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SUPPORTING INFORMATION

Carboxylate-directed C–H allylation with allyl alcohols or ethers

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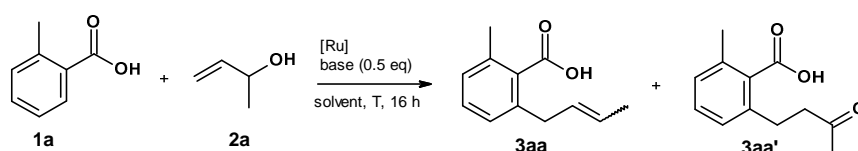
General methods

All reactions were performed in oven-dried glassware containing a Teflon-coated stirring bar and dry septum under argon atmosphere. All optimisation reactions were monitored by ^1H NMR using dibenzyl ether as internal standard. NMR spectra were recorded at ambient temperature using CDCl_3 as solvent, with proton, carbon, and fluorine resonances at 400/300/200, 101/75/63 and 377/235 MHz, respectively. All NMR data are reported in ppm relative to the solvent signal. Column chromatography was performed on a CombiFlash Companion (Isco) or on a Reveleris X2 (BUCHI) Flash Chromatography-System using Reveleris packed columns (12 g). GC analyses were carried out using an HP-5 capillary column (Phenyl methyl siloxane, 30 m \times 320 \times 0.25, 100/2.3-30-300/3, 2 min at 60 $^\circ\text{C}$, heating rate 30 $^\circ\text{C}/\text{min}$, 8 min at 300 $^\circ\text{C}$). Mass spectrometric data were acquired on a GC-MS Agilent 5977B MSD. HRMS analyses and mass spectral data were acquired on a Waters GCT Premier CAB163 with a TOF mass analyser or on a Thermo Scientific LTQ Orbitrap XL with positive ion mod. Melting points were measured on a Mettler Toledo MP70. The MS ionisation was achieved by EI^+ . GC Melting points were measured on a Mettler FP 61. Infrared spectra were recorded on Bruker Vertex 70 Spectrometer with Universal ATR Sampling Accessory.

Commercial substrates were used as received unless otherwise stated. Solvents were purchased (puriss p.A.) from commercial suppliers and dried by standard procedures.^[1] 2,2,2-Trichloroethanol (TCE) and 2,2,2-trifluoroethanol (TFE) were purchased from Sigma Aldrich and used as received. Perdeuterated 2-methylbenzoic acid was synthesised following a literature procedure starting from *o*-xylene- d_{10} .^[2] Allyl-1,1- d_2 alcohol was synthesised following a literature procedure starting from acryloyl chloride.^[3] All solvents and liquid reactants were degassed by Argon sparge prior to use. Potassium phosphate tribasic (K_3PO_4) and potassium carbonate (K_2CO_3) were dried prior to use by heating at 120 $^\circ\text{C}$ under vacuum (10^{-3} mbar). Ruthenium catalysts were donated by Umicore. *E/Z* ratios were determined via ^1H NMR unless otherwise stated.

Screening of the reaction conditions

Table S1: Screening of the *ortho*-allylation conditions^[a]



Entry	Solvent	T ($^\circ\text{C}$)	Base	3aa (%) (<i>E:Z</i>)	3aa' (%)
1	TCE	60	K_3PO_4	80 (2:1)	--
2	TFE	60	K_3PO_4	68 (1.7:1)	--
3	MeOH	60	K_3PO_4	6 (2.1:1)	--
4	HFIP	60	K_3PO_4	27 (2:1)	trace
5	CH_3CN	60	K_3PO_4	8 (2.1:1)	3
6	acetic acid	60	K_3PO_4	--	--
7	toluene	60	K_3PO_4	13 (2.5:1)	6
8	NMP	60	K_3PO_4	--	--
9	dioxane	60	K_3PO_4	trace	--
10	TCE	60	K_2CO_3	73 (2:1)	--
11	TCE	60	Cs_2CO_3	68 (2:1)	--
12	TCE	60	K_2HPO_4	58 (2:1)	--
13	TCE	70	K_3PO_4	51 (1.8:1)	5
14	TCE	50	K_3PO_4	89 (2:1)	--
15	TCE	40	K_3PO_4	81 (2:1)	--
16 ^[b]	TCE	50	K_3PO_4	trace	--
17 ^[c]	TCE	50	K_3PO_4	--	--
18 ^[d]	TCE	50	K_3PO_4	28 (2:1)	10
19 ^[e]	TCE	50	K_3PO_4	--	--
20 ^[f]	TCE	50	K_3PO_4	--	--

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), [Ru] (2 mol%), base, solvent (0.5 mL), 60 °C, 16 h, yields determined by ¹H NMR spectroscopy using dibenzyl ether as internal standard, *E/Z* ratios in parentheses. [b] [(C₆Me₆)RuCl₂]₂ (2 mol%). [c] Ru(COD)Cl₂ (2 mol%). [d] Ph₃P (4 mol%). [e] dppb (2 mol%). [f] Without catalyst. [g] Without base. [Ru] = [Ru(*p*-cymene)Cl₂]₂. HFIP = hexafluoro-2-propanol. TFE = 2,2,2-trifluoroethanol. TCE = 2,2,2-trichloroethanol. Ph₃P = triphenylphosphine. dppb = 1,4-bis(diphenylphosphino)butane.

General procedure for the *ortho*-allylation

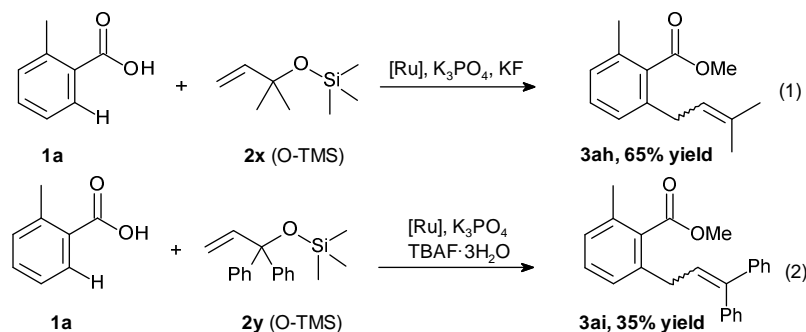
General procedure for the *ortho*-allylation using allyl alcohols

An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (6.46 mg, 0.01 mmol), K₃PO₄ (53.2 mg, 0.25 mmol) and a benzoic acid (0.50 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and an allyl alcohol (0.75 mmol) were added via syringe. The resulting mixture was stirred at 50 °C for 16 h. After the reaction was complete, MeCN (3 mL), K₂CO₃ (207 mg, 1.50 mmol) and MeI (358 mg, 2.50 mmol) were added and the mixture was stirred at 50 °C for 2 h. H₂O (20 mL) was added and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO₂, ethyl acetate/cyclohexane gradient) yielding the corresponding *ortho*-allylated product in the form of its methyl ester.

General procedure for the *ortho*-allylation using allyl ethers

An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (12.9 mg, 0.02 mmol), K₃PO₄ (53.2 mg, 0.25 mmol) and a benzoic acid (0.50 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and an allyl methyl ether (0.75 mmol) were added via syringe. The resulting mixture was stirred at 50 °C for 16 h. The crude reaction mixture was diluted with CDCl₃ (1.5 mL), 1,2-dibenzylether (30.0 μL, 0.15 mmol) as internal standard was added and the mixture was analysed via ¹H NMR spectroscopy. For internal olefins, *E/Z* ratios could not be determined.

General procedure for the *ortho*-allylation using allyl silyl ethers



An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (6.46 mg, 0.01 mmol), K₃PO₄ (53.2 mg, 0.25 mmol), KF (34.8 mg, 0.6 mmol) and benzoic acid **1a** (0.50 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and **2x** (0.75 mmol) were added via syringe. The resulting mixture was stirred at 50 °C for 16 h. The crude reaction mixture was diluted with CDCl₃ (1.5 mL), 1,2-dibenzylether (30.0 μL, 0.15 mmol) as internal standard was added and the mixture was analysed via ¹H NMR spectroscopy.

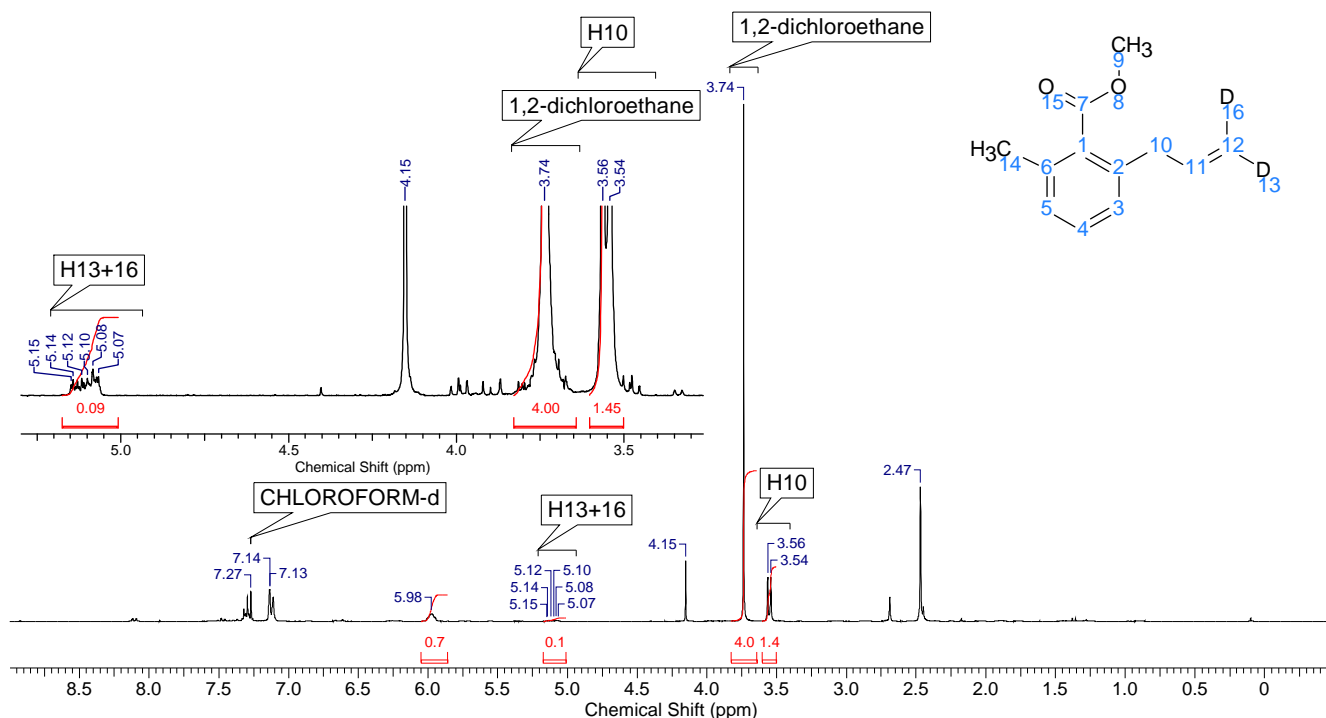
In presence of KF, **2x** reacted smoothly to yield the corresponding allylated product **3ah** in 65% yield (Eq.1). Using allyl silyl ether **2y**, a 35% yield of desired product **3ai** was obtained in the presence of TBAF·3H₂O salt (Eq.2).

Mechanistic investigations

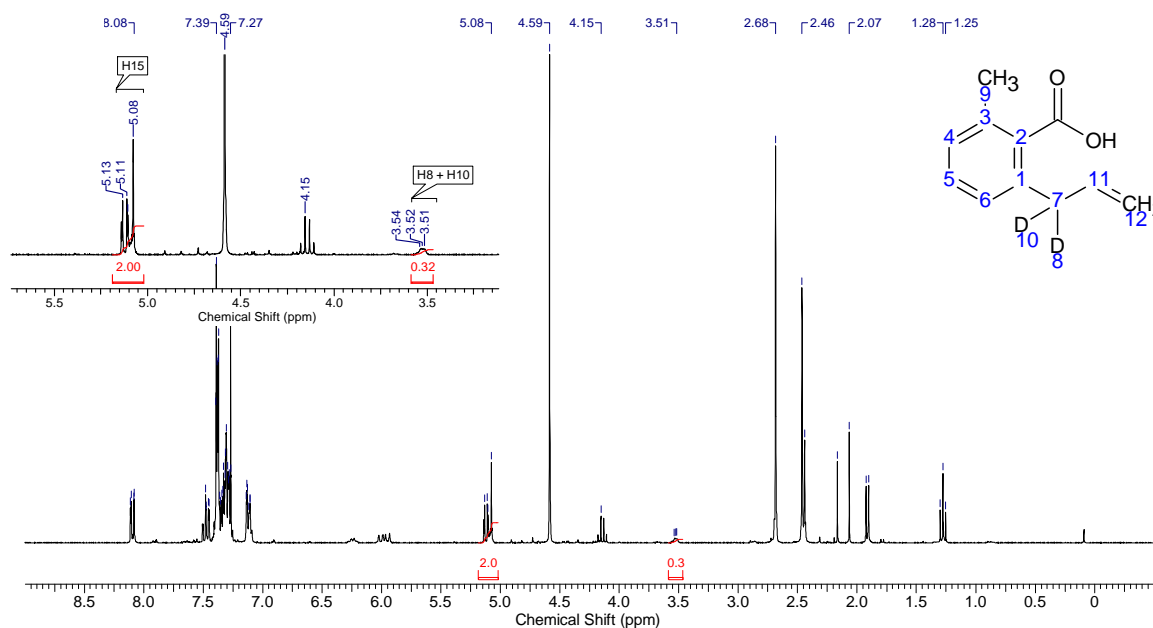
Intermediacy of allyl-ruthenium experiment

An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (3.87 mg, 6.00 μmol), K₃PO₄ (32.8 mg, 0.15 mmol) and 2-methylbenzoic acid (41.3 mg, 0.30 mmol), and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and allyl-1,1-d₂ alcohol (32.1 μL, 0.45 mmol) were added via syringe. The resulting mixture was stirred at 50 °C for 16 h. The

reaction mixture was diluted with EtOAc (10 mL) and extracted with aq. K_2CO_3 solution (3x10 mL). The combined aqueous phases were acidified with 2M HCl (pH 1-2), then extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. $CDCl_3$ (1 mL) and 1,2-dichloroethane (24.0 μ L, 0.30 mmol) as internal standard and were added and the mixture was analysed via 1H NMR spectroscopy. The determined ratio of $\gamma[D_2]3at/\alpha[D_2]3at$ was 14:1.

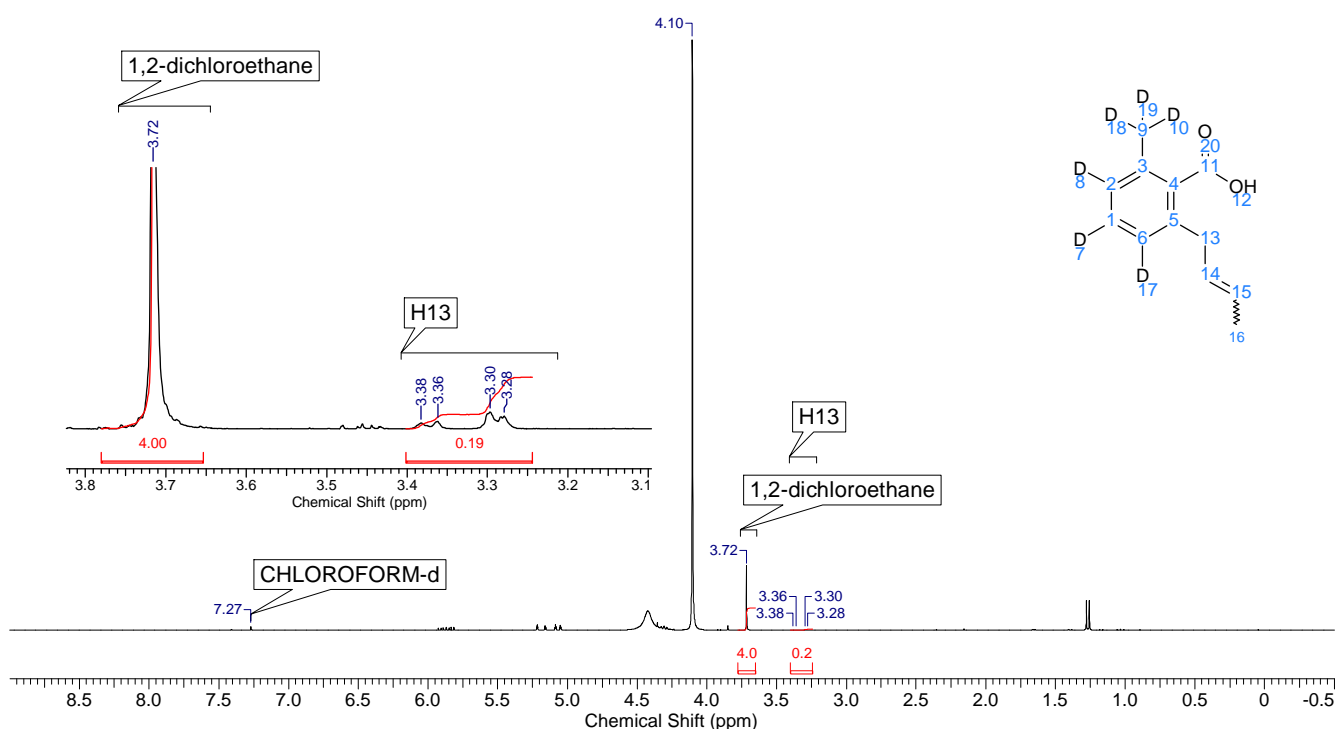
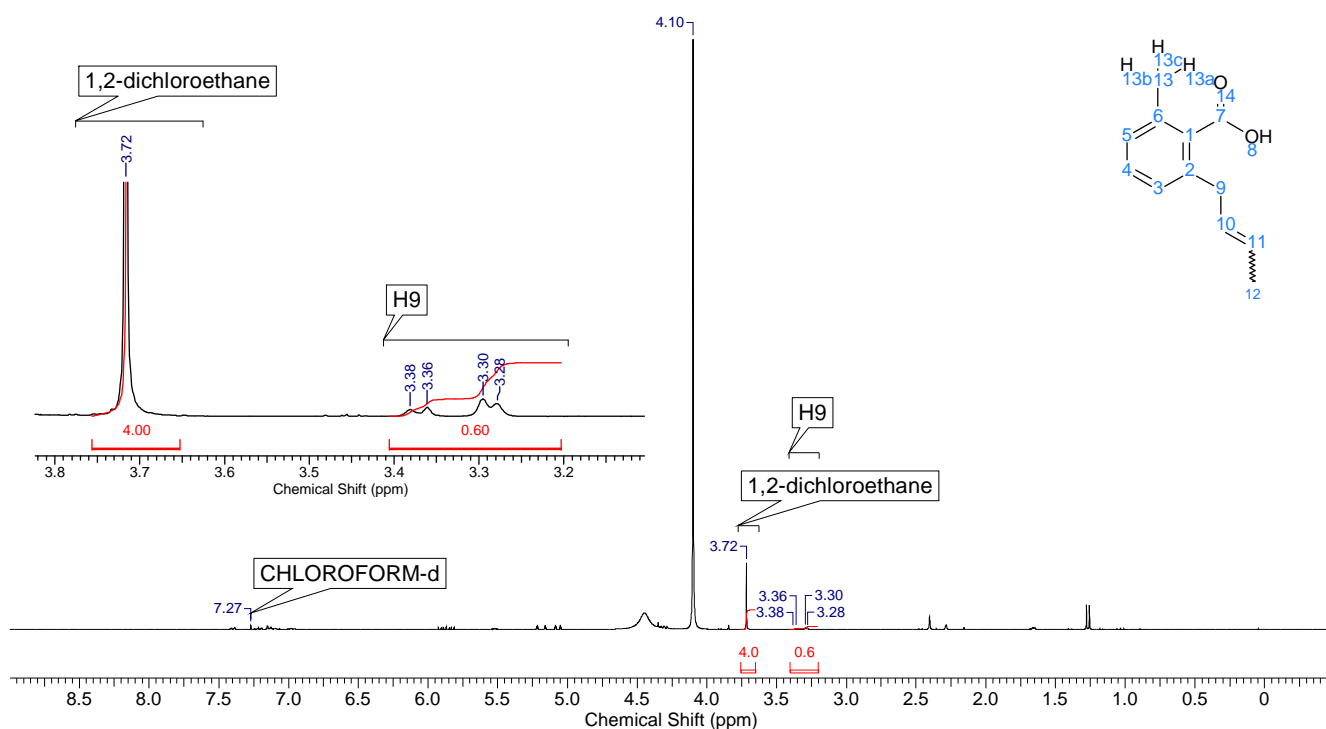


An oven-dried 20 mL vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (3.87 mg, 6.00 μ mol), K_3PO_4 (32.8 mg, 0.15 mmol) and 2-methylbenzoic acid (41.3 mg, 0.30 mmol), and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and allyl-3,3- d_2 alcohol (32.1 μ L, 0.45 mmol) with 77% D incorporation were added via syringe. The resulting mixture was stirred at 50 $^\circ$ C for 16 h. The reaction mixture was diluted with EtOAc (10 mL) and extracted with aq. K_2CO_3 solution (3x10 mL). The combined aqueous phases were acidified with 2M HCl (pH 1-2), then extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. $CDCl_3$ (1 mL) and dibenzyl ether as internal standard and were added and the mixture was analysed via 1H NMR spectroscopy. The determined ratio of $\alpha[D_2]3at/\gamma[D_2]3at$ was 6.3:1.



Parallel kinetic isotope effect

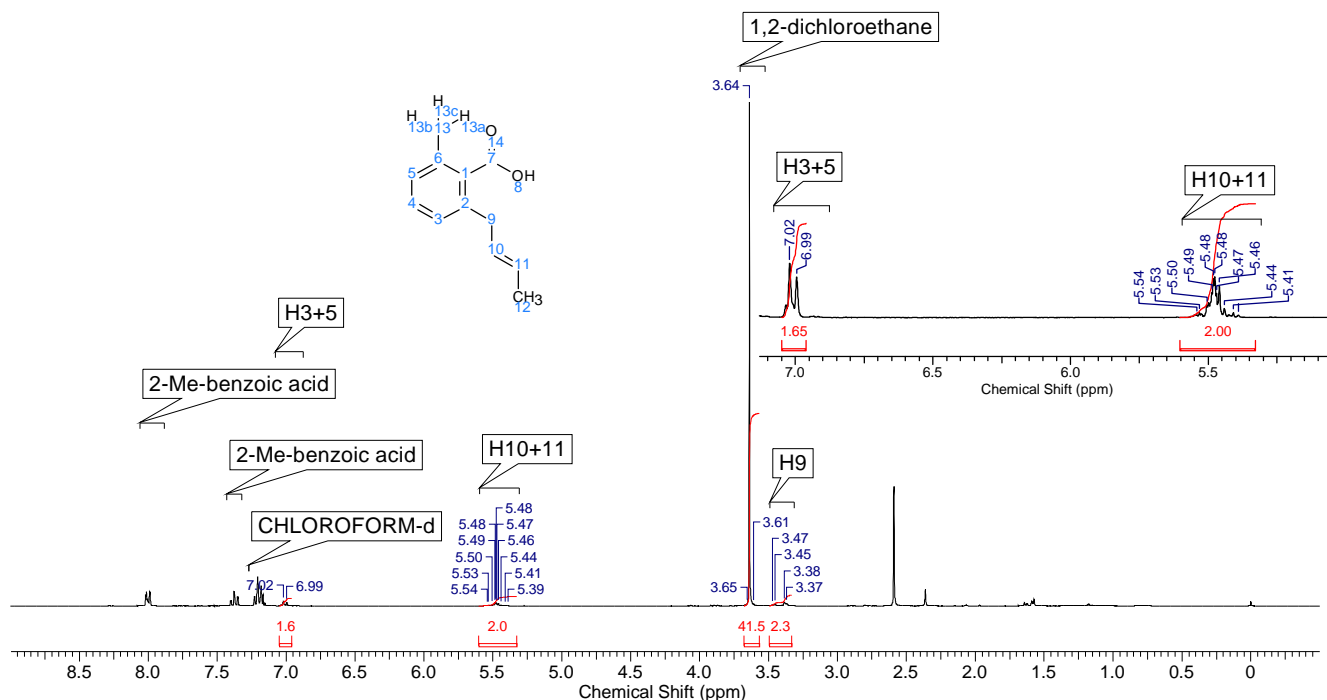
An oven-dried 20 mL vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (1.93 mg, 3.00 μmol), K_3PO_4 (16.4 mg, 75.0 μmol), 2-methylbenzoic acid (20.6 mg, 0.15 mmol) or 2,3,4,5-tetradeuterio-6-(trideuteriomethyl)benzoic acid (21.5 mg, 0.15 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.4 mL) and 3-buten-2-ol (20.1 μL , 225 μmol) were added via syringe. The resulting mixture was stirred at 50 $^\circ\text{C}$ for 1 h. The crude reaction mixture was diluted with CDCl_3 (1.5 mL), 1,2-dichloroethane (11.9 μL , 0.15 mmol) as internal standard was added and the mixture was analysed via ^1H NMR spectroscopy. The yields were 30% and 10% respectively, resulting in a $k_{\text{H}}/k_{\text{D}}$ of 3.0.



Competitive kinetic isotope effect measurement

An oven-dried 20 mL vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.87 mg, 8.00 μmol), K_3PO_4 (32.8 mg, 0.15 mmol), 2-methylbenzoic acid (20.6 mg, 0.15 mmol), 2,3,4,5-tetradeuterio-6-(trideuteriomethyl)benzoic acid (21.5 mg, 0.15 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and allyl acetate (40.2 μL , 0.45 mmol) were added via syringe. The resulting mixture was stirred at 50 $^\circ\text{C}$ for 1 h. The reaction mixture was diluted with EtOAc (10 mL) and extracted with aq.

K_2CO_3 solution (3x10 mL). The combined aqueous phases were acidified with 2M HCl (pH 1-2), then extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. $CDCl_3$ (1 mL) and 1,2-dichloroethane (24 μ L, 0.30 mmol) as internal standard were added and the mixture was analysed via 1H NMR spectroscopy. Based on the integration ratios, the determined k_H/k_D was 4.0.

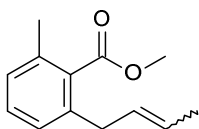


Competitive kinetic isotope effect measurement

An oven-dried 20 mL vial was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (3.87 mg, 8.00 μ mol), K_3PO_4 (32.8 mg, 0.15 mmol), 2-methylbenzoic acid (20.6 mg, 0.15 mmol), 2,3,4,5-tetradeuterio-6-(trideuteriomethyl)benzoic acid (21.5 mg, 0.15 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and allyl acetate (40.2 μ L, 0.45 mmol) were added via syringe. The resulting mixture was stirred at 50 $^{\circ}C$ for 1 h. The reaction mixture was diluted with EtOAc (10 mL) and extracted with aq. K_2CO_3 solution (3x10 mL). The combined aqueous phases were acidified with 2M HCl (pH 1-2), then extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. $CDCl_3$ (1 mL) and 1,2-dichloroethane (24 μ L, 0.30 mmol) as internal standard were added and the mixture was analysed via 1H NMR spectroscopy. Based on the integration ratios, the determined k_H/k_D was 4.0.

Synthesis and characterisation of products

Methyl 2-[but-2-enyl]-6-methyl-benzoate (3aa):



Compound **3aa** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μ L, 0.75 mmol) and isolated as a colorless oil (89 mg, 87%, *E/Z* 2.0:1).

1H NMR (300 MHz, $CDCl_3$) δ (*E*-isomer) = 7.23 (t, J = 7.7 Hz, 1 H), 7.06 (d, J = 7.7 Hz, 2 H), 5.18 - 5.84 (m, 2 H), 3.90 (s, 3 H), 3.27 - 3.35 (d, J = 5.1 Hz, 2 H), 2.32 (s, 3 H), 1.58 - 1.77 (m, 3 H) ppm; δ (*Z*-isomer) = 7.23 (t, J = 7.7 Hz, 1 H), 7.06 (d, J = 7.7 Hz, 2 H), 5.18 - 5.84 (m, 2 H), 3.90 (s, 3 H), 3.40 (d, J = 6.8 Hz, 2 H), 2.32 (s, 3 H), 1.58 - 1.77 (m, 3 H) ppm.

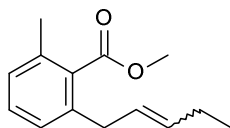
^{13}C NMR (75 MHz, $CDCl_3$) δ (*E*-isomer) = 170.27 (s), 138.0 (s), 135.0 (s), 133.45 (s), 129.39 (s), 129.2 (s), 127.9 (s), 126.8 (s), 126.7 (s), 51.7 (s), 36.9 (s), 19.6 (s), 17.8 (s) ppm; δ (*Z*-isomer) = 170.32 (s), 138.1 (s), 135.0 (s), 133.54 (s), 129.43 (s), 128.4 (s), 127.8 (s), 126.6 (s), 125.0 (s), 51.8 (s), 31.1 (s), 19.6 (s), 12.8 (s) ppm.

IR (ATR) 2950, 1726, 1435, 1266, 1114, 1070, 964, 827 cm^{-1} .

MS (EI-TOF) m/z (%) 204 (61) $[M]^+$, 172 (100), 157 (45), 145 (37), 129 (48), 115 (22).

HRMS (EI-TOF) m/z calcd. for $C_{13}H_{16}O_2$ $[M]^+$ 204.1150, found 204.1149.

Methyl 2-methyl-6-(-pent-2-enyl)benzoate (3ab):



Compound **3ab** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-penten-3-ol (77.9 μ L, 0.75 mmol) and isolated as a colorless oil (97.0 mg, 89%, *E/Z* 3:1).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ (*E*-isomer) = 7.24 (t, J = 7.7 Hz, 1 H), 7.00 - 7.11 (m, 2 H), 5.37 - 5.61 (m, 2 H), 3.90 (s, 3 H), 3.34 (d, J = 5.0 Hz, 2 H), 2.32 (s, 3 H), 1.94 - 2.08 (m, 2 H), 0.99 (t, J = 7.5 Hz, 3 H) ppm; δ (*Z*-isomer) = 7.24 (t, J = 7.7 Hz, 1 H), 7.00 - 7.11 (m, 2 H), 5.37 - 5.61 (m, 2 H), 3.91 (s, 3 H), 3.39 (d, J = 6.1 Hz, 2 H), 2.32 (s, 3 H), 2.08 - 2.21 (m, 2 H), 1.02 (t, J = 7.5 Hz, 3 H) ppm.

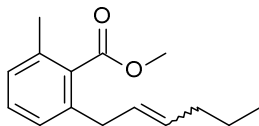
$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ (*E*-isomer) = 170.3 (s), 138.1 (s), 134.99 (s), 133.9 (s), 133.5 (s), 129.4 (s), 127.9 (s), 127.0 (s), 126.9 (s), 51.8 (s), 36.9 (s), 25.5 (s), 19.68 (s), 13.7 (s) ppm; δ (*Z*-isomer) = 170.4 (s), 138.2 (s), 134.95 (s), 133.6 (s), 132.9 (s), 129.5 (s), 127.8 (s), 126.7 (s), 126.5 (s), 51.9 (s), 31.3 (s), 20.6 (s), 19.66 (s), 14.2 (s) ppm.

IR (ATR) 2962, 1721, 1436, 1266, 1111, 1070, 967, 775 cm^{-1} .

MS (EI-TOF) m/z (%) 218 (100) $[\text{M}]^+$, 186 (79), 171 (64), 158 (66), 143 (31), 128 (36), 115 (27), 105 (19).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 218.1307, found 218.1299.

Methyl 2-(hex-2-enyl)-6-methyl-benzoate (3ac):



Compound **3ac** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-hexen-3-ol (90.3 μ L, 0.75 mmol) and isolated as a colorless oil (100 mg, 86%, *E/Z* 4:1).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ (*E*-isomer) = 7.25 (t, J = 7.5 Hz, 1 H), 7.02 - 7.12 (m, 2 H), 5.33 - 5.62 (m, 2 H), 3.90 (s, 3 H), 3.35 (d, J = 5.0 Hz, 2 H), 2.33 (s, 3 H), 1.93 - 2.05 (m, 2 H), 1.25 - 1.52 (m, 2 H), 0.91 (t, J = 7.3 Hz, 3 H) ppm; δ (*Z*-isomer) = 7.25 (t, J = 7.5 Hz, 1 H), 7.02 - 7.12 (m, 2 H), 5.33 - 5.62 (m, 2 H), 3.91 (s, 3 H), 3.41 (d, J = 5.5 Hz, 2 H), 2.33 (s, 3 H), 2.06 - 2.18 (m, 2 H), 1.25 - 1.52 (m, 2 H), 0.95 (t, J = 7.3 Hz, 3 H) ppm.

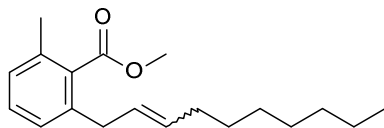
$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ (*E*-isomer) = 170.26 (s), 138.1 (s), 135.0 (s), 133.47 (s), 132.1 (s), 129.39 (s), 128.1 (s), 127.9 (s), 126.8 (s), 51.7 (s), 36.9 (s), 34.6 (s), 22.5 (s), 19.7 (s), 13.6 (s) ppm; δ (*Z*-isomer) = 170.34 (s), 138.2 (s), 134.9 (s), 133.54 (s), 131.0 (s), 129.42 (s), 127.8 (s), 127.5 (s), 126.5 (s), 51.8 (s), 31.3 (s), 29.3 (s), 22.7 (s), 19.6 (s), 13.8 (s) ppm.

IR (ATR) 2956, 1758, 1435, 1266, 1238, 1111, 1070, 968, 774 cm^{-1} .

MS (EI-TOF) m/z (%) 232 (18) $[\text{M}]^+$, 175 (10), 158 (100).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 232.1463, found 232.1454.

Methyl 2-(dec-2-enyl)-6-methyl-benzoate (3ad):



Compound **3ad** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-decen-3-ol (143 μ L, 0.75 mmol) and isolated as a colorless oil (121 mg, 84%, *E/Z* 4:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (*E*-isomer) = 7.24 (t, J = 7.6 Hz, 1 H), 7.07 (m, 2 H), 5.39 - 5.57 (m, 2 H), 3.90 (s, 3 H), 3.34 (d, J = 5.1 Hz, 2 H), 2.33 (s, 3 H), 1.89 - 2.06 (m, 2 H), 1.18 - 1.44 (m, 10 H), 0.80 - 0.98 (m, 3 H) ppm; δ (*Z*-isomer) = 7.24 (t, J = 7.6 Hz, 1 H), 7.07 (m, 2 H), 5.39 - 5.57 (m, 2 H), 3.91 (s, 3 H), 3.40 (d, J = 5.8 Hz, 2 H), 2.33 (s, 3 H), 2.07 - 2.20 (m, 2 H), 1.18 - 1.44 (m, 10 H), 0.80 - 0.98 (m, 3 H) ppm.

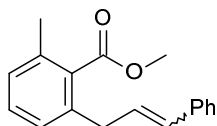
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (*E+Z*) = 170.34 (s, *Z*), 170.27 (s, *E*), 138.2 (s, *Z*), 138.1 (s, *E*), 134.94 (s, *E*), 134.91 (s, *Z*), 133.54 (s, *Z*), 133.48 (s, *E*), 132.4 (s, *E*), 131.3 (s, *Z*), 129.42 (s, *Z*), 129.39 (s, *E*), 127.9 (s, *E*), 127.8 (s, *Z*), 127.3 (s, *Z*), 126.8 (s, *E*), 126.5 (s, *Z*), 51.8 (s, *Z*), 51.7 (s, *E*), 36.9 (s, *E*), 32.5 (s, *E*), 31.8 (s, *E+Z*), 31.3 (s, *Z*), 29.6 (s, *E* or *Z*), 29.4 (s, *E* or *Z*), 29.3 (s, *E* or *Z*), 29.2 (s, *E* or *Z*), 29.1 (s, *E* or *Z*), 27.3 (s, *Z*), 22.6 (s, *E+Z*), 19.7 (s, *E+Z*), 14.0 (s, *E+Z*) ppm.

IR (ATR) 2953, 1729, 1436, 1266, 1112, 1072, 967, 774 cm^{-1} .

MS (EI-TOF) m/z (%) 288 (42) $[\text{M}]^+$, 257 (10), 175 (25), 158 (100), 143 (14), 128 (26).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{19}\text{H}_{28}\text{O}_2$ $[\text{M}]^+$ 288.2089, found 288.2087.

Methyl 2-(cinnamyl)-6-methyl-benzoate (3ae):



Compound **3ae** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-phenylprop-2-en-1-ol (103 μ L, 0.75 mmol) and isolated as a colorless oil (105 mg, 79%, *E/Z* 1:1).

^1H NMR (400 MHz, CDCl_3) δ (*E*-isomer) = 7.18 - 7.42 (m, 6 H), 7.06 - 7.18 (m, 2 H), 6.45 (d, J = 15.9 Hz, 1 H), 6.31 (dt, J = 15.7, 6.8 Hz, 1 H), 3.89 (s, 3 H), 3.58 (dd, J = 7.3, 1.3 Hz, 2 H), 2.36 (s, 3 H) ppm; δ (*Z*-isomer) = 7.18 - 7.42 (m, 6 H), 7.06 - 7.18 (m, 2 H), 6.58 (d, J = 11.4 Hz, 1 H), 5.79 (dt, J = 11.4, 7.3 Hz, 1 H), 3.73 (s, 3 H), 3.70 (dd, J = 7.3, 1.5 Hz, 2 H), 2.34 (s, 3 H) ppm.

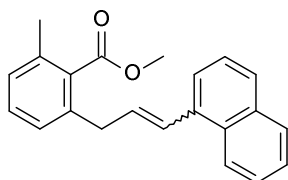
^{13}C NMR (101 MHz, CDCl_3) δ (*E+Z*) = 170.3 (s, *E* or *Z*), 170.1 (s, *E* or *Z*), 137.8 (s, *E* or *Z*), 137.3 (s, *E* or *Z*), 137.2 (s, *E* or *Z*), 137.0 (s, *E* or *Z*), 135.2 (s, *E* or *Z*), 133.7 (s, *E* or *Z*), 133.6 (s, *E* or *Z*), 131.3 (s, *E*), 130.1 (s, *Z*), 129.9 (s, *Z*), 129.6 (s, *E* or *Z*), 128.7 (s, *E* or *Z*), 128.5 (s, *E* or *Z*), 128.4 (s, *E*), 128.2 (s, *E* or *Z*), 128.1 (s, *E* or *Z*), 127.13 (s, *E* or *Z*), 127.08 (s, *E* or *Z*), 126.9 (s, *E* or *Z*), 126.5 (s, *E* or *Z*), 126.1 (s, *E* or *Z*), 51.9 (s, *E* or *Z*), 51.8 (s, *E* or *Z*), 37.3 (s, *E*), 32.7 (s, *Z*), 19.72 (s, *E* or *Z*), 19.67 (s, *E* or *Z*) ppm.

IR (ATR) 3024, 1725, 1435, 1267, 1113, 1071, 963, 755, 694 cm^{-1} .

MS (EI-TOF) m/z (%) 234 (100) [M-OMe-H], 191 (13), 175 (13).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{17}\text{H}_{14}\text{O}$ [M-OMe-H] 234.1045, found 234.1039.

Methyl 2-methyl-6-[3-(1-naphthyl)allyl]benzoate (3af):



Compound **3af** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-(1-naphthyl)prop-2-en-1-ol (141 μ L, 0.75 mmol) and isolated as a colorless oil (130 mg, 82%, *E/Z* 1.9:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 8.08 - 8.19 (m, 1 H), 7.70 - 7.93 (m, 2 H), 7.35 - 7.62 (m, 4 H), 6.96 - 7.34 (m, 4 H), 6.32 (dt, J = 15.5, 6.8 Hz, 1 H), 3.88 (s, 3 H), 3.70 (dd, J = 6.4, 1.3 Hz, 2 H), 2.37 (s, 3 H) ppm; δ (*Z*-isomer) = 7.97 - 8.08 (m, 1 H), 7.70 - 7.93 (m, 2 H), 7.35 - 7.62 (m, 4 H), 6.96 - 7.34 (m, 4 H), 6.06 (dt, J = 11.3, 7.3 Hz, 1 H), 3.59 (s, 3 H), 3.52 (dd, J = 7.3, 1.7 Hz, 2 H), 2.29 (s, 3 H) ppm.

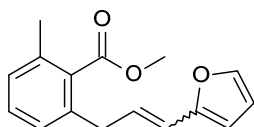
^{13}C NMR (101 MHz, CDCl_3) δ (*E+Z*) = 170.3 (s, *E*), 170.1 (s, *Z*), 137.6 (s, *Z*), 137.2 (s, *E*), 135.3 (s, *E* or *Z*), 135.1 (s, *E* or *Z*), 134.0 (s, *E*), 133.7 (s, *Z*), 133.5 (s, *E* or *Z*), 131.9 (s, *E* or *Z*), 131.8 (s, *E* or *Z*), 131.6 (s, *E* or *Z*), 131.1 (s, *E* or *Z*), 129.6 (s, *E* or *Z*), 129.5 (s, *E* or *Z*), 128.6 (s, *E* or *Z*), 128.4 (s, *E* or *Z*), 128.3 (s, *E* or *Z*), 128.0 (s, *E* or *Z*), 127.51 (s, *E* or *Z*), 127.48 (s, *E* or *Z*), 127.1 (s, *E* or *Z*), 126.6 (s, *E* or *Z*), 126.3 (s, *E* or *Z*), 125.9 (s, *E* or *Z*), 125.84 (s, *E* or *Z*), 125.79 (s, *E* or *Z*), 125.63 (s, *E* or *Z*), 125.58 (s, *E* or *Z*), 125.3 (s, *E* or *Z*), 125.0 (s, *E* or *Z*), 123.8 (s, *E* or *Z*), 123.7 (s, *E* or *Z*), 51.9 (s, *E*), 51.7 (s, *Z*), 37.6 (s, *E*), 32.8 (s, *Z*), 19.8 (s, *E*), 19.6 (s, *Z*), 12.8 (s, *Z*) ppm.

IR (ATR) 2949, 1724, 1435, 1268, 1113, 1072, 779 cm^{-1} .

MS (EI-TOF) m/z (%) 316 (55) [M]⁺, 284 (95), 266 (63), 255 (28), 239 (52), 175 (100), 153 (23).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_2$ [M]⁺ 316.1463, found: 316.1480.

Methyl 2-[3-(2-furyl)allyl]-6-methyl-benzoate (3ag):



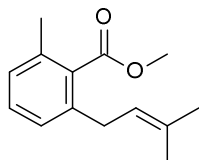
Compound **3ag** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-(2-furyl)prop-2-en-1-ol (95.3 μ L, 0.75 mmol) and isolated as a colorless oil (86 mg, 67%, *E/Z* 1.5:1).

^1H NMR (400 MHz, CDCl_3) δ (*E*-isomer) = 7.27 (d, J = 1.3 Hz, 1 H), 7.17 - 7.24 (m, 1 H), 7.01 - 7.13 (m, 2 H), 6.03 - 6.44 (m, 4 H), 3.84 (s, 3 H), 3.50 (d, J = 5.6 Hz, 2 H), 2.31 (s, 3 H) ppm; δ (*Z*-isomer) = 7.39 (d, J = 1.3 Hz, 1 H), 7.17 - 7.24 (m, 1 H), 7.01 - 7.13 (m, 2 H), 6.03 - 6.44 (m, 3 H), 5.59 (dt, J = 11.6, 7.3 Hz, 1 H), 3.84 (dd, J = 7.3, 1.8 Hz, 2 H), 3.77 (s, 3 H), 2.31 (s, 3 H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ (*E+Z*) = 170.1 (s, *E+Z*), 152.83 (s, *Z*), 152.76 (s, *E*), 141.6 (s, *Z*), 141.4 (s, *E*), 137.7 (s, *E* or *Z*), 136.9 (s, *E* or *Z*), 135.2 (s, *E* or *Z*), 133.6 (s, *E* or *Z*), 129.5 (s, *E+Z*), 128.2 (s, *E+Z*), 128.1 (s, *Z*), 127.2 (s, *E+Z*), 127.1 (s, *E+Z*), 126.7 (s, *E+Z*),

119.9 (s, *E*), 117.7 (s, *Z*), 111.1 (s, *Z*), 111.0 (s, *E*), 109.5 (s, *Z*), 106.7 (s, *E*), 51.73 (s, *E* or *Z*), 51.70 (s, *E* or *Z*), 36.8 (s, *E*), 33.5 (s, *Z*), 19.7 (s, *E* or *Z*), 19.6 (s, *E* or *Z*) ppm.
IR (ATR) 2927, 1722, 1436, 1269, 1114, 1072, 776, 733 cm^{-1} .
MS (EI-TOF) m/z (%) 256 (14) $[\text{M}]^+$, 224 (100), 195 (49), 181 (26), 175 (14), 153 (16), 147 (17).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_3$ $[\text{M}]^+$ 256.1099, found 256.1110.

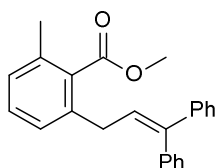
Methyl 2-methyl-6-(3-methylbut-2-enyl)benzoate (3ah):



Compound **3ah** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 2-methyl-3-buten-2-ol (107 μL , 0.75 mmol) and isolated as a colorless oil (97 mg, 89%).

^1H NMR (300 MHz, CDCl_3) δ = 7.23 (t, J = 7.5 Hz, 1 H), 7.01 - 7.09 (m, 2 H), 5.24 (tq, J = 7.2, 1.3 Hz, 1 H), 3.90 (s, 3 H), 3.35 (d, J = 7.2 Hz, 2 H), 2.32 (s, 3 H), 1.74 (s, 3 H), 1.70 (s, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ = 170.4 (s), 138.7 (s), 134.9 (s), 133.5 (s), 132.8 (s), 129.4 (s), 127.7 (s), 126.6 (s), 122.5 (s), 51.8 (s), 32.3 (s), 25.7 (s), 19.6 (s), 17.8 (s) ppm.
IR (ATR) 2950, 1727, 1436, 1267, 1111, 1070, 774 cm^{-1} .
MS (EI-TOF) m/z (%) 218 (2) $[\text{M}]^+$, 186 (100).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 218.1307, found 218.1313.

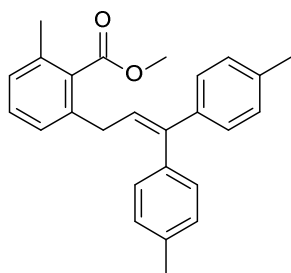
Methyl 2-(3,3-diphenylallyl)-6-methyl-benzoate (3ai):



Compound **3ai** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1,1-diphenylprop-2-en-1-ol (157 μL , 0.75 mmol) and isolated as a colorless oil (154 mg, 90%).

^1H NMR (300 MHz, CDCl_3) δ = 7.19 - 7.39 (m, 3 H), 7.08 - 7.19 (m, 8 H), 6.97 (d, J = 7.7 Hz, 2 H), 6.09 (t, J = 7.2 Hz, 1 H), 3.69 (s, 3 H), 3.39 (d, J = 7.3 Hz, 2 H), 2.22 (s, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ = 170.2 (s), 142.5 (s), 142.4 (s), 139.6 (s), 138.0 (s), 135.1 (s), 133.6 (s), 129.9 (s), 129.5 (s), 128.2 (s), 128.07 (s), 128.05 (s), 127.4 (s), 127.3 (s), 127.2 (s), 127.1 (s), 126.7 (s), 51.9 (s), 33.9 (s), 19.7 (s) ppm.
IR (ATR) 3023, 1725, 1463, 1113, 1072, 760, 698 cm^{-1} .
MS (EI-TOF) m/z (%) 342 (5) $[\text{M}]^+$, 310 (100), 295 (27), 282 (11), 267 (21), 233 (11), 175 (15), 162 (24).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_2$ $[\text{M}]^+$ 342.1620, found 342.1635.

Methyl 2-[3,3-bis(p-tolyl)allyl]-6-methyl-benzoate (3aj):

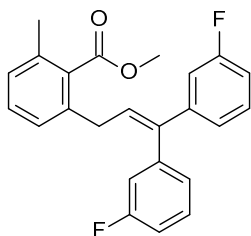


Compound **3aj** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1,1-bis(p-tolyl)prop-2-en-1-ol (216 μL , 0.75 mmol) and isolated as a colorless oil (170 mg, 92%).

^1H NMR (400 MHz, CDCl_3) δ = 7.21 - 7.27 (m, 3 H), 7.13 - 7.20 (m, 4 H), 7.04 - 7.13 (m, 4 H), 6.15 (t, J = 7.2 Hz, 1 H), 3.82 (s, 3 H), 3.53 (d, J = 7.3 Hz, 2 H), 2.42 (s, 3 H), 2.35 (s, 3 H), 2.34 (s, 3 H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ = 170.2 (s), 142.3 (s), 139.8 (s), 138.2 (s), 136.71 (s), 136.66 (s), 136.62 (s), 135.0 (s), 133.6 (s), 129.8 (s), 129.4 (s), 128.9 (s), 128.7 (s), 127.9 (s), 127.3 (s), 126.7 (s), 126.1 (s), 51.8 (s), 33.9 (s), 21.2 (s), 21.0 (s), 19.6 (s) ppm.
IR (ATR) 2948, 1721, 1269, 1112, 1073, 822, 780, 729 cm^{-1} .
MS (EI-TOF) m/z (%) 370 (5) $[\text{M}]^+$, 338 (17), 323 (25), 219 (44), 210 (40), 195 (52), 147 (21), 119 (100).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{26}\text{H}_{26}\text{O}_2$ $[\text{M}]^+$ 370.1933, found 370.1937.

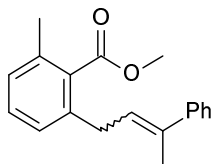
Methyl 2-[3,3-bis(3-fluorophenyl)allyl]-6-methyl-benzoate (3ak):



Compound **3ak** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1,1-bis(3-fluorophenyl)prop-2-en-1-ol (223 μL , 0.75 mmol) and isolated as a colorless oil (161 mg, 85%).

^1H NMR (400 MHz, CDCl_3) δ = 7.33 - 7.44 (m, 1 H), 7.15 - 7.30 (m, 2 H), 6.99 - 7.15 (m, 5 H), 6.86 - 6.98 (m, 3 H), 6.24 (t, J = 7.3 Hz, 1 H), 3.82 (s, 3 H), 3.48 (d, J = 7.3 Hz, 2 H), 2.33 (s, 3 H) ppm.
 ^{13}C NMR (101 MHz, CDCl_3) δ = 170.1 (s), 162.8 (d, J = 247.1 Hz), 144.0 (d, J = 8.3 Hz), 141.2 (d, J = 6.6 Hz), 140.3 (s), 137.3 (s), 135.3 (s), 133.6 (s), 130.0 (d, J = 8.3 Hz), 129.6 (d, J = 9.9 Hz), 129.1 (s), 128.3 (s), 126.7 (s), 125.6 (d, J = 3.3 Hz), 122.9 (d, J = 8.3 Hz), 116.8 (d, J = 19.9 Hz), 114.5 (d, J = 19.9 Hz), 114.2 (d, J = 21.6 Hz), 114.1 (d, J = 19.9 Hz), 51.9 (s), 33.9 (s), 19.7 (s) ppm.
 ^{19}F NMR (235 MHz, CDCl_3) δ = -112.79, -113.46 ppm.
IR (ATR) 2951, 1725, 1580, 1435, 1264, 1230, 1113, 1072, 780, 731 cm^{-1} .
MS (EI-TOF) m/z (%) 378 (3) $[\text{M}]^+$, 360 (39), 346 (100), 331 (31), 317 (19), 303 (20), 251 (15), 175 (13).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_2\text{F}_2$ $[\text{M}]^+$ 378.1413, found: 378.1447.

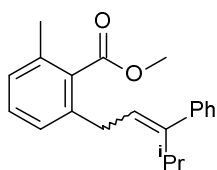
Methyl 2-methyl-6-(3-phenylbut-2-enyl)benzoate (3al):



Compound **3al** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 2-phenylbut-3-en-2-ol (134 μL , 0.75 mmol) and isolated as a colorless oil (135 mg, 96%, *E/Z* 4:1).

^1H NMR (400 MHz, CDCl_3) δ (*E*-isomer) = 7.23 - 7.51 (m, 6 H), 7.15 (dd, J = 13.3, 7.7 Hz, 2 H), 5.93 (tq, J = 7.1, 1.3 Hz, 1 H), 3.92 (s, 3 H), 3.63 (d, J = 7.3 Hz, 2 H), 2.39 (s, 3 H), 2.18 (d, J = 1.3 Hz, 3 H) ppm; δ (*Z*-isomer) = 7.23 - 7.51 (m, 6 H), 7.06 - 7.11 (m, 2 H), 5.65 (td, J = 7.1, 1.3 Hz, 1 H), 3.81 (s, 3 H), 3.39 (d, J = 7.3 Hz, 2 H), 2.35 (s, 3H), 2.13 (d, J = 1.3 Hz, 3 H) ppm.
 ^{13}C NMR (101 MHz, CDCl_3) δ (*E*-isomer) = 170.3 (s), 143.4 (s), 138.1 (s), 135.8 (s), 135.1 (s), 133.6 (s), 129.5 (s), 128.1 (s), 128.0 (s), 126.7 (s), 126.1 (s), 125.7 (s), 51.9 (s), 33.0 (s), 19.7 (s), 15.9 (s) ppm; δ (*Z*-isomer) = 170.2 (s), 141.5 (s), 138.4 (s), 137.5 (s), 134.9 (s), 133.5 (s), 129.4 (s), 128.1 (s), 127.9 (s), 127.8 (s), 126.5 (s), 125.1 (s), 51.8 (s), 33.2 (s), 25.6 (s), 19.6 (s) ppm.
IR (ATR) 2949, 1725, 1434, 1267, 1113, 1070, 761, 696 cm^{-1} .
MS (EI-TOF) m/z (%) 249 (26) $[\text{M-OMe}]$, 248 (100), 233 (50), 205 (33), 175 (28), 162 (39), 147 (23).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{18}\text{H}_{17}\text{O}$ $[\text{M-OMe}]$ 249.1279, found 249.1281.

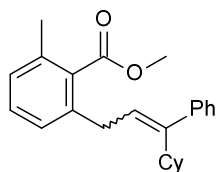
Methyl 2-methyl-6-(4-methyl-3-phenyl-pent-2-enyl)benzoate (3am):



Compound **3am** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 4-methyl-3-phenyl-pent-1-en-3-ol (160 μL , 0.75 mmol) and isolated as a colorless oil (150 mg, 97%, *E/Z* >20:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.21 - 7.31 (m, 4 H), 7.16 - 7.21 (m, 2 H), 7.15 (d, J = 7.0 Hz, 1 H), 7.08 (d, J = 7.2 Hz, 1 H), 5.38 (s, 1 H), 3.91 (s, 3 H), 3.57 (d, J = 7.2 Hz, 2 H), 3.02 - 3.25 (m, 1 H), 2.33 (s, 3 H), 1.08 (d, J = 7.0 Hz, 6 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 170.4 (s), 147.9 (s), 142.8 (s), 138.3 (s), 135.0 (s), 133.6 (s), 129.5 (s), 128.6 (s), 127.9 (s), 127.4 (s), 126.5 (s), 126.4 (s), 126.3 (s), 51.9 (s), 31.6 (s), 29.2 (s), 21.7 (s), 19.7 (s) ppm.
 IR (ATR) 2961, 1727, 1439, 1268, 1111, 1071, 763, 701 cm^{-1} .
 MS (EI-TOF) m/z (%) 308 (7) [M] $^+$, 276 (22), 233 (100), 218 (10), 162 (18).
 HRMS (EI-TOF) m/z calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_2$ [M] $^+$ 308.1776, found 308.1771.

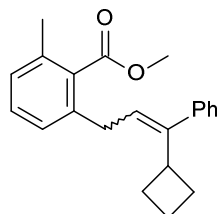
Methyl 2-(3-cyclohexyl-3-phenyl-allyl)-6-methyl-benzoate (3an):



Compound **3an** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-cyclohexyl-1-phenyl-prop-2-en-1-ol (196 μL , 0.75 mmol) and isolated as a colorless oil (160 mg, 92%, *E/Z* >20:1).

