Supporting Information

Photoinduced Nickel-Catalyzed Chemo- and Regioselective Hydroalkylation of Internal Alkynes with Ether and Amide α-Hetero C(sp^3)–H Bonds

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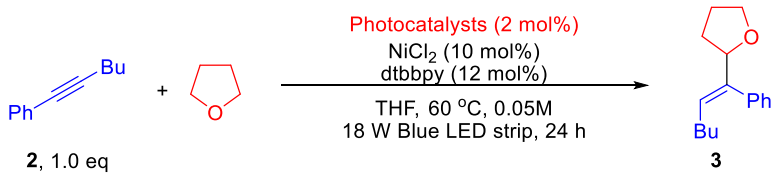
I. General Information

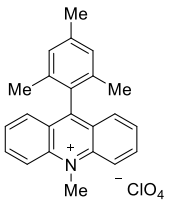
Chemicals and anhydrous solvents were purchased from commercial suppliers and used as received. Tetrahydrofuran (THF), diethyl ether (Et_2O) was freshly distilled. Uncommercial available internal alkynes were synthesized according to literature. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker AV-III400 (400 MHZ) or AMX500 (500 MHz) spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^1H NMR, 77.0 ppm ^{13}C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). All high resolution mass spectra (HRMS) were obtained on a Finnigan/MAT 95XL-T spectrometer. All GC analysis was performed on Aglilent 7820A&5977E GC-MS. The Blue LED strips (2 meter, 18 W) were purchased from Inwares Pte Ltd (Singapore). The Asia Syringe Pump was purchased from Syrris Company (UK) for continuous flow setup. The Tefzel shut-off valves, and PFA, HPFA micro tubings were purchased from IDEX Health & Science (Oak Harbor, WA). Further visualization was achieved by staining with iodine.

II. Reaction Optimization

Table S1. Evaluating other photocatalysts.

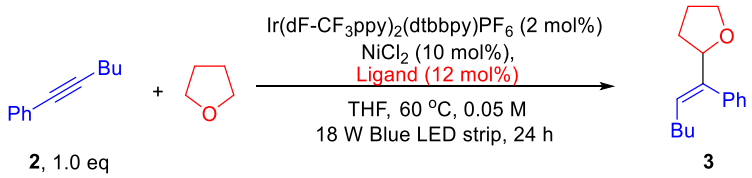


2, 1.0 eq **3**

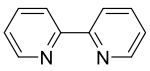
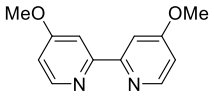
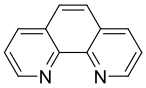
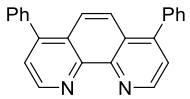
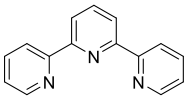
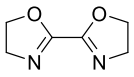
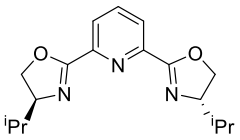
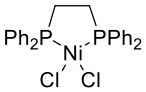
entry	photocatalyst	yield[a]	entry	photocatalyst	yield[a]
1	$Ir(ppy)_2(dtbbpy)PF_6$	0	4	$Ru(bpz)_3(PF_6)_2$	0
2	*fac*-$Ir(ppy)_3$	0	5	Eosin Y	0
3	$Ru(bpy)_3(PF_6)_2$	0	6	 Mes-Acr^+ ClO_4^-	0

[a] Reactions were carried out with alkyne (0.2 mmol), yields were determined by crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. [b] *E*/*Z* Ratios of major products were determined by crude ^{1}H NMR spectra. [c] Ratios of regioisomers were determined by crude ^{1}H NMR spectra.

Table S2. Ligand investigation.[a]



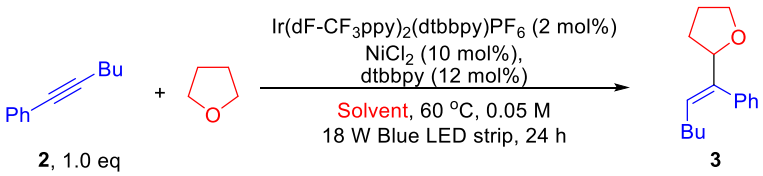
2, 1.0 eq **3**

entry	ligand	yield[a]
1		20%, (>20:1)[b], (5:1)[c]
2		0
3		0
4		20%, (>20:1)[b], (5:1)[c]
5		0
6		0
7		0
8[d]	 (dppe)$NiCl_2$	0

[a] Reactions were carried out with alkyne (0.2 mmol), yields were determined by crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. [b] *E*/*Z* Ratios of major products were determined by crude ^{1}H NMR spectra. [c] Ratios of regioisomers were determined by crude ^{1}H

NMR spectra. [d] Using (dppe)$NiCl_2$ as catalyst.

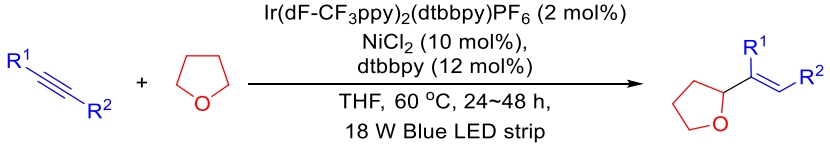
Table S3. Solvent investigation.



entry	solvent (volume ratio)	yield[a]
1	ACN/THF (1:1)	0
2	MeOH/THF (1:1)	0
3	DCM/THF (1:1)	0
4	DCE/THF (1:1)	trace
5	DMF/THF (1:1)	4%, (>20:1)[b], (5:1)[c]
6	DMSO/THF (1:1)	7%, (>20:1)[b], (>20:1)[c]
7	Acetone/THF (1:1)	trace
8	$PhCF_3$/THF (1:1)	trace
9	Benzene/THF (1:1)	58%, (>20:1)[b], (5:1)[c]
10	Benzene[d]	62%, (>20:1)[b], (5:1)[c]

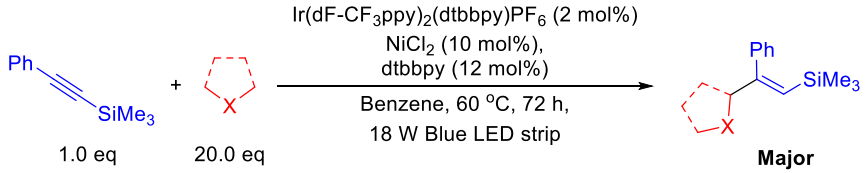
[a] Reactions were carried out with alkyne (0.2 mmol), yields was determined by crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. [b] *E*/*Z* Ratios of major products were determined by crude ^{1}H NMR spectra. [c] Ratios of regioisomers were determined by crude ^{1}H NMR spectra. [d] Reaction was carried out with THF (10.0 equiv).

III. Typical Procedure for Ir/Ni Catalyzed Alkenylation of C(Sp^3)–H Bonds with Internal Alkyne in Batch Reactors



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the corresponding alkyne

(0.2 mmol, 1.0 equiv.), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (4.4 mg, 0.004 mmol, 2 mol%), nickel chloride anhydrous (2.6 mg, 0.02 mmol, 10 mol%), and 4,4′-Di-*tert*-butyl-2,2′-dipyridyl (6.4 mg, 0.024 mmol, 12 mol%). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. Then anhydrous THF (4.0 mL) was added, and the mixture was cooed to 0 °C, and bubbled with argon balloon for 10~15 min (if alkyne was volatile, the alkyne was added after bubbling). After that, the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by elution with hexane to hexane / ethyl acetate (20:1) to give the corresponding product.



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added trimethyl(phenylethynyl)silane (35 mg, 0.2 mmol, 1.0 equiv.), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (4.4 mg, 0.004 mmol, 2 mol%), nickel chloride anhydrous (2.6 mg, 0.02 mmol, 10 mol%), and 4,4′-Di-*tert*-butyl-2,2′-dipyridyl (6.4 mg, 0.024 mmol, 12 mol%). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. Then benzene (4.0 mL) was added, and the mixture was cooed to 10 °C, and bubbled with argon balloon for 10~15 min, then the corresponding ether or amide (4 mmol, 20.0 equiv) was added. After that, the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 72 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by elution with hexane to hexane / ethyl acetate (20:1-3:1) to give the corresponding product.

IV. Typical Procedure for Ir/Ni Catalyzed Alkenylation of C(Sp^3)–H Bonds with Internal Alkyne in Continuous Flow Reactors (Preparation of 12 as an Example)

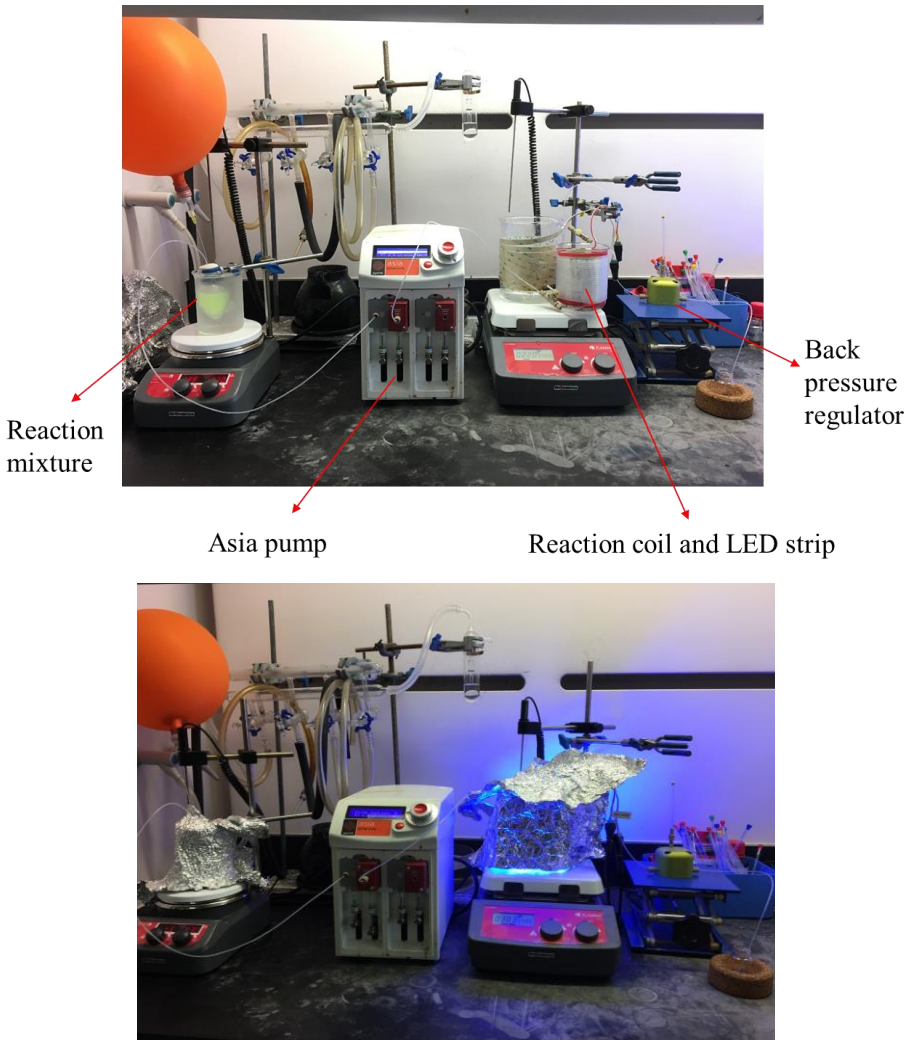
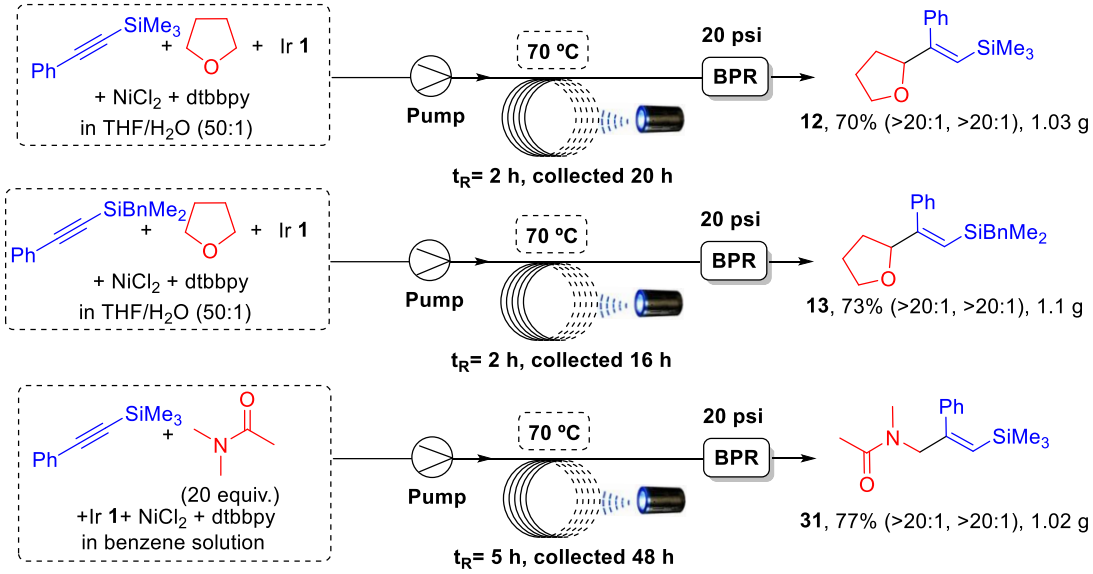


Figure S1. Continuous-flow setup

Under Argon atmosphere, a 200 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with phenyl trimethylsilyl acetylene (1.218 g, 7 mmol, 1.0 equiv.), $Ir(dF\text{-}CF_3ppy)_2(dtbbpy)PF_6$ (154 mg, 0.14 mmol, 2 mol%), nickel chloride anhydrous (91 mg, 0.7 mmol, 10 mol%), and 4,4′-Di-*tert*-butyl-2,2′-dipyridyl (224 mg, 0.84 mmol, 12 mol%). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. Then anhydrous THF (140 mL) and distilled H_2O (2.8 mL) was added, and the mixture was cooed to 0 °C, and bubbled with argon balloon for 10~15 min. As shown in Figure S1, an Asia pump was filled with the pre-heat (60 °C) solution (the solution became a clear

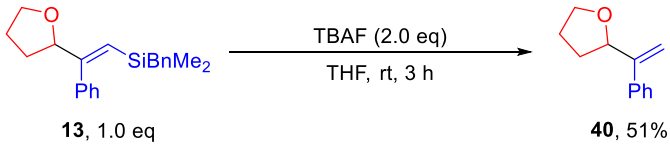
solution at 60 °C, which was better for injection of flow synthesis.) and then attached to the flow apparatus with 20 psi back-pressure regulator (BPR). The tubing (PFA, O.D. 1/8", I.D. 0.062", 600 cm, volume = 11.7 mL) was placed into the water bath equipped with 36 W blue LED strip at around 70 °C. The flow apparatus itself was set up with t_R = 2 h, flow rate = 97.5 μL/min, After approximately 4 h of equilibration, the solution was collected for 20 h, after evaporating under reduced pressure, the residue was purified by flash chromatography with deactivated silica gel (eluent: from hexane to hexane:EA = 20 :1), affording the colorless oil product 1.03 g, in 70% yield.

V. Large-Scale Continuous-Flow Synthesis



VI. Further Diversification of Alkene Products

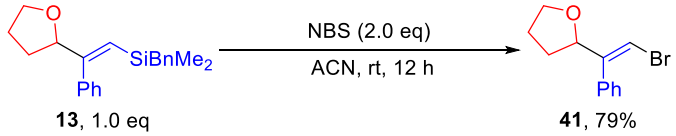
Synthesis of 2-(1-phenylvinyl)tetrahydrofuran (40)[1]



Under Ar atmosphere, TBAF (0.2 mmol) was added to a solution of compound **13** (32 mg, 0.1 mmol) in dry THF (2.0 mL), then the solution was stirred at room temperature for 3 h. After evaporation of the solvent, the residue was purified by chromatography (hexane:ethyl acetate =

20:1) to afford the desired product 40 9 mg, in 51% yield.

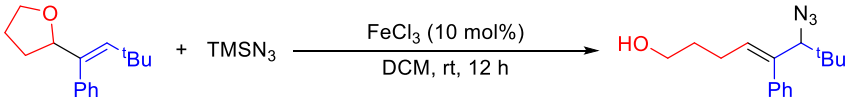
Synthesis of (*E*)-2-(2-bromo-1-phenylvinyl)tetrahydrofuran (41)



13, 1.0 eq **41**, 79%

Under Ar atmosphere, NBS (0.2 mmol) was added to a solution of compound **13** (32 mg, 0.1 mmol) in dry ACN (2.0 mL), then the solution was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was purified by chromatography (hexane:ethyl acetate = 20:1) to afford the desired product **41**, 20 mg, in 79% yield.

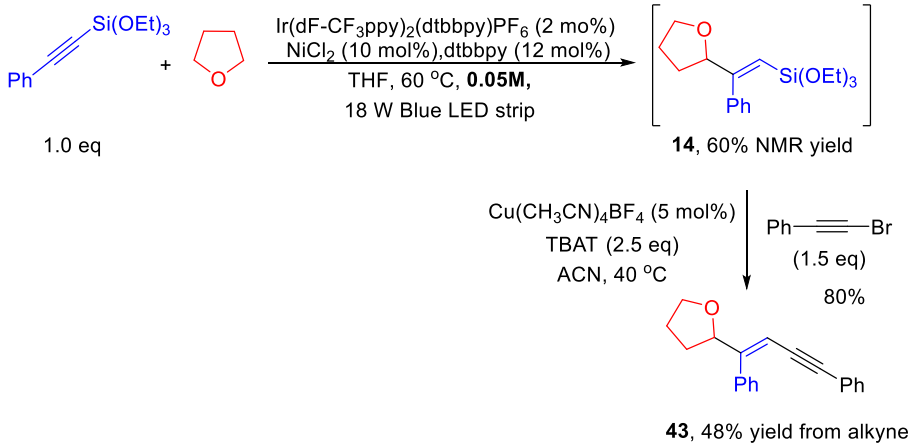
Synthesis of (*E*)-6-azido-7,7-dimethyl-5-phenyloct-4-en-1-ol (42)[2]



9, 1.0 eq 3.0 eq (major) **42**, 91% regioisomer (6.6 :1)

Under Ar atmosphere, to a solution of compound **9** (23 mg, 0.1 mmol) and $FeCl_3$ (1.6 mg, 0.01 mmol) in dry CH_2Cl_2 (2.0 mL) was added $TMSN_3$ (35 mg, 0.30 mmol) and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was quenched with n-Bu_4NF (0.30 mmol) and water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (hexane: ethyl acetate = 4:1) to afford light yellow oil **42** 25 mg, in 91% yield.

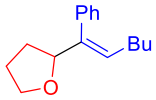
Synthesis of (*E*)-2-(1,4-diphenylbut-1-en-3-yn-1-yl)tetrahydrofuran (43)[3]



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the triethoxy(phenylethynyl)silane (53 mg, 0.2 mmol, 1.0 equiv.), $Ir(dF\text{-}CF_3ppy)_2(dtbbpy)PF_6$ (4.4 mg, 0.004 mmol, 2 mol%), nickel chloride anhydrous (2.6 mg, 0.02 mmol, 10 mol%), and 4,4′-Di-*tert*-butyl-2,2′-dipyridyl (6.4 mg, 0.024 mmol, 12 mol%). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. Then anhydrous THF (4.0 mL) was added, and the mixture was cooed to 0 °C, and bubbled with argon balloon for 10~15 min. After that, the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the residue was used for next step without further purification, according to crude ^1H NMR, indicated the desired product **14** in 60% yield.

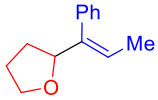
To a solution of the residue of last step (0.12 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added the bromoalkyne (32 mg, 0.18 mmol, 1.5 equiv.). The mixture was transferred to a Shlenck flask containing $Cu(MeCN)_4PF_6$ (2.0 mg, 0.006 mmol, 5 mol%) and tetrabutylammonium difluorotriphenylsilicate (TBAT) (162 mg, 0.30 mmol, 2.5 equiv.) under argon. The resulting mixture was stirred at 40 °C for 16 hours. The solution was diluted with diethyl ether (6 mL), filtrated trough a short pad of silica and eluted with diethyl ether (30 mL). The solution was evaporated under reduced pressure, and the residue was purified by flash chromatography (hexane:ethyl acetate = 4:1) to afford the desired product **43** 26 mg, in 80% yield (in 48% yield from alkyne).

VII. Product Characterization



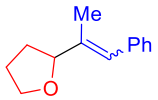
(*E*)-2-(1-phenylhex-1-en-1-yl)tetrahydrofuran (3) (major product)

Following the typical procedure **III** with hex-1-yn-1-ylbenzene (31.6 mg, 0.2 mmol) to give the product **3** and **3'** (33 mg) in 72% yield (containing all isomers, major:minor = 5:1, *E*/*Z* of major product > 20:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.17-7.16 (m, 2H), 5.72 (t, *J* = 7.5 Hz, 1H), 4.54 (t, *J* = 7.0 Hz, 1H), 3.85 (dd, *J* = 7.0, 14.0 Hz, 1H), 3.79 (dd, *J* = 7.0, 14.0 Hz, 1H), 1.92-1.86 (m, 3H), 1.84-1.70 (m, 2H), 1.61-1.54 (m, 1H), 1.34-1.22 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C MR (125 MHz, $CDCl_3$) δ 141.3, 138.9, 129.4, 128.3, 127.9, 126.6, 83.2, 68.3, 32.0, 30.9, 28.1, 25.7, 22.2, 13.9; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{22}NaO$ 253.1563, found 253.1563.



(*E*)-2-(1-phenylprop-1-en-1-yl)tetrahydrofuran (4) (major product)

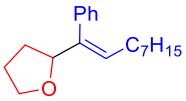
Following the typical procedure **III** with prop-1-yn-1-ylbenzene (23.2 mg, 0.2 mmol) to give the product **4** and **4'** (24 mg) in 64% yield (containing all isomers, major : minor = 2:1, *E*/*Z* of major product > 20:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 3H), 7.19-7.17 (m, 2H), 5.83 (dq, *J* = 0.8, 6.8 Hz, 1H), 4.55 (t, *J* = 6.8 Hz, 1H), 3.86-3.77 (m, 2H), 2.02-1.71 (m, 3H), 1.62-1.57 (m, 1H), 1.55 (dd, *J* = 0.8, 6.8 Hz, 1H); ^{13}C MR (100 MHz, $CDCl_3$) δ 142.2, 138.6, 129.4, 127.9, 126.6, 122.4, 83.2, 68.3, 30.8, 25.8, 14.2; HRMS–ESI $[M+Na]^+$ Calcd for $C_{13}H_{16}NaO$ 211.1093, found 211.1089.



2-(1-phenylprop-1-en-2-yl)tetrahydrofuran (4') (minor product)

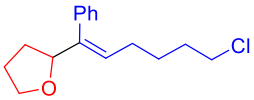
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 3H), 7.24-7.19 (m, 2H), 6.55 (6.45) (s, 1H), 4.74 (4.39) (t, *J* = 7.2 Hz, 1H), 4.03-3.88 (m, 2H), 2.01-1.71 (m, 7H); ^{13}C MR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 137.9, 137.5, 129.0, 128.7, 128.2, 128.0, 127.98, 126.3, 126.2, 124.5, 84.0, 77.2, 76.8, 68.6, 30.9, 30.5, 26.8, 26.0, 17.8, 13.9; HRMS–ESI $[M+Na]^+$ Calcd for $C_{13}H_{16}NaO$

211.1093, found 211.1089.



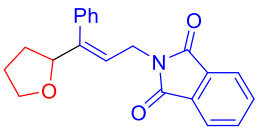
(*E*)-2-(1-phenylnon-1-en-1-yl)tetrahydrofuran (5) (major product)

Following the typical procedure **III** with non-1-yn-1-ylbenzene (40.0 mg, 0.2 mmol) to give the product **5** and **5'** (37 mg) in 68% yield (containing all isomers, major:minor = 7:1, *E*/*Z* of major product > 20:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.17-7.16 (m, 2H), 5.72 (t, *J* = 7.5 Hz, 1H), 4.54 (t, *J* = 7.0 Hz, 1H), 3.85 (dd, *J* = 7.0, 14.0 Hz, 1H), 3.79 (dd, *J* = 7.0, 14.0 Hz, 1H), 1.92-1.86 (m, 3H), 1.84-1.70 (m, 2H), 1.61-1.54 (m, 1H), 1.34-1.20 (m, 10H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C MR (125 MHz, $CDCl_3$) δ 141.2, 138.9, 129.4, 128.4, 127.9, 126.6, 83.2, 68.3, 31.8, 30.9, 29.7, 29.14, 29.09, 28.4, 25.7, 22.6, 14.0; HRMS–ESI $[M+Na]^+$ Calcd for $C_{19}H_{28}NaO$ 295.2032, found 295.2024.



(*E*)-2-(6-chloro-1-phenylhex-1-en-1-yl)tetrahydrofuran (6) (major product)

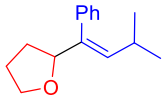
Following the typical procedure **III** with (7-chlorohept-1-yn-1-yl)benzene (41.3 mg, 0.2 mmol) to give the product **6** and **6'** (37 mg) in 70% yield (containing all isomers, major:minor = 7:1, *E*/*Z* of major product > 20:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.27-7.26 (m, 1H), 7.16-7.14 (m, 2H), 5.70 (t, *J* = 7.2 Hz, 1H), 4.54 (t, *J* = 6.8 Hz, 1H), 3.88-3.77 (m, 2H), 3.42 (t, *J* = 6.8 Hz, 1H), 1.92-1.66 (m, 7H), 1.62-1.55 (m, 1H), 1.51-1.44 (m, 2H); ^{13}C MR (100 MHz, $CDCl_3$) δ 142.2, 138.6, 129.2, 128.0, 127.0, 126.8, 83.0, 68.3, 44.8, 32.0, 30.9, 27.5, 26.8, 25.7; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{21}ClNaO$ 287.1173, found 287.1178.



(*E*)-2-(3-phenyl-3-(tetrahydrofuran-2-yl)allyl)isoindoline-1,3-dione (7)

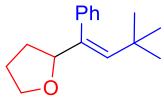
Following the typical procedure **III** with 2-(3-phenylprop-2-yn-1-yl)isoindoline-1,3-dione (52.2 mg, 0.2 mmol) to give the product **7** (31 mg) in 46% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.79 (m, 2H), 7.69-7.67, 7.39-7.36 (m, 2H), 7.31-7.28 (m, 3H), 5.75 (t, *J* = 7.5 Hz, 1H), 4.55 (t, *J* = 7.0 Hz, 1H), 4.20 (t, *J* = 7.5 Hz, 1H), 3.86 (dd, *J* = 7.0, 15.0 Hz, 1H), 3.79 (dd, *J*

= 7.0, 15.0 Hz, 1H), 1.92-1.86 (m, 1H), 1.82-1.76 (m, 2H), 1.65-1.58 (m, 1H); ^{13}C MR (125 MHz, $CDCl_3$) δ 167.9, 156.5, 145.5, 137.4, 133.8, 132.2, 129.0, 128.2, 127.4, 123.1, 120.0, 82.1, 68.5, 36.6, 30.9, 25.5; HRMS–ESI $[M+Na]^+$ Calcd for $C_{21}H_{19}NNaO_3$ 356.1257, found 356.1264.



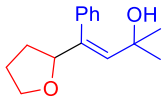
(*E*)-2-(3-methyl-1-phenylbut-1-en-1-yl)tetrahydrofuran (8)

Following the typical procedure **III** with (3-methylbut-1-yn-1-yl)benzene (28.8 mg, 0.2 mmol) to give the product **8** (32 mg) in 74% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.27-7.26 (m, 1H), 7.17-7.16 (m, 2H), 5.52 (d, *J* = 8.0 Hz, 1H), 4.49 (t, *J* = 7.0 Hz, 1H), 3.84 (dd, *J* = 7.0, 13.5 Hz, 1H), 3.79 (dd, *J* = 7.0, 13.5 Hz, 1H), 2.27-2.20 (m, 1H), 1.91-1.84 (m, 1H), 1.82-1.69 (m, 2H), 1.61-1.54 (m, 1H), 0.92 (d, *J* = 4.5 Hz, 3H), 0.90 (d, *J* = 4.5 Hz, 3H); ^{13}C MR (125 MHz, $CDCl_3$) δ 139.0, 135.5, 129.3, 129.3, 127.9, 126.6, 83.1, 68.3, 30.8, 27.5, 25.7, 23.2, 23.1; HRMS–ESI $[M+H]^+$ Calcd for $C_{15}H_{21}O$ 217.1587, found 217.1589.



(*E*)-2-(3,3-dimethyl-1-phenylbut-1-en-1-yl)tetrahydrofuran (9)

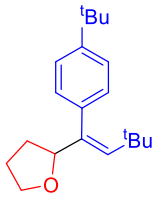
Following the typical procedure **III** with (3,3-dimethylbut-1-yn-1-yl)benzene (31.6 mg, 0.2 mmol) to give the product **9** (33 mg) in 71% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.24 (m, 3H), 7.17-7.16 (m, 2H), 5.72 (s, 1H), 4.39 (t, *J* = 7.0 Hz, 1H), 3.80-3.73 (m, 2H), 1.92-1.85 (m, 1H), 1.81-1.74 (m, 1H), 1.70-1.60 (m, 2H), 0.88 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 139.1, 138.6, 137.8, 130.3, 127.3, 126.5, 84.9, 68.3, 33.2, 31.3, 30.6, 25.6; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{22}NaO$ 253.1563, found 253.1559.



(*E*)-2-methyl-4-phenyl-4-(tetrahydrofuran-2-yl)but-3-en-2-ol (10)

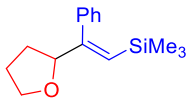
Following the typical procedure **III** with 2-methyl-4-phenylbut-3-yn-2-ol (32.0 mg, 0.2 mmol) to give the product **10** (24 mg) in 52% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.30-7.28 (m, 1H), 7.21-7.19 (m, 2H), 5.88 (s, 1H), 4.41 (t, *J* = 7.0 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 1H), 1.92-1.85 (m, 1H), 1.83-1.60 (m, 3H), 1.223 (s, 3H), 1.216 (s, 3H); ^{13}C MR (125 MHz, $CDCl_3$) δ 139.6, 138.0, 134.3, 129.5, 128.1, 127.2, 83.7, 71.5, 68.5, 31.4, 31.3,

30.7, 25.7; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{20}NaO_2$ 255.1356, found 255.1353.



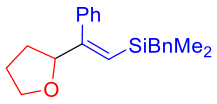
(*E*)-2-(1-(4-(tert-butyl)phenyl)-3,3-dimethylbut-1-en-1-yl)tetrahydrofuran (11)

Following the typical procedure **III** with 1-(tert-butyl)-4-(3,3-dimethylbut-1-yn-1-yl)benzene (42.8 mg, 0.2 mmol) to give the product **11** (45 mg) in 78% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.68 (s, 1H), 4.34 (t, *J* = 7.0 Hz, 1H), 3.79-3.72 (m, 2H), 1.88-1.82 (m, 1H), 1.79-1.58 (m, 3H), 1.31 (s, 9H), 0.85 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 149.3, 138.8, 137.4, 136.0, 129.8, 124.1, 84.8, 68.3, 34.4, 33.1, 31.3, 30.7, 25.7; HRMS–ESI $[M+Na]^+$ Calcd for $C_{20}H_{30}NaO$ 309.2189, found 309.2195.



(*E*)-trimethyl(2-phenyl-2-(tetrahydrofuran-2-yl)vinyl)silane (12)

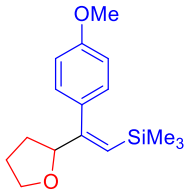
Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) to give the product **12** (35 mg) in 70% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.16-7.14 (m, 2H), 5.88 (d, *J* = 1.2 Hz, 1H), 4.54 (dt, *J* = 1.2, 6.8 Hz, 1H), 3.93 (dd, *J* = 6.8, 14.4 Hz, 1H), 3.85 (dd, *J* = 6.8, 14.4 Hz, 1H), 1.95-1.78 (m, 3H), 1.66-1.60 (m, 1H), -0.19 (s, 9H); ^{13}C MR (100 MHz, $CDCl_3$) δ 158.9, 141.5, 128.9, 127.7, 127.1, 125.4, 83.8, 68.6, 31.2, 25.6, -0.1; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{22}NaOSi$ 269.1332, found 269.1333.



(*E*)-benzyldimethyl(2-phenyl-2-(tetrahydrofuran-2-yl)vinyl)silane (13)

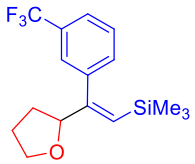
Following the typical procedure **III** with benzyldimethyl(phenylethynyl)silane (50.0 mg, 0.2 mmol) to give the product **13** (47 mg) in 73% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.27 (m, 3H), 7.21-7.18 (m, 2H), 7.08-7.03 (m, 3H), 6.94-6.93 (m, 2H), 5.88 (d, *J* = 1.0 Hz, 1H), 4.56 (t, *J* = 7.0 Hz, 1H), 3.94 (dd, *J* = 6.5, 14.5 Hz, 1H), 3.87 (dd, *J* = 6.5, 14.5 Hz, 1H), 1.98-1.977 (m, 2H), 1.93-1.88 (m, 1H), 1.86-1.80 (m, 2H), 1.66-1.59 (m, 1H), -0.23 (s, 3H), -0.30 (s, 3H); ^{13}C MR (125 MHz, $CDCl_3$) δ 159.8, 141.2, 140.3, 128.8, 128.2, 128.0, 127.7, 127.2,

123.8, 123.2, 83.7, 68.6, 31.1, 26.7, 25.5, -2.2, -2.4; HRMS–APCI $[M+H]^+$ Calcd for $C_{16}H_{27}OSi$ 323.1826, found 323.1828.



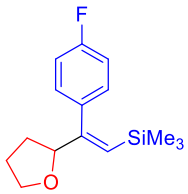
(*E*)-(2-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)vinyl)trimethylsilane (15)

Following the typical procedure **III** with ((4-methoxyphenyl)ethynyl)trimethylsilane (40.9 mg, 0.2 mmol) to give the product **15** (47 mg) in 88% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.85 (d, *J* = 1.0 Hz, 1H), 4.51 (dt, *J* = 1.0, 7.0 Hz, 1H), 3.93 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.84 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.81 (s, 3H), 1.94-1.88 (m, 1H), 1.84-1.78 (m, 2H), 1.63-1.58 (m, 1H), -0.18 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 158.8, 158.6, 133.8, 129.9, 125.3, 113.1, 84.0, 68.6, 55.2, 31.2, 25.6, -0.03; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{24}NaO_2Si$ 299.1438, found 299.1438.



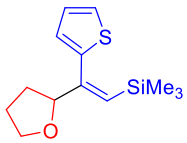
(*E*)-trimethyl(2-(tetrahydrofuran-2-yl)-2-(3-(trifluoromethyl)phenyl)vinyl)silane (16)

Following the typical procedure **III** with trimethyl((3-(trifluoromethyl)phenyl)ethynyl)silane (48.5 mg, 0.2 mmol) to give the product **16** (54 mg) in 87% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 1H), 7.45-7.41 (m, 2H), 7.38-7.36 (m, 1H), 5.96 (d, *J* = 1.2 Hz, 1H), 4.54 (t, *J* = 6.8 Hz, 1H), 3.92-3.82 (m, 2H), 1.98-1.90 (m, 1H), 1.88-1.77 (m, 2H), 1.63-1.56 (m, 1H), -0.20 (s, 9H); ^{13}C MR (100 MHz, $CDCl_3$) δ 157.2, 142.1, 132.2, 130.2 (d, J_{C-F} = 32 Hz), 128.2, 127.8, 126.8 (q, J_{C-F} = 71 Hz), 125.9 (q, J_{C-F} = 4.0 Hz), 123.9 (q, J_{C-F} = 4.0 Hz), 83.8, 68.6, 31.3, 25.7, -0.2; ^{19}F MR (376 MHz, $CFCl_3$) δ -62.7; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{21}F_3NaOSi$ 337.1206, found 337.1205.



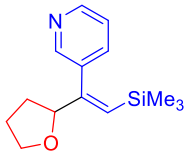
(*E*)-(2-(4-fluorophenyl)-2-(tetrahydrofuran-2-yl)vinyl)trimethylsilane (17)

Following the typical procedure **III** with ((4-fluorophenyl)ethynyl)trimethylsilane (38.4 mg, 0.2 mmol) to give the product **17** (41 mg) in 78% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.11 (m, 2H), 7.01-6.98 (m, 2H), 5.89 (d, *J* = 1.0 Hz, 1H), 4.50 (dt, *J* = 1.0, 7.0 Hz, 1H), 3.90 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.84 (dd, *J* = 7.0, 14.5 Hz, 1H), 1.94-1.88 (m, 1H), 1.85-1.76 (m, 2H), 1.61-1.55 (m, 1H), -0.18 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 162.2 (d, J_{C-F} = 243.8 Hz), 157.7, 137.2 (d, J_{C-F} = 3.2 Hz), 130.5 (d, J_{C-F} = 6.2 Hz), 126.6, 114.6 (d, J_{C-F} = 21.2 Hz), 84.0, 68.6, 31.1, 25.6, -0.1; ^{19}F MR (376 MHz, $CFCl_3$) δ -115.5; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{21}FNaOSi$ 287.1238, found 287.1237.



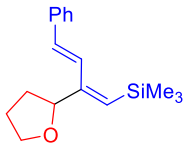
(*Z*)-trimethyl(2-(tetrahydrofuran-2-yl)-2-(thiophen-2-yl)vinyl)silane (**18**)

Following the typical procedure **III** with trimethyl(thiophen-2-ylethynyl)silane (36.0 mg, 0.2 mmol) to give the product **18** (33 mg) in 65% yield as a colorless oil. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.43 (d, *J* = 5.0 Hz, 1H), 7.02 (dd, *J* = 3.5, 5.0 Hz, 1H), 6.95 (d, *J* = 3.5 Hz, 1H), 5.98 (s, 1H), 4.49 (t, *J* = 7.0 Hz, 1H), 3.88 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.77 (dd, *J* = 7.0, 14.5 Hz, 1H), 2.02-1.96 (m, 1H), 1.85-1.76 (m, 2H), 1.62-1.55 (m, 1H), -0.08 (s, 9H); ^{13}C MR (125 MHz, $(CD_3)_2CO$) δ 153.1, 142.2, 129.5, 127.7, 127.2, 126.5, 84.8, 69.1, 32.4, 26.3, -0.02; HRMS–ESI $[M+Na]^+$ Calcd for $C_{13}H_{20}NaOSSi$ 275.0896, found 275.0901.



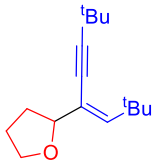
(*E*)-3-(1-(tetrahydrofuran-2-yl)-2-(trimethylsilyl)vinyl)pyridine (**19**)

Following the typical procedure **III** with 3-((trimethylsilyl)ethynyl)pyridine (35.0 mg, 0.2 mmol) to give the product **19** (25 mg) in 50% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 2.0, 4.5 Hz, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 7.50 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.24 (dd, *J* = 4.5, 8.0 Hz, 1H), 5.99 (d, *J* = 1.0 Hz, 1H), 4.50 (t, *J* = 6.5 Hz, 1H), 3.88-3.80 (m, 2H), 1.97-1.91 (m, 1H), 1.85-1.74 (m, 2H), 1.60-1.53 (m, 1H), -0.18 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 154.8, 149.6, 148.5, 136.7, 136.3, 128.9, 122.7, 84.1, 68.6, 31.0, 25.7, -0.1; HRMS–ESI $[M+H]^+$ Calcd for $C_{12}H_{22}NOSi$ 248.1465, found 248.1467.



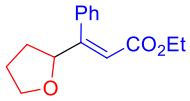
trimethyl((1E,3E)-4-phenyl-2-(tetrahydrofuran-2-yl)buta-1,3-dien-1-yl)silane (**20**)

Following the typical procedure **III** with (*E*)-trimethyl(4-phenylbut-3-en-1-yn-1-yl)silane (40.0 mg, 0.2 mmol) to give the product **20** (40 mg) in 73% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.18 (m, 1H), 6.45 (d, *J* = 12.5 Hz, 1H), 6.25 (d, *J* = 12.5 Hz, 1H), 5.87 (s, 1H), 4.34 (t, *J* = 7.0 Hz, 1H), 3.97 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.79 (dd, *J* = 7.0, 14.5 Hz, 1H), 2.02-1.96 (m, 1H), 1.90-1.78 (m, 2H), 1.70-1.63 (m, 1H), 0.02 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 155.7, 137.1, 131.1, 129.7, 128.9, 128.2, 127.3, 124.3, 81.7, 68.4, 31.8, 25.5, -0.6; HRMS–ESI $[M+Na]^+$ Calcd for $C_{17}H_{24}NaOSi$ 295.1489, found 295.1492.



(*E*)-2-(2,2,7,7-tetramethyloct-3-en-5-yn-4-yl)tetrahydrofuran (**21**)

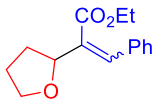
Following the typical procedure **III** with 2,2,7,7-tetramethylocta-3,5-diyne (32.4 mg, 0.2 mmol) to give the product **21** (34 mg) in 73% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (d, *J* = 1.0 Hz, 1H), 4.24 (t, *J* = 7.0 Hz, 1H), 3.93 (dd, *J* = 7.5, 14.5 Hz, 1H), 3.80 (t, *J* = 7.5, 14.5 Hz, 1H), 2.04-1.92 (m, 3H), 1.88-1.82 (m, 1H), 1.25 (s, 9H), 1.18 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 145.8, 122.5, 105.1, 83.2, 75.8, 68.9, 32.3, 31.0, 30.7, 29.9, 28.2, 26.1; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{26}NaO$ 257.1876, found 257.1879.



ethyl (*E*)-3-phenyl-3-(tetrahydrofuran-2-yl)acrylate (**22**) **(major product)**

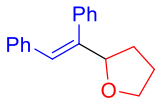
Following the typical procedure **III** with ethyl 3-phenylpropiolate (34.8 mg, 0.2 mmol) to give the product **22** and **22'** (33 mg) in 68% yield (containing all isomers, major : minor = 1.5:1, E/Z of major product > 20:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.26-7.24 (1H, m), 7.15-7.13 (m, 2H), 6.15 (d, *J* = 1.2 Hz, 1H), 4.64 (dt, *J* = 1.2, 7.2 Hz, 1H), 4.02-3.85 (m, 4H), 1.98-1.81 (m, 3H), 1.69-1.61 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C MR (100 MHz, $CDCl_3$) δ 166.2, 159.0, 131.4, 128.3, 127.9, 127.6, 115.6, 81.9, 69.0, 59.8, 31.2, 25.4, 13.9;

HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{18}NaO_3$ 269.1148, found 269.1152.



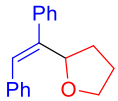
ethyl 3-phenyl-2-(tetrahydrofuran-2-yl)acrylate (22') (minor product)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (6.85) (s, 1H), 7.35-7.29 (m, 3H), 7.26-7.24 (m, 2H), 4.86 (t, *J* = 8.0 Hz, 1H) (4.71 (t, *J* = 6.0 Hz, 1H)), 4.26 (4.12) (q, *J* = 7.2 Hz, 2H), 4.02-3.85 (m, 2H), 1.98-1.81 (m, 4H), 1.33 (1.10) (t, *J* = 7.2 Hz, 3H); ^{13}C MR (100 MHz, $CDCl_3$) δ 168.4, 167.0, 141.2, 137.8, 135.74, 135.72, 135.0, 133.7, 129.2, 128.4, 128.3, 128.0, 127.8, 127.7, 79.5, 74.9, 69.1, 68.7, 60.6, 60.5, 31.7, 31.1, 27.2, 25.6, 14.2, 13.8; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{18}NaO_3$ 269.1148, found 269.1152.



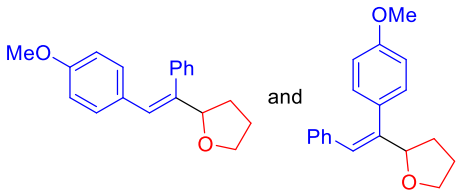
(*E*)-2-(1,2-diphenylvinyl)tetrahydrofuran (23)

Following the typical procedure **III** with 1,2-diphenylethyne (35.6 mg, 0.2 mmol), product **23** (22 mg) was isolated in 45% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.21-7.19 (m, 2H), 7.08-7.07 (m, 3H), 6.95-6.93 (m, 2H), 7.00 (s, 1H), 4.70 (t, *J* = 7.0 Hz, 1H), 3.97 (dd, *J* = 7.0, 15.0 Hz, 1H), 3.89 (dd, *J* = 7.0, 15.0 Hz, 1H), 2.02-1.96 (m, 1H), 1.89-1.83 (m, 2H), 1.74-1.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 139.0, 136.8, 129.3, 129.2, 128.5, 127.8, 127.1, 126.5, 125.8, 83.5, 68.7, 31.1, 25.8; HRMS–ESI $[M+Na]^+$ Calcd for $C_{18}H_{18}NaO$ 273.1250, found 273.1242.



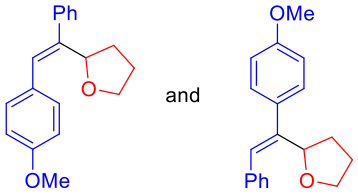
(Z)-2-(1,2-diphenylvinyl)tetrahydrofuran (23')

Following the typical procedure **III** with 1,2-diphenylethyne (35.6 mg, 0.2 mmol), the product **23'** (22 mg) was isolated in 44% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.39 (m, 2H), 7.26-7.14 (m, 8H), 6.62 (s, 1H), 4.86 (t, *J* = 7.0 Hz, 1H), 3.72 (dd, *J* = 7.0, 15.0 Hz, 1H), 3.60 (dd, *J* = 7.0, 15.0 Hz, 1H), 1.83-1.62 (m, 3H), 1.60-1.52 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 141.3, 137.0, 132.0, 129.0, 128.8, 128.2, 127.8, 127.0, 127.0, 77.0, 68.3, 30.6, 26.6; HRMS–ESI $[M+Na]^+$ Calcd for $C_{18}H_{18}NaO$ 273.1250, found 273.1242.



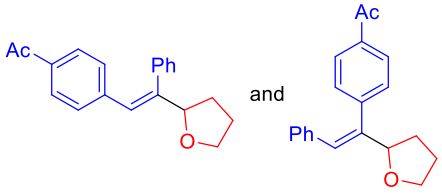
(*E*)-2-(2-(4-methoxyphenyl)-1-phenylvinyl)tetrahydrofuran (24a) and (E)-2-(1-(4-methoxyphenyl)-2-phenylvinyl)tetrahydrofuran (24b)

Following the typical procedure **III** with 1-methoxy-4-(phenylethynyl)benzene (41.6 mg, 0.2 mmol), the product **24a** and **24b** (24 mg) were isolated in 43% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 1H), 7.22-7.20 (m, 1H), 7.13-7.06 (m, 3H), 6.98 (6.96) (s, 1H), 6.87-8.85 (m, 2H), 6.66-6.61 (m, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 4.00-3.86 (m, 2H), 3.82 (3.72) (s, 3H), 2.03-1.94 (m, 1H), 1.90-1.80 (m, 1H), 1.74-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.2, 142.6, 140.9, 139.2, 137.0, 131.0, 130.4, 129.4, 129.3, 129.2, 128.6, 128.3, 127.8, 127.0, 126.4, 125.7, 125.4, 114.0, 113.3, 83.8, 83.7, 68.7, 68.6, 55.14, 55.1, 31.1, 31.0, 25.8, 25.8; HRMS–ESI $[M+Na]^+$ Calcd for $C_{19}H_{20}NaO_2$ 303.1356, found 303.1357.



(*Z*)-2-(2-(4-methoxyphenyl)-1-phenylvinyl)tetrahydrofuran (24a') and (*Z*)-2-(1-(4-methoxyphenyl)-2-phenylvinyl)tetrahydrofuran (24b')

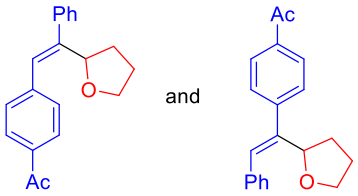
Following the typical procedure **III** with 1-methoxy-4-(phenylethynyl)benzene (41.6 mg, 0.2 mmol), the product **24a'** and **24b'** (24 mg) were isolated in 43% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.37-7.32 (m, 5H), 6.93-6.88 (m, 2H), 6.72 (6.70) (s, 1H), 5.01-4.96 (m, 1H), 3.94-3.75 (m, 5H), 1.96-1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.7, 141.9, 141.6, 141.1, 137.1, 133.7, 132.8, 132.3, 130.3, 129.9, 129.4, 129.0, 128.7, 128.3, 128.1, 127.8, 126.8, 113.6, 113.2, 77.1, 77.0, 68.3, 68.2, 55.3, 55.2, 30.6, 30.5, 26.6, 26.6; HRMS–ESI $[M+Na]^+$ Calcd for $C_{19}H_{20}NaO_2$ 303.1356, found 303.1362.



(*E*)-1-(4-(2-phenyl-2-(tetrahydrofuran-2-yl)vinyl)phenyl)ethan-1-one (25a) and

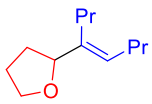
(*E*)-1-(4-(2-phenyl-1-(tetrahydrofuran-2-yl)vinyl)phenyl)ethan-1-one (25b)

Following the typical procedure **III** with 1-(4-(phenylethynyl)phenyl)ethan-1-one (44 mg, 0.2 mmol), the product **25a** and **25b** (20 mg) were isolated in 34% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.33-7.30 (m, 3H), 7.18-7.16 (m, 1H), 7.09-7.08 (m, 1H), 7.01 (6.99) (s, 1H), 6.93-6.91 (m, 1H), 6.75-6.74 (m, 1H), 4.73-4.69 (m, 1H), 4.03-3.86 (m, 2H), 2.60 (2.50) (s, 3H), 2.04-1.96 (m, 1H), 1.92-1.81 (m, 1H), 1.74-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 197.6, 146.1, 144.3, 141.92, 141.86, 138.5, 136.2, 135.9, 135.0, 129.7, 129.2, 129.0, 128.7, 128.5, 128.0, 127.6, 127.1, 126.8, 124.4, 83.3, 83.2, 68.8, 68.7, 31.2, 31.1, 26.6, 26.4, 25.8, 25.7; HRMS–ESI $[M+Na]^+$ Calcd for $C_{20}H_{20}NaO_2$ 315.1356, found 315.1350.



(*Z*)-1-(4-(2-phenyl-2-(tetrahydrofuran-2-yl)vinyl)phenyl)ethan-1-one (25a') and (*Z*)-1-(4-(2-phenyl-1-(tetrahydrofuran-2-yl)vinyl)phenyl)ethan-1-one (25b')

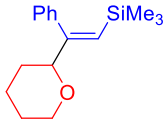
Following the typical procedure **III** with 1-(4-(phenylethynyl)phenyl)ethan-1-one (44 mg, 0.2 mmol), the product **25a'** and **25b'** (20 mg) were isolated in 34% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.93 (m, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.52-7.47 (m, 2H), 7.39-7.29 (m, 4H), 6.79 (6.74) (s, 1H), 4.99 (4.92) (dd, *J* = 6.8, 8.8 Hz, 1H), 3.93-3.87 (m, 1H), 3.81-3.76 (m, 1H), 2.624 (2.619) (s, 3H), 1.98-1.74 (m, 3H), 1.71-1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 197.7, 146.4, 144.4, 141.9, 141.5, 140.9, 136.4, 135.8, 135.6, 134.0, 131.9, 129.2, 129.0, 128.9, 128.6, 128.3, 128.3, 128.0, 127.9, 127.34, 127.31, 77.2, 76.8, 68.4, 68.3, 30.7, 30.7, 26.60 26.60, 26.58, 26.58; HRMS–ESI $[M+Na]^+$ Calcd for $C_{20}H_{20}NaO_2$ 315.1356, found 315.1352.



(*E*)-2-(oct-4-en-4-yl)tetrahydrofuran (26)

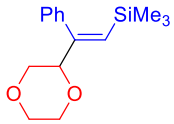
Following the typical procedure **III** with 4-octyne (22.0 mg, 0.2 mmol) to give the product **26** (18 mg) in 50% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (t, *J* = 7.5 Hz, 1H), 4.22 (t, *J* = 7.5 Hz, 1H), 3.91 (dd, *J* = 7.5, 14.0 Hz, 1H), 3.77 (dd, *J* = 7.5, 14.0 Hz, 1H), 2.08-1.84 (m,

7H), 1.66-1.60 (m, 1H), 1.46-1.34 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C MR (125 MHz, $CDCl_3$) δ 139.5, 125.5, 82.7, 68.0, 31.2, 30.2, 29.6, 25.8, 23.0, 22.8, 14.5, 13.9; HRMS–ESI $[M+Na]^+$ Calcd for $C_{12}H_{22}NaO$ 205.1563, found 205.1565.



