

Supporting Information

Diene-Transmissive Diels–Alder Sequences With Benzyne

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General Methods

NMR Spectroscopy

^1H NMR spectra were recorded at 400 MHz using a Bruker AVANCE 400 spectrometer. Residual solvent peaks were used as an internal reference for ^1H NMR spectra (CDCl_3 δ 7.26 ppm, CD_2Cl_2 δ 5.32 ppm, $(\text{CD}_3)_2\text{SO}$ δ 2.50). Coupling constants (J) are quoted to the nearest 0.1 Hz. The assignment of proton signals was assisted by COSY, HSQC and HMBC experiments. ^{13}C NMR spectra were recorded at 100 MHz using a Bruker AVANCE 400 spectrometer. Solvent peaks were used as an internal reference for ^{13}C NMR spectra (CDCl_3 δ 77.16 ppm, CD_2Cl_2 δ 53.84 ppm, $(\text{CD}_3)_2\text{SO}$ δ 39.52). Assignment of carbon signals was assisted by HSQC and HMBC experiments. The following abbreviations (or combinations thereof) are used to denote ^1H NMR multiplicities: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplet, t = triplet, m = multiplet.

Infrared Spectroscopy

IR spectra were recorded on a Perkin–Elmer UATR Two spectrometer as a thin film or solid.

Mass Spectrometry

Low-resolution EI mass spectra were recorded on a Finnigan Polaris Q ion trap mass spectrometer using electron impact (EI^+) ionization mode at 70 eV. High-resolution EI mass spectra were recorded on a VG Autospec mass spectrometer operating at 70 eV. Low-resolution ESI mass spectra were recorded on a ZMD Micromass spectrometer with Waters Alliance 2690 HPLC. High-resolution ESI mass spectra were recorded on a Waters LCT Premier time-of-flight (TOF) mass spectrometer.

Melting Points

Melting points were measured on a Stanford Research Systems Optimelt Automated Melting Point System and are uncorrected.

X-ray Crystallography

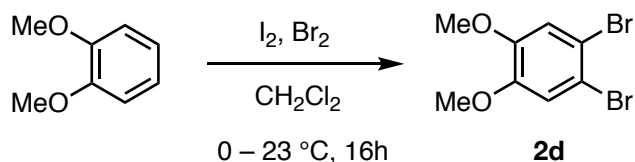
Single crystal X-ray data was collected on a SuperNova (Dual Source) diffractometer using a SuperNova (Cu) X-ray radiation source. Crystallographic structures were solved using CryaAlis PRO.

Experimental Procedures, Reagents, Chromatography and Glassware

Reactions were conducted under a positive pressure of dry nitrogen in oven dried glassware and at room temperature, unless specified otherwise. Anhydrous solvents were either obtained from commercial sources or dried according to the procedure outlined by Grubbs and co-workers.¹ Commercially available chemicals were used as purchased, or where specified, purified by standard techniques. Analytical thin-layer chromatography was conducted with aluminum-backed silica gel 60 F₂₅₄ (0.2 mm) plates supplied by Merck, and visualized using UV fluorescence ($\lambda_{\text{max}} = 254 \text{ nm}$), or developed using KMnO₄ or *p*-anisaldehyde or phosphomolybdic acid followed by heating. Flash chromatography employed Merck Kiesegel 60 silica gel (230–400 mesh). Solvent compositions are given in (v/v). PS 40–60 °C refers to petroleum spirits, boiling point fraction 40–60 °C. The unsubstituted benzyne precursors, 1,2-dibromobenzene and 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate were purchased from Sigma–Aldrich and used as received. 1 M TBAF in THF and CsF were purchased from Sigma–Aldrich and used as received. Substituted dendralenes were synthesised as per the reported procedure.²

Synthesis of Substituted Benzyne Precursors

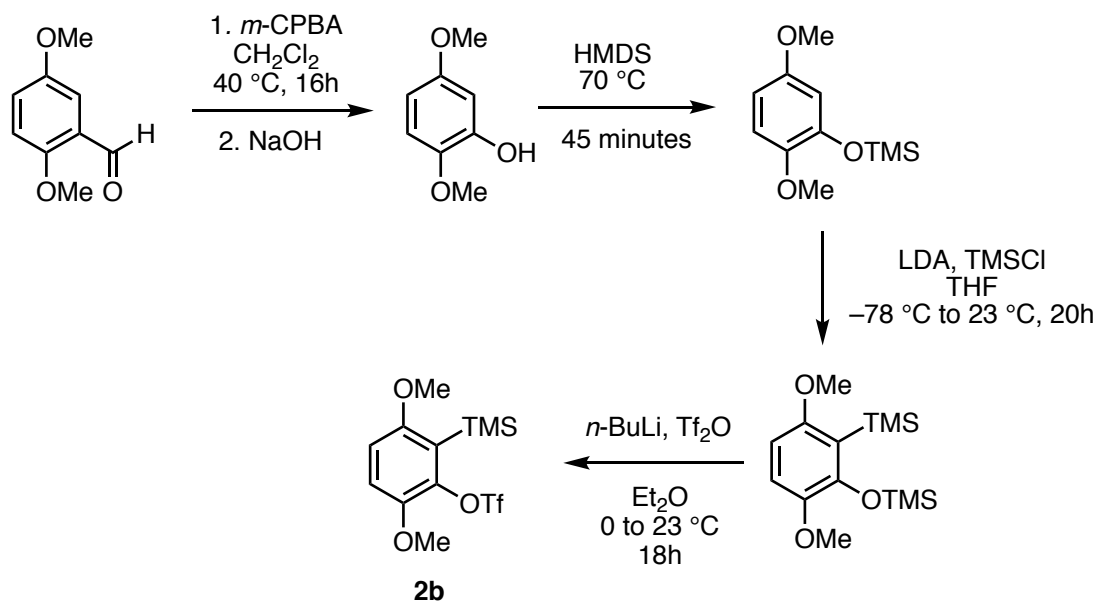
1,2-Dibromo-4,5-dimethoxybenzene (**2d**)



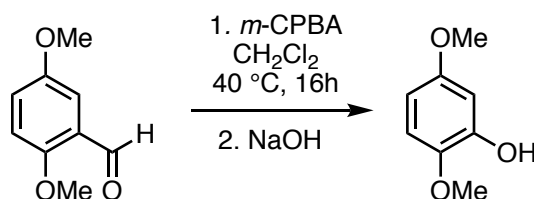
1,2-Dibromo-4,5-dimethoxybenzene **2d** was prepared according to the reported procedure by Sun and co-workers from 1,2-dimethoxybenzene (17.0 g, 123 mmol) as a white solid (20.8 g, 70.3 mmol, 57%) and characterization data was consistent with the literature.³

3,6-Dimethoxy-2-trimethylsilyl-benzene-1-trifluoromethanesulfonate (**2b**)

The title compound was prepared in four steps as shown in the below scheme.

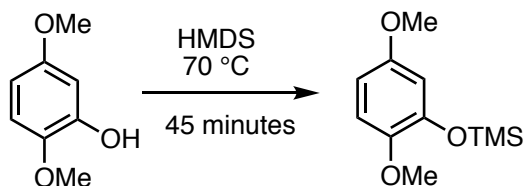


2,5-Dimethoxyphenol



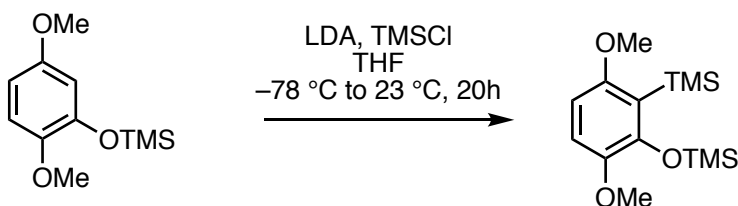
2,5-Dimethoxyphenol was synthesised using a modified protocol from Michael and co-workers.⁴ A solution of 2,5-dimethoxybenzaldehyde (20.0 g, 120 mmol) in dry CH₂Cl₂ (40 mL) was added dropwise to a solution of *m*-CPBA (27.6 g, 160 mmol) in CH₂Cl₂ (160 mL) at 0 °C. The solution was heated to reflux with stirring for 16 hours. After cooling to room temperature, the solution was washed with saturated aqueous NaHCO₃ solution and saturated aqueous Na₂S₂O₃ and dried over MgSO₄. The solvent was removed under reduced pressure to give the crude ester as a yellow oil. This yellow oil was dissolved in MeOH (100 mL) and 10% NaOH was added (100 mL). The reaction mixture was stirred at 23 °C for 3 h. The solution was acidified to pH 1 (6M HCl) and extracted with CH₂Cl₂ (200 mL). The solvent was removed under reduced pressure and purification by flash column chromatography (SiO₂, 10% EtOAc in PS 40–60) gave 2,5-dimethoxyphenol as a colorless oil (16.1 g, 104 mmol, 87%).

(2,5-Dimethoxyphenoxy)trimethylsilane



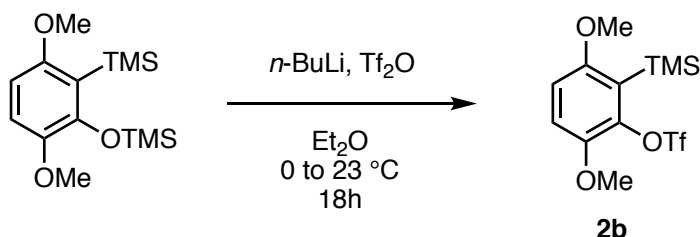
(2,5-Dimethoxyphenoxy)trimethylsilane was synthesised using a modified protocol from Castedo and co-workers.⁵ 2,5-Dimethoxyphenol (16.1 g, 104 mmol) and hexamethyldisilazane (10.1 g, 13.1 mL, 63.0 mmol) were combined in a round bottom flask and heated to 70 °C for 45 minutes. The reaction mixture was cooled to room temperature and excess hexamethyldisilazane was removed under reduced pressure to give the TMS ether in quantitative yield (23.5 g, 103 mmol, 99%).

(3,6-Dimethoxy-2-((trimethylsilyl)oxy)phenyl)trimethylsilane



The title compound was synthesised using a modified protocol from Castedo and co-workers.⁵ A solution of TMS ether (4.16 g, 18.4 mmol) in dry THF (25 mL) was added dropwise to a solution of freshly prepared LDA (2.16 g, 20.2 mmol) at -78 °C under N₂. The solution was warmed to room temperature and stirred for two hours. The solution was then cooled to -78 °C and freshly distilled TMSCl (2.38 g, 2.80 mL, 22.0 mmol) was added dropwise. The solution was allowed to warm to 23 °C and stirred for 20h. The reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL) and extracted with Et₂O (50 mL). The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure to give crude product as a colorless oil. The crude product was used without further purification.

3,6-Dimethoxy-2-trimethylsilyl-benzene-1-trifluoromethanesulfonate (2b)

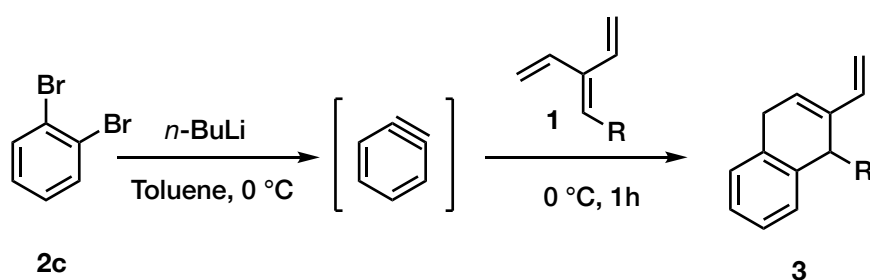


The title compound was synthesised using a modified protocol from Castedo and co-workers.⁵ *n*-BuLi (11.7 mL, 1.6 M, 18.6 mmol) was added dropwise to a solution of TMS ether (5.29 g, 17.7 mmol) in dry Et₂O (190 mL) at 0 °C under N₂. The solution was warmed to room temperature and allowed to stir for 4 hours. The solution was then cooled to 0 °C and triflic anhydride (10.0 g, 9.66 mL, 35.4 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 18 hours. The reaction mixture was quenched with saturated aqueous NH₄Cl (70 mL) and the layers were separated. The aqueous layer was further extracted with Et₂O (50 mL). The combined organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 33% CH₂Cl₂ in PS 40–60) gave the product **2b** as a pale brown solid (4.56 g, 12.7 mmol, 69% over two steps). m.p. 40 – 45 °C (CH₂Cl₂).

¹H NMR (400 MHz, (CD₃)₂SO) δ 7.26 (d, *J* = 9.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 0.32 (s, 9H) ppm; ¹³C NMR (100 MHz, (CD₃)₂SO) δ 157.6 (Cq), 144.4 (Cq), 141.6 (Cq), 122.1 (Cq), 118.4 (q, *J* = 321 Hz, CF₃), 115.3 (CH), 111.4 (CH), 56.1 (CH₃), 56.1 (CH₃), 0.64 (3×CH₃) ppm; IR (thin film): *v*_{max} = 2946, 2904, 2841, 1574 cm⁻¹; LRMS (EI⁺): *m/z* (%): 358([M]⁺⁺, 18), 343 ([M-CH₃]⁺⁺, 58), 328 ([M-2×CH₃]⁺⁺, 58), 210 (100); HRMS (EI⁺): calculated for C₁₂H₁₇O₅F₃SiS: 358.0518; found: 358.0519.

General Protocols for Single Diels–Alder Reactions of [3]Dendralenes with Benzyne as Dienophile

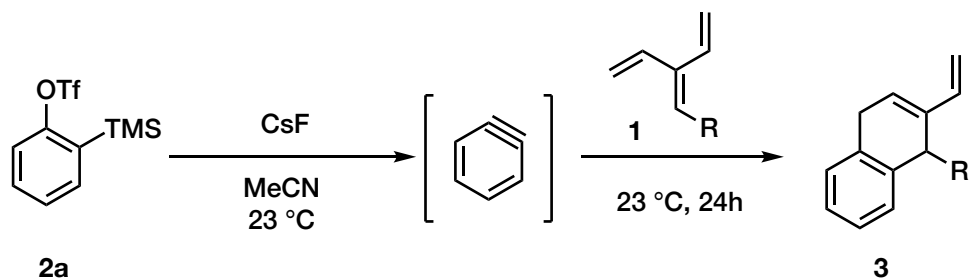
General Method A: 1,2-Dibromide as the benzyne precursor



1,2-Dibromobenzene **2c** (1.0 mol equiv) and dendralene **1** (1.0 mol equiv) were mixed in toluene (1.0 mL/0.1 g of dendralene) under N₂. The reaction mixture was cooled to 0 °C and *n*-BuLi (1.2 mol equiv, 1.2 M – 1.5 M in hexane) was added dropwise over 5 minutes. The reaction mixture was stirred at 0 °C for 1h. The reaction mixture was quenched with saturated aqueous NH₄Cl (1 mL/0.1 g dendralene) and the resulting heterogeneous solution was filtered through a plug of Celite and diluted with CH₂Cl₂ (10 mL/0.1 g dendralene) and water (10 mL/0.1 g dendralene). The aqueous layer was extracted with CH₂Cl₂ (5 mL/0.1 g dendralene). The combined organic layer was

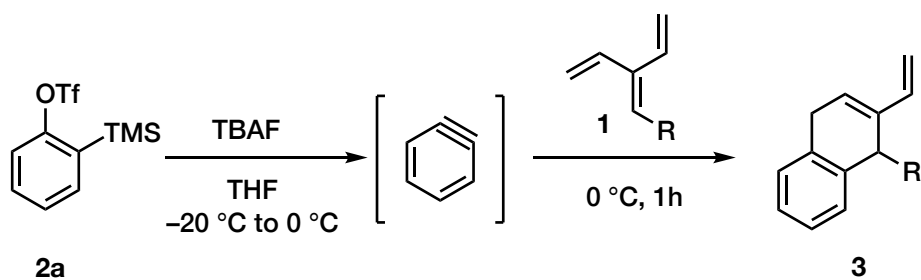
washed with saturated brine (5 mL/0.1 g dendralene), dried over Na₂SO₄ and concentrated under reduced pressure.

General Method B: 2-Trimethylsilyl-benzene-1-trifluoromethanesulfonate as the benzyne precursor and CsF as the fluoride source



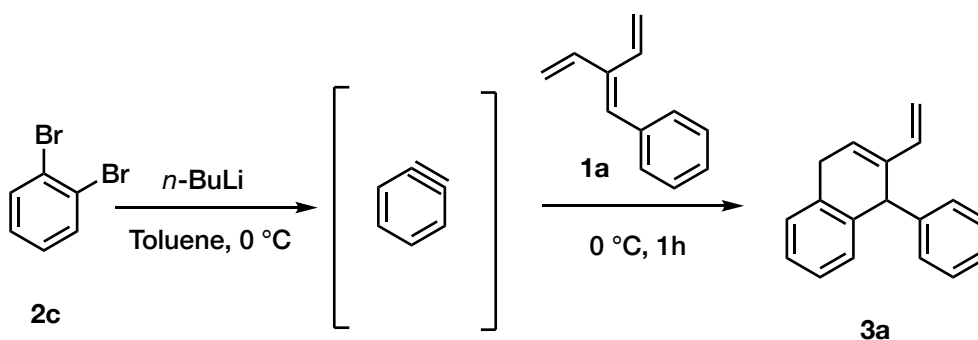
2-Trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (1.5 mol equiv) and dendralene **1** (1.0 mol equiv) were dissolved in MeCN (1 mL/0.1 g of dendralene) under N₂. CsF (up to 6 mol equiv) was added and the reaction mixture was stirred at 23 °C for 24h. The reaction mixture was diluted with CH₂Cl₂ (10 mL/0.1 g dendralene) and water (10 mL/0.1 g dendralene) shaken well and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (5 mL/0.1 g dendralene). The combined organic layer was washed with saturated brine (5 mL/0.1 g dendralene), dried over Na₂SO₄ and concentrated under reduced pressure.

General Method C: 2-Trimethylsilyl-benzene-1-trifluoromethanesulfonate as the benzyne precursor and TBAF as the fluoride source

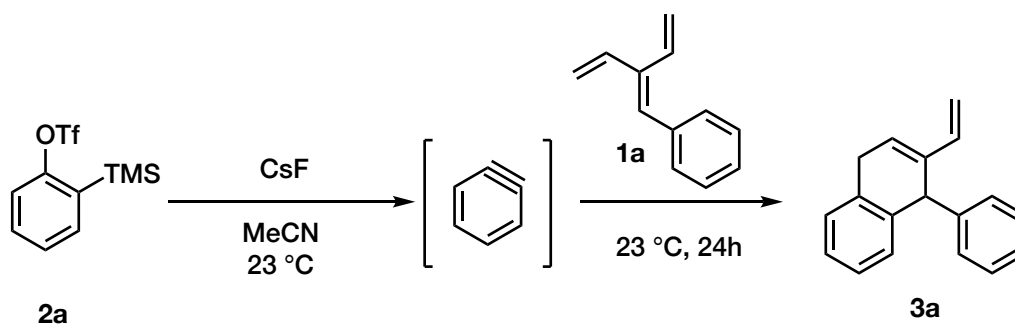


2-Trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (2.0 – 3.0 mol equiv) and dendralene **1** (1.0 mol equiv) were dissolved in THF (1.0 mL/0.1 g of dendralene) under N₂. The reaction mixture was cooled to -20 °C and TBAF (up to 3.5 mol equiv, 1 M in THF) was added dropwise over 20 minutes. The resulting pale yellow reaction mixture was brought to 0 °C and stirred for 1h. The reaction mixture was quenched with saturated aqueous NH₄Cl solution (1 mL/0.1 g dendralene). The resulting solution was diluted with CH₂Cl₂ (10 mL/0.1 g dendralene) and washed with water (10 mL/0.1 g dendralene). The aqueous layer was extracted with CH₂Cl₂ (5 mL/0.1 g dendralene). The combined organic layer was washed with saturated brine (5 mL/0.1 g dendralene), dried over Na₂SO₄ and concentrated under reduced pressure.

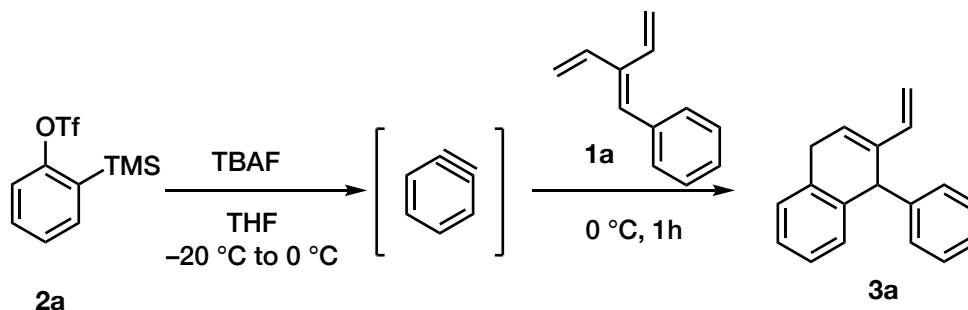
1-Phenyl-2-vinyl-1,4-dihydronaphthalene (**3a**)



Following **General Method A**, the reaction mixture containing dendralene **1a** (73 mg, 0.46 mmol), 1,2-dibromobenzene **2c** (56 μ L, 0.46 mmol) and *n*-BuLi (0.46 mL, 1.2 M, 0.56 mmol) in toluene (0.75 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (5 g SiO₂, 100% PS 40–60) gave the mono DA adduct **3a** as a colorless liquid (42 mg, 0.18 mmol, 39%). *R_f* = 0.43 (100% PS 40–60).



Following **General Method B**, the reaction mixture containing CsF (233 mg, 1.54 mmol), dendralene **1a** (40 mg, 0.26 mmol) and 2-trimethylsilylbenzene-1-trifluoromethanesulfonate **2a** (93 μ L, 0.38 mmol) in MeCN (1 mL) was stirred at 23 °C for 24h. After work up, purification by flash column chromatography (4 g SiO₂, 100% PS 40–60) gave the mono DA adduct **3a** as a colorless liquid (24 mg, 0.103 mmol, 40%).

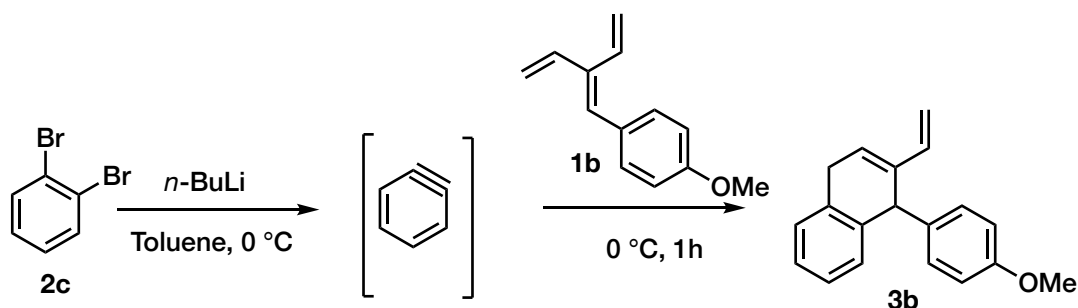


Following **General Method C**, the reaction mixture containing dendralene **1a** (70 mg, 0.45 mmol), 2-trimethylsilylbenzene-1-trifluoromethanesulfonate **2a** (0.33 mL, 1.34 mmol) and TBAF (1.60 mL, 1 M, 1.57 mmol) in THF (2 mL) was stirred at 0 °C for 1h. After work up, purification by flash

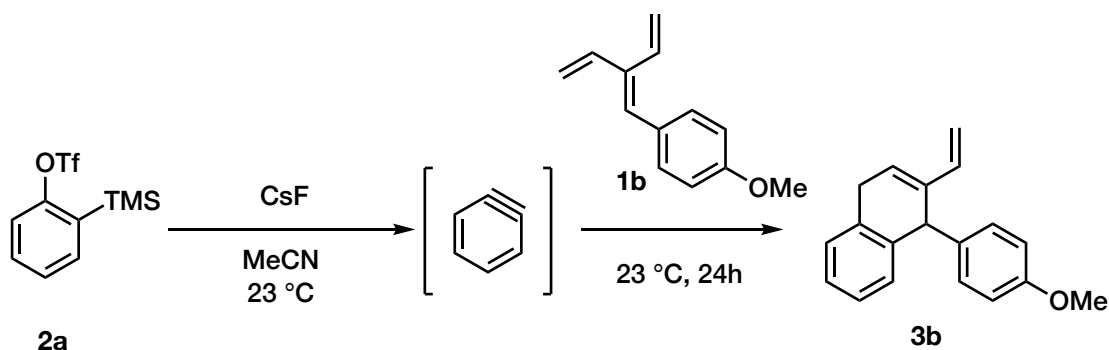
column chromatography (4 g SiO₂, 100% PS 40–60) gave the mono DA adduct **3a** as a colorless liquid (62 mg, 0.27 mmol, 59%).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.04 (m, 9H), 6.41 (dd, J = 17.6, 10.9 Hz, 1H), 6.26 (dd, J = 5.6, 2.7 Hz, 1H), 5.21 (d, J = 17.6 Hz, 1H), 4.98 (d, J = 10.9 Hz, 1H), 4.91 (t, J = 2.8 Hz, 1H), 3.75 (d, J = 22.0 Hz, 1H), 3.56 (ddd, J = 22.0, 5.2, 2.4 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 145.4 (Cq), 138.9 (Cq), 138.1 (Cq), 137.8 (CH), 133.0 (Cq), 129.0 (CH), 128.8 (2×CH), 128.3 (CH), 127.7 (CH), 127.6 (2×CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 113.0 (CH₂), 46.3 (CH), 31.2 (CH₂) ppm; IR (thin film): ν_{max} = 3060, 3023, 2813, 1650, 1597, 1491 cm⁻¹; LRMS (EI⁺): m/z (%): 232([M]⁺, 100), 217 ([M-CH₃]⁺, 50); HRMS (EI⁺): calculated for C₁₈H₁₆: 232.1252; found: 232.1252.

1-(4-Methoxyphenyl)-2-vinyl-1,4-dihydronaphthalene (**3b**)

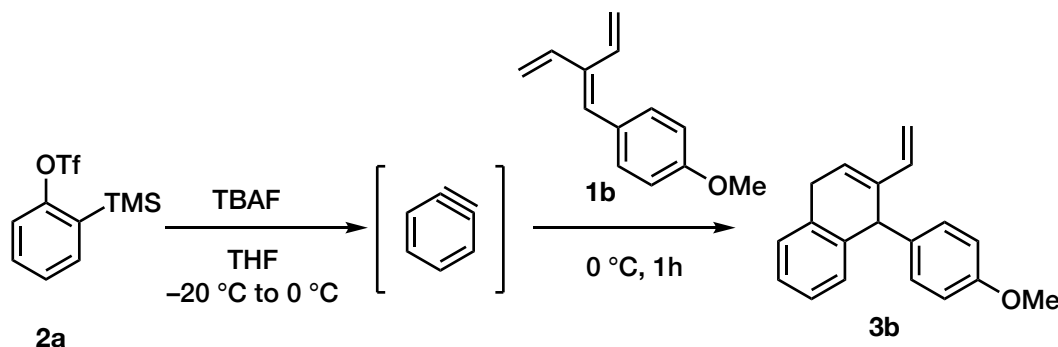


Following **General Method A**, the reaction mixture containing dendralene **1b** (62 mg, 0.33 mmol), 1,2-dibromobenzene **2c** (40 μ L, 0.33 mmol) and *n*-BuLi (0.32 mL, 1.23 M, 0.40 mmol) in toluene (0.75 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (4 g SiO₂, 3% EtOAc in PS 40–60) gave the mono DA adduct **3b** as a colorless liquid (35 mg, 0.13 mmol, 40%). R_f = 0.33 (5% EtOAc in PS 40–60).



Following **General Method B**, the reaction mixture containing dendralene **1b** (75 mg, 0.40 mmol), 2-trimethylsilylbenzene-1-trifluoromethanesulfonate **2a** (0.12 mL, 0.48 mmol) and CsF (110 mg, 0.73 mmol) in MeCN (0.75 mL) was stirred at 23 °C for 24h. After work up, purification by flash

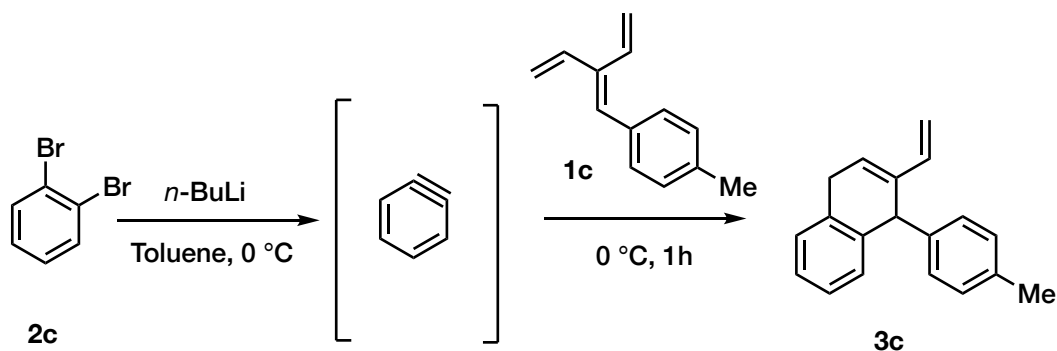
column chromatography (4 g SiO₂, 3% EtOAc in PS 40–60) gave the mono DA adduct **3b** as a colorless liquid (40 mg, 0.15 mmol, 38%).



Following **General Method C**, the reaction mixture containing dendralene **1b** (75 mg, 0.40 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.29 mL, 1.21 mmol) and TBAF (1.41 mL, 1 M, 1.41 mmol) in THF (0.75 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (5 g SiO₂, 3% EtOAc in PS 40–60) gave the mono DA adduct **3b** as a colorless liquid (51 mg, 0.19 mmol, 49%).

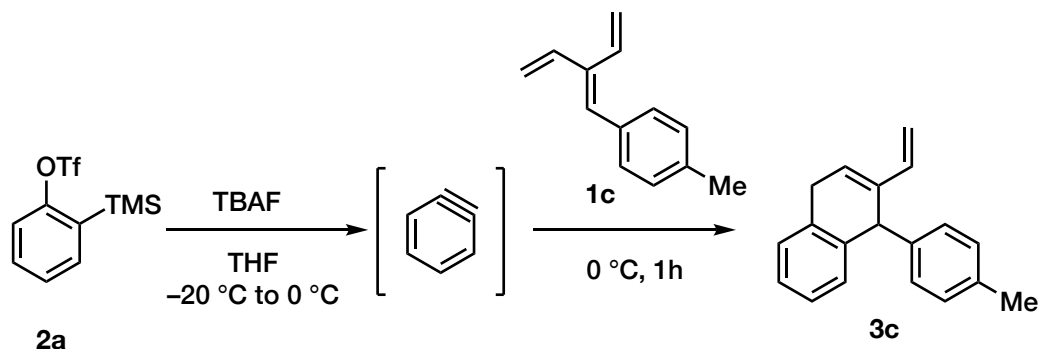
¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.22 (m, 1H), 7.22 – 7.06 (m, 5H), 6.77 (d, J = 8.7 Hz, 2H), 6.41 (dd, J = 17.6, 10.9 Hz, 1H), 6.25 (dd, J = 5.4, 2.6 Hz, 1H), 5.23 (d, J = 17.6 Hz, 1H), 5.00 (d, J = 10.9 Hz, 1H), 4.87 (t, J = 2.8 Hz, 1H), 3.79 – 3.65 (m, 4H), 3.55 (ddd, J = 22.2, 5.6, 2.4 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 158.1 (Cq), 139.2 (Cq), 138.3 (Cq), 137.9 (CH), 137.7 (Cq), 132.9 (Cq), 128.9 (CH), 128.4 (2×CH), 128.3 (CH), 127.6 (CH), 126.6 (CH), 126.0 (CH), 114.1 (2×CH), 113.0 (CH₂), 55.3 (CH₃), 45.3 (CH), 31.1 (CH₂) ppm; IR (thin film): ν_{max} = 3033, 3003, 2901, 2834, 1608, 1507 cm⁻¹; LRMS (EI⁺): m/z (%): 262([M]⁺, 21), 247([M-CH₃]⁺, 13), 154([M-C₇H₈O]⁺, 100); HRMS (EI⁺): calculated for C₁₉H₁₈O: 262.1358; found: 262.1358.

1-(*p*-Tolyl)-2-vinyl-1,4-dihydronaphthalene (**3c**)



Following **General Method A**, the reaction mixture containing dendralene **1c** (98 mg, 0.58 mmol), 1,2-dibromobenzene **2c** (68 μ L, 0.58 mmol) and *n*-BuLi (0.56 mL, 1.23 M, 0.69 mmol) in toluene (1 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography

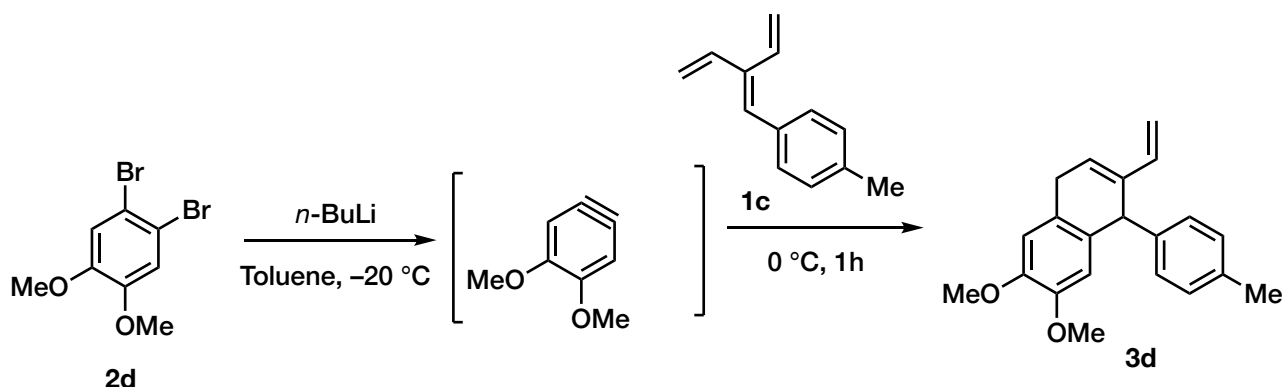
(5 g SiO₂, 1% EtOAc in PS 40–60) gave the mono DA adduct **3c** as a colorless liquid (56 mg, 0.23 mmol, 39%). *R_f* = 0.40 (5% EtOAc in PS 40–60).



Following **General Method C**, the reaction mixture containing dendralene **1c** (110 mg, 0.65 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.31 mL, 1.3 mmol) and TBAF (1.4 mL, 1 M, 1.4 mmol) in THF (2 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (7 g SiO₂, 1% EtOAc in PS 40–60) gave the mono DA adduct **3c** as a colorless liquid (96 mg, 0.39 mmol, 60%).

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.23 (m, 1H), 7.18 – 7.08 (m, 5H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.40 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.25 (dd, *J* = 5.4, 2.6 Hz, 1H), 5.22 (d, *J* = 17.6 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.88 (t, *J* = 2.9 Hz, 1H), 3.74 (d, *J* = 22.1 Hz, 1H), 3.54 (ddd, *J* = 22.1, 5.4, 2.2 Hz, 1H), 2.25 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 142.5 (Cq), 139.1 (Cq), 138.2 (Cq), 137.9 (CH), 135.9 (Cq), 132.9 (Cq), 129.5 (2×CH), 129.0 (CH), 128.2 (CH), 127.6 (CH), 127.4 (2×CH), 126.6 (CH), 126.0 (CH), 113.0 (CH₂), 45.8 (CH), 31.2 (CH₂), 21.1 (CH₃) ppm; IR (thin film): ν_{max} = 3020, 2920, 1687, 1610, 1509 cm⁻¹; LRMS (EI⁺): *m/z* (%): 246([M]⁺, 81), 231([M-CH₃]⁺, 96), 215 (100); HRMS (EI⁺): calculated for C₁₉H₁₈: 246.1409; found: 246.1407.

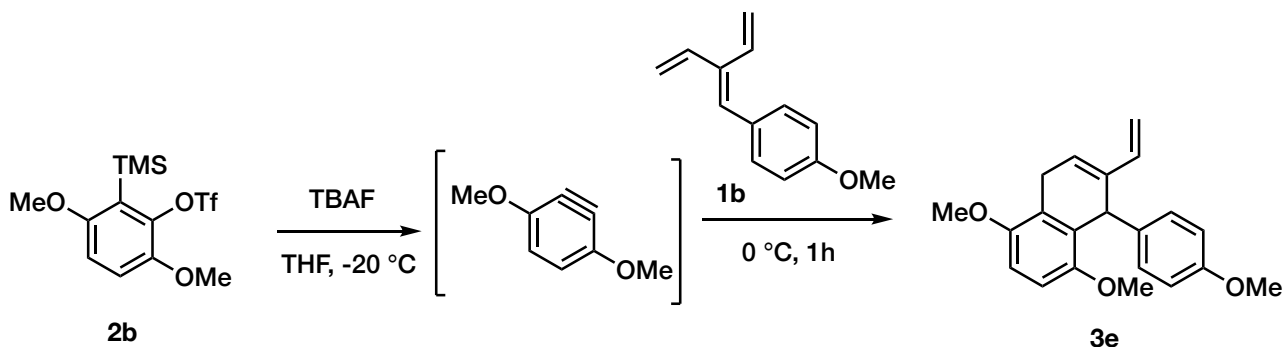
(S)-6,7-Dimethoxy-1-(*p*-tolyl)-2-vinyl-1,4-dihydronaphthalene (3d)



Following **General Method A**, the reaction mixture containing dendralene **1c** (50 mg, 0.29 mmol), 1,2-dibromo-4,5-dimethoxybenzene **2d** (260 mg, 0.881 mmol) and *n*-BuLi (0.69 mL, 1.37 M, 0.94 mmol) in toluene (1 mL) was brought from -20 °C to 0 °C and stirred for 1h. After work up, purification by flash column chromatography (10 g SiO₂, 6% EtOAc in PS 40–60) gave the mono DA adduct **3d** as a colorless liquid (45 mg, 0.15 mmol, 51%). *R*_f = 0.50 (10% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 6.64 (s, 1H), 6.38 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.27 – 6.15 (m, 1H), 5.21 (d, *J* = 17.6 Hz, 1H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.77 (t, *J* = 3.1 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.77 – 3.62 (m, 1H), 3.57 – 3.35 (m, 1H), 2.26 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 147.8 (Cq), 147.5 (Cq), 142.9 (Cq), 138.1 (Cq), 137.9 (CH), 135.8 (Cq), 131.0 (Cq), 129.5 (2×CH), 127.5 (CH), 127.3 (2×CH), 124.7 (Cq), 112.9 (CH₂), 111.5 (CH), 110.8 (CH), 56.0 (2×CH₃), 45.5 (CH), 30.9 (CH₂), 21.1 (CH₃) ppm; IR (thin film): ν_{max} = 3000, 2932, 2833, 1737, 1610, 1508 cm⁻¹; LRMS: (EI⁺): *m/z* (%): 306 ([M]⁺, 100), 291 ([M-CH₃]⁺, 23), 275 ([M-OCH₃]⁺, 16); HRMS (EI⁺): calculated for C₂₁H₂₂O₂: 306.1620; found: 306.1619.

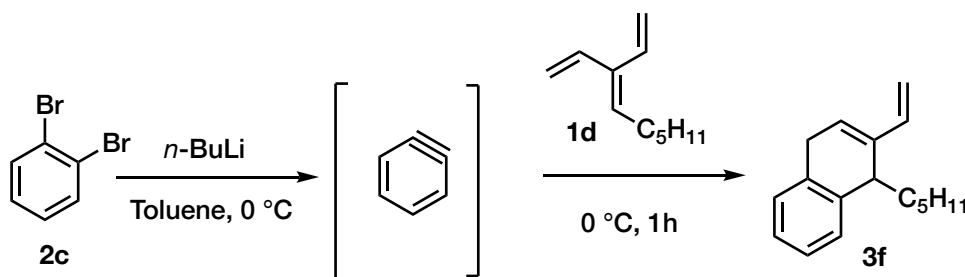
(S)-5,8-Dimethoxy-1-(4-methoxyphenyl)-2-vinyl-1,4-dihydronaphthalene (3e)



Following **General Method C**, the reaction mixture containing dendralene **1b** (246 mg, 1.32 mmol), 3,6-dimethoxy-2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2b** (947 mg, 2.64 mmol) and TBAF (4.00 mL, 1 M, 3.96 mmol) in THF (2.5 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (25 g SiO₂, 3% EtOAc in PS 40–60) gave the mono DA adduct **3e** as a white solid (238 mg, 0.738 mmol, 56%). *R_f* = 0.50 (10% EtOAc in PS 40–60); m.p. 127 – 131 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.63 (s, 2H), 6.37 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.17 (dd, *J* = 5.5, 2.4 Hz, 1H), 5.32 (d, *J* = 17.6 Hz, 1H), 5.17 (t, *J* = 2.7 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.70 – 3.59 (m, 1H), 3.43 (d, *J* = 23.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 157.7 (Cq), 150.9 (Cq), 150.8 (Cq), 138.8 (Cq), 137.7 (CH), 137.2 (Cq), 129.8 (Cq), 129.3 (2×CH), 126.9 (CH), 123.7 (Cq), 113.4 (2×CH), 112.5 (CH₂), 108.4 (CH), 107.4 (CH), 55.8 (CH₃), 55.7 (CH₃), 55.2 (CH₃), 38.8 (CH), 26.0 (CH₂) ppm; IR (thin film): *v*_{max} = 2998, 2934, 2833, 1607, 1507 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 323 ([*M*+H]⁺, 35), 345 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₁H₂₃O₃: 323.1642; found: 323.1645.

1-Pentyl-2-vinyl-1,4-dihydronaphthalene (**3f**)

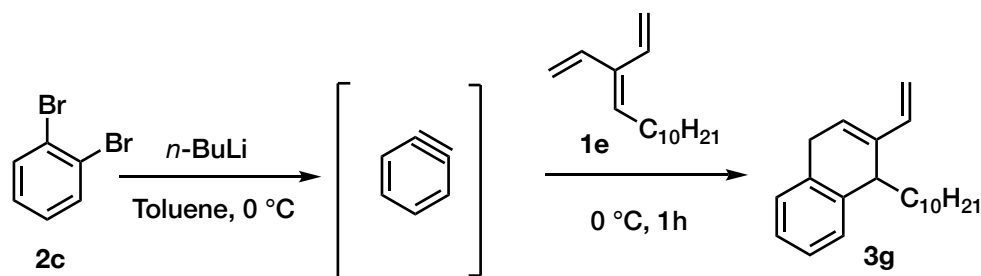


Following **General Method A**, the reaction mixture containing dendralene **1d** (46 mg, 0.31 mmol), 1,2-dibromobenzene **2c** (36 μL, 0.31 mmol) and *n*-BuLi (0.30 mL, 1.23 M, 0.37 mmol) in toluene (0.5 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (4 g SiO₂, 100% PS 40–60) gave the mono DA adduct **3f** as a colorless liquid (22 mg, 0.10 mmol, 32%). *R_f* = 0.50 (100% PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.12 (m, 4H), 6.42 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.04 (dd, *J* = 5.8, 2.4 Hz, 1H), 5.28 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 10.9 Hz, 1H), 3.76 – 3.69 (m, 1H), 3.52 (d, *J* = 21.3 Hz, 1H), 3.37 (dd, *J* = 21.2, 5.6 Hz, 1H), 1.72 – 1.49 (m, 2H), 1.33 – 1.04 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 140.1 (Cq), 139.7 (Cq), 137.9 (CH), 135.2 (Cq), 128.6 (CH), 127.8 (CH), 127.5 (CH), 125.9 (CH), 125.8 (CH), 111.1 (CH₂), 39.7 (CH), 36.2 (CH₂), 32.1 (CH₂), 31.3 (CH₂), 26.0 (CH₂), 22.8 (CH₂), 14.2 (CH₃) ppm; IR (thin film):

ν_{\max} = 3021, 2954, 2927, 2856, 1646 cm^{-1} ; LRMS (EI^+): m/z (%): 226($[\text{M}]^{++}$, 21), 155 ($[\text{M}-\text{C}_5\text{H}_{11}]^{++}$, 100), 128 ($[\text{M}-\text{C}_7\text{H}_{14}]^{++}$, 22); HRMS (EI^+): calculated for $\text{C}_{17}\text{H}_{22}$: 226.1722; found: 226.1727.

