

Cyclopropenation of Internal Alkynylsilanes and Diazoacetates Catalyzed by Copper(I) *N*-Heterocyclic Carbene Complexes

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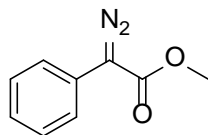
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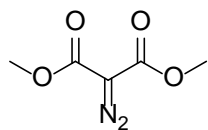
1. General Methods: Chemicals and Instrumentation

All organic chemicals and transition metal catalysts were ordered from Sigma-Aldrich. They were used as received and stored on benchtop in a desiccator over CaSO₄ when they were not in use. Bulk chemicals were obtained from the College of Science Chemistry Stockroom at the Rochester Institute of Technology. Diethyl ether and hexanes were obtained from Fisher Scientific (20 L) for column chromatography. All reactions were conducted under dry argon gas with anhydrous solvents from Sigma-Aldrich (Sure/Seal™). Ethyl diazoacetate was purchased from Sigma-Aldrich as a 15% solution in toluene and degassed with argon for 15 minutes. Infrared spectroscopic analyses were performed neat on a Shimadzu IR Prestige-21 Fourier Transform Infrared Spectrometer. High resolution mass spectral (HRMS) samples (<1mg) were dissolved in dichloromethane and sent for analysis on the Thermo Finnigan MAT 95XL Mass Spectrometer at State University of New York at Buffalo's Mass Spectrometry Facility. Nuclear Magnetic Resonance Spectroscopic data for ¹H and ¹³C NMR spectra was collected on RIT's Bruker Avance DRX-500 MHz NMR spectrometer. NMR chemical shifts are reported in ppm and referenced to the residual solvent peak CDCl₃ (δ = 7.26 ppm, ¹H; δ = 77.00 ppm ¹³C) as an internal standard or tetramethylsilane (δ = 0.00 ppm, ¹H) as an external standard. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz. All samples were dissolved in CDCl₃ with a TMS internal standard prior to analysis. X-ray crystallography samples were sent for analysis on a Bruker-AXS SMART Platform diffractometer equipped with an APEX II CCD detector at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester.

2. Diazoacetate Synthesis



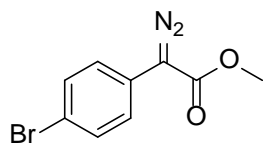
Methyl 2-diazo-2-phenylacetate (2a) To a solution of *p*-acetamidobenzenesulfonyl azide (19.5 g, 81.2 mmol), methyl phenylacetate (10 mL, 62.5 mmol) and ACN (200 mL) was added DBU (12.1 mL, 80.9 mmol) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et₂O (200 mL) and washed with saturated NH₄Cl (3 x 100 mL), dried with MgSO₄, filtered, and reduced *in vacuo* on a rotary evaporator. The crude residue was purified by column chromatography (SiO₂, 1/5: Et₂O/hexanes) to afford **2a** (7.06 g, 40.1 mmol, 64% yield) as a red oil. ¹H NMR (300 MHz, CDCl₃) δ 3.87 (s, 3H), 7.19 (t, 1H), 7.39 (t, 2H), 7.49 (d, *J* = 7.5 Hz, 2H). Compound **2a** is a known compound and the analytical data is consistent with the literature.¹



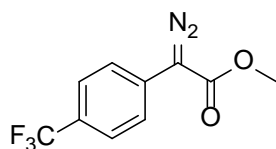
Dimethyl 2-diazomalonate (26c) To a solution of *p*-acetamidobenzenesulfonyl azide (10.0 g, 41.6 mmol), methyl malonate (5.00 g, 37.8 mmol), and ACN (95.0 mL) was added Et₃N (5.80 mL, 41.6 mmol) dropwise via syringe. The reaction mixture was stirred at 0°C and allowed to stir to room temperature overnight. The crude was then reduced *in vacuo* on a rotary evaporator and dissolved in 100mL of 50% Et₂O/hexanes. The mixture was then filtered through a plug of celite and washed with 50% Et₂O/hexanes (3 x 100 mL). Subsequently, the solvent removed *in vacuo* on a rotary evaporator and purified by column chromatography (SiO₂, 2/3: Et₂O/hexanes) to afford **26c** (2.59 g, 16.4 mmol, 39% yield) as a yellow oil. ¹H NMR (300 Hz,

¹ Zhao, W.J.; Yan, M.; Huang, D.; Ji, S-J. *Tetrahedron*, **2005**, *61*, 5585-5593.

CDCl₃) δ 3.85 (s, 6H). Compound **26c** is a known compound and the analytical data is consistent with the literature.²



methyl 2-(4-bromophenyl)-2-diazoacetate (27d) To a solution of *p*-acetamidobenzenesulfonyl azide (11.75 g, 48.84 mmol) and methyl 4-bromophenylacetate (10.17 g, 44.4 mmol) in ACN (100 mL) at 0°C, was added DBU (7.44 g, 48.84 mmol) dropwise over 1 hour. The reaction mixture was allowed to stir at room temperature for 16 hrs. The crude was diluted with Et₂O (200 mL) and washed with saturated NH₄Cl (3 x 100 mL), dried with MgSO₄, filtered, and reduced *in vacuo* on a rotary evaporator. The crude residue was purified by column chromatography (SiO₂, 1/5: Et₂O/hexanes) to afford **27d** (9.6 g, 37.6 mmol, 85% yield) as an orange solid. ¹H NMR (300 MHz, CDCl₃): δ 3.87 (s, 3H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H). Compound **27d** is a known compound and the analytical data is consistent with the literature.³

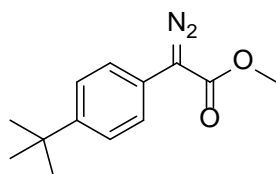


methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (28e) In a flamed dried and argon purged round bottom (100 mL) charged with methanol was added SOCl₂ (1.533 g, 12.89 mmol) dropwise at 0°C. After 15 minutes, 4-(Trifluoromethyl)phenylacetic acid (2.63 g, 12.89 mmol) was added and allowed to stir to room temperature for 16 hrs. The reaction mixture was diluted with an aqueous saturated solution of NaHCO₃ (100 mL) and washed with Et₂O (3 x 50 mL). The organic layers were collected, dried over MgSO₄, and concentrated to dryness with a rotary evaporator. ¹H NMR (300 MHz, CDCl₃) indicated a

² Ramachary, D.; Narayana, V.; Ramakumar, K. *Tetrahedron Lett.* **2008**, *49*, 2704-2709.

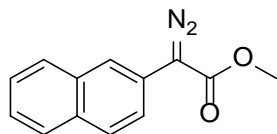
³ Yu, W.Y.; Tsoi, Y.T.; Zhou, Z.; Chan, A.S.C. *Org. Lett.* **2009**, *11*, 469-472.

clean conversion and was used as is. To a solution of *p*-acetamidobenzenesulfonyl azide (4.65 g, 19.3 mmol), methyl phenylacetate (2.8 g, 12.89 mmol) and ACN (25 mL) was added DBU (2.94 g, 19.3 mmol) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et₂O (100 mL) and washed with saturated NH₄Cl (3 x 100 mL), dried with MgSO₄, filtered, and reduced *in vacuo* on a rotary evaporator. Purified by column chromatography (SiO₂, 1/5: Et₂O/hexanes) to afford **28e** (1.982 g, 8.12 mmol, 63% yield) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ 3.89 (s, 3H), 7.62 (s, 4H). Compound **28e** is a known compound and the analytical data is consistent with the literature.⁴

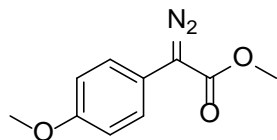


methyl 2-(4-(tert-butyl)phenyl)-2-diazoacetate (29f) To a solution of *p*-acetamidobenzenesulfonyl azide (34.98 g, 145.4 mmol), methyl 4-(*tert*-butyl)phenylacetate (25 g, 121.2 mmol) and ACN (330 mL) was added DBU (22.14 g, 145.4 mmol) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et₂O (500 mL) and washed with saturated NH₄Cl (3 x 200 mL), dried with MgSO₄, filtered, and reduced *in vacuo* on a rotary evaporator. The crude residue was purified by column chromatography (SiO₂, 1/5: Et₂O/hexanes) to afford **29f** (14.35 g, 61.81 mmol, 51% yield) as an orange solid. IR (neat) 1705, 2081 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.41 (s, 4H), 3.86 (s, 3H), 1.32 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz) δ = 31.25, 34.45, 51.95, 122.16, 124.04, 125.96, 149.11, 165.87. HRMS (ESI) *m/z* calcd for C₁₇H₂₆Si, 232.12, found 232.12112 [M⁺].

⁴ Rubina, M.; Woodward, E.W.; Rubin, M. *Org. Lett.* **2007**, *9*, 5501-5504.



methyl 2-diazo-2-(naphthalen-2-yl)acetate (30g) In a flamed dried and argon purged round bottom (250 mL) charged with acetone (100 mL) was added 2-naphthylacetic acid (5.46 g, 29.35 mmol) and CsCO₃ (6.50 g, 19.95 mmol). A reflux condenser and methyl iodide was added to the reaction vessel and it was allowed to stir at 60°C for 16 hrs. The reaction mixture was concentrated under reduced vacuum with a rotary evaporator, diluted with Et₂O (100 mL), washed with a saturated solution of NaHCO₃ (2 X 100 mL), dried over MgSO₄, filtered, and concentrated to dryness under reduced vacuum with a rotary evaporator. ¹H NMR (300 MHz, CDCl₃) indicated a clean conversion and was used as is. To a solution of *p*-acetamidobenzenesulfonyl azide (9.64 g, 40.0 mmol), methyl 2-naphthylacetate (5.35 g, 26.72 mmol) and ACN (50 mL) was added DBU (6.10 g, 40.0 mmol) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et₂O (100 mL) and washed with saturated NH₄Cl (2 x 100 mL), dried with MgSO₄, filtered, and reduced *in vacuo* on a rotary evaporator. The crude residue was purified by column chromatography (SiO₂, 1/5: Et₂O/hexanes) to afford **30g** (3.57 g, 15.7 mmol, 59% yield) as an orange solid. ¹H NMR (300 MHz, CDCl₃): δ 3.91 (s, 3H), 7.55 - 7.44 (m, 3H), 7.86 - 7.80 (m, 3H), 8.02 (s, 1H). Compound **30g** is a known compound and the analytical data is consistent with the literature.⁵



methyl 2-diazo-2-(4-methoxyphenyl)acetate (31h) In an argon purged round bottom (25 mL) charged with water (3 mL) was added NaOH (300 mg, 7.5 mmol) and cooled to 0°C. After 15 minutes, 4-hydroxyphenylacetic acid (500 mg, 3.28 mmol) was added while stirring and Me₂SO₄ (946 mg 7.5 mmol) was added via syringe pump at 1 mL/hr. The ice bath was removed and allowed to stir to room temperature

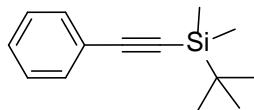
⁵ Chan, W.W.; Yeung, S.H.; Zhou, Z.; Chan, A.S.C.; Yu, W.Y. *Org. Lett.* **2010**, *12*, 604-607.

for 16 hrs. The reaction mixture was diluted with an aqueous saturated solution of NaHCO₃ (10 mL) and washed with Et₂O (3 x 5 mL). The organic layers were collected, dried over MgSO₄, and concentrated to dryness with a rotary evaporator. ¹H NMR (300 MHz, CDCl₃) indicated a clean conversion and was used as is. To a solution of *p*-acetamidobenzenesulfonyl azide (788 mg, 3.28 mmol), methyl (4-methoxyphenyl)acetate (591 mg, 3.28 mmol) and ACN (15 mL) was added DBU (500 mg, 3.28 mmol) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et₂O (25 mL) and washed with saturated NH₄Cl (3 x 10 mL), dried with MgSO₄, filtered, and reduced *in vacuo* on a rotary evaporator. The crude residue was purified by column chromatography (SiO₂, 1/5: Et₂O/hexanes) to afford **31h** (350 mg, 1.70 mmol, 52% yield) as a red solid. ¹H NMR (300 MHz, CDCl₃): δ H 3.80 (s, 3H), 3.84 (s, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H). Compound **31h** is a known compound and the analytical data is consistent with the literature.⁶

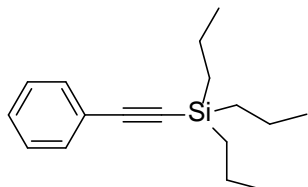
3. Synthetic Procedure and Characterization of Internal Alkynylsilanes

A 1M solution of phenylacetylene (1.00 eq) in THF was cooled to -78°C and a 1.0 M solution of *n*-butyllithium (1.1 eq) in hexanes was added dropwise over 1 hr. After stirring for 30 minutes, an appropriate 1.0 M solution of silyl chloride (1.2 eq) in THF was added dropwise via cannula. The reaction mixture was then allowed to warm to room temperature overnight. A cold saturated solution of NH₄Cl in water was carefully added and the resultant solution was washed with diethyl ether (3x), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude oil was fractionally distilled under reduced pressure to afford the product.

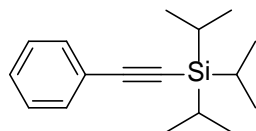
⁶ Chan, W.W.; Yeung, S.H.; Zhou, Z.; Chan, A.S.C.; Yu, W.Y. *Org. Lett.* **2010**, *12*, 604-607.



tert-butyl dimethyl(phenylethynyl)silane (6) (2.22 g, 10.3 mmol, 89% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 0.32 (s, 6H); 1.26 (s, 9H); 7.44 - 1.52 (m, 6H); 7.25 - 7.49 (m, 3H). Compound **6** is a known compound and the analytical data is consistent with the literature.⁷



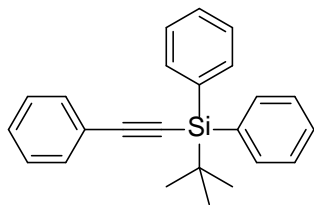
(phenylethynyl)-tripropylsilane (7) (5.22 g, 20.19 mmol, 78% yield). IR (neat) 2149 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 0.64 - 0.70 (m, 6H); 1.01 (t, 9H); 1.44-1.52 (m, 6H); 7.25 - 7.30 (m, 3H); 7.44 - 7.47 (m, 2H). $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz) δ = 16.12, 17.55, 18.21, 92.39, 106.32, 123.43, 128.15, 128.31, 131.98. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{Si}$, 258.18, found 258.179.



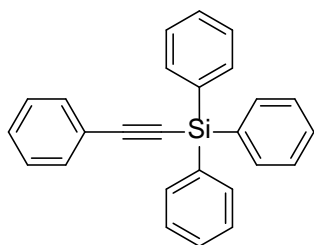
triisopropylphenylethynylsilane (8) (5.27 g, 20.39 mmol, 79% yield) as an oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 1.13 (s, 21H), 7.26 - 7.30 (m, 3H), 7.46-7.48 (m, 2H). Compound **8** is a known compound and the analytical data is consistent with the literature.⁸

⁷ Fitzmaurice, N.J.; Jackson, W.R.; Perlmutter, P.; *J. Organomet. Chem.*, **1985**, 285, 375-381.

⁸ Komaromi, A.; Novak, Z. *Chem. Commun.* **2008**, 40, 4968-70.



tert-butyl(diphenyl)(phenylethynyl)silane (9) (2.019 g, 6.18 mmol, 85% yield) as an oil. ^1H NMR (500 MHz, CDCl_3) δ 1.14 (s, 9H), 7.33 – 7.42 (m, 9H), 7.58 – 7.61 (m, 2H), 7.85 – 7.87 (m, 4H). Compound **9** is a known compound and the analytical data is consistent with the literature.⁹



triphenyl(phenylethynyl)silane (10) (3.47 g, 9.62 mmol, 94% yield) as an oil. ^1H NMR (500 MHz, CDCl_3) δ 7.23– 7.72 (m, 20H). ^{13}C NMR (CDCl_3 , 125 MHz) δ = 89.03, 109.57, 122.75, 127.98, 128.27, 129.03, 129.92, 132.25, 133.58, 135.60. Compound **10** is a known compound and the analytical data is consistent with the literature.¹⁰

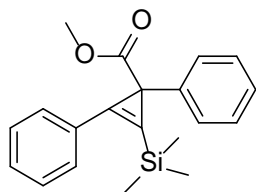
General Procedure for Cu(I)-Catalyzed Cycloaddition

A flame-dried round bottom (50 mL) equipped with a reflux condenser was charged with a solution of alkynylsilane (1.00 mmol, 1 eq) in anhydrous α,α,α -trifluorotoluene (CF_3Ph , 2 mL). The appropriate transition-metal salt (0.05 mmol, 0.05 eq) was added and allow stir 10 minutes at an oil bath temperature ranging from 100 - 110°C. The appropriate diazoacetate (3.00 mmol, 3 eq) was dissolved in anhydrous CF_3Ph (20 mL) and syringe pumped over a 24 hour period at a rate of 1.00 mL/min. The reaction mixture

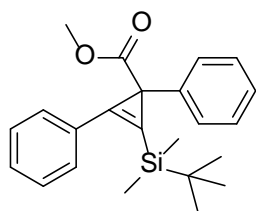
⁹ Yamaguchi, K.; Wang, Y.; Oishi, T.; Kuroda, Y.; Mizuno, N. *Angew. Chem., Int. Ed.*, **2013**, 52, 5627-30.

¹⁰ Selina, A.A.; Karlov, S.S.; Gauchenova, E.V.; Churakov, A.V.; Kuz'mina, L.G.; Howard, J.A.K.; Lorberth, J.; Zaitseva, G.S. *Heteroat. Chem.* **2004**, 15, 43-56.

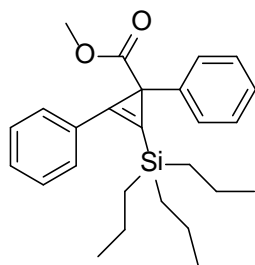
was then cooled to room temperature and the concentrated under reduced pressure to afford a crude oil. It was dissolved in toluene (10 mL) and dry mounted on silica gel prior to chromatography.



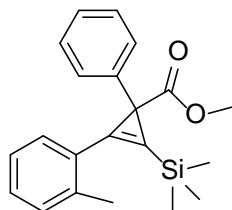
methyl 1,2-diphenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (5a) Purified by column chromatography (SiO₂, 1/10 - 1/5 : Et₂O/hexanes) to afford **5a** as an oil (272 mg, 0.84 mmol, 84% yield). R_f = 0.45; 1/5; Et₂O/hexanes. IR (neat) 1715 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.67 (s, 3H), 7.14 - 7.19 (m, 1H), 7.22-7.25 (m, 2H), 7.34 - 7.43 (m, 5H), 7.58 - 7.61 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.04, 34.63, 51.78, 113.71, 125.91, 126.07, 127.11, 127.84, 128.04, 129.70, 129.78, 141.93, 175.35. HRMS (ESI) *m/z* calcd for C₂₀H₂₂O₂Si, 322.14, found 322.1384 [M]⁺.



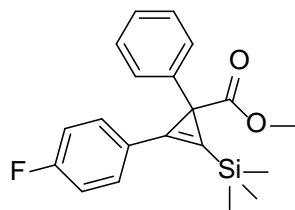
methyl 2-(tert-butyl dimethylsilyl)-1,3-diphenylcycloprop-2-ene-1-carboxylate (11a) Purified by column chromatography (SiO₂, 1/10 : Et₂O/hexanes) to afford **11a** as an oil (295 mg, 0.81 mmol, 81% yield). R_f = 0.44; 1/5; Et₂O/hexanes. IR (neat) 1717 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.21 (d, 6H), 0.91 (s, 9H), 3.67 (s, 3H), 7.12 - 7.16 (m, 1H), 7.20 - 7.24 (m, 2H), 7.33 - 7.44 (m, 5H), 7.62 - 7.64 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -5.30, -5.16, 17.12, 26.20, 34.36, 51.67, 113.52, 125.82, 126.0, 127.23, 127.77, 128.03, 128.93, 129.71, 129.78, 142.04, 175.30. HRMS (ESI) *m/z* calcd for C₂₃H₂₈O₂Si, 364.19, found 364.1860 [M]⁺.



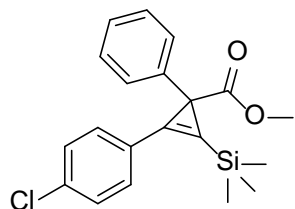
methyl 1,2-diphenyl-3-(triisopropylsilyl)cycloprop-2-ene-1-carboxylate (12a) Purified by column chromatography (SiO₂, 1/50; Et₂O/hexanes) to afford **12a** as an oil (34 mg, 0.084 mmol, 8% yield). R_f = 0.27; 1/5; Et₂O/hexanes. IR (neat) 1717 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.71 – 0.78 (m, 6H), .9102 (t, 9H), 1.26 – 1.38 (m, 6H), 3.66 (s, 3H), 7.12 – 7.16 (m, 1H), 7.20 – 7.26 (m, 2H), 7.33 – 7.45 (m, 5H), 7.58 – 7.60 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 15.44, 17.26, 18.31, 34.32, 51.71, 113.0, 125.81, 126.04, 127.33, 127.77, 128.03, 128.95, 129.64, 129.71, 142.09, 175.43. HRMS (ESI) *m/z* calcd for C₂₆H₃₄O₂Si, 406.23, found 406.2329 [M]⁺.



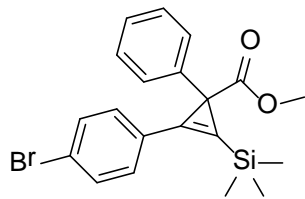
methyl 1-phenyl-2-(o-tolyl)-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (13a) Purified by column chromatography (SiO₂, 1/20 : Et₂O/hexanes) to afford **13a** as an oil (238 mg, 0.71 mmol, 71% yield). R_f = 0.46; 1/5; Et₂O/hexanes. IR (neat) 1715 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 9H), 2.54 (s, 3H), 3.69 (s, 3H), 7.13 – 7.16 (m, 1H), 7.21 – 7.31 (m, 5H), 7.33 – 7.36 (m, 2H), 7.47 – 7.48 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ -0.60, 20.57, 33.22, 51.76, 114.17, 122.58, 125.70, 126.00, 126.21, 127.78, 127.94, 129.68, 130.36, 131.17, 139.10, 142.20, 175.57. HRMS (ESI) *m/z* calcd for C₂₁H₂₄O₂Si, 336.15, found 336.1540 [M]⁺.



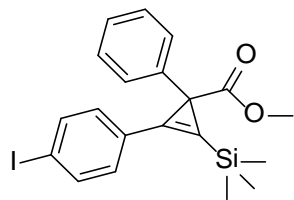
methyl 2-(4-fluorophenyl)-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (14a) Purified by column chromatography (SiO₂, 1/100 – 1/20 : Et₂O/hexanes) to afford **14a** as a solid m.p. (°C) 64-72 (119 mg, 0.35 mmol, 35% yield). R_f = 0.54; 1/5; Et₂O/hexanes. IR (neat) 1717 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.68 (s, 3H), 7.09 – 7.18 (m, 3H), 7.23 – 7.26 (m, 2H), 7.31 – 7.34 (m, 2H), 7.55 – 7.59 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.02, 34.70, 51.85, 113.07, 116.24 (d, J_{C-F} = 21.3 Hz), 123.46 (d, J_{C-F} = 2.4 Hz), 125.14, 126.01, 127.91, 127.94, 131.71 (d, J_{C-F} = 8.8 Hz), 141.72, 163.50 (d, J_{C-F} = 250.0 Hz), 175.23. HRMS (ESI) *m/z* calcd for C₂₀H₂₁FO₂Si, 340.13, found 340.1289 [M]⁺.



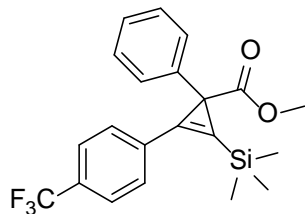
methyl 2-(4-chlorophenyl)-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (15a) Purified by column chromatography (SiO₂, 1/100 – 1/10 : Et₂O/hexanes) to afford **15a** as a solid m.p. (°C) 95 - 100 (160 mg, 0.45 mmol, 45% yield). R_f = 0.40; 1/5; Et₂O/hexanes. IR (neat) 1715 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.67 (s, 3H), 7.14 – 7.18 (m, 1H), 7.22 – 7.26 (m, 2H), 7.30 – 7.33 (m, 2H), 7.38 – 7.40 (m, 2H), 7.50 – 7.53 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.07, 34.68, 51.85, 114.67, 125.09, 125.68, 126.05, 127.92, 129.23, 130.89, 135.67, 141.58, 175.09. HRMS (ESI) *m/z* calcd for C₂₀H₂₁ClO₂Si, 356.10, found 356.0991 [M]⁺.



methyl 2-(4-bromophenyl)-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (16a) Purified by column chromatography (SiO₂, 1/100 – 1/10 : Et₂O/hexanes) to afford **16a** as an oil (99.1 mg, 0.25 mmol, 25% yield). $R_f = 0.48$; 1/5; Et₂O/hexanes. IR (neat) 1721 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.67 (s, 3H), 7.14 – 7.18 (m, 1H), 7.22 – 7.27 (m, 2H), 7.30 – 7.33 (m, 2H), 7.43 – 7.46 (m, 2H), 7.54 – 7.57 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -7.30, 28.45, 45.65, 108.78, 117.78, 118.95, 119.85, 119.91, 121.71, 124.88, 125.98, 135.33, 168.85. HRMS (ESI) m/z calcd for C₂₀H₂₁BrO₂Si, 400.05, found 400.0492 [M]⁺.

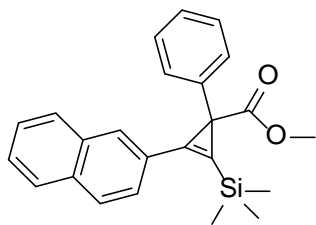


methyl 2-(4-iodophenyl)-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (17a) Purified by column chromatography (SiO₂, 1/100 – 1/10 : Et₂O/hexanes) to afford **17a** as a solid m.p. (°C) 113 - 115 (17.2 mg, 0.038 mmol, 3.8% yield). $R_f = 0.48$; 1/5; Et₂O/hexanes. IR (neat) 1717 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 9H), 3.67 (s, 3H), 7.16 – 7.18 (m, 1H), 7.22 – 7.25 (m, 2H), 7.29 – 7.32 (m, 4H), 7.75 – 7.77 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.09, 34.63, 51.87, 95.88, 115.34, 125.29, 126.07, 126.66, 127.93, 131.16, 138.16, 141.55, 175.06. HRMS (ESI) m/z calcd for C₂₀H₂₁IO₂Si, 448.04, found 448.0353 [M]⁺.

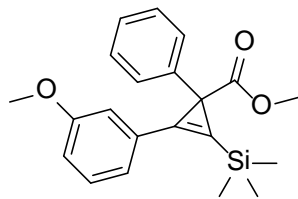


methyl 1-phenyl-2-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate

(18a) Purified by column chromatography (SiO₂, 1/100 – 1/5 : Et₂O/hexanes) to afford **18a** as an oil (191 mg, 0.49 mmol, 49% yield). R_f = 0.44; 1/5; Et₂O/hexanes. IR (neat) 1720 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.30 (s, 9H), 3.69 (s, 3H), 7.16 – 7.20 (m, 1H), 7.21 – 7.27 (m, 2H), 7.29 – 7.33 (m, 2H), 7.64 – 7.73 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ -1.12, 34.87, 51.94, 117.62, 125.13, 125.89 (d, J_{C-F} = 32.6 Hz), 126.10 (q, J_{C-F} = 271.3), 126.21, 127.91, 128.01, 128.10, 129.82, 130.64 (d, J_{C-F} = 32.6), 141.30, 174.87. HRMS (ESI) *m/z* calcd for C₂₁H₂₁F₃O₂Si, 390.13, found 390.1261 [M]⁺.

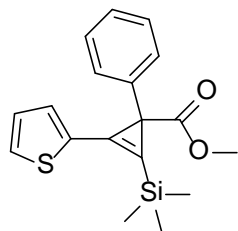


methyl 2-(naphthalen-2-yl)-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (19a) Purified by column chromatography (SiO₂, 1/50 – 1/5 : Et₂O/hexanes) to afford **19a** as an oil (216 mg, 0.579 mmol, 58% yield). R_f = 0.24; 1/5; Et₂O/hexanes. IR (neat) 1715 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.35 (s, 9H), 3.69 (s, 3H), 7.14 – 7.16 (m, 1H), 7.21 – 7.25 (m, 1H), 7.40 – 7.42 (m, 2H), 7.48 – 7.51 (m, 2H), 7.55 – 7.64 (m, 2H), 7.68 – 7.70 (m, 1H), 7.88 – 7.92 (m, 2H), 8.48 – 8.50 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ -0.71, 30.93, 32.72, 51.82, 115.30, 121.89, 123.53, 124.77, 125.68, 125.80, 126.39, 126.88, 127.83, 128.02, 128.64, 130.08, 130.43, 131.90, 133.65, 141.88, 175.47. HRMS (ESI) *m/z* calcd for C₂₄H₂₄O₂Si, 372.15, found 372.1618 [M]⁺.

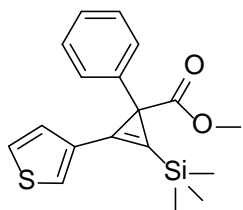


methyl 2-(3-methoxyphenyl)-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (20a)

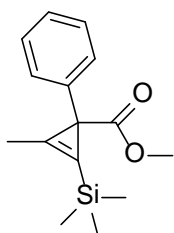
Purified by column chromatography (SiO₂, 1/20 : Et₂O/hexanes) to afford **20a** as an oil (201 mg, 0.57 mmol, 57% yield). R_f = 0.36; 1/5; Et₂O/hexanes. IR (neat) 1713 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.67 (s, 3H), 3.82 (s, 3H), 6.92 – 6.92 (m, 1H), 7.11 – 7.25 (m, 5H), 7.32 – 7.36 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ -1.04, 34.83, 51.82, 55.31, 114.30, 114.69, 115.69, 122.32, 125.94, 126.12, 127.87, 128.07, 128.35, 129.94, 141.91, 159.83, 175.31. HRMS (ESI) *m/z* calcd for C₂₁H₂₄O₃Si, 352.15, found 352.1491 [M]⁺.