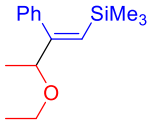
(*E*)-trimethyl(2-phenyl-2-(tetrahydro-2H-pyran-2-yl)vinyl)silane (27)

Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) and tetrahydropyran (344 mg, 4 mmol) in benzene (8.0 mL) to give the product **27** (25 mg) in 49% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 3H), 7.16-7.14 (m, 2H), 5.92 (d, *J* = 1.0 Hz, 1H), 4.16-4.12 (m, 1H), 3.94-3.91 (m, 1H), 3.55 (dt, *J* = 2.5, 11.5 Hz, 1H), 1.81-1.77 (m, 1H), 1.64-1.55 (m, 2H), 1.51-1.47 (m, 1H), 1.45-1.37 (m, 1H), 1.28-1.20 (m, 1H), -0.20 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 159.6, 141.8, 128.8, 127.7, 127.1, 125.0, 82.1, 68.9, 31.3, 25.9, 23.9, -0.04; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{24}NaOSi$ 283.1489, found 283.1496.



(*E*)-(2-(1,4-dioxan-2-yl)-2-phenylvinyl)trimethylsilane (28)

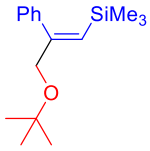
Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) and 1,4-dioxane (352 mg, 4 mmol) in benzene (8.0 mL) to give the product **28** (28 mg) in 53% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 3H), 7.14-7.12 (m, 2H), 6.00 (d, *J* = 1.0 Hz, 1H), 4.26 (dd, *J* = 1.0, 10.0 Hz, 1H), 3.94 (dd, *J* = 2.5, 11.5 Hz, 1H), 3.85 (dt, *J* = 3.0, 11.5 Hz, 1H), 3.71-3.66 (m, 2H), 3.60 (dt, *J* = 2.5, 11.5 Hz, 1H), 3.24 (dd, *J* = 10.0, 11.5 Hz, 1H), -0.18 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 154.7, 140.8, 128.5, 128.1, 128.0, 127.6, 79.9, 70.8, 67.2, 66.2, -0.1; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{22}NaO_3Si$ 285.1281, found 285.1289.



(*E*)-(3-ethoxy-2-phenylbut-1-en-1-yl)trimethylsilane (29)

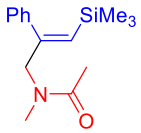
Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) and diethyl ether (308 mg, 4 mmol) in benzene (4.0 mL) to give the product **29** (21 mg) in 42% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 3H), 7.12-7.10 (m, 2H), 5.81 (s,

1H), 3.98 (q, *J* = 6.4 Hz, 1H), 3.70-3.62 (m, 1H), 3.48-3.40 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 1H), -0.18 (s, 9H); ^{13}C MR (100 MHz, $CDCl_3$) δ 159.2, 141.4, 128.8, 127.6, 127.6, 127.0, 81.5, 63.8, 20.8, 15.4, -0.1; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{24}NaOSi$ 271.1489, found 271.1488.



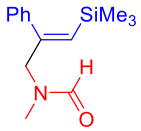
(*E*)-(3-(tert-butoxy)-2-phenylprop-1-en-1-yl)trimethylsilane (30)

Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) and tert-butyl methyl ether (352 mg, 4 mmol) in benzene (8.0 mL) to give the product **30** (32 mg) in 61% yield as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.36-7.30 (m, 3H), 7.22-7.20 (m, 2H), 5.92 (s, 1H), 4.06 (s, 2H), 1.19 (s, 9H), -0.18 (s, 9H); ^{13}C MR (100 MHz, $(CD_3)_2CO$) δ 158.8, 143.6, 129.8, 129.2, 128.7, 125.9, 74.3, 68.7, 28.5, -0.9; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{26}NaOSi$ 285.1645, found 285.1647.



(*E*)-*N*-methyl-N-(2-phenyl-3-(trimethylsilyl)allyl)acetamide (31)

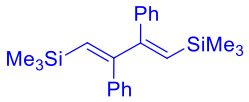
Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) and N,N'-dimethylacetamide (348 mg, 4 mmol) in benzene (4.0 mL) to give the product **31** (50 mg) in 96% yield as a colorless oil. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.36-7.28 (m, 3H), 7.13-7.11 (7.21-7.19) (m, 2H), 5.61 (5.56) (s, 1H), 4.07 (4.31) (s, 2H), 2.96 (2.93) (s, 3H), 2.00 (2.05) (s, 3H), -0.17 (-0.16) (s, 9H); ^{13}C MR (125 MHz, $(CD_3)_2CO$) δ 171.3 (170.5), 152.1 (153.2), 140.9 (141.2), 128.2 (128.1), 128.0 (127.8), 127.7 (127.6), 127.5 (127.4), 59.8 (55.6), 33.9 (35.7), 20.1 (21.6), -0.2 (-0.1); HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{23}NNaOSi$ 284.1441, found 284.1449.



(*E*)-*N*-methyl-N-(2-phenyl-3-(trimethylsilyl)allyl)formamide (32)

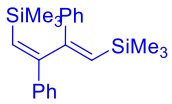
Following the typical procedure **III** with trimethyl(phenylethynyl)silane (34.8 mg, 0.2 mmol) and N,N'-dimethylacetamide (348 mg, 4 mmol) in benzene (4.0 mL) to give the product **32** (27 mg) in

55% yield (containing all isomers, major:minor > 20:1, E/Z of major product = 10:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (8.06) (s, 1H), 7.34-7.28 (m, 3H), 7.10-7.09 (7.20-7.19) (m, 2H), 5.71 (5.62) (s, 1H), 4.04 (4.24) (s, 2H), 2.85 (2.86) (s, 3H), -0.17 (-0.16) (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 163.2, 152.4 (151.8), 140.5 (140.8), 130.7 (128.8), 128.24 (128.18), 128.0 (127.9), 127.8 (127.7), 59.0 (52.8), 29.7 (34.3), -0.2 (-0.1); HRMS–ESI $[M+H]^+$ Calcd for $C_{14}H_{22}NOSi$ 248.1465, found 248.1464.



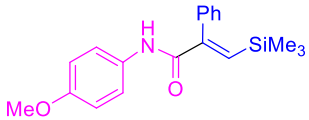
((1*E*,3*E*)-2,3-diphenylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (35)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 6H), 7.20-7.18 (m, 4H), 5.45 (s, 2H), -0.31 (s, 18H); ^{13}C MR (100 MHz, $CDCl_3$) δ 160.2, 142.5, 134.2, 130.2, 127.9, 127.2, 0.0; HRMS–APCI $[M+H]^+$ Calcd for $C_{22}H_{31}Si_2$ 351.1959, found 351.1954.



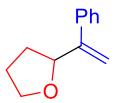
((1*Z*,3*E*)-2,3-diphenylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (36)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.28-7.25 (m, 2H), 7.20-7.12 (m, 6H), 6.00 (s, 2H), 0.19 (s, 9H), 0.05 (s, 9H); ^{13}C MR (100 MHz, $CDCl_3$) δ 161.4, 158.1, 141.9, 140.9, 133.4, 129.6, 128.9, 127.9, 127.5, 127.3, 127.1, 0.5, 0.4; HRMS–APCI $[M+H]^+$ Calcd for $C_{22}H_{31}Si_2$ 351.1959, found 351.1958.



(*E*)-*N*-(4-methoxyphenyl)-2-phenyl-3-(trimethylsilyl)acrylamide (38)

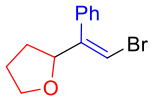
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 3H), 7.36-7.29 (m, 5H), 7.07 (br, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), -0.13 (s, 9H); ^{13}C MR (100 MHz, $CDCl_3$) δ 163.8, 156.5, 149.5, 142.1, 138.0, 131.0, 129.7, 128.8, 128.6, 121.6, 114.1, 55.4, -0.8; HRMS–ESI $[M+Na]^+$ Calcd for $C_{19}H_{23}NNaO_2Si$ 348.1390, found 348.1388.



2-(1-phenylvinyl)tetrahydrofuran (40)

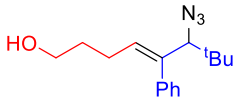
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.26-7.23 (m, 1H), 5.34 (s,

1H), 5.27 (s, 1H), 4.83 (t, *J* = 7.0 Hz, 1H), 4.00 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.86 (dd, *J* = 7.0, 14.5 Hz, 1H), 2.09-2.02 (m, 1H), 1.91-1.85 (m, 2H), 1.64-1.59 (m, 1H); ^{13}C MR (125 MHz, $CDCl_3$) δ 149.6, 140.0, 128.2, 127.4, 126.7, 111.6, 80.1, 68.4, 31.7, 25.6; HRMS–APCI $[M+H]^+$ Calcd for $C_{12}H_{15}O$ 175.1117, found 175.1120.



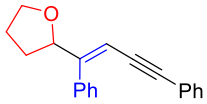
(*E*)-2-(2-bromo-1-phenylvinyl)tetrahydrofuran (41)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.35-7.32 (m, 1H), 7.25-7.23 (m, 2H), 6.55 (d, *J* = 1.0 Hz, 1H), 4.66 (dt, *J* = 1.0, 7.0 Hz, 1H), 3.94-3.89 (m, 1H), 3.87-3.82 (m, 1H), 1.97-1.90 (m, 1H), 1.86-1.80 (m, 2H), 1.68-1.62 (m, 1H); ^{13}C MR (125 MHz, $CDCl_3$) δ 147.1, 137.4, 128.6, 128.2, 127.8, 104.7, 80.1, 68.7, 31.0, 25.4; HRMS–APCI $[M-H]^+$ Calcd for $C_{12}H_{12}BrO$ 251.0066, found 251.0057.



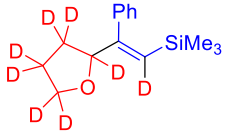
(*E*)-6-azido-7,7-dimethyl-5-phenyloct-4-en-1-ol (42)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.30-7.24 (m, 1H), 7.20-7.18 (m, 2H), 5.74 (t, *J* = 7.5 Hz, 1H), 4.02 (s, 1H), 3.58 (t, *J* = 6.5 Hz, 1H), 2.14-2.10 (m, 2H), 1.66-1.61 (m, 2H), 0.78 (s, 9H); ^{13}C MR (125 MHz, $CDCl_3$) δ 139.5, 137.9, 133.5, 129.3, 128.1, 127.0, 79.3, 62.1, 35.7, 32.7, 27.0, 24.9; HRMS–ESI $[M+Na]^+$ Calcd for $C_{16}H_{23}N_3NaO$ 296.1733, found 296.1731.



(*E*)-2-(1,4-diphenylbut-1-en-3-yn-1-yl)tetrahydrofuran (43)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 2H), 7.31-7.21 (m, 4H), 7.16-7.14 (m, 4H), 6.01 (d, *J* = 1.6 Hz, 1H), 4.78 (dt, *J* = 1.6, 7.6 Hz, 1H), 3.95-3.90 (m, 1H), 3.84-3.78 (m, 1H), 1.99-1.90 (m, 1H), 1.84-1.76 (m, 2H), 1.58-1.50 (m, 1H); ^{13}C MR (100 MHz, $CDCl_3$) δ 153.6, 137.9, 131.3, 128.4, 128.2, 128.0, 127.9, 127.8, 123.8, 105.1, 92.8, 88.0, 81.0, 68.8, 32.0, 25.6; HRMS–ESI $[M+Na]^+$ Calcd for $C_{20}H_{18}NaO$ 297.1250, found 297.1249.

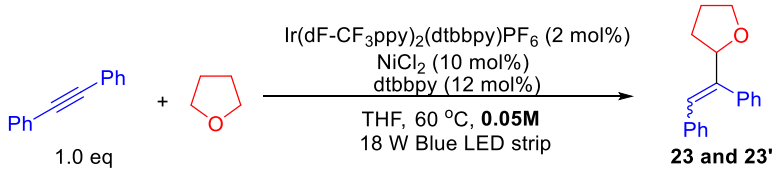


(*E*)-trimethyl(2-phenyl-2-(tetrahydrofuran-2-yl-d7)vinyl-1-d)silane (39)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.16-7.14 (m, 2H), -0.19 (s, 9H); ^{13}C MR (100 MHz, $CDCl_3$) δ 158.8, 141.5, 128.9, 127.7, 127.1, 125.0 (t), 83.3 (t), 67.8 (m), 30.2 (m), 24.5 (m), -0.1; HRMS–ESI $[M+Na]^+$ Calcd for $C_{15}H_{14}D_8NaOSi$ 277.1834, found 277.1830.

VIII. Additional Control Experiments to Elucidate the Mechanistic Pathway

a) Light ON/OFF experiments over time



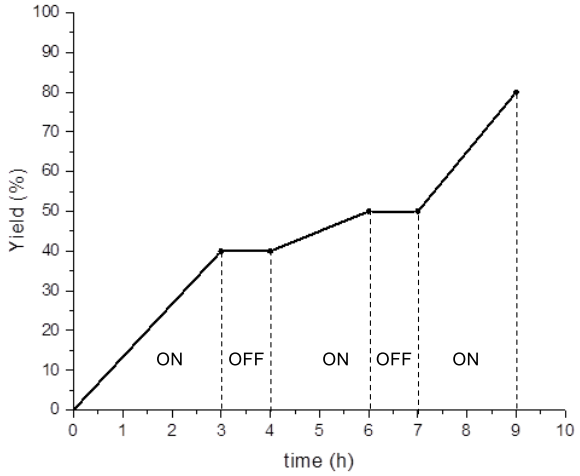
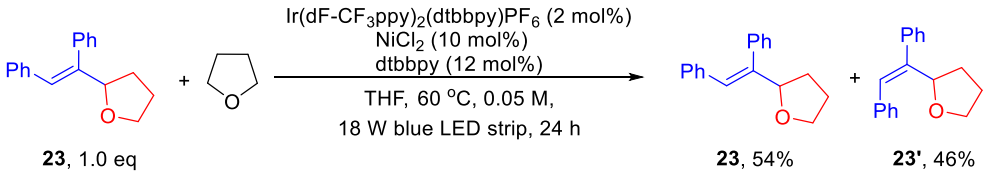


Figure S2. Time profile of the transformation with the light ON/OFF over time

To examine the impact of light, we conducted experiments under alternating periods of irradiation and darkness. These resulted in a total interruption of the reaction progress in the absence of light and recuperation of reactivity on further illumination, which allows precise temporal control over the entire reaction period. These results demonstrate that light is a necessary component of the reaction. Even though they do not definitively rule out a radical-chain process, the data show that any chain-propagation process must be short-lived.

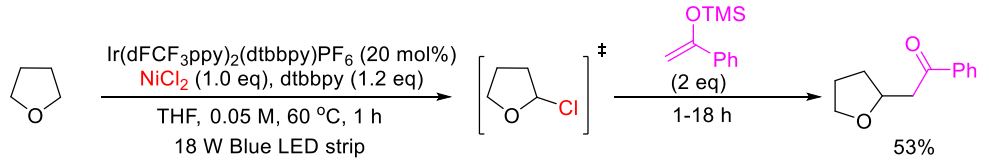
b) Isomerization of product 23



Scheme S1. Isomerization of product **23**

Under the standard alkenylation reaction conditions, 46% of **23** was converted to its isomer **23'**.

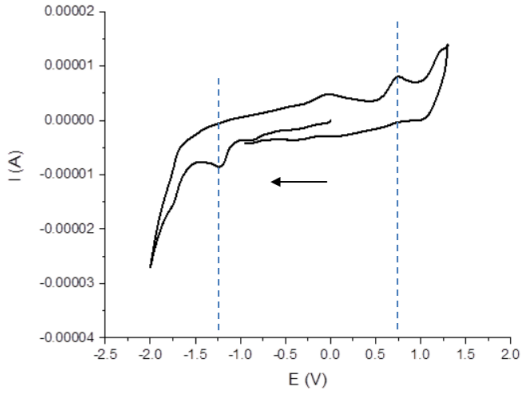
c) Trapping 2-Cl-THF with silyl enol ether[4]



Scheme S2. Trapping 2-Cl-THF with silyl enol ether.

We obtained the desired THF ketone product in 53% yield (based on Ni catalyst). However, we cannot exclude the possibility that the THF ketone is generated by THF radical coupling with the silyl enol ether.

IX. Cyclic Voltammetry of (dtbbpy)$NiCl_2$ in ACN



Voltage vs Ag/AgCl

Figure S3. Cyclic Voltammetry of (dtbbpy)$NiCl_2$ in ACN

Cyclic Voltammetry was performed using a CHI 620C electrochemical analyzer at a rate of 0.1 V/s in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. Polished glassy carbon, platinum wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. The (dtbbpy)$NiCl_2$ complex was formed in situ by adding $NiCl_2$ (0.01

mmol) and dtbbpy (0.012 mmol) into acetonitrile (20 mL). The solutions were degassed with nitrogen gas for 15 mins and stirred for 30 mins. As showed in Figure S3, the reduction peak at -1.22 V (-1.27 V SCE) is corresponding to the Ni(II)/Ni(0) couple and the oxidation peak at +0.77 V (+0.72 V SCE) is corresponding to the Ni(II)/Ni(III) couple.

X. Emission Spectrum of Blue LED Strips

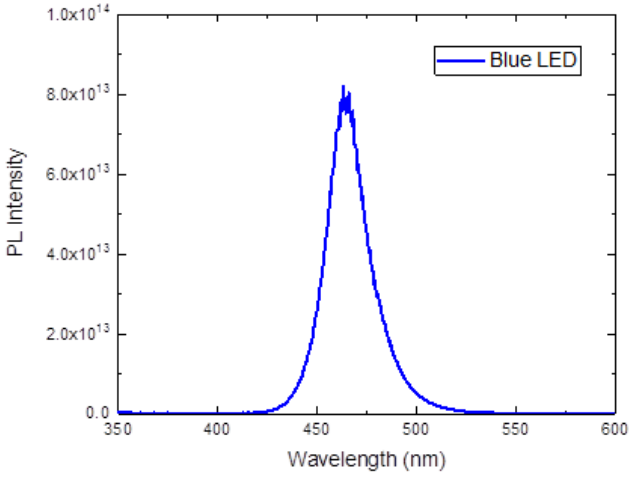


Figure S4. Emission spectra of 18 W blue LED strips (maximum Emission at around 470 nm)

XI. Fluorescence Quenching Studies

a) Absorption spectrum of (dtbbpy)$NiCl_2$ in THF

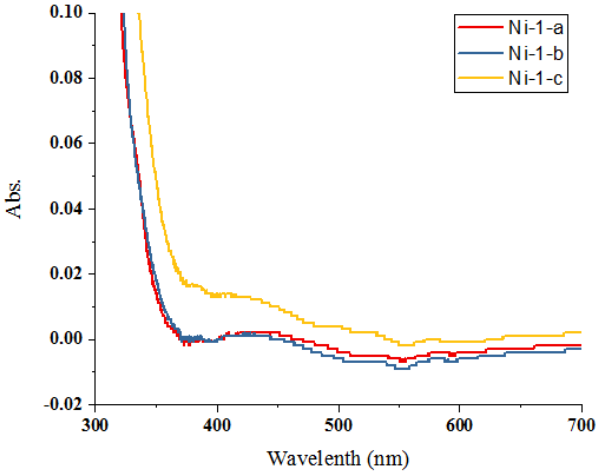


Figure S5. Absorption spectrum of (dtbbpy)$NiCl_2$ in THF with different concentrations.

Ni-1-a: 66.7 μM, **Ni-1-b**: 133 μM, **Ni-1-c**: 200 μM.

b) Absorption spectrum of Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 in THF

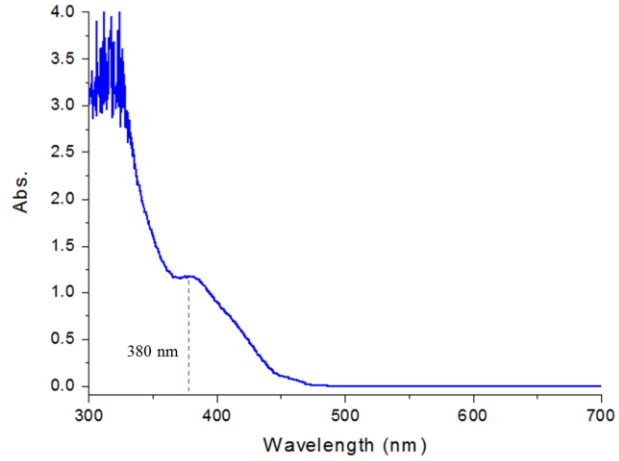


Figure S6. Absorption spectrum of Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 in THF (100 μM)

c) Fluorescence quenching study of Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 in THF, benzene and DMSO

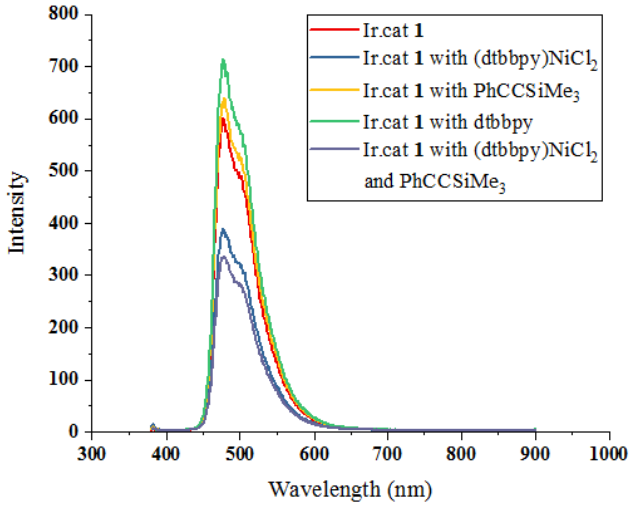


Figure S7. Samples were excited at 380 nm. Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 in THF (100 μM) (red line), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (100 μM) with (dtbbpy)$NiCl_2$ (200 μM) in THF (blue line), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (100 μM) with trimethyl(phenylethynyl)silane (1 mM) in THF (yellow line), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (100 μM) with dtbbpy (200 μM) in THF (green line), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (100 μM) with (dtbbpy)$NiCl_2$ (200 μM) and trimethyl(phenylethynyl)silane (1 mM) in THF (purple line).

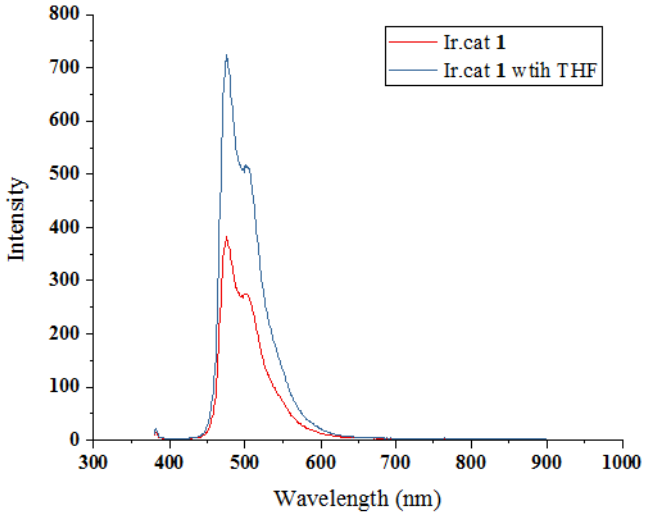


Figure S8. Samples were excited at 380 nm. Emission spectrum of Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 in benzene (100 μM) (red line), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (100 μM) with THF (1 mM) in benzene (blue line).

The quenching studies demonstrated that only (dtbbpy)$NiCl_2$ can quench the excited state of the Ir catalyst (**1***), whereas alkynes, THF, and dtbbpy ligand cannot.

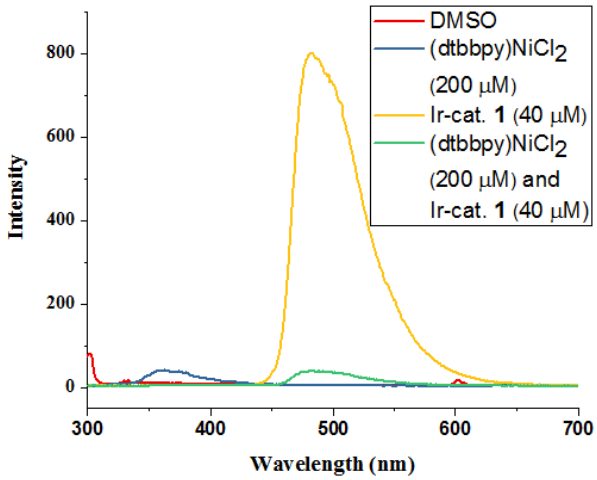


Figure S9. Samples were excited at 300 nm. DMSO (red line), (dtbbpy)$NiCl_2$ (200 μM) in DMSO (blue line), Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (40 μM) in THF (yellow line), (dtbbpy)$NiCl_2$ (200 μM) with Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (40 μM) in DMSO (green line).

Maximum emission of (dtbbpy)$NiCl_2$ in DMSO was monitored at 358 nm, and maximum emission of Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 in DMSO was monitored at 480 nm. Adding Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 into a solution of (dtbbpy)$NiCl_2$ in DMSO, quenching effect of both (dtbbpy)$NiCl_2$ and Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 were detected.

d) PL quenching of (dtbbpy)$NiCl_2$ by Ir 1 at various concentrations

In a typical experiment, a solution of (dtbbpy)$NiCl_2$ in DMSO (800 μM, 2.5 mL) was added the appropriate amount of quencher (Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6) in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 358 nm was collected with excited wavelength of 300 nm.

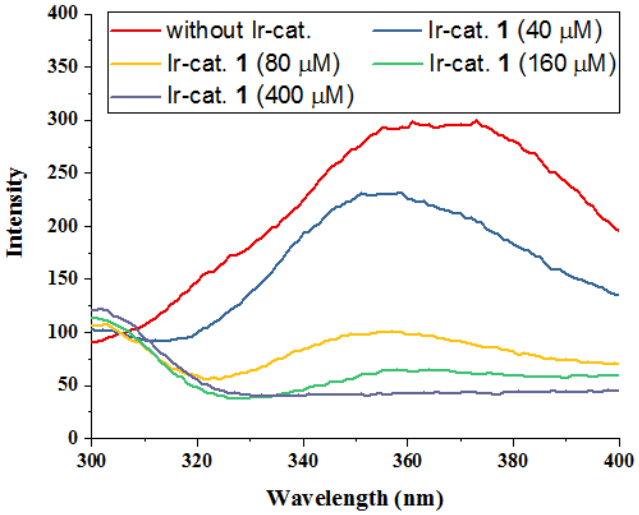


Figure S10. PL quenching experiments. Without Ir-cat.: (dtbbpy)$NiCl_2$ (800 μM) in DMSO; Ir-cat. (40 μM): (dtbbpy)$NiCl_2$ (800 μM) with Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (40 μM) in DMSO; Ir-cat. (80 μM): (dtbbpy)$NiCl_2$ (800 μM) with Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (80 μM) in DMSO; Ir-cat. (160 μM): (dtbbpy)$NiCl_2$ (800 μM) with Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (1600 μM) in DMSO; Ir-cat. (400 μM): (dtbbpy)$NiCl_2$ (800 μM) with Ir(dF-CF_3ppy)$_2$(dtbbpy)PF_6 (400 μM) in DMSO.

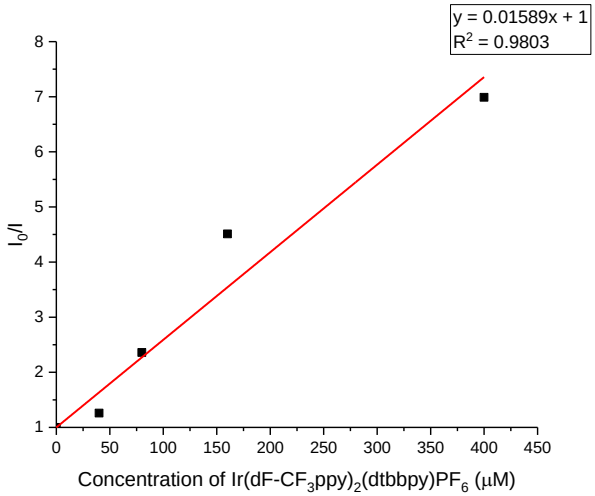
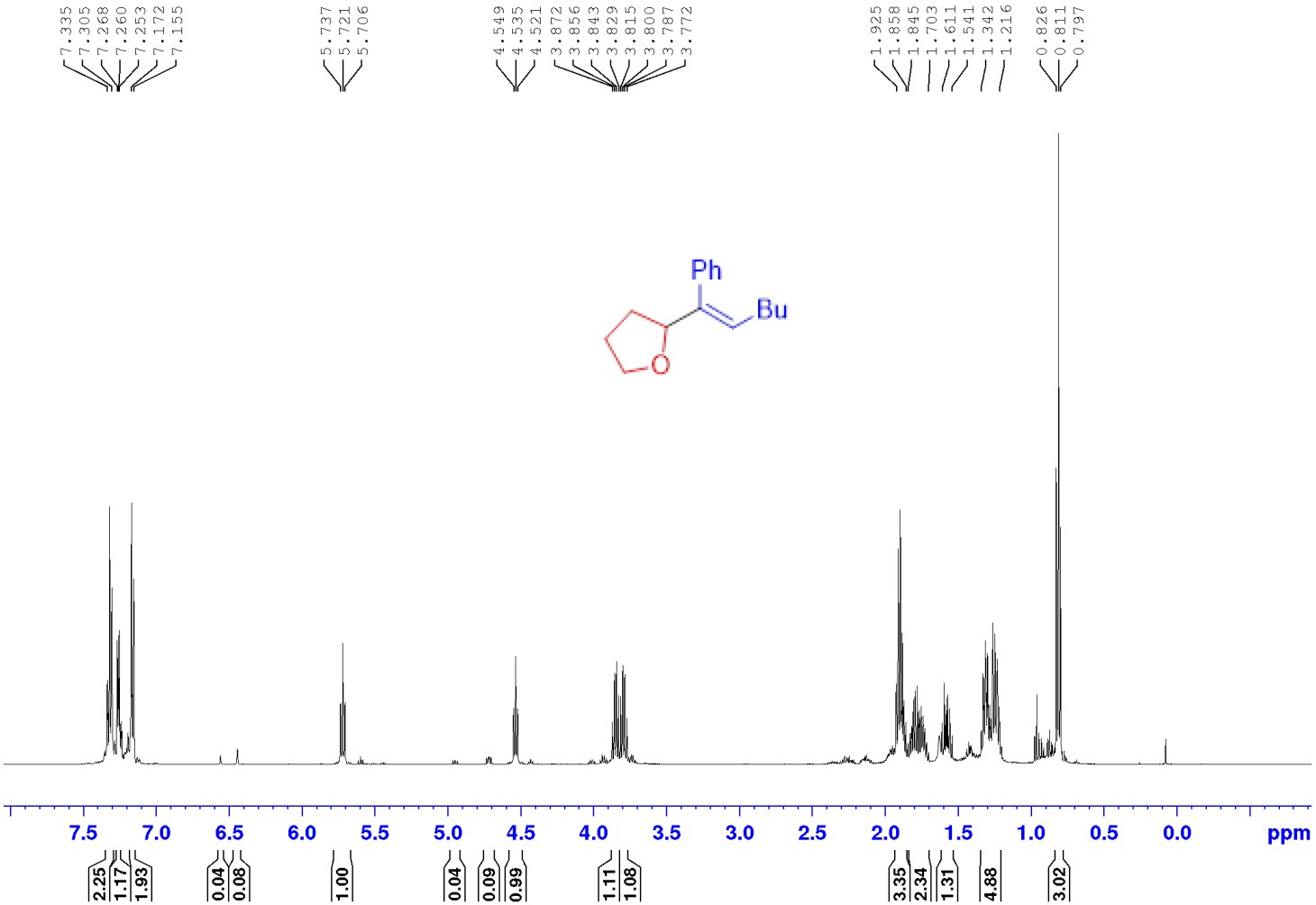


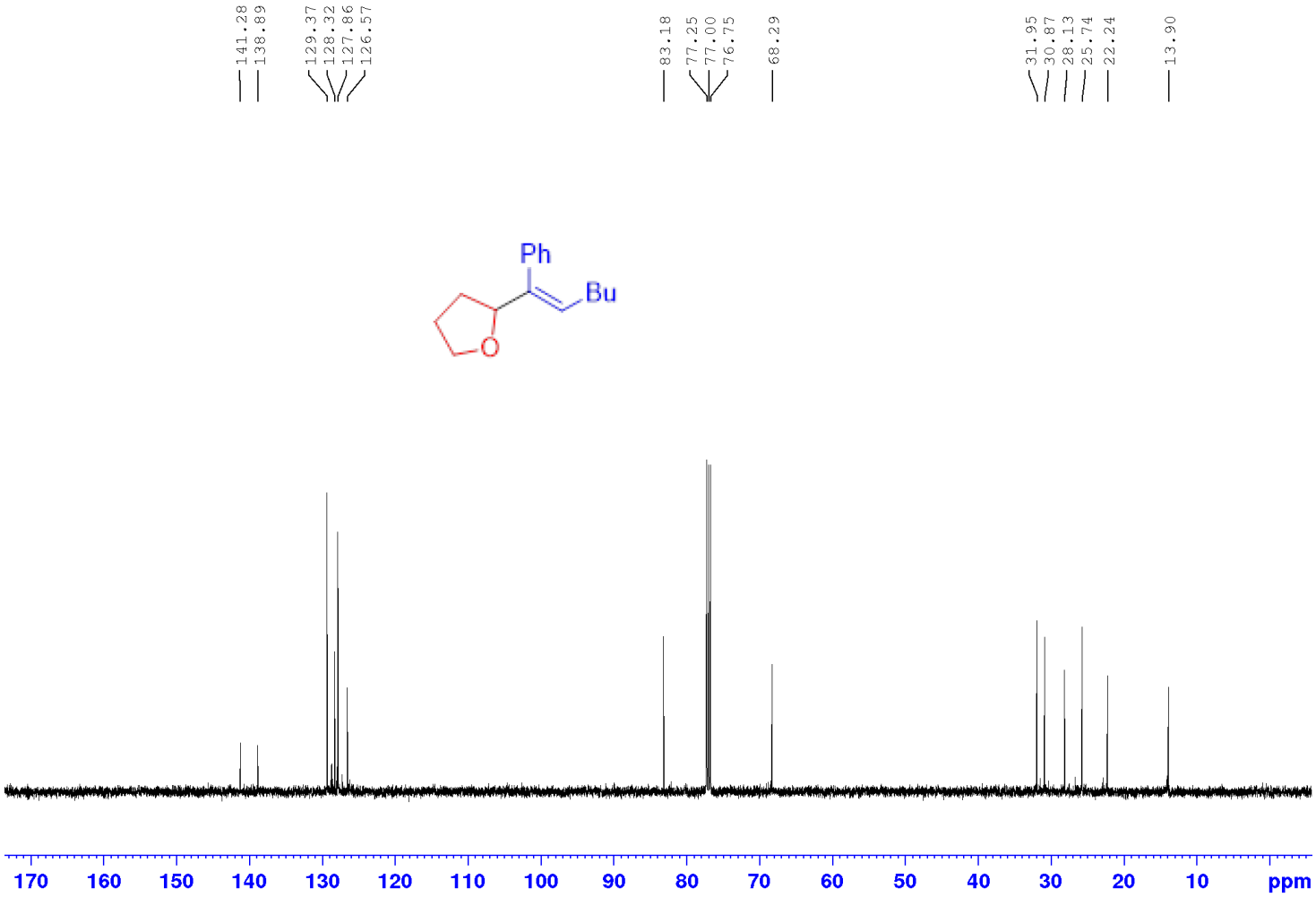
Figure S11. Combined Quenching Data

XIII. References

1. Wang, X.; Nakajima, M.; Serrano, E.; Martin, R. *J. Am. Chem. Soc.* **2016**, *138*, 15531-15534.
2. Sawama, Y., Shibata, K., Sawama, Y.; Takubo, M., Monguchi, Y.; Krause, N.; Sajiki, H. *Org. Lett.*, **2013**, *15*, 5282.
3. Cornelissen, L.; Lefrancq, M.; Riant, O. *Org. Lett.*, **2014**, *16*, 3024.
4. Lee, S.; Kaib, P. J.; List, B. *J. Am. Chem. Soc.* **2017**, *139*, 2156-2159.