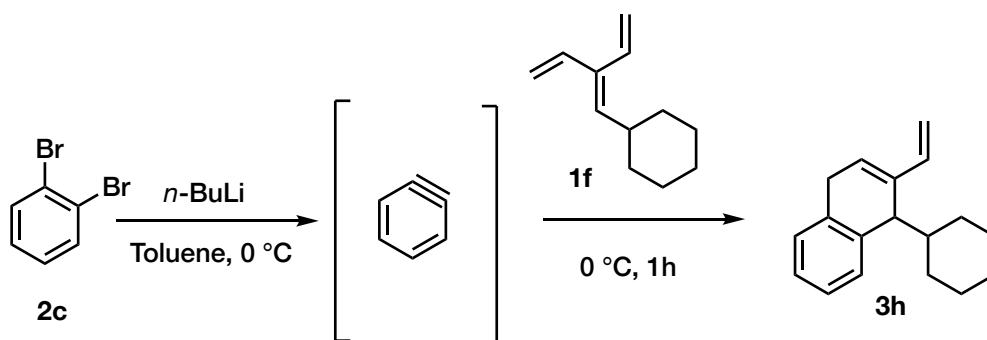
1-Decyl-2-vinyl-1,4-dihydronaphthalene (3g)



Following **General Method A**, the reaction mixture containing dendralene **1e** (90 mg, 0.41 mmol), 1,2-dibromobenzene **2c** (49 μL , 0.41 mmol) and $n\text{-BuLi}$ (0.40 mL, 1.23 M, 0.49 mmol) in toluene (1 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (6 g SiO_2 , 100% PS 40–60) gave the mono DA adduct **3g** as a colorless liquid (35 mg, 0.12 mmol, 29%). R_f = 0.50 (100% PS 40–60).

^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.10 (m, 4H), 6.43 (dd, J = 17.6, 10.9 Hz, 1H), 6.04 (dd, J = 5.7, 2.3 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.05 (d, J = 10.9 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.52 (d, J = 21.2 Hz, 1H), 3.37 (dd, J = 5.9, 1.4 Hz, 1H), 1.76 – 1.47 (m, 2H), 1.35 – 1.05 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 140.1 (Cq), 139.8 (Cq), 137.9 (CH), 135.2 (Cq), 128.6 (CH), 127.8 (CH), 127.5 (CH), 125.9 (CH), 125.8 (CH), 111.1 (CH_2), 39.8 (CH), 36.3 (CH_2), 32.1 (CH_2), 31.3 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 14.3 (CH_3) ppm; IR (thin film): ν_{\max} = 2922, 2852, 1685, 1646, 1607, 1456 cm^{-1} ; LRMS (EI^+): m/z (%): 296($[\text{M}]^{++}$, 14), 155 ($[\text{M}-\text{C}_{10}\text{H}_{21}]^{++}$, 100), 128 ($[\text{M}-\text{C}_{12}\text{H}_{24}]^{++}$, 100); HRMS (EI^+): calculated for $\text{C}_{22}\text{H}_{32}$: 296.2504; found: 296.2509.

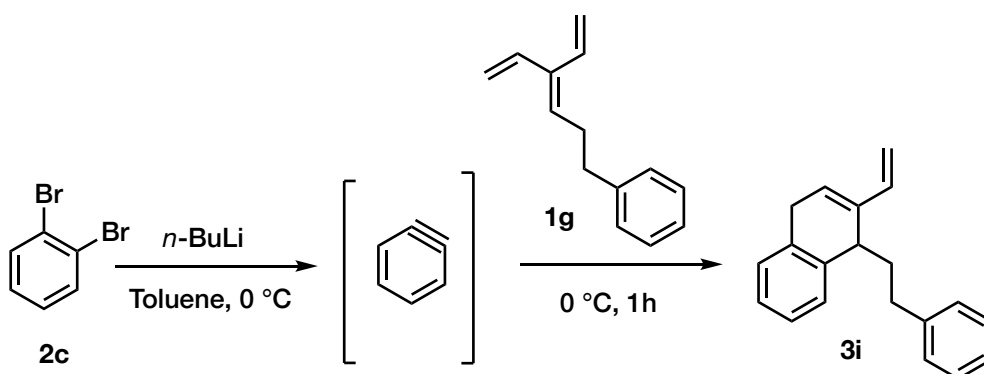
1-Cyclohexyl-2-vinyl-1,4-dihydronaphthalene (3h)



Following **General Method A**, the reaction mixture containing dendralene **1f** (49 mg, 0.30 mmol), 1,2-dibromobenzene **2c** (36 μ L, 0.30 mmol) and *n*-BuLi (0.29 mL, 1.23 M, 0.36 mmol) in toluene (0.6 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (4 g SiO₂, 100% PS 40–60) gave the mono DA adduct **3h** as a colorless liquid (25 mg, 0.105 mmol, 35%). *R_f* = 0.50 (100% PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.18 – 7.13 (m, 4H), 6.44 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.10 (dd, *J* = 6.2, 2.4 Hz, 1H), 5.25 (d, *J* = 17.6 Hz, 1H), 5.03 (d, *J* = 10.8 Hz, 1H), 3.59 (brs, 1H), 3.52 (d, *J* = 21.3 Hz, 1H), 3.32 (dd, *J* = 21.2, 6.0 Hz, 1H), 1.82 – 1.46 (m, 6H), 1.32 – 0.85 (m, 4H), 0.61 (qd, *J* = 12.9, 12.3, 4.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 139.9 (Cq), 138.6 (CH), 137.9 (Cq), 136.2 (Cq), 129.6 (CH), 128.2 (CH), 127.7 (CH), 125.8 (CH), 125.3 (CH), 111.1 (CH₂), 46.1 (CH), 44.7 (CH), 32.5 (CH₂), 32.2 (CH₂), 28.8 (CH₂), 27.1 (CH₂), 26.7 (CH₂), 26.4 (CH₂) ppm; IR (thin film): ν_{max} = 2922, 2850, 1678, 1646, 1448 cm⁻¹; LRMS (EI⁺): *m/z* (%): 238([M]⁺, 25), 155 ([M–C₆H₁₁]⁺, 96), 154 ([M–C₆H₁₂]⁺, 100); HRMS (EI⁺): calculated for C₁₈H₂₂: 238.1722; found: 238.1722.

1-Phenethyl-2-vinyl-1,4-dihydronaphthalene (**3i**)

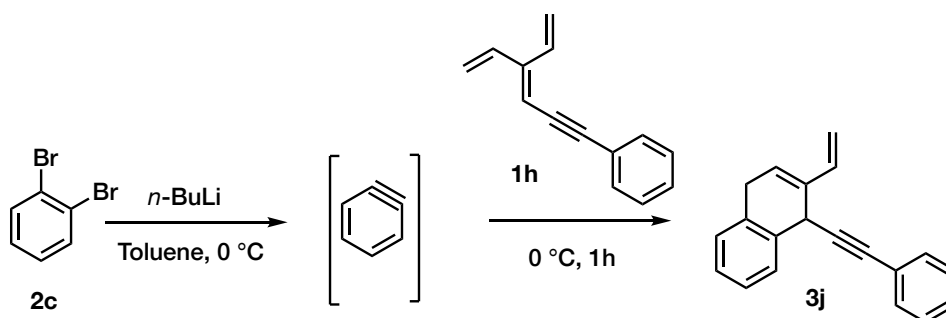


Following **General Method A**, the reaction mixture containing dendralene **1g** (102 mg, 0.55 mmol), 1,2-dibromobenzene **2c** (66 μ L, 0.55 mmol) and *n*-BuLi (0.54 mL, 1.23 M, 0.66 mmol) in toluene (1 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (6 g SiO₂, 100% PS 40–60) gave the mono DA adduct **3i** as a colorless liquid (38 mg, 0.15 mmol, 27%). *R_f* = 0.29 (100% PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.17 (m, 6H), 7.17 – 7.11 (m, 1H), 7.08 (d, *J* = 7.0 Hz, 2H), 6.44 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.08 (dd, *J* = 5.8, 2.4 Hz, 1H), 5.22 (d, *J* = 17.6 Hz, 1H), 5.04 (d, *J* = 10.9 Hz, 1H), 3.87 – 3.77 (m, 1H), 3.56 (d, *J* = 21.5 Hz, 1H), 3.42 (dd, *J* = 21.4, 5.7 Hz, 1H), 2.62 – 2.50 (m, 1H), 2.45 – 2.33 (m, 1H), 2.06 – 1.86 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 142.5 (Cq), 139.5 (Cq), 139.1 (Cq), 137.7 (CH), 135.2 (Cq), 128.6 (CH), 128.5 (2×CH), 128.4

(2×CH), 128.0 (CH), 127.8 (CH), 126.1 (CH), 126.0 (CH), 125.8 (CH), 111.4 (CH₂), 39.4 (CH), 37.9 (CH₂), 32.3 (CH₂), 31.3 (CH₂) ppm; IR (thin film): ν_{max} = 3084, 3061, 3024, 2920, 2856, 1646, 1604, 1494 cm⁻¹; LRMS (EI⁺): m/z (%): 260 ([M]⁺⁺, 4), 155 ([M-C₆H₅CH₂CH₂]⁺⁺, 100), 128 ([M-C₁₀H₁₂]⁺⁺, 29); HRMS (EI⁺): calculated for C₂₀H₂₀: 260.1565; found: 260.1571.

1-(Phenylethynyl)-2-vinyl-1,4-dihydronaphthalene (**3j**)



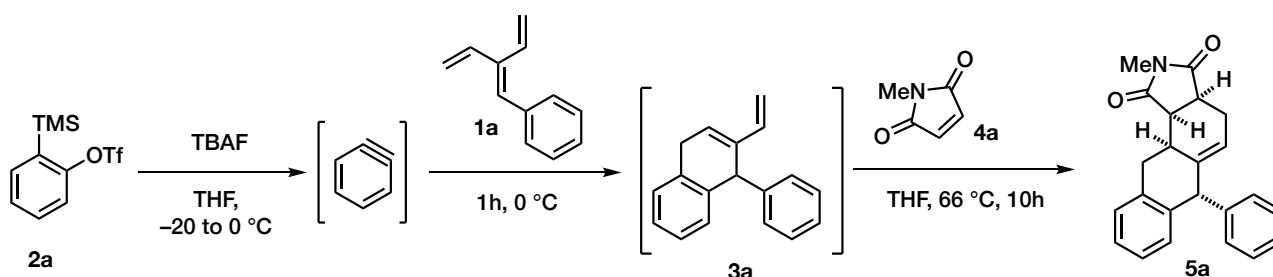
Following **General Method A**, the reaction mixture containing dendralene **1h** (78 mg, 0.43 mmol), 1,2-dibromobenzene **2c** (51 μ L, 0.43 mmol) and *n*-BuLi (0.35 mL, 1.5 M, 0.52 mmol) in toluene (1 mL) was stirred at 0 °C for 1h. After work up, purification by flash column chromatography (5 g SiO₂, 1% EtOAc in PS 40–60) gave the mono DA adduct **3j** as a colorless liquid (39 mg, 0.15 mmol, 35%). *R_f* = 0.40 (5% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.16 (m, 8H), 6.51 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.12 (dd, *J* = 5.3, 2.8 Hz, 1H), 5.59 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H), 4.86 (t, *J* = 3.2 Hz, 1H), 3.69 (d, *J* = 22.1 Hz, 1H), 3.48 (ddd, *J* = 22.0, 5.2, 2.8 Hz, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 137.0 (CH), 134.9 (2×Cq), 133.5 (Cq), 131.8 (2×CH), 129.1 (CH), 128.2 (CH), 128.2 (2×CH), 127.8 (CH), 127.7 (CH), 127.0 (CH), 126.8 (CH), 123.8 (CH₂), 113.1 (Cq), 90.9 (Cq), 80.7 (Cq), 31.9 (CH), 30.6 (CH₂) ppm; IR (thin film): ν_{max} = 3059, 3020, 2962, 2925, 2856, 1657, 1597 cm⁻¹; LRMS: (EI⁺): m/z (%): 256([M]⁺⁺, 65), 255 ([M-H]⁺⁺, 72), 154 (100); HRMS (EI⁺): calculated for C₂₀H₁₆: 256.1252; found: 256.1253.

Twofold Cycloadditions to Substituted [3]Dendralenes

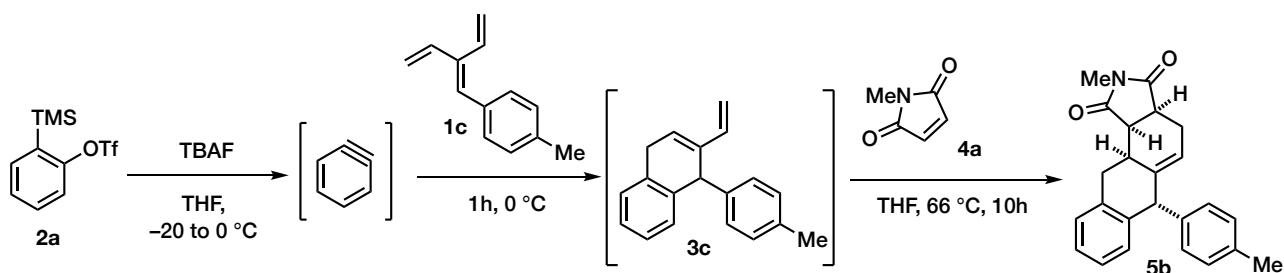
(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-2-Methyl-6-phenyl-3a,4,6,11,11a,11b-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (**5a**)



Following **General Method C**, the reaction mixture containing dendralene **1a** (95 mg, 0.61 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.44 mL, 1.8 mmol) and TBAF (2.1 mL, 1 M, 2.1 mmol) in THF (3 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (405 mg, 3.65 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (20 g SiO₂, 25% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5a** as a white solid (123 mg, 0.360 mmol, 59%). *R*_f = 0.34 (30% EtOAc in PS 40–60); m.p. 153 – 159 °C (10% EtOAc in hexane).

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.24 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.07 (m, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.47 – 5.35 (m, 1H), 4.47 (s, 1H), 3.62 (dd, *J* = 14.8, 9.9 Hz, 1H), 3.23 (dd, *J* = 8.5, 6.7 Hz, 1H), 3.12 (t, *J* = 7.6 Hz, 1H), 3.02 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.83 (s, 3H), 2.76 – 2.61 (m, 2H), 2.18 – 2.06 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.8 (Cq), 178.3 (Cq), 143.8 (Cq), 139.4 (Cq), 139.3 (Cq), 138.0 (Cq), 130.2 (2×CH), 128.6 (2×CH), 128.1 (CH), 127.0 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 120.7 (CH), 51.5 (CH), 43.8 (CH), 40.4 (CH), 35.8 (CH), 31.3 (CH₂), 24.9 (CH₂), 24.7 (CH₃) ppm; IR (thin film): ν_{max} = 3029, 2951, 2851, 1772, 1696 cm⁻¹; LRMS (EI⁺): *m/z* (%): 343 ([M]⁺, 100), 231 (79), 215 (60); HRMS (EI⁺): calculated for C₂₃H₂₁NO₂: 343.1572; found: 343.1570.

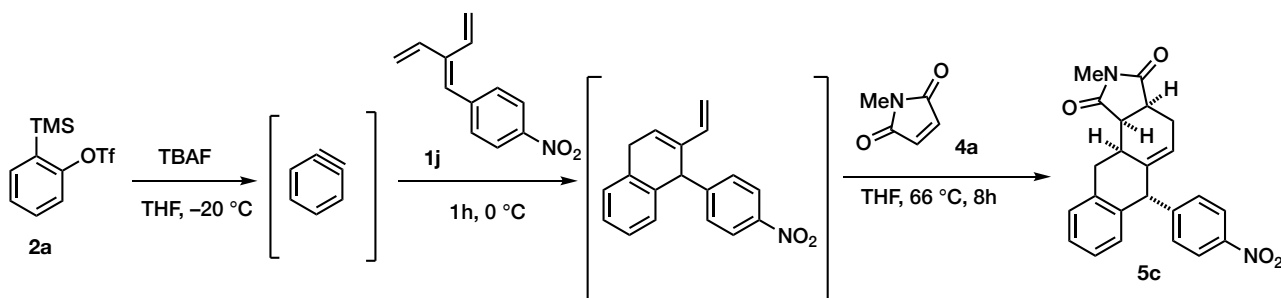
(rel)-(3*aR*,6*R*,11*aR*,11*bS*)-2-Methyl-6-(*p*-tolyl)-3*a*,4,6,11,11*a*,11*b*-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (5*b*)



Following **General Method C**, the reaction mixture containing dendralene **1c** (103 mg, 0.600 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.37 mL, 1.5 mmol) and TBAF (1.8 mL, 1 M, 1.8 mmol) in THF (2 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) were added and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (403 mg, 3.63 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 20% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5b** as a colorless liquid (121 mg, 0.340 mmol, 56%). *R*_f = 0.33 (30% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.23 (m, 1H), 7.22 – 7.14 (m, 3H), 7.14 – 7.07 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.46 – 5.39 (m, 1H), 4.44 (s, 1H), 3.63 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.23 (dd, *J* = 8.7, 6.5 Hz, 1H), 3.16 – 3.06 (m, 1H), 3.02 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.83 (s, 3H), 2.75 – 2.61 (m, 2H), 2.37 (s, 3H), 2.17 – 2.06 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.8 (Cq), 178.3 (Cq), 143.9 (Cq), 139.5 (Cq), 138.0 (Cq), 136.6 (Cq), 136.2 (Cq), 130.1 (2×CH), 129.3 (2×CH), 128.0 (CH), 126.6 (CH), 126.4 (CH), 126.3 (CH), 120.4 (CH), 51.1 (CH), 43.8 (CH), 40.4 (CH), 35.9 (CH), 31.3 (CH₂), 24.8 (CH₂), 24.8 (CH₃), 21.2 (CH₃) ppm; IR (thin film): *ν*_{max} = 3021, 2946, 2843, 1772, 1698 cm⁻¹; LRMS (EI⁺): *m/z* (%): 357 ([*M*]⁺, 100), 342 ([*M*–CH₃]⁺, 28); HRMS (EI⁺): calculated for C₂₄H₂₃NO₂: 357.1729; found: 357.1729.

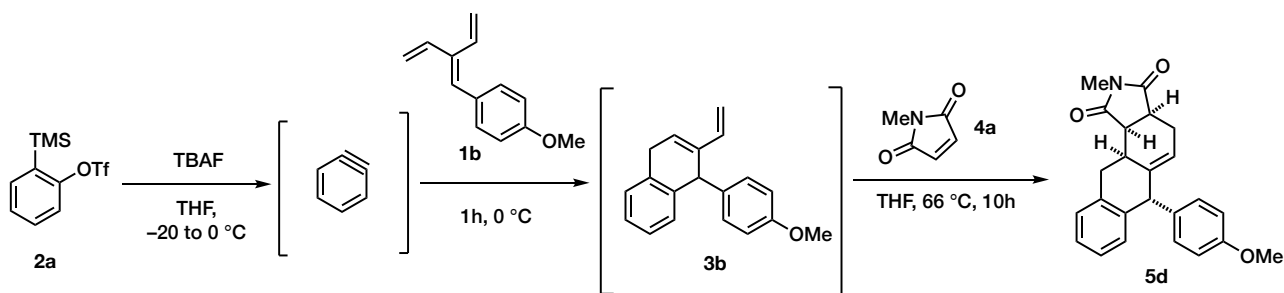
(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-2-Methyl-6-(4-nitrophenyl)-3a,4,6,11,11a,11b-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (5c)



Following **General Method C**, the reaction mixture containing dendralene **1j** (69 mg, 0.34 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.17 mL, 0.69 mmol) and TBAF (1.0 mL, 1 M, 1.0 mmol) in THF (1.5 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (229 mg, 2.06 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 8h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 25% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5c** as a yellow solid (59 mg, 0.15 mmol, 44%). *R_f* = 0.42 (50% EtOAc in PS 40–60); m.p. 188 – 194 °C (hexane:EtOAc, 7:3).

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.23 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 5.47 (s, 1H), 4.62 (s, 1H), 3.63 (dd, *J* = 14.9, 9.2 Hz, 1H), 3.32 – 3.23 (m, 1H), 3.21 – 3.13 (m, 1H), 3.00 (dd, *J* = 15.0, 6.4 Hz, 1H), 2.91 – 2.66 (m, 5H), 2.26 – 2.10 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.5 (Cq), 177.9 (Cq), 147.7 (Cq), 147.1 (Cq), 142.9 (Cq), 137.7 (Cq), 137.7 (Cq), 130.9 (2×CH), 128.7 (CH), 127.1 (CH), 126.7 (CH), 126.5 (CH), 123.8 (2×CH), 121.8 (CH), 51.3 (CH), 43.7 (CH), 40.2 (CH), 35.4 (CH), 31.1 (CH₂), 24.9 (CH₃), 24.6 (CH₂) ppm; IR (thin film): *ν*_{max} = 3071, 2947, 2848, 2254, 1772, 1691 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 389 ([*M*+1]⁺, 20), 411 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₃H₂₁N₂O₄: 389.1496; found: 389.1497.

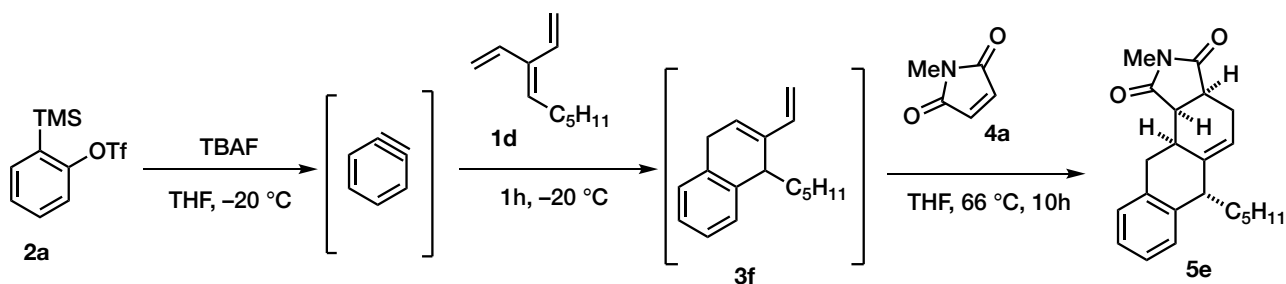
(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-6-(4-Methoxyphenyl)-2-methyl-3a,4,6,11,11a,11b-hexahydro-1H-naphtho[2,3-*c*]isoindole-1,3(2H)-dione (5d)



Following **General Method C**, the reaction mixture containing dendralene **1b** (55 mg, 0.30 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (215 mL, 0.886 mmol) and TBAF (1.0 mL, 1 M, 1.03 mmol) in THF (1.5 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (131 mg, 1.18 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 25% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5d** as a white solid (53 mg, 0.142 mmol, 48%). *R_f* = 0.30 (40% EtOAc in PS 40–60); m.p. 169 – 173 °C (hexane:EtOAc, 8:2).

¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.24 (m, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.46 – 5.36 (m, 1H), 4.42 (s, 1H), 3.83 (s, 3H), 3.63 (dd, *J* = 14.7, 10.2 Hz, 1H), 3.23 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.12 (t, *J* = 7.4 Hz, 1H), 3.02 (dd, *J* = 14.8, 6.1 Hz, 1H), 2.84 (s, 3H), 2.76 – 2.59 (m, 2H), 2.16 – 2.04 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.8 (Cq), 178.3 (Cq), 158.7 (Cq), 144.1 (Cq), 139.7 (Cq), 138.1 (Cq), 131.3 (2×CH), 131.2 (Cq), 128.0 (CH), 126.6 (CH), 126.4 (CH), 126.4 (CH), 120.4 (CH), 114.0 (2×CH), 55.4 (CH₃), 50.6 (CH), 43.8 (CH), 40.4 (CH), 36.0 (CH), 31.4 (CH₂), 24.9 (CH₂), 24.8 (CH₃) ppm; IR (thin film): *v*_{max} = 2946, 2835, 1772, 1694, 1611, 1511 cm⁻¹; LRMS (EI⁺): *m/z* (%): 373 ([M]⁺, 100), 358 ([M–CH₃]⁺, 3), 342 ([M–OCH₃]⁺, 22); HRMS (EI⁺): calculated for C₂₄H₂₃NO₃: 373.1678; found: 373.1678.

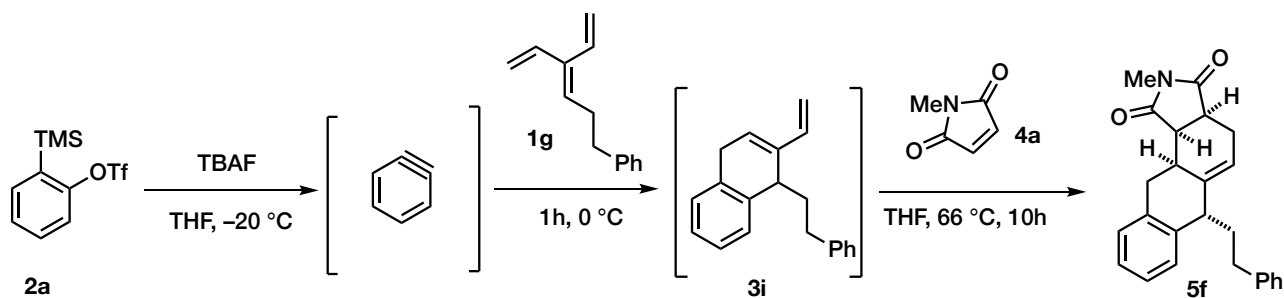
(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-2-Methyl-6-pentyl-3a,4,6,11,11a,11b-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (5e)



Following **General Method C**, the reaction mixture containing dendralene **1d** (61 mg, 0.41 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.25 mL, 1.0 mmol) and TBAF (1.2 mL, 1 M, 1.2 mmol) in THF (1.5 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (271 mg, 2.44 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 15% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5e** as a colorless liquid (69 mg, 0.20 mmol, 50%). *R_f* = 0.66 (40% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.18 (m, 1H), 7.18 – 7.12 (m, 2H), 7.08 – 7.01 (m, 1H), 5.71 – 5.60 (m, 1H), 3.41 (dd, *J* = 15.1, 7.1 Hz, 1H), 3.23 – 3.04 (m, 4H), 2.84 – 2.70 (m, 4H), 2.68 – 2.57 (m, 1H), 2.16 – 2.00 (m, 1H), 1.77 – 1.60 (m, 2H), 1.45 – 1.18 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.9 (Cq), 177.9 (Cq), 143.2 (Cq), 140.1 (Cq), 137.4 (Cq), 128.6 (CH), 126.3 (CH), 126.0 (CH), 125.4 (CH), 118.5 (CH), 45.8 (CH), 43.9 (CH), 40.7 (CH), 35.2 (CH), 32.1 (CH₂), 31.4 (CH₂), 31.0 (CH₂), 27.7 (CH₂), 24.7 (CH₃), 24.2 (CH₂), 22.7 (CH₂), 14.2 (CH₃) ppm; IR (thin film): *ν*_{max} = 2952, 2928, 2855, 1773, 1696 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 338 ([*M*+1]⁺, 42), 360 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₂H₂₈NO₂: 338.2115; found: 338.2111.

(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-2-Methyl-6-phenethyl-3a,4,6,11,11a,11b-hexahydro-1H-naphtho[2,3-*c*]isoindole-1,3(2H)-dione (5f)

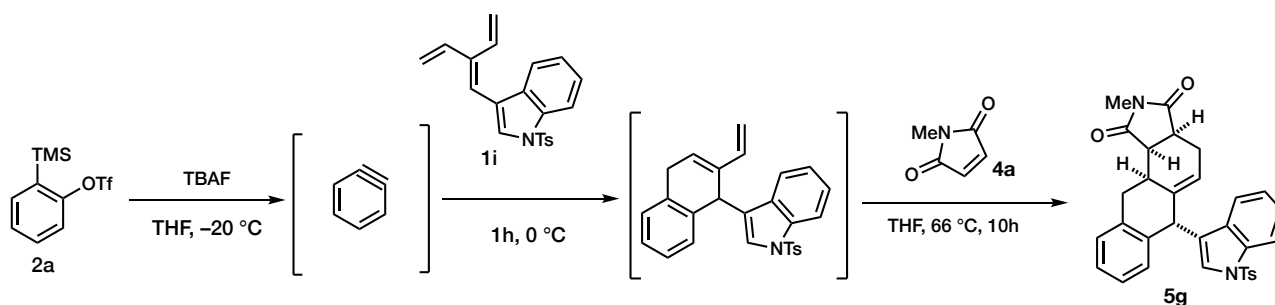


Following **General Method C**, the reaction mixture containing dendralene **1g** (59 mg, 0.32 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.23 mL, 0.96 mmol) and TBAF (1.1 mL, 1 M, 1.1 mmol) in THF (1.5 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (231 mg, 1.91 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 17% EtOAc in PS 40–60 gave the double Diels–Alder adduct **5f** as a colorless liquid (52 mg, 0.14 mmol, 44%). *R_f* = 0.30 (30% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.11 (m, 8H), 7.11 – 7.02 (m, 1H), 5.78 – 5.66 (m, 1H), 3.40 (dd, *J* = 15.2, 6.8 Hz, 1H), 3.24 (t, *J* = 6.7 Hz, 1H), 3.21 – 3.06 (m, 3H), 2.79 (ddd, *J* = 15.3, 7.1, 2.0 Hz, 1H), 2.73 (s, 3H), 2.71 – 2.65 (m, 3H), 2.16 – 1.97 (m, 3H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 179.8 (Cq), 177.8 (Cq), 142.8 (Cq), 142.1 (Cq), 139.6 (Cq), 137.3 (Cq), 128.9 (CH), 128.5 (2×CH), 128.5 (2×CH), 126.4 (CH), 126.2 (CH), 126.0 (CH), 125.5 (CH), 119.1 (CH), 45.5 (CH), 43.9 (CH), 40.6 (CH), 35.0 (CH), 34.1 (CH₂), 33.3 (CH₂), 31.0 (CH₂), 24.7 (CH₃), 24.1 (CH₂) ppm; IR (thin film): *v*_{max} = 3023, 2928, 2851, 1772, 1696 cm⁻¹; LRMS (EI⁺): *m/z* (%): 371 ([M]⁺⁺, 47), 266 ([M–C₆H₅CH₂CH₂]⁺⁺, 100), 178 (31), 155 (57); HRMS (EI⁺): calculated for C₂₅H₂₅NO₂: 371.1885; found: 371.1883.

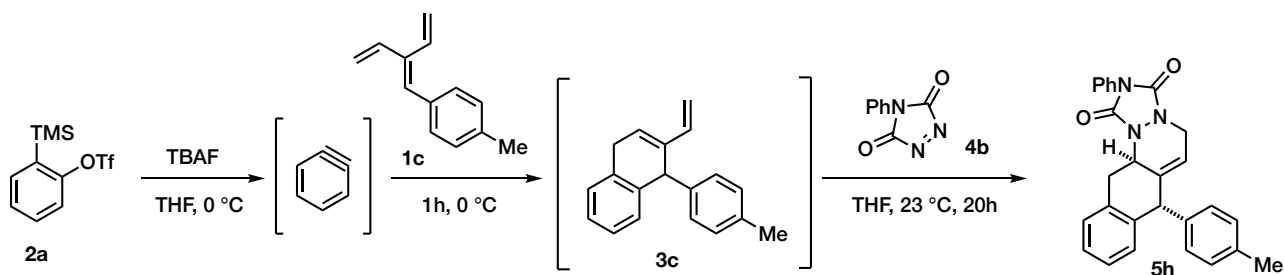
(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-2-Methyl-6-(1-tosyl-1*H*-indol-3-yl)-3a,4,6,11,11a,11b-hexahydro-1*H*-naphtho[2,3-*c*]isoindole-1,3(2*H*)-dione (5g)



Following **General Method C**, the reaction mixture containing dendralene **1i** (91 mg, 0.26 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.16 mL, 0.65 mmol) and TBAF (0.78 mL, 1 M, 0.78 mmol) in THF (3 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (174 mg, 1.6 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 30% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5g** as a white solid (63 mg, 0.12 mmol, 45%). *R*_f = 0.34 (40% EtOAc in PS 40–60); m.p. 157 – 161 °C (Et₂O:CH₂Cl₂, 5:5).

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.39 (s, 1H), 7.28 – 7.15 (m, 4H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 5.21 – 5.02 (m, 1H), 4.67 (s, 1H), 3.74 – 3.55 (m, 1H), 3.21 – 3.13 (m, 1H), 3.11 – 2.99 (m, 2H), 2.87 (s, 3H), 2.63 – 2.52 (m, 1H), 2.51 (dd, *J* = 15.2, 7.2 Hz, 1H), 2.32 (s, 3H), 2.08 – 1.88 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.7 (Cq), 178.3 (Cq), 145.1 (Cq), 141.4 (Cq), 138.1 (Cq), 137.3 (Cq), 136.1 (Cq), 135.1 (Cq), 130.0 (Cq), 130.0 (2×CH), 127.7 (CH), 126.9 (2×CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 126.1 (CH), 124.8 (CH), 123.0 (CH), 121.9 (CH), 120.6 (Cq), 120.3 (CH), 114.3 (CH), 43.6 (CH), 42.5 (CH), 40.2 (CH), 36.2 (CH), 31.5 (CH₂), 25.0 (CH₃), 24.9 (CH₂), 21.7 (CH₃) ppm; IR (thin film): *ν*_{max} = 3057, 2945, 2854, 1771, 1694 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 537 ([*M*+1]⁺, 8), 559 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₃₂H₂₉N₂O₄S: 537.1843; found: 537.1843.

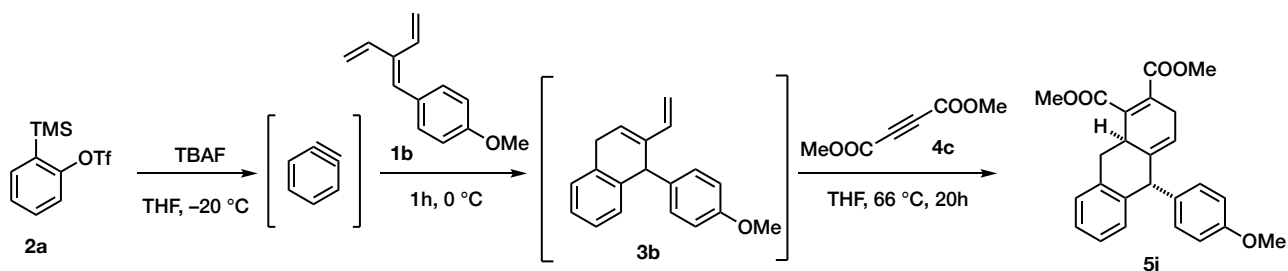
(rel)-(7*S*,12*aS*)-2-Phenyl-7-(*p*-tolyl)-5,7,12,12*a*-tetrahydro-1*H*-benzo[*g*][1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (5h)



Following **General Method C**, the reaction mixture containing dendralene **1c** (53 mg, 0.31 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.19 mL, 0.78 mmol) and TBAF (0.93 mL, 1 M, 0.93 mmol) in THF (2 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. PTAD **4b** (162 mg, 0.93 mmol) was added and the reaction mixture was stirred at 23 °C for 20h. The reaction mixture was filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 30% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5h** as a white solid (83 mg, 0.20 mmol, 63%). *R*_f = 0.60 (40% EtOAc in PS 40–60); m.p. 175 – 180 °C (hexane:EtOAc, 8:2).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.33 (m, 1H), 7.25 – 7.17 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 4.98 (s, 1H), 4.83 – 4.68 (m, 1H), 4.35 (dd, *J* = 16.1, 4.3 Hz, 1H), 4.07 (dt, *J* = 16.1, 2.3 Hz, 1H), 3.72 (dd, *J* = 15.4, 5.9 Hz, 1H), 3.01 (dd, *J* = 15.3, 11.3 Hz, 1H), 2.32 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 152.6 (Cq), 151.6 (Cq), 141.0 (Cq), 137.8 (Cq), 136.8 (Cq), 136.4 (Cq), 134.0 (Cq), 131.3 (Cq), 130.1 (CH), 129.4 (3×CH), 129.3 (2×CH), 128.2 (CH), 128.2 (2×CH), 127.2 (2×CH), 125.6 (2×CH), 113.1 (CH), 52.3 (CH), 49.9 (CH), 43.3 (CH₂), 34.6 (CH₂), 21.1 (CH₃) ppm; IR (thin film): *ν*_{max} = 3048, 3020, 2920, 2852, 2249, 1772, 1706 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 422 ([M+H]⁺, 30), 444 ([M+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₇H₂₄N₃O₂: 422.1863; found: 422.1862.

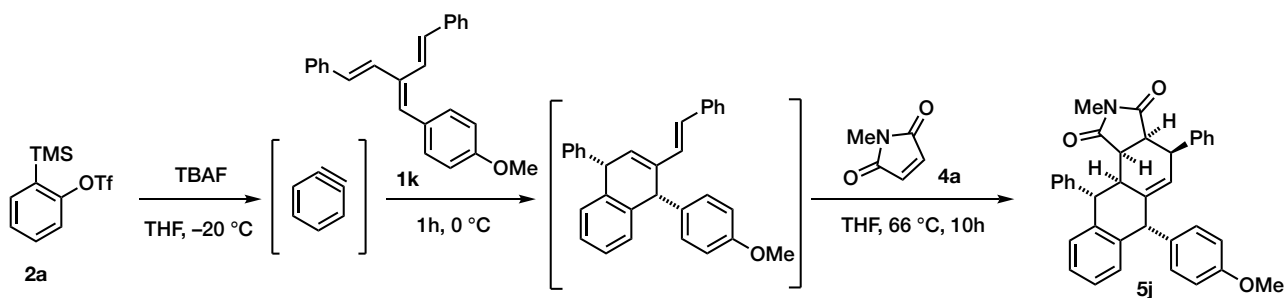
(rel)-Dimethyl (9a*S*,10*R*)-10-(4-methoxyphenyl)-3,9,9a,10-tetrahydroanthracene-1,2-dicarboxylate (5i**)**



Following **General Method C**, the reaction mixture containing dendralene **1b** (56 mg, 0.30 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.22 mL, 0.90 mmol) and TBAF (1.1 mL, 1 M, 1.05 mmol) in THF (1.5 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. DMAD **4c** (0.37 mL, 3.0 mmol) was added and the reaction mixture was heated under reflux for 20h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 8% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5i** as a white solid (36 mg, 0.09 mmol, 30%). *R_f* = 0.26 (20% EtOAc in PS 40–60); m.p. 88 – 91 °C (hexane:EtOAc, 8:2).

¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.11 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.83 (t, *J* = 3.4 Hz, 1H), 4.72 (s, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.76 (s, 3H), 3.48 – 3.37 (m, 1H), 3.24 (dd, *J* = 16.0, 5.5 Hz, 1H), 3.16 (ddd, *J* = 23.3, 7.0, 2.9 Hz, 1H), 2.99 (ddd, *J* = 23.3, 6.5, 3.8 Hz, 1H), 2.79 (dd, *J* = 15.9, 12.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 168.7 (Cq), 168.2 (Cq), 158.3 (Cq), 137.8 (Cq), 137.8 (Cq), 137.2 (Cq), 136.9 (Cq), 135.8 (Cq), 131.5 (Cq), 130.2 (CH), 129.3 (2×CH), 128.9 (CH), 126.7 (CH), 126.6 (CH), 115.5 (CH), 113.8 (2×CH), 55.4 (CH₃), 52.4 (CH₃), 52.4 (CH₃), 52.1 (CH), 37.2 (CH₂), 33.0 (CH), 28.1 (CH₂) ppm; IR (thin film): *v*_{max} = 3001, 2950, 2895, 2836, 2255, 1720 cm⁻¹; LRMS (EI⁺): *m/z* (%): 404 ([M]⁺, 11), 370 (41), 264 (70), 207 (100); HRMS (EI⁺): calculated for C₂₅H₂₄O₅: 404.1624; found: 404.1611.

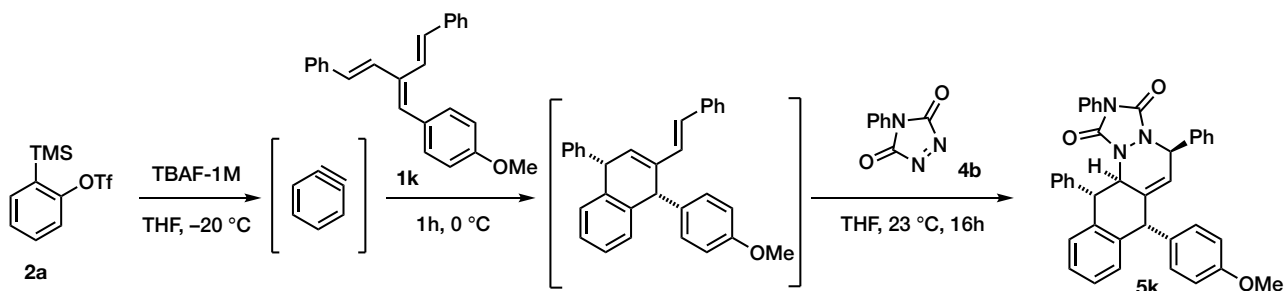
(rel)-(3a*R*,4*R*,6*R*,11*R*,11a*R*,11b*S*)-6-(4-Methoxyphenyl)-2-methyl-4,11-diphenyl-3a,4,6,11,11a,11b-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (5j)



Following **General Method C**, the reaction mixture containing dendralene **1k** (74 mg, 0.22 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.13 mL, 0.55 mmol) and TBAF (0.66 mL, 1 M, 0.66 mmol) in THF (2.5 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (121 mg, 1.10 mmol) was added and the reaction mixture was refluxed at 66 °C for 10h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 18% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5j** as a white solid (62 mg, 0.12 mmol, 54%). *R_f* = 0.49 (30% EtOAc in PS 40–60); m.p. 191 – 195 °C (hexane:CH₂Cl₂, 9:1).

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.35 – 7.15 (m, 5H), 7.14 – 7.03 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 6.2 Hz, 1H), 5.65 (s, 1H), 5.32 (d, *J* = 11.6 Hz, 1H), 4.67 (s, 1H), 3.87 (s, 3H), 3.62 – 3.51 (m, 1H), 3.18 (t, *J* = 8.1 Hz, 1H), 3.05 – 2.96 (m, 1H), 2.92 (d, *J* = 11.4 Hz, 1H), 2.85 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 178.0 (Cq), 175.9 (Cq), 158.9 (Cq), 145.5 (Cq), 141.4 (Cq), 140.5 (Cq), 140.0 (Cq), 139.5 (Cq), 132.3 (2×CH), 130.2 (2×CH), 129.9 (Cq), 129.2 (2×CH), 128.9 (2×CH), 128.4 (2×CH), 127.5 (CH), 127.1 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 122.6 (CH), 114.3 (2×CH), 55.4 (CH₃), 50.5 (CH), 47.3 (CH), 45.2 (CH), 44.6 (CH), 43.3 (CH), 42.4 (CH), 24.8 (CH₃) ppm; IR (thin film): *v*_{max} = 3057, 3031, 2956, 2925, 2856, 1771, 1694 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 526 ([*M*+H]⁺, 45), 548 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₃₆H₃₂NO₃: 526.2382; found: 526.2385.

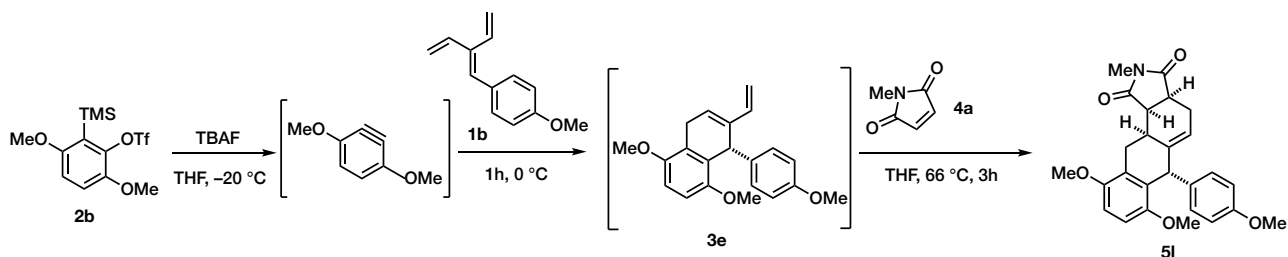
(rel)-(5*S*,7*S*,12*R*,12*aS*)-7-(4-Methoxyphenyl)-2,5,12-triphenyl-5,7,12,12*a*-tetrahydro-1*H*-benzo[*g*][1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (5k)



Following **General Method C**, the reaction mixture containing dendralene **1k** (94 mg, 0.28 mmol), 2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2a** (0.17 mL, 0.69 mmol) and TBAF (0.83 mL, 1 M, 0.83 mmol) in THF (3 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. PTAD **4b** (146 mg, 0.833 mmol) was added and the reaction mixture was stirred at 23 °C for 16h. The reaction mixture was filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 20% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5k** as an amorphous solid (91 mg, 0.15 mmol, 55%). *R_f* = 0.40 (40% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.30 (m, 8H), 7.30 – 7.18 (m, 5H), 7.17 – 7.11 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.88 (s, 1H), 5.34 (s, 1H), 5.05 (s, 1H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 10.5 Hz, 1H), 3.84 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 158.9 (Cq), 155.0 (Cq), 148.7 (Cq), 141.0 (Cq), 139.0 (Cq), 138.9 (Cq), 137.0 (Cq), 136.6 (Cq), 135.3 (Cq), 131.4 (Cq), 130.4 (CH), 130.1 (CH), 130.0 (2×CH), 129.4 (2×CH), 129.1 (2×CH), 128.9 (2×CH), 128.9 (2×CH), 128.6 (CH), 128.2 (CH), 127.9 (CH), 127.8 (2×CH), 127.6 (CH), 127.3 (CH), 125.5 (2×CH), 119.4 (CH), 114.4 (2×CH), 62.0 (CH), 55.5 (CH₃), 55.4 (CH), 54.5 (CH), 52.4 (CH) ppm; IR (thin film): *ν*_{max} = 3062, 3028, 2836, 2252, 1778, 1720 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 590 ([M+H]⁺, 100), 612 ([M+Na]⁺, 65); HRMS (ESI⁺): calculated for C₃₉H₃₁N₃O₃Na: 612.2263; found: 612.2275.