^1H NMR (400 MHz, CDCl_3) δ (*E*-isomer) = 7.20 - 7.30 (m, 4 H), 7.10 - 7.19 (m, 3 H), 7.06 (d, J = 7.6 Hz, 1 H), 5.35 (t, J = 7.2 Hz, 1 H), 3.91 (s, 3 H), 3.56 (d, J = 7.1 Hz, 2 H), 2.58 - 2.80 (m, 1 H), 2.32 (s, 3 H), 1.59 - 1.82 (m, 6 H), 1.20 - 1.42 (m, 4 H), 0.99 - 1.18 (m, 1 H) ppm.
 ^{13}C NMR (101 MHz, CDCl_3) δ (*E*-isomer) = 170.4 (s), 147.6 (s), 143.5 (s), 138.3 (s), 135.0 (s), 133.6 (s), 129.5 (s), 128.6 (s), 127.9 (s), 127.4 (s), 126.6 (s), 126.5 (s), 126.2 (s), 51.9 (s), 40.4 (s), 31.9 (s), 31.6 (s), 26.7 (s), 26.0 (s), 19.7 (s) ppm.
 IR (ATR) 2925, 1728, 1441, 1268, 1113, 1071, 768, 702 cm^{-1} .
 MS (EI-TOF) m/z (%) 348 (6) [M] $^+$, 316 (13), 234 (100), 175 (14), 162 (25), 129 (12).
 HRMS (EI-TOF) m/z calcd. for $\text{C}_{24}\text{H}_{28}\text{O}_2$ [M] $^+$ 348.2089, found 348.2073.

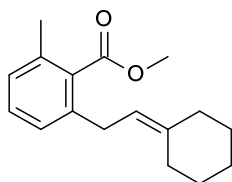
Methyl 2-(3-cyclobutyl-3-phenyl-allyl)-6-methyl-benzoate (3ao):



Compound **3ao** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-cyclobutyl-1-phenyl-prop-2-en-1-ol (170 μL , 0.75 mmol) and isolated as a colorless oil (148 mg, 92%, *E/Z* 9:1).

^1H NMR (400 MHz, CDCl_3) δ (*E*-isomer) = 7.18 - 7.36 (m, 4 H), 7.07 - 7.17 (m, 3 H), 6.98 - 7.07 (m, 1 H), 5.35 - 5.56 (m, 1 H), 3.89 (s, 3 H), 3.58 - 3.73 (m, 1 H), 3.50 (d, J = 7.1 Hz, 2 H), 2.31 (s, 3 H), 2.07 - 2.23 (m, 2 H), 1.77 - 2.02 (m, 3 H), 1.58 - 1.71 (m, 1 H) ppm; δ (*Z*-isomer) = 7.18 - 7.36 (m, 4 H), 7.07 - 7.17 (m, 3 H), 6.98 - 7.07 (m, 1 H), 5.35 - 5.56 (m, 1 H), 3.77 (s, 3 H), 3.58 - 3.73 (m, 1 H), 3.25 (d, J = 6.8 Hz, 2 H), 2.31 (s, 3 H), 2.07 - 2.23 (m, 2 H), 1.77 - 2.02 (m, 3 H), 1.58 - 1.71 (m, 1 H) ppm.
 ^{13}C NMR (101 MHz, CDCl_3) δ (*E*-isomer) = 170.3 (s), 145.4 (s), 142.9 (s), 138.3 (s), 135.0 (s), 133.6 (s), 129.5 (s), 127.9 (s), 127.74 (s), 127.69 (s), 126.6 (s), 126.5 (s), 126.2 (s), 51.9 (s), 37.1 (s), 32.2 (s), 29.1 (s), 19.7 (s), 18.9 (s) ppm; δ (*Z*-isomer, detectable signals) = 145.8 (s), 138.5 (s), 129.4 (s), 128.4 (s), 128.0 (s), 122.5 (s), 51.8 (s), 42.6 (s), 32.8 (s), 27.8 (s), 19.6 (s), 17.7 (s) ppm.
 IR (ATR) 2947, 1726, 1440, 1267, 1112, 1070, 762, 700 cm^{-1} .
 MS (EI-TOF) m/z (%) 320 (12) [M] $^+$, 288 (27), 260 (64), 245 (78), 233 (100), 215 (29), 202 (26), 162 (32), 147 (30).
 HRMS (EI-TOF) m/z calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_2$ [M] $^+$ 320.1776, found 320.1786.

Methyl 2-(2-cyclohexylideneethyl)-6-methyl-benzoate (3ap):



Compound **3ap** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 1-ethenylcyclohexan-1-ol (104 μ L, 0.75 mmol) and isolated as a colorless oil (117 mg, 90%).

^1H NMR (300 MHz, CDCl_3) δ = 7.22 (d, J = 7.7 Hz, 1 H), 7.06 (d, J = 7.2 Hz, 1 H), 5.15 - 5.25 (m, 1 H), 3.91 (s, 3 H), 3.36 (d, J = 7.2 Hz, 2 H), 2.32 (s, 3 H), 2.04 - 2.26 (m, 4 H), 1.48 - 1.62 (m, 6 H) ppm.

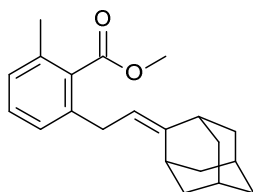
^{13}C NMR (75 MHz, CDCl_3) δ = 170.4 (s), 140.9 (s), 138.9 (s), 134.8 (s), 133.5 (s), 129.4 (s), 127.6 (s), 126.5 (s), 119.0 (s), 51.8 (s), 37.1 (s), 31.2 (s), 28.7 (s), 28.5 (s), 27.7 (s), 26.8 (s), 19.6 (s) ppm.

IR (ATR) 2925, 1728, 1445, 1267, 1112, 1071, 825 cm^{-1} .

MS (EI-TOF) m/z (%) 258 (15) $[\text{M}]^+$, 226 (100), 171 (16), 162 (29), 145 (24), 132 (22), 115 (12).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_2$ $[\text{M}]^+$ 258.1620, found 258.1604.

Methyl 2-[2-(2-adamantylidene)ethyl]-6-methyl-benzoate (**3aq**):



Compound **3aq** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 2-vinyladamantan-2-ol (135 mg, 0.75 mmol) and isolated as a colorless oil (83 mg, 53%).

^1H NMR (400 MHz, CDCl_3) δ = 7.24 (t, J = 7.6 Hz, 1 H), 7.10 (d, J = 7.6 Hz, 1 H), 7.05 (d, J = 7.6 Hz, 1 H), 5.18 (t, J = 7.2 Hz, 1 H), 3.93 (s, 3 H), 3.34 (d, J = 7.3 Hz, 2 H), 2.84 - 2.97 (m, 1 H), 2.36 - 2.42 (m, 1 H), 2.33 (s, 3 H), 1.94 - 2.02 (m, 2 H), 1.69 - 1.94 (m, 10 H) ppm.

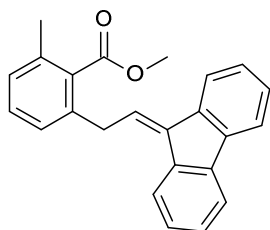
^{13}C NMR (101 MHz, CDCl_3) δ = 170.5 (s), 148.8 (s), 139.1 (s), 134.0 (s), 133.5 (s), 129.4 (s), 127.5 (s), 126.4 (s), 114.0 (s), 51.8 (s), 40.5 (s), 39.7 (s), 38.9 (s), 37.2 (s), 32.1 (s), 30.5 (s), 28.6 (s), 19.6 (s), ppm.

IR (ATR) 2901, 1728, 1447, 1266, 1112, 1069, 774, 716 cm^{-1} .

MS (EI-TOF) m/z (%) 310 (7) $[\text{M}]^+$, 278 (100), 162 (30).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_2$ $[\text{M}]^+$ 310.1933, found 310.1938.

Methyl 2-(2-(9-fluorenylidene)ethyl)-6-methyl-benzoate (**3ar**):



An oven-dried 20 mL vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (6.46 mg, 0.01 mmol), K_2CO_3 (69.2 mg, 0.5 mmol) and 2-methylbenzoic acid (0.50 mmol) and closed with a septum cap. Under exclusion of air and water, MeCN (2 mL) and 9-vinylfluoren-9-ol (188 μ L, 0.75 mmol) were added via syringe. The resulting mixture was stirred at 80 $^\circ\text{C}$ for 16 h. After the reaction was complete, MeCN (2 mL), K_2CO_3 (207 mg, 1.50 mmol) and MeI (358 mg, 2.50 mmol) were added and the mixture was stirred at 50 $^\circ\text{C}$ for 2 h. H_2O (20 mL) was added and the resulting mixture was extracted with EtOAc (3 \times 20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO_4 , filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2 , ethyl acetate/cyclohexane gradient) yielding compound **3ar** as a colorless oil (49 mg, 29%).

^1H NMR (300 MHz, CDCl_3) δ = 7.89 - 7.97 (m, 1 H), 7.77 - 7.83 (m, 1 H), 7.70 - 7.76 (m, 1 H), 7.61 - 7.69 (m, 1 H), 7.25 - 7.47 (m, 5 H), 7.23 (d, J = 7.0 Hz, 1 H), 7.18 (d, J = 7.3 Hz, 1 H), 6.79 (t, J = 7.2 Hz, 1 H), 4.24 (d, J = 7.3 Hz, 2 H), 3.78 (s, 3 H), 2.41 (s, 3 H) ppm.

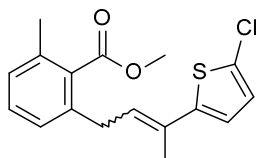
^{13}C NMR (75 MHz, CDCl_3) δ = 170.1 (s), 141.0 (s), 139.2 (s), 138.7 (s), 137.1 (s), 137.0 (s), 135.9 (s), 135.6 (s), 133.7 (s), 129.8 (s), 128.6 (s), 128.1 (s), 128.0 (s), 127.7 (s), 127.04 (s), 126.95 (s), 126.9 (s), 124.9 (s), 119.92 (s), 119.86 (s), 119.5 (s), 52.0 (s), 33.7 (s), 19.8 (s) ppm.

IR (ATR) 2949, 1723, 1446, 1268, 1113, 1073, 776, 728 cm^{-1} .

MS (EI-TOF) m/z (%) 340 (18) $[\text{M}]^+$, 308 (100), 249 (25), 265 (68), 180 (67), 162 (54), 147 (55), 132 (47).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 340.1463, found 340.1468.

Methyl 2-[3-(5-chloro-2-thienyl)but-2-enyl]-6-methyl-benzoate (3as):



Compound **3as** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 2-(5-chloro-2-thienyl)but-3-en-2-ol (171 μL , 0.75 mmol) and isolated as a colorless oil (118 mg, 73%, *E/Z* 1.3:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.26 (t, J = 7.7 Hz, 1 H), 7.05 - 7.14 (m, 2 H), 6.77 (d, J = 7.9 Hz, 1 H), 6.76 (d, J = 7.7 Hz, 1 H), 5.82 - 5.98 (m, 1 H), 3.89 (s, 3 H), 3.56 (d, J = 7.3 Hz, 2 H), 2.35 (s, 3 H), 2.08 (d, J = 1.1 Hz, 3 H) ppm; δ (*Z*-isomer) = 7.26 (t, J = 7.7 Hz, 1 H), 7.05 - 7.14 (m, 2 H), 6.87 (d, J = 3.9 Hz, 1 H), 6.80 (d, J = 3.9 Hz, 1 H), 5.54 - 5.66 (m, 1 H), 3.83 (s, 3 H), 3.64 (dt, J = 7.4, 0.7 Hz, 2 H), 2.35 (s, 3 H), 2.12 (q, J = 1.4 Hz, 3 H) ppm.

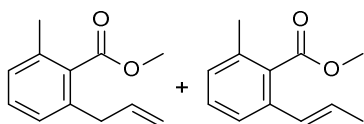
^{13}C NMR (75 MHz, CDCl_3) δ (*E+Z*) = 170.2 (s, *E*), 170.0 (s, *Z*), 145.8 (s, *E* or *Z*), 141.5 (s, *E* or *Z*), 137.6 (s, *E* or *Z*), 137.3 (s, *E* or *Z*), 135.20 (s, *Z*), 135.17 (s, *E*), 133.5 (s, *E*), 133.4 (s, *Z*), 129.5 (s, *E*), 129.4 (s, *Z*), 128.9 (s, *Z*), 128.6 (s, *E*), 128.2 (s, *E*), 128.1 (s, *Z*), 127.44 (s, *E+Z*), 127.39 (s, *Z*), 126.6 (s, *E*), 126.5 (s, *Z*), 126.2 (s, *E*), 125.8 (s, *Z*), 125.1 (s, *E*), 124.7 (s, *Z*), 121.6 (s, *E*), 51.9 (s, *E*), 51.8 (s, *Z*), 33.9 (s, *E*), 32.6 (s, *E*), 25.2 (s, *Z*), 19.6 (s, *E+Z*), 15.2 (s, *E*), ppm.

IR (ATR) 2990, 1724, 1463, 1113, 1071, 958, 785 cm^{-1} .

MS (EI-TOF) m/z (%) 322 (6) $[\text{M} (^{37}\text{Cl})]^+$, 320 (18) $[\text{M} (^{35}\text{Cl})]^+$, 288 (84), 273 (33), 253 (100), 225 (26), 175 (28), 162 (54), 147 (36).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_2\text{S}^{37}\text{Cl}$ $[\text{M}]^+$ 322.0608 and $\text{C}_{17}\text{H}_{17}\text{O}_2\text{S}^{35}\text{Cl}$ 320.0638, found 322.0625 and 320.0653.

Methyl 2-allyl-6-methyl-benzoate (3at):

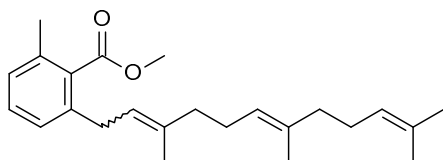


Compound **3at** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and allyl alcohol (51.9 mg, 0.75 mmol) and isolated as a 2:1 mixture with its isomer (68 mg, 71%).

^1H NMR (300 MHz, CDCl_3) δ = 7.18 - 7.29 (m, 1 H), 7.02 - 7.11 (m, 2 H), 5.79 - 6.01 (m, 1 H), 4.96 - 5.15 (m, 2 H), 3.90 (s, 3 H), 3.40 (d, J = 6.8 Hz, 1 H), 2.33 (s, 3 H) ppm; δ (isomer) = 7.31 - 7.37 (m, 1 H), 7.18 - 7.29 (m, 1 H), 7.02 - 7.11 (m, 1 H), 6.40 (dq, J = 15.6, 1.7 Hz, 1 H), 6.20 (dq, J = 15.4, 6.6 Hz, 1 H), 3.94 (s, 3 H), 2.31 (s, 3 H), 1.88 (dd, J = 6.6, 1.7 Hz, 3 H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ (mixture) = 170.4 (s), 170.2 (s), 137.0 (s), 136.7 (s), 135.3 (s), 135.1 (s), 134.8 (s), 133.5 (s), 132.2 (s), 129.5 (s), 129.3 (s), 128.7 (s), 128.4 (s), 128.1 (s), 127.9 (s), 126.9 (s), 122.9 (s), 116.0 (s), 52.0 (s), 51.8 (s), 38.1 (s), 19.7 (s), 19.5 (s), 18.7 (s) ppm.

Methyl 2-methyl-6-[(6E)-3,7,11-trimethyldodeca-2,6,10-trienyl]benzoate (4aa):



Compound **4aa** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and nerolidol (170 mg, 0.75 mmol) and isolated as a colorless oil (153 mg, 86%, *E/Z* determined by GC analysis and by analogy with the other compounds 1.4:1).

Gram-scale synthesis of **4aa**: An oven-dried 100 mL vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (129 mg, 0.20 mmol), K_3PO_4 (1.06 g, 5.00 mmol) and 2-methylbenzoic acid (1.38 g, 10.0 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (10 mL) and nerolidol (3.40 g, 15.0 mmol) were added via syringe. The resulting mixture was stirred at 50 $^\circ\text{C}$ for 16 h.

After the reaction was complete, MeCN (30 mL), K₂CO₃ (4.15 g, 30.0 mmol) and MeI (3.11 mL, 50.0 mmol) were added and the mixture was stirred at 50 °C for 10 h. H₂O (50 mL) was added and the resulting mixture was extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO₄, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO₂, ethyl acetate/cyclohexane gradient) yielding the corresponding *ortho*-allylated product in the form of its methyl ester.

¹H NMR (300 MHz, CDCl₃) δ(*E+Z*) = 7.23 (t, *J* = 7.5 Hz, 1 H), 7.07 (t, *J* = 6.4 Hz, 2 H), 5.24 - 5.35 (m, 1 H), 5.08 - 5.23 (m, 2 H), 3.91 (s, 3 H), 3.38 (dt, *J* = 7.2, 1.6 Hz, 2 H), 2.34 (s, 3 H), 2.12 - 2.21 (m, 3 H), 2.02 - 2.12 (m, 5 H), 1.75 - 1.80 (m, 2 H), 1.67 - 1.74 (m, 7 H), 1.58 - 1.66 (m, 3 H) ppm.

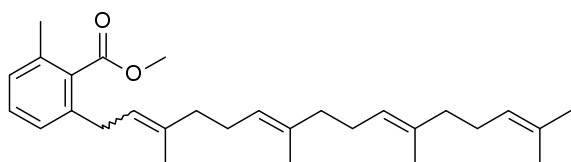
¹³C NMR (75 MHz, CDCl₃) δ(*E+Z*) = 170.36 (s), 170.24 (s), 138.7 (s), 138.6 (s), 136.48 (s), 136.45 (s), 135.4 (s), 135.1 (s), 134.8 (s), 133.49 (s), 133.47 (s), 131.42 (s), 131.39 (s), 129.3 (s), 127.6 (s), 126.6 (s), 126.4 (s), 124.84 (s), 124.78 (s), 124.3 (s), 124.2 (s), 123.1 (s), 122.3 (s), 51.8 (s), 51.7 (s), 39.9 (s), 32.2 (s), 32.0 (s), 31.92 (s), 31.90 (s), 31.88 (s), 26.6 (s), 26.5 (s), 26.3 (s), 26.2 (s), 25.6 (s), 23.4 (s), 23.32 (s), 23.31 (s), 19.6 (s), 17.6 (s), 17.5 (s), 16.1 (s) ppm.

IR (ATR) 2950, 1730, 1268, 1112, 1071, 775 cm⁻¹.

MS (EI-TOF) *m/z* (%) 354 (16) [M]⁺, 253 (12), 211 (21), 185 (39), 171 (18), 157 (100), 142 (56), 128 (28).

HRMS (EI-TOF) *m/z* calcd. for C₂₄H₃₄O₂ [M]⁺ 354.2559, found 354.2574.

Methyl 2-methyl-6-[(6*E*,10*E*)-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraenyl]benzoate (**4ab**):



An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (6.46 mg, 0.01 mmol), K₂CO₃ (69.2 mg, 0.5 mmol) and 2-methylbenzoic acid (0.50 mmol) and closed with a septum cap. Under exclusion of air and water, MeCN (2 mL) and geranylinalool (260 μL, 0.75 mmol) were added via syringe. The resulting mixture was stirred at 80 °C for 16 h. After the reaction was complete, MeCN (2 mL), K₂CO₃ (207 mg, 1.50 mmol) and MeI (358 mg, 2.50 mmol) were added and the mixture was stirred at 50 °C for 2 h. H₂O (20 mL) was added and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO₂, ethyl acetate/cyclohexane gradient) yielding compound **4ab** as a colorless oil (115 mg, 54%, *E/Z* determined by GC analysis and by analogy with the other compounds 1.8:1).

¹H NMR (300 MHz, CDCl₃) δ(*E+Z*) = 7.23 (d, *J* = 7.7 Hz, 1 H), 7.07 (dd, *J* = 6.7, 6.1 Hz, 2 H), 5.24 - 5.32 (m, 1 H), 5.07 - 5.23 (m, 3 H), 3.90 (s, 3 H), 3.37 (d, *J* = 7.0 Hz, 2 H), 2.33 (s, 3 H), 1.95 - 2.18 (m, 12 H), 1.76 (d, *J* = 1.3 Hz, 2 H), 1.71 (s, 4 H), 1.65 (d, *J* = 0.9 Hz, 2 H), 1.63 (s, 6 H) ppm.

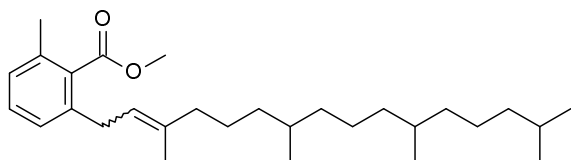
¹³C NMR (75 MHz, CDCl₃) δ(*E+Z*) = 170.4 (s), 138.68 (s), 138.67 (s), 136.6 (s), 136.5 (s), 135.3 (s), 135.1 (s), 134.9 (s), 134.82 (s), 134.77 (s), 133.49 (s), 133.47 (s), 131.2 (s), 129.3 (s), 127.66 (s), 127.65 (s), 126.54 (s), 126.46 (s), 124.4 (s), 124.19 (s), 124.16 (s), 124.0 (s), 123.9 (s), 123.0 (s), 122.3 (s), 51.8 (s), 39.68 (s), 39.65 (s), 32.01 (s), 31.97 (s), 31.9 (s), 26.7 (s), 26.6 (s), 26.5 (s), 26.4 (s), 25.7 (s), 23.4 (s), 19.6 (s), 17.6 (s), 16.1 (s), 15.98 (s), 15.95 (s) ppm.

IR (ATR) 2916, 1730, 1436, 1267, 1112, 1071, 826, 774 cm⁻¹.

MS (EI) *m/z* (%) 422 (5) [M]⁺, 353 (8), 253 (15), 211 (27), 185 (35), 157 (79), 109 (35), 81 (59), 69 (100).

HRMS (ESI) *m/z* calcd. for C₂₉H₄₂NaO₂ [M+Na]⁺ 455.3077, found 455.3087.

Methyl 2-methyl-6-(3,7,11,15-tetramethylhexadec-2-enyl)benzoate (**4ac**):



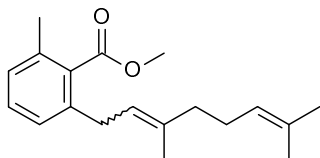
Compound **4ac** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and isophytol (273 μL, 0.75 mmol) and isolated as a colorless oil (154 mg, 72%, *E/Z* 1.9:1).

¹H NMR (300 MHz, CDCl₃) δ(*E+Z*) = 7.25 (t, *J* = 7.5 Hz, 1 H), 7.03 - 7.12 (m, 2 H), 5.28 (t, *J* = 7.1 Hz, 1 H), 3.92 (s, 3 H), 3.37 (d, *J* = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.11 (t, *J* = 7.3 Hz, 2 H-*E*), 2.02 (t, *J* = 7.5 Hz, 2 H-*Z*), 1.76 (d, *J* = 1.3 Hz, 3 H-*E*), 1.71 (s, 3 H-*Z*), 1.01 - 1.62 (m, 19 H), 0.82 - 0.94 (m, 12 H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ = 170.4 (s), 138.8 (s), 137.1 (s), 136.9 (s), 134.81 (s), 134.79 (s), 133.5 (s), 129.4 (s), 127.7 (s), 126.6 (s), 126.5 (s), 122.7 (s), 122.1 (s), 51.8 (s), 40.0 (s), 37.43 (s), 37.42 (s), 37.39 (s), 37.38 (s), 37.34 (s), 37.27 (s), 37.1 (s), 37.0 (s), 36.8

(s), 36.7 (s), 32.77 (s), 32.75 (s), 32.72 (s), 32.69 (s), 32.66 (s), 32.6 (s), 32.12 (s), 32.08 (s), 31.9 (s), 28.0 (s), 25.41 (s), 25.39 (s), 25.36 (s), 25.35 (s), 24.8 (s), 24.4 (s), 23.4 (s), 22.7 (s), 22.6 (s), 19.73 (s), 19.68 (s), 16.1 (s) ppm.
IR (ATR) 2925, 1731, 1463, 1267, 1112, 1071, 774, 733 cm^{-1} .
MS (EI) m/z (%) 428 (10) $[\text{M}]^+$, 396 (13), 381 (5), 213 (16), 186 (54), 172 (100), 146 (39), 132 (12), 105 (13).
HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{48}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 451.3546, found 451.3544.

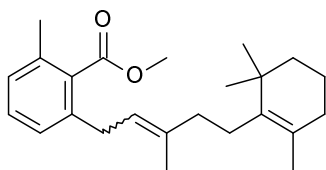
Methyl 2-(3,7-dimethylocta-2,6-dienyl)-6-methyl-benzoate (4ad):



Compound **4ad** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and linalool (139 μL , 0.75 mmol) and isolated as a colorless oil (115 mg, 80%, *E/Z* determined by GC analysis and by analogy with the other compounds 1.3:1).

^1H NMR (300 MHz, CDCl_3) δ (*E+Z*) = 7.22 (d, J = 7.7 Hz, 1 H), 7.02 - 7.11 (m, 2 H), 5.22 - 5.33 (m, 1 H), 5.07 - 5.20 (m, 1 H), 3.91 (s, 3 H), 3.37 (dt, J = 7.2, 1.5 Hz, 2 H), 2.33 (s, 3 H), 2.03 - 2.18 (m, 4 H), 1.68 - 1.79 (m, 6 H), 1.59 - 1.66 (m, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ = 170.4 (s), 138.68 (s), 138.67 (s), 136.6 (s), 136.5 (s), 134.78 (s), 134.76 (s), 133.48 (s), 131.6 (s), 131.4 (s), 129.3 (s), 127.7 (s), 126.54 (s), 126.46 (s), 124.2 (s), 124.1 (s), 123.1 (s), 122.3 (s), 51.8 (s), 39.6 (s), 32.0 (s), 31.94 (s), 31.86 (s), 26.5 (s), 26.4 (s), 25.7 (s), 25.6 (s), 23.4 (s), 19.6 (s), 19.59 (s), 17.63 (s), 17.58 (s), 16.1 (s) ppm.
IR (ATR) 2949, 1729, 1436, 1267, 1111, 1070, 774, 749 cm^{-1} .
MS (EI) m/z (%) 286 (13) $[\text{M}]^+$, 254 (31), 211 (43), 185 (76), 157 (100), 123 (83).
HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{26}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 309.1825, found 309.1825.

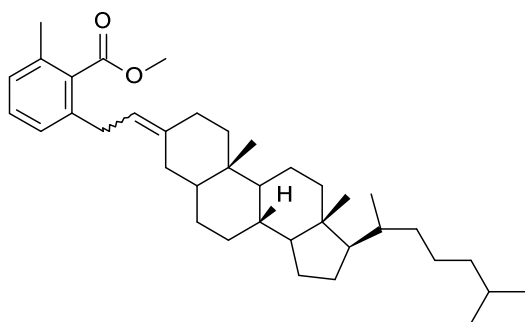
Methyl 2-methyl-6-[3-methyl-5-(2,6,6-trimethylcyclohexen-1-yl)pent-2-enyl]benzoate (4ae):



Compound **4ae** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and 3-methyl-5-(2,6,6-trimethylcyclohexen-1-yl)pent-1-en-3-ol (171 mg, 0.75 mmol) and isolated as a colorless oil (158 mg, 89%, *E/Z* determined by GC analysis and by analogy with the other compounds 2.4:1).

^1H NMR (300 MHz, CDCl_3) δ (*E+Z*) = 7.20 - 7.27 (m, 1 H), 7.00 - 7.13 (m, 2 H), 5.18 - 5.35 (m, 1 H), 3.90 (s, 3 H), 3.34 - 3.46 (m, 2 H), 2.33 (s, 3 H), 2.04 - 2.23 (m, 4 H), 1.94 (q, J = 6.2 Hz, 2 H), 1.81 (q, J = 1.3 Hz, 2 H), 1.72 - 1.78 (m, 1 H), 1.68 (s, 2 H), 1.53 - 1.66 (m, 3 H), 1.39 - 1.50 (m, 2 H), 1.05 (s, 4 H), 1.02 (s, 2 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ (*E+Z*) = 170.4 (s), 170.3 (s), 138.8 (s), 138.7 (s), 137.5 (s), 137.3 (s), 136.92 (s), 136.89 (s), 134.84 (s), 134.81 (s), 133.52 (s), 133.50 (s), 129.4 (s), 127.7 (s), 127.2 (s), 127.0 (s), 126.54 (s), 126.48 (s), 122.5 (s), 121.7 (s), 51.8 (s), 40.2 (s), 39.8 (s), 34.9 (s), 32.74 (s), 32.70 (s), 32.66 (s), 32.1 (s), 32.0 (s), 28.60 (s), 28.57 (s), 27.8 (s), 27.2 (s), 23.3 (s), 19.84 (s), 19.78 (s), 19.63 (s), 19.60 (s), 19.5 (s), 16.2 (s), ppm.
IR (ATR) 2926, 1730, 1435, 1267, 1112, 1070, 774, 732 cm^{-1} .
MS (EI-TOF) m/z (%): 354 (12) $[\text{M}]^+$, 216 (67), 186 (42), 157 (66), 137 (100), 121 (17), 95 (53).
HRMS (EI-TOF) m/z calcd. for $\text{C}_{24}\text{H}_{34}\text{O}_2$ $[\text{M}]^+$ 354.2559, found 354.2555.

Methyl 2-[2-[(8R,10S,13R,17R)-17-(1,5-dimethylhexyl)-10,13-dimethyl-1,2,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydrocyclopenta[a]phenanthren-3-ylidene]ethyl]-6-methyl-benzoate (4af):



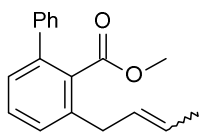
Compound **4af** was prepared following the general procedure for the *ortho*-allylation from 2-methylbenzoic acid (68.9 mg, 0.50 mmol) and (8R,10S,13R,17R)-17-(1,5-dimethylhexyl)-10,13-dimethyl-3-vinyl-1,2,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydrocyclopenta[*a*]phenanthren-3-ol (371 μ L, 0.75 mmol) and isolated as a colorless oil (110 mg, 44%, *E/Z* determined by GC analysis and by analogy with the other compounds 1.5:1).

^1H NMR (300 MHz, CDCl_3) δ (*E+Z*) = 7.22 (d, J = 7.7 Hz, 1 H), 6.99 - 7.09 (m, 2 H), 5.17 (t, J = 7.3 Hz, 1 H), 3.91 (s, 3 H), 3.34 (d, J = 7.9 Hz, 2 H), 2.31 (s, 3 H), 2.15 - 2.59 (m, 4 H), 1.45 - 2.13 (m, 10 H), 0.96 - 1.45 (m, 18 H), 0.78 - 0.96 (m, 14 H), 0.67 (s, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ = 170.5 (s), 140.8 (s), 140.7 (s), 138.9 (s), 134.8 (s), 133.5 (s), 129.42 (s), 129.40 (s), 127.6 (s), 126.52 (s), 126.51 (s), 118.7 (s), 118.6 (s), 56.5 (s), 56.3 (s), 54.44 (s), 54.39 (s), 51.9 (s), 48.2 (s), 47.4 (s), 42.58 (s), 42.57 (s), 40.04 (s), 40.00 (s), 39.5 (s), 39.42 (s), 39.36 (s), 36.5 (s), 36.4 (s), 36.2 (s), 35.8 (s), 35.5 (s), 32.5 (s), 32.02 (s), 31.96 (s), 31.4 (s), 31.2 (s), 29.1 (s), 28.8 (s), 28.2 (s), 28.0 (s), 24.4 (s), 24.2 (s), 23.8 (s), 22.8 (s), 22.6 (s), 21.12 (s), 21.07 (s), 19.7 (s), 18.7 (s), 12.1 (s), 11.82 (s), 11.78 (s) ppm.

IR (ATR) 2925, 1731, 1443, 1267, 1112, 1071, 774, 733 cm^{-1} .

HRMS (ESI) m/z calcd. for $\text{C}_{38}\text{H}_{58}\text{NaO}_2$ [$\text{M}+\text{Na}$] $^+$ 569.4329, Found 569.4329.

Methyl 2-(but-2-enyl)-6-phenyl-benzoate (3ba):



Compound **3ba** was prepared following the general procedure for the *ortho*-allylation from 2-phenylbenzoic acid (101 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μ L, 0.75 mmol) and isolated as a colorless oil (74 mg, 56%, *E/Z* 2:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.31 - 7.44 (m, 6 H), 7.21 - 7.30 (m, 2 H), 5.43 - 5.71 (m, 2 H), 3.56 (s, 3 H), 3.44 (d, J = 5.1 Hz, 2 H), 1.67 - 1.71 (m, 3 H) ppm; δ (*Z*-isomer) = 7.31 - 7.44 (m, 6 H), 7.21 - 7.30 (m, 2 H), 5.43 - 5.71 (m, 2 H), 3.57 (s, 3 H), 3.50 (d, J = 6.2 Hz, 2 H), 1.71 - 1.76 (m, 3 H) ppm.

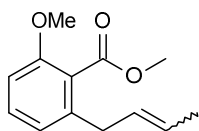
^{13}C NMR (75 MHz, CDCl_3) δ (*E+Z*) = 170.2 (s), 170.1 (s), 140.88 (s), 140.87 (s), 140.2 (s), 138.6 (s), 138.5 (s), 132.9 (s), 132.8 (s), 129.6 (s), 129.5 (s), 129.1 (s), 128.4 (s), 128.24 (s), 128.19 (s), 128.1 (s), 127.6 (s), 127.5 (s), 127.3 (s), 126.9 (s), 125.3 (s), 51.8 (s), 51.7 (s), 36.7 (s), 30.9 (s), 17.9 (s), 12.9 (s), ppm.

IR (ATR) 2948, 1725, 1427, 1265, 1103, 1064, 806, 729, 700 cm^{-1} .

MS (EI) m/z (%) 266 (66) [M] $^+$, 233 (100), 209 (25), 191 (37), 179 (23), 165 (46), 152 (22).

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{NaO}_2$ [$\text{M}+\text{Na}$] $^+$ 289.1199, found 289.1198.

Methyl 2-(but-2-enyl)-6-methoxy-benzoate (3ca):

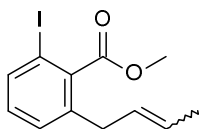


Compound **3ca** was prepared following the general procedure for the *ortho*-allylation from 2-methoxybenzoic acid (76.8 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μ L, 0.75 mmol) and isolated as a colorless oil (82 mg, 75%, *E/Z* 1.9:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.28 (t, J = 8.1 Hz, 1 H), 6.83 (d, J = 7.7 Hz, 1 H), 6.78 (d, J = 8.3 Hz, 1 H), 5.39 - 5.68 (m, 2 H), 3.90 (s, 3 H), 3.82 (s, 3 H), 3.28 (d, J = 4.4 Hz, 2 H), 1.64 - 1.68 (m, 3 H) ppm; δ (*Z*-isomer) = 7.28 (t, J = 8.1 Hz, 1 H), 6.85 (d, J = 7.7 Hz, 1 H), 6.78 (d, J = 8.3 Hz, 1 H), 5.39 - 5.68 (m, 2 H), 3.90 (s, 3 H), 3.82 (s, 3 H), 3.37 (d, J = 6.6 Hz, 2 H), 1.68 - 1.72 (m, 3 H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 168.6 (s), 156.3 (s), 139.4 (s), 130.3 (s), 128.8 (s), 126.8 (s), 123.25 (s), 121.5 (s), 108.68 (s), 55.79 (s), 52.0 (s), 36.5 (s), 17.8 (s) ppm; δ (*Z*-isomer) = 168.7 (s), 156.3 (s), 139.6 (s), 130.4 (s), 127.9 (s), 125.2 (s), 123.2 (s), 121.3 (s), 108.65 (s), 55.81 (s), 52.1 (s), 30.7 (s), 12.8 (s) ppm.
IR (ATR) 2949, 1728, 1261, 1110, 1067, 964, 760, 735 cm^{-1} .
MS (EI) m/z (%) 220 (85) [M^+], 189 (70), 173 (100), 161 (49), 145 (64), 129 (46), 115 (81).
HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{NaO}_3$ [$\text{M}+\text{Na}$] $^+$ 243.0992, Found 243.0999.

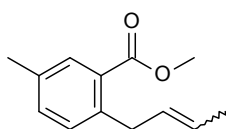
Methyl 2-(but-2-enyl)-6-iodo-benzoate (3da):



Compound **3da** was prepared following the general procedure for the *ortho*-allylation from 2-iodobenzoic acid (127 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (85 mg, 54%, *E/Z* 1.9:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.67 (dd, J = 7.9, 1.3 Hz, 1 H), 7.21 (dd, J = 7.7, 1.1 Hz, 1 H), 7.03 (t, J = 8.1 Hz, 1 H), 5.37 - 5.69 (m, 2 H), 3.93 (s, 3 H), 3.24 - 3.34 (m, 2 H), 1.66 - 1.68 (m, 3 H) ppm; δ (*Z*-isomer) = 7.67 (dd, J = 7.9, 1.3 Hz, 1 H), 7.21 (dd, J = 7.7, 1.1 Hz, 1 H), 7.03 (t, J = 8.1 Hz, 1 H), 5.37 - 5.69 (m, 2 H), 3.94 (s, 3 H), 3.39 (d, J = 7.2 Hz, 2 H), 1.69 - 1.71 (m, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 169.3 (s), 139.8 (s), 136.7 (s), 130.8 (s), 129.0 (s), 128.2 (s), 127.5 (s), 92.2 (s), 52.4 (s), 37.2 (s), 17.8 (s) ppm; δ (*Z*-isomer) = 169.4 (s), 139.9 (s), 139.7 (s), 136.6 (s), 130.7 (s), 128.6 (s), 127.3 (s), 125.9 (s), 92.1 (s), 52.5 (s), 31.3 (s), 12.8 (s) ppm.
IR (ATR) 2948, 1729, 1558, 1438, 1269, 1097, 1058, 956, 823, 689 cm^{-1} .
MS (EI) m/z (%) 316 (96) [M^+], 284 (99), 259 (40), 157(41), 129 (100), 115 (48).
HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_2$ [$\text{M}+\text{H}$] $^+$ 317.0033, Found 317.0032.

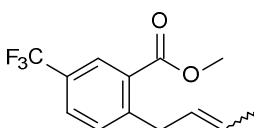
Methyl 2-(but-2-enyl)-5-methyl-benzoate (3ea):



Compound **3ea** was prepared following the general procedure for the *ortho*-allylation from 3-methylbenzoic acid (68.8 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (73 mg, 72%, *E/Z* 2.1:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.68 (m, 1 H), 7.24 (dd, J = 7.9, 1.7 Hz, 1 H), 7.18 (t, J = 6.2 Hz, 1 H), 5.33 - 5.69 (m, 2 H), 3.89 (s, 3 H), 3.64 (d, J = 6.4 Hz, 2 H), 2.35 (s, 3 H), 1.67 (dq, J = 6.2, 1.5 Hz, 3 H) ppm; δ (*Z*-isomer) = 7.68 (m, 1 H), 7.24 (dd, J = 7.9, 1.7 Hz, 1 H), 7.18 (t, J = 6.2 Hz, 1 H), 5.33 - 5.69 (m, 2 H), 3.90 (s, 3 H), 3.72 (d, J = 5.7 Hz, 2 H), 2.35 (s, 3 H), 1.70 - 1.76 (m, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 168.34 (s), 139.5 (s), 135.5 (s), 132.68 (s), 130.86 (s), 130.7 (s), 130.1 (s), 129.35 (s), 126.0 (s), 51.79 (s), 36.8 (s), 20.74 (s), 17.9 (s) ppm; δ (*Z*-isomer) = 168.29 (s), 139.4 (s), 135.4 (s), 132.70 (s), 130.94 (s), 130.3 (s), 129.42 (s), 129.1 (s), 124.6 (s), 51.84 (s), 31.2 (s), 20.74 (s), 12.9 (s) ppm.
IR (ATR) 2950, 1720, 1434, 1265, 1206, 1075, 967, 827, 788, 679 cm^{-1} .
MS (EI) m/z (%) 204 (54) [M^+], 172 (100), 157 (32), 145 (47), 129 (79), 115 (34).
HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_2$ [$\text{M}+\text{H}$] $^+$ 205.1223, found 205.1222.

Methyl 2-(but-2-enyl)-5-(trifluoromethyl)benzoate (3fa):



Compound **3fa** was prepared following the general procedure for the *ortho*-allylation from 3-(trifluoromethyl)benzoic acid (97 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (69 mg, 53%, *E/Z* 2.3:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 8.14 (m, 1 H), 7.67 (dd, J = 8.2, 1.7 Hz, 1 H), 7.43 (t, J = 6.4 Hz, 1 H), 5.42 - 5.73 (m, 2 H), 3.93 (s, 3 H), 3.74 (d, J = 5.9 Hz, 2 H), 1.64 - 1.70 (m, 3 H) ppm; δ (*Z*-isomer) = 8.13 (m, 1 H), 7.67 (dd, J = 8.2, 1.7 Hz, 1 H), 7.43 (t, J = 6.4 Hz, 1 H), 5.42 - 5.73 (m, 2 H), 3.93 (s, 3 H), 3.83 (d, J = 6.8 Hz, 2 H), 1.71 - 1.76 (m, 3 H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ (*E+Z*) = 166.9 (s, *E*), 166.8 (s, *Z*), 146.8 (q, $J = 1.7$ Hz, *Z*), 146.7 (q, $J = 1.7$ Hz, *E*), 131.4 (s, *E*), 131.0 (s, *Z*), 130.2 (s, *Z*), 130.1 (s, *E*), 128.7 (s, *E* or *Z*), 128.2 - 128.4 (m, *E+Z*), 128.4 (q, $J = 33.2$ Hz, *E+Z*), 127.6 (s, *E* or *Z*), 127.5 (q, $J = 4.3$ Hz, *E+Z*), 127.4 (s, *E* or *Z*), 126.0 (s, *E* or *Z*), 127.2 (q, $J = 272.0$ Hz, *E+Z*), 52.3 (s, *E* or *Z*), 52.2 (s, *E* or *Z*), 37.1 (s, *E*), 31.5 (s, *Z*), 17.9 (s, *E*), 12.9 (s, *Z*) ppm.

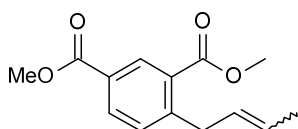
^{19}F NMR (235 MHz, CDCl_3) $\delta = -62.63$ ppm.

IR (ATR) 2955, 1727, 1336, 1241, 1168, 1123, 1076, 969, 838, 812 cm^{-1} .

MS (EI) m/z (%) 258 (29) $[\text{M}]^+$, 226 (100), 201 (32), 177 (27), 129 (48), 115 (14).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{O}_2$ $[\text{M}]^+$ 258.0868, found 258.0860.

Dimethyl 4-(but-2-enyl)benzene-1,3-dicarboxylate (3ga):



Compound **3ga** was prepared following the general procedure for the *ortho*-allylation from 3-methoxycarbonylbenzoic acid (92.9 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (82 mg, 66%, *E/Z* 1.4:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 8.49 - 8.54 (m, 1 H), 8.07 (dd, $J = 8.0, 1.9$ Hz, 1 H), 7.36 (d, $J = 8.1$ Hz, 1 H), 5.38 - 5.69 (m, 2 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.72 (d, $J = 6.1$ Hz, 2 H), 1.63 - 1.69 (m, 3 H) ppm; δ (*Z*-isomer) = 8.49 - 8.54 (m, 1 H), 8.07 (dd, $J = 8.0, 1.9$ Hz, 1 H), 7.39 (d, $J = 8.1$ Hz, 1 H), 5.38 - 5.69 (m, 2 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.81 (d, $J = 7.0$ Hz, 2 H), 1.69 - 1.74 (m, 3 H) ppm.

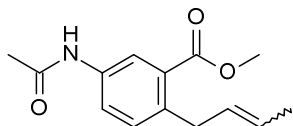
^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 167.28 (s), 166.3 (s), 147.8 (s), 132.67 (s), 131.8 (s), 131.7 (s), 129.8 (s), 128.9 (s), 129.1 (s), 127.2 (s), 52.23 (s), 52.16 (s), 37.3 (s), 18.0 (s) ppm; δ (*Z*-isomer) = 167.35 (s), 163.3 (s), 148.0 (s), 132.70 (s), 131.9 (s), 130.7 (s), 129.9 (s), 128.0 (s), 127.8 (s), 125.8 (s), 52.23 (s), 52.21 (s), 31.7 (s), 24.2 (s), 13.0 (s) ppm.

IR (ATR) 2953, 1718, 1434, 1303, 1228, 1118, 1074, 991, 761 cm^{-1} .

MS (EI) m/z (%) 248 (44) $[\text{M}]^+$, 219 (100), 185 (34), 157 (77), 129 (60), 115 (25).

HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 271.0941, Found 271.0588.

Methyl 5-acetamido-2-(but-2-enyl)benzoate (3ha):



Compound **3ha** was prepared following the general procedure for the *ortho*-allylation from 3-acetamidobenzoic acid (91.4 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a white solid (86 mg, 70%, *E/Z* 1.9:1).

m.p. 88 - 89 $^{\circ}\text{C}$

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 8.25 (br. s, 1 H), 7.93 - 7.99 (m, 1 H), 7.61 - 7.69 (m, 1 H), 7.17 (d, $J = 8.3$ Hz, 1 H), 5.34 - 5.62 (m, 2 H), 3.81 (s, 3 H), 3.59 (d, $J = 6.4$ Hz, 2 H), 2.15 (s, 3 H), 1.63 (dq, $J = 6.2, 1.3$ Hz, 3 H) ppm; δ (*Z*-isomer) = 8.25 (br. s, 1 H), 7.93 - 7.99 (m, 1 H), 7.61 - 7.69 (m, 1 H), 7.21 (d, $J = 8.3$ Hz, 1 H), 5.34 - 5.62 (m, 2 H), 3.82 (s, 3 H), 3.68 (d, $J = 6.2$ Hz, 2 H), 2.15 (s, 3 H), 1.66 - 1.72 (m, 3 H) ppm.

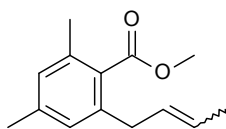
^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 169.0 (s), 167.76 (s), 138.2 (s), 136.02 (s), 131.3 (s), 129.70 (s), 129.65 (s), 126.2 (s), 123.6 (s), 121.8 (s), 51.9 (s), 36.6 (s), 24.2 (s), 17.8 (s) ppm; δ (*Z*-isomer) = 169.0 (s), 167.81 (s), 138.3 (s), 135.96 (s), 130.9 (s), 129.8 (s), 128.7 (s), 124.8 (s), 123.7 (s), 121.9 (s), 52.0 (s), 31.0 (s), 24.2 (s), 12.8 (s) ppm.

IR (ATR) 3296, 2950, 1724, 1665, 1536, 1499, 1279, 1212, 1074, 967, 807 cm^{-1} .

MS (EI) m/z (%) 247 (42) $[\text{M}]^+$, 215 (29), 173 (100), 146 (38), 130 (29), 115 (12).

HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{17}\text{NaNO}_3$ $[\text{M}+\text{Na}]^+$ 270.1101, Found 270.1108.

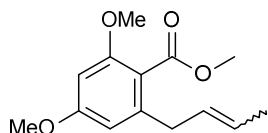
Methyl 2-(but-2-enyl)-4,6-dimethylbenzoate (3ia):



Compound **3ia** was prepared following the general procedure for the *ortho*-allylation from 2,4-dimethylbenzoic acid (76.6 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (88 mg, 81%, *E/Z* 2:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 6.80 - 6.92 (m, 2 H), 5.40 - 5.64 (m, 2 H), 3.88 (s, 3 H), 3.29 (d, J = 5.3 Hz, 2 H), 2.30 (s, 3 H), 2.29 (s, 3 H), 1.65 - 1.69 (m, 3 H) ppm; δ (*Z*-isomer) = 6.80 - 6.92 (m, 2 H), 5.40 - 5.64 (m, 2 H), 3.88 (s, 3 H), 3.38 (d, J = 6.6 Hz, 1 H), 2.30 (s, 3 H), 2.29 (s, 3 H), 1.69 - 1.73 (m, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3): δ (*E*-isomer) = 170.53 (s), 139.42 (s), 138.3 (s), 135.1 (s), 130.7 (s), 129.4 (s), 128.8 (s), 127.6 (s), 126.5 (s), 51.7 (s), 36.9 (s), 21.16 (s), 19.7 (s), 17.9 (s) ppm; δ (*Z*-isomer) = 170.48 (s), 139.39 (s), 138.1 (s), 135.1 (s), 130.6 (s), 128.7 (s), 128.6 (s), 127.3 (s), 124.9 (s), 51.8 (s), 31.1 (s), 21.18 (s), 19.7 (s), 12.9 (s) ppm.
 IR (ATR) 2950, 1725, 1379, 1265, 1164, 1081, 966, 854, 811 cm^{-1} .
 MS (EI) m/z (%) 218 (74) $[\text{M}]^+$, 186 (100), 171 (76), 159 (63), 143 (66), 128 (51), 115 (32).
 HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 241.1199, Found 241.1199.

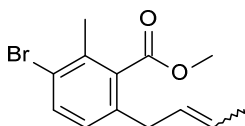
Methyl 2-(but-2-enyl)-4,6-dimethoxy-benzoate (3ja):



Compound **3ja** was prepared following the general procedure for the *ortho*-allylation from 2,4-dimethoxybenzoic acid (127 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (105 mg, 84%, *E/Z* 1.9:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 6.28 - 6.37 (m, 2 H), 5.38 - 5.66 (m, 2 H), 3.85 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.23 - 3.30 (m, 2 H), 1.61 - 1.73 (m, 3 H) ppm; δ (*Z*-isomer) = 6.28 - 6.37 (m, 2 H), 5.38 - 5.66 (m, 2 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.34 (d, J = 7.0 Hz, 2 H), 1.61 - 1.73 (m, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 168.48 (s), 161.37 (s), 158.0 (s), 141.1 (s), 128.7 (s), 126.8 (s), 116.6 (s), 105.9 (s), 96.22 (s), 55.76 (s), 55.21 (s), 52.0 (s), 36.9 (s), 17.8 (s) ppm; δ (*Z*-isomer) = 168.53 (s), 161.41 (s), 158.0 (s), 141.3 (s), 127.9 (s), 125.3 (s), 116.1 (s), 105.6 (s), 96.18 (s), 55.78 (s), 55.20 (s), 51.9 (s), 31.0 (s), 12.8 (s) ppm.
 IR (ATR) 2947, 1722, 1602, 1429, 1325, 1261, 1155, 1097, 1045, 966, 831 cm^{-1} .
 MS (EI) m/z (%) 250 (62) $[\text{M}]^+$, 219 (100), 191 (45), 175 (40), 145 (21), 115 (21).
 HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 273.1097, found 273.1102.

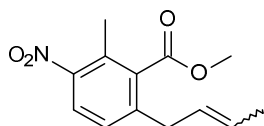
Methyl 3-bromo-6-(but-2-enyl)-2-methyl-benzoate (3ka):



Compound **3ka** was prepared following the general procedure for the *ortho*-allylation from 3-bromo-2-methylbenzoic acid (111 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (110 mg, 78%, *E/Z* 1.9:1).

^1H NMR (300 MHz, CDCl_3) δ (*E*-isomer) = 7.50 (d, J = 8.3 Hz, 1 H), 6.93 (dd, J = 8.3, 0.6 Hz, 1 H), 5.38 - 5.67 (m, 2 H), 3.91 (s, 3 H), 3.18 - 3.27 (m, 2 H), 2.35 (s, 3 H), 1.64 - 1.69 (m, 3 H) ppm; δ (*Z*-isomer) = 7.50 (d, J = 8.3 Hz, 1 H), 6.95 (dd, J = 8.4, 0.7 Hz, 1 H), 5.38 - 5.67 (m, 2 H), 3.91 (s, 3 H), 3.32 (d, J = 7.0 Hz, 2 H), 2.35 (s, 3 H), 1.69 - 1.72 (m, 3 H) ppm.
 ^{13}C NMR (75 MHz, CDCl_3) δ (*E*-isomer) = 169.61 (s), 137.1 (s), 135.5 (s), 134.2 (s), 133.43 (s), 128.5 (s), 128.4 (s), 127.3 (s), 123.1 (s), 52.2 (s), 36.6 (s), 20.4 (s), 17.9 (s) ppm; δ (*Z*-isomer) = 168.55 (s), 137.3 (s), 135.4 (s), 134.2 (s), 132.40 (s), 128.1 (s), 127.6 (s), 125.7 (s), 123.0 (s), 52.3 (s), 30.7 (s), 20.4 (s), 12.9 (s) ppm.
 IR (ATR) 2949, 1728, 1434, 1266, 1236, 1147, 1089, 964, 835, 737 cm^{-1} .
 MS (EI) m/z (%) 284 (42) $[\text{M}^{+}(^{81}\text{Br})]$, 282 (43) $[\text{M}^{+}(^{79}\text{Br})]$, 253 (50), 225 (35), 171 (100), 143 (59), 128 (75), 115 (32).
 HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{NaO}_2\text{Br}$ $[\text{M}+\text{Na}]^+$ 305.0148, Found 305.0147.

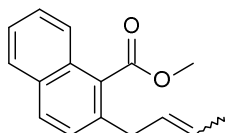
Methyl 6-(but-2-enyl)-2-methyl-3-nitro-benzoate (3la):



Compound **3la** was prepared following the general procedure ($T = 60\text{ }^\circ\text{C}$) for the *ortho*-allylation from 2-methyl-3-nitrobenzoic acid (91.5 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL , 0.75 mmol) and isolated as a colorless oil (47 mg, 38%, *E/Z* 2.3:1).

¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) = 7.86 (d, *J* = 8.4 Hz, 1 H), 7.22 (d, *J* = 8.4 Hz, 1 H), 5.35 - 5.74 (m, 2 H), 3.94 (s, 3 H), 3.33 (d, *J* = 5.1 Hz, 2 H), 2.46 (s, 3 H), 1.64 - 1.73 (m, 3 H) ppm; δ (*Z*-isomer) = 7.86 (d, *J* = 8.4 Hz, 1 H), 7.22 (d, *J* = 8.4 Hz, 1 H), 5.35 - 5.74 (m, 2 H), 3.95 (s, 3 H), 3.41 (d, *J* = 7.2 Hz, 2 H), 2.46 (m, 3 H), 1.64 - 1.73 (m, 3 H) ppm.
¹³C NMR (75 MHz, CDCl₃) δ (*E*-isomer) = 168.56 (s), 148.3 (s), 143.2 (s), 136.6 (s), 128.5 (s), 127.9 (s), 127.4 (s), 126.8 (s), 125.25 (s), 52.4 (s), 36.3 (s), 17.8 (s), 16.7 (s) ppm; δ (*Z*-isomer) = 168.61 (s), 148.3 (s), 143.4 (s), 136.7 (s), 130.1 (s), 127.5 (s), 126.7 (s), 126.4 (s), 125.30 (s), 52.5 (s), 31.1 (s), 16.7 (s), 12.9 (s) ppm.
 IR (ATR) 2953, 1731, 1522, 1436, 1415, 1275, 1239, 1116, 968, 867 cm⁻¹.
 MS (EI) *m/z* (%) 249 (77) [M]⁺, 220 (91), 192 (52), 172 (52), 156 (29), 128 (100), 103 (18).
 HRMS (EI-TOF) *m/z* calcd. for C₁₃H₁₅NO₂ [M]⁺ 249.1001, found 249.1007.

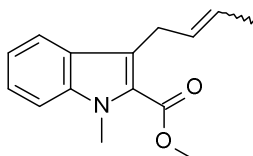
Methyl 2-(but-2-enyl)naphthalene-1-carboxylate (3ma):



Compound **3ma** was prepared following the general procedure for the *ortho*-allylation from 1-naphthalenecarboxylic acid (89.7 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL, 0.75 mmol) and isolated as a colorless oil (105 mg, 87%, *E/Z* 1.9:1).

¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) = 7.75 - 7.90 (m, 3 H), 7.50 (ddd, *J* = 9.4, 7.7, 1.5 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 1 H), 5.43 - 5.71 (m, 2 H), 4.04 (s, 3 H), 3.50 (dd, *J* = 5.2, 1.4 Hz, 2 H), 1.70 (dt, *J* = 4.8, 1.4 Hz, 3 H) ppm; δ (*Z*-isomer) = 7.75 - 7.90 (m, 3 H), 7.50 (ddd, *J* = 9.4, 7.7, 1.5 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 1 H), 5.43 - 5.71 (m, 2 H), 4.05 (s, 3 H), 3.57 (d, *J* = 6.4 Hz, 2 H), 1.75 - 1.80 (m, 3 H) ppm.
¹³C NMR (75 MHz, CDCl₃) δ (*E+Z*) = 170.01 (s), 170.96 (s), 136.4 (s), 136.1 (s), 131.8 (s), 131.7 (s), 130.0 (s), 129.9 (s), 129.80 (s), 129.77 (s), 129.0 (s), 128.2 (s), 128.0 (s), 127.4 (s), 127.2 (s), 127.0 (s), 126.9 (s), 125.61 (s), 125.59 (s), 125.2 (s), 124.6 (s), 124.5 (s), 52.2 (s), 52.1 (s), 37.3 (s), 31.5 (s), 17.8 (s), 12.9 (s) ppm.
 IR (ATR) 2949, 1724, 1434, 1245, 1210, 1136, 1034, 968, 850, 746 cm⁻¹.
 MS (EI) *m/z* (%) 240 (69) [M]⁺, 211 (100), 181 (45), 165 (99), 152 (22), 139 (21), 115 (13).
 HRMS (ESI) *m/z* calcd. for C₁₆H₁₆NaO₂ [M+Na]⁺ 263.1043, Found 263.1047.

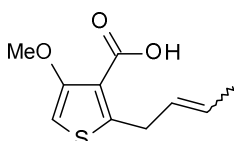
Methyl 3-(but-2-enyl)-1-methyl-indole-2-carboxylate (3na):



Compound **3na** was prepared following the general procedure for the *ortho*-allylation from 1-methylindole-2-carboxylic acid (89.4 mg, 0.50 mmol) and 3-buten-2-ol (67.3 μL, 0.75 mmol) and isolated as a colorless oil (100 mg, 75%, *E/Z* 1.2:1).

¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) = 7.70 (ddt, *J* = 8.1, 3.1, 0.9 Hz, 1 H), 7.37 (d, *J* = 3.9 Hz, 2 H), 7.09 - 7.19 (m, 1 H), 5.38 - 5.70 (m, 2 H), 4.02 (s, 3 H), 3.96 (s, 3 H), 3.88 (d, *J* = 6.1 Hz, 2 H), 1.83 - 1.89 (m, 3 H) ppm; δ (*Z*-isomer) = 7.70 (ddt, *J* = 8.1, 3.1, 0.9 Hz, 1 H), 7.37 (d, *J* = 3.9 Hz, 2 H), 7.09 - 7.19 (m, 1 H), 5.38 - 5.70 (m, 2 H), 4.02 (s, 3 H), 3.96 (s, 3 H), 3.80 (d, *J* = 5.9 Hz, 2 H), 1.61 - 1.67 (m, 3 H) ppm.
¹³C NMR (75 MHz, CDCl₃) δ (*E+Z*) = 163.2 (s), 138.8 (s), 129.7 (s), 129.5 (s), 126.4 (s), 125.22 (s), 125.20 (s), 125.1 (s), 124.4 (s), 123.7 (s), 123.3 (s), 120.89 (s), 120.86 (s), 119.8 (s), 110.1 (s), 51.4 (s), 51.3 (s), 32.0 (s), 28.6 (s), 23.4 (s), 17.8 (s), 13.0 (s) ppm.
 IR (ATR) 2948, 1701, 1438, 1342, 1239, 1129, 1102, 965, 737 cm⁻¹.
 MS (EI) *m/z* (%) 243 (100) [M]⁺, 228 (35), 184 (66), 168 (54), 128 (12), 115 (12).
 HRMS (ESI) *m/z* calcd. for C₁₅H₁₇NaNO₂ [M+Na]⁺ 266.1152, Found 266.1158.

2-(But-2-enyl)-4-methoxy-thiophene-3-carboxylic acid (3oa):



An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (6.46 mg, 0.01 mmol), K₃PO₄ (53.2 mg, 0.25 mmol) and 4-methoxythiophene-3-carboxylic acid (83.3 g, 0.50 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-

trichloroethanol (0.5 mL) and 3-buten-2-ol (67.3 μ L, 0.75 mmol) were added via syringe. The resulting mixture was stirred at 50 °C for 16 h. After the reaction was complete, it was diluted with EtOAc (10 mL) and extracted with aq. K₂CO₃ solution (3 \times 10 mL). The combined aqueous phases were acidified with 2M HCl (pH 1-2), then extracted with EtOAc (3 \times 30 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO₂, ethyl acetate/cyclohexane gradient, 1% HCOOH) and compound **30a** was isolated as a white solid (69 mg, 64%, *E/Z* 1.9:1).

m.p. 62 – 63 °C.

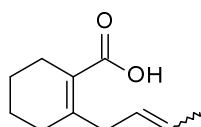
¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) = 6.20 (s, 1 H), 5.56 - 5.80 (m, 2 H), 3.99 (s, 3 H), 3.86 - 3.92 (m, 2 H), 1.65 - 1.75 (m, 3 H) ppm; δ (*Z*-isomer) = 6.20 (s, 1 H), 5.56 - 5.80 (m, 2 H), 3.99 (s, 3 H), 3.97 - 4.01 (m, 2 H), 1.65 - 1.75 (m, 3 H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ (*E*-isomer) = 162.76 (s), 157.4 (s), 155.2 (s), 129.2 (s), 126.8 (s), 116.6 (s), 94.93 (s), 58.1 (s), 38.8 (s), 17.8 (s) ppm; δ (*Z*-isomer) = 162.82 (s), 157.1 (s), 155.2 (s), 128.0 (s), 125.7 (s), 116.7 (s), 94.87 (s), 58.1 (s), 28.4 (s), 12.8 (s) ppm.

IR (ATR) 3305, 2938, 1729, 1676, 1554, 1468, 1381, 1287, 1089, 967, 705 cm⁻¹.

HRMS (ESI) *m/z* calcd. for C₁₀H₁₂NaSO₃ [M+Na⁺] 235.0399, Found 235.0400.

2-(but-2-enyl)cyclohexene-1-carboxylic acid (**3pa**):



An oven-dried 20 mL vial was charged with [Ru(*p*-cymene)Cl₂]₂ (6.46 mg, 0.01 mmol), K₂CO₃ (69.1 mg, 0.50 mmol) and 1-cyclohexene-1-carboxylic acid (65.0 mg, 0.50 mmol) and closed with a septum cap. Under exclusion of air and water, 2,2,2-trichloroethanol (0.5 mL) and 3-buten-2-ol (67.3 μ L, 0.75 mmol) were added via syringe. The resulting mixture was stirred at 60 °C for 16 h. After the reaction was complete, it was diluted with EtOAc (10 mL) and extracted with aq. K₂CO₃ solution (3 \times 10 mL). The combined aqueous phases were acidified with 2M HCl (pH 1-2), then extracted with EtOAc (3 \times 30 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO₂, ethyl acetate/cyclohexane gradient, 1% HCOOH) and compound **3pa** was isolated as a white solid (average of 2 runs, 39 mg, 43%, *E/Z* 1.9:1).

m.p. 76 – 77 °C

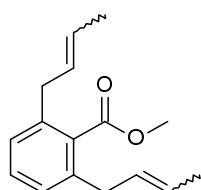
¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) = 5.31 - 5.63 (m, 2 H), 3.14 (d, *J* = 5.3 Hz, 2 H), 2.26 - 2.39 (m, 2 H), 2.08 - 2.23 (m, 2 H), 1.64 - 1.68 (m, 3 H), 1.53 - 1.64 (m, 4 H) ppm; δ (*Z*-isomer) = 5.31 - 5.63 (m, 2 H), 3.26 (d, *J* = 7.0 Hz, 2 H), 2.26 - 2.39 (m, 2 H), 2.08 - 2.23 (m, 2 H), 1.68 - 1.71 (m, 3 H), 1.53 - 1.64 (m, 4 H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ (*E*-isomer) = 174.2 (s), 152.0 (s), 128.4 (s), 126.6 (s), 123.6 (s), 38.9 (s), 31.4 (s), 26.3 (s), 22.3 (s), 22.15 (s), 17.9 (s) ppm; δ (*Z*-isomer) = 174.3 (s), 152.2 (s), 127.8 (s), 125.1 (s), 123.8 (s), 33.3 (s), 31.6 (s), 26.4 (s), 22.24 (s), 22.18 (s), 13.0 (s) ppm.

IR (ATR) 2939, 2627, 1663, 1615, 1289, 980, 966, 746, 647 cm⁻¹.

HRMS (ESI) *m/z* calcd. for C₁₁H₁₆NaO₂ [M+Na]⁺ 203.1043, Found 203.1047.

Methyl 2,6-bis(but-2-enyl)benzoate (**3qa**):



Compound **3qa** was prepared following the general procedure for the *ortho*-allylation from benzoic acid (61.7 mg, 0.50 mmol) and 3-buten-2-ol (112 μ L, 1.25 mmol) and isolated as a colorless oil (100 mg, 82%, *E/Z* 2.1:1).

¹H NMR (300 MHz, CDCl₃) δ (*E+Z*) = 7.27 (t, *J* = 8.4 Hz, 1 H), 7.09 (d, *J* = 7.7 Hz, 2 H), 5.40 - 5.65 (m, 4 H), 3.88 (m, 3 H), 3.40 (d, *J* = 6.6 Hz, 4 H-*Z*), 3.32 (d, *J* = 4.8 Hz, 4 H-*E*), 1.65 - 1.73 (m, 6 H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ (*E+Z*) = 170.21 (s), 170.15 (s), 138.2 (s), 138.1 (s), 133.2 (s), 133.1 (s), 129.6 (s), 129.5 (s), 129.2 (s), 128.33 (s), 128.31 (s), 127.23 (s), 127.18 (s), 127.0 (s), 126.9 (s), 126.7 (s), 125.1 (s), 51.8 (s), 51.7 (s), 36.9 (s), 31.1 (s), 17.9 (s), 12.8 (s) ppm.

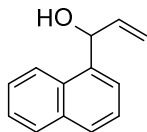
IR (ATR) 2964, 1727, 1430, 1266, 1114, 1101, 965, 826 cm⁻¹.

MS (EI) *m/z* (%) 244 (83) [M]⁺, 213 (53), 183 (100), 168 (38), 155 (33), 128 (72), 115 (49).

HRMS (ESI) *m/z* calcd. for C₁₆H₂₀NaO₂ [M+Na]⁺ 267.1356, Found 267.1361.

Synthesis of starting materials

1-(1-naphthyl)prop-2-en-1-ol (**2f**) [CAS 61619-02-1]:

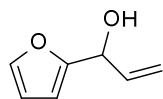


Compound **2f** was synthesised following a literature procedure^[4] from 1-naphthaldehyde (1.64 g, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (93% yield).

¹H NMR (300 MHz, CDCl₃) δ = 8.16 - 8.24 (m, 1 H), 7.76 - 7.94 (m, 2 H), 7.64 (dt, J = 6.9, 1.1 Hz, 1 H), 7.41 - 7.59 (m, 3 H), 6.27 (ddd, J = 17.2, 10.5, 5.3 Hz, 1 H), 5.85 - 6.01 (m, 1 H), 5.47 (dt, J = 17.2, 1.5 Hz, 1 H), 5.30 (dt, J = 10.3, 1.4 Hz, 1 H), 2.11 (d, J = 4.2 Hz, 1 H) ppm.

The analytical data matched those reported in the literature.^[5]

1-(2-furyl)prop-2-en-1-ol (**2g**) [CAS: 116914-87-5]:

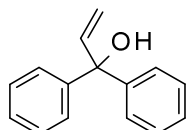


Compound **2g** was synthesised following a literature procedure^[4] from 2-furaldehyde (0.82 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (52% yield).

¹H NMR (300 MHz, CDCl₃) δ = 7.41 (dd, J = 2.0, 0.9 Hz, 1 H), 6.35 (dd, J = 3.3, 1.8 Hz, 1 H), 6.22 - 6.29 (m, 1 H), 6.13 (ddd, J = 17.2, 10.3, 5.7 Hz, 1 H), 5.43 (dt, J = 17.2, 1.4 Hz, 1 H), 5.29 (dt, J = 10.4, 1.3 Hz, 1 H), 5.24 (t, J = 5.1 Hz, 1 H), 2.18 (d, J = 5.1 Hz, 1 H) ppm.

The analytical data matched those reported in the literature.^[6]

1,1-diphenylprop-2-en-1-ol (**2i**) [CAS: 3923-51-1]:

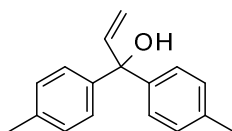


Compound **2i** was synthesised following a literature procedure^[4] from benzophenone (1.28 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (93% yield).

¹H NMR (300 MHz, CDCl₃) δ = 7.09 - 7.54 (m, 10 H), 6.53 (dd, J = 17.2, 10.3 Hz, 1 H), 5.11 - 5.51 (m, 2 H), 2.28 (d, J = 1.7 Hz, 1 H) ppm.

The analytical data matched those reported in the literature.^[7]

1,1-bis(p-tolyl)prop-2-en-1-ol (**2j**) [CAS: 278188-16-2]:

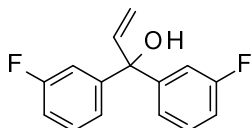


Compound **2j** was synthesised following a literature procedure^[4] from 4,4'-dimethylbenzophenone (2.12 g, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (63% yield).

¹H NMR (300 MHz, CDCl₃) δ = 7.20 - 7.29 (m, 4 H), 7.06 - 7.15 (m, 4 H), 6.47 (dd, J = 17.1, 10.6 Hz, 1 H), 5.33 (dd, J = 17.1, 1.3 Hz, 0 H), 5.27 (dd, J = 10.6, 1.3 Hz, 1 H), 2.33 (s, 6 H), 2.22 (s, 1 H) ppm.

The analytical data matched those reported in the literature.^[7]

1,1-bis(3-fluorophenyl)prop-2-en-1-ol (2k) [CAS: 1639040-60-0]:



Compound **2k** was synthesised following a literature procedure from 3,3'-difluorobenzophenone (0.98 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (92% yield).

^1H NMR (300 MHz, CDCl_3) δ = 7.19 - 7.32 (m, 2 H), 7.03 - 7.15 (m, 4 H), 6.87 - 7.00 (m, 2 H), 6.42 (dd, J = 17.1, 10.6 Hz, 1 H), 5.23 - 5.40 (m, 2 H), 2.31 (s, 1 H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ = 162.7 (d, J = 246.0 Hz), 147.8 (d, J = 6.6 Hz), 142.4 (s), 129.7 (d, J = 7.7 Hz), 122.5 (d, J = 2.8 Hz), 115.2 (s), 114.4 (d, J = 21.0 Hz), 114.0 (d, J = 23.2 Hz), 78.7 (d, J = 1.7 Hz) ppm.

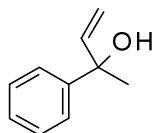
^{19}F NMR (235 MHz, CDCl_3) δ = -112.46 ppm.

IR (ATR) 3444, 1587, 1483, 1409, 1230, 1141, 862, 780, 697 cm^{-1} .

MS (EI) m/z (%) 246 (43) $[\text{M}]^+$, 228 (13), 151 (17), 123 (100), 109 (12).

HRMS (EI-TOF) m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{O}$ $[\text{M}]^+$ 246.0856, found, 246.0855.

2-phenylbut-3-en-2-ol (2l) [CAS: 6051-52-1]:

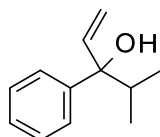


Compound **2l** was synthesised following a literature procedure^[4] from acetophenone (1.28 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (89% yield).

^1H NMR (300 MHz, CDCl_3) δ = 7.45 - 7.53 (m, 2 H), 7.32 - 7.40 (m, 2 H), 7.23 - 7.31 (m, 1 H), 6.19 (dd, J = 17.2, 10.6 Hz, 1 H), 5.31 (dd, J = 17.3, 1.2 Hz, 1 H), 5.16 (dd, J = 10.6, 1.1 Hz, 1 H), 1.88 (br. s, 1 H), 1.68 (s, 3 H) ppm.

The analytical data matched those reported in the literature.^[9]

4-methyl-3-phenyl-pent-1-en-3-ol (2m) [CAS: 201789-85-7]:

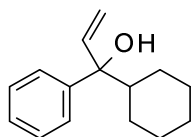


Compound **2m** was synthesised following a literature procedure^[4] from isobutyrophenone (1.55 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (76% yield).

^1H NMR (300 MHz, CDCl_3) δ = 7.41 - 7.53 (m, 2 H), 7.30 - 7.40 (m, 2 H), 7.18 - 7.29 (m, 1 H), 6.32 (dd, J = 17.1, 10.7 Hz, 1 H), 5.34 (dd, J = 17.2, 1.3 Hz, 1 H), 5.21 (dd, J = 10.8, 1.3 Hz, 1 H), 2.21 (quin, J = 6.8 Hz, 1 H), 1.79 (s, 1 H), 0.93 (d, J = 7.0 Hz, 3 H), 0.80 (d, J = 6.8 Hz, 3 H) ppm.

The analytical data matched those reported in the literature.^[9]

1-cyclohexyl-1-phenyl-prop-2-en-1-ol (2n) [CAS: 136779-82-3]:

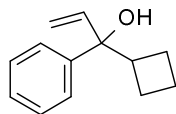


Compound **2n** was synthesised following a literature procedure^[4] from cyclohexyl phenyl ketone (1.92 g, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (71% yield).

^1H NMR (300 MHz, CDCl_3) δ = 7.16 - 7.55 (m, 5 H), 6.32 (dd, J = 17.1, 10.7 Hz, 1 H), 5.33 (dd, J = 17.2, 1.3 Hz, 1 H), 5.20 (dd, J = 10.6, 1.3 Hz, 1 H), 1.54 - 1.93 (m, 6 H), 1.42 - 1.54 (m, 1 H), 0.90 - 1.27 (m, 5 H) ppm.

The analytical data matched those reported in the literature.^[10]

1-cyclobutyl-1-phenyl-prop-2-en-1-ol (**2o**):



Compound **2o** was synthesised following a literature procedure^[4] from cyclobutyl phenyl ketone (1.56 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (80% yield).

¹H NMR (300 MHz, CDCl₃) δ = 7.40 - 7.49 (m, 2 H), 7.30 - 7.38 (m, 2 H), 7.19 - 7.29 (m, 1 H), 6.14 (dd, J = 17.2, 10.6 Hz, 1 H), 5.30 (dd, J = 17.2, 1.3 Hz, 1 H), 5.18 (dd, J = 10.8, 1.3 Hz, 1 H), 2.86 - 3.03 (m, 1 H), 1.91 - 2.14 (m, 3 H), 1.89 (s, 1 H), 1.63 - 1.88 (m, 3 H) ppm.

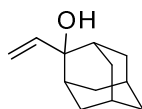
¹³C NMR (75 MHz, CDCl₃) δ = 144.6 (s), 142.3 (s), 128.0 (s), 126.7 (s), 125.5 (s), 131.1 (s), 77.2 (s), 44.0 (s), 22.7 (s), 22.2 (s), 16.9 (s) ppm.

IR (ATR) 3471, 1492, 1446, 1159, 992, 918, 754, 698 cm⁻¹.

MS (EI) m/z (%) 188 (2) [M]⁺, 155 (11), 141 (22), 133 (100), 105 (30).

HRMS (ESI) m/z calcd. for C₁₃H₁₆NaO [M+Na]⁺ 211.1093, Found 211.1091.

2-vinyladamantan-2-ol (**2q**) [CAS: 1597185-77-7]:



Compound **2q** was synthesised following a literature procedure^[4] from 2-adamantanone (1.53 g, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as white solid (84% yield).

m.p.: 60 – 61 °C

¹H NMR (300 MHz, CDCl₃) δ = 6.28 (dd, J = 17.5, 10.9 Hz, 1 H), 5.36 (dd, J = 17.6, 1.5 Hz, 1 H), 5.08 - 5.22 (m, 1 H), 2.21 - 2.35 (m, 2 H), 1.67 - 1.97 (m, 9 H), 1.51 - 1.63 (m, 2 H), 1.38 (s, 1 H) ppm.

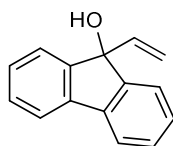
¹³C NMR (75 MHz, CDCl₃) δ = 144.8 (s), 113.5 (s), 74.7 (s), 38.0 (s), 37.9 (s), 34.7 (s), 32.8 (s), 27.4 (s), 27.1 (s) ppm.

IR (ATR) 3335, 2896, 1451, 1334, 991, 922, 663 cm⁻¹.

MS (EI) m/z (%) 178 (100) [M]⁺, 149 (30), 135 (47), 109 (26), 91 (31).

HRMS (ESI) m/z calcd. for C₁₂H₁₈NaO [M+Na]⁺ 201.1250, Found 201.1252.

9-vinylfluoren-9-ol (**2r**) [CAS: 92496-21-4]:

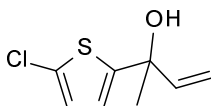


Compound **2r** was synthesised following a literature procedure^[4] from 9-fluorenone (1.82 g, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (56% yield).

¹H NMR (300 MHz, CDCl₃) δ = 7.44 - 7.51 (m, 2 H), 7.36 - 7.43 (m, 2 H), 7.28 - 7.36 (m, 2 H), 6.01 (ddd, J = 17.1, 10.5, 0.6 Hz, 1 H), 5.57 (dd, J = 17.1, 1.5 Hz, 1 H), 5.23 (dd, J = 10.5, 1.5 Hz, 1 H), 2.20 (d, J = 0.7 Hz, 1 H) ppm.

The analytical data (NMR) matched the ones reported in the literature.^[11]

2-(5-chloro-2-thienyl)but-3-en-2-ol (**2s**):



Compound **2s** was synthesised following a literature procedure^[4] from 2-acetyl-5-chlorothiophene (1.62 g, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (87% yield).

^1H NMR (300 MHz, CDCl_3) δ = 6.75 (d, J = 3.9 Hz, 1 H), 6.70 (d, J = 3.9 Hz, 1 H), 6.15 (dd, J = 17.1, 10.5 Hz, 1 H), 5.36 (dd, J = 17.2, 0.9 Hz, 1 H), 5.18 (dd, J = 10.5, 1.0 Hz, 1 H), 2.26 (s, 1 H), 1.69 (s, 3 H) ppm.

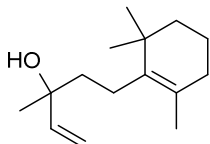
^{13}C NMR (75 MHz, CDCl_3) δ = 150.2 (s), 143.3 (s), 129.1 (s), 125.7 (s), 122.4 (s), 113.1 (s), 73.3 (s), 29.8 (s) ppm.

IR (ATR) 3363, 2980, 1445, 1369, 1217, 983, 922, 792 cm^{-1} .

MS (EI) m/z (%) 190 (18) [M^+ (^{37}Cl)], 188 (49) [M^+ (^{35}Cl)], 173 (100), 145 (70), 131 (92), 118 (25).

HRMS (EI-TOF) m/z calcd. for $\text{C}_8\text{H}_7\text{Cl}(35)\text{S}$ [$\text{M}^+ - \text{H}_2\text{O}$] 169.9957, found 169.9972; $\text{C}_8\text{H}_7\text{Cl}(37)\text{S}$ [$\text{M}^+ - \text{H}_2\text{O}$] 171.9927, found 171.9947.

3-methyl-5-(2,6,6-trimethylcyclohexen-1-yl)pent-1-en-3-ol (4e) [CAS 99733-97-8]:

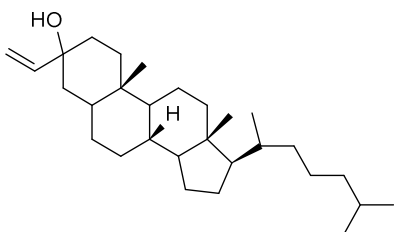


Compound **4e** was synthesised following a literature procedure^[4] from 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone (1.96 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as colorless oil (80% yield).

^1H NMR (300 MHz, CDCl_3) δ = 5.96 (dd, J = 17.3, 10.7 Hz, 1 H), 5.24 (dd, J = 17.4, 1.3 Hz, 1 H), 5.08 (dd, J = 10.8, 1.3 Hz, 1 H), 1.96 - 2.09 (m, 2 H), 1.90 (t, J = 6.1 Hz, 2 H), 1.50 - 1.66 (m, 7 H), 1.36 - 1.48 (m, 3 H), 1.31 (s, 3 H), 0.99 (s, 6 H) ppm.

The analytical data (NMR) matched the ones reported in the literature.^[12]

(8R,10S,13R,17R)-17-(1,5-dimethylhexyl)-10,13-dimethyl-3-vinyl-1,2,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydrocyclopenta[a]phenanthren-3-ol (4f) [CAS 27335-30-4]:



Compound **4f** was synthesised following a literature procedure^[4] from 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone (1.96 mL, 10.0 mmol) and vinyl magnesium bromide (1M in THF, 15.0 mL, 15.0 mmol) and isolated as white solid (40% yield).

^1H NMR (300 MHz, CDCl_3) δ = 6.11 (dd, J = 17.4, 10.8 Hz, 1 H), 5.31 (dd, J = 17.4, 1.3 Hz, 1 H), 5.15 (dd, J = 10.8, 1.3 Hz, 1 H), 1.97 (d, J = 12.1 Hz, 1 H), 1.76 - 1.90 (m, 1 H), 1.59 - 1.76 (m, 5 H), 1.42 - 1.58 (m, 5 H), 0.94 - 1.41 (m, 19 H), 0.81 - 0.93 (m, 13 H), 0.63 - 0.66 (m, 3 H) ppm.

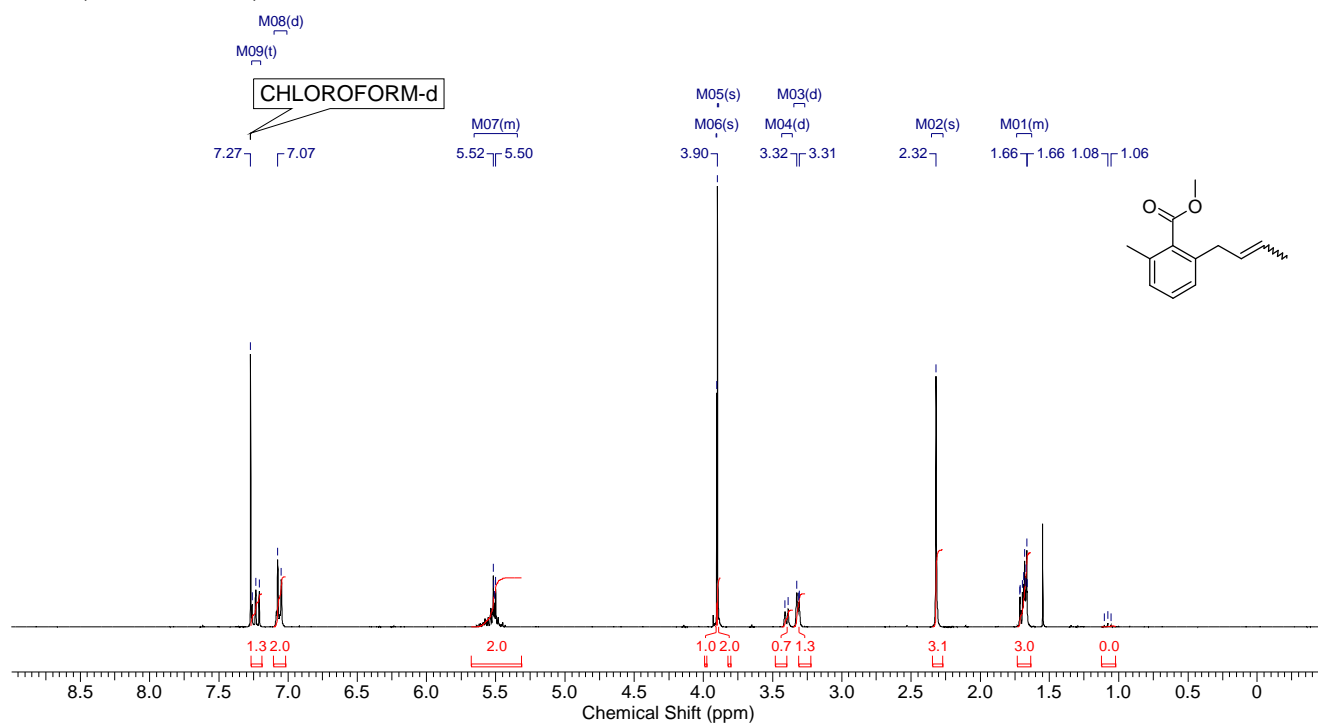
The analytical data (NMR) matched the ones reported in the literature.^[13]

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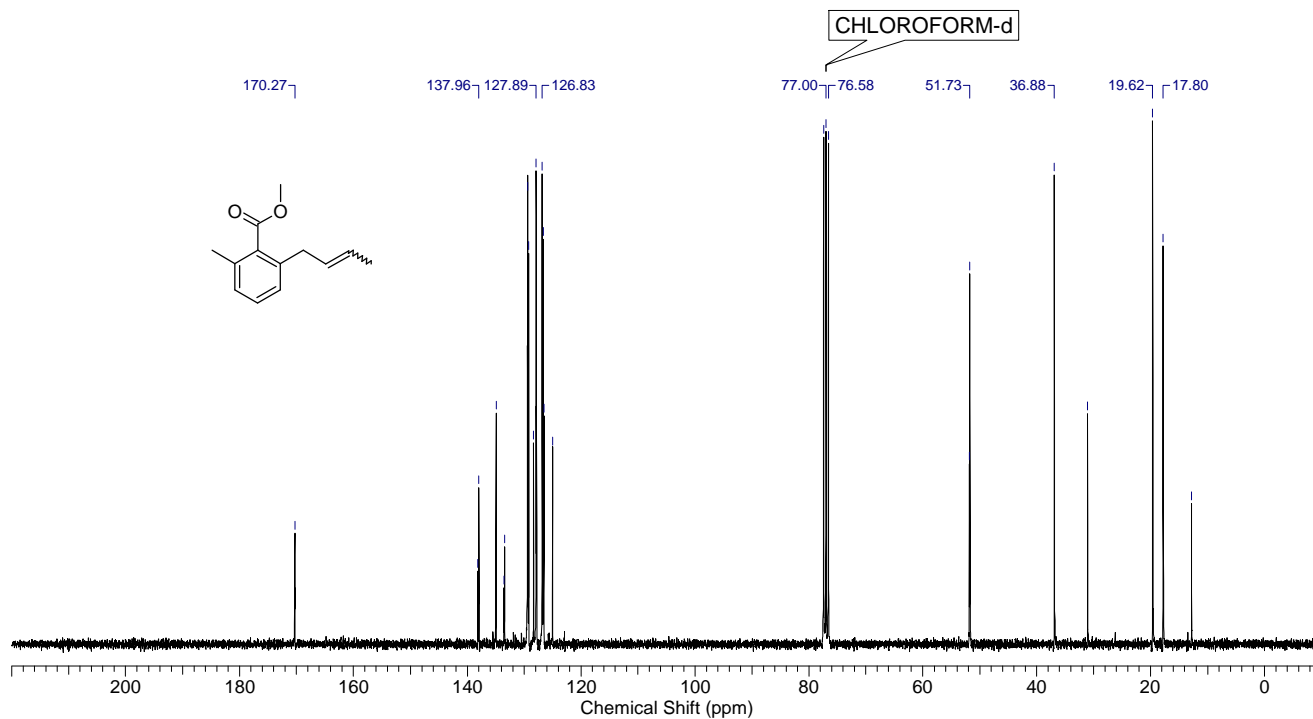
NMR spectra

Methyl 2-[but-2-enyl]-6-methyl-benzoate (3aa)

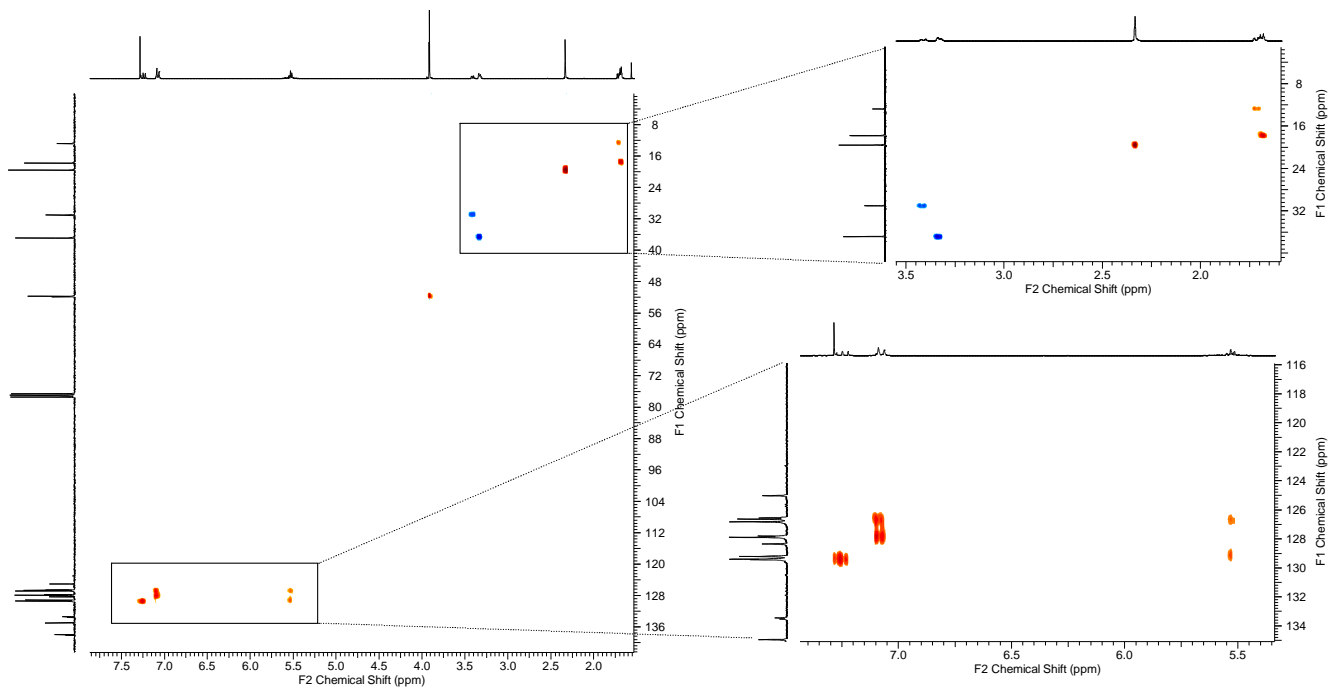
^1H NMR (300 MHz, CDCl_3)



^{13}C NMR (75 MHz, CDCl_3)

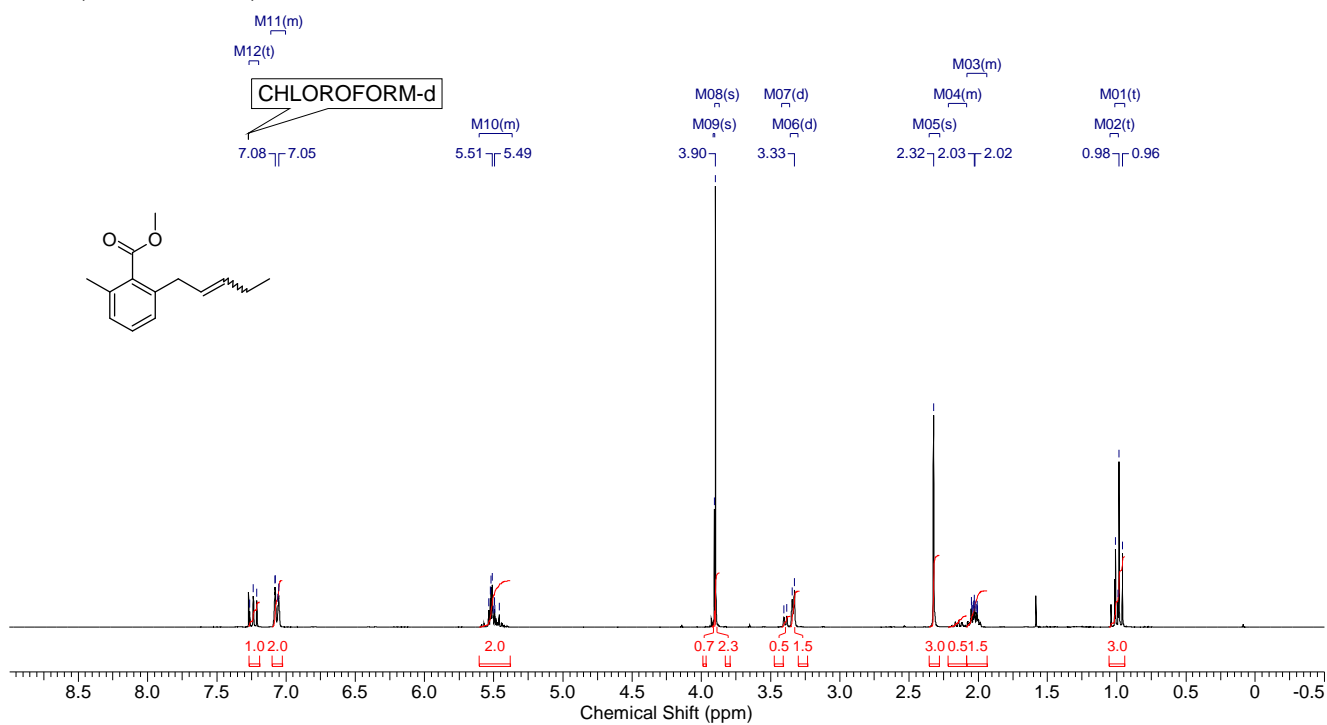


$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

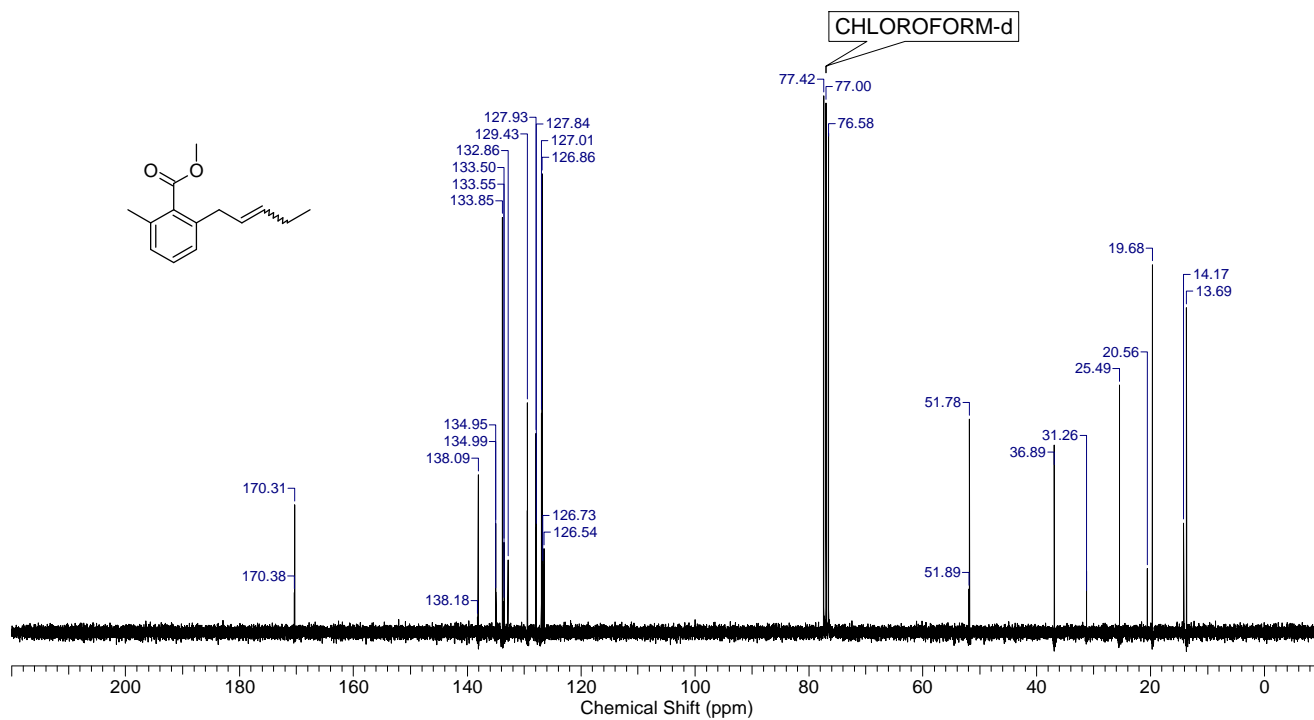


Methyl 2-methyl-6-(-pent-2-enyl)benzoate (3ab)

¹H NMR (300 MHz, CDCl₃)

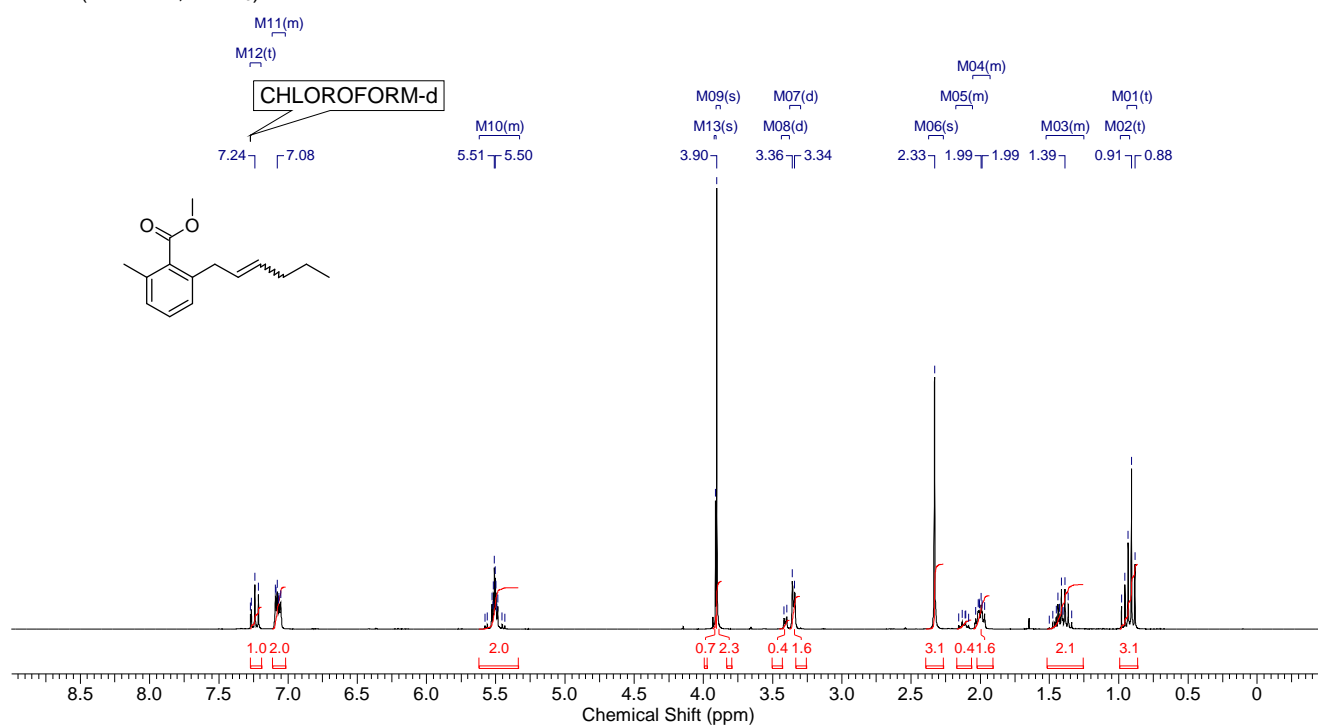


¹³C NMR (75 MHz, CDCl₃)

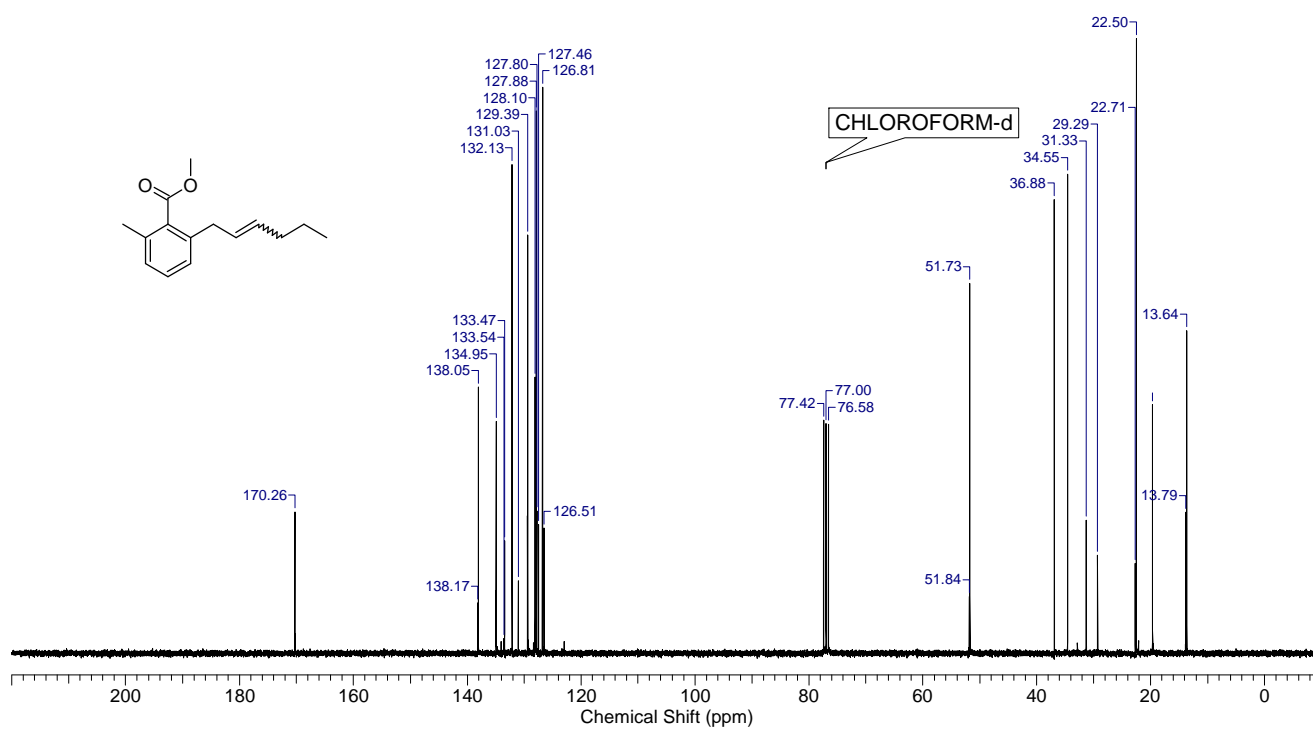


Methyl 2-(hex-2-enyl)-6-methyl-benzoate (3ac)

¹H NMR (300 MHz, CDCl₃)

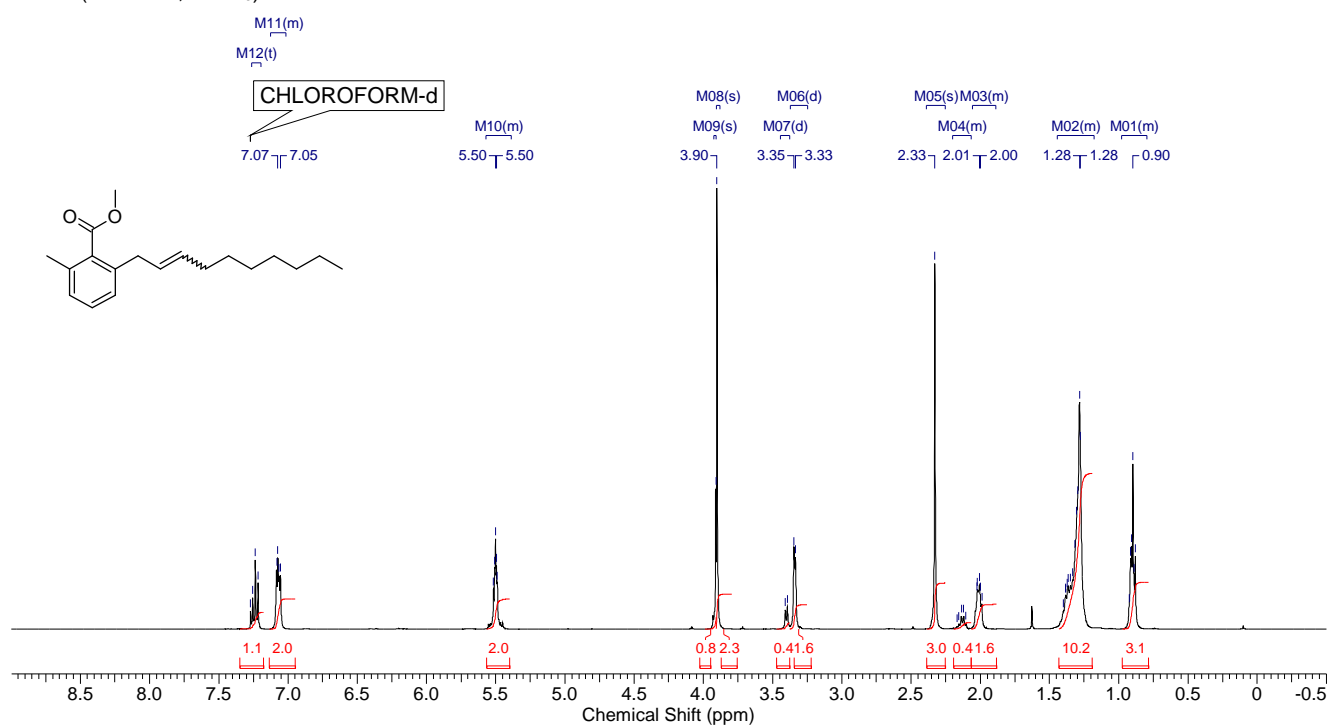


¹³C NMR (75 MHz, CDCl₃)

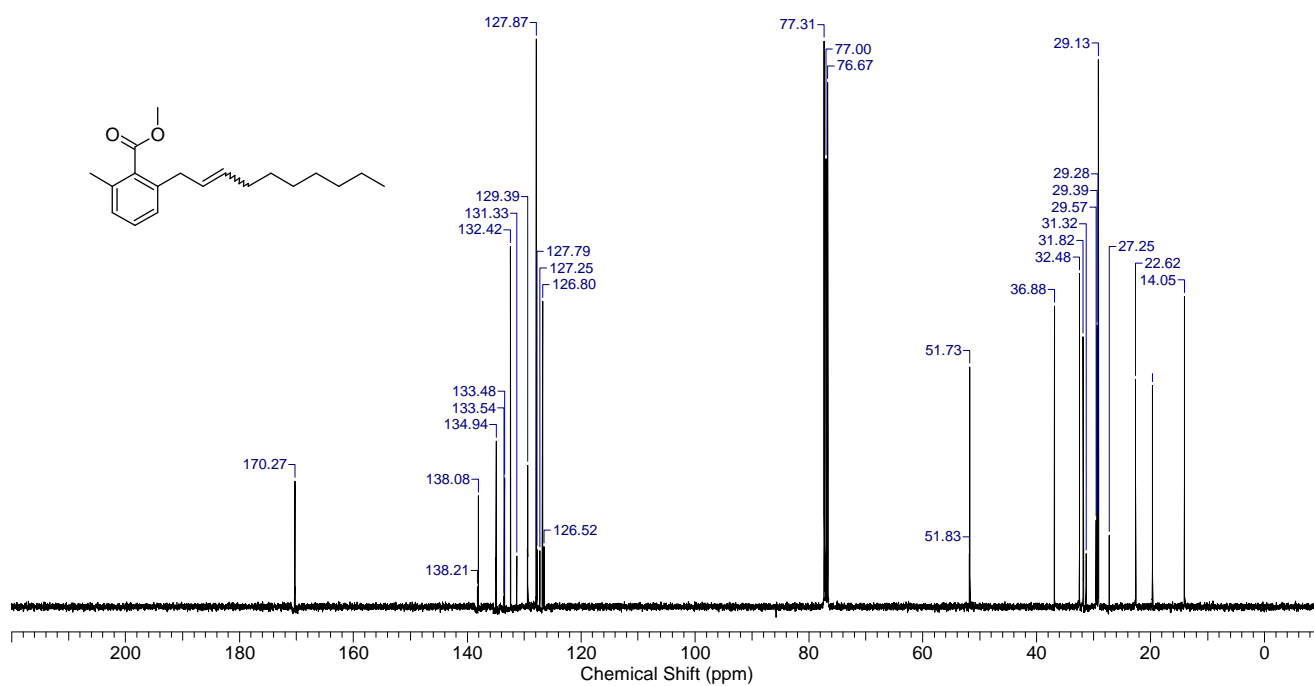


Methyl 2-(dec-2-enyl)-6-methyl-benzoate (3ad)

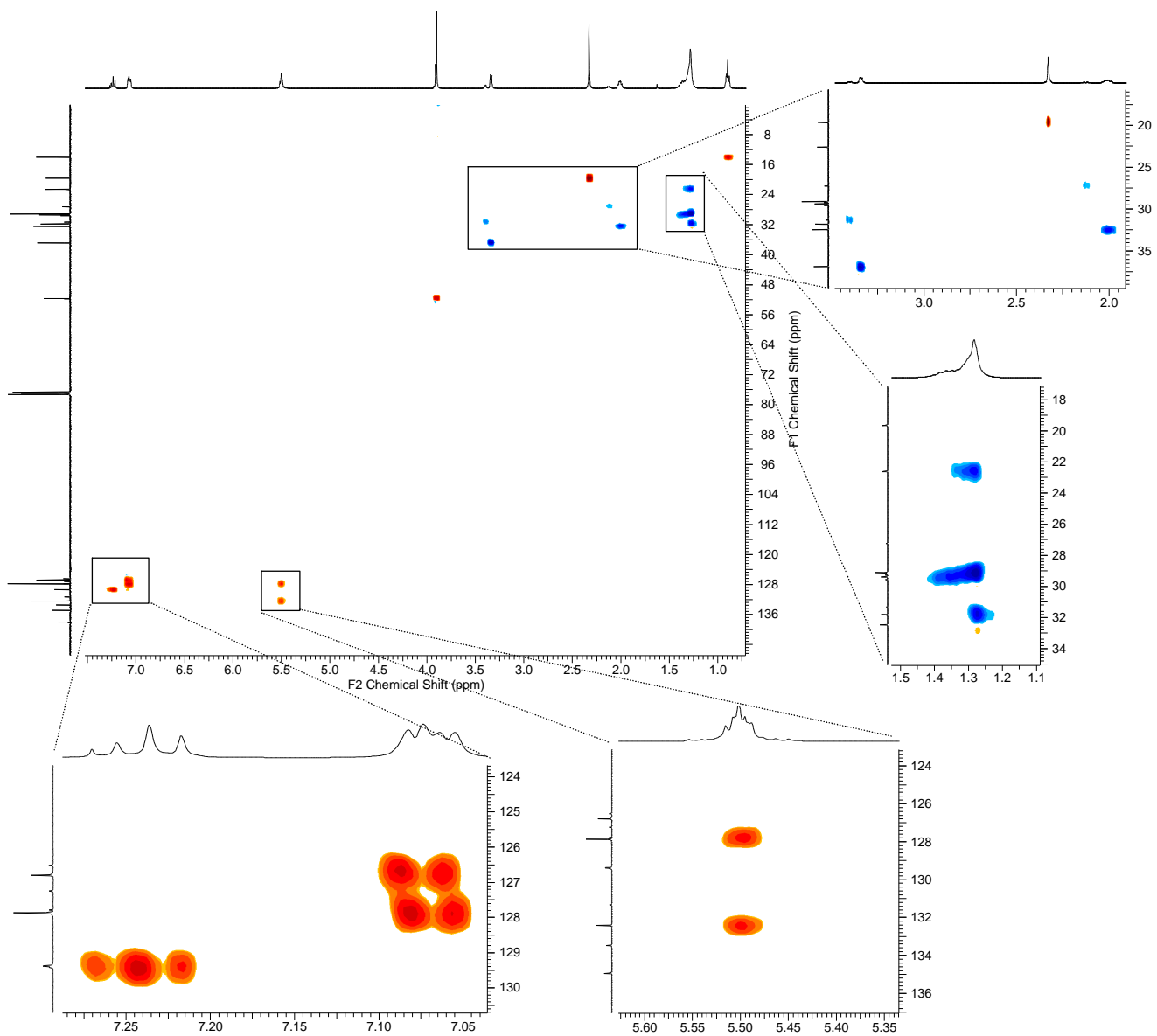
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

