Electronic supplementary information

A Half-Sandwich 1,2-Azaborolyl Ruthenium Complex: Synthesis, Characterization, and Preliminary Evaluation of Its Catalytic Activities

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General Remarks

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox unless otherwise stated. Solvents were distilled under nitrogen from sodium (*n*-hexane, ether, THF, dioxane, toluene), or calcium hydride ($CHCl_3$, DCE). The starting materials such as $RuCl_2(PPh_3)_3$,[1] $RuHCl(PPh_3)_3$,[2] 1,2-azaborole **LH-1**,[3] and lithium 1,2-azaborolide **L-1**[3] were prepared according to the literature. All other reagents were used as purchased from commercial suppliers and used without further purification.

Thin layer chromatography (TLC) was performed on Huanghai precoated glass-backed TLC plates and visualized by UV lamp (254 nm). Silica gel column chromatography (300~400 mesh) was carried out using analytical grade *n*-hexane and ethyl acetate or ether. All the NMR spectra were recorded with a Bruker AV400 or a Bruker AV500 spectrometer. Chemical shifts are given in ppm with reference to the residual solvent resonance of the deuterated solvents for ^1H NMR and ^{13}C NMR, and 85% H_3PO_4 and $BF_3{\cdot}Et_2O$ as the external standard for ^{31}P NMR and ^{11}B NMR, respectively. Mass spectra were recorded by Bruke Dalton Esquire 3000 plus or Agilent 5973 MS detector. Elemental analyses data were obtained on an Elementar Analysensysteme GmbH Vario EL III instrument.

Procedures

Syntheses of Half-Sandwich Ab Ruthenium Complexes

(η^5-1-*t*-Bu-2-PhC≡C-Ab)RuCl(PPh_3)$_2$ (1): Method A: A mixture of $RuCl_2(PPh_3)_3$ (796 mg, 0.83 mmol) and lithium 1,2-azaborolide **L-1** (211 mg, 0.92 mmol) in toluene (25 mL) was stirred at room temperature for 1 h to give a dark orange solution, which was filtered to remove LiCl. The filtrate was concentrated to *ca.* 1 mL and *n*-hexane (10 mL) was added to give a yellow precipitate, which was collected by filtration, washed with diethyl ether/*n*-hexane (1:5) (3×8 mL), and dried under vacuum; yield: 570 mg (78 %). **Method B:** A solution of complex **2** (399 mg, 0.47 mmol) in chloroform (10 mL) was stirred at room temperature for 30 min to give a yellow solution. The volatiles were removed under vacuum, and the residue was washed with cool *n*-hexane (3×5 mL) and dried under vacuum to give complex **1** as a yellow powder; yield: 345 mg (83%). **Method C:** To a solution of $RuCl_2(PPh_3)_3$ (499 mg, 0.52 mmol) in toluene (15 mL) was added 1,2-azaborole **LH-1** (152 mg, 0.68 mmol) and NEt_3 (131 μL, 0.94 mmol). The reaction mixture was refluxed at 130 ^oC for 8 h to give an orange solution accompanied with formation of a white precipitate of $Et_3N{\cdot}HCl$, which was then filtered. The filtrate was concentrated to *ca.* 1 mL and *n*-hexane (10 mL) was added to give a yellow precipitate, which was collected by

filtration, washed with diethyl ether/*n*-hexane (1:5) (3×5 mL), and dried under vacuum; yield: 320 mg (70 %). **Method D:** To a solution of $RuHCl(PPh_3)_3$ (499 mg, 0.54 mmol) in toluene (15 mL) was added 1,2-azaborole **LH-1** (156 mg, 0.70 mmol). The reaction mixture was stirred at 90 ^oC for 6 h to give an orange solution. The volume of the solution was reduced to *ca.* 1 mL under vacuum. Addition of *n*-hexane (10 mL) to the residue gave a yellow precipitate, which was collected by filtration, washed with diethyl ether/*n*-hexane (1:5) (3×5 mL), and dried under vacuum; yield: 362 mg (76 %). ^{11}B NMR (128.4 MHz, $CDCl_3$): δ5.2 (br). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 49.7 (d, *J*(PP) = 33.4 Hz, Ru*P*Ph_3), 36.4 (d, *J*(PP) = 33.4 Hz, Ru*P*Ph_3). ^1H NMR (500.1 MHz, $CDCl_3$): δ 7.68 (br, 6 H, P*Ph*$_3$), 7.42 (t, ^3J(HH) = 8.8 Hz, 6 H, P*Ph*$_3$), 7.16 (m , 9 H, P*Ph*$_3$, *Ph*), 7.06 (t, ^3J(HH) = 7.1 Hz, 12 H, P*Ph*$_3$), 7.02 (br ,6 H, P*Ph*$_3$), 6.82 (d, ^3J (HH) = 7.0 Hz, 2 H, *Ph*), 6.32 (unresolved dt (brs in $^1H\{^{31}P\}$ spectrum), ^3J(PH) = 3.8 Hz, ^3J(HH) = 1.6 Hz, 1 H, 5-C*H*), 4.88 (brs (unresolved dd in $^1H\{^{31}P\}$ spectrum), ^3J(HH) = 3.8 Hz, 1.6 Hz, 1 H, 4-C*H*), 1.56 (d, ^3J(HH) = 3.8 Hz, 1 H, 3-C*H*), 1.04 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 137.0 (d, *J* (PC) = 43.6 Hz, *ipso*-P*Ph*$_3$), 136.0 (br, *ipso*-P*Ph*$_3$), 133.8 (d, *J*(PC) = 9.4 Hz, *ortho*-P*Ph*$_3$), 131.1 (s, Ph), 128.7 (br, *para*-P*Ph*$_3$, *Ph*), 127.9 (s, *Ph*), 127.8 (s, *Ph*), 127.5 (d, *J*(PC) = 9.6 Hz, *meta*-P*Ph*$_3$), 126.8 (d, *J*(PC) = 8.9 Hz, *meta*-P*Ph*$_3$), 124.4 (s, *ipso*-*Ph*C≡C), 108.6 (s, BC≡*C*Ph), 98.8 (br, B*C*≡CPh), 90.7 (d, *J*(PC) = 9.6 Hz, 5-*C*), 89.0 (d, *J*(PC) = 3.4 Hz, 4-*C*), 61.0 (br, 3-*C*), 59.4 (s, *C*(CH$_3$)$_3$), 30.8 (s, C(*C*H$_3$)$_3$). Anal. Calcd. for $C_{51}H_{47}BClNP_2Ru$: C, 69.35; H, 5.36; N, 1.59. Found: C, 69.08; H, 5.75; N, 1.56.

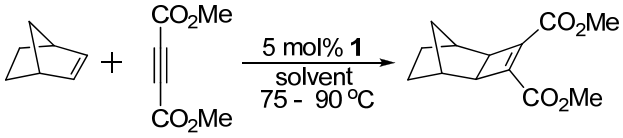
(η^5-1-*t*-Bu-2-PhC≡C-Ab)RuH(PPh$_3$)$_2$ (2): A mixture of $RuHCl(PPh_3)_3$ (767 mg, 0.83 mmol) and lithium 1,2-azaborolide **L-1** (211 mg, 0.92 mmol) in toluene (20 mL) was stirred at room temperature for 30 min. The original purple suspension changed to an orange solution, which was filtered to remove the LiCl solid. The filtrate was concentrated to *ca.* 1 mL. Addition of *n*-hexane (8 mL) to the residue led to the formation of an orange precipitate, which was collected by filtration, washed with diethyl ether/*n*-hexane (1:5) (3 × 8 mL), and dried under vacuum; yield: 567 mg (80%). ^{11}B NMR (128.4 MHz, C_6D_6): δ 8.3 (br). ^{31}P NMR (202.4 MHz, C_6D_6, 298 K): δ 59.5 (br, Ru*P*Ph_3), 61.8 (br, Ru*P*Ph_3). ^1H NMR (500.1 MHz, C_6D_6): δ 7.66 (m, 6 H, P*Ph*$_3$), 7.56 (t, 6 H, P*Ph*$_3$), 7.15 (br, 3 H, *Ph*), 6.94 (m, 20 H, P*Ph*$_3$, *Ph*), 5.33 (brs, 1 H, 4-C*H*), 4.55 (brs, 1 H, 5-C*H*), 4.06 (brs, 1 H, 3-C*H*), 1.24 (s, 9 H, *t*-Bu), -16.90 (brs, 1 H, Ru-*H*). ^{13}C NMR (125.7 MHz, C_6D_6): δ 141.8 (d, *J*(PC) = 34.7 Hz, *ipso*-P*Ph*$_3$), 140.7 (d, *J*(PC) = 38.3 Hz, *ipso*-P*Ph*$_3$), 134.7 (d, *J*(PC) = 11.8 Hz, *ortho*-P*Ph*$_3$), 131.6 (s, *Ph*), 128.3-128.2 (m, P*Ph*$_3$, *Ph*), 125.8 (s, *ipso*-*Ph*C≡C), 106.9 (s, BC≡*C*Ph), 99.6 (br, B*C*≡CPh), 96.1 (br, 4-*C*), 82.7 (br, 5-*C*), 74.3 (br, 3-*C*), 56.5 (s, *C*(CH$_3$)$_3$), 31.4 (s, C(*C*H$_3$)$_3$). **Characteristic NMR data at 348 K**, ^{31}P NMR (162.0 MHz, toluene-d_8, 348 K): δ 62.3 (d (unresolved), J(PP) = 15.7 Hz, Ru*P*Ph_3), 65.6 (br, Ru*P*Ph_3). ^1H

NMR (400.1 MHz, toluene-d_8, 348 K): δ 5.16 (d (unresloved), J(HH) = 4.0 Hz, 1 H, 4-C*H*), 4.48 (brs, 1 H, 5-C*H*), 3.88 (d (unresloved), J(HH) = 4.0 Hz, 1 H, 3-C*H*), 1.20 (s, 9 H, *t*-Bu), -16.68 (brs, 1 H, Ru-*H*). **Characteristic NMR data at 228 K**, two sets of signals in about a ration of 10:1 are observed, **Major isomer:** ^{31}P NMR (162.0 MHz, toluene-d_8, 228 K): δ 60.6 (d, *J*(PP) = 15.1 Hz, Ru*P*Ph$_3$), 63.1 (d, *J*(PP) = 15.1 Hz, Ru*P*Ph$_3$). ^{1}H NMR (400.1 MHz, toluene-d_8, 228 K): 5.51 (brs, 1 H, 4-C*H*), 4.46 (brs, 1 H, 5-C*H*), 3.91 (brs, 1 H, 3-C*H*), 1.23 (s, 9 H, *t*-Bu), -17.05 (dd, *J*(PH) = 36.5, 28.0 Hz, 1 H, Ru-*H*). **Minor isomer:** ^{31}P NMR (162.0 MHz, toluene-d_8, 228 K): δ 65.8 (d, *J*(PP) = 22.0 Hz, Ru*P*Ph$_3$), 76.4 (d, *J*(PP) = 22.0 Hz, Ru*P*Ph$_3$). ^{1}H NMR (400.1 MHz, toluene-d_8, 228 K): 5.10 (brs, 2 H, 4, 5-C*H*), 4.38 (brs, 1 H, 3-C*H*), 0.98 (brs, 9 H, *t*-Bu), -11.18 (t, *J*(PH) = 32.8 Hz, 1 H, Ru-*H*). Anal. Calcd. for $C_{51}H_{48}BNP_2Ru$: C, 72.17; H, 5.70; N, 1.65. Found: C, 71.84; H, 5.72; N, 1.64.

[2+2] Cycloadditions of Norbornene Derivatives 3 with DMAD 4 Catalyzed by Complex 1

Solvents screening: Several solvents such as dioxane, THF, DCE, toluene, and *n*-hexane were firstly screened in the model reaction of **3a** with **4** in the presence of 5 mol% of complex **1** (Table S1). The reaction in dioxane at 90 °C for 12 h proved to be most effective, which afforded the desired product **5a** in 86% yield.

Table S1. Solvents screening.[a]



3a **4** **5a**

Entry	Solvent	T [°C]	Yield [%][b]
1	dioxane	90	86
2	THF	90	80
3	DCE[c]	75	38
4	toluene	90	25
5	*n*-hexane	90	4

[a]Experimental conditions: Norbornene **3a** (1.20 mmol), DMAD **4** (0.40 mmol), precatalyst **1** (0.02 mmol), solvent (3.0 mL), at 90 °C for 12 h. [b]Isolated yield. [c]DCE = 1,2-dichloroethane.

General Procedure: A solution of complex **1** (18 mg, 0.02 mmol) in dioxane (1 mL) was stirred for 10 min in a Schlenk tube. A solution of norbornene derivatives **3** (1.20 mmol) and DMAD **4** (57 mg, 49 μL, 0.40 mmol) in dioxane (2 mL) was added, and the mixture was heated at 90 °C for 5-12 h. The reaction was monitored by TLC until complete consumption of **4**. Then the solvent was removed under vacuum and the

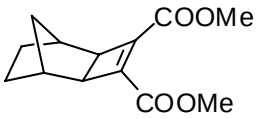
residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane as eluent) to give the corresponding products **5**.

ATRA Reaction Catalyzed by Complex 1

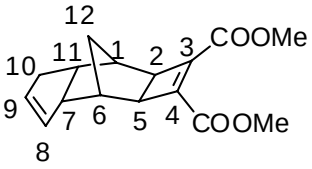
General Procedure: A solution of complex **1** (11.5-68.0 mg, 0.013-0.077 mmol), olefins **6** (3.84 mmol) and chlorine species **7** (11.52-19.20 mmol) in toluene (2 mL) was stirred in a sealed Schlenk tube at room temperature to 90 °C for 3-48 h. The reaction was monitored by TLC until complete consumptions of olefins **6**. The solvent was then concentrated and the residue was purified by silica gel column chromatography (ether/*n*-hexane as eluent) to yield the corresponding adducts **8**.

Characterization of organic products in the catalytic reactions

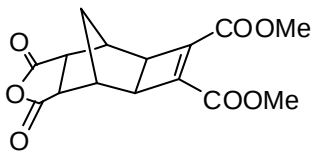
[2+2] Cycloadditions of Norbornene Derivatives 3 with DMAD 4



5a[4]**:** colorless liquid (EA/*n*-hexane = 1/10 as eluant). Yield: 81 mg, 86%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.77 (s, 6 H, OCH_3), 2.66 (s, 2 H, C*H*-*endo*-cyclobutene), 2.24 (t, app. s, br, 2 H, C*H*-bridgehead), 1.60 (m, 2 H, CH*H*-*endo*), 1.31 (dt, app. d, *J*(HH) = 10.8 Hz, 1 H, C*H*-bridge), 1.11 (m, 2 H, C*H*H-*exo*), 1.06 (dt, *J*(HH) = 10.8, 1.2 Hz, 1 H, C*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ161.8, 142.3, 51.9, 47.5, 33.9, 30.5, 27.9. MS (ESI) *m/z* (%): 259 (100) (*M*+Na^+).



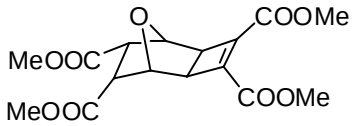
5b[5]**:** colorless liquid (EA/*n*-hexane = 1/10 as eluant). Yield: 103 mg, 94%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ5.64 (m, 1 H, 8-C*H*), 5.54 (m, 1 H, 9-C*H*), 3.76 (s, 6 H, OCH_3), 3.18 (m, 1 H, 7-C*H*), 2.79 (d, *J*(HH) = 3.4 Hz, 1 H, C*H*-*endo*-cyclobutene), 2.70 (m, 2 H, C*H*-*endo*-cyclobutene, 11-C*H*), 2.36 (dd, *J*(HH) = 5.1, 1.3 Hz, 1 H, C*H*-bridgehead), 2.26 (m, 2 H, 10-CH_2), 2.23 (d, *J*(HH) = 4.7 Hz, 1 H, C*H*-bridgehead), 1.46 (dt, app. d, *J*(HH) = 10.8 Hz, 1 H, C*H*-bridge), 1.29 (dt, app. d, *J*(HH) = 10.8, 1.2 Hz, 1 H C*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ161.69, 161.67, 142.7, 141.5, 131.8, 130.8, 52.3, 51.9, 44.4, 41.7, 41.4, 37.7, 35.9, 34.0, 31.3. MS (ESI) *m/z* (%): 297 (3.4) (*M*+Na^+).



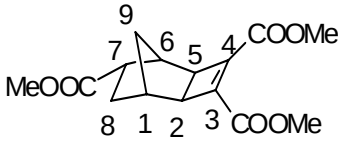
5c[6]**:** white solid (EA/*n*-hexane = 1/1 as eluant). Yield: 103 mg, 84%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.79 (s, 6 H, OCH_3), 3.54 (dd, *J*(HH) = 3.6, 2.1 Hz, 2 H, C*H*-*exo*), 2.99 (s, 2 H, C*H*-*endo*-cyclobutene), 2.24 (dd, app. d, *J*(HH) =

1.4 Hz, 2 H, C*H*-bridgehead), 1.82 (d, *J*(HH) = 11.6 Hz, C*H*-bridge), 1.51 (d, *J*(HH) = 11.6 Hz, CHH-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.8, 160.6, 141.2, 52.3, 48.6, 42.4, 37.4, 34.6. MS (ESI) *m/z* (%): 329 (1.8) (*M*+Na^+).

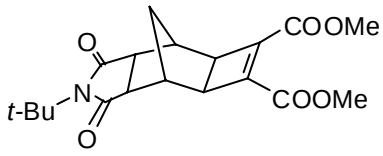
5d[4]**:** white solid (EA/*n*-hexane = 1/5 as eluant). Yield: 120 mg, 85%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.75 (s, 6 H, OCH_3-cyclobutene), 3.64 (s, 6 H, OCH_3-norbornene), 3.33 (s, 2 H, C*H*-*endo*-cyclobutene), 3.11 (t, *J*(HH) = 2.0 Hz, 2 H, C*H*-*exo*), 2.63 (s, br, 2 H, C*H*-bridgehead), 1.62 (dt, app. d, *J*(HH) = 11.4 Hz, 1 H, C*H*-bridge), 1.06 (dt, app. d, *J*(HH) = 11.4, 1.2 Hz, 1 H, C*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 172.0, 161.4, 141.7, 52.0, 51.7, 45.8, 42.2, 37.4, 31.8. MS (ESI) *m/z* (%): 375 (100) (*M*+Na^+).



5e[4]**:** white solid (EA/*n*-hexane = 1/1 as eluant). Yield: 135 mg, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.76 (s, 2 H, C*H*-bridgehead), 3.78 (s, 6 H, OCH_3-cyclobutene), 3.66 (s, 6 H, OCH_3-oxanorbornene), 2.97 (s, 2 H, C*H*-*endo*-cyclobutene) 2.89 (s, 2 H, C*H*-*exo*). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.8, 160.7, 141.2, 75.3, 52.4, 52.2, 50.7, 46.6. MS (ESI) *m/z* (%): 377 (100) (*M*+Na^+).

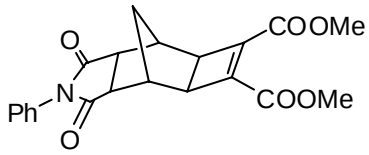


5f: colorless liquid (EA/*n*-hexane = 1/3 as eluant). Yield: 112 mg, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.774 (s, 3 H, OCH_3), 3.771 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 2.88 (dt, *J*(HH) = 11.2, 4.8 Hz, 1 H, 7-C*H*), 2.79 (m, 2 H, C*H*-*endo*-cyclobutene), 2.61 (d, 1 H, *J*(HH) = 4.3 Hz, C*H*-bridgehead), 2.34 (d, 1 H, *J*(HH) = 4.3 Hz, C*H*-bridgehead), 1.84 (ddd, *J*(HH) = 12.6, 11.4, 4.7 Hz, 1 H, *endo*-8-C*H*H), 1.61 (m, 1 H, *exo*-8-CH*H*), 1.49 (dt, app. d, *J*(HH) = 11.1 Hz, 1 H, CH-bridge), 1.25 (dt, *J*(HH) = 11.1, 1.2 Hz, 1 H, C*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 174.5, 161.6, 161.5, 142.0, 141.7, 52.0(2), 51.9, 46.8, 45.1, 43.4, 37.7, 34.3, 32.2, 30.3. MS (ESI) *m/z* (%): 317 (100) (*M*+Na^+). Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16. Found: C, 61.41; H, 6.23.

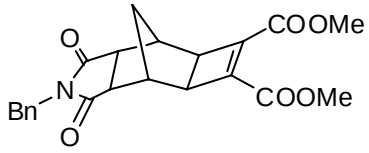


5g: white solid (EA/*n*-hexane = 1/2 as eluant). Yield: 128 mg, 89%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.76 (s, 6 H, OCH_3), 3.04 (dd, *J*(HH) = 3.5, 2.0 Hz, 2 H, C*H*-*exo*), 2.84 (s, 2 H, C*H*-*endo*-cyclobutene), 2.79 (q, *J*(HH) = 1.6 Hz, 2 H, C*H*-bridgehead), 1.69 (dt, app. d, *J*(HH) = 11.4 Hz, C*H*H-bridge), 1.55 (s, 9 H, C(CH_3)$_3$), 1.40 (dt, *J*(HH) = 11.4, 1.2 Hz, CHH-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 178.2, 160.9, 141.3, 58.9, 52.1, 47.0, 42.6, 36.8,

33.9, 28.6. MS(ESI) *m/z* (%): 384 (100) (*M*+Na^+). Anal. Calcd. for $C_{19}H_{23}NO_6$: C, 63.15; H, 6.41; N, 3.88. Found: C, 63.48; H, 6.67; N, 3.56.

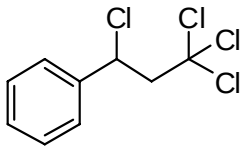


5h: white solid (EA/*n*-hexane = 1/3 as eluant). Yield: 145 mg, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.45 (m, 3 H, Ph), 7.22 (m, 2 H, Ph), 3.78 (s, 6 H, OC*H*$_3$), 3.40 (dd, *J*(HH) = 3.5, 2.0 Hz, 2 H, C*H*-*exo*), 3.01 (s, 2 H, C*H*-*endo*-cyclobutene), 2.96 (q, *J*(HH) = 1.5 Hz, 2 H, C*H*-bridgehead), 1.83 (d, *J*(HH) = 11.5 Hz, C*H*H-bridge), 1.55 (d, *J*(HH) = 11.5 Hz, CH*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 176.0, 160.8, 141.3, 131.7, 129.4, 129.0, 126.7, 52.2, 47.6, 42.7, 36.8, 34.4. MS (ESI) *m/z* (%): 404 (100) (*M*+Na^+). Anal. Calcd. for $C_{21}H_{19}NO_6$: C, 66.13; H, 5.02; N, 3.67. Found: C, 65.94; H, 5.31; N, 3.72.

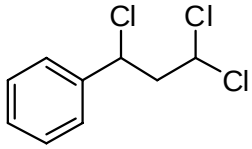


5i: white solid (EA/*n*-hexane = 1/3 as eluant). Yield: 134 mg, 85%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.40 (dd, app. d, *J*(HH) = 4.0 Hz, 2 H, Ph), 7.29 (m, 3 H, Ph), 4.61 (s, 2 H, C*H*$_2$Ph), 3.75 (s, 6 H, OC*H*$_3$), 3.21 (dd, *J*(HH) = 3.3, 1.9 Hz, 2 H, C*H*-*exo*), 2.82 (q, *J*(HH) = 1.3 Hz, 2 H, C*H*-bridgehead), 2.54 (s, 2 H, C*H*-*endo*-cyclobutene),1.71 (d, *J*(HH) = 11.4 Hz, C*H*H-bridge), 1.44 (d, *J*(HH) = 11.4 Hz, CH*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 176.6, 160.8, 141.1, 135.9, 129.1, 128.8, 128.3, 52.1, 47.5, 42.4(2), 36.4, 34.4. MS (ESI) *m/z* (%): 418 (100) (*M*+Na^+). Anal. Calcd. for $C_{22}H_{21}NO_6$: C, 66.83; H, 5.35; N, 3.54. Found: C, 66.87; H, 5.19; N, 3.39.

ATRA Reactions Catalyzed by Complex 1

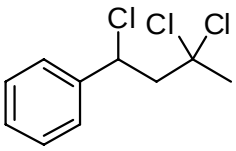


8aa[7]**:** obtained from the reaction of styrene **6a** (400 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.10 mL, 1.77 g, 11.52 mmol) in the presence of complex **1** (11.5 mg, 0.013 mmol) at room temperature for 3 h, colorless liquid (*n*-hexane as eluant), yield: 914 mg, 93%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.45 (m, 2 H, Ph), 7.38 (m, 3 H, Ph), 5.32 (t, *J*(HH) = 6.0 Hz, 1 H, C*H*Cl), 3.64 (dd, *J*(HH) = 15.4, 5.5 Hz, 1 H, C*H*H), 3.56 (dd, *J*(HH) = 15.4, 6.6 Hz, 1 H, C*H*H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 140.5, 129.0 (br, 2 C), 127.5, 96.3, 62.8, 58.4. MS (EI) *m/z* (%): 258 (*M*$^+$).

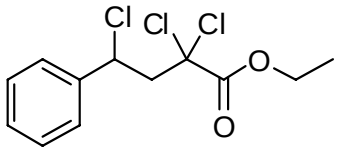


8ab[8]**:** obtained from the reaction of styrene **6a** (400 mg, 3.84 mmol) with chloroform **7b** (1.54 mL, 2.29 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 60 °C for 24 h, colorless liquid (*n*-hexane as eluant), yield: 755 mg, 88%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.40 (m, 5 H, Ph), 5.83 (dd, *J*(HH) = 7.0, 5.2 Hz, 1 H,

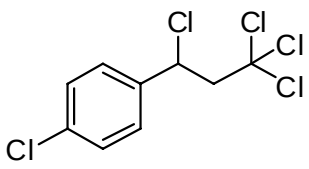
C*H*Cl_2), 5.10 (dd, *J*(HH) = 8.7, 5.0 Hz, 1 H, C*H*Cl), 3.00 (m, 1 H, C*H*H), 2.81 (m, 1 H, C*H*H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 139.5, 129.0 (2 C), 127.1, 70.4, 59.5, 52.8. MS (EI) *m/z* (%): 152 (M^+-Cl_2).



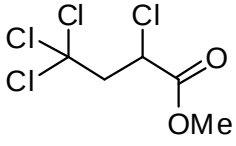
8ac[9]**:** obtained from the reaction of styrene **6a** (400 mg, 3.84 mmol) with 1,1,1-trichloroethane **7c** (1.75 mL, 2.56 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 5 h, colorless liquid (*n*-hexane as eluant), yield: 848 mg, 93%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.44 (m, 2 H, Ph), 7.39 (m, 2 H, Ph), 7.34 (m, 1 H, Ph), 5.27 (t, *J*(HH) = 6.1 Hz, 1 H, C*H*Cl_2), 3.19 (dd, *J*(HH) = 15.3, 6.4 Hz, 1 H, C*H*H), 3.12 (dd, *J*(HH) = 15.3, 5.7 Hz, 1 H, CH*H*), 2.11 (s, 3 H, CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 141.4, 129.0, 128.9, 127.2, 88.1, 59.1, 58.5, 37.7. MS (EI) *m/z* (%): 236 (M^+).



8ad[7]**:** obtained from the reaction of styrene **6a** (400 mg, 3.84 mmol) with ethyl trichloroacetate **7d** (3.68 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077mmol) at 85 °C for 5 h, colorless liquid (*n*-hexane/ether = 1/4 as eluant), yield: 965 mg, 85%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.41 (m, 2 H, Ph), 7.36 (m, 3 H, Ph), 5.23 (dd, *J*(HH) = 7.7, 6.0 Hz, 1 H, C*H*Cl), 4.13 (qd, *J*(HH) = 10.7, 7.1 Hz, 1 H, OC*H*H), 4.07 (qd, *J*(HH) = 10.7, 7.1 Hz, 1 H, OCH*H*), 3.45 (dd, *J*(HH) = 15.3, 6.4 Hz, 1 H, C*H*Cl), 3.21 (dd, *J*(HH) = 15.1, 6.0 Hz, 1 H, C*H*H), 1.30 (s, 3 H, CH_8H_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 165.1, 139.8, 129.0, 128.9, 127.5, 82.4, 64.2, 58.7, 54.0, 13.8. MS (EI) *m/z* (%): 294 (M^+).