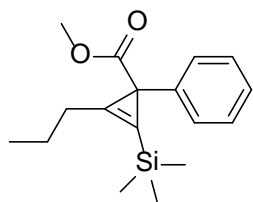
methyl 1-phenyl-2-(thiophen-2-yl)-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (21a) Purified by column chromatography (SiO₂, 1/100 – 1/20 : Et₂O/hexanes) to afford **21a** as an oil (161 mg, 0.49 mmol, 49% yield). R_f = 0.45; 1/5; Et₂O/hexanes. IR (neat) 1713 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 9H), 3.67 (s, 3H), 7.15 – 7.18 (m, 1H), 7.23 – 7.26 (m, 2H), 7.30 – 7.38 (m, 4H), 7.55 – 7.56 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ -1.07, 34.64, 51.84, 110.94, 121.01, 126.00, 126.70, 127.66, 127.90, 128.08, 128.20, 128.67, 141.92, 175.30. HRMS (ESI) *m/z* calcd for C₁₈H₂₀O₂SSi, 328.10, found 328.1026 [M]⁺.



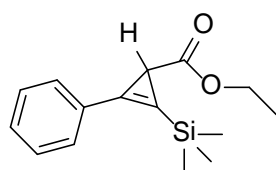
methyl 1-phenyl-2-(thiophen-3-yl)-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (22a) Purified by column chromatography (SiO₂, 1/50 – 1/20 : Et₂O/hexanes) to afford **22a** as a solid m.p. (°C) 84 - 87 (151 mg, 0.46 mmol, 46% yield). R_f = 0.40; 1/5; Et₂O/hexanes. IR (neat) 1714 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 9H), 3.67 (s, 3H), 7.15 – 7.18 (m, 1H), 7.23 – 7.26 (m, 2H), 7.30 – 7.38 (m, 4H), 7.55 – 7.56 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ -1.07, 34.64, 51.83, 110.94, 121.01, 125.99, 126.70, 127.65, 127.90, 128.08, 128.19, 128.67, 141.92, 175.30. HRMS (ESI) *m/z* calcd for C₁₈H₂₀O₂Si, 328.10, found 328.0855 [M]⁺.



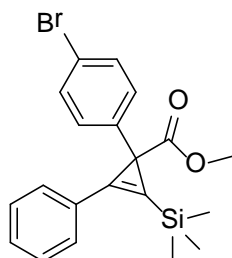
methyl 2-methyl-1-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (23a) Purified by column chromatography (SiO₂, 1/20 : Et₂O/hexanes) to afford **23a** as an oil (158.6 mg, 0.61 mmol, 61% yield). R_f = 0.44; 1/5; Et₂O/hexanes. IR (neat) 1717 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.20 (s, 9H), 2.26 (s, 3H), 3.65 (s, 3H), 7.15 – 7.18 (m, 1H), 7.26 – 7.27 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ -1.13, 10.81, 34.36, 51.62, 109.12, 125.71, 126.03, 127.86, 128.11, 142.69, 176.11. HRMS (ESI) *m/z* calcd for C₁₂H₂₀O₂Si, 260.12, found 260.1125 [M]⁺.



methyl 1-phenyl-2-propyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (24a) Purified by column chromatography (SiO₂, 1/20 : Et₂O/hexanes) to afford **24a** as an oil (185 mg, 0.64 mmol, 64% yield). R_f = 0.40; 1/5; Et₂O/hexanes. IR (neat) 1715 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.20 (s, 9H) 0.98 (t, 3H), 1.63 – 1.67 (m, 2H), 2.55 – 2.59 (m, 2H), 3.65 (s, 3H), 7.13 – 7.17 (m, 1H), 7.23 – 7.27 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ -1.02, 13.82, 20.64, 27.84, 34.44, 51.53, 108.14, 125.58, 127.78, 128.08, 129.98, 142.85, 176.18. HRMS (ESI) *m/z* calcd for C₁₇H₂₄O₂Si, 288.15, found 288.1540 [M]⁺.

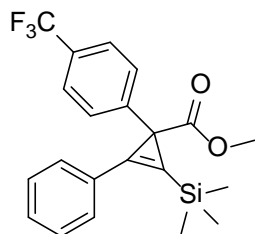


ethyl 2-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (32b) Purified by column chromatography (SiO₂, 1/20 – 1/10 : Et₂O/hexanes) to afford **32b** as an oil (200 mg, 0.77 mmol, 77% yield). R_f = 0.31; 1/5; Et₂O/hexanes. IR (neat) 1721 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.34 (s, 9H), 1.25 (t, 3H), 2.41 (s, 1H), 4.10 – 4.22 (m, 2H), 7.37 – 7.46 (m, 3H), 7.55 – 7.57 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.39, 14.04, 20.67, 60.01, 108.08, 124.08, 127.67, 128.70, 129.56, 129.83, 176.13. HRMS (ESI) *m/z* calcd for C₁₅H₂₀O₂Si, 260.12, found 260.1233 [M]⁺.



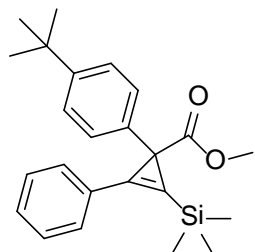
methyl 1-(4-bromophenyl)-2-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (33d) Purified by column chromatography (SiO₂, 1/100 – 1/20 : Et₂O/hexanes) to afford **33d** as an oil (253 mg, 0.63

mmol, 63% yield). $R_f = 0.44$; 1/5; Et₂O/hexanes. IR (neat) 1713 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 9H), 3.66 (s, 3H), 7.23 – 7.26 (m, 2H), 7.34 – 7.45 (m, 5H), 7.55 – 7.57 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.08, 33.99, 51.87, 113.43, 119.69, 125.25, 126.67, 128.98, 129.77, 129.93, 130.90, 141.13, 174.91. HRMS (ESI) m/z calcd for C₂₀H₂₁BrO₂Si, 400.05, found 400.0489 [M]⁺.



methyl 2-phenyl-1-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate

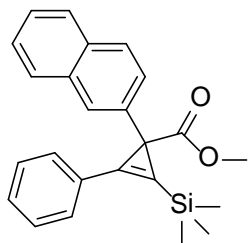
(34e) Purified by column chromatography (SiO₂, 1/20 – 1/10 : Et₂O/hexanes) to afford **34e** as an oil (210.9 mg, 0.54 mmol, 54% yield). $R_f = 0.56$; 1/5; Et₂O/hexanes. IR (neat) 1720 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.68 (s, 3H), 7.38 – 7.45 (m, 3H), 7.49 (s, 4H), 7.53 – 7.58 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.10, 34.28, 51.91, 113.03, 124.40 (q, $J_{C-F} = 270.0$ Hz), 124.80 (d, $J_{C-F} = 2.5$ Hz), 124.99, 126.47, 128.00 (d, $J_{C-F} = 32.5$ Hz), 128.20, 129.03, 129.82, 130.07, 146.20, 174.66. HRMS (ESI) m/z calcd for C₂₁H₂₁F₃O₂Si, 390.13, found 390.1239 [M]⁺.



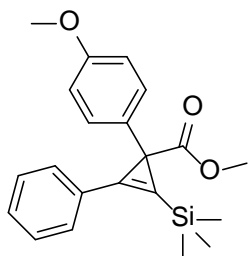
methyl 1-(4-(tert-butyl)phenyl)-2-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (35f)

Purified by column chromatography (SiO₂, 1/20 – 1/5 : Et₂O/hexanes) to afford **35f** as an oil (261 mg, 0.69 mmol, 69% yield). $R_f = 0.44$; 1/5; Et₂O/hexanes. IR (neat) 1721 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.31 (s, 9H), 1.29 (s, 9H), 3.68 (s, 3H), 7.25 – 7.33 (m, 4H), 7.34 – 7.44 (m, 3H), 7.59 - 7.62 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -0.95, 31.19, 31.34, 34.33, 51.77, 113.37, 124.78, 126.86, 127.25, 127.71,

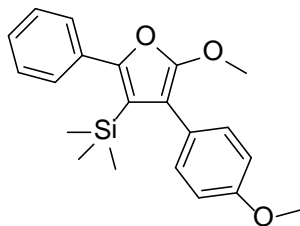
128.84, 129.62, 129.80, 138.69, 148.60, 175.58. HRMS (ESI) m/z calcd for $C_{24}H_{30}O_2Si$, 378.20, found 378.2018 $[M]^+$.



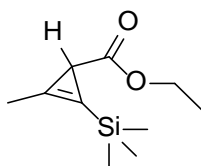
methyl 1-(naphthalen-2-yl)-2-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (36g) Purified by column chromatography (SiO_2 , 1/100 – 1/20 : Et_2O /hexanes) to afford **36g** as an oil (227 mg, 0.609 mmol, 61% yield). $R_f = 0.39$; 1/5; Et_2O /hexanes. IR (neat) 1715 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 9H), 3.36 (s, 3H), 7.18 (s, 1H), 7.30 – 7.38 (m, H), 7.43 – 7.45 (m, 1H), 7.56 – 7.58 (m, 2H), 7.64 – 7.73 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.98, 34.79, 51.85, 113.75, 125.25, 125.70, 126.03, 126.29, 126.77, 127.10, 127.25, 127.47, 127.75, 128.94, 129.79, 129.87, 132.02, 133.34, 139.68, 175.38. HRMS (ESI) m/z calcd for $C_{24}H_{24}O_2Si$, 372.15, found 372.1438 $[M]^+$.



methyl 1-(4-methoxyphenyl)-2-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (37h) Purified by column chromatography (SiO_2 , 1/20 : Et_2O /hexanes) to afford **37h** as an oil (243 mg, 0.69 mmol, 69% yield). $R_f = 0.43$; 1/5; Et_2O /hexanes. IR (neat) 1713 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 0.30 (s, 9H), 3.80 (s, 3H), 3.81 (s, 3H), 6.86 – 6.89 (m, 2H), 7.24 – 7.26 (m, 1H), 7.31 – 7.34 (m, 4H), 7.46 – 7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.45, 52.11, 55.75, 98.79, 105.19, 113.85, 124.83, 127.15, 128.12, 128.78, 129.09, 134.77, 158.81, 167.89, 213.03. HRMS (ESI) m/z calcd for $C_{21}H_{24}O_3Si$, 352.15, found 352.1385 $[M]^+$.



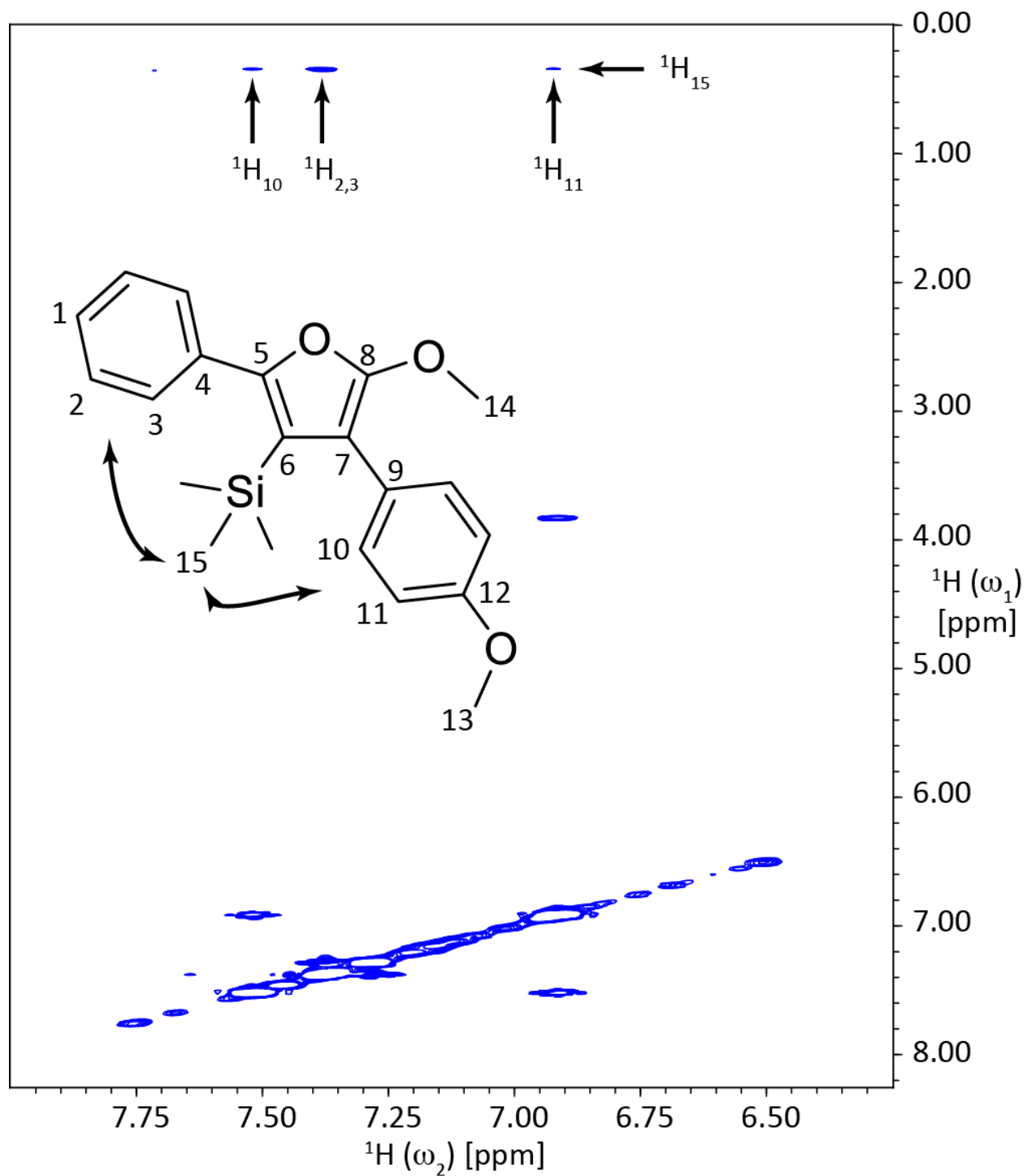
(5-methoxy-4-(4-methoxyphenyl)-2-phenylfuran-3-yl)trimethylsilane (38h) Purified by column chromatography (SiO₂, 1/20 : Et₂O/hexanes) to afford **38h** as an oil (74 mg, 0.21 mmol, 21% yield). R_f = 0.35; 1/5; Et₂O/hexanes. IR (neat) 1713 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.28 (s, 9H), 3.66 (s, 3H), 3.75 (s, 3H), 6.77 – 6.80 (m, 2H), 7.24 – 7.29 (m, 1H), 7.35 – 7.43 (m, 3H), 7.57 – 7.60 (m, 2H). ¹³C NMR (125 MHz, CDCl₃,) δ -1.03, 33.94, 51.76, 55.16, 113.32, 114.08, 126.33, 127.20, 128.86, 129.15, 129.63, 129.72, 134.14, 157.81, 165.63. HRMS (ESI) *m/z* calcd for C₂₁H₂₄O₃Si, 352.15, found 352.1384 [M]⁺.



ethyl 2-phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (39b) Purified by column chromatography (SiO₂, 1/20 – 1/10 : Et₂O/hexanes) to afford **39b** as an oil (141 mg, 0.71 mmol, 71% yield). ¹H NMR (500 MHz, CDCl₃) δ = 0.16 (s, 9H), 1.21 (t, 3H), 1.95 (s, 1H), 2.17 (s, 3H), 4.04 – 4.10 (m, 2H). Compound **39b** is a known compound and the analytical data is consistent with the literature.¹¹

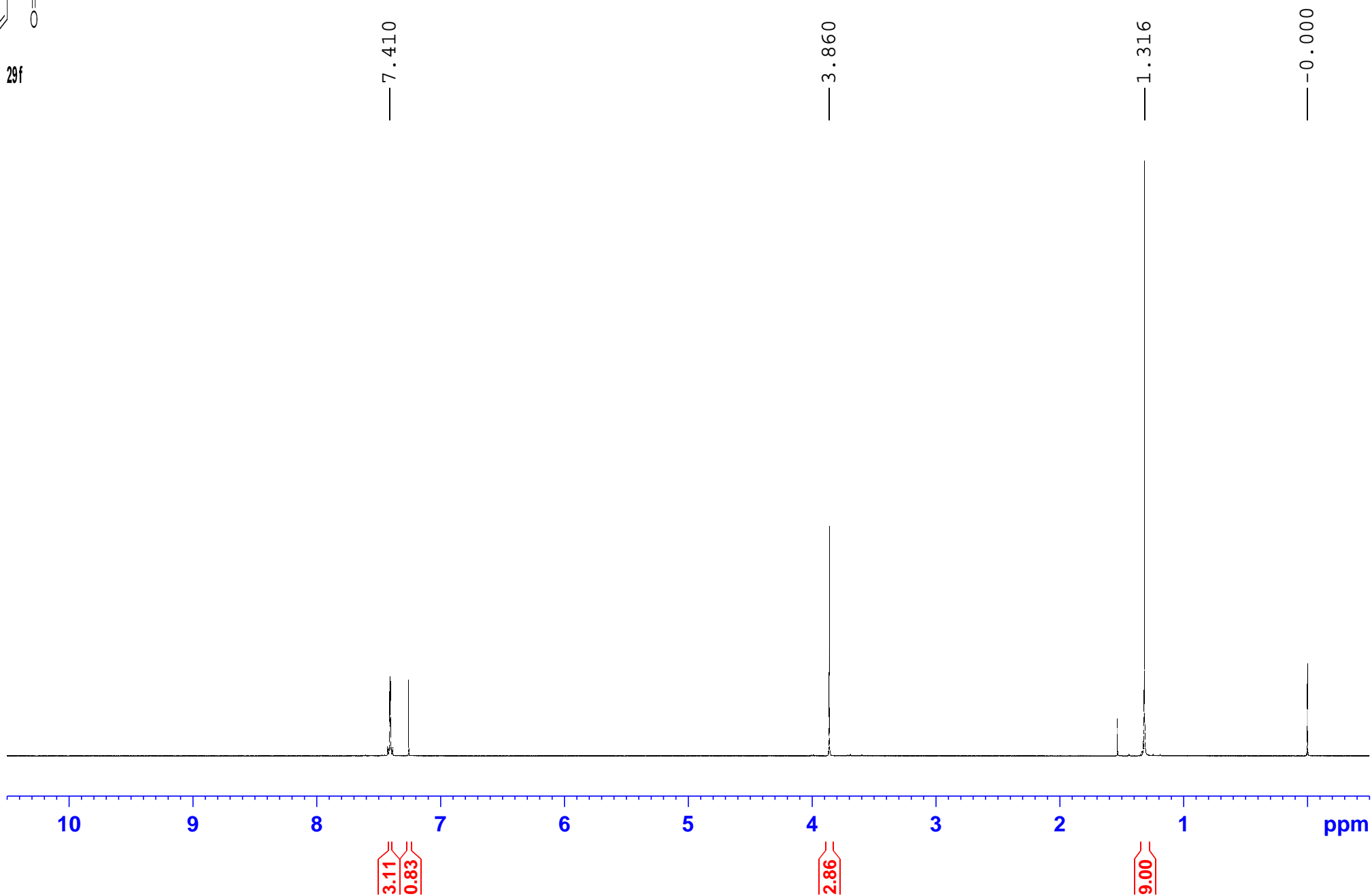
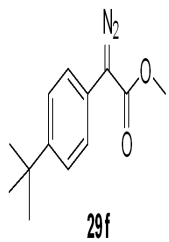
¹¹ Pallerla, M.K.; Fox, J.M. *Org. Lett.* **2005**, *7*, 3593.

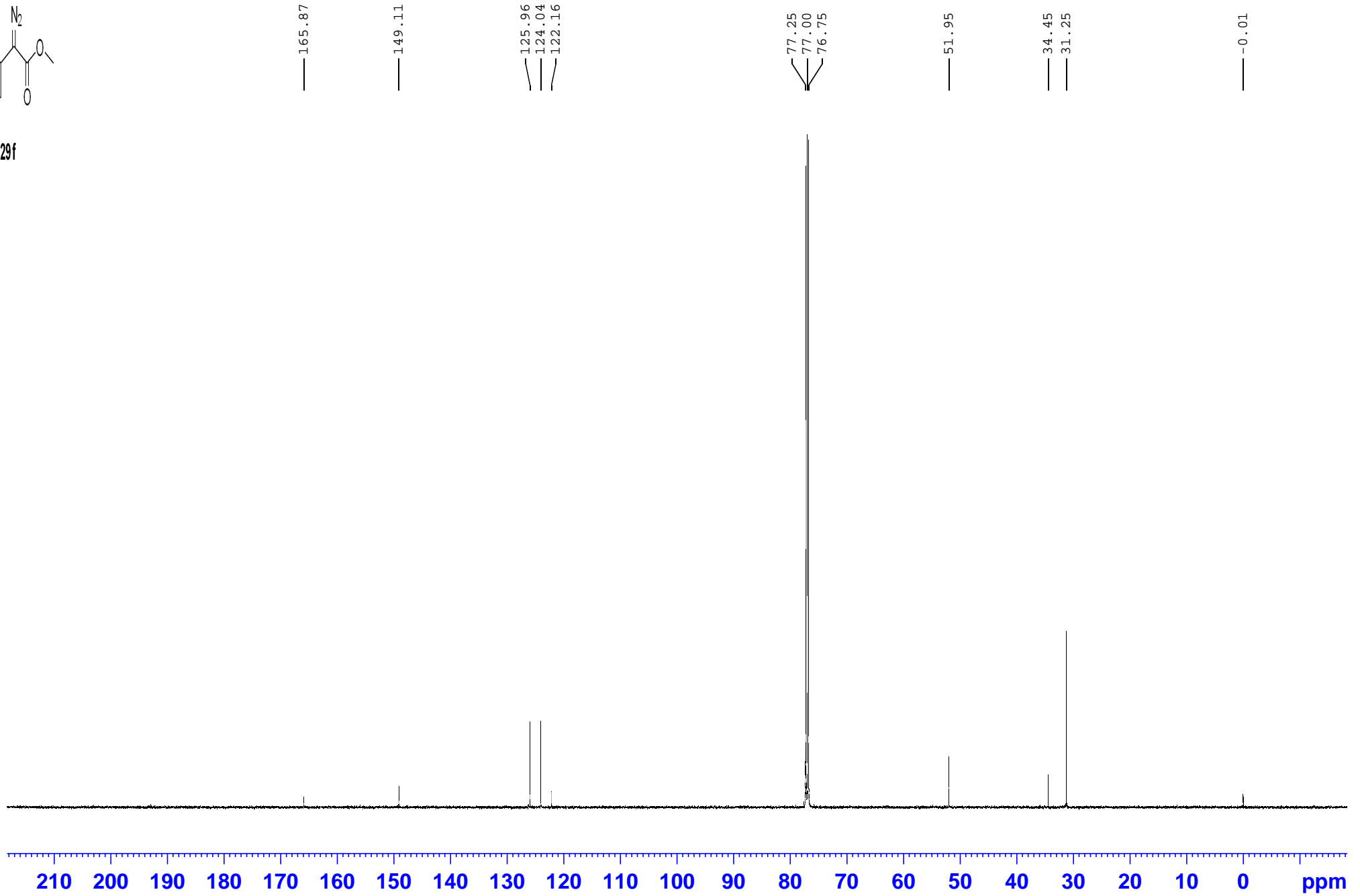
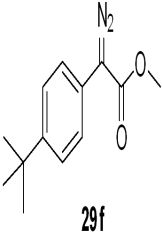
^{13}C Chemical Shift Assignments for **38h**

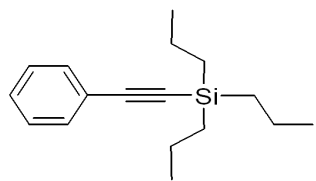


Moiety [#]	¹ H shift [ppm]	¹³ C shift [ppm]
1	7.28	127.17
2	7.37*	128.18
3	7.37*	128.80
4	NA	134.80
5	NA	-
6	NA	105.22
7	NA	-
8	NA	167.93
9	NA	-
10	7.51	129.08
11	6.91	113.86
12	NA	158.82
13	3.82	55.29
14	3.83	52.16
15	0.35	-0.43

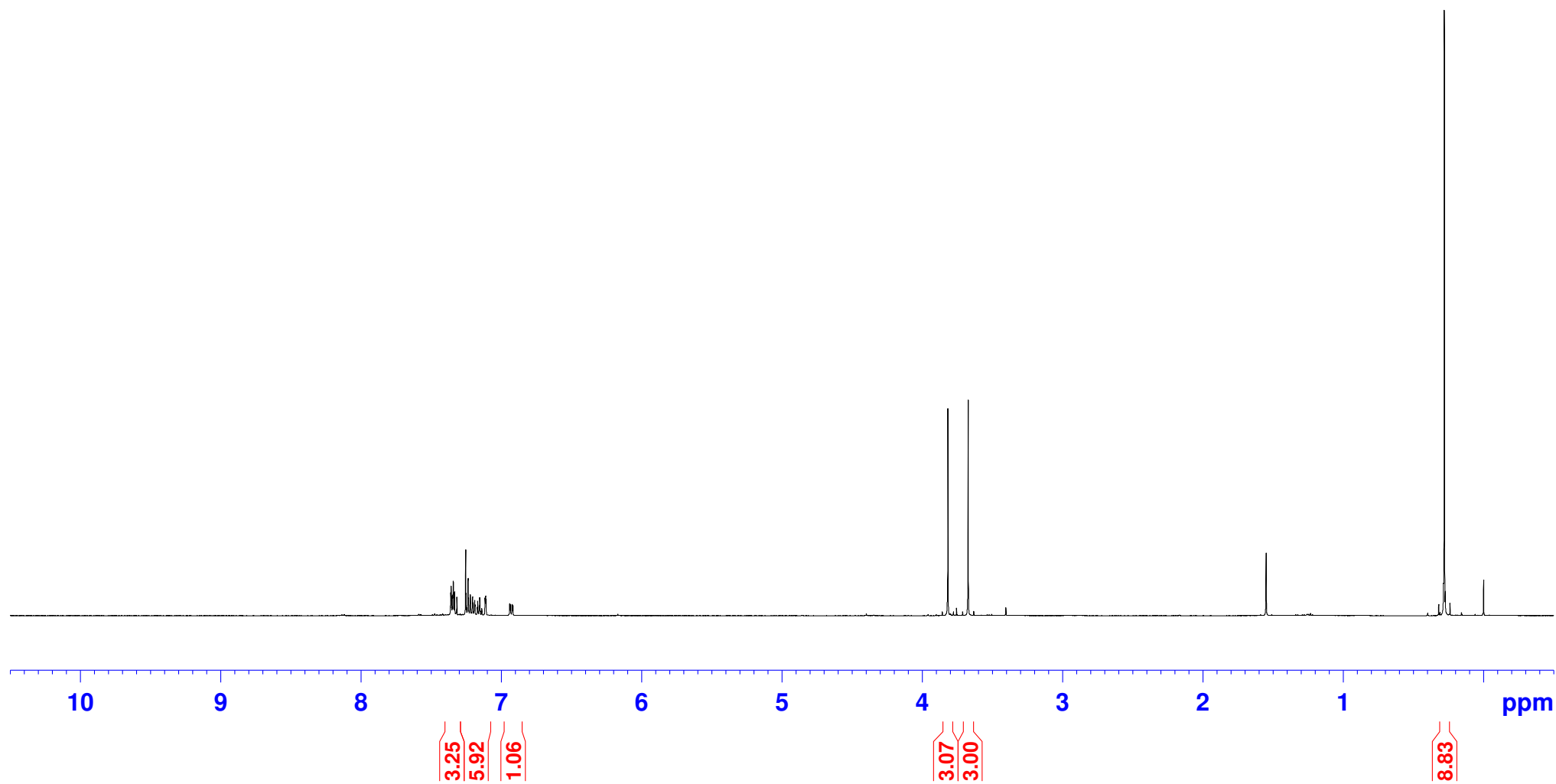
Table 1. "*" denotes degenerate ¹H chemical shifts between aromatic ¹Hs 2 and 3, which resulted in an ambiguous assignment of the attached ¹³C chemical shifts. "NA" indicates a quaternary ¹³C that has no associated ¹H chemical shift. A "-" indicates that the chemical shift was not observed or could not be unambiguously identified.