(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-7,10-Dimethoxy-6-(4-methoxyphenyl)-2-methyl-3a,4,6,11,11a,11b-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (5l**)**

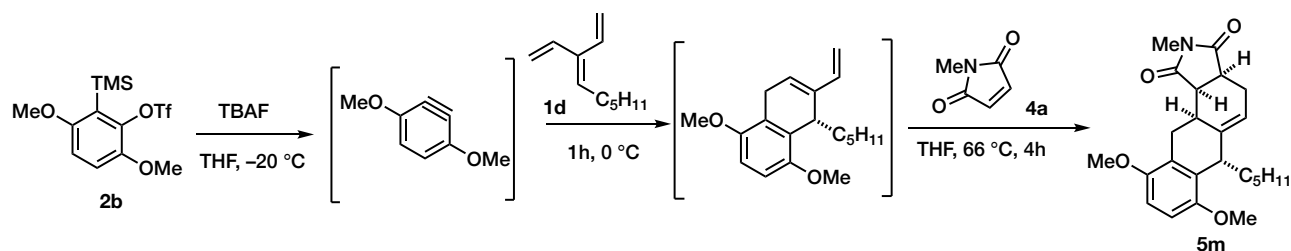


Following **General Method C**, the reaction mixture containing dendralene **1b** (72 mg, 0.39 mmol), 3,6-dimethoxy-2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2b** (277 mg, 0.773 mmol) and TBAF (1.2 mL, 1 M, 1.2 mmol) in THF (2 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (257 mg, 2.32 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 3h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂, then the filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 30% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5l** as a white solid (83 mg, 0.19 mmol, 49%). *R*_f = 0.24 (40% EtOAc in PS 40–60); m.p. 173 – 175 °C (Et₂O:CH₂Cl₂, 9.8:0.2).

¹H NMR (400 MHz, CDCl₃) δ 6.90 (d, *J* = 8.5 Hz, 2H), 6.82 – 6.61 (m, 4H), 6.05 – 5.87 (m, 1H), 5.04 (s, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 3.68 (s, 3H), 3.24 – 2.98 (m, 3H), 2.90 – 2.82 (m, 1H), 2.82 – 2.73 (m, 1H), 2.70 (s, 3H), 2.62 (dd, *J* = 16.1, 7.7 Hz, 1H), 2.40 – 2.26 (m, 1H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 179.9 (Cq), 177.5 (Cq), 158.0 (Cq), 151.7 (Cq), 150.4 (Cq), 141.7 (Cq), 134.3 (Cq), 128.3 (2×CH), 128.3 (Cq), 127.1 (Cq), 120.4 (CH), 113.6 (2×CH), 108.7 (CH), 108.4 (CH), 56.2 (CH₃), 56.1 (CH₃), 55.3 (CH₃), 45.0 (CH), 43.5 (CH), 39.4 (CH), 31.5 (CH), 24.6 (CH₃), 24.5 (CH₂), 23.1 (CH₂) ppm; IR (thin film): ν_{max} = 2997, 2941, 2901, 2834, 2250, 1774, 1698 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 456 ([M+Na]⁺, 100), 434 ([M+H]⁺, 15); HRMS (ESI⁺): calculated for C₂₆H₂₇NO₅Na: 456.1781; found: 456.1770.

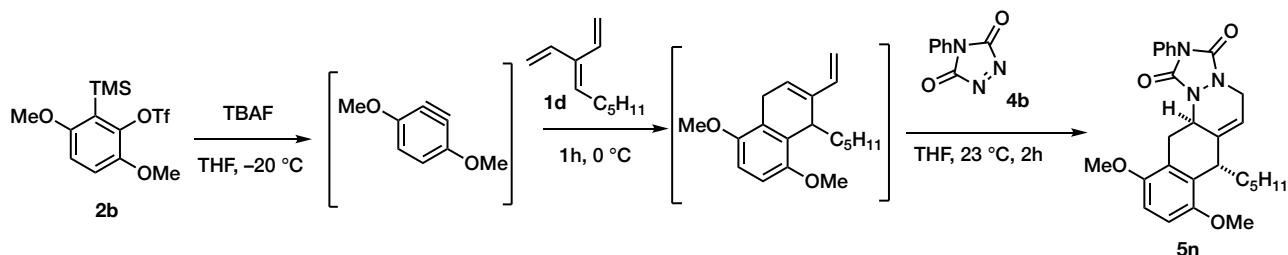
(rel)-(3*aR*,6*R*,11*aR*,11*bS*)-7,10-Dimethoxy-2-methyl-6-pentyl-3*a*,4,6,11,11*a*,11*b*-hexahydro-1*H*-naphtho[2,3-*e*]isoindole-1,3(2*H*)-dione (5*m*)



Following **General Method C**, the reaction mixture containing dendralene **1d** (82 mg, 0.55 mmol), 3,6-dimethoxy-2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2b** (391 mg, 1.09 mmol) and TBAF (1.4 mL, 1 M, 1.4 mmol) in THF (2 mL) was stirred at 0 °C for 1h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. *N*-Methylmaleimide **4a** (182 mg, 1.64 mmol) was added and the reaction mixture was heated under reflux at 66 °C for 4h. The reaction mixture was cooled to 23 °C and filtered through a plug of Celite. The filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 20% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5m** as a white solid (124 mg, 0.312 mmol, 57%). *R*_f = 0.41 (40% EtOAc in PS 40–60); m.p. 113 – 117 °C (hexane:CH₂Cl₂, 9.5:0.5).

¹H NMR (400 MHz, CDCl₃) δ 6.76 – 6.49 (m, 2H), 5.76 – 5.58 (m, 1H), 3.85 (s, 3H), 3.73 (s, 3H), 3.69 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.39 – 3.27 (m, 1H), 3.18 – 3.11 (m, 1H), 3.10 – 3.02 (m, 1H), 2.96 – 2.84 (m, 2H), 2.77 – 2.63 (m, 4H), 2.31 – 2.15 (m, 1H), 1.58 – 1.44 (m, 1H), 1.44 – 1.31 (m, 1H), 1.31 – 1.14 (m, 6H), 0.85 (t, *J* = 6.7 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 180.0 (Cq), 177.5 (Cq), 151.5 (Cq), 150.0 (Cq), 141.6 (Cq), 130.3 (Cq), 126.0 (Cq), 119.8 (CH), 108.0 (CH), 107.9 (CH), 56.2 (CH₃), 55.8 (CH₃), 44.1 (CH), 40.9 (CH), 39.8 (CH), 34.4 (CH₂), 31.7 (CH₂), 31.6 (CH), 27.5 (CH₂), 24.6 (CH₃), 24.1 (CH₂), 23.4 (CH₂), 22.7 (CH₂), 14.2 (CH₃) ppm; IR (thin film): *v*_{max} = 2928, 2853, 1775, 1702, 1699, 1600 cm⁻¹; LRMS (EI⁺): *m/z* (%): 397 ([M]⁺, 43), 326 ([M–C₅H₁₁]⁺, 100); HRMS (EI⁺): calculated for C₂₄H₃₁NO₄: 397.2253; found: 397.2254.

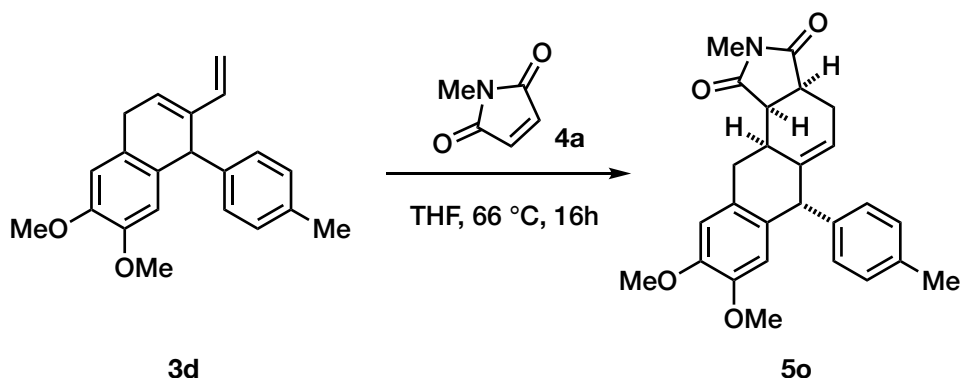
(rel)-(7*R*,12*as*)-8,11-Dimethoxy-7-pentyl-2-phenyl-5,7,12,12*a*-tetrahydro-1*H*-benzo[*g*][1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (5*n*)



Following **General Method C**, the reaction mixture containing dendralene **1d** (74 mg, 0.49 mmol), 3,6-dimethoxy-2-trimethylsilyl-benzene-1-trifluoromethanesulfonate **2b** (353 mg, 0.985 mmol) and TBAF (1.2 mL, 1 M, 1.2 mmol) in THF (2 mL) was stirred at 0 °C for 1 h. Methanol (1 mL) was added to the reaction mixture, followed by CaCO₃ (120 mg) and Dowex 50WX8–400 resin (420 mg) and stirring was continued for 10 minutes. PTAD **4b** (130 mg, 0.74 mmol) was added and the reaction mixture was stirred at 23 °C for 2 h. The reaction mixture was filtered through a plug of Celite. The Celite pad was washed with 5 mL CH₂Cl₂. The filtrate was further diluted with CH₂Cl₂ (5 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (10 g SiO₂, 15% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5n** as a white solid (122 mg, 0.264 mmol, 54%). *R_f* = 0.40 (30% EtOAc in PS 40–60); m.p. 158 – 161 °C (hexane:EtOAc, 9:1).

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 5.76 (s, 1H), 4.92 – 4.83 (m, 1H), 4.31 (dd, *J* = 16.0, 4.5 Hz, 1H), 4.09 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H), 3.79 – 3.65 (m, 5H), 2.55 (dd, *J* = 16.4, 10.7 Hz, 1H), 2.00 – 1.86 (m, 1H), 1.5 – 1.08 (m, 7H), 0.91 (t, *J* = 6.0 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 153.0 (Cq), 151.8 (Cq), 151.5 (Cq), 150.5 (Cq), 136.0 (Cq), 131.5 (Cq), 130.1 (Cq), 129.3 (2×CH), 128.2 (CH), 125.6 (2×CH), 123.0 (Cq), 113.3 (CH), 108.5 (CH), 107.7 (CH), 55.7 (CH₃), 55.7 (CH₃), 49.5 (CH), 43.5 (CH₂), 43.1 (CH), 34.4 (CH₂), 31.5 (CH₂), 29.5 (CH₂), 27.6 (CH₂), 22.8 (CH₂), 14.3 (CH₃) ppm; IR (thin film): ν_{max} = 2950, 2928, 2855, 1774, 1710, 1600 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 462 ([*M*+H]⁺, 75), 484 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₇H₃₁N₃O₄Na: 484.2207; found: 484.2201.

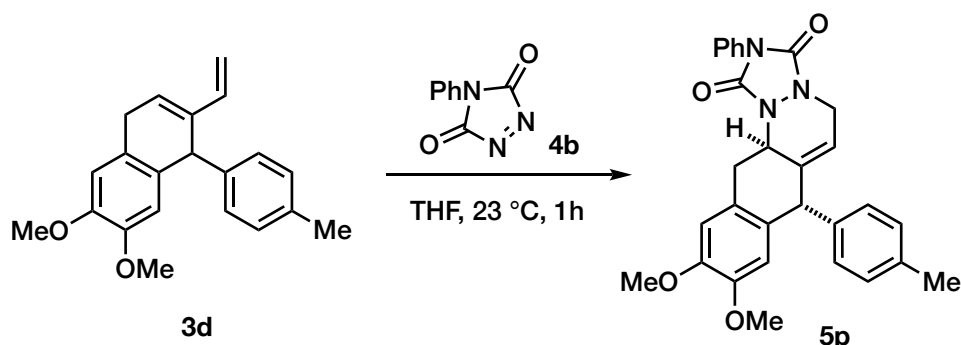
(rel)-(3a*R*,6*R*,11a*R*,11b*S*)-8,9-Dimethoxy-2-methyl-6-(*p*-tolyl)-3a,4,6,11,11a,11b-hexahydro-1H-naphtho[2,3-*e*]isoindole-1,3(2H)-dione (5o**)**



The reaction mixture containing the 2-vinyl-1,4-dihydronaphthalene **3d** (39 mg, 0.13 mmol) and *N*-methylmaleimide **4a** (18 mg, 0.17 mmol) in THF (1 mL) was heated under reflux for 16h. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (6 g SiO₂, 50% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5o** as a white amorphous solid (41 mg, 0.10 mmol, 77%). *R_f* = 0.29 (50% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.79 (s, 1H), 6.39 (s, 1H), 5.46 (brs, 1H), 4.40 (s, 1H), 3.89 (s, 3H), 3.68 (s, 3H), 3.43 (dd, *J* = 14.7, 9.2 Hz, 1H), 3.22 – 3.15 (m, 1H), 3.13 – 3.04 (m, 1H), 2.90 (dd, *J* = 14.8, 6.3 Hz, 1H), 2.81 (s, 3H), 2.75 – 2.62 (m, 2H), 2.35 (s, 3H), 2.20 – 2.07 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 179.8 (Cq), 178.2 (Cq), 147.4 (Cq), 147.4 (Cq), 143.8 (Cq), 137.0 (Cq), 136.5 (Cq), 131.3 (Cq), 129.9 (Cq), 129.7 (2×CH), 129.2 (2×CH), 120.2 (CH), 112.0 (CH), 111.0 (CH), 56.2 (CH₃), 56.1 (CH₃), 51.0 (CH), 43.6 (CH), 40.2 (CH), 35.3 (CH), 30.9 (CH₂), 24.8 (CH₃), 24.3 (CH₂), 21.2 (CH₃) ppm; IR (thin film): *v*_{max} = 2935, 2833, 1771, 1698, 1609 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 418 ([M+H]⁺, 15), 440 ([M+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₆H₂₈NO₄: 418.2018; found: 418.2014; calculated for C₂₆H₂₇NO₄Na: 440.1838; found: 440.1841.

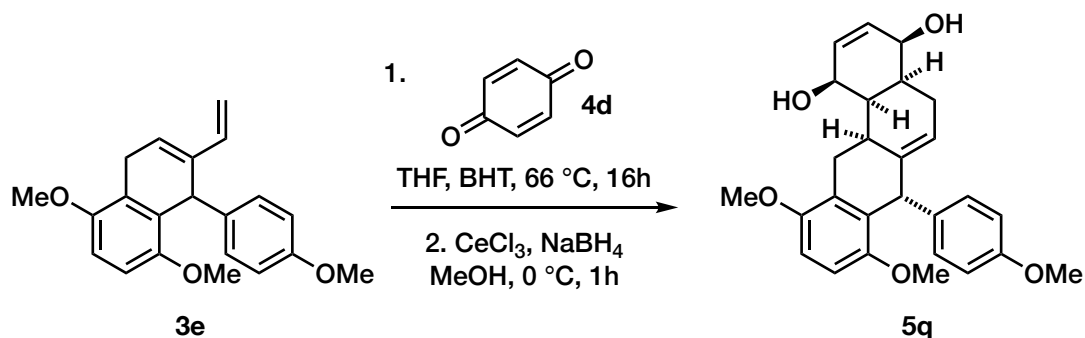
(rel)-(7*S*,12*aS*)-9,10-Dimethoxy-2-phenyl-7-(*p*-tolyl)-5,7,12,12*a*-tetrahydro-1*H*-benzo[*g*][1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (5p)



A reaction mixture containing the 2-vinyl-1,4-dihydronaphthalene **3d** (39 mg, 0.13 mmol) and PTAD **4b** (29 mg, 0.17 mmol) in THF (1 mL) was stirred at 23 °C for 1h. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and water (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. After work up, purification by flash column chromatography (6 g SiO₂, 40% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5p** as a white amorphous solid (54 mg, 0.11 mmol, 88%). *R_f* = 0.33 (50% EtOAc in PS 40–60).

¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.31 (m, 5H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.65 (s, 1H), 6.47 (s, 1H), 6.05 (s, 1H), 4.89 (s, 1H), 4.69 (brs, 1H), 4.34 (d, *J* = 16.0 Hz, 1H), 4.06 (d, *J* = 16.2 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 3.62 (dd, *J* = 15.1, 5.7 Hz, 1H), 3.00 – 2.83 (m, 1H), 2.32 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 152.6 (Cq), 151.7 (Cq), 148.5 (Cq), 148.4 (Cq), 140.9 (Cq), 138.0 (Cq), 136.8 (Cq), 131.3 (Cq), 129.4 (2×CH), 129.3 (2×CH), 128.3 (CH), 128.1 (2×CH), 128.0 (Cq), 126.0 (Cq), 125.6 (2×CH), 112.7 (CH), 112.1 (CH), 111.3 (CH), 56.1 (CH₃), 56.0 (CH₃), 52.1 (CH), 49.9 (CH), 43.3 (CH₂), 34.2 (CH₂), 21.1 (CH₃) ppm; IR (thin film): ν_{max} = 3002, 2935, 2853, 2252, 1771, 1705, 1609 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 482 ([*M*+*H*]⁺, 10), 504 ([*M*+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₉H₂₈N₃O₄: 482.2074; found: 482.2074;

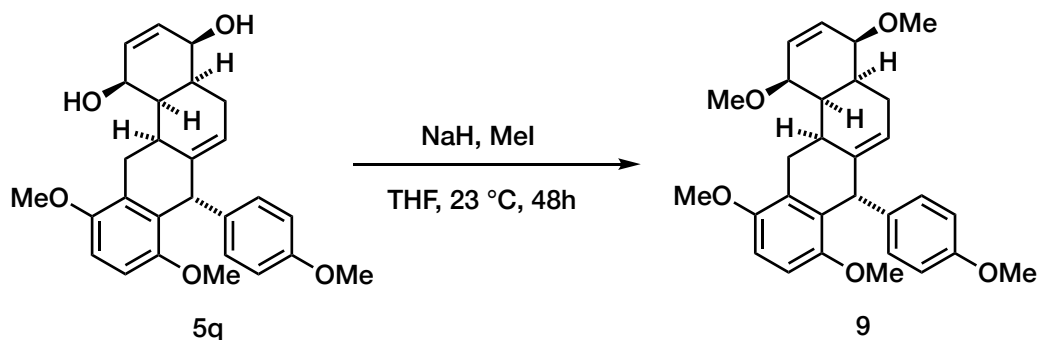
(rel)-(1*S*,4*R*,4*aS*,7*S*,12*aS*,12*bR*)-8,11-Dimethoxy-7-(4-methoxyphenyl)-1,4,4*a*,5,7,12,12*a*,12*b*-octahydrotetraphene-1,4-diol (5q**)**



The reaction mixture containing the 2-vinyl-1,4-dihydronaphthalene **3e** (80 mg, 0.25 mmol), benzoquinone **4d** (70 mg, 0.65 mmol) and a crystal of BHT in THF (2 mL) was heated under reflux for 16h. The reaction mixture was cooled to 0 °C and methanol (1 mL), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (185 mg, 0.500 mmol) and NaBH_4 (19 mg, 0.50 mmol) were added. The reaction mixture was stirred at 0 °C for 1h then quenched with saturated aqueous NH_4Cl (2mL) and diluted with water (10 mL) and CH_2Cl_2 (10 mL) shaken well and the layers were separated. The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure. After work up, purification by flash column chromatography (6 g SiO_2 , 45% EtOAc in PS 40–60) gave the double Diels–Alder adduct **5q** as a white solid (78 mg, 0.18 mmol, 72%). R_f = 0.36 (40% EtOAc in PS 40–60). m.p. 181 – 188 °C (hexane:EtOAc, 1:1).

^1H NMR (400 MHz, CD_2Cl_2) δ 6.96 (d, J = 8.4 Hz, 2H), 6.83 – 6.64 (m, 4H), 5.95 (s, 1H), 5.84 – 5.69 (m, 1H), 5.62 (d, J = 10.1 Hz, 1H), 4.94 (s, 1H), 4.42 – 4.23 (m, 2H), 3.82 (s, 3H), 3.73 (s, 3H), 3.66 (s, 3H), 3.16 (dd, J = 17.5, 5.9 Hz, 1H), 2.86 (brs, 1H), 2.69 (dd, J = 17.4, 9.9 Hz, 1H), 2.29 – 2.06 (m, 3H), 2.09 – 1.96 (m, 1H), 1.63 (d, J = 6.4 Hz, 1H), 1.51 (d, J = 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 158.3 (Cq), 151.4 (Cq), 150.9 (Cq), 141.9 (Cq), 136.0 (Cq), 130.9 (CH), 129.2 (CH), 129.1 (Cq), 128.5 (2×CH), 127.0 (Cq), 122.1 (CH), 113.7 (2×CH), 108.6 (2×CH), 70.4 (CH), 65.1 (CH), 56.2 (CH_3), 56.1 (CH_3), 55.5 (CH_3), 46.7 (CH), 39.4 (CH), 37.6 (CH), 33.2 (CH), 23.9 (CH_2), 23.4 (CH_2) ppm; IR (thin film): ν_{max} = 3288, 2928, 2887, 2824, 1601 cm^{-1} ; LRMS (ESI^+): m/z (%): 457 ($[\text{M}+\text{Na}]^{+}$, 100); HRMS (ESI^+): calculated for $\text{C}_{27}\text{H}_{30}\text{O}_5\text{Na}$: 457.1991; found: 457.1989.

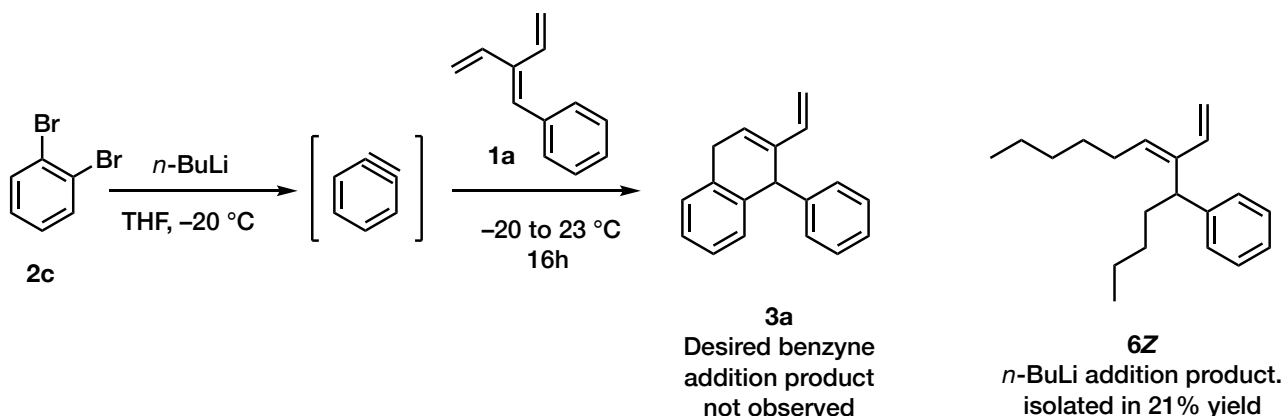
(rel)-(1*S*,4*R*,4*aS*,7*S*,12*aS*,12*bR*)-1,4,8,11-Tetramethoxy-7-(4-methoxyphenyl)-1,4,4*a*,5,7,12,12*a*,12*b*-octahydrotetraphene (9**)**



NaH (3 mg, 0.10 mmol) was dispensed in THF (0.5 mL) under N₂. The reaction mixture was cooled to 0 °C and a solution of diol **5q** (20 mg, 0.05 mmol) in THF (0.5 mL) was added, followed by MeI (9 µL, 0.14 mmol) and stirring was continued at 23 °C for 48h. The reaction mixture was quenched with saturated aqueous NH₄Cl (2mL) and diluted with water (10 mL) and CH₂Cl₂ (10 mL), shaken well and the layers were separated. The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. After work up, purification by flash column chromatography (4 g SiO₂, 40% EtOAc in PS 40–60) gave the product **9** as a white solid (16 mg, 0.030 mmol, 75%). *R_f* = 0.47 (20% EtOAc in PS 40–60); m.p. 137 – 140 °C (hexane:EtOAc, 9:1).

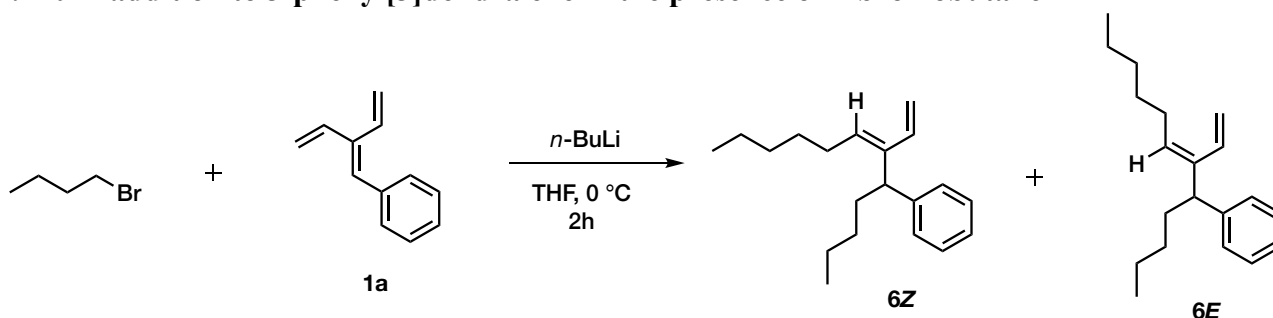
¹H NMR (400 MHz, CDCl₃) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.72 – 6.60 (m, 2H), 5.96 (d, *J* = 9.3 Hz, 1H), 5.86 (brs, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 4.94 (s, 1H), 3.82 (s, 4H), 3.75 (s, 4H), 3.63 (s, 3H), 3.38 (s, 3H), 2.98 (dd, *J* = 17.1, 6.0 Hz, 1H), 2.90 (s, 3H), 2.78 (brs, 1H), 2.63 (dd, *J* = 17.1, 9.8 Hz, 1H), 2.30 – 2.21 (m, 1H), 2.21 – 2.09 (m, 1H), 2.08 – 1.90 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 157.6 (Cq), 150.9 (Cq), 150.8 (Cq), 140.1 (Cq), 136.5 (Cq), 129.7 (Cq), 129.4 (CH), 128.3 (2×CH), 127.8 (Cq), 124.8 (CH), 120.8 (CH), 113.3 (2×CH), 107.6 (2×CH), 79.6 (CH), 73.5 (CH), 56.5 (CH₃), 56.4 (CH₃), 56.1 (CH₃), 55.7 (CH₃), 55.3 (CH₃), 46.4 (CH), 39.2 (CH), 34.6 (CH), 33.1 (CH), 23.4 (CH₂), 22.5 (CH₂) ppm; IR (thin film): *ν*_{max} = 3028, 2929, 2901, 2831, 1602, 1506 cm⁻¹; LRMS (ESI⁺): *m/z* (%): 463 ([M+H]⁺, 10), 485 ([M+Na]⁺, 100); HRMS (ESI⁺): calculated for C₂₉H₃₅O₅: 463.2484; found: 463.2483, calculated for C₂₉H₃₄O₅Na: 485.2304; found: 485.2302.

n-BuLi addition to 3-phenyl[3]dendralene in the presence of 1,2-dibromobenzene



Following **General Method A**, *n*-BuLi (0.40 mL, 0.96 M, 0.38 mmol) was added to the reaction mixture containing dendralene **1a** (54 mg, 0.35 mmol) and 1,2-dibromobenzene **2c** (41 μ L, 0.35 mmol) in THF (1.4 mL) at -20 °C over 10 minutes and brought to 23 °C slowly and stirring continued for 16h. After work up, purification by flash column chromatography (5 g SiO₂, 100% PS 40–60) gave the adduct **6Z** as a colorless liquid (19 mg, 0.07 mmol, 20%) along with unreacted dendralene.

n-BuLi addition to 3-phenyl[3]dendralene in the presence of 1-bromobutane



n-BuLi (0.65 mL, 1.36 M, 0.89 mmol) was added to the reaction mixture containing dendralene **1a** (63 mg, 0.40 mmol) and 1-bromobutane (87 μ L, 0.81 mmol) in THF (1.5 mL) at 0 °C over 5 minutes and the reaction mixture was stirred at the same temperature for 2h. The reaction mixture was quenched by saturated aqueous NH₄Cl and extracted with CH₂Cl₂. The organic layer was washed with water, dried over Na₂SO₄ and concentrated under reduced pressure to give the crude product as a mixture of geometrical isomers (dr = 7:3). Purification by preparative HPLC (Grace Altima C18 5u 250×22 mm (P/N 81105), eluting with water/MeCN/2-propanol in 5:47.5:47.5 ratio) gave the major product **6Z** (*t*_R = 18.49) as a colorless liquid (66 mg, 0.24 mmol, 60%) and the minor product **6E** (*t*_R = 16.97) as a colorless liquid (18 mg, 0.067 mmol, 17%).

Major isomer **6Z**. *R*_f = 0.77 (100% PS 40–60); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.28 (d, *J* = 4.3 Hz, 4H), 7.22 – 7.05 (m, 1H), 6.17 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.71 (t, *J* = 7.3 Hz, 1H), 5.14

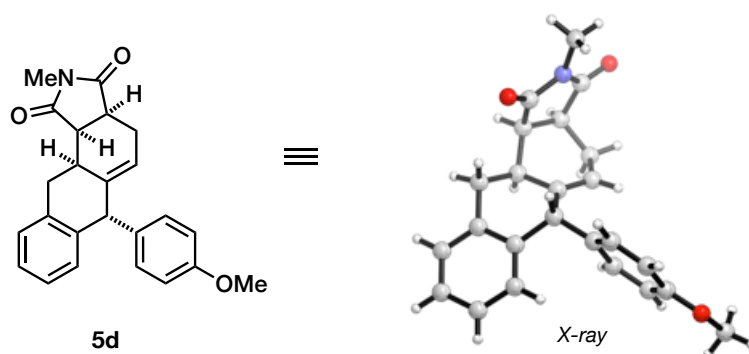
(d, $J = 17.4$ Hz, 1H), 4.84 (d, $J = 10.9$ Hz, 1H), 3.95 (dd, $J = 9.6, 5.9$ Hz, 1H), 2.24 (q, $J = 7.3$ Hz, 2H), 2.05 – 1.91 (m, 1H), 1.91 – 1.76 (m, 1H), 1.50 – 1.19 (m, 10H), 1.02 – 0.82 (m, 6H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 144.7 (Cq), 140.9 (Cq), 138.4 (CH), 131.4 (CH), 128.5 (2 \times CH), 128.0 (2 \times CH), 126.1 (CH), 113.0 (CH_2), 43.5 (CH), 32.2 (CH_2), 31.8 (CH_2), 30.5 (CH_2), 29.9 (CH_2), 28.7 (CH_2), 23.4 (CH_2), 23.0 (CH_2), 14.3 (CH_3), 14.3 (CH_3) ppm; IR (thin film): $\nu_{\text{max}} = 3084, 3025, 2956, 2927, 2857, 1601\text{ cm}^{-1}$; LRMS (EI^+): m/z (%): 270($[\text{M}]^+$, 52), 213 ($[\text{M}-\text{C}_4\text{H}_9]^+$, 35), 129 (100); HRMS (EI^+): calculated for $\text{C}_{20}\text{H}_{30}$: 270.2348; found: 270.2347.

Minor isomer **6E**. $R_f = 0.77$ (100% PS 40–60); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.35 – 7.06 (m, 5H), 6.61 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.61 (t, $J = 7.4$ Hz, 1H), 5.19 (d, $J = 17.6$ Hz, 1H), 5.00 (d, $J = 11.2$ Hz, 1H), 3.59 (t, $J = 7.5$ Hz, 1H), 2.25 (q, $J = 7.4$ Hz, 2H), 1.91 – 1.62 (m, 2H), 1.50 – 1.39 (m, 2H), 1.39 – 1.14 (m, 8H), 1.03 – 0.78 (m, 6H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 145.9 (Cq), 139.1 (Cq), 133.8 (CH), 130.9 (CH), 128.4 (2 \times CH), 128.2 (2 \times CH), 126.1 (CH), 113.9 (CH_2), 47.5 (CH), 35.3 (CH_2), 32.0 (CH_2), 30.6 (CH_2), 30.1 (CH_2), 28.0 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 14.3 (CH_3), 14.3 (CH_3) ppm; IR (thin film): $\nu_{\text{max}} = 3086, 3062, 2956, 2927, 2857, 1598\text{ cm}^{-1}$; LRMS (EI^+): m/z (%): 270($[\text{M}]^+$, 94), 213 ($[\text{M}-\text{C}_4\text{H}_9]^+$, 78), 143 (100); HRMS (EI^+): calculated for $\text{C}_{20}\text{H}_{30}$: 270.2348; found: 270.2348.

X-Ray Crystallography

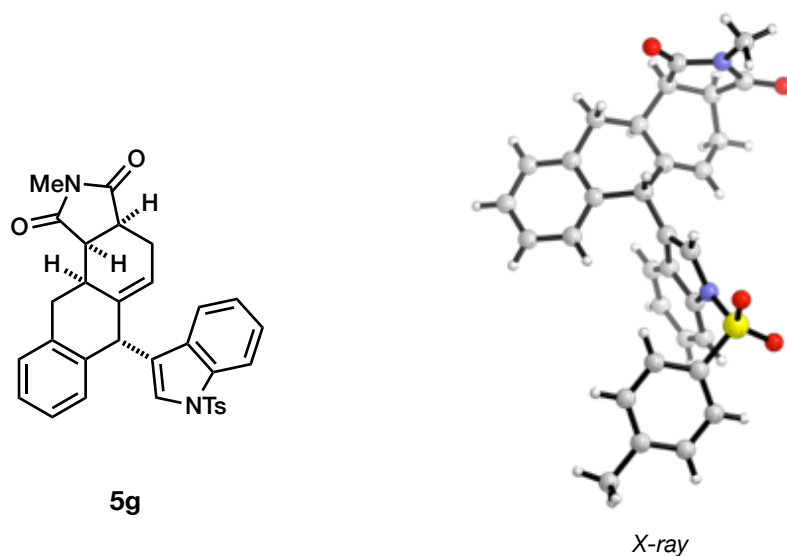
Single crystal X-ray data for compounds were collected on a Supernova diffractometer using Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$ except for compound **9** that used Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$. Data reduction was performed using the CrysAlis PRO package.⁶ Structure solutions for all compounds were determined by ShelXT,⁷ and the structures refined using ShelXL in the OLEX2 program package.^{8,9}

1. Compound 5d



$\text{C}_{24}\text{H}_{23}\text{NO}_3$ ($M = 373.43 \text{ g/mol}$): monoclinic, space group $P2_1/n$ (no. 14), $a = 8.71981(10) \text{ \AA}$, $b = 9.17689(10) \text{ \AA}$, $c = 23.8890(3) \text{ \AA}$, $\beta = 93.4208(11)^\circ$, $V = 1908.21(4) \text{ \AA}^3$, $Z = 4$, $T = 150.00(10) \text{ K}$, $\mu(\text{CuK}\alpha) = 0.683 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.300 \text{ g/cm}^3$, 37421 reflections measured ($7.4144^\circ \leq 2\theta \leq 147.597^\circ$), 3868 unique ($R_{\text{int}} = 0.0396$) which were used in all calculations. The final R_1 was 0.0355 ($I > 2\sigma(I)$) and wR_2 was 0.0934 (all data). CCDC 1922955.

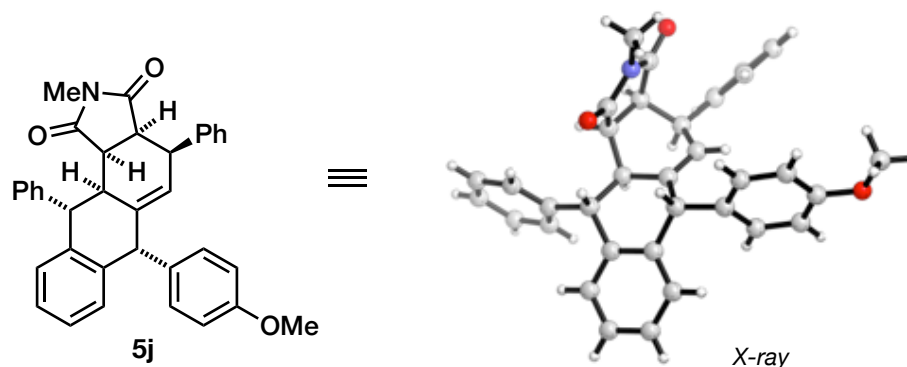
2. Compound 5g



$\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_4\text{S}$ ($M = 536.62 \text{ g/mol}$): monoclinic, space group $C2/c$ (no. 15), $a = 10.6976(2) \text{ \AA}$, $b = 24.7999(3) \text{ \AA}$, $c = 21.9739(4) \text{ \AA}$, $\beta = 103.752(2)^\circ$, $V = 5662.55(17) \text{ \AA}^3$, $Z = 8$, $T = 149.99(10) \text{ K}$,

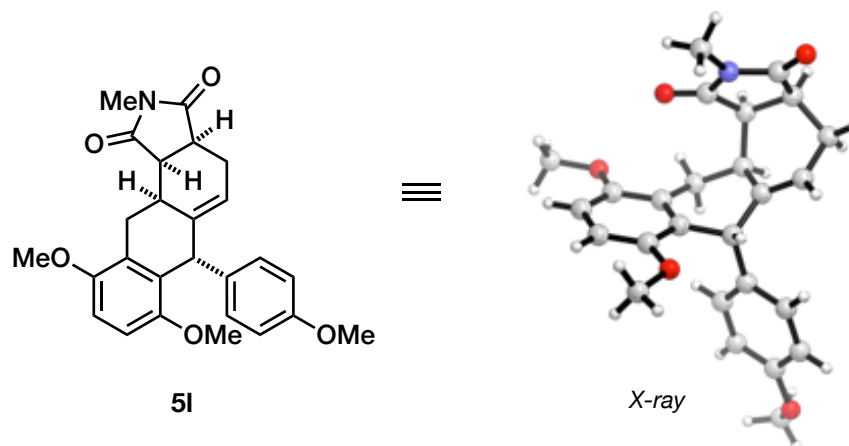
$\mu(\text{CuK}\alpha) = 1.332 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.259 \text{ g/cm}^3$, 19587 reflections measured ($7.128^\circ \leq 2\theta \leq 147.68^\circ$), 5674 unique ($R_{\text{int}} = 0.0290$) which were used in all calculations. The final R_1 was 0.0512 ($I > 2\sigma(I)$) and wR_2 was 0.1397 (all data). CCDC 1922954.

3. Compound 5j



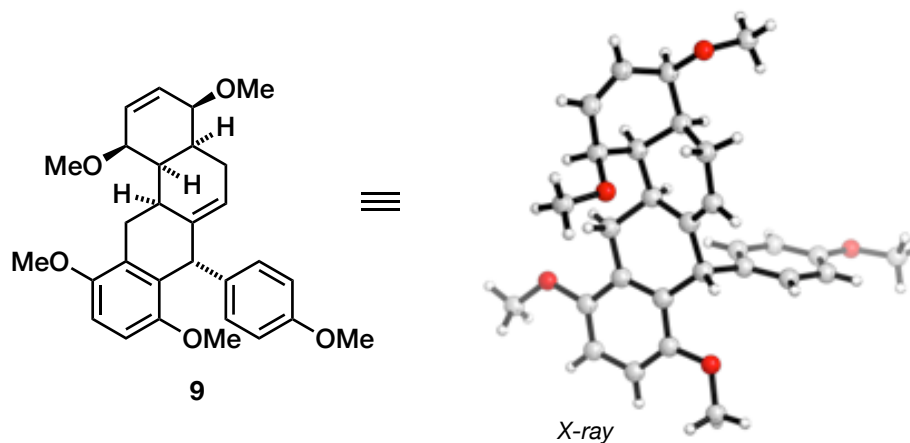
$\text{C}_{36}\text{H}_{31}\text{NO}_3$ ($M = 525.62 \text{ g/mol}$): triclinic, $P-1$ (No. 2), $a = 12.7985(3) \text{ \AA}$, $b = 14.6201(3) \text{ \AA}$, $c = 16.1015(3) \text{ \AA}$, $\alpha = 102.171(2)^\circ$, $\beta = 103.096(2)^\circ$, $\gamma = 102.187(2)^\circ$, $V = 2760.45(11) \text{ \AA}^3$, $T = 150.01(10) \text{ K}$, $Z = 4$, $Z' = 2$, $\mu(\text{CuK}\alpha) = 0.629 \text{ mm}^{-1}$, 60801 reflections measured, 11099 unique ($R_{\text{int}} = 0.0424$) which were used in all calculations. The final wR_2 was 0.1065 (all data) and R_1 was 0.0399 ($I > 2\sigma(I)$). CCDC 1922951.

4. Compound 5l



$\text{C}_{26}\text{H}_{27}\text{NO}_5$ ($M = 433.48 \text{ g/mol}$): triclinic, space group $P-1$ (no. 2), $a = 6.1902(3) \text{ \AA}$, $b = 12.4868(6) \text{ \AA}$, $c = 14.2390(5) \text{ \AA}$, $\alpha = 89.146(4)^\circ$, $\beta = 80.837(4)^\circ$, $\gamma = 78.564(4)^\circ$, $V = 1064.84(8) \text{ \AA}^3$, $Z = 2$, $T = 150.01(10) \text{ K}$, $\mu(\text{CuK}\alpha) = 0.760 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.352 \text{ g/cm}^3$, 7316 reflections measured ($7.224^\circ \leq 2\theta \leq 147.214^\circ$), 4208 unique ($R_{\text{int}} = 0.0304$) which were used in all calculations. The final R_1 was 0.0513 ($I > 2\sigma(I)$) and wR_2 was 0.1442 (all data). CCDC 1922953.

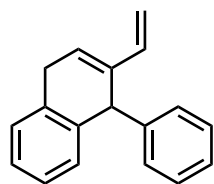
5. Compound 9



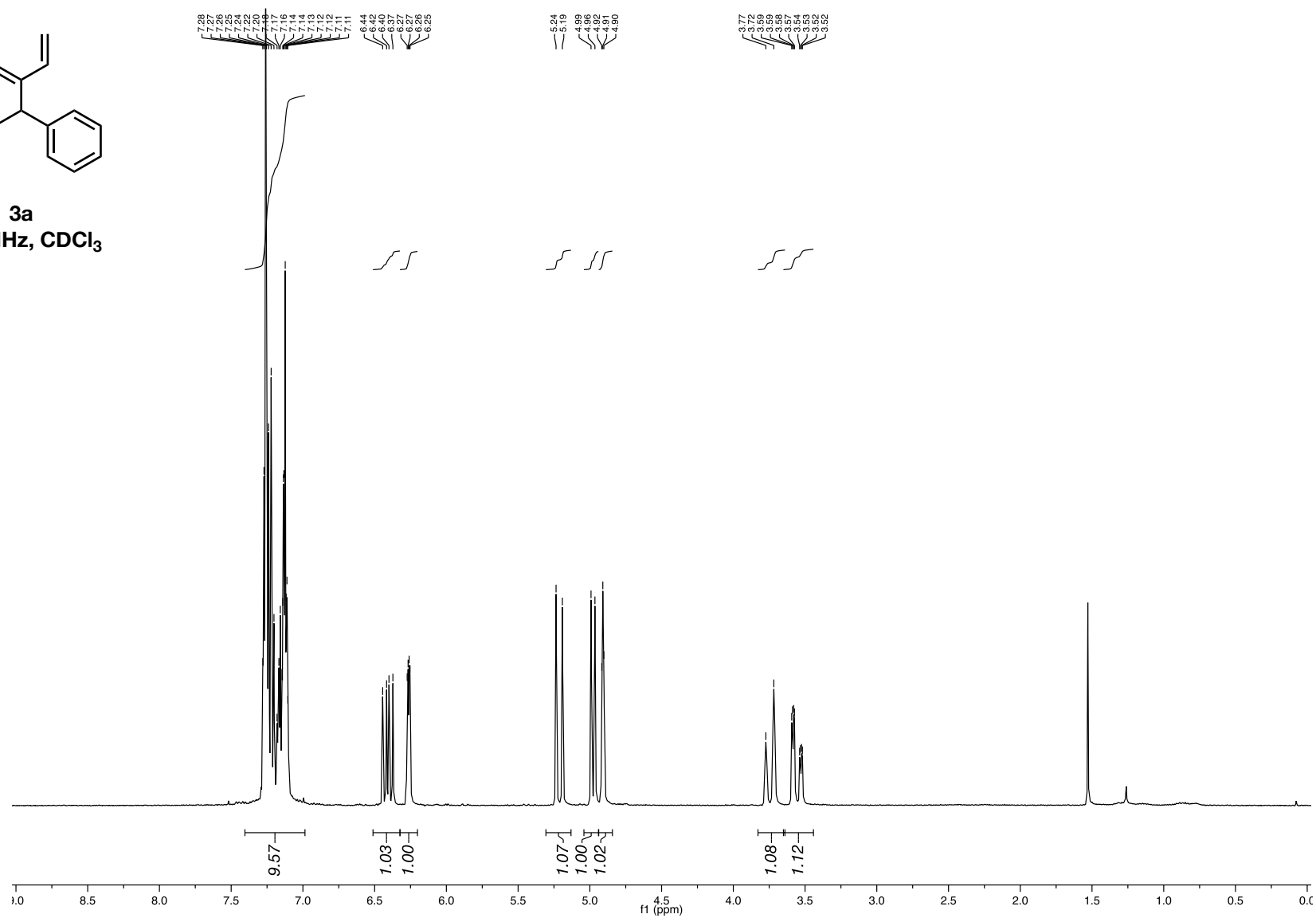
$C_{29}H_{34}O_5$ ($M = 462.56$): triclinic, $P-1$ (No. 2), $a = 8.4029(5) \text{ \AA}$, $b = 12.8926(10) \text{ \AA}$, $c = 12.9902(8) \text{ \AA}$, $\alpha = 63.249(7)^\circ$, $\beta = 88.299(5)^\circ$, $\gamma = 75.429(6)^\circ$, $V = 1210.56(16) \text{ \AA}^3$, $T = 150.00(10) \text{ K}$, $Z = 2$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 0.085 \text{ mm}^{-1}$, 26071 reflections measured, 5886 unique ($R_{\text{int}} = 0.0329$) which were used in all calculations. The final wR_2 was 0.1323 (all data) and R_1 was 0.0525 ($I > 2\sigma(I)$). CCDC 1922952.