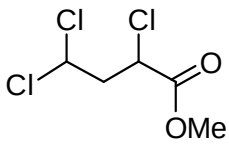


8ba[7]**:** obtained from the reaction of 4-chlorostyrene **6b** (484 μL, 532 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.10 mL, 1.77 g, 11.52 mmol) in the presence of complex **1** (11.5 mg, 0.013 mmol) at room temperature for 4 h, colorless liquid (*n*-hexane as eluant), yield: 1068 mg, 95%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.37 (m, 4 H, Ph), 5.28 (dd, *J*(HH) = 7.2, 5.2 Hz,1 H, C*H*Cl), 3.60 (dd, *J*(HH) = 15.4, 5.1 Hz, 1 H, CH*H*), 3.50 (dd, *J*(HH) = 15.4, 6.7 Hz, 1 H, CH*H*). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 138.9, 134.9, 129.2, 129.0, 96.0, 62.7, 57.5. MS (EI) *m/z* (%): 292 (M^+).

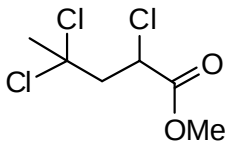


8ca [10]**:** obtained from the reaction of methyl acrylate **6c** (330 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.10 mL, 1.77 g, 11.52 mmol) in the presence of complex **1** (33.6 mg, 0.038 mmol) at 85

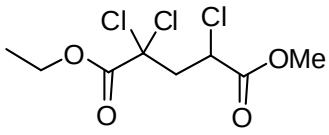
°C for 3 h, colorless liquid (*n*-hexane/ether = 1/20 as eluant), yield: 737 mg, 80%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 4.61 (dd, *J*(HH) = 8.1, 3.8 Hz, 1 H, C*H*Cl), 3.82 (s, 3 H, OCH_3), 3.22 (dd, *J*(HH) = 15.6, 8.0 Hz, 1 H, CH*H*), 3.76 (dd, *J*(HH) = 15.6, 3.7 Hz, 1 H, C*H*H), ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.8, 95.5, 58.3, 53.6, 51.5. MS (EI) *m/z* (%): 240 (M^+).



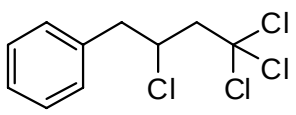
8cb[8]**:** obtained from the reaction of methyl acrylate **6c** (330 mg, 3.84 mmol) with chloroform **7b** (1.54 mL, 2.29 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 24 h, colorless liquid (*n*-heaxne /ether = 1/40 as eluant), yield: 521 mg, 66%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 5.92 (dd, *J*(HH) = 8.9, 4.4 Hz, 1 H, C*H*Cl_2), 4.52 (dd, *J*(HH) = 9.8, 5.6 Hz, 1 H, C*H*Cl), 3.83 (s, 3 H, OCH_3), 2.89 (ddd, *J*(HH) = 14.9, 8.8, 4.6 Hz, 1 H, C*H*H), 2.78 (ddd, *J*(HH) = 14.9, 9.6, 4.5 Hz, 1 H, CH*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ168.6, 69.5, 53.6, 53.5, 47.5. MS (EI) *m/z* (%): 205 (M^+).



8cc[9]**:** obtained from the reaction of methyl acrylate **6c** (330 mg, 3.84 mmol) with 1,1,1-trichloroethane **7c** (1.75 mL, 2.56 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 5 h, colorless liquid (*n*-hexane/ether = 1/50 as eluant), yield: 506 mg, 60%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.64 (dd, *J*(HH) = 7.8, 4.4 Hz, 1 H, C*H*Cl), 3.82 (s, 3 H, OCH_3), 3.27 (dd, *J*(HH) = 15.5, 7.6 Hz, 1 H, C*H*H), 3.05 (d, *J*(HH) = 15.5, 4.4 Hz, 1 H, CH*H*), 2.20 (s, 3 H, CCl_8H_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 169.6, 86.8, 53.6, 53.5, 52.3. MS (EI) *m/z* (%): 218 (M^+).

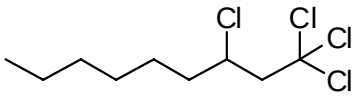


8cd[11]**:** obtained from the reaction of methyl acrylate **6c** (330 mg, 3.84 mmol) with ethyl trichloroacetate **7d** (3.68 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 24h, colorless liquid (*n*-hexane/ether = 1/100 as eluant), yield: 693 mg, 65%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.62 (dd, *J*(HH) = 7.3, 5.6 Hz, 1 H, CHCl), 4.30 (qd, *J*(HH) = 7.0, 0.9 Hz, 2 H, CH_8H_3), 3.82 (s, 3 H, OCH_3), 3.39 (dd, *J*(HH) = 15.3, 6.9 Hz, 1 H, C*H*HCCl_2), 3.41 (dd, *J*(HH) = 15.3, 5.7 Hz, 1 H, CH*H*CCl_2), 1.37 (t, *J*(HH) = 7.1 Hz, CH_8H_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 169.1, 165.1, 81.3, 64.5, 53.6, 52.1, 49.1, 13.9. MS (EI) *m/z* (%): 276 (M^+).

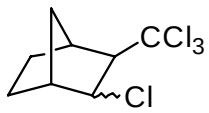


8da[12]**:** obtained from the reaction of allylbenzene **6d** (454 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.10 mL, 1.77

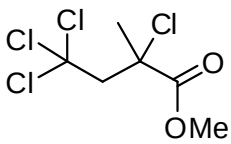
g, 11.52 mmol) in the presence of complex **1** (33.6 mg, 0.038 mmol) at 85 °C for 24 h, colorless liquid (*n*-hexane as eluant), yield: 762 mg, 73%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.36 (d, *J*(HH) = 2.3 Hz, 2 H, Ph), 7.29 (m, 3 H, Ph), 4.50 (m, 1 H, C*H*Cl), 3.30-3.24 (m, 3 H, CH_2Ph, C*H*HCCl$_3$), 3.16 ppm (dd, *J*(HH) = 14.4, 8.1 Hz, 1 H, CH*H*CCl$_3$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 136.7, 129.6, 128.9, 128.8, 127.4, 97.0, 61.2, 57.8, 45.4. MS (EI) *m/z* (%): 272 (M^+).



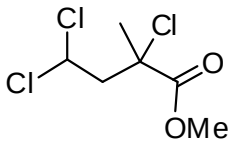
8ea[7]**:** obtained from the reaction of 1-octene **6e** (431 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.85 mL, 2.95 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 25 h, colorless liquid (*n*-hexane as eluant), yield: 625 mg, 72%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.26 (m, 1 H, C*H*Cl), 3.27 (dd, *J*(HH) = 15.7, 6.1 Hz, 1 H, C*H*HCCl$_3$), 3.27 (dd, *J*(HH) = 15.7, 4.2 Hz, 1 H, CH*H*CCl$_3$), 1.93 (m, 1 H, C*H*HCHCl), 1.84 (m, 1 H, CH*H*CHCl), 1.52 (m, 2 H, CH_2), 1.32 (m, 6 H, CH_2), 0.90 (t, *J*(HH) = 7.0 Hz, 3 H, CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 97.1, 62.4, 57.9, 39.2, 31.8, 28.7, 26.1, 22.7, 14.2. MS (EI) *m/z* (%): 266 (M^+).



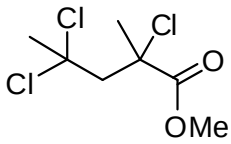
8fa [7]**:** obtained from the reaction of norbornene **6f** (362 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.85 mL, 2.95 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 25 h, colorless liquid (*n*-hexane as eluant), yield: 876 mg, 92%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.22 (m, 1 H, C*H*Cl), 2.65 (d, *J*(HH) = 3.0 Hz, 1 H, C*H*-bridgehead), 2.62 (dd, *J*(HH) = 5.8, 1.4 Hz, 1 H, C*H*-bridgehead), 2.53 (m, 1 H, C*H*CCl$_3$), 2.10 (d(quint), *J*(HH) = 10.9, 2.0 Hz, 1 H, C*H*H-bridge), 2.04 (m, 1 H, C*H*H-*endo*), 1.69 (m, 1 H, CH*H*-*endo*), 1.58 (m, 1 H, CH*H*-*exo*), 1.43 (m, 1 H, CH*H*-*exo*), 1.37 (dq, *J*(HH) = 10.9, 2.0 Hz, 1 H, C*H*H-bridge), 1.37 (dq, *J*(HH) = 10.9, 1.6 Hz, 1 H, CH*H*-bridge). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 101.4, 71.9, 63.4, 44.8, 42.3, 35.8, 30.6, 21.8. MS (EI) *m/z* (%): 211 [M^+-Cl].



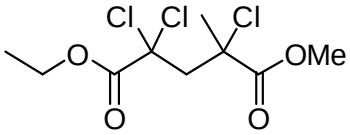
8ga[7]: obtained from the reaction of methyl methacrylate **6g** (384 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.10 mL, 1.77 g, 11.52 mmol) in the presence of complex **1** (11.5 mg, 0.013mmol) at room temperature for 3 h, colorless liquid (*n*-hexane/ether = 1/20 as eluant), yield: 702 mg, 72%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.97 (d, *J*(HH) = 15.4 Hz, 1 H, C*H*H), 3.80 (s, 3 H, OCH_3), 3.45 (d, *J*(HH) = 15.4 Hz, 1 H, CH*H*), 1.99 (s, 3 H, CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.2, 94.7, 64.7, 62.3, 53.6, 26.4. MS (EI) *m/z* (%): 254 (M^+).



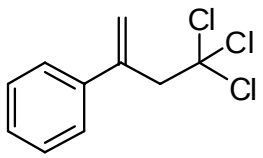
8gb[8]**:** obtained from the reaction of methyl methacrylate **6g** (384 mg, 3.84 mmol) with chloroform **7b** (1.54 mL, 2.29 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 24, colorless liquid (*n*-hexane/ether = 1/40 as eluant), yield: 657 mg, 78%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 5.99 (dd, *J*(HH) = 7.3, 5.2 Hz, 1 H, C*H*Cl$_2$), 3.80 (s, 3 H, OC*H*$_3$), 3.12 (dd, *J*(HH) = 15.0, 7.4 Hz, 1 H, C*H*H), 2.93 (dd, *J*(HH) = 15.0, 5.4 Hz, 1 H, CH*H*), 1.84 (s, 3 H, C*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.6, 69.0, 66.4, 54.4, 53.7, 29.1. MS (EI) *m/z* (%): 125 (*M*$^+$-Cl and CO_2Me).



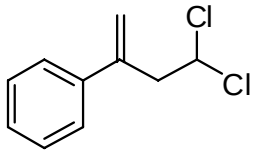
8gc[9]**:** obtained from the reaction of methyl methacrylate **6g** (384 mg, 3.84mmol) with 1,1,1-trichloroethane **7c** (1.75 mL, 2.56 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 12 h, colorless liquid (*n*-hexane/ether = 1/100 as eluant), yield: 628 mg, 70%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.80 (s, 3 H, OC*H*$_3$), 3.38 (d, *J*(HH) = 15.2 Hz, 1 H, C*H*H), 3.05 (d, *J*(HH) = 15.2 Hz, 1 H, CH*H*), 2.23 (s, 3 H, CHCl$_8$*H*$_3$), 1.99 (s, 3 H, CHClC*H*$_3$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.8, 86.0, 66.0, 58.1, 53.5, 39.0, 27.8. MS (EI) *m/z* (%): 232 (*M*$^+$).



8gd[11]**:** obtained from the reaction of methyl methacrylate **6g** (384 mg, 3.84 mmol) with ethyl trichloroacetate **7d** (3.68 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 12 h, colorless liquid (*n*-hexane/ether = 1/100 as eluant), yield: 739 mg, 66%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.30 (q, *J*(HH) = 7.2 Hz, 2 H, C*H*$_8$H$_3$), 3.77 (s, 3 H, OC*H*$_3$), 3.54 (d, *J*(HH) = 15.1 Hz, 1 H, C*H*HCCl$_2$), 3.41 (d, *J*(HH) = 15.1 Hz, 1 H, CH*H*CCl$_2$), 1.78 (s, 3 H, CHClC*H*$_3$), 1.33 (t, *J*(HH) = 7.1 Hz, CH$_8$*H*$_3$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.7, 165.4, 81.0, 65.4, 64.4, 53.6, 53.5, 28.0, 13.8. MS (EI) *m/z* (%): 290 (*M*$^+$).



9ha[13]**:** obtained from the reaction of α-methylstyrene **6h** (454 mg, 3.84 mmol) with carbon tetrachloride **7a** (1.85 mL, 2.95 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 85 °C for 15 h, colorless liquid (*n*-hexane/ether = 1/40 as eluant), yield: 651 mg, 72%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.42 (d, *J*(HH) = 7.6 Hz, 2 H, Ph), 7.36 (t, *J*(HH) = 7.6 Hz, 2 H, Ph), 7.30 (t, *J*(HH) = 7.3 Hz, 1 H, Ph), 5.64 (s, 1 H, =C*H*H), 5.51 (s, 1 H, =CH*H*), 3.91 (s, 2 H, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ141.9, 141.1, 128.5, 127.9, 126.8, 122.3, 98.3, 58.9. MS (EI) *m/z* (%): 234 (*M*$^+$).



9hb[14]**:** obtained from the reaction of α-methylstyrene **6h** (454 mg, 3.84 mmol) with chloroform **7b** (1.54 mL, 2.29 g, 19.20 mmol) in the presence of complex **1** (68 mg, 0.077 mmol) at 90 °C for 48 h, colorless liquid (*n*-hexane as eluant), yield: 540 mg, 70%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.37 (d, *J*(HH) = 4.4 Hz, 4 H, Ph), 7.32 (m, 1 H, Ph), 5.66 (t, *J*(HH) = 6.7 Hz, 1 H, C*H*Cl_2), 5.45 (d, app. s, 1 H, =CH*H*), 5.27 (d, *J*(HH) = 0.75 Hz, 1 H, C*H*H), 3.41 (d, *J*(HH) = 6.7 Hz, 2 H, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 142.8, 139.3, 128.5, 128.2, 126.4, 117.8, 71.3, 50.0. MS (EI) *m/z* (%): 200 (M^+).

X-Ray Crystallographic Analysis

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into the toluene solution for crystal **1**, and by slow diffusion of *n*-hexane into the ether solution for crystal **2**. The crystals of **5c** (Figure S1) and **5i** (Figure S2) suitable for X-ray diffraction analysis were grown from ethyl acetate solution layered with *n*-hexane. Data collections were performed on an Oxford CCD area detector using graphite-monochromated Mo Kα radiation (λ =0.71073 Å). Empirical absorption corrections (multiscan) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL-97 program package.[15] Non-H atoms were refined anisotropically. The metal-bound hydrido ligand of complex **2** could be located satisfactorily in a final difference Fourier synthesis with reasonable Ru-H bond distance and was refined with isotropic thermal parameter. The remaining hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Although compound **5c** crystallizes in the non-centrosymmetric space group $P2_1$， there is no significant anomalous scattering due to the absence of heavy atoms, so the Friedel pairs were merged in the final refinement and the absolute configuration was unknown. Details on crystal data, data collection, and refinements are summarized in Table S2. Selected bond lengths and bond angles for complexes **1** and **2** are shown in Tables S3 and S4. CCDC 908726 (**1**), 908727 (**2**), 908728 (**5c**) and 908729 (**5i**) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

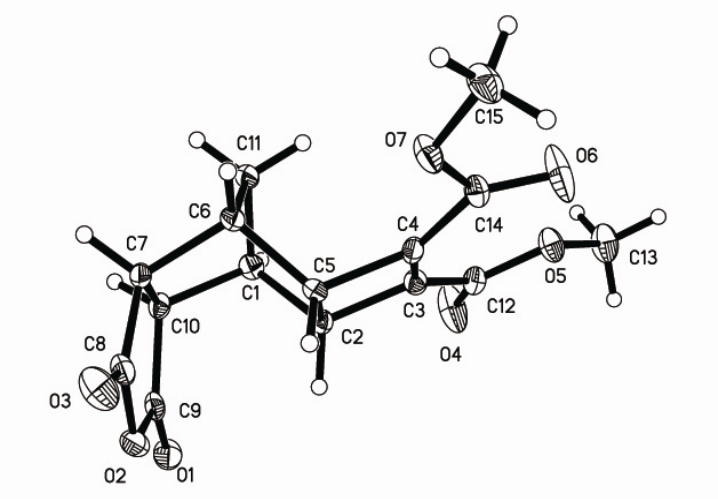


Figure S1. Molecular structure for cycloadduct **5c**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C2-C3 1.515(3), C3-C4 1.349(4), C4-C5 1.510 (3), C5-C2 1.581(3); C5-C2-C3 85.66(17), C2-C3-C4 94.1(2), C3-C4-C5 94.7(2), C4-C5-C2 85.54(18). CCDC 908728

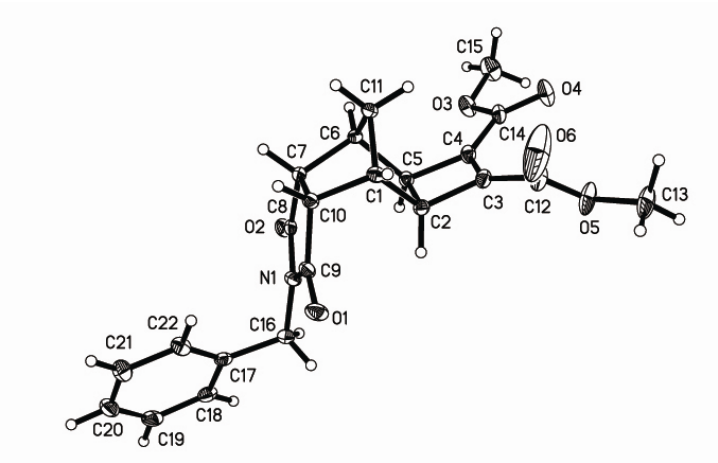


Figure S2. Molecular structure for cycloadduct **5i**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C2-C3 1.507(3), C3-C4 1.335(4), C4-C5 1.516 (3), C5-C2 1.580(3),; C5-C2-C3 85.74(18), C2-C3-C4 94.6(2), C3-C4-C5 94.7(2), C4-C5-C2 84.95(18). CCDC 908729

Table S2. Crystallographic Details for complex **1** and **2**, **5c** and **5i**.

complex	**1**	**2**	**5c**	**5i**
empirical formula	$C_{58}H_{55}BClNP_2Ru$	$C_{51}H_{48}BNP_2Ru$	$C_{15}H_{14}O_7$	$C_{22}H_{21}NO_6$
formula weight	975.30	848.72	306.26	395.40
temperature, K	173(2)	123(2)	173(2)	173(2)
radiation (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	P-1	P2(1)2(1)2(1)	P2(1)	P2(1)/c
a, Å	13.1299(3)	9.9813(4)	9.1386(7)	8.8506(3)
b, Å	13.8383(3)	14.1738(5)	6.5567(5)	9.5121(3)
c, Å	27.1041(6)	29.0404(11)	11.6157(8)	22.9522(8)
α, °	79.247(2)	90	90	90
β, °	84.900(2)	90	94.023(6)	96.001(3)
γ, °	81.114(2)	90	90	90
V, Å^3	4770.99(18)	4108.4(3)	694.29(9)	1921.71(11)
Z	4	4	2	4
d_{calcd}, g cm^{-3}	1.358	1.372	1.465	1.367
F(000)	2024	1760	320	832
crystal size, mm	0.48 x 0.40 x0.20	0.36 x 0.28 x 0.18	0.38 x 0.24x0.20	0.36 x 0.28 x0.22
θ range, °	2.78 to 26.00	2.81 to 26.00°.	2.74 to 25.99	2.79 to 26.00
reflns collected	42377	12358	3444	15519
indep reflns	18722	7826	1489	3764
obsd reflns ($I>2\sigma(I)$)	12643	6617	1231	2840
data-restraints-params	18722 / 18 / 1153	7826 / 0 / 508	1489 / 1 / 199	3764 / 0 / 266
GOF on F^2	0.995	0.915	1.009	1.086
final R ($I > 2\sigma(I)$)	R_1 = 0.0336, wR_2 = 0.0779	R_1 = 0.0308, wR_2 = 0.0403	R_1 = 0.0331, wR_2 = 0.0632	R_1 = 0.0423, wR_2 = 0.1102
R indices (all data)	R_1 = 0.0585, wR_2 = 0.0822	R_1 = 0.0394, wR_2 = 0.0412	R_1 = 0.0426, wR_2 = 0.0647	R_1 = 0.0583, wR_2 = 0.1143
peak and hole, e.Å^{-3}	1.085 and -0.675	0.614 and -0.448	0.166 and -0.151	0.438 and -0.421

Table S3. Selected Bond Lengths and Bond Angles for complex **1**

Bond Distances (Å)			
Ru(1)-N(1)	2.280(2)	Ru(2)-N(2)	2.288(2)
Ru(1)-B(1)	2.357(3)	Ru(2)-B(2)	2.355(3)
Ru(1)-C(11)	2.244(2)	Ru(2)-C(21)	2.247(2)
Ru(1)-C(12)	2.202(2)	Ru(2)-C(22)	2.205(2)
Ru(1)-C(13)	2.157(3)	Ru(2)-C(23)	2.152(3)
Ru(1)-P(1)	2.2834(7)	Ru(2)-P(3)	2.3499(7)
Ru(1)-P(2)	2.3542(7)	Ru(2)-P(4)	2.2868(7)
Ru(1)-Cl(1)	2.4514(6)	Ru(2)-Cl(2)	2.4509(6)
B(1)-N(1)	1.489(4)	B(2)-N(2)	1.493(4)
B(1)-C(11)	1.515(4)	B(2)-C(21)	1.514(4)
N(1)-C(13)	1.426(3)	N(2)-C(23)	1.426(3)
N(1)-C(14)	1.506(3)	N(2)-C(24)	1.503(3)
C(11)-C(12)	1.426(4)	C(21)-C(22)	1.430(4)
C(12)-C(13)	1.392(4)	C(22)-C(23)	1.389(3)
B(1)-C(18)	1.531(4)	B(2)-C(28)	1.534(4)
C(18)-C(19)	1.201(3)	C(28)-C(29)	1.194(3)
Bond Angels (°)			
C(13)-Ru(1)-Cl(1)	92.68(7)	C(23)-Ru(2)-Cl(2)	92.12(7)
C(12)-Ru(1)-Cl(1)	120.57(7)	C(22)-Ru(2)-Cl(2)	119.99(7)
C(11)-Ru(1)-Cl(1)	155.77(7)	C(21)-Ru(2)-Cl(2)	155.21(7)
N(1)-Ru(1)-Cl(1)	99.23(6)	N(2)-Ru(2)-Cl(2)	98.82(5)
B(1)-Ru(1)-Cl(1)	133.82(8)	B(2)-Ru(2)-Cl(2)	133.53(7)
P(1)-Ru(1)-Cl(1)	92.25(2)	P(3)-Ru(2)-Cl(2)	92.03(2)
P(2)-Ru(1)-Cl(1)	91.35(2)	P(4)-Ru(2)-Cl(2)	92.41(2)
P(1)-Ru(1)-P(2)	100.84(2)	P(3)-Ru(2)-P(4)	100.12(2)
N(1)-B(1)-C(11)	105.0(2)	N(2)-B(2)-C(21)	105.0(2)
N(1)-B(1)-C(18)	126.8(2)	N(2)-B(2)-C(28)	126.1(2)
C(11)-B(1)-C(18)	128.0(3)	C(21)-B(2)-C(28)	128.6(2)
N(1)-B(1)-Ru(1)	68.48(14)	N(2)-B(2)-Ru(2)	68.81(13)
C(11)-B(1)-Ru(1)	66.82(14)	C(21)-B(2)-Ru(2)	66.98(14)
C(18)-B(1)-Ru(1)	132.25(19)	C(28)-B(2)-Ru(2)	132.02(19)

Table S4. Selected Bond Lengths and Bond Angles for complex **2**

Bond Distances (Å)			
Ru(1)-N(1)	2.384(2)	N(1)-B(1)	1.486(4)
Ru(1)-B(1)	2.402(3)	C(8)-B(1)	1.528(4)
Ru(1)-C(1)	2.256(3)	C(1)-B(1)	1.517(4)
Ru(1)-C(2)	2.217(2)	C(4)-N(1)	1.518(3)
Ru(1)-C(3)	2.194(3)	C(3)-N(1)	1.411(3)
Ru(1)-H(1)	1.463(18)	C(4)-C(5)	1.503(4)
Ru(1)-P(1)	2.2897(8)	C(8)-C(9)	1.204(4)
Ru(1)-P(2)	2.2893(7)	C(11)-C(12)	1.366(4)
Bond Angels (°)			
C(3)-Ru(1)-H(1)	121.8(8)	P(1)-Ru(1)-H(1)	79.1(8)
C(2)-Ru(1)-H(1)	92.3(8)	P(2)-Ru(1)-H(1)	79.5(8)
C(1)-Ru(1)-H(1)	96.0(9)	N(1)-B(1)-C(8)	126.6(3)
N(1)-Ru(1)-H(1)	152.7(9)	N(1)-B(1)-C(1)	104.4(3)
B(1)-Ru(1)-H(1)	130.8(9)	C(8)-B(1)-C(1)	129.0(3)
P(2)-Ru(1)-P(1)	99.32(3)	N(1)-B(1)-Ru(1)	71.25(16)

