Supporting Information for

Pursuing the active species in an aluminum-based Lewis acid system for catalytic Diels Alder cycloadditions

Zhizhou Liu, Rakesh Ganguly, Dragoslav Vidović*

School of Physical and Mathematical Sciences, Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore, 637371.
Email: dvidovic@ntu.edu.sg

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Figure S1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(3,4-Dimethylcyclohex-3-en-1-yl)ethanone, **20**).

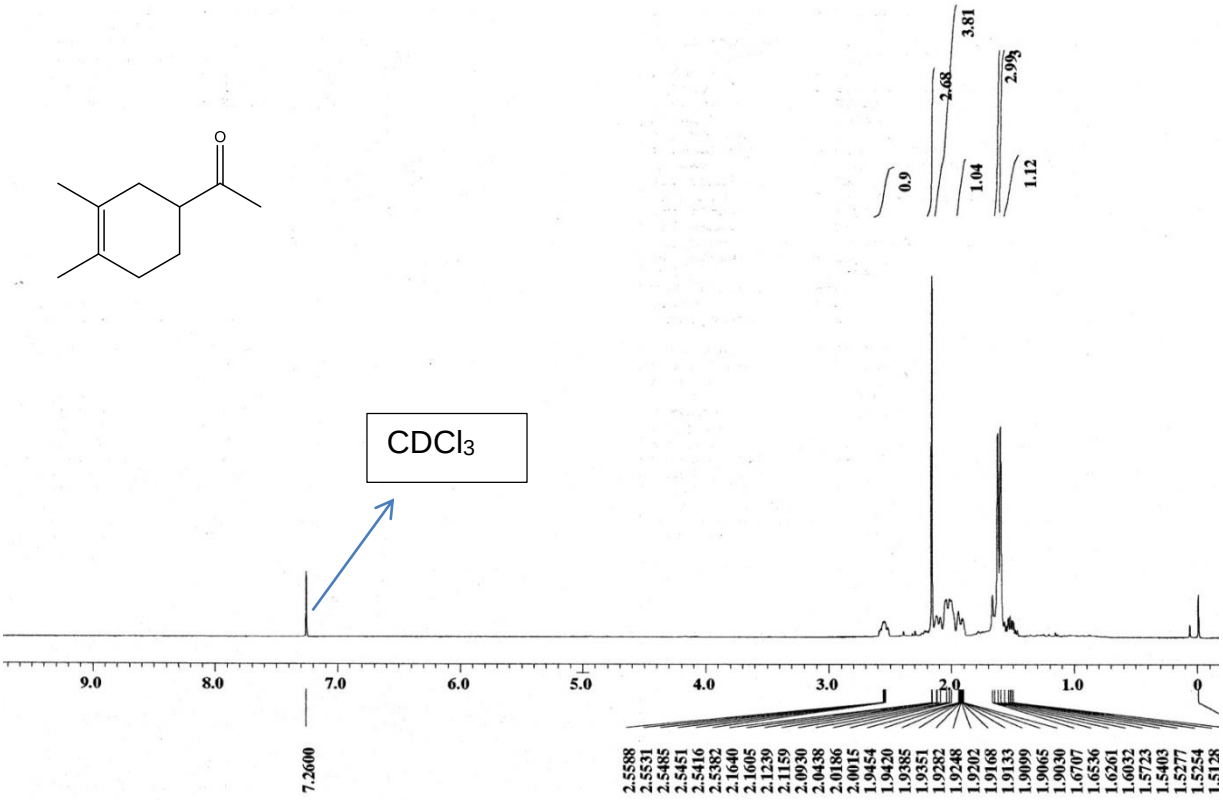


Figure S2: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of 1-(3,4-Dimethylcyclohex-3-en-1-yl)ethanone, **20**).

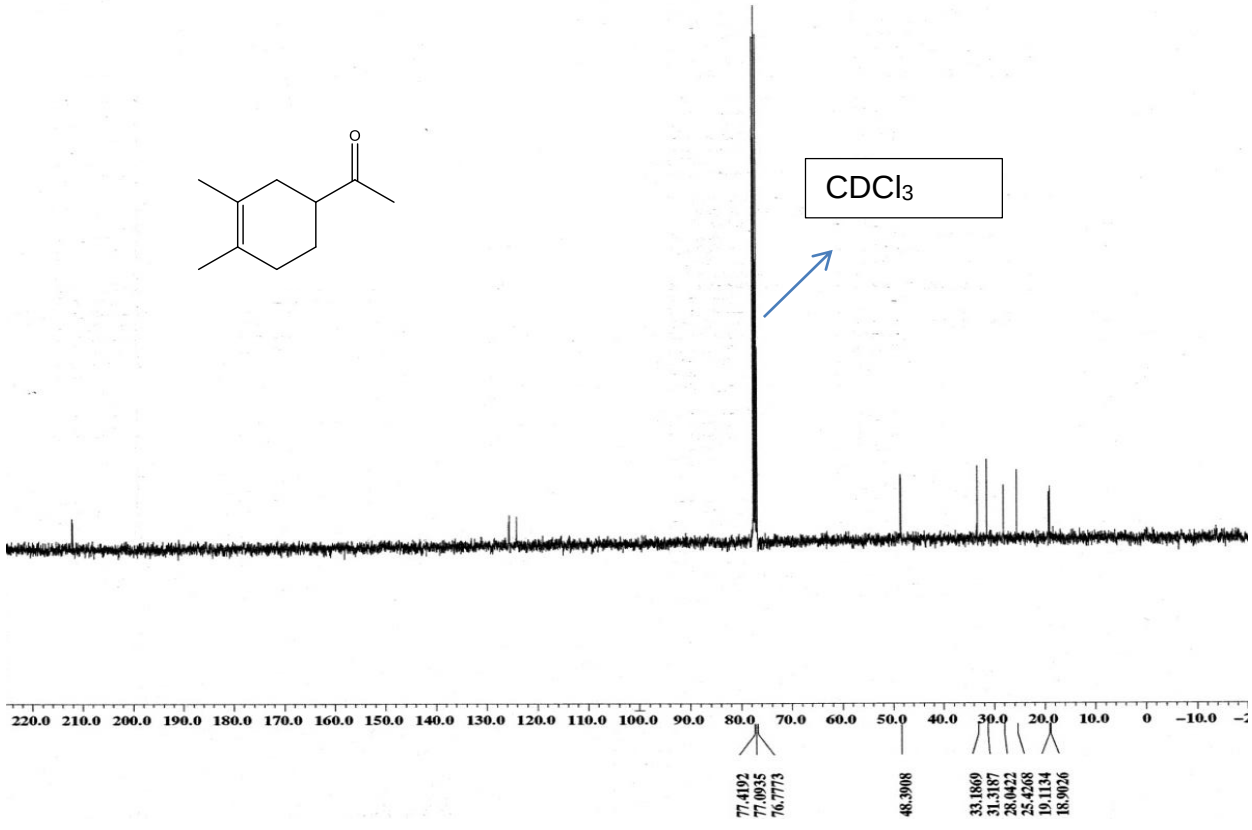


Figure S3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(3,4-dimethylcyclohex-3-en-1-yl)propan-1-one, **21**).

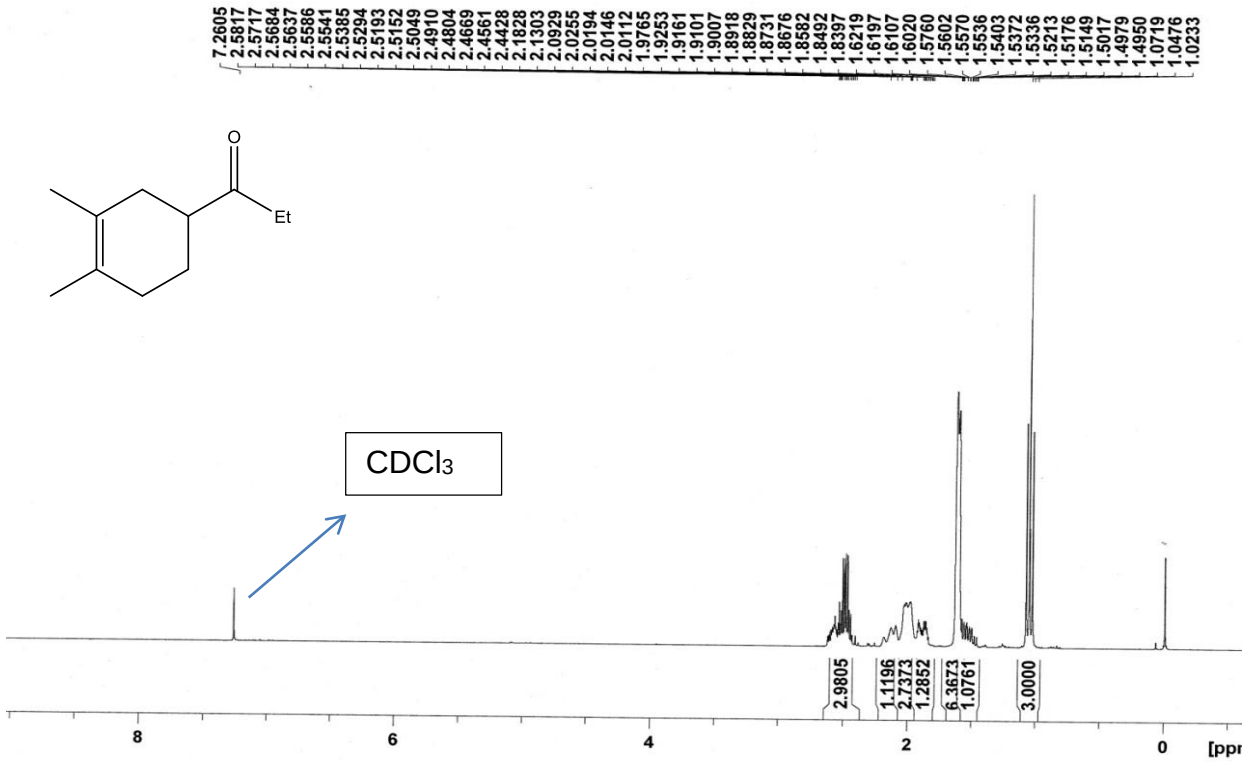


Figure S4: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of 1-(3,4-dimethylcyclohex-3-en-1-yl)propan-1-one, **21**).

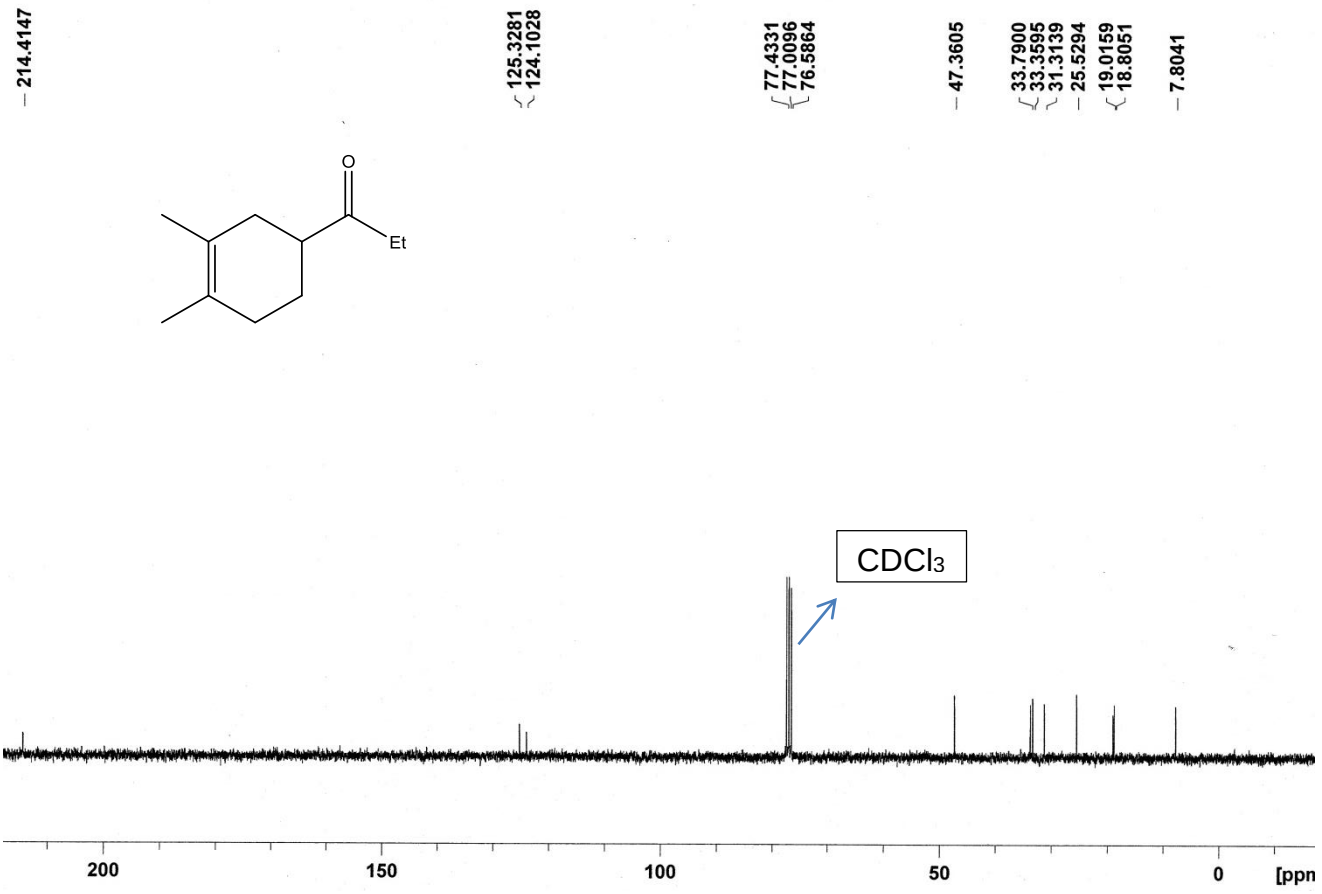


Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one, **22**).

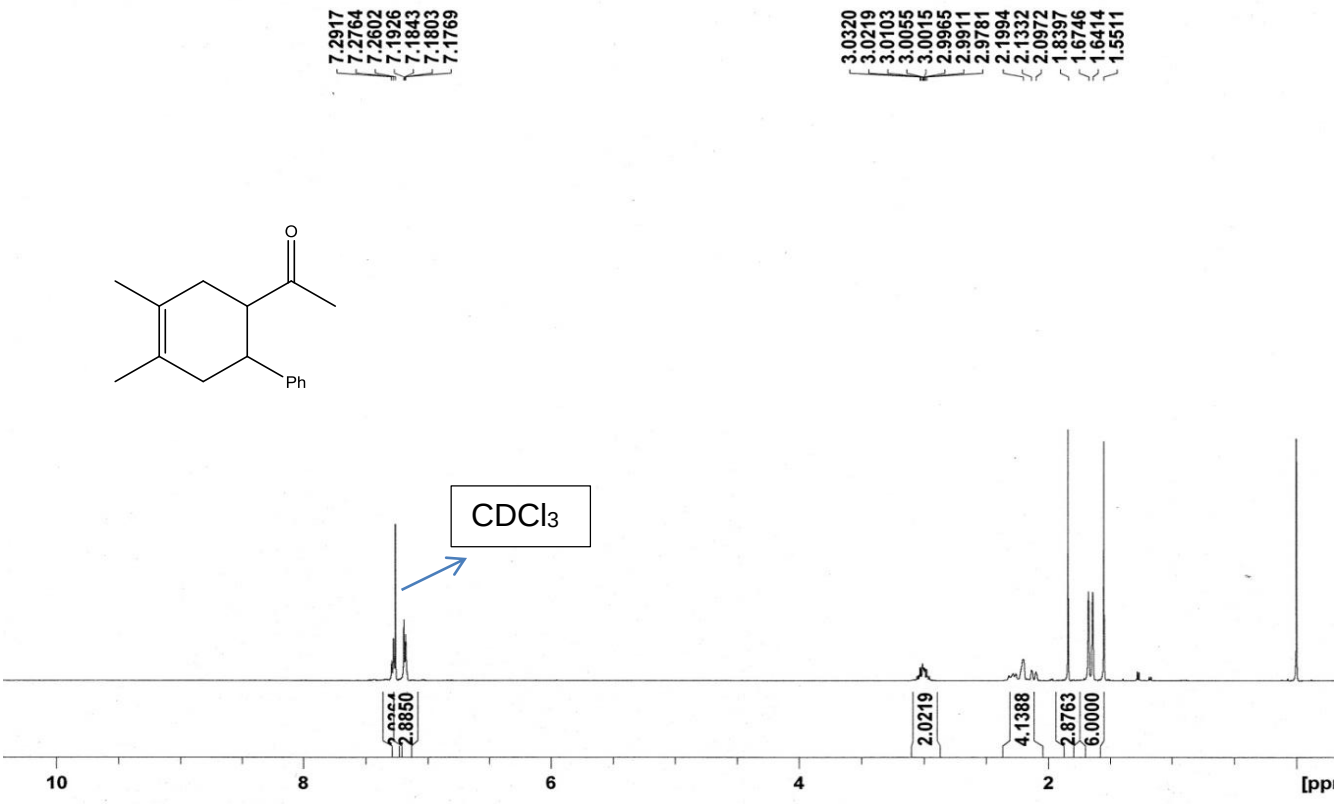


Figure S6: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of 1-(4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one, **22**).