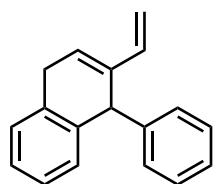
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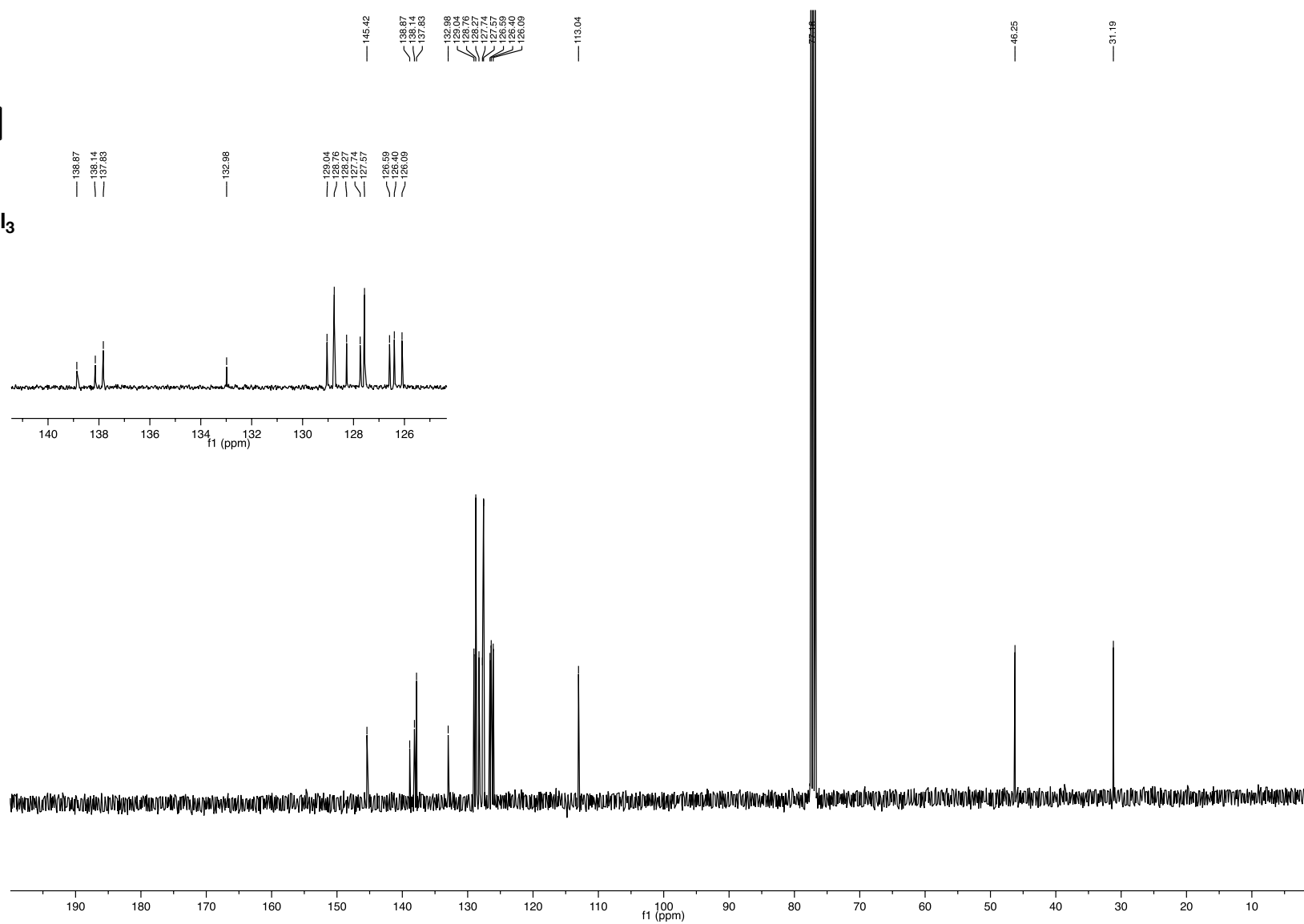


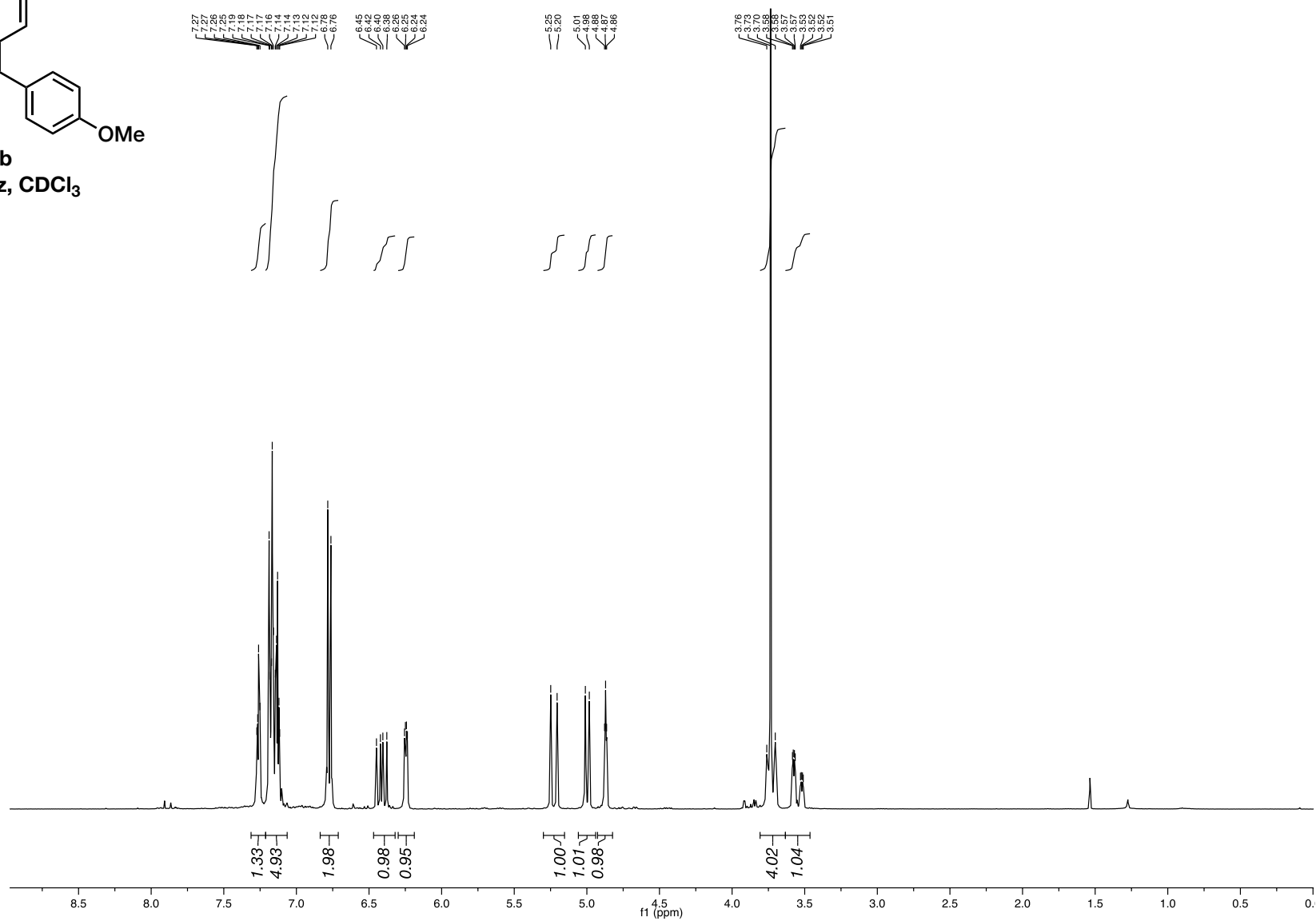
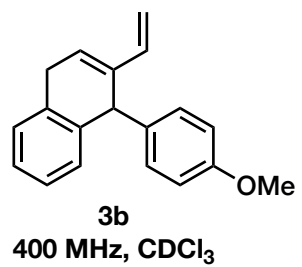
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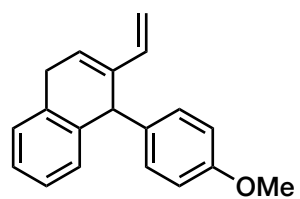




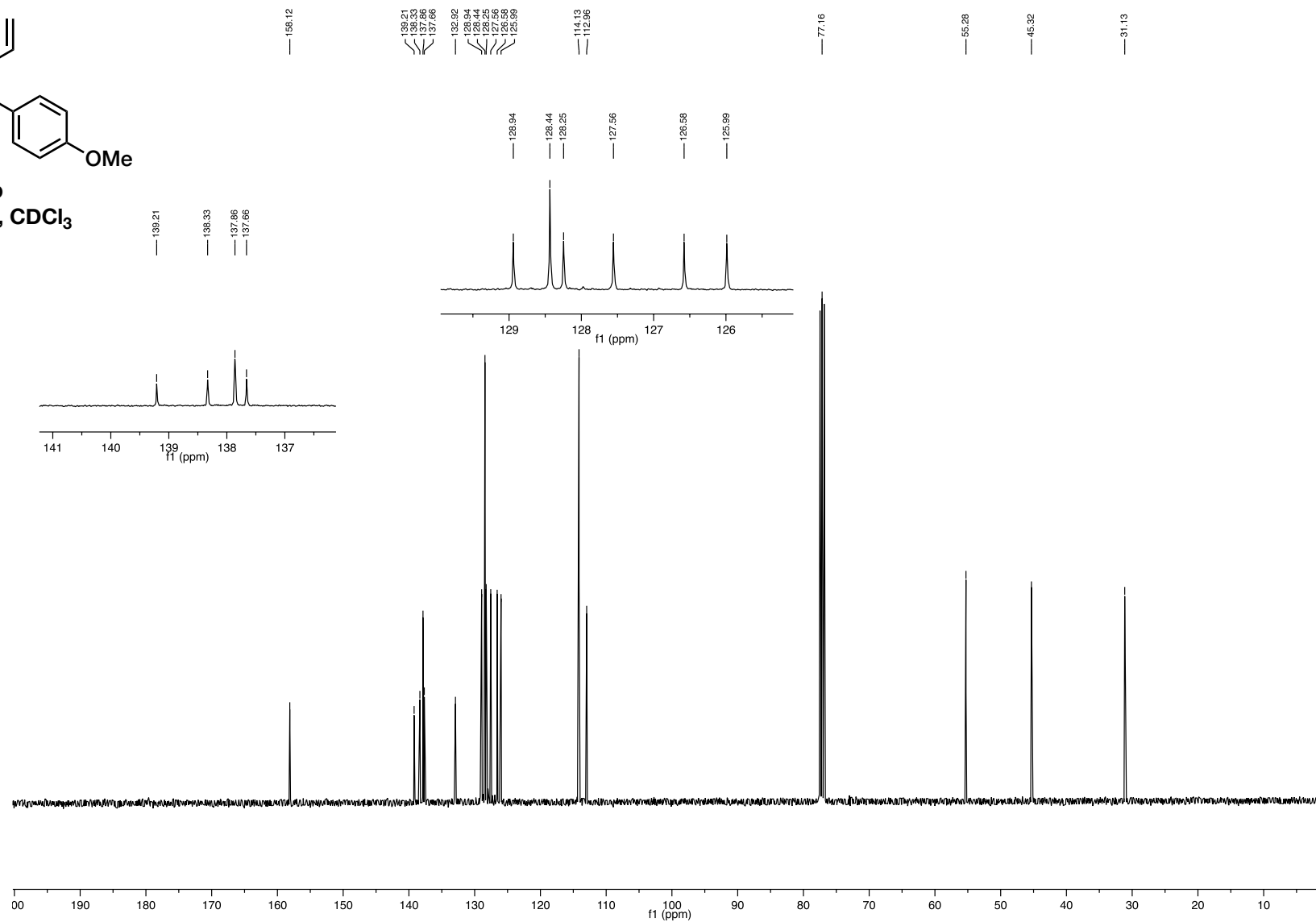
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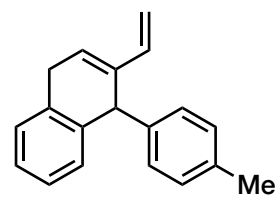




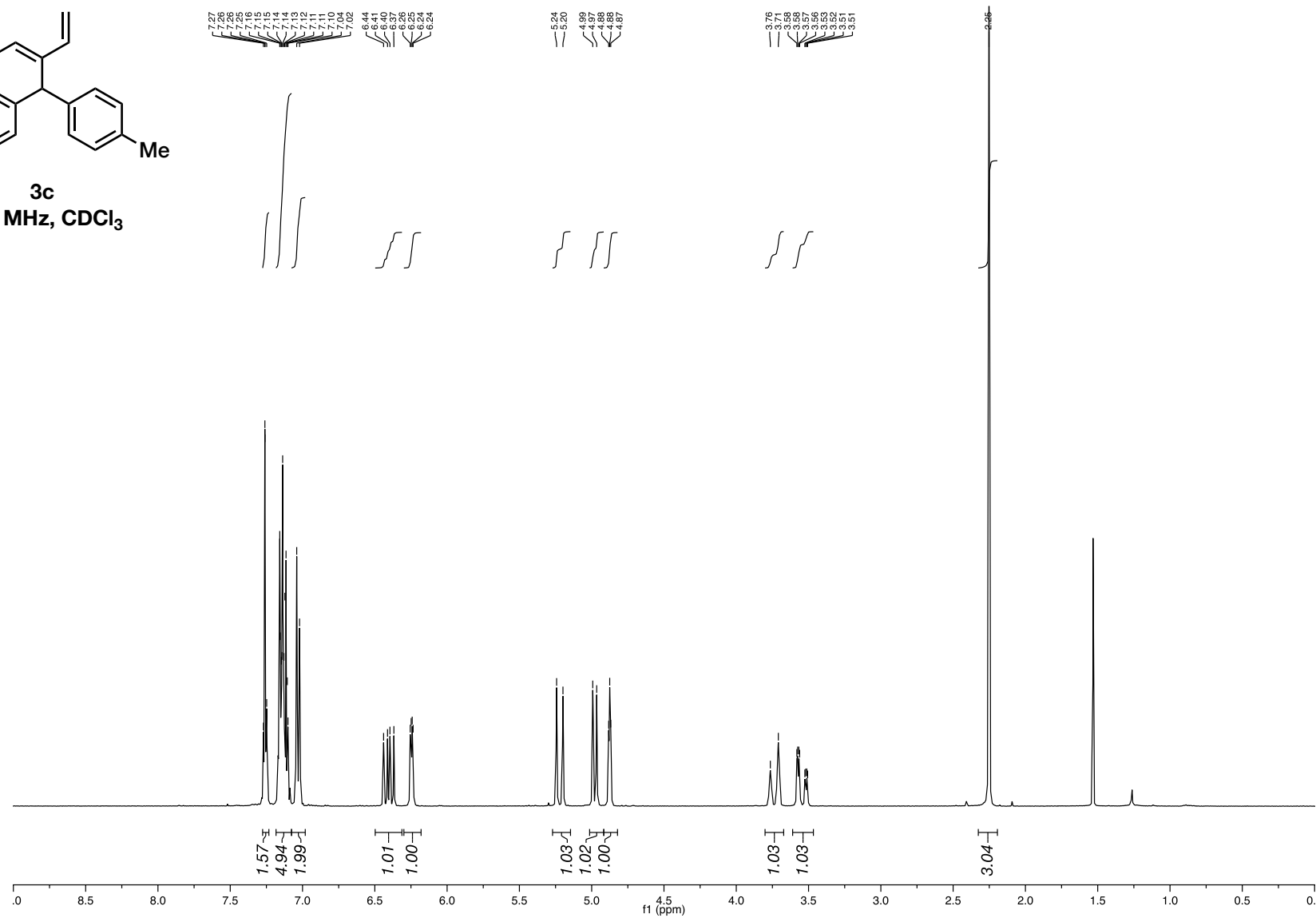


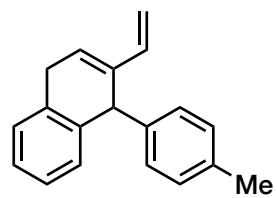
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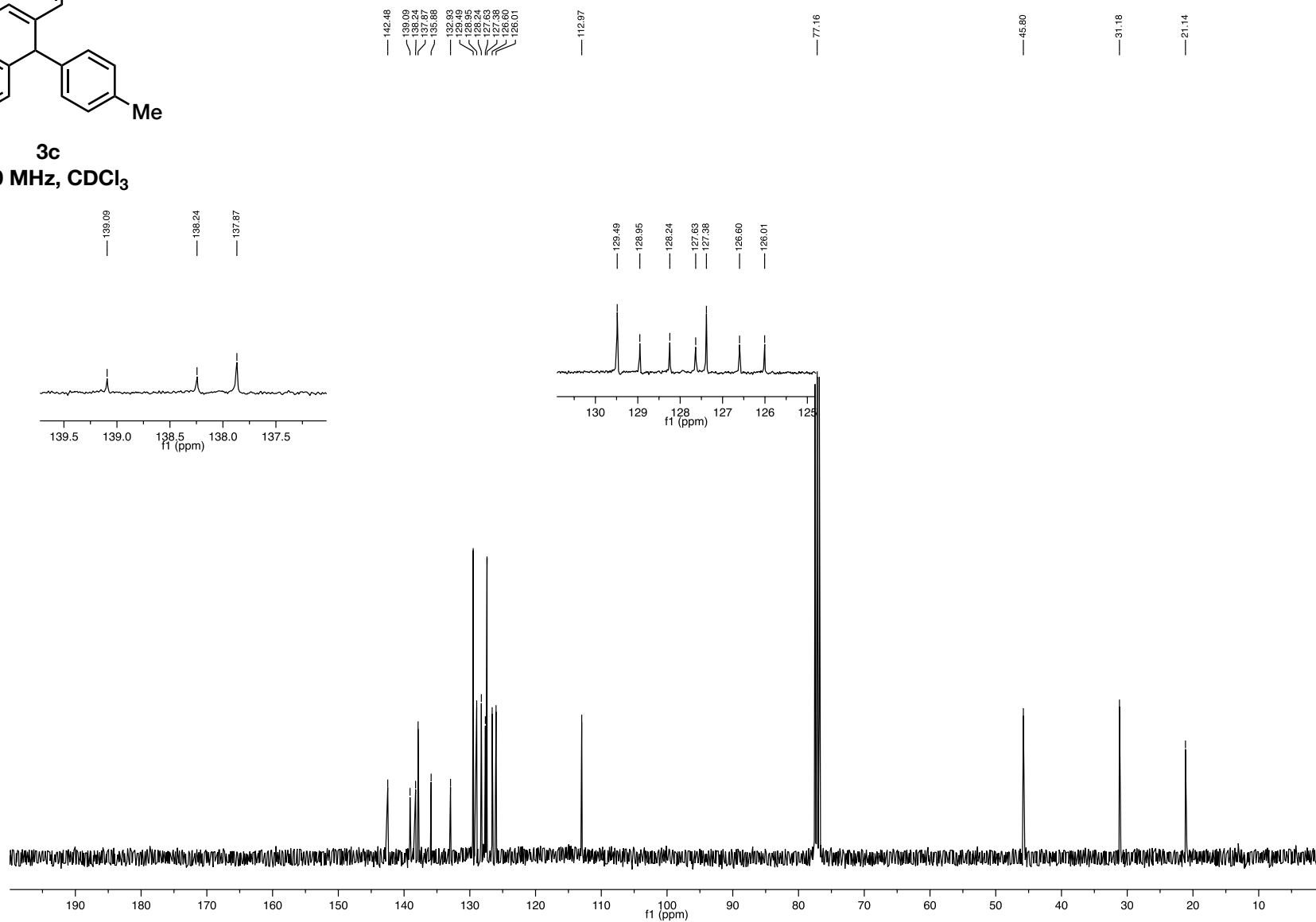


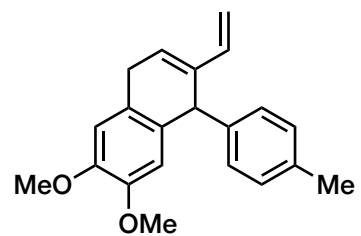
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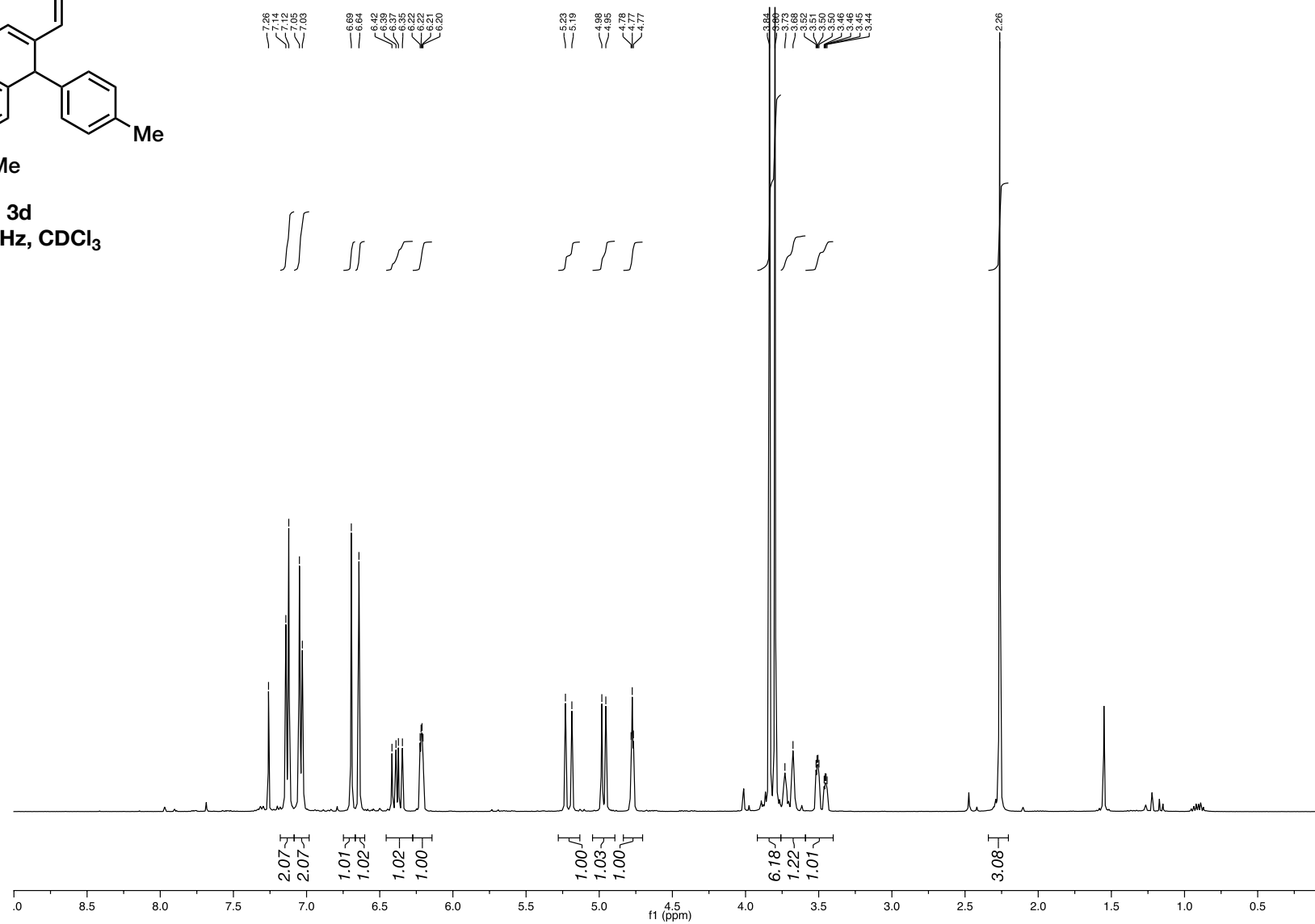


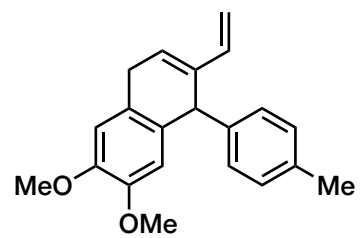
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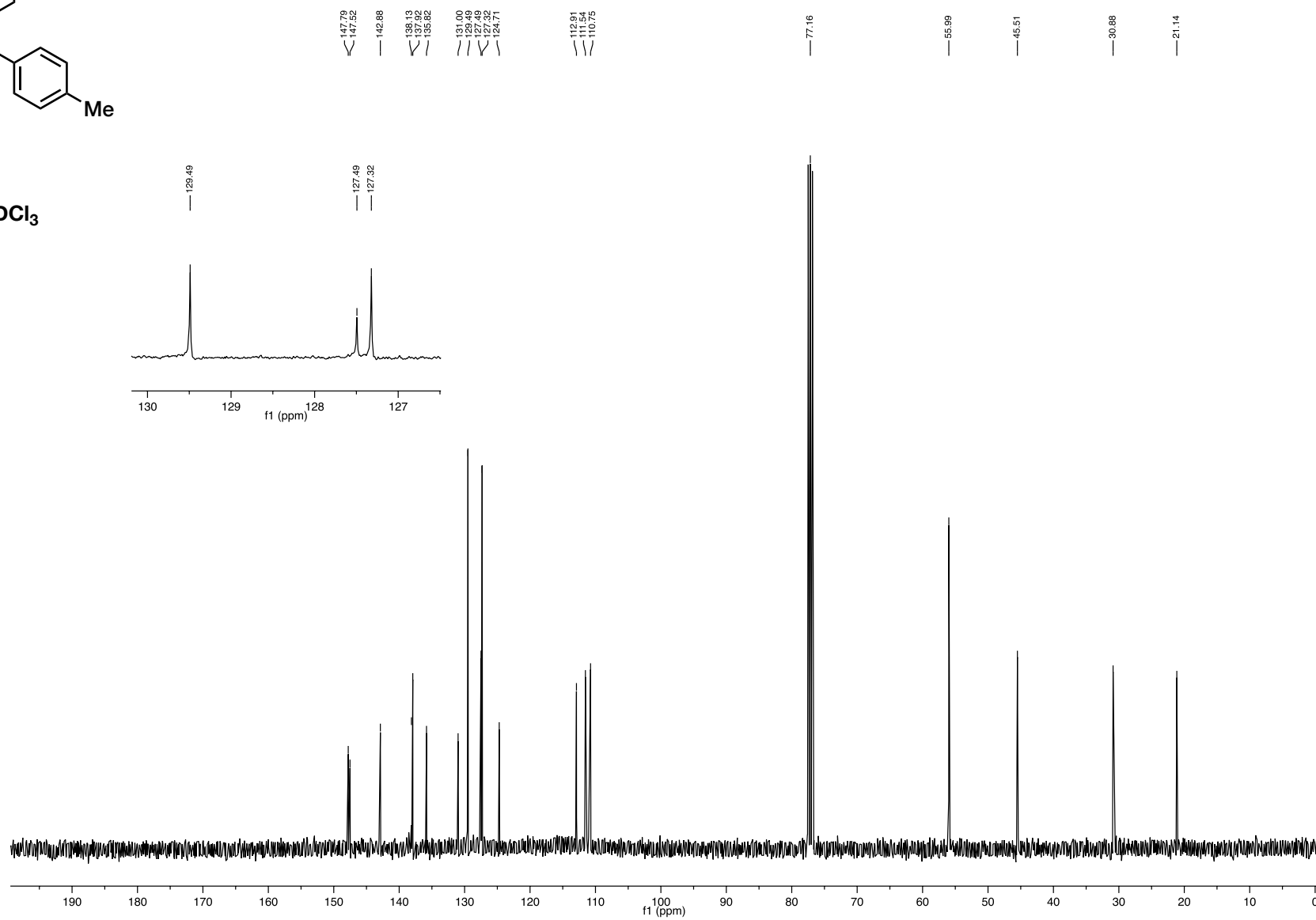


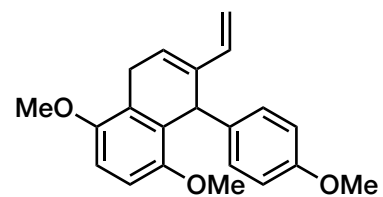
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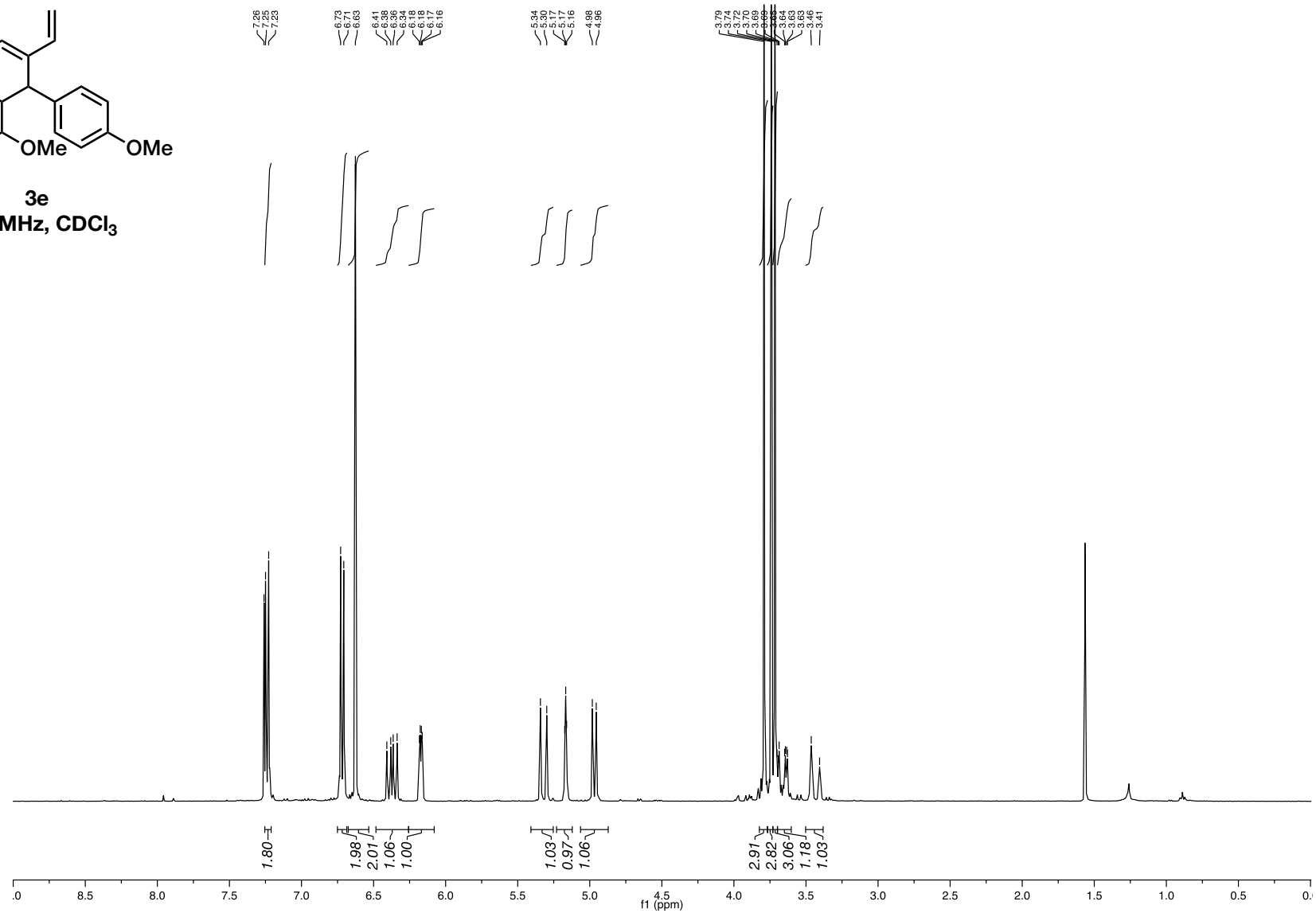


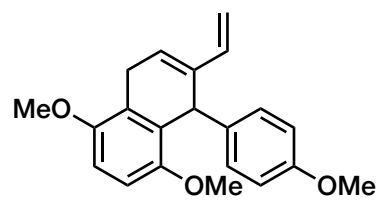
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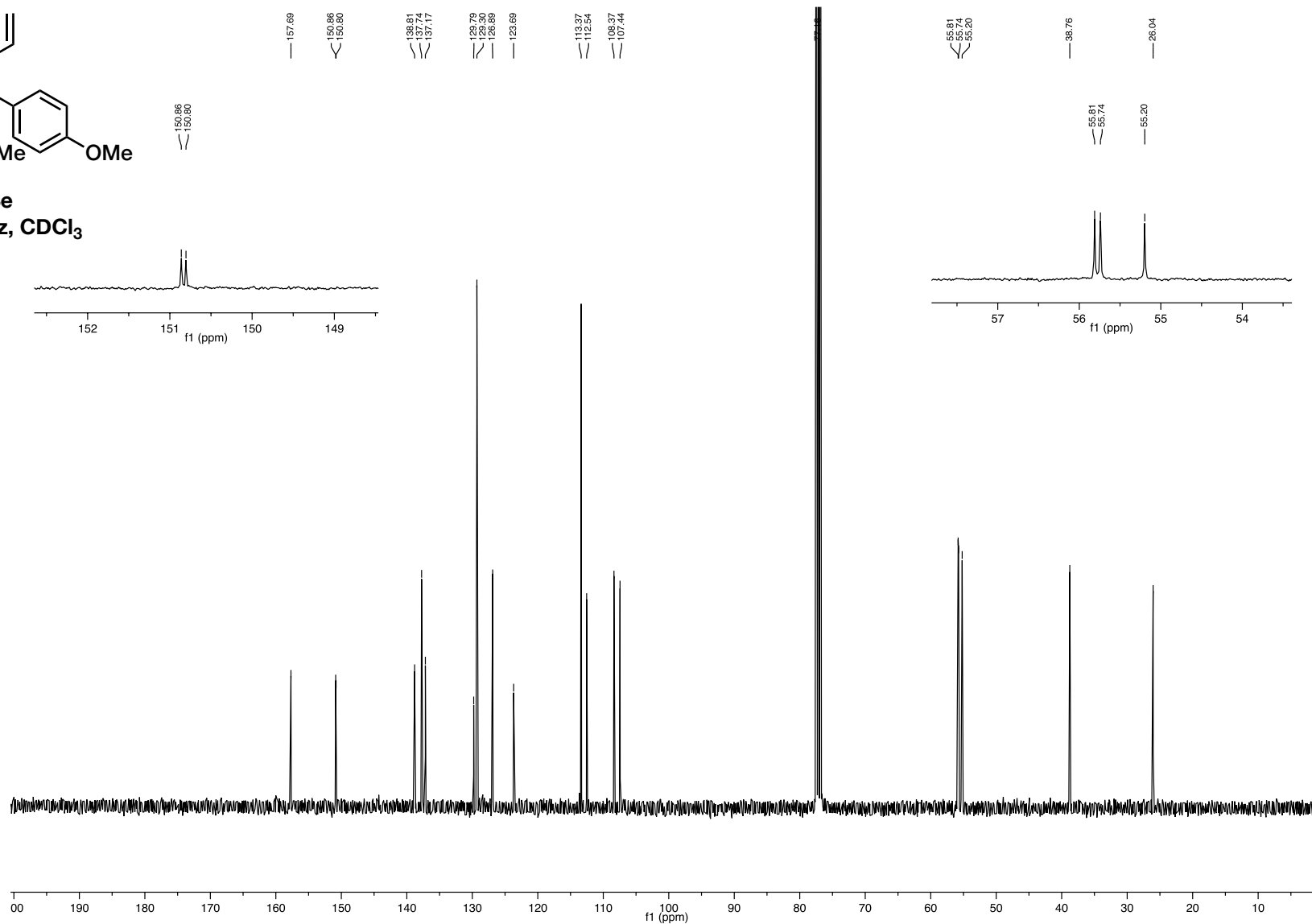


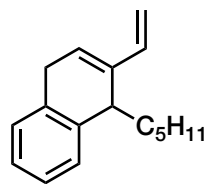
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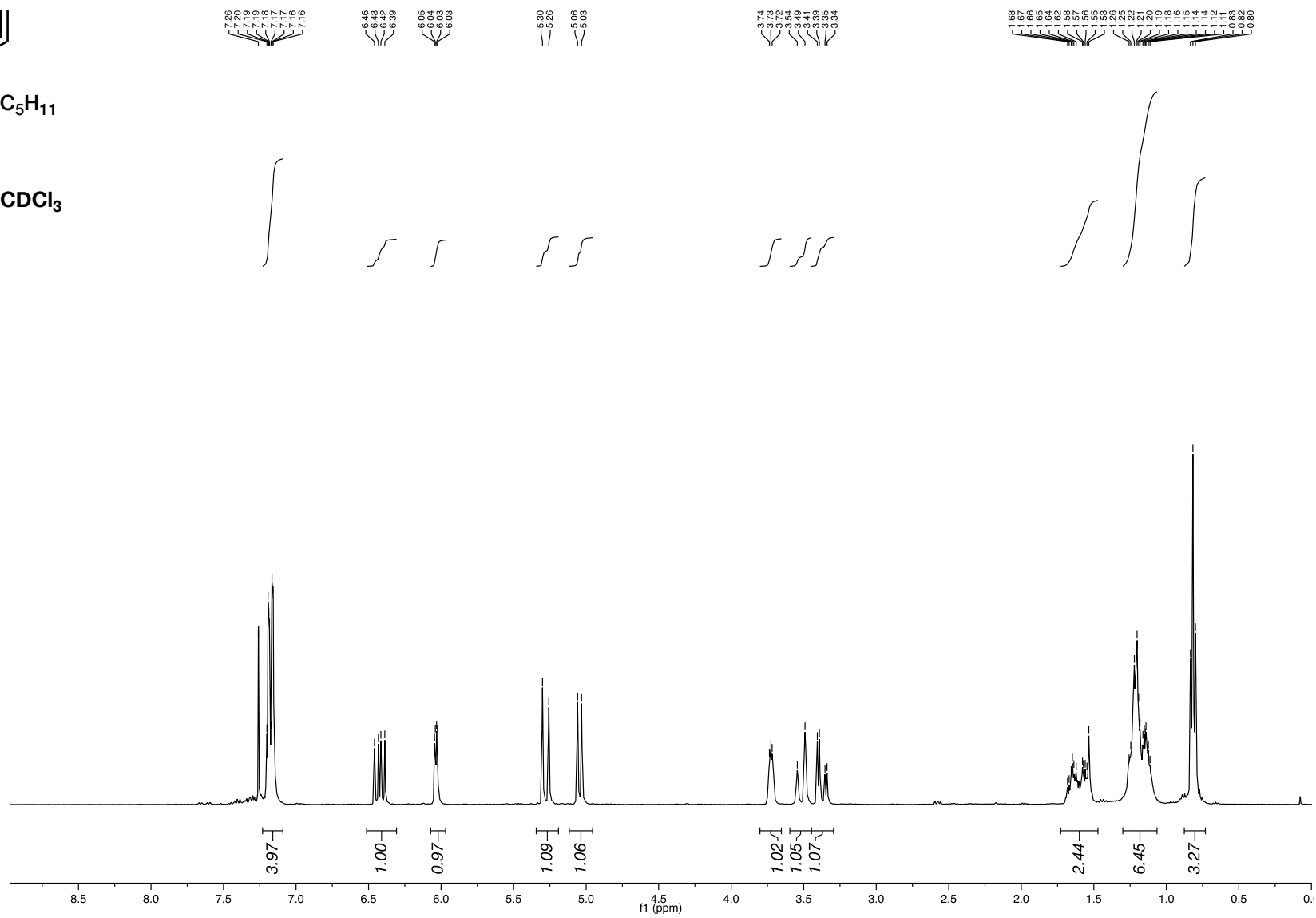


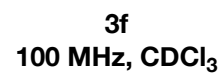
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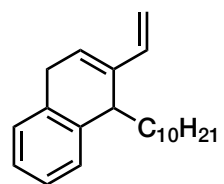




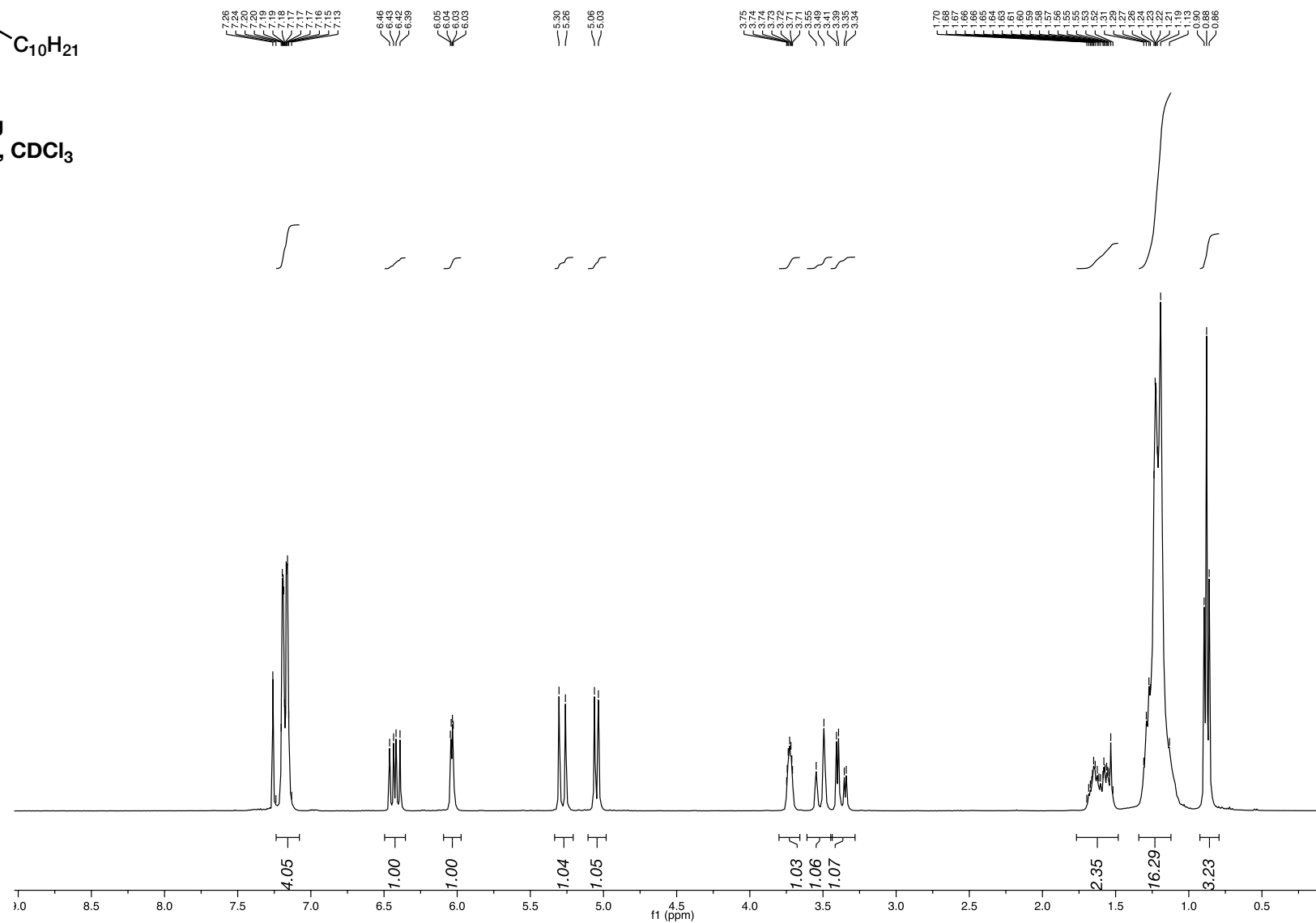
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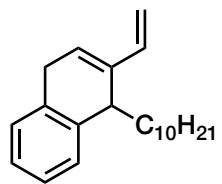