XIV. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products

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76.75
68.29
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28.13
25.74
22.24
13.90
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90
80
70
60
50
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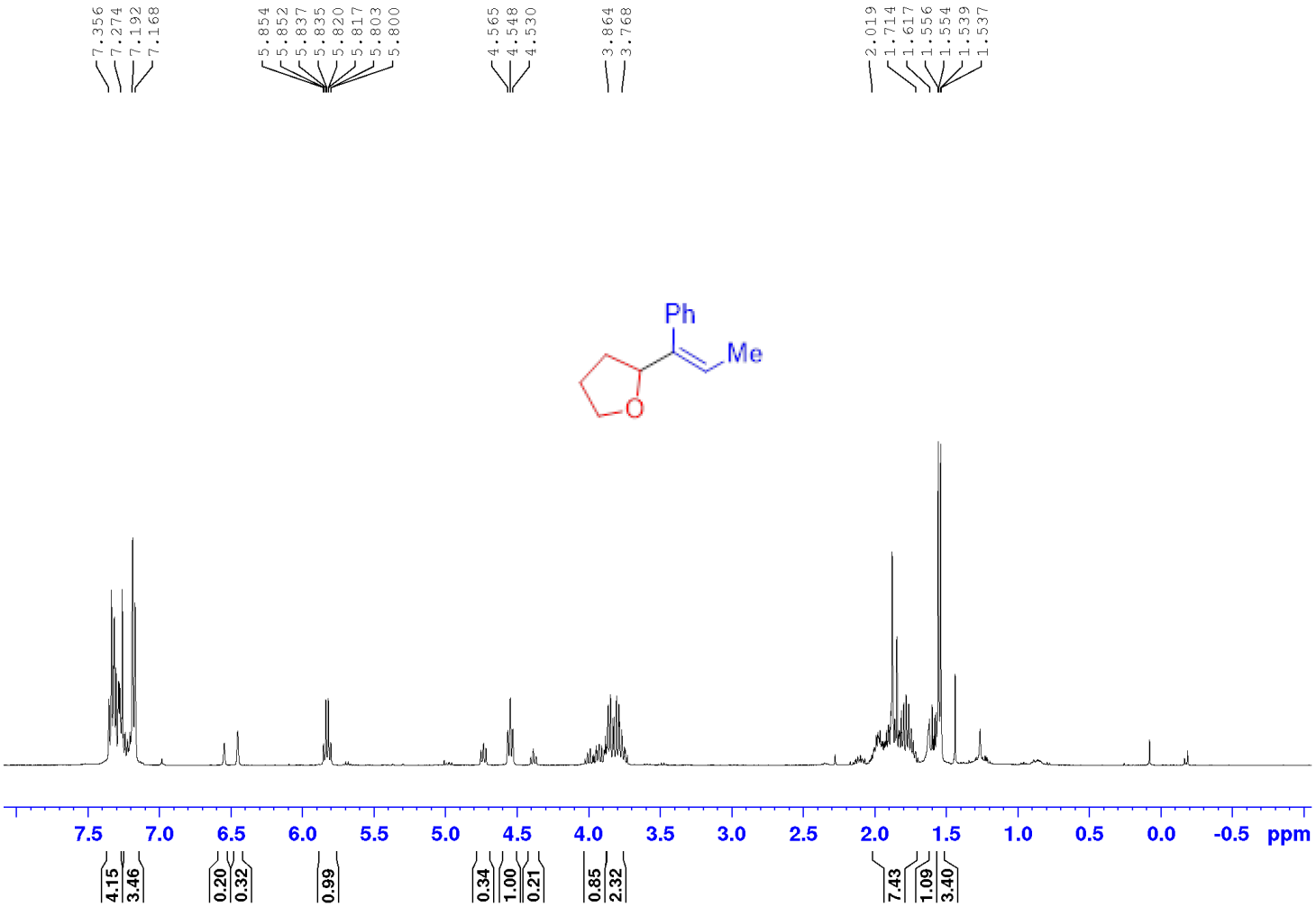
30
20
10
ppm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7.168
5.854
5.852
5.837
5.835
5.820
5.817
5.803
5.800
4.565
4.548
4.530
3.864
3.768
2.019
1.714
1.617
1.556
1.554
1.539
1.537
Ph
Me
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
4.15
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0.20
0.32
0.99
0.34
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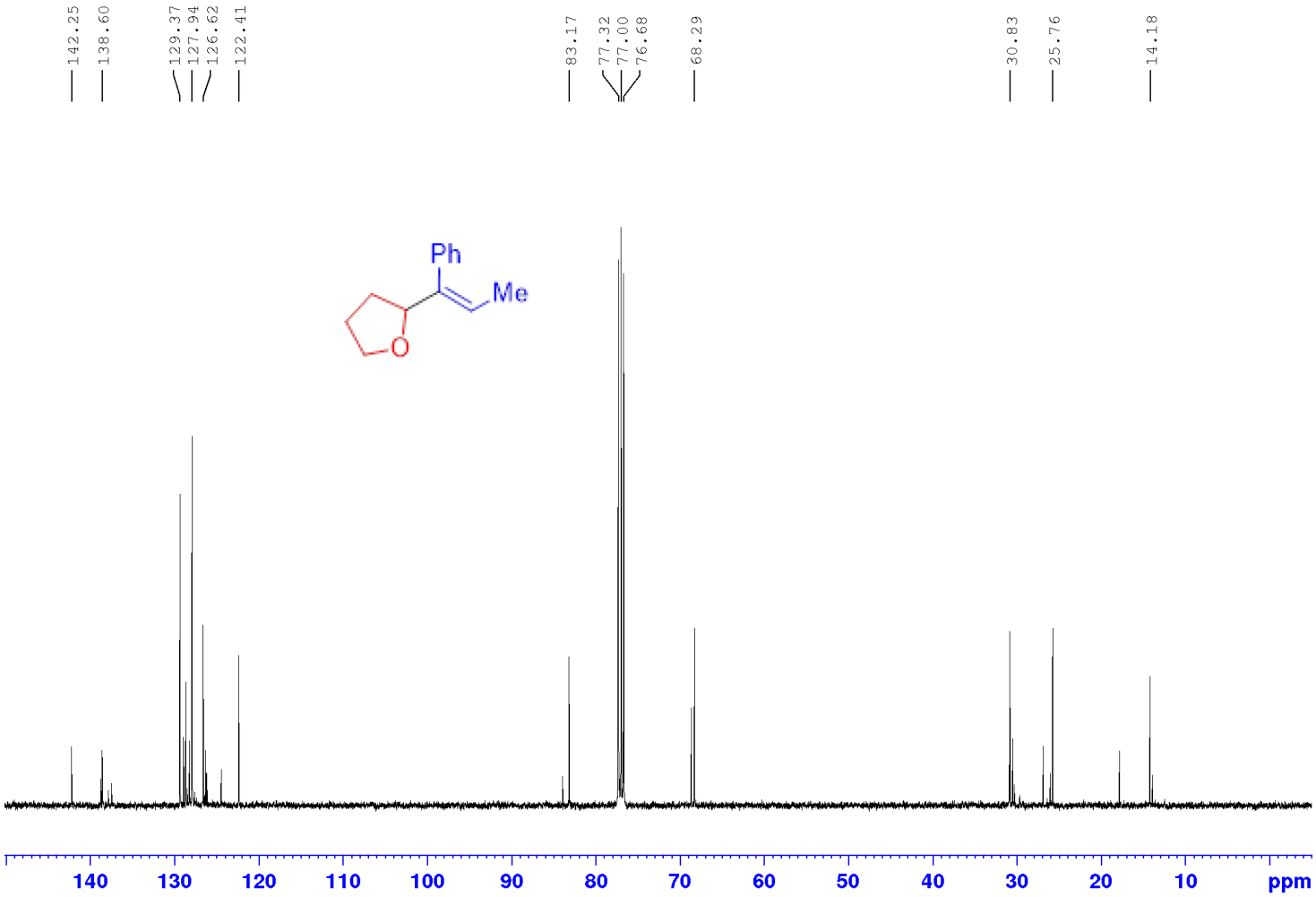
7.43
1.09
3.40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14.18
Ph
Me
O
140
130
120
110
100
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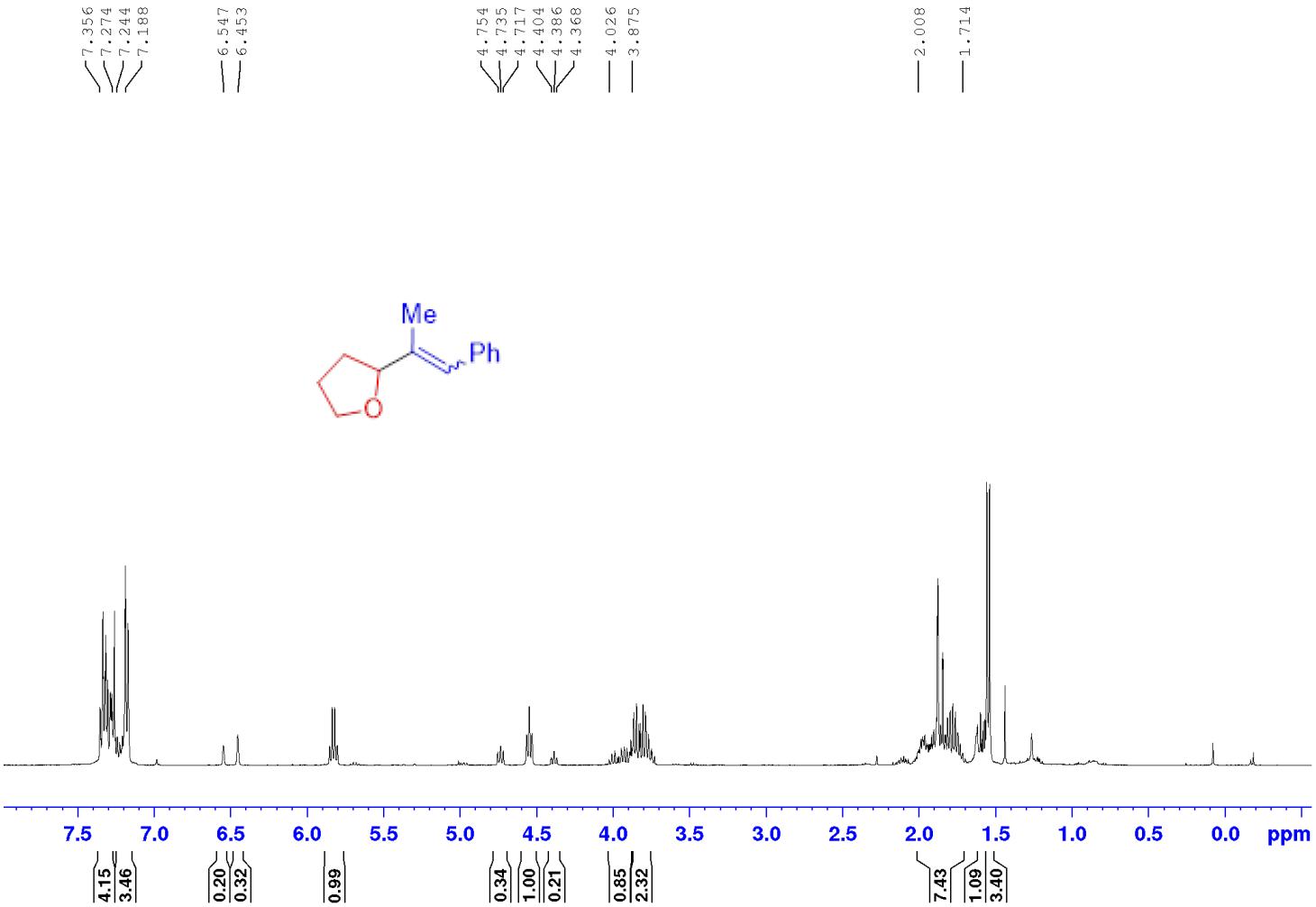
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Me
Ph
O
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6.0
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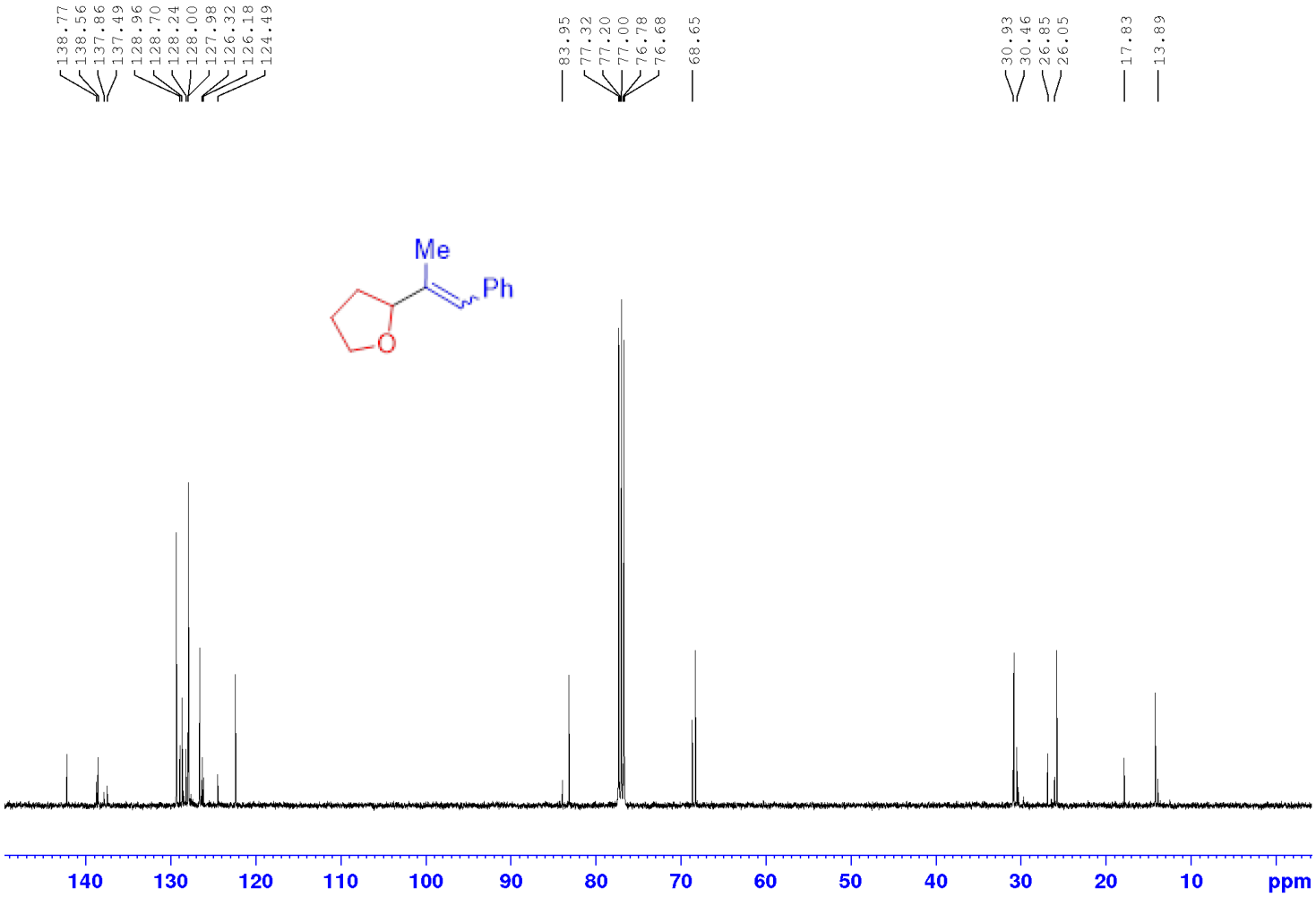
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26.05
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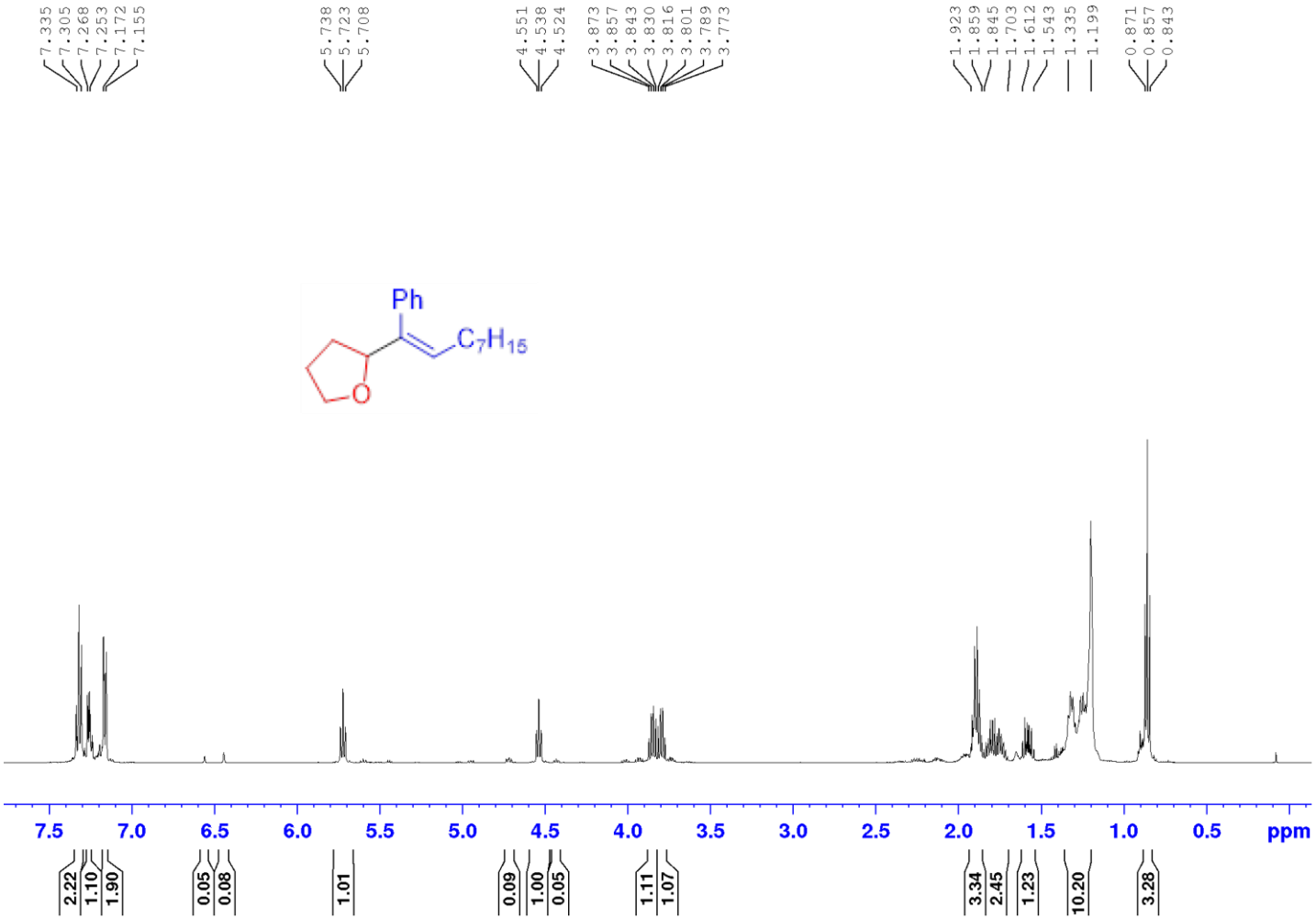
ppm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O
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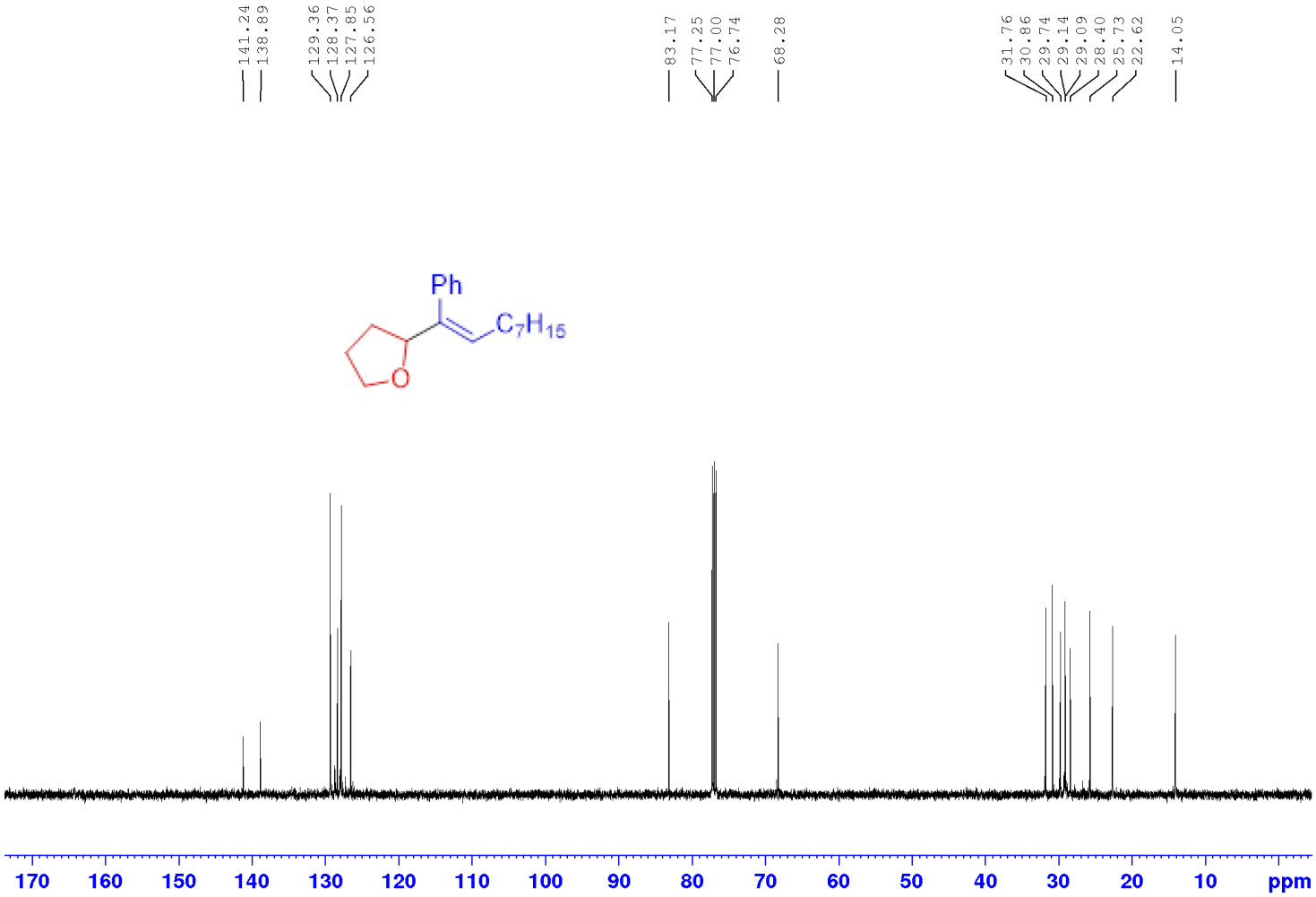
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28.40
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22.62
14.05
Ph
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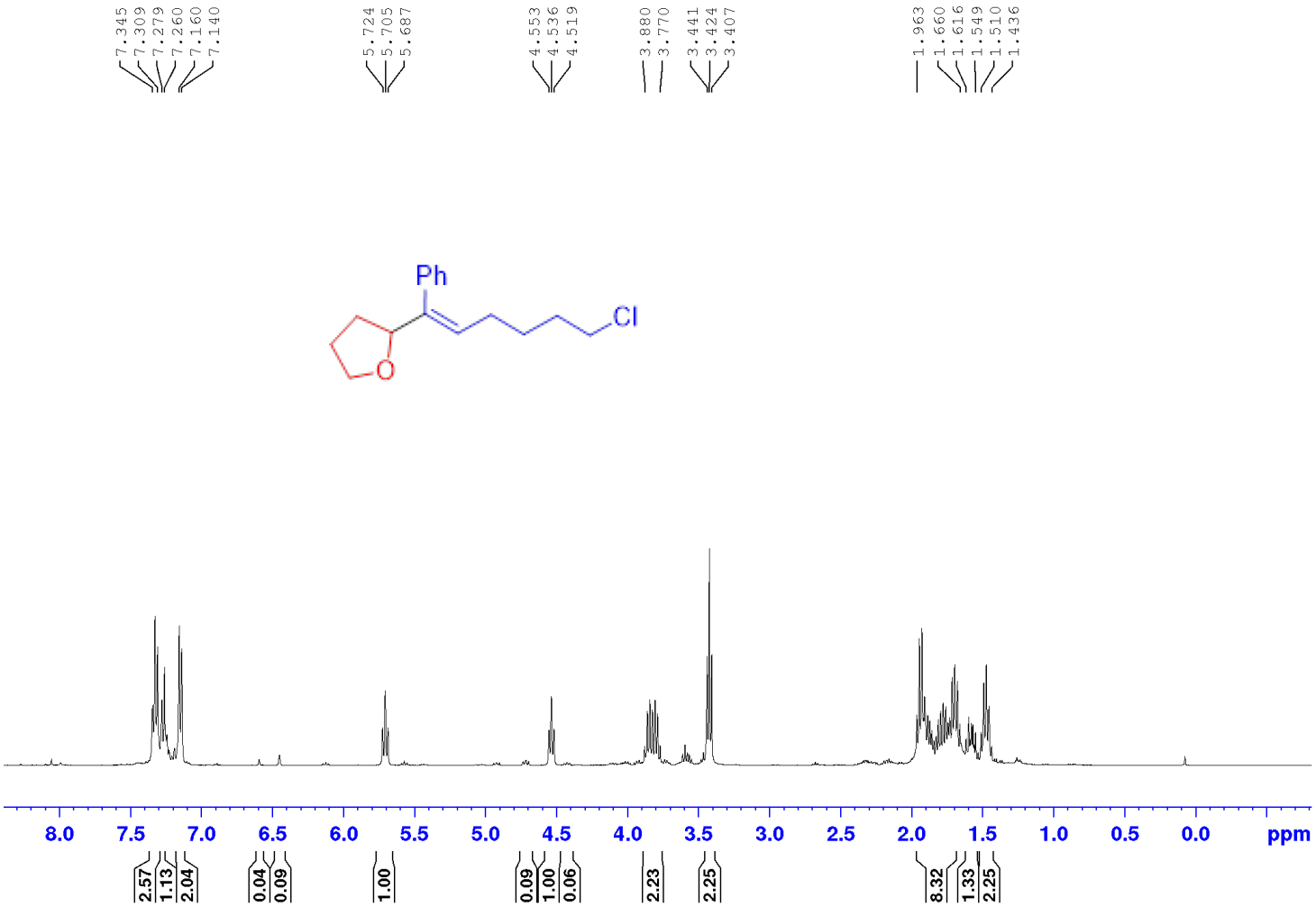
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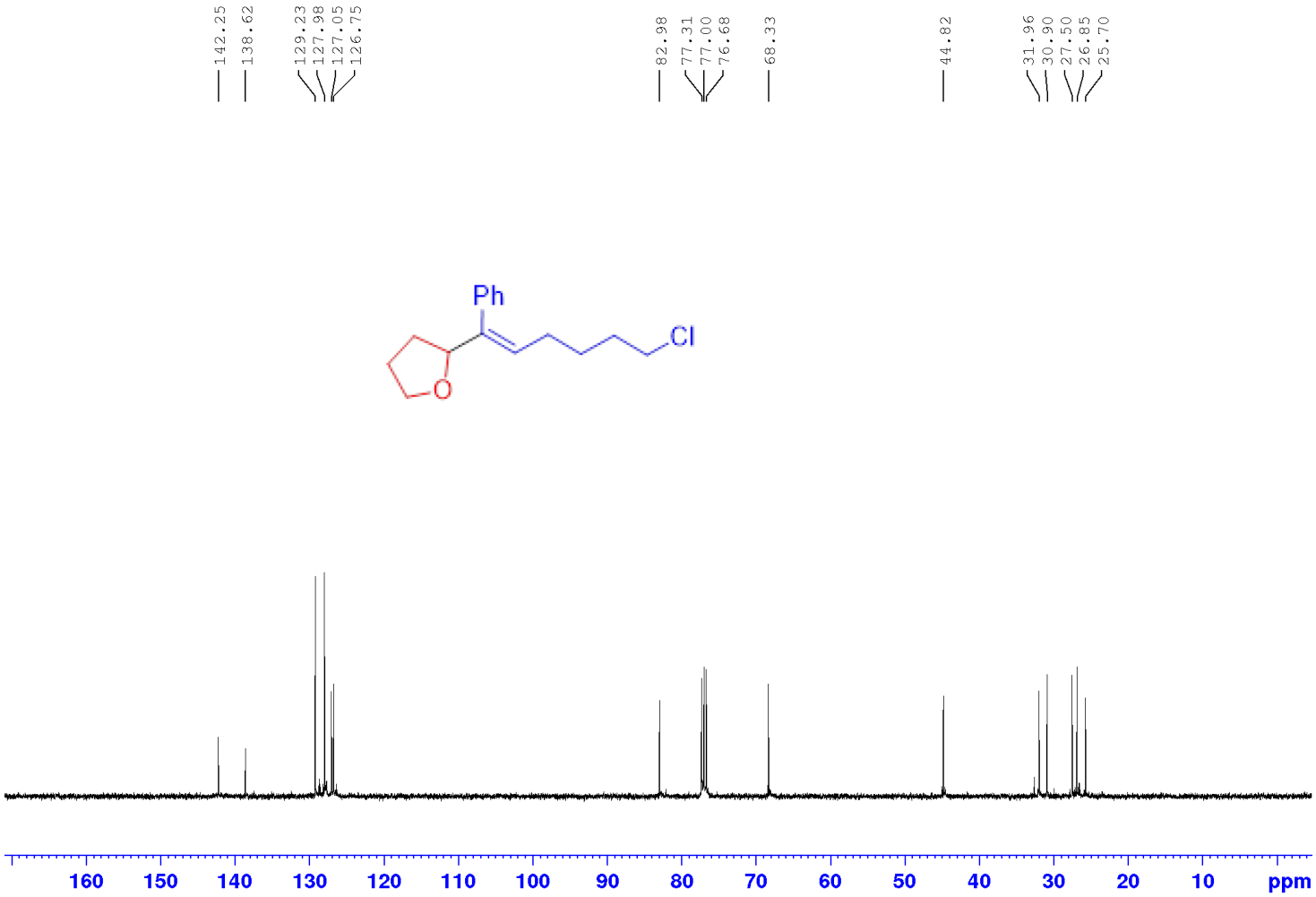
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Cl
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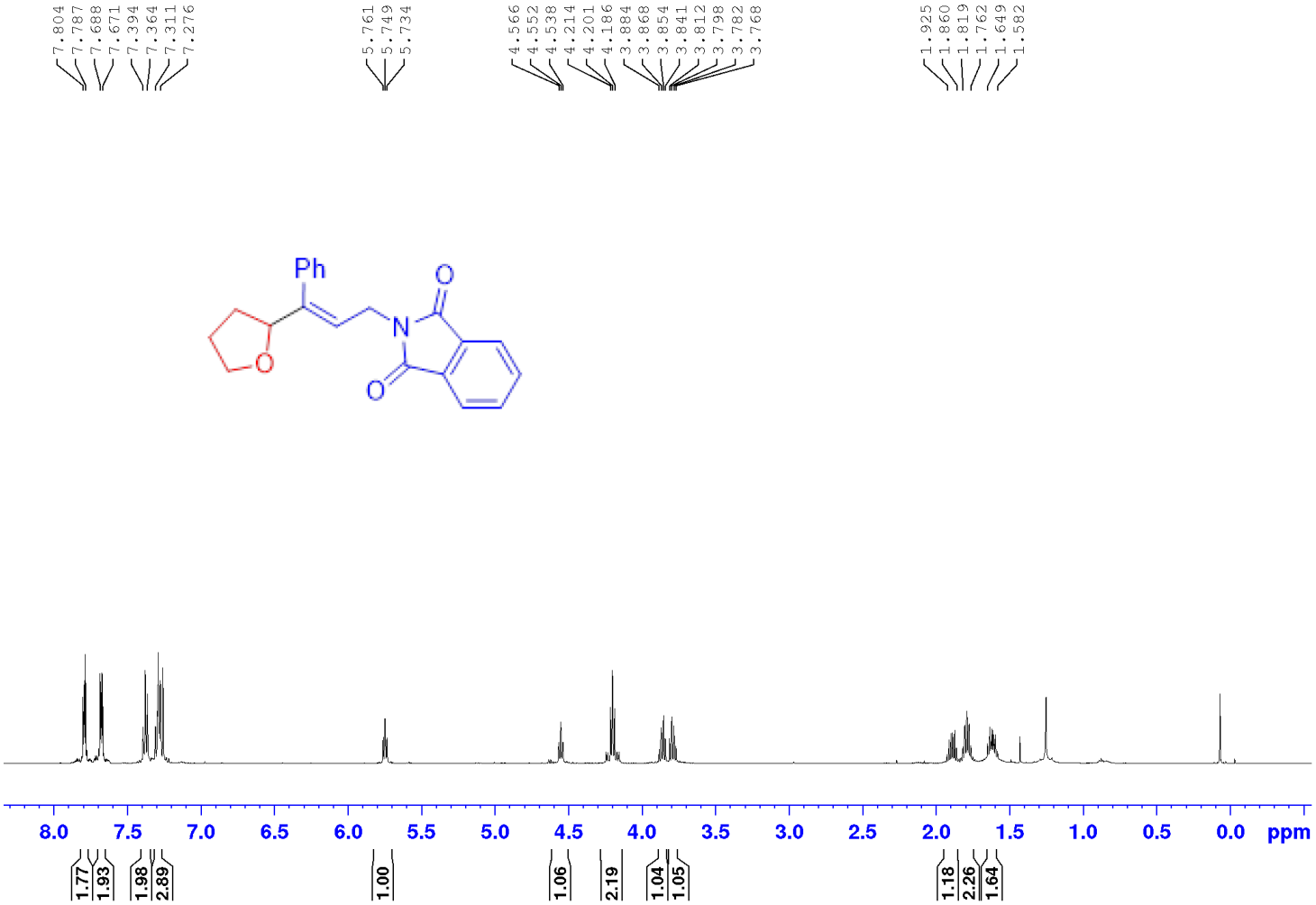
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3.841
3.812
3.798
3.782
3.768
1.925
1.860
1.819
1.762
1.649
1.582
Ph
O
N
O
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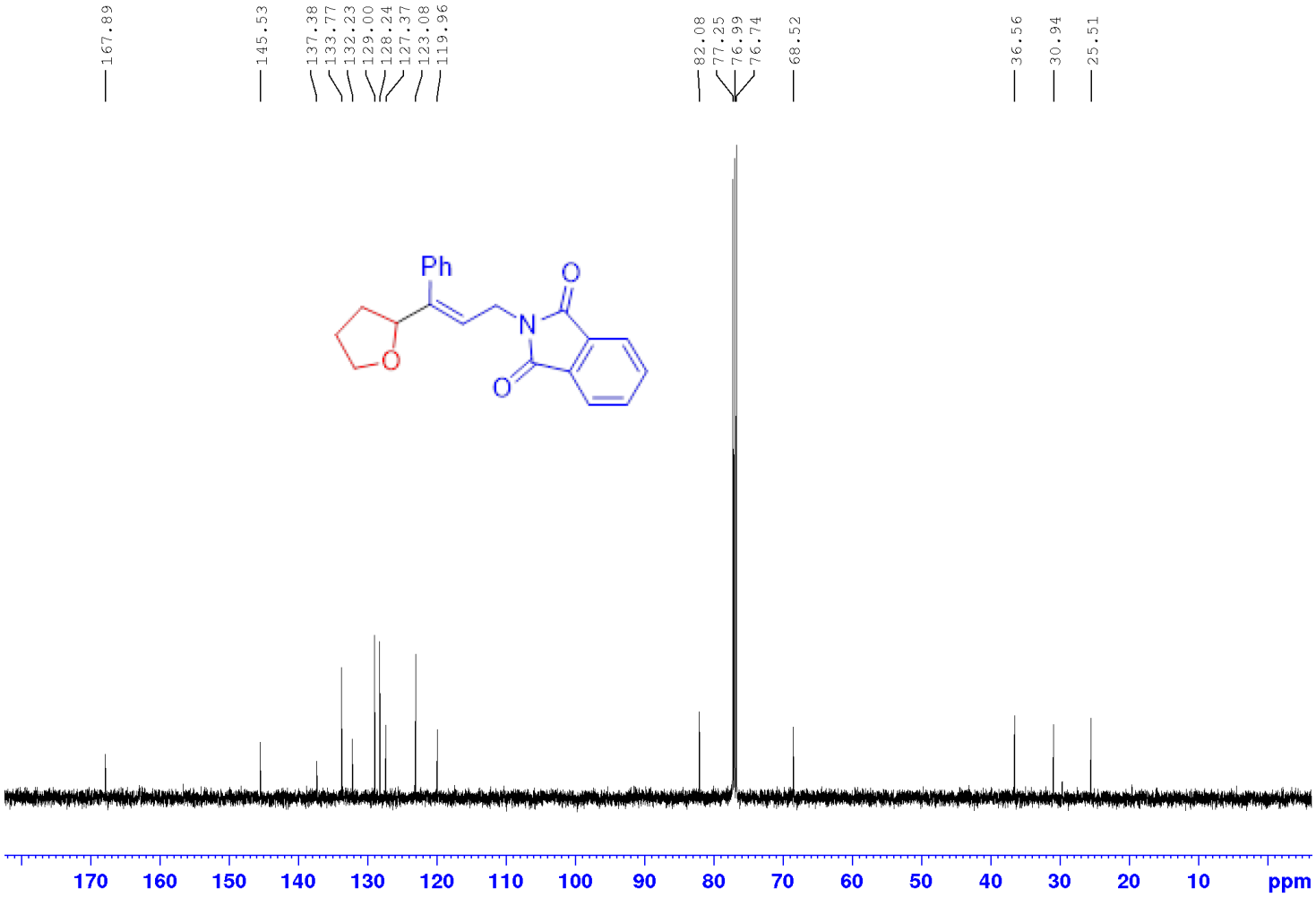
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Ph
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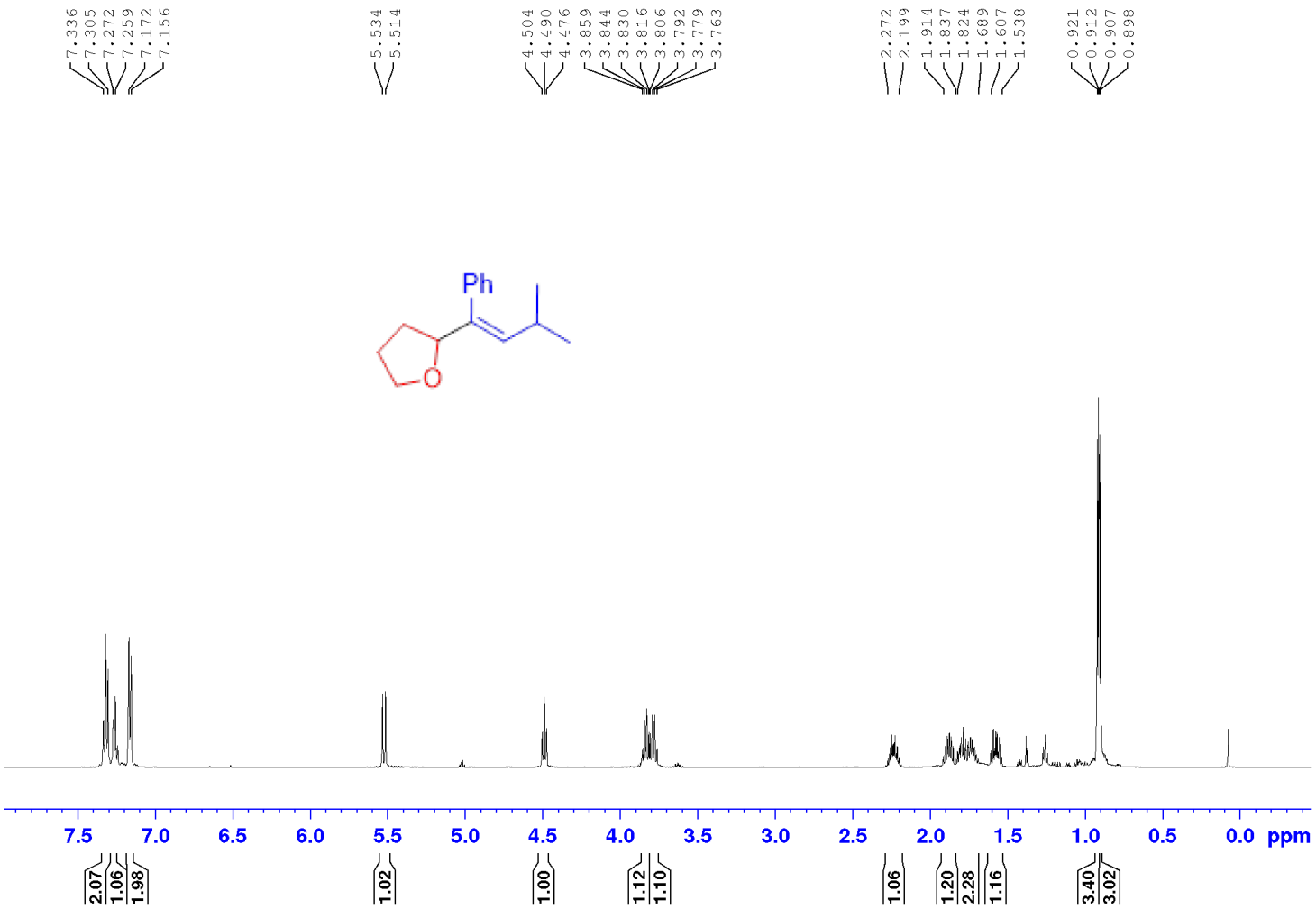
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3.830
3.816
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0.912
0.907
0.898
Ph
O
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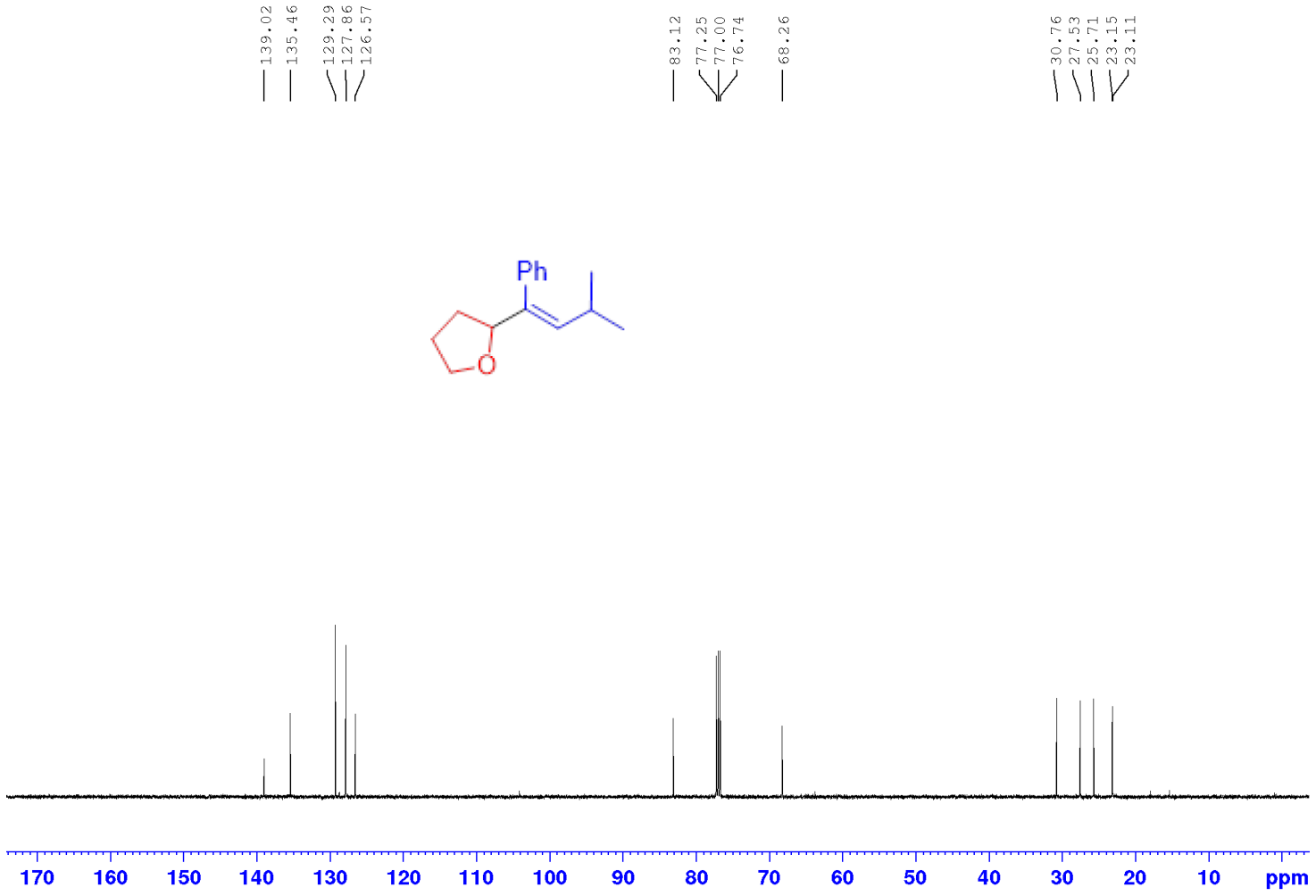
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23.15
23.11
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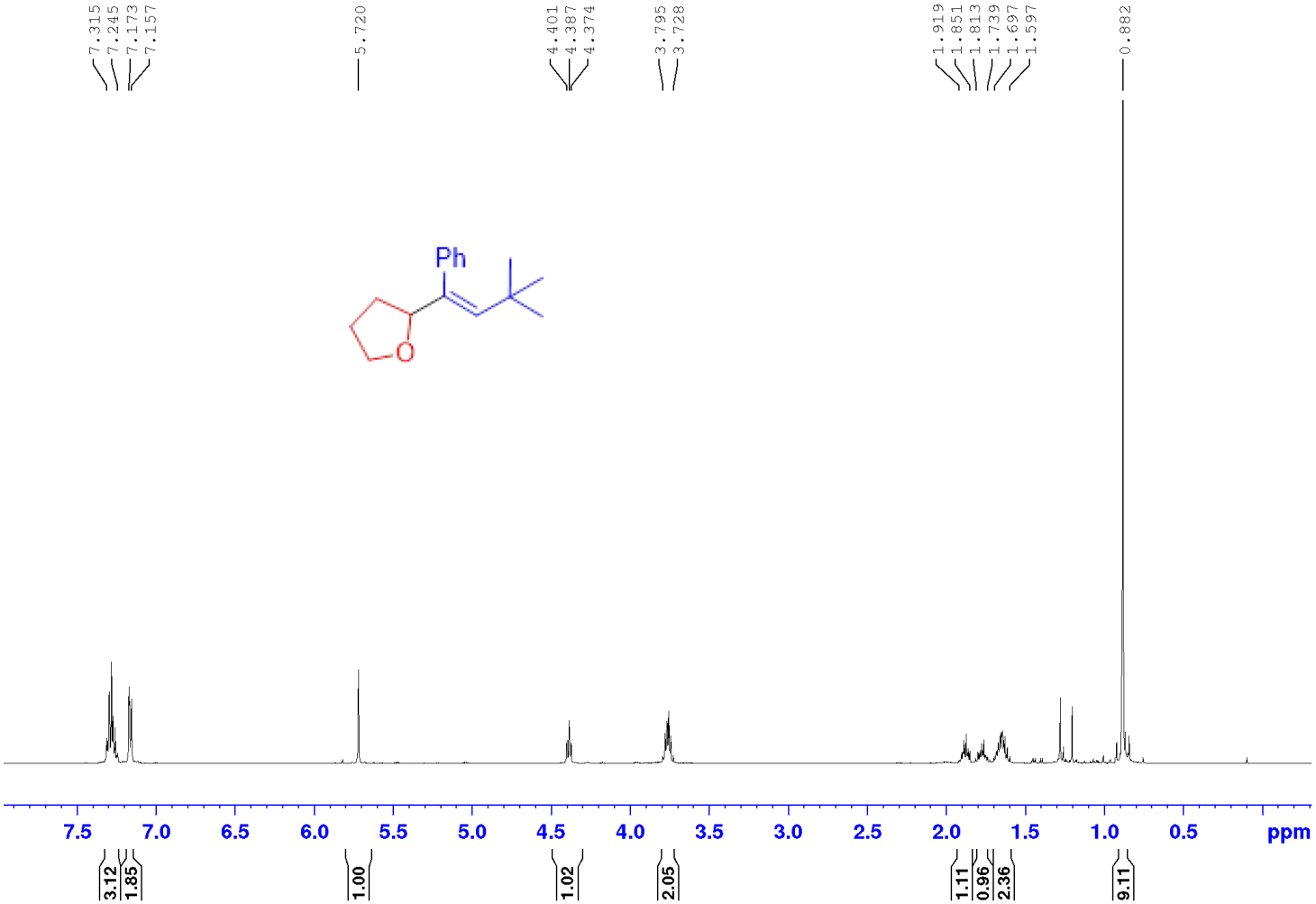
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O
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5.0
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4.0
3.5
3.0
2.5
2.0
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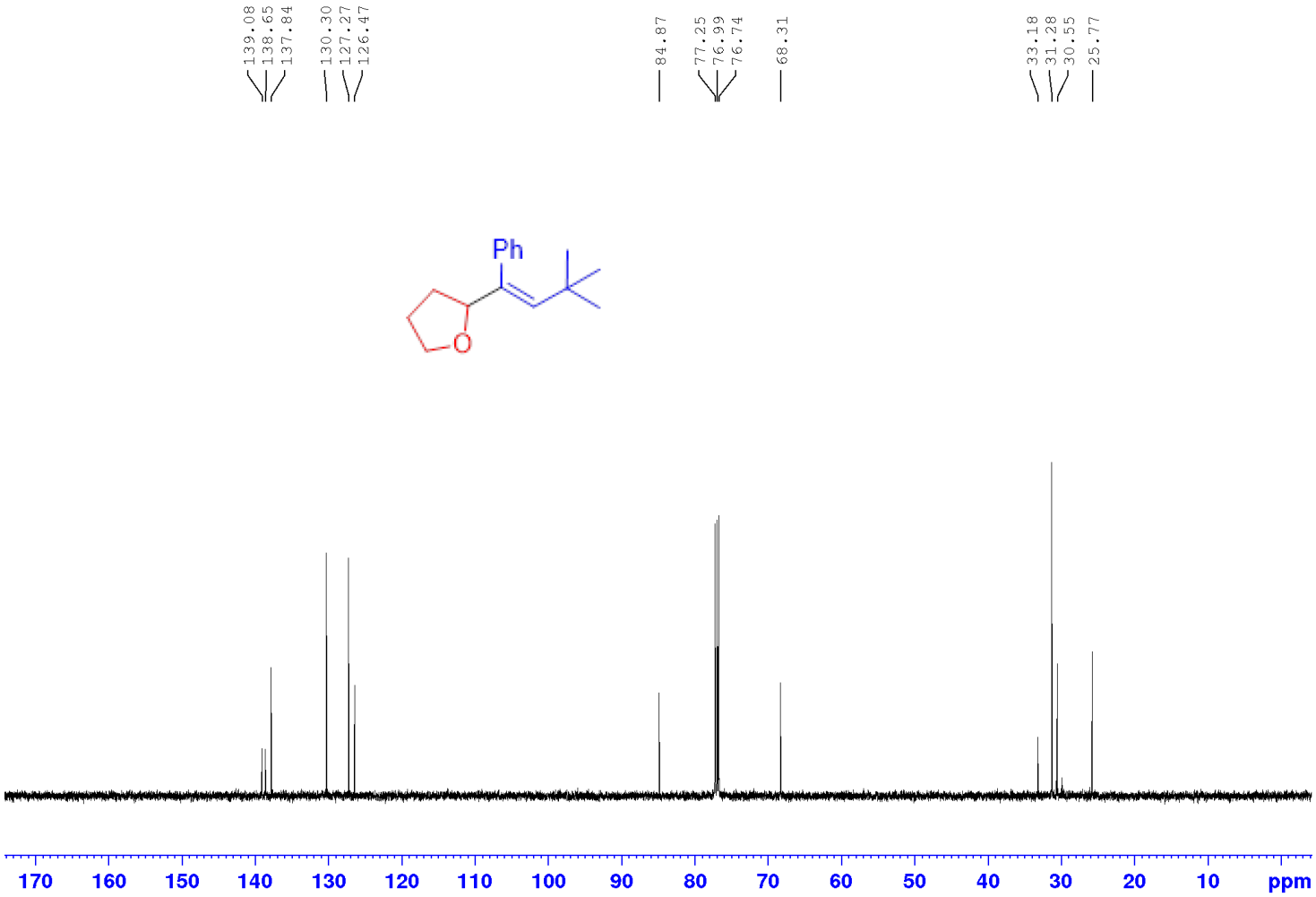
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33.18
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30.55
25.77
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70
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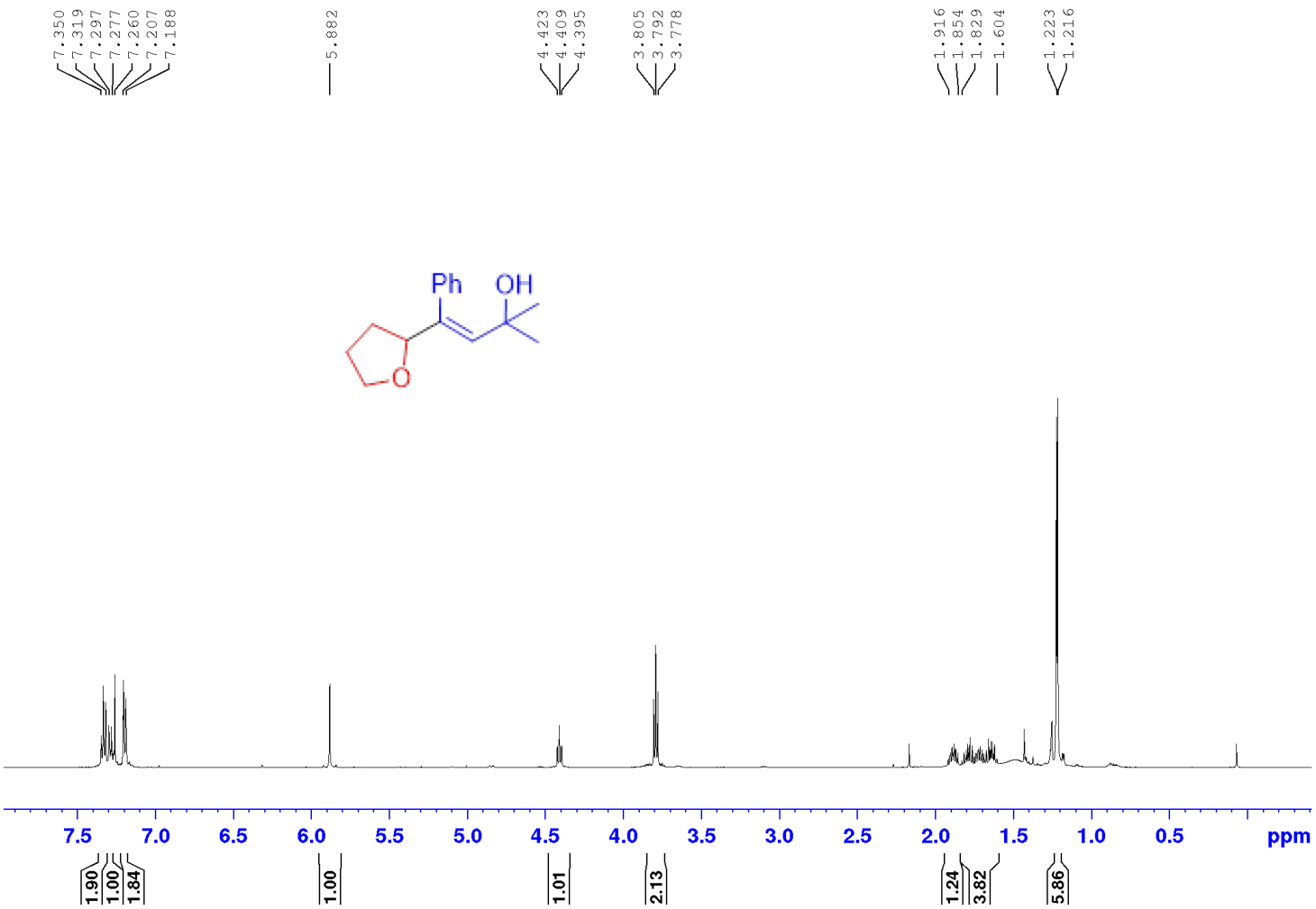
ppm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3.778
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1.854
1.829
1.604
1.223
1.216
Ph
OH
O
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5.0
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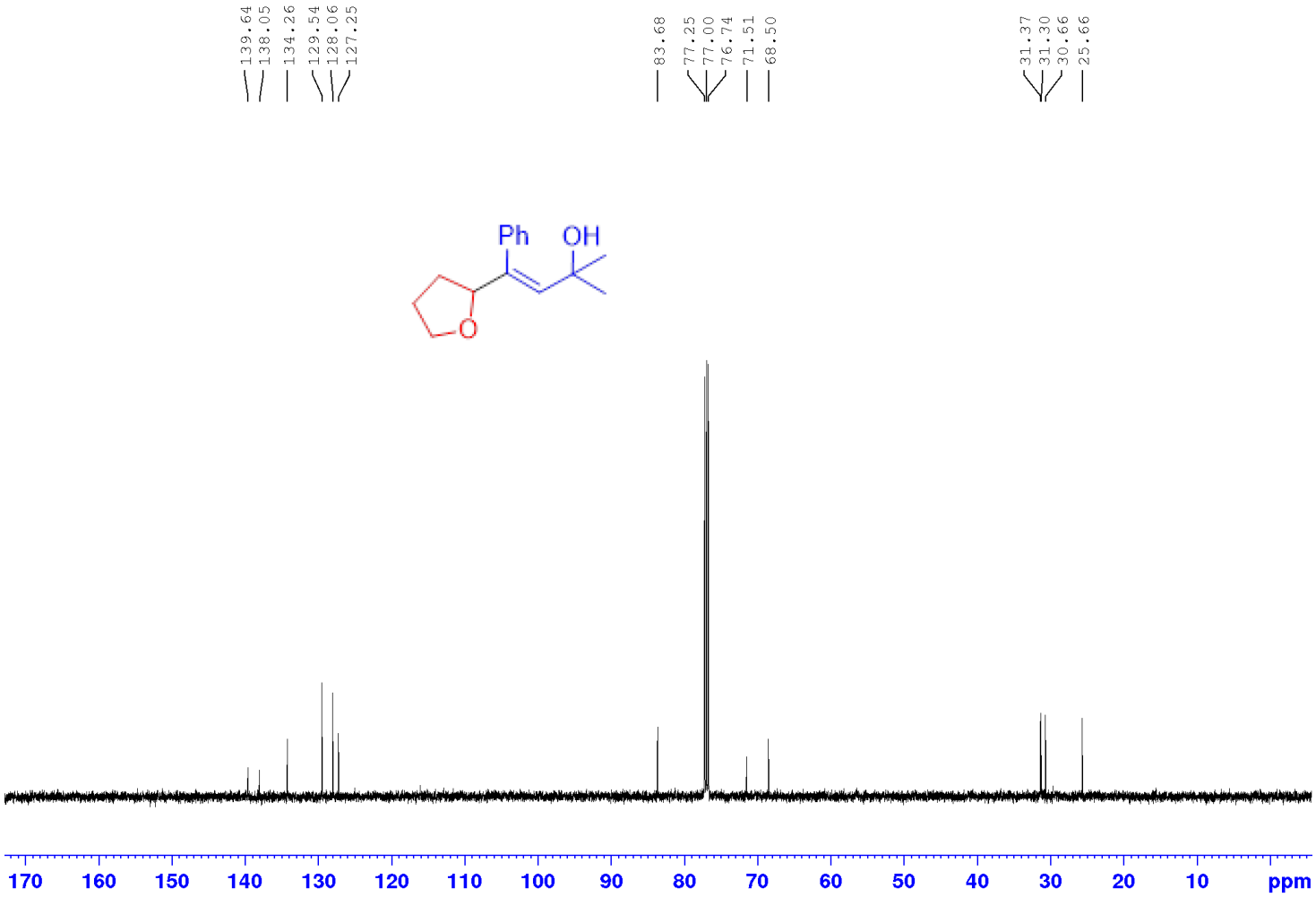
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76.74
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31.37
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30.66
25.66
Ph
OH
O
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140
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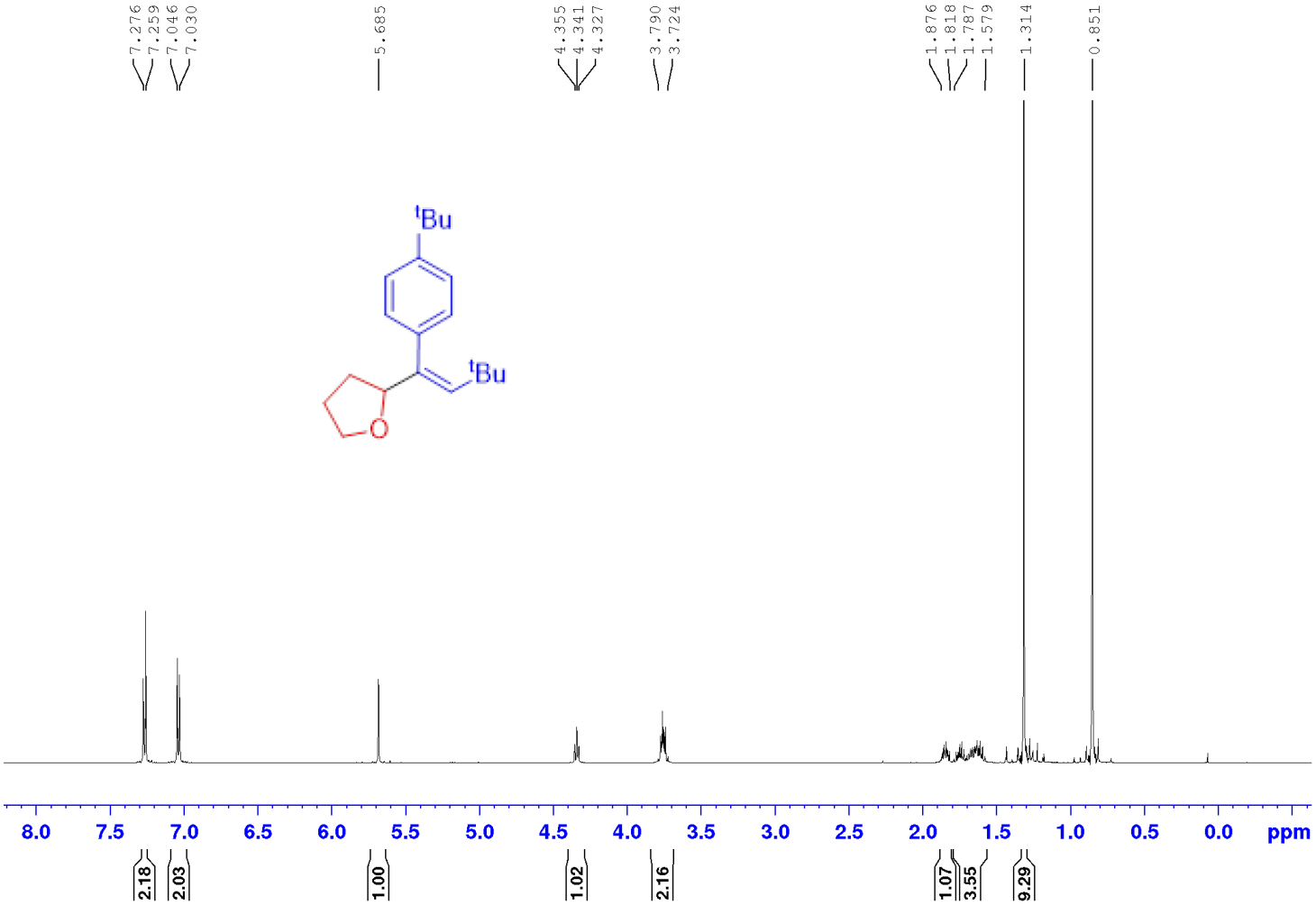
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tBu
O
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4.0
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3.0
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2.0
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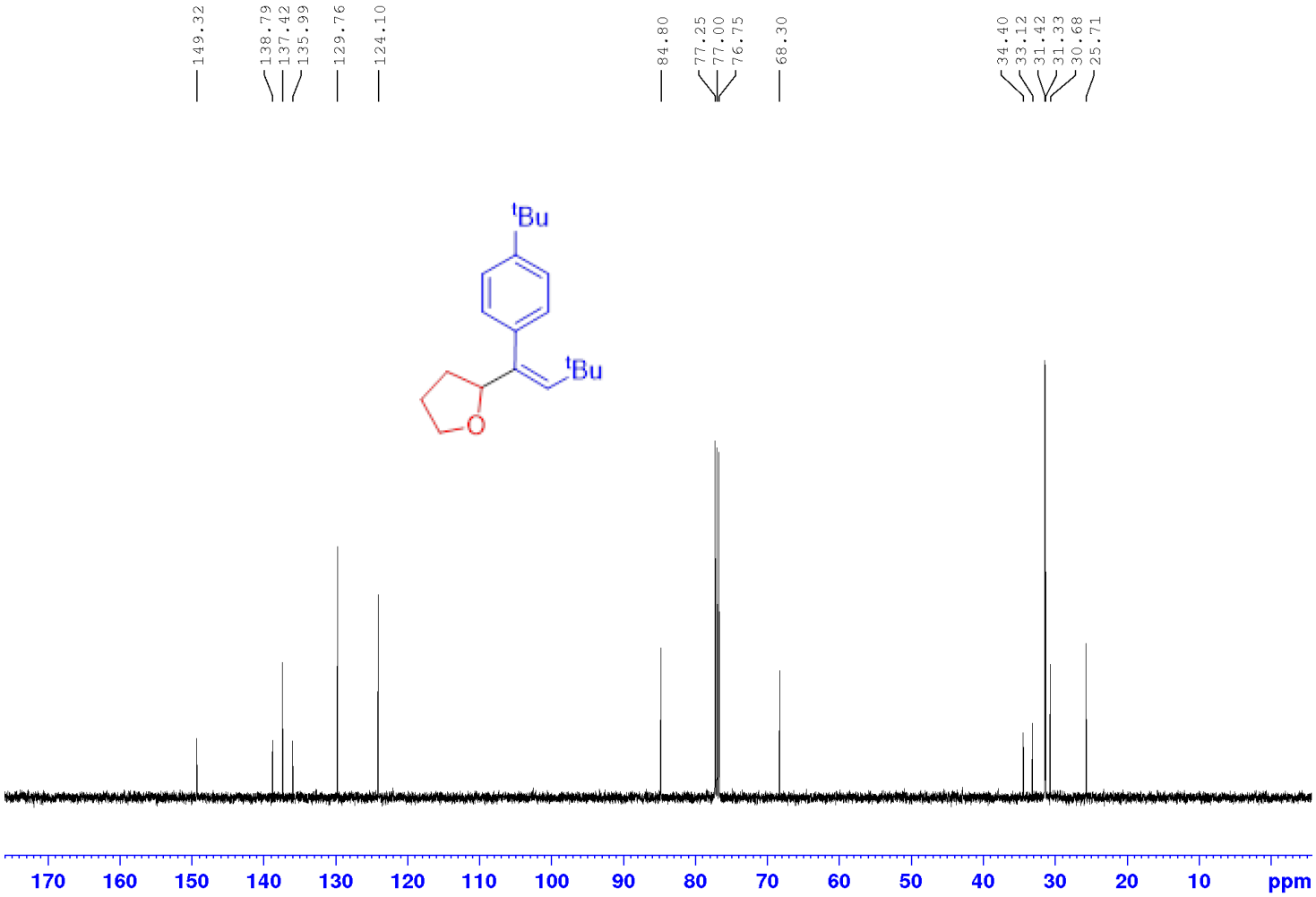
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33.12
31.42
31.33
30.68
25.71
tBu
tBu
O
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150