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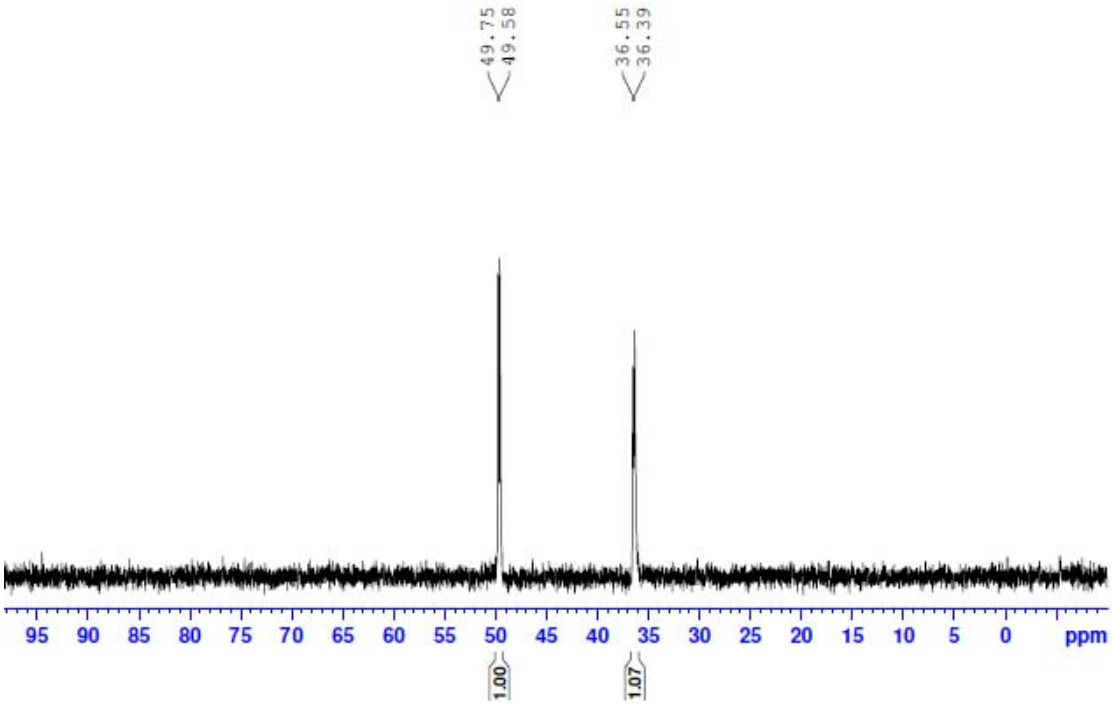
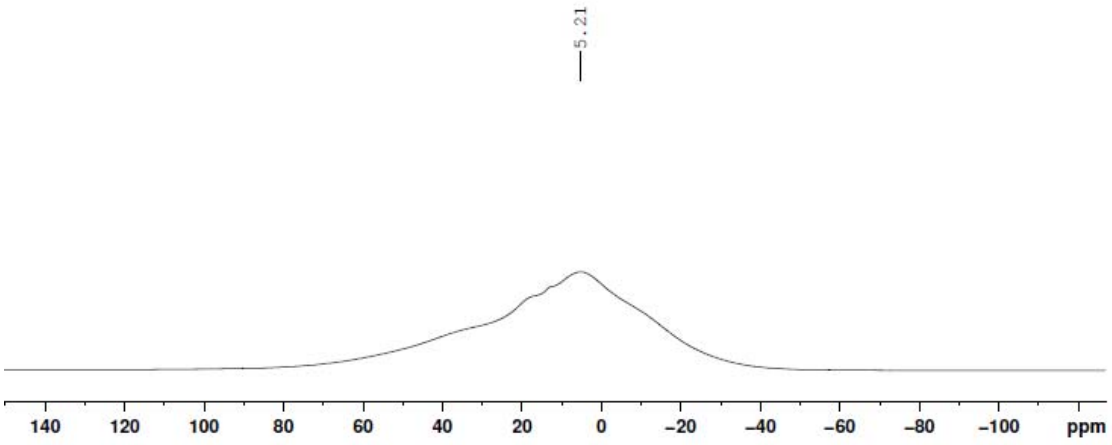
^{31}P, ^{11}B, ^{1}H, and ^{13}C NMR Spectra

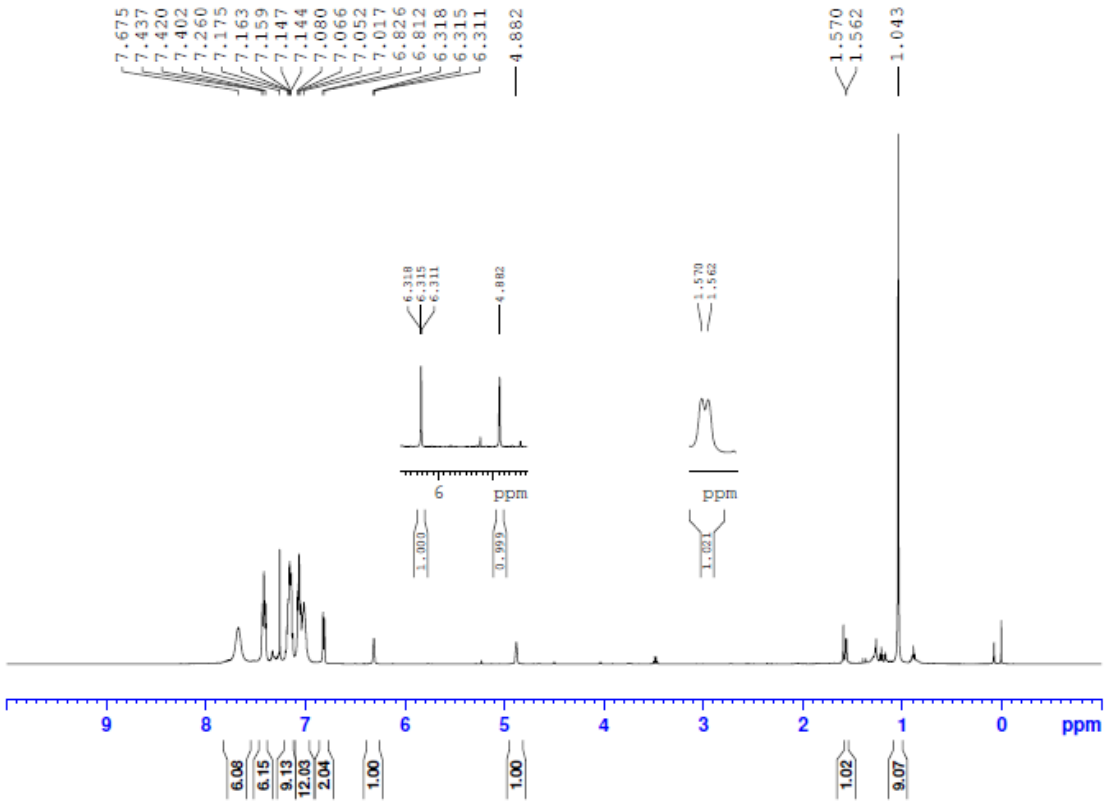
^{31}P NMR spectrum for complex **1**



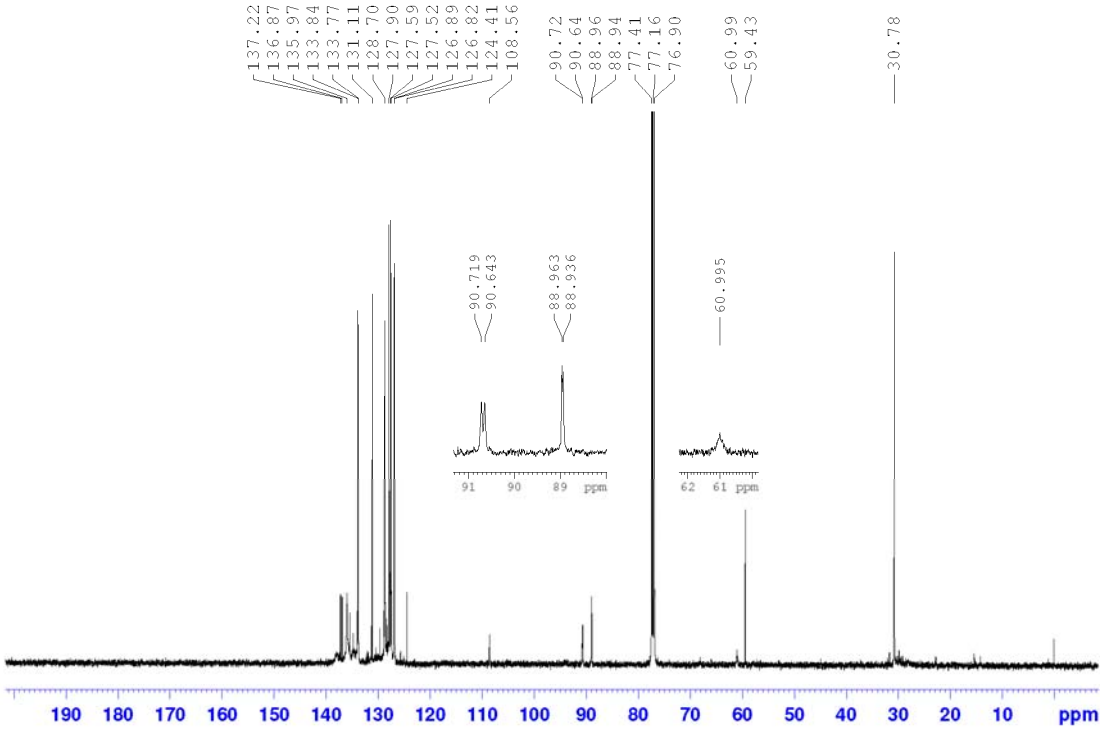
^{11}B NMR spectrum for complex **1**



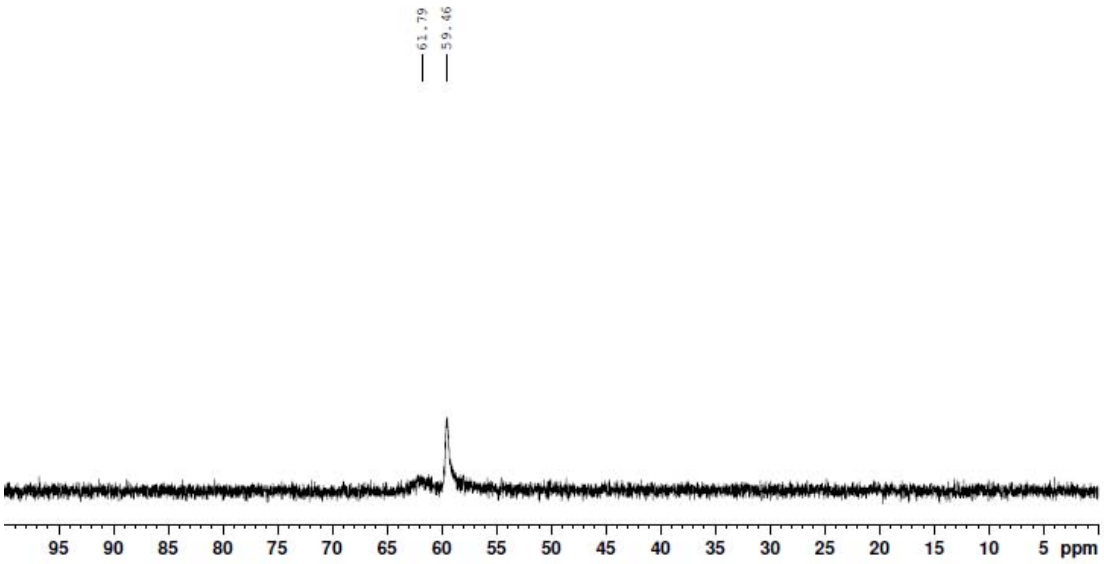
^{1}H NMR spectrum for complex **1**



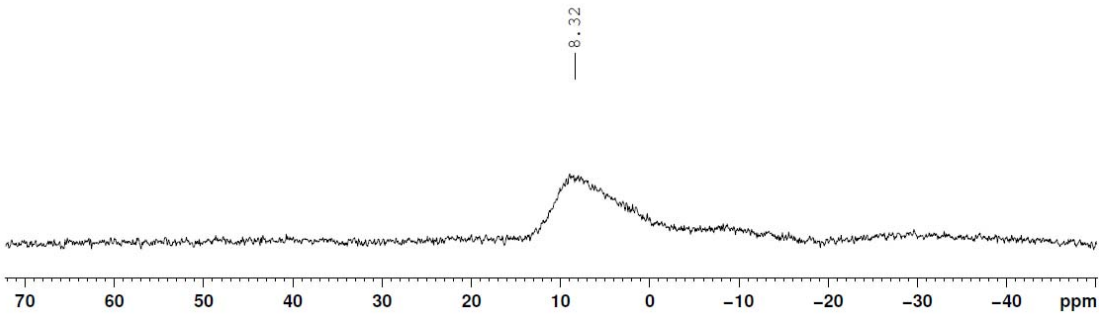
^{13}C NMR spectrum for complex **1**



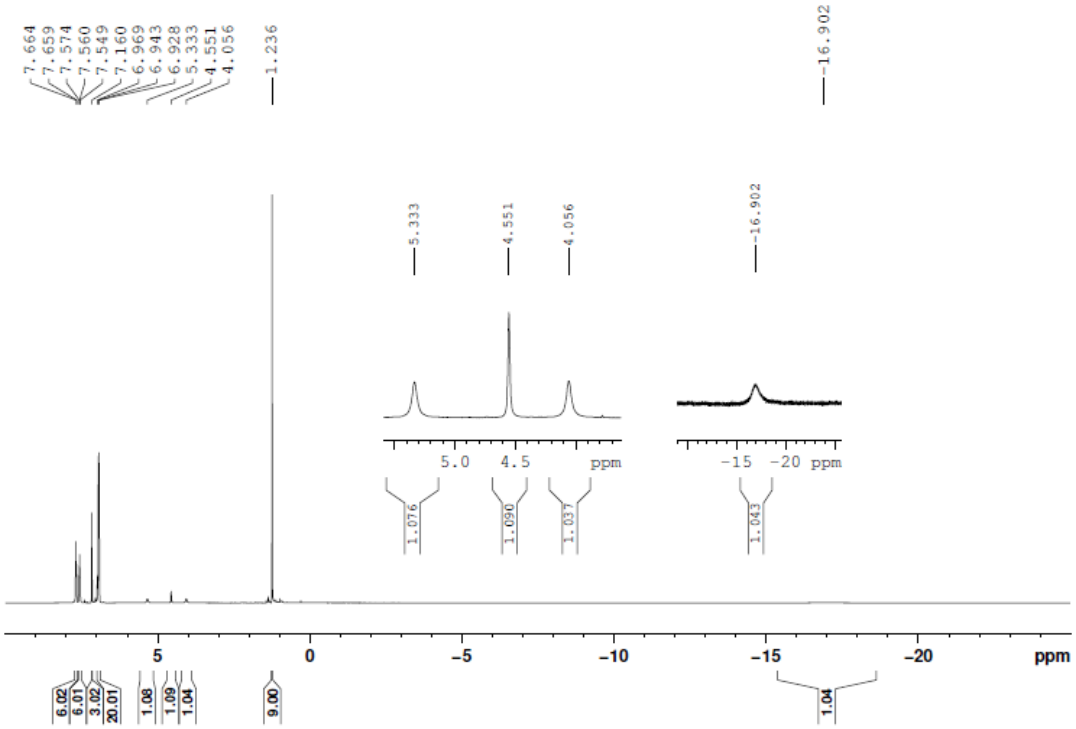
^{31}P NMR spectrum (298 K) for complex **2** in C_6D_6 at 202.4 MHz



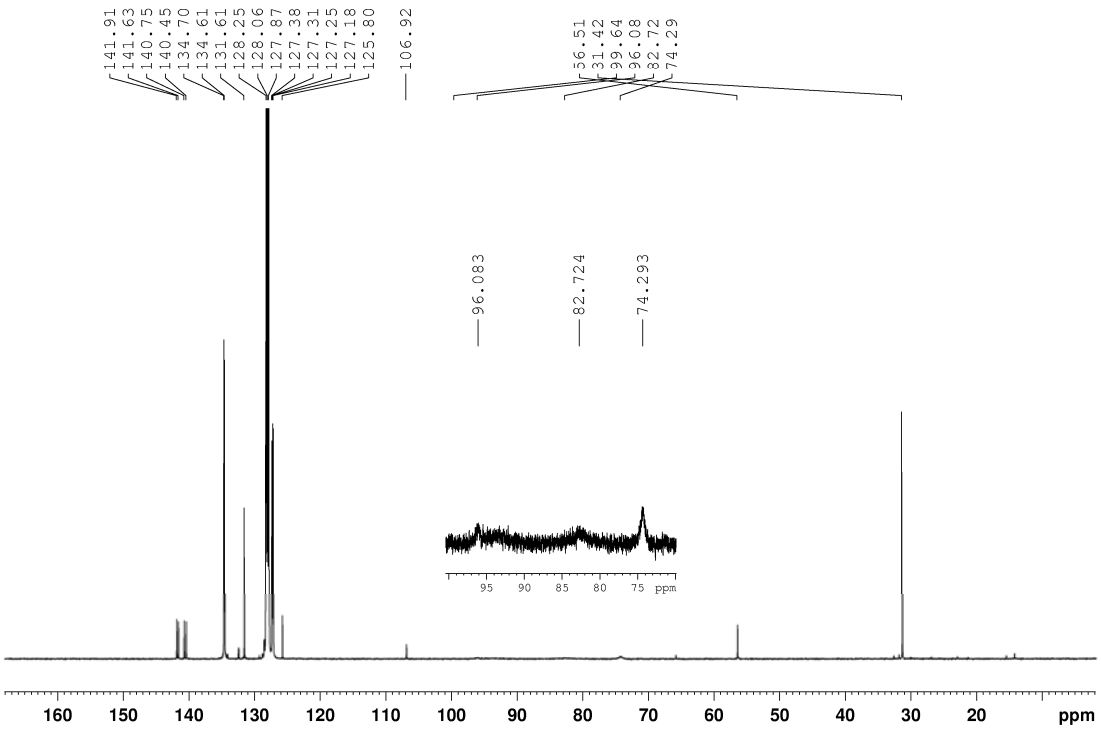
^{11}B NMR spectrum for complex **2** in C_6D_6 at 128.4 MHz



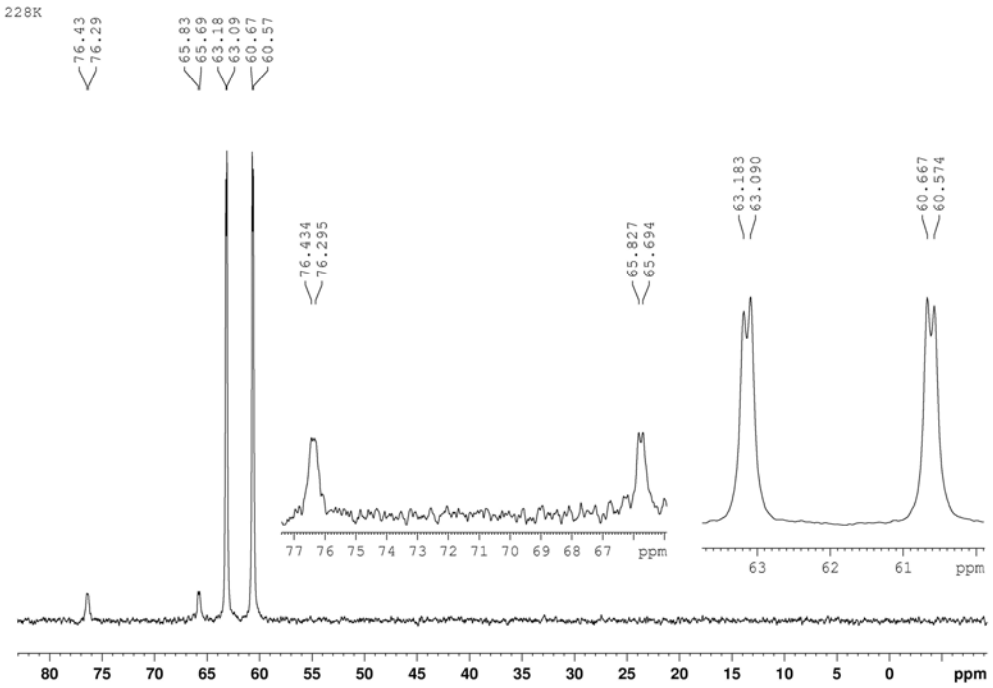
^{1}H NMR spectrum (298 K) for complex **2** in C_6D_6 at 500.1 MHz



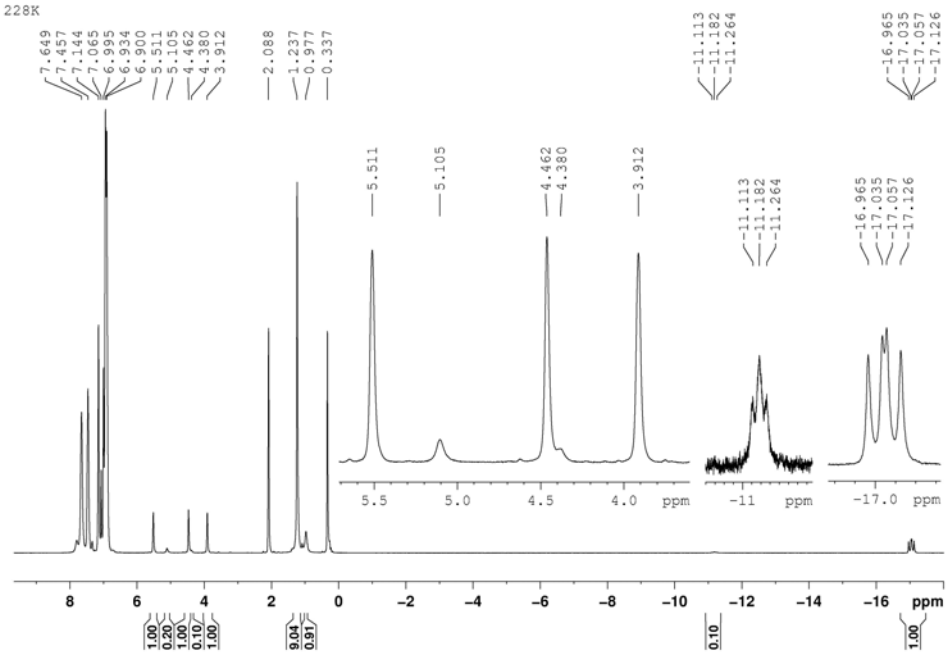
^{13}C NMR spectrum for complex **2** in C_6D_6 at 125.7 MHz



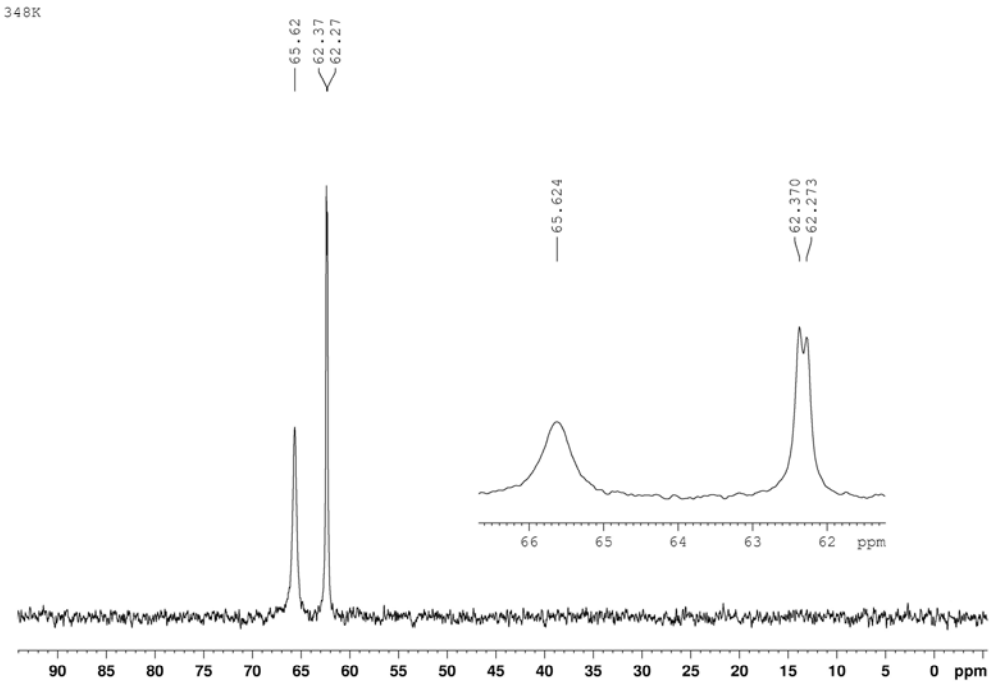
^{31}P NMR spectrum (228 K) for complex **2** in toluene-d_8 at 162.0 MHz



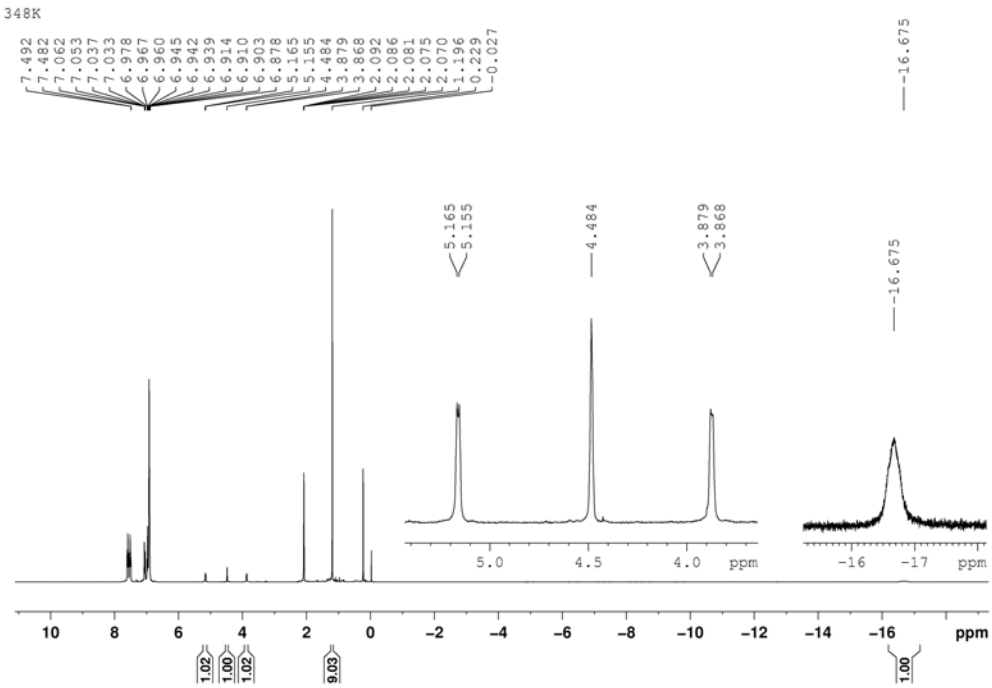
^{1}H NMR spectrum (228 K) for complex **2** in C_6D_6 at 400.1 MHz



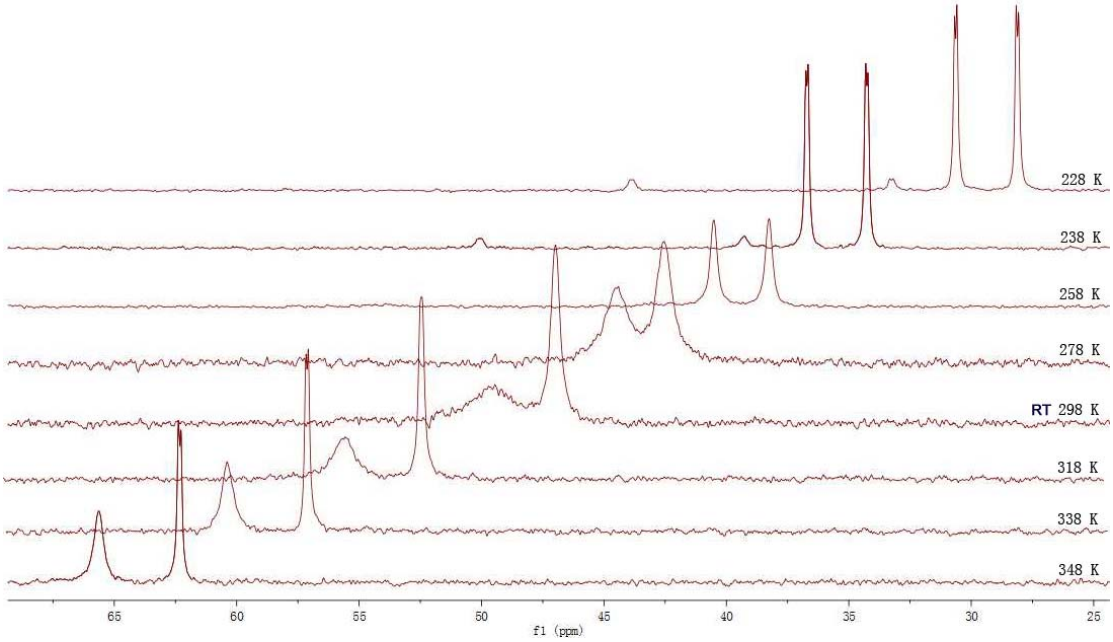
^{31}P NMR spectrum (348 K) for complex **2** in toluene-d_8 at 162.0 MHz



