Supporting Information

Waste-Minimized, Ecofriendly, and Chemoselective Room-Temperature Hydrogenation of C=C Bonds Using a Homogeneous Recyclable Imidazole-Based Ru(II)-p-Cym Catalyst

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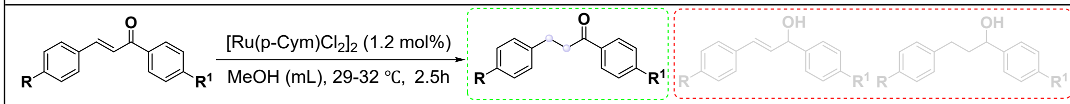
Table of Content

1. [Ru(p-Cym)Cl$_2$]$_2$ promoted hydrogenation of different chalcones under Optimized reaction condition

Table S1. [Ru(p-Cym)Cl$_2$]$_2$ screening for hydrogenation of α,β-unsaturated ketone



Sr. No	R	R¹	Substrate	Conversion (%)
1	Br	Cl	**3a**	19
2	OMe	Cl	**4a**	15
3	Me	Br	**5a**	19
4	Me	Cl	**6a**	17
5	Cl	Cl	**11a**	23

2. Determination of green metrics parameters

2.1 The CHEM21 green metrics toolkit

Supplementary Information: Appendix 2 — Summary of Zero Pass Metrics Toolkit

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density (g ml^{-1})	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml^{-1})	Mass (g)
Chalcone	42.00	208.26	0.20	Mn	5.00		4.00	Toluene-d8	0.40	0.94	0.38						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	42.00	210.28			5.00		4.00				0.38		0.00				0.00

$$AE = \frac{molecular\ weight\ of\ product}{total\ molecualr\ weight\ of\ reactants} \times 100$$

$$RME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ reactants} \times 100$$

		Flag	
Yield	98.2	●	98.2
Conversion	100.0	●	100.0
Selectivity	98.2	●	98.2
AE	100.0		
RME	99.2		

	mass (mg)	mw	mol (mM)
Product	41.660	210.280	0.1981168
	mass		
Unreacted limiting reactant			

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Fig. S1 **Zero pass for** *Org. Lett.*, **2024**, 26, 4173-4177 (reference 21)

Supplementary Information: Appendix 2 **Summary of First Pass Metrics Toolkit**

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density (g ml^{-1})	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml^{-1})	Mass (g)
Chalcone	42.00	208.26	0.20	Mn	5.00		4.00	Toluene-d8	0.40	0.94	0.38						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	42.00	210.28			5.00		4.00				0.38		0.00				0.00

		Flag	
Yield	98.2		98.2
Conversion	100.0		100.0
Selectivity	98.2		98.2
AE	100.0		
RME	99.2	OE	99.2
PMI total	1.2		
PMI Reaction	1.2		
PMI reactants, reagents, catlyst	1.2		
PMI reaction solvents	0.0		
PMI Workup	0.0		
PMI Workup chemical	0.0		
PMI workup solvents	0.0		

	Mass	MW	Mol
Product	41.660	210.280	0.198116797
	mass		
Unreacted limiting reactant	0.00		

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$\text{mass intensity} = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$

$$OE = \frac{RME}{AE} \times 100$$

Experimental:
"Inside a N2-filled glovebox, a J. Young NMR tube suitable for intermediate pressure (up to 10.5 bar) was charged with substrate (0.1/0.2 mmol, or 0.05 mmol), manganese hydride catalyst 1 [(PCNHCP)Mn(CO)2H] (5 mol%; 0.1/0.2 mL from a 50 mM stock solution of 1 in toluene), and toluene-d8 to make the total volume of 0.4 mL. The tube was sealed and was taken out of the glovebox. Hereafter, the tube was degassed by freeze-pump-thaw cycles (3×) using Schlenk techniques and connected to an intermediate pressure hydrogen line. The line was purged by subsequent evacuation and filling with H2 (3×). The tube was opened and was filled with hydrogen at desired pressure (1-5 bar). Next, the tube was sealed again and placed on a preheated oil bath at 110 °C. The reaction progress was monitored by 1 H-NMR spectroscopy at room temperature. Either (i) after >90% substrate consumption or (ii) after a maximum of 48 h, the reaction mixture was cooled to room temperature, and the contents of the J. Young tube were transferred to a 20 ml vial. The J. Young tube was repeatedly rinsed with dichloromethane (5 × 0.6 mL). Then, the reaction mixture was filtered through a short alumina pad (4 cm; 7 mm O.D) using a gradient of either ethyl acetate/hexane mixture or 0-2 % methanol in dichloromethane (depending on the polarity and solubility of the product) to separate the organic products from the manganese catalyst. The complete elution of the organic products from the alumina pad was confirmed by thin layer chromatography analysis. Hereafter, the solvent was evaporated under reduced pressure and the crude reaction mixture was purified by silica gel column. For every substrate, reactions were run in duplicate. In one reaction, 1,3,5-trimethoxybenzene (0.33 equiv.) was added as internal standard to the crude reaction mixture after filtration over alumina to determine the yield by 1 H-NMR spectroscopy. For substrate 5ae the yield was determined by Gas Chromatography. Isolated yields have been averaged from two independent catalysis runs.."

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	
Problematic solvents: (acceptable only if substitution does not offer advantages)	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene, MTBE, **cyclohexane**, chlorobenzene, formic acid, pyridine, Me-THF	Toluene
Hazardous solvents: These solvents have significant health and/or safety concerns.	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	
Highly hazardous solvents: The solvents which are agreed not to be used, even in screening	Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	

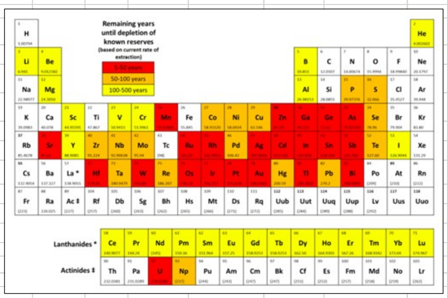
Catalyst/enzyme (First Pass)

		Tick
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	X
Use of stoichiometric quantities of reagents	Amber Flag	
Use of reagents in excess	Red Flag	

		Tick
Facile recovery of catalyst/enzyme	Green Flag	
catalyst/enzyme not recovered	Amber Flag	X

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	Mn
50-500 years	Amber Flag	
+500 years	Green Flag	



Energy (First Pass)

		Tick
Reaction run between 0 to 70^{o}C	Green Flag	
Reaction run between -20 to 0 or 70 to 140^{o}C	Amber Flag	X
Reaction run below -20 or above 140^{o}C	Red Flag	

		Tick
Reaction run at reflux	Red Flag	X
Reaction run 5^{o}C or more below the solvent boiling point	Green Flag	

Batch/flow

		Tick
Flow	Green Flag	
Batch	Amber Flag	X

Work Up

		List
quenching filtration centrifugation crystallisation Low temperature distillation/evaporation/ sublimation (< 140 ^{o}C at atmospheric	Green Flag	
solvent exchange, quenching into aqueous solvent	Amber Flag	
chromatography/ion exchange high temperature multiple recrystallisation	Red Flag	X

Health & safety

	Red Flag	Amber Flag	Green Flag	List substances and H-codes	List substances and H-codes	List substances and H-codes
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			
Explosive thermal runaway	H230, H240, H250	H241				
Toxic	H300, H310, H330	H301, H311, H331,				
Long Term toxicity	H340, H350, H360, H370, H372	H341, H351, H361, H371, H373				
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern

		List substances of very high concern
Chemical identified as Substances of Very High Concern by ChemSec which are utilised	Red Flag	

Fig. S2 **First pass for** *Org. Lett.*, **2024**, 26, 4173-4177 (reference 21).

Supplementary Information: Appendix 2 | **Summary of Zero Pass Metrics Toolkit**

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density (g ml^{-1})	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml^{-1})	Mass (g)
Chalcone	104.00	208.26	0.50	Fe	2.00	Cs2CO3	400.00	ethanol	2.00	0.79	1.58						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	104.00	210.28			2.00		400.00				1.58		0.00				0.00

$$AE = \frac{\text{molecular weight of product}}{\text{total molecuair weight of reactants}} \times 100$$

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

		Flag
Yield	93.3	93.3
Conversion	100.0	100.0
Selectivity	93.3	93.3
AE	100.0	
RME	94.2	

	mass (mg)	mw	mol (mM)
Product	98.000	210.280	0.4660453
	mass		
Unreacted limiting reactant			

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Fig. S3 **Zero pass** for *Chem. Eur. J.*, **2018**, 24, 5770-5774 (reference 19).

Supplementary Information: Appendix 2 — **Summary of First Pass Metrics Toolkit**

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm³)	Density (g ml⁻¹)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml⁻¹)	Mass (g)
Chalcone	104.00	208.26	0.50	Fe	2.00	Cs2CO3	400.00	ethanol	2.00	0.79	1.58						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	104.00	210.28			2.00		400.00				1.58		0.00				0.00

$$RME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ reactants} \times 100$$

$$AE = \frac{molecular\ weight\ of\ product}{total\ molecuair\ weight\ of\ reactants} \times 100$$

$$mass\ intensity = \frac{total\ mass\ in\ a\ process\ or\ process\ step}{mass\ of\ product}$$

$$OE = \frac{RME}{AE} \times 100$$

		Flag	
Yield	93.3		93.3
Conversion	100.0		100.0
Selectivity	93.3		93.3
AE	100.0		
RME	94.2	OE	94.2
PMI total	5.2		
PMI Reaction	5.2		
PMI reactants, reagents, catlyst	5.2		
PMI reaction solvents	0.0		
PMI Workup	0.0		
PMI Workup chemical	0.0		
PMI workup solvents	0.0		

	Mass	MW	Mol
Product	98.000	210.280	0.466045273
	mass		
Unreacted limiting reactant	0.00		

Experimental:
"Procedure A In a 10 mL reaction tube equipped with a stirring bar, the substrate (0.5 mmol), Fe2 (2 mol%, 6.90 mg), and Cs2CO3 (2.5 mol%, 4.41 mg) were solubilised in 2 mL of free-O2 propan-2-ol and heated for 16 h at 70° C. Solvent was removed and hydrogenated chalcone was purified by silica gel chromatography. ! Procedure B In a 10 mL reaction tube equipped with a stirring bar, substrate (0.5 mmol), Fe2 (2 mol%, 6.90 mg), and Cs2CO3 (2.5 mol%, 4.41 mg) were solubilised in 2 mL of free-O2 propan-2-ol and heated for 16 h at 90° C. Conversion was calculated by GC analysis, the corresponding commercially available saturated ketone was used for comparison. ! Procedure C In a 10 mL reaction tube equipped with a stirring bar, substrate (0.5 mmol), complex Fe2 (2 mol%, 6.90 mg), Cs2CO3 (2.5 mol%, 4.41 mg) were solubilised in 2 mL of free-O2 propan-2-ol and heated for 16 h at 90° C. Solvent was removed and hydrogenated enone was purified by silica gel chromatography

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	EtOH
Problematic solvents: (acceptable only if substitution does not offer advantages)	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene, MTBE, **cyclohexane**, chlorobenzene, formic acid, pyridine, Me-THF	
Hazardous solvents: These solvents have significant health and/or safety concerns.	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	
Highly hazardous solvents: The solvents which are agreed not to be used, even in screening	Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	

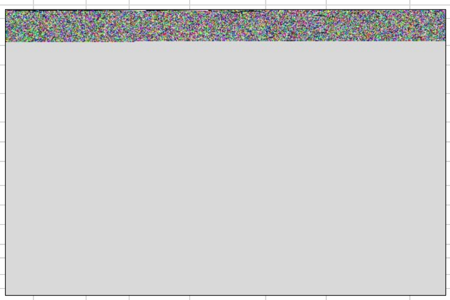
Catalyst/enzyme (First Pass)

		Tick
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	X
Use of stoichiometric quantities of reagents	Amber Flag	
Use of reagents in excess	Red Flag	

		Tick
Facile recovery of catalyst/enzyme	Green Flag	
catalyst/enzyme not recovered	Amber Flag	X

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	
50-500 years	Amber Flag	
+500 years	Green Flag	Fe



Energy (First Pass)

		Tick
Reaction run between 0 to 70°C	Green Flag	
Reaction run between -20 to 0 or 70 to 140°C	Amber Flag	X
Reaction run below -20 or above 140°C	Red Flag	

		Tick
Reaction run at reflux	Red Flag	X
Reaction run 5°C or more below the solvent boiling point	Green Flag	

Batch/flow

		Tick
Flow	Green Flag	
Batch	Amber Flag	X

Work Up

		List
quenching filtration centrifugation crystallisation Low temperature distillation/evaporation/ sublimation (< 140 °C at atmospheric	Green Flag	
solvent exchange, quenching into aqueous solvent	Amber Flag	
chromatography/ion exchange high temperature multiple recrystallisation	Red Flag	X

Health & safety

	Red Flag	Amber Flag	Green Flag	List substances and H-codes	List substances and H-codes	List substances and H-codes
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			
Explosive thermal runaway	H230, H240, H250	H241				
Toxic	H300, H310, H330	H301, H311, H331,				
Long Term toxicity	H340, H350, H360, H370, H372	H341, H351, H361, H371, H373				
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern		List substances of very high concern
Chemical identified as Substances of Very High Concern by ChemSec which are utilised	Red Flag	

Fig. S4 **First pass** for *Chem. Eur. J.*, **2018**, 24, 5770-5774 (reference 19).

Supplementary Information: Appendix 2 **Summary of Zero Pass Metrics Toolkit**

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density ($g\ ml^{-1}$)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density ($g\ ml^{-1}$)	Mass (g)
Chalcone	42.00	208.26	0.20	**Rh-H**	3.00			Methanol	4.00	0.79	3.16			Ethyl acetate	10.00	0.89	8.90
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	42.00	210.28			3.00		0.00				3.16		0.00				8.90

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

		Flag	
Yield	99.0		99.0
Conversion	100.0		100.0
Selectivity	99.0		99.0
AE	100.0		
RME	100.0		

	mass (mg)	mw	mol (mM)
Product	42.000	210.280	0.1997337
	mass		
Unreacted limiting reactant			

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Fig. S5 **Zero pass** for *J. Am. Chem. Soc.,* **2021**, 143, 9657-9663 (reference 24).

Supplementary Information: Appendix 2 — **Summary of First Pass Metrics Toolkit**

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density (g ml^{-1})	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml^{-1})	Mass (g)
Chalcone	42.00	208.26	0.20	Rh-H	3.00			Methanol	4.00	0.79	3.16			ethyl acetate	10.00	0.89	8.90
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	42.00	210.28			3.00		0.00				3.16		0.00				8.90

		Flag	
Yield	99.0		99.0
Conversion	100.0		100.0
Selectivity	99.0		99.0
AE	100.0		
RME	100.0	OE	100.0
PMI total	1.4		
PMI Reaction	1.1		
PMI reactants, reagents, catlyst	1.1		
PMI reaction solvents	0.1		
PMI Workup	0.2		
PMI Workup chemical	0.0		
PMI workup solvents	0.2		

	Mass	MW	Mol
Product	42.000	210.280	0.199733688
	mass		
Unreacted limiting reactant	0.00		

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

$$AE = \frac{\text{molecular weight of product}}{\text{total molecular weight of reactants}} \times 100$$

$$\text{mass intensity} = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$

$$OE = \frac{RME}{AE} \times 100$$

Experimental:
"A Fisher-Porter tube containing a stirring bar was charged with α,β-unsaturated carbonyl compounds/isolated olefins (0.2 mmol). Then, it was introduced in an argon-filled glovebox where, RhH-1 catalyst (3 mol%), anhydrous methanol (4 mL) were added. The tube was then placed behind an appropriate blast shield and pressurized to 40 psi of H2 gas. In order to remove the inert atmosphere, the vessel was vented and repressurized with H2 gas for twenty times. Increase the pressure of H2 to 80 psi for 30 seconds. If no change in H2 pressure, the reaction tube was taken out of the glovebox, and stirred at room temperature for 24 hours. (NOTE: The pressurized Fisher-Porter tube should always be placed behind an appropriate blast shield!) The Fisher-Porter was then allowed to release H2 gas, and the apparatus was disassembled. The crude mixture was filtered through a Celite® plug, eluting with additional EtOAc (10 mL). The filtrate was concentrated and the products were purified S-6 by flash chromatography to afford hydrogenation product. The yields reported in the manuscript refer to isolated yields and represent an average of at least two independent runs.."

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	MeOH
Problematic solvents: (acceptable only if substitution does not offer advantages)	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene, MTBE, **cyclohexane**, chlorobenzene, formic acid, pyridine, Me-THF	
Hazardous solvents: These solvents have significant health and/or safety concerns.	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	
Highly hazardous solvents: The solvents which are agreed not to be used, even in screening	Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	

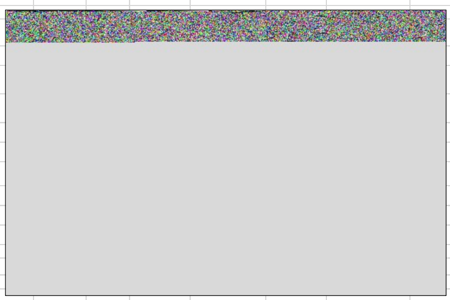
Catalyst/enzyme (First Pass)

		Tick
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	X
Use of stoichiometric quantities of reagents	Amber Flag	
Use of reagents in excess	Red Flag	

		Tick
Facile recovery of catalyst/enzyme	Green Flag	
catalyst/enzyme not recovered	Amber Flag	X

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	Rh
50-500 years	Amber Flag	
+500 years	Green Flag	



Energy (First Pass)

		Tick
Reaction run between 0 to 70°C	Green Flag	X
Reaction run between -20 to 0 or 70 to 140°C	Amber Flag	
Reaction run below -20 or above 140°C	Red Flag	

		Tick
Reaction run at reflux	Red Flag	
Reaction run 5°C or more below the solvent boiling point	Green Flag	X

Batch/flow

		Tick
Flow	Green Flag	
Batch	Amber Flag	X

Work Up

		List
quenching filtration centrifugation crystallisation Low temperature distillation/evaporation/ sublimation (< 140 °C at atmospheric	Green Flag	
solvent exchange, quenching into aqueous solvent	Amber Flag	
chromatography/ion exchange high temperature multiple recrystallisation	Red Flag	X

Health & safety

	Red Flag	Amber Flag	Green Flag	List substances and H-codes	List substances and H-codes	List substances and H-codes
						MeOH: H225
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			
Explosive thermal runaway	H230, H240, H250	H241				
Toxic	H300, H310, H330	H301, H311, H331,			MeOH: H301, H311	
Long Term toxicity	H340, H350, H360, H370, H372	H341, H351, H361, H371, H373		MeOH: H370		
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern		List substances of very high concern
Chemical identified as Substances of Very High Concern by ChemSec which are utilised	Red Flag	

Fig. S6 **First pass** for *J. Am. Chem. Soc.,* **2021**, 143, 9657-9663 (reference 24).

Supplementary Information: Appendix 2 **Summary of Zero Pass Metrics Toolkit**

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density ($g\ ml^{-1}$)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density ($g\ ml^{-1}$)	Mass (g)
ethyl-1-phenylpent-2-en	35.00	174.24	0.20	Ir	0.50			DCM	2.00	1.33	2.66						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	35.00	176.26			0.50		0.00				2.66		0.00				0.00

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

		Flag	
Yield	98.9	●	98.9
Conversion	100.0	●	100.0
Selectivity	98.9	●	98.9
AE	100.0		
RME	100.0		

	mass (mg)	mw	mol (mM)
Product	35.000	176.250	0.1985816
	mass		
Unreacted limiting reactant			

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Fig. S7 **Zero pass** for *Org. Lett.,* **2021**, 23, 242-246 (reference 23).

Supplementary Information: Appendix 2 — Summary of First Pass Metrics Toolkit

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density ($g\ ml^{-1}$)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density ($g\ ml^{-1}$)	Mass (g)
(E)-2-methyl-1-phenylpent-2-en-1-one	35.00	174.24	0.20	Ir	0.50			DCM	2.00	1.33	2.66						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	35.00	176.26			0.50		0.00				2.66		0.00				0.00

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$\text{mass intensity} = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$

$$OE = \frac{RME}{AE} \times 100$$

		Flag	
Yield	98.9		98.9
Conversion	100.0		100.0
Selectivity	98.9		98.9
AE	100.0		
RME	100.0	OE	100.0
PMI total	1.1		
PMI Reaction	1.1		
PMI reactants, reagents, catlyst	1.0		
PMI reaction solvents	0.1		
PMI Workup	0.0		
PMI Workup chemical	0.0		
PMI workup solvents	0.0		

	Mass	MW	Mol
Product	35.000	176.250	0.19858156
	mass		
Unreacted limiting reactant	0.00		

Experimental:
"An oven-dried glass vial equipped with magnetic stirring bar was charged with substrate (0.2 mmol), iridium complex (0.5 mol%) and dry DCM (2.0 ml). The vial was placed in a low-pressure hydrogenation apparatus, purged three times with nitrogen, purged three times with hydrogen gas and then pressurized to 20.0 bar with hydrogen gas. After stirring for 16 h at room temperature, the pressure was released and the solvent was removed under vacuum. The crude product was then purified by column chromatography on silica gel (pentane/Et2O, 50:50) to give the corresponding product. Conversions were determined by 1H NMR spectroscopy and the ee values were determined by GC or SFC analysis using a chiral stationary phase. The configuration of the products was determined by comparing their optical rotation with literature data. If no reference is given, the assignment is tentative.

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	
Problematic solvents: (acceptable only if substitution does not offer advantages)	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene, MTBE, **cyclohexane**, chlorobenzene, formic acid, pyridine, Me-THF	
Hazardous solvents: These solvents have significant health and/or safety concerns.	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	DCM
Highly hazardous solvents: The solvents which are agreed not to be used, even in screening	Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	

Catalyst/enzyme (First Pass)

		Tick
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	X
Use of stoichiometric quantities of reagents	Amber Flag	
Use of reagents in excess	Red Flag	

		Tick
Facile recovery of catalyst/enzyme	Green Flag	
catalyst/enzyme not recovered	Amber Flag	X

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	Ir
50-500 years	Amber Flag	
+500 years	Green Flag	

Energy (First Pass)

		Tick
Reaction run between 0 to 70°C	Green Flag	X
Reaction run between -20 to 0 or 70 to 140°C	Amber Flag	
Reaction run below -20 or above 140°C	Red Flag	

		Tick
Reaction run at reflux	Red Flag	
Reaction run 5°C or more below the solvent boiling point	Green Flag	X

Batch/flow

		Tick
Flow	Green Flag	
Batch	Amber Flag	X

Work Up

		List
quenching filtration centrifugation crystallisation Low temperature distillation/evaporation/ sublimation (< 140 °C at atmospheric	Green Flag	
solvent exchange, quenching into aqueous solvent	Amber Flag	
chromatography/ion exchange high temperature multiple recrystallisation	Red Flag	X

Health & safety

	Red Flag	Amber Flag	Green Flag	List substances and H-codes	List substances and H-codes	List substances and H-codes
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			
Explosive thermal runaway	H230, H240, H250	H241				
Toxic	H300, H310, H330	H301, H311, H331,				
Long Term toxicity	H340, H350, H360, H370, H372	H341, H351, H361, H371, H373				
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern		List substances of very high concern
Chemical identified as Substances of Very High Concern by ChemSec which are utilised	Red Flag	

Fig. S8 **First pass** for *Org. Lett.,* **2021**, 23, 242-246 (reference 23).

Supplementary Information: Appendix 2 **Summary of Zero Pass Metrics Toolkit**

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density (g ml^{-1})	Mass (g)
Chalcone	42.00	208.26	0.20	Mn	5.00	K3PO4	4.00	Methanol	1.00	0.79	0.79
H2		2.02									0.00
											0.00
											0.00
											0.00
											0.00
											0.00
Total	42.00	210.28			5.00		4.00				0.79

Reactant (Limiting Reactant First)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml^{-1})	Mass (g)
Chalcone						0.00
H2						0.00
						0.00
						0.00
						0.00
						0.00
						0.00
Total		0.00				0.00

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

		Flag	
Yield	95.3		95.3
Conversion	100.0		100.0
Selectivity	95.3		95.3
AE	100.0		
RME	96.2		

	mass (mg)	mw	mol (mM)
Product	40.400	210.280	0.1921248
	mass		
Unreacted limiting reactant			

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Fig. S9 **Zero pass** for *Chem. Sci.,* **2022**, 13, 13764-13773 (reference 25).

Supplementary Information: Appendix 2 — **Summary of First Pass Metrics Toolkit**

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm³)	Density (g ml⁻¹)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml⁻¹)	Mass (g)
Chalcone	42.00	208.26	0.20	Mn	5.00	K3PO4	4.00	Methanol	1.00	0.79	0.79						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	42.00	210.28			5.00		4.00				0.79		0.00				0.00

		Flag	
Yield	95.3		95.3
Conversion	100.0		100.0
Selectivity	95.3		95.3
AE	100.0		
RME	96.2	OE	96.2
PMI total	1.3		
PMI Reaction	1.3		
PMI reactants, reagents, catlyst	1.3		
PMI reaction solvents	0.0		
PMI Workup	0.0		
PMI Workup chemical	0.0		
PMI workup solvents	0.0		

	Mass	MW	Mol
Product	40.400	210.280	0.192124786
	mass		
Unreacted limiting reactant	0.00		

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

$$AE = \frac{\text{molecular weight of product}}{\text{total molecular weight of reactants}} \times 100$$

$$\text{mass intensity} = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$

$$OE = \frac{RME}{AE} \times 100$$

Experimental:
"To a dry vial with magnetic bar was introduced Mn-3 (0.005 g, 0.01 mmol), K3PO4 (0.0043 g, 0.02 mmol), and (E)-chalcone (4a; 0.042 g, 0.202 mmol) inside the glove box. The reaction vial was transferred to an autoclave under argon atmosphere. Then MeOH (1.0 mL) was added and the autoclave was pressurized with H2 (5 bar) and vented for five times. Finally, the autoclave was pressurized with 5 bar H2 and stirred (700 rpm) at room temperature (27 °C) for 1 h. After reaction time, the reaction mixture was concentrated and subjected to column chromatography on silica gel (petroleum ether/EtOAc: 70/1) to yield 4 (0.041 g, 96%) as white solid."

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	MeOH
Problematic solvents: (acceptable only if substitution does not offer advantages)	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene, MTBE, **cyclohexane**, chlorobenzene, formic acid, pyridine, Me-THF	
Hazardous solvents: These solvents have significant health and/or safety concerns.	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	
Highly hazardous solvents: The solvents which are agreed not to be used, even in screening	Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	

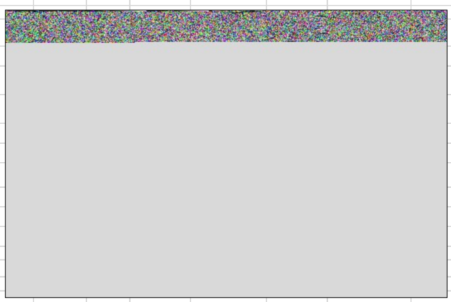
Catalyst/enzyme (First Pass)

		Tick
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	X
Use of stoichiometric quantities of reagents	Amber Flag	
Use of reagents in excess	Red Flag	

		Tick
Facile recovery of catalyst/enzyme	Green Flag	
catalyst/enzyme not recovered	Amber Flag	X

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	Mn
50-500 years	Amber Flag	
+500 years	Green Flag	



Energy (First Pass)

		Tick
Reaction run between 0 to 70°C	Green Flag	X
Reaction run between -20 to 0 or 70 to 140°C	Amber Flag	
Reaction run below -20 or above 140°C	Red Flag	

		Tick
Reaction run at reflux	Red Flag	
Reaction run 5°C or more below the solvent boiling point	Green Flag	X

Batch/flow

		Tick
Flow	Green Flag	
Batch	Amber Flag	X

Work Up

		List
quenching filtration centrifugation crystallisation Low temperature distillation/evaporation/sublimation (< 140 °C at atmospheric	Green Flag	
solvent exchange, quenching into aqueous solvent	Amber Flag	
chromatography/ion exchange high temperature multiple recrystallisation	Red Flag	X

Health & safety

	Red Flag	Amber Flag	Green Flag	List substances and H-codes	List substances and H-codes	List substances and H-codes
						MeOH: H225
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			
Explosive thermal runaway	H230, H240, H250	H241				
Toxic	H300, H310, H330	H301, H311, H331,			MeOH: H301, H311	
Long Term toxicity	H340, H350, H360, H370, H372	H341, H351, H361, H371, H373		MeOH: H370		
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern		List substances of very high concern
Chemical identified as Substances of Very High Concern by ChemSec which are utilised	Red Flag	

Fig. S10 **First pass** for *Chem. Sci.,* **2022**, 13, 13764-13773 (reference 25).

Supplementary Information: Appendix 2 — **Summary of Zero Pass Metrics Toolkit**

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density ($g\ ml^{-1}$)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density ($g\ ml^{-1}$)	Mass (g)
Chalcone	52.00	208.26	0.25	Ru	1.20			Methanol	10.00	0.79	7.90						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	52.00	210.28			1.20		0.00				7.90		0.00				0.00

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

		Flag
Yield	99.0	99.0
Conversion	100.0	100.0
Selectivity	99.0	99.0
AE	100.0	
RME	100.0	

	mass (mg)	mw	mol (mM)
Product	52.000	210.280	0.2472893
	mass		
Unreacted limiting reactant			

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Fig. S11 **Zero pass** for this work.