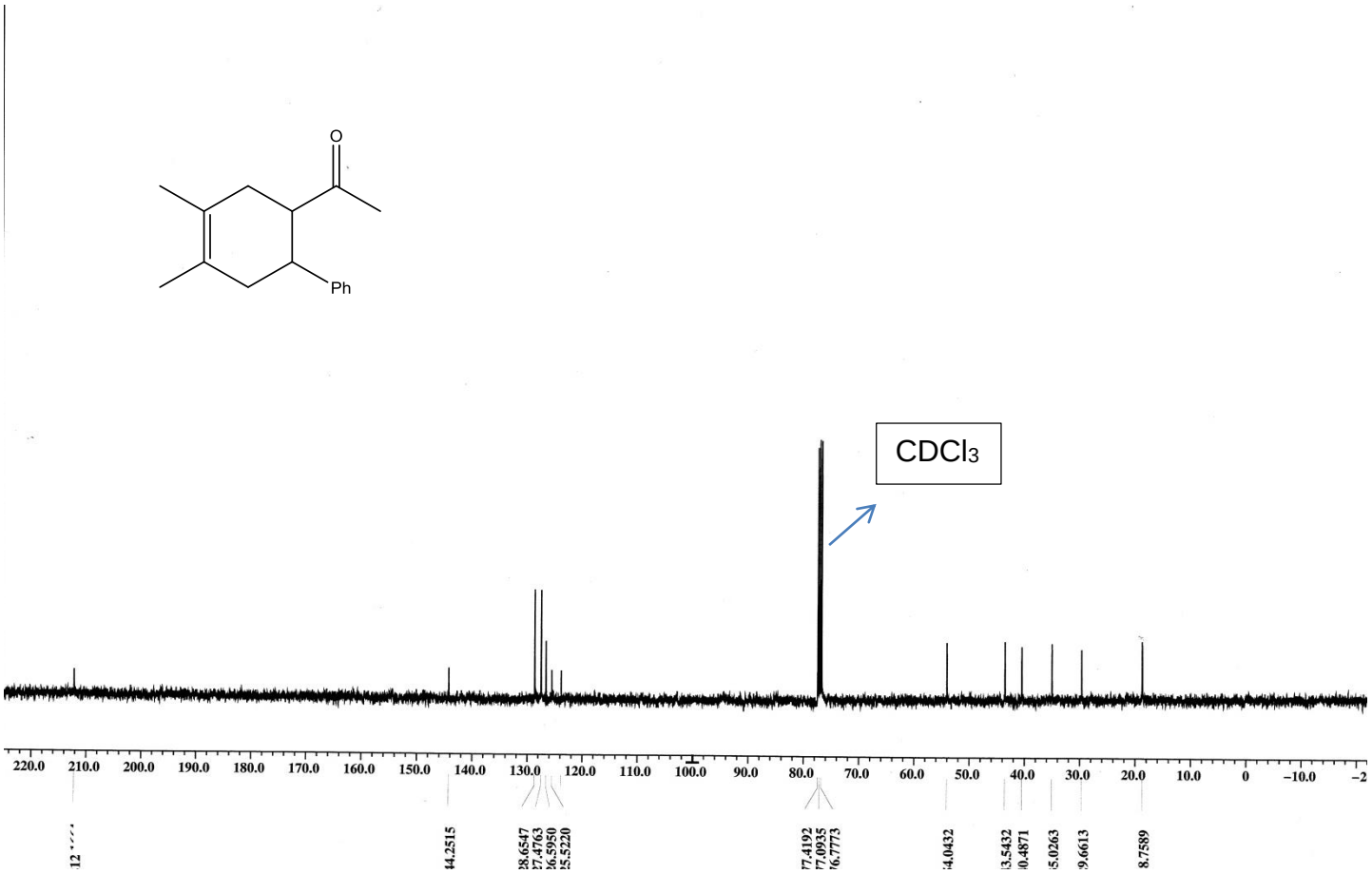


Figure S7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone, **9**).

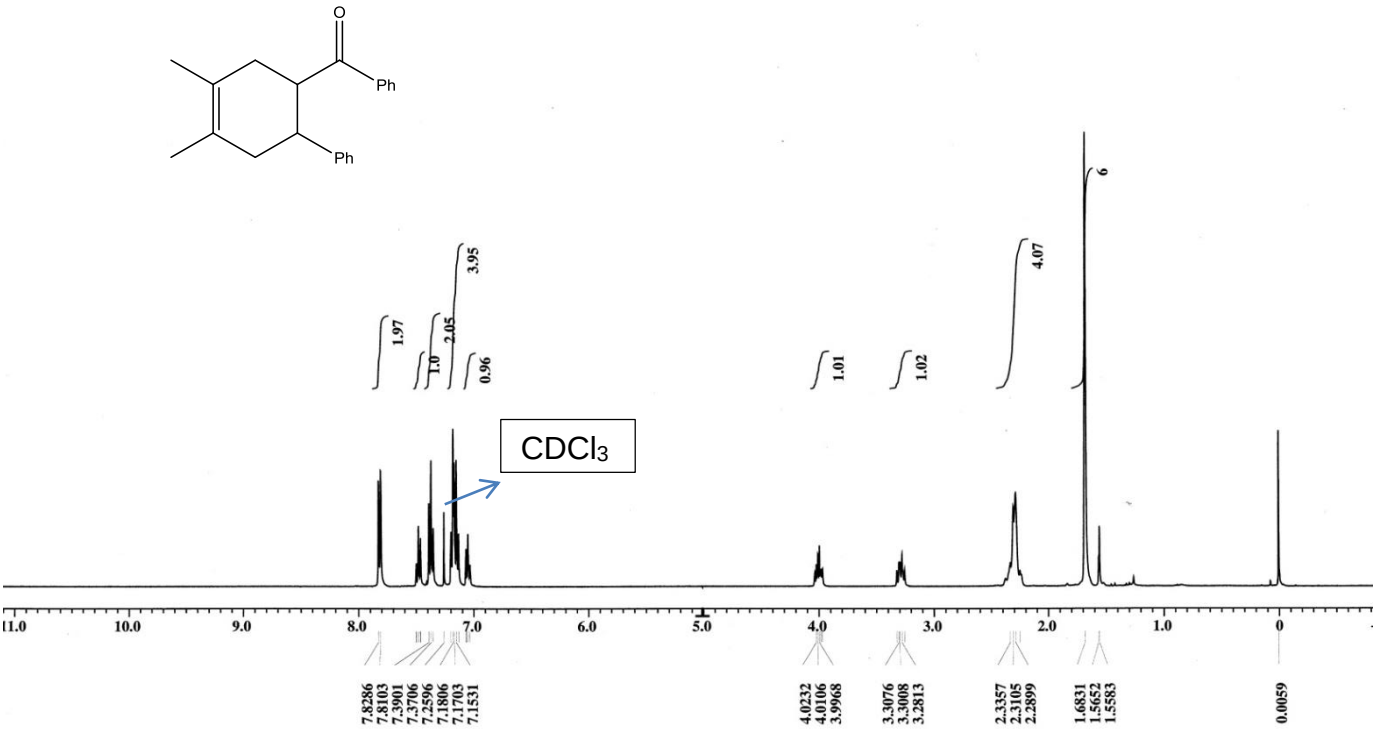


Figure S8: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone, **9**).

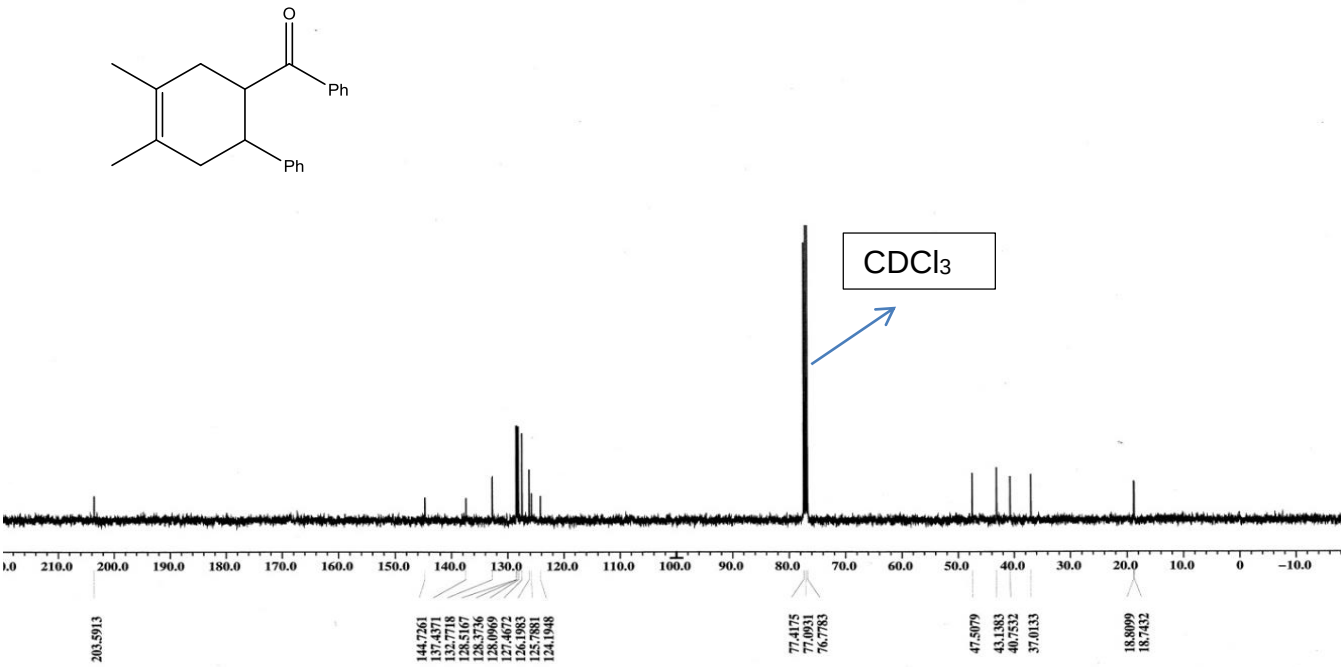


Figure S9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (6,7-dimethyl-3,4,4a,5,8,8a-hexahydronaphthalen-1(2H)-one, **24**).

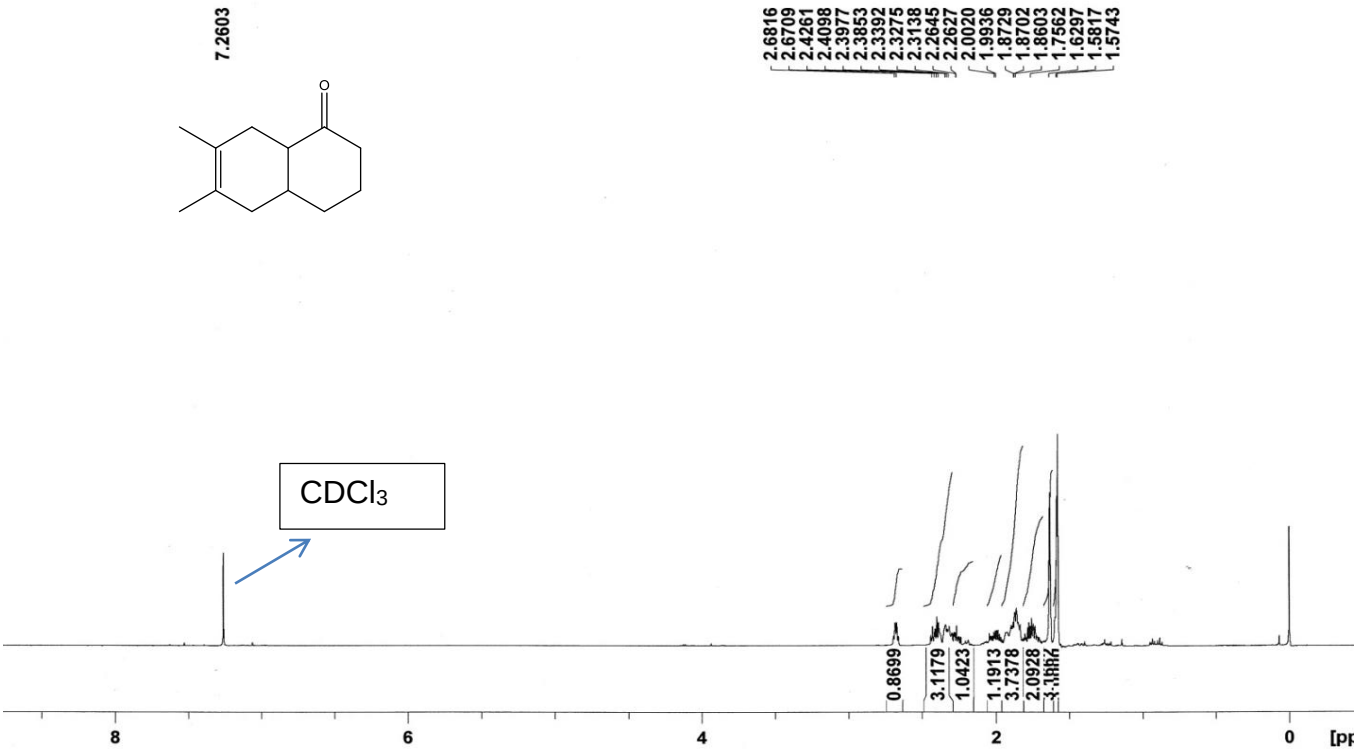


Figure S10: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (6,7-dimethyl-3,4,4a,5,8,8a-hexahydronaphthalen-1(2H)-one, **24**).

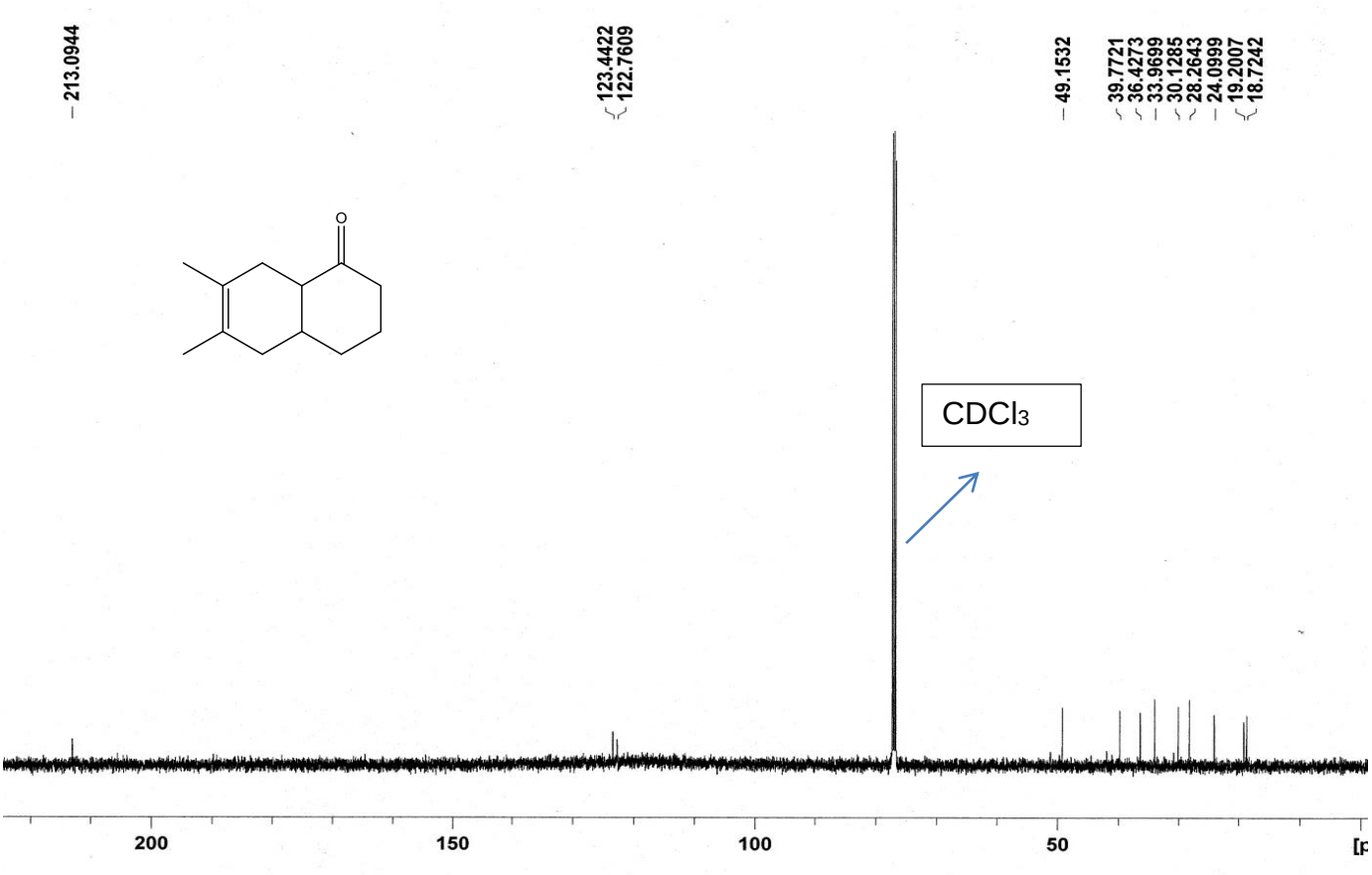


Figure S11: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (3,4,6-trimethylcyclohex-3-ene-1-carbaldehyde, **25**).