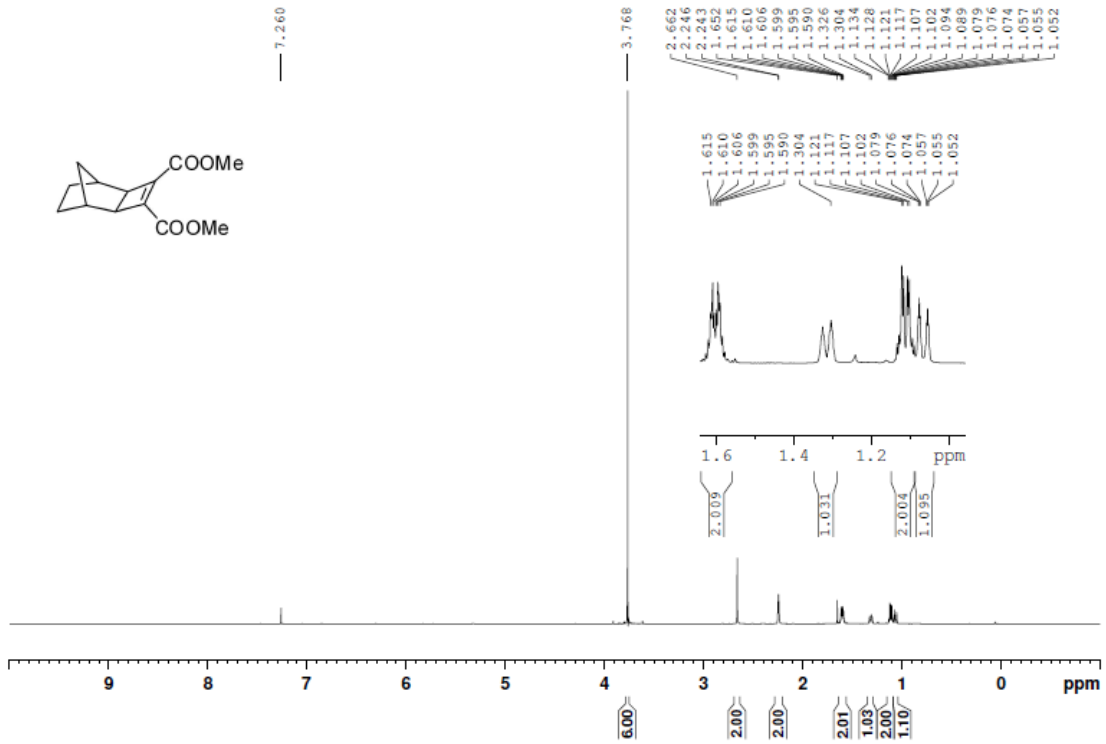
^{1}H NMR spectrum (228 K) for complex **2** in C_6D_6 at 400.1 MHz



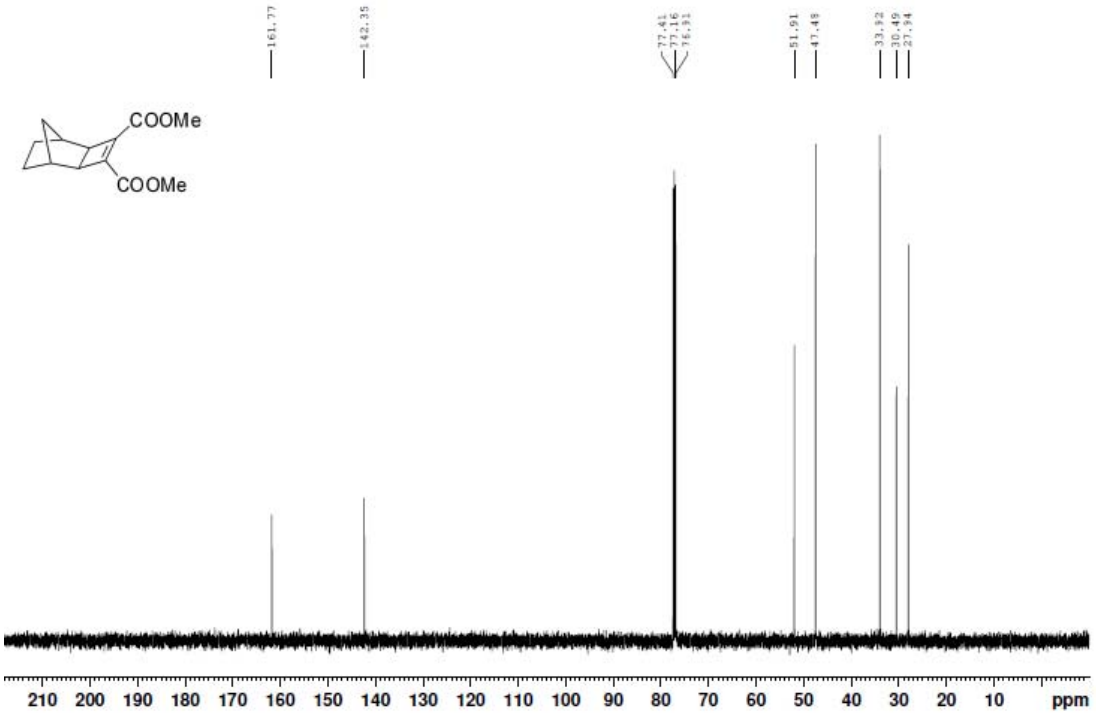
Stacked plot of variable-temperature ^{31}P NMR spectra for **2** in toluene-d_8 at 202.4 MHz