Supplementary Information: Appendix 2 — Summary of First Pass Metrics Toolkit

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (mg)	MW	Mol (mM)	Catalyst	Mass (mol%)	Reagent	Mass (mg)	Reaction solvent	Volume (cm^3)	Density (g ml^{-1})	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml^{-1})	Mass (g)
Chalcone	52.00	208.26	0.25	Ru	1.20			Methanol	10.00	0.79	7.90						0.00
H2		2.02									0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
											0.00						0.00
Total	52.00	210.28			1.20		0.00				7.90		0.00				0.00

$$RME = \frac{\text{mass of isolated product}}{\text{total mass of reactants}} \times 100$$

$$AE = \frac{\text{molecular weight of product}}{\text{total molecualr weight of reactants}} \times 100$$

$$\text{mass intensity} = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$

$$OE = \frac{RME}{AE} \times 100$$

		Flag	
Yield	99.0		99.0
Conversion	100.0		100.0
Selectivity	99.0		99.0
AE	100.0		
RME	100.0	OE	100.0
PMI total	1.2		
PMI Reaction	1.2		
PMI reactants, reagents, catlyst	1.0		
PMI reaction solvents	0.2		
PMI Workup	0.0		
PMI Workup chemical	0.0		
PMI workup solvents	0.0		

	Mass	MW	Mol
Product	52.000	210.280	0.247289329
	mass		
Unreacted limiting reactant	0.00		

Experimental

"For the reaction, 0.25 mmol of α,β-unsaturated ketones(1a) were mixed with 1.2 mol% of the **Ru-1** catalyst and 10 mL of methanol in a high-pressure reactor. The mixture was stirred at room temperature (29–32°C) under 20 bar of H_2 pressure for the required reaction time. Upon completion of the reaction, the volatile components were removed under high vacuum to yield the crude product, which was analyzed using 1H NMR spectroscopy with unreacted substrates serving as the internal standard.

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	MeOH
Problematic solvents: (acceptable only if substitution does not offer advantages)	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene, MTBE, **cyclohexane**, chlorobenzene, formic acid, pyridine, Me-THF	
Hazardous solvents: These solvents have significant health and/or safety concerns.	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	
Highly hazardous solvents: The solvents which are agreed not to be used, even in screening	Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	

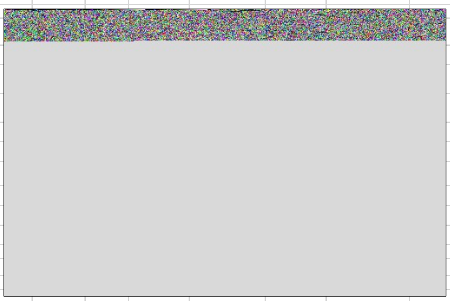
Catalyst/enzyme (First Pass)

		Tick
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	X
Use of stoichiometric quantities of reagents	Amber Flag	
Use of reagents in excess	Red Flag	

		Tick
Facile recovery of catalyst/enzyme	Green Flag	X
catalyst/enzyme not recovered	Amber Flag	

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	Ru
50-500 years	Amber Flag	
+500 years	Green Flag	



Energy (First Pass)

		Tick
Reaction run between 0 to 70°C	Green Flag	X
Reaction run between -20 to 0 or 70 to 140°C	Amber Flag	
Reaction run below -20 or above 140°C	Red Flag	

		Tick
Reaction run at reflux	Red Flag	
Reaction run 5°C or more below the solvent boiling point	Green Flag	X

Batch/flow

		Tick
Flow	Green Flag	
Batch	Amber Flag	X

Work Up

		List
quenching filtration centrifugation crystallisation Low temperature distillation/evaporation/ sublimation (< 140 °C at atmospheric	Green Flag	X
solvent exchange, quenching into aqueous solvent	Amber Flag	
chromatography/ion exchange high temperature multiple recrystallisation	Red Flag	

Health & safety

	Red Flag	Amber Flag	Green Flag	List substances and H-codes	List substances and H-codes	List substances and H-codes
						MeOH: H225
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			
Explosive thermal runaway	H230, H240, H250	H241				
Toxic	H300, H310, H330	H301, H311, H331,			MeOH: H301, H311	
Long Term toxicity	H340, H350, H360, H370, H372	H341, H351, H361, H371, H373		MeOH: H370		
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern

		List substances of very high concern
Chemical identified as Substances of Very High Concern by ChemSec which are utilised	Red Flag	

Fig. S12 **First pass** for this work.

2.2 E-factor calculations

E-factor for 1.5 mM hydrogenation of 1a

E-factor (with solvent recovery) = [0.312 g (**1a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.295 g (Product **1b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.295 g (Product **1b**) = **15.4**

E-factor (without solvent recovery) = [0.312 g (**1a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.295 g (Product **1b**) – 0.01 g (**Ru-1** isolated)] / 0.295 g (Product **1b**) = **116.9**

E-factor for 1.5 mM hydrogenation of 2a

E-factor (with solvent recovery) = [0.384 g (**2a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.345 g (Product **2b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.345 g (Product **2b**) = **13.2**

E-factor (without solvent recovery) = [0.384 g (**2a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.345 g (Product **2b**) – 0.01 g (**Ru-1** isolated)] / 0.345 g (Product **2b**) = **99.9**

E-factor for 1.5 mM hydrogenation of 8a

E-factor (with solvent recovery) = [0.458 g (**8a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.410 g (Product **8b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.410 g (Product **8b**) = **11.1**

E-factor (without solvent recovery) = [0.458 g (**8a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.410 g (Product **8b**) – 0.01 g (**Ru-1** isolated)] / 0.410 g (Product **8b**) = **84.2**

E-factor for 1.5 mM hydrogenation of 11a

E-factor (with solvent recovery) = [0.420 g (**11a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.380 g (Product **11b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.380 g (Product **11b**) = **11.9**

E-factor (without solvent recovery) = [0.420 g (**11a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.380 g (Product **11b**) – 0.01 g (**Ru-1** isolated)] / 0.380 g (Product **11b**) = **90.8**

E-factor for 1.5 mM hydrogenation of 14a

E-factor (with solvent recovery) = [0.390 g (**14a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.350 g (Product **14b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.350 g (Product **14b**) = **13**

E-factor (without solvent recovery) = [0.390 g (**14a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.350 g (Product **14b**) – 0.01 g (**Ru-1** isolated)] / 0.350 g (Product **14b**) = **98.6**

E-factor for 1.5 mM hydrogenation of 15a

E-factor (with solvent recovery) = [0.445 g (**15a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.410 g (Product **15b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.410 g (Product **15b**) = **11.4**

E-factor (without solvent recovery) = [0.445 g (**15a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.410 g (Product **15b**) – 0.01 g (**Ru-1** isolated)] / 0.410 g (Product **15b**) = **84.1**

E-factor for 1.5 mM hydrogenation of 16a

E-factor (with solvent recovery) = [0.520 g (**16a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.465 g (Product **16b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.465 g (Product **16b**) = **9.8**

E-factor (without solvent recovery) = [0.520 g (**16a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.465 g (Product **16b**) – 0.01 g (**Ru-1** isolated)] / 0.465 g (Product **16b**) = **74.2**

E-factor for 1.5 mM hydrogenation of 17a

E-factor (with solvent recovery) = [0.410 g (**17a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.375 g (Product **17b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.375 g (Product **17b**) = **12.1**

E-factor (without solvent recovery) = [0.410 g (**17a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.375 g (Product **17b**) – 0.01 g (**Ru-1** isolated)] / 0.375 g (Product **17b**) = **91.9**

E-factor for 1.5 mM hydrogenation of 19a

E-factor (with solvent recovery) = [0.415 g (**19a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.370 g (Product **19b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.370 g (Product **19b**) = **12.2**

E-factor (without solvent recovery) = [0.415 g (**19a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.370 g (Product **19b**) – 0.01 g (**Ru-1** isolated)] / 0.370 g (Product **19b**) = **93.2**

E-factor for 1.5 mM hydrogenation of 20a

E-factor (with solvent recovery) = [0.480 g (**20a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.440 g (Product **20b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.440 g (Product **20b**) = **10.4**

E-factor (without solvent recovery) = [0.480 g (**20a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.440 g (Product **20b**) – 0.01 g (**Ru-1** isolated)] / 0.440 g (Product **20b**) = **78.4**

E-factor for 1.5 mM hydrogenation of 23a

E-factor (with solvent recovery) = [0.370 g (**23a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.330 g (Product **23b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.330 g (Product **23b**) = **13.8**

E-factor (without solvent recovery) = [0.370 g (**23a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.330 g (Product **23b**) – 0.01 g (**Ru-1** isolated)] / 0.330 g (Product **23b**) = **104.5**

E-factor for 1.5 mM hydrogenation of 25a

E-factor (with solvent recovery) = [0.435 g (**25a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.410 g (Product **25b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.410 g (Product **25b**) = **11**

E-factor (without solvent recovery) = [0.435 g (**25a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.410 g (Product **25b**) – 0.01 g (**Ru-1** isolated)] / 0.410 g (Product **25b**) = **84.1**

E-factor for 1.5 mM hydrogenation of 27a

E-factor (with solvent recovery) = [0.370 g (**27a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.330 g (Product **27b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.330 g (Product **27b**) = **13.8**

E-factor (without solvent recovery) = [0.370 g (**27a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.330 g (Product **27b**) – 0.01 g (**Ru-1** isolated)] / 0.330 g (Product **27b**) = **104.5**

E-factor for 1.5 mM hydrogenation of 28a

E-factor (with solvent recovery) = [0.340 g (**28a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.305 g (Product **28b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.305 g (Product **28b**) = **14.9**

E-factor (without solvent recovery) = [0.340 g (**28a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.305 g (Product **28b**) – 0.01 g (**Ru-1** isolated)] / 0.305 g (Product **28b**) = **113.1**

E-factor for 1.5 mM hydrogenation of 30a

E-factor (with solvent recovery) = [0.360 g (**30a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.330 g (Product **30b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.330 g (Product **30b**) = **14.8**

E-factor (without solvent recovery) = [0.360 g (**30a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.330 g (Product **30b**) – 0.01 g (**Ru-1** isolated)] / 0.330 g (Product **30b**) = **104.5**

E-factor for 1.5 mM hydrogenation of 31a

E-factor (with solvent recovery) = [0.345 g (**31a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.310 g (Product **31b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.310 g (Product **31b**) = **14.7**

E-factor (without solvent recovery) = [0.345 g (**31a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.310 g (Product **31b**) – 0.01 g (**Ru-1** isolated)] / 0.310 g (Product **31b**) = **111.3**

E-factor for 1.5 mM hydrogenation of 33a

E-factor (with solvent recovery) = [0.345 g (**33a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.315 g (Product **33b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.315 g (Product **33b**) = **14.4**

E-factor (without solvent recovery) = [0.345 g (**33a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.315 g (Product **33b**) – 0.01 g (**Ru-1** isolated)] / 0.315 g (Product **33b**) = **109.4**

E-factor for 1.5 mM hydrogenation of 34a

E-factor (with solvent recovery) = [0.395 g (**34a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.360 g (Product **34b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.360 g (Product **34b**) = **12.7**

E-factor (without solvent recovery) = [0.395 g (**34a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.360 g (Product **34b**) – 0.01 g (**Ru-1** isolated)] / 0.360 g (Product **34b**) = **95.8**

E-factor for 1.5 mM hydrogenation of 35a

E-factor (with solvent recovery) = [0.450 g (**35a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.405 g (Product **35b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.405 g (Product **35b**) = **11.3**

E-factor (without solvent recovery) = [0.450 g (**35a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.405 g (Product **35b**) – 0.01 g (**Ru-1** isolated)] / 0.405 g (Product **35b**) = **85.2**

E-factor for 1.5 mM hydrogenation of 37a

E-factor (with solvent recovery) = [0.250 g (**37a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.220 g (Product **37b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.220 g (Product **37b**) = **20.7**

E-factor (without solvent recovery) = [0.250 g (**37a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.220 g (Product **37b**) – 0.01 g (**Ru-1** isolated)] / 0.220 g (Product **37b**) = **156.8**

E-factor for 1.5 mM hydrogenation of 38a

E-factor (with solvent recovery) = [0.295 g (**38a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.275 g (Product **38b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.275 g (Product **38b**) = **16.5**

E-factor (without solvent recovery) = [0.295 g (**38a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.275 g (Product **38b**) – 0.01 g (**Ru-1** isolated)] / 0.275 g (Product **38b**) = **125.4**

E-factor for 1.5 mM hydrogenation of 42a

E-factor (with solvent recovery) = [0.325 g (**42a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.290 g (Product **42b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.290 g (Product **42b**) = **15.7**

E-factor (without solvent recovery) = [0.325 g (**42a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.290 g (Product **42b**) – 0.01 g (**Ru-1** isolated)] / 0.290 g (Product **42b**) = **118.9**

E-factor for 1.5 mM hydrogenation of 43a

E-factor (with solvent recovery) = [0.355 g (**43a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.335 g (Product **43b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.335 g (Product **43b**) = **13.5**

E-factor (without solvent recovery) = [0.355 g (**43a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.335 g (Product **43b**) – 0.01 g (**Ru-1** isolated)] / 0.335 g (Product **43b**) = **102.9**

E-factor for 1.5 mM hydrogenation of 48a

E-factor (with solvent recovery) = [0.380 g (**48a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.340 g (Product **48b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.340 g (Product **48b**) = **13.4**

E-factor (without solvent recovery) = [0.380 g (**48a**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.340 g (Product **48b**) – 0.01 g (**Ru-1** isolated)] / 0.340 g (Product **48b**) = **101.5**

E-factor for 1.5 mM hydrogenation of 1e

E-factor (with solvent recovery) = [0.360 g (**1e**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.320 g (Product **1f**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.320 g (Product **1f**) = **14.3**

E-factor (without solvent recovery) = [0.360 g (**1e**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.320 g (Product **1f**) – 0.01 g (**Ru-1** isolated)] / 0.320 g (Product **1f**) = **107.8**

E-factor for 1.5 mM hydrogenation of 3e

E-factor (with solvent recovery) = [0.465 g (**3e**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.430 g (Product **3f**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.430 g (Product **3f**) = **10.6**

E-factor (without solvent recovery) = [0.465 g (**3e**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.430 g (Product **3f**) – 0.01 g (**Ru-1** isolated)] / 0.430 g (Product **3f**) = **80.2**

E-factor for 1.5 mM hydrogenation of 5e

E-factor (with solvent recovery) = [0.520 g (**5e**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.460 g (Product **5f**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.460 g (Product **5f**) = **9.9**

E-factor (without solvent recovery) = [0.520 g (**5e**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.460 g (Product **5f**) – 0.01 g (**Ru-1** isolated)] / 0.460 g (Product **5f**) = **75**

E-factor for 1.5 mM hydrogenation of 1h

E-factor (with solvent recovery) = [0.275 g (**1h**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.260 g (Product **1i**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.260 g (Product **1i**) = **17.4**

E-factor (without solvent recovery) = [0.275 g (**1h**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.260 g (Product **1i**) – 0.01 g (**Ru-1** isolated)] / 0.260 g (Product **1i**) = **132.6**

E-factor for 1.5 mM hydrogenation of 3h

E-factor (with solvent recovery) = [0.350 g (**3h**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.320 g (Product **3i**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.320 g (Product **3i**) = **14.1**

E-factor (without solvent recovery) = [0.350 g (**3h**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.320 g (Product **3i**) – 0.01 g (**Ru-1** isolated)] / 0.320 g (Product **3i**) = **107.8**

E-factor for 1.5 mM hydrogenation of 7h

E-factor (with solvent recovery) = [0.350 g (**7h**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.310 g (Product **7i**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.01 g (**Ru-1** isolated)] / 0.310 g (Product **7i**) = **14.7**

E-factor (without solvent recovery) = [0.350 g (**7h**) + 0.012 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.310 g (Product **7i**) – 0.01 g (**Ru-1** isolated)] / 0.310 g (Product **7i**) = **111.3**

E-factor for 2.5 mM hydrogenation of 1a

E-factor (with solvent recovery) = [0.520 g (**1a**) + 0.010 g (**Ru-1**) +15.84 g (MeOH) + 7.13 g (Diethyl ether) – 0.490 g (Product **1b**) – 13.464 g (MeOH recovered) – 4.991 g (Diethyl ether recovered) – 0.007 g (**Ru-1** isolated)] / 0.490 g (Product **1b**) = **9.3**

E-factor (without solvent recovery) = [0.520 g (**1a**) + 0.010 g (**Ru-1**) +15.84 g (MeOH) + 7.13 g (Diethyl ether) – 0.490 g (Product **1b**) – 0.007 g (**Ru-1** isolated)] / 0.490 g (Product **1b**) = **46.9**

E-factor for 5 mM hydrogenation of 1a

E-factor (with solvent recovery) = [1.040 g (**1a**) + 0.020 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.875 g (Product **1b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.016 g (**Ru-1** isolated)] / 0.875 g (Product **1b**) = **5.4**

E-factor (without solvent recovery) = [1.040 g (**1a**) + 0.020 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.875 g (Product **1b**) – 0.016 g (**Ru-1** isolated)] / 0.875 g (Product **1b**) = **39.6**

E-factor for 2.5 mM hydrogenation of 2a

E-factor (with solvent recovery) = [0.640 g (**2a**) + 0.010 g (**Ru-1**) +15.84 g (MeOH) + 7.13 g (Diethyl ether) – 0.585 g (Product **2b**) – 13.464 g (MeOH recovered) – 4.991 g (Diethyl ether recovered) – 0.007 g (**Ru-1** isolated)] / 0.585 g (Product **2b**) = **7.8**

E-factor (without solvent recovery) = [0.640 g (**2a**) + 0.010 g (**Ru-1**) +15.84 g (MeOH) + 7.13 g (Diethyl ether) – 0.585 g (Product **2b**) – 0.007 g (**Ru-1** isolated)] / 0.585 g (Product **2b**) = **39.4**

E-factor for 5 mM hydrogenation of 2a

E-factor (with solvent recovery) = [1.280 g (**2a**) + 0.020 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 1.150 g (Product **2b**) – 21.384 g (MeOH recovered) – 8.556 g (Diethyl ether recovered) – 0.016 g (**Ru-1** isolated)] / 1.150 g (Product **2b**) = **4.0**

E-factor (without solvent recovery) = [1.280 g (**2a**) + 0.020 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 1.150 g (Product **2b**) – 0.016 g (**Ru-1** isolated)] / 1.150 g (Product **2b**) = **30.1**

E-factor for 2.5 mM hydrogenation of 37a

E-factor (with solvent recovery) = [0.405 g (**37a**) + 0.010 g (**Ru-1**) +15.84 g (MeOH) + 7.13 g (Diethyl ether) – 0.375 g (Product **37b**) – 13.464 g (MeOH recovered) – 5.348 g (Diethyl ether recovered) – 0.006 g (**Ru-1** isolated)] / 0.375 g (Product **37b**) = **11.2**

E-factor (without solvent recovery) = [0.405 g (**37a**) + 0.010 g (**Ru-1**) +15.84 g (MeOH) + 7.13 g (Diethyl ether) – 0.375 g (Product **37b**) – 0.006 g (**Ru-1** isolated)] / 0.375 g (Product **37b**) = **61.3**

E-factor for 5 mM hydrogenation of 37a

E-factor (without solvent recovery) = [0.810 g (**37a**) + 0.020 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.780 g (Product **37b**) – 22.176 g (MeOH recovered) – 8.1995 g (Diethyl ether recovered) – 0.017 g (**Ru-1** isolated)] / 0.780 g (Product **37b**) = **5.3**

E-factor (without solvent recovery) = [0.810 g (**37a**) + 0.020 g (**Ru-1**) +23.76 g (MeOH) + 10.695 g (Diethyl ether) – 0.780 g (Product **37b**) – 0.017 g (**Ru-1** isolated)] / 0.780 g (Product **37b**) = **44.2**

2.3 EcoScale analysis

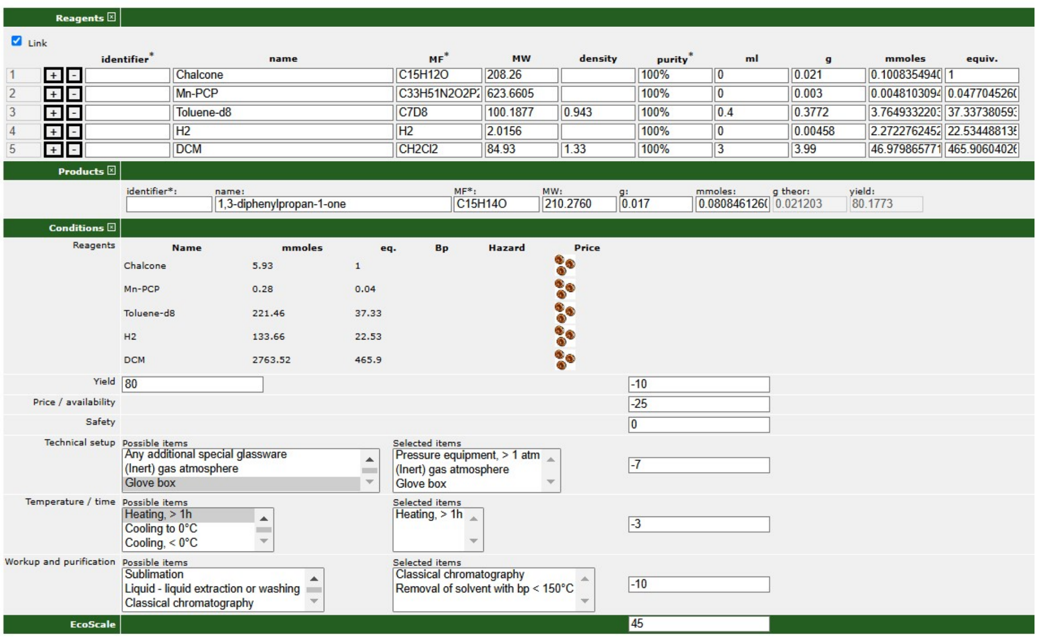
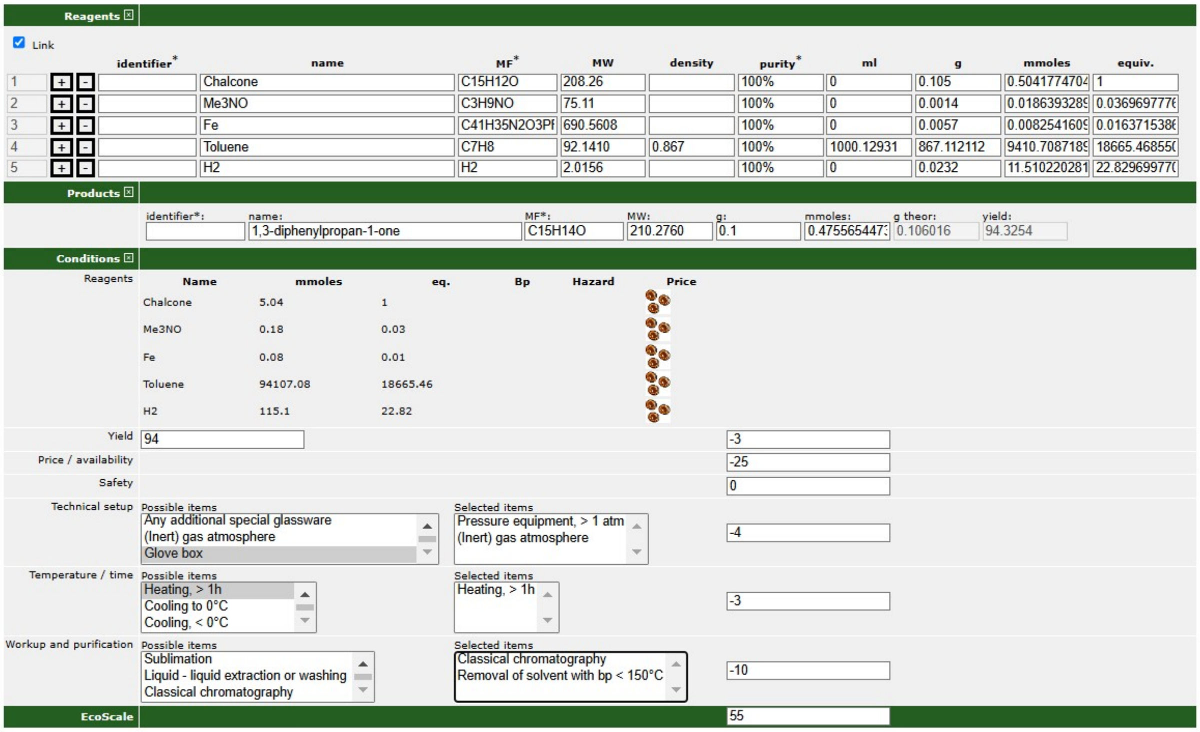


Fig. S13 EcoScale analysis for *Org. Lett.*, **2024**, 26, 4173-4177 (reference 21)



Reagents

Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1		Chalcone	C15H12O	208.26		100%	0	0.105	0.504177470	1
2		Me3NO	C3H9NO	75.11		100%	0	0.0014	0.018639328	0.03696977
3		Fe	C41H35N2O3P	690.5608		100%	0	0.0057	0.008254160	0.01637153
4		Toluene	C7H8	92.1410	0.867	100%	1000.12931	867.112112	9410.708718	18665.4685
5		H2	H2	2.0156		100%	0	0.0232	11.510220281	22.8296997

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	1,3-diphenylpropan-1-one	C15H14O	210.2760	0.1	0.47556544	0.106016	94.3254

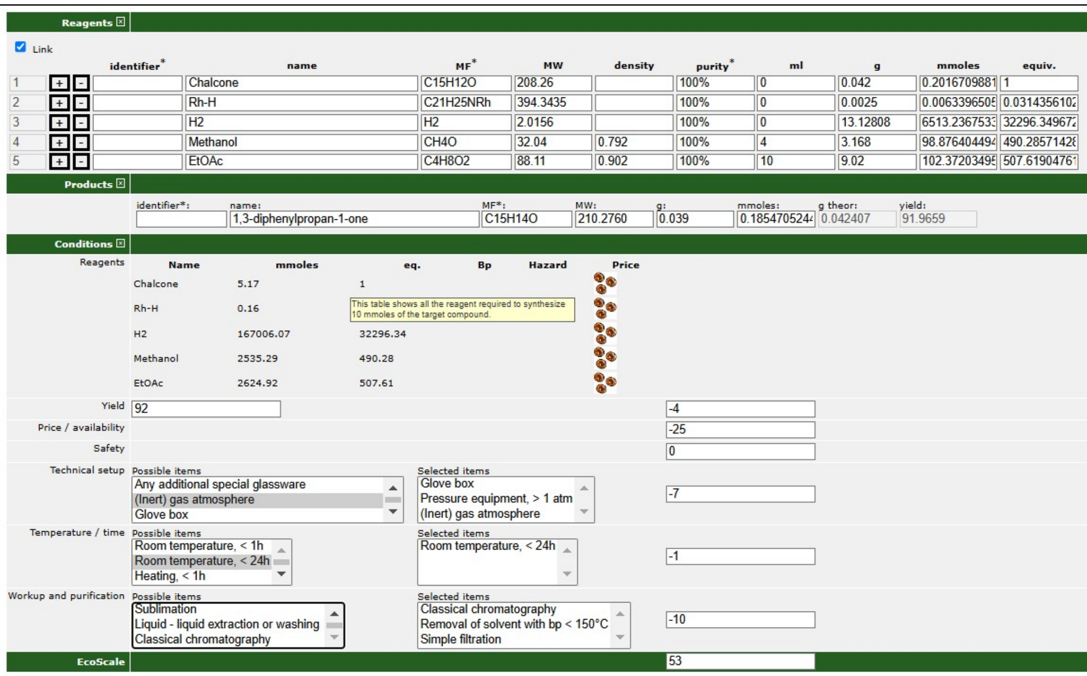
Conditions

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
Chalcone	5.04	1			
Me3NO	0.18	0.03			
Fe	0.08	0.01			
Toluene	94107.08	18665.46			
H2	115.1	22.82			

	Possible items	Selected items	Penalty
Yield	94		-3
Price / availability			-25
Safety			0
Technical setup	Any additional special glassware; (Inert) gas atmosphere; Glove box	Pressure equipment, > 1 atm; (Inert) gas atmosphere	-4
Temperature / time	Heating, > 1h; Cooling to 0°C; Cooling, < 0°C	Heating, > 1h	-3
Workup and purification	Sublimation; Liquid - liquid extraction or washing; Classical chromatography	Classical chromatography; Removal of solvent with bp < 150°C	-10
EcoScale			55

Fig. S14 EcoScale analysis for *Chem. Eur. J.,* **2018**, 24, 5770-5774 (reference 19).



Reagents

Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1		Chalcone	C15H12O	208.26		100%	0	0.042	0.2016709881	1
2		Rh-H	C21H25NRh	394.3435		100%	0	0.0025	0.006339650	0.03143561
3		H2	H2	2.0156		100%	0	13.12808	6513.236753	32296.3496
4		Methanol	CH4O	32.04	0.792	100%	4	3.168	98.87640449	490.285714
5		EtOAc	C4H8O2	88.11	0.902	100%	10	9.02	102.3720349	507.619047

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	1,3-diphenylpropan-1-one	C15H14O	210.2760	0.039	0.18547052	0.042407	91.9659

Conditions

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
Chalcone	5.17	1			
Rh-H	0.16				
H2	167006.07	32296.34			
Methanol	2535.29	490.28			
EtOAc	2624.92	507.61			

This table shows all the reagent required to synthesize 10 mmoles of the target compound.

	Possible items	Selected items	Penalty
Yield	92		-4
Price / availability			-25
Safety			0
Technical setup	Any additional special glassware; (Inert) gas atmosphere; Glove box	Glove box; Pressure equipment, > 1 atm; (Inert) gas atmosphere	-7
Temperature / time	Room temperature, < 1h; Room temperature, < 24h; Heating, < 1h	Room temperature, < 24h	-1
Workup and purification	Sublimation; Liquid - liquid extraction or washing; Classical chromatography	Classical chromatography; Removal of solvent with bp < 150°C; Simple filtration	-10
EcoScale			53

Fig. S15 EcoScale analysis for *J. Am. Chem. Soc.,* **2021**, 143, 9657-9663 (reference 24).

Reagents

Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1		(E)-1,3-diphenylbut-2-en-1-one	C16H14O	222.2870		100%	0	0.02223	0.1000058482	0.991772284(
2		Ir	C34H37NPSArE	783.9018		100%	0	0.0004	0.000510267(	0.005060400(
3		DCM	CH2Cl2	84.93	1.33	100%	1	1.33	15.659955257	155.30201342
4		H2	H2	2.0156		100%	0	0.0476	23.61579678	234.2012304(

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	1,3-diphenylbutan-1-one	C16H16O	224.3030	0.0205	0.091394230	0.022618	90.6358

Conditions

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
(E)-1,3-diphenylbut-2-en-1-one	4.87	0.99			
Ir	0.02	0			
DCM	763.9	155.3			
H2	1151.99	234.2			

	Possible items	Selected items	
Yield	91		-5
Price / availability			-20
Safety			0
Technical setup	Any additional special glassware; (Inert) gas atmosphere; Glove box	Pressure equipment, > 1 atm; (Inert) gas atmosphere	-4
Temperature / time	Room temperature, < 1h; Room temperature, < 24h; Heating, < 1h	Room temperature, < 24h	-1
Workup and purification	Sublimation; Liquid - liquid extraction or washing; Classical chromatography	Classical chromatography; Removal of solvent with bp < 150°C	-10
EcoScale			60

Fig. S16 EcoScale analysis for *Org. Lett.*, **2021**, 23, 242-246 (reference 23).