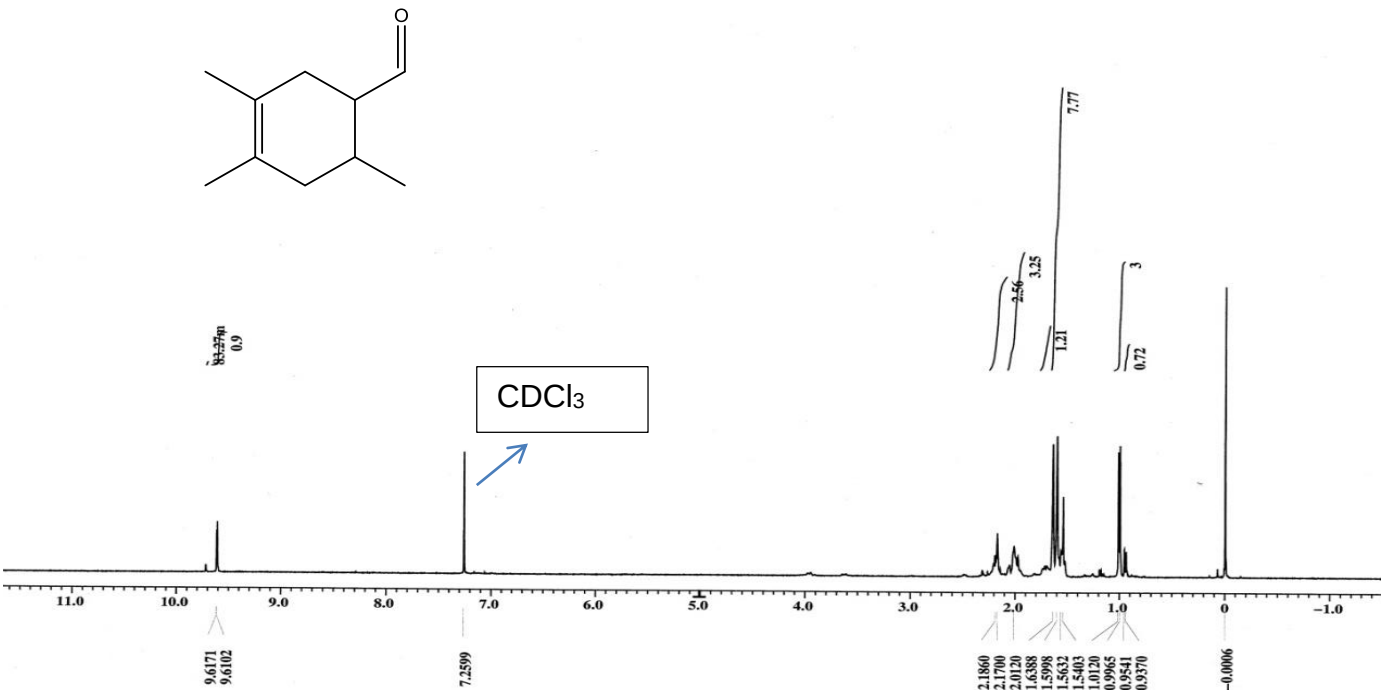


Figure S12: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (3,4,6-trimethylcyclohex-3-ene-1-carbaldehyde, **25**).

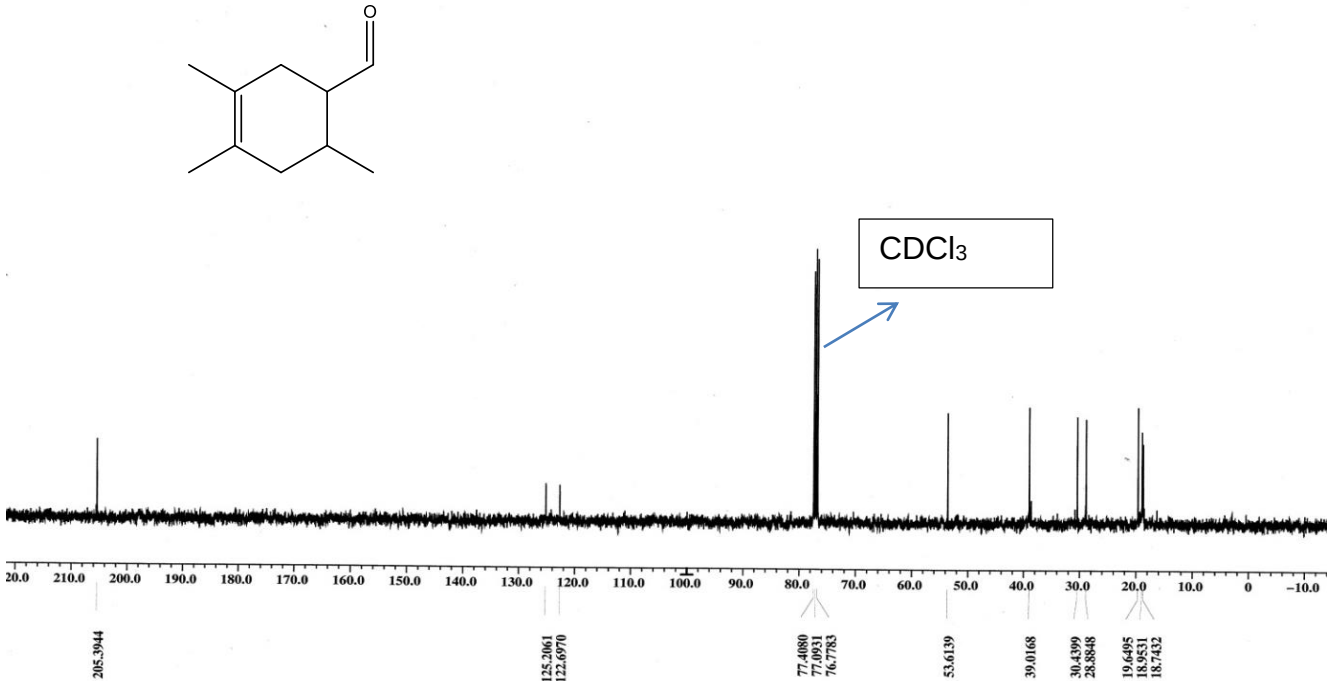


Figure S13: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (ethyl 3,4,6-trimethylcyclohex-3-ene-1-carboxylate, **26**).

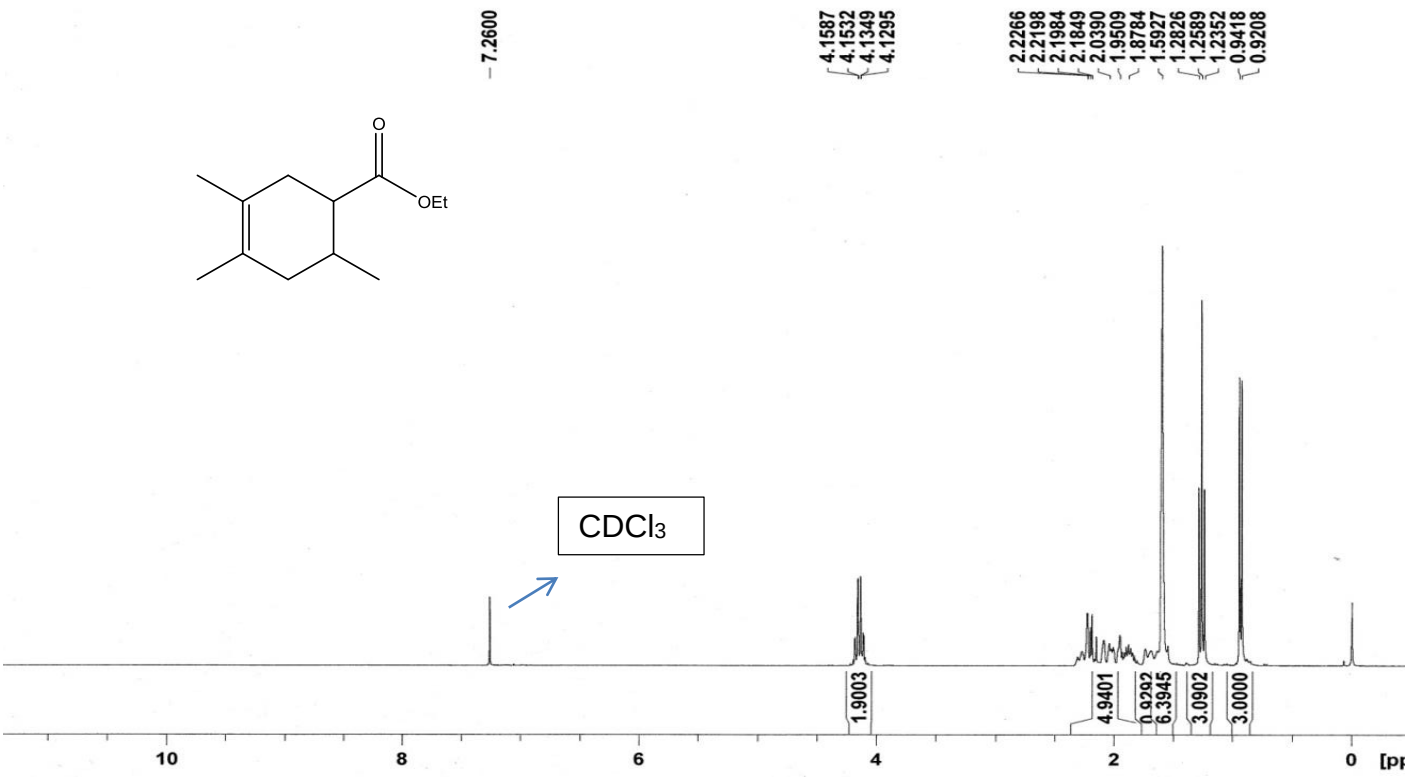


Figure S14: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (ethyl 3,4,6-trimethylcyclohex-3-ene-1-carboxylate, **26**).

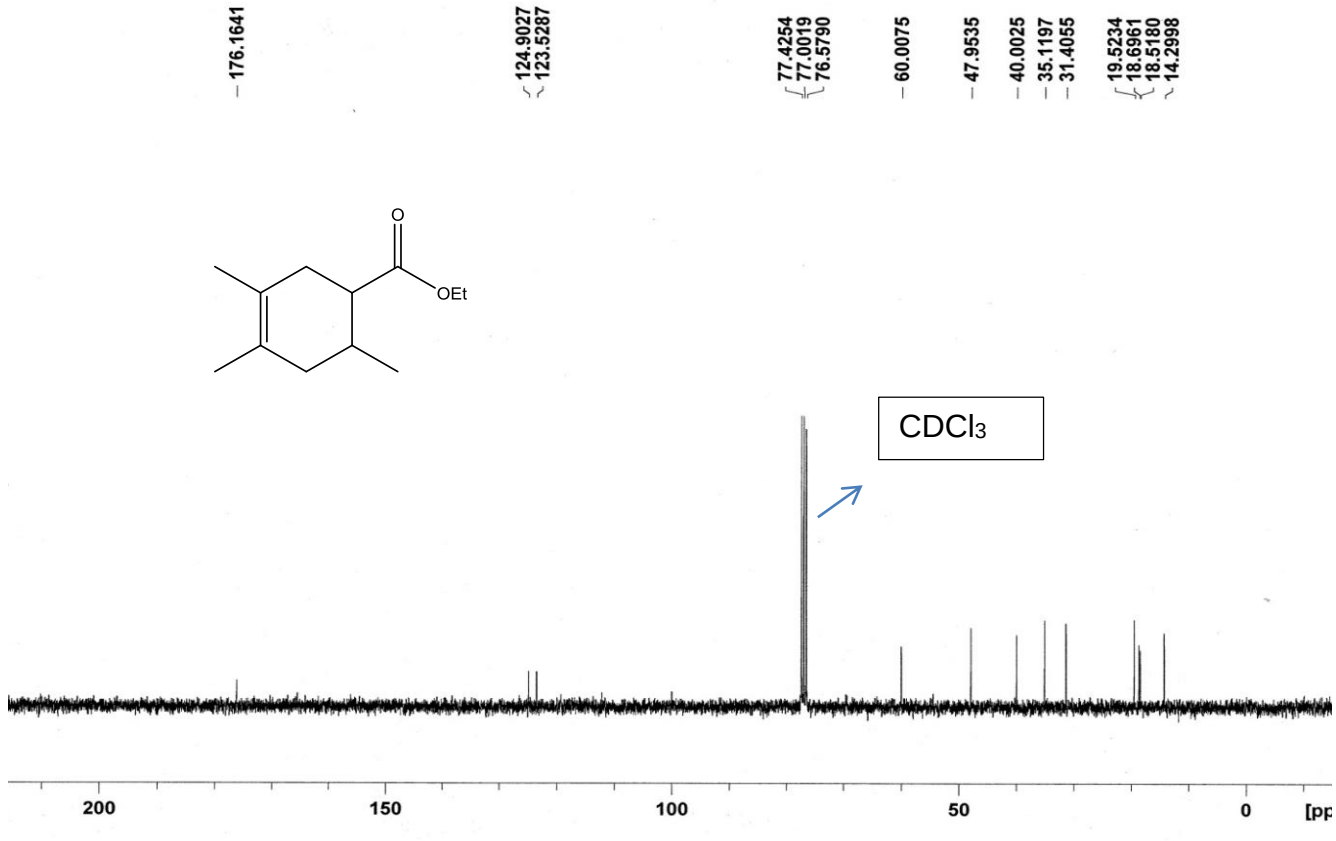


Figure S15: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1-((1R,2R,4R)-bicyclo[2.2.2]oct-5-en-2-yl)ethan-1-one, **27**).

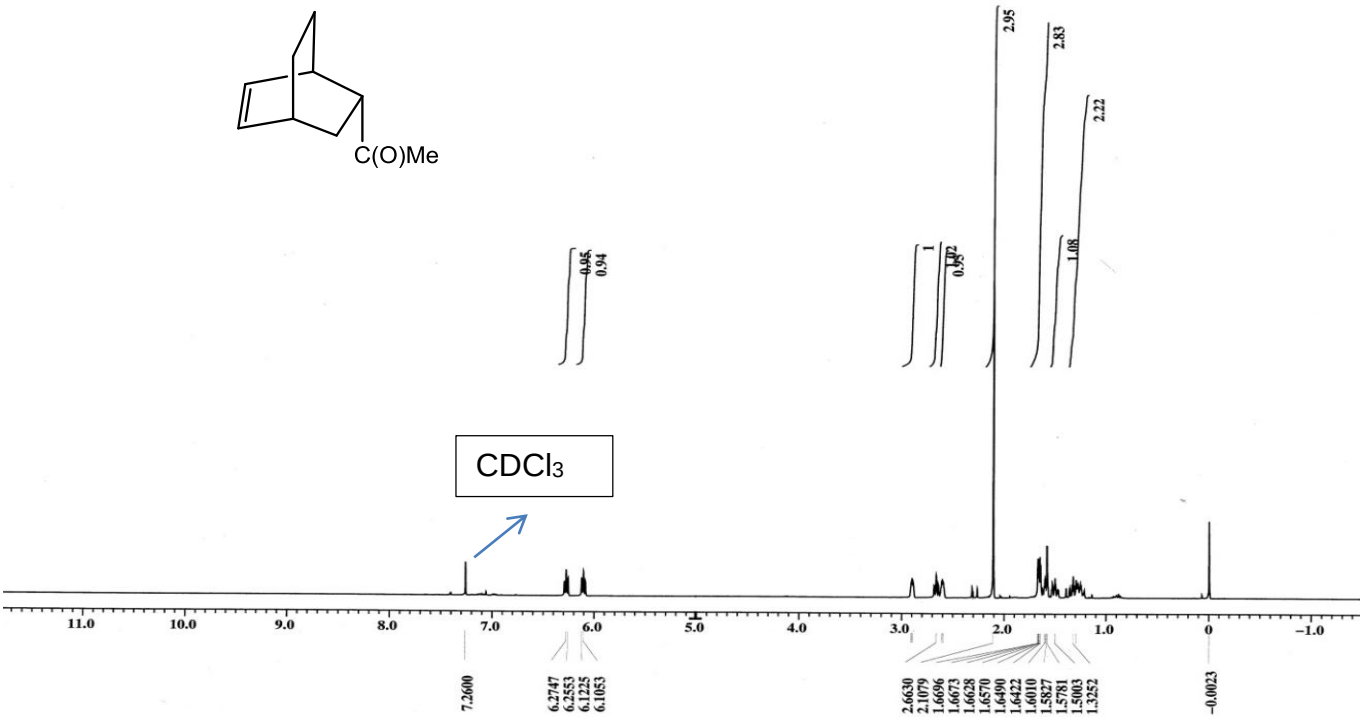


Figure S16: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (1-((1R,2R,4R)-bicyclo[2.2.2]oct-5-en-2-yl)ethan-1-one, **27**).

