31.4, 27.6, 25.5, 24.7, 24.7, 23.4, 22.0, 21.8, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.94.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{16}H_{30}BO_2$: 265.2333. Found: 265.2337.



2-(2-(2,3-Dihydro-1H-inden-2-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17).

This compound was prepared according to the general procedure using tertiary alkyl oxalate (80 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 71% yield (61 mg, 0.21 mmol) as a white solid.

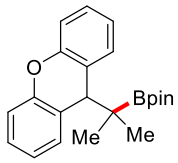
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.11 (dd, *J* = 5.5, 3.2 Hz, 2H), 2.92 (dd, *J* = 15.3, 8.4 Hz, 2H), 2.83 (dd, *J* = 15.4, 9.9 Hz, 2H), 2.41 (m, 1H), 1.22 (s, 12H), 1.01 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 125.8, 124.2, 82.9, 48.9, 35.3, 24.7, 23.1, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.69.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{28}BO_2$: 287.2177. Found: 287.2175.

M.P. 94-95 ℃



2-(2-(9H-xanthen-9-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (99 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4 equiv). After purification by flash column chromatograph (EA : PE = 1: 15), the title compound was isolated in 30% yield (32.2 mg, 0.09 mmol) as a white solid.

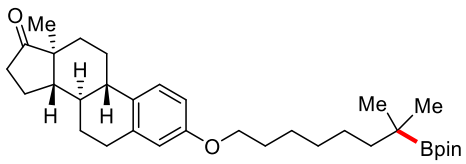
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 2H), 4.09 (s, 1H), 1.26 (s, 12H), 0.77 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 130.0, 127.4, 124.4, 122.5, 116.1, 83.4, 45.7, 24.8, 21.0, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.53.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{22}H_{28}BO_3$: 351.2126. Found: 351.2124.

M.P. 48-49 ℃



(8R,9S,13S,14S)-13-methyl-3-((7-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (19).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (152 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 10), the title compound was isolated in 58% yield (91 mg, 0.17 mmol) as a white solid.

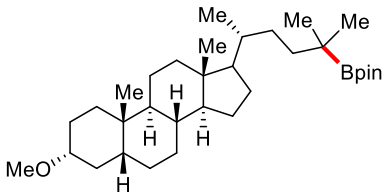
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 1H), 6.71 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.64 (s, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.89 (m, 2H), 2.50 (dd, *J* = 18.9, 9.0 Hz, 1H), 2.39 (m, 1H), 2.24 (m, 1H), 2.13 (dd, *J* = 18.9, 9.0 Hz, 1H), 2.02 (m, 2H), 1.95 (m, 1H), 1.75 (m, 2H), 1.61 (m, 2H), 1.50 (m, 3H), 1.44 (m, 3H), 1.33 (m, 2H), 1.26 (br, 4H), 1.22 (s, 12H), 0.91 (s, 6H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 220.9, 157.1, 137.6, 131.7, 126.2, 114.5, 112.1, 82.8, 67.9, 50.4, 48.0, 44.0, 41.1, 38.4, 35.8, 31.6, 30.2, 29.6, 29.3, 26.5, 26.3, 26.0, 25.9, 24.9, 24.7, 21.6, 13.8, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.20.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{33}H_{52}BO_4$: 523.3953. Found: 523.3934.

M.P. 104-105 ℃



2-((5R)-5-((3R,5R,8R,9S,10S,13R,14S)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-methylhexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (149 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 65% yield (101 mg, 0.20 mmol) as an off-white solid.

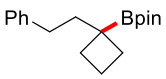
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.31 (s, 3H), 3.12 (m, 1H), 1.92 (m, 1H), 1.80 (m, 3H), 1.72 (m, 1H), 1.66 (m, 1H), 1.53 (m, 2H), 1.31 (m, 12H), 1.19 (s, 12H), 1.01 (m, 8H), 0.87 (m, 12H), 0.59 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 80.4, 56.4, 56.0, 55.4, 42.6, 42.0, 40.3, 40.1, 37.5, 36.3, 35.8, 35.3, 34.8, 32.7, 32.6, 28.2, 27.3, 26.7, 26.4, 25.1, 24.8, 24.7, 24.7, 24.2, 23.4, 20.7, 18.7, 11.9, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.72.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{33}H_{60}BO_3$: 515.4630. Found: 515.4632.

M.P. 86-87 ℃



4,4,5,5-Tetramethyl-2-(1-phenethylcyclobutyl)-1,3,2-dioxaborolane (21).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (79 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column

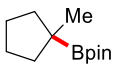
chromatograph (EA : PE = 1: 20), the title compound was isolated in 87% yield (75 mg, 0.26 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.23 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 2.54 (m, 2H), 2.22 (m, 2H), 1.98 (m, 2H), 1.92 (m, 2H), 1.79 (m, 2H), 1.33 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 128.3, 128.2, 125.4, 83.0, 42.0, 33.2, 30.2, 24.7, 18.2, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.00.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{28}BO_2$: 287.2177. Found: 287.2172.



4,4,5,5-Tetramethyl-2-(1-methylcyclopentyl)-1,3,2-dioxaborolane (22).

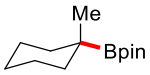
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (56.5 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 63% yield (40 mg, 0.19 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.77 (m, 2H), 1.65 (m, 2H), 1.55 (m, 2H), 1.25 (m, 2H), 1.22 (m, 12H), 0.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 37.0, 25.2, 24.6, 23.4, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.16.

MS (EI) m/z [M$^+$]) calcd for $C_{12}H_{23}BO_2$: 210. Found: 210 [M$^+$], 195 [M-15]$^+$.



4,4,5,5-Tetramethyl-2-(1-methylcyclohexyl)-1,3,2-dioxaborolane (23).

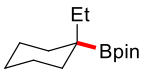
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (60 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 71% yield (48 mg, 0.21 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.82 (d, *J* = 12.8 Hz, 2H), 1.62 (m, 4H), 1.30 (m, 1H), 1.24 (s, 12H), 1.12 (m, 1H), 0.90 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 37.0, 26.4, 25.9, 25.5, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.98.

MS (EI) m/z [M^+]) calcd for $C_{13}H_{25}BO_2$: 224. Found: 224 [M^+], 209 [M-15]$^+$.



2-(1-Ethylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24).

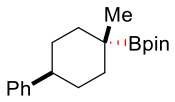
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (65 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 39% yield (28 mg, 0.12 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.87 (d, *J* = 12.9 Hz, 2H), 1.61 (m, 4H), 1.29 (m, 3H), 1.25 (s, 12H), 1.12 (m, 1H), 0.87 (m, 2H), 0.83 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 35.0, 33.3, 26.8, 25.3, 24.9, 9.9, carbon attached to boron not observed..

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.96.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{14}H_{28}BO_2$: 239.2177. Found: 239.2250.



Cis-4,4,5,5-tetramethyl-2-(1-methyl-4-phenylcyclohexyl)-1,3,2-dioxaborolane (25).

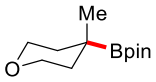
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (84 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 54% (cis / syn = 4.4: 1) yield (49 mg, 0.16 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.19 (m, 3H), 2.46 (m, 1H), 1.91 (m, 1H), 1.69 (m, 5H), 1.54 (m, 2H), 1.25 (m, 12H), 1.08 (s, 2.40H, cis), 0.96 (s, 0.55H, syn).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 128.2, 126.8, 125.7, 82.8, 44.1, 32.9, 28.0, 24.6, 18.6, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.66.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{30}BO_2$: 301.2333. Found: 301.2336.



4-Methyl-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)tetrahydro-2H-pyran (26).

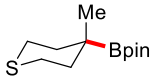
This compound was prepared according to the general procedure using according tertiary alkyl oxalate (61 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 285.4 mg, 4.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 15), the title compound was isolated in 59% yield (40 mg, 0.18 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (ddd, *J* = 6.4, 3.5, 2.4 Hz, 2H), 3.38 (td, *J* = 11.8, 2.0 Hz, 2H), 1.75 (dd, *J* = 13.1, 1.8 Hz, 2H), 1.28 (m, 2H), 1.24 (s, 12H), 0.95 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.2, 67.4, 36.7, 25.5, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.76.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{12}H_{24}BO_3$: 227.1813. Found: 227.1819.



4,4,5,5-Tetramethyl-2-(4-methyltetrahydro-2H-thiopyran-4-yl)-1,3,2-dioxaborolane (27).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (67 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 285.4 mg, 4.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 15), the title compound was isolated in 46% yield (34 mg, 0.14 mmol) as a white solid.

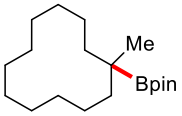
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.69 (m, 2H), 2.51 (m, 2H), 2.09 (m, 2H), 1.30 (m, 2H), 1.23 (s, 12H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.1, 37.4, 27.5, 26.1, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.57.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{12}H_{24}BO_2S$: 243.1585. Found: 243.1585.

M.P. 62-63 ℃.



4,4,5,5-Tetramethyl-2-(1-methylcyclododecyl)-1,3,2-dioxaborolane (28).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (87 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.35 mmol, 322 mg, 4.5 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 43% yield (40 mg, 0.13 mmol) as a white solid.

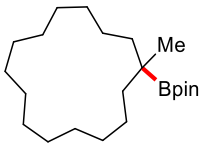
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.36 (m, 22H), 1.22 (s, 12H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 30.8, 26.8, 26.3, 24.7, 22.6, 22.5, 22.1, 19.2, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.01.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{38}BO_2$: 309.2959. Found: 309.2984.

M.P. 82-83 ℃



4,4,5,5-Tetramethyl-2-(1-methylcyclopentadecyl)-1,3,2-dioxaborolane (29).

This compound was prepared according to the general procedure using according tertiary alkyl oxalate (100 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.35 mmol, 322 mg, 4.5 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 67% yield (70 mg, 0.20 mmol) as an off-white oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.43 (m, 2H), 1.28 (m, 26H), 1.22 (s, 12H), 0.89 (s, 3H).

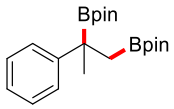
^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 34.9, 28.2, 27.0, 27.0, 26.8, 26.3, 24.7, 22.9, 22.3, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 35.07.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{44}BO_2$: 351.3429. Found: 351.3467.

(2) Borylation of alkenes under thermal conditions.

The tube was capped with a rubber septum. After being evacuated and backfilled nitrogen for 5 times, DMF (1.2 mL) was added to the tube via a syringe. The reaction mixture was stirred for 15 min at 40 ^{o}C followed by addition of alkenes (1.0 equiv, 0.3 mmol, if it is a liquid) via a syringe. The reaction mixture was stirred under at 55 ^{o}C for 32 h. After the reaction was completed, pinacol (4.0 equiv) dissolved in Et_3N (1.0 mL) was added via a syringe. The resultant mixture was stirred for additional 1 h, after which point, the reaction mixture was partitioned between EtOAc and water. The organic layer was collected and washed with an aqueous solution of NH_4Cl, which was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatograph to give the target compound.



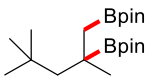
2,2'-(2-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (30).

This compound was prepared according to the general procedure using according alkenes (35.5 mg, 3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 91% yield (101.2 mg, 0.27 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 1.49 (d, *J* = 15.6 Hz, 1H), 1.41 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 1.15 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.12, 127.83, 126.41, 124.76, 83.20, 82.91, 27.28, 25.06, 24.66, 24.64, 24.51, 24.40, 22.05, carbon attached to boron not observed..

HRMS (ESI) m/z ([M+H]$^{+}$) calcd for $C_{21}H_{35}B_2O_4$: 373.2723. Found: 373.2720.



2,2'-(2,4,4-Trimethylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (31).

This compound was prepared according to the general procedure using according alkenes (33.5 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 95 % yield (104 mg, 0.28 mmol)

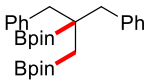
as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.53 (d, *J* = 14.1 Hz, 1H), 1.29 (d, *J* = 14.1 Hz, 1H), 1.21 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.03 (s, 3H), 0.95 (t, *J* = 10.6 Hz, 1H), 0.90 (s, 9H), 0.72 (d, *J* = 15.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.9, 82.6, 54.9, 31.8, 31.5, 25.2, 25.0, 25.0, 25.0, 24.7, 24.4, 21.8, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.59.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{20}H_{41}B_2O_4$: 367.3192. Found: 367.3197.



2,2'-(2-Benzyl-3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (32).

This compound was prepared according to the general procedure using according alkenes (63 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 40% yield (56 mg, 0.12 mmol) as a white solid.

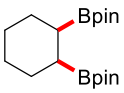
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.1 Hz, 4H), 7.21 (t, *J* = 7.5 Hz, 4H), 7.15 (t, *J* = 7.1 Hz, 2H), 3.00 (d, *J* = 13.2 Hz, 2H), 2.67 (d, *J* = 13.2 Hz, 2H), 1.27 (s, 12H), 1.17 (s, 12H), 0.80 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.91, 130.83, 127.55, 125.60, 83.34, 82.67, 43.73, 25.10, 24.99, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.23.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{28}H_{41}B_2O_4$: 463.3195. Found: 463.3193.

M.P. 96-98 ℃.



***cis*-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (33).[3]**

This compound was prepared according to the general procedure using according alkenes (25 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 96% yield (96 mg, 0.29 mmol)

as a white solid.

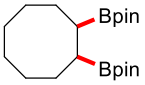
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.61 (br m, 2H), 1.54 (br m, 2H), 1.47 – 1.40 (m, 2H), 1.40 – 1.34 (m, 2H), 1.25 – 1.23 (m, 2H), 1.23 (s, 12H), 1.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 28.1, 26.8, 24.9, 24.8, 23.2, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.08.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{35}B_2O_4$: 337.2722. Found: 337.2728.

M.P. 66-68 ℃.



1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclooctane (34).

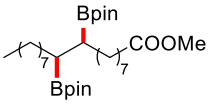
This compound was prepared according to the general procedure using according alkenes (33 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 93% yield (102 mg, 0.28 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.74 – 1.65 (m, 2H), 1.64 – 1.54 (m, 4H), 1.53 – 1.43 (m, 6H), 1.39 – 1.35 (m, 2H), 1.21 (s, 12H), 1.21 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.68, 28.19, 27.66, 26.60, 24.85, 24.77, 21.75, carbon attached to boron not observed..

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.52.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{20}H_{39}B_2O_4$: 365.3029. Found: 365.3034.



Methyl 9,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octadecanoate (35).

This compound was prepared according to the general procedure using according alkenes (90 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (0.9 mmol, 215 mg, 3.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 86% yield (141 mg, 0.26 mmol) as a colorless oil.

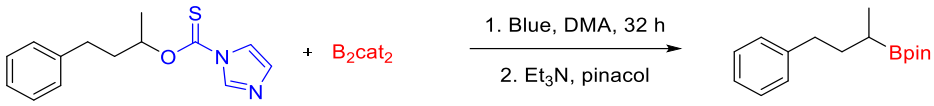
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (s, 3H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.43 – 1.39 (m, 2H), 1.29 – 1.19 (m, 46H), 1.11 – 1.06 (m, 2H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 82.7, 51.4, 34.1, 31.9, 30.8, 30.7, 29.9, 29.7, 29.6, 29.5, 29.2, 29.1, 29.1, 25.8, 25.0, 24.9, 24.8, 22.7, 14.1, carbon attached to boron not observed.

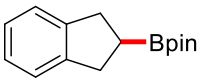
^{11}B NMR (193 MHz, $CDCl_3$) δ 34.50.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{31}H_{61}B_2O_6$: 551.4659. Found: 551.4657.

(3) Photo-induced Borylation of Secondary Imidazole-1-carbothioates



General Procedure-2: To a flame-dried tube equipped with a stir bar was charged with secondary imidazole-1-carbothioates (1.0 equiv, 0.2 mmol, if it is a solid), B_2cat_2 (5.0 equiv). The tube was capped with a rubber septum. After being evacuated and backfilled nitrogen for 5 times, **(Note: The reaction is sensitive to H_2O and O_2)**. DMA (0.6 mL) was added to the tube via a syringe. Secondary imidazole-1-carbothioates (1.0 equiv, 0.2 mmol, if it is a liquid) was added to the reaction mixture via a syringe. The reaction mixture was stirred under hν 450nm LED irradiation at 55 °C for 32 h **(Note: the internal temperature of the reaction vessel was determined to be 55 °C during the course of photo-irradiation)**. After the reaction was completed, pinacol (10.0 equiv) dissolved in Et_3N (1.0 mL) was added via a syringe. The resultant mixture was stirred for additional 1 h, after which point, the reaction mixture was partitioned between EtOAc and water. The organic layer was collected and washed with an aqueous solution of NH_4Cl, which was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatograph to give the target compound.



2-(2,3-Dihydro-1H-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)[4]

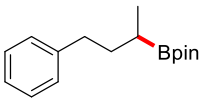
This compound was prepared according to the general procedure-2 using secondary imidazole-1-carbothioates (50 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 43% yield (21.2 mg, 0.087 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.11 (dd, *J* = 5.3, 3.2 Hz, 2H), 3.06 (dd, *J* = 15.3, 9.4 Hz, 2H), 2.97 (dd, *J* = 15.4, 10.3 Hz, 2H), 1.88 (p, *J* = 9.8 Hz, 1H), 1.27 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 125.9, 124.2, 83.2, 35.1, 24.8, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.46.

MS (EI) m/z [M^+]) calcd for $C_{15}H_{21}BO_2$: 244. Found: 244 [M^+], 229 [M-15]$^+$.



4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (37)[5]

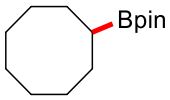
This compound was prepared according to the general procedure-2 using secondary imidazole-1-carbothioates (53 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 46% yield (23.8 mg, 0.091 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 2.74 – 2.64 (m, 2H), 1.89 – 1.82 (m, 1H), 1.69 – 1.62 (m, 1H), 1.32 (s, 12H), 1.15 (dt, *J* = 13.6, 7.0 Hz, 1H), 1.09 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 128.4, 128.2, 125.5, 82.9, 35.3, 35.3, 24.8, 24.7, 16.8, 15.4, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.51.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{16}H_{26}BO_2$: 261.2023. Found: 261.2028.



2-Cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)[5]

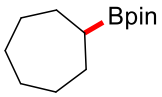
This compound was prepared according to the general procedure using according secondary imidazole-1-carbothioates (48 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 40% yield (18.9 mg, 0.079 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.76 – 1.68 (m, 2H), 1.68 – 1.59 (m, 2H), 1.59 – 1.42 (m, 10H), 1.22 (s, 12H), 1.14 – 1.07 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 27.5, 27.0, 26.8, 26.6, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.54.

MS (EI) m/z ($[M^+]$) calcd for $C_{14}H_{27}BO_2$: 238. Found: 238 ($[M^+]$), 223 $[M-15]^+$.



2-Cycloheptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)[6]

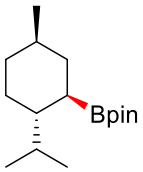
This compound was prepared according to the general procedure-2 using secondary imidazole-1-carbothioates (45 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 38% yield (16.8 mg, 0.075 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.78 – 1.70 (m, 2H), 1.70 – 1.60 (m, 2H), 1.60 – 1.52 (m, 2H), 1.52 – 1.39 (m, 6H), 1.23 (s, 12H), 1.10 – 1.03 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 29.6, 29.0, 28.3, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.61.

MS (EI) m/z [M^+]) calcd for $C_{13}H_{25}BO_2$: 224. Found: 224 [M^+], 209 [M-15]$^+$.



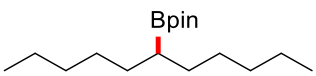
2-((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40)[7]

This compound was prepared according to the general procedure-2 using secondary imidazole-1-carbothioates (54 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 12% yield (6.5 mg, 0.024 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.74 – 1.66 (m, 1H), 1.66 – 1.54 (m, 3H), 1.34 – 1.24 (m, 2H), 1.21 (s, 12H), 0.98 – 0.89 (m, 4H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.81(d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.6, 43.7, 37.2, 35.3, 33.4, 32.0, 25.9, 24.7, 24.6, 22.7, 21.6, 16.5, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.88.



4,4,5,5-Tetramethyl-2-(undecan-6-yl)-1,3,2-dioxaborolane (41)

This compound was prepared according to the general procedure-2 using secondary

imidazole-1-carbothioates (57 mg, 0.2 mmol, 1.0 equiv), B_2cat_2 (1.0 mmol, 238 mg, 5.0 equiv). After purification by flash column chromatograph (EA : PE = 1: 20), the title compound was isolated in 25% yield (14.2 mg, 0.050 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.39 (ddd, *J*=14.0, 11.7, 6.4, 2H), 1.35 – 1.24 (m, 14H), 1.23 (s, 12H), 0.94 (dq, *J*=9.3, 5.5, 1H), 0.86 (t, *J*=6.9, 6H).

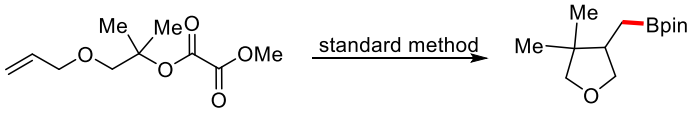
^{13}C NMR (151 MHz, $CDCl_3$) δ 82.6, 43.7, 37.2, 35.3, 32.2, 31.5, 29.0, 24.8, 22.6, 14.0, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.61.

MS (EI) m/z [M^+]) calcd for $C_{17}H_{35}BO_2$: 282. Found: 282 [M^+], 267 [M-15]$^+$.

(4) Cyclization of 44.

2-((4,4-dimethyltetrahydrofuran-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (44).



43 **44**

This compound was prepared according to the general procedure using according tertiary alkyl oxalate **38** (65 mg, 0.3 mmol, 1.0 equiv), B_2cat_2 (1.2 mmol, 285.4 mg, 4.5 equiv). After purification by flash column chromatograph (EA : PE = 1: 10), the title compound **39** was isolated in 51% yield (37 mg, 0.15 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.06 (t, *J* = 8.1 Hz, 1H), 3.54 (d, *J* = 7.9 Hz, 1H), 3.46 (d, *J* = 7.9 Hz, 1H), 3.41 – 3.35 (m, 1H), 2.04 – 1.98 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 0.98 (s, 3H), 0.87 (s, 3H), 0.84 (m, 1H), 0.58 (dd, *J* = 15.4, 11.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.2, 80.9, 74.1, 44.7, 40.8, 24.9, 24.8, 24.7, 24.2, 20.3, carbon attached to boron not observed.

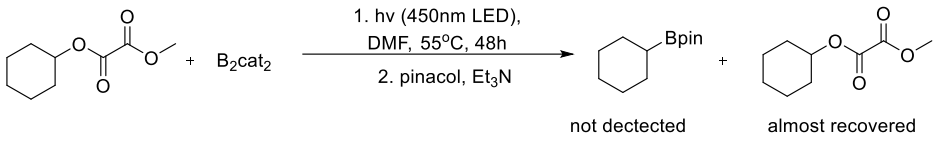
^{11}B NMR (193 MHz, $CDCl_3$) δ 33.92.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{13}H_{26}BO_3$: 241.1972. Found: 241.1979.

(5) Borylation of secondary and primary alkyl methyl oxalates

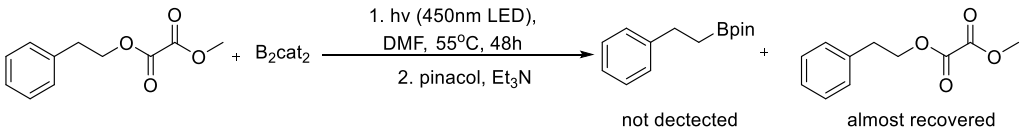
To a flame-dried tube equipped with a stir bar was charged with B_2cat_2 (3.0 equiv). The tube was capped with a rubber septum. After being evacuated and backfilled nitrogen for 5 times, DMF (1.2 mL)

was added to the tube via a syringe. The reaction mixture was stirred for 15 min at 40 °C followed by addition of cyclohexyl methyl oxalate (1.0 equiv, 0.3 mmol,) via a syringe. The reaction mixture was stirred under 450 nm LED (Blue light) irradiation at 55 °C for 48 h. After the reaction was completed, pinacol (4.0 equiv) dissolved in Et_3N (1.0 mL) was added via a syringe. The resultant mixture was stirred for additional 1 h, the resulting mixture was analyzed by ^{11}B NMR and GC-MS, respectively, and the cyclohexyl methyl oxalate was recovered almost completely.



Scheme S2

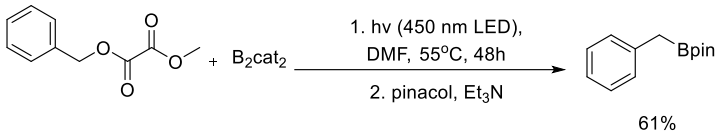
To a flame-dried tube equipped with a stir bar was charged with B_2Cat_2 (3.0 equiv). The tube was capped with a rubber septum. After being evacuated and backfilled nitrogen for 5 times, DMF (1.2 mL) was added to the tube via a syringe. The reaction mixture was stirred for 15 min at 40 °C followed by addition of methyl phenethyl oxalate (1.0 equiv, 0.3 mmol,) via a syringe. The reaction mixture was stirred under 450 nm LED (Blue light) irradiation at 55 °C for 48 h. After the reaction was completed, pinacol (4.0 equiv) dissolved in Et_3N (1.0 mL) was added via a syringe. The resultant mixture was stirred for additional 1 h, the resulting mixture was analyzed by ^{11}B NMR and GC-MS, respectively, and the cyclohexyl methyl oxalate was recover almost completely.



Scheme S3

To a flame-dried tube equipped with a stir bar was charged with B_2Cat_2 (3.0 equiv). The tube was capped with a rubber septum. After being evacuated and backfilled nitrogen for 5 times, DMF (1.2 mL) was added to the tube via a syringe. The reaction mixture was stirred for 15 min at 40 °C followed by addition of methyl phenethyl oxalate (1.0 equiv, 0.3 mmol,) via a syringe. The reaction mixture was

stirred under Blue LED (450nm) irradiation at 55 °C for 48 h. After the reaction was completed, pinacol (4.0 equiv) dissolved in Et_3N (1.0 mL) was added via a syringe. The resultant mixture was stirred for additional 1 h, after which point, the reaction mixture was partitioned between EtOAc and water. The organic layer was collected and washed with an aqueous solution of NH_4Cl, which was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatograph to give the target compound. The title compound was isolated in 61% yield as an off-white oil.



Scheme S4

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 2.30 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 129.0, 128.2, 124.8, 83.4, 24.7, carbon attached to boron not observed.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.05.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{20}BO_2$: 219.1551. Found 219.1557.

II. Mechanistic Investigations

1. ^{11}B NMR Data and ^{13}C NMR measurements

All ^{11}B NMR data was recorded at 0.2 M. See Figure S1 for details of reagents and solvents. Where 1 and B_2cat_2 were mixed, a 1:1.25 ratio was used.

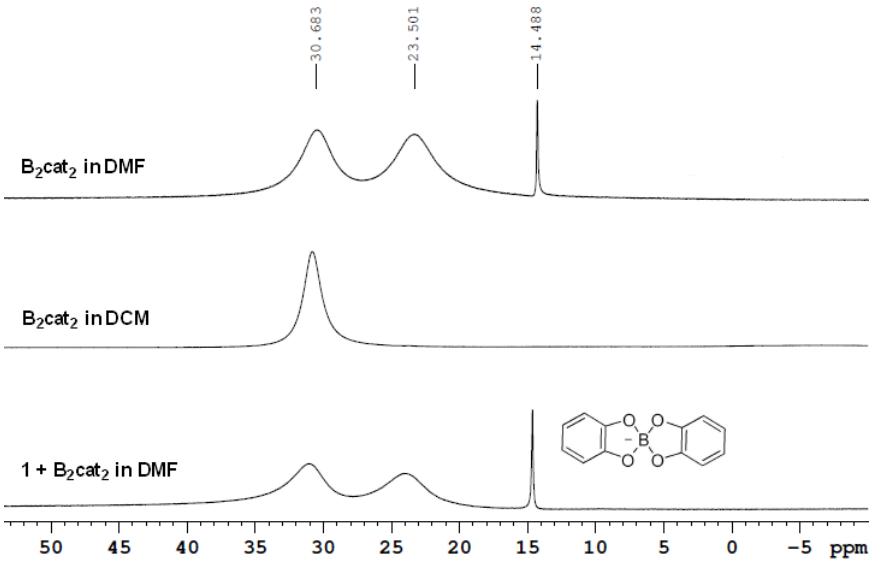


Figure S1. ^{11}B NMR of complexation of 1 with B_2cat_2 in DMF-d^7

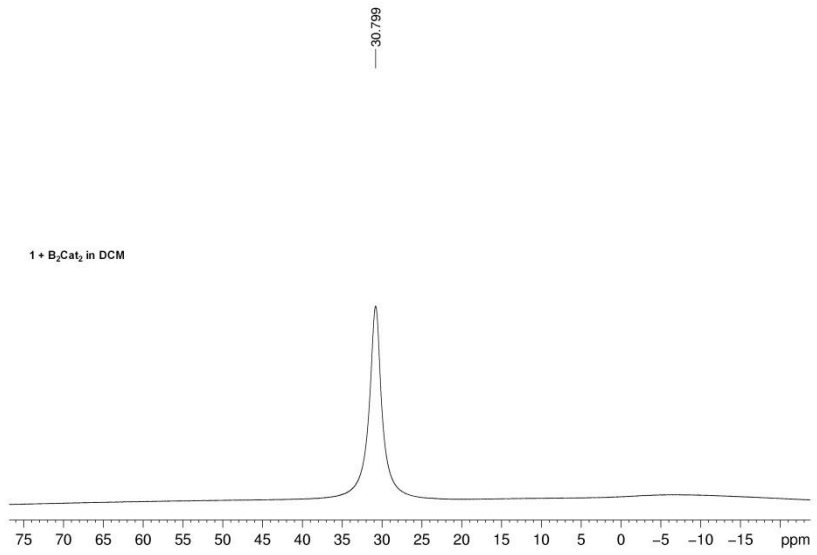


Figure S2. ^{11}B NMR of complexation of **1** with B_2cat_2 in CD_2Cl_2

The chelation of diboron with DMF was confirmed by ^{11}B NMR spectroscopic studies, wherein a diagnostic chemical shift at 23.5 ppm for a solution of B_2cat_2 in DMF corresponds to the complexation of DMF with B_2cat_2 (Figure S1). This interaction is evidenced by a sharp peak at 14.5 ppm, and a

general broadening and lower chemical shift of the largest peak (at 30.7 ppm in DCM and 23.5 ppm in DMF), in the spectra of B_2cat_2 with DMF. The sharp peak at 13.8 ppm is indicative of the $[Bcat_2]^-$ anion, which was confirmed by its independent synthesis.[8] The broadening of the peak at 23.5 ppm is indicative of a rapid interconversion of **1** and B_2cat_2.

Considering B_2cat_2 with DMF versus **1** + B_2cat_2 with DMF in Figure S1, there is almost no difference between the two spectra. This doesn't exclude the possibility of an interaction between B_2cat_2 and **1** since, relatively, there is far more DMF than **1** present. Considering Figure S1 versus Figure S2, there is also no interaction between B_2cat_2 and **1** occurring in DCM since there is no upfield shift or peak broadening. This, also, doesn't necessarily suggest that there is no complex of B_2cat_2 and **1** present in solution, since it could be in very low concentration and thus not detectable. This complex is likely a weak interaction between a carbonyl oxygen of **1** and the boron atoms of B_2cat_2. Whilst any Lewis basic centre could interact with B_2cat_2,[9] only interaction of one of the imide carbonyl oxygens will result in any reaction. [8] ^{13}C NMR of a 1:1.25 mixture of **1** and B_2cat_2 in DMF-d_7 showed that all peaks of **1** were shifted very slightly (0.05ppm, Figure S3)

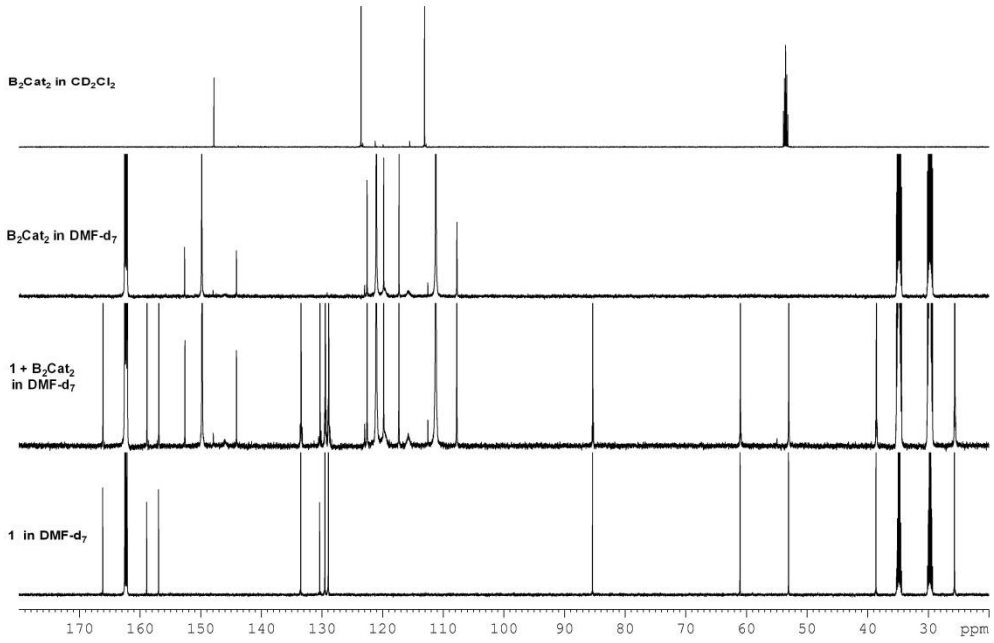


Figure S3. ^{13}C NMR of B_2cat_2 and 1 in DCM or DMF

The use of Blue LED gave a complex reaction mixture containing B_2cat_2, a DMF solvent molecule

bind to the boron centers of B_2cat_2, forming heteroleptic complex (23.5 ppm) and a new product (20.4 ppm). As the reaction time increases, the concentration of heteroleptic complex becomes lower and lower, and the concentration of the new product becomes higher and higher as shown in Figure S4.

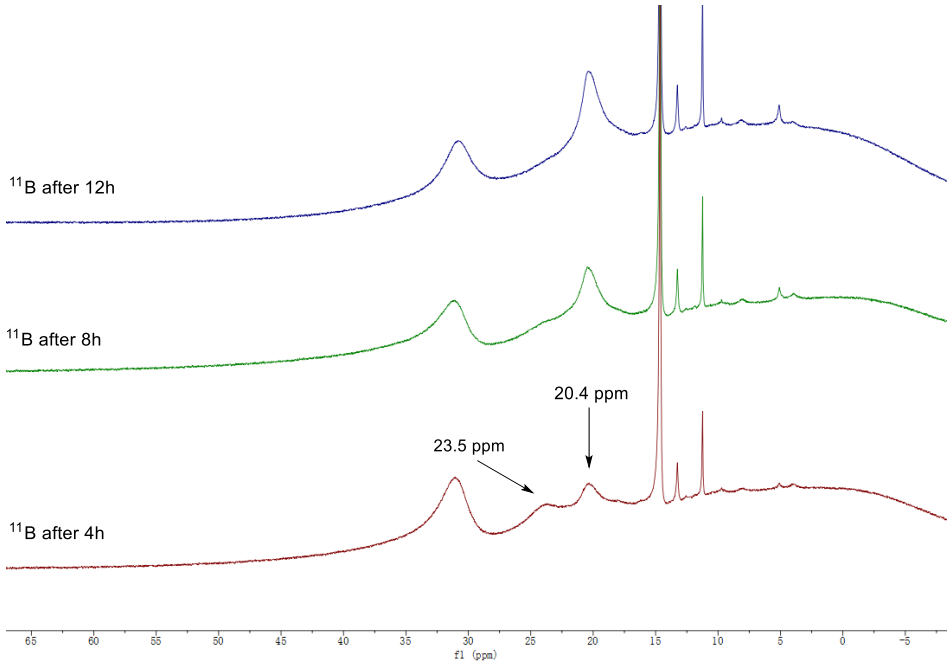
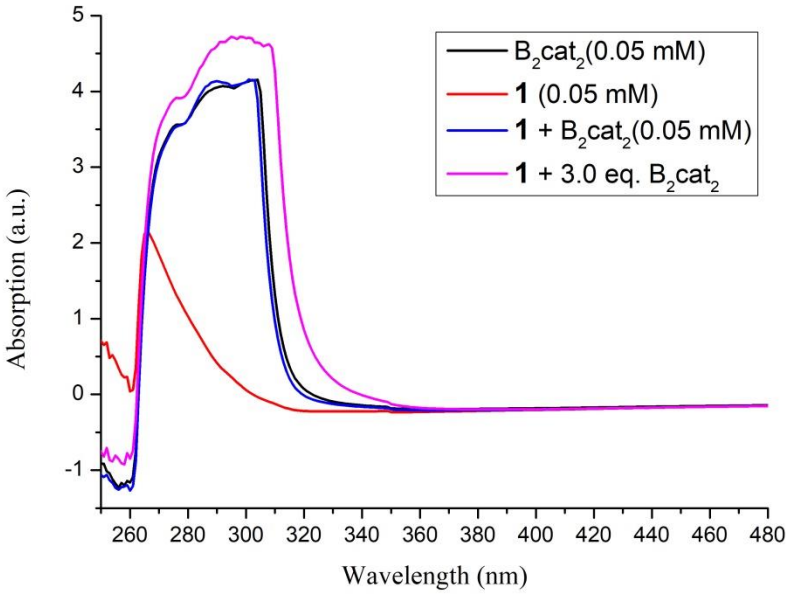


Figure S4. ^{11}B NMR signals showing in synthesis reactions at different time

2. UV-vis absorption spectroscopic measurements

Figure S5 shows the results of measuring the UV-vis. spectrum of B_2cat_2, tertiary alkyl oxalates **1**, and B_2cat_2 and **1** combined, in DMF at 0.05 M with respect to **1**. From these measurements, it is clear that there is a slight blue shift while mixing **1** and B_2cat_2, but not in the separate compounds. UV-vis spectra for oxalate+B_2cat_2 with **1** showed absorption in a region of ~400 nm to <460 nm (Figure S7 in the SI and below), which did provide meaningful information for the complexation of DMF + oxalate 1 + B_2cat_2.



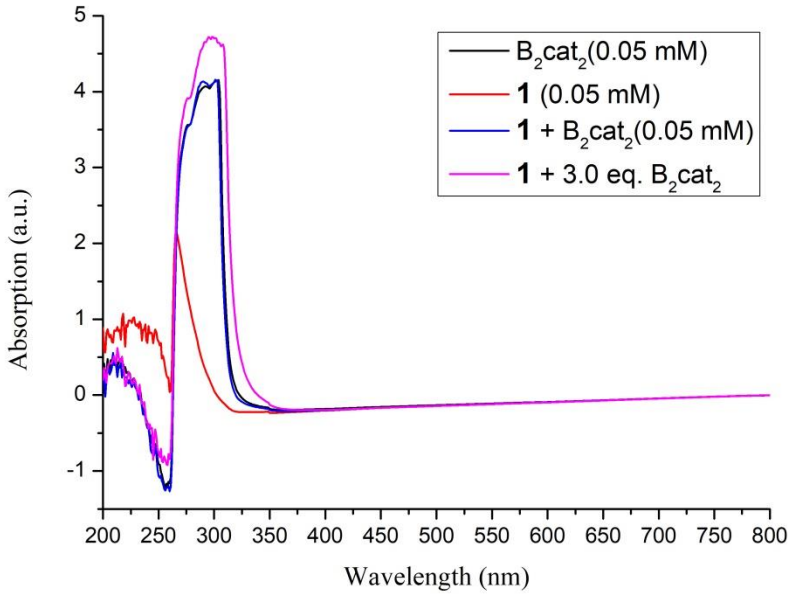


Figure S5. UV/vis absorption spectra of B_2cat_2 (0.05 mM), oxalate 1 (0.05 mM), 1 (0.05 mM) and B_2cat_2 (0.05 mM), and 1 (0.05 mM) and B_2cat_2 (0.15 mM) in DMF.

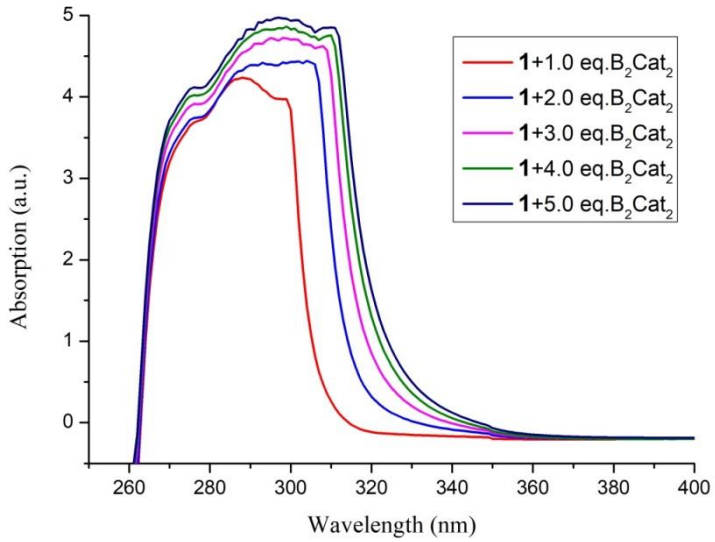


Figure S6. UV/vis absorption spectra from varying the quantity of B_2cat_2 in the presence of 1 (0.05mM).

The concentration of **1** under standard reaction conditions was set as 0.3 M. We carried out UV-vis studies for a set of mixtures of B_2cat_2 with oxalate **1** in a fixed ratio of 3:1 at different concentrations of **1** (0.1, 0.2 and 0.3 M) in DMF. UV-vis spectra showed weak absorption at λ_{max} ~437 nm in the three separate experiments (Figure S7 in the SI and below). It was observed that when the concentration of **1** increases from 0.1 to 0.3 M, the absorption intensity at ~437 nm decreases.

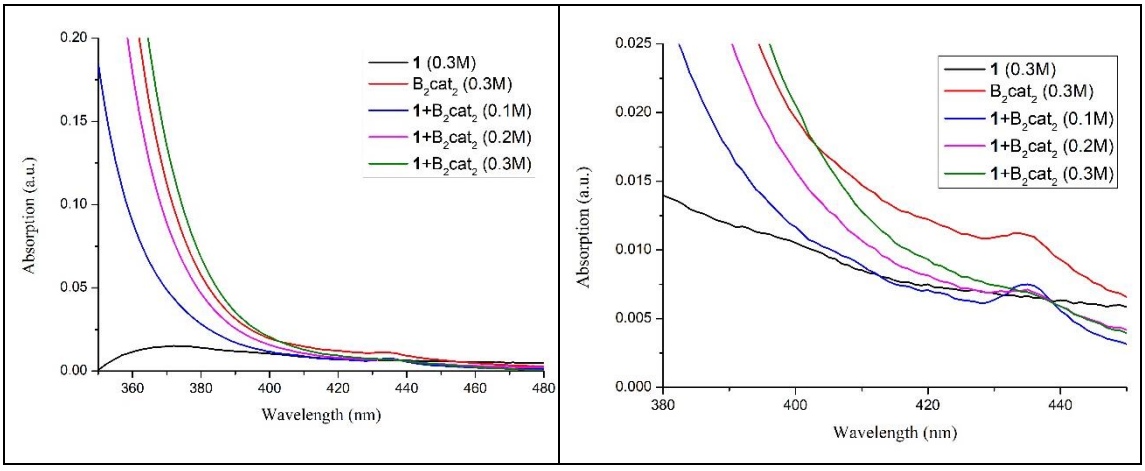


Figure S7. UV/vis absorption spectra of **1** (0.3 M) and B_2Cat_2 (0.3 M) and mixtures of **1** (0.1, 0.2 and 0.3 M) and B_2cat_2 in DMF (**1**: B_2cat_2 = 1:3). Left box: full region; Right box: expanded region.

When the concentration of 1 was fixed at 0.3 M, variation of B2cat2 at 0.6 M and 0.9 M also

showed the absorption peak at λ_{max} ~437 nm (Figure S8 in the SI and below). An independent spectroscopic study of B_2cat_2 (0.3 and 0.9 M in DMF, see the right boxes of Figures S7 and S8) indicated the absorption at ~437 nm arise solely from B_2cat_2 or B_2cat_2/DMF, as a control in DCM did not result in any observable new peaks over the UV ranges of 300-500 nm (Figure S9).

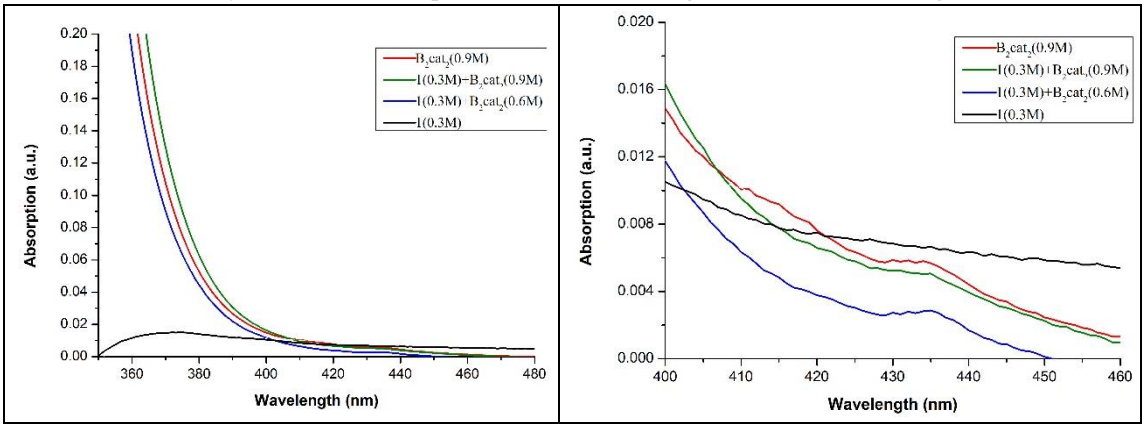


Figure S8. UV/vis absorption spectra B_2Cat_2 (0.9 M) and mixtures of **1** (0.3 M) and B_2cat_2 (0.6 and 0.9 M) in DMF. Left box: full region; Right box: expanded region.

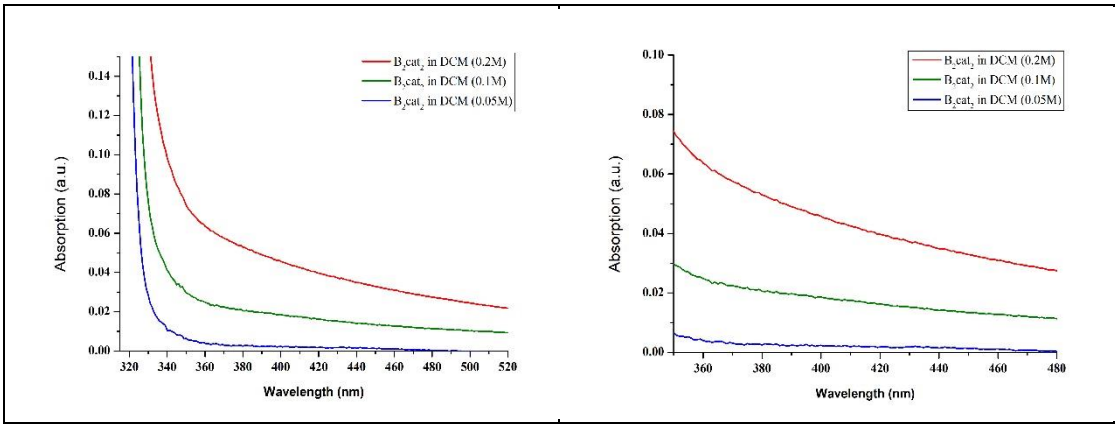
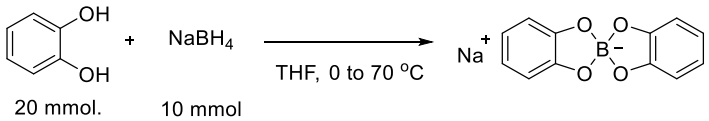


Figure S9. UV/vis absorption spectra for $B_2(cat)_2$ (0.05, 0.1 and 0.2 M) in DCM. Left box: full region; Right box: expanded region.

3. Synthesis and Characterization of NaBcat2 [4a]:



$NaBcat_2$ was synthesised by mixing catechol (2.20 g, 20.0 mmol, 2.0 eq.) and $NaBH_4$ (380 mg, 10.0 mmol, 1.0 eq.) in anhydrous THF (50 mL) at 0 °C for 2 h, room temperature for 1 h and 70°C for 1 h. The solvent was removed under vacuum and the resulting white solid was dissolved in DMF for HRMS and UV/vis absorption spectra analysis.

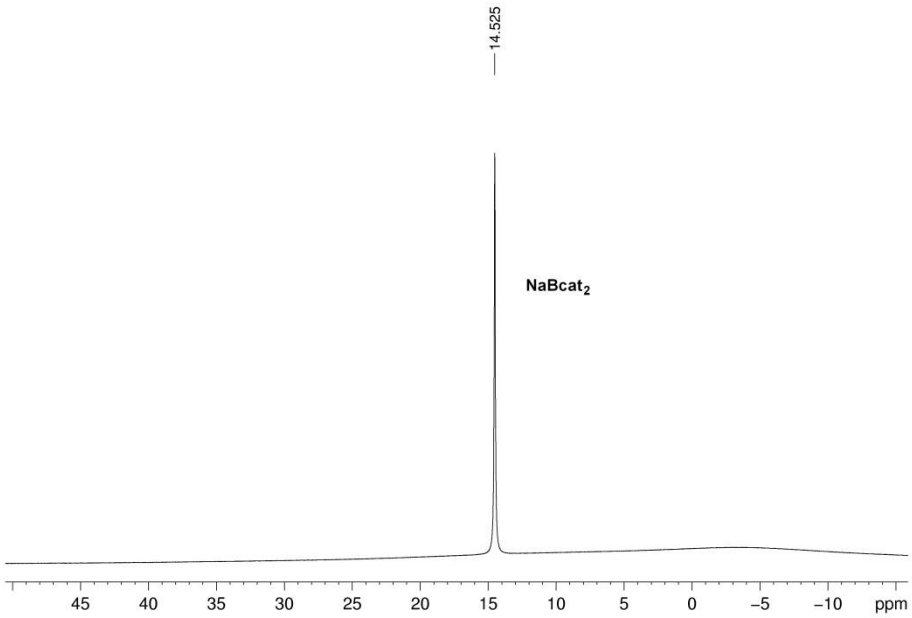


Figure S10. ^{11}B NMR of $NaBcat_2$ in DMF-d^7

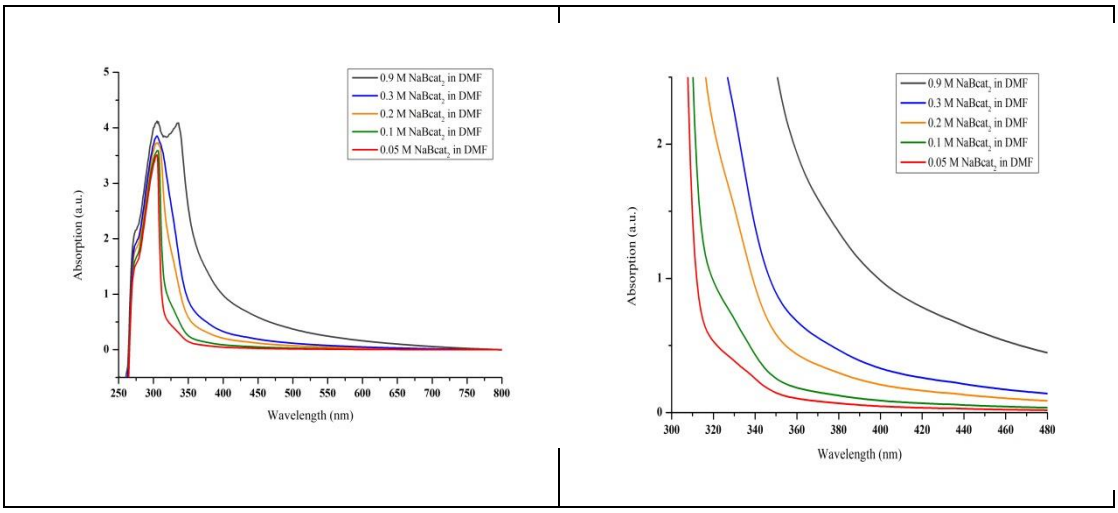


Figure S11. UV/vis absorption spectra from various concentrations of $NaBcat_2$ in DMF. Left box: full region; Right box: expanded region.

4. ESI spectra of $NaBcat_2$ in DMF.

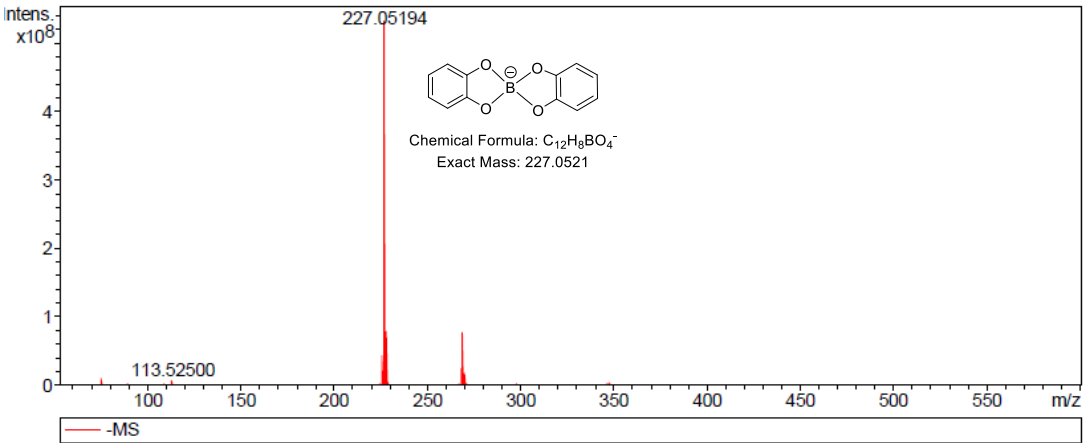


Figure S12. HRMS analysis of $NaBcat_2$ ($^{-}Bcat_2$ Expected Mass: 227.0521, negative mode)

5. ESI spectra of B_2cat_2 in DMF.

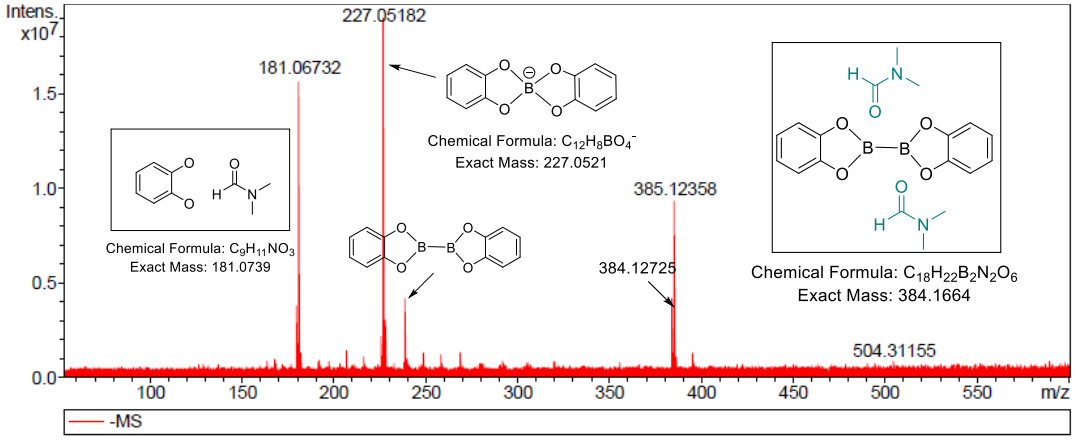


Figure S13. HRMS analysis of B_2cat_2 in DMF (negative mode)

Based on the ^{11}B NMR spectrum of $B_2(cat)_2$ (0.1 M) in DMF (Figure S1), the peak 14.5 ppm was attributed to $(DMF)_2$-$B_2(cat)_2$ complex and $[B(cat)_2]^-$, respectively. The formation of $[B(cat)_2]^-$ was confirmed by ESI-MS (Figure S12) and ^{11}B NMR by comparison with a sample of $NaB(cat)_2$ prepared according to a literature (Figure S10, *Science*, 2017, **357**, 283), wherein the counter cation was not determined. A small mass error between the calculated (384.1664) and experimental mass (384.1273) for $(DMF)_2$-B_2cat_2 was found in Figure S13 (anionic mode of ESI) led us to tentatively reason that $(DMF)_2$-B_2cat_2 complex indeed forms in the solution. It should correspond to the peak at 23.5 ppm in the ^{11}B NMR (Figure S1) and the UV absorption peak at λ_{max} ~437 nm (Figures S7 and S8).

Thus, the collective experiments are in agreement with our mechanistic proposal that highlights formation of a putative $(DMF)_2$-B_2Cat_2 complex. This complex acts as a photosensitizer or initiator, which results in a boryl radical under visible light irradiation. Addition of the boryl radical to the carbonyl oxygen atom within the alkyl oxalates gives a carbon-center radical as shown in our proposed mechanistic cycle in Figure 1 (see the revised manuscript).

6. Calibration of Photoreactor

The emission spectra of the Blue LEDs (450 nm) were recorded on an UV-NIR spectrometer. The spectra was normalised to 1 at the maximum 450 nm.

The emission spectra of the Blue LEDs (405 nm) were recorded on an UV-NIR spectrometer. The spectra was normalised to 1 at the maximum 405 nm.

