

Metal Free C–H Functionalization of Alkanes by Aryldiazoacetates

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Supporting Information

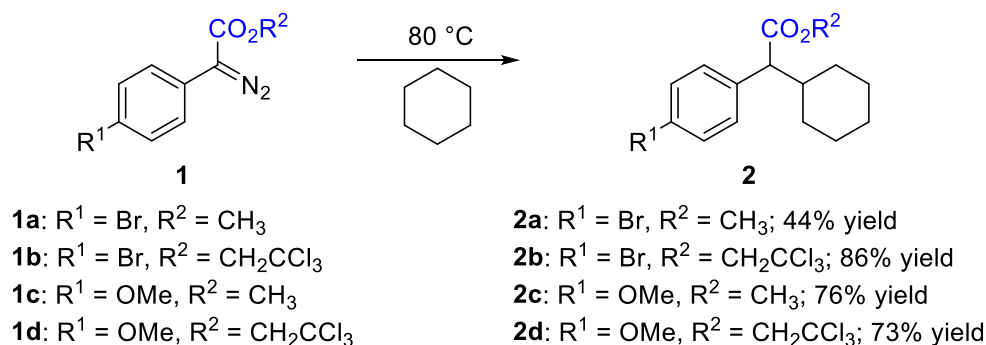
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1. General remarks

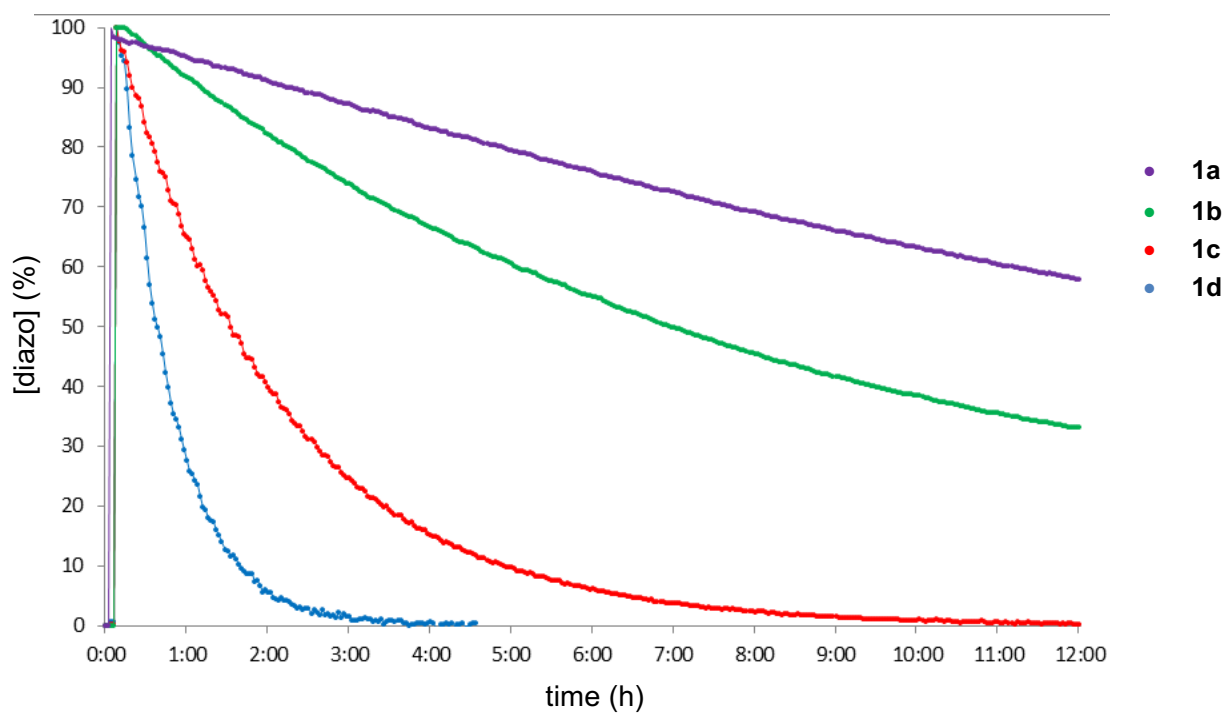
All solvents were purified and dried by a Glass Contour Solvent System unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded at either 400 MHz (^{13}C at 100 MHz) on Varian-400 spectrometer or at 500 MHz on a I-Nova spectrometer. NMR spectra were run in solutions of deuterated chloroform (CDCl_3) with residual chloroform taken as an internal standard (7.26 ppm for ^1H , and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm). Abbreviations for signal multiplicity are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublet, app t = apparent triplet, etc. Coupling constants (J values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic analysis was performed with glass-backed silica gel plates, visualizing with UV light and/or staining with PMA or aqueous KMnO_4 stain. Melting points (mp) were measured in open capillary tubes with a Mel-Temp Electrothermal melting points apparatus and are uncorrected. *In situ* IR monitoring experiments were carried out with a Mettler Toledo ReactIRTM 45m instrument equipped with a 9.5 mm x 12'' AgX 1.5 m SiComp probe. Unless otherwise stated, all chemicals were obtained from Fluka, Aldrich or Acros and used as received or purified according to standard literature procedures.

2. General procedure for kinetic measurements on ReactIR



Experiments were carried out with a Mettler Toledo ReactIRTM 45m instrument equipped with a 9.5 mm x 12'' AgX 1.5 m SiComp probe. A 2-necked round bottom flask was equipped with a stir bar, a condenser and the ReactIR probe. The instrument was set up for a continuous scan experiment. Cyclohexane (6 mL) was warmed to 80 °C under argon. The scan was started and IR spectra recorded every 2 min. Few IR spectra were recorded before the addition of the diazo (1 equiv, 0.8 mmol). The reaction mixture was stirred at 80 °C until complete conversion of the diazo. Then, solvent was evaporated and the mixture purified by column chromatography over silica gel. The reaction was run twice to ensure the validity of the procedure. It was possible to observe the signals relative to the diazo reagents **1a**, **1b**, **1c** and **1d** (at 2085 cm⁻¹, 2095 cm⁻¹, 2090 cm⁻¹ and 2096 cm⁻¹ respectively) decreasing over the time following a first order behavior.

Representation of the concentration of diazo 1a, 1b, 1c and 1d in M (%) versus time (hh:mm)

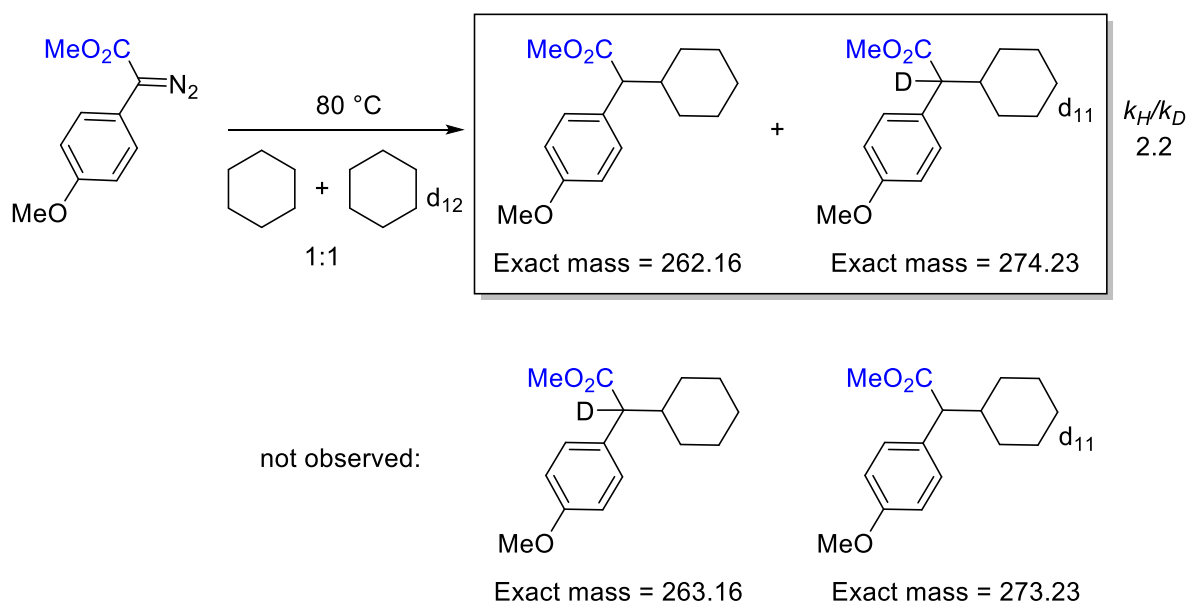


Compd	R ¹	R ²	<i>k</i> ₁ (h ⁻¹)	<i>t</i> _{1/2} (min)
1a	Br	OMe	0.044 ± 0.001	942
1b	Br	OCH ₂ CCl ₃	0.099 ± 0.001	418
1c	OMe	OMe	0.45 ± 0.01	92
1d	OMe	OCH ₂ CCl ₃	1.07 ± 0.03	39

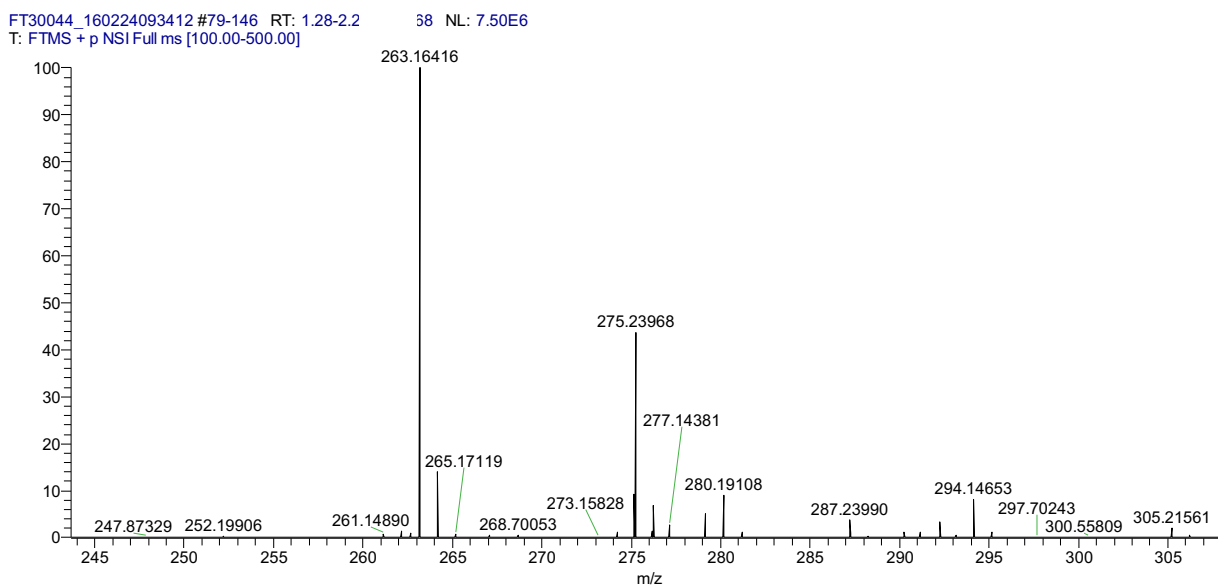
3. General procedure for isotope effect study

In a 4 mL screw-cap vial equipped with a magnetic stirring bar, diazo (0.2 mmol) was dissolved in in 0.50 mL of dry cyclohexane and 0.50 mL of dry cyclohexane- d_{12} . The vial is flushed with argon and capped. The resulting solution is stirred at 80 °C for 15 hours and until complete conversion of the diazo compound (IR check). The solvent is evaporated and the mixture purified by column chromatography over silica gel. k_H/k_D were determined by ^1H NMR of the crude reaction mixture.

FTMS-NSI and ^1H NMR spectrum of substrate 3a shown as example:

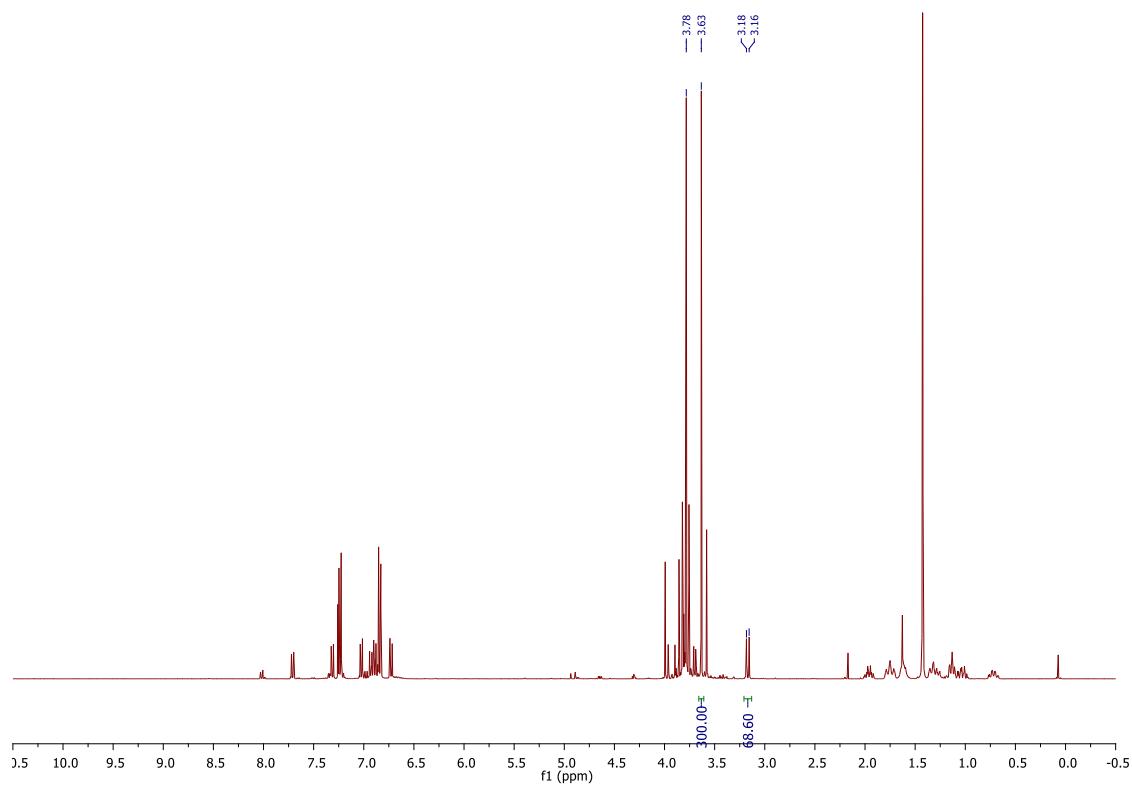


Mass Spectroscopic analysis (all masses plus 1)

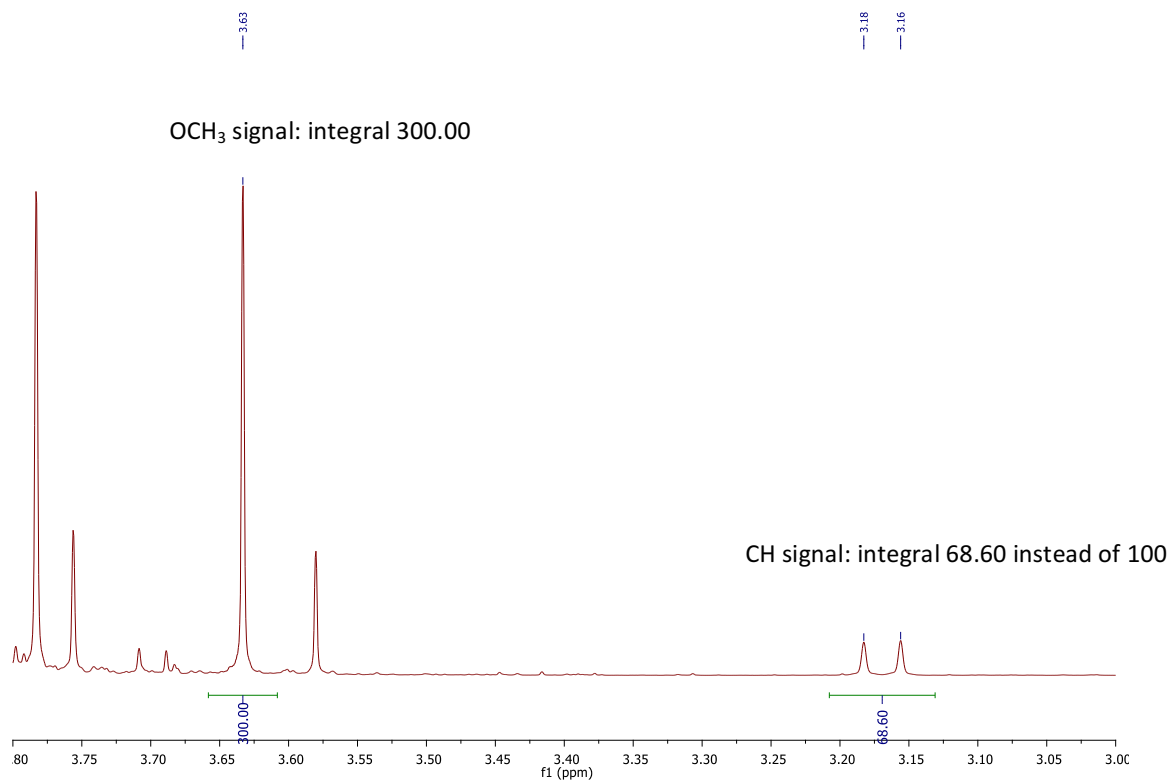


^1H NMR spectra (400 MHz, CDCl_3)

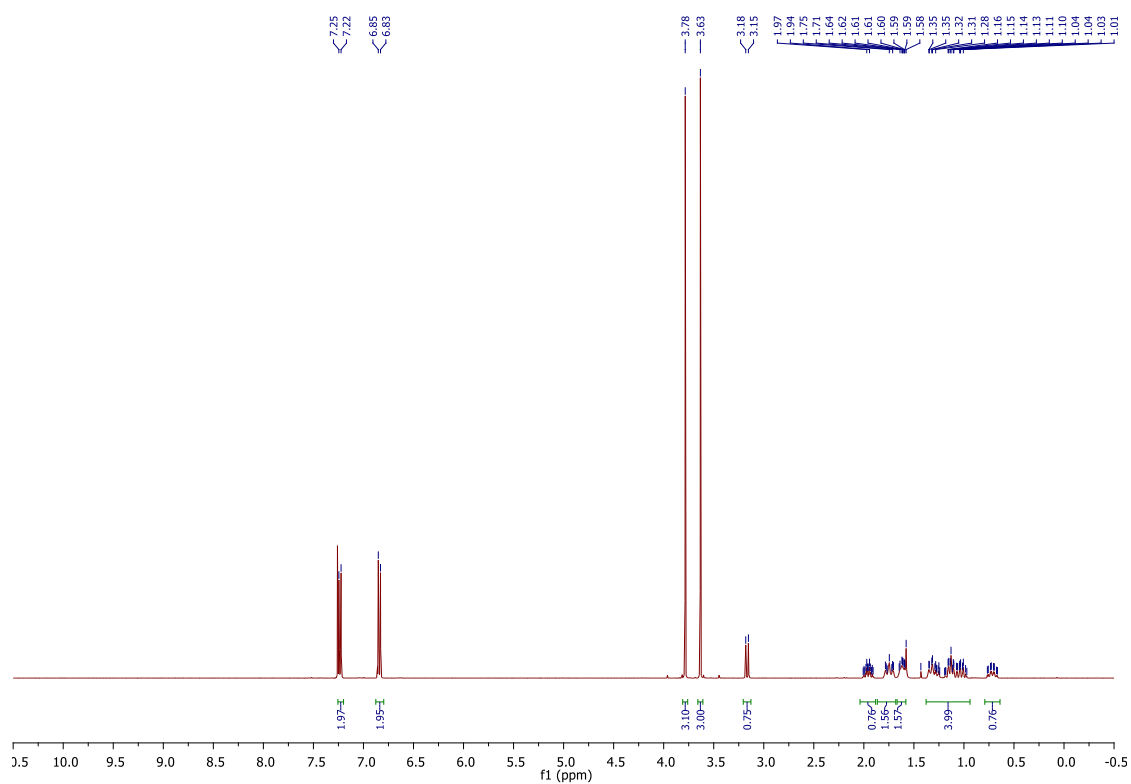
Crude mixture - General view



Crude mixture - Detailed view

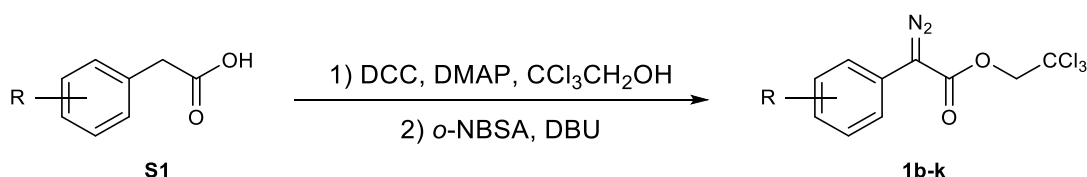


Purified compound - General view



4. General procedure for the synthesis and analysis data of diazo compounds

Diazo compounds with methyl esters were prepared following the procedure reported in the literature.¹ Yields for diazo compounds containing the 2,2,2-trichloroethyl ester were higher when prepared using *o*-nitrobenzenesulfonyl azide (*o*-NBSA) as the diazo transfer reagent² (CAUTION! POTENTIALLY EXPLOSIVE! USE PROPER PRECAUTIONS FOR HANDLING THIS AZIDE). This reagent was prepared according to a literature protocol.³



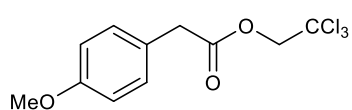
First step: preparation of the trichloroethyl ester

A solution of desired phenylacetic acid **S1** (49 mmol, 1.0 equiv), 2,2,2-trichloroethanol (8.8 g, 5.6 mL, 58.8 mmol, 1.2 equiv) and DMAP (599 mg, 4.9 mmol, 0.1 equiv) in CH₂Cl₂ (100 mL) was cooled to 0 °C in an ice/water bath. A solution of DCC (11.1 g, 53.9 mmol, 1.1 equiv) in CH₂Cl₂ (25 mL) was poured into the cold reaction mixture. The solution was stirred overnight, at which point it had reached ambient temperature. The precipitate was filtered and washed with Et₂O. The filtrate was concentrated and filtered on a short plug of silica gel. The product obtained was used without further purification in the diazo transfer reaction.

Second step: diazo transfer reaction

The ester from the previous step (14.9 mmol, 1.0 equiv) and *o*-NBSA (22.4 mmol, 1.5 equiv) were dissolved in acetonitrile (100 mL) and cooled to 0 °C. Then DBU (4.5 g, 4.4 mL, 29.8 mmol, 2.0 equiv) was added dropwise. The solution was stirred until full conversion of the ester and quenched with saturated aqueous NH₄Cl (75 mL) and water (20 mL) and extracted with Et₂O (100 mL). The organic layer was washed with water (50 mL) and brine (50 mL) and dried over MgSO₄.

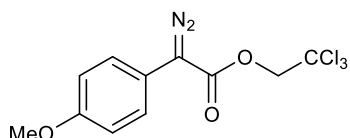
2,2,2-trichloroethyl 2-(4-methoxyphenyl)acetate (**S1d**)



Starting from the corresponding phenylacetic acid (23.3 g, 140 mmol) and following the general procedure, the desired compound was obtained after as a colorless oil (40 g, 96% yield) and used in the following step without further purification.

Rf = 0.48 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.74 (s, 2H), 3.80 (s, 3H) and 3.71 (s, 2H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 170.35 (C), 158.99 (C), 130.54 (2xCH), 125.03 (C), 114.14 (2xCH), 94.97 (C), 74.21 (CH₂), 55.33 (CH₃) and 40.08 (CH₂) ppm; **IR (neat)**: 2116, 1752, 1512, 1247 and 1125 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₁H₁₂Cl₃O₃⁺ 296.9847, observed 296.9848.

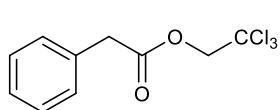
2,2,2-trichloroethyl 2-diazo-2-(4-methoxyphenyl)acetate (1d)



Starting from the corresponding ester **S1d** (9 g, 50 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as an orange solid (2.2 g, 21% yield). Spectroscopic data are consistent with those reported in the literature.^{2b}

Mp: >70 °C; **Rf** = 0.53 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (600 MHz, CDCl₃)**: δ 7.38 (d, 2H, *J* = 8.7 Hz), 6.94 (d, 2H, *J* = 8.7 Hz), 4.88 (s, 2H) and 3.08 (s, 3H) ppm; **¹³C NMR (150 MHz, CDCl₃)**: δ 158.6 (C), 126.3 (2xCH), 116.2 (C), 114.9 (2xCH), 95.3 (C), 74.0 (CH₂) and 55.6 (CH₃) ppm (note: the resonances resulting from the diazo carbon and the carbonyl carbon were not observed); **IR (neat)**: 2085, 1704, 1511, 1239 and 1136 cm⁻¹; **HR-MS (APCI)** *m/z*: [M+H-N₂]⁺ calculated for C₁₁H₁₀O₃Cl₃ 294.9690, observed 294.9688.

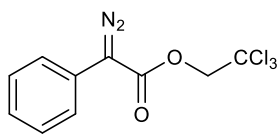
2,2,2-trichloroethyl 2-phenylacetate (S1e)



Starting from the corresponding phenylacetic acid (11.6 g, 70 mmol) and following the general procedure, the desired compound was obtained as a colorless oil (19 g, quantitative yield) and used in the following step without further purification.

Rf = 0.70 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.39-7.29 (m, 5H), 4.77 (s, 2H) and 3.79 (s, 2H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 170.00 (C), 132.99 (C), 129.49 (2xCH), 128.74 (2xCH), 127.51 (CH), 94.91 (C), 74.23 (CH₂) and 40.97 (CH₂) ppm; **IR (neat)**: 2117, 1752 and 1125 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₀H₁₀Cl₃O₂⁺ 266.9741, observed 266.9742.

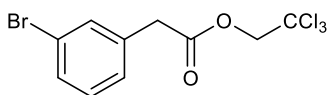
2,2,2-trichloroethyl 2-diazo-2-phenylacetate (1e)



Starting from the corresponding ester **S1e** (5.3 g, 20 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as an orange solid (4 g, 68% yield).

Mp: 55 °C; **Rf** = 0.75 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (600 MHz, CDCl₃):** δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H) and 7.24 (t, *J* = 7.4 Hz, 1H) and 4.93 (s, 2H) ppm; **¹³C NMR (126 MHz, CDCl₃):** δ 163.43 (C), 129.21 (2xCH), 126.45 (2xCH), 124.74 (C), 124.19 (CH), 95.16 (C) and 73.95 (CH₂) ppm (note: the resonance resulting from the diazo carbon was not observed); **IR (neat):** 2094, 1707, 1498 and 1140 cm⁻¹; **HR-MS (EI) *m/z*:** calculated for C₁₀H₇O₂Cl₃N₂Na⁺ 314.9471, observed 315.1891.

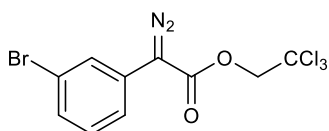
2,2,2-trichloroethyl 2-(3-bromophenyl)acetate (S1f)



Starting from the corresponding phenylacetic acid (15 g, 70 mmol) and following the general procedure, the desired compound was obtained as a white solid (21.4 g, 88 % yield) and used in the following step without further purification.

Mp: 31 °C; **Rf** = 0.63 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃):** δ 7.53-7.47 (m, 1H), 7.47-7.39 (m, 1H), 7.30-7.16 (m, 2H), 4.76 (s, 2H) and 3.74 (s, 2H) ppm; **¹³C NMR (100 MHz, CDCl₃):** δ 169.33 (C), 135.04 (C), 132.59 (CH), 130.70 (CH), 130.25 (CH), 128.19 (CH), 122.66 (C), 94.78 (C), 74.31 (CH₂) and 40.47 (CH₂) ppm; **IR (neat):** 2116, 1754 and 1129 cm⁻¹; **HR-MS (EI) *m/z*** calculated for C₁₀H₇BrCl₃O₂⁻ 342.8701, observed 342.8692.

2,2,2-trichloroethyl 2-(3-bromophenyl)-2-diazoacetate (1f)

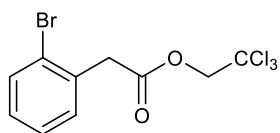


Starting from the corresponding ester **S1f** (2.0 g, 5.8 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as an orange solid (794 mg, 36% yield).

Mp: 43 °C; **Rf** = 0.75 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃):** δ 7.71 (t, *J* = 1.9 Hz, 1H), 7.43-7.38 (m, 1H), 7.36-7.33 (m, 1H), 7.30-7.26 (m, 1H) and 4.92 (s, 2H); **¹³C NMR (126 MHz, CDCl₃):** δ 162.75 (C), 130.44 (CH), 129.20 (CH), 127.07 (C), 126.64 (C), 123.28 (CH), 122.16 (CH), 94.94 (C) and 73.92 (CH₂) ppm (note: the resonance resulting from the diazo carbon was not observed).

carbon was not observed); **IR (neat)**: 2094, 1710, 1479, 1237 and 1139 cm^{-1} ; **HR-MS (EI)** m/z : calculated for $\text{C}_{10}\text{H}_7\text{BrO}_2\text{Cl}_3\text{N}_2^+$ 375.0316, observed 375.0320.

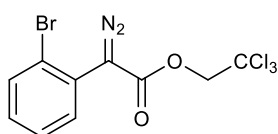
2,2,2-trichloroethyl 2-(2-bromophenyl)acetate (**S1g**)



Starting from the corresponding phenylacetic acid (5.1 g, 23.7 mmol) and following the general procedure, the desired compound was obtained as a colourless oil (8.0 g, 99% yield) and used in the following step without further purification.

R_f = 0.60 (SiO_2 , pentane: Et_2O , 9:1); **^1H NMR (400 MHz, CDCl_3)**: δ 7.58 (dd, J = 8.0 and 1.2 Hz, 1H), 7.37-7.25 (m, 2H), 7.21-7.12 (m, 1H), 4.78 (s, 2H) and 3.95 (s, 2H) ppm; **^{13}C NMR (100 MHz, CDCl_3)**: δ 169.07 (C), 133.30 (C), 133.00 (CH), 131.72 (CH), 129.36 (CH), 127.75 (CH), 125.14 (C), 94.85 (CCl_3), 74.40 (CH_2) and 41.33 (CH_2) ppm; **IR (neat)**: 2929, 2114, 1756 and 1352 cm^{-1} ; **HR-MS (EI)** m/z calculated for $\text{C}_{10}\text{H}_7\text{BrCl}_3\text{O}_2^-$ 342.87005, observed 342.86980.

2,2,2-trichloroethyl 2-(2-bromophenyl)-2-diazoacetate (**1g**)



Starting from the corresponding ester **S1g** (8.2 g, 23.7 mmol) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 97:3) as an orange oil (6.6 g, 75% yield).

R_f = 0.60 (SiO_2 , pentane: Et_2O , 9:1); **^1H NMR (400 MHz, CDCl_3)**: δ 7.65 (dd, J = 8.1, 1.3 Hz, 1H), 7.56 (dd, J = 7.9 and 1.7 Hz, 1H), 7.44-7.35 (m, 1H), 7.25 (ddd, J = 8.1, 7.4 and 1.7 Hz, 1H) and 4.89 (s, 2H) ppm; **^{13}C NMR (100 MHz, CDCl_3)**: δ 163.9 (C), 133.5 (CH), 133.2 (C), 130.6 (CH), 127.9 (CH), 125.0 (CH), 124.7 (C), 95.2 (CCl_3) and 74.1 (CH_2) ppm (note: the resonance resulting from the diazo carbon was not observed); **IR (neat)**: 2100, 1705, 1235 and 1142 cm^{-1} ; **HR-MS (EI)** m/z : $[\text{M}+\text{H}-\text{N}_2]^+$ calculated for $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2\text{BrCl}_3$ 370.8751, observed 370.8754.

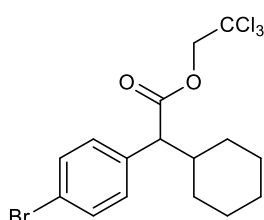
5. General procedure for C–H functionalization reactions

In a 4 mL screw-cap vial equipped with a magnetic stirring bar, diazo (0.2 mmol) was dissolved in 1.5 mL of alkane. The vial is flushed with argon and capped. The resulting solution is stirred at 80 °C for the time indicated in the table and until complete conversion of the diazo compound (IR check). The solvent is evaporated and the mixture purified by column chromatography over silica gel.

Products **5**, **7** and **9** were prepared adding the diazo dropwise over 3 hours by the help of a syringe pump. The experimental data correspond to previously reported material.⁴

6. Analysis data of adducts of C-H insertion reactions

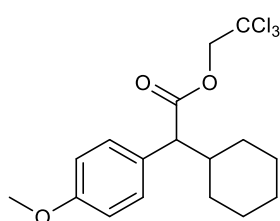
2,2,2-trichloroethyl 2-cyclohexyl-2-phenylacetate (2b)



Starting from the corresponding aryl diazo **1b** (74.5 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (74 mg, 86 % yield).

