

Supporting information for

Synthesis of Highly Polarized [3]Dendralenes And Their Diels-Alder Reactions

Rastislav Antal, Monika Staš, Stefanie M. Perdomo, Marie Štemberová, Zbyněk Brůža,
Petr Matouš, Jiří Kratochvíl, Aleš Růžička, Lubomír Rulíšek, Jiří Kuneš, Pavel Kočovský,
Erik Andris* and Milan Pour*

R. Antal, S. M. Perdomo, M. Štemberová, Dr. Z. Brůža, Dr. P. Matouš, Dr. J. Kratochvíl, Prof. Dr. J. Kuneš, Prof. Dr. P. Kočovský,
Prof. Dr. M. Pour*
Department of Organic and Bioorganic Chemistry
Charles University, Faculty of Pharmacy in Hradec Králové
Heyrovského 1203, 500 05 Hradec Králové, Czech Republic
E-mail: pour@faf.cuni.cz

Dr. M. Staš, Prof. Dr. L. Rulíšek, Prof. Dr. P. Kočovský, Dr. E. Andris*
Institute of Organic Chemistry and Biochemistry
Academy of Science of the Czech Republic
Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic
E-mail: erik.andris@uochb.cas.cz

Dr. M. Staš
Faculty of Chemistry
University of Opole
48 Oleska Street, 45-052 Opole, Poland

Prof. Dr. A. Růžička
Department of General and Inorganic Chemistry
University of Pardubice, Faculty of Chemical Technology
Studentská 573, 532 10 Pardubice, Czech Republic

Prof. Dr. P. Kočovský
Department of Organic Chemistry
Charles University, Faculty of Science
Hlavova 8, 128 43 Prague 2, Czech Republic

Table of Contents

1 General Information	3
2 Experimental Section	4
2.1 Preparation of Catalysts	4
2.2 Preparation of Diene Coupling Partners (5 and 6)	5
2.3 Preparation of Stannylated Alkene Coupling Partners (5o–5s)	6
2.4 General Procedures for Migita-Stille Coupling: Preparation of Electron-Poor [3]Dendralenes (9a–9v).....	7
2.5 Selective Diels-Alder monoadditions of 9e and 9g.....	17
2.6 General procedure for DTDA reactions	18
2.7 Selective Second Stage Diels-Alder Cycloadditions	23
3. X-Ray Structures	24
4. Computational Section	27
4.1 Computational Details.....	27
4.2 CCSD(T) Benchmark.....	27
4.3 Tables S6 and S7	30
5. References	32
6. NMR spectra	34

1 General Information

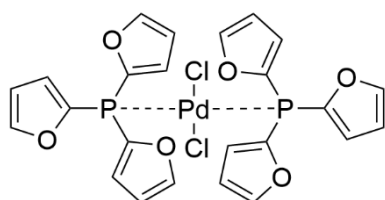
All reagents and solvents were purchased from Sigma-Aldrich (Merck, KGaA, Darmstadt, Germany) and used without further purification. Solvents (DCM, THF) were dried using the solvent purification system (PureSolv PS-Micro, Innovative Technologies). The reactions were carried out under Ar atmosphere in oven-dried glassware using Schlenk line techniques with magnetic stirring and dried solvents. TLC analyses were performed using Merck TLC Silica gel F254 plates and visualized by UV (254 nm) in combination with staining (using the solution of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (2 g), $\text{H}_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ (4 g), conc. H_2SO_4 (10 mL) and H_2O (200 mL) or KMnO_4 (1.5 g), K_2CO_3 (10 g), NaOH (1.5 g) and H_2O (200 mL) with subsequent heating). Column chromatography was carried out on a Merck Silica gel 60 (0.040–0.063 mm). ^1H , ^{13}C and ^{31}P NMR spectra were recorded with a Varian VNMR S500 or Jeol JNM-ECZ600R instrument. The chemical shifts were recorded as δ values in parts per million (ppm) reported relative to TMS and referenced to the residual solvent peaks; the chemical shifts in ^{31}P spectra were indirectly referenced to an 85% phosphoric acid external standard (0.00 ppm). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublets of doublets, m = multiplet. Coupling constants (J) are given in Hz. HR-MS data were recorded on a QTOF mass spectrometer using the electrospray ionization (Synapt G2Si Q-TOF, Waters, USA). ESI-MS spectra were obtained on an Agilent LC/MSD SL spectrometer or Expression^L CMS in connection with Plate Express®, Advion, Inc. (USA) instrument. IR spectra were recorded on a Nicolet 6700 FT-IR equipped with an ATR device. Melting points were determined on a Stuart SMP30 apparatus without correction. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was verified by the comparison of their NMR, IR, and MS data, and TLC behaviour.

2 Experimental Section

2.1 Preparation of Catalysts

The catalysts were synthesized according to modified literature procedure.^[1] A mixture of PdCl₂ (0.887 g, 5 mmol) and LiCl (0.424 g, 10 mmol) in MeOH (10 mL) was stirred at 50 °C for approximately 10 min until a homogeneous dark-red solution was formed. A phosphine ligand (**L**, 10.5 mmol) was added, and the resultant mixture was stirred at 50 °C until the red colour completely faded and a precipitate formed (ca 1 h). The reaction mixture was cooled down to RT, the precipitate filtered off, washed with MeOH (20 mL), and dried under vacuum to afford the desired catalysts in nearly quantitative yields. Two novel ([Pd(JohnPhos)₂Cl₂] and [Pd(CyJohnPhos)₂Cl₂]), and a known catalyst ([Pd(TFP)₂Cl₂]), were prepared.^[2] The complexes were also characterized by their melting points with decomposition (mpd) and temperature-dependant colour change.

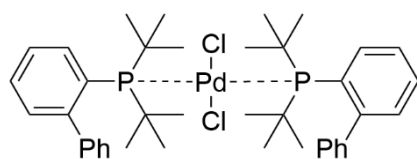
Dichloridobis[tris(furan-2-yl)phosphine]palladium(II) [Pd(TFP)₂Cl₂]



L: tri(furan-2-yl)phosphine (TFP, 2.438 g, 10.5 mmol); yellow powder, mpd 263.5–264.6 °C, from yellow to brown at around 219 °C, quantitative yield (3.202 g), mixture of *cis* and *trans* isomers (A:B 1:2); the former is a mixture of two rotamers (A' and A''). Spectral data were in agreement with those reported in the literature.^[2] ¹H NMR (500 MHz, CDCl₃):

δ 7.78–7.74 (m, isomer A, 6H), 7.57–7.53 (m, isomer B, 6H), 7.36–7.30 (m, isomer A, 6H), 7.08–7.03 (m, isomer B, 6H), 6.56–6.51 (m, isomer A, 6H), 6.45–6.40 (m, isomer B, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 149.0 (d, *J* = 3.0 Hz, isomer A'), 149.0 (d, *J* = 2.8 Hz, isomer A''), 148.7 (d, *J* = 6.7 Hz, isomer B), 140.9 (d, *J* = 92.0 Hz, isomers A + B), 125.9 (d, *J* = 11.5 Hz, isomer A'), 125.8 (d, *J* = 11.4 Hz, isomer A''), 125.4 (d, *J* = 20.7 Hz, isomer B), 111.5 (d, *J* = 9.1 Hz, isomer B), 111.3 (d, *J* = 4.1 Hz, isomer A'), 111.3 (d, *J* = 4.1 Hz, isomer A''); ³¹P NMR (202 MHz, CDCl₃): δ -22.37 (4/3P, isomer B), -29.16 (2/3P, isomer A); **IR** (ATR-Ge): ν_{max} 3114, 1548, 1450, 1368, 1261, 1168, 1126, 1064, 1013, 910, 882, 834, 750, 664, 646, 633 cm⁻¹.

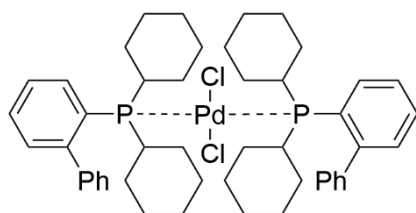
Dichloridobis[(biphenyl-2-yl)di-*t*-butylphosphine]palladium(II) [Pd(JohnPhos)₂Cl₂]



L: (biphenyl-2-yl)di-*t*-butylphosphine (JohnPhos, 3.133 g, 10.5 mmol); white powder, mpd 287.6–288.4 °C, no colour change, 99% yield (3.836 g), mixture of isomers;

¹H NMR (500 MHz, CDCl₃): δ 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43–7.28 (m, 12H), 7.20 (t, overlap, *J* = 7.6 Hz, 1H), 7.14 (t, overlap, *J* = 7.6 Hz, 1H), 7.04–6.97 (m, 2H), 1.38 (s, 9H), 1.34 (s, 18H), 1.31 (s, 9H); ¹³C NMR (126 MHz, CDCl₃): δ 142.4 (d, *J* = 115.0 Hz), 129.4, 129.2, 129.1, 129.1, 128.9, 127.8, 127.7, 127.5, 127.5, 127.4, 36.0 (d, *J* = 12.8 Hz), 35.9 (d, *J* = 12.8 Hz), 30.4, 30.4; ³¹P NMR (202 MHz, CDCl₃): δ -17.93 (2P); **IR** (ATR-Ge): ν_{max} 3052, 2973, 2961, 2896, 2866, 1567, 1535, 1495, 1471, 1456, 1440, 1390, 1366, 1178, 1139, 1101, 1072, 1041, 1026, 1016, 967, 938, 915, 812, 785, 758, 729, 702, 643, 625, 619 cm⁻¹.

Dichloridobis[(biphenyl-2-yl)dicyclohexylphosphine]palladium(II) [Pd(CyJohnPhos)₂Cl₂]



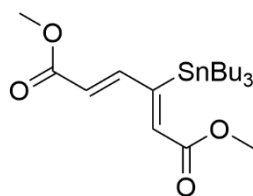
L: (biphenyl-2-yl)dicyclohexylphosphine (CyJohnPhos, 3.680 g, 10.5 mmol); golden yellow powder, mpd 327.8–328.9 °C, from golden yellow to gray at around 170 °C, 99% yield (4.342 g); ¹H and ¹³C NMR: spectra are not reported due to complete insolubility of the compound; **IR** (ATR-Ge): ν_{\max} 3051, 2931, 2854, 1541, 1496, 1447,

1428, 1327, 1291, 1231, 1175, 1131, 1074, 1007, 918, 897, 848, 771, 758, 745, 699, 672, 658, 649, 644, 637, 616 cm⁻¹.

2.2 Preparation of Diene Coupling Partners (5 and 6)

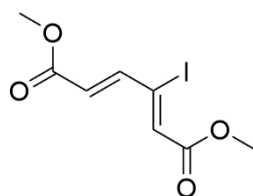
Both diene coupling partners **5** and **6** were synthesized from dimethyl (*E*)-hex-2-en-4-ynedioate **4**, which was prepared from methyl propiolate.^[3]

Dimethyl (2*Z*,4*E*)-3-(tributylstannyl)hexa-2,4-dienedioate (5)



Tributylstannane (26.9 mL, 100 mmol) was added dropwise to a solution of dimethyl (*E*)-hex-2-en-4-ynedioate **4** (16.815 g, 100 mmol) in anhydrous toluene (150 mL) under reflux. After 1 h at reflux, the reaction mixture was cooled down, and the solvent evaporated to dryness. The crude product was purified by column chromatography on silica gel (gradient elution, hexane → hexane/EtOAc 97 : 3) to afford the desired stannylated diene as a yellow oil, 80% yield (36.737 g); ¹H NMR (500 MHz, CDCl₃): δ 7.63 (dd, $J = 15.5$ Hz, $J = 1.5$ Hz, 1H), 6.55 (d, $J = 1.5$ Hz, 1H), 5.88 (d, $J = 15.5$ Hz), 3.77 (s, 3H), 3.77 (s, 3H), 1.56–1.37 (m, 6H), 1.34–1.23 (m, 6H), 1.13–0.94 (m, 6H), 0.88 (t, $J = 7.3$ Hz, 9H); ¹³C NMR (126 MHz, CDCl₃): δ 167.7, 166.8, 166.7, 150.6, 130.6, 119.8, 51.8, 51.7, 29.0, 27.3, 13.6, 11.8; **IR** (ATR-Ge): ν_{\max} 2954, 2922, 2871, 2853, 1724, 1710, 1621, 1463, 1434, 1321, 1302, 1268, 1200, 1183, 1167, 1080 cm⁻¹; **LR-MS** (APCI⁺): m/z (rel. intensity) 461.3 [M+H]⁺ (100), 403.1 [M-C₄H₉] (63); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₂₀H₃₆NaO₄Sn⁺ [M+Na]⁺ 483.1533, found 483.1528; configuration was assigned using the NOESY experiment.

Dimethyl (2*Z*,4*E*)-3-iodohexa-2,4-dienedioate (6)



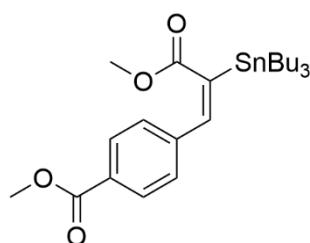
Modified literature conditions were used.^[4] A solution of dimethyl (*E*)-hex-2-en-4-ynedioate **4** (5.045 g, 30 mmol) and NaI (4.497 g, 30 mmol) in glacial acetic acid (17.2 mL, 300 mmol) was heated at 110 °C for 20 min. The reaction mixture was cooled down, diluted with Et₂O (100 mL) and washed with water (1 × 100 mL). The aqueous phase was reextracted with diethyl ether (1 × 50 mL). The combined organic phases were washed with a 5% solution of Na₂CO₃ (2 × 150 mL) and a saturated solution of Na₂S₂O₃ (1 × 150 mL). The organic layer was dried over anhydrous Na₂SO₄, evaporated to dryness, and the residue purified by recrystallization from hot Et₂O to afford the desired pure (*Z*)-isomer of iododiene **6** as white crystalline solid, mp 82.9–84.0 °C (EtOAc/hexane), 76% yield (6.750 g). All spectral data were in agreement with those reported in the literature.^[4] ¹H NMR (500 MHz, CDCl₃): δ 7.08 (d, $J = 14.8$ Hz, 1H), 6.80 (s, 1H), 6.49 (d, $J = 14.8$ Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 165.9, 164.7, 145.7, 132.7,

132.0, 110.7, 52.2, 52.1; **IR** (ATR-Ge): ν_{\max} 2955, 1722, 1698, 1435, 1297, 1232, 1177 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 297.1 [M+H]⁺ (100), 169.2 (50), 165.3 (34); **HR-MS** (TOF-ESI⁺): calcd. for C₇H₉IO₄⁺ [M+H]⁺ 296.9618, found 296.9627.

2.3 Preparation of Stannylated Alkene Coupling Partners (5o–5s)

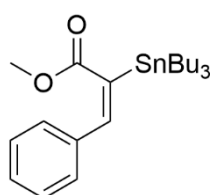
The starting propiolates were either purchased or prepared according to standard literature conditions, as specified below. Pd(PPh₃)₄ (0.02 eq) was suspended in dry THF (1 mL per 1 mmol of the propiolate) in a dry argon-filled flask, equipped with a stirring bar. A propiolate (1 mmol) was added to the mixture, and the resultant solution was placed in an ice bath. BHT-stabilized tributylstannane (1.05–1.1 eq) was slowly added dropwise, and the resultant mixture was stirred at RT until TLC showed complete consumption of the starting material. Solvent was evaporated, and the crude product purified by chromatography on silica gel using hexane as the eluent.

Methyl (*E*)-4-(3-methoxy-3-oxo-2-(tributylstannyl)prop-1-en-1-yl)benzoate (5o)



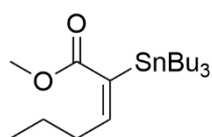
Starting with methyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate^[5] (0.872 g, 4.0 mmol). Reaction time 3 h. Yield 76% (1.54 g) of the product as a colourless oil. R_f = 0.55 (hexane/EtOAc 9 : 1). **¹H NMR** (500 MHz, CDCl₃) δ 8.02–7.96 (m, AA'BB', 2H), 7.39–7.32 (m, AA'BB', 2H), 6.75 (s, 1H), 3.92 (s, 3H), 3.69 (s, 3H), 1.65–1.47 (m, 6H), 1.37–1.33 (m, 6H), 1.16–1.00 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 173.3, 166.7, 142.8, 141.3, 140.9, 129.7, 129.3, 127.7, 52.1, 51.5, 28.7, 27.2, 13.7, 10.7; **IR** ν_{\max} 2955; 2927; 2871; 2852; 1723; 1607; 1463; 1434; 1278; 1208; 1191; 1179; 1108; 1018; 919; 794; 767; 697 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 453.2 [M–Bu]⁺ (100); 509.3 [M]⁺ (4); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₂₄H₃₈NaO₄Sn⁺ [M+Na]⁺ 533.1684; found 533.1698.

Methyl (*E*)-2-tributylstannyl-3-phenylacrylate (5p)



Starting with methyl 3-phenylpropiolate^[6] (1.2 mL, 8.11 mmol). Reaction time 1.5 h. Yield 77% (2.8 g) of the product as a colourless oil. R_f = 0.55 (hexane/EtOAc 9 : 1). All spectral data were in agreement with those reported in the literature.^[7] **¹H NMR** (500 MHz, CDCl₃) δ , 7.37–7.21 (m, 5H), 6.72 (s, 1H), 3.71 (s, 3H), 1.66–1.47 (m, 6H), 1.4–1.3 (m, 6H), 1.17–0.99 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 173.7, 142.2, 139.4, 136.9, 128.4, 128.1, 127.9, 51.4, 28.8, 27.2, 13.7, 10.6; **IR** ν_{\max} 2955; 2926; 2871; 2853; 1705; 1596; 1494; 1463; 1207; 1191; 1171; 1011; 929; 875; 754; 694; 615 cm^{-1} ; **HR-MS** (TOF-ESI⁺): m/z calcd. for C₂₂H₃₇O₂Sn⁺ [M+H]⁺ 453.1810; found 453.1818.

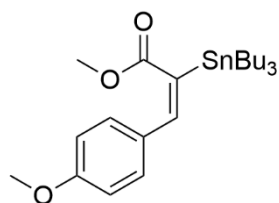
Methyl (*E*)-2-tributylstannylhex-2-enoate (5q)



Starting with methyl hex-2-ynoate^[6] (1.34 mL, 10 mmol). Reaction time 4 h. Yield 74% (3.1 g) of the product as a colourless oil. R_f = 0.50 (hexane). **¹H NMR** (600 MHz, CDCl₃) δ 6.08–5.94 (m, 1H), 3.67 (s, 3H), 2.41–2.33 (m, 2H), 1.55–1.39 (m, 8H) 1.32–1.25, (m, 8H), 0.94–0.84 (m, 16H); **¹³C NMR** (151 MHz, CDCl₃) δ 171.9, 153.4, 153.4, 135.6, 51.2, 34.2, 28.9, 27.3, 22.5, 13.8, 10.3; **IR** ν_{\max} 2956; 2927; 2872; 2854; 1712; 1603; 1464; 1431; 1376; 1355; 1191; 1130; 1072;

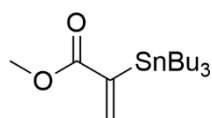
1046; 961; 914; 874; 768; 745; 690 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 361.2 [M-Bu]⁺ (100); 419.2 [M+H]⁺ (9).

Methyl (*E*)-2-tributylstannyl-3-(4-methoxyphenyl)acrylate (**5r**)



Starting with methyl *p*-methoxyphenylpropiolate^[8] (2.852 g, 15.0 mmol). Reaction time 2.5 h. Yield 82% (5.9 g) of the product as a colourless oil. R_f = 0.55 (hexane/EtOAc 9 : 1). All spectral data were in agreement with those reported in the literature.^[7] **¹H NMR** (500 MHz, CDCl_3) δ 7.31–7.24 (m, AA'BB', 2H), 6.89–6.81 (m, AA'BB', 2H), 6.65 (s, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 1.61–1.51 (m, 6H), 1.41–1.30 (m, 6H), 1.08–1.03 (m, 6H), 0.95–0.87 (m, 9H); **¹³C NMR** (126 MHz, CDCl_3) δ 159.5, 142.0, 136.4, 129.5, 126.3, 113.7, 55.3, 51.4, 28.8, 27.2, 13.7, 11.9, 10.6; **IR** ν_{max} 2954; 2924; 2871; 2851; 1701; 1604; 1509; 1463; 1442; 1431; 1293; 1252; 1207; 1169; 1114; 1034; 915; 822; 665 cm^{-1} ; **HR-MS** (TOF-ESI⁺): m/z calcd. for $\text{C}_{23}\text{H}_{38}\text{NaO}_3\text{Sn}^+$ [M+Na]⁺ 505.1735; found 505.1753.

Methyl 2-tributylstannylacrylate (**5s**)



Starting with methyl propiolate^[6] (1.775 mL, 20.0 mmol). Reaction time 4 h. Yield 82% (6.2 g) of the product as colourless oil. R_f = 0.50 (hexane). All spectral data were in agreement with those reported in the literature.^[9] **¹H NMR** (500 MHz, CDCl_3) δ 7.02–6.77 (m, 1H), 6.02–5.82 (m, 1H), 3.74 (s, 3H), 1.59–1.43 (m, 6H), 1.36–1.26 (m, 6H), 1.02–0.95 (m, 6H), 0.92–0.86 (m, 9H); **¹³C NMR** (126 MHz, CDCl_3) δ 170.9, 145.9, 139.8, 51.7, 28.9, 27.2, 13.7, 10.1; **IR** ν_{max} 3839; 3734; 3648; 3614; 3566; 2923; 2871; 2853; 1719; 1689; 1456; 1390; 1259; 1213; 1129; 1113; 962; 865 cm^{-1} .

2.4 General Procedures for Migita-Stille Coupling: Preparation of Electron-Poor [3]Dendralenes (**9a–9v**)

All [3]dendralenes were synthesized by the optimized Migita-Stille coupling reaction. Compounds **9a–9n** were prepared from the stannylated diene **5** and the corresponding iodoalkenes, which were either purchased or prepared according to standard literature conditions specified below. Pd(TFP)₂Cl₂ (Methods A and B), Pd(JohnPhos)₂Cl₂ (Method C), and Pd(CyJohnPhos)₂Cl₂ (Method D) were used as catalysts. The majority of the compounds **9a–9n** were prepared using Pd(TFP)₂Cl₂. The JohnPhos and CyJohnPhos ligands were suitable only for the coupling of the iodoalkenes with an ester group. While the efficiency of both Pd(TFP)₂Cl₂ and Pd(JohnPhos)₂Cl₂ were comparable in the preparation of **9a–9c**, the use of the latter led to a substantial increase of the yield of **9l**. For substrates without the ester group **9e** and **9g**, only the dimerization of the stannylated diene **5** was observed when Pd(JohnPhos)₂Cl₂ was used. Compounds **9a**, **9c**, **9e**, **9g**, and **9i** were also prepared on a large scale (Method B). Compounds **9o–9v** were synthesized from dimethyl (2*Z*,4*E*)-3-iodohexa-2,4-dienedioate **6** and the appropriate alkenyl stannanes according to the protocol of Kratochvíl et al.^[5] (Method E); iododiene **6** was used in excess (1.2 eq) due to the limited stability of the stannane coupling partners. The alkenyl stannanes **5o–5s** were prepared as described above, the remaining compounds (see the preparation of **9t**, **9u**, **9v** and **9w**) are commercially available. The methods and yields are summarized in **Table S1**.

Table S1: Yields of products.

[3]dendralene	Yield (%)				
	Method A	Method B	Method C	Method D	Method E
9a	84	82	80	79	-
9b	86	-	91	-	-
9c	80	79	75	-	-
9d	58	-	-	-	-
9e	60	60	dimer ~10	-	-
9f	73	-	-	-	-
9g	76	74	dimer ~10	-	-
9h	47	-	-	-	-
9i	65	62	-	-	-
9j	53	-	-	-	-
9k	46	-	-	-	-
9l	28	-	53	51	-
9m	48	-	21	-	-
9n	57	-	18	-	-
9o	-	-	-	-	70
9p	-	-	-	-	79
9q	-	-	-	-	78
9r	-	-	-	-	57
9s	-	-	-	-	30
9t	-	-	-	-	82
9u	-	-	-	-	60
9v	-	-	-	-	34
9w	-	-	-	-	10

Method A: A 2.5 M solution of *n*-BuLi in THF (48 μ L, 0.12 mmol) was added dropwise to a suspension of [Pd(TFP)₂Cl₂] (38.5 mg, 0.06 mmol) and CuI (0.343 g, 1.8 mmol) in anhydrous THF (2 mL) at -78 °C. The resultant mixture was gradually allowed to warm up to -30 °C over 3 h. After 15 min at this temperature, the solution of an iodoalkene (2.5 mmol) in anhydrous DMF (2 mL) was cannulated into the reaction mixture, and after another 15 min, a solution of dimethyl (2*Z*,4*E*)-3-(tributylstannyl)hexa-2,4-dienedioate **5** (0.918 g, 2 mmol) in anhydrous DMF (2 mL) was added. The cooling bath was then removed, the reaction mixture stirred overnight, diluted with EtOAc (20 mL) and washed with a saturated solution of NH₄Cl (2 \times 20 mL). The aqueous phases were extracted with EtOAc (10 mL), and the combined organic phases washed with a 4% solution of NaF (2 \times 30 mL). The precipitate formed was removed by filtration, the solution dried over Na₂SO₄, and the solvent evaporated. Purification of the residue by column chromatography on silica gel, using gradient elution with a mixture of hexane/EtOAc (hexane \rightarrow hexane : EtOAc) afforded the corresponding [3]dendralene.

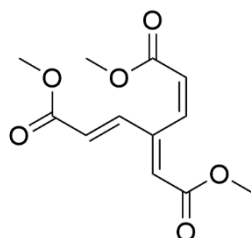
Method B: Identical to Method A, performed on a larger scale. Reagent amount: 2.5 M solution of *n*-BuLi in THF (240 μ L, 0.6 mmol), [Pd(TFP)₂Cl₂] (192.5 mg, 0.3 mmol), CuI (1.714 g, 9 mmol), anhydrous THF (10 mL), the solution of an iodoalkene (12.5 mmol) in anhydrous DMF (10 mL) and a solution of dimethyl (2*Z*,4*E*)-3-(tributylstannyl)hexa-2,4-dienedioate **5** (4.592 g, 10 mmol) in anhydrous DMF (10 mL).

Method C: Identical to Method A, Pd(JohnPhos)₂Cl₂ was used instead of Pd(TFP)₂Cl₂. Reagent amount: 2.5 M solution of *n*-BuLi in THF (24 μ l, 0.06 mmol), [Pd(JohnPhos)₂Cl₂] (23.2 mg, 0.03 mmol), CuI (0.191 g, 0.9 mmol) in anhydrous THF (1 mL), the solution of an iodoalkene (1.25 mmol) in anhydrous DMF (1 mL), a solution of dimethyl (2*Z*,4*E*)-3-(tributylstannyl)hexa-2,4-dienedioate **5** (0.459 g, 1 mmol) in anhydrous DMF (1 mL).

Method D: Identical to Method C, Pd(CyJohnPhos)₂Cl₂ (26.3 mg, 0.03 mmol) was used instead of Pd(JohnPhos)₂Cl₂.

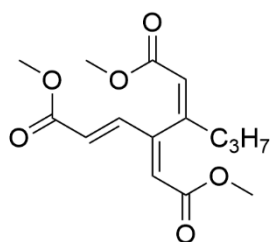
Method E: Pd black (0.07 mmol, 7.5 mg) was added to a solution of dimethyl (2*Z*,4*E*)-3-iodohexa-2,4-dienedioate **6** (1.243 g, 4.2 mmol) and an alkenyl stannane (3.5 mmol) in DMF (7 mL). The resultant mixture was heated at 70 °C with vigorous stirring until TLC analysis indicated complete consumption of the stannane. The catalyst was then filtered off, rinsed with EtOAc (15 mL) and the filtrate worked up as described in Method A.

Dimethyl (2*Z*,5*E*)-4-((*Z*)-2-methoxy-2-oxoethylidene)hepta-2,5-dienedioate (**9a**)



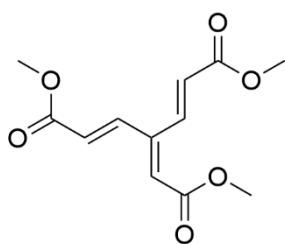
Method A, B, C, D: methyl (*Z*)-3-iodoacrylate^[5] (0.530 g, 2.5 mmol for A; 2.650 g, 12.5 mmol for B; 0.212 g, 1.25 mmol for C and D); elution with hexane/EtOAc (hexane \rightarrow 9 : 1), white crystalline solid, mp 82.9–84.0 °C (EtOAc/hexane), A – 84% yield (0.427 g), B – 82% yield (2.084 g), C – 80% yield (0.204 g), D – 79% (0.200 g). All spectral data were in agreement with those reported in the literature^[10] for dracomolphesin C: ¹H NMR (500 MHz, CDCl₃): δ 7.37 (d, *J* = 15.8 Hz, 1H), 6.95 (dd, *J* = 12.0 Hz, *J* = 2.0 Hz, 1H), 6.15 (d, *J* = 12.0 Hz, 1H), 6.12 (d, *J* = 2.0 Hz, 1H), 6.07 (d, *J* = 15.8 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 166.4, 165.7, 165.1, 148.5, 143.1, 139.8, 124.4, 123.9, 122.9, 51.9, 51.7, 51.5; IR (ATR-Ge): ν_{max} 3080, 3001, 2950, 1731, 1715, 1702, 1647, 1629, 1590, 1457, 1441, 1435, 1412, 1360, 1318, 1293, 1229, 1174, 1155, 1003 cm⁻¹; LR-MS (APCI⁺): *m/z* (rel. intensity) 536.4 (16), 255.0 [M+H]⁺ (100), 223.0 [M+H-CH₃OH]⁺ (90); HR-MS (TOF-ESI⁺): *m/z* calcd. for C₁₂H₁₄NaO₆⁺ [M+Na]⁺ 277.0683, found 277.0692, C₁₁H₁₁O₅⁺ [M+H-CH₃OH]⁺ 223.0601, found 223.0610.

Dimethyl (2*Z*,5*E*)-4-((*Z*)-2-methoxy-2-oxoethylidene)-3-propylhepta-2,5-dienedioate (**9b**)



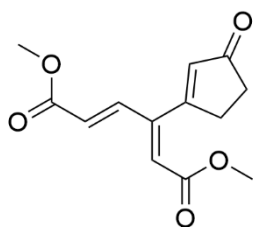
Method A, C: methyl (*Z*)-3-iodohex-2-enoate^[5] (0.635 g, 2.5 mmol for A; 0.318g, 1.25 mmol for C); elution with hexane/EtOAc (hexane \rightarrow 85 : 15); yellowish amorphous solid, A – 86% yield (0.512 g), C – 91% yield (0.269 g); ¹H NMR (500 MHz, CDCl₃): δ 7.35 (d, *J* = 15.8 Hz, 1H), 6.07 (s, 1H), 5.98 (d, *J* = 15.8, 1H), 5.95 (s, 1H) 3.76 (s, 3H), 3.70 (s, 3H), 3.61 (s, 3H), 2.41–2.14 (m, 2H) 1.62–1.48 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 166.4, 165.3, 165.2, 156.0, 153.4, 143.5, 124.1, 122.9, 117.0, 51.9, 51.5, 51.1, 39.8, 20.1, 13.8; IR (ATR-Ge): ν_{max} 2954, 1711, 1650, 1623, 1598, 1455, 1435, 1406, 1329, 1309, 1285, 1229, 1193, 1169, 1079, 1002 cm⁻¹; LR-MS (APCI⁺): *m/z* (rel. intensity) 578.4 (15), 297.1 [M+H]⁺ (100), 265.0 [M+H-CH₃OH]⁺ (65); HR-MS (TOF-ESI⁺): *m/z* calcd. for C₁₅H₂₀NaO₆⁺ [M+Na]⁺ 319.1152, found 319.1164, C₁₄H₁₇O₅⁺ [M+H-CH₃OH]⁺ 265.1071, found 265.1082.

Dimethyl (2*E*,5*E*)-4-(2-methoxy-2-oxoethylidene)hepta-2,5-dienedioate (9c):



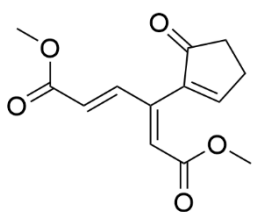
Method A, B, C: methyl (*E*)-3-iodoacrylate^[5] (0.530 g, 2.5 mmol for A; 2.650 g, 12.5 mmol for B; 0.212 g, 1.25 mmol for C); elution with hexane/EtOAc (hexane → 9 : 1), white amorphous solid, A – 80% yield (0.406 g), B – 78% yield (1.982 g), C – 75% yield (0.191 g); **¹H NMR** (500 MHz, CDCl₃): δ 8.30 (d, *J* = 16.4 Hz, 1H), 7.43 (d, *J* = 15.8 Hz, 1H), 6.28 (d, *J* = 15.8 Hz, 1H), 6.18 (d, overlap, *J* = 16.4 Hz, 1H), 6.17 (s, 1H), 3.81 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.2, 166.0, 165.3, 145.7, 141.8, 138.4, 125.9, 125.4, 124.1, 52.1, 52.0, 51.9; **IR** (ATR-Ge): ν_{\max} 3063, 2952, 1716, 1643, 1586, 1449, 1432, 1374, 1327, 1276, 1250, 1217, 1205, 1181, 1165, 1035, 1014 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 536.4 (29), 509.2 [2M+H]⁺ (42), 287.0 (30), 255.0 [M+H]⁺ (100), 223.0 [M+H-CH₃OH]⁺ (67); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₂H₁₄NaO₆⁺ [M+Na]⁺ 277.0683, found 277.0695, C₁₁H₁₁O₅⁺ [M+H-CH₃OH]⁺ 223.0601, found 223.0612.

Dimethyl (2*Z*,4*E*)-3-(3-oxocyclopent-1-en-1-yl)hexa-2,4-dienedioate (9d):



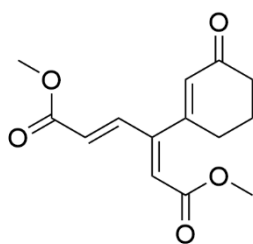
Method A: 3-iodocyclopent-2-en-1-one^[11] (0.520 g, 2.5 mmol); elution with hexane/EtOAc (hexane → 8 : 2); beige crystalline solid, mp 122.7–124.2 °C (EtOAc/hexane; decomposition at 111.3 °C); 58% yield (0.292 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.36 (d, *J* = 15.8 Hz, 1H), 6.12 (s, 1H), 6.02 (s, 1H), 6.00 (d, overlap, *J* = 15.8 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.86–2.80 (m, 2H), 2.60–2.55 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃): δ 208.3, 172.7, 166.0, 164.7, 148.4, 142.1, 132.4, 126.1, 124.5, 52.1, 52.0, 35.2, 31.8; **IR** (ATR-Ge): ν_{\max} 3068, 2955, 1699, 1673, 1634, 1609, 1584, 1435, 1398, 1368, 1313, 1274, 1252, 1239, 1227, 1192, 1175, 1057, 1041, 1008 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 532.4 (28), 501.3 [2M+H]⁺ (78), 282.8 (14), 251.0 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₃H₁₅O₅⁺ [M+H]⁺ 251.0914, found 251.0921, C₁₂H₁₁O₄⁺ [M+H-CH₃OH]⁺ 219.0652, found 219.0659.

Dimethyl (2*Z*,4*E*)-3-(5-oxocyclopent-1-en-1-yl)hexa-2,4-dienedioate (9e):



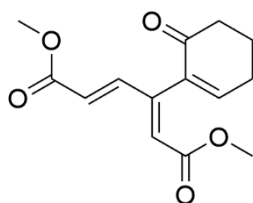
Method A, B: 2-iodocyclopent-2-en-1-one^[12] (0.520g, 2.5 mmol for A; 2.600 g, 12.5 mmol for B); elution with hexane/EtOAc (hexane → 8 : 2); white crystalline solid, mp 93.8–94.2 °C (EtOAc/hexane); A – 60% yield (0.298 g), B – 60% yield (1.502 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.48 (t, *J* = 2.8 Hz, 1H), 7.40 (d, *J* = 15.6 Hz, 1H), 6.27 (s, 1H), 5.96 (d, *J* = 15.6 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.84–2.78 (m, 2H), 2.61–2.56 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃): δ 205.3, 166.2, 165.2, 160.1, 144.3, 142.8, 141.3, 127.1, 125.2, 52.0, 51.7, 34.3, 27.3; **IR** (ATR-Ge): ν_{\max} 1726, 1706, 1643, 1624, 1586, 1433, 1387, 1314, 1294, 1252, 1226, 1210, 1189, 1171 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 532.5 (34), 502.2 (43), 501.4 [2M+H]⁺ (59), 277.1 (31), 251.1 [M+H]⁺ (100), 219.0 [M+H-CH₃OH]⁺ (89); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₃H₁₄NaO₅⁺ [M+Na]⁺ 273.0733, found 273.0743.

Dimethyl (2Z,4E)-3-(3-oxocyclohex-1-en-1-yl)hexa-2,4-dienedioate (9f):



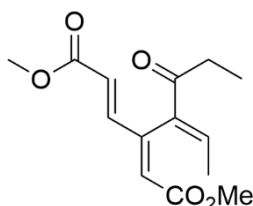
Method A: 3-iodocyclohex-2-en-1-one^[11] (0.555 g, 2.5 mmol); elution with hexane/EtOAc (hexane → 8 : 2); beige crystalline solid, mp 103.1–103.9 °C (EtOAc/hexane); 73% yield (0.385 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.31 (d, *J* = 15.8 Hz, 1H), 6.04 (s, 1H), 6.04 (d, overlap, *J* = 15.8 Hz, 1H), 5.78 (s, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.54–2.49 (m, 2H), 2.48–2.43 (m, 2H), 2.23–2.14 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃): δ 198.4, 166.1, 164.8, 158.4, 151.2, 142.6, 127.7, 126.0, 124.0, 52.1, 51.9, 37.2, 29.7, 22.8; **IR** (ATR-Ge): ν_{\max} 3071, 2953, 1716, 1706, 1662, 1634, 1611, 1589, 1507, 1442, 1434, 1413, 1399, 1351, 1335, 1311, 1271, 1258, 1225, 1189, 1167, 1138, 1074, 1036, 1008 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 546.4 (35), 530.3 (53), 529.4 [2M+H]⁺ (64), 265.3 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₄H₁₇O₅⁺ [M+H]⁺ 265.1071, found 265.1079, C₁₄H₁₆NaO₅⁺ [M+Na]⁺ 287.0890, found 287.0896, C₁₃H₁₃O₄⁺ [M+H-CH₃OH]⁺ 233.0809, found 233.0819.

Dimethyl (2Z,4E)-3-(6-oxocyclohex-1-en-1-yl)hexa-2,4-dienedioate (9g):



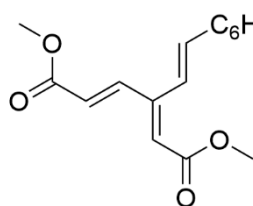
Method A, B: 2-iodocyclohex-2-en-1-one^[12] (0.555 g, 2.5 mmol for A; 2.775 g, 12.5 mmol for B); elution with hexane/EtOAc (hexane → 8 : 2); white crystalline solid, mp 108.3–109.4 °C (EtOAc/hexane); A – 76% yield (0.401 g), B – 74% yield (1.956 g); **¹H NMR** (600 MHz, CDCl₃): δ 7.36 (d, *J* = 15.7 Hz, 1H), 6.65 (t, *J* = 4.1 Hz, 1H), 6.17 (s, 1H), 5.96 (d, *J* = 15.7 Hz, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.60–2.54 (m, 2H), 2.51–2.46 (m, 2H), 2.16–2.08 (m, 2H); **¹³C NMR** (151 MHz, CDCl₃): δ 196.4, 166.5, 165.4, 147.7, 147.2, 145.2, 136.3, 126.5, 125.3, 52.0, 51.7, 38.4, 26.1, 22.8; **IR** (ATR-Ge): ν_{\max} 2955, 2882, 1715, 1706, 1672, 1639, 1597, 1559, 1508, 1432, 1426, 1398, 1340, 1314, 1265, 1258, 1221, 1172, 1155, 1131, 1121, 1071, 1041, 1013 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 530.3 (34), 529.4 [2M+H]⁺ (49), 277.1 (36), 265.1 [M+H]⁺ (100), 233.1 [M+H-CH₃OH]⁺ (85), 205.0 (24); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₄H₁₆NaO₅⁺ [M+Na]⁺ 287.0890, found 287.0901, C₁₃H₁₃O₄⁺ [M+H-CH₃OH]⁺ 233.0809, found 233.0820.

Dimethyl (2Z,4E)-3-((E)-4-oxohex-2-en-3-yl)hexa-2,4-dienedioate (9h):



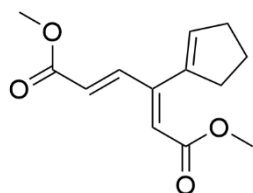
Method A: (Z)-4-iodohex-4-en-3-one^[12] (0.560 g, 2.5 mmol); elution with hexane/EtOAc (hexane → 8 : 2); yellow oil; 47% yield (0.251 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.40 (d, *J* = 15.6 Hz, 1H), 6.96 (q, *J* = 7.0 Hz, 1H), 6.30 (s, 1H), 5.93 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.75–2.62 (m, 2H), 1.67 (d, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 198.7, 166.4, 165.1, 148.1, 143.8, 138.3, 137.8, 127.2, 125.2, 51.9, 51.6, 31.2, 15.5, 8.1; **IR**: (ATR-Ge) ν_{\max} 2952, 1717, 1674, 1629, 1600, 1559, 1540, 1517, 1507, 1490, 1458, 1435, 1405, 1374, 1349, 1304, 1276, 1228, 1193, 1169, 1153, 1107, 1060, 1038, 1006 cm⁻¹; **LR-MS**: (APCI⁺): *m/z* (rel. intensity) 360.3 (15), 345.2 (28), 269.3 (26), 267.1 [M+H]⁺ (100), 235.1 (43); **HR-MS**: (TOF-ESI⁺): *m/z* calcd. for C₁₄H₁₈O₅Na⁺ [M+Na]⁺ 289.1046, found 289.1054.

Dimethyl (2*E*,4*E*)-3-((*E*)-oct-1-en-1-yl)hexa-2,4-dienedioate (9i):



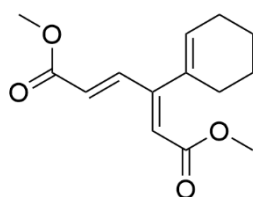
Method A, B: (*E*)-1-iodooct-1-ene ^[6] (2.5 mmol, 0.595 g for A; 12.5 mmol, 2.976 g for B); elution with hexane/EtOAc (hexane → 97 : 3); yellowish oil; A – 65% yield (0.365 g), B – 62% yield (1.737 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.51 (d, *J* = 15.7 Hz, 1H), 7.31 (d, *J* = 16.1, 1H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.14 (dt, *J* = 16.1 Hz, *J* = 7.1 Hz, 1H), 5.85 (s, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 2.23 (q, *J* = 7.1 Hz, 2H), 1.50–1.40 (m, 2H), 1.37–1.24 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.5, 166.3, 149.0, 143.9, 141.6, 125.2, 123.9, 116.7, 51.9, 51.4, 33.5, 31.6, 28.9, 28.8, 22.5, 14.0; **IR** (ATR-Ge): ν_{\max} 2952, 2927, 2856, 1716, 1635, 1587, 1433, 1376, 1310, 1272, 1225, 1192, 1156, 1037, 1011 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 562.4 (16), 561.4 [2M+H]⁺ (25), 281.1 (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₇H₂₄O₄⁺ [M+H]⁺ 281.1747, found 281.1757, C₁₅H₂₁O₃⁺ [M+H-CH₃OH]⁺ 249.1485, found 249.1495.

Dimethyl (2*Z*,4*E*)-3-(cyclopent-1-en-1-yl)hexa-2,4-dienedioate (9j):



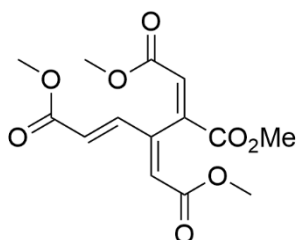
Method A: 1-iodocyclopent-1-ene ^[13] (0.485 g, 2.5 mmol); elution with hexane/EtOAc (hexane → 95 : 5); yellowish crystalline solid, mp 44.6–45.2 °C (EtOAc/hexane); 53% yield (0.250 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.30 (d, *J* = 15.6 Hz, 1H), 6.13 (d, *J* = 15.6 Hz, 1H), 6.01 (s, 1H), 5.58–5.55 (m, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.55–2.47 (m, 4H), 2.06–1.96 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.8, 165.6, 150.4, 145.3, 138.1, 130.5, 125.1, 124.1, 51.9, 51.5, 36.2, 33.5, 23.9; **IR** (ATR-Ge): ν_{\max} 2954, 2846, 1720, 1713, 1684, 1623, 1584, 1559, 1507, 1434, 1391, 1305, 1296, 1225, 1201, 1172, 1155, 1070, 1039, 1003 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 354.4 (14), 237.1 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₃H₁₇O₄⁺ [M+H]⁺ 237.1121, found 237.1129, C₁₂H₁₃O₃⁺ [M+H-CH₃OH]⁺ 205.0859, found 205.0867.

Dimethyl (2*Z*,4*E*)-3-(cyclohex-1-en-1-yl)hexa-2,4-dienedioate (9k):



Method A: 1-iodocyclohex-1-ene ^[13] (0.520 g, 2.5 mmol); elution with hexane/EtOAc (hexane → 95 : 5); yellowish crystalline solid, mp 66.9–67.2 °C (EtOAc/hexane); 46% yield (0.231 g); **¹H NMR** (600 MHz, CDCl₃): δ 7.24 (d, *J* = 15.5 Hz, 1H), 6.16 (d, *J* = 15.5 Hz, 1H), 5.92 (s, 1H), 5.45–5.37 (m, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 2.16–2.09 (m, 2H), 2.08–2.02 (m, 2H), 1.78–1.70 (m, 2H), 1.69–1.61 (m, 2H); **¹³C NMR** (151 MHz, CDCl₃): δ 167.0, 165.7, 155.1, 145.7, 133.5, 126.1, 125.2, 124.0, 51.9, 51.5, 28.5, 25.1, 22.7, 21.9; **IR** (ATR-Ge): ν_{\max} 2948, 1717, 1627, 1590, 1439, 1391, 1308, 1293, 1267, 1218, 1195, 1160, 1077, 1005 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 251.1 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₄H₁₉O₄⁺ [M+H]⁺ 251.1278, found 251.1286, C₁₃H₁₅O₃⁺ [M+H-CH₃OH]⁺ 219.1016, found 219.1022.

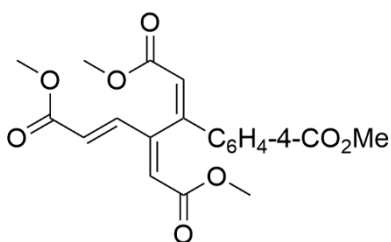
Dimethyl (2Z, 5E)-3-(methoxy-3-oxomethyl)-4-((Z)-2-methoxy-2-oxoethylidene)hepta-2,5-dienedioate (9l):



Method A, C, D: dimethyl 2-iodofumarate ^[14] (0.675 g, 2.5 mmol for A; 0.338 g, 1.25 mmol for C and D); elution with hexane/EtOAc (hexane → 8 : 2); white crystalline solid, mp 110.0–112.0 °C (EtOAc/hexane); A – 28% yield (0.177 g), C – 53% yield (0.166 g), D – 51% yield (0.160 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.46 (d, *J* = 15.8 Hz, 1H), 7.05 (s, 1H), 6.26 (s, 1H), 5.93 (d, *J* = 15.8 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H);

¹³C NMR (126 MHz, CDCl₃): δ 166.2, 165.5, 164.4, 164.3, 146.8, 143.2, 141.6, 128.6, 125.8, 124.3, 53.1, 52.1, 51.9, 51.8; **IR** (ATR-Ge): ν_{\max} 2955, 1730, 1713, 1659, 1629, 1606, 1433, 1412, 1340, 1317, 1287, 1261, 1236, 1199, 1171, 1060, 1005 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 594.4 (23), 313.1 [M+H]⁺ (100), 280.9 [M+H-CH₃OH]⁺ (19); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₄H₁₆NaO₈⁺ [M+Na]⁺ 335.0737, found 335.0740, C₁₃H₁₃O₇⁺ [M+H-CH₃OH]⁺ 281.0656, found 281.0663.

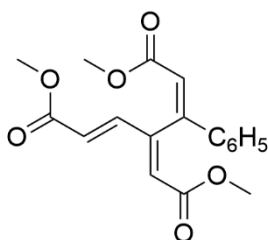
Dimethyl (2Z, 5E)-4-((Z)-2-methoxy-2-oxoethylidene)-3-(4-methoxycarbonylphenyl)hepta-2,5-dienedioate (9m):



Method A, C: methyl (Z)-4-(1-iodo-3-methoxy-3-oxoprop-1-en-1-yl)benzoate ^[5] (0.865 g, 2.5 mmol for A; 0.433 g, 1.25 mmol for C); elution with hexane/EtOAc (hexane → 85 : 15); white crystalline solid, mp 110.0–112.0 °C (EtOAc/hexane); A – 53% yield (0.412 g), C – 21% yield (0.081 g); **¹H NMR** (500 MHz, CDCl₃): δ 8.05–7.99 (m, AA'BB', 2H), 7.58 (d, *J* = 15.8 Hz, 1H), 7.55–7.49

(m, AA'BB', 2H), 6.59 (s, 1H), 6.36 (s, 1H), 5.99 (d, *J* = 15.8 Hz, 1H), 3.93 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.61 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.4, 166.3, 164.9, 164.8, 150.5, 150.1, 144.0, 141.1, 131.2, 130.0, 126.8, 125.5, 125.1, 119.1, 52.3, 52.0, 51.7, 51.6; **IR** (ATR-Ge): ν_{\max} 2955, 1717, 1710, 1644, 1608, 1507, 1432, 1412, 1331, 1278, 1264, 1246, 1219, 1200, 1173, 1163, 1111, 1041, 1014 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 389.2 [M+H]⁺ (100), 357.1 [M+H-CH₃OH]⁺ (24); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₂₀H₂₀NaO₈⁺ [M+Na]⁺ 411.1050, found 411.1060, C₁₉H₁₇O₇⁺ [M+H-CH₃OH]⁺ 357.0977, found 357.0976.

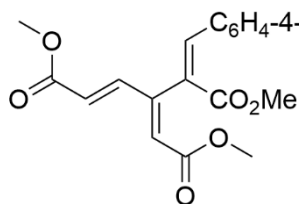
Dimethyl (2Z,5E)-4-((Z)-2-methoxy-2-oxoethylidene)-3-phenylhepta-2,5-dienedioate (9n):



Method A, C: methyl (Z)-3-iodo-3-phenylacrylate ^[5] (0.720 g, 2.5 mmol for A; 0.360g, 1.25 mmol for C); elution with hexane/EtOAc (hexane → 9 : 1); white crystalline solid, mp 126.9–127.6 °C (EtOAc/hexane); A – 57% yield (0.376 g), C – 18% yield (0.060 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.57 (d, *J* = 15.7 Hz, 1H), 7.50–7.42 (m, 2H), 7.41–7.31 (m, 3H), 6.53 (s, 1H), 6.35 (s, 1H), 6.01 (d, *J* = 15.7 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.4,

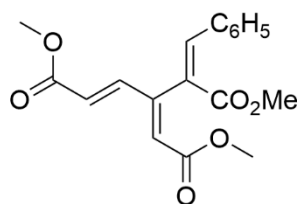
165.3, 164.8, 151.6, 150.6, 144.3, 136.7, 130.0, 128.8, 126.8, 125.2, 125.0, 117.2, 51.9, 51.6, 51.5; **IR** (ATR-Ge): ν_{\max} 2951, 1707, 1620, 1594, 1575, 1496, 1450, 1432, 1397, 1331, 1310, 1285, 1256, 1218, 1191, 1170 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 612.4 (13), 331.2 [M+H]⁺ (100), 299.0 [M+H-CH₃OH]⁺ (63); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₈H₁₈NaO₆⁺ [M+Na]⁺ 353.0996, found 353.1001, C₁₇H₁₅O₅⁺ [M+H-CH₃OH]⁺ 299.0914, found 299.0923.

Dimethyl (2Z,4E)-3-[(Z)-3-methoxy-3-oxo-1-(4-methoxycarbonylphenyl)prop-1-en-2-yl]-hexa-2,4-dienedioate (9o):



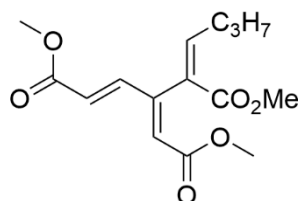
Method E: methyl (*E*)-4-[3-methoxy-3-oxo-2-(tributylstannyl)prop-1-en-1-yl]benzoate **5o** (1.782 g, 3.5 mmol); t. 18 h; elution with hexan/EtOAc (95 : 5 → 92 : 8); white amorphous solid; 70% yield (0.951 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.97–7.92 (m, AA'BB', 2H), 7.90 (s, 1H), 7.44–7.40 (m, AA'BB', 2H), 7.39 (d, overlap, *J* = 15.7 Hz, 1H), 6.40 (s, 1H), 5.99 (d, *J* = 15.7 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.3, 166.1, 165.8, 165.1, 147.1, 142.5, 139.2, 138.0, 130.7, 129.7, 129.6, 128.6, 128.3, 125.4, 52.7, 52.2, 51.9, 51.8; **IR** (ATR-Ge): ν_{max} 3735, 3650, 3566, 2954, 1713, 1633, 1597, 1435, 1275, 1256, 1241, 1225, 1204, 1185, 1173, 1152, 1107, 979, 863, 779, 766, 703 cm⁻¹. **LR-MS** (ESI⁺): *m/z* (rel. intensity) 318.9 (22), 361.0 (19), 411.1 [M+Na]⁺ (100); **HR-MS** (TOF-ESI⁺): calcd. for C₂₀H₂₀NaO₈⁺ [M+Na]⁺ 411.1050, found 411.1055.

Dimethyl (2Z,4E)-3-[(Z)-3-methoxy-3-oxo-1-phenylprop-1-en-2-yl]hexa-2,4-dienedioate (9p):



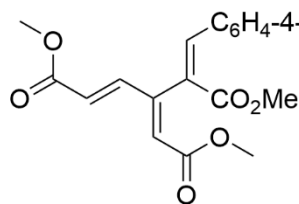
Method E: methyl (*E*)-3-phenyl-2-(tributylstannyl)acrylate **5p** (1.579 g, 3.5 mmol); t. 7 h; elution with hexan/EtOAc (9 : 1 → 75 : 25); white amorphous solid; 79% yield (0.913 g); **¹H NMR** (600 MHz, CDCl₃): δ 7.87 (s, 1H), 7.39 (d, *J* = 15.6 Hz, 1H), 7.37–7.33 (m, 2H), 7.30–7.25 (m, 3H), 6.37 (s, 1H), 6.01 (d, *J* = 15.6 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H); **¹³C NMR** (151 MHz, CDCl₃): δ 166.5, 166.3, 165.3, 147.7, 142.9, 140.7, 133.8, 130.1, 129.9, 128.7, 128.1, 126.4, 125.4, 52.6, 52.0, 51.9; **IR** (ATR-Ge): ν_{max} 2951, 2359, 1705, 1624, 1596, 1451, 1429, 1302, 1276, 1247, 1221, 1161, 1152, 1055, 1004, 971, 852, 761, 690 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 277.1 (8); 353.0 [M+Na]⁺ (100); **HR-MS** (TOF-ESI⁺): calcd. for C₁₈H₁₈NaO₆⁺ [M+Na]⁺ 353.0996; found 353.1000.