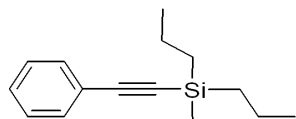




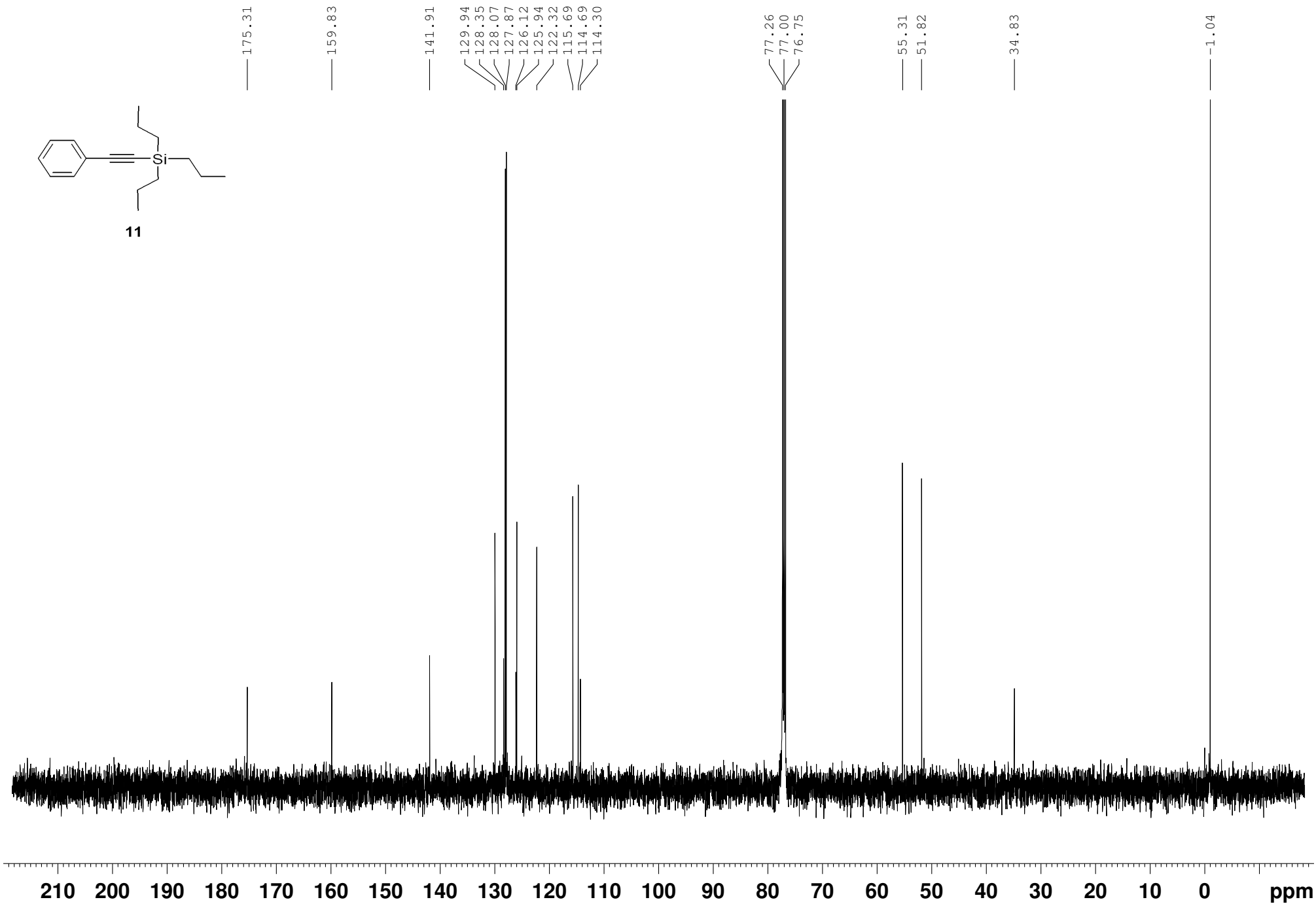


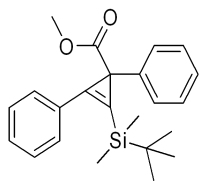
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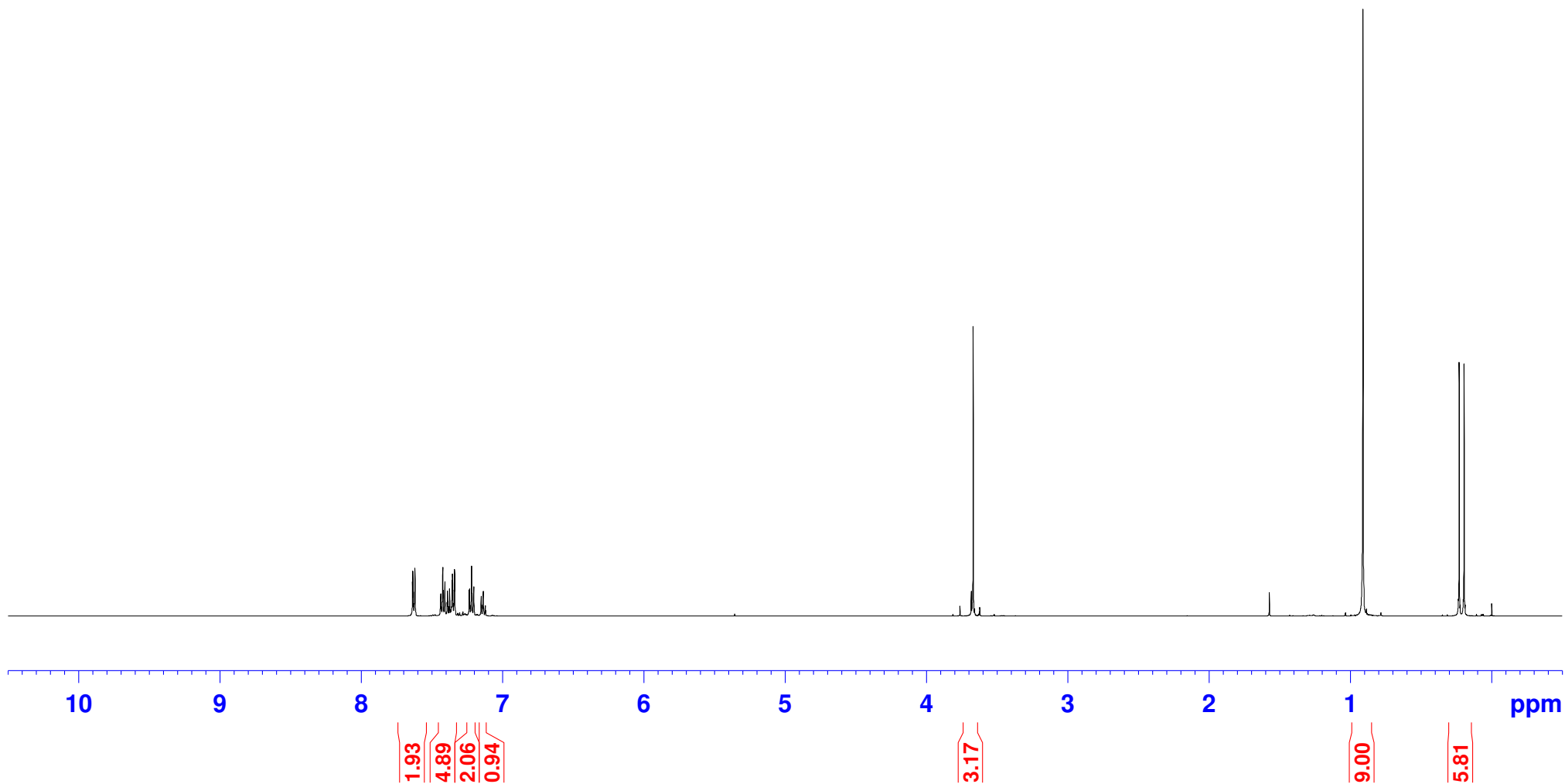


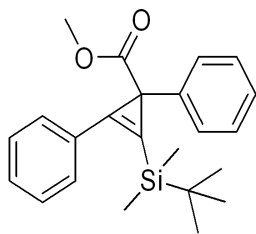
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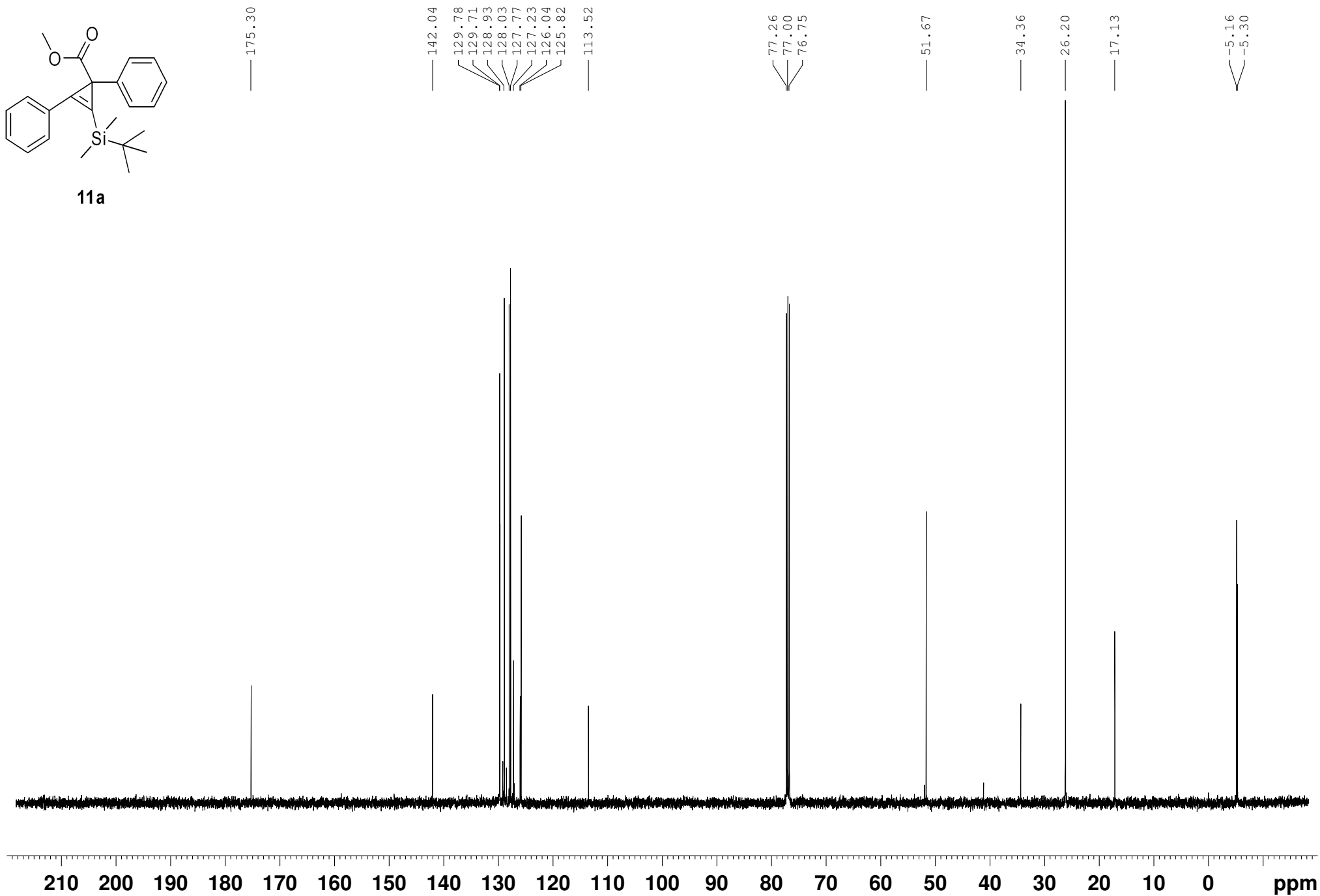


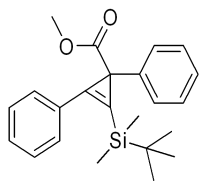
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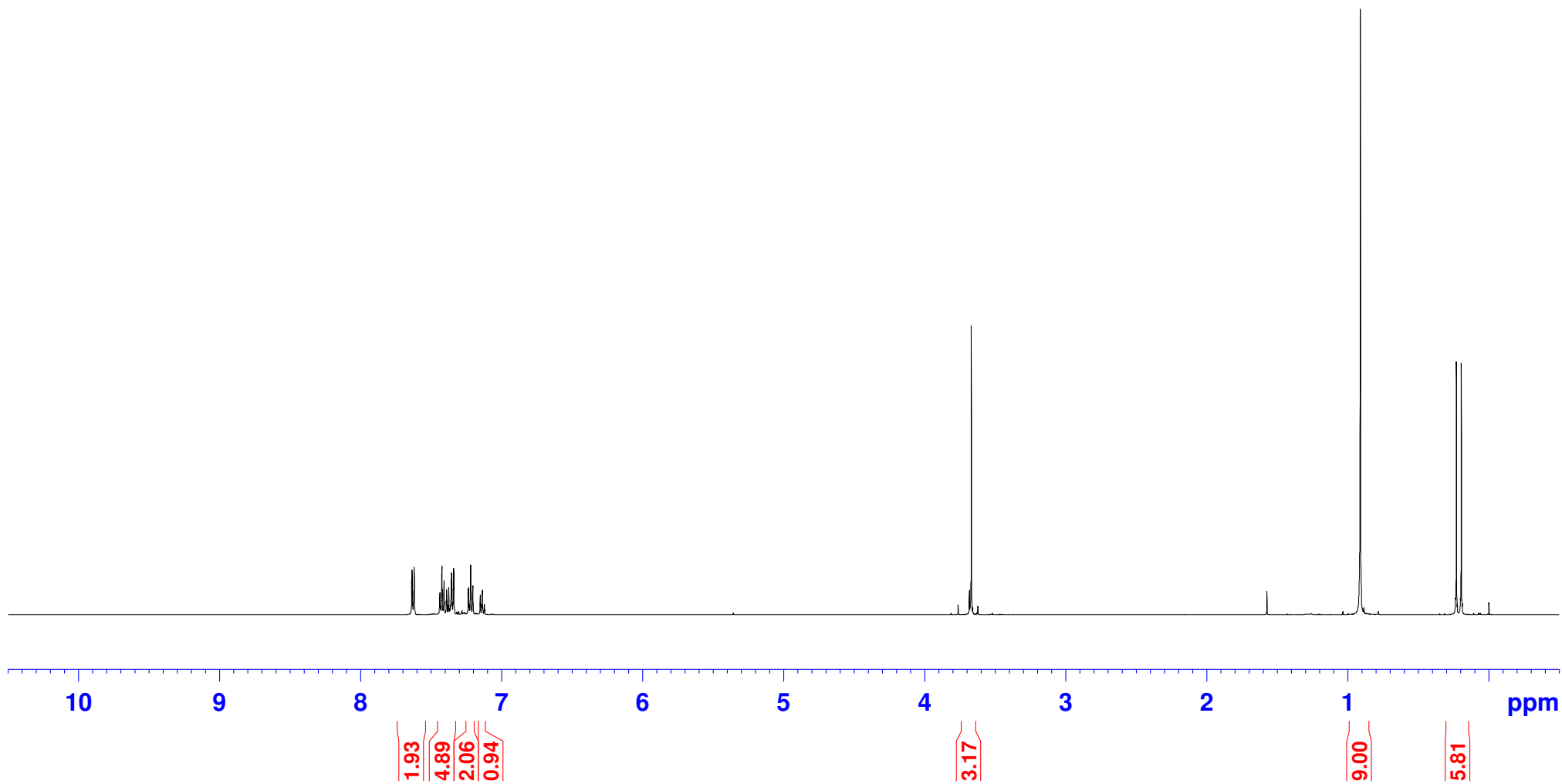


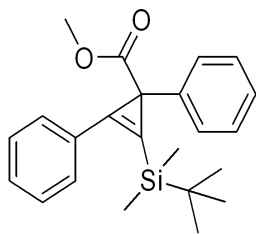
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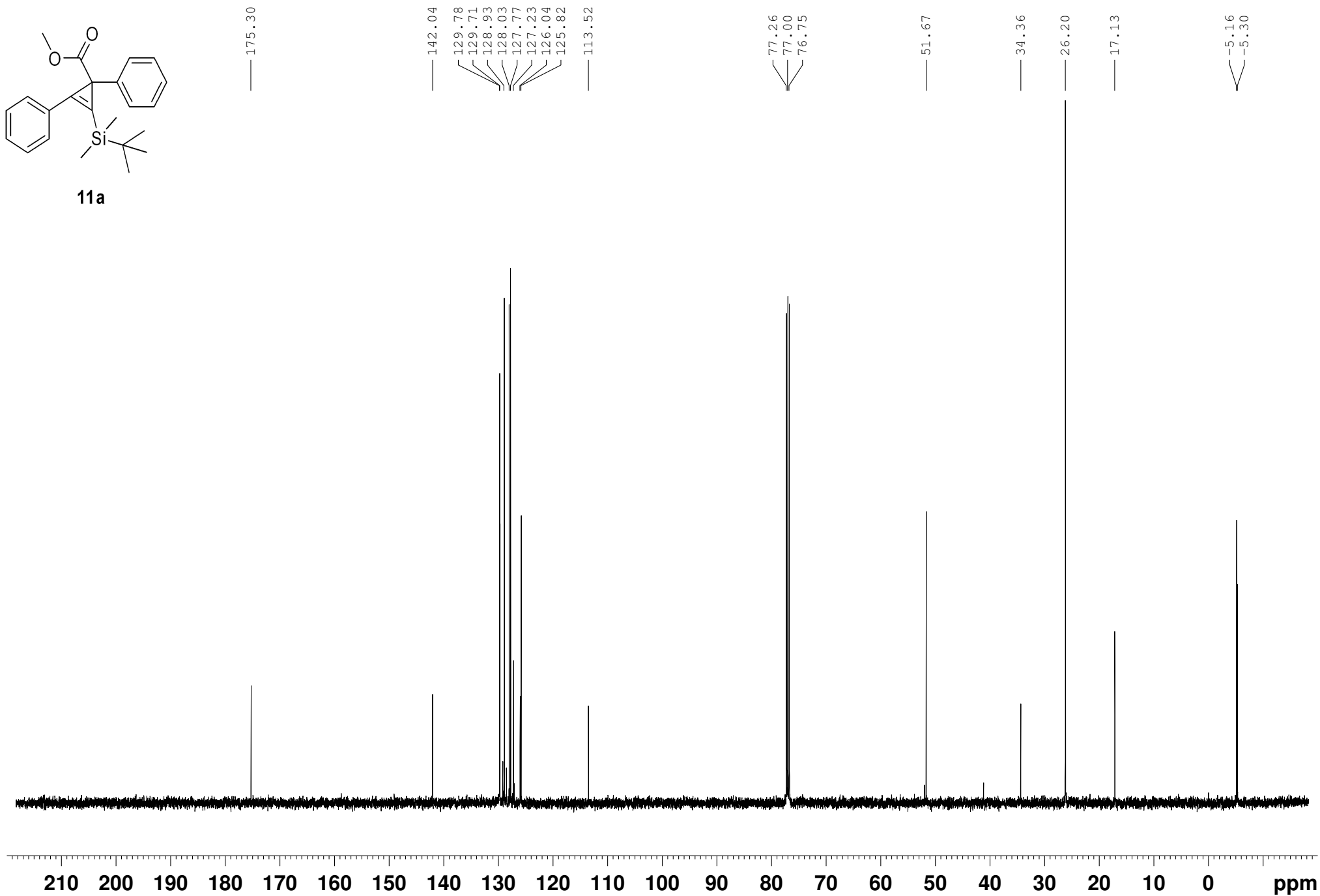


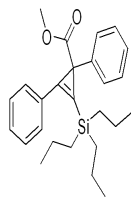
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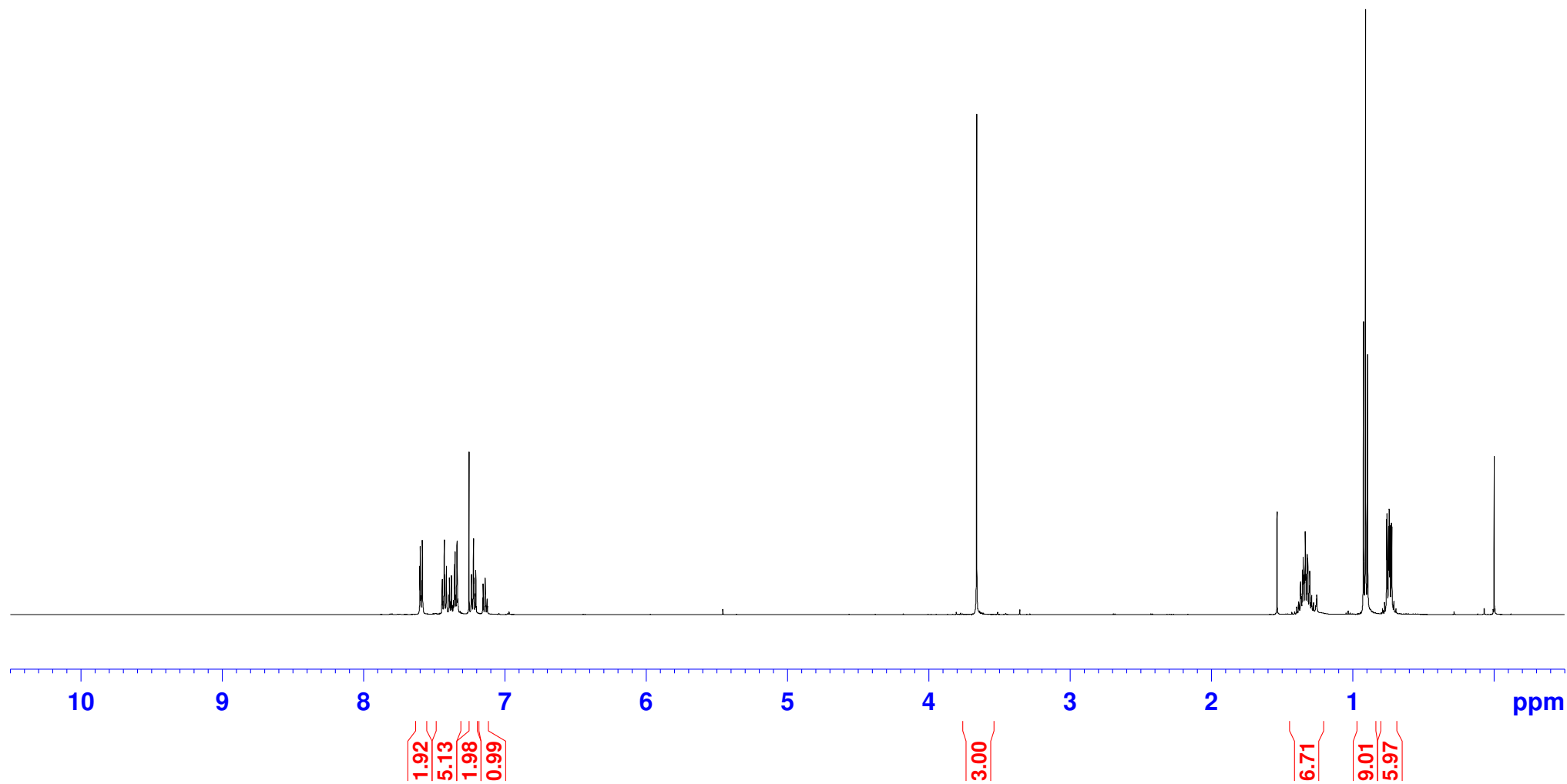


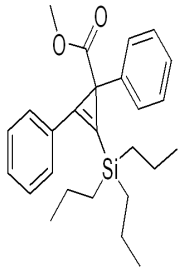
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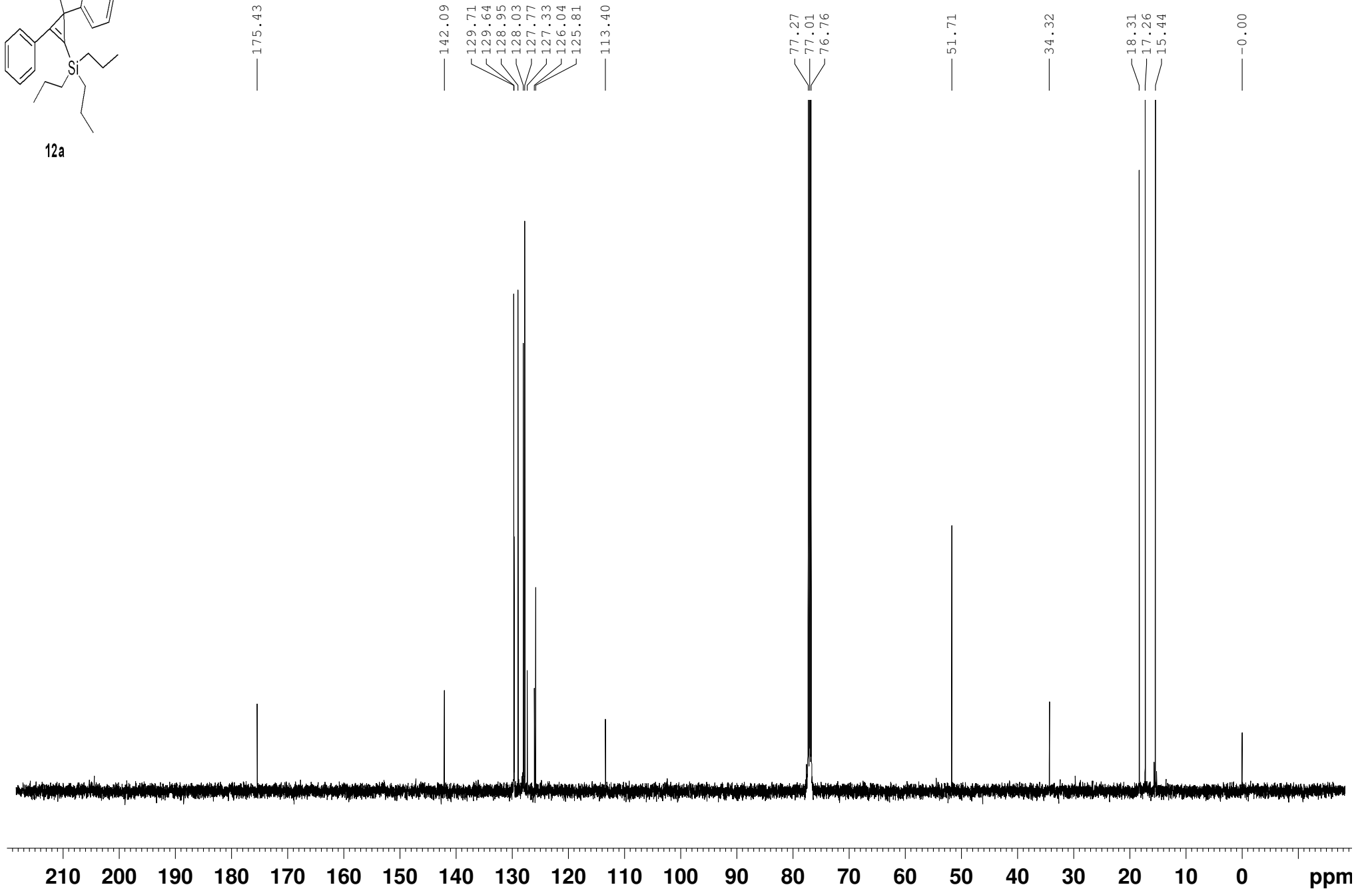


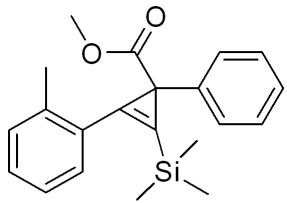
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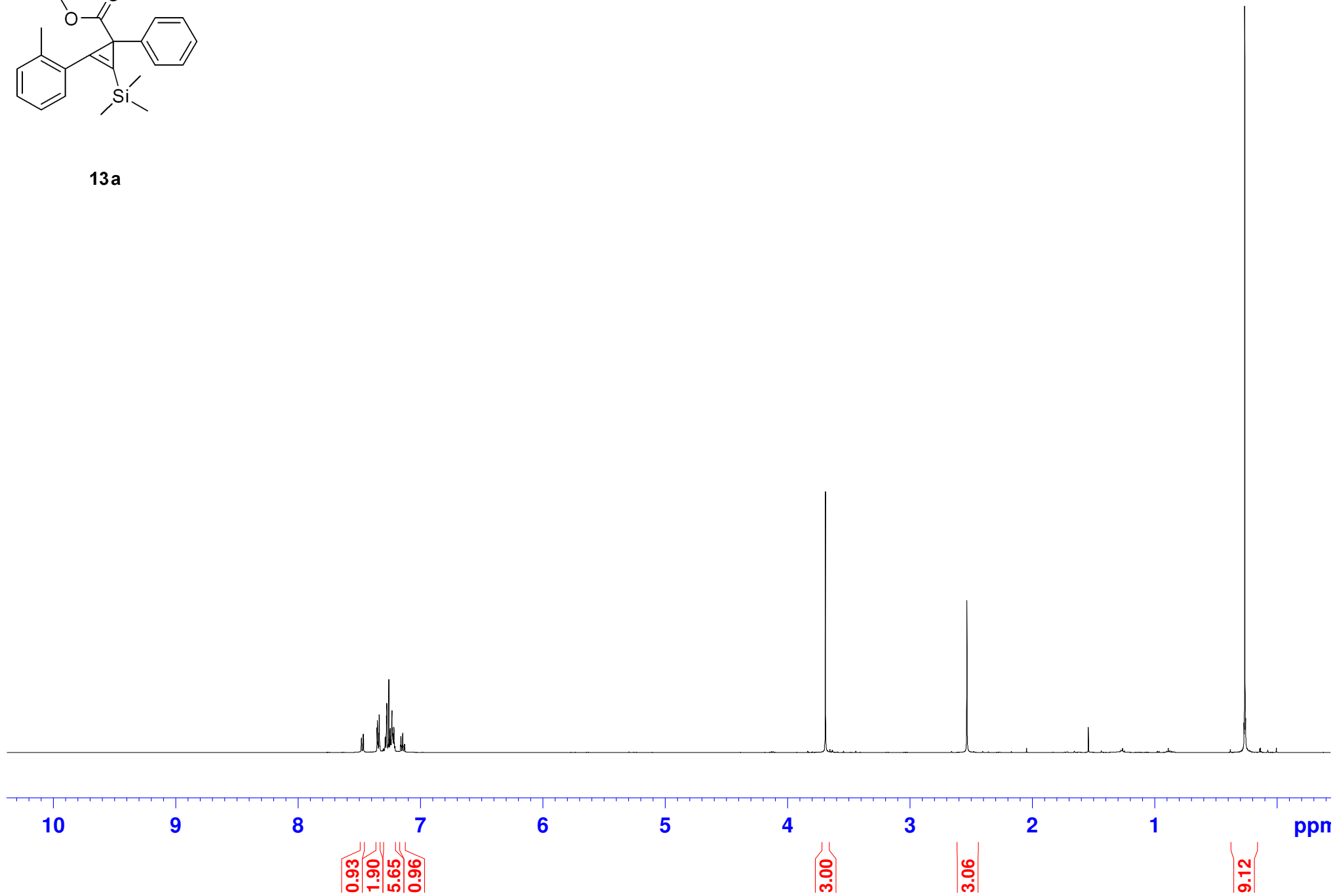