R_f = 0.75 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.34 (d, *J* = 10.7 Hz, 1H), 2.12-1.99 (m, 1H), 1.90-1.81 (m, 1H), 1.80-1.69 (m, 1H), 1.68-1.59 (m, 2H), 1.39-1.04 (m, 5H) and 0.89-0.70 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.86 (C), 136.04 (C), 131.80 (2xCH), 130.54 (2xCH), 121.65 (C), 94.89 (CCl₃), 74.25 (CH₂), 58.23 (CH), 40.96 (CH), 31.98 (CH₂), 30.37 (CH₂), 26.26 (CH₂), 25.98 (CH₂) and 25.94 (CH₂) ppm; **IR (neat)**: 2927, 1748, 1488, 1173 and 1122 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₆H₁₈NBrCl₃O₂⁺ 439.9581 observed 439.9584.

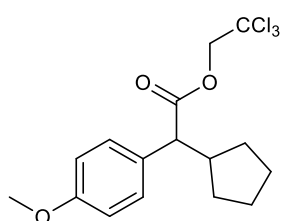
2,2,2-trichloroethyl 2-cyclohexyl-2-(4-methoxyphenyl)acetate (2d)



Starting from the corresponding aryl diazo **1d** (16.5 mg, 0.05 mmol) and cyclohexane (0.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (15 mg, 70 % yield).

R_f = 0.42 (SiO₂, pentane:Et₂O, 95:5); **¹H NMR (400 MHz, CDCl₃)**: δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.32 (d, *J* = 10.8 Hz, 1H), 2.05 (qt, *J* = 11.0, 3.3 Hz, 1H), 1.96-1.78 (m, 1H), 1.75 (m, 1H), 1.64 (m, 2H), 1.46-1.01 (m, 5H) and 0.76 (ddd, *J* = 24.4, 12.2 and 3.3 Hz, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.58 (C), 159.05 (C), 129.83 (2xCH), 129.08 (C), 114.01 (2xCH), 95.05 (CCl₃), 74.17 (CH₂), 57.96 (CH), 55.37 (CH₃), 40.92 (CH), 32.08 (CH₂), 30.41 (CH₂), 26.38 (CH₂), 26.05 (CH₂) and 26.02 (CH₂) ppm; **IR (neat)**: 2924, 1750, 1511, 1248 and 1121 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₇H₂₂Cl₃O₃⁺ 379.0629 observed 379.0635.

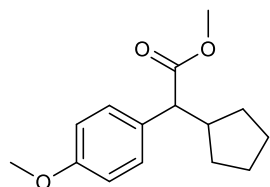
2,2,2-trichloroethyl 2-cyclopentyl-2-(4-methoxyphenyl)acetate (4)



Starting from the corresponding aryl diazo **1d** (41 mg, 0.2 mmol) and cyclopentane (1.5 mL) and following the general procedure with hexafluorobenzene (1.5 mL) as solvent, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (33 mg, 66 % yield).

R_f = 0.65 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.36 (d, *J* = 11.2 Hz, 1H), 2.69-2.53 (m, 1H), 2.01-1.88 (m, 1H), 1.75-1.59 (m, 2H), 1.50-1.43 (m, 2H), 1.36-1.21 (m, 2H) and 1.11-0.95 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.67 (C), 159.01 (C), 130.28 (C), 129.53 (2xCH), 114.00 (2xCH), 95.08 (CCl₃), 74.09 (CH₂), 57.00 (CH), 55.36 (CH₃), 43.24 (CH), 31.62 (CH₂), 30.87 (CH₂), 25.42 (CH₂) and 25.01 (CH₂) ppm; **IR (neat)**: 2953, 1748, 1511, 1249, 1123 and 719 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₆H₁₉Cl₃O₃Na⁺ 387.0292 observed 387.0294.

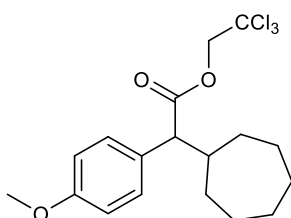
Methyl 2-cyclopentyl-2-(4-methoxyphenyl)acetate (5)



Starting from the corresponding aryl diazo **1c** (41 mg, 0.2 mmol) and cyclopentane (1.5 mL) and following the general procedure with hexafluorobenzene (1.5 mL) as solvent, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (32 mg, 65 % yield). The experimental data correspond to previously reported material.⁴

¹H NMR (300 MHz, CDCl₃): δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.63 (s, 3H), 3.22 (d, *J* = 11.0 MHz, 1H), 2.53-2.51 (m, 1H), 1.88-1.39 (m, 6H), 1.25-1.18 (m, 1H) and 1.01-0.90 (m, 1H) ppm.

2,2,2-trichloroethyl 2-cycloheptyl-2-(4-methoxyphenyl)acetate (6)

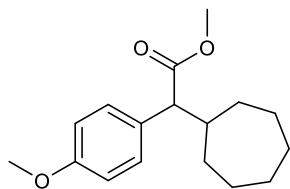


Starting from the corresponding aryl diazo **1d** (129.4 mg, 0.4 mmol) and cycloheptane (0.242 mL, 5 equiv) and following the general procedure, the

desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (84 mg, 53 % yield).

R_f = 0.65 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.39 (d, *J* = 11.1 Hz, 1H), 2.45-2.23 (m, 1H), 1.90-1.79 (m, 1H), 1.74-1.24 (m, 10H) and 1.06-0.94 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.74 (C), 159.01 (C), 129.90 (2xCH), 129.63 (C), 114.00 (2xCH), 95.03 (C), 74.14 (CH₂), 58.12 (CH), 55.32 (CH₃), 41.97 (CH), 33.25 (CH₂), 31.35 (CH₂), 28.41 (CH₂), 28.35 (CH₂), 26.45 (CH₂) and 26.31 (CH₂) ppm; **IR (neat)**: 2925, 1747, 1510, 1248 and 1118 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₈H₂₄Cl₃O₃⁺ 393.0786 observed 393.0783.

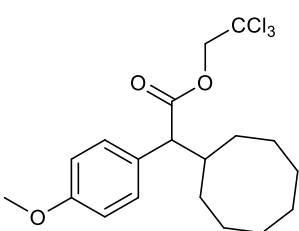
Methyl 2-cycloheptyl-2-(4-methoxyphenyl)acetate (7)



Starting from the corresponding aryl diazo **1c** (82 mg, 0.4 mmol) and cycloheptane (0.242 mL, 5 equiv) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (31 mg, 28 % yield). The experimental data correspond to previously reported material.⁴

¹H NMR (300 MHz, CDCl₃): δ 7.23 (d, *J* = 6.6 Hz, 2H), 6.82 (d, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 3.63 (s, 3H), 3.24 (d, *J* = 8.2 Hz, 1H), 2.21-2.19 (m, 1H), 1.86-1.24 (m, 11H) and 0.96-0.94 (m, 1H) ppm.

2,2,2-trichloroethyl 2-cyclooctyl-2-(4-methoxyphenyl)acetate (8)

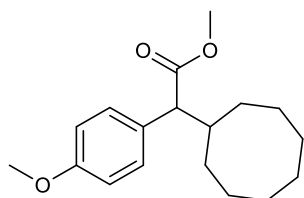


Starting from the corresponding aryl diazo **1d** (129.4 mg, 0.4 mmol) and cyclooctane (0.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (121 mg, 74 % yield).

R_f = 0.65 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.38 (d, *J* = 11.2 Hz, 1H), 2.45-2.25 (m, 1H), 1.75-1.23 (m, 13H) and 1.13-1.05 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.79 (C), 159.01 (C), 129.91 (2xCH), 129.61 (C), 114.00 (2xCH), 95.04 (C), 74.14 (CH₂), 58.30 (CH), 55.30 (CH₃), 40.06 (CH), 31.30 (CH₂), 29.20 (CH₂), 27.03 (CH₂), 26.99

(CH₂), 26.52 (CH₂), 25.51 (CH₂) and 25.31 (CH₂) ppm; **IR (neat)**: 2918, 1747, 1510, 1248 and 1118 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₉H₂₆Cl₃O₃⁺ 407.0942 observed 407.0943.

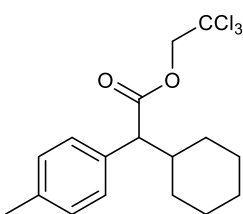
Methyl 2-cyclooctyl-2-(4-methoxyphenyl)acetate (9)



Starting from the corresponding aryl diazo **1c** (41.0 mg, 0.2 mmol) and cyclooctane (0.135 mL) and following the general procedure (slow addition of the diazo), the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (21.3 mg, 37 % yield).

R_f = 0.45 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.63 (s, 3H), 3.24 (d, *J* = 11.1 Hz, 1H), 2.35-2.21 (m, 1H), 1.69-1.24 (m, 13H) and 1.11-1.00 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 175.14 (C), 158.82 (C), 130.62 (C), 129.74 (2xCH), 113.95 (2xCH), 58.27 (CH), 55.34 (CH₃), 51.85 (CH₃), 40.42 (CH), 31.35 (CH₂), 29.14 (CH₂), 27.14 (CH₂), 27.00 (CH₂), 26.53 (CH₂), 25.64 (CH₂) and 25.29 (CH₂) ppm; **IR (neat)**: 2918, 1732, 1510, 1248 and 1152 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₈H₂₇O₃⁺ 291.1955 observed 291.1956.

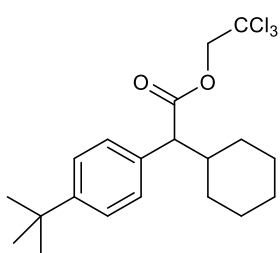
2,2,2-trichloroethyl 2-cyclohexyl-2-(p-tolyl)acetate (10)



Starting from the corresponding aryl diazo (26.3 mg, 0.086 mmol) and cyclohexane (1 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (20.4 mg, 65 % yield).

R_f = 0.70 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (500 MHz, CDCl₃)**: δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.77 (dd, *J* = 12.0 and 0.9 Hz, 1H), 4.59 (dd, *J* = 12.0 and 0.9 Hz, 1H), 3.34 (d, *J* = 10.7 Hz, 1H), 2.32 (s, 3H), 2.07 (qd, *J* = 11.1, 7.8 Hz, 1H), 1.87 (d, *J* = 12.8 Hz, 1H), 1.75 (d, *J* = 11.8 Hz, 1H), 1.68-1.57 (m, 2H), 1.42-1.27 (m, 2H), 1.27-1.03 (m, 3H) and 0.76 (qd, *J* = 12.3, 3.6 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)**: δ 172.48 (C), 137.28 (C), 134.03 (C), 129.37 (2xCH), 128.72 (2xCH), 95.07 (CCl₃), 74.23 (CH₂), 58.45 (CH), 40.90 (CH), 32.10 (CH₂), 30.46 (CH₂), 26.40 (CH₂), 26.08 (CH₂), 26.04 (CH₂) and 21.23 (CH₃) ppm; **IR (neat)**: 2923, 1749, 1142, 1121 and 719 cm⁻¹.

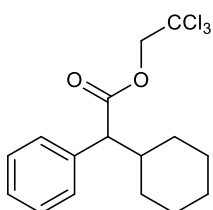
2,2,2-trichloroethyl 2-(4-(tert-butyl)phenyl)-2-cyclohexylacetate (11)



Starting from the corresponding aryl diazo (70 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (51 mg, 63 % yield).

R_f = 0.88 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.30 (q, *J* = 8.6 Hz, 4H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 3.35 (d, *J* = 10.8 Hz, 1H), 2.08 (qt, *J* = 11.0, 3.3 Hz, 1H), 1.88 (d, *J* = 12.6 Hz, 1H), 1.75 (d, *J* = 11.4 Hz, 1H), 1.64 (dd, *J* = 8.8, 4.1 Hz, 2H), 1.48-1.32 (m, 2H), 1.30 (s, 9H), 1.29-1.06 (m, 3H) and 0.77 (qd, *J* = 12.4, 3.4 Hz, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.54 (C), 150.44 (C), 133.92 (C), 128.43 (2xCH), 125.54 (2xCH), 95.05 (CCl₃), 74.22 (CH₂), 58.37 (CH), 40.91 (CH), 34.60 (C), 32.07 (CH₂), 31.48 (3xCH₃), 30.48 (CH₂), 26.39 (CH₂), 26.06 (CH₂) and 26.03 (CH₂) ppm; **IR (neat)**: 2926, 1749, 1142, 1124, 1112 and 728 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₂₀H₂₈Cl₃O₂⁺ 405.1149 observed 405.1153.

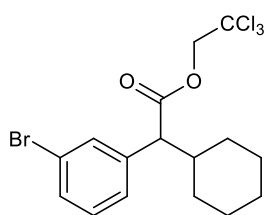
2,2,2-trichloroethyl 2-cyclohexyl-2-phenylacetate (12)



Starting from the corresponding aryl diazo (59 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (38 mg, 54 % yield).

R_f = 0.85 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.40-7.23 (m, 5H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 3.38 (d, *J* = 10.8 Hz, 1H), 2.10 (qt, *J* = 11.0, 3.4 Hz, 1H), 1.94-1.83 (m, 1H), 1.80-1.71 (m, 1H), 1.63 (dt, *J* = 7.1, 5.5, 2.7 Hz, 2H), 1.42-1.25 (m, 2H), 1.24-1.05 (m, 3H) and 0.78 (ddd, *J* = 24.5, 12.2, 3.5 Hz, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.32 (C), 137.04 (C), 128.85 (2xCH), 128.66 (2xCH), 127.62 (CH), 95.00 (CCl₃), 74.19 (CH₂), 58.85 (CH), 40.91 (CH), 32.08 (CH₂), 30.44 (CH₂), 26.36 (CH₂), 26.04 (CH₂) and 26.01 (CH₂) ppm; **IR (neat)**: 2925, 1732, 1510, 1248 and 1152 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₆H₂₀Cl₃O₂⁺ 349.0523 observed 349.0526.

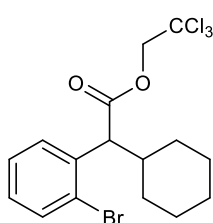
2,2,2-trichloroethyl 2-(3-bromophenyl)-2-cyclohexylacetate (13)



Starting from the corresponding aryl diazo (74.5 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (35 mg, 41 % yield).

R_f = 0.78 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.54 (t, *J* = 1.8 Hz, 1H), 7.40 (ddd, *J* = 7.9, 2.0 and 1.1 Hz, 1H), 7.29 (dt, *J* = 7.8 and 1.3 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 3.34 (d, *J* = 10.7 Hz, 1H), 2.06 (d, *J* = 11.1 Hz, 1H), 1.86 (d, *J* = 12.6 Hz, 1H), 1.80-1.71 (m, 1H), 1.69-1.60 (m, 2H), 1.42-1.05 (m, 5H) and 0.85 and 0.72 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.67 (C), 139.27 (C), 131.79 (CH), 130.81 (CH), 130.17 (CH), 127.62 (CH), 122.75 (C), 94.86 (CCl₃), 74.29 (CH₂), 58.51 (CH), 40.98 (CH₂), 31.96 (CH₂), 30.42 (CH₂), 26.26 (CH₂), 25.97 (CH₂) and 25.92 (CH₂) cm⁻¹; **IR (neat)**: 2926, 1742, 1143, 1120 and 715 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₆H₂₀NBrCl₃O₂⁺ 441.9738 observed 441.9739.

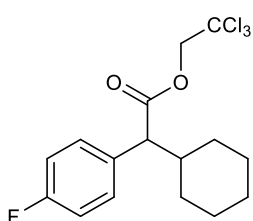
2,2,2-trichloroethyl 2-(3-bromophenyl)-2-cyclohexylacetate (14)



Starting from the corresponding aryl diazo (94 mg, 0.25 mmol) and cyclohexane (2 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 9:1) as a colourless oil (93 mg, 87 % yield).

R_f = 0.78 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.56 (ddd, *J* = 12.3, 8.0 and 1.5 Hz, 2H), 7.29 (td, *J* = 7.6 and 1.3 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.3 and 1.7 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.18 (d, *J* = 10.7 Hz, 1H), 2.11 (qt, *J* = 10.9 and 3.3 Hz, 1H), 1.97-1.87 (m, 1H), 1.82-1.72 (m, 1H), 1.70-1.60 (m, 2H), 1.40-1.08 (m, 5H) and 1.00-0.87 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.66 (C), 136.66 (C), 133.06 (CH), 129.29 (CH), 128.88 (CH), 127.83 (CH), 126.06 (C), 94.91 (CCl₃), 74.13 (CH₂), 55.94 (CH), 41.43 (CH), 31.87 (CH₂), 29.72 (CH₂), 26.28 (CH₂), 26.07 (CH₂) and 26.02 (CH₂) ppm; **IR (neat)**: 2925, 1749, 1147, 1128 and 719 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₆H₁₉BrCl₃O₂⁺ 426.9629 observed 426.9632.

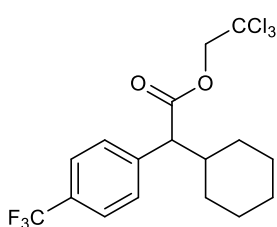
2,2,2-trichloroethyl 2-cyclohexyl-2-(4-fluorophenyl)acetate (15)



Starting from the corresponding aryl diazo (62.3 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (57 mg, 78 % yield).

Rf = 0.82 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.33 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.36 (d, *J* = 10.7 Hz, 1H), 2.05 (qt, *J* = 11.1, 3.4 Hz, 1H), 1.86 (d, *J* = 12.6 Hz, 1H), 1.80-1.71 (m, 1H), 1.71-1.58 (m, 2H), 1.40-1.03 (m, 5H) and 0.76 (ddd, *J* = 16.1, 12.3, 3.4 Hz, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 172.17 (d, *J* = 1.1 Hz, C), 162.32 (d, *J*_{C-F} = 246.0 Hz, C), 132.74 (d, *J*_{C-F} = 3.2 Hz, C), 130.34 (d, *J*_{C-F} = 8.0 Hz, 2xCH), 115.55 (d, *J*_{C-F} = 21.3 Hz, 2xCH), 94.93 (CCl₃), 74.19 (CH₂), 58.00 (CH), 41.00 (CH), 32.01 (CH₂), 30.36 (CH₂), 26.30 (CH₂), 25.99 (CH₂) and 25.96 (CH₂) ppm; **¹⁹F NMR (282 MHz, CDCl₃)**: δ -115.07 ppm; **IR (neat)**: 2927, 1749, 1508, 1142 and 1120 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₆H₁₉Cl₃FO₂⁺ 367.0429 observed 367.0434.

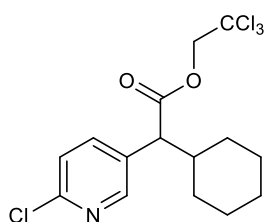
2,2,2-trichloroethyl 2-cyclohexyl-2-(4-(trifluoromethyl)phenyl)acetate (16)



Starting from the corresponding aryl diazo (72 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (30 mg, 36 % yield).

Rf = 0.76 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (500 MHz, CDCl₃)**: δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 3.46 (d, *J* = 10.7 Hz, 1H), 2.11 (qt, *J* = 11.0 and 3.4 Hz, 1H), 1.89 (d, *J* = 12.7 Hz, 1H), 1.84-1.68 (m, 1H), 1.64 (ddd, *J* = 7.8, 6.9 and 3.7 Hz, 2H), 1.38-1.23 (m, 3H), 1.23-1.04 (m, 3H) and 0.79 (qd, *J* = 12.2 and 3.6 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)**: δ 171.62 (C), 141.09 (C), 129.99 (dd, *J* = 65.0 and 32.5 Hz, C), 129.27 (2xCH), 125.63 (q, *J* = 3.7 Hz, 2xCH), 124.21 (q, *J* = 272.0 Hz, CF₃), 94.84 (CCl₃), 74.35 (CH₂), 58.64 (CH), 41.11 (CH), 31.98 (CH₂), 30.42 (CH₂), 26.24 (CH₂), 25.98 (CH₂) and 25.93 (CH₂) ppm; **¹⁹F NMR (282 MHz, CDCl₃)**: δ -62.57 ppm; **IR (neat)**: 2928, 1749, 1322, 1121 and 1107 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₇H₁₉Cl₃F₃O₂⁺ 418.6817 observed 418.7090.

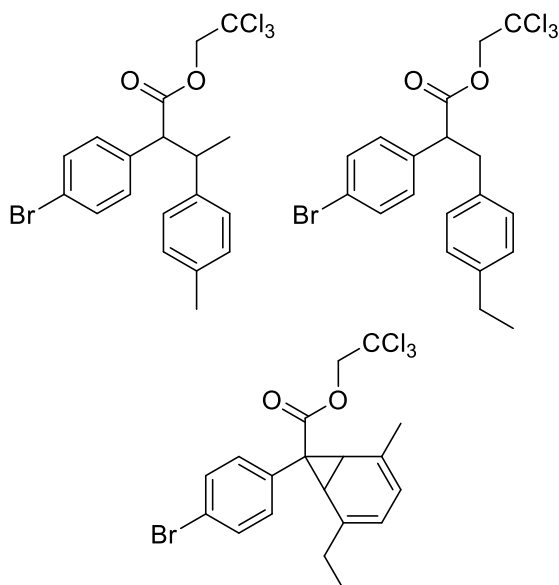
2,2,2-trichloroethyl 2-cyclohexyl-2-(4-(trifluoromethyl)phenyl)acetate (17)



Starting from the corresponding aryl diazo **1h** (65.8 mg, 0.2 mmol) and cyclohexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 9:1) as a colourless oil (40 mg, 52 % yield).

Rf = 0.50 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 8.32 (d, *J* = 2.4 Hz, 1H), 7.74 (dd, *J* = 8.3 and 2.5 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 3.42 (d, *J* = 10.4 Hz, 1H), 2.05 (qt, *J* = 11.1 and 3.3 Hz, 1H), 1.90-1.72 (m, 2H), 1.66 (dd, *J* = 11.6 and 8.7 Hz, 2H), 1.39-1.03 (m, 5H) and 0.88-0.74 (m, 1H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.21 (C), 150.93 (C), 150.12 (CH), 138.77 (CH), 131.71 (C), 124.41 (CH), 94.65 (C), 74.37 (CH₂), 55.33 (CH), 41.07 (CH), 31.83 (CH₂), 30.31 (CH₂), 26.07 (CH₂), 25.86 (CH₂) and 25.80 (CH₂) ppm; **IR (neat)**: 2928, 1748, 1462, 1449, 1174, 1121 and 1105 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₅H₁₈Cl₄NO₂⁺ 384.0086 observed 384.0085.

2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(p-tolyl)butanoate (18), 2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-ethylphenyl)propanoate (19), 2,2,2-trichloroethyl 7-(4-bromophenyl)-2-ethyl-5-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (S2a)

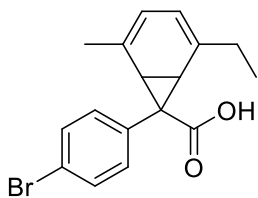


Starting from the corresponding aryl diazo **1b** (74 mg, 0.2 mmol) and 4-ethyltoluene (1.5 mL, 49 equiv) and following the general procedure, an inseparable mixture^{2a,b} of the two C–H insertion products and the cyclopropanation product (2:1:5.2) was obtained after purification by column of silica gel (hexanes:diethyl ether 100:0 to 99:1) as a colourless oil (56 mg, 60 % yield).

The NMR spectra of the product mixture was compared with authentic samples of both C–H insertion compounds,^{2a,b} leaving the cyclopropanation product (**S2a**) as the only uncharacterized compound: **R_f** = 0.50 (SiO₂, hexanes:Et₂O, 6:1); ¹H NMR (300 MHz, CDCl₃): δ 7.34 – 7.27 (m, 2H), 6.88 – 6.82 (m, 2H), 5.60 – 5.50 (m, 2H), 4.71 (s, 2H), 3.17 – 3.02 (m, 2H), 2.08 (s, 3H), 1.15 (t, *J* = 7.4 Hz, 3H).

The cyclopropane product 2,2,2-trichloroethyl 7-(4-bromophenyl)-2-ethyl-5-methylbicyclo[4.1.0]-hepta-2,4-diene-7-carboxylate (**S2a**) was fully characterized as its carboxylic acid (**S2b**):

7-(4-bromophenyl)-2-ethyl-5-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylic acid (S2b)

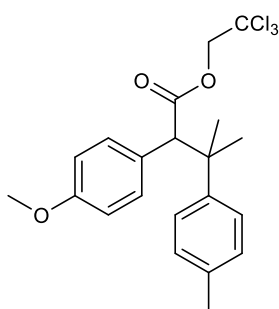


A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with the mixture of **18**, **19**, and 2,2,2-trichloroethyl 7-(4-bromophenyl)-2-ethyl-5-methylbicyclo[4.1.0]-hepta-2,4-diene-7-carboxylate (**S2a**) (84 mg, 0.181 mmol, 1 equiv.) and acetic acid (1.8 mL) to give a colourless solution. Zinc (70.9 mg, 1.09 mmol, 6.0 equiv.) was added. The reaction mixture was magnetically stirred at 600 rpm for 7 d until full consumption of starting material was evident by TLC control. The reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 15 mL). The organic layers were washed with water (20 mL) and brine (20 mL), dried over Na₂SO₄, filtered, and evaporated under reduced pressure. An aliquot of the reaction mixture was subjected to preparative HPLC

(normal phase, 0–2% *i*PrOH in hexanes) to give 7-(4-bromophenyl)-2-ethyl-5-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylic acid (**S2b**) as a white solid.

Mp: 155–157 °C; **Rf** = 0.36 (SiO₂, hexanes:EtOAc, 2:1); **¹H NMR (500 MHz, CDCl₃)**: δ 7.33 – 7.29 (m, 2H), 6.85 – 6.80 (m, 2H), 5.59 – 5.49 (m, 2H), 3.08 – 2.99 (m, 2H), 2.40 (qq, *J* = 15.3, 7.3 Hz, 2H), 2.08 (s, 3H) and 1.16 (t, *J* = 7.4 Hz, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃)**: δ 182.53 (C), 135.69 (C), 133.57 (2xCH), 131.23 (C), 130.72 (2xCH), 130.41 (C), 122.68 (CH), 121.31 (C), 120.55 (CH), 29.98 (CH₂), 25.26 (C), 23.60 (CH₂) and 12.00 (CH₃) ppm; **IR (neat)**: 2964, 2929, 2875, 1671, 1489, 1419, 1270, 1073, 907, 887, 835, 819, 731, 711 and 690 cm⁻¹; **HR-MS (NSI)** *m/z* calculated for C₁₇H₁₈O₂Br⁺ 333.04847 observed 333.04843.

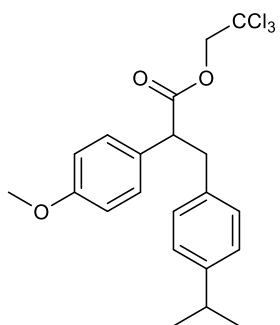
2,2,2-trichloroethyl 2-(4-methoxyphenyl)-3-methyl-3-(*p*-tolyl)butanoate^{2b} (**20**)



Starting from the corresponding aryl diazo **1d** (65 mg, 0.2 mmol) and *p*-cymene (1.5 mL, 49 equiv) and following the general procedure, the desired compound was obtained after purification by column of silica gel (hexanes:diethyl ether 98:2 to 95:5) as a colourless oil (20 mg, 24 % yield).

Rf = 0.58 (SiO₂, pentane:Et₂O, 8:2); **¹H NMR (500 MHz, CDCl₃)**: δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 3.97 (s, 1H), 3.79 (s, 3H), 2.30 (s, 3H), 1.51 (s, 3H) and 1.31 (s, 3H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.18 (C), 159.11 (C), 143.96 (C), 135.86 (C), 131.36 (2xCH), 128.83 (2xCH), 126.90 (C), 126.52 (2xCH), 113.30 (2xCH), 94.86 (CCl₃), 74.13 (CH₂), 61.68 (CH), 55.35 (CH₃), 41.16 (C), 27.21 (CH₃), 24.58 (CH₃) and 21.01 (CH₃) ppm; **IR (neat)**: 2972, 2360, 1472, 1087 and 1044 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₂₁H₂₄Cl₃O₃⁺ 429.0786 observed 429.0792.

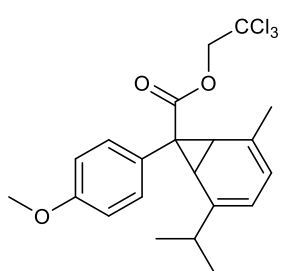
2,2,2-trichloroethyl 3-(4-isopropylphenyl)-2-(4-methoxyphenyl)propanoate (**21**)



Starting from the corresponding aryl diazo **1d** (65 mg, 0.2 mmol) and *p*-cymene (1.5 mL, 49 equiv) and following the general procedure, the desired compound was obtained after purification by column of silica gel (hexanes:diethyl ether 98:2 to 95:5) as a white solid (11 mg, 13 % yield).

Mp: 66 °C; **Rf** = 0.55 (SiO₂, pentane:Et₂O, 8:2); **¹H NMR (600 MHz, CDCl₃):** δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.08 (s, 4H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.68 (dd, *J* = 11.9, 0.7 Hz, 1H), 4.55 (dd, *J* = 11.9, 0.7 Hz, 1H), 3.94 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.78 (s, 3H), 3.39 (dd, *J* = 13.8, 9.5 Hz, 1H), 3.03 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.83 (hept, *J* = 6.9 Hz, 1H) and 1.19 (d, *J* = 6.9 Hz, 6H) ppm; **¹³C NMR (126 MHz, CDCl₃):** δ 172.05 (C), 159.05 (C), 147.09 (C), 135.89 (C), 129.88 (C), 129.15 (2xCH), 128.87 (2xCH), 126.45 (2xCH), 114.04 (2xCH), 94.76 (CCl₃), 74.01 (CH₂), 55.28 (CH₃), 52.65 (CH), 39.17 (CH₂), 33.70 (CH) and 24.02 (2xCH₃) ppm; **IR (neat):** 2959, 2360, 2342, 1751, 1611, 1520, 1458, 1252, 1134, 1036, 824, 791 and 721 cm⁻¹; **HR-MS (NSI)** *m/z* calculated for C₂₁H₂₂Cl₃O₃⁻ 427.0640 observed 427.06502.

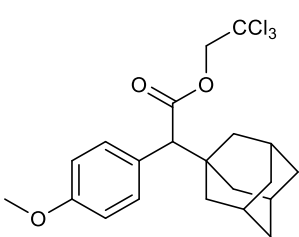
2,2,2-trichloroethyl 2-isopropyl-7-(4-methoxyphenyl)-5-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (S3)



Starting from the corresponding aryl diazo **1d** (65 mg, 0.2 mmol) and p-cymene (1.5 mL, 49 equiv) and following the general procedure, the desired compound was obtained after purification by column of silica gel (hexanes:diethyl ether 98:2 to 95:5) as a colourless oil (29 mg, 34 % yield).

Rf = 0.50 (SiO₂, pentane:Et₂O, 8:2); **¹H NMR (600 MHz, CDCl₃):** δ 6.99 – 6.91 (m, 2H), 6.75 – 6.69 (m, 2H), 5.65 – 5.50 (m, 2H), 4.78 – 4.68 (m, 2H), 3.76 (s, 3H), 3.21 (d, *J* = 8.9 Hz, 1H), 3.09 (d, *J* = 8.9 Hz, 1H), 2.65 (hept, *J* = 6.8 Hz, 1H), 2.10 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H) and 1.18 (d, *J* = 6.9 Hz, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃):** δ 175.79 (C), 158.41 (C), 139.75 (C), 133.13 (2xCH), 130.66 (C), 123.98 (C), 122.81 (CH), 119.28 (CH), 112.67 (2xCH), 95.23 (CCl₃), 74.38 (CH₂), 55.02 (CH₃), 34.51 (CH), 23.62 (CH₃), 21.85 (CH₃) and 21.25 (CH₃); **IR (neat):** 2959, 1721, 1613, 1515, 1245, 1220, 1173, 1151, 1106, 1034, 942, 829, 807 and 722 cm⁻¹; **HR-MS (NSI)** *m/z* calculated for C₂₁H₂₂Cl₃O₃⁻ 427.06290 observed 427.06290.

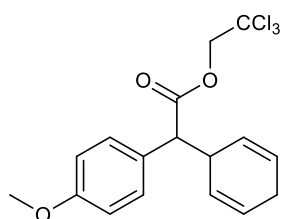
2,2,2-trichloroethyl 2-((1s,3s)-adamantan-1-yl)-2-(4-methoxyphenyl)acetate (22)



Starting from the corresponding aryl diazo **1d** (64.7 mg, 0.2 mmol) and adamantane (27.2 mg, 0.2 mmol) in hexafluorobenzene (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (14 mg, 16 % yield).

Rf = 0.70 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.80 (s, 3H), 3.37 (s, 1H), 1.96 (s, 3H), 1.77-1.61 (m, 6H) and 1.57-1.54 (d, *J* = 12.3 Hz, 6H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.39 (C), 159.00 (C), 131.35 (2xCH), 126.14 (C), 113.27 (2xCH), 95.08 (CCl₃), 74.24 (CH₂), 62.35 (CH₃), 55.35 (CH), 39.95 (3xCH₂), 36.81 (3xCH₂), 36.56 (C) and 28.68 (3xCH) ppm; **IR (neat)**: 2904, 1746, 1510, 1249 and 1118 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₂₁H₂₆Cl₃O₃⁺ 431.0942 observed 431.0947.

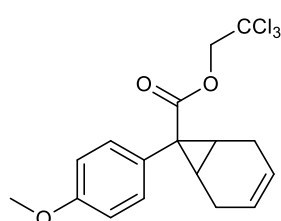
2,2,2-trichloroethyl 2-(cyclohexa-2,5-dien-1-yl)-2-(4-methoxyphenyl) (23)



Starting from the corresponding aryl diazo **1d** (41 mg, 0.2 mmol) and 1,4-cyclohexadiene (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (22 mg, 30 % yield).