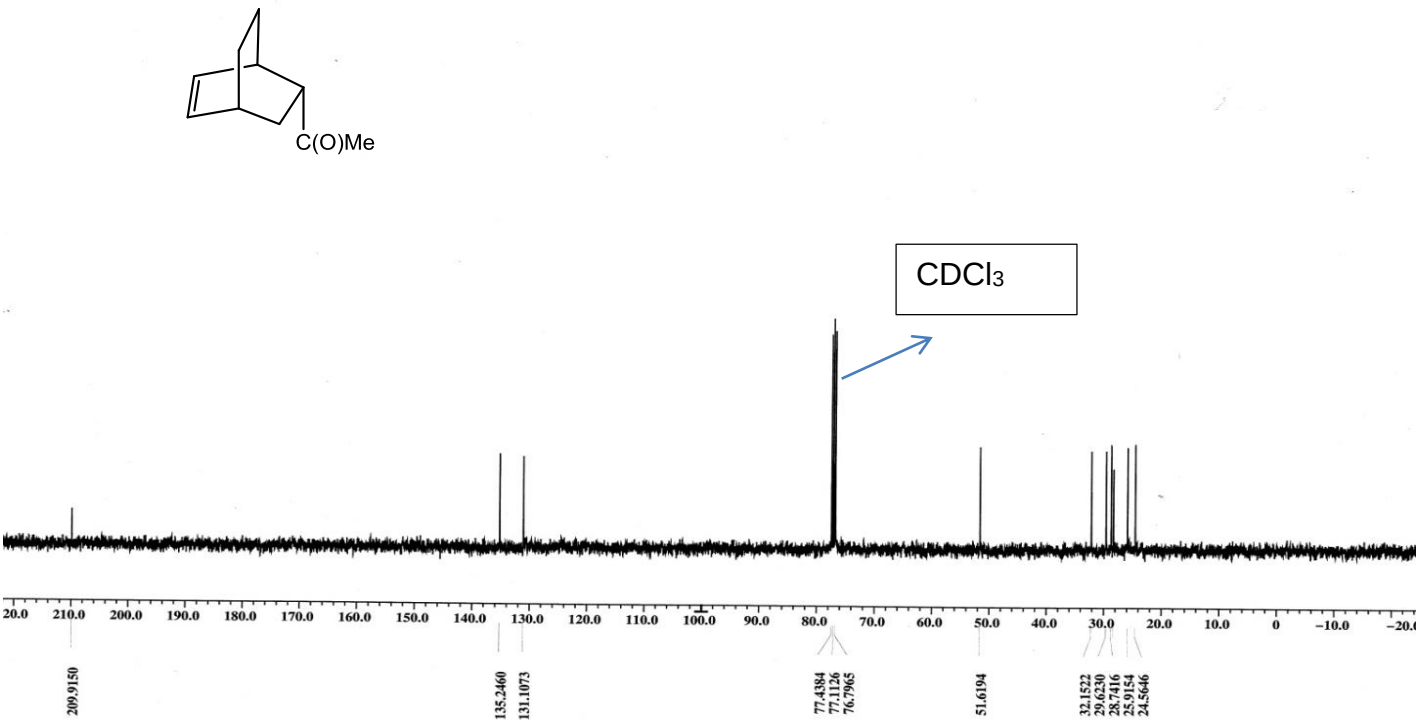


Figure S17: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (phenyl((1R,2S,3R,4S)-3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone, **28**).

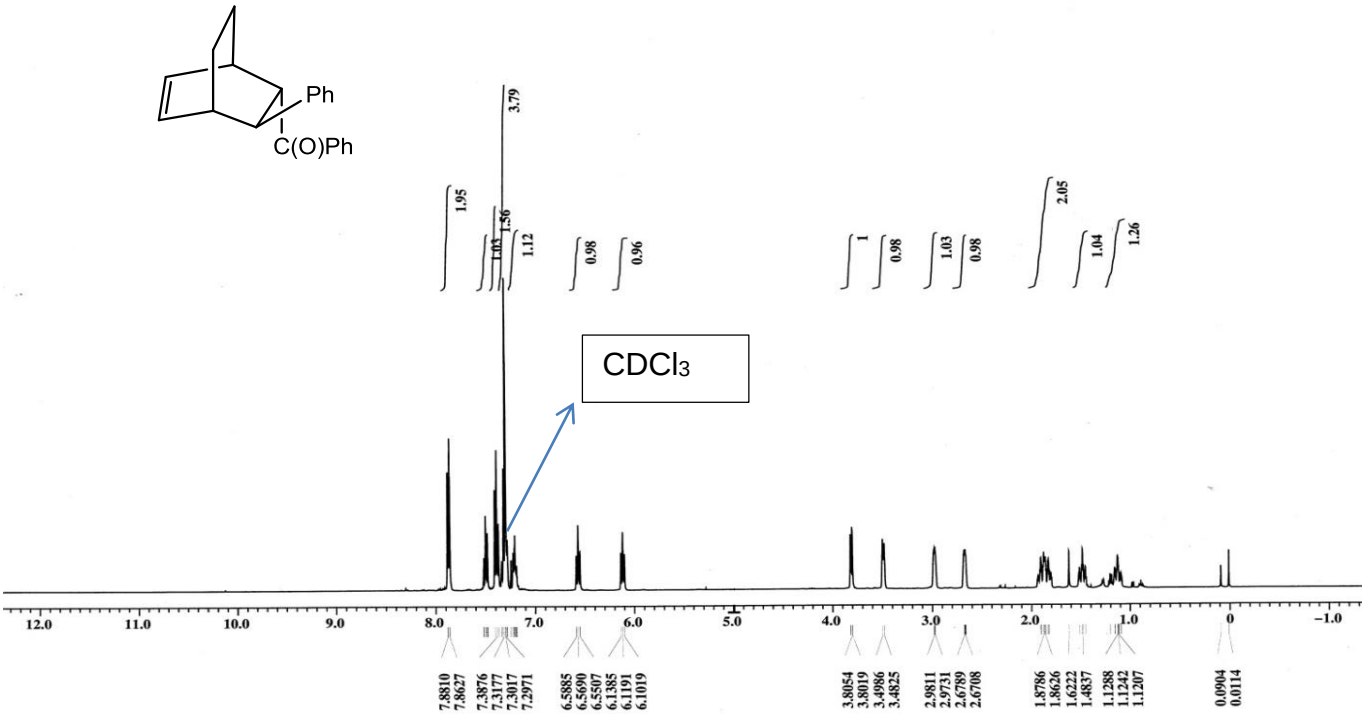


Figure S18: ^{1}H NMR spectrum (100.5 MHz, $CDCl_3$) of (phenyl((1R,2S,3R,4S)-3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone, **28**).

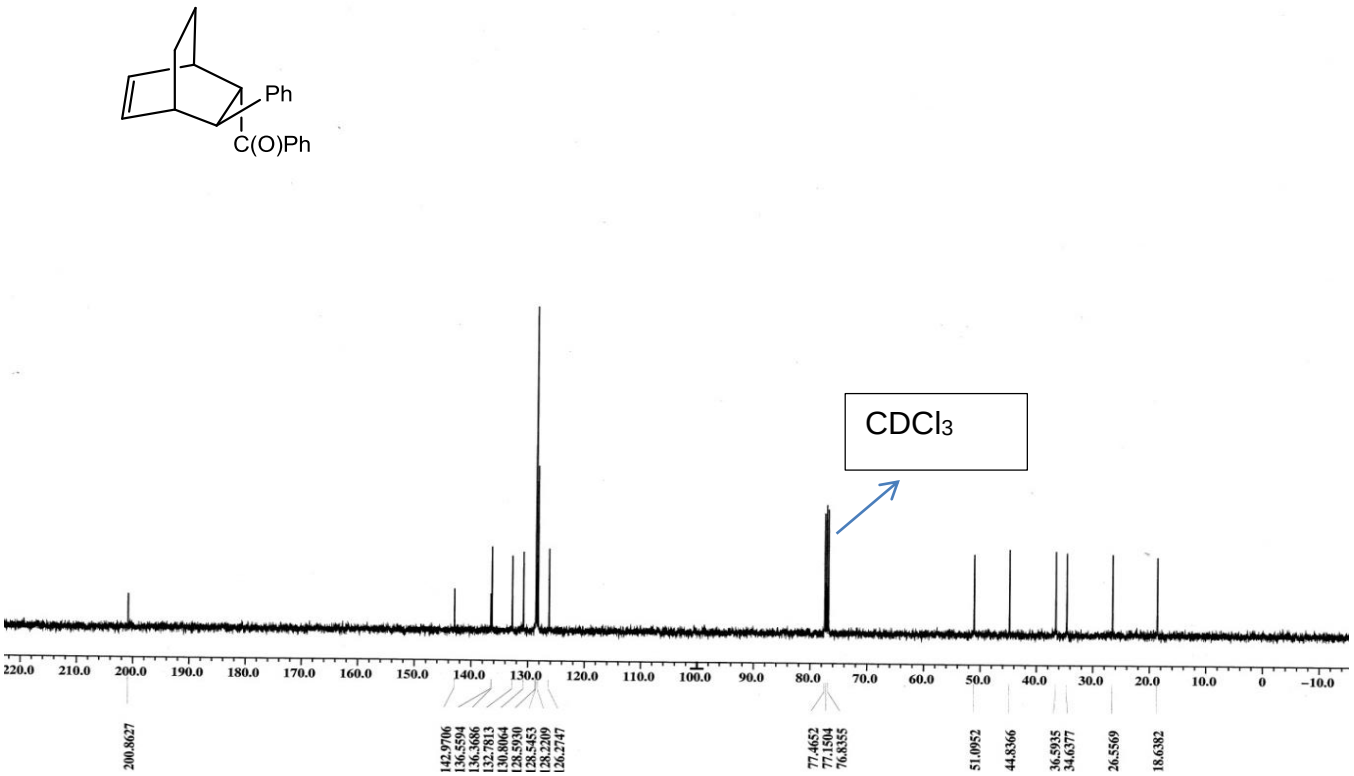


Figure S19: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1-(4-methylcyclohex-3-en-1-yl)ethan-1-one, **29**).

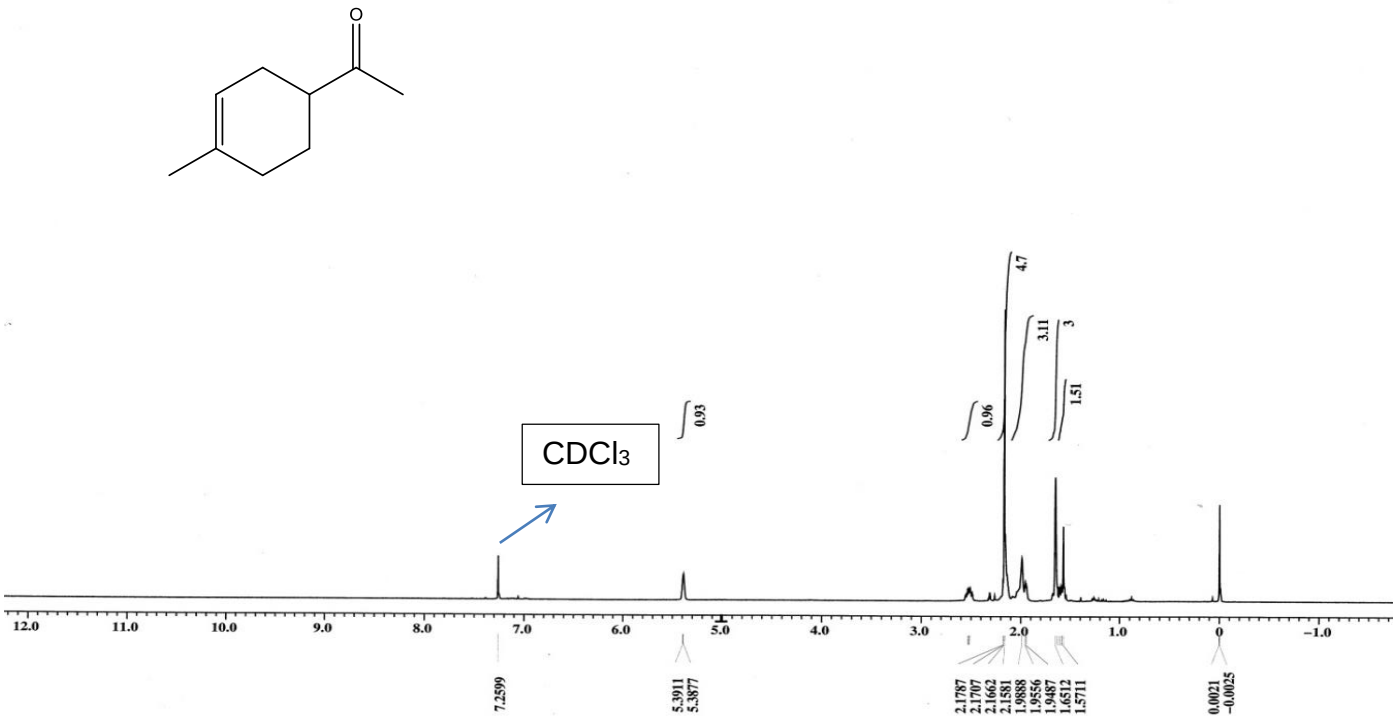


Figure S20: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (1-(4-methylcyclohex-3-en-1-yl)ethan-1-one, **29**).

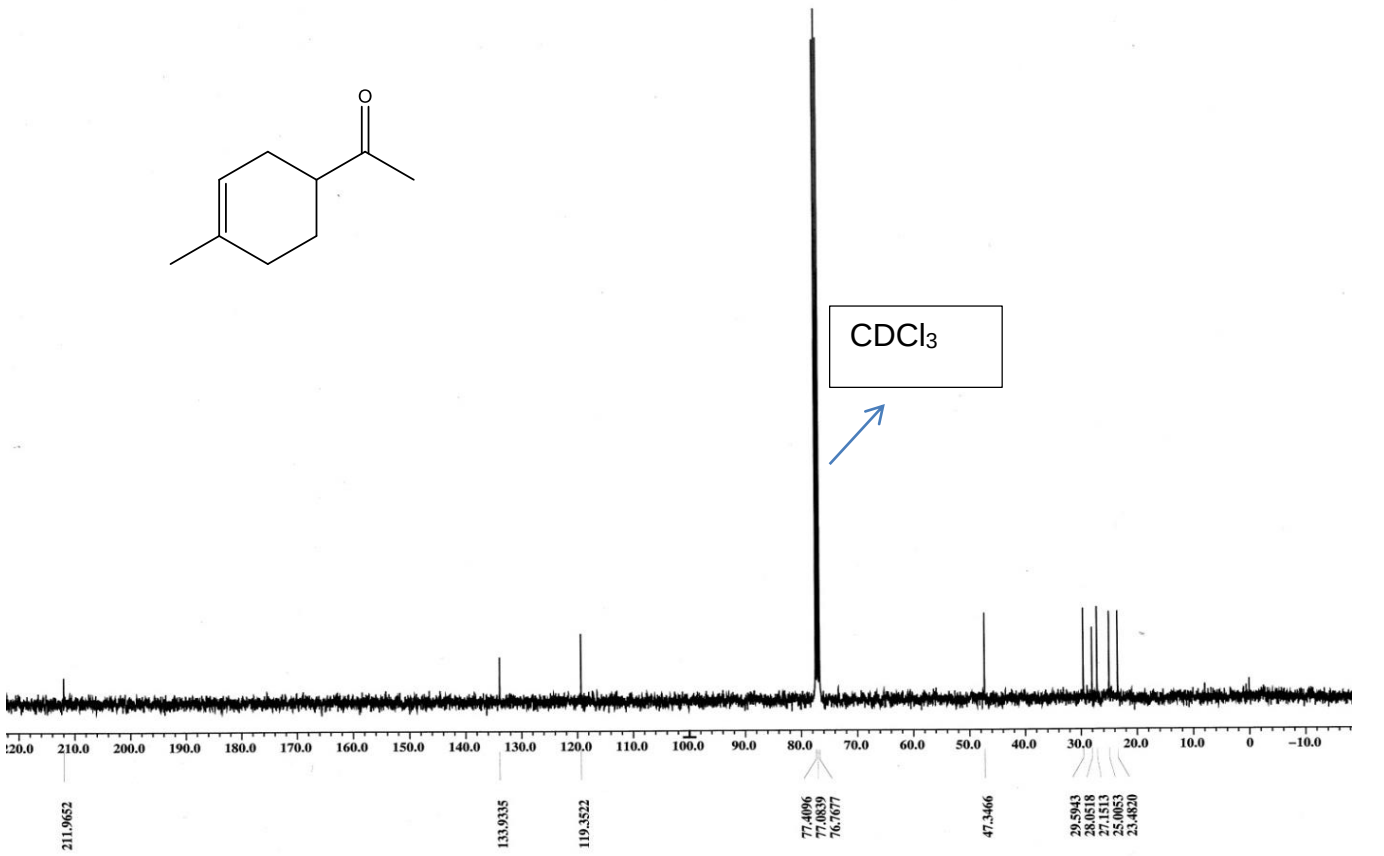


Figure S21: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1-(4-methylcyclohex-3-en-1-yl)ethan-1-one, **30**).