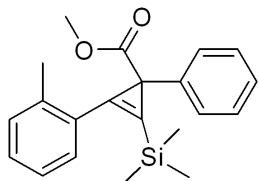
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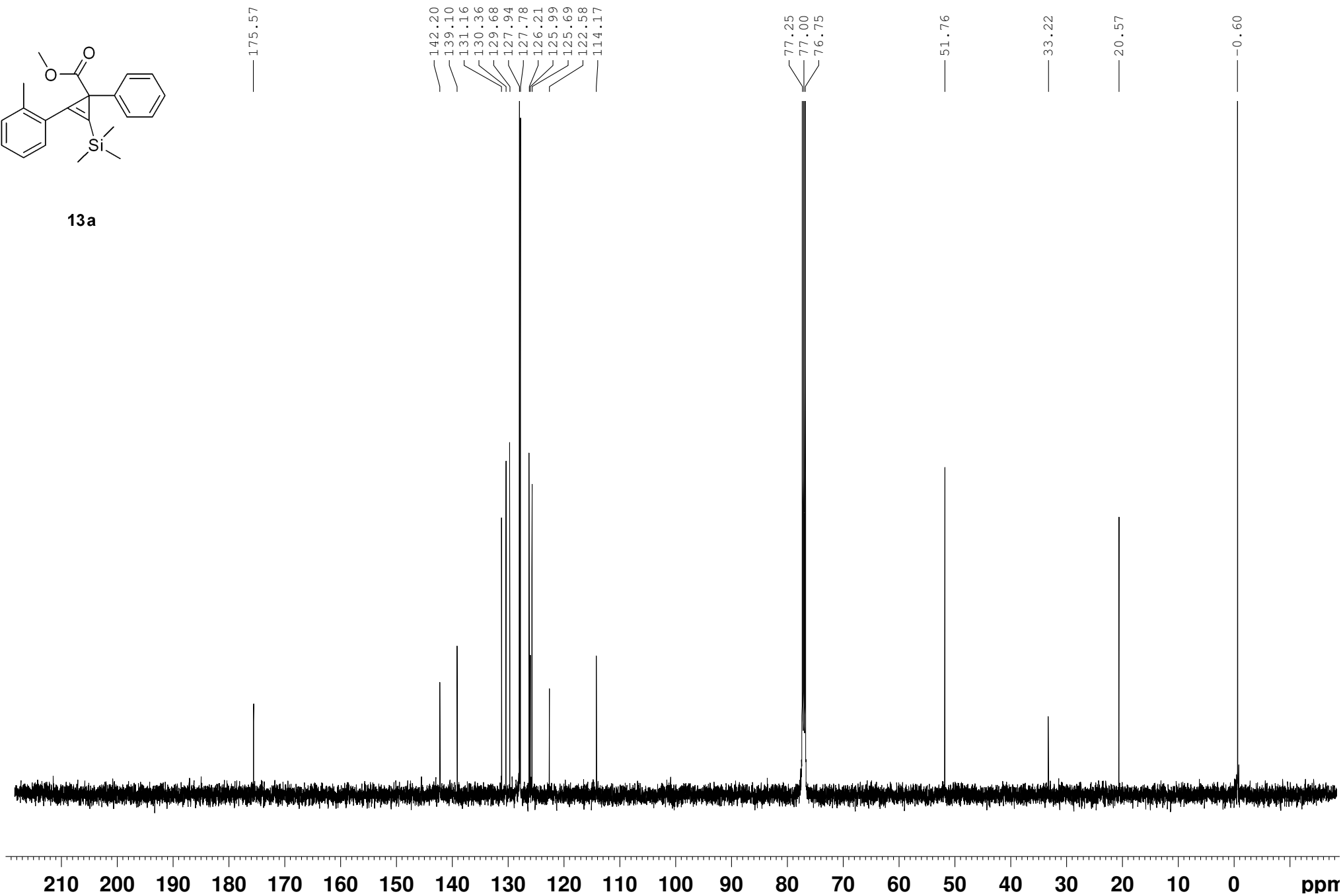


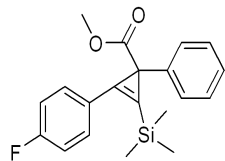
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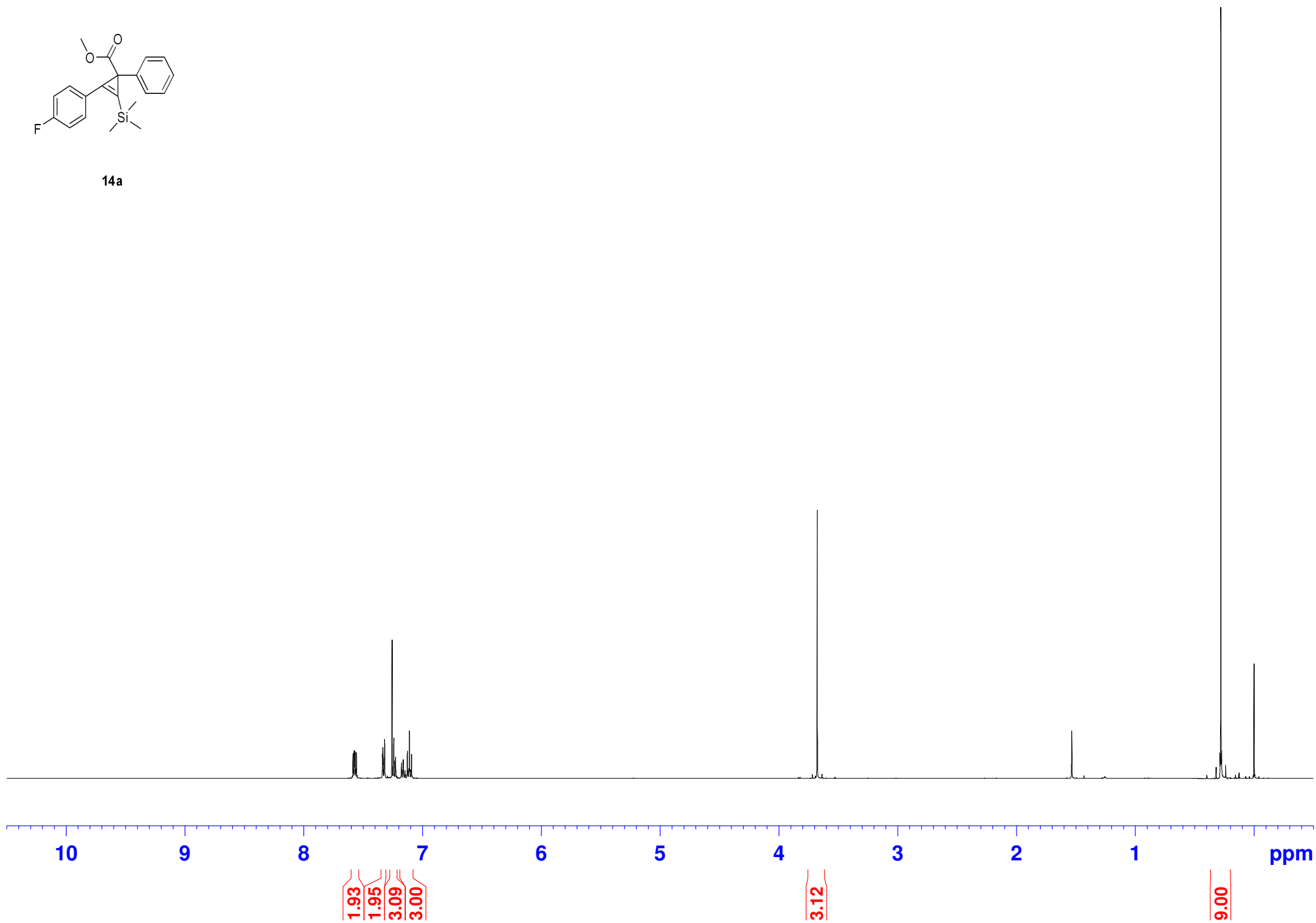


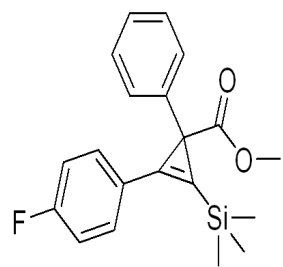
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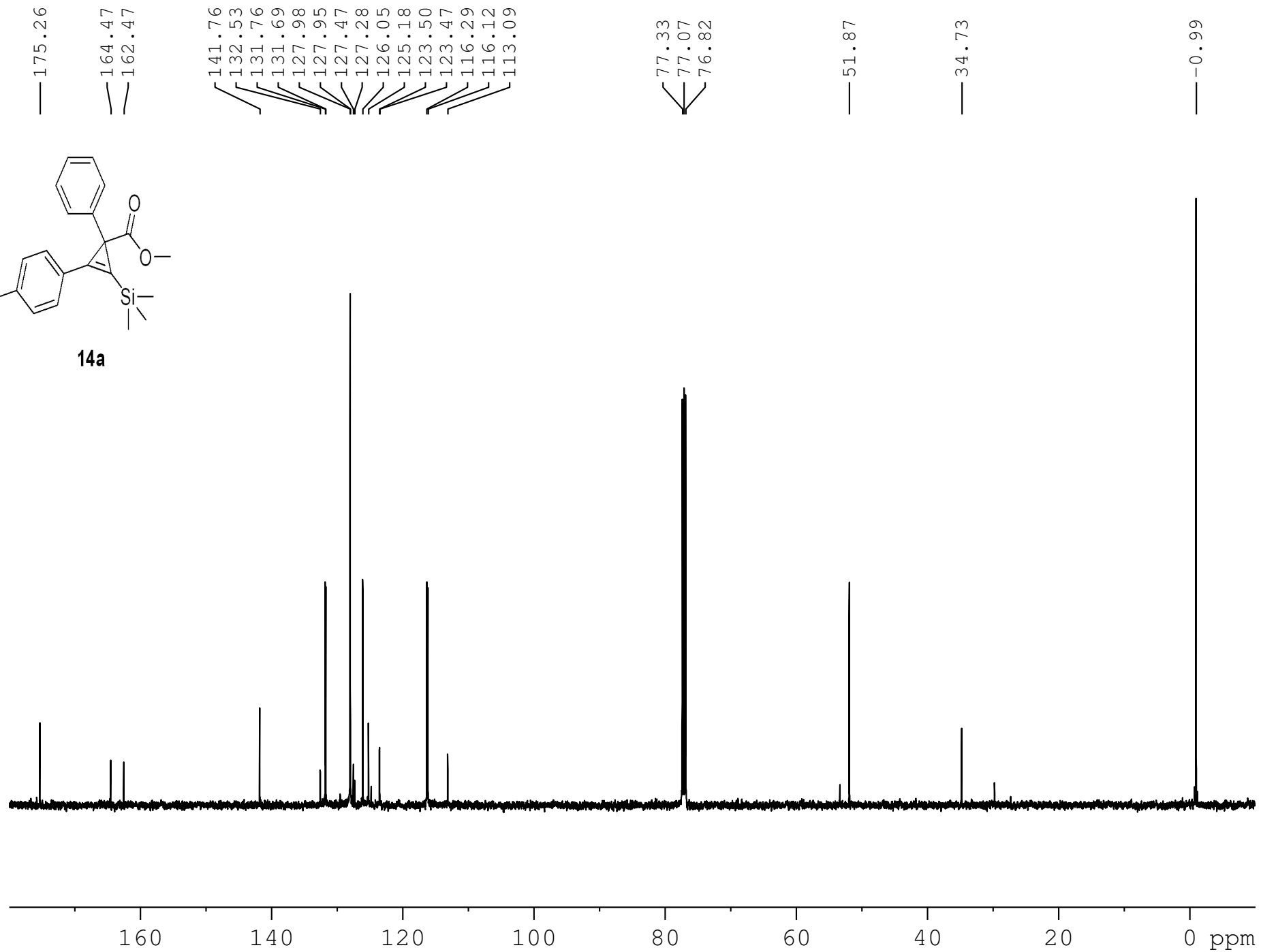


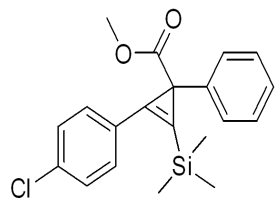
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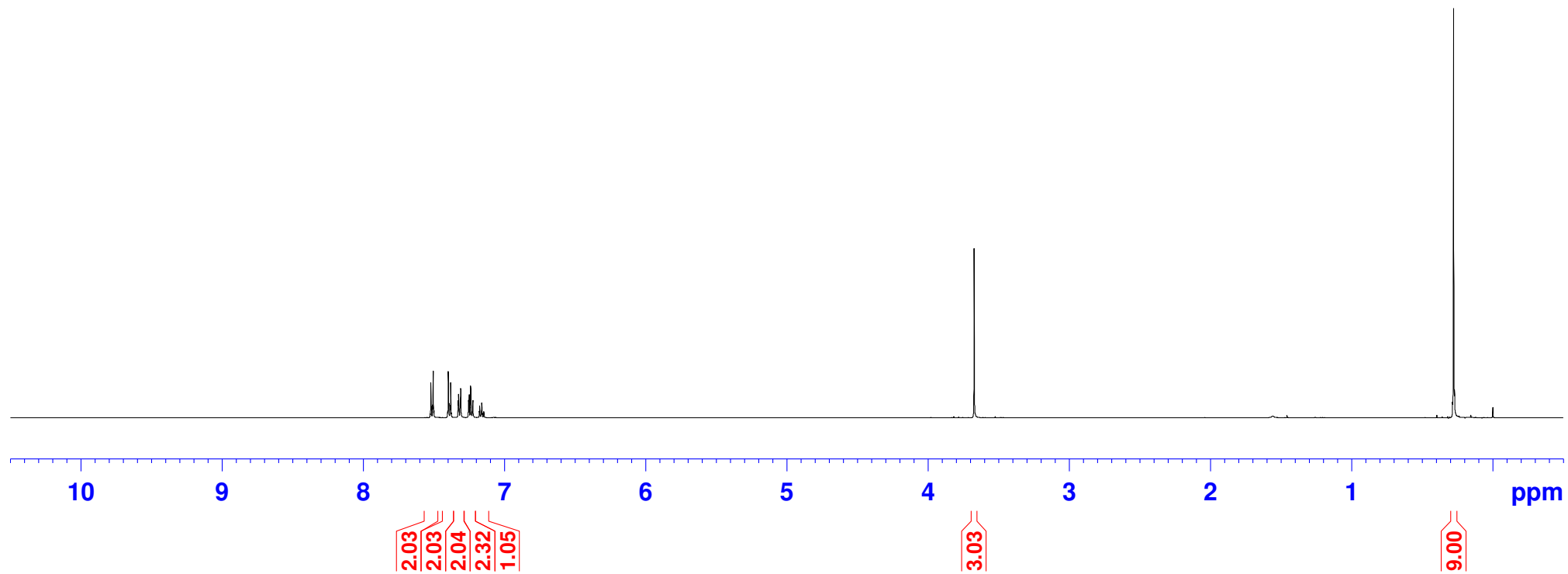


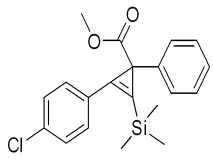
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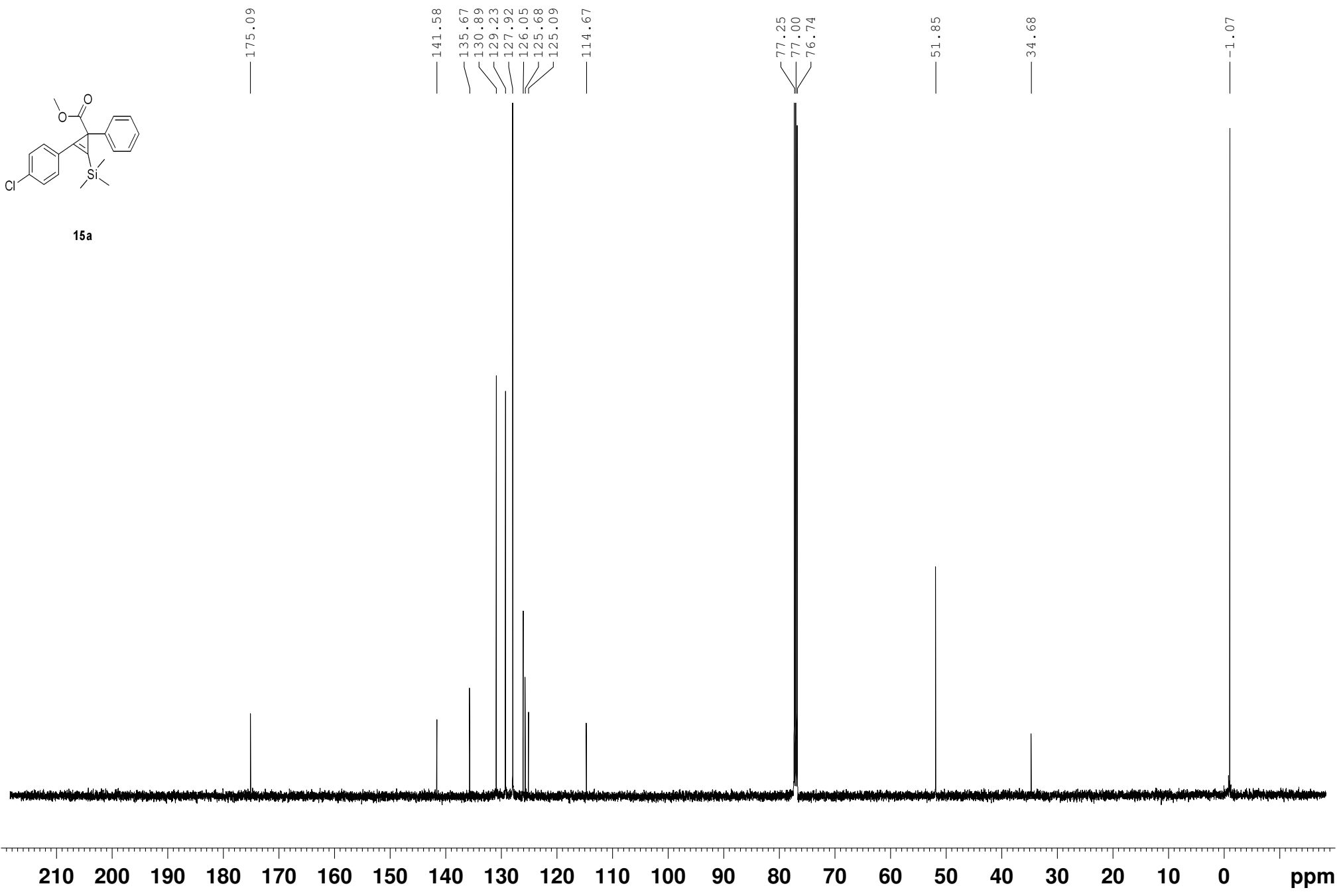


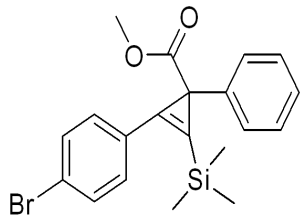
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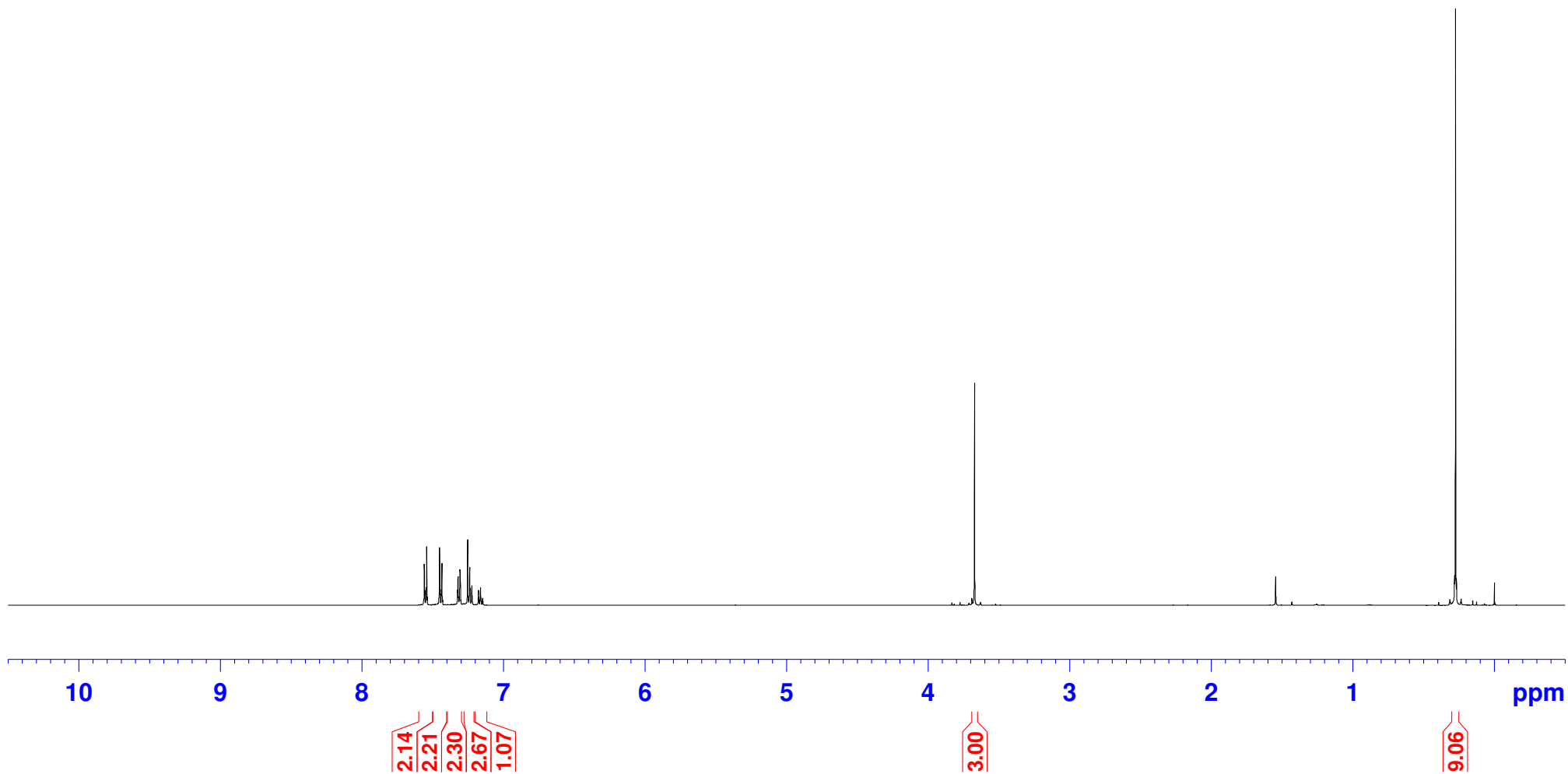


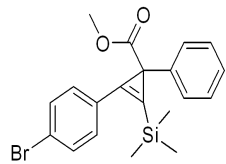
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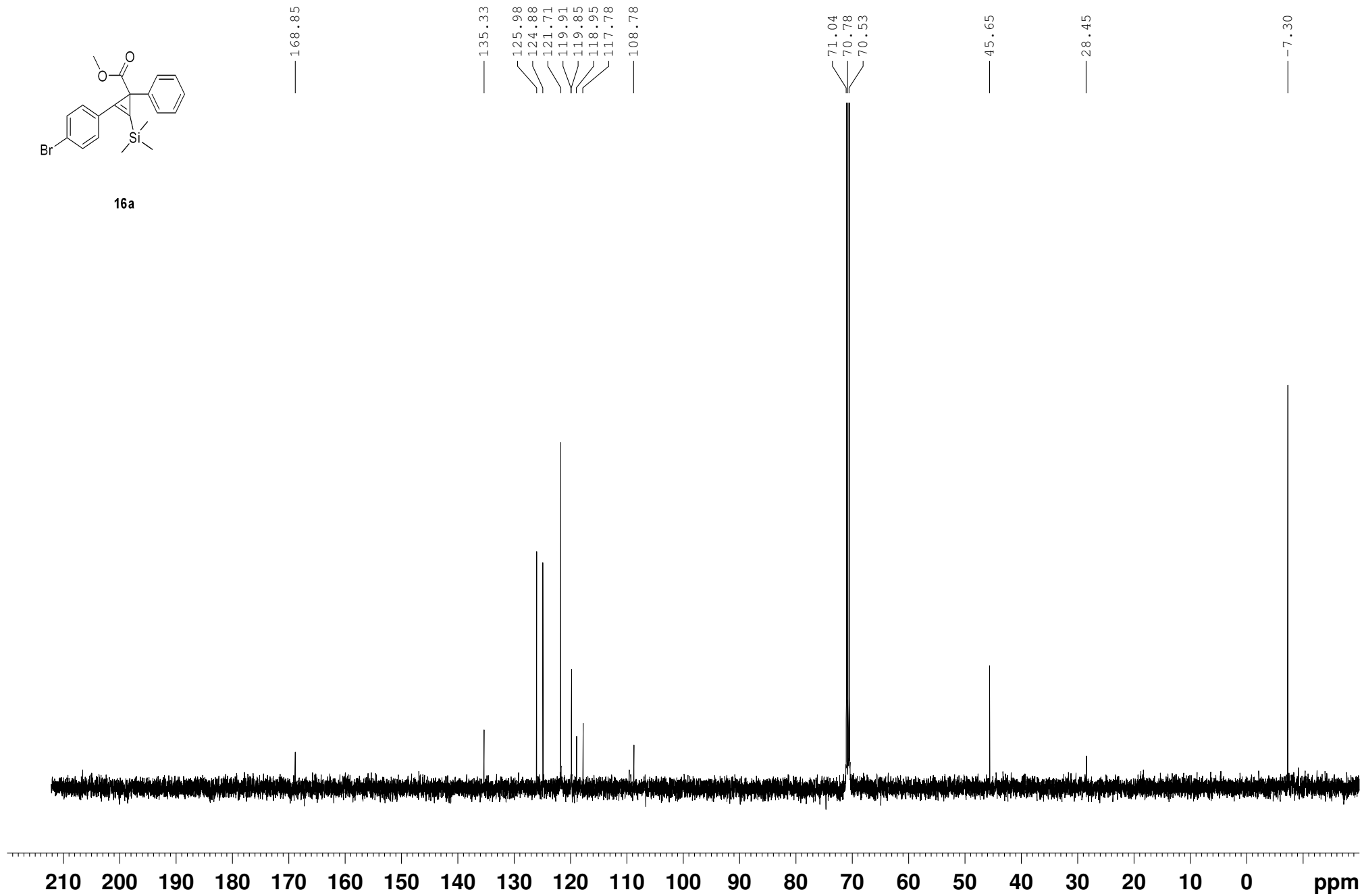


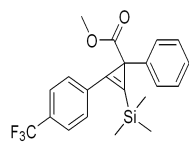
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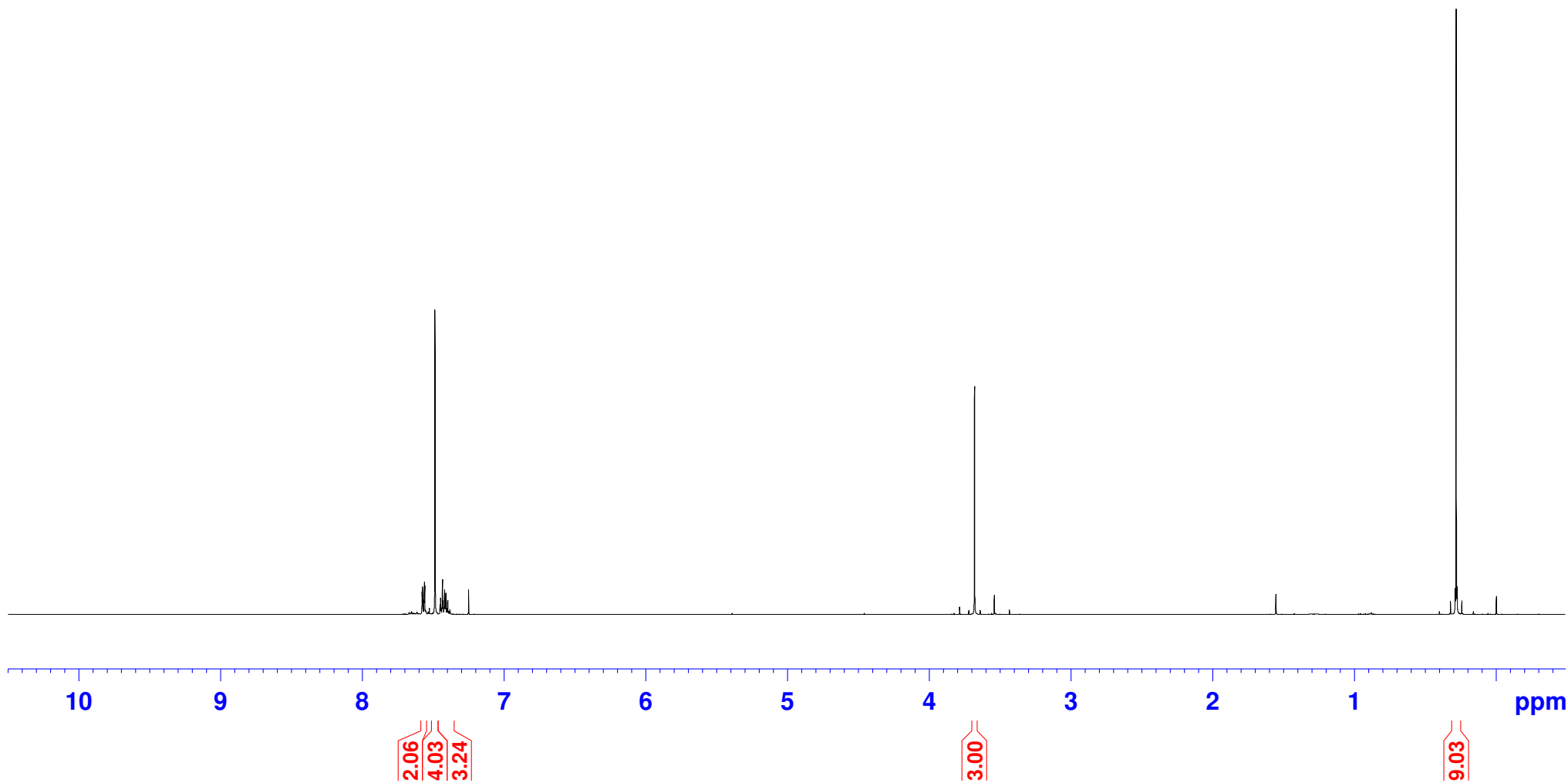