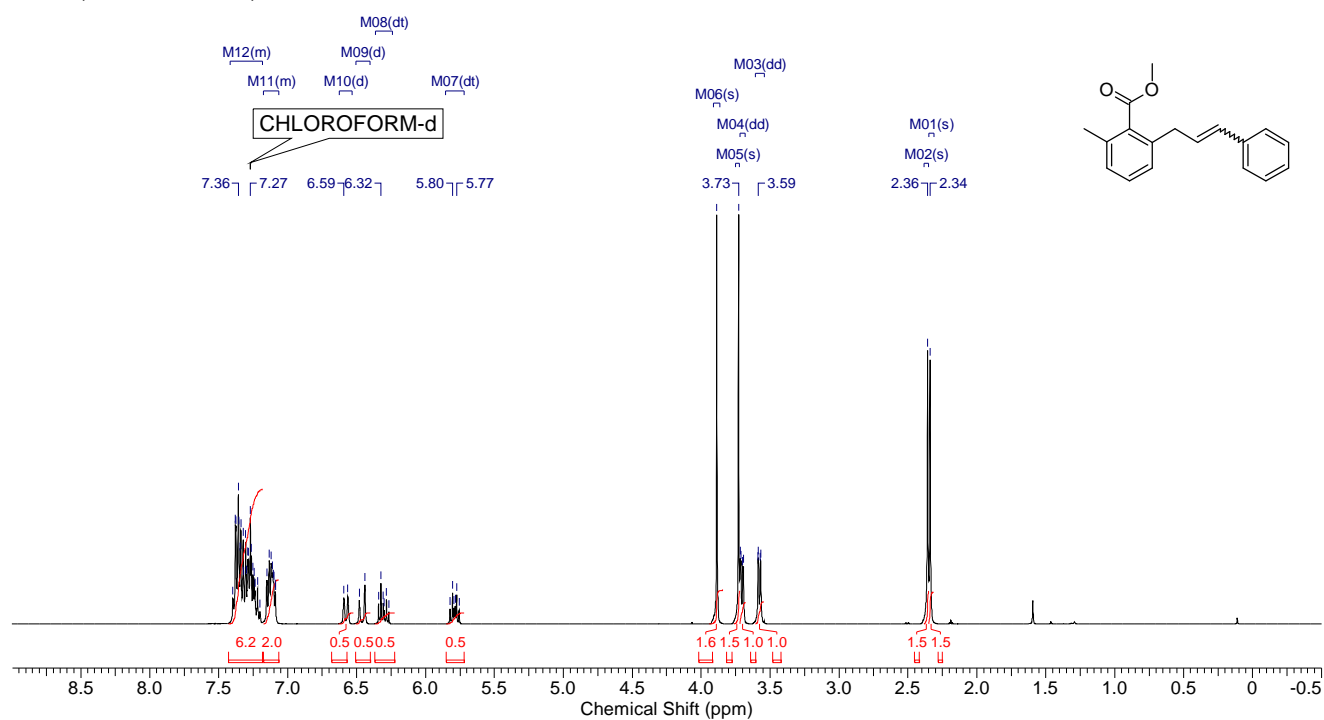


$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

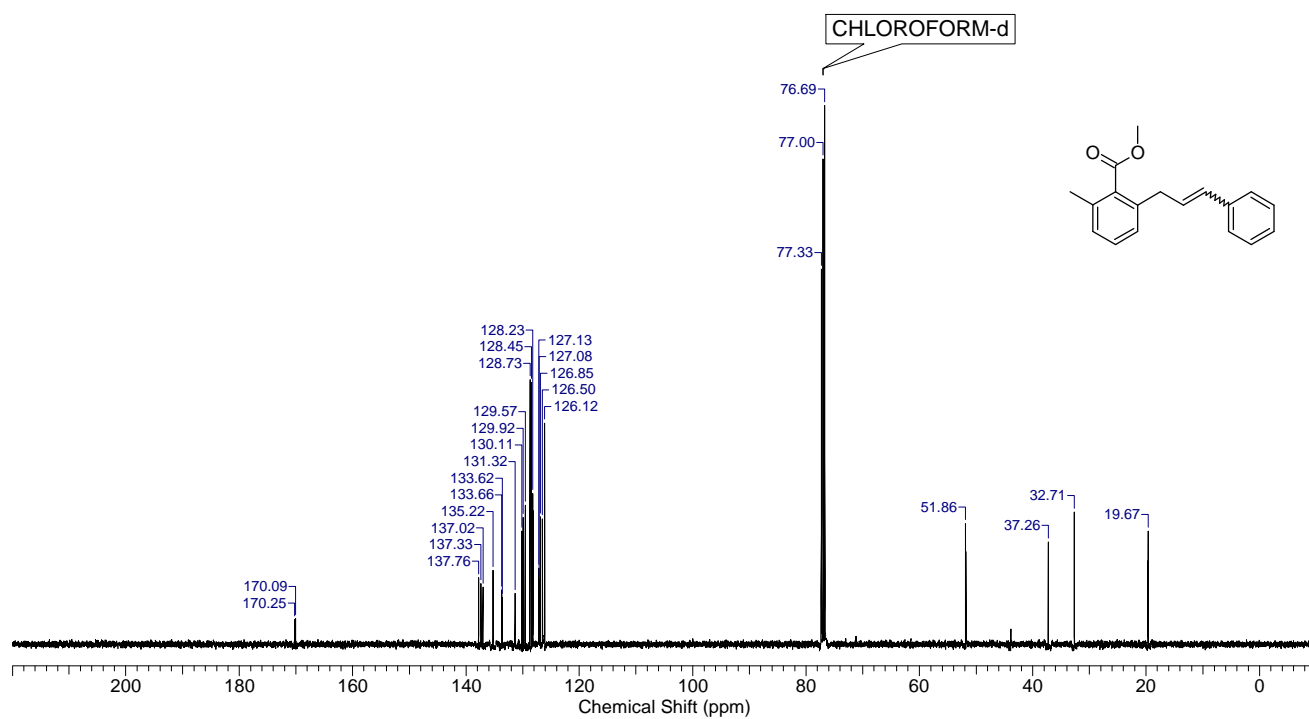


Methyl 2-(cinnamyl)-6-methyl-benzoate (3ae)

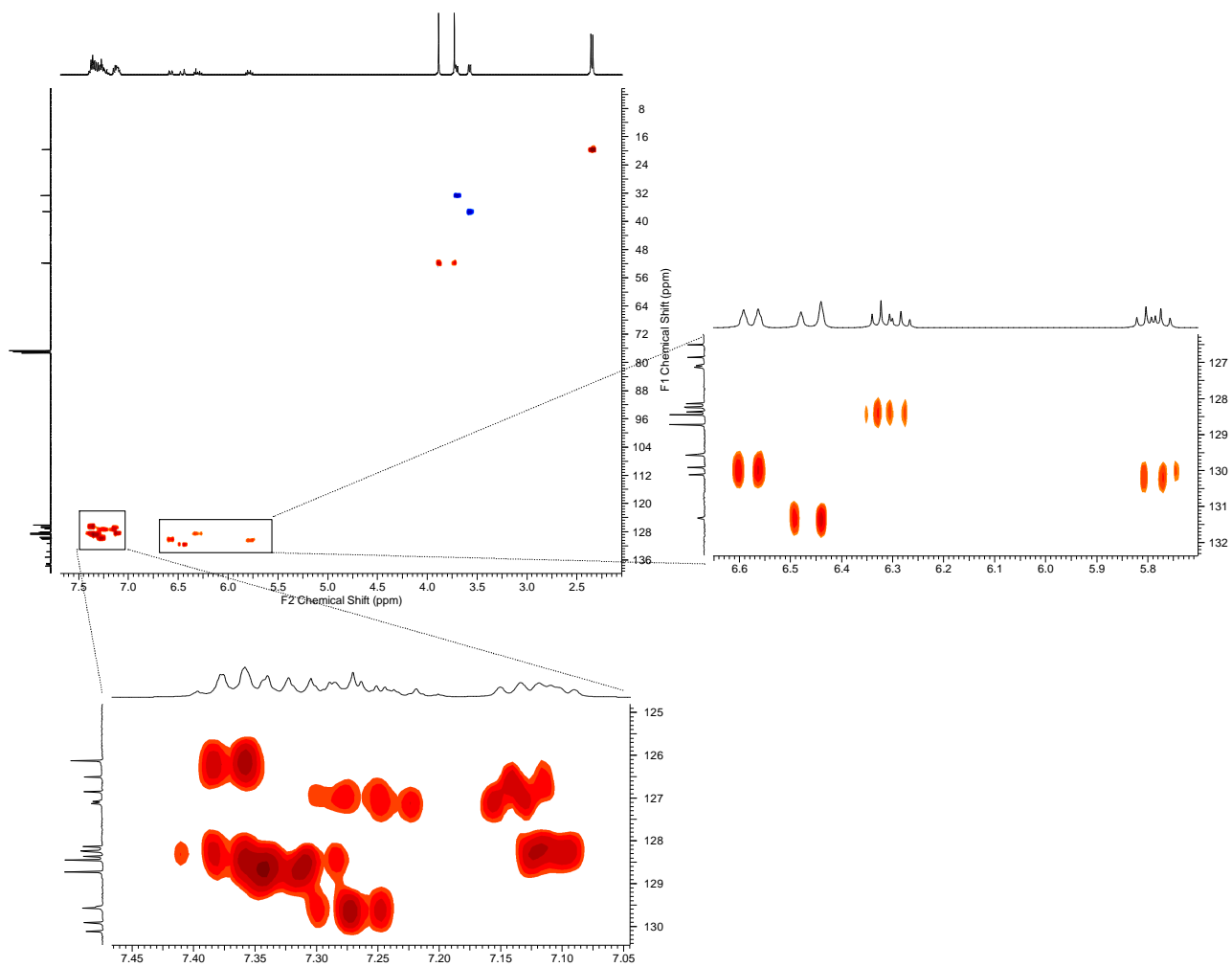
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

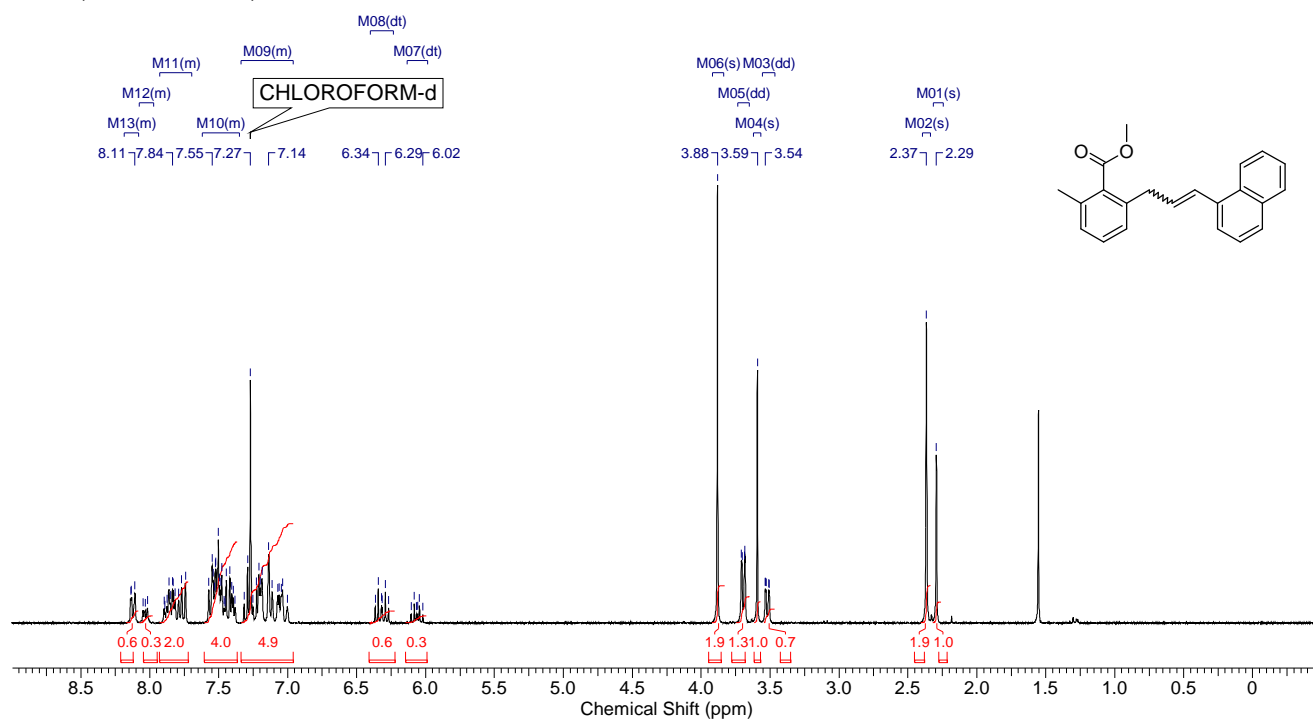


$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

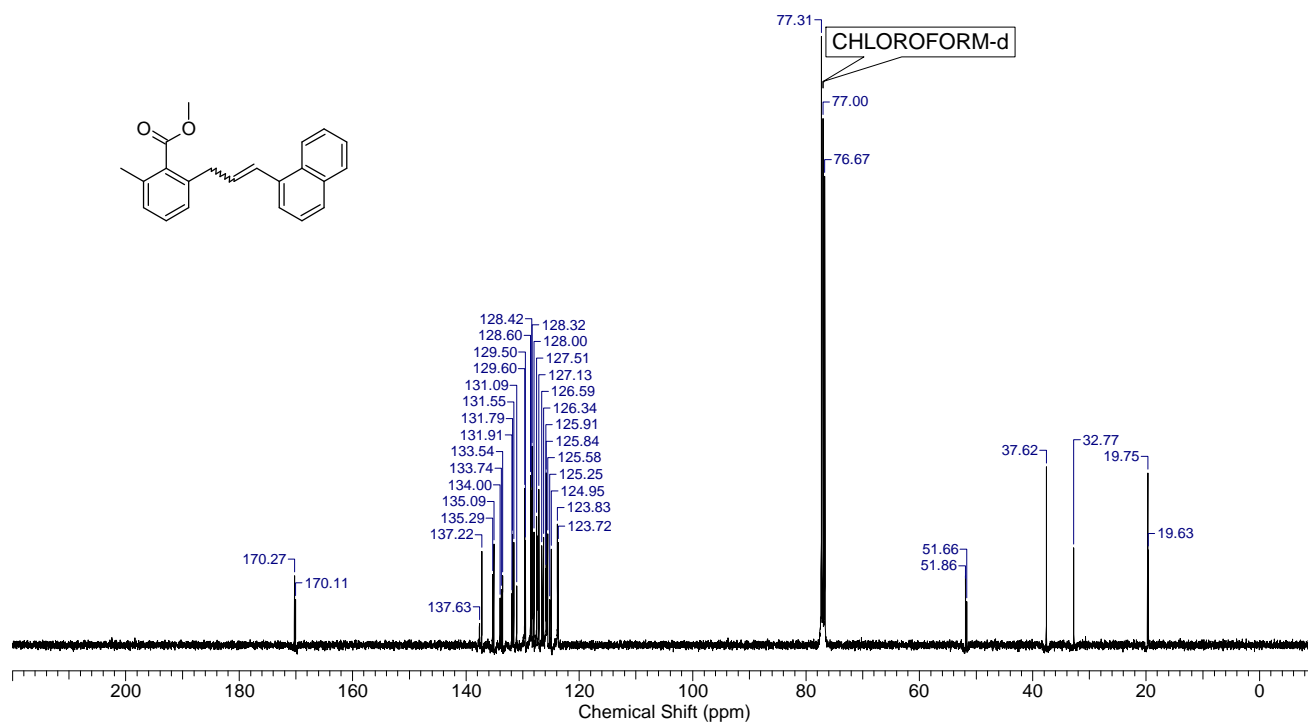


Methyl 2-methyl-6-[3-(1-naphthyl)allyl]benzoate (3af)

¹H NMR (300 MHz, CDCl₃)

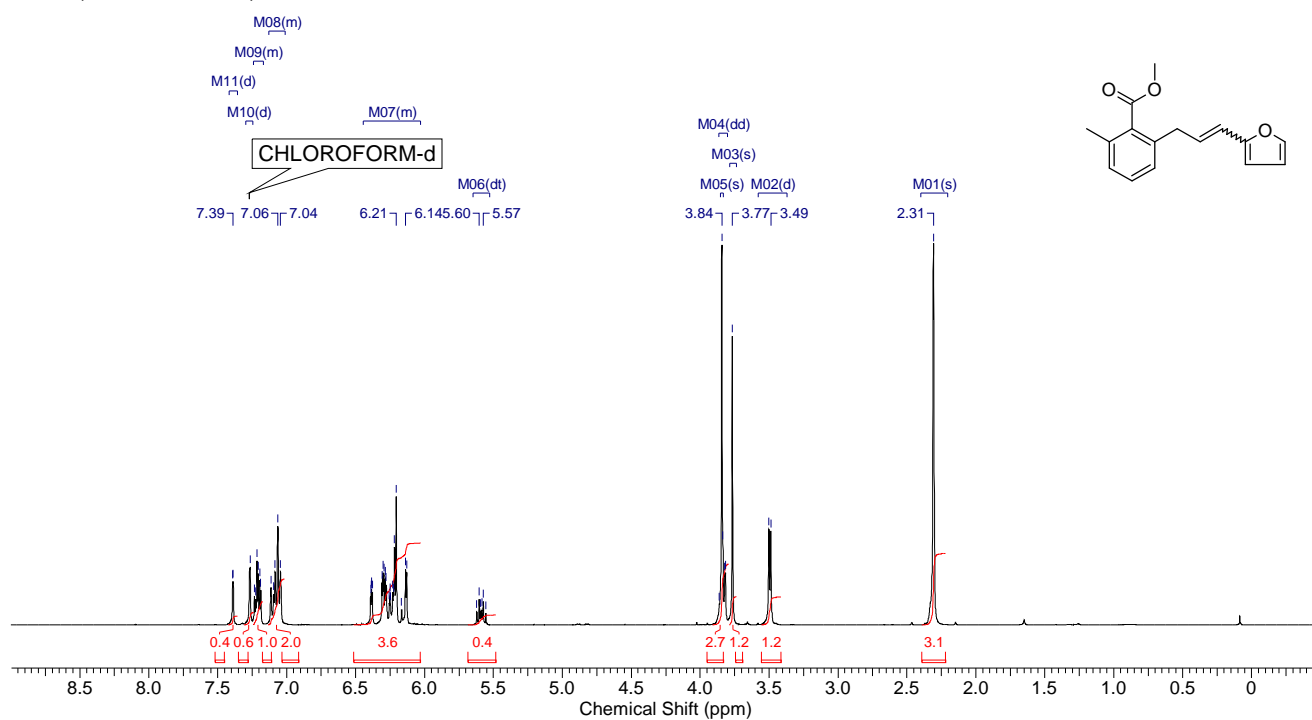


¹³C NMR (101 MHz, CDCl₃)

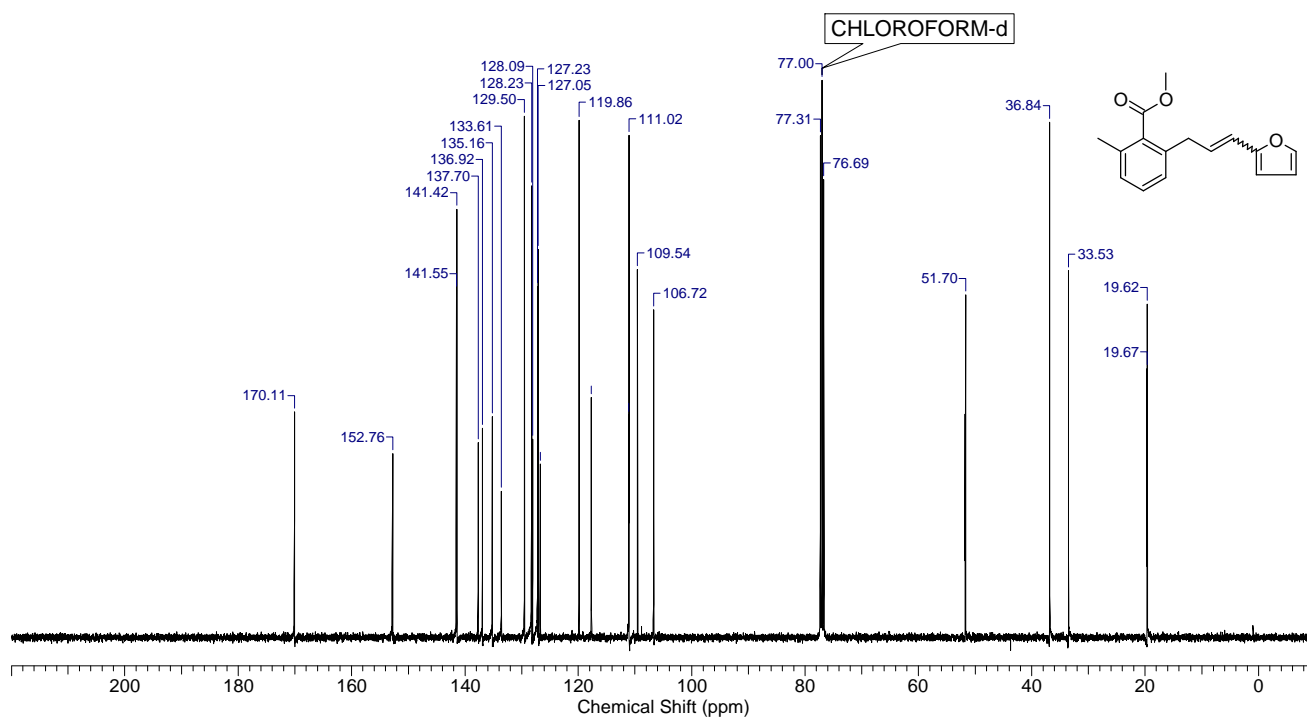


Methyl 2-[3-(2-furyl)allyl]-6-methyl-benzoate (3ag)

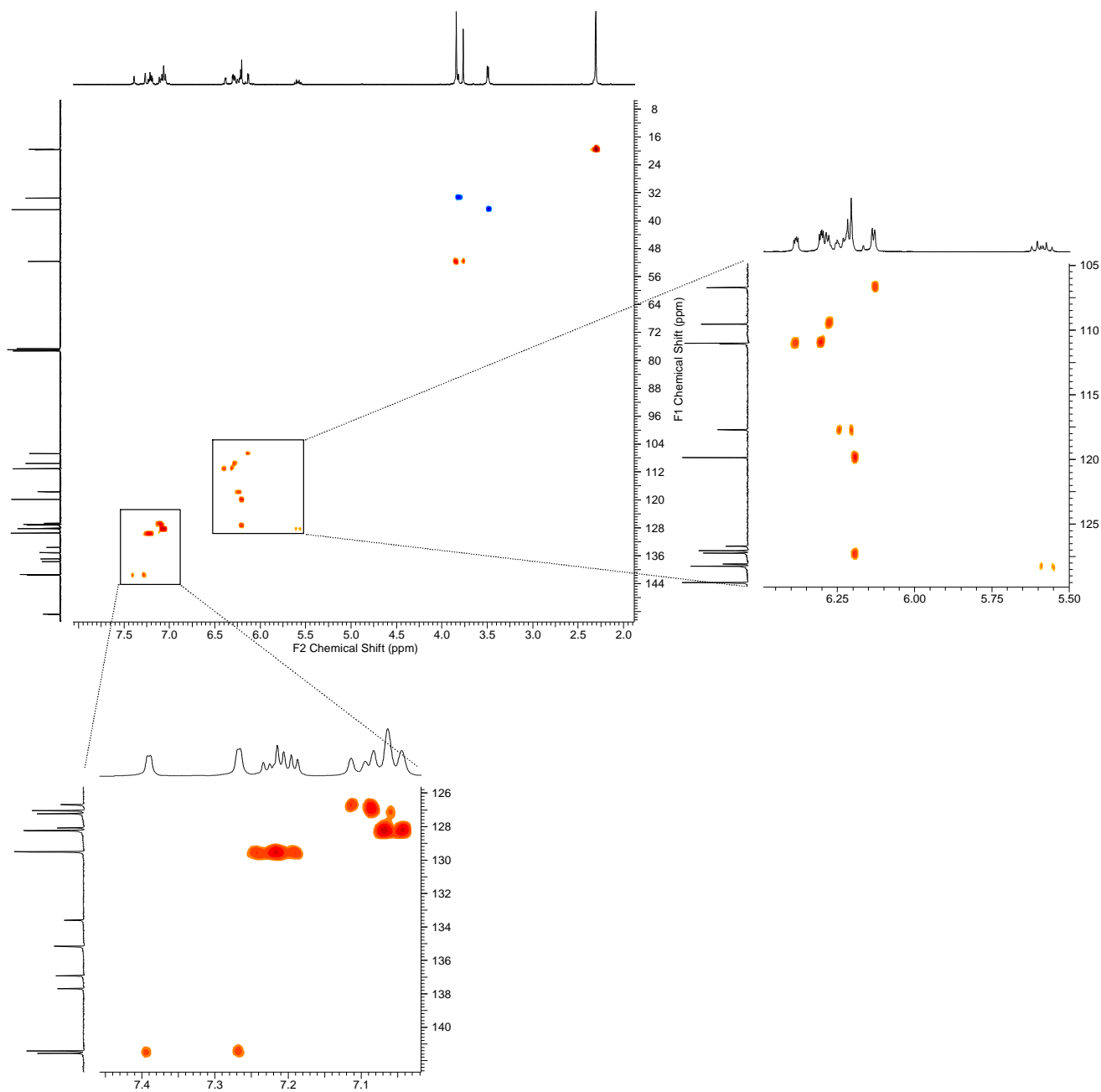
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

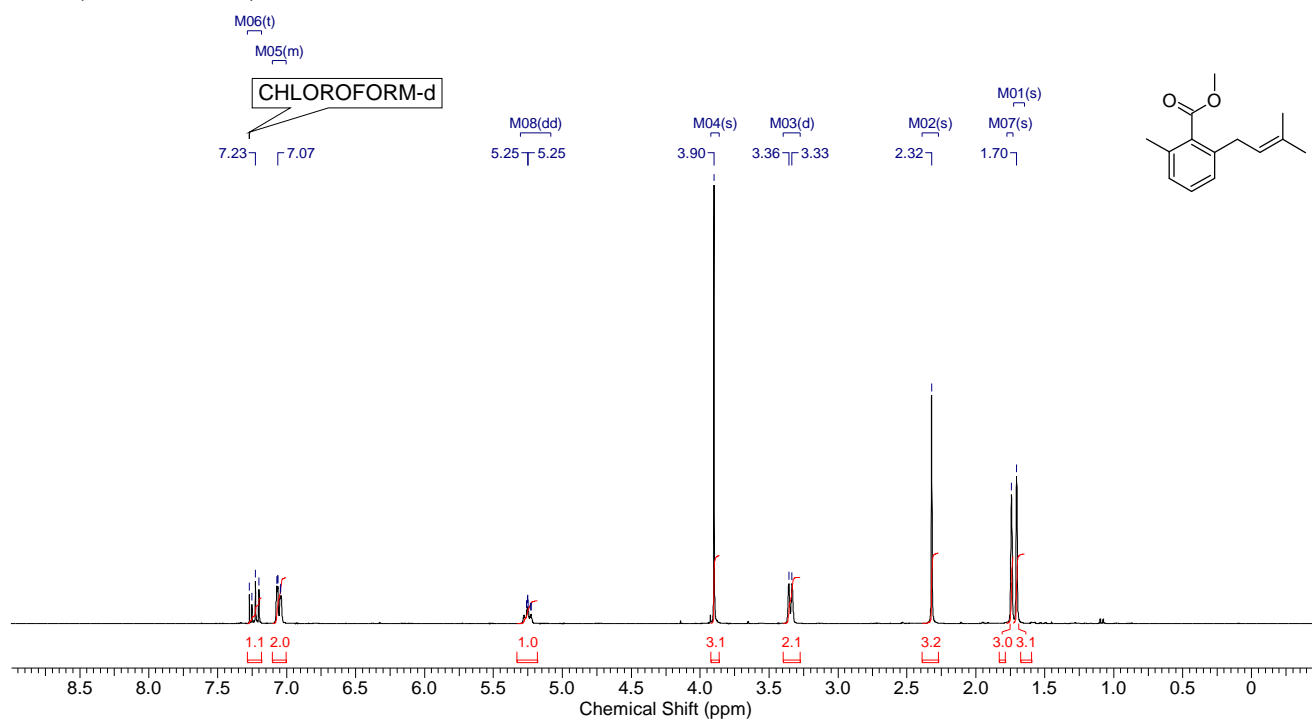


$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

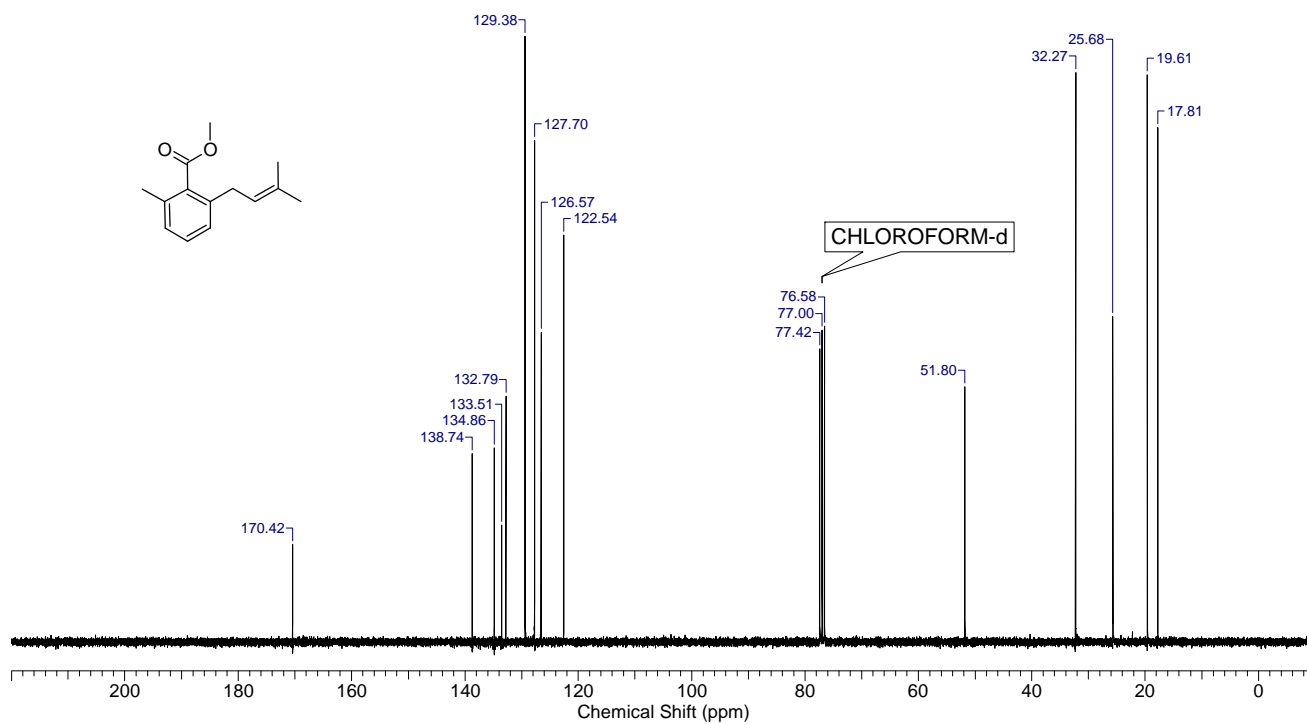


Methyl 2-methyl-6-(3-methylbut-2-enyl)benzoate (3ah)

¹H NMR (300 MHz, CDCl₃)

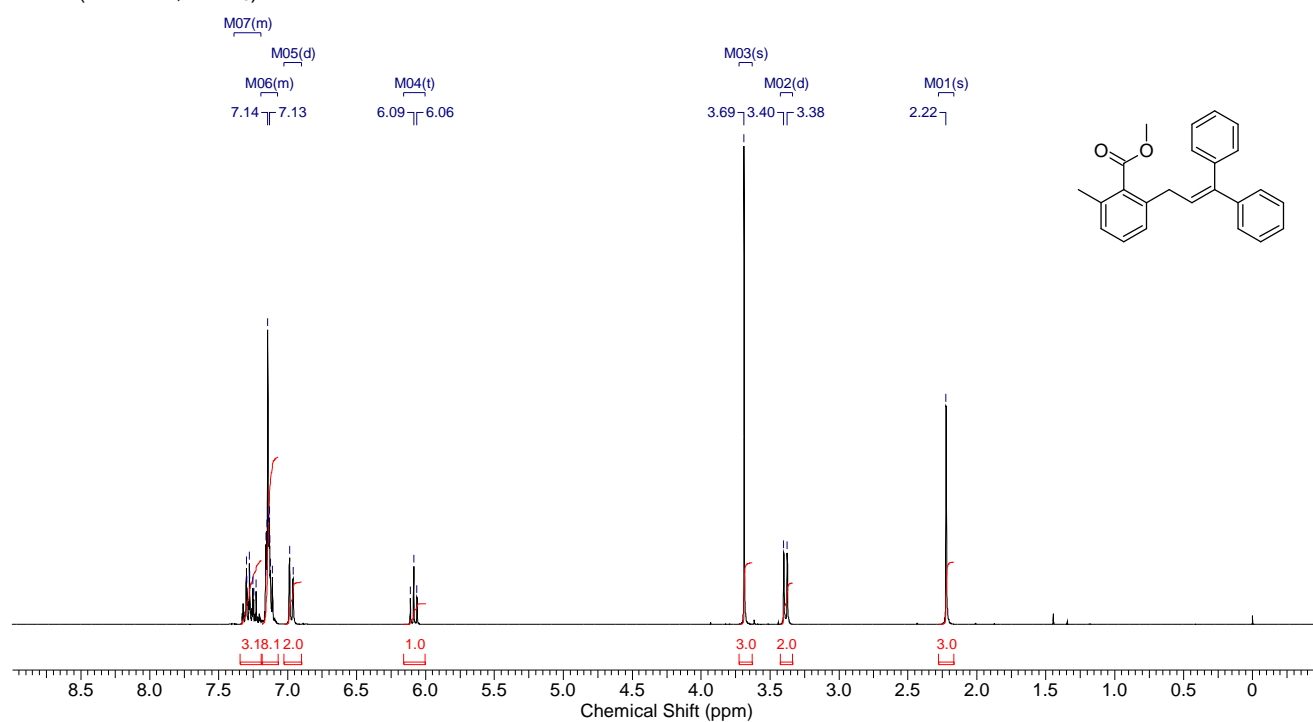


¹³C NMR (75 MHz, CDCl₃)

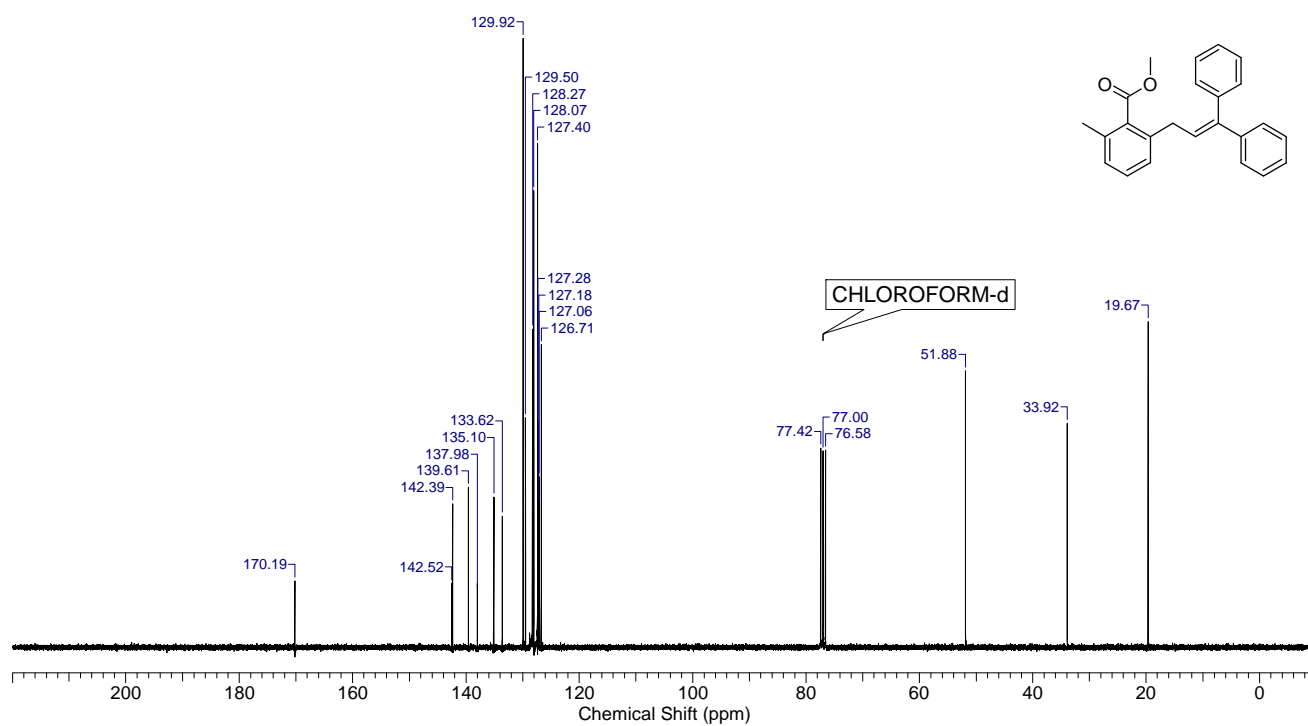


Methyl 2-(3,3-diphenylallyl)-6-methyl-benzoate (3ai)

^1H NMR (300 MHz, CDCl_3)

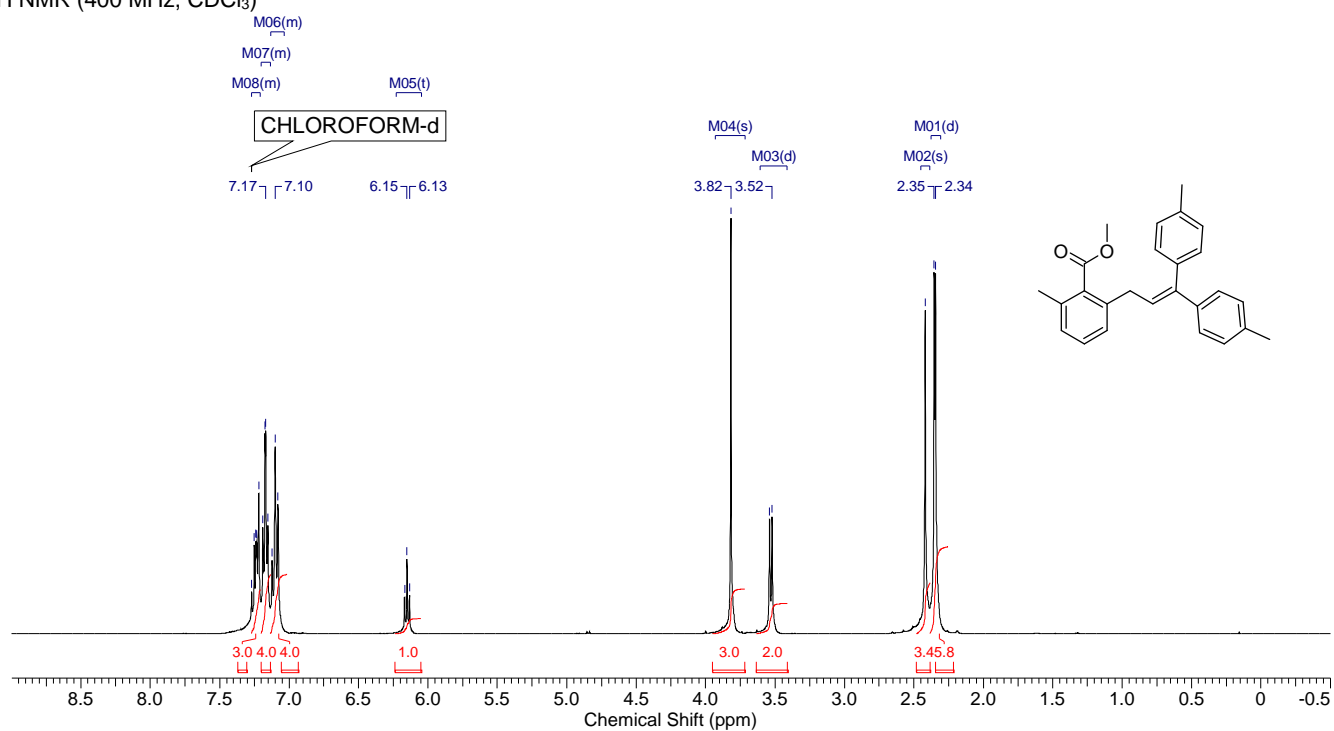


^{13}C NMR (75 MHz, CDCl_3)

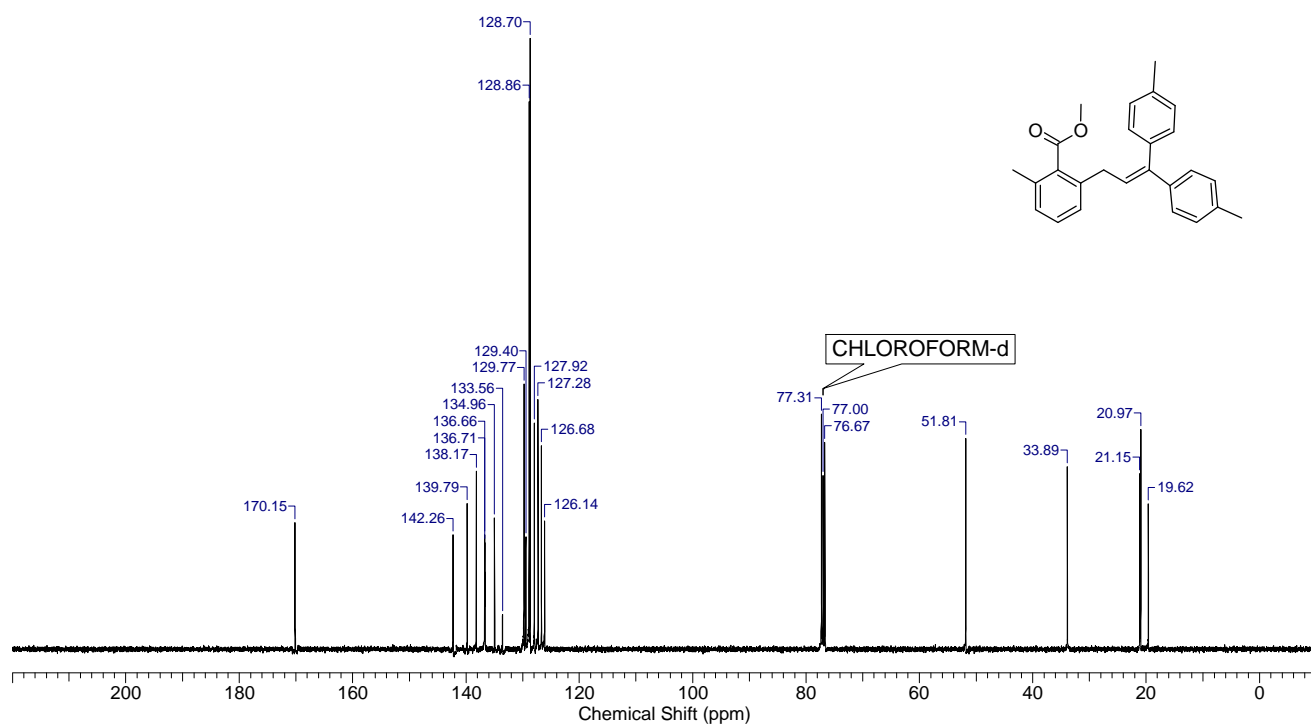


Methyl 2-[3,3-bis(p-tolyl)allyl]-6-methyl-benzoate (3aj)

¹H NMR (400 MHz, CDCl₃)

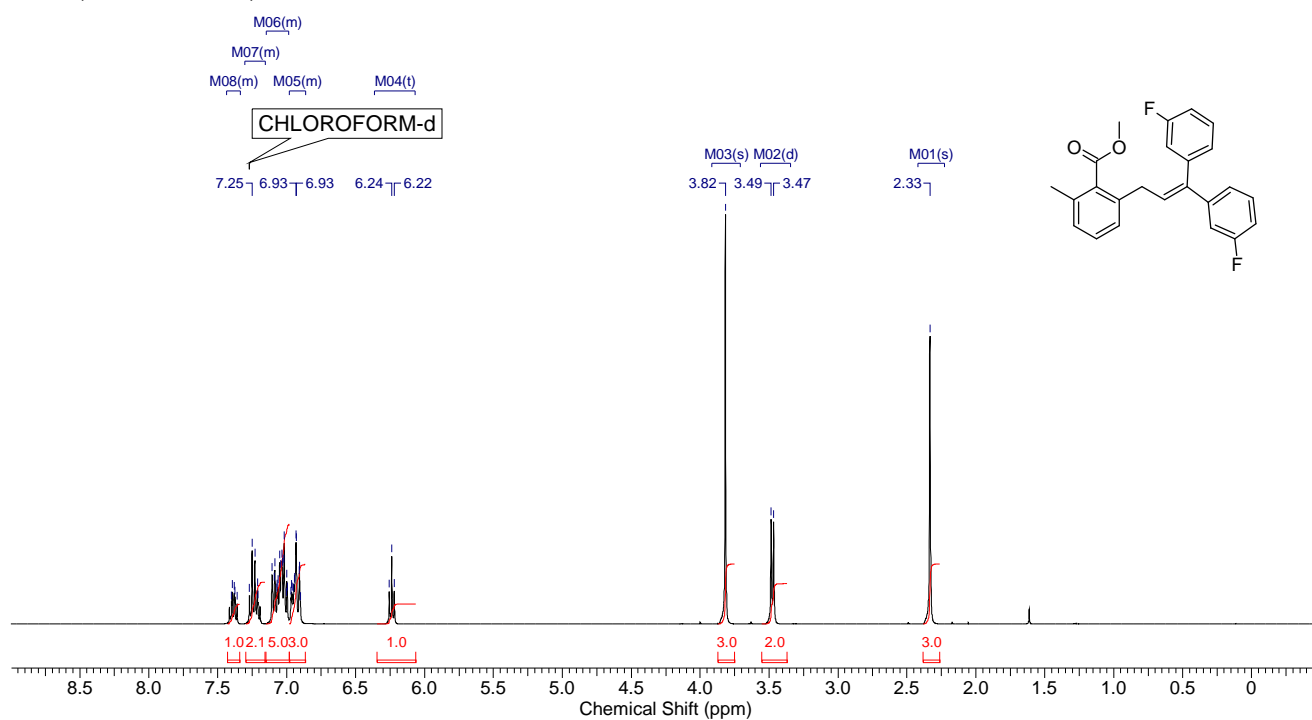


¹³C NMR (101 MHz, CDCl₃)

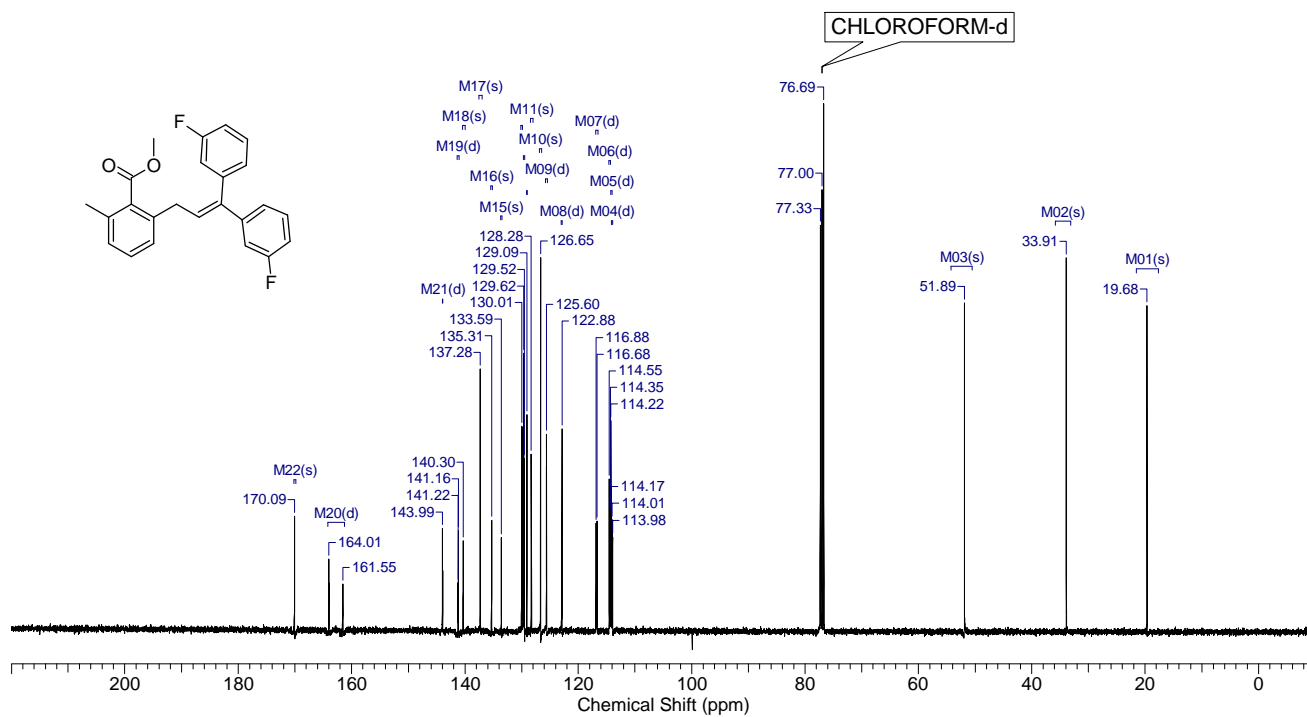


Methyl 2-[3,3-bis(3-fluorophenyl)allyl]-6-methyl-benzoate (3ak)

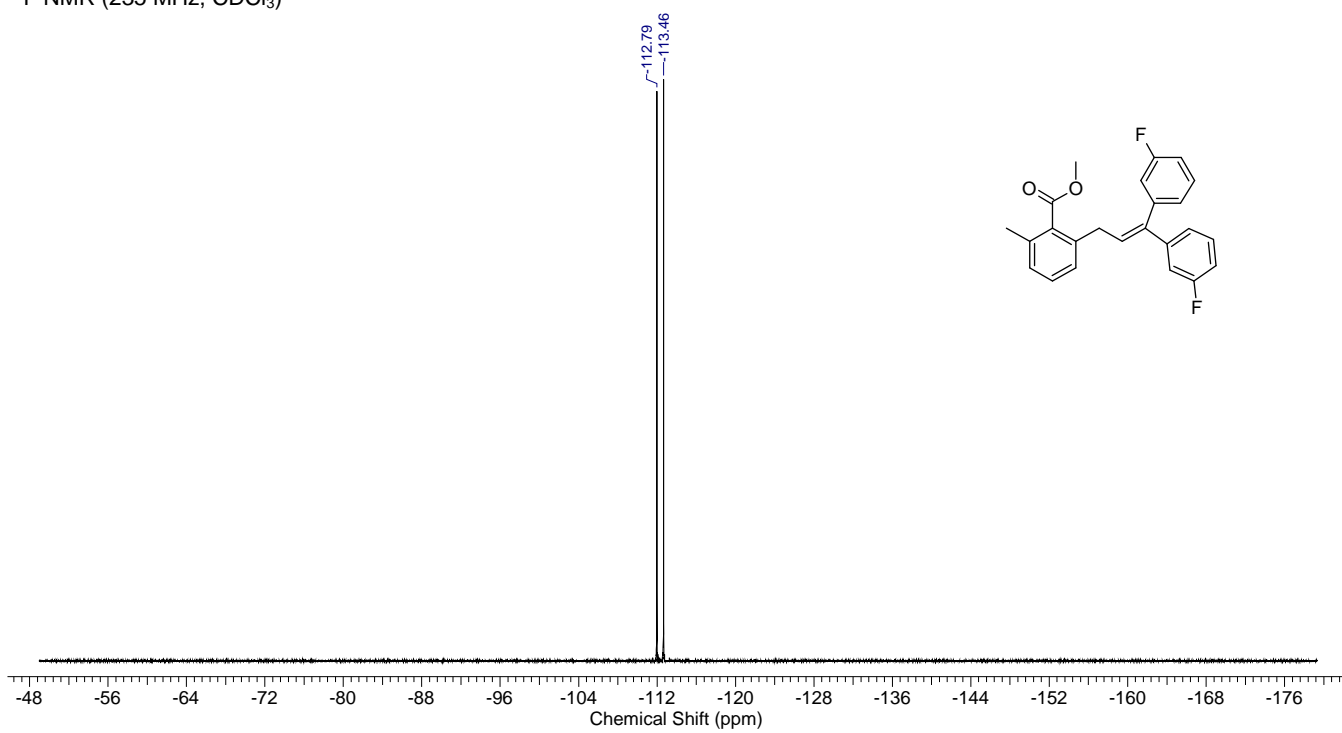
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

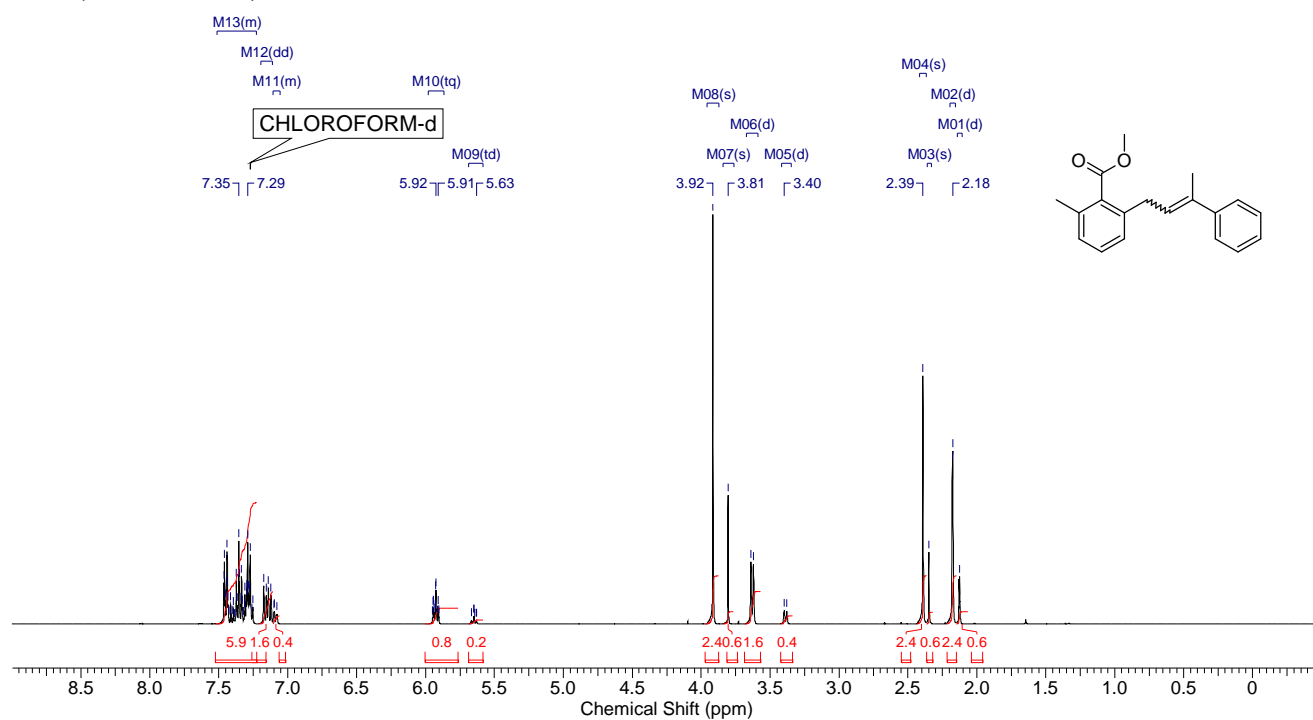


^{19}F NMR (235 MHz, CDCl_3)