Reagents

Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1		Chalcone	C15H12O	208.26		100%	0	0.042	0.2016709881	1
2		K3PO4	K3PO4	212.27		100%	0	0.004245	0.0199981156	0.099162084(
3		Mn-PNN	C19H25O3N4PI	443.3458		100%	0	0.002217	0.005	0.0247928571
4		H2	H2	2.0156		100%	0	0.0119	5.9039491962	29.27515380(
5		MeOH	CH4O	32.04	0.792	100%	1	0.792	24.719101123	122.57142857

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	1,3-diphenylpropan-1-one	C15H14O	210.2760	0.04	0.190226178(	0.042407	94.3241

Conditions

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
Chalcone	5.04	1			
K3PO4	0.49	0.09			
Mn-PNN	0.12	0.02			
H2	147.59	29.27			
MeOH	617.97	122.57			

	Possible items	Selected items	
Yield	94		-3
Price / availability			-25
Safety			0
Technical setup	Any additional special glassware; (Inert) gas atmosphere; Glove box	Glove box; Pressure equipment, > 1 atm; (Inert) gas atmosphere	-7
Temperature / time	Room temperature, < 1h; Room temperature, < 24h; Heating, < 1h	Room temperature, < 24h	-1
Workup and purification	Adding solvent; Simple filtration; Removal of solvent with bp < 150°C	Classical chromatography; Removal of solvent with bp < 150°C	-10
EcoScale			54

Fig. S17 EcoScale analysis for *Chem. Sci.*, **2022**, 13, 13764-13773 (reference 25).

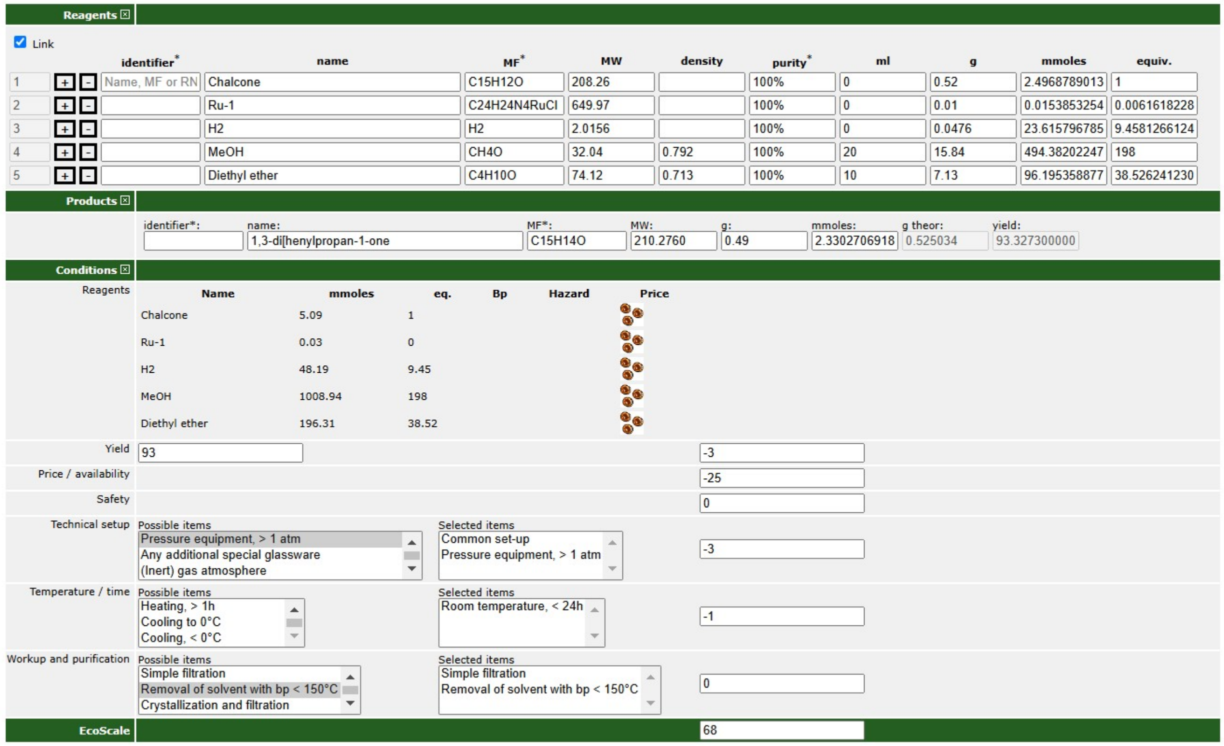


Fig. S18 EcoScale analysis for this work.

2.4 Calculation of catalyst price

Table S2. Price calculation of reported catalysts and our catalyst.

Chemicals	**Company**	**Price per gram or mL**	**Required amount (g or mL)**	**Price for the required amount in INR**
Mn(PCP) catalyst by Ruiter et. al (*Org. Lett.*, **2024**, 26, 4173-4177) (reference 17)				
Ligand	**2,10-di-tert-butyl-4,8-bis(isopropyl-l2-phosphaneyl)imidazo[1,5-a:3,4-a']dipyridin-5-ium-6-ide**			
Step 1	2,10-di-tert-butyl-6H-imidazo[1,5-a:3,4-a']dipyridine			
4,4'-di-tert-butyl-2,2'-bipyridine	Sigma-Aldrich	1387.6/-	0.134	185.94/-
$Ph_3As^+CH_2OTf$	SRL Chem.	138/-	0.237	32.7/-
			Price for (Yield = 0.295 g)	218.64/-
			Price per gram or mL	743.38/-
Step 2	2,10-di-tert-butyl-6H-imidazo[1,5-a:3,4-a']dipyridine-6-thione			
2,10-di-tert-butyl-6H-imidazo[1,5-a:3,4-a']dipyridine	From Step 1	743.38/-	0.14	108.82/-
K^tOBu	Sigma-Aldrich	2.4/-	0.056	0.134/-
S_8	Sigma-Aldrich	4.8/-	0.128	0.614/-

			Price for (Yield = 0.190 g)	109.57/-
			Price per gram or mL	580.71/-
Step 3	2,10-di-tert-butyl-4,8-bis(isopropyl-l2-phosphaneyl)-6-(methylthio)-6H-imidazo[1,5-a:3,4-a']dipyridine			
2,10-di-tert-butyl-6H-imidazo[1,5-a:3,4-a']dipyridine-6-thione	From Step 2	580.71/-	0.196	113.82/-
THF	SRL Chem.	1.32/-	30	39.6/-
^{t}BuLi	Sigma-Aldrich	46.36/-	0.85	39.41/-
$^{i}Pr_2PCl$	Sigma-Aldrich	1085.52/-	0.213	231.22/-
MeI	Sigma-Aldrich	59.96/-	0.13	7.79/-
			Price for (Yield = 0.465 g)	434.84/-
			Price per gram or mL	939.25/-
Step 4	2,10-di-tert-butyl-4,8-bis(isopropyl-l2-phosphaneyl)-5l4-imidazo[1,5-a:3,4-a']dipyridine			
2,10-di-tert-butyl-4,8-bis(isopropyl-l2-phosphaneyl)-6-(methylthio)-6H-imidazo[1,5-a:3,4-a']dipyridine	From step 3	939.25/-	0.412	386.97/-
MeOH	SRL Chem.	0.2/-	20	4/-
$NaBH_4$	Sigma-Aldrich	32.22/-	0.04	1.29/-
			Price for (Yield = 0.231 g)	392.26/-
			Price per gram or mL	1706.33/-
Step 5 (Final Ligand)	2,10-di-tert-butyl-4,8-bis(isopropyl-l2-phosphaneyl)imidazo[1,5-a:3,4-a']dipyridin-5-ium-6-ide			
2,10-di-tert-butyl-4,8-bis(isopropyl-l2-phosphaneyl)-5l4-imidazo[1,5-a:3,4-a']dipyridine	From step 4	1706.33/-	0.04	68.25/-
LiHMDS	Sigma-Aldrich	33.63/-	0.055	1.85/-
THF	SRL Chem.	1.32/-	5	6.6/-
			Price for (Yield = 0.031 g)	76.7/-
			Price per gram or mL in INR	2492.75/-
Mn-Precursor	$Mn(CO)_5Br$	Price per gram = 7738/-		
Mn-PCP Complex				
$Mn(CO)_5Br$	Sigma-Aldrich	7738/-	0.163	1261.29/-
Ligand	From step 5	1706.33/-	0.32	797.68/-
Toluene	SRL Chem.	0.8	30	24
			Price for (Yield = 0.338 g)	2082.97/-
			Price per gram of Mn-PCP complex in INR	6165.59/-
Fe catalyst Renaud et al. (*Chem. Eur. J.,* **2018**, 24, 5770-5774) (reference 13)				
Ligand	1,4-dimethyl-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one			
Step 1	4-hydroxy-2,5-diphenylcyclopent-4-ene-1,3-dione			
1,3- diphenyl-2-propanone	Sigma-Aldrich	96.34/-	5.6	539.504

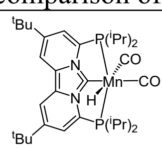
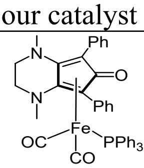
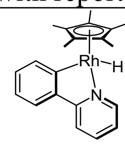
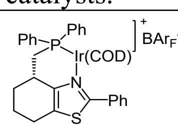
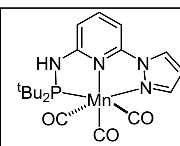
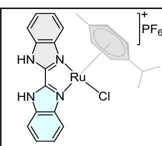
diethyl oxalate	Sigma-Aldrich	3.7/-	3.9	14.43/-
sodium	Sigma-Aldrich	10.98/-	1.31	14.39/-
ethanol	SRL Chem.	1.82/-	27	49.30/-
			Price for (Yield = 5.79 g)	617.63/-
			Price per gram in INR	106.67/-
Step 2	1,4-dimethyl-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one			
4-hydroxy-2,5-diphenylcyclopent-4-ene-1,3-dione	From step 1	106.67/-	5	533.35
N,N'-dimethylethylenediamine	Sigma-Aldrich	28.4/-	2.04	57.94
Methanol	SRL Chem.	0.2/-	30	5
			Price for (Yield = 5.96 g)	597.29/-
			Price per gram in INR	100.22/-
Metal Precursor	$Fe_2(CO)_9$	Price per gram in INR = 643.65/-		
Fe-Complex				
1,4-dimethyl-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one	From step 2	100.22/-	0.8	80.18/-
$Fe_2(CO)_9$	Sigma-Aldrich	643.65/-	1.84	1184.32/-
Toluene	SRL Chem.	0.8/-	10	8/-
			Price for (Yield = 0.560 g)	1272.5/-
			Price per gram of Fe-Complex in INR	2277.78/-
Rh-H catalyst Norton et al. (*J. Am. Chem. Soc.*, **2021**, 143, 9657-9663) (reference 15)				
Ligand	2-phenylpyridine	Price per mL in INR = 536/-		
Rh Precursor	$[Cp^*Rh(Cl)_2]_2$			
$RhCl_3.H_2O$	Sigma-Aldrich	57697.8/-	0.15	8654.67/-
Cp*	Sigma-Aldrich	3086/-	0.11	333.29/-
EtOH		1.83/-	3	5.48/-
			Price for (Yield = 0.180 g)	8993.44/-
			Price per gram in INR	50,004/-
Cp*Rh(2-phenylpyridine)Cl				
$[Cp^*Rh(Cl)_2]_2$	From above	50004/-	0.05	2500.2/-
2-phenylpyridine	Sigma-Aldrich	536/-	0.0282	15.12/-
NaOAc	Sigma-Aldrich	11094/-	0.04	443.76
DCM	SRL Chem.	0.54/-	20	10.8/-
			Price for (Yield = 0.0646g)	2969.88/-
			Price per gram in INR	46,003/-
Rh-H Complex	Cp*Rh(2-phenylpyridine)H			
Cp*Rh(2-phenylpyridine)Cl	From above	46003/-	0.4	18401.2/-
$NaBH_4$	Sigma-Aldrich	32.22/-	0.08	2.58/-
THF	SRL Chem.	1.32	80	105.6/-
			Price for (Yield = 0.1625 g)	18,509.38/-
			Price of Rh-H complex per gram in INR	1,14,758/-

Ir catalyst Anderson et al. (*Org. Lett.,* **2021**, 23, 242-246) (reference 14)				
Ligand	(S)-4-((diphenylphosphino)methyl)-2-phenyl-4,5,6,7tetrahydrobenzo[d]thiazole			
Step 1	Methyl 2-phenyl-5,6,7,8-tetrahydro-4H-cyclohexa[d]thiazole-4-carboxylate			
Ethyl 3-bromo-2-oxocyclohexanecarboxylate	Sigma-Aldrich	275.52/-	3	826.56/-
EtOH	SRL Chem.	1.826/-	15	27.39/-
$PhC(S)NH_2$	Sigma-Aldrich	68/-	2.45	166.6/-
			Price for (Yield = 4.75g)	1020.55/-
			Price per gram in INR	214.85/-
Step 2	(S)-(2-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazol-4-yl)methanol			
Methyl 2-phenyl-5,6,7,8-tetrahydro-4H-cyclohexa[d]thiazole-4-carboxylate	From step 1	214.85/-	1	214.85/-
THF	SRL Chem.	1.32/-	10	13.2/-
$LiAlH_4$	Sigma-Aldrich	127.69/-	0.14	17.88/-
			Price for (Yield = 0.85 g)	245.93/-
			Price per gram in INR	290.19/-
Step 3	(S)-(2-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazol-4-yl)methyl 4-methylbenzenesulfonate			
(S)-(2-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazol-4-yl)methanol	From step 2	290.19/-	1.2	348.23/-
DCM	SRL Chem.	0.54/-	15	8.1/-
Pyridine	Sigma-Aldrich	6.52/-	10	65.2/-
Tosyl chloride	Sigma-Aldrich	2.7/-	1.39	3.75/-
			Price for (Yield = 2.046 g)	425.28/-
			Price per gram in INR	207.86/-
Step 4	(S)-4-((diphenylphosphino)methyl)-2-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazole Borane adduct			
(S)-(2-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazol-4-yl)methyl 4-methylbenzenesulfonate	From step 3	207.86/-	0.301	62.56/-
Diphenylphospine-borane adduct	Sigma-Aldrich	5304/-	0.23	1219.92/-
n-BuLi (1.6 M in hexane)	Sigma-Aldrich	46.36/-	0.71	32.92/-
THF	SRL Chem.	1.32/-	2	2.64/-
DMF	SRL Chem.	0.8/-	2	1.6/-
			Price for (Yield = 0.440 g)	1257.08/-
			Price per gram in INR	2866.14/-
Step 5	(S)-4-((diphenylphosphino)methyl)-2-phenyl-4,5,6,7tetrahydrobenzo[d]thiazole			
(S)-4-((diphenylphosphino)methyl)-2-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazo	From step 5	2866.14/-	0.25	716.54/-

le Borane adduct				
Et_2NH	Sigma-Aldrich	9.2/-	5	46/-
			Price for (Yield = 0.232 g)	762.54
			Price per gram in INR	3317.05/-
Metal Precursor	$[IrCl(COD)_2]_2$			
$IrCl_3$	Sigma-Aldrich	33161.25/-	0.02418	801.84/-
COD	Sigma-Aldrich	13.34/-	0.022	0.29/-
MeOH	SRL Chem.	0.2/-	20	4/-
			Price for (Yield = 0.018 g)	806.13/-
			Price per gram in INR	44,821/-
Complex				
$[IrCl(COD)_2]_2$	From above	44821/-	0.12	5378.52/-
Ligand	From step 5	3317.05/-	0.14	464.39/-
DCM	SRL Chem.	0.54/-	10	5.4/-
NaBArF	Sigma-Aldrich	33092/-	0.4	13236.8/-
			Price for (Yield = 0.203 g)	19,085.11/-
			Price of Ir-complex per gram in INR	94,090/-
Mn catalyst Punji et al. (*Chem. Sci.,* **2022**, 13, 13764-13773) (reference 16)				
Ligand	N-(di-tert-butylphosphaneyl)-6-(1H-pyrazol-1- yl)pyridin-2-amine			
Step 1	2-Bromo-6-(1H-pyrazol-1-yl)pyridine			
2,6-dibromopyridine	Sigma-Aldrich	209/-	2.37	495.33/-
1H-pyrazole	Sigma-Aldrich	101/-	0.68	68.68/-
Potassium ter-butoxide	Sigma-Aldrich	2.4/-	1.2	2.88/-
Dioxane	SRL Chem.	0.84/-	30	25.2
			Price for (Yield = 2.01 g)	592/-
			Price per gram in INR	296/-
Step 2	2-Amino-6-(1H-pyrazol-1-yl)pyridine			
N-(di-tert-butylphosphaneyl)-6-(1H-pyrazol-1-yl)pyridin-2-amine	From step 1	296/-	0.669	198/-
Cu_2O	Sigma-Aldrich	17.02/-	0.016	0.27/-
			Price for (Yield = 0.388 g)	198.27/-
			Price per gram in INR	515.5/-
Step 3	N-(di-tert-butylphosphino)-6-(1H-pyrazol-1-yl)-2- aminopyridine			
2-Amino-6-(1H-pyrazol-1-yl)pyridine	From step 2	515.5/-	0.32	164.96/-
NEt_3	Sigma-Aldrich	15.32/-	0.27	4.14/-
$^tBu_2PCl$	Sigma-Aldrich	635.75/-	0.39	247.94/-
^nBuLi	Sigma-Aldrich	46.36/-	1.28	59.34/-
			Price for (Yield = 0.550 g)	476.38/-
			Price per gram in INR	905.12/-
Metal Precursor	$Mn(CO)_5Br$	7738/- per gram		
Mn Complex				
$Mn(CO)_5Br$	Sigma-Aldrich	7738/-	0.045	348.21/-
Ligand	From step 3	905.12/-	0.05	45.26/-
THF		1.32/-	10	13.2/-
			Price for (Yield = 0.064 g)	406.67/-
			Price of Mn-complex per gram in INR	6506.72/-

Ru(II)-paracymene catalysts (This Work)				
Ligand	Bis-benzimidazole			
O-phenylenediamine	Sigma-Aldrich	14/-	13.6	190/-
Orthoposphoric acid	Sigma-Aldrich	4.5/-	50	225/-
Trichloroacetic acid	Sigma-Aldrich	26/-	16.3	424/-
			Price for (Yield = 11.8 g)	839/-
			Price per gram in INR	70/-
Metal Precursor	$[Ru(p\text{-}cym)Cl_2]_2$			
RuCl3	Sigma-Aldrich	1944/-	2	3888/-
α-phelandrene	Sigma-Aldrich	14/-	5	70/-
MeOH	SRL Chem.	0.2/-	20	4/-
			Price for (Yield = 2 g)	3962/-
			Price per gram in INR	1981/-
Ru(II)P-cym complex				
$[Ru(p\text{-}cym)Cl_2]_2$	From above	1981/-	0.153	303/-
Bis-benzimidazole	From above	70/-	0.117	8.19/-
KPF_6	Sigma-Aldrich	5/-	0.184	0.92/-
MeOH		0.2/-	20	4/-
			Price for (Yield = 0.230 g)	316.11/-
			Price of Ru(II)P-cym complex per gram in INR	1374.38/-

Table S3. Price comparison of our catalyst with reported catalysts.

Complex						
Reference No.	17	13	15	14	16	This work
Catalyst Price per gram in INR (₹)	6,166/-	2,278/-	1,14,758/-	94,090/-	6,507/-	1,375/-
Catalyst Price per gram in US-dollar ($)	70.87	26.18	1319.06	1081.49	74.79	15.80
Reported catalysts cost comparison with our catalysts per times	4.48	1.66	83.48	68.45	4.73	1

3. *Substrate Scope for catalytic hydrogenation of α,β*-**unsaturated ketones/nitro.**

3.1 ^{1}H, and $^{13}C\{^{1}H\}$ NMR for catalytic hydrogenation of α,β-unsaturated ketone/nitro to saturated ketone/nitro.

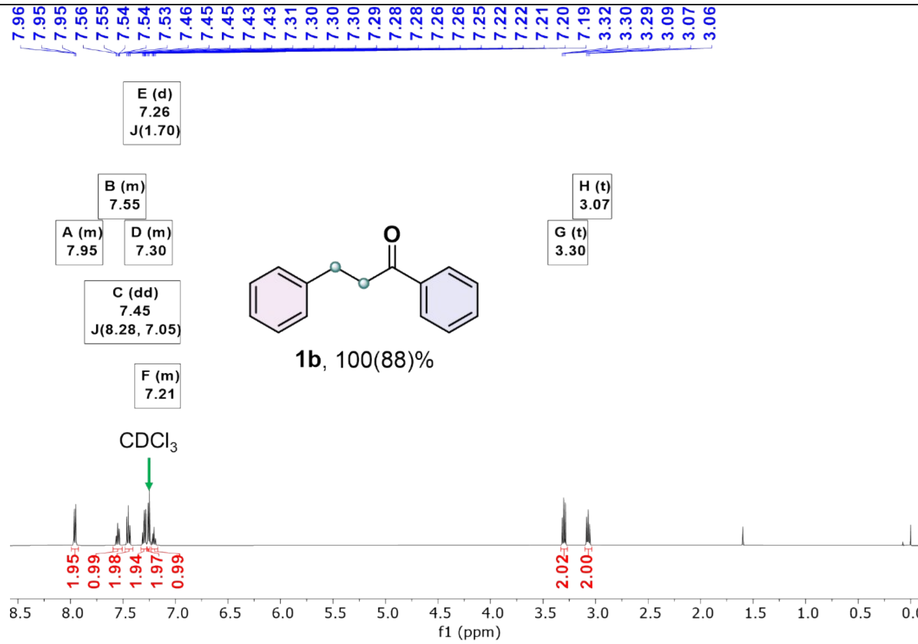


Fig. S19 ^{1}H–NMR of **1b** in $CDCl_3$ at 298K.

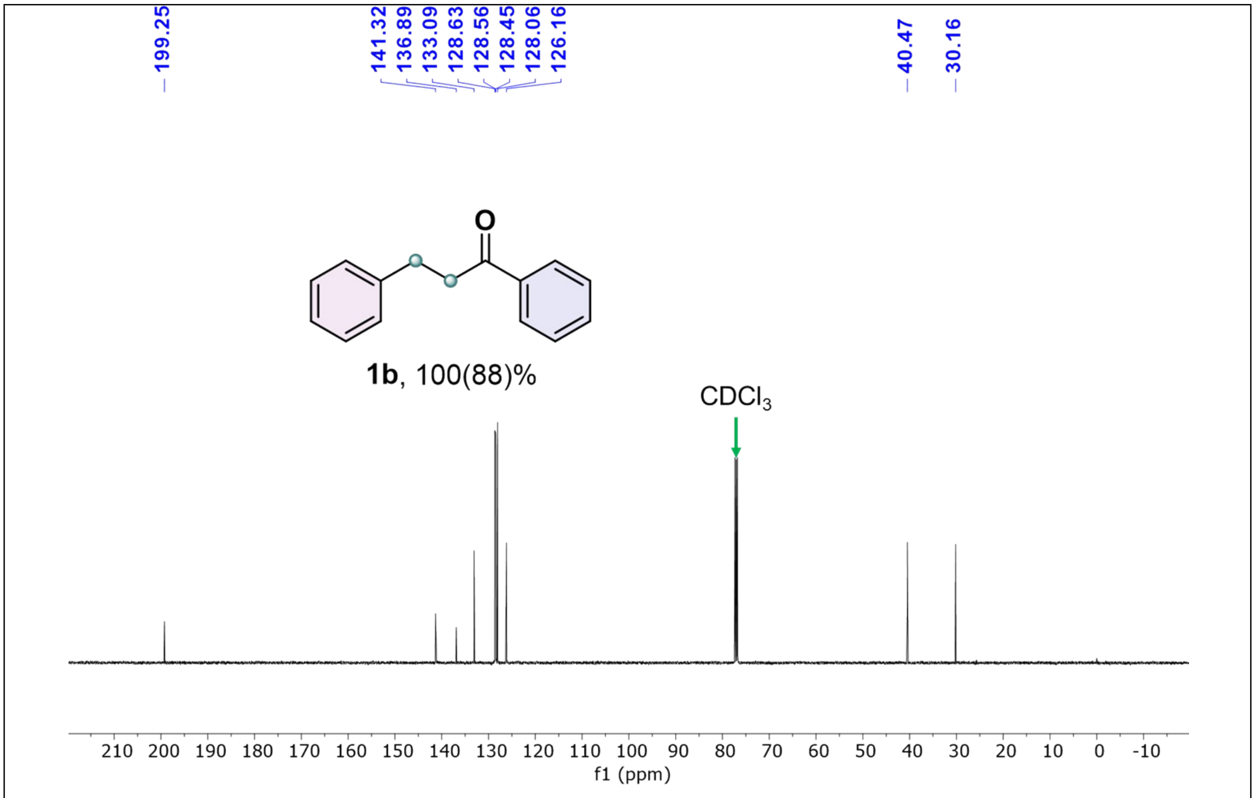


Fig. S20 $^{13}C\{^{1}H\}$ –NMR of **1b** in $CDCl_3$ at 298K.

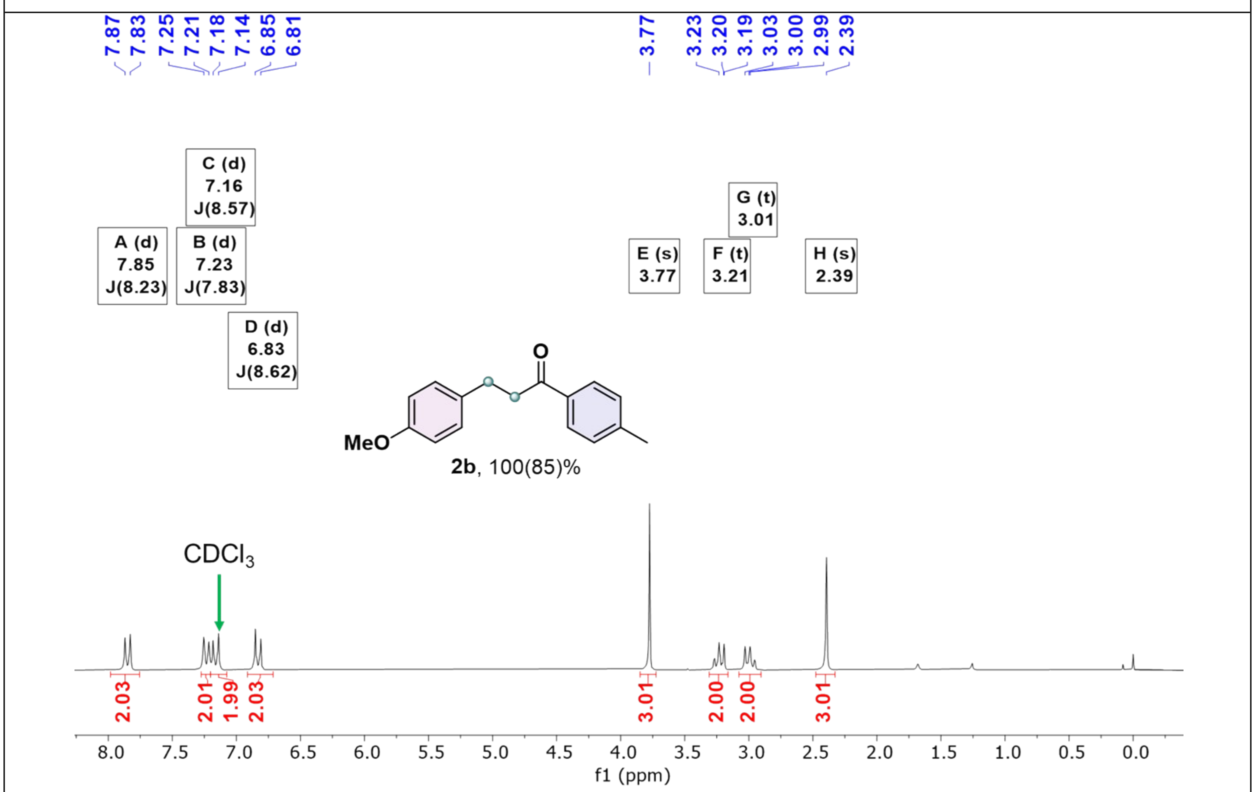


Fig. S21 ^{1}H–NMR of **2b** in $CDCl_3$ at 298K.

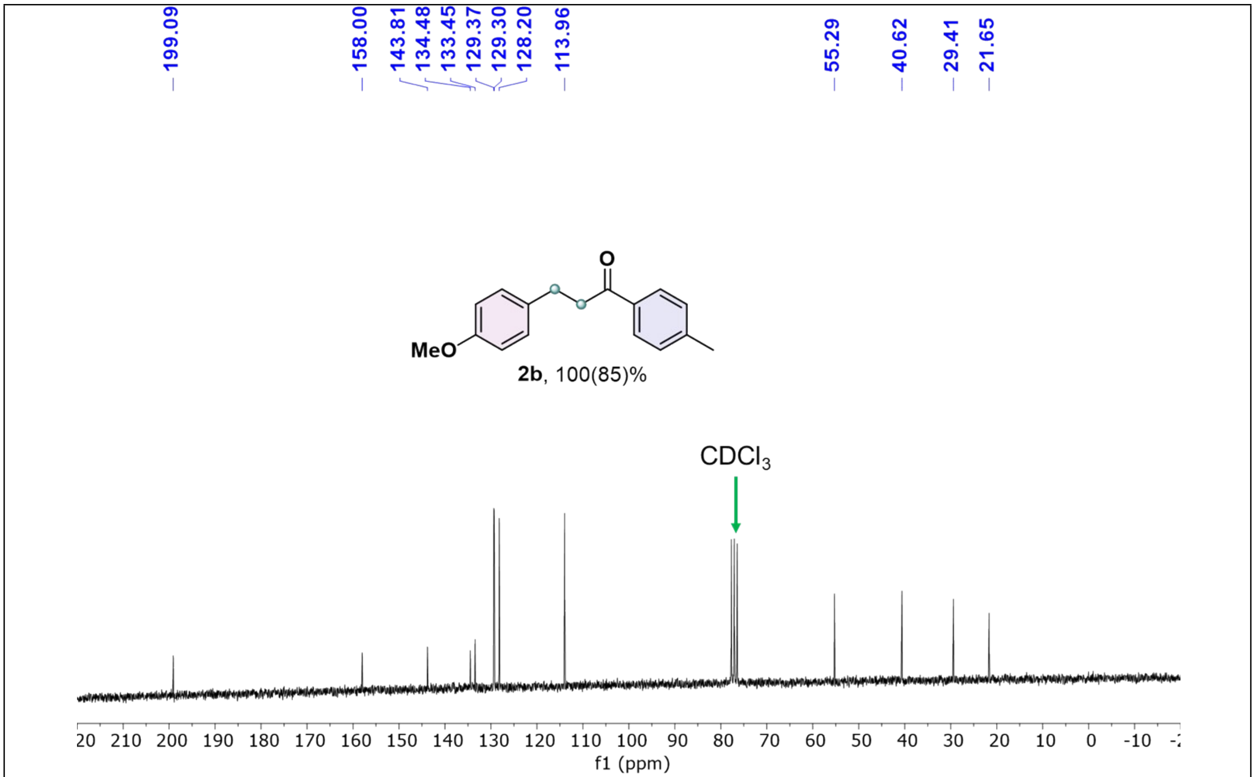


Fig. S22 $^{13}C\{^{1}H\}$ –NMR of **2b** in $CDCl_3$ at 298K.