Rf = 0.73 (SiO₂, pentane:Et₂O, 8:2); **¹H NMR (500 MHz, CDCl₃)**: δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.86-5.64 (m, 3H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 3.80 (s, 3H), 3.52 (s, 2H) and 2.63-2.61 (m, 2H) ppm; **¹³C NMR (126 MHz, CDCl₃)**: δ 171.62 (C), 159.22 (C), 129.93 (2xCH), 127.99 (C), 126.71 (CH), 126.38 (CH), 126.31 (CH), 125.62 (CH), 114.09 (2xCH), 94.98 (CCl₃), 74.21 (CH₂), 57.52 (CH), 55.39 (CH₃), 38.39 (CH) and 26.54 (CH₂) ppm; **IR (neat)**: 2919, 1750, 1598, 1512, 1251 and 1156 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₇H₁₈Cl₃O₃⁺ 375.0316 observed 375.0320.

2,2,2-trichloroethyl 7-(4-methoxyphenyl)bicyclo[4.1.0]hept-3-ene-7-carboxylate (24)

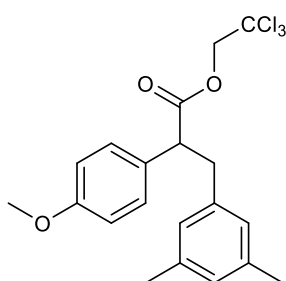


Starting from the corresponding aryl diazo **1d** (41 mg, 0.2 mmol) and 1,4-cyclohexadiene (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (18 mg, 24 % yield).

Rf = 0.58 (SiO₂, pentane:Et₂O, 8:2); **¹H NMR (500 MHz, CDCl₃)**: δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.06 (s, 2H), 4.62 (s, 2H), 3.79 (s, 3H), 2.59-2.40 (m, 4H) and 2.26-2.21 (m, 2H) ppm; **¹³C NMR (126 MHz, CDCl₃)**: δ 173.48 (C), 158.81 (C), 131.24 (2xC), 125.60 (C), 123.29 (2xCH), 113.61 (2xCH), 74.44 (CH₂), 55.23 (OCH₃), 29.86 (C), 25.63 (2xCH) and 21.12 (2xCH₂) ppm (note: the resonance resulting from the CCl₃ carbon was not observed); **IR (neat)**:

2954, 1652 and 1540 cm^{-1} ; **HR-MS (EI)** m/z calculated for $\text{C}_{17}\text{H}_{18}\text{Cl}_3\text{O}_3^+$ 375.0316 observed 375.0321.

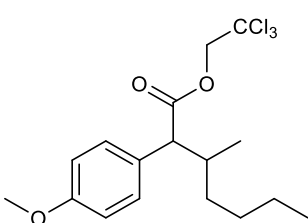
2,2,2-trichloroethyl 3-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)propanoate (25)



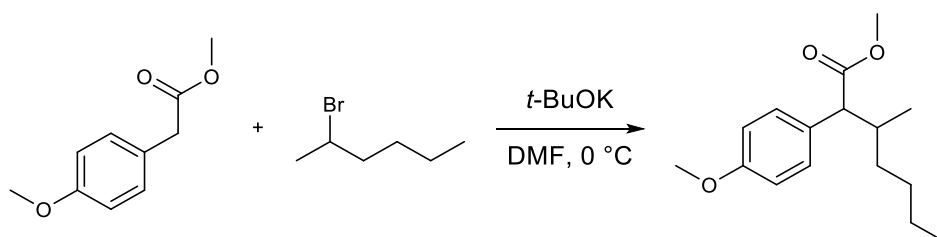
Starting from the corresponding aryl diazo **1b** (65 mg, 0.2 mmol) and mesitylene (139 μL , 5 equiv) in hexafluorobenzene (1.5 mL) and following the general procedure, the desired compound was obtained after purification by preparative TLC over silica gel (pentane:diethyl ether 95:5) as a colourless oil (13 mg, 16 % yield).

R_f = 0.45 (SiO_2 , pentane: Et_2O , 9:1); **^1H NMR (500 MHz, CDCl_3)**: 7.30 (d, J = 8.7 Hz, 2H), 6.91-6.77 (m, 5H), 4.69 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 3.96 (dd, J = 9.6 and 6.1 Hz, 1H), 3.80 (s, 3H), 3.37 (dd, J = 13.8 and 9.6 Hz, 1H), 2.99 (dd, J = 13.8 and 6.0 Hz, 1H) and 2.25 (s, 6H) ppm; **^{13}C NMR (126 MHz, CDCl_3)**: δ 172.19 (C), 159.19 (C), 138.62 (C), 137.96 (2xC), 130.12, 130.09, 129.59, 129.28 (CH), 128.29, 126.87 (CH), 114.18 (2xCH), 94.94 (CCl_3), 74.21 (CH_2), 55.43 (OCH_3), 52.64 (CH), 39.51 (CH_2), 21.38 (CH_3) and 21.06 (CH_3) ppm; **IR (neat)**: 2953, 1751, 1511, 1250 and 1131 cm^{-1} ; **HR-MS (EI)** m/z calculated for $\text{C}_{20}\text{H}_{22}\text{Cl}_3\text{O}_3^+$ 415.0629 observed 415.0638.

2,2,2-trichloroethyl 2-(4-methoxyphenyl)-3-methylheptanoate (28)

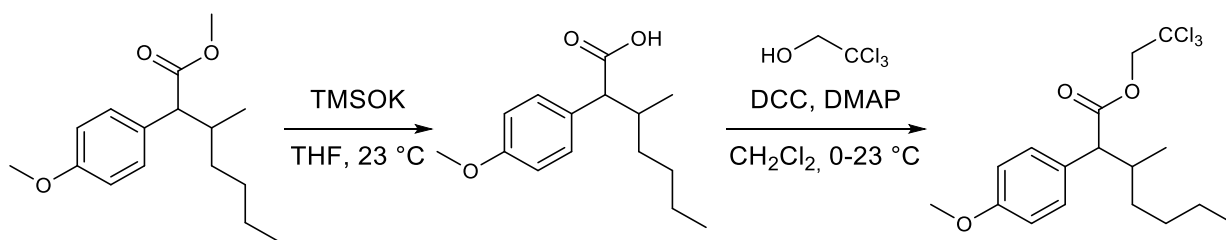


Starting from the corresponding aryl diazo **1d** (64.7 mg, 0.2 mmol) and n-hexane (1.5 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (21.1 mg, 30 % yield). The product is obtained as a 2:1 mixture of two diastereoisomers that could not be separated from the product **13** derived from an insertion into the C3. In order to characterize it, product **12** was prepared by $\text{S}_{\text{N}}2$, according to the following procedure:



Methyl 2-(4-methoxyphenyl)-3-methylheptanoate (S4): potassium *tert*-butoxide (1.2 equiv, 0.72 mmol, 81 mg) was suspended in DMF (1 mL) at 0 °C under argon. Methyl 2-(4-methoxyphenyl)acetate (1 equiv, 0.6 mmol, 108 mg) was added followed, after 10 min, by 2-bromohexane (1.2 equiv, 0.72 mmol, 119 mg, 100 μ L). The reaction mixture was allowed to warm up to 23 °C and it was stirred for 1 h. After quenching with water, the product was extracted with CH_2Cl_2 . Collected organic phase was washed with $\text{NH}_4\text{Cl}_{\text{aq}}$ and water and dried over MgSO_4 . The crude obtained was purified by column chromatography over SiO_2 (eluent: pentane/ Et_2O = 9/1) to give the desired product as a colorless oil in 50% yield. The product was obtained as an inseparable 1:1 mixture of two diastereoisomers.

R_f = 0.67 (SiO_2 , pentane: Et_2O , 8:2); **^1H NMR (500 MHz, CDCl_3):** δ 7.24 (two overlapped d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.79 (d, J = 1.5 Hz, 3H), 3.64 (d, J = 1.3 Hz, 3H), 3.20 (two overlapped d, J = 10.6 Hz, 1H), 2.23-2.10 (m, 1H), 1.47-1.03 (m, 6H) and 1.02-0.60 (m, 7H) ppm; **^{13}C NMR (126 MHz, CDCl_3):** δ 174.95 (C), 158.86 (C), 158.85 (C), 130.44, 130.37 (C), 129.76 (C), 129.69 (2xCH), 129.65 (2xCH), 113.95 (2xCH), 113.93 (2xCH), 58.00 (CH), 57.98 (CH), 55.32 (OCH_3), 51.79 (OCH_3), 51.77 (OCH_3), 36.52 (CH_2), 36.37 (CH_2), 35.17 (CH), 33.10 (CH), 29.14 (CH_2), 28.67 (CH_2), 22.97 (CH_2), 22.77 (CH_2), 18.00 (CH_3), 16.82 (CH_3), 14.18 (CH_3) and 14.12 (CH_3) ppm; **IR (neat):** 2955, 1732, 1511, 1247 and 1159 cm^{-1} ; **HR-MS (EI) m/z** calculated for $\text{C}_{16}\text{H}_{25}\text{O}_3^+$ 265.1798 observed 265.1799.

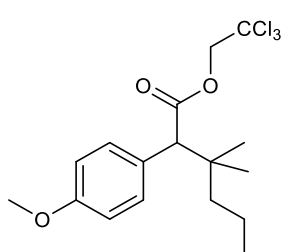


2,2,2-trichloroethyl 2-(4-methoxyphenyl)-3-methylheptanoate (28): Methyl 2-(4-methoxyphenyl)-3-methylheptanoate (**S4**) (1 equiv, 0.28 mmol, 74 mg) was dissolved in THF (3 mL) and TMSOK (10 equiv, 2.8 mmol) was added. The mixture was stirred at 23 °C for 48 h then citric acid (2 mL) was added. The biphasic mixture was stirred for 1 h then the product was extracted with Et_2O . The acid obtained was used in the following step without further purification. It was dissolved in CH_2Cl_2 (1 mL) and 2,2,2-trichloroethyl alcohol (1.2 equiv, 0.33 mmol, 50 mg, 32 μ L) was added, followed by DMAP (0.3 equiv, 0.08 mmol, 10 mg). The mixture was cooled to 0 °C before the addition of a solution of DCC (1.1 equiv, 0.3 mmol, 63 mg) in CH_2Cl_2 (1 mL). The resulting mixture was stirred at 23 °C. After 15 h, the solid was filtered and the mixture was

purified by column chromatography over SiO₂ (eluent: pentane/Et₂O = 9/1) to give the desired product **12** as a colorless oil. The product was obtained as a 1:1.5 mixture of two diastereoisomers.

Rf = 0.70 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (500 MHz, CDCl₃)**: δ 7.23 (m, 1H), 6.93 (m, 2H), 6.81 (two overlapped d, *J* = 8.2 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.62 (two overlapped d, *J* = 12.0 Hz, 1H), 3.80 (s, 3H), 3.41-3.33 (m, 1H), 2.39-2.11 (m, 1H), 2.00-1.85 (m, 0.6H), 1.74 (m, 0.6H), 1.57-1.09 (m, 7H), 1.05 (d, *J* = 6.5 Hz, 1.2H), 1.00-0.73 (m, 3H) and 0.72 (d, *J* = 6.7 Hz, 1.8H) ppm; **¹³C NMR (126 MHz, CDCl₃)**: δ 172.33 (C), 172.27 (C), 159.81 (C), 159.80 (C), 138.93 (C), 138.85 (C), 129.56 (2xCH), 121.39 (2xCH), 121.37 (2xCH), 114.44 (2xCH), 114.41 (2xCH), 113.09 (2xCH), 113.06 (2xCH), 113.02 (2xCH), 95.05 (CCL₃), 95.03 (CCL₃), 74.24 (CH₂), 74.23 (CH₂), 58.91 (CH), 58.85 (CH), 55.35 (OCH₃), 36.33 (CH₂), 36.13 (CH₂), 35.16 (CH₂), 35.06 (CH₂), 33.09 (CH₂), 29.03 (CH₂), 28.65 (CH₂), 25.60 (CH₂), 24.84 (CH₂), 23.01 (CH₂), 22.76 (CH₂), 18.00 (CH₃), 16.80 (CH₃), 14.21 (CH₃) and 14.13 (CH₃) ppm; **IR (neat)**: 2931, 1748, 1511, 1249 and 1119 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₇H₂₂Cl₃O₃⁻ 379.0640 observed 379.0642.

2,2,2-trichloroethyl 2-(4-methoxyphenyl)-3,3-dimethylhexanoate (**30**)



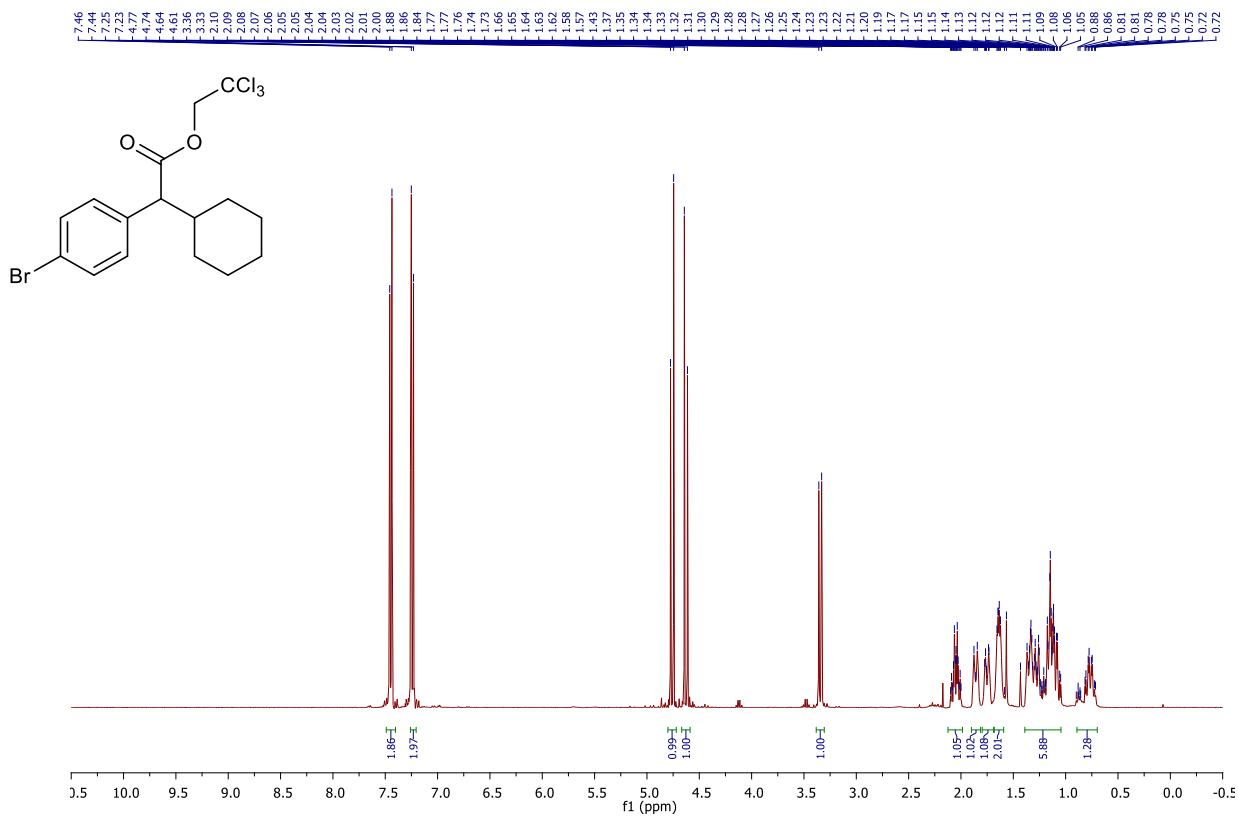
Starting from the corresponding aryl diazo **1d** (65.9 mg, 0.32 mmol) and 2-methylpentane (2 mL) and following the general procedure, the desired compound was obtained after purification by column of silica gel (pentane:diethyl ether 95:5) as a colourless oil (22.1 mg, 18 % yield).

Rf = 0.73 (SiO₂, pentane:Et₂O, 9:1); **¹H NMR (400 MHz, CDCl₃)**: δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 3.80 (s, 3H), 3.61 (s, 1H), 1.38-1.31 (m, 3H), 1.27-1.18 (m, 1H), 1.04 (s, 3H), 0.92 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm; **¹³C NMR (100 MHz, CDCl₃)**: δ 171.84 (C), 159.03 (C), 131.35 (2xCH), 127.37 (C), 113.39 (2xCH), 95.07 (CCL₃), 74.19 (CH₂), 59.60 (CH), 55.36 (CH₃), 43.25 (CH₂), 37.46 (C), 24.74 (CH₃), 24.42 (CH₃), 17.20 (CH₂) and 14.98 (CH₃) ppm; **IR (neat)**: 2958, 1748, 1511, 1249 and 1117 cm⁻¹; **HR-MS (EI)** *m/z* calculated for C₁₇H₂₄Cl₃O₃⁺ 381.0786 observed 381.0789.

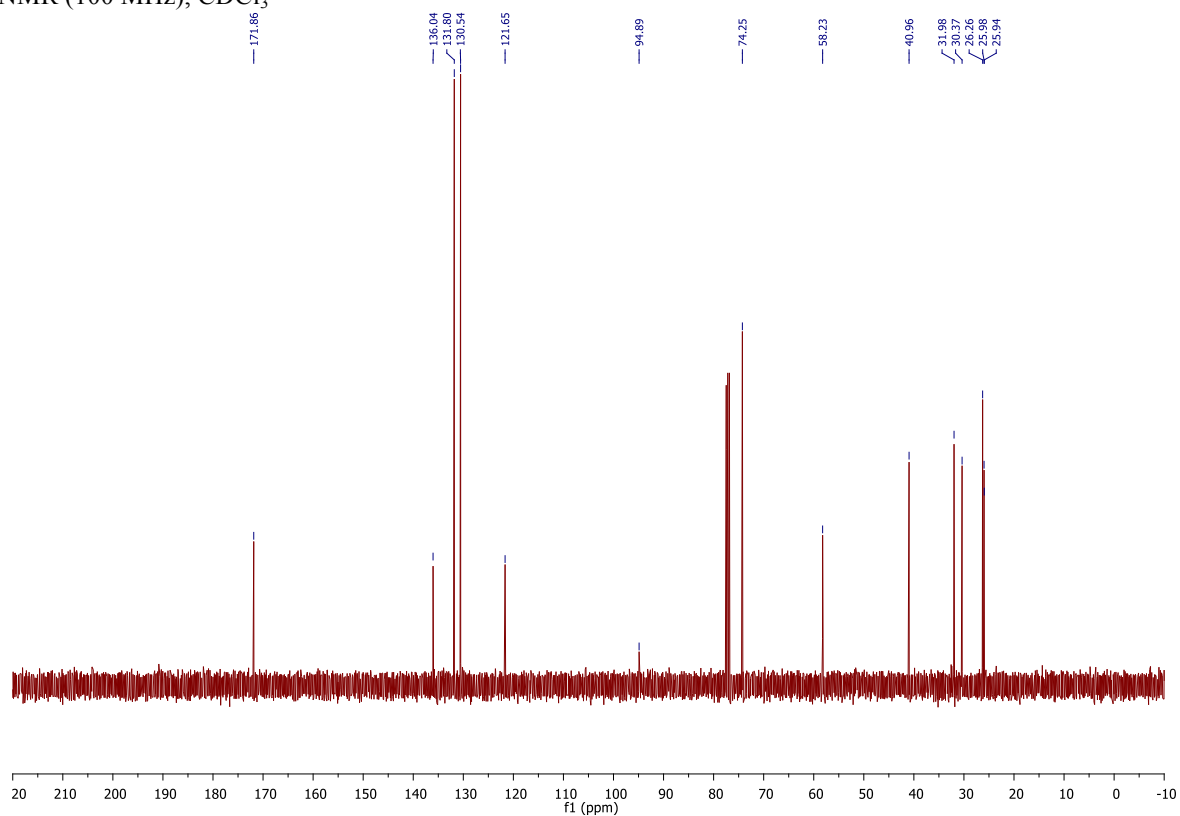
7. ^1H NMR and ^{13}C -NMR spectra of all novel compounds

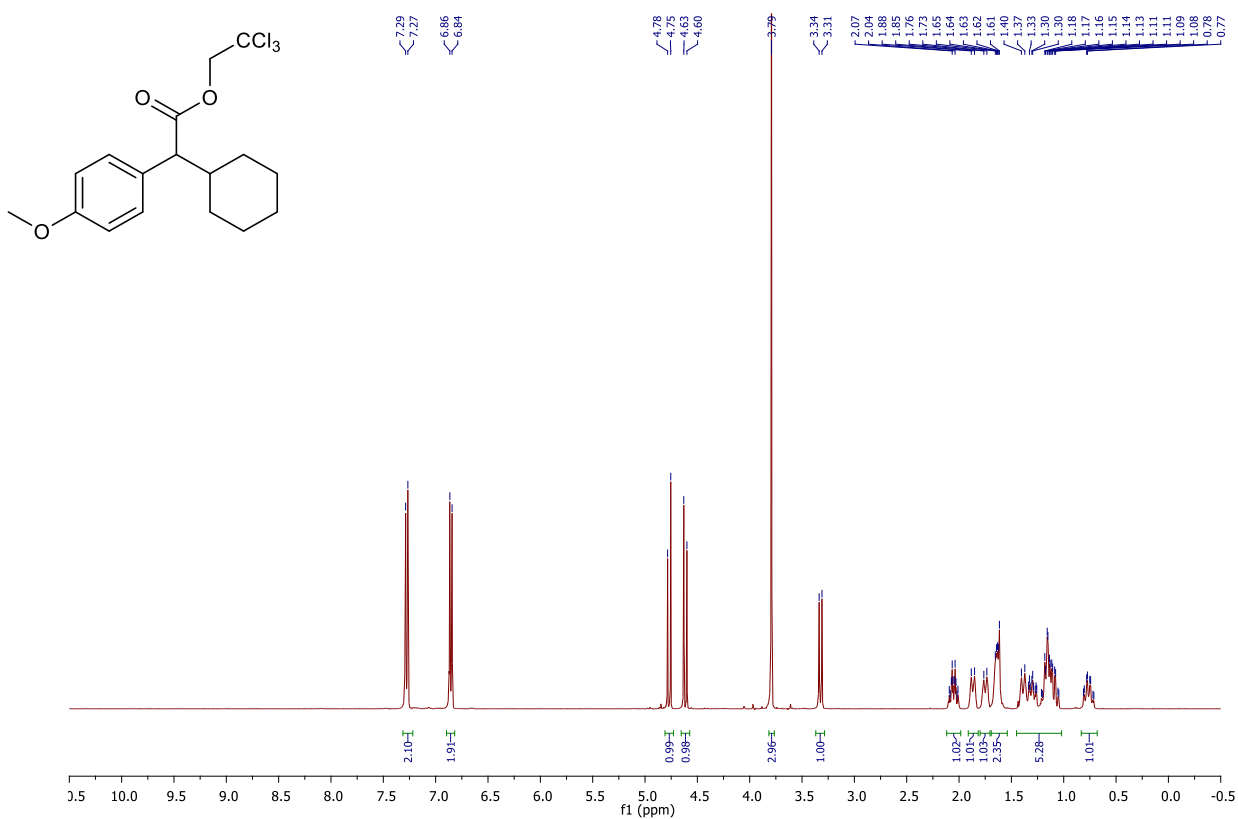
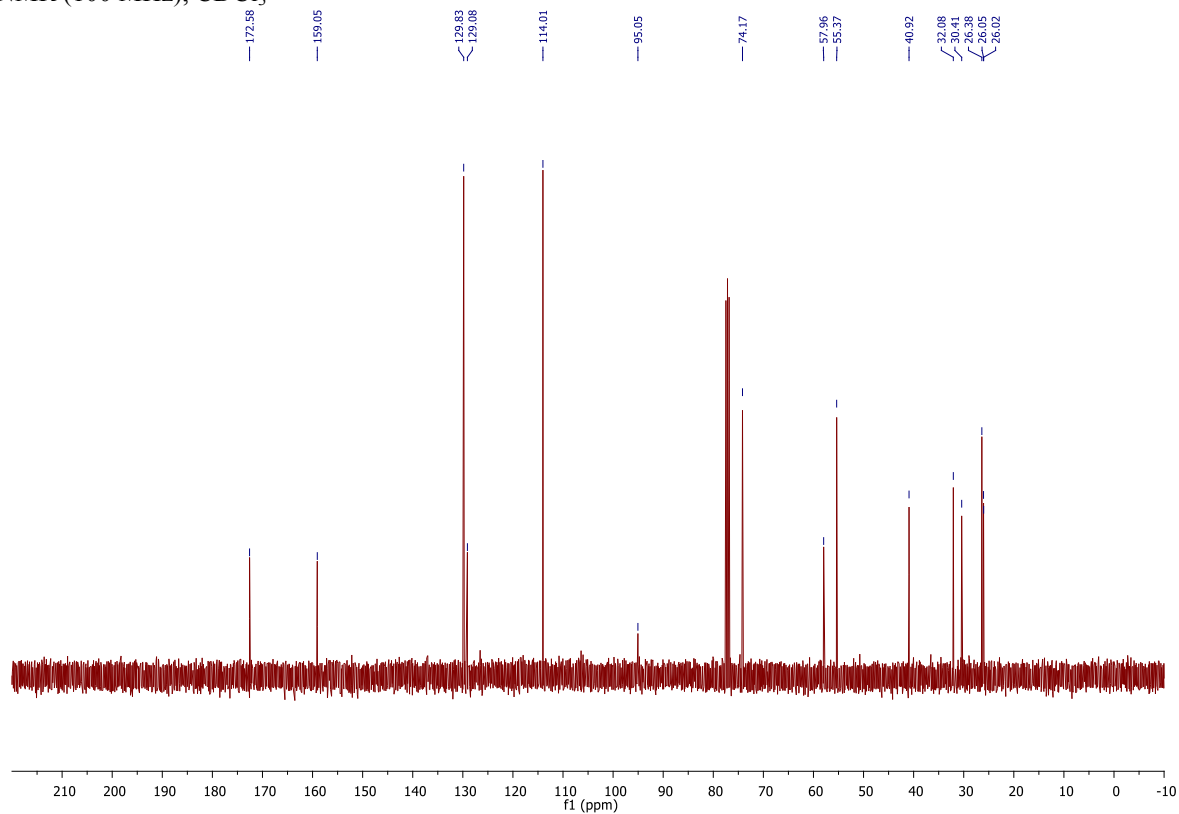
Adduct 2b