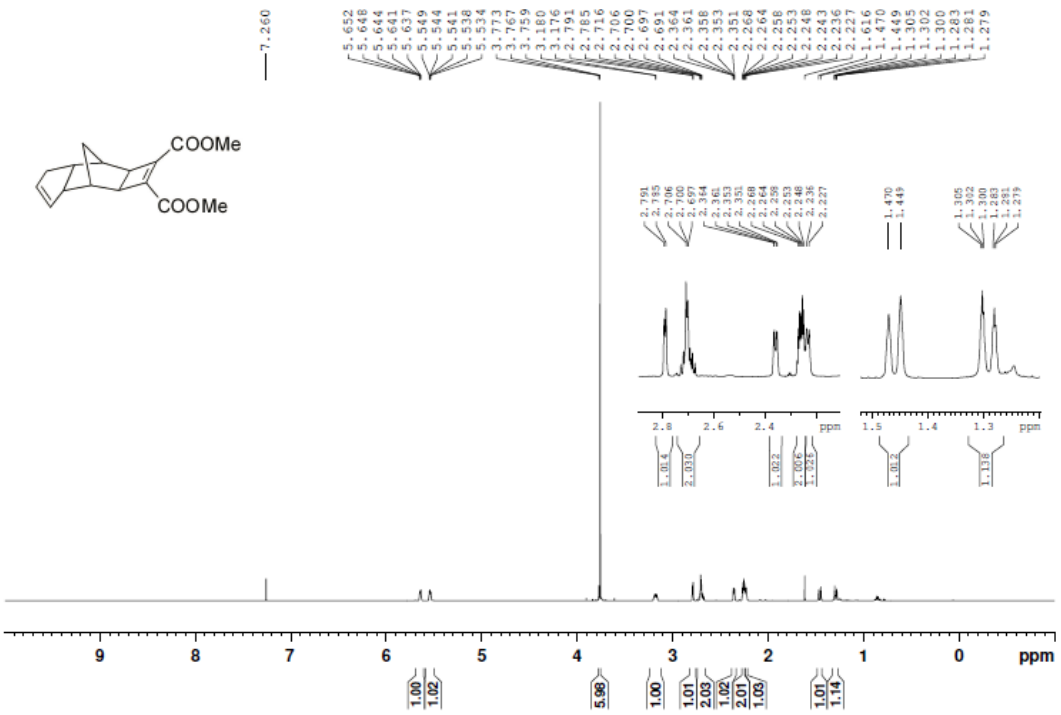
^{1}H NMR spectrum for **5a**



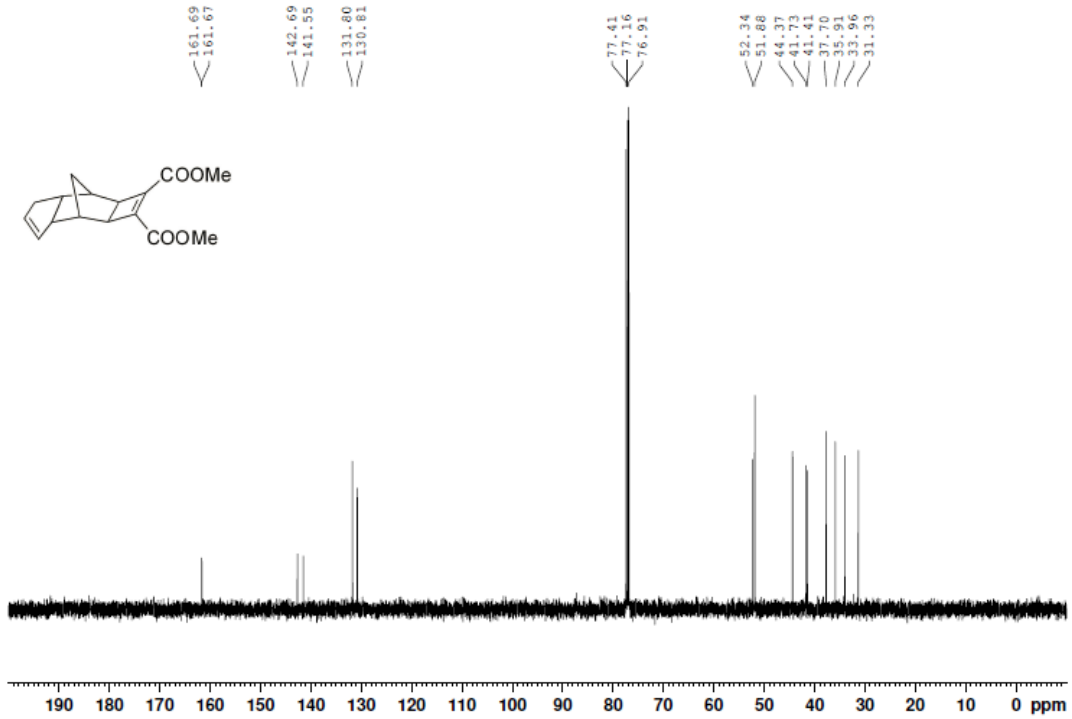
^{13}C NMR spectrum for **5a**



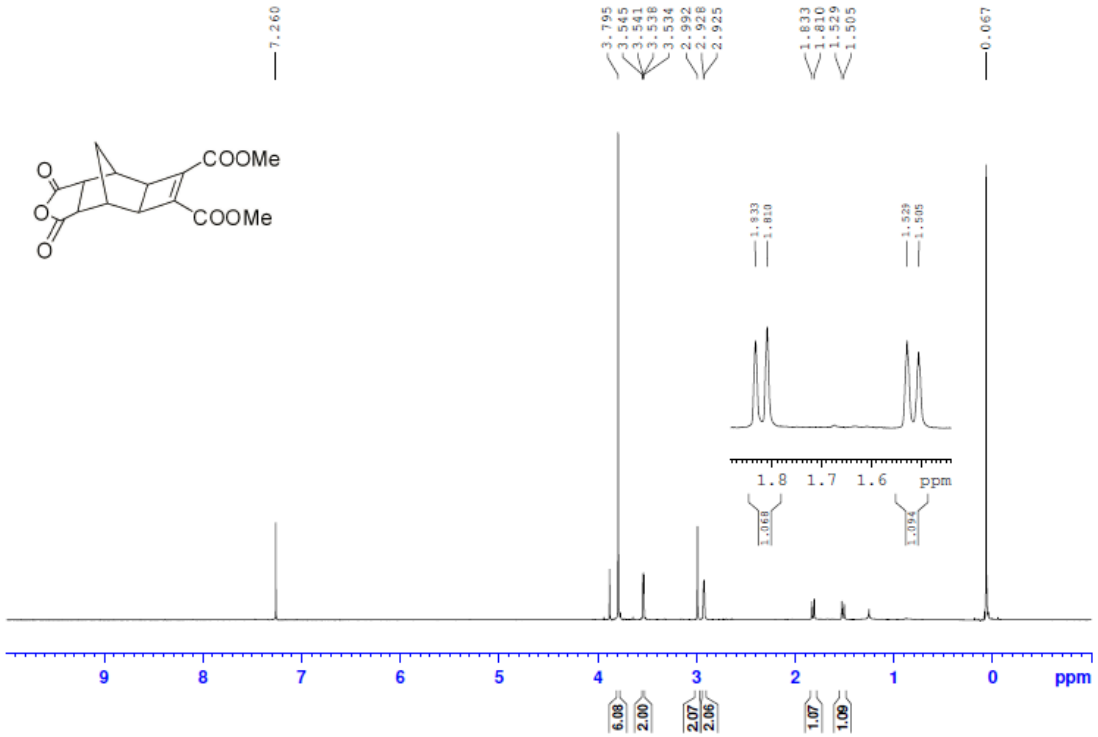
^{1}H NMR spectrum for **5b**



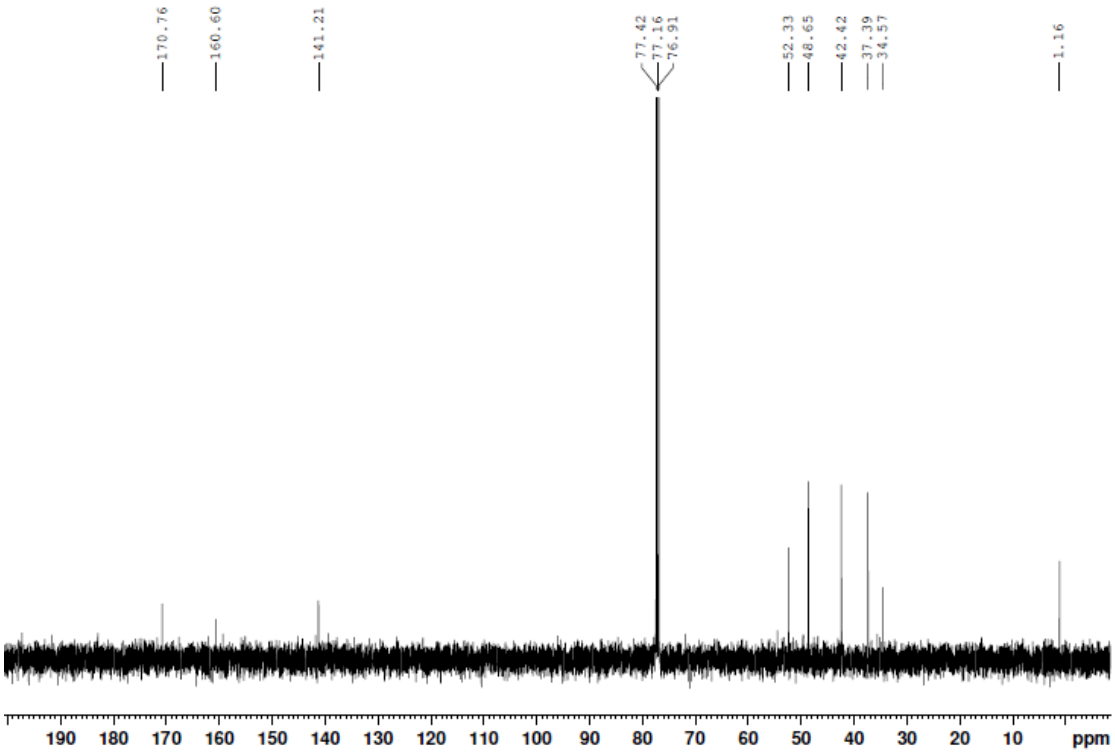
^{13}C NMR spectrum for **5b**



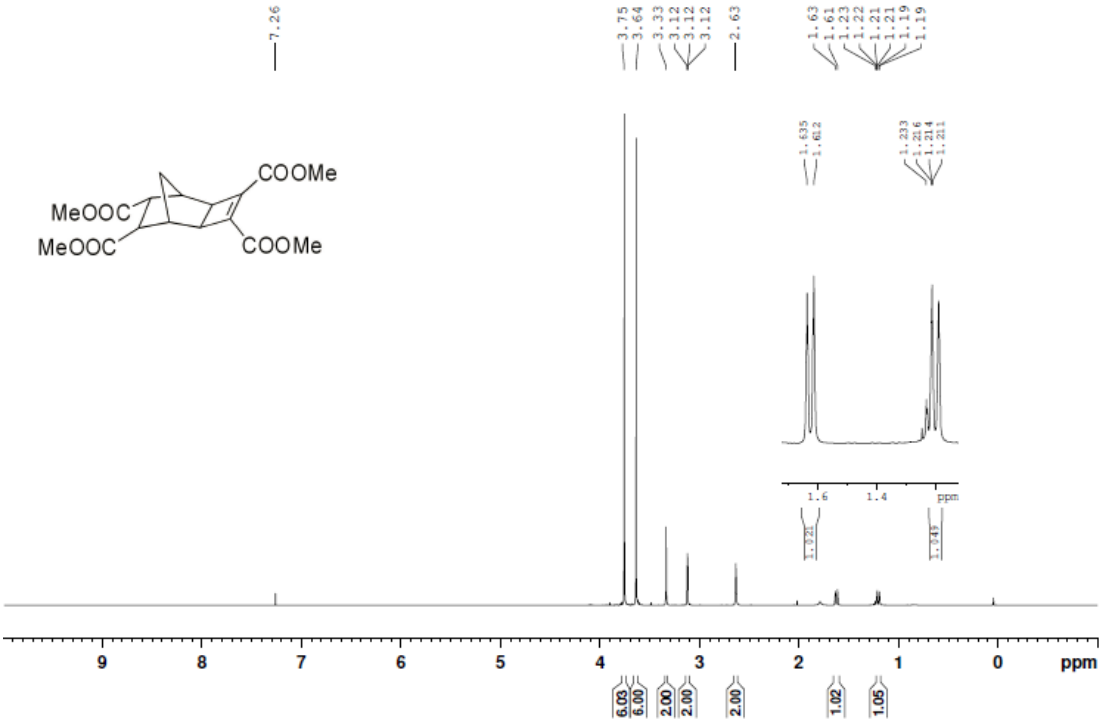
^{1}H NMR spectrum for **5c**



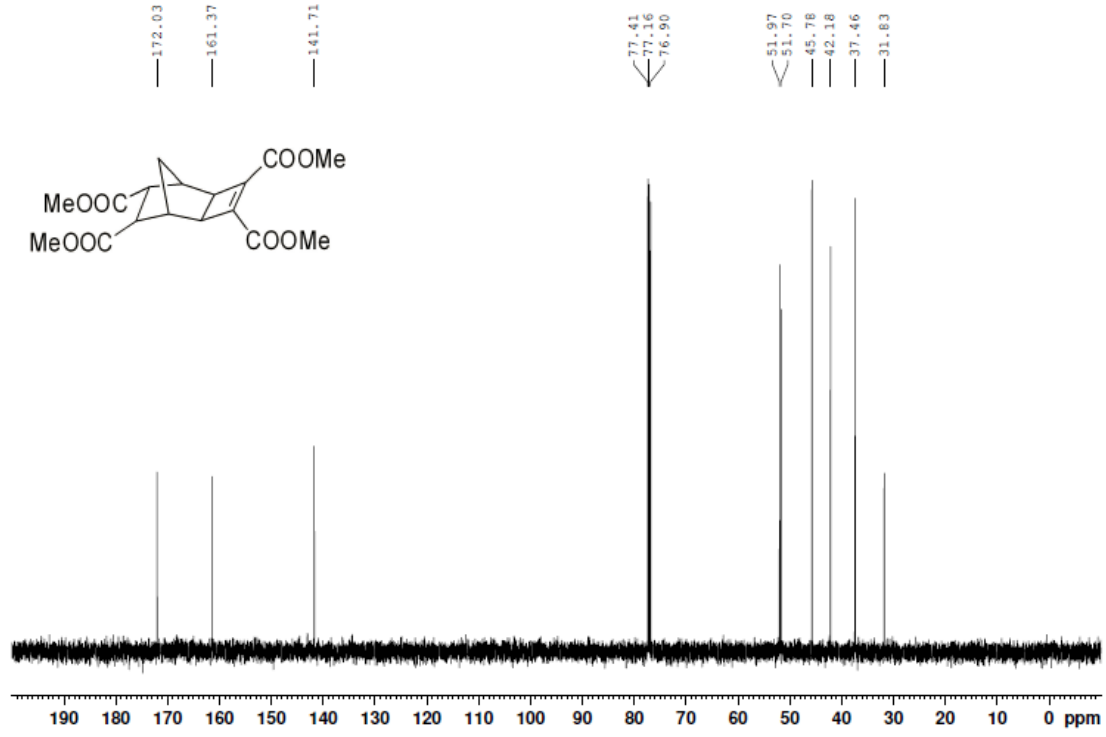
^{13}C NMR spectrum for **5c**



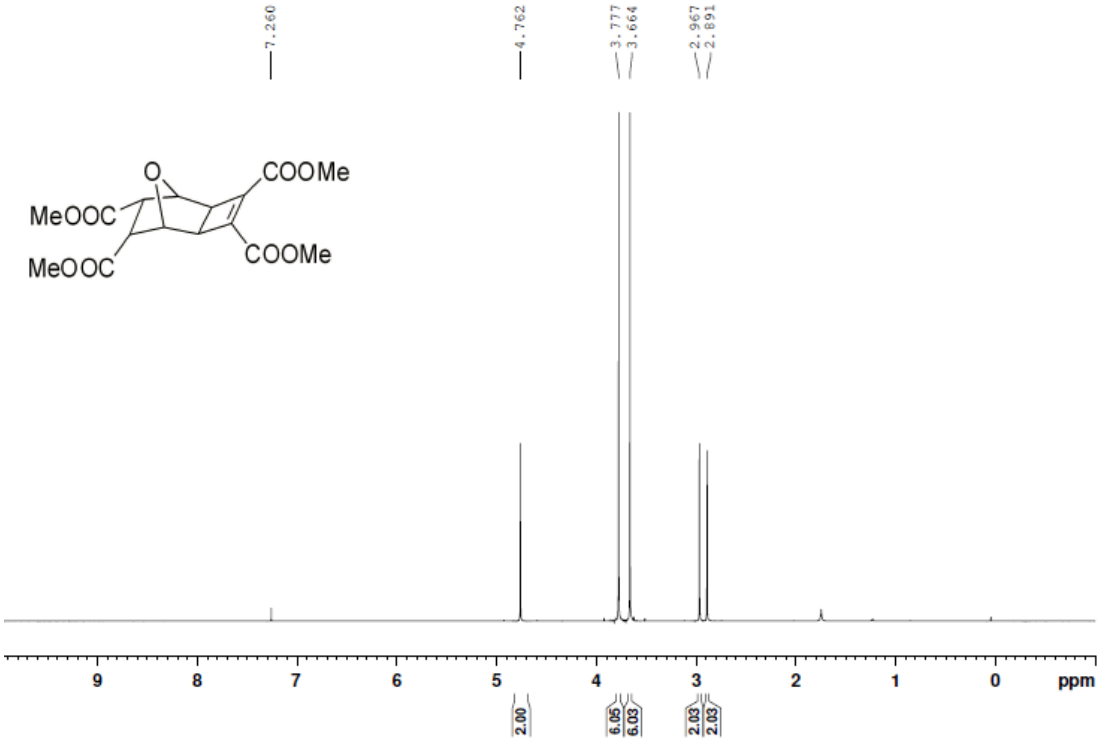
^{1}H NMR spectrum for **5d**



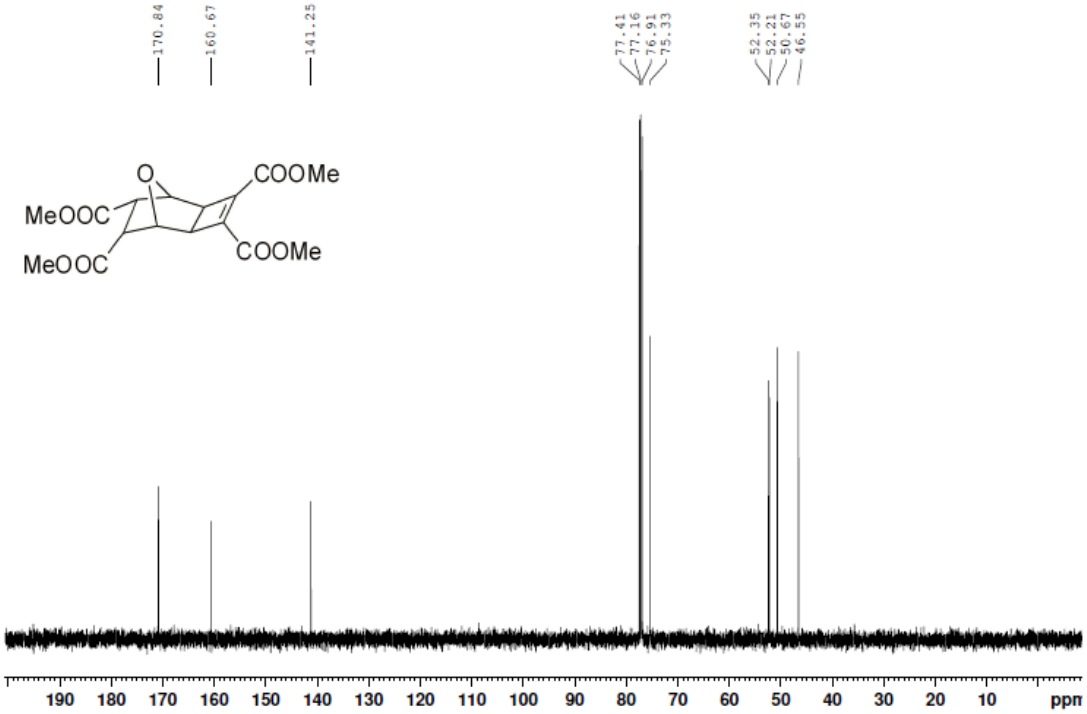
^{13}C NMR spectrum for **5d**



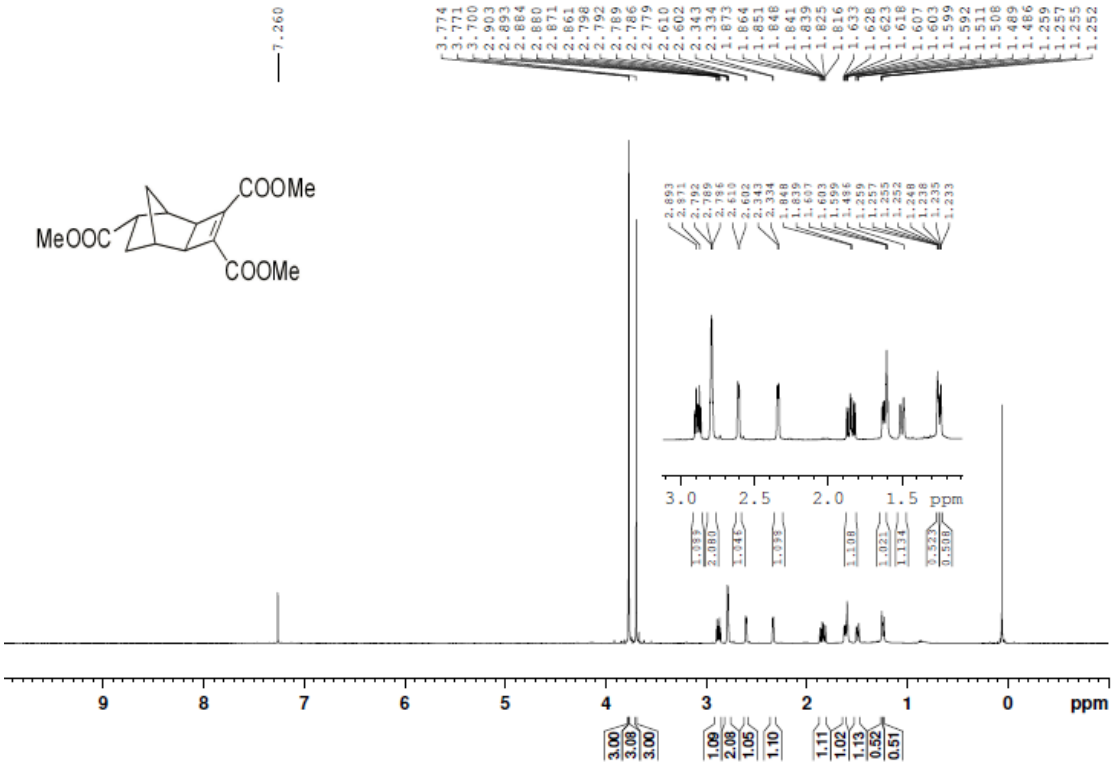
^{1}H NMR spectrum for **5e**



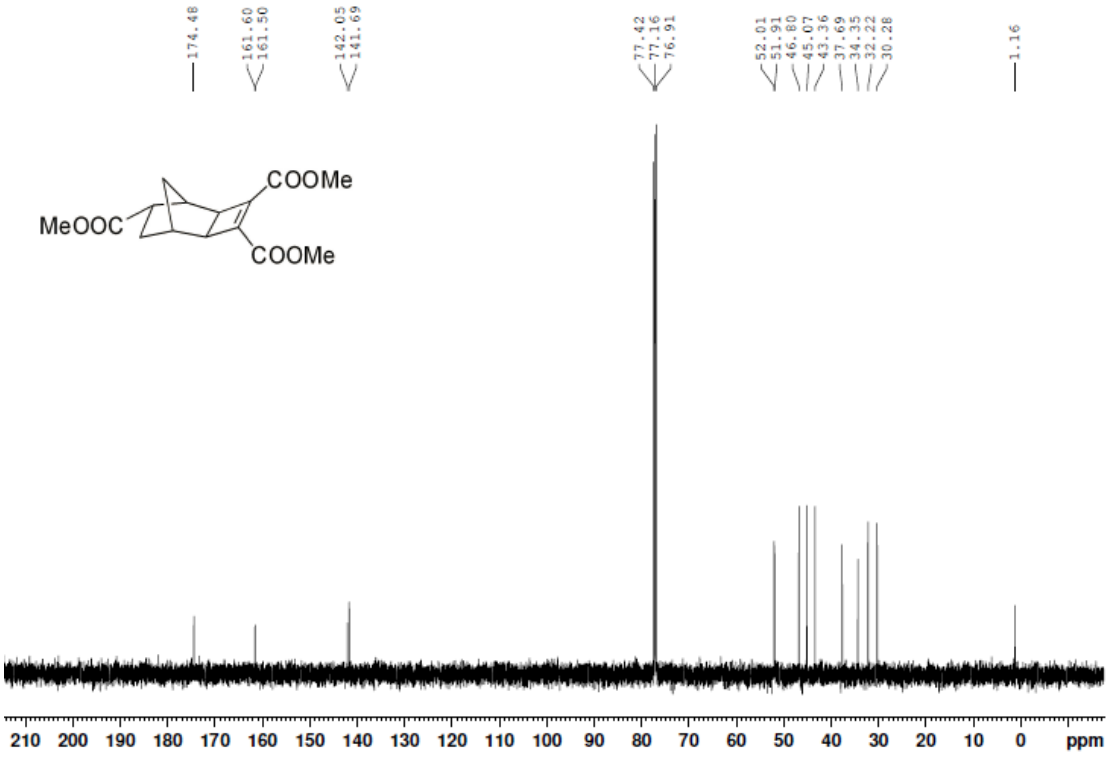
^{13}C NMR spectrum for **5e**



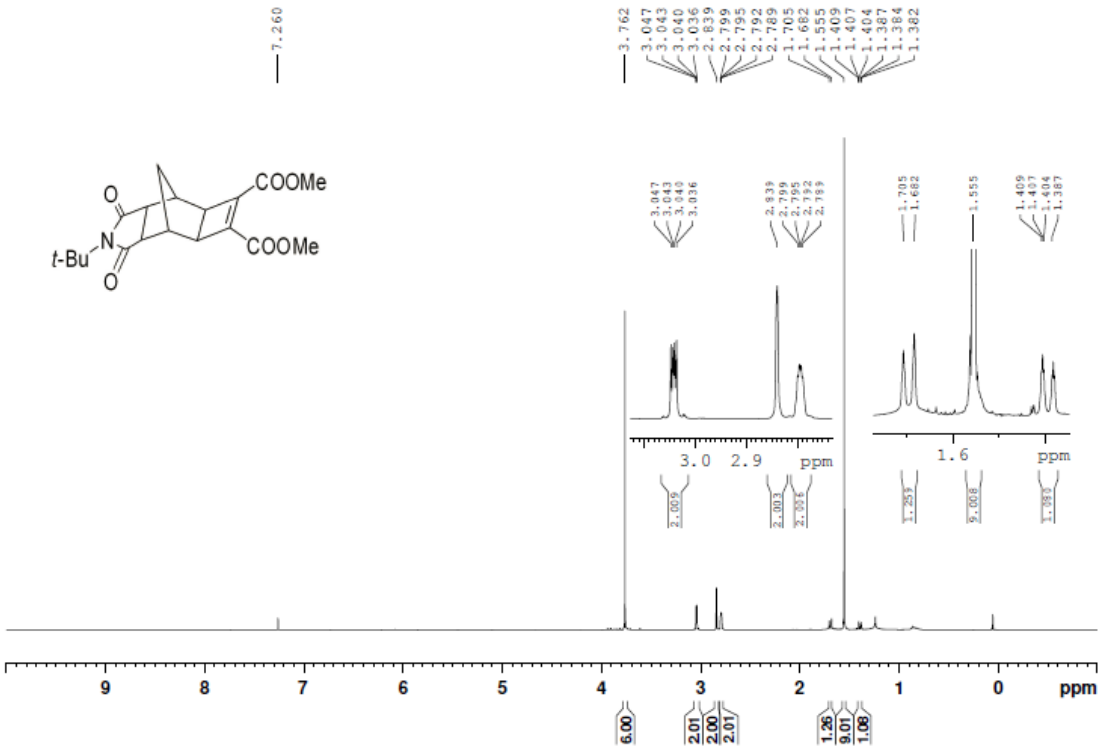
^{1}H NMR spectrum for **5f**



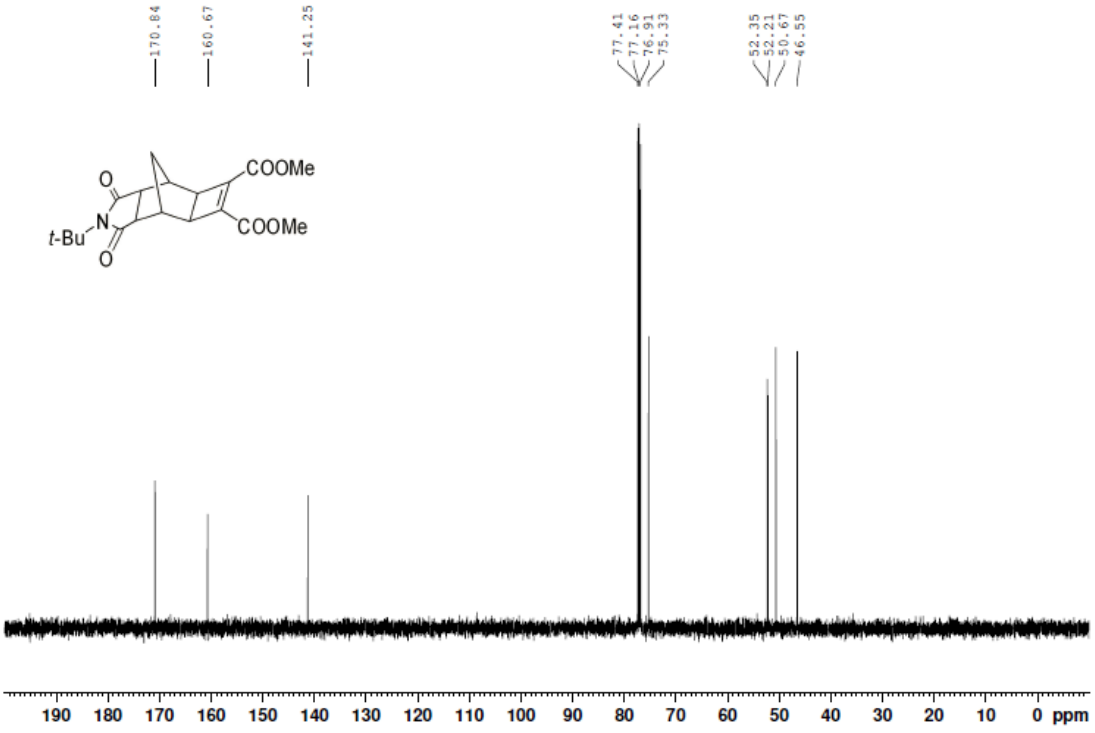
^{13}C NMR spectrum for **5f**



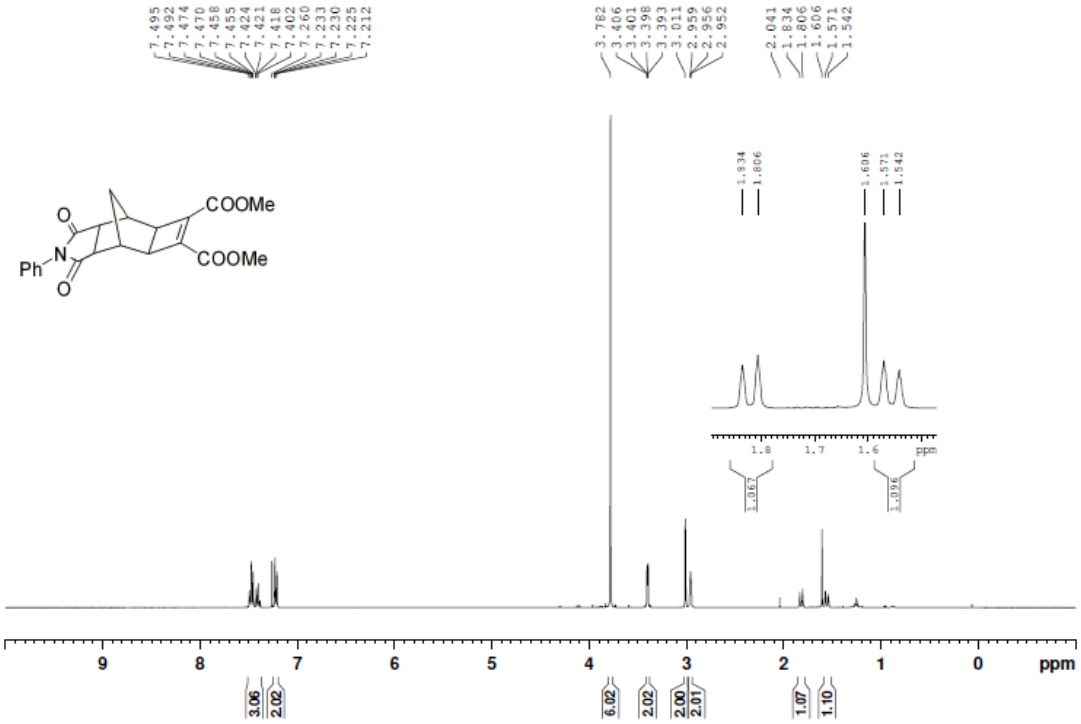
^{1}H NMR spectrum for **5g**