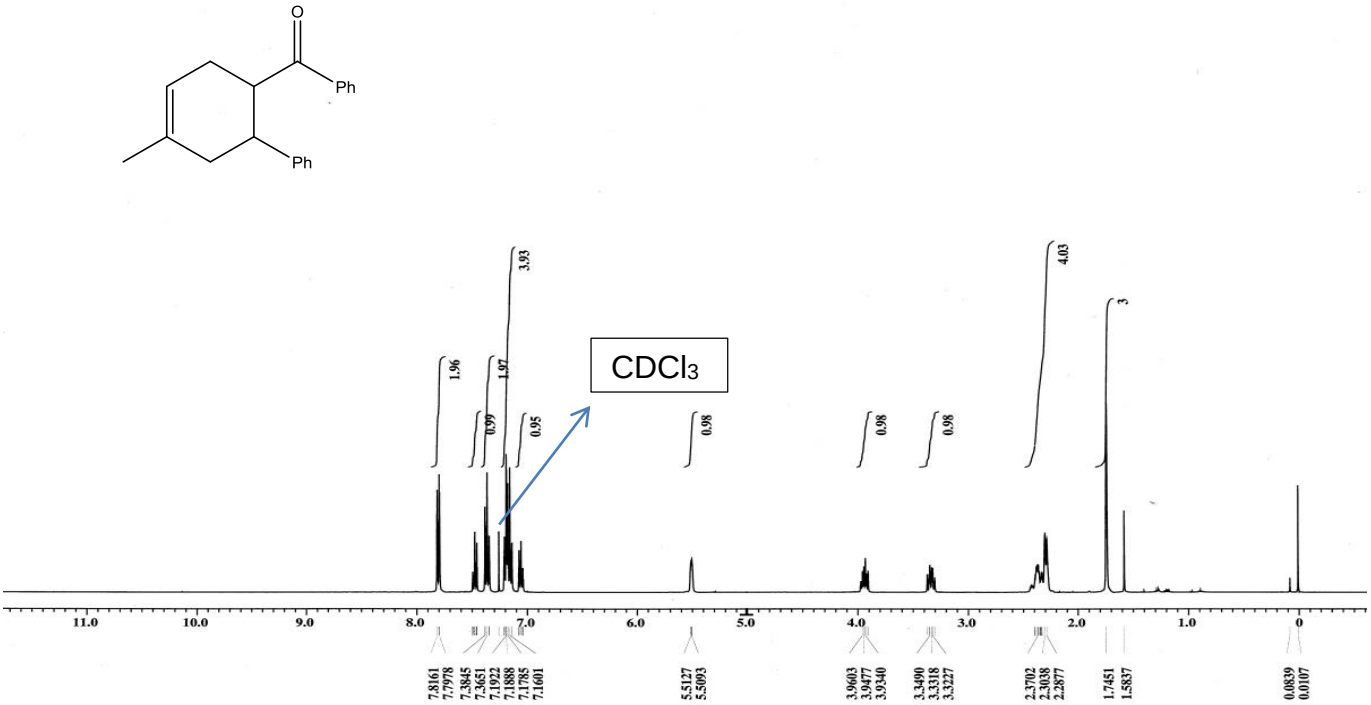
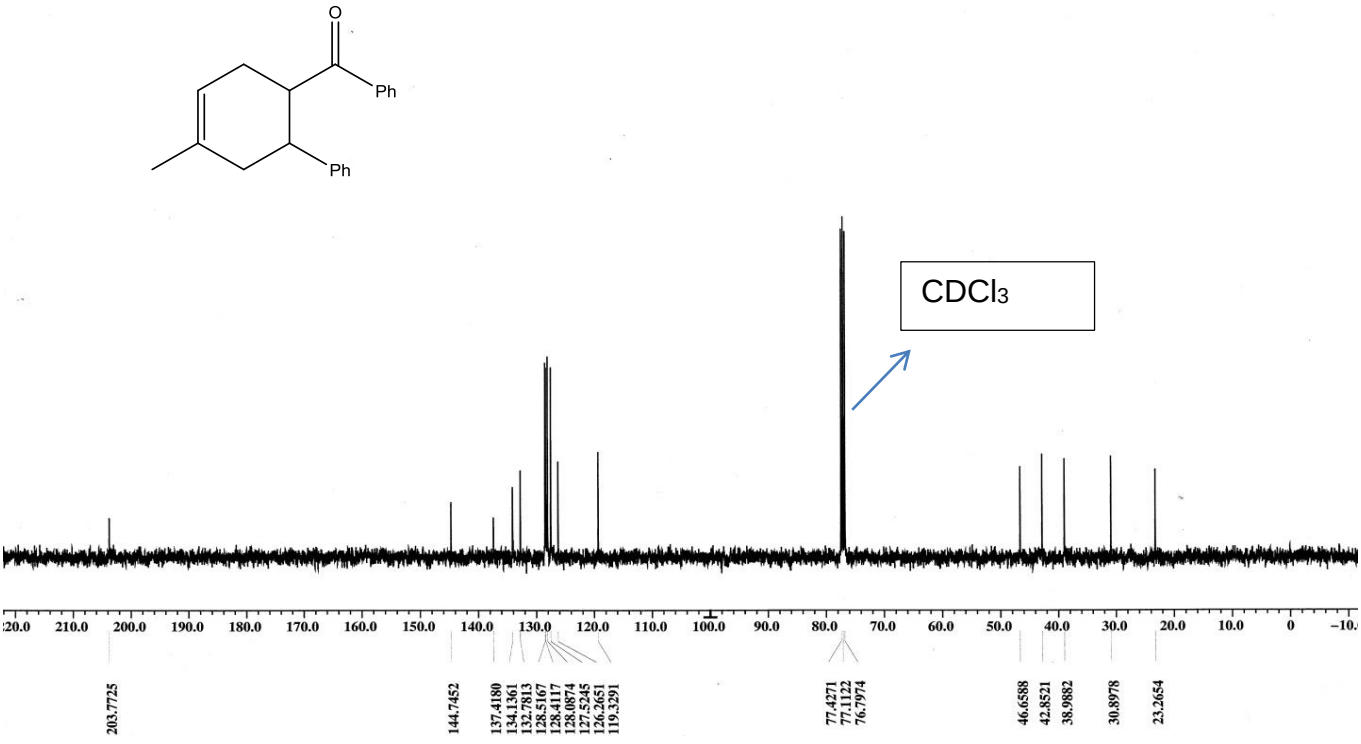


Figure S22: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of (1-(4-methylcyclohex-3-en-1-yl)ethan-1-one, **30**).



2. NMR spectra of Aluminum complexes 2 - 6

Figure S23: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ($LAlCl_2$, **3**).

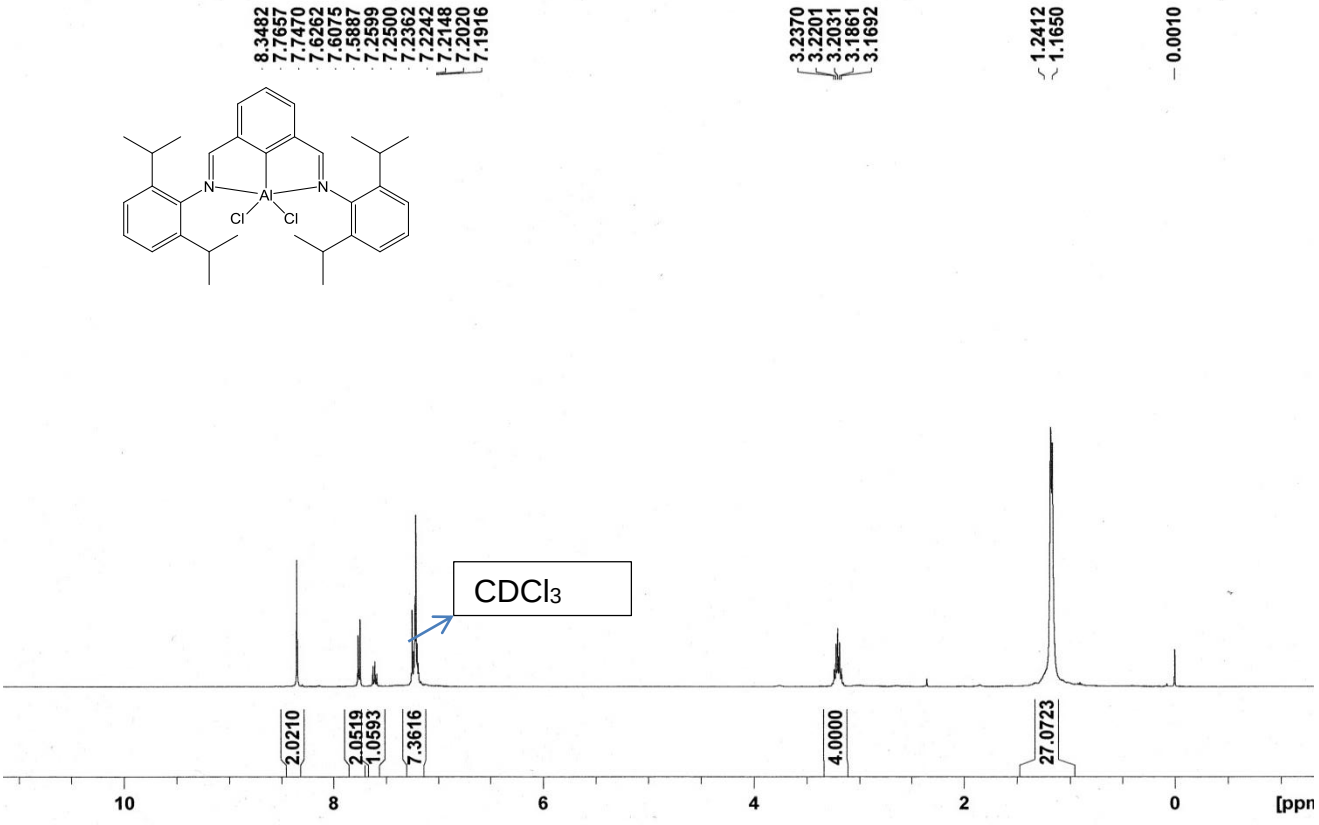


Figure S24: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ($LAlCl_2$, **3**) at - 50°C.

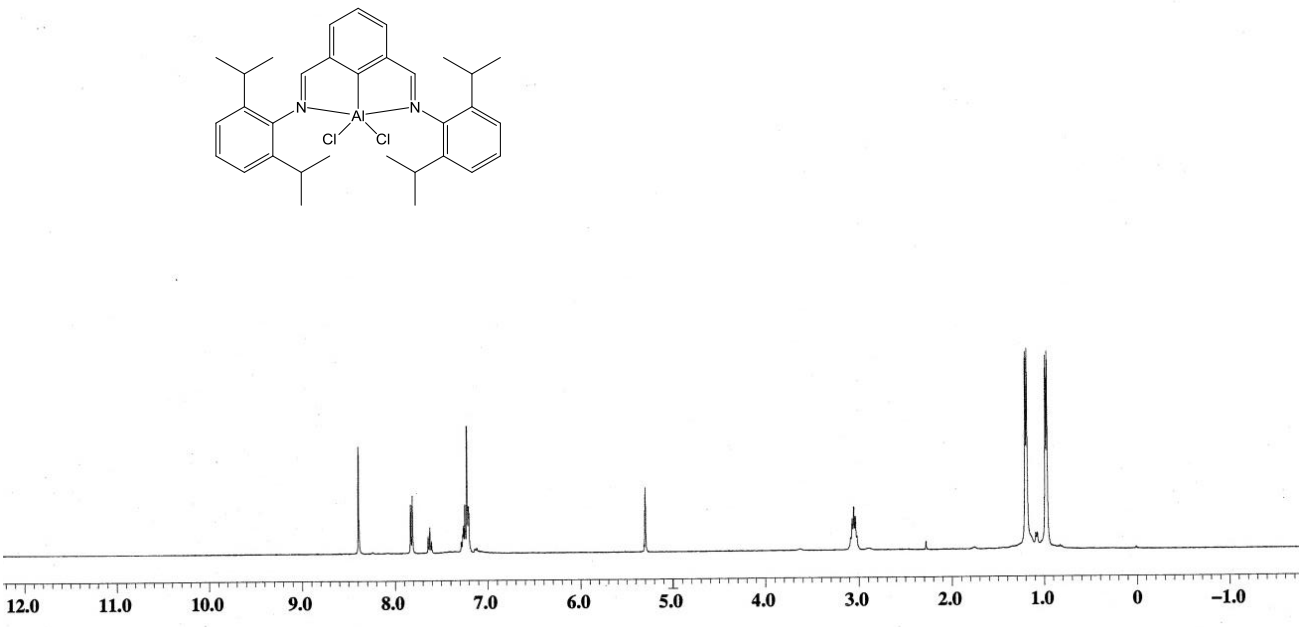


Figure S25: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of ($LAlCl_2$, **3**).

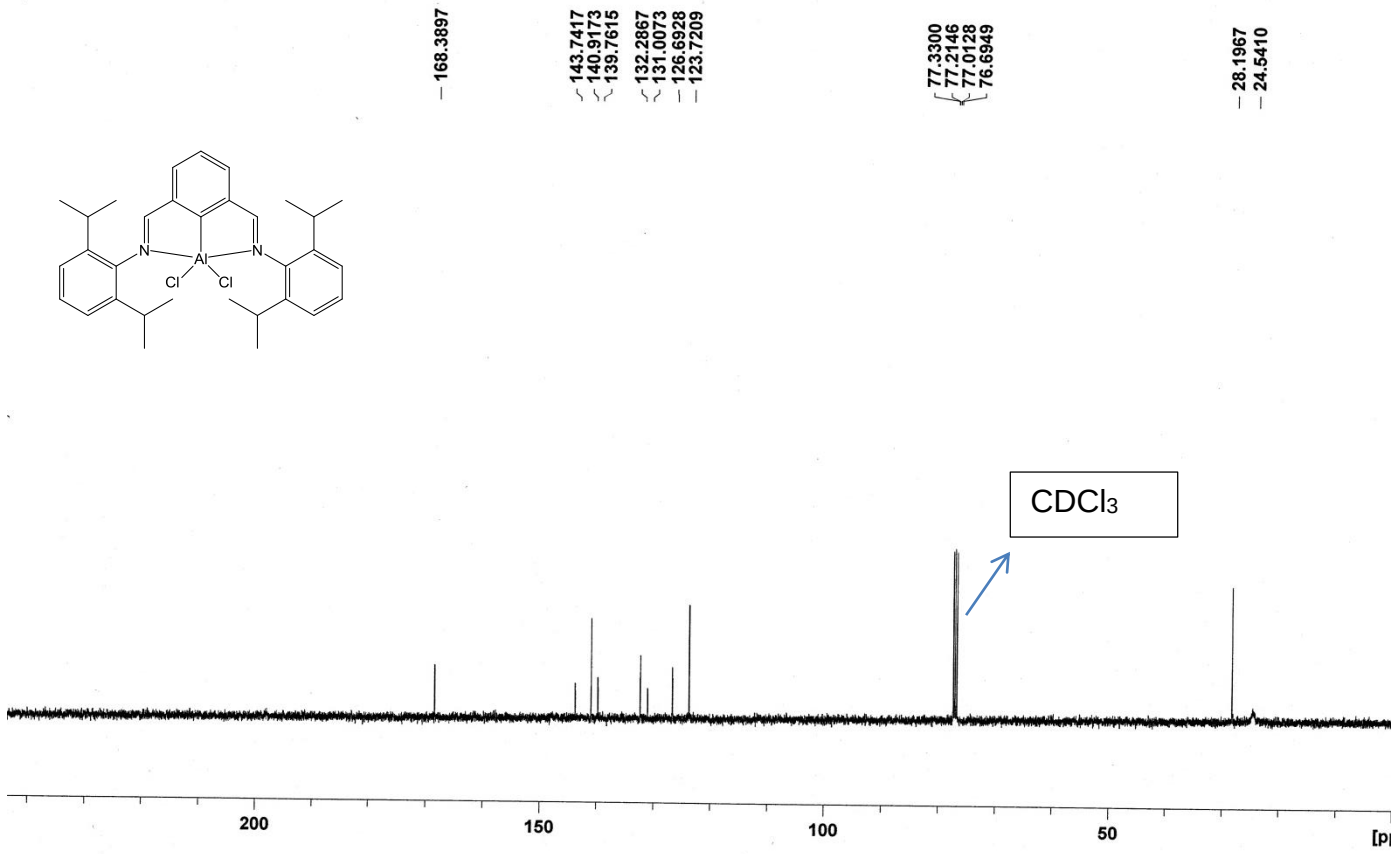


Figure S26: ^{27}Al NMR spectrum (104.2 MHz, $CDCl_3$) of ($LAlCl_2$, **3**).