^1H NMR (400 MHz), CDCl_3



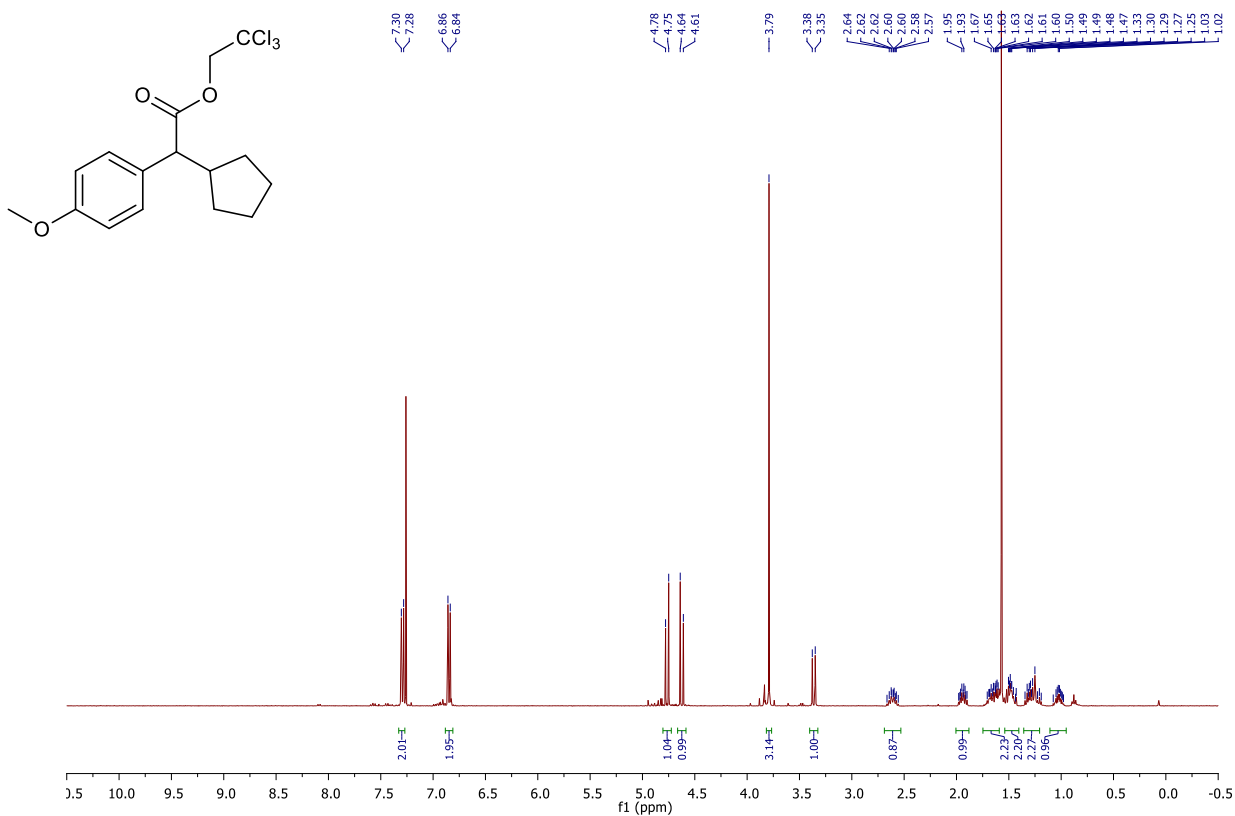
^{13}C NMR (100 MHz), CDCl_3



Adduct 2d¹H NMR (400 MHz), CDCl₃¹³C NMR (100 MHz), CDCl₃

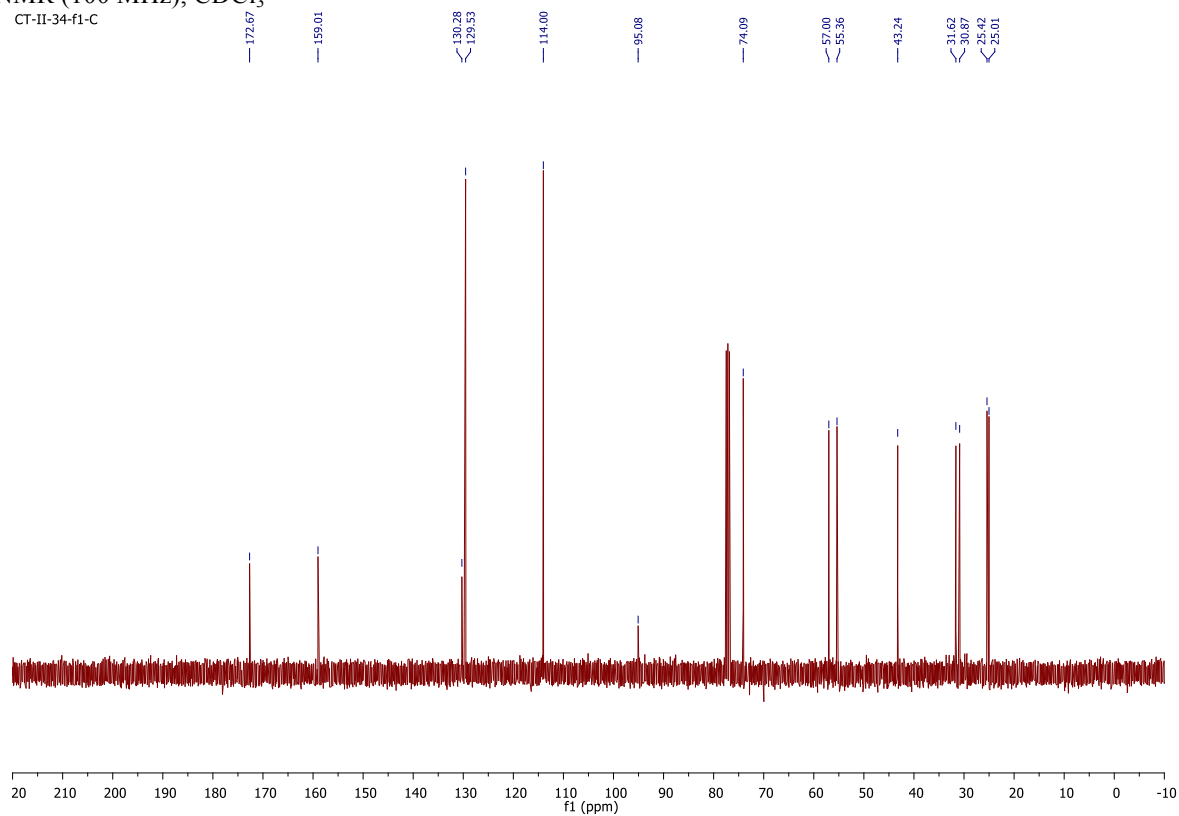
Adduct 4

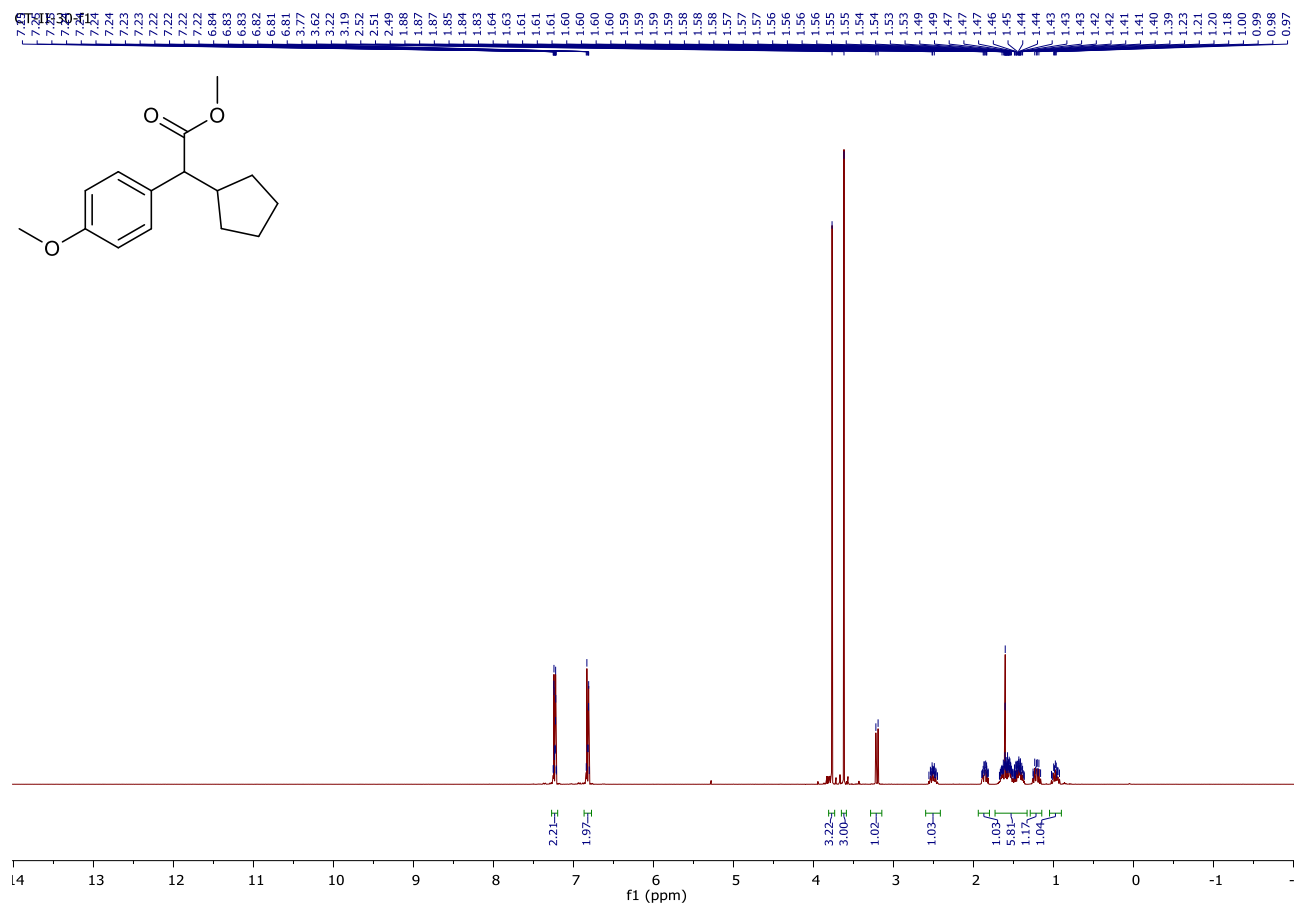
^1H NMR (400 MHz), CDCl_3



^{13}C NMR (100 MHz), CDCl_3

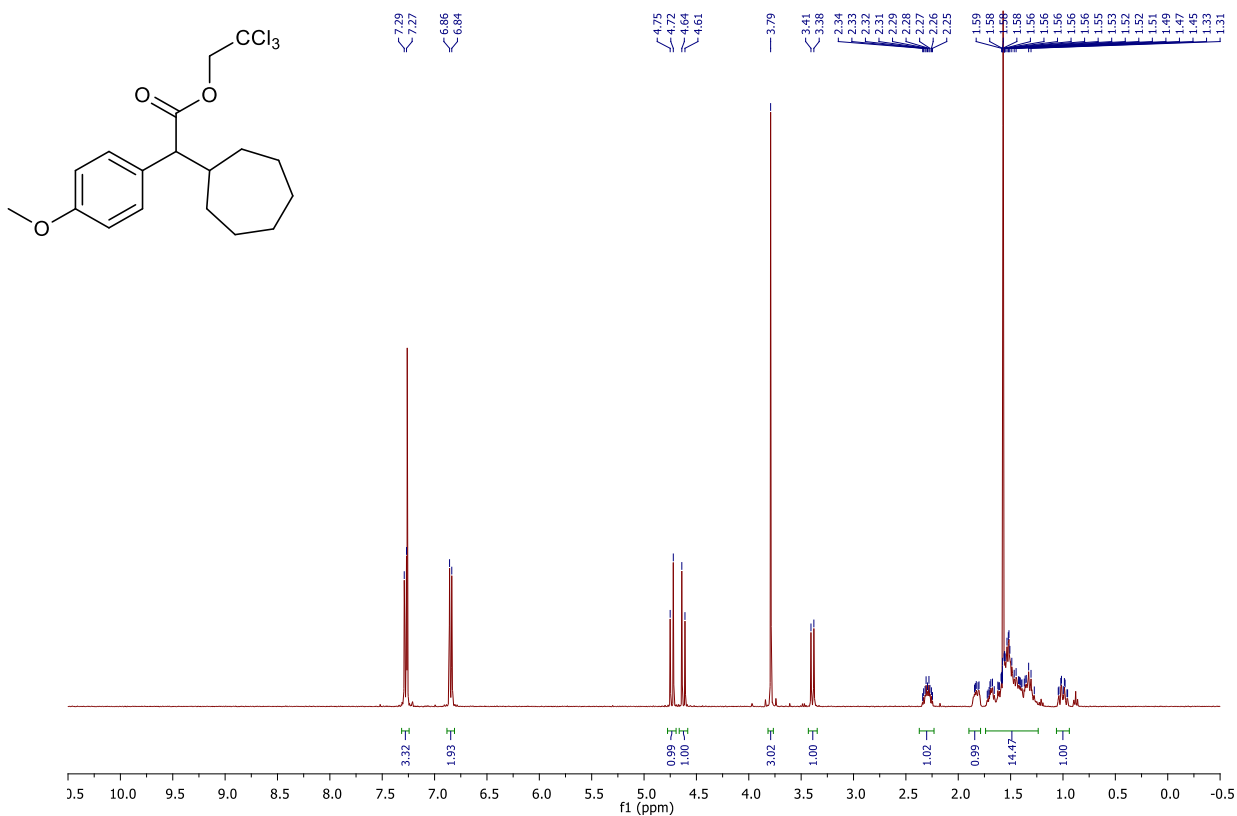
CT-II-34-f1-C



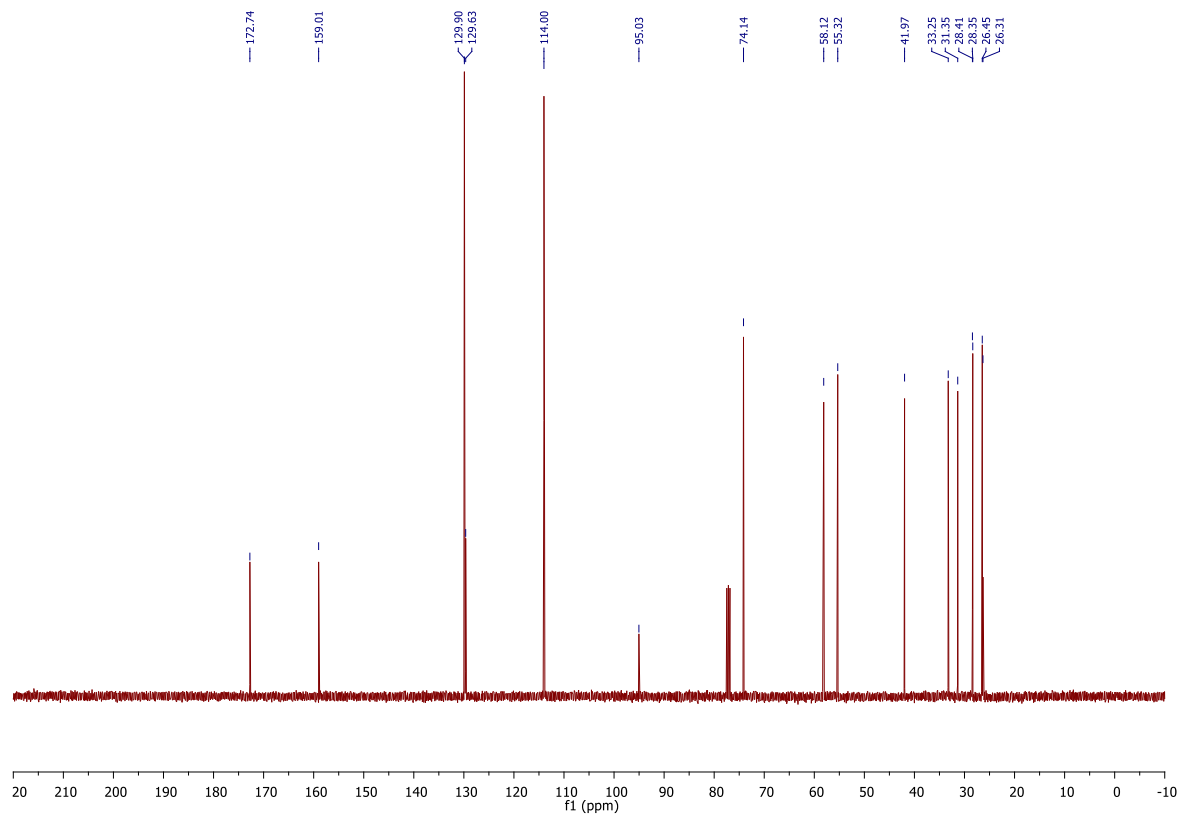
¹H NMR (400 MHz), CDCl₃

Adduct 6

^1H NMR (400 MHz), CDCl_3

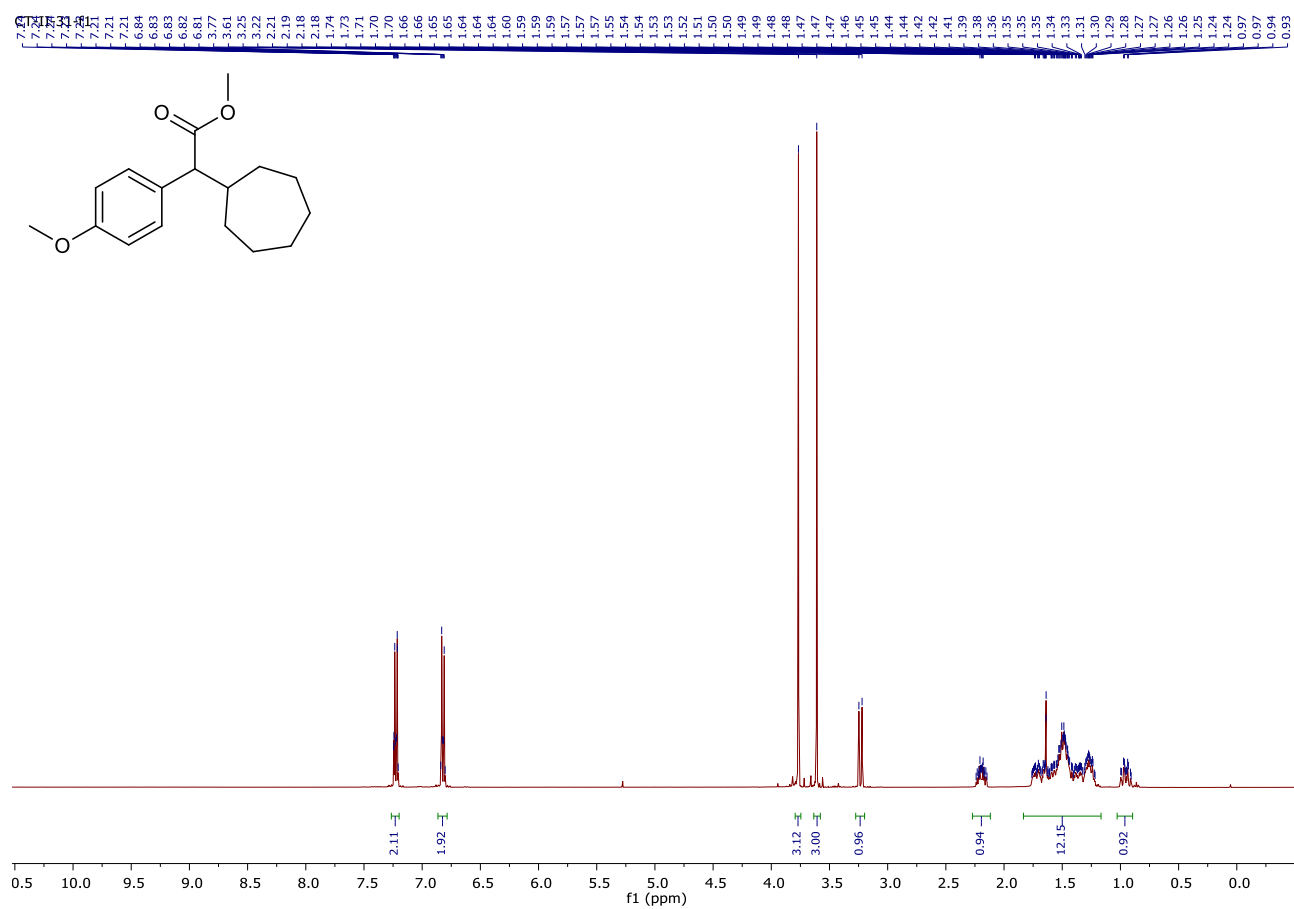


^{13}C NMR (100 MHz), CDCl_3



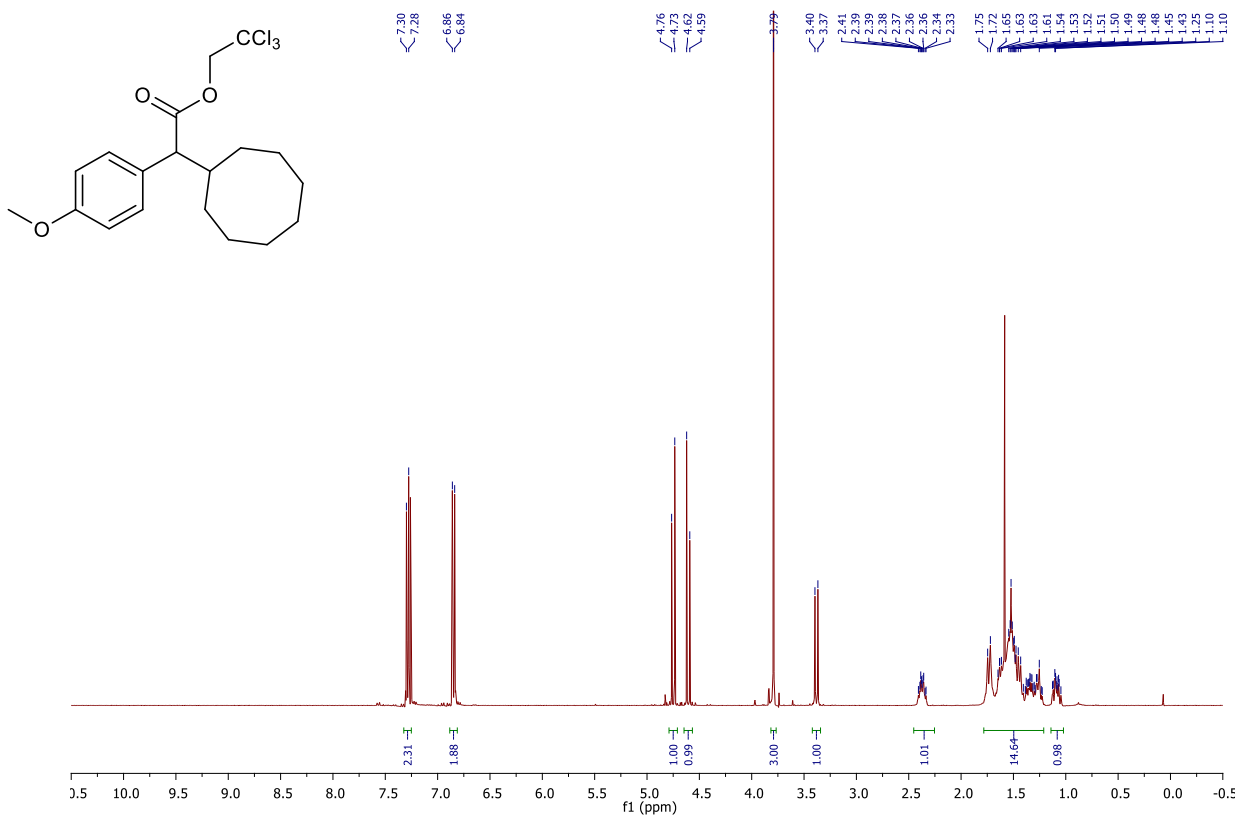
Adduct 7

^1H NMR (400 MHz), CDCl_3

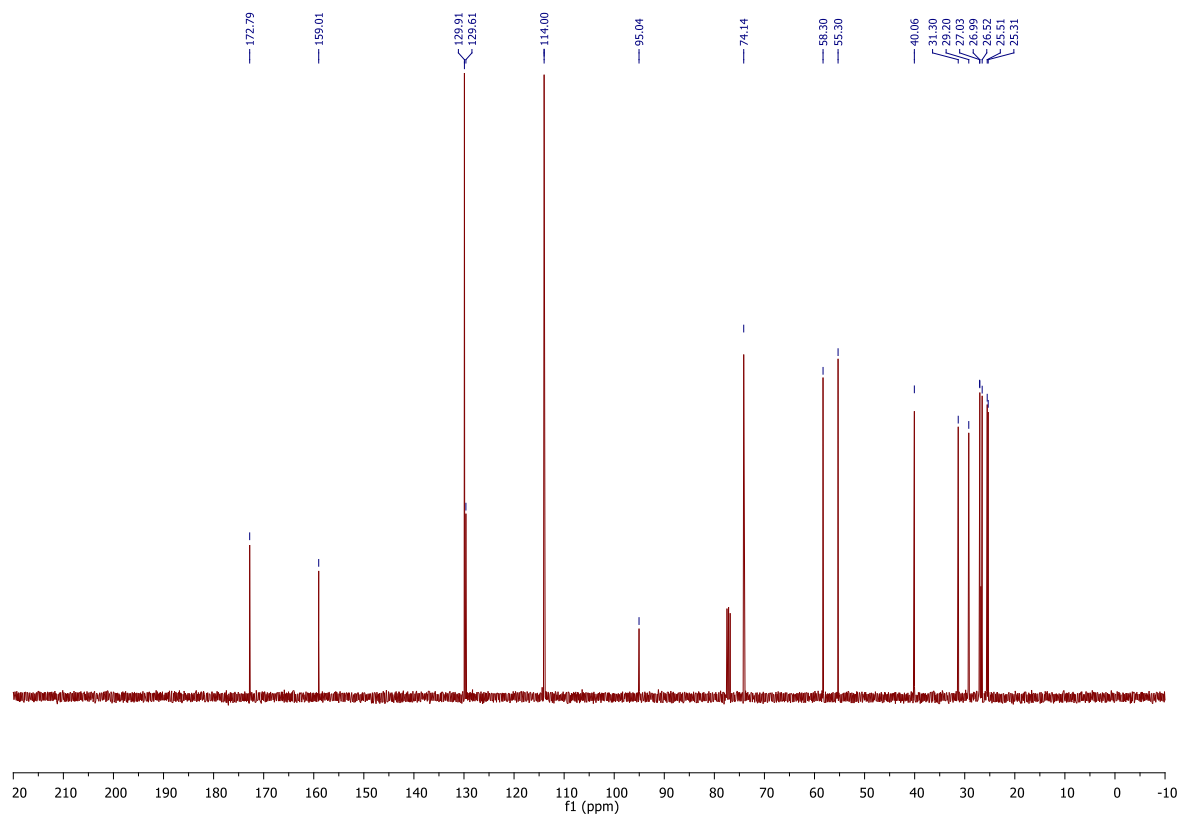


Adduct 8

^1H NMR (400 MHz), CDCl_3

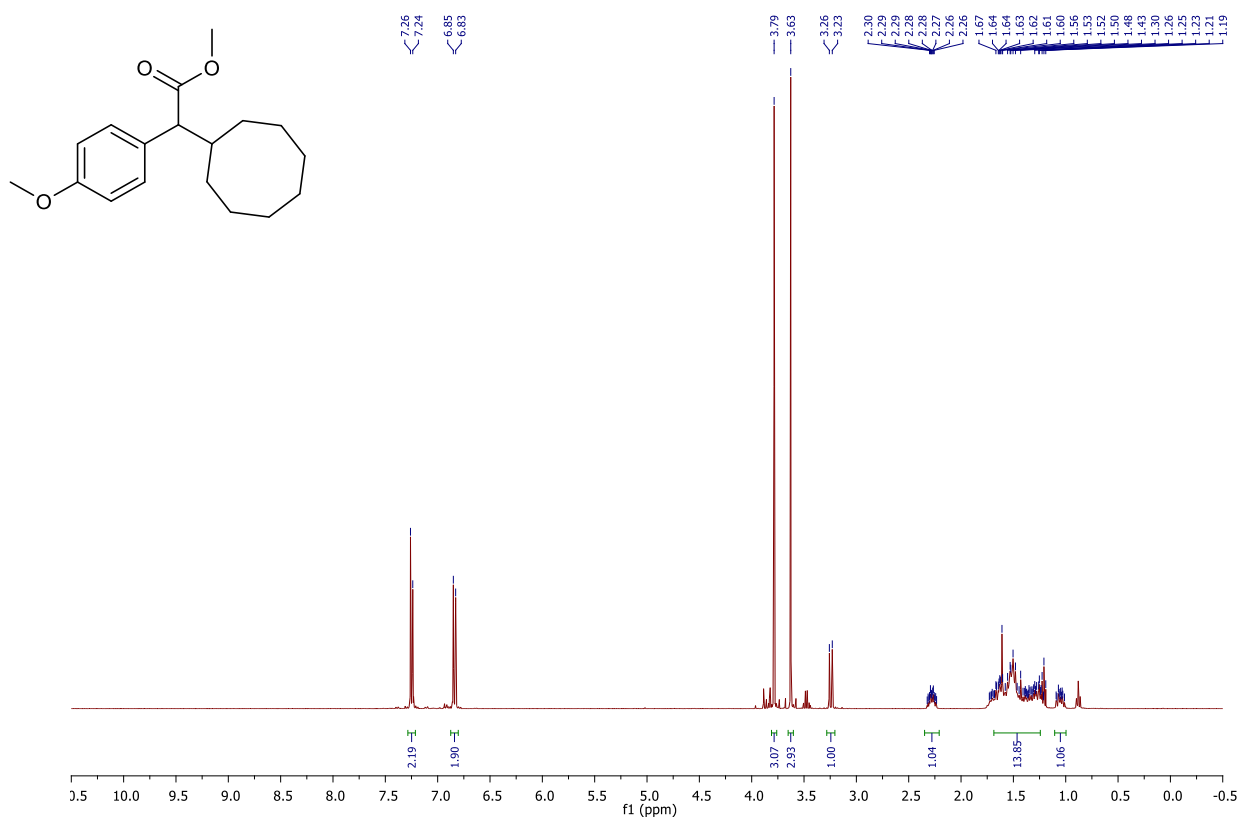


^{13}C NMR (100 MHz), CDCl_3

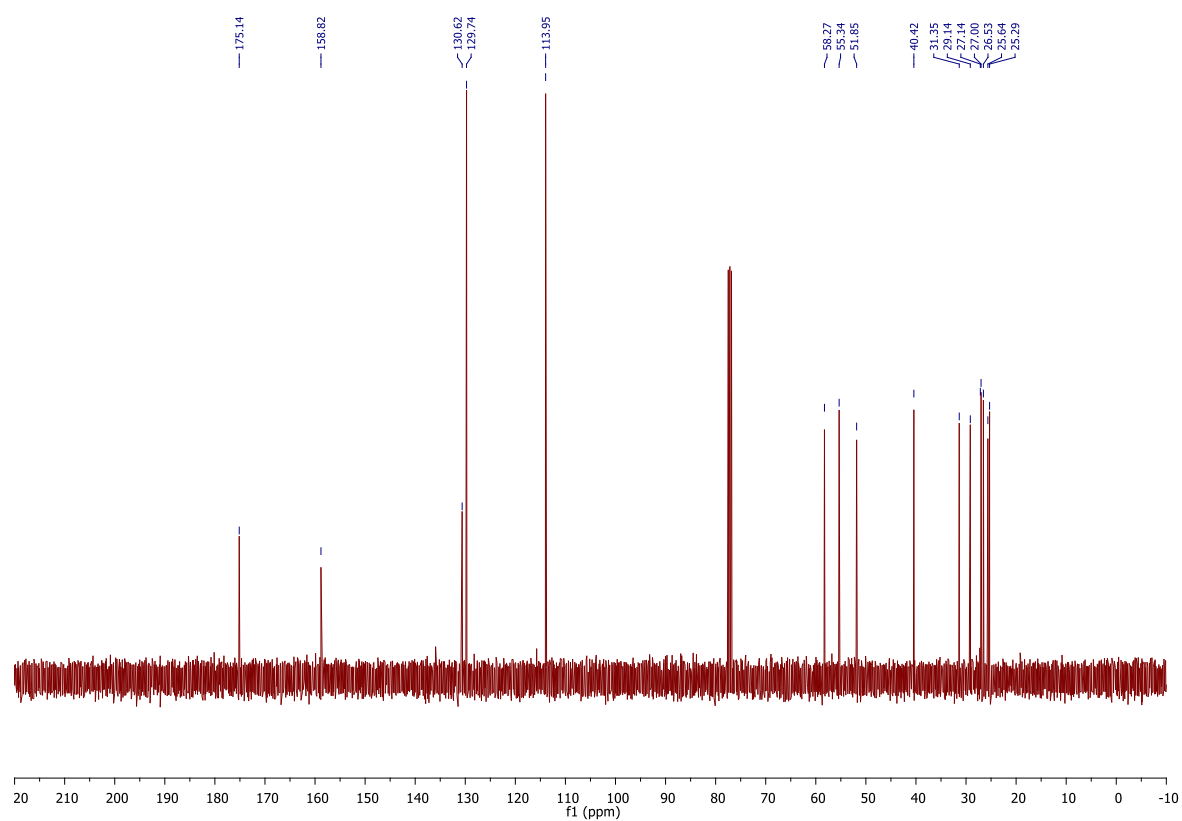


Adduct 9

^1H NMR (400 MHz), CDCl_3