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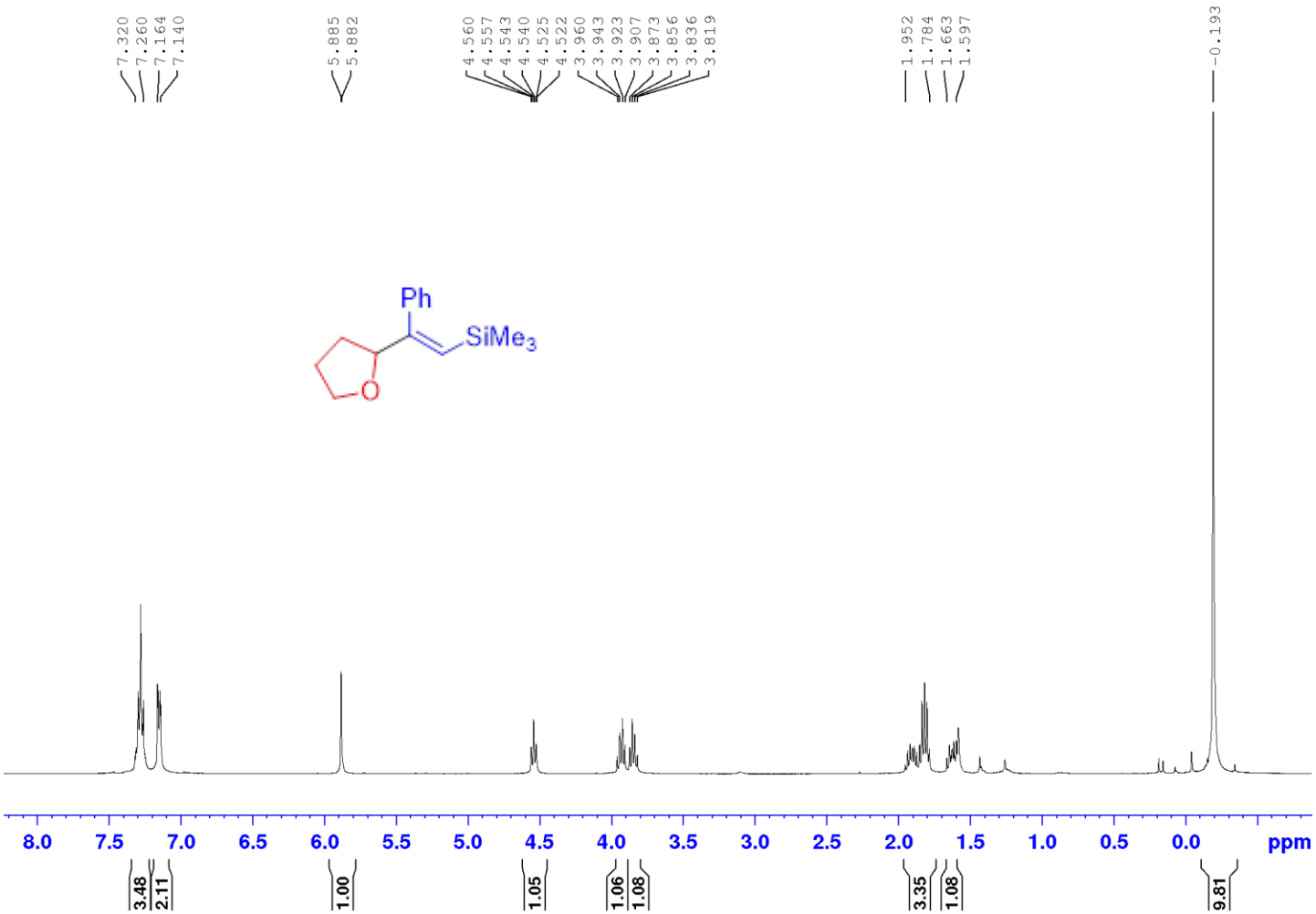
10
ppm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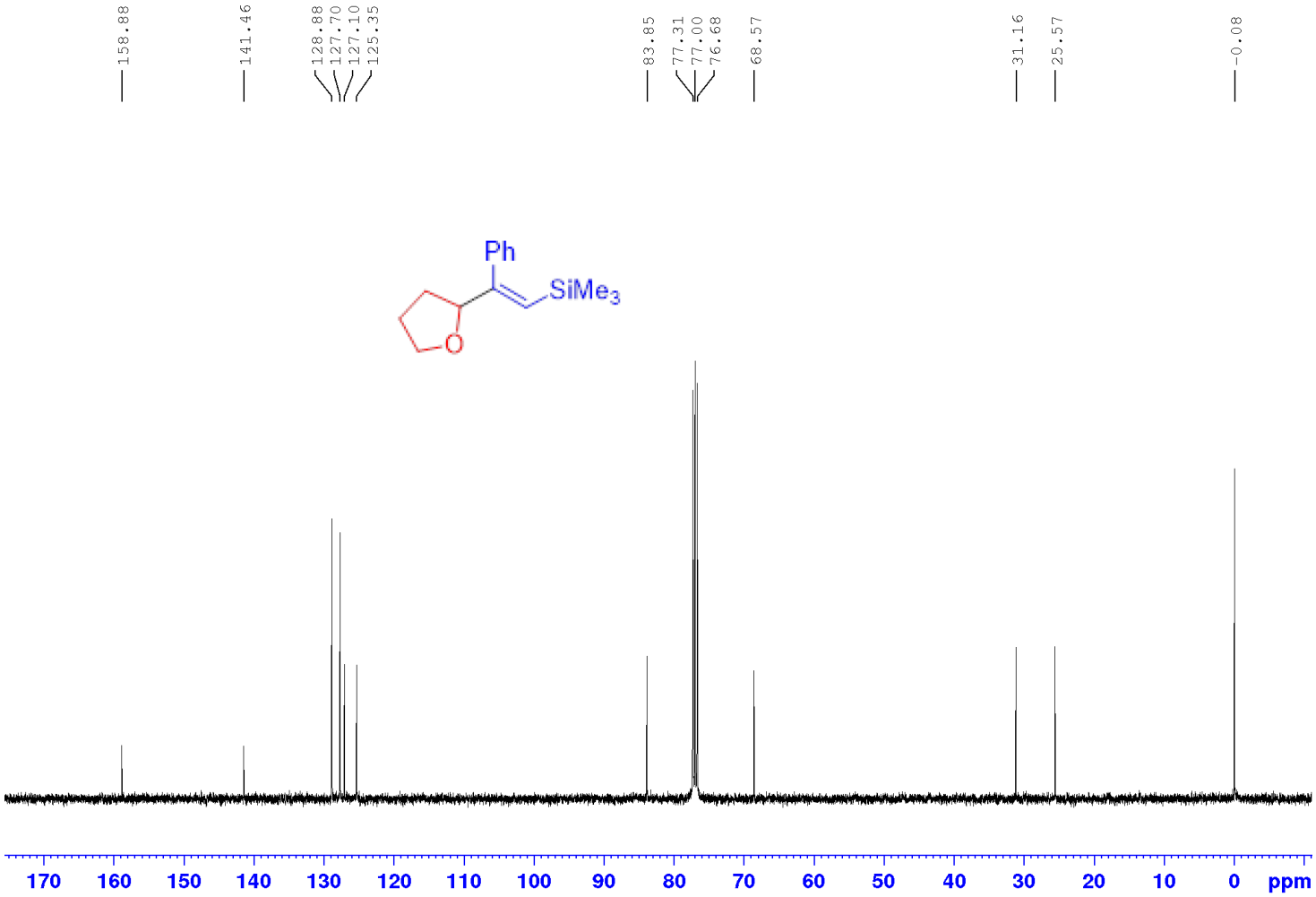
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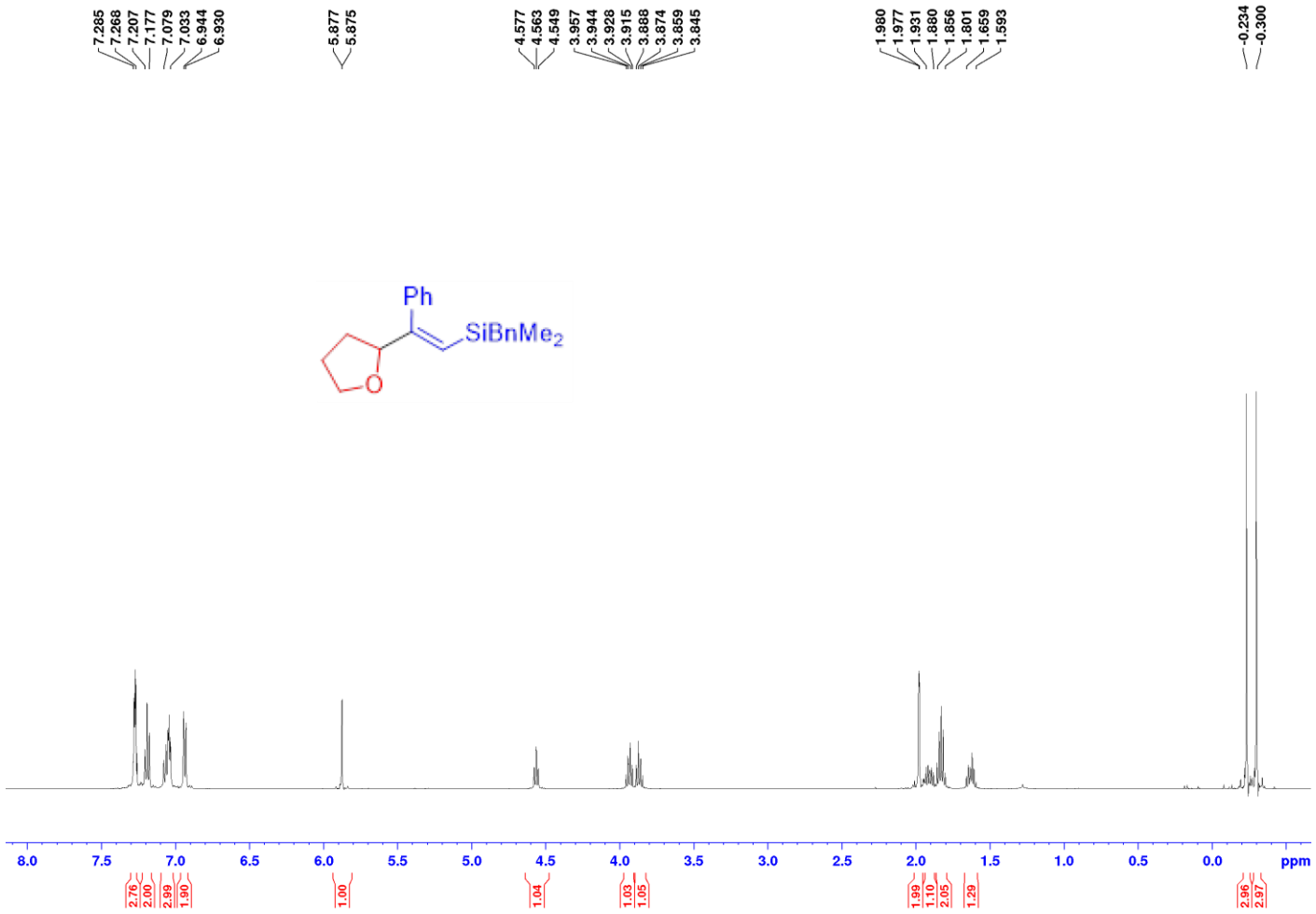
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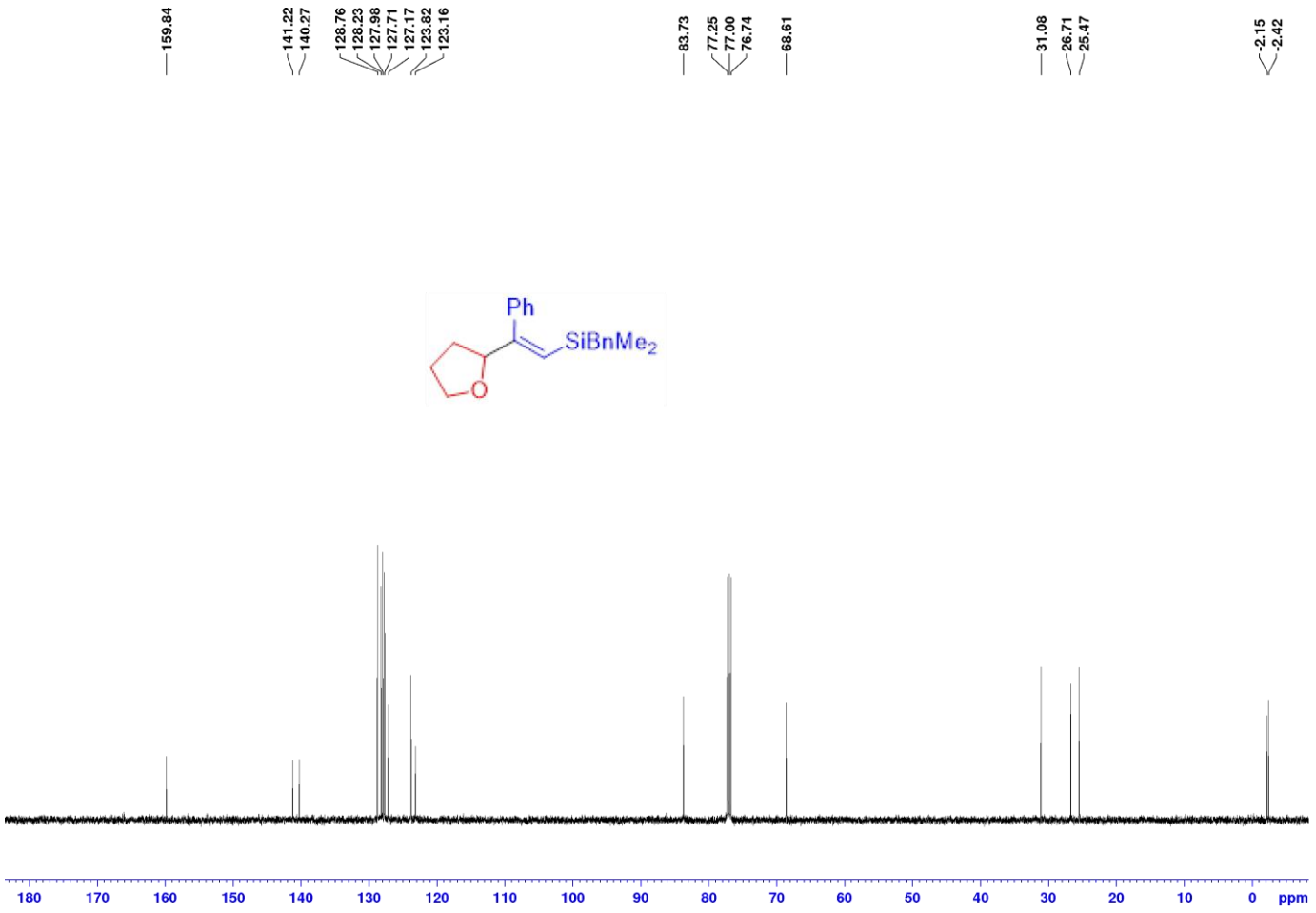
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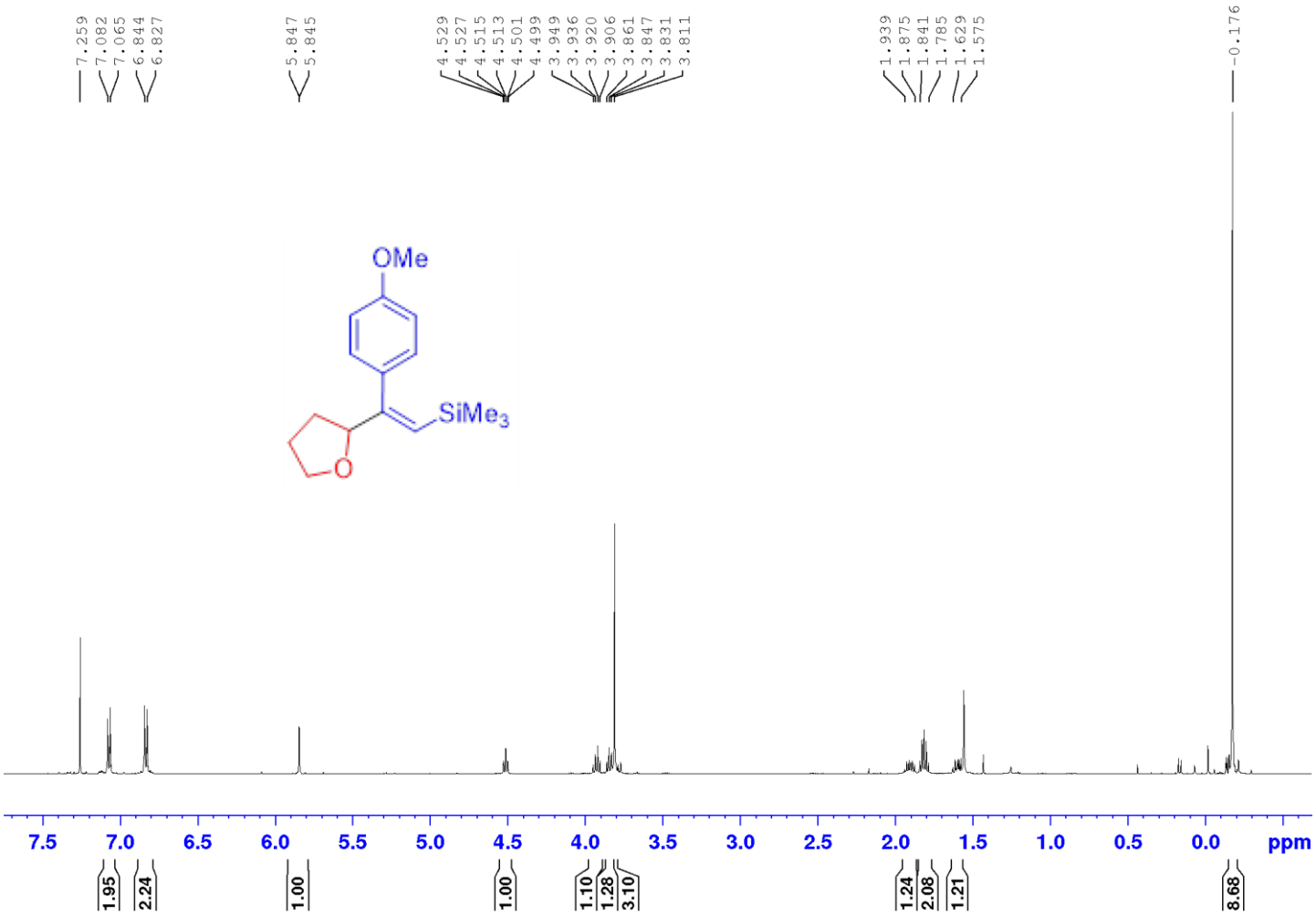
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4.499
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3.811
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OMe
SiMe3
O
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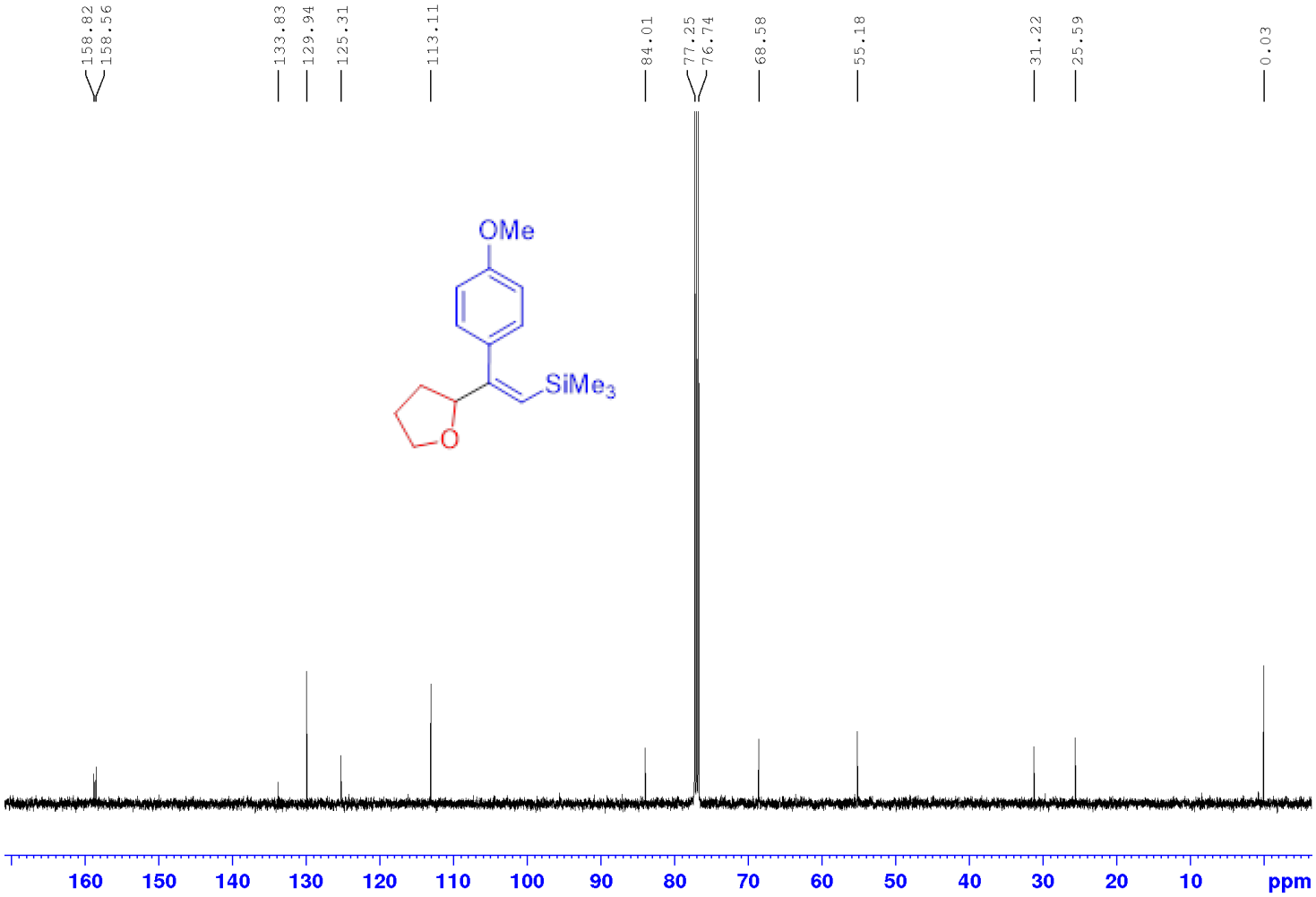
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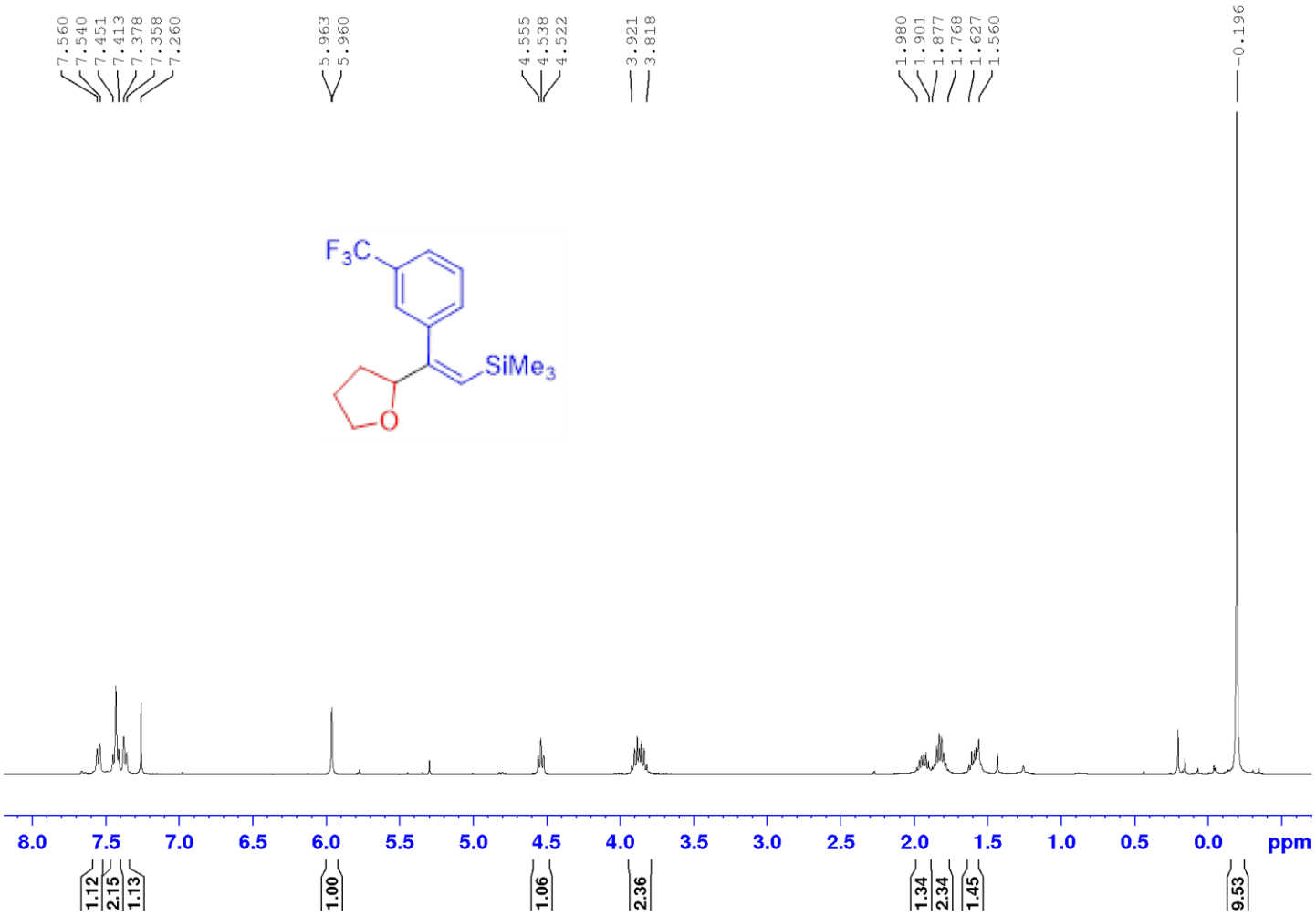
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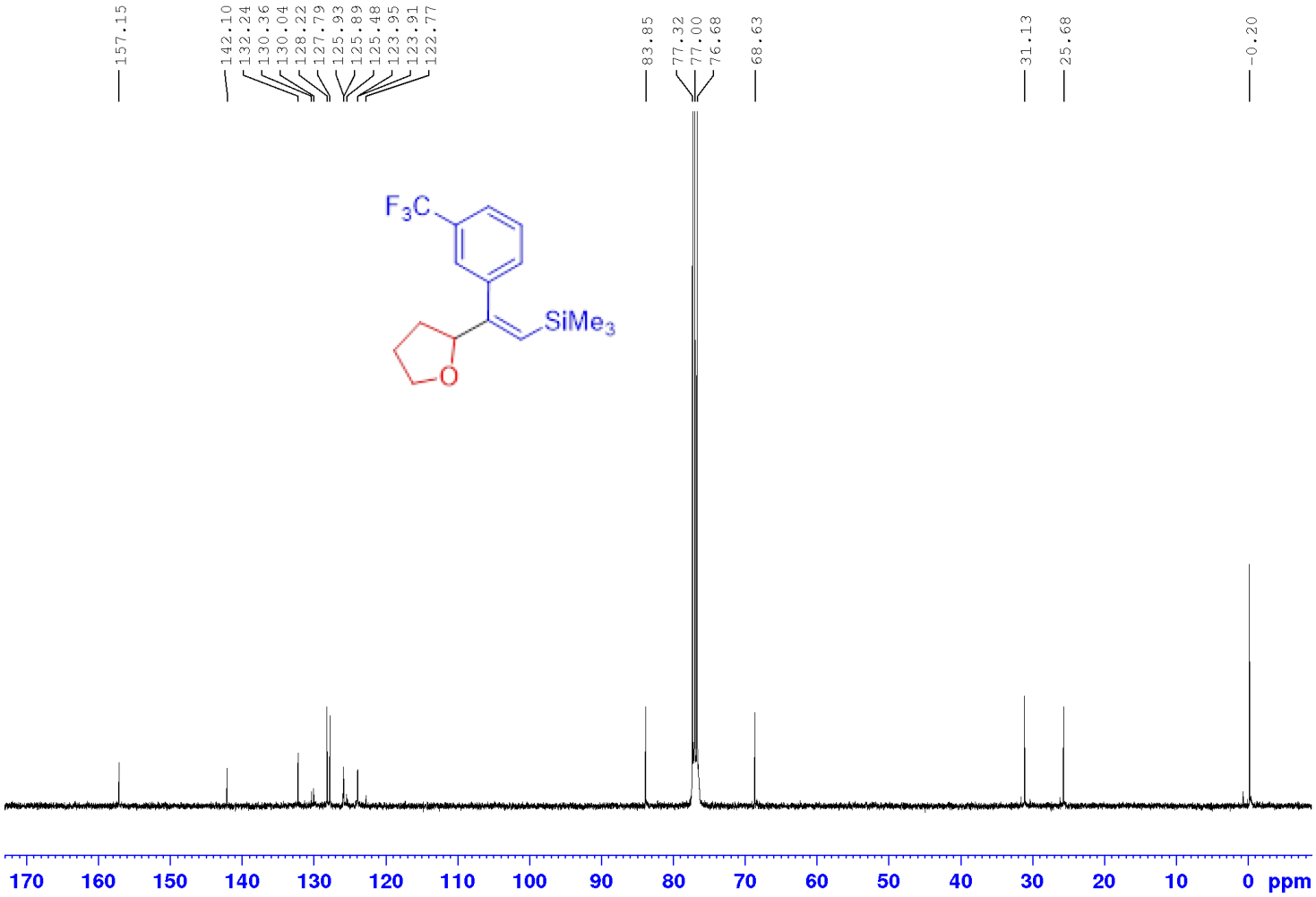
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122.77
83.85
77.32
77.00
76.68
68.63
31.13
25.68
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F3C
SiMe3
O
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140
130
120
110
100
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60
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20
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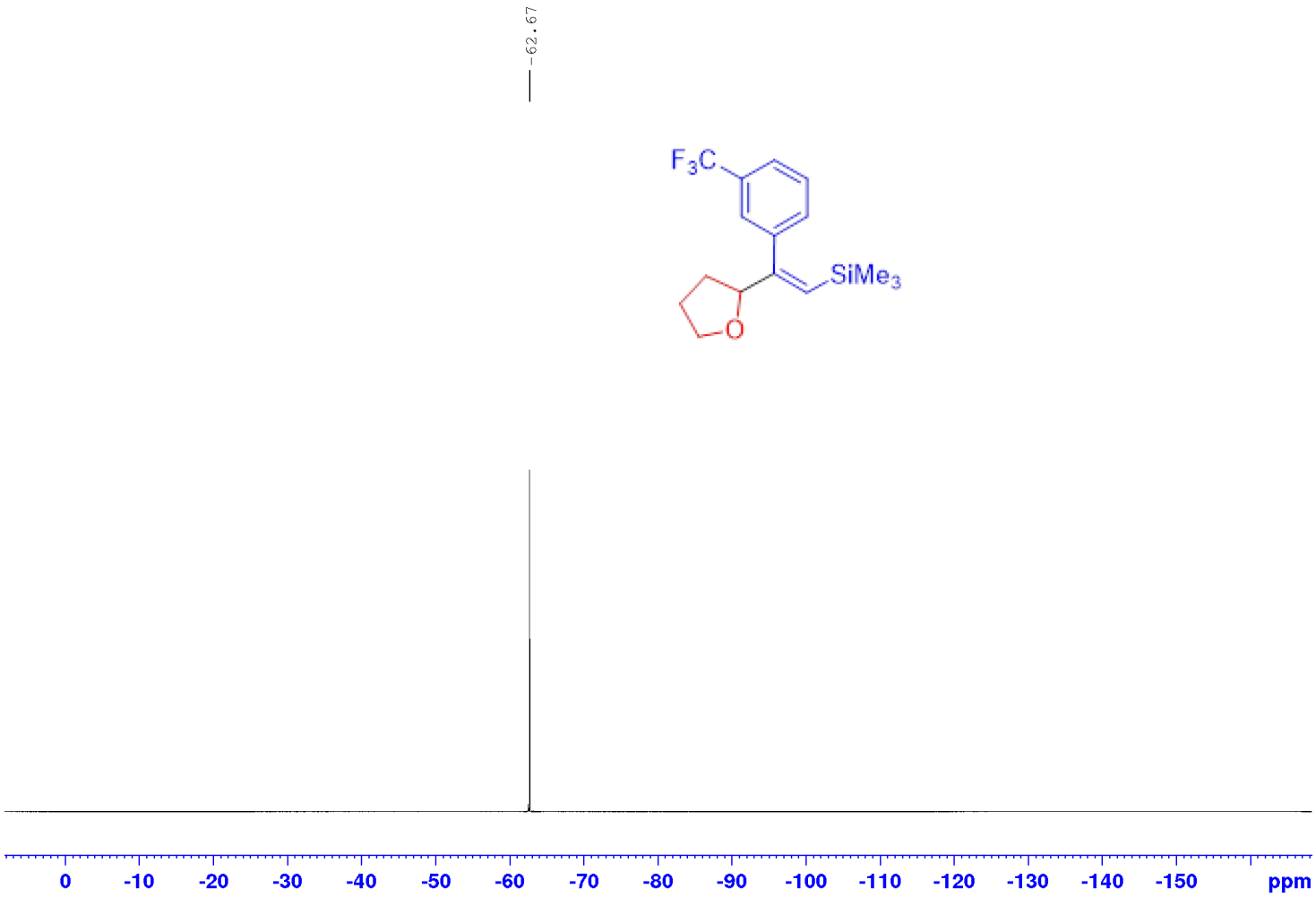
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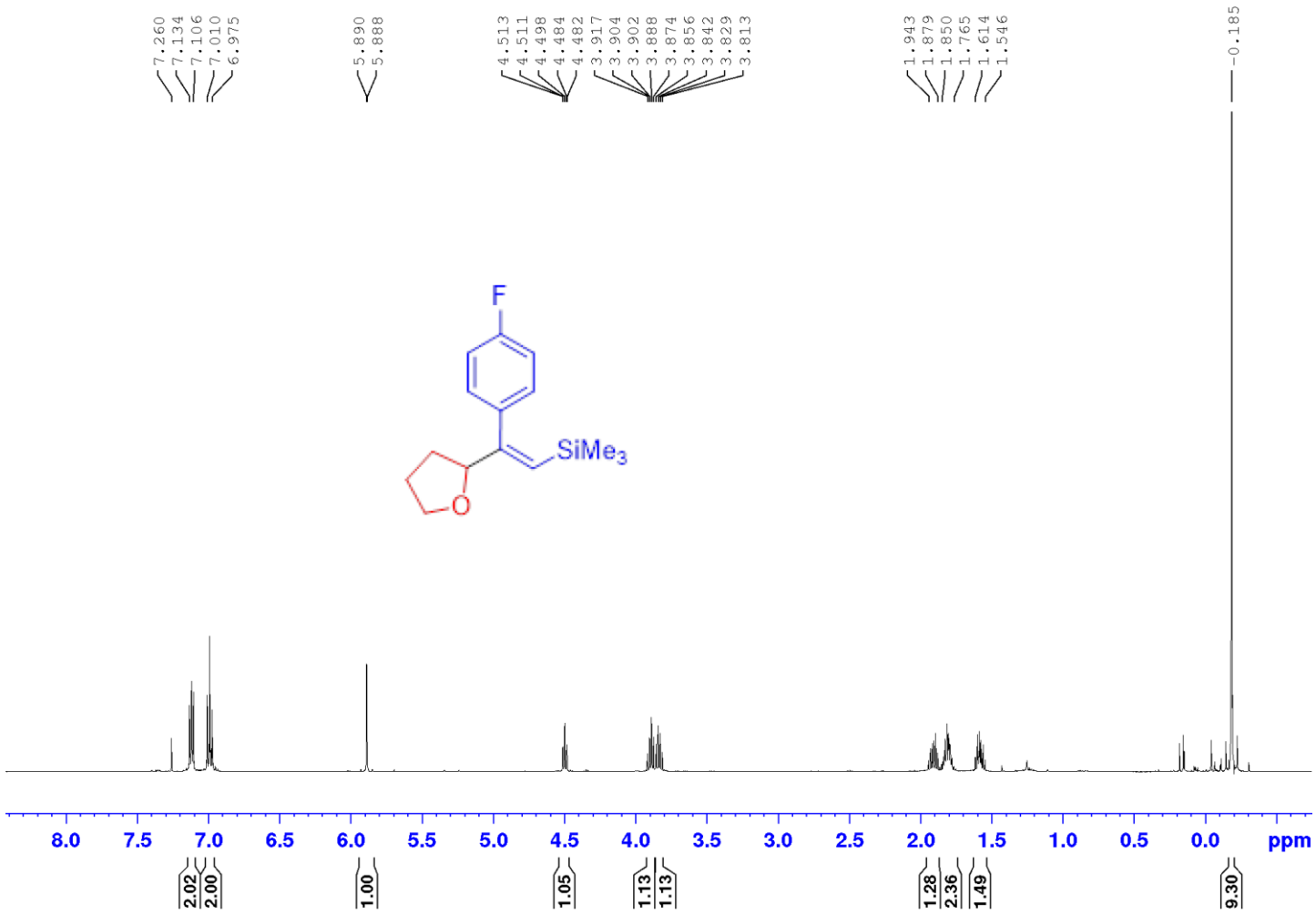
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3.904
3.902
3.888
3.874
3.856
3.842
3.829
3.813
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1.879
1.850
1.765
1.614
1.546
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F
SiMe3
O
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5.0
4.5
4.0
3.5
3.0
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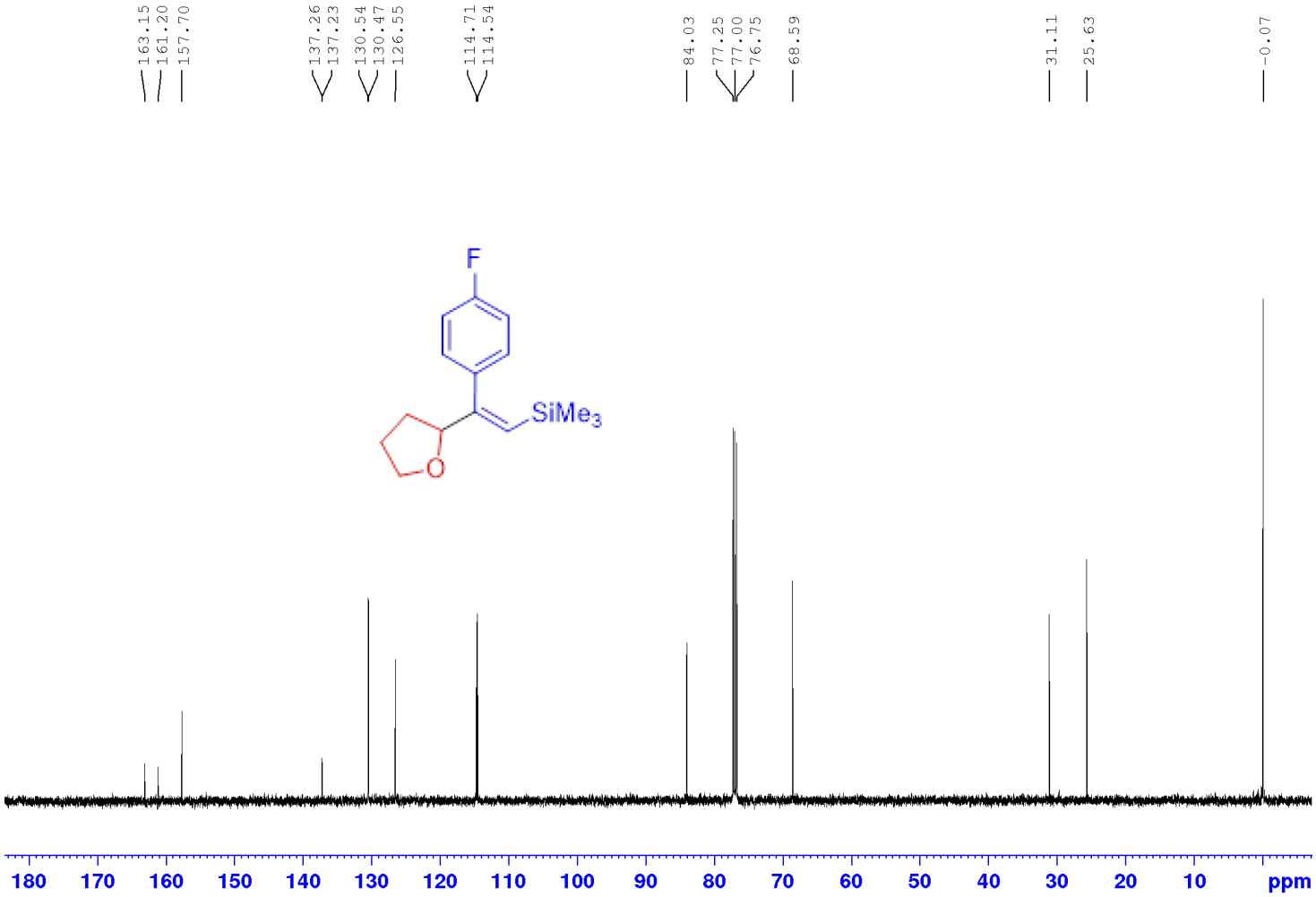
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77.00
76.75
68.59
31.11
25.63
-0.07
F
SiMe3
O
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100
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20
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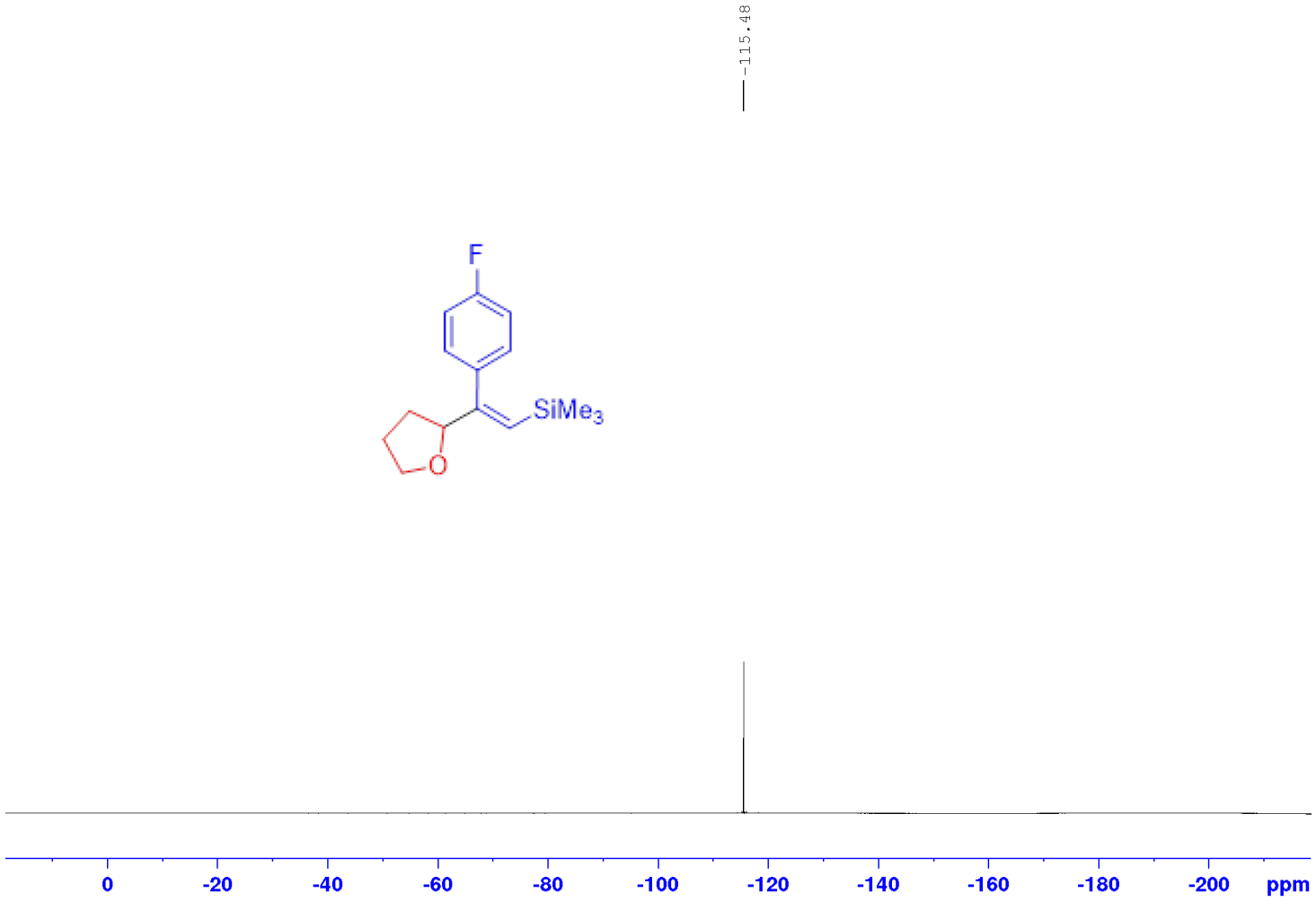
ppm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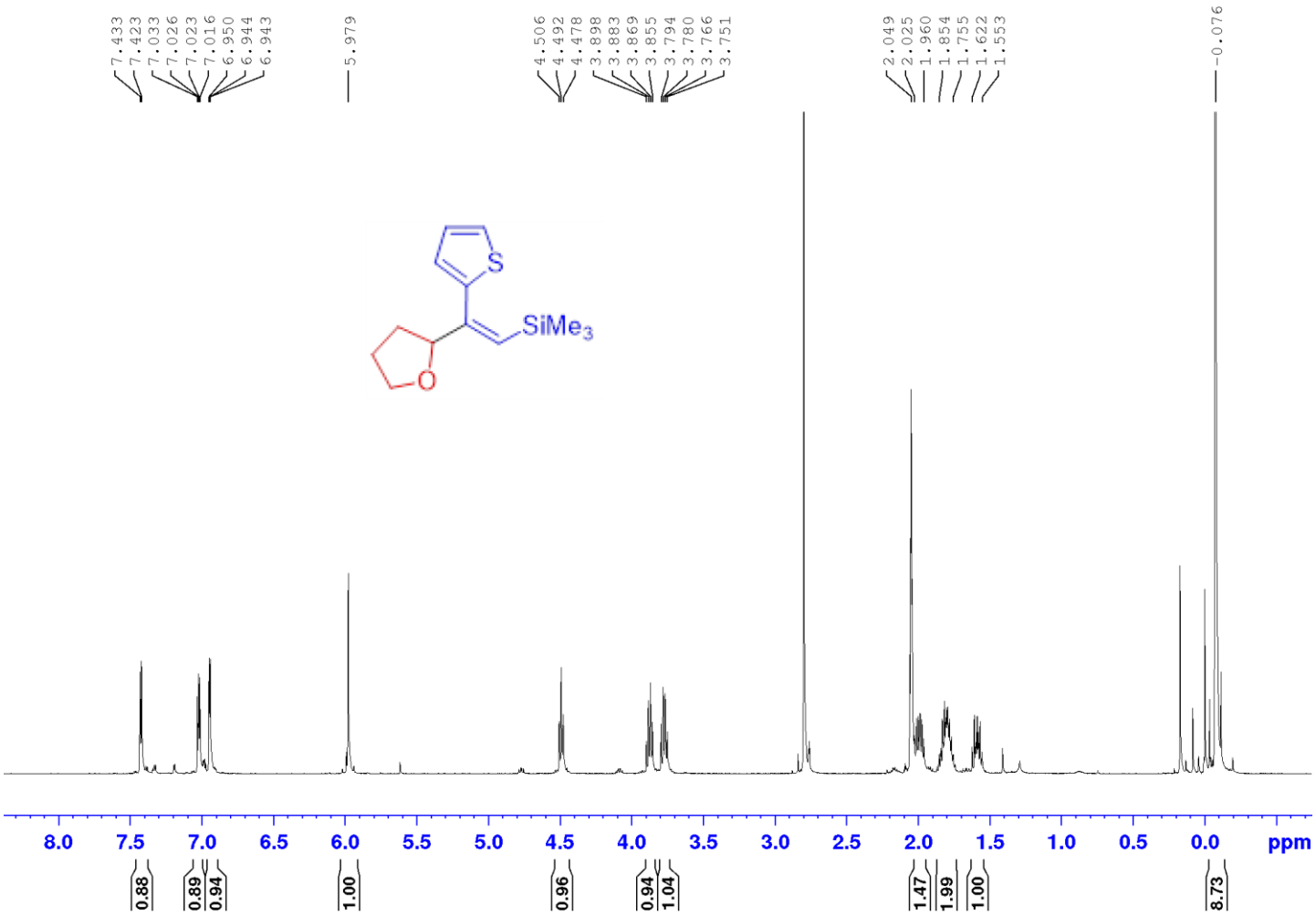
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4.478
3.898
3.883
3.869
3.855
3.794
3.780
3.766
3.751
2.049
2.025
1.960
1.854
1.755
1.622
1.553
-0.076
S
SiMe3
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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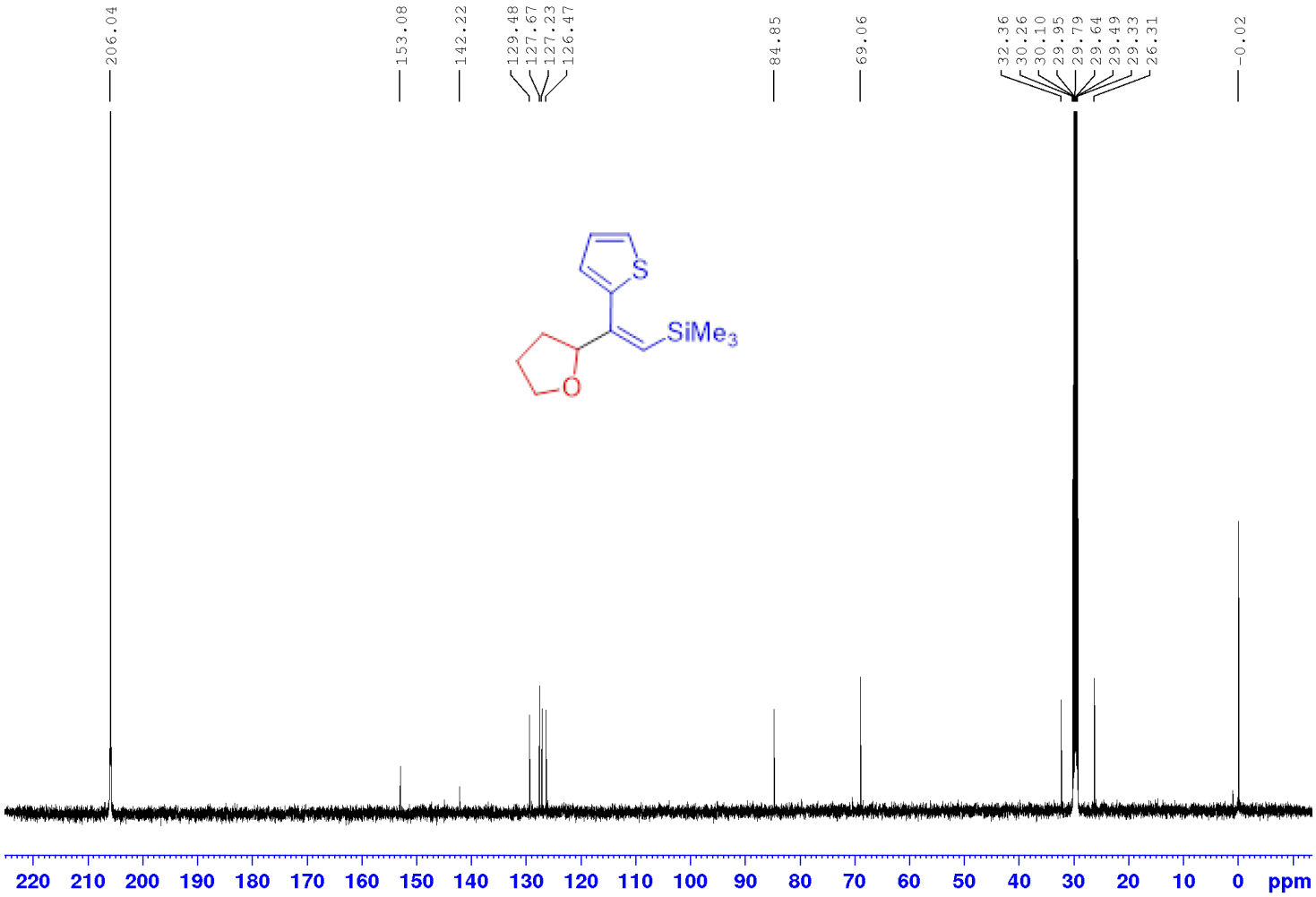
8.73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84.85
69.06
32.36
30.26
30.10
29.95
29.79
29.64
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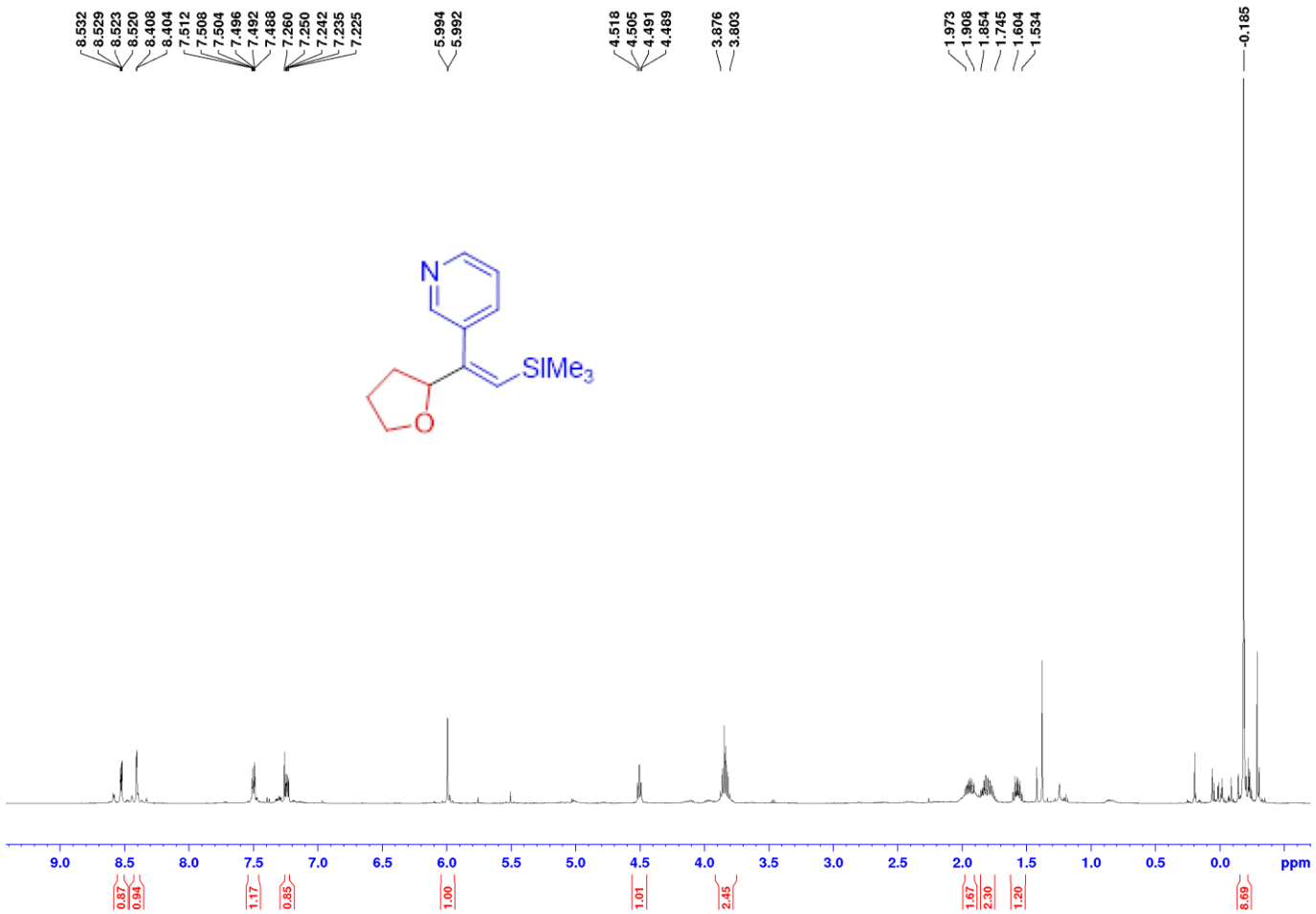
29.33
26.31
-0.02
S
SiMe3
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.508
7.504
7.496
7.492
7.488
7.260
7.250
7.242
7.235
7.225
5.994
5.992
4.518
4.505
4.491
4.489
3.876
3.803
1.973
1.908
1.854
1.745
1.604
1.534
-0.185
N
SiMe3
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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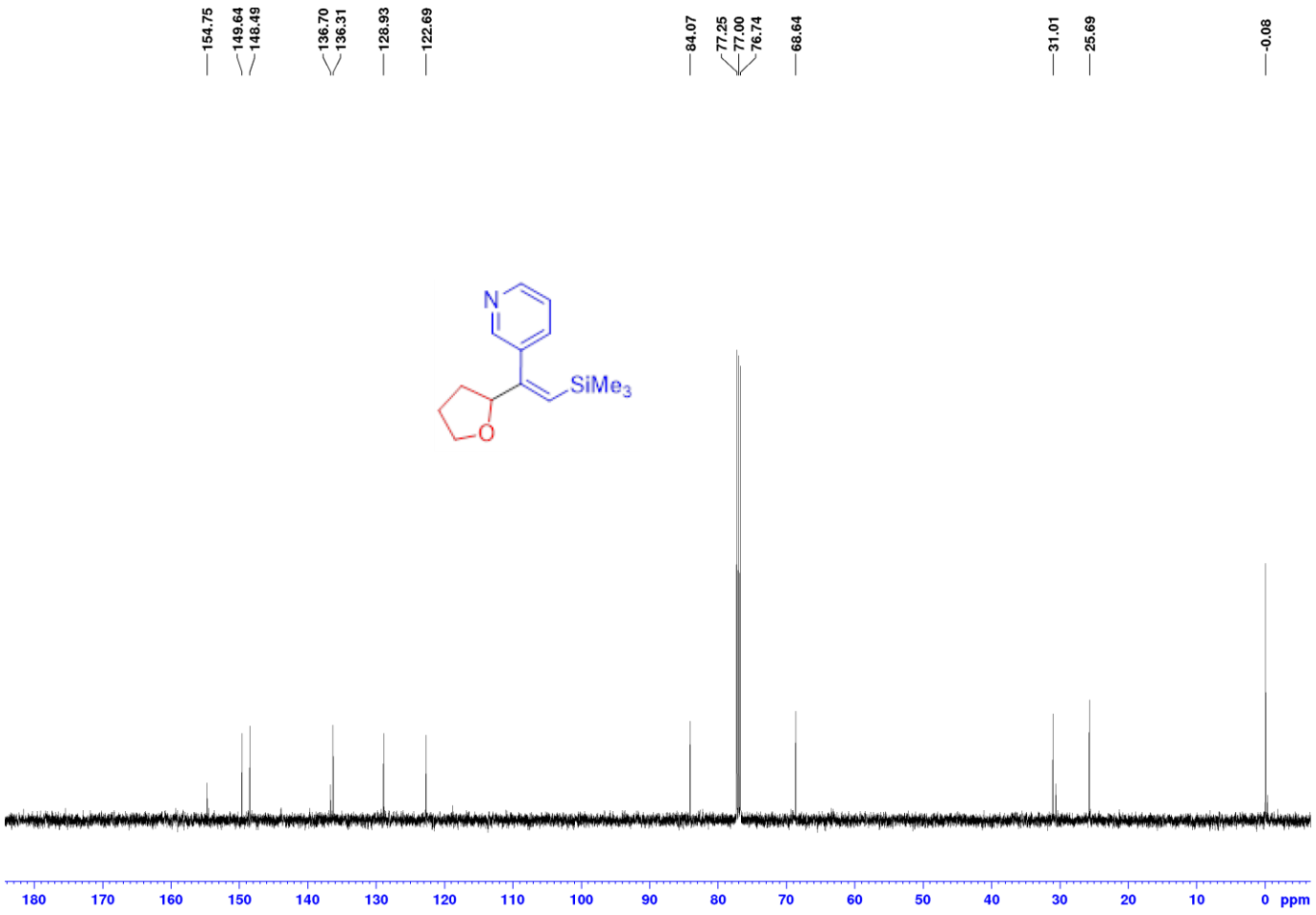
8.69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122.69
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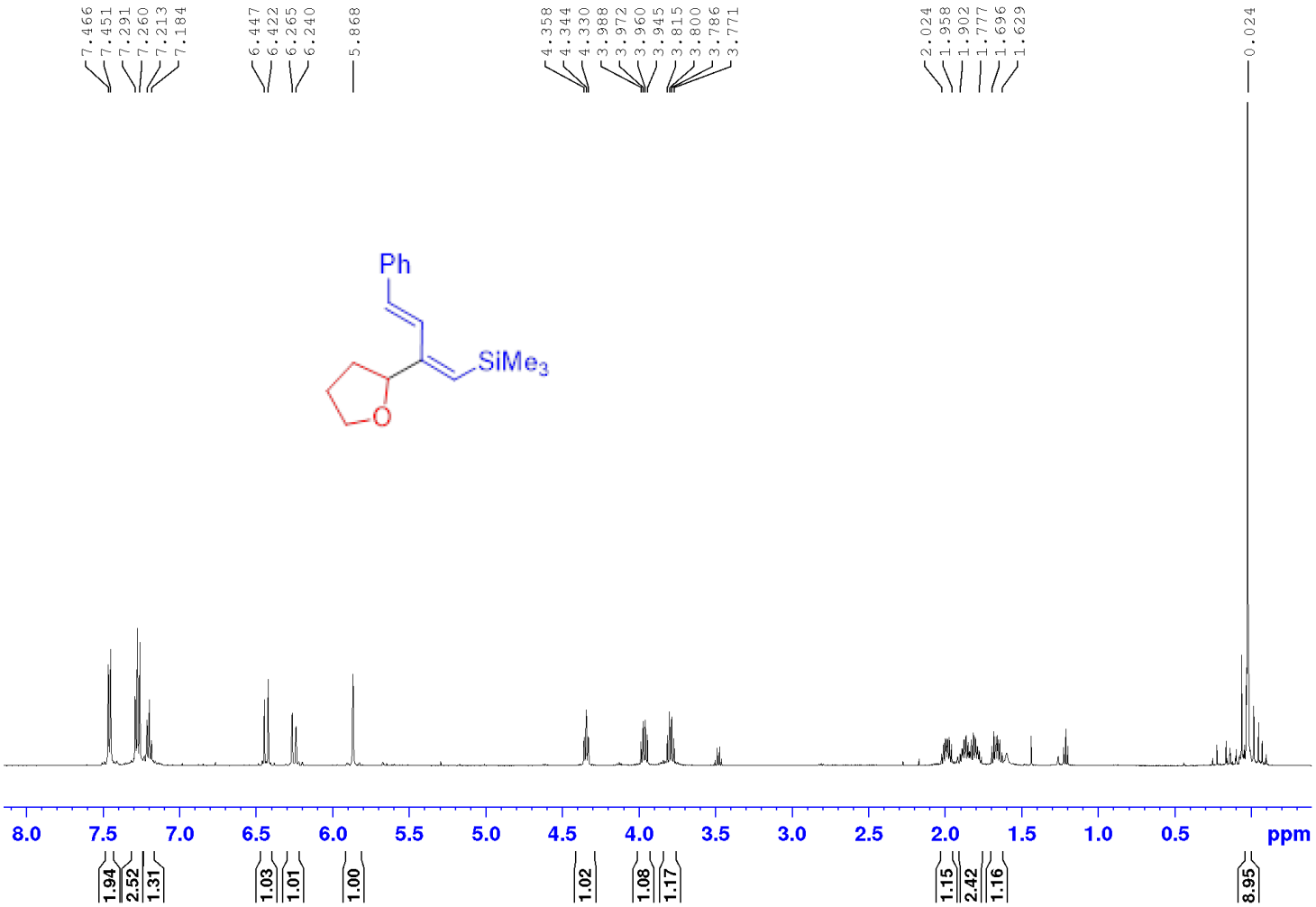
77.00
76.74
68.64
31.01
25.69
-0.08
N
SiMe3
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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4.344
4.330
3.988
3.972
3.960
3.945
3.815
3.800
3.786
3.771
2.024
1.958
1.902
1.777
1.696
1.629
0.024
Ph
SiMe3
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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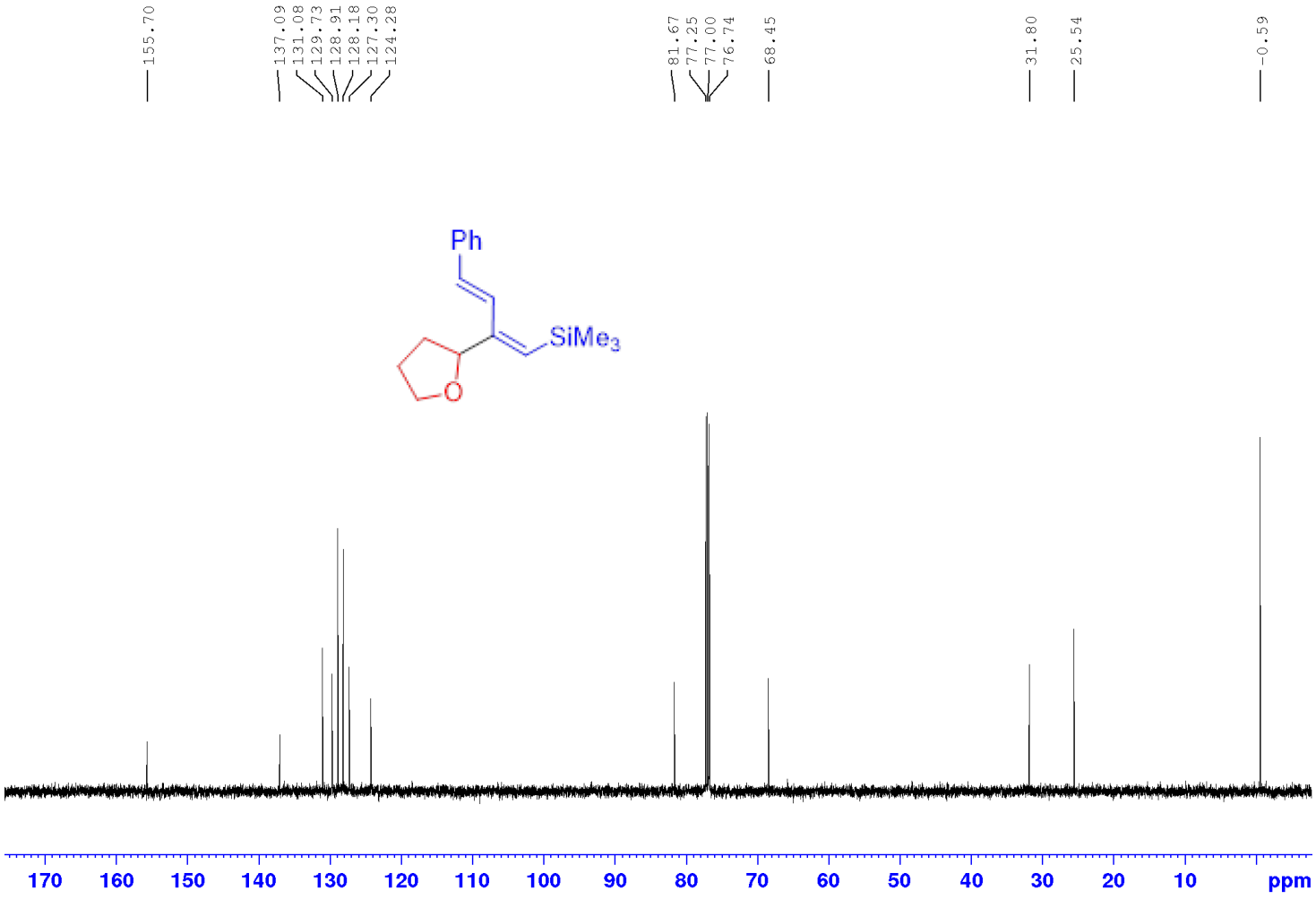
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124.28
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77.00
76.74
68.45
31.80
25.54
-0.59
Ph
SiMe3
O
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140
130
120
110
100
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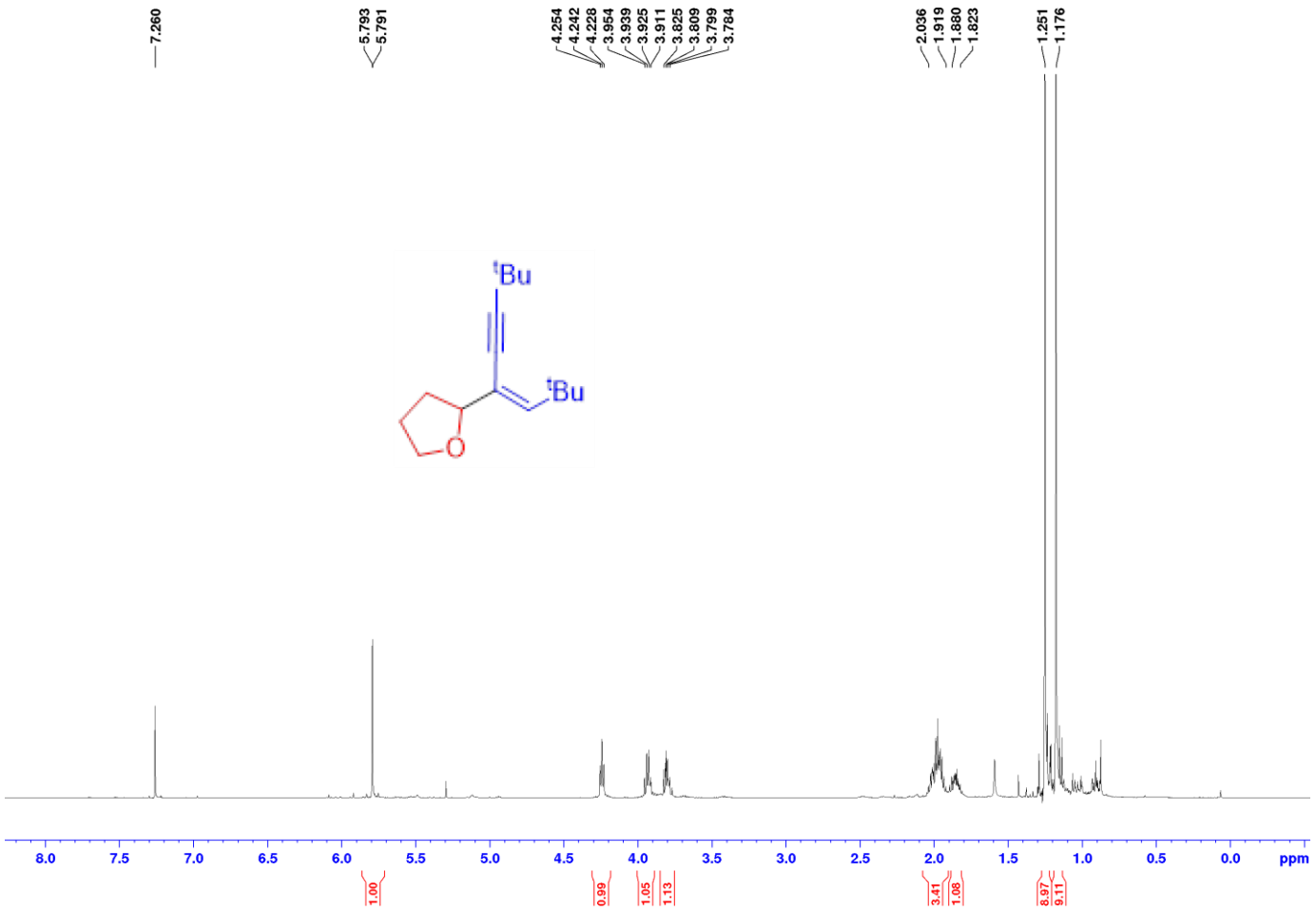
70
60
50
40
30
20
10
ppm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3.925
3.911
3.825
3.809
3.799
3.784
2.036
1.919
1.880
1.823
1.251
1.176
tBu
tBu
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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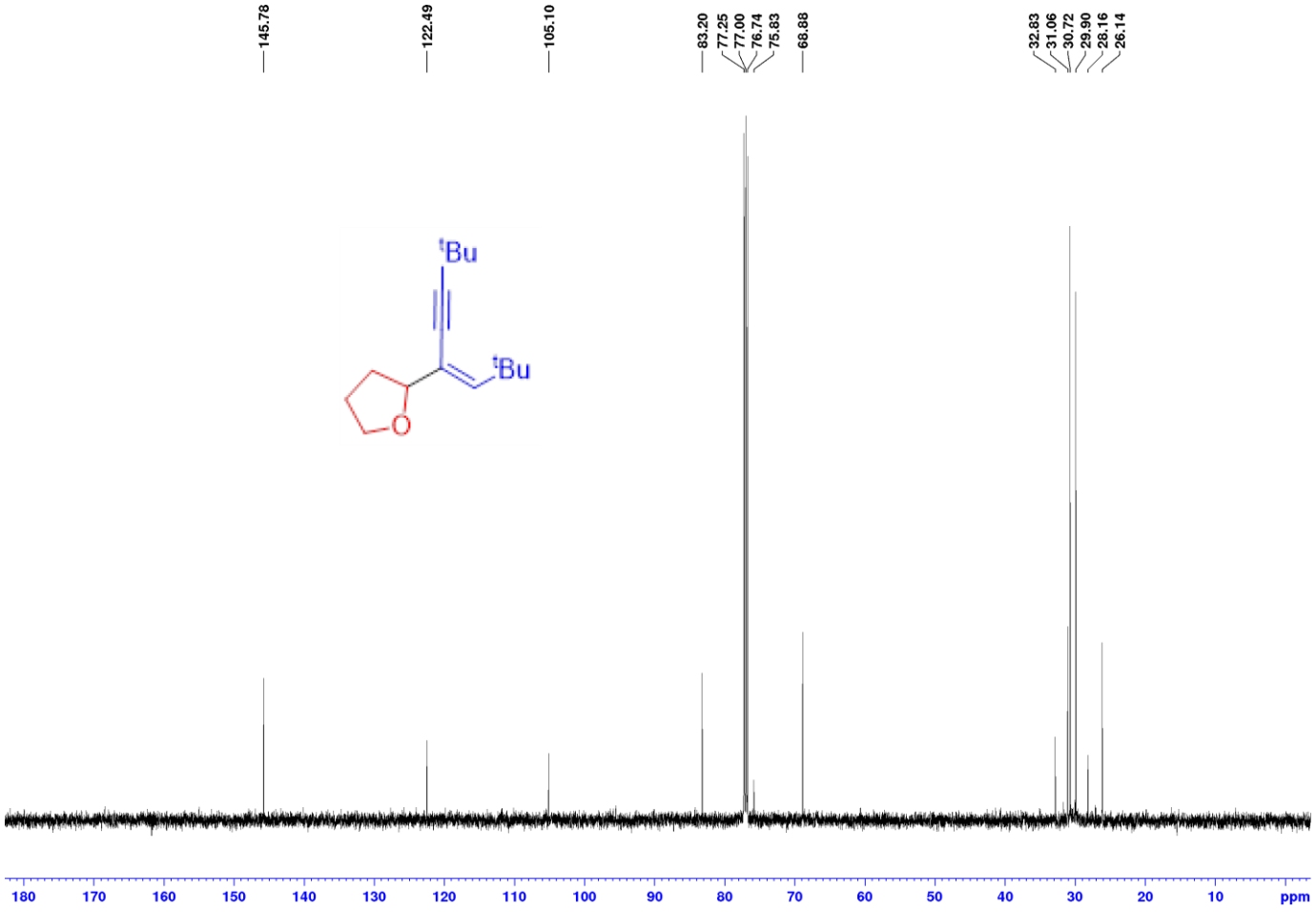
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32.83
31.06
30.72
29.90
28.16
26.14
tBu
tBu
O