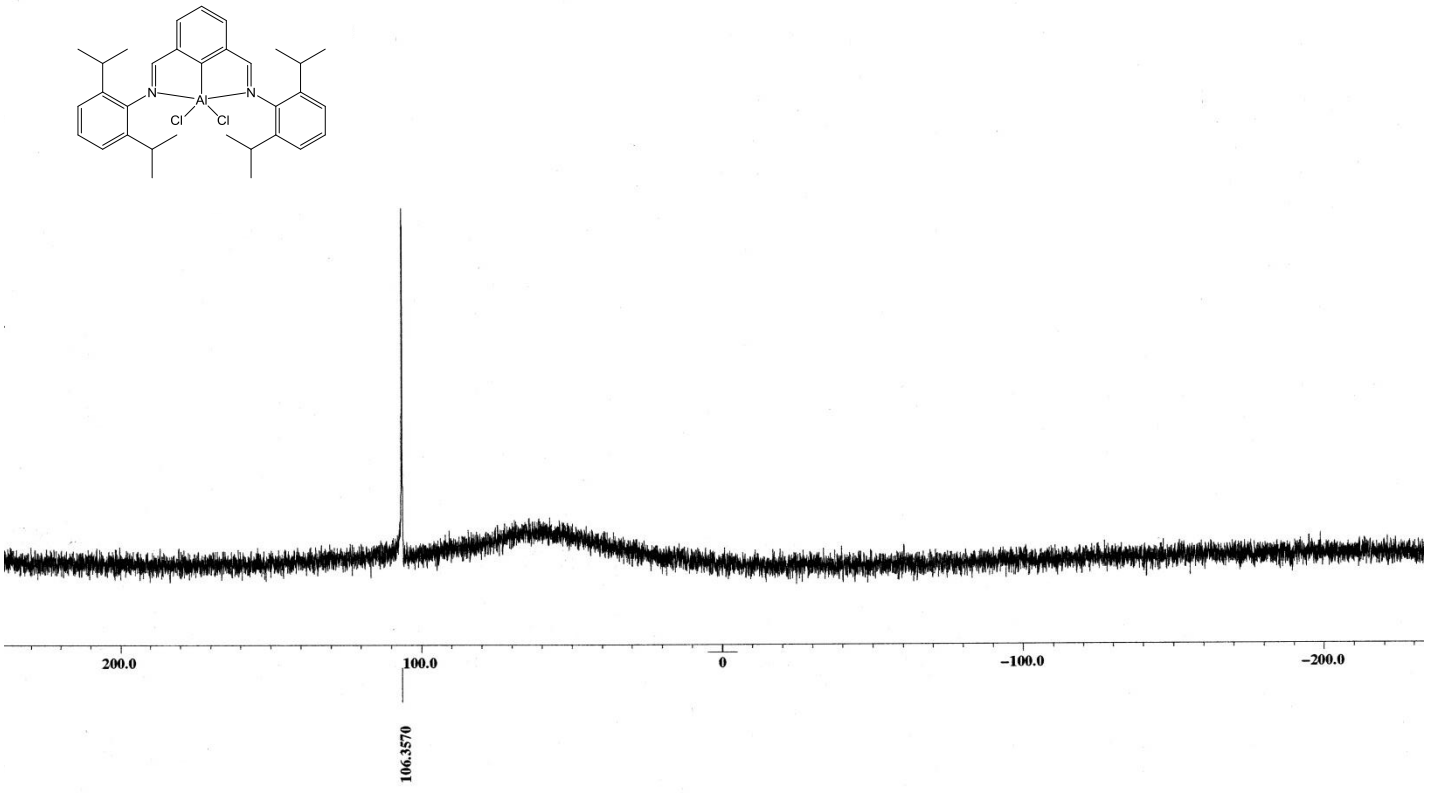


Figure S27: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ($LAlCl_2THF$, **2**).

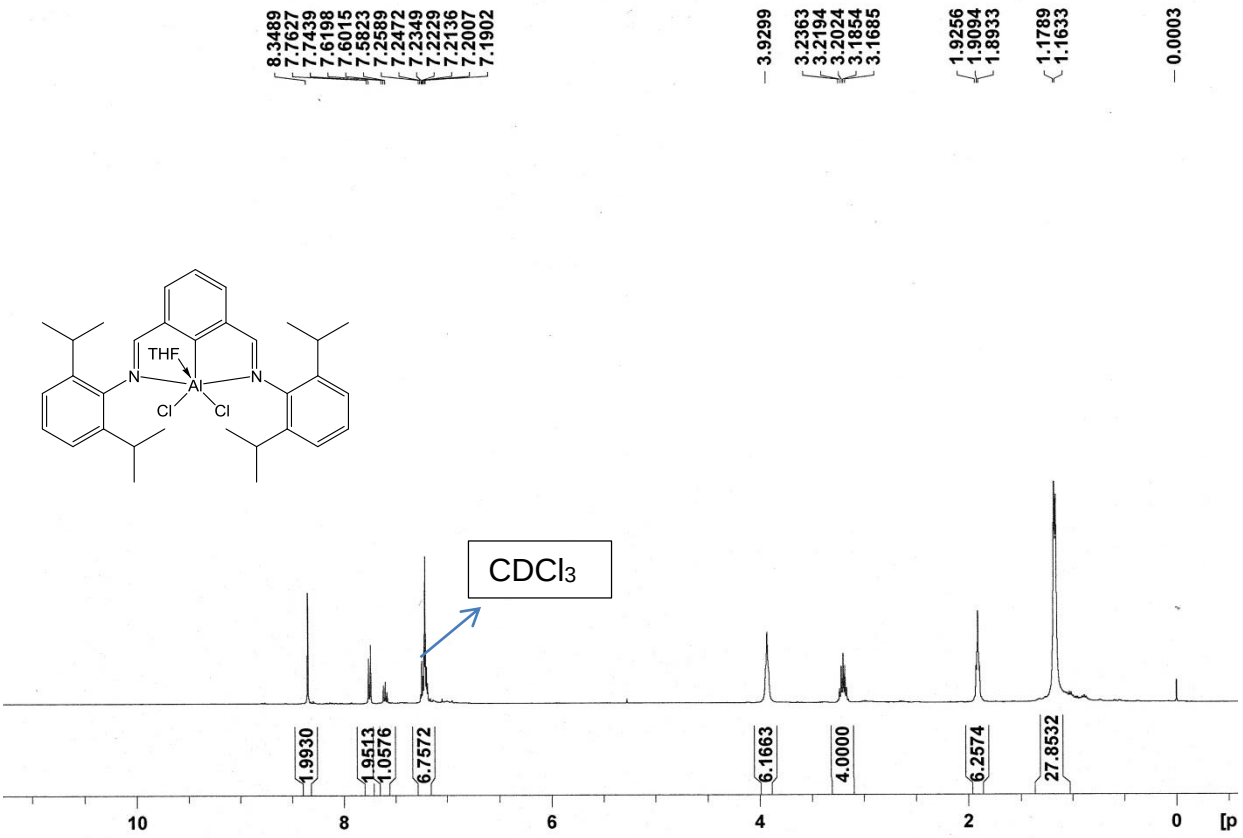


Figure S28: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of ($LAlCl_2THF$, **2**).

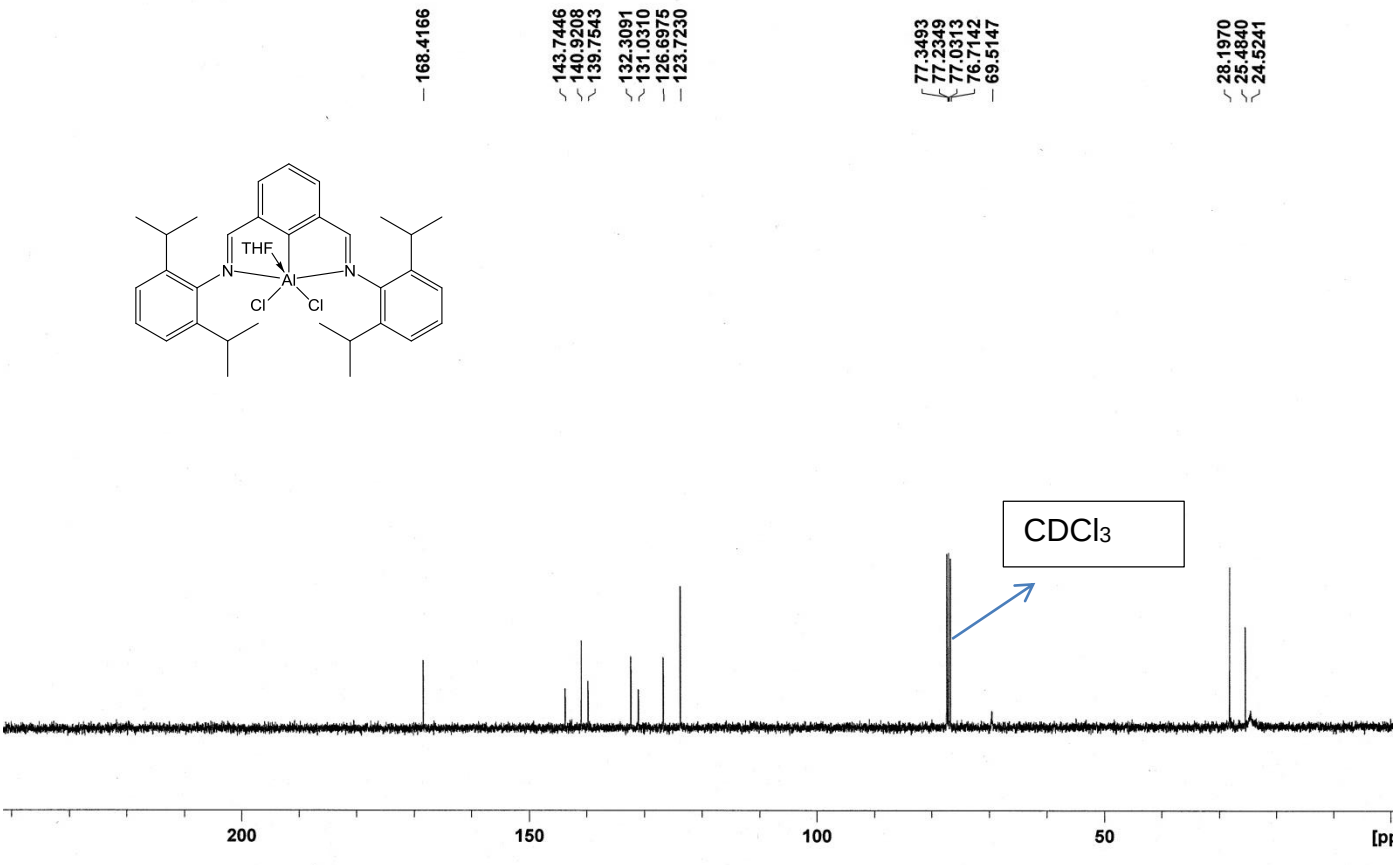


Figure S29: ^{27}Al NMR spectrum (104.2 MHz, $CDCl_3$) of ($LAlCl_2THF$, **2**).

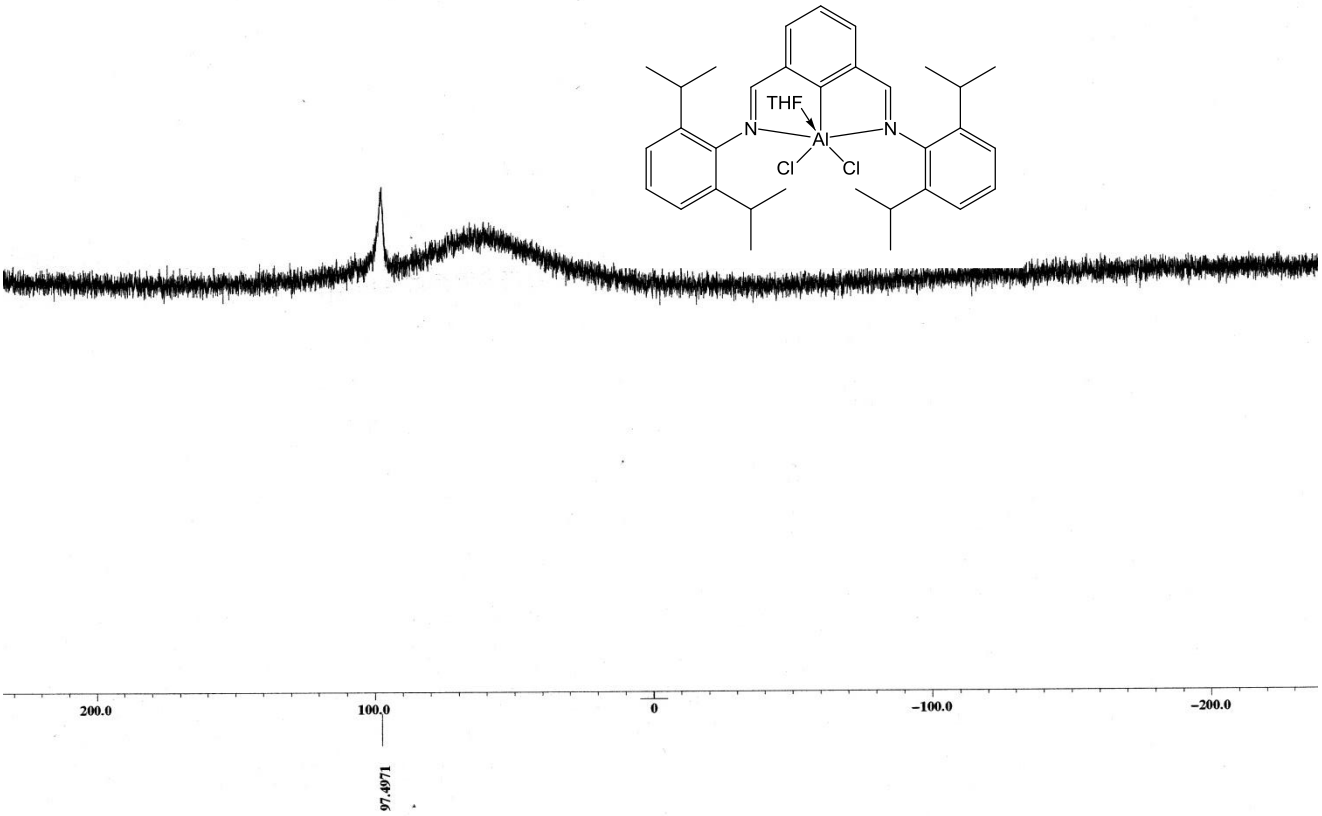


Figure S30: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ($[LAlCl_2NaCl_2AlL][NaBAr^{Cl}_4]$, **5**).

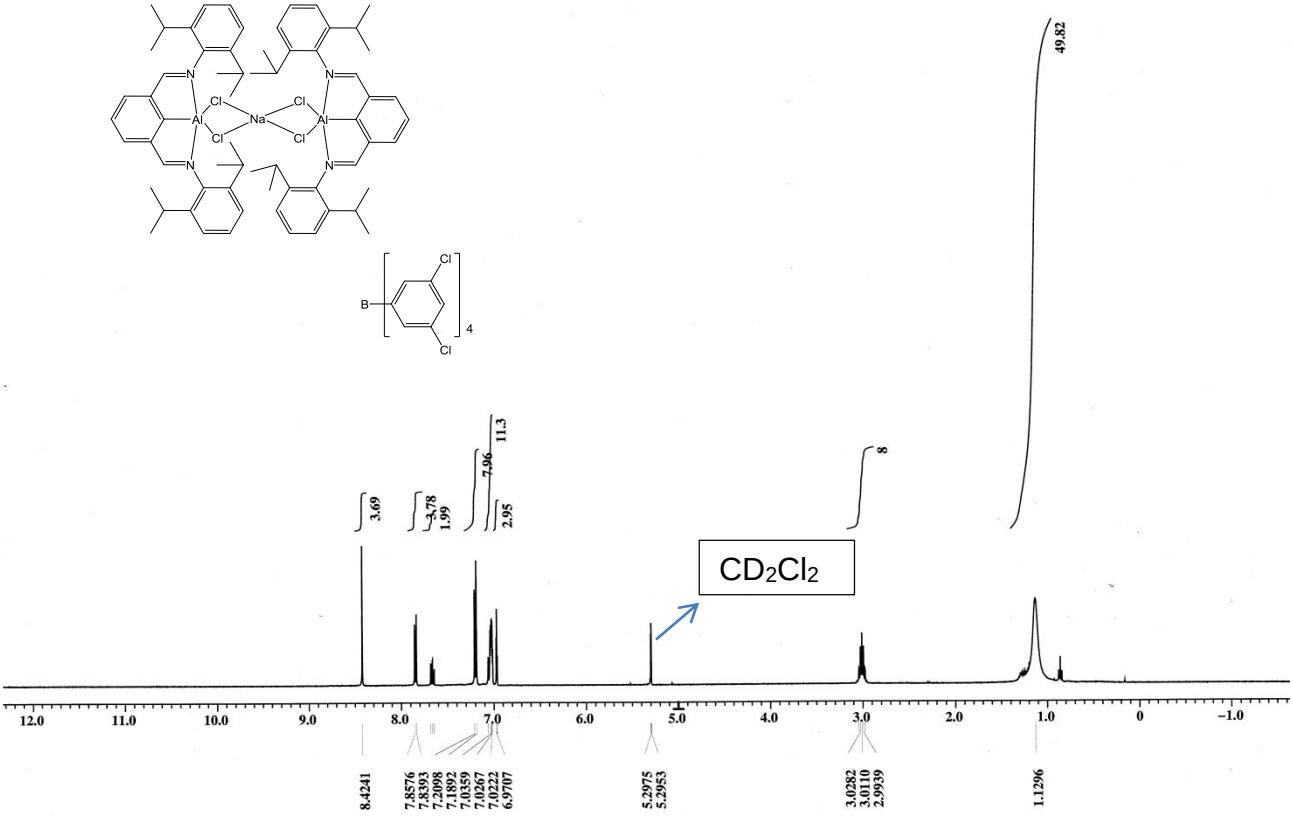
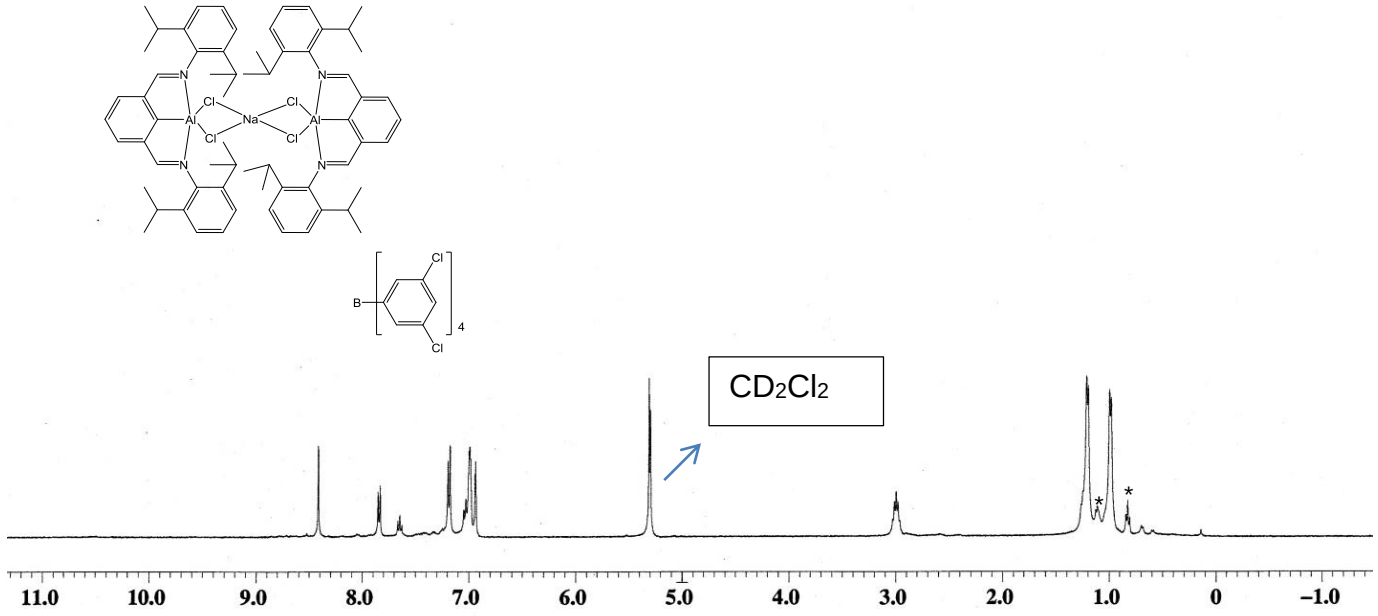


Figure S31: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ([$LAlCl_2NaCl_2AlL$][$NaBAr^{Cl}_4$], **5**) at - 50°C.