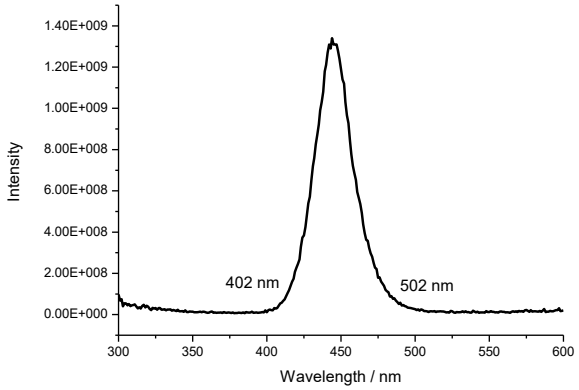


Figure S14. Emission spectrum of 450 nm LEDs

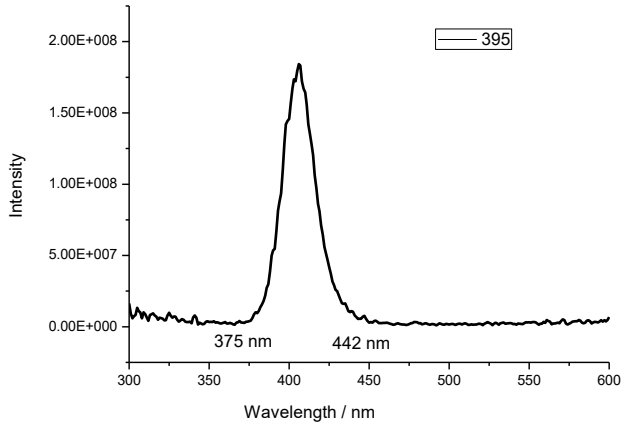
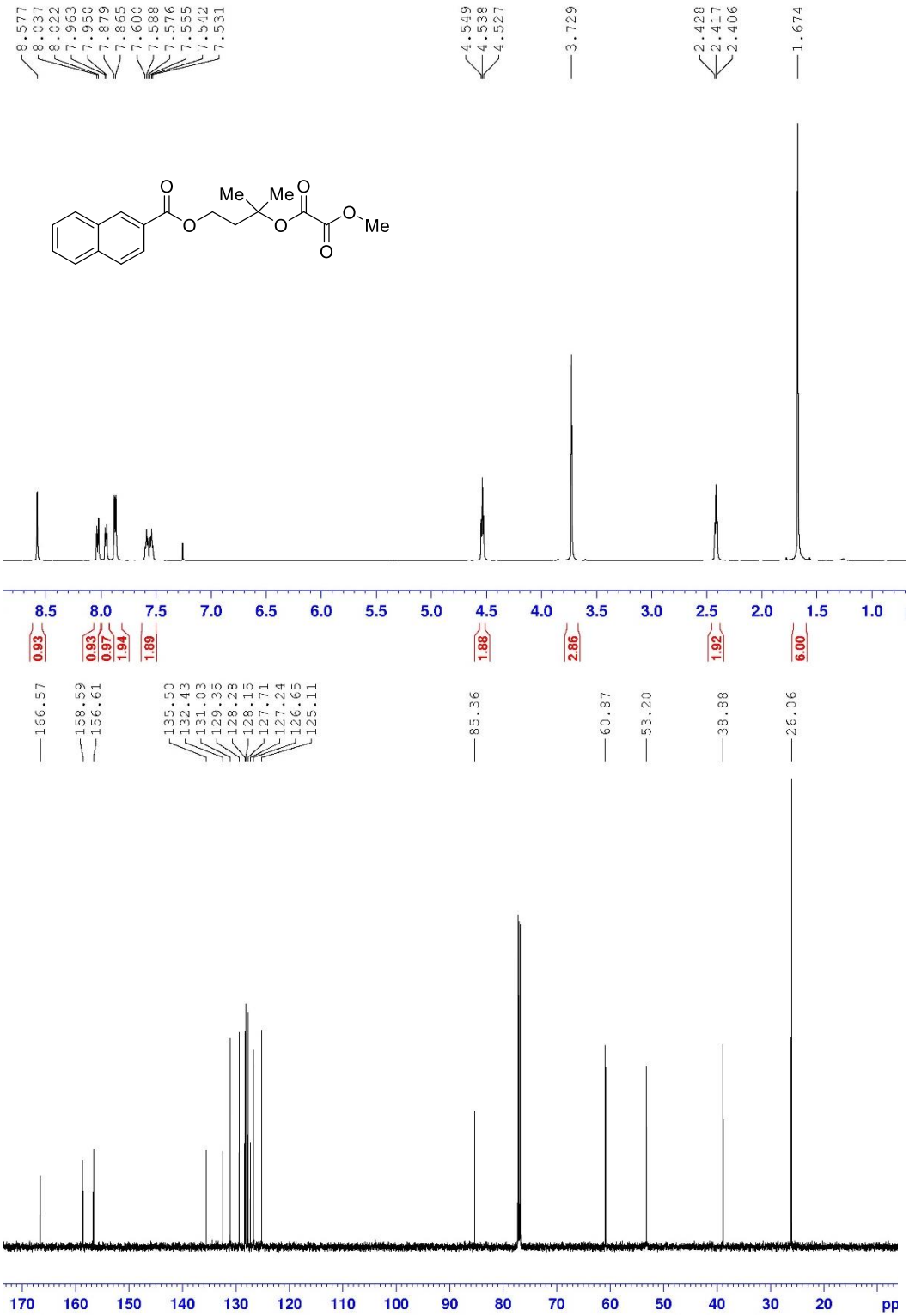
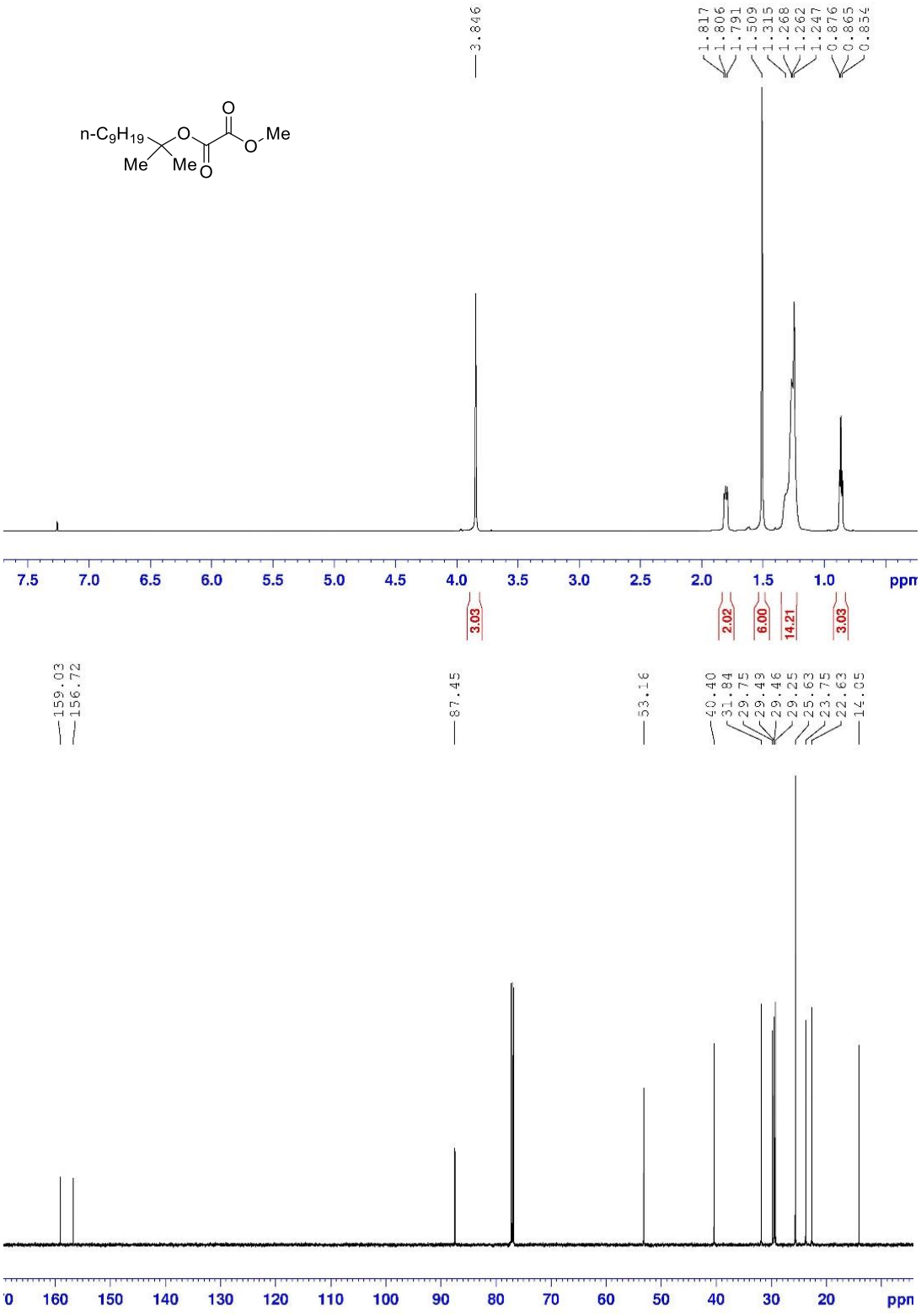