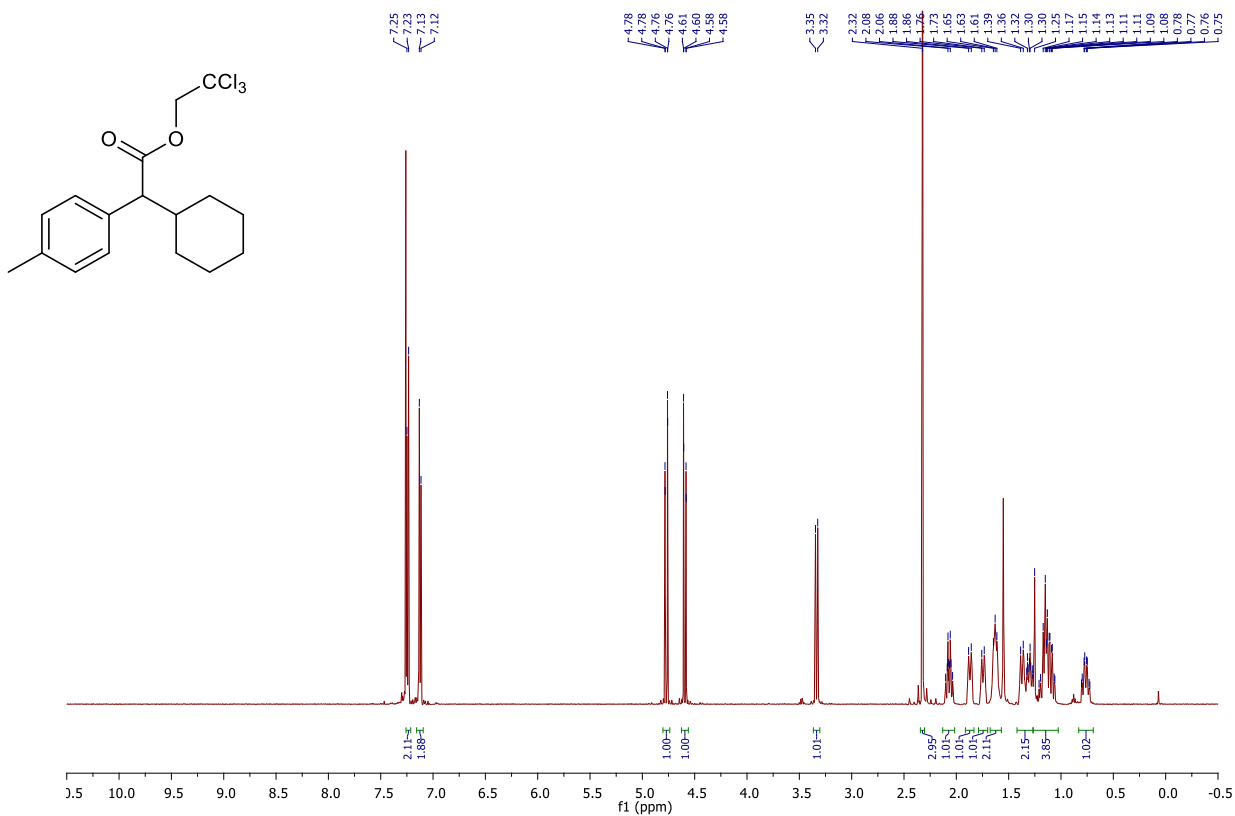


^{13}C NMR (100 MHz), CDCl_3

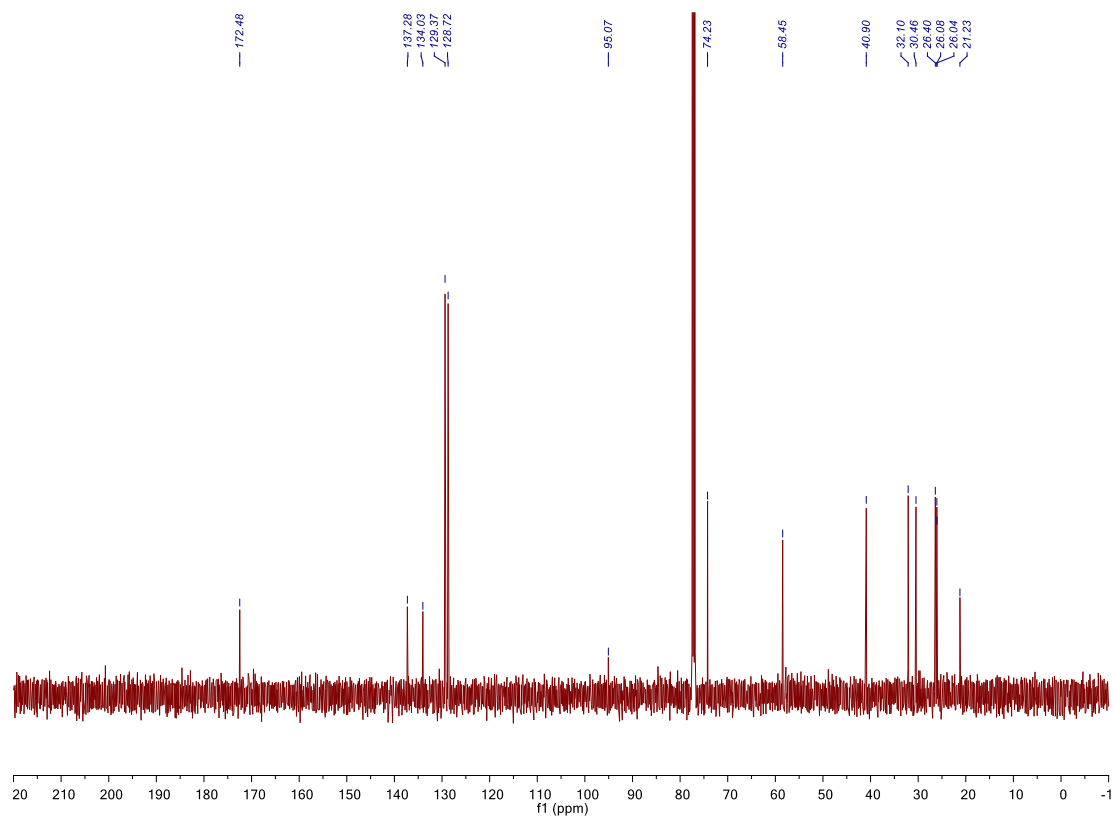


Adduct 10

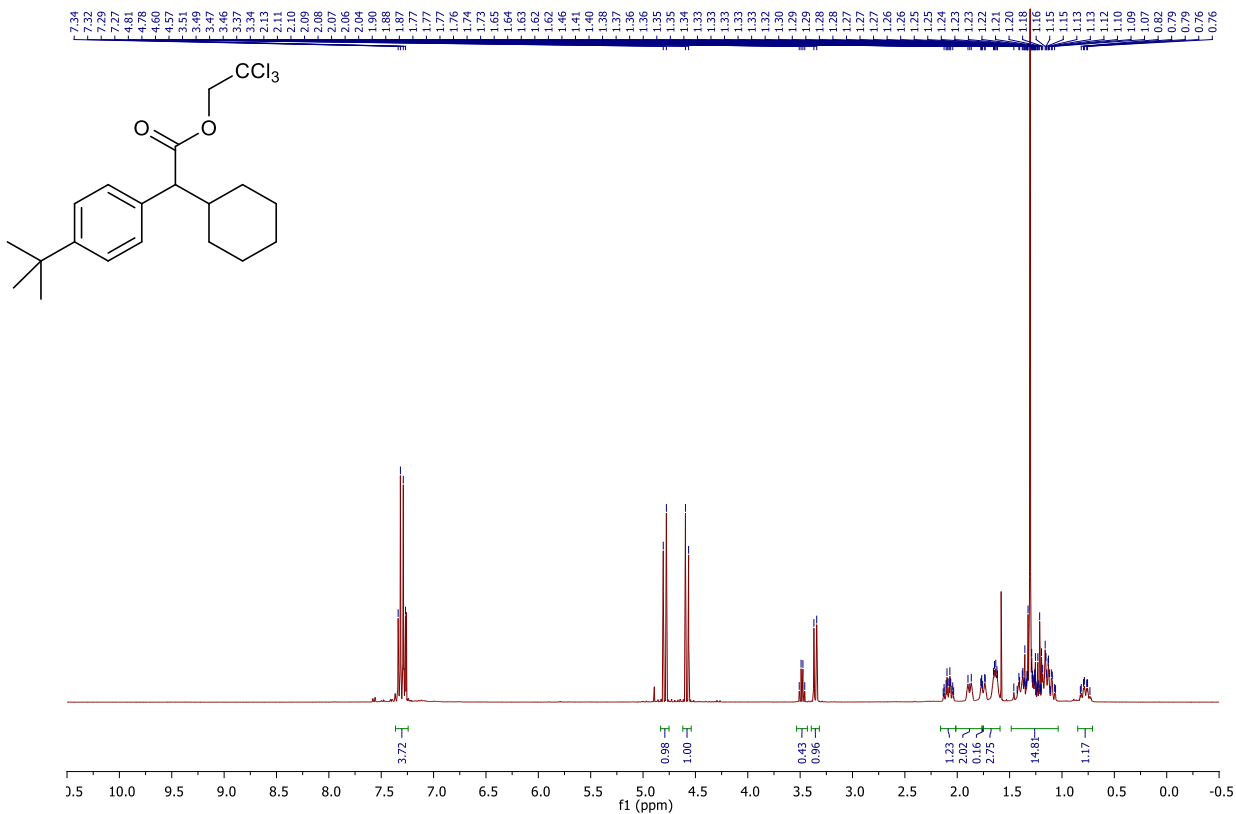
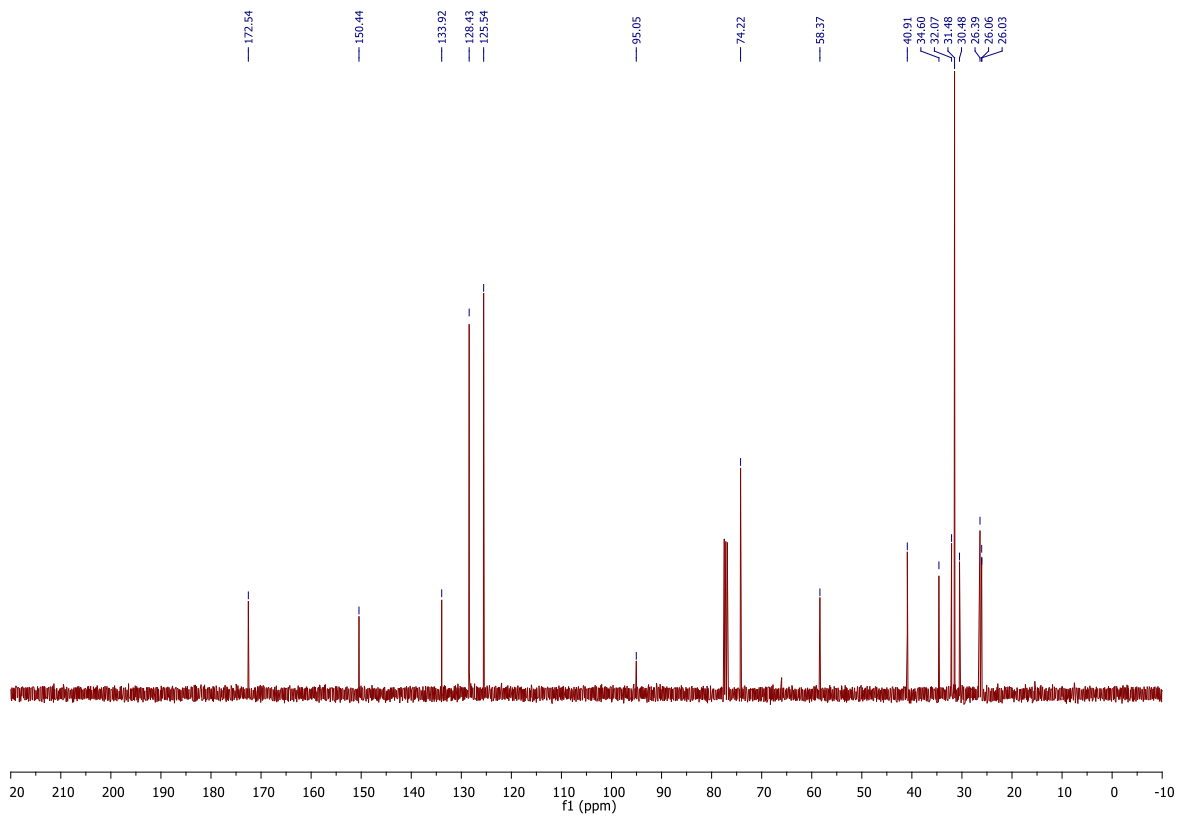
^1H NMR (500 MHz), CDCl_3



^{13}C NMR (126 MHz), CDCl_3

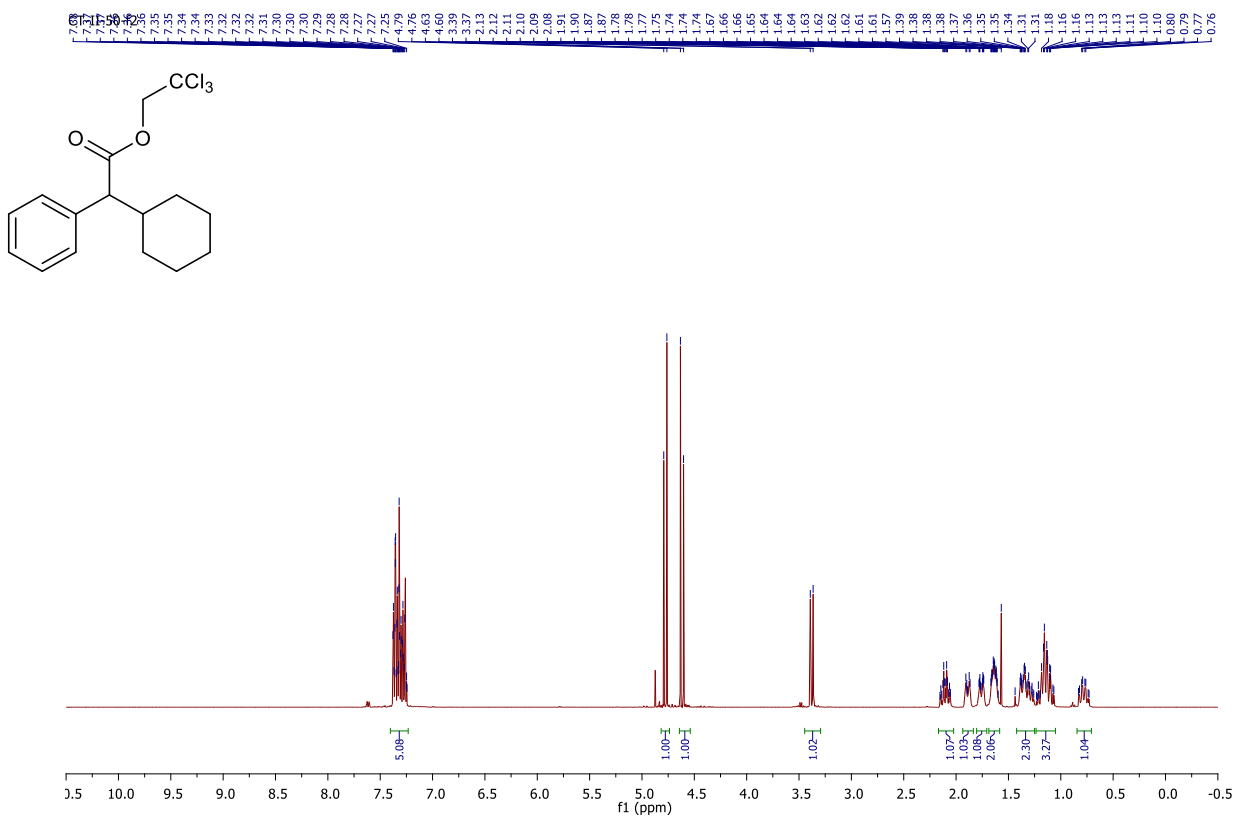


Adduct 11

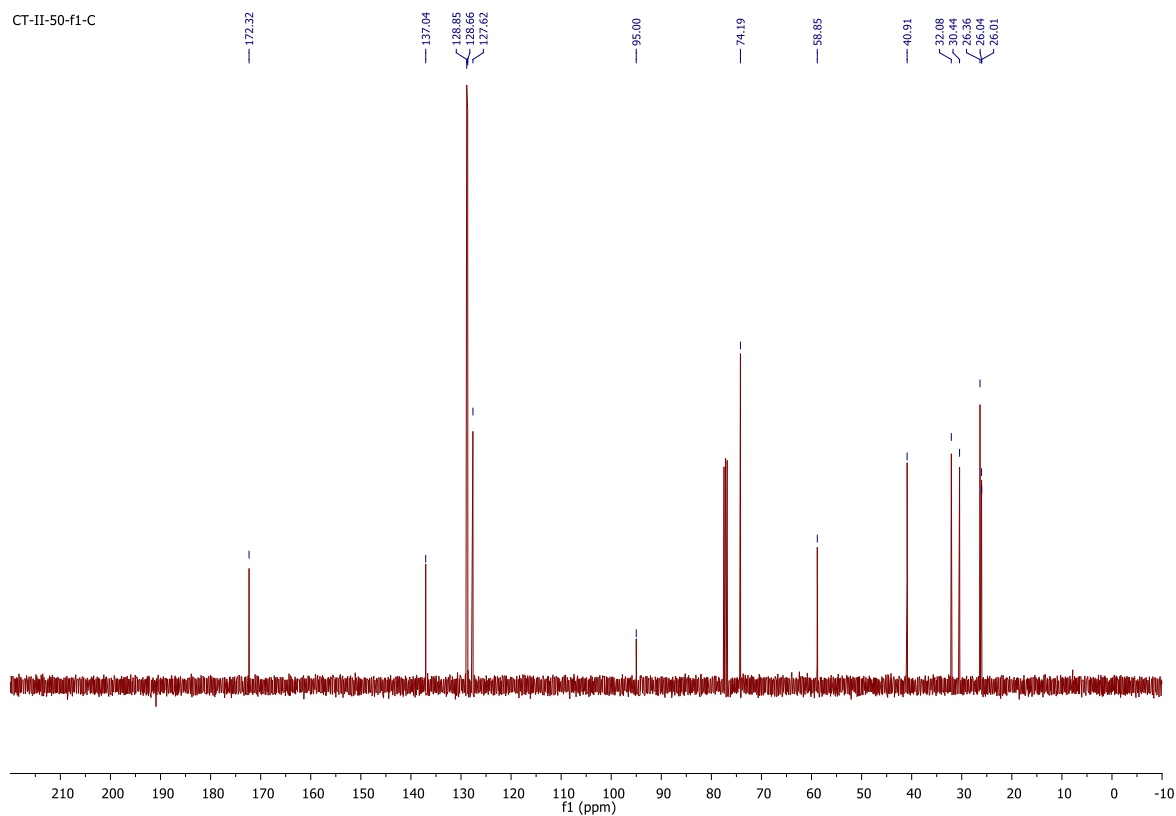
 ^1H NMR (400 MHz), CDCl_3  ^{13}C NMR (100 MHz), CDCl_3 

Adduct 12

^1H NMR (400 MHz), CDCl_3

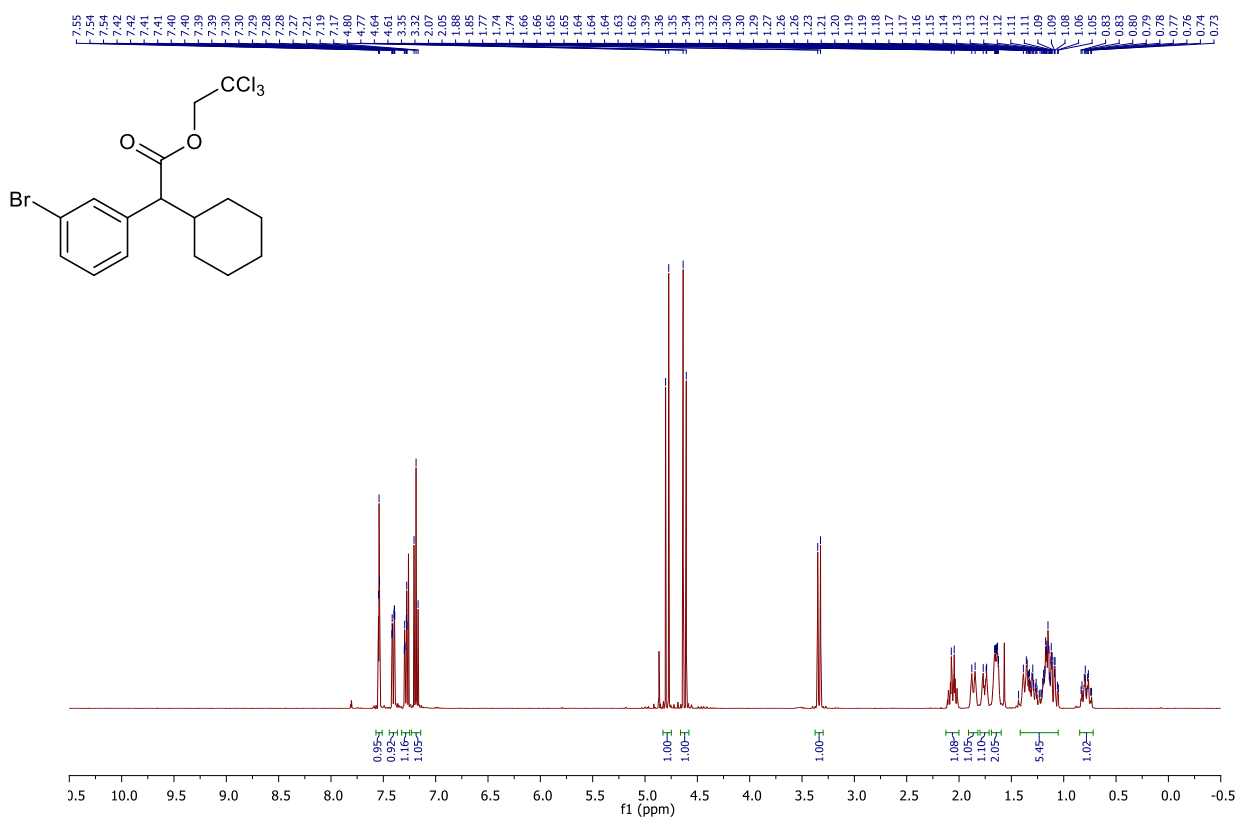


^{13}C NMR (100 MHz), CDCl_3

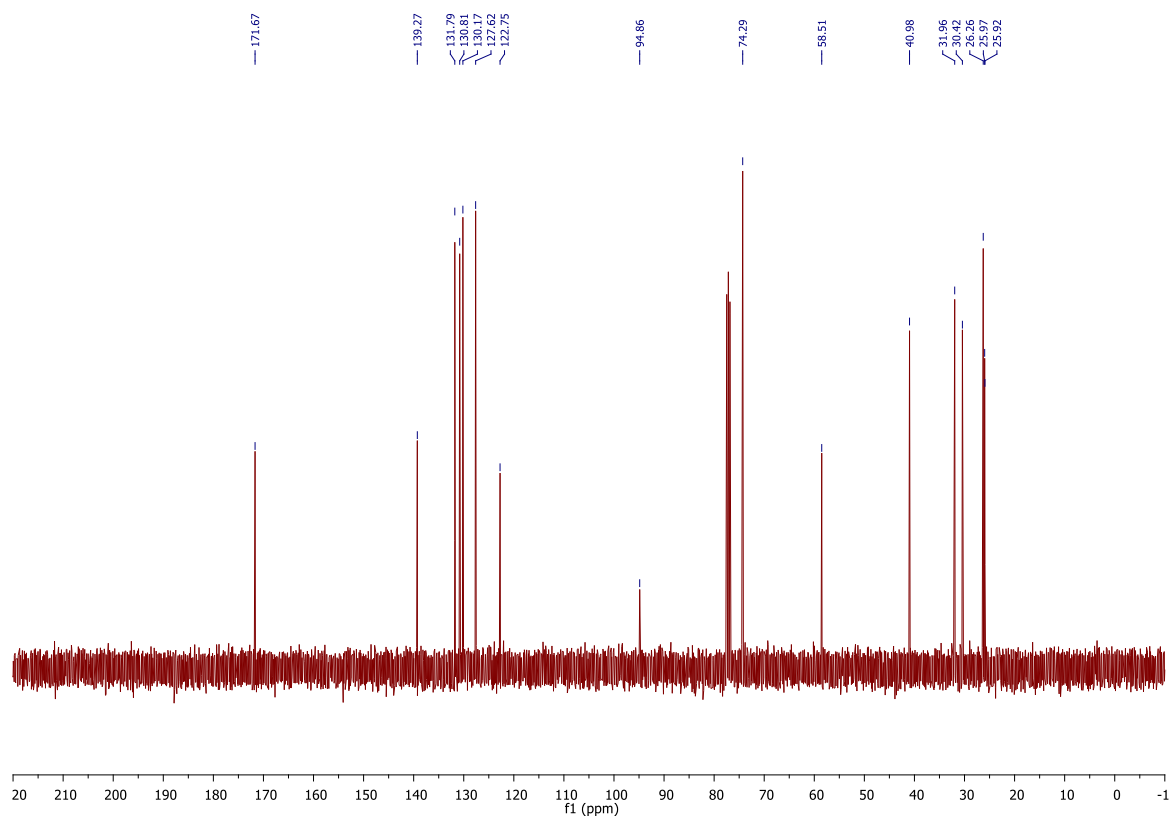


Adduct 13

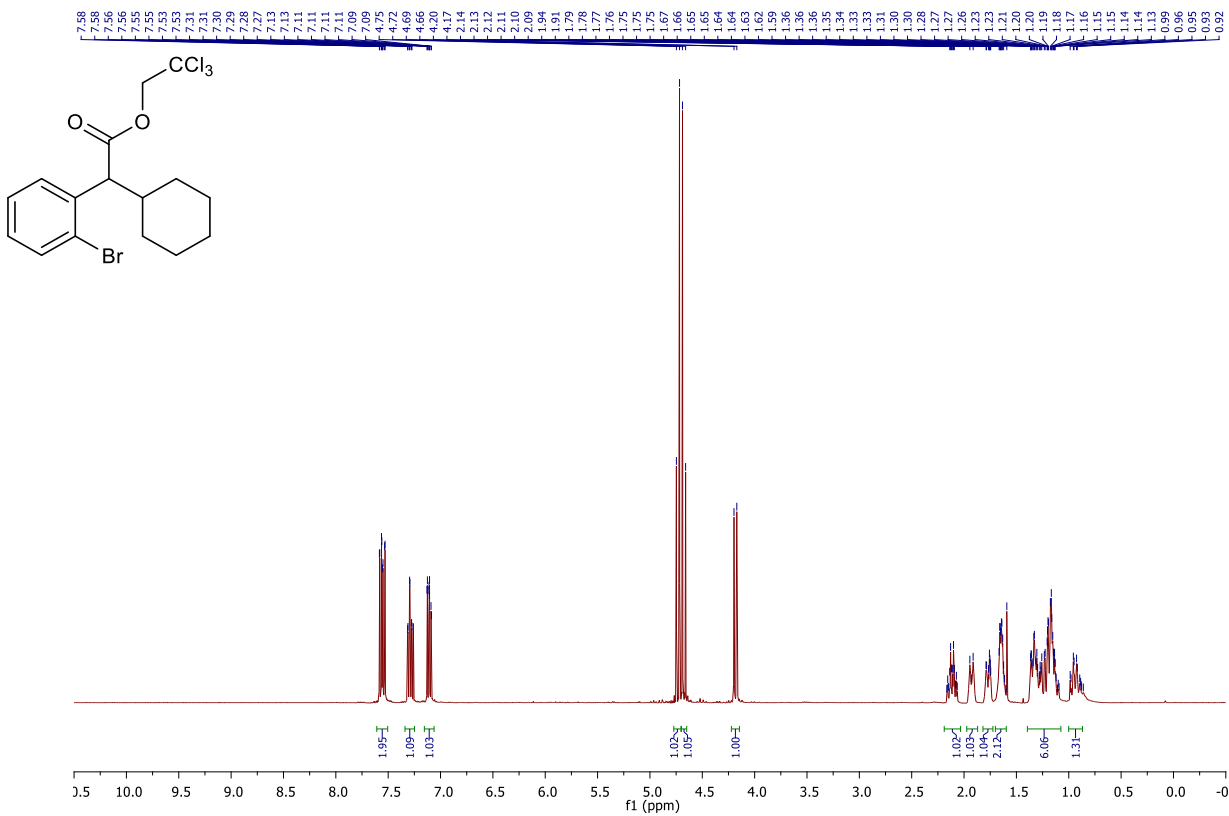
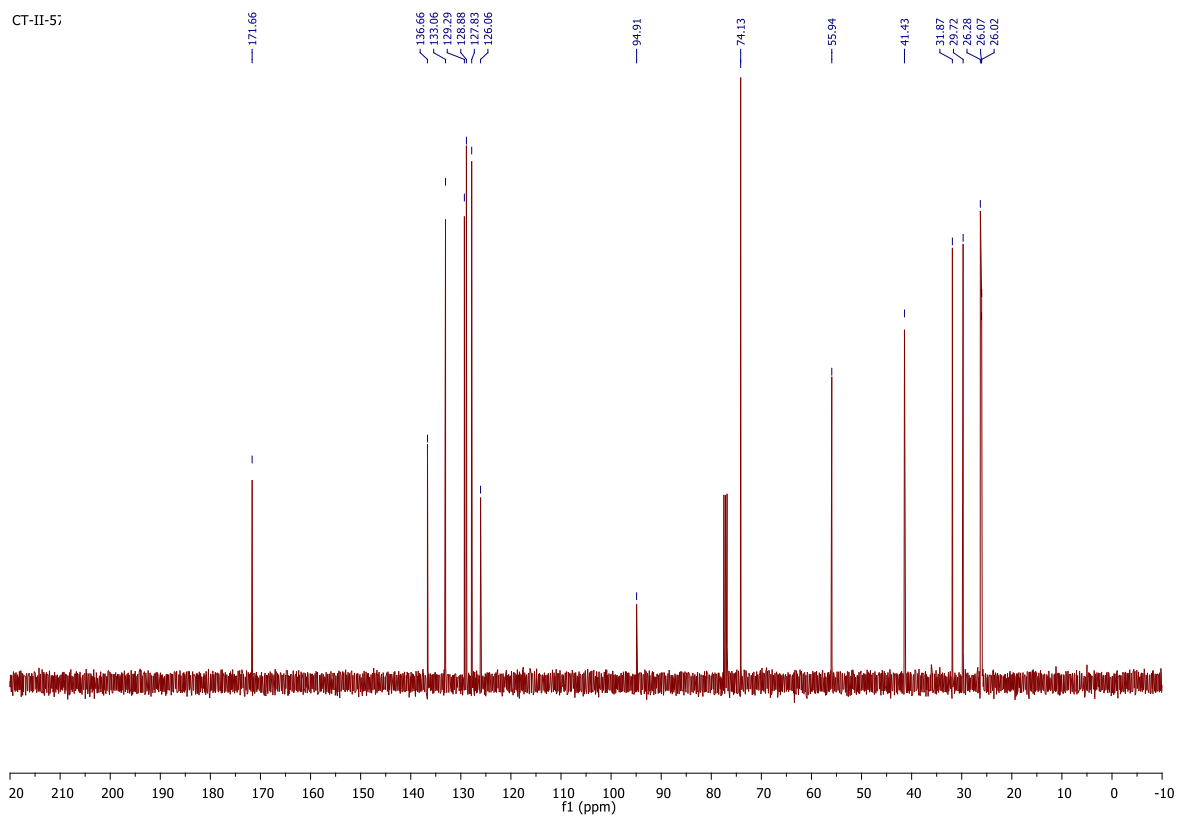
^1H NMR (400 MHz), CDCl_3



^{13}C NMR (100 MHz), CDCl_3

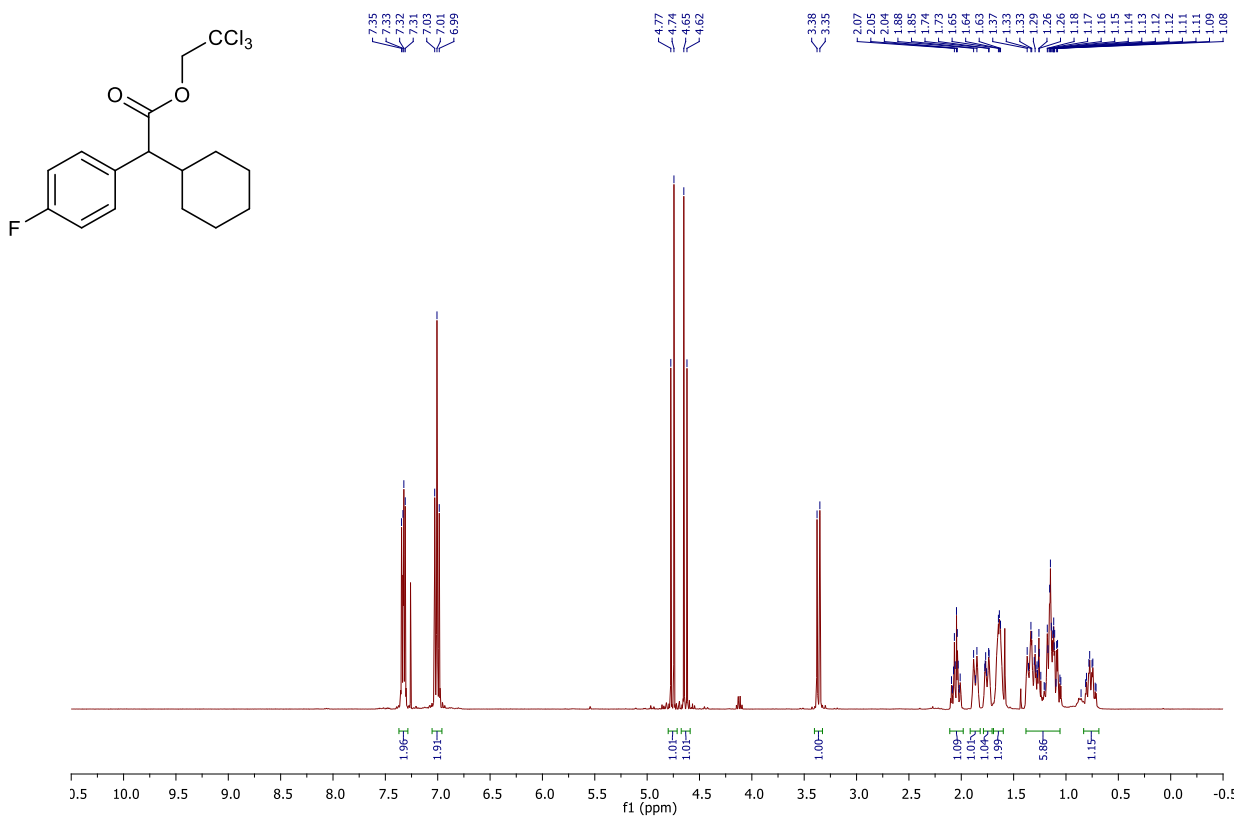


Adduct 14

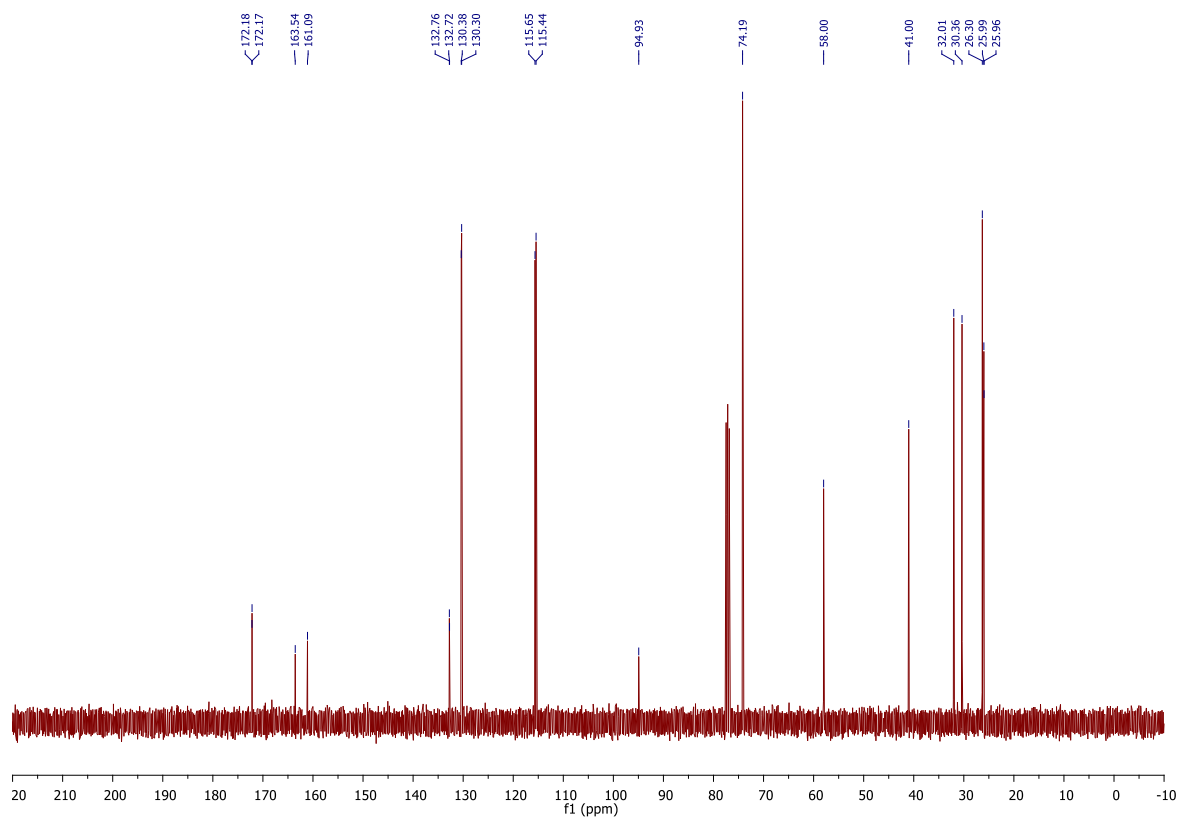
¹H NMR (400 MHz), CDCl₃ ^{13}C NMR (100 MHz), CDCl_3 