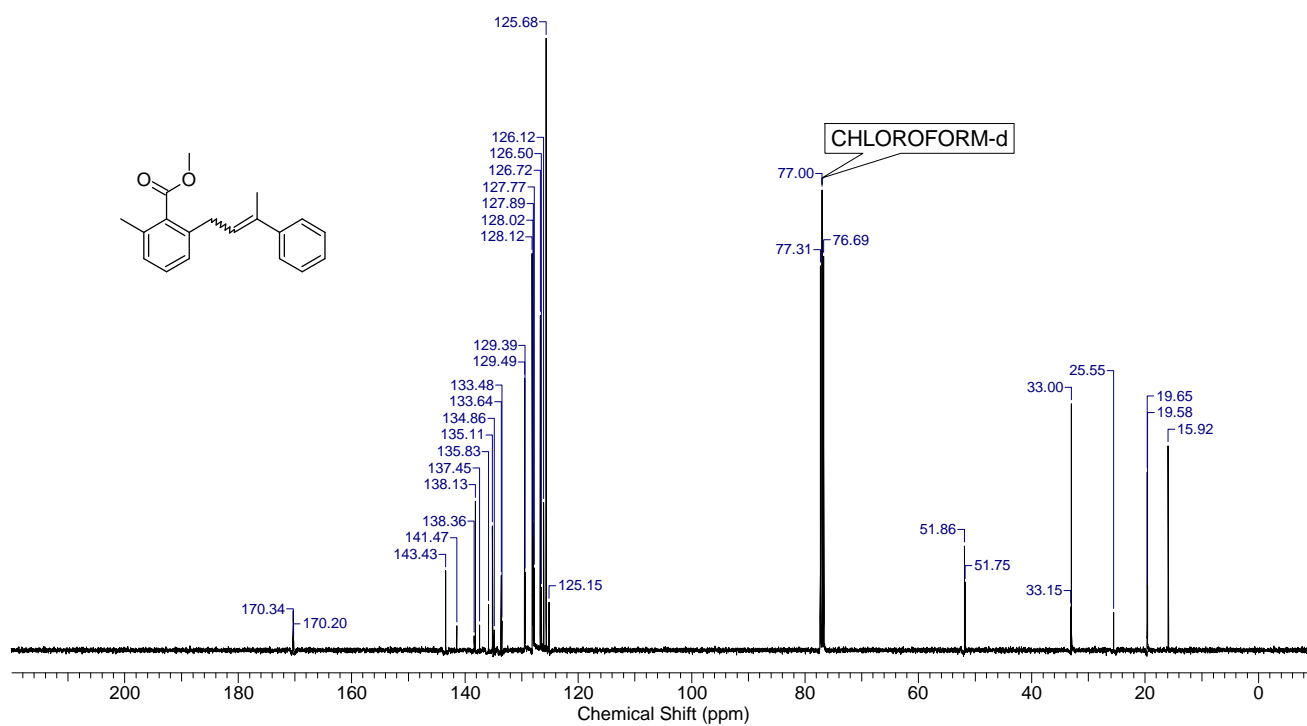


Methyl 2-methyl-6-(3-phenylbut-2-enyl)benzoate (3a)

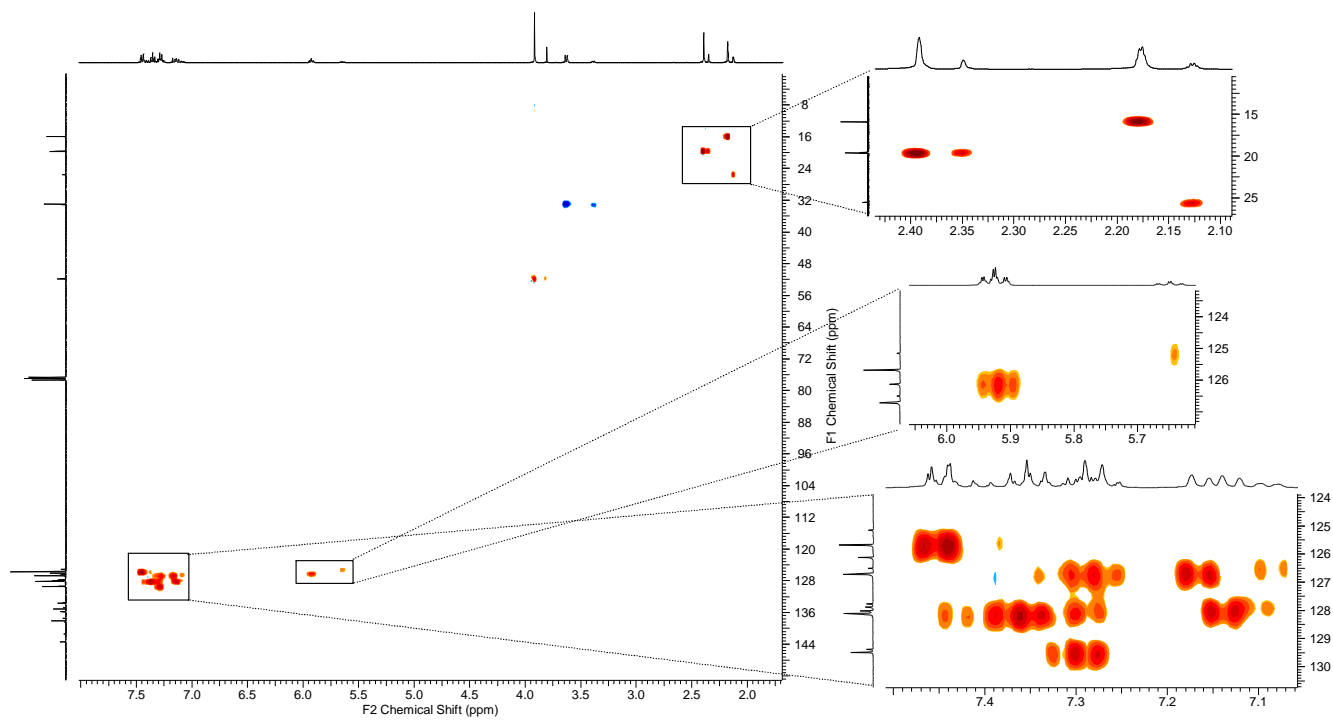
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

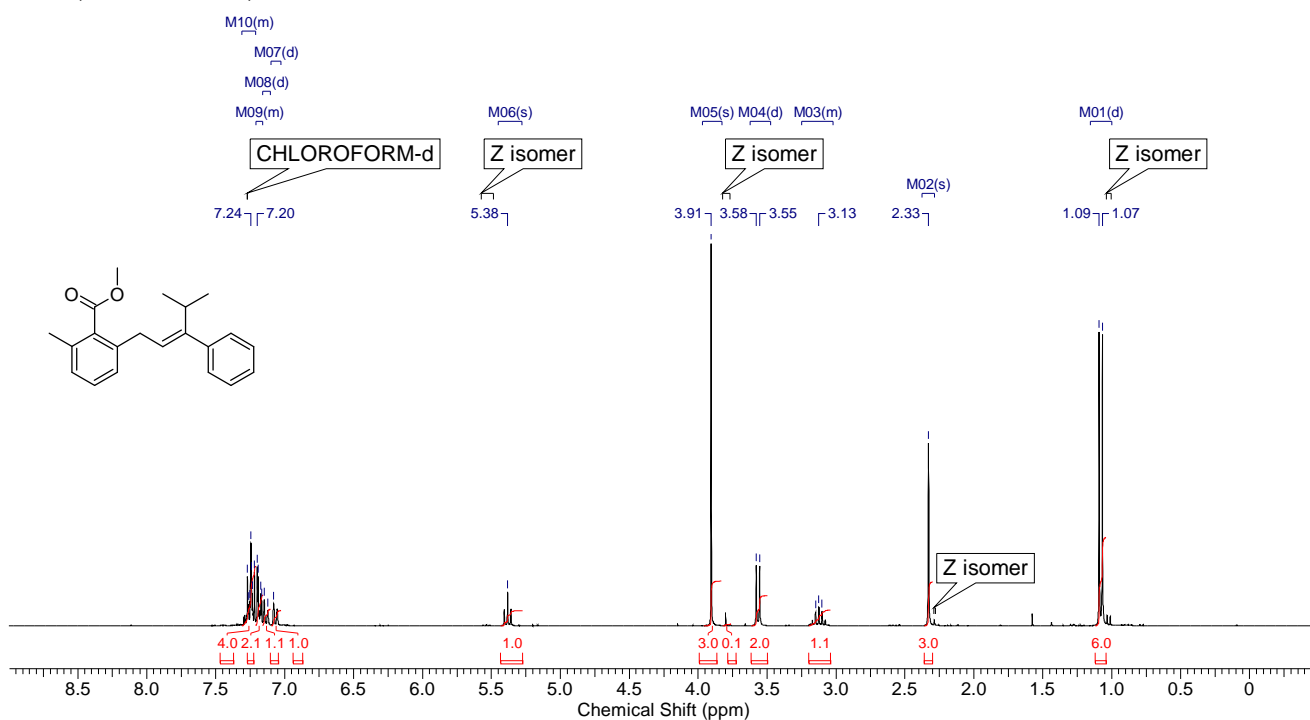


$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

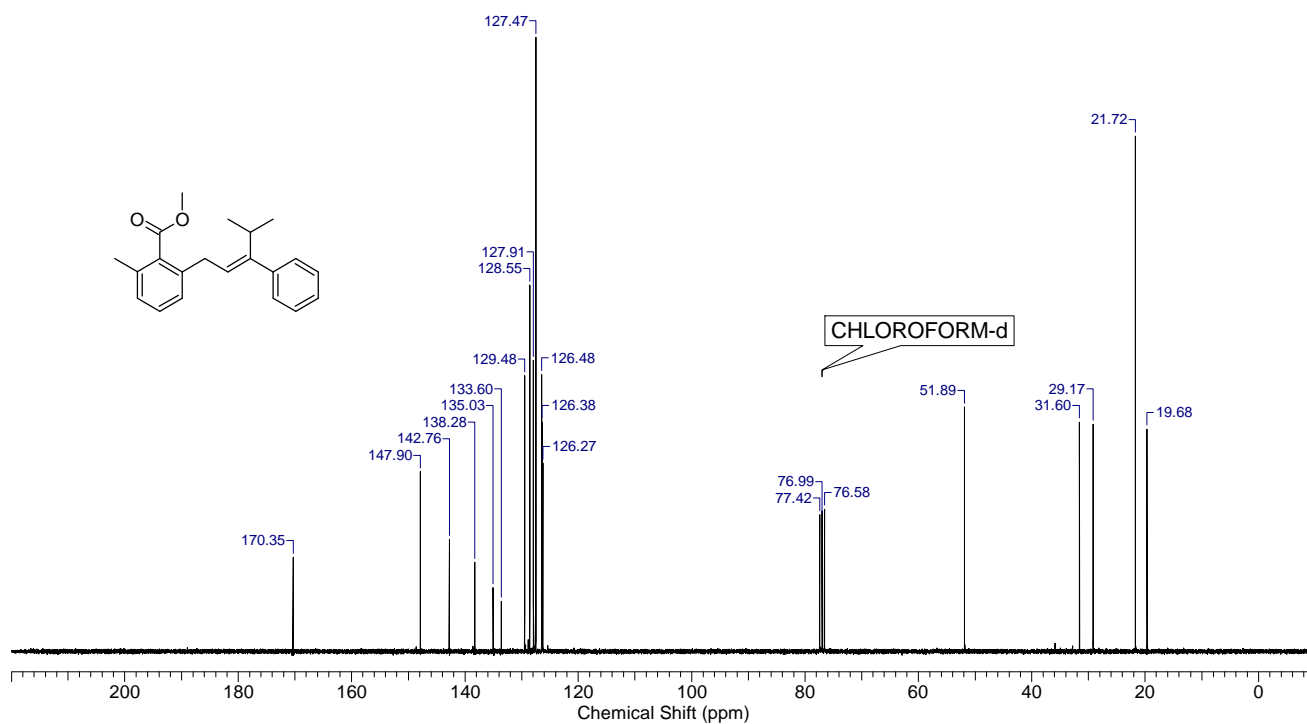


Methyl 2-methyl-6-[4-methyl-3-phenyl-pent-2-enyl]benzoate (3am)

¹H NMR (300 MHz, CDCl₃)

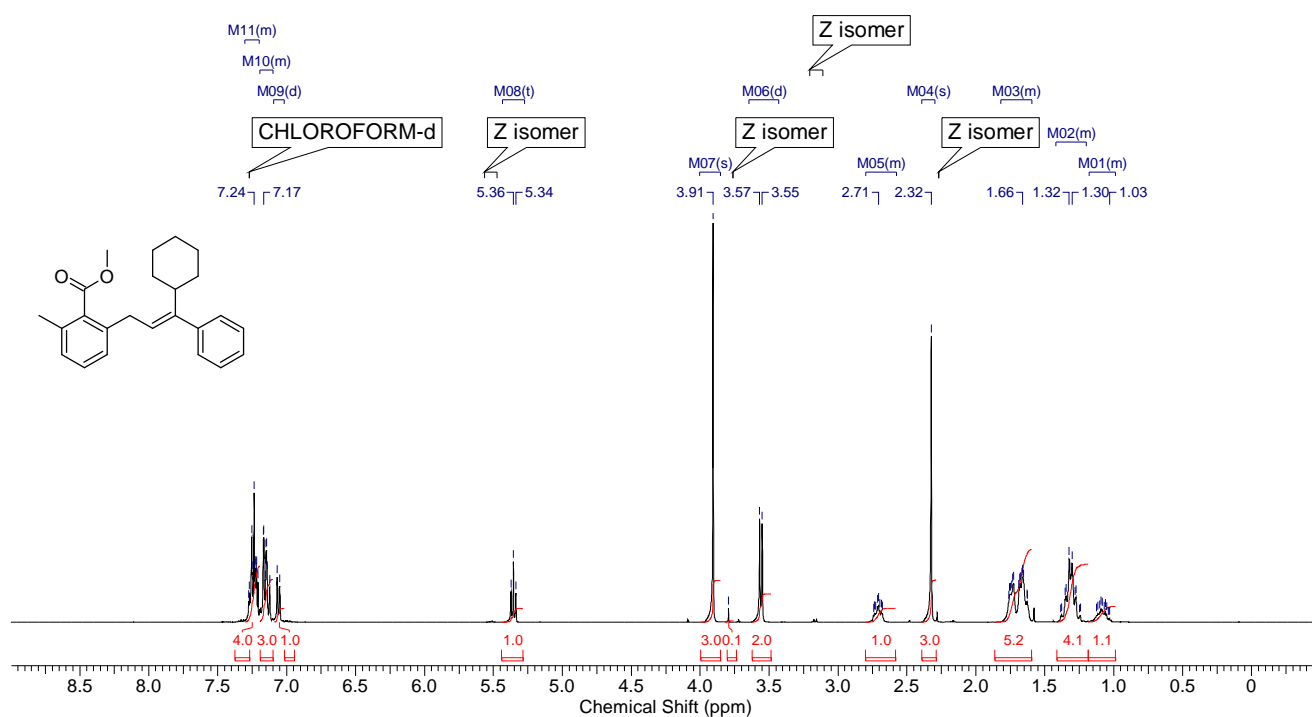


¹³C NMR (75 MHz, CDCl₃)

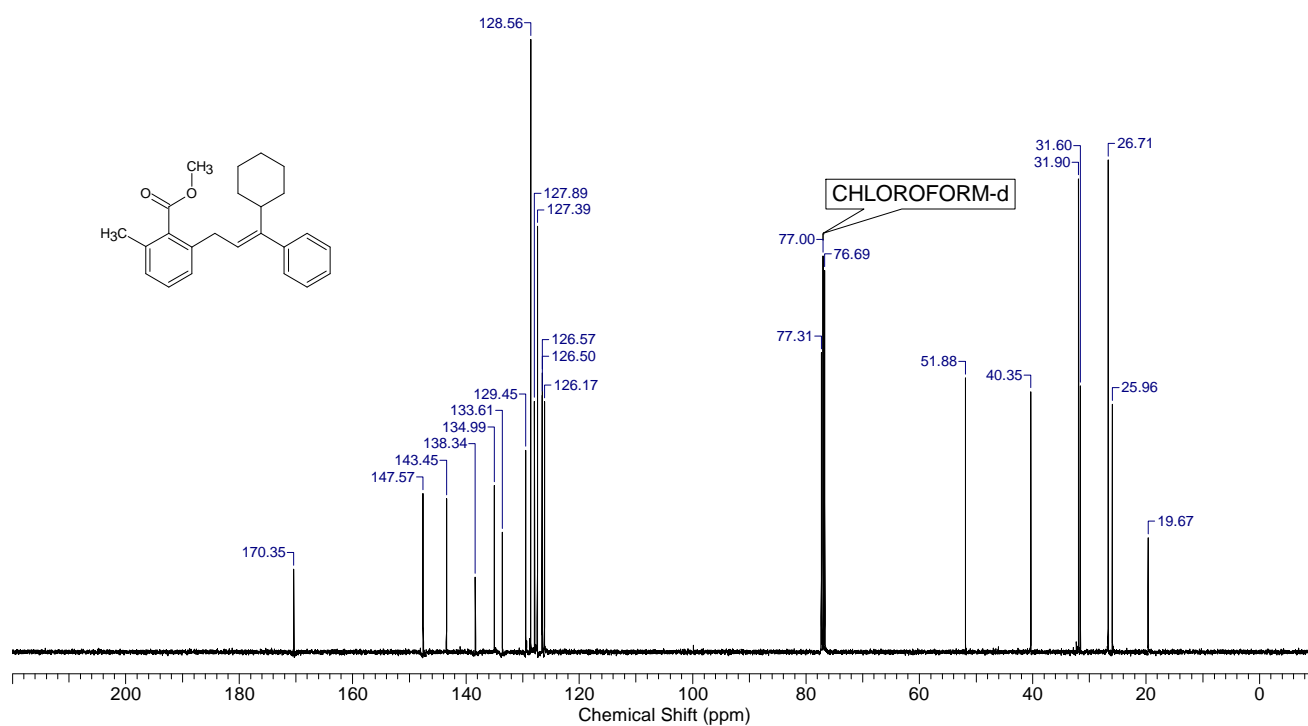


Methyl 2-(3-cyclohexyl-3-phenyl-allyl)-6-methyl-benzoate (3an)

¹H NMR (400 MHz, CDCl₃)

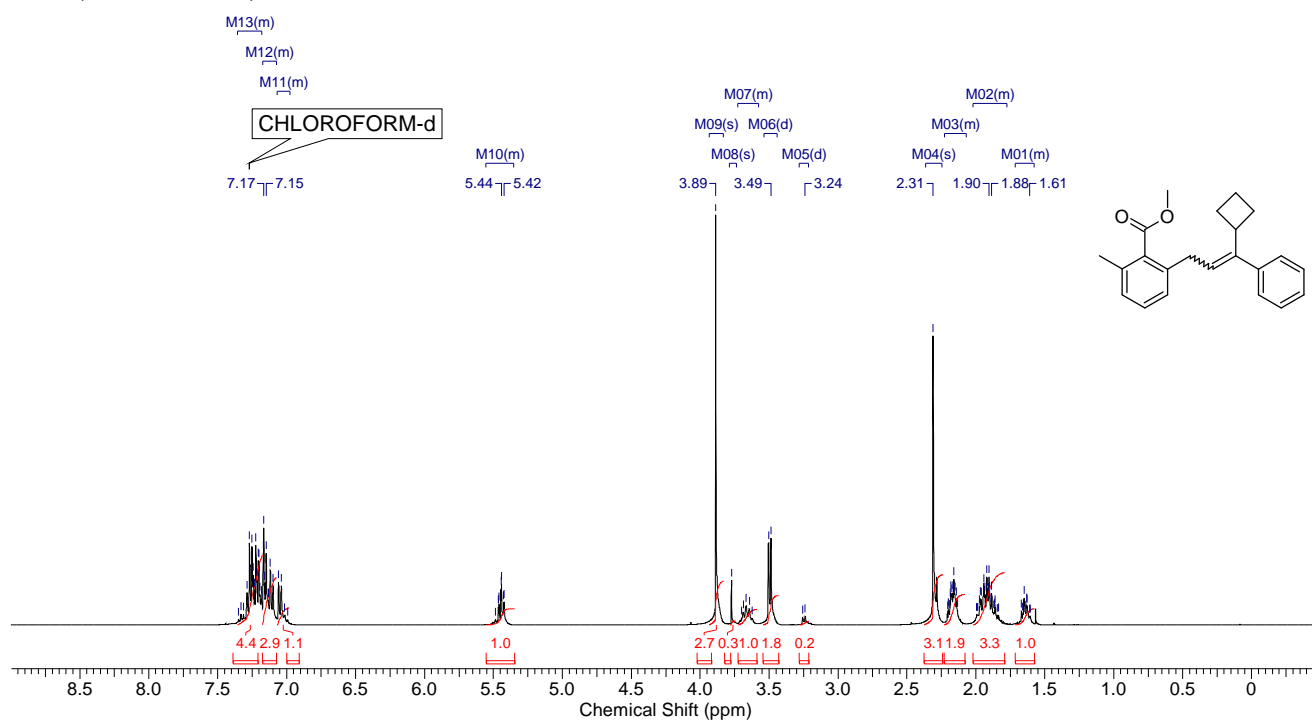


¹³C NMR (101 MHz, CDCl₃)

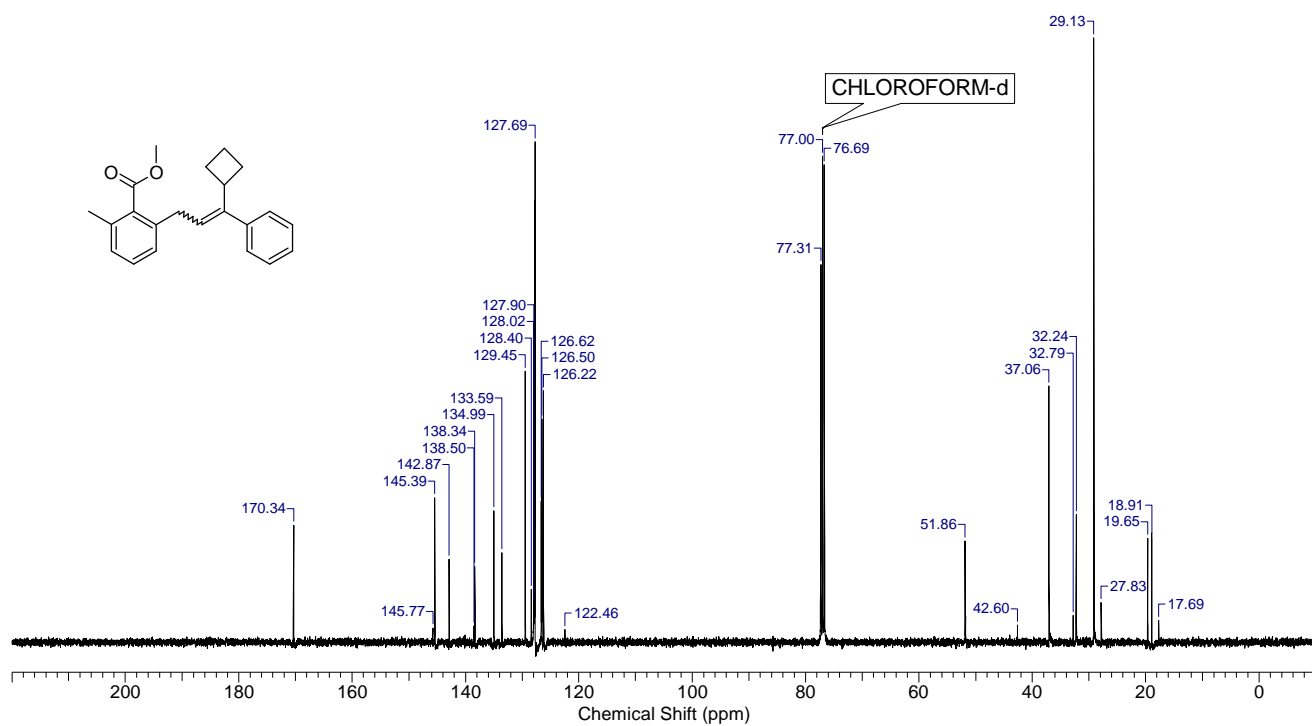


Methyl 2-(3-cyclobutyl-3-phenyl-allyl)-6-methyl-benzoate (3ao)

¹H NMR (400 MHz, CDCl₃)

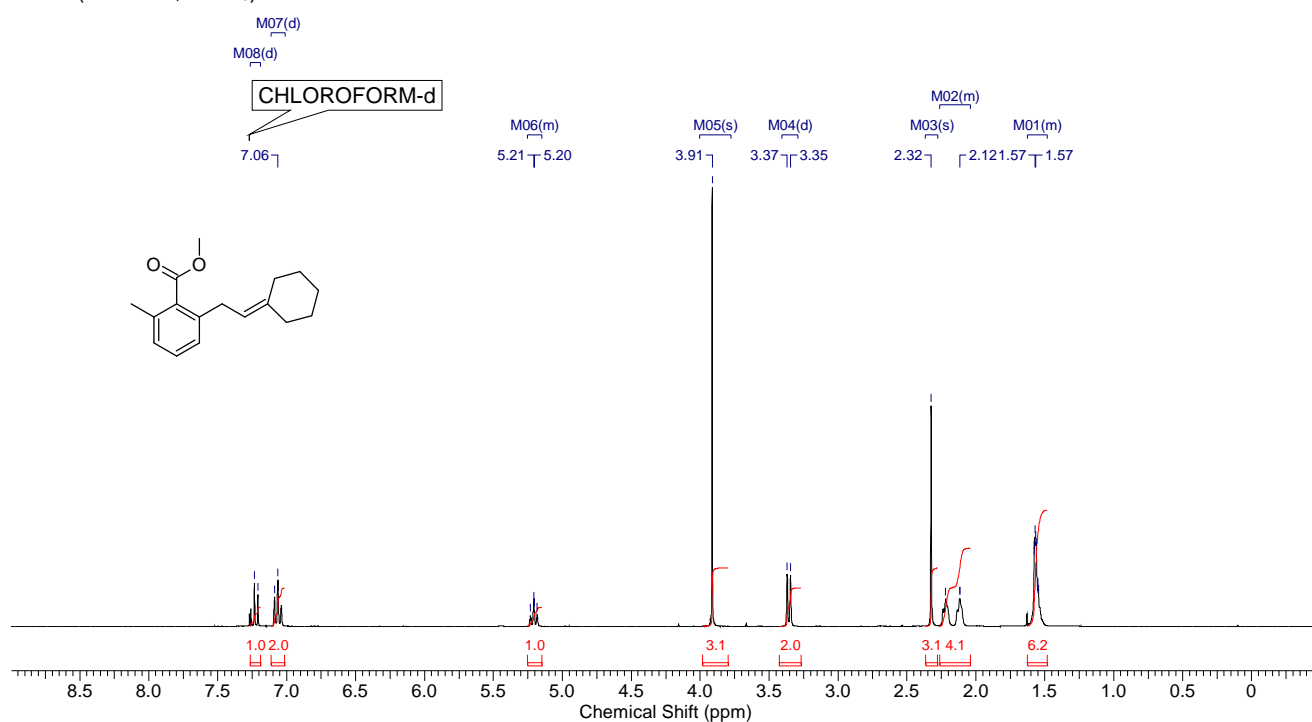


¹³C NMR (101 MHz, CDCl₃)

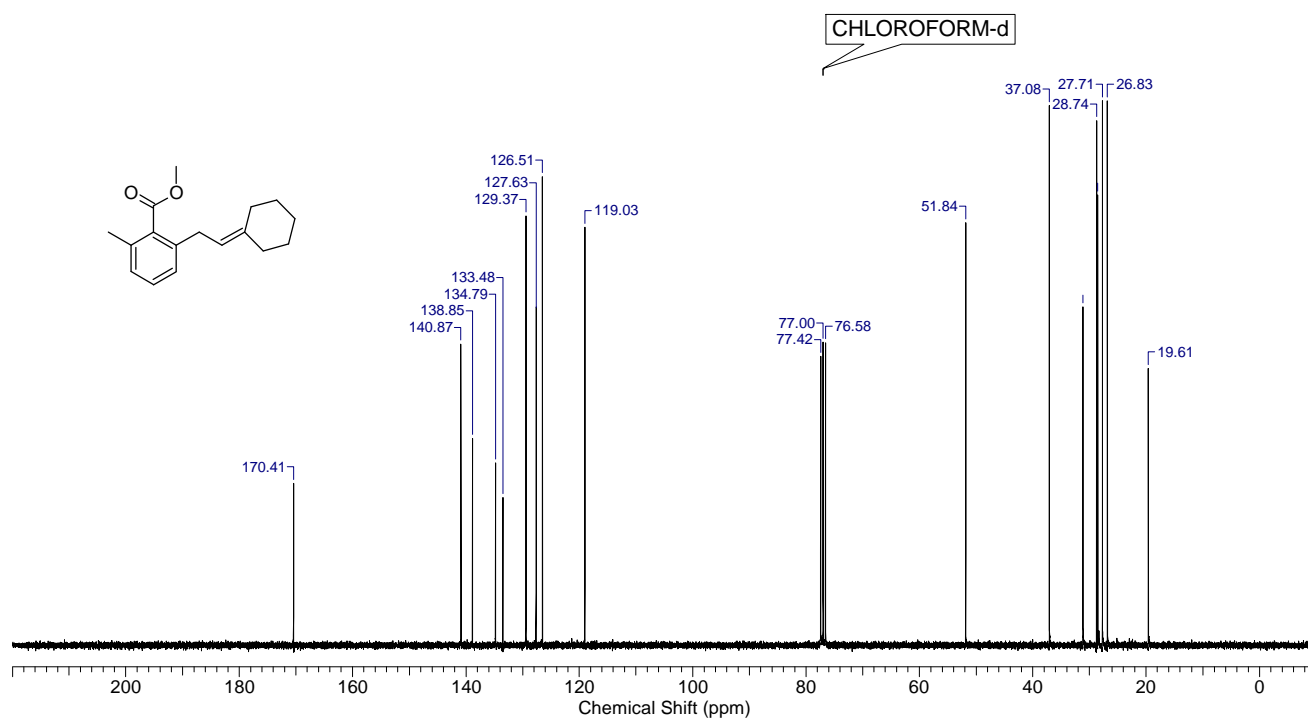


2-(2-cyclohexylideneethyl)-6-methyl-benzoate (3ap)

^1H NMR (300 MHz, CDCl_3)

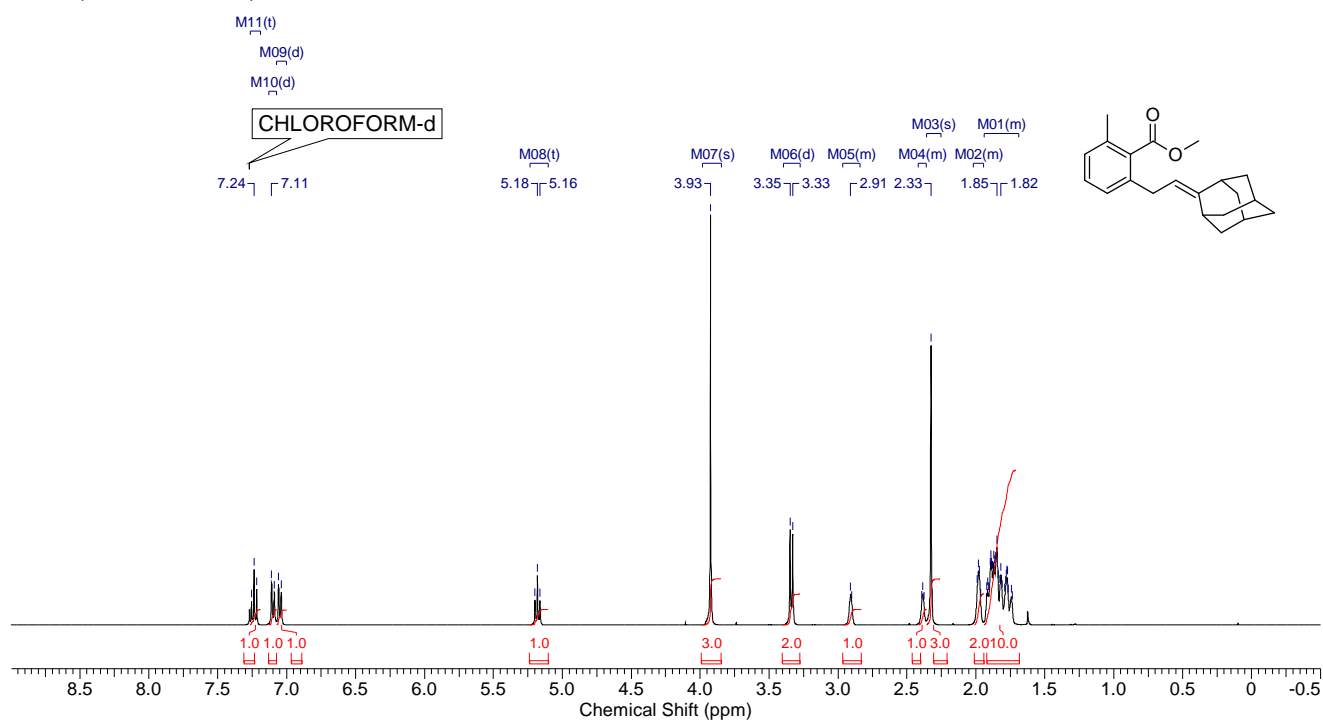


^{13}C NMR (75 MHz, CDCl_3)

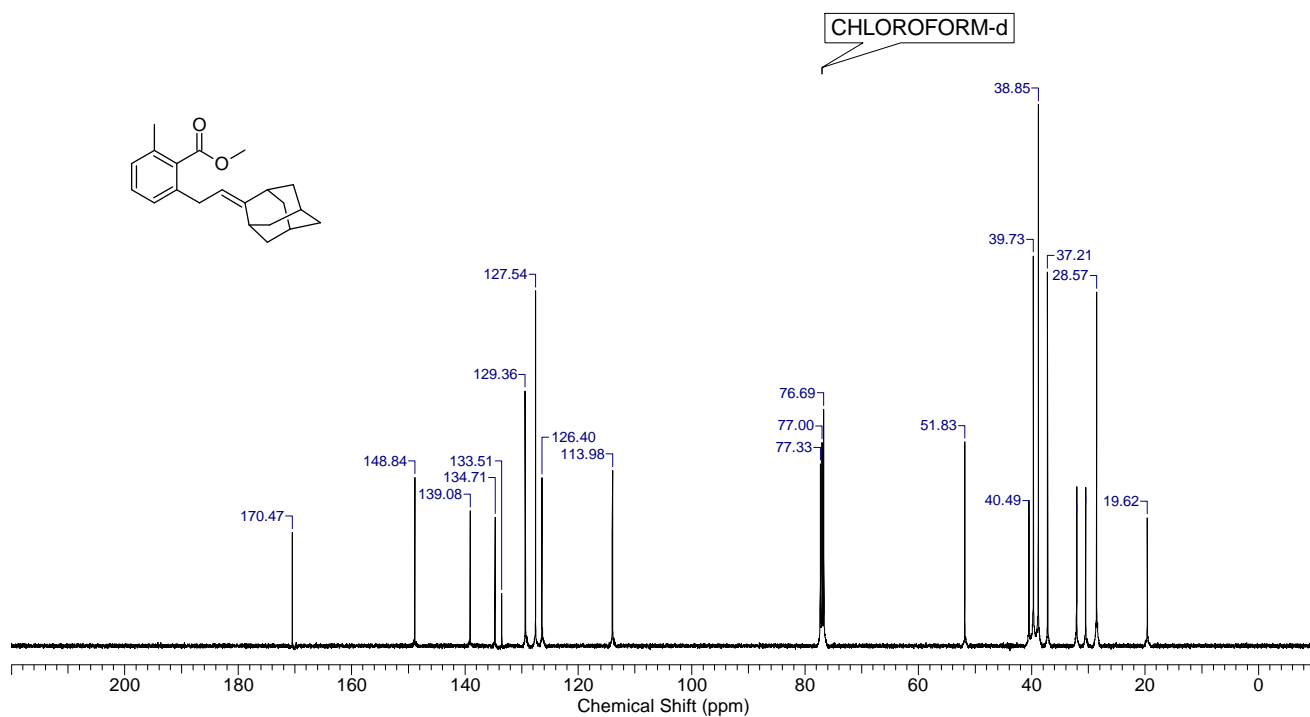


Methyl 2-[2-(2-adamantylidene)ethyl]-6-methyl-benzoate (3aq)

¹H NMR (400 MHz, CDCl₃)

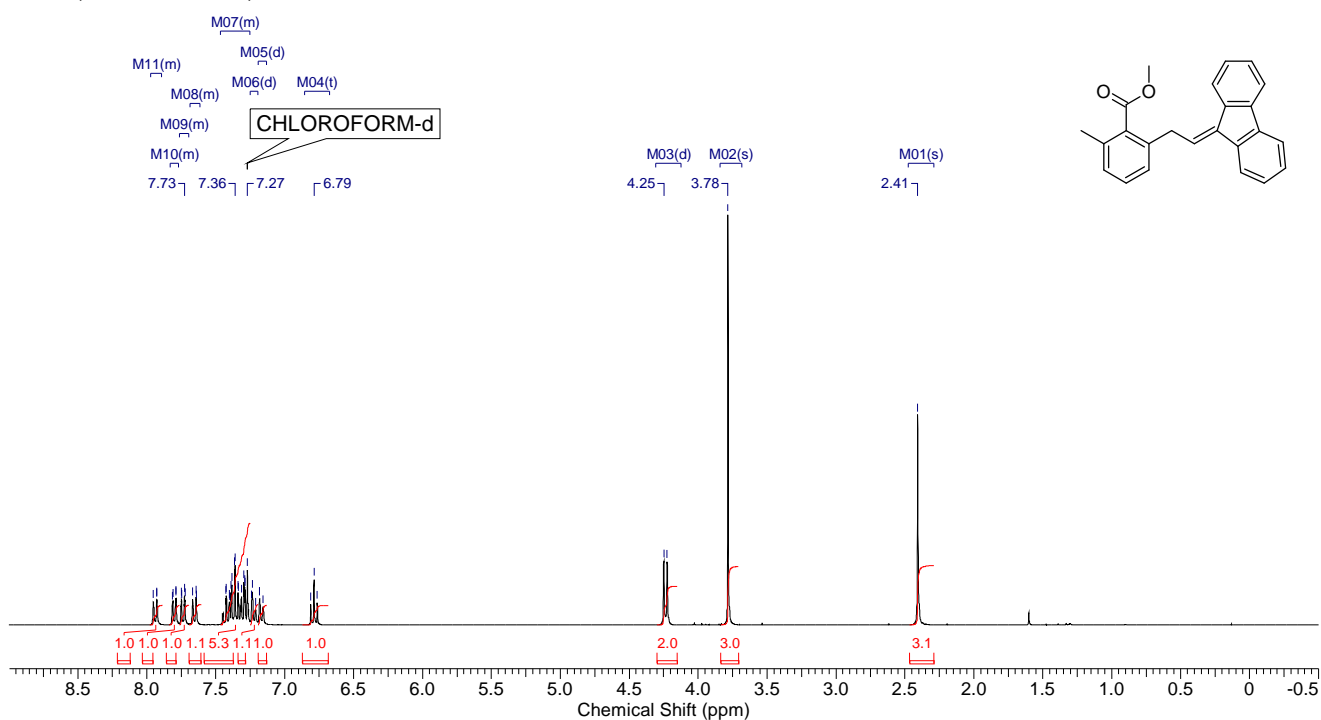


¹³C NMR (101 MHz, CDCl₃)

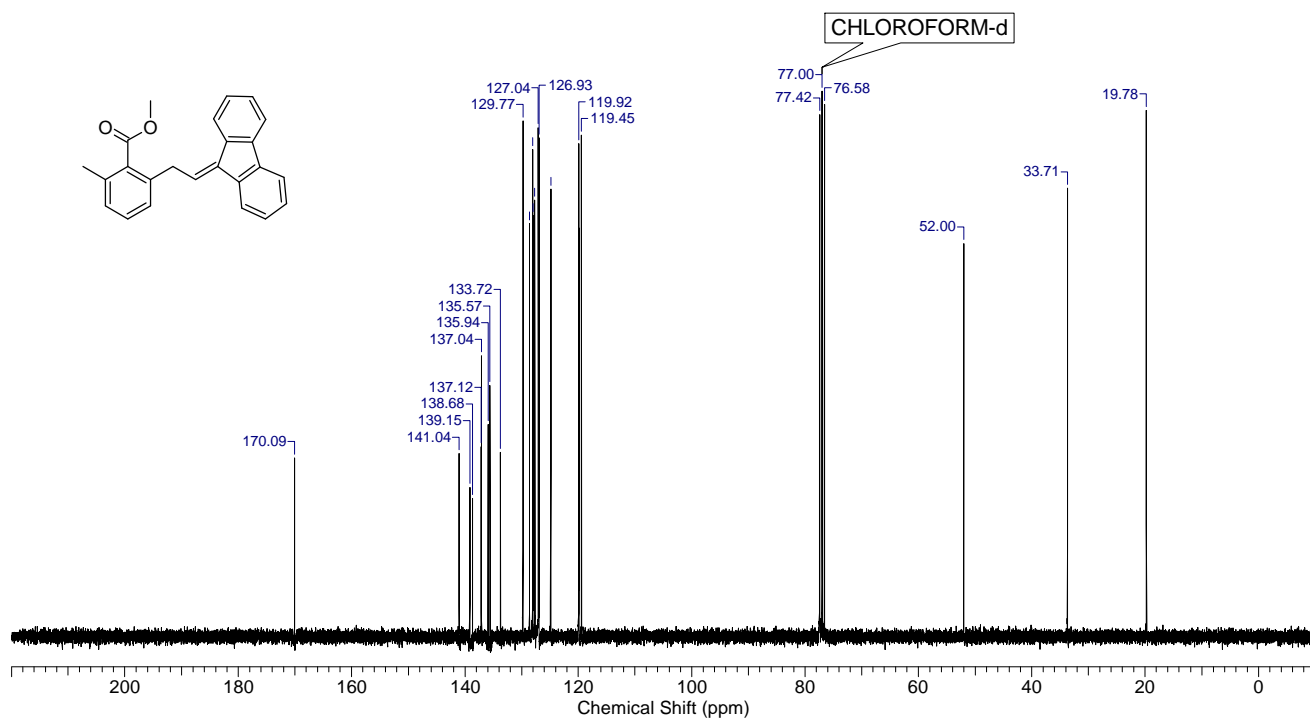


Methyl 2-(2-fluorenylideneethyl)-6-methyl-benzoate (3ar)

^1H NMR (300 MHz, CDCl_3)

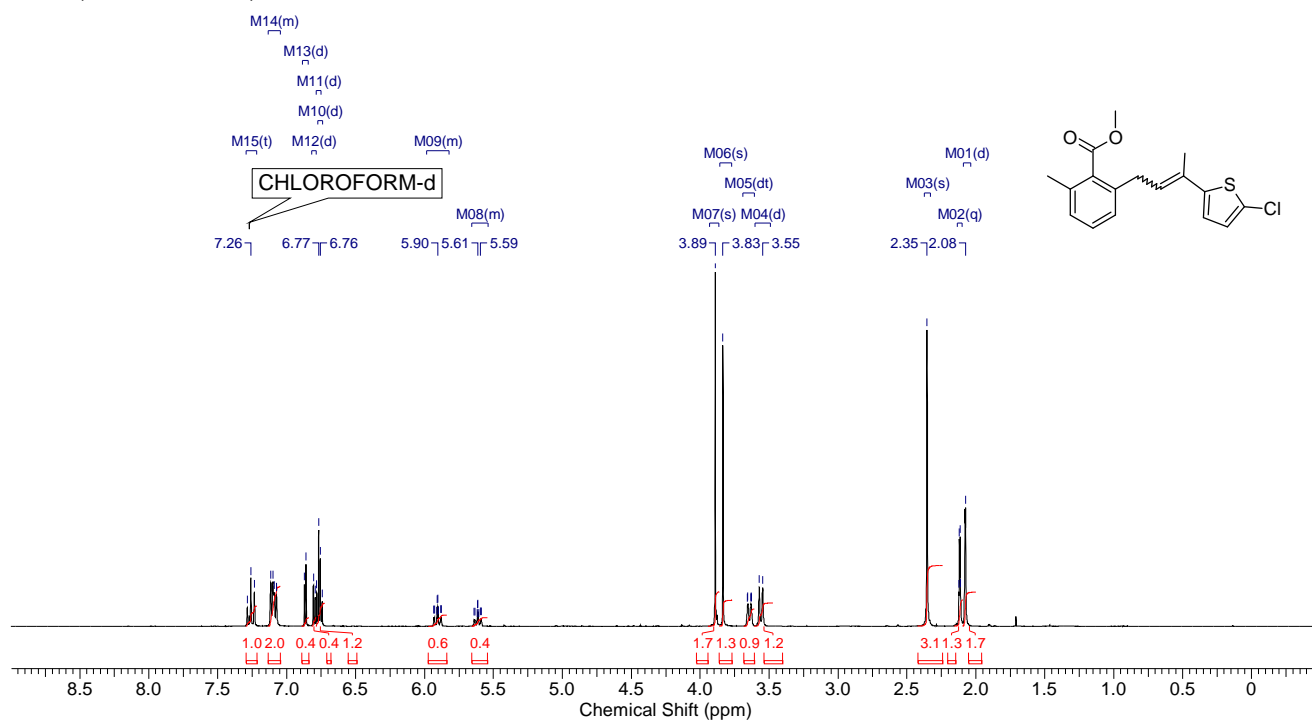


^{13}C NMR (75 MHz, CDCl_3)

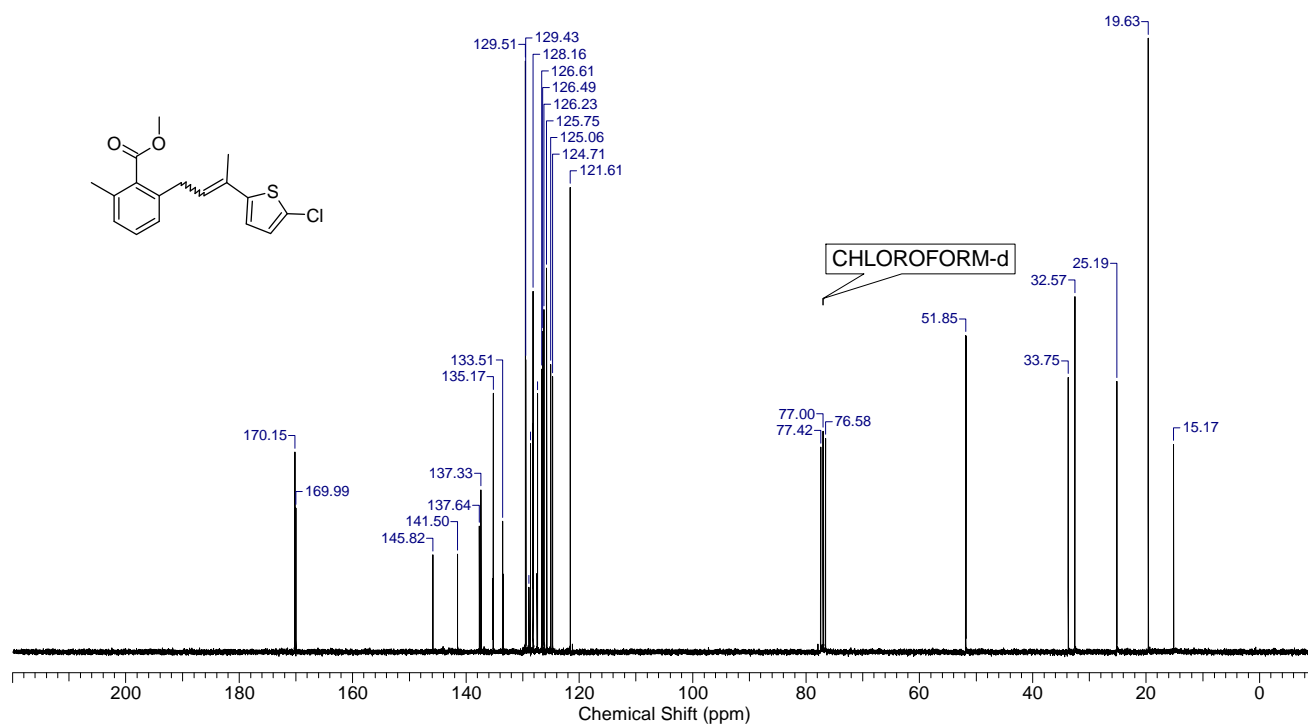


Methyl 2-[3-(5-chloro-2-thienyl)but-2-enyl]-6-methyl-benzoate (3as)

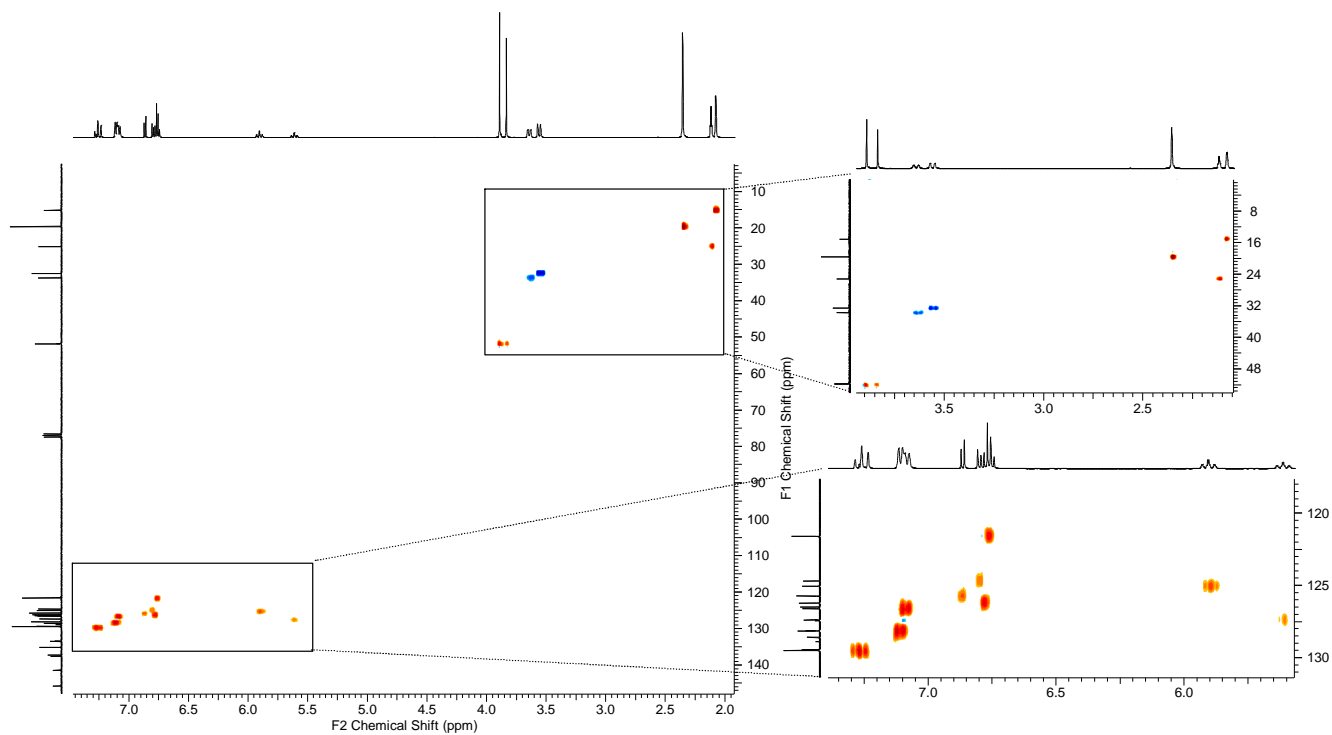
¹H NMR (300 MHz, CDCl₃)



¹³C NMR (75 MHz, CDCl₃)

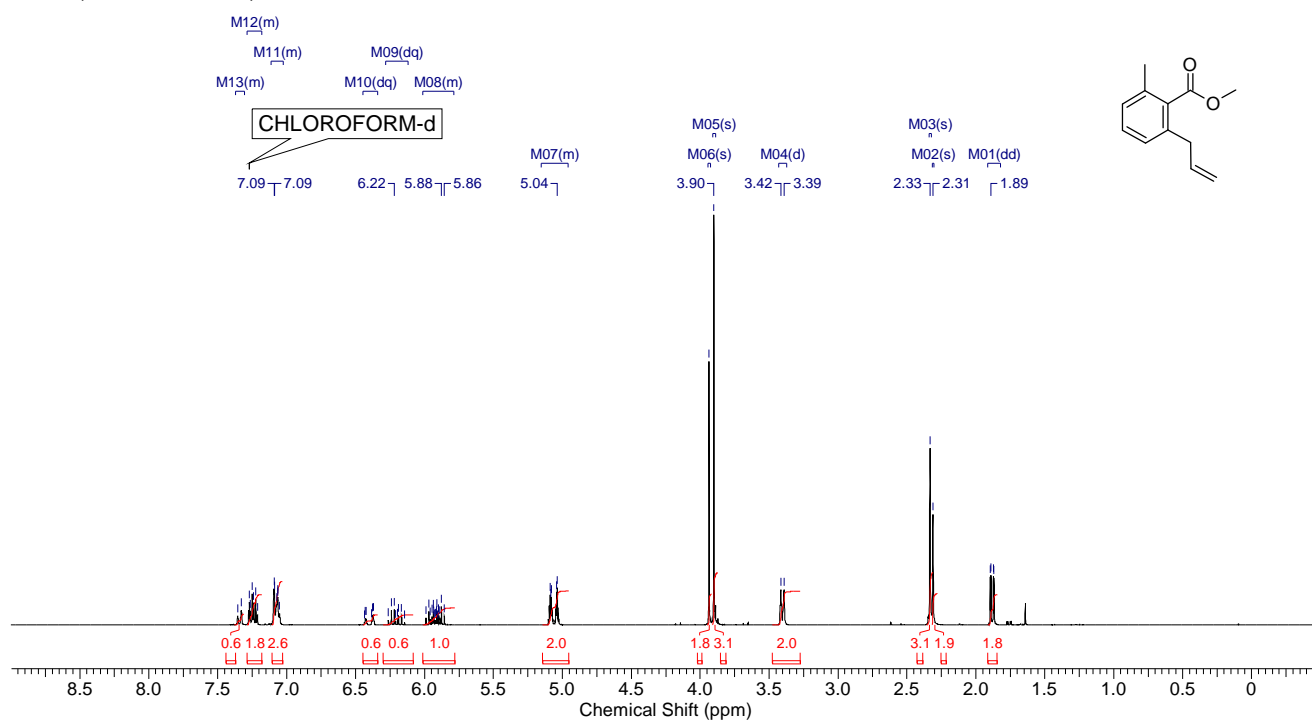


$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

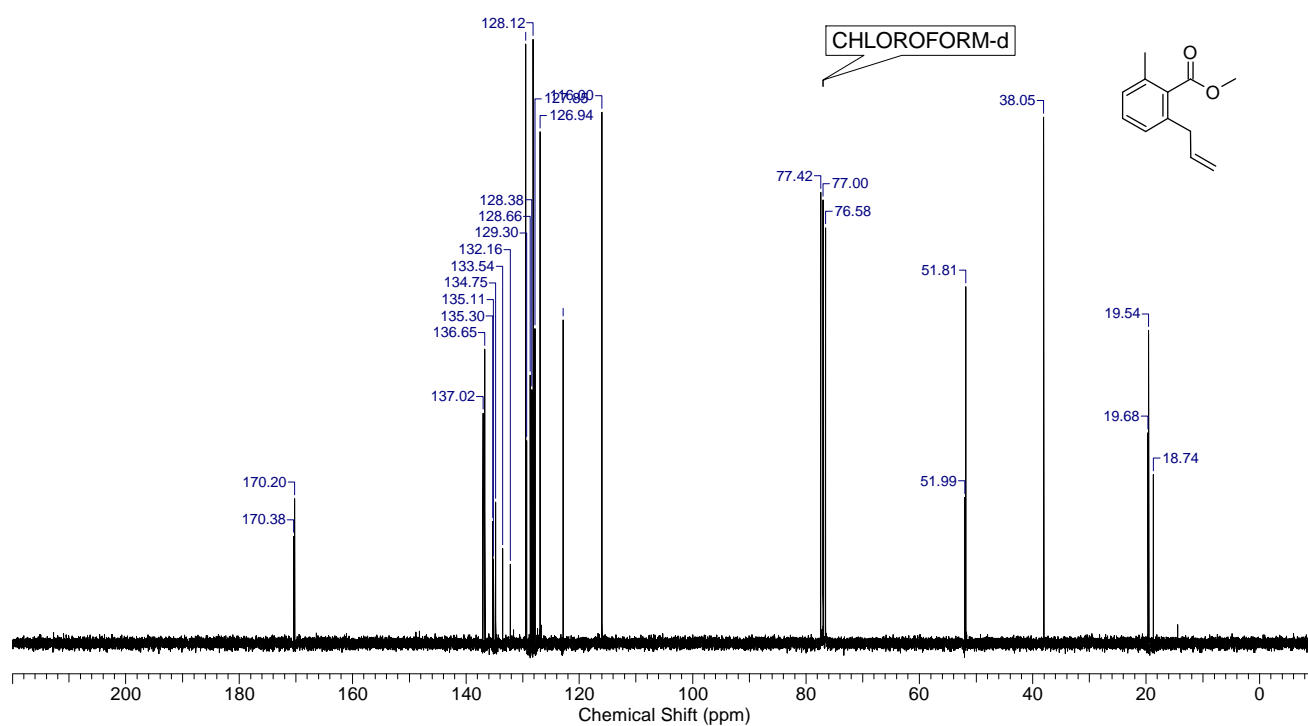


Methyl 2-allyl-6-methyl-benzoate (3at)