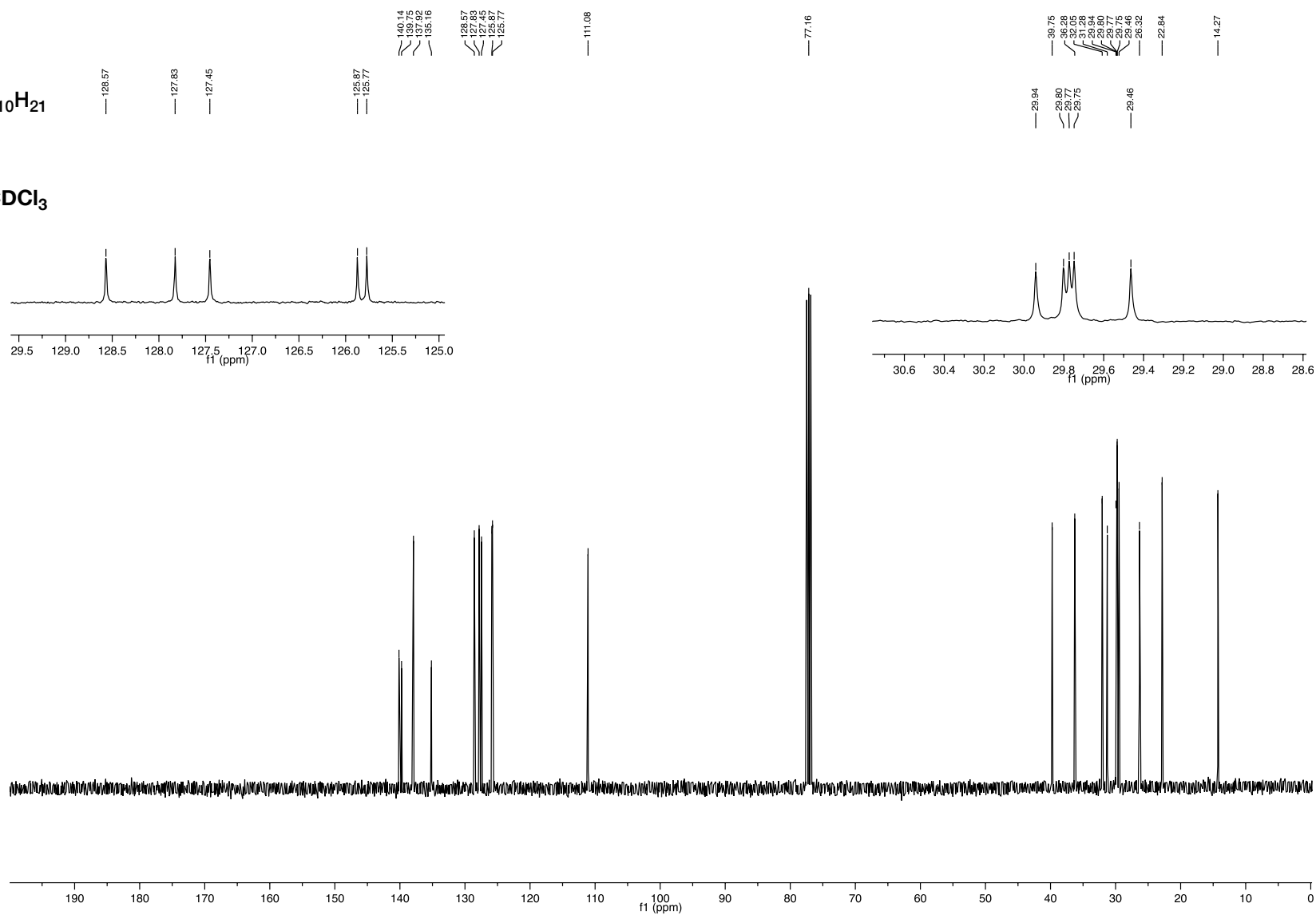


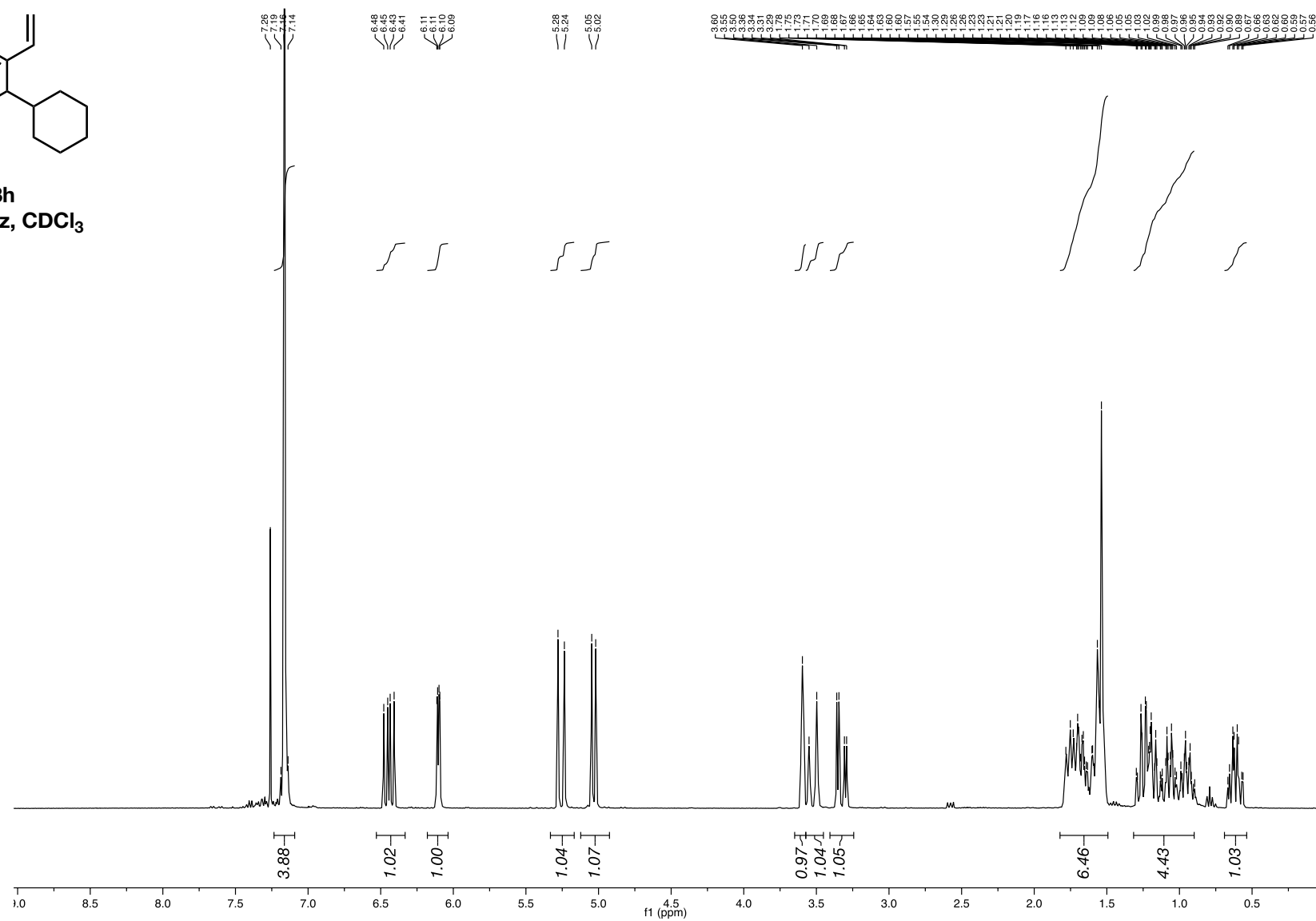
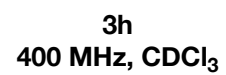
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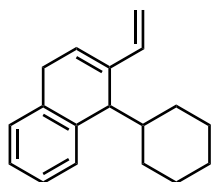




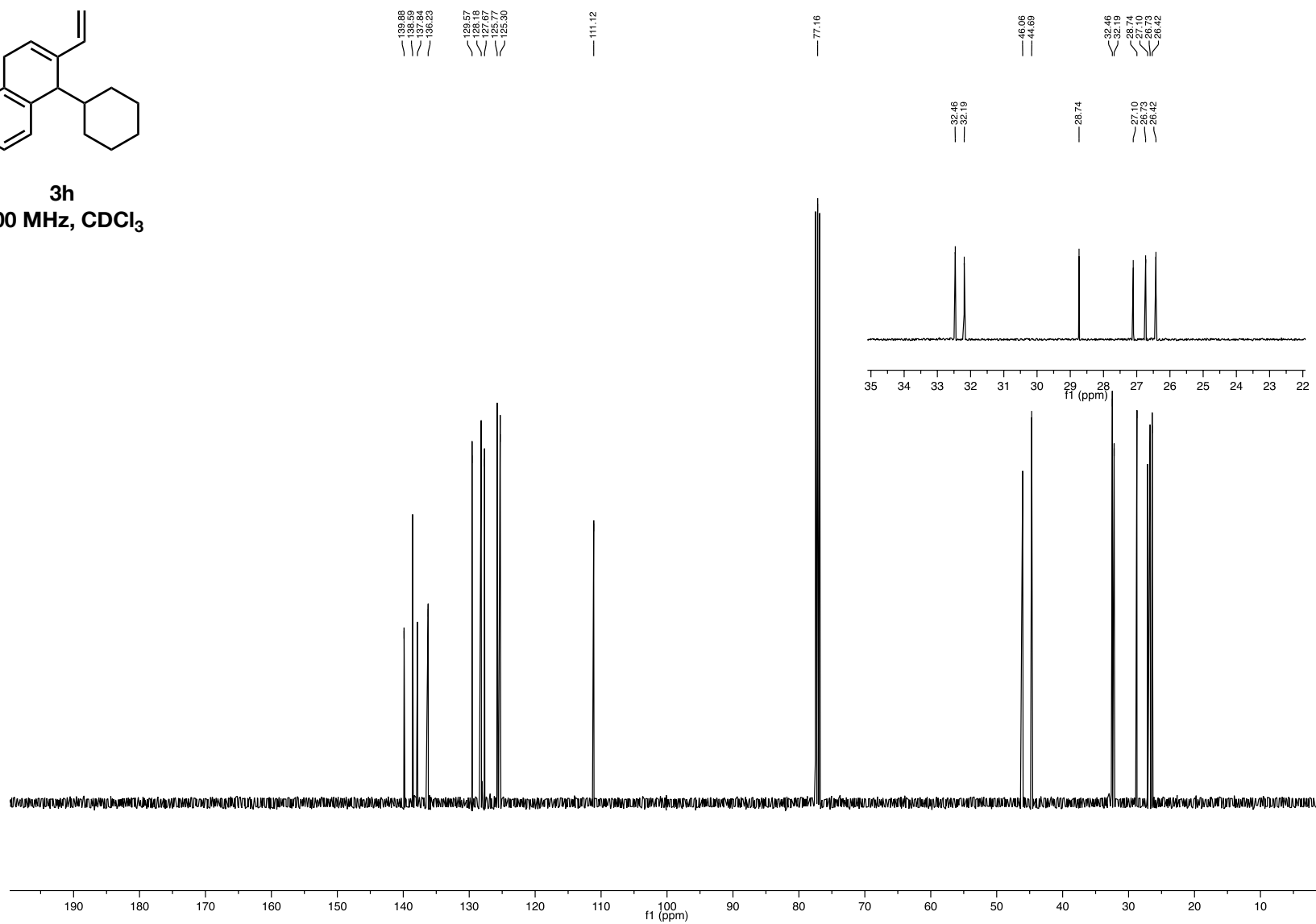
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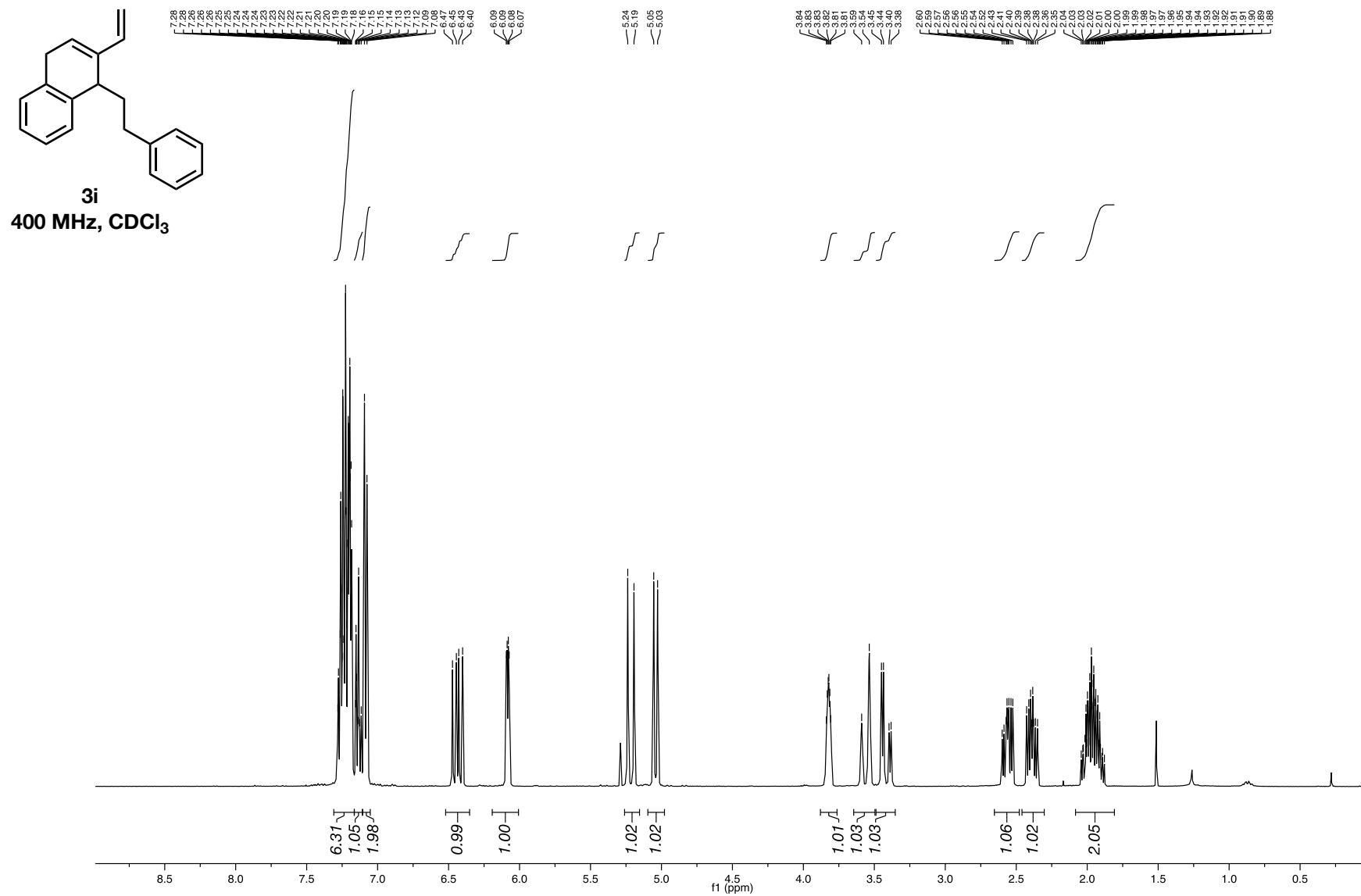


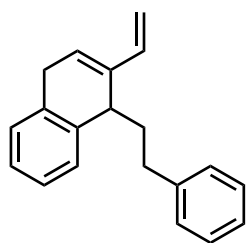




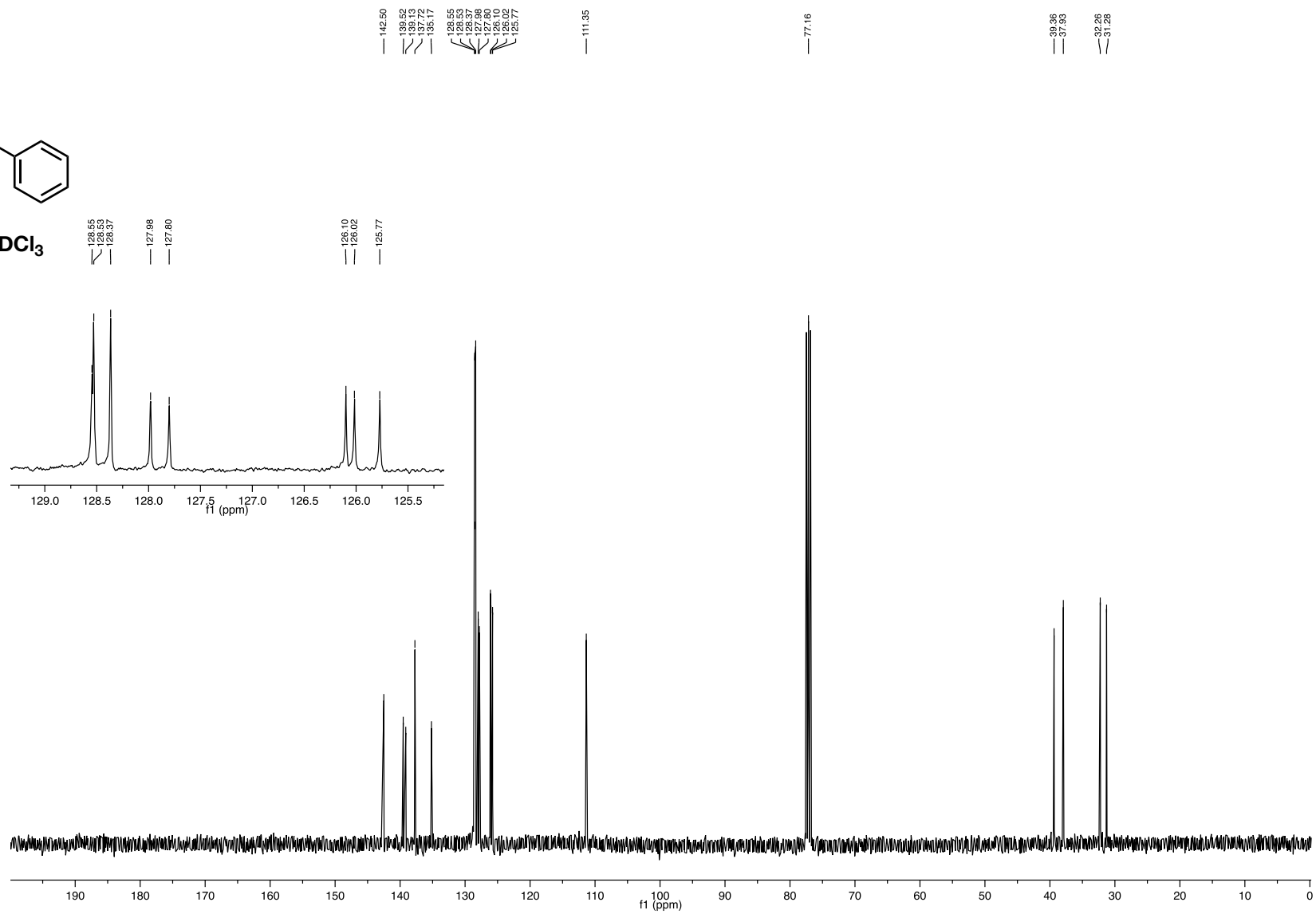
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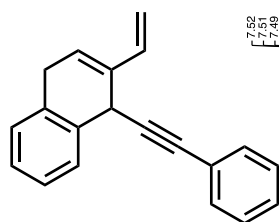




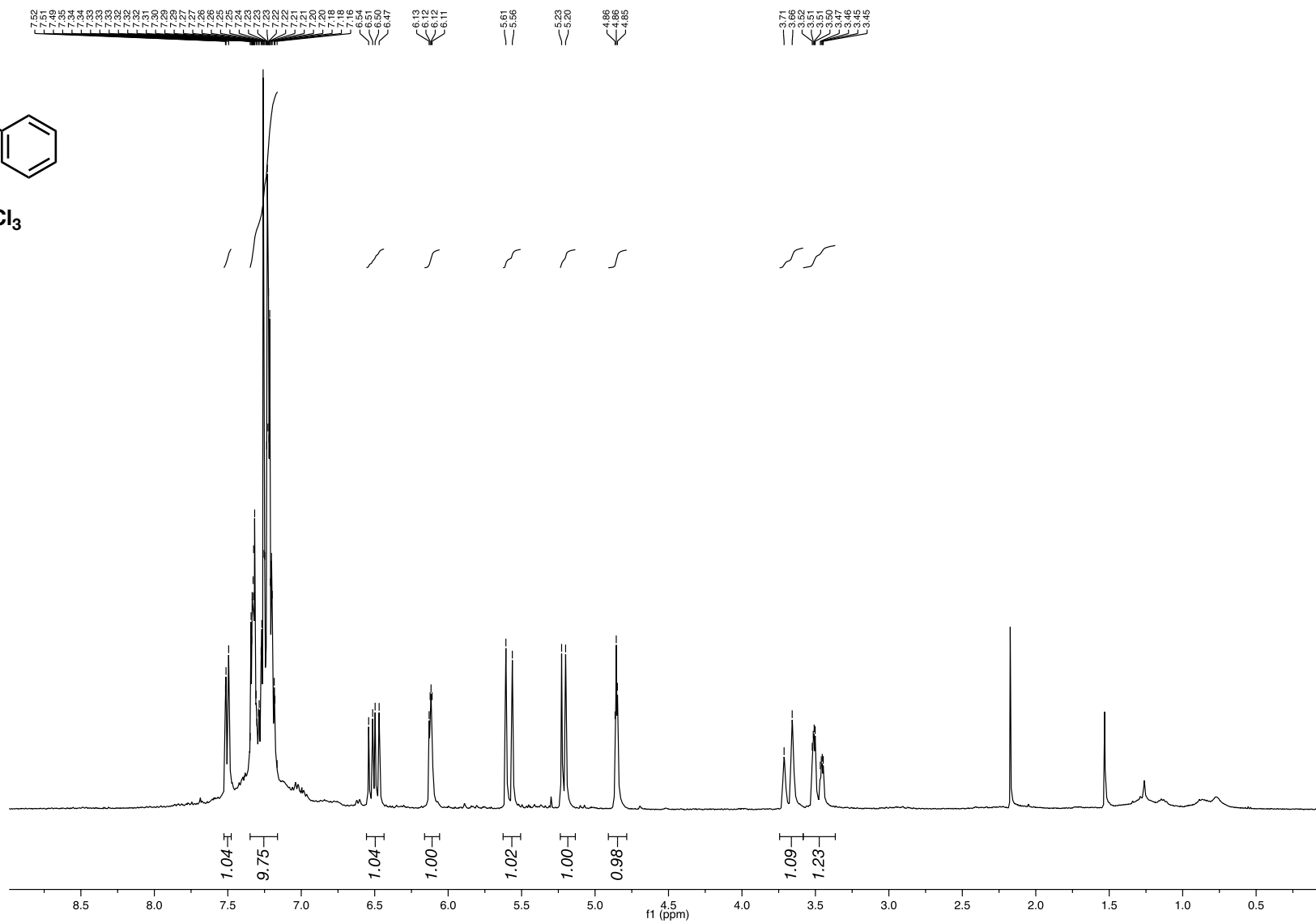


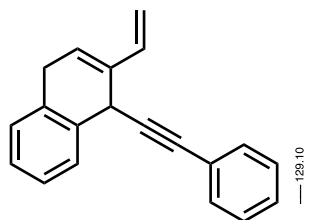
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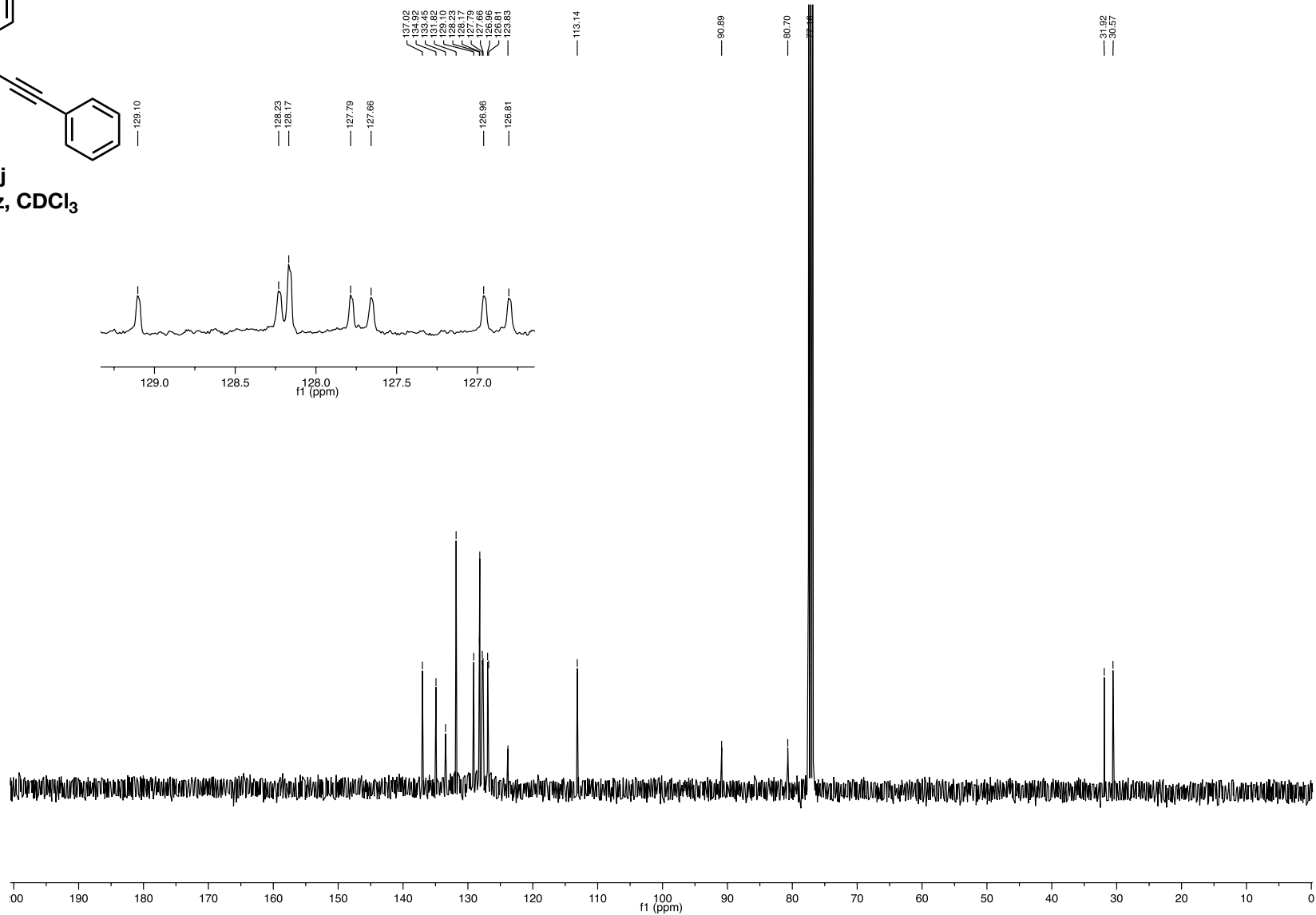


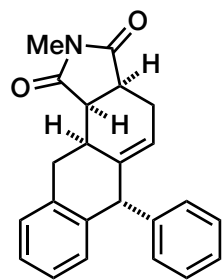
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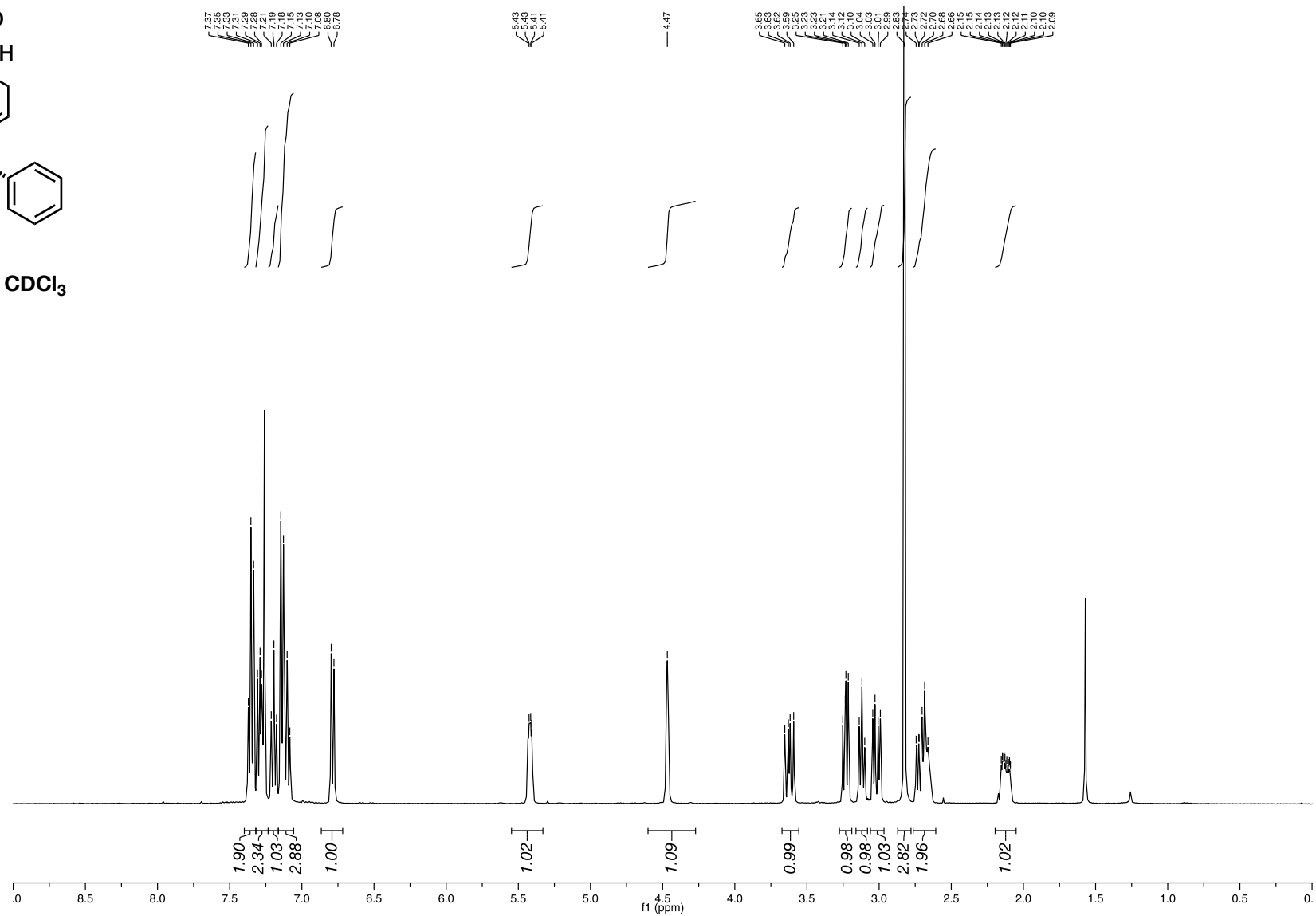


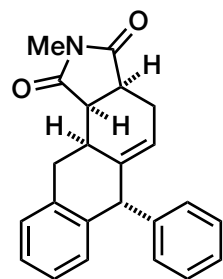
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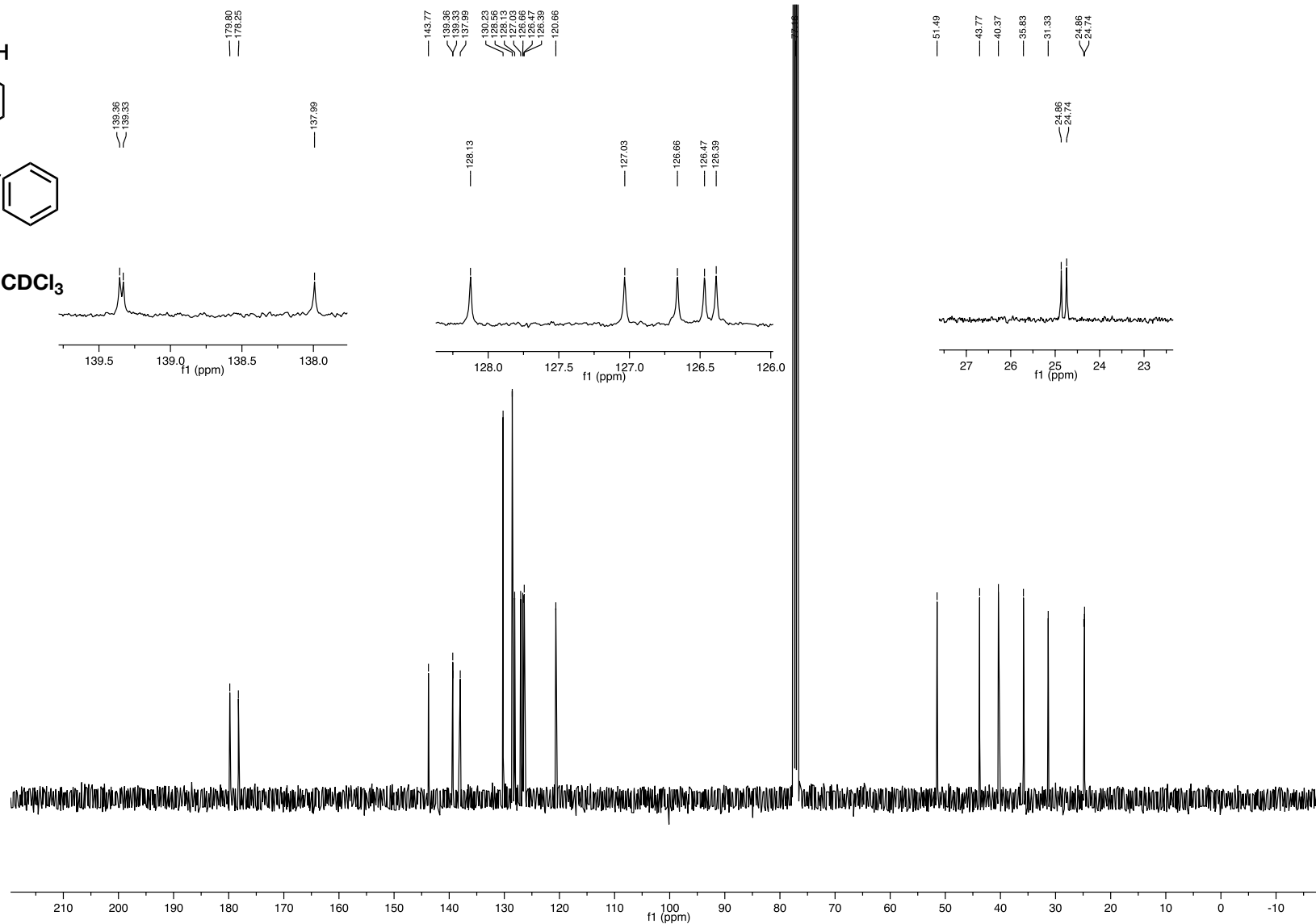


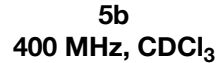
5a
400 MHz, CDCl₃

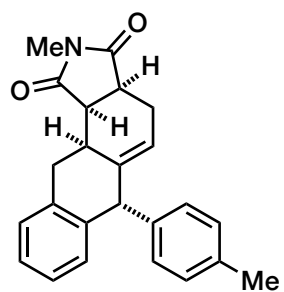




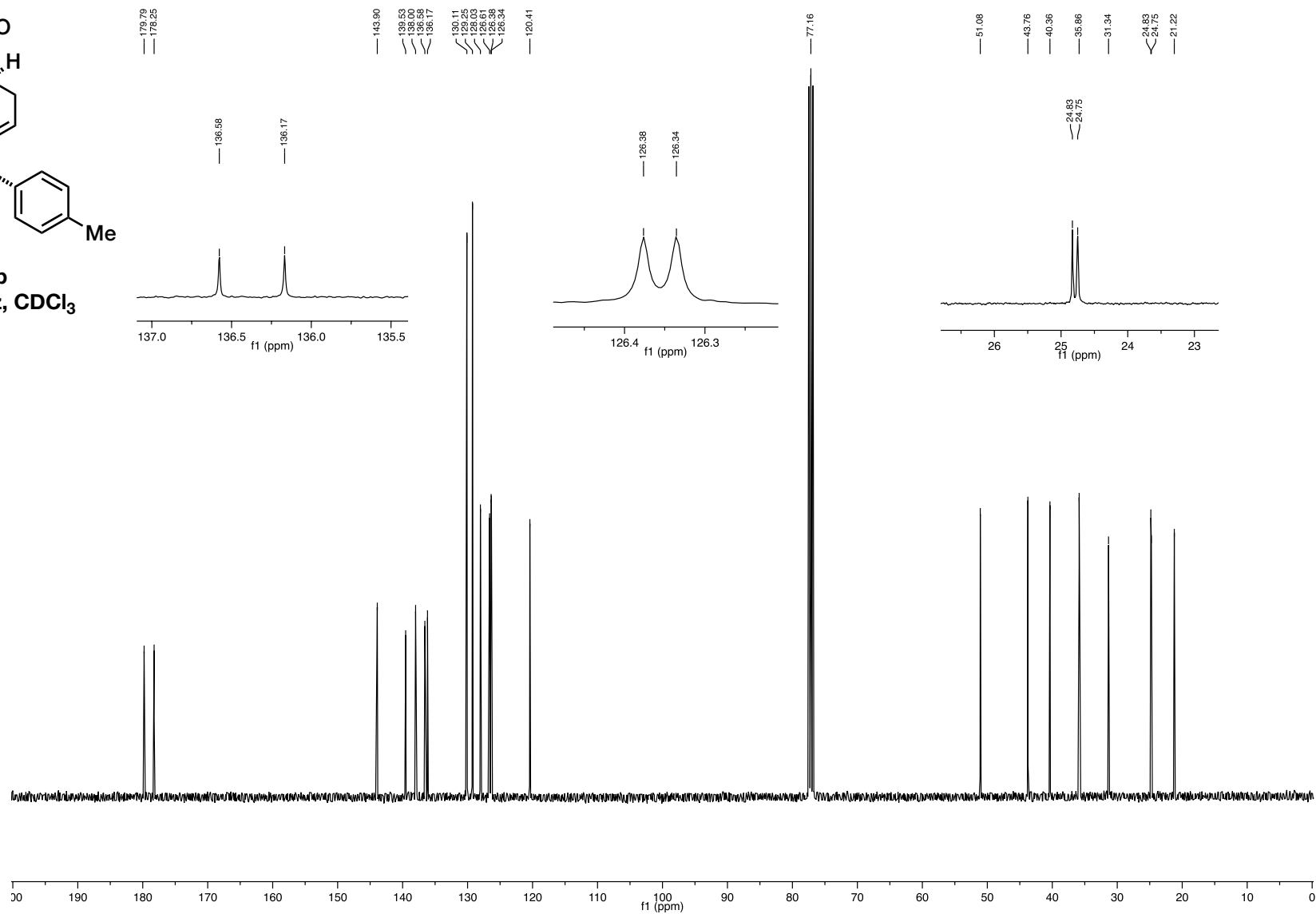
5a
100 MHz, CDCl₃

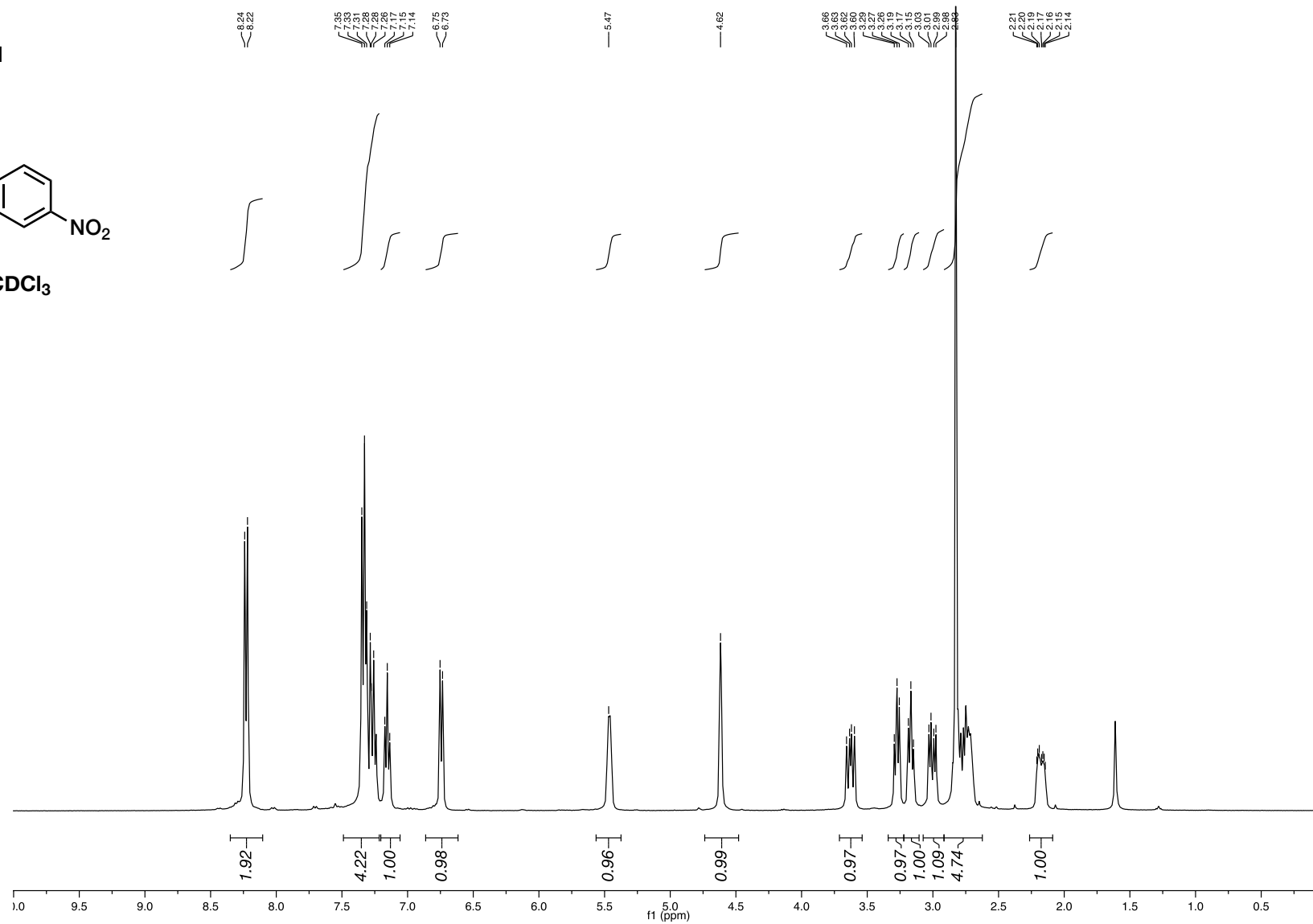
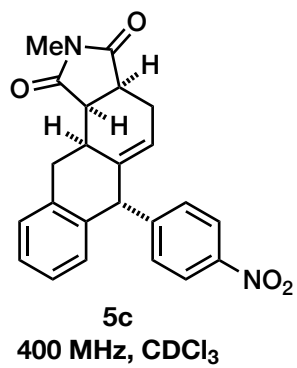