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150
140
130
120
110
100
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70
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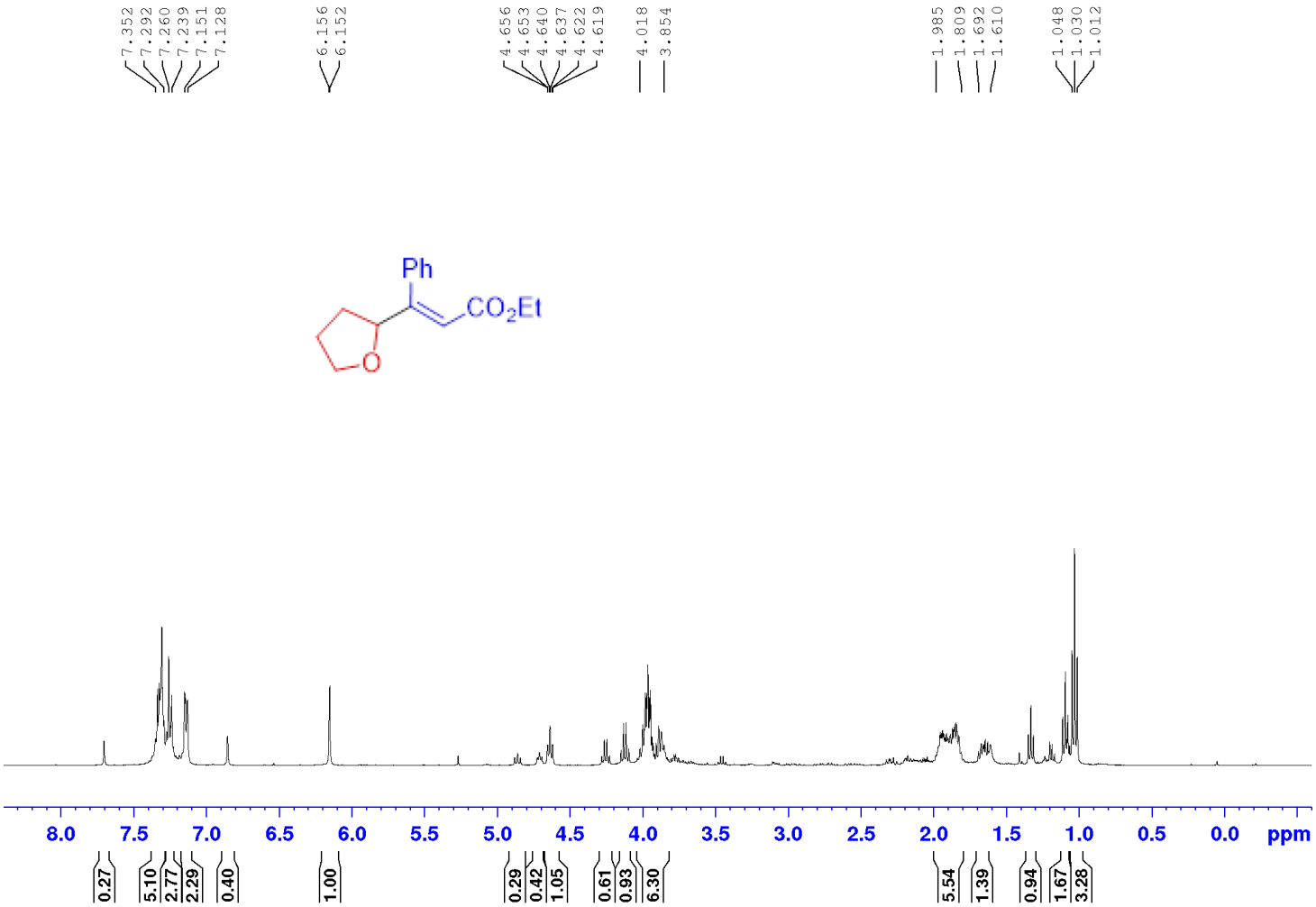
30
20
10
ppm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7.128
6.156
6.152
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4.653
4.640
4.637
4.622
4.619
4.018
3.854
1.985
1.809
1.692
1.610
1.048
1.030
1.012
Ph
CO2Et
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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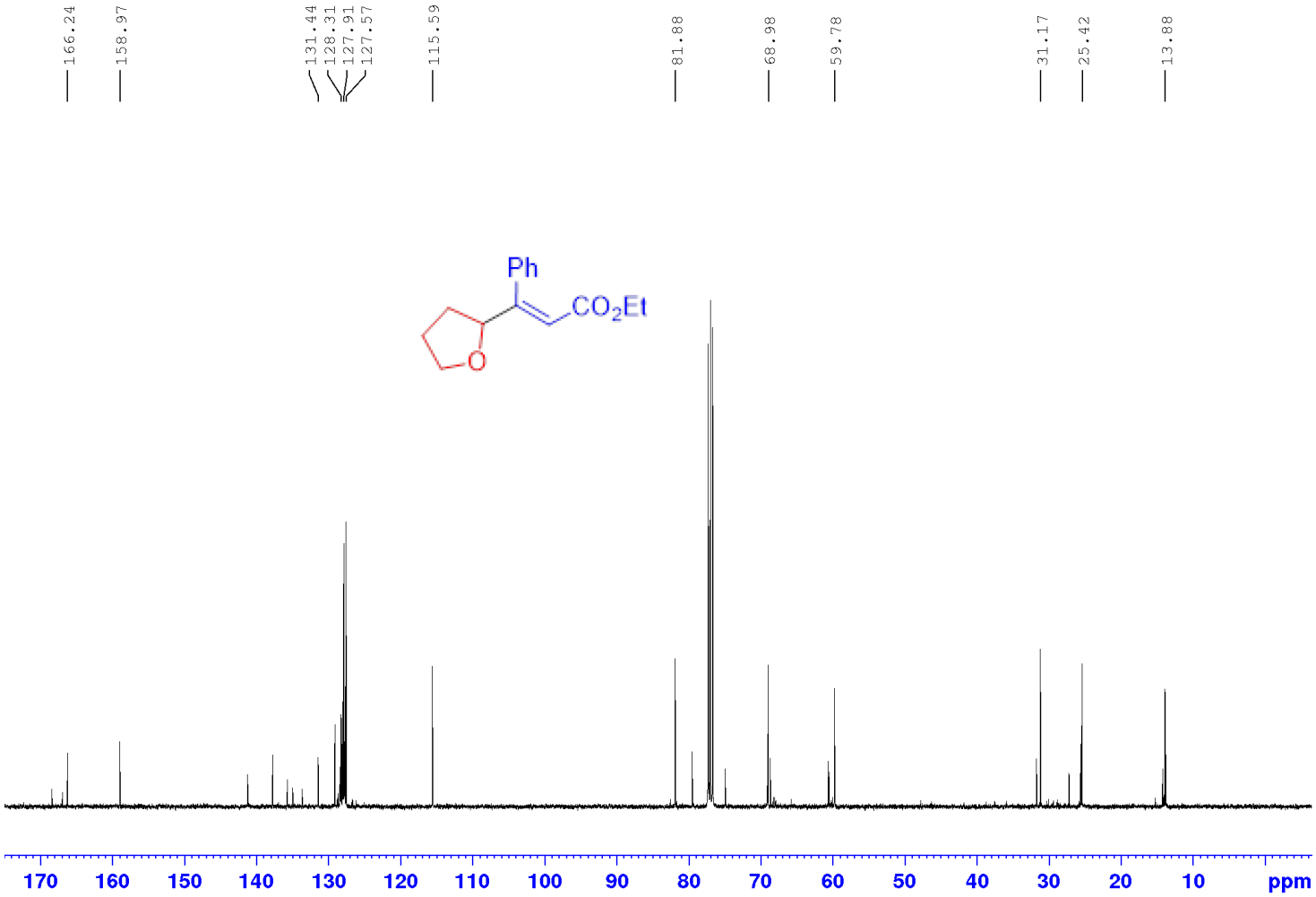
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59.78
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13.88
Ph
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O
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150
140
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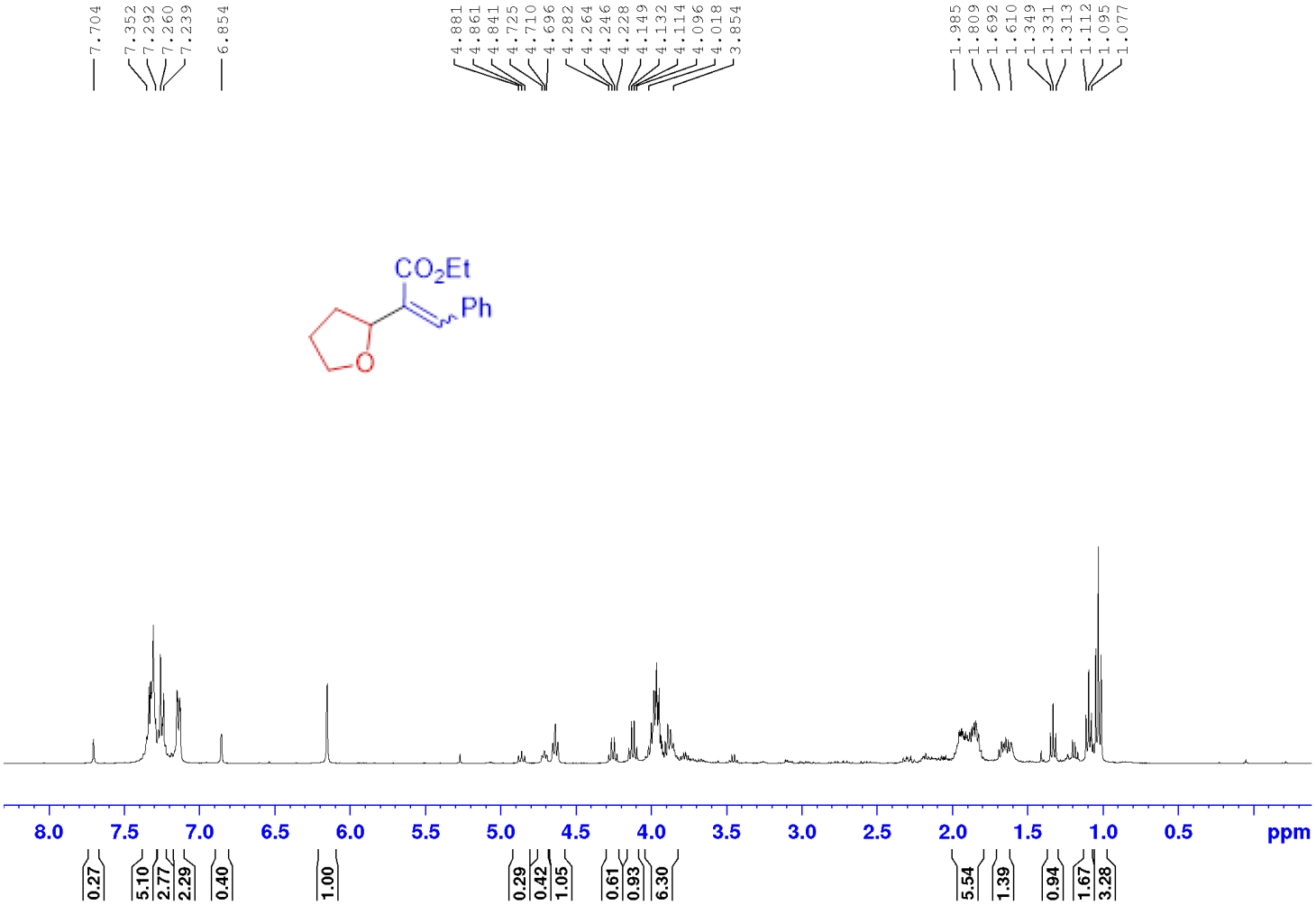
20
10
ppm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4.246
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4.018
3.854
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1.809
1.692
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1.112
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1.077
CO2Et
Ph
O
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7.0
6.5
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1.0
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ppm
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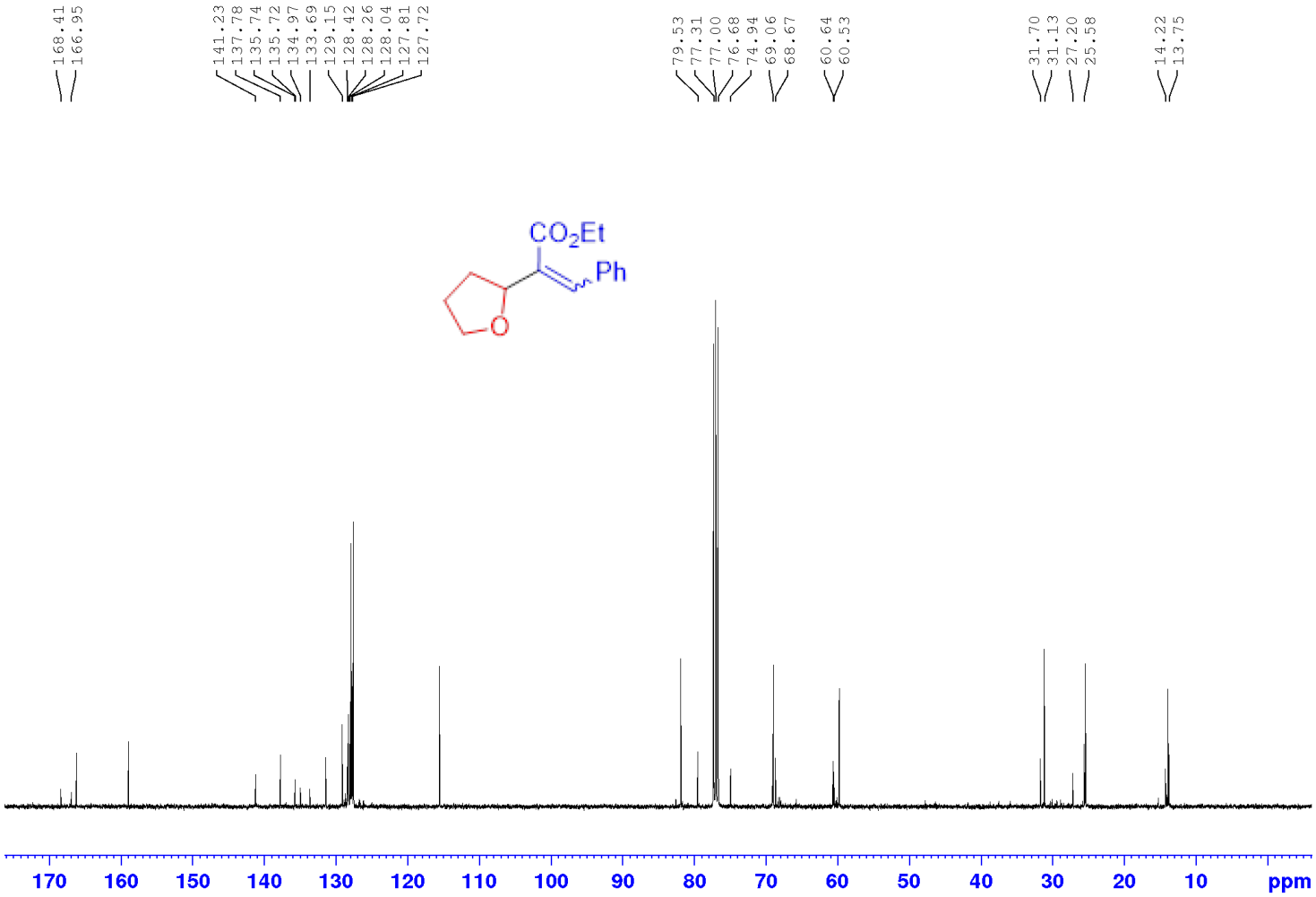
3.28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128.04
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127.72
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77.31
77.00
76.68
74.94
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60.53
31.70
31.13
27.20
25.58
14.22
13.75
CO2Et
Ph
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140
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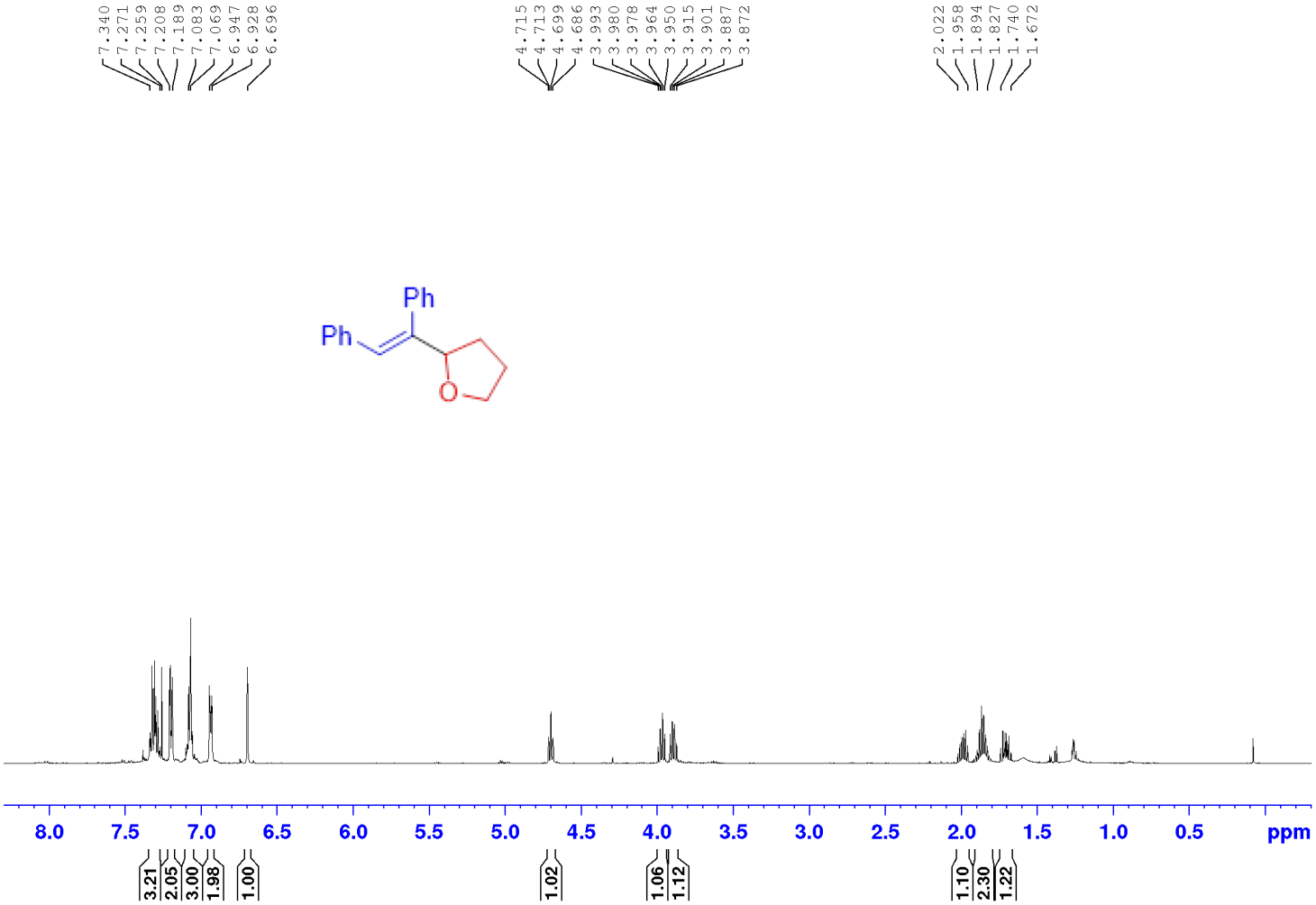
ppm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Ph
Ph
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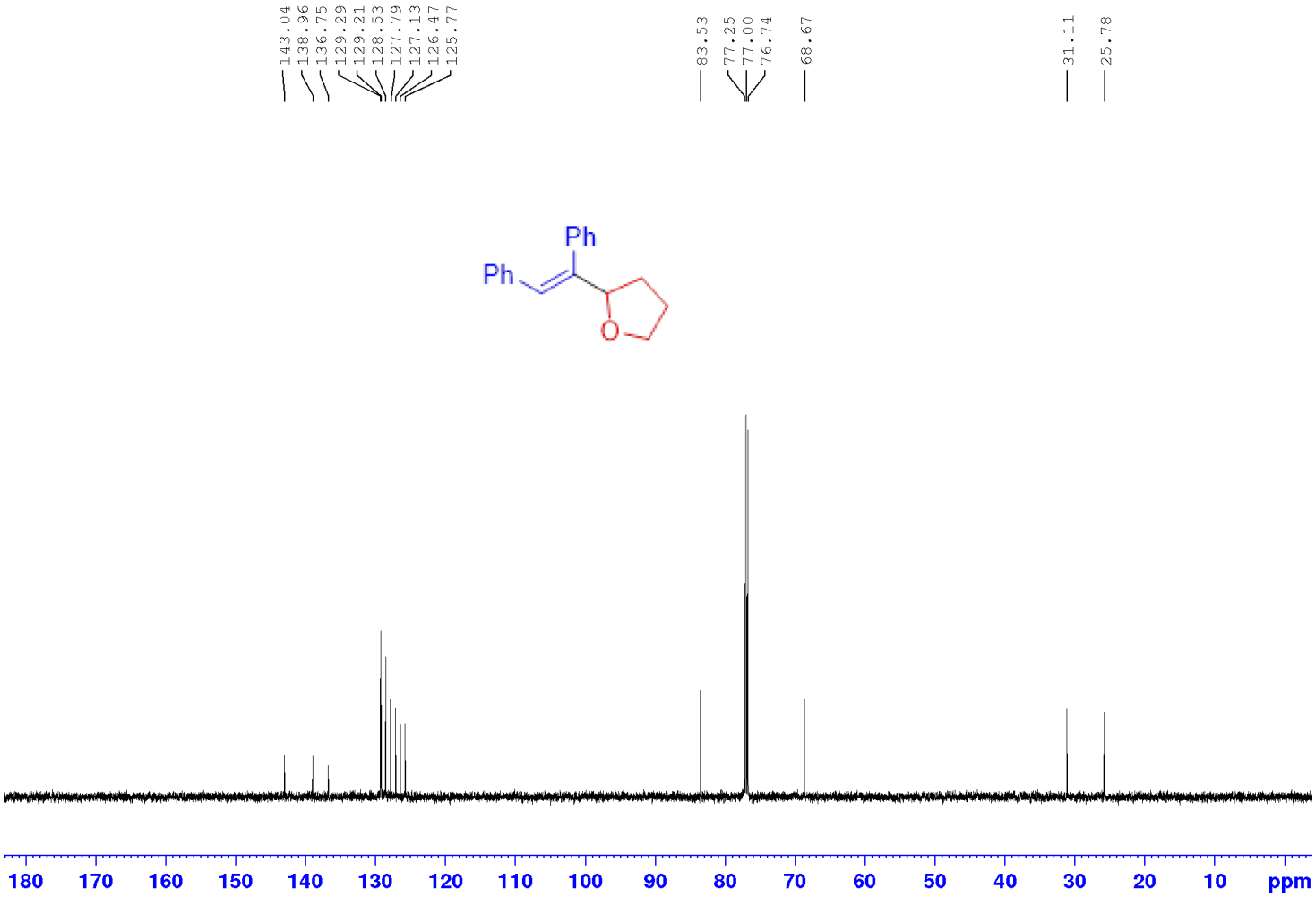
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25.78
Ph
Ph
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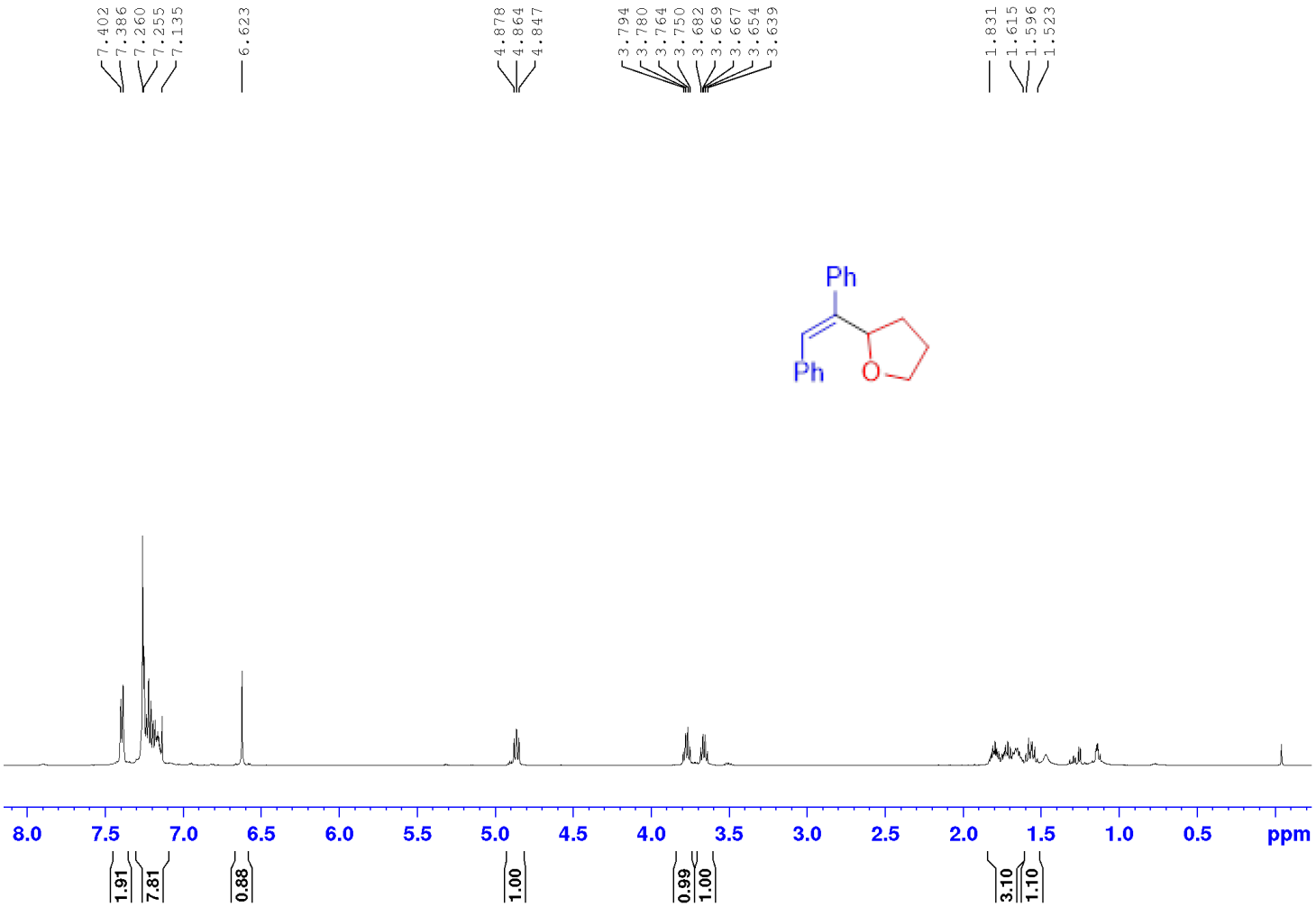
10
ppm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3.682
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3.667
3.654
3.639
1.831
1.615
1.596
1.523
Ph
Ph
O
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7.0
6.5
6.0
5.5
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4.5
4.0
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3.0
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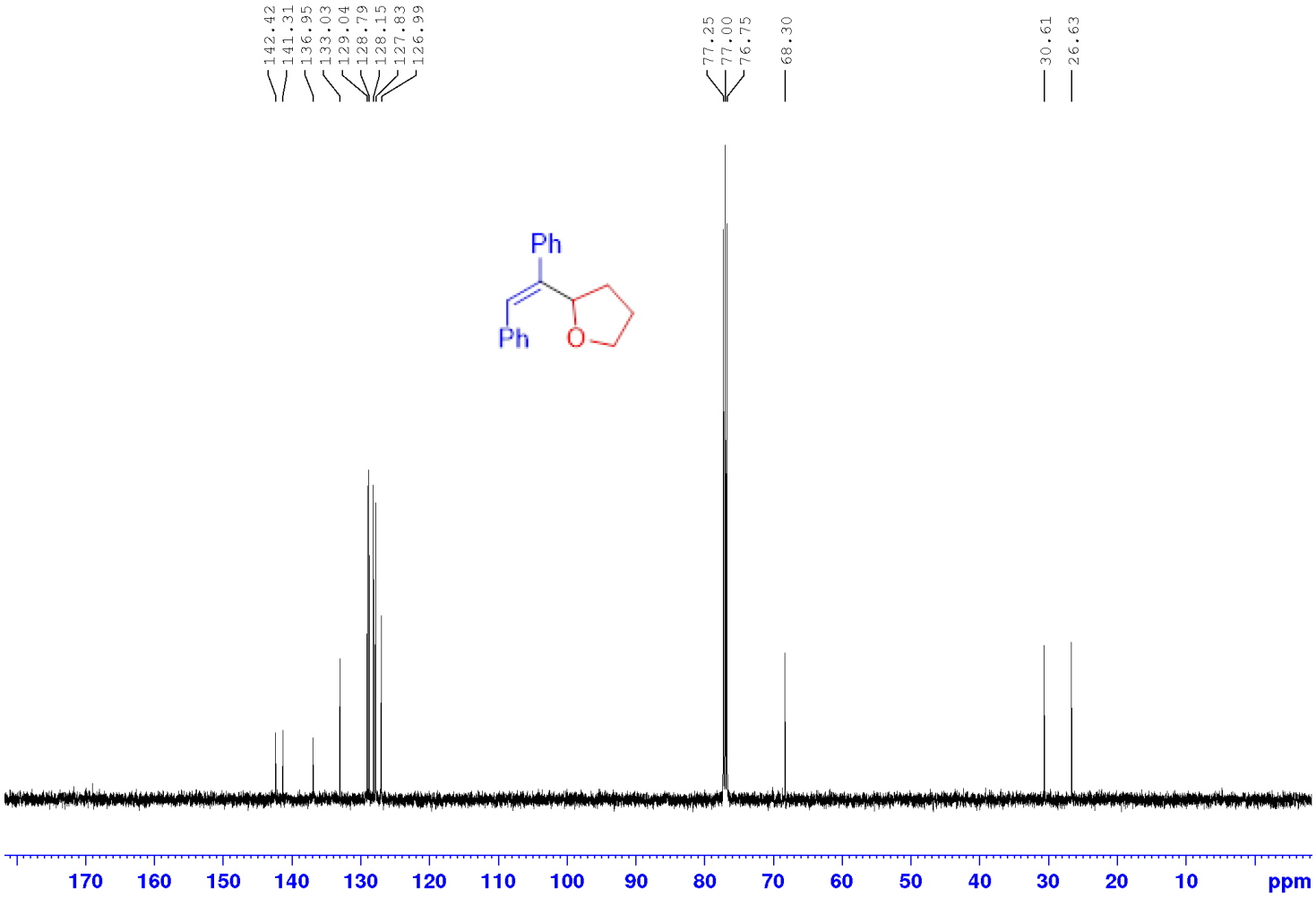
1.10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127.83
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77.00
76.75
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30.61
26.63
Ph
Ph
O
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140
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110
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80
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30
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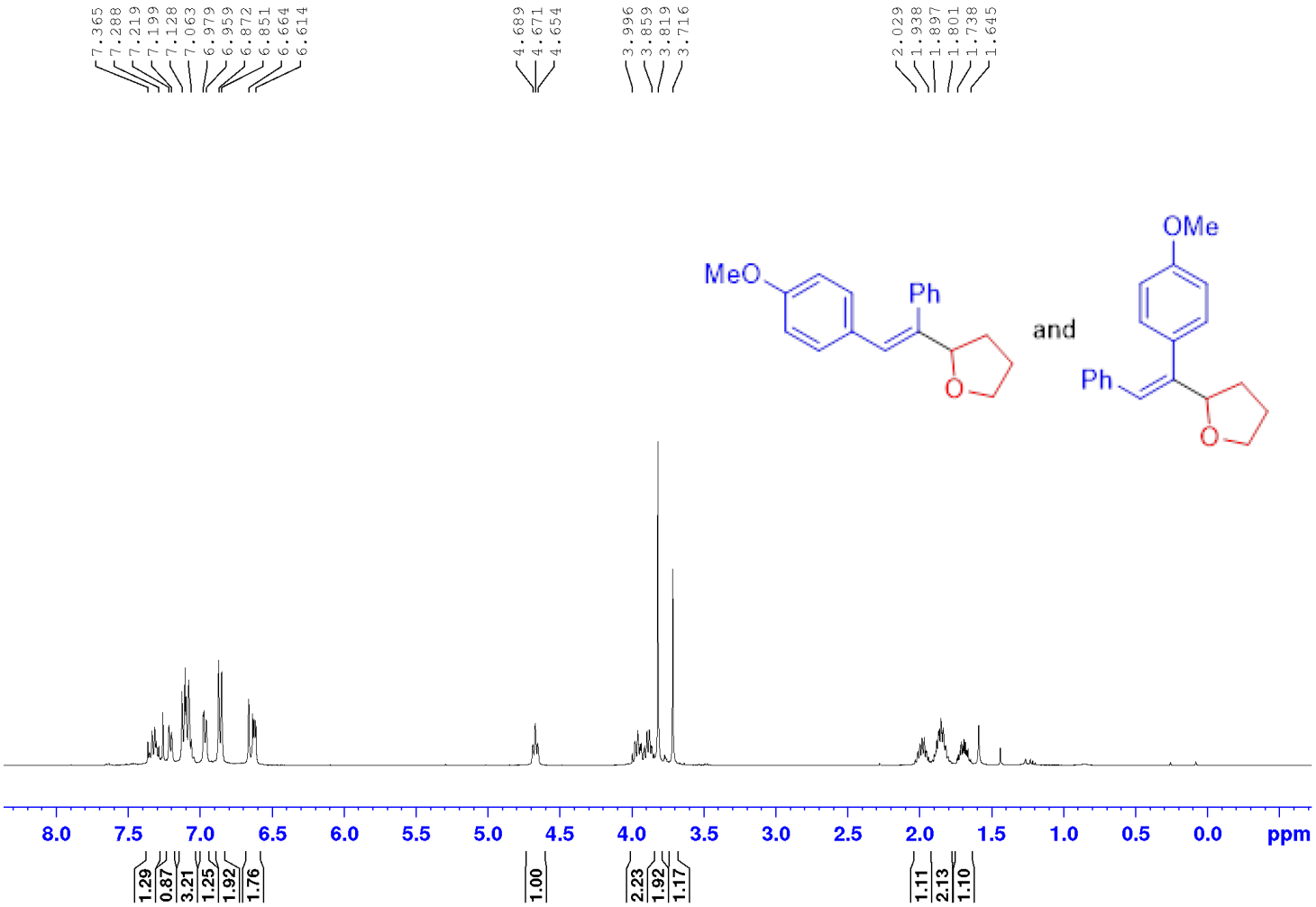
10
ppm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4.654
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3.819
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1.897
1.801
1.738
1.645
MeO
Ph
O
and
OMe
Ph
O
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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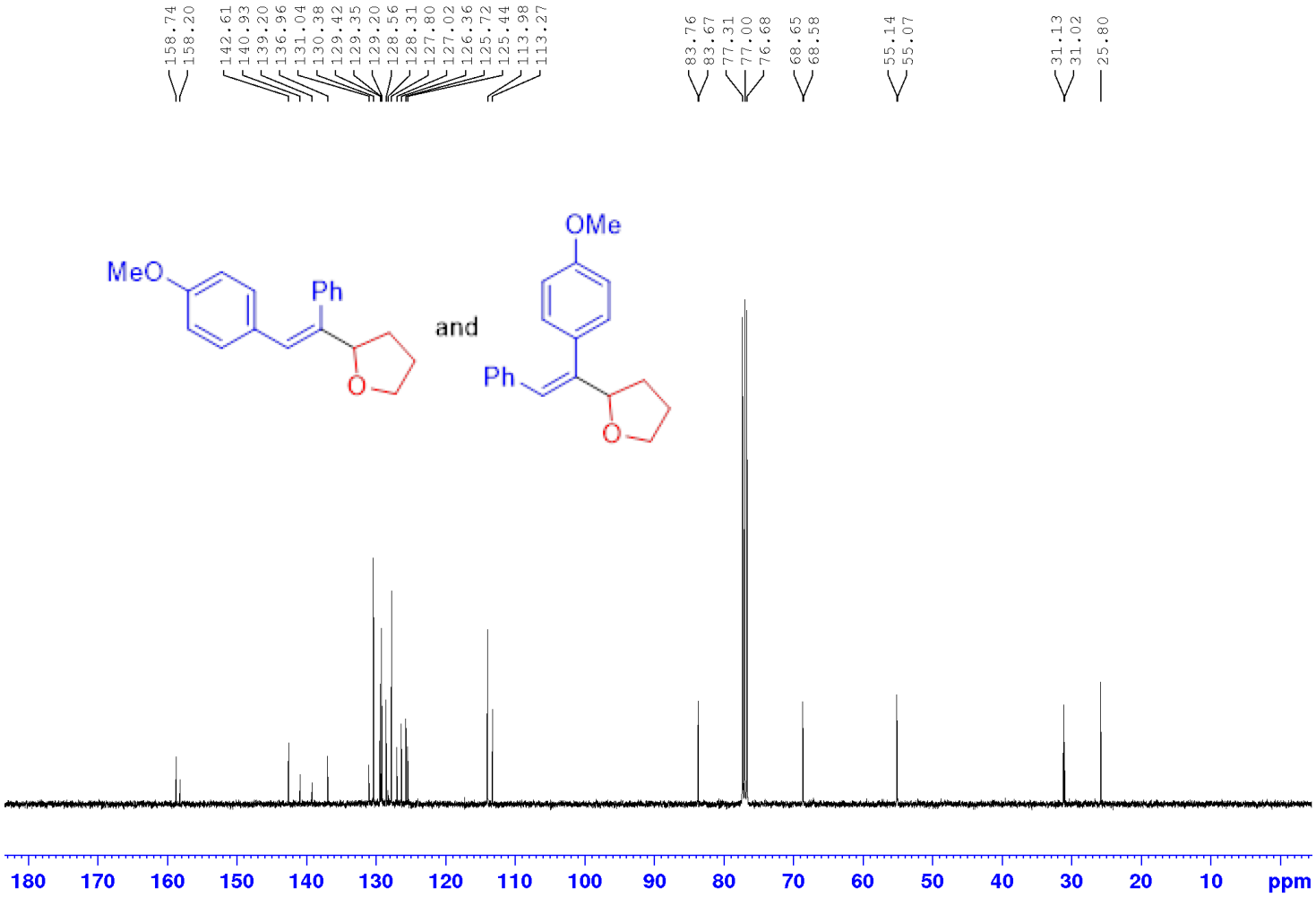
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126.36
125.72
125.44
113.98
113.27
83.76
83.67
77.31
77.00
76.68
68.65
68.58
55.14
55.07
31.13
31.02
25.80
MeO
Ph
O
and
OMe
Ph
O
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140
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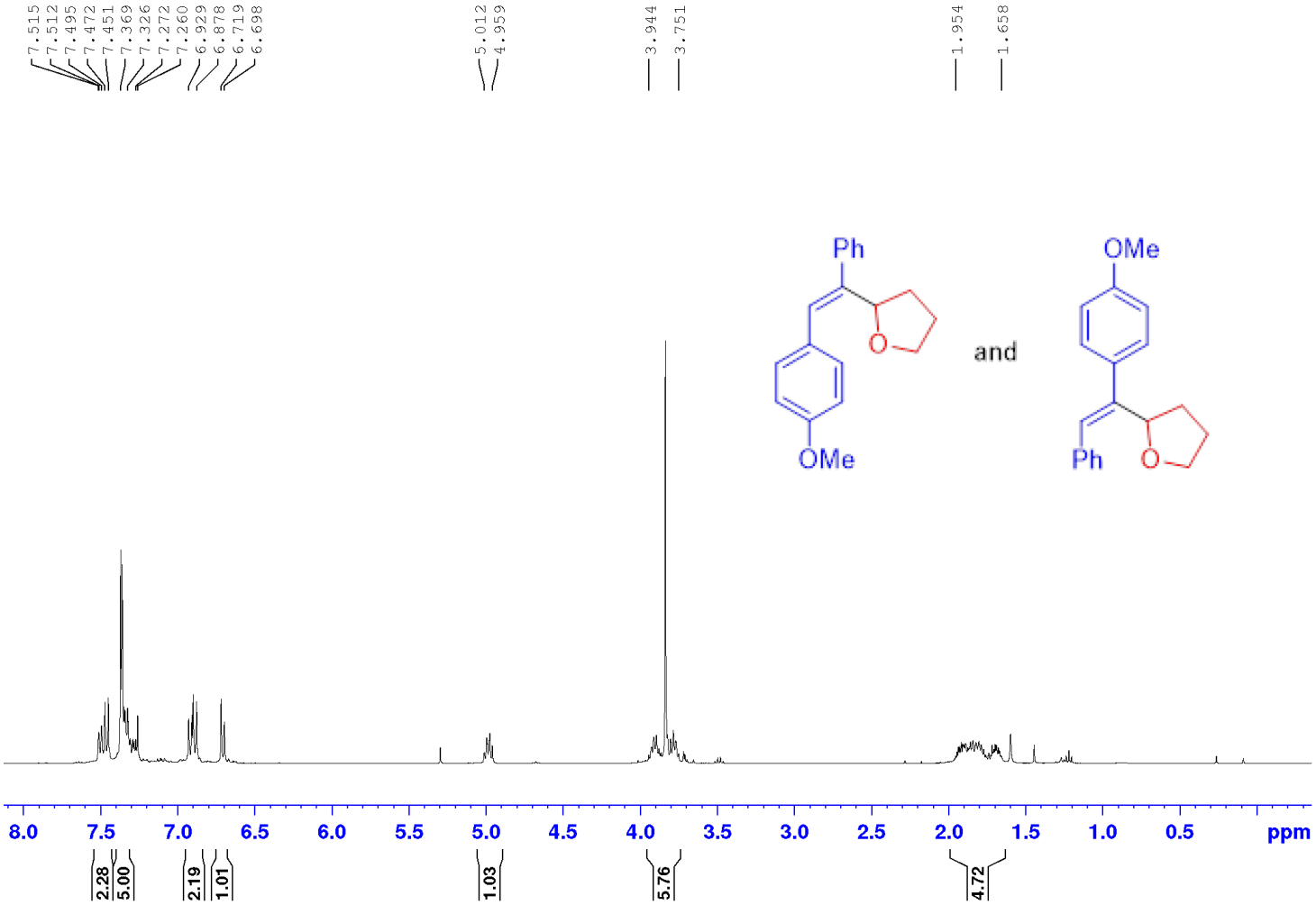
10
ppm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5.012
4.959
3.944
3.751
1.954
1.658
Ph
O
OMe
and
OMe
Ph
O
8.0
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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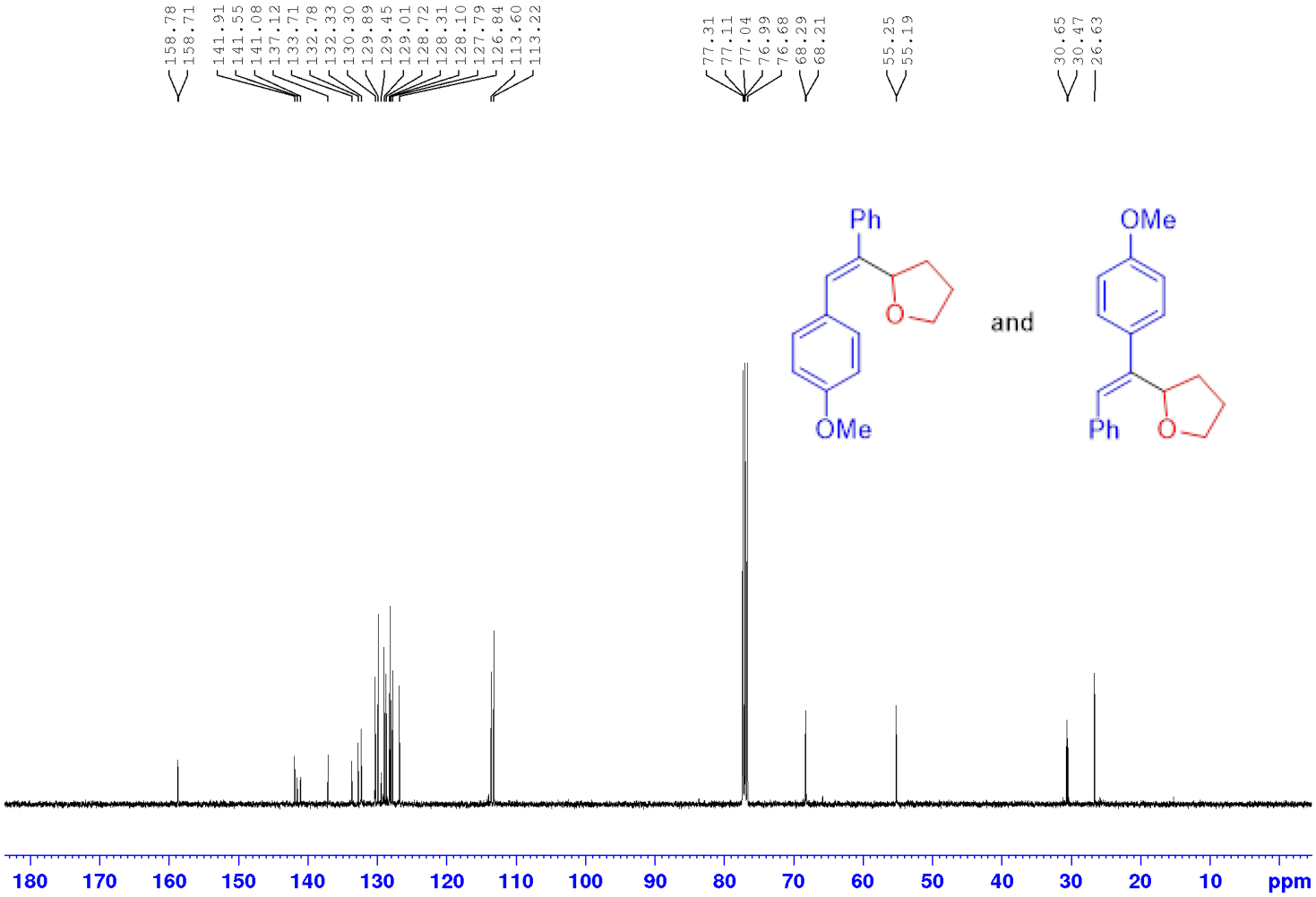
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128.31
128.10
127.79
126.84
113.60
113.22
77.31
77.11
77.04
76.99
76.68
68.29
68.21
55.25
55.19
30.65
30.47
26.63
Ph
O
OMe
and
OMe
Ph
O