Figure S15. Emission spectrum of 405 nm LEDs

III. NMR Data for New Compounds

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1.262
1.247
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0.854
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7.0
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3.5
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2.5
2.0
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29.49
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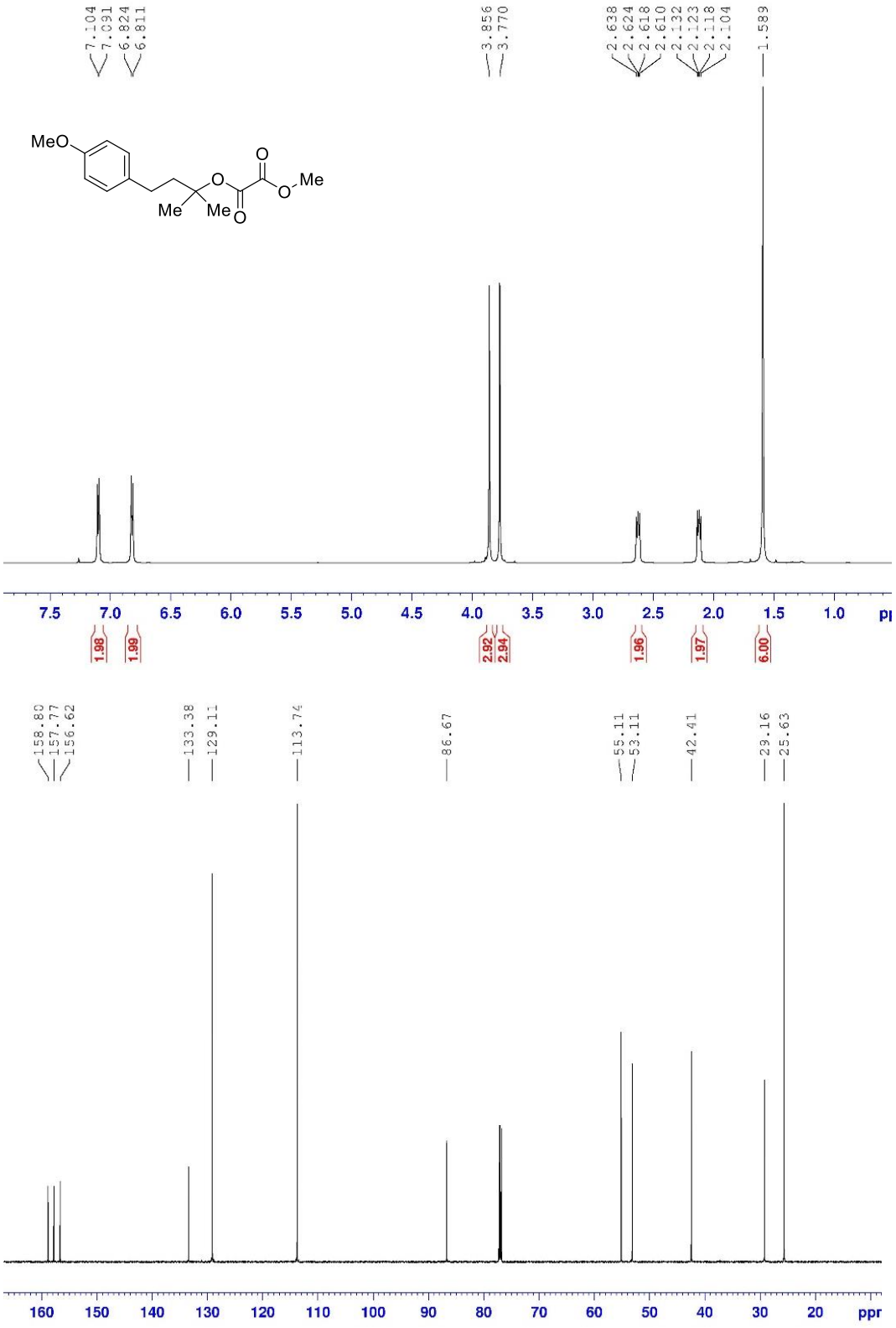
ppm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2.610
2.132
2.123
2.118
2.104
1.583
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O
O
O
Me
Me
Me
O
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7.0
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6.0
5.5
5.0
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3.5
3.0
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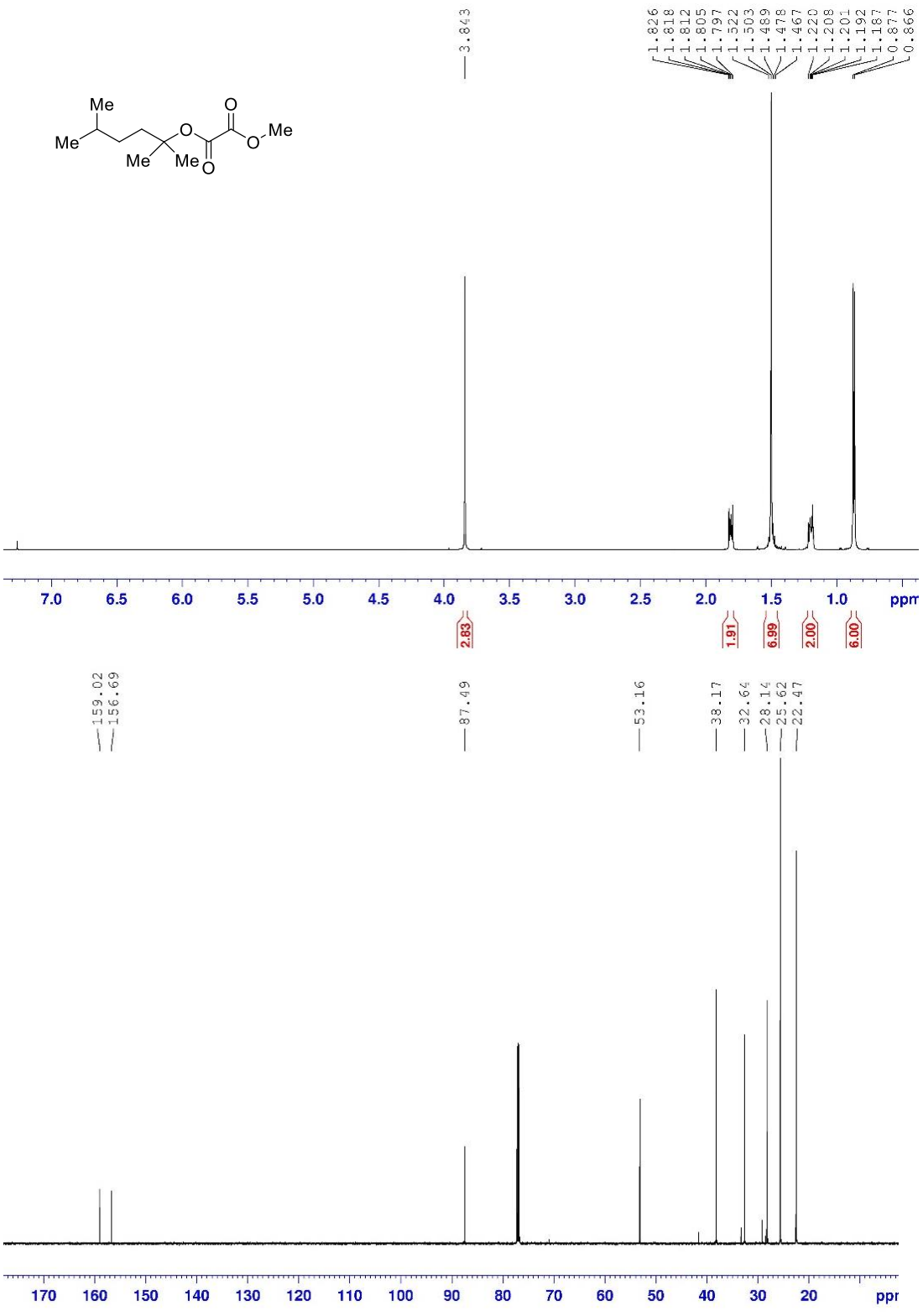
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1.201
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1.187
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6.5
6.0
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4.5
4.0
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1.5
1.0
ppm
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6.99
2.00
6.00
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156.69
87.49
53.16
38.17
32.64
28.14
25.62
22.47
170
160
150
140
130
120
110
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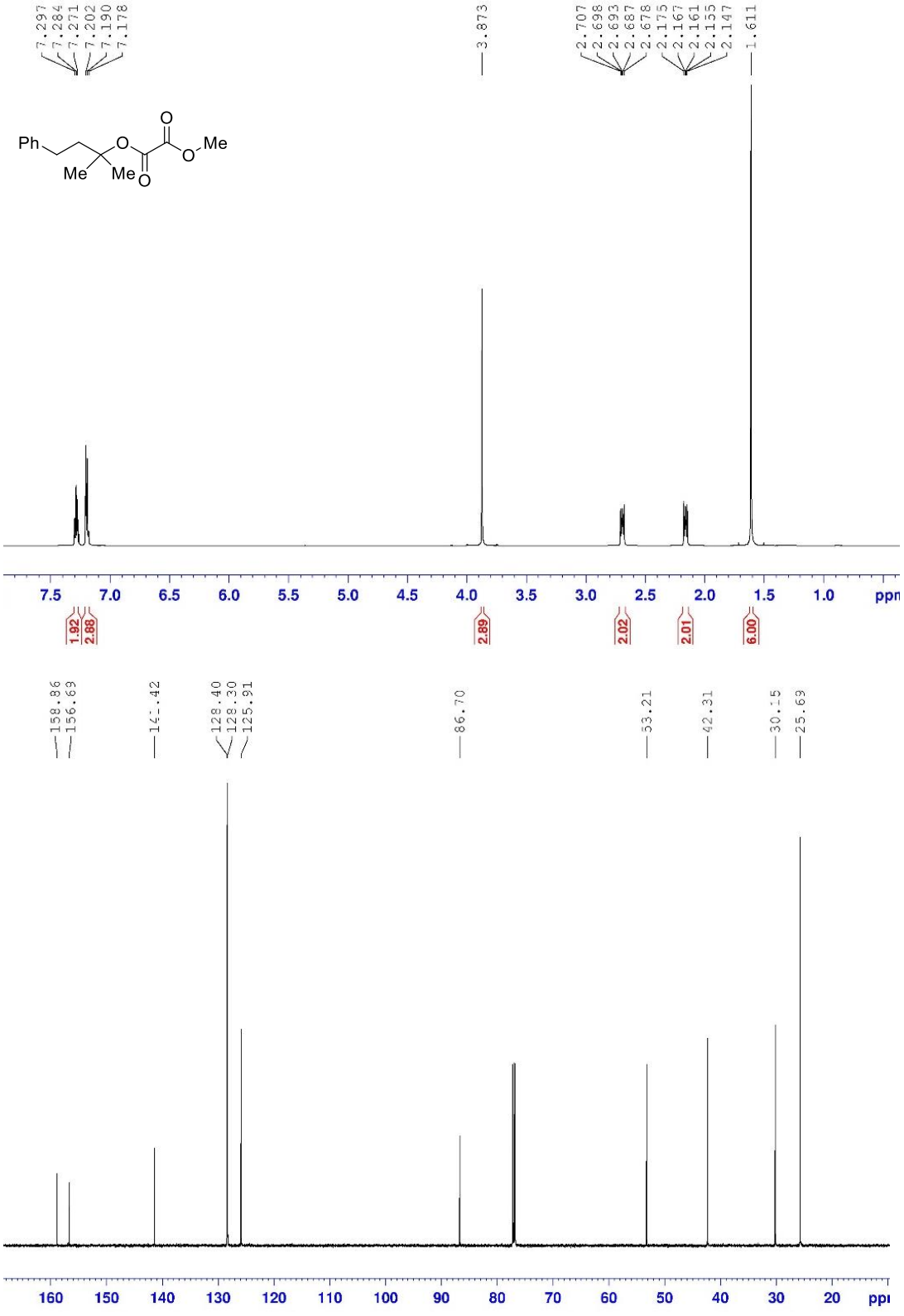
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2.167
2.161
2.155
2.147
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Ph
O
O
O
Me
Me
Me
O
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2.01
6.00
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128.40
128.30
125.91
86.70
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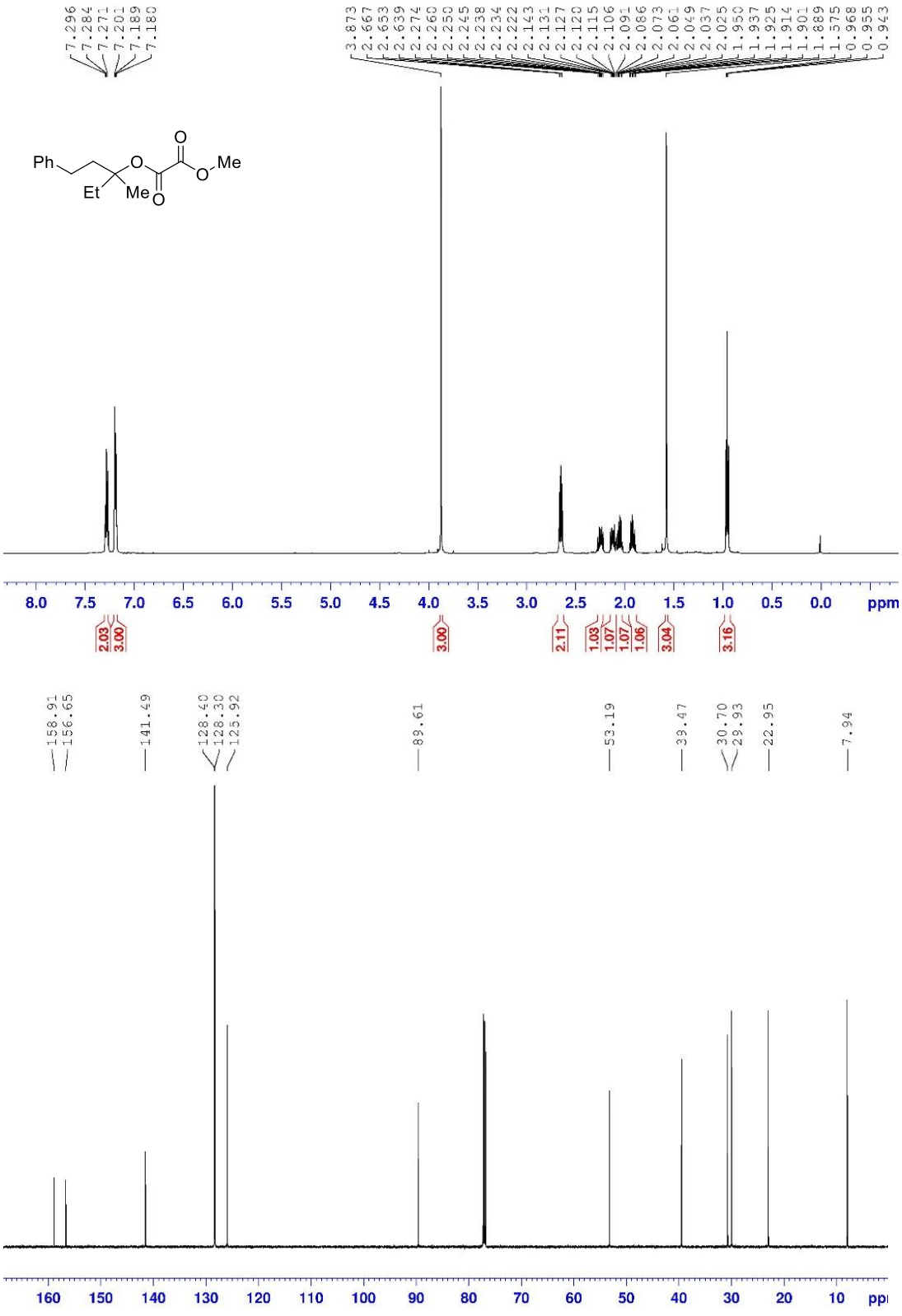
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2.234
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2.061
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1.901
1.889
1.575
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0.955
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O
Me
Et
Me
O
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3.00
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1.06
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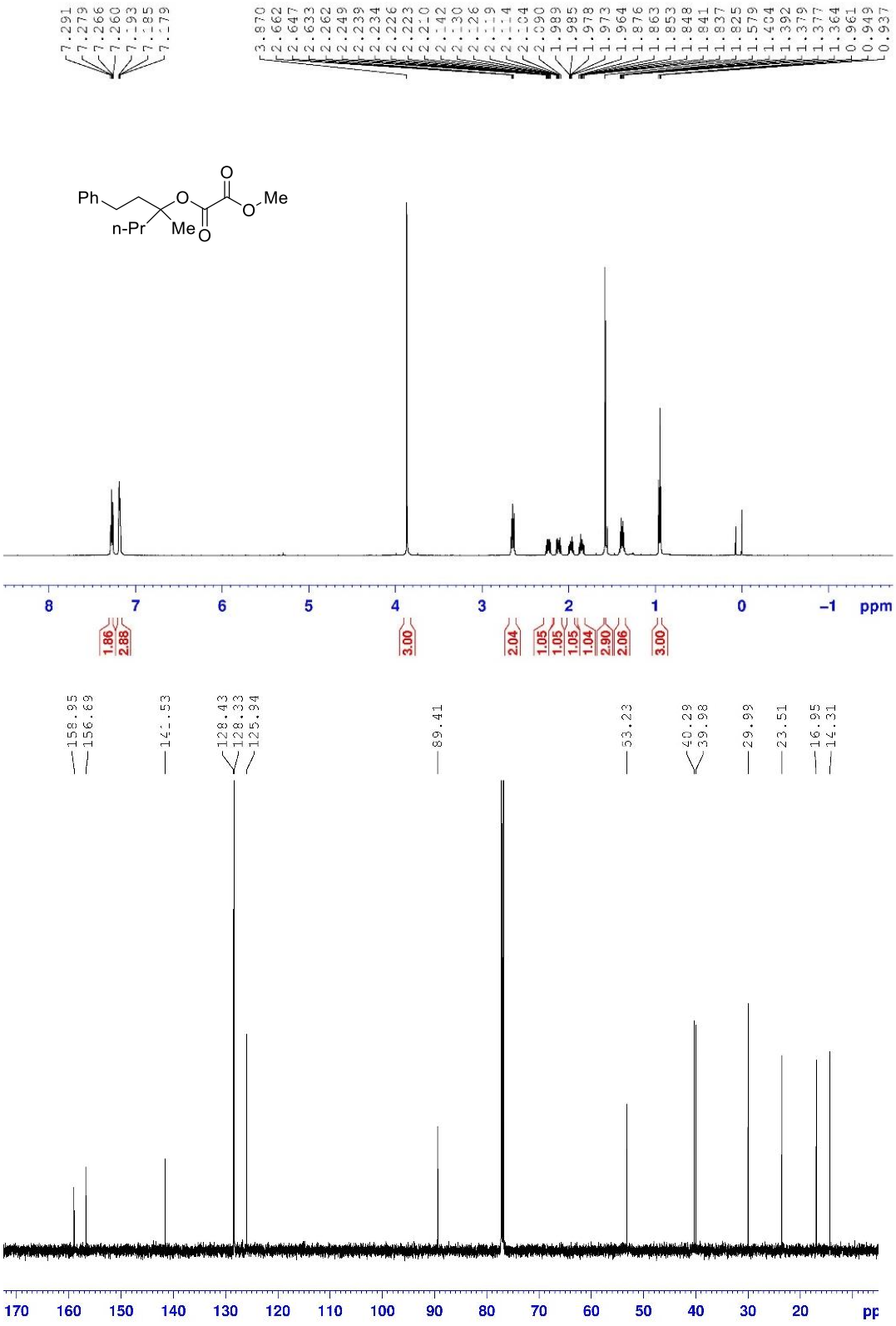
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2.223
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2.130
2.126
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1.379
1.377
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n-Pr
Me
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O
Me
O
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7
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4
3
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−1
ppm
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1.05
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1.04
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2.06
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23.51
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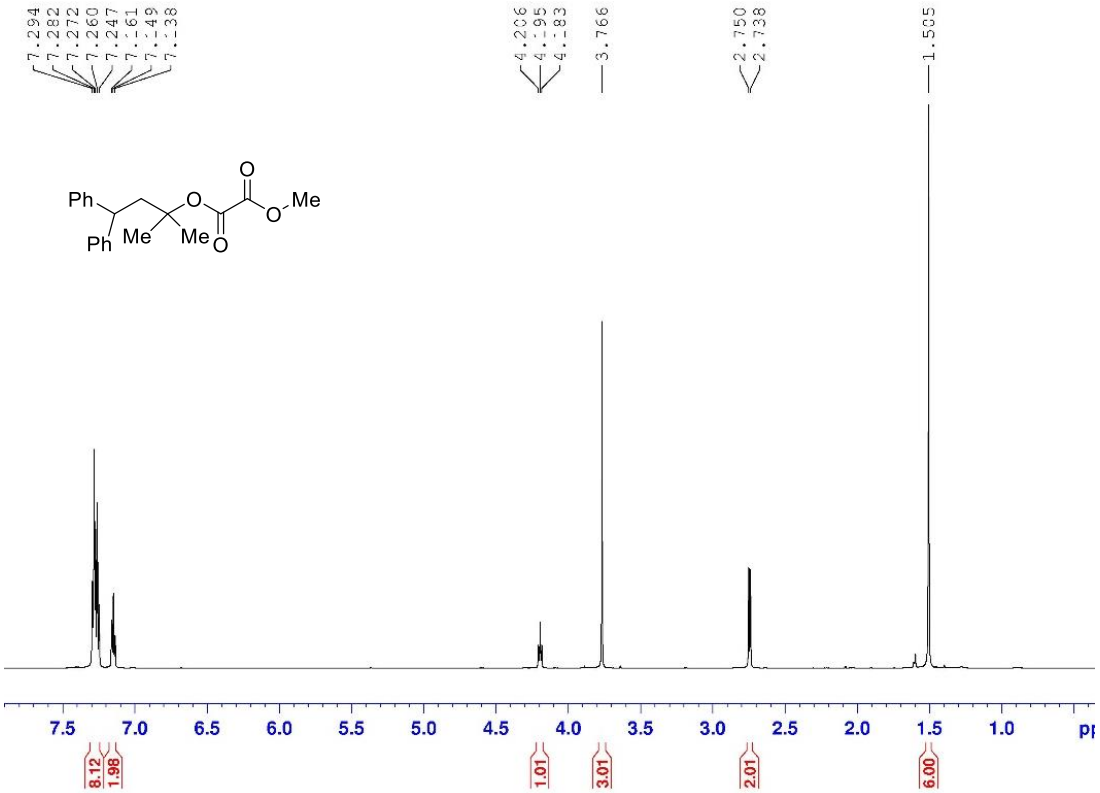
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Me
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O
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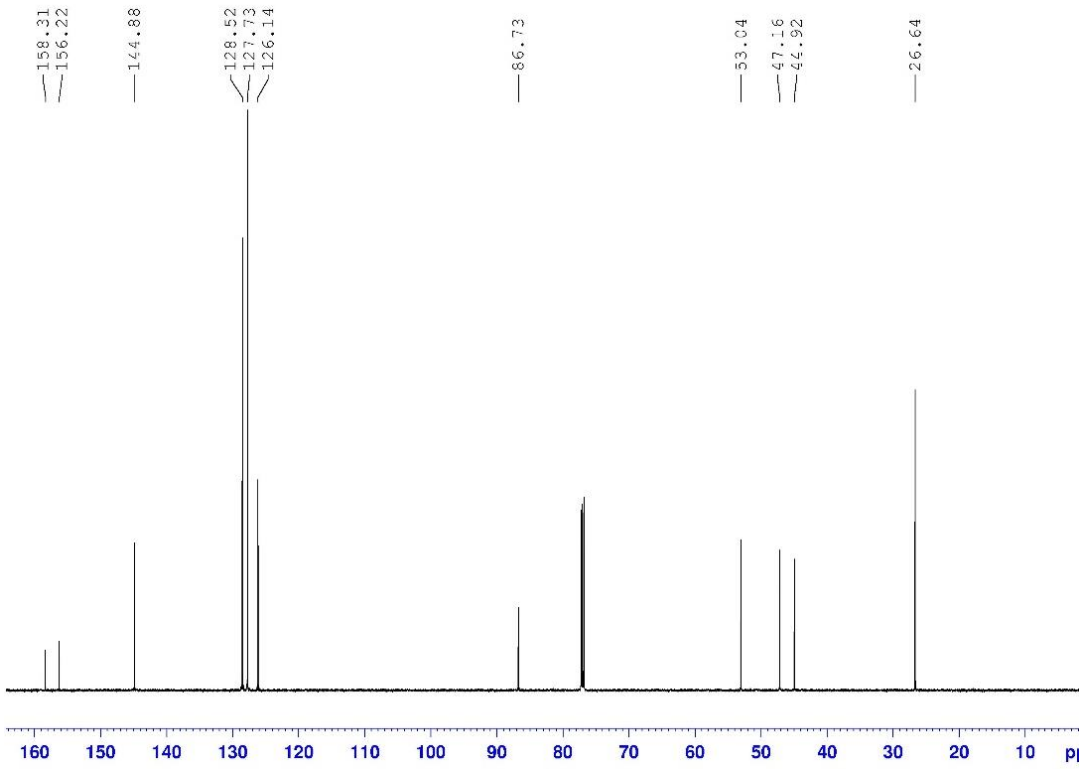
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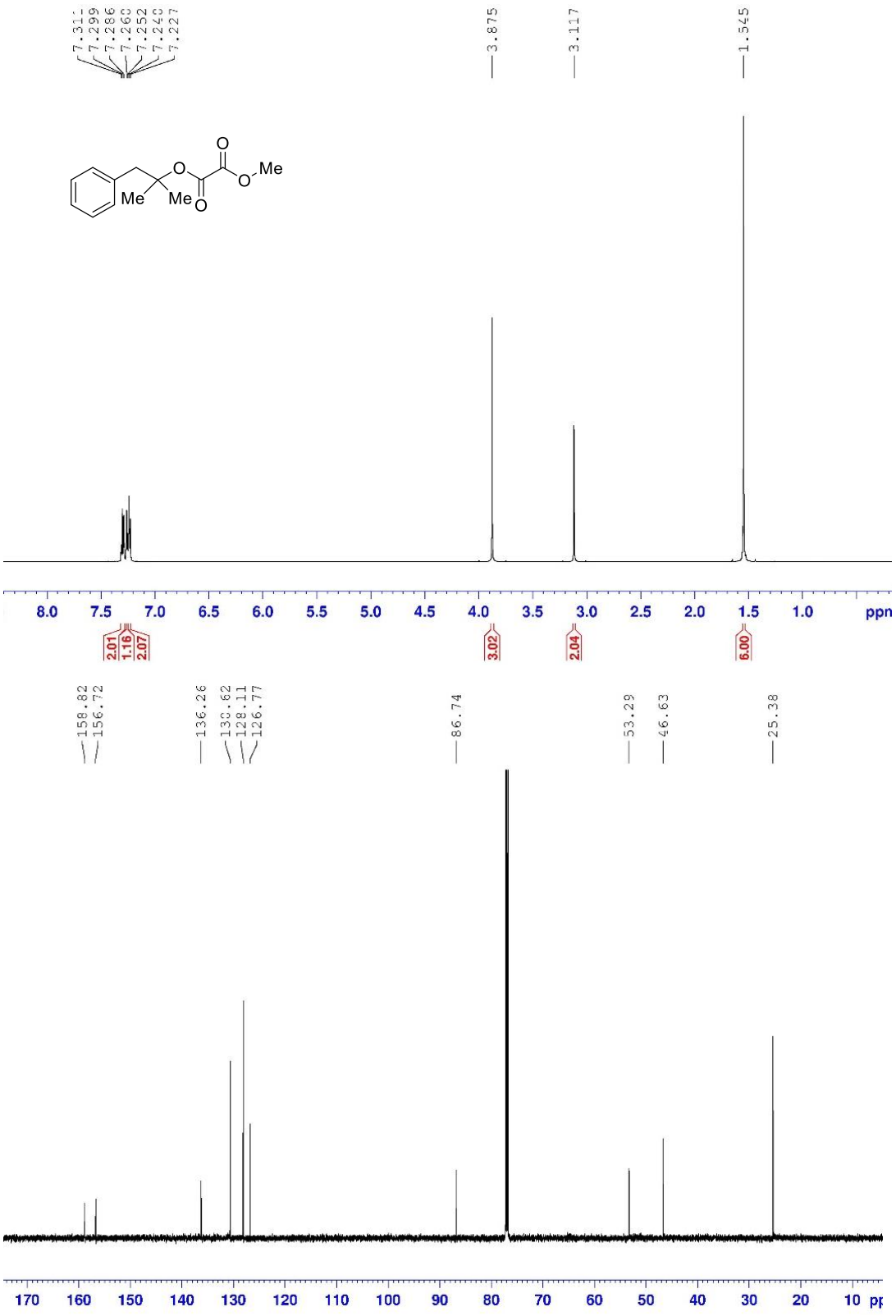
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O
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Me
Me
O
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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1.16
2.07
3.02
2.04
6.00
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20
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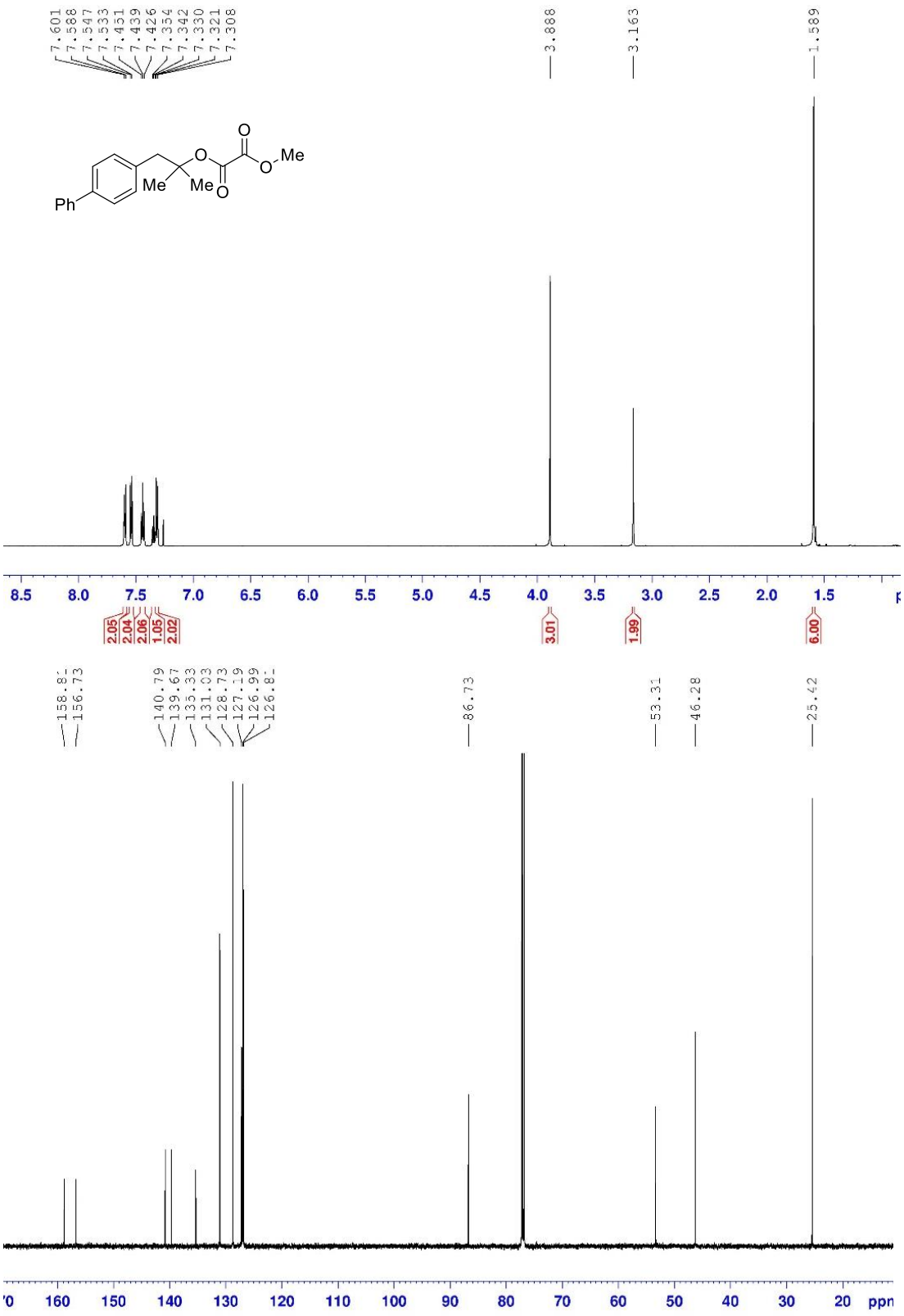
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7.330
7.321
7.308
3.888
3.163
1.589
O
O
Me
O
Me
Me
Ph
8.5
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7.5
7.0
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5.0
4.5
4.0
3.5
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1.5
2.05
2.04
2.06
1.05
2.02
3.01
1.99
6.00
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127.19
126.99
126.8
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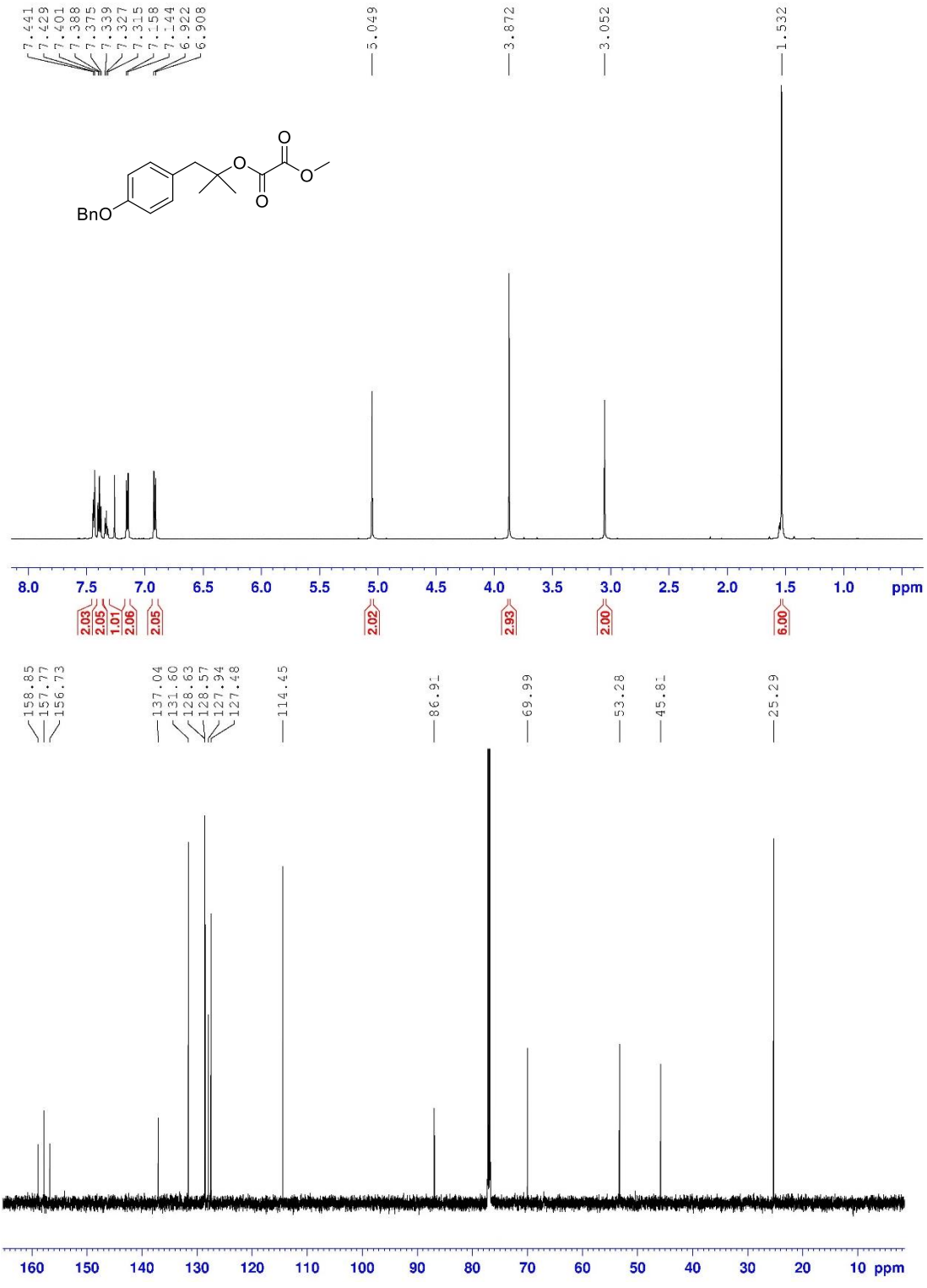
20
ppm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5.049
3.872
3.052
1.532
BnO
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O
O
O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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1.0
ppm
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2.05
1.01
2.06
2.05
2.02
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2.00
6.00
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156.73
137.04
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128.57
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127.48
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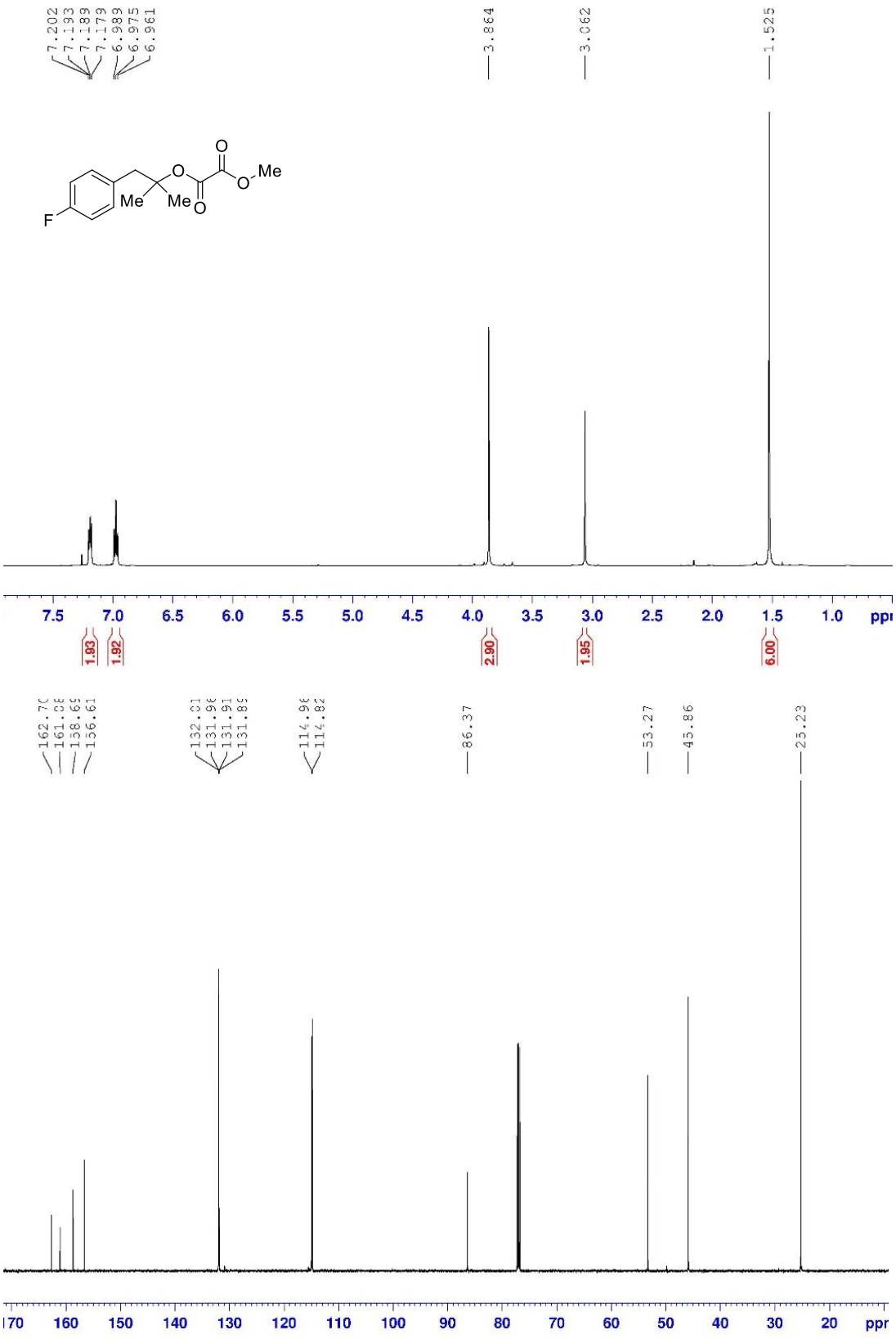
10 ppm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Me
Me
O
F
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5.0
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4.0
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2.5
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1.5
1.0
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1.95
6.00
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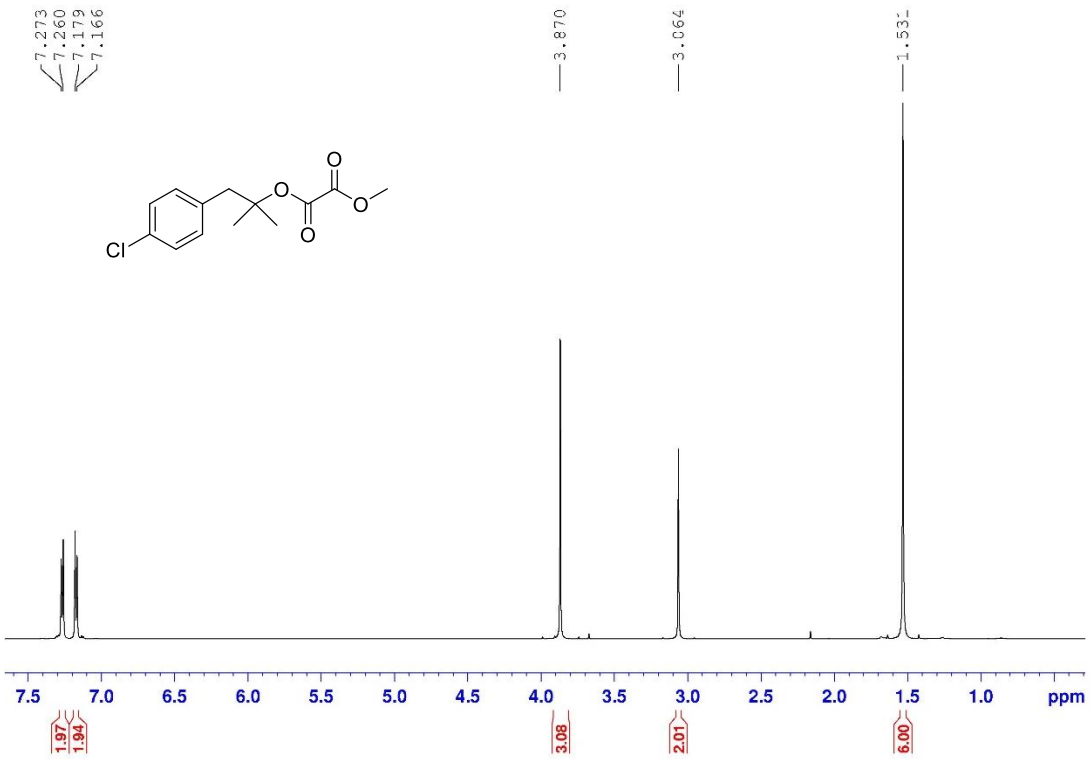
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6.5
6.0
5.5
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4.5
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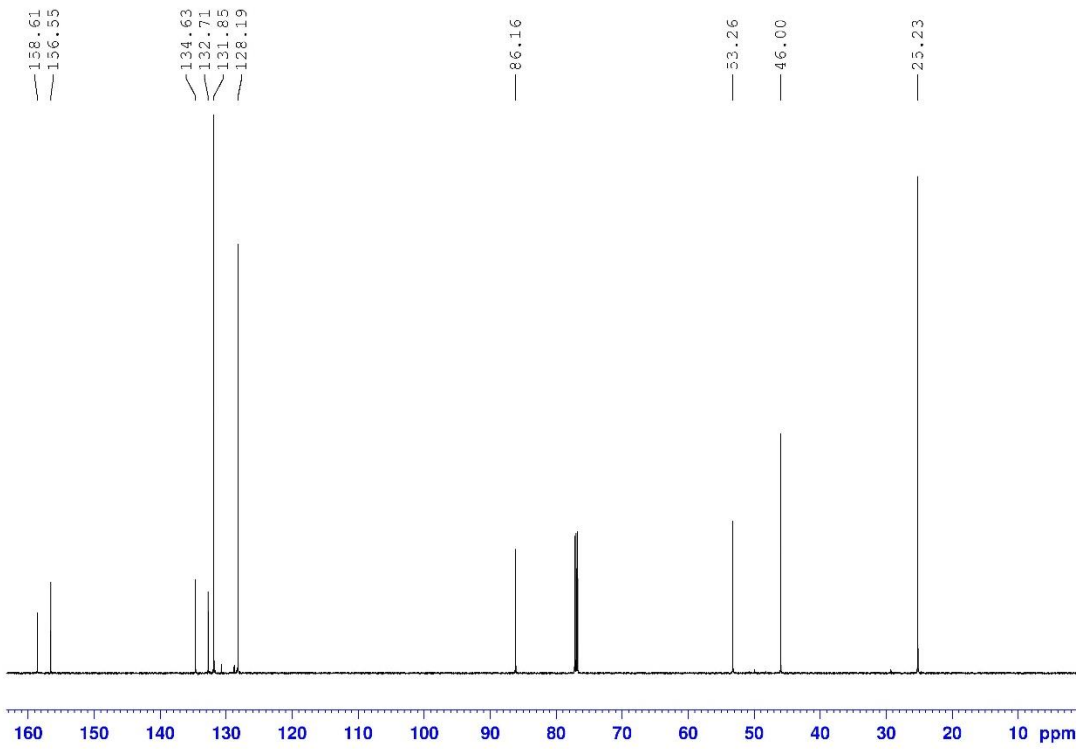
6.00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140
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120
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80
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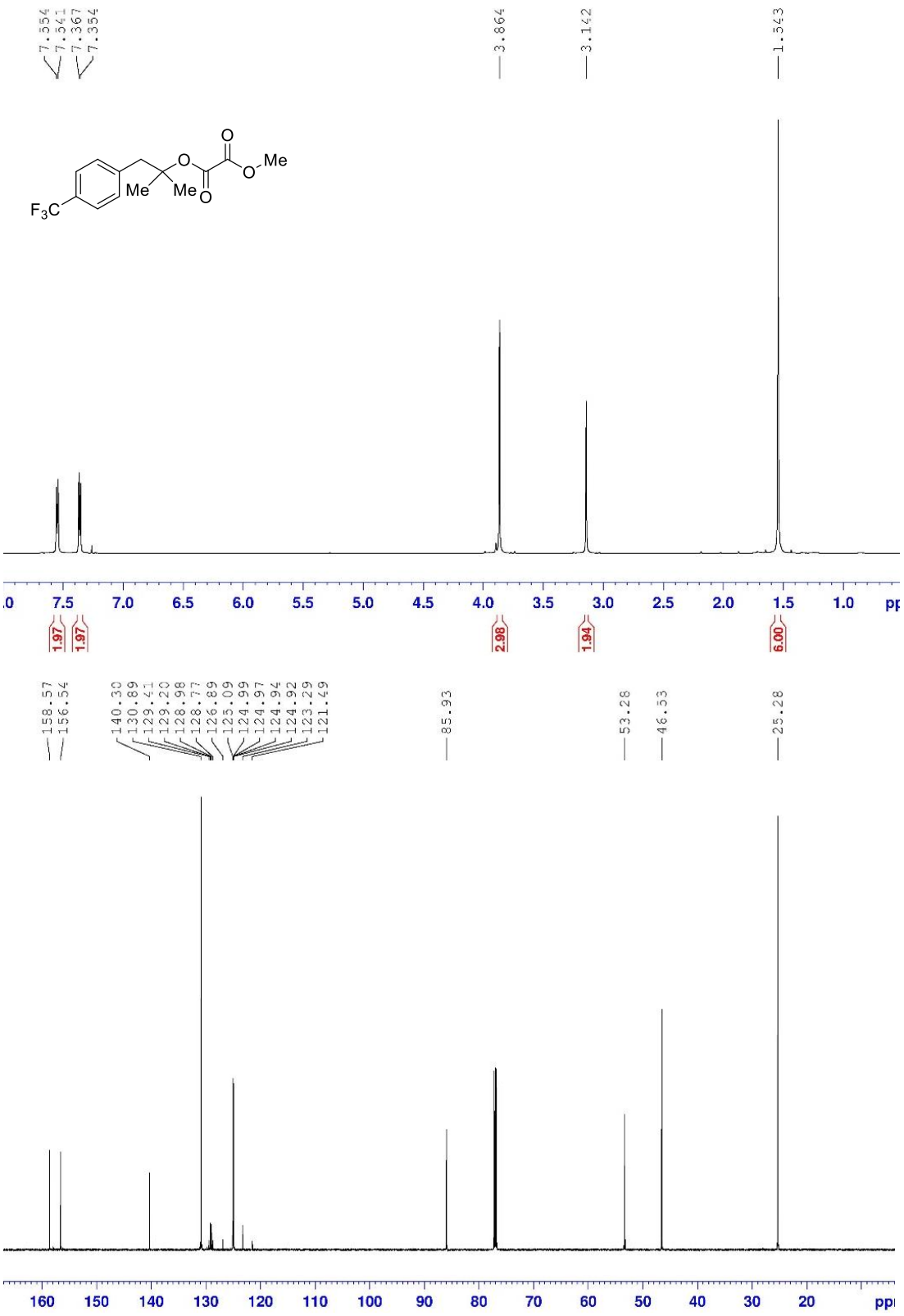
40
30
20
10 ppm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Me
O
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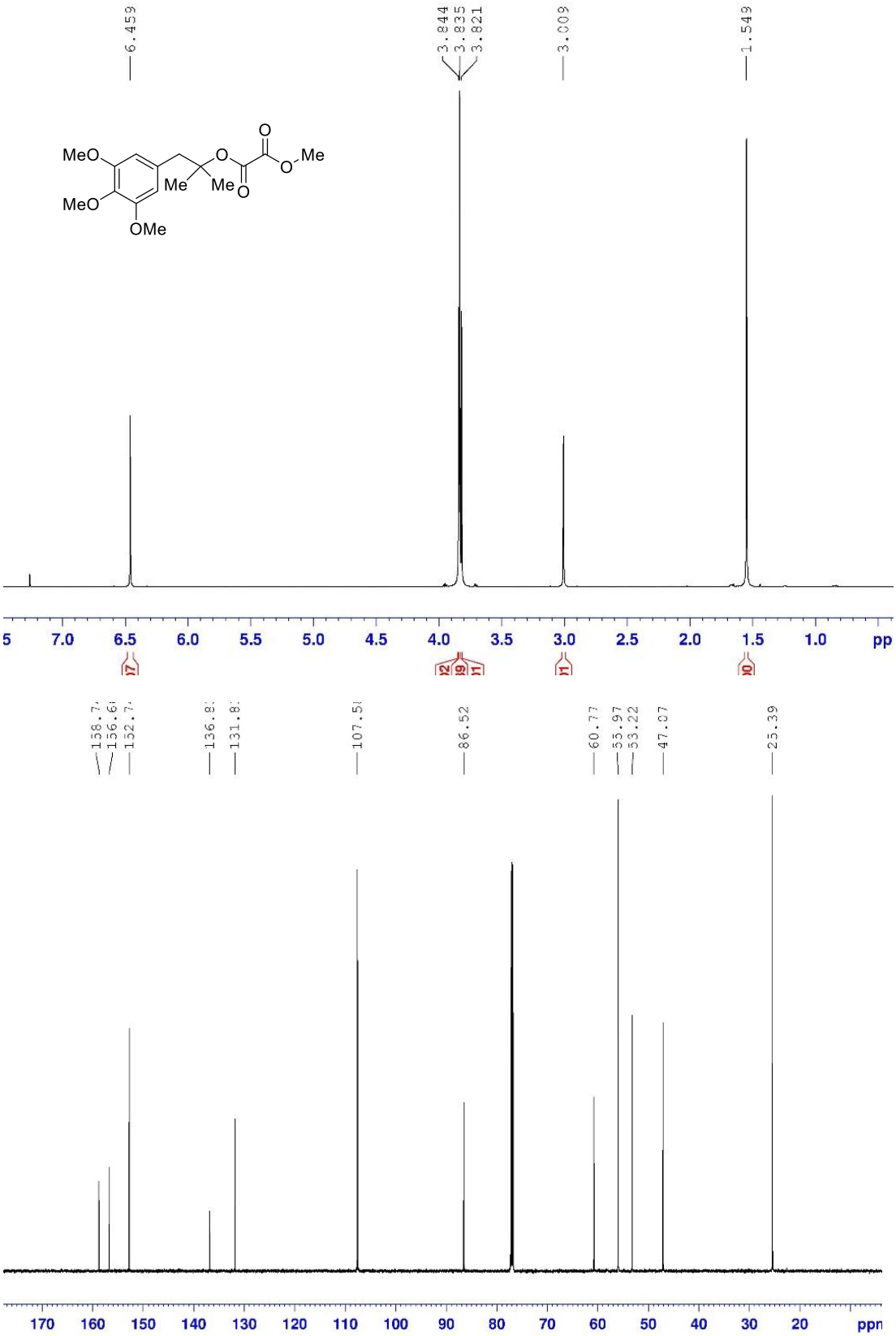
25.28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Me
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O
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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152.7
136.8
131.8
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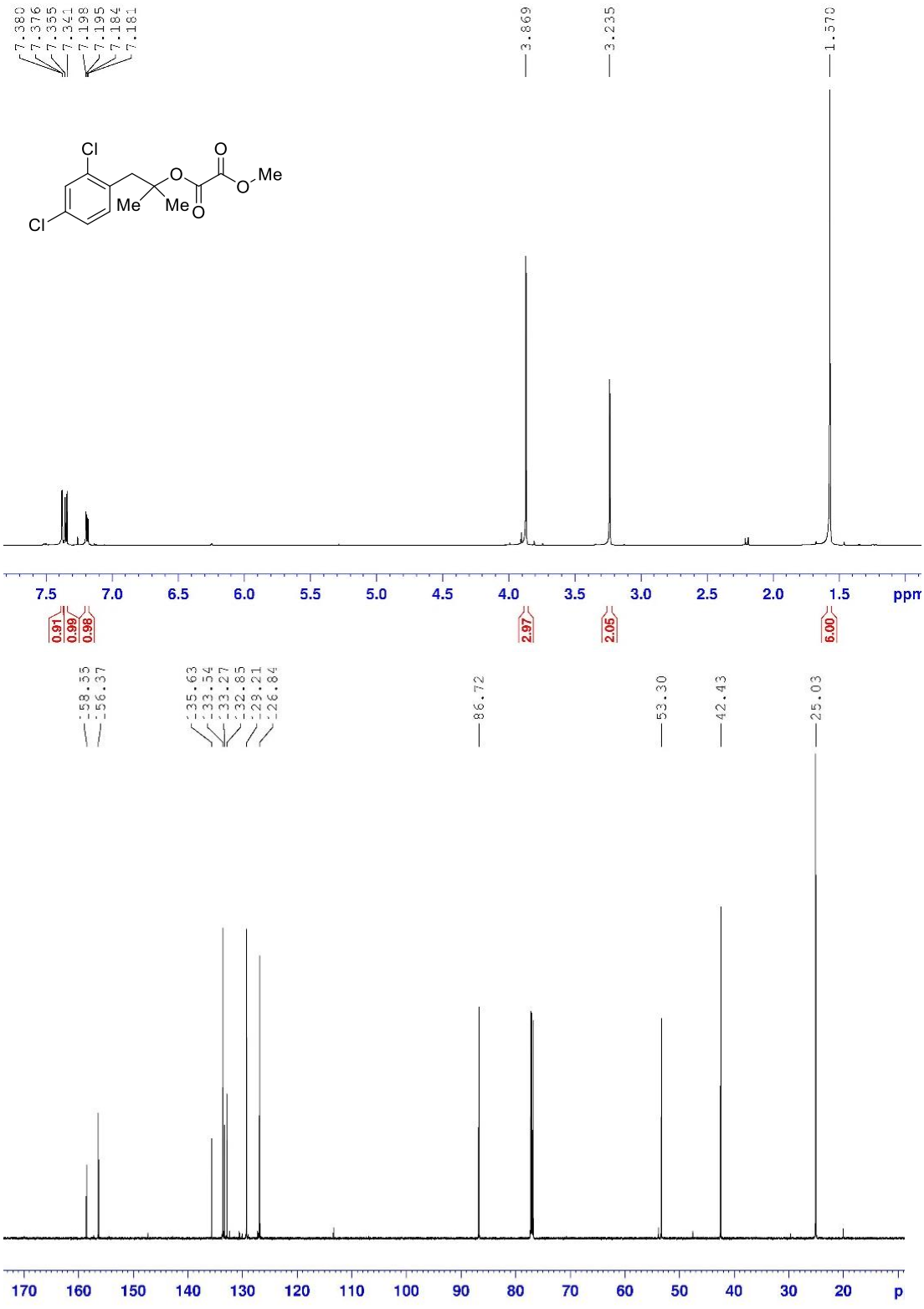
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Cl
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Me
O
O
O
O
Me
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6.0
5.5
5.0
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20
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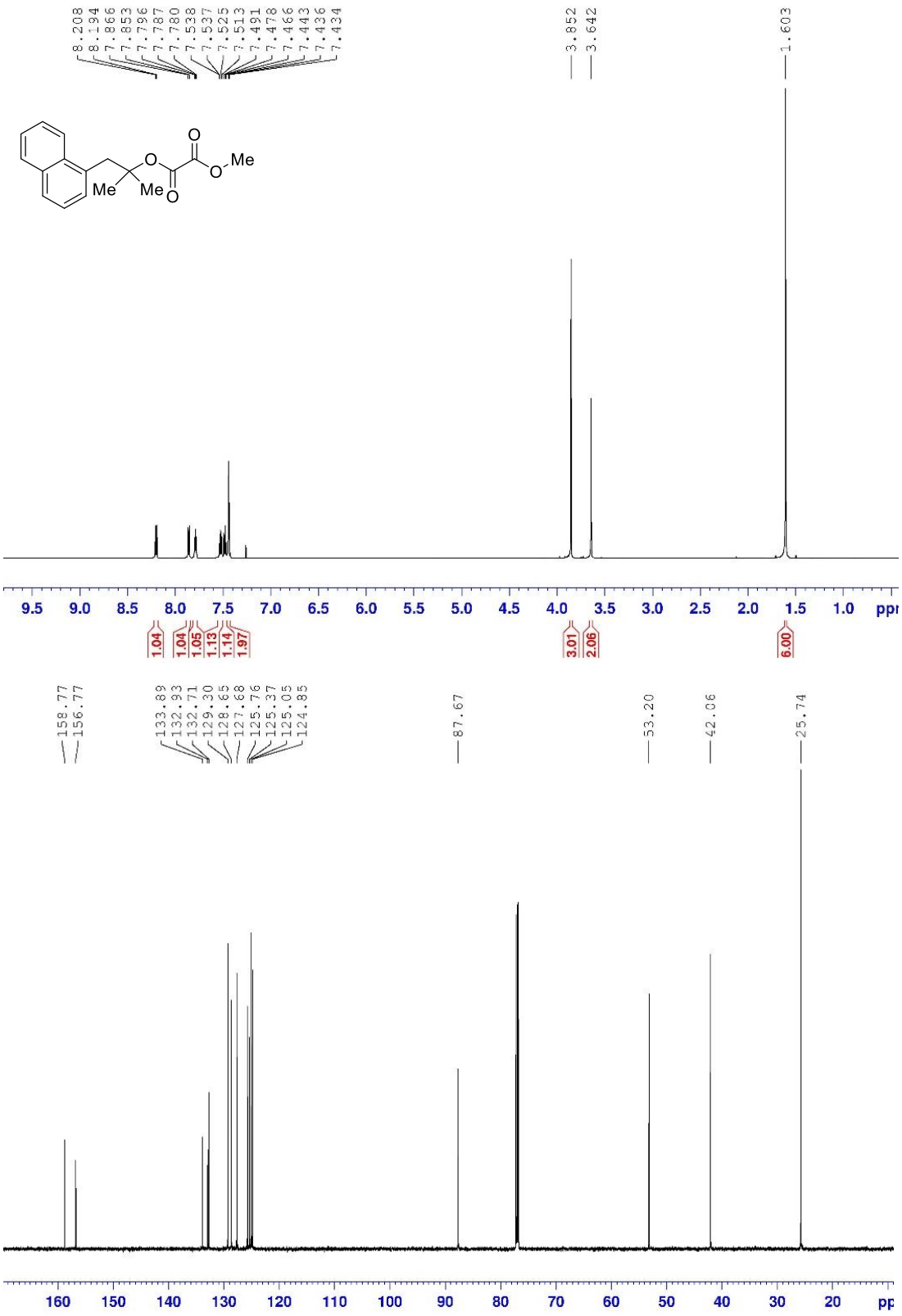
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7.443
7.436
7.434
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Me
Me
O
O
O
O
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1.04
1.05
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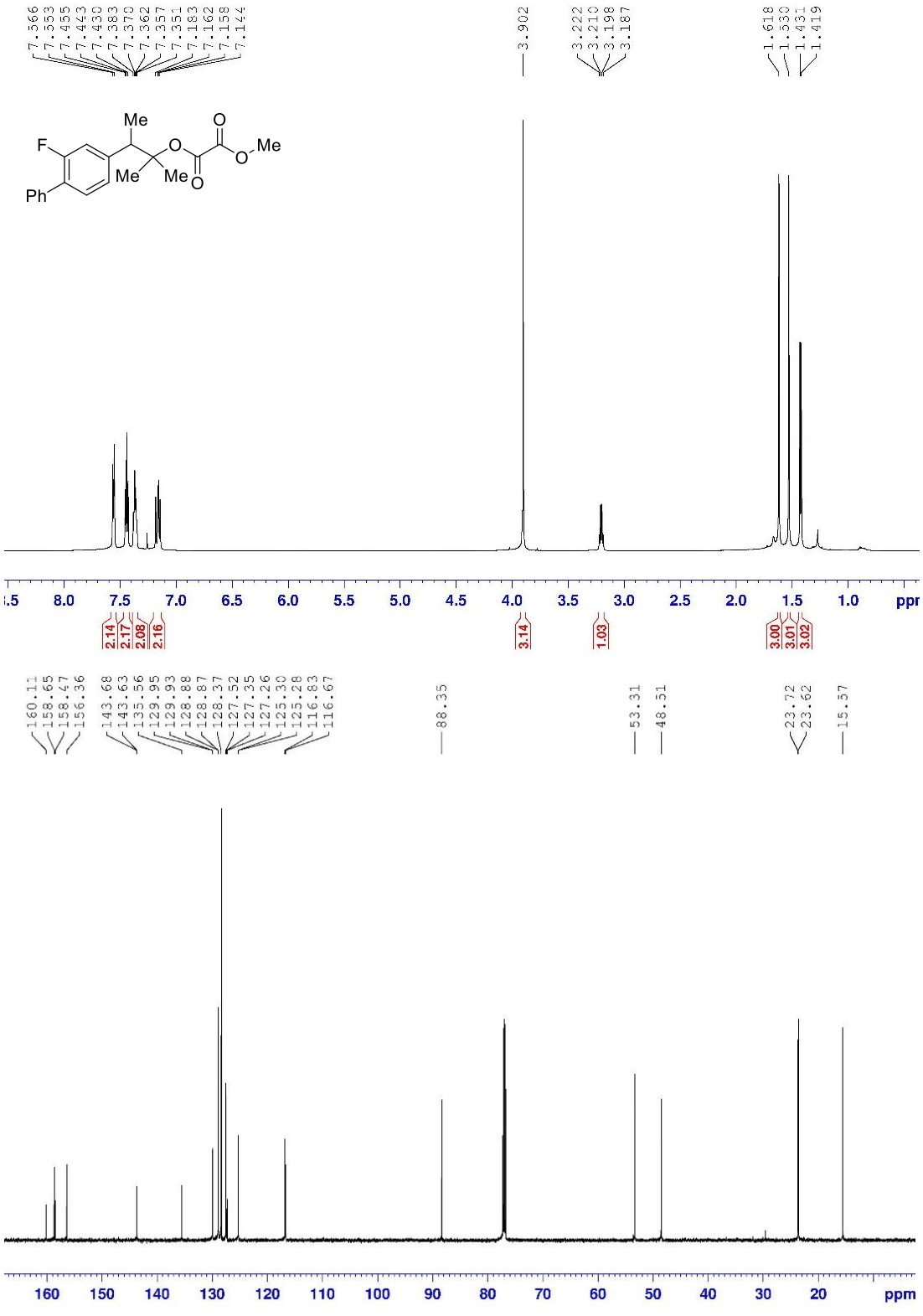
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Me
Me
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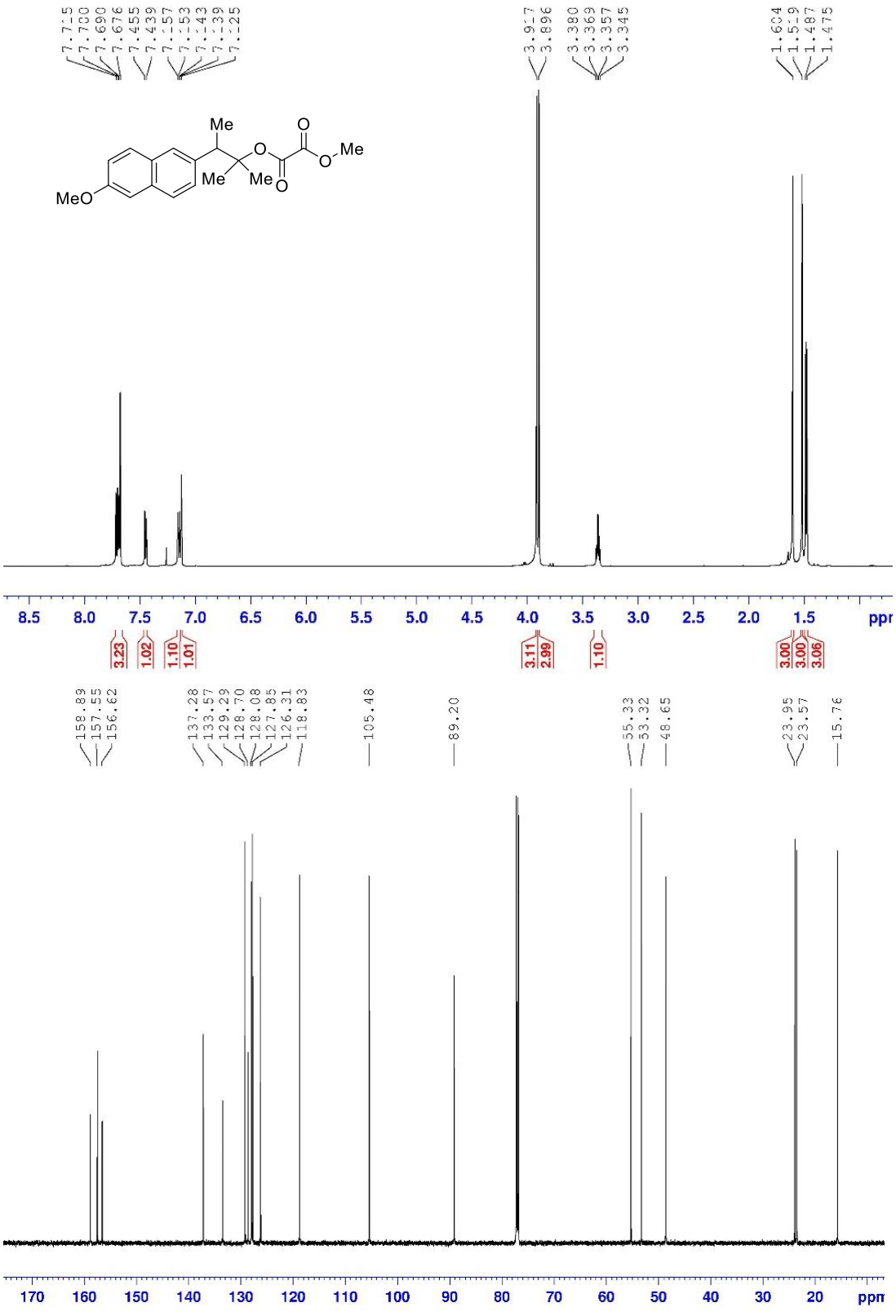
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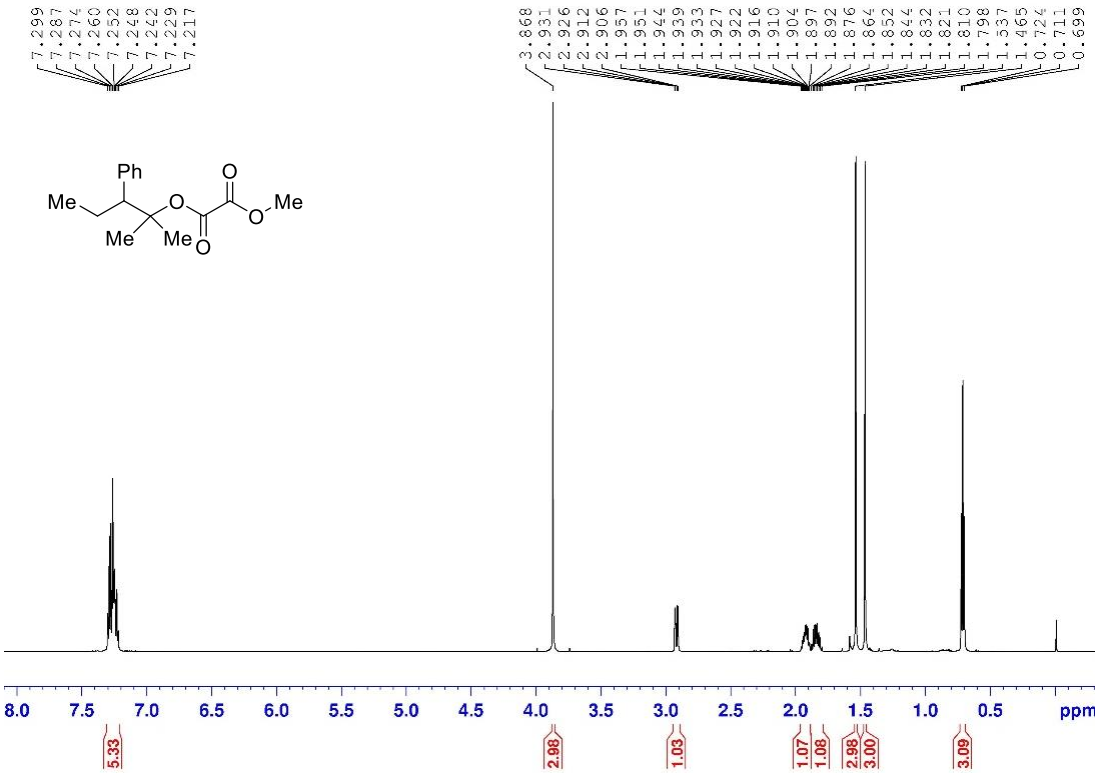
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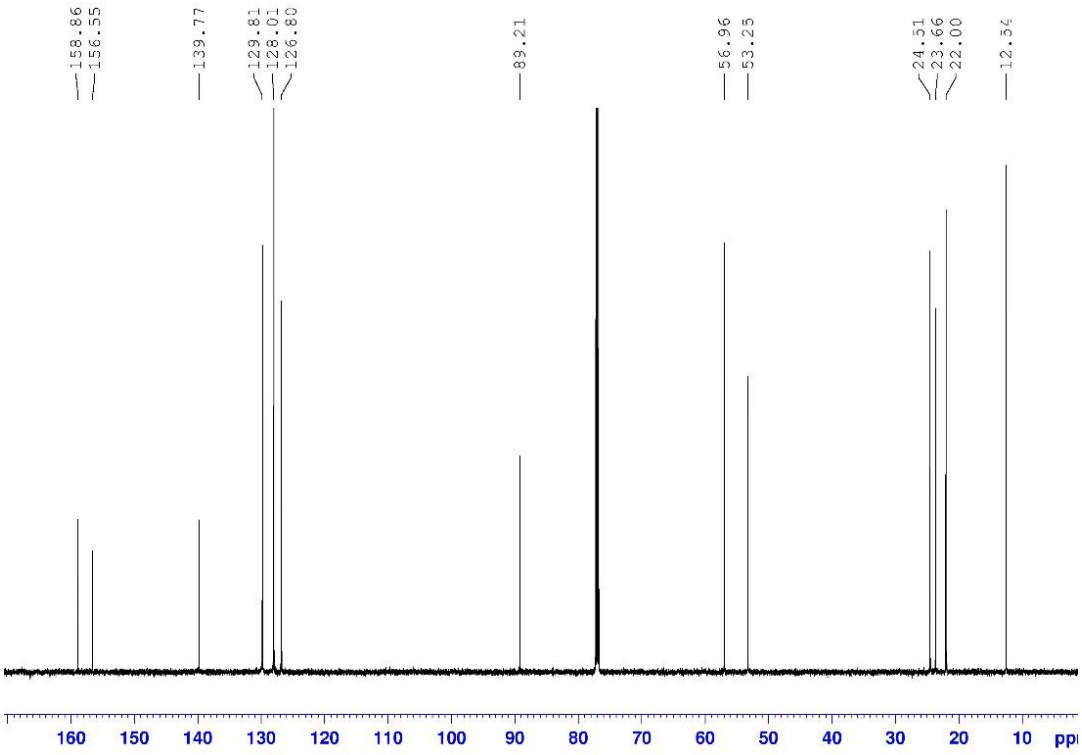
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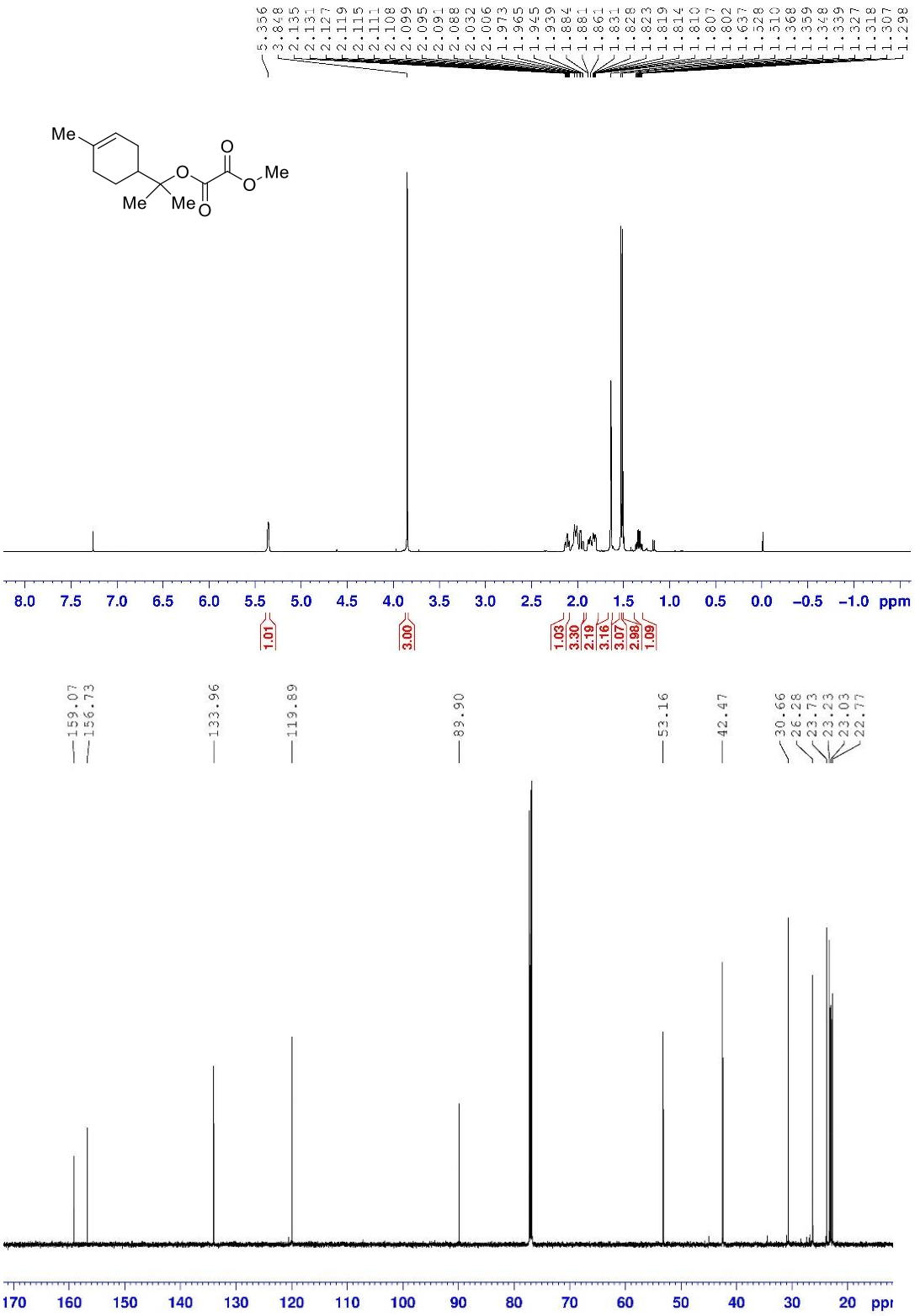
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Me
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 ppm
1.01
3.00
1.03
3.30
2.19
3.16
3.07
2.98
1.09
159.07
156.73
133.96
119.89
89.90
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26.28
23.73
23.23
23.03
22.77
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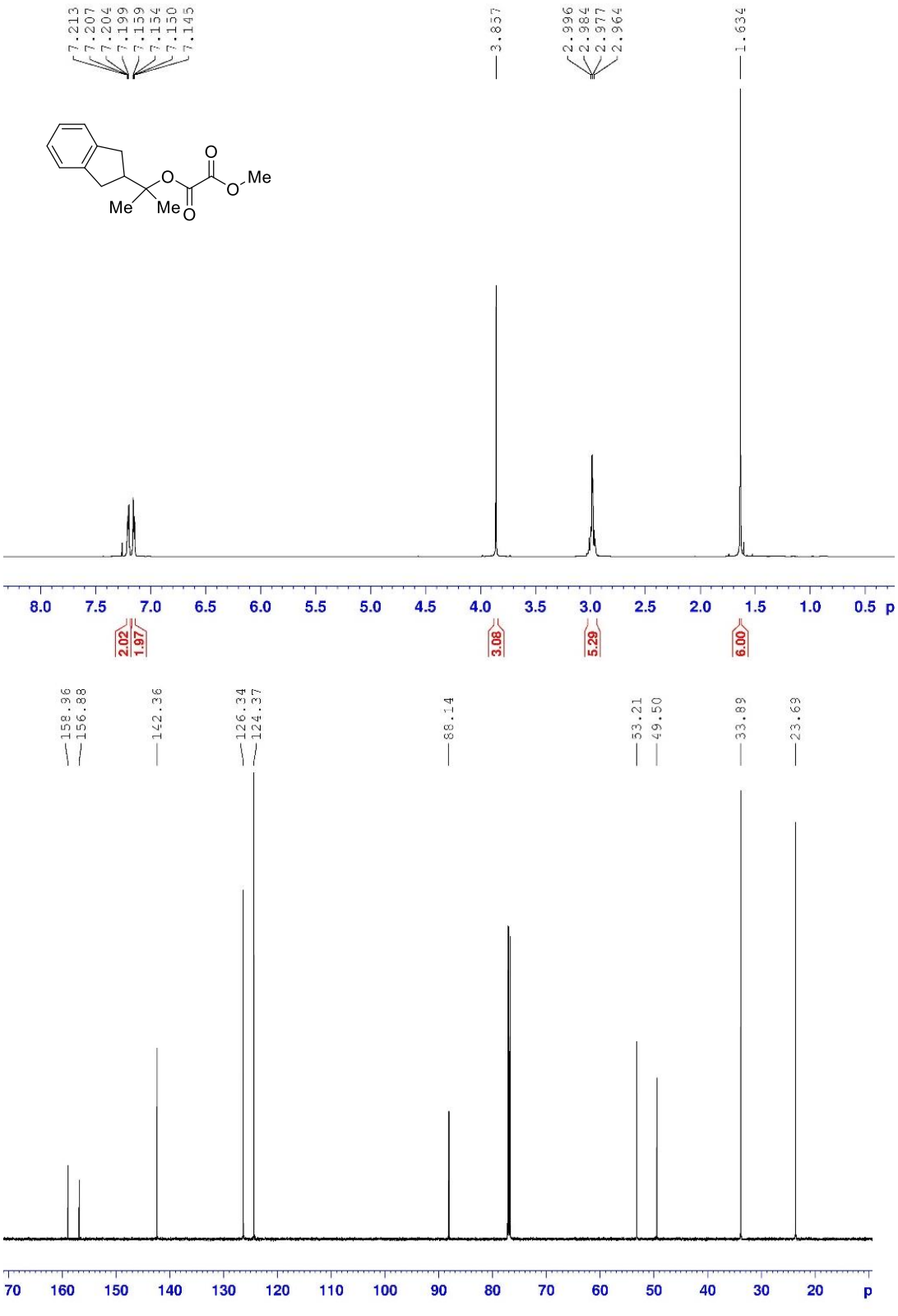
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7.204
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7.145
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2.984
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2.964
1.634
Me
Me
Me
O
O
O
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 p
2.02
1.97
3.08
5.29