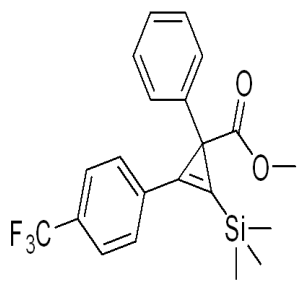
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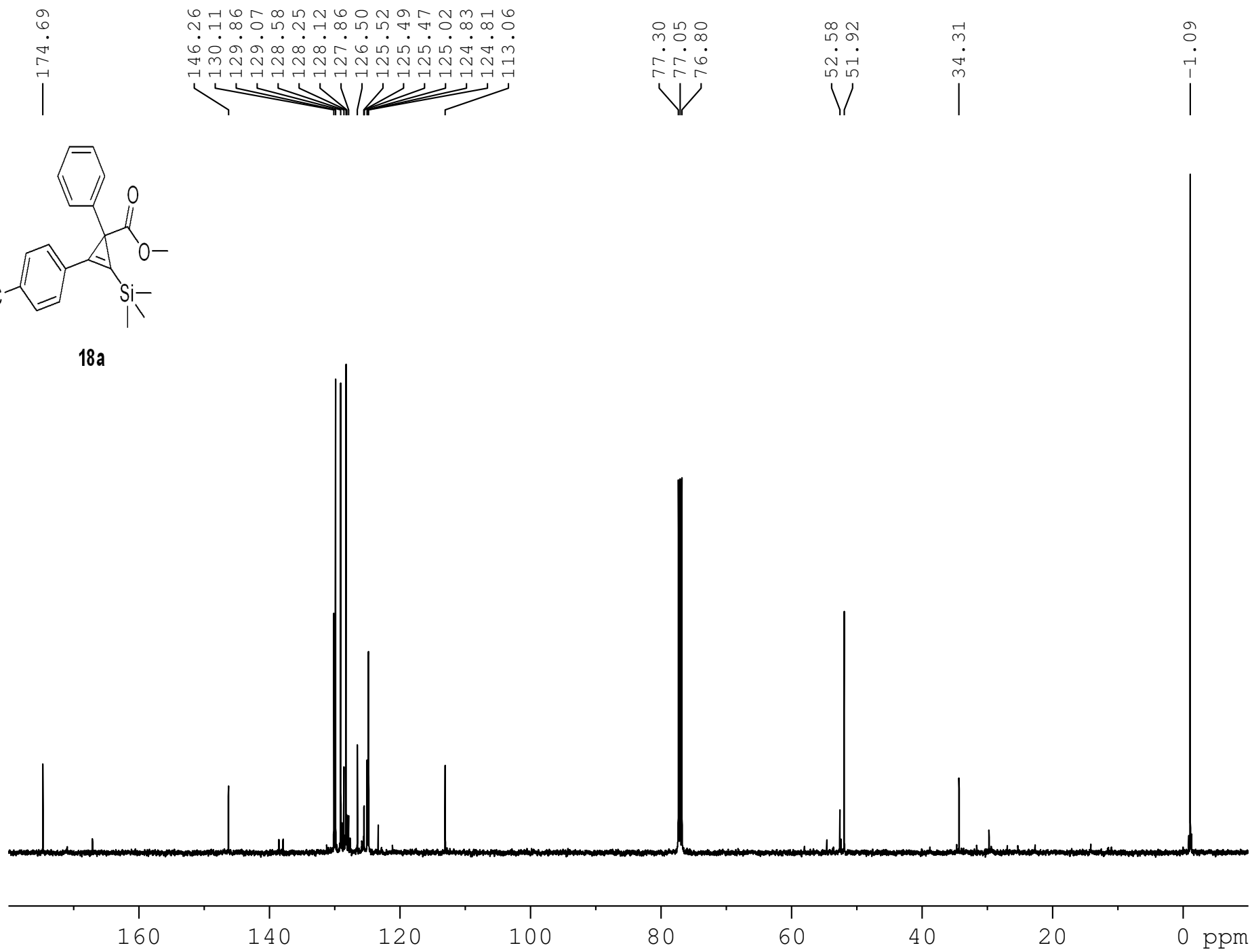


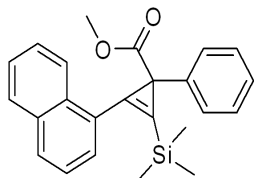
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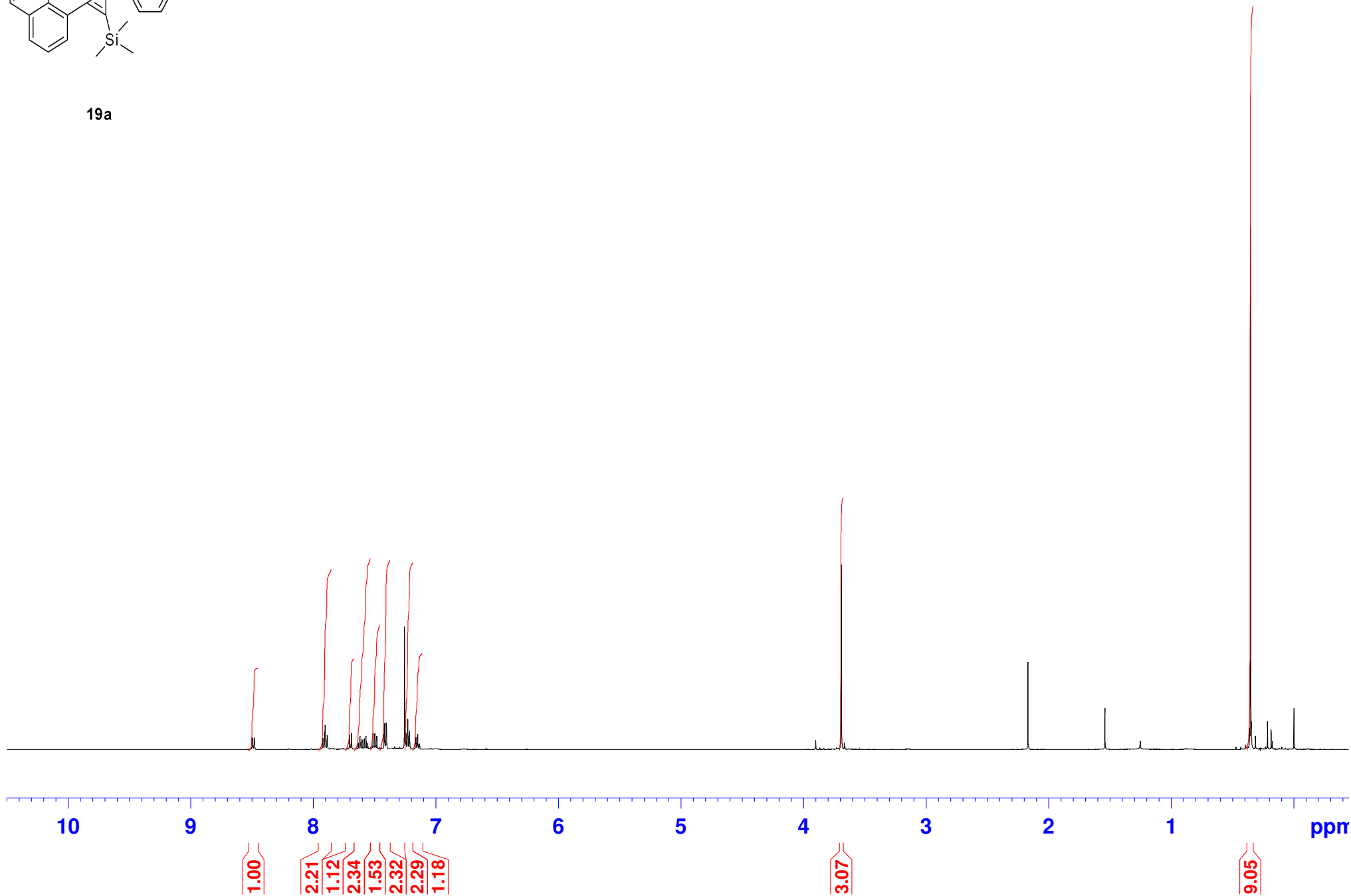


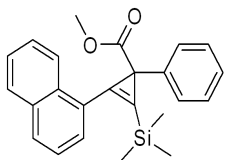
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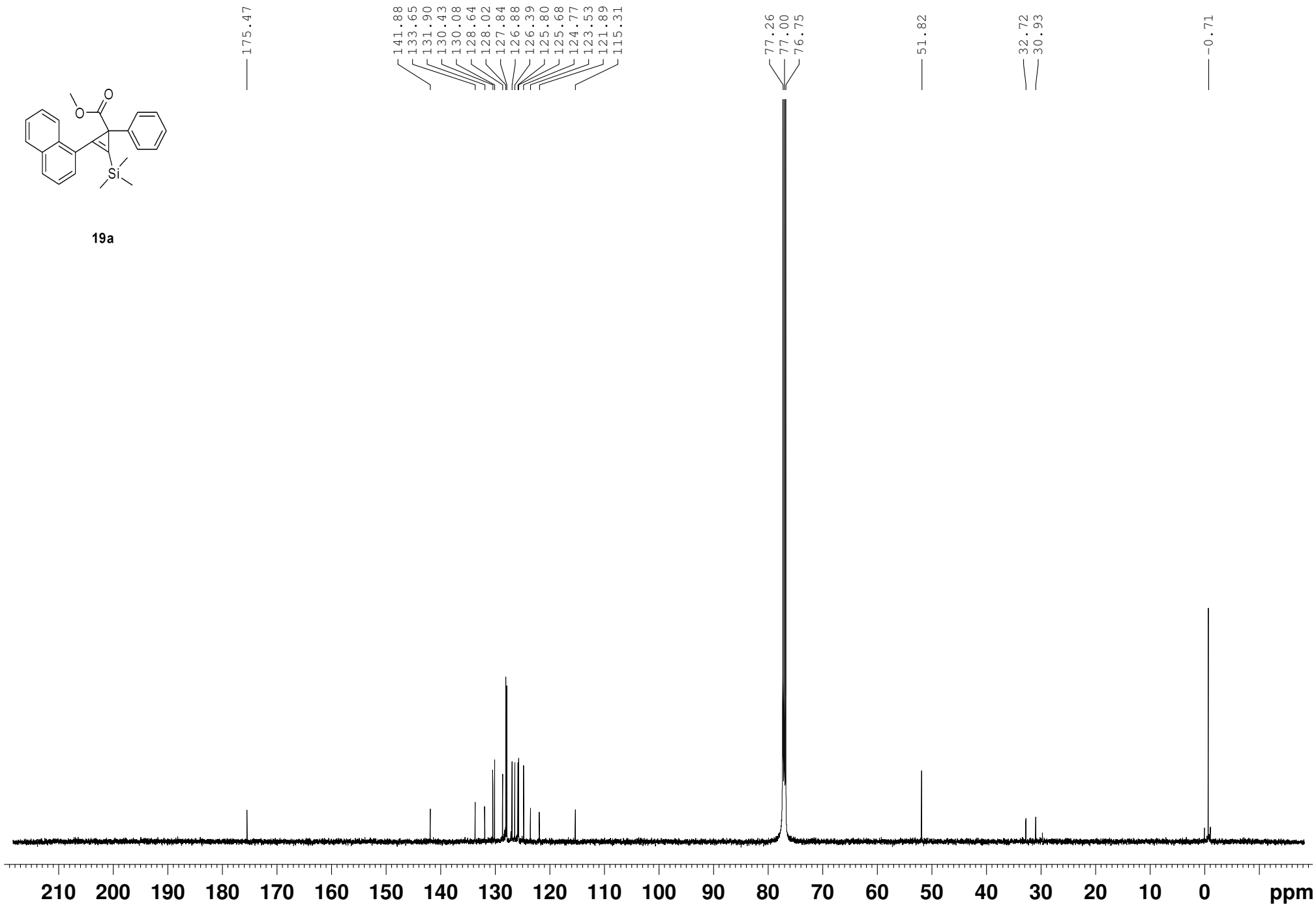


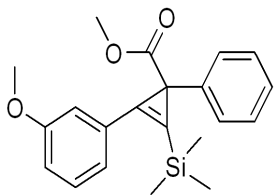
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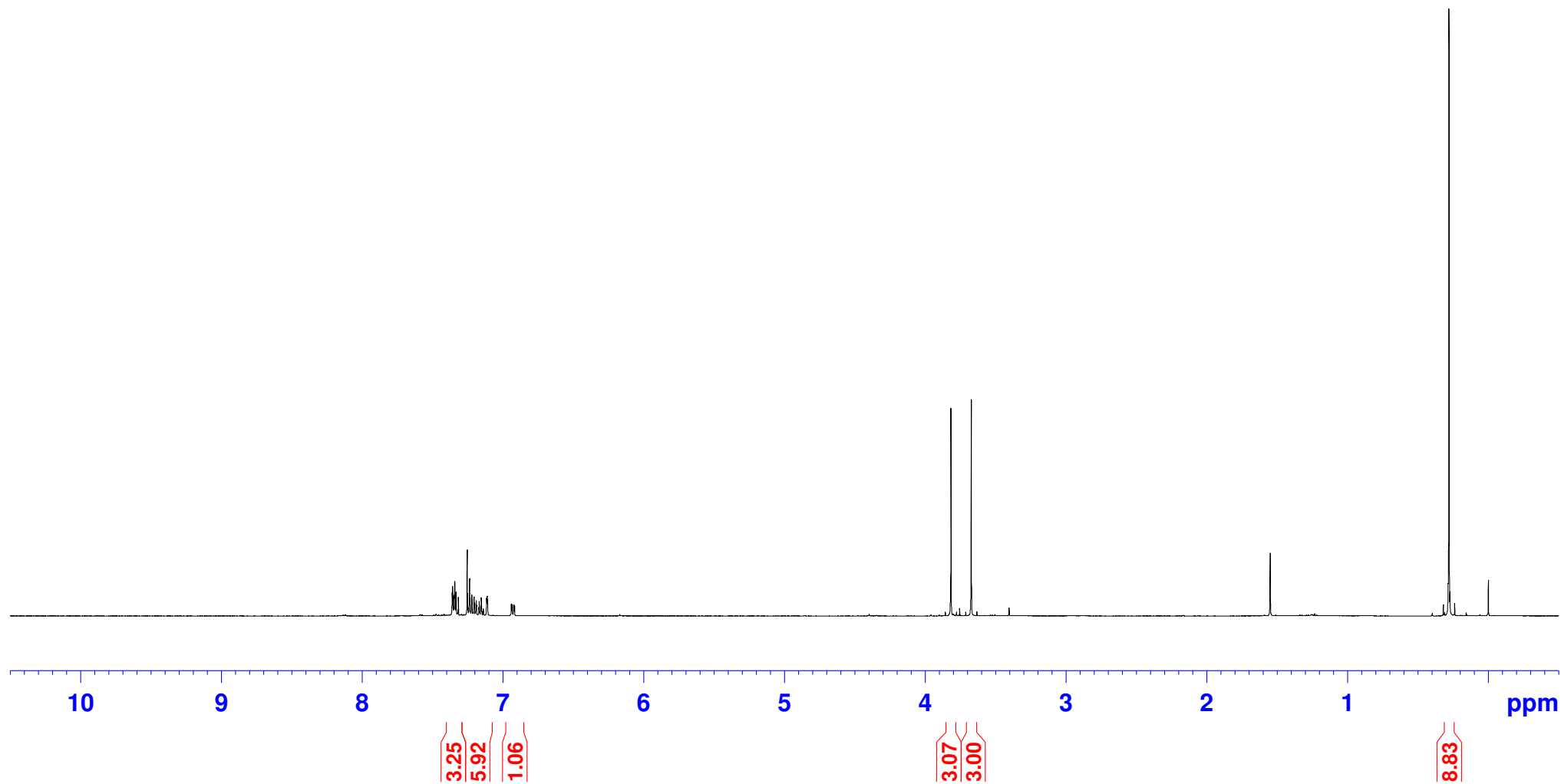


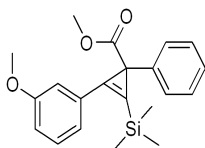
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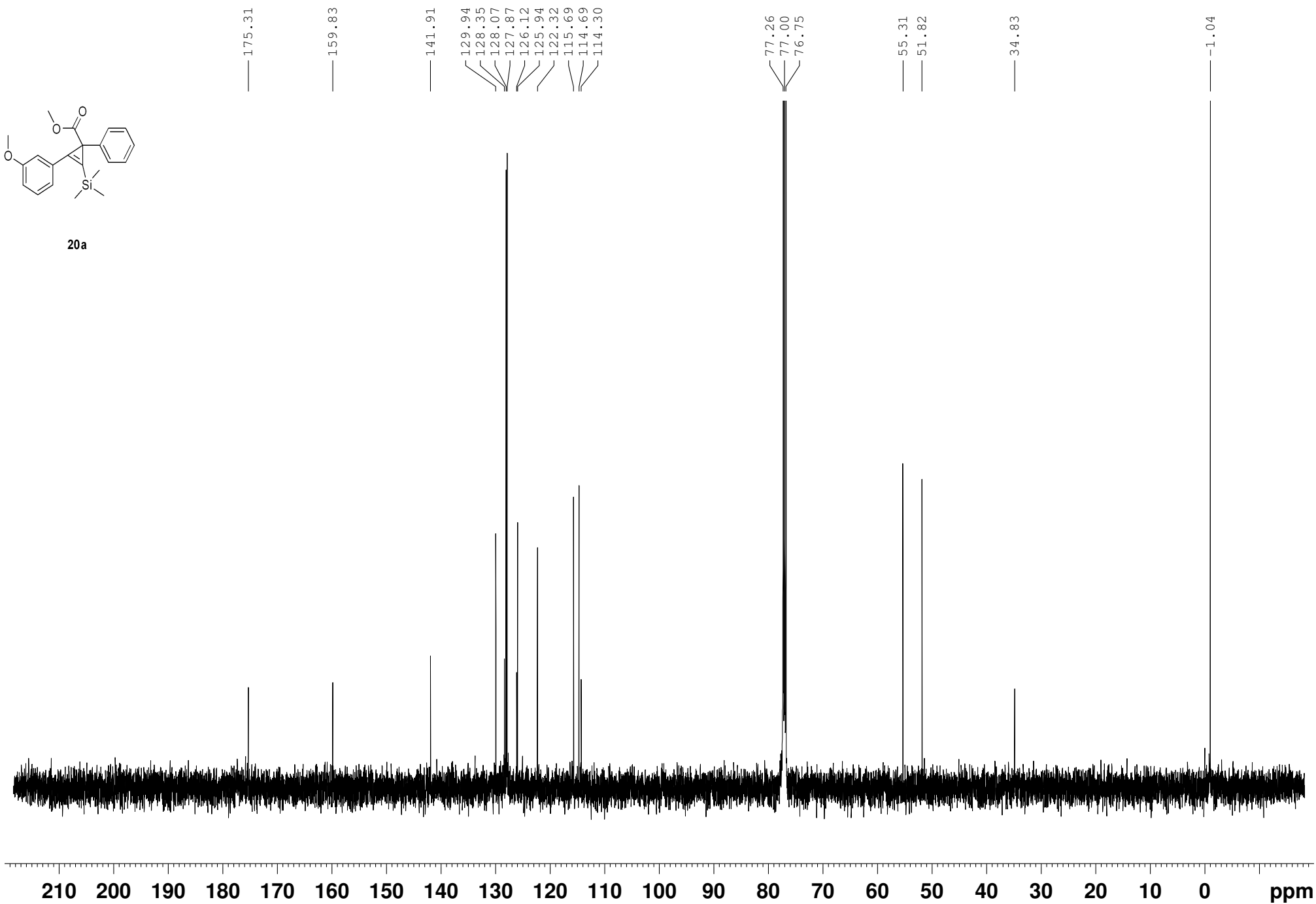


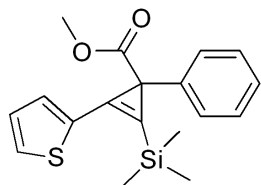
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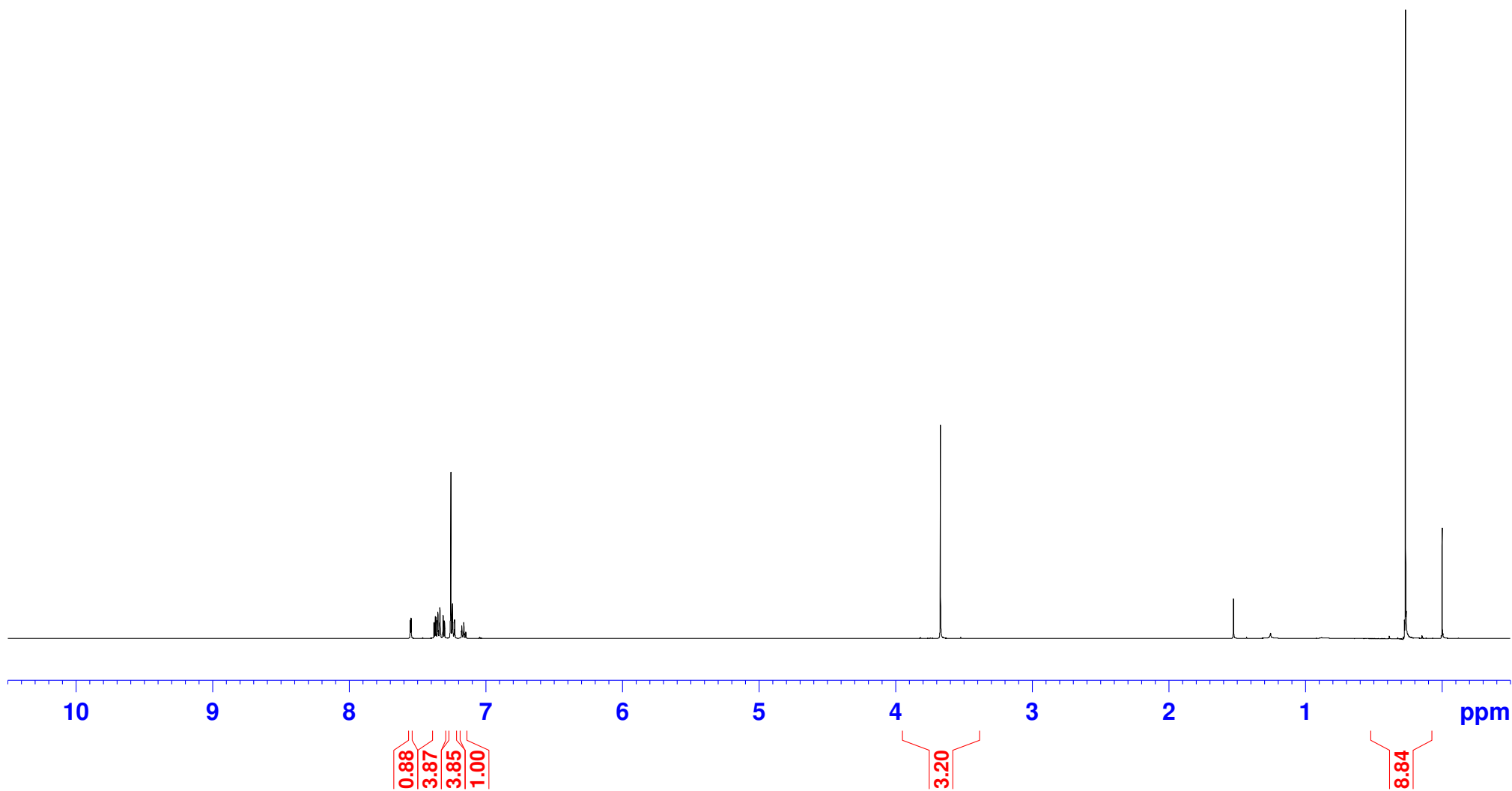


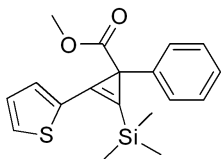
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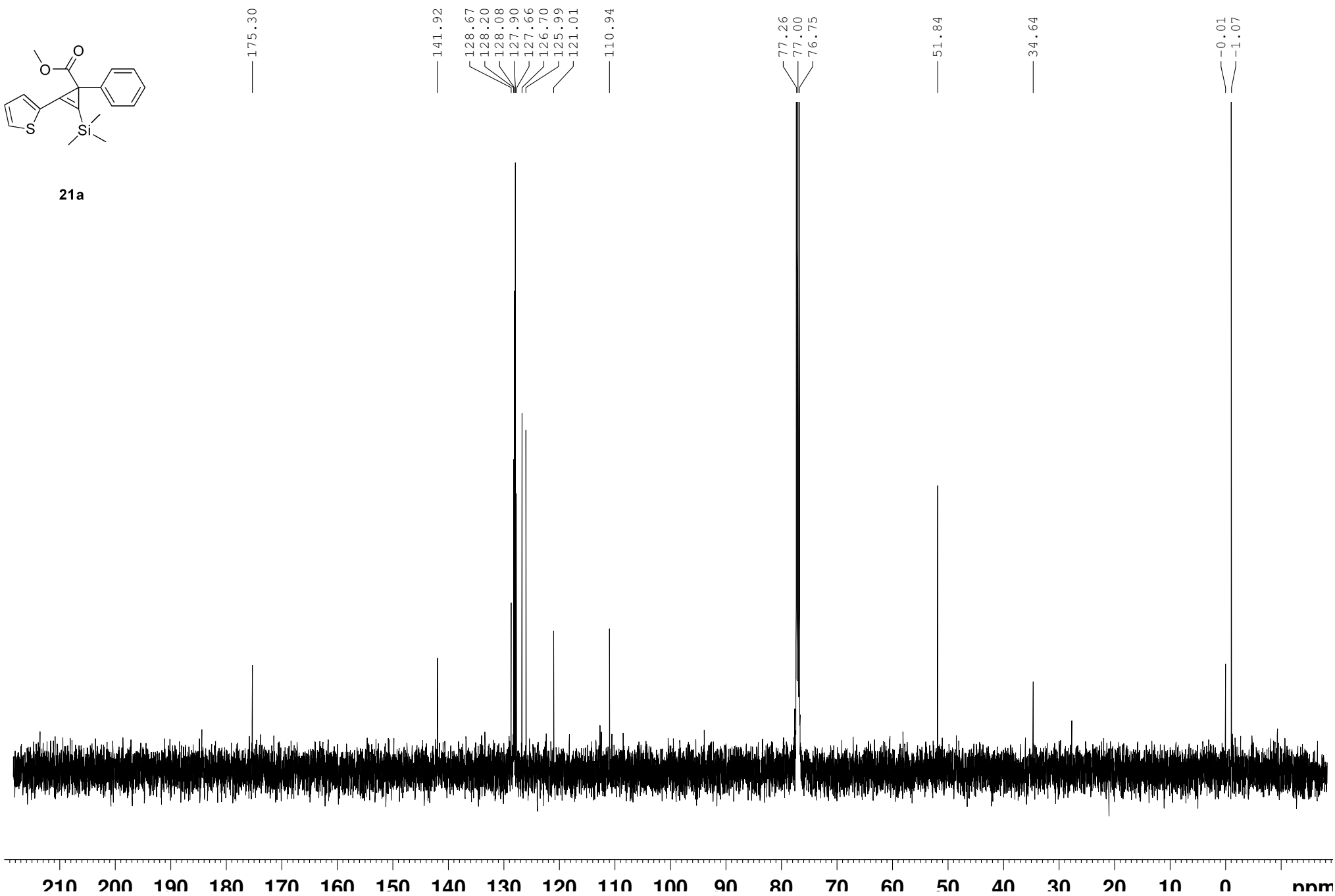


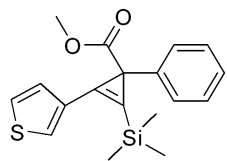
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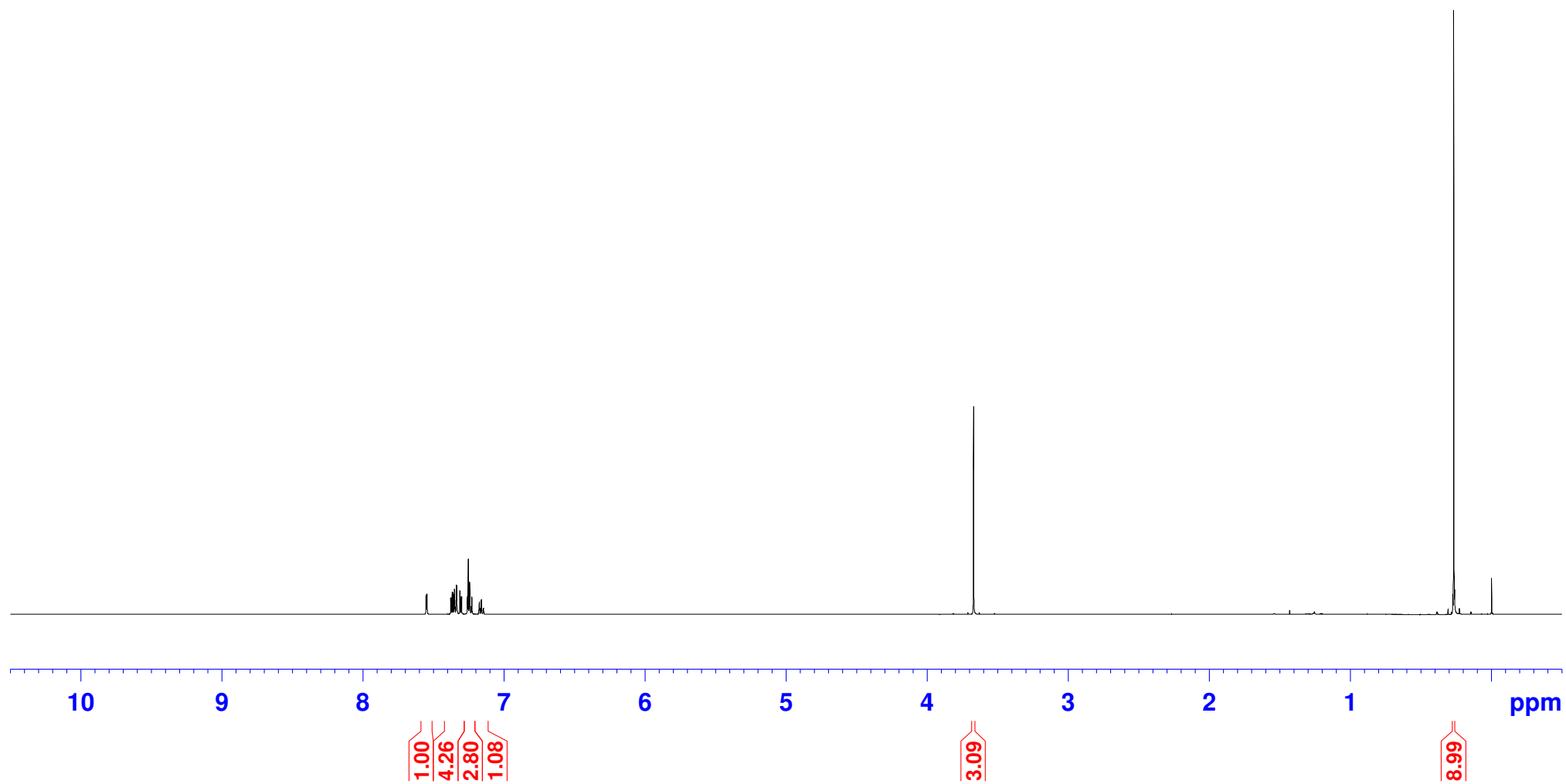