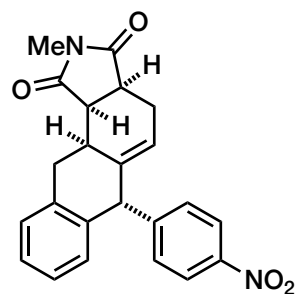




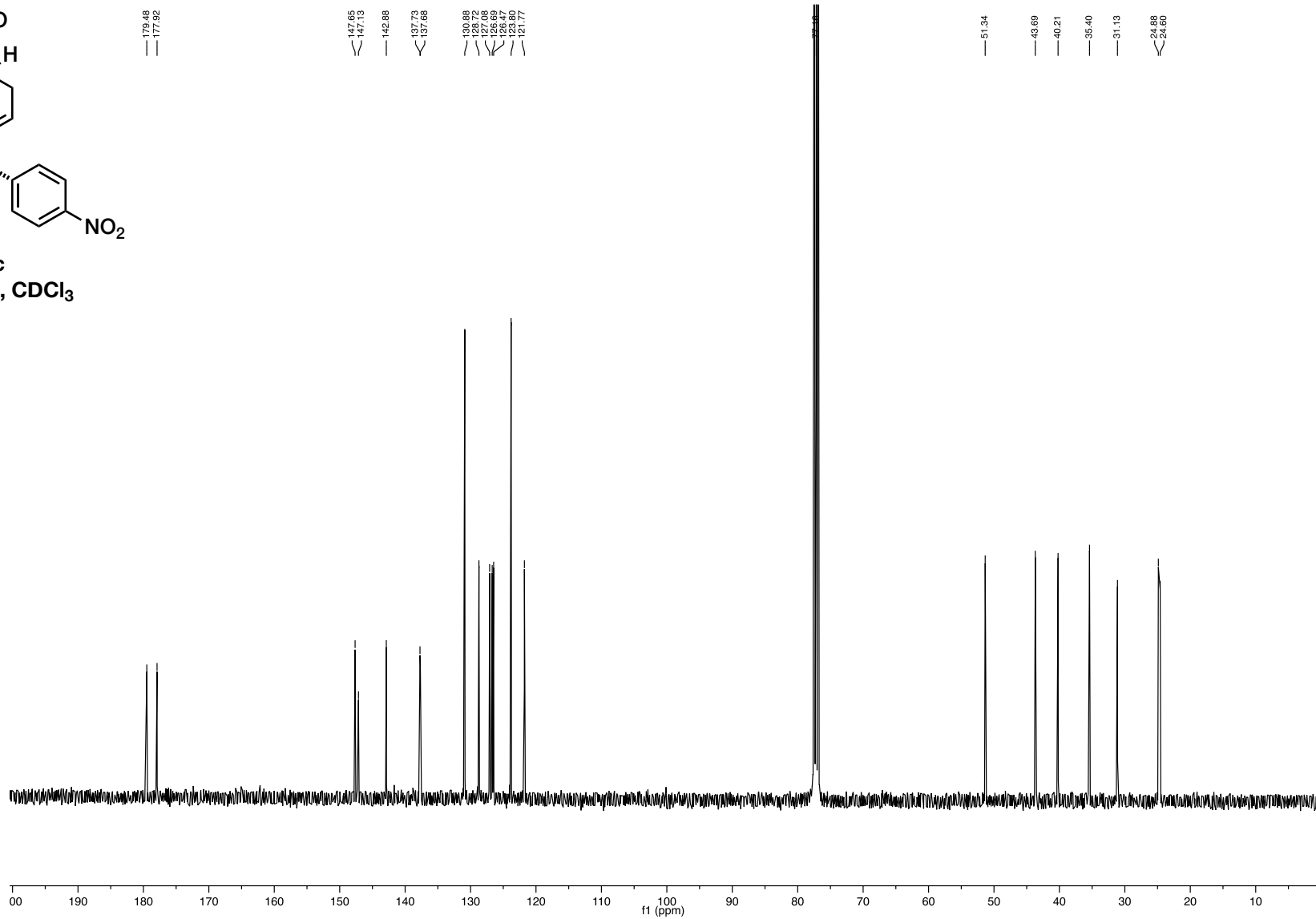
5b
100 MHz, CDCl₃

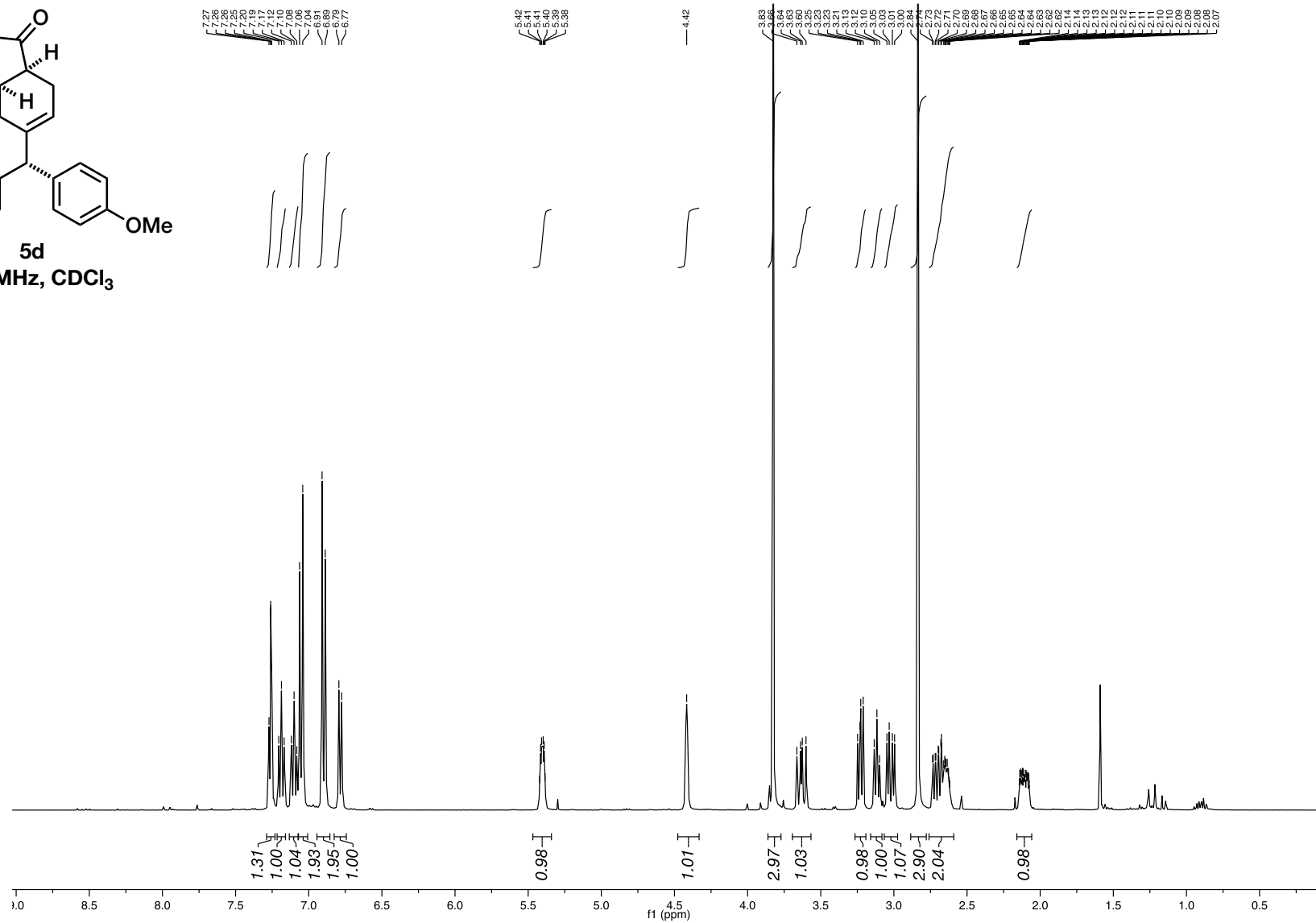
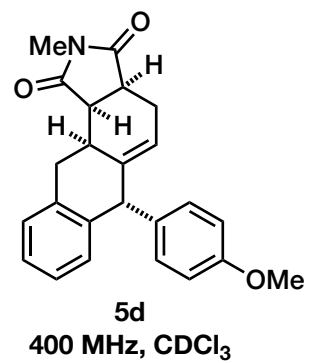


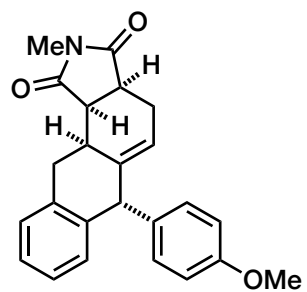




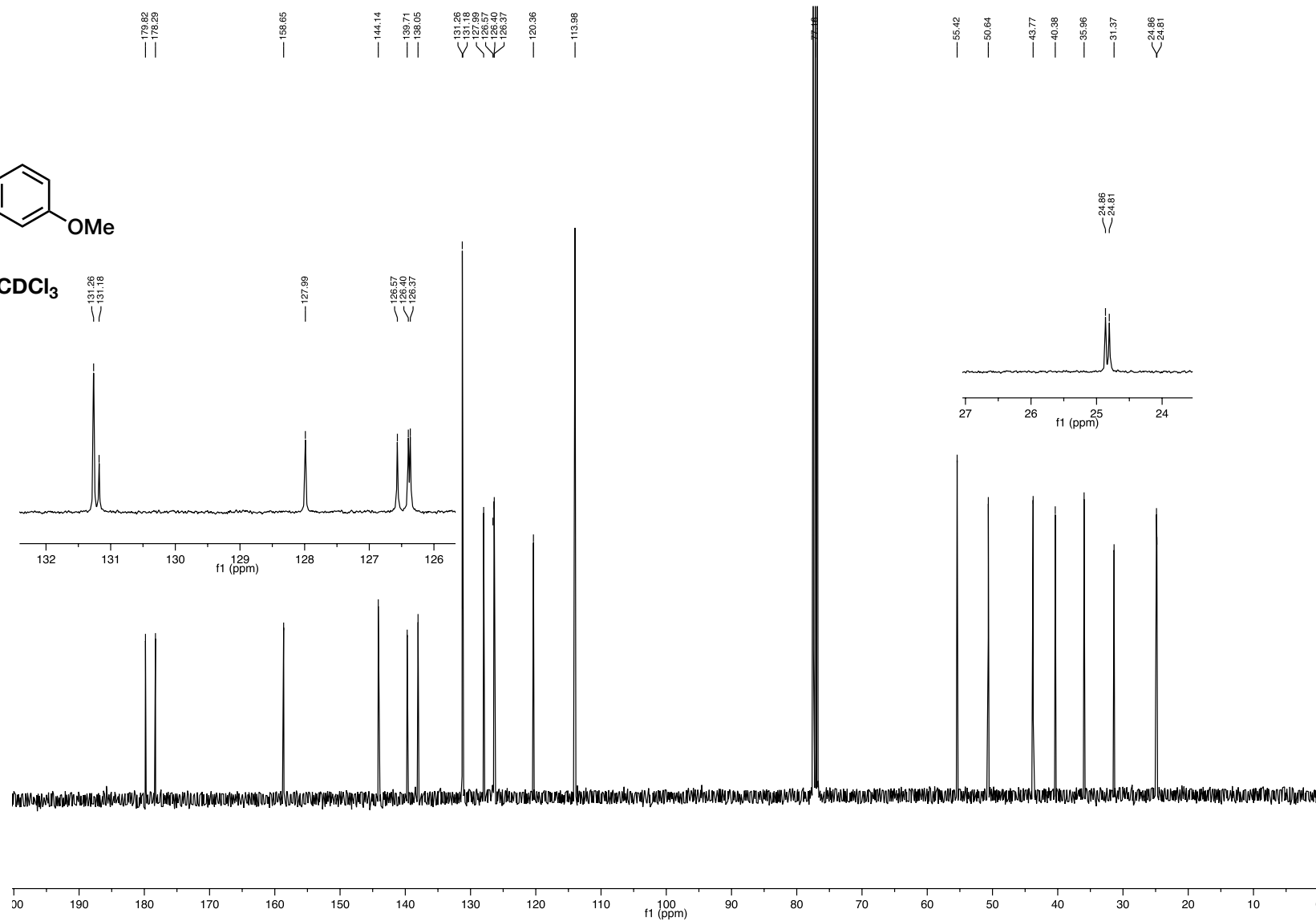
5c
100 MHz, CDCl₃

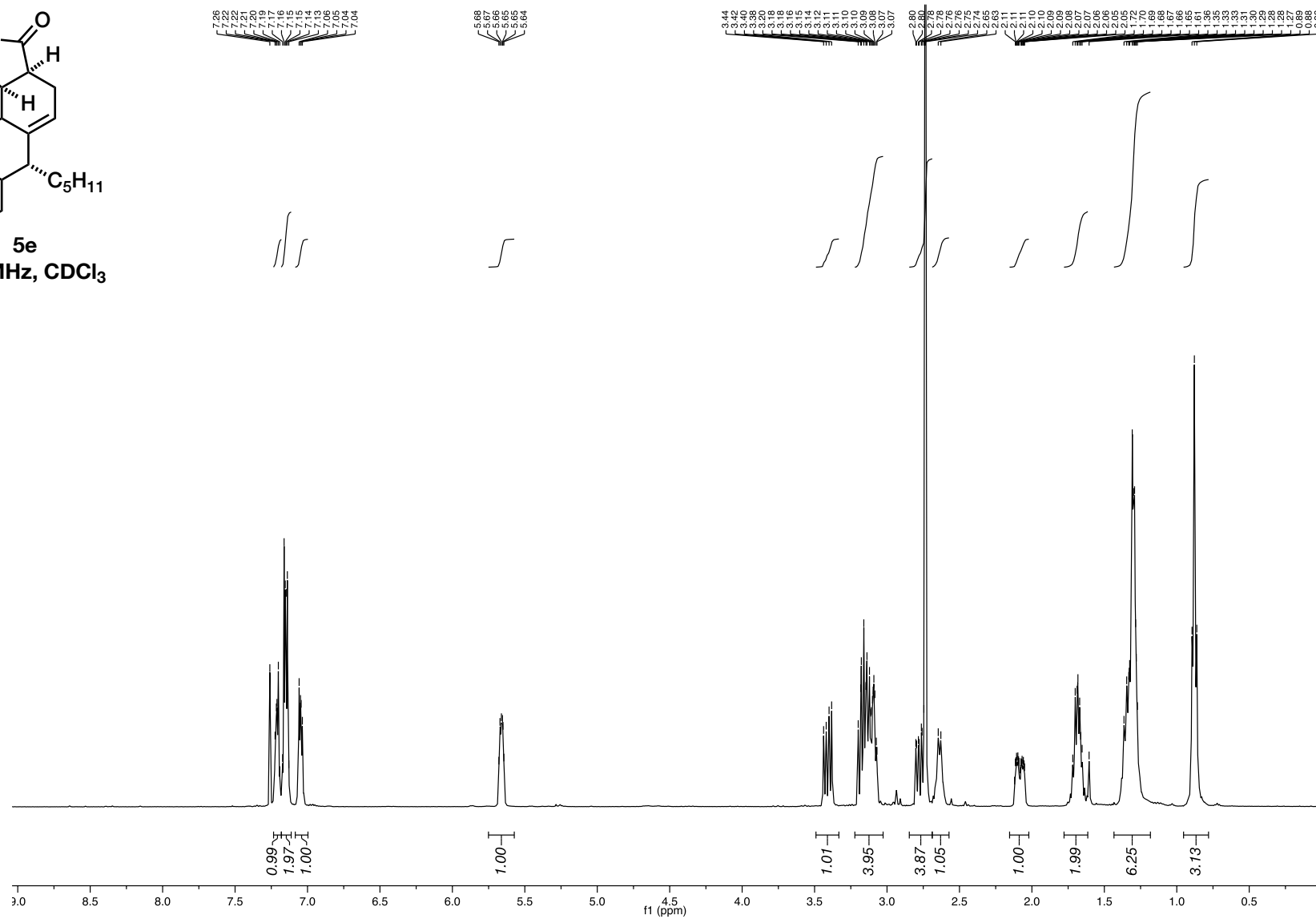
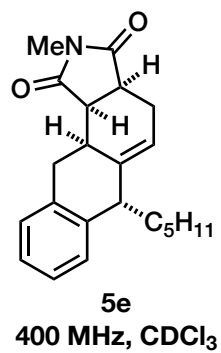


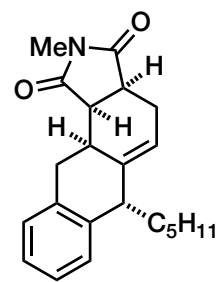




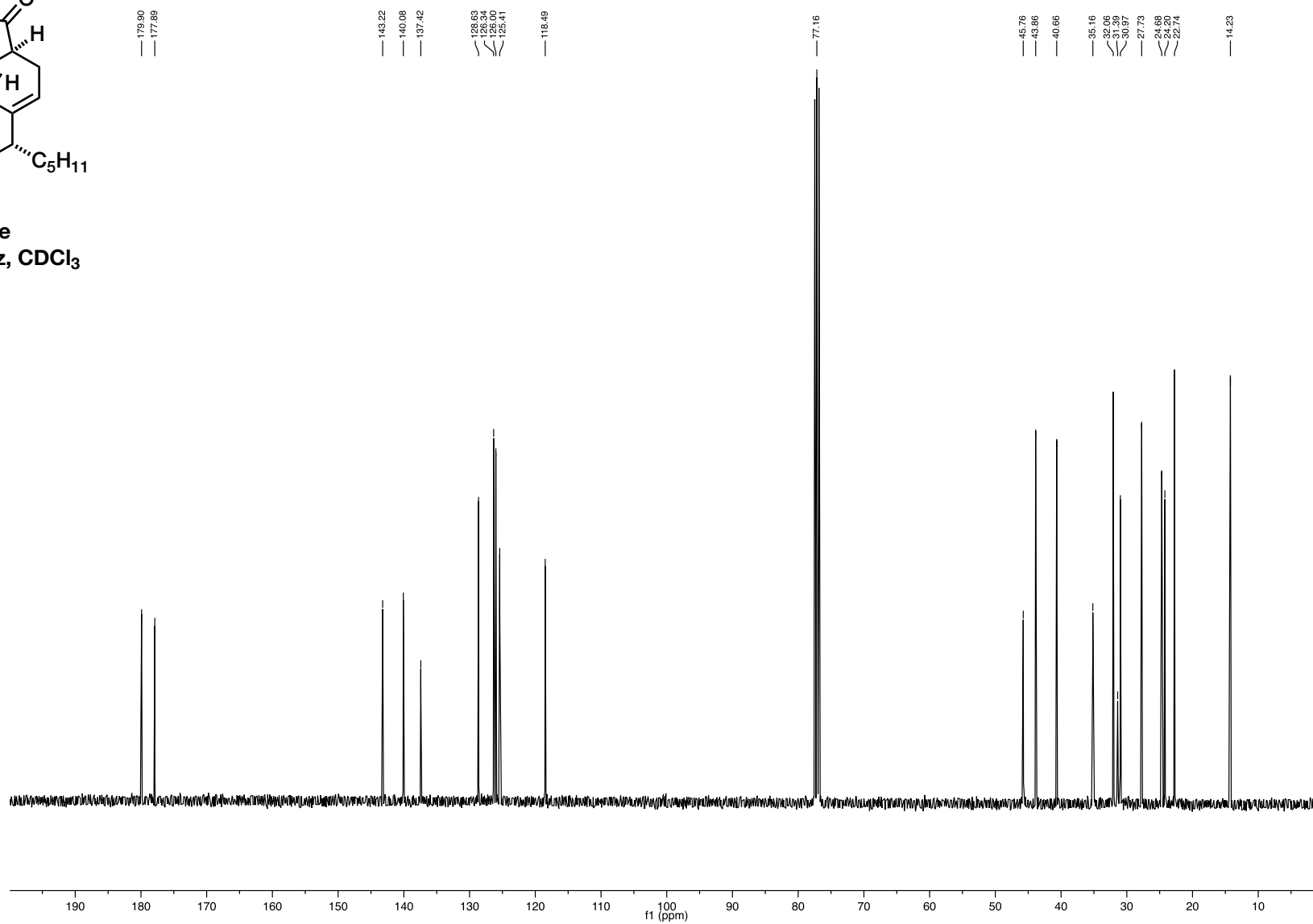
5d
100 MHz, CDCl₃

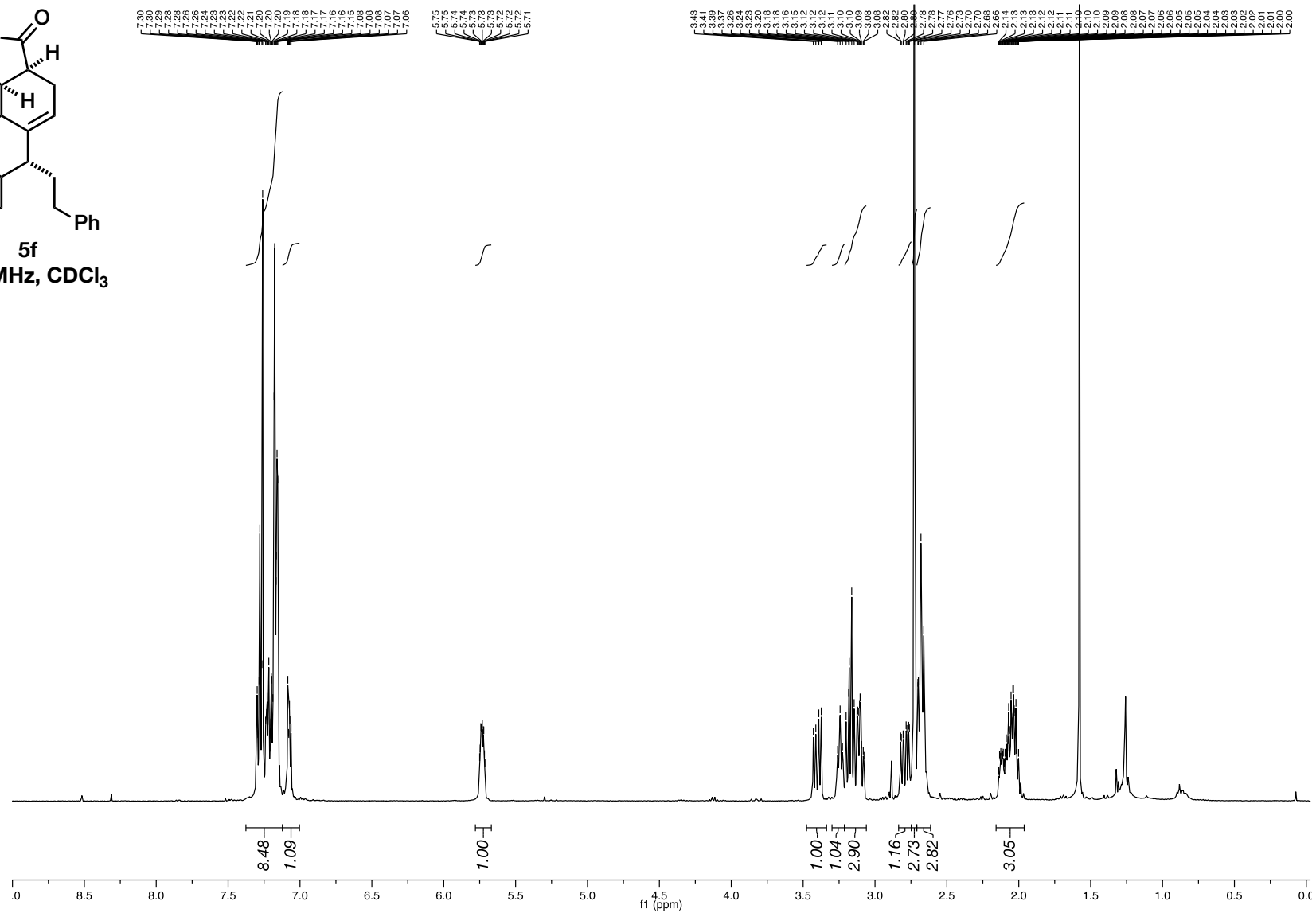
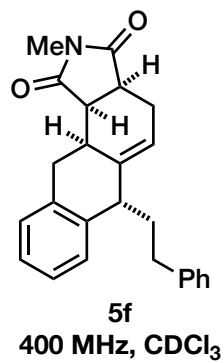


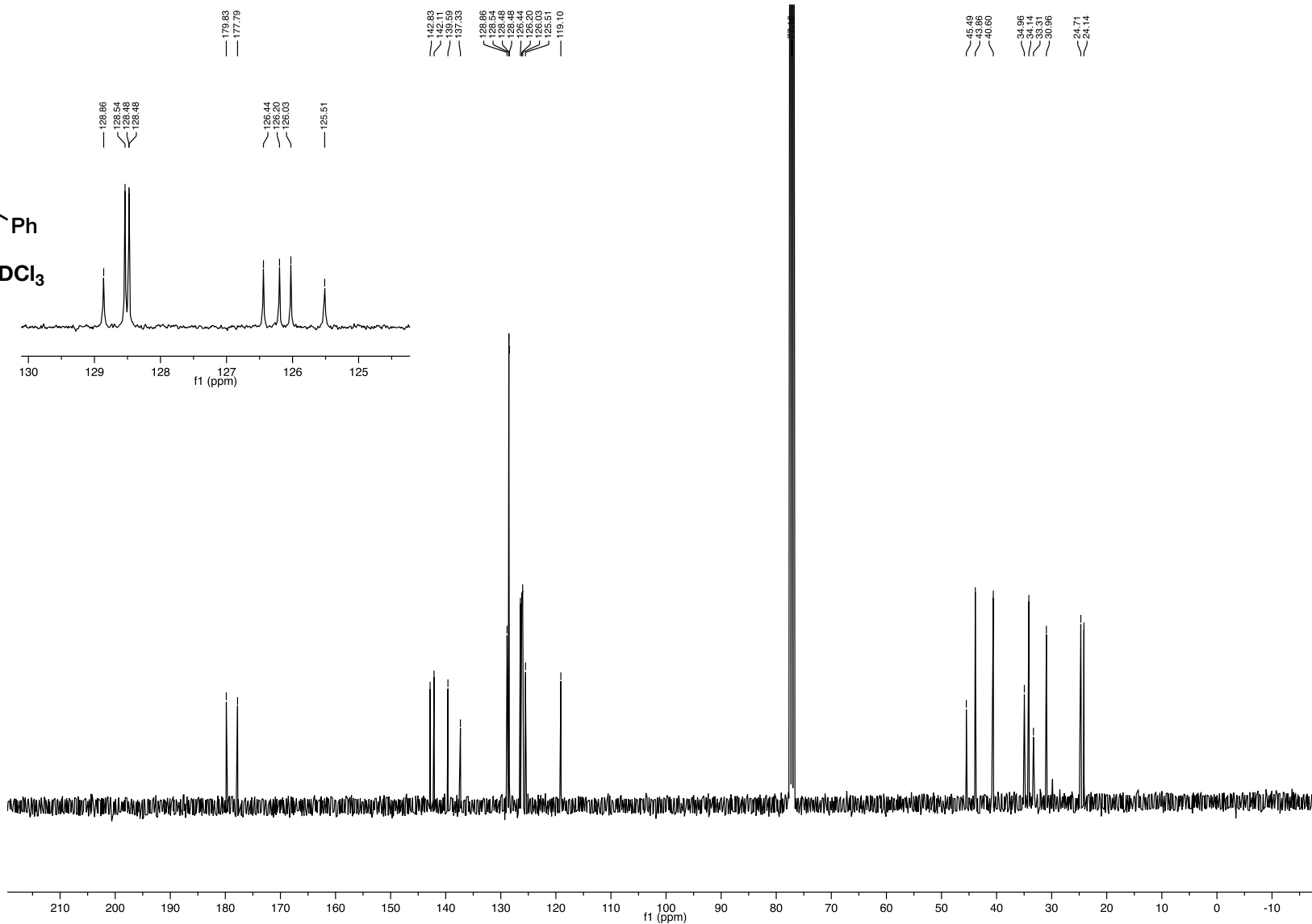
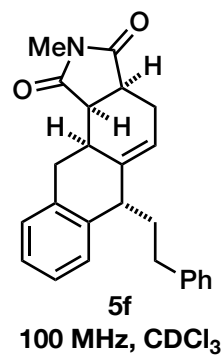


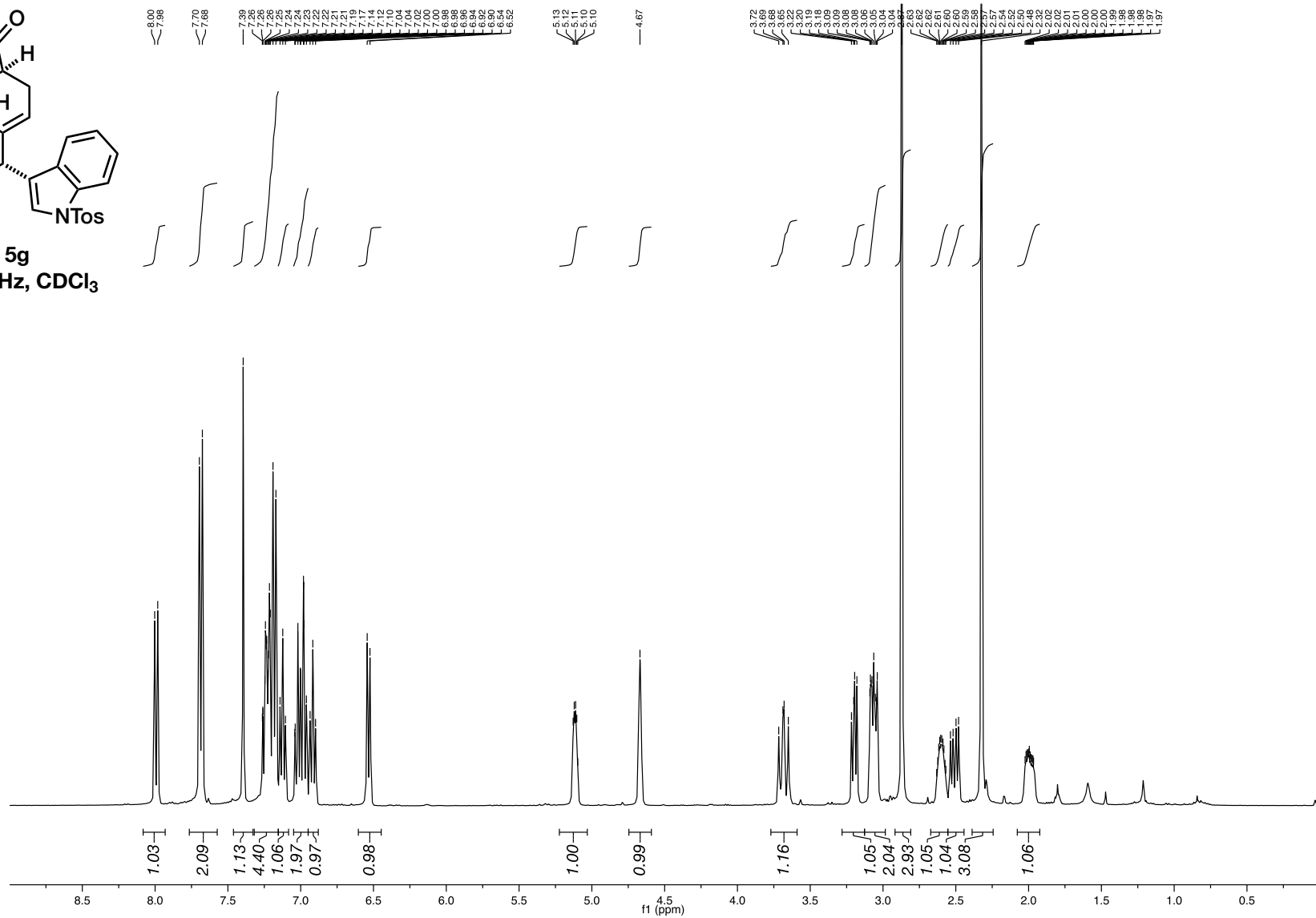
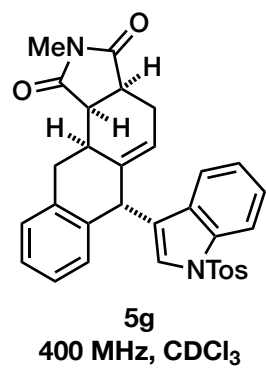


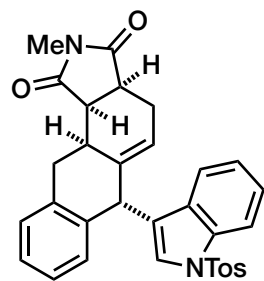
5e
100 MHz, CDCl₃



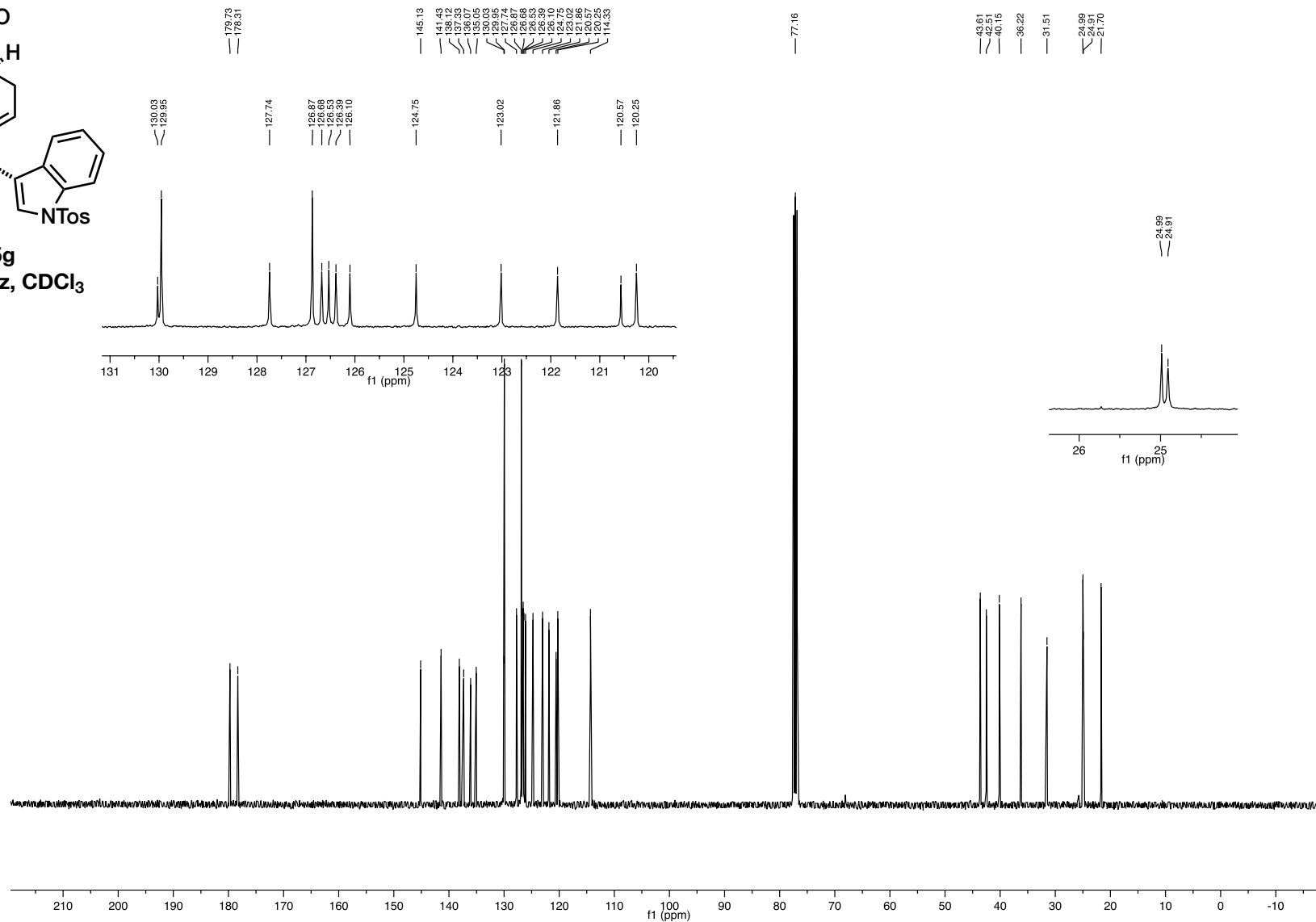


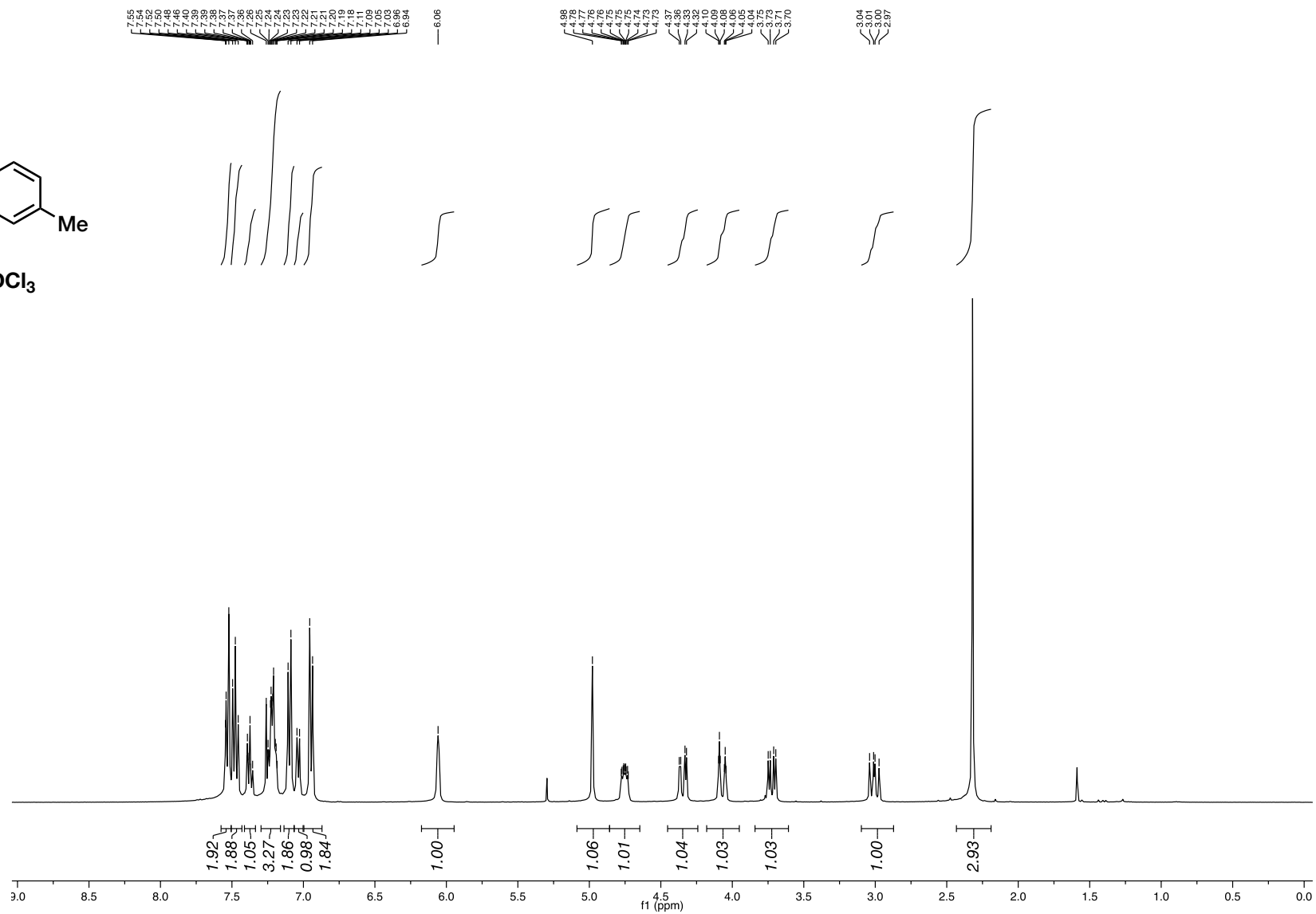
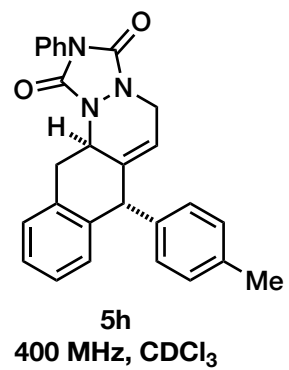


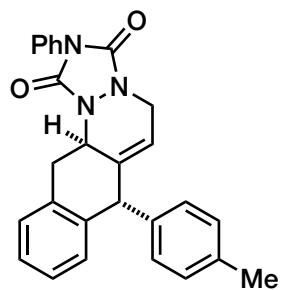




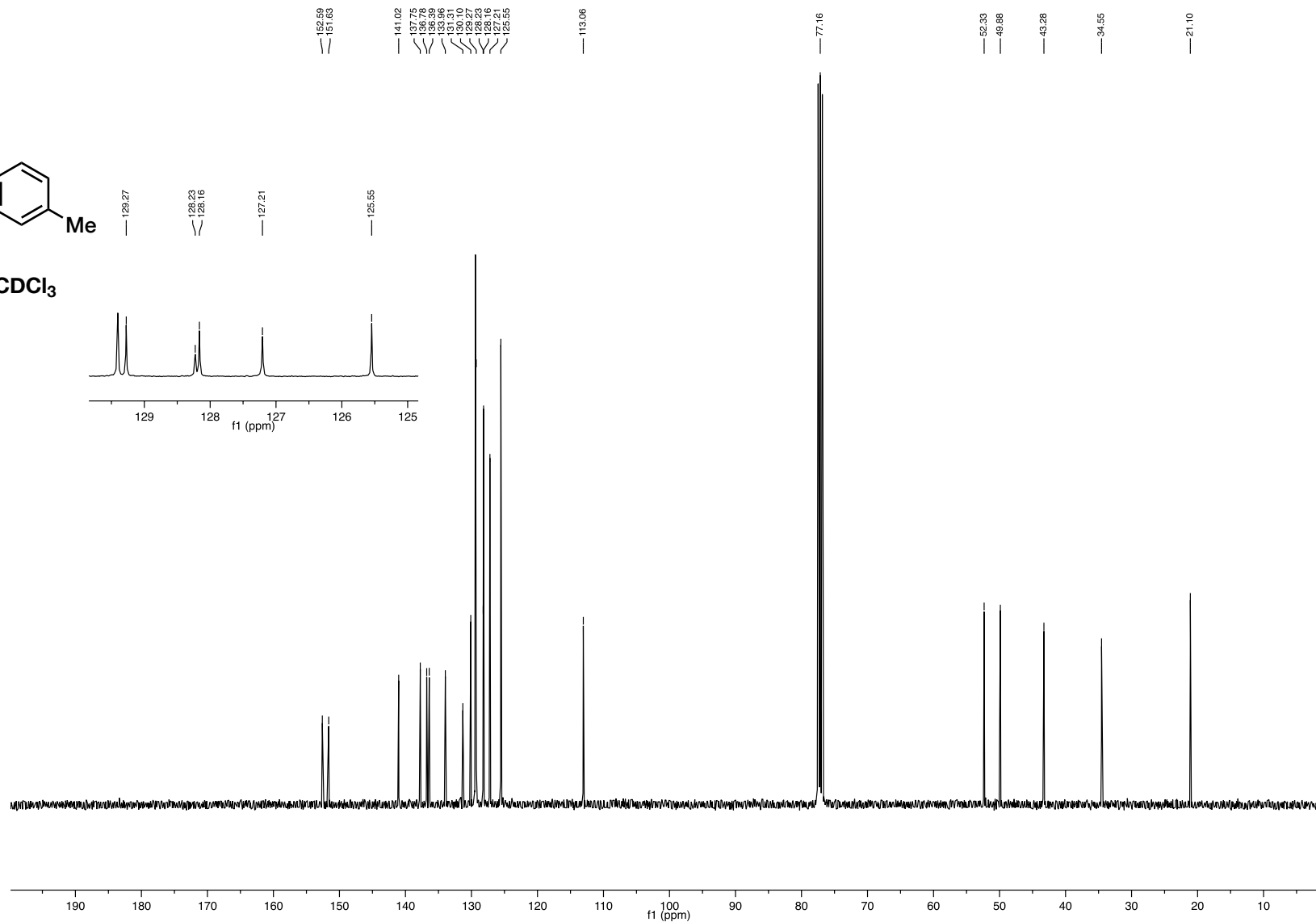
5g
100 MHz, CDCl₃

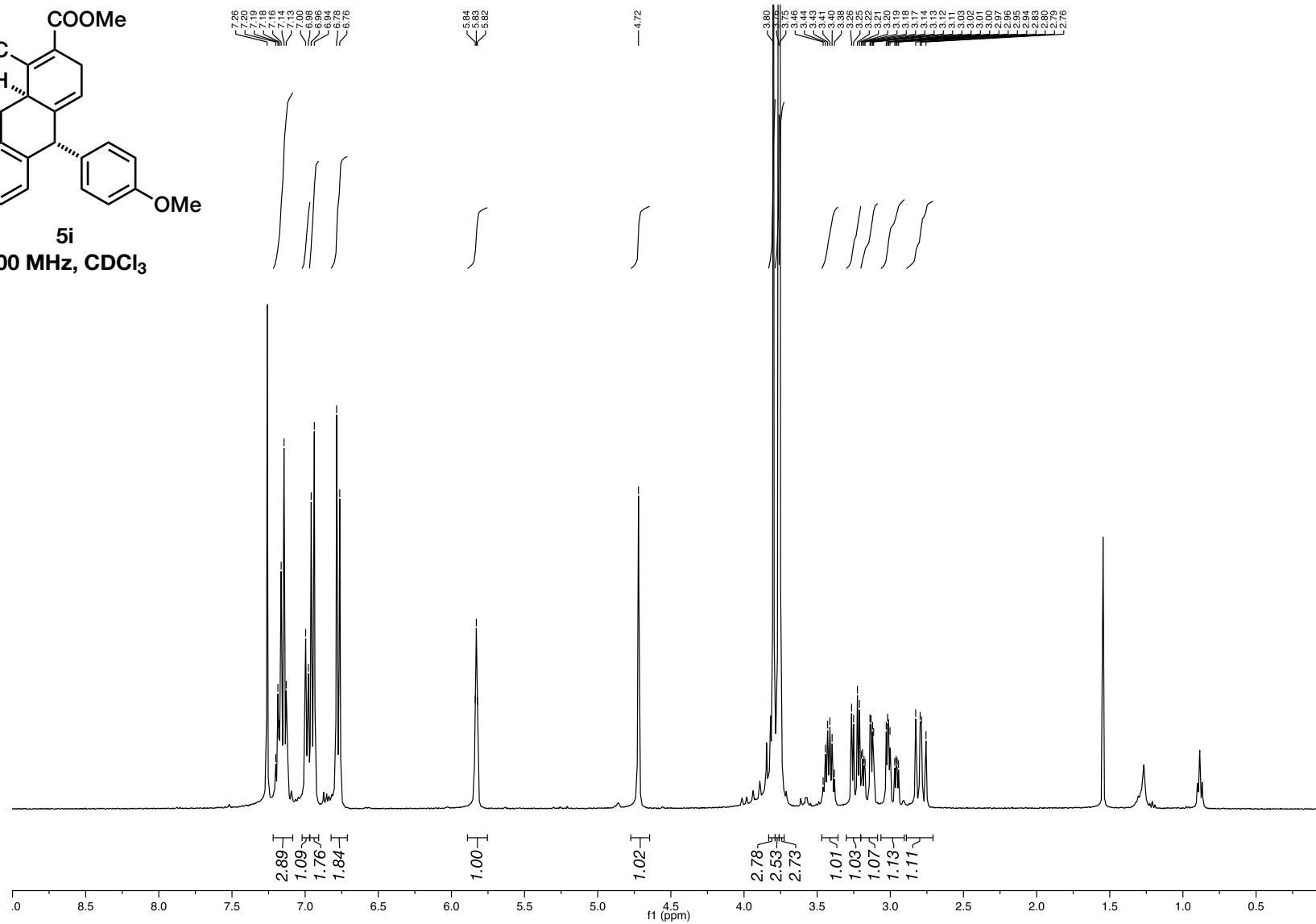
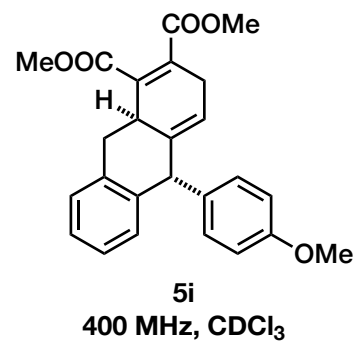