*Solvent (pantane) and/or impurity

Figure S32: ^{13}C NMR spectrum (100.5 MHz, CD_2Cl_2) of ([$LAlCl_2NaCl_2AlL$][$NaBAr^{Cl}_4$], **5**).

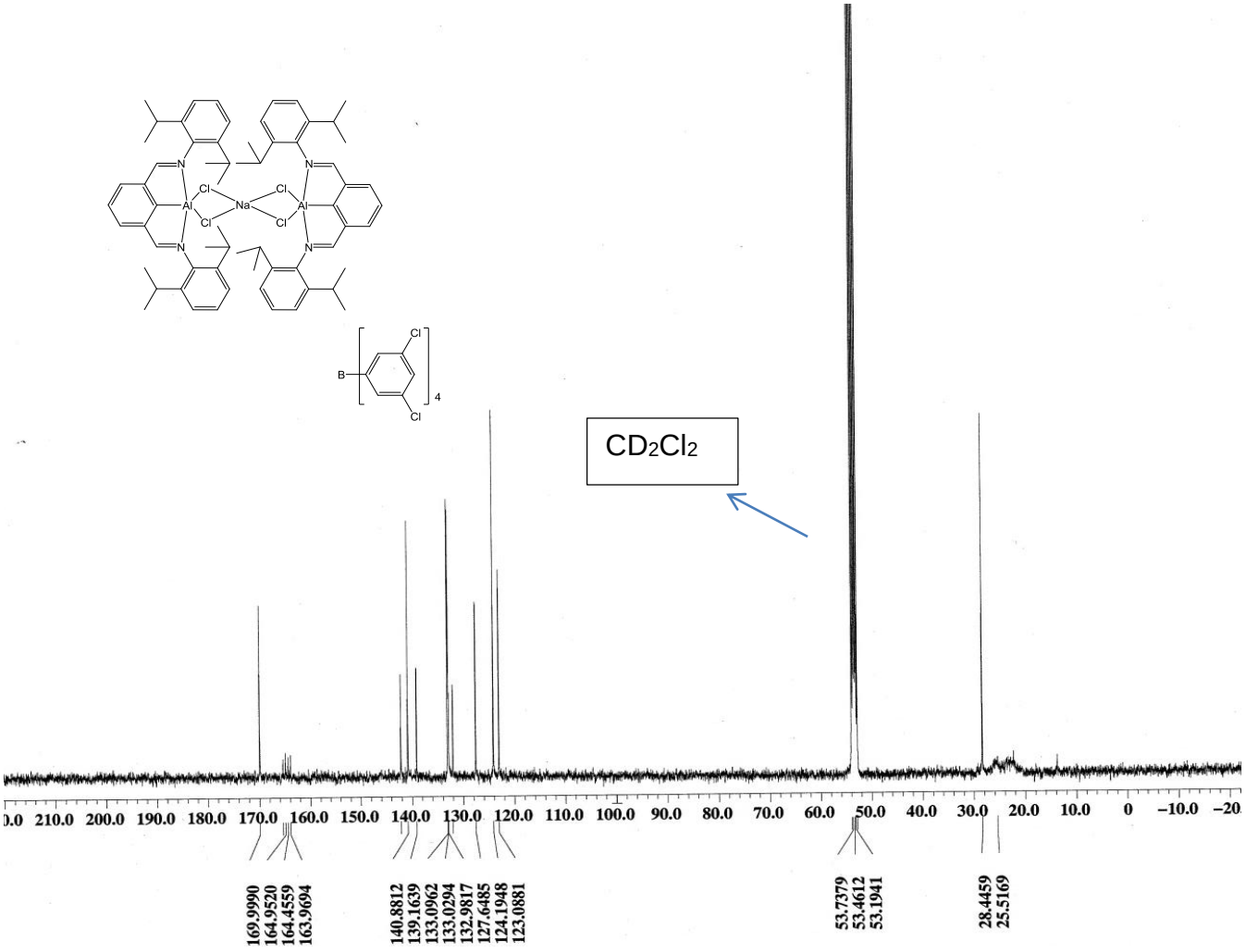


Figure S33: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ([LAlCl(THF)][BAr^{Cl}_4], **6**).

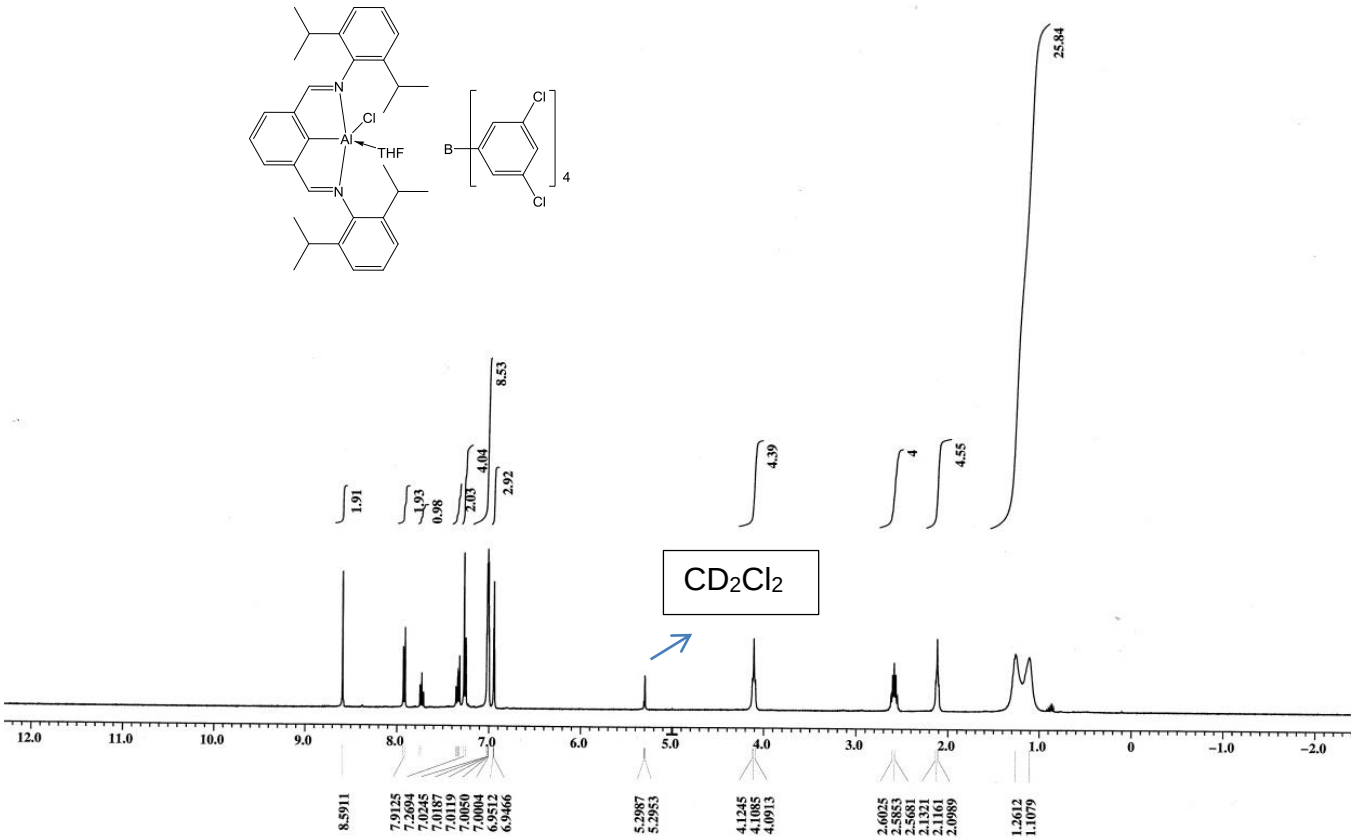
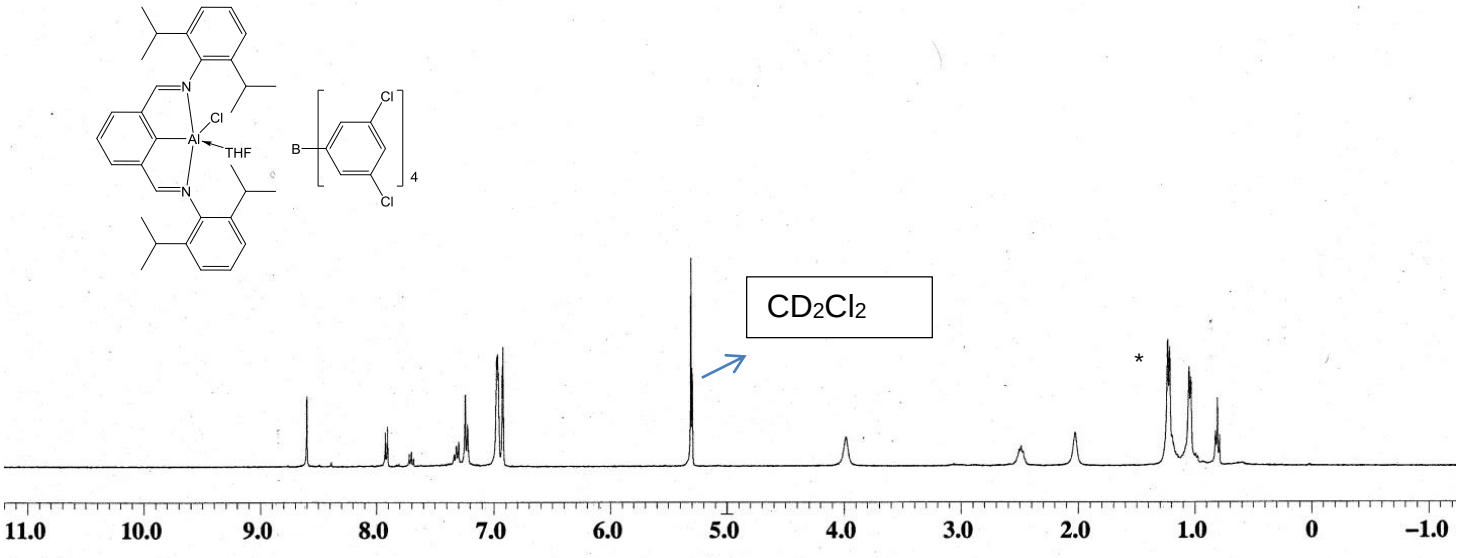
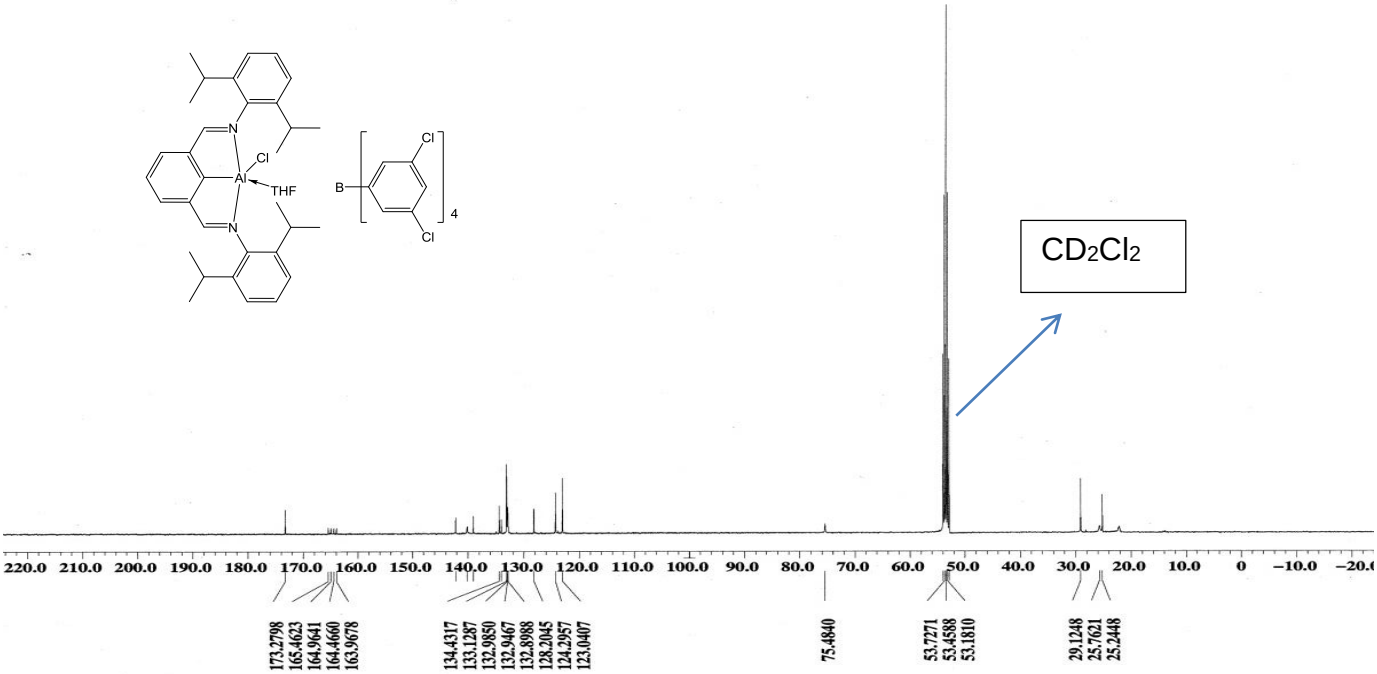


Figure S34: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ([LAlCl(THF)][BAr^{Cl}_4], **6**) at - 50°C.



*Solvent (pantane)

Figure S35: ^{13}C NMR spectrum (100.5 MHz, CD_2Cl_2) of ([LAlCl(THF)][BAr^{Cl}_4], **6**).



3. NMR spectra of 6 + 8/dbpy

Figure S36: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ([LAlCl(THF)][BAr^{Cl}_4] + 5 eq **8**).