6.00
158.96
156.88
142.36
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124.37
88.14
53.21
49.50
33.89
23.69
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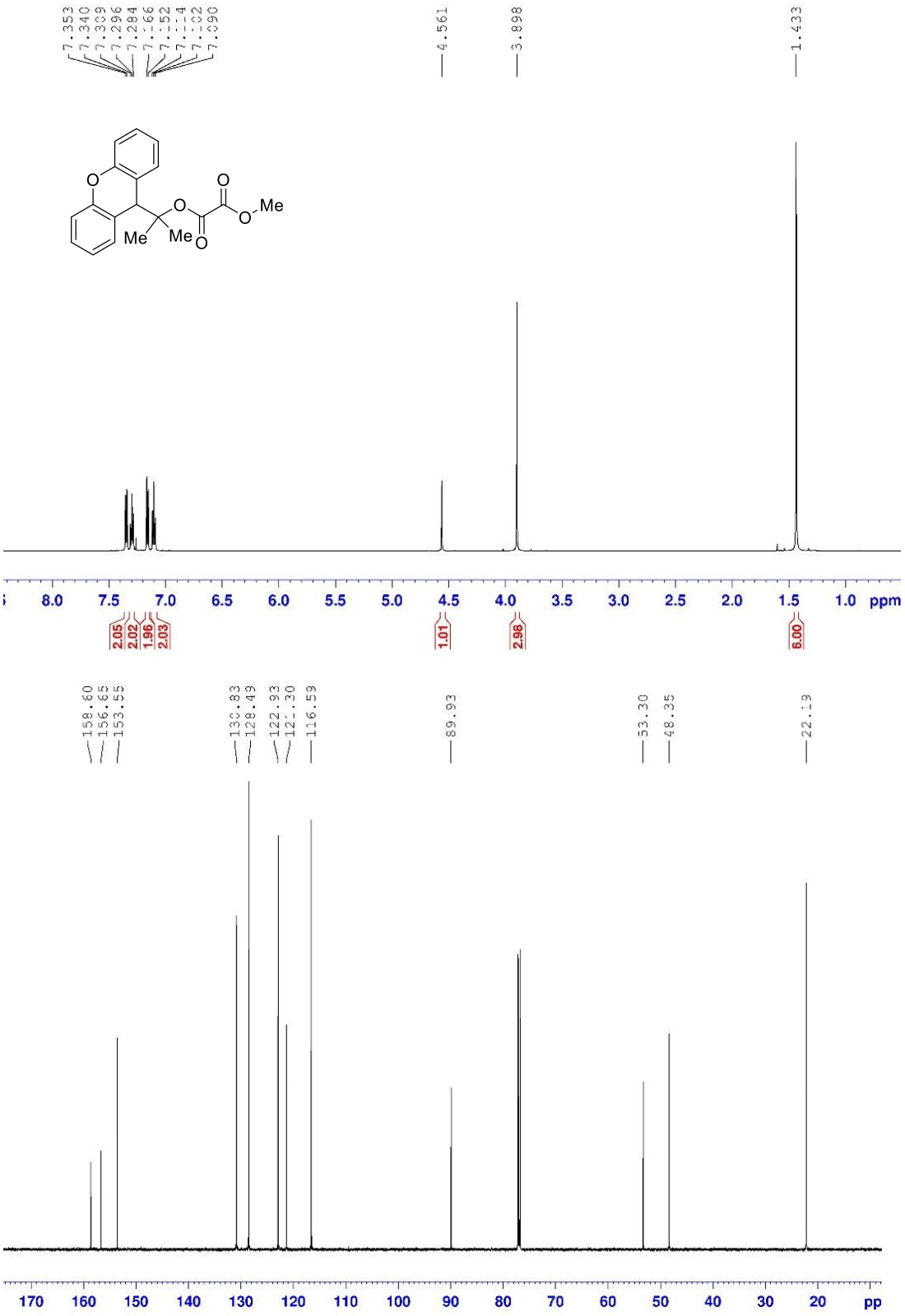
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7.309
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3.898
1.433
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O
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O
Me
Me
Me
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.05
2.02
1.96
2.03
1.01
2.98
6.00
158.60
156.65
153.55
130.83
128.49
122.93
122.30
116.59
89.93
53.30
48.35
22.19
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160
150
140
130
120
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80
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40
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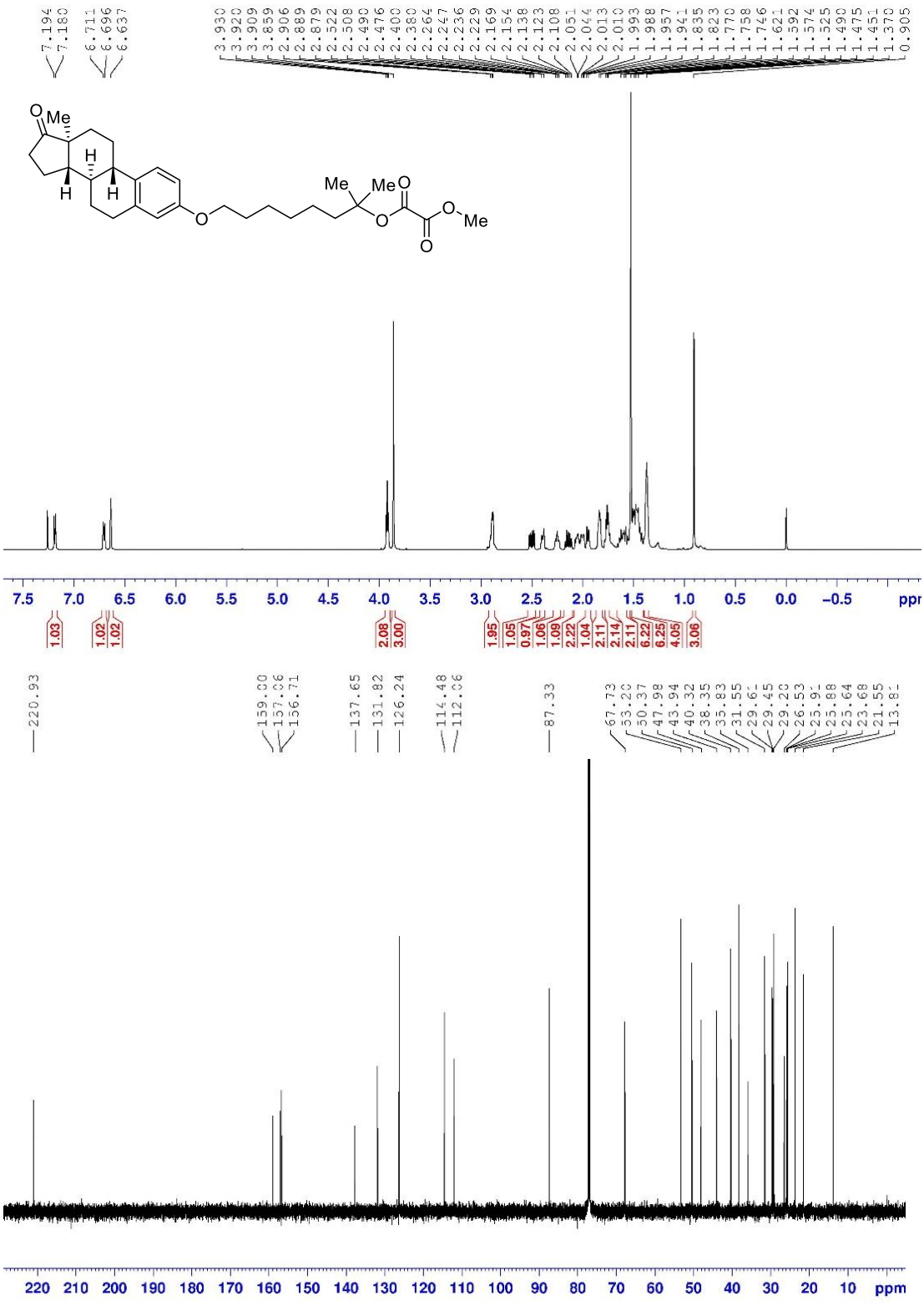
20
pp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2.879
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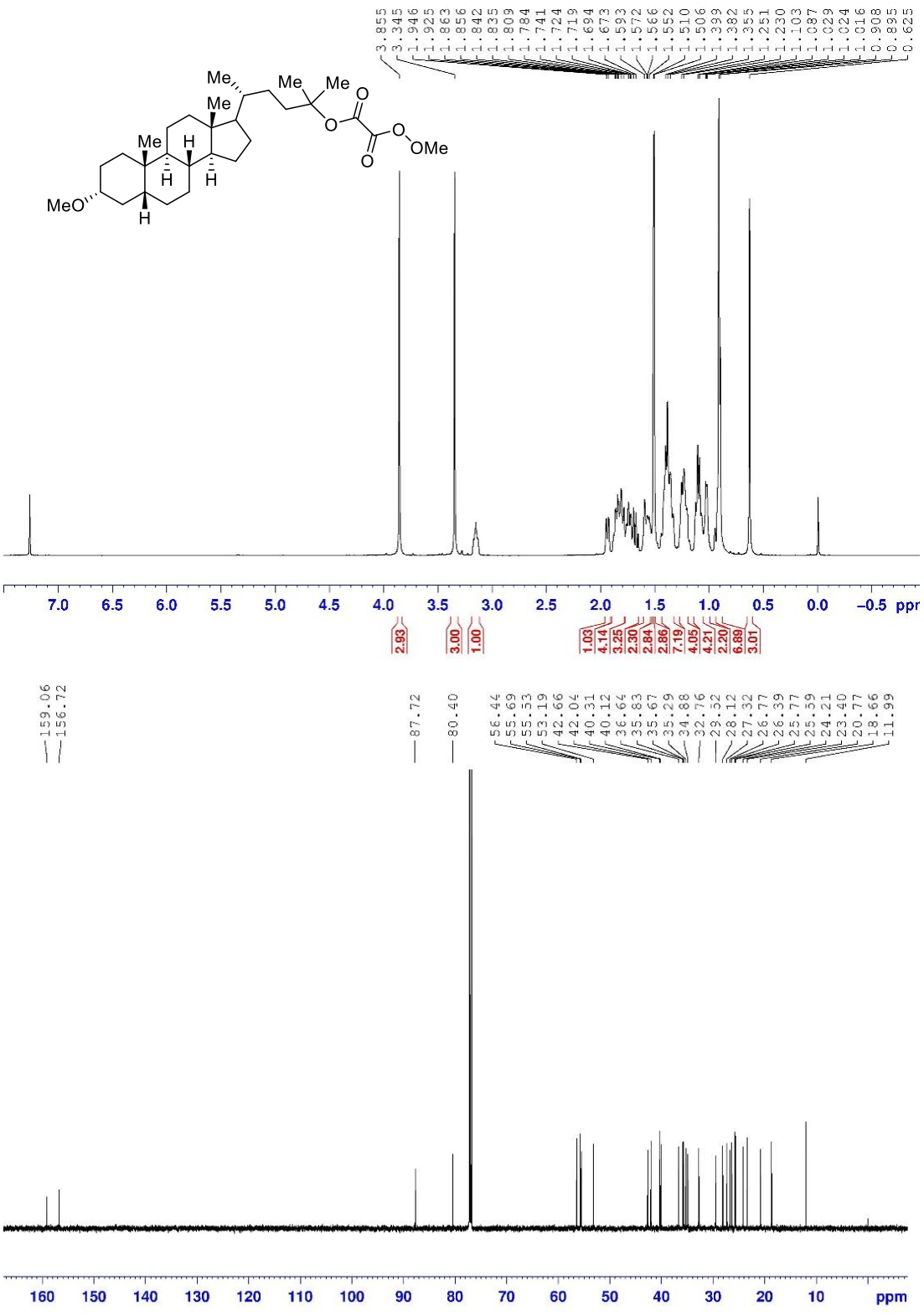
2.508
2.490
2.476
2.400
2.380
2.264
2.247
2.236
2.229
2.169
2.154
2.138
2.123
2.108
2.051
2.044
2.013
2.010
1.993
1.988
1.957
1.941
1.835
1.823
1.770
1.758
1.746
1.621
1.592
1.574
1.525
1.490
1.475
1.451
1.370
0.905
O
Me
H
H
H
O
Me
Me
O
O
O
O
Me
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.03
1.02
1.02
2.08
3.00
1.95
1.05
0.97
1.06
1.09
2.22
1.04
2.11
2.14
2.11
6.22
6.25
4.05
3.06
220.93
159.00
157.66
156.71
137.65
131.82
126.24
114.48
112.66
87.33
67.73
53.23
50.37
47.98
43.94
40.32
38.35
35.83
31.55
29.6
29.45
29.23
26.53
25.9
25.88
23.64
23.68
21.55
13.8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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1.719
1.694
1.673
1.593
1.572
1.566
1.552
1.510
1.506
1.399
1.382
1.355
1.251
1.230
1.103
1.087
1.029
1.024
1.016
0.908
0.895
0.625
Me
Me
Me
Me
Me
H
H
H
H
MeO
O
O
O
O
OMe
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm
2.93
3.00
1.00
1.03
4.14
3.25
2.30
2.84
2.86
7.19
4.05
4.21
2.20
6.89
3.01
159.06
156.72
87.72
80.40
56.44
55.69
55.53
53.19
42.66
42.04
40.31
40.12
36.64
35.83
35.67
35.29
34.88
32.76
29.32
28.12
27.32
26.77
26.39
25.77
25.39
24.21
23.40
20.77
18.66
11.99
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150
140
130
120
110
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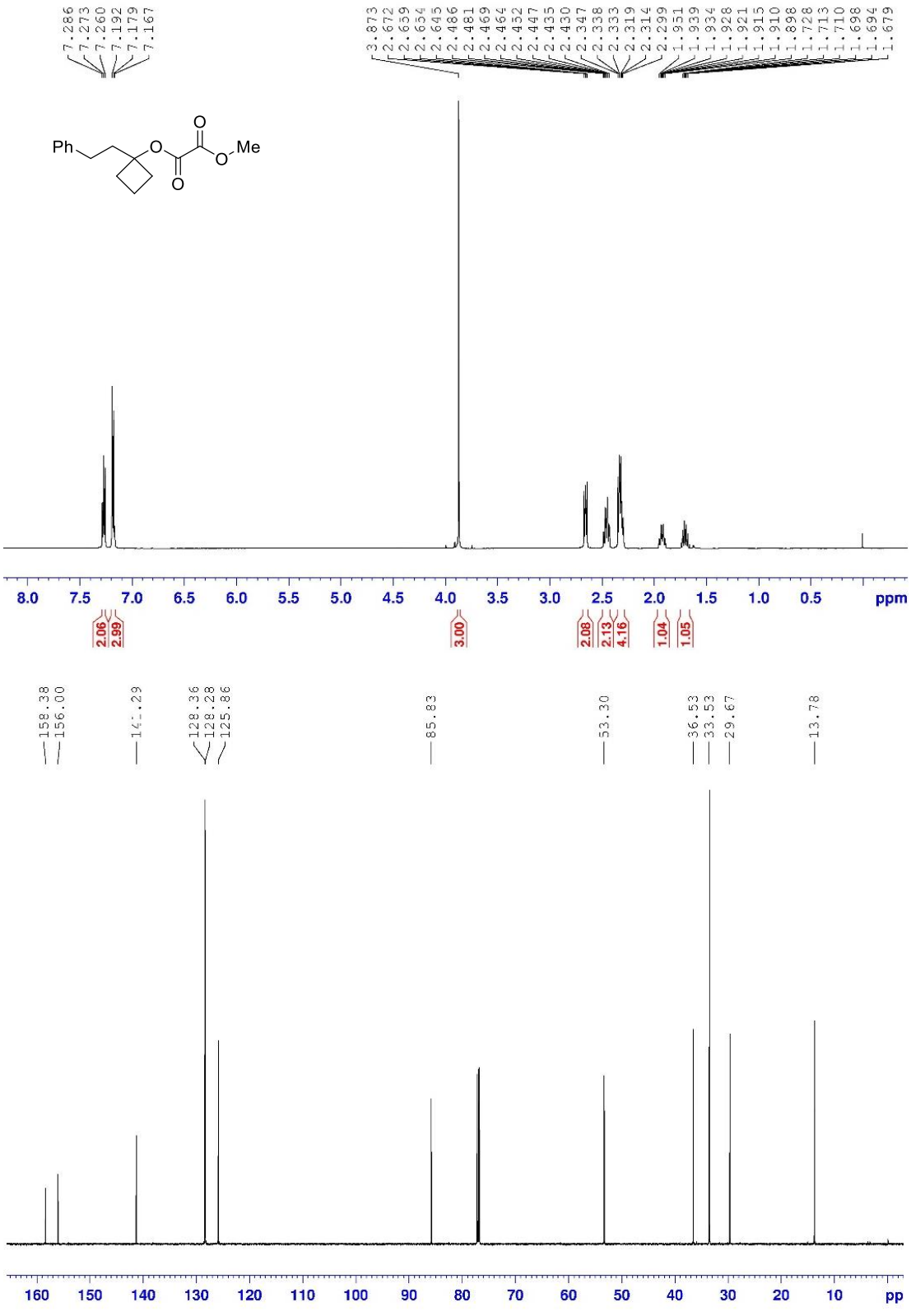
80
70
60
50
40
30
20
10
ppm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7.179
7.167
3.873
2.672
2.659
2.654
2.645
2.486
2.481
2.469
2.464
2.452
2.447
2.435
2.430
2.347
2.338
2.333
2.319
2.314
2.299
1.951
1.939
1.934
1.928
1.921
1.915
1.910
1.898
1.728
1.713
1.710
1.698
1.694
1.679
Ph
O
O
O
O
Me
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
2.06
2.99
3.00
2.08
2.13
4.16
1.04
1.05
158.38
156.00
141.29
128.36
128.28
125.86
85.83
53.30
36.53
33.53
29.67
13.78
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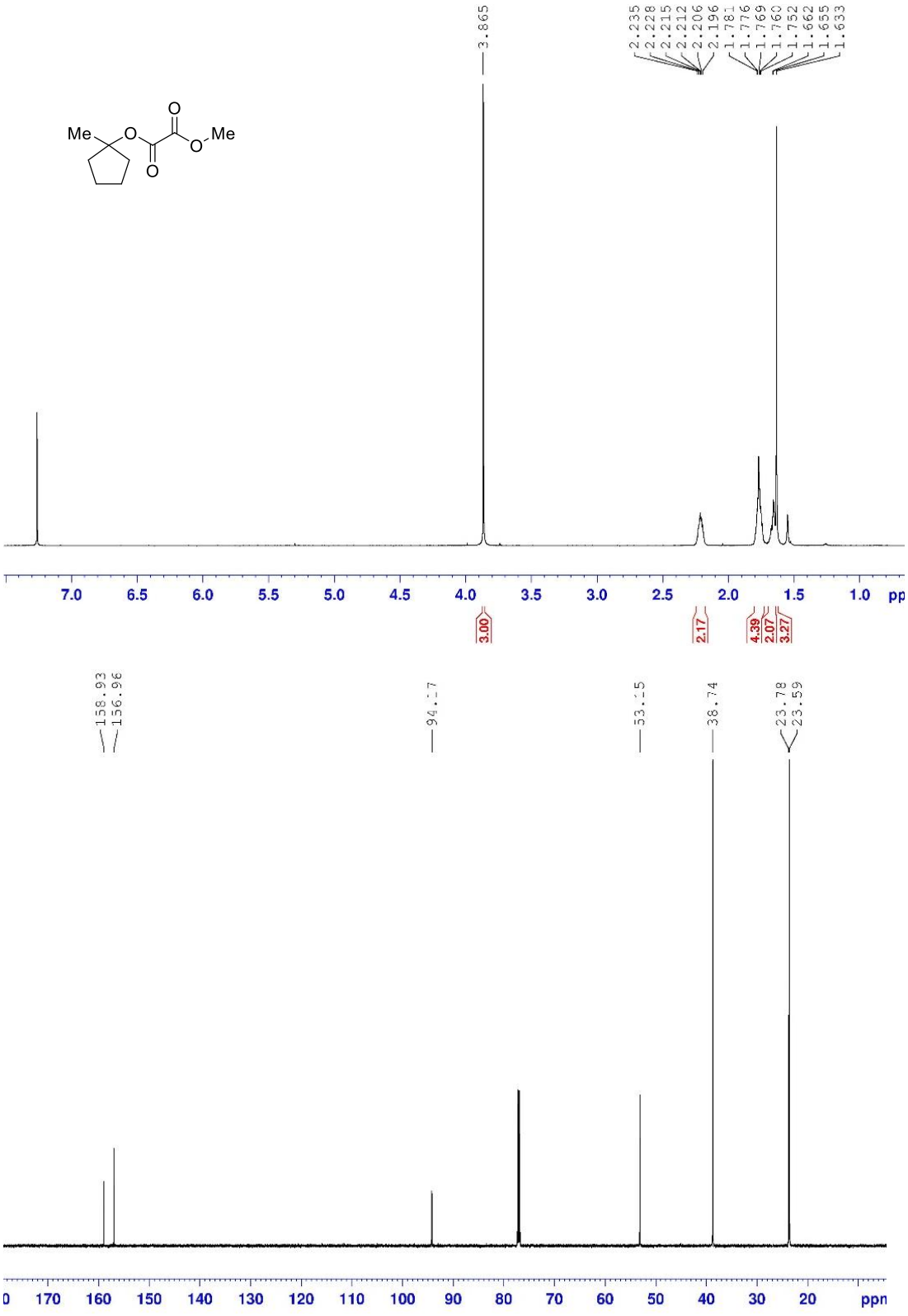
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
pp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O
O
O
O
Me
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2.228
2.215
2.212
2.206
2.196
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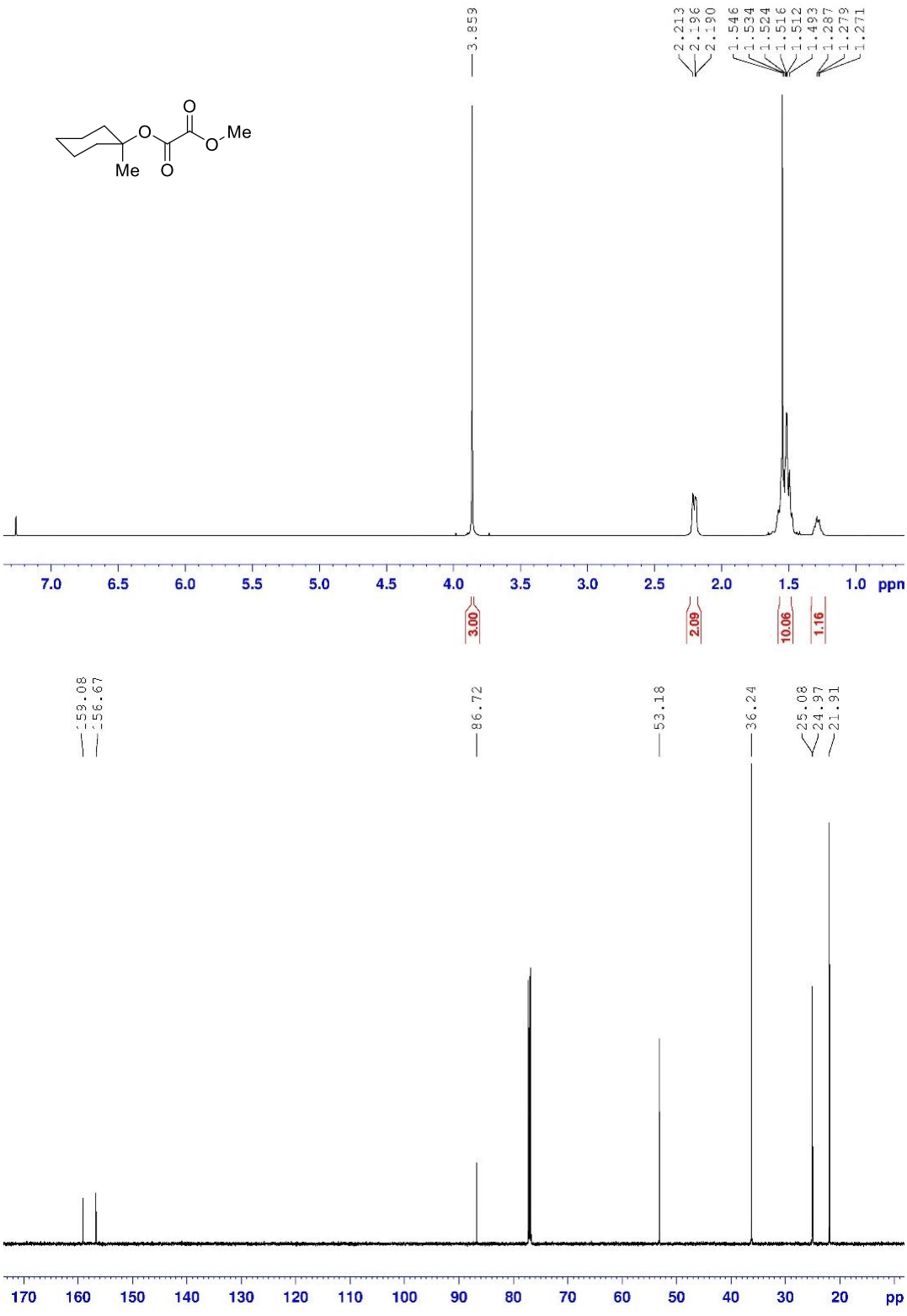
1.776
1.769
1.760
1.752
1.662
1.655
1.633
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
pp
3.00
2.17
4.39
2.07
3.27
158.93
156.96
94.17
53.15
38.74
23.78
23.59
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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1.516
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1.287
1.279
1.271
O
O
Me
O
Me
O
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
ppm
3.00
2.09
10.06
1.16
159.08
156.67
86.72
53.18
36.24
25.08
24.97
21.91
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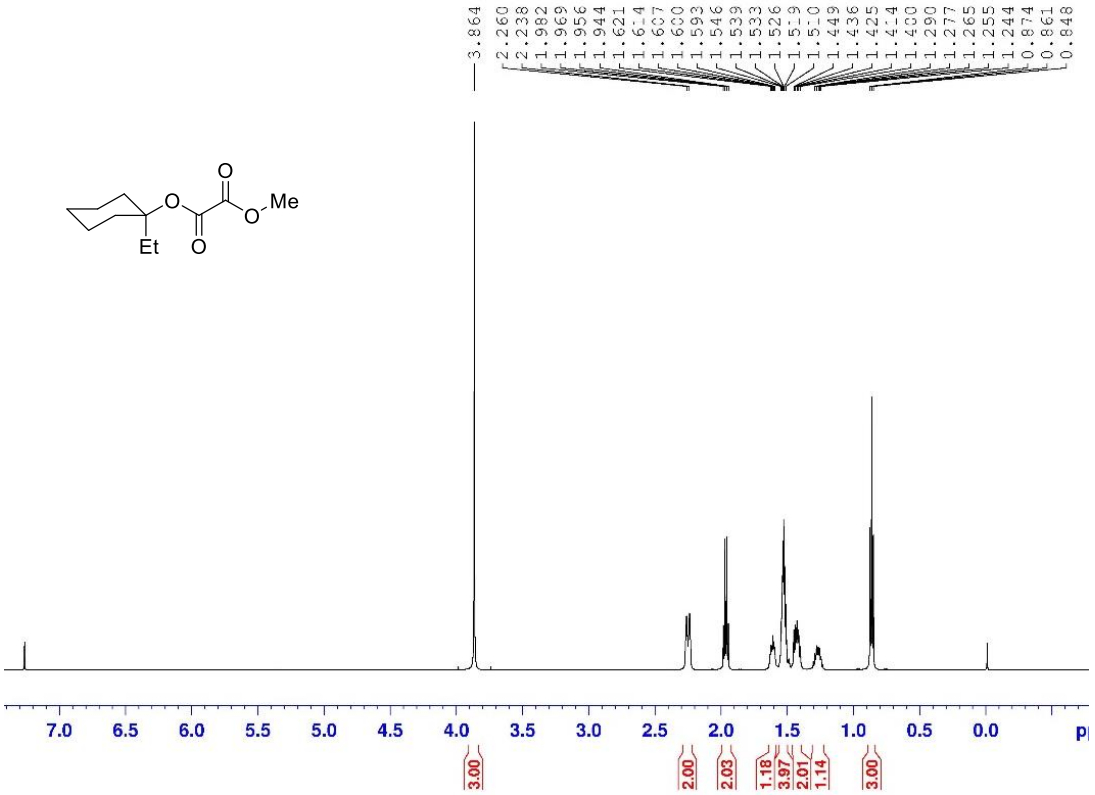
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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1.614
1.607
1.600
1.593
1.546
1.539
1.533
1.526
1.519
1.510
1.449
1.436
1.425
1.414
1.400
1.290
1.277
1.265
1.255
1.244
0.874
0.861
0.848
O
O
Me
O
Et
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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0.0
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1.18
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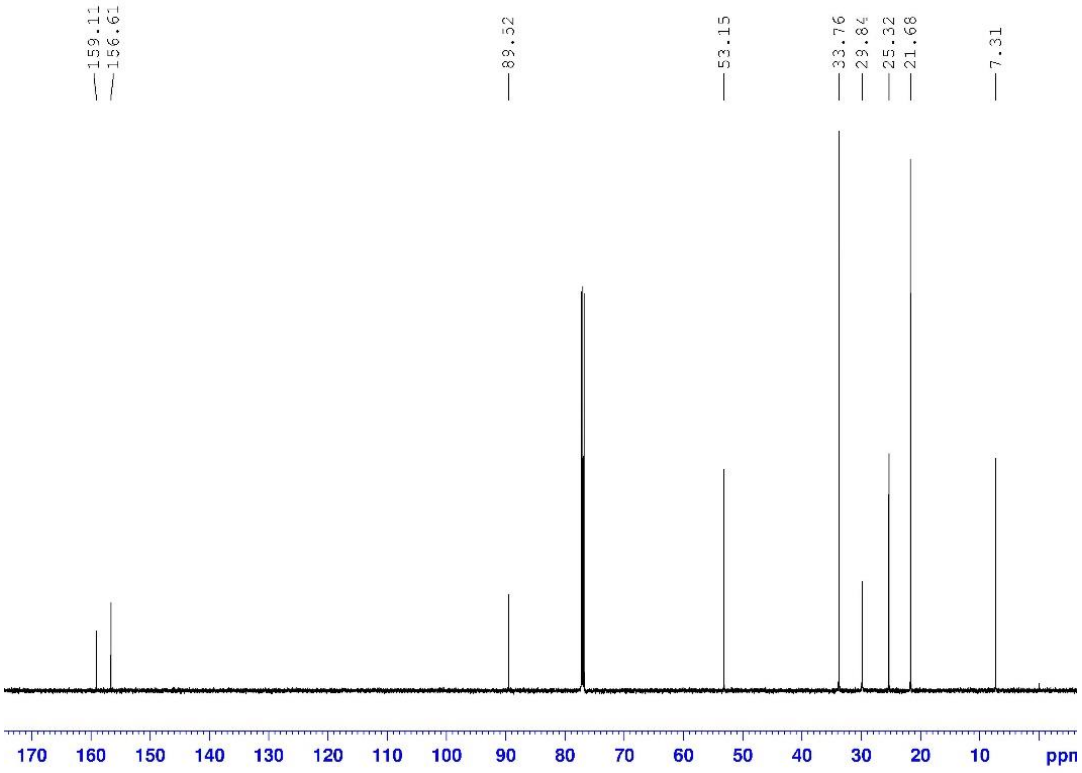
1.14
3.00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156.61
89.32
53.15
33.76
29.84
25.32
21.68
7.31
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150
140
130
120
110
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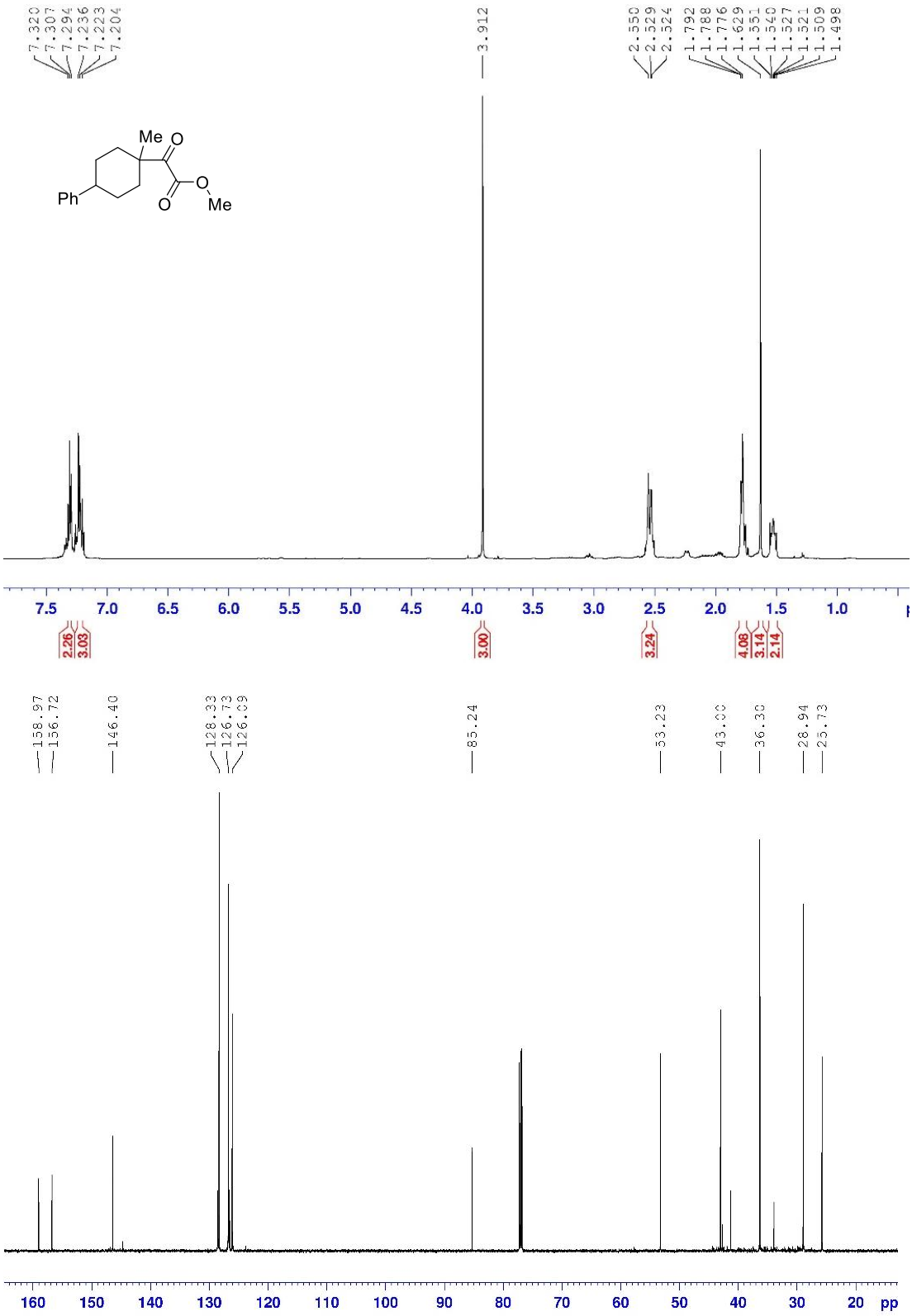
80
70
60
50
40
30
20
10
ppm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7.204
3.912
2.550
2.529
2.324
1.792
1.788
1.776
1.629
1.551
1.540
1.527
1.521
1.509
1.498
Me
O
Ph
O
O
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
2.26
3.03
3.00
3.24
4.08
3.14
2.14
158.97
156.72
146.40
128.33
126.73
126.09
85.24
33.23
43.00
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120
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80
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30
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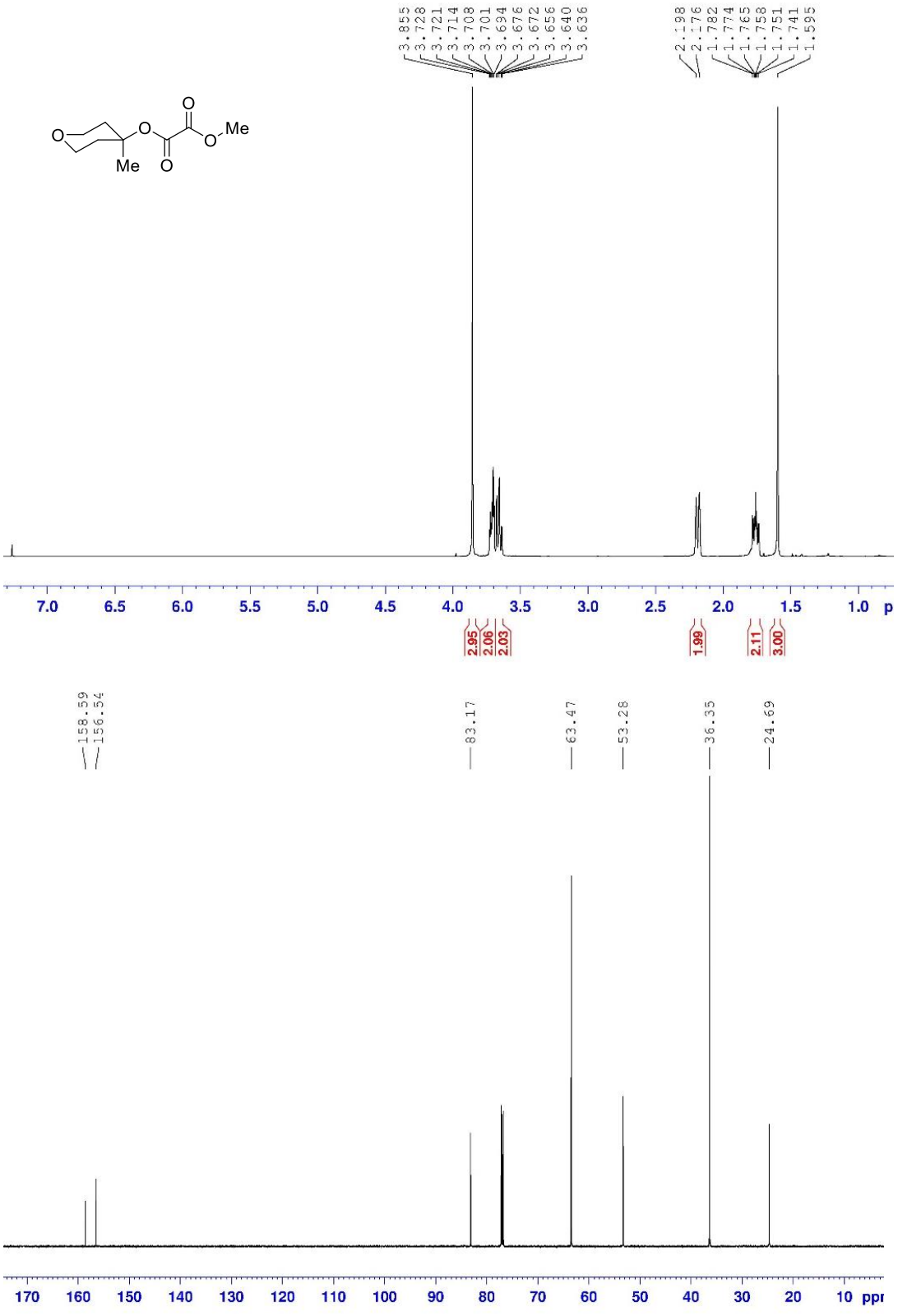
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3.636
2.198
2.176
1.782
1.774
1.765
1.758
1.751
1.741
1.595
Me
Me
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
p
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2.06
2.03
1.99
2.11
3.00
158.59
156.54
83.17
63.47
53.28
36.35
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10
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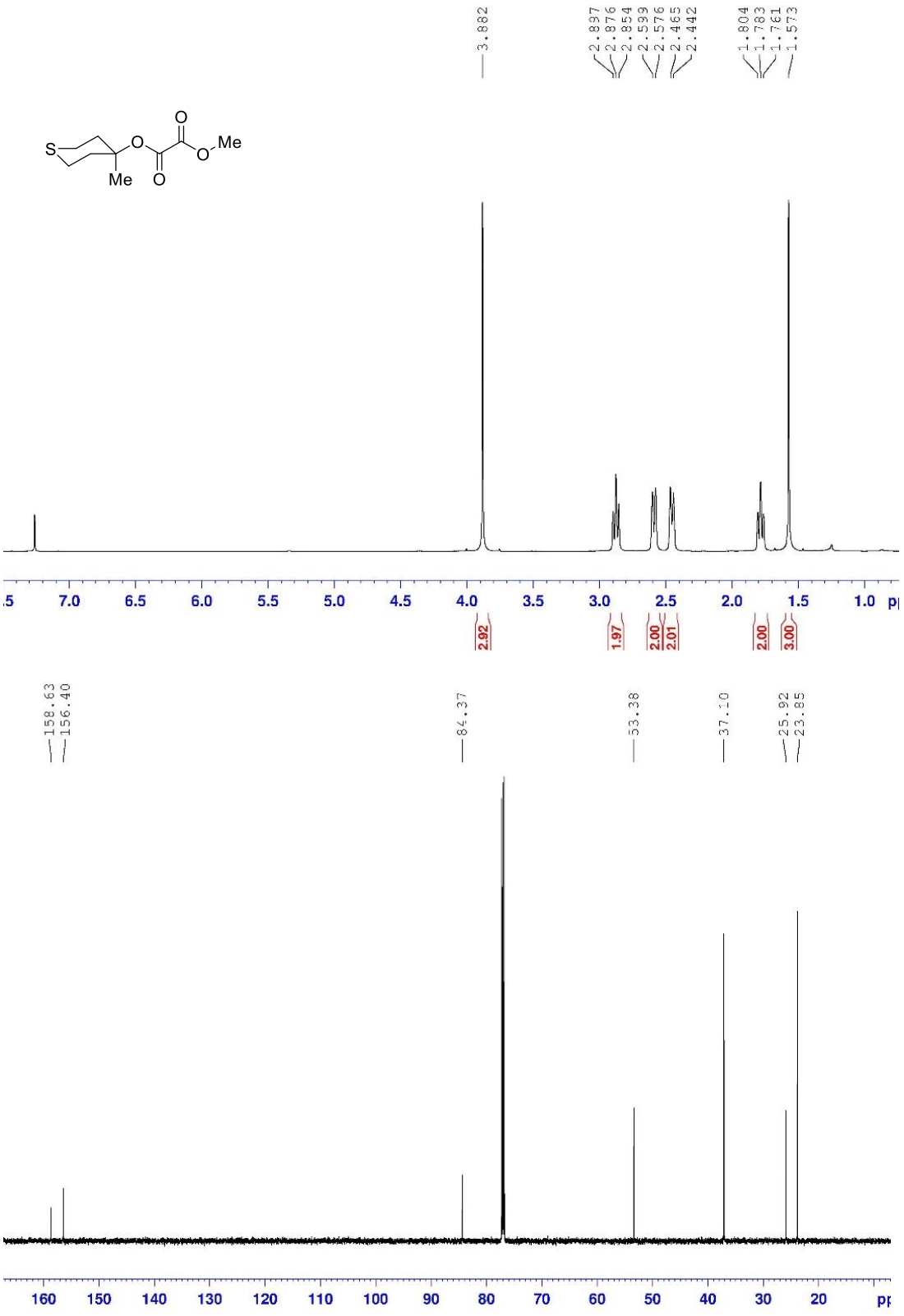
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1.761
1.573
S
O
O
O
O
Me
Me
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
2.92
1.97
2.00
2.01
2.00
3.00
158.63
156.40
84.37
53.38
37.10
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130
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90
80
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50
40
30
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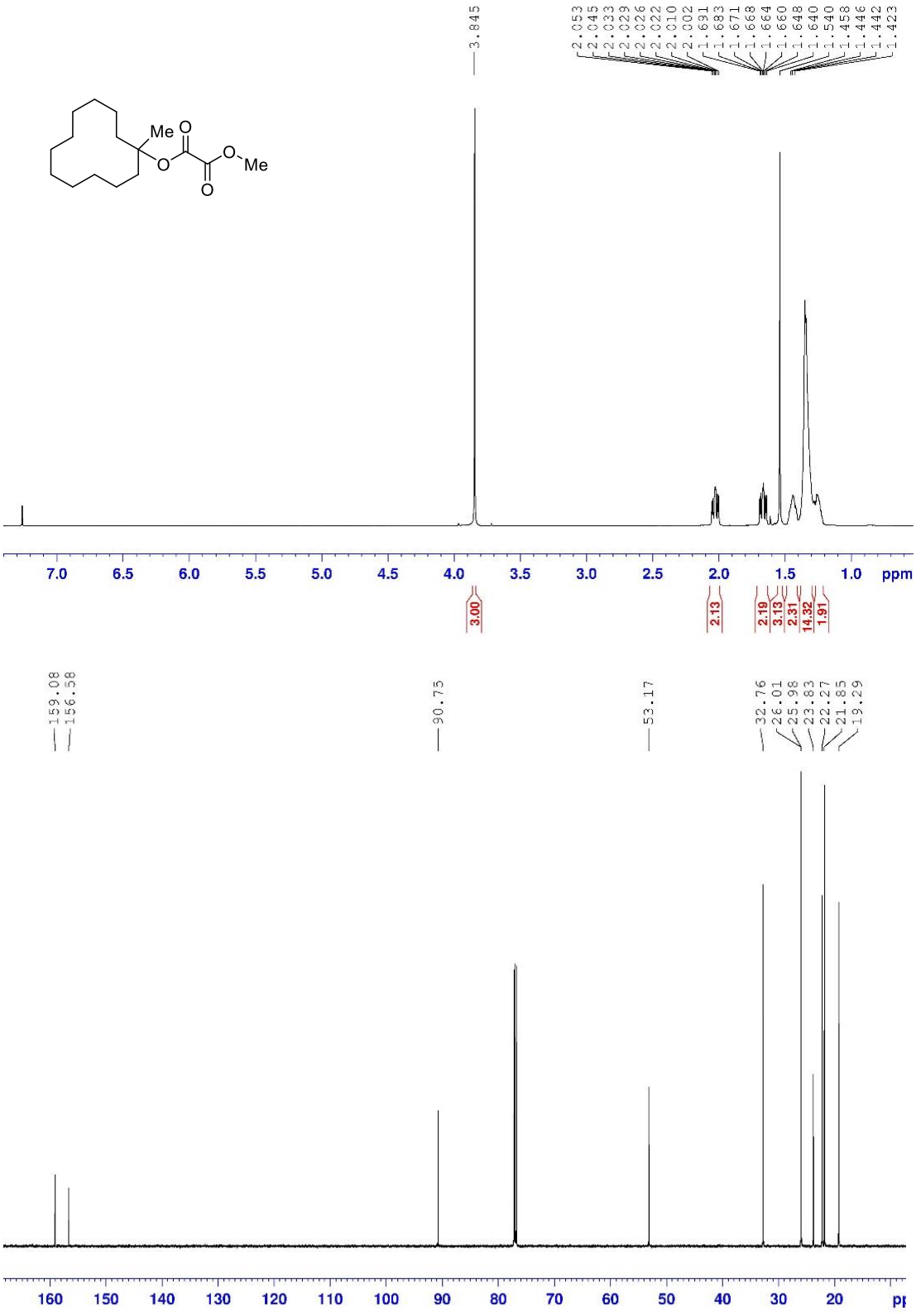
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O
O
Me
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2.033
2.029
2.026
2.022
2.010
2.002
1.691
1.683
1.671
1.668
1.664
1.660
1.648
1.640
1.540
1.458
1.446
1.442
1.423
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.00
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2.19
3.13
2.31
14.32
1.91
159.08
156.58
90.75
53.17
32.76
26.01
25.98
23.83
22.27
21.85
19.29
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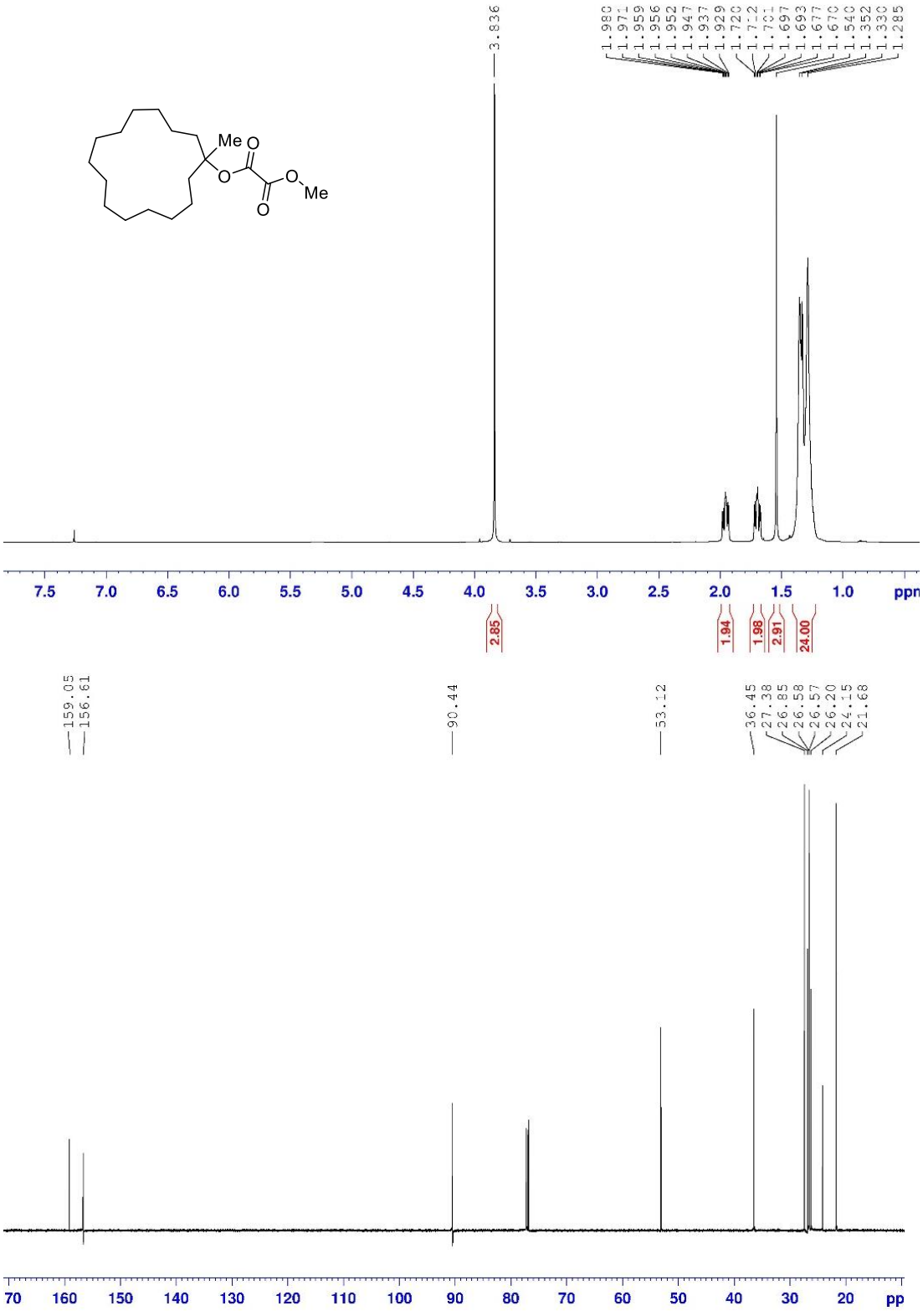
130
120
110
100
90
80
70
60
50
40
30
20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O
Me
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1.952
1.947
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1.720
1.697
1.693
1.677
1.670
1.540
1.352
1.330
1.285
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.85
1.94
1.98
2.91
24.00
159.05
156.61
90.44
53.12
36.45
27.38
26.85
26.58
26.57
26.20
24.15
21.68
70
160
150
140
130
120
110
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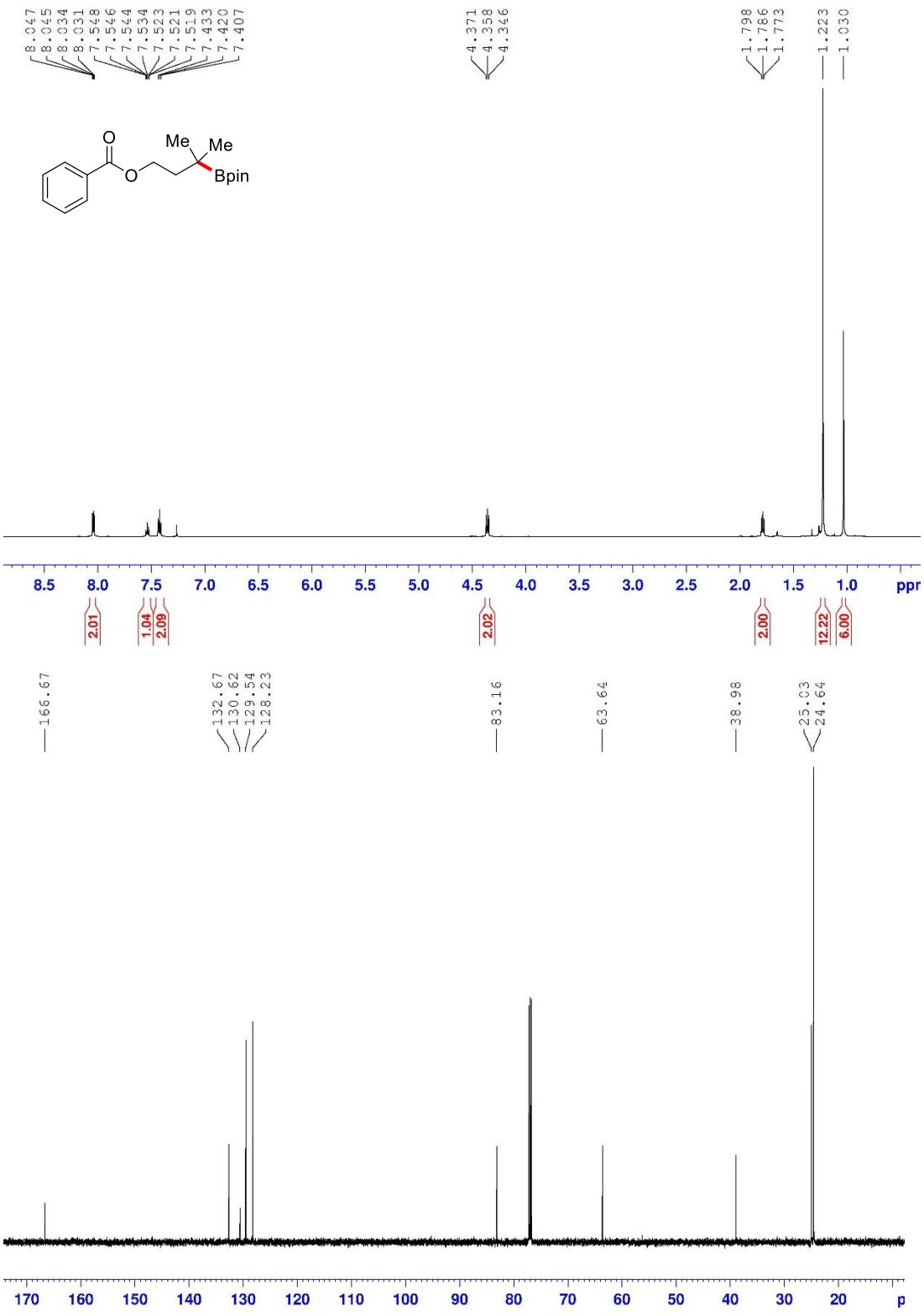
90
80
70
60
50
40
30
20
ppm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7.534
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7.521
7.519
7.433
7.420
7.407
4.371
4.358
4.346
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1.786
1.773
1.223
1.030
O
O
Me
Me
Bpin
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.04
2.09
2.02
2.00
12.22
6.00
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132.67
130.62
129.54
128.23
83.16
63.64
38.98
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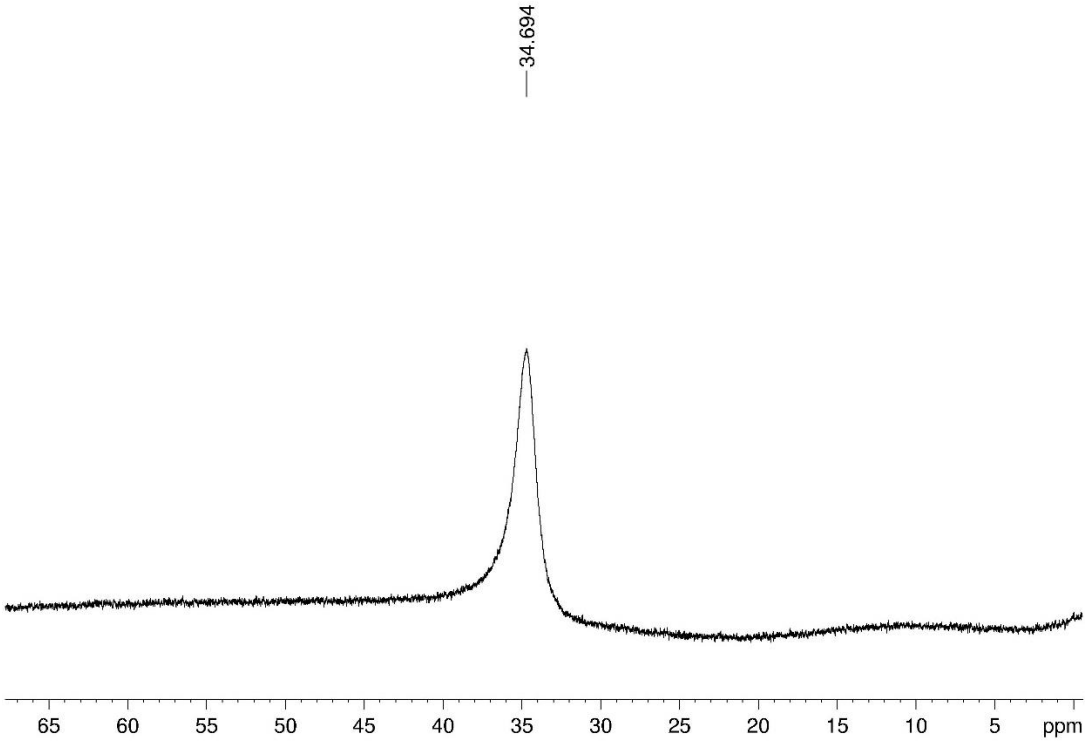
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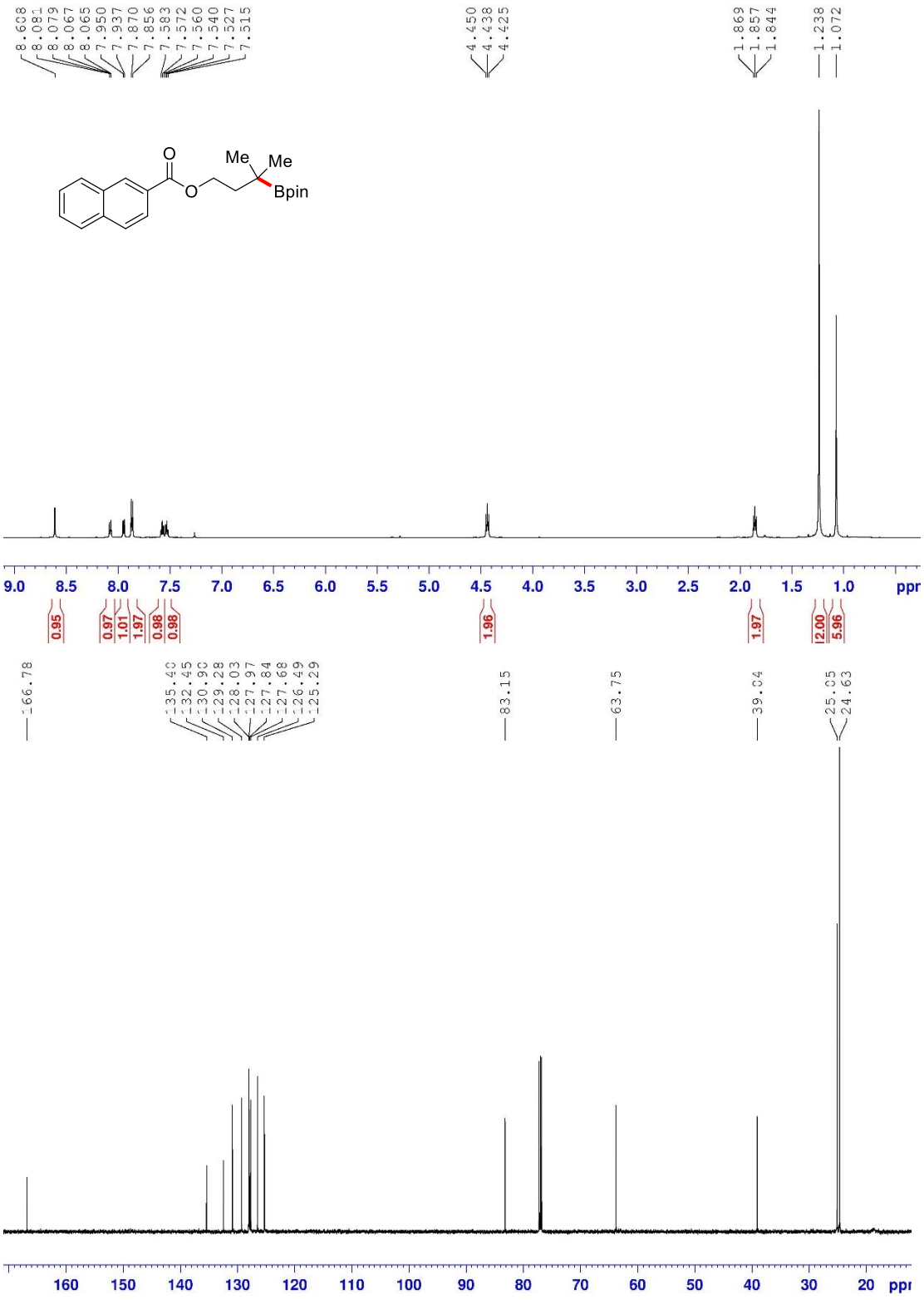
20
15
10
5
ppm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7.527
7.515
4.450
4.438
4.425
1.869
1.857
1.844
1.238
1.072
O
O
Me
Me
Bpin
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8.0
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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0.97
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1.97
0.98
0.98
1.96
1.97
2.00
5.96
166.78
135.40
132.45
130.90
129.28
128.03
127.97
127.84
127.68
126.49
125.29
83.15
63.75
39.04
25.05