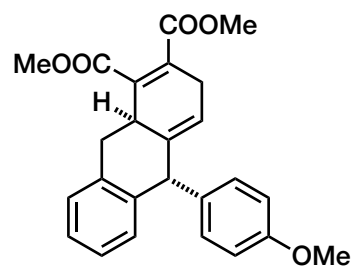




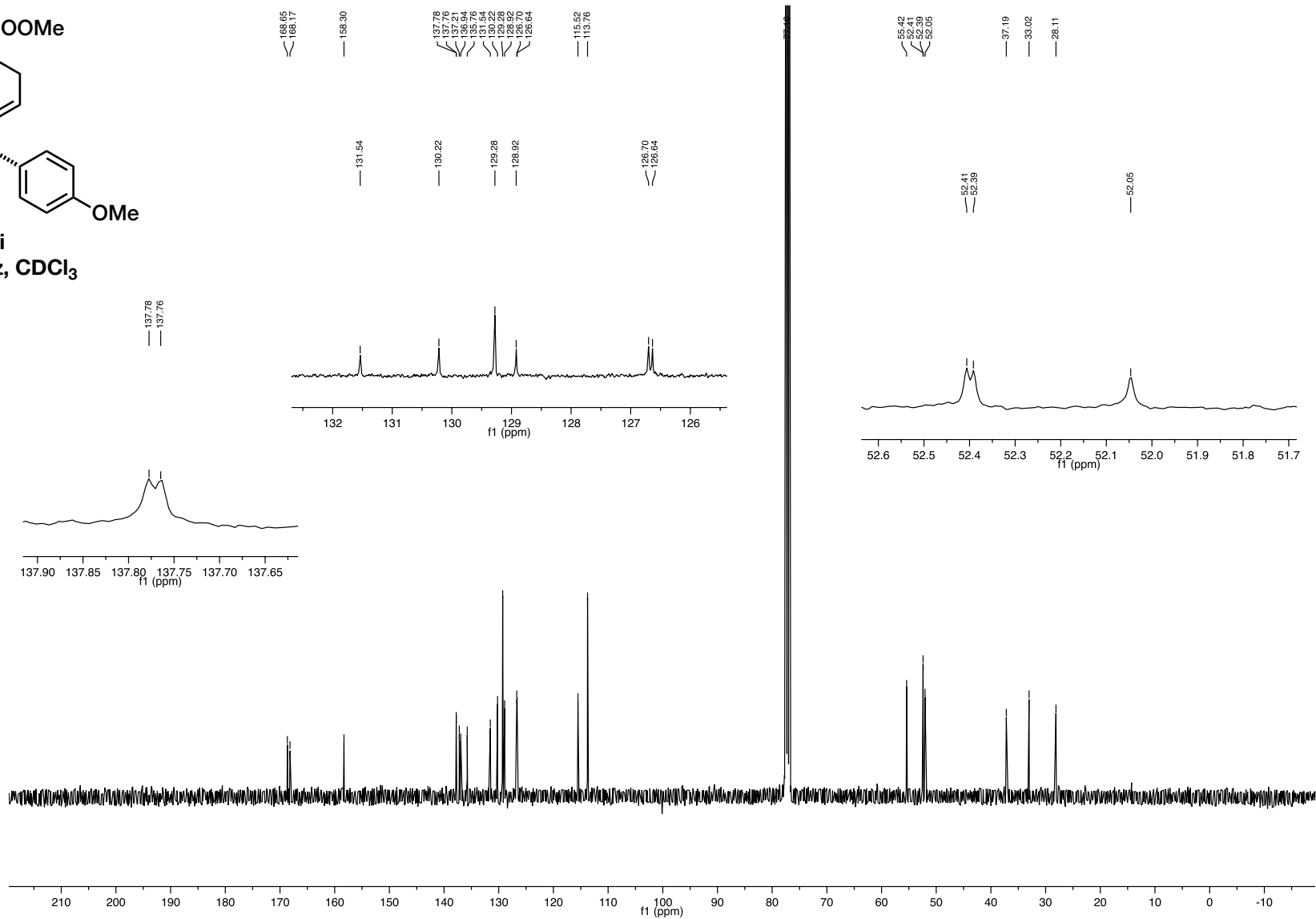
5h
100 MHz, CDCl₃

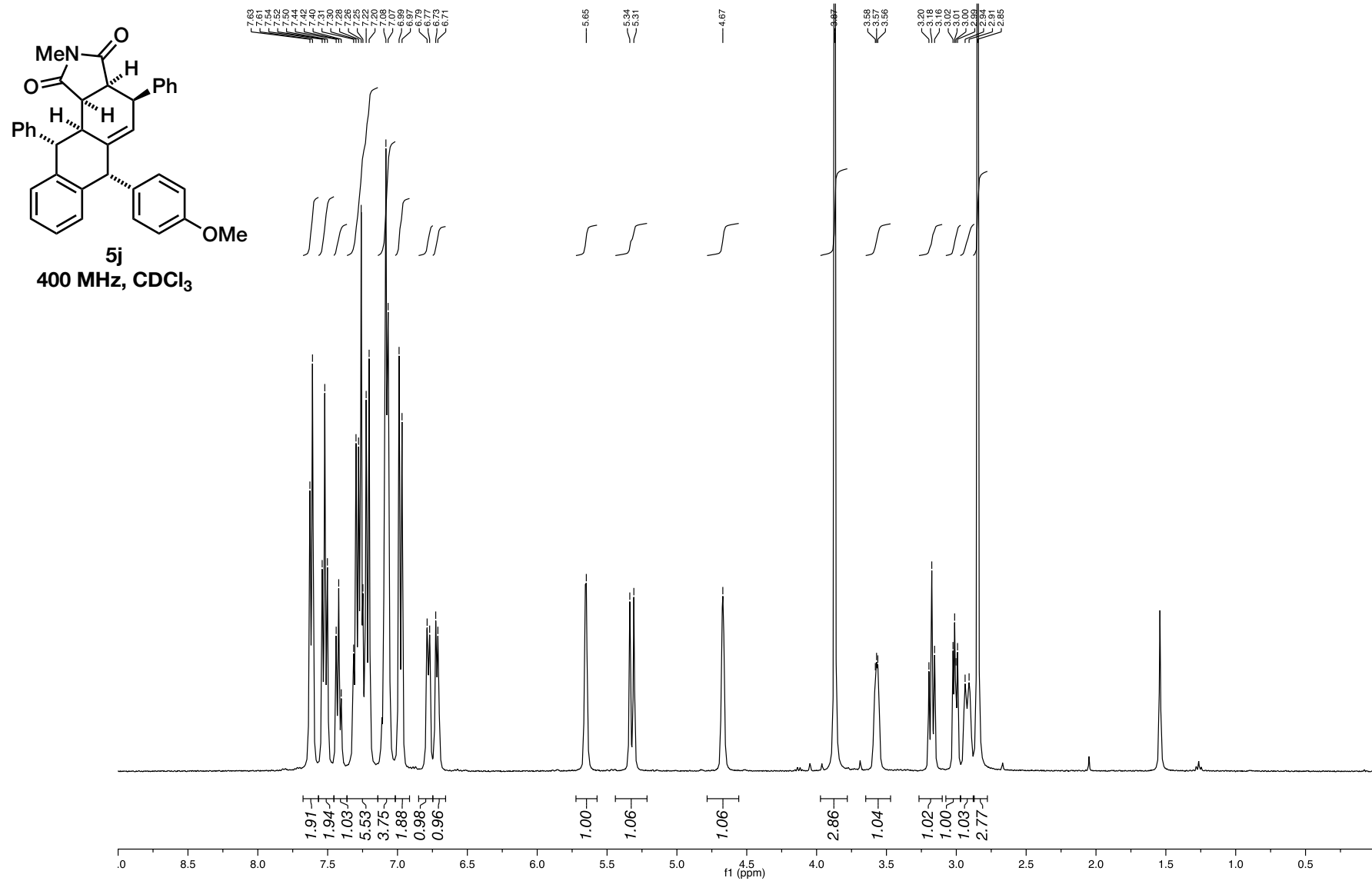


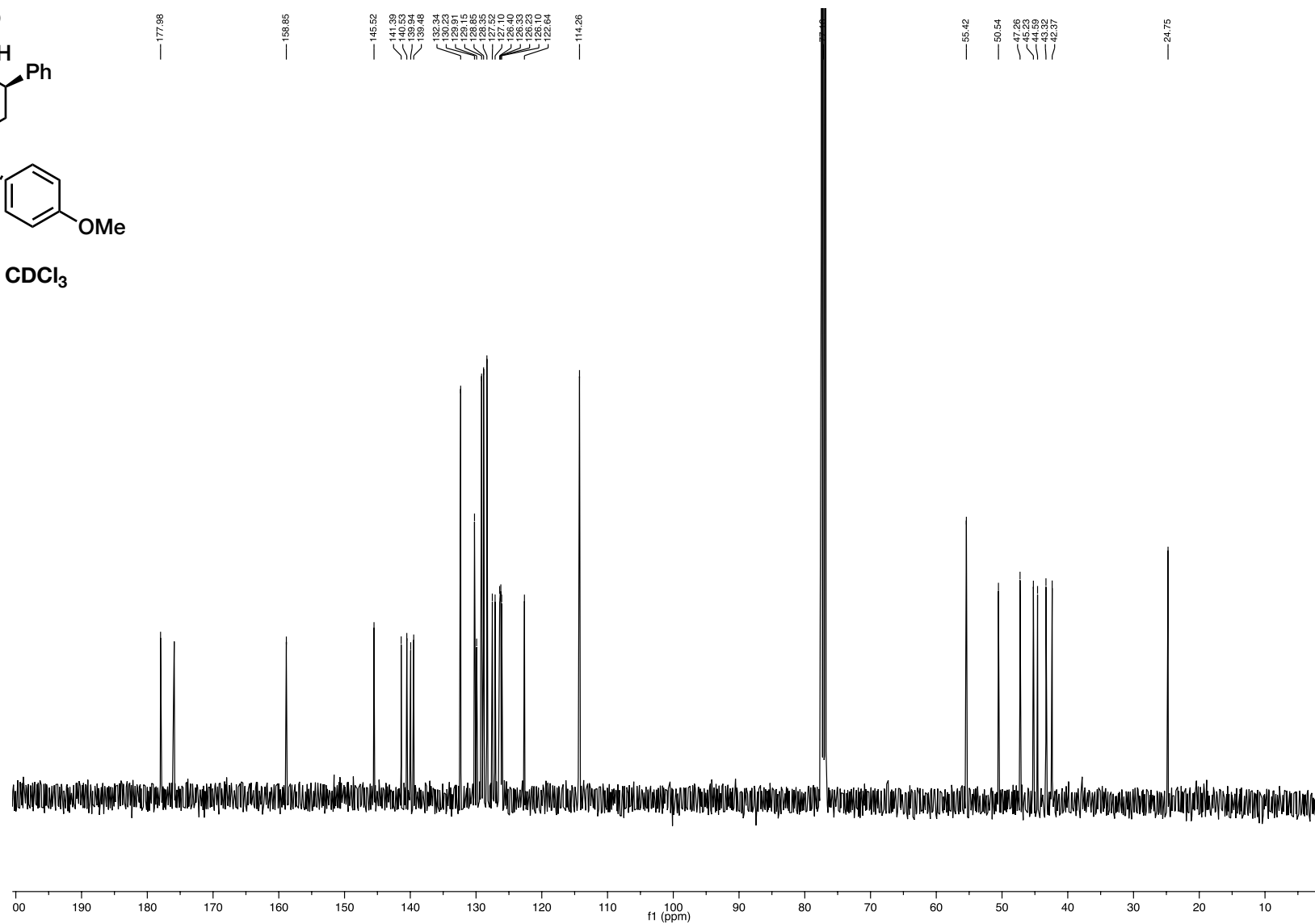
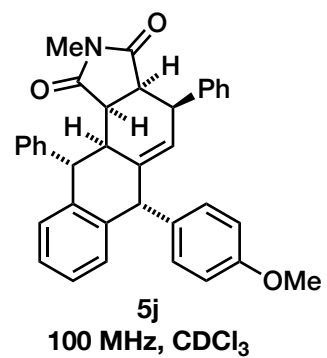


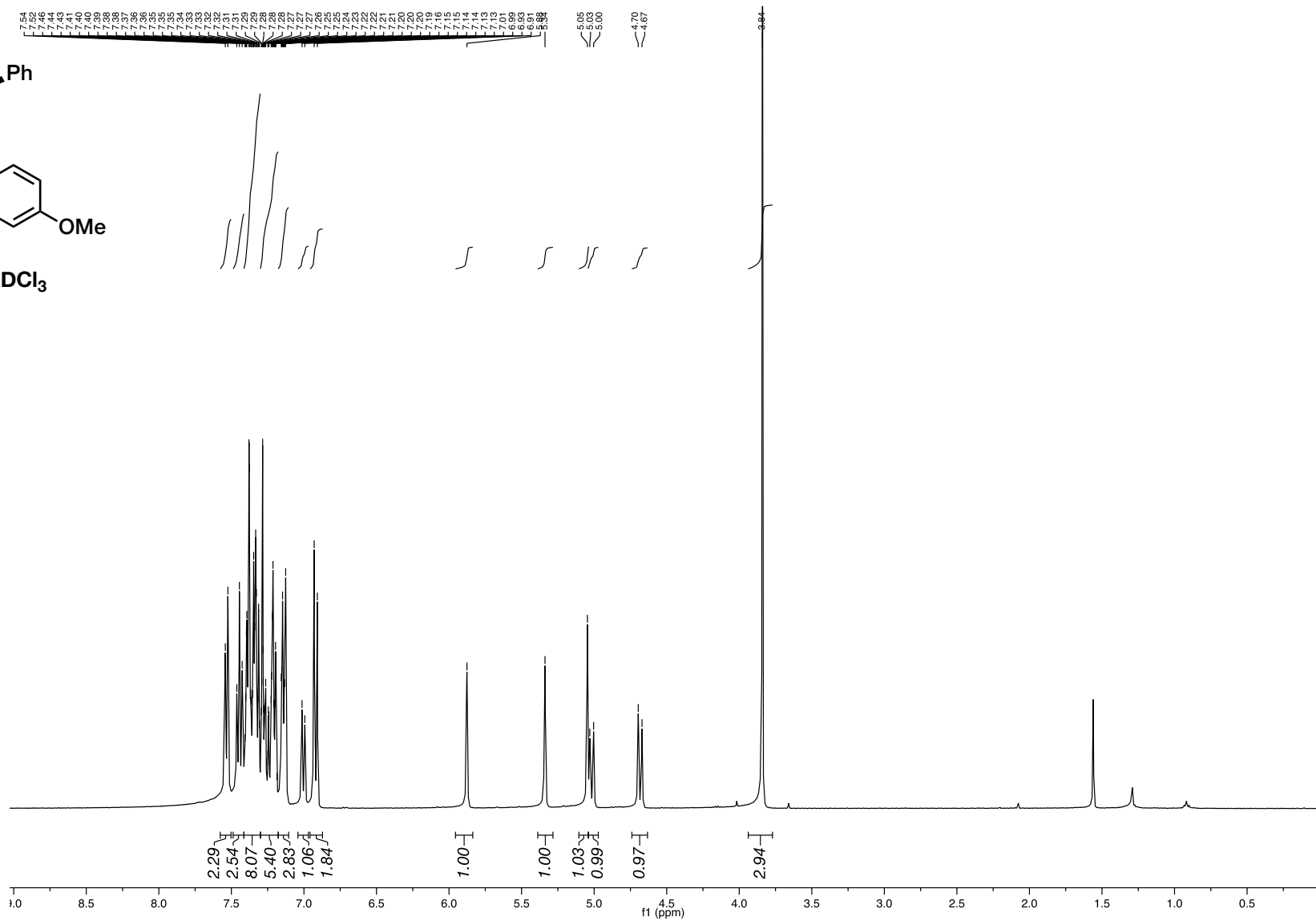
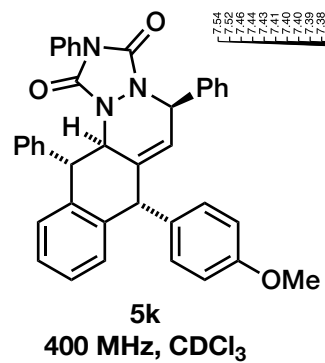


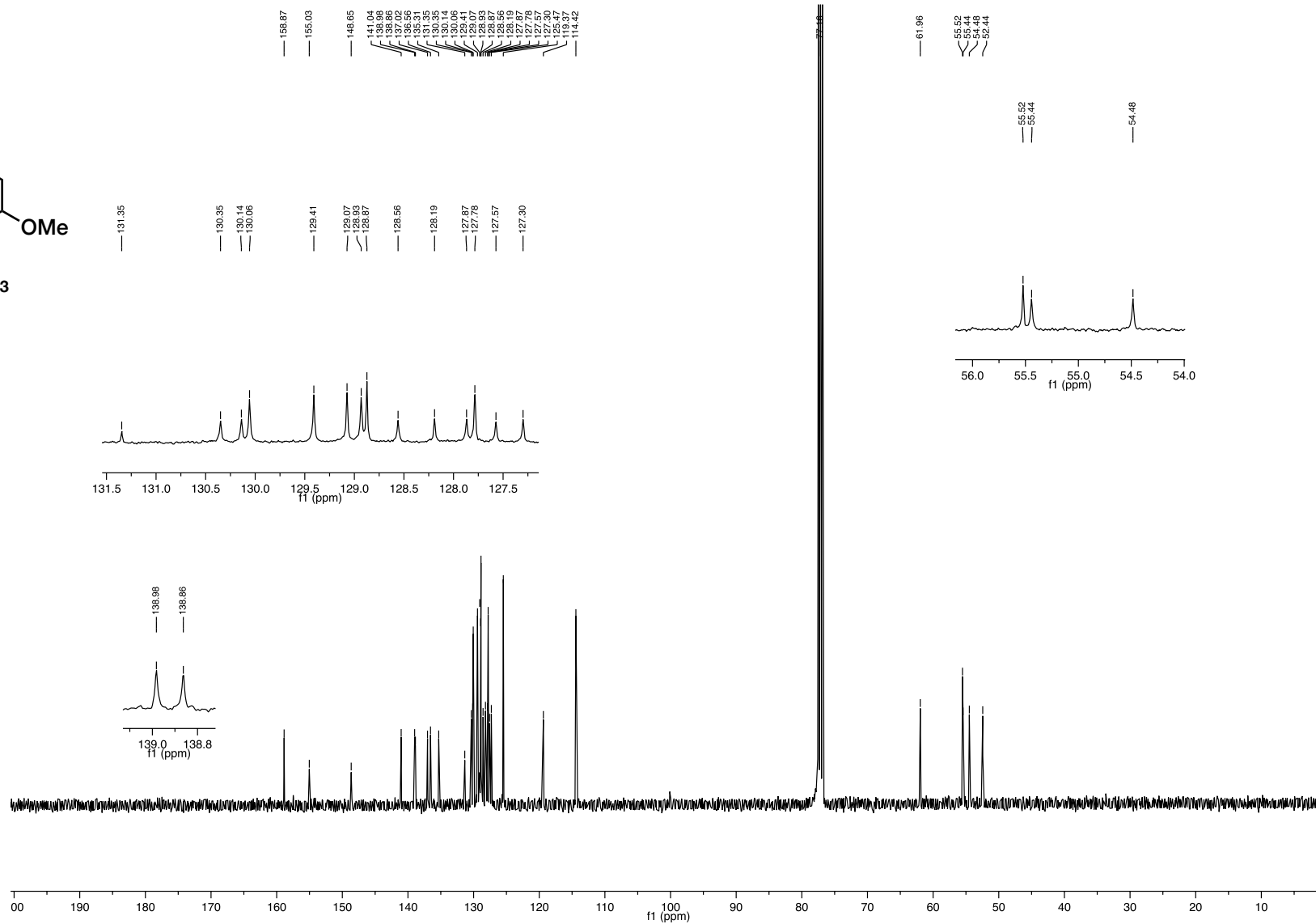
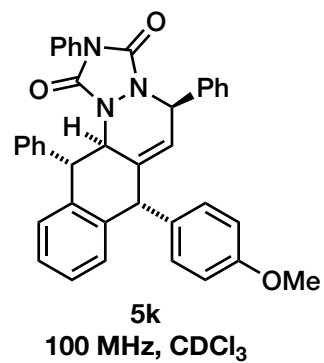
5i
100 MHz, CDCl₃

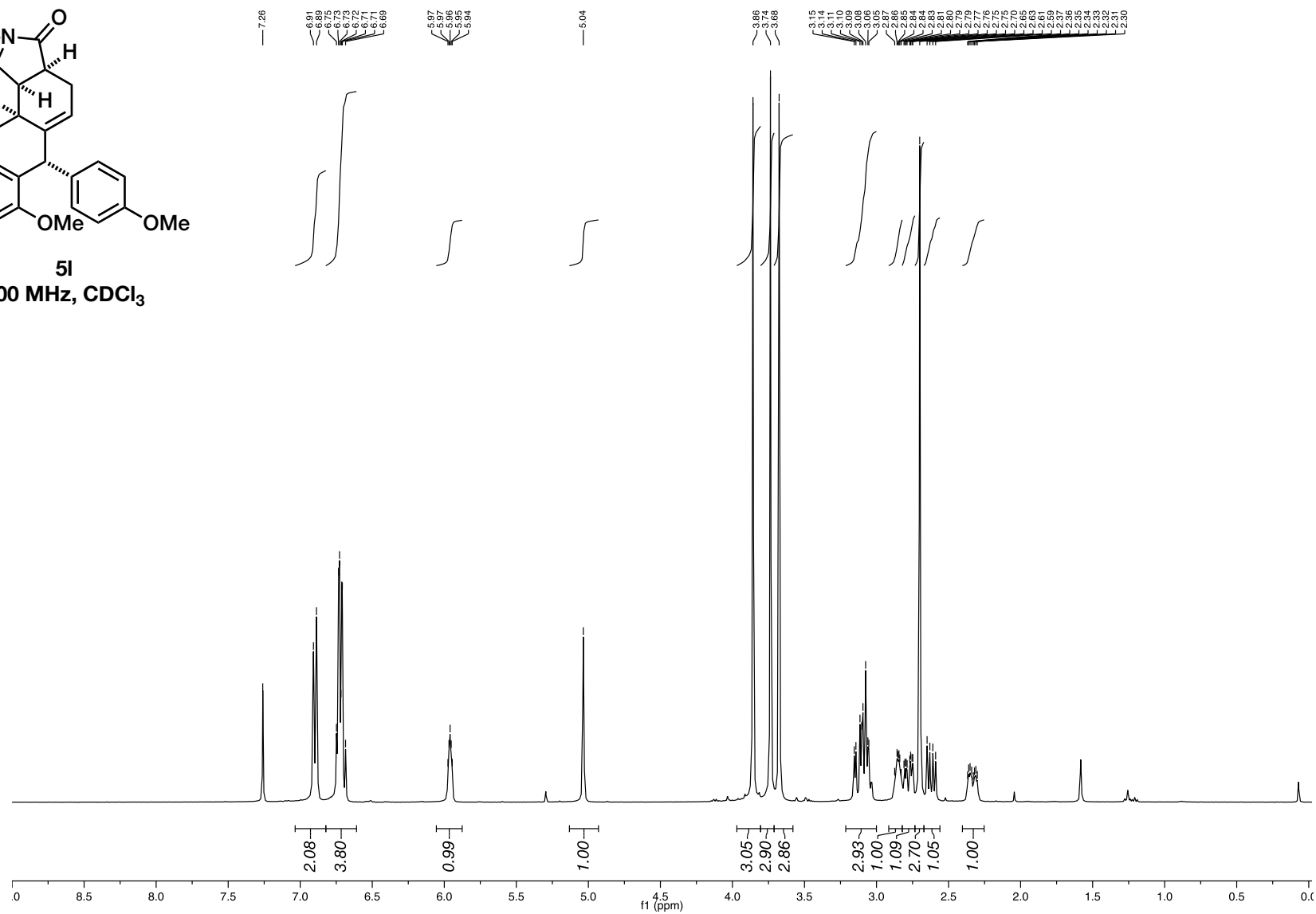
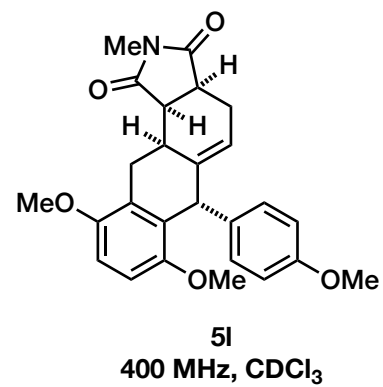


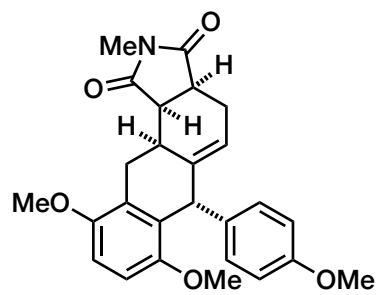




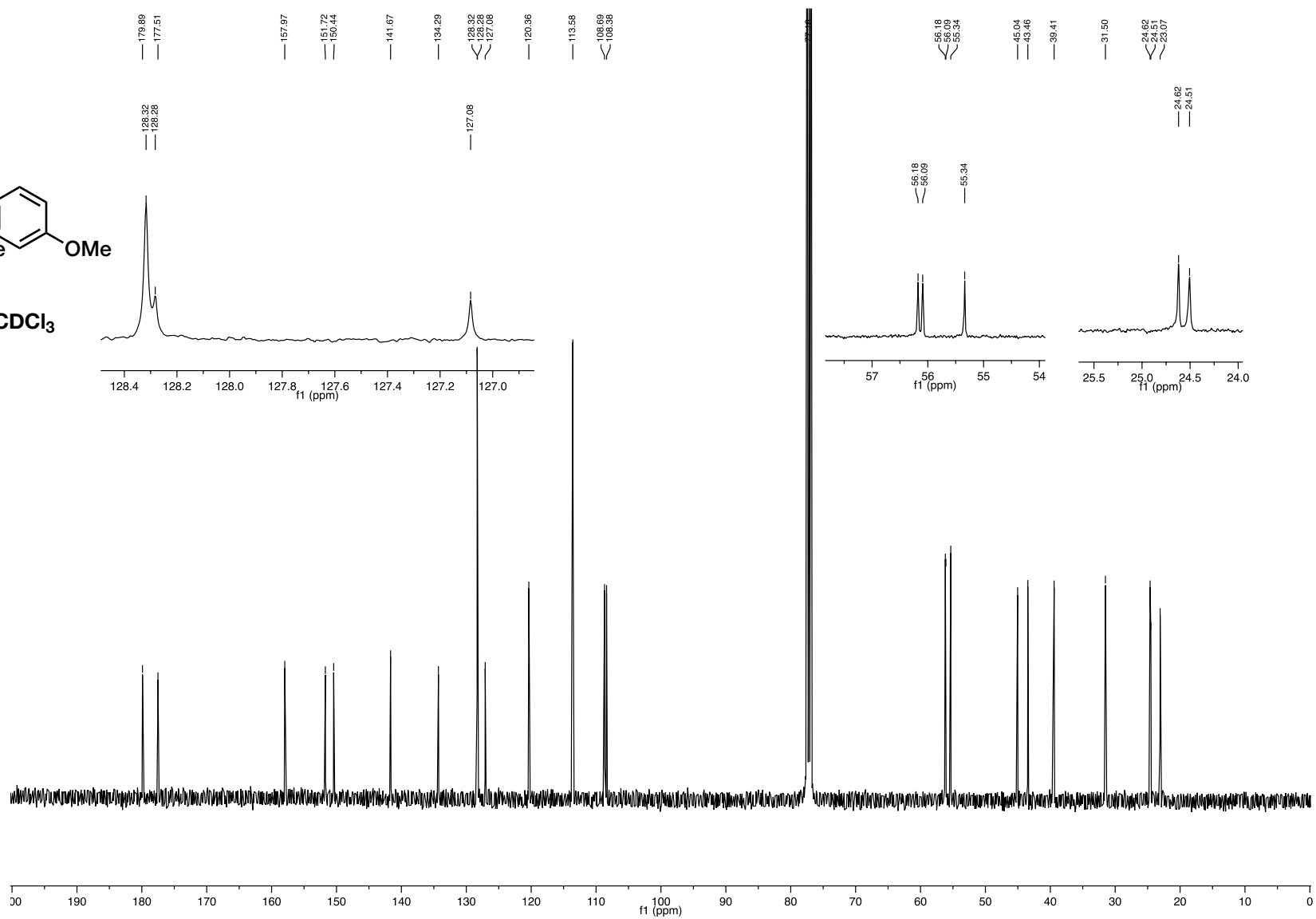


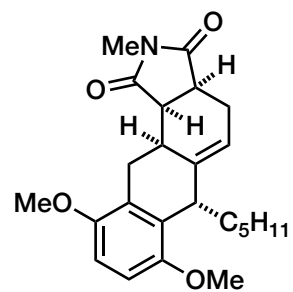




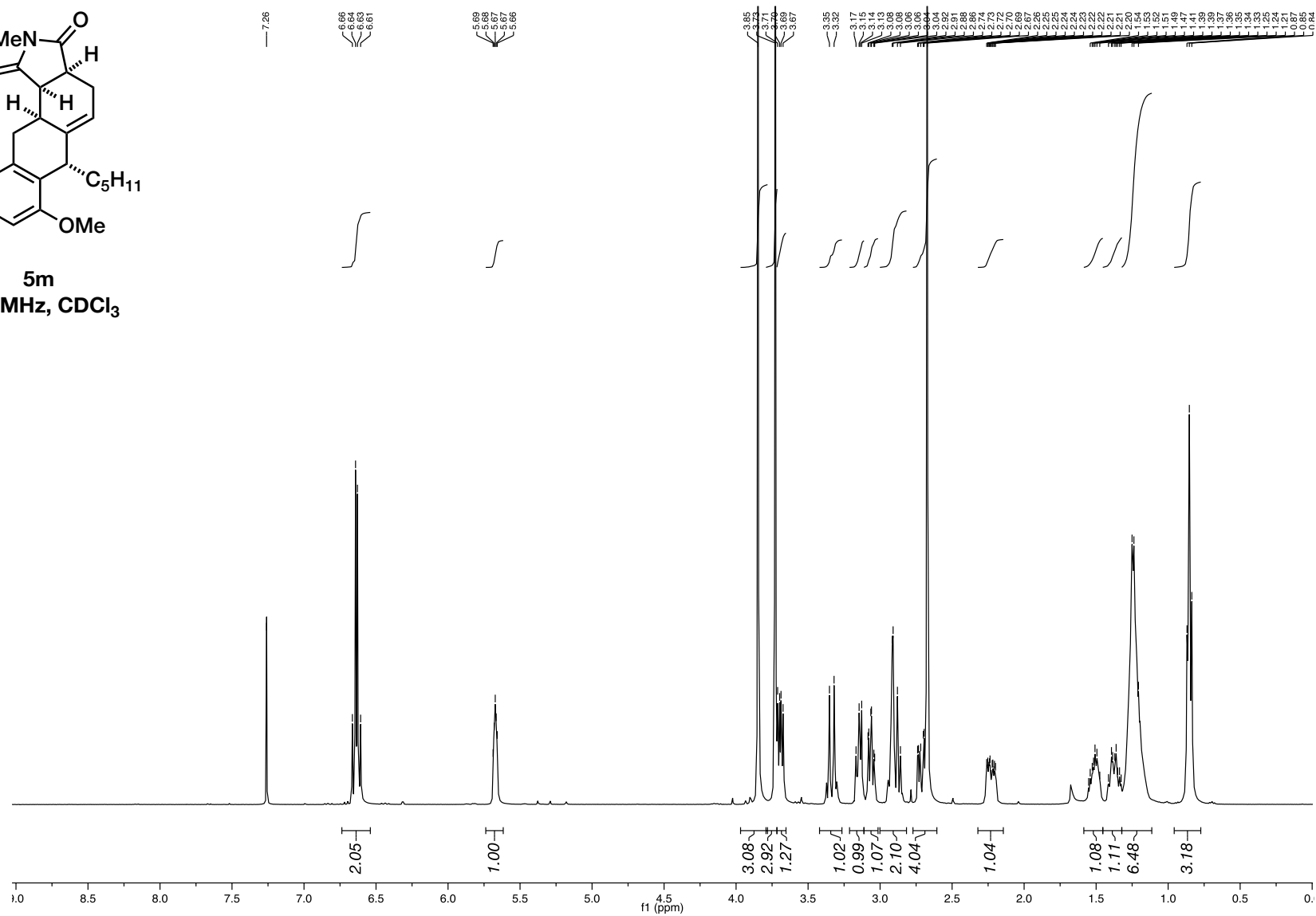


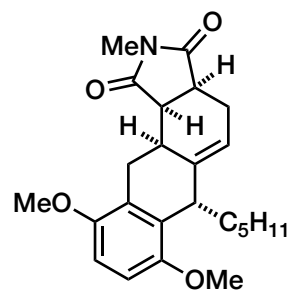
5l
100 MHz, CDCl₃



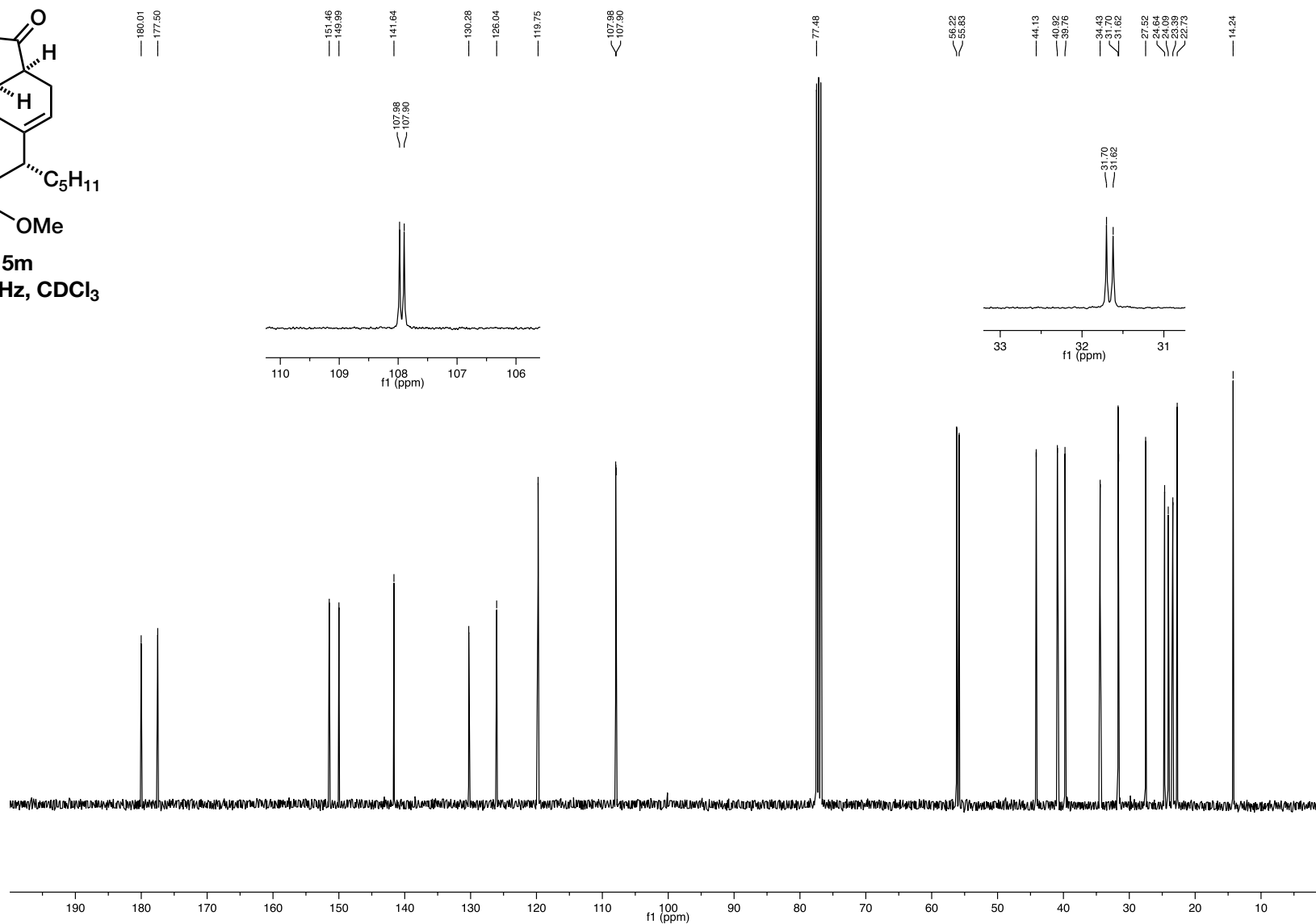


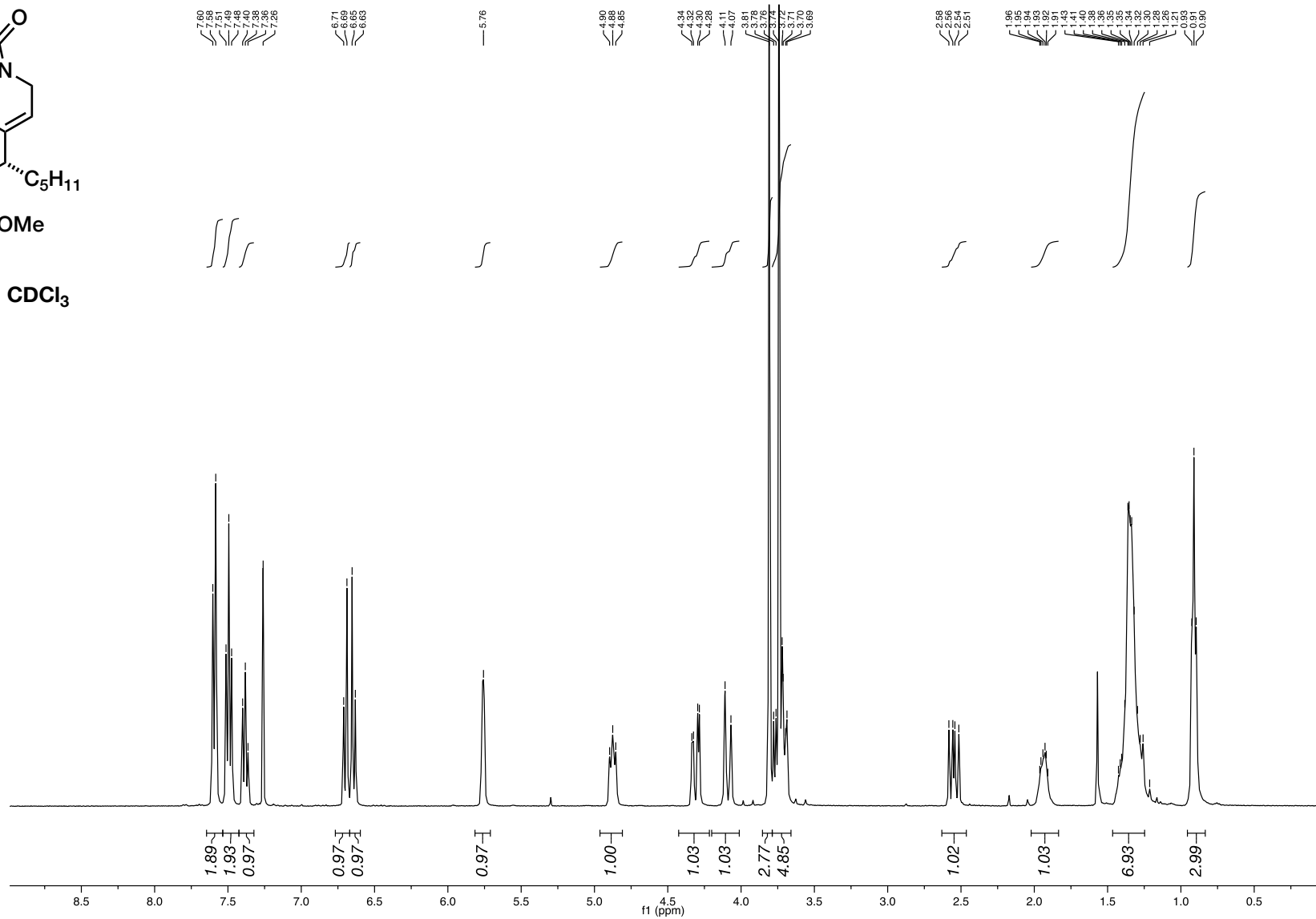
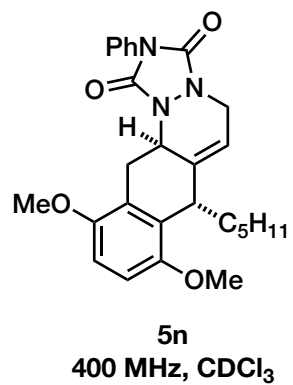
5m
400 MHz, CDCl₃