Adduct 15

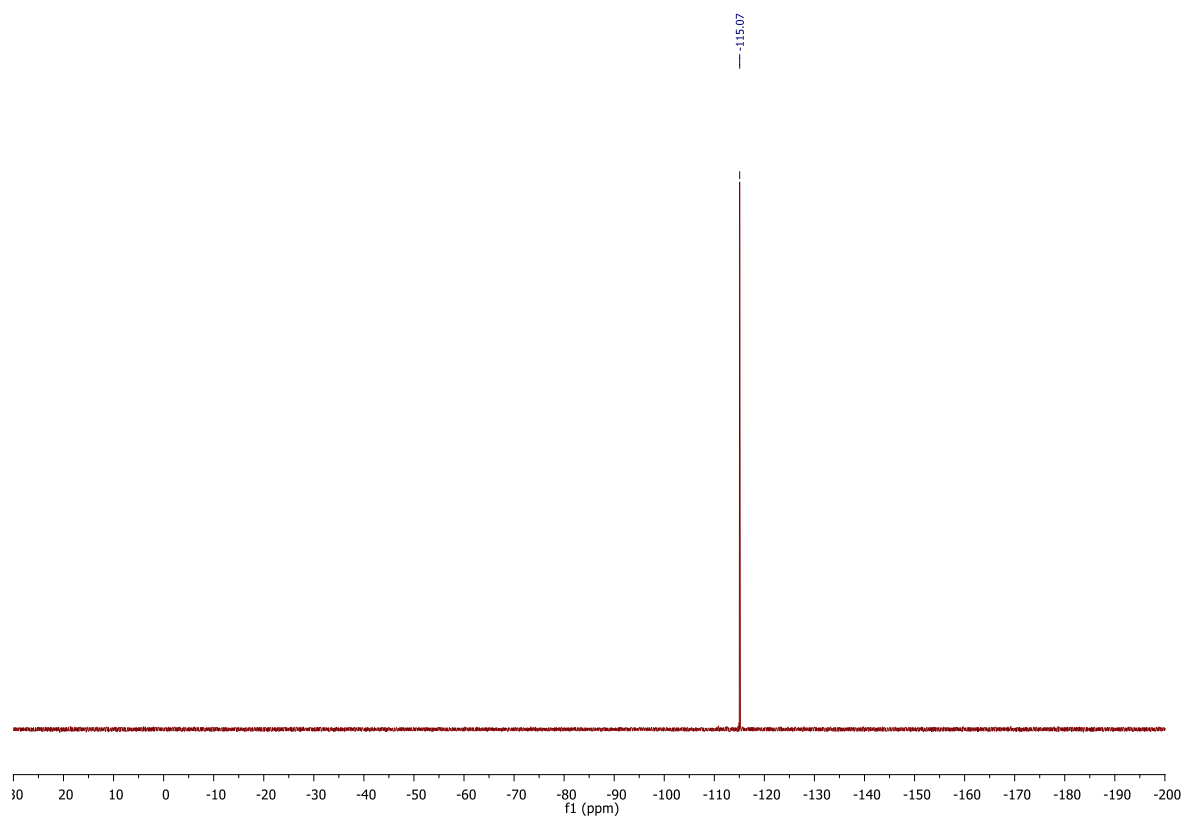
^1H NMR (400 MHz), CDCl_3



^{13}C NMR (100 MHz), CDCl_3

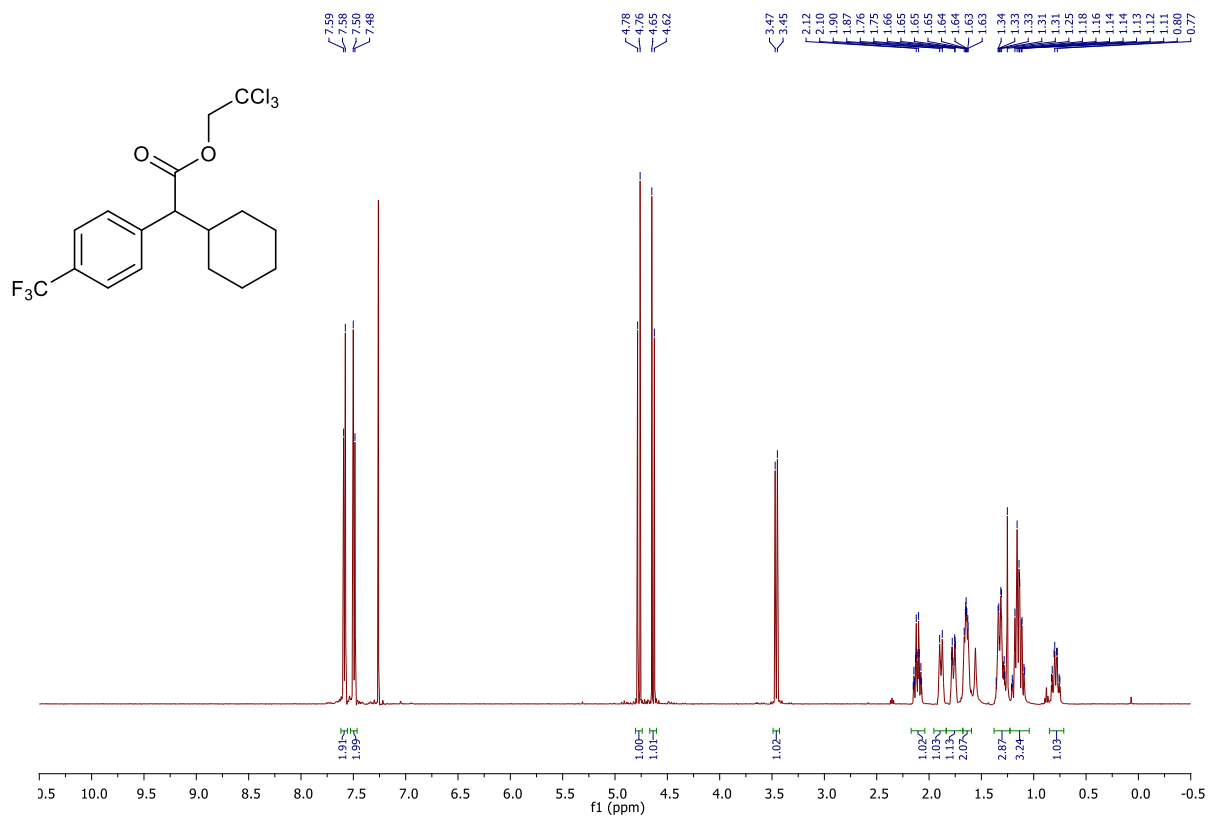


^{19}F NMR (282 MHz), CDCl_3

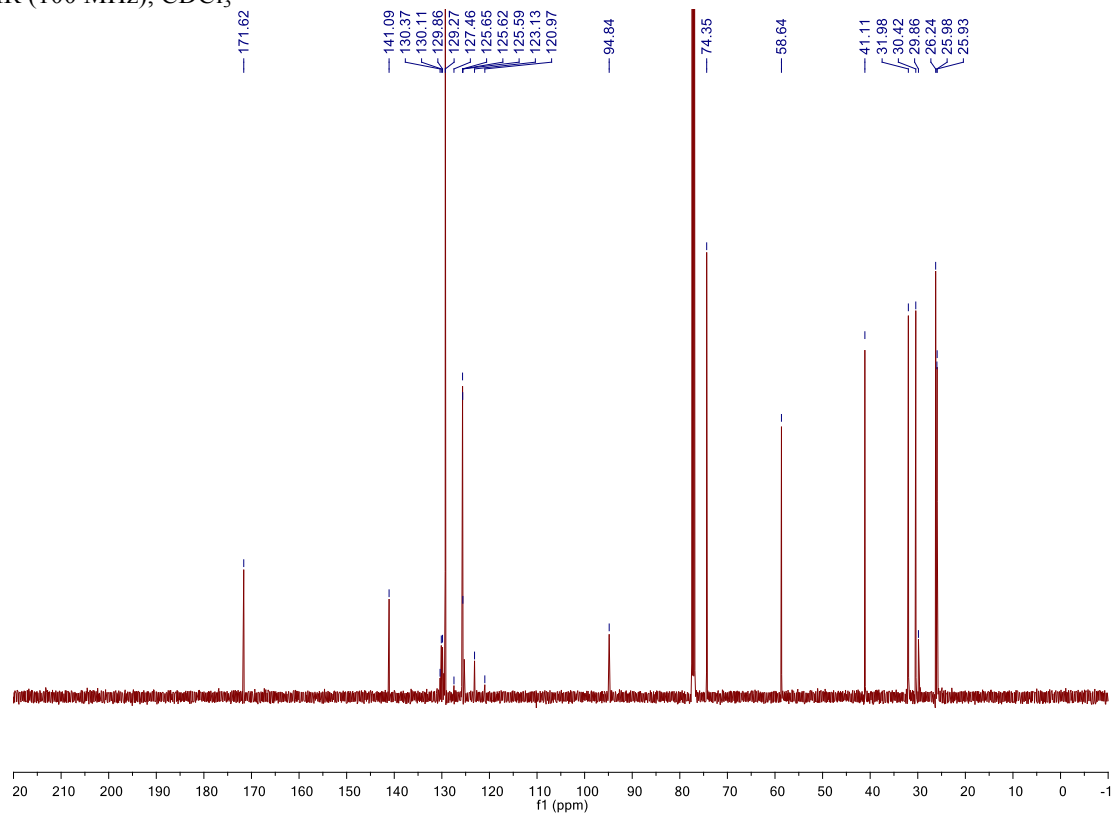


Adduct 16

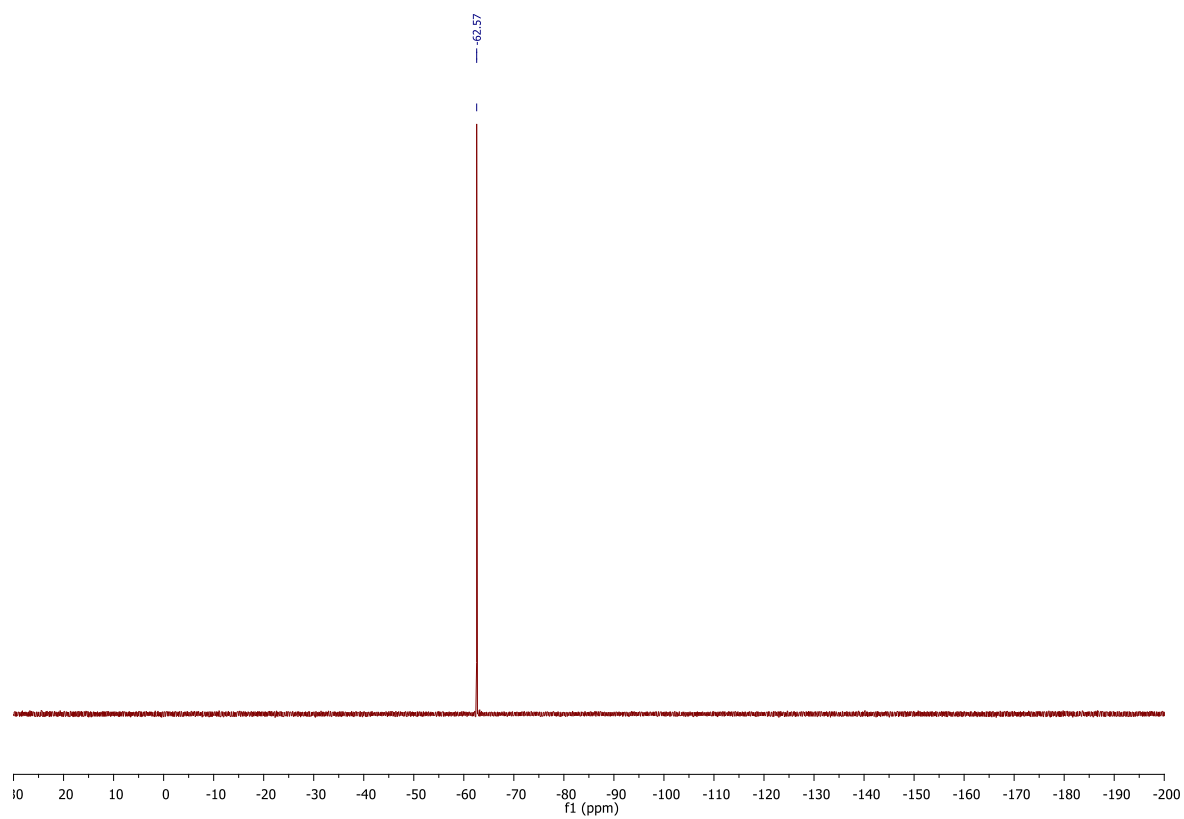
^1H NMR (500 MHz), CDCl_3



^{13}C NMR (100 MHz), CDCl_3

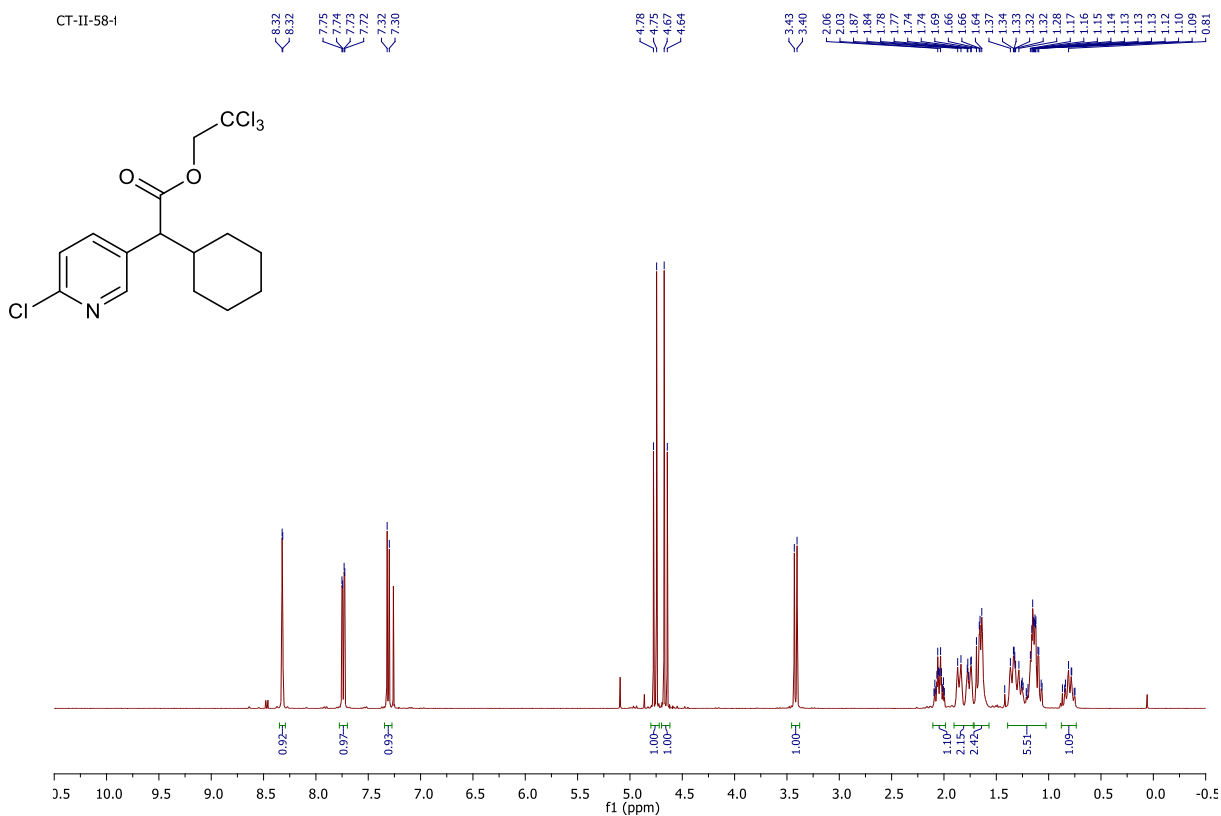


^{19}F NMR (282 MHz), CDCl_3

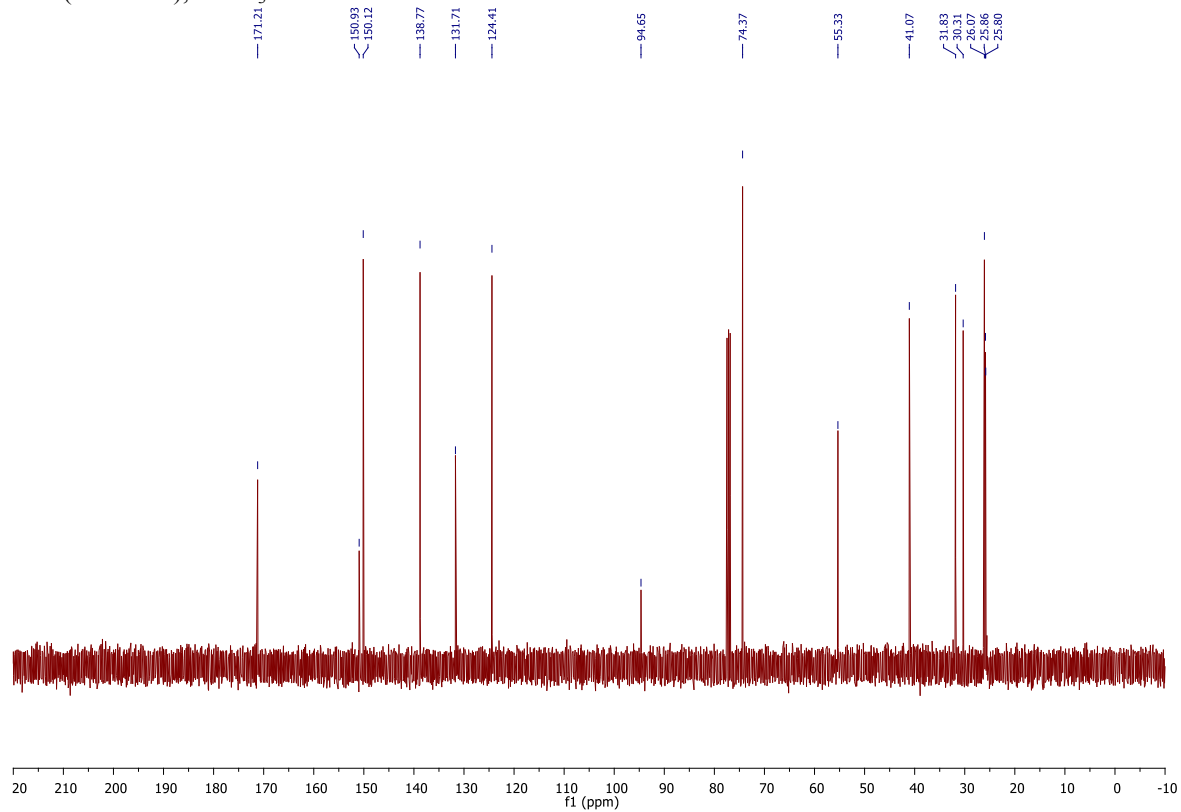


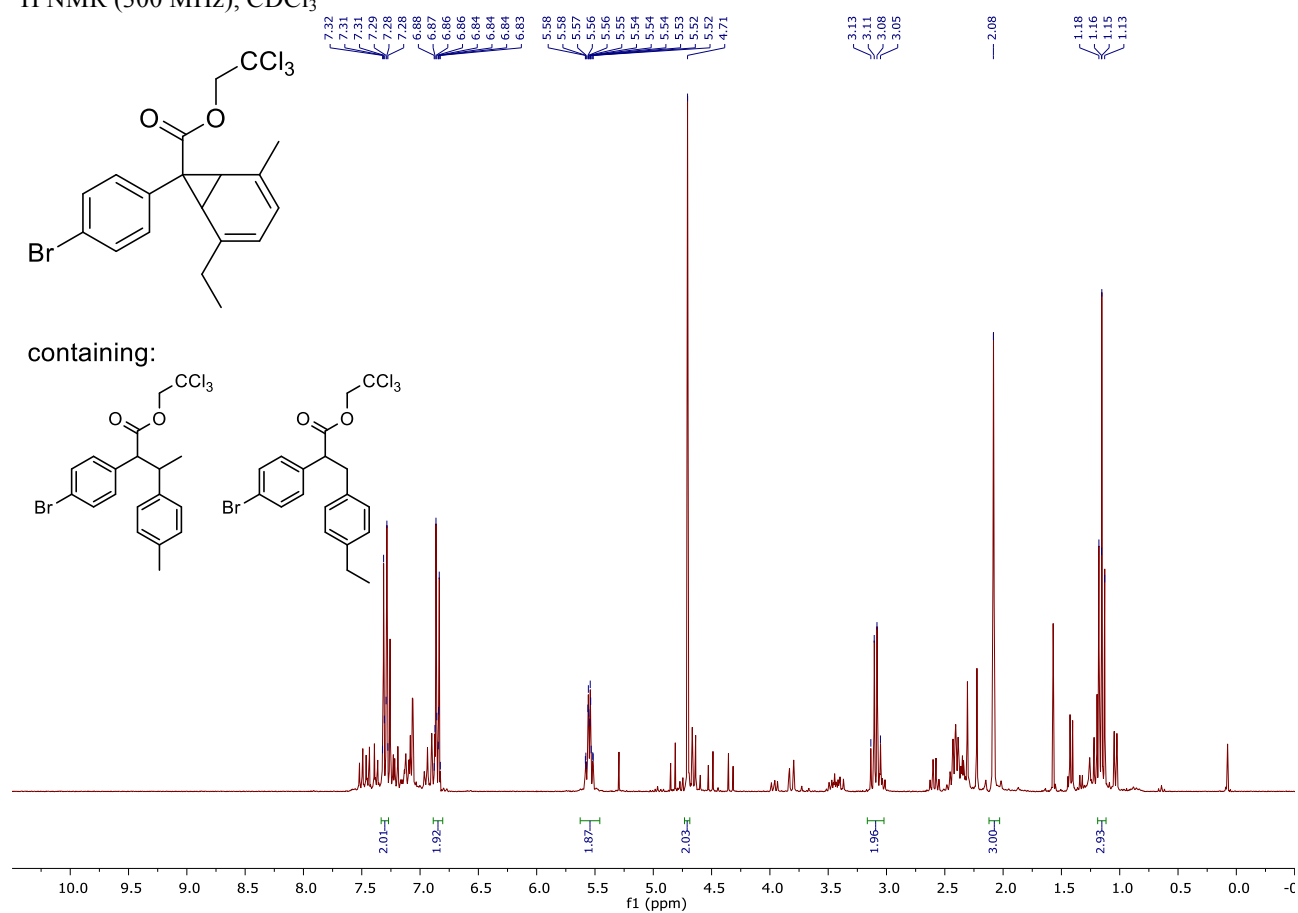
Adduct 17

^1H NMR (400 MHz), CDCl_3



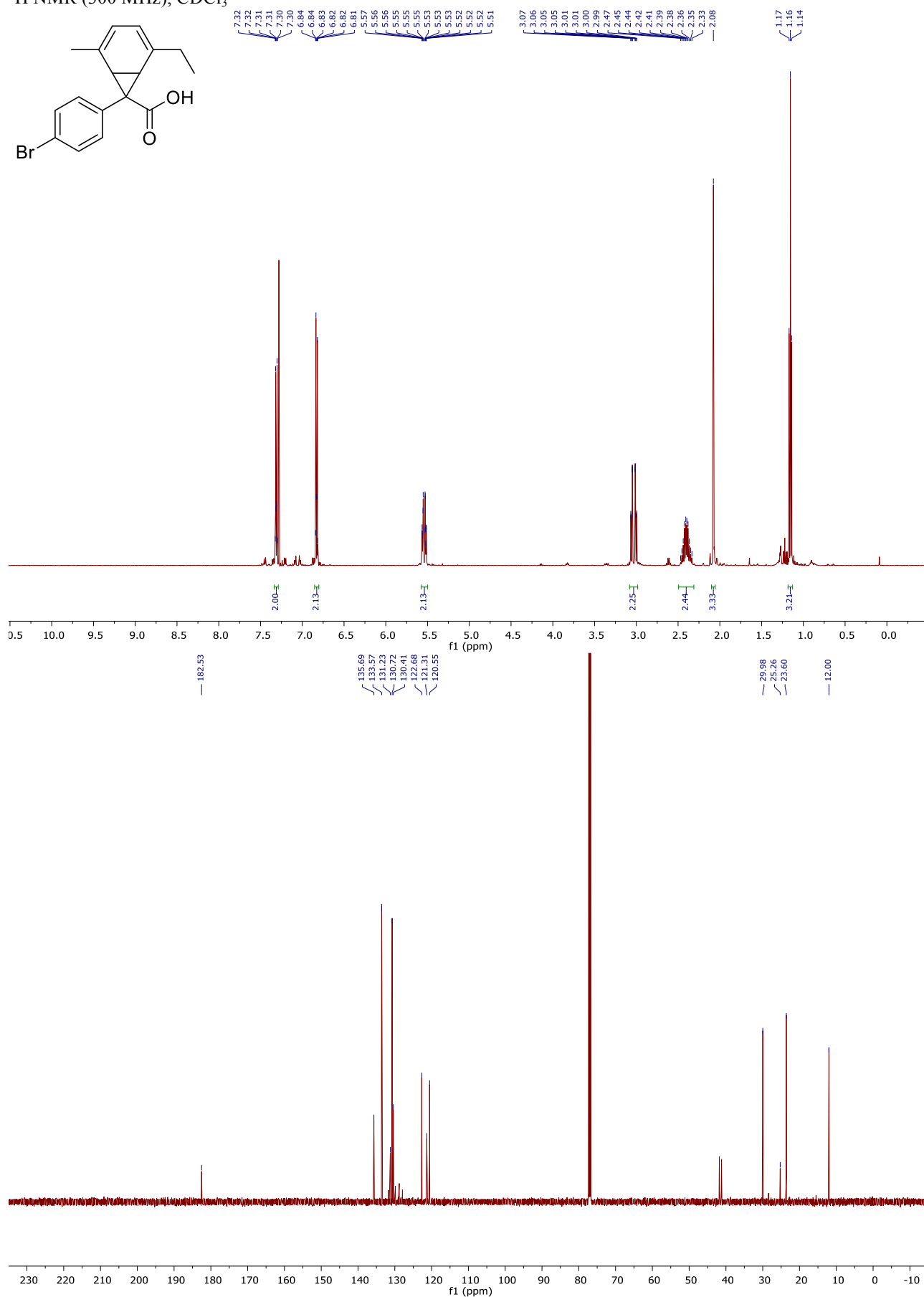
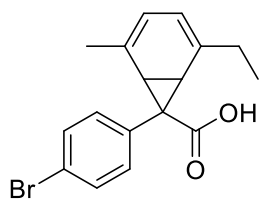
^{13}C NMR (100 MHz), CDCl_3

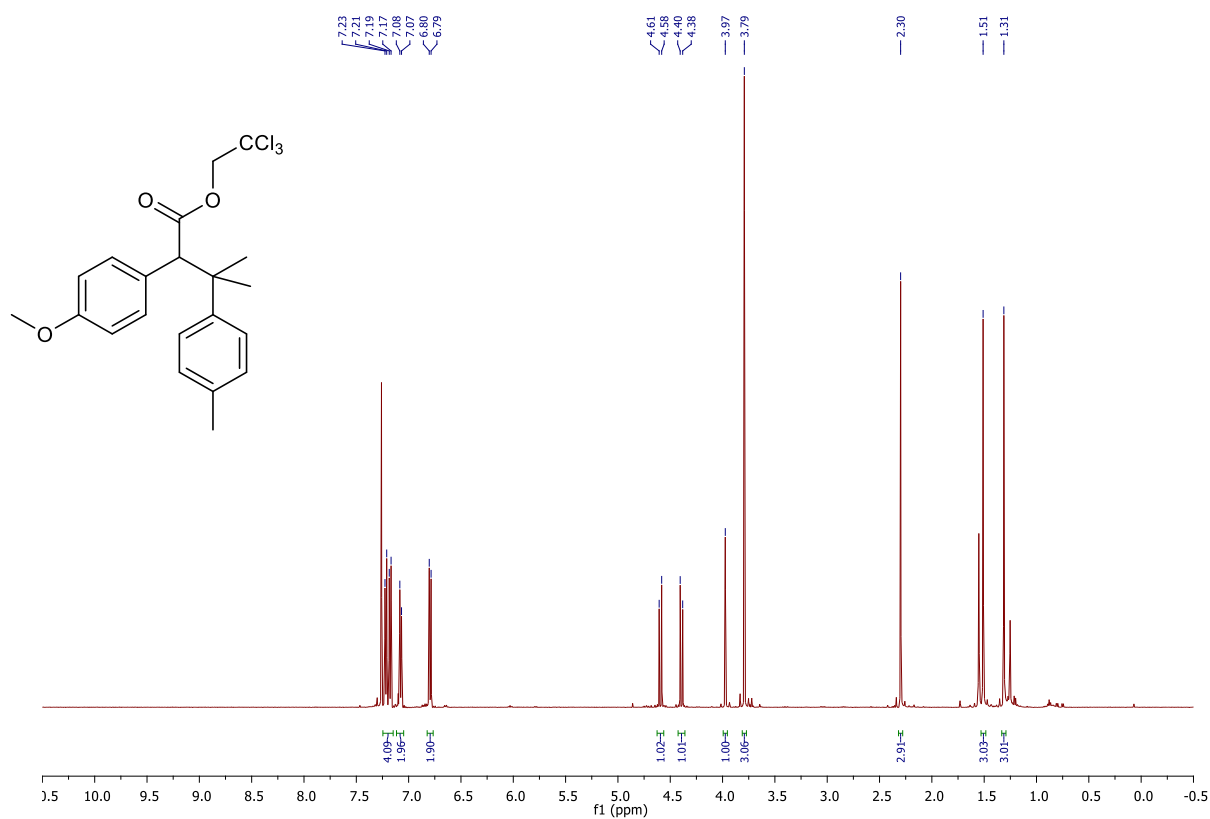
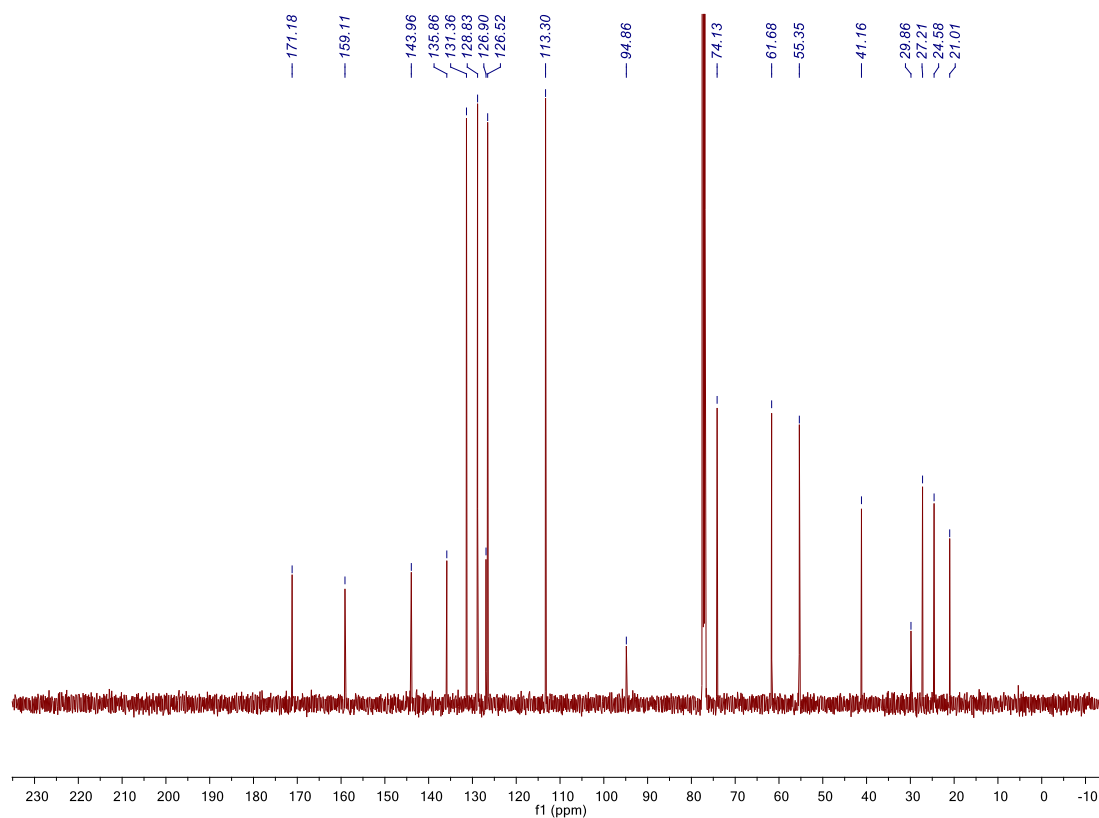


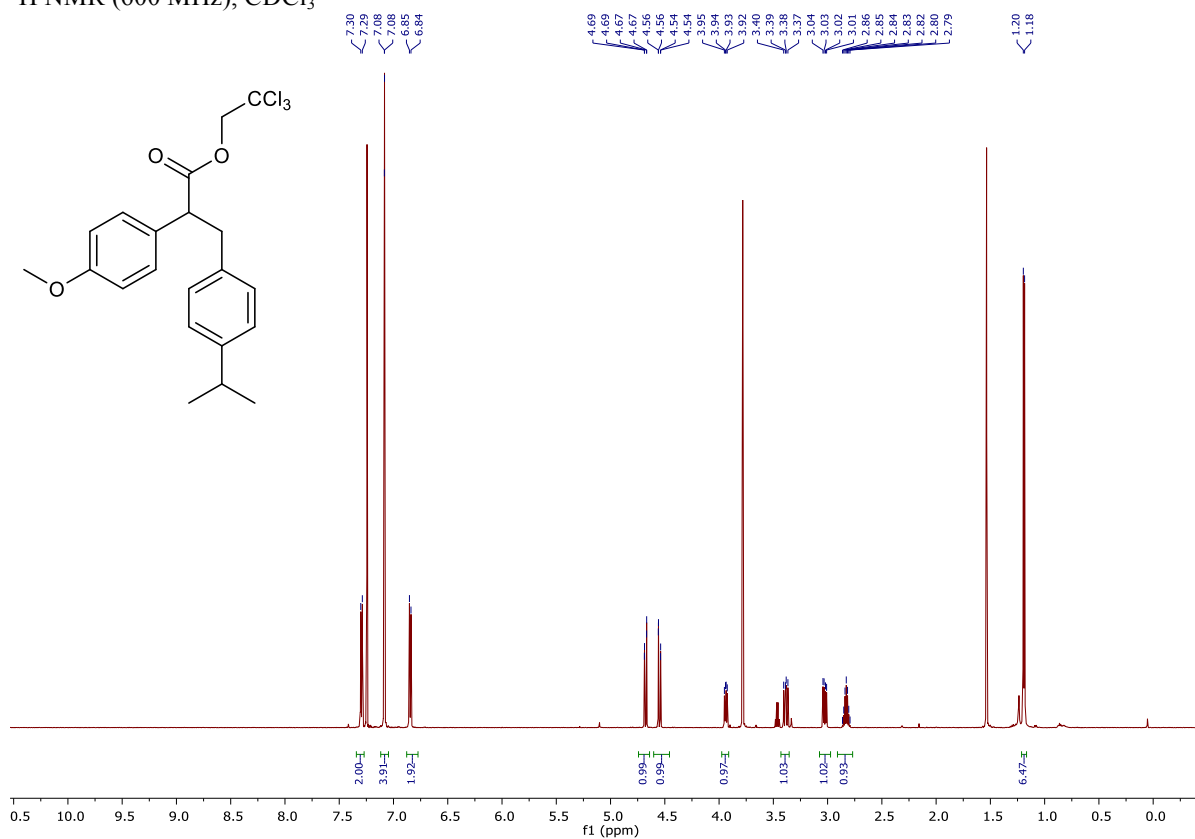
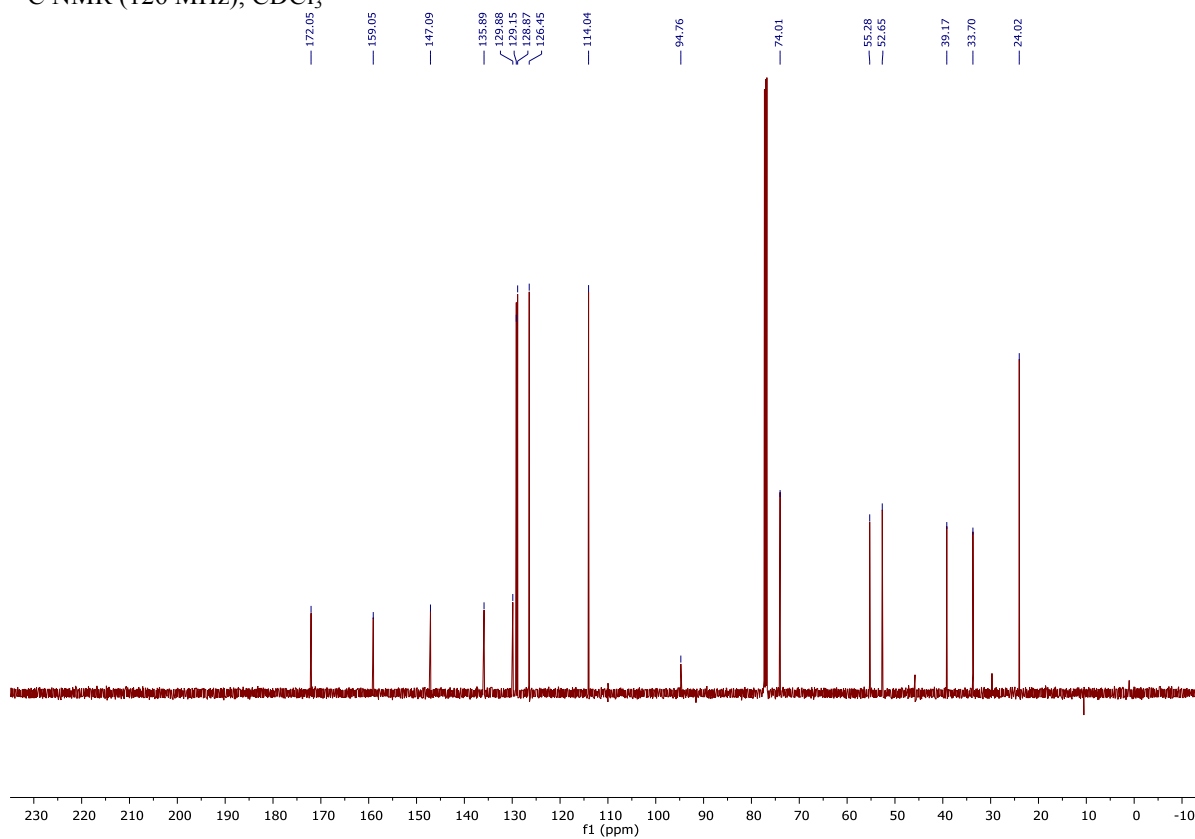
Adduct S2a¹H NMR (300 MHz), CDCl₃