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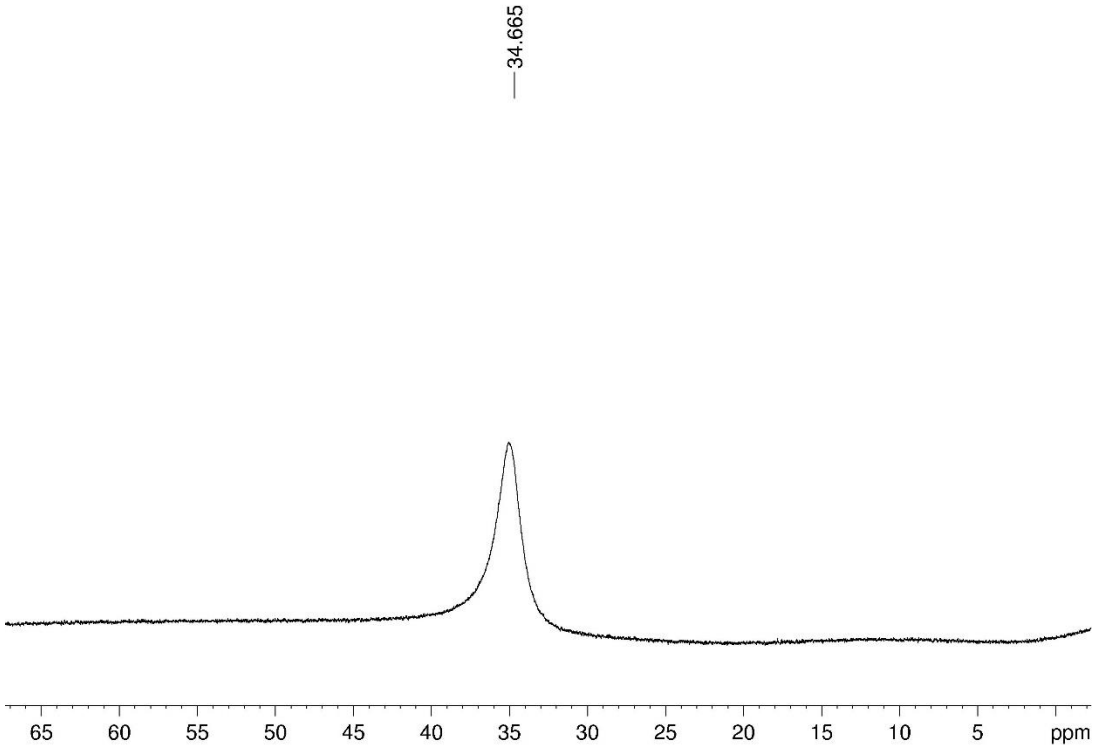
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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20
15
10
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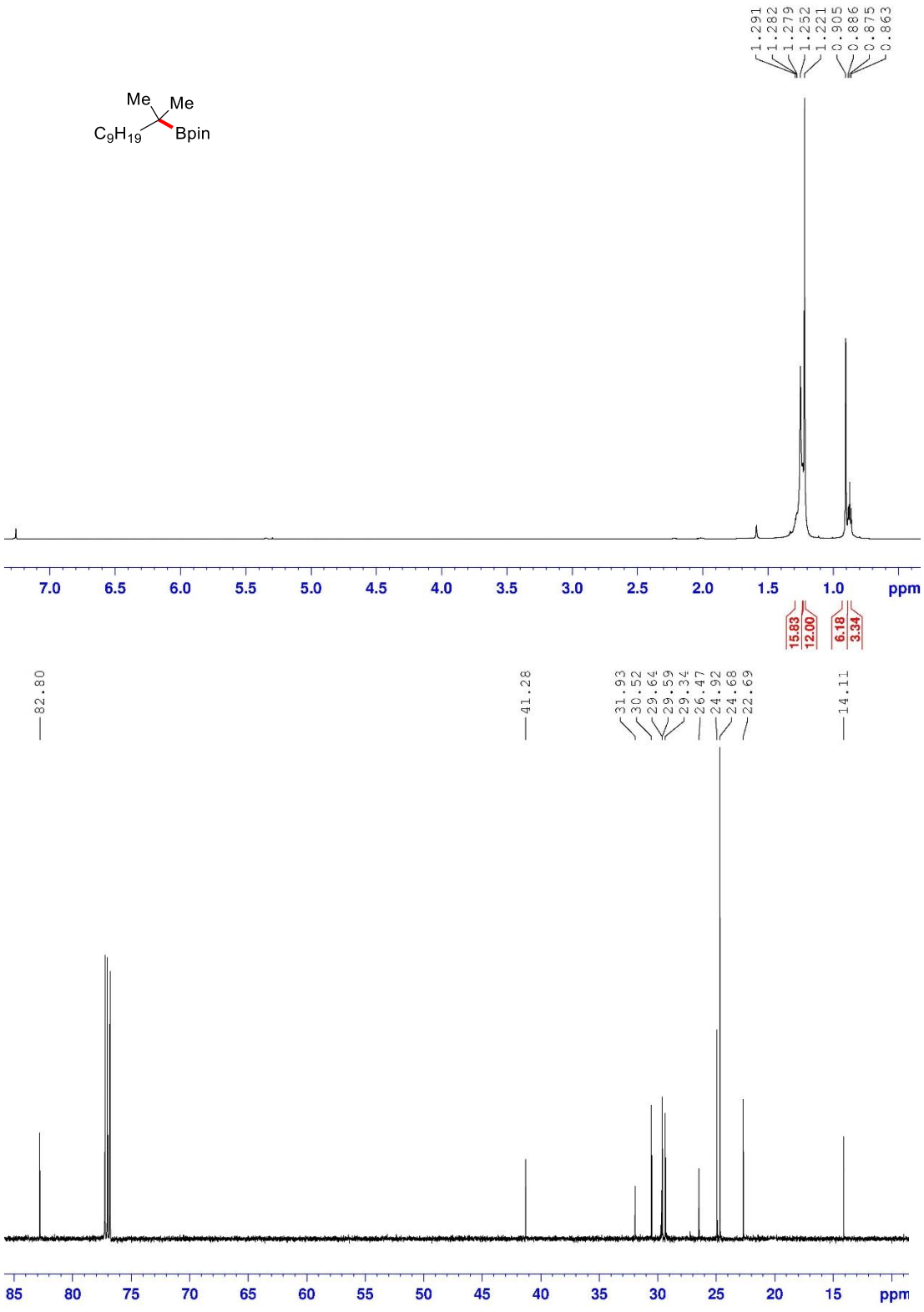
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26.47
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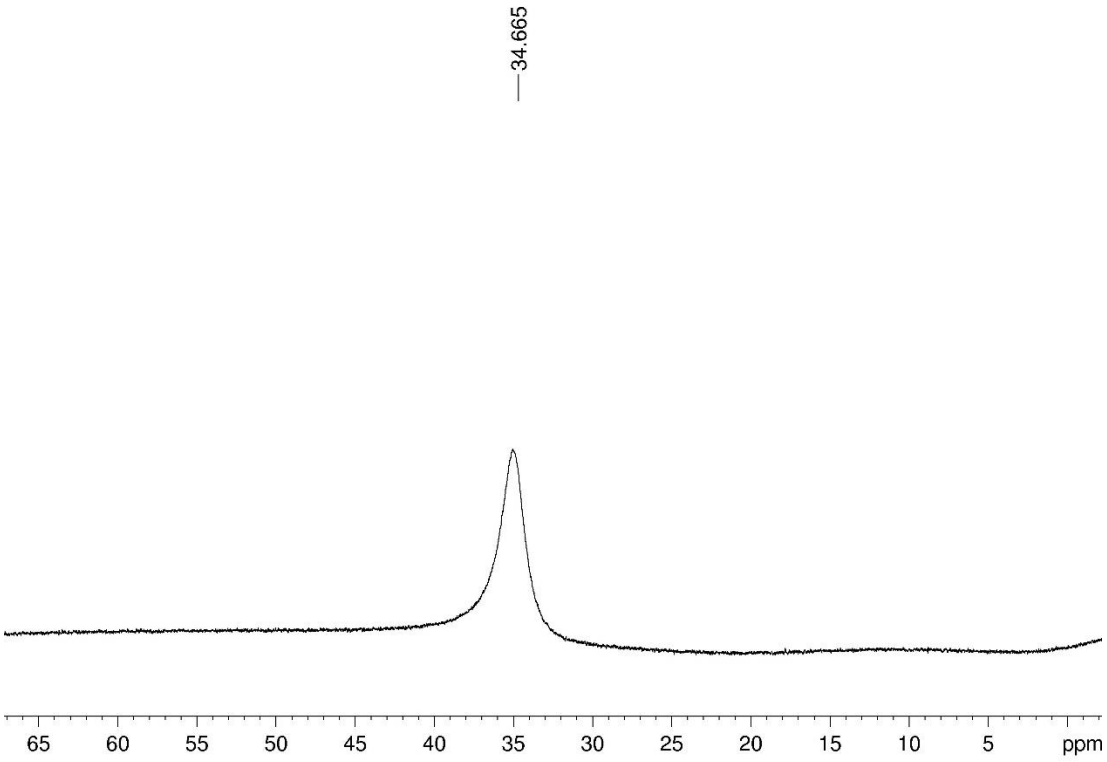
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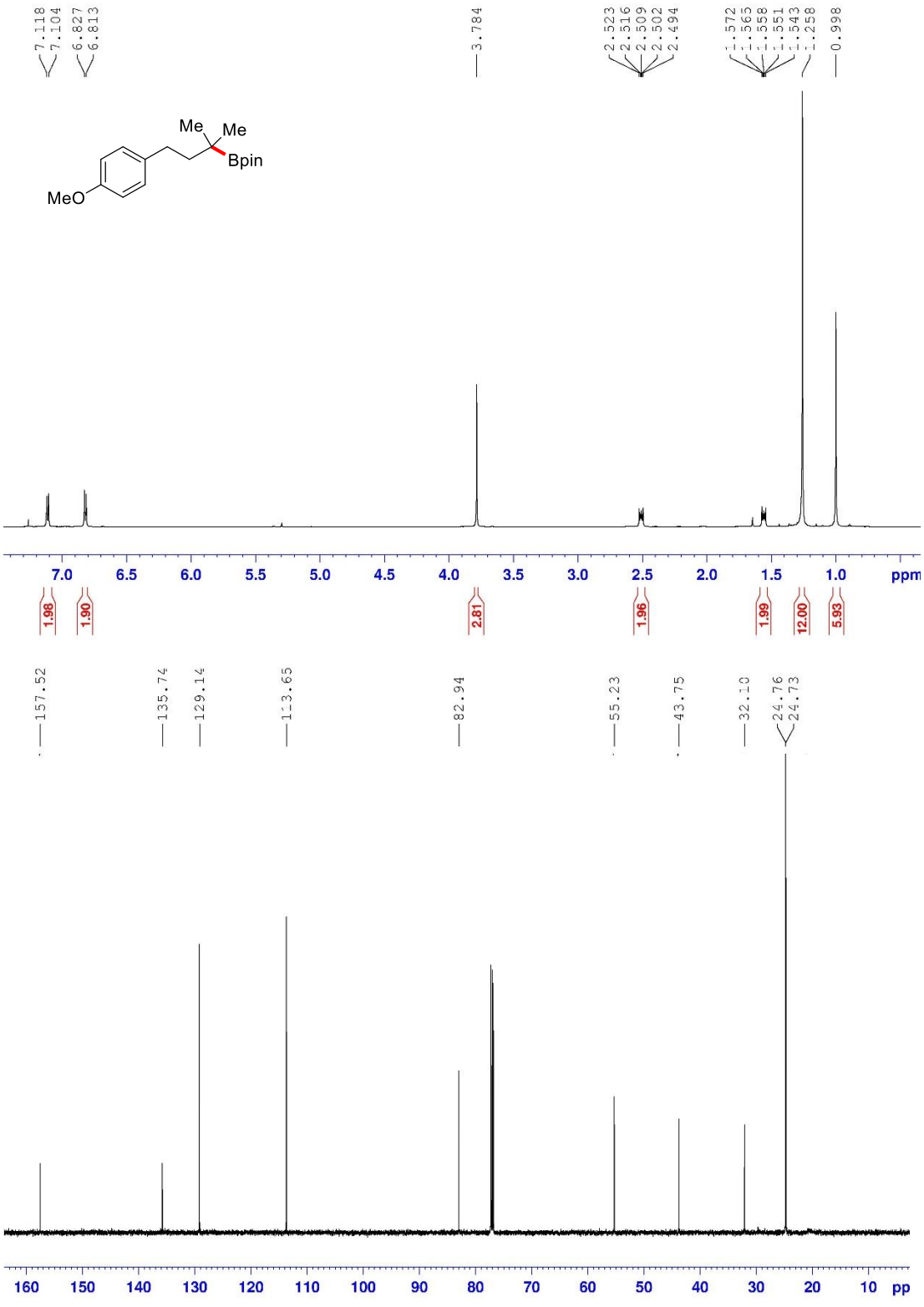
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Me
Bpin
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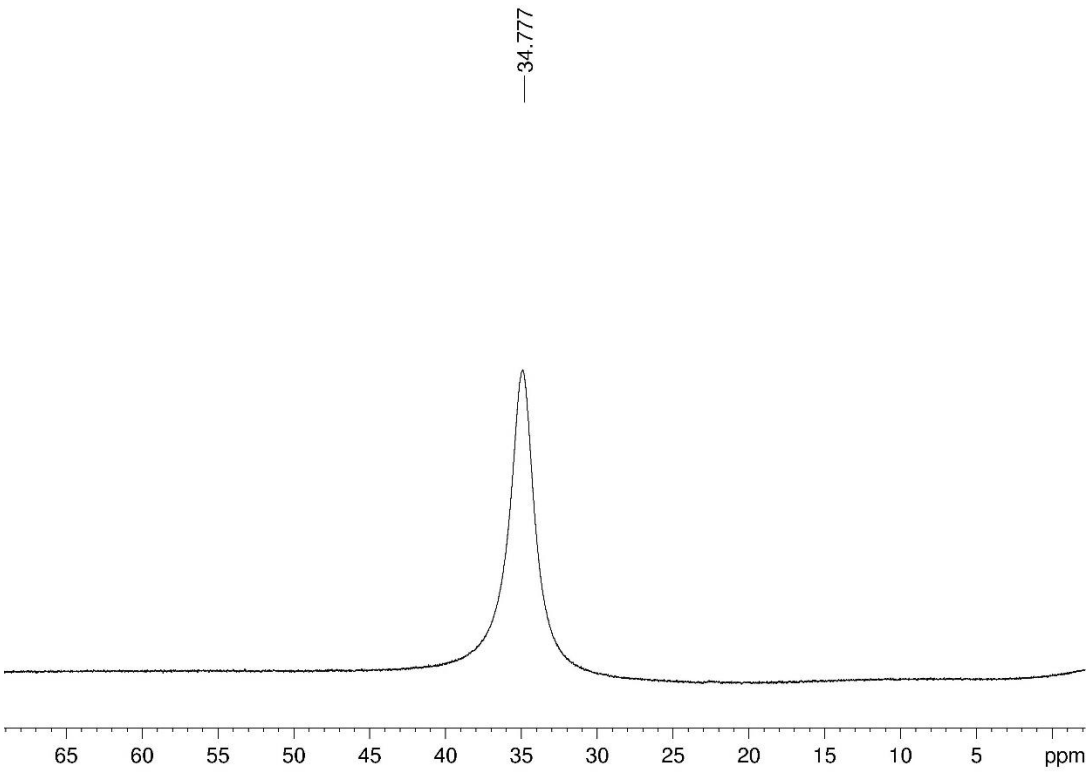
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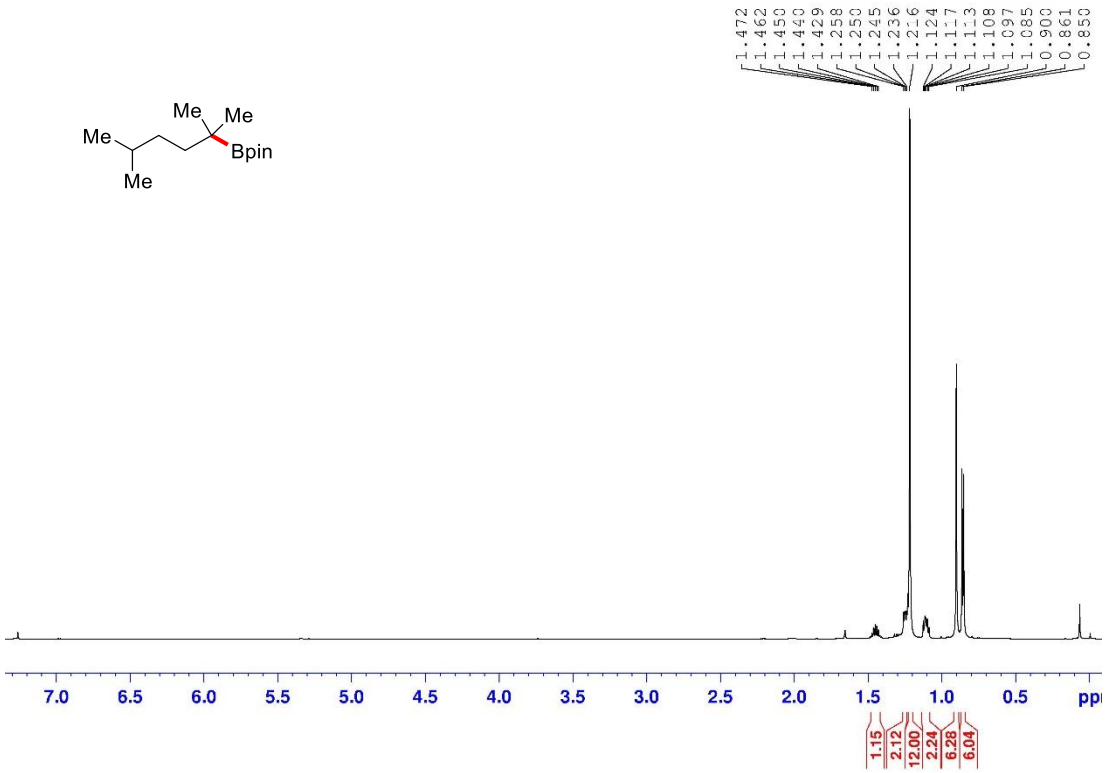
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1.113
1.108
1.097
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0.861
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4.0
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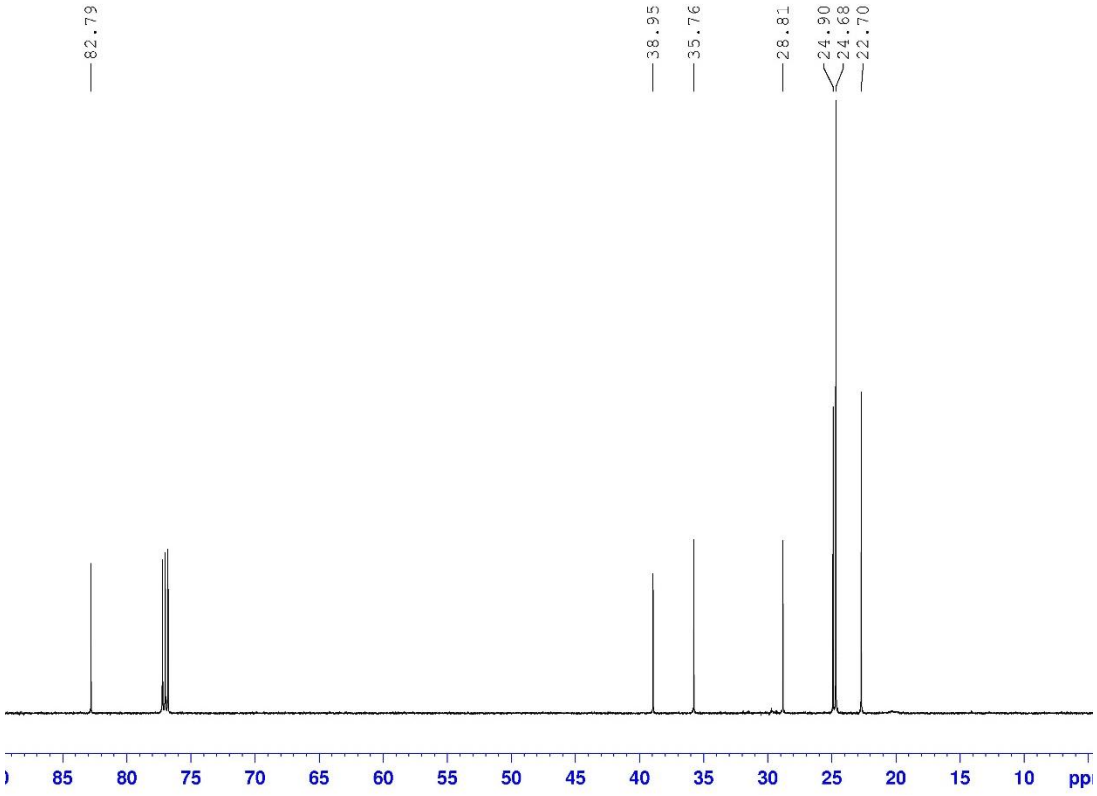
6.04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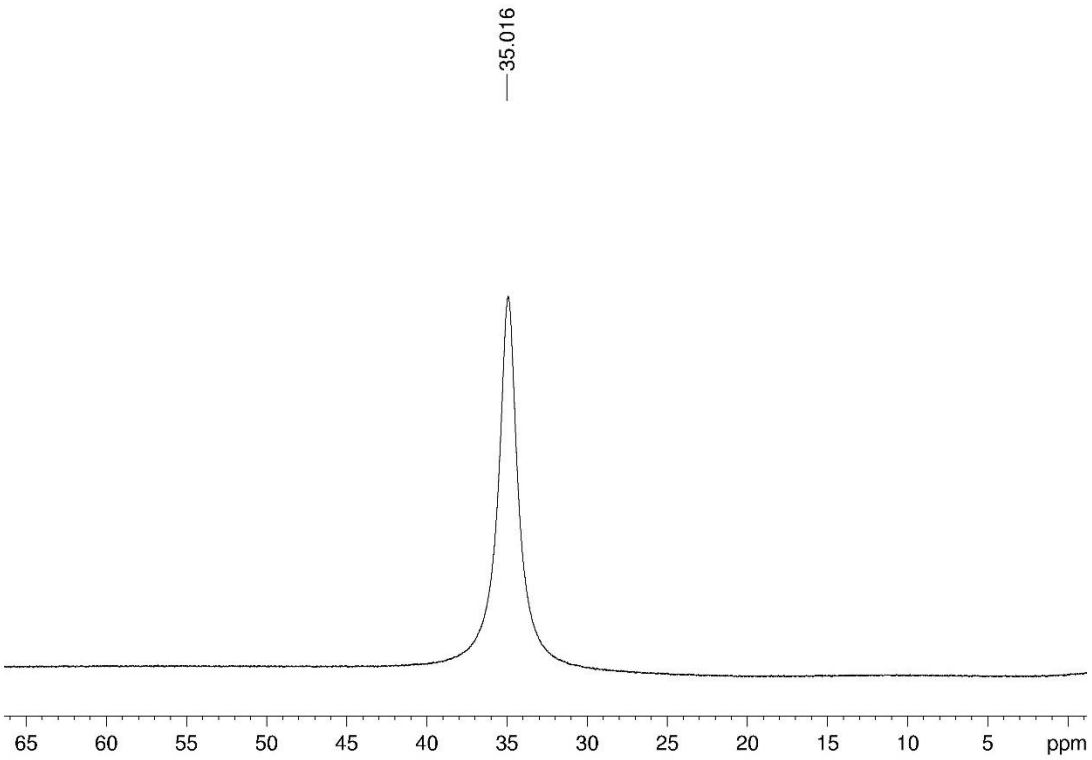
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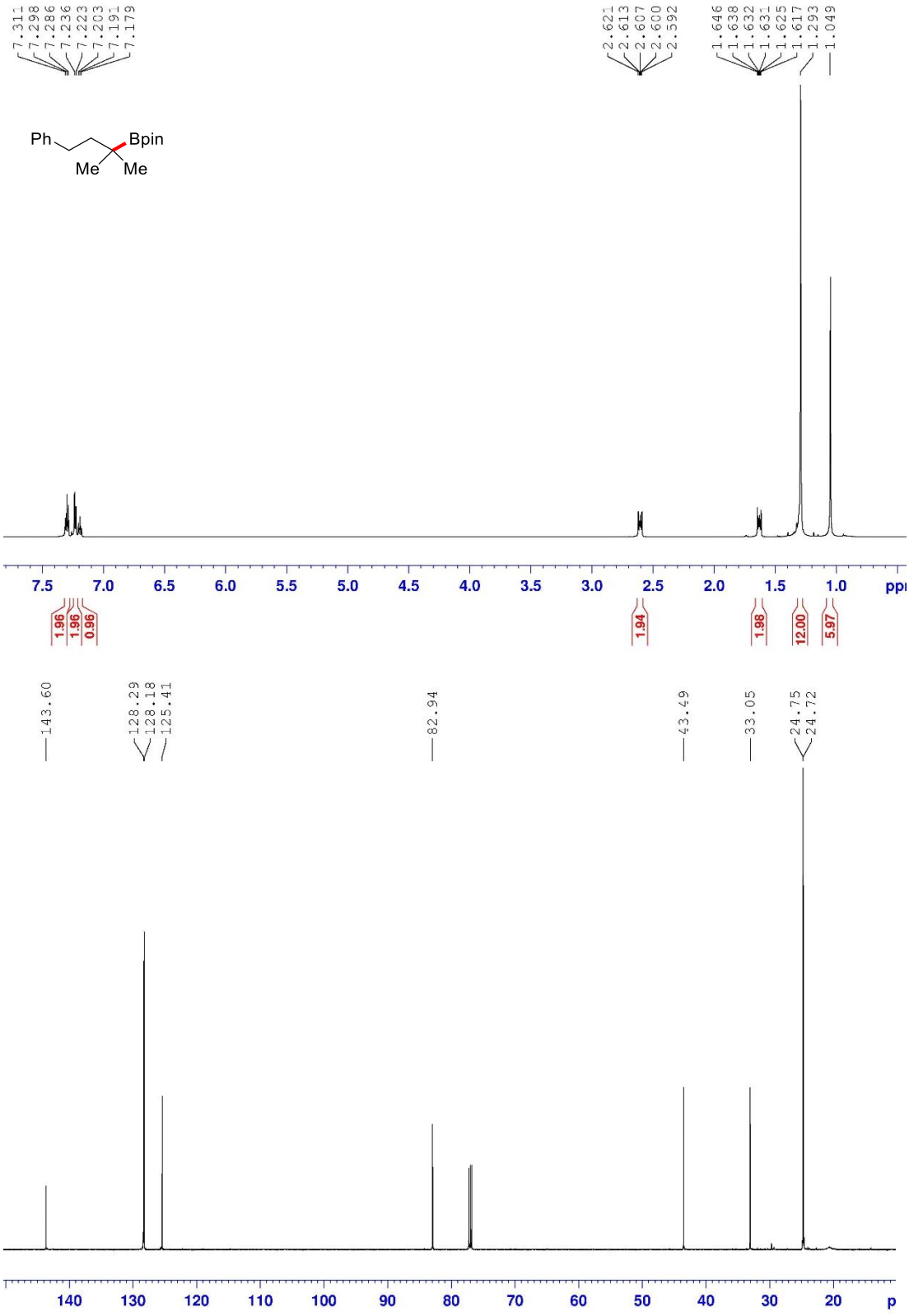
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2.592
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1.638
1.632
1.631
1.625
1.617
1.293
1.049
Ph
Bpin
Me
Me
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6.0
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3.5
3.0
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2.0
1.5
1.0
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1.96
0.96
1.94
1.98
12.00
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143.60
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128.18
125.41
82.94
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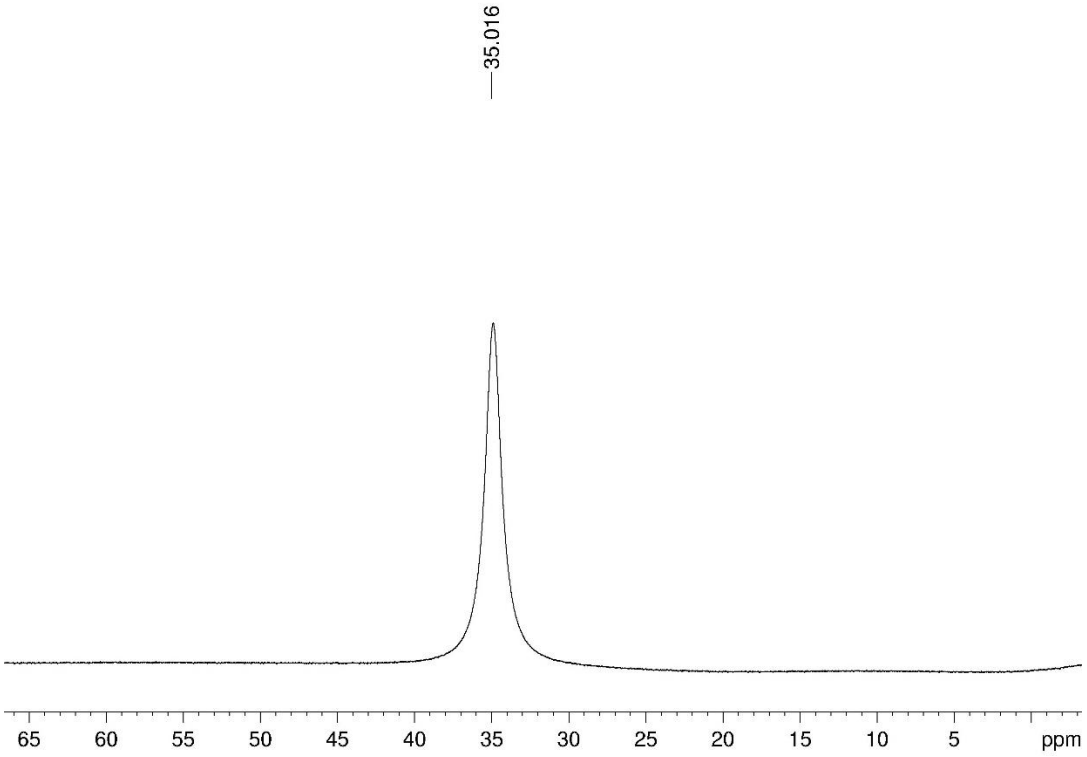
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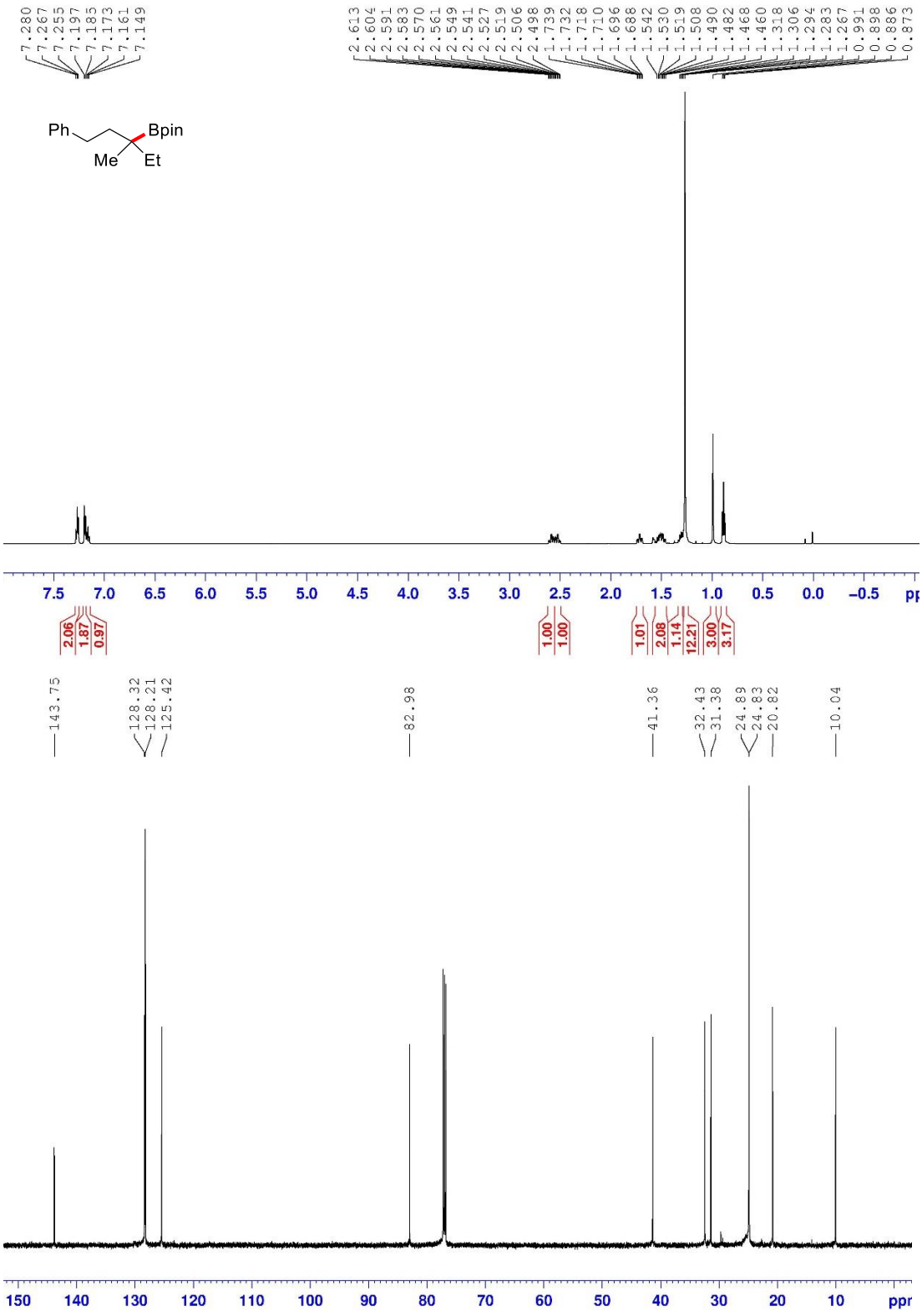
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2.561
2.549
2.541
2.527
2.519
2.506
2.498
1.739
1.732
1.718
1.710
1.696
1.688
1.542
1.530
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1.482
1.468
1.460
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1.306
1.294
1.283
1.267
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0.886
0.873
Ph
Bpin
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Et
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6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
1.5
1.0
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0.0
−0.5
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1.00
1.01
2.08
1.14
12.21
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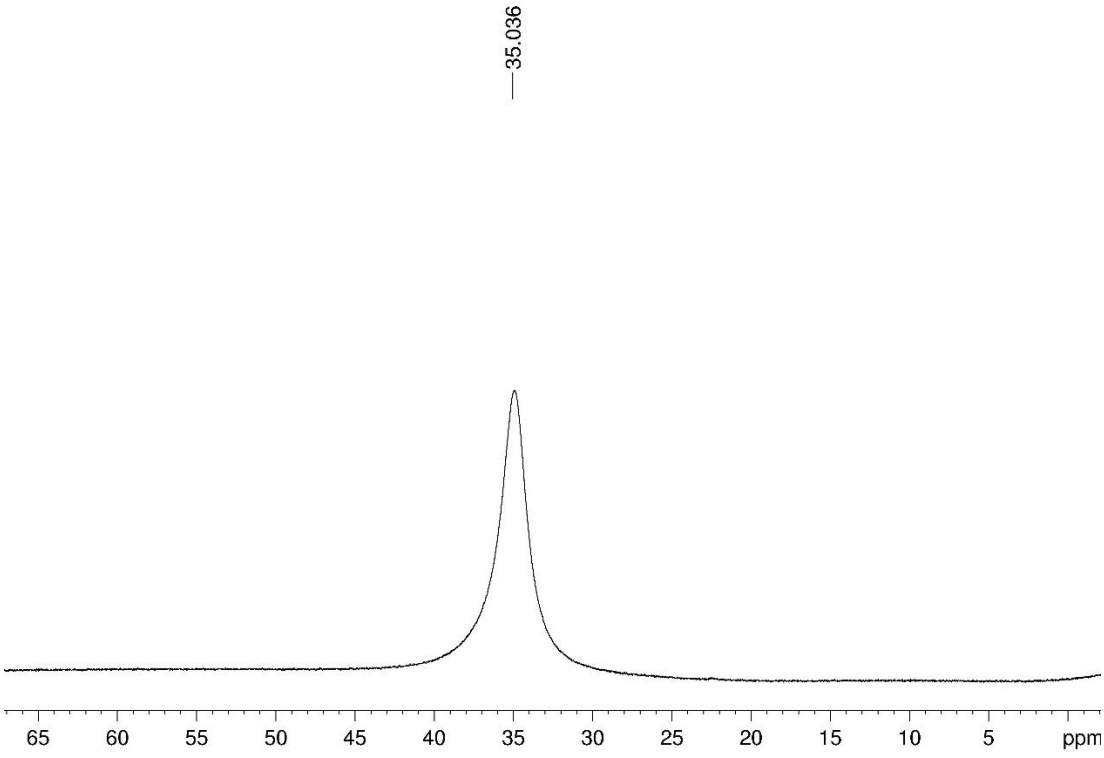
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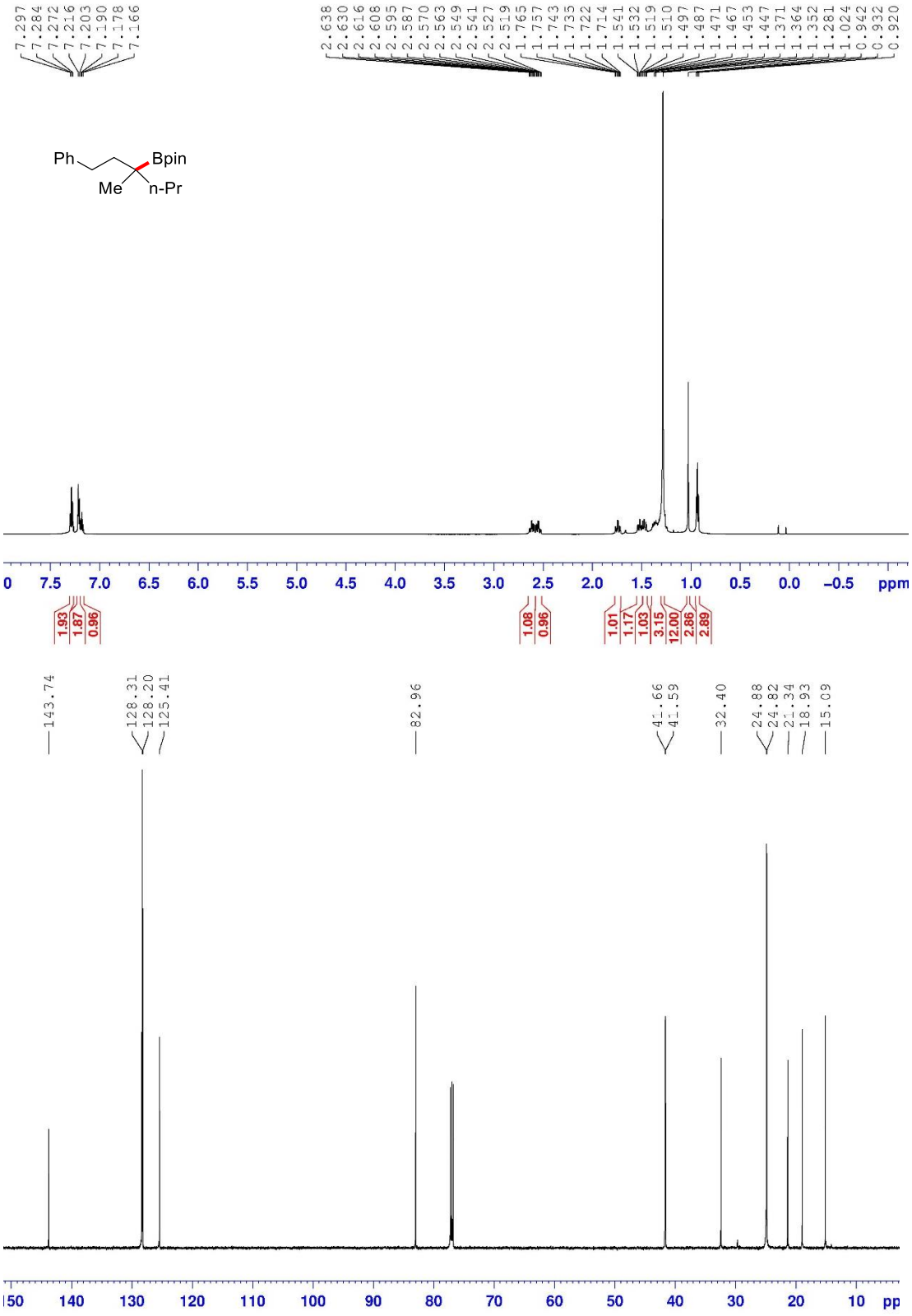
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2.587
2.570
2.563
2.549
2.541
2.527
2.519
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1.757
1.743
1.735
1.722
1.714
1.541
1.532
1.519
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1.447
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0.932
0.920
Ph
Bpin
Me
n-Pr
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1.87
0.96
1.08
0.96
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1.17
1.03
3.15
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2.89
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128.20
125.41
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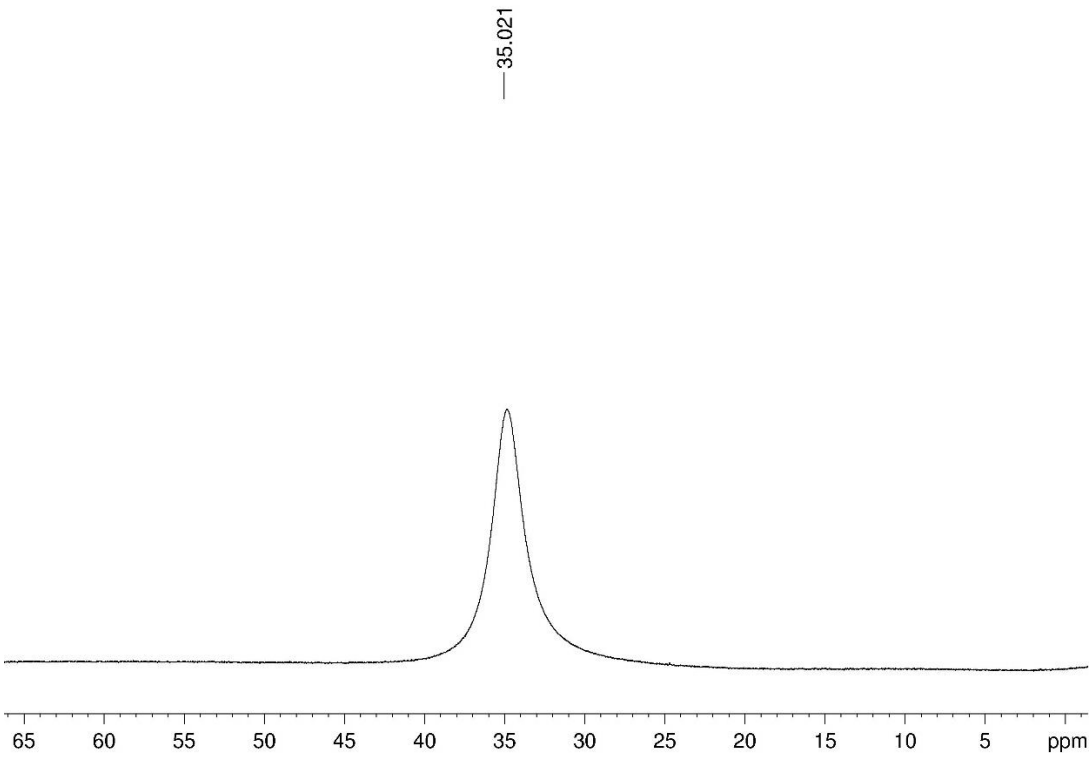
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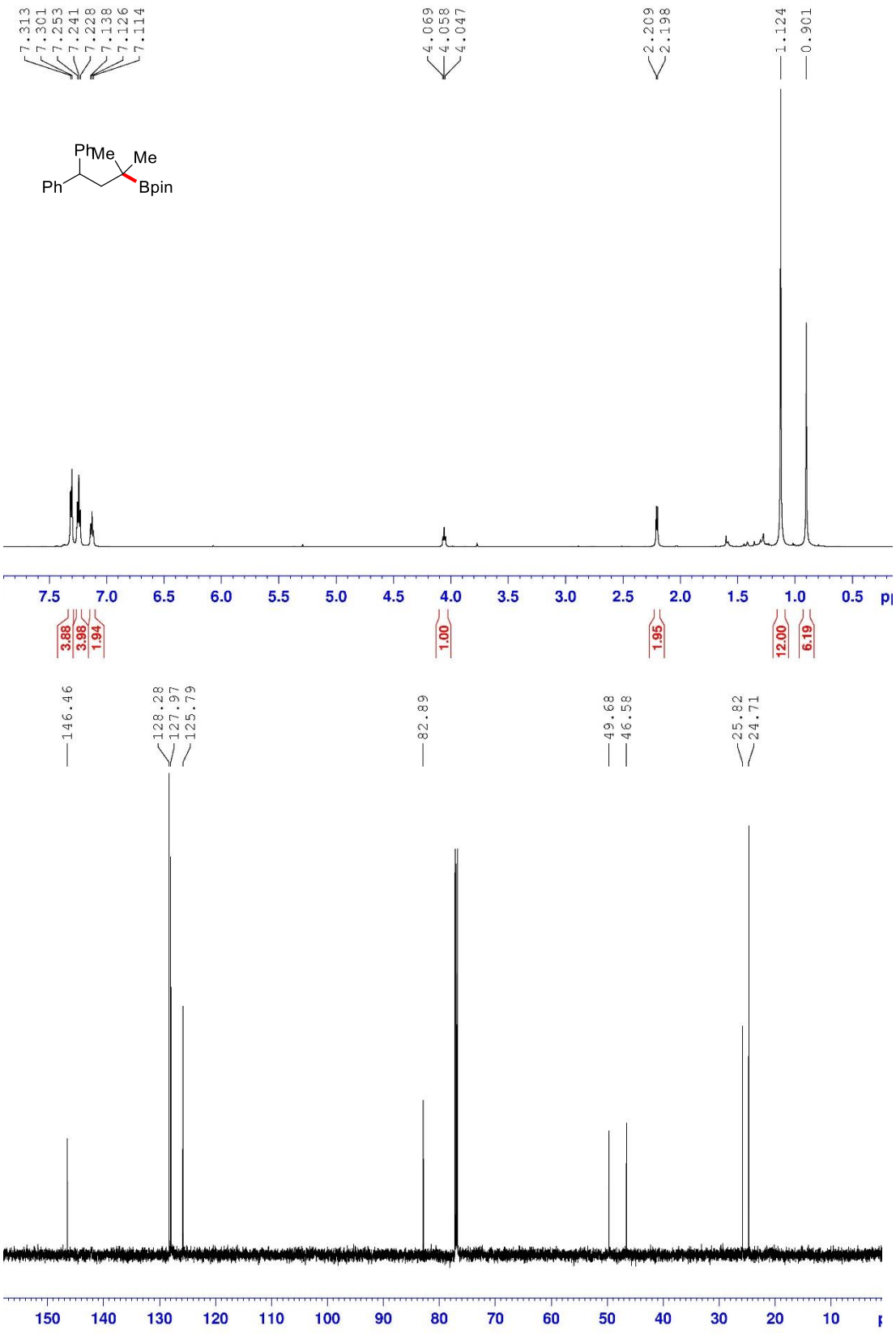
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Me
Me
Ph
Bpin
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5.0
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4.0
3.5
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2.5
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1.00
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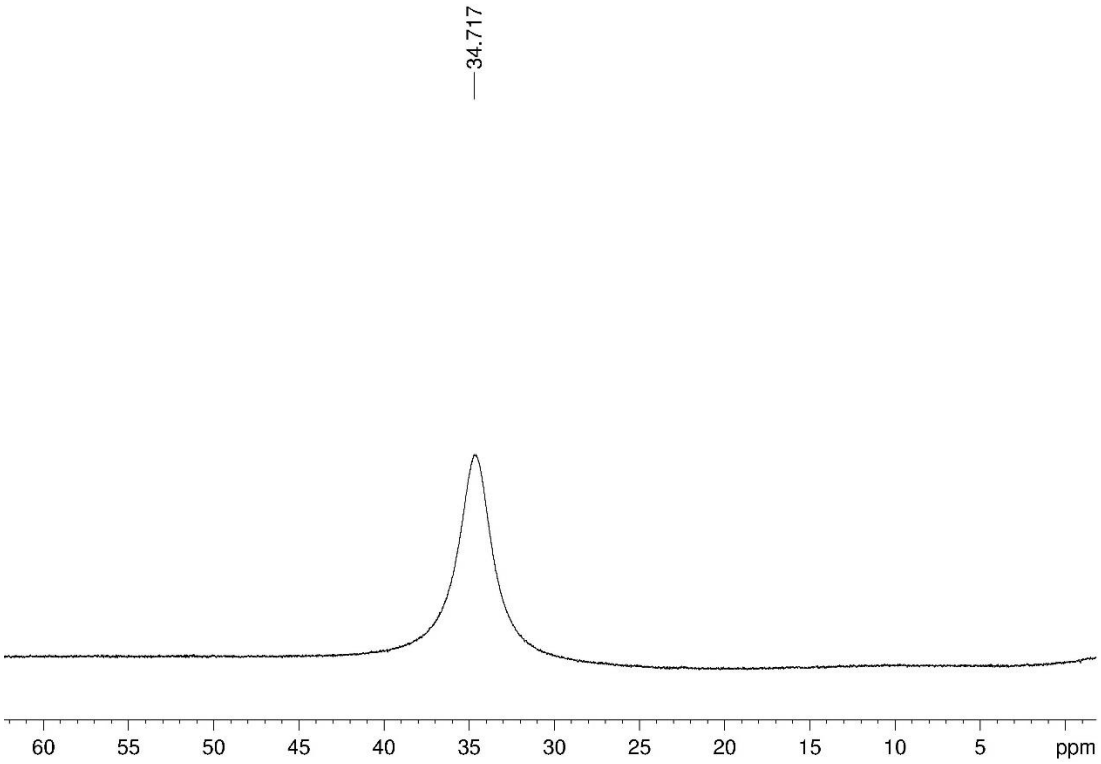
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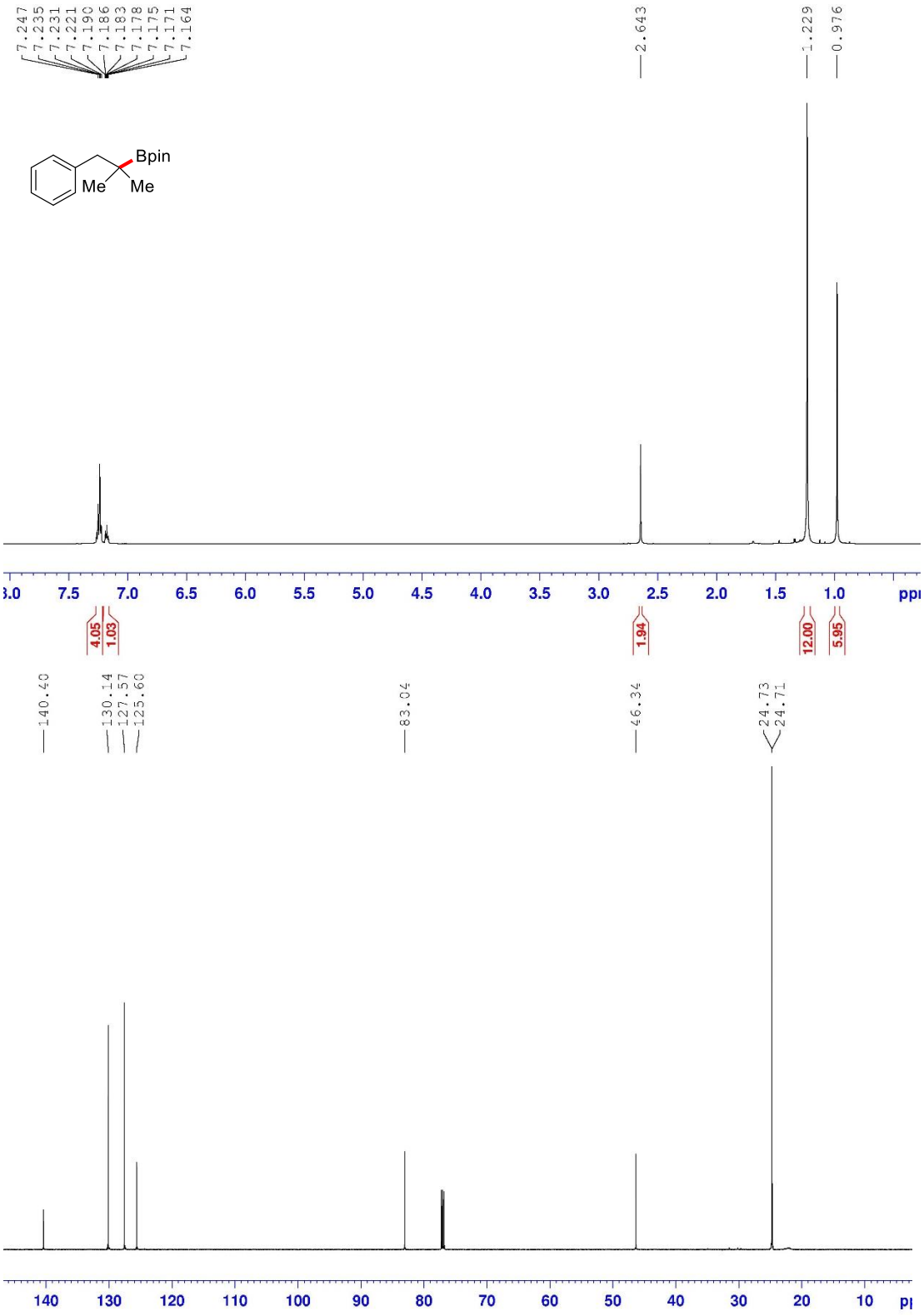
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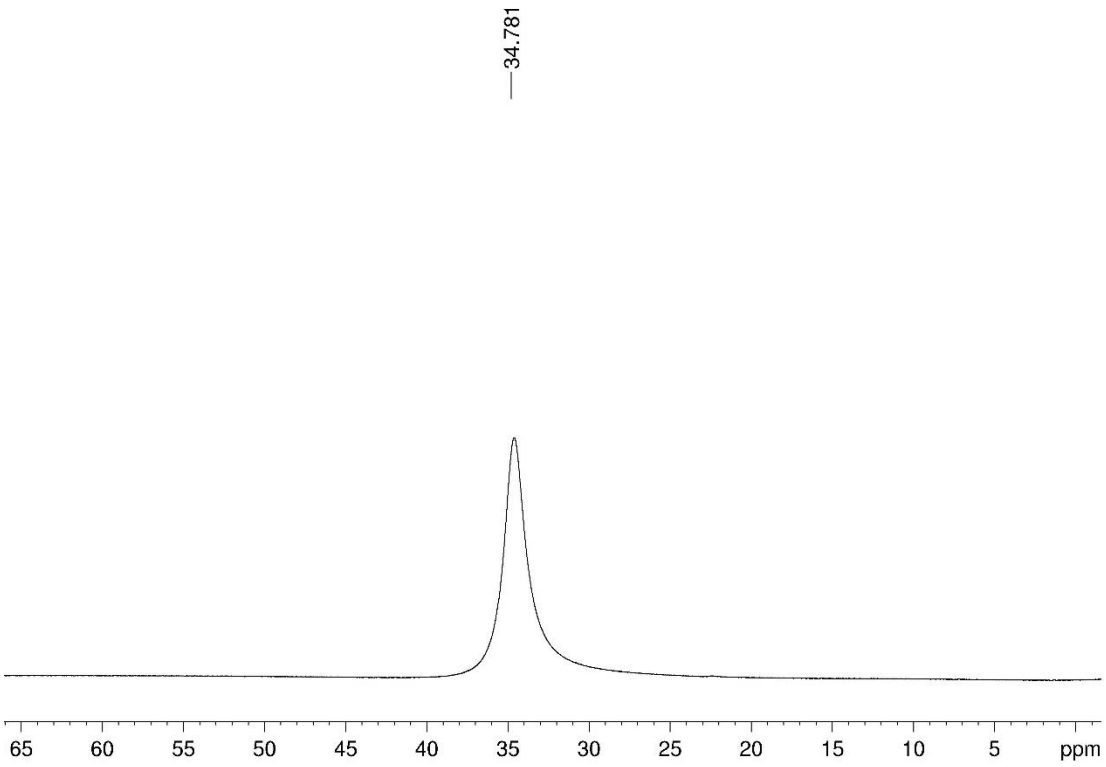
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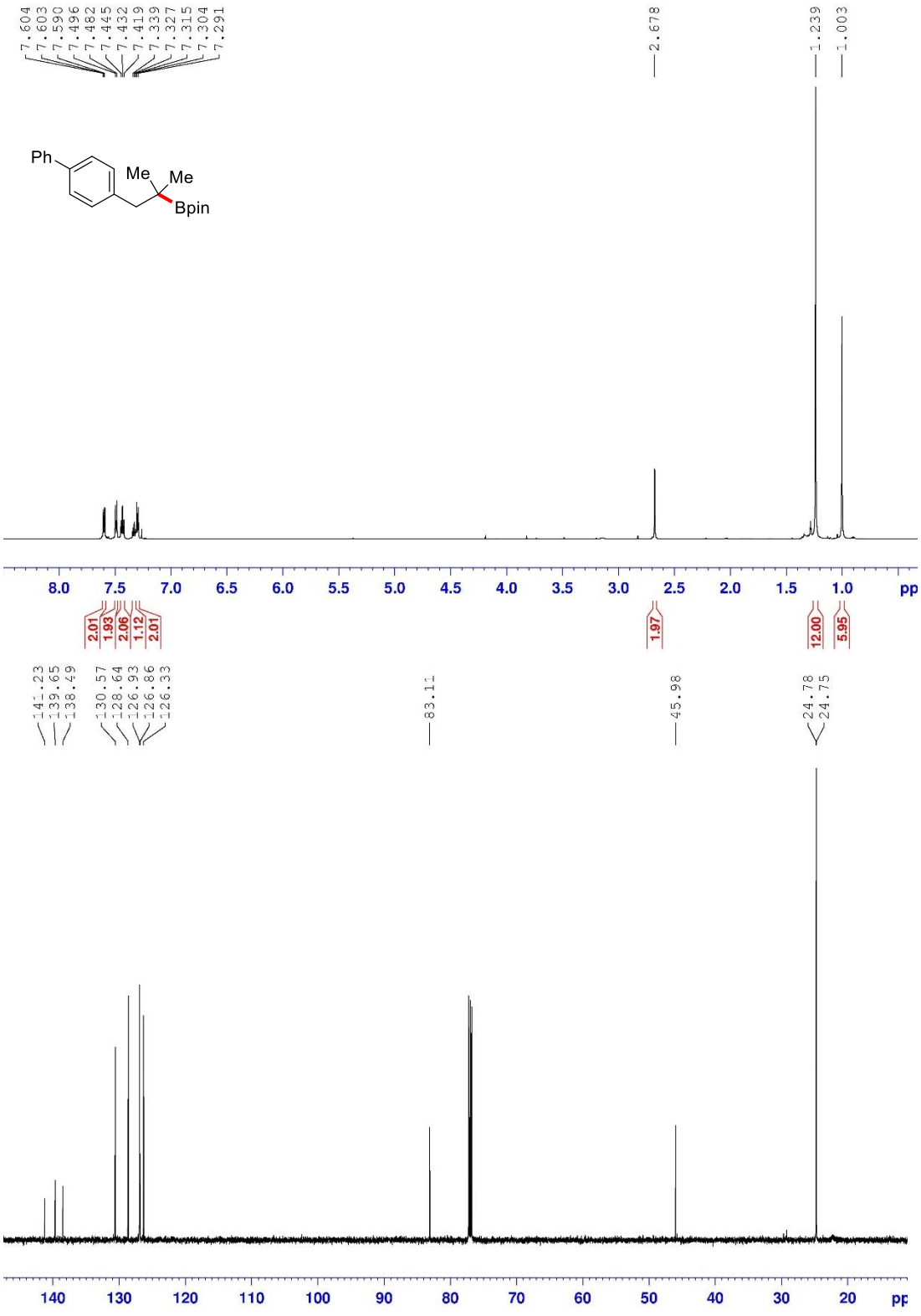
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Me
Me
Bpin
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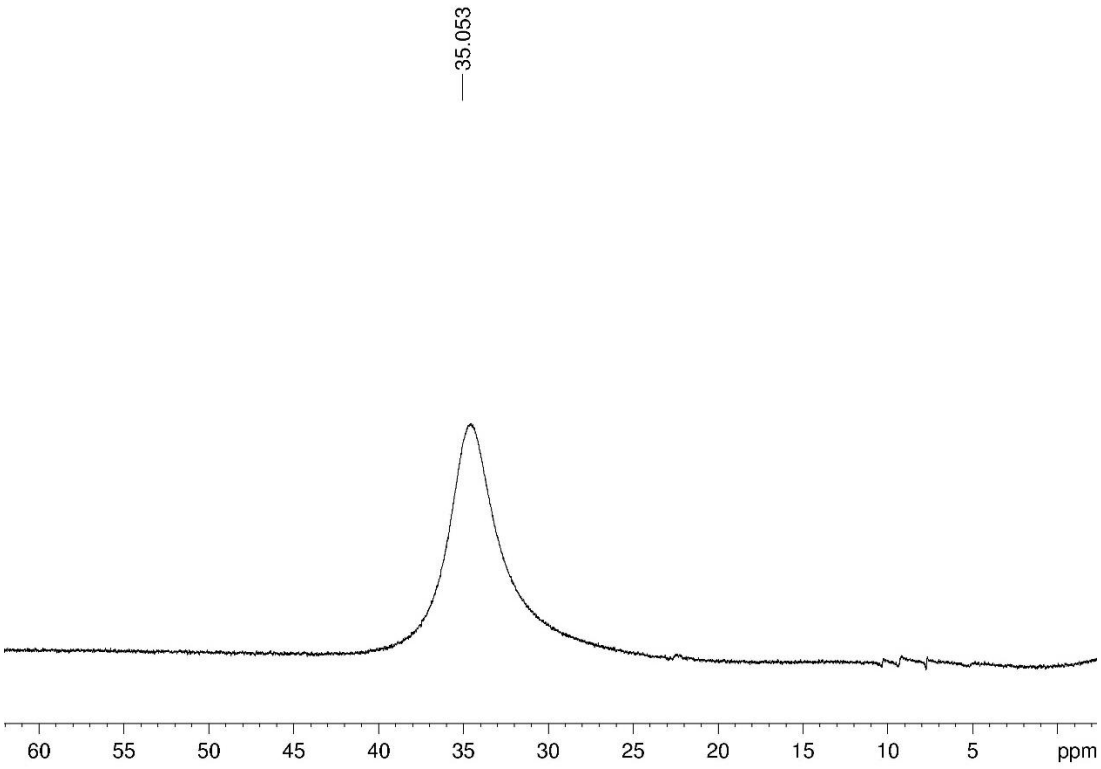
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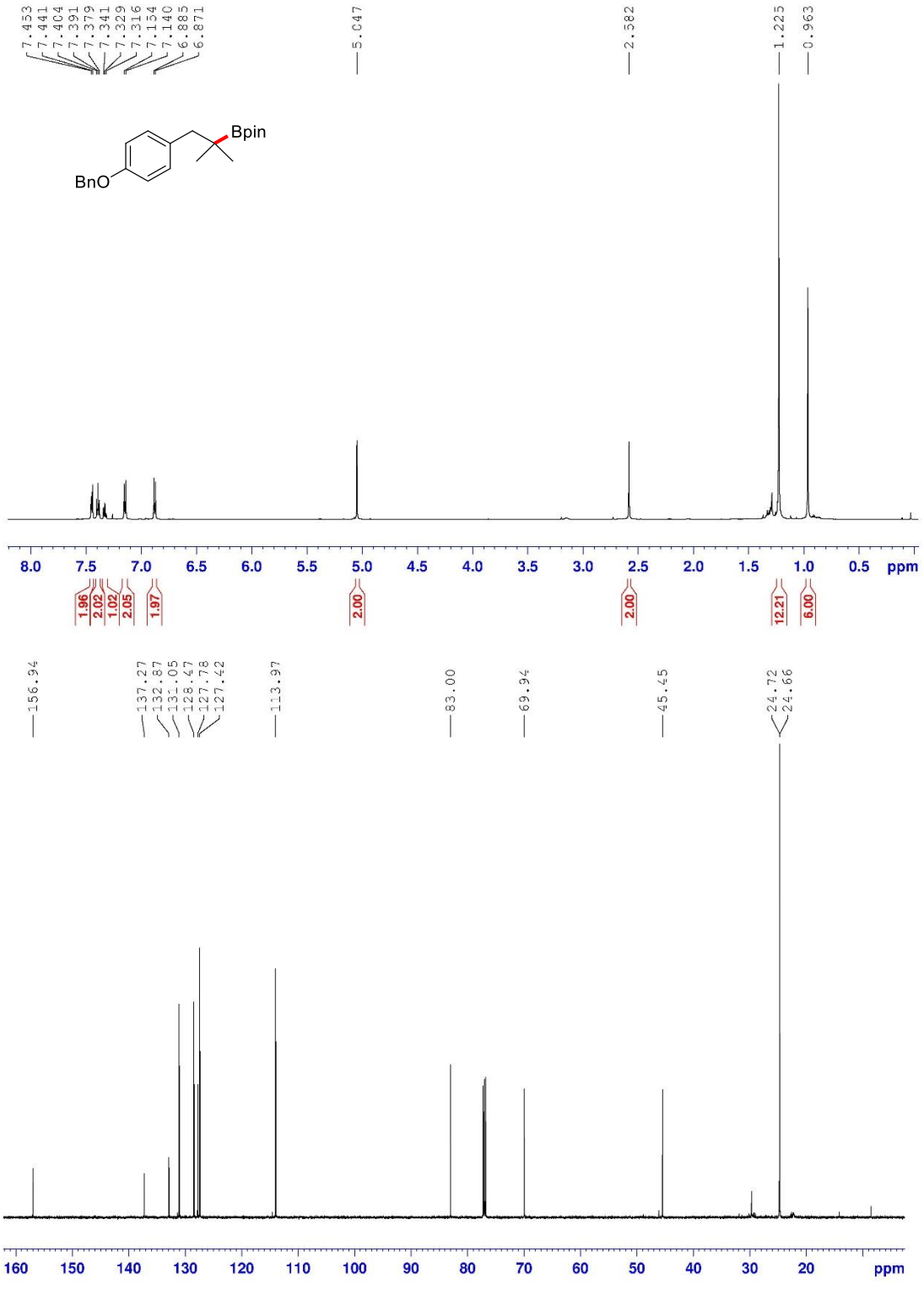
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BnO
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1.02
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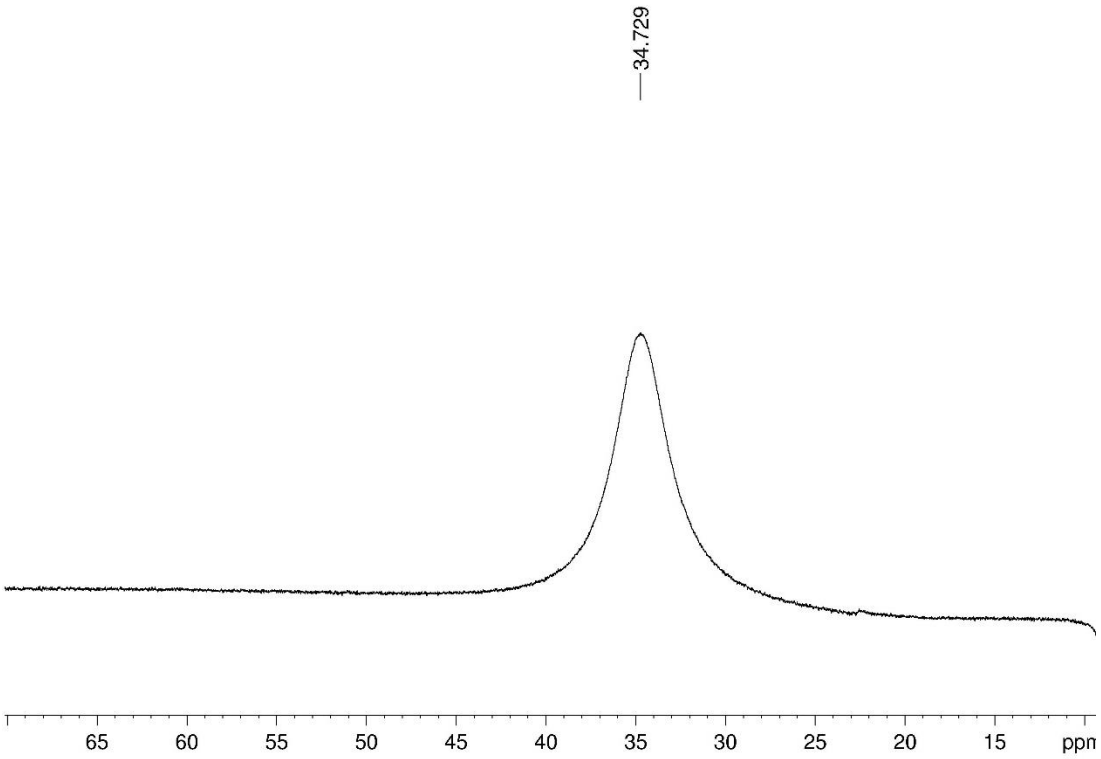
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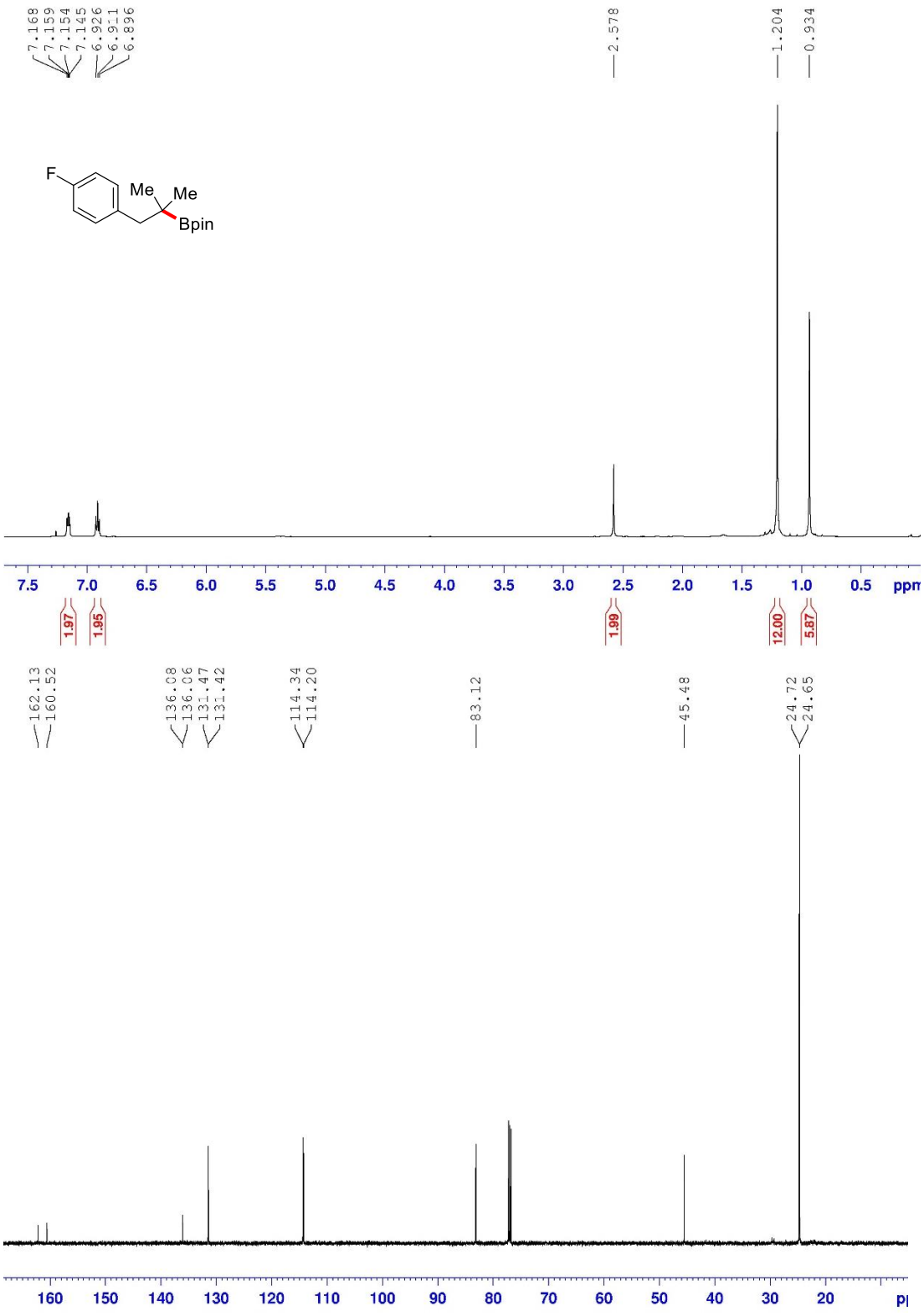
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Me
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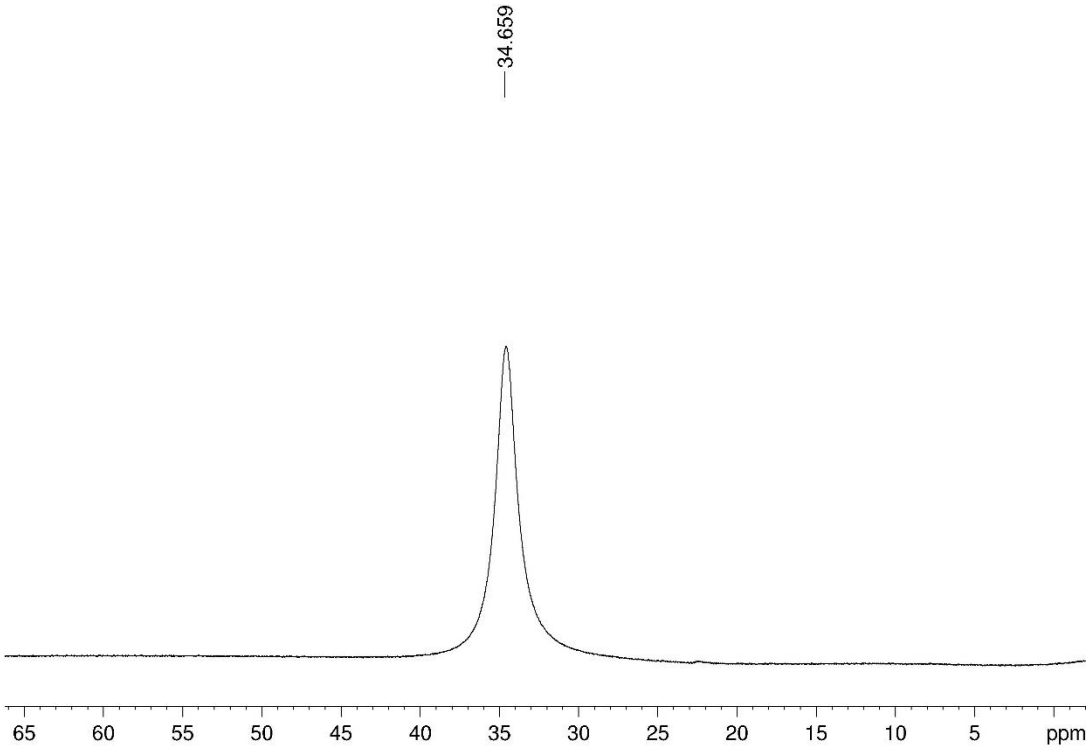
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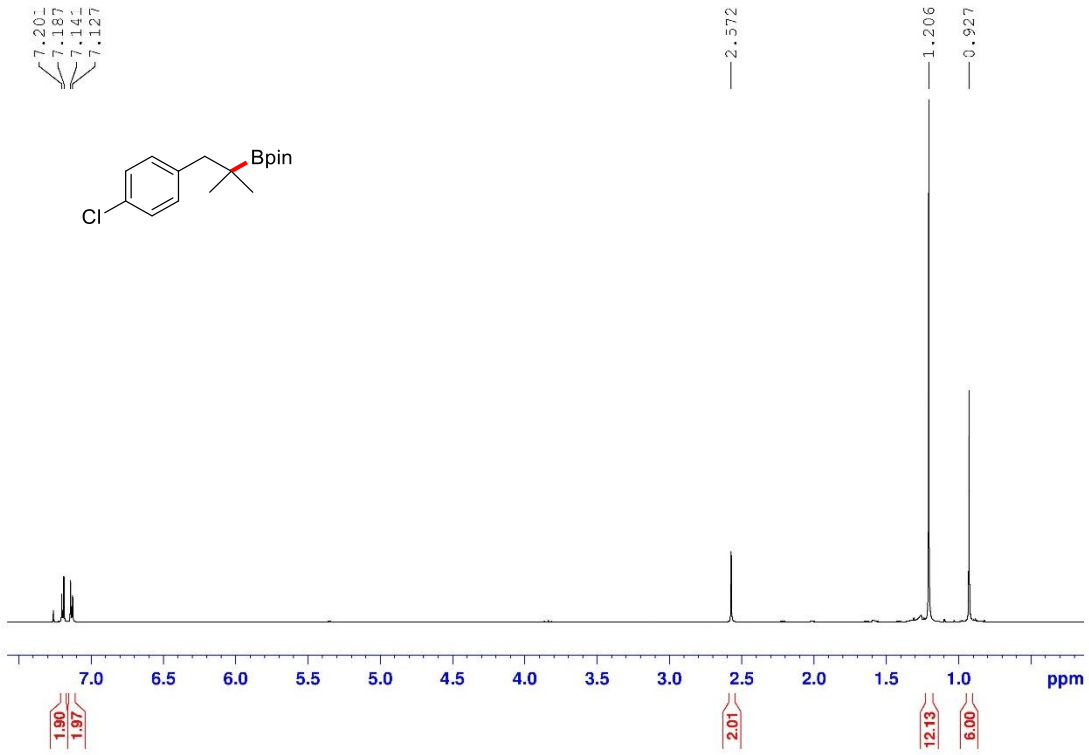
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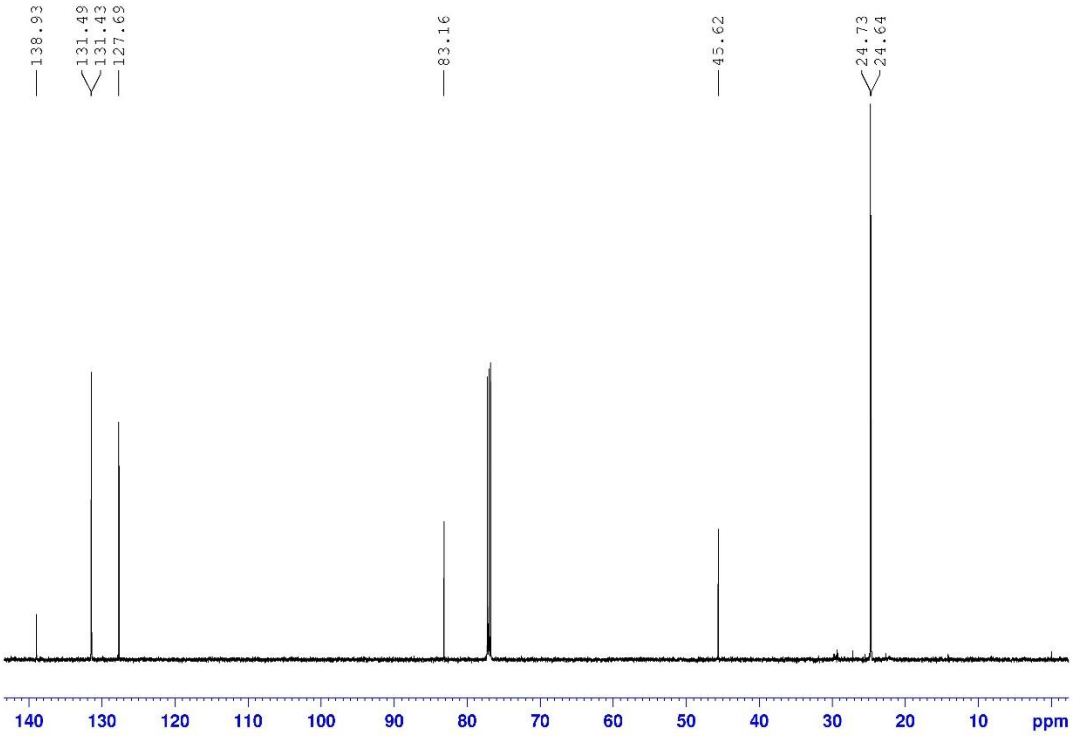
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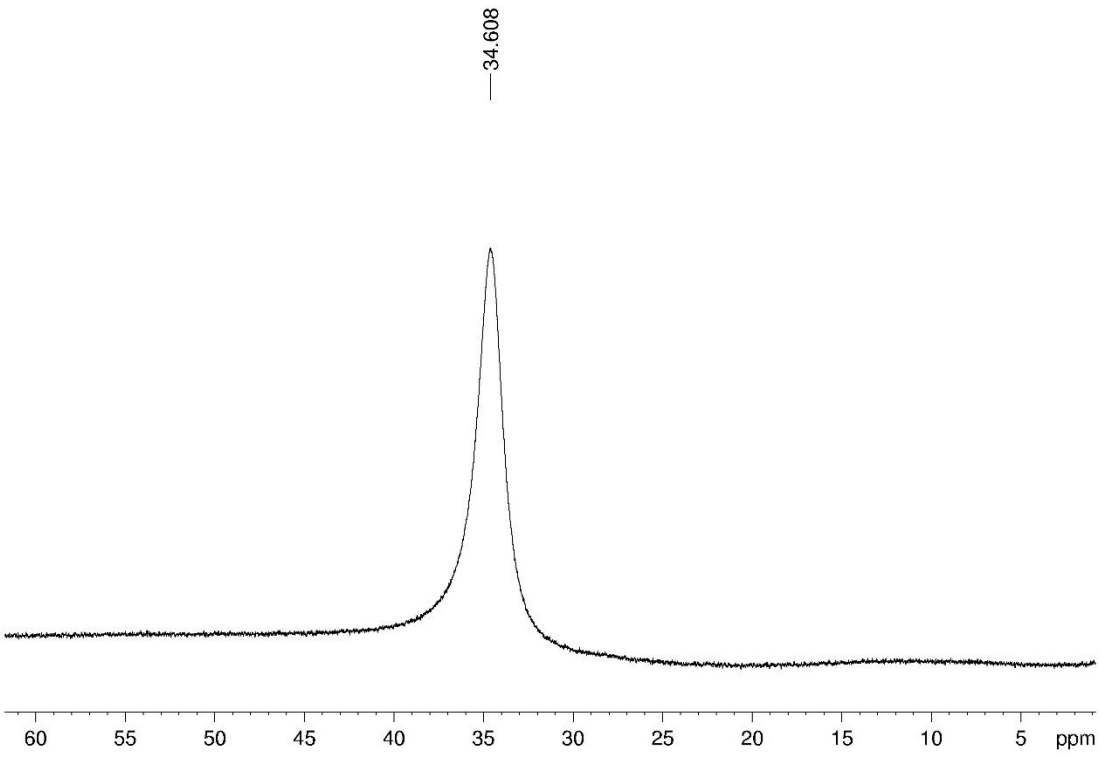
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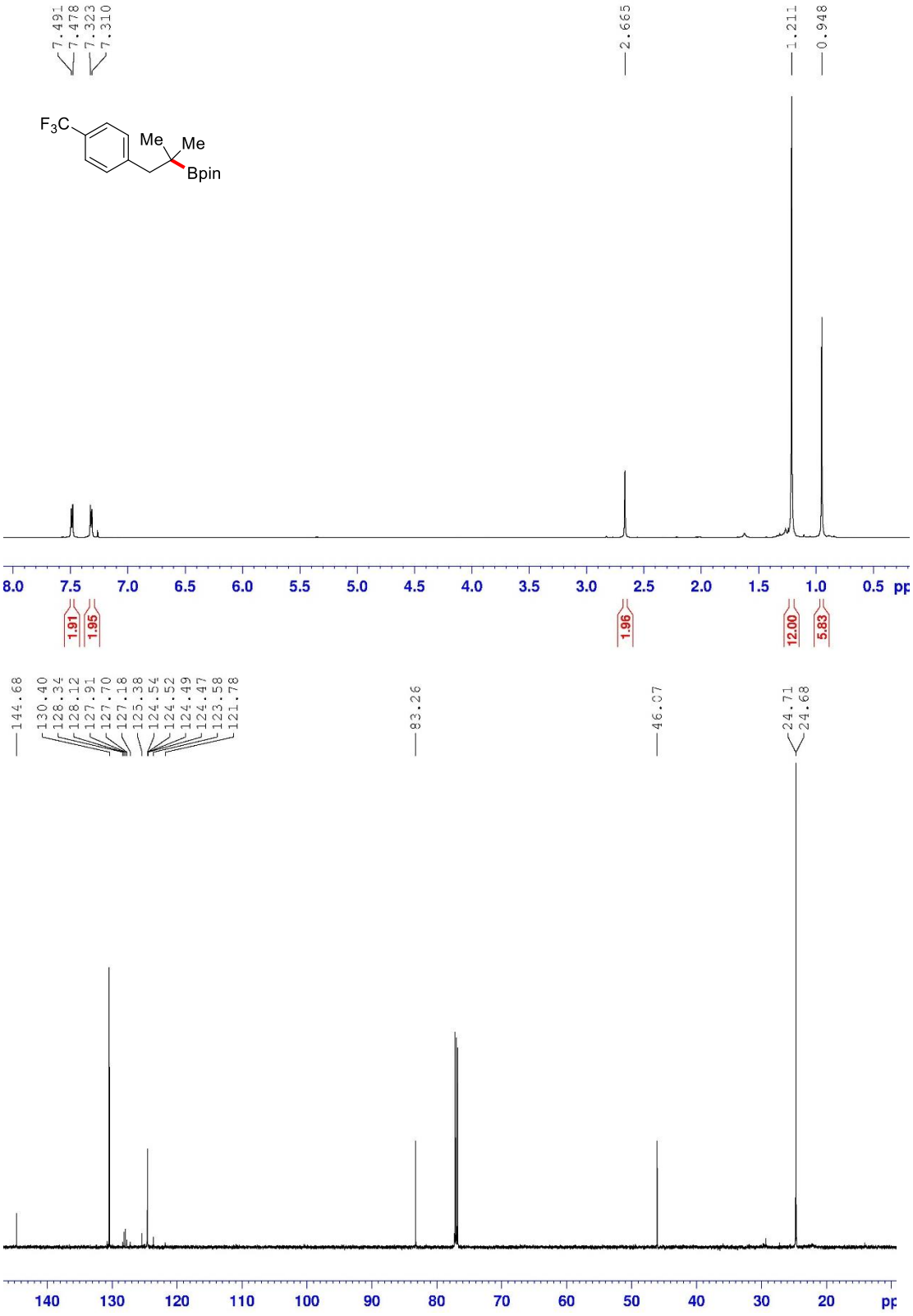
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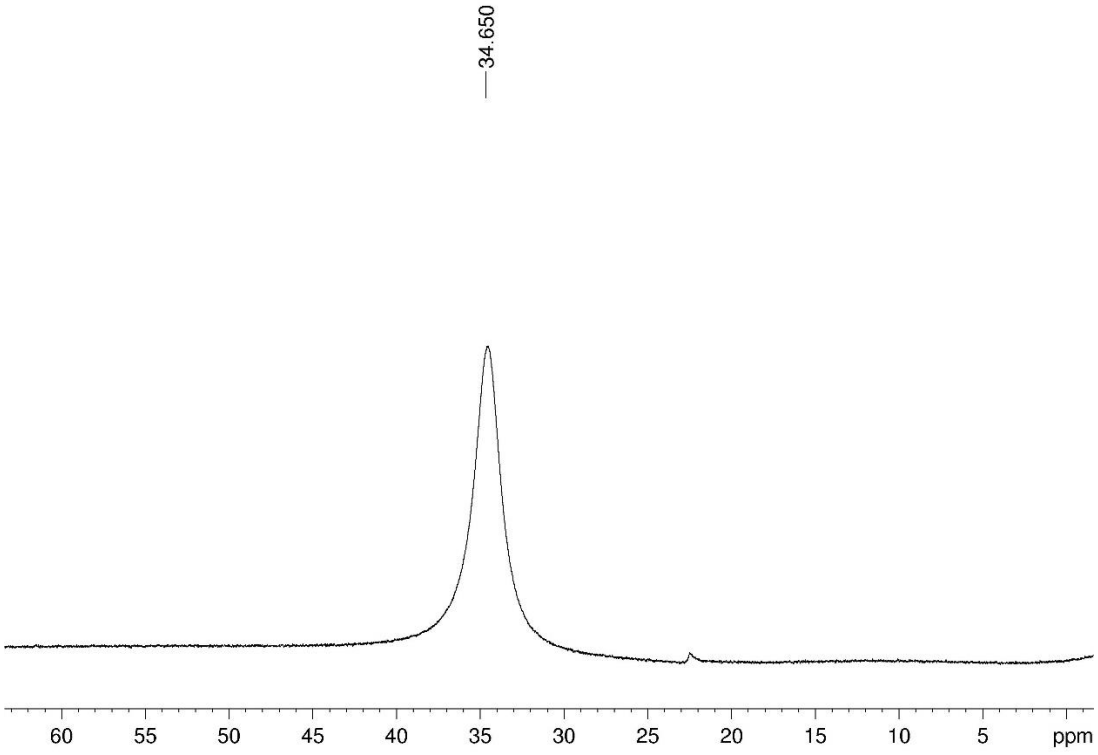
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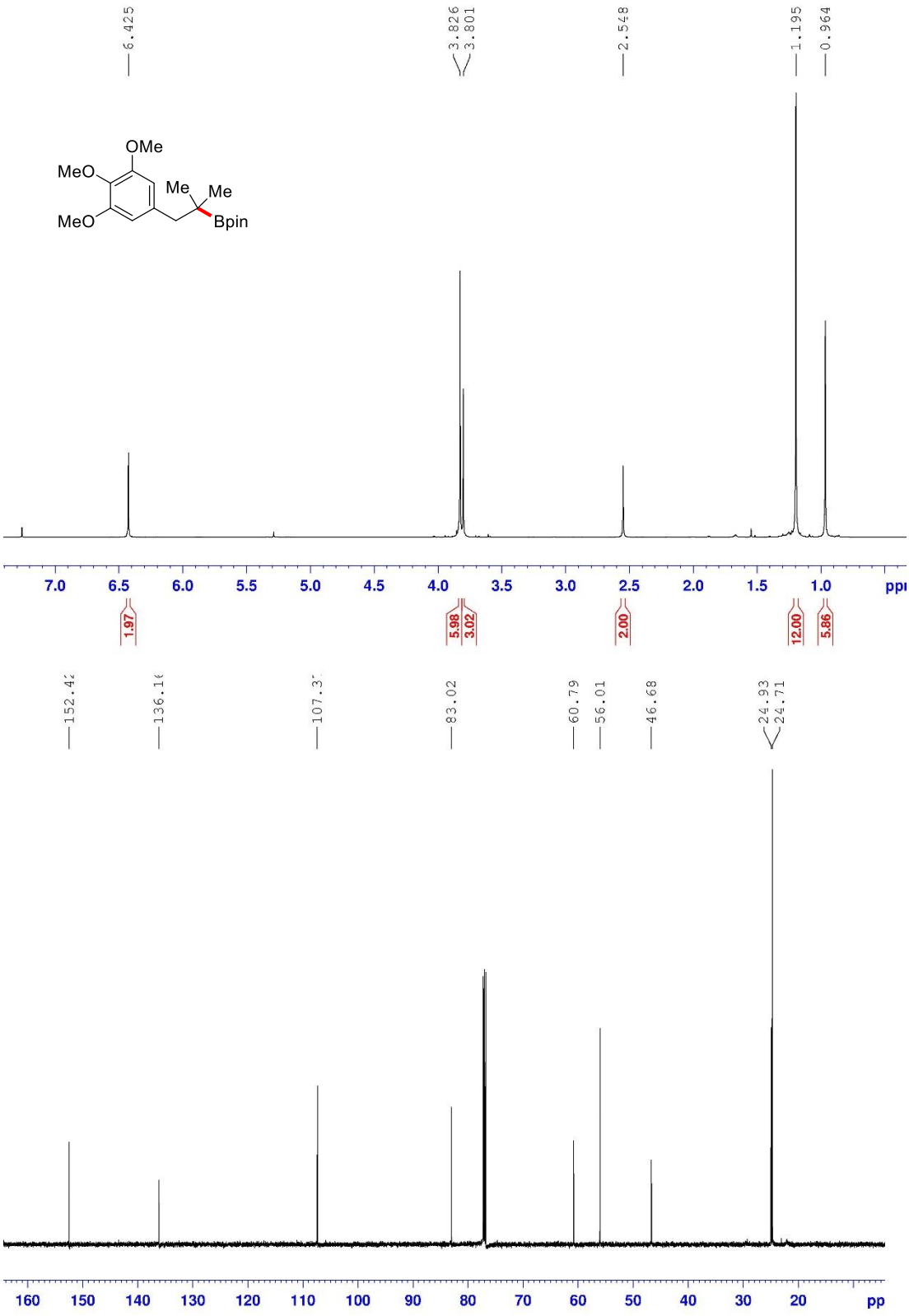
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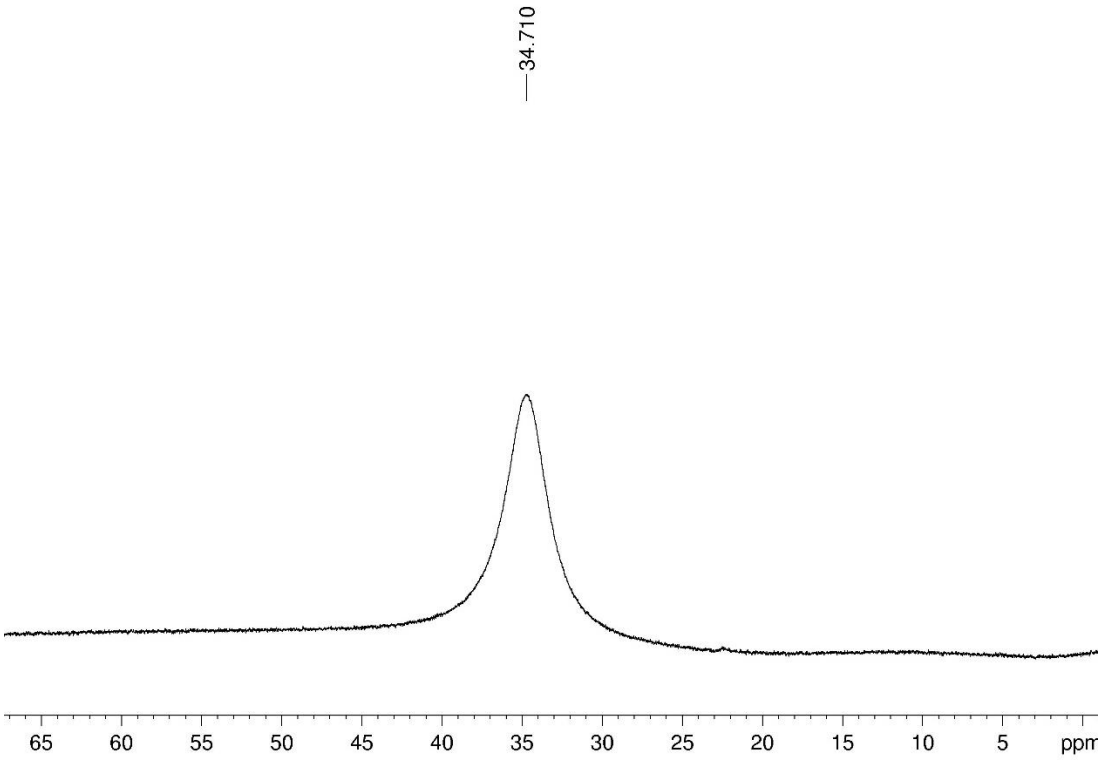
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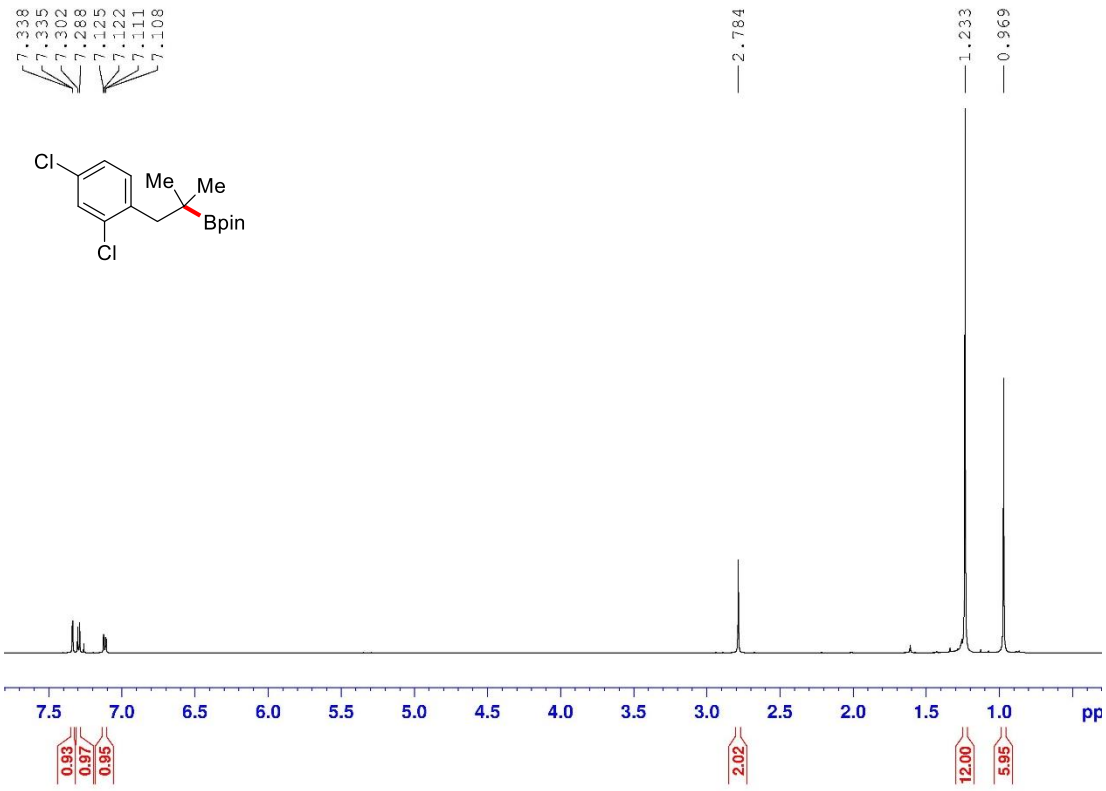
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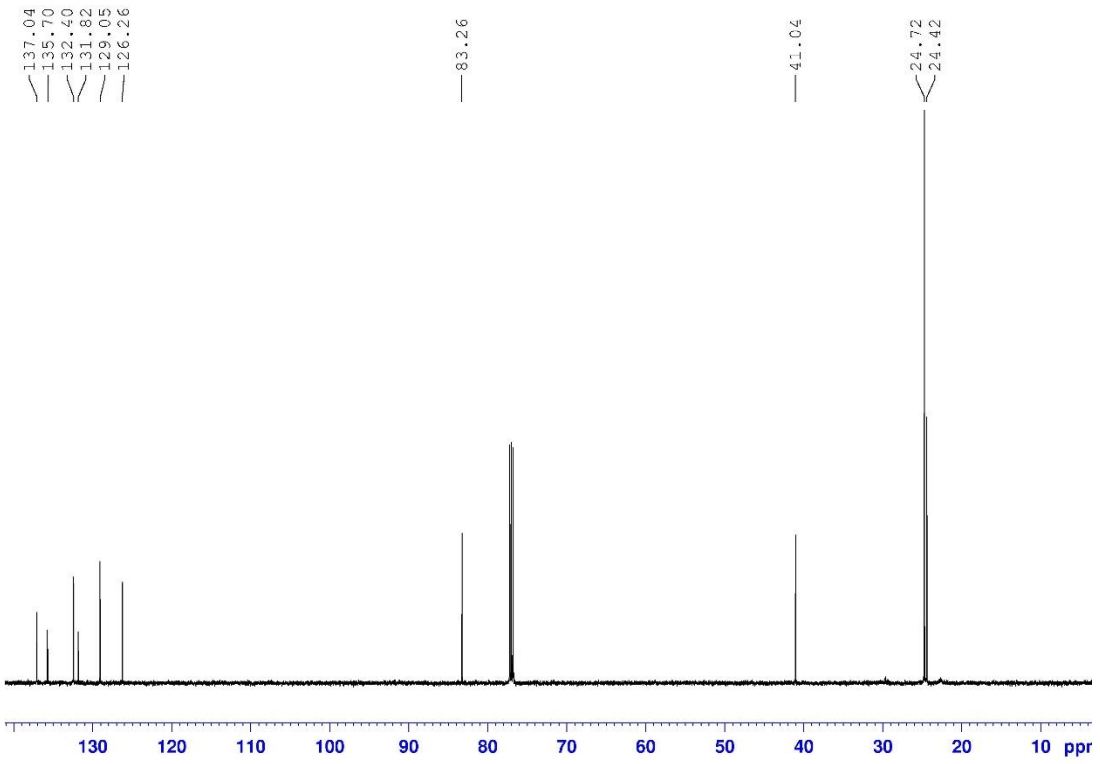
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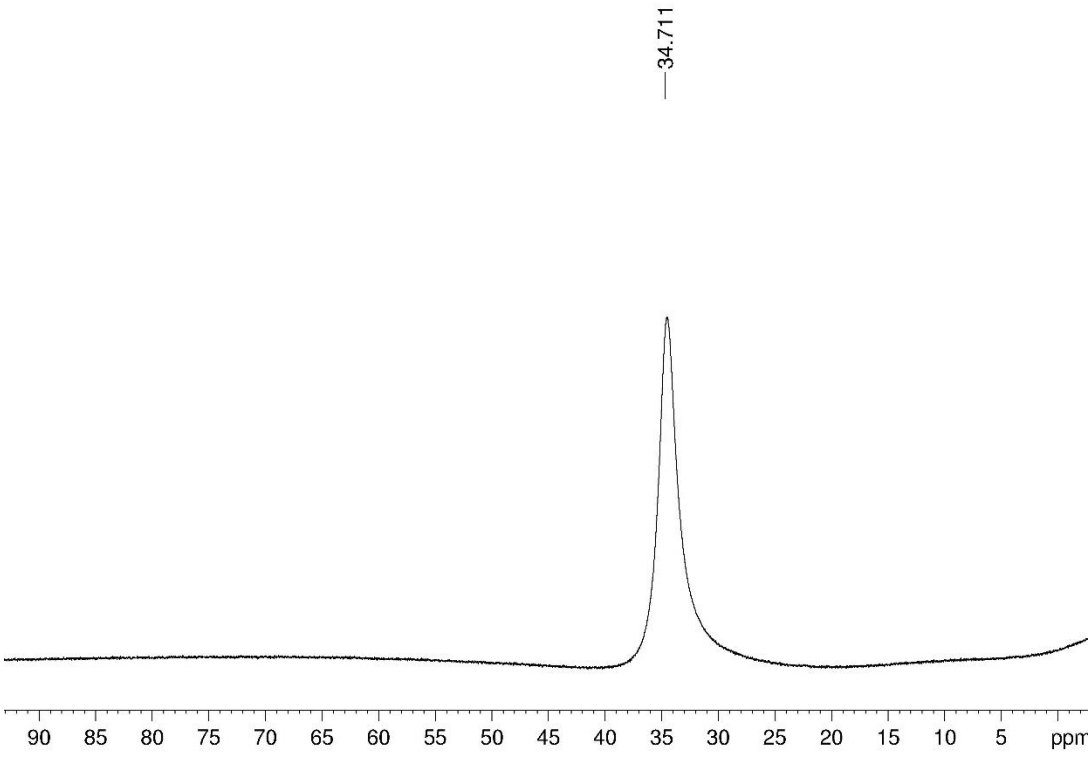
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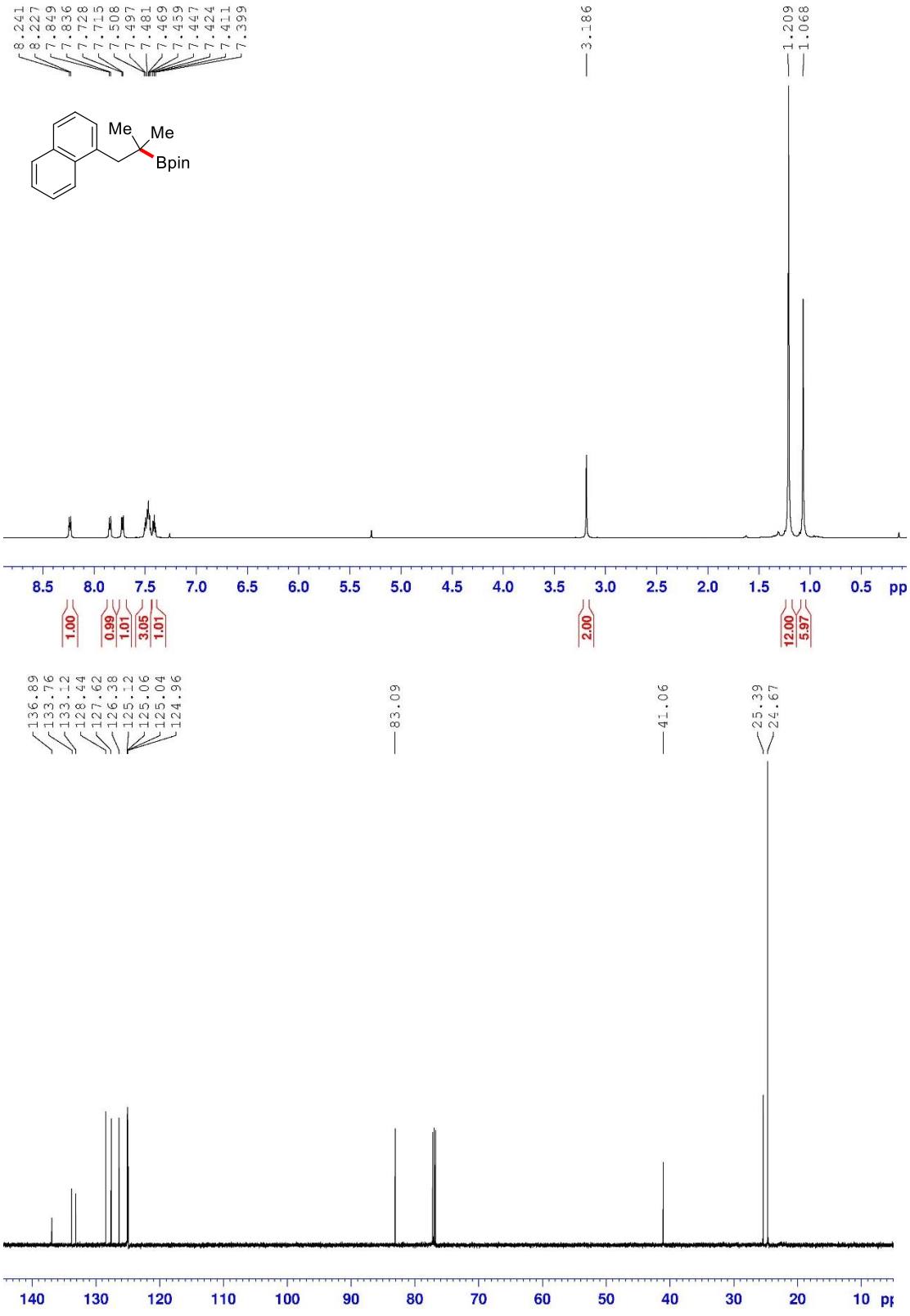
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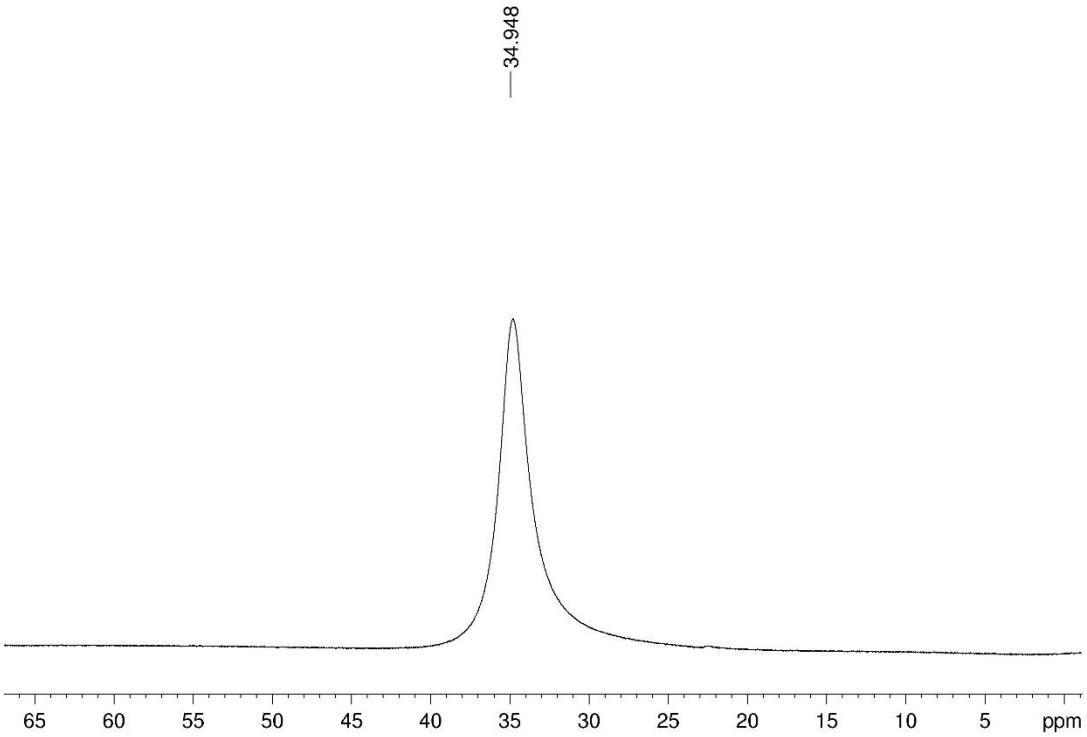
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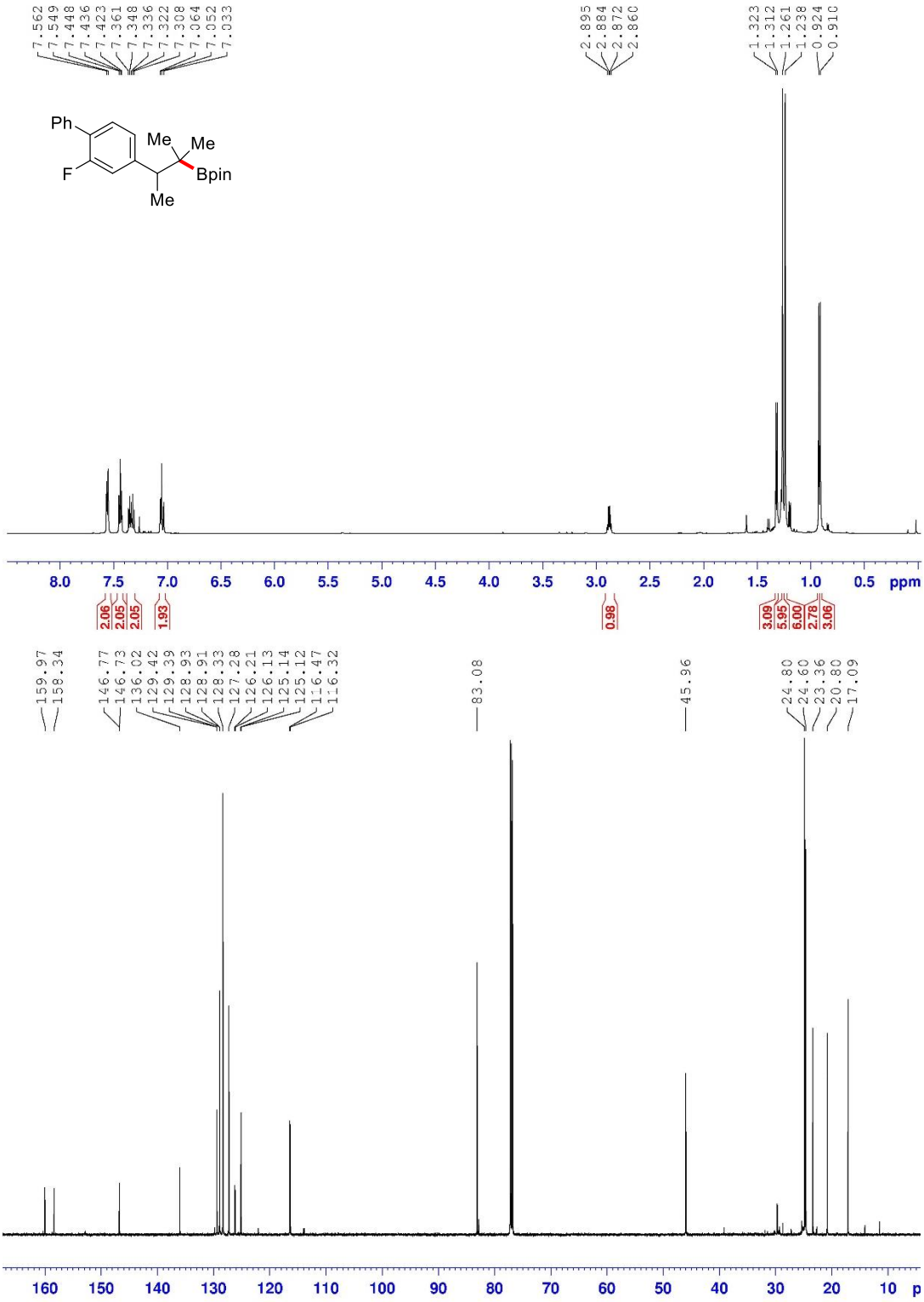
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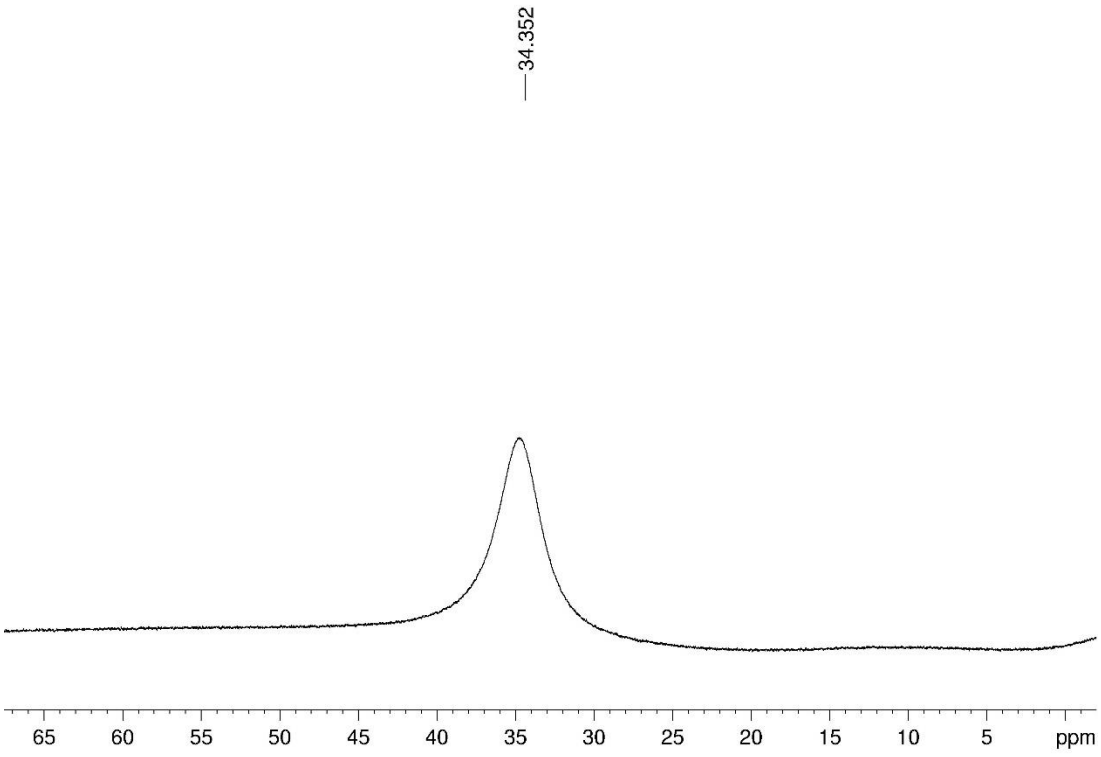
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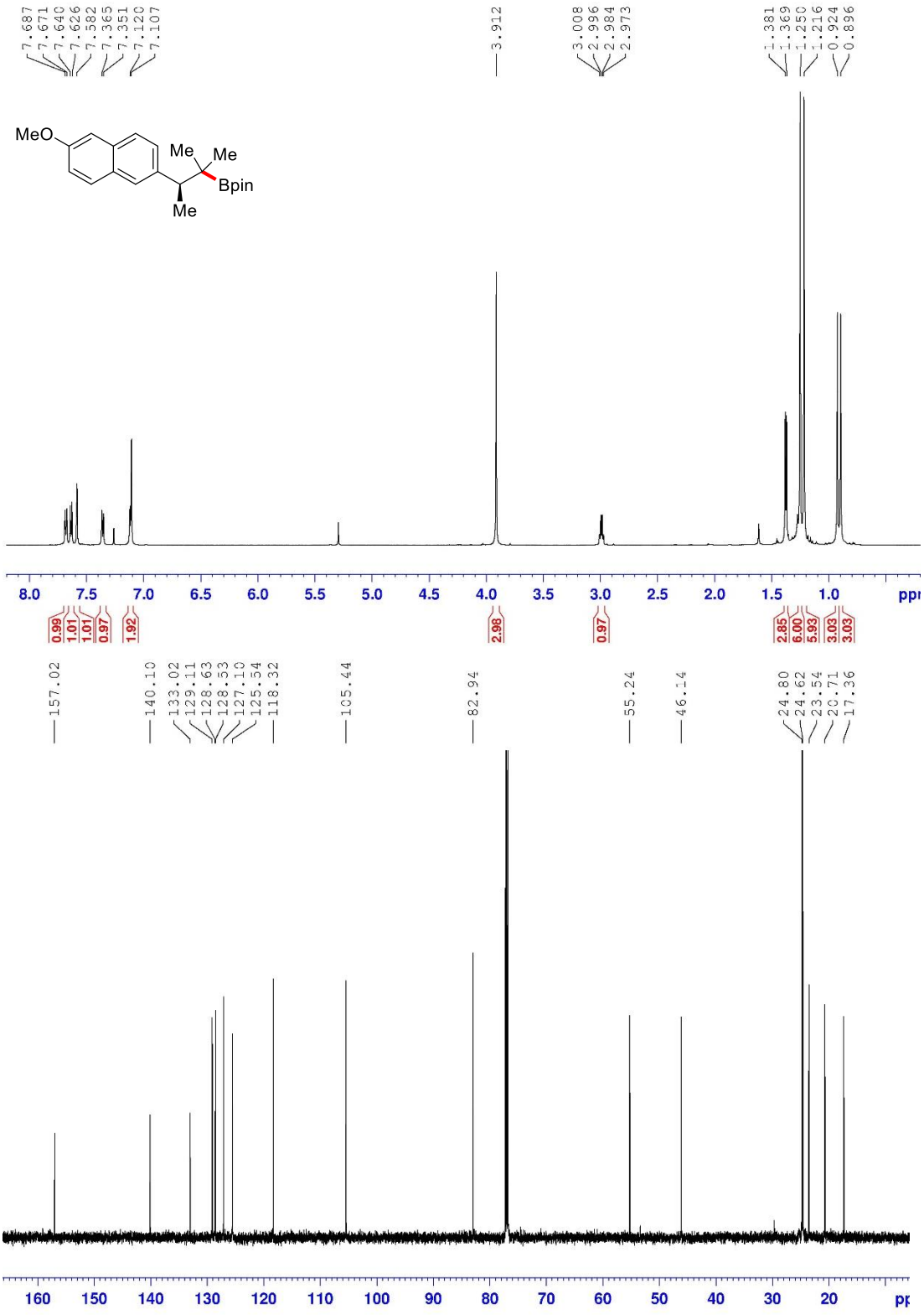
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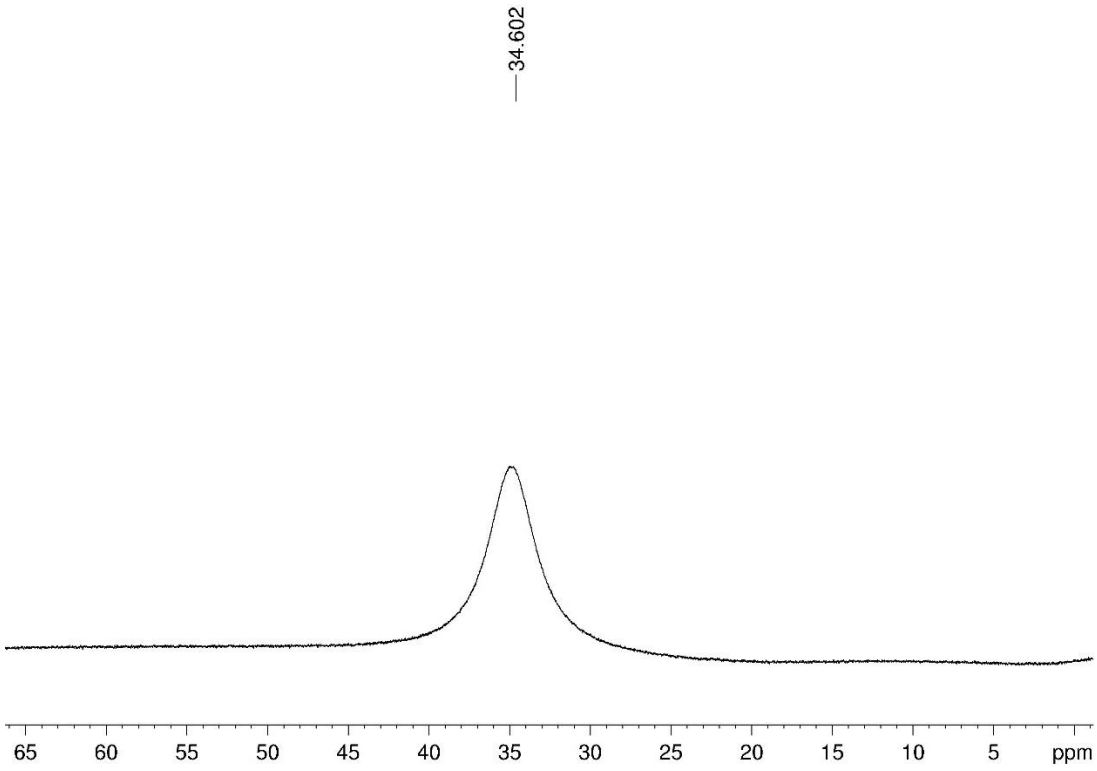
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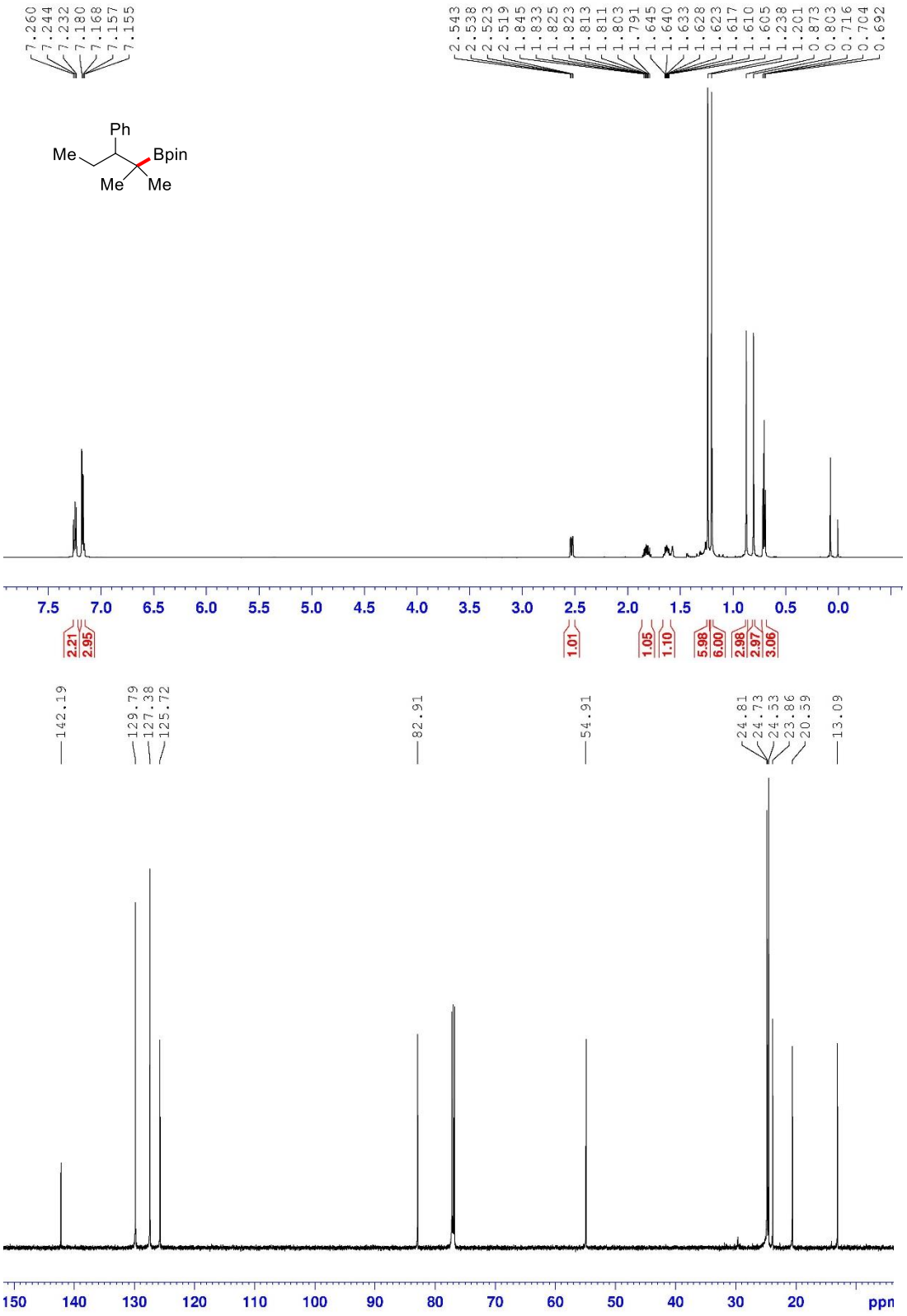
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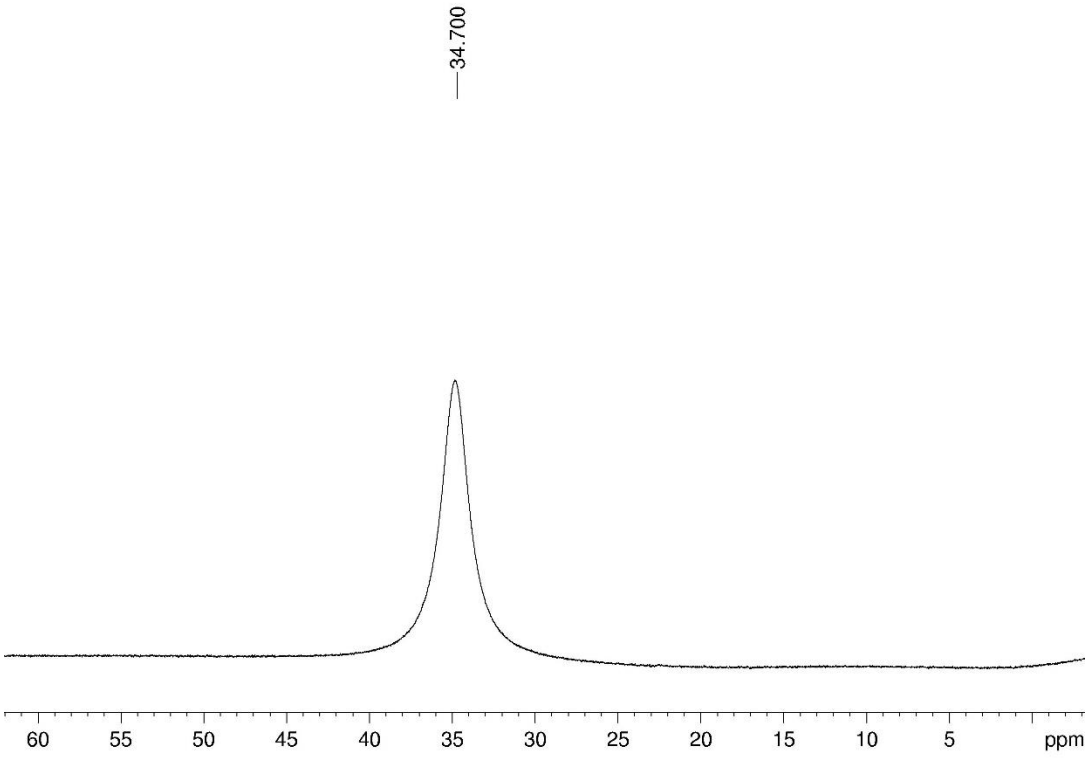
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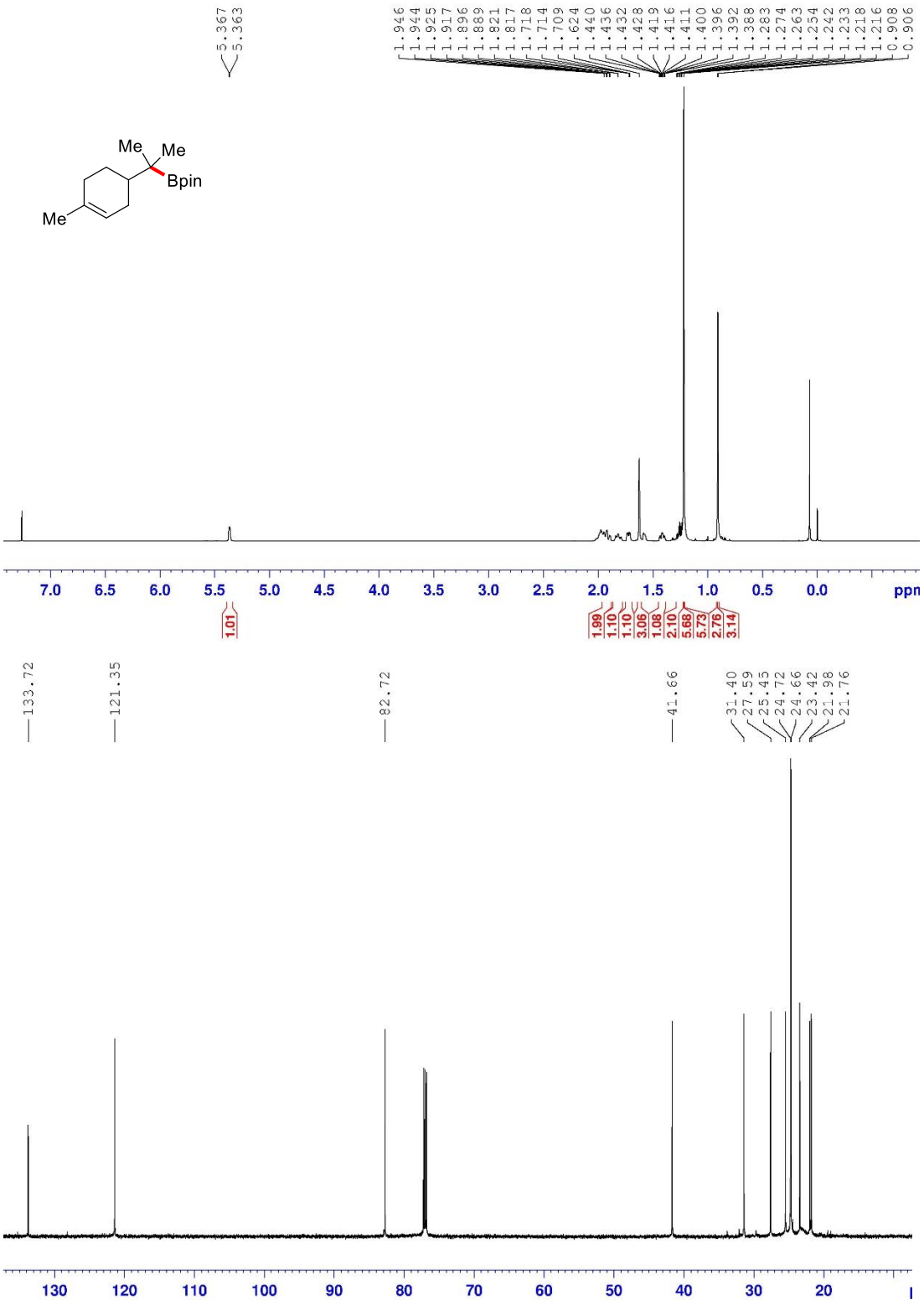
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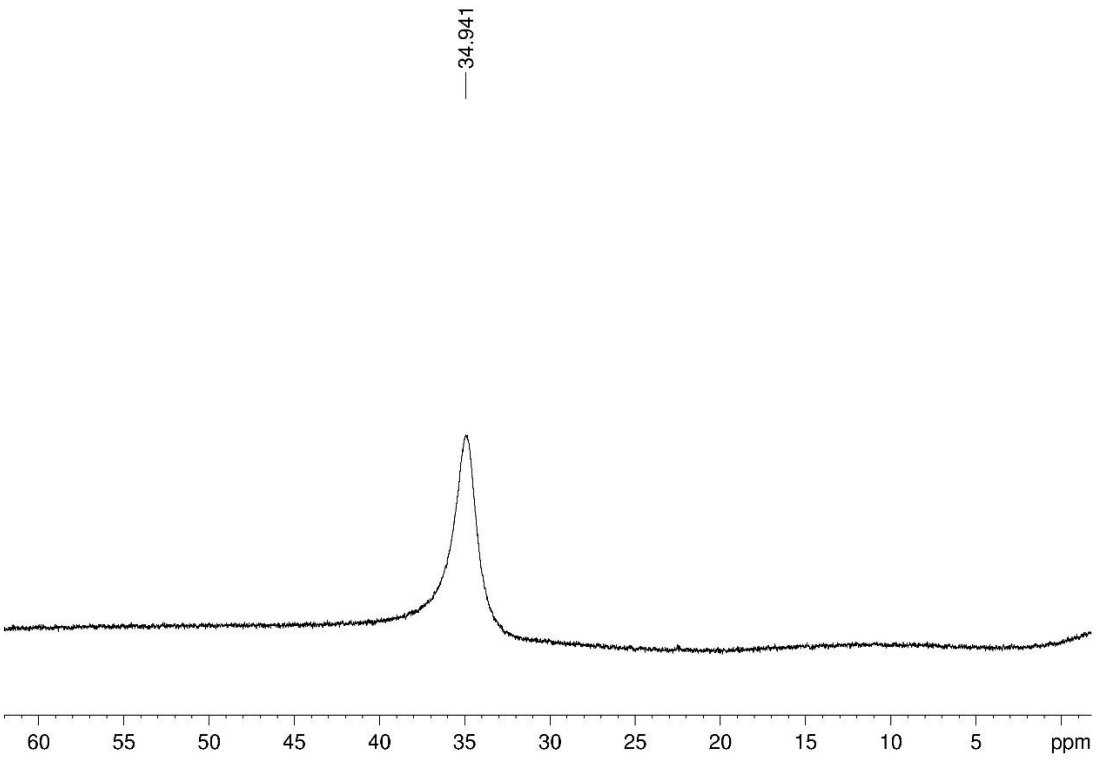
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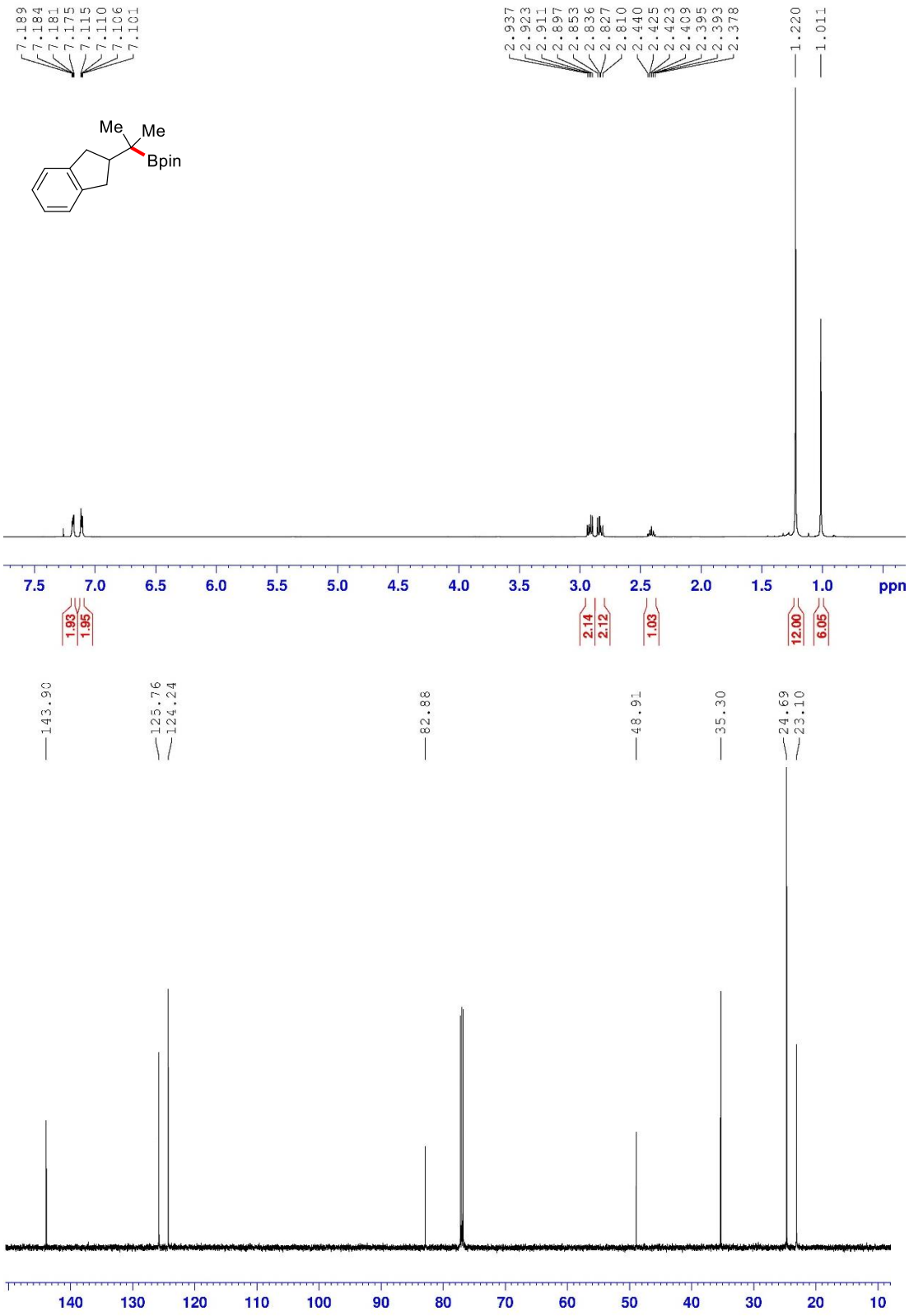
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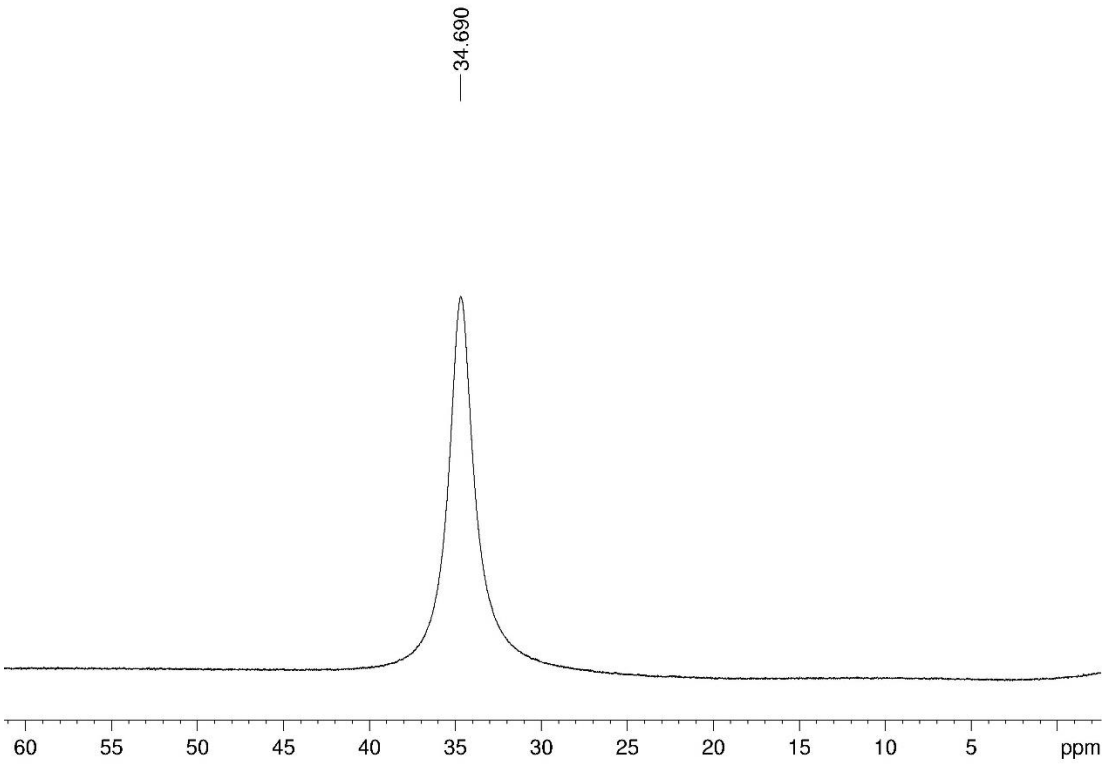
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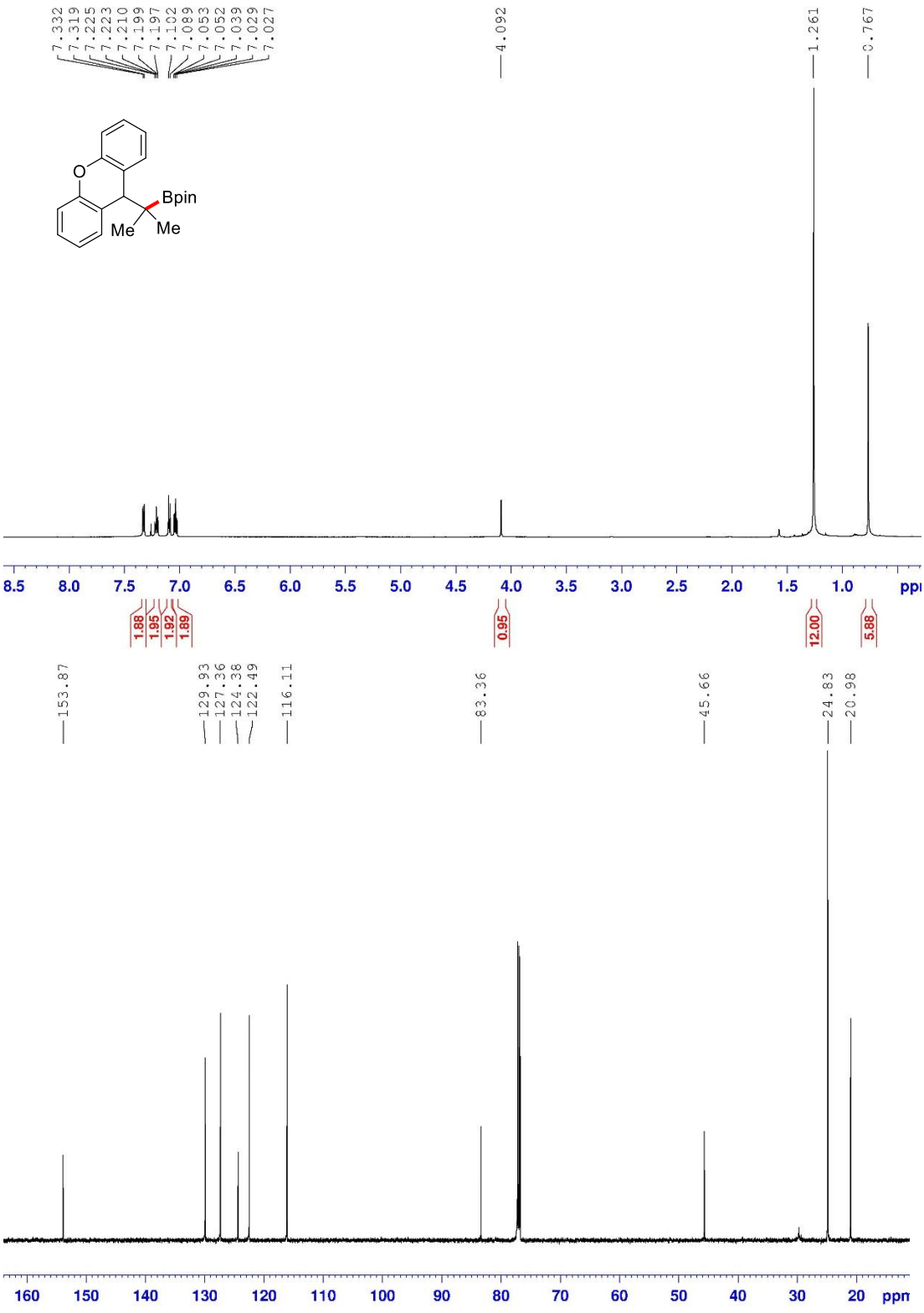
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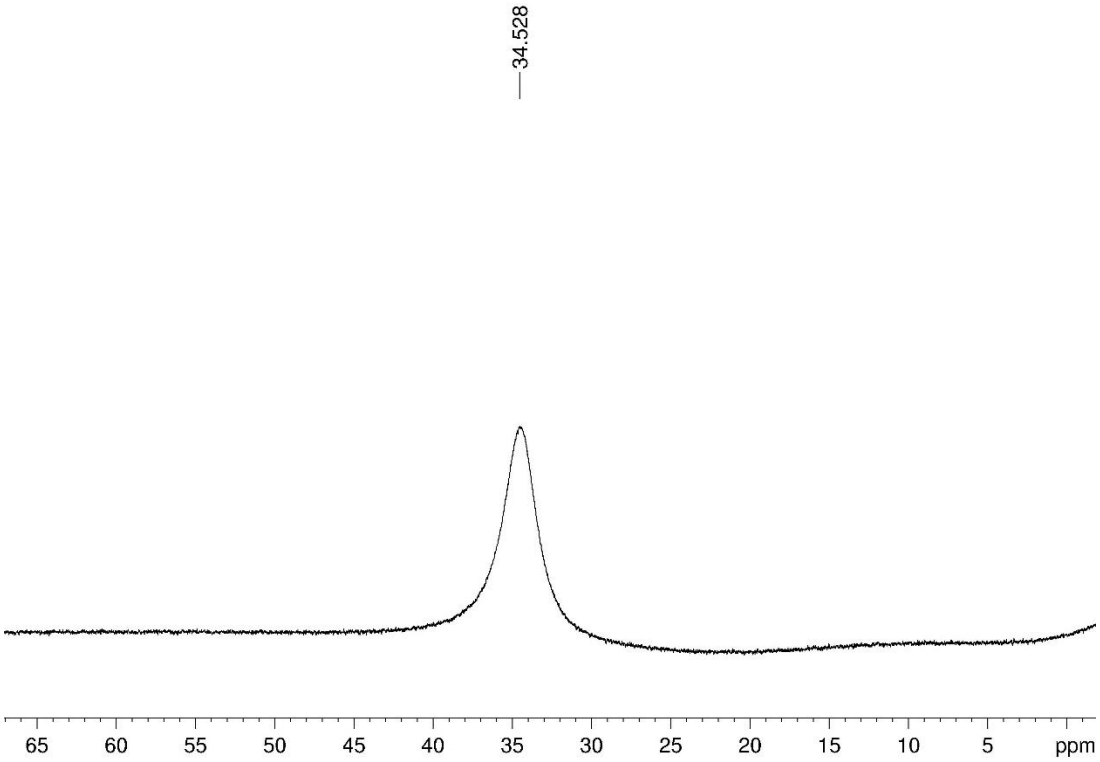
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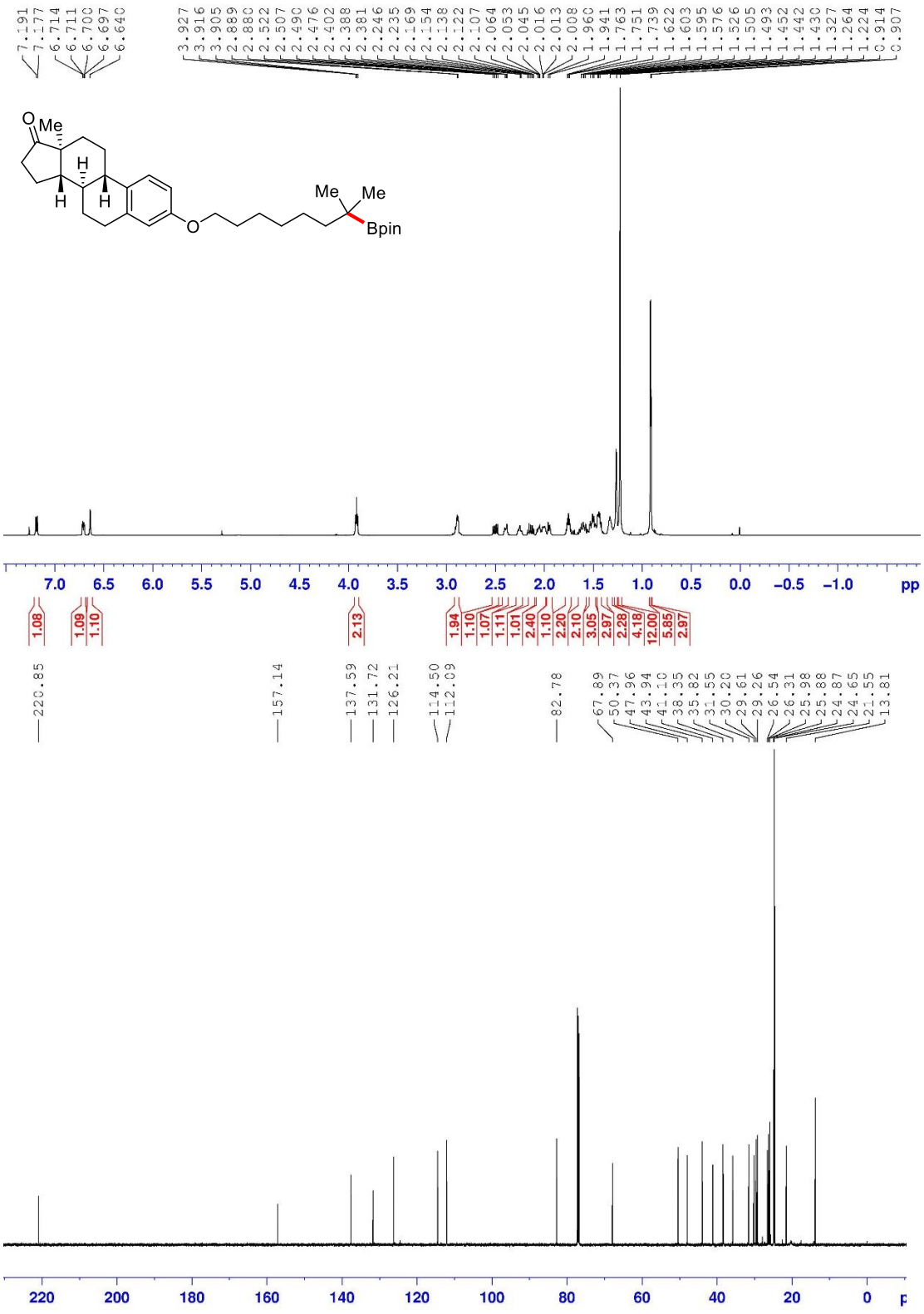
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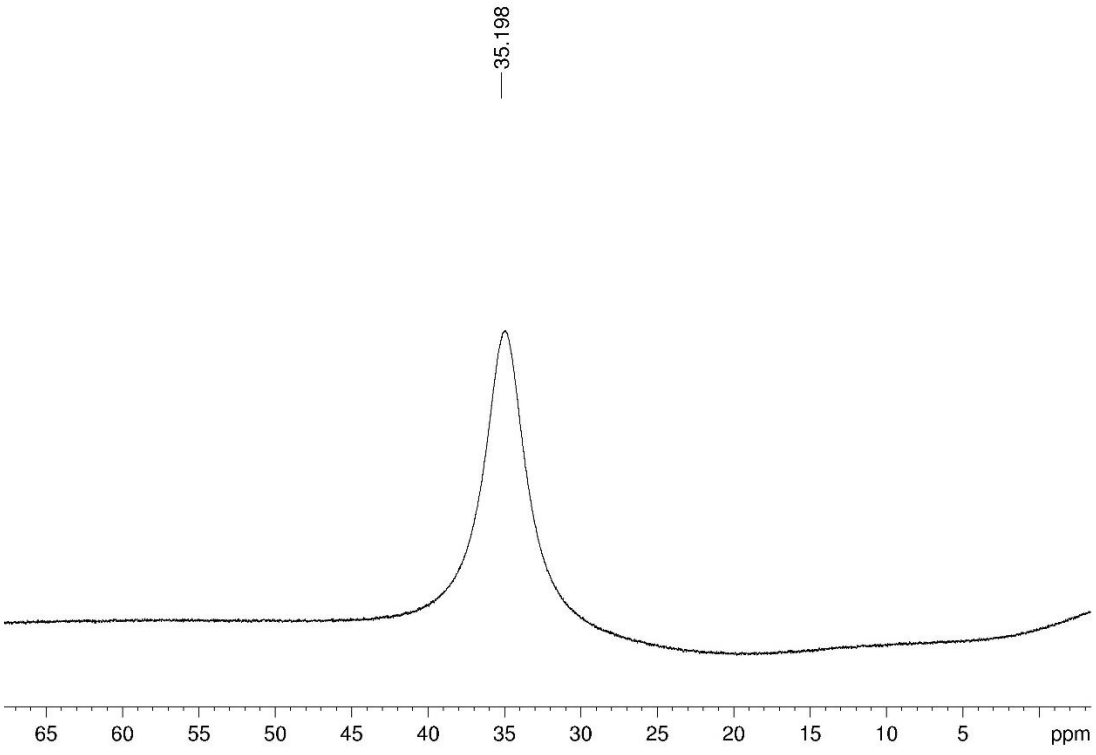
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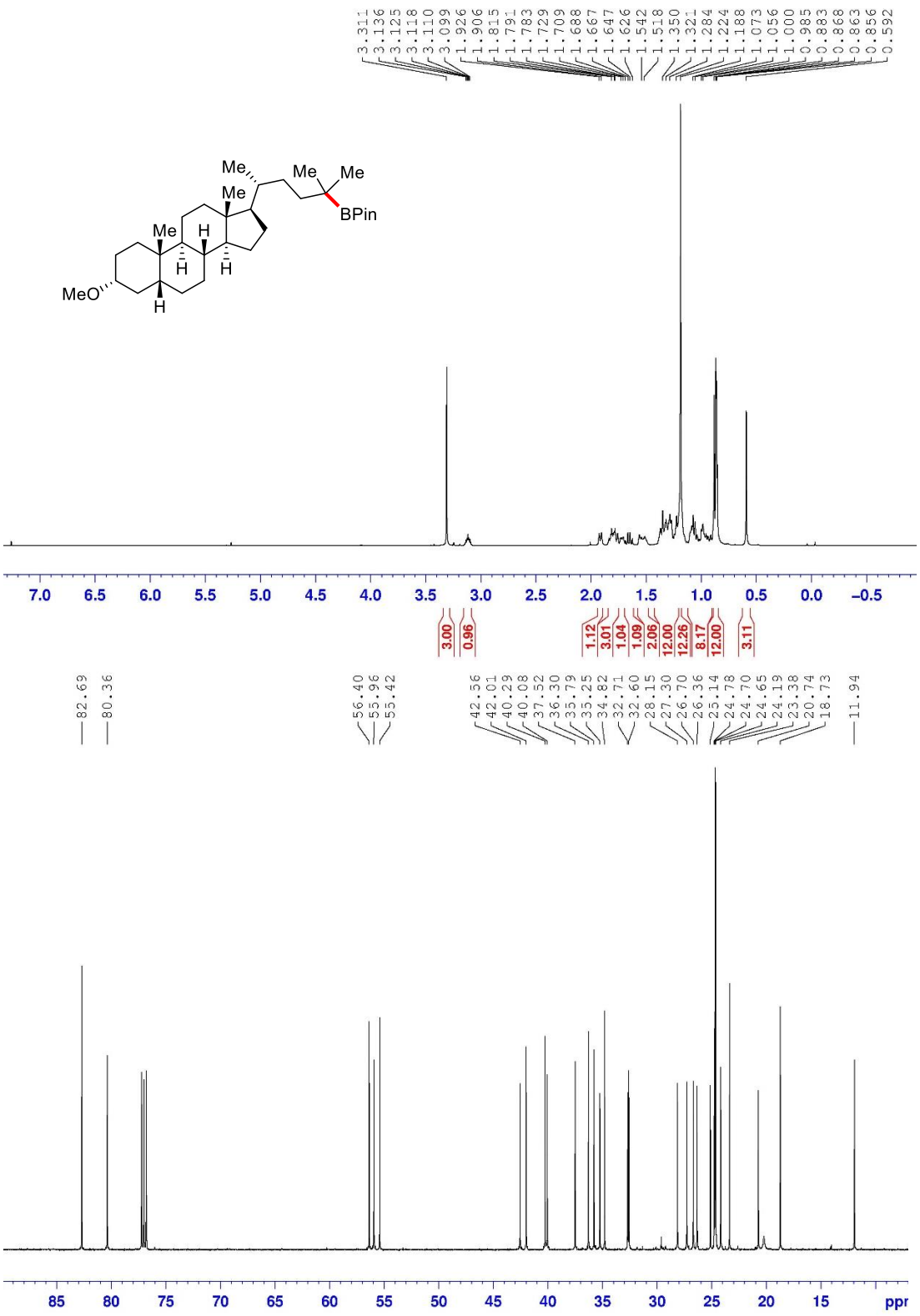
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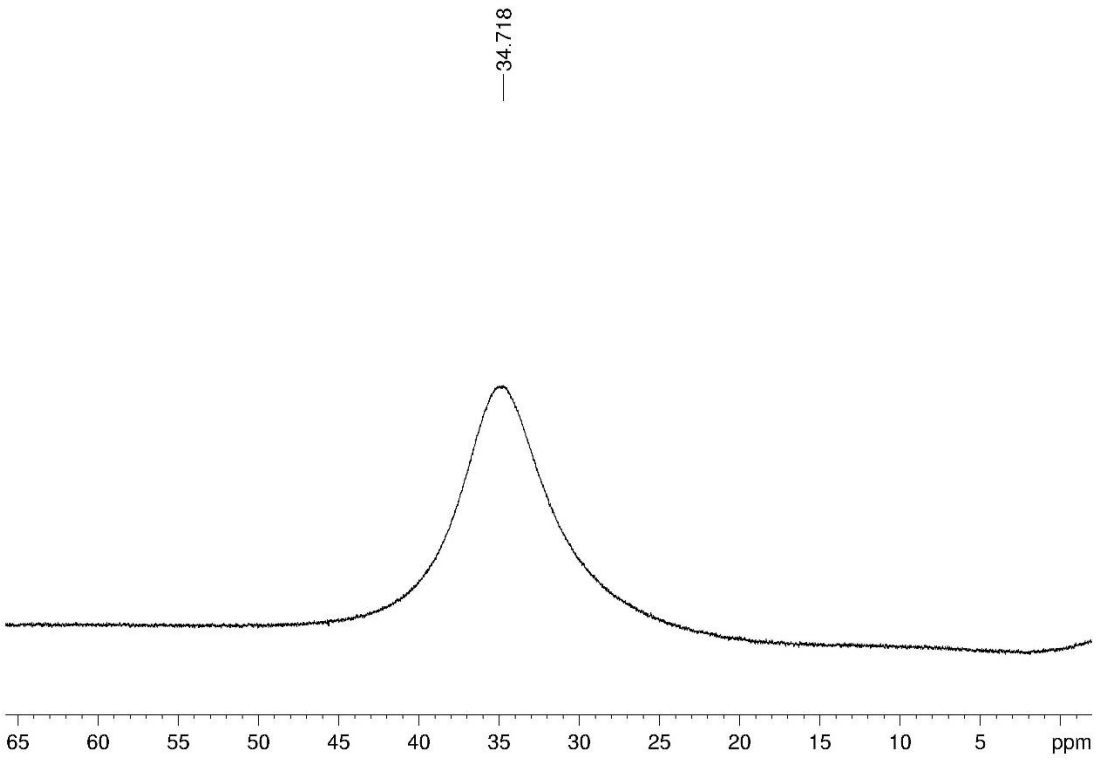
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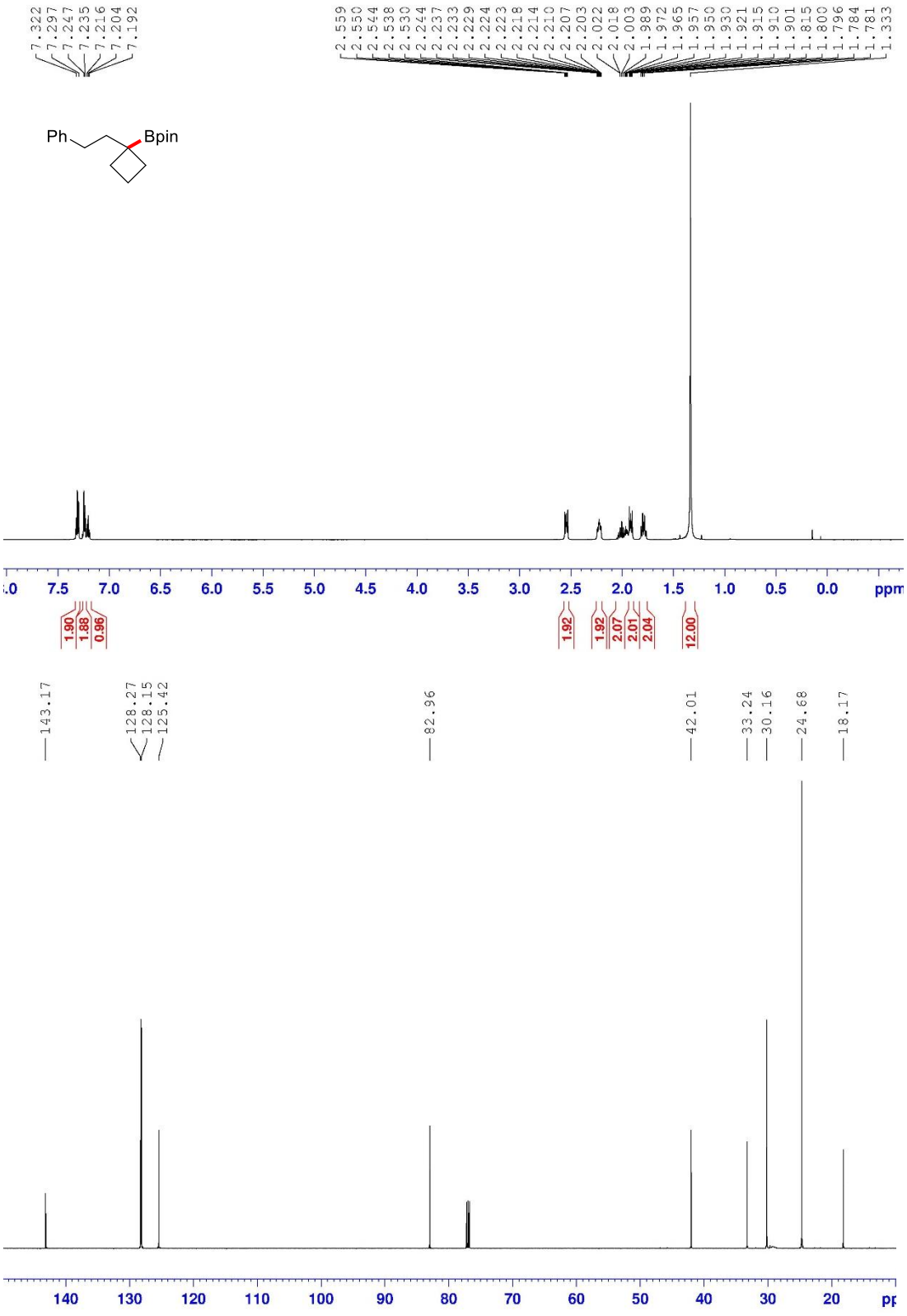
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2.224
2.223
2.218
2.214
2.210
2.207
2.203
2.022
2.018
2.003
1.989
1.972
1.965
1.957
1.950
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1.921
1.915
1.910
1.901
1.815
1.800
1.796
1.784
1.781
1.333
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Bpin
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2.0
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0.0
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0.96
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1.92
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2.01
2.04