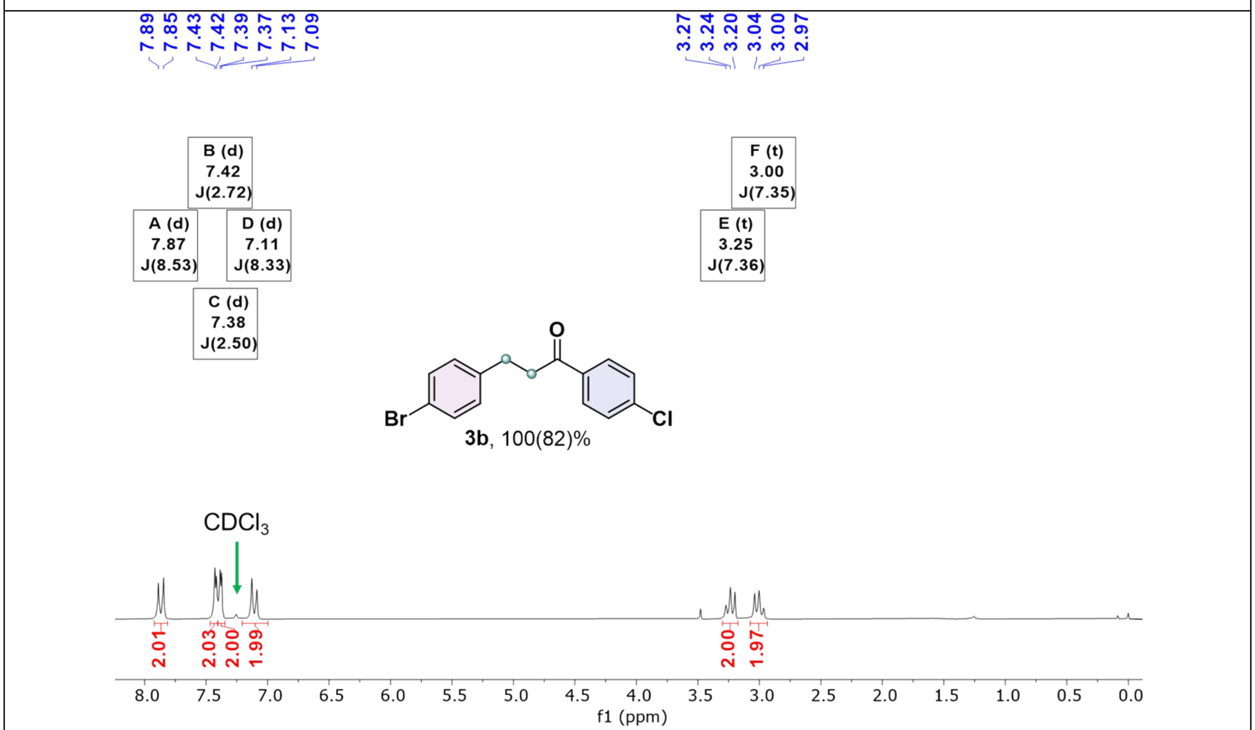


Fig. S23 ^{1}H–NMR of **3b** in $CDCl_3$ at 298K.

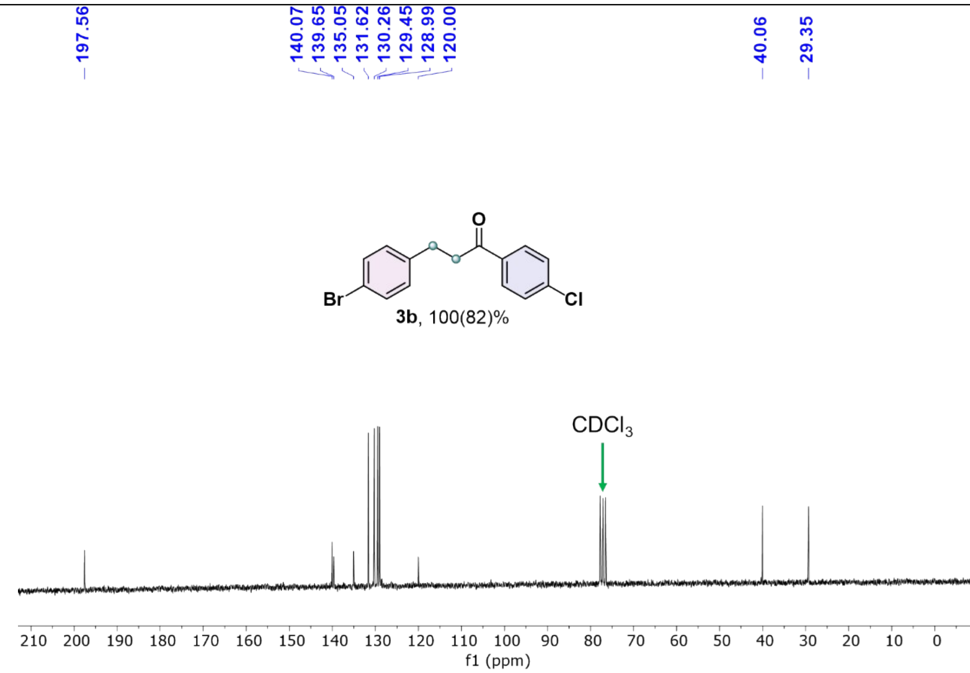


Fig. S24 $^{13}C\{^1H\}$ –NMR of **3b** in $CDCl_3$ at 298K.

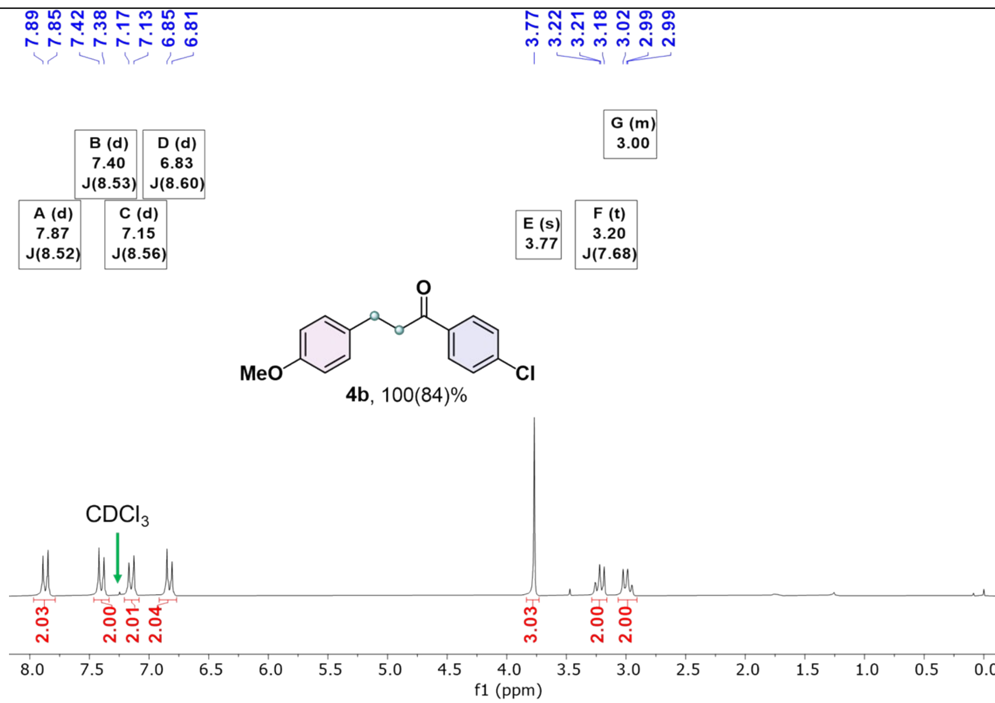


Fig. S25 ^1H–NMR of **4b** in $CDCl_3$ at 298K.

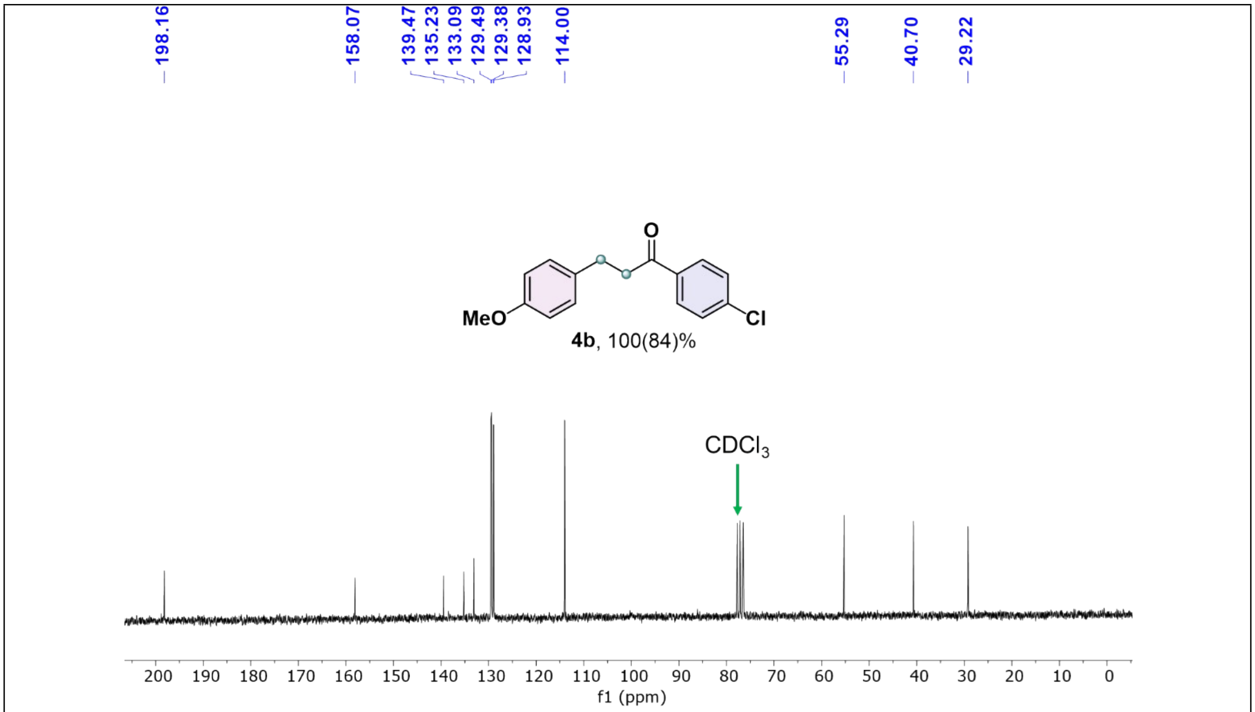


Fig. S26 $^{13}C\{^{1}H\}$ –NMR of **4b** in $CDCl_3$ at 298K.

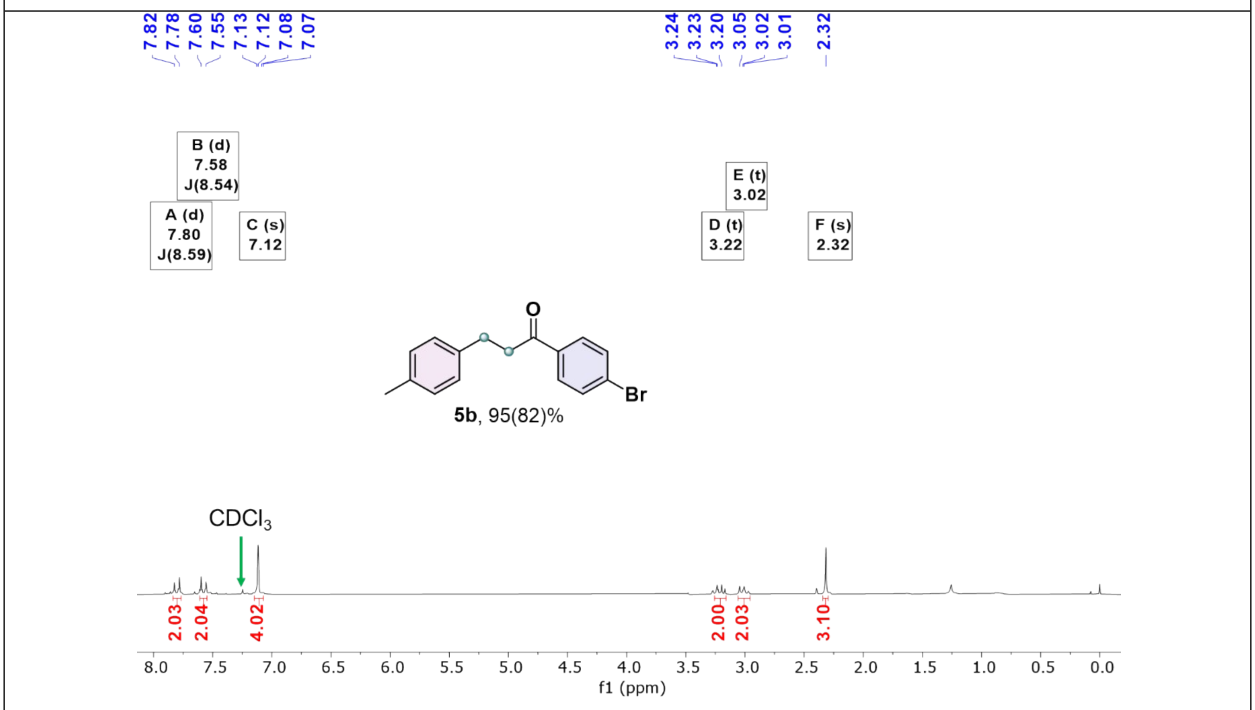


Fig. S27 ^{1}H–NMR of **5b** in $CDCl_3$ at 298K.

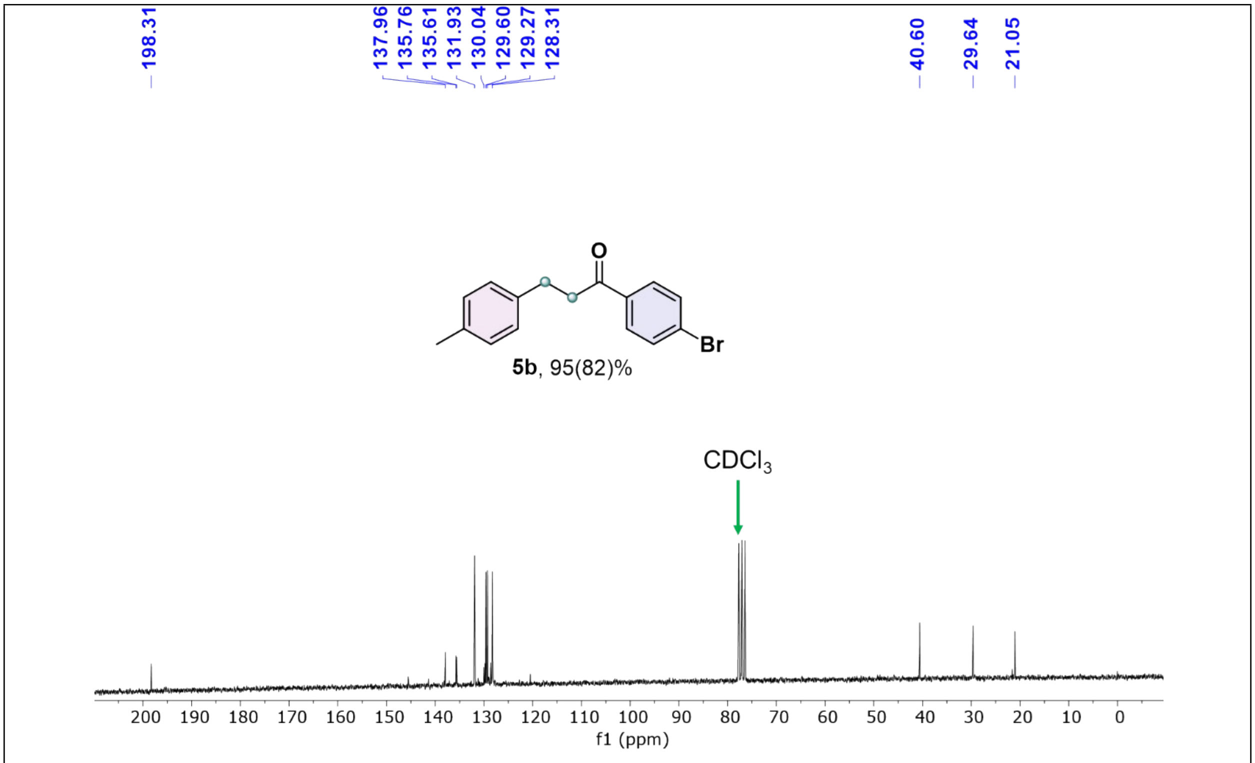


Fig. S28 $^{13}C\{^{1}H\}$ –NMR of **5b** in $CDCl_3$ at 298K.

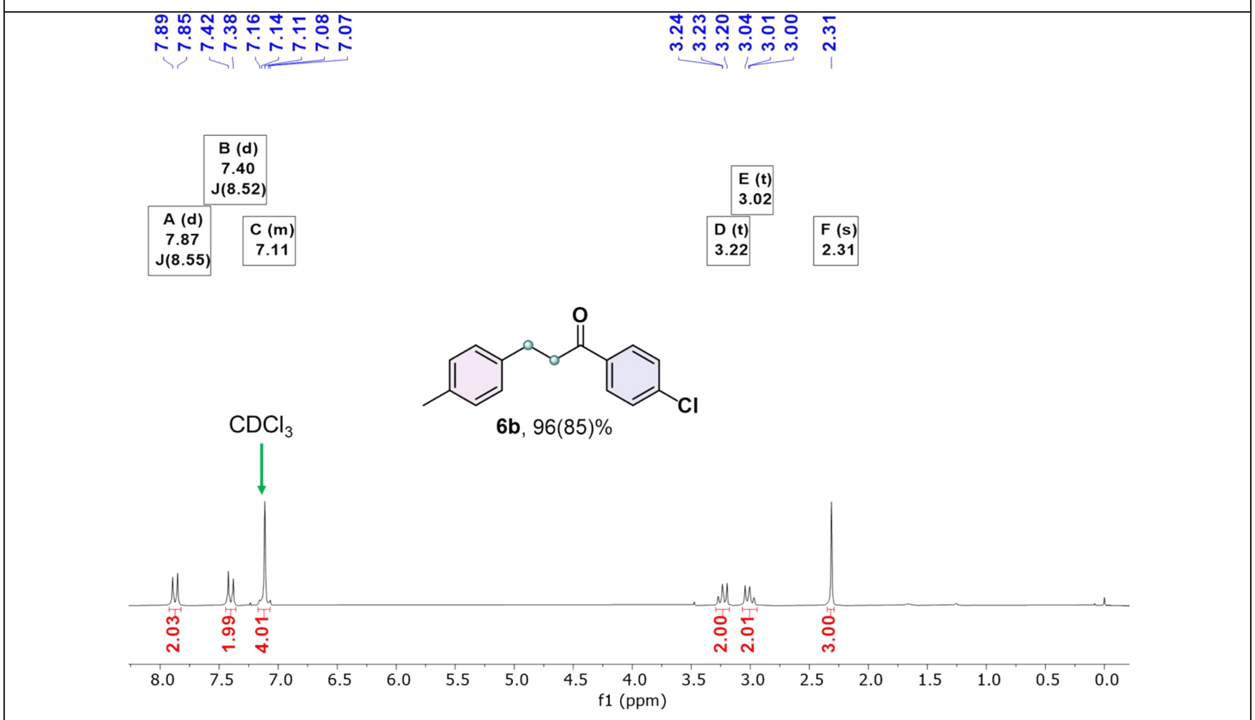


Fig. S29 ^{1}H–NMR of **6b** in $CDCl_3$ at 298K.

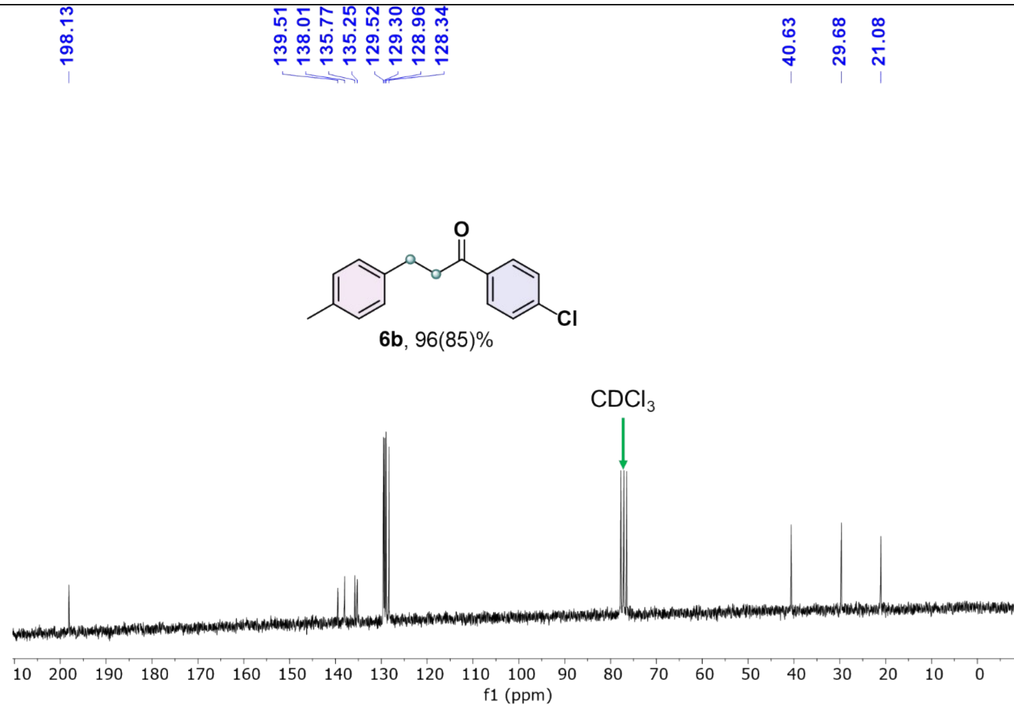


Fig. S30 $^{13}C\{^{1}H\}$ –NMR of **6b** in $CDCl_3$ at 298K.

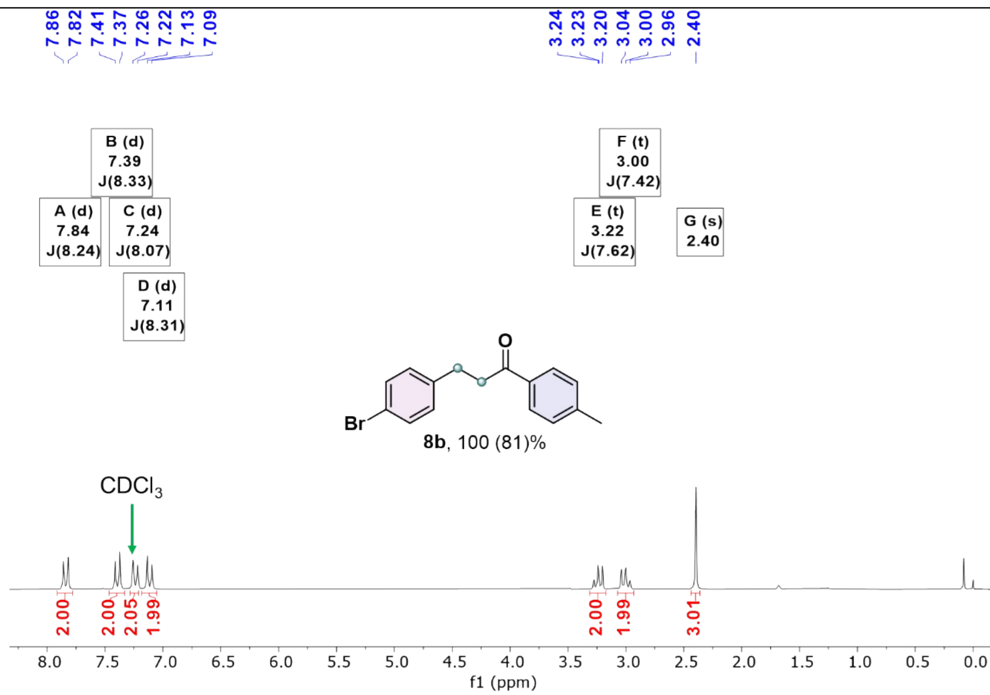


Fig. S31 ^{1}H–NMR of **8b** in $CDCl_3$ at 298K.

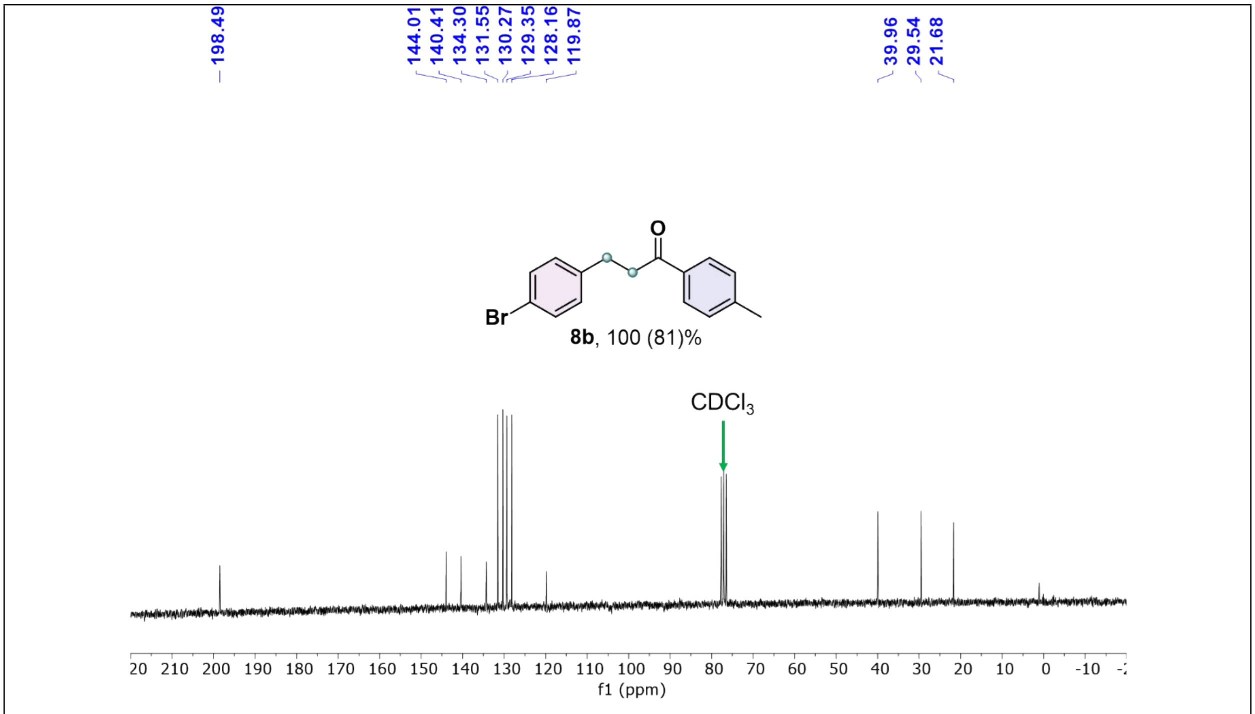


Fig. S32 $^{13}C\{^{1}H\}$ –NMR of **8b** in $CDCl_3$ at 298K.

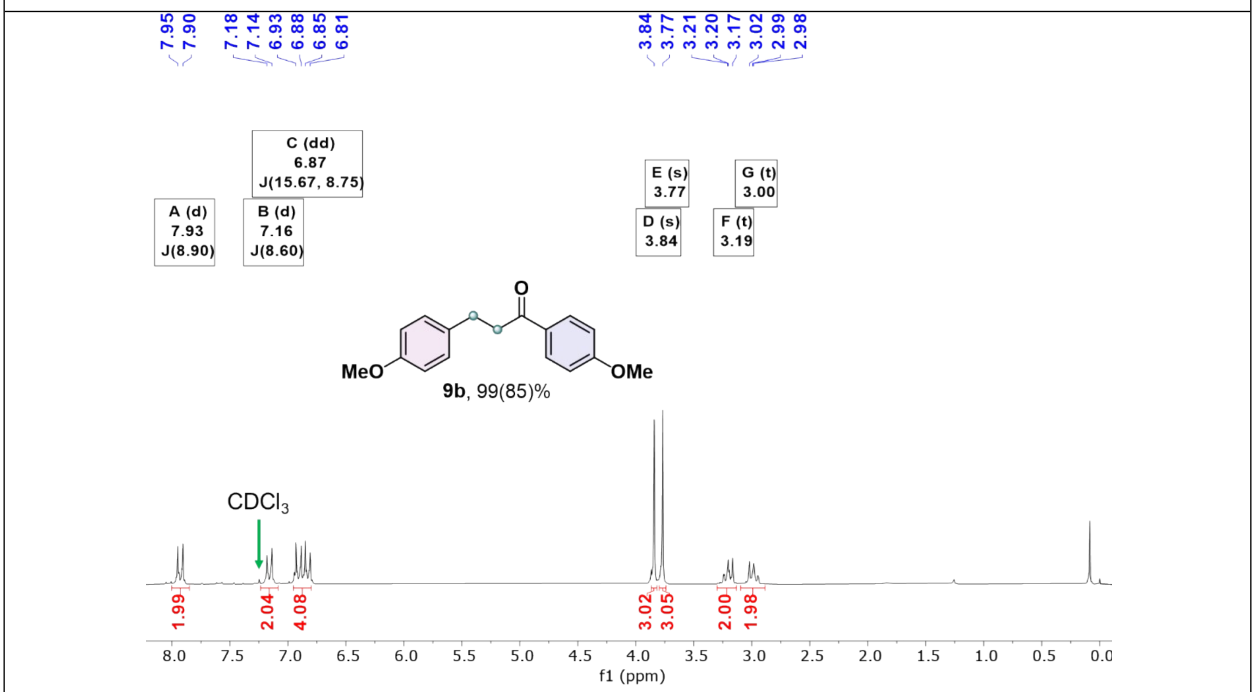


Fig. S33 ^{1}H–NMR of **9b** in $CDCl_3$ at 298K.