^1H NMR (300 MHz, CDCl_3)

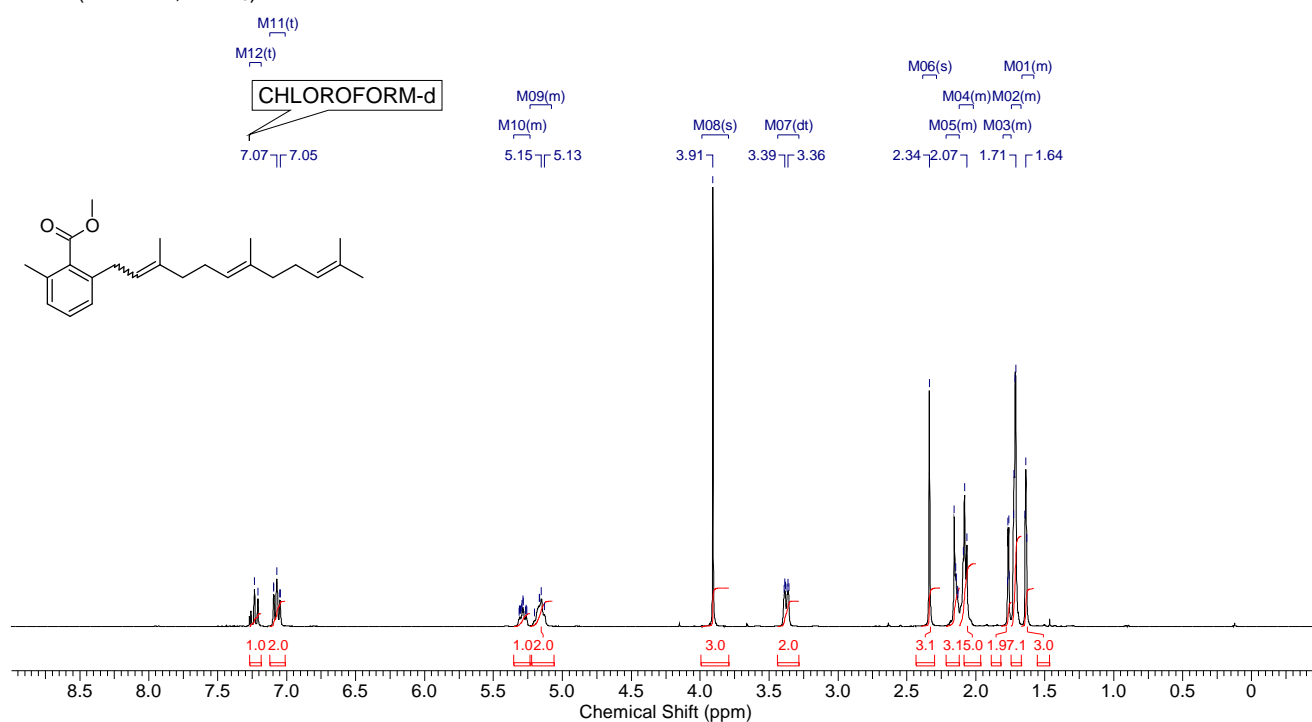


^{13}C NMR (75 MHz, CDCl_3)

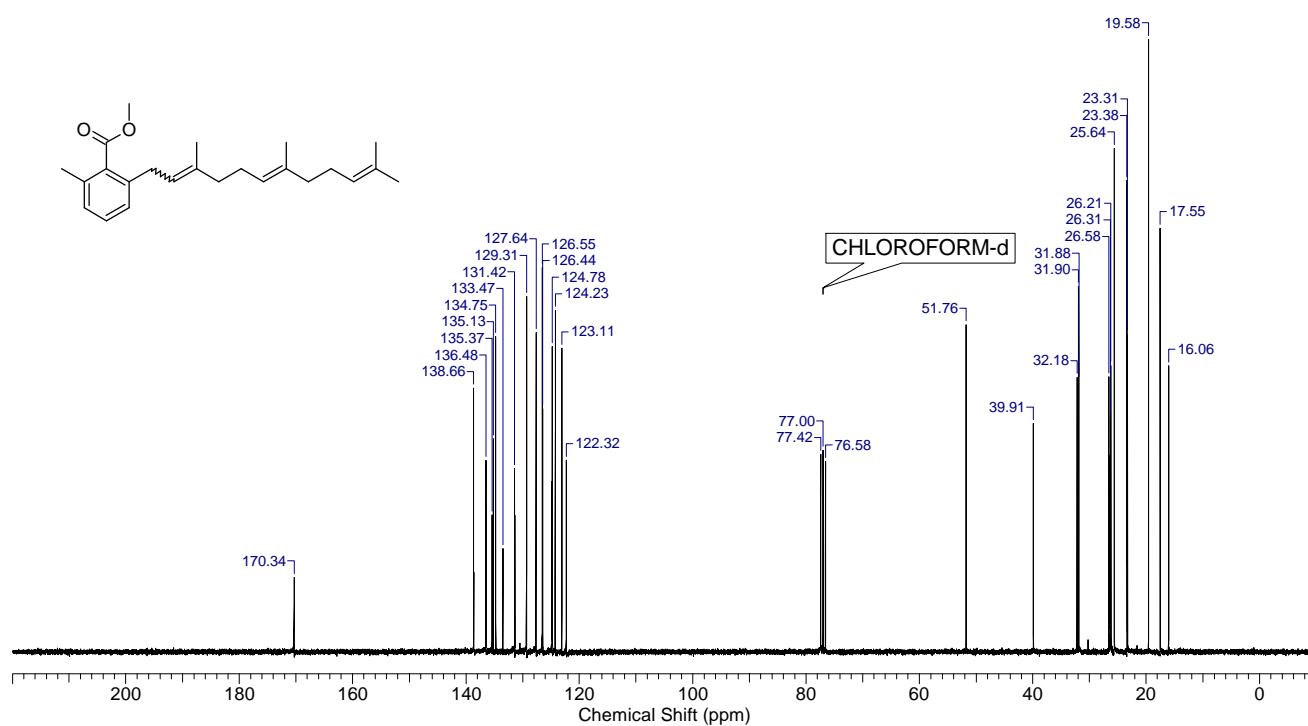


Methyl 2-methyl-6-[(6E)-3,7,11-trimethyldodeca-2,6,10-trienyl]benzoate (4aa)

^1H NMR (300 MHz, CDCl_3)

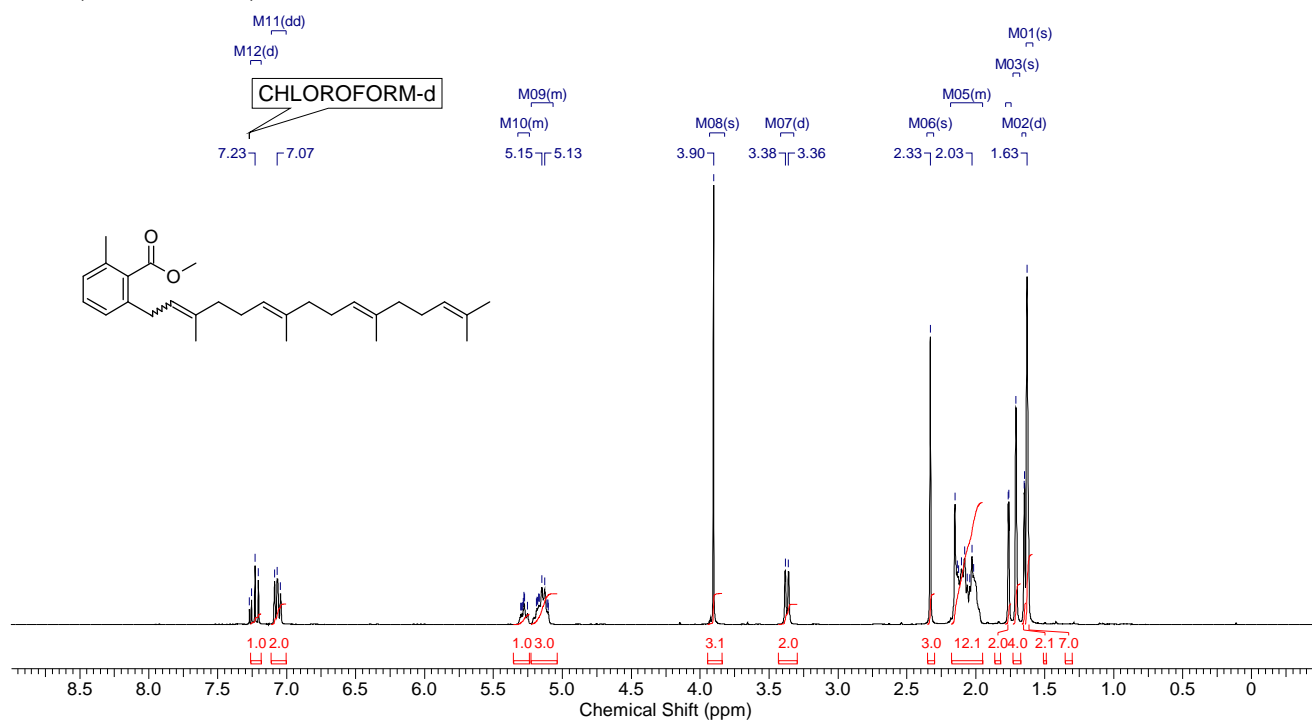


^{13}C NMR (75 MHz, CDCl_3)

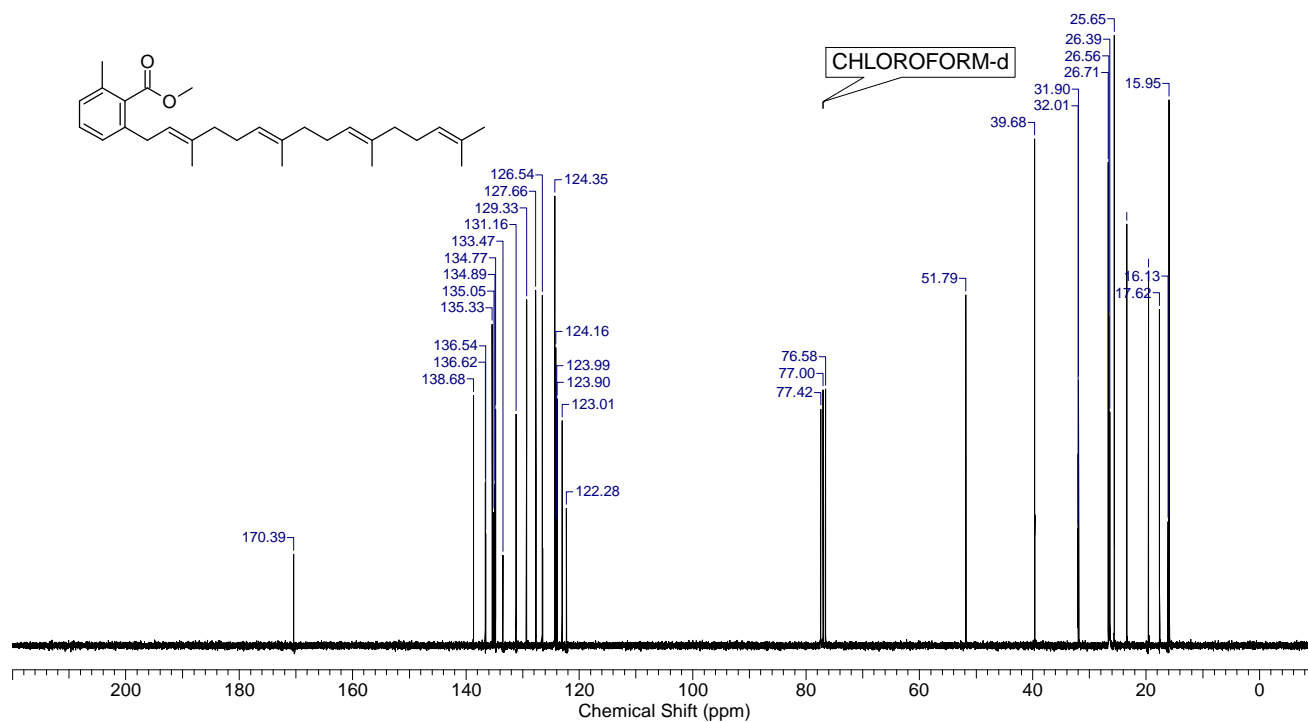


Methyl 2-methyl-6-[(6E,10E)-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraenyl]benzoate (4ab)

¹H NMR (300 MHz, CDCl₃)

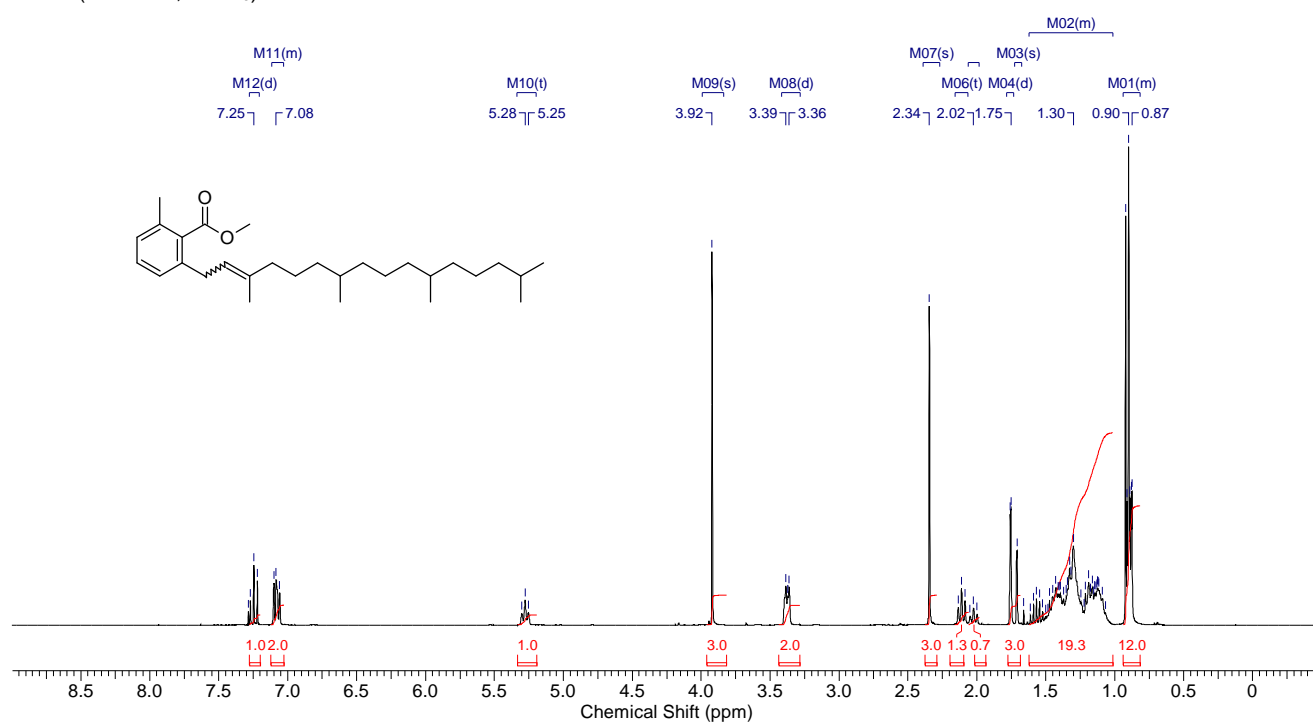


¹³C NMR (75 MHz, CDCl₃)

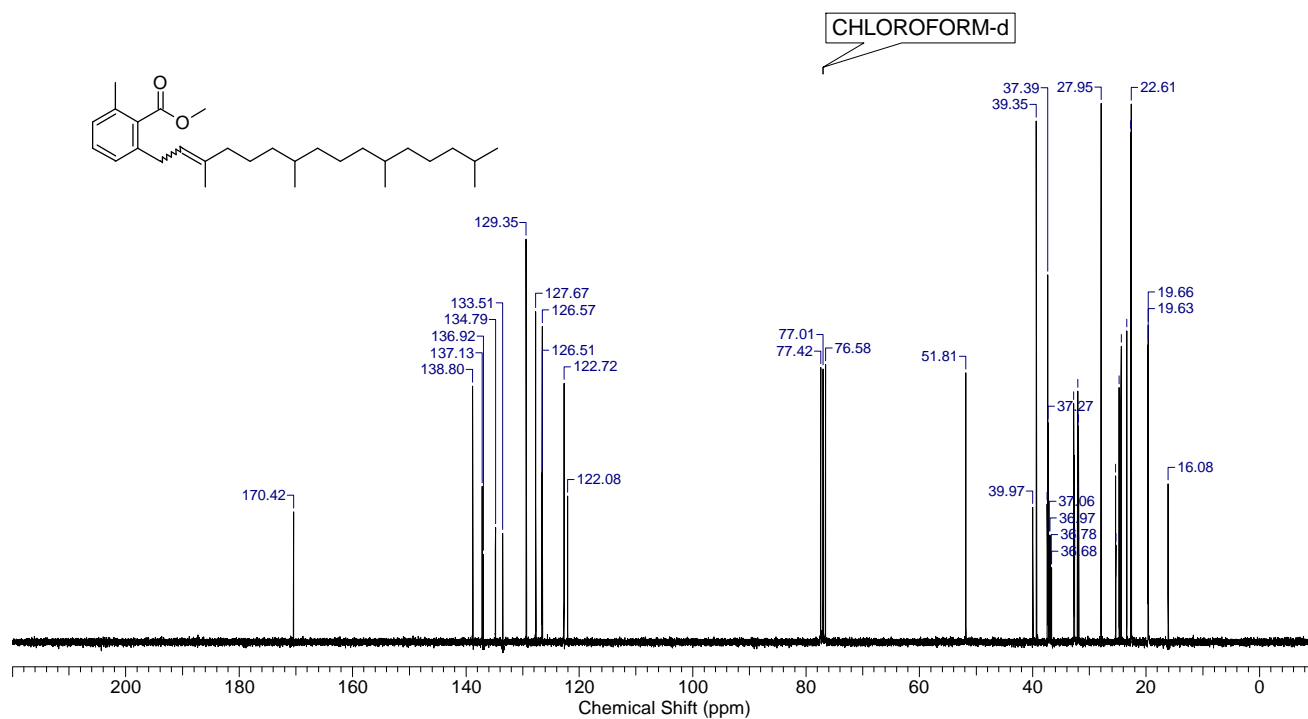


Methyl 2-methyl-6-(3,7,11,15-tetramethylhexadec-2-enyl)benzoate (4ac)

¹H NMR (300 MHz, CDCl₃)

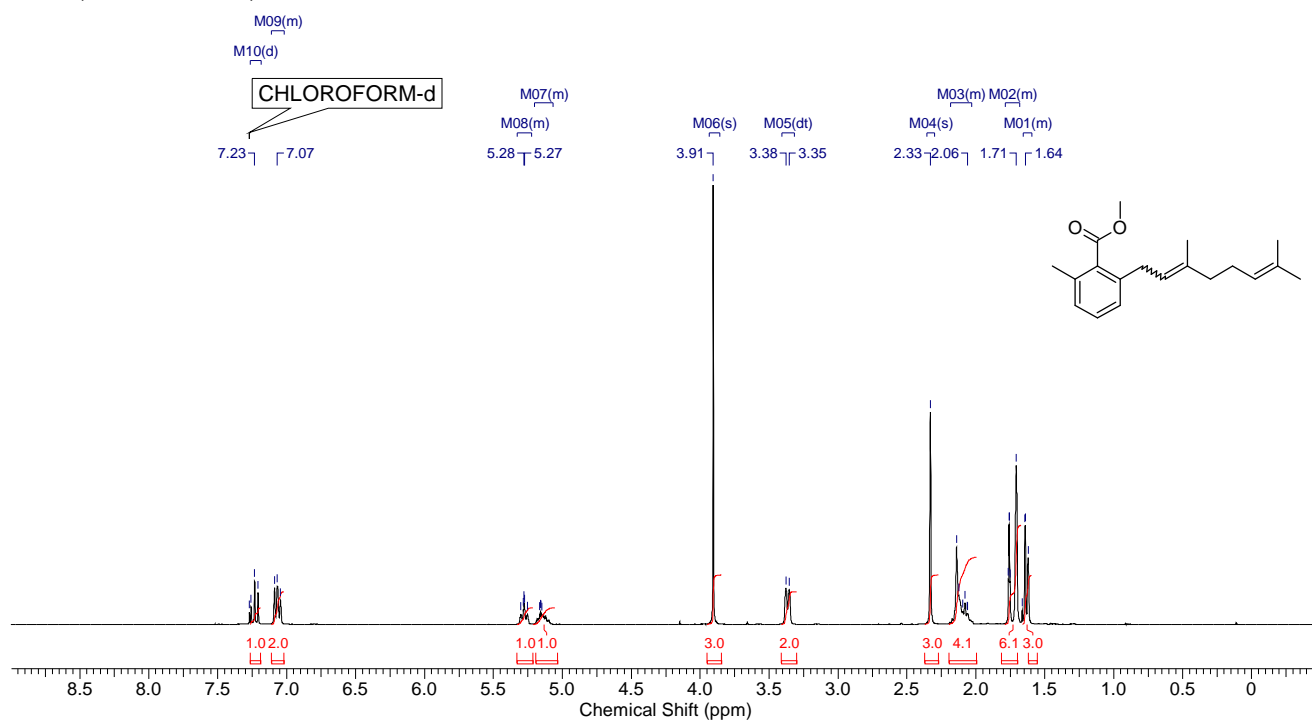


¹³C NMR (75 MHz, CDCl₃)

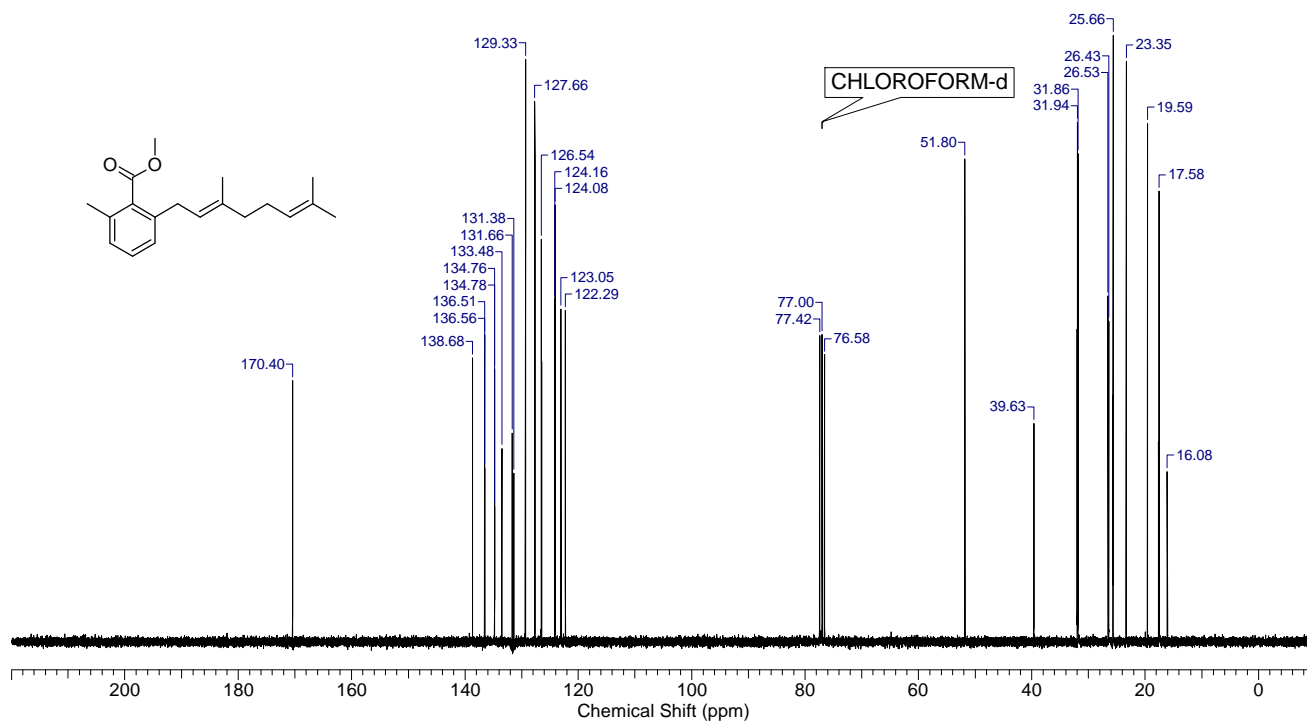


Methyl 2-(3,7-dimethylocta-2,6-dienyl)-6-methyl-benzoate (4ad)

¹H NMR (300 MHz, CDCl₃)

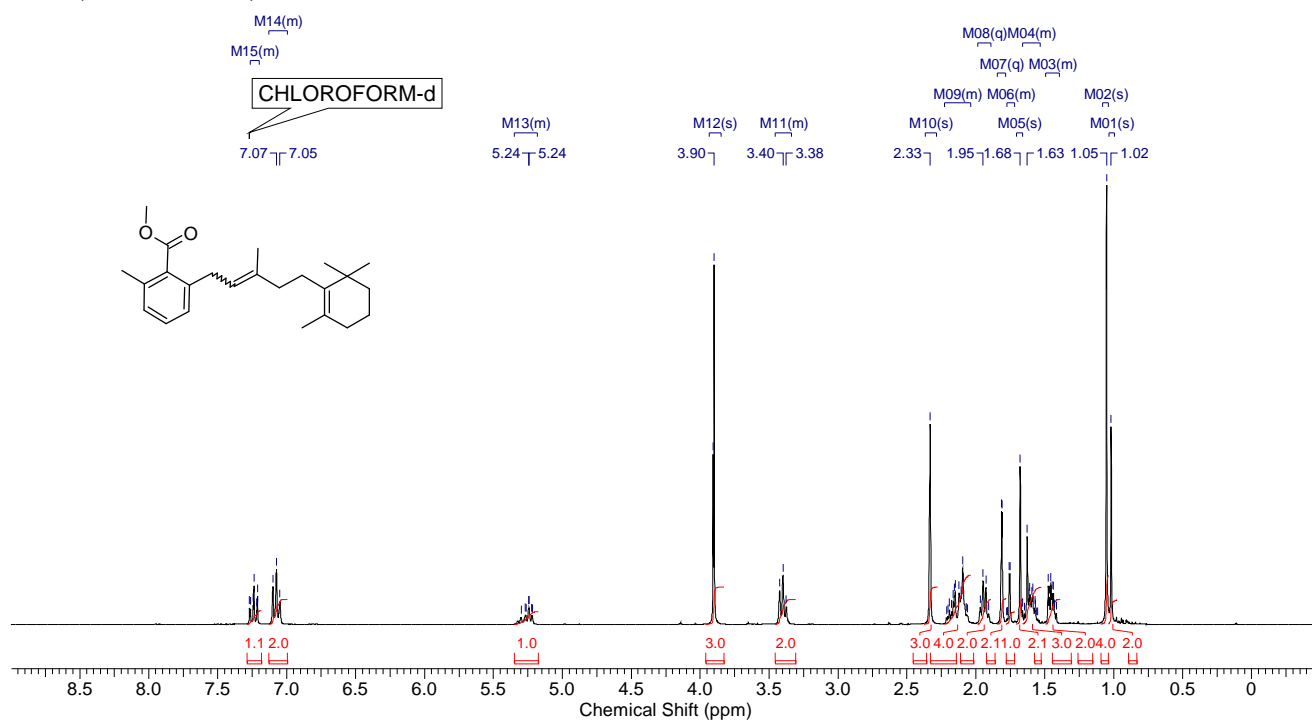


¹³C NMR (75 MHz, CDCl₃)

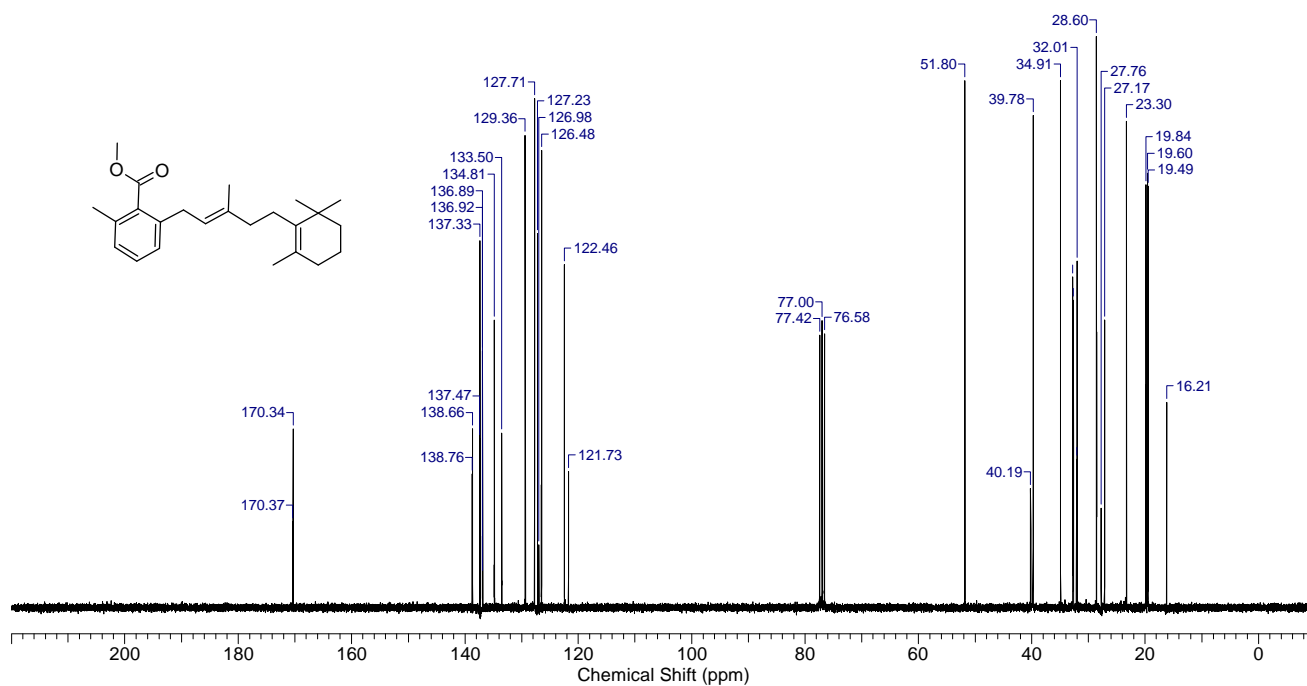


Methyl 2-methyl-6-[3-methyl-5-(2,6,6-trimethylcyclohexen-1-yl)pent-2-enyl]benzoate (4ae)

¹H NMR (300 MHz, CDCl₃)

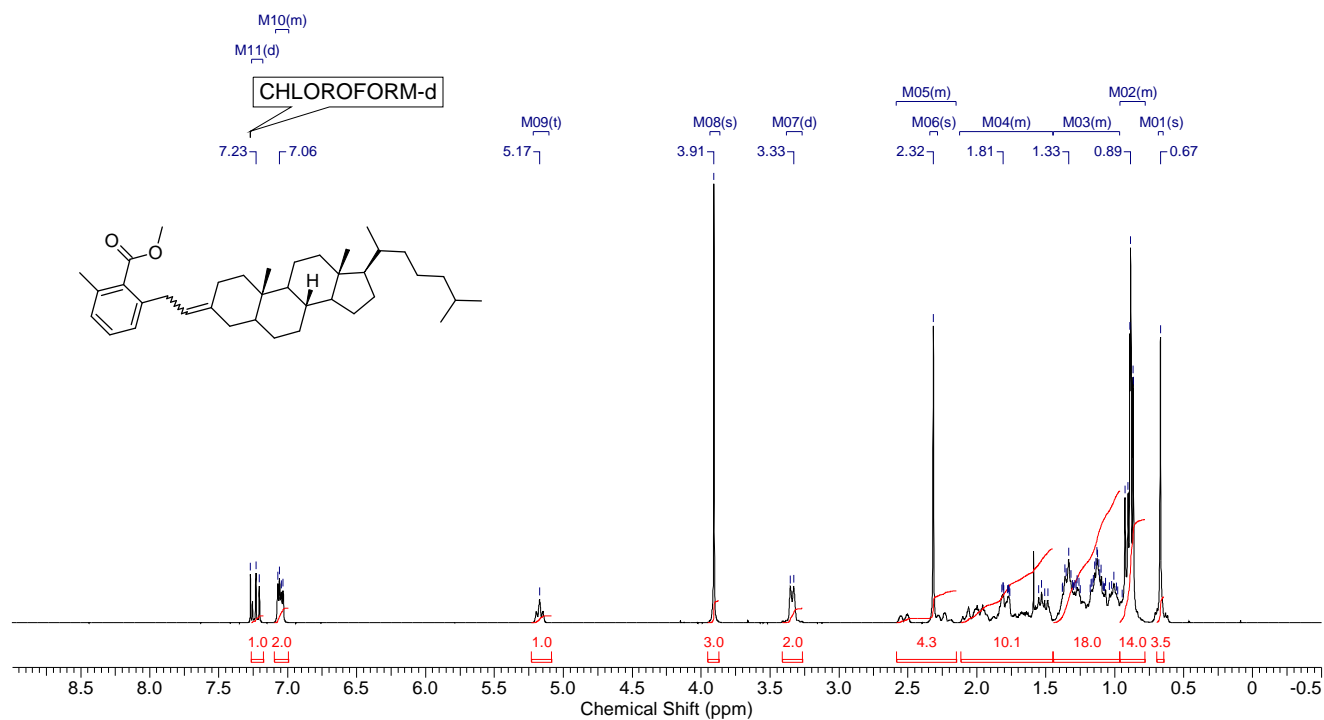


¹³C NMR (75 MHz, CDCl₃)

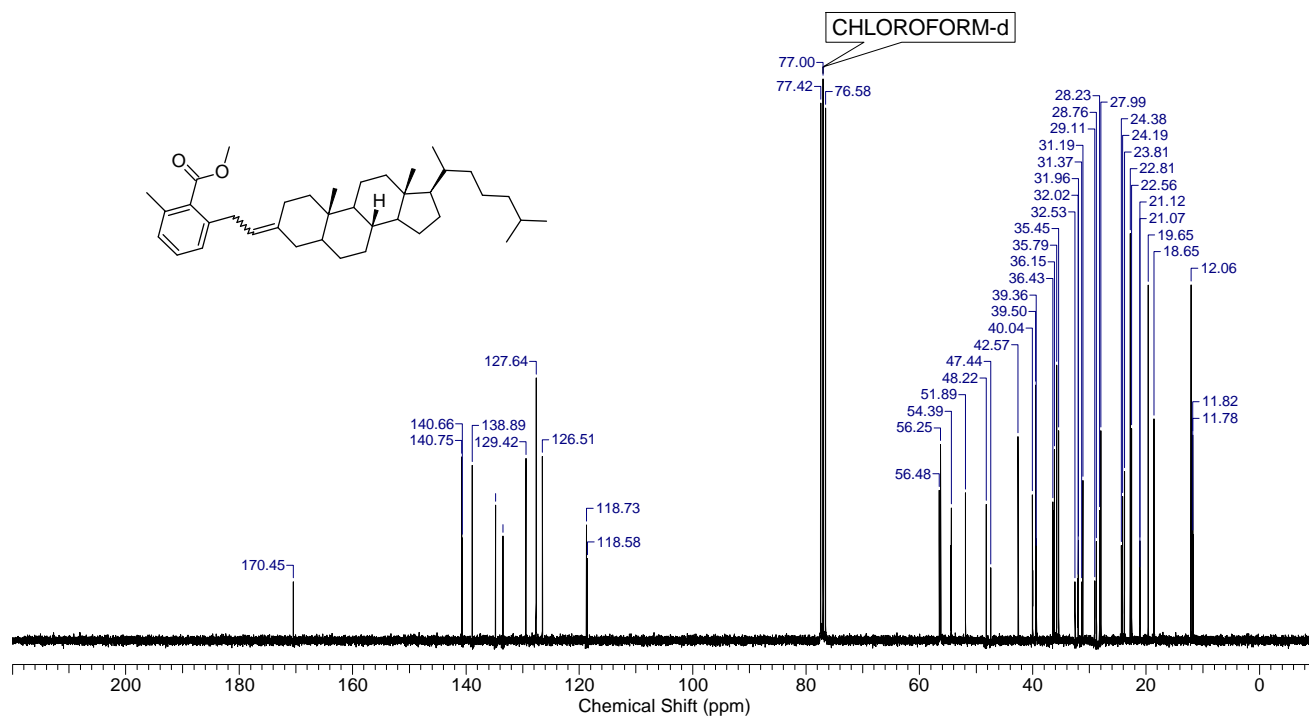


Methyl 2-[2-[(8R,10S,13R,17R)-17-(1,5-dimethylhexyl)-10,13-dimethyl-1,2,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydrocyclopenta[a]phenanthren-3-ylidene]ethyl]-6-methyl-benzoate (4af)

¹H NMR (300 MHz, CDCl₃)

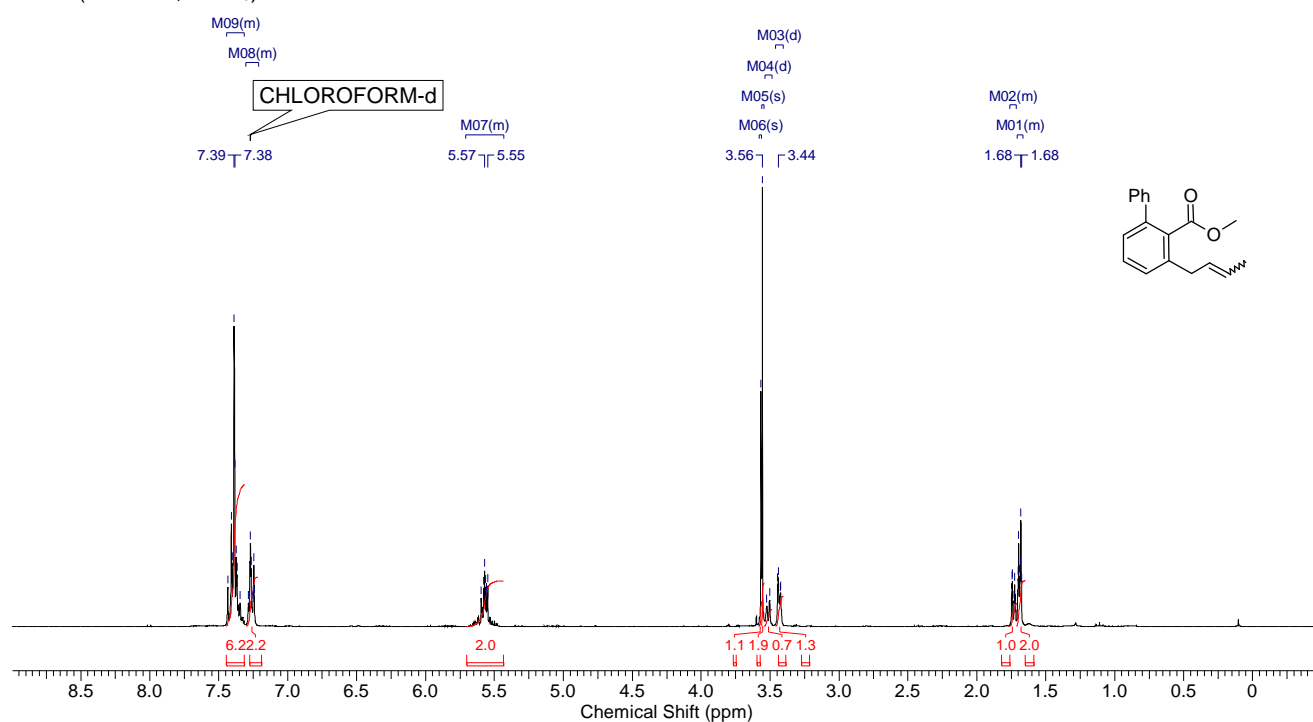


¹³C NMR (75 MHz, CDCl₃)

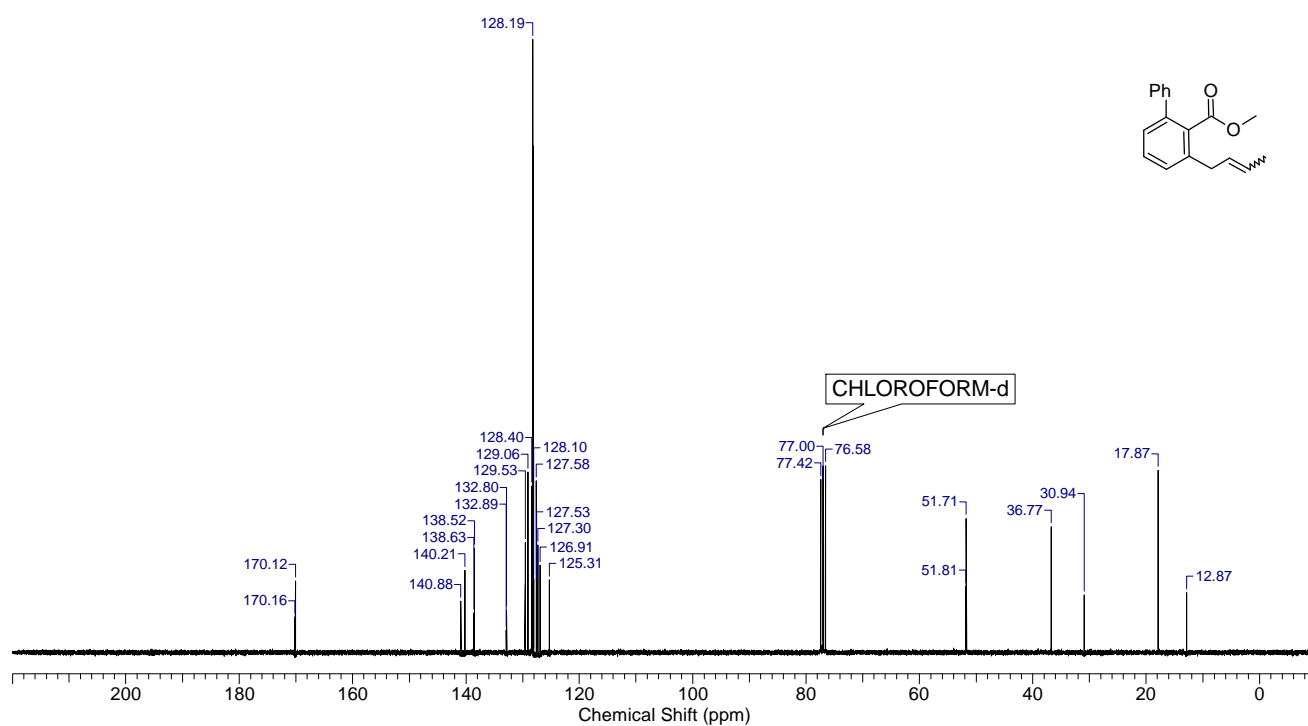


Methyl 2-(but-2-enyl)-6-phenyl-benzoate (3ba)

^1H NMR (300 MHz, CDCl_3)

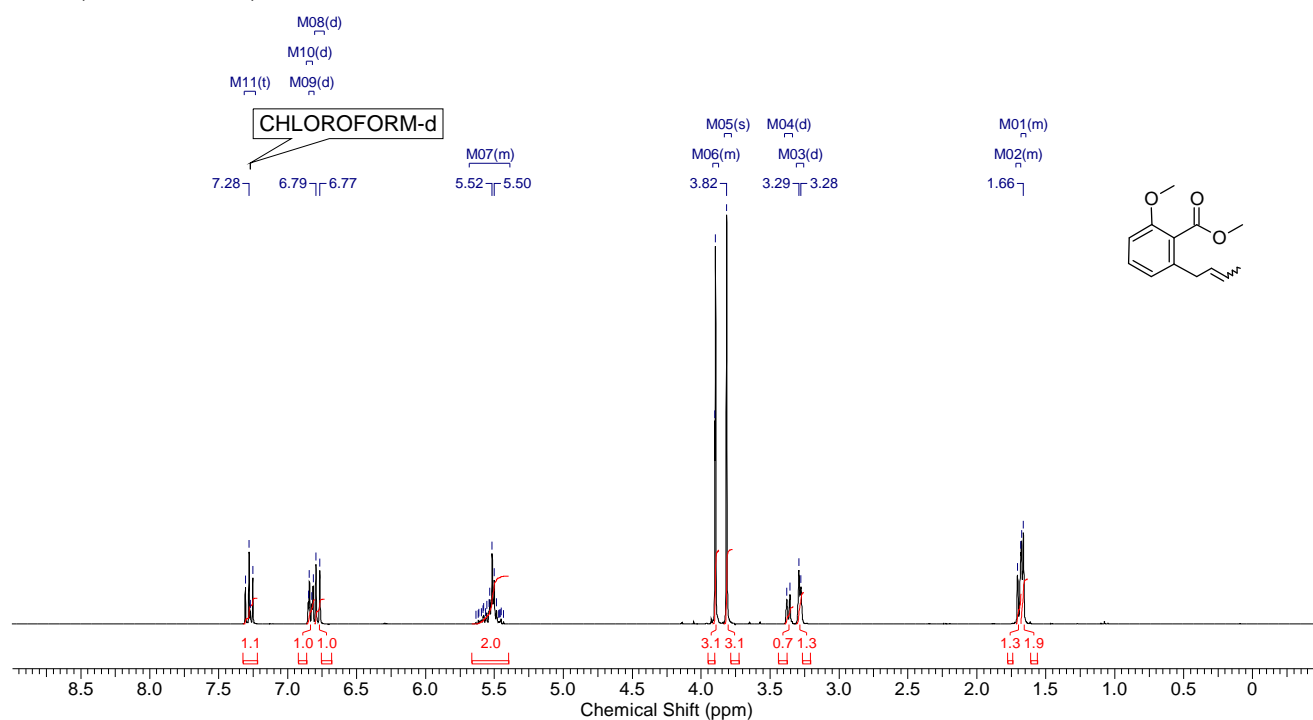


^{13}C NMR (75 MHz, CDCl_3)

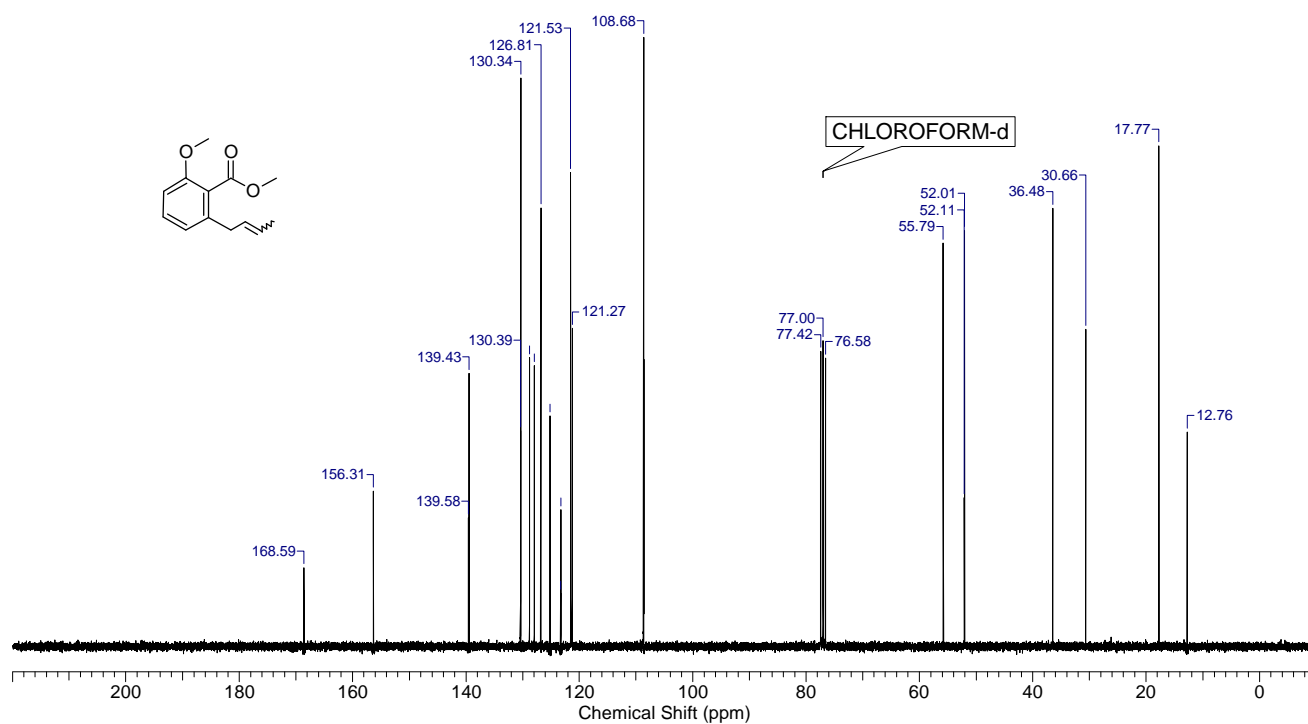


Methyl 2-(but-2-enyl)-6-methoxy-benzoate (3ca)

¹H NMR (300 MHz, CDCl₃)

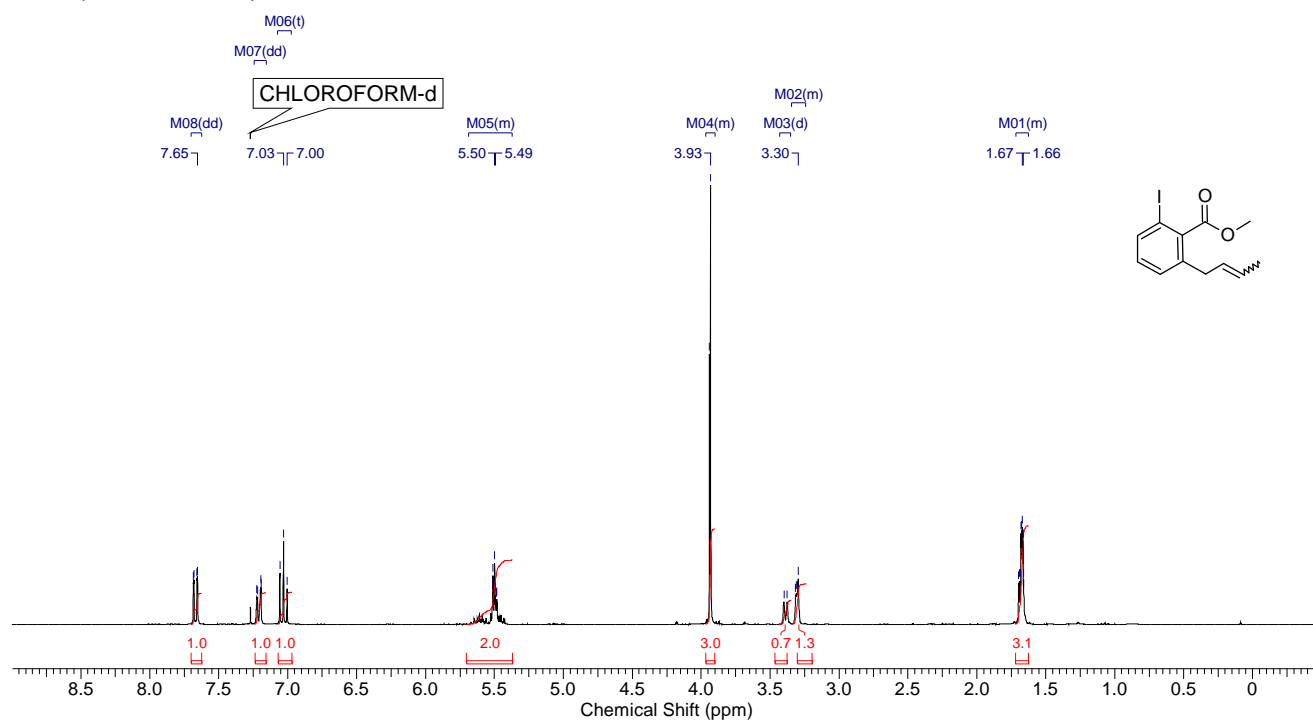


¹³C NMR (75 MHz, CDCl₃)

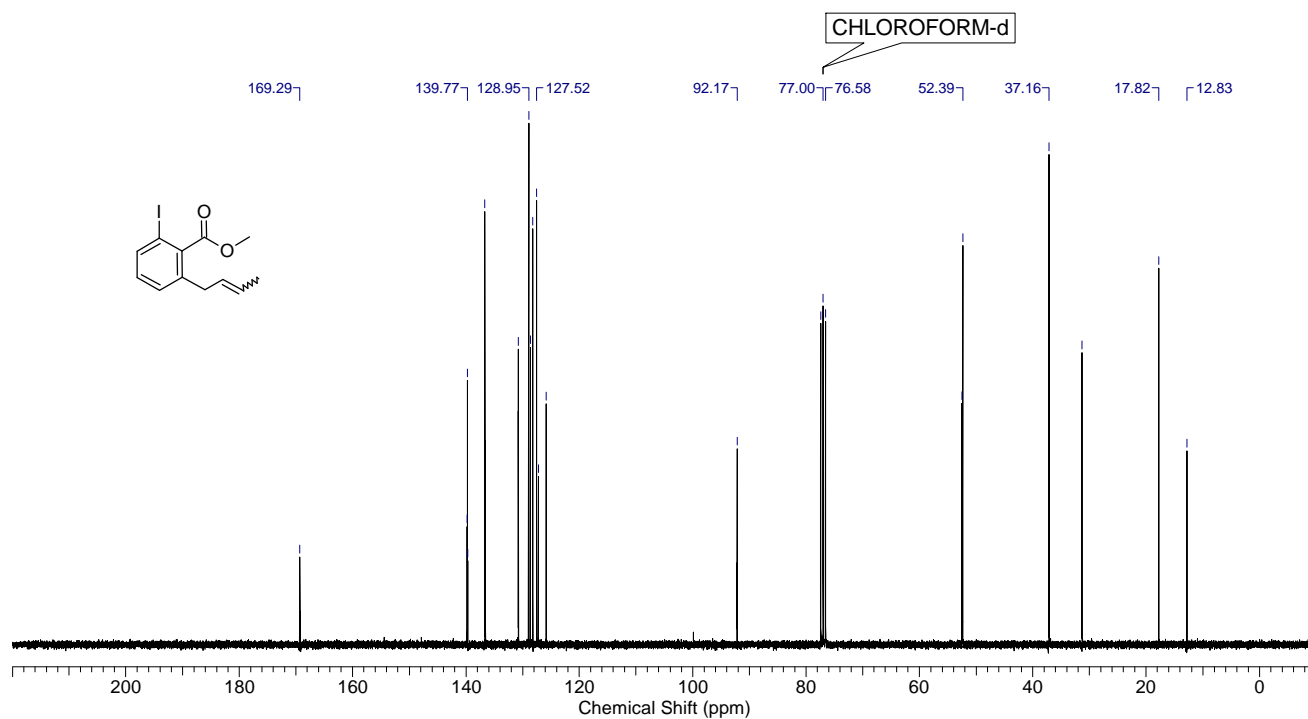


Methyl 2-(but-2-enyl)-6-iodo-benzoate (3da)