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128.15
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82.96
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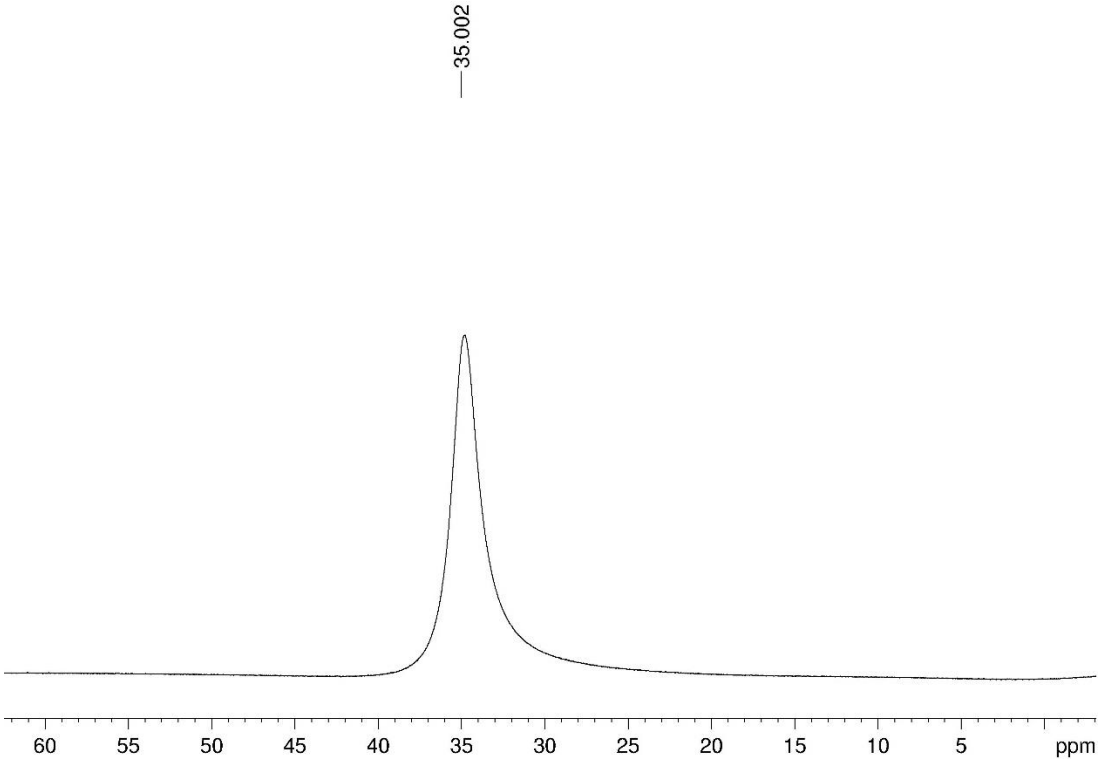
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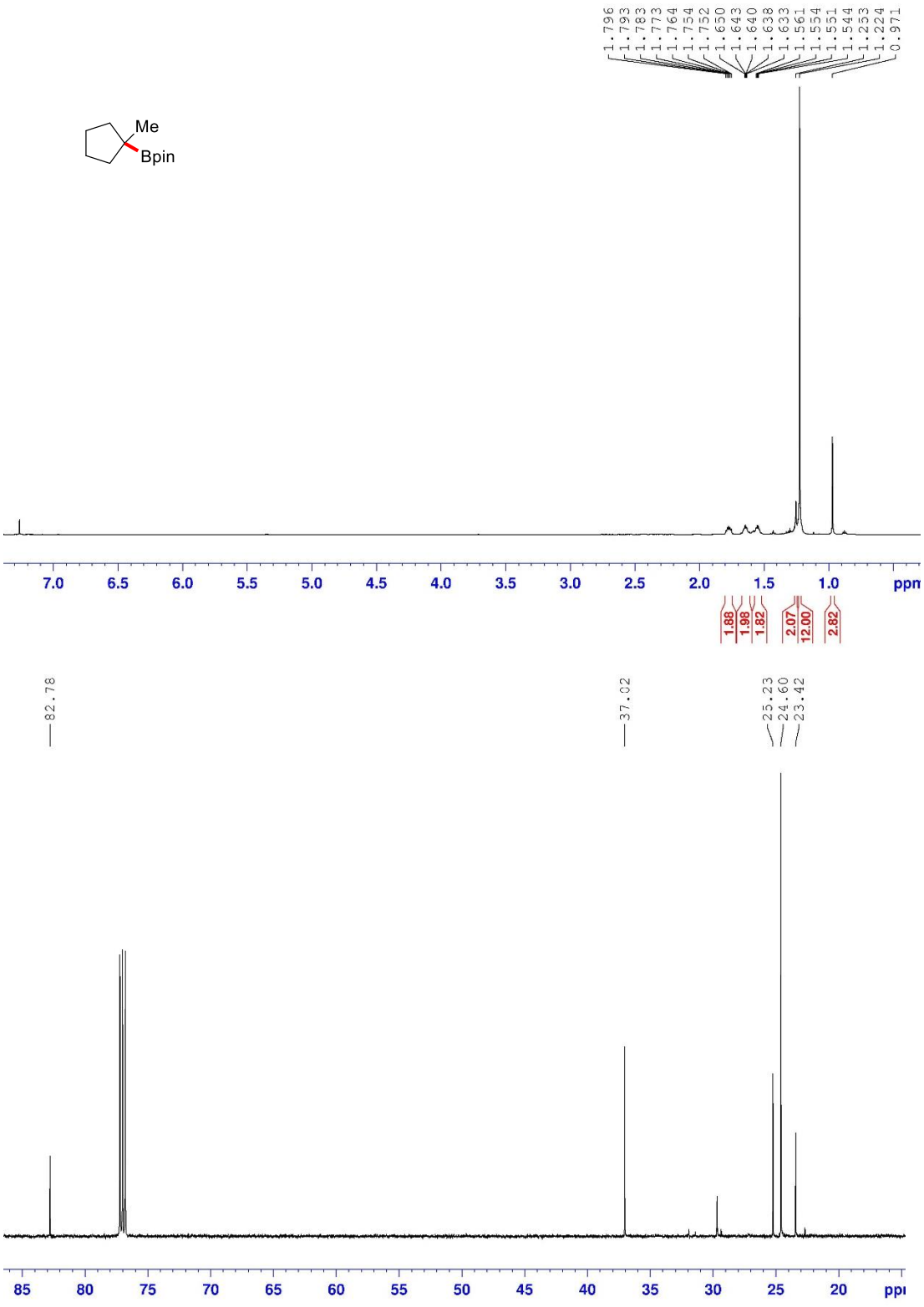
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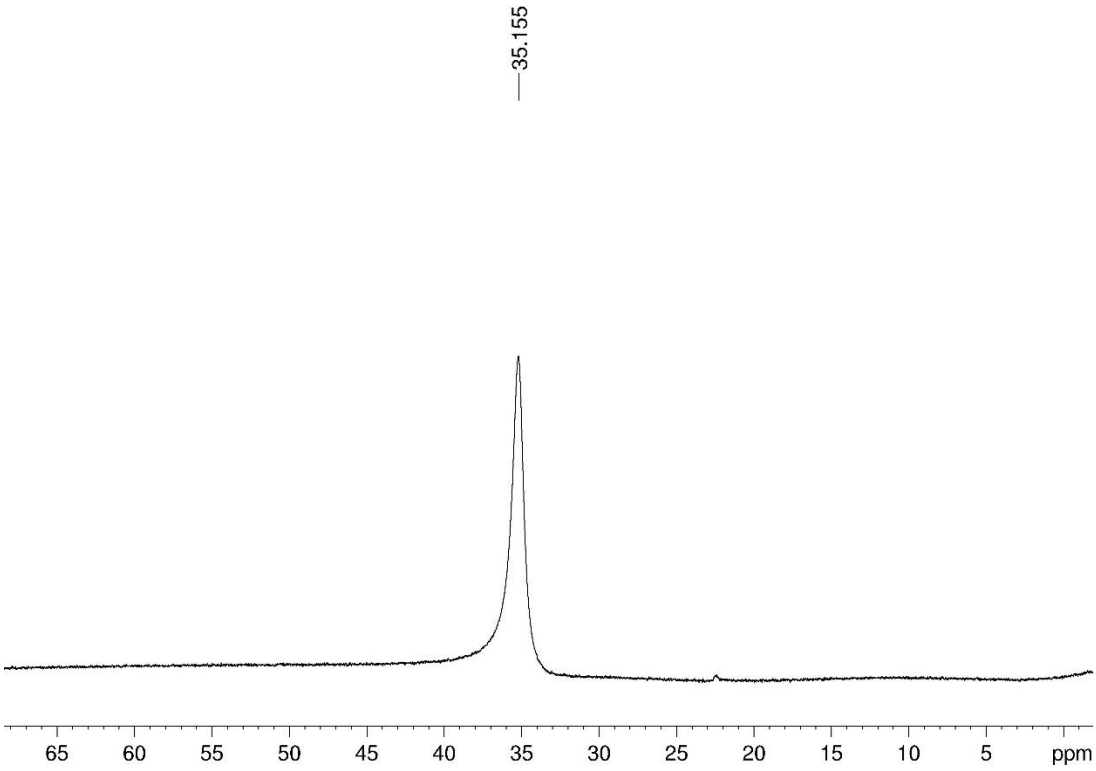
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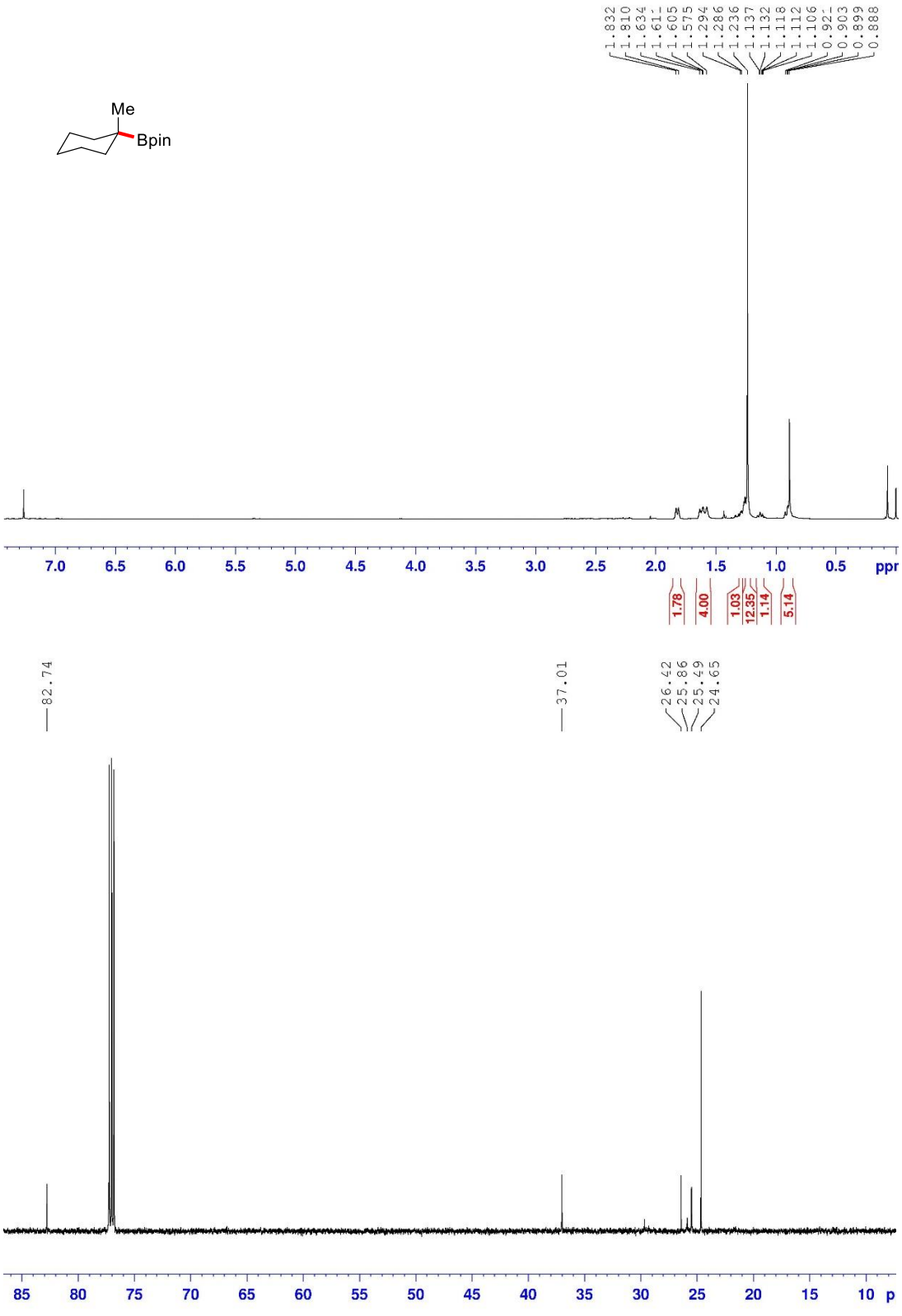
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2.0
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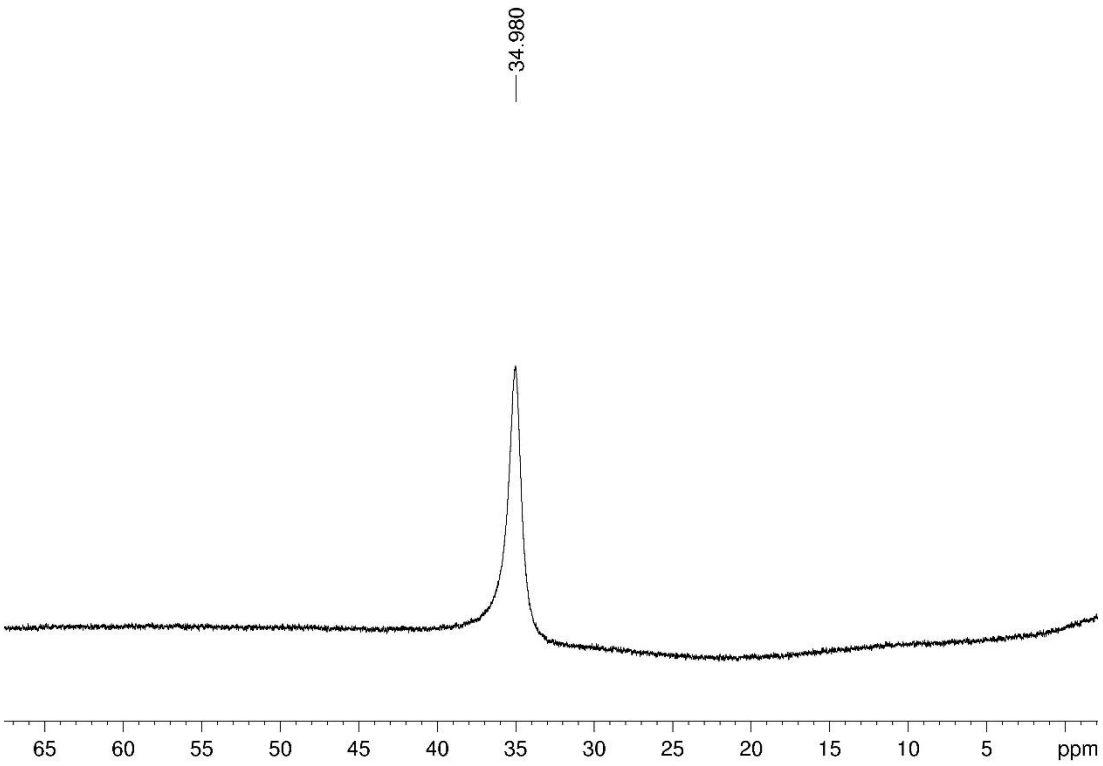
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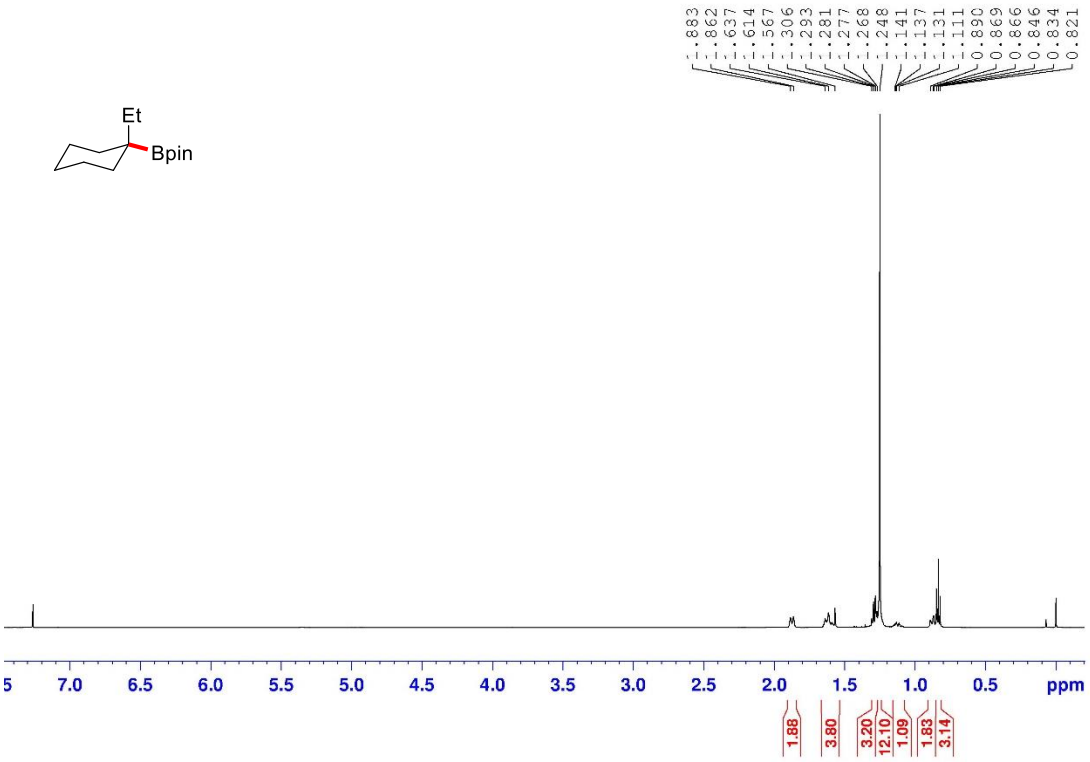
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1.141
1.137
1.131
1.111
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0.866
0.846
0.834
0.821
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3.5
3.0
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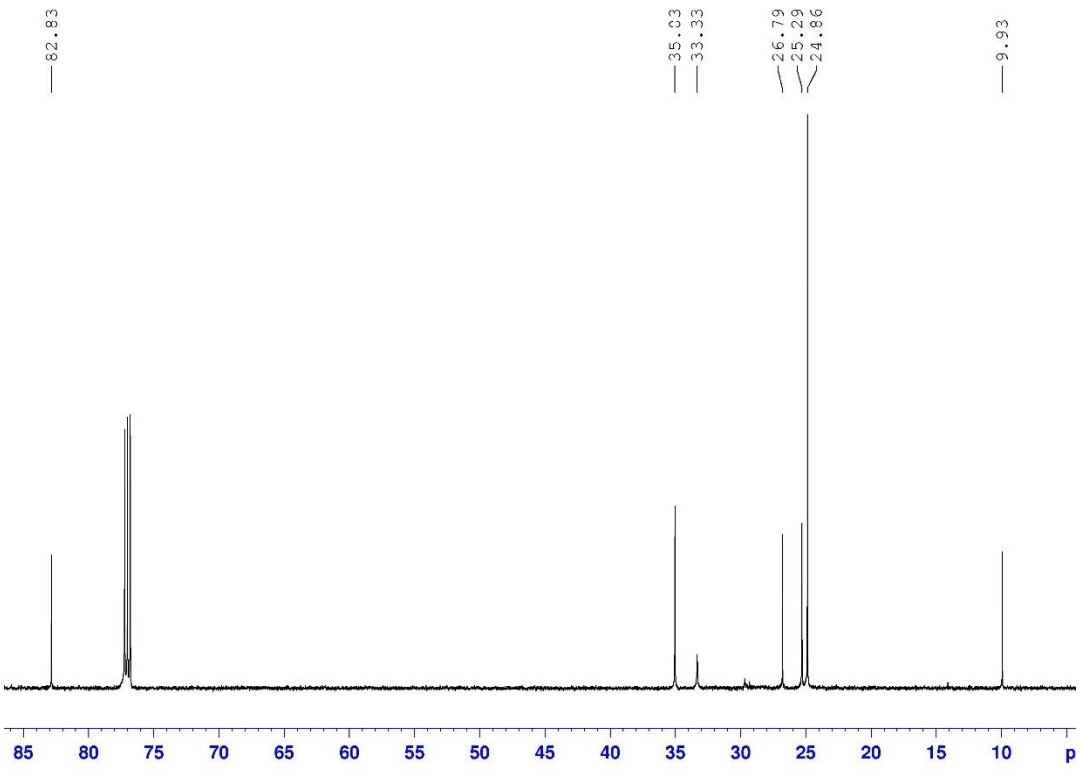
3.14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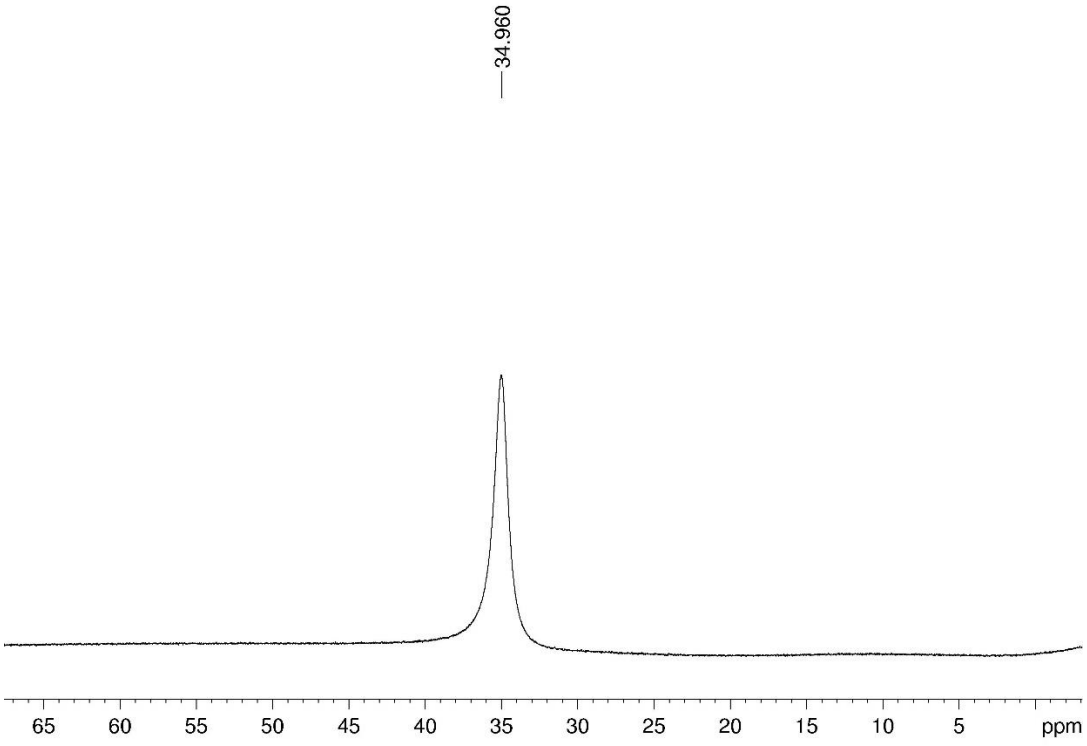
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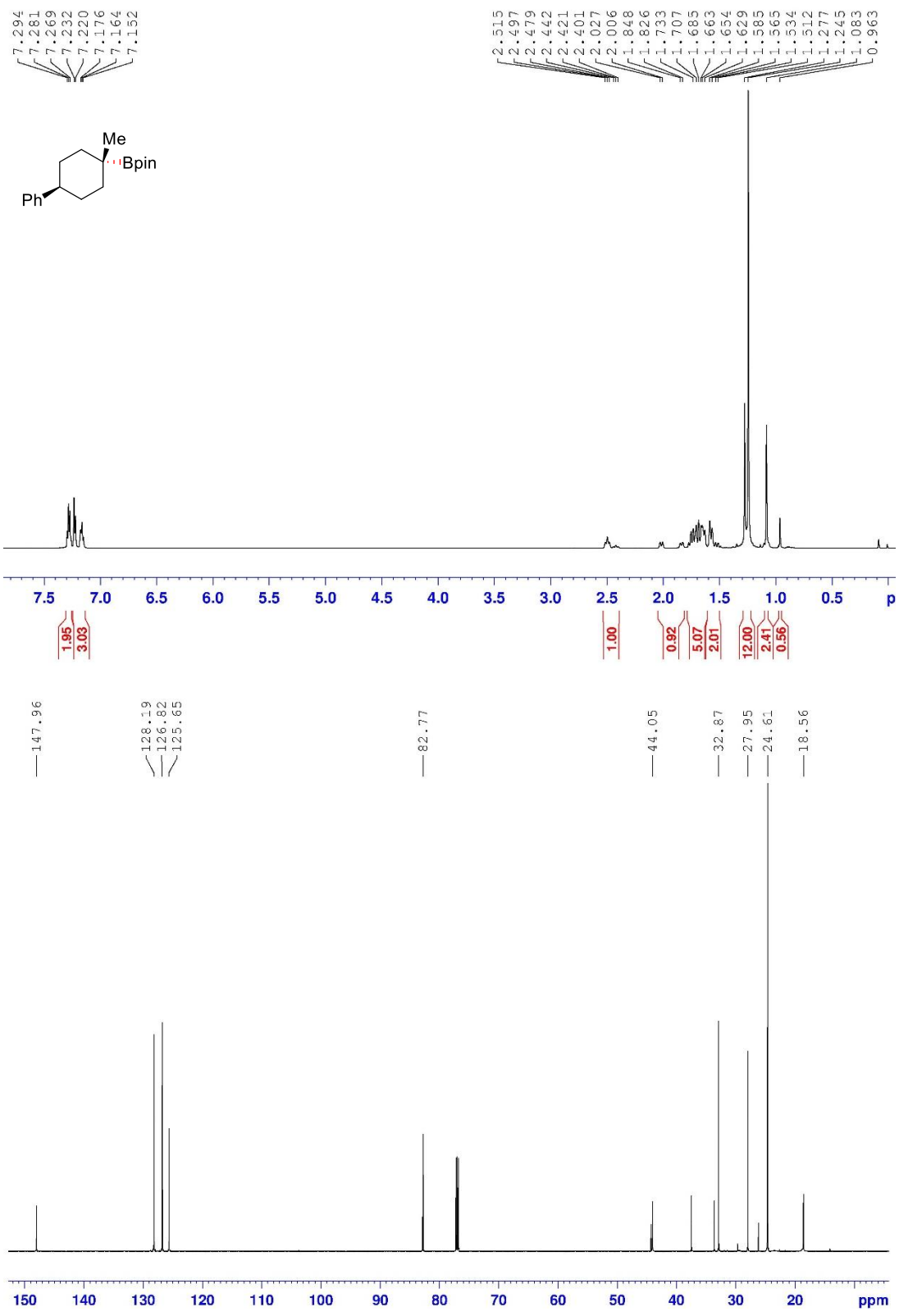
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2.421
2.401
2.027
2.006
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1.733
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1.585
1.565
1.334
1.312
1.277
1.245
1.083
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Me
Bpin
Ph
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
p
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3.03
1.00
0.92
5.07
2.01
12.00
2.41
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126.82
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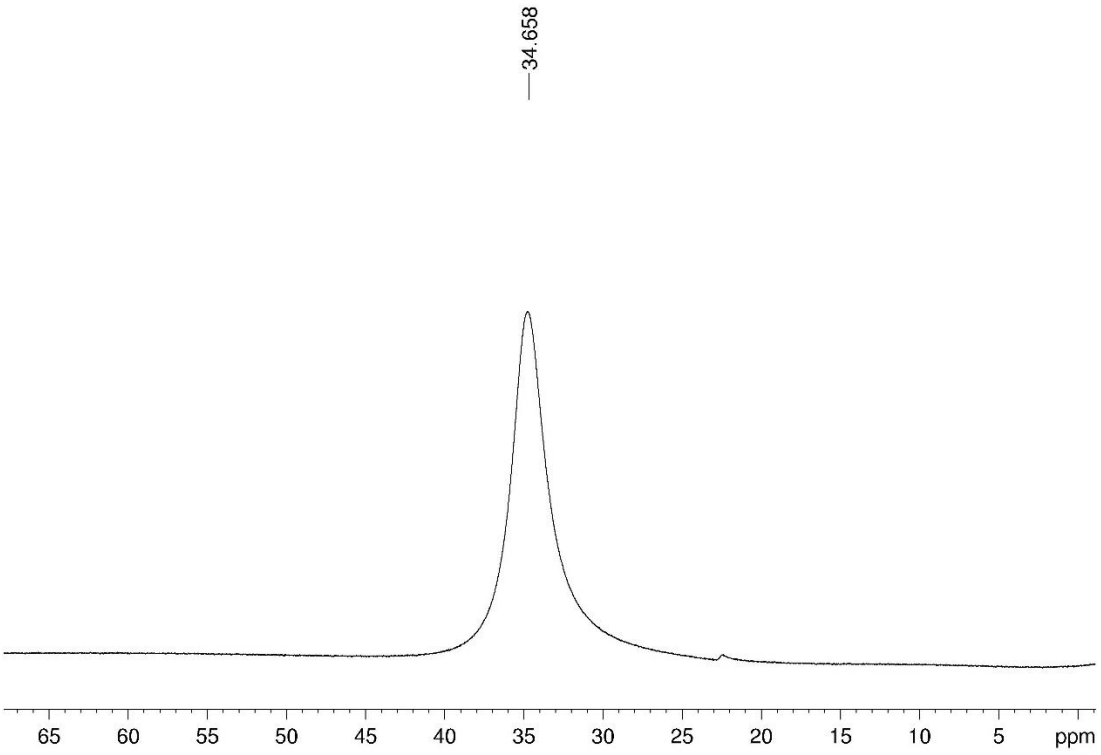
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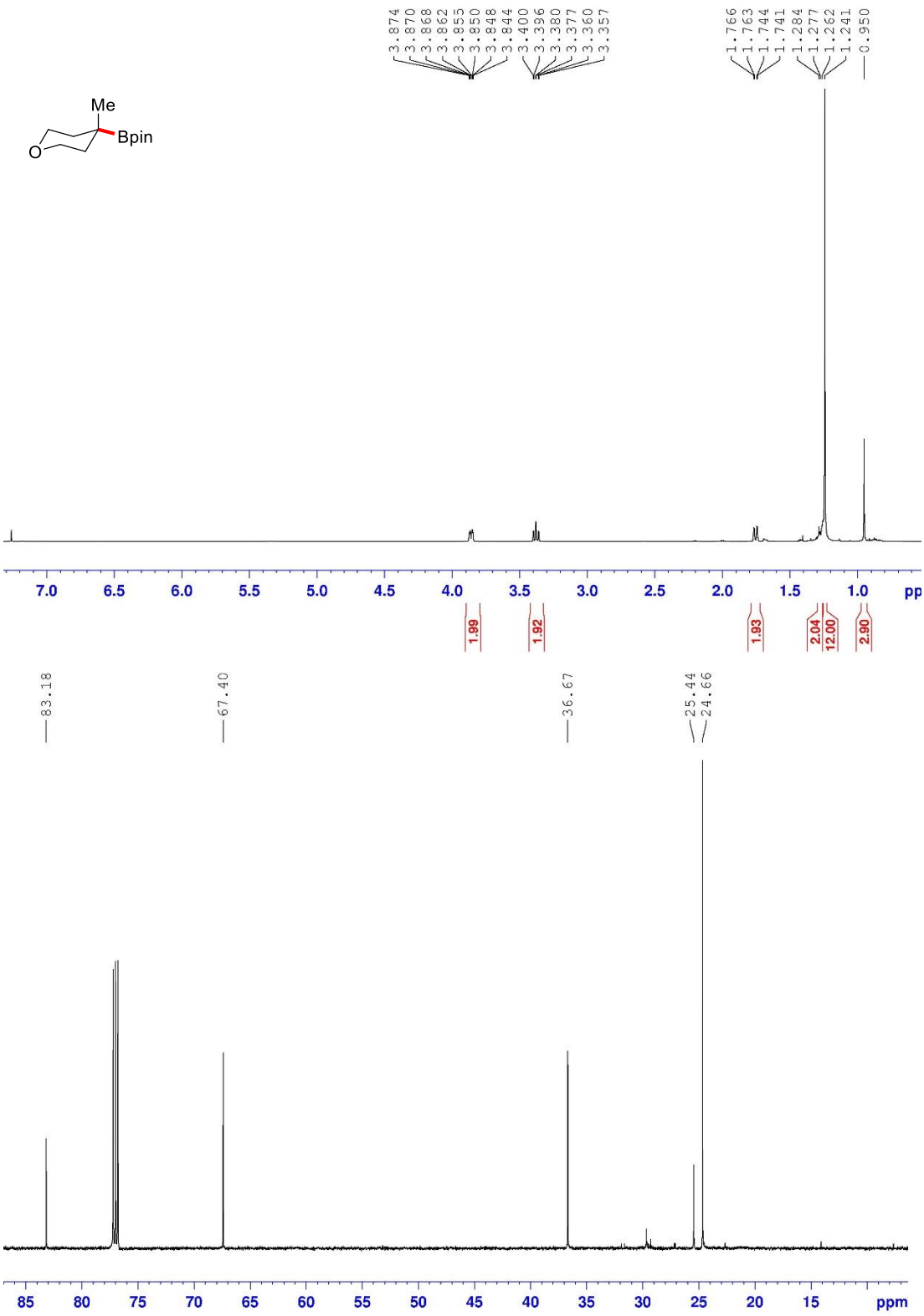
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3.377
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1.0
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1.93
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2.90
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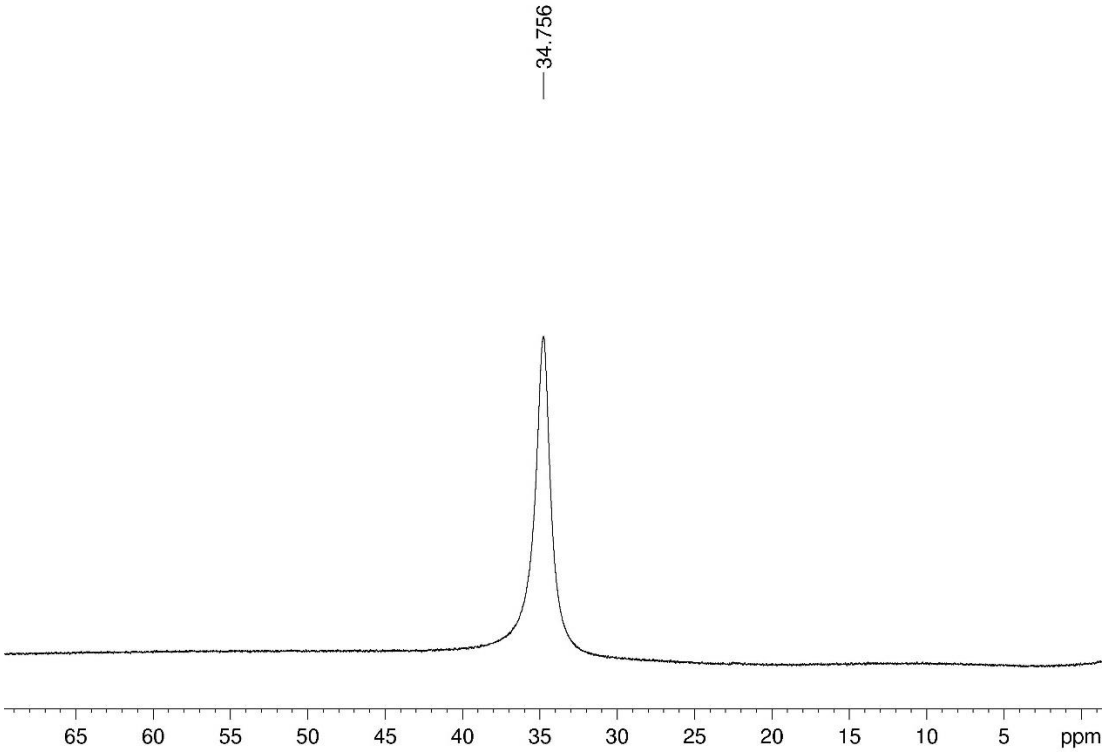
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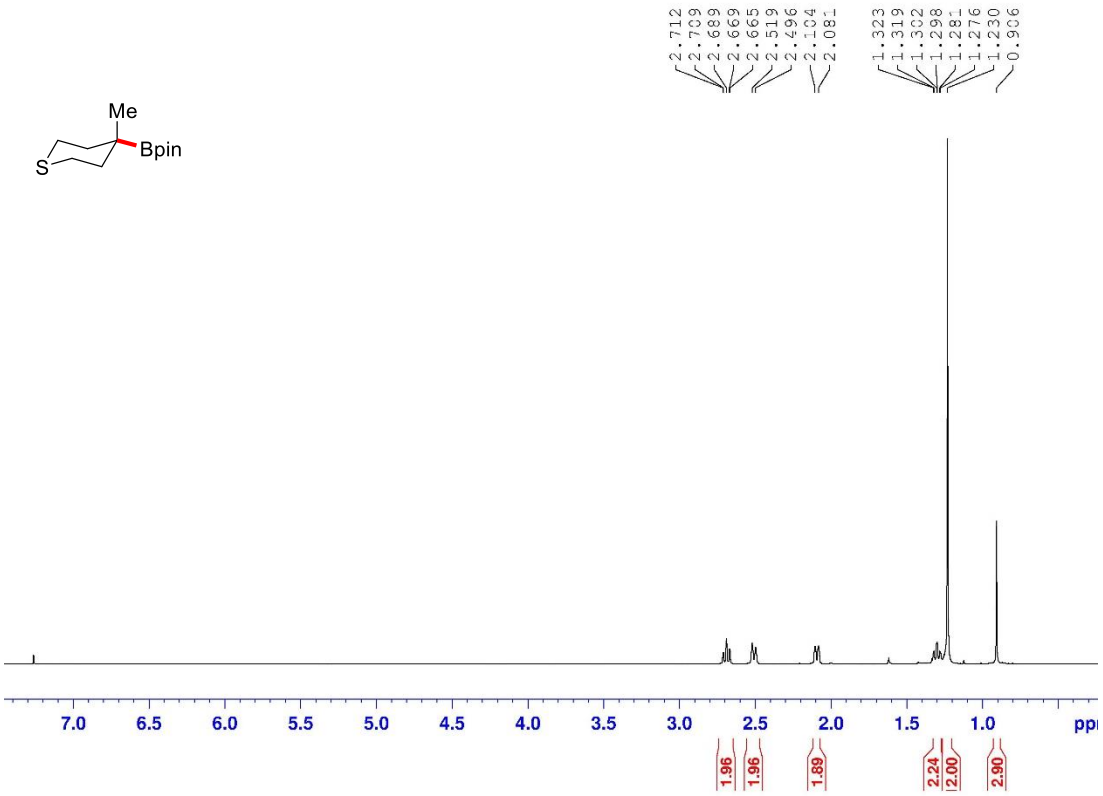
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1.298
1.276
1.230
0.906
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6.0
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5.0
4.5
4.0
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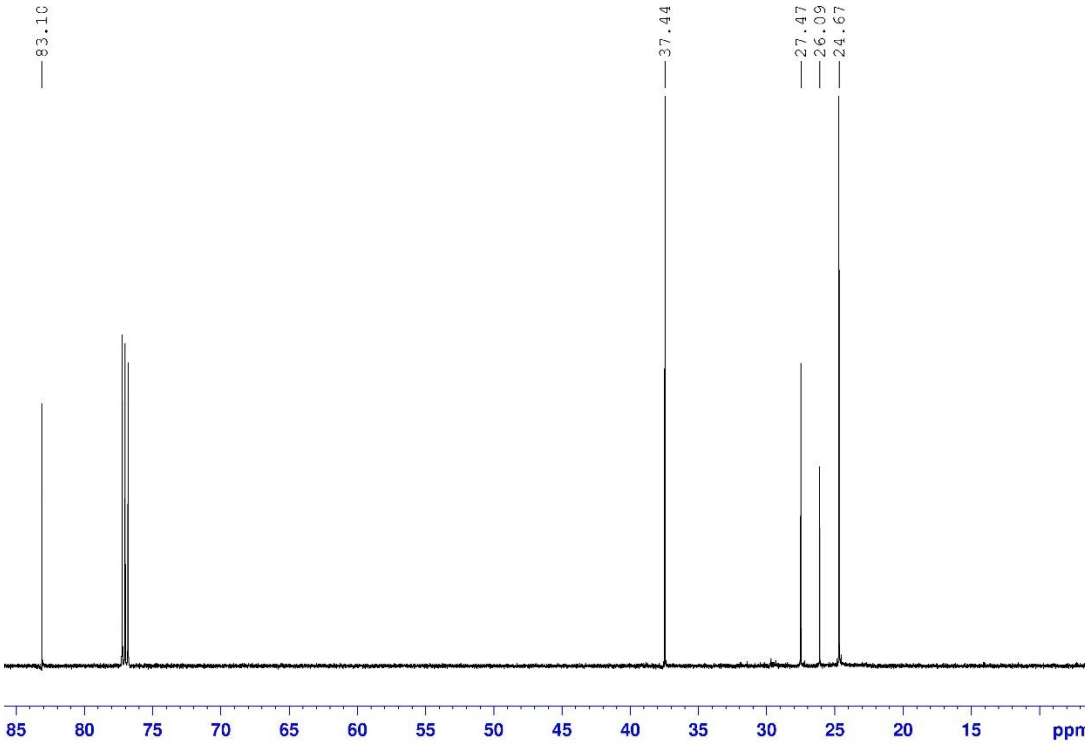
2.00
2.90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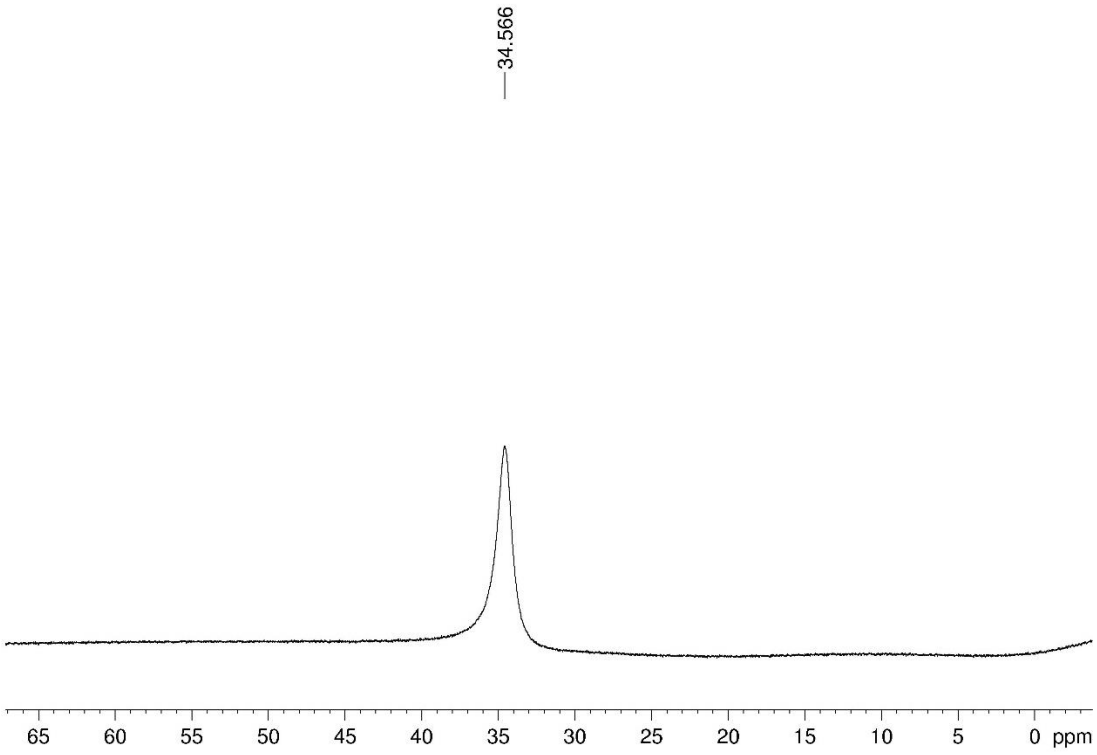
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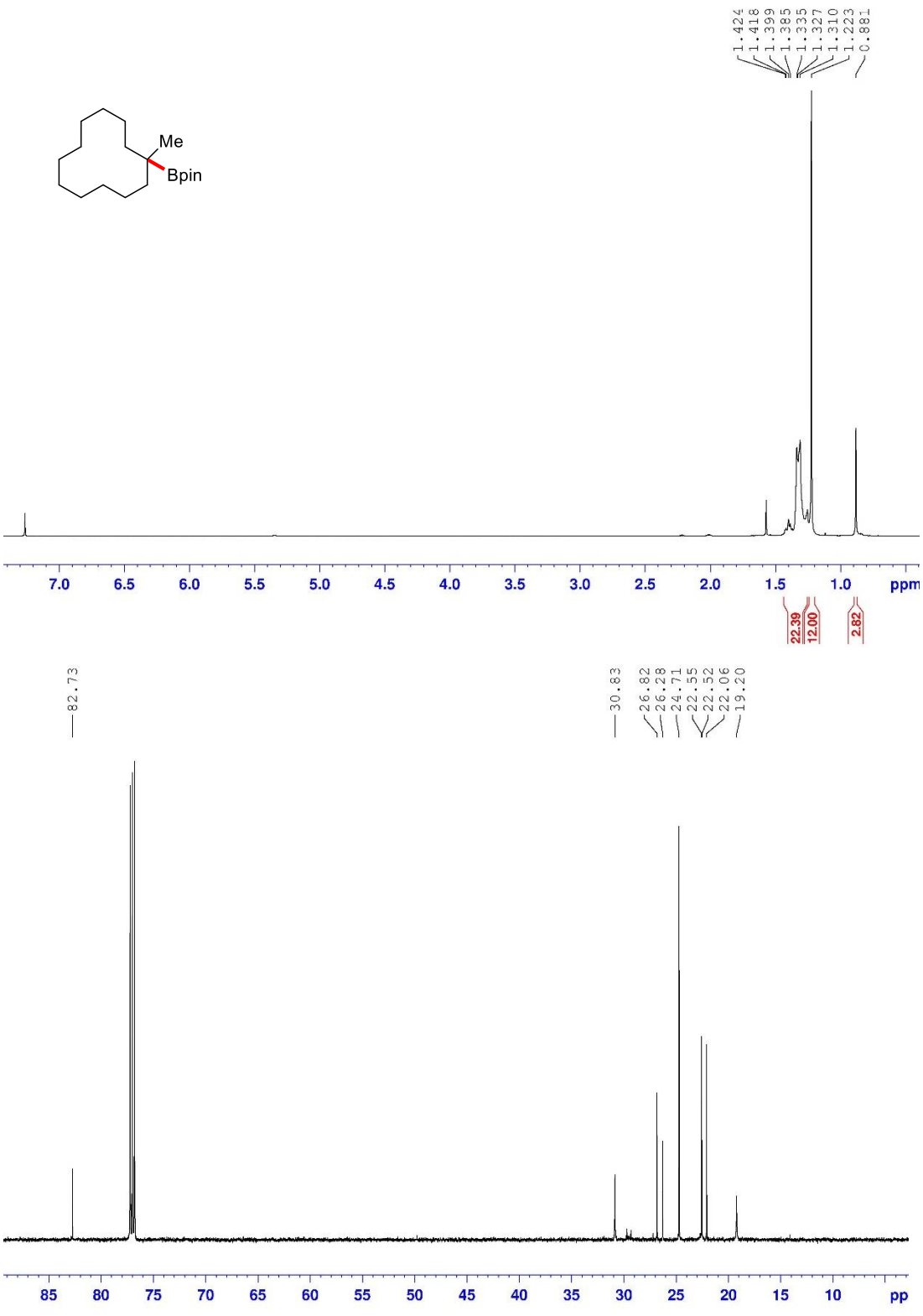
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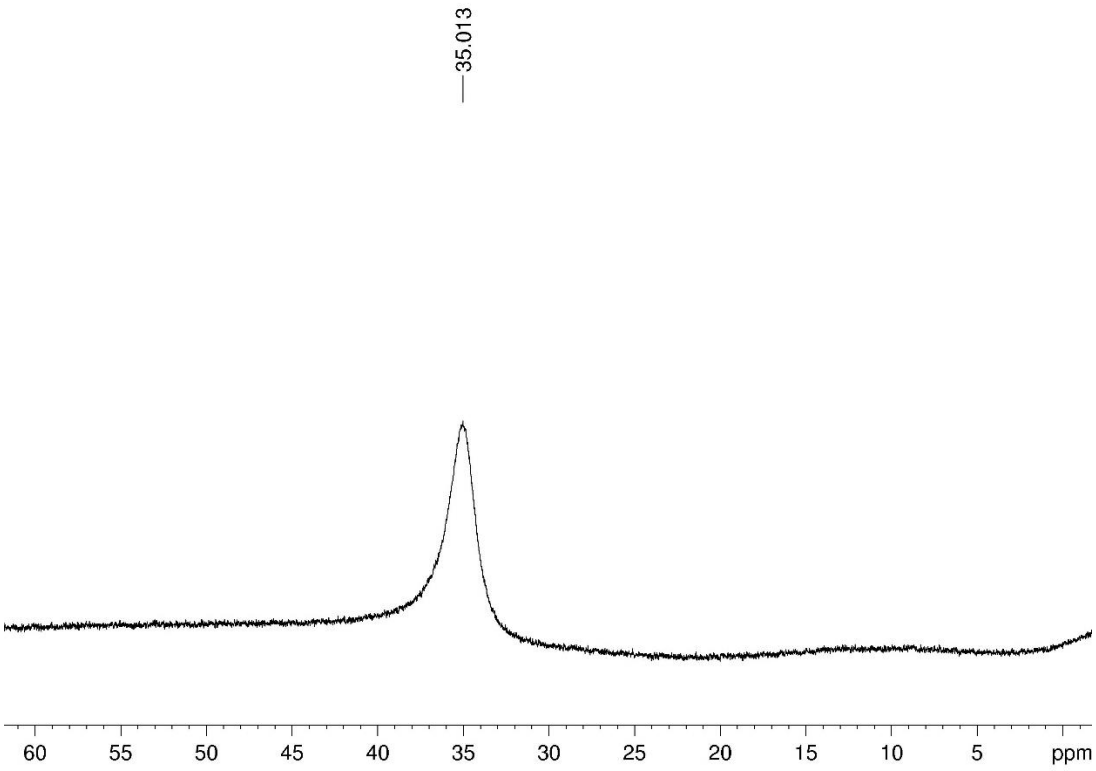
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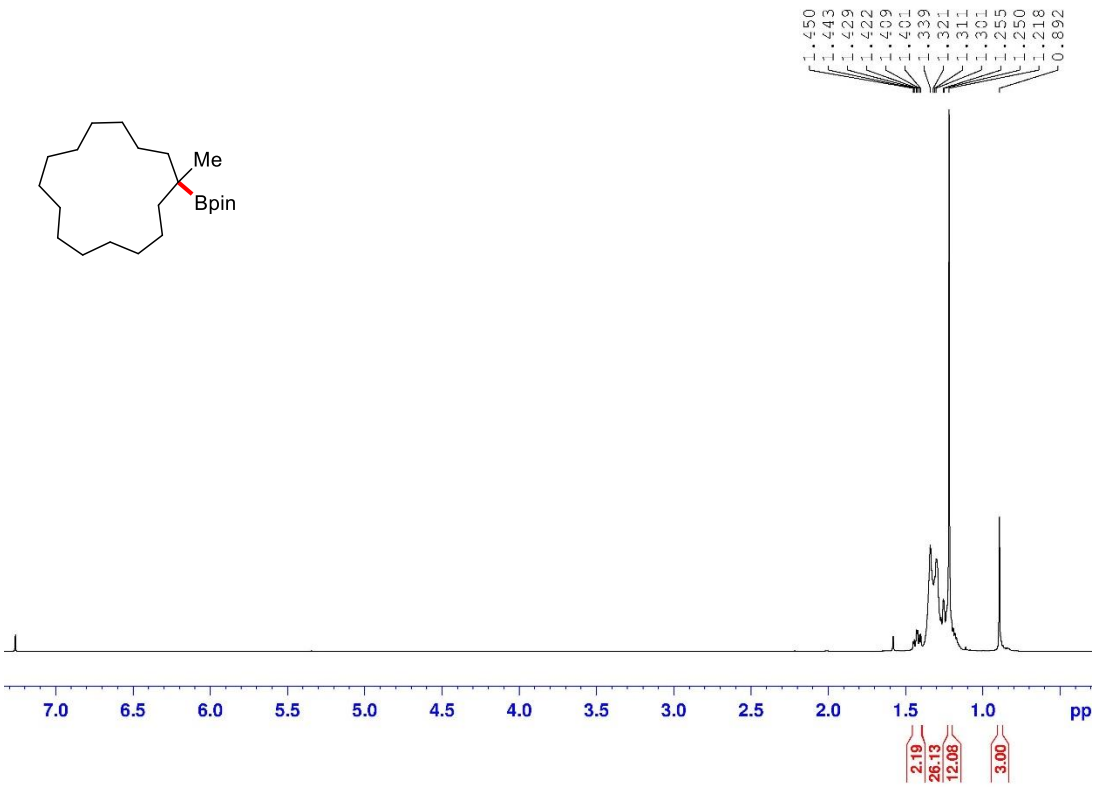
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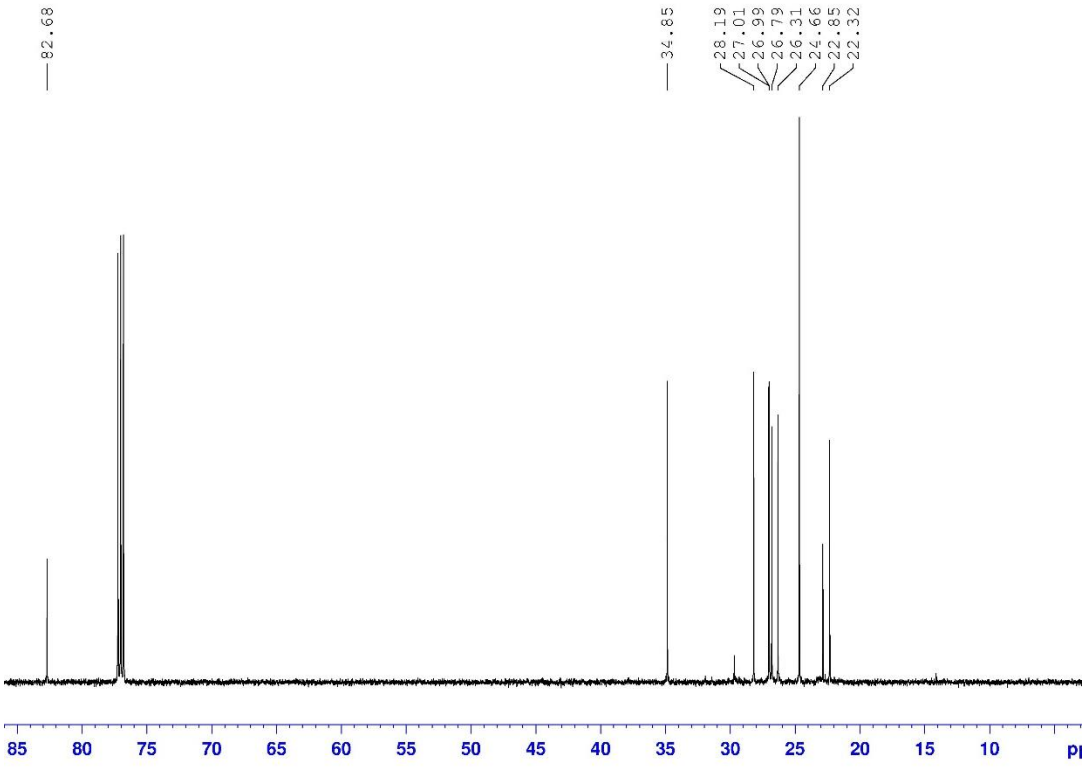
3.00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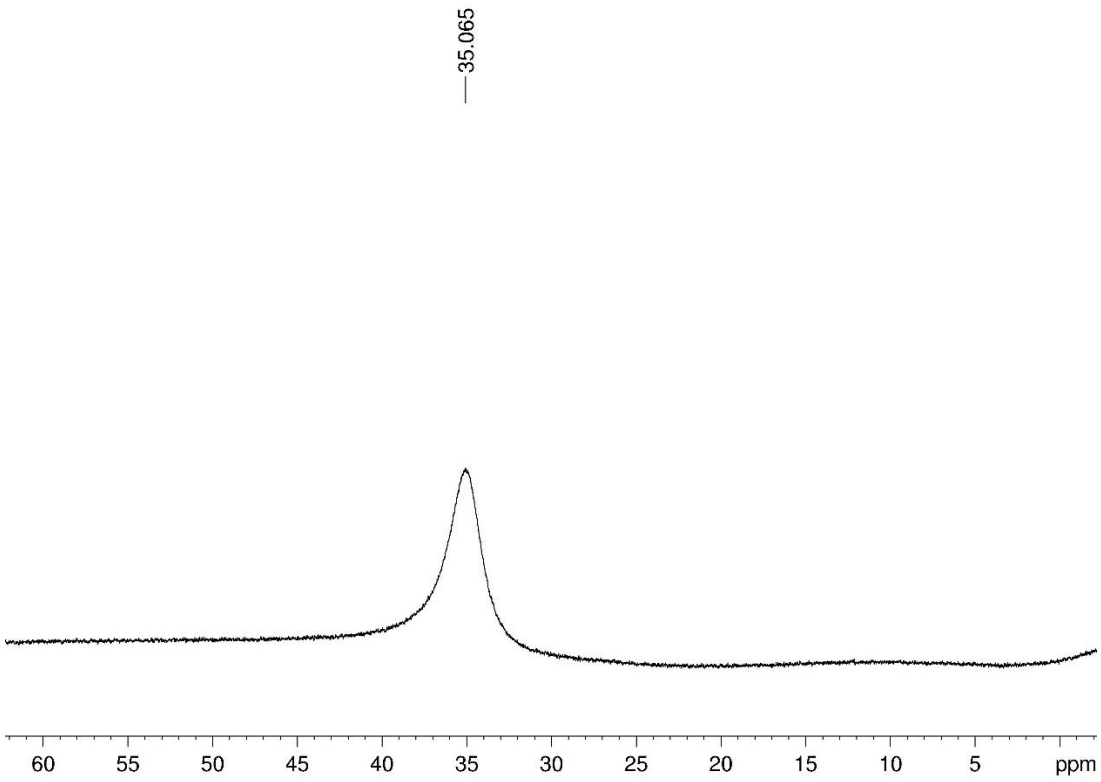
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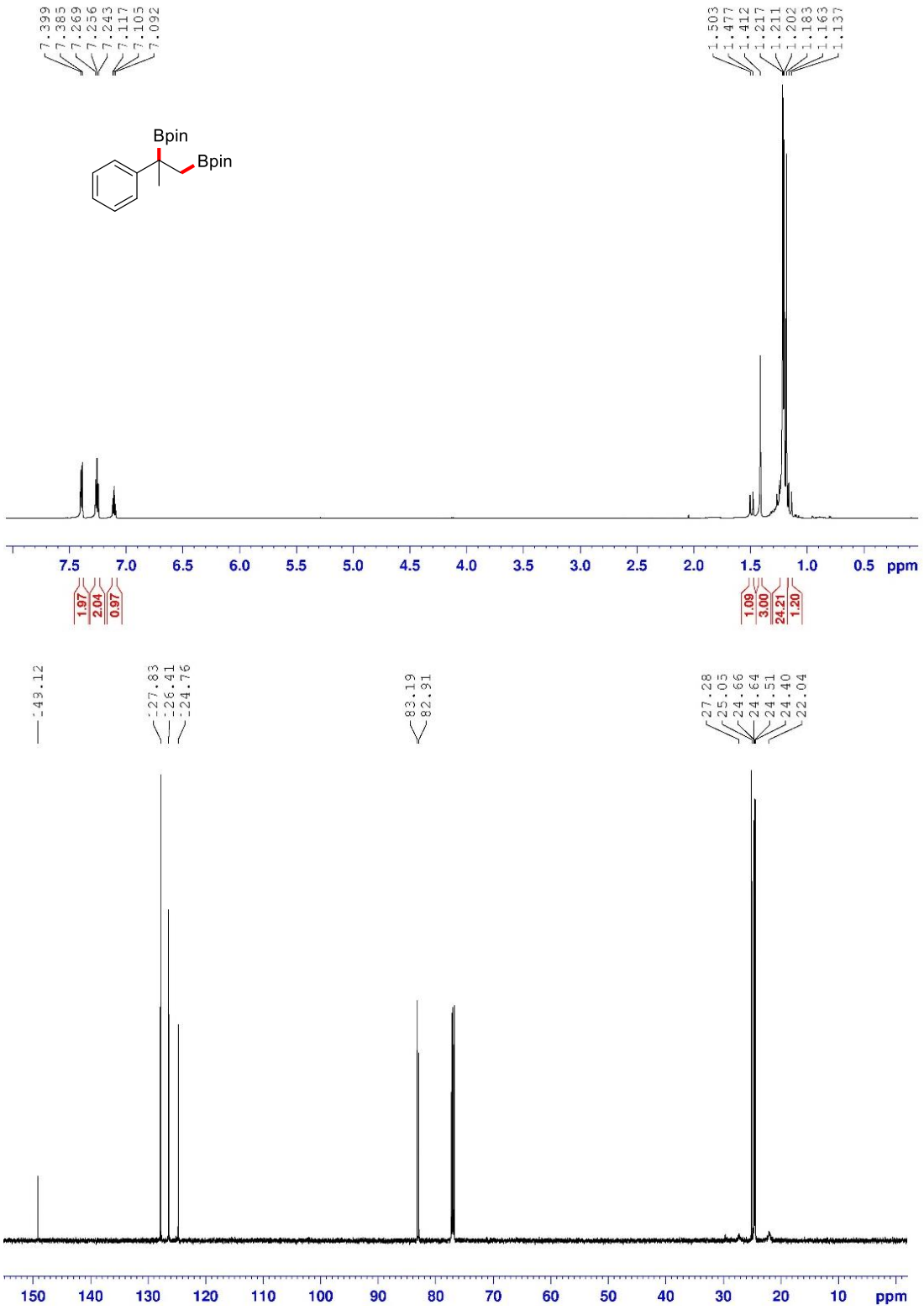
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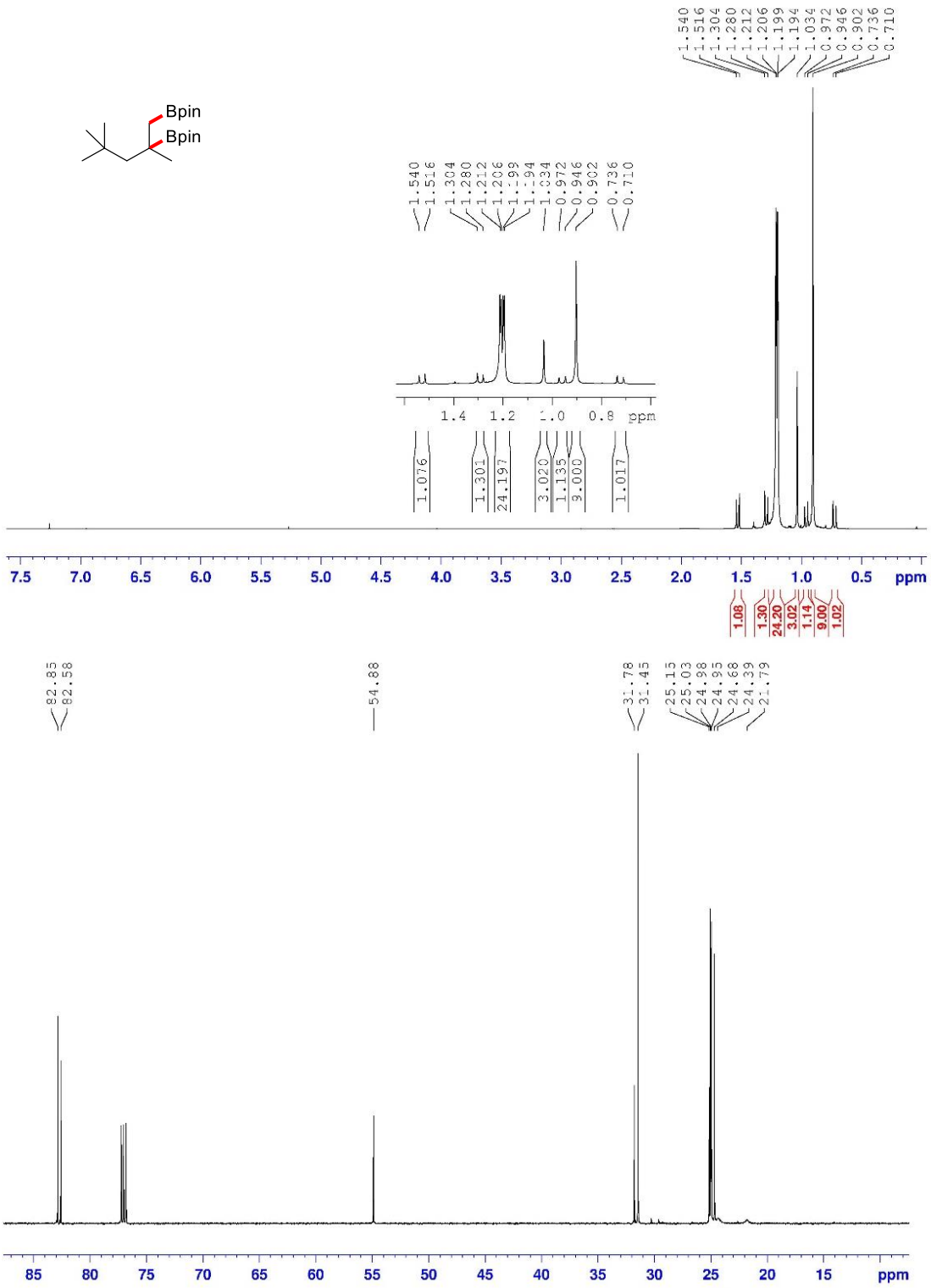
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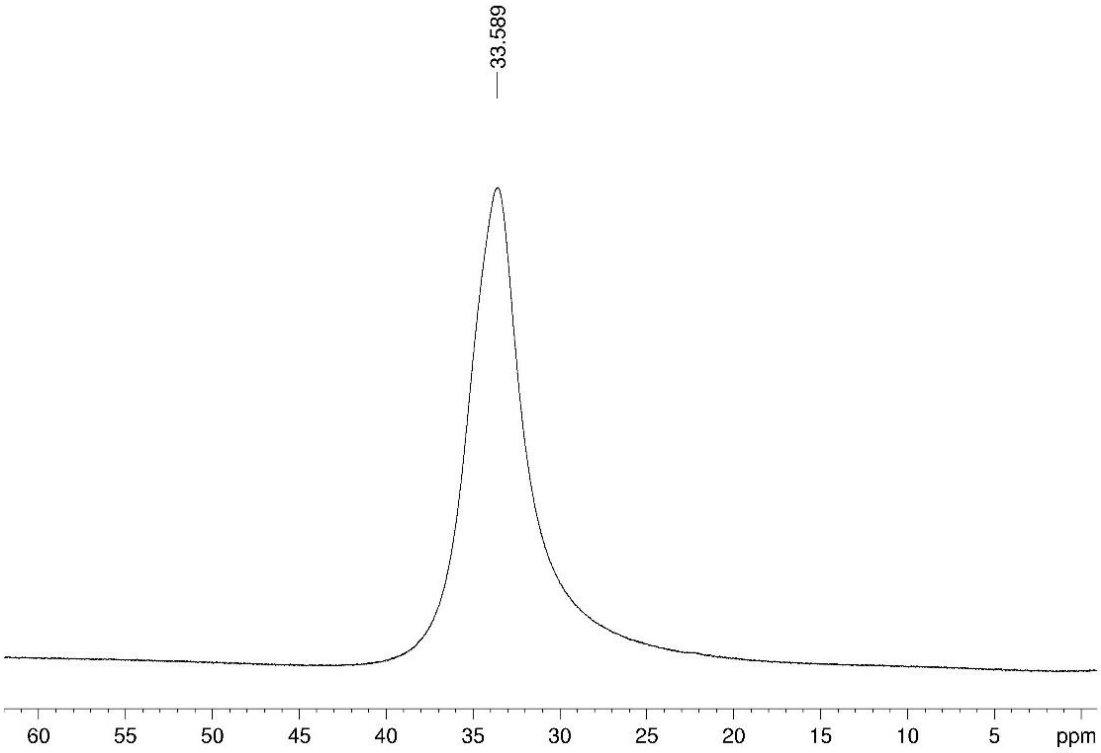
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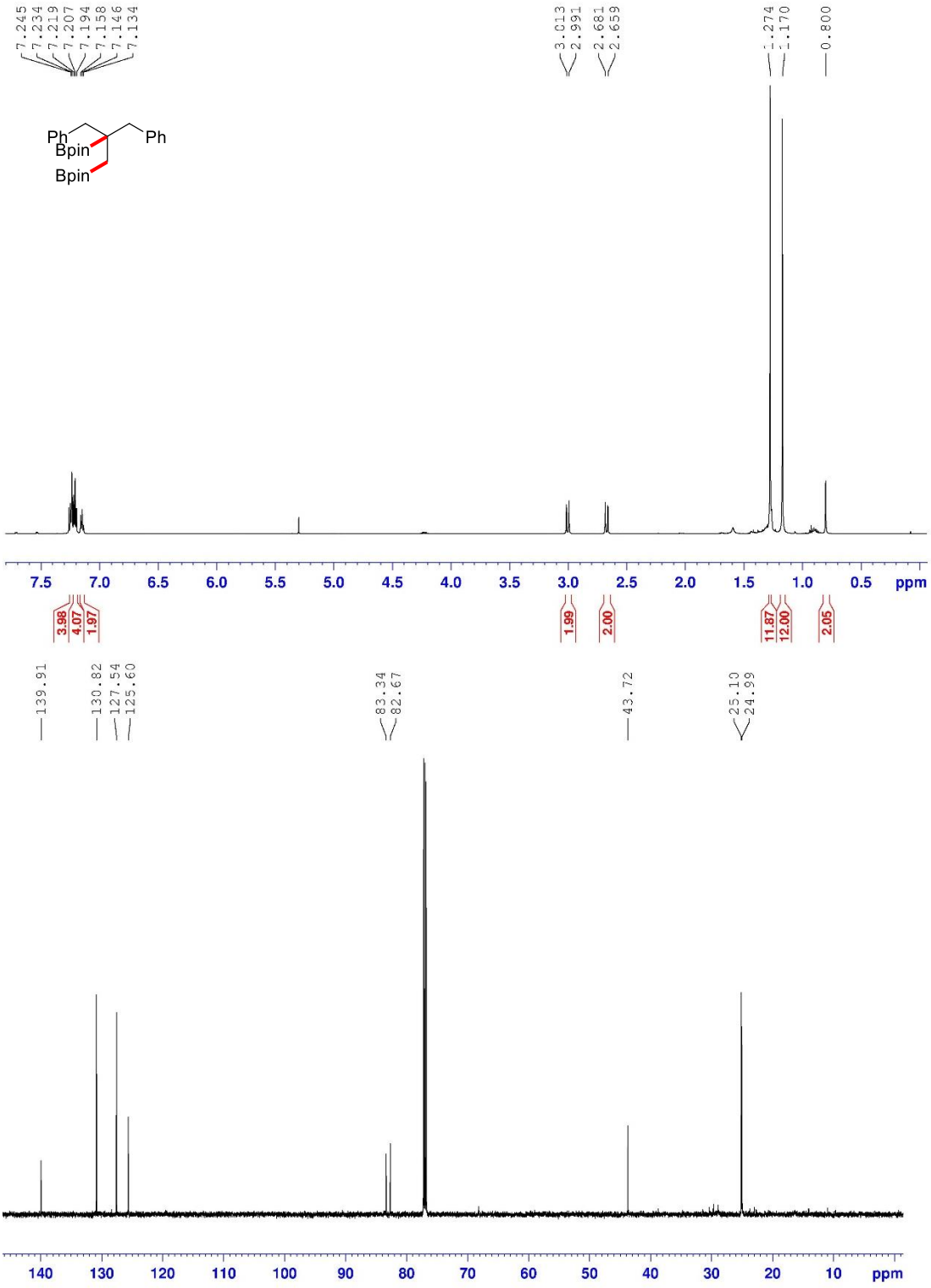
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1.170
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Bpin
Bpin
Ph
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4.0
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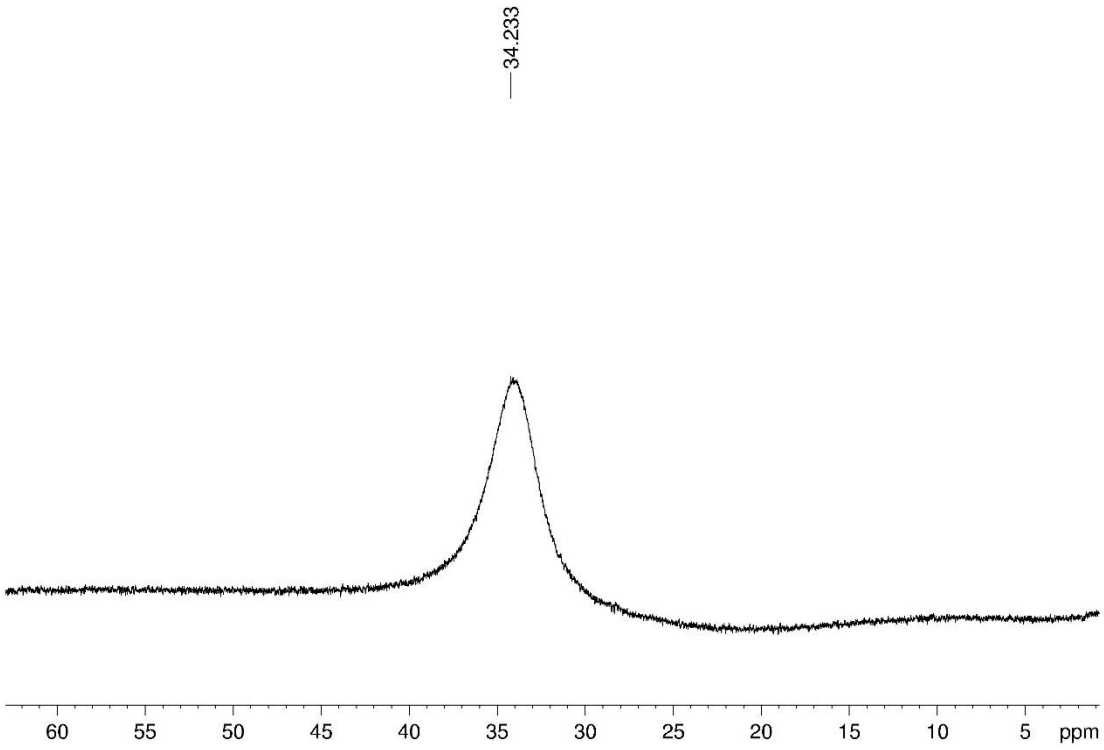
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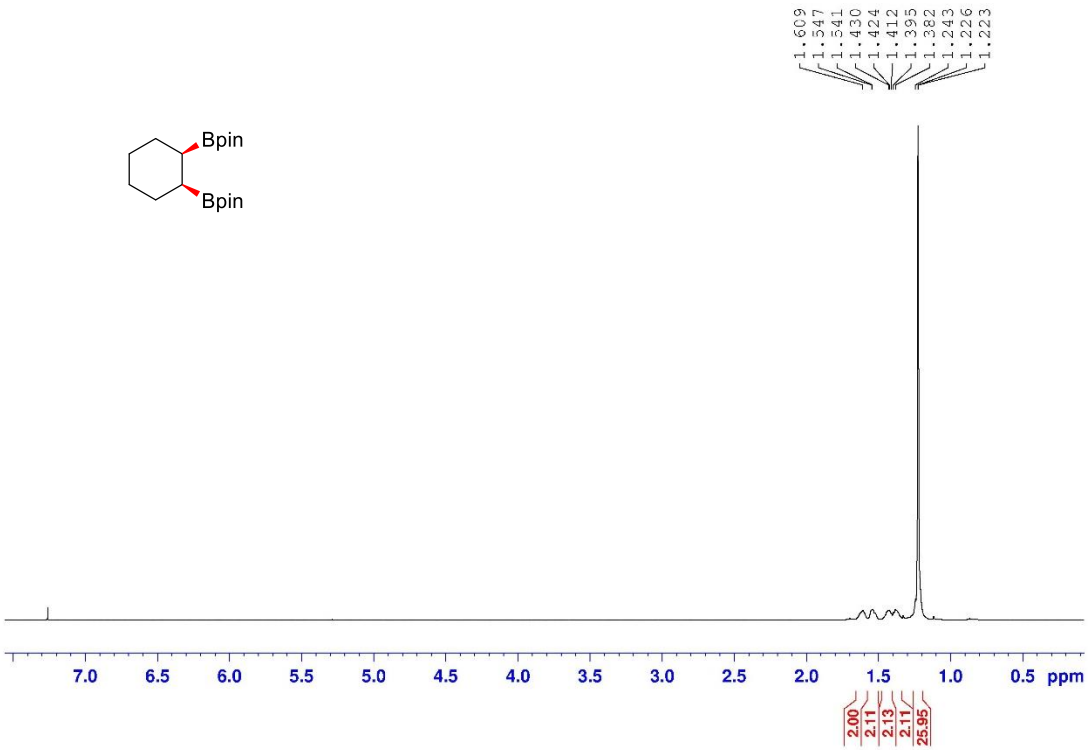
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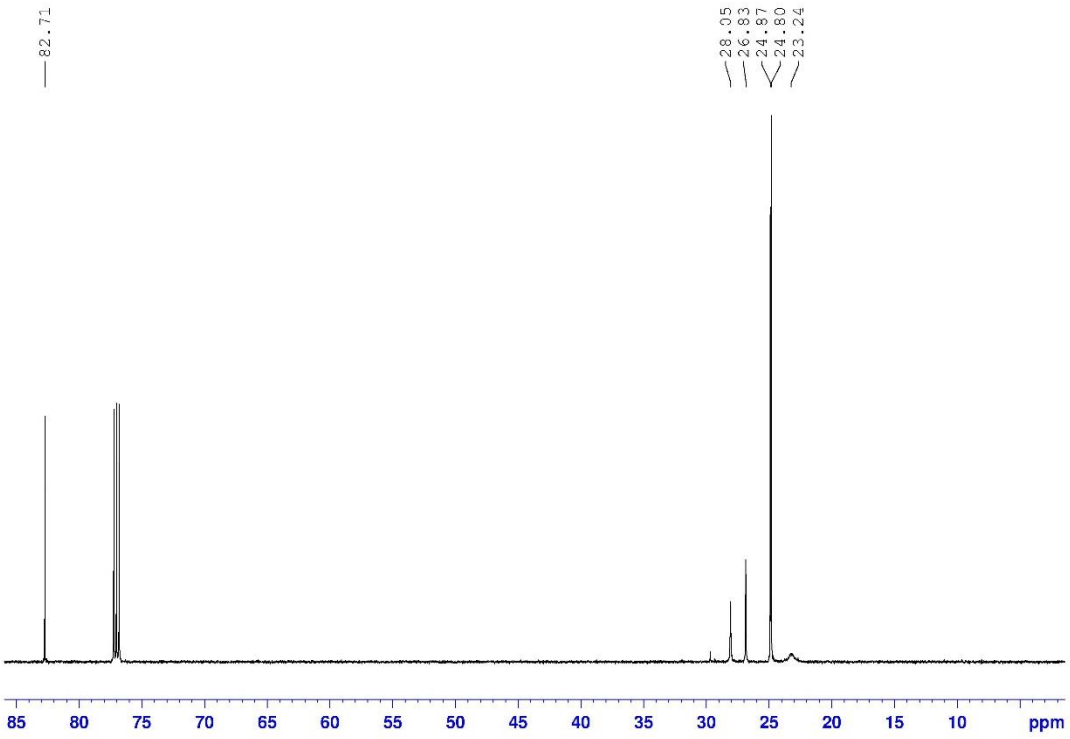
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25
20
15
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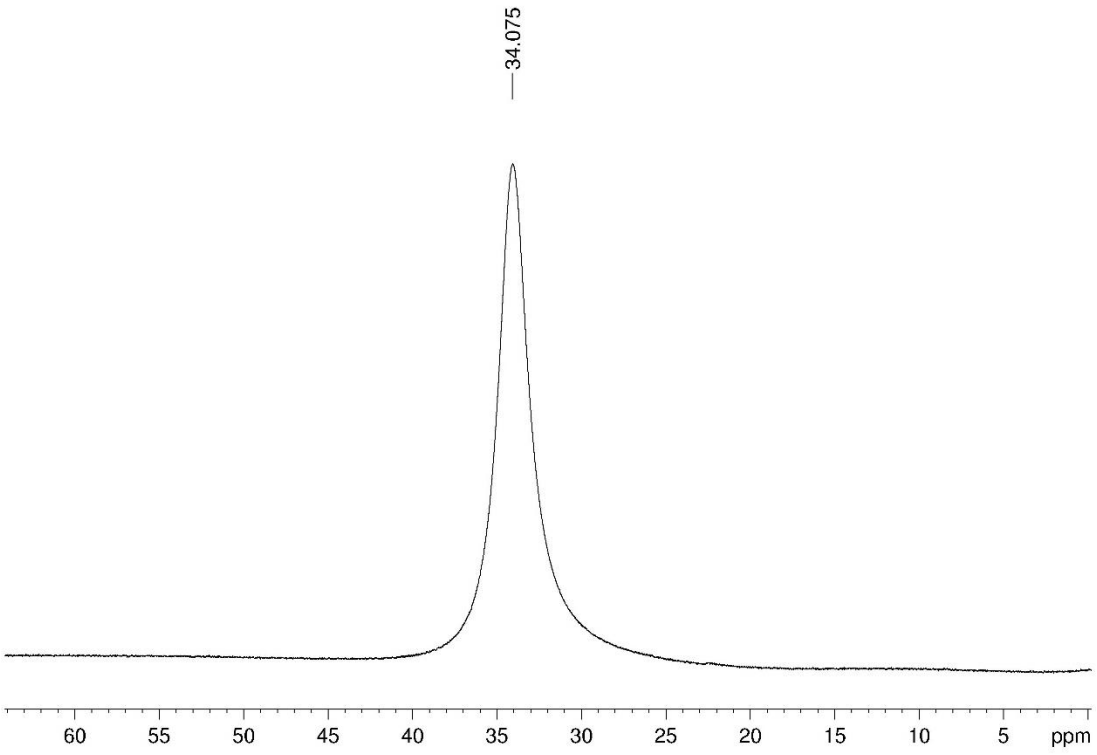
ppm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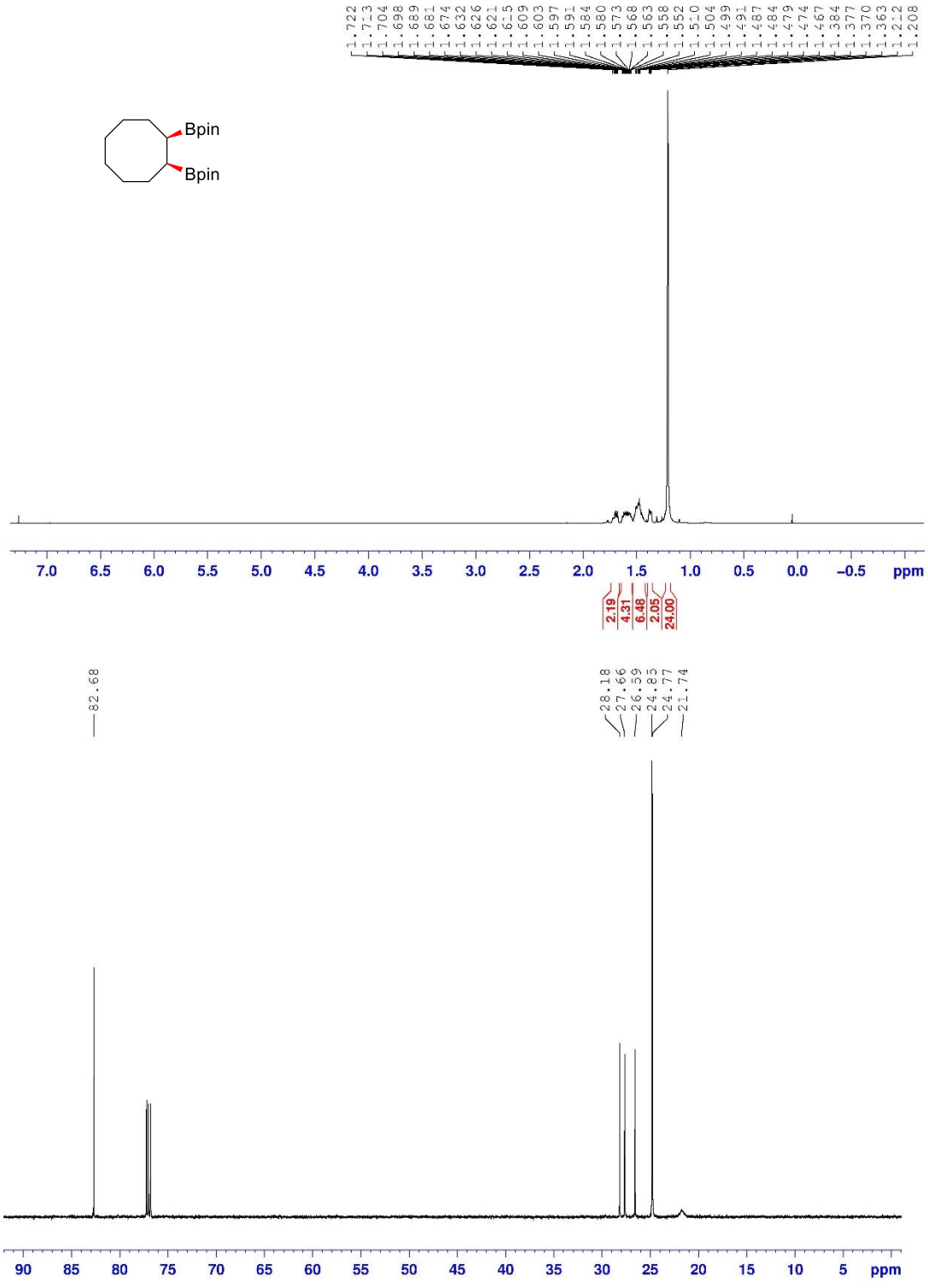
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1.597
1.591
1.584
1.580
1.573
1.568
1.563
1.558
1.552
1.510
1.504
1.499
1.491
1.487
1.484
1.479
1.474
1.467
1.384
1.377
1.370
1.363
1.212
1.208
Bpin
Bpin
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm
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4.31
6.48
2.05
24.00
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28.18
27.66
26.59
24.85
24.77
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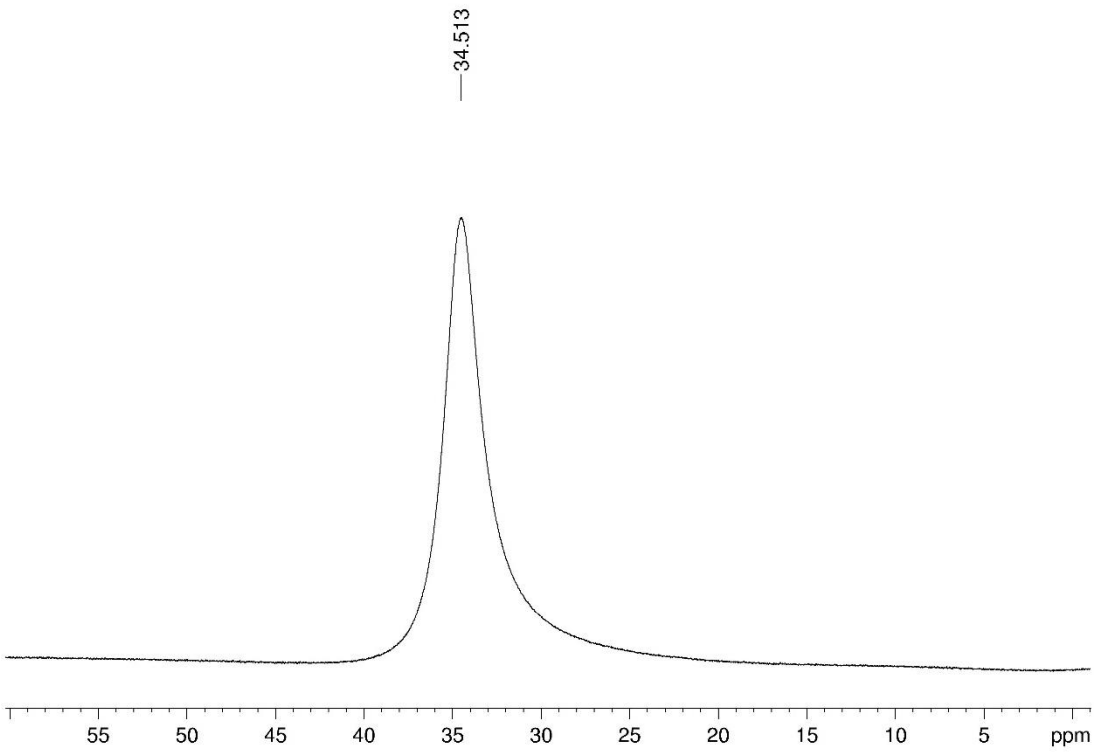
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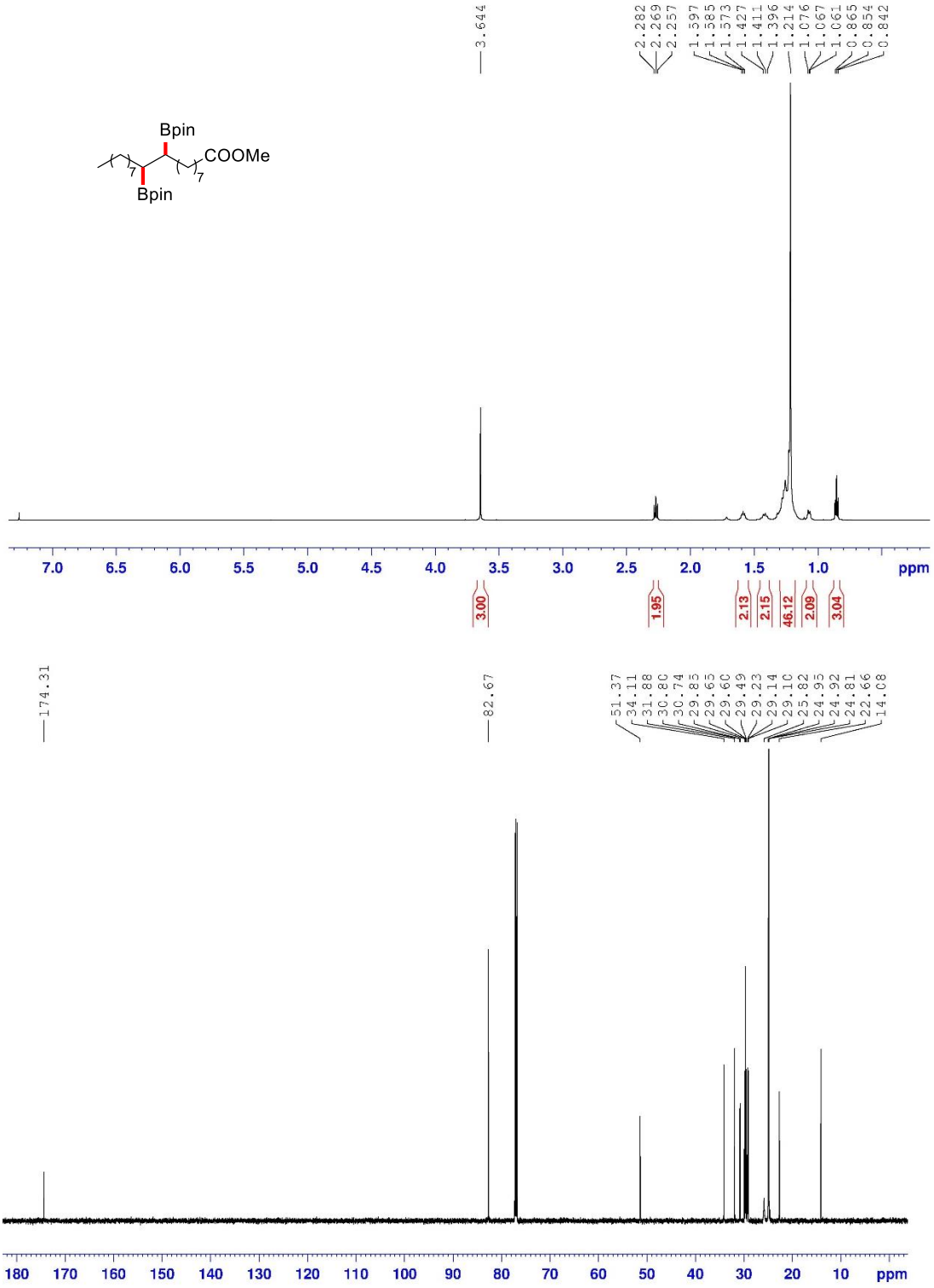
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COOMe
Bpin
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1.214
1.076
1.067
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0.854
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.00
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2.13
2.15
46.12
2.09
3.04
174.31
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51.37
34.11
31.88
30.80
30.74
29.85
29.65
29.60
29.49
29.23
29.14
29.10
25.82
24.95
24.92
24.81
22.66
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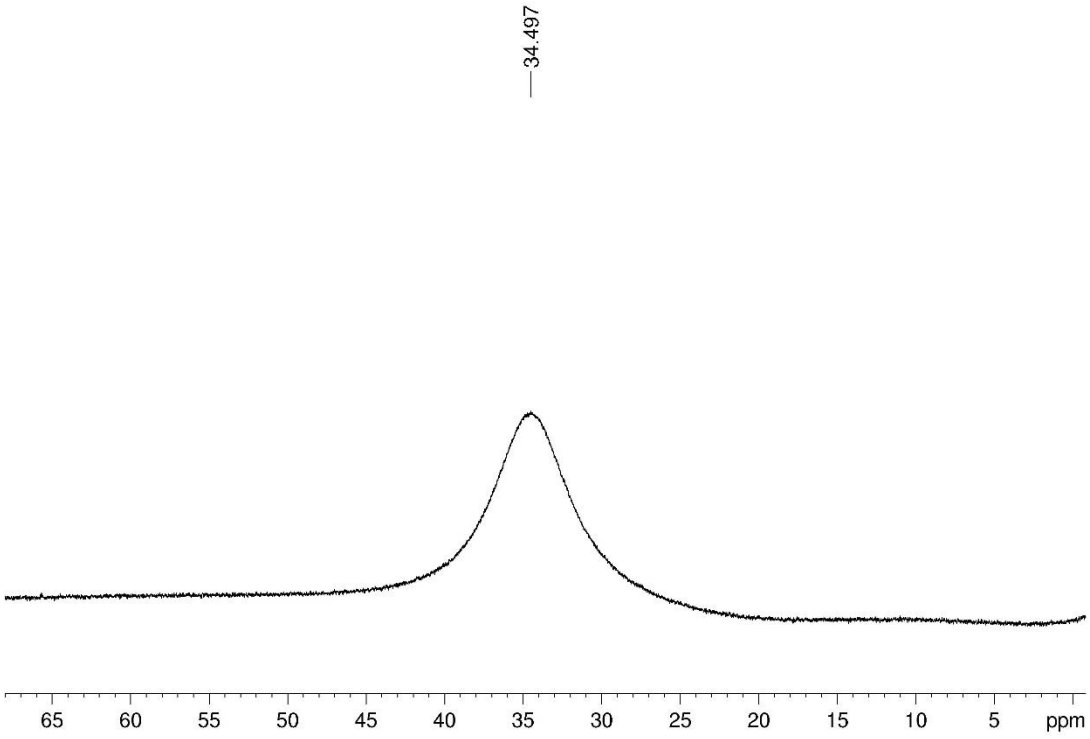
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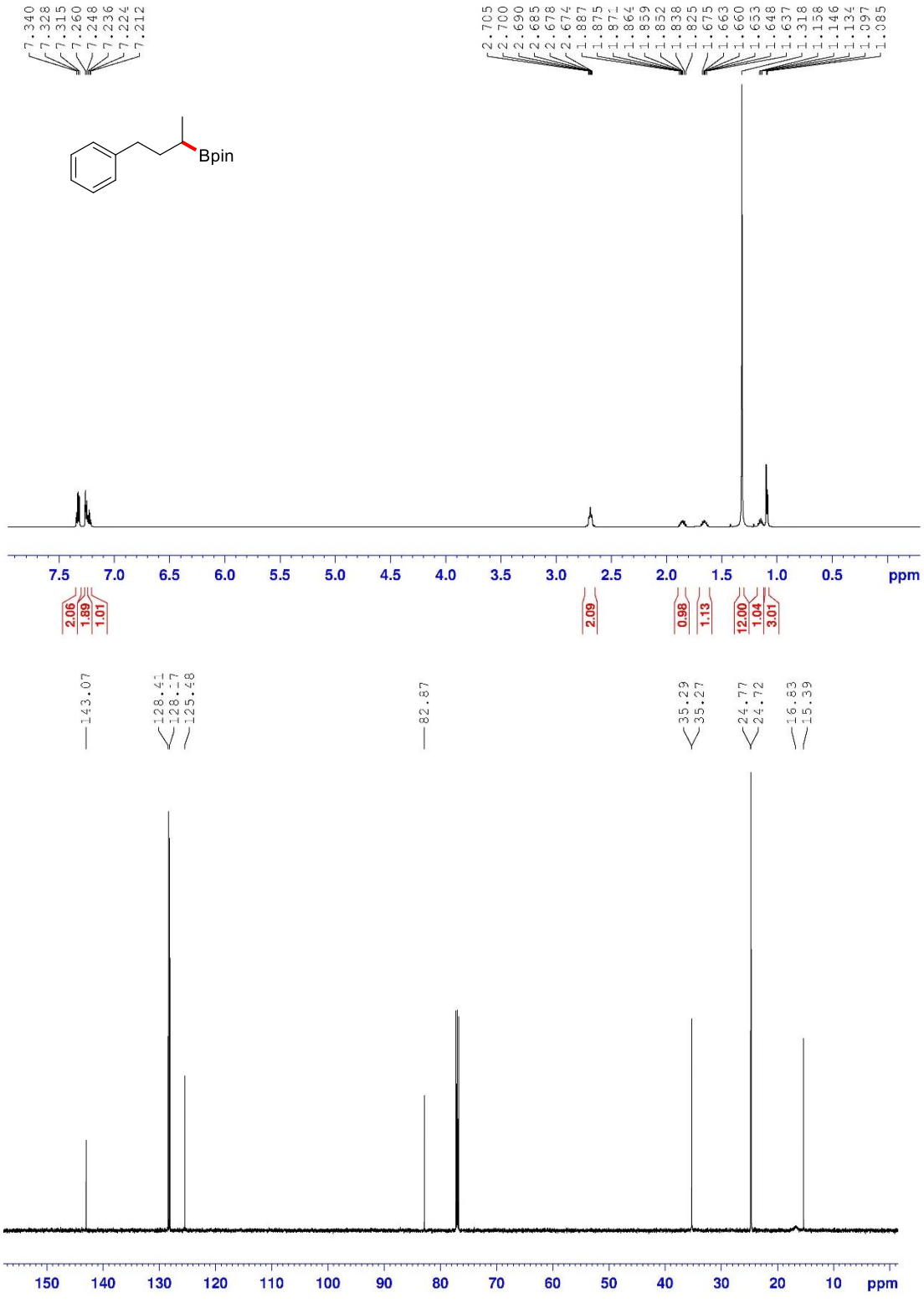
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2.678
2.674
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1.864
1.859
1.852
1.838
1.825
1.675
1.663
1.660
1.653
1.648
1.637
1.318
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1.134
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1.085
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3.0
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1.0
0.5
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3.01
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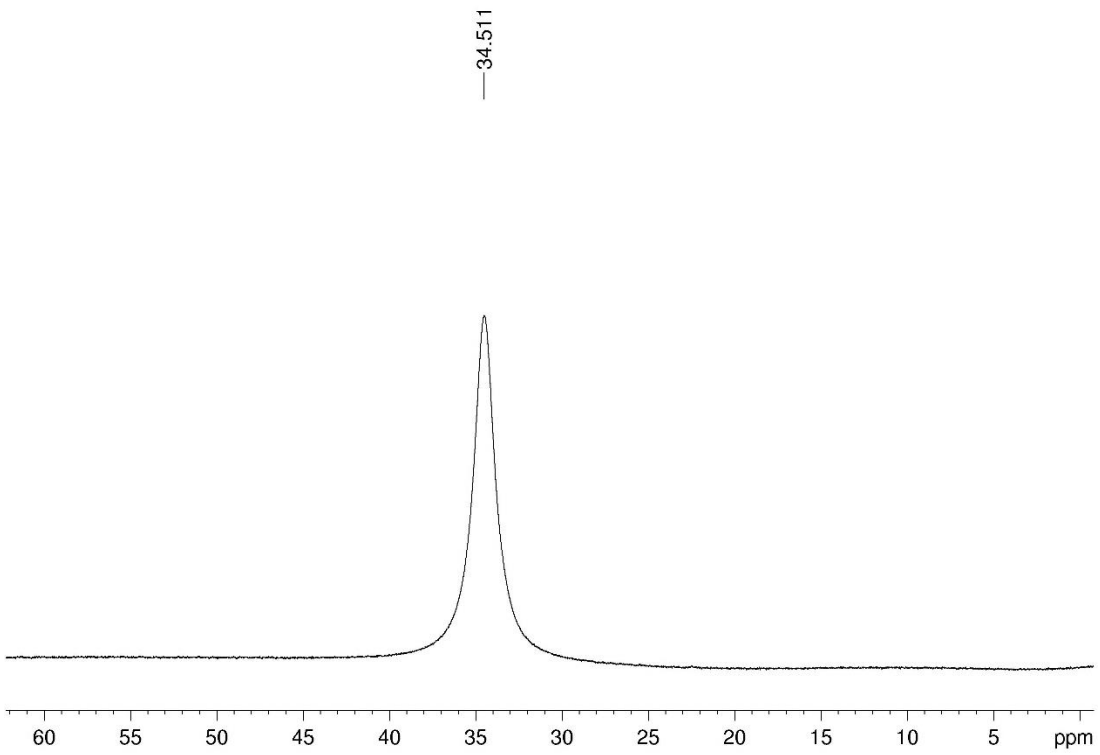
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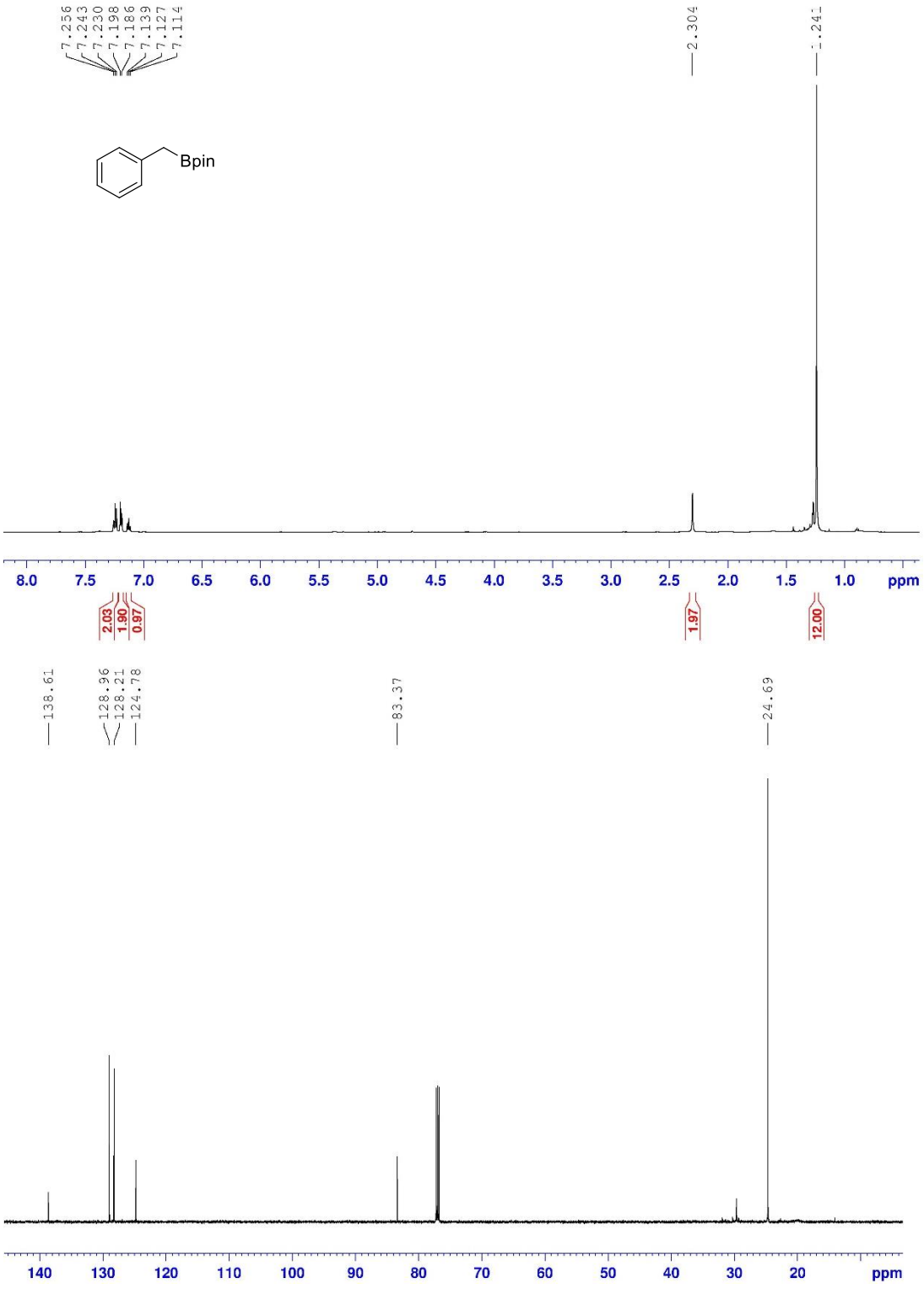
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7.230
7.198
7.186
7.139
7.127
7.114
2.304
1.241
Bpin
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.03
1.90
0.97
1.97
12.00
138.61
128.96
128.21
124.78
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24.69
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130
120
110
100
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80
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60
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40
30
20
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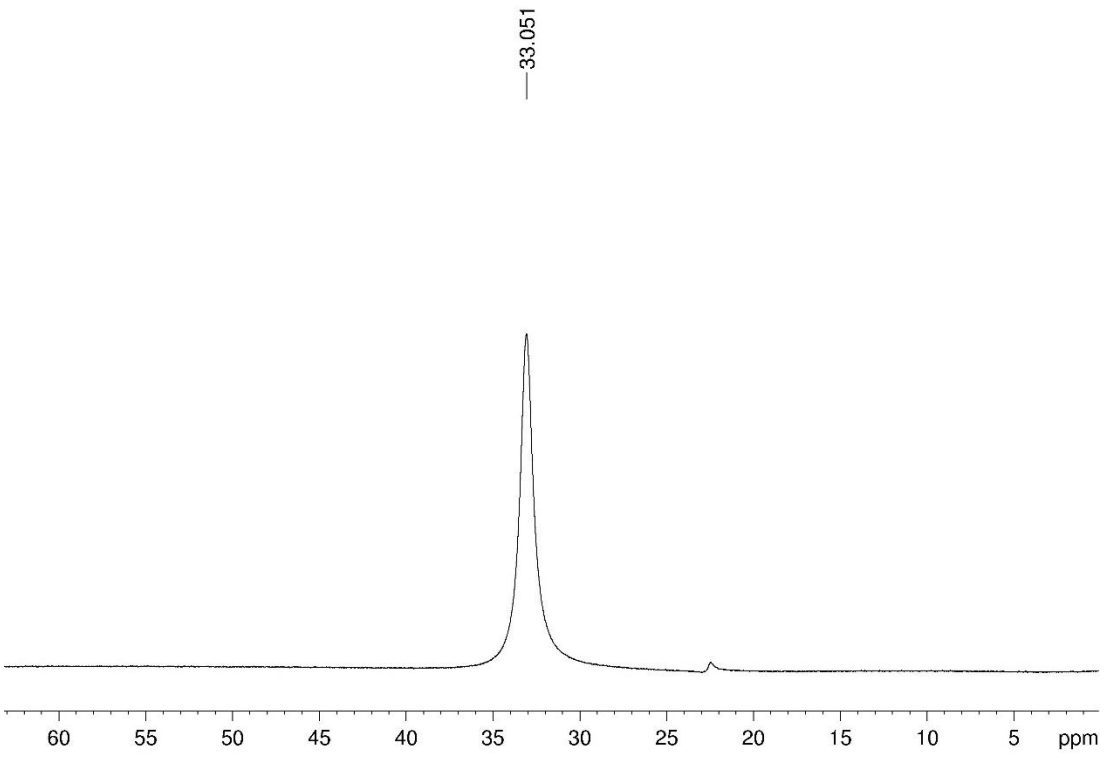
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15
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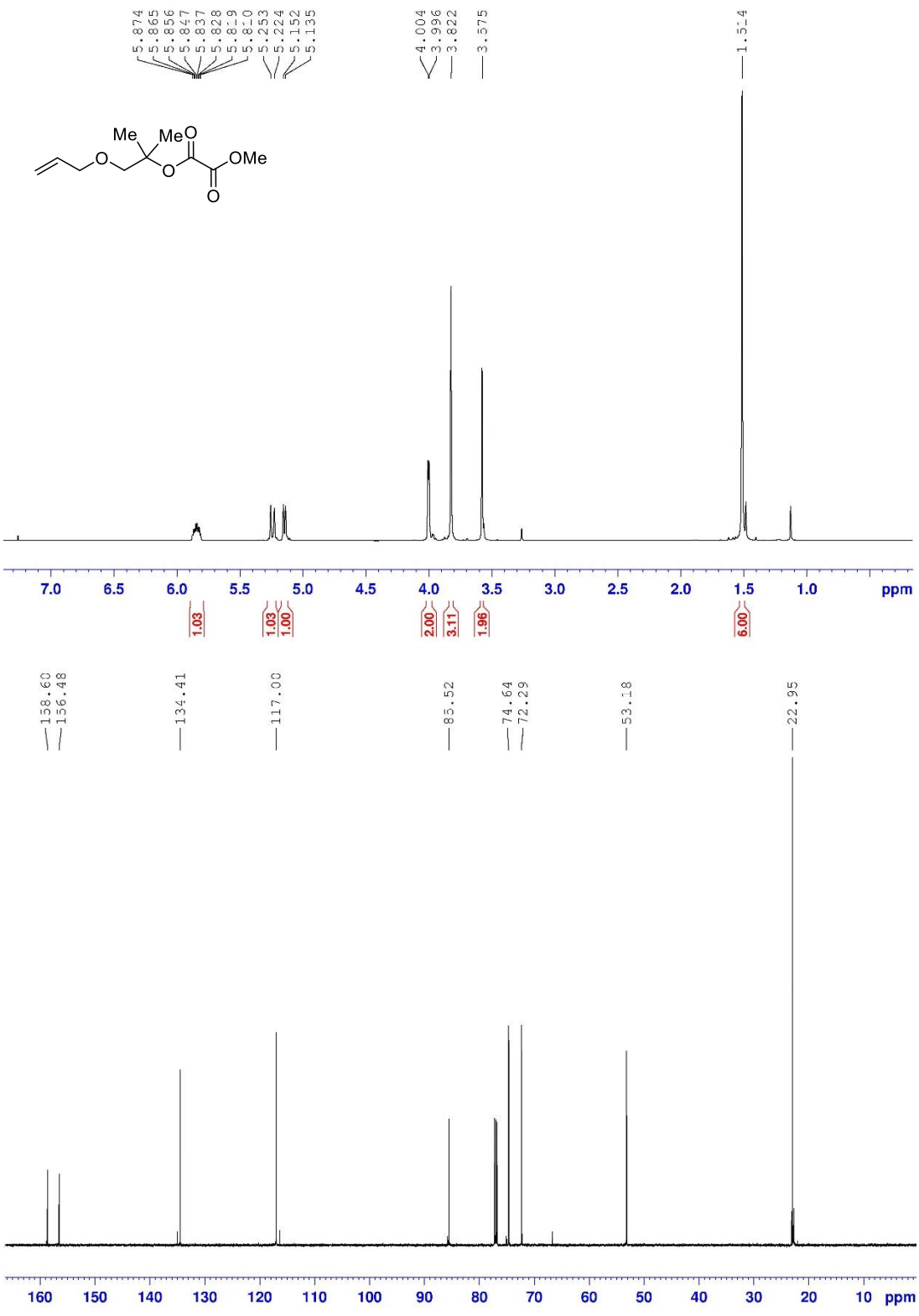
5
ppm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5.810
5.253
5.224
5.152
5.135
4.004
3.996
3.822
3.575
1.534
Me
Me
O
O
O
OMe
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.03
1.03
1.00
2.00
3.11
1.96
6.00
158.60
156.48
134.41
117.00
85.52
74.64
72.29
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150
140
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110
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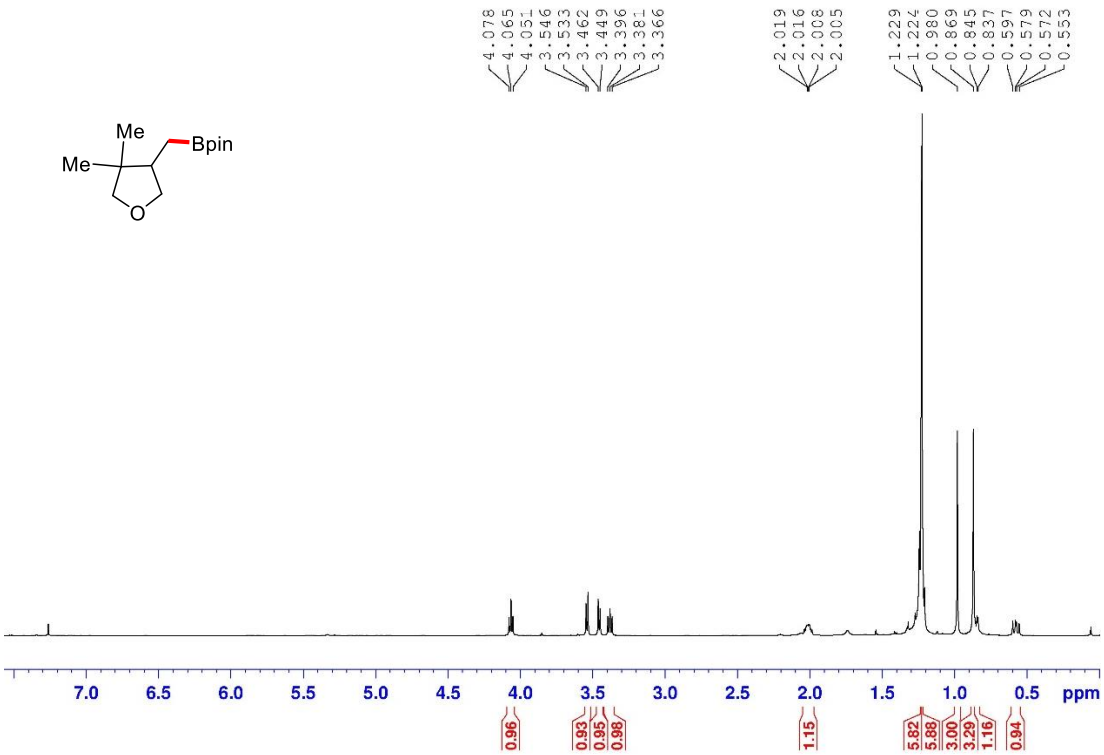
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2.016
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2.005
1.229
1.224
0.980
0.869
0.845
0.837
0.597
0.579
0.572
0.553
Me
Me
Bpin
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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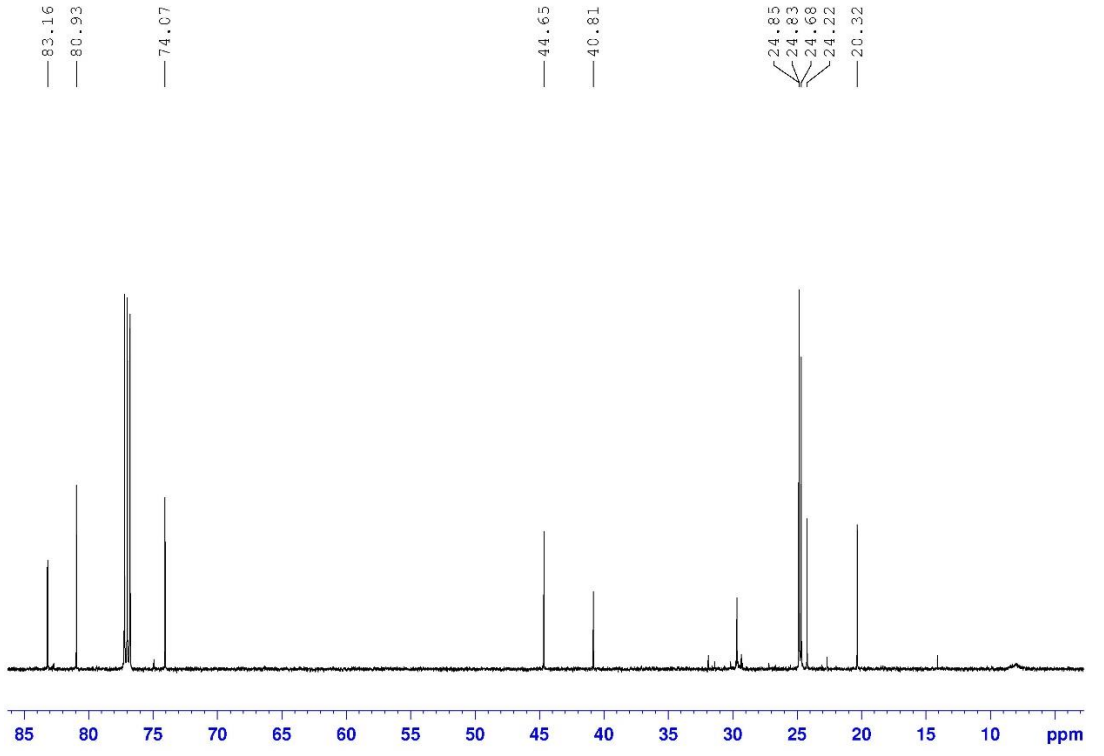
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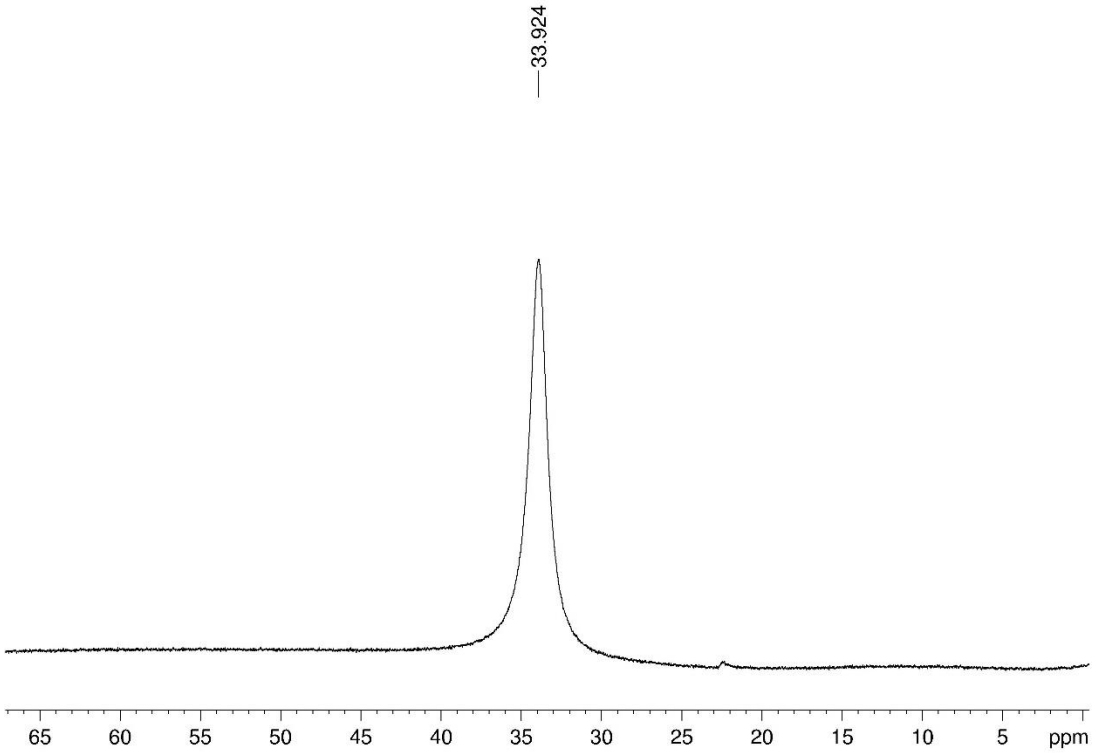
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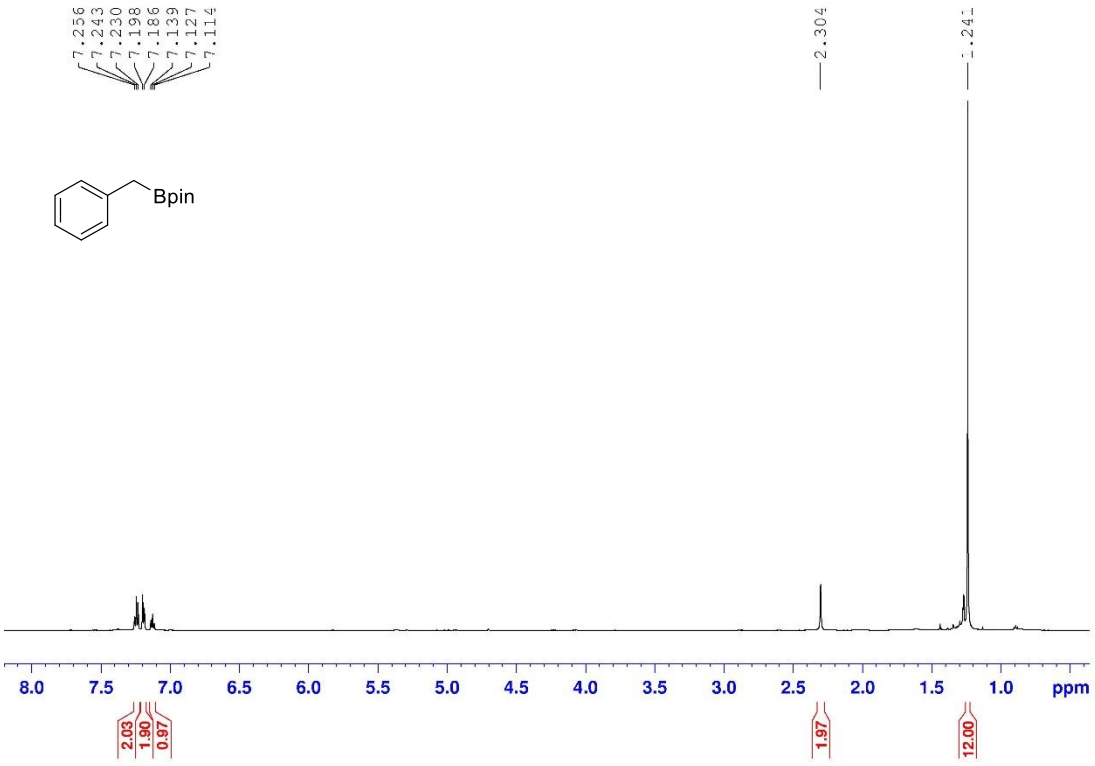
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7.243
7.230
7.198
7.186
7.139
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2.304
1.241
Bpin
8.0
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6.5
6.0
5.5
5.0
4.5
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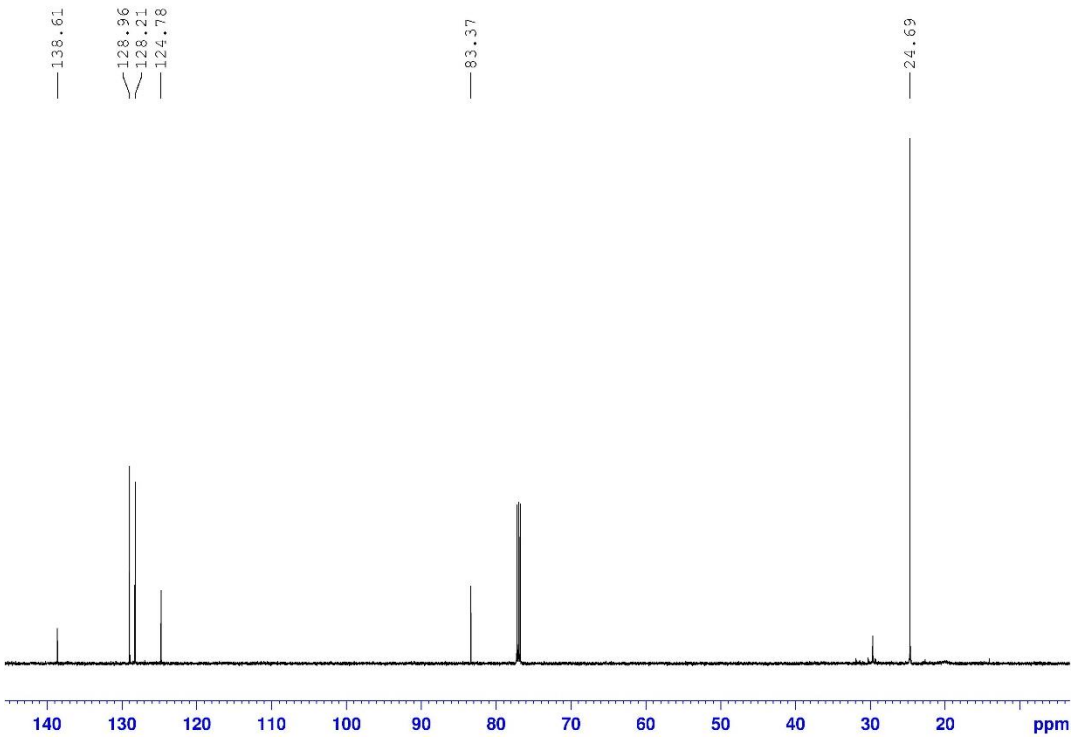
2.5
2.0
1.5
1.0
ppm
2.03
1.90
0.97
1.97
12.00