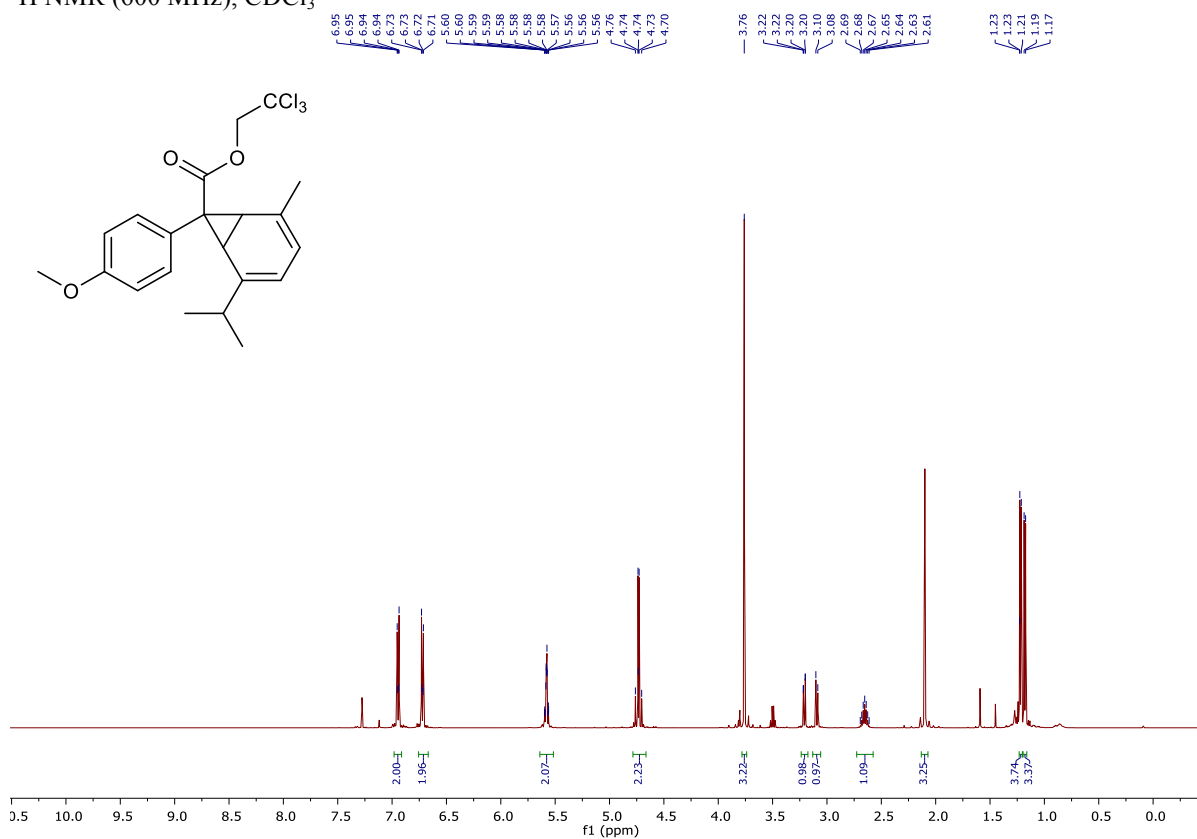
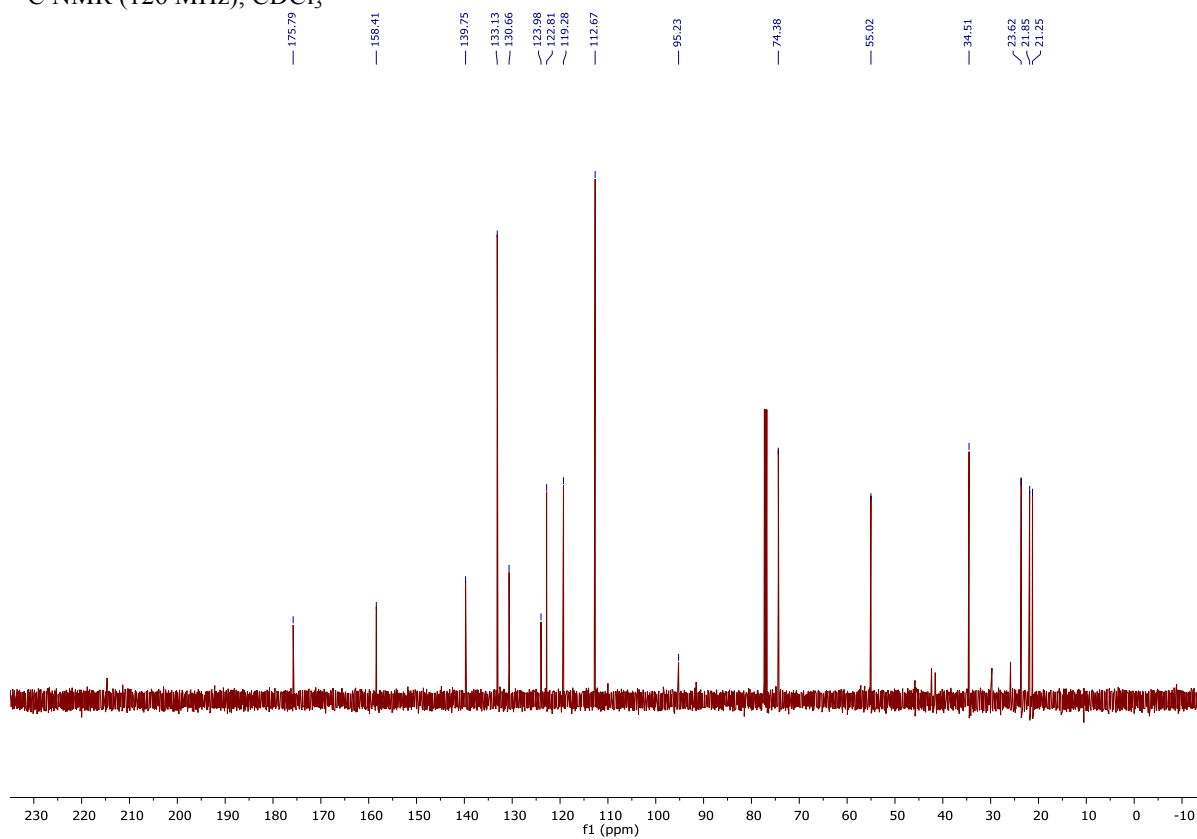
Adduct S2b

¹H NMR (300 MHz), CDCl₃



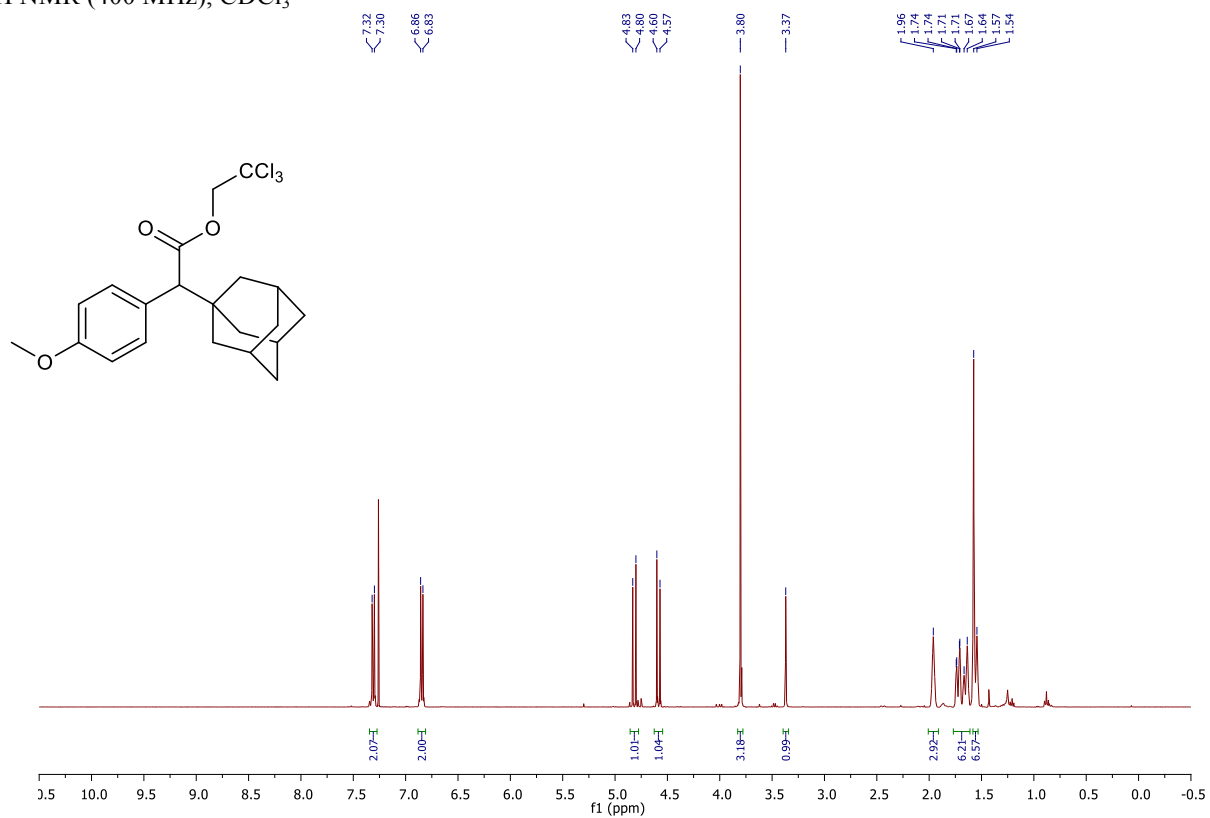
Adduct 20¹H NMR (500 MHz), CDCl₃¹³C NMR (126 MHz), CDCl₃

Adduct 21 ^1H NMR (600 MHz), CDCl_3  ^{13}C NMR (126 MHz), CDCl_3 

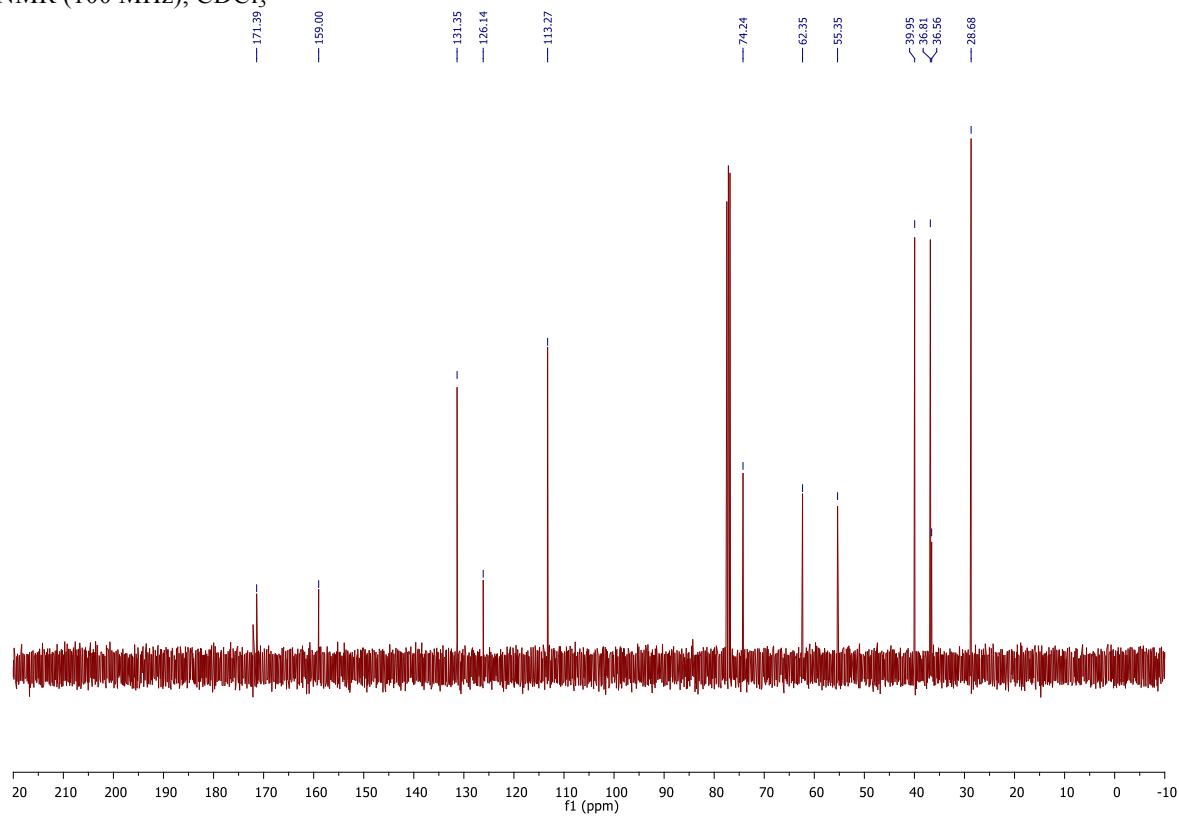
Adduct S3¹H NMR (600 MHz), CDCl₃¹³C NMR (126 MHz), CDCl₃