^1H NMR (300 MHz, CDCl_3)

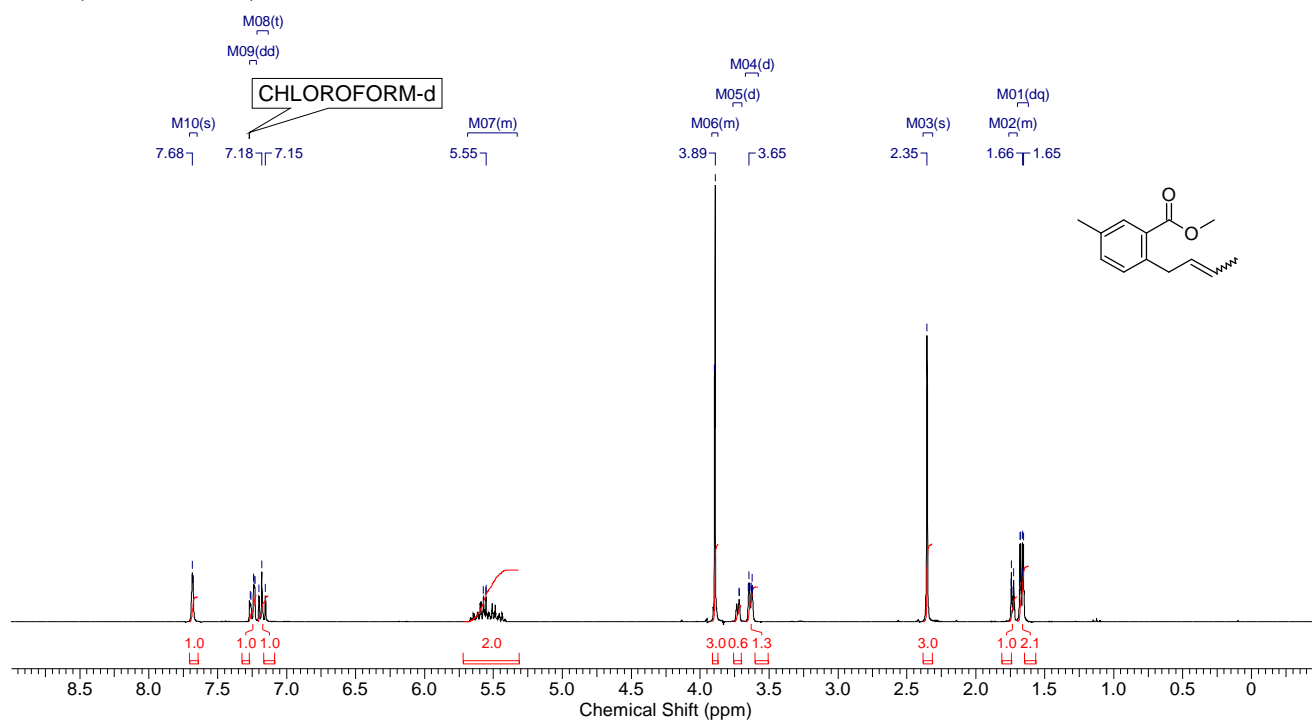


^{13}C NMR (75 MHz, CDCl_3)

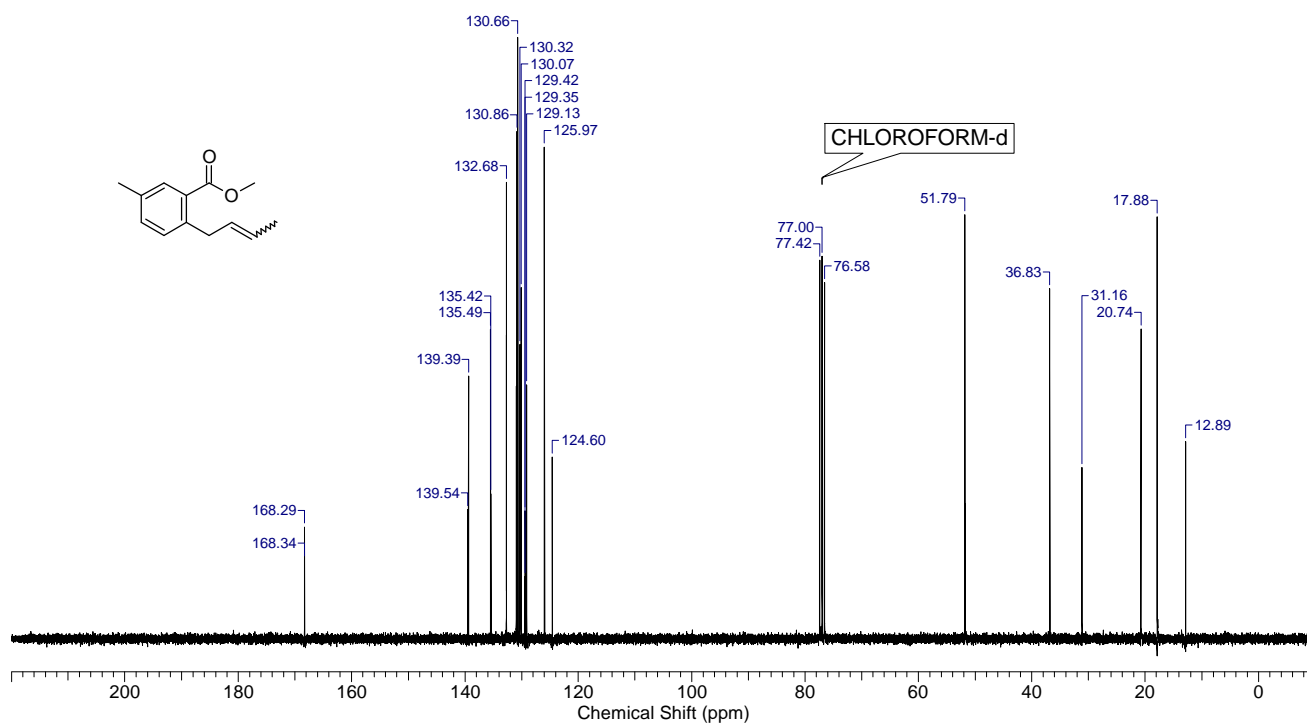


Methyl 2-(but-2-enyl)-5-methyl-benzoate (3ea)

^1H NMR (300 MHz, CDCl_3)

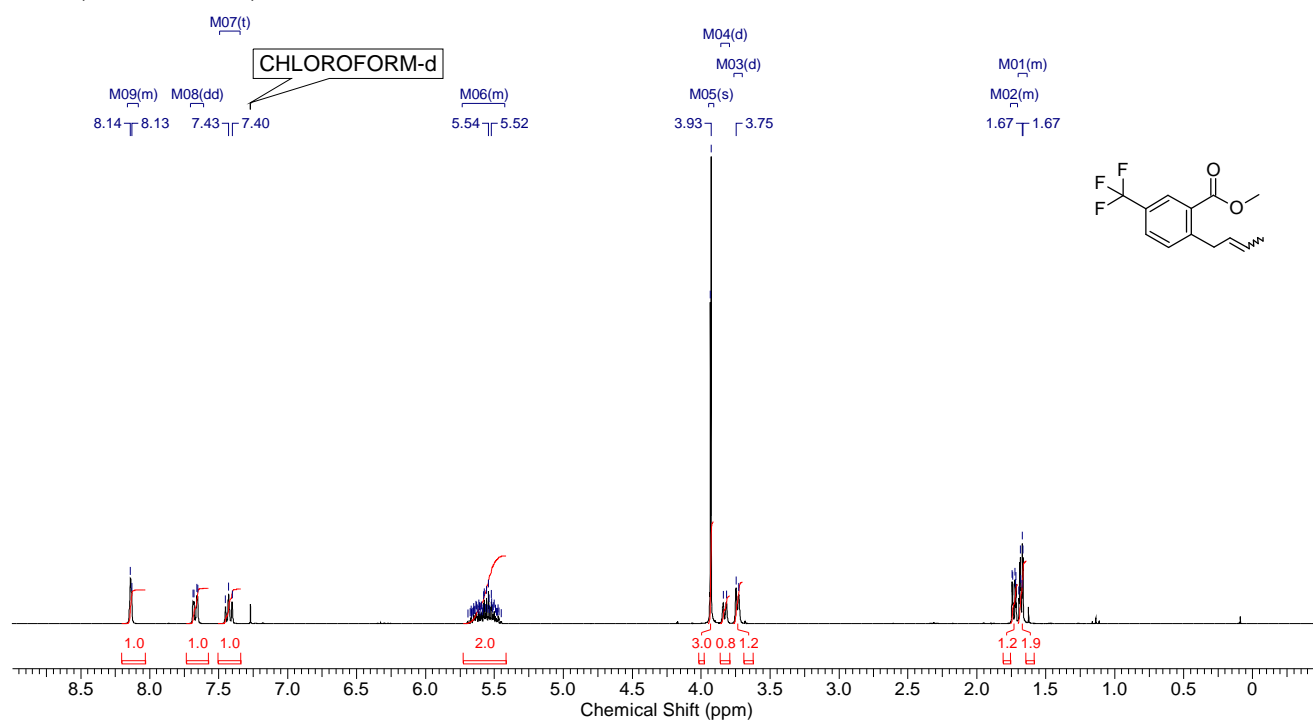


^{13}C NMR (75 MHz, CDCl_3)

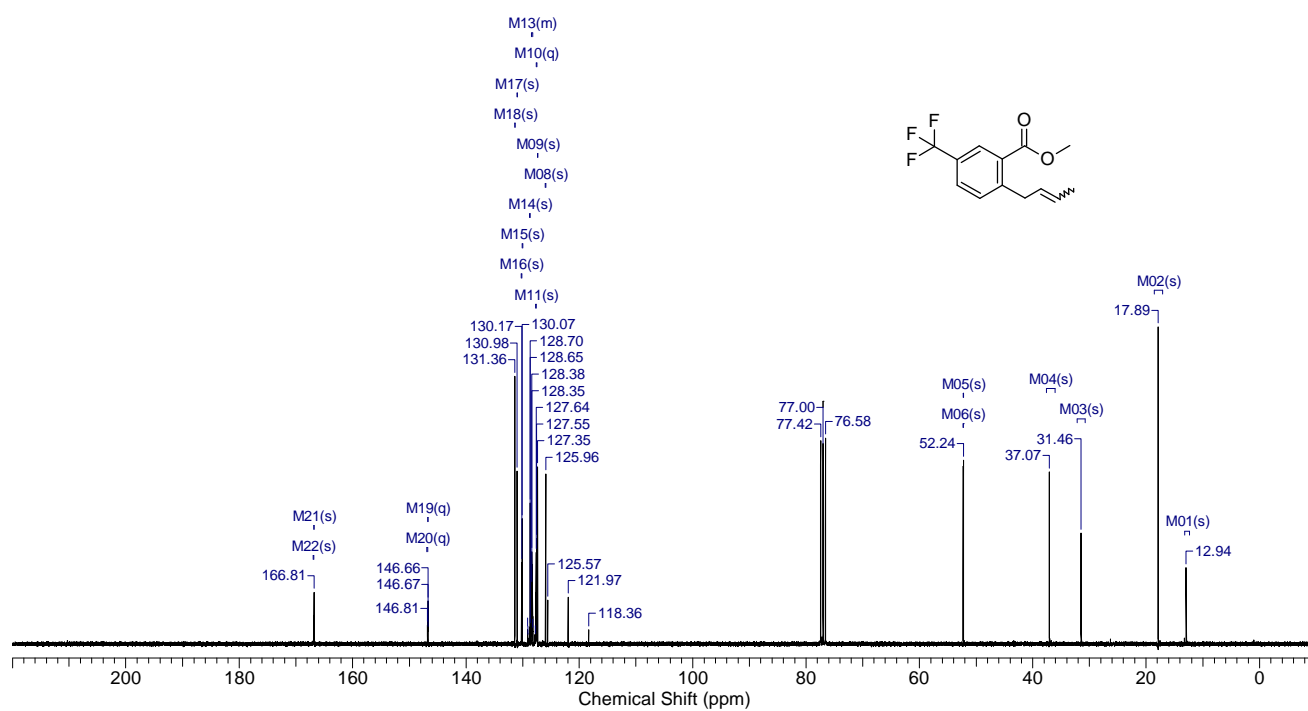


Methyl 2-(but-2-enyl)-5-(trifluoromethyl)benzoate (3fa)

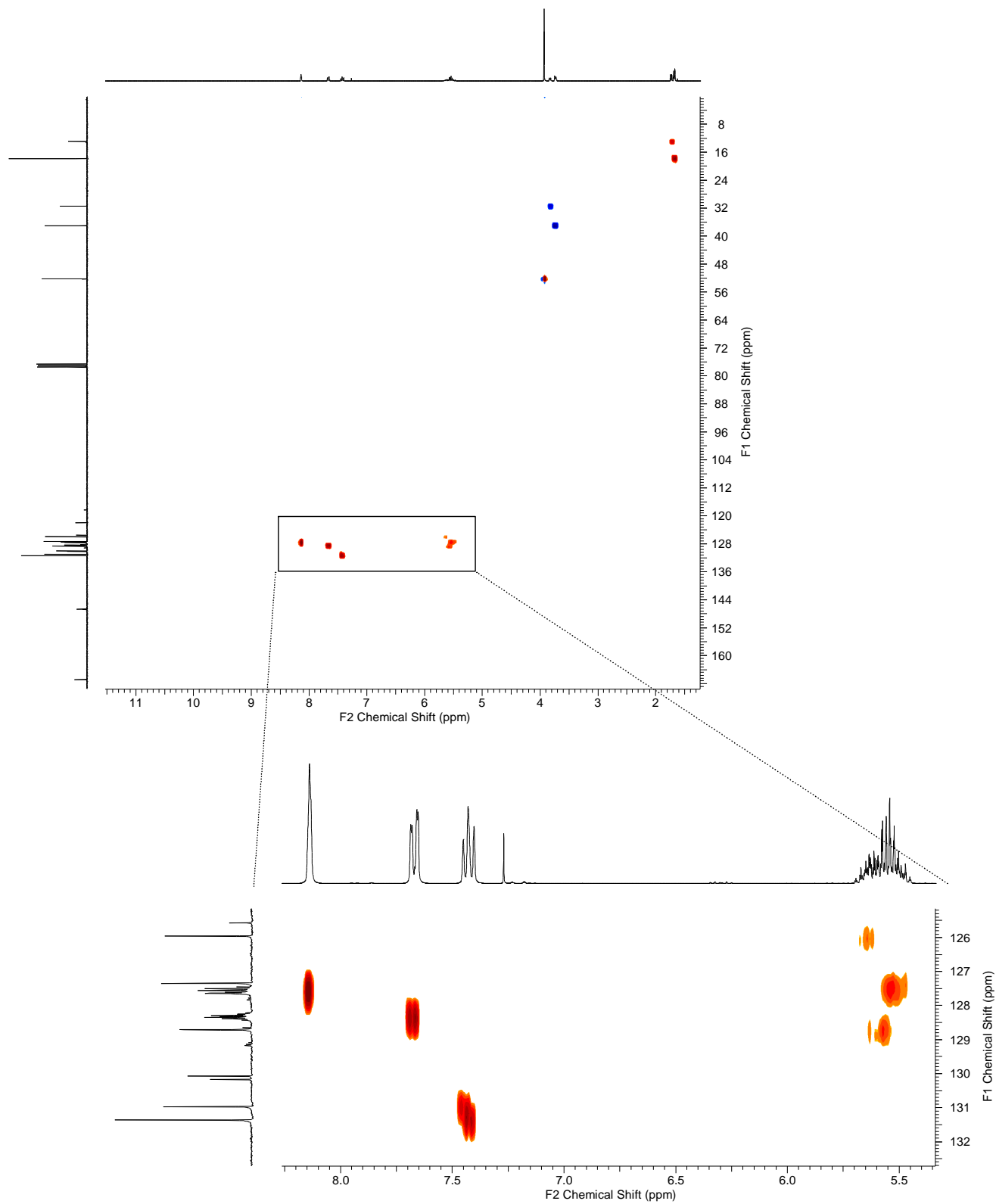
¹H NMR (300 MHz, CDCl₃)



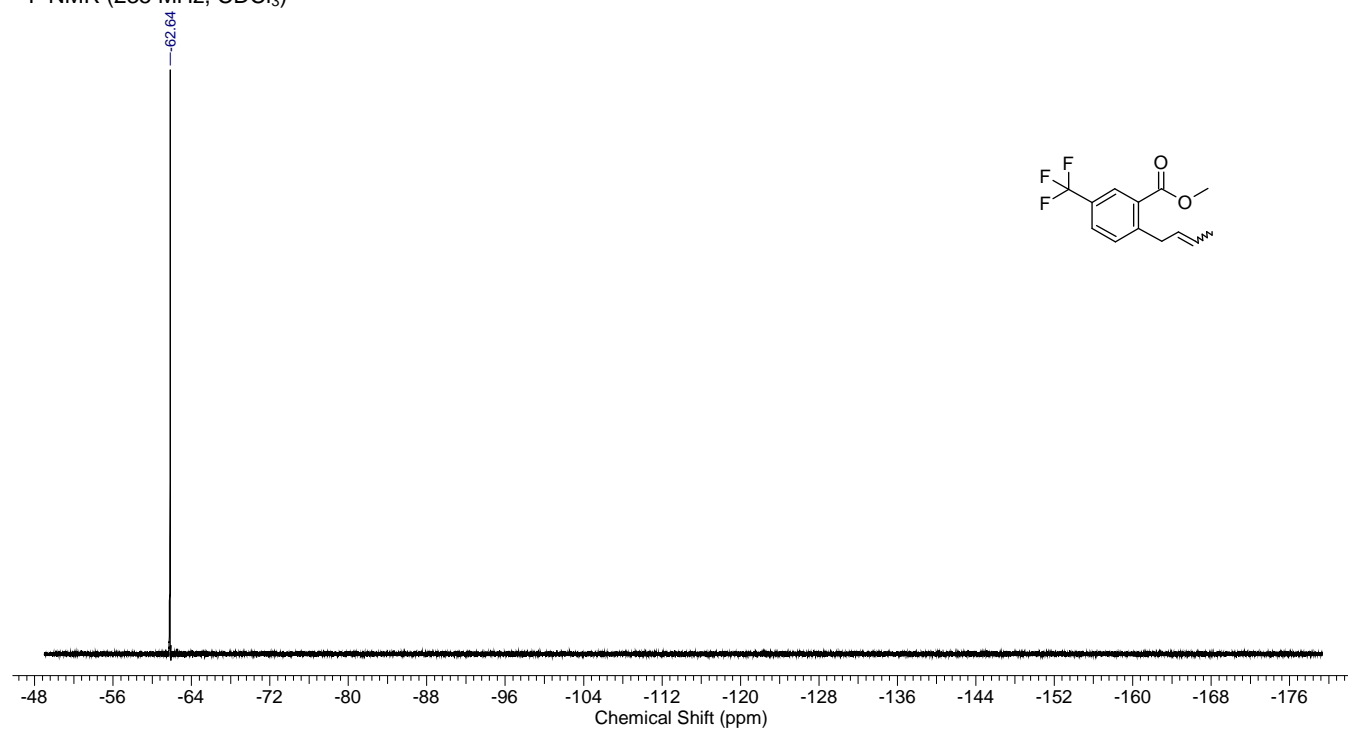
¹³C NMR (75 MHz, CDCl₃)



$^1\text{H}/^{13}\text{C}$ HSQC NMR (300 MHz, CDCl_3)

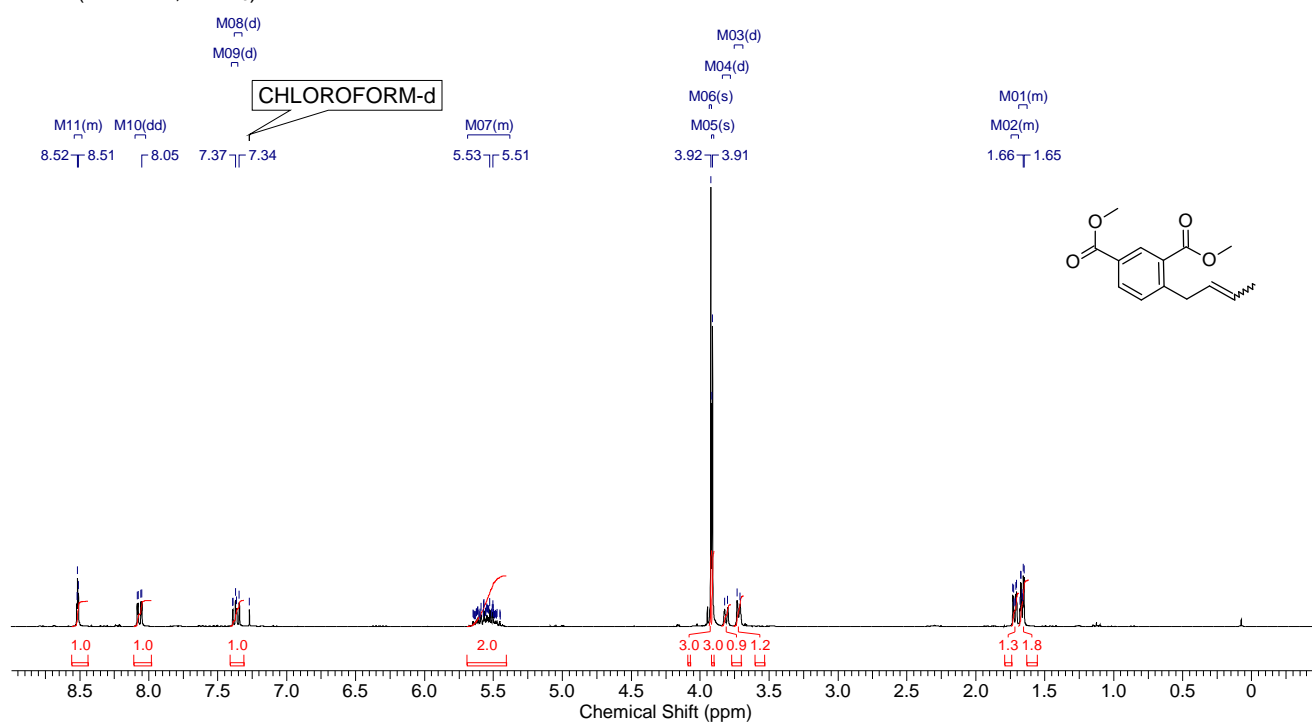


^{19}F NMR (235 MHz, CDCl_3)

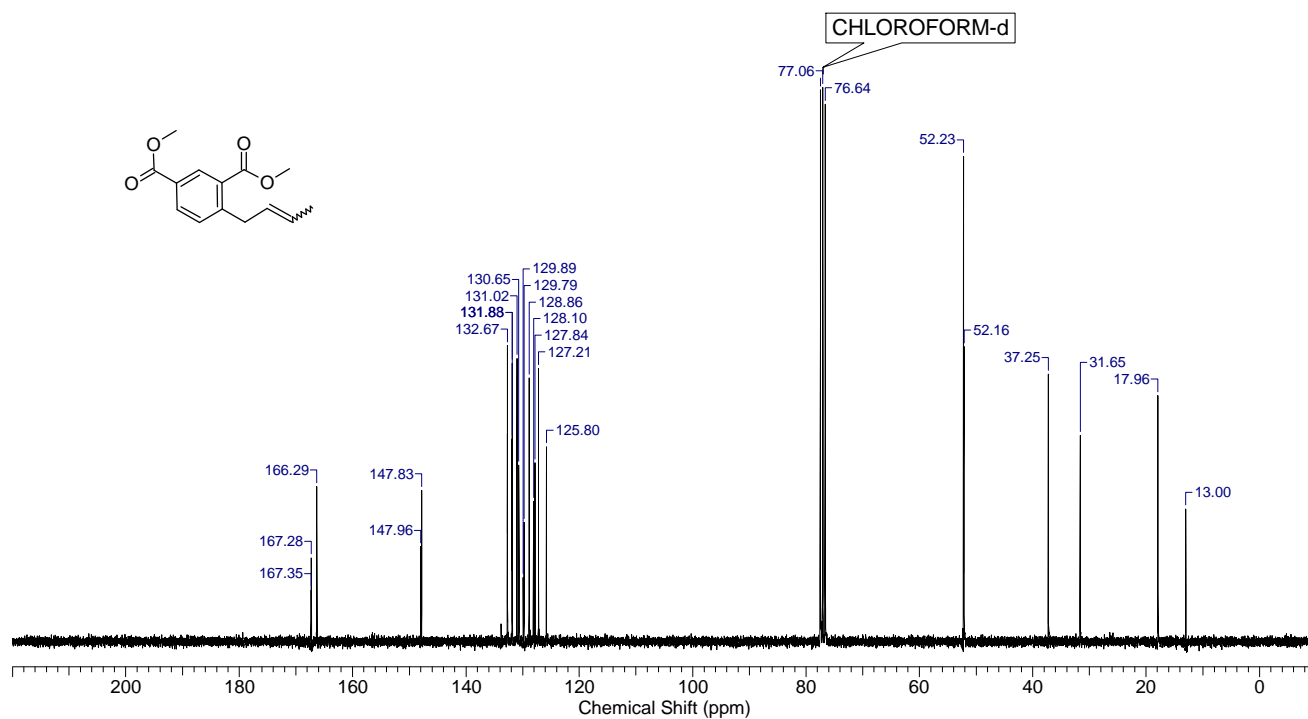


Dimethyl 4-(but-2-enyl)benzene-1,3-dicarboxylate (3ga)

¹H NMR (300 MHz, CDCl₃)

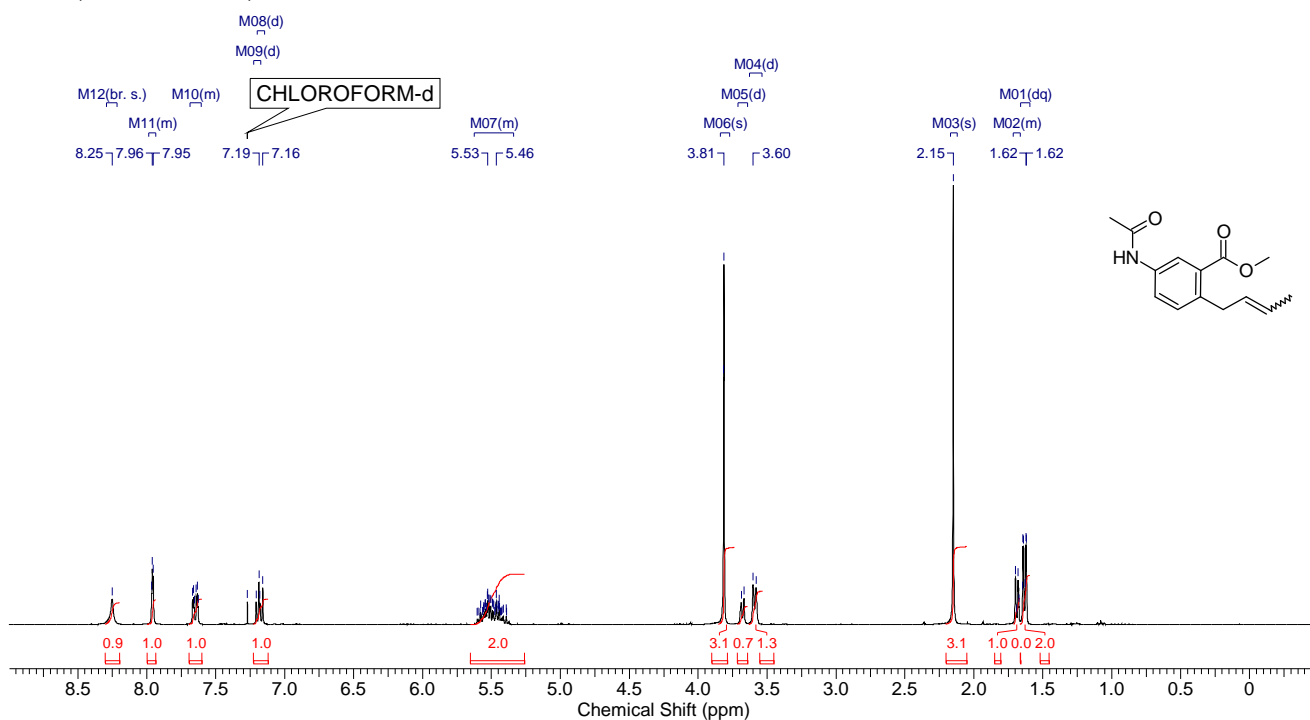


¹³C NMR (75 MHz, CDCl₃)

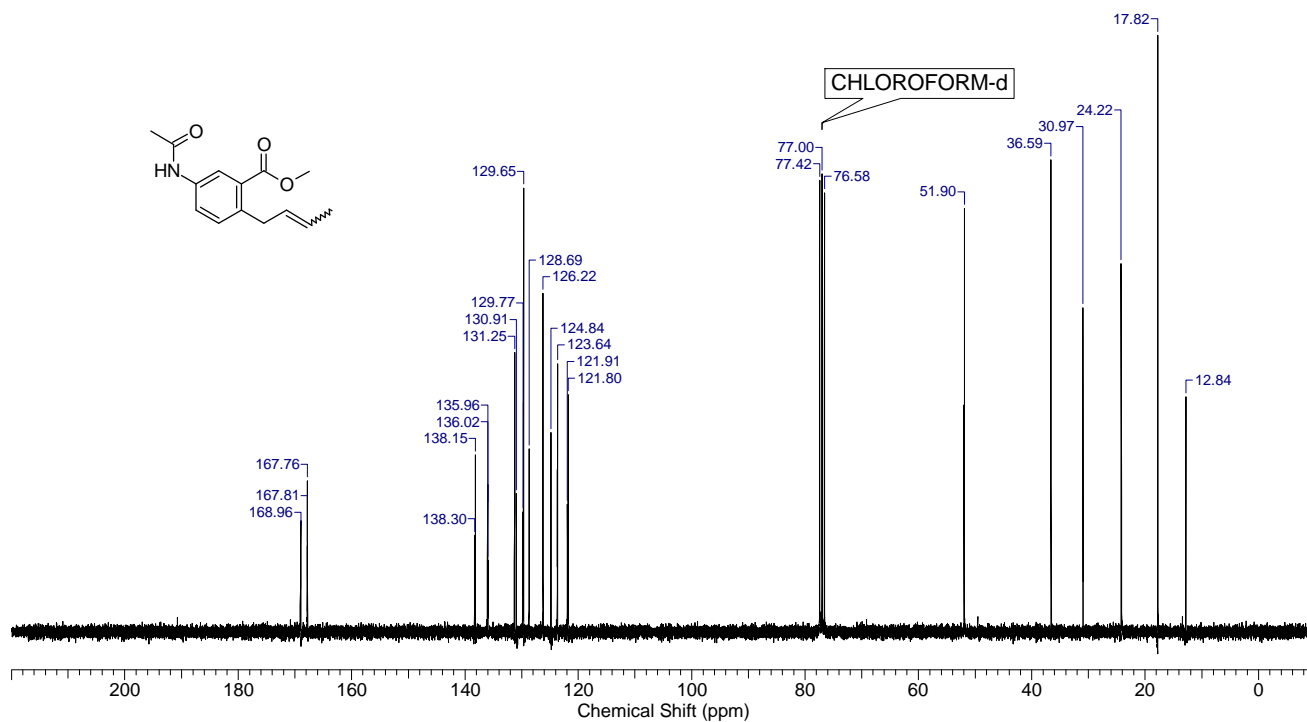


Methyl 5-acetamido-2-(but-2-enyl)benzoate (3ha)

¹H NMR (300 MHz, CDCl₃)

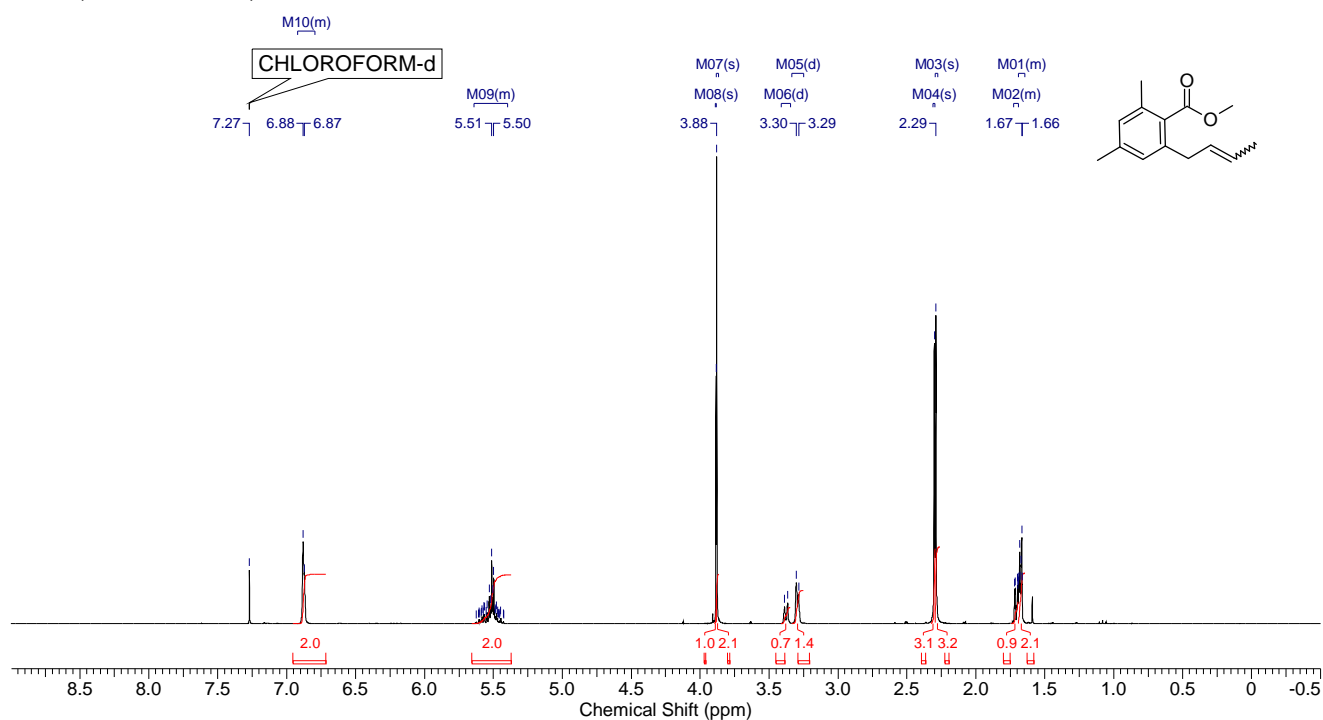


¹³C NMR (75 MHz, CDCl₃)

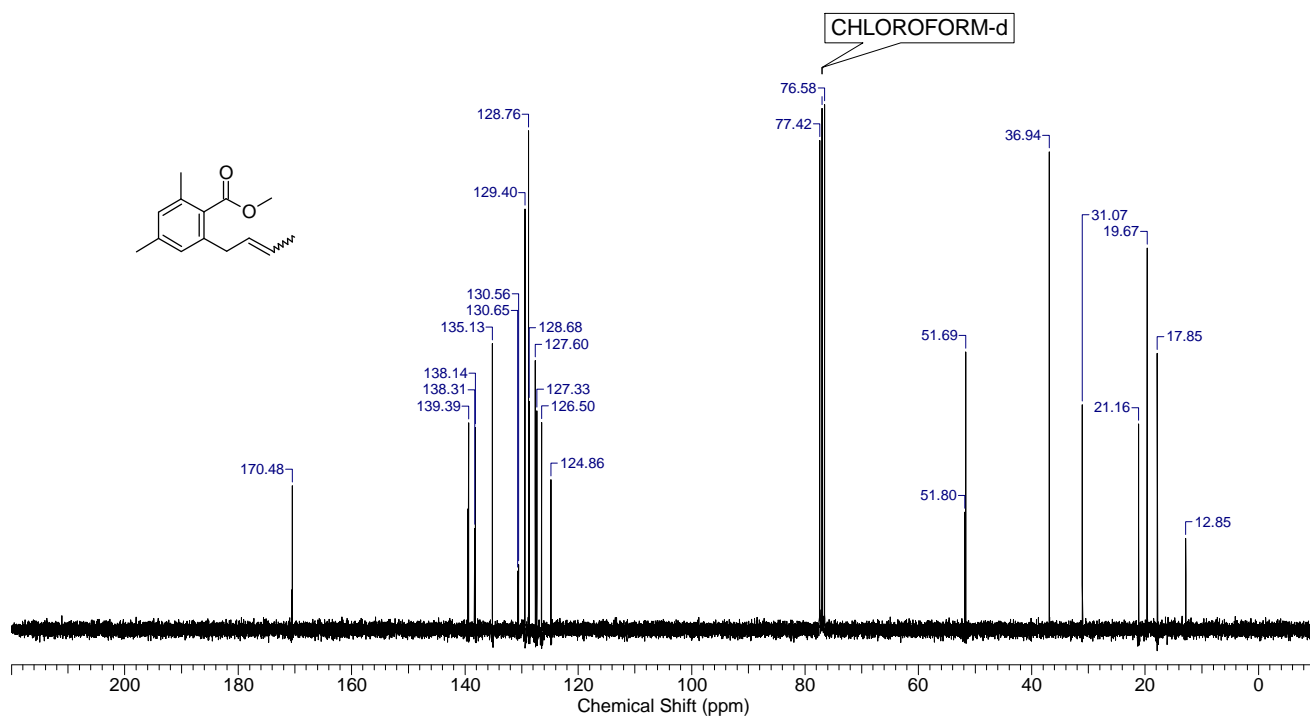


Methyl 2-(but-2-enyl)-4,6-dimethyl-benzoate (3ia)

^1H NMR (300 MHz, CDCl_3)

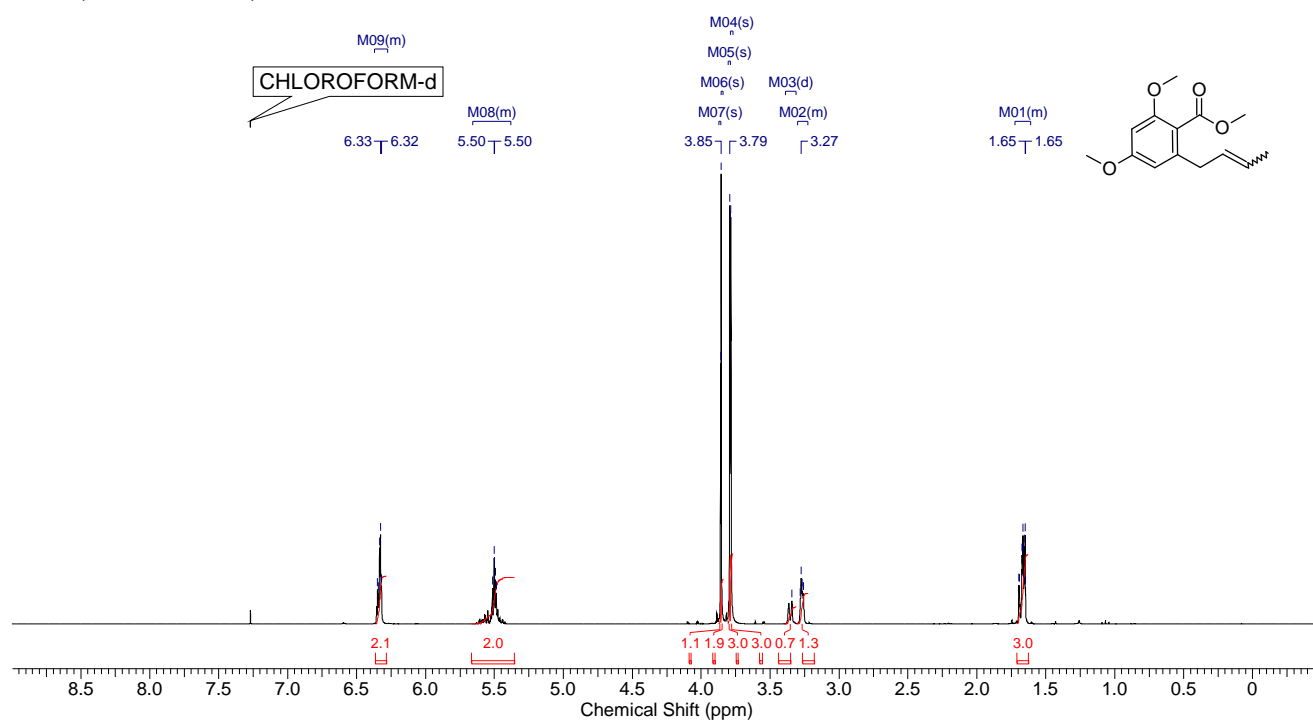


^{13}C NMR (75 MHz, CDCl_3)

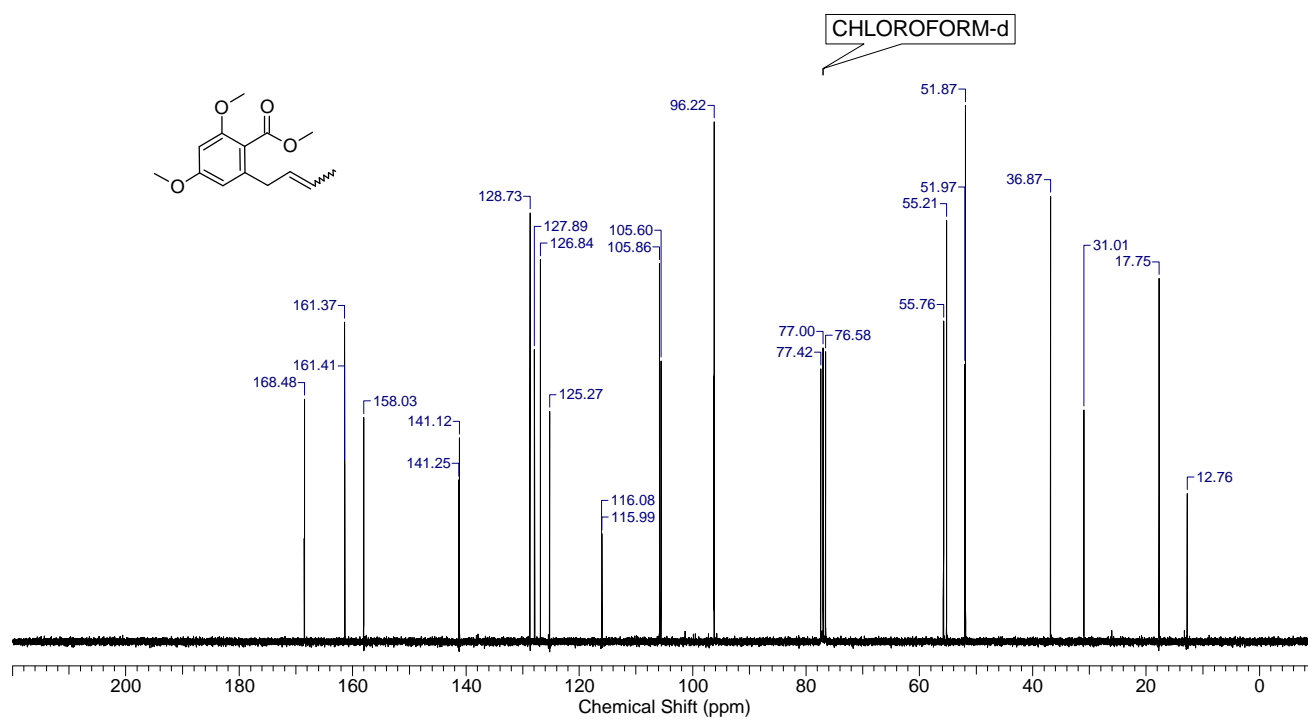


Methyl 2-(but-2-enyl)-4,6-dimethoxy-benzoate (3ja)

¹H NMR (300 MHz, CDCl₃)

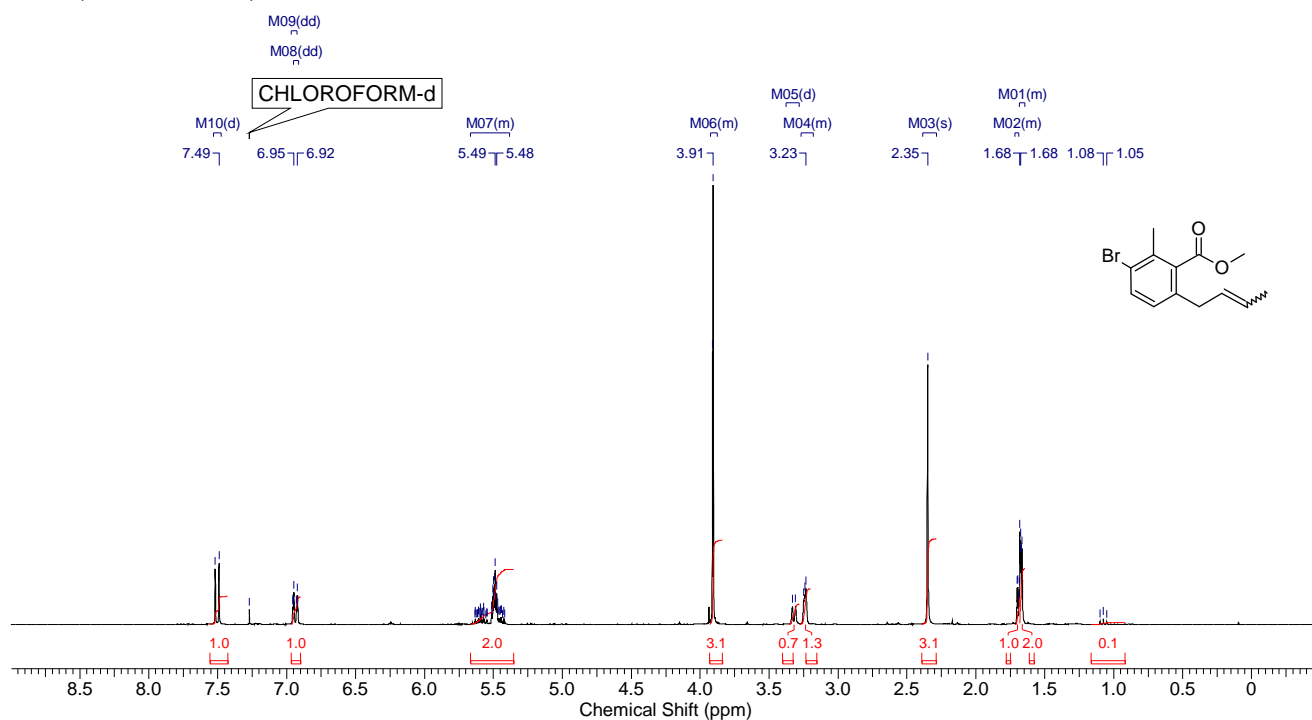


¹³C NMR (75 MHz, CDCl₃)

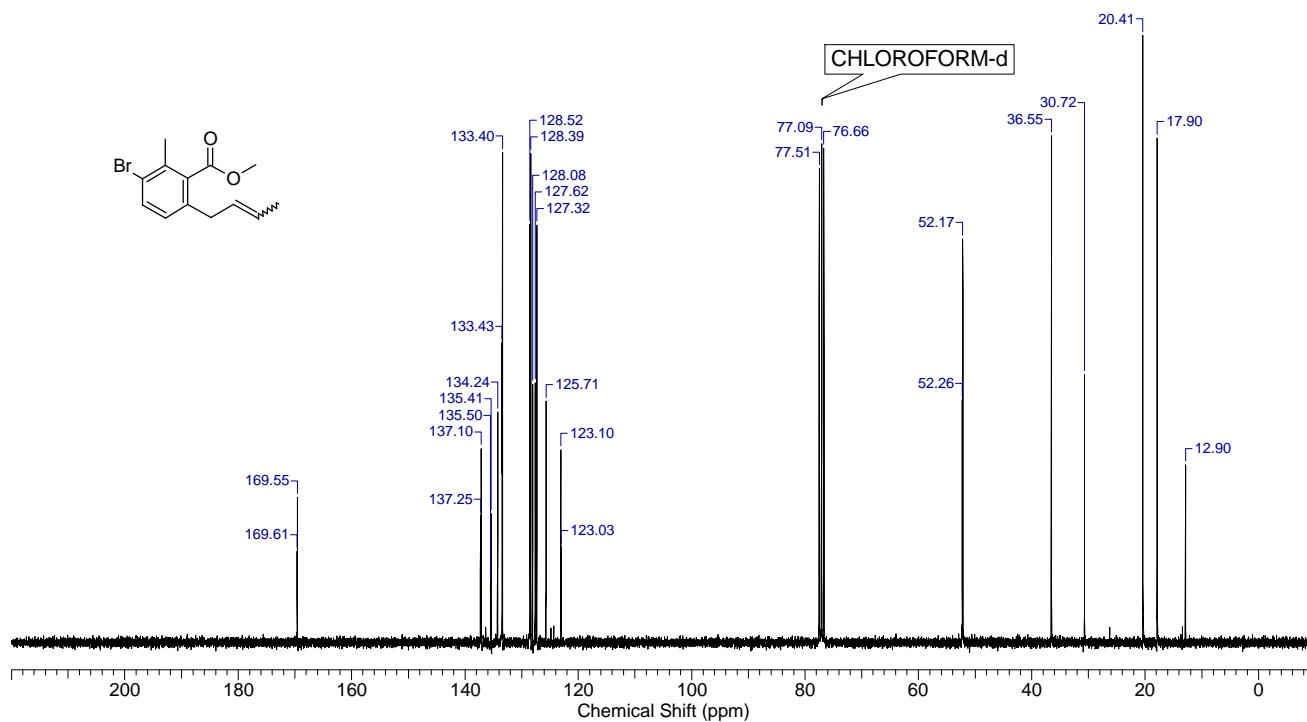


Methyl 3-bromo-6-(but-2-enyl)-2-methyl-benzoate (3ka)

^1H NMR (300 MHz, CDCl_3)

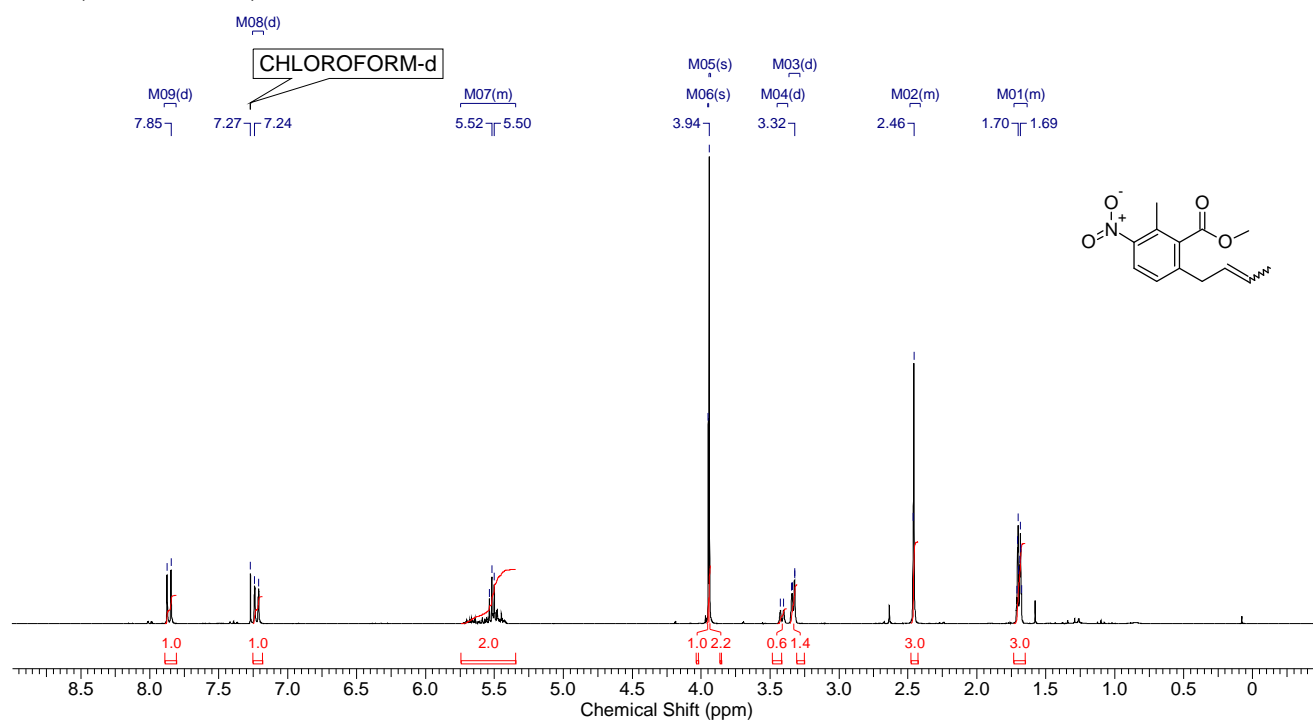


^{13}C NMR (75 MHz, CDCl_3)

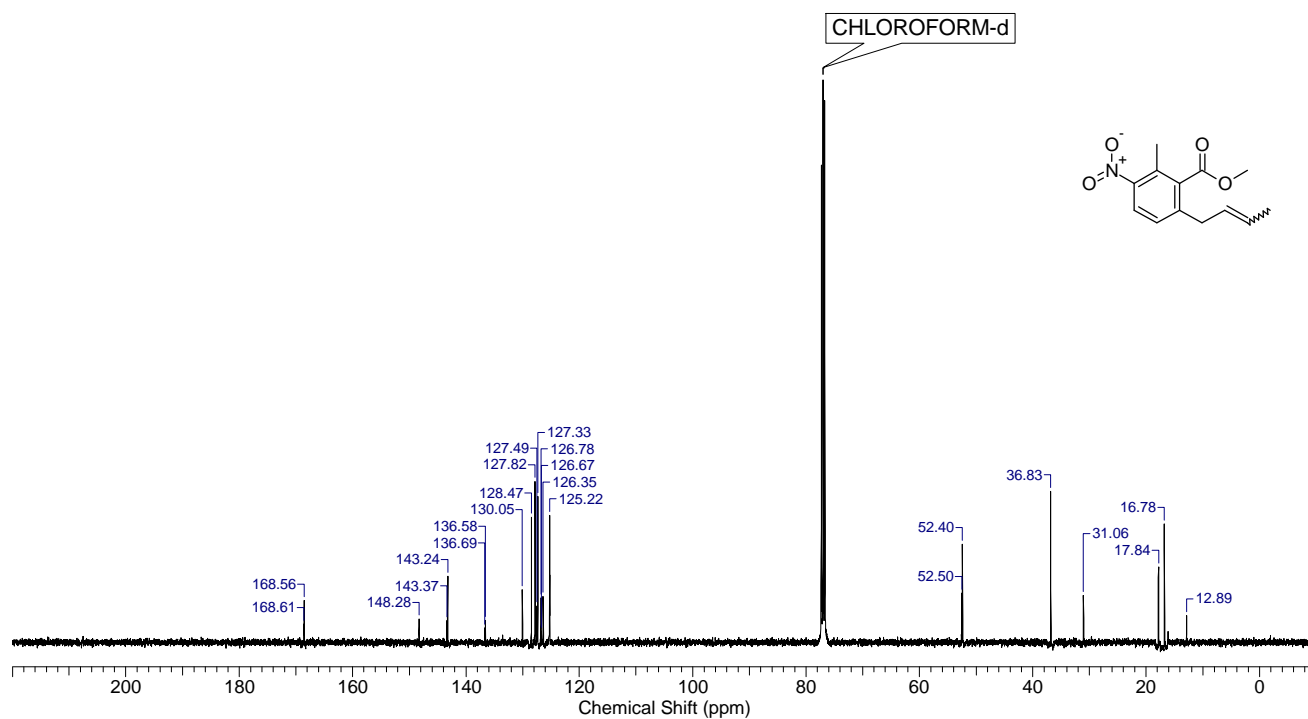


Methyl 6-(but-2-enyl)-2-methyl-3-nitro-benzoate (31a)