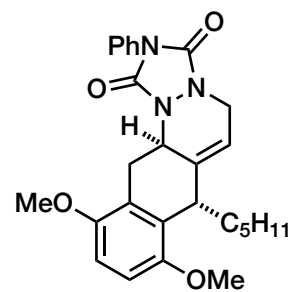




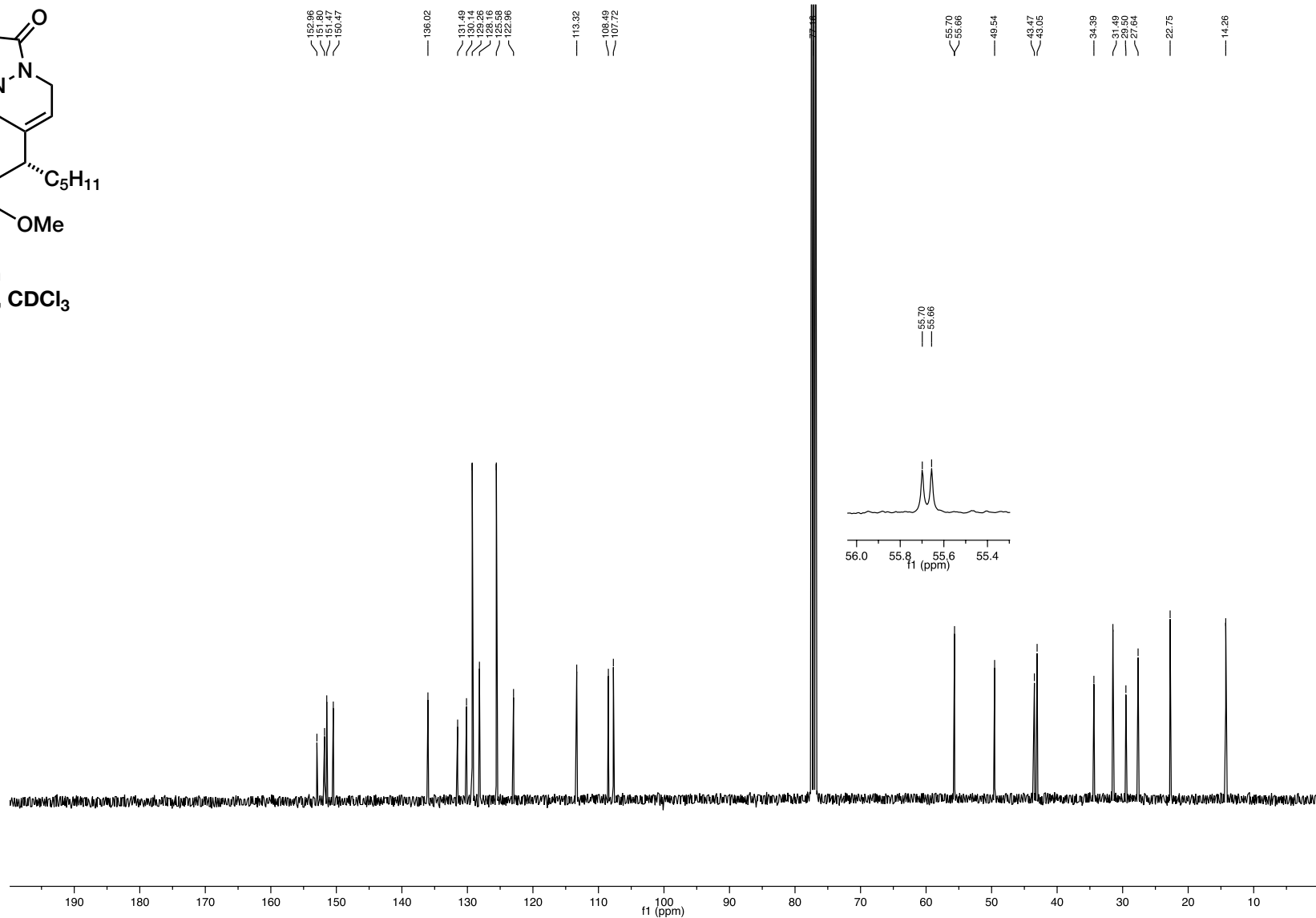
5m
100 MHz, CDCl₃

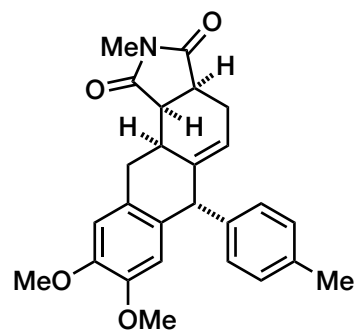




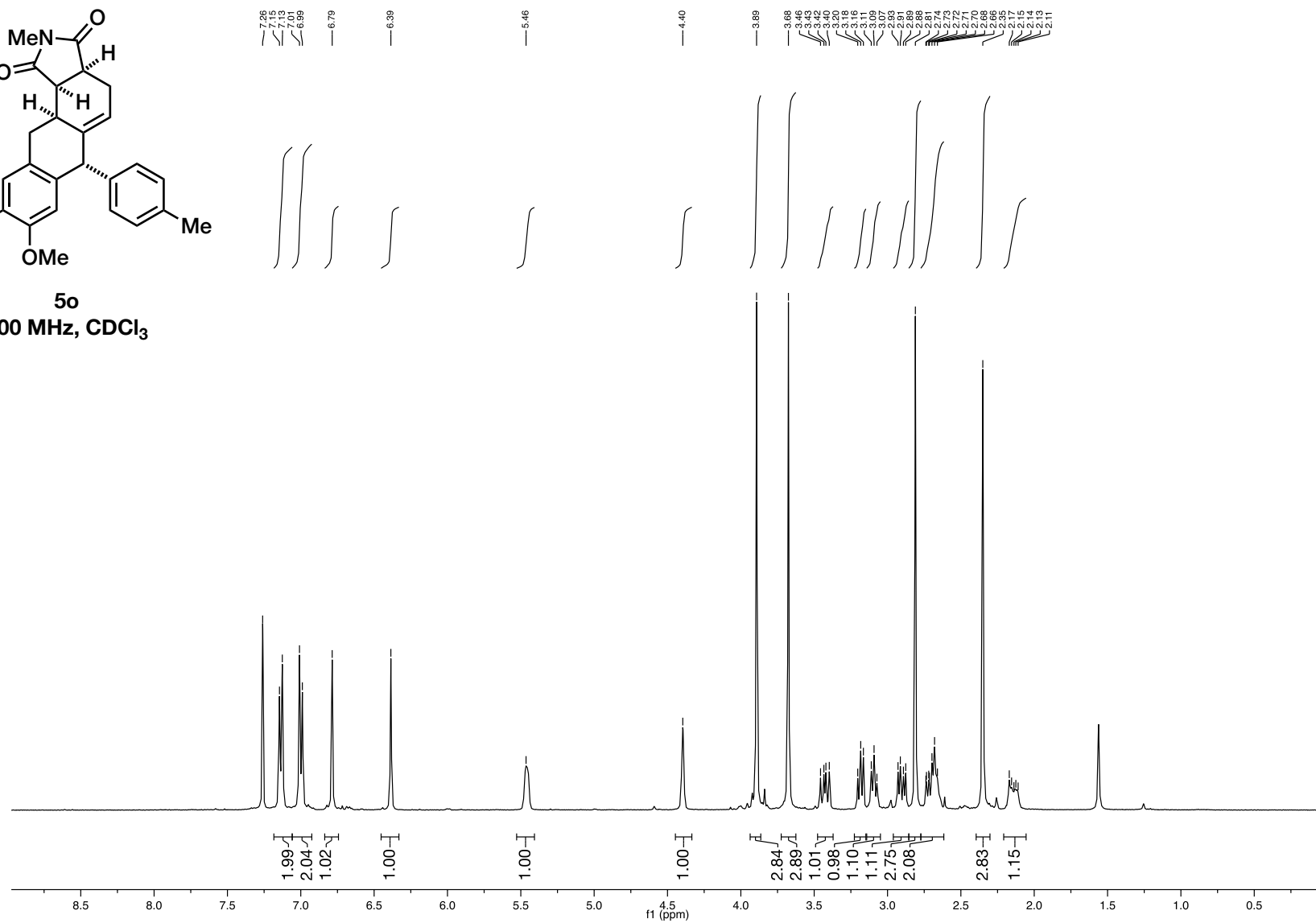


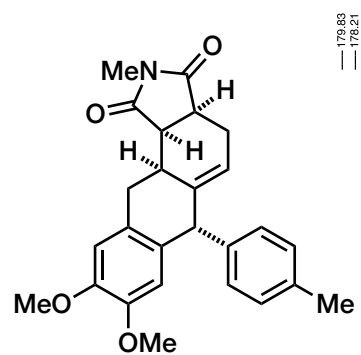
5n
100 MHz, CDCl₃



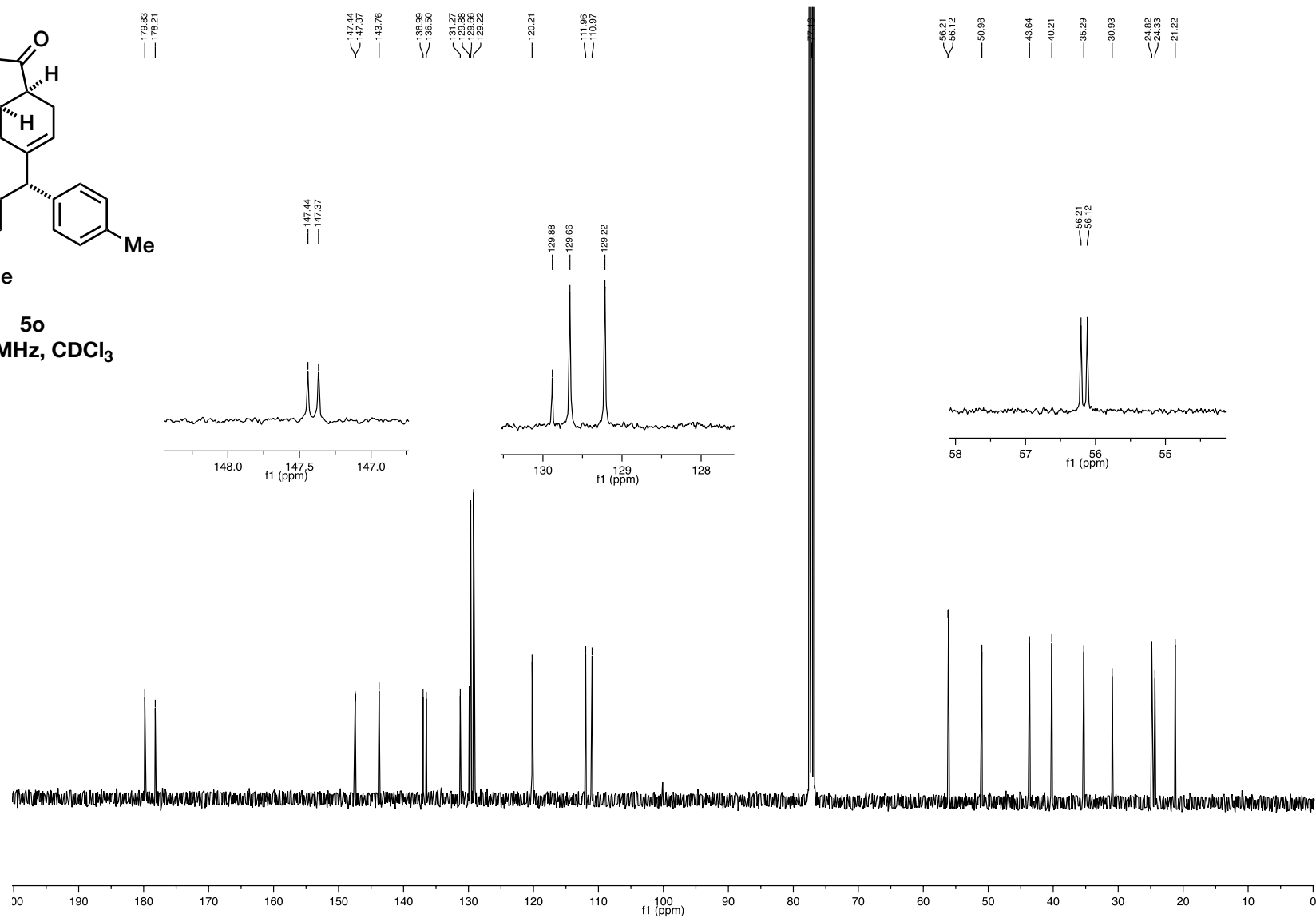


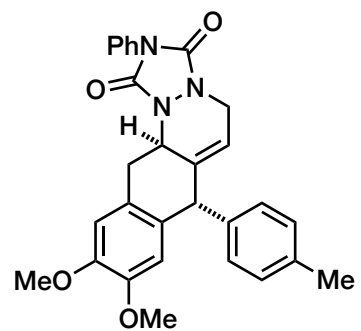
5o
400 MHz, CDCl₃



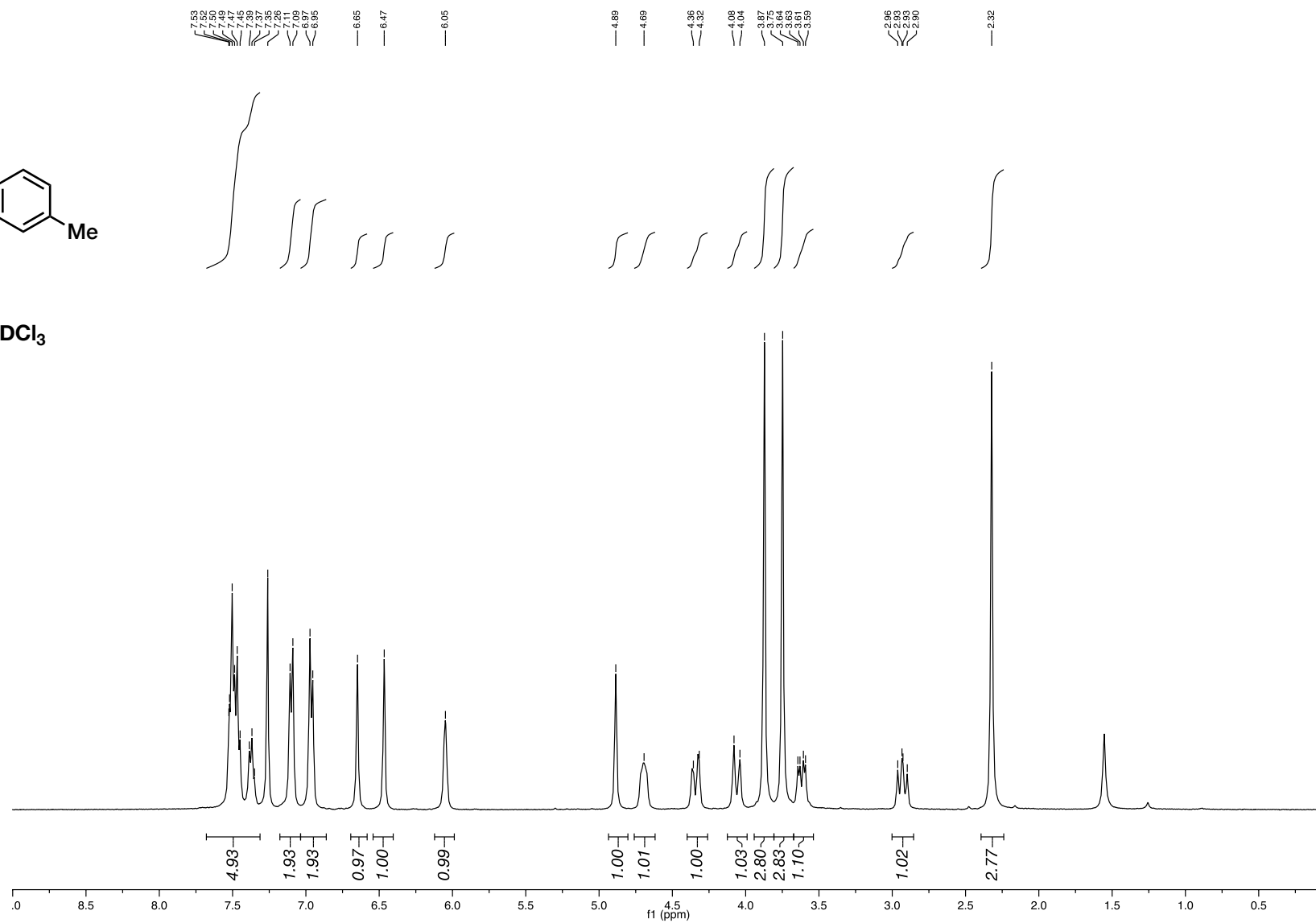


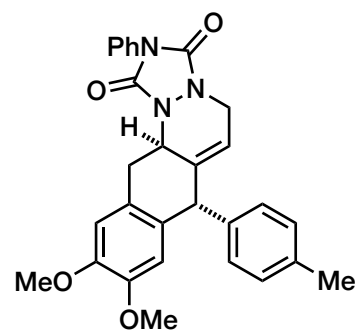
5o
100 MHz, CDCl₃



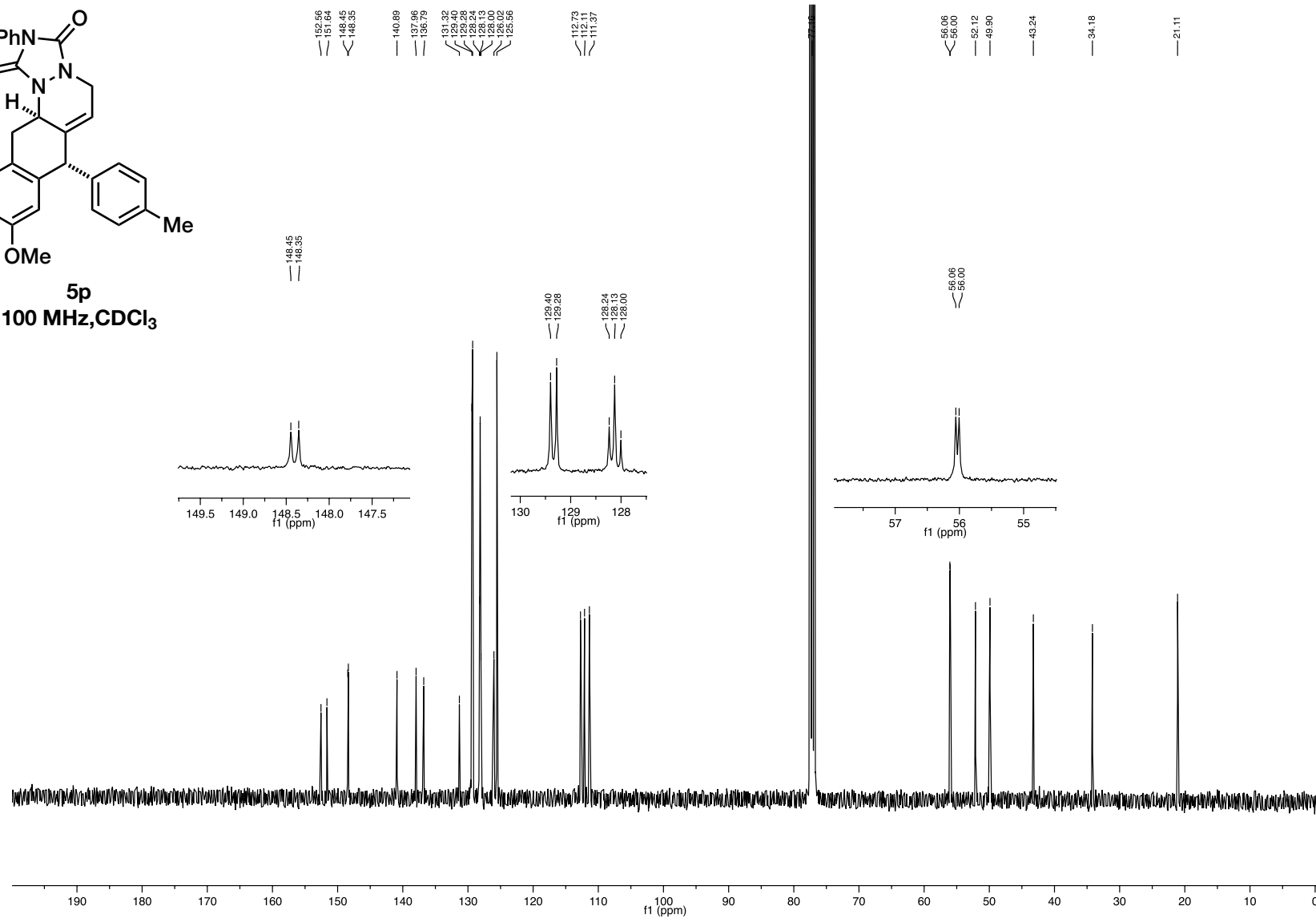


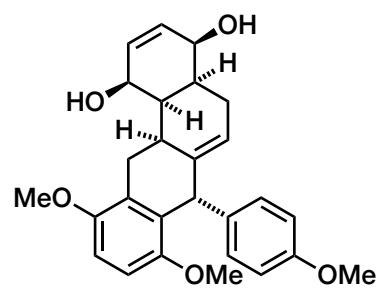
5p
400 MHz, CDCl_3



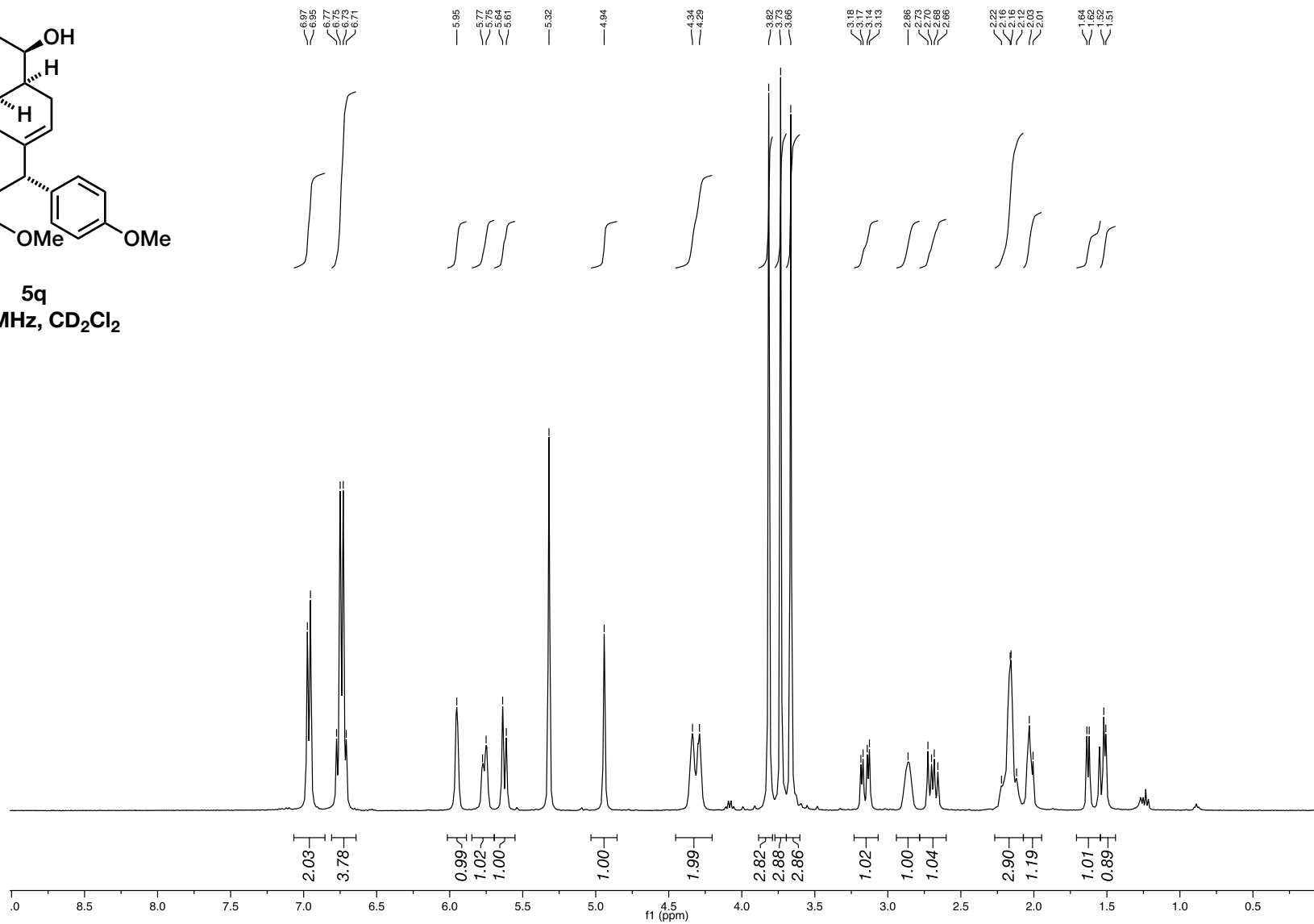


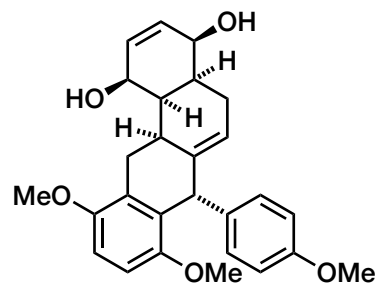
5p
100 MHz, CDCl₃



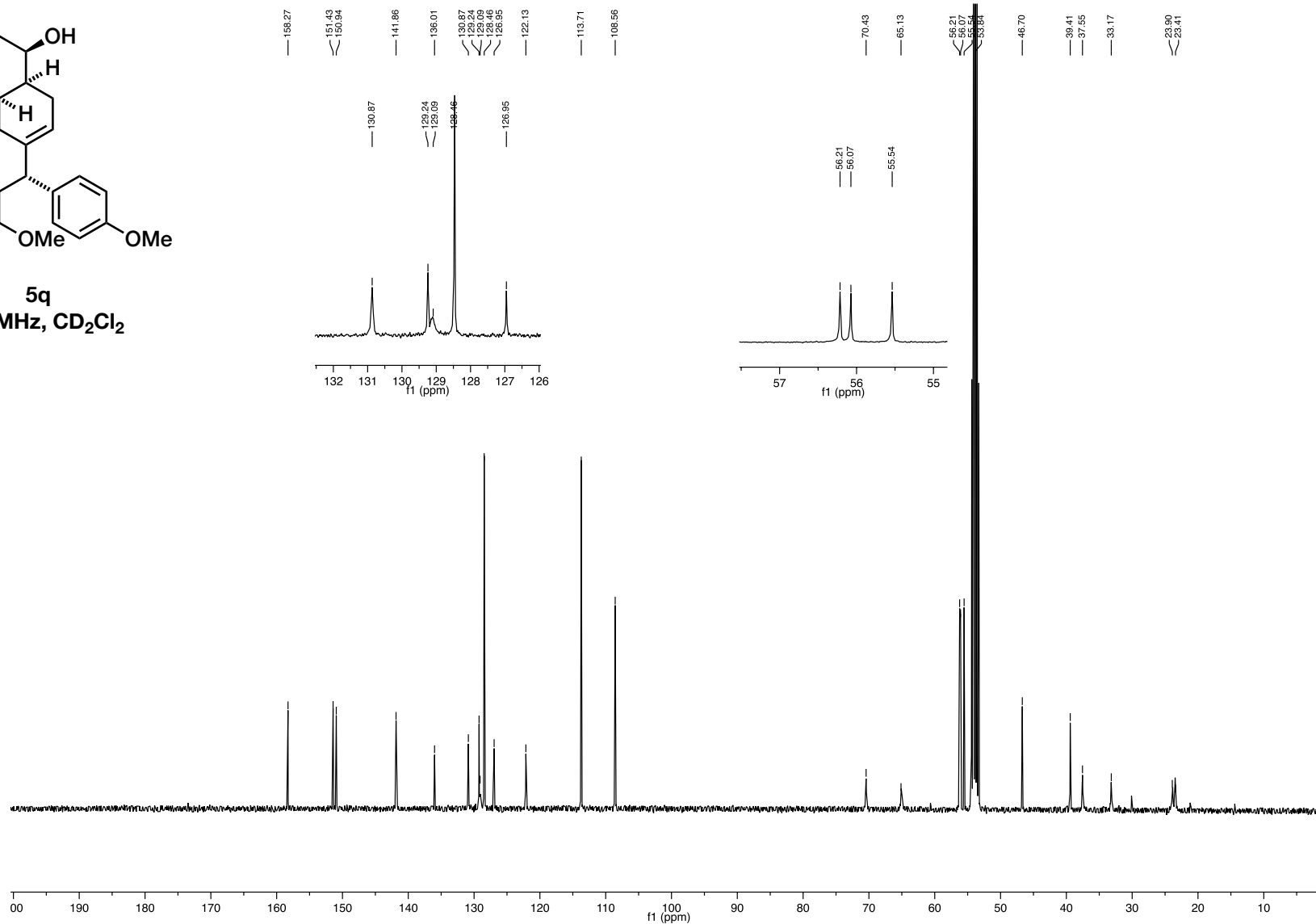


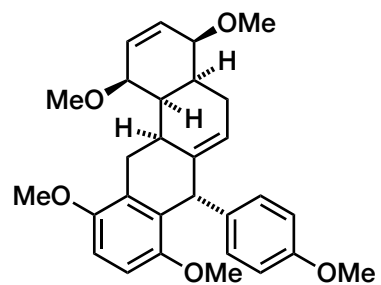
5q
400 MHz, CD₂Cl₂



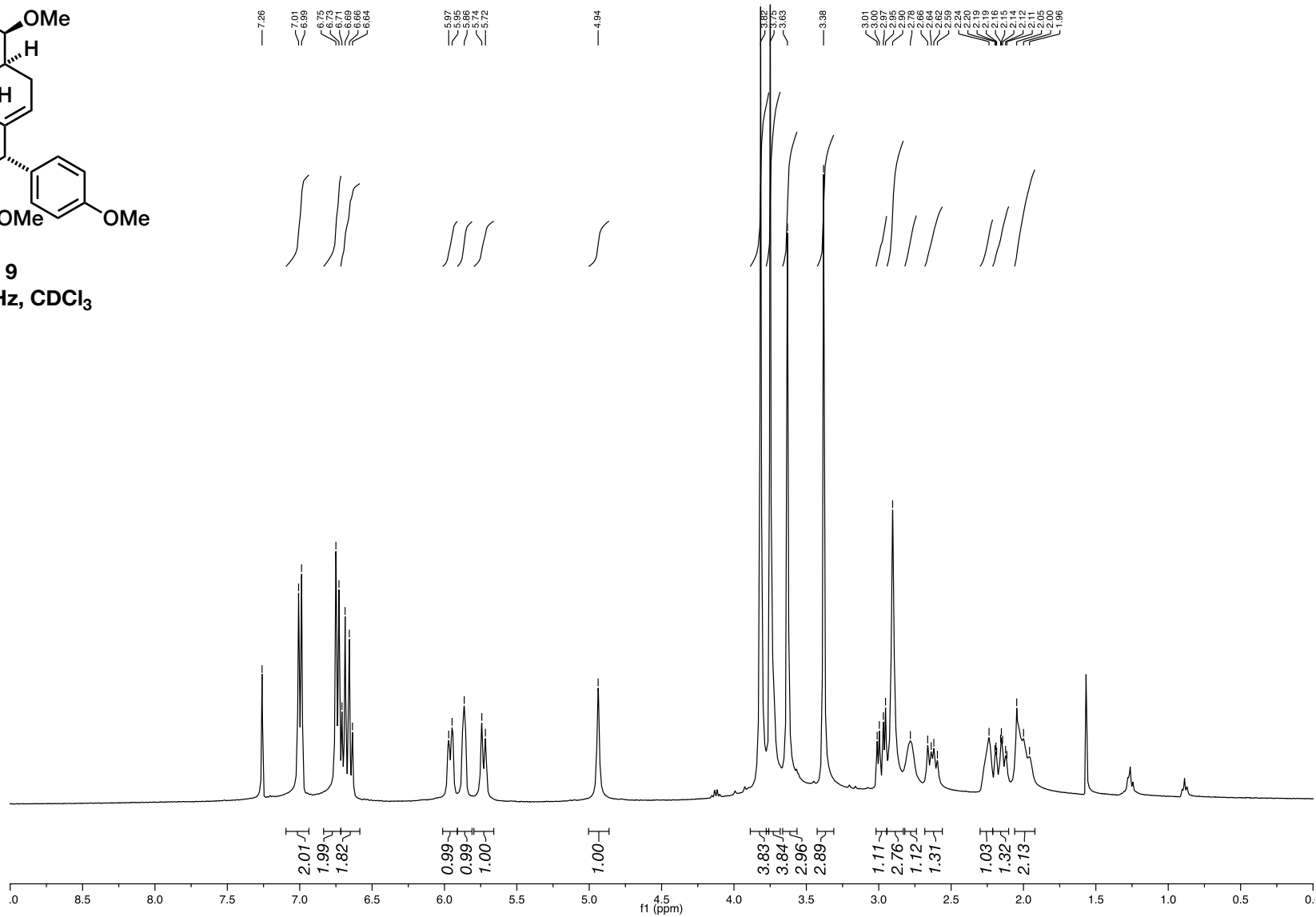


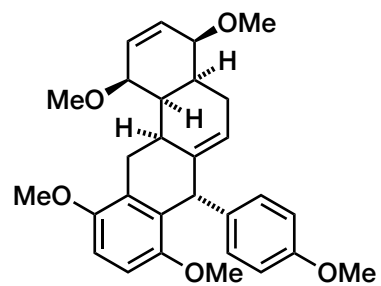
5q
100 MHz, CD₂Cl₂



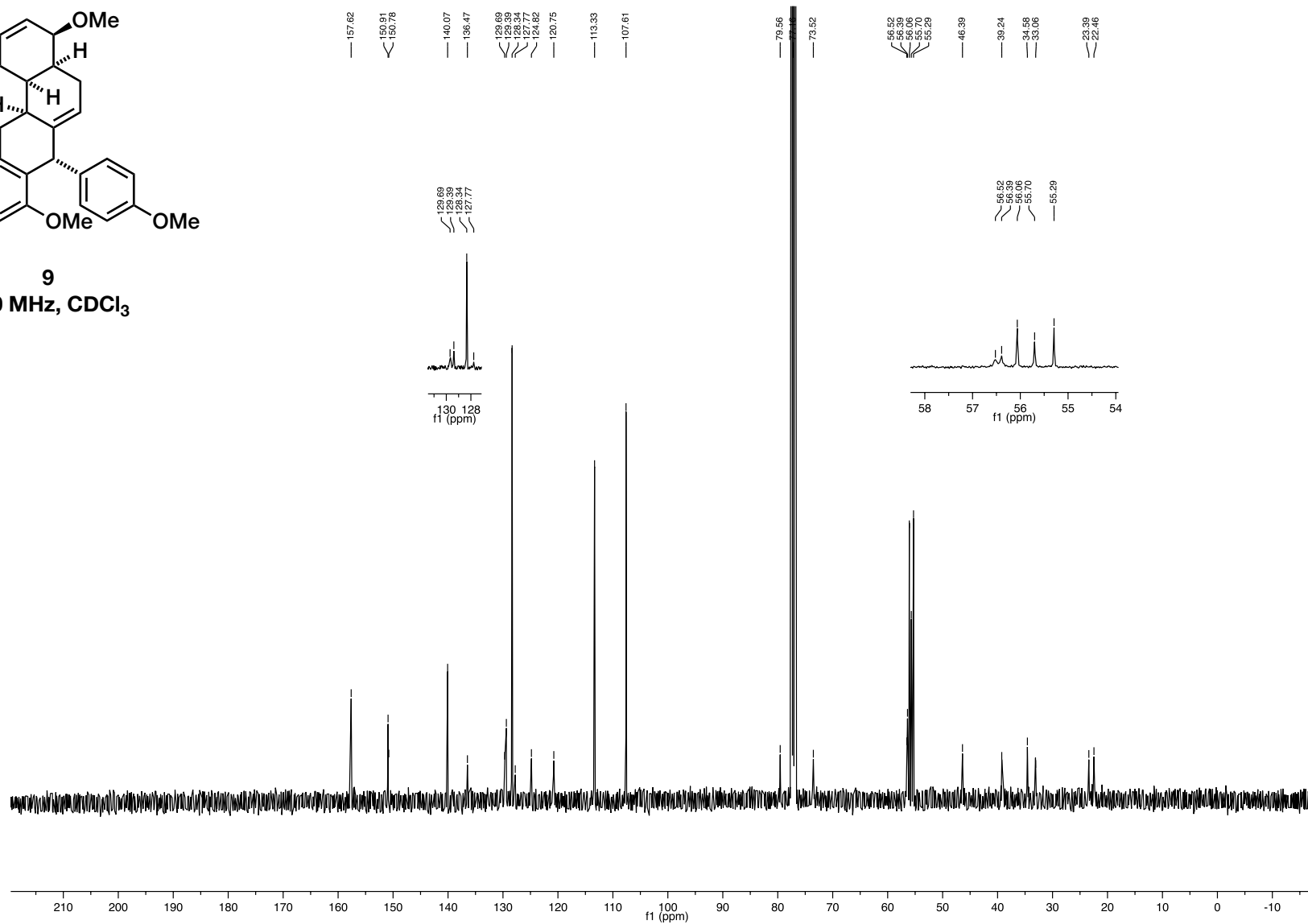


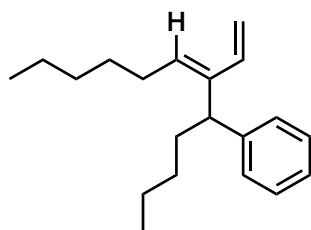
9
400 MHz, CDCl₃



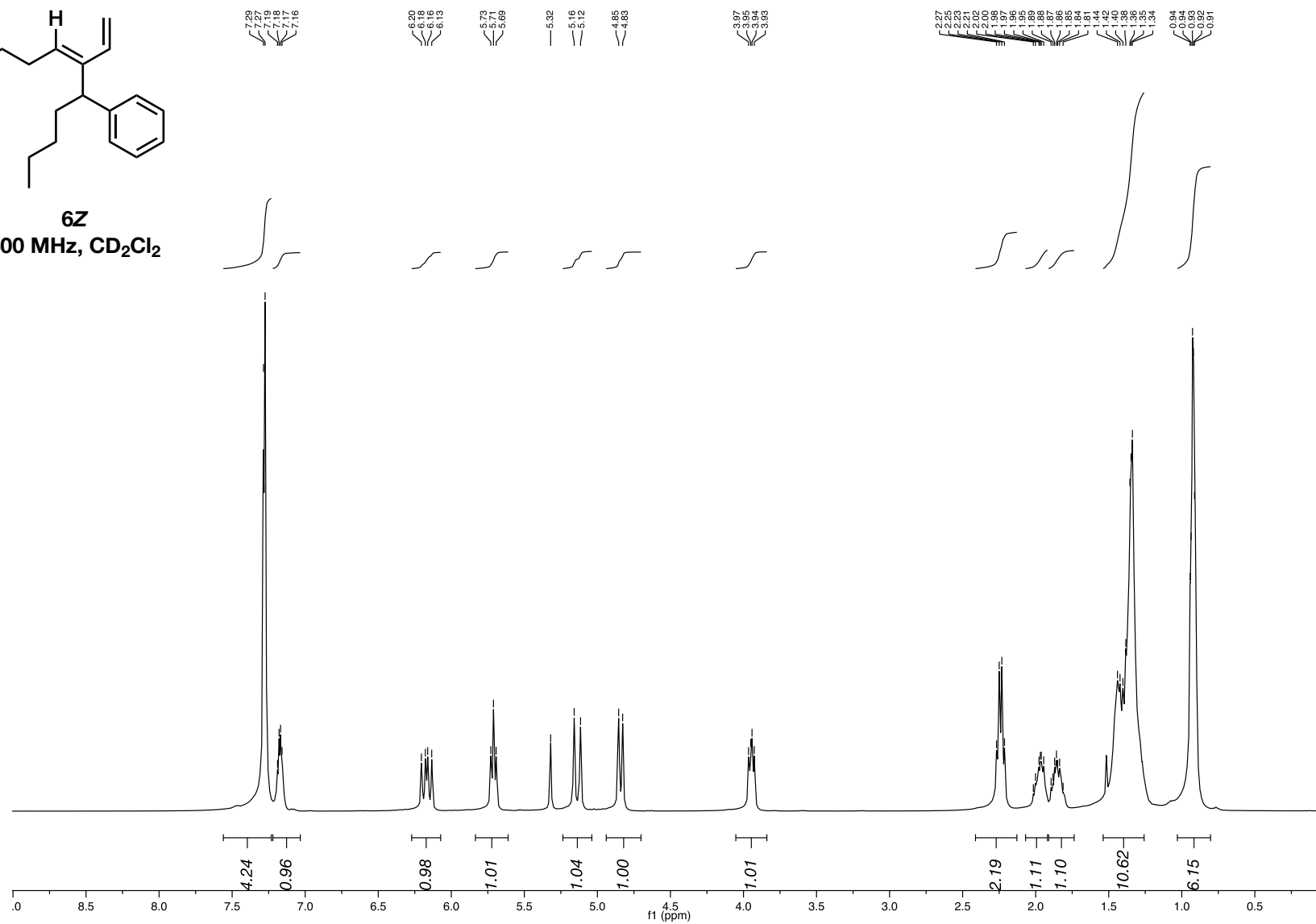


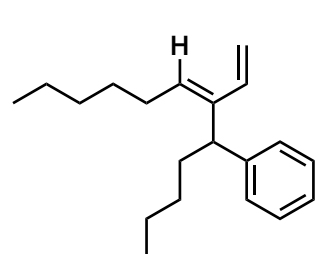
9
100 MHz, CDCl₃



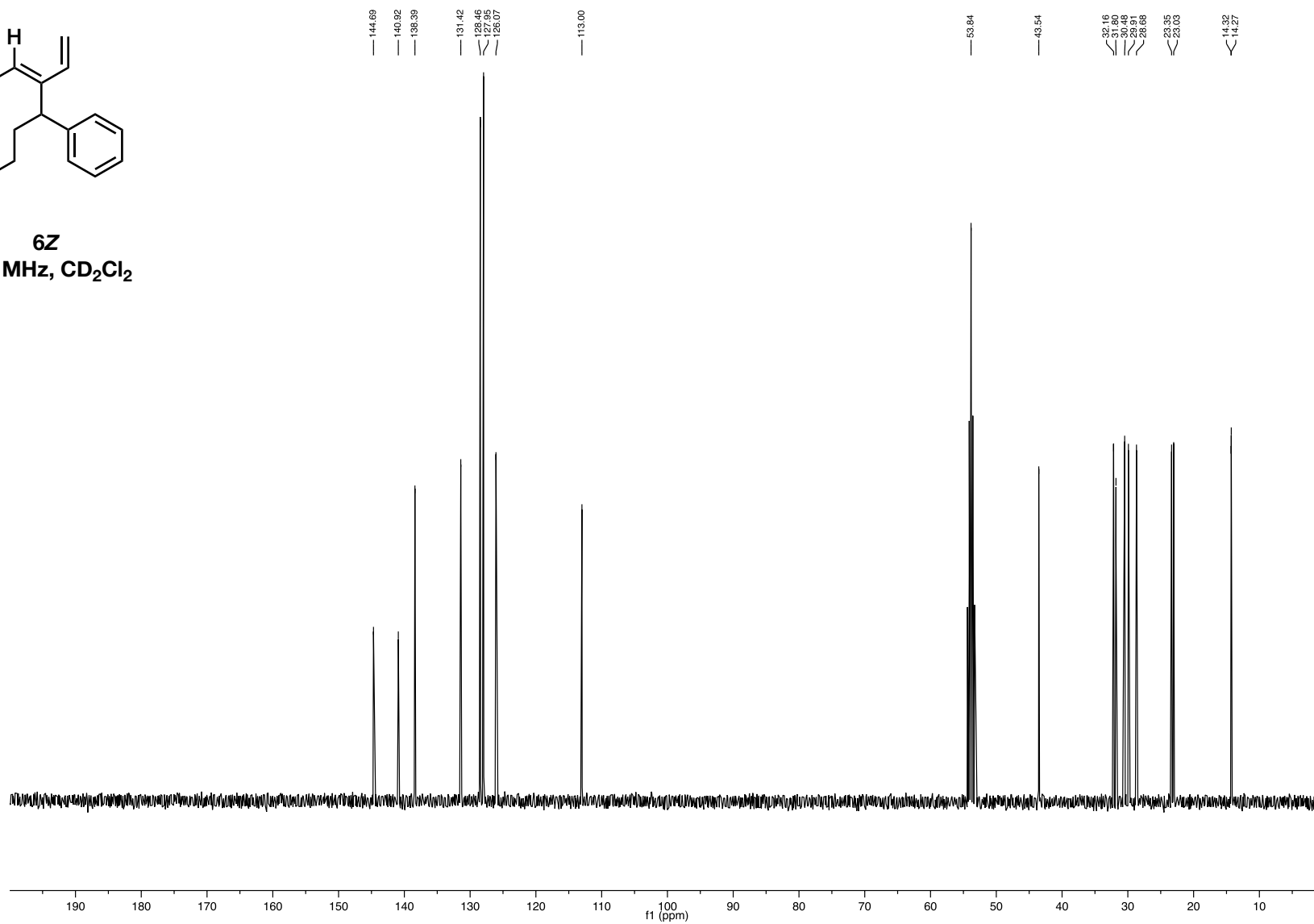


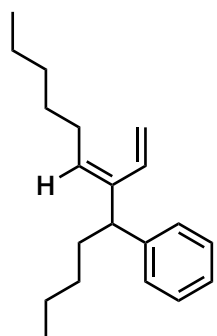
6Z
400 MHz, CD₂Cl₂





6Z
100 MHz, CD₂Cl₂





6E
400 MHz, CD₂Cl₂