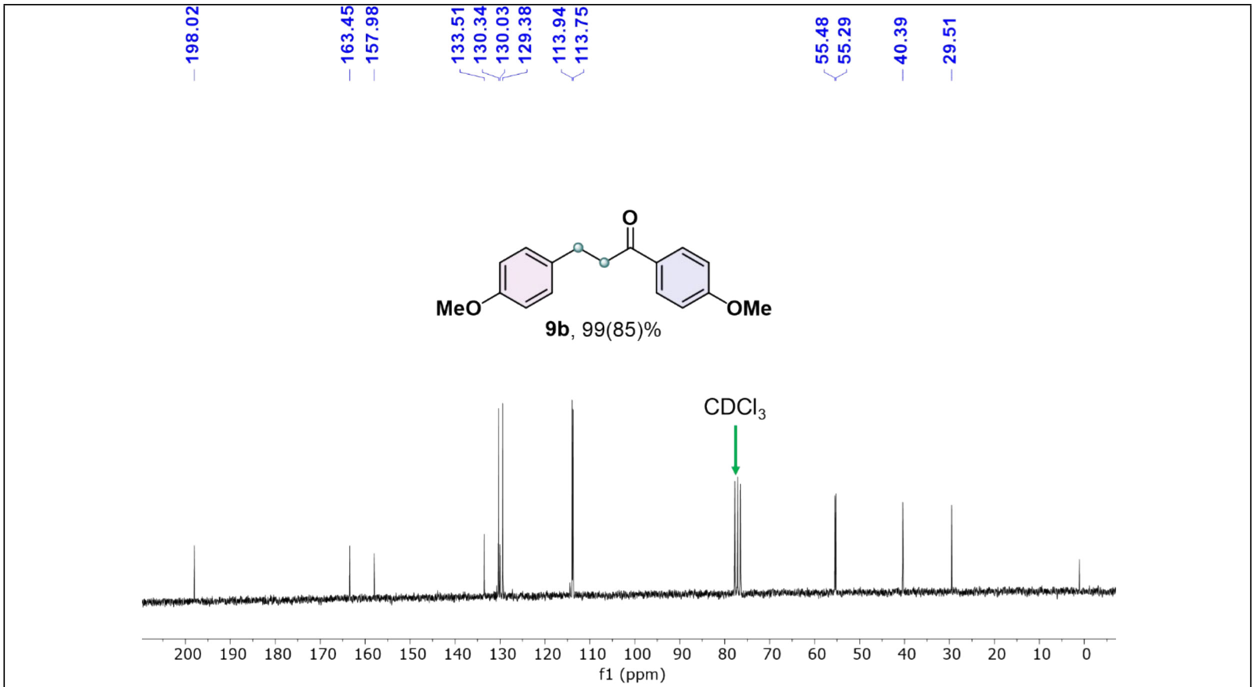


Fig. S34 $^{13}C\{^{1}H\}$ –NMR of **9b** in $CDCl_3$ at 298K.

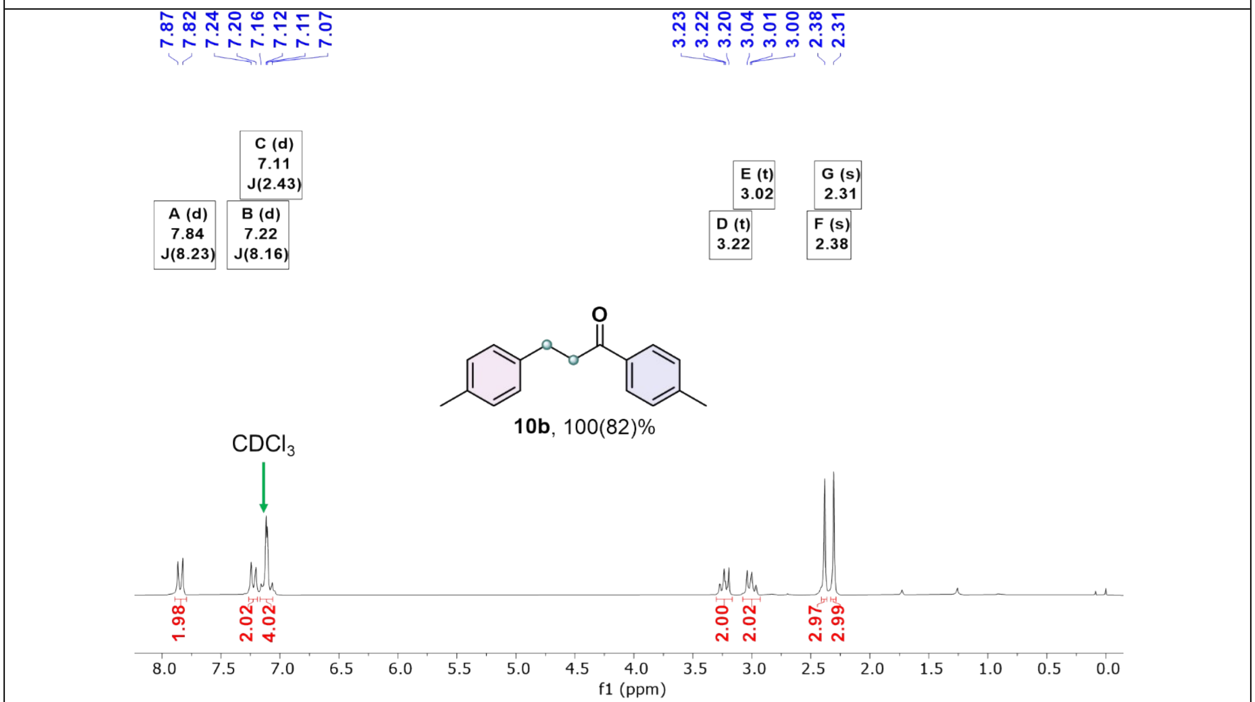


Fig. S35 ^{1}H–NMR of **10b** in $CDCl_3$ at 298K.

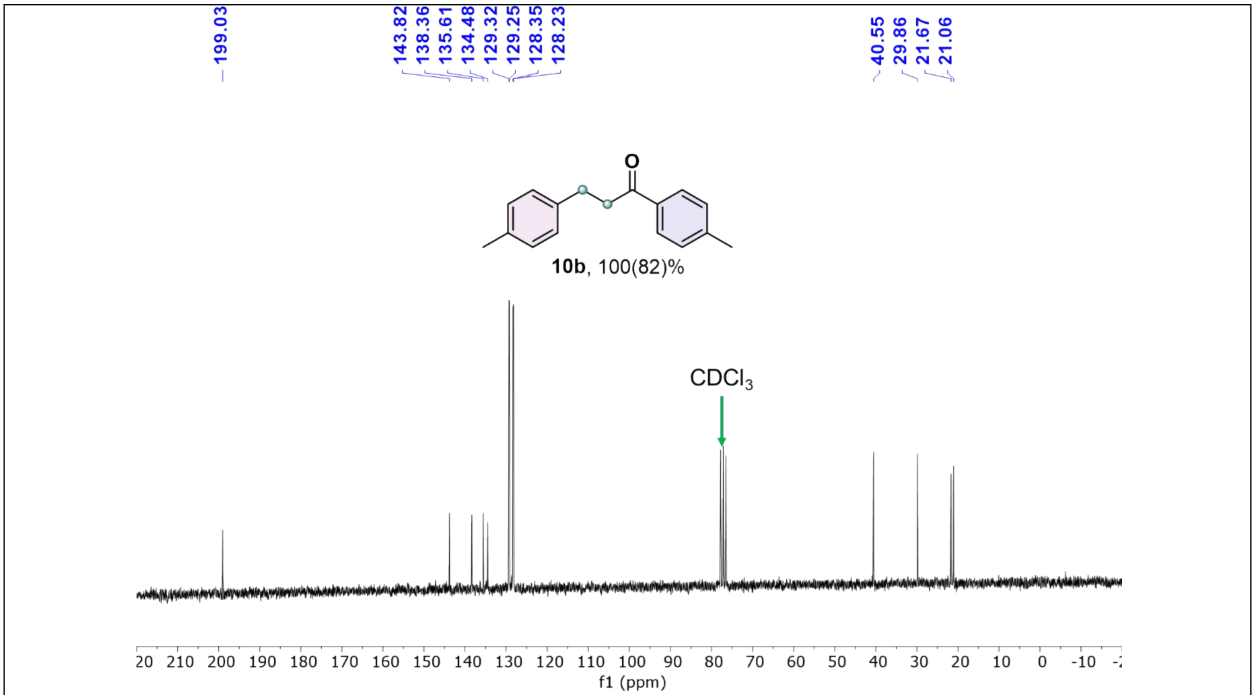


Fig. S36 $^{13}C\{^{1}H\}$ –NMR of **10b** in $CDCl_3$ at 298K.

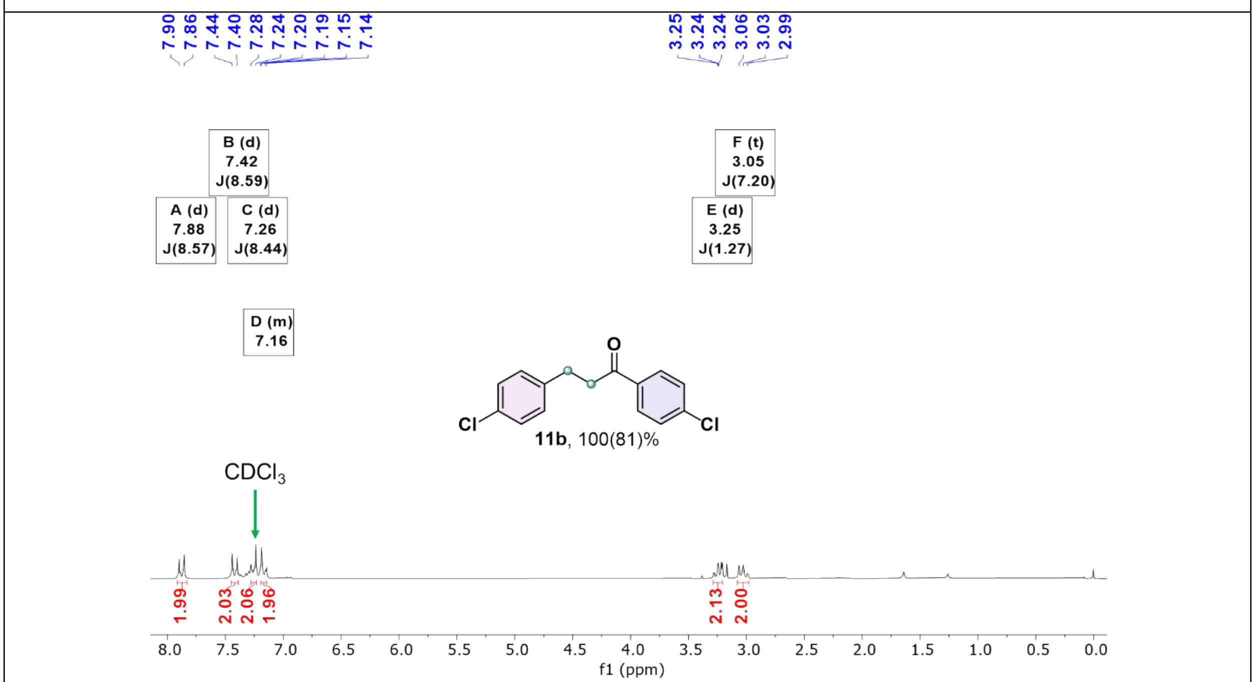


Fig. S37 ^{1}H–NMR of **11b** in $CDCl_3$ at 298K.

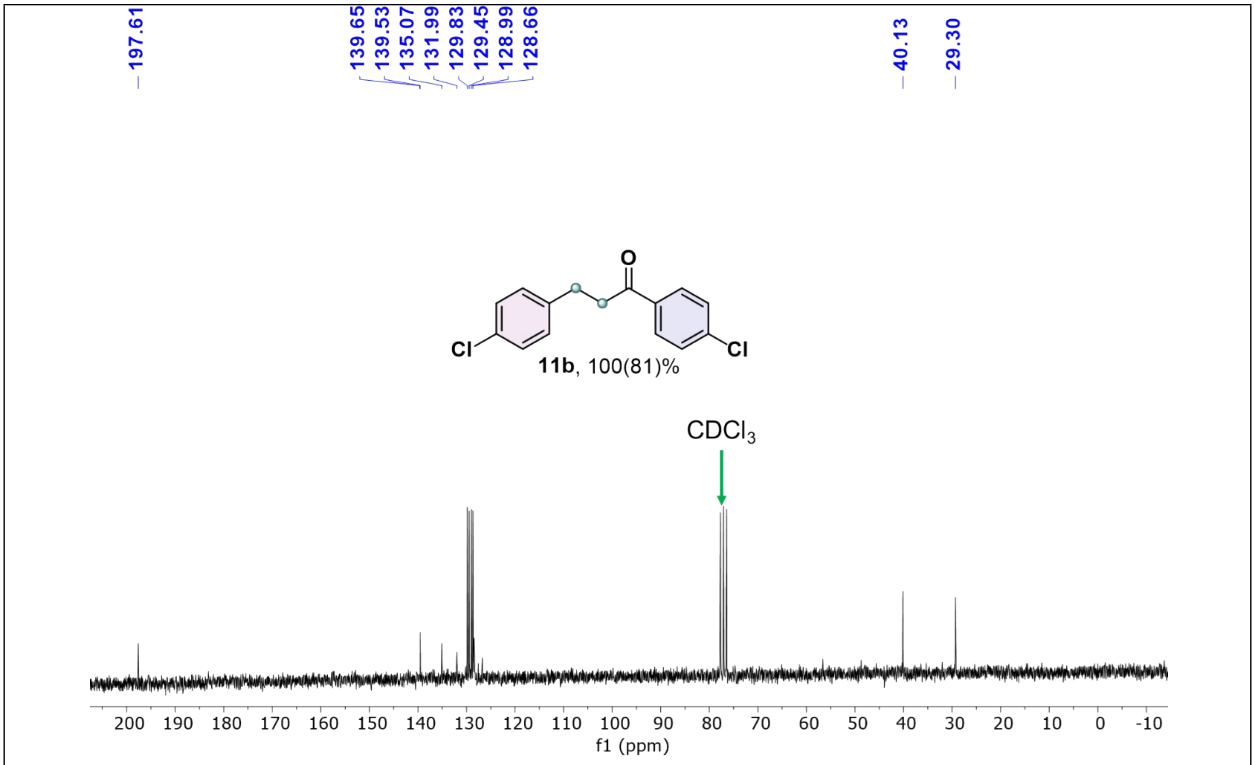


Fig. S38 $^{13}C\{^{1}H\}$ –NMR of **11b** in $CDCl_3$ at 298K.

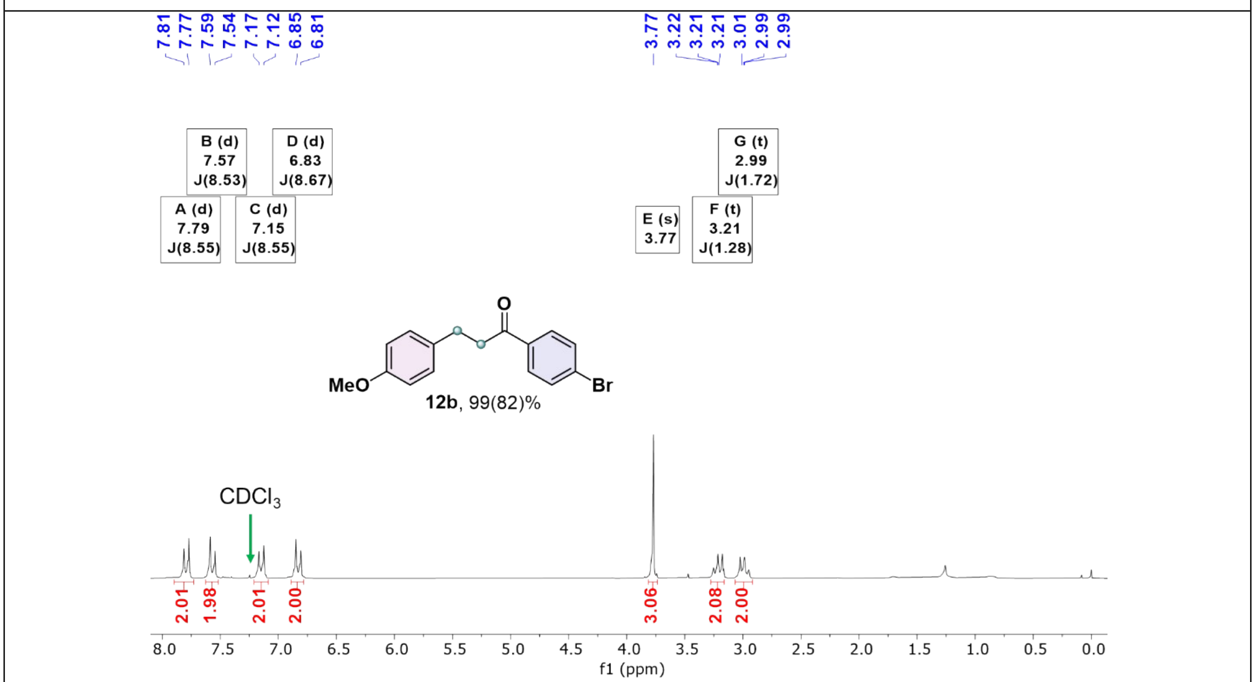


Fig. S39 ^{1}H–NMR of **12b** in $CDCl_3$ at 298K.

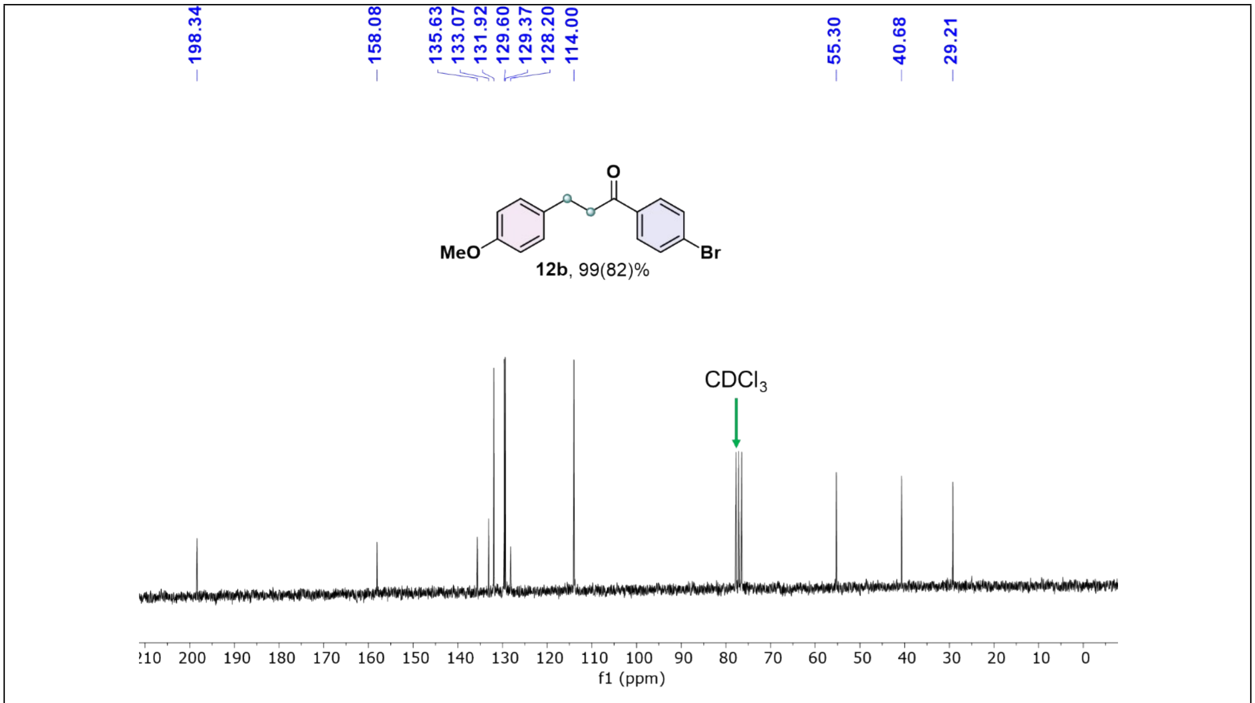


Fig. S40 $^{13}C\{^{1}H\}$ –NMR of **12b** in $CDCl_3$ at 298K.

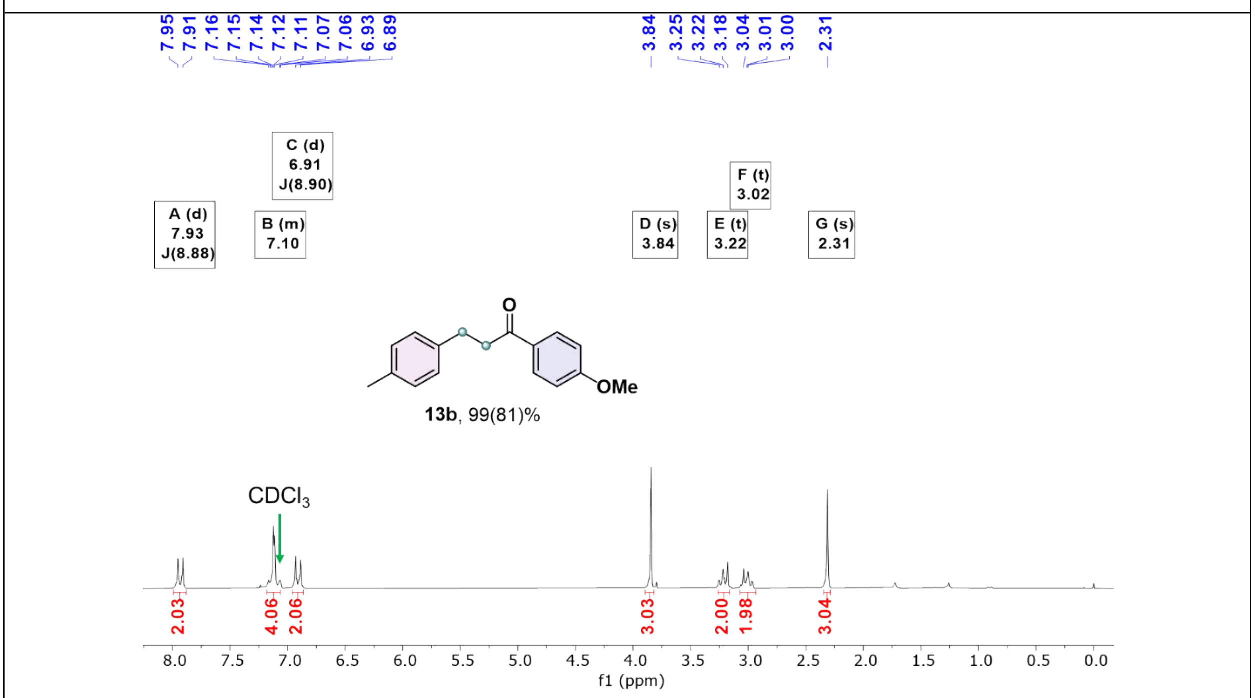


Fig. S41 ^{1}H–NMR of **13b** in $CDCl_3$ at 298K.

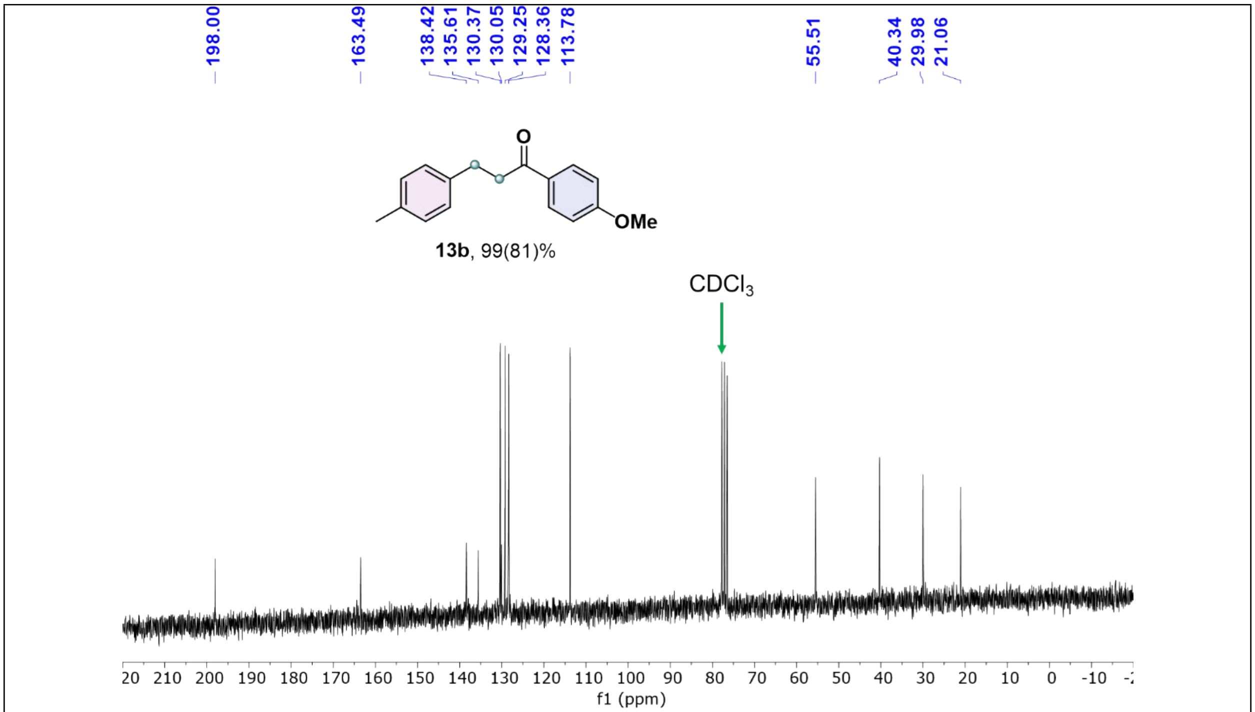


Fig. S42 $^{13}C\{^{1}H\}$ –NMR of **13b** in $CDCl_3$ at 298K.

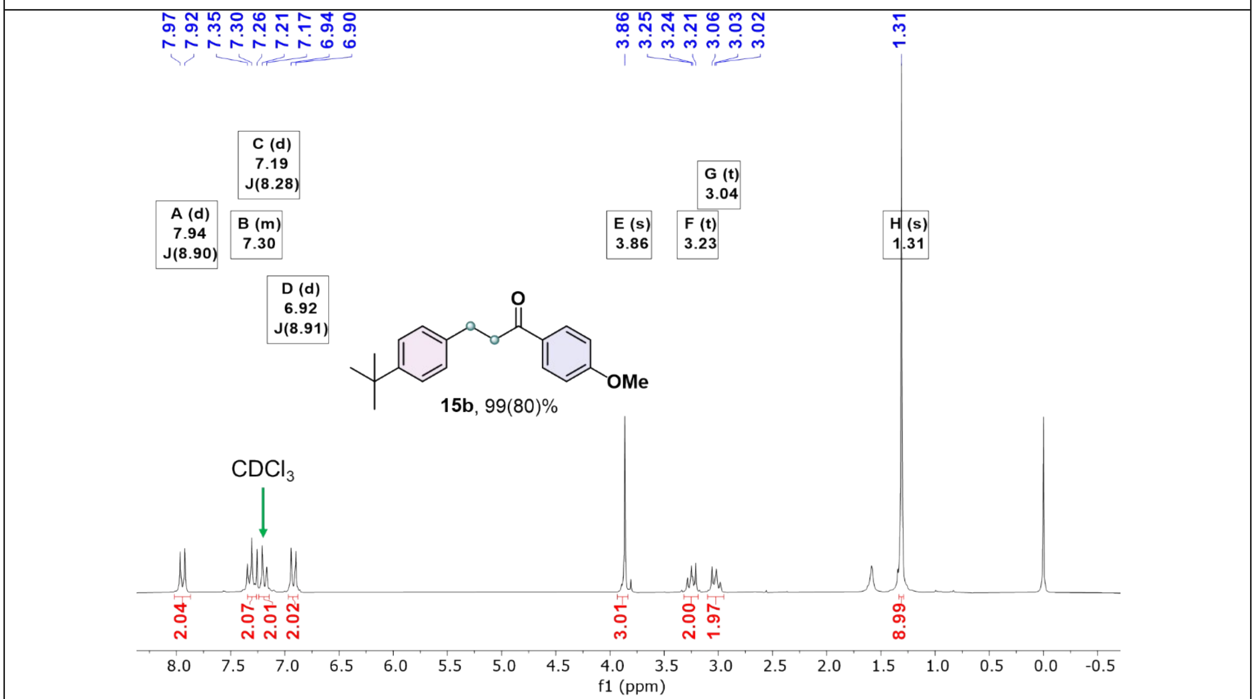


Fig. S43 ^{1}H–NMR of **15b** in $CDCl_3$ at 298K.