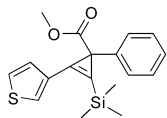
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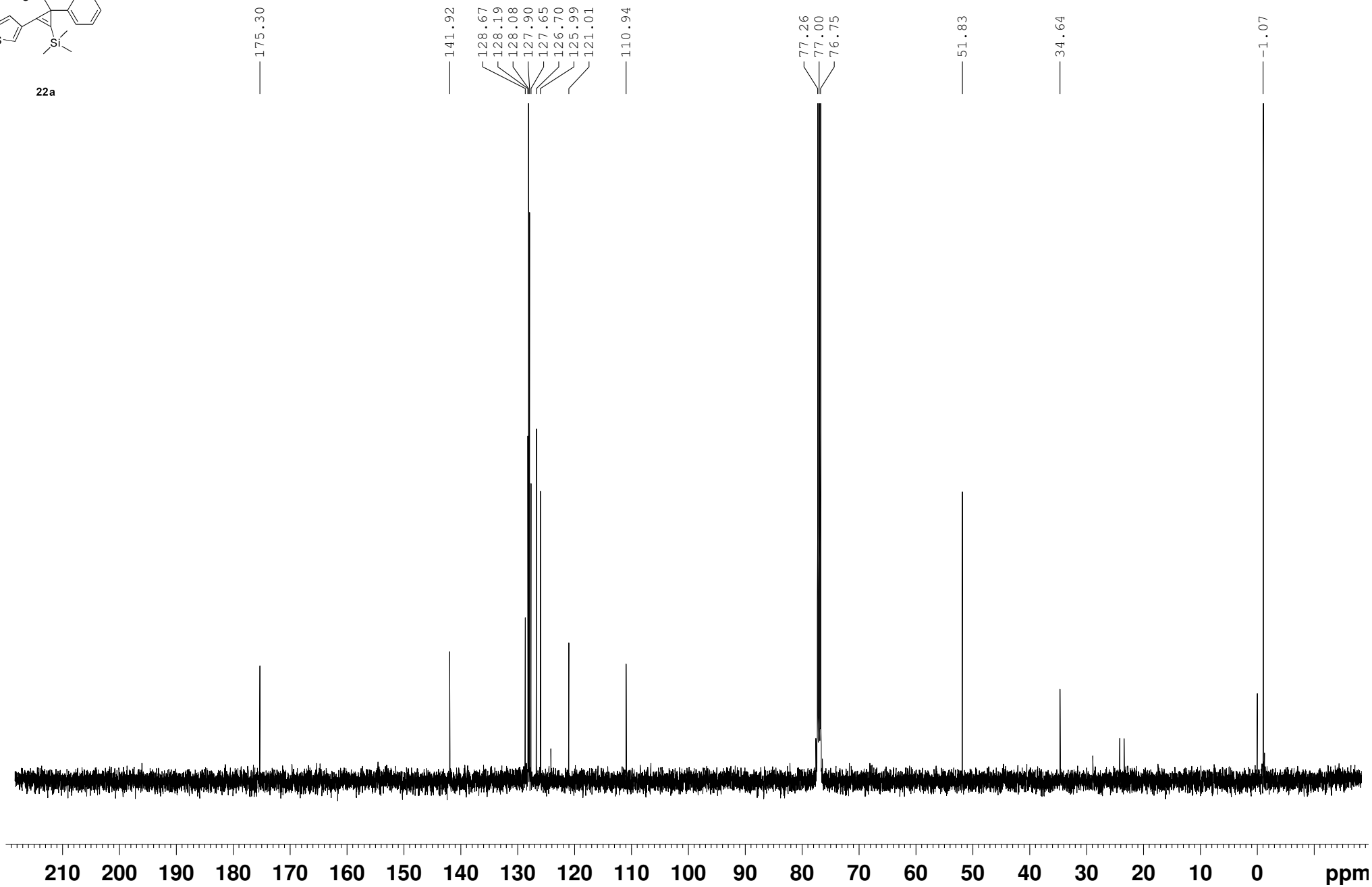


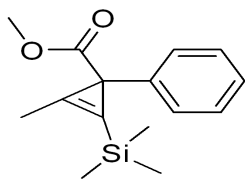
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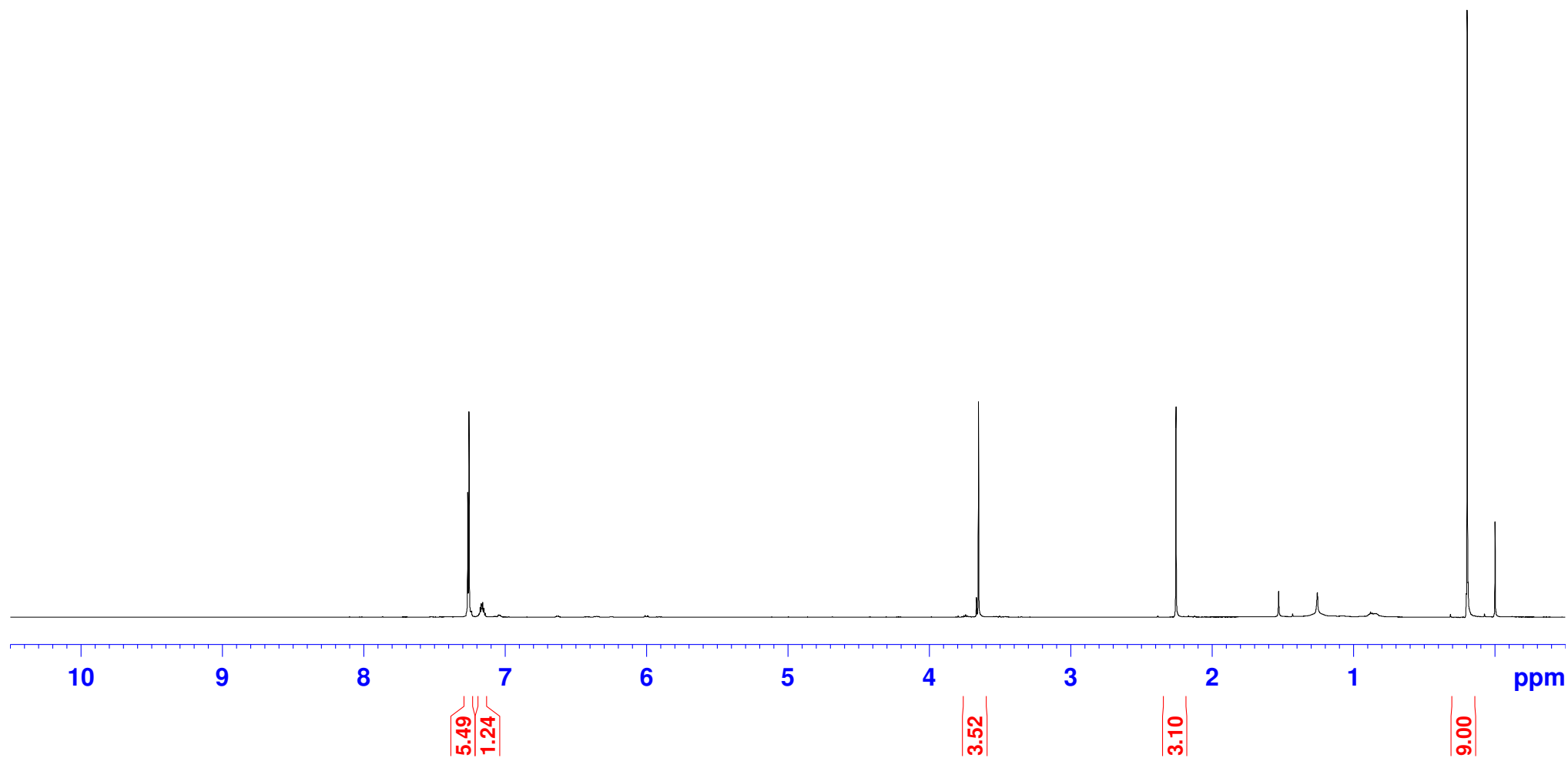


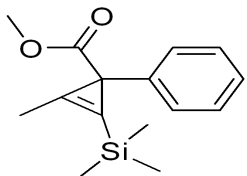
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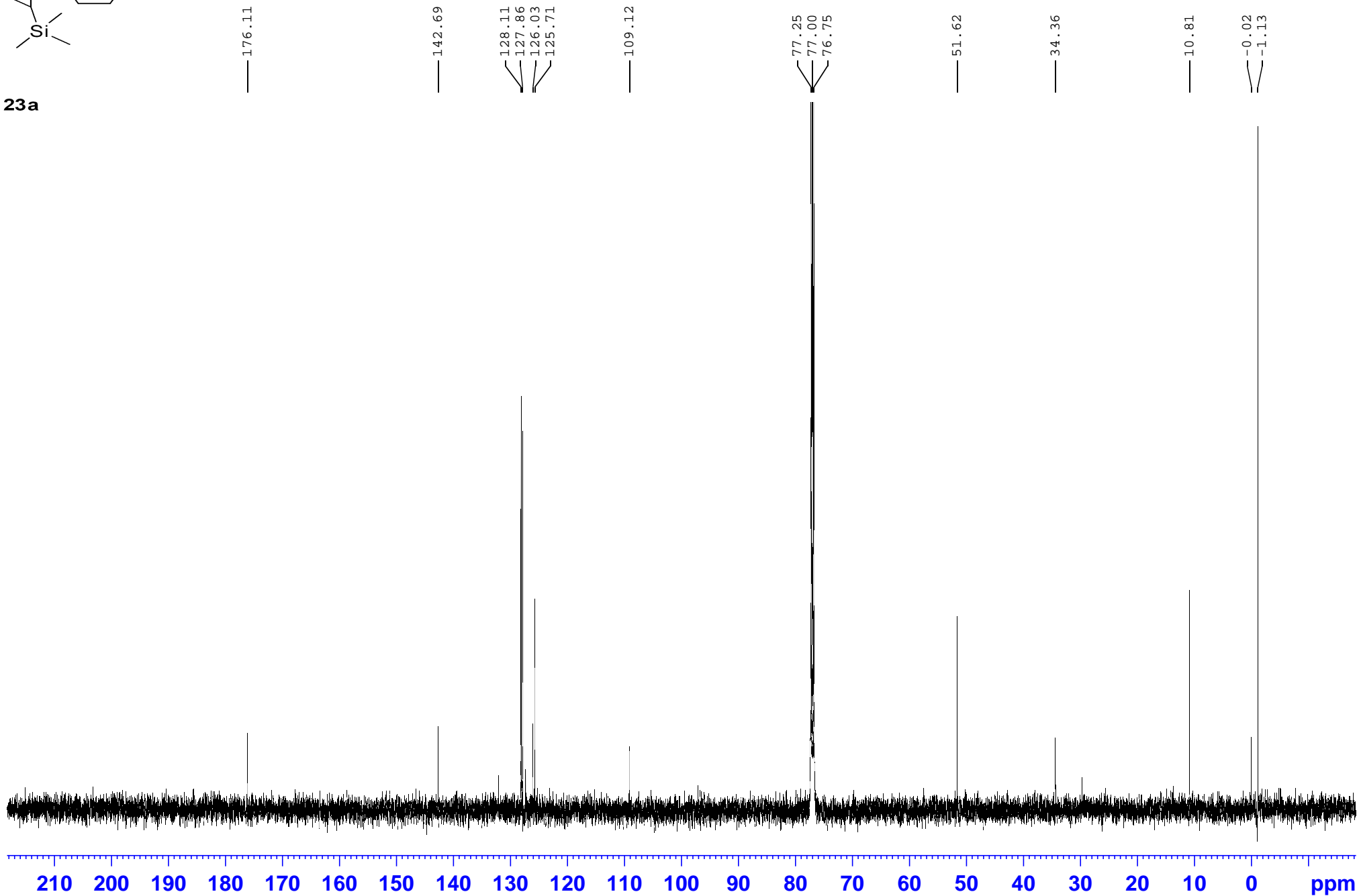


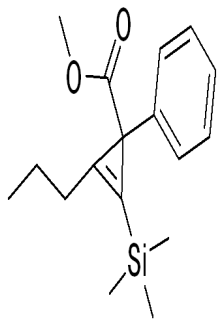
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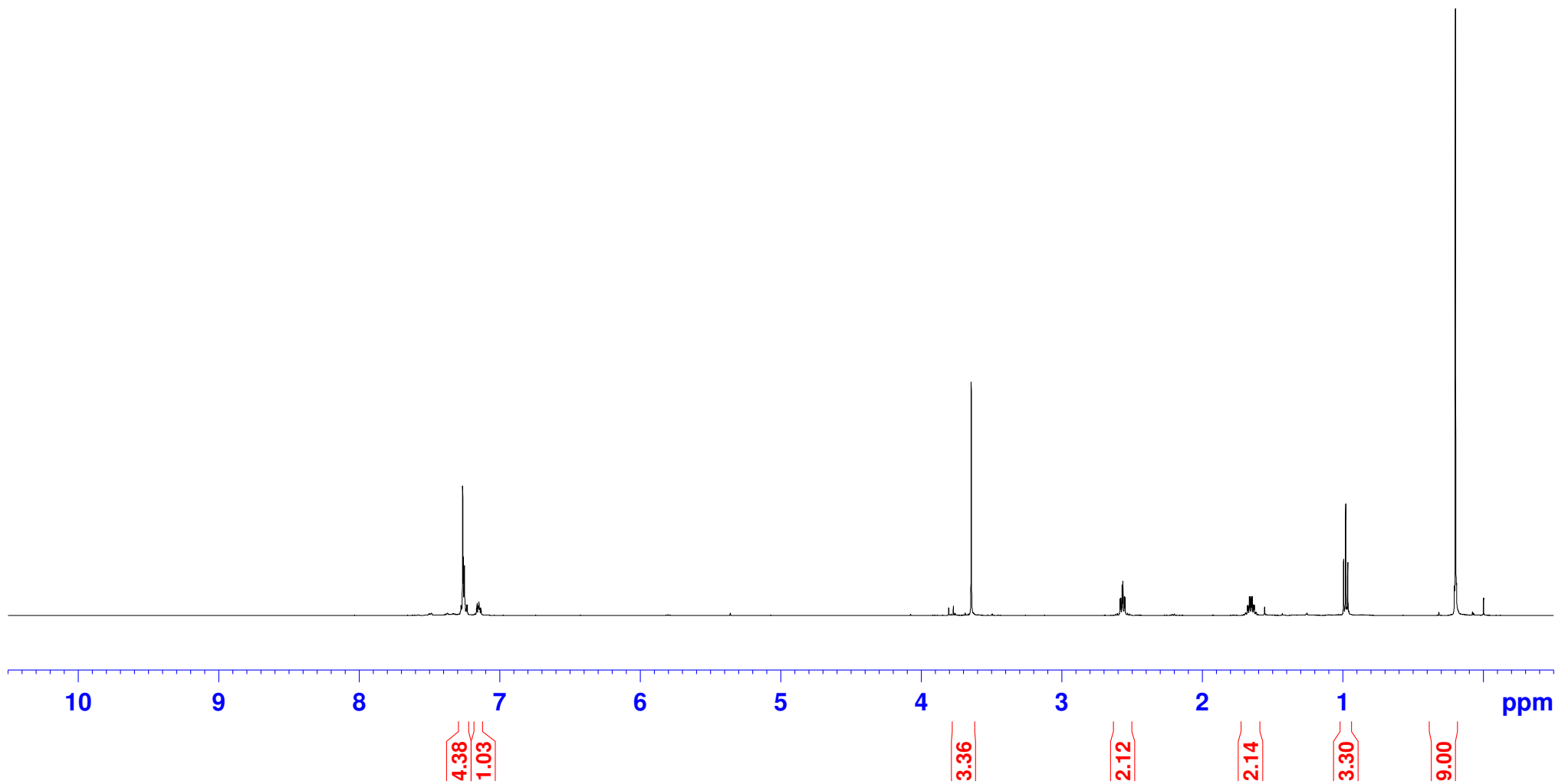


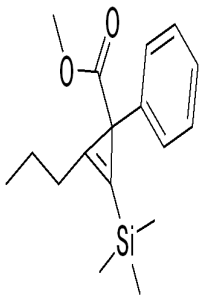
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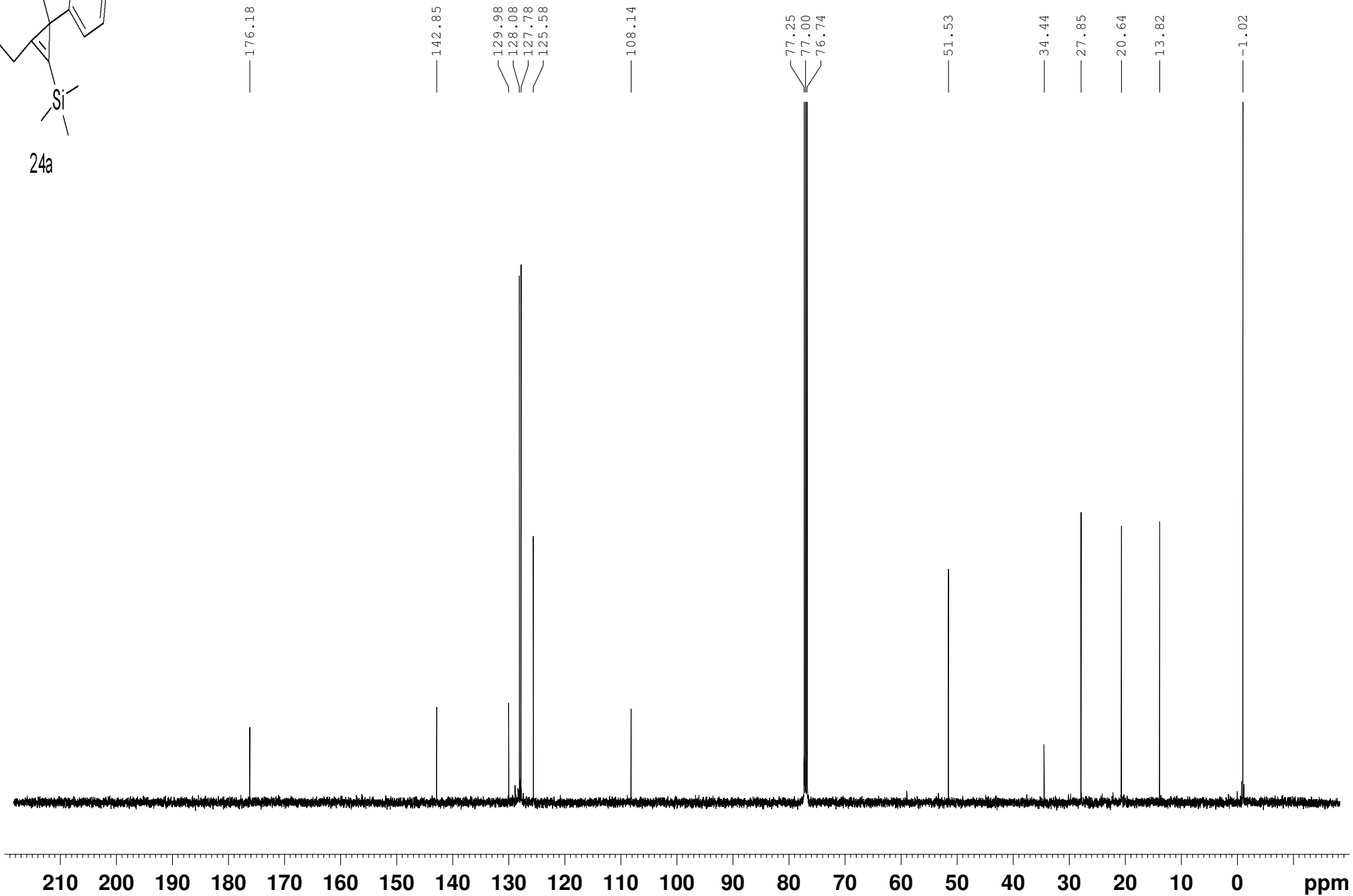


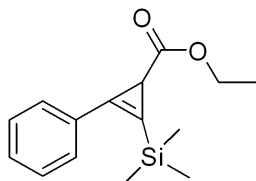
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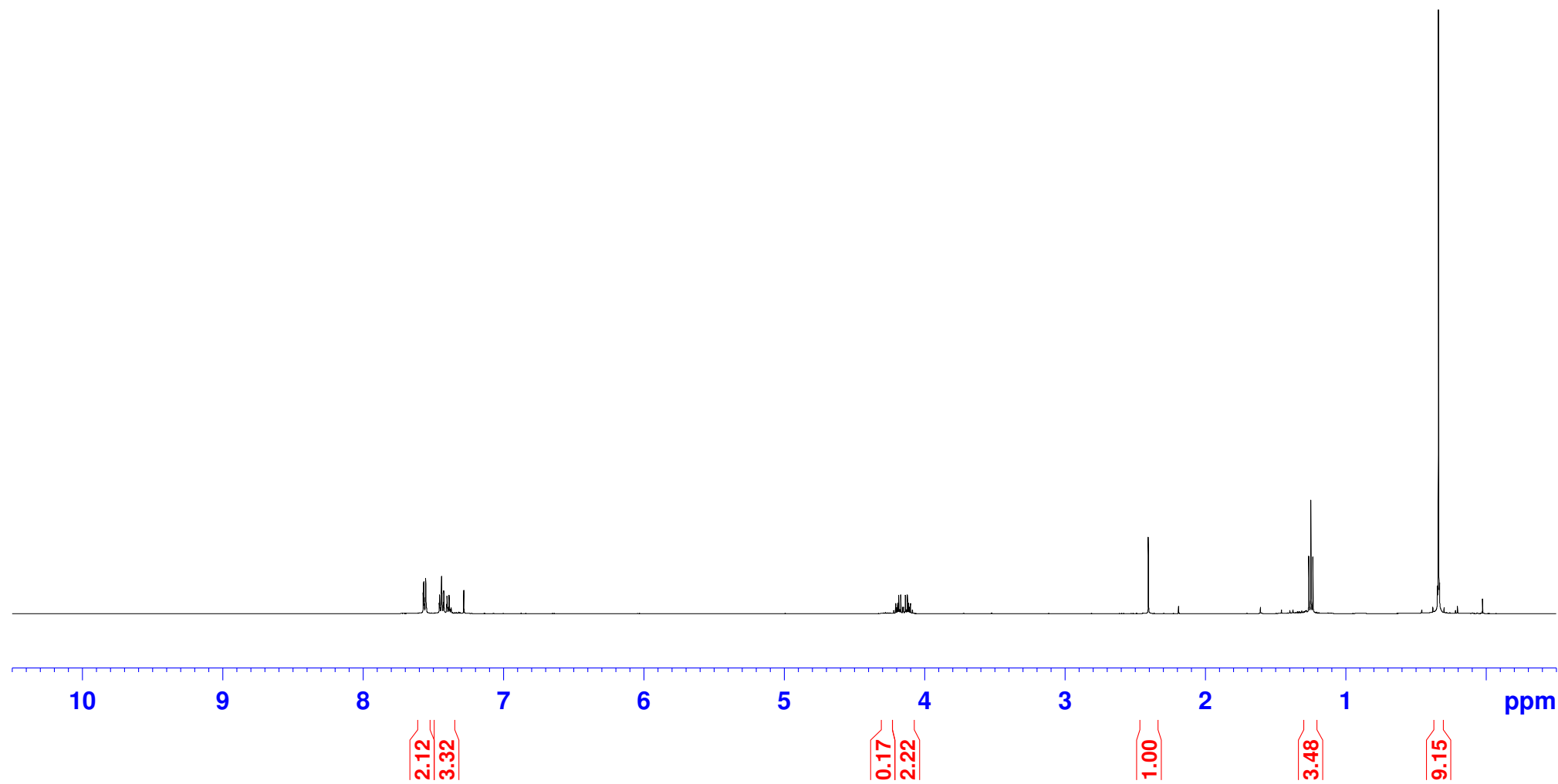


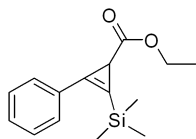
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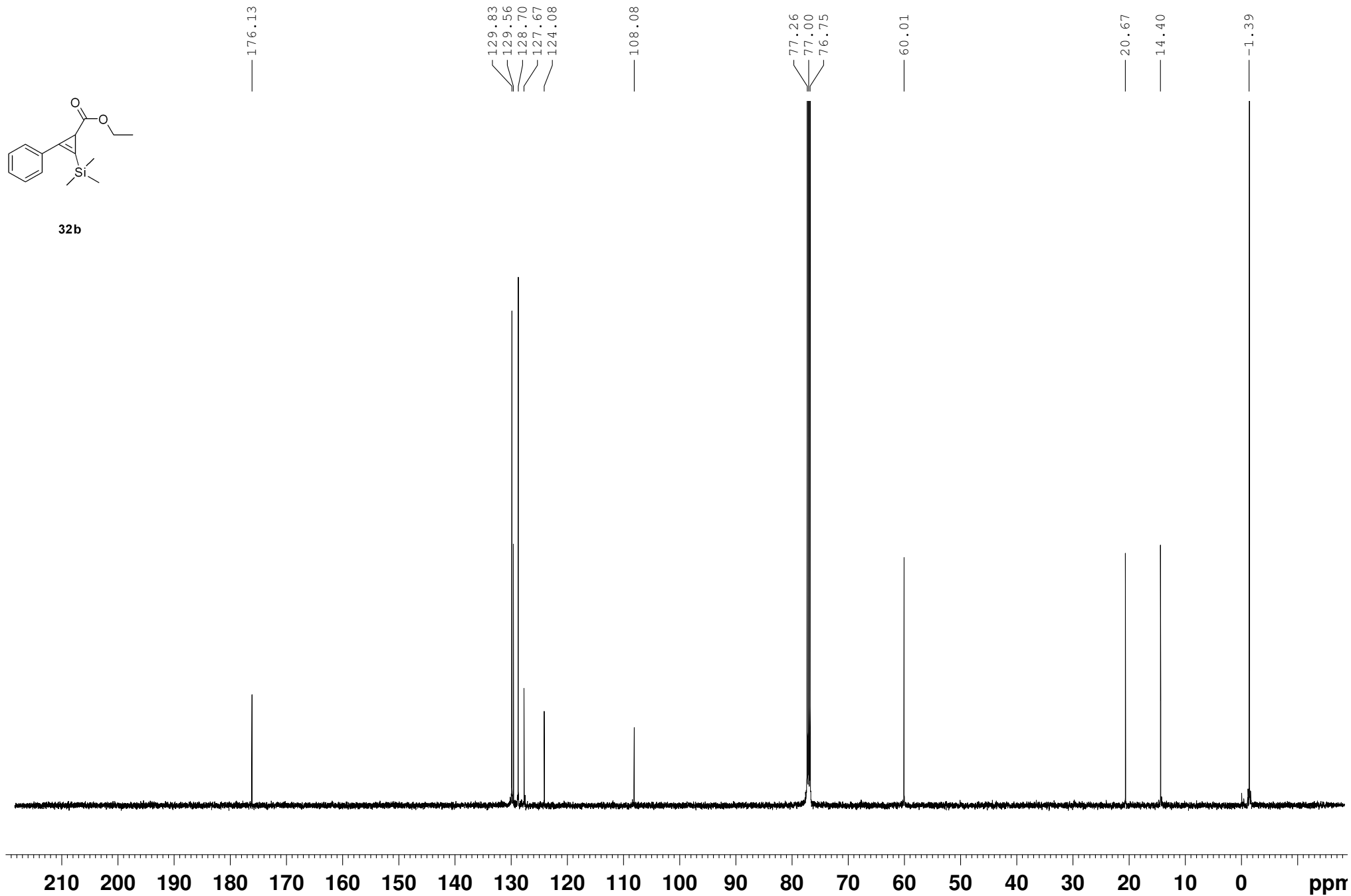


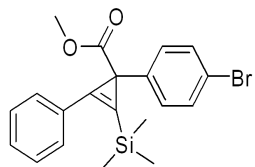
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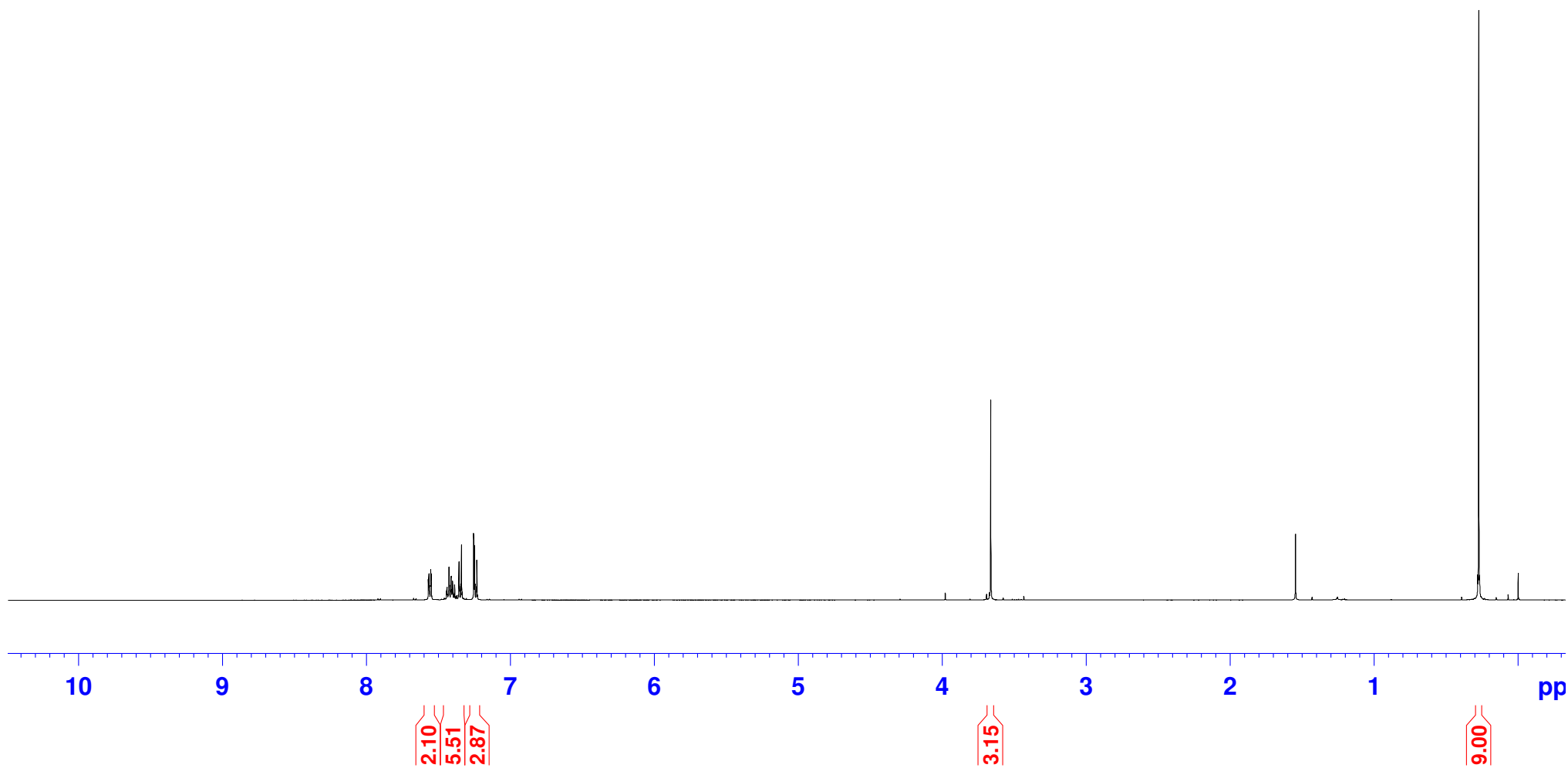