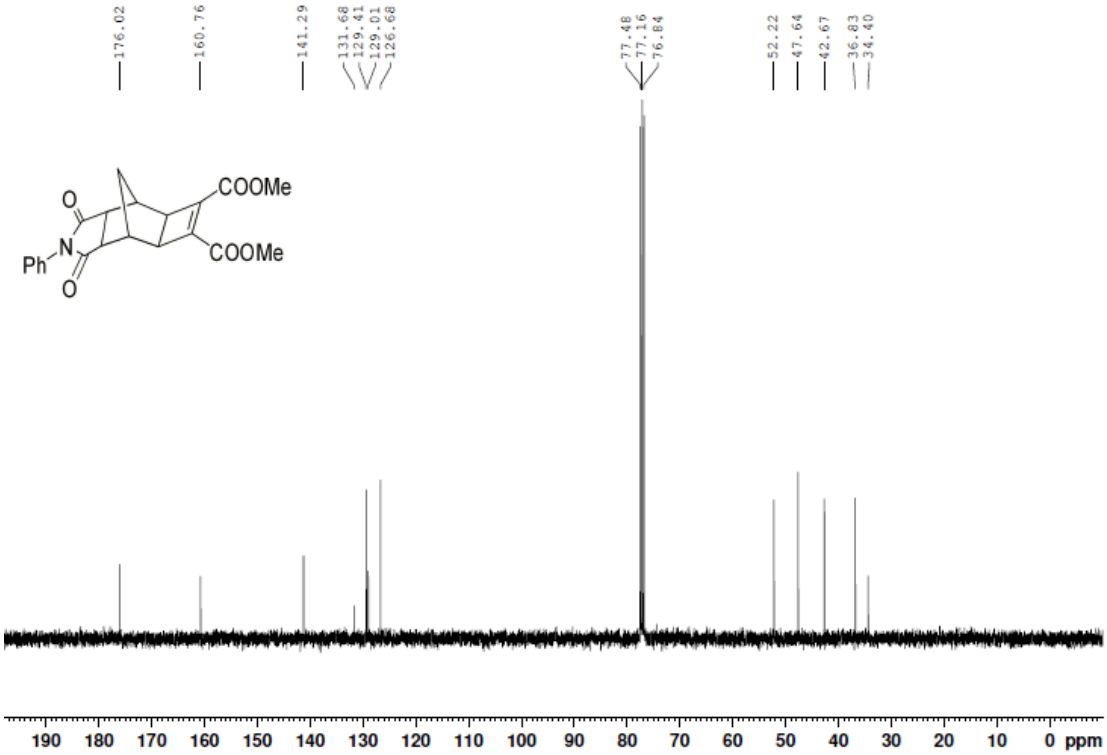
^{13}C NMR spectrum for **5g**



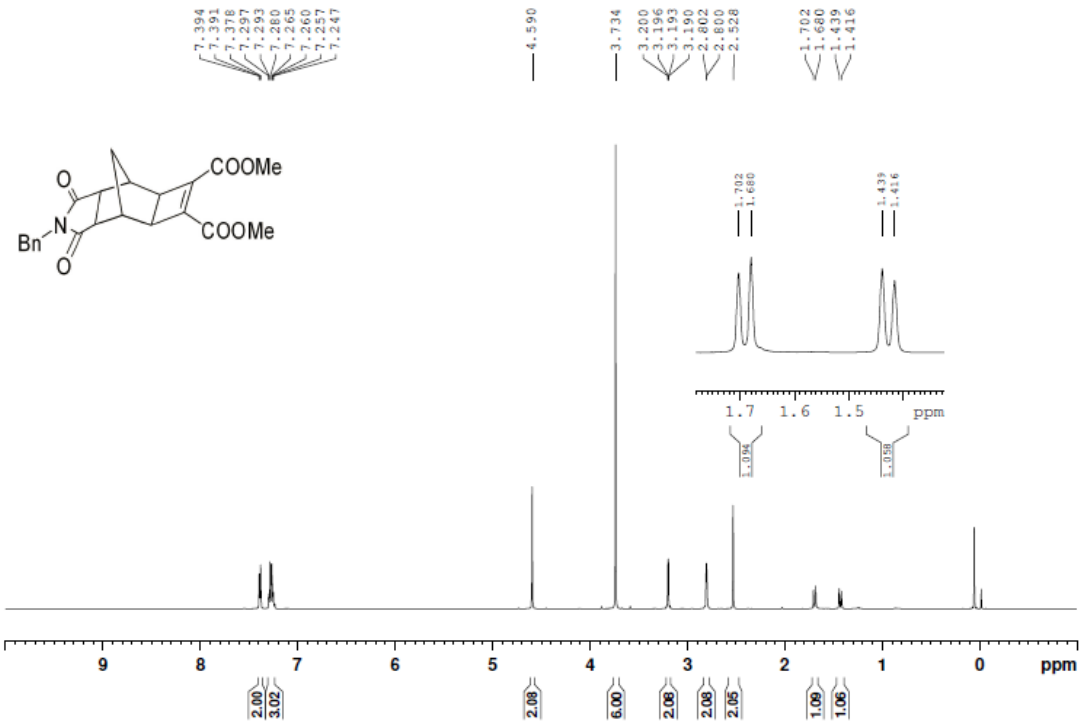
^{1}H NMR spectrum for **5h**



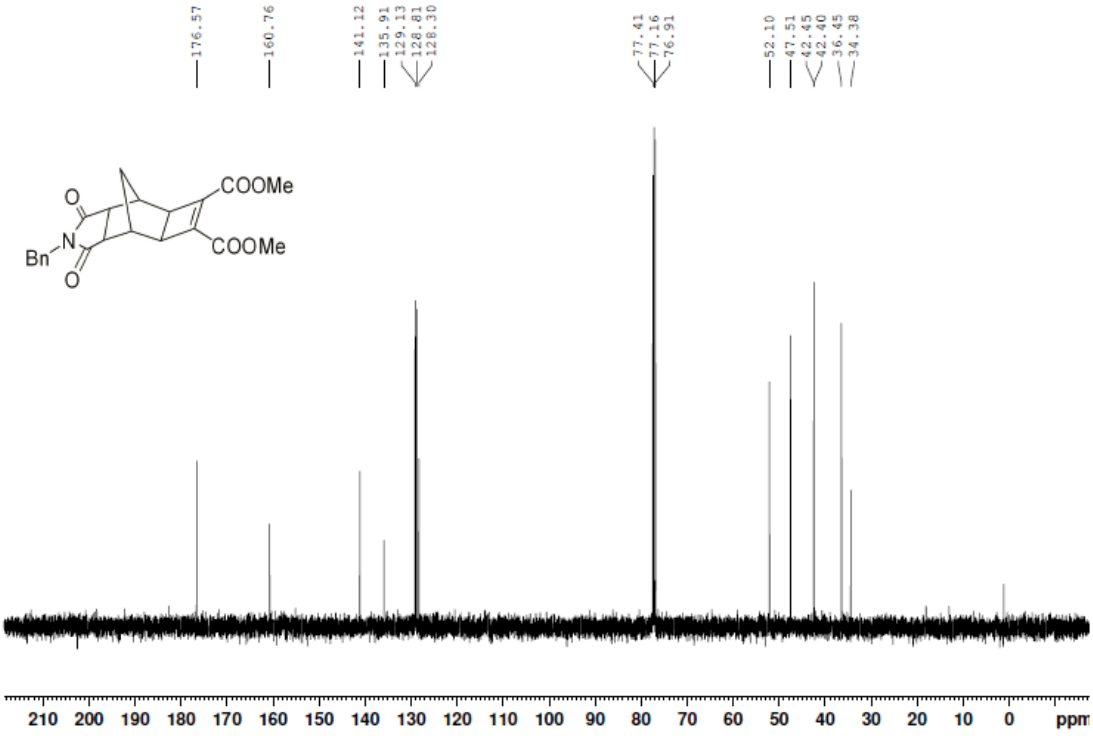
^{13}C NMR spectrum for **5h**



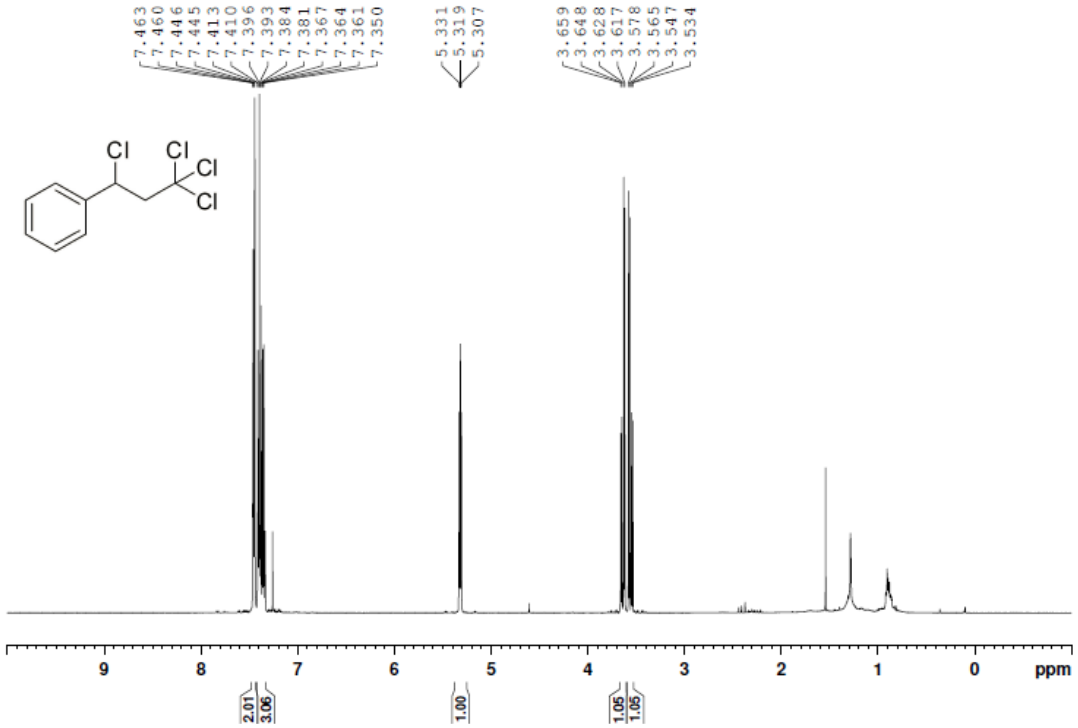
^{1}H NMR spectrum for **5i**



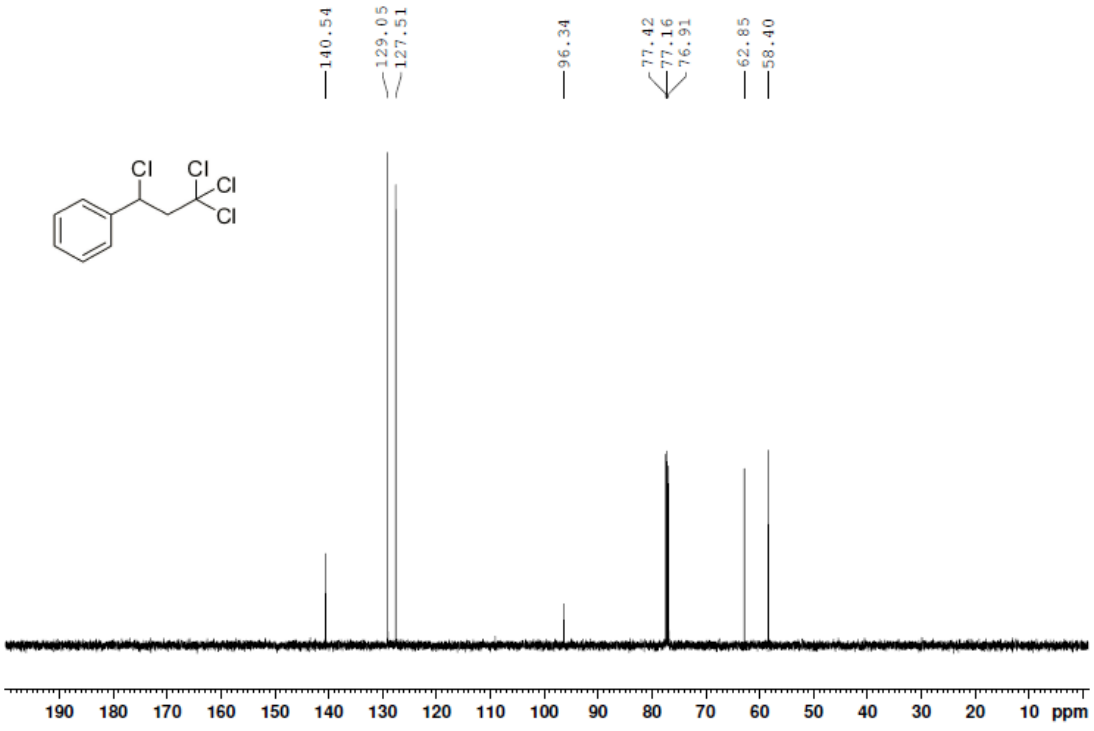
^{13}C NMR spectrum for **5i**



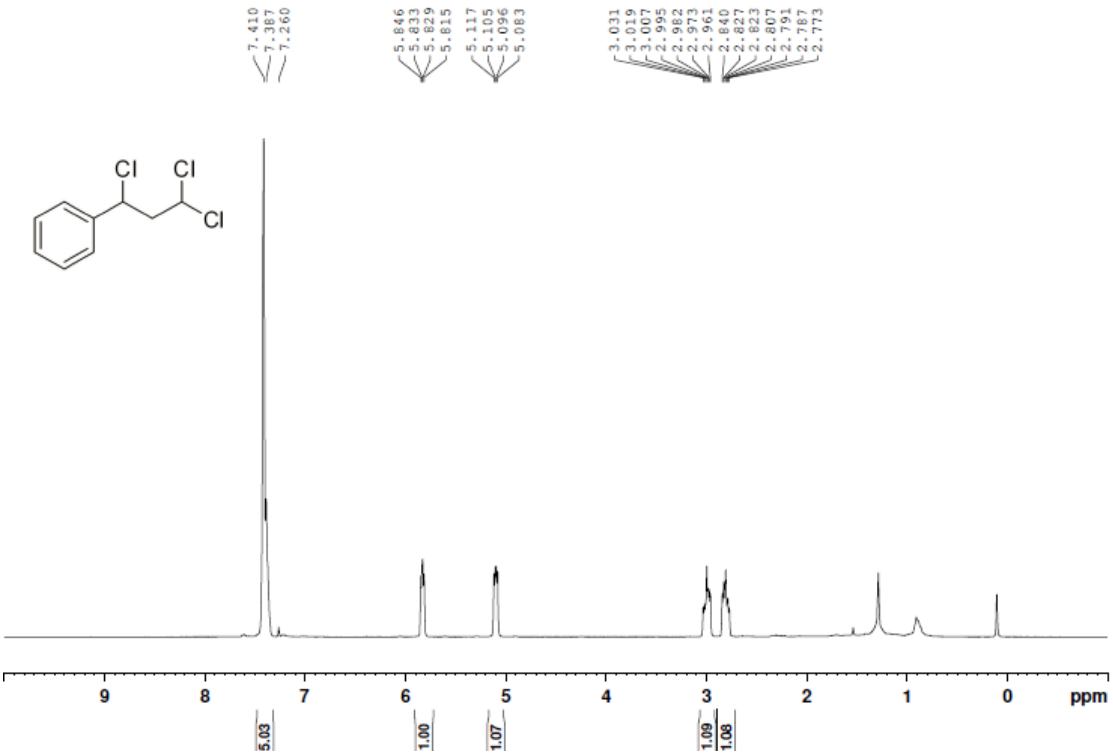
^{1}H NMR spectrum for **8aa**



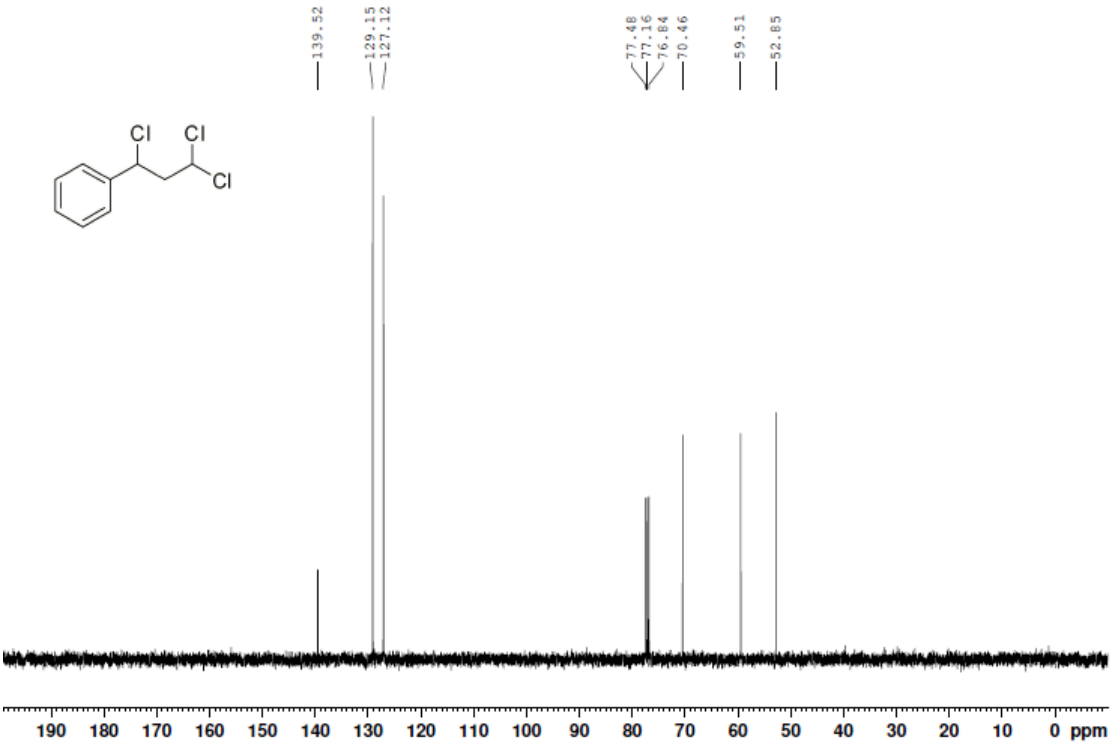
^{13}C NMR spectrum for **8aa**



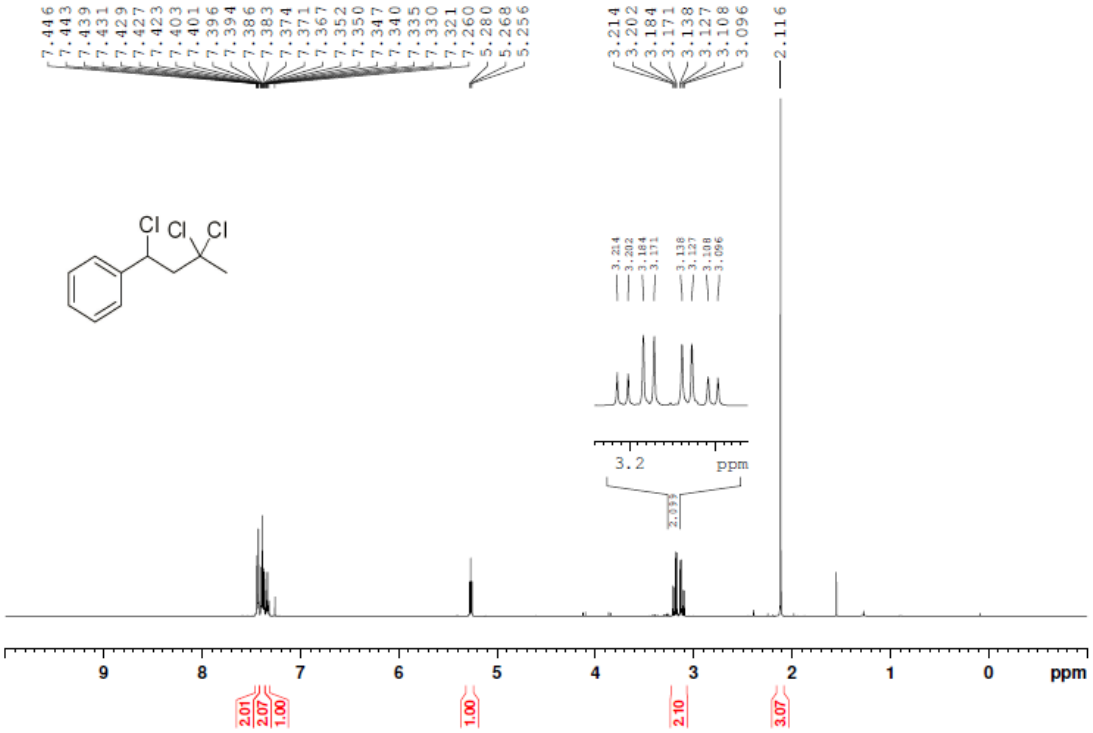
^{1}H NMR spectrum for **8ab**



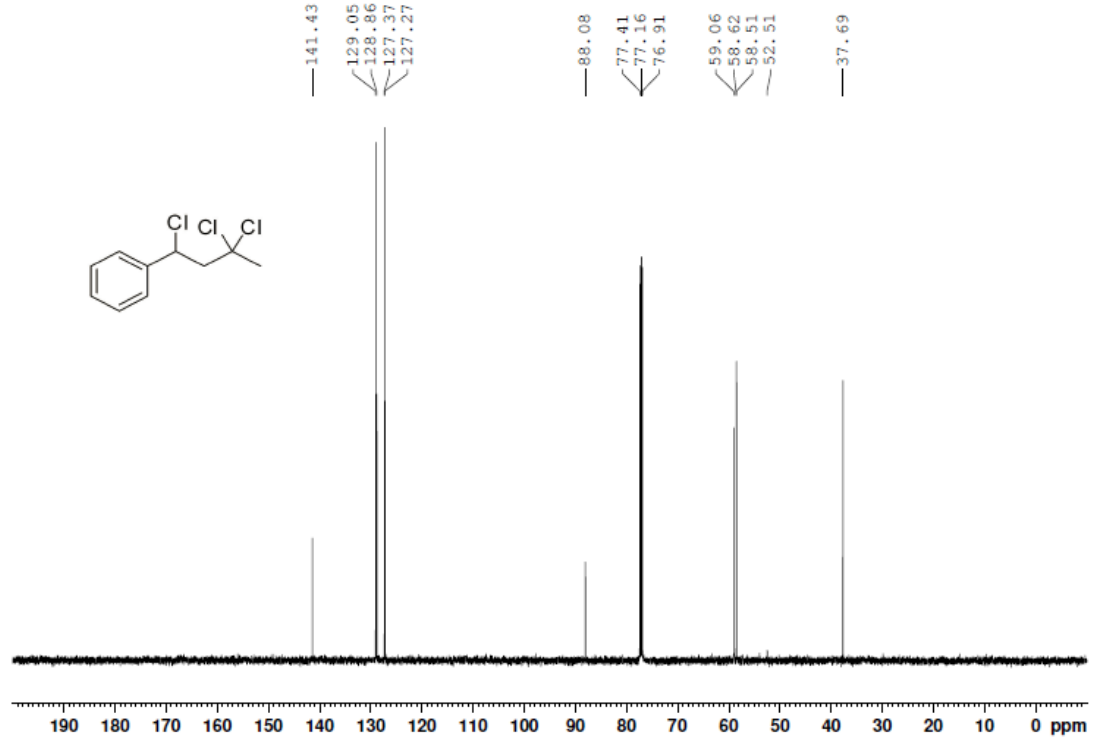
^{13}C NMR spectrum for **8ab**



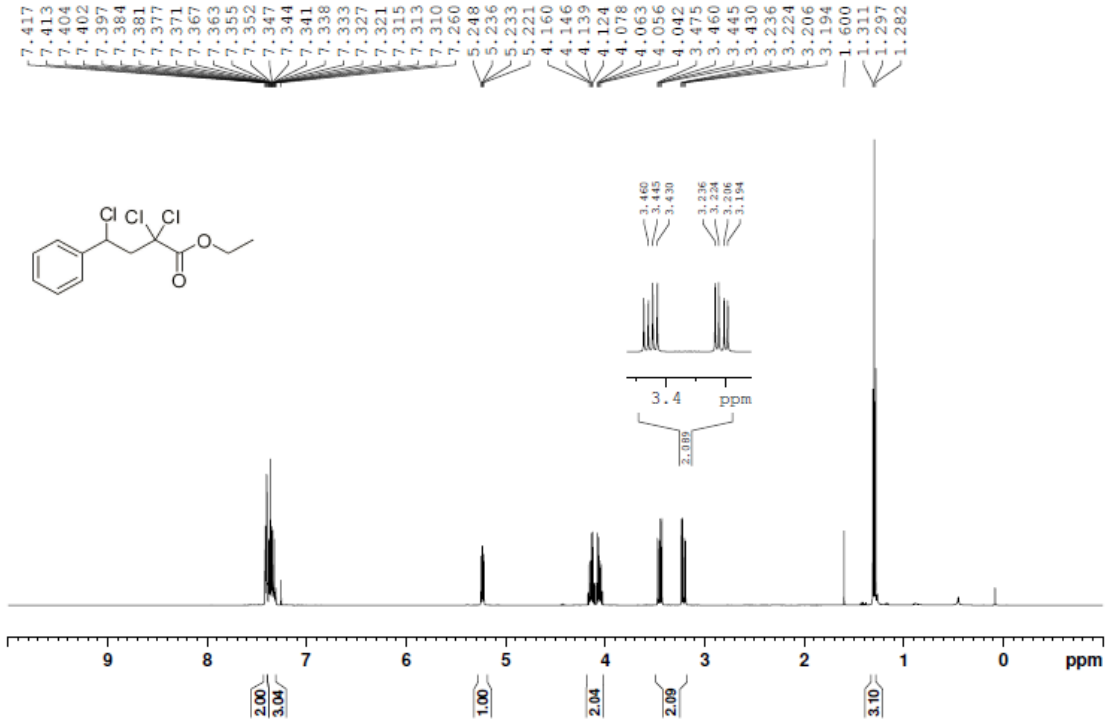
^{1}H NMR spectrum for **8ac**



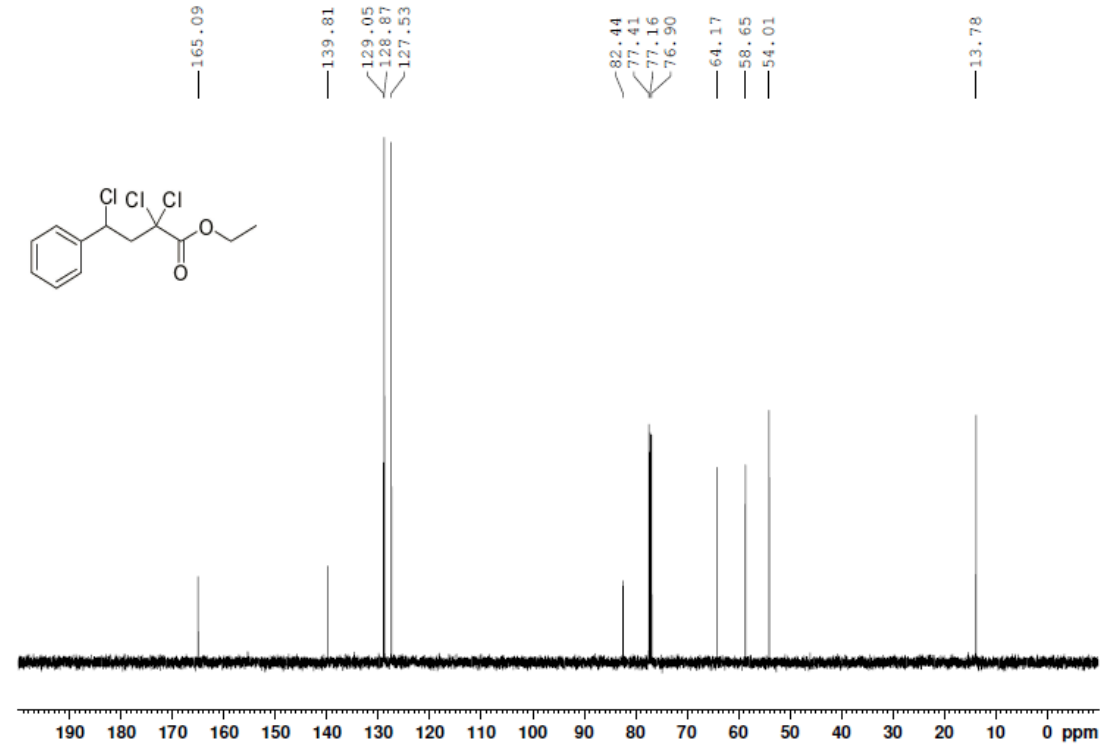
^{13}C NMR spectrum for **8ac**



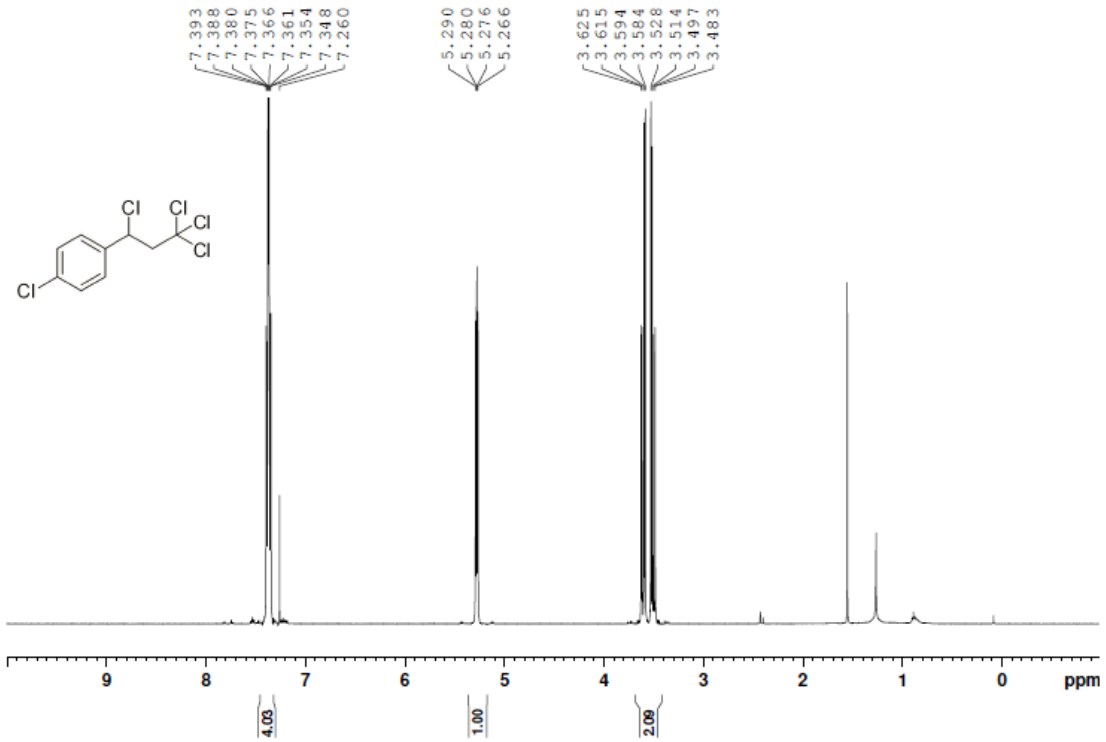
^{1}H NMR spectrum for **8ad**



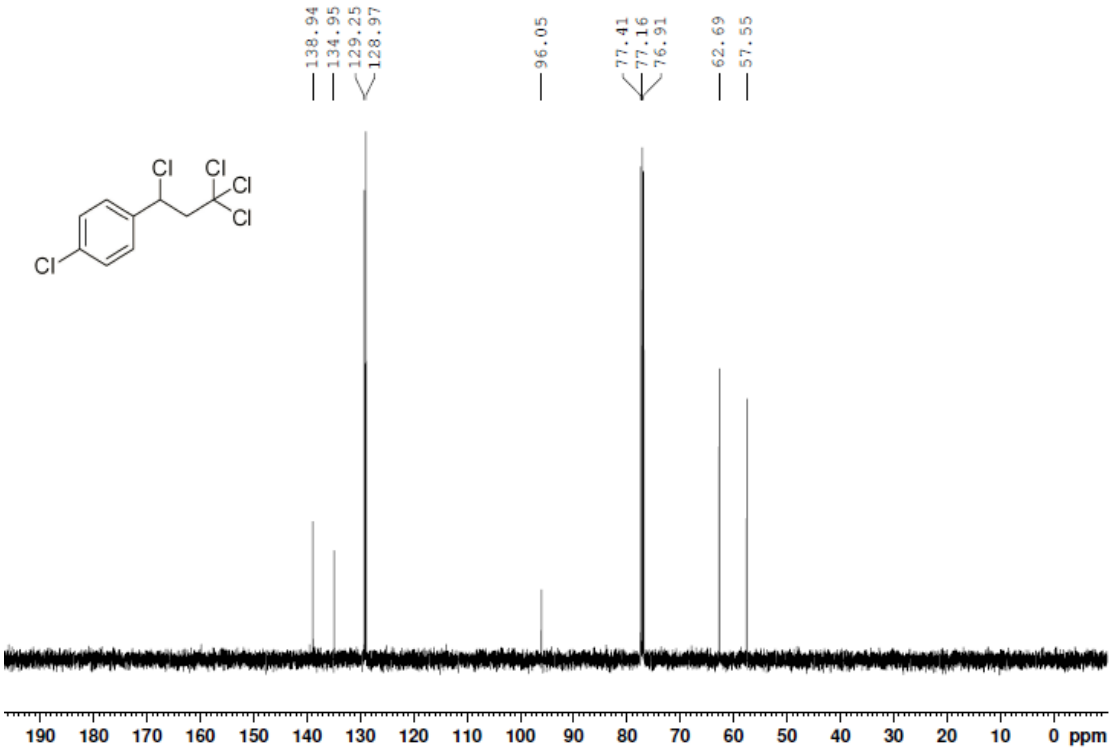
^{13}C NMR spectrum for **8ad**



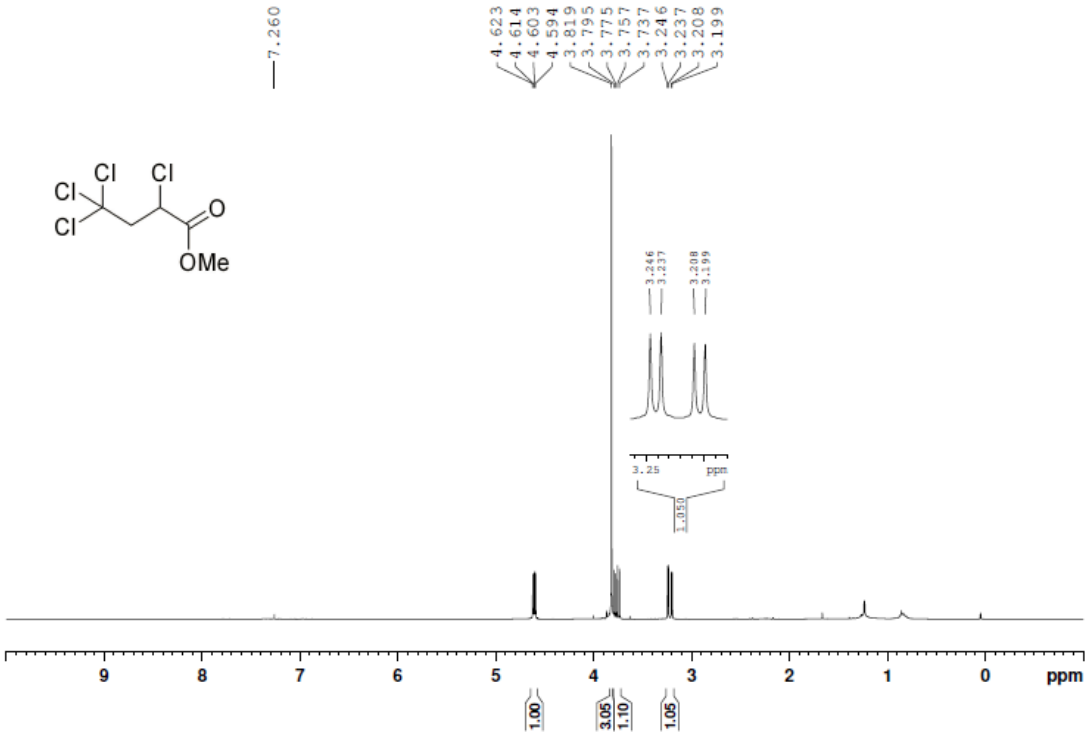