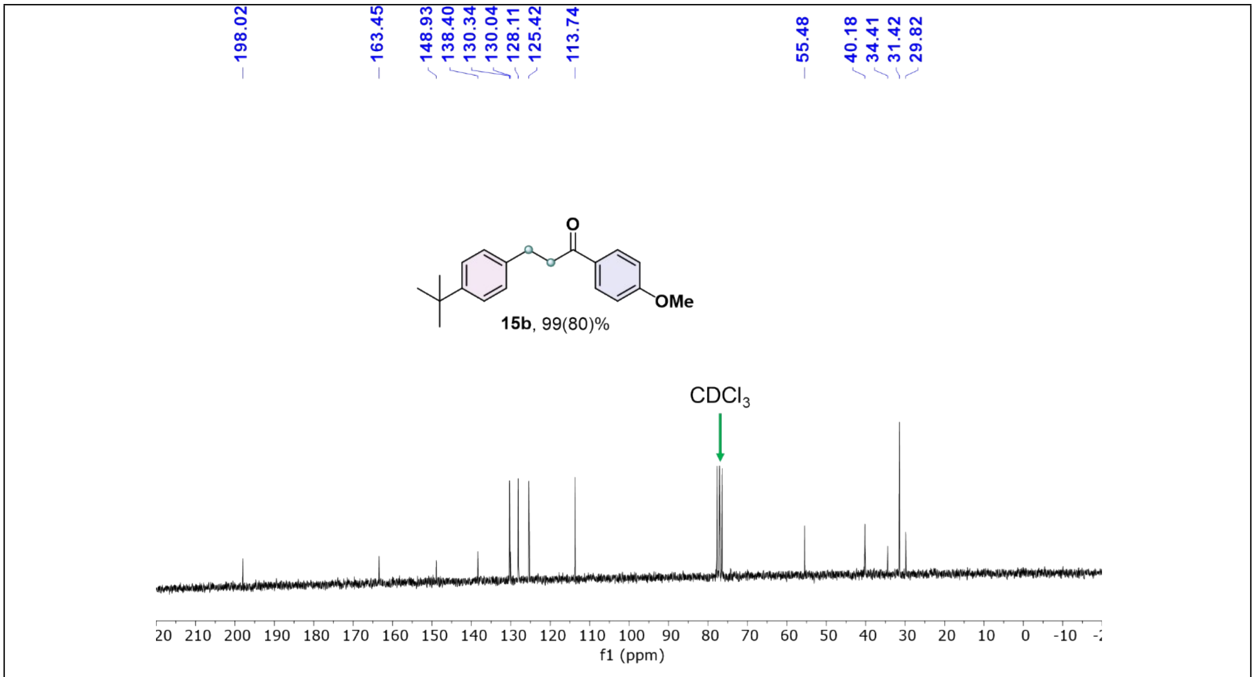


Fig. S44 $^{13}C\{^{1}H\}$ –NMR of **15b** in $CDCl_3$ at 298K.

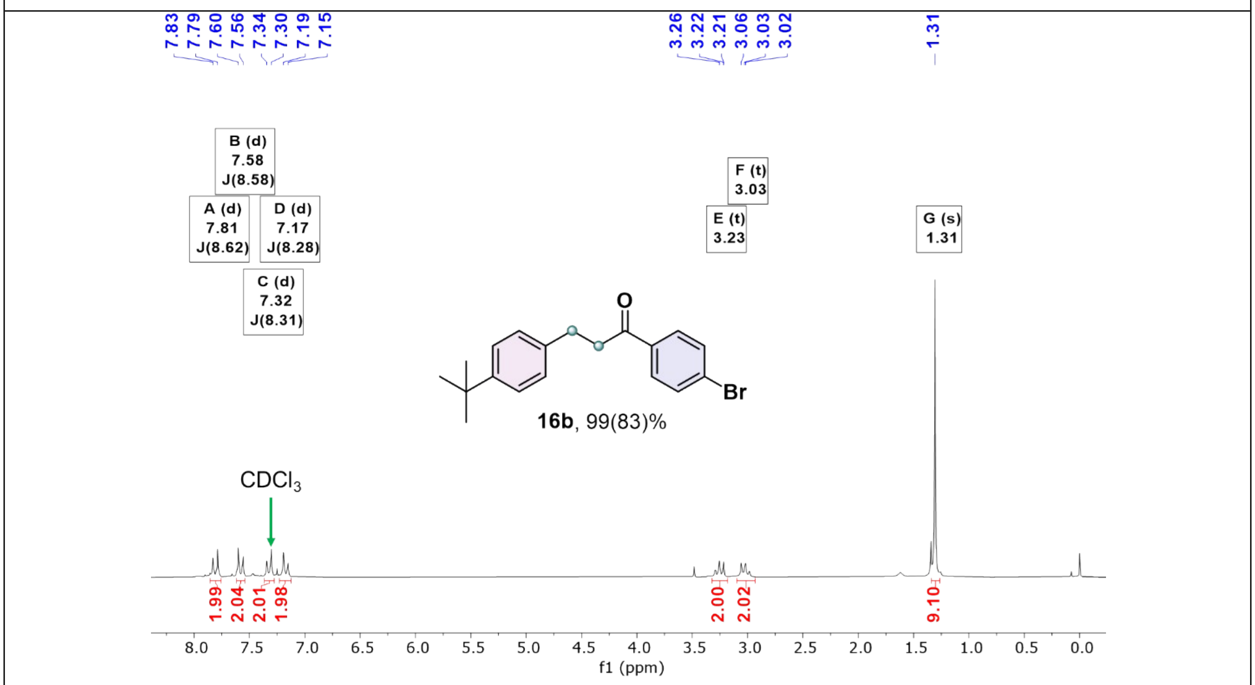


Fig. S45 ^{1}H–NMR of **16b** in $CDCl_3$ at 298K.

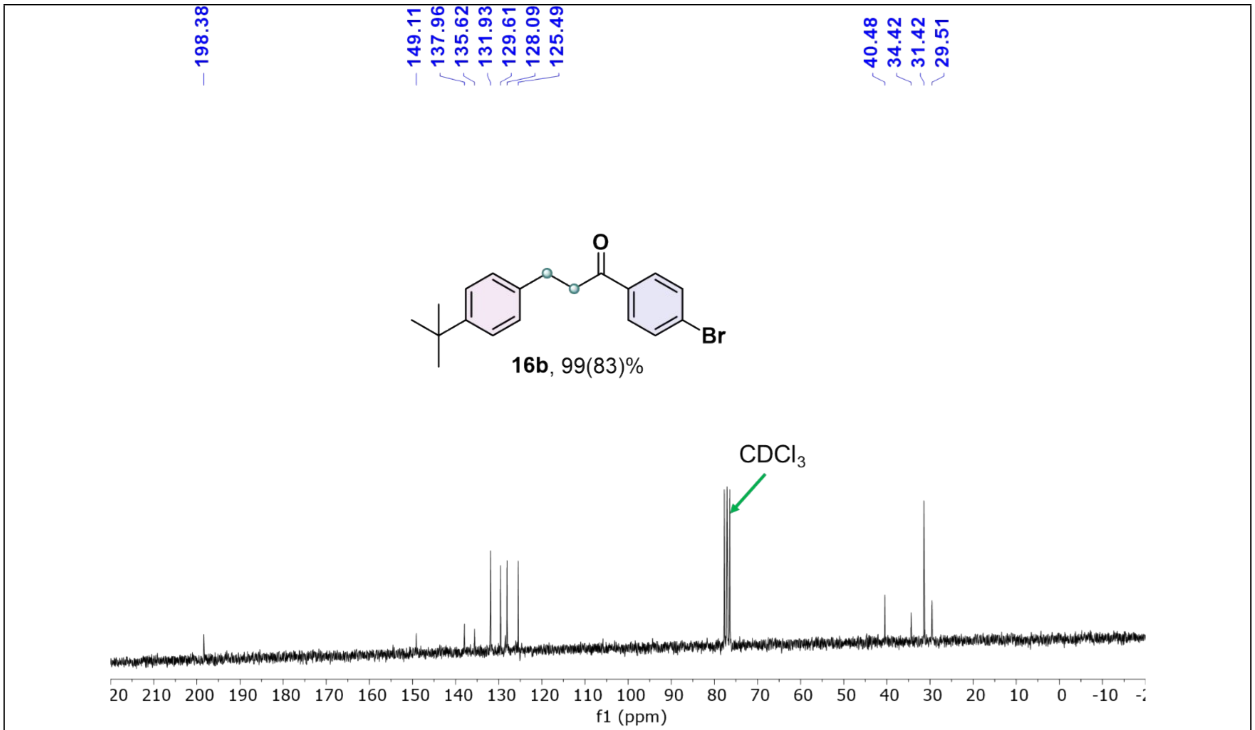


Fig. S46 $^{13}C\{^{1}H\}$ –NMR of **16b** in $CDCl_3$ at 298K.

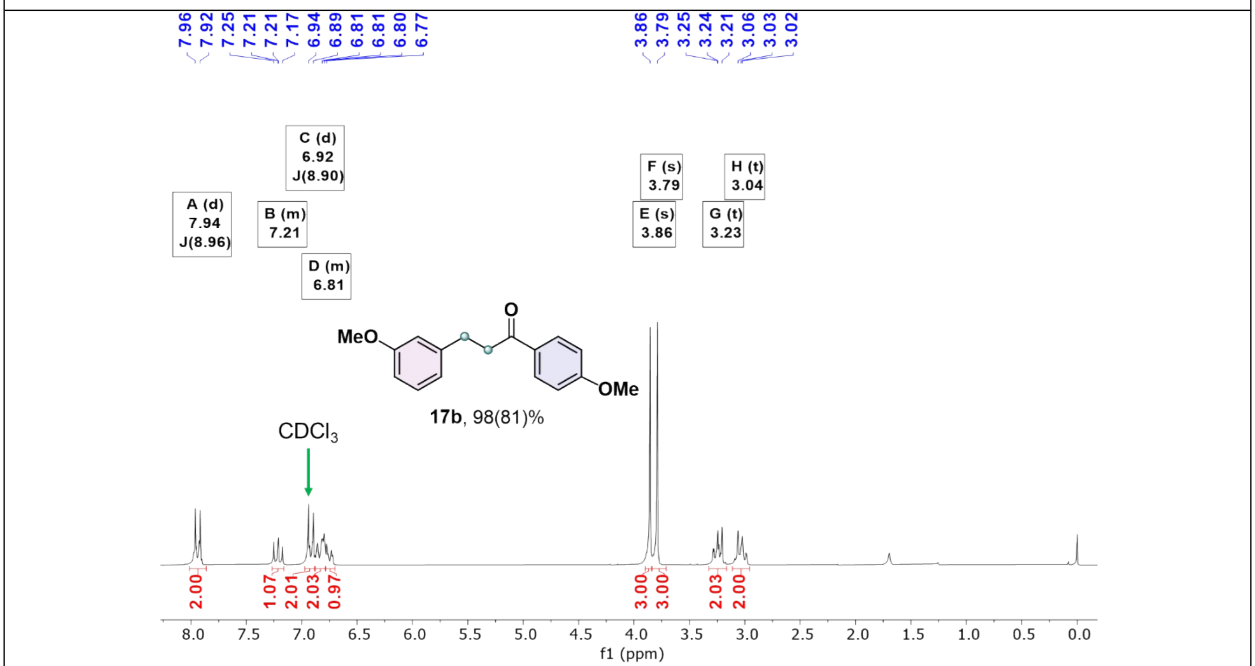


Fig. S47 ^{1}H–NMR of **17b** in $CDCl_3$ at 298K.

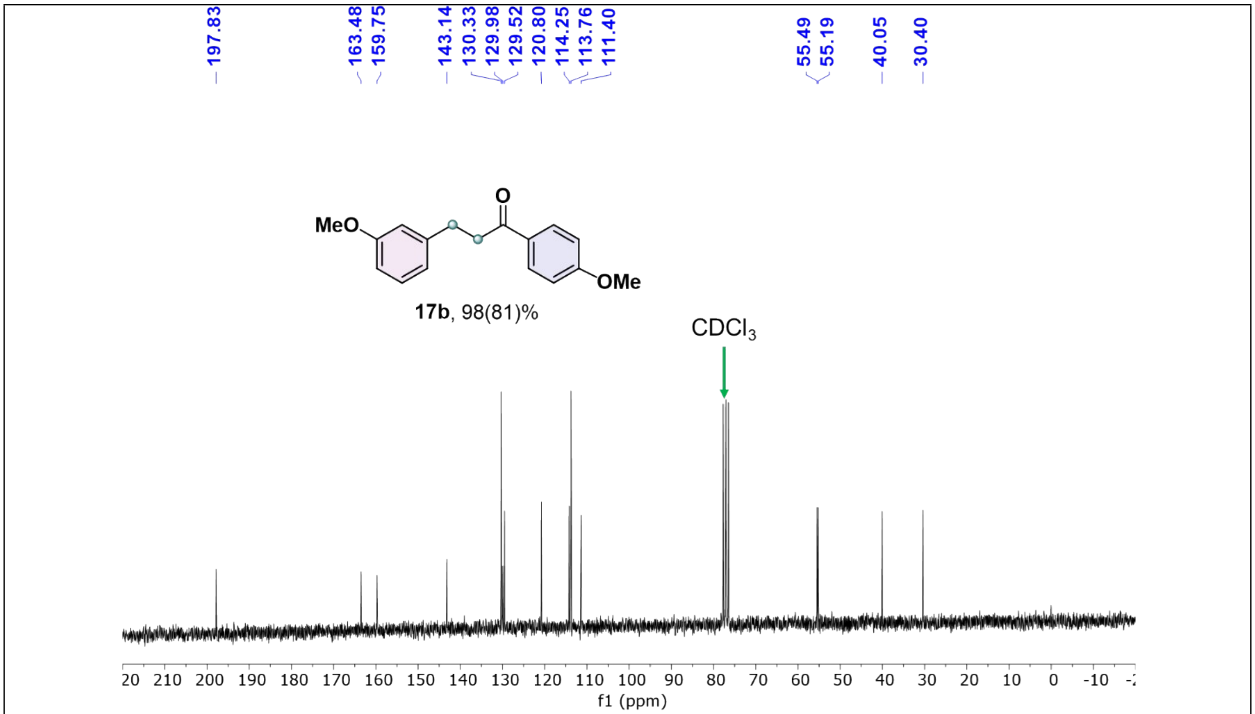


Fig. S48 $^{13}C\{^{1}H\}$ –NMR of **17b** in $CDCl_3$ at 298K.

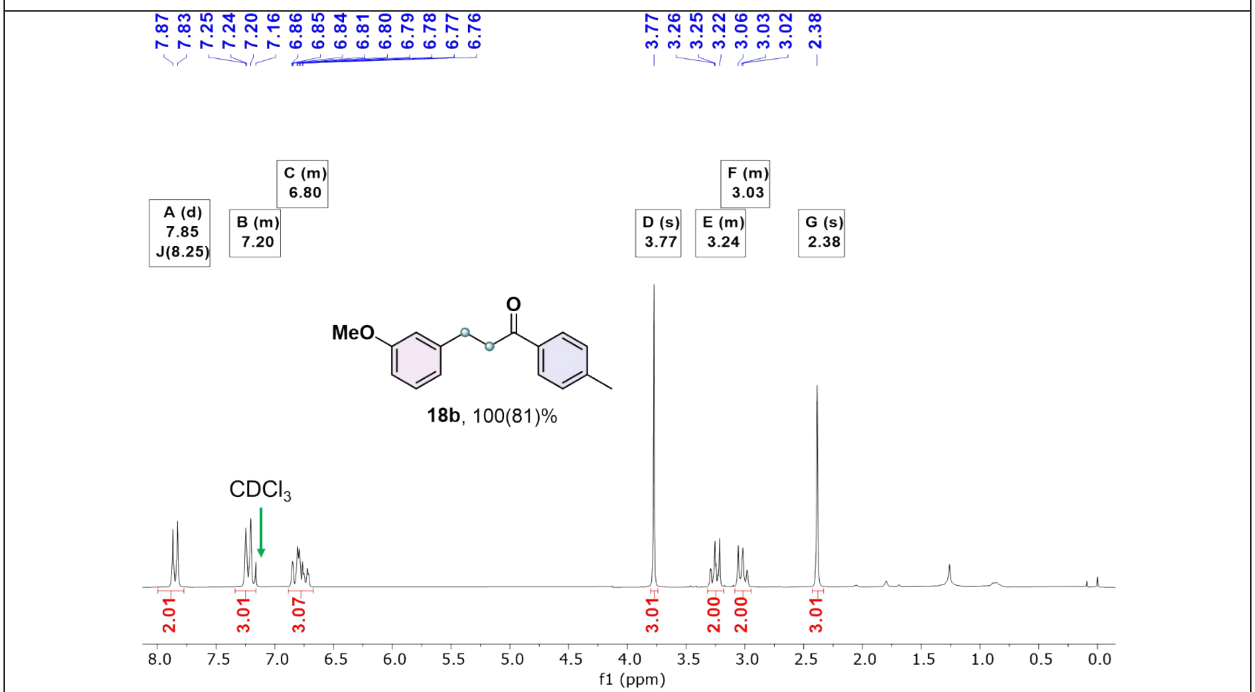


Fig. S49 ^{1}H–NMR of **18b** in $CDCl_3$ at 298K.

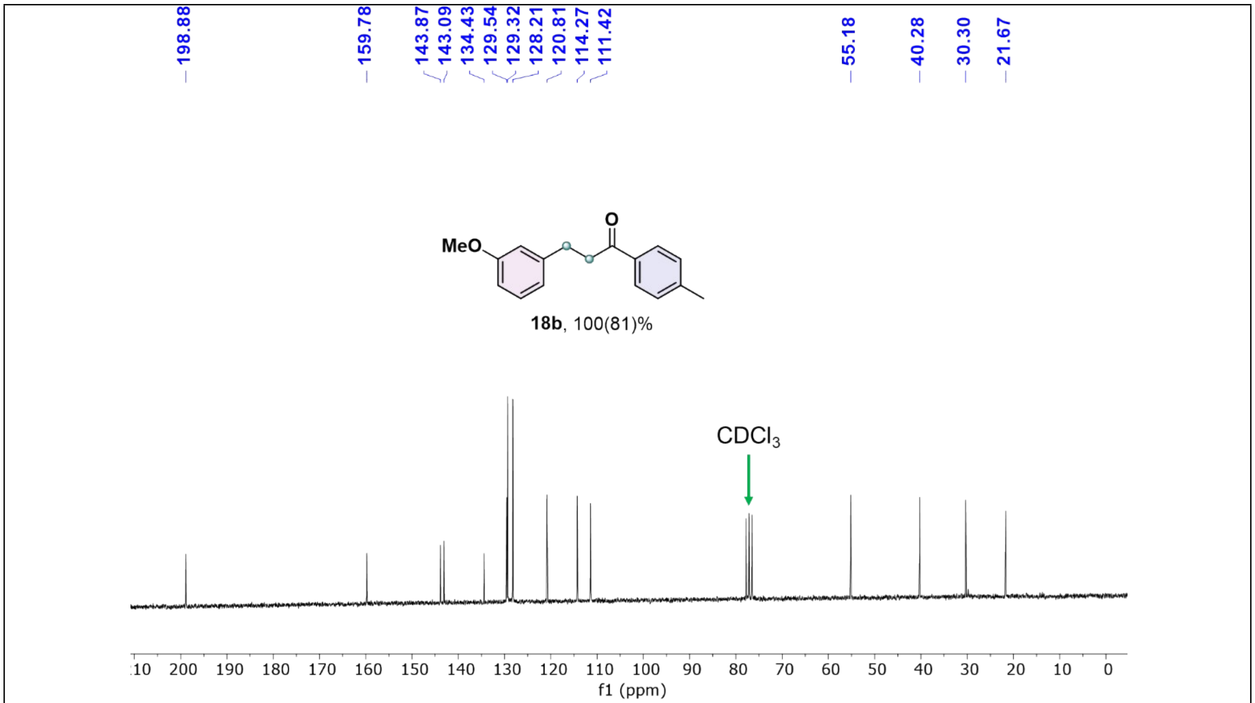


Fig. S50 $^{13}C\{^{1}H\}$ –NMR of **18b** in $CDCl_3$ at 298K.

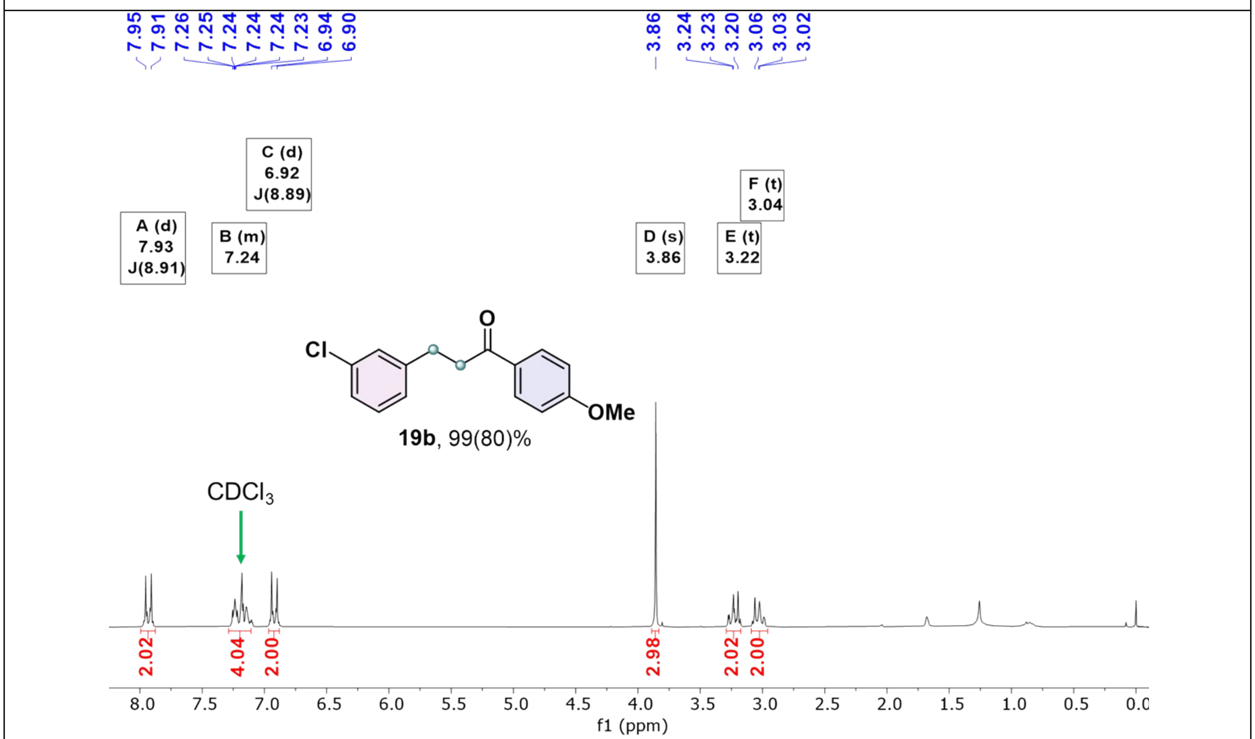


Fig. S51 ^{1}H–NMR of **19b** in $CDCl_3$ at 298K.

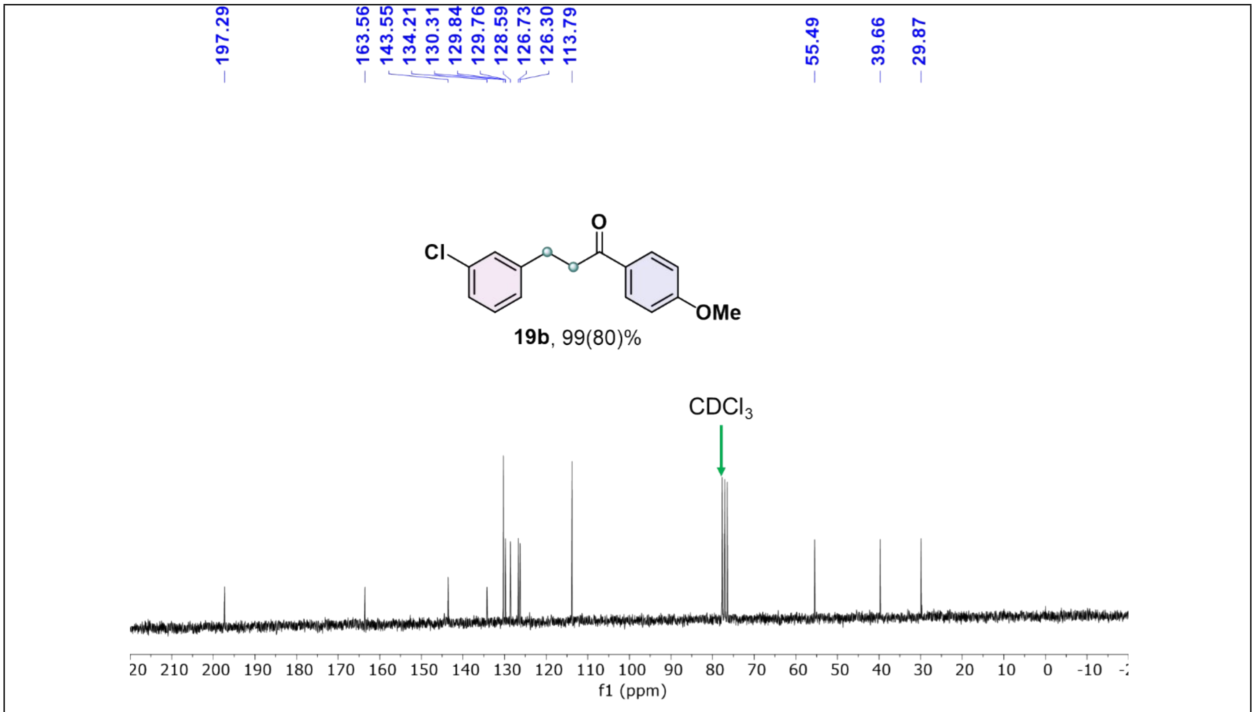


Fig. S52 $^{13}C\{^{1}H\}$ –NMR of **19b** in $CDCl_3$ at 298K.

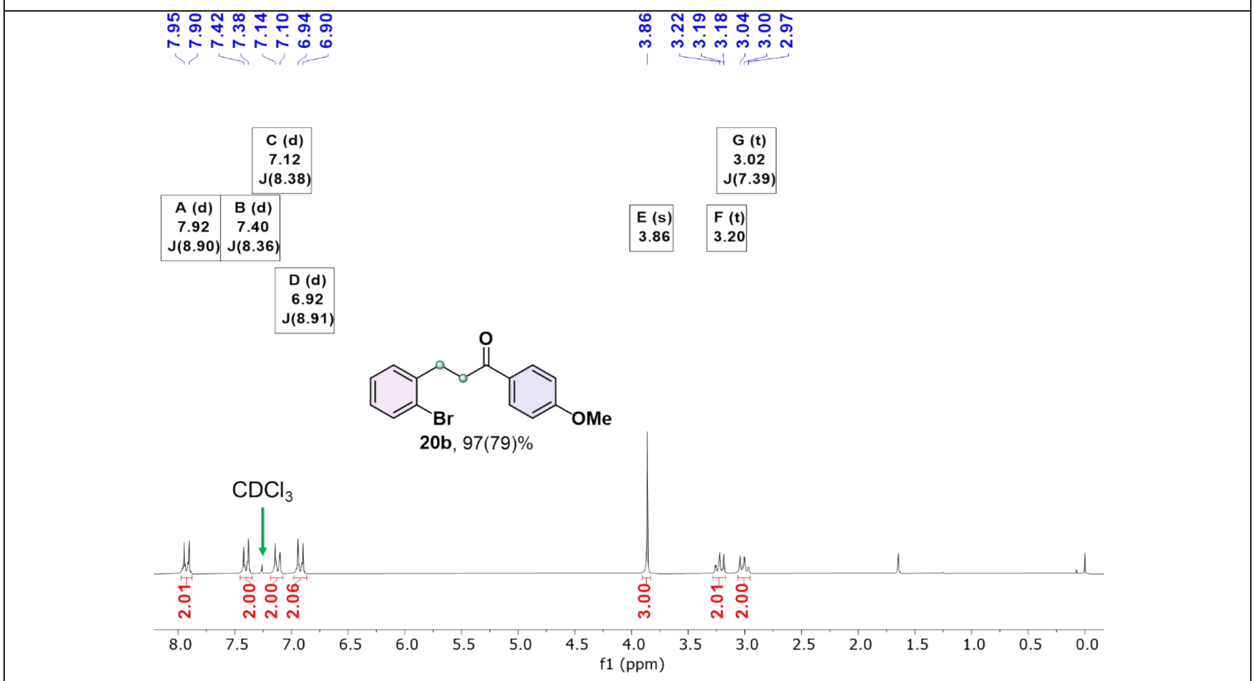


Fig. S53 ^{1}H–NMR of **20b** in $CDCl_3$ at 298K.

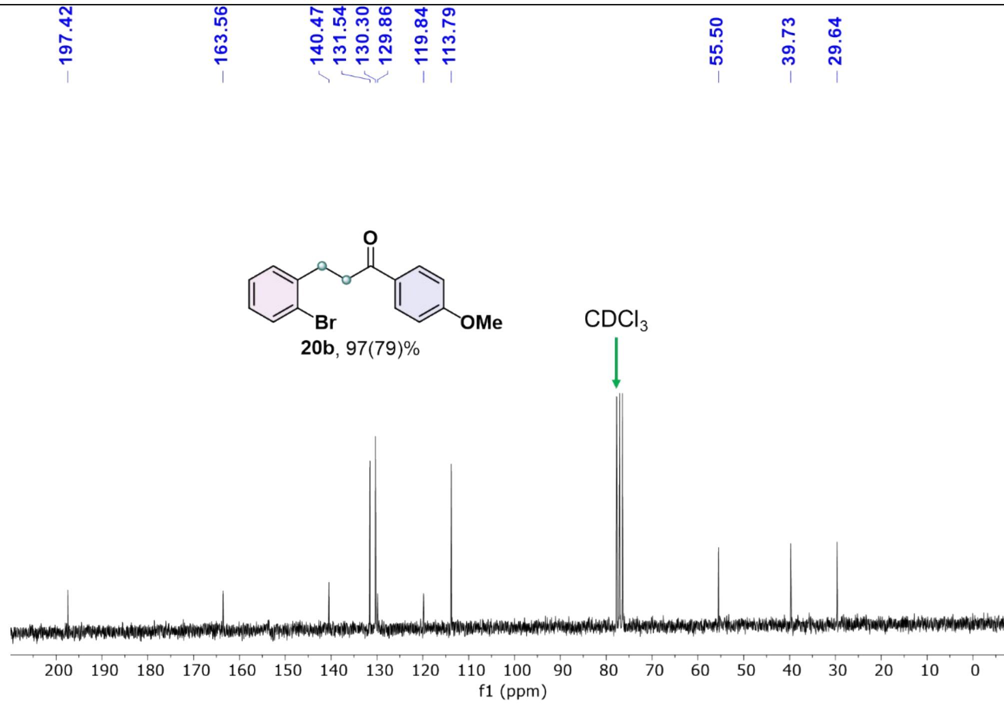


Fig. S54 $^{13}C\{^{1}H\}$ –NMR of **20b** in $CDCl_3$ at 298K.