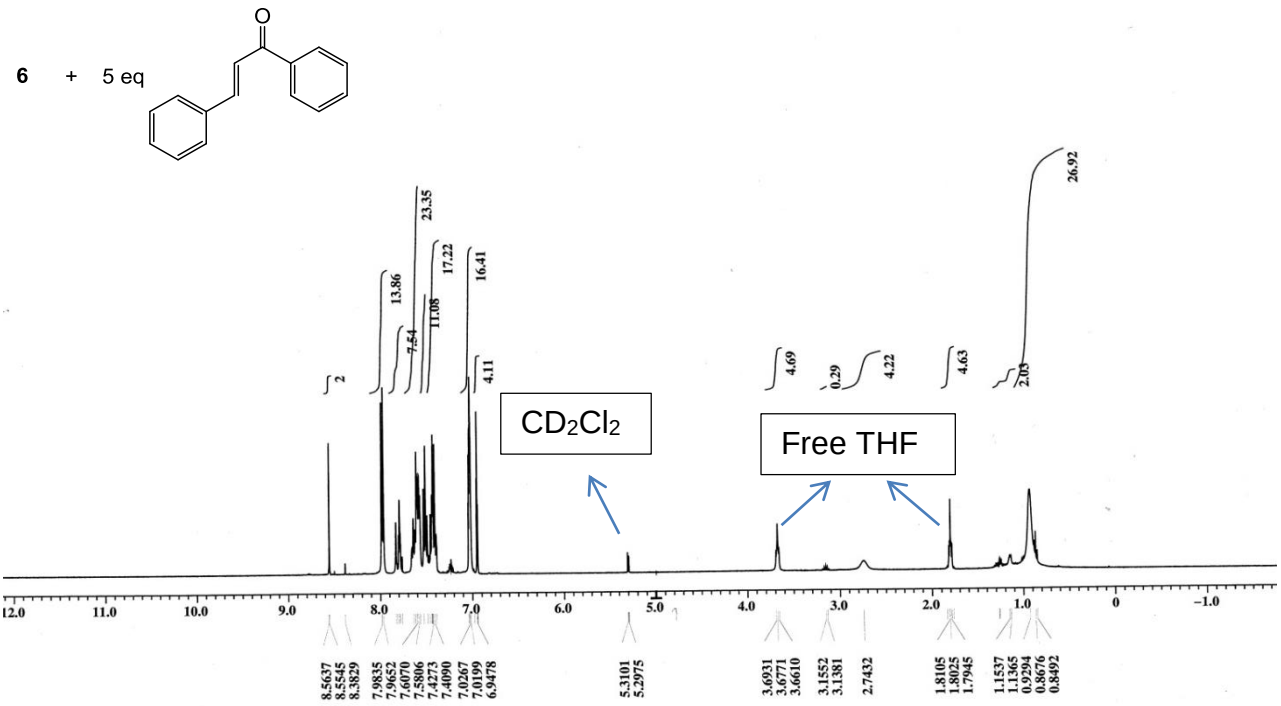
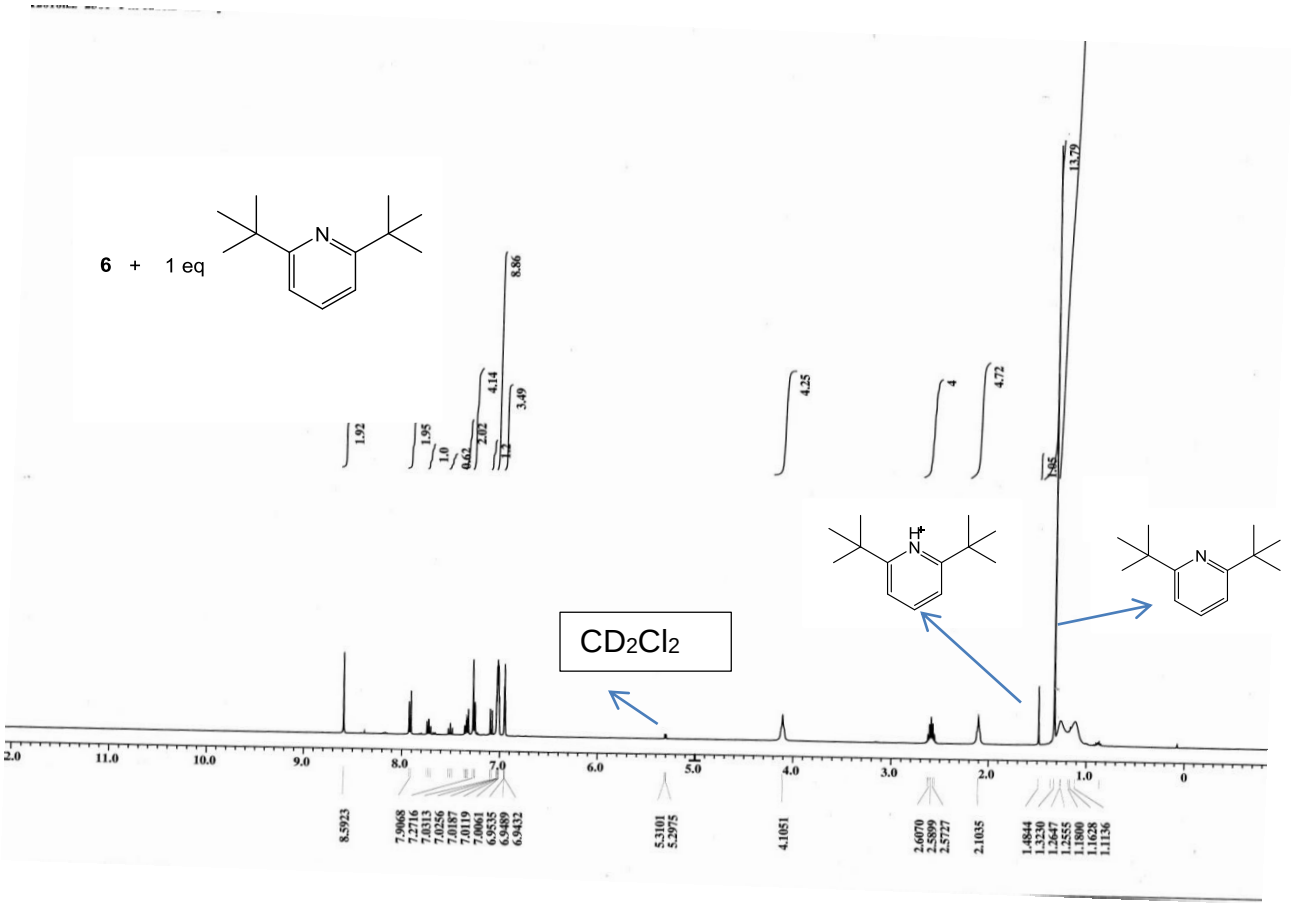


Figure S37: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ([LAlCl(THF)][BAr^{Cl}_4] + 1 eq dbpy).



4. NMR spectra of pyridinium triflate, [dbpy-H][OTf]

Figure S38: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ([dbpy-H][OTf]).

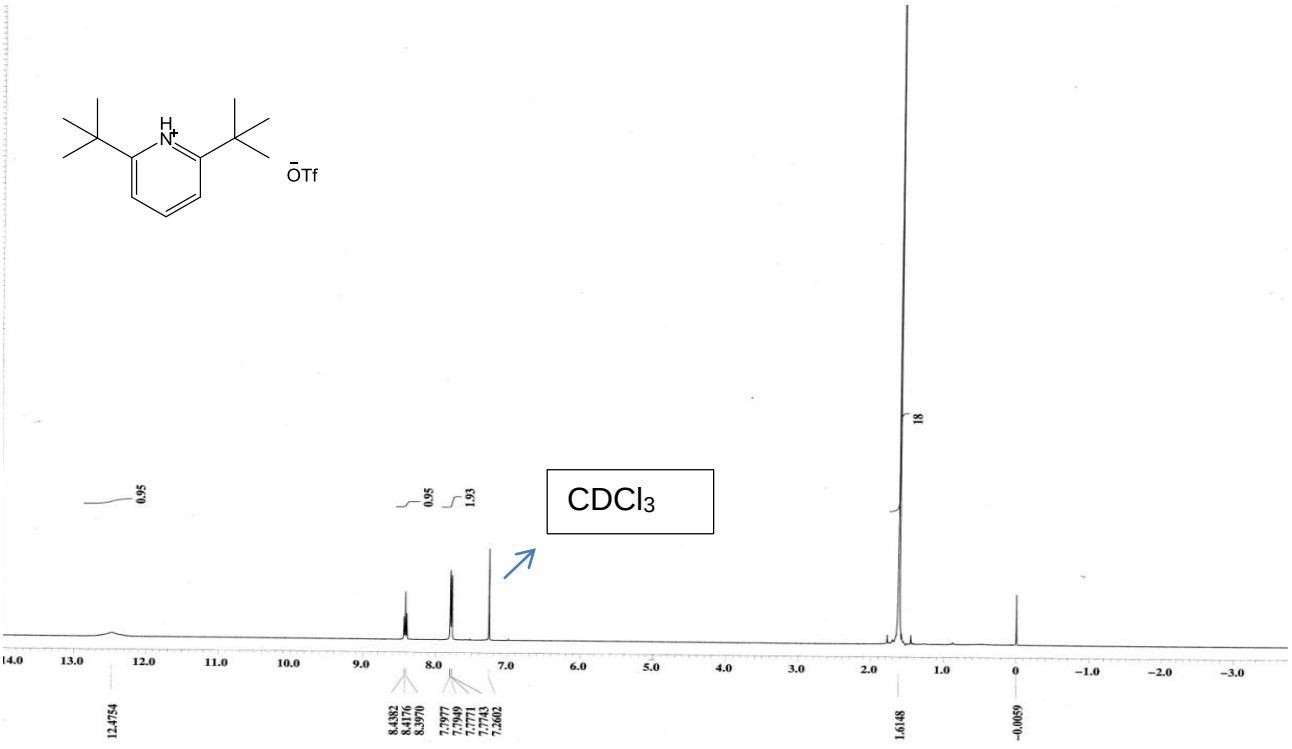


Figure S39: ^{13}C NMR spectrum (100.5 MHz, $CDCl_3$) of ([dbpy-H][OTf]).

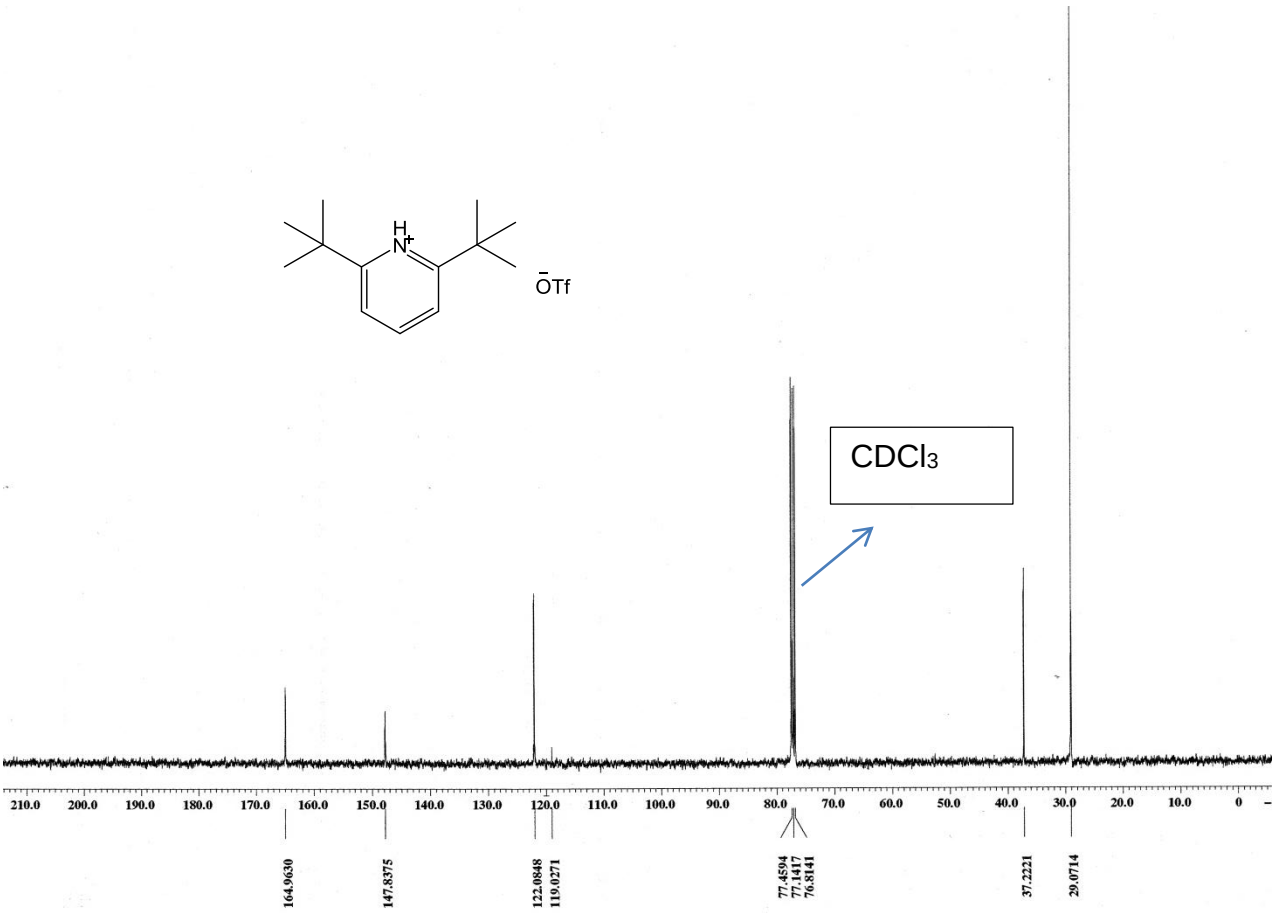
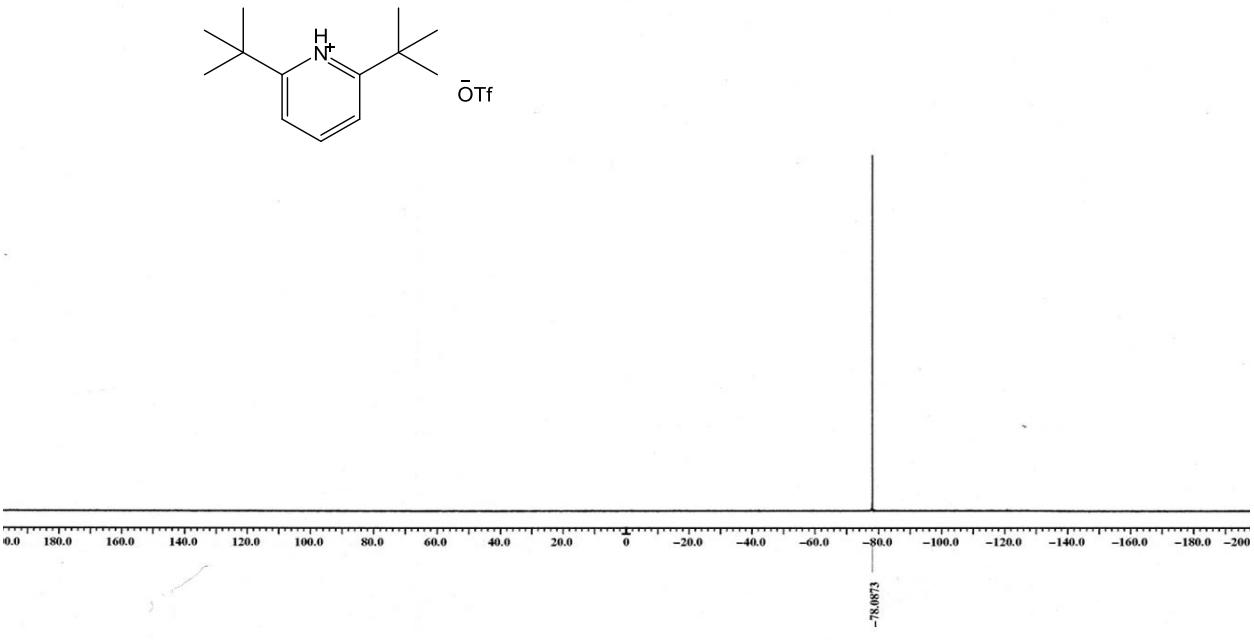


Figure S40: ^{19}F NMR spectrum (376.4 MHz, $CDCl_3$) of ([dbpy-H][OTf]).



Crystallographic Details. Single crystals were mounted on quartz fiber and the X-ray intensity data were collected a Bruker X8 APEX system, using Mo Kα radiation, with the SMART suite of programs.[S1a] Data were processed and corrected for Lorentz and polarization effects with SAINT[S1b] and for absorption effects with SABADS.[S1c] Structural solution and refinement were carried out with the SHELXTL suite of programs.[S1d] The structure was solved by direct methods and refined for all data by full-matrix least-squares methods on F^2. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters.

5. Table S1. Summary of crystallographic data for 3, 4, 5, and 6.

	3	**4**	**5**	**6**
CCDC	1471553	1471555	1471554	1471556
Formula	C_{32} H_{39} Al Cl_2 N_2	$C_{96}H_{134}Al_2F_{12}$ $N_4O_{19}S_4$	$C_{92}H_{98}Al_2BCl_2$ $_0N_4Na$	$C_{64.36}H_{68.91}AlB$ $Cl_{11.82}N_2O$
Formula weight	549.53	2058.26	2056.50	1343.31
Crystal system	Monoclinic	monoclinic	monoclinic	triclinic
Space group	P2(1)/n	P 1 21/c 1	C 1 2/c 1	P -1
a /Å	9.5204(11)	9.7628(8)	16.9979(7)	14.2999(7)
b /Å	25.954(3)	27.367(2)	27.9699(11)	16.7422(9)
c /Å	12.6419(16)	19.2292(14)	20.6231(9)	17.0542(9)
β/°	98.612(5)	101.133(3)	92.6642(16)	104.6772(19)
V / $Å^3$	3088.5(6)	5040.9(7)	9794.2(7)	3280.3(3)
Z	4	2	4	2
Temperature / K	103	153	153	103
Dc/ g cm^{-3}	1.182	1.356	1.395	1.360
F(000)	1168	2176	4240	1392
Crystal size/ mm	0.20 x 0.16 x 0.12	0.140 x 0.160 x 0.200	0.220 x 0.320 x 0.360	0.390 x 0.400 x 0.420
θ range/°	2.26 to 29.00	2.48 to 26.48	1.40 to 29.19	1.46 to 27.13°
No. of reflns collected	35460	60773	31329	106602
No. of indep reflns	8162	10354	13109	14392
R1 [I >2σ (I)]	0.0619	0.0650	0.0792	0.0510
wR2 (all data)	0.1754	0.1876	0.2458	0.1380
Peak and hole/e $Å^{-3}$	0.324 and -0.349	0.800 and -0.537	1.462 and -1.397	1.628 and -0.817

Refrences

S1 (a) SMART version 5.628; Bruker AXS Inc.: Madison, WI, **2001**. (b)SAINT+ version 6.22a; Bruker AXS Inc.: Madison, WI, **2001**. (c) Sheldrick, G. M. SADABS; **1996**. (d) SHELXTL version 5.1; Bruker AXS Inc.: Madison, WI, **1997**.