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150
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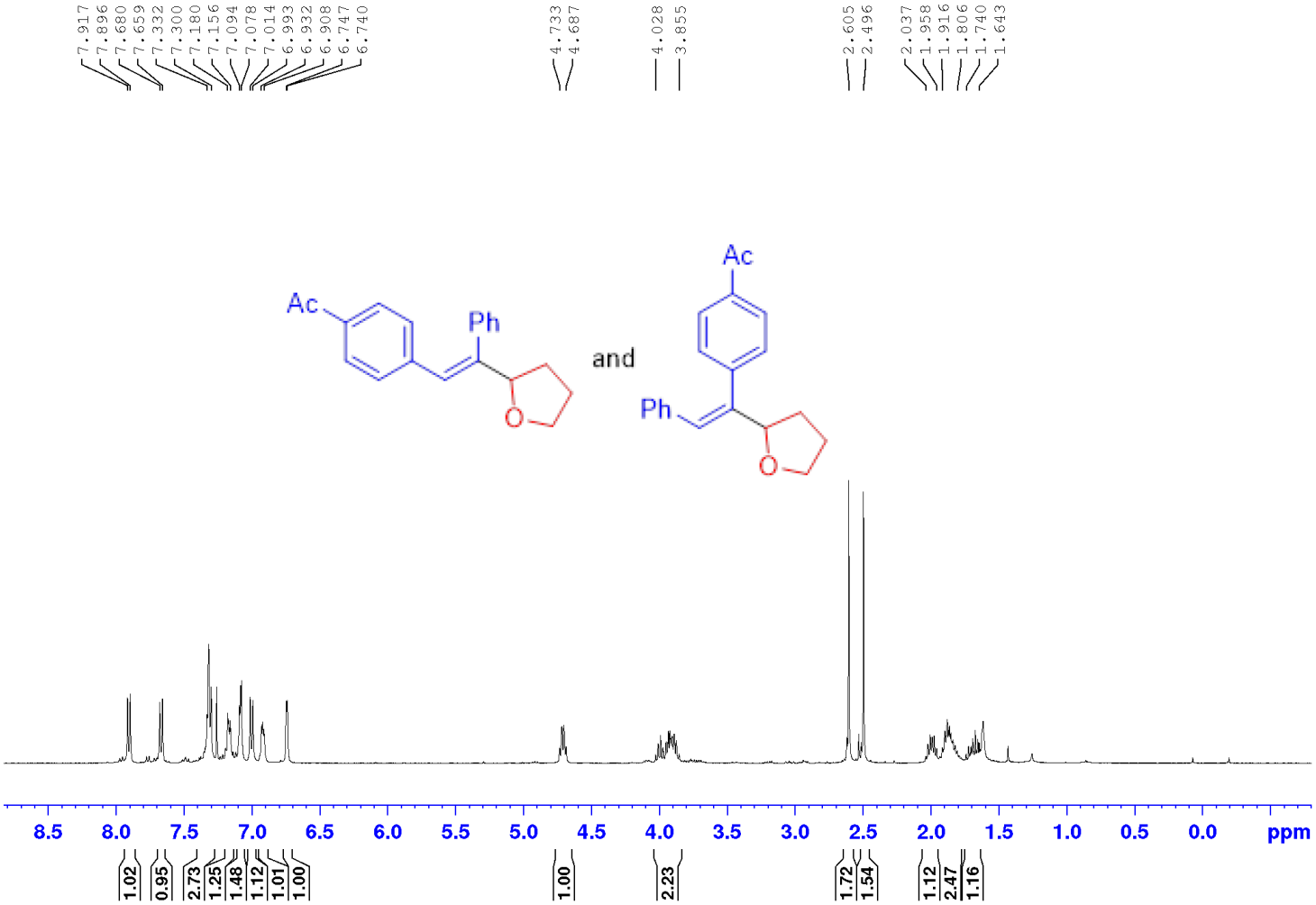
ppm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6.932
6.908
6.747
6.740
4.733
4.687
4.028
3.855
2.605
2.496
2.037
1.958
1.916
1.806
1.740
1.643
Ac
Ph
O
and
Ac
Ph
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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0.95
2.73
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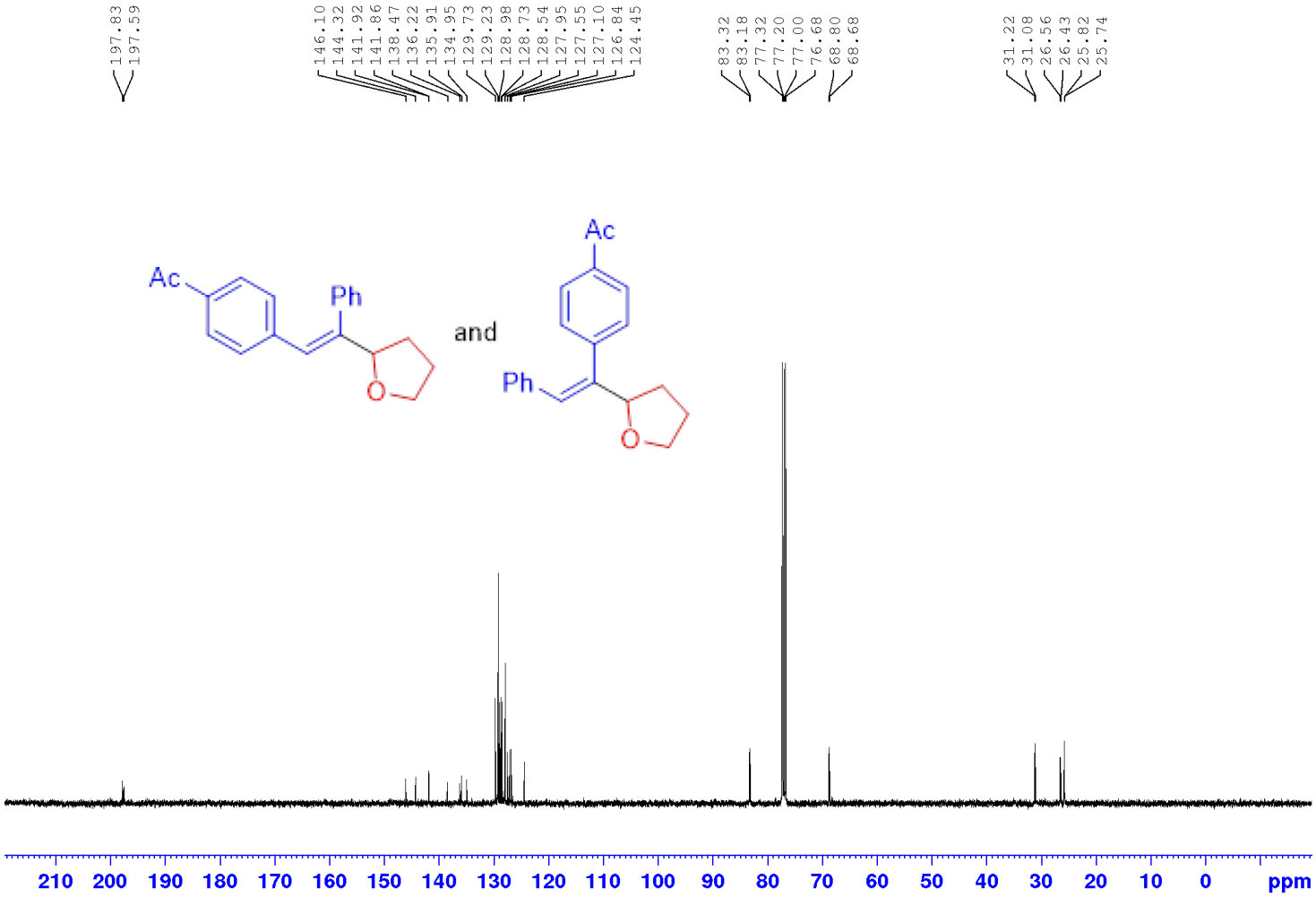
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128.98
128.73
128.54
127.95
127.55
127.10
126.84
124.45
83.32
83.18
77.32
77.20
77.00
76.68
68.80
68.68
31.22
31.08
26.56
26.43
25.82
25.74
Ac
Ph
O
and
Ac
Ph
O
210
200
190
180
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140
130
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100
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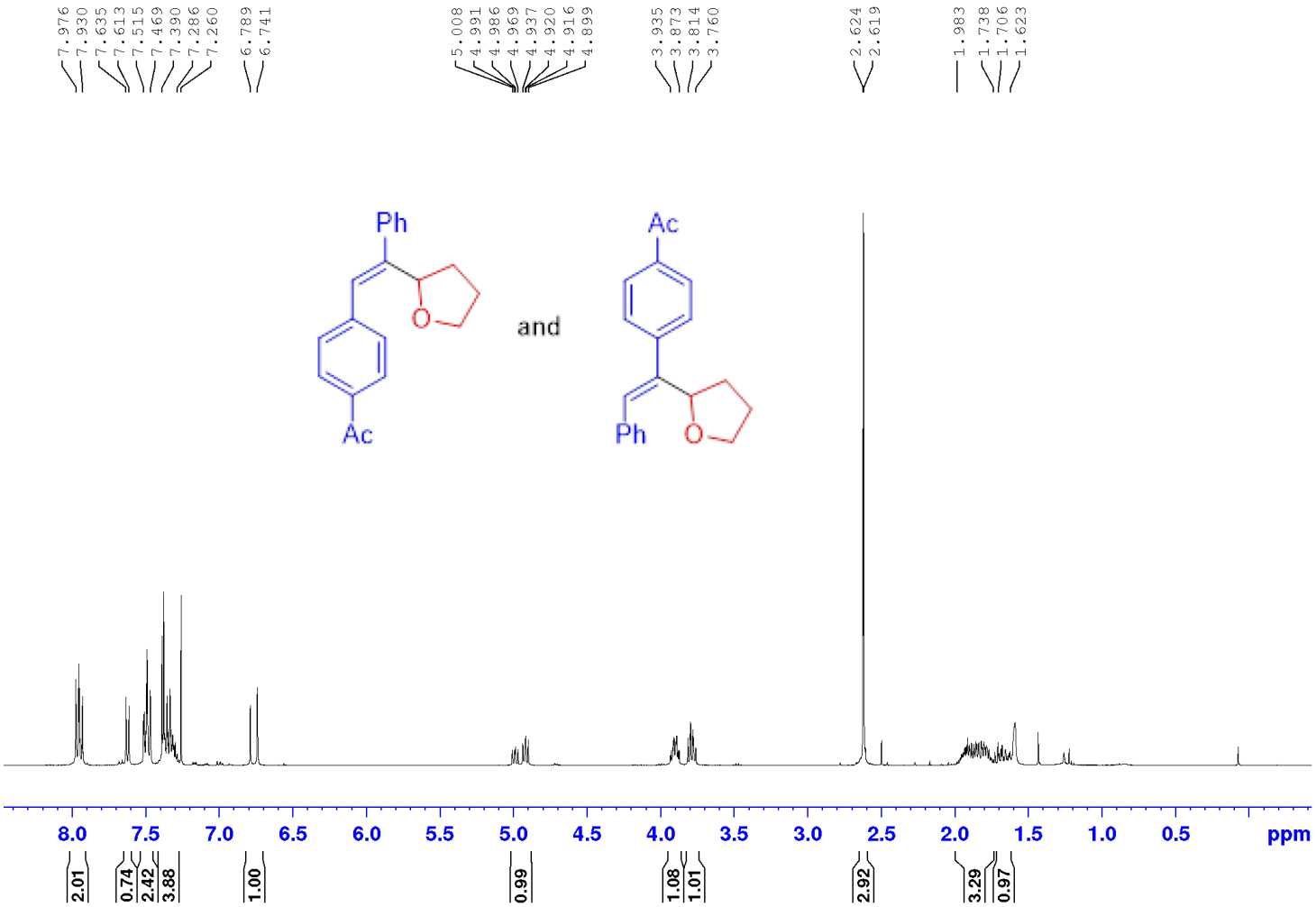
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6.741
5.008
4.991
4.986
4.969
4.937
4.920
4.916
4.899
3.935
3.873
3.814
3.760
2.624
2.619
1.983
1.738
1.706
1.623
Ph
O
Ac
and
Ac
Ph
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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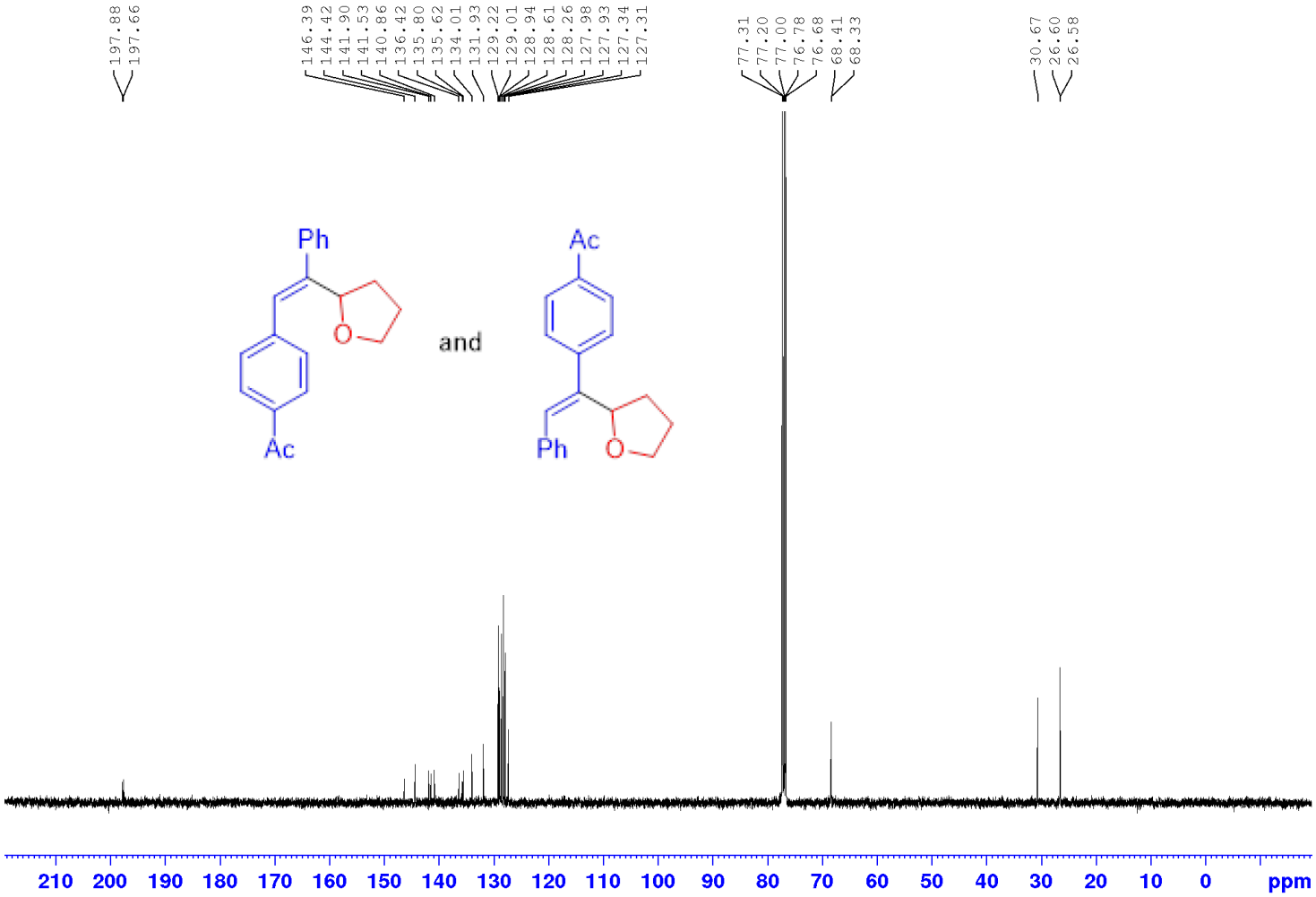
0.97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129.01
128.94
128.61
128.26
127.98
127.93
127.34
127.31
77.31
77.20
77.00
76.78
76.68
68.41
68.33
30.67
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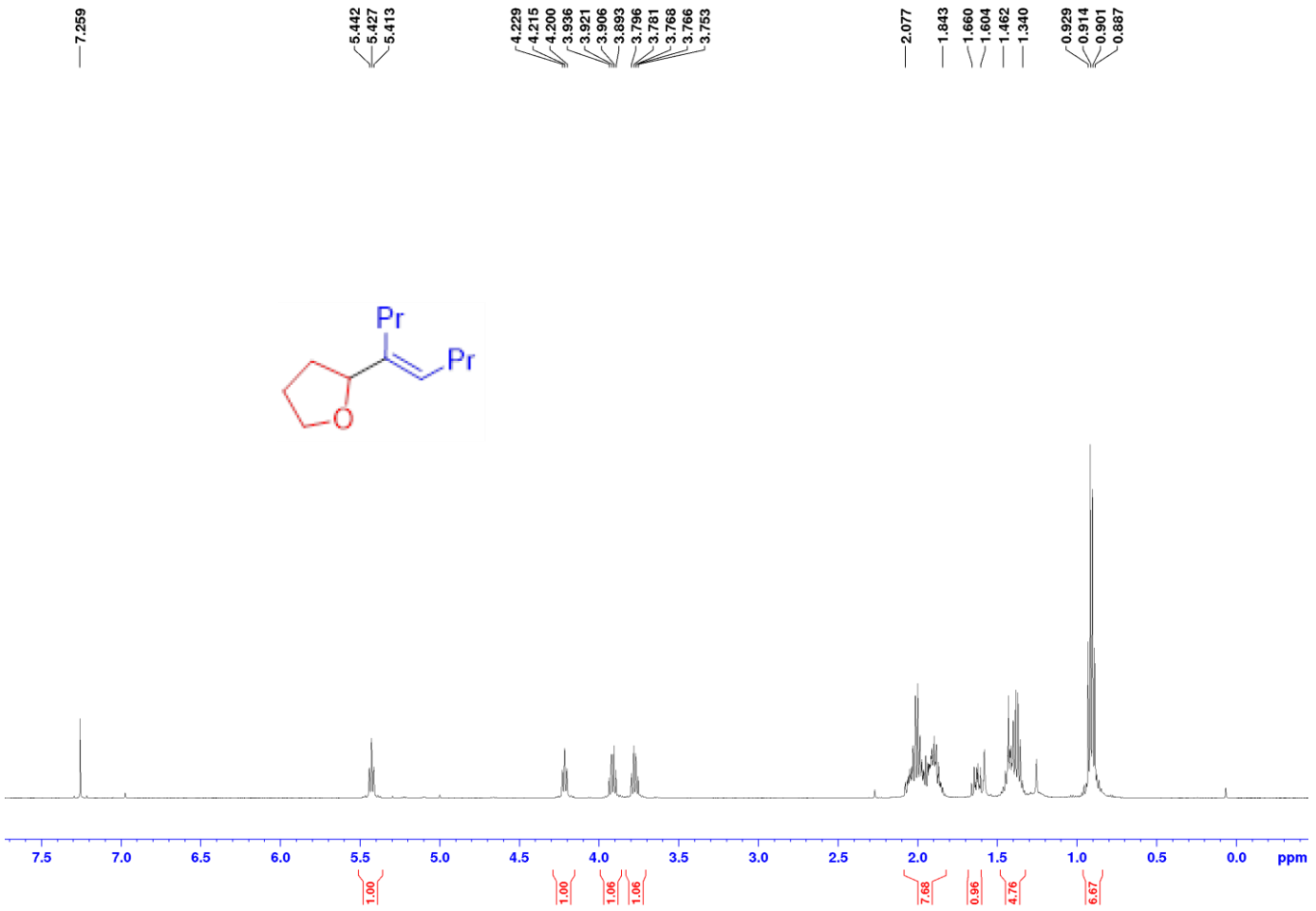
26.58
Ph
O
Ac
and
Ac
Ph
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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5.427
5.413
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4.200
3.936
3.921
3.906
3.893
3.796
3.781
3.768
3.766
3.753
2.077
1.843
1.660
1.604
1.462
1.340
0.929
0.914
0.901
0.887
Pr
Pr
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
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1.06
7.68
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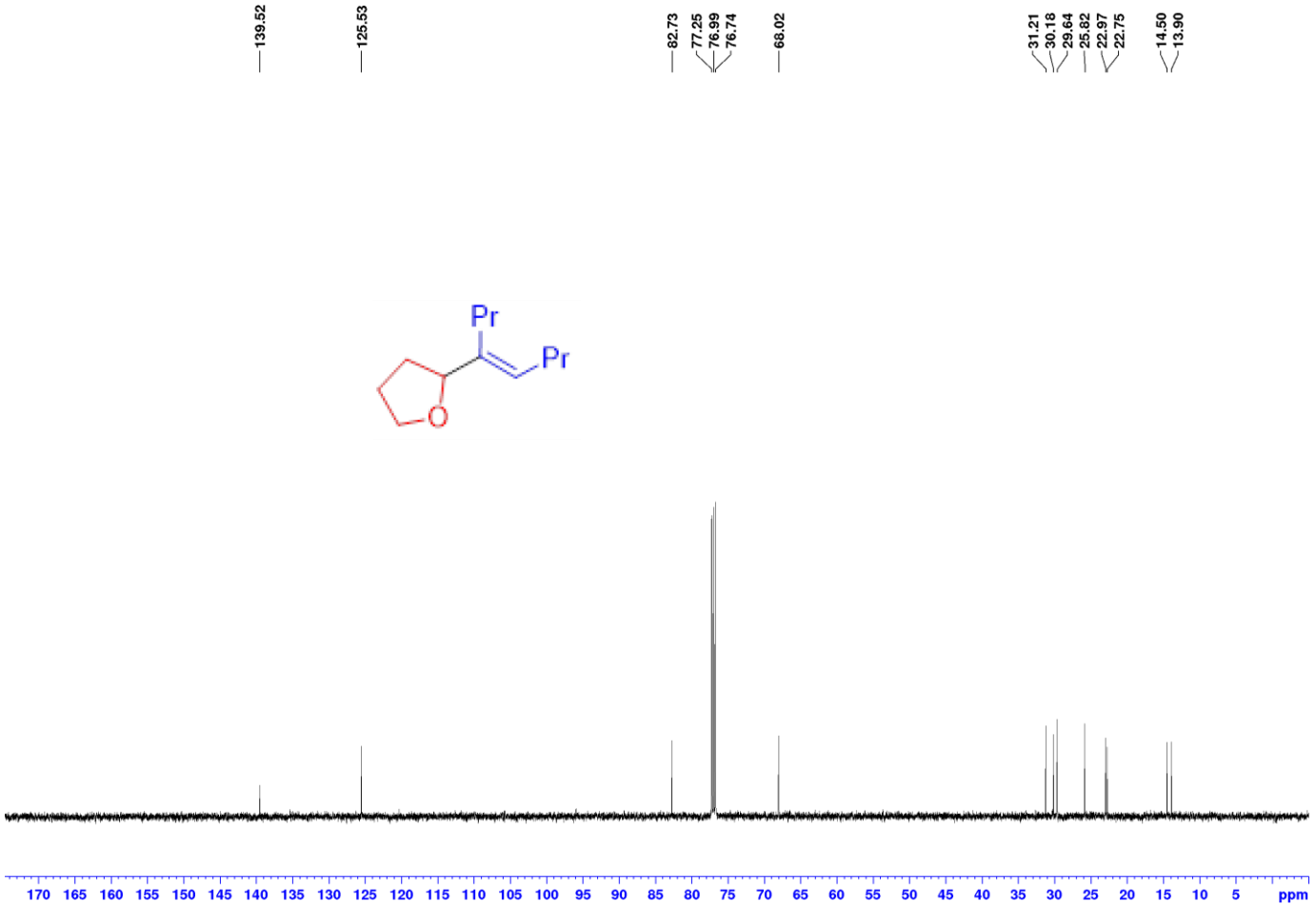
4.76
6.67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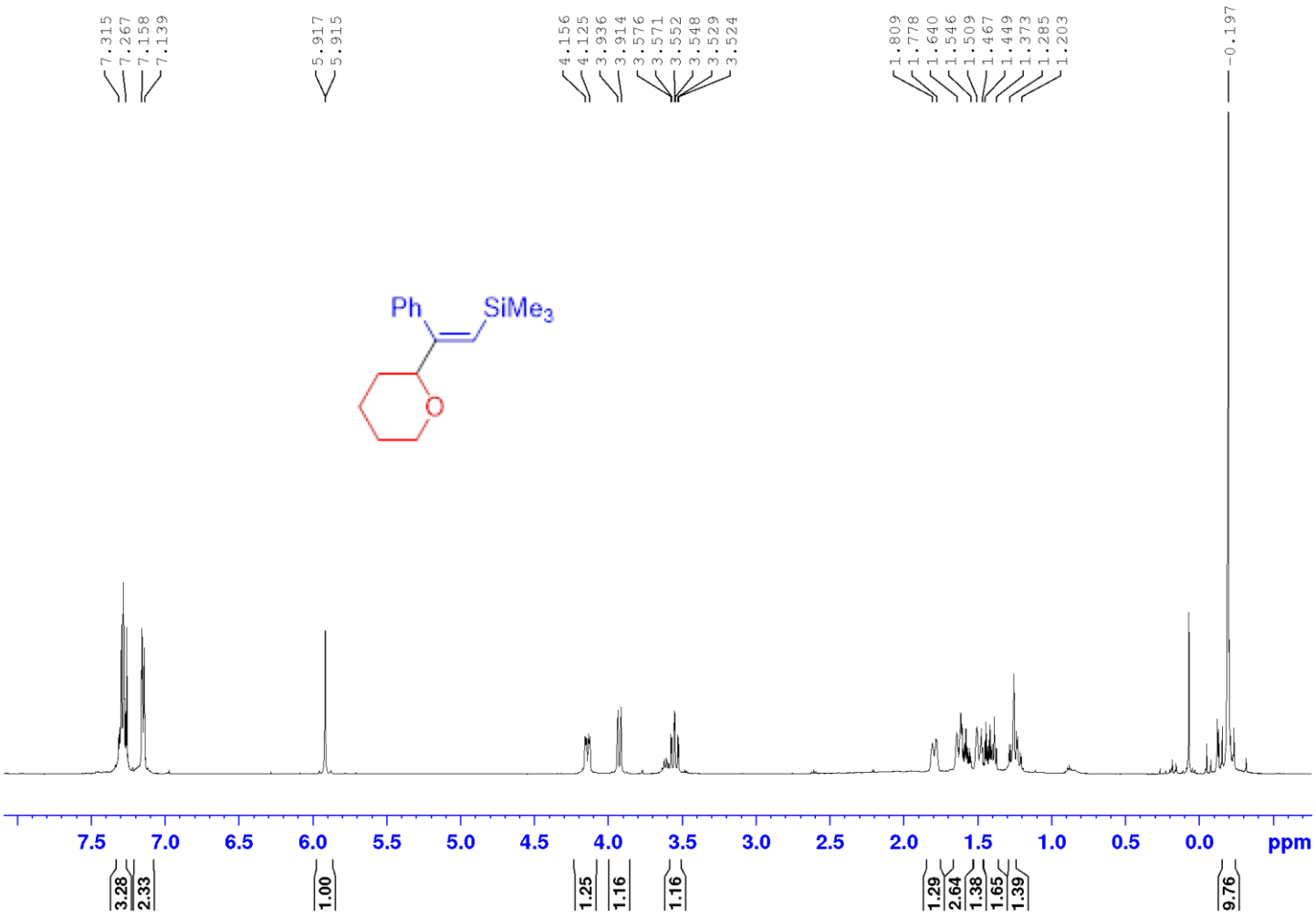
125.53
82.73
77.25
76.99
76.74
68.02
31.21
30.18
29.64
25.82
22.97
22.75
14.50
13.90
Pr
Pr
O
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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7.267
7.158
7.139
5.917
5.915
4.156
4.125
3.936
3.914
3.576
3.571
3.552
3.548
3.529
3.524
1.809
1.778
1.640
1.546
1.509
1.467
1.449
1.373
1.285
1.203
-0.197
Ph
SiMe3
O
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
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1.25
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1.16
1.29
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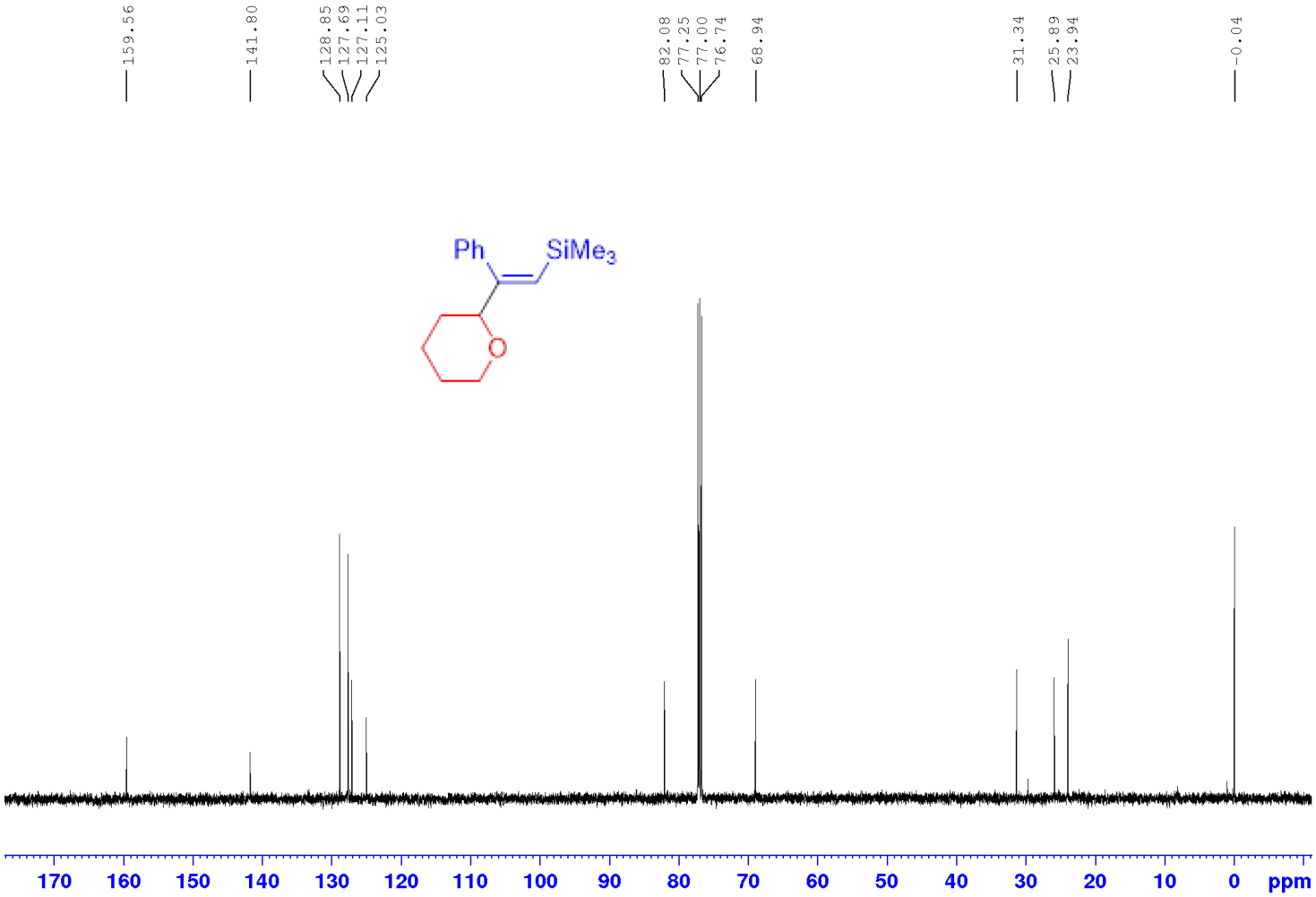
1.39
9.76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128.85
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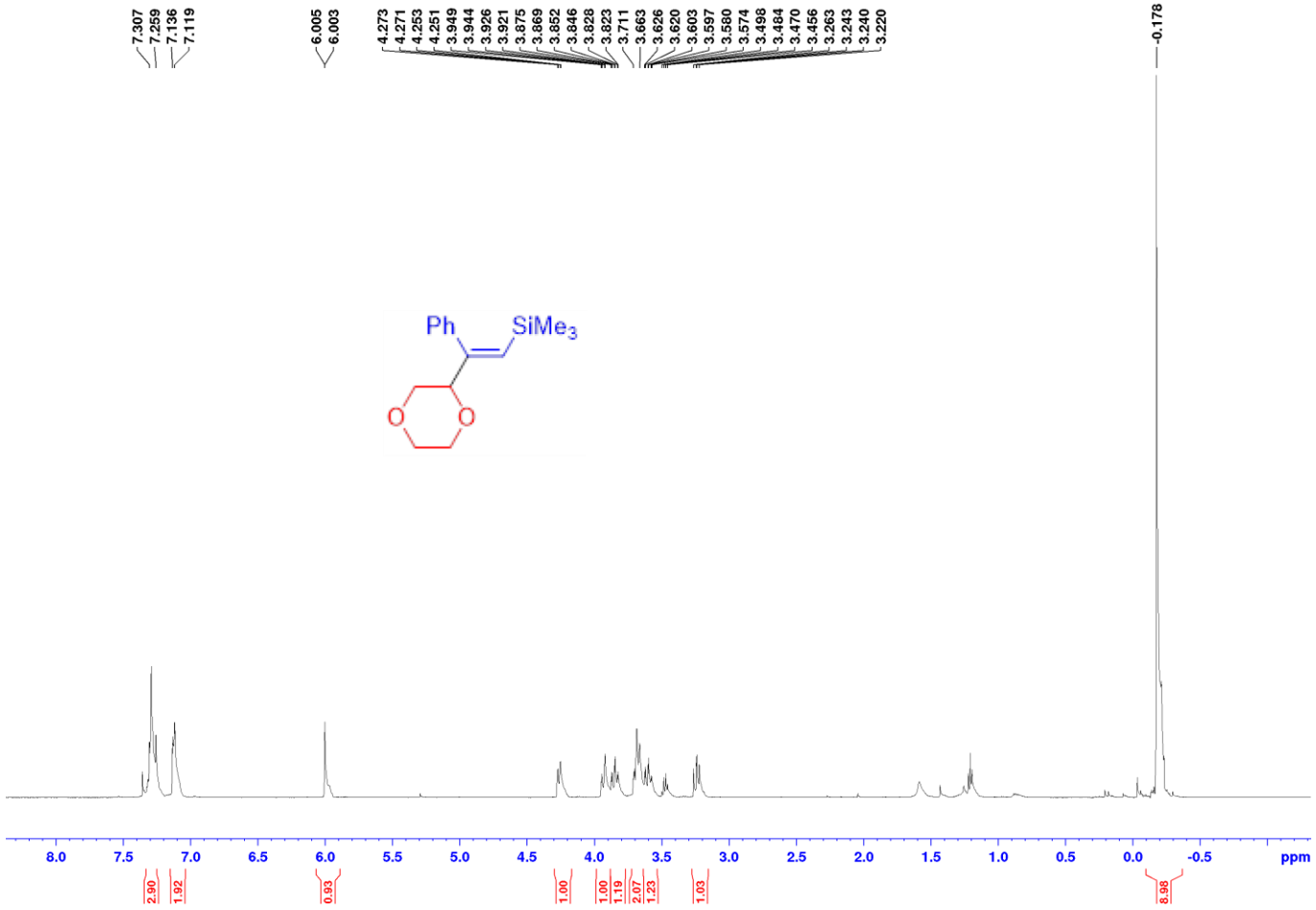
125.03
82.08
77.25
77.00
76.74
68.94
31.34
25.89
23.94
-0.04
Ph
SiMe3
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.136
7.119
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6.003
4.273
4.271
4.253
4.251
3.949
3.944
3.926
3.921
3.875
3.869
3.852
3.846
3.828
3.823
3.711
3.663
3.626
3.620
3.603
3.597
3.580
3.574
3.498
3.484
3.470
3.456
3.263
3.243
3.240
3.220
-0.178
Ph
SiMe3
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
0.0
-0.5
ppm
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1.92
0.93
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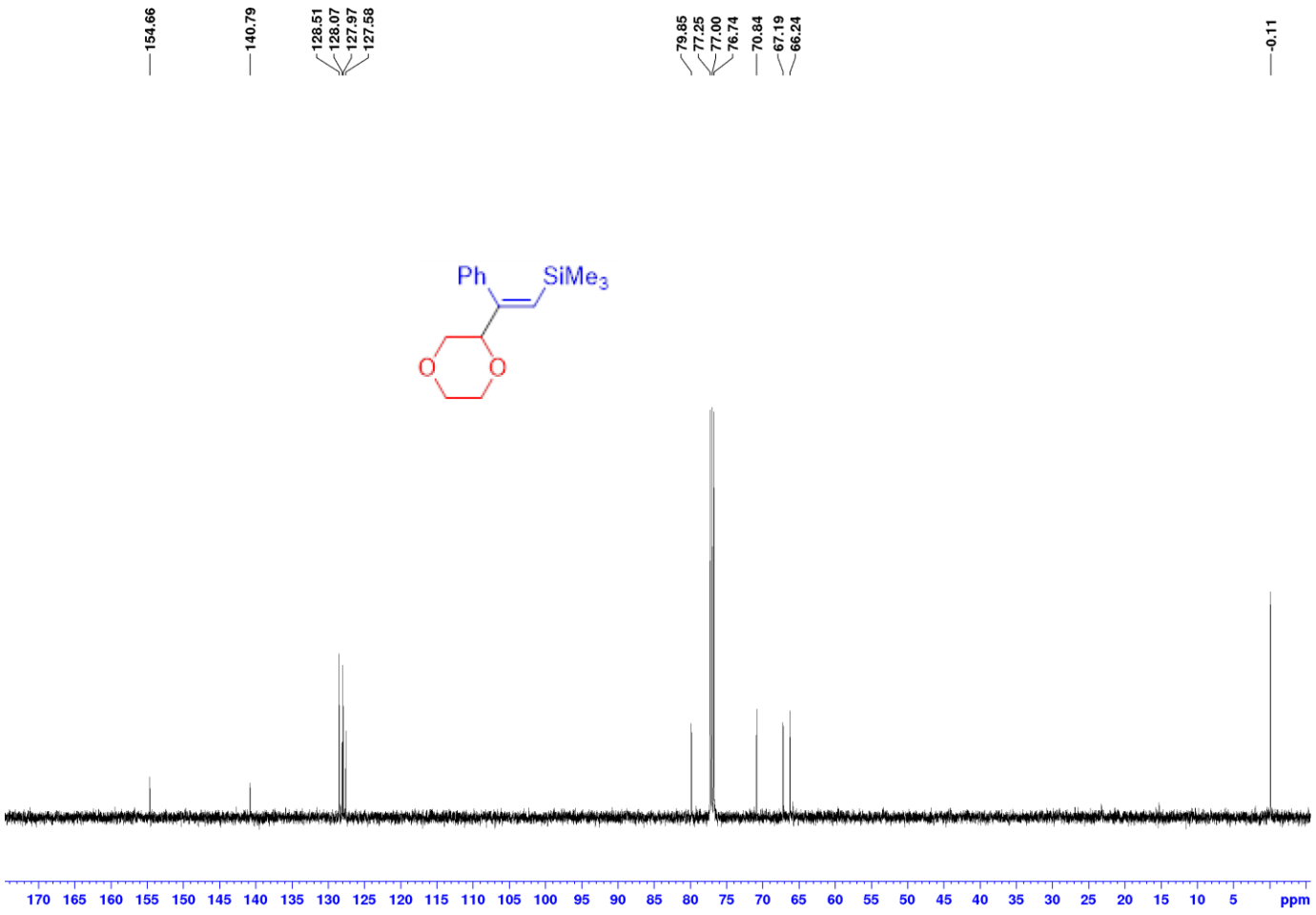
1.00
1.19
2.07
1.23
1.03
8.98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140.79
128.51
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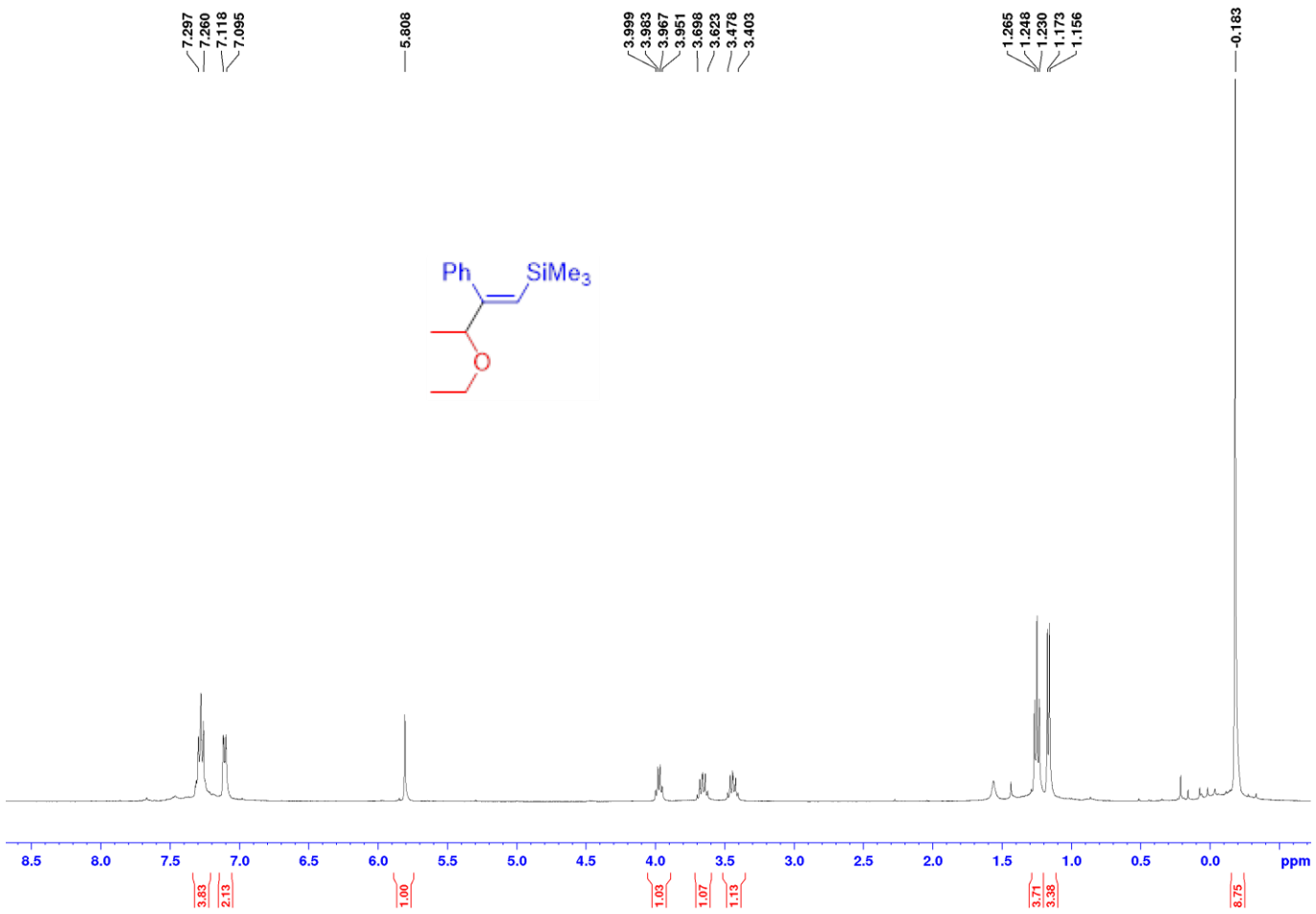
127.97
127.58
79.85
77.25
77.00
76.74
70.84
67.19
66.24
-0.11
Ph
SiMe3
O
O
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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3.967
3.951
3.698
3.623
3.478
3.403
1.265
1.248
1.230
1.173
1.156
-0.163
Ph
SiMe3
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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ppm
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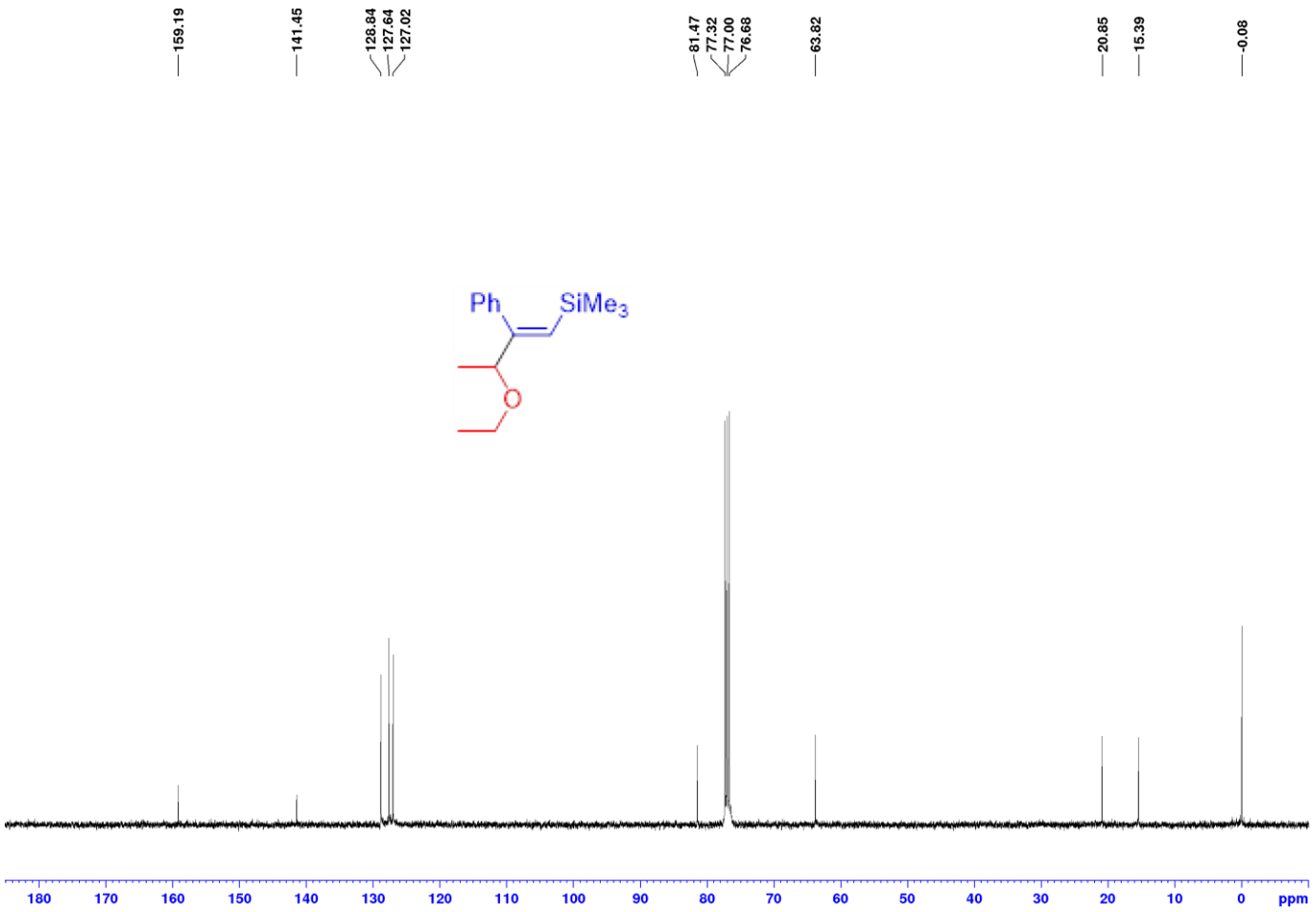
1.00
1.03
1.07
1.13
3.71
3.38
8.75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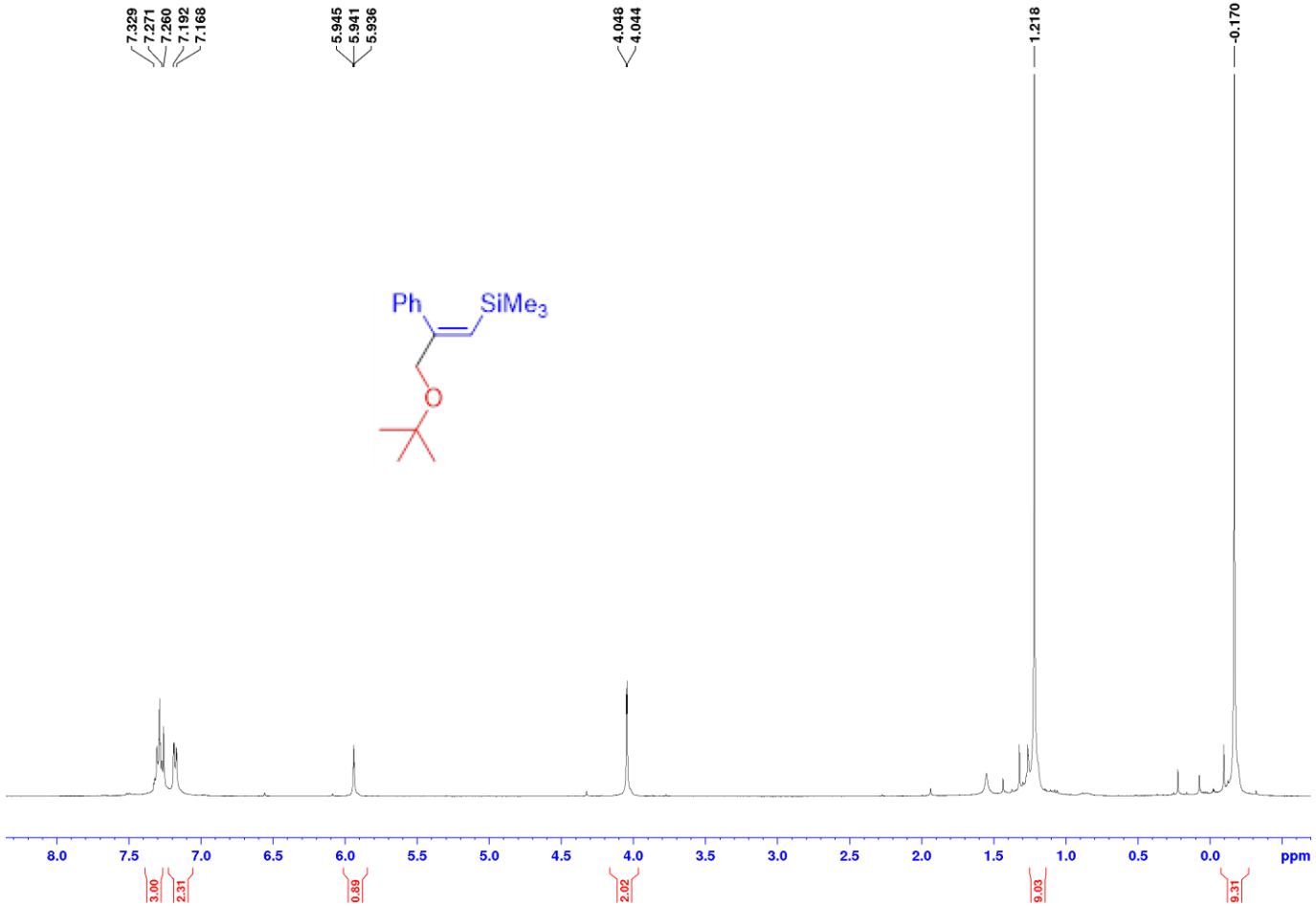
141.45
128.84
127.64
127.02
81.47
77.32
77.00
76.68
63.82
20.85
15.39
-0.08
Ph