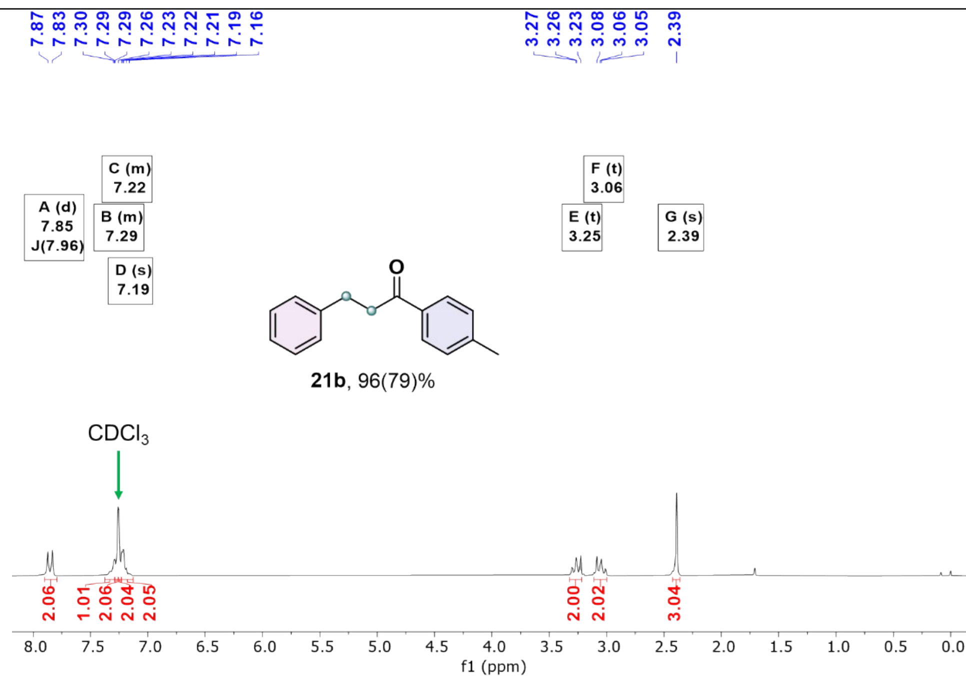


Fig. S55 ^{1}H–NMR of **21b** in $CDCl_3$ at 298K.

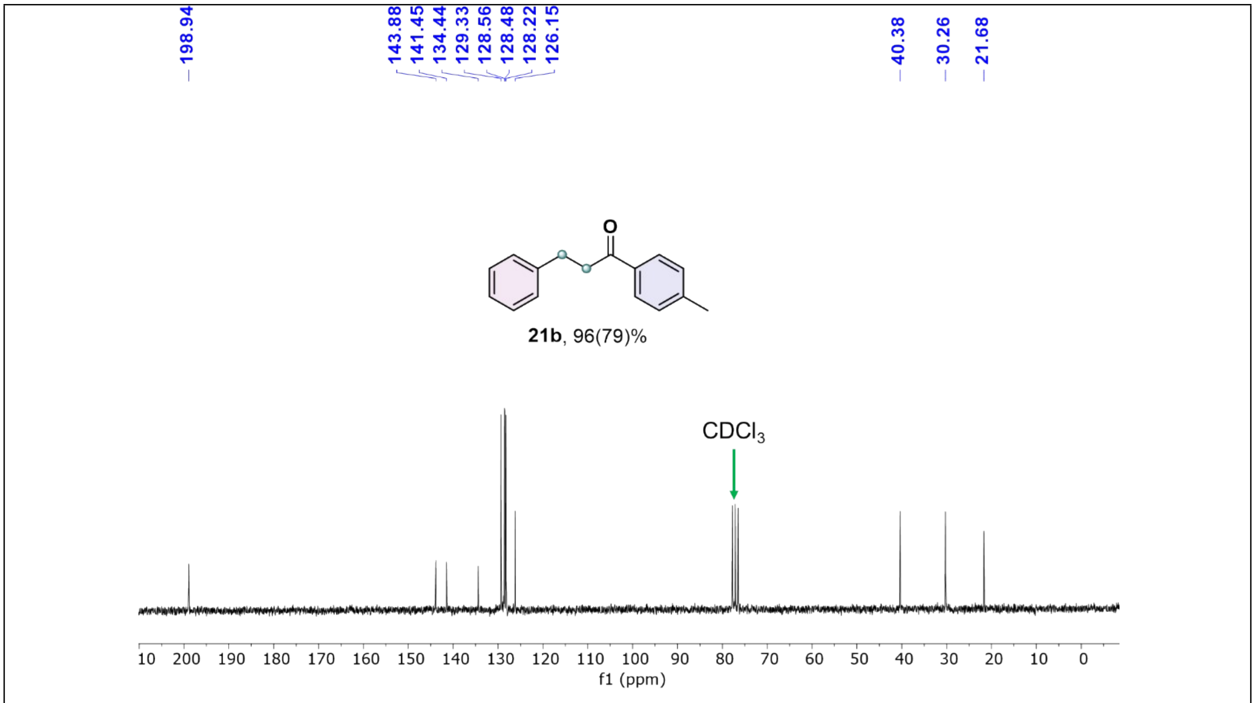


Fig. S56 $^{13}C\{^1H\}$ –NMR of **21b** in $CDCl_3$ at 298K.

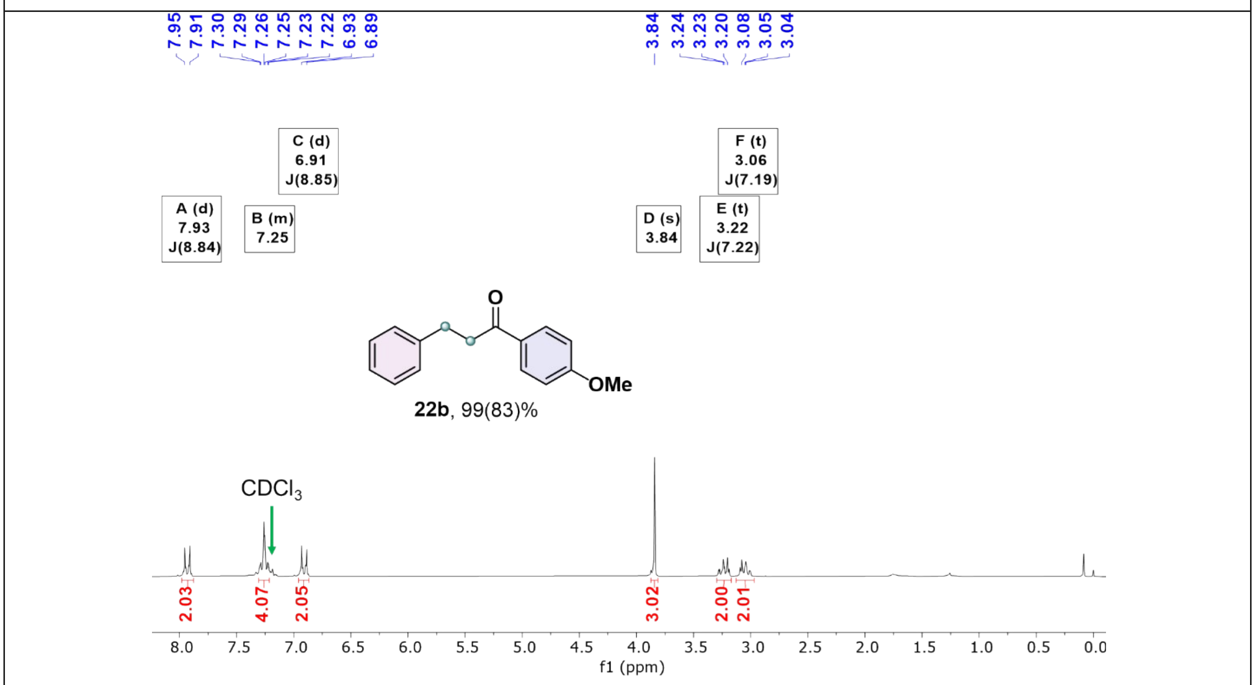


Fig. S57 ^1H–NMR of **22b** in $CDCl_3$ at 298K.

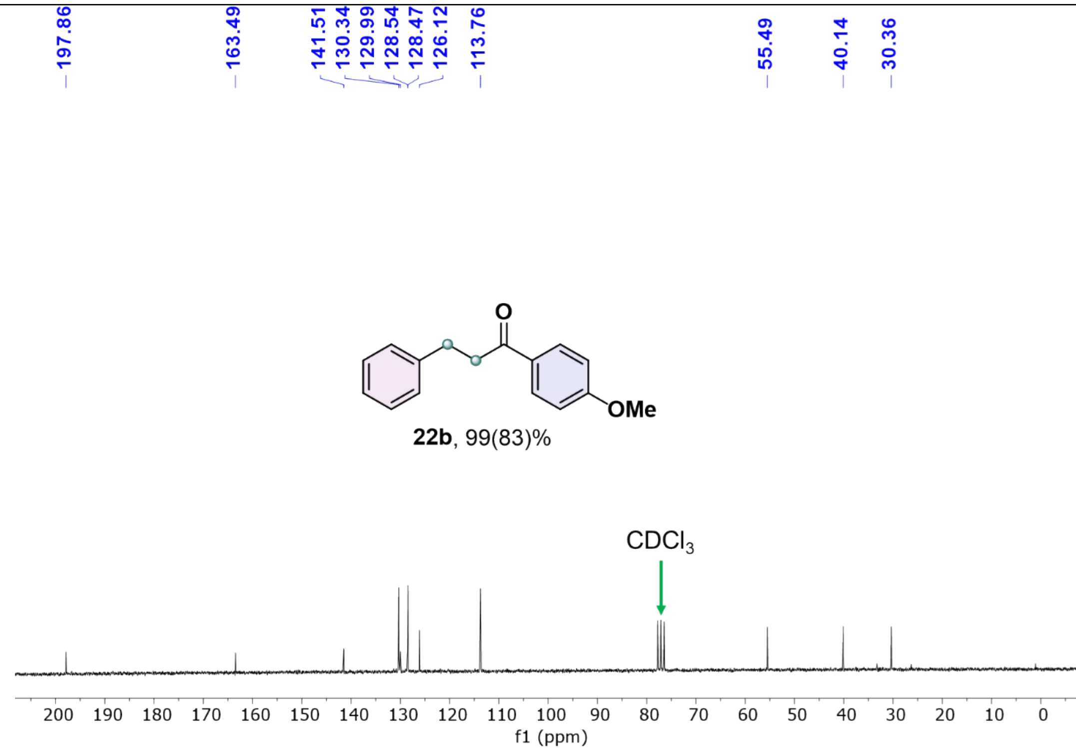


Fig. S58 $^{13}C\{^{1}H\}$ –NMR of **22b** in $CDCl_3$ at 298K.

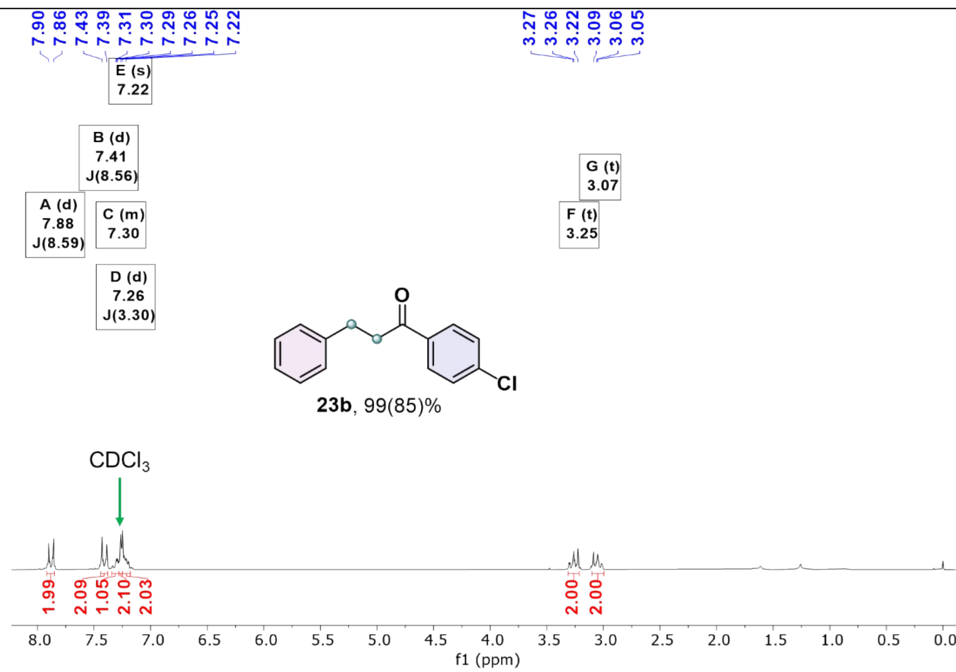


Fig. S59 ^{1}H–NMR of **23b** in $CDCl_3$ at 298K.

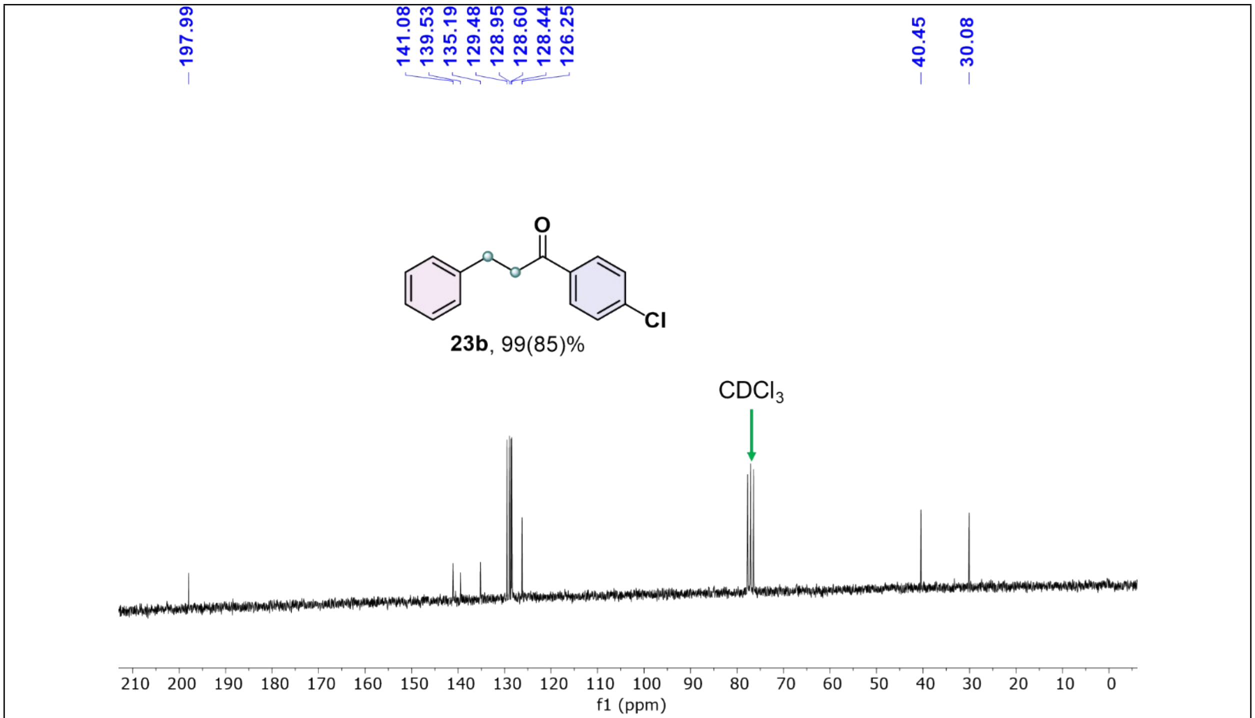


Fig. S60 $^{13}C\{^{1}H\}$ –NMR of **23b** in $CDCl_3$ at 298K.

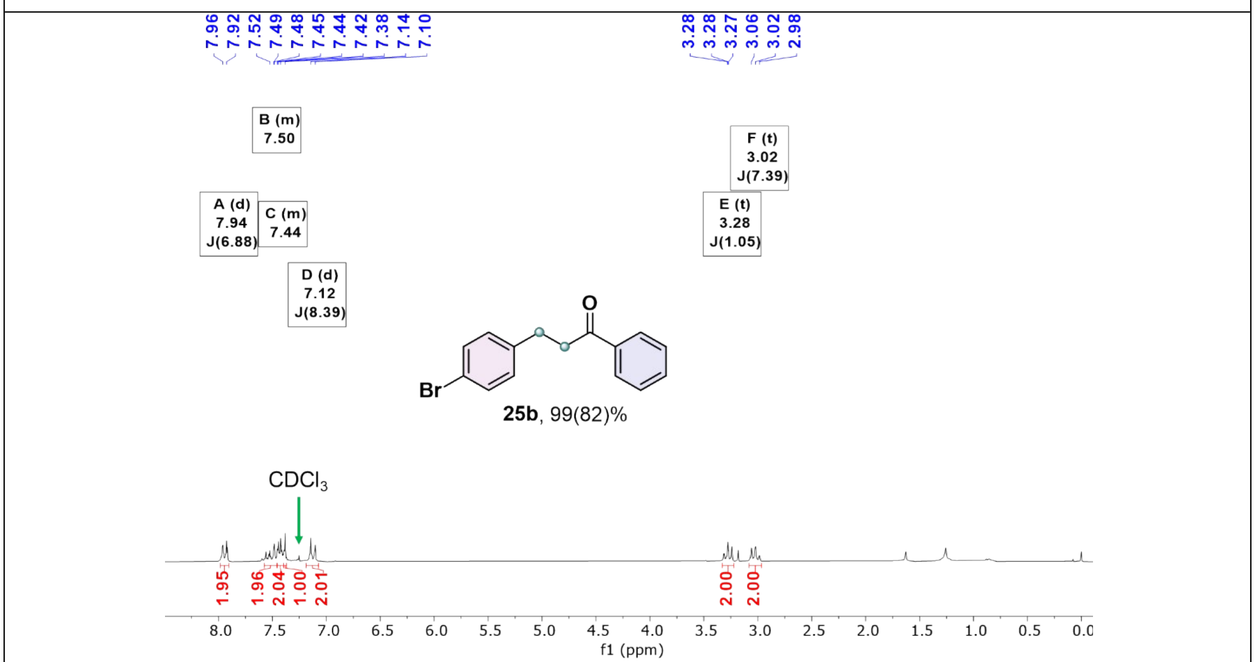


Fig. S61 ^{1}H–NMR of **25b** in $CDCl_3$ at 298K.

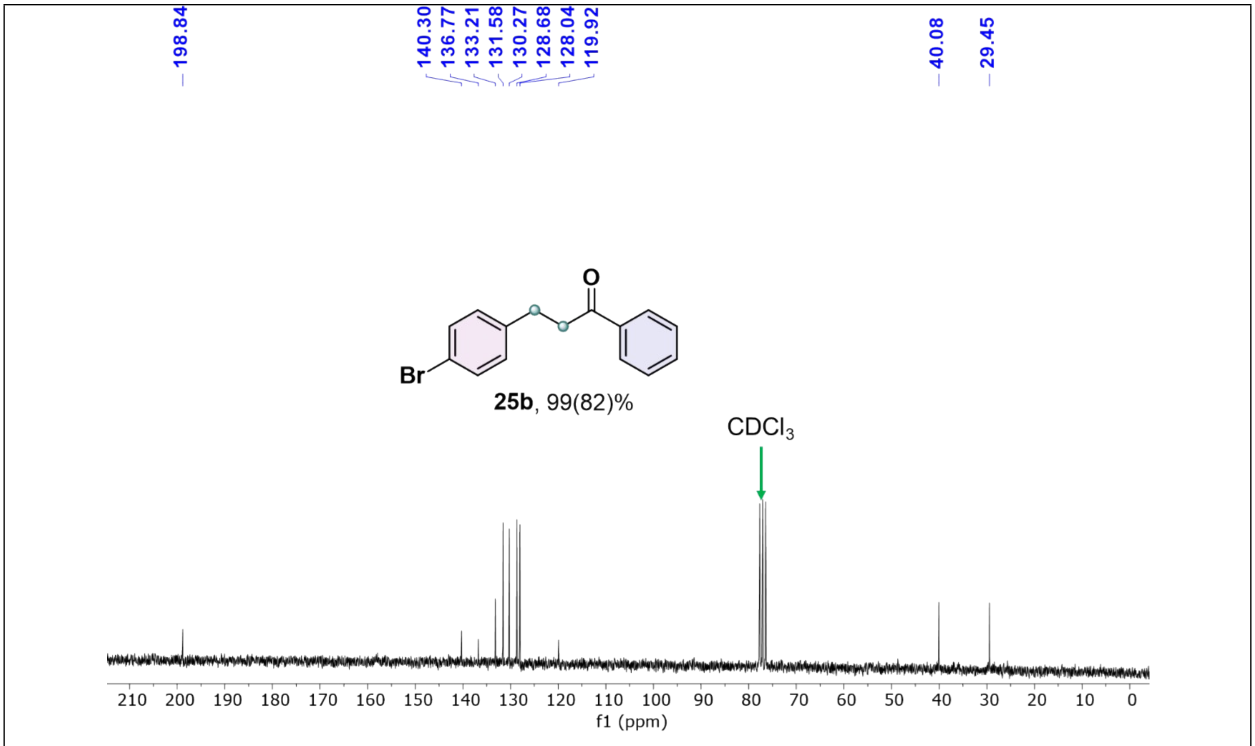


Fig. S62 $^{13}C\{^{1}H\}$ –NMR of **25b** in $CDCl_3$ at 298K.

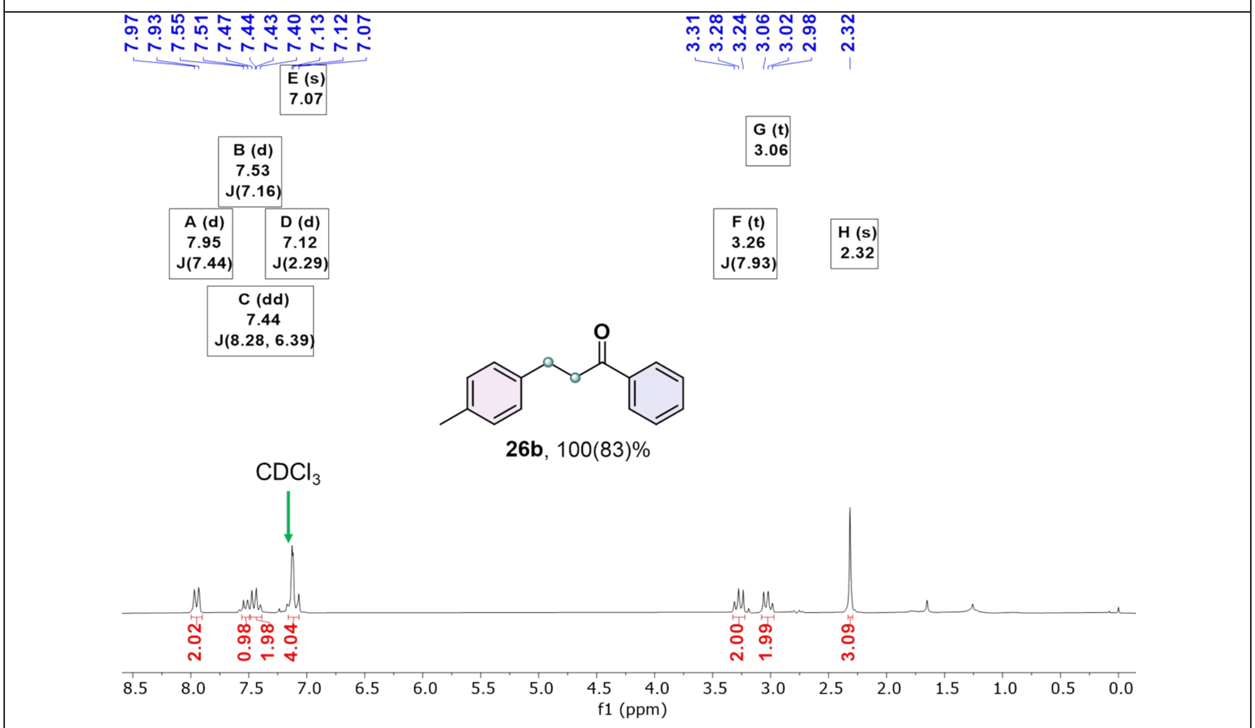


Fig. S63 ^{1}H–NMR of **26b** in $CDCl_3$ at 298K.

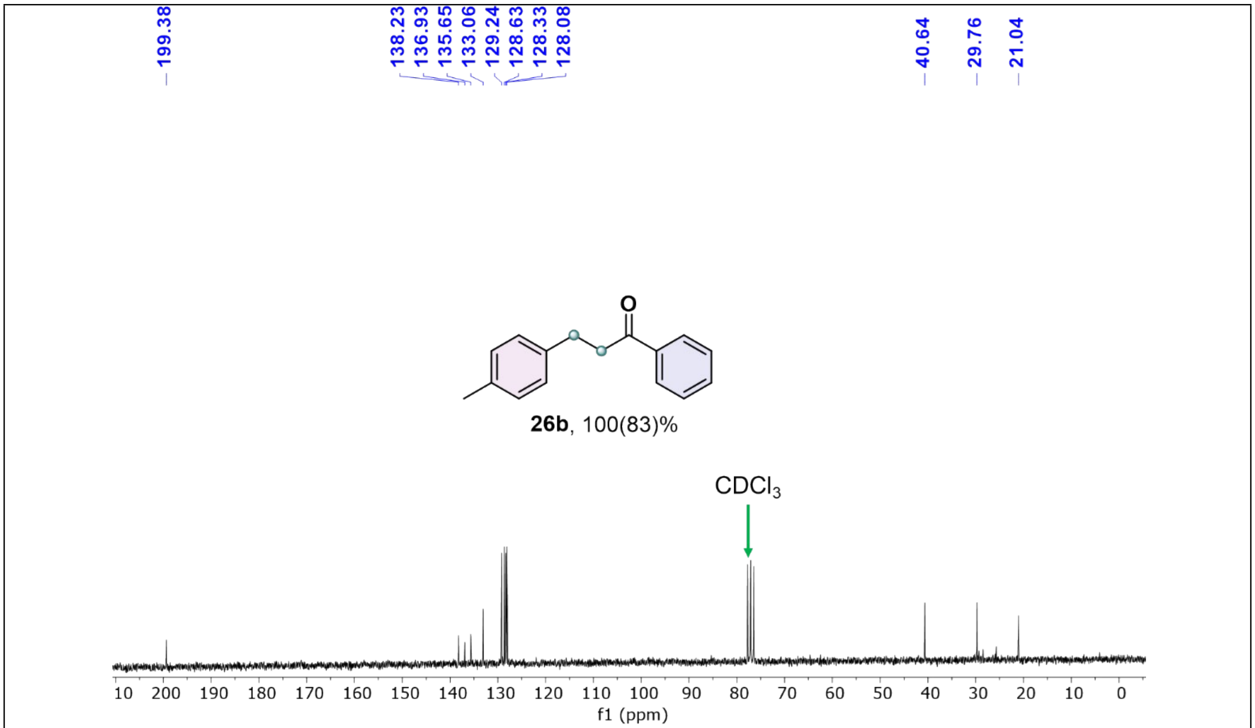


Fig. S64 $^{13}C\{^{1}H\}$ –NMR of **26b** in $CDCl_3$ at 298K.

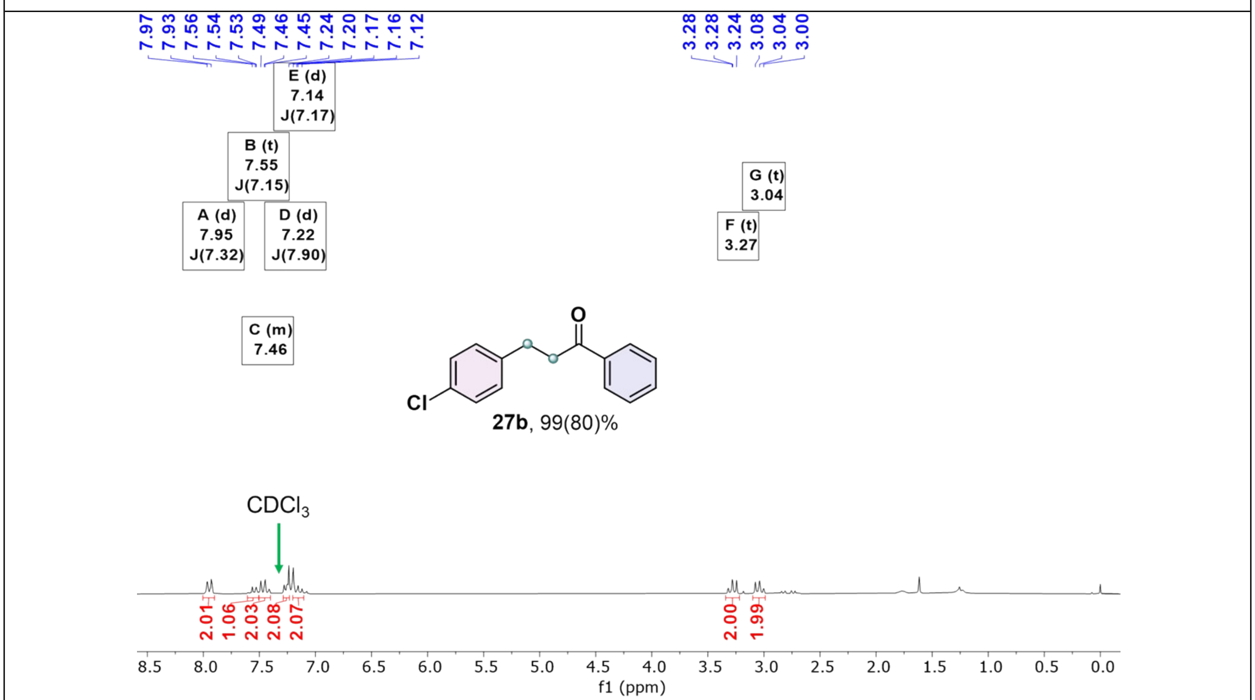


Fig. S65 ^{1}H–NMR of **27b** in $CDCl_3$ at 298K.