Dimethyl (2Z,4E)-3-[(Z)-1-methoxy-1-oxohex-2-en-2-yl]hexa-2,4-dienedioate (9q)



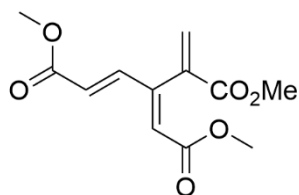
Method E: methyl (*E*)-2-(tributylstannyl)hex-2-enoate **5q** (1.460 g, 3.5 mmol); t. 4.5 h; elution with hexane/EtOAc (95 : 5 → 85 : 15); white amorphous solid; 78% yield (0.808 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.38 (d, *J* = 15.5 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.25 (s, 1H), 6.00 (d, *J* = 15.5 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 1.96–1.87 (m, 2H), 1.46–1.35 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.4, 165.5, 165.1, 146.7, 145.3, 144.0, 127.9, 127.3, 125.2, 52.1, 51.9, 51.6, 31.7, 21.5, 13.8; **IR** (ATR-Ge): ν_{max} 2959, 2929, 2870, 2359, 1727, 1713, 1649, 1624, 1601, 1458, 1435, 1306, 1281, 1257, 1239, 1193, 1172, 1063, 1003, 870 cm⁻¹; **LR-MS** (ESI⁺): *m/z* (rel. intensity) 319.0 [M+Na]⁺ (100); **HR-MS** (TOF-ESI⁺): calcd. for C₁₅H₂₀NaO₆⁺ [M+Na]⁺ 319.1152, found 319.1165.

Dimethyl (2Z,4E)-3-[(Z)-3-methoxy-3-oxo-1-(4-methoxyphenyl)prop-1-en-2-yl]hexa-2,4-dienedioate (9r):



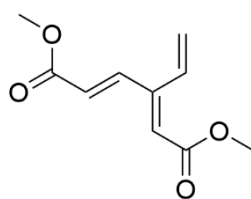
Method E: methyl (E)-3-(4-methoxyphenyl)-2-(tributylstannyl)acrylate **5r** (1.684 g, 3.5 mmol); t. 3 h; elution with hexane/EtOAc (95 : 5 → 85 : 15); white amorphous solid; 57% yield (0.718 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.84 (s, 1H), 7.44 (d, *J* = 15.6 Hz, 1H), 7.38–7.32 (m, AA'BB', 2H), 6.85–6.79 (m, AA'BB', 2H), 6.40 (s, 1H), 6.05 (d, *J* = 15.6 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.5, 166.5, 165.2, 160.8, 148.0, 142.9, 140.2, 132.0, 127.9, 126.3, 125.2, 123.5, 114.1, 55.3, 52.4, 51.9, 51.7; **IR** (ATR-Ge): ν_{\max} 2948, 1714, 1622, 1601, 1570, 1514, 1458, 1433, 1410, 1306, 1279, 1252, 1219, 1202, 1173, 1147, 1060, 1033, 1002, 867, 835 cm⁻¹; **LR-MS** (ESI⁺): *m/z* (rel. intensity) 304.3 (32), 353.0 (72), 383.0 [M+Na]⁺ (100); **HR-MS** (TOF-ESI⁺): calcd. for C₁₉H₂₀NaO₇⁺ [M+Na]⁺ 383.1101, found 383.1107.

Dimethyl (2Z,4E)-3-(3-methoxy-3-oxoprop-1-en-2-yl)hexa-2,4-dienedioate (9s):



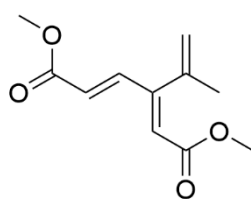
Method E: methyl 2-tributylstannylacrylate **5s** (2.07 g, 5.53 mmol); t. 17 h; elution with hexane; white amorphous solid; 30% yield (0.421 g); **¹H NMR** (500 MHz, CDCl₃) δ 7.42 (dd, *J* = 15.6 Hz, *J* = 0.9 Hz, 1H), 6.57 (d, *J* = 0.8 Hz, 1H), 6.19 (s, 1H), 6.10 (dd, *J* = 15.6 Hz, *J* = 0.9 Hz, 1H), 5.57 (d, *J* = 0.8 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 166.3, 165.3, 165.1, 147.5, 144.5, 136.1, 128.3, 126.3, 125.8, 52.3, 51.9, 51.7; **IR** ν_{\max} 3002; 2957; 1711; 1703; 1634; 1624; 1458; 1436; 1310; 1279; 1194; 1169; 1126; 1029; 1012; 991; 971; 861; 824; 700; 665 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 223.0 [M+H-CH₃OH]⁺ (100); 255.0 [M+H]⁺ (51); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₂H₁₄O₆Na⁺ [M+Na]⁺ 277,0683; found 277,0691.

Dimethyl (2E,4E)-3-vinylhexa-2,4-dienedioate (9t):



Method E: tributyl(vinyl)stannane^[6] (1.110 g, 3.5 mmol); t. 12 h; elution with hexane/EtOAc (hexane → 97 : 3); colourless oil; 82% yield (0.562 g); **¹H NMR** (500 MHz, CDCl₃): δ 7.48 (d, overlap, *J* = 15.8 Hz, 1H), 7.48 (dd, overlap, *J* = 17.7 Hz, *J* = 11.4 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.99 (s, 1H), 5.59 (d, overlap, *J* = 17.7 Hz, 1H), 5.58 (d, overlap, *J* = 11.4 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃): δ 166.4, 165.9, 148.5, 143.0, 131.7, 124.6, 122.7, 119.7, 51.9, 51.5; **IR** (ATR-Ge): ν_{\max} 2952, 1716, 1624, 1580, 1435, 1358, 1315, 1273, 1229, 1193, 1160, 1036, 1004 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 393.2 [2M+H]⁺ (29), 354.4 (22), 196.9 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₁₀H₁₃O₄⁺ [M+H]⁺ 197.0808, found 197.0814, C₉H₉O₃⁺ [M+H-CH₃OH]⁺ 165.0546, found 165.0551.

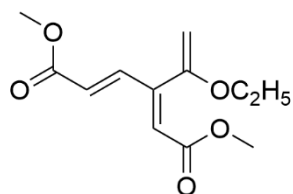
Dimethyl (2Z,4E)-3-(prop-1-en-2-yl)hexa-2,4-dienedioate (9u):



Method E: tributyl(prop-1-en-2-yl)stannane^[6] (1.159 g, 3.5 mmol); t. 14 h; elution with hexane/EtOAc (hexane → 97 : 3); white amorphous solid; 60% yield (0.440 g); **¹H NMR** (600 MHz, CDCl₃): δ 7.25 (d, *J* = 15.6 Hz, 1H), 6.19 (d, *J* = 15.6 Hz, 1H), 5.95 (s, 1H), 5.22–5.17 (m, 1H), 4.73–4.70 (m, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 1.94 (s, 3H);

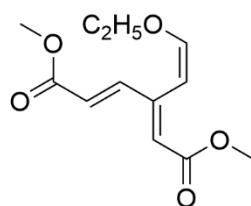
^{13}C NMR (151 MHz, CDCl_3): δ 166.8, 165.5, 154.5, 144.6, 140.5, 125.5, 123.9, 115.0, 52.0, 51.6, 22.7; **IR** (ATR-Ge): ν_{max} 2953, 1713, 1622, 1600, 1437, 1373, 1308, 1296, 1249, 1194, 1167, 1005 cm^{-1} ; **LR-MS** (APCI $^+$): m/z (rel. intensity) 563.6 (10), 354.4 (14), 211.0 $[\text{M}+\text{H}]^+$ (100); **HR-MS** (TOF-ESI $^+$): m/z calcd. for $\text{C}_{11}\text{H}_{15}\text{O}_4^+$ $[\text{M}+\text{H}]^+$ 211.0965, found 211.0974, $\text{C}_{10}\text{H}_{11}\text{O}_3^+$ $[\text{M}+\text{H}-\text{CH}_3\text{OH}]^+$ 179.0703, found 179.0708.

Dimethyl (2Z,4E)-3-(1-ethoxyvinyl)hexa-2,4-dienedioate (9v):



Method E: tributyl(1-ethoxyvinyl)stannane ^[6] (1.264 g, 3.5 mmol); t. 18 h; elution with hexane/EtOAc (hexane \rightarrow 9 : 1); yellowish amorphous solid; 34% yield (0.285 g); **^1H NMR** (600 MHz, CDCl_3): δ 7.27 (d, $J = 15.6$ Hz, 1H), 6.29 (d, $J = 15.6$ Hz, 1H), 6.06 (s, 1H), 4.34 (d, $J = 2.8$ Hz, 1H), 4.07 (d, $J = 2.8$ Hz, 1H), 3.84 (q, $J = 7.0$ Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 1.31 (t, $J = 7.0$ Hz, 3H); **^{13}C NMR** (151 MHz, CDCl_3): δ 166.8, 165.4, 155.1, 146.5, 143.6, 126.3, 125.5, 86.8, 63.7, 52.0, 51.7, 14.4; **IR** (ATR-Ge): ν_{max} 3043, 2989, 2956, 2364, 1713, 1672, 1625, 1600, 1435, 1407, 1378, 1354, 1310, 1250, 1197, 1172, 1143, 1119, 1059, 1000 cm^{-1} ; **LR-MS** (APCI $^+$): m/z (rel. intensity) 354.4 (10), 241.1 $[\text{M}+\text{H}]^+$ (100); **HR-MS** (TOF-ESI $^+$): m/z calcd. for $\text{C}_{12}\text{H}_{17}\text{O}_5^+$ $[\text{M}+\text{H}]^+$ 241.1071, found 241.1080, $\text{C}_{12}\text{H}_{16}\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$ 263.0890, found 263.0893, $\text{C}_{11}\text{H}_{13}\text{O}_4^+$ $[\text{M}+\text{H}-\text{CH}_3\text{OH}]^+$ 209.0809, found 209.0812.

Dimethyl (2Z,4E)-3-((Z)-2-ethoxyvinyl)hexa-2,4-dienedioate (9w):

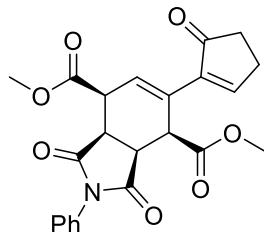


Method E: (*E*)-tributyl(2-ethoxyvinyl)stannane ^[6] (1.264 g, 3.5 mmol); t. 18 h; elution with hexane/EtOAc (hexane \rightarrow 9 : 1); yellowish amorphous solid; 10% yield (0.084 g); **^1H NMR** (600 MHz, CDCl_3): δ 7.44 (d, $J = 15.6$ Hz, 1H), 7.00–6.91 (m, 2H), 6.23 (d, $J = 15.6$ Hz, 1H), 5.64 (s, 1H), 3.94 (q, $J = 7.1$ Hz, 2H), 3.76 (s, 3H), 3.70 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** (151 MHz, CDCl_3): δ 167.0, 166.5, 155.8, 148.6, 143.6, 124.0, 112.9, 102.6, 65.9, 52.0, 51.2, 14.6; **IR** (ATR-Ge): ν_{max} 2925, 2854, 2206, 1720, 1710, 1643, 1607, 1577, 1509, 1456, 1436, 1416, 1362, 1308, 1294, 1255, 1199, 1184, 1168, 1122, 1078, 1035 cm^{-1} ; **LR-MS** (APCI $^+$): m/z (rel. intensity) 359.2 (30), 341.2 (35), 279.4 (19), 241.1 $[\text{M}+\text{H}]^+$ (100), 209.0 $[\text{M}+\text{H}-\text{CH}_3\text{OH}]^+$ (70), 191.0 (33), 178.9 (36); **HR-MS** (TOF-ESI $^+$): m/z calcd. for $\text{C}_{12}\text{H}_{17}\text{O}_5^+$ $[\text{M}+\text{H}]^+$ 241.1071, found 241.1079, $\text{C}_{12}\text{H}_{16}\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$ 263.0890, found 263.0895, $\text{C}_{11}\text{H}_{13}\text{O}_4^+$ $[\text{M}+\text{H}-\text{CH}_3\text{OH}]^+$ 209.0809, found 209.0813.

2.5 Selective Diels-Alder monoadditions of **9e** and **9g**

A dienophile (1 eq), a dendralene (1.8–2 eq) in xylene at the given temperature. Products **11e** and **11g** are prone to isomerization even under mildly acidic conditions (CDCl₃, silica gel).

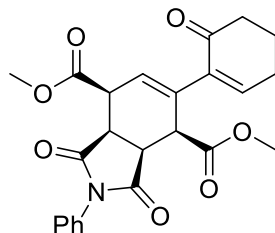
DA product **11e**



Dendralene **9e** (3.4 mmol; 0.852 g), *N*-phenylmaleimide (1.7 mmol; 0.294 g) in 8.5 mL of xylene at 70 °C, reaction time 7 days. The product was precipitated by hexane as a yellowish powder. The precipitate was filtered off, and further washed with hexane. The powder was then suspended in pure hexane, the suspension heated, and the solid filtered off to remove the excess of dendralene **9e**. The solid obtained was further

washed with a minimum amount of EtOAc (RT or lukewarm) to remove the residual maleimide to furnish 57% (0.97 mmol; 0.412 g) of the product as a white powder. **¹H NMR** (600 MHz, CD₃CN) δ 7.75–7.71 (m, 1H), 7.52–7.46 (m, 2H), 7.45–7.37 (m, 1H), 7.36–7.29 (m, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.96 (t, *J* = 7.6 Hz, 1H), 3.59 (s, 3H), 3.58–3.54 (m, 1H), 3.53 (s, 3H), 3.50–3.44 (m, 1H), 2.62–2.58 (m, 2H), 2.47–2.38 (m, 2H); **¹³C NMR** (151 MHz, CD₃CN) δ 207.4, 176.2, 170.6, 159.9, 159.9, 141.1, 133.2, 130.8, 128.9, 128.5, 127.1, 127.1, 125.9, 51.8, 51.6, 41.8, 41.4, 40.2, 39.9, 35.5, 25.8; **IR** (ATR) ν_{\max} 2951; 1775; 1742; 1732; 1708; 1686; 1599; 1504; 1429; 1392; 1292; 1235; 1186; 1169; 1154; 1110; 1003 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 392.3 (64); 424.4 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₂₃H₂₂NO₇⁺ [M+H]⁺ 424.1391, found 424.1398.

DA product **11g**



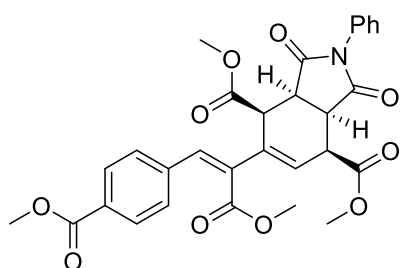
Dendralene **9g** (1.0 mmol; 0.258 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 2.5 mL of xylene at 70 °C, reaction time 5 days. The product was precipitated by hexane as a yellowish powder. The precipitate was filtered off, and further washed with hexane. The powder was then suspended in pure hexane, the suspension heated, and the solid filtered off to remove the excess of dendralene **9g**. The powder obtained was

further washed with a minimum amount of EtOAc (RT or lukewarm) to remove the residual maleimide to furnish 81% (0.405 mmol; 0.177 g) of the product as a white powder; *R_f* = 0.46 (hexane/EtOAc 3 : 7). **¹H NMR** (600 MHz, CD₃CN) δ 7.49–7.32 (m, 3H), 7.25–7.16 (m, 2H), 6.69 (t, *J* = 4.2 Hz, 1H), 6.17 (dd, *J* = 4.4 Hz, *J* = 1.9 Hz, 1H), 3.85–3.79 (m, 1H), 3.75–3.70 (m, 2H), 3.69 (s, 3H), 3.55 (s, 3H), 3.49–3.47 (m, 1H), 2.45–2.28 (m, 4H), 2.02–1.86 (m, 2H); **¹³C NMR** (151 MHz, CD₃CN) δ 198.8, 176.3, 175.5, 170.7, 170.1, 145.3, 141.2, 137.9, 132.5, 129.1, 128.7, 126.9, 125.7, 51.8, 51.4, 43.5, 42.7, 42.2, 39.9, 38.1, 25.8, 22.6; **IR** (ATR) ν_{\max} 2949; 1752; 1730; 1707; 1671; 1596; 1492; 1457; 1435; 1396; 1328; 1317; 1262; 1217; 1197; 1181; 1161; 1075; 1049; 1035 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 406.2 (100); 438.2 [M+H]⁺ (36); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₂₄H₂₃NNaO₇⁺ [M+Na]⁺ 460.1367, found 460.1370.

2.6 General procedure for DTDA reactions

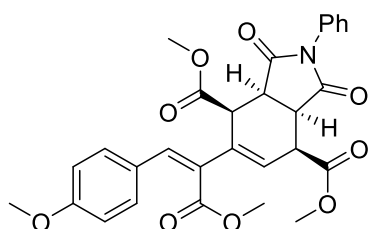
Unless otherwise stated, a dendralene (0.2 mmol) and a selected dienophile (2.5 eq, 0.5 mmol) were stirred in xylene (0.5 mL per 0.1 mmol of the dendralene) in a flask sealed with a rubber septum. The reaction was heated at 100 °C for 48 hours or until a large amount of precipitate was formed. The solvent was replenished, if needed. The reaction mixture was then cooled to RT, diluted with hexane, and the precipitated product filtered off.

DA product 11o



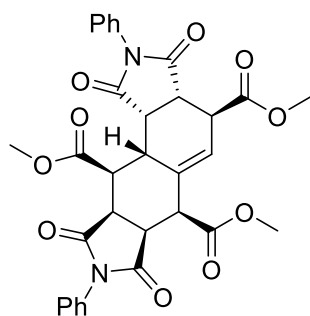
Dendralene **9o** (0.5 mmol; 0.194 g), *N*-phenylmaleimide (1.25 mmol; 0.216 g) in 2.5 mL of xylene, reaction time 5 days at 100 °C plus another 23 hours at 150 °C. The pale yellowish solid was purified by reprecipitation from hot EtOAc/hexane mixture yielding 91% (0.46 mmol; 0.255 g) of the product as a white amorphous powder. *R*_f = 0.67 (hexane/EtOAc 1 : 1). ¹H NMR (500 MHz, CDCl₃) δ 8.04–7.98 (m, AA'BB', 2H), 7.81–7.77 (m, AA'BB', 2H), 7.76 (s, 1H), 7.52–7.47 (m, 2H), 7.45–7.36 (m, 3H), 6.21 (d, *J* = 8.2 Hz, 1H), 4.17–4.07 (m, 2H), 4.05–4.00 (m, 1H), 3.94 (s, 3H), 3.93–3.91 (m, 1H), 3.84 (s, 3H), 3.55 (s, 3H), 3.39 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 177.4, 176.7, 170.9, 170.7, 166.7, 166.5, 140.6, 138.3, 133.1, 132.4, 131.9, 130.7, 130.3, 129.4, 129.1, 128.8, 128.6, 126.5, 52.9, 52.6, 52.5, 52.3, 44.5, 41.2, 40.7, 40.6; IR (ATR) ν_{max} 2957; 1733; 1710; 1599; 1511; 1497; 1436; 1381; 1241; 1202; 1172; 1128; 1117; 1029; 871; 827; 810; 773; 767; 696; 641 cm⁻¹; LR-MS (APCI⁺): *m/z* (rel. intensity) 562.2 [M+H]⁺ (100); HR-MS (TOF-ESI⁺): *m/z* calcd. for C₃₀H₂₇NO₁₀Na⁺ [M+Na]⁺ 584.1527, found 584.1534.

DA product 11r



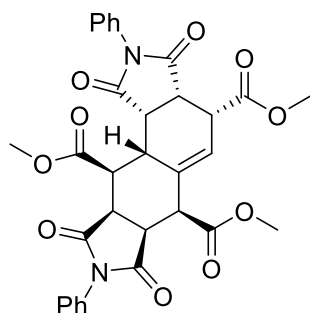
Dendralene **9r** (1 mmol; 0.360 g), *N*-phenylmaleimide (2.5 mmol; 0.434 g) in 5 mL of xylene at 100 °C, reaction time 14 days. The pale yellowish solid was purified by reprecipitation from hot EtOAc/hexane yielding 62% (0.62 mmol; 0.330 g) of product as a white amorphous powder. ¹H NMR (600 MHz, CDCl₃) δ 7.72–7.70 (m, AA'BB', 2H), 7.68 (s, 1H), 7.49–7.42 (m, AA'BB', 2H), 7.42–7.33 (m, 3H), 6.86–6.80 (m, 2H), 6.25–6.20 (m, 1H), 4.14–4.07 (m, 2H), 4.02–3.97 (m, 1H), 3.88 (d, *J* = 1.1 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.48 (s, 3H), 3.36 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 177.6, 176.9, 171.4, 171.1, 167.5, 161.1, 141.7, 133.9, 132.8, 132.1, 129.2, 128.8, 127.6, 127.6, 126.6, 126.6, 113.8, 55.4, 52.8, 52.5, 52.4, 44.9, 41.4, 40.9, 40.7; IR (ATR) ν_{max} 3566; 2957; 1710; 1598; 1511; 1497; 1379; 1241; 1226; 1172; 1127; 1117; 1029; 849; 826; 767; 696; 621 cm⁻¹; LR-MS (APCI⁺): *m/z* (rel. intensity) 534.2 [M+H]⁺ (100); HR-MS (TOF-ESI⁺): *m/z* calcd. for C₂₉H₂₇NO₉Na⁺ [M+Na]⁺ 556.1578, found 556.1588.

DTDA product 12a



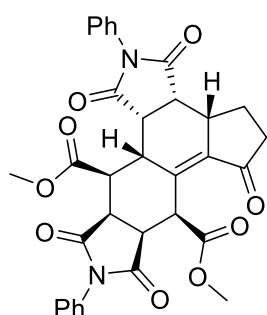
Dendralene **9a** (0.2 mmol; 0.051 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 1 mL of xylene at 100 °C, reaction time 48 h. Yield 74% (0.015 mmol; 0.089 g) of the product as a white amorphous precipitate. On a larger scale, dendralene **9a** (3 mmol; 0.763 g), *N*-phenylmaleimide (7.5 mmol; 1.299 g) in 15 mL of xylene, at 100 °C, reaction time 48 h. Yield 78% (2.34 mmol; 1.4 g) of the product as a white amorphous precipitate. **¹H NMR**(500 MHz, pyridine-*d*₅) δ 7.59–7.49 (m, 3H), 7.45–7.24 (m, 8H), 4.70 (dd, *J* = 8.9 Hz, *J* = 5.7 Hz, 1H), 4.54 (dd, *J* = 12.8 Hz, *J* = 5.5 Hz, 1H), 4.42–4.34 (m, 2H), 4.30 (dd, *J* = 10.1 Hz, *J* = 5.5 Hz, 1H), 4.24–4.17 (m, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 3.51–3.41 (m, 1H), 3.35 (s, 3H); **¹³C NMR**(126 MHz, pyridine-*d*₅) δ 177.8, 177.8, 176.1, 175.9, 172.0, 171.5, 169.9, 132.8, 132.6, 129.3, 129.3, 129.0, 128.8, 127.2, 127.2, 124.4, 123.8, 52.5, 52.3, 51.9, 43.1, 43.1, 43.0, 42.9, 42.1, 42.0, 39.7, 34.7; **IR** (ATR) ν_{max} 2956; 1745; 1733; 1716; 1705; 1499; 1433; 1387; 1338; 1275; 1201; 1155; 1121; 1019; 958; 816; 758; 710; 694 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 601.2 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₃₂H₂₉N₂O₁₀⁺ [M+H]⁺ 601.1817, found 601.1823.

DTDA product 12c



Dendralene **9c** (0.2 mmol; 0.051 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 1 mL of xylene at 100 °C, reaction time 24 h. Yield 78% (0.156 mmol; 0.093 g) of the product as a white amorphous precipitate. The same reaction terminated after 6 h yielded 70 % (0.14 mmol; 0.084 g). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.48–7.42 (m, 4H), 7.42–7.38 (m, 2H), 7.21–7.06 (m, 5H), 4.03–3.94 (m, 2H), 3.93–3.86 (m, 2H), 3.86–3.79 (m, 2H), 3.75–3.72 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 2.70–2.64 (m, 1H); **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 176.9, 176.7, 176.3, 176.2, 171.8, 171.6, 169.9, 132.3, 132.3, 131.7, 129.4, 129.3, 129.1, 129.0, 127.8, 127.3, 124.7, 52.2, 52.2, 52.0, 43.3, 42.6, 42.5, 41.4, 40.8, 40.2, 38.8, 35.7; **IR** (ATR) ν_{max} 2956; 1746; 1733; 1715; 1705; 1499; 1433; 1386; 1336; 1275; 1201; 1155; 1121; 1019; 958; 816; 758; 710; 694 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 601.2 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₃₂H₂₉N₂O₁₀⁺ [M+H]⁺ 601.1817, found 601.1823.

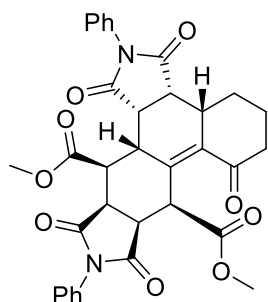
DTDA product 12e



Dendralene **9e** (0.2 mmol; 0.050 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 1 mL of xylene at 100 °C, reaction time 48 h. Yield 86% (0.17 mmol; 0.103 g) of the product as a white amorphous precipitate. **¹H NMR** (500 MHz, pyridine-*d*₅) δ 7.50–7.25 (m, 10H), 4.58 (dd, *J* = 8.9 Hz, *J* = 6.3 Hz, 1H), 4.49–4.36 (m, 3H), 3.89 (s, 3H), 3.72–3.58 (m, 2H), 3.25 (s, 3H), 3.16–3.07 (m, 2H), 2.92–2.82 (m, 1H), 2.63–2.53 (m, 1H), 2.41–2.30 (m, 1H), 2.18–2.07 (m, 1H); **¹³C NMR** (126 MHz, pyridine-*d*₅) δ 204.9, 176.8, 176.8, 176.7, 176.3, 171.9, 170.9, 140.0, 138.1, 132.8, 132.6, 129.3, 129.2, 128.9, 128.8, 127.3, 127.1, 53.2, 52.4, 43.3, 42.6, 41.8, 41.7, 40.4, 40.3, 39.2, 38.6, 37.5, 20.4; **IR** (ATR) ν_{max} 2955; 1732; 1703; 1646; 1495; 1389; 1294; 1232; 1193; 1167; 1075 995; 932; 793; 761; 709;

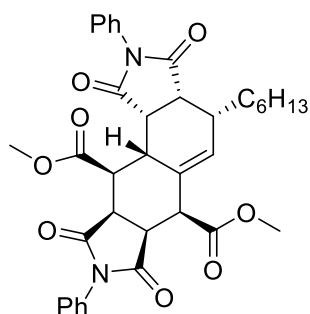
697 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 597.2 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₃₃H₂₉N₂O₉⁺ [M+H]⁺ 597.1868, found 697.1877.

DTDA product 12g



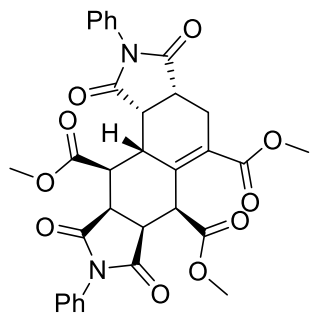
Dendralene **9g** (0.2 mmol; 0.053 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 1 mL of xylene at 100 °C, reaction time 48 h. Yield 72% (0.14 mmol; 0.088 g) of the product as a white amorphous powder. **¹H NMR** (600 MHz, pyridine-*d*₅) δ 7.48–7.19 (m, 10H), 5.93 (d, $J = 1.7$ Hz), 4.43 (dd, $J = 9.3$ Hz, $J = 6.8$ Hz, 1H), 4.39–4.27 (m, 2H), 4.18 (dd, $J = 13.0$ Hz, $J = 5.6$ Hz, 1H), 3.85 (s, 3H), 3.36 (dd, $J = 9.3$ Hz, $J = 5.8$ Hz, 1H), 3.18 (s, 3H), 3.06–2.99 (m, 1H), 2.71–2.64 (m, 1H), 2.65–2.53 (m, 1H), 2.45–2.31 (m, 2H), 1.97–1.88 (m, 1H), 1.78–1.72 (m, 1H), 1.47–1.37 (m, 1H). **¹³C NMR** (151 MHz, pyridine-*d*₅) δ 198.6, 176.8, 176.8, 176.1, 176.1, 171.6, 171.3, 143.6, 138.1, 132.8, 132.5, 129.3, 128.9, 128.5, 127.2, 127.1, 126.9, 52.8, 52.2, 43.5, 43.2, 42.5, 41.7, 41.6, 39.7, 39.2, 38.5, 36.9, 25.0, 21.5; **IR** (ATR) ν_{max} 2955; 1739; 1728; 1703; 1682; 1592; 1493; 1457; 1437; 1390; 1337; 1295; 1266; 1235; 1195; 1161; 1129; 1005; 994 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 579.2 [M+H–MeOH]⁺ (100); 611.2 [M+H]⁺ (22); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₃₄H₃₁N₂O₉⁺ [M+H]⁺ 611.2024, found 611.2026.

DTDA product 12i



Dendralene **9i** (0.2 mmol; 0.056 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 1 mL of xylene at 100 °C. Reaction time 48 h, yield 83% (0.166 mmol; 0.104 g) of the product as a white precipitate. Recrystallization from hot acetonitrile afforded crystalline product, mp 215.8–216.3 °C. **¹H NMR** (500 MHz, pyridine-*d*₅) δ 7.45–7.23 (m, 11H;), 4.61 (dd, $J = 12.8$ Hz, $J = 3.9$ Hz, 1H), 4.38–4.31 (m, 3H), 4.06 (d, $J = 3.9$ Hz, 1H), 3.90 (s, 3H;), 3.73 (s, 3H), 3.41 (dd, $J = 8.5$ Hz, $J = 6.9$ Hz, 1H), 3.06 (d, $J = 12.9$ Hz, 1H), 2.25 (s, 1H), 2.06–1.85 (m, 2H), 1.51–1.33 (m, 2H), 1.28–1.10 (m, 6H), 0.82 (t, $J = 6.5$ Hz, 3H); **¹³C NMR** (126 MHz, pyridine-*d*₅) δ 178.0, 176.6, 176.5, 176.2, 172.3, 170.0, 133.0, 132.7, 132.2, 131.9, 129.4, 129.3, 129.0, 128.7, 127.4, 127.1, 52.3, 51.8, 44.2, 43.5, 43.4, 43.2, 42.1, 39.4, 38.0, 36.8, 31.9, 31.5, 29.5, 28.5, 22.9, 14.2; **IR** (ATR) ν_{max} 2958; 2932; 2872; 1771; 1738; 1710; 1599; 1499; 1458; 1435; 1382; 1339; 1192; 1025; 758; 692; 611 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 627.2 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₃₆H₃₉N₂O₈⁺ [M+H]⁺ 627.2701, found 627.2698.

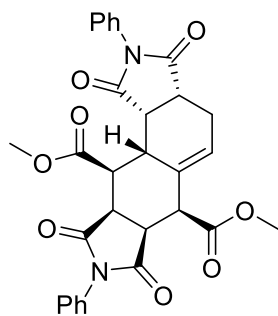
DTDA product 12s



Dendralene **9s** (0.5 mmol; 0.127 g), *N*-phenylmaleimide (1.25 mmol; 0.216 g) in 2.5 mL of xylene at 100 °C. Reaction time 24 h, the pale yellowish precipitate obtained upon layering the reaction mixture with hexane was purified by reprecipitation from hot EtOAc/hexane to furnish 74% (0.37 mmol; 0.223 g) of the product as a white amorphous powder. **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.57–7.44 (m, 4H), 7.44–7.38 (m, 2H), 7.20–7.10 (m, 4H), 4.27 (d, $J = 5.9$ Hz, 1H), 4.06–3.93 (m, 2H), 3.86 (dd, $J = 8.9$ Hz, $J = 5.6$ Hz, 1H), 3.69

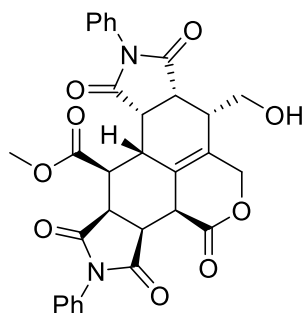
(s, 3H), 3.68–3.63 (m, 1H), 3.54 (s, 3H), 3.53 (s, 3H), 3.51–3.47 (m, 1H), 3.09 (d, $J = 15.5$ Hz, 1H), 2.88–2.81 (m, 1H), 2.57–2.51 (m, 1H); $^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ 178.1, 177.5, 176.3, 174.5, 172.3, 168.9, 166.7, 140.6, 132.9, 132.6, 129.4, 129.3, 129.1, 129.0, 128.8, 127.5, 127.5, 52.6, 52.2, 51.8, 43.9, 43.1, 41.3, 40.4, 40.3, 39.0, 38.3, 27.6. **IR** (ATR) ν_{max} 2957; 1742; 1704; 1621; 1597; 1499; 1456; 1440; 1392; 1328; 1311; 1272; 1218; 1178; 1150; 1104; 1078; 1030; 1078 cm^{-1} ; **LR-MS** (APCI $^+$): m/z (rel. intensity) 601.2 $[\text{M}+\text{H}]^+$ (100); **HR-MS** (TOF-ESI $^+$): m/z calcd. for $\text{C}_{32}\text{H}_{29}\text{N}_2\text{O}_{10}^+$ $[\text{M}+\text{H}]^+$ 601.1817, found 601.1820.

DTDA product 12t



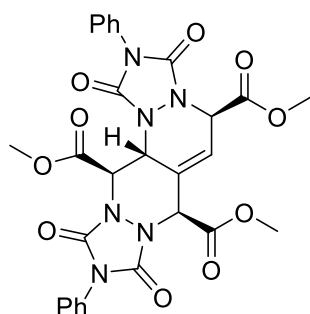
Dendralene **9t** (0.2 mmol; 0.039 g), *N*-phenylmaleimide (0.5 mmol; 0.086 g) in 1 mL of xylene at 100°C. Reaction time 48 h, yield 71% (0.14 mmol; 0.077 g) of the product as a white amorphous powder. $^1\text{H NMR}$ (600 MHz, pyridine- d_5) δ 7.38–7.30 (m, 6H), 7.30–7.23 (m, 3H), 7.22–7.18 (m, 2H), 4.52–4.47 (m, 1H), 4.28–4.23 (m, 3H), 3.99 (s, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 3.32 (t, $J = 8.9$, 1H), 2.97–2.90 (m, 1H), 2.86–2.80 (m, 1H), 2.07–2.01 (m, 1H); $^{13}\text{C NMR}$ (151 MHz, pyridine- d_5) δ 178.8, 178.1, 176.2, 175.9, 172.1, 169.8, 132.9, 132.8, 132.5, 129.2, 129.1, 128.8, 128.6, 127.1, 126.9, 126.2, 52.1, 51.6, 43.1, 42.9, 42.3, 41.9, 40.4, 39.3, 35.9, 25.3; **IR** (ATR) ν_{max} 2954; 1742; 1702; 1597; 1499; 1435; 1334; 1273; 1169; 1155; 1024; 760; 716; 699 cm^{-1} ; **LR-MS** (APCI $^+$): m/z (rel. intensity) 543.2 $[\text{M}+\text{H}]^+$ (100); **HR-MS** (TOF-ESI $^+$): m/z calcd. for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_8\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 565.1581, found 564.1584.

DTDA product 12x



Dendralene **9x** (0.56 mmol; 0.112 g), *N*-phenylmaleimide (1.4 mmol; 0.243 g) in 1 mL of xylene at 75 °C. Reaction time 19 h, yield 62% (0.34 mmol; 0.198 g) of the product as a white amorphous precipitate. $^1\text{H NMR}$ (500 MHz, pyridine- d_5) δ 7.44–7.33 (m, 4H), 7.33–7.22 (m, 6H), 5.86–5.77 (d, $J = 17.2$ Hz, 1H), 5.46 (d, $J = 17.2$ Hz, 1H), 4.63–4.51 (m, 3H), 4.50–4.40 (m, 2H), 4.37–4.30 (m, 2H), 3.95 (s, 3H), 3.88–3.80 (m, 1H), 3.30 (t, $J = 9.7$ Hz, 1H), 3.22 (s, 1H); $^{13}\text{C NMR}$ (126 MHz, pyridine- d_5) δ 177.2, 177.0, 177.0, 176.2, 171.9, 167.8, 132.8, 132.5, 130.9, 129.4, 129.2, 128.9, 128.7, 127.3, 127.1, 124.6, 70.3, 59.4, 52.4, 43.9, 43.4, 43.1, 42.9, 40.7, 40.6, 36.3, 34.3; **IR** (ATR) ν_{max} 3476; 2948; 1742; 1736; 1712; 1691; 1387; 1212; 1192; 1175; 1054; 1043; 968; 915; 887; 799; 766; 739; 710; 698; 680; 654 cm^{-1} ; **LR-MS** (ESI $^+$): m/z (rel. intensity) 609.0 $[\text{M}+\text{K}]^+$ (70), 593.1 $[\text{M}+\text{Na}]^+$ (100); **HR-MS** (TOF-ESI $^+$): m/z calcd. for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_9^+$ $[\text{M}+\text{H}]^+$ 571.1711, found 571.1718.

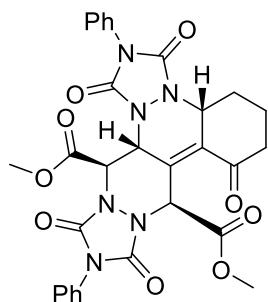
DTDA product 15a



Dendralene **9a** (0.5 mmol; 0.127 g), 4-phenyl-1,2,4-triazoline-3,5-dione (1.25 mmol; 0.226 g) in 2.5 mL of xylene at 100 °C. Reaction time 48 h, yield 75% (0.38 mmol; 0.226 g) of the product as a white amorphous precipitate. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59–7.32 (m, 10H), 6.53 (d, $J = 5.9$ Hz, 1H), 5.39 (s, 1H), 5.24 (d, $J = 5.9$ Hz, 1H), 5.18–5.13 (m, 1H), 4.31 (d, $J = 9.2$ Hz, 1H), 3.91 (s, 3H), 3.85 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.0, 165.7, 165.6, 154.7, 151.5, 151.3, 150.5, 130.6, 130.6, 129.4, 129.2, 128.9, 128.7, 127.7,

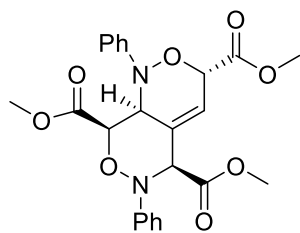
126.2, 125.5, 122.9, 60.9, 60.8, 56.9, 54.1, 53.6, 53.6, 51.4; **IR** (ATR) ν_{\max} 1786; 1748; 1724; 1501; 1418; 1271; 1219; 1167; 1146; 976; 767; 731; 723; 705; 654 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 605.1 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₂₈H₂₅N₆O₁₀⁺ [M+H]⁺ 605.1627, found 605.1634.

DTDA product 15g



Dendralene **9g** (1.6 mmol; 0.421 g), 4-phenyl-1,2,4-triazoline-3,5-dione (0.8 mmol; 0.140 g) in 3.5 mL of xylene at 70 °C. Reaction time 16 h, precipitation with hexane gave 64% yield (0.26 mmol; 0.158 g) of the product as a pale yellow amorphous powder. **¹H NMR** (600 MHz, CDCl₃) δ 7.55–7.30 (m, 10H), 5.83 (s, 1H), 5.35 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1H), 4.53 (d, $J = 8.8$ Hz, 1H), 4.51–4.45 (m, 1H), 3.93 (s, 3H), 3.78 (s, 3H), 3.42–3.40 (m, 1H), 2.82–2.78 (m, 1H), 2.54–2.48 (m, 1H), 2.27–2.14 (m, 1H), 2.00–1.82 (m, 2H); **¹³C NMR** (151 MHz, CDCl₃) δ 198.0, 166.2, 165.9, 154.9, 152.1, 151.2, 149.9, 137.7, 130.7, 130.5, 129.5, 129.4, 129.2, 129.0, 128.8, 125.9, 125.6, 61.5, 60.2, 58.7, 54.2, 53.7, 51.7, 41.9, 29.9, 19.7; **IR** (ATR) ν_{\max} 1784; 1725; 1642; 1504; 1415; 1361; 1299; 1256; 1202; 1156; 1073; 999 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 583.2 (15); 615.2 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₃₀H₂₆N₆NaO₉⁺ [M+Na]⁺ 637.1653, found 637.1655.

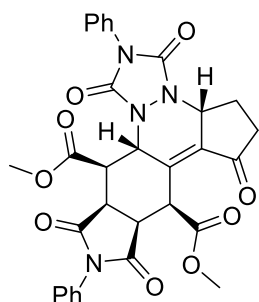
DTDA product 17a



Dendralene **9a** (0.5 mmol; 0.127 g), nitrosobenzene (1.25 mmol; 0.113 g) in 2.5 mL of dry xylene at RT. Reaction time 48 h (the mixture underwent several colour changes from light clear turquoise, emerald green, yellow to red), yield 20% (0.1 mmol; 0.047 g) of the product as a white amorphous precipitate. **¹H NMR** (600 MHz, CDCl₃) δ 7.33–7.24 (m, 5H), 7.22–7.16 (m, 2H), 6.99–6.93 (m, 3H), 6.45–6.44 (m, 1H), 5.39–5.37 (m, 1H), 5.29 (d, $J = 7.5$ Hz, 1H), 5.16 (d, $J = 7.5$ Hz, 1H), 4.97–4.97 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.47 (s, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 169.3, 168.6, 167.4, 147.16, 147.0, 129.2, 129.0, 128.9, 122.4, 121.8, 121.3, 114.5, 114.3, 76.3, 75.7, 67.7, 55.0, 52.5, 52.5, 52.2; **IR** (ATR) ν_{\max} 3751; 3735; 3675; 3566; 2953; 1760; 1734; 1598; 1491; 1548; 1455; 1280; 1271; 1227; 1209; 1184; 1099; 1081; 1030; 1009; 843 cm^{-1} ; **LR-MS** (APCI⁺): m/z (rel. intensity) 469.2 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): m/z calcd. for C₂₄H₂₄N₂O₈Na⁺ [M+Na]⁺ 491.1425, found 491.1428.

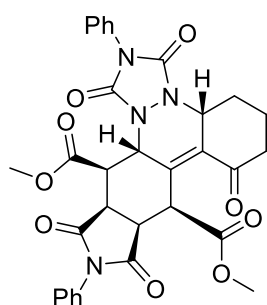
2.7 Selective Second Stage Diels-Alder Cycloadditions

DTDA product 14e



Diene **11e** (0.2 mmol; 0.085 g), 4-phenyl-1,2,4-triazoline-3,5-dione (0.3 mmol; 0.052 g) in 2 mL of acetonitrile at RT. Reaction time 17 h, the resultant precipitate was filtered off and washed with hexane to give 91% (0.182 mmol; 0.109 g) of the product as a white amorphous powder. **¹H NMR** (600 MHz, CD₃CN) δ 7.53–7.40 (m, 8H), 7.28–7.24 (m, 2H), 5.69 (d, *J* = 8.5 Hz, 1H), 5.29 (dd, *J* = 9.3 Hz, *J* = 2.4 Hz, 1H), 4.60–4.83 (m, 1H), 3.84–3.79 (m, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.56–3.48 (m, 2H), 2.82–2.74 (m, 1H), 2.54–2.48 (m, 2H), 2.13–2.06 (m, 1H); **¹³C NMR** (151 MHz, CD₃CN) δ 202.3, 174.9, 174.6, 170.5, 169.5, 156.6, 149.8, 136.6, 133.1, 132.5, 131.7, 129.2, 129.2, 128.9, 128.6, 127.0, 126.5, 59.9, 52.9, 51.9, 49.6, 45.4, 42.2, 40.5, 39.7, 37.2, 26.3; **IR** (ATR) ν_{\max} 2954; 1781; 1716; 1657; 1598; 1499; 1456; 1417; 1387; 1231; 1200; 1178; 1144; 1074; 1061; 1014; 946; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 599.3 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₃₁H₂₆N₄NaO₉⁺ [M+Na]⁺ 621.1592, found 621.1597.

DTDA product 14g



Diene **11g** (0.2 mmol; 0.087 g), 4-phenyl-1,2,4-triazoline-3,5-dione (0.3 mmol; 0.052 g) in 2 mL of xylene at RT. Reaction time 24 h, the resultant precipitate was then filtered off and washed with hexane to furnish 73% (0.15 mmol; 0.089 g) of the product as a white amorphous solid. **¹H NMR** (500 MHz, CD₃CN) δ 7.59–7.45 (m, 8H), 7.34–7.31 (m, 2H), 5.34 (dd, *J* = 9.4 Hz, *J* = 2.1 Hz, 1H), 4.71 (d, *J* = 8.8 Hz, 1H), 4.56–4.44 (m, 1H), 3.99–3.88 (m, 1H), 3.83–3.79 (m, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.61–3.58 (m, 1H), 3.07–2.97 (m, 1H), 2.66–2.60 (m, 1H), 2.21–2.01 (m, 2H), 1.95–1.88 (m, 2H); **¹³C NMR** (126 MHz, CD₃CN) δ 201.2, 175.9, 175.3, 172.0, 170.4, 156.3, 150.9, 137.2, 133.3, 133.1, 132.5, 130.0, 129.9, 129.7, 129.4, 127.82, 127.4, 60.7, 53.7, 52.7, 50.3, 44.7, 44.4, 43.4, 43.2, 40.8, 31.5, 20.8; **IR** (ATR) ν_{\max} 3647; 1786; 1712; 1625; 1502; 1434; 1395; 1358; 1314; 1221; 1201; 1180 1125; 1044; 966 cm⁻¹; **LR-MS** (APCI⁺): *m/z* (rel. intensity) 613.4 [M+H]⁺ (100); **HR-MS** (TOF-ESI⁺): *m/z* calcd. for C₃₂H₂₉N₄O₉⁺ [M+H]⁺ 613.1929, found 613.1935.

3. X-Ray Structures

The X-ray data for colourless crystals of **12i** were obtained at 150K using Oxford Cryostream low-temperature device with a Bruker D8-Venture diffractometer equipped with Mo (Mo/ K_{α} radiation; $\lambda = 0.71073 \text{ \AA}$) microfocus X-ray ($I_{\mu S}$) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection. Obtained data were treated by XT-version 2014/5 and SHELXL-2017/1 (or higher) software implemented in APEX3 v2016.9-0 (Bruker AXS) system. ^[15] $R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2$, $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$ for all data, $R(F) = \sum | |F_o| - |F_c| | / \sum |F_o|$ for observed data, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ for all data. Crystallographic data for all structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 2238545. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

The frames for all compounds were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structures were solved and refined using the Bruker SHELXTL Software Package.

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen atoms except of those involved in H-bonds were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (pivot atom) or of $1.5U_{\text{eq}}$ (methyl). H atoms in methyl, methylene and methine moieties and C-H in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98 and 0.93 \AA . Static disorders were treated by standard procedures implemented in SHELXTL Software.

The compound **12i** crystallizes in monoclinic system within the achiral $P2_1/c$ space group with two independent, but very similar, molecules in asymmetric unit. The molecule of **12i** reveals eight centers of chirality, where, in the measured crystal, atoms C3, C5, C6, C8 and C9 (C103, C105, C106, C108 and C109 of the second molecule) were assigned to have *R* configuration, and atoms C2, C10 and C11 (C102, C110 and C111) are stereocenters with *S* configuration. Inside this S-shaped dendralene molecule core all the carbon atoms are sp^3 hybridized except of the C7 and C12 (C107, C112) ones, which are interconnected by typical double bond with separation of 1.331(4) \AA . Although the core lacks a π -electron conjugation, most of the C-C single bonds are a bit elongated in comparison to the standard 1.51 \AA due to the presence of steric strain. Also the interatomic angles within the core are a bit different from what we can expect for sp^3 and sp^2 hybridized atoms – for example C12-C7-C8 129.4(2) or C5-C6-C9 115.2(2) $^\circ$. On the other hand, similar S-shape arrangement with close interatomic separations and angle was found for about fifty related structures. ^[16] The only U-shaped structure was described for 2,5,8-trimethyl-6-(phenylethynyl)-3a,4,6,6a,9a,10,10a,10b-octahydroisindolo[5,6-e]isindole-1,3,7,9(2*H*,8*H*)-tetrone together with its S-shaped isomer recently. ^[17] The only difference is the opposite configuration and thus orientation of phenylethynyl substituent on carbon in position 6.

Table S3: Experimental details for **12i**.

Crystal data	
Chemical formula	C ₃₆ H ₃₈ N ₂ O ₈
<i>M_r</i>	626.68
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.7805(16), 30.4609(19), 8.9360(6)
β (°)	100.235(3)
<i>V</i> (Å ³)	6370.0(7)
<i>Z</i>	8
Radiation type	MoKα
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.59 × 0.27 × 0.26
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan <i>SADABS2016/2</i> - Bruker AXS area detector scaling and absorption correction
<i>T_{min}</i> , <i>T_{max}</i>	0.629, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	56914, 11191, 9106
<i>R_{int}</i>	0.053
(sin θ/λ) _{max} (Å ⁻¹)	0.595
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.067, 0.150, 1.12
No. of reflections	11191
No. of parameters	823
No. of restraints	14
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.59, -0.84

Computer prog: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), *XT*, VERSION 2014/5, *SHELXL2016/6* (Sheldrick, 2016), *PLATON* (Spek, 2009).

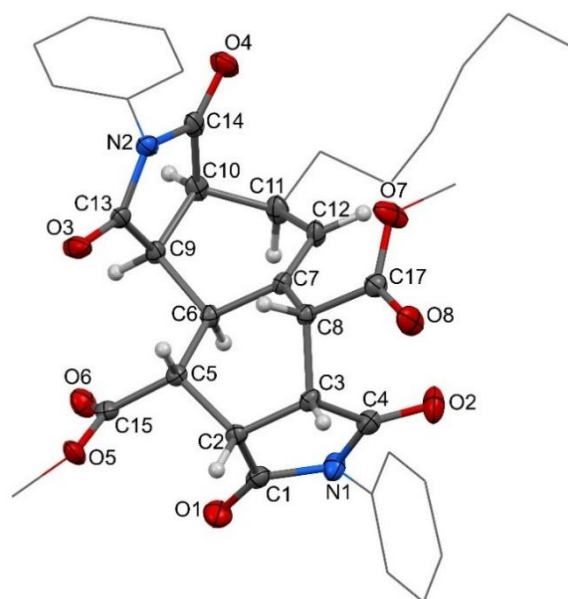


Figure S1: The molecular structure of **12i**, one of the disordered molecules is shown for clarity, ORTEP view 50% probability level. Interatomic distances (\AA , the second independent molecule exhibits nearly the same values): O1-C1 1.204(3), N1-C4, 1.394(4), N1-C1 1.395(4), N1-C19 1.443(4), C1-C2 1.515(4), O2-C4 1.204(3), N2-C13 1.382(3), N2-C14 1.401(3), N2-C25 1.437(3), C2-C3 1.542(3), C2-C5 1.548(3), O3-C13 1.212(3), C3-C4 1.523(4), C3-C8 1.544(3), O4-C14 1.210(3), C5-C15 1.511(4), C5-C6 1.535(3), O5-C15 1.337(3), O5-C16 1.446(3), O6-C15 1.202(3), C6-C7 1.525(3), C6-C9 1.562(3), O7-C17 1.331(3), O7-C18 1.453(4), C7-C12 1.331(4), C7-C8 1.521(3), C8-C17 1.522(4), O8-C17 1.197(3), C9-C13 1.505(4), C9-C10 1.545(3).

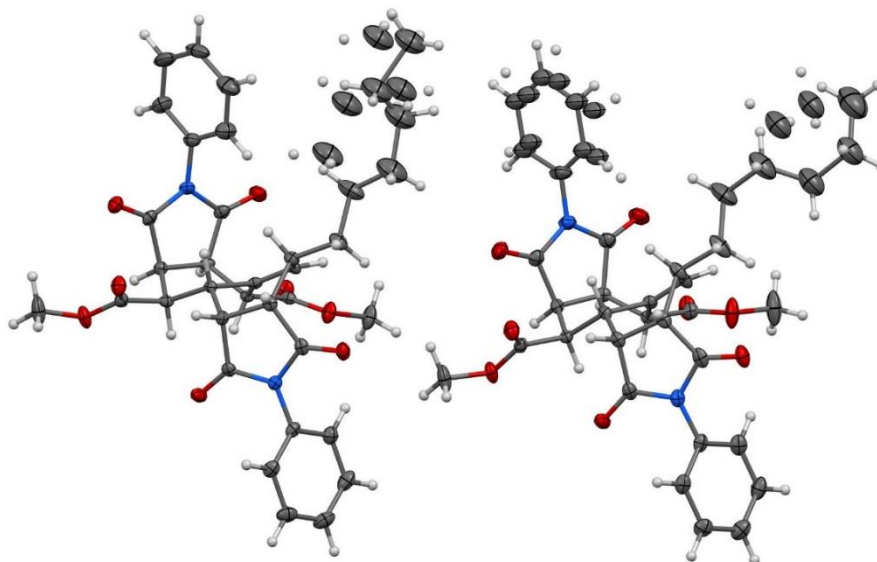


Figure S2: The molecular structure of **12i**, ORTEP view of both independent molecules with disordered parts - 50% probability level.

4. Computational Section

4.1 Computational Details

Calculations were performed in Gaussian 16 rev. A.03 and C.01.^[18] The reaction paths were studied by the DFT method in xylene. Full geometry optimization and frequencies were calculated at ω B97X-D/6-31+G(d,p) level of theory,^[19] which was selected based on benchmark against CCSD(T) energies described in the Section 4.1 of the SI. SCRf (self-consistent reaction field theory) with CPCM solvent model^[20] (conductor-like polarizable continuum model) was used, (xylene $\epsilon = 2.3879$). After optimization, single point calculations were performed in 6-311+G(2d,p) basis set, applying the same method. The studied structures were characterized by harmonic vibrational frequencies as minima (no imaginary frequencies) and transition states (one imaginary frequency), respectively. The unscaled vibrational frequencies were used to obtain the free energies ΔG and ΔG^\ddagger ($T = 298.15$ K; $p = 1$ atm). Reported Natural population analysis charges and electrostatic potential maps were calculated at ω B97X-D/6-311+G(2d,p) level of theory in the gas phase.

For our calculations, we considered the *s-cis/s-trans* isomerism in diene fragments, and different orientations of the CO₂Me groups were considered. When necessary (chiral compounds), attacks of the dienophile from both faces to the diene fragment were considered. In parallel, we also applied a more systematic approach, consisting of systematic conformational sampling with the CREST^[21] program and GFN2-xTB^[22] method in ALPB solvation model (toluene),^[23] followed by BP86-D3BJ/DGauss-DZVP^[24] single point calculations in COSMO-RS^[25] solvation model (at the semiempirical geometry). These calculations were carried out in Turbomole 7.6^[26] and COSMOTerm 2022,^[27] using “BP_TZVPD_FINE_22.ctd” parameter file.