^{1}H NMR spectrum for **8ba**



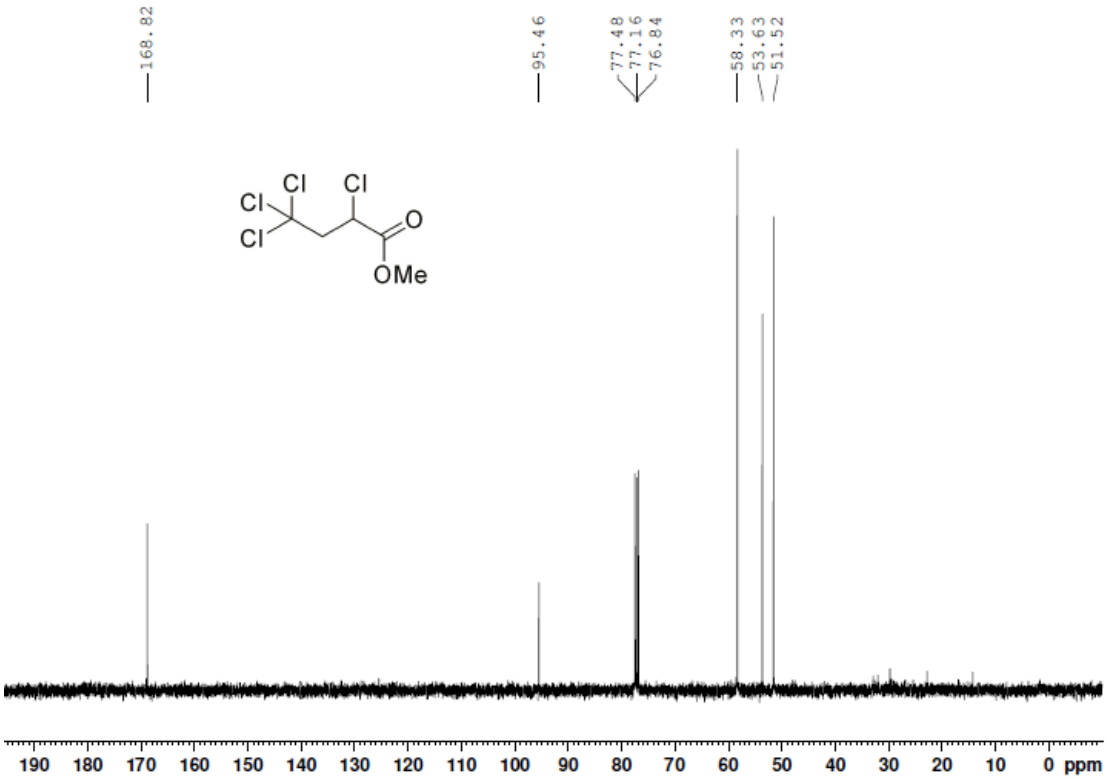
^{13}C NMR spectrum for **8ba**



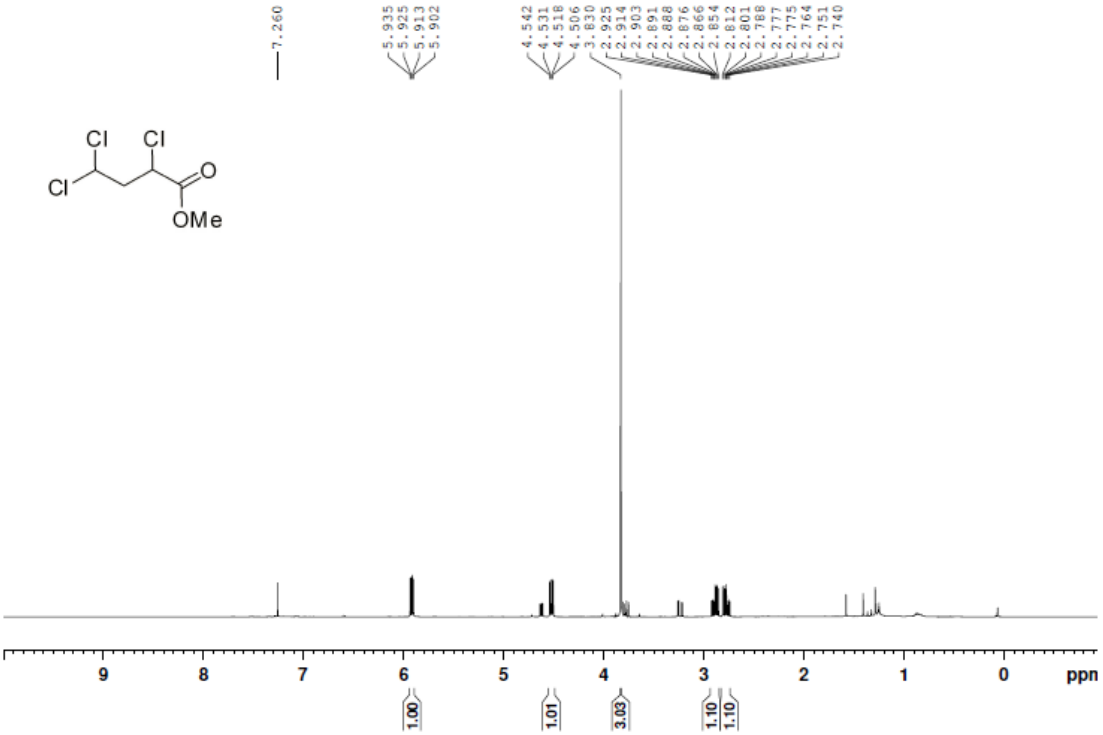
^{1}H NMR spectrum for **8ca**



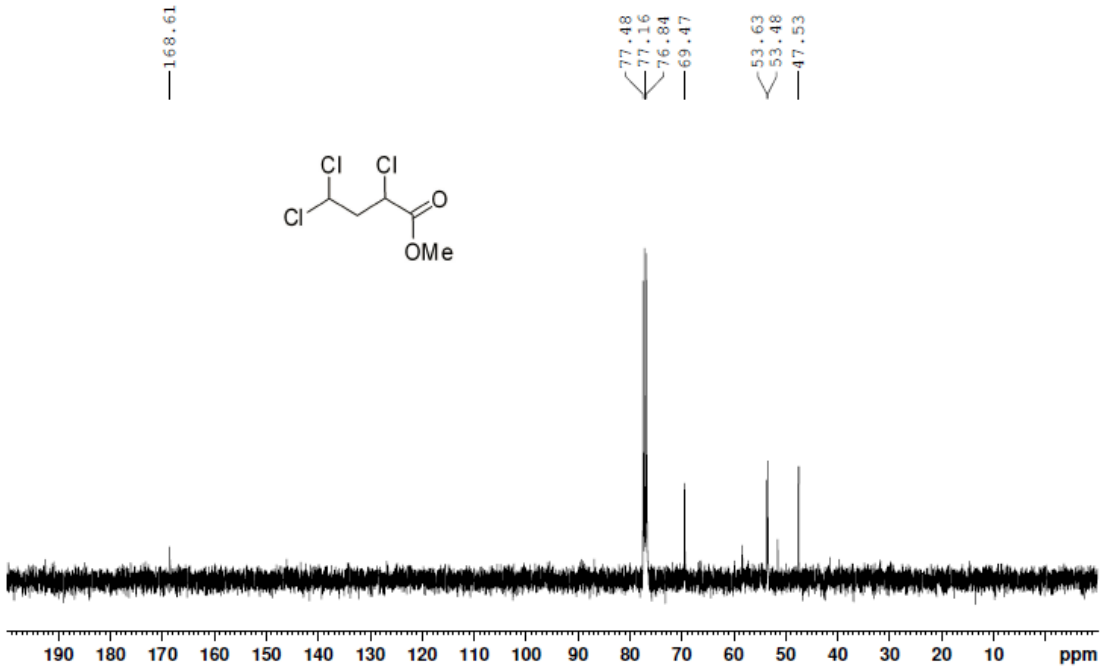
^{13}C NMR spectrum for **8ca**



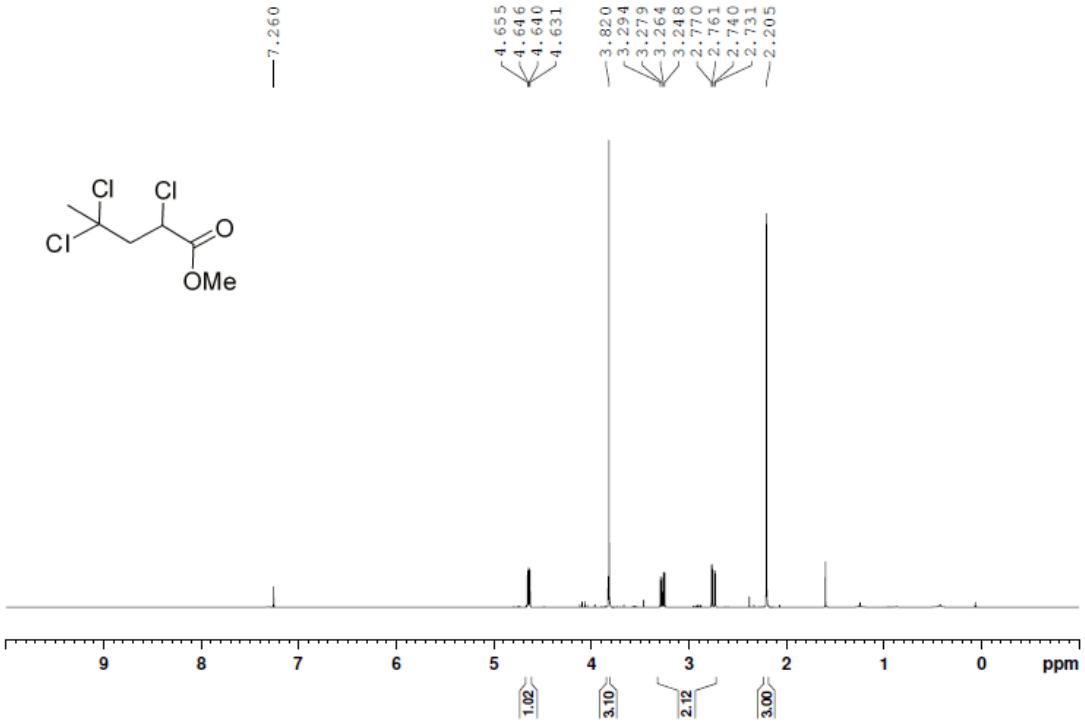
^{1}H NMR spectrum for **8cb**



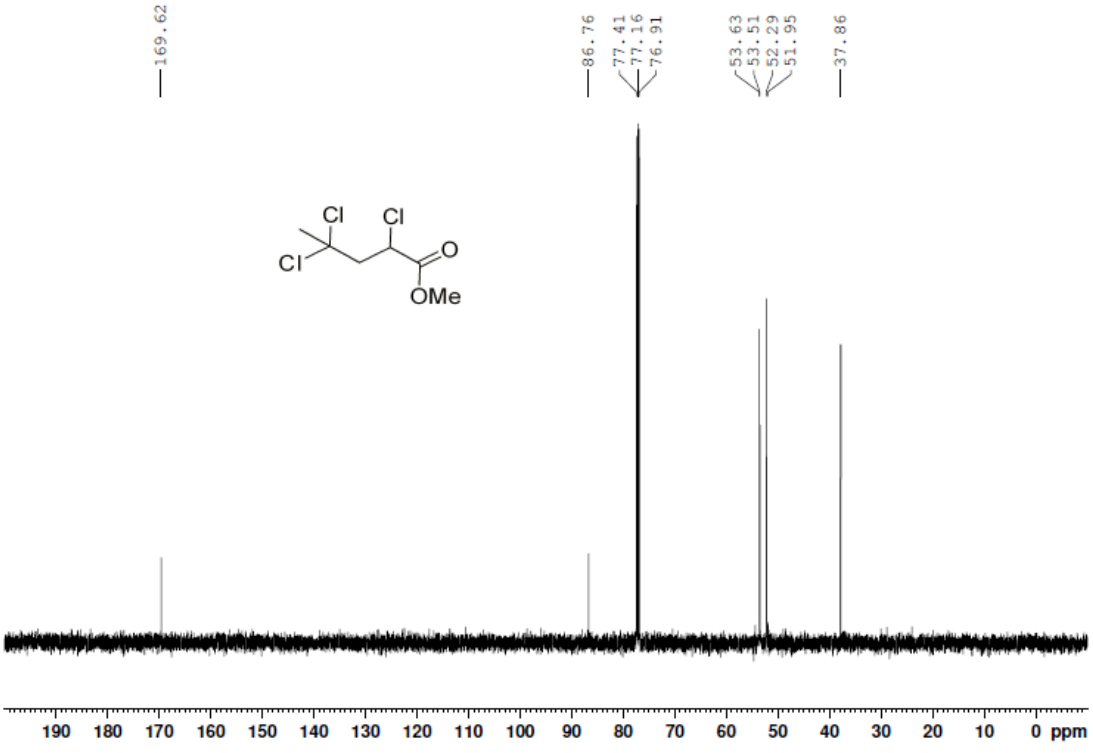
^{13}C NMR spectrum for **8cb**



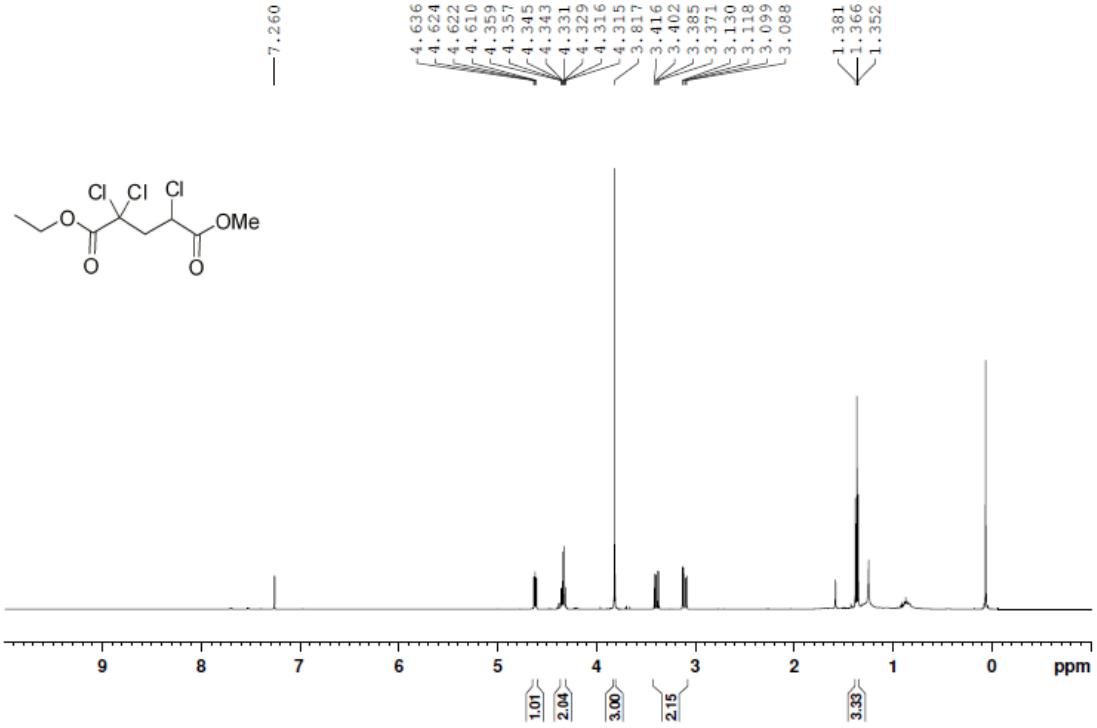
^{1}H NMR spectrum for 8**cc**



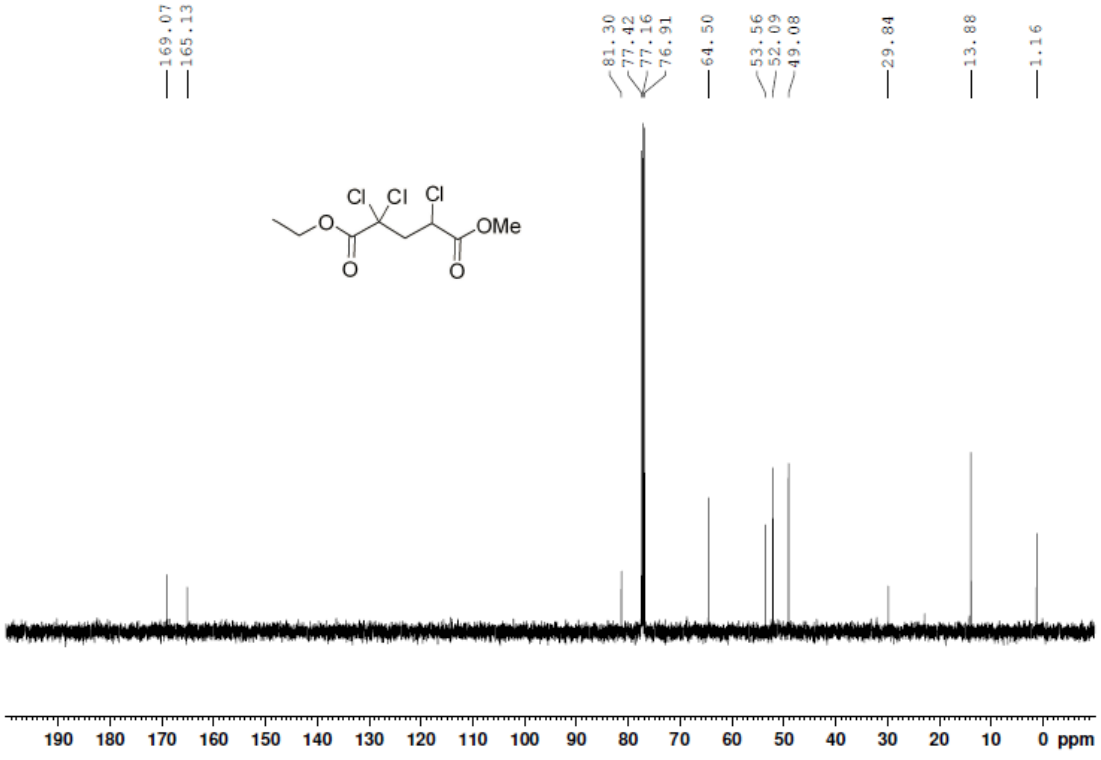
^{13}C NMR spectrum for **8cc**



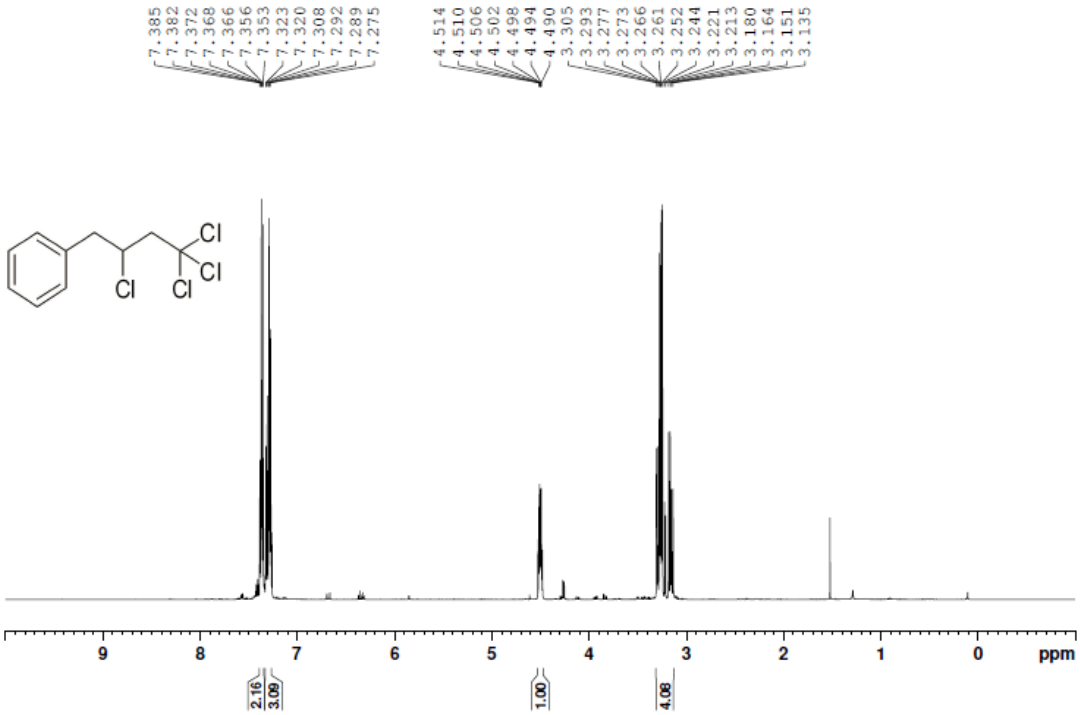
^{1}H NMR spectrum for **8cd**



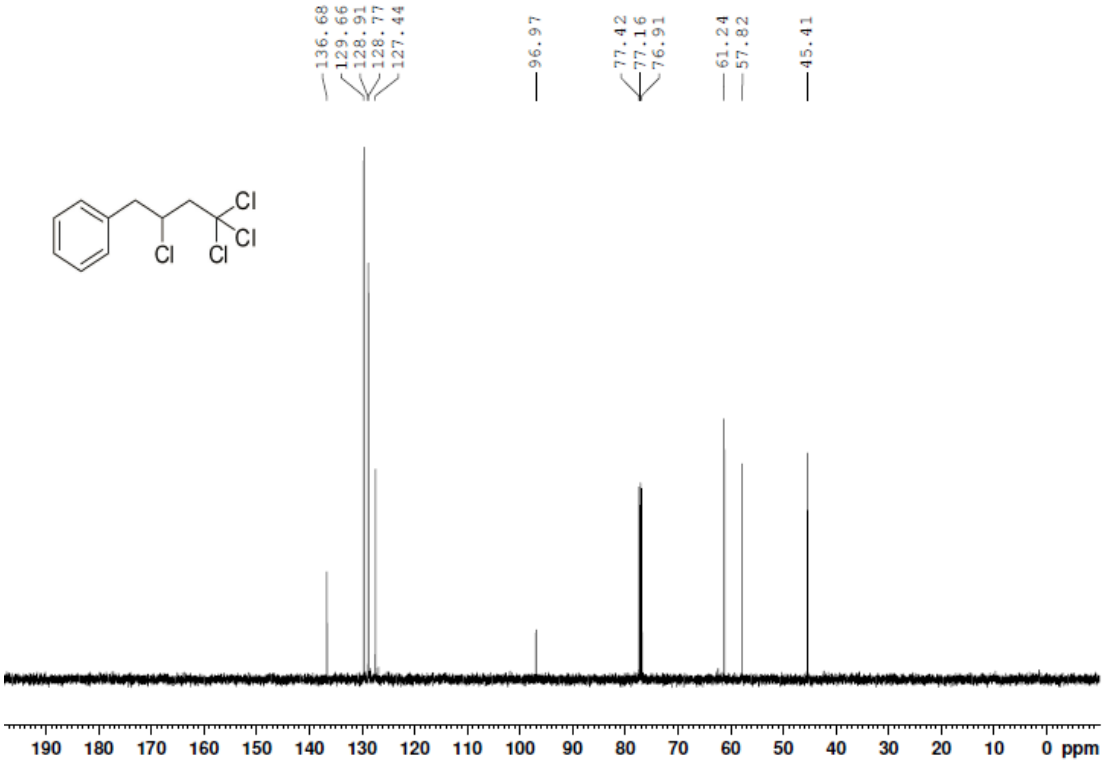
^{13}C NMR spectrum for **8cd**



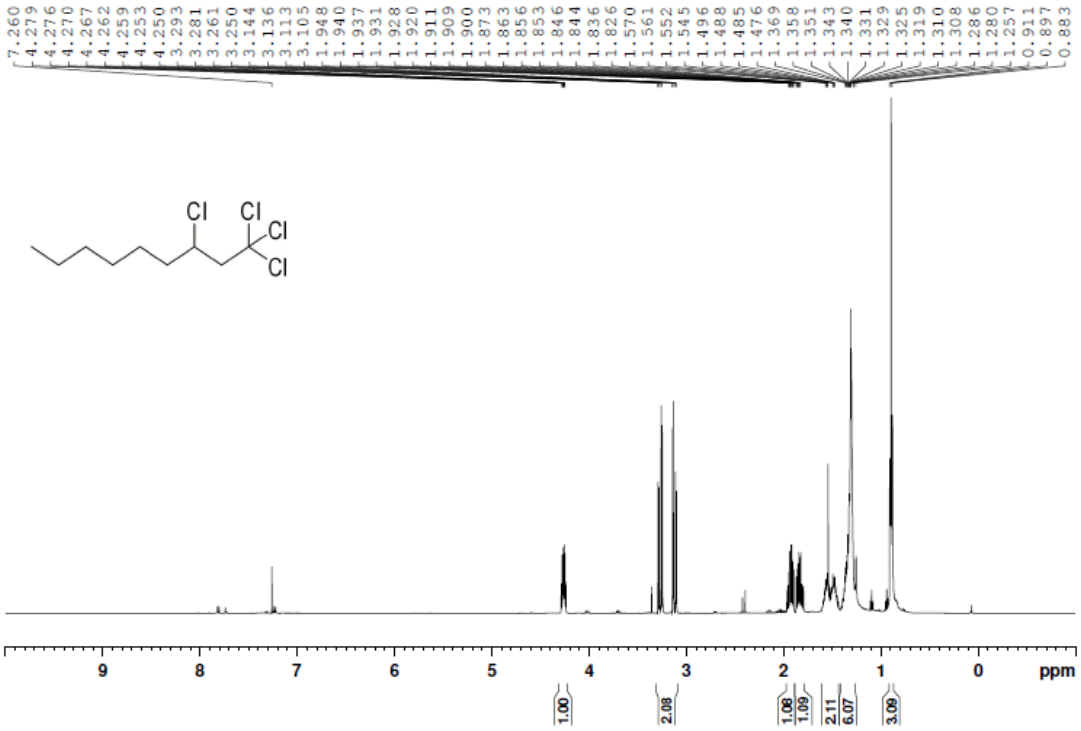
^{1}H NMR spectrum for **8da**



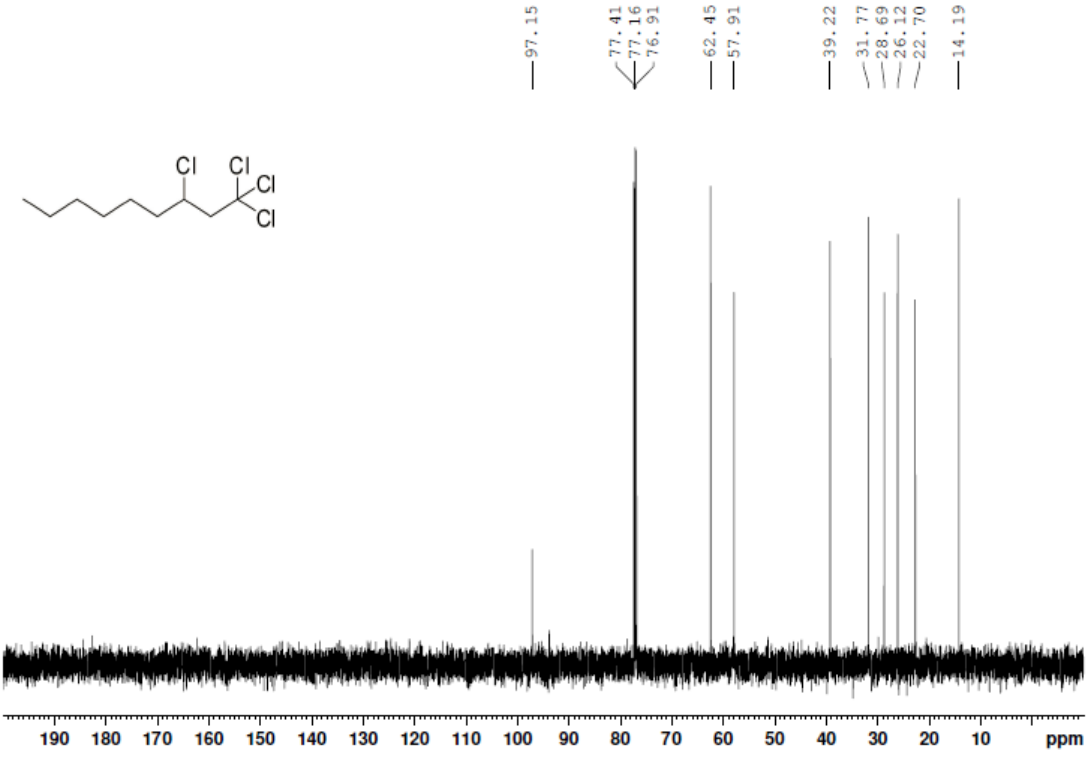
^{13}C NMR spectrum for **8da**



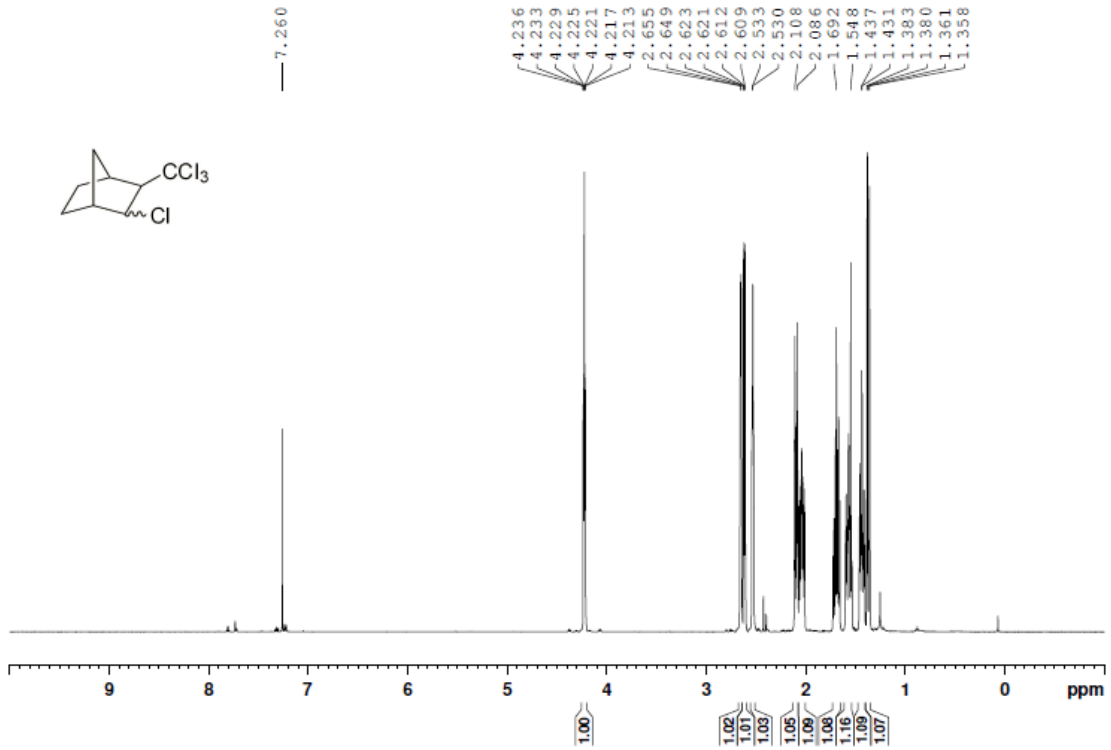
^{1}H NMR spectrum for **8ea**



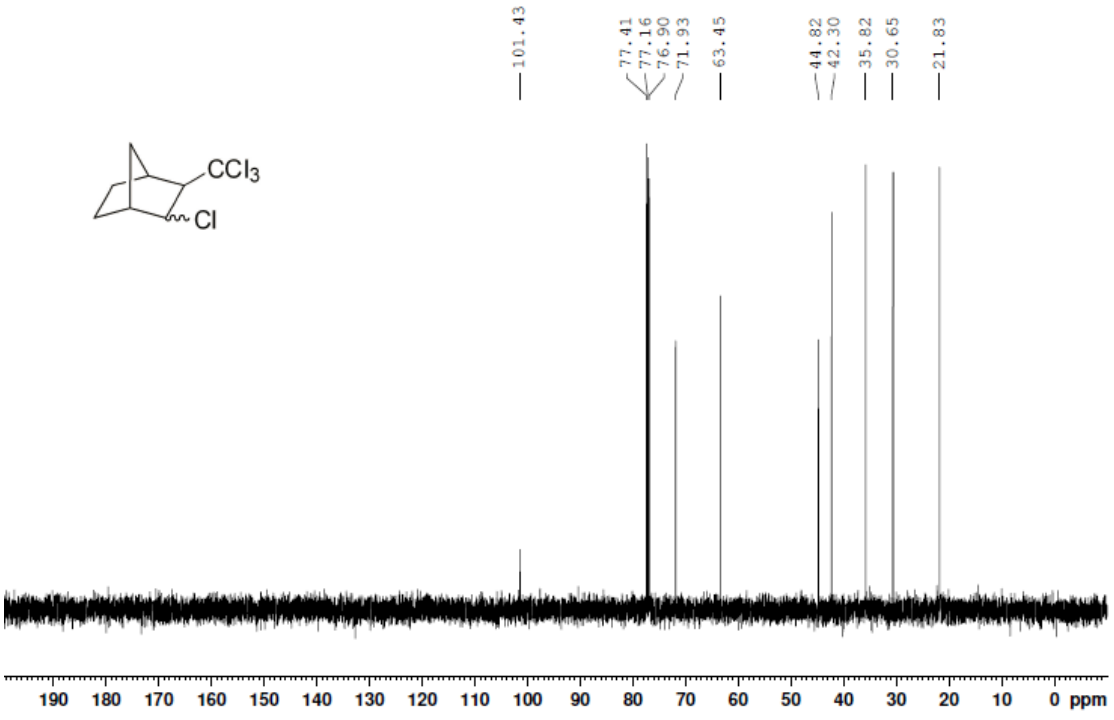