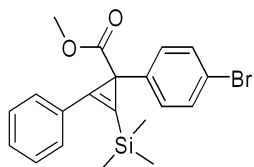
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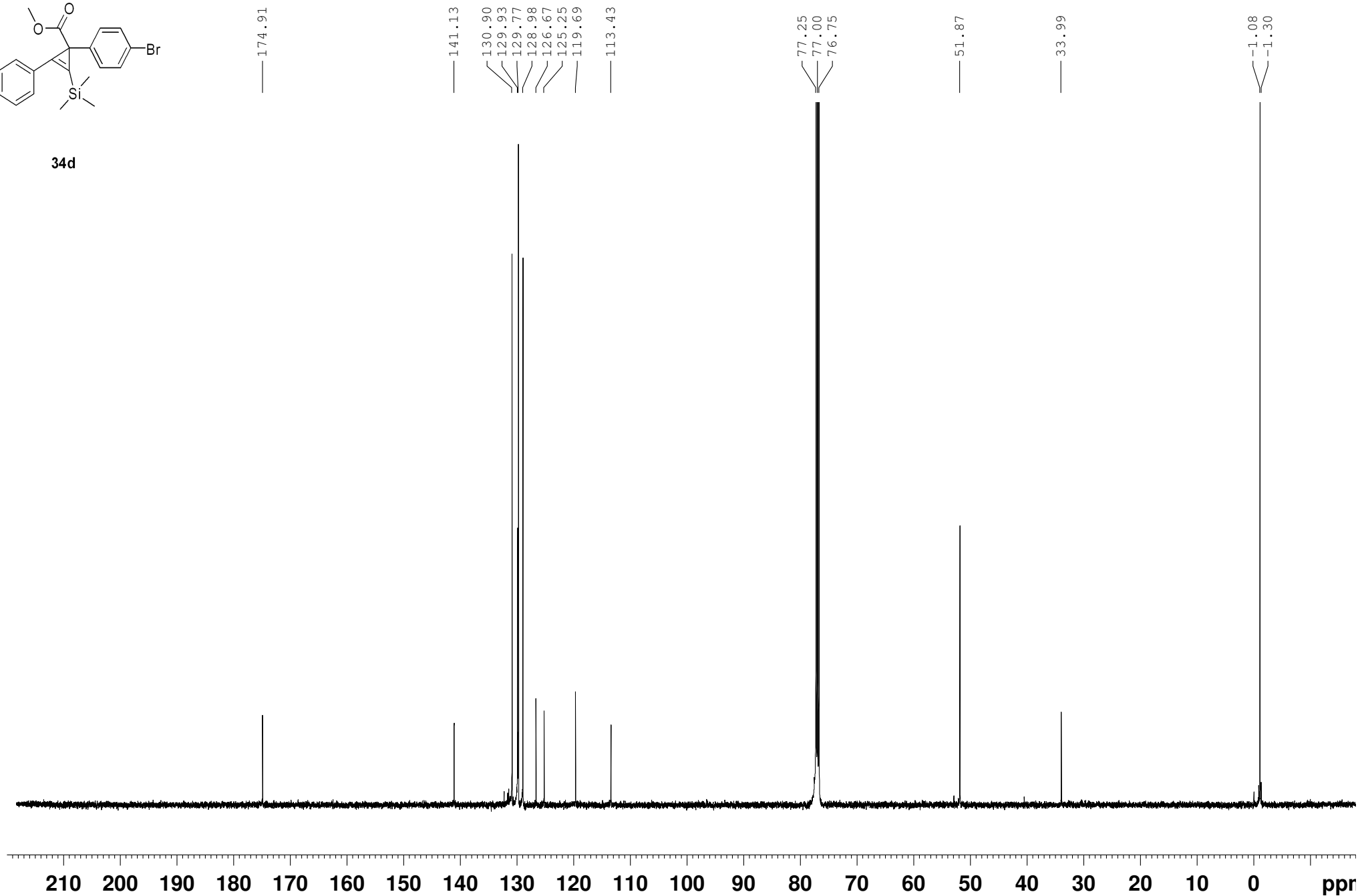


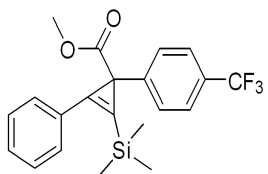
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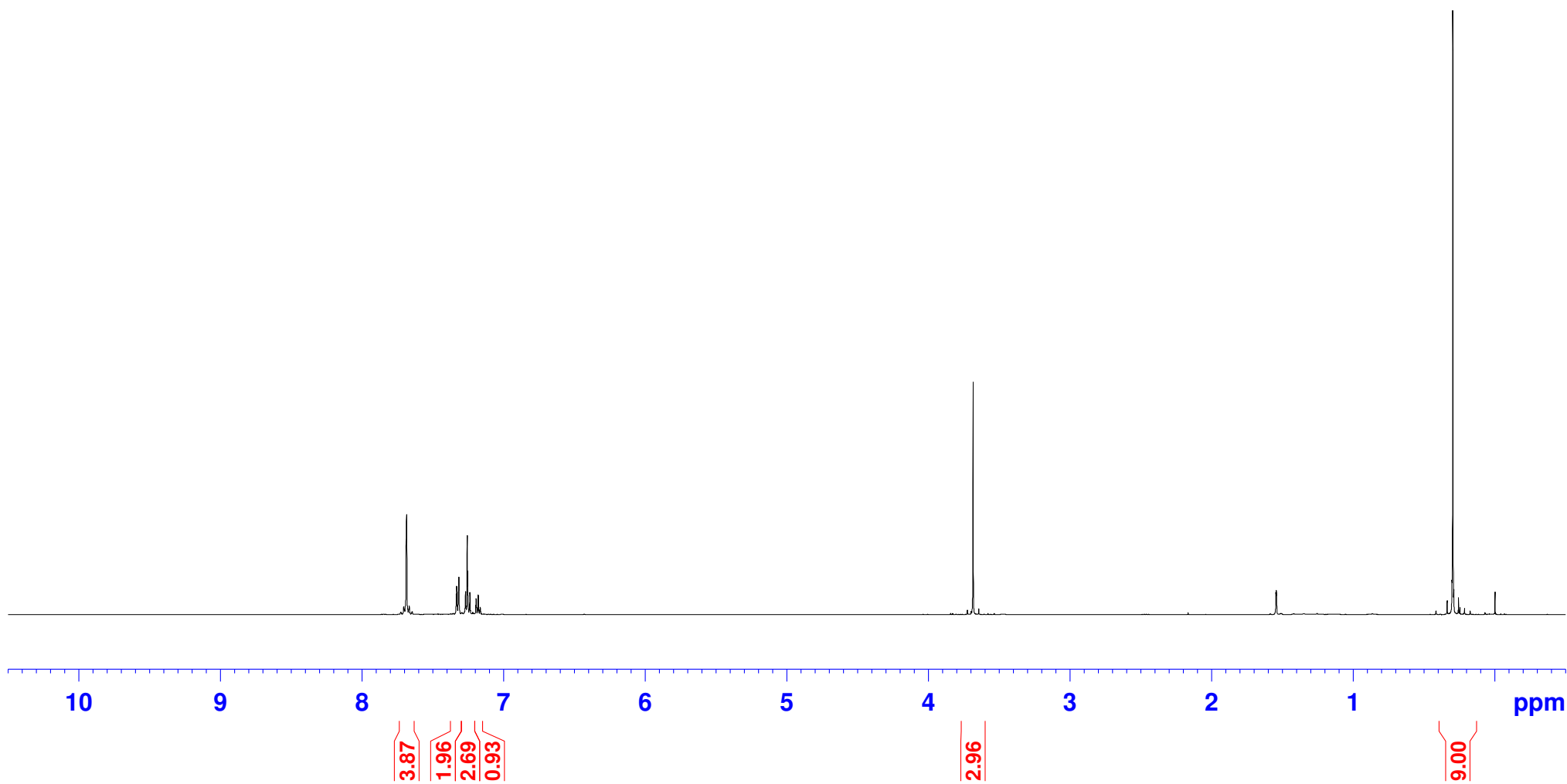


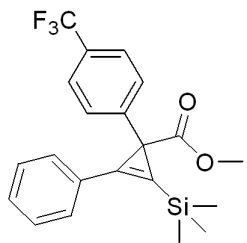
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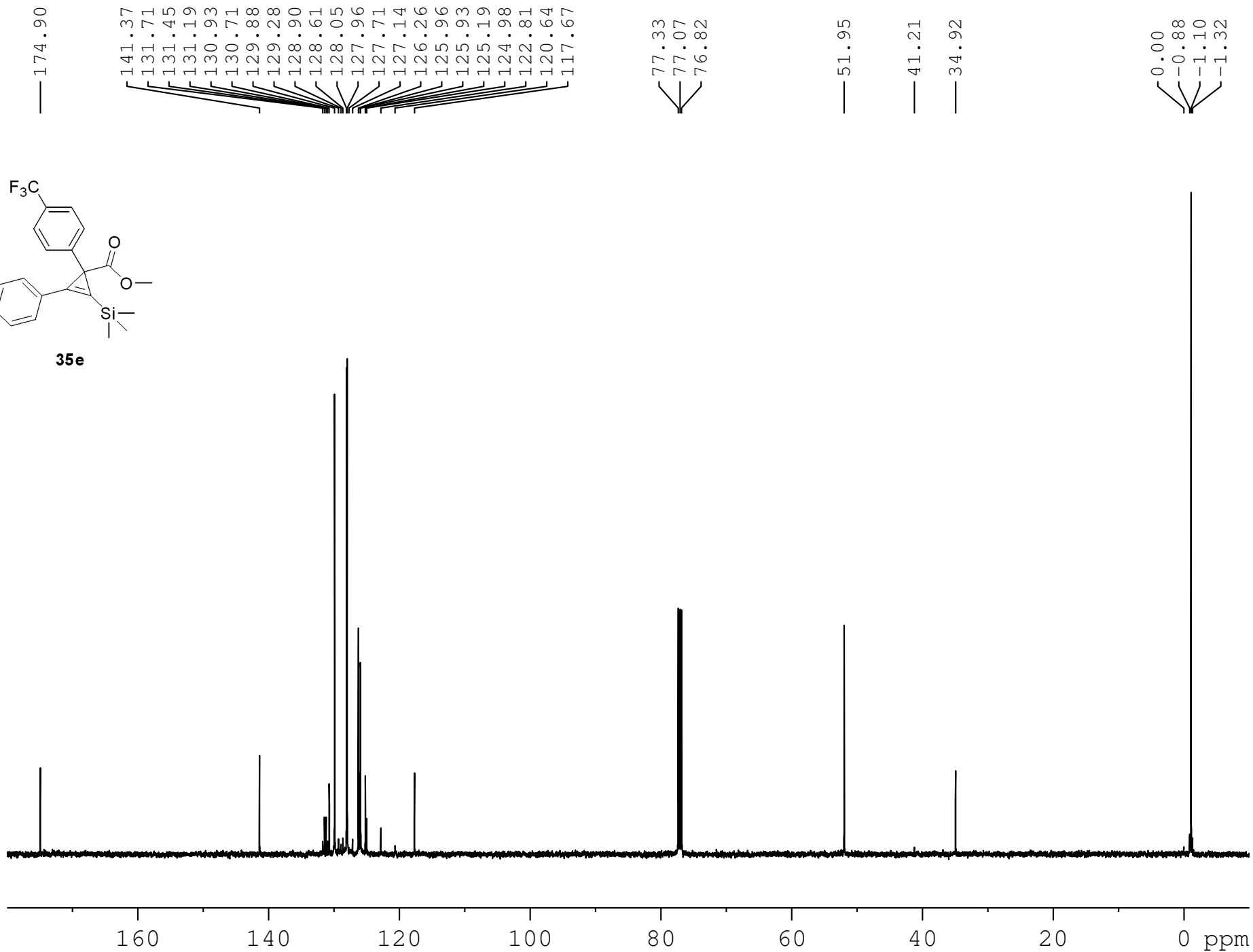


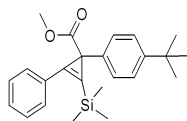
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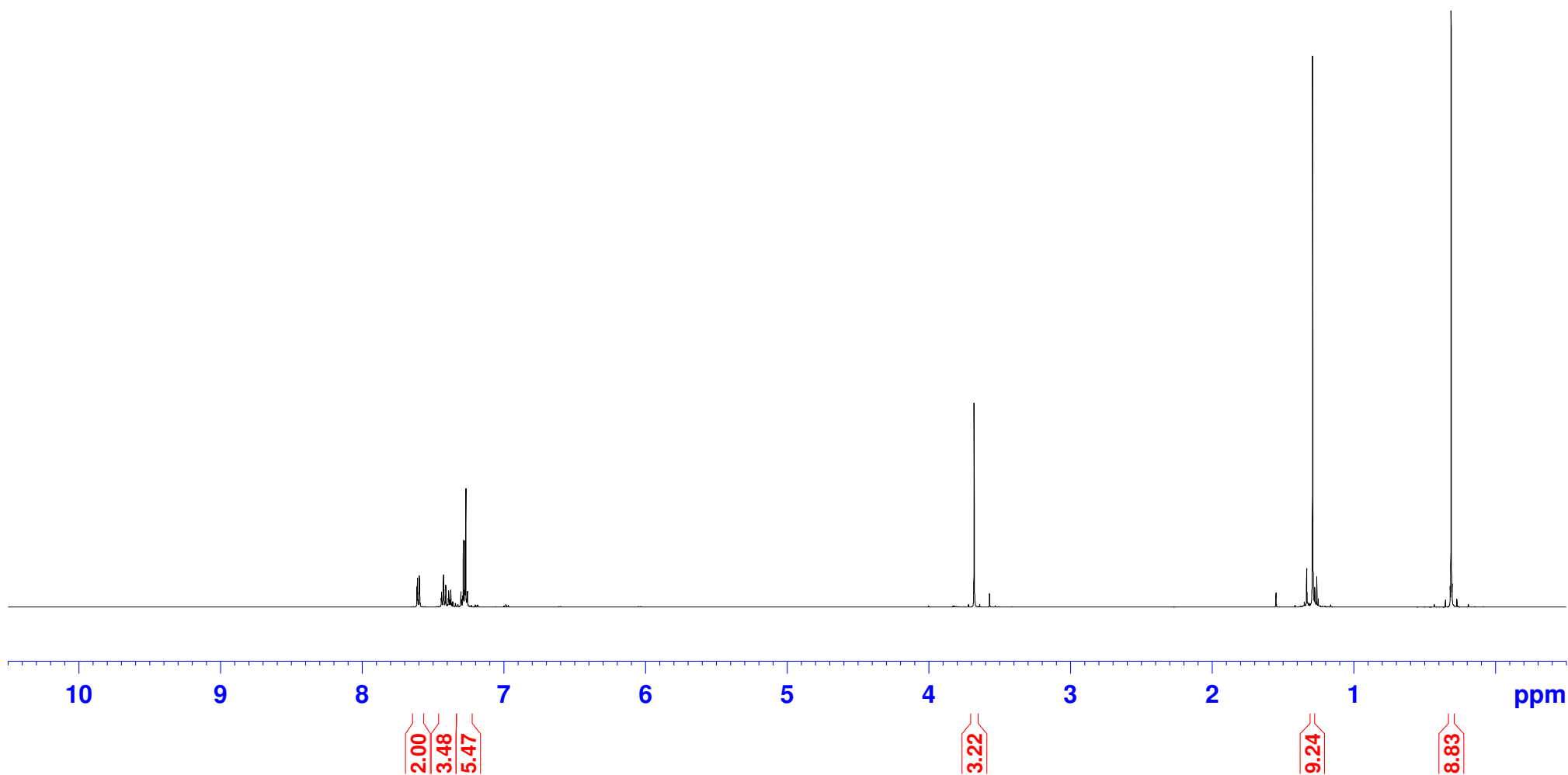


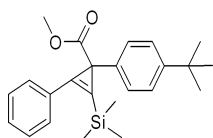
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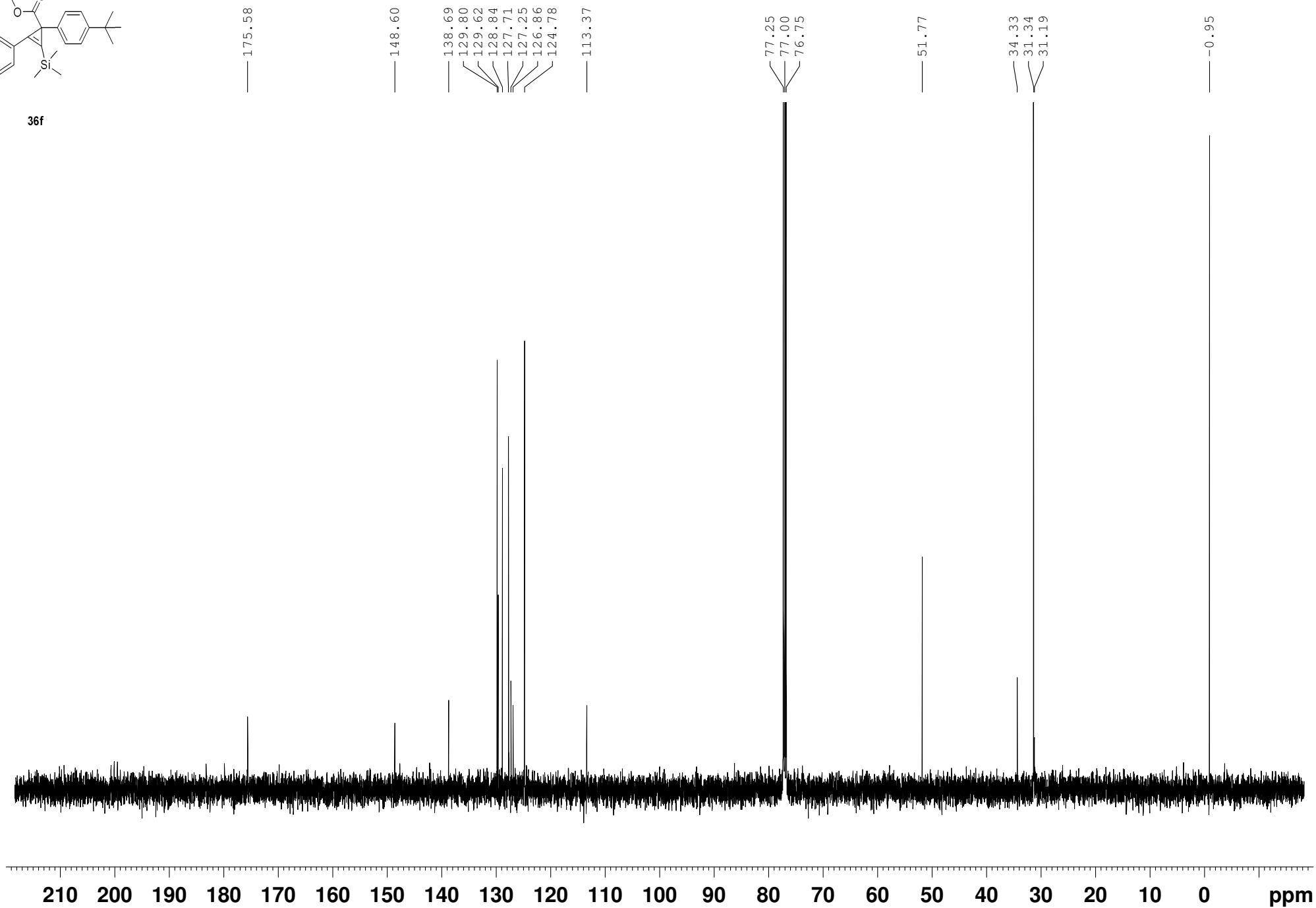


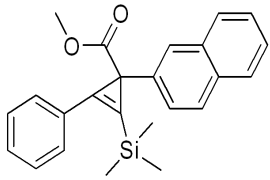
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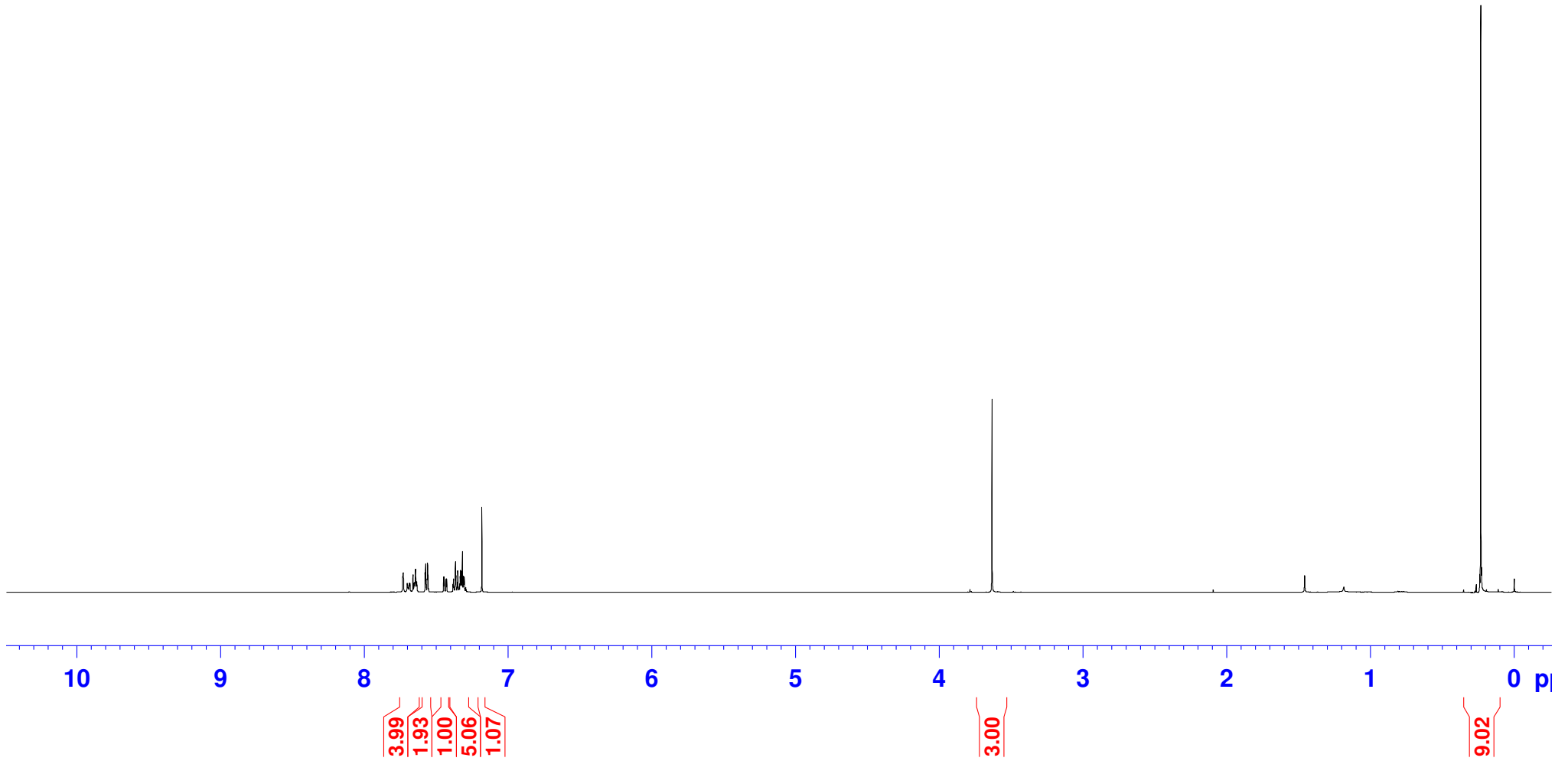


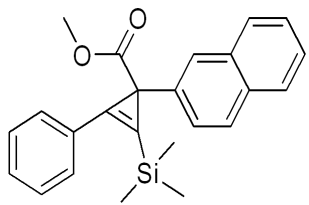
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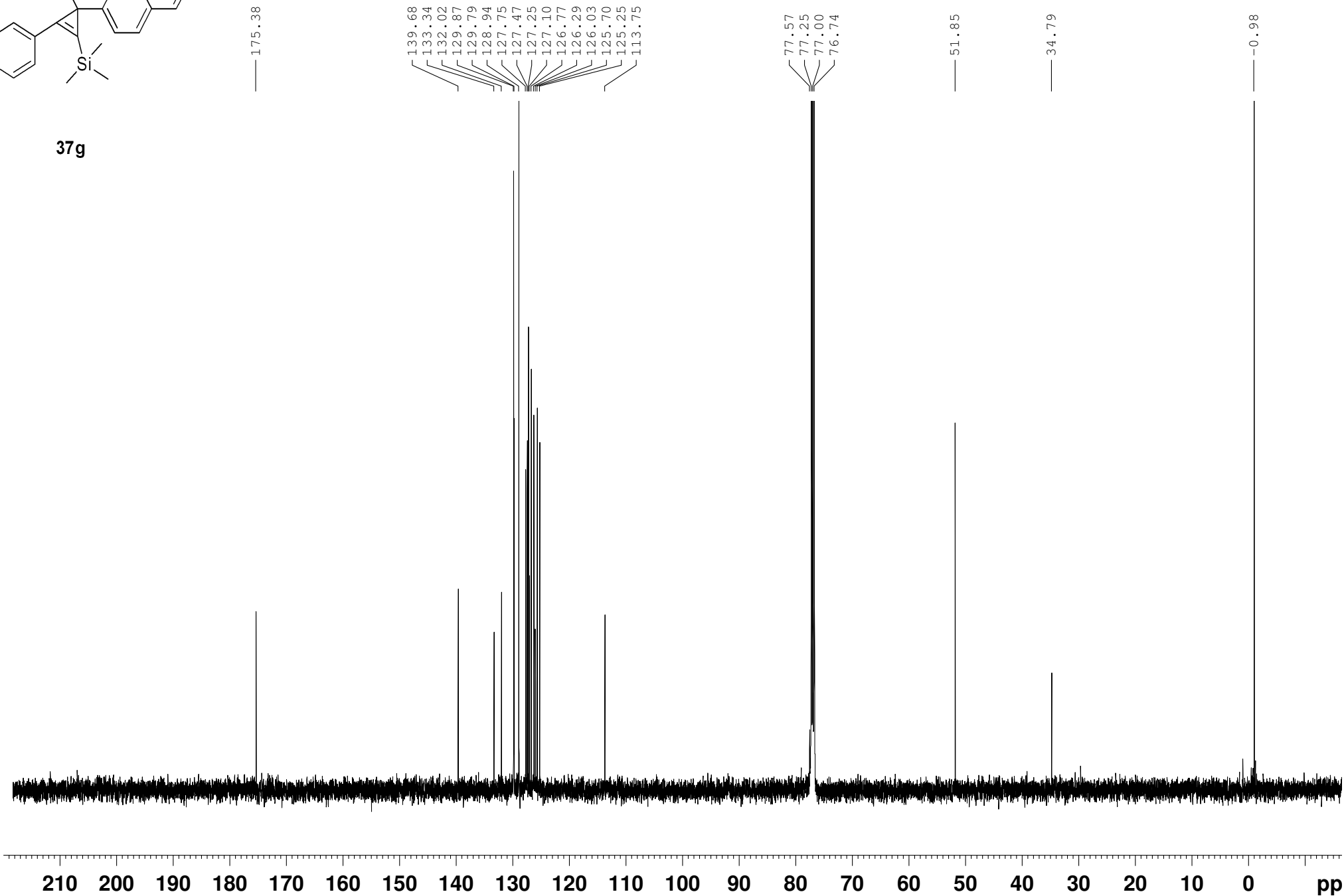


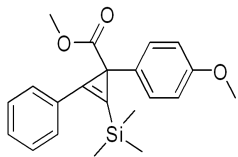
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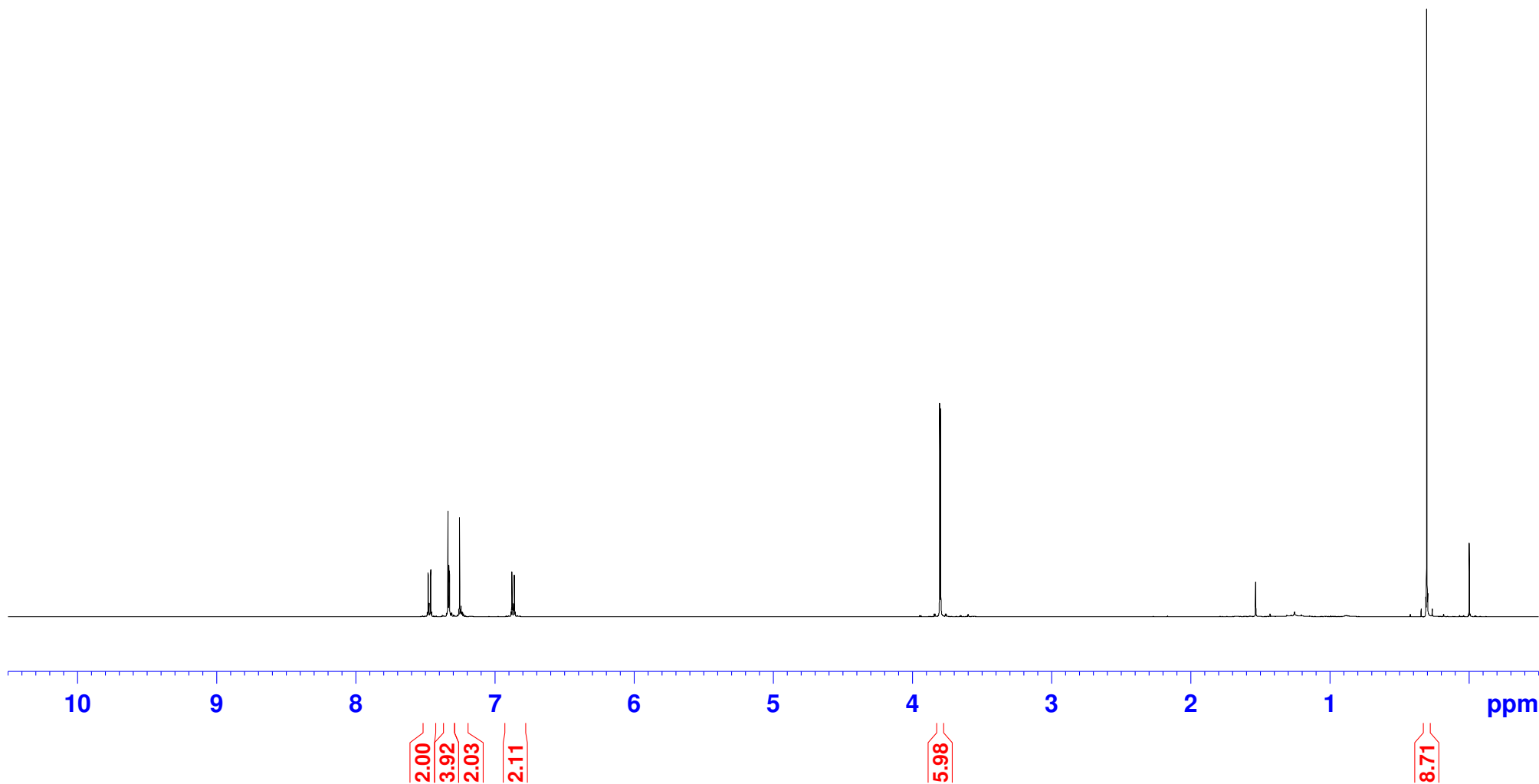