4.2 CCSD(T) Benchmark

The Diels-Alder reaction (DA) between furan and maleimide (and cyclopenta-2,4-dien-1-one and nitrosomethane) was studied with various functionals in gas phase (**Table S4** and **Table S5**). Both forms: endo and exo were considered. Firstly, all structures were optimized by B3LYP, M062X, ω B97X-D and MP2 methods in combination with the 6-31+g(d,p) or aug-cc-pVDZ basis sets. Afterwards, the energy values were recalculated with 6-311+g(2d,p) basis set and corresponding functional. For this purpose, we used Gaussian 16. In the next step, we performed CCSD(T) calculations on the geometries obtained with different methods in two basis sets: aug-cc-pVDZ and aug-cc-pVTZ. CCSD(T) calculations were done in Turbomole 7.4.1 program.^[26, 28] The extrapolation to the complete basis set was calculated according to the equation:^[29]

$$E_{\text{CCSD(T)/CBS}} = E_{\text{HF/aug-cc-pVTZ}} + (3^3 E_{\text{corr,CCSD(T)/aug-cc-pVTZ}} - 2^3 E_{\text{corrCCSD(T)/aug-cc-pDTZ}})/(3^3 - 2^3),$$

where E_{HF} is the Hartree-Fock energy and $E_{\text{corr,CCSD(T)}}$ is the CCSD(T) correlation energy.

Table S4: Calculated values of studied DA reaction electronic energies (ΔE^\ddagger - transition state barriers; ΔE - energy value of the substrates or the products) between furan and maleimide.




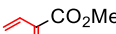

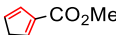



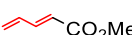
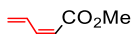
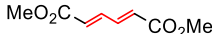
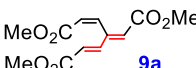
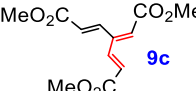
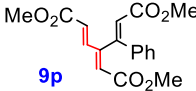
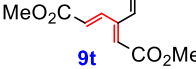
Optimization level	$E_{\text{Product_Exo}}$	$E_{\text{Product_Endo}}$	E_{Furan}	$E_{\text{Maleimide}}$	$E_{\text{TS_Exo}}$	$E_{\text{TS_Endo}}$	$\Delta E^\ddagger_{\text{Exo}}$	$\Delta E^\ddagger_{\text{Endo}}$	ΔE_{Exo}	ΔE_{Endo}
	[a.u.]						[kcal/mol]			
Optimization										
B3LYP-D3/6-31+g(d,p)	-589.5196	-589.5160	-230.0412	-359.4591	-589.4591	-589.4588	25.9	26.1	-12.1	-9.8
M062X/6-31+g(d,p)	-589.2720	-589.2687	-229.9366	-359.3051	-589.2230	-589.2234	11.8	11.5	-19.0	-16.9
ω B97X-D/6-31+g(d,p)	-589.3219	-589.3189	-229.9570	-359.3321	-589.2668	-589.2679	14.0	13.3	-20.6	-18.7
MP2/aug-cc-pVDZ	-586.1274	-586.1219	-228.6508	-357.4537	-586.0500	-586.0497	34.3	34.5	-14.3	-10.8
MP2/6-31+G(d)	-586.0626	-586.0572	-228.6295	-357.4115	-585.9859	-585.9856	34.6	34.8	-13.5	-10.2
Single point with the same functional as optimization, 6-311+g(2d,p) basis set										
B3LYP D3/6-31+g(d,p)	-589.6657	-589.6620	-230.0966	-359.5532	-589.6251	-589.6249	15.5	15.6	-10.0	-7.7
M062X/6-31+g(d,p)	-589.4306	-589.4272	-229.9962	-359.4064	-589.3821	-589.3825	12.8	12.6	-17.6	-15.5
ω B97X-D/6-31+g(d,p)	-589.4624	-589.4594	-230.0096	-359.4227	-589.4079	-589.4089	15.3	14.8	-18.8	-16.9
MP2/aug-cc-pVDZ	-586.2102	-586.2046	-228.6853	-357.5064	-586.1342	-586.1335	36.1	36.5	-11.7	-8.2
MP2/6-31+G(d)	-586.2131	-586.2079	-228.6879	-357.5077	-586.1372	-586.1368	36.6	36.9	-11.0	-7.7
Single point CCSD(T)/aug-cc-pVDZ										
B3LYP D3/6-31+g(d,p)	-588.0898	-588.0864	-229.4501	-358.5986	-588.0375	-588.0382	7.0	6.6	-25.8	-23.7
E_{corr}	-1.9573	-1.9588	-0.7964	-1.1412	-1.9832	-1.9835				
M062X/6-31+g(d,p)	-588.0880	-588.0848	-229.4490	-358.5975	-588.0360	-588.0370	6.6	6.0	-26.0	-24.0
E_{corr}	-1.9534	-1.9551	-0.7944	-1.1383	-1.9796	-1.9804				
ω B97X-D/6-31+g(d,p)	-588.0880	-588.0846	-229.4490	-358.5976	-588.0358	-588.0368	6.8	6.2	-25.9	-23.8
E_{corr}	-1.9533	-1.9549	-0.7944	-1.1386	-1.9793	-1.9800				
MP2/aug-cc-pVDZ	-588.0912	-588.0879	-229.4510	-358.5995	-588.0398	-588.0408	6.7	6.1	-25.5	-23.5
E_{corr}	-1.9638	-1.9661	-0.8002	-1.1458	-1.9899	-1.9911				
MP2/6-31+G(d)	-588.0899	-588.0867	-229.4503	-358.5990	-588.0382	-588.0390	6.9	6.4	-25.5	-23.5
E_{corr}	-1.9605	-1.9624	-0.7976	-1.1442	-1.9862	-1.9871				
Single point CCSD(T)/aug-cc-pVTZ										
B3LYP D3/6-31+g(d,p)	-588.5838	-588.5805	-229.6512	-358.8994	-588.5320	-588.5327	11.7	11.3	-20.8	-18.8
E_{HF}	-586.2598	-586.2550	-228.7086	-357.5382	-586.1847	-586.1850				
E_{corr}	-2.3240	-2.3255	-0.9426	-1.3613	-2.3473	-2.3477				
M062X/6-31+g(d,p)	-588.5838	-588.5806	-229.6510	-358.8993	-588.5325	-588.5332	11.2	10.7	-21.0	-19.0
E_{HF}	-586.2629	-586.2579	-228.7099	-357.5406	-586.1878	-586.1878				
E_{corr}	-2.3209	-2.3227	-0.9411	-1.3587	-2.3446	-2.3454				
ω B97X-D/6-31+g(d,p)	-588.5837	-588.5805	-229.6510	-358.8994	-588.5324	-588.5332	11.3	10.8	-20.9	-18.9
E_{HF}	-586.2628	-586.2580	-228.7099	-357.5403	-586.1881	-586.1882				
E_{corr}	-2.3209	-2.3225	-0.9411	-1.3591	-2.3443	-2.3450				
MP2/aug-cc-pVDZ	-588.5827	-588.5795	-229.6503	-358.8989	-588.5318	-588.5324	10.9	10.5	-21.0	-19.0
E_{HF}	-586.2533	-586.2478	-228.7047	-357.5335	-586.1787	-586.1782				
E_{corr}	-2.3294	-2.3317	-0.9456	-1.3650	-2.3530	-2.3542				
MP2/6-31+G(d)	-588.5833	-588.5801	-229.6510	-358.8986	-588.5321	-588.5328	10.9	10.5	-21.2	-19.1
E_{HF}	-586.2562	-586.2511	-228.7074	-357.5349	-586.1819	-586.1816				
E_{corr}	-2.3271	-2.3290	-0.9436	-1.3639	-2.3502	-2.3512				
Single point CCSD(T)/CBS										
B3LYP D3/6-31+g(d,p)	-588.7382	-588.7349	-229.7127	-358.9921	-588.6854	-588.6860	12.2	11.8	-20.9	-18.9
M062X/6-31+g(d,p)	-588.7385	-588.7354	-229.7127	-358.9922	-588.6862	-588.6869	11.7	11.3	-21.1	-19.1
ω B97X-D/6-31+g(d,p)	-588.7385	-588.7353	-229.7127	-358.9922	-588.6860	-588.6868	11.9	11.4	-21.0	-19.0
MP2/aug-cc-pVDZ	-588.7366	-588.7334	-229.7115	-358.9909	-588.6847	-588.6853	11.1	10.7	-21.5	-19.5
MP2/6-31+G(d)	-588.7376	-588.7344	-229.7125	-358.9914	-588.6854	-588.6861	11.6	11.2	-21.2	-19.2
Average value							11.7	11.3	-21.2	-19.1

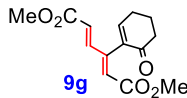
Table S5: Calculated values of studied DA reaction electronic energies (ΔE^\pm - transition state barriers; ΔE - energy value of the substrates or the products) between cyclopenta-2,4-dien-1-one and nitrosomethane.

Optimization level	$E_{\text{Product_Exo}}$	$E_{\text{Product_Endo}}$	$E_{\text{cyclopentadienone}}$	$E_{\text{nitrosomethane}}$	$E_{\text{TS_Exo}}$	$E_{\text{TS_Endo}}$	$\Delta E^\pm_{\text{Exo}}$	$\Delta E^\pm_{\text{Endo}}$	ΔE_{Exo}	ΔE_{Endo}
	[a.u.]						[kcal/mol]			
Optimization										
B3LYP-D3/6-31+g(d,p)	-437.9574	-437.9588	-268.1277	-169.8104	-437.9052	-437.9127	20.6	15.9	-12.1	-13.0
M062X/6-31+g(d,p)	-437.7599	-437.7612	-268.0021	-169.7272	-437.7014	-437.7108	17.5	11.6	-19.2	-20.0
ω B97X-D/6-31+g(d,p)	-437.8034	-437.8049	-268.0265	-169.7488	-437.7480	-437.7574	17.1	11.3	-17.6	-18.5
MP2/aug-cc-pVDZ	-435.3717	-435.3719	-266.5113	-168.8531	-435.2973	-435.3120	42.1	32.9	-4.6	-4.7
MP2/6-31+g(d)	-435.3240	-435.3246	-266.4863	-168.8289	-435.2419	-435.2599	46.0	34.8	-5.5	-5.9
Single point with the same functional as optimization, 6-311+g(2d,p) basis set										
B3LYP-D3/6-31+g(d,p)	-438.0648	-438.0659	-268.1918	-169.8556	-438.0267	-438.0343	13.0	8.3	-10.9	-11.6
M062X/6-31+g(d,p)	-437.8775	-437.8783	-268.0721	-169.7760	-437.8190	-437.8284	18.2	12.3	-18.5	-19.0
ω B97X-D/6-31+g(d,p)	-437.9068	-437.9080	-268.0882	-169.7922	-437.8516	-437.8612	18.1	12.1	-16.6	-16.6
MP2/aug-cc-pVDZ	-435.4339	-435.4342	-266.5509	-168.8778	-435.3589	-435.3742	43.8	34.2	-3.3	-3.5
MP2/6-31+g(d)	-435.4369	-435.4373	-266.5532	-168.8773	-435.3549	-435.3730	47.4	36.0	-4.0	-4.3
Single point CCSD(T)/aug-cc-pVDZ										
B3LYP D3/6-31+g(d,p)	-436.8802	-436.8807	-267.4388	-169.4139	-436.8329	-436.8412	12.5	7.3	-17.2	-17.5
E_{corr}	-1.5036	-1.5035	-0.9238	-0.5575	-1.5452	-1.5330				
M062X/6-31+g(d,p)	-436.8784	-436.8788	-267.4378	-169.4132	-436.8318	-436.8414	12.0	6.0	-17.2	-17.4
E_{corr}	-1.4987	-1.4988	-0.9217	-0.5553	-1.5399	-1.5359				
ω B97X-D/6-31+g(d,p)	-436.8783	-436.8787	-267.4379	-169.4134	-436.8325	-436.8407	11.8	6.7	-16.9	-17.2
E_{corr}	-1.4987	-1.4989	-0.9219	-0.5560	-1.5421	-1.5320				
MP2/aug-cc-pVDZ	-436.8817	-436.8820	-267.4402	-169.4143	-436.8347	-436.8456	12.4	5.6	-17.1	-17.3
E_{corr}	-1.5100	-1.5101	-0.9289	-0.5612	-1.5427	-1.5336				
MP2/6-31+g(d)	-436.8805	-436.8809	-267.4392	-169.4140	-436.8347	-436.8432	11.6	6.3	-17.1	-17.4
E_{corr}	-1.5067	-1.5068	-0.9264	-0.5615	-1.5427	-1.5332				
Single point CCSD(T)/aug-cc-pVTZ										
B3LYP D3/6-31+g(d,p)	-437.2513	-437.2520	-267.6669	-169.5578	-437.2006	-437.2093	15.1	9.6	-16.8	-17.2
E_{HF}	-435.4724	-435.4730	-266.5751	-168.8948	-435.3827	-435.4034				
E_{corr}	-1.7790	-1.7790	-1.0918	-0.6630	-1.8179	-1.8058				
M062X/6-31+g(d,p)	-437.2511	-437.2517	-267.6667	-169.5575	-437.2008	-437.2109	14.6	8.3	-16.9	-17.3
E_{HF}	-435.4761	-435.4765	-266.5767	-168.8966	-435.3872	-435.4010				
E_{corr}	-1.7750	-1.7752	-1.0900	-0.6609	-1.8136	-1.8099				
ω B97X-D/6-31+g(d,p)	-437.2510	-437.2517	-267.6667	-169.5576	-437.2015	-437.2100	14.4	9.0	-16.7	-17.1
E_{HF}	-435.4760	-435.4764	-266.5765	-168.8960	-435.3859	-435.4045				
E_{corr}	-1.7750	-1.7753	-1.0902	-0.6616	-1.8156	-1.8056				
MP2/aug-cc-pVDZ	-437.2506	-437.2511	-267.6660	-169.5573	-437.2012	-437.2106	13.9	8.0	-17.1	-17.5
E_{HF}	-435.4661	-435.4664	-266.5701	-168.8910	-435.3863	-435.4057				
E_{corr}	-1.7845	-1.7847	-1.0958	-0.6663	-1.8149	-1.8049				
MP2/6-31+g(d)	-437.2511	-437.2517	-267.6665	-169.5572	-437.2012	-437.2099	14.2	8.7	-17.2	-17.5
E_{HF}	-435.4691	-435.4696	-266.5724	-168.8905	-435.3863	-435.4046				
E_{corr}	-1.7820	-1.7822	-1.0941	-0.6667	-1.8149	-1.8053				
Single point CCSD(T)/CBS										
B3LYP D3/6-31+g(d,p)	-437.3673	-437.3680	-267.7376	-169.6021	-437.3155	-437.3241	15.2	9.8	-17.3	-17.7
M062X/6-31+g(d,p)	-437.3674	-437.3680	-267.7375	-169.6020	-437.3161	-437.3262	14.7	8.4	-17.5	-17.9
ω B97X-D/6-31+g(d,p)	-437.3673	-437.3680	-267.7376	-169.6021	-437.3166	-437.3252	14.5	9.1	-17.3	-17.8
MP2/aug-cc-pVDZ	-437.3662	-437.3667	-267.7363	-169.6016	-437.3158	-437.3248	13.9	8.2	-17.8	-18.1
MP2/6-31+g(d)	-437.3670	-437.3677	-267.7371	-169.6016	-437.3158	-437.3245	14.4	8.9	-17.8	-18.2
Average value							14.5	8.9	-17.5	-17.9

4.3 Tables S6 and S7

Table S6. Relative enthalpies^[a] for transition states ($\Delta H^{0K\dagger}$) and products (ΔH^{0K}) of the DA reaction in of various substituted dienes (diene functionality highlighted in red) with dienophile (DP; **10** or **13**) as well as the energy difference between *s-cis* and *s-trans* conformers ($\Delta H_{t\rightarrow c}$) for selected dienes. DFT HOMO/LUMO orbital energies in eV.

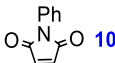






Entry	Diene	DP	ΔH^{0K} <i>t</i> → <i>c</i>	$\Delta H^{0K\dagger}$ <i>endo</i>	$\Delta H^{0K\dagger}$ <i>exo</i>	ΔH^{0K} <i>endo</i>	ΔH^{0K} <i>exo</i>	E_{HOMO} diene ^[b]	E_{LUMO} diene ^[b]
1		10	2.8	14.1	17	-44.9	-8.6	0.8	
2		10	-1	10.3	14.3	-49.7	-8.5	0.5	
3		10	-	10.1	13.2	-30	-30.1	-8.2	1.2
4		10	-0.3	9.1	13	-50.2	-9.0	0.0	
5		10	-	9.6	12.1	-32.6	-32.2	-8.0	0.8
6		10	-	9.5	13.1	-31.3	-30.8	-8.6	0.3
7		10	2.6	13.9	16.8	-47.1	-9.3	-0.2	
8		10	2	11.5	15.8	-47.9	-8.5	0.8	
9		10	-1.5	9.7	13.5	-50.9	-8.6	1.0	
10		10	2.9	14.3	17.7	-40.8	-42	-9.0	-0.2
11		10	5.7	18.2	20.3	-44	-42.9	-8.9	-0.2
12		10	2.8	15.6	18.5	-37.3	-39	-9.2	-0.9
13		10	2.2	13.9	15.9	-39	-43.3	-9.1	-0.9
14		10	-3.8	12.1	15.3	-42.7	-47.4	-9.2	-1.2
15		10	2	11.6	15.5	-41	-46.4	-8.8	-1.0
16		10	-0.3	13	16	-40.9	-45.8	-9.0	-0.8

Entry	Diene	DP	ΔH^{0K} <i>t</i> → <i>c</i>	$\Delta H^{0K\dagger}$ <i>endo</i>	$\Delta H^{0K\dagger}$ <i>exo</i>	ΔH^{0K} <i>endo</i>	ΔH^{0K} <i>exo</i>	E_{HOMO} diene ^[b]	E_{LUMO} diene ^[b]
17		10	2.5	12.7	15.8	-39.3	-44.8	-9.0	-0.9
18	9g	13	2.5	7.1	17.5	-46.6	-46.8	-9.0	-0.9

[a] Enthalpies at 0 K in kcal mol⁻¹. Calculations were carried out with ω B97X-D/6-311+G(2d,p)//6-31+G(d,p) level of theory for xylene as the solvent.

[b] Orbital energies for the most stable diene conformation.

Table S7. Enthalpies ΔH^{0K} for transition states and products of the DA reaction of dendralene **9a** with various dienophiles (DPs).^[a]

Entry	Dienophile	$\Delta H^{0K\dagger}$ <i>endo</i>	$\Delta H^{0K\dagger}$ <i>exo</i>	ΔH^{0K} <i>endo</i>	ΔH^{0K} <i>exo</i>	E_{HOMO} DP	E_{LUMO} DP
1	 10	13.9	15.9	-39	-43.3	-9	-1.1
2	PhN=O 14	14.2	22	-20.9	-20.2	-8.8	-1.2
3		16.7	19.7	-31.5	-32.9	-8.2	1.2
4		24.7	26	-19.5	-20.9	-8.6	1.8
5		18.2	18.1	-30.3	-34.6	-9.5	-1
6		16.5	17.6	-32.6	-35.9	-9.9	-1.9
7		15.2	16.9	-33.6	-36	-9.7	-1.7
8		24	23.8	-32.7	-36	-8.2	1.8

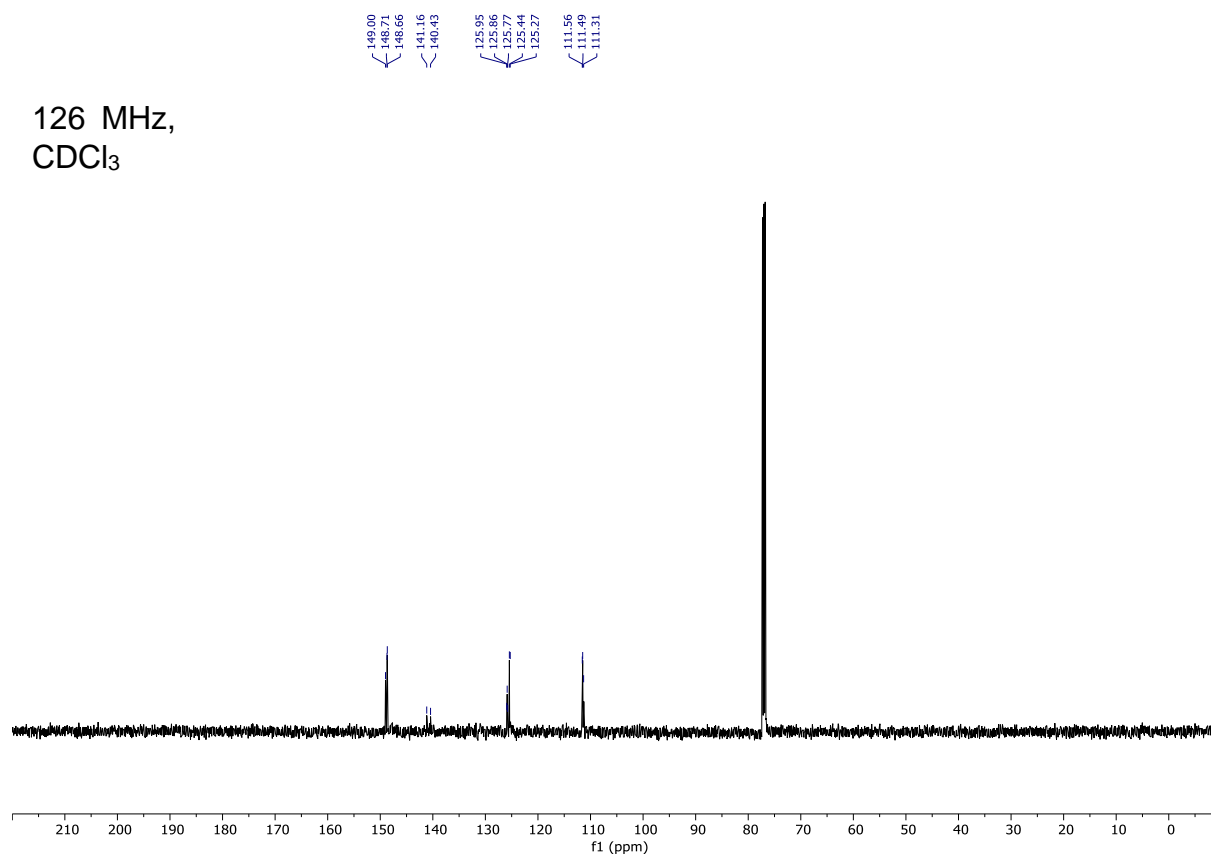
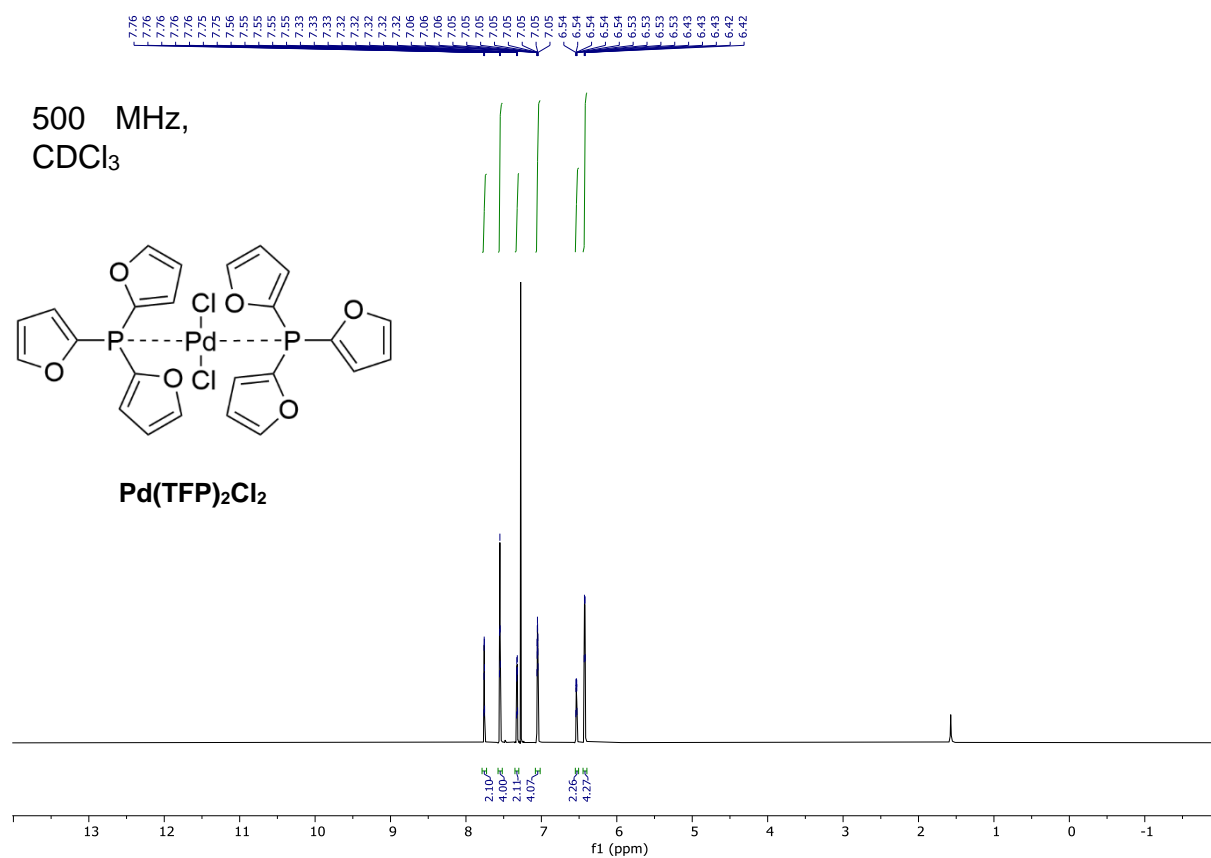
[a] Enthalpies at 0 K in kcal mol⁻¹. Calculations were carried out with ω B97X-D/6-311+G(2d,p)//6-31+G(d,p) level of theory in xylene.

5. References

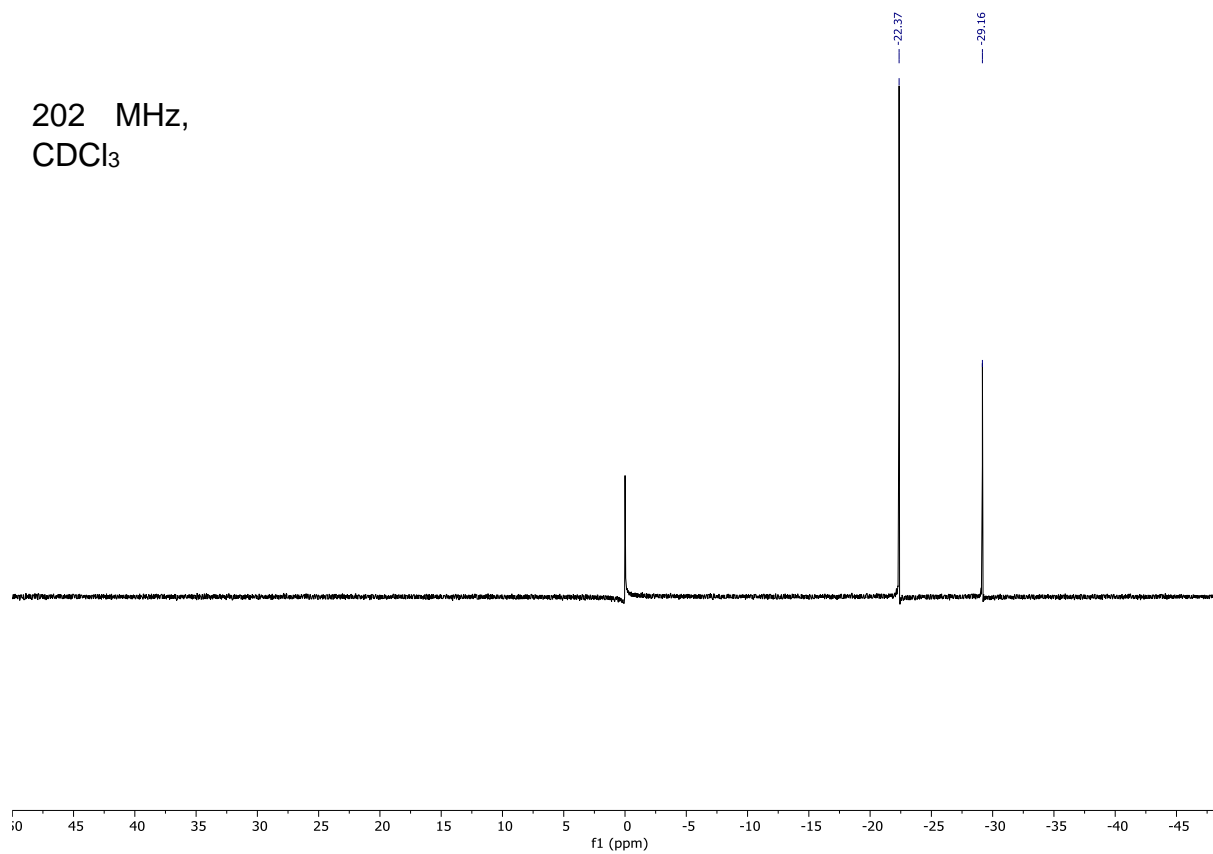
- [1] X. Zeng, Q. Hu, M. Qian, E. Negishi, *J. Am. Chem. Soc.* **2003**, *125*, 13636–13637.
- [2] C. M. Hettrick, W. J. Scott, *J. Am. Chem. Soc.* **1991**, *113*, 4903–4910.
- [3] F. Pünner, G. Hilt, *Chem. Commun.* **2012**, *48*, 3617–3619.
- [4] Z. Brůža, J. Kratochvíl, J. N. Harvey, L. Rulíšek, L. Nováková, J. Maříková, J. Kuneš, P. Kočovský, M. Pour, *Chem. Eur. J.* **2019**, *25*, 8053–8060.
- [5] J. Kratochvíl, Z. Novák, M. Ghavre, L. Nováková, A. Růžička, J. Kuneš, M. Pour, *Org. Lett.* **2015**, *17*, 520–523.
- [6] Commercially available starting material.
- [7] S. Fujiwara, R. Cadou, Y. Yamaoka, K. Takasu, K.-i. Yamada, *Eur. J. Org. Chem.* **2015**, *2015*, 1264–1272.
- [8] I. N. Michaelides, B. Darses, D. J. Dixon, *Org. Lett.* **2011**, *13*, 664–667.
- [9] T. Peez, J.-N. Luy, K. Harms, R. Tonner, U. Koert, *Chem. Eur. J.* **2018**, *24*, 17686–17690.
- [10] H. Zhang, L. Xu, X. Liu, J. Fan, X. Wang, T. Shen, S. Wang, D. Ren, *Chin. Chem. Lett.* **2020**, *31*, 1259–1262.
- [11] E. Piers, J. R. Grierson, C. K. Lau, I. Nagakura, *Canad. J. Chem.* **1982**, *60*, 210–223.
- [12] M. E. Krafft, J. W. Cran, *Synlett* **2005**, 1263–1266.
- [13] D. H. R. Barton, G. Bashiardes, J.-L. Fourrey, *Tetrahedron* **1988**, *44*, 147–162.
- [14] J. Salazar, F. Fernández, J. Restrepo, S. E. López, *J. Chem. Res.* **2007**, *2007*, 170–172.
- [15] G. Sheldrick, *Acta Crystall. Section A* **2015**, *71*, 3–8.
- [16] for example: a) O. Kwon, S. B. Park, S. L. Schreiber, *J. Am. Chem. Soc.* **2002**, *124*, 13402–13404; b) S. M. Tan, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem., Int. Ed.* **2016**, *55*, 3081–3085; c) G. Bojase, A. D. Payne, A. C. Willis, M. S. Sherburn, *Angew. Chem., Int. Ed.* **2008**, *47*, 910; d) T. A. Bradford, A. D. Payne, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *J. Org. Chem.* **2010**, *75*, 491–494.
- [17] J. George, J. S. Ward, M. S. Sherburn, *Chem. Sci.* **2019**, *10*, 9969–9973.
- [18] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [19] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B Condens. Matter* **1988**, *37*, 785–789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- [20] a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001; b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* **2003**, *24*, 669–681.
- [21] P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192.
- [22] C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671.
- [23] S. Ehlert, M. Stahn, S. Spicher, S. Grimme, *J. Chem. Theory Comput.* **2021**, *17*, 4250–4261.

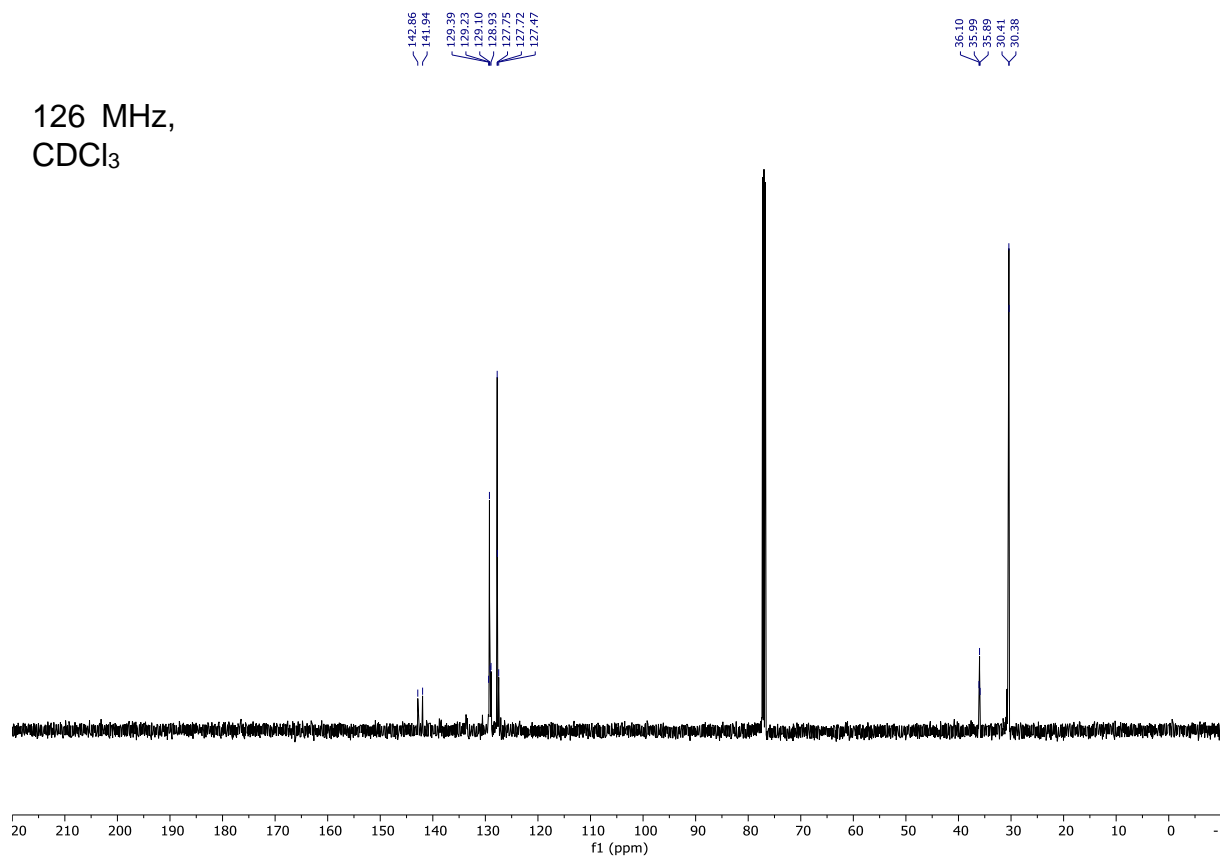
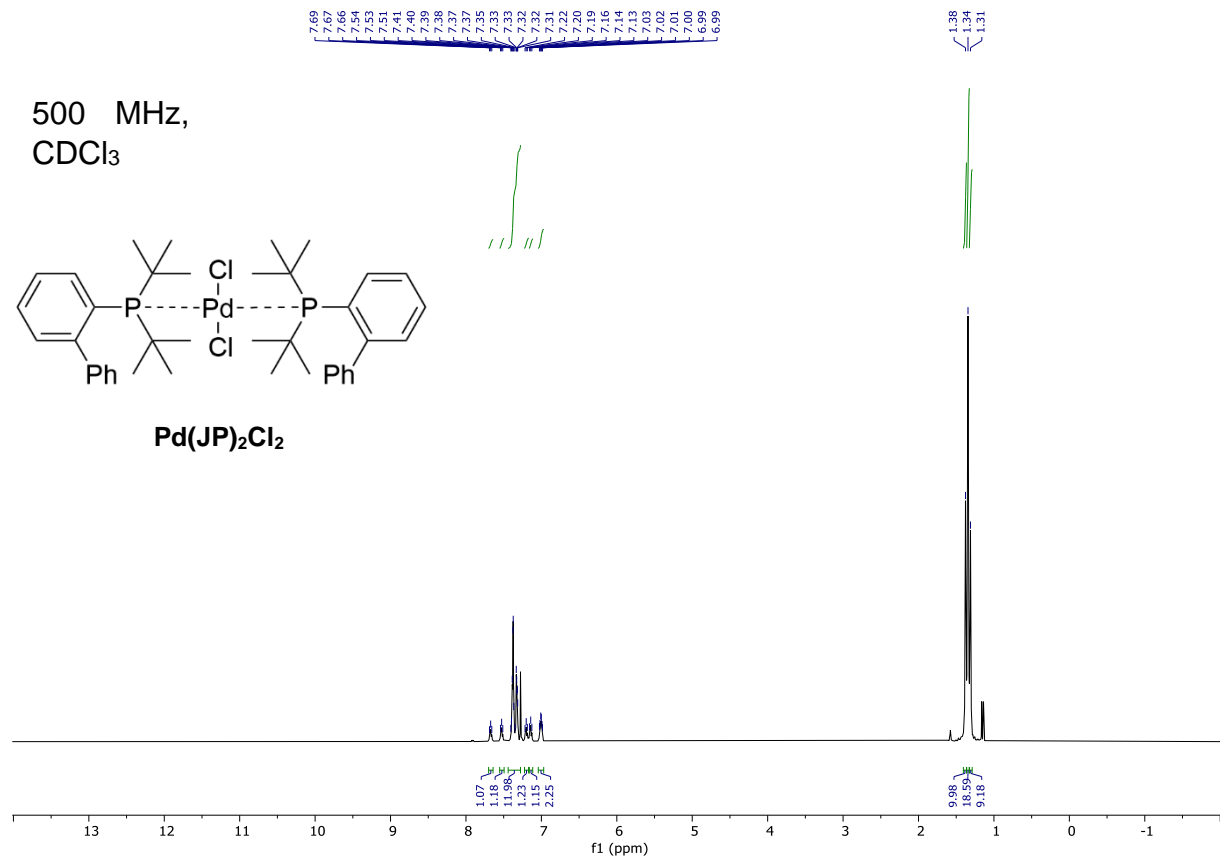
- [24] a) A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098–3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822–8824; c) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, 132, 154104; d) J. Hostaš, J. Řezáč, *J. Chem. Theory Comput.* **2017**, 13, 3575–3585.
- [25] F. Eckert, A. Klamt, *AIChE Journal* **2002**, 48, 369–385.
- [26] TURBOMOLE V7.4.1 2019, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [27] Biovia COSMOTHERM, Release 2022, Dassault Systèmes. <https://www.3ds.com>.
- [28] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, 4, 91–100.
- [29] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, *Chem. Phys. Lett.* **1998**, 286, 243–252.

6. NMR spectra

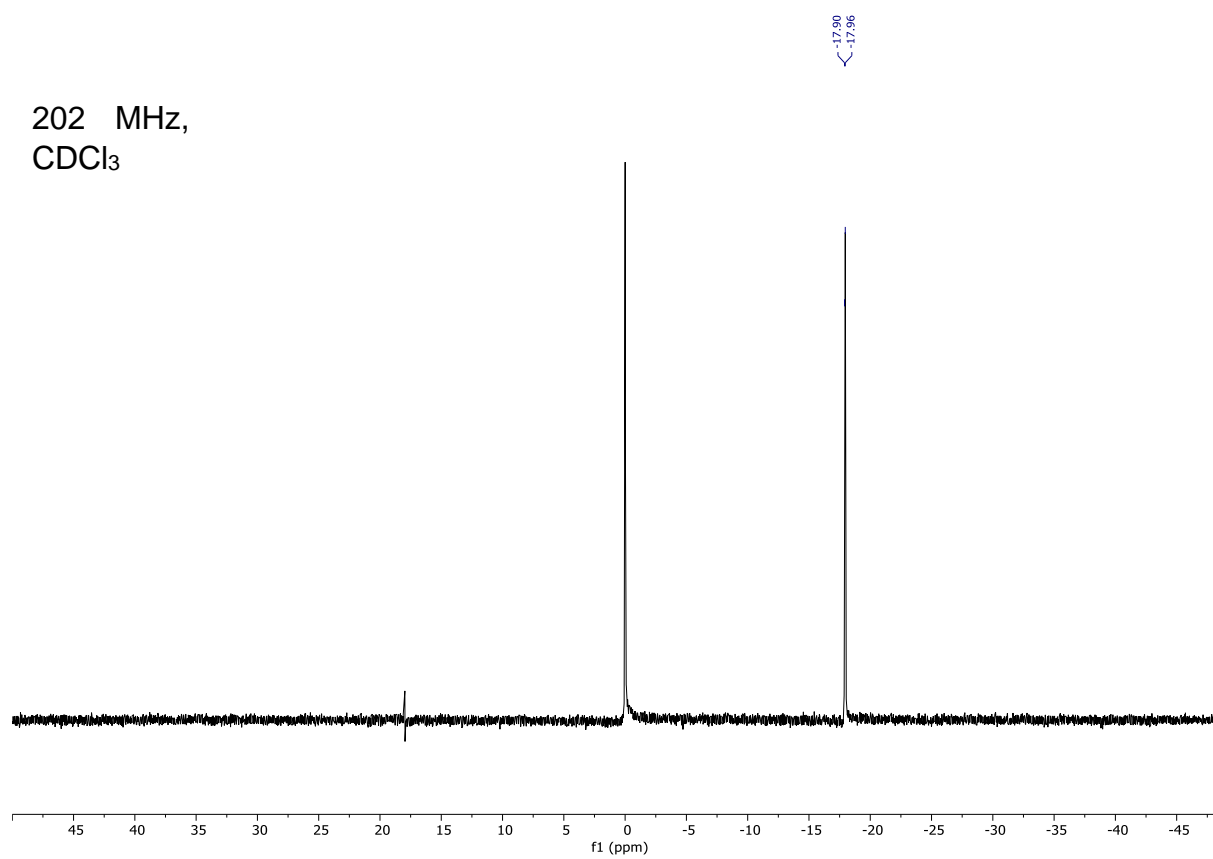


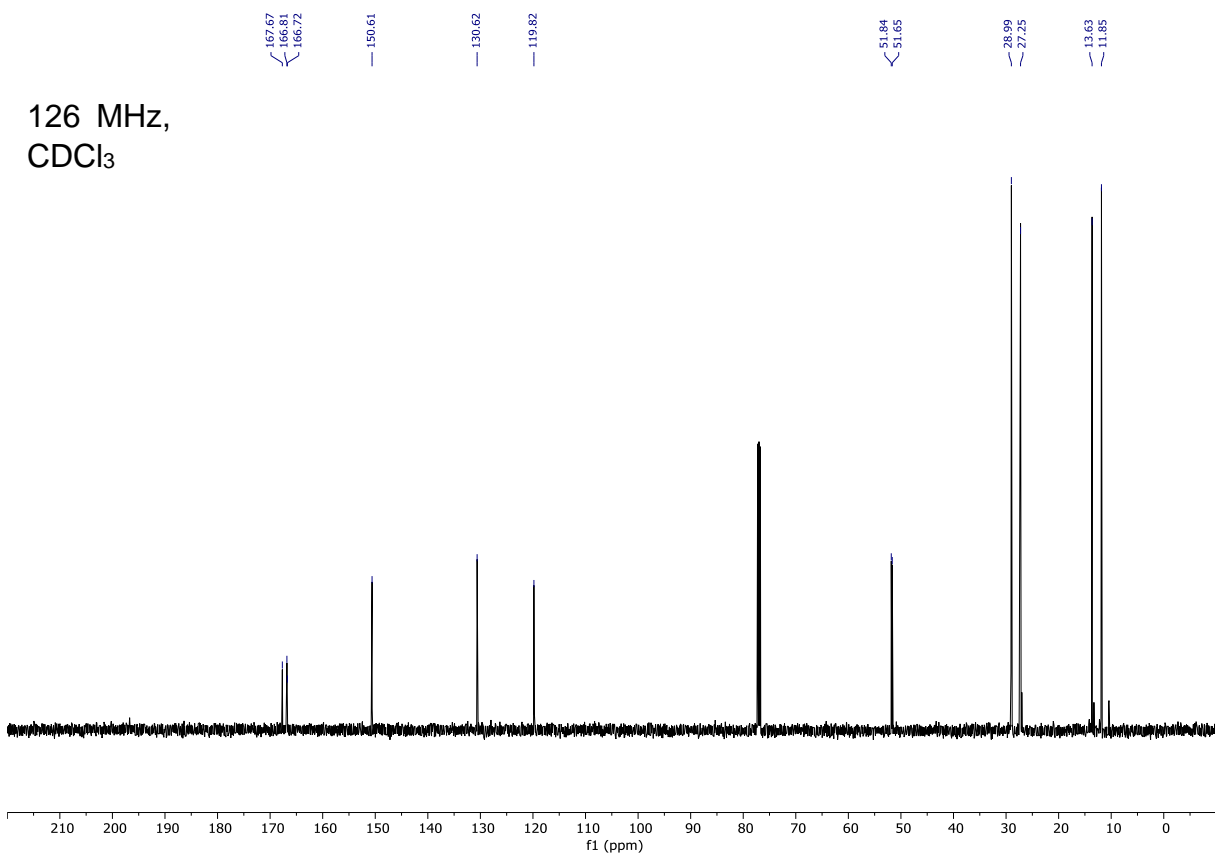
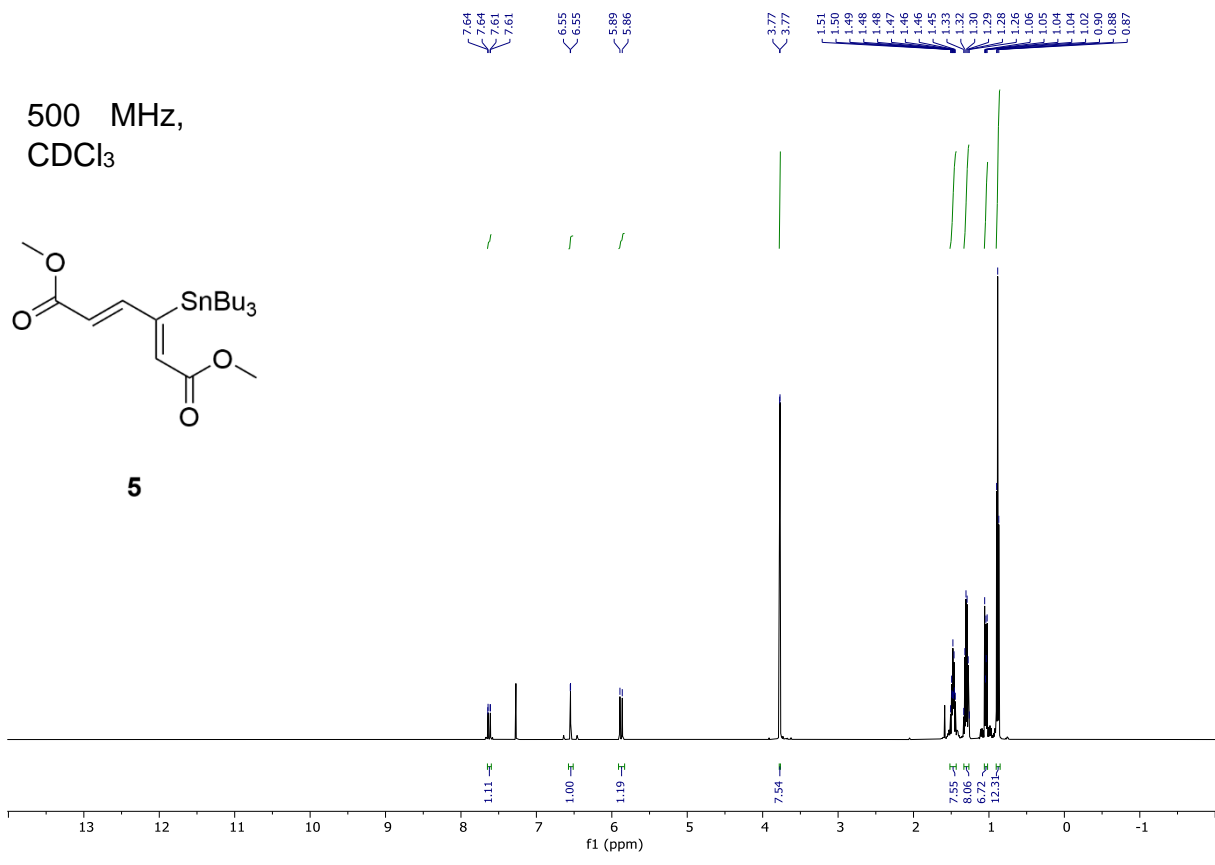
202 MHz,
CDCl₃