SiMe3
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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5.936
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4.044
1.218
-0.170
Ph
SiMe3
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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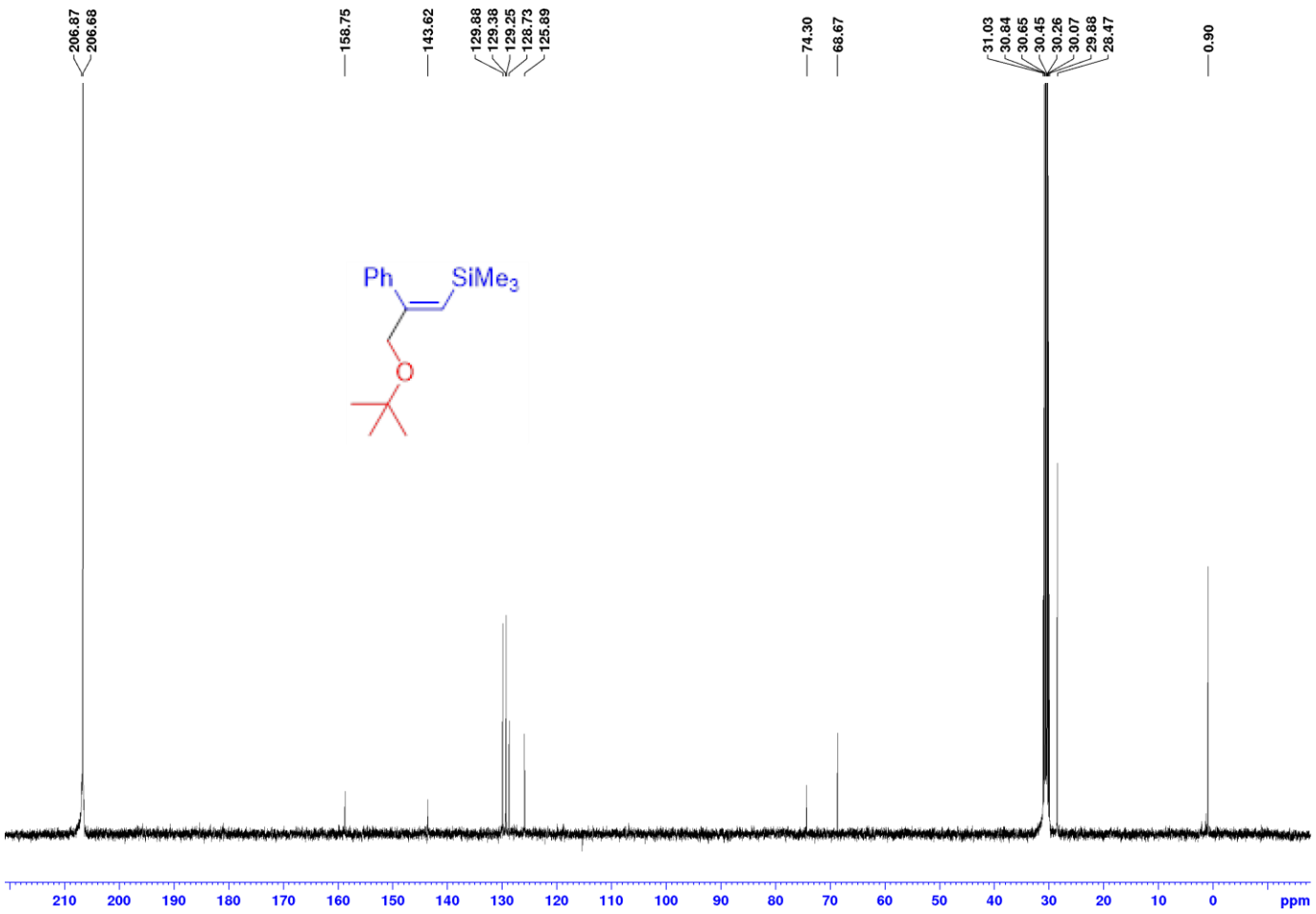
9.03
9.31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143.62
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129.38
129.25
128.73
125.89
74.30
68.67
31.03
30.84
30.65
30.45
30.26
30.07
29.88
28.47
0.90
Ph
SiMe3
O
210
200
190
180
170
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140
130
120
110
100
90
80
70
60
50
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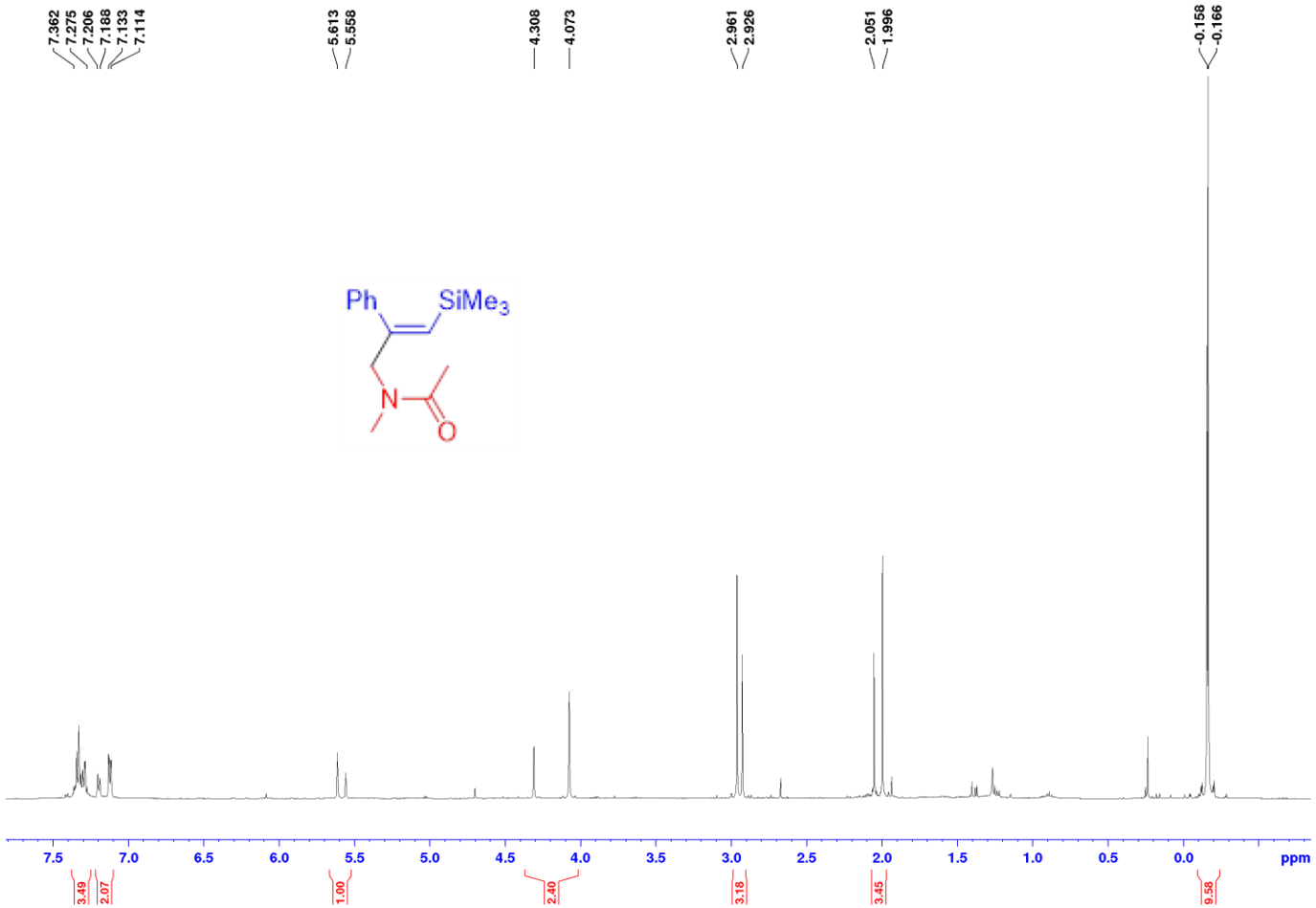
30
20
10
0
ppm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5.558
4.308
4.073
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2.926
2.051
1.996
-0.158
-0.166
Ph
SiMe3
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.00
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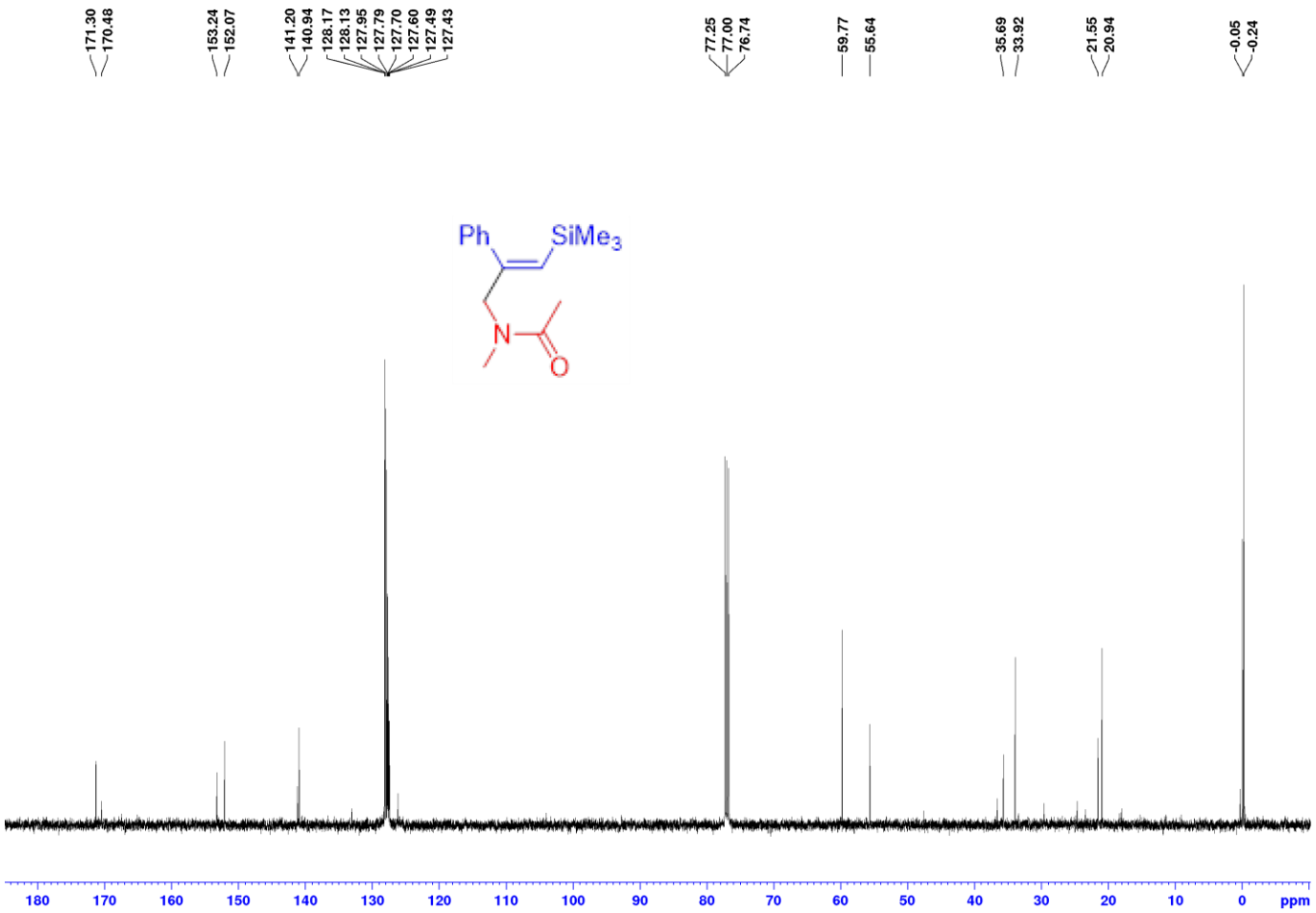
3.45
9.58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140.94
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128.13
127.95
127.79
127.70
127.60
127.49
127.43
77.25
77.00
76.74
59.77
55.64
35.69
33.92
21.55
20.94
-0.05
-0.24
Ph
SiMe3
N
O
180
170
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140
130
120
110
100
90
80
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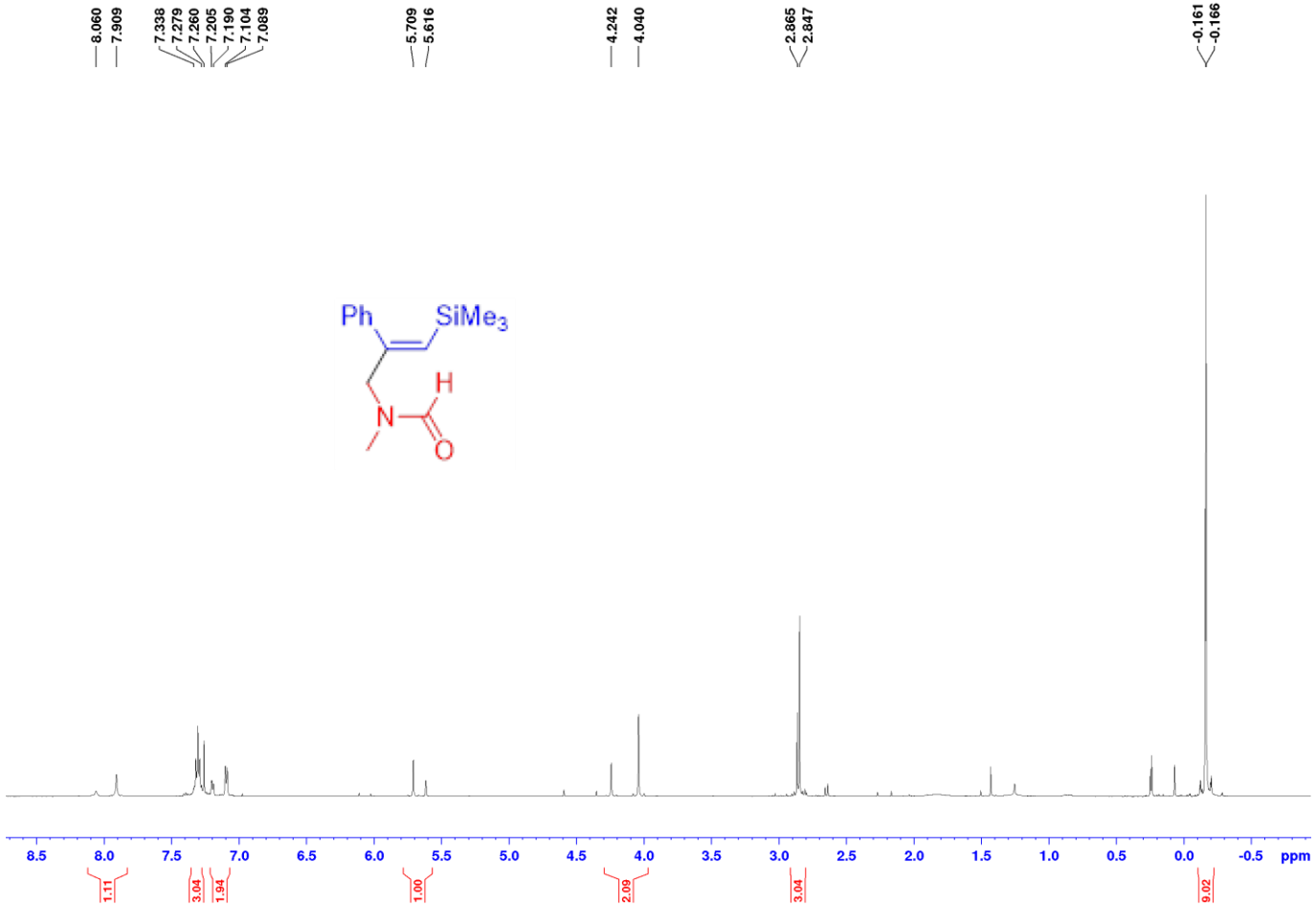
60
50
40
30
20
10
0
ppm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7.190
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7.089
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5.616
4.242
4.040
2.865
2.847
-0.161
-0.166
Ph
SiMe3
H
N
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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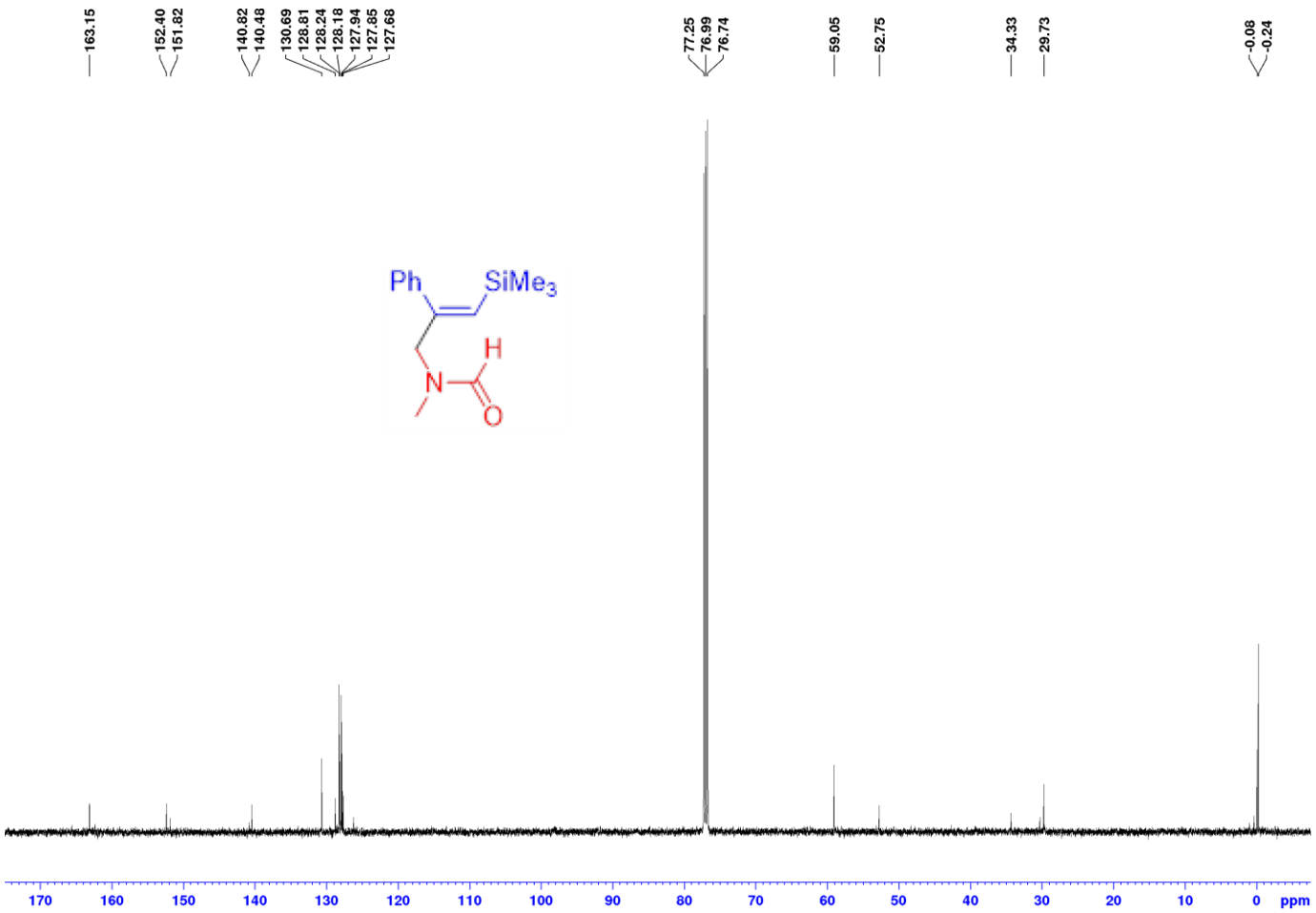
3.04
9.02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140.82
140.48
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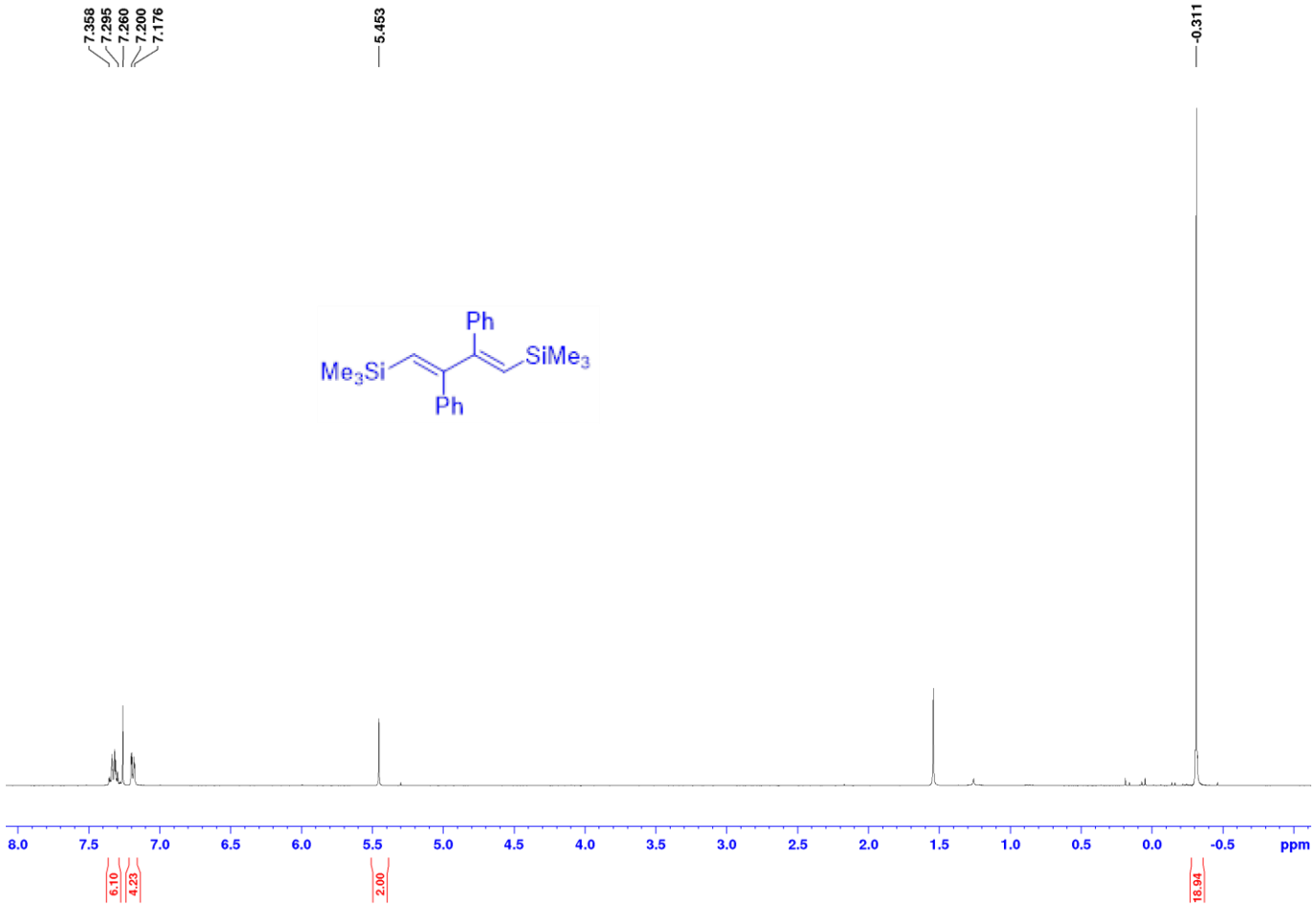
128.81
128.24
128.18
127.94
127.85
127.68
77.25
76.99
76.74
59.05
52.75
34.33
29.73
-0.08
-0.24
Ph
SiMe3
H
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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Ph
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SiMe3
Ph
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
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-0.5
ppm
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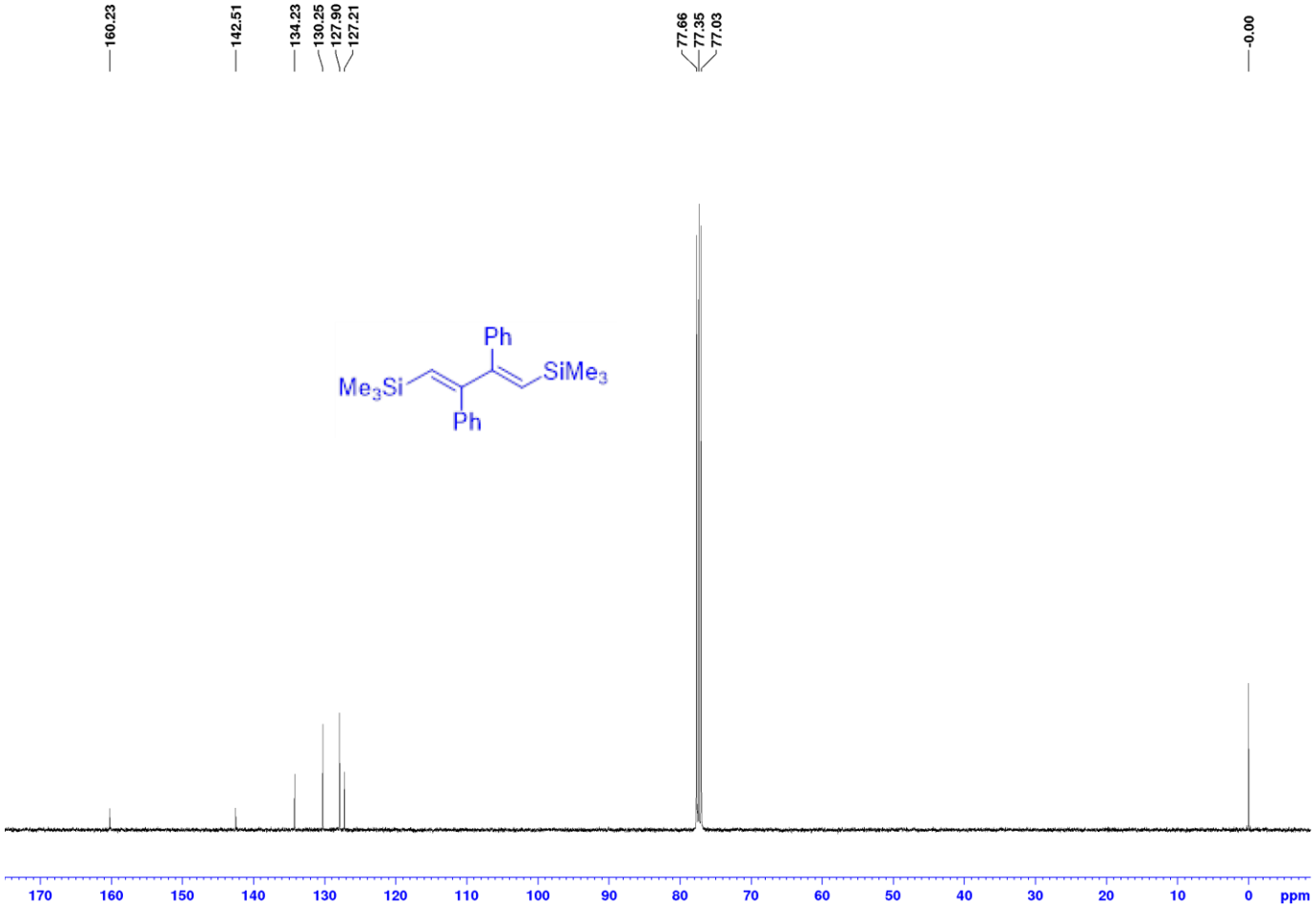
4.23
2.00
18.94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142.51
134.23
130.25
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127.21
77.66
77.35
77.03
0.00
Ph
Me3Si
SiMe3
Ph
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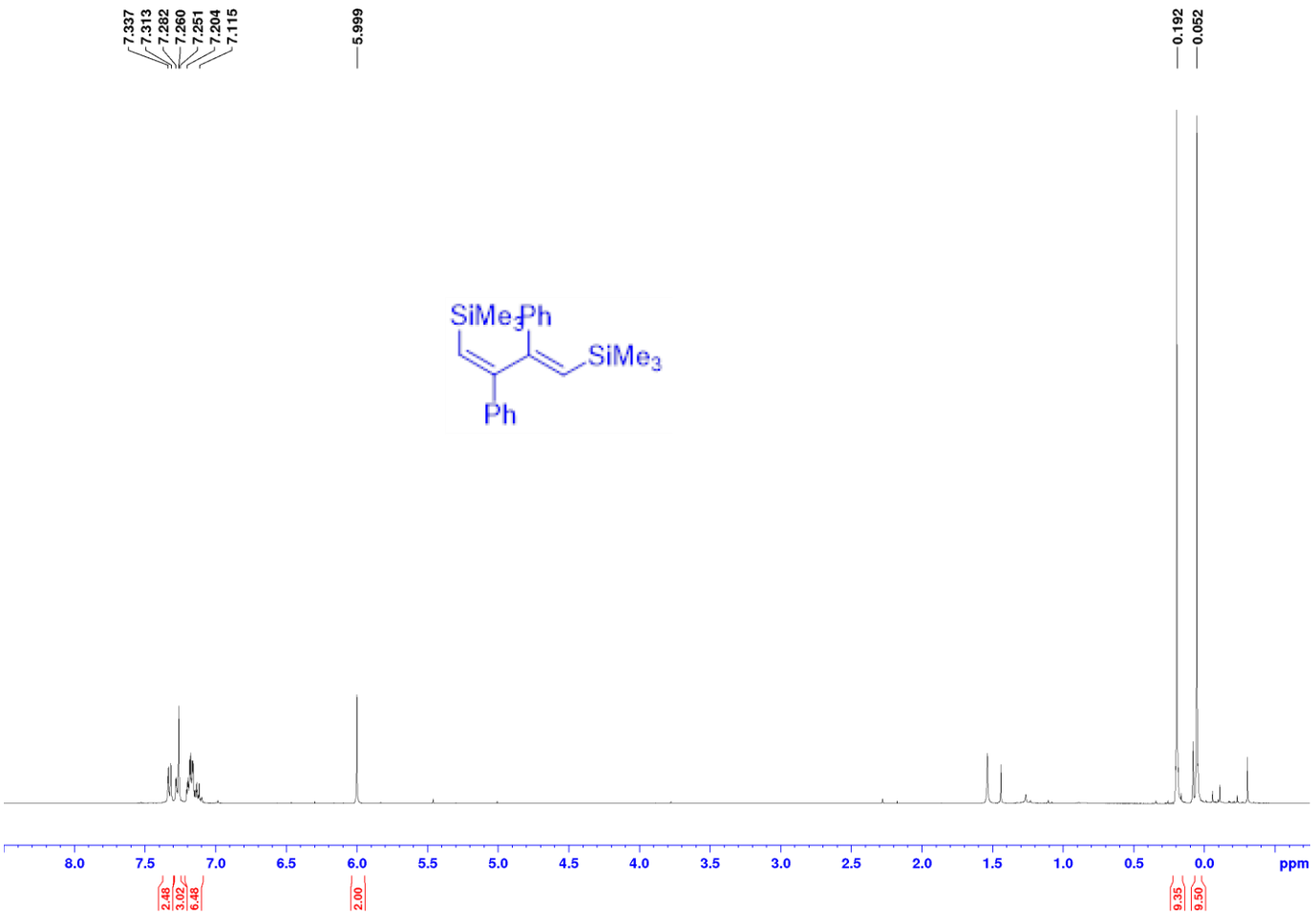
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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0.052
SiMe3
Ph
SiMe3
Ph
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
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ppm
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3.02
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2.00
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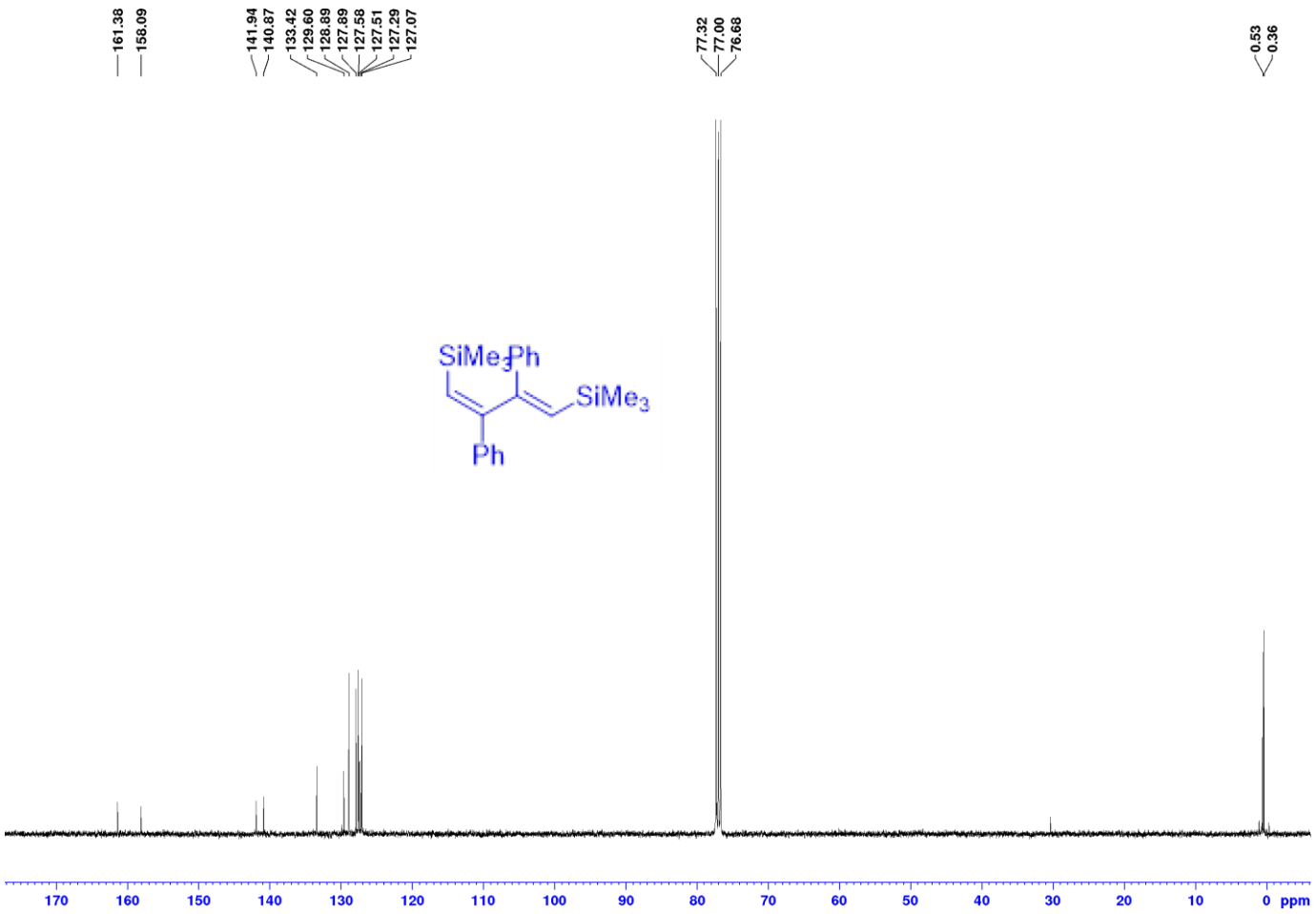
9.50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127.89
127.58
127.51
127.29
127.07
77.32
77.00
76.68
0.53
0.36
SiMe3
Ph
SiMe3
Ph
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160
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140
130
120
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100
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60
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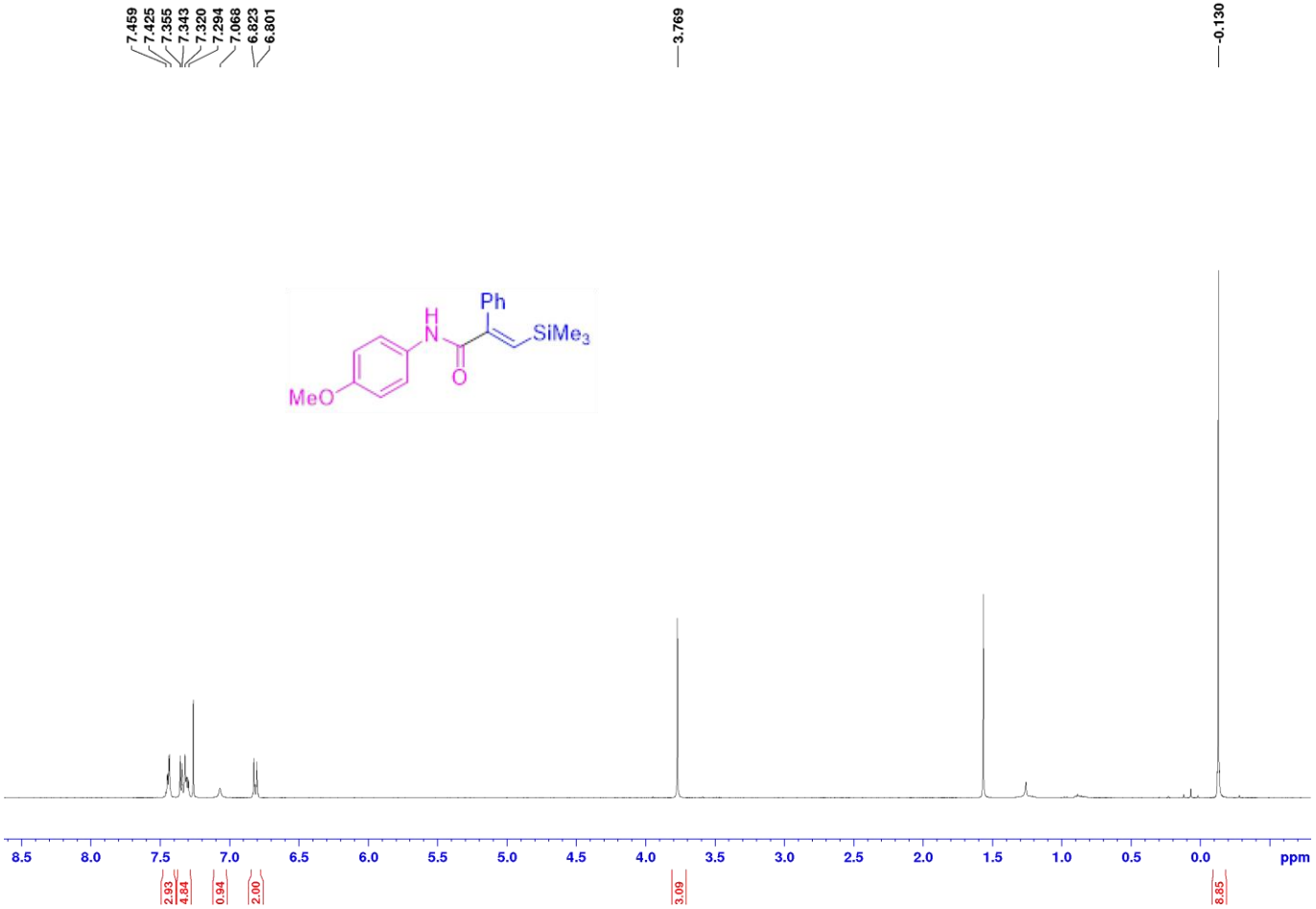
0
ppm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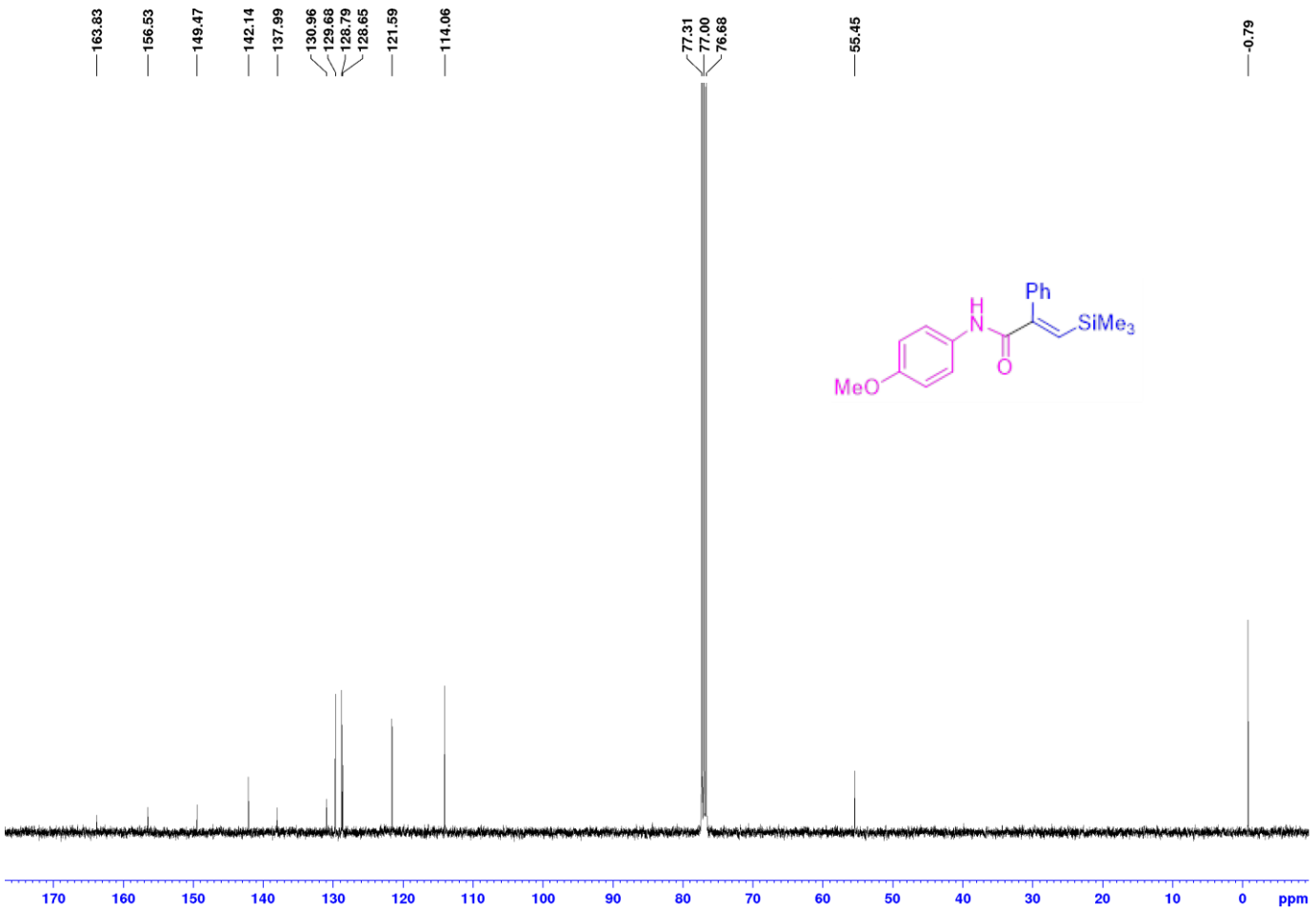
7.068
6.823
6.801
3.769
0.130
Ph
SiMe3
H
N
O
MeO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.93
4.84
0.94
2.00
3.09
8.85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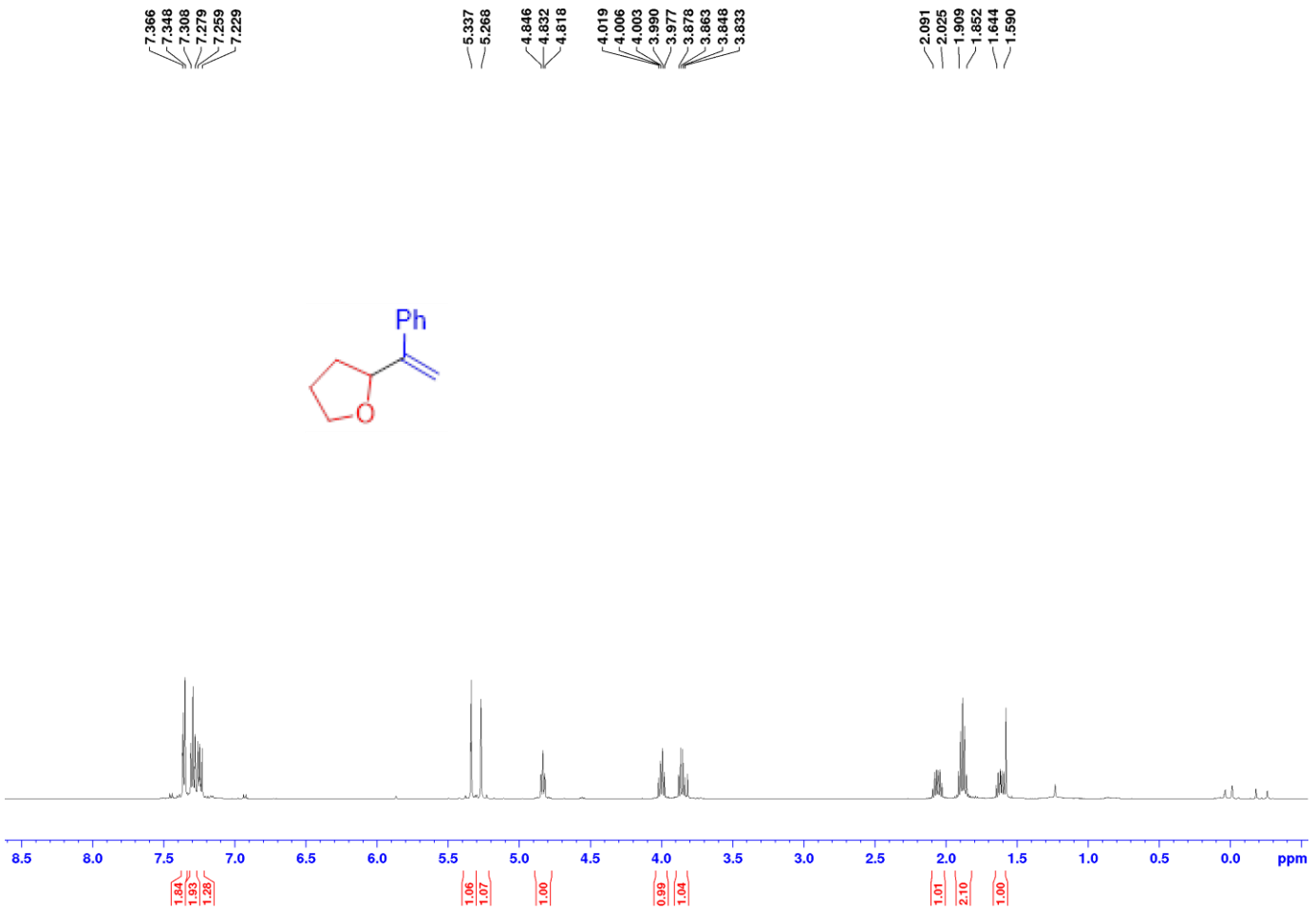
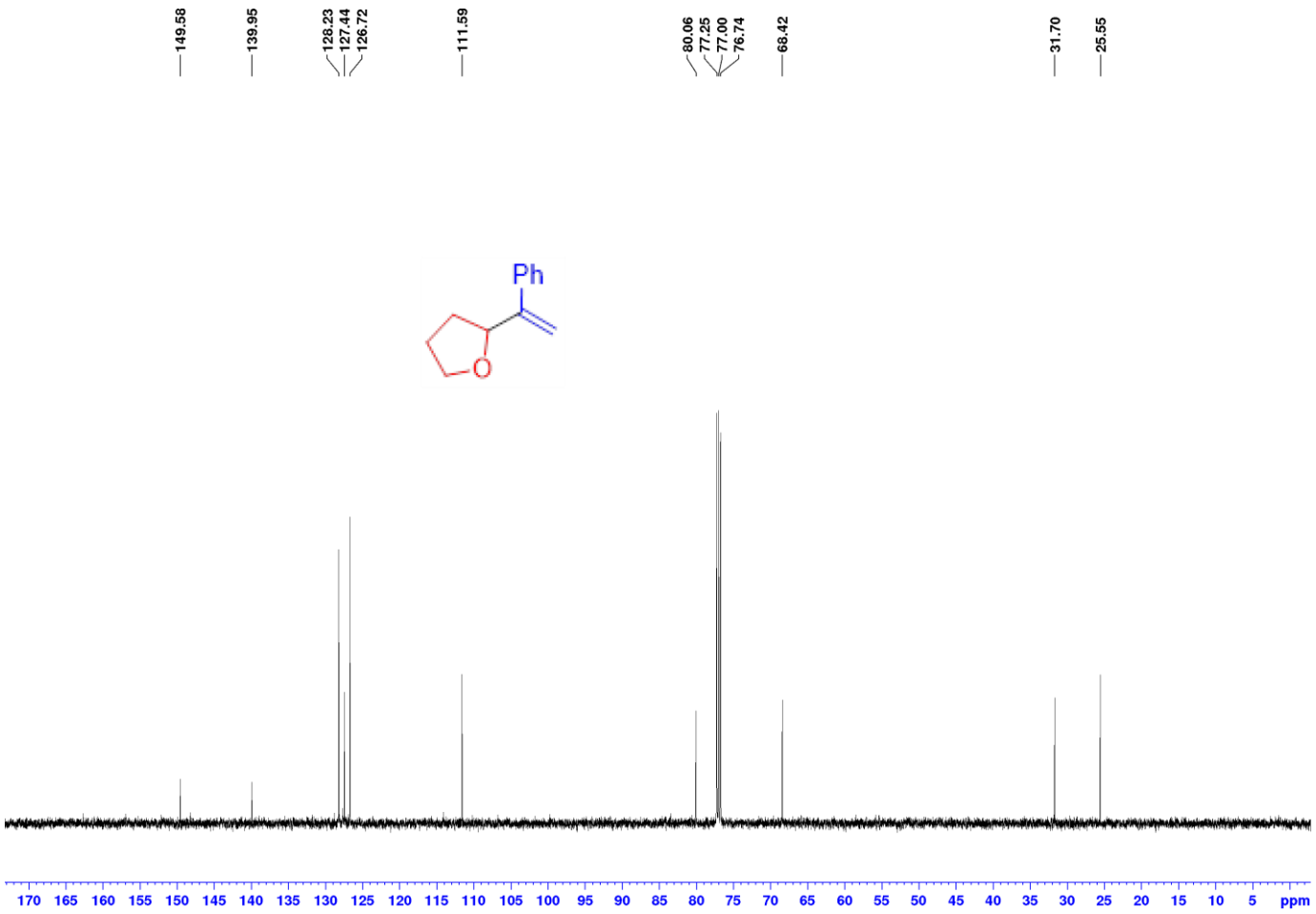
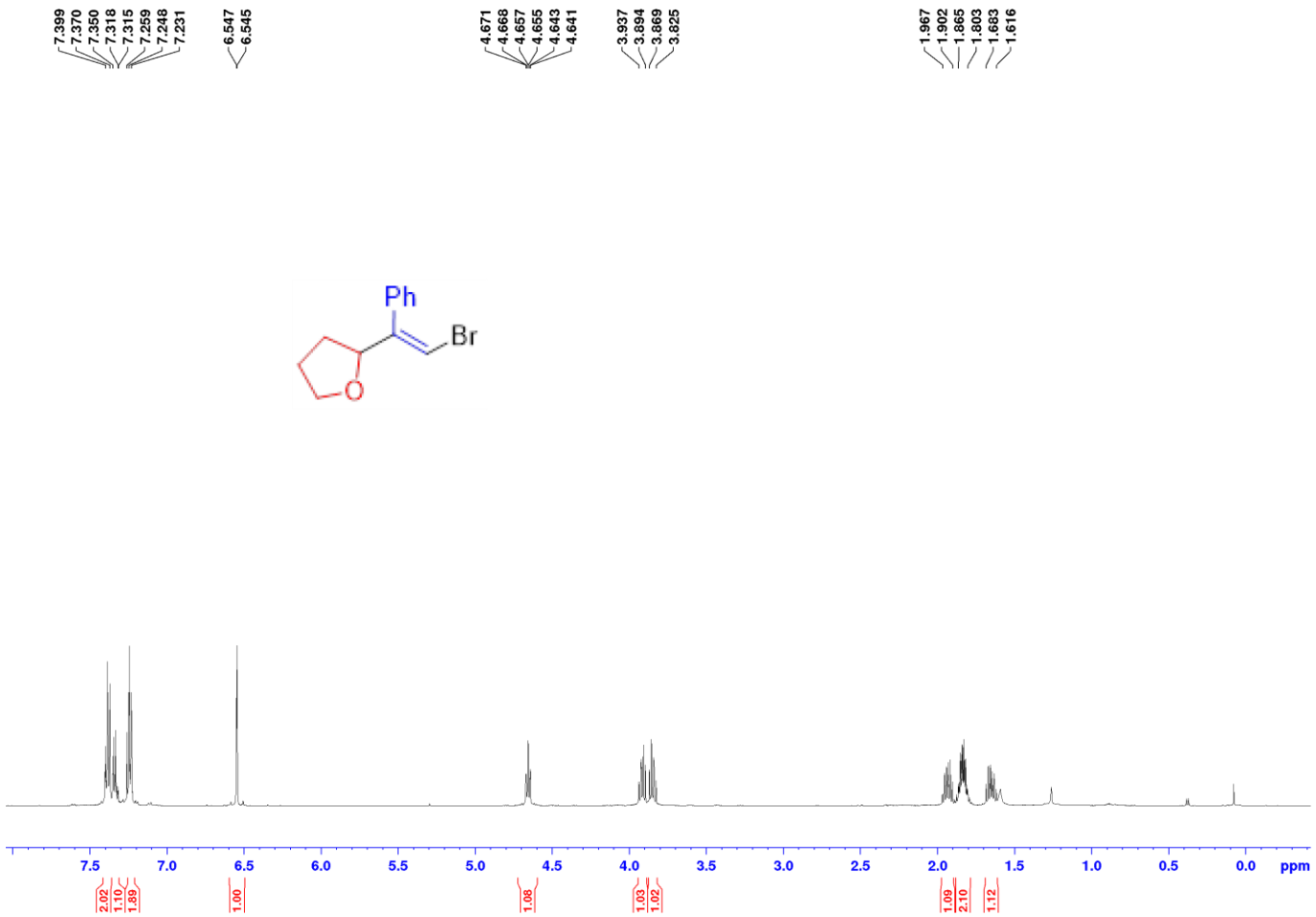
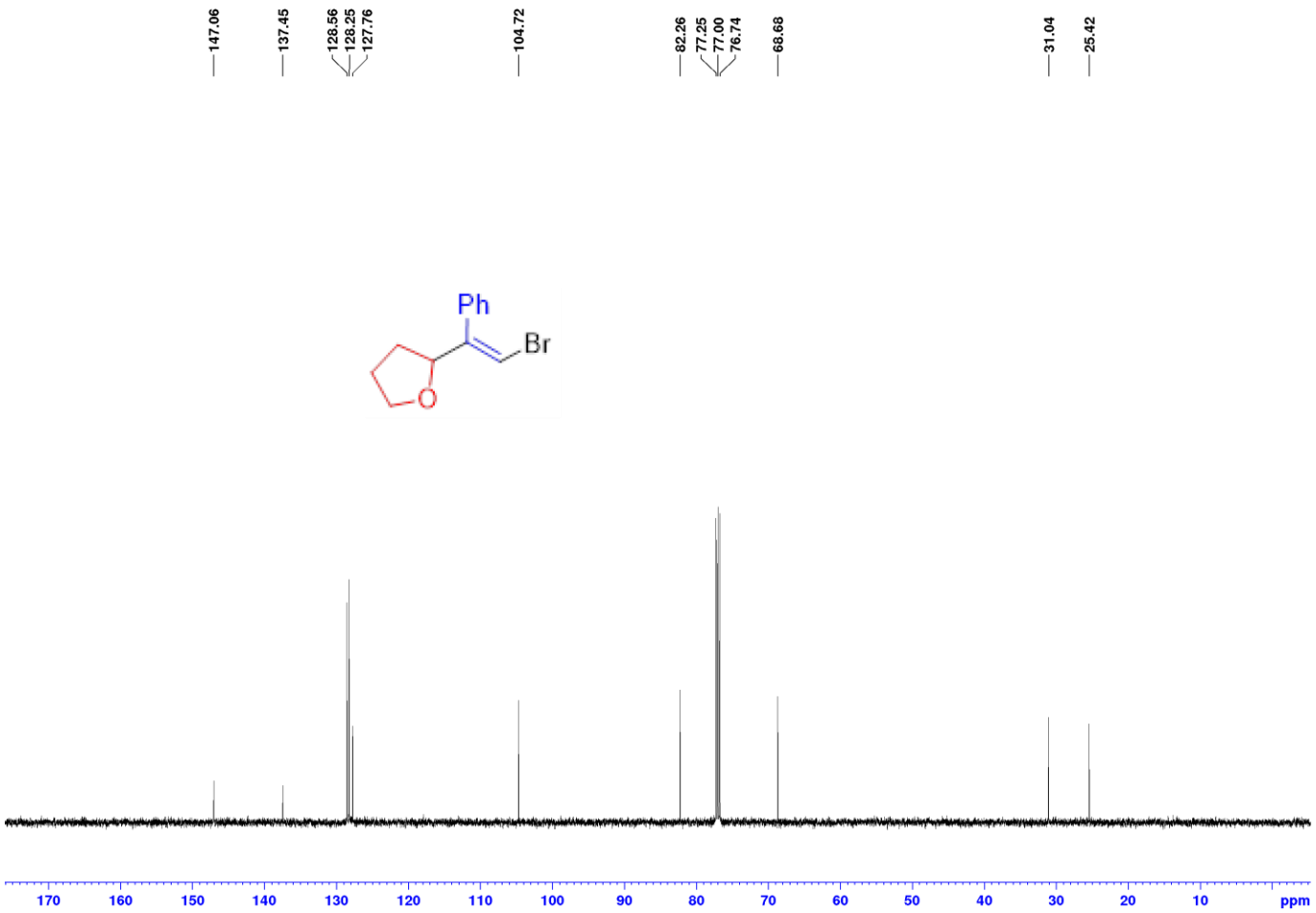
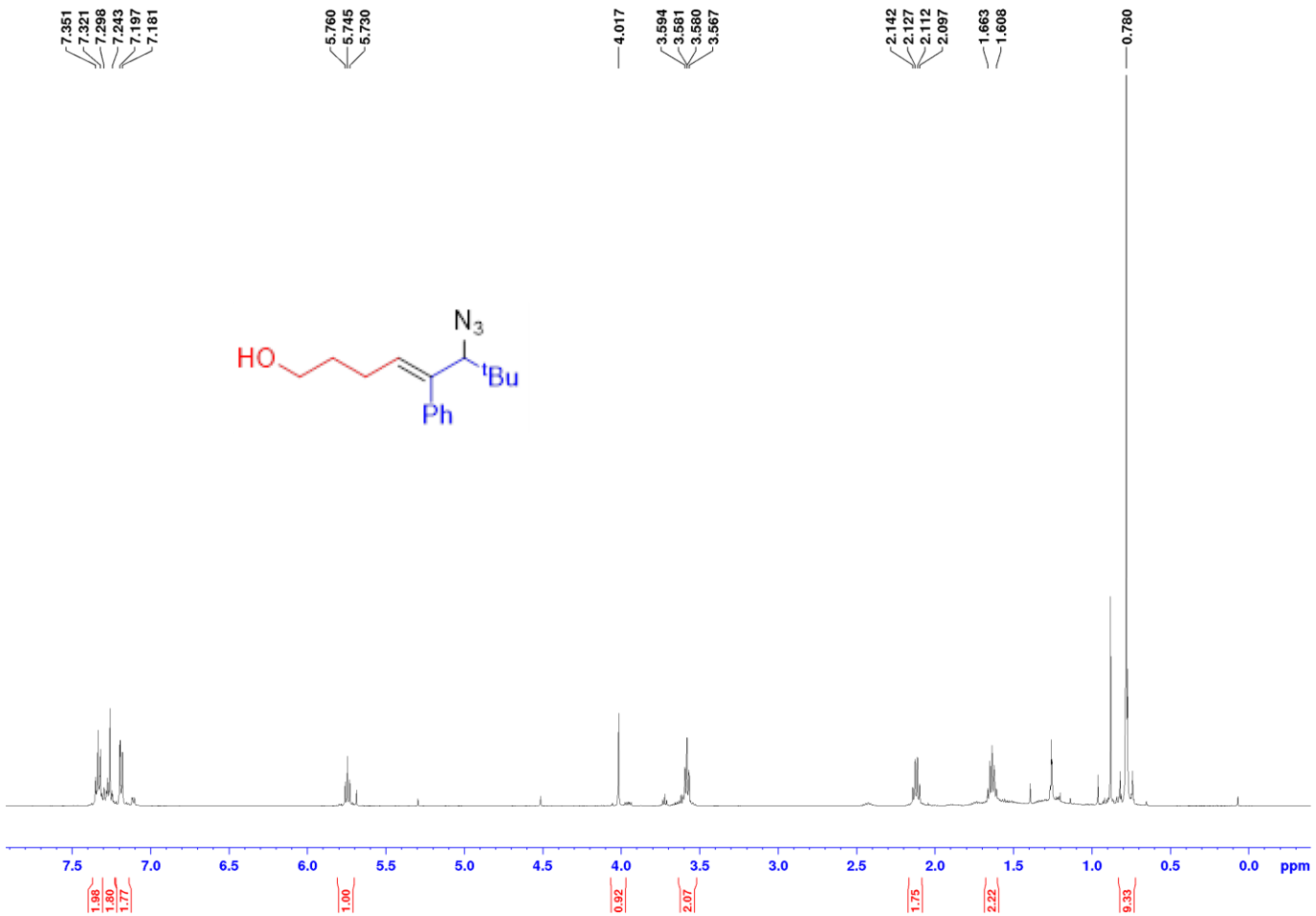
156.53
149.47
142.14
137.99
130.96
129.68
128.79
128.65
121.59
114.06
77.31
77.00
76.68
55.45
-0.79
Ph
SiMe3
H
N
O
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