138.61
128.96
128.21
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140
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120
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80
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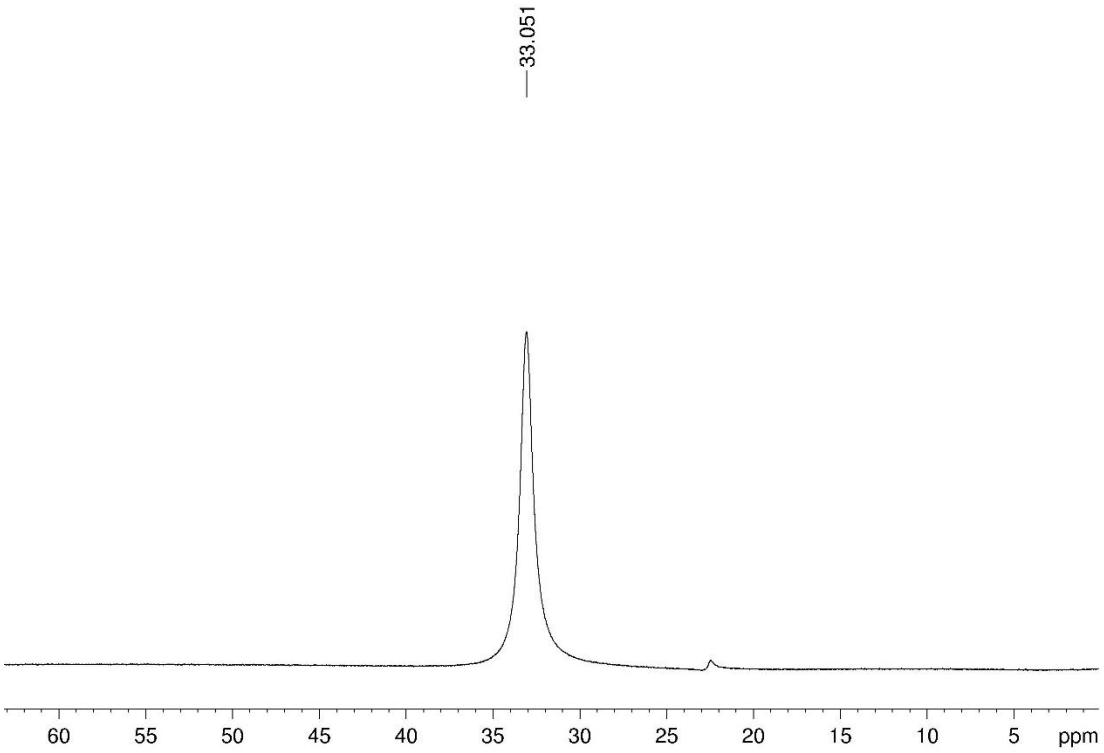
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ppm