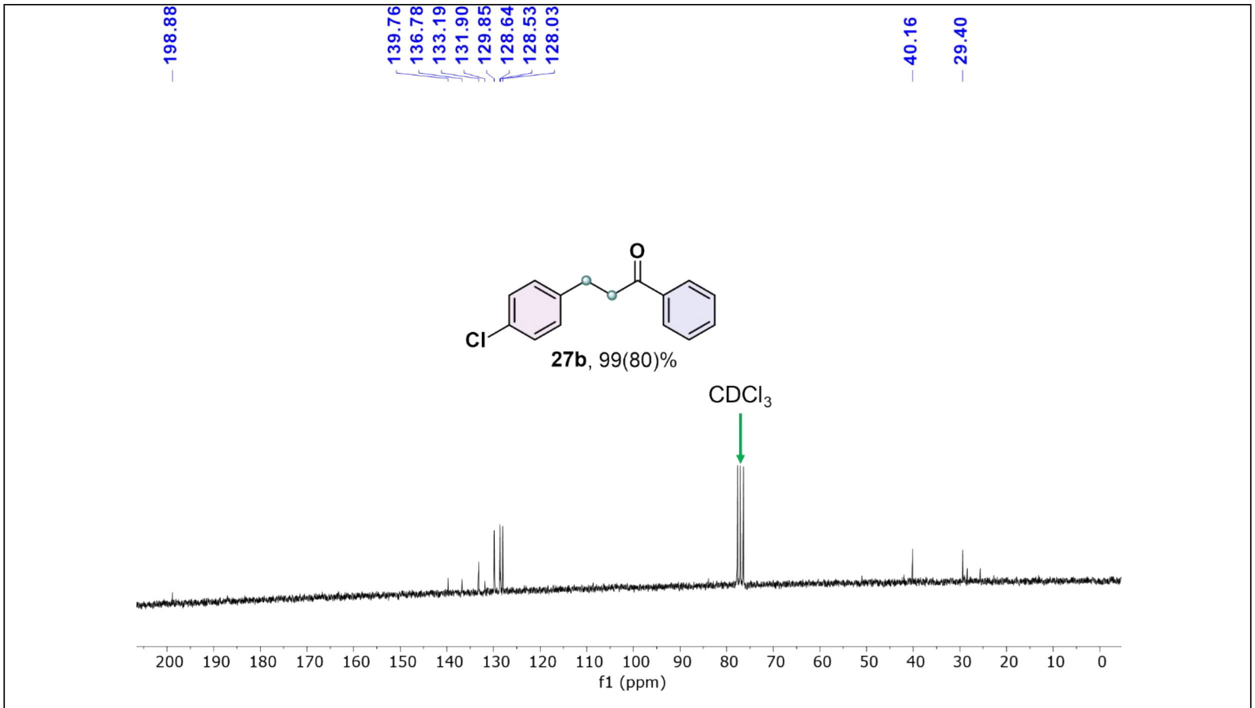


Fig. S66 $^{13}C\{^{1}H\}$ –NMR of **27b** in $CDCl_3$ at 298K.

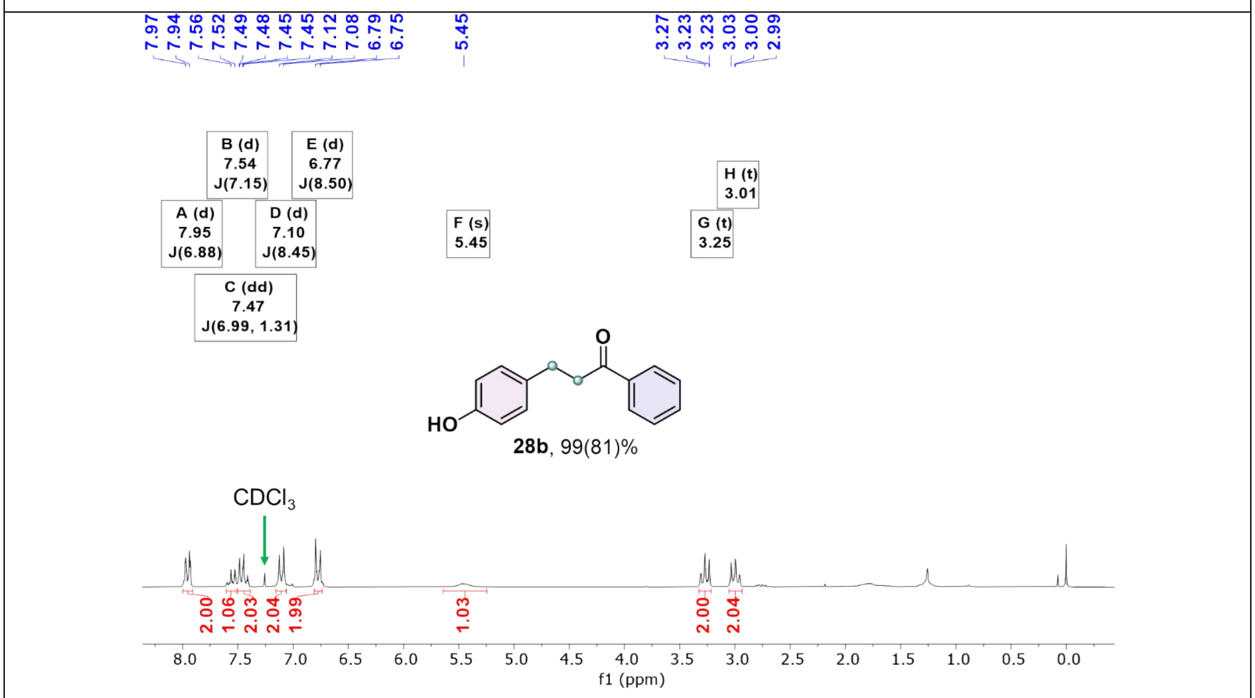


Fig. S67 ^{1}H–NMR of **28b** in $CDCl_3$ at 298K.

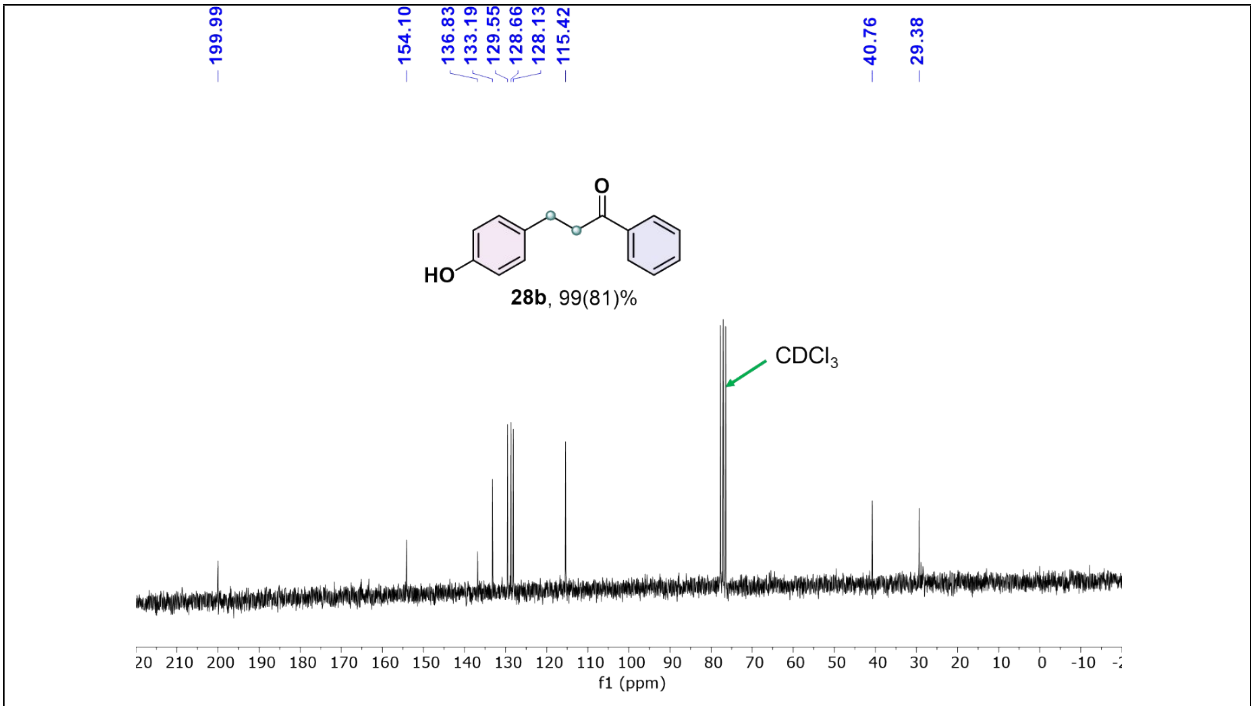


Fig. S68 $^{13}C\{^{1}H\}$ –NMR of **28b** in $CDCl_3$ at 298K.

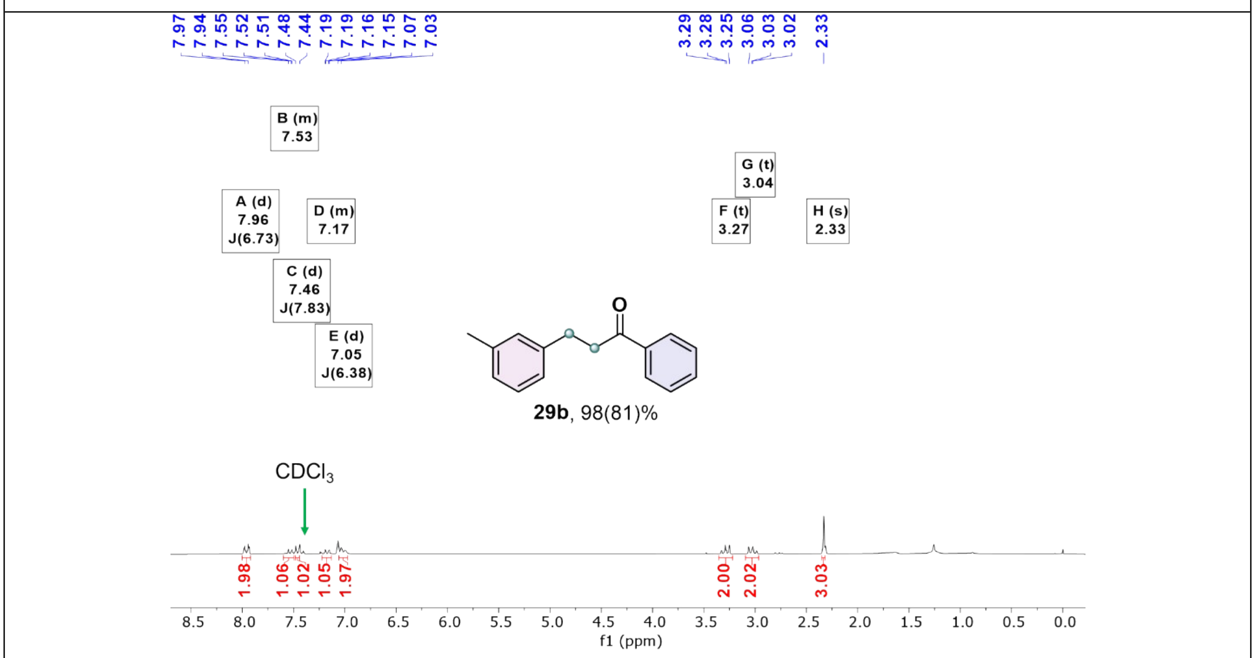


Fig. S69 ^{1}H–NMR of **29b** in $CDCl_3$ at 298K.

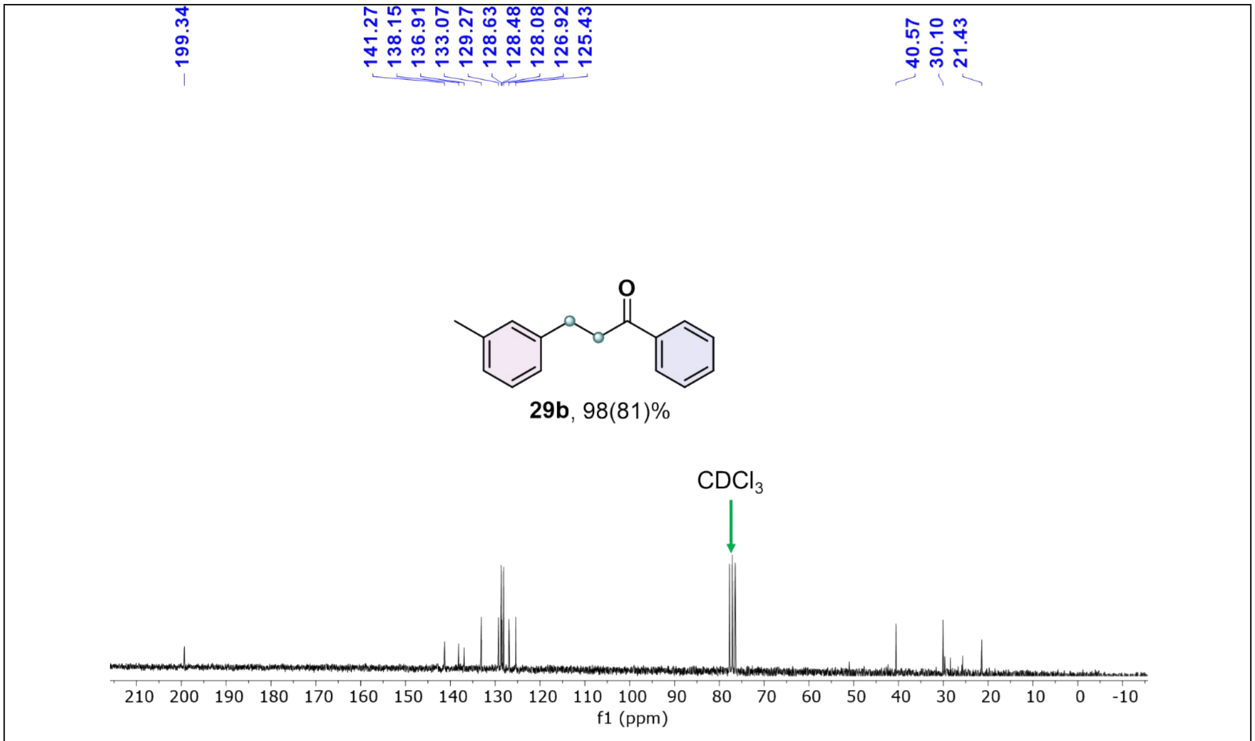


Fig. S70 $^{13}C\{^{1}H\}$ –NMR of **29b** in $CDCl_3$ at 298K.

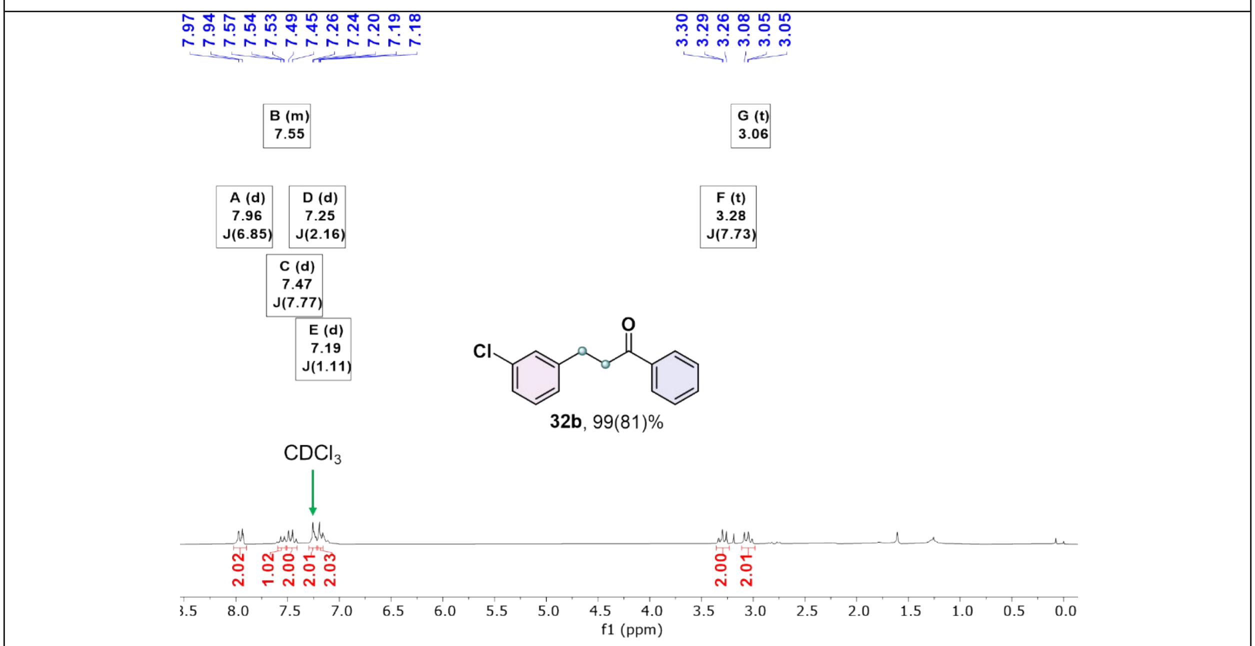


Fig. S71 ^{1}H–NMR of **32b** in $CDCl_3$ at 298K.

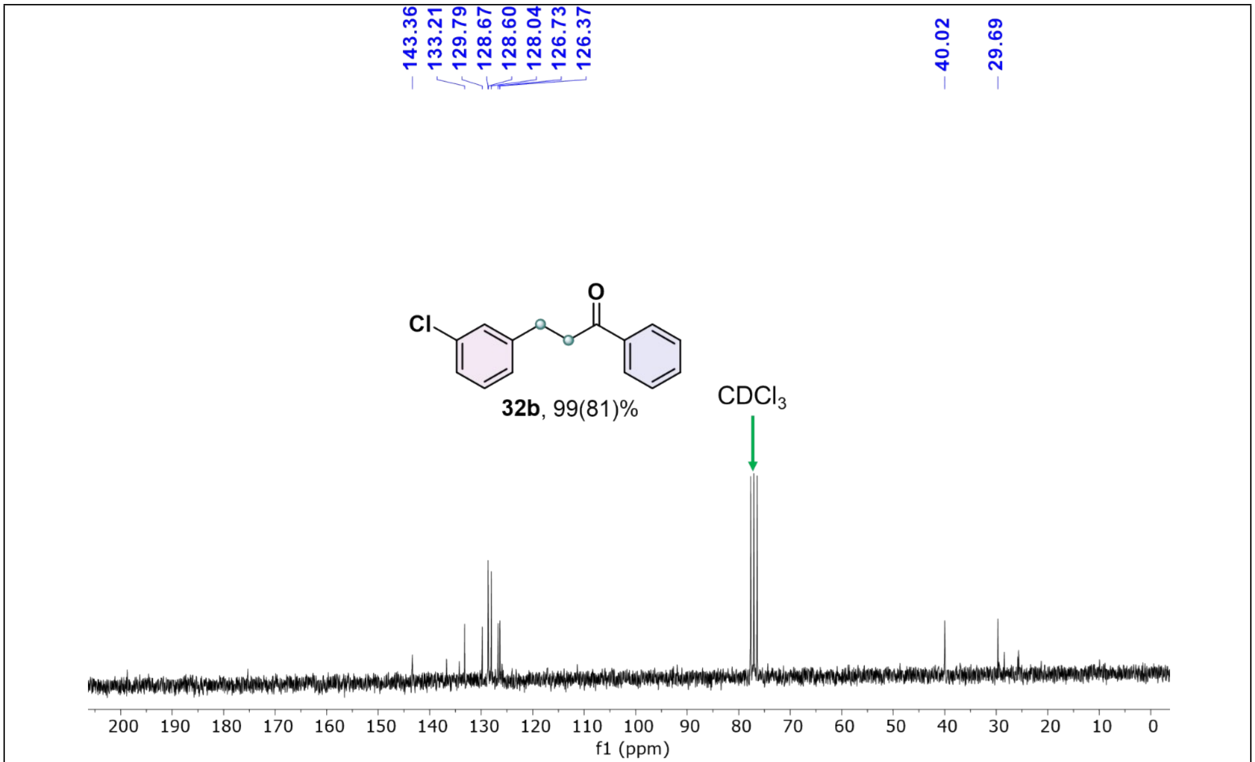


Fig. S72 $^{13}C\{^{1}H\}$ –NMR of **32b** in $CDCl_3$ at 298K.

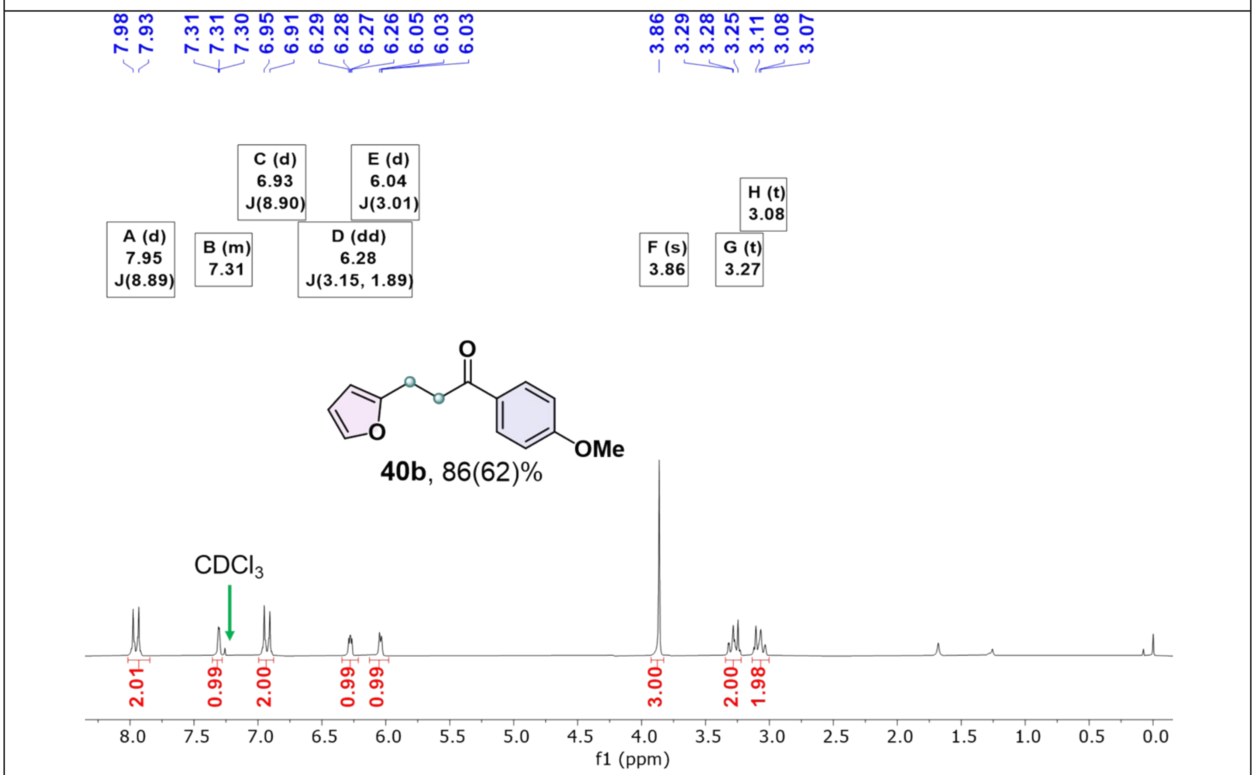


Fig. S73 ^{1}H–NMR of **40b** in $CDCl_3$ at 298K.

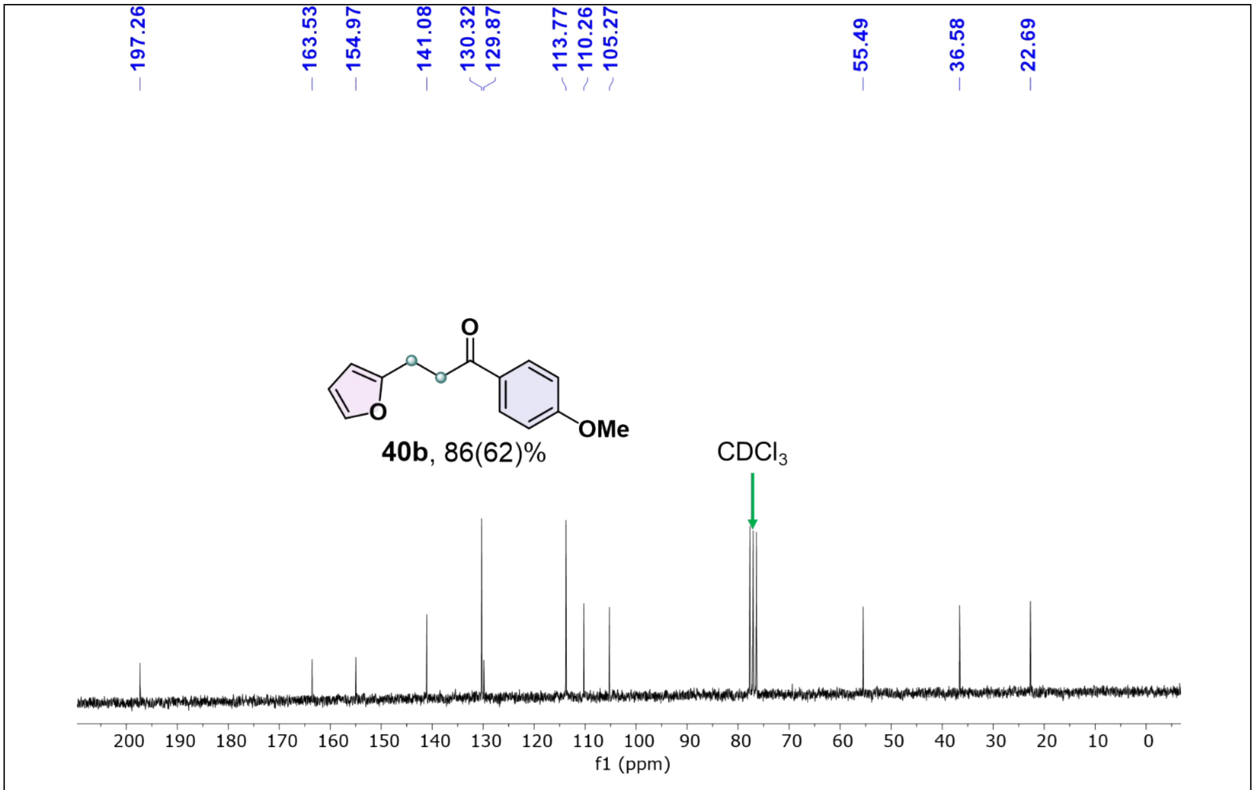


Fig. S74 $^{13}C\{^{1}H\}$ –NMR of **40b** in $CDCl_3$ at 298K.

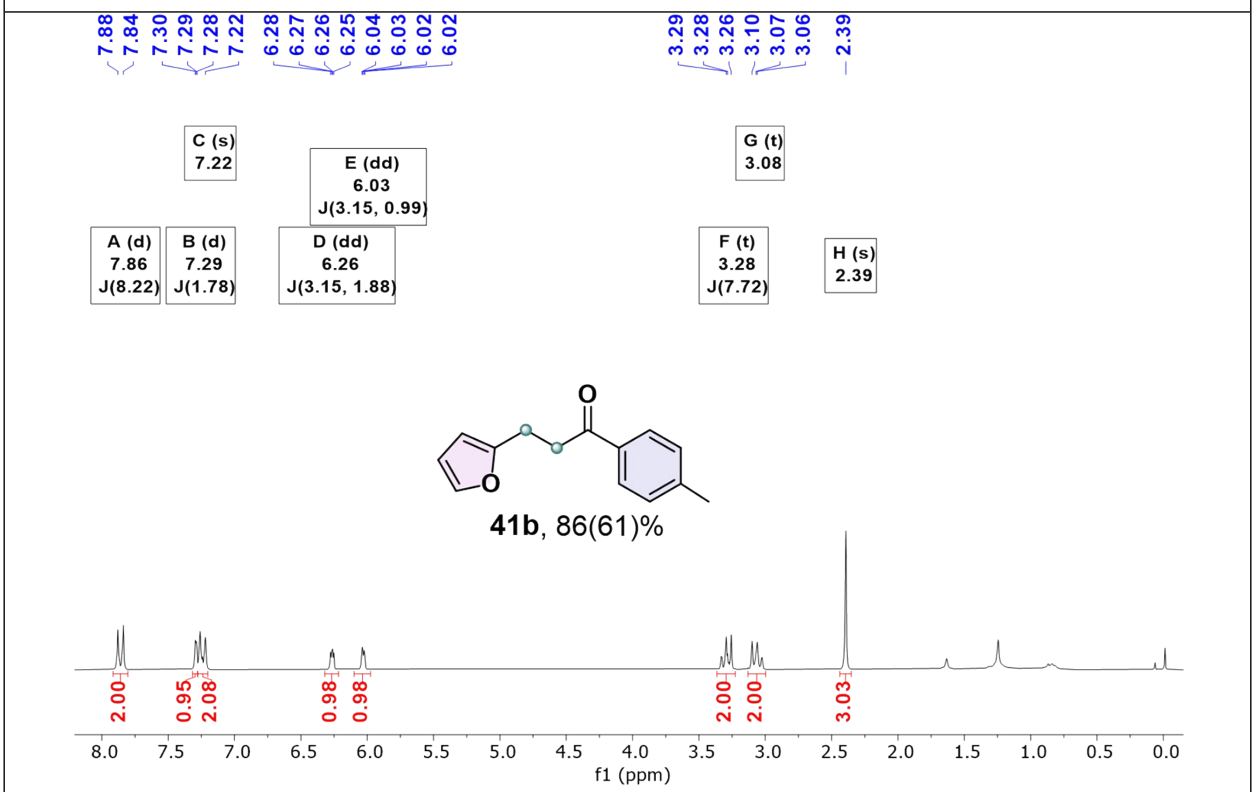


Fig. S75 ^{1}H–NMR of **41b** in $CDCl_3$ at 298K.