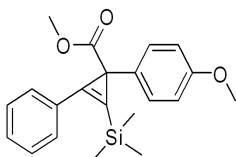
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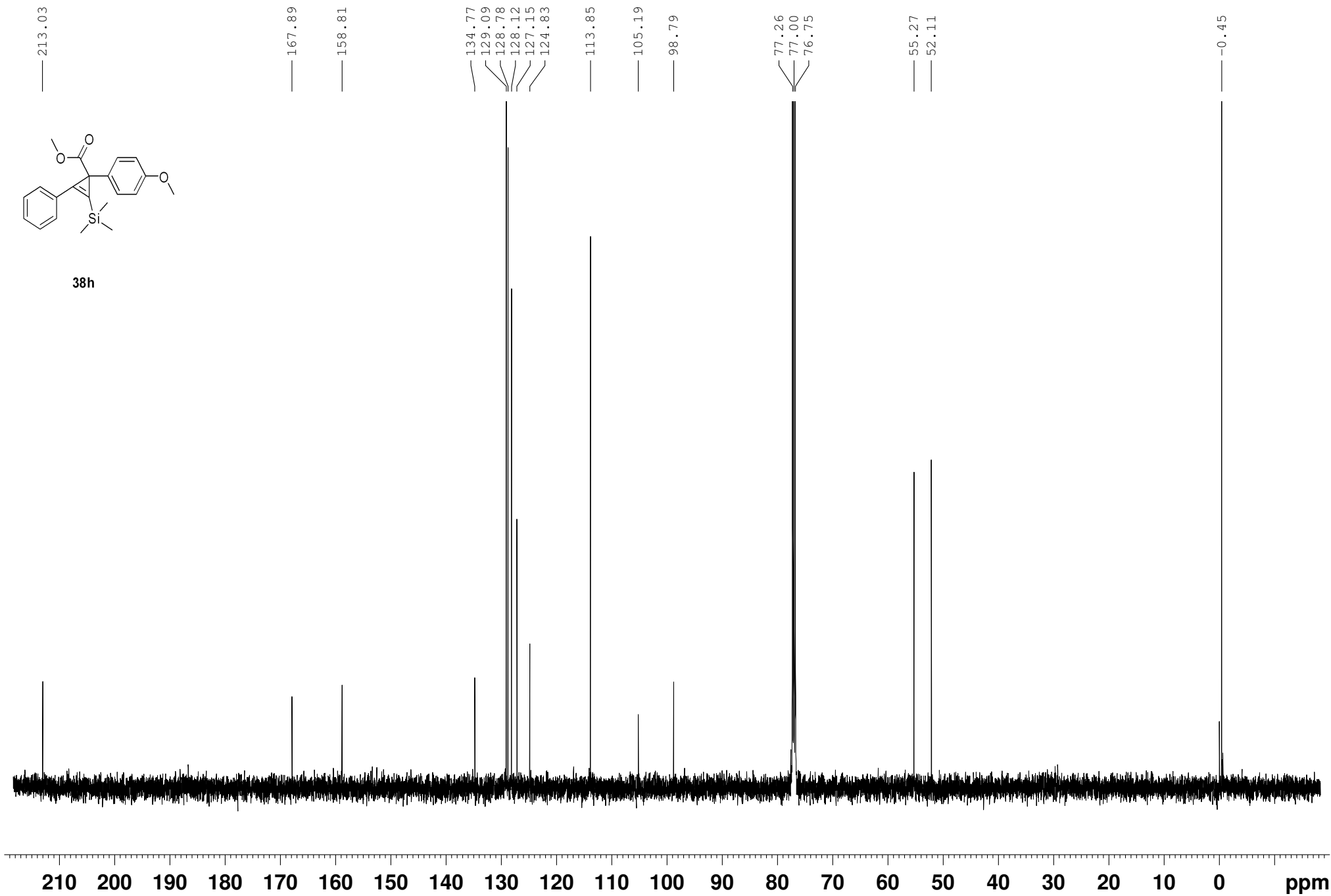


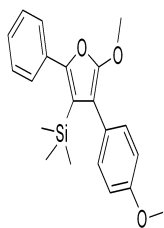
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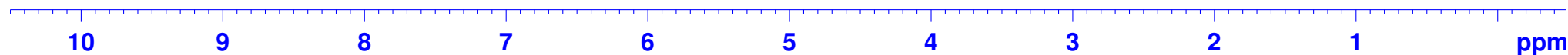
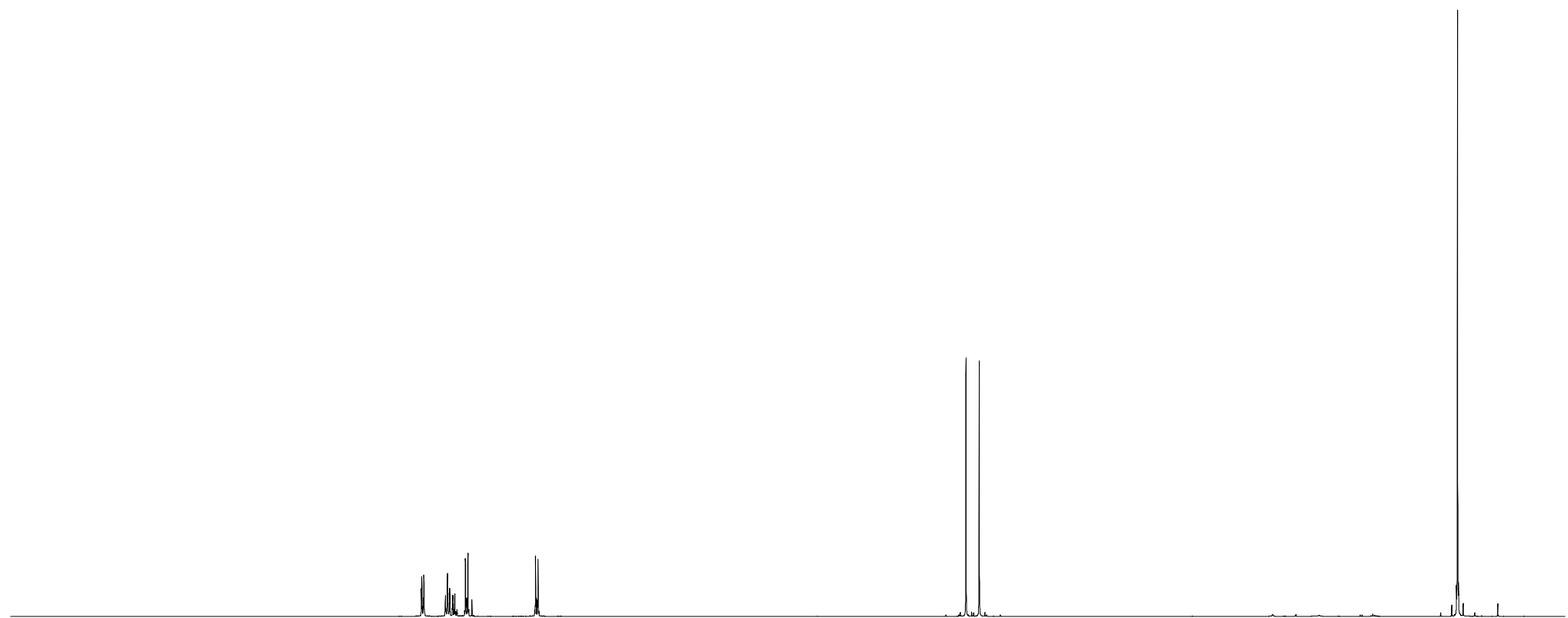


38h





39h

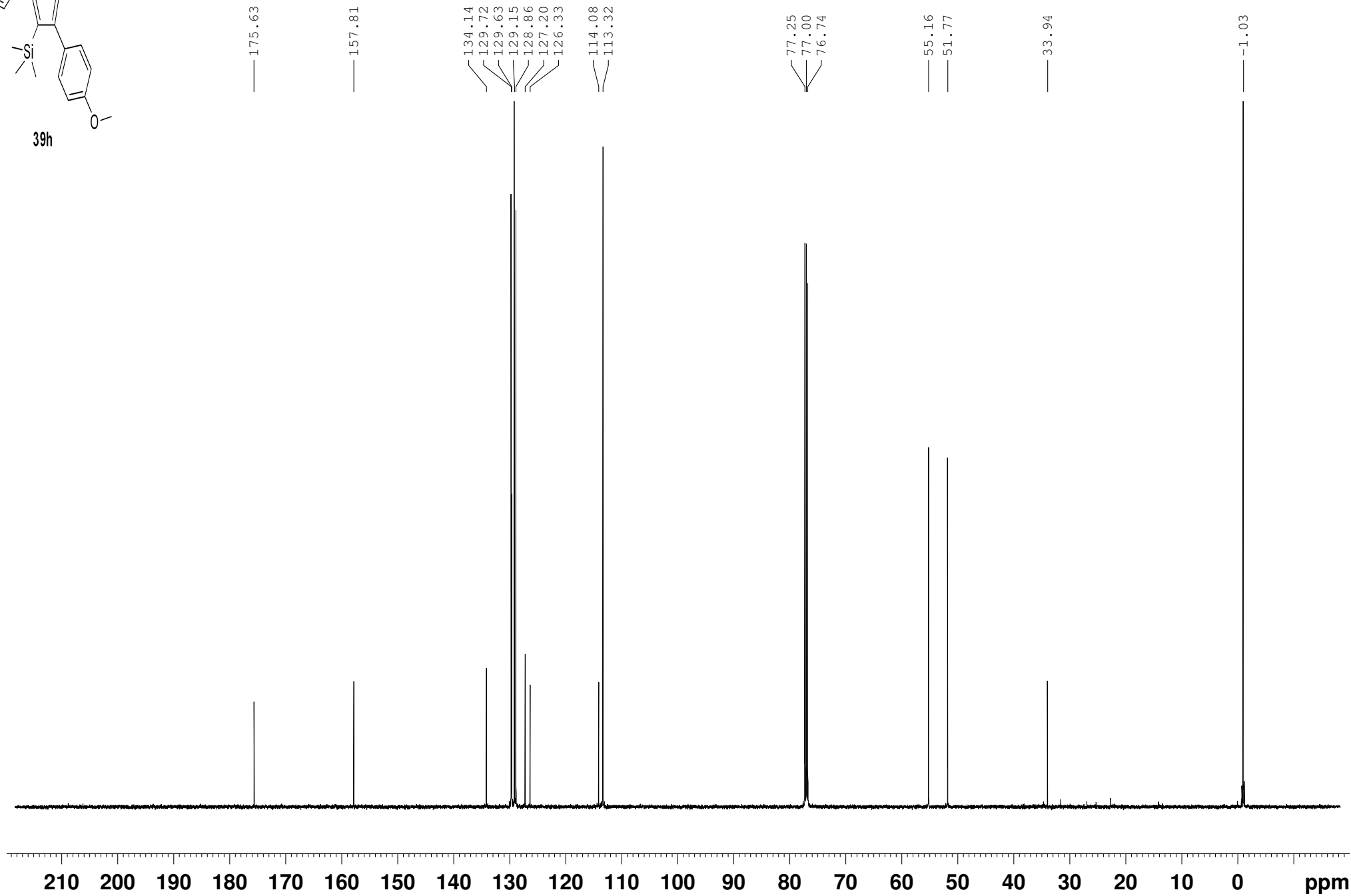
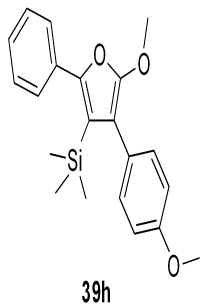


1.97
3.05
2.13
2.00

2.94
2.93

8.70

ppm

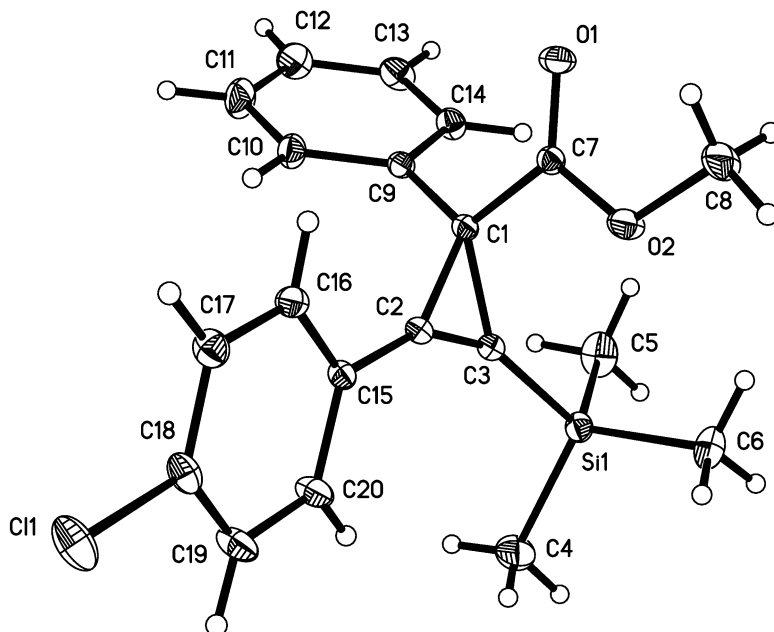


Compound **15a**
REFERENCE NUMBER: ritmc11

CRYSTAL STRUCTURE REPORT

C₂₀ H₂₁ Cl O₂ Si

Report prepared for:
M. G. Coleman, Ph.D.



William W. Brennessel
X-ray Crystallographic Facility
Department of Chemistry, University of Rochester
120 Trustee Road
Rochester, NY 14627

Data collection

A crystal (0.45 x 0.45 x 0.35 mm³) was placed onto the tip of a thin glass optical fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50° steps in ω at six different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 4013 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR2011⁴ and refined using SHELXL-2014/7.⁵ The space group $P-1$ was determined based on intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of methyl group C8 were given a geometric riding model; all others were refined freely. The final full matrix least squares refinement converged to $R1 = 0.0334$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.0985$ (F^2 , all data).

Structure description

The structure is the one suggested. The asymmetric unit contains one molecule in a general position.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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- ¹ *APEX2*, version 2014.7-1; Bruker AXS: Madison, WI, 2014.
- ² Sheldrick, G. M. *SADABS*, version 2014/3; University of Göttingen: Göttingen, Germany, 2014.
- ³ *SAINT*, version 8.32B; Bruker AXS: Madison, WI, 2013.
- ⁴ Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.
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Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max (0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for ritmc11.

Identification code	ritmc11	
Empirical formula	C ₂₀ H ₂₁ Cl O ₂ Si	
Formula weight	356.91	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 8.9739(13) Å	α = 108.891(3)°
	<i>b</i> = 9.8320(14) Å	β = 91.301(3)°
	<i>c</i> = 11.4770(16) Å	γ = 95.799(3)°
Volume	951.5(2) Å ³	
<i>Z</i>	2	
Density (calculated)	1.246 Mg/m ³	
Absorption coefficient	0.272 mm ⁻¹	
<i>F</i> (000)	376	
Crystal color, morphology	colorless, plate	
Crystal size	0.45 x 0.45 x 0.35 mm ³	
Theta range for data collection	1.879 to 38.589°	
Index ranges	-15 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 16, -19 ≤ <i>l</i> ≤ 20	
Reflections collected	35515	
Independent reflections	10249 [<i>R</i> (int) = 0.0242]	
Observed reflections	8669	
Completeness to theta = 37.785°	98.5%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7476 and 0.6483	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	10249 / 0 / 293	
Goodness-of-fit on <i>F</i> ²	1.041	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0334, <i>wR</i> 2 = 0.0930	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0417, <i>wR</i> 2 = 0.0985	
Largest diff. peak and hole	0.569 and -0.269 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ritmc11. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C11	5996(1)	9952(1)	13766(1)	25(1)
Si1	8636(1)	8018(1)	6478(1)	14(1)
O1	9363(1)	3654(1)	7680(1)	20(1)
O2	7354(1)	4715(1)	7386(1)	21(1)
C1	9591(1)	6242(1)	8247(1)	12(1)
C2	8761(1)	7460(1)	8974(1)	12(1)
C3	8952(1)	7446(1)	7846(1)	13(1)
C4	8485(1)	9993(1)	7021(1)	29(1)
C5	10228(1)	7549(1)	5467(1)	27(1)
C6	6847(1)	6991(1)	5652(1)	23(1)
C7	8792(1)	4738(1)	7755(1)	12(1)
C8	6537(1)	3292(1)	6867(1)	24(1)
C9	11259(1)	6300(1)	8452(1)	12(1)
C10	11972(1)	6896(1)	9626(1)	18(1)
C11	13531(1)	6969(1)	9784(1)	24(1)
C12	14384(1)	6440(1)	8772(1)	24(1)
C13	13679(1)	5843(1)	7599(1)	20(1)
C14	12128(1)	5770(1)	7442(1)	17(1)
C15	8136(1)	8078(1)	10156(1)	12(1)
C16	8042(1)	7328(1)	11004(1)	15(1)
C17	7390(1)	7908(1)	12122(1)	17(1)
C18	6836(1)	9236(1)	12378(1)	17(1)
C19	6935(1)	10014(1)	11558(1)	20(1)
C20	7587(1)	9426(1)	10444(1)	18(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for ritmc11.

Cl(1)-C(18)	1.7430(7)	C(12)-H(12)	0.907(15)
Si(1)-C(3)	1.8562(7)	C(13)-C(14)	1.3909(10)
Si(1)-C(4)	1.8573(9)	C(13)-H(13)	0.944(13)
Si(1)-C(5)	1.8614(9)	C(14)-H(14)	0.951(13)
Si(1)-C(6)	1.8653(8)	C(15)-C(16)	1.3969(9)
O(1)-C(7)	1.2074(8)	C(15)-C(20)	1.4014(9)
O(2)-C(7)	1.3451(8)	C(16)-C(17)	1.3932(9)
O(2)-C(8)	1.4427(9)	C(16)-H(16)	0.925(13)
C(1)-C(2)	1.4984(8)	C(17)-C(18)	1.3881(10)
C(1)-C(7)	1.4989(9)	C(17)-H(17)	0.980(14)
C(1)-C(9)	1.5024(9)	C(18)-C(19)	1.3910(11)
C(1)-C(3)	1.5558(9)	C(19)-C(20)	1.3906(10)
C(2)-C(3)	1.3051(9)	C(19)-H(19)	0.940(14)
C(2)-C(15)	1.4476(8)	C(20)-H(20)	0.960(13)
C(4)-H(4A)	0.974(17)	C(3)-Si(1)-C(4)	108.42(4)
C(4)-H(4B)	0.940(18)	C(3)-Si(1)-C(5)	108.28(4)
C(4)-H(4C)	1.018(19)	C(4)-Si(1)-C(5)	112.08(5)
C(5)-H(5A)	1.000(17)	C(3)-Si(1)-C(6)	107.35(3)
C(5)-H(5B)	1.008(15)	C(4)-Si(1)-C(6)	110.53(5)
C(5)-H(5C)	0.999(19)	C(5)-Si(1)-C(6)	110.03(4)
C(6)-H(6A)	0.987(17)	C(7)-O(2)-C(8)	115.19(6)
C(6)-H(6B)	0.975(16)	C(2)-C(1)-C(7)	119.60(5)
C(6)-H(6C)	0.968(17)	C(2)-C(1)-C(9)	120.97(5)
C(8)-H(8A)	0.9800	C(7)-C(1)-C(9)	114.00(5)
C(8)-H(8B)	0.9800	C(2)-C(1)-C(3)	50.55(4)
C(8)-H(8C)	0.9800	C(7)-C(1)-C(3)	118.09(5)
C(9)-C(10)	1.3933(9)	C(9)-C(1)-C(3)	119.17(5)
C(9)-C(14)	1.3986(9)	C(3)-C(2)-C(15)	149.81(6)
C(10)-C(11)	1.3985(10)	C(3)-C(2)-C(1)	67.00(4)
C(10)-H(10)	0.928(14)	C(15)-C(2)-C(1)	143.08(6)
C(11)-C(12)	1.3905(12)	C(2)-C(3)-C(1)	62.45(4)
C(11)-H(11)	0.949(15)	C(2)-C(3)-Si(1)	154.81(5)
C(12)-C(13)	1.3898(12)	C(1)-C(3)-Si(1)	142.13(4)

Si(1)-C(4)-H(4A)	110.6(10)	C(11)-C(10)-H(10)	119.2(9)
Si(1)-C(4)-H(4B)	113.1(10)	C(12)-C(11)-C(10)	120.35(7)
H(4A)-C(4)-H(4B)	110.5(14)	C(12)-C(11)-H(11)	120.7(9)
Si(1)-C(4)-H(4C)	110.6(10)	C(10)-C(11)-H(11)	119.0(9)
H(4A)-C(4)-H(4C)	104.4(14)	C(13)-C(12)-C(11)	119.63(7)
H(4B)-C(4)-H(4C)	107.3(15)	C(13)-C(12)-H(12)	119.3(9)
Si(1)-C(5)-H(5A)	112.1(10)	C(11)-C(12)-H(12)	121.0(9)
Si(1)-C(5)-H(5B)	111.2(9)	C(12)-C(13)-C(14)	120.06(7)
H(5A)-C(5)-H(5B)	110.1(13)	C(12)-C(13)-H(13)	120.6(8)
Si(1)-C(5)-H(5C)	110.6(11)	C(14)-C(13)-H(13)	119.3(8)
H(5A)-C(5)-H(5C)	105.4(14)	C(13)-C(14)-C(9)	120.81(6)
H(5B)-C(5)-H(5C)	107.1(14)	C(13)-C(14)-H(14)	119.5(8)
Si(1)-C(6)-H(6A)	110.1(10)	C(9)-C(14)-H(14)	119.7(8)
Si(1)-C(6)-H(6B)	112.5(9)	C(16)-C(15)-C(20)	119.54(6)
H(6A)-C(6)-H(6B)	109.2(13)	C(16)-C(15)-C(2)	120.66(6)
Si(1)-C(6)-H(6C)	108.7(10)	C(20)-C(15)-C(2)	119.78(6)
H(6A)-C(6)-H(6C)	109.0(14)	C(17)-C(16)-C(15)	120.27(6)
H(6B)-C(6)-H(6C)	107.3(13)	C(17)-C(16)-H(16)	120.8(9)
O(1)-C(7)-O(2)	122.92(6)	C(15)-C(16)-H(16)	118.9(9)
O(1)-C(7)-C(1)	124.51(6)	C(18)-C(17)-C(16)	119.05(6)
O(2)-C(7)-C(1)	112.57(5)	C(18)-C(17)-H(17)	120.5(8)
O(2)-C(8)-H(8A)	109.5	C(16)-C(17)-H(17)	120.5(8)
O(2)-C(8)-H(8B)	109.5	C(17)-C(18)-C(19)	121.85(6)
H(8A)-C(8)-H(8B)	109.5	C(17)-C(18)-Cl(1)	119.15(5)
O(2)-C(8)-H(8C)	109.5	C(19)-C(18)-Cl(1)	119.00(5)
H(8A)-C(8)-H(8C)	109.5	C(20)-C(19)-C(18)	118.63(6)
H(8B)-C(8)-H(8C)	109.5	C(20)-C(19)-H(19)	120.4(9)
C(10)-C(9)-C(14)	118.89(6)	C(18)-C(19)-H(19)	120.9(9)
C(10)-C(9)-C(1)	121.60(5)	C(19)-C(20)-C(15)	120.64(6)
C(14)-C(9)-C(1)	119.51(5)	C(19)-C(20)-H(20)	120.3(8)
C(9)-C(10)-C(11)	120.27(7)	C(15)-C(20)-H(20)	119.0(8)
C(9)-C(10)-H(10)	120.5(9)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ritmc11. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	28(1)	23(1)	19(1)	0(1)	12(1)	-1(1)
Si1	17(1)	14(1)	13(1)	5(1)	0(1)	0(1)
O1	18(1)	12(1)	30(1)	6(1)	-5(1)	3(1)
O2	12(1)	12(1)	35(1)	4(1)	-5(1)	1(1)
C1	12(1)	10(1)	12(1)	2(1)	1(1)	2(1)
C2	14(1)	11(1)	12(1)	2(1)	1(1)	3(1)
C3	14(1)	11(1)	13(1)	3(1)	0(1)	2(1)
C4	42(1)	16(1)	31(1)	10(1)	-4(1)	3(1)
C5	24(1)	36(1)	20(1)	9(1)	6(1)	-1(1)
C6	21(1)	28(1)	19(1)	9(1)	-5(1)	-3(1)
C7	12(1)	12(1)	12(1)	3(1)	1(1)	2(1)
C8	16(1)	15(1)	37(1)	4(1)	-5(1)	-2(1)
C9	12(1)	11(1)	14(1)	3(1)	0(1)	1(1)
C10	16(1)	20(1)	15(1)	3(1)	-2(1)	1(1)
C11	16(1)	28(1)	23(1)	3(1)	-7(1)	1(1)
C12	12(1)	24(1)	33(1)	5(1)	-3(1)	1(1)
C13	13(1)	19(1)	27(1)	3(1)	4(1)	3(1)
C14	13(1)	17(1)	17(1)	2(1)	2(1)	3(1)
C15	13(1)	11(1)	11(1)	2(1)	1(1)	2(1)
C16	17(1)	14(1)	14(1)	5(1)	1(1)	4(1)
C17	20(1)	17(1)	14(1)	5(1)	3(1)	2(1)
C18	17(1)	16(1)	14(1)	1(1)	4(1)	0(1)
C19	27(1)	14(1)	18(1)	3(1)	8(1)	7(1)
C20	26(1)	13(1)	16(1)	5(1)	6(1)	7(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ritmc11.

	x	y	z	U(eq)
H4A	7600(19)	10204(17)	7494(15)	45(4)
H4B	9350(20)	10546(18)	7479(16)	51(5)
H4C	8310(20)	10350(20)	6293(17)	59(5)
H5A	10140(19)	7860(18)	4723(16)	48(4)
H5B	10324(17)	6481(17)	5209(14)	40(4)
H5C	11200(20)	8070(20)	5913(17)	61(5)
H6A	5995(18)	7277(18)	6172(16)	47(4)
H6B	6858(17)	5946(17)	5423(14)	41(4)
H6C	6702(19)	7213(18)	4898(16)	48(4)
H8A	6689	2726	7414	58(5)
H8B	6902	2805	6056	70(6)
H8C	5465	3380	6778	72(6)
H10	11418(15)	7239(14)	10312(13)	30(3)
H11	13996(16)	7384(16)	10591(14)	35(4)
H12	15390(16)	6445(16)	8868(14)	35(4)
H13	14243(14)	5482(14)	6903(12)	24(3)
H14	11655(15)	5365(14)	6636(12)	25(3)
H16	8458(15)	6465(14)	10826(12)	28(3)
H17	7337(15)	7393(14)	12724(12)	26(3)
H19	6596(16)	10931(15)	11759(13)	32(3)
H20	7685(14)	9948(14)	9869(12)	25(3)

Table 6. Torsion angles [°] for ritmc11.

C7-C1-C2-C3	-103.52(6)	C7-C1-C9-C10	-116.30(7)
C9-C1-C2-C3	104.02(6)	C3-C1-C9-C10	96.68(7)
C7-C1-C2-C15	73.07(11)	C2-C1-C9-C14	-141.16(6)
C9-C1-C2-C15	-79.38(11)	C7-C1-C9-C14	64.96(8)
C3-C1-C2-C15	176.59(11)	C3-C1-C9-C14	-82.06(7)
C15-C2-C3-C1	-175.93(13)	C14-C9-C10-C11	0.47(11)
C15-C2-C3-Si1	-6.6(2)	C1-C9-C10-C11	-178.28(7)
C1-C2-C3-Si1	169.37(13)	C9-C10-C11-C12	-0.42(13)
C7-C1-C3-C2	106.61(6)	C10-C11-C12-C13	0.32(13)
C9-C1-C3-C2	-107.69(6)	C11-C12-C13-C14	-0.29(13)
C2-C1-C3-Si1	-172.65(9)	C12-C13-C14-C9	0.35(11)
C7-C1-C3-Si1	-66.04(9)	C10-C9-C14-C13	-0.44(10)
C9-C1-C3-Si1	79.65(9)	C1-C9-C14-C13	178.33(6)
C4-Si1-C3-C2	37.97(13)	C3-C2-C15-C16	163.99(10)
C5-Si1-C3-C2	159.78(12)	C1-C2-C15-C16	-9.77(12)
C6-Si1-C3-C2	-81.45(13)	C3-C2-C15-C20	-14.50(15)
C4-Si1-C3-C1	-157.49(8)	C1-C2-C15-C20	171.74(8)
C5-Si1-C3-C1	-35.67(8)	C20-C15-C16-C17	0.80(10)
C6-Si1-C3-C1	83.09(8)	C2-C15-C16-C17	-177.70(6)
C8-O2-C7-O1	-1.16(10)	C15-C16-C17-C18	0.09(10)
C8-O2-C7-C1	178.14(6)	C16-C17-C18-C19	-1.03(11)
C2-C1-C7-O1	-144.48(7)	C16-C17-C18-C11	179.10(5)
C9-C1-C7-O1	9.79(9)	C17-C18-C19-C20	1.06(12)
C3-C1-C7-O1	157.19(6)	C11-C18-C19-C20	-179.07(6)
C2-C1-C7-O2	36.22(8)	C18-C19-C20-C15	-0.14(12)
C9-C1-C7-O2	-169.50(5)	C16-C15-C20-C19	-0.77(11)
C3-C1-C7-O2	-22.10(8)	C2-C15-C20-C19	177.74(7)
C2-C1-C9-C10	37.58(9)		