IV. Reference

1. (a) C. C. Nawrat, C. R. Jamison, Y. Slutskyy, D. W. C. MacMillan and L. E. Overman, *J. Am. Chem. Soc*., 2015, **137**, 11270;(b) X. Zhang and D. W. C. MacMillan, *J. Am. Chem. Soc*., 2016, **138**, 13862; (c) G. L. Lackner, K. W. Quasdorf and L. E. Overman, *J. Am. Chem. Soc*., 2013, **135**, 15342; (d) G. L. Lackner, K. W. Quasdorf, G. Pratsch and L. E. Overman, *J. Org. Chem*., 2015, **80**, 6012.
2. A. S. Dudnik and G. C. Fu, *J. Am. Chem. Soc*., 2012, **134**, 10693.
3. C. Pubill-Ulldemolins, M. Poyatos, C. Bo and E. Fernández, *Dalton Trans*., 2013, **42**, 746.
4. (a) A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers and V. K. Aggarwal, *Science*, 2017, **357**, 283; (b) J. Hu, G. Wang, S. Li and Z. Shi, *Angew. Chem. Int. Ed*., 2018, **57**, 15227; (c) J. Wu, L. He, A. Noble and V. K. Aggarwal, J. *Am. Chem. Soc.*, 2018, **140**, 10700.
5. F. W. Friese and A. Studer, *Angew. Chem., Int. Ed*., 2019, **58**, 9561.
6. C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder and L. Liu, *Angew. Chem. Int. Ed*., 2012, **51**, 528;
7. H. Ito, K. Kubota, *Org. Lett*., 2012, **14**, 890.
8. A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers and V. K. Aggarwal, *Science*, 2017, **357**, 283.
9. R. D. Dewhurst, E.C. Neeve, H. Braunschweig, and T.B. Marder, *Chem. Commun*., 2015 **51**, 9594.