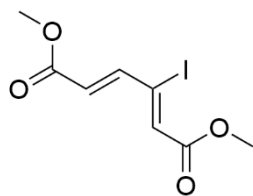


202 MHz,
CDCl₃

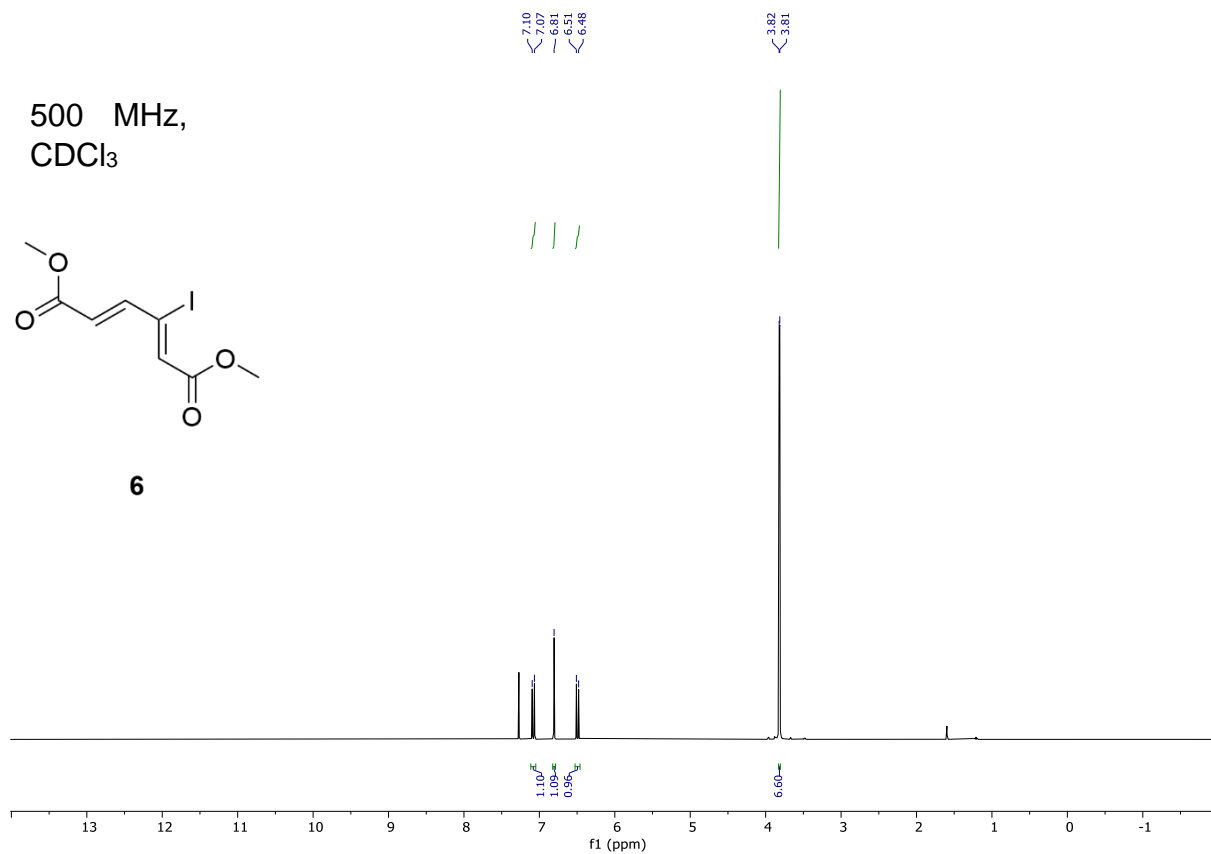




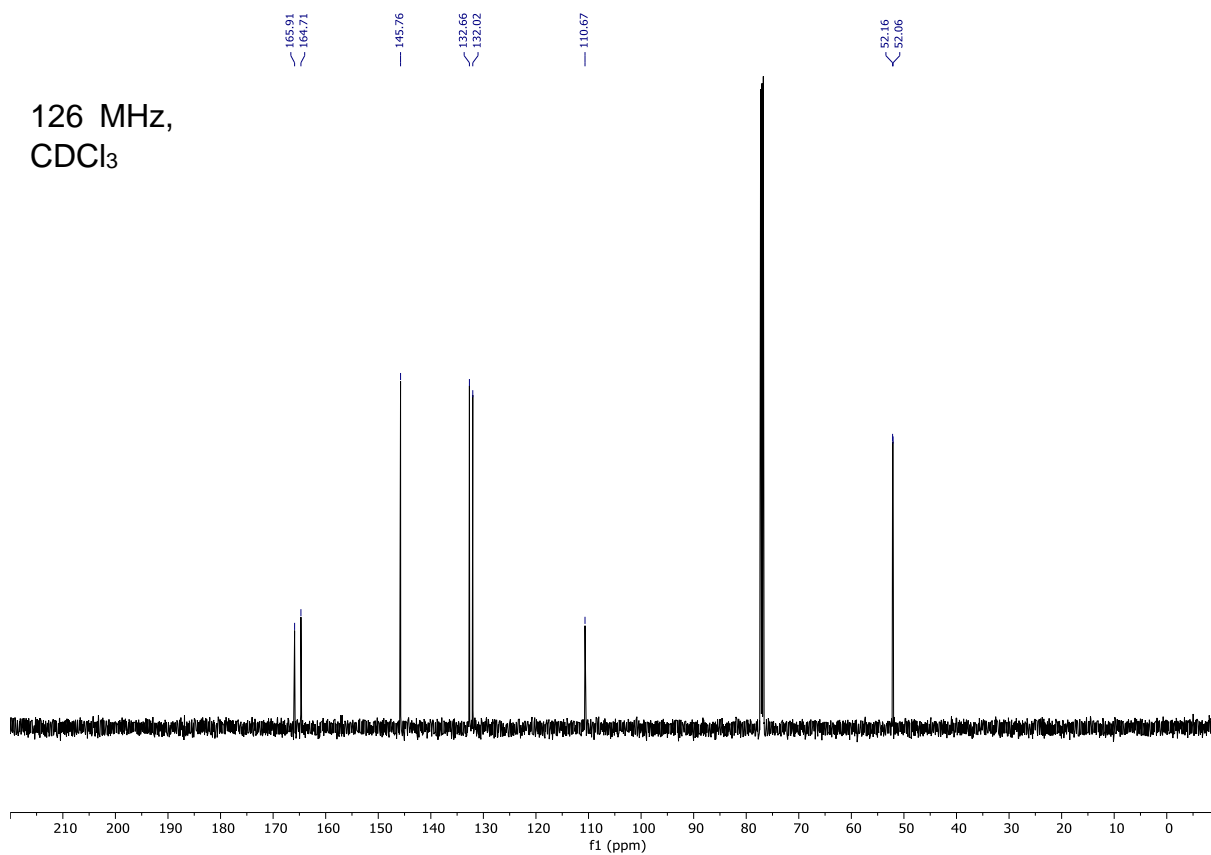
500 MHz,
CDCl₃

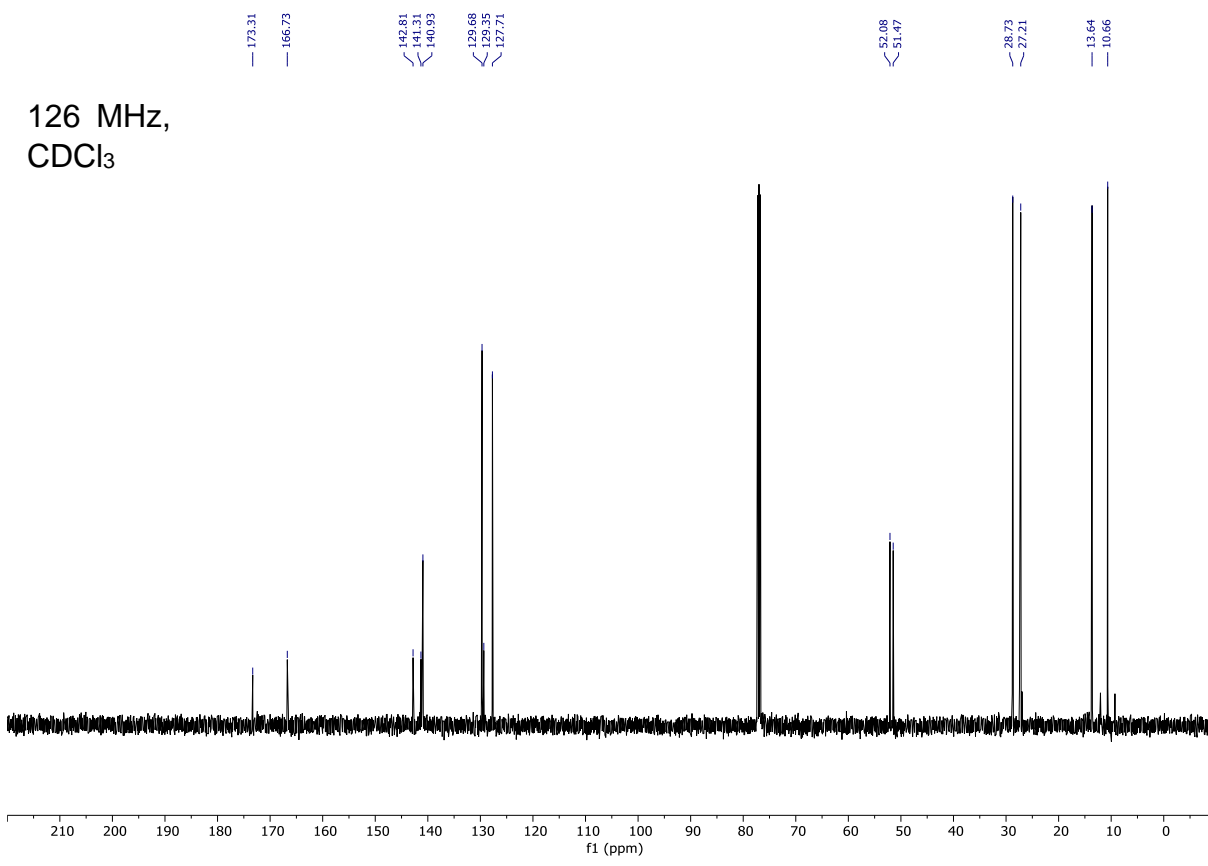
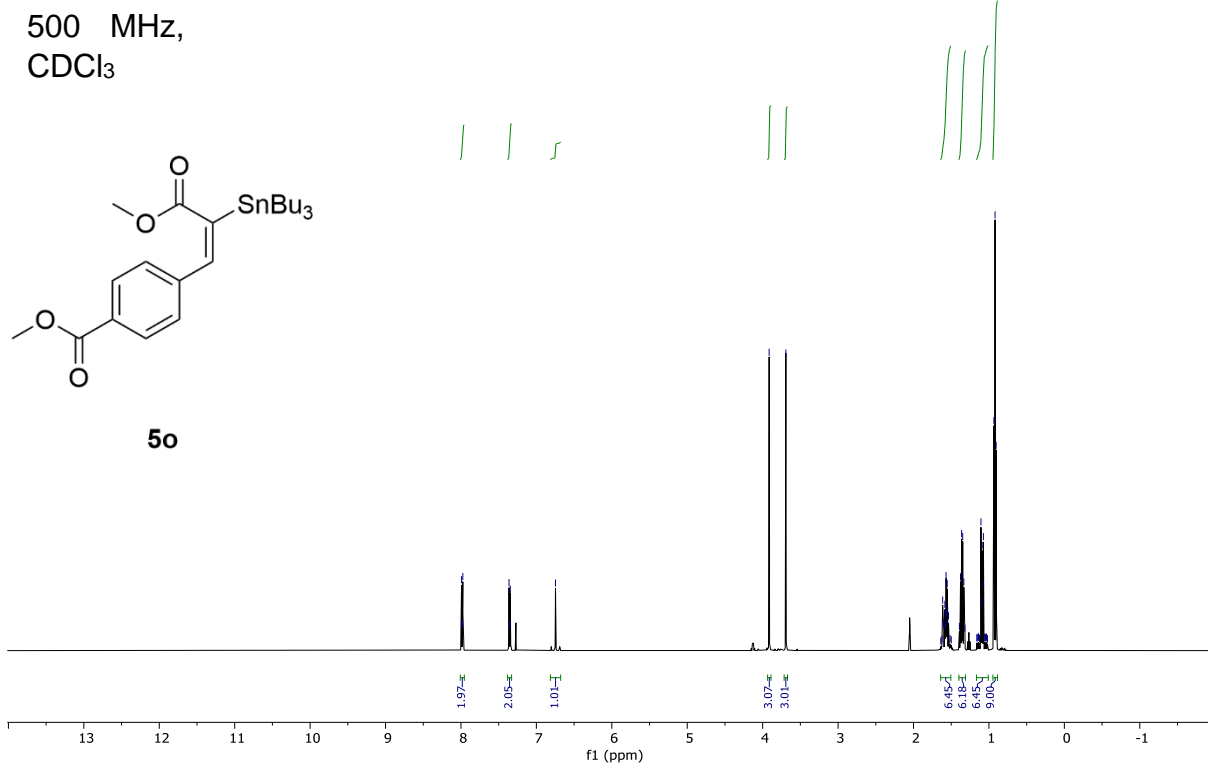


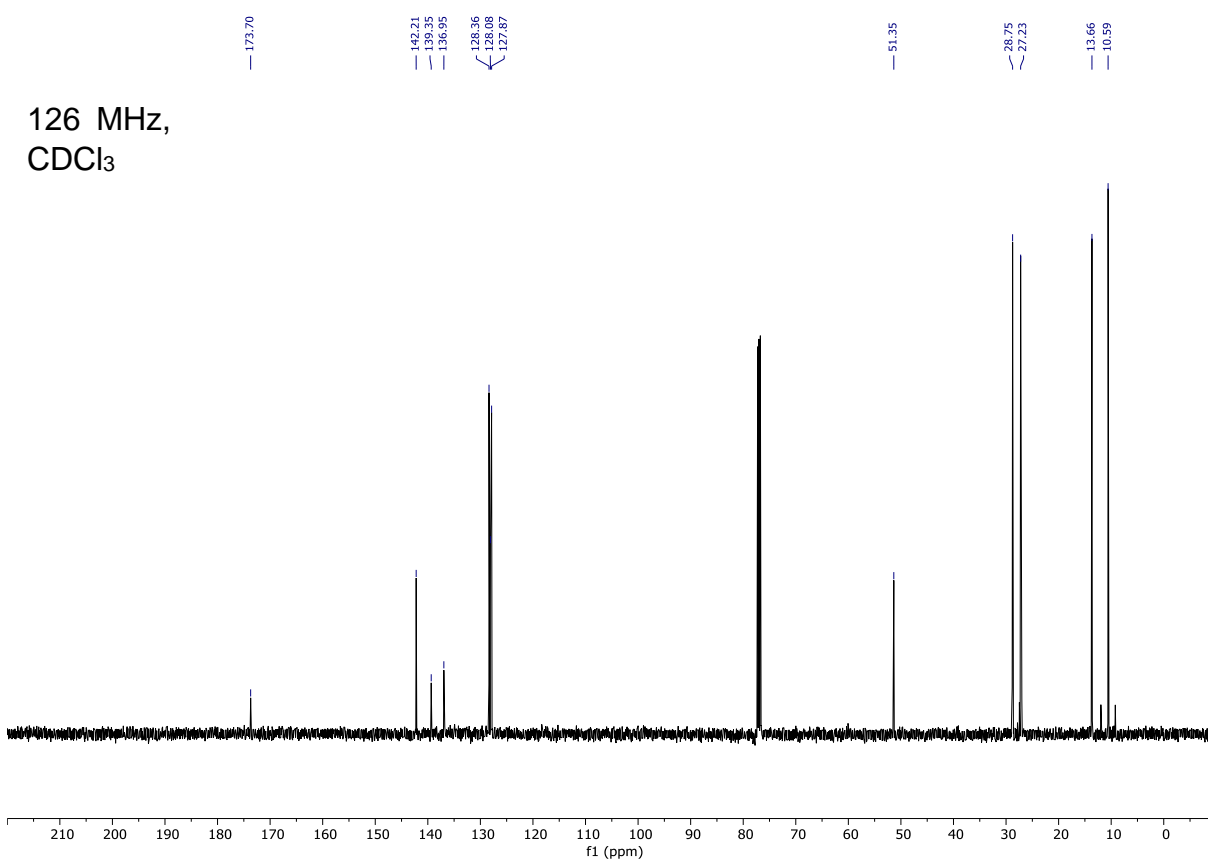
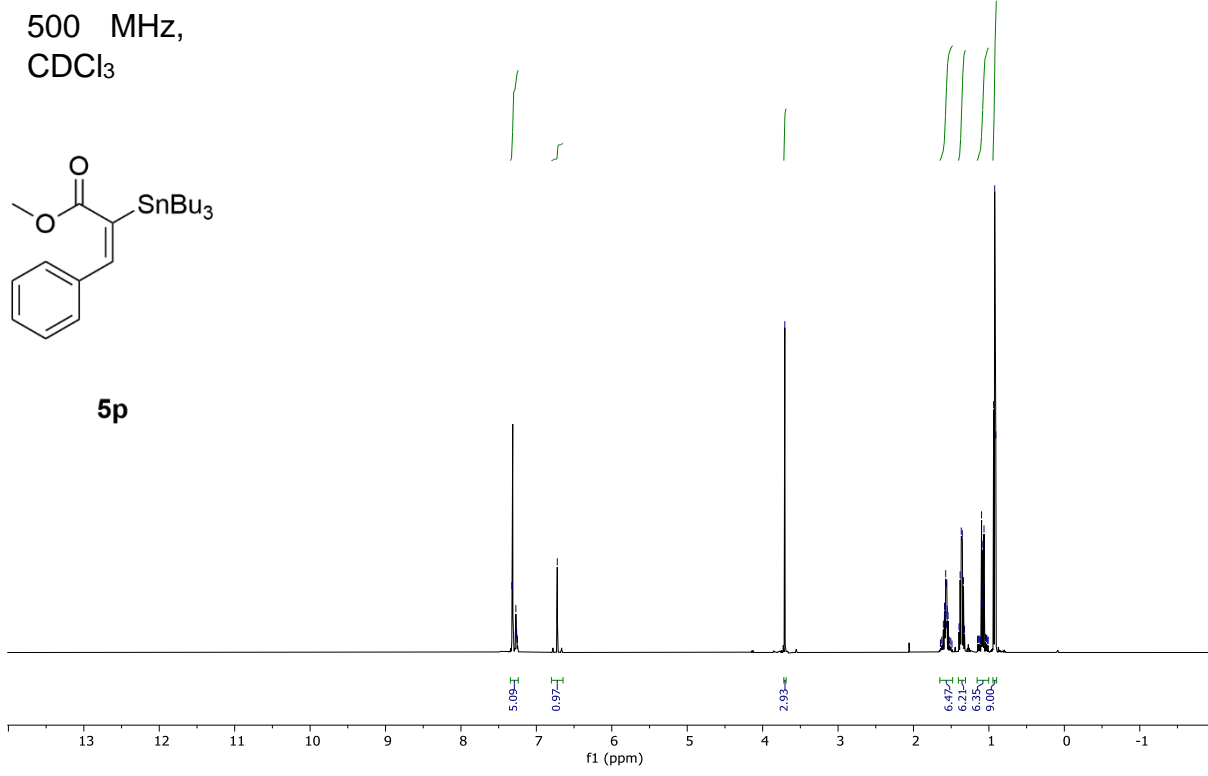
6



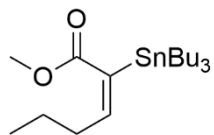
126 MHz,
CDCl₃



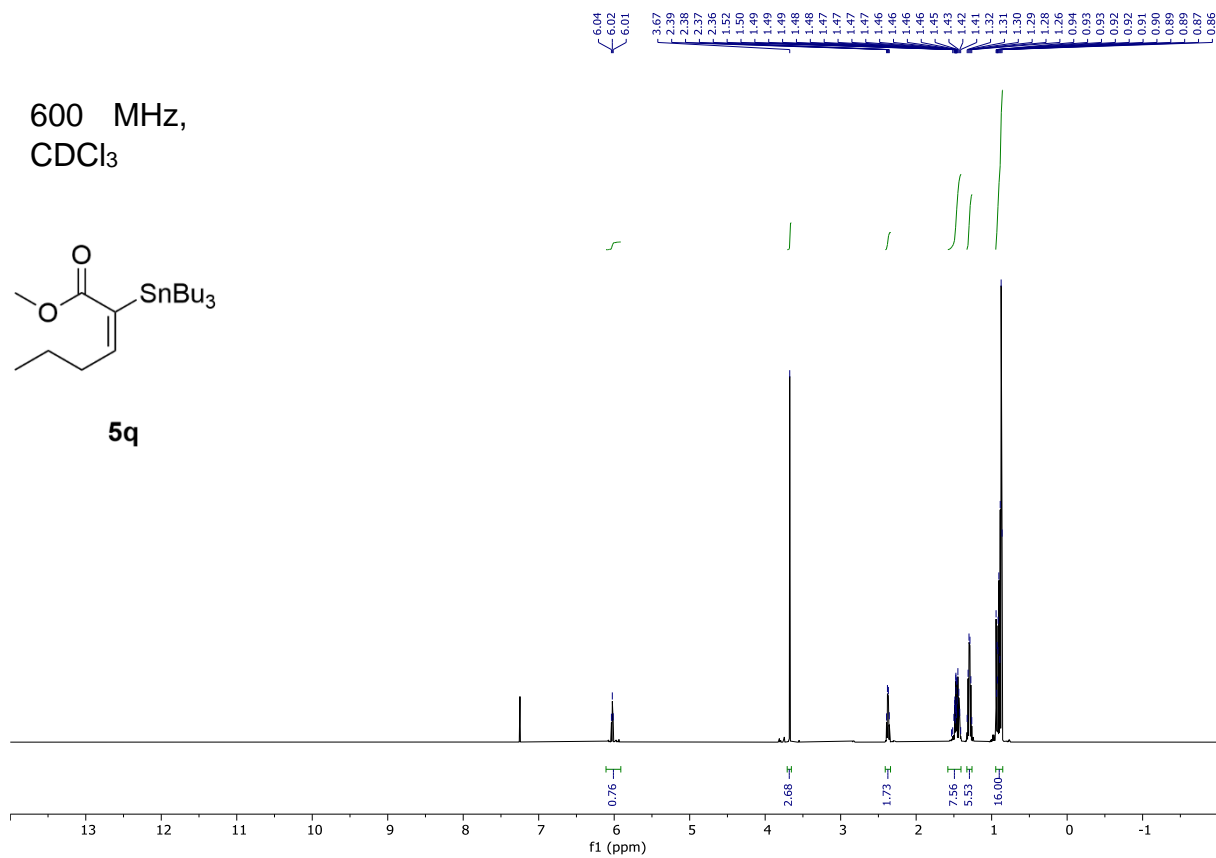




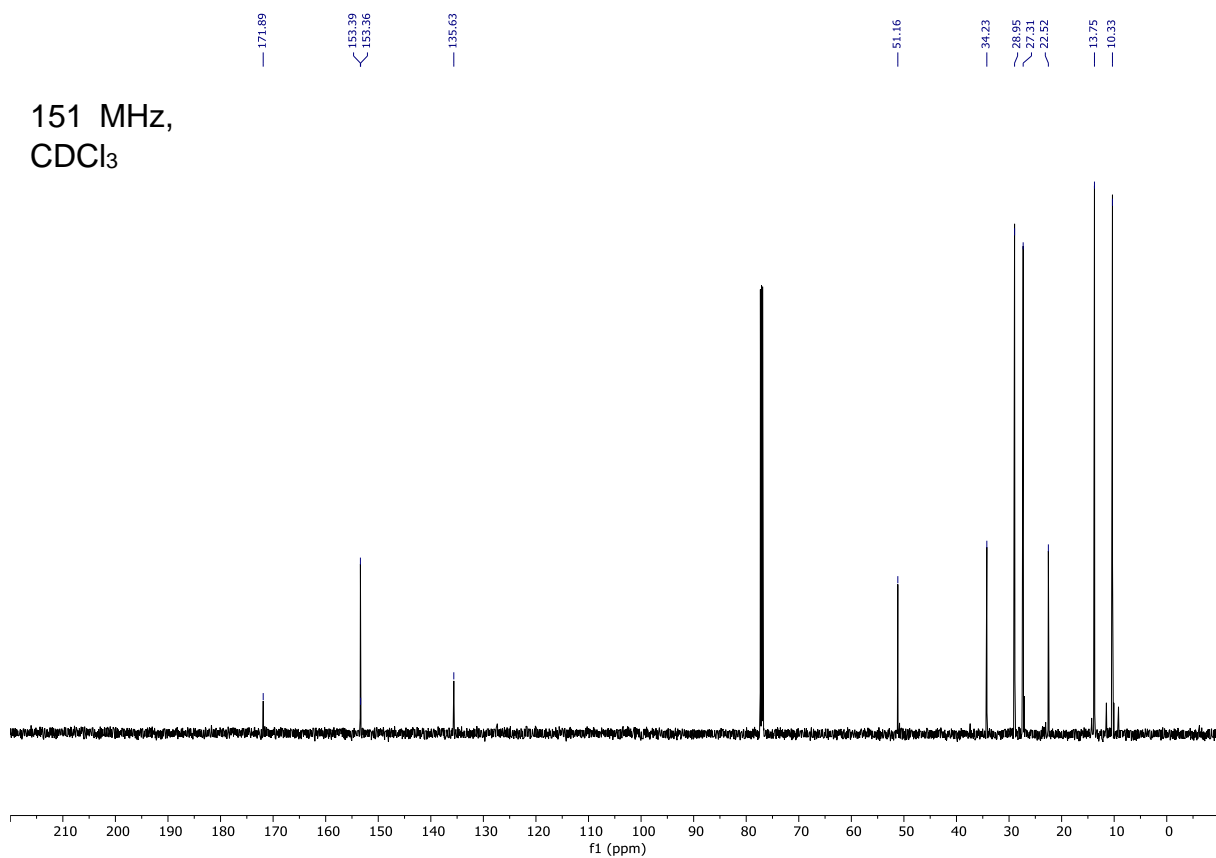
600 MHz,
CDCl₃

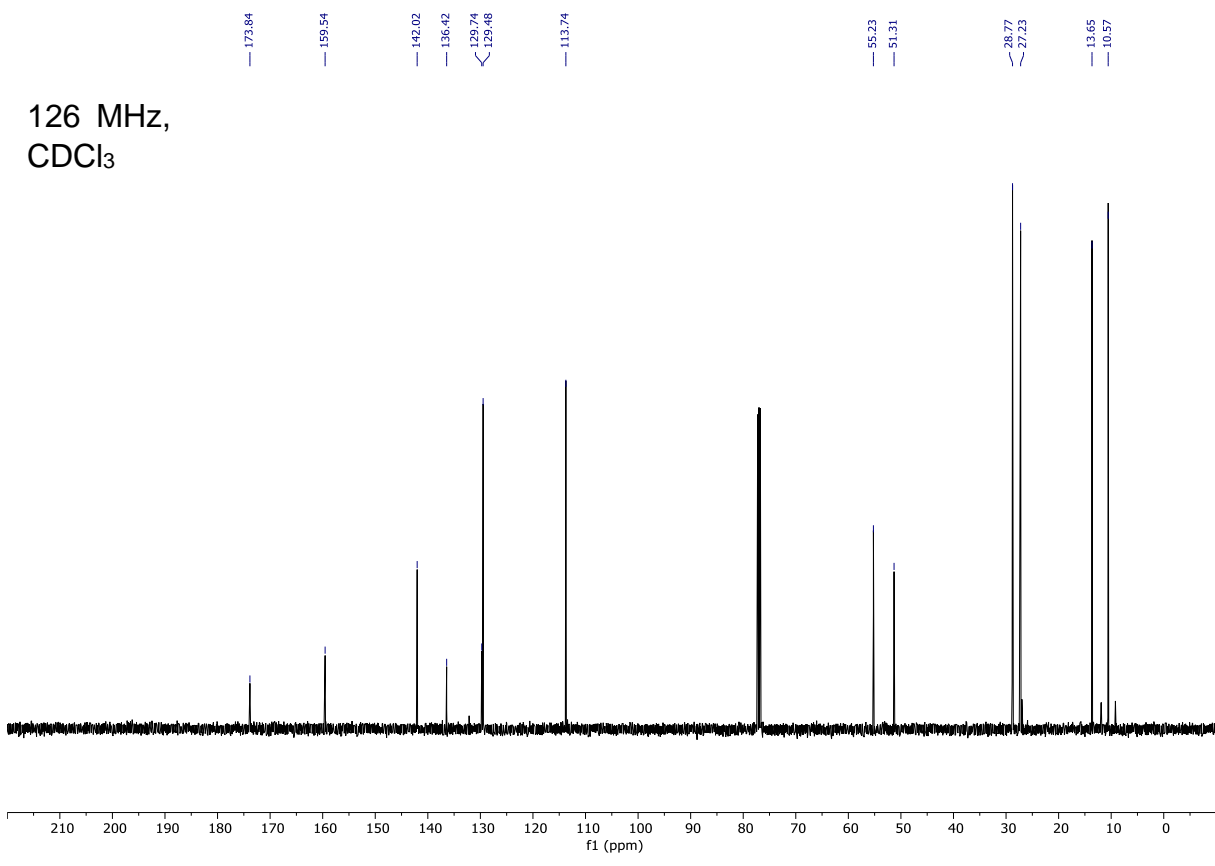
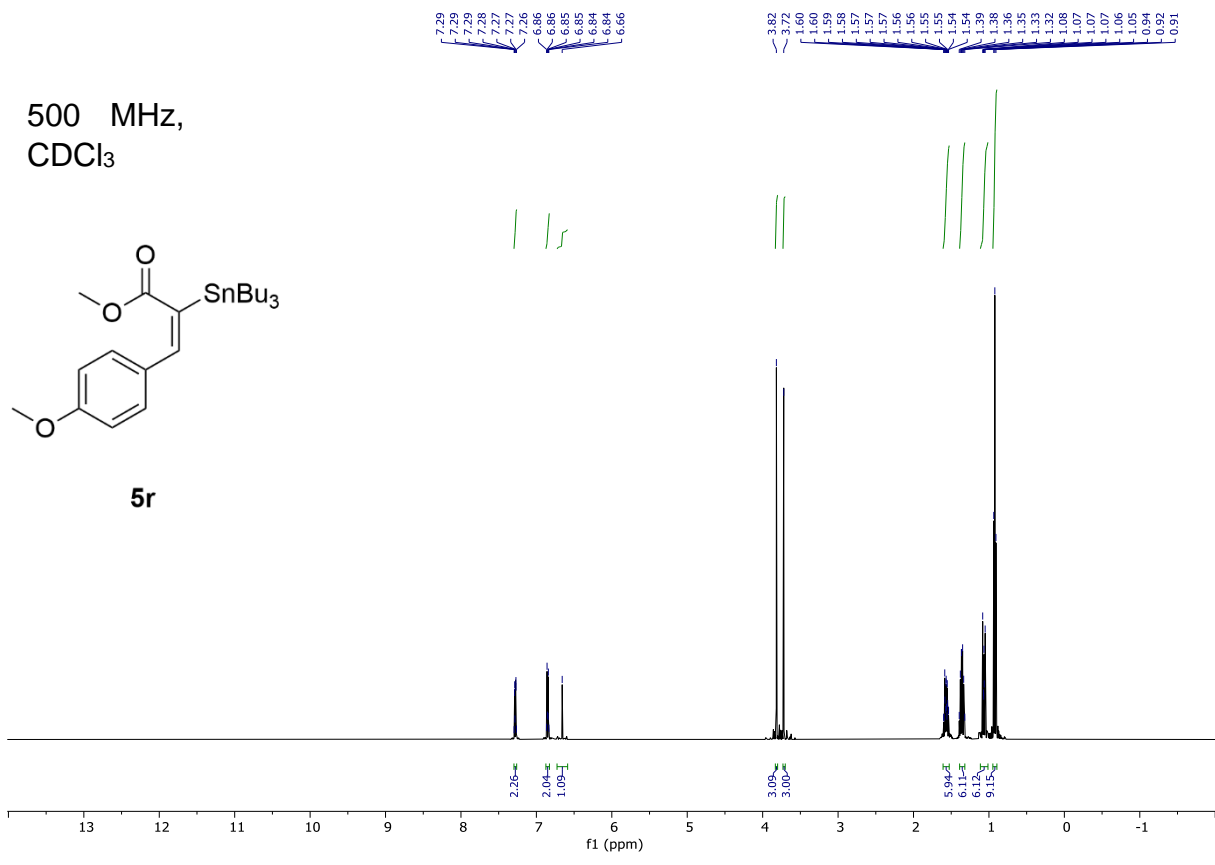


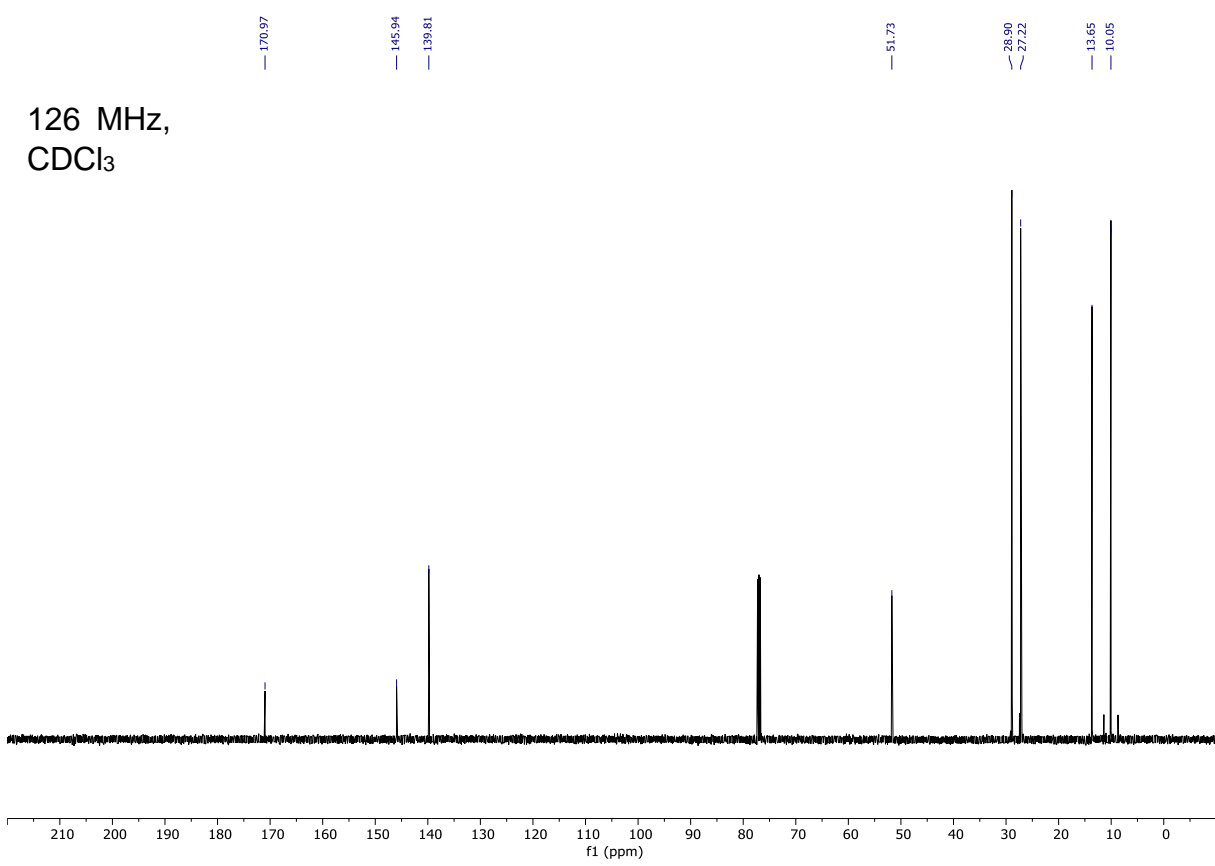
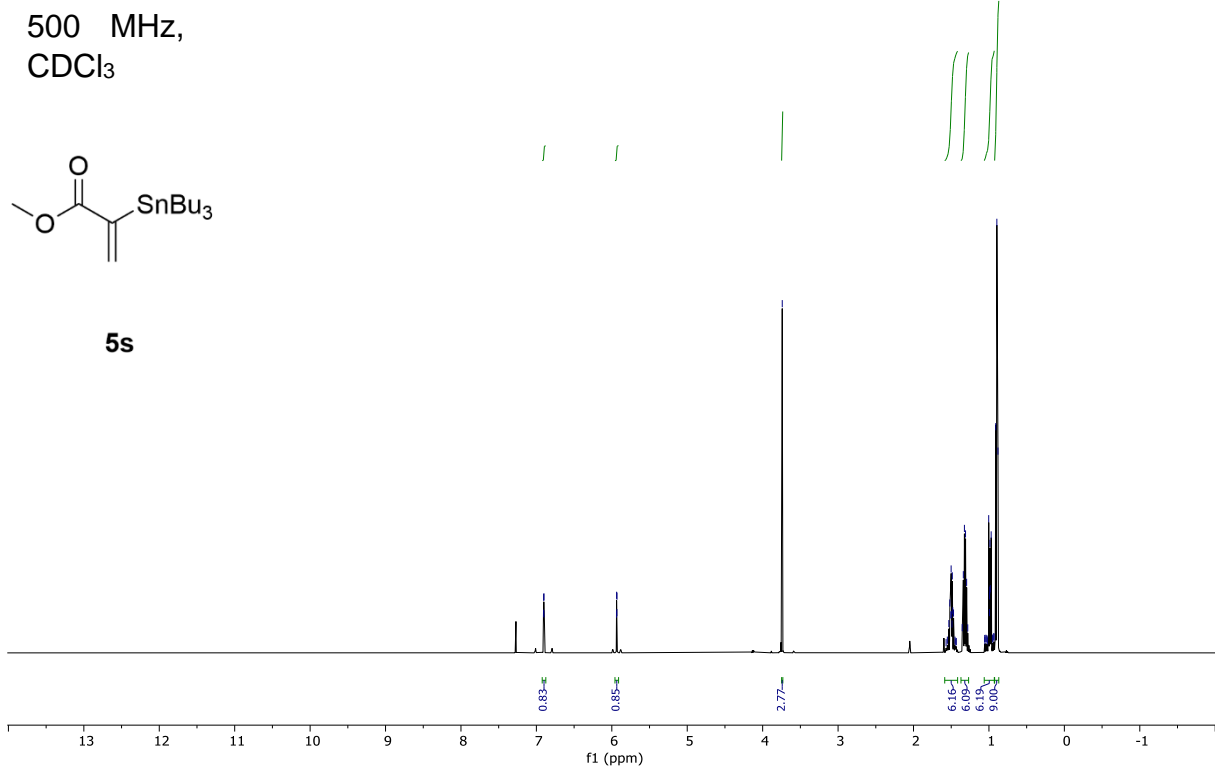
5q

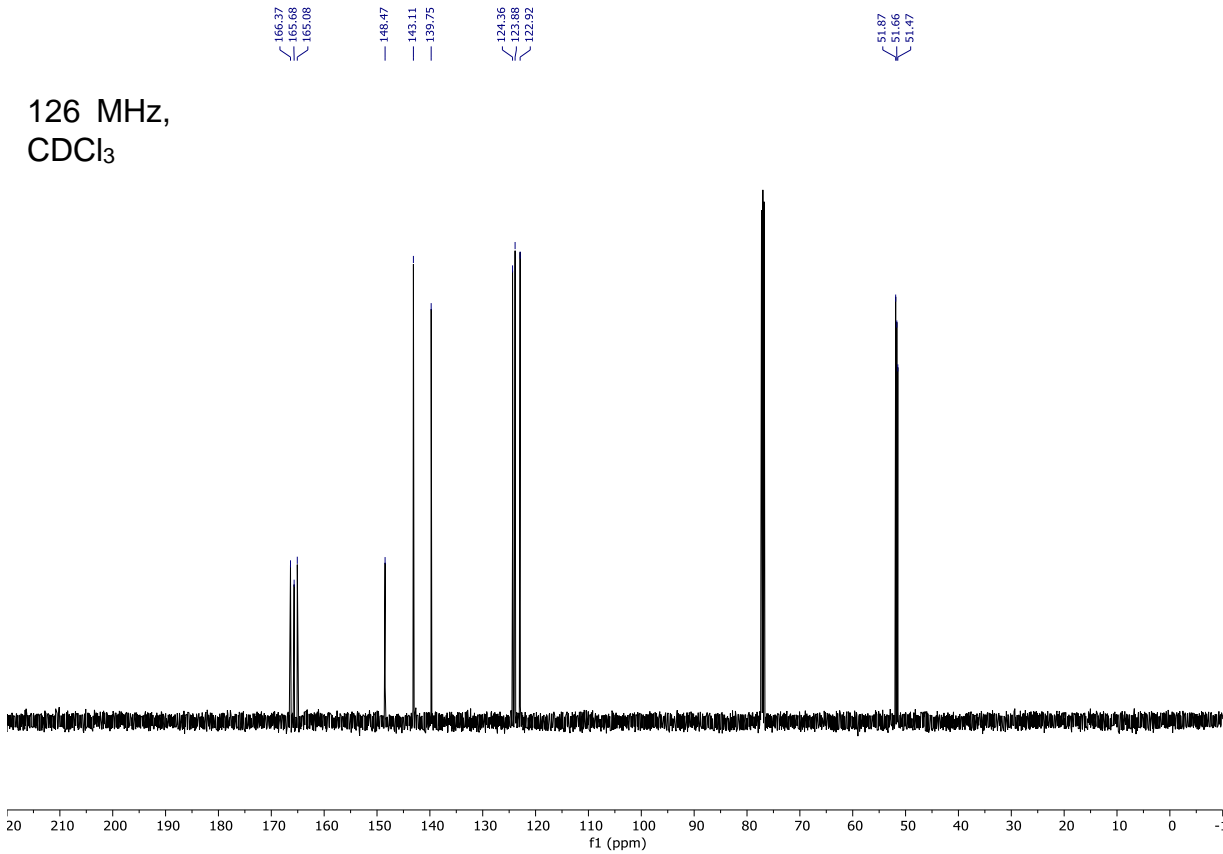
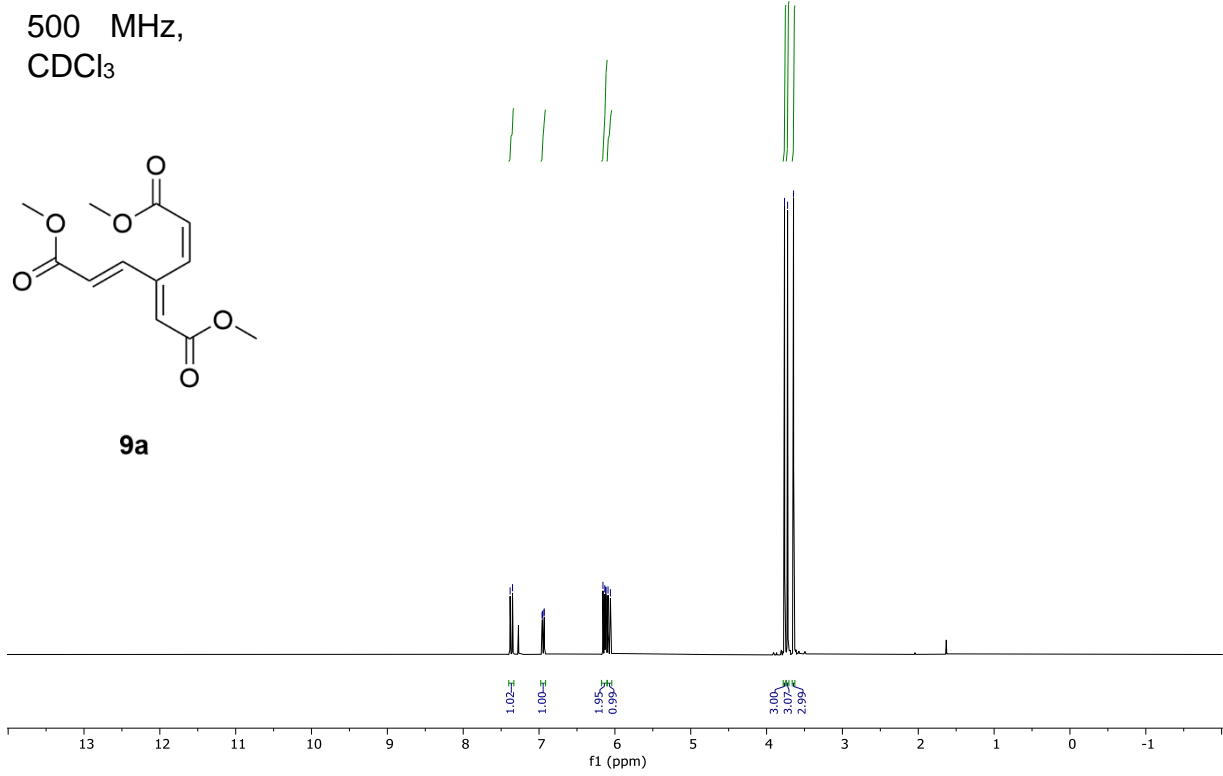


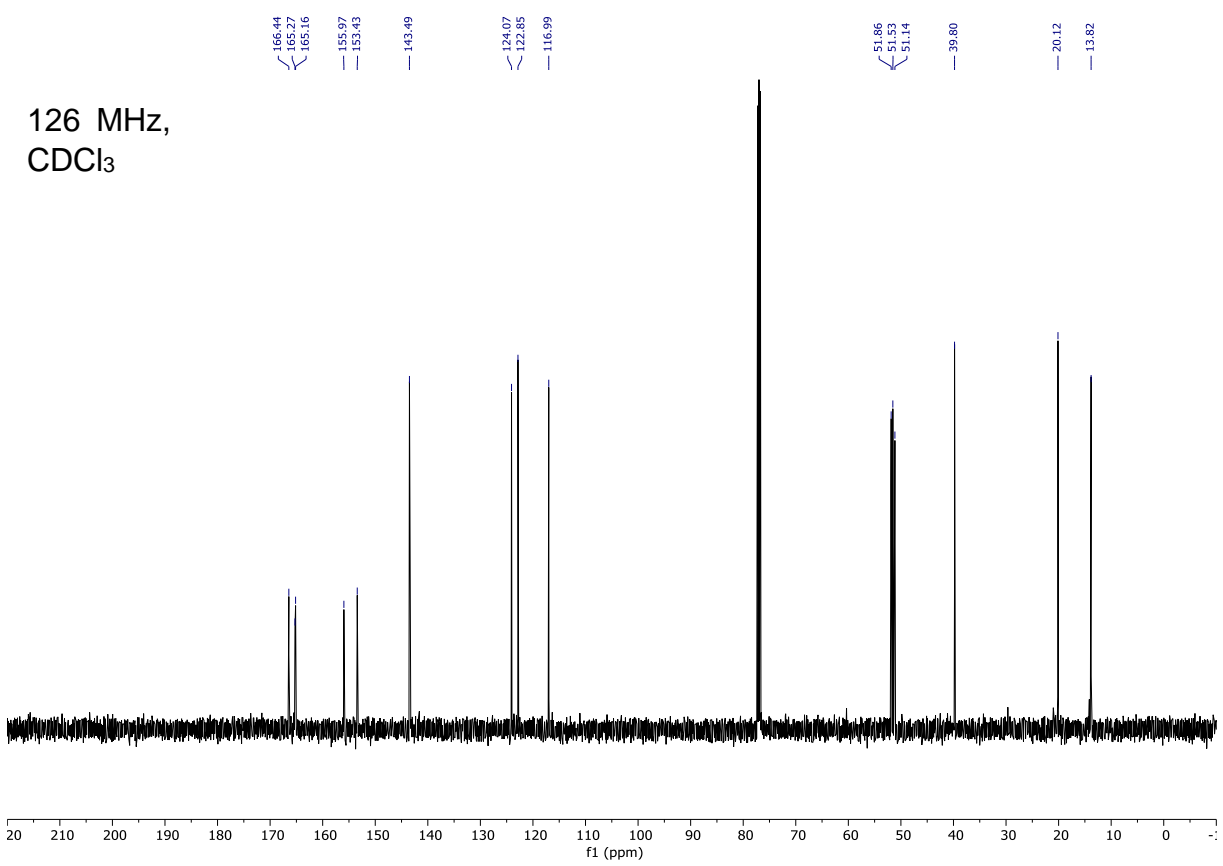
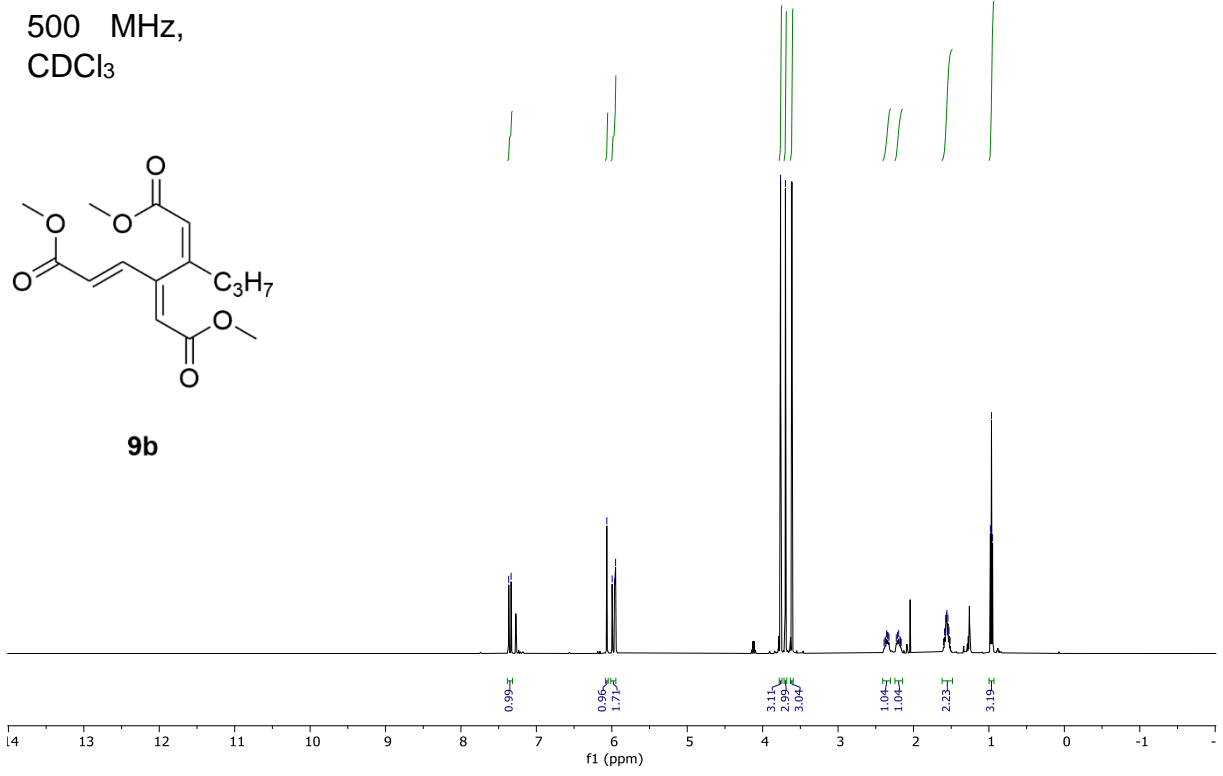
151 MHz,
CDCl₃

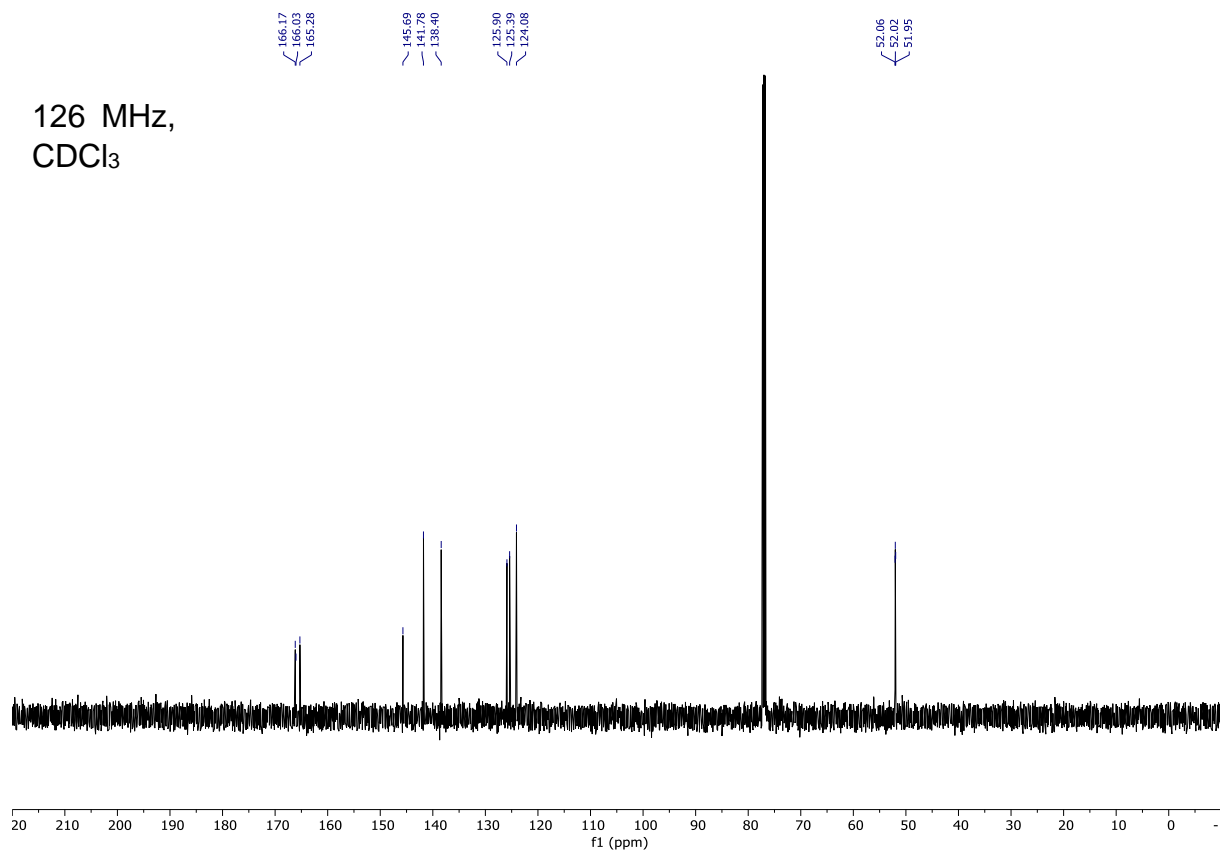
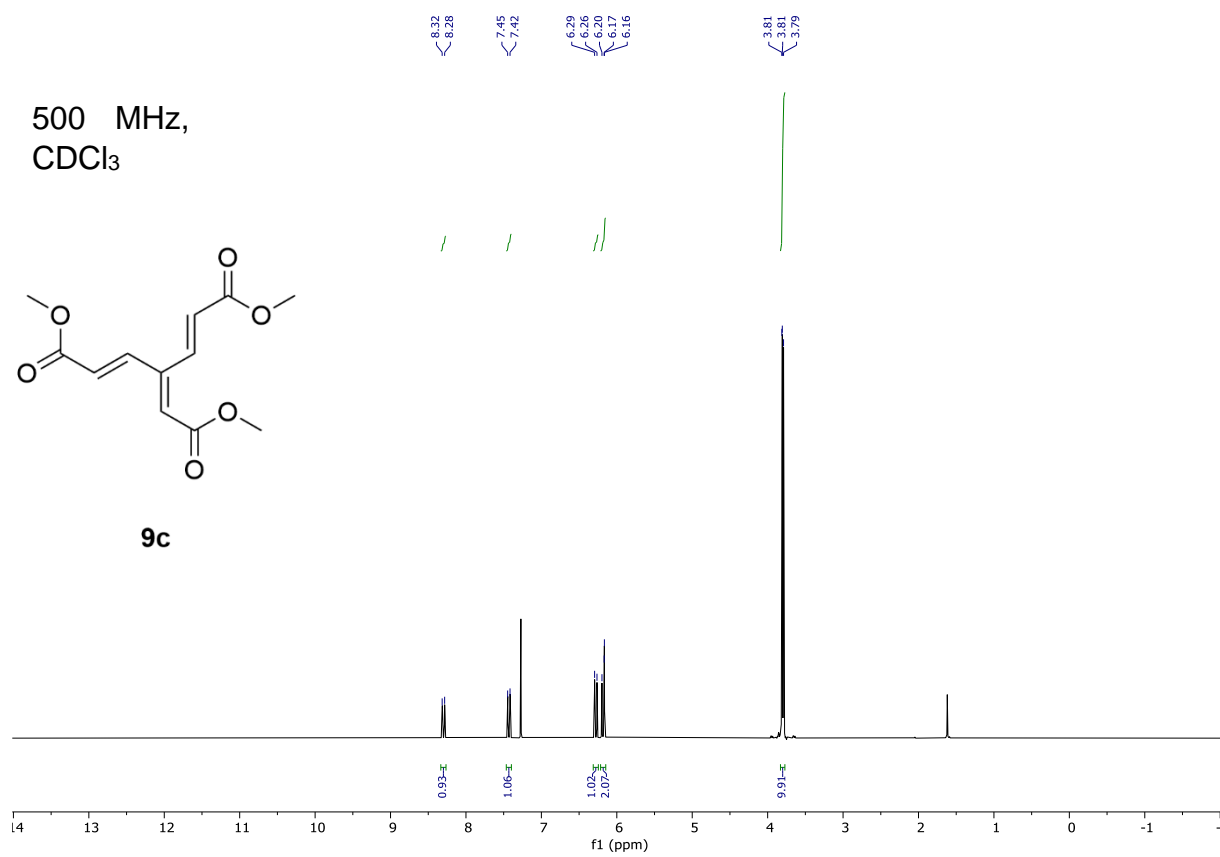


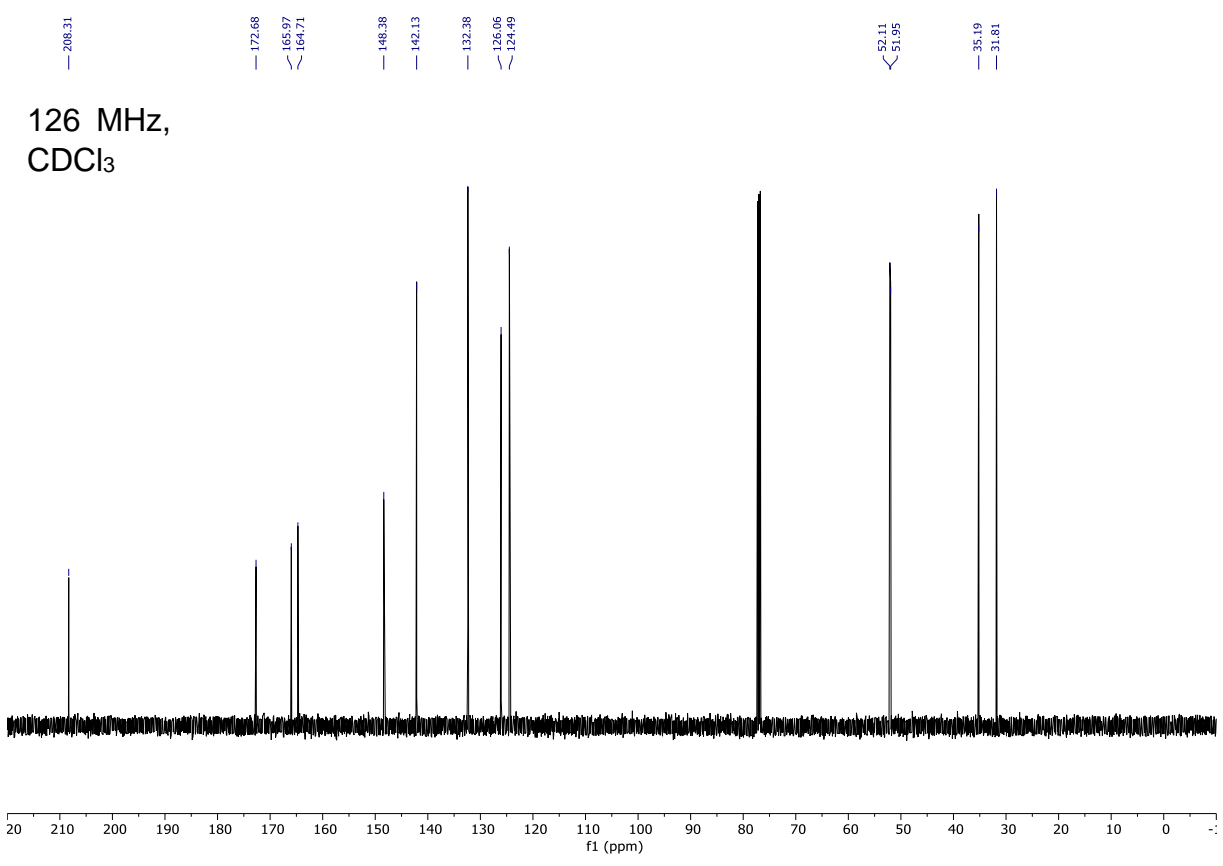
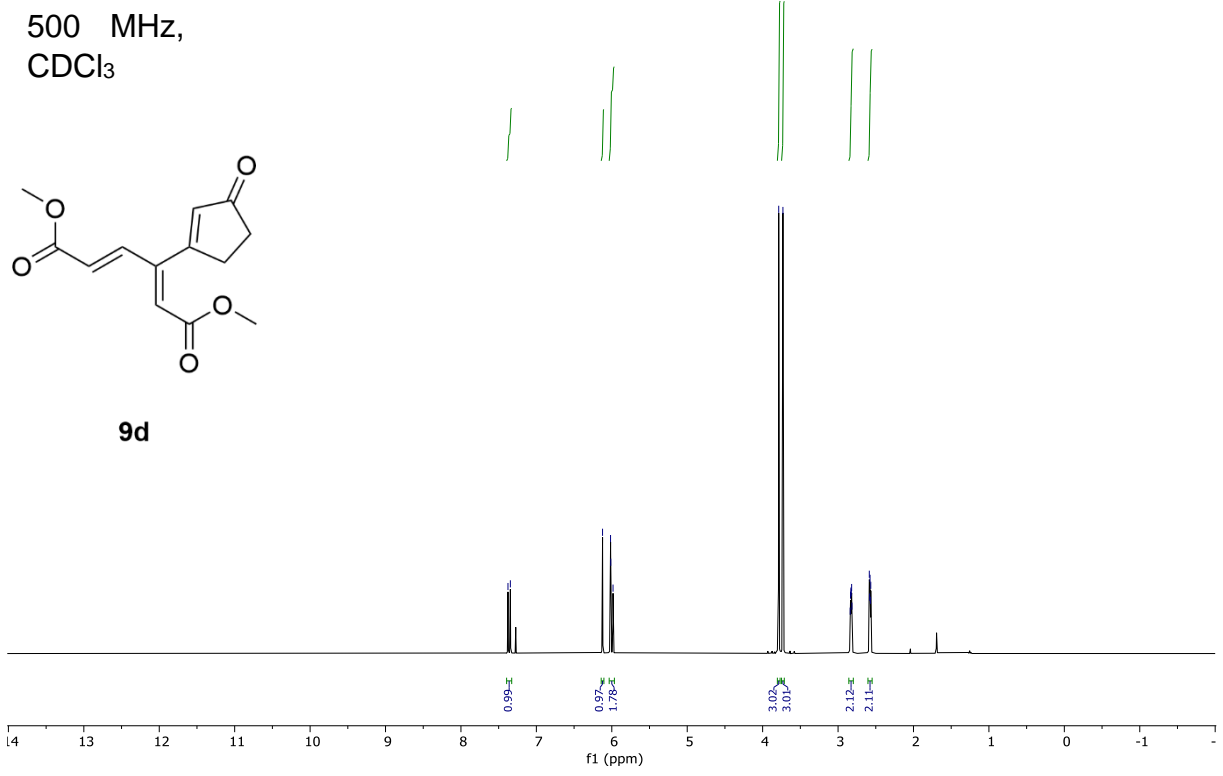


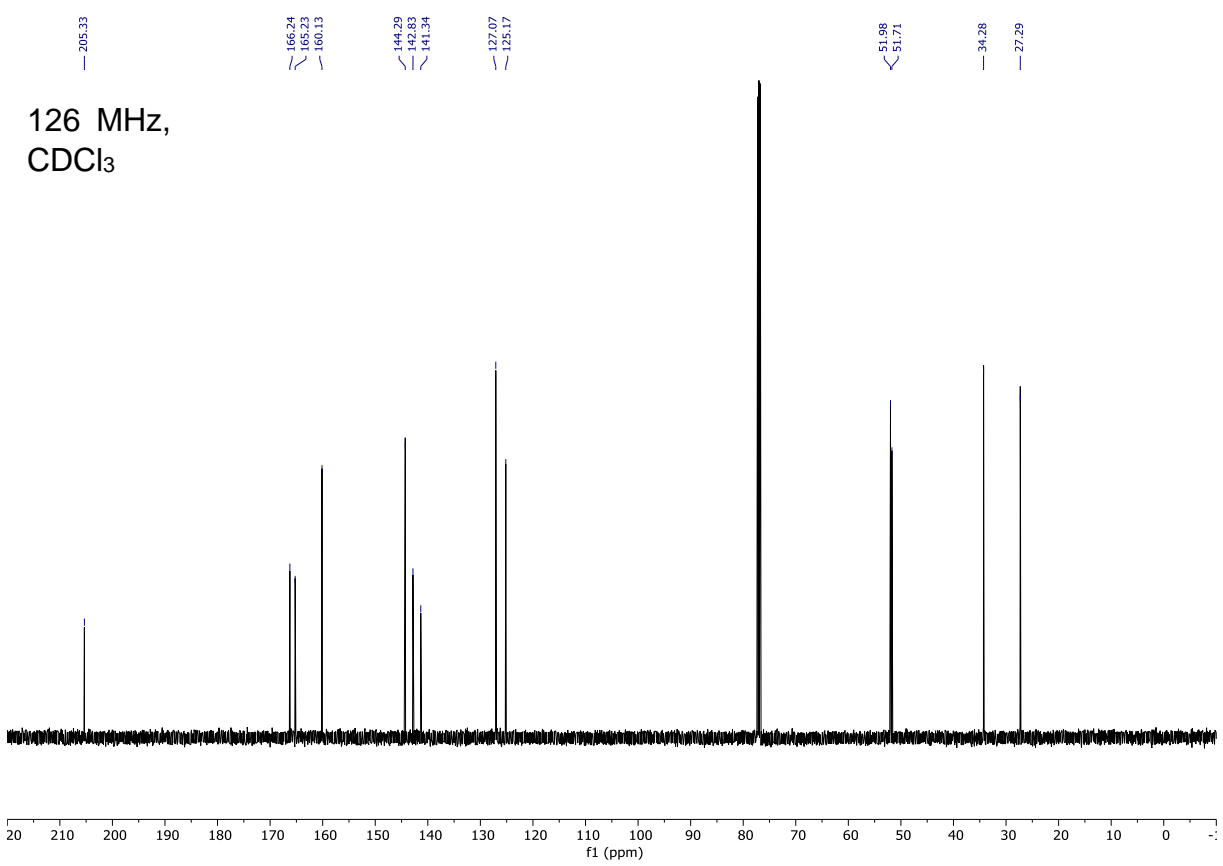
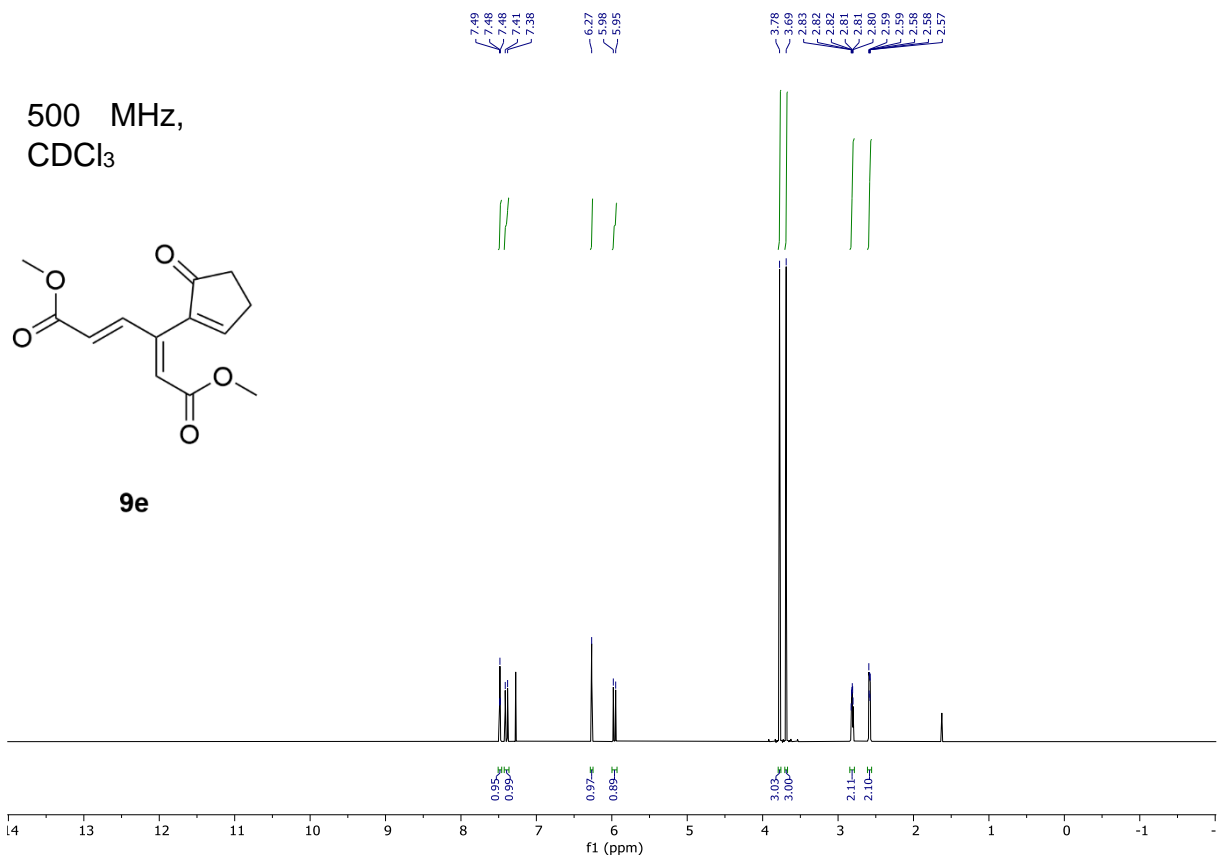


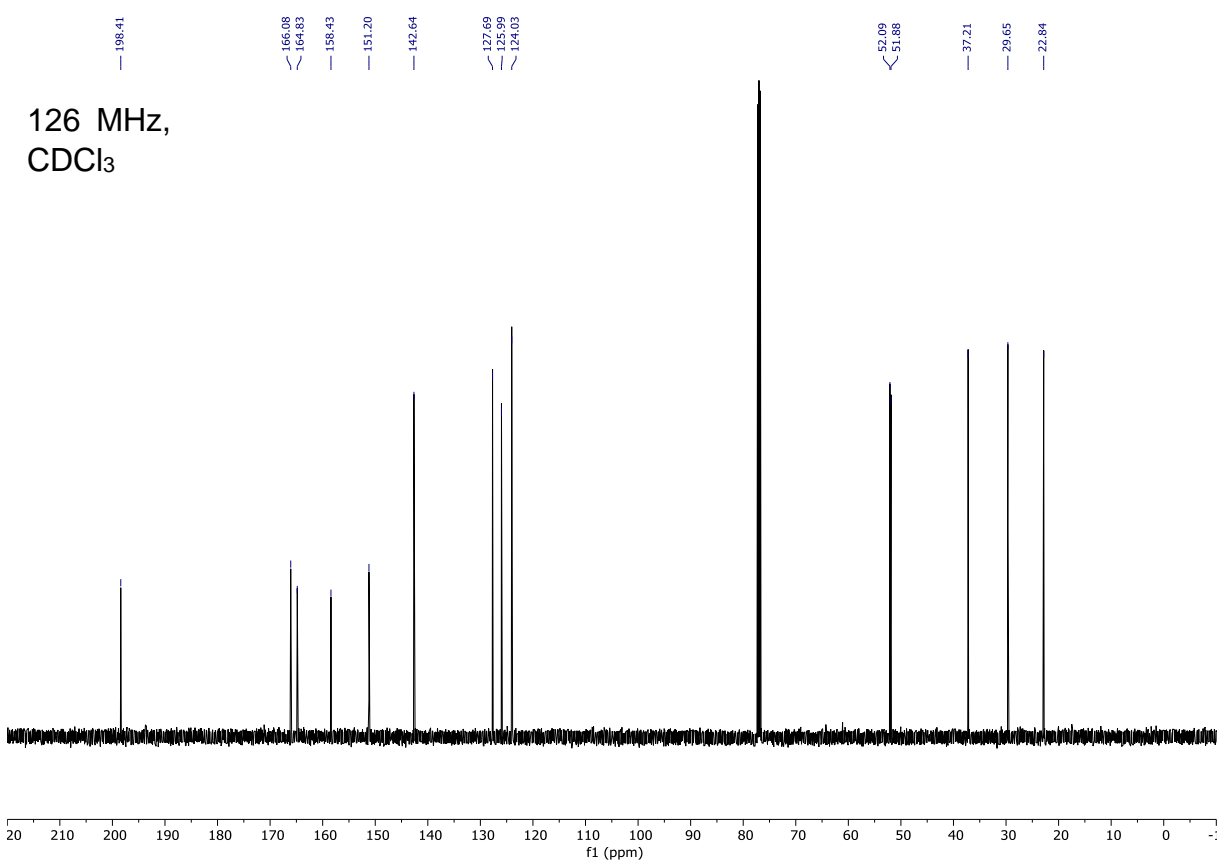
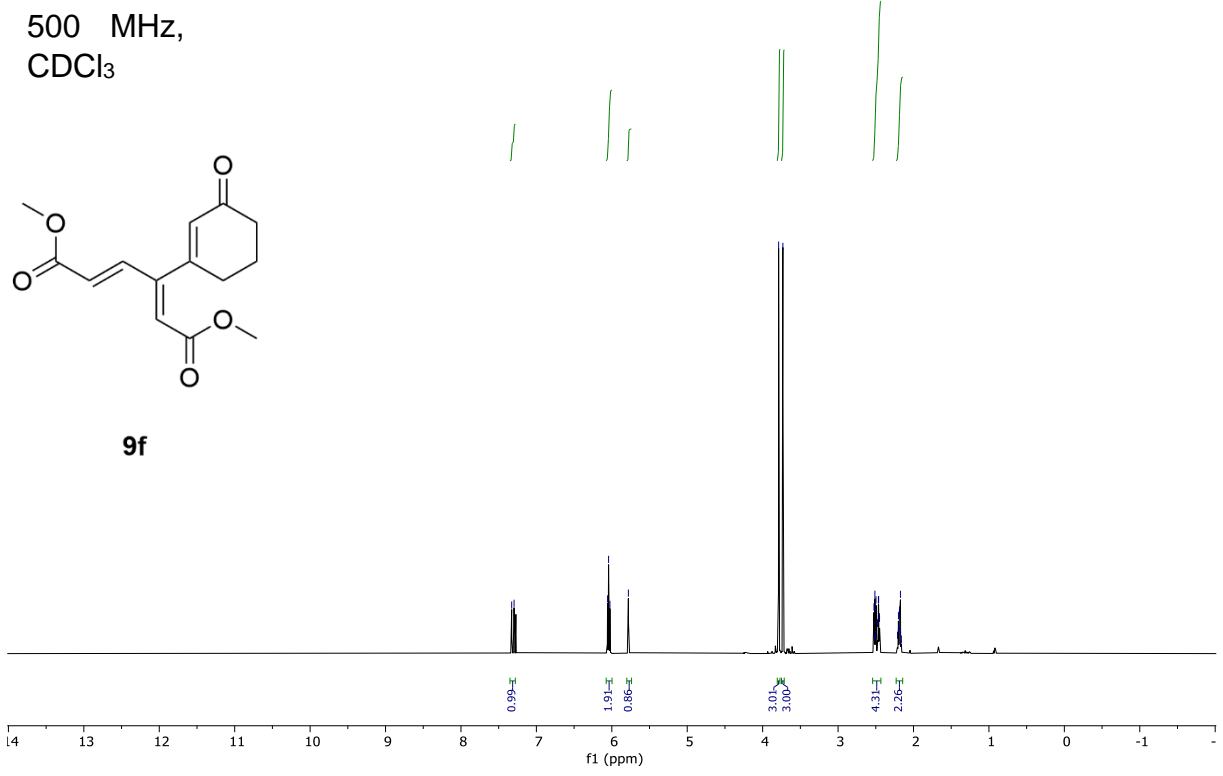


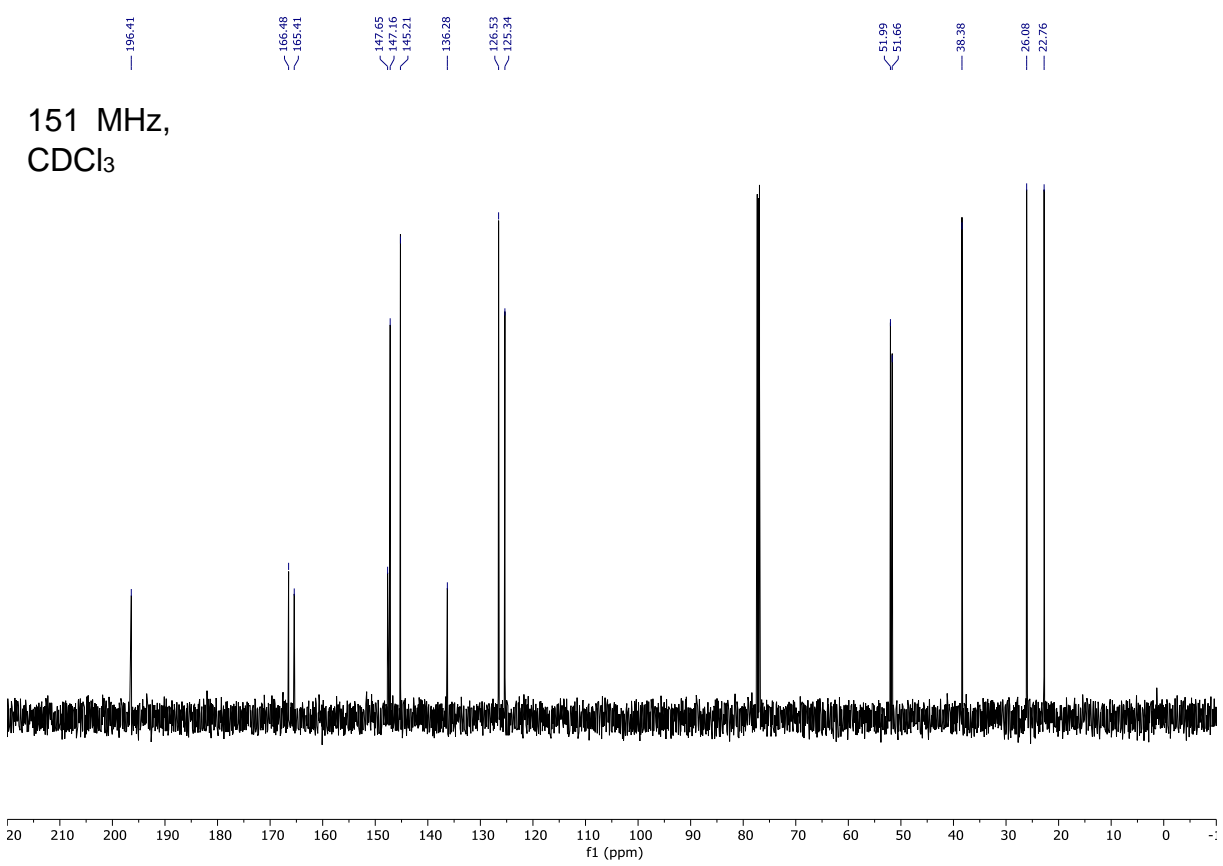
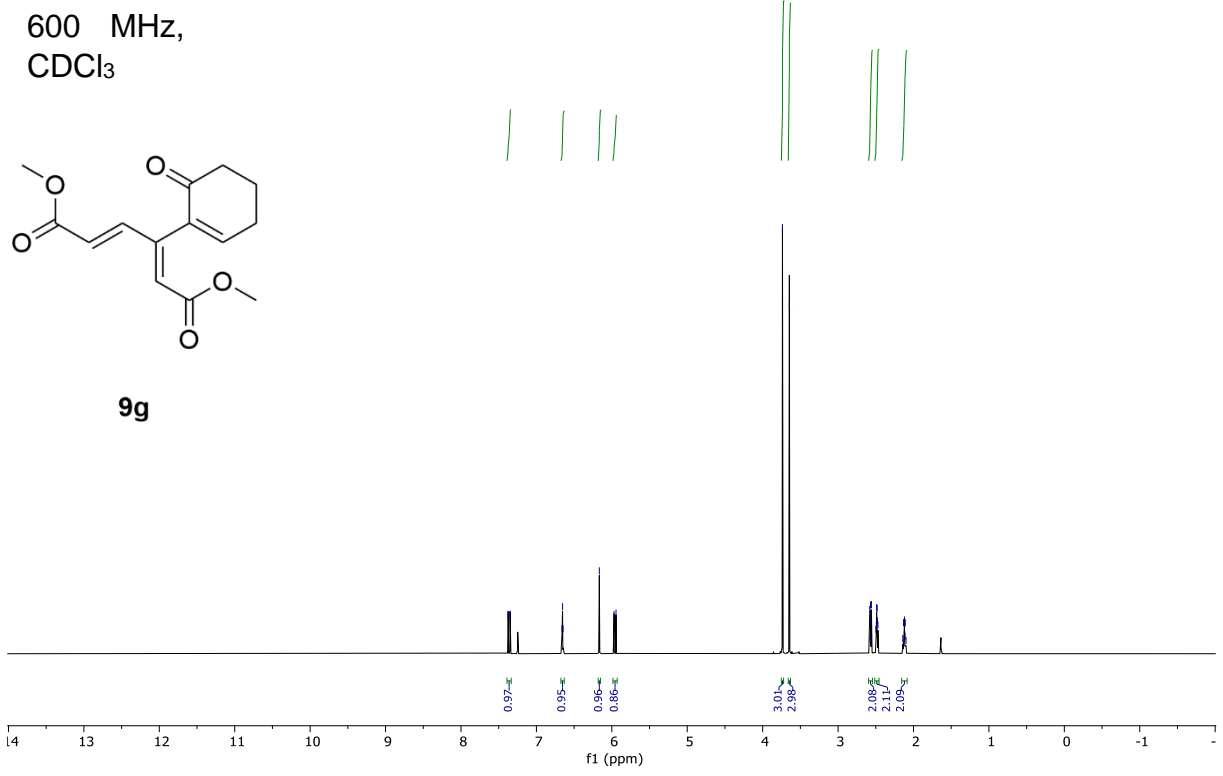


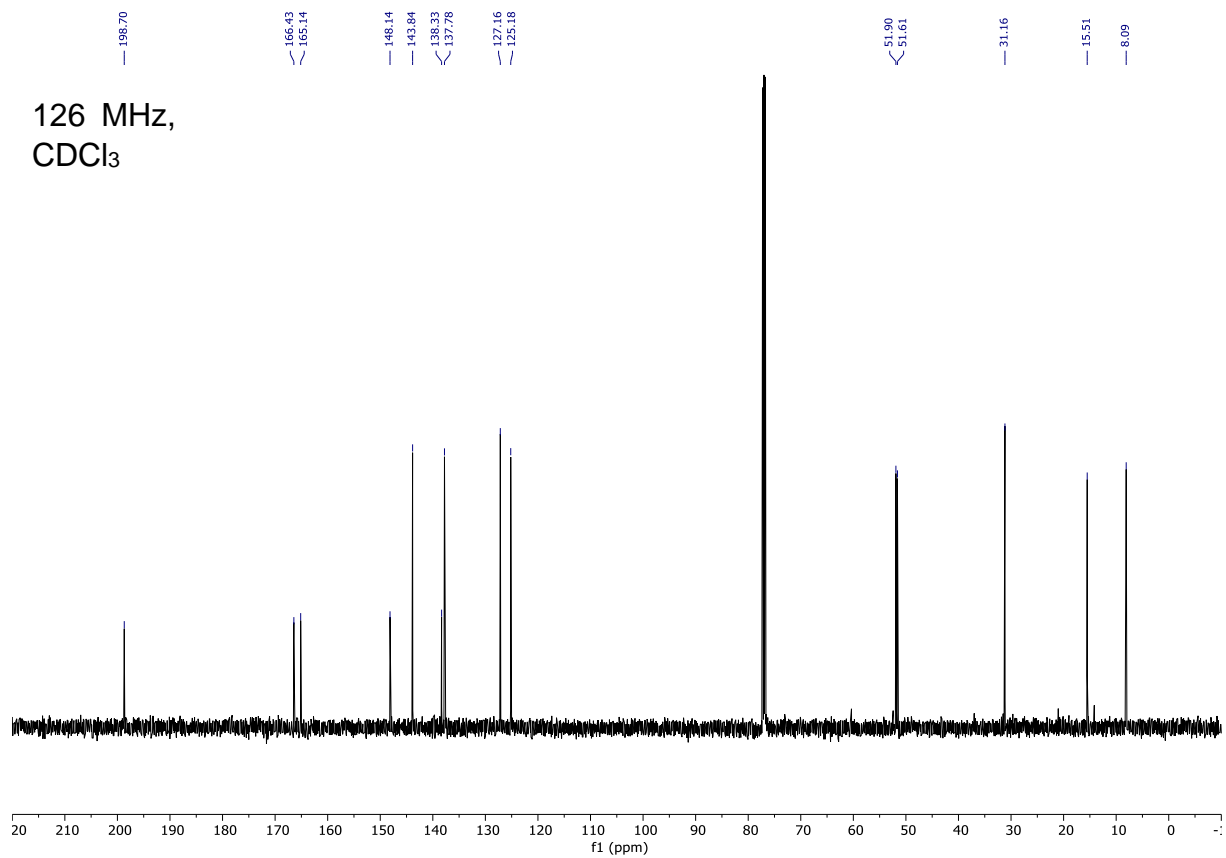
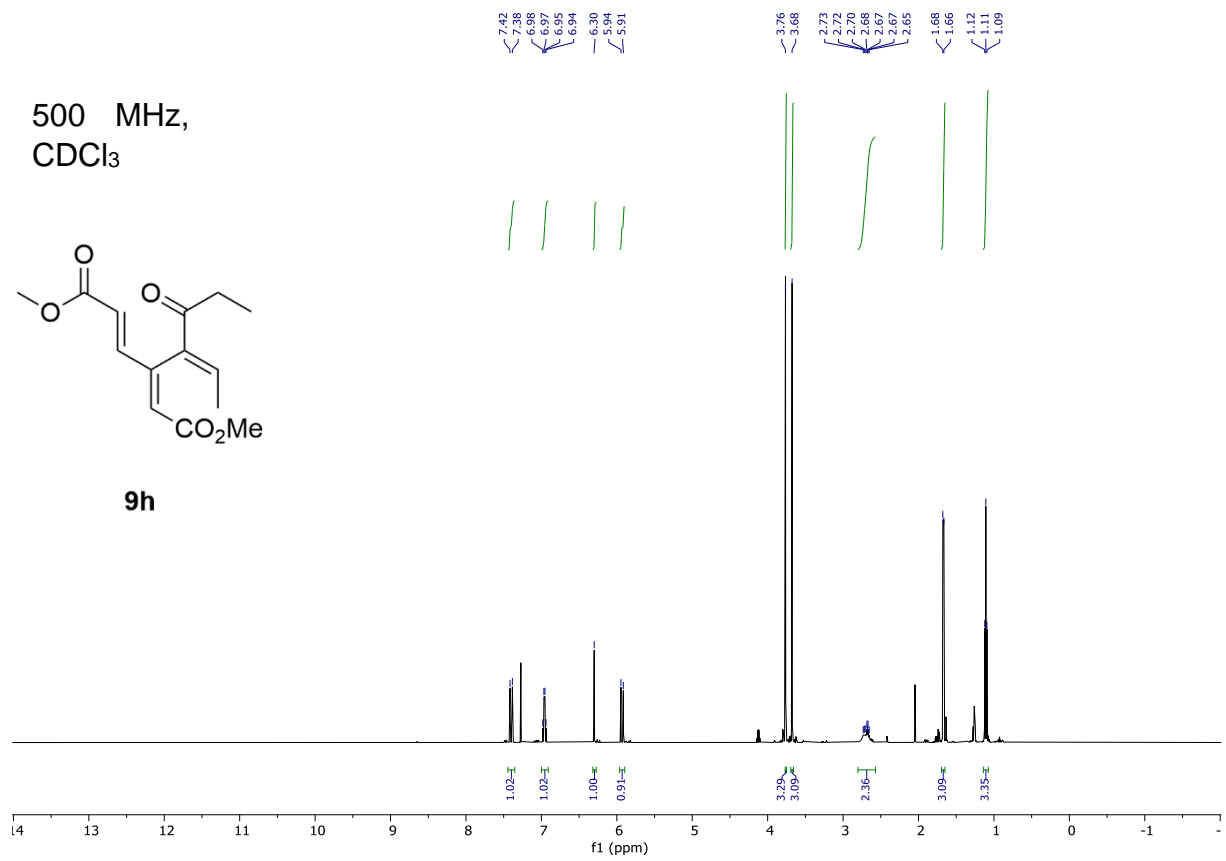


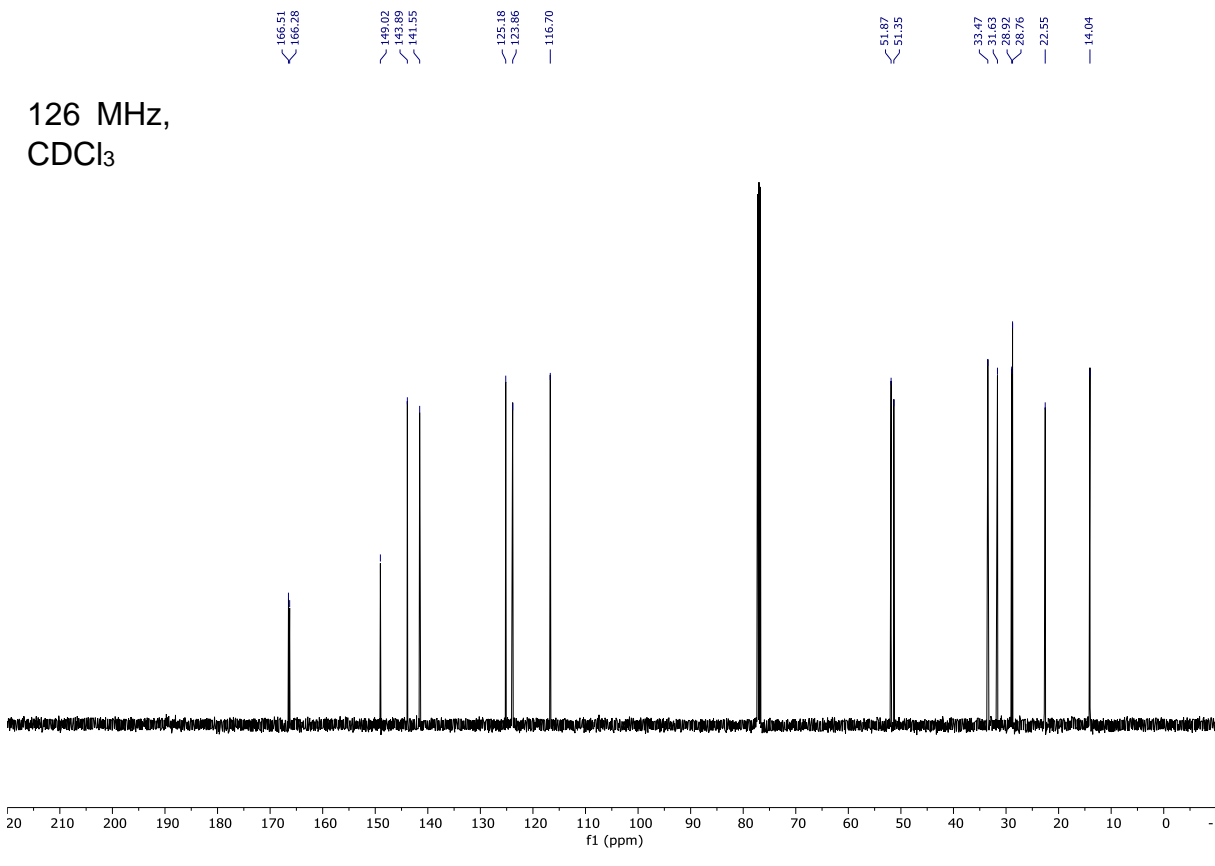
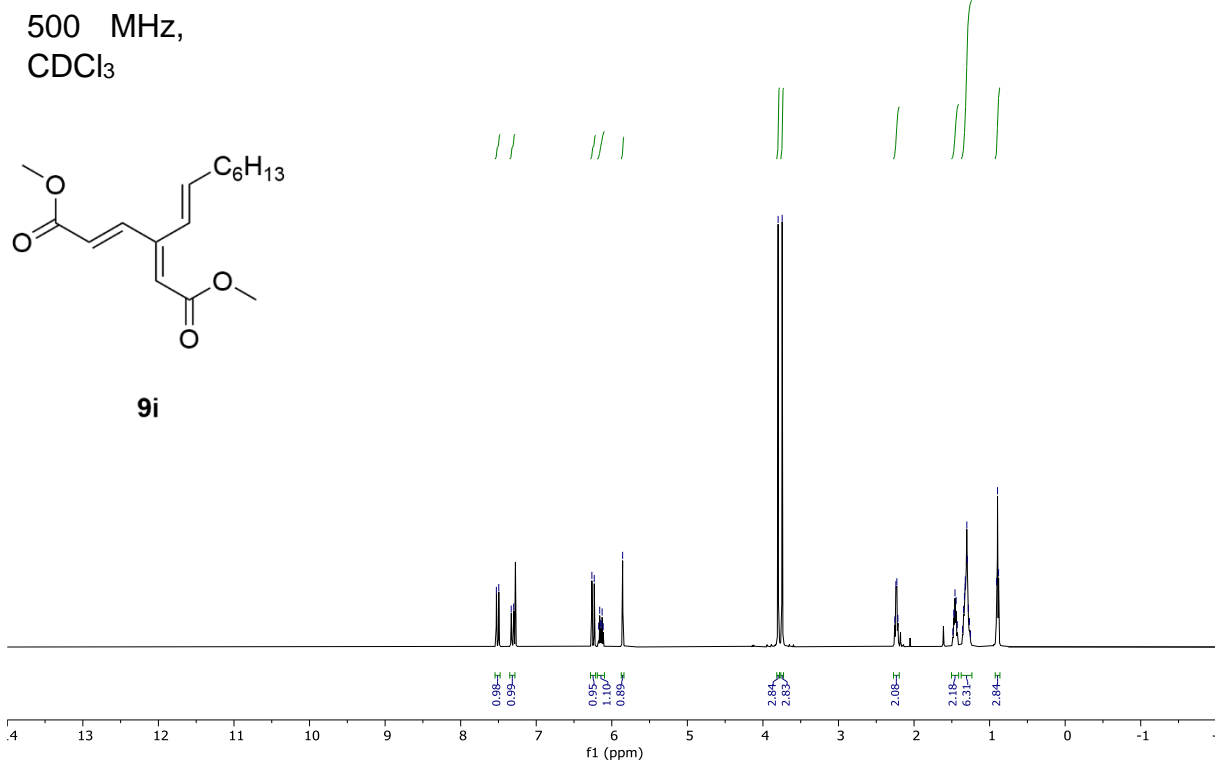


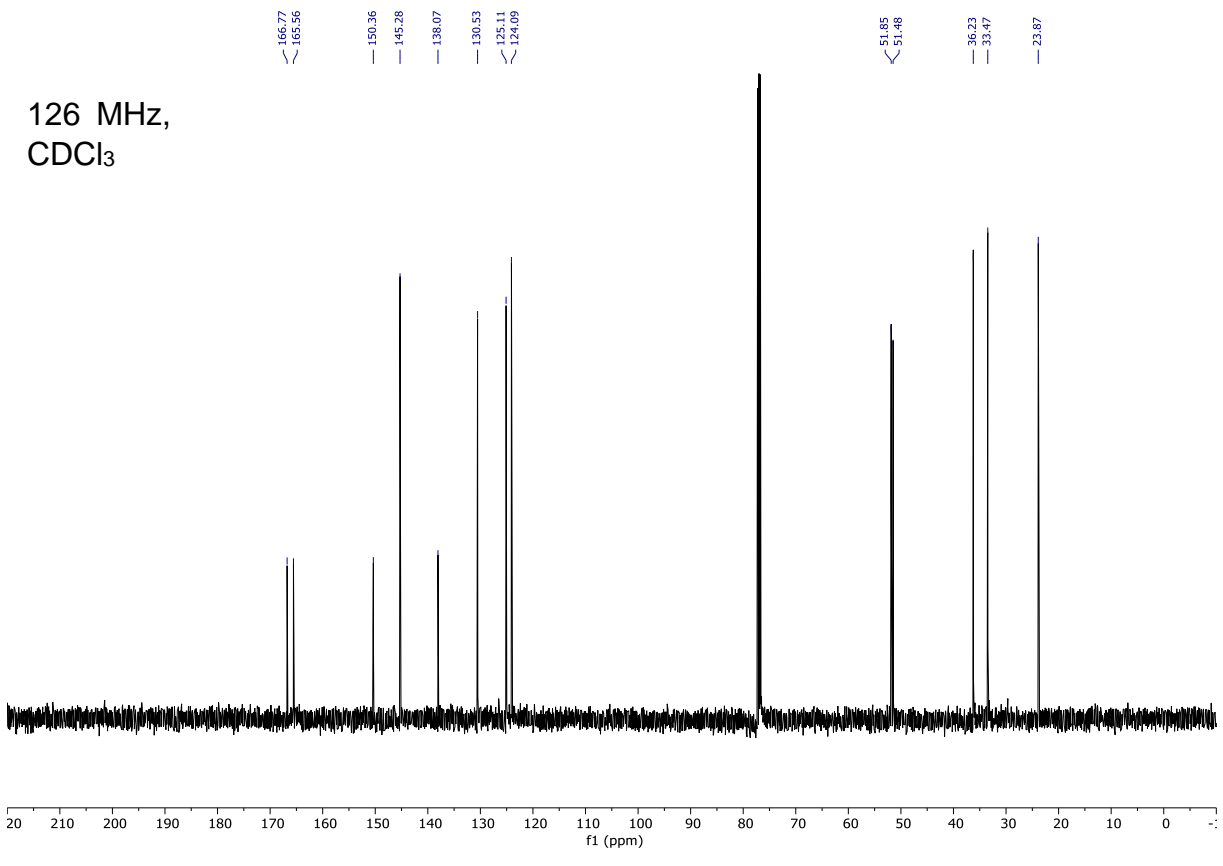
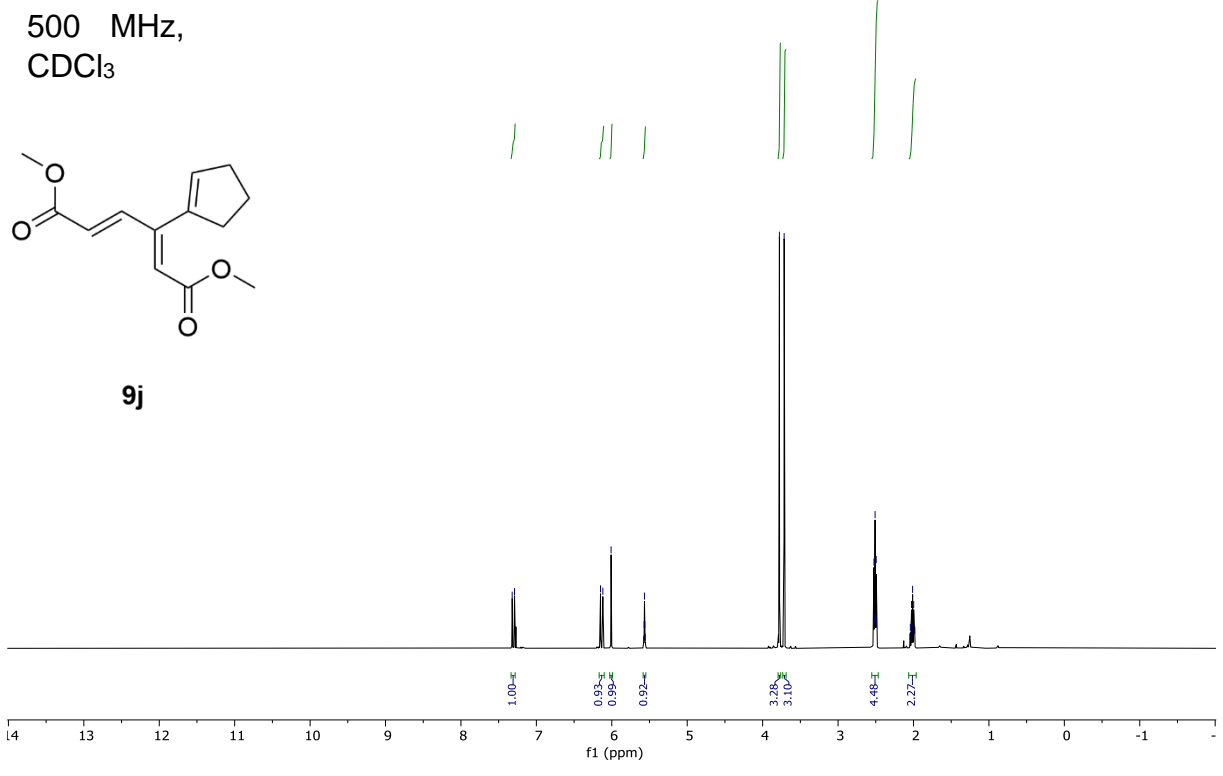


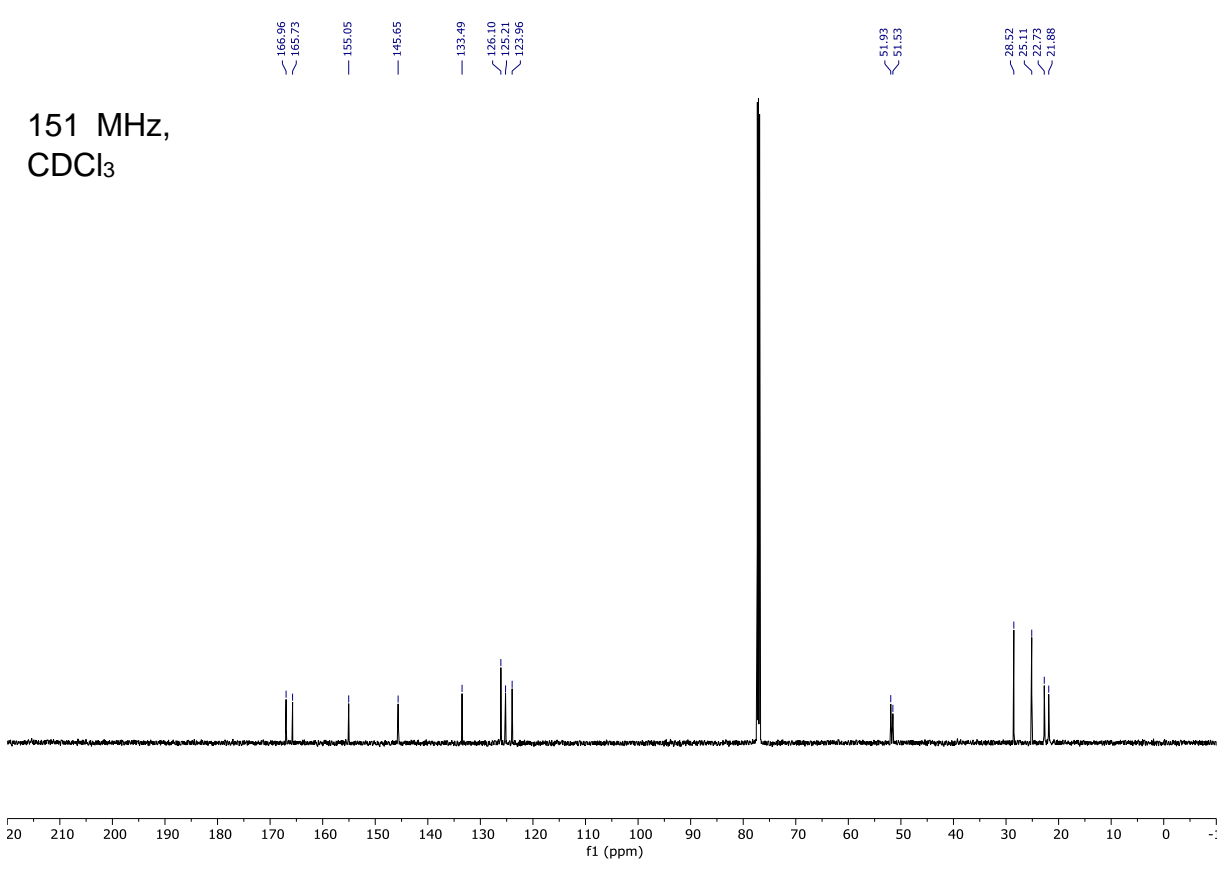
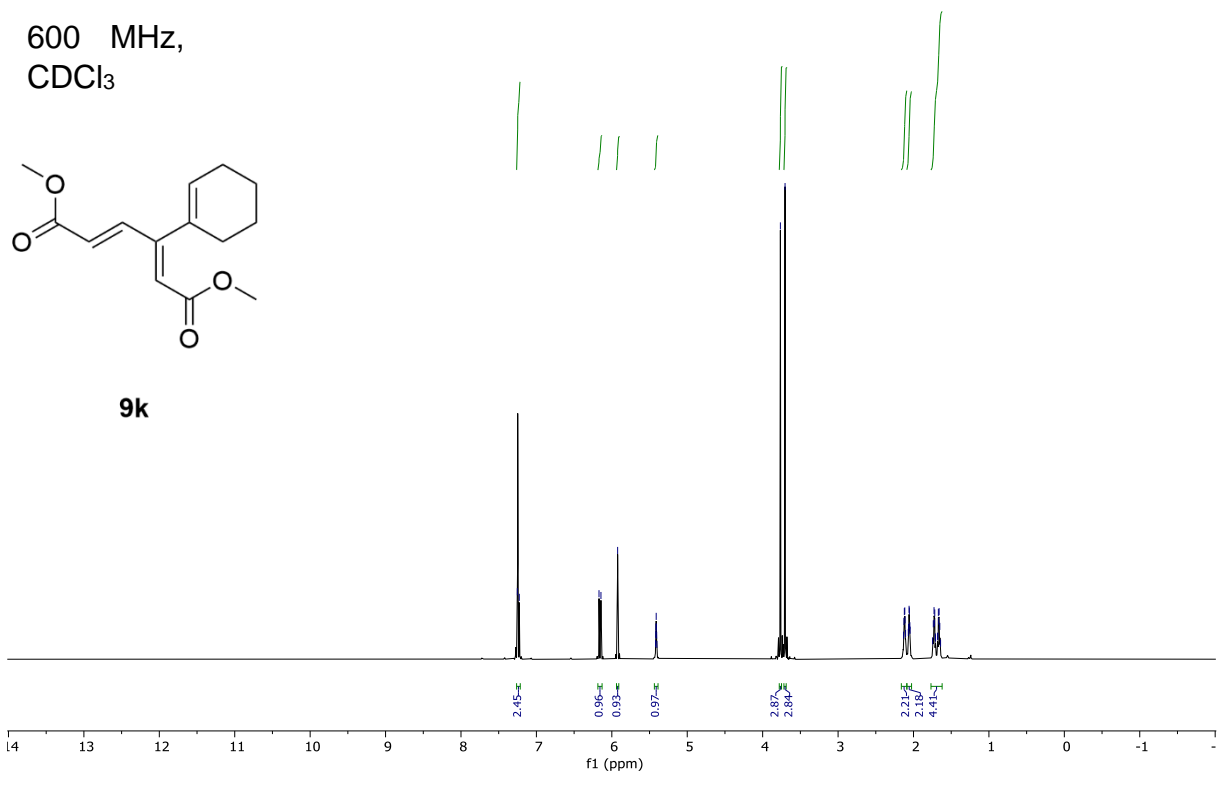


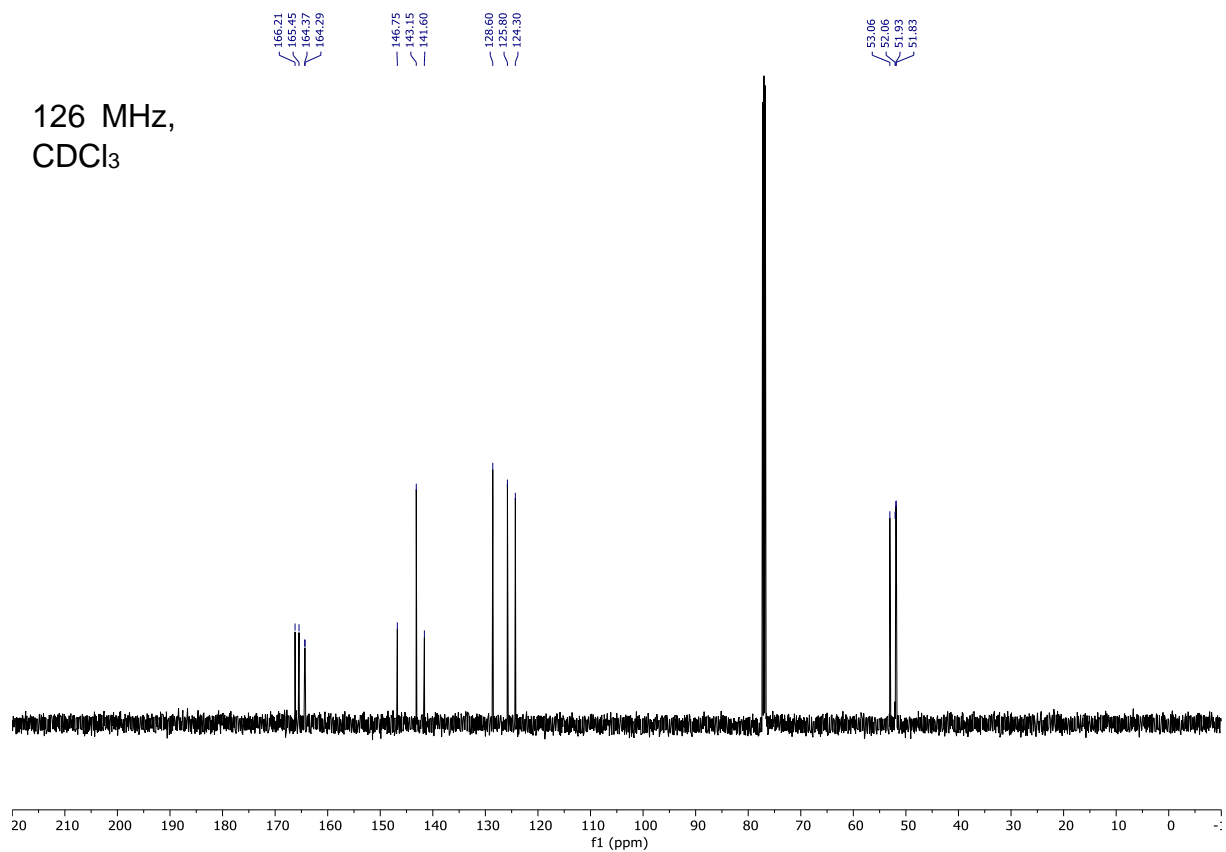
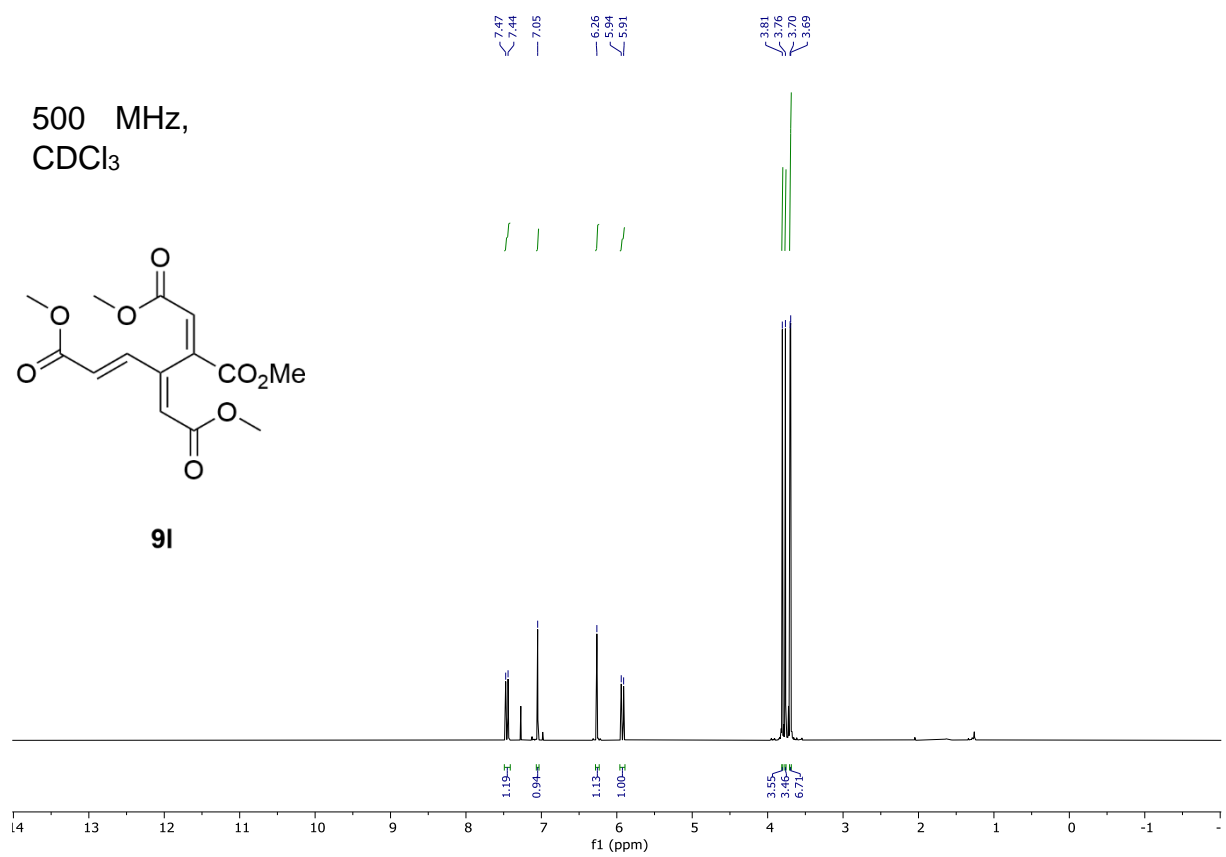


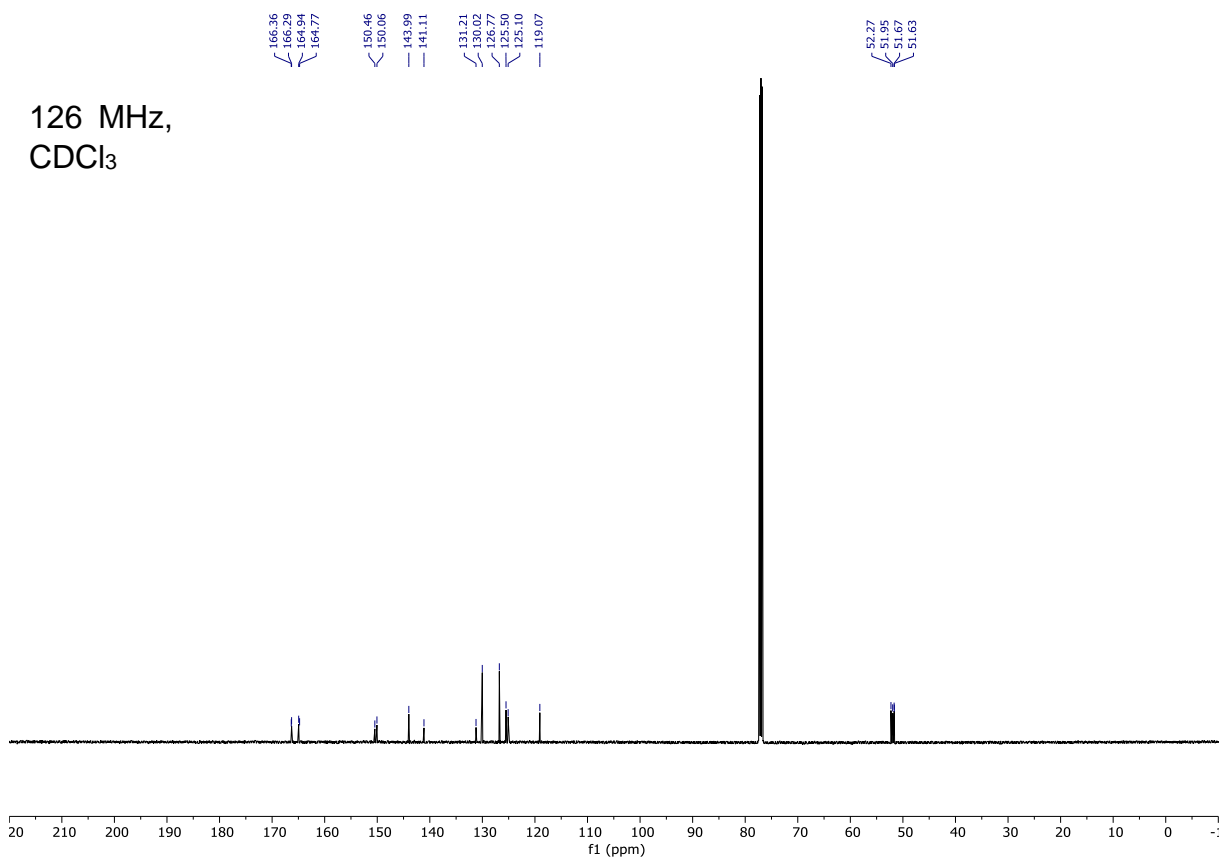
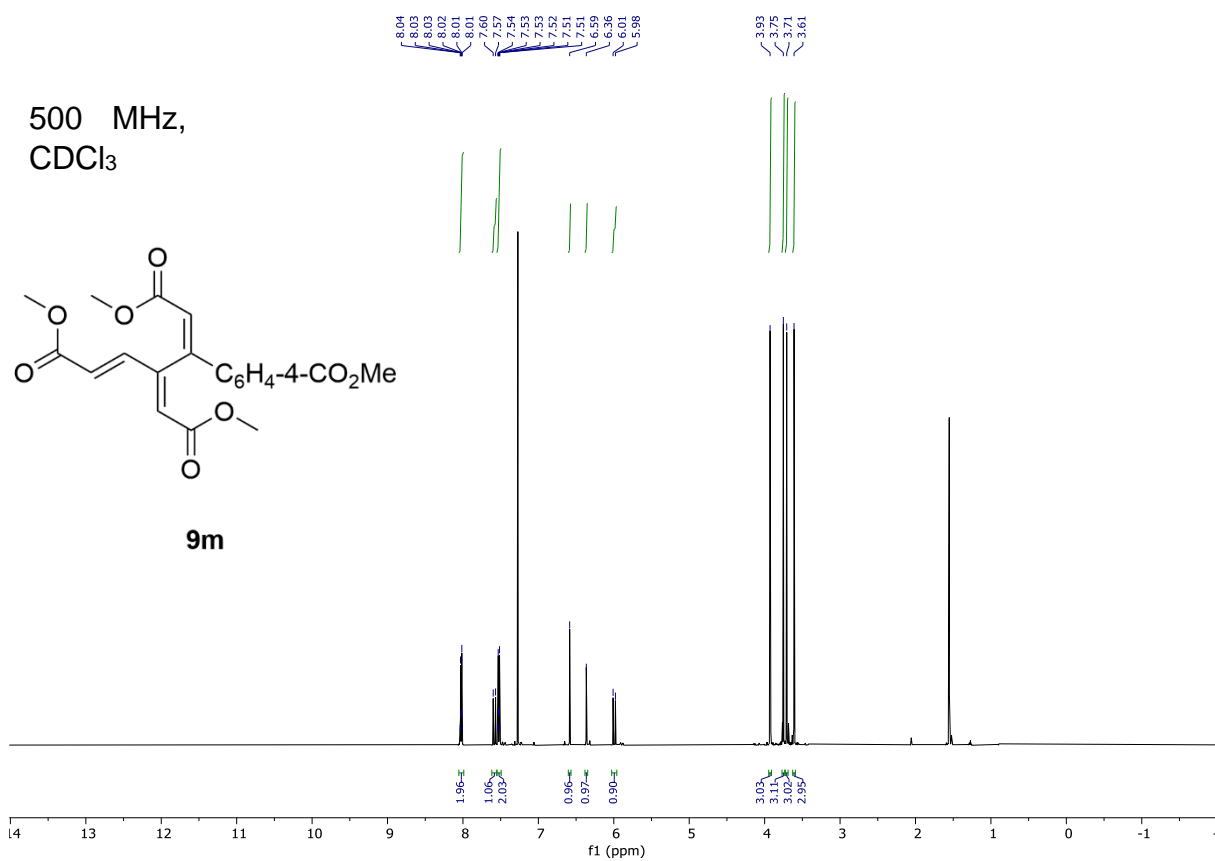


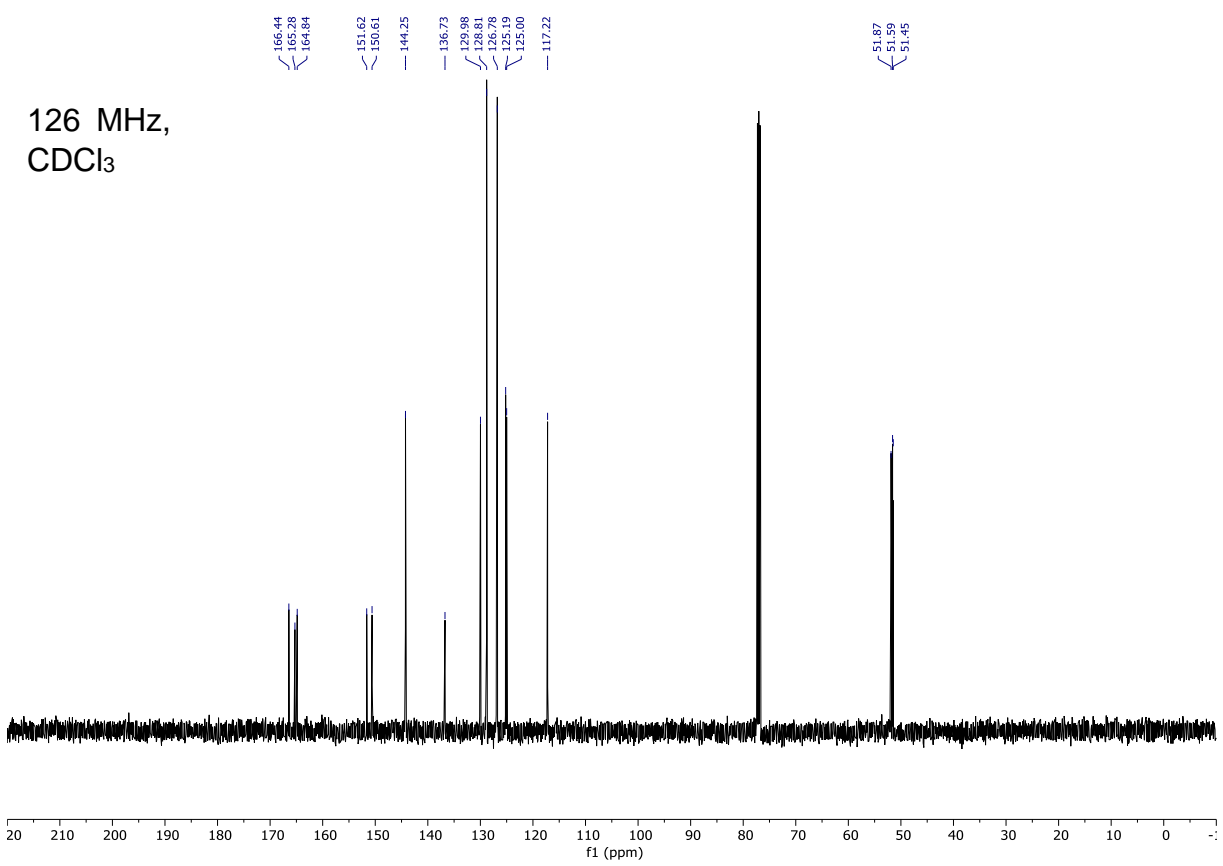
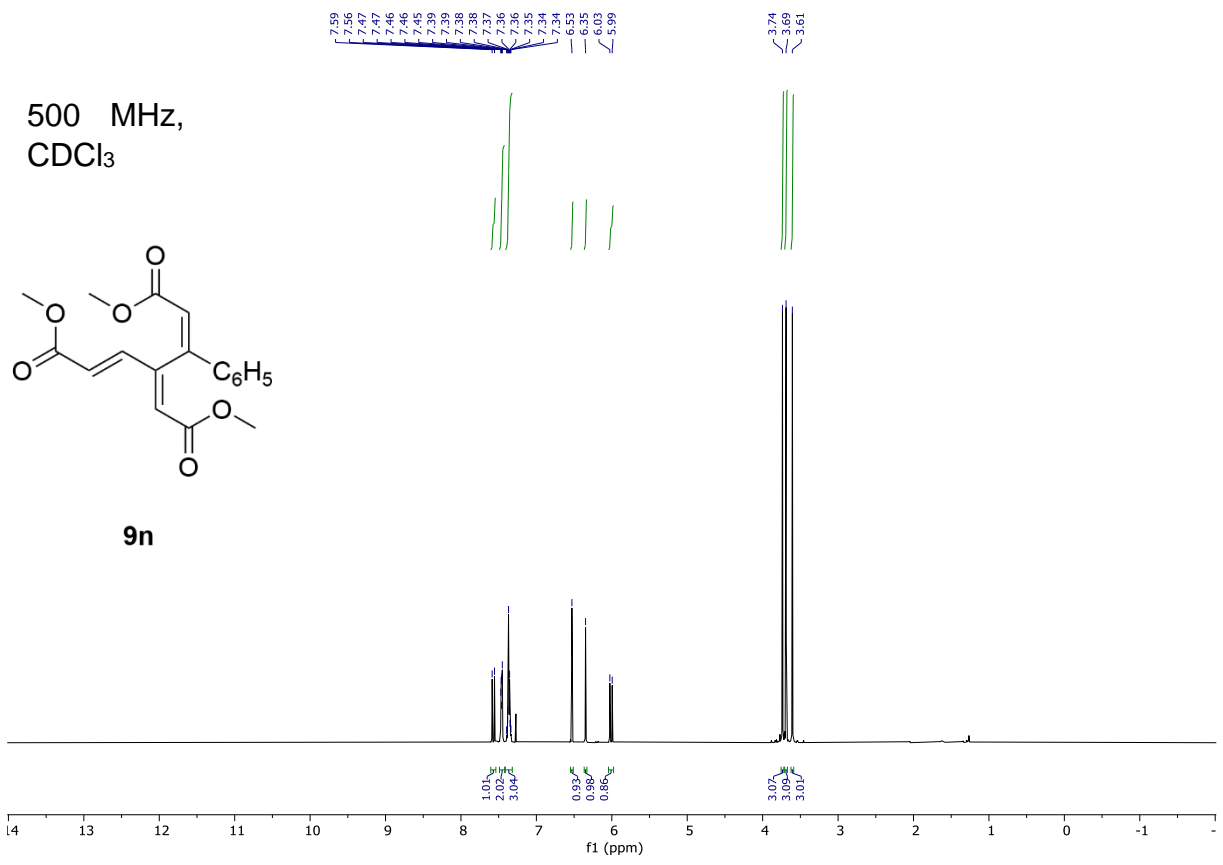


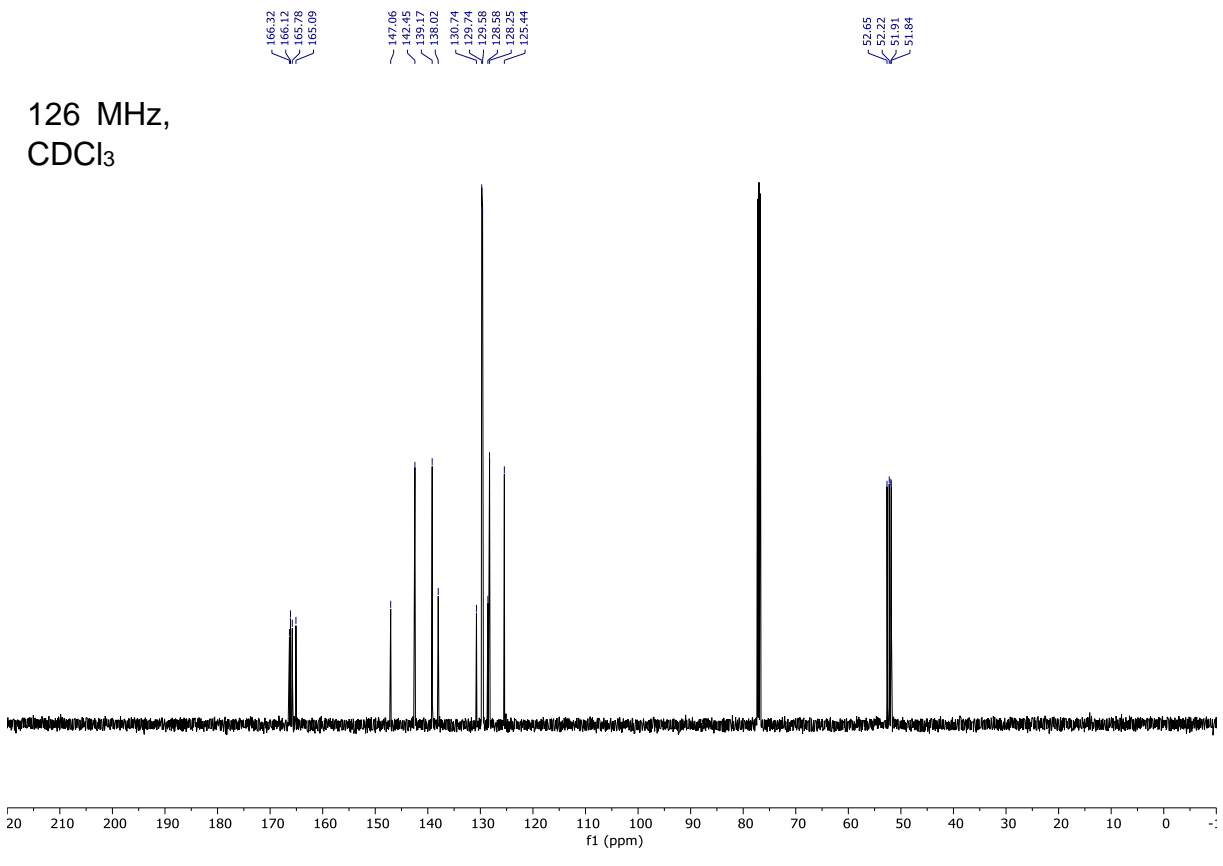
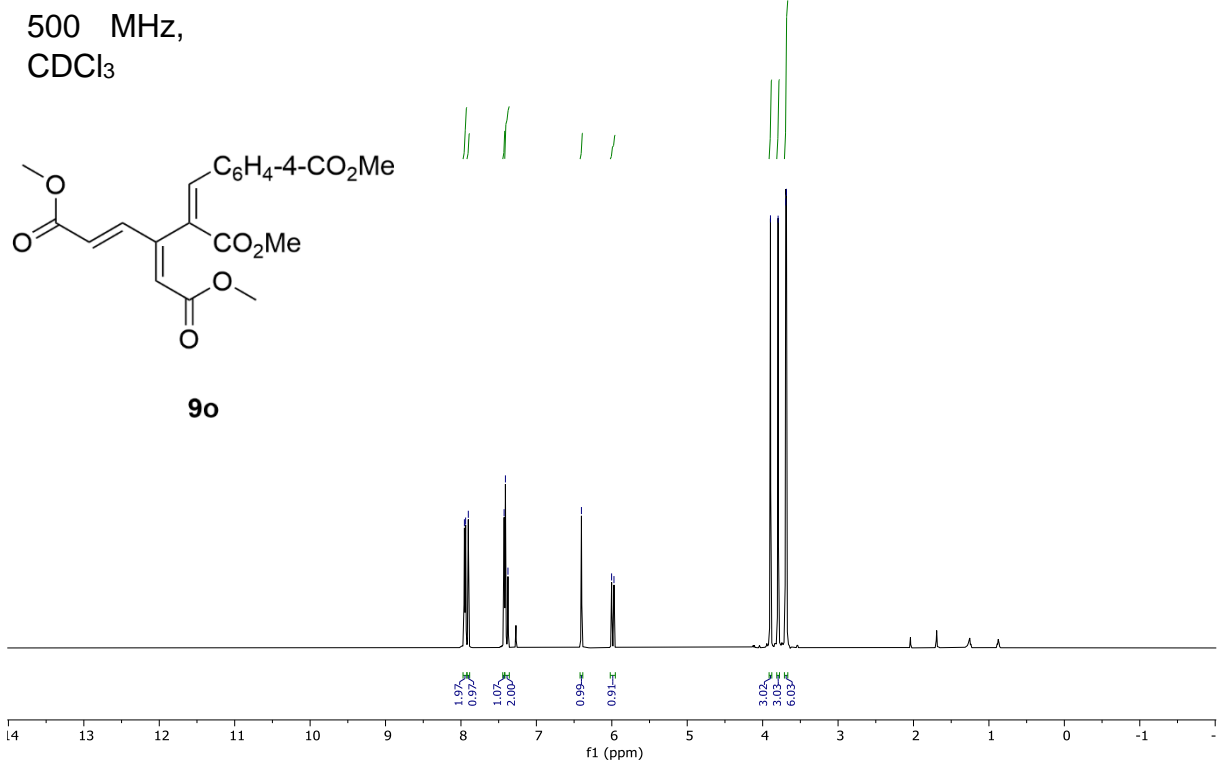


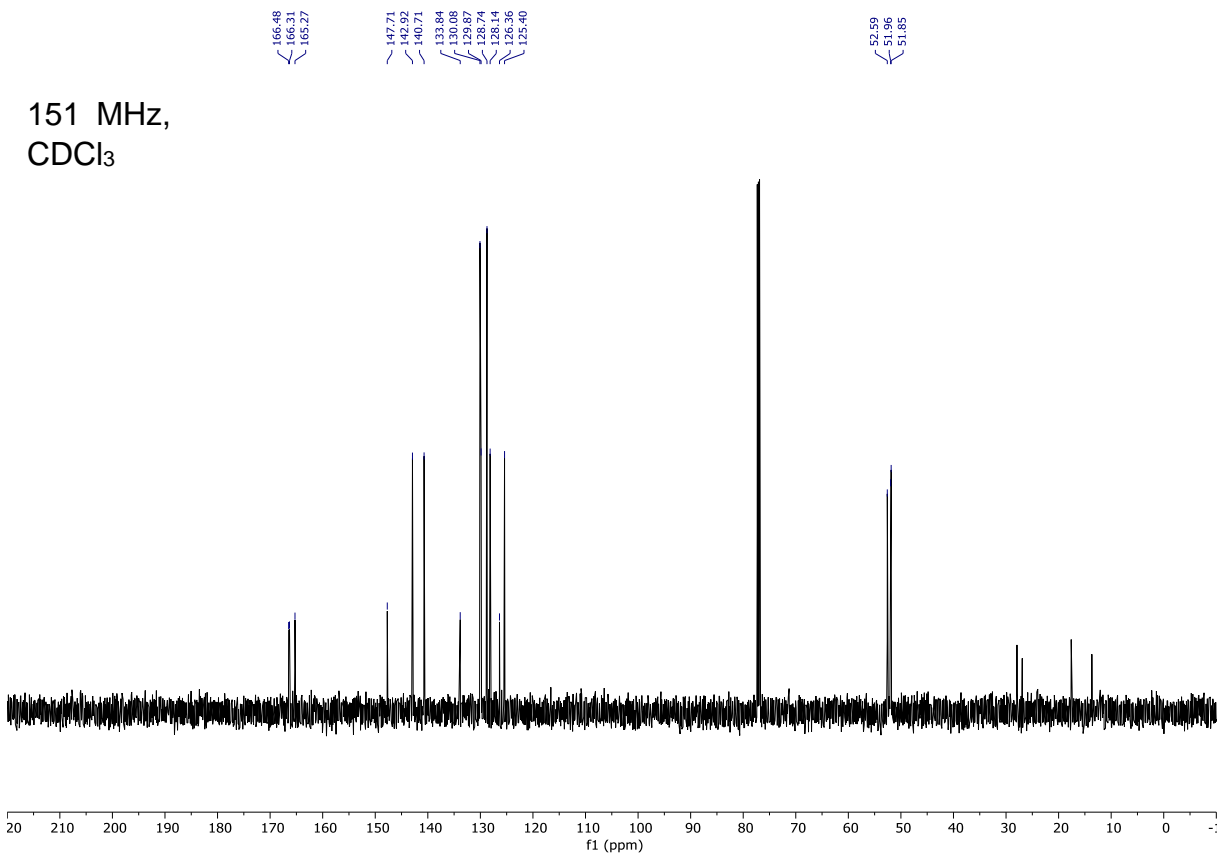
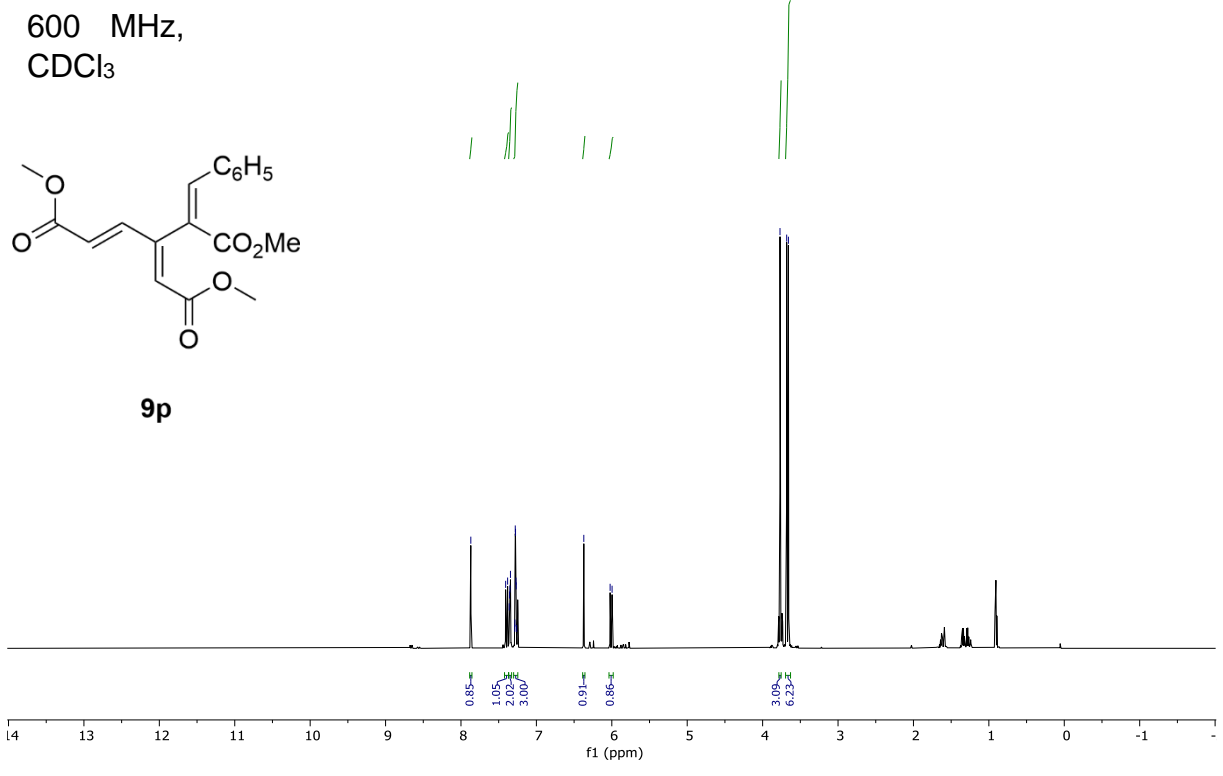


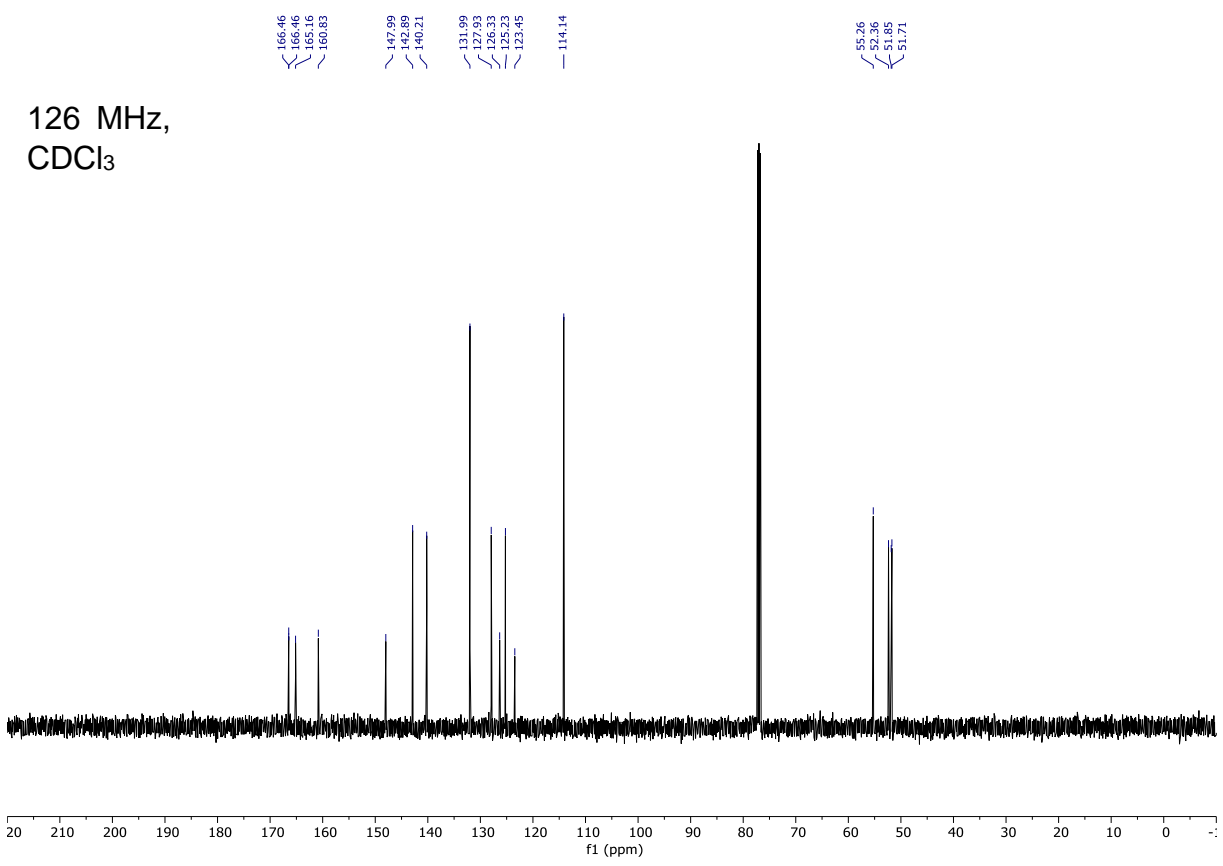
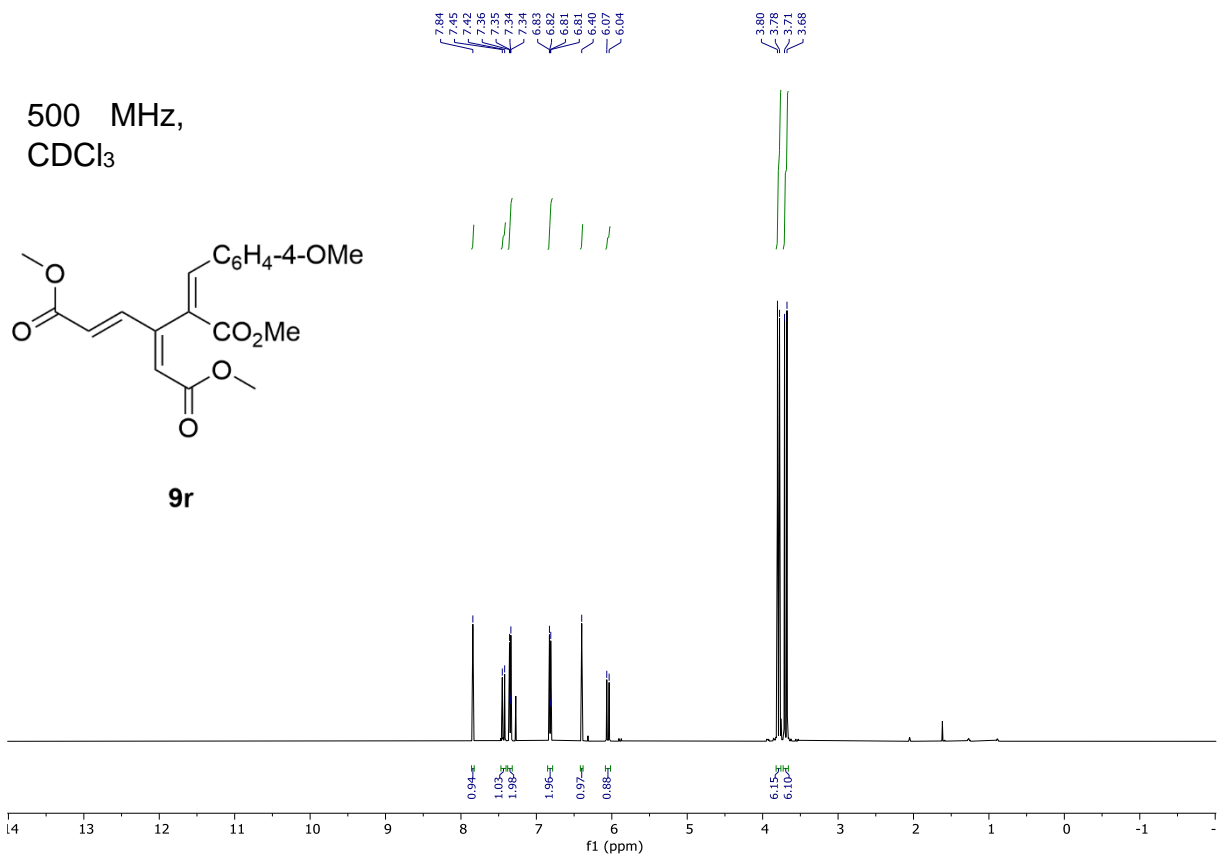


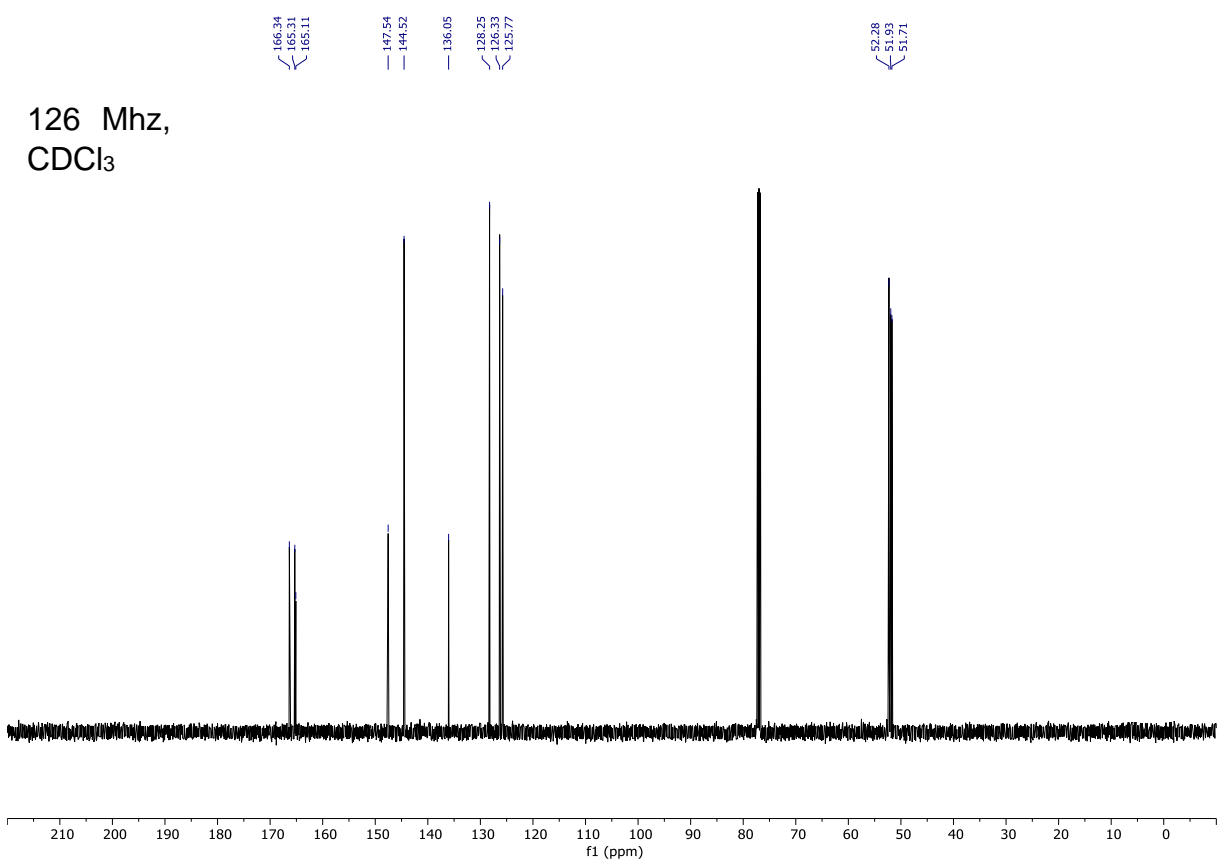
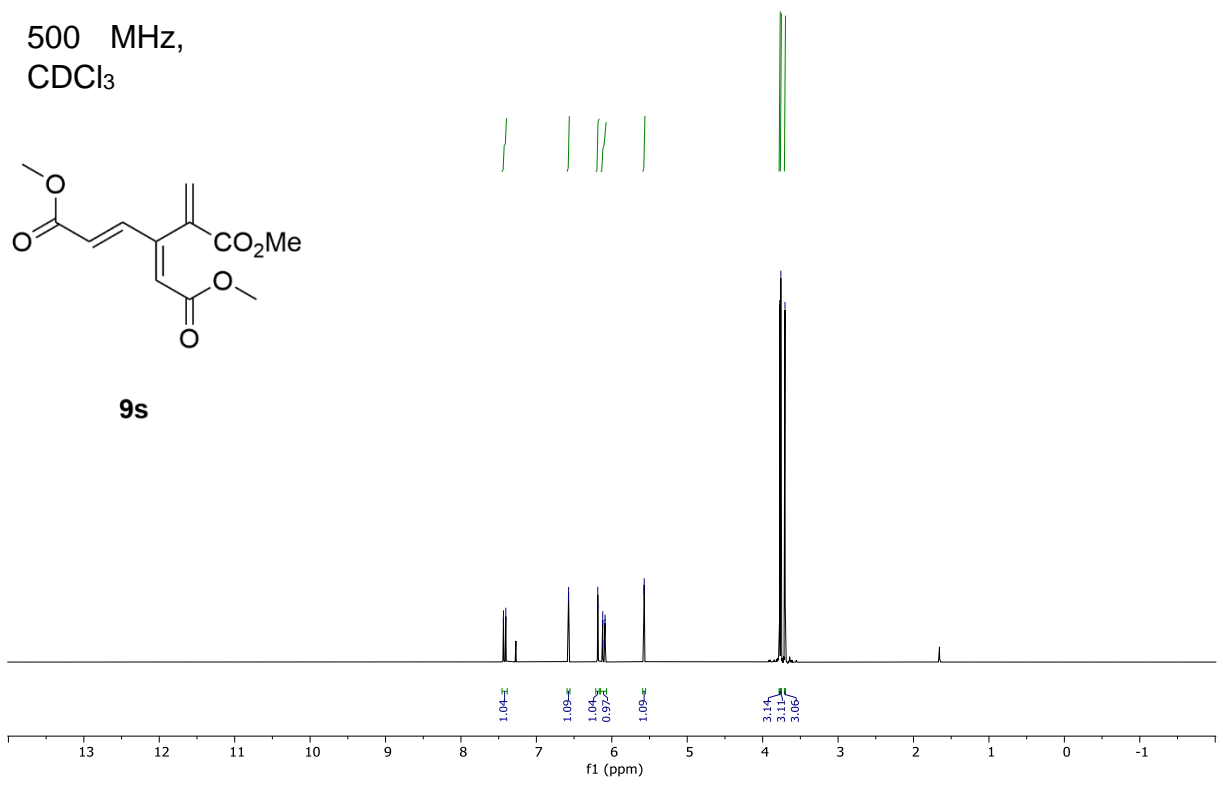


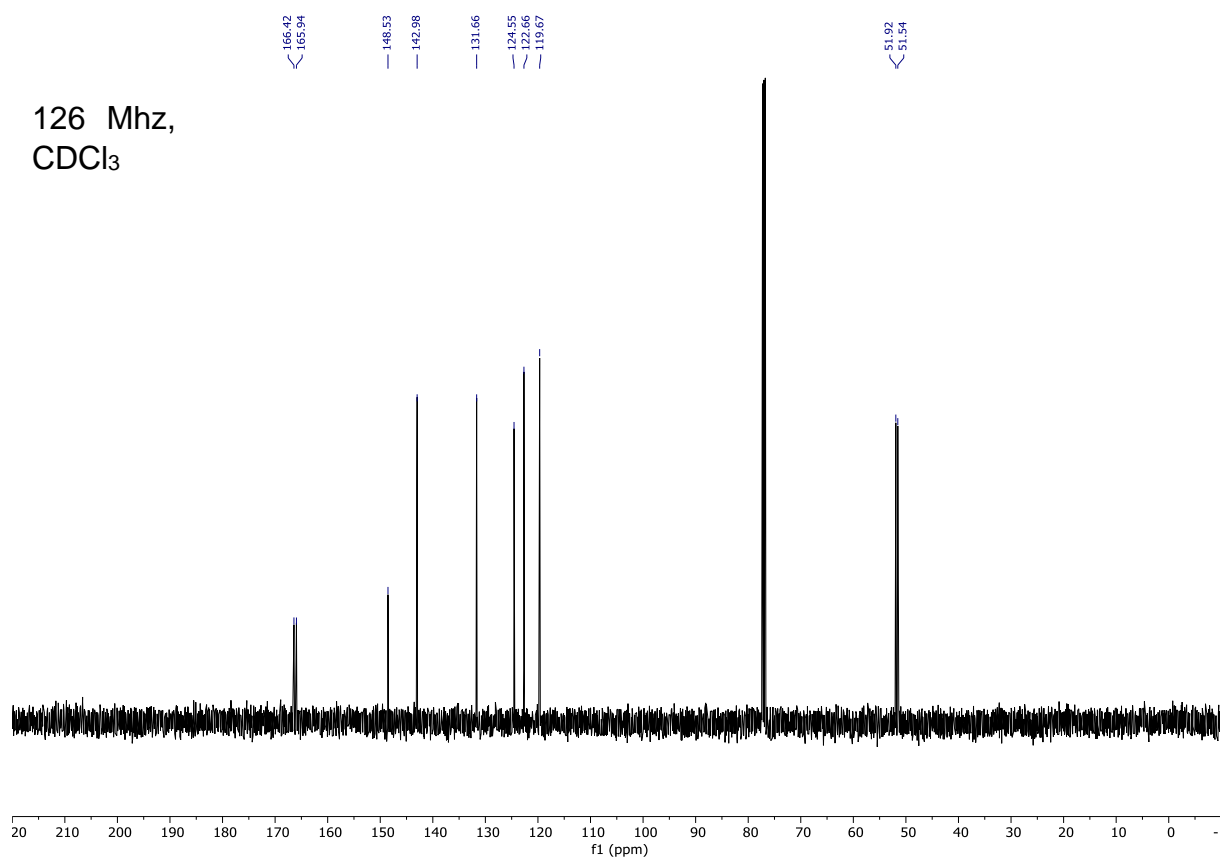
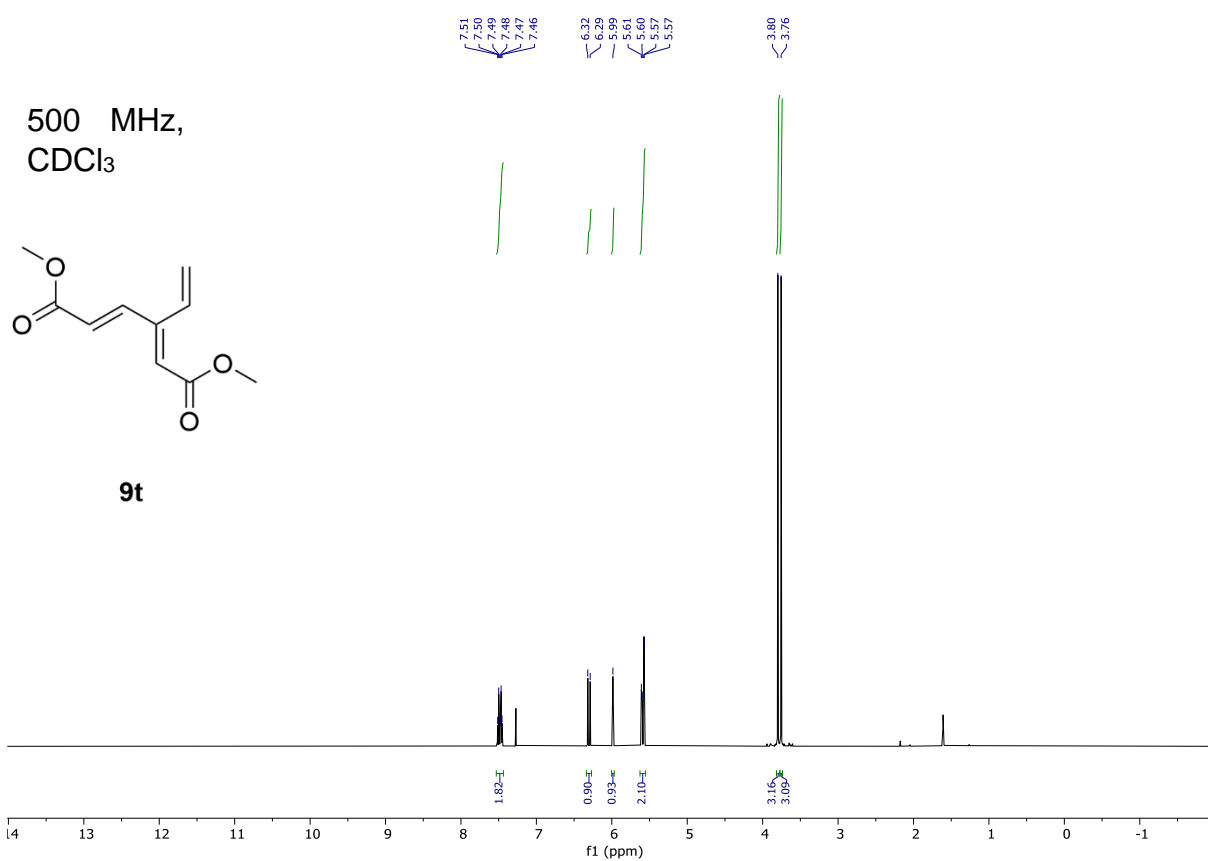


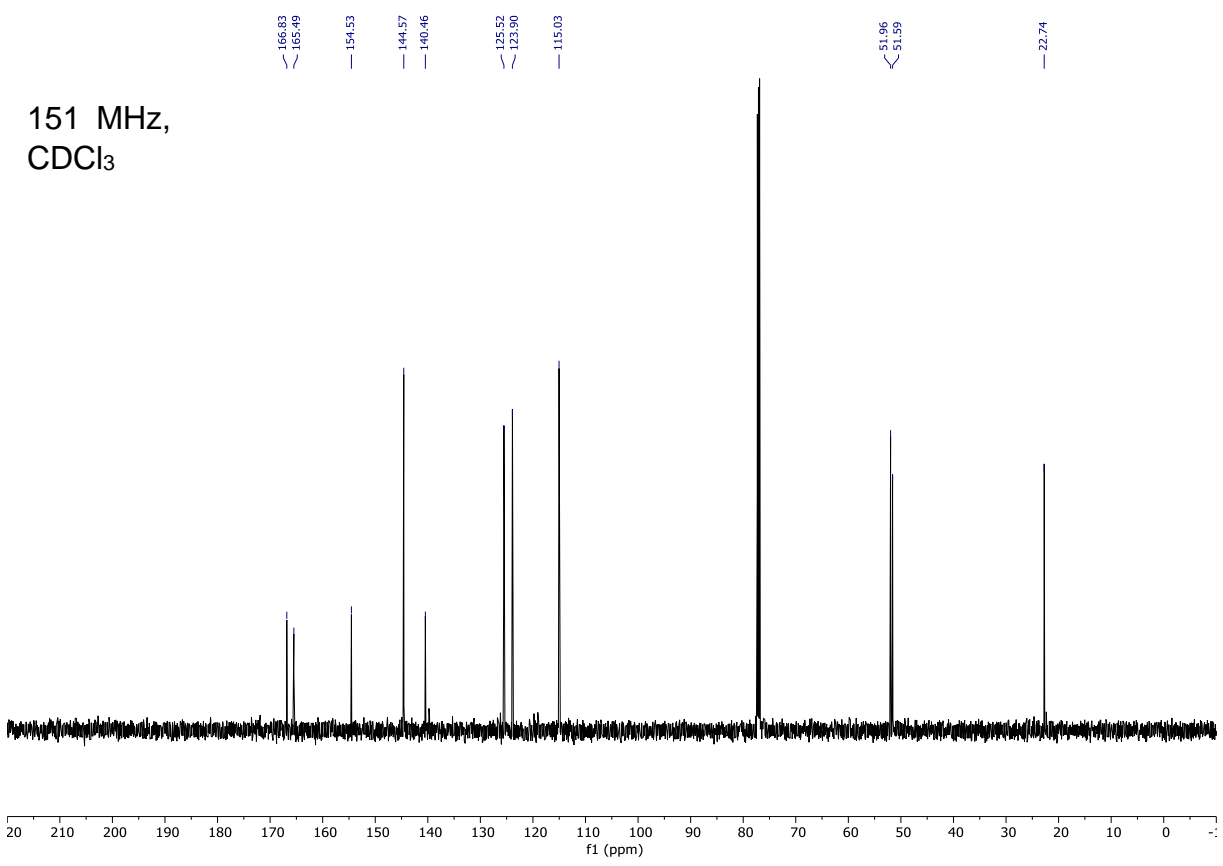
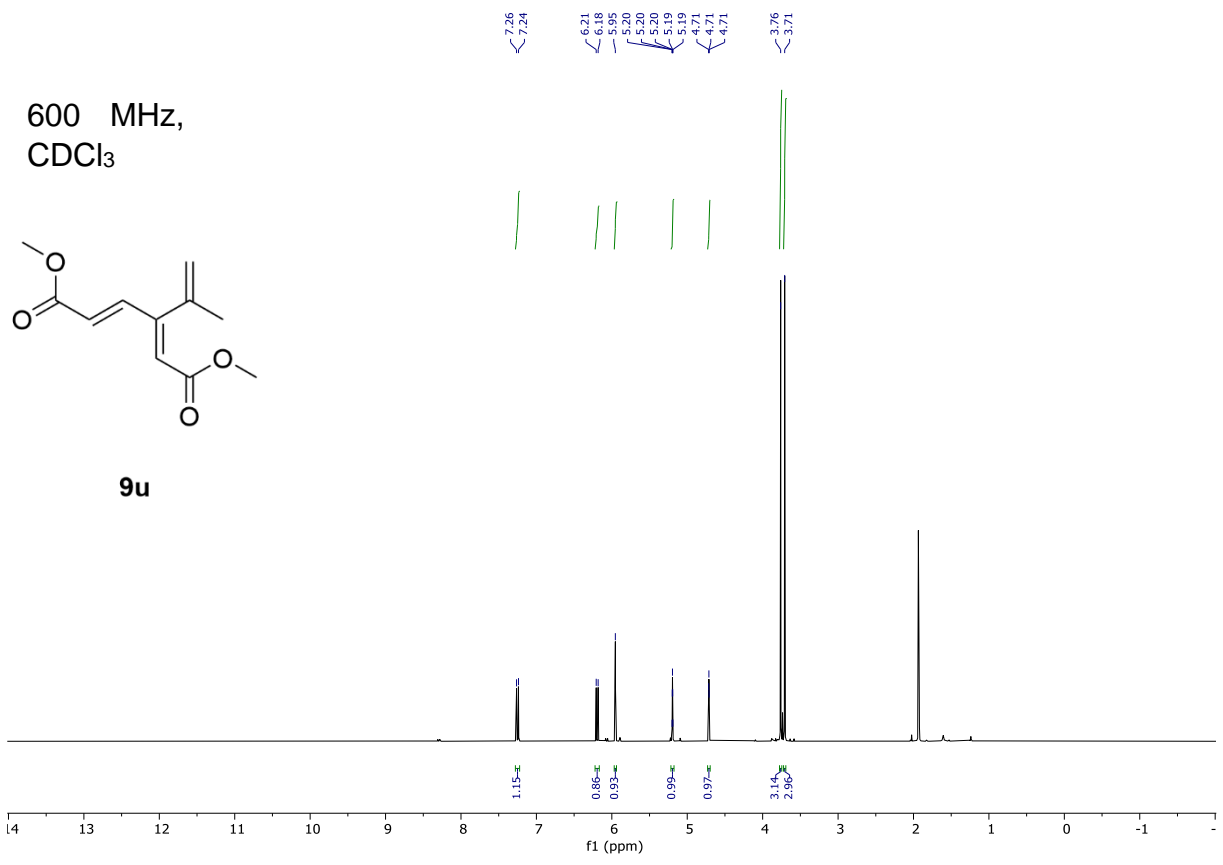


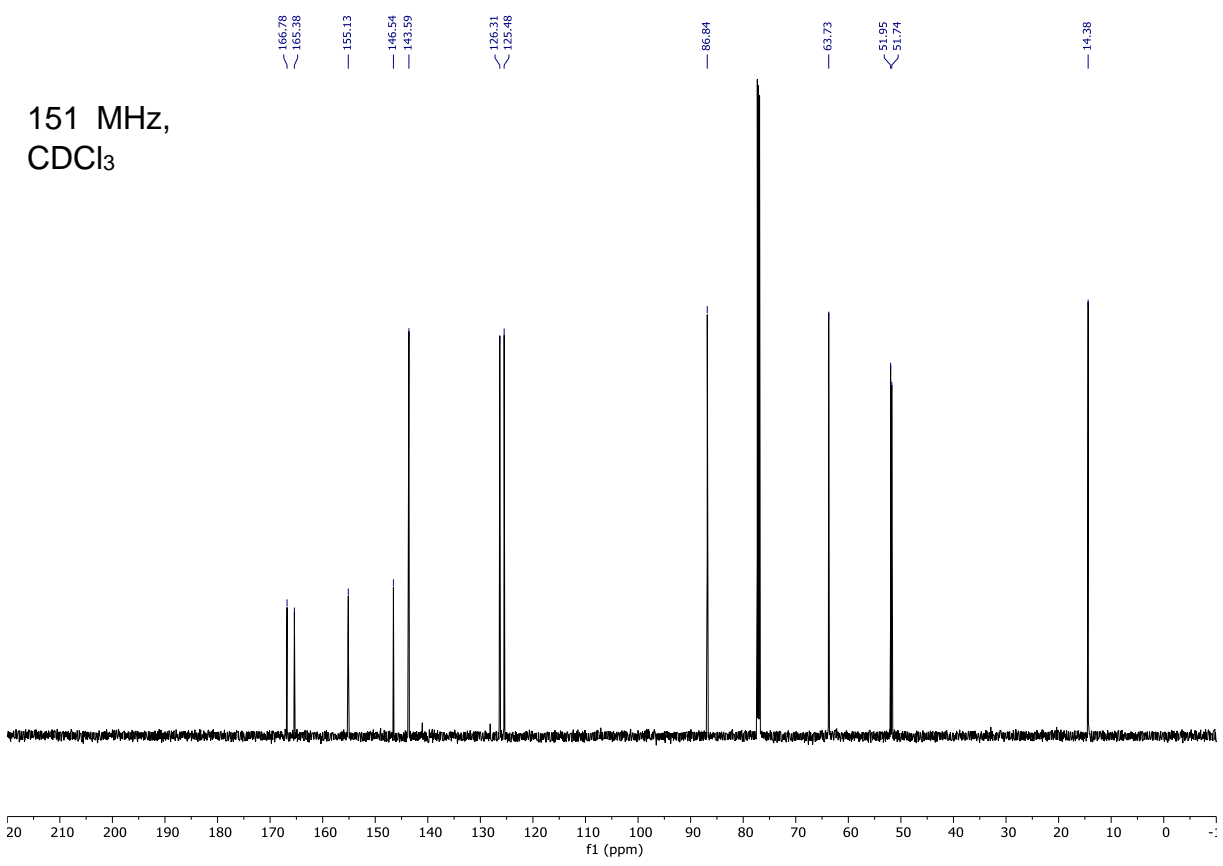
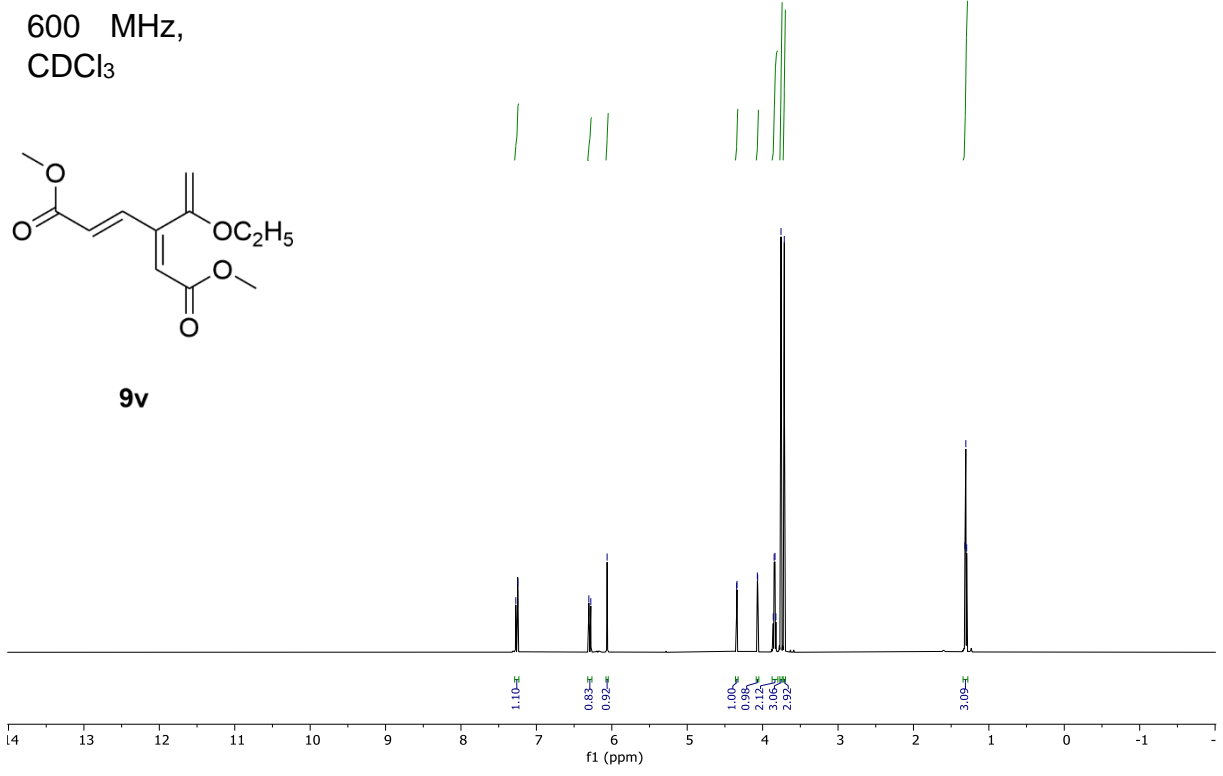


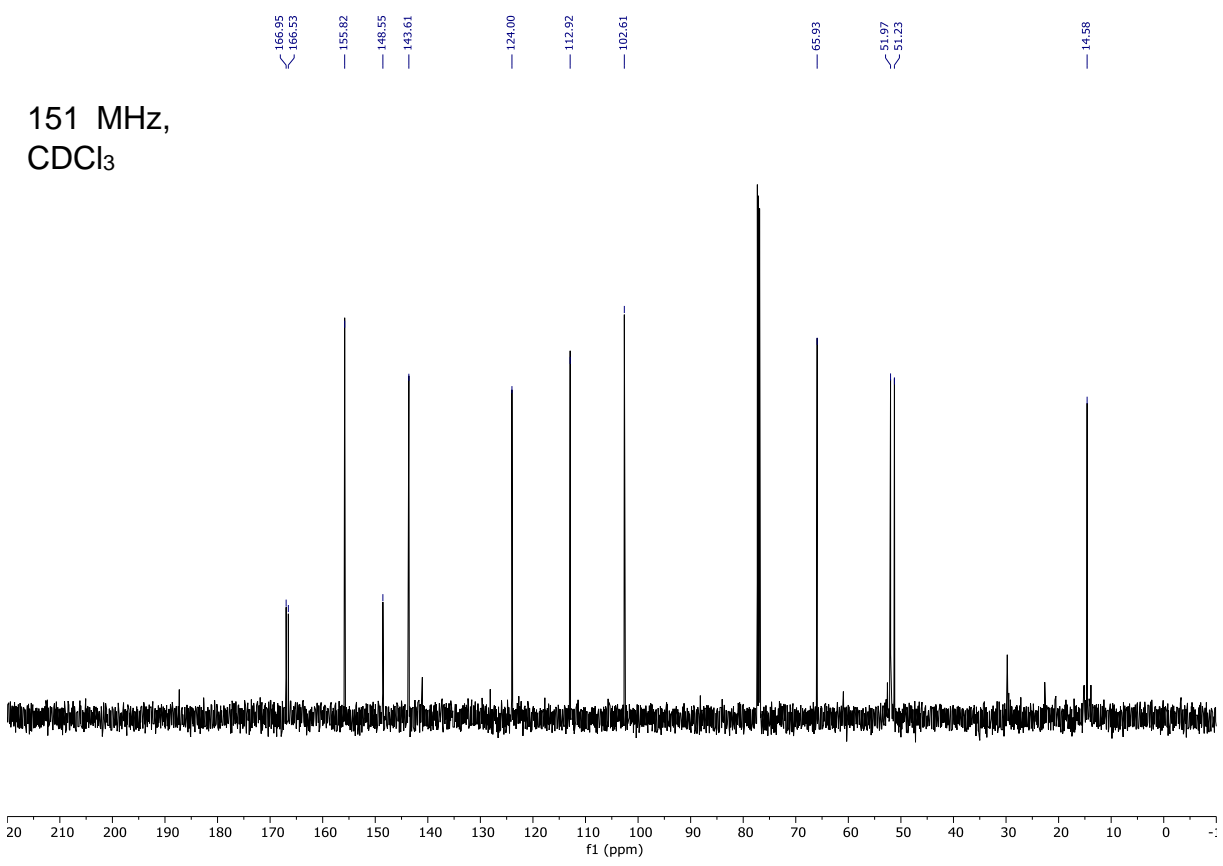
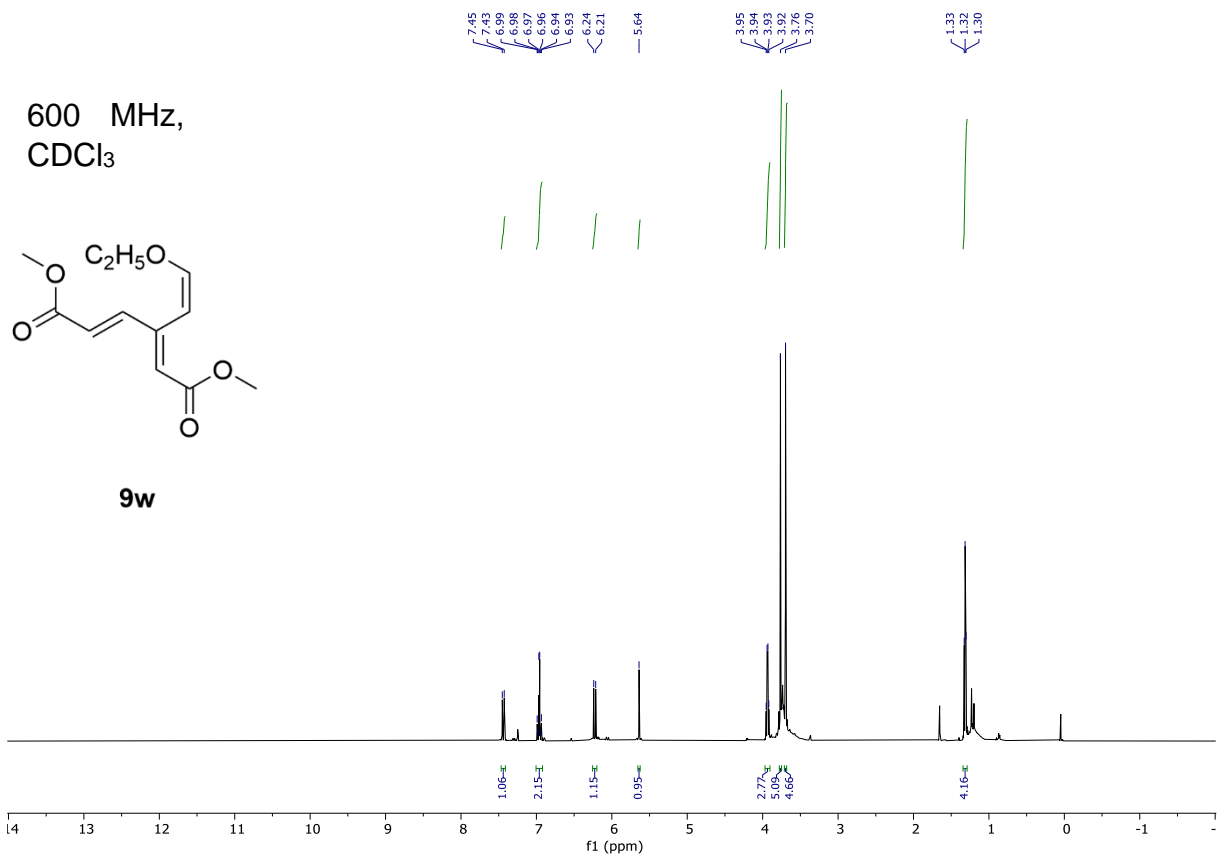


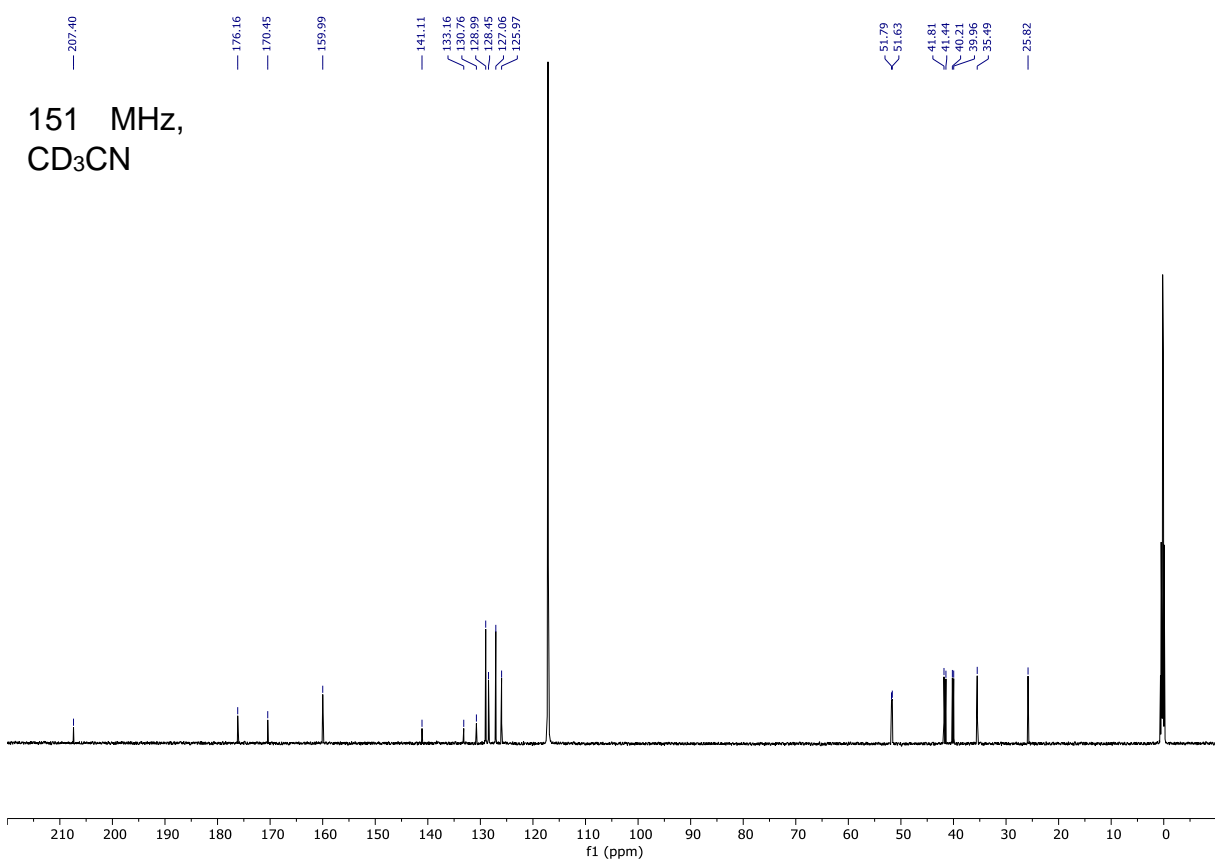
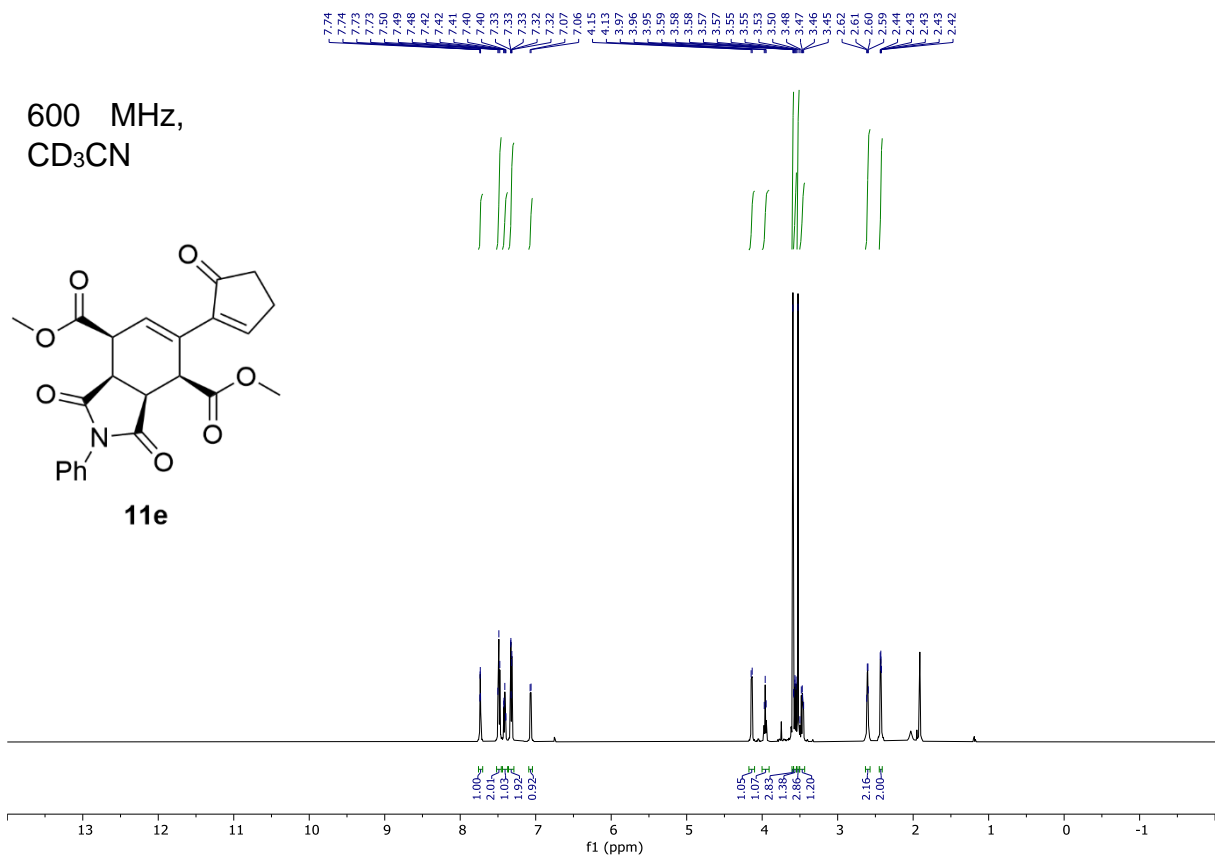


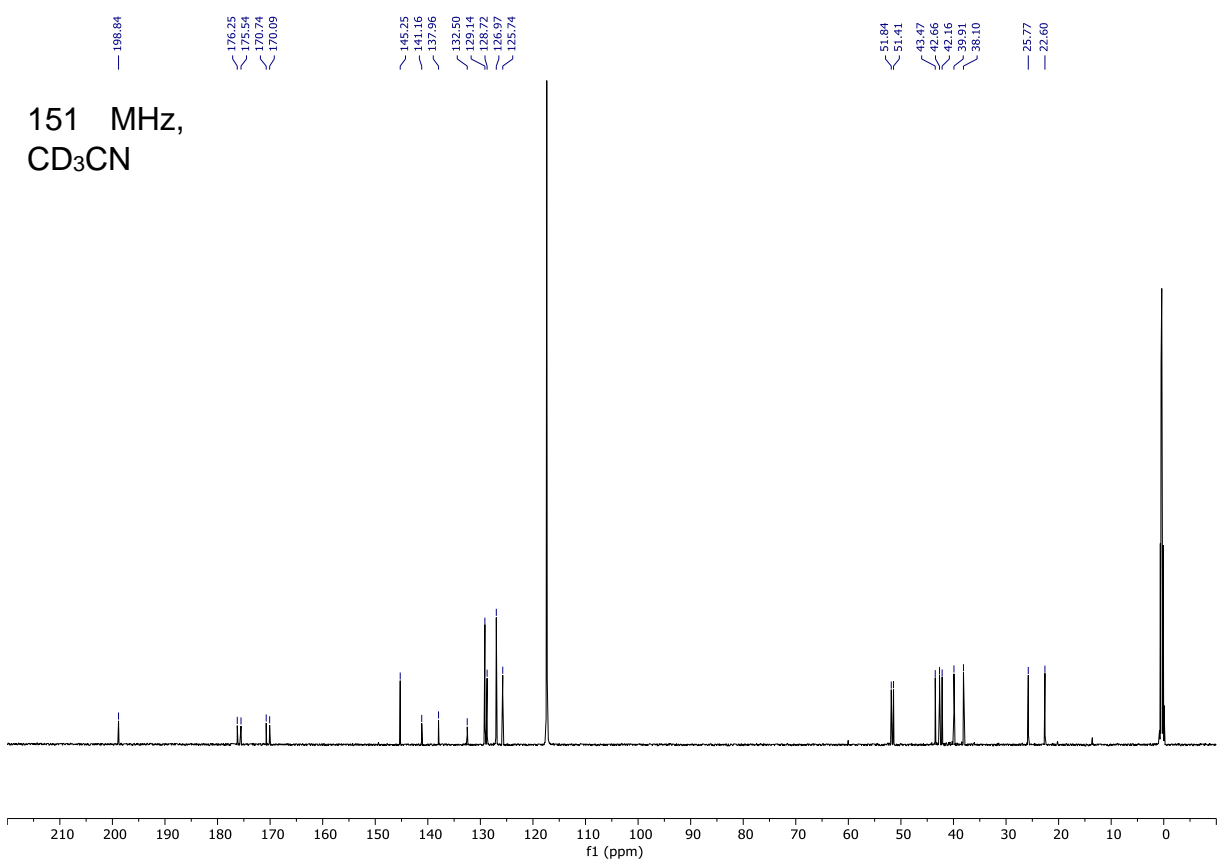
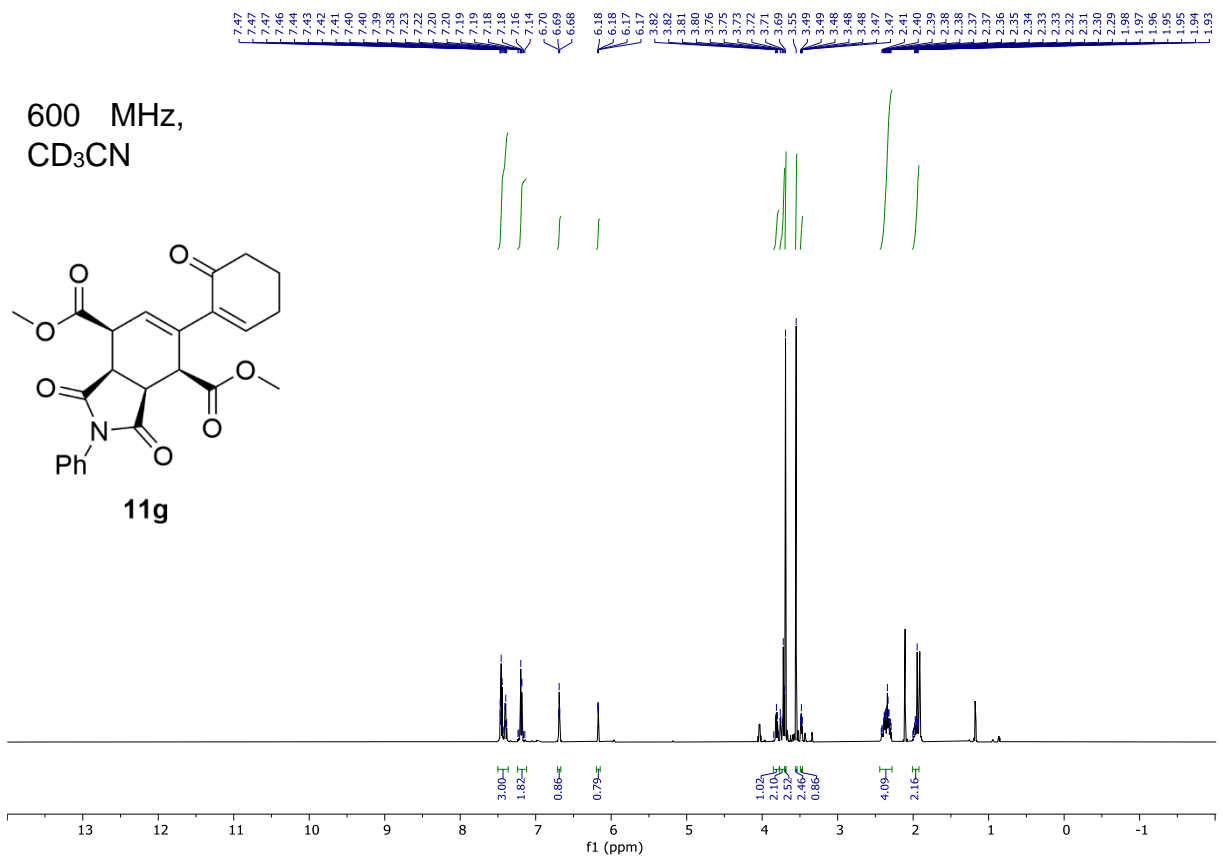


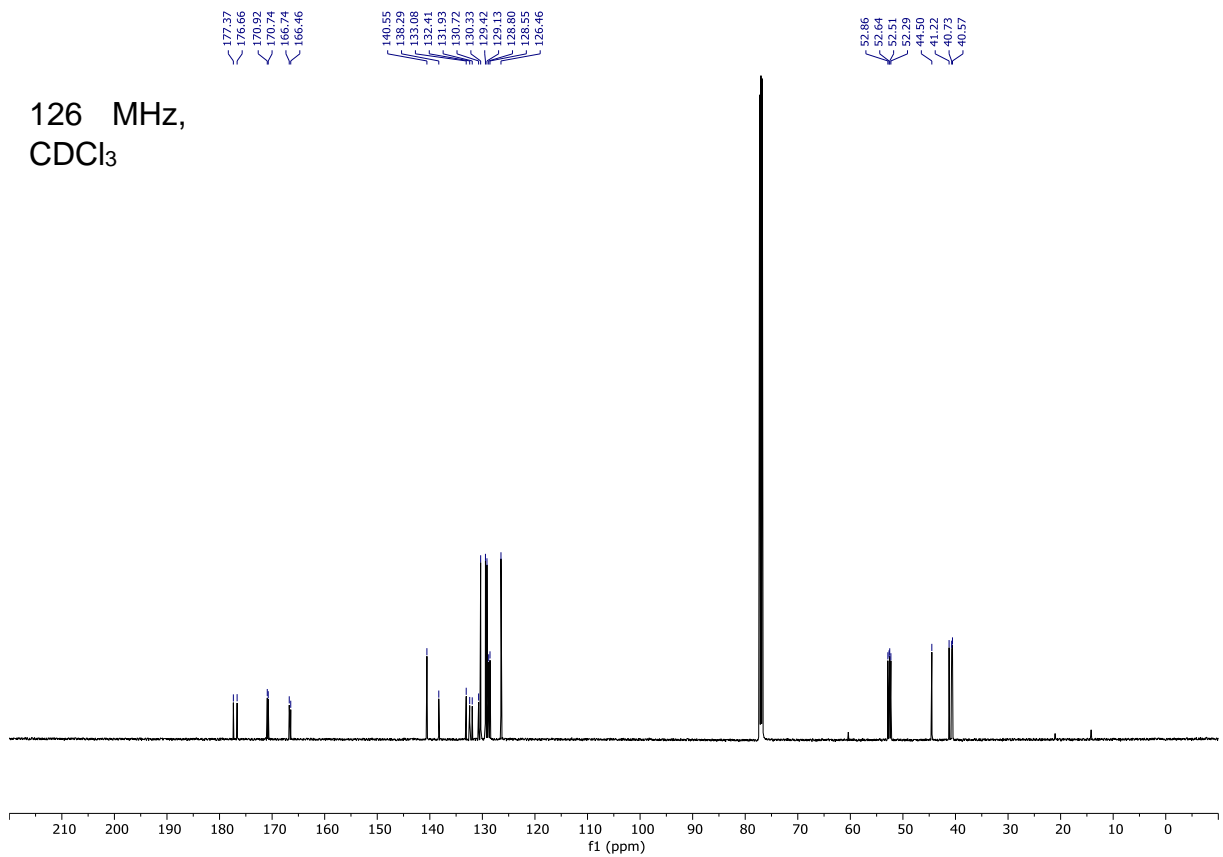
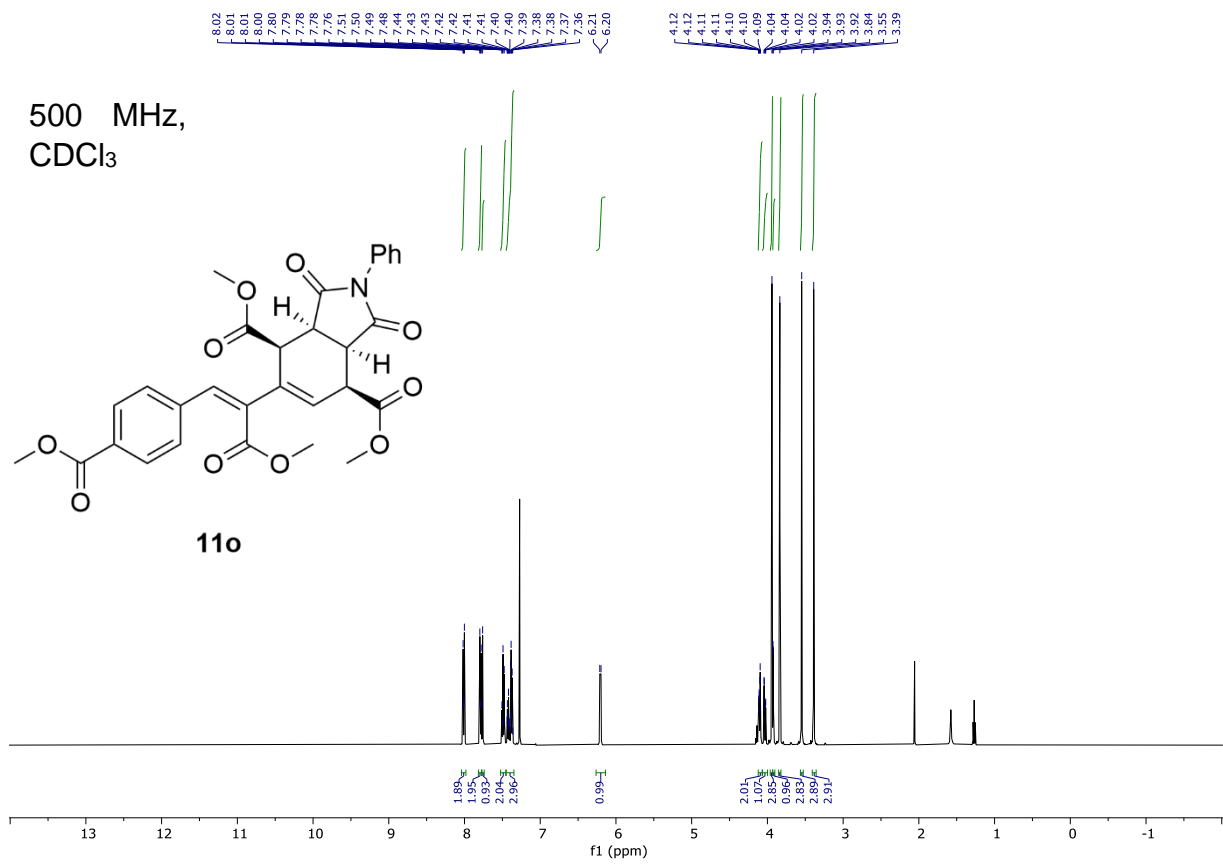


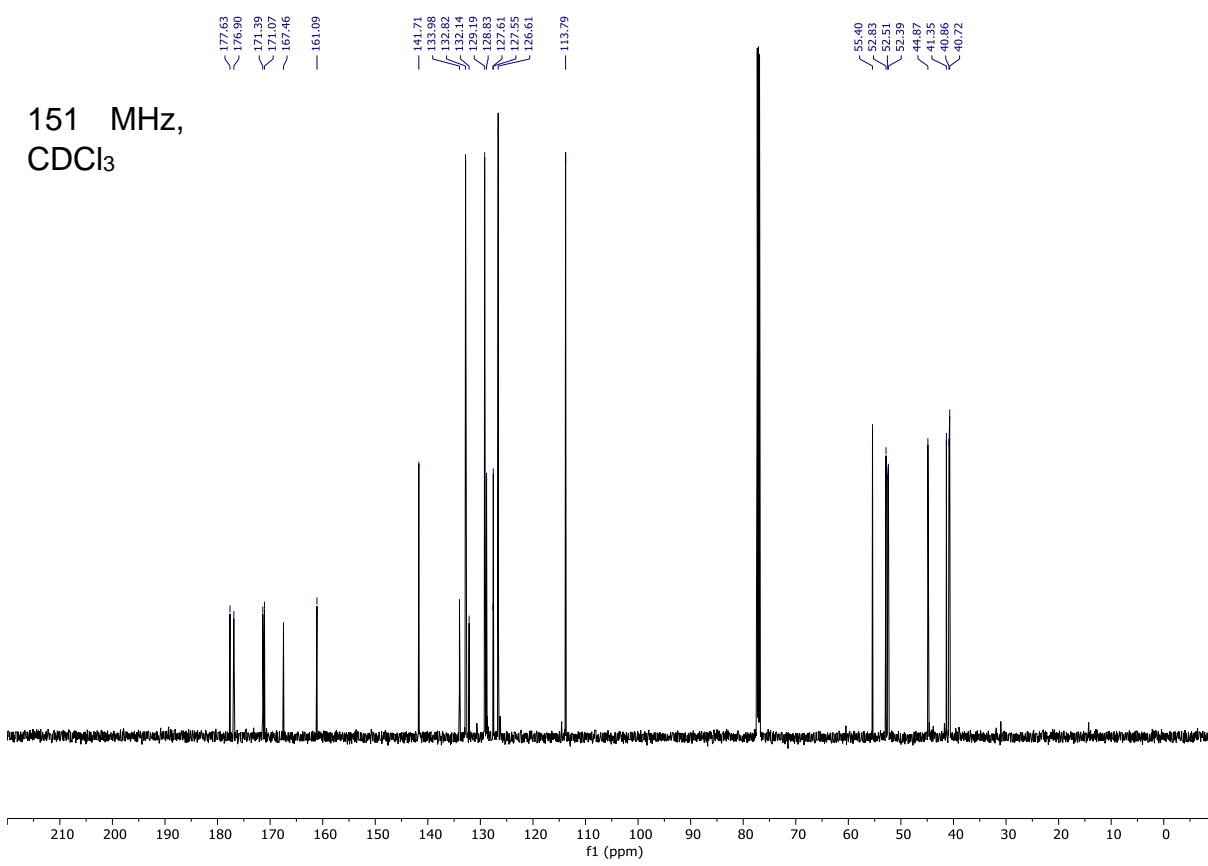
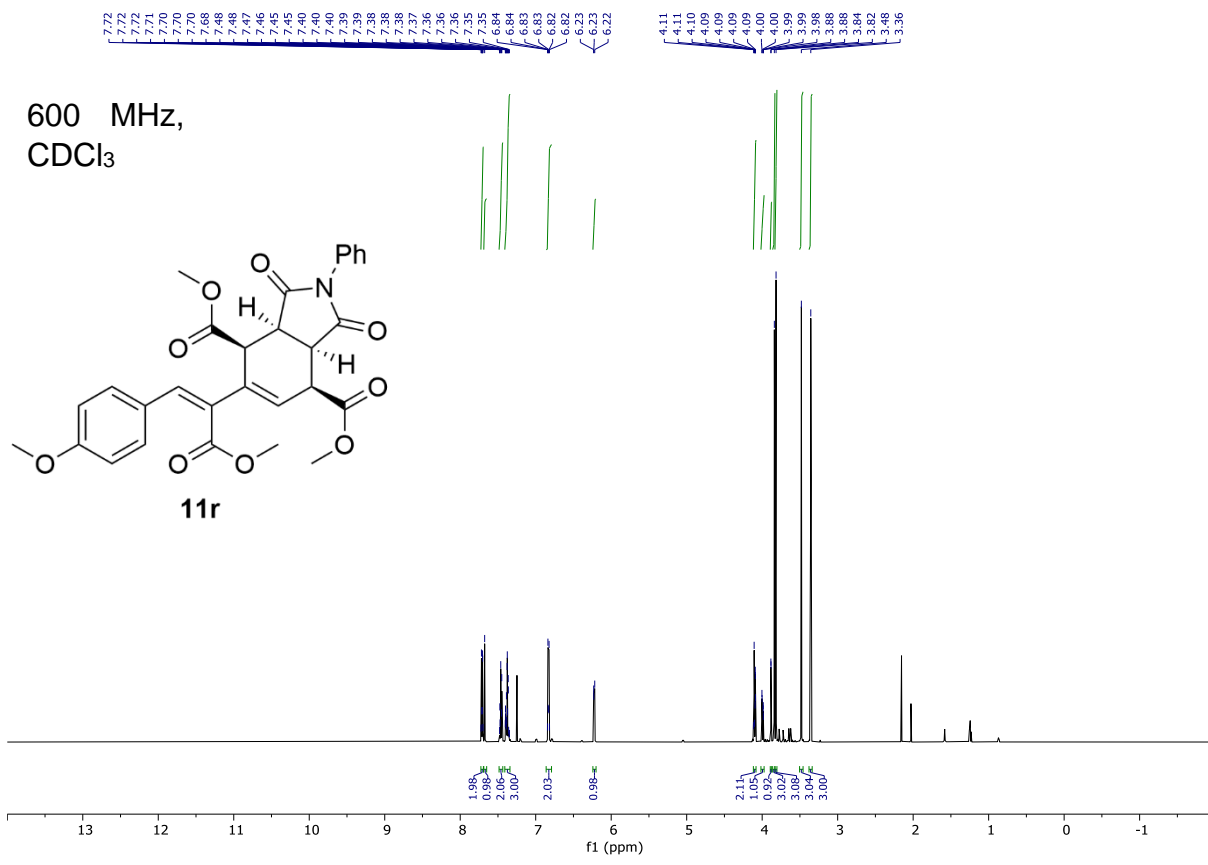




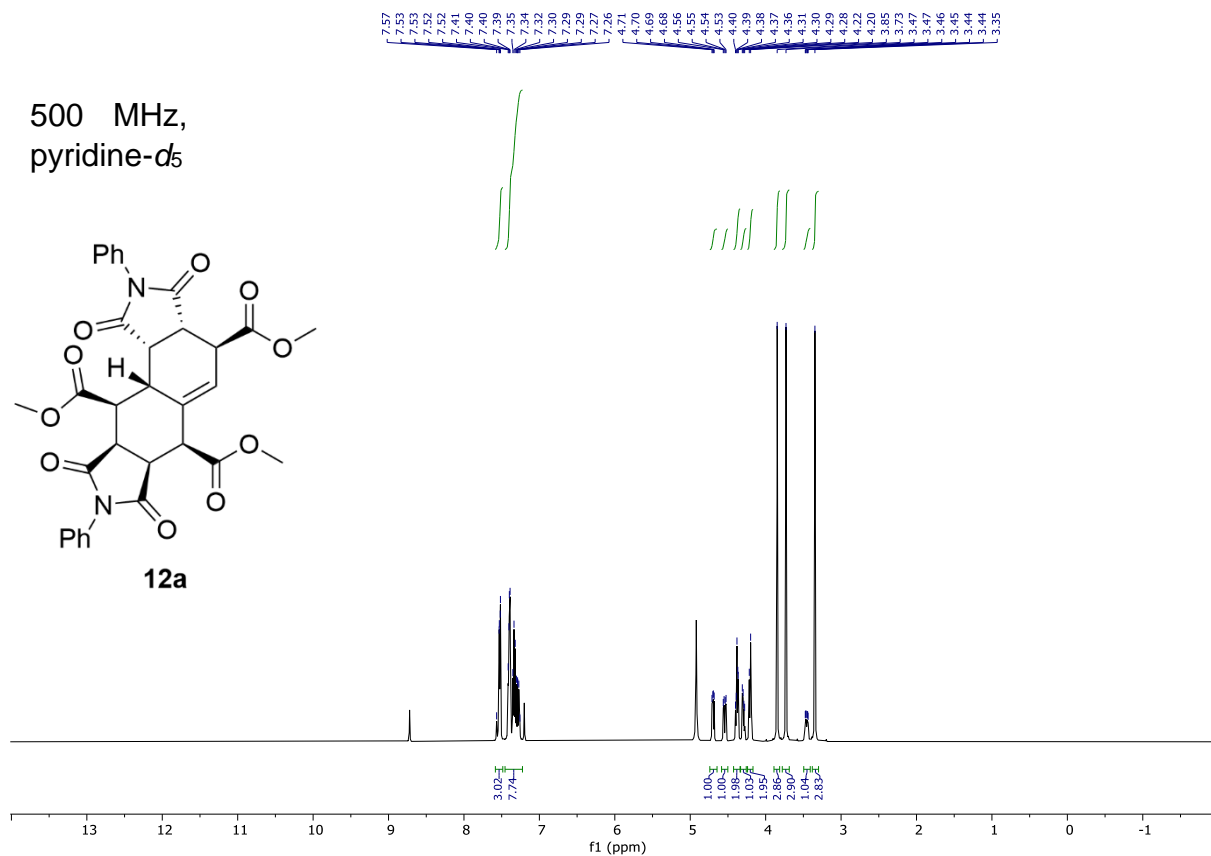
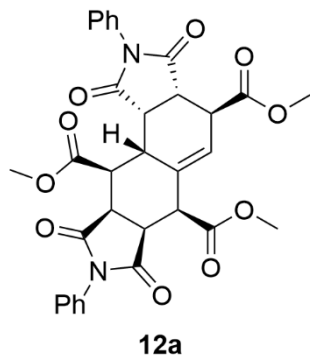




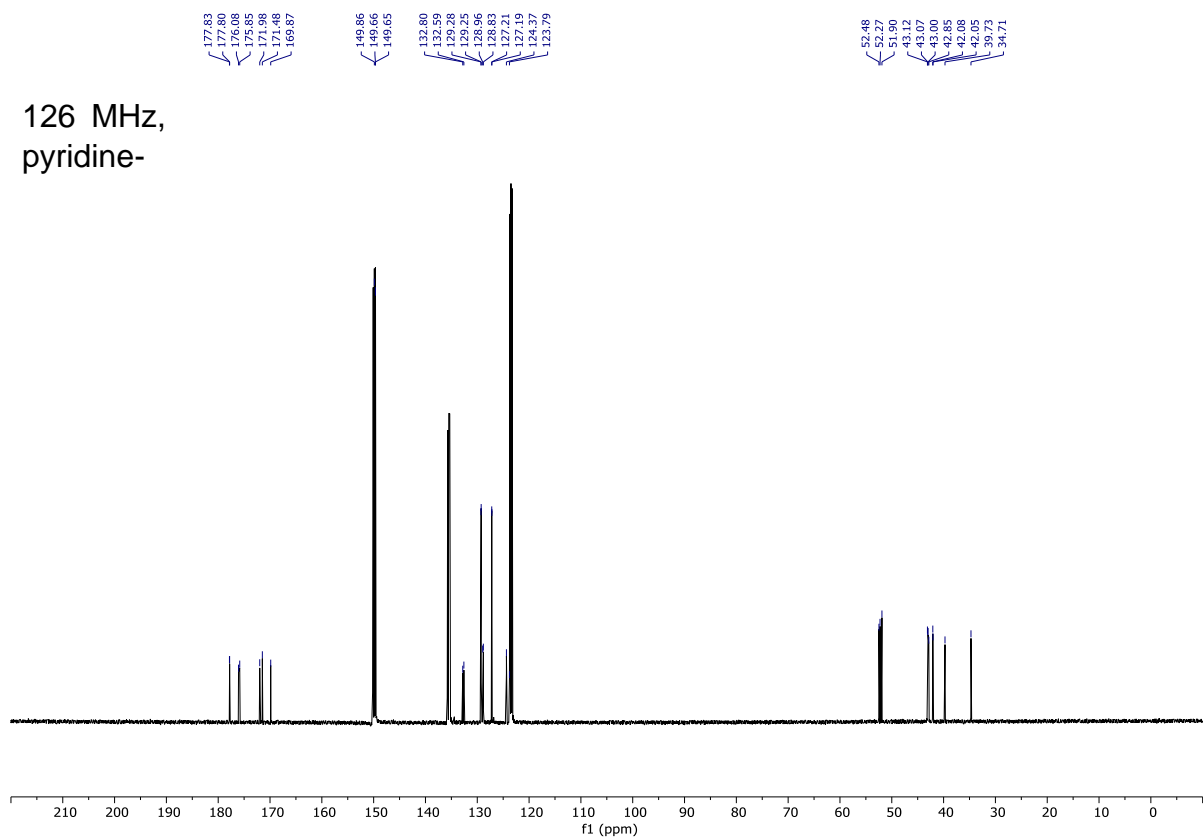


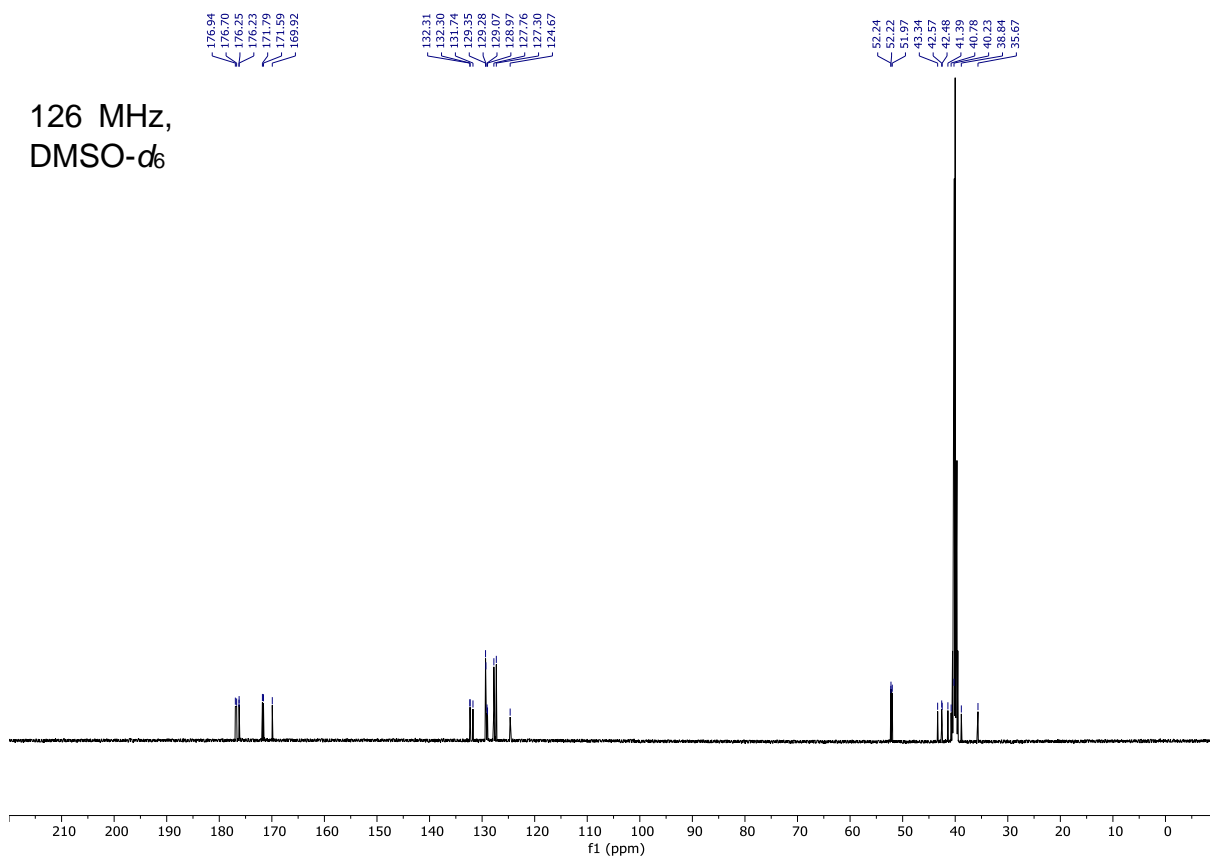
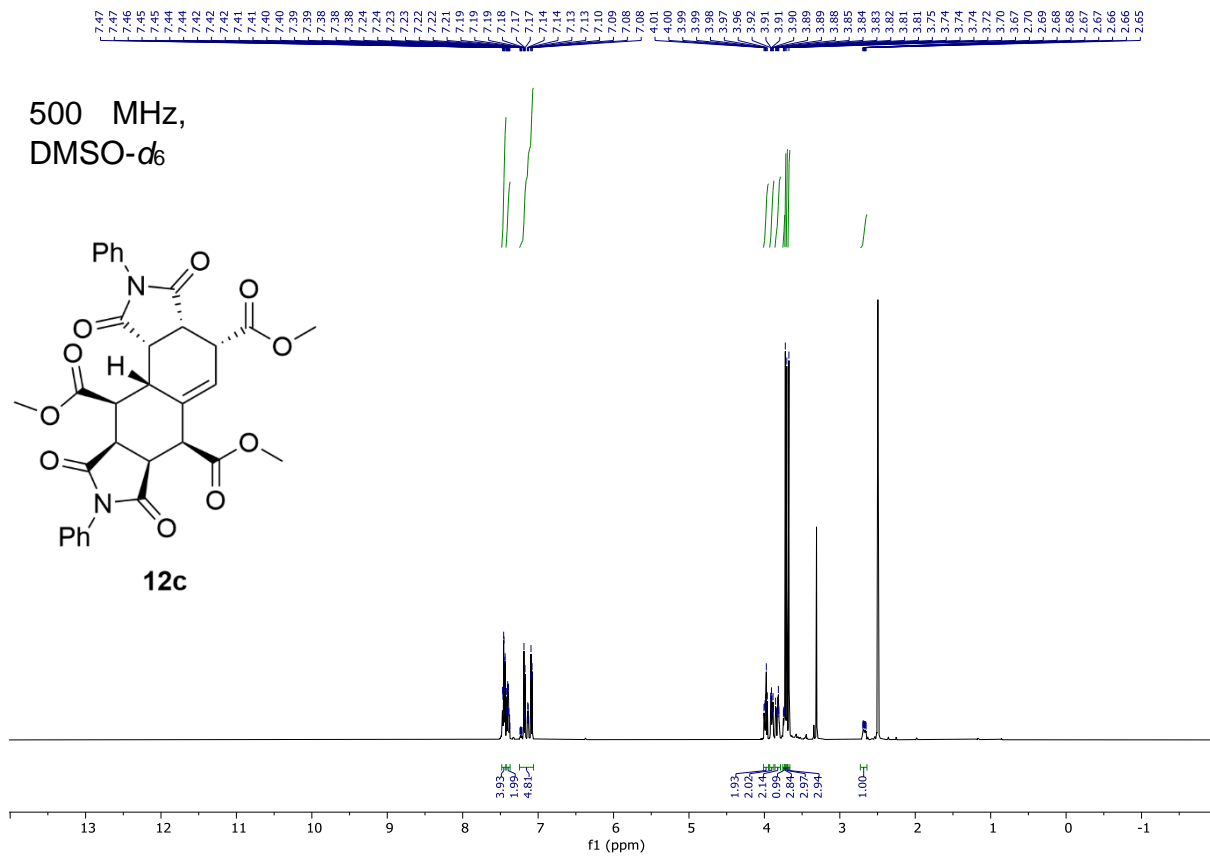


500 MHz,
pyridine-*d*₅

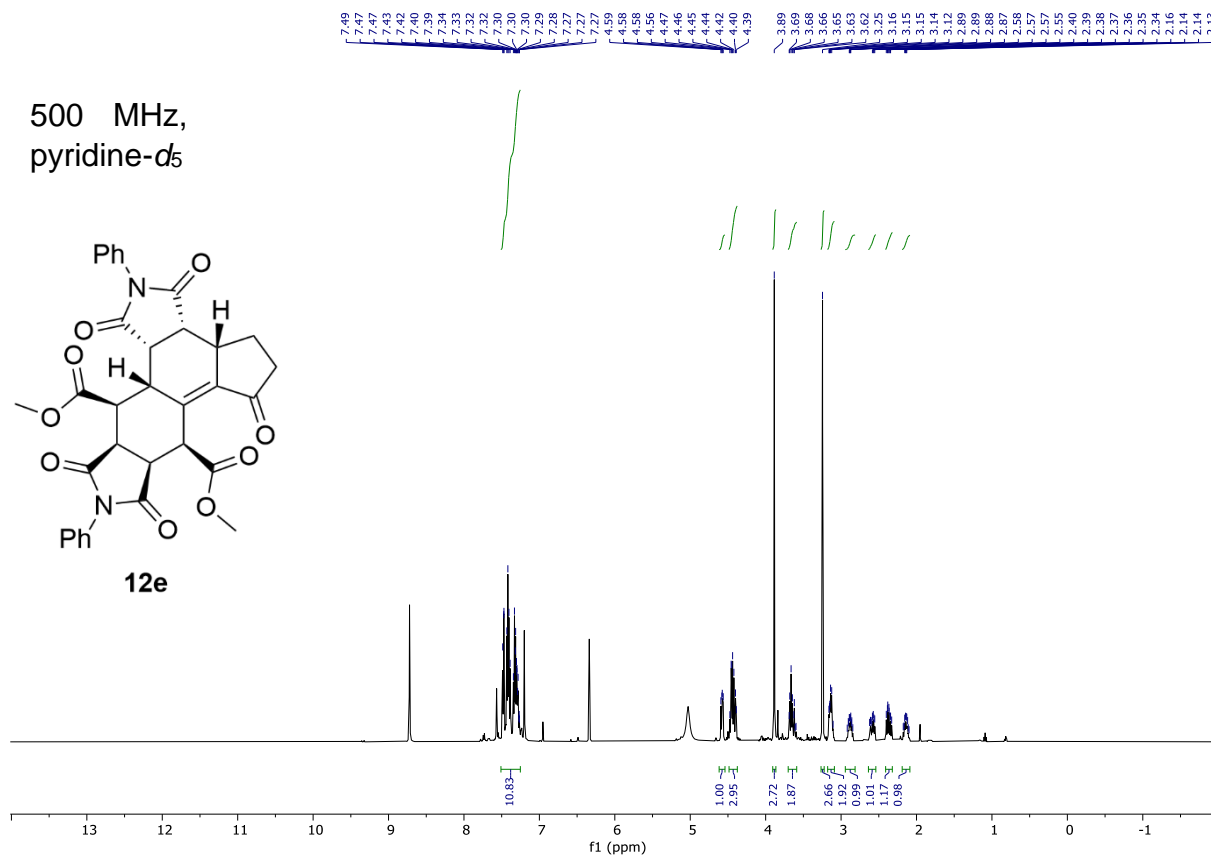
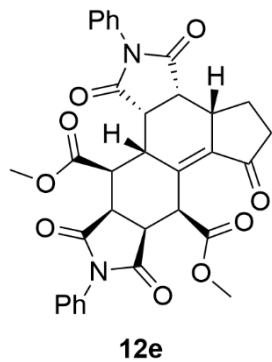