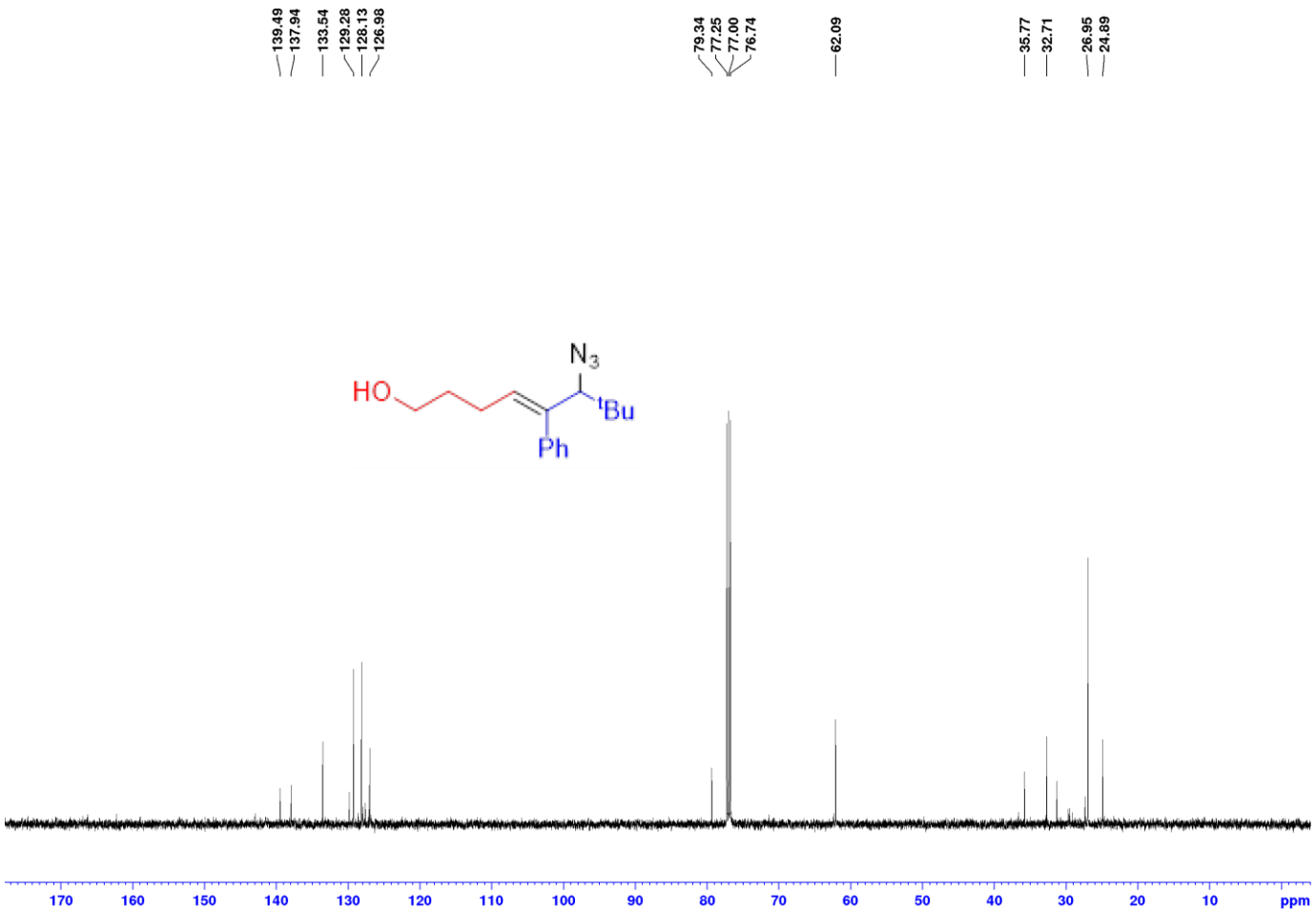

7.366
7.348
7.308
7.279
7.259
7.229
5.337
5.268
4.846
4.832
4.818
4.019
4.006
4.003
3.990
3.977
3.878
3.863
3.848
3.833
2.091
2.025
1.909
1.852
1.644
1.590
Ph
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.84
1.93
1.28
1.06
1.07
1.00
0.99
1.04
1.01
2.10
1.00

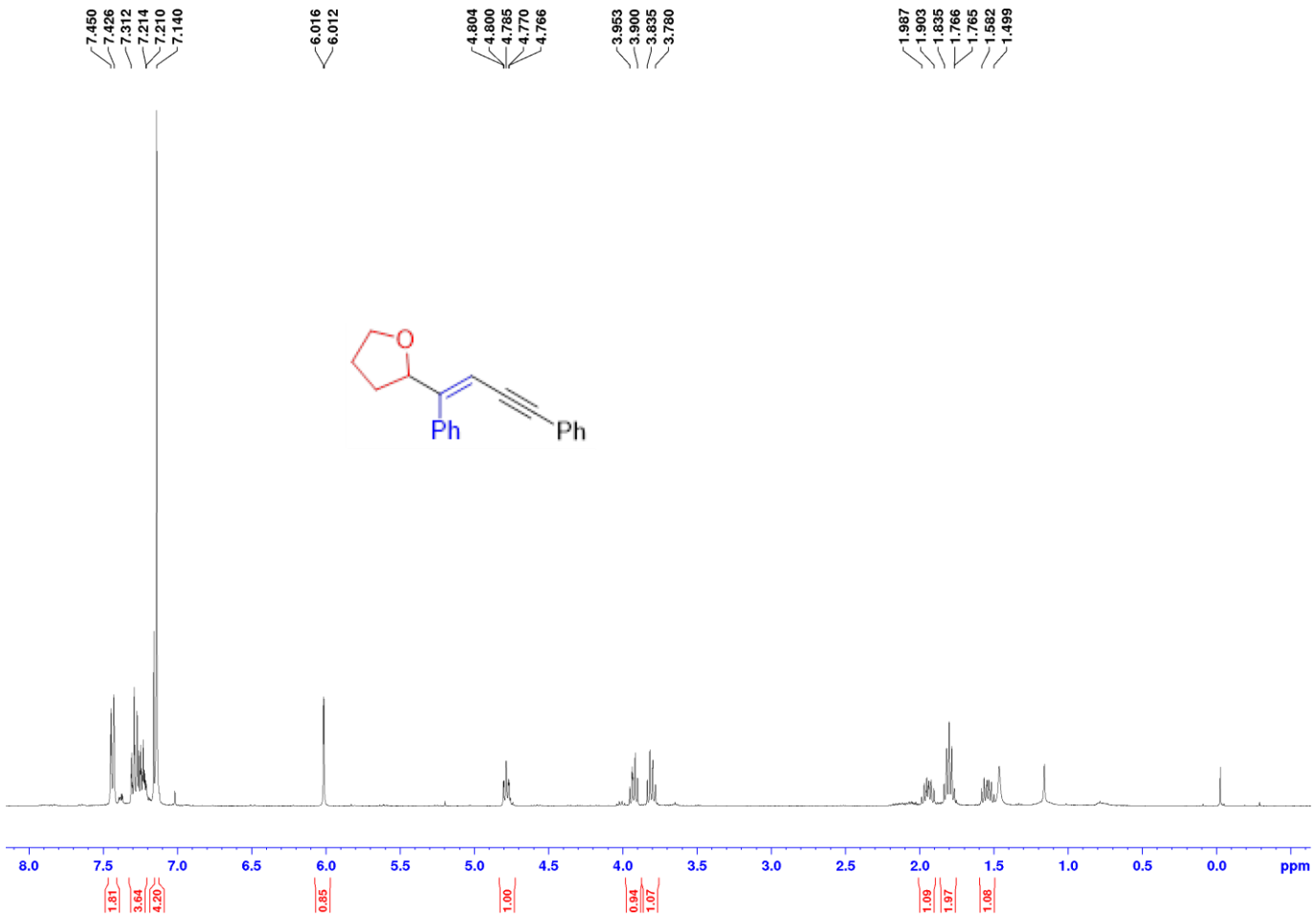

149.58
139.95
128.23
127.44
126.72
111.59
80.06
77.25
77.00
76.74
68.42
31.70
25.55
Ph
O
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

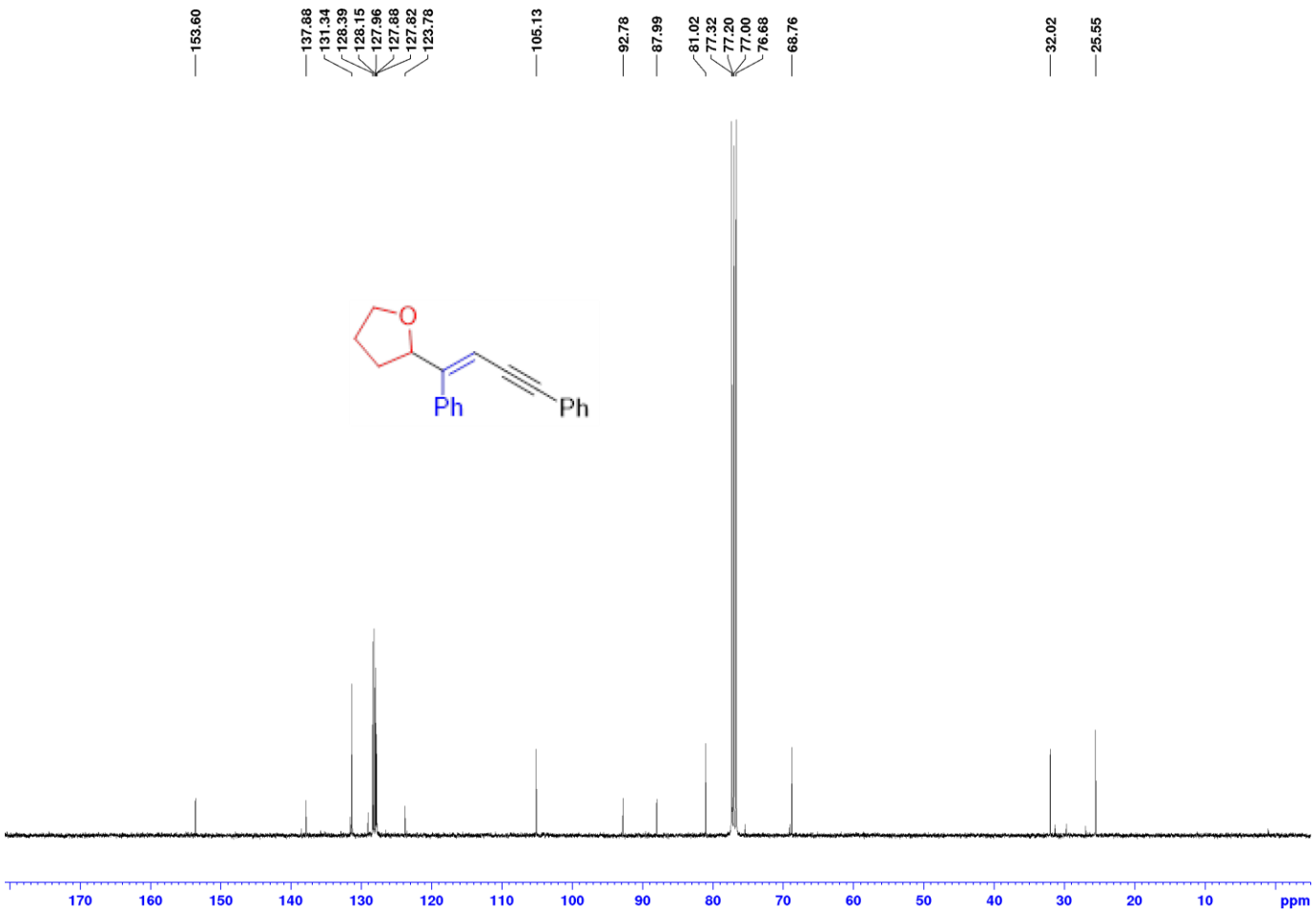

7.399
7.370
7.350
7.318
7.315
7.259
7.248
7.231
6.547
6.545
4.671
4.668
4.657
4.655
4.643
4.641
3.937
3.894
3.869
3.825
1.967
1.902
1.865
1.803
1.683
1.616
Ph
Br
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
1.10
1.89
1.00
1.08
1.03
1.02
1.09
2.10
1.12

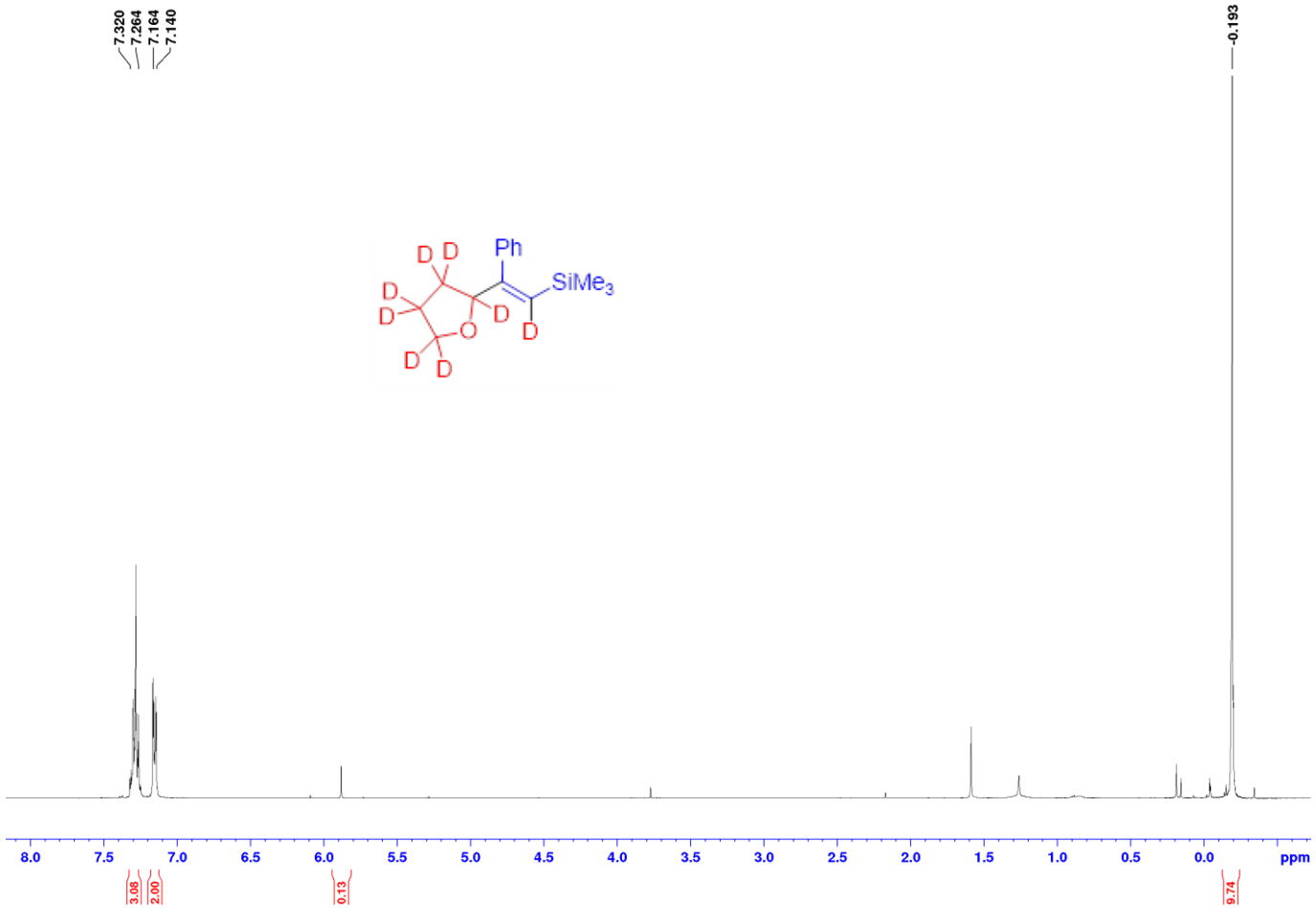

147.06
137.45
128.56
128.25
127.76
104.72
82.26
77.25
77.00
76.74
68.68
31.04
25.42
Ph
Br
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

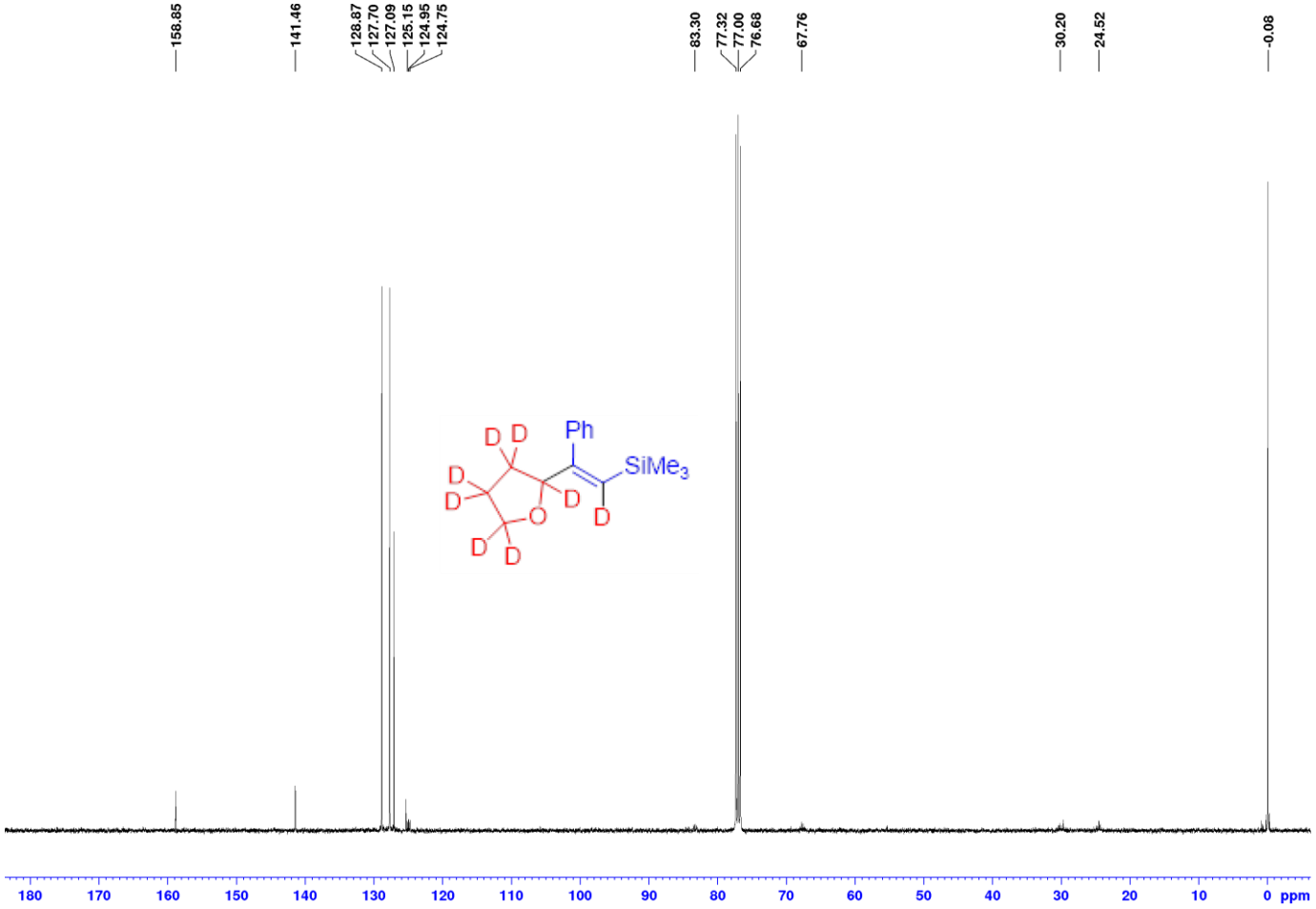

7.351
7.321
7.298
7.243
7.197
7.181
5.760
5.745
5.730
4.017
3.594
3.581
3.580
3.567
2.142
2.127
2.112
2.097
1.663
1.608
0.780
HO
N3
tBu
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.98
1.80
1.77
1.00
0.92
2.07
1.75
2.22
9.33


139.49
137.94
133.54
129.28
128.13
126.98
79.34
77.25
77.00
76.74
62.09
35.77
32.71
26.95
24.89
HO
N3
tBu
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

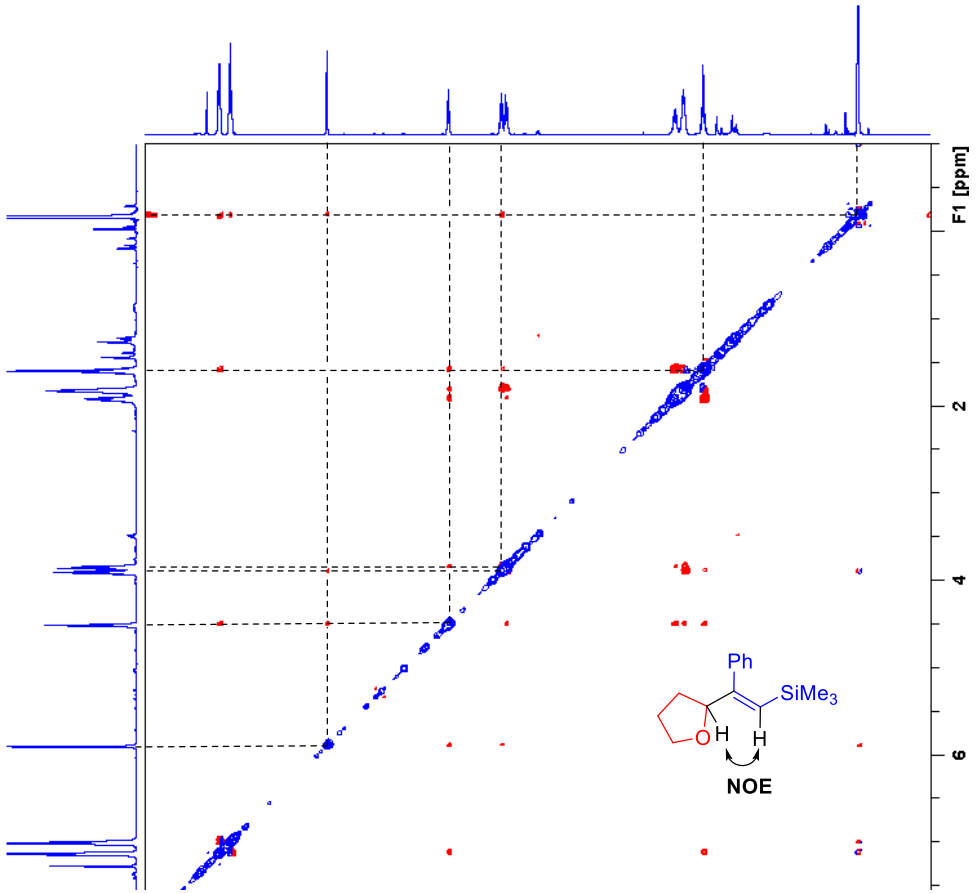

7.450
7.426
7.312
7.214
7.210
7.140
6.016
6.012
4.804
4.800
4.785
4.770
4.766
3.953
3.900
3.835
3.780
1.987
1.903
1.835
1.766
1.765
1.582
1.499
O
Ph
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.61
3.64
4.20
0.85
1.00
0.94
1.07
1.09
1.97
1.08

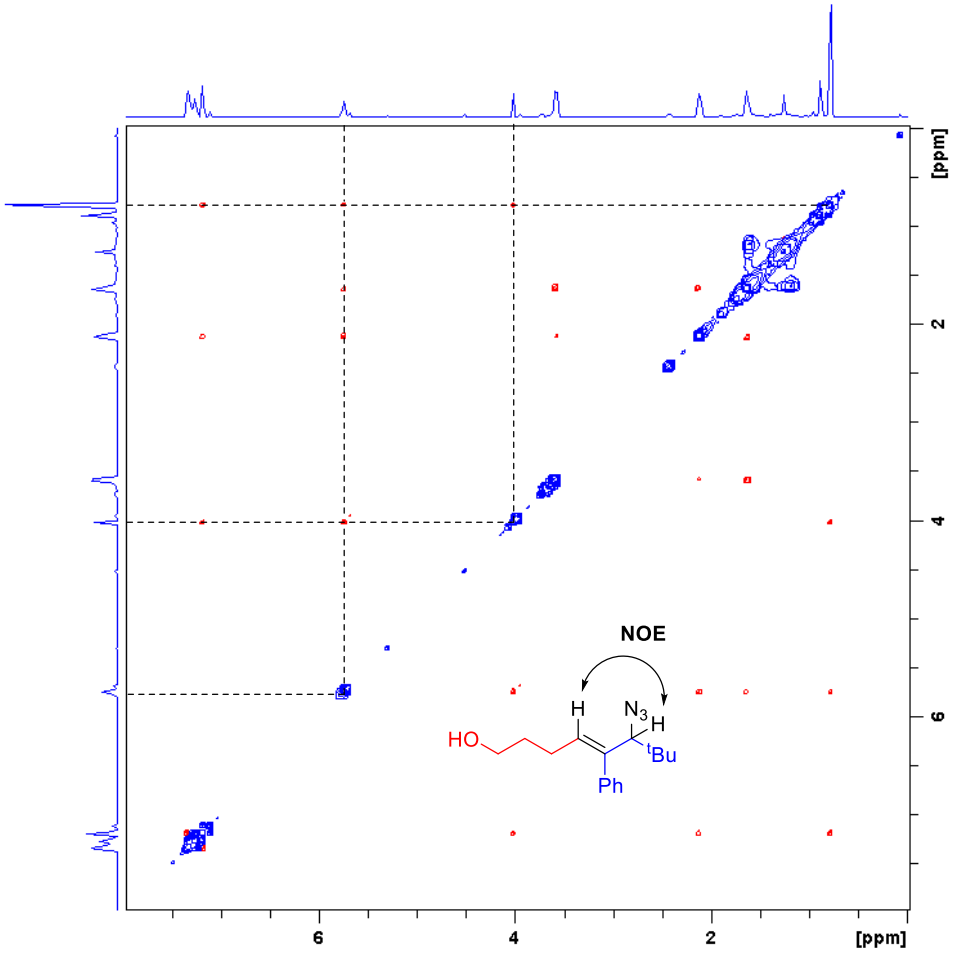

153.60
137.88
131.34
128.39
128.15
127.96
127.88
127.82
123.78
105.13
92.78
87.99
81.02
77.32
77.20
77.00
76.68
68.76
32.02
25.55
O
Ph
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.320
7.264
7.164
7.140
-0.193
D
D
Ph
SiMe3
D
D
D
O
D
D
D
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
ppm
3.08
2.00
0.13
9.74


158.85
141.46
128.87
127.70
127.09
125.15
124.95
124.75
83.30
77.32
77.00
76.68
67.76
30.20
24.52
-0.08
Ph
SiMe3
D
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

XV. NOESY Spectra of Representative Compounds




NOE
H
N3
H
HO
tBu
Ph
6
4
2
[ppm]
6
4
2
[ppm]