^{13}C NMR spectrum for **8ea**



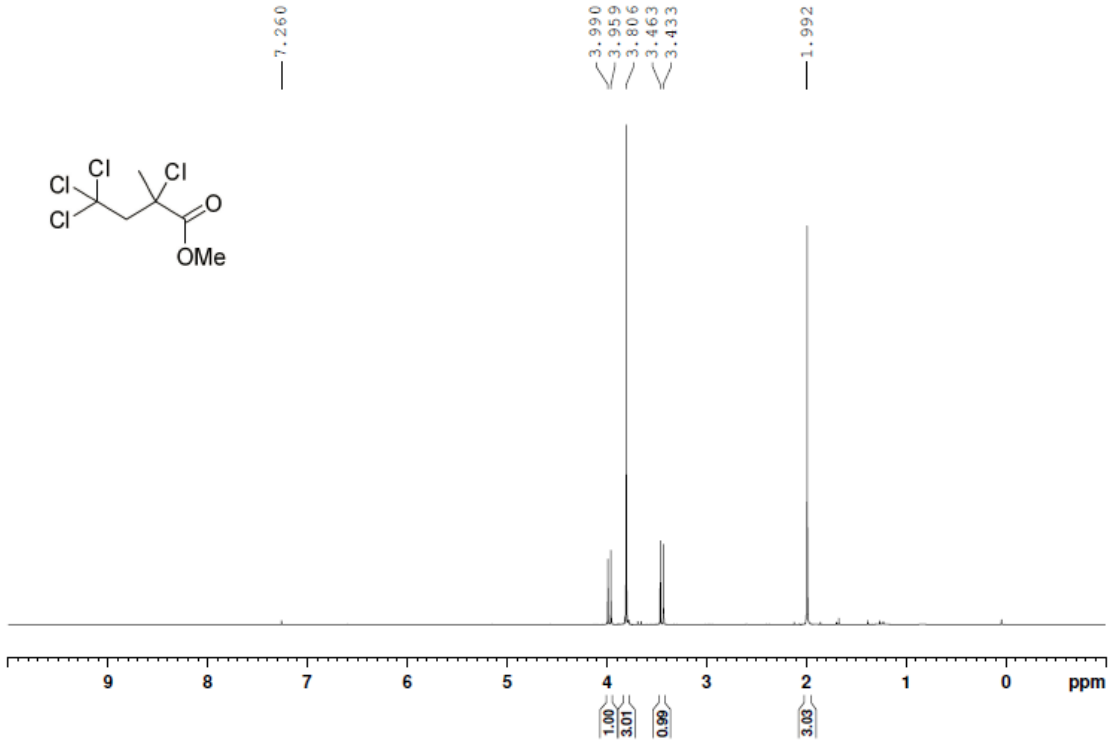
^{1}H NMR spectrum for **8fa**



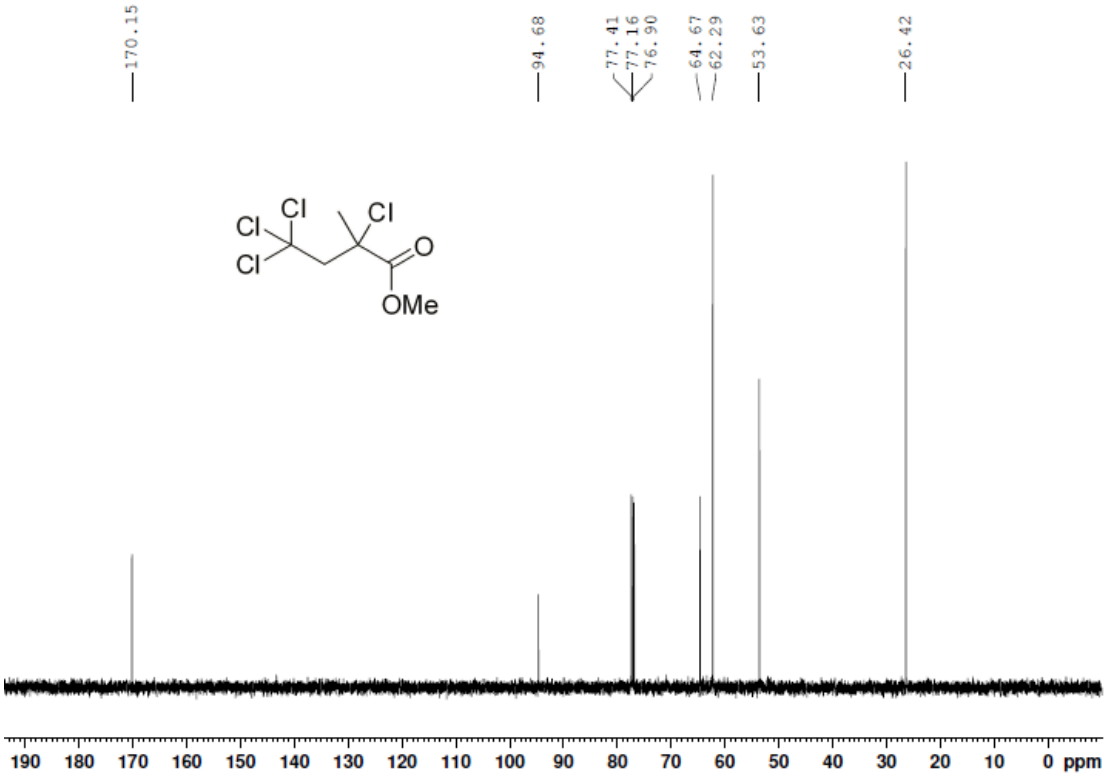
^{13}C NMR spectrum for **8fa**



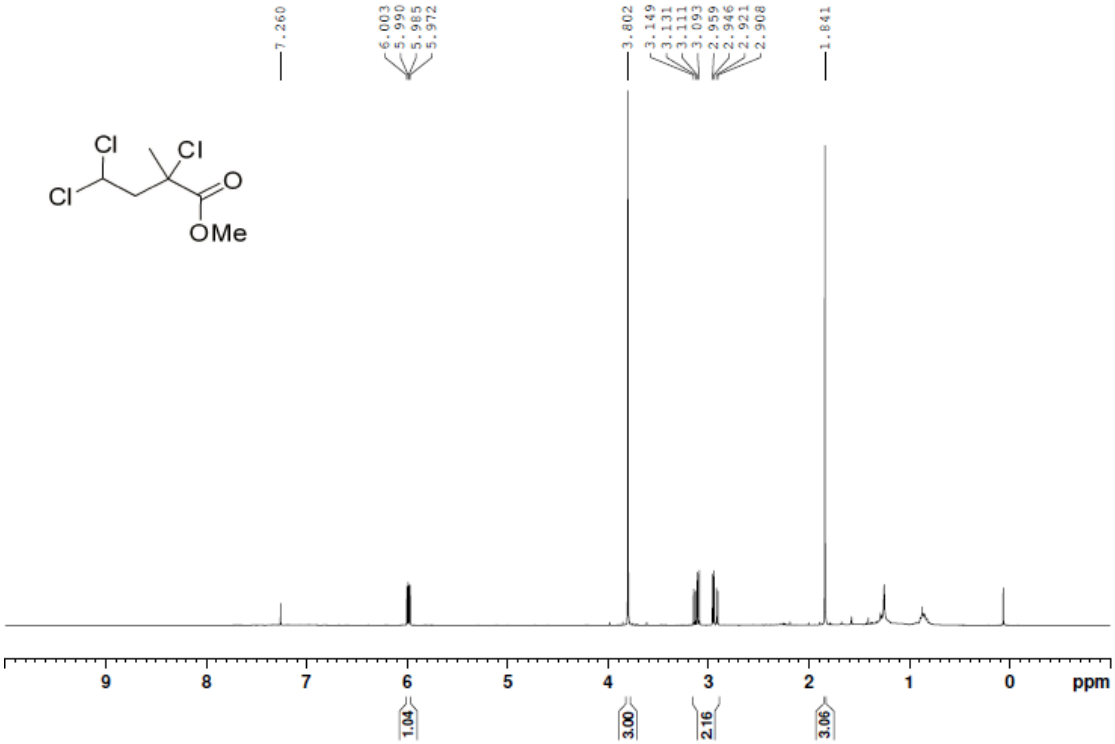
^{1}H NMR spectrum for **8ga**



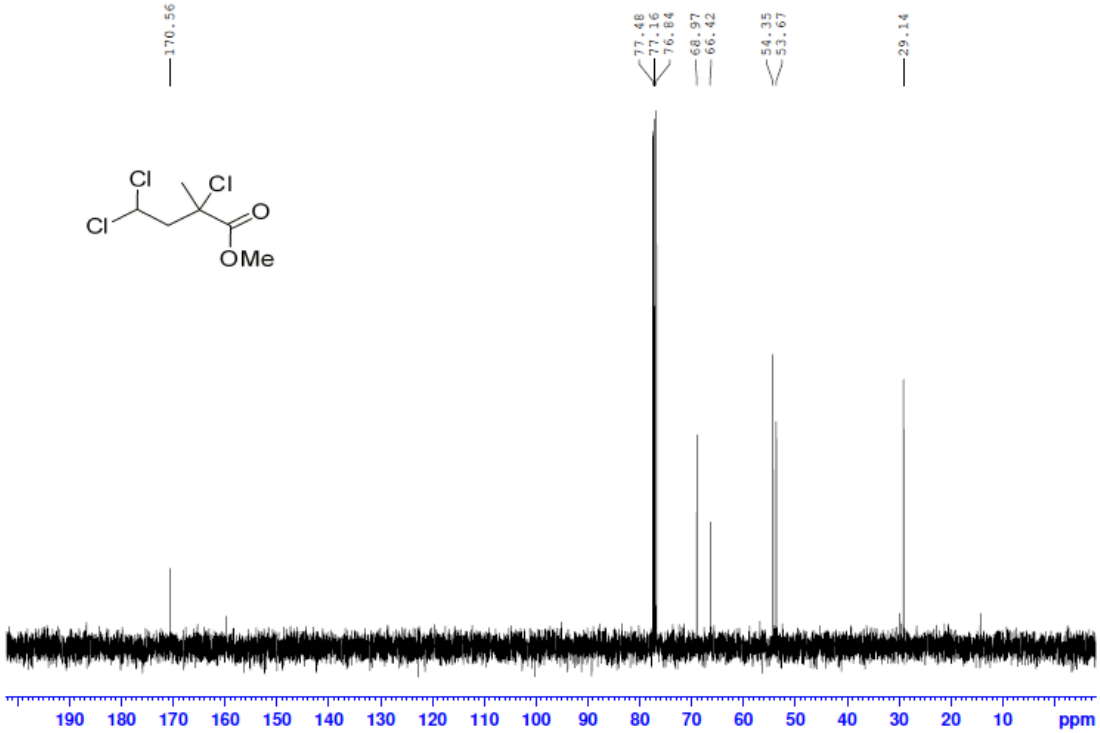
^{13}C NMR spectrum for **8ga**



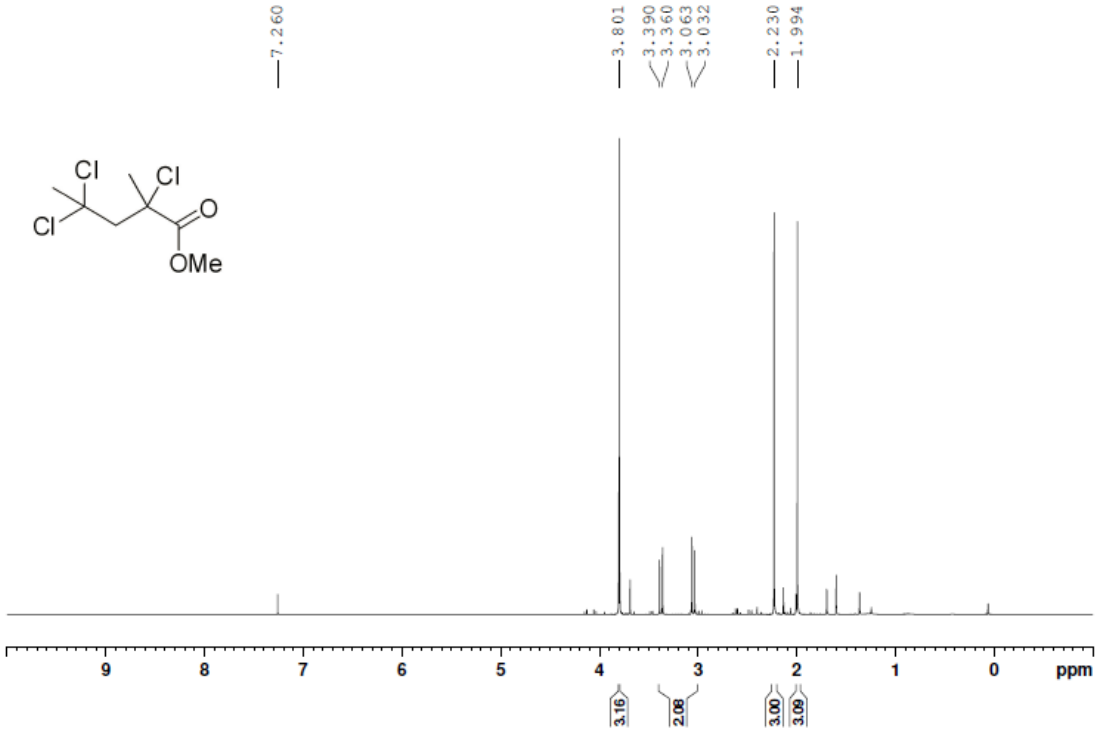
^{1}H NMR spectrum for **8gb**



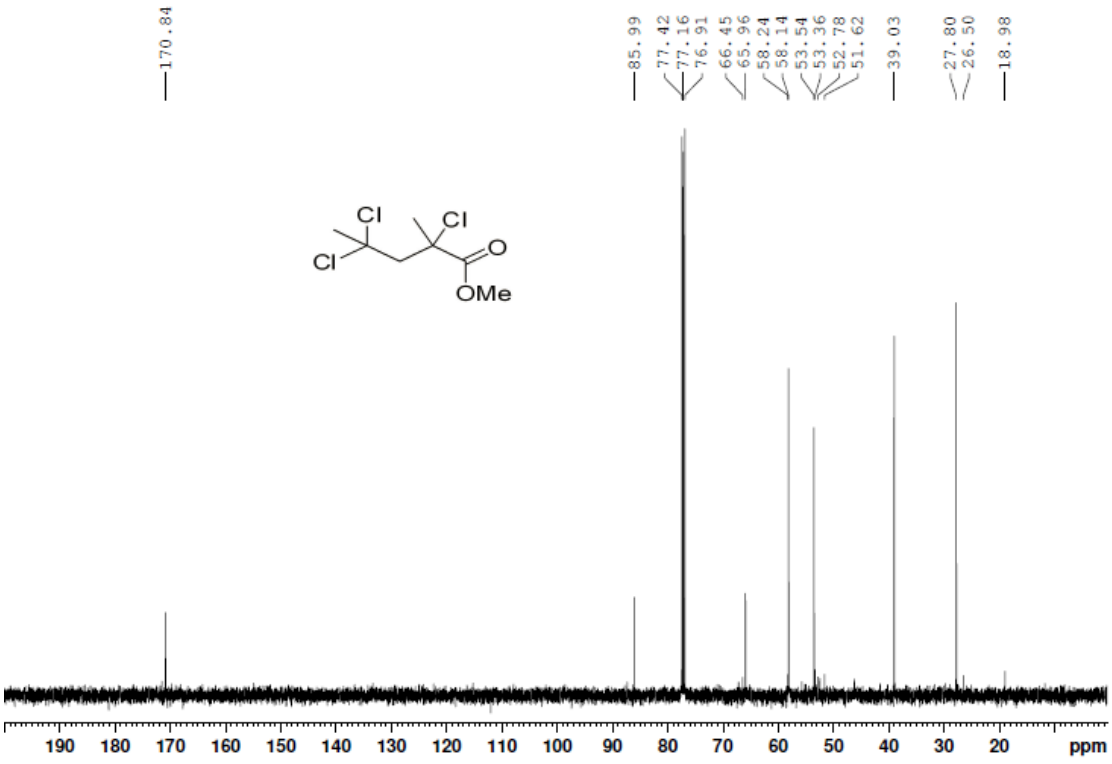
^{13}C NMR spectrum for **8gb**



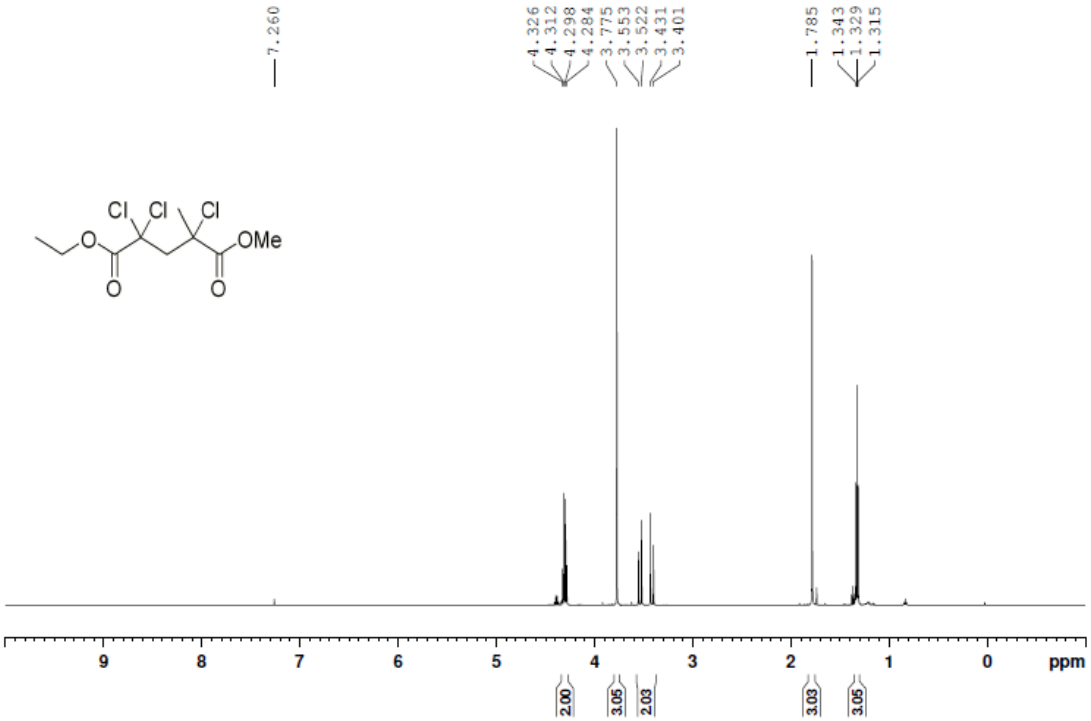
^{1}H NMR spectrum for **8gc**



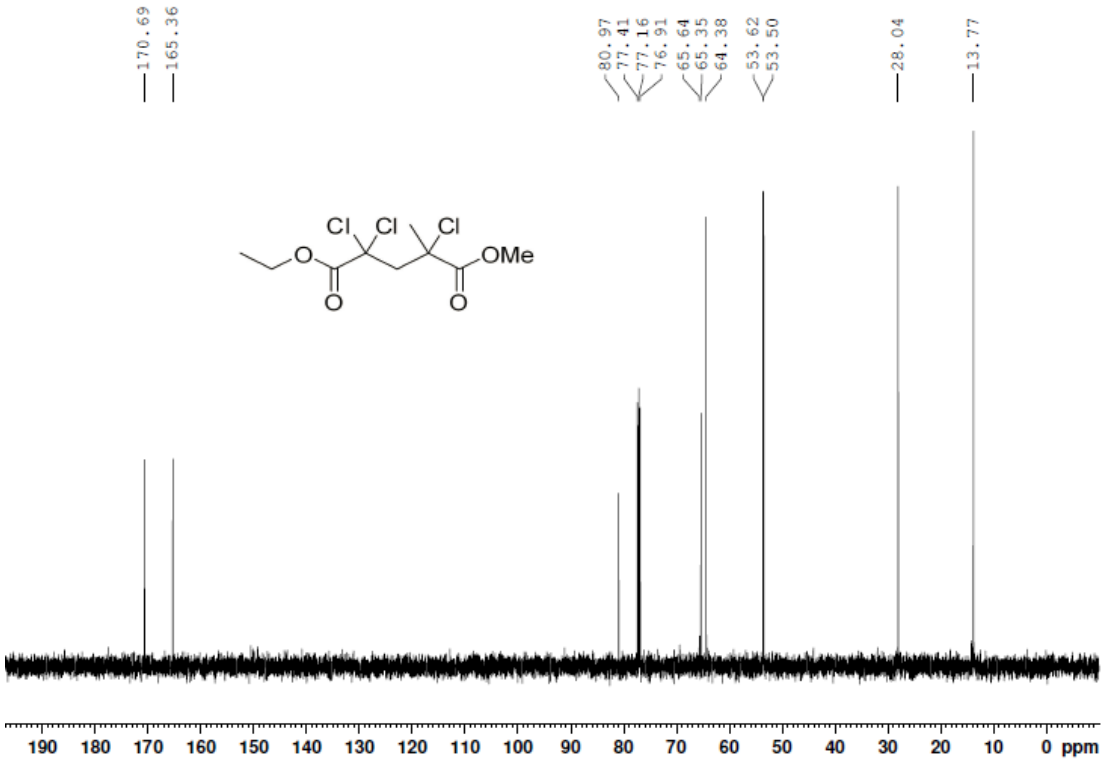
^{13}C NMR spectrum for **8gc**



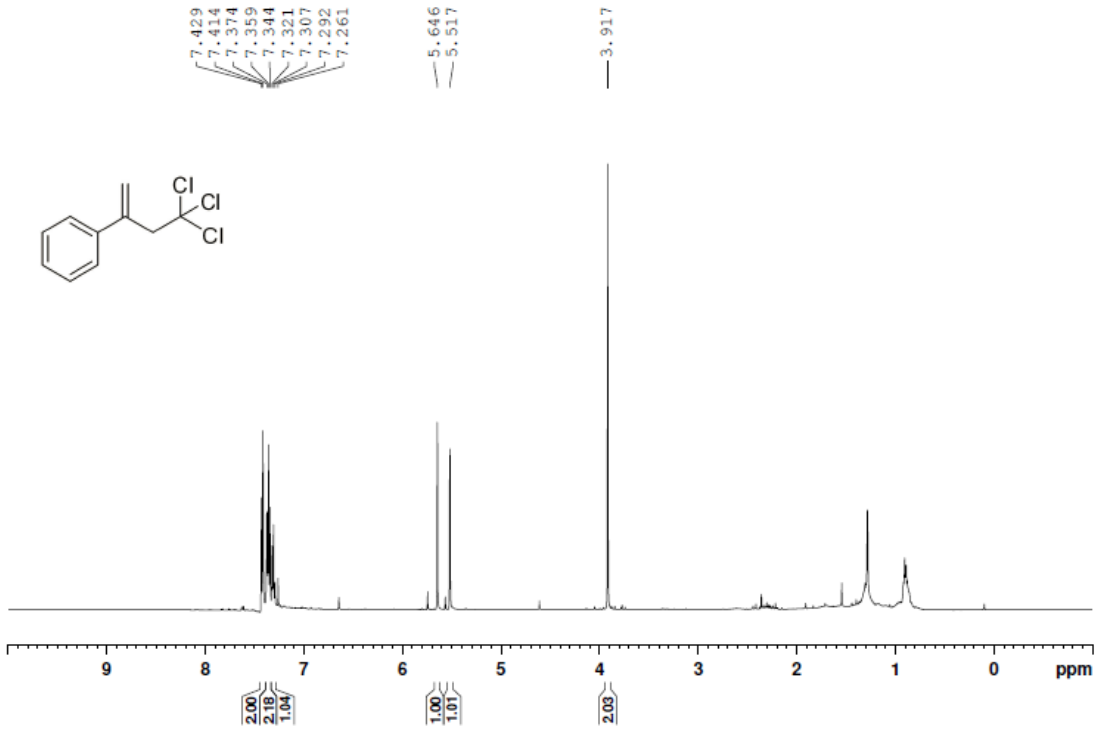
^{1}H NMR spectrum for **8gd**



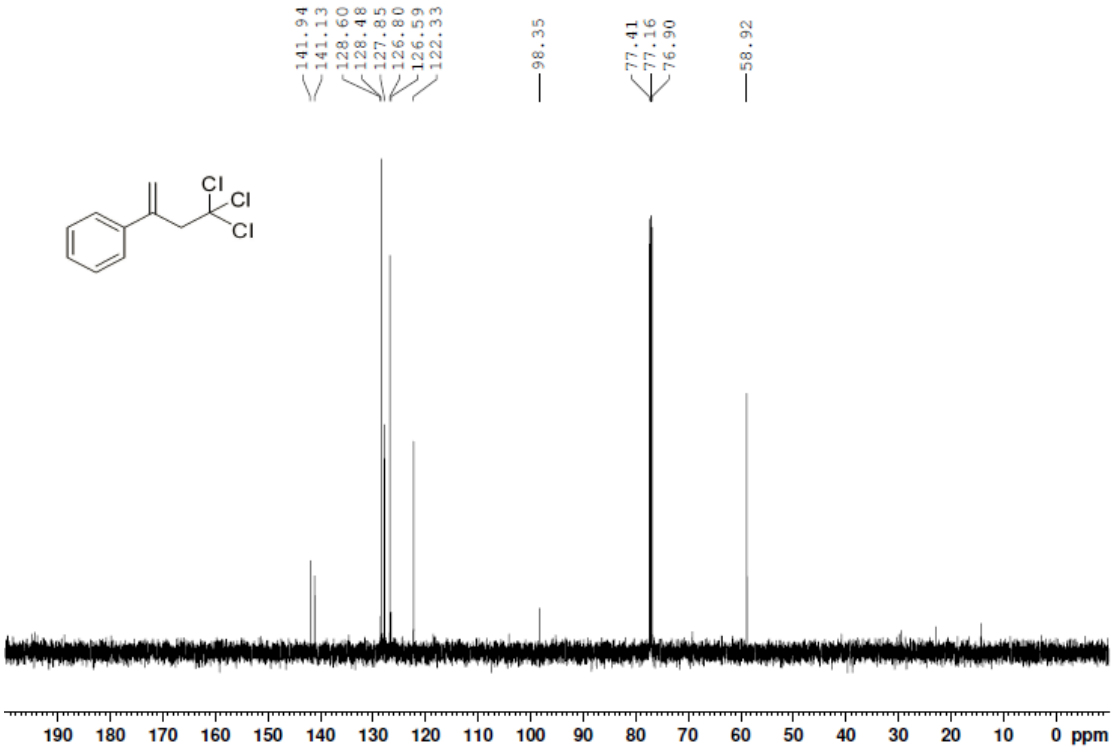
^{13}C NMR spectrum for **8gd**



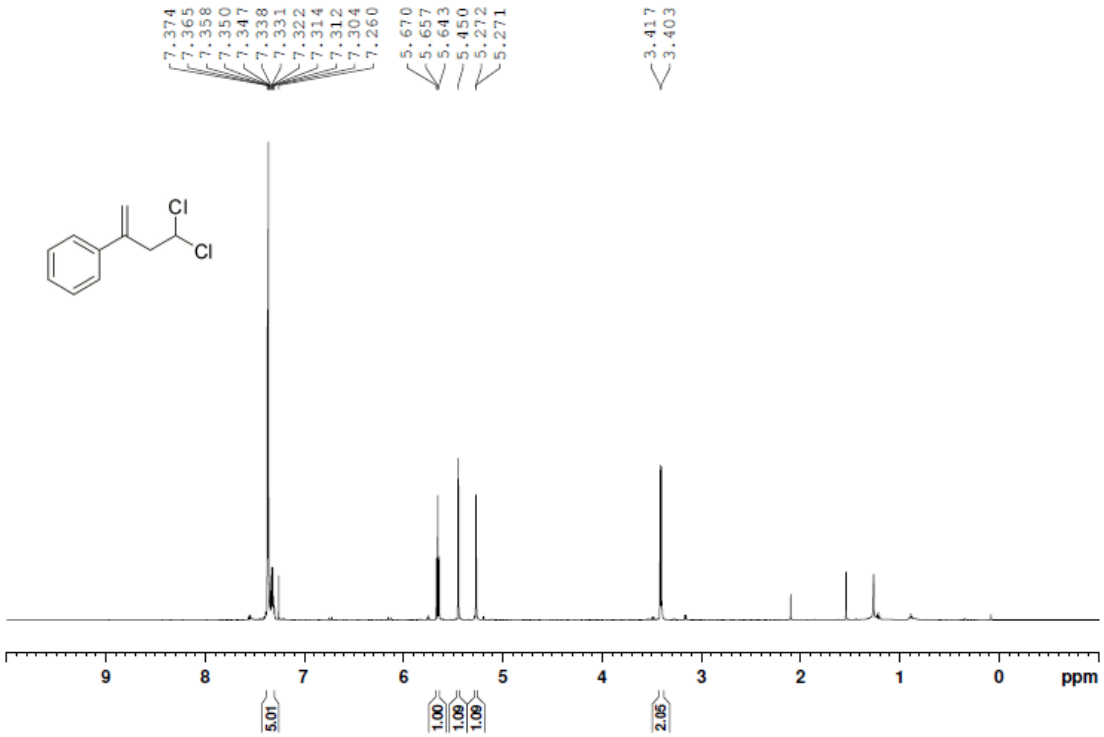
^{1}H NMR spectrum for **9ha**



^{13}C NMR spectrum for **9ha**



^{1}H NMR spectrum for **9hb**



^{13}C NMR spectrum for **9hb**