126 MHz,
pyridine-

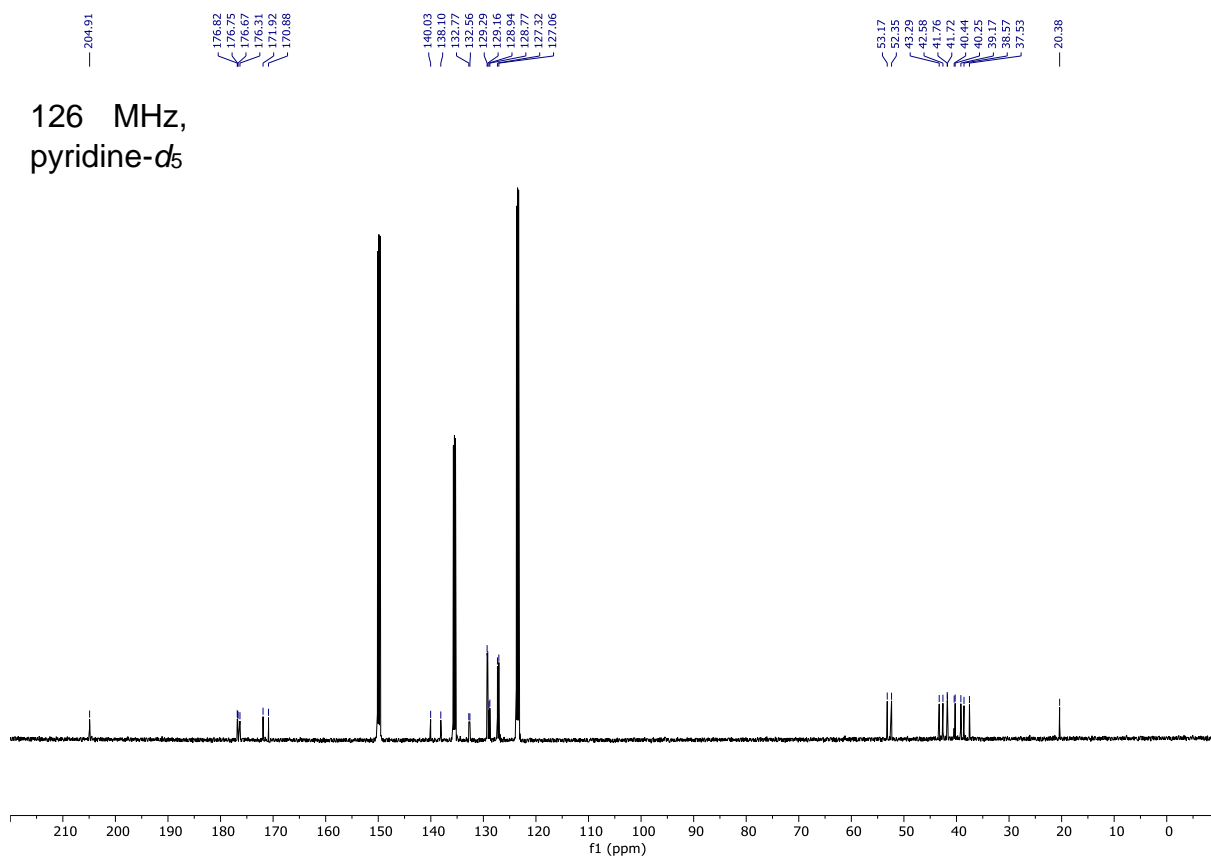


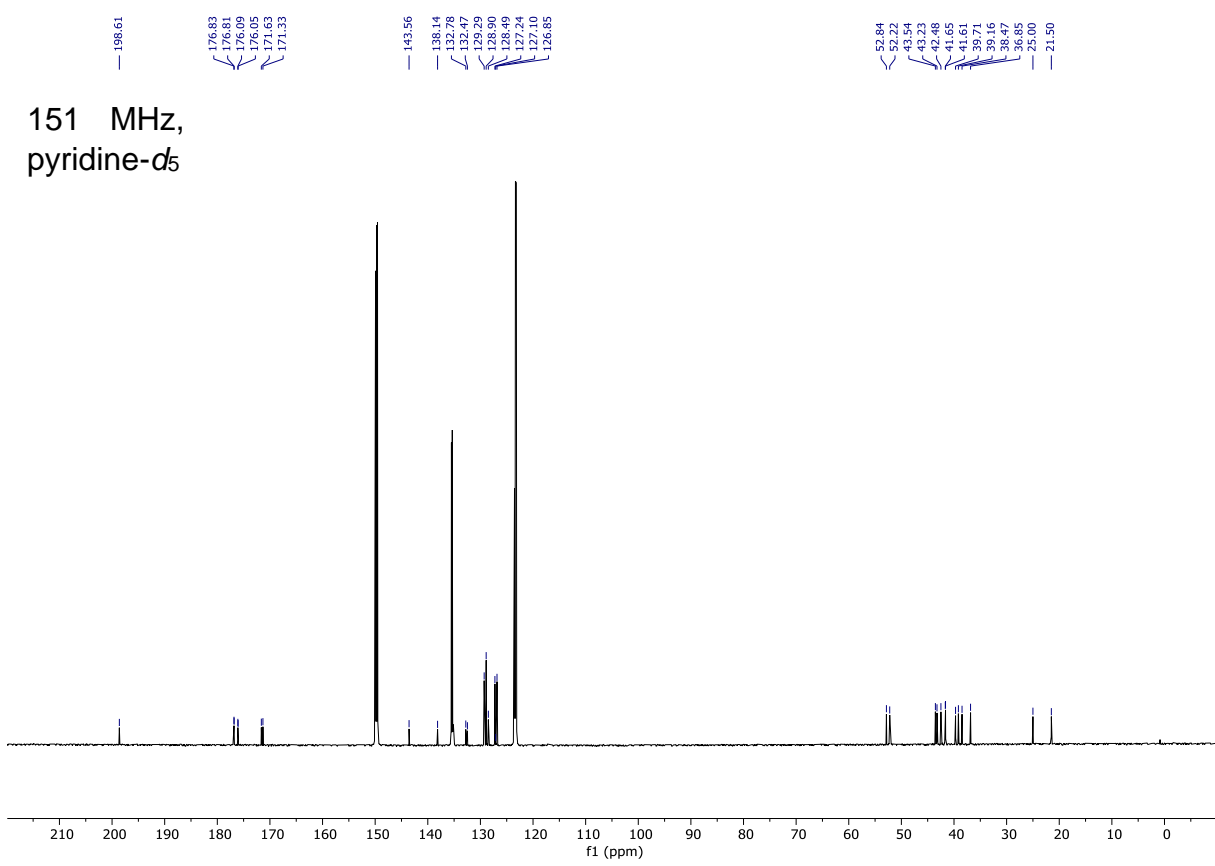
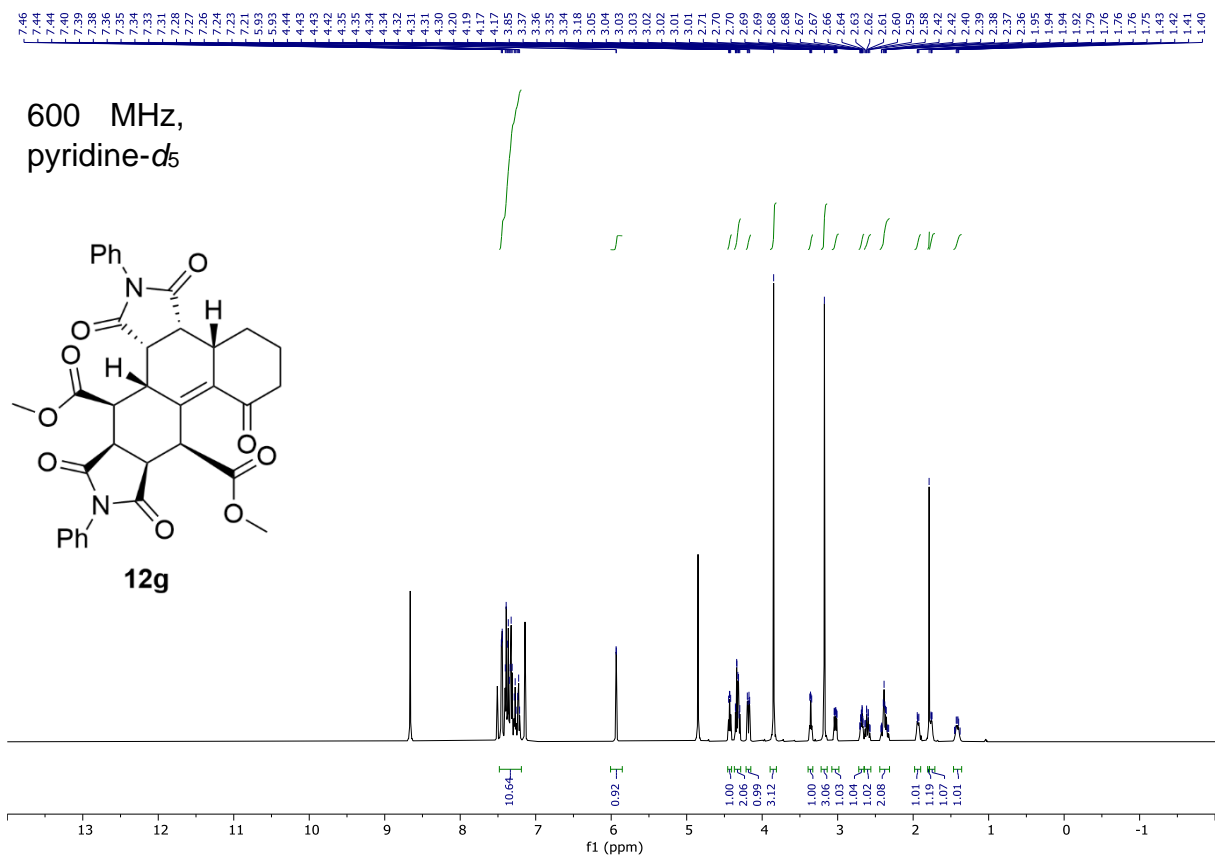


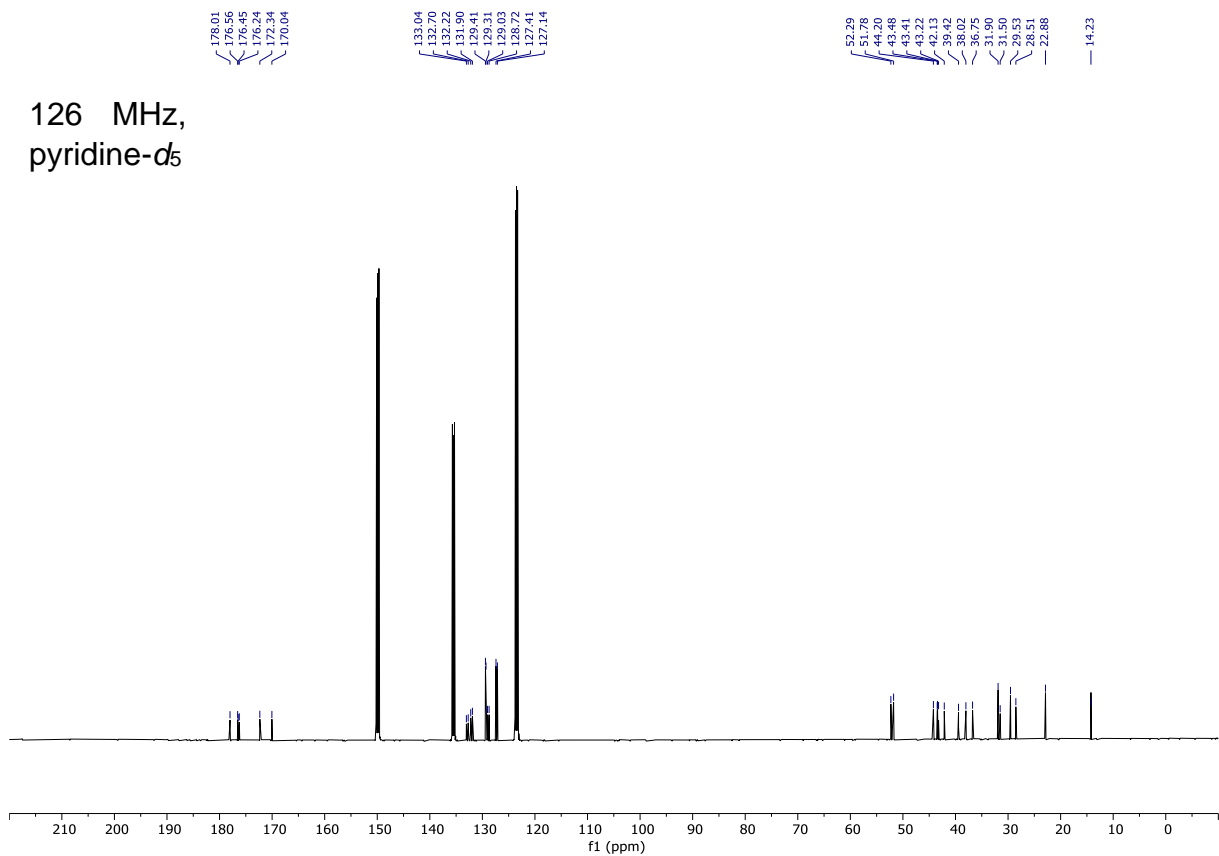
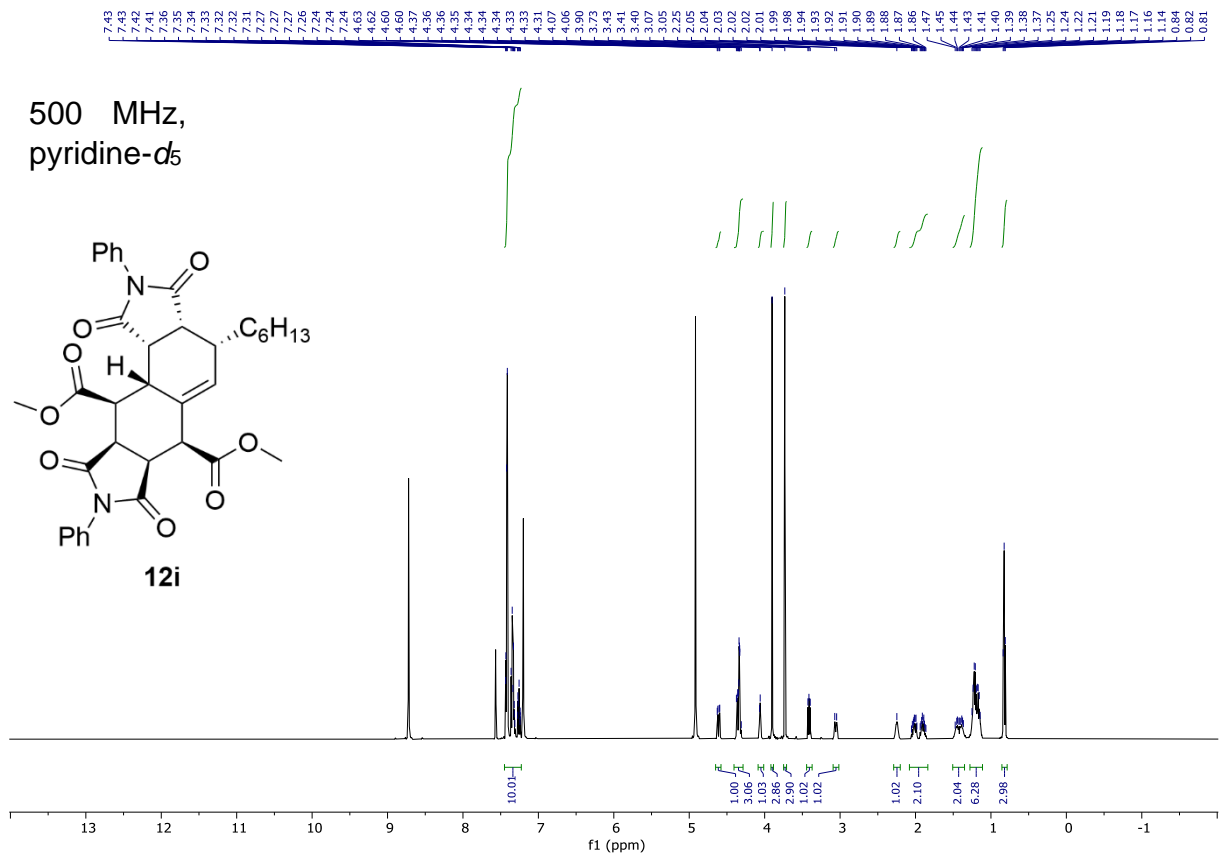
500 MHz,
pyridine-*d*₅

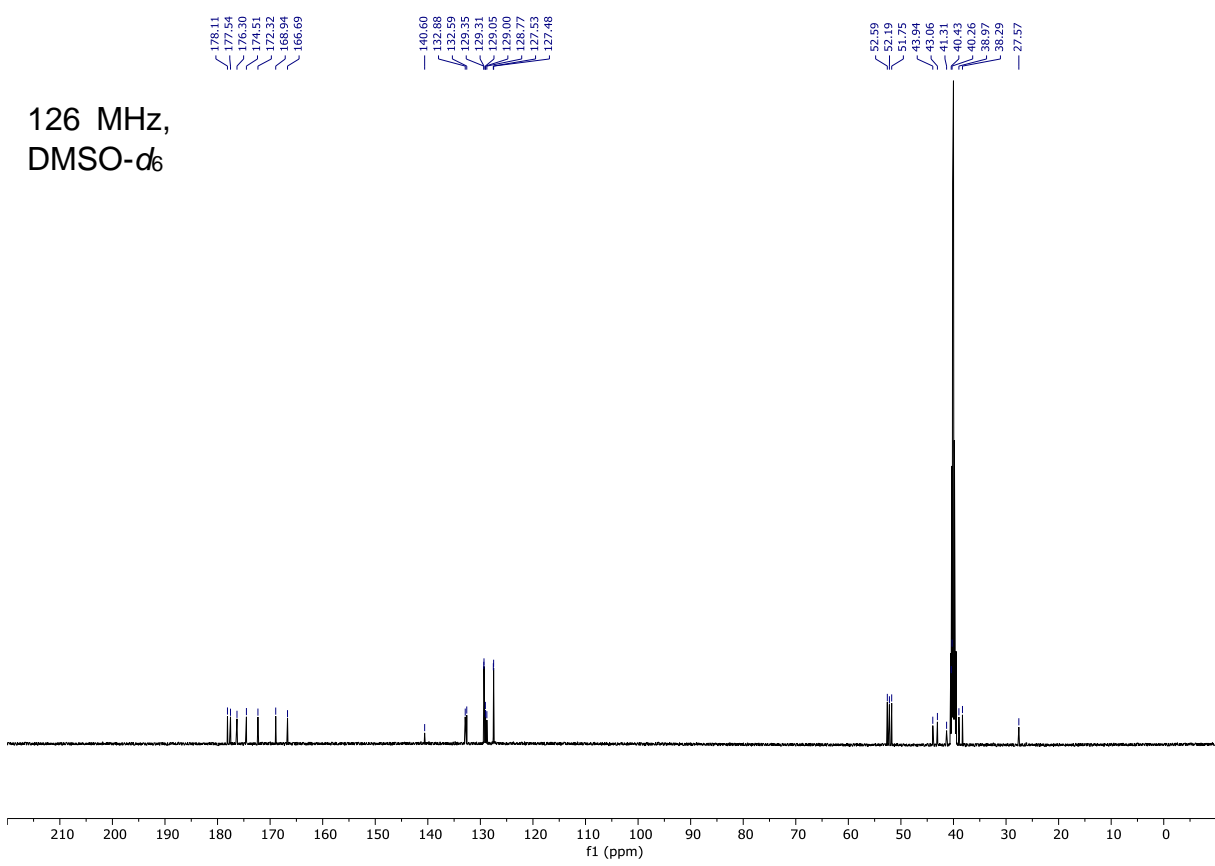
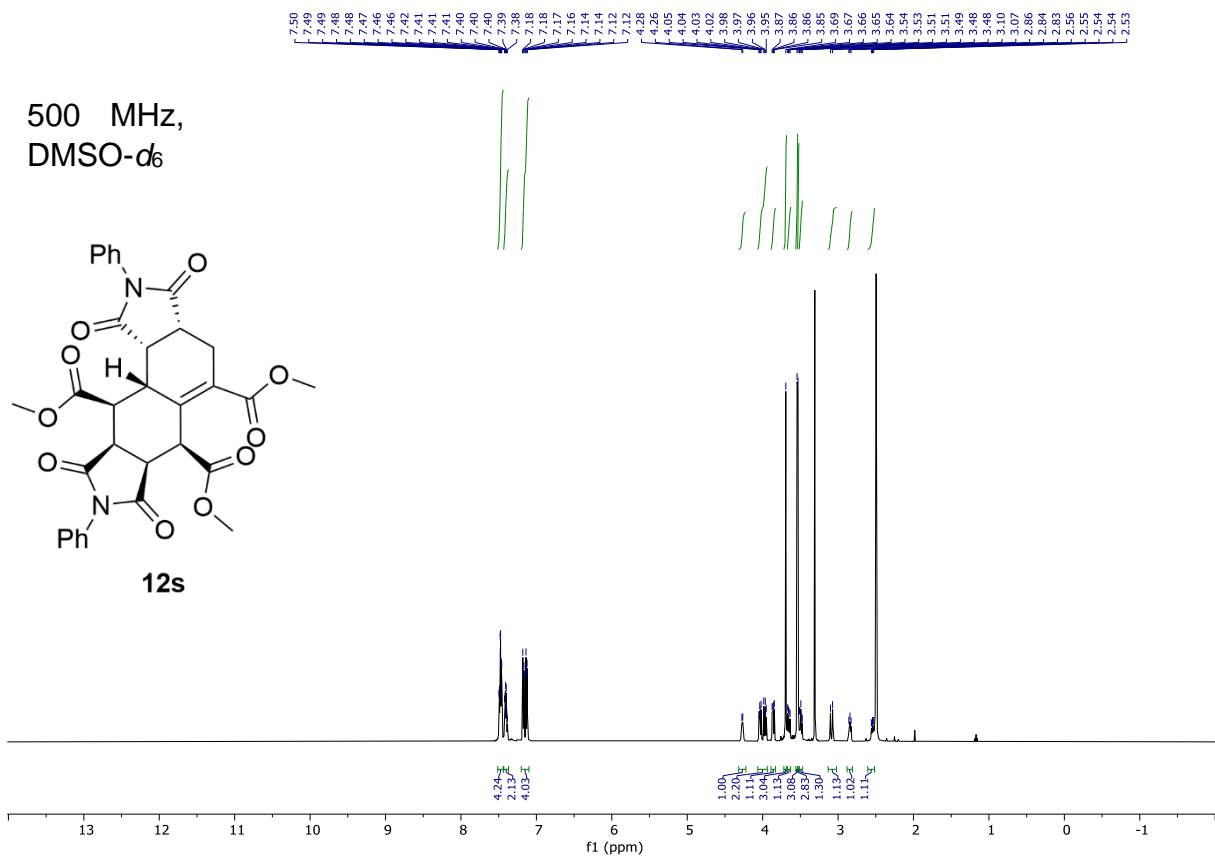


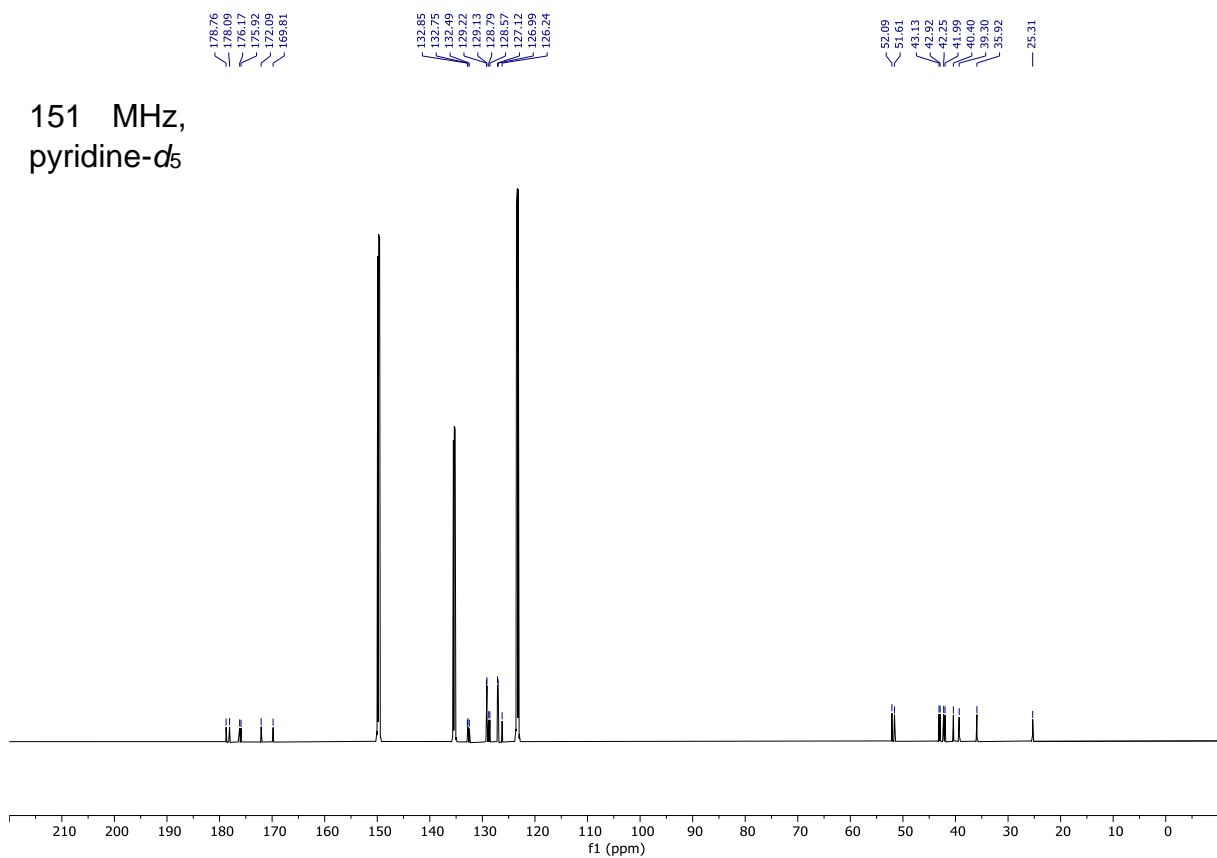
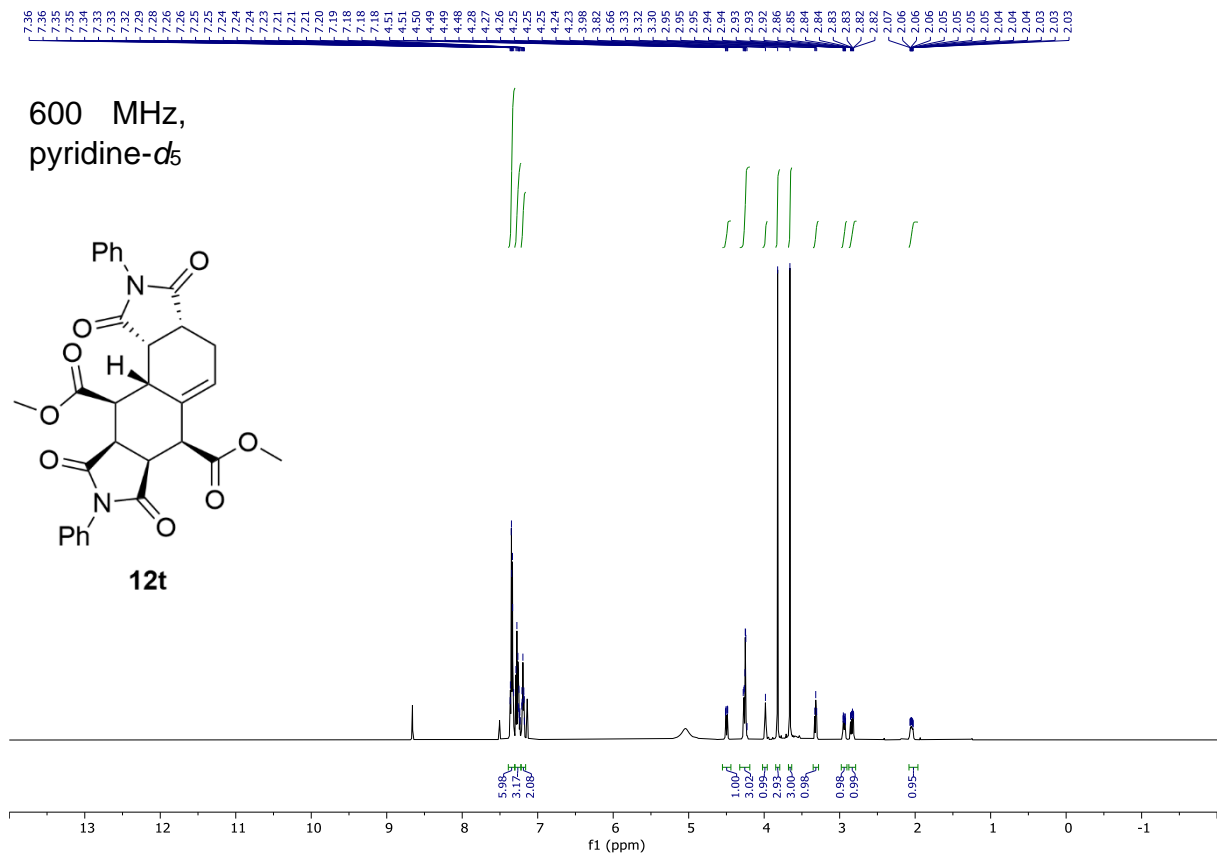
126 MHz,
pyridine-*d*₅



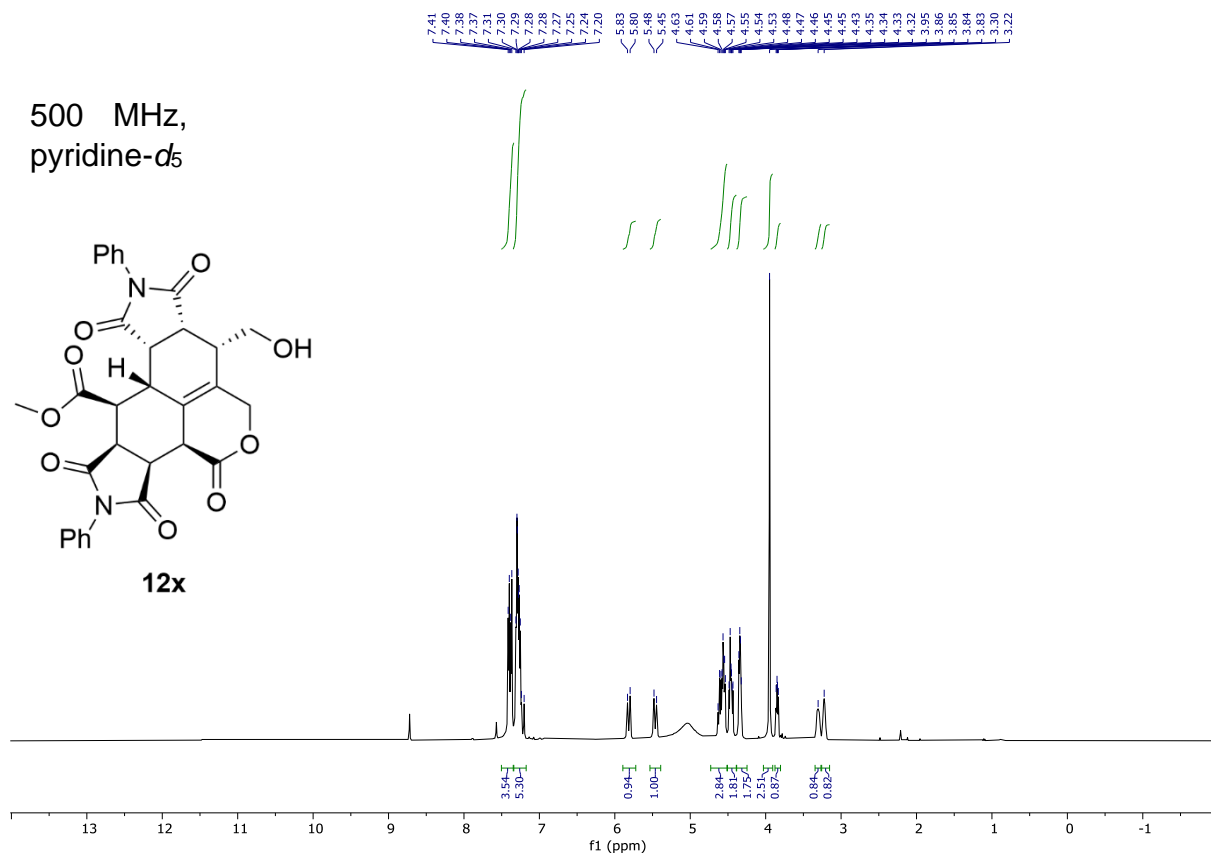
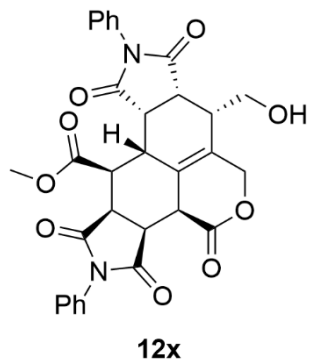




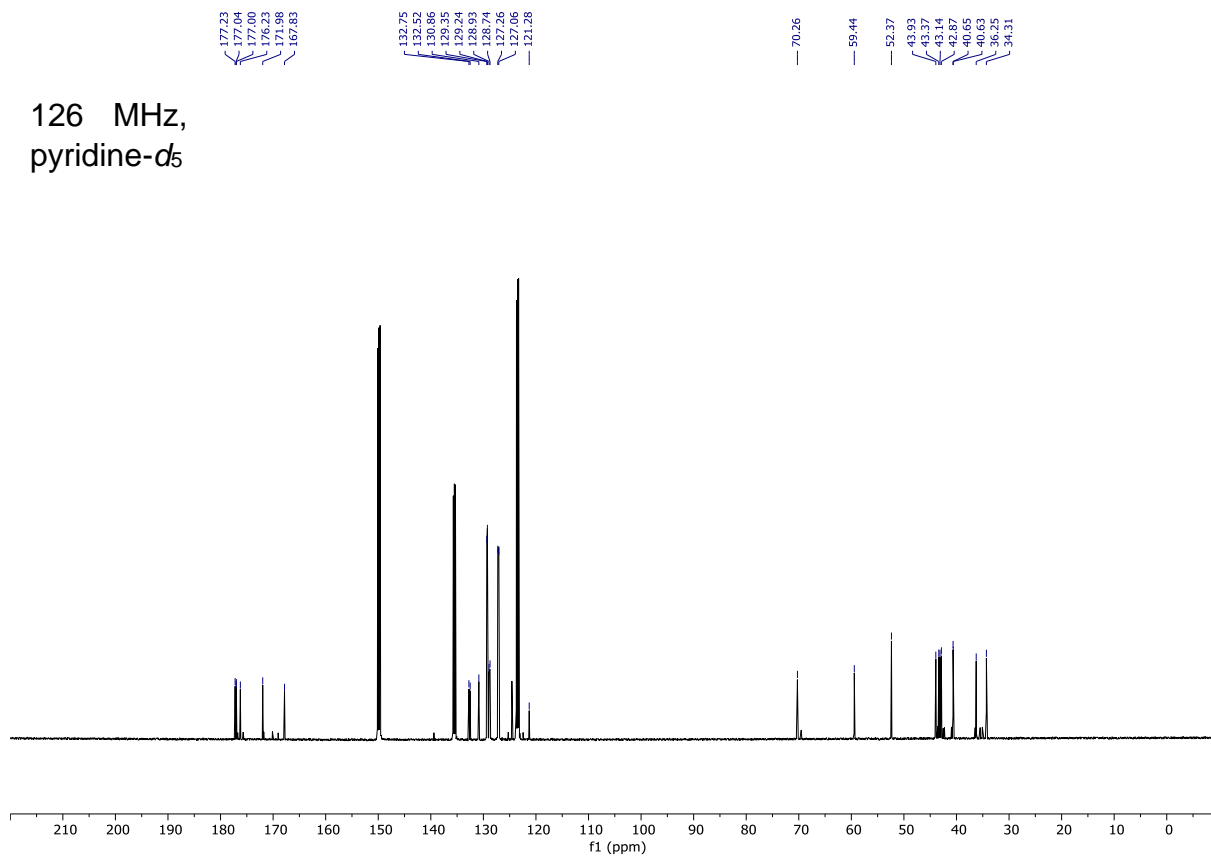


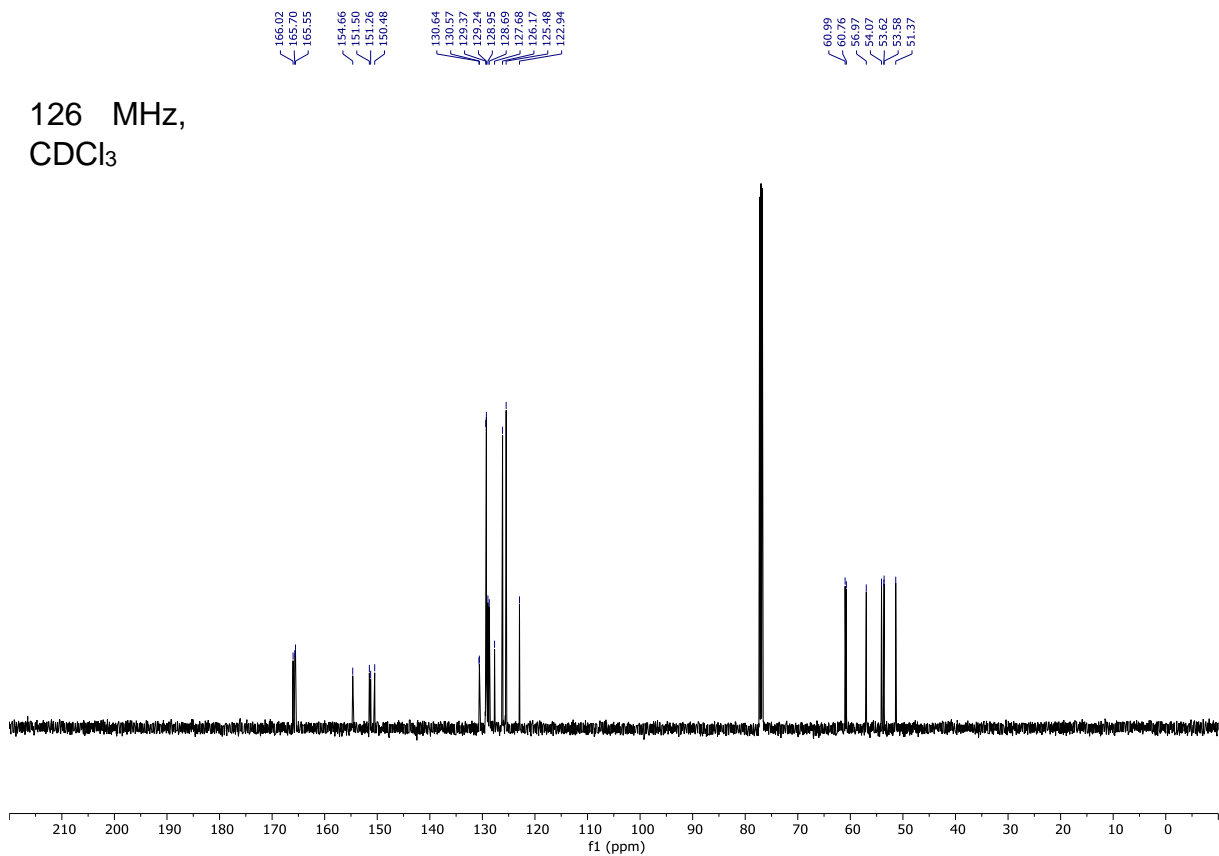
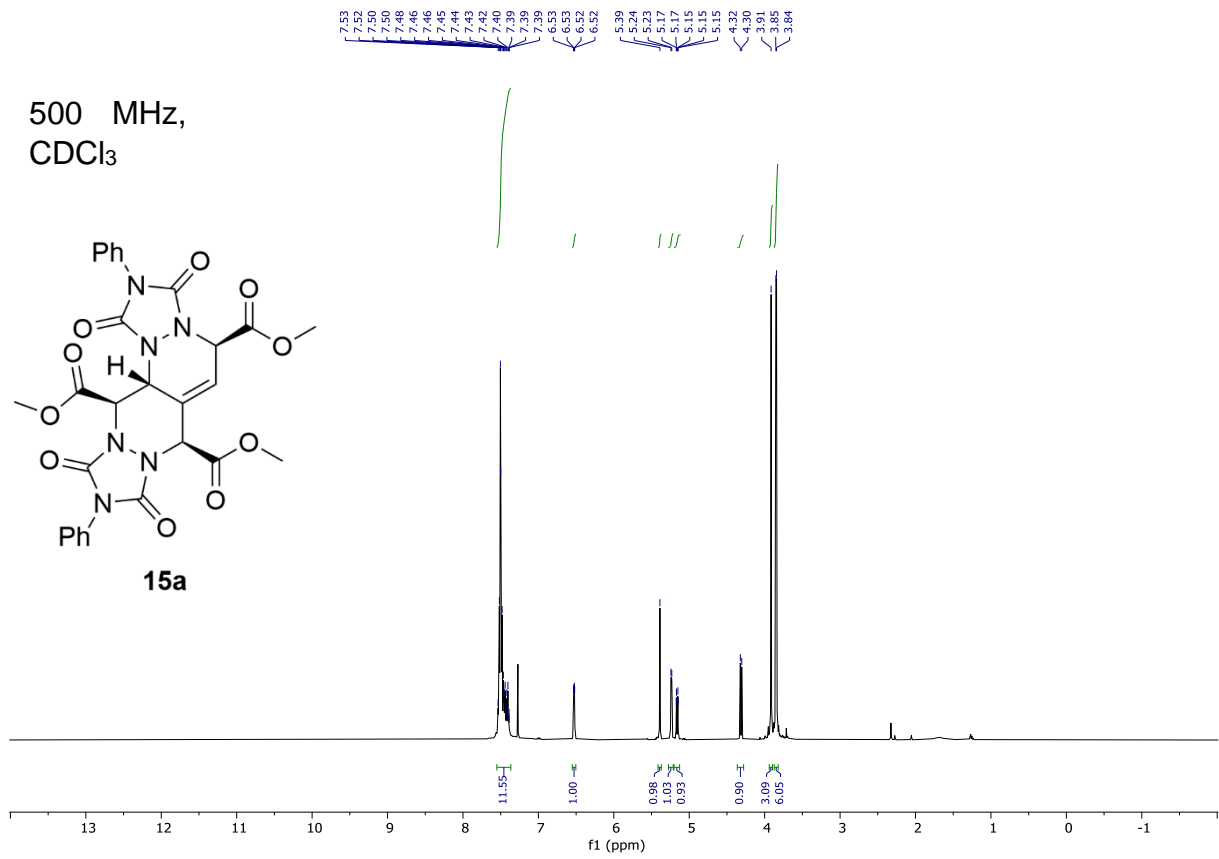


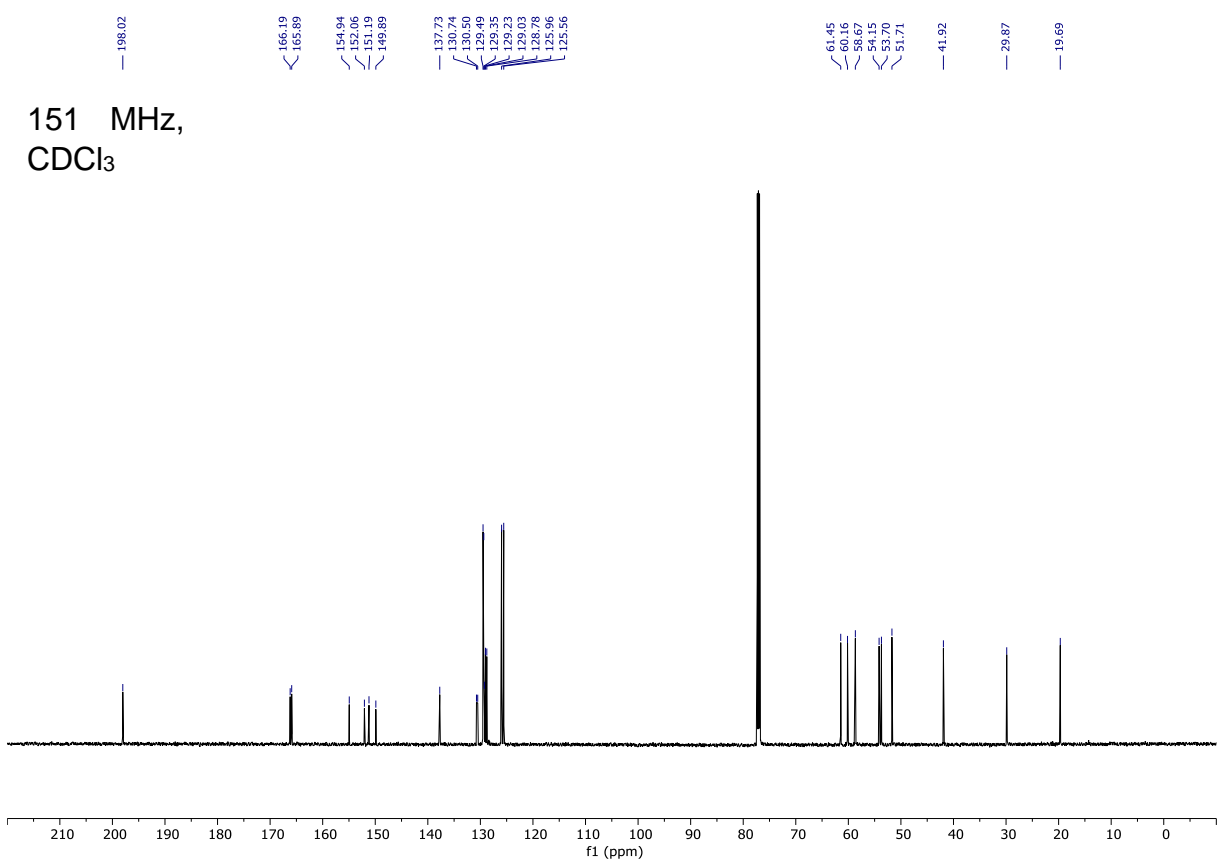
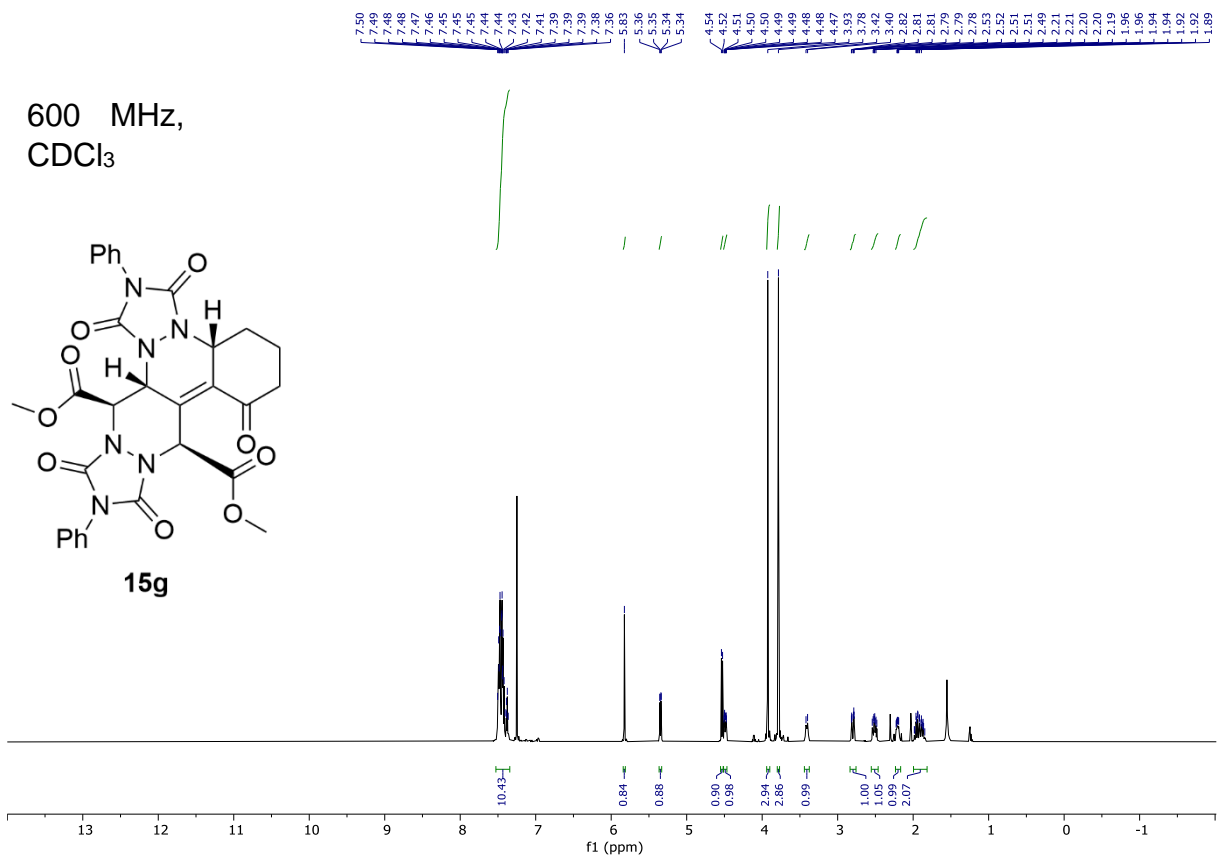
500 MHz,
pyridine-*d*₅

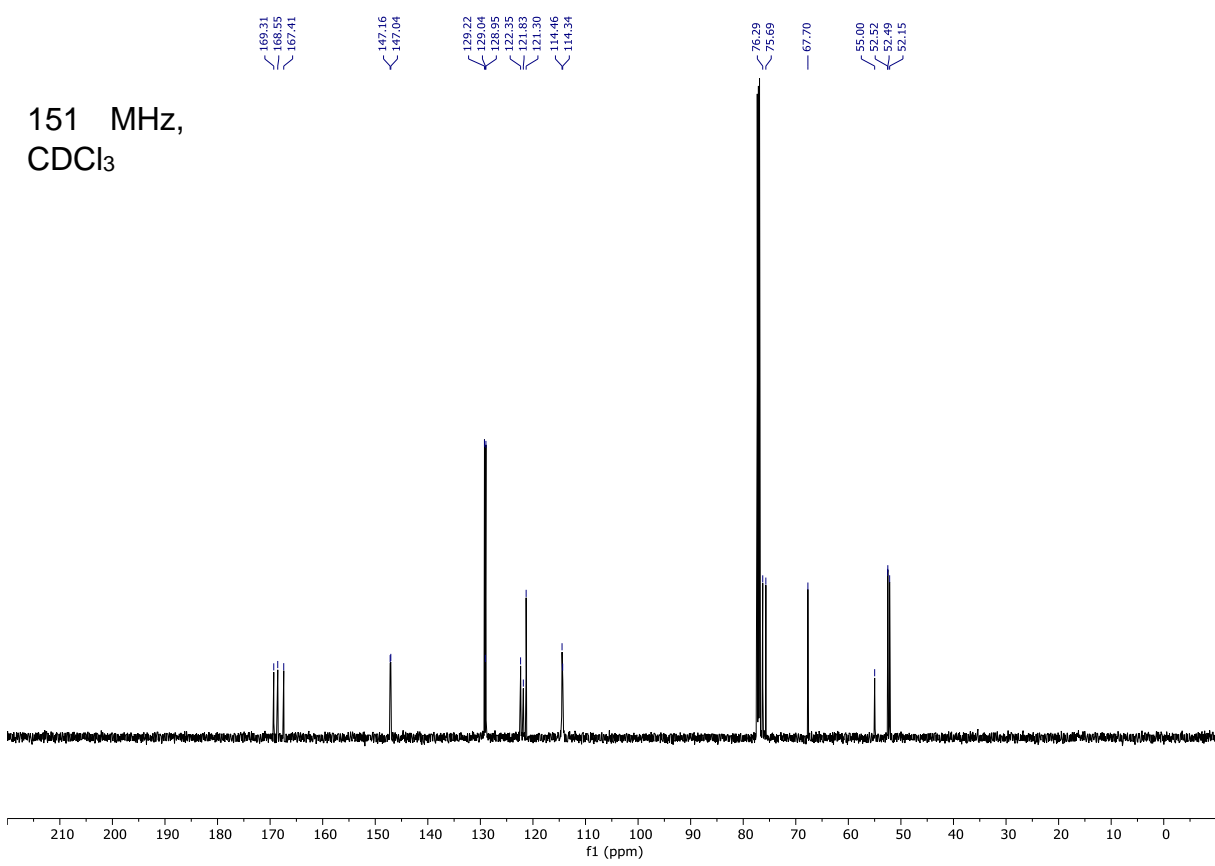
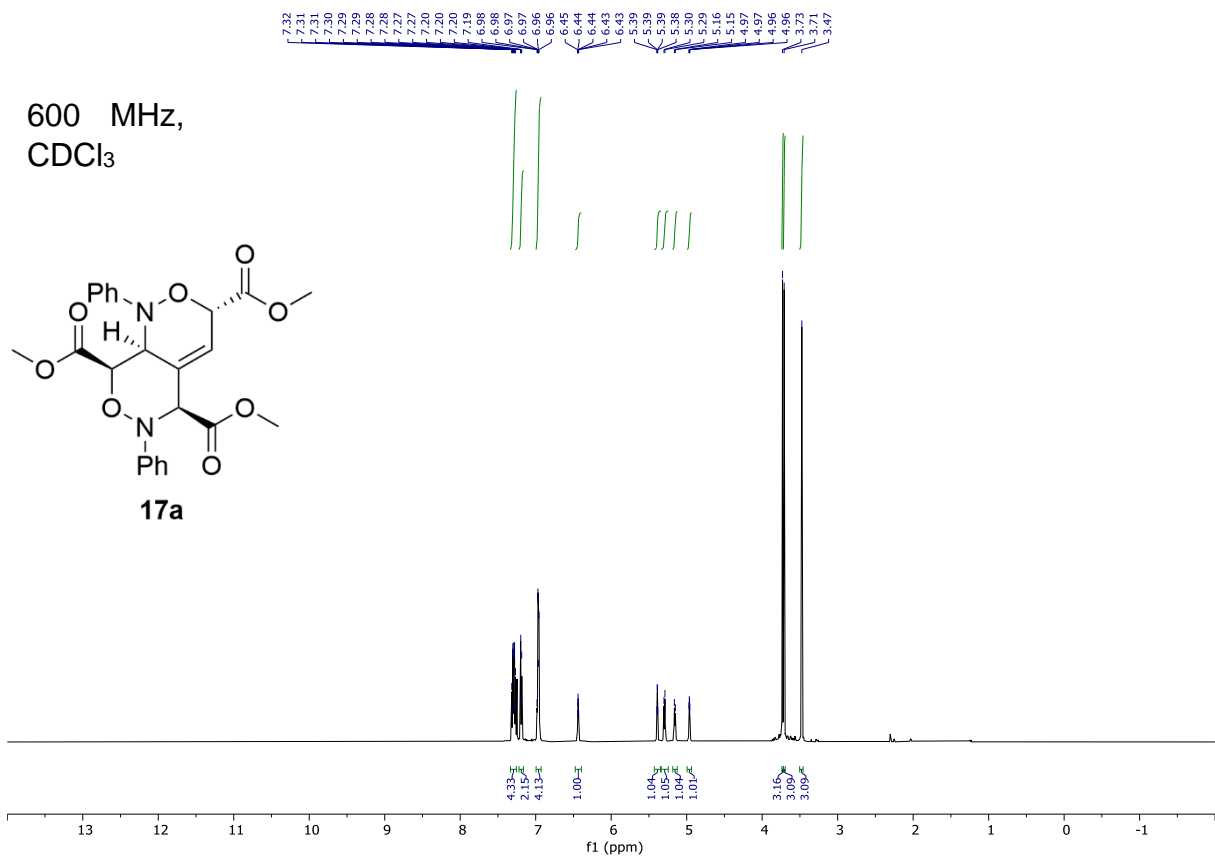


126 MHz,
pyridine-*d*₅

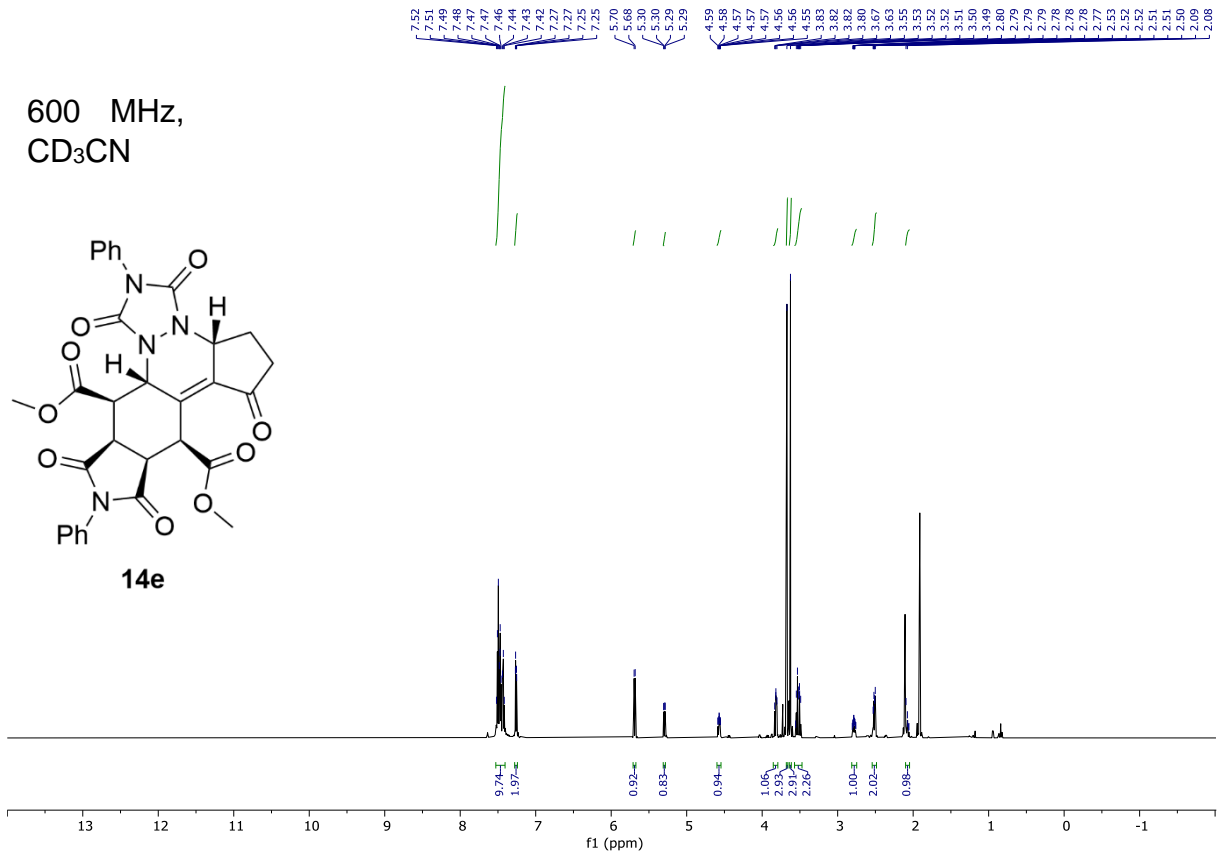
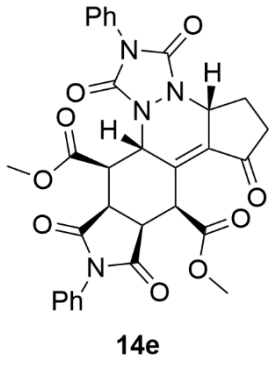








600 MHz,
CD₃CN



151 MHz,
CD₃CN