¹H NMR (300 MHz, CDCl₃)

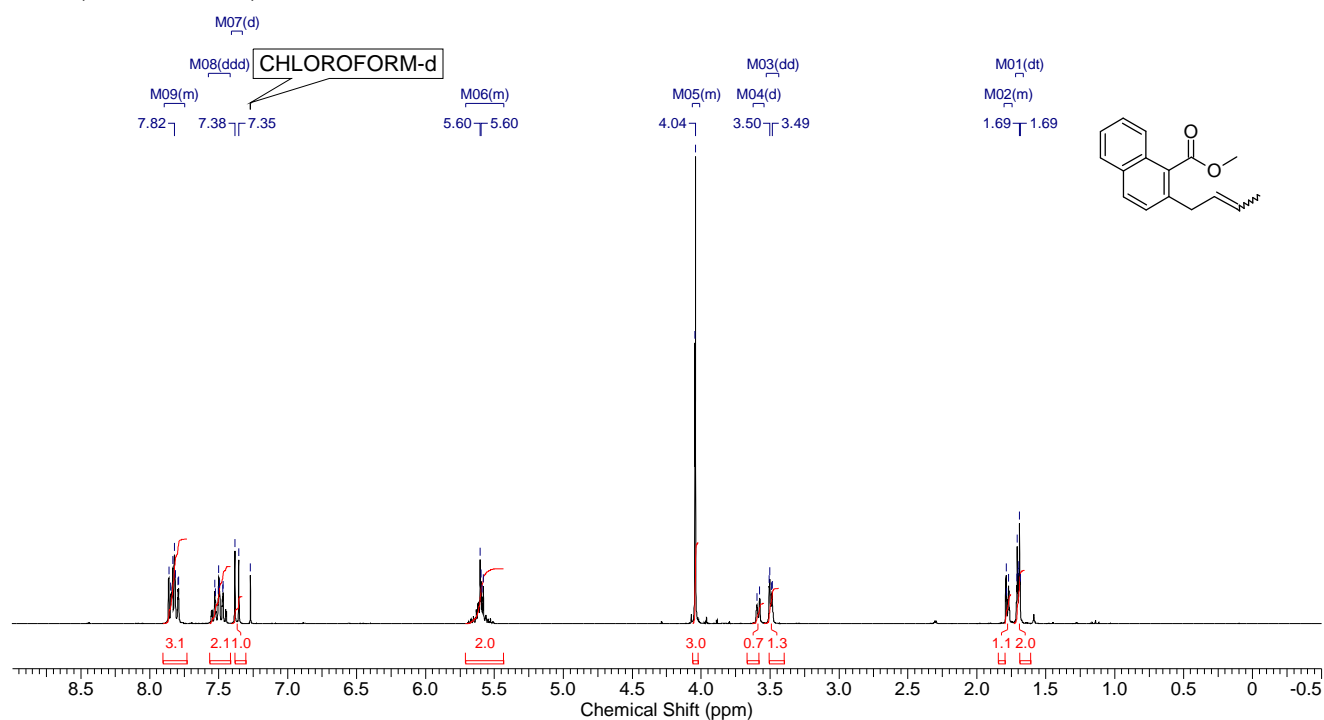


¹³C NMR (75 MHz, CDCl₃)

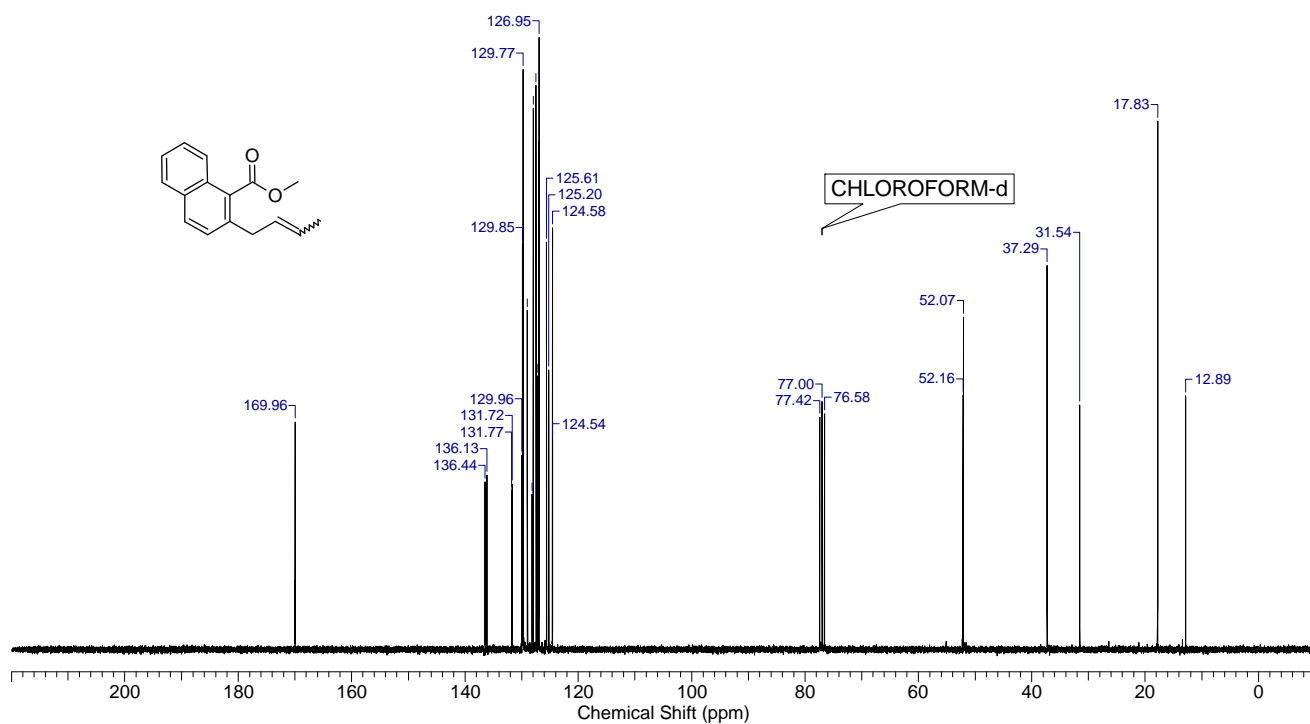


Methyl 2-(but-2-enyl)naphthalene-1-carboxylate (3ma)

¹H NMR (300 MHz, CDCl₃)

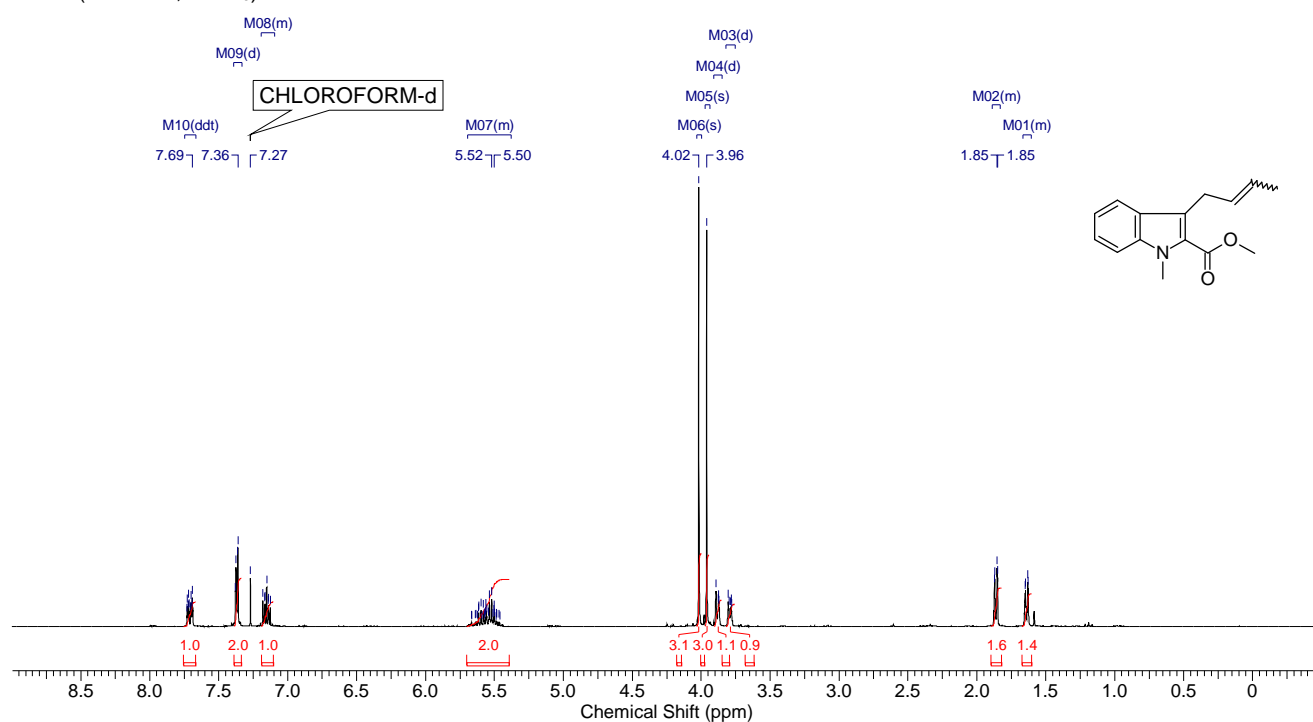


¹³C NMR (75 MHz, CDCl₃)

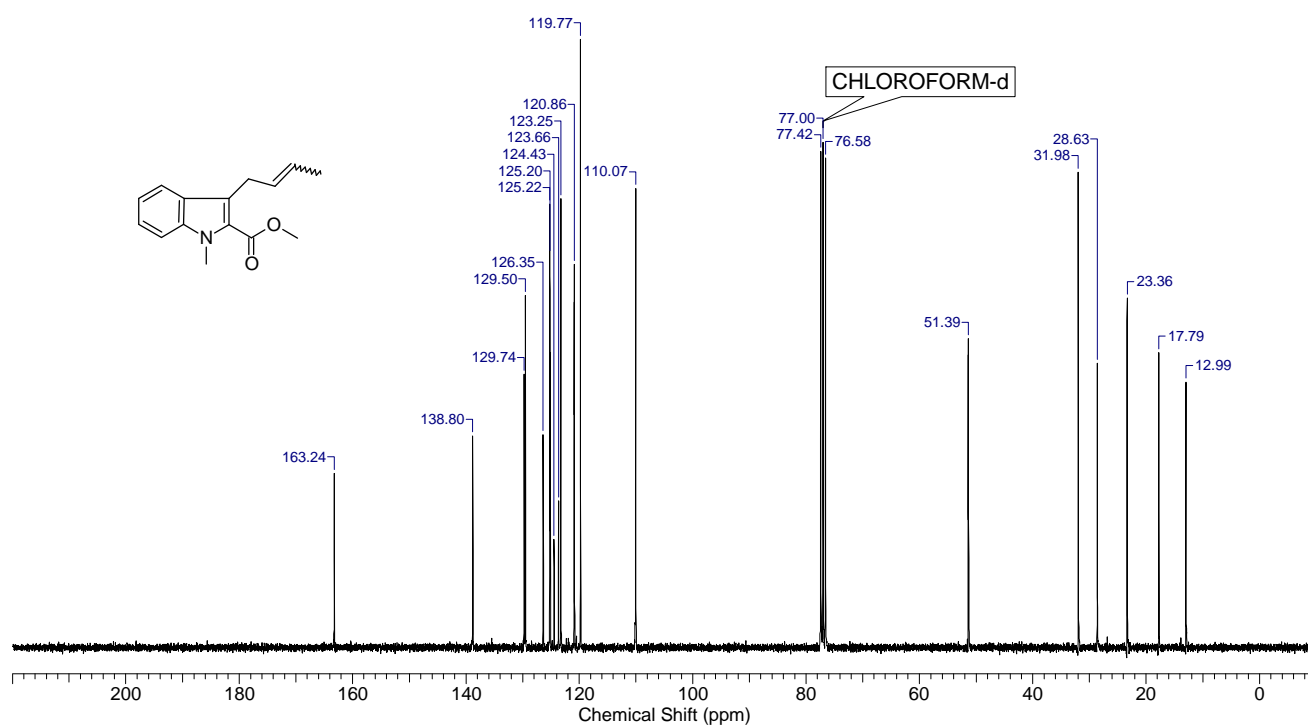


Methyl 3-(but-2-enyl)-1-methyl-indole-2-carboxylate (3na)

¹H NMR (300 MHz, CDCl₃)

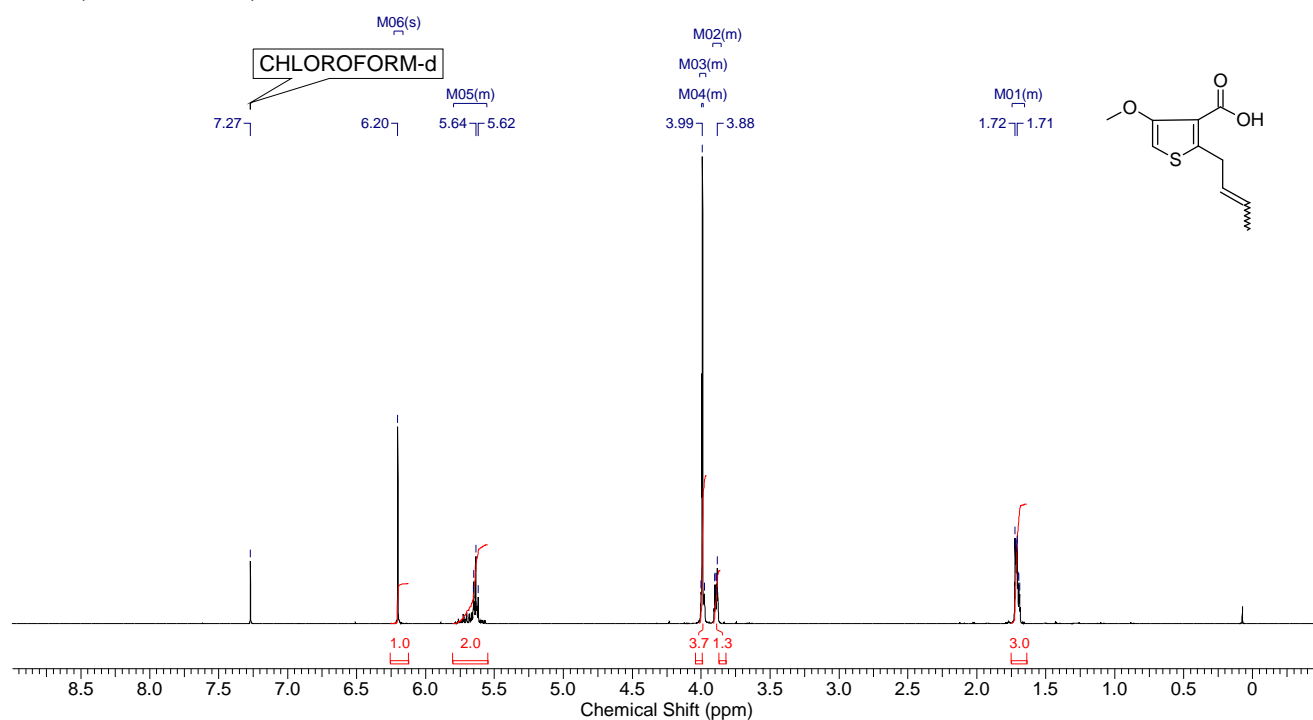


¹³C NMR (75 MHz, CDCl₃)

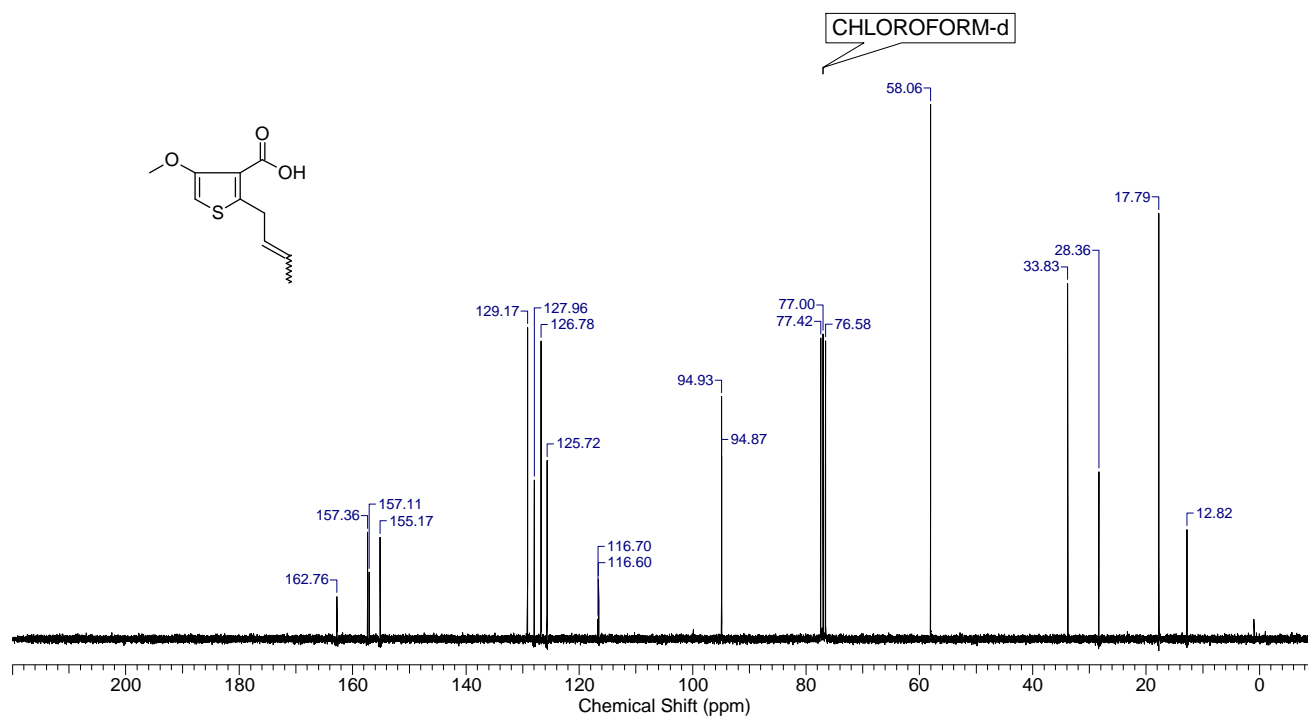


2-(But-2-enyl)-4-methoxy-thiophene-3-carboxylic acid (3oa)

^1H NMR (300 MHz, CDCl_3)

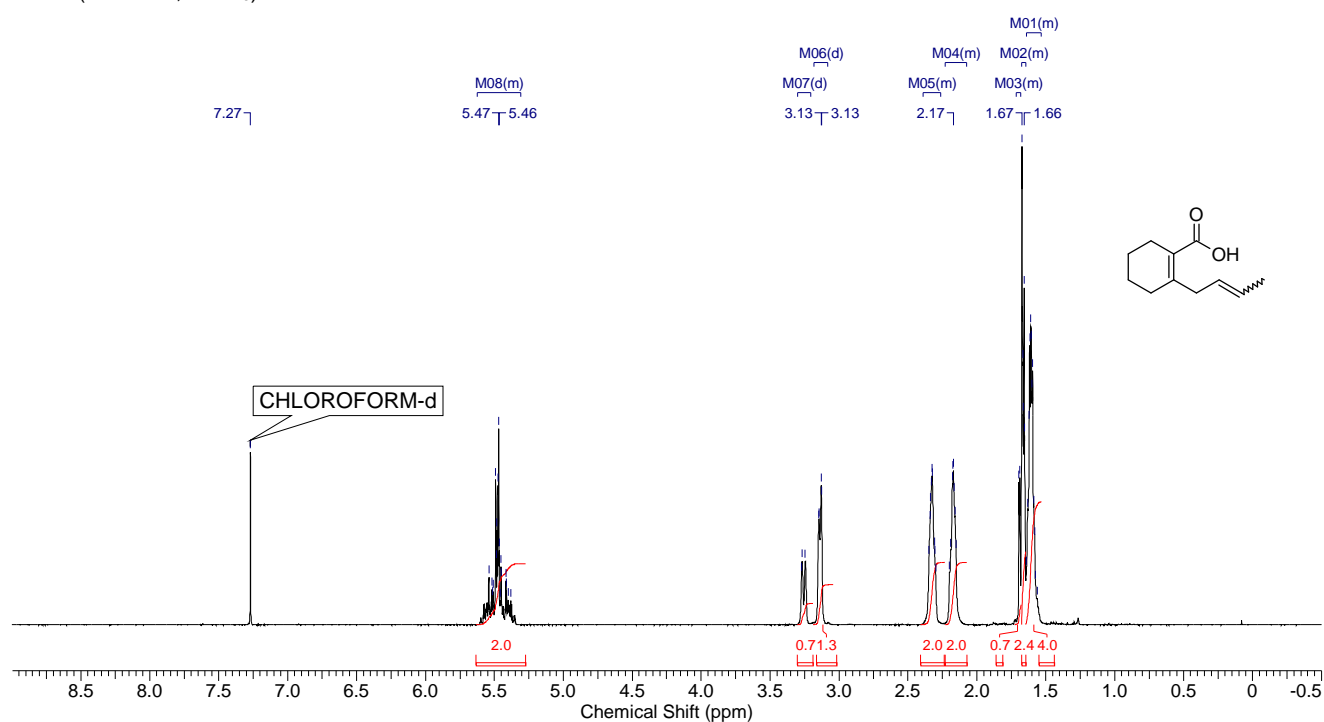


^{13}C NMR (75 MHz, CDCl_3)

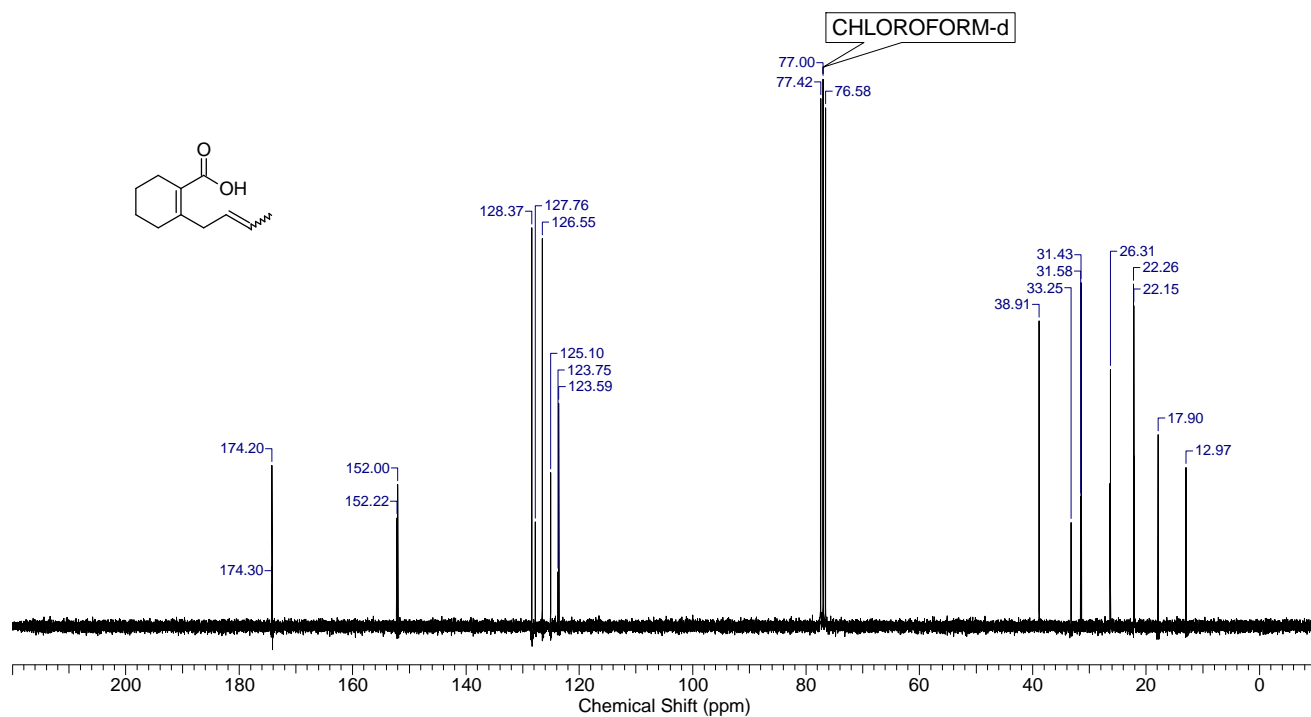


2-(but-2-enyl)cyclohexene-1-carboxylic acid (3pa)

^1H NMR (300 MHz, CDCl_3)

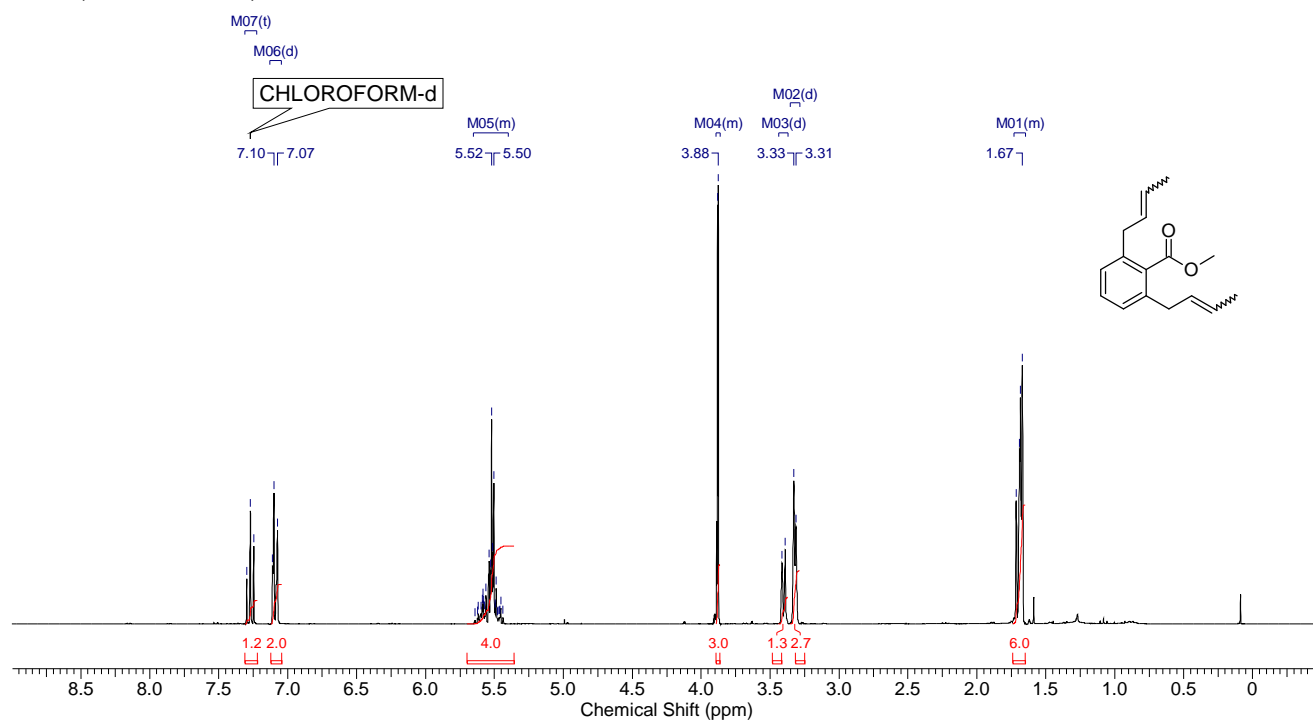


^{13}C NMR (75 MHz, CDCl_3)

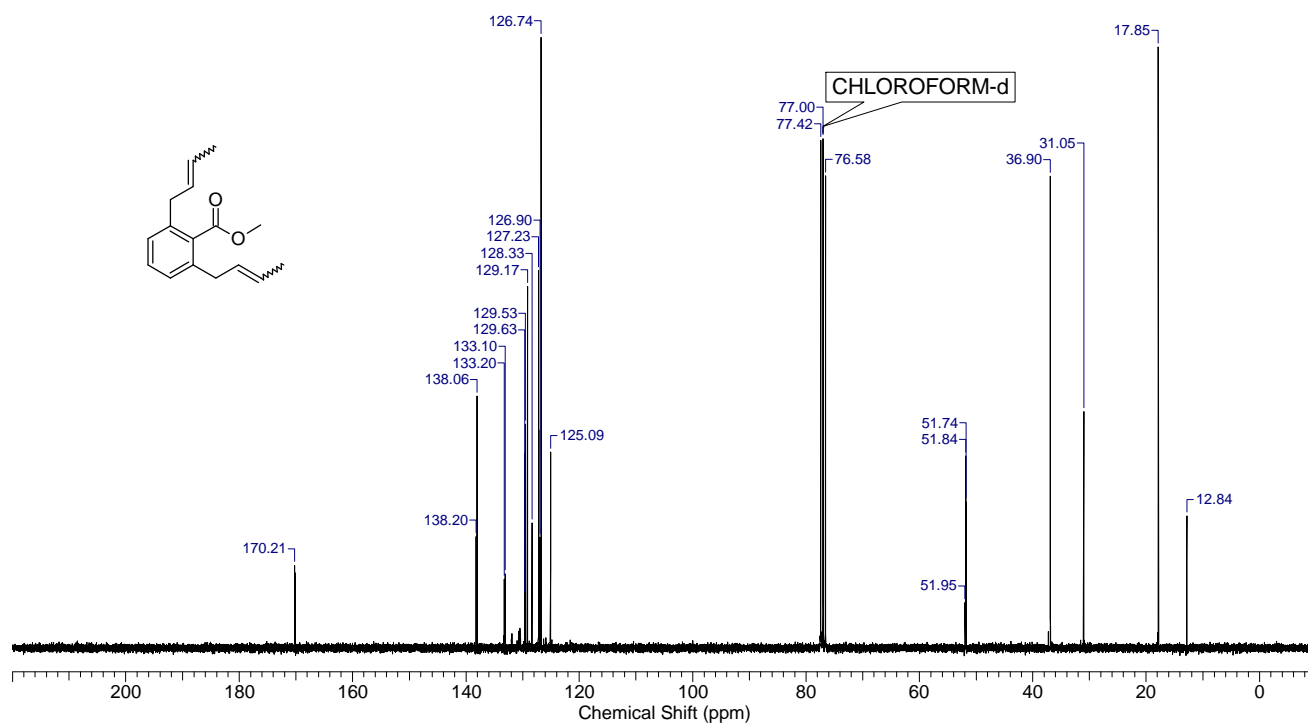


Methyl 2,6-bis(but-2-enyl)benzoate (3qa)

¹H NMR (300 MHz, CDCl₃)

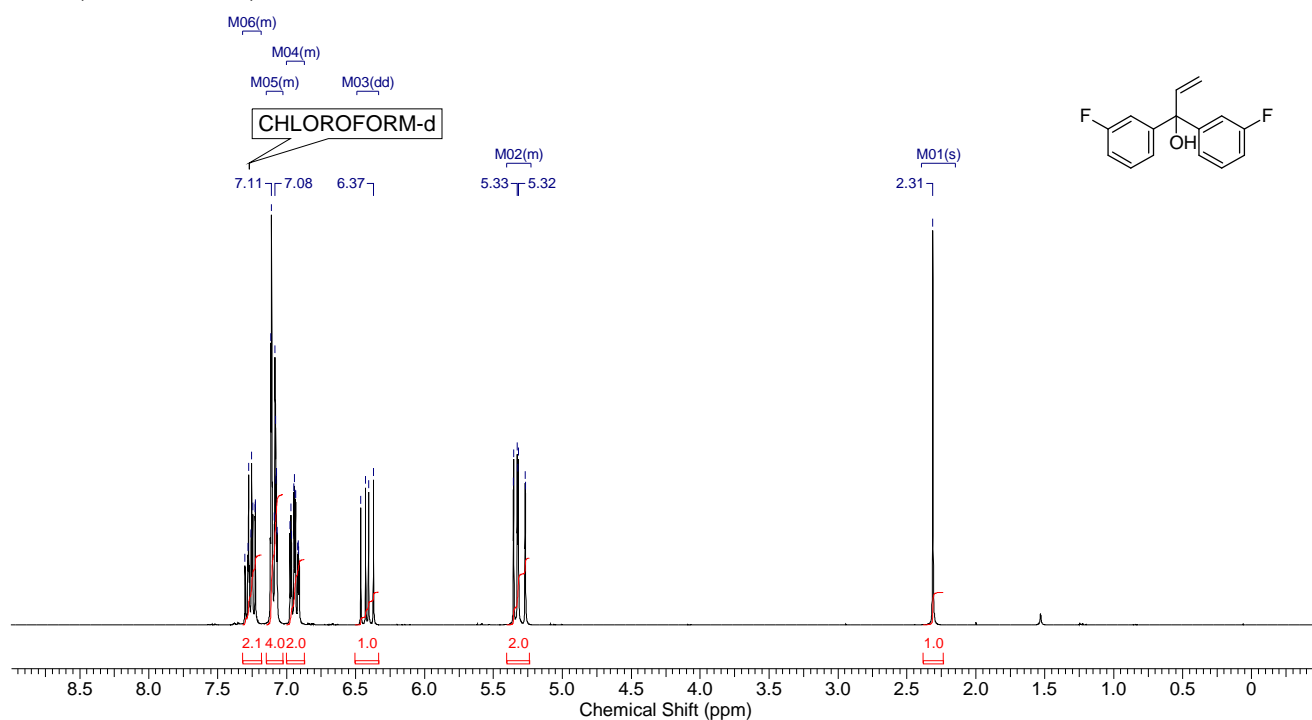


¹³C NMR (75 MHz, CDCl₃)

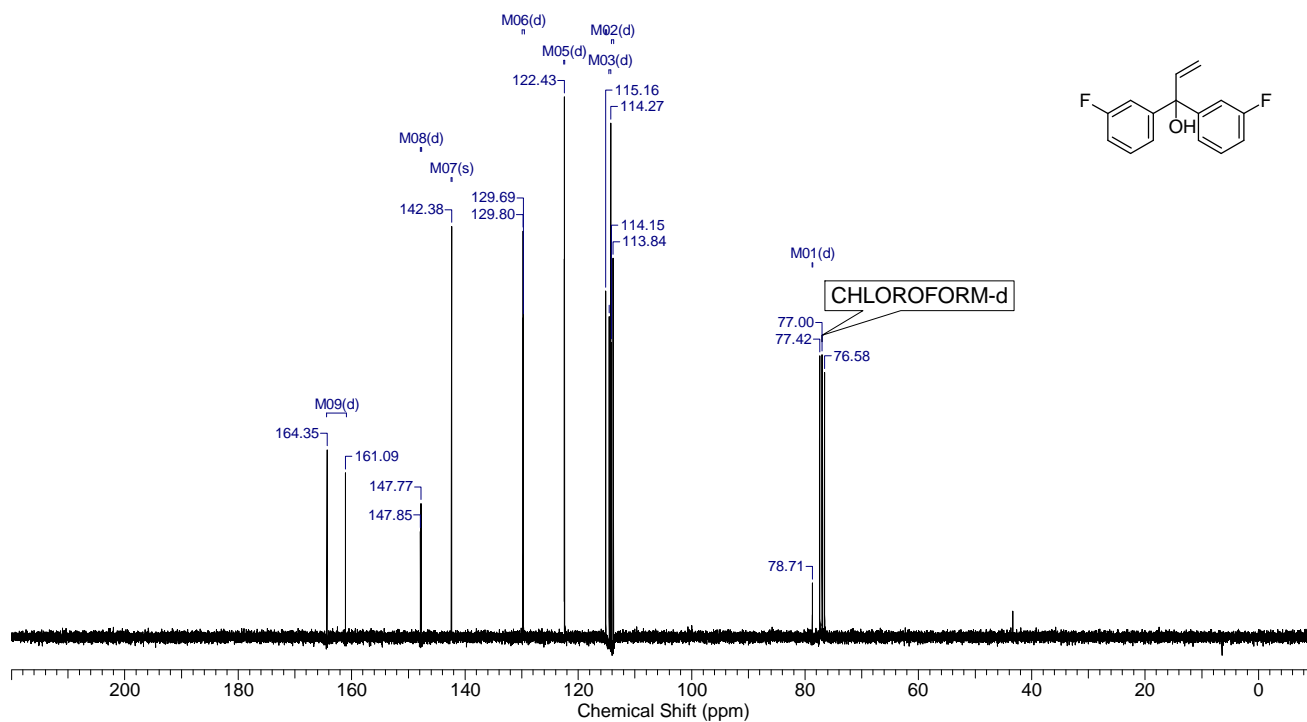


1,1-bis(3-fluorophenyl)prop-2-en-1-ol (2k)

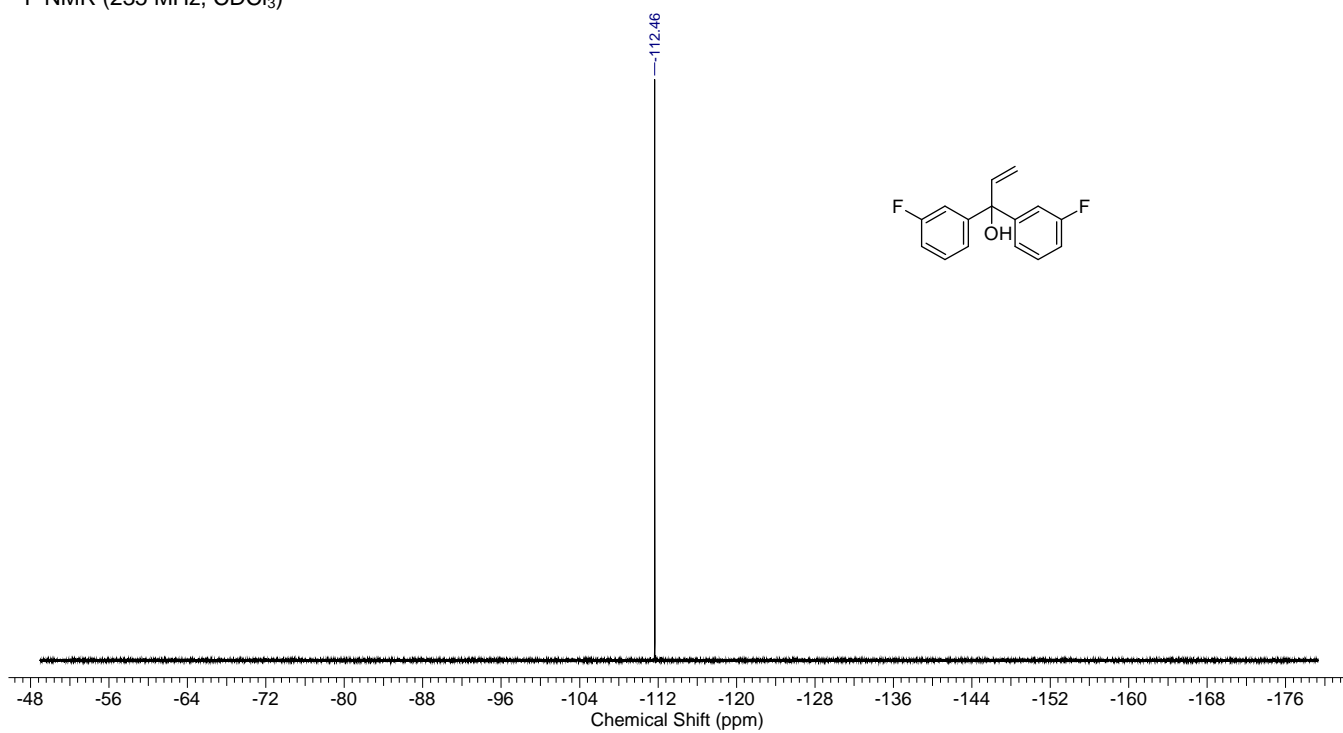
¹H NMR (300 MHz, CDCl₃)



¹³C NMR (75 MHz, CDCl₃)

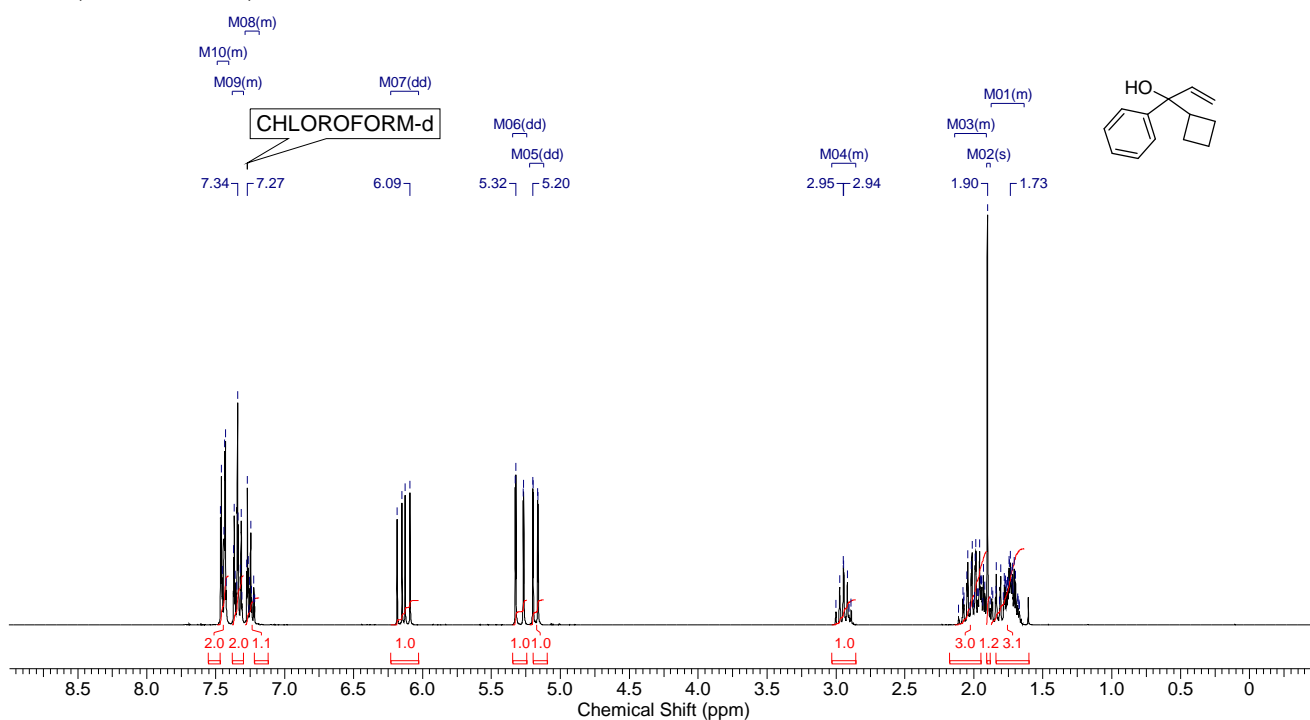


^{19}F NMR (235 MHz, CDCl_3)

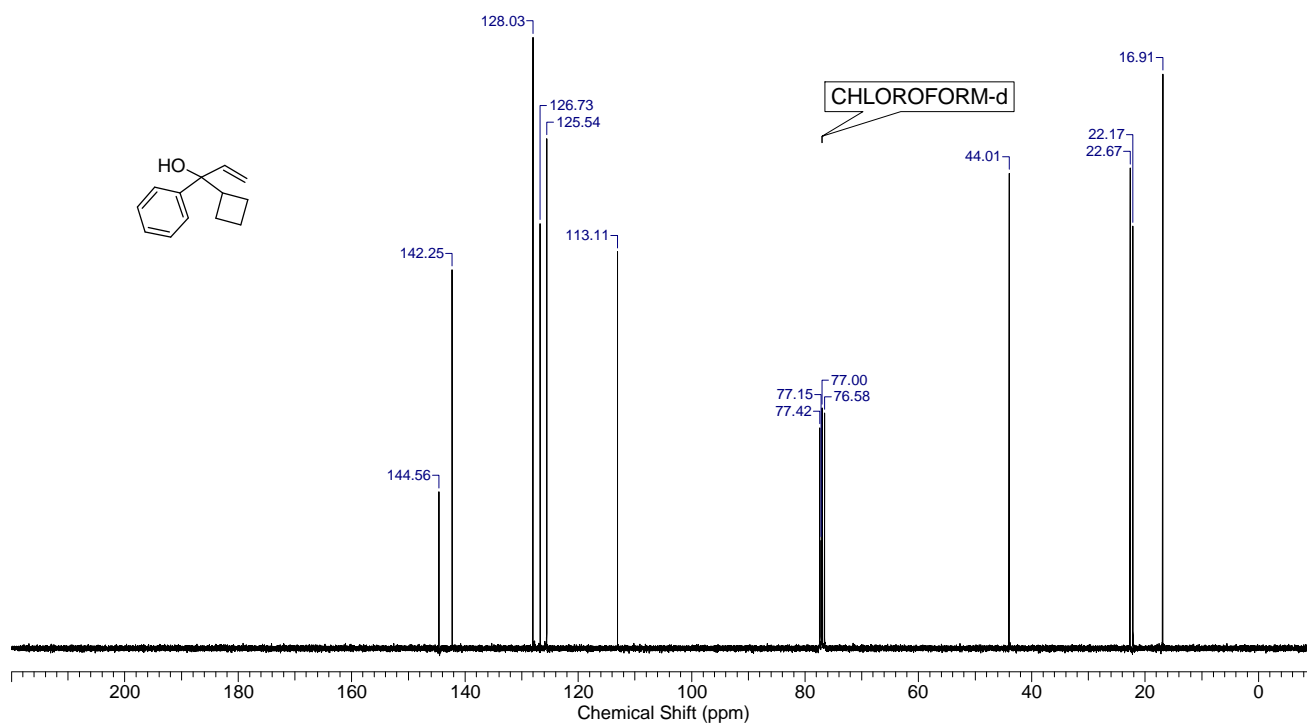


1-cyclobutyl-1-phenyl-prop-2-en-1-ol (2o)

¹H NMR (300 MHz, CDCl₃)

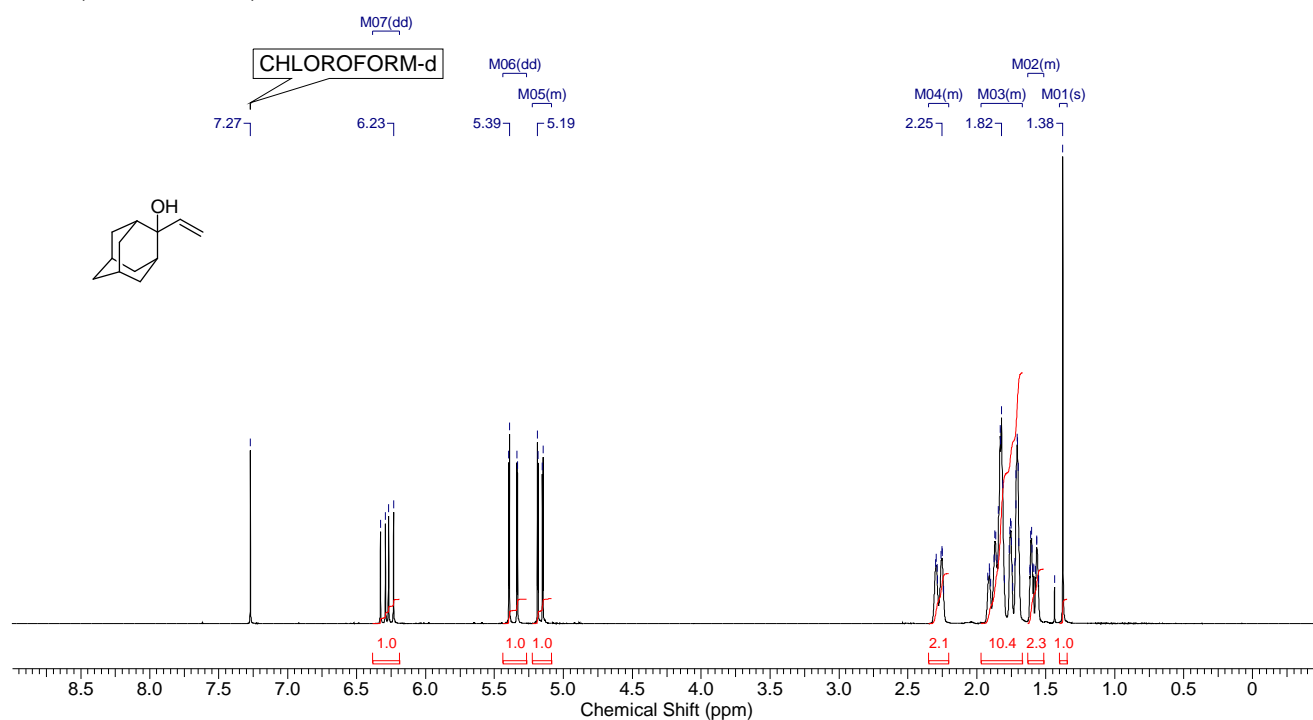


¹³C NMR (75 MHz, CDCl₃)

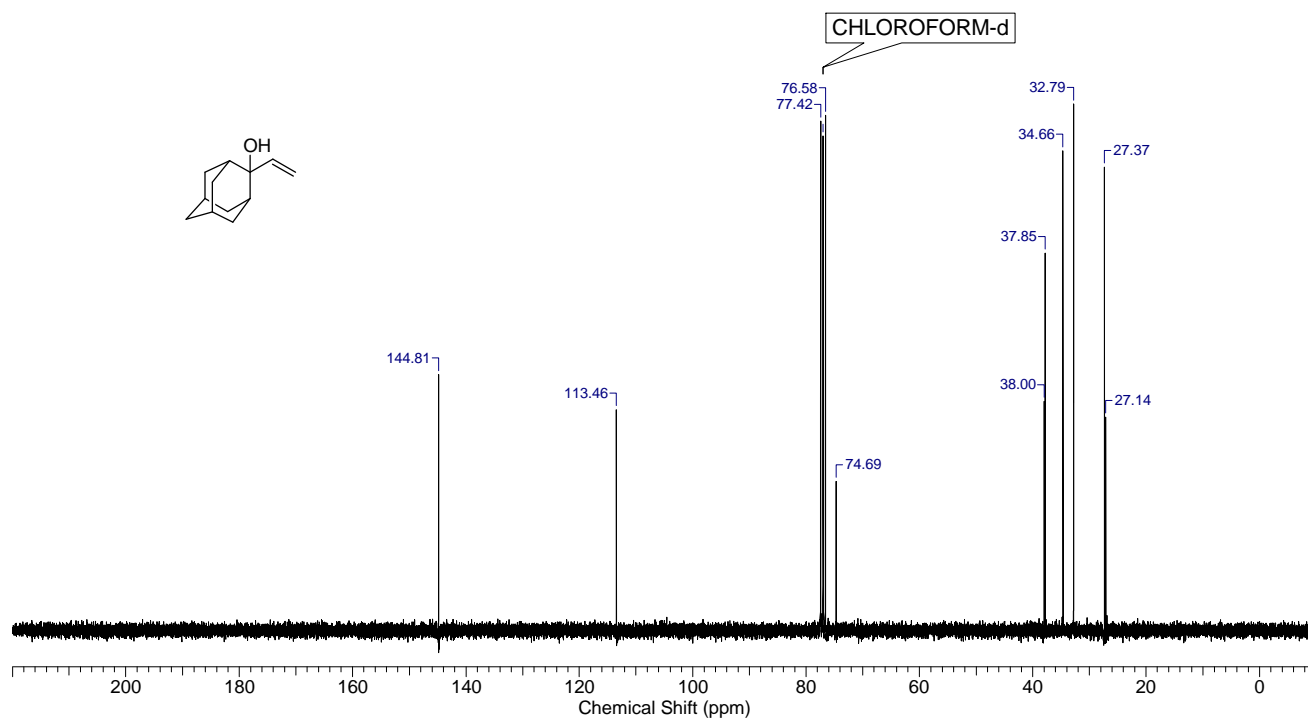


2-vinyladamantan-2-ol (2q)

^1H NMR (300 MHz, CDCl_3)

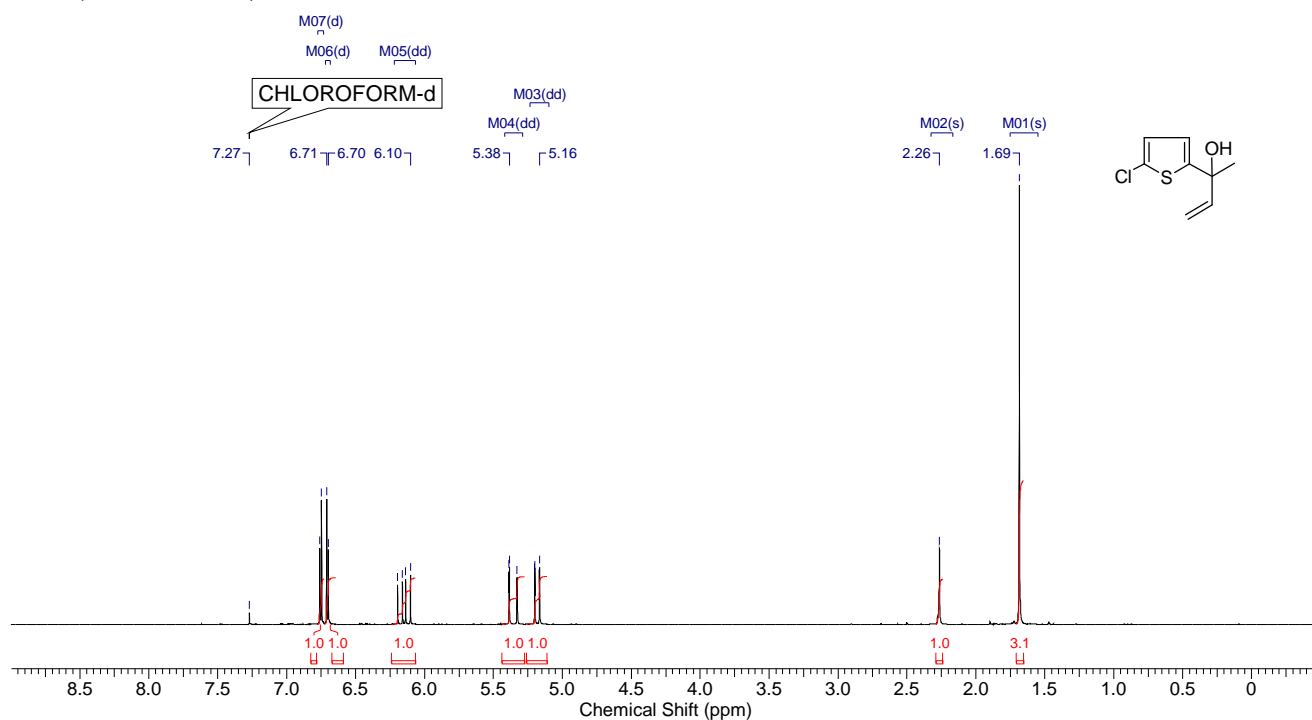


^{13}C NMR (75 MHz, CDCl_3)



2-(5-chloro-2-thienyl)but-3-en-2-ol (2s)

^1H NMR (300 MHz, CDCl_3)



^{13}C NMR (75 MHz, CDCl_3)