Adduct 22

^1H NMR (400 MHz), CDCl_3

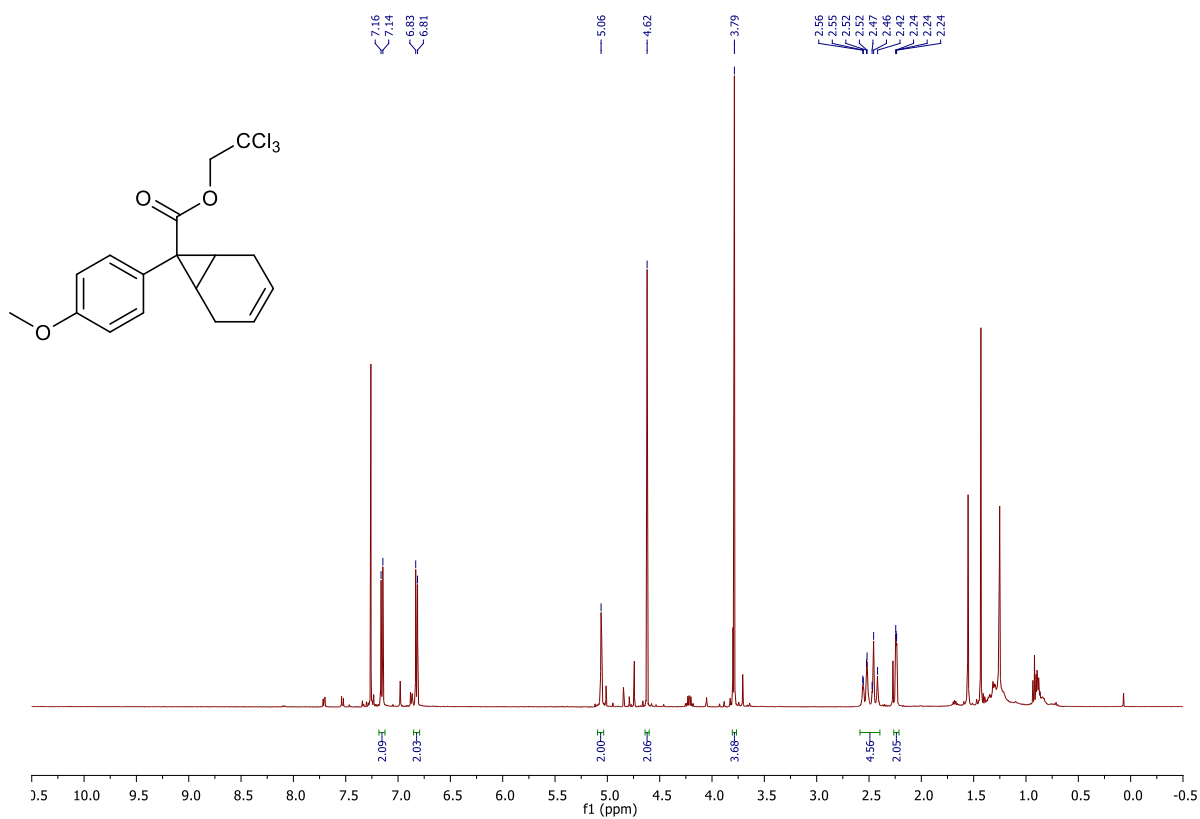


^{13}C NMR (100 MHz), CDCl_3

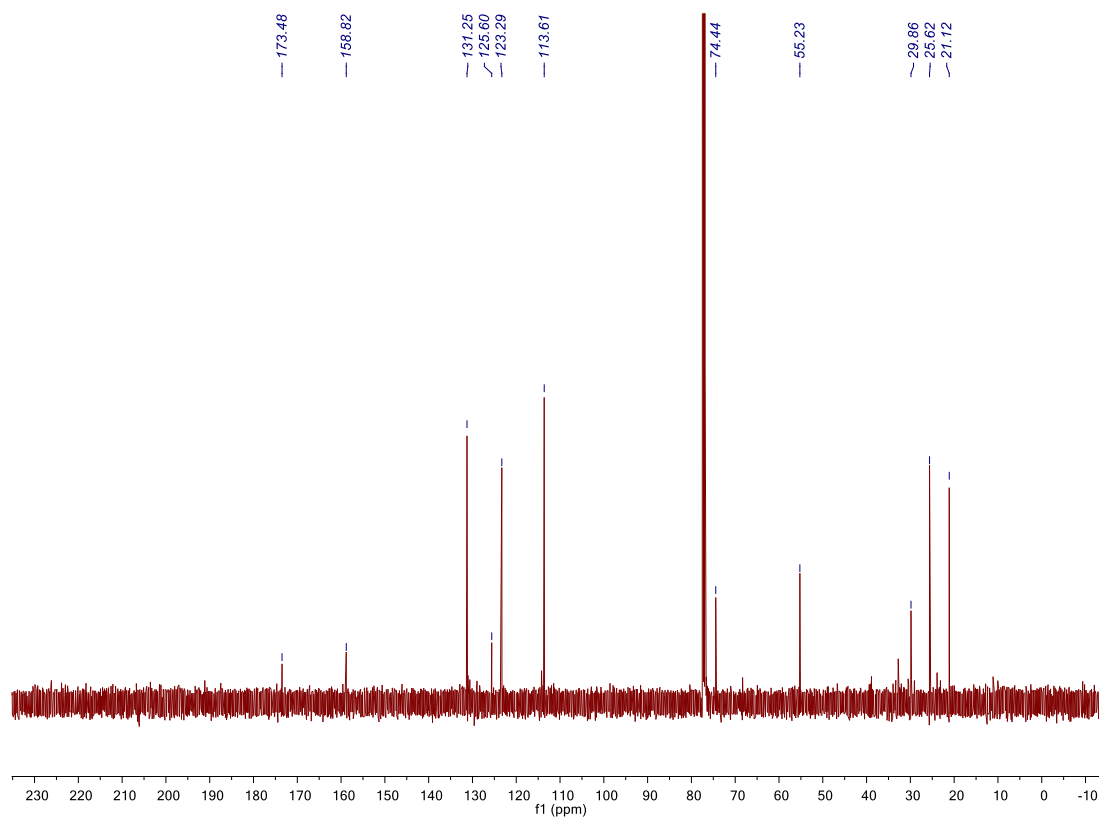


Adduct 24

^1H NMR (500 MHz), CDCl_3

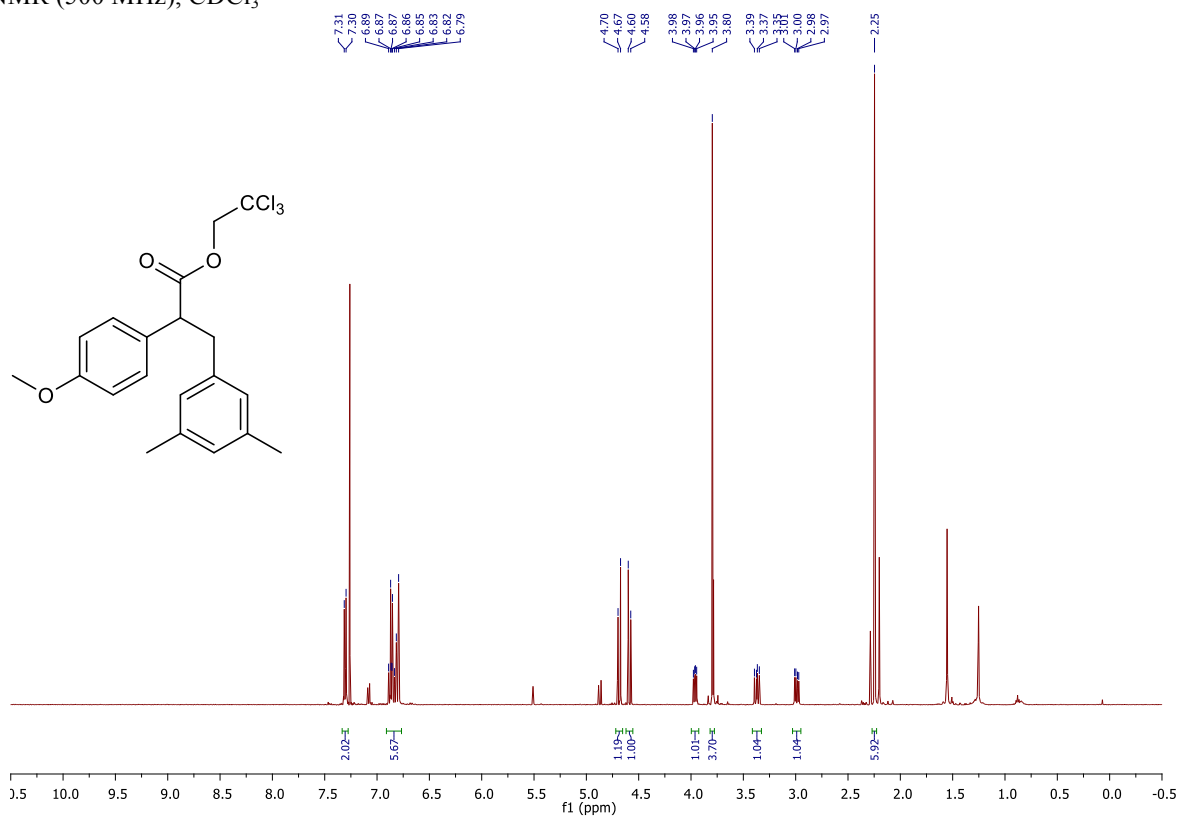


^{13}C NMR (100 MHz), CDCl_3

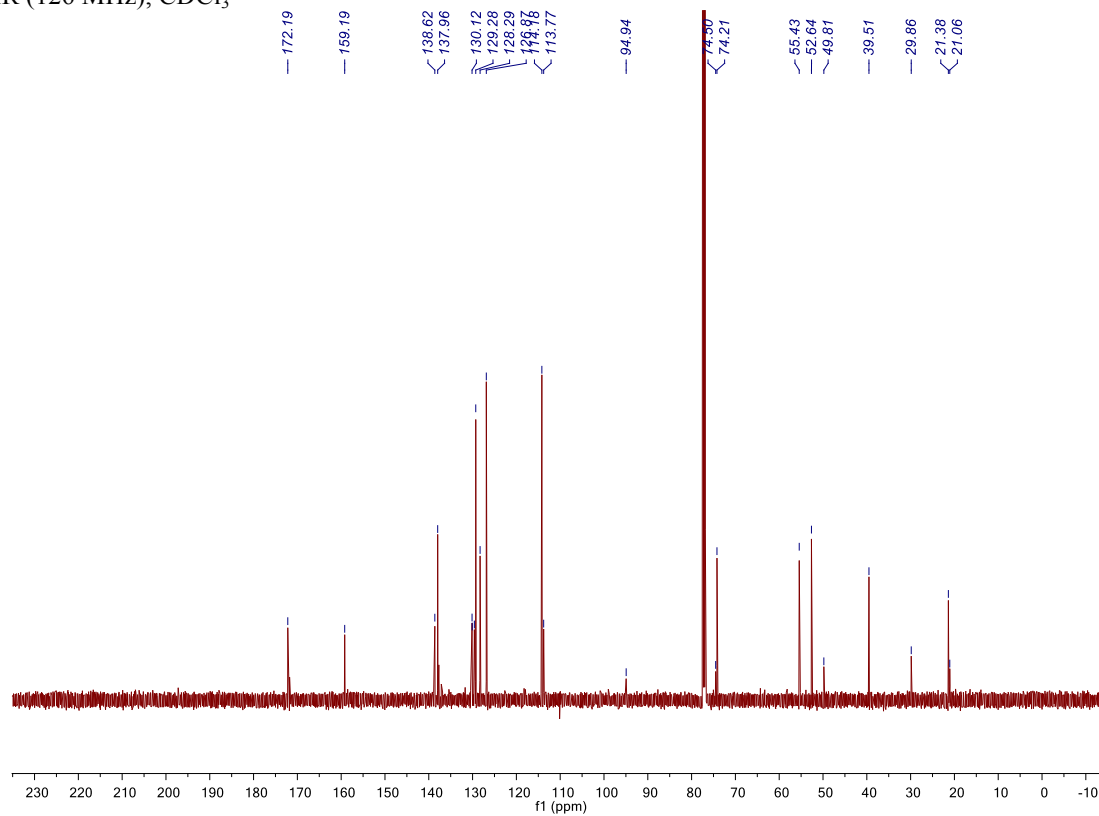


Adduct 25

^1H NMR (500 MHz), CDCl_3

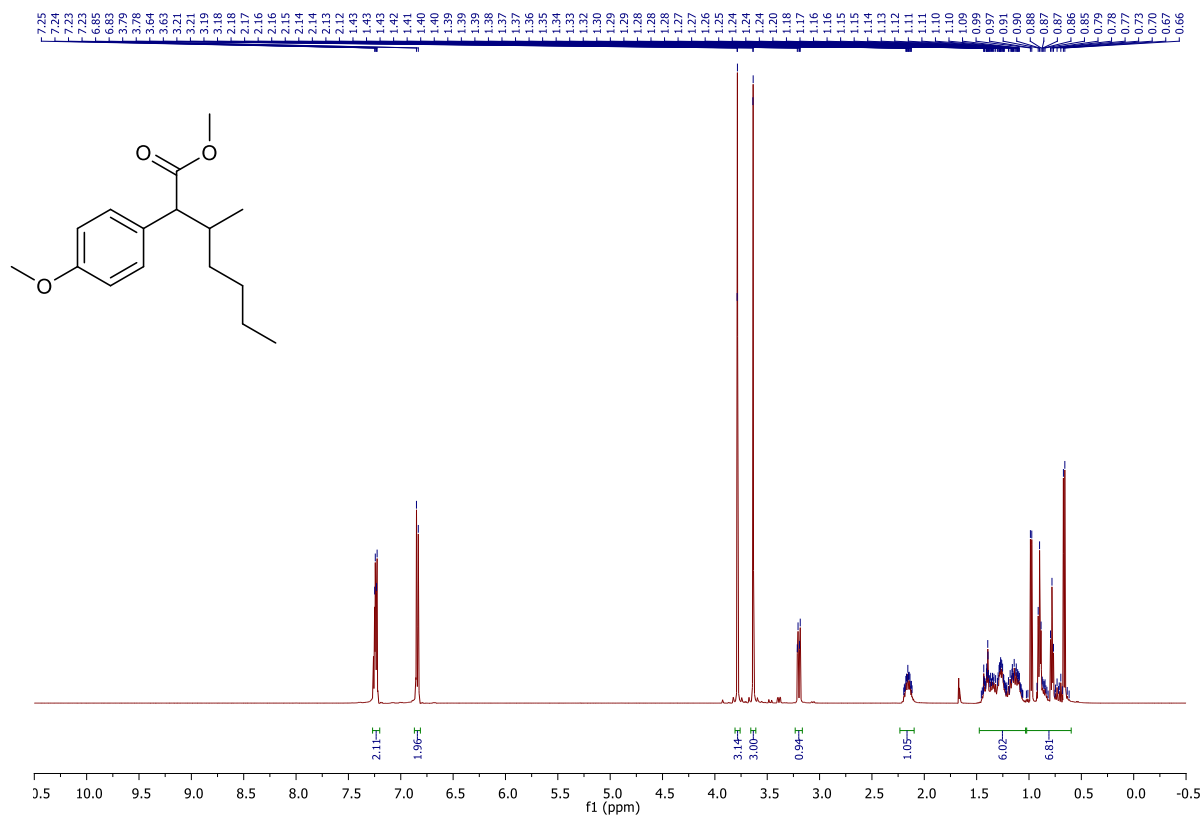


^{13}C NMR (126 MHz), CDCl_3

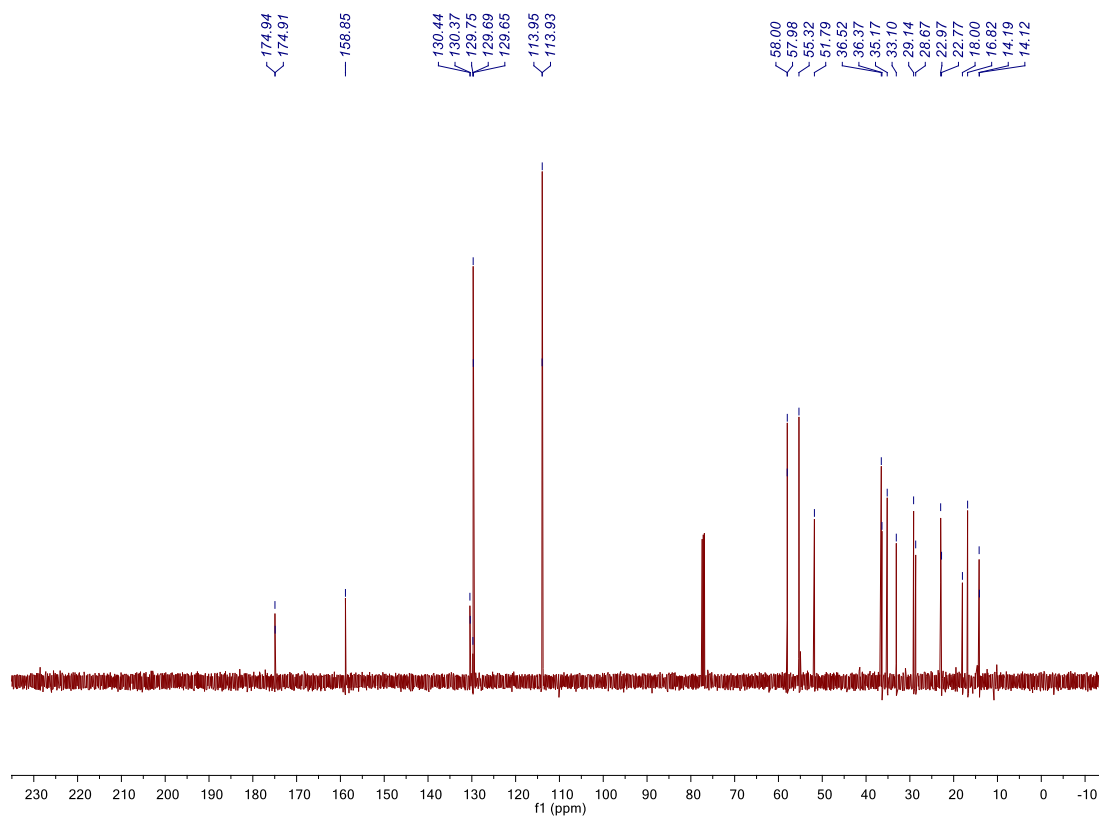


Adduct S4

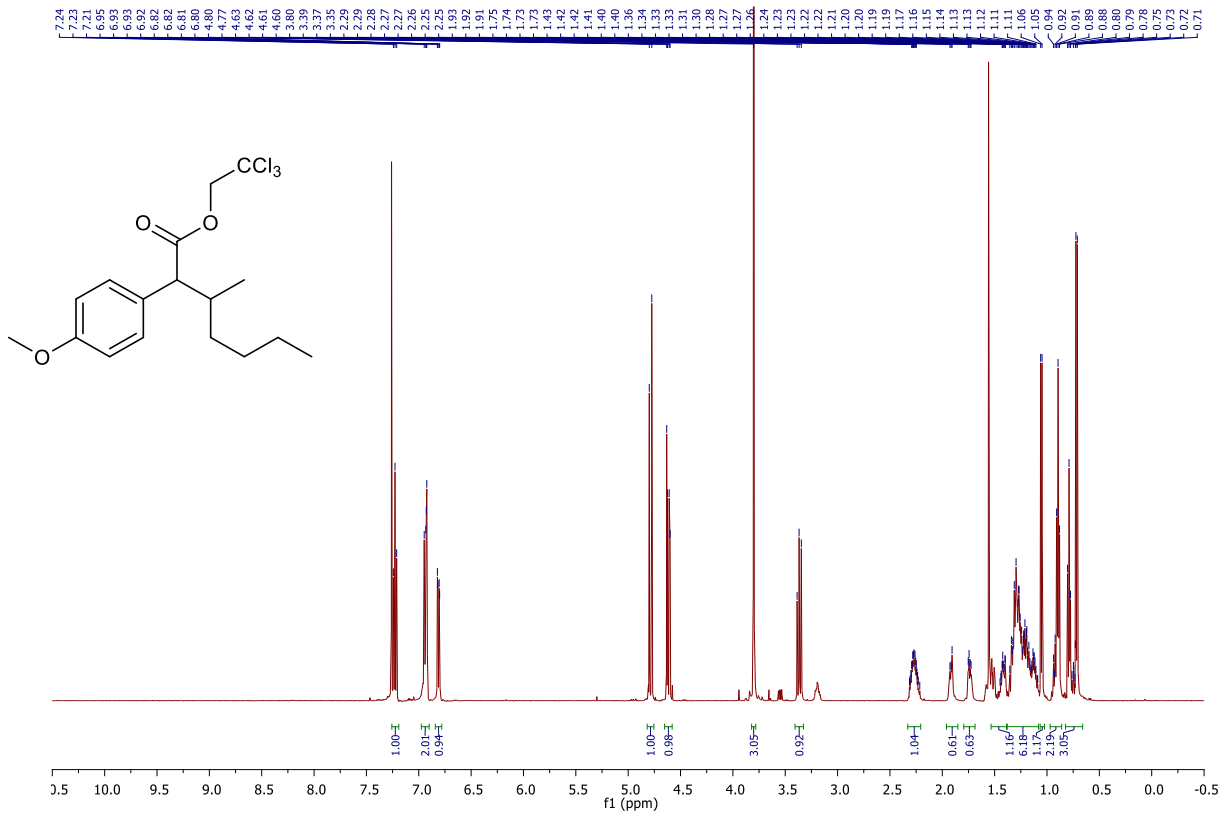
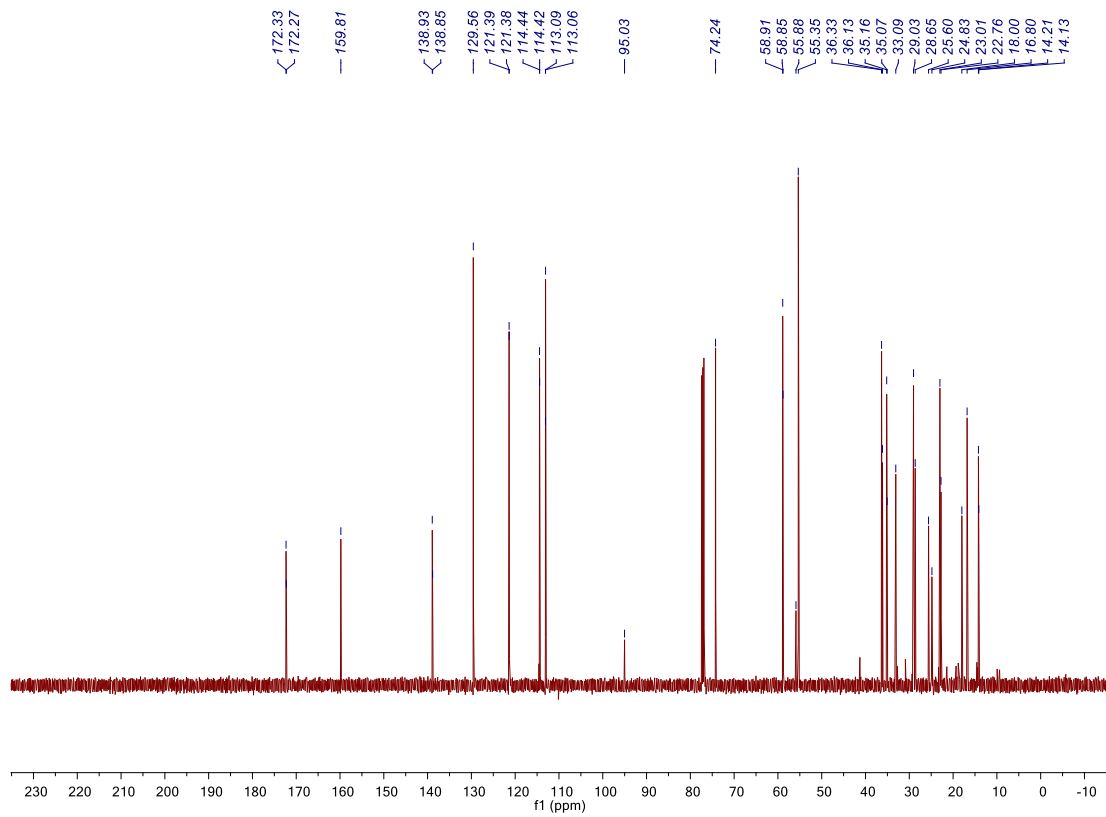
^1H NMR (500 MHz), CDCl_3



^{13}C NMR (126 MHz), CDCl_3

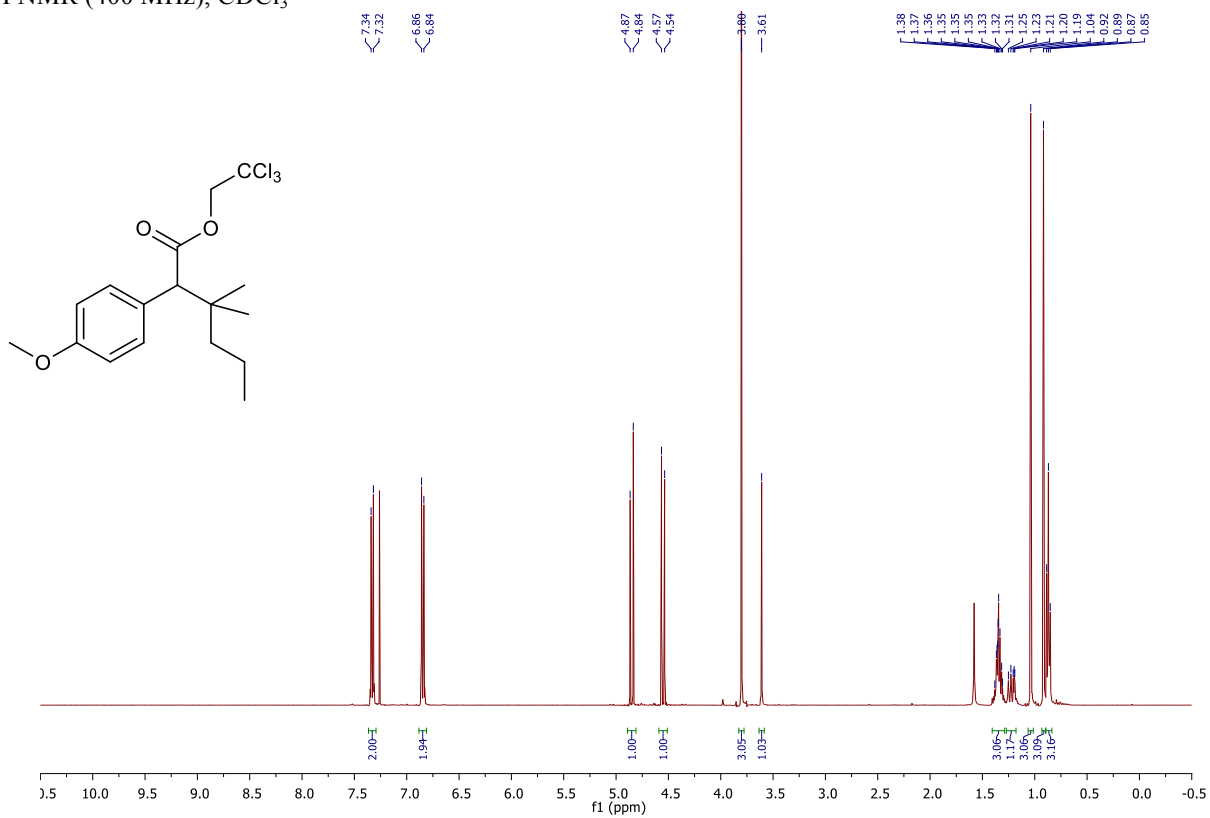


Adduct 28

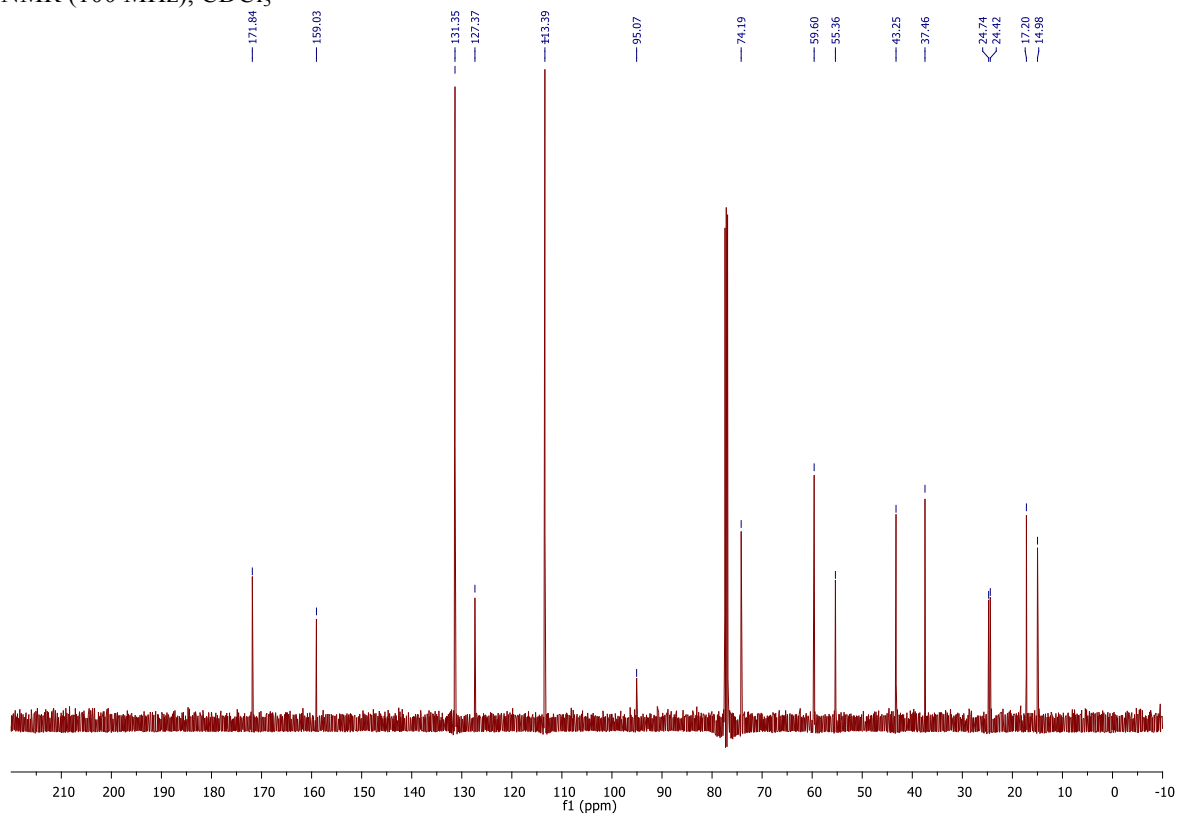
¹H NMR (500 MHz), CDCl₃ ^{13}C NMR (126 MHz), CDCl_3 

Adduct 30

^1H NMR (400 MHz), CDCl_3



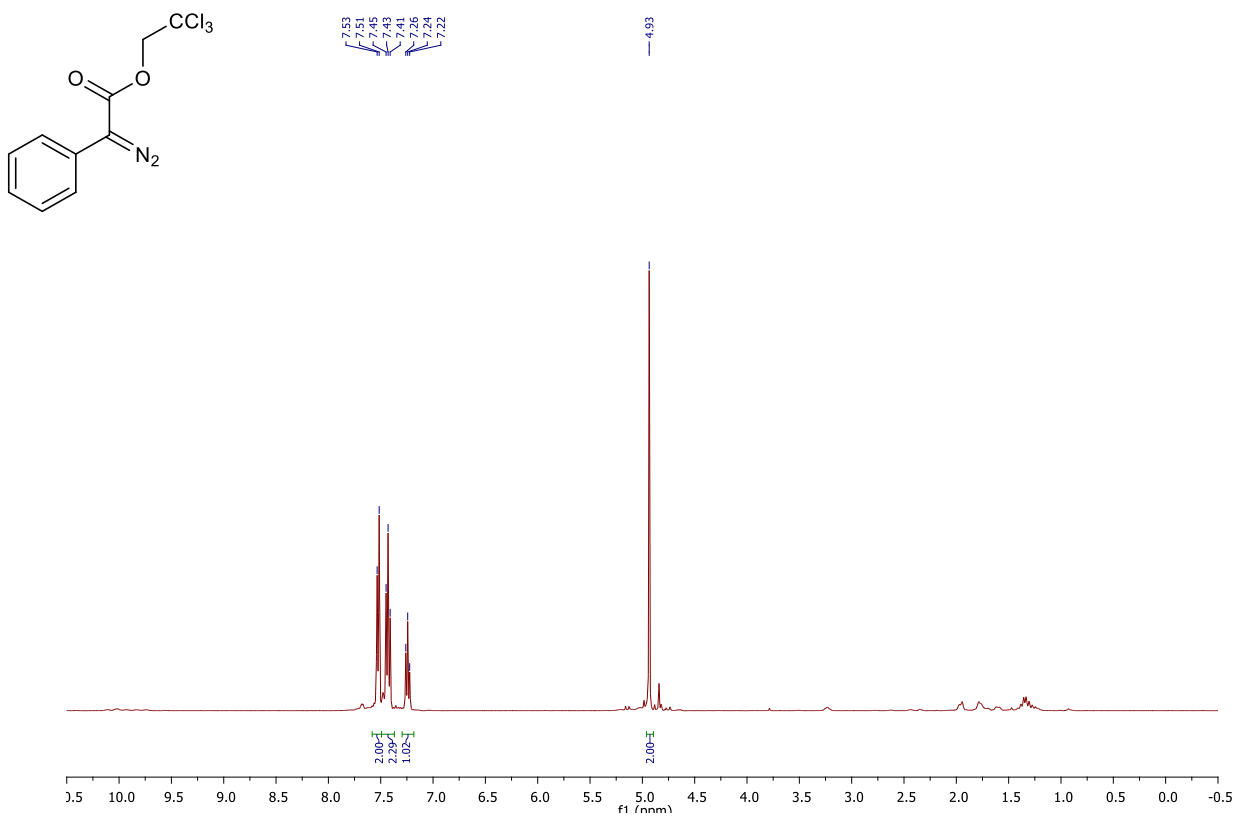
^{13}C NMR (100 MHz), CDCl_3



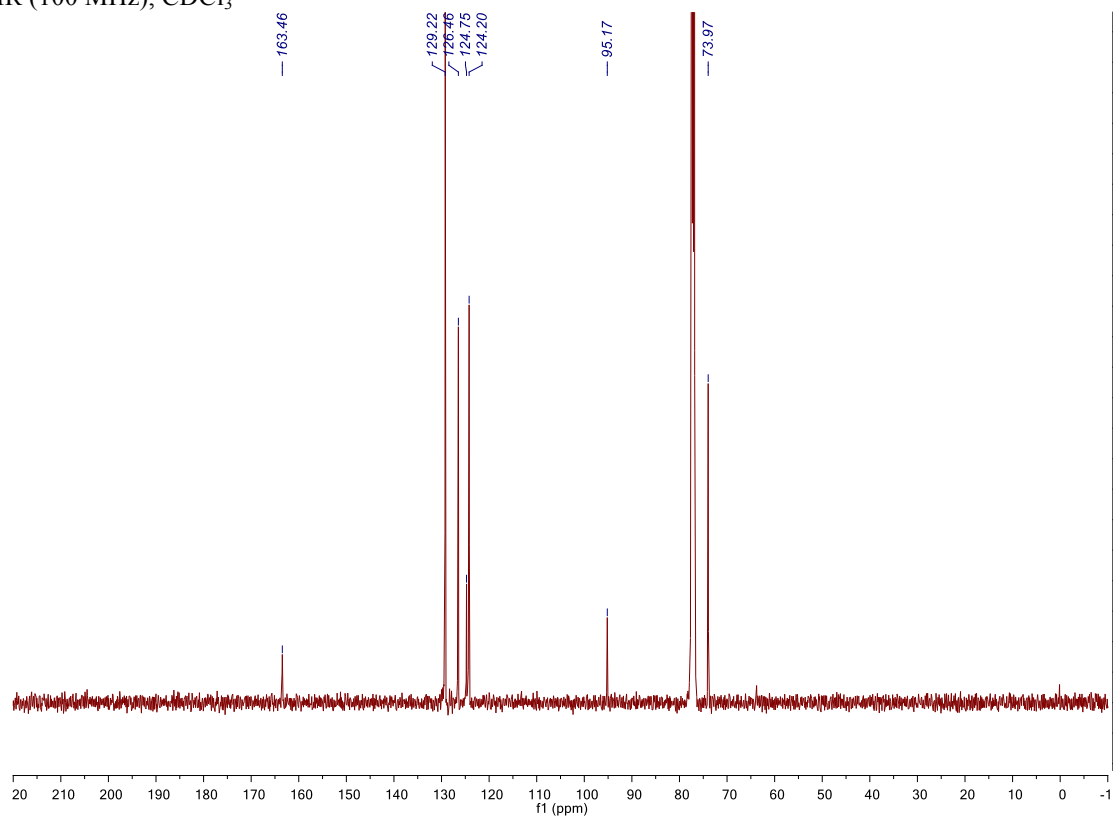
8. ^1H NMR and ^{13}C -NMR spectra of new diazo compounds

Diazo 1e

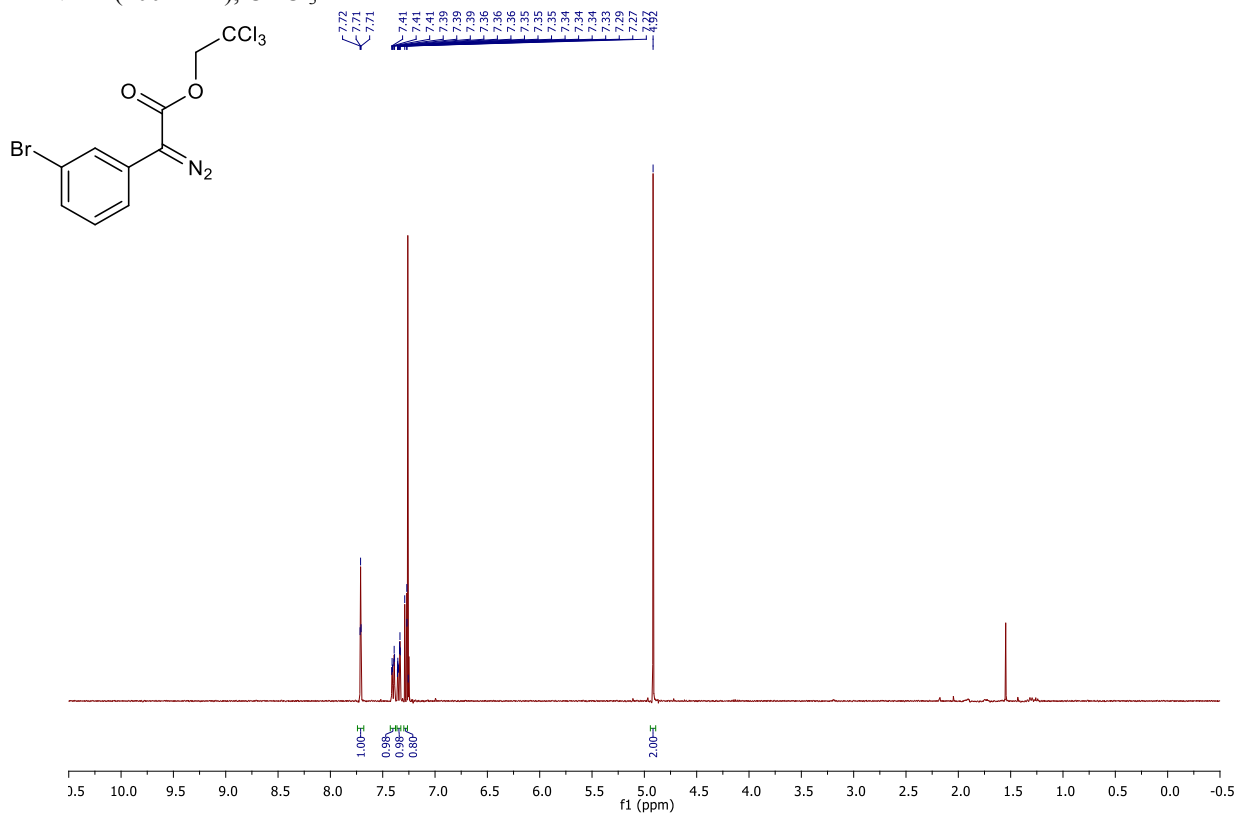
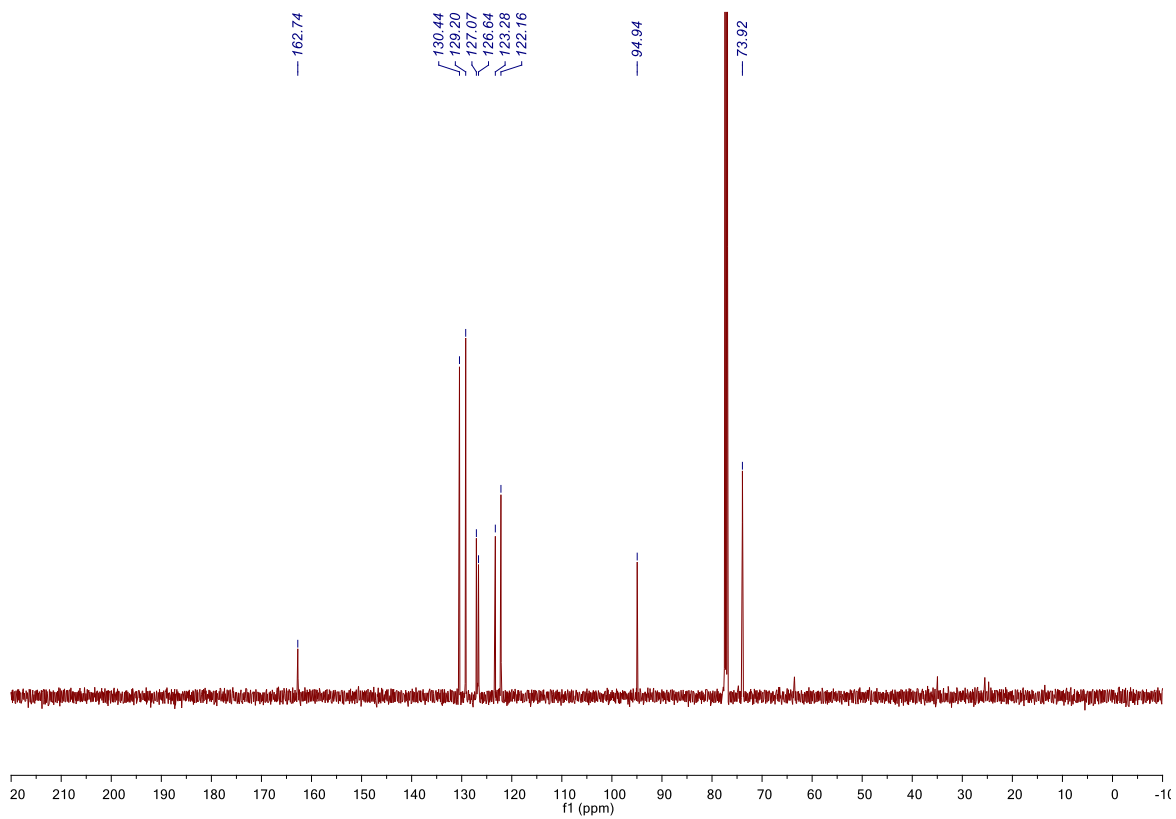
^1H NMR (400 MHz), CDCl_3



^{13}C NMR (100 MHz), CDCl_3

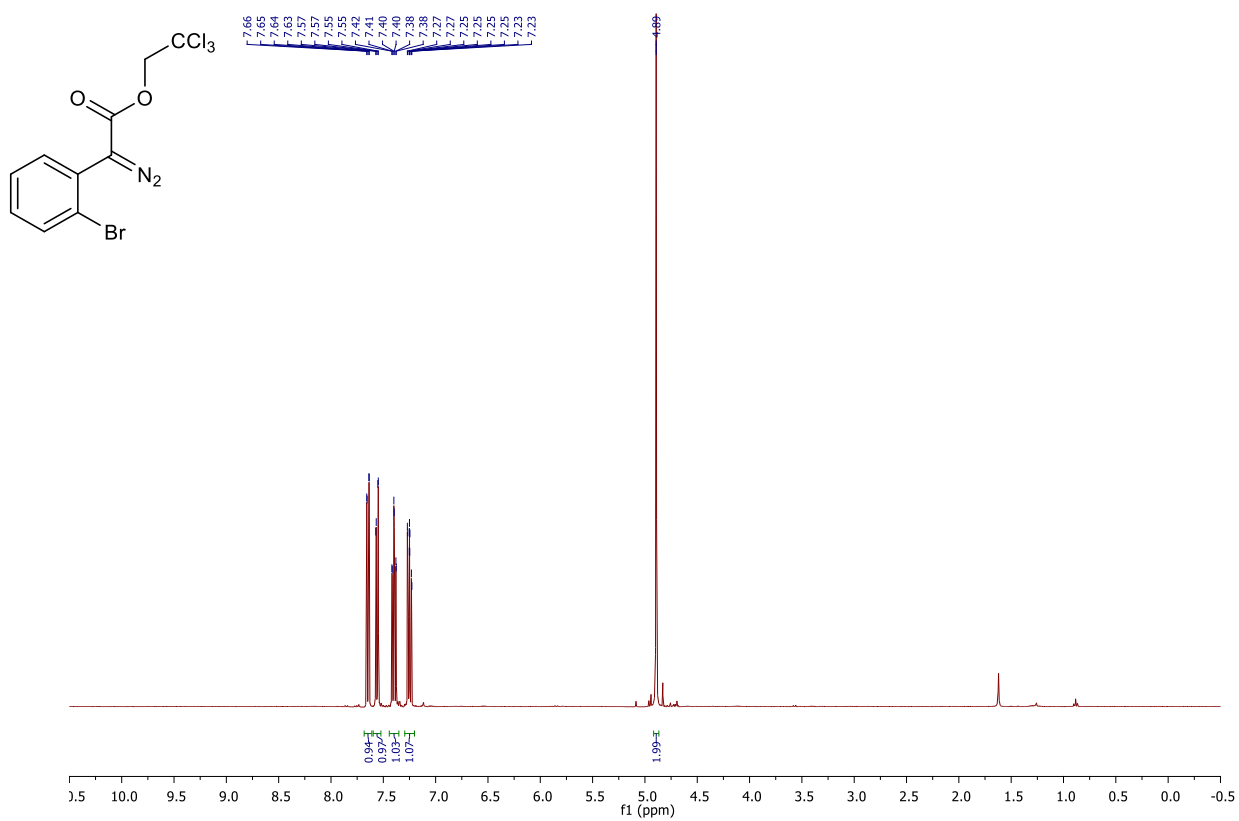


Diazo 1f

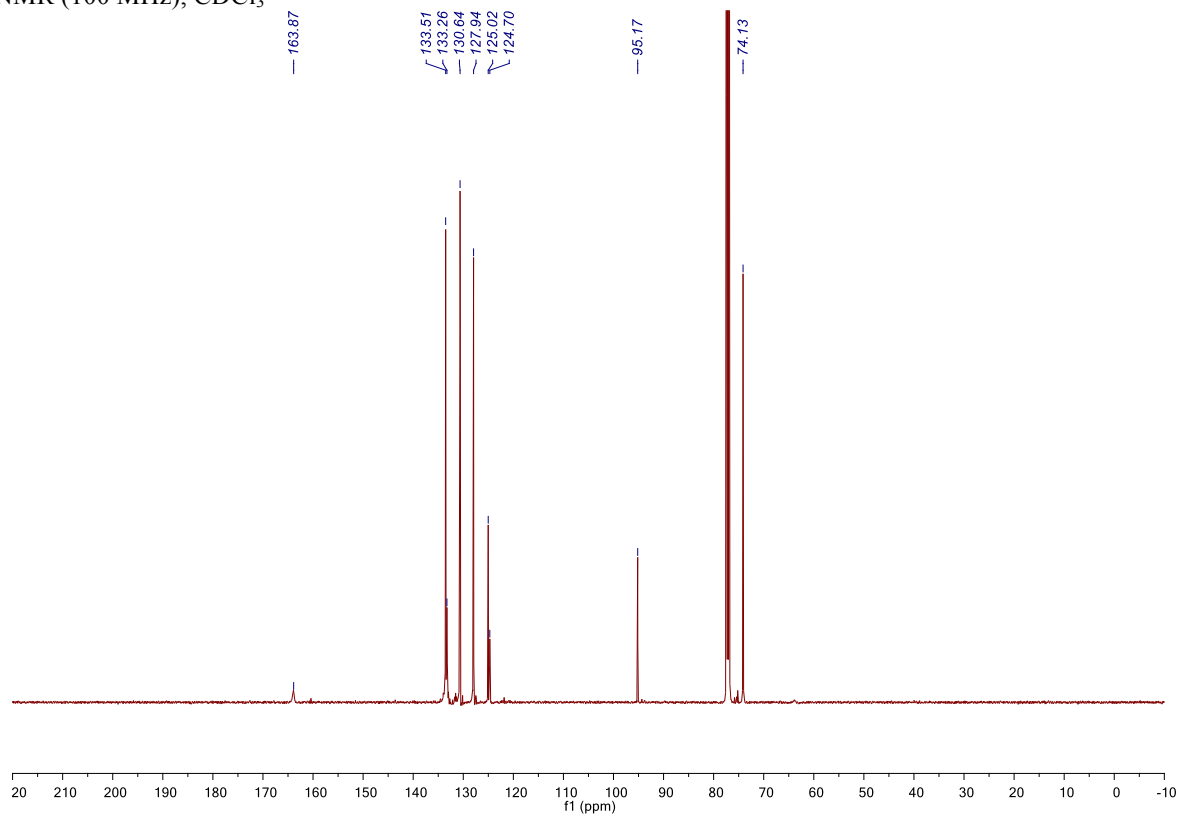
¹H NMR (400 MHz), CDCl₃ ^{13}C NMR (100 MHz), CDCl_3 

Diazo 1g

^1H NMR (400 MHz), CDCl_3



^{13}C NMR (100 MHz), CDCl_3



9. References

1. Baum, J. S.; Shook, D. A.; Davies, H. M. L.; Smith, H. D., *Synthetic Communications* **1987**, *17* (14), 1709-1716.
2. (a) Guptill, D. M.; Davies, H. M. L., *J. Am. Chem. Soc.* **2014**, *136* (51), 17718-17721; (b) Bess, E. N.; Guptill, D. M.; Davies, H. M. L.; Sigman, M. S., *Chem Sci* **2015**, *6* (5), 3057-3062.
3. Brodsky, B. H.; Du Bois, J., *Org. Lett.* **2004**, *6* (15), 2619-2621.
4. Davies, H. M. L.; Hansen, T., *J. Am. Chem. Soc.* **1997**, *119* (38), 9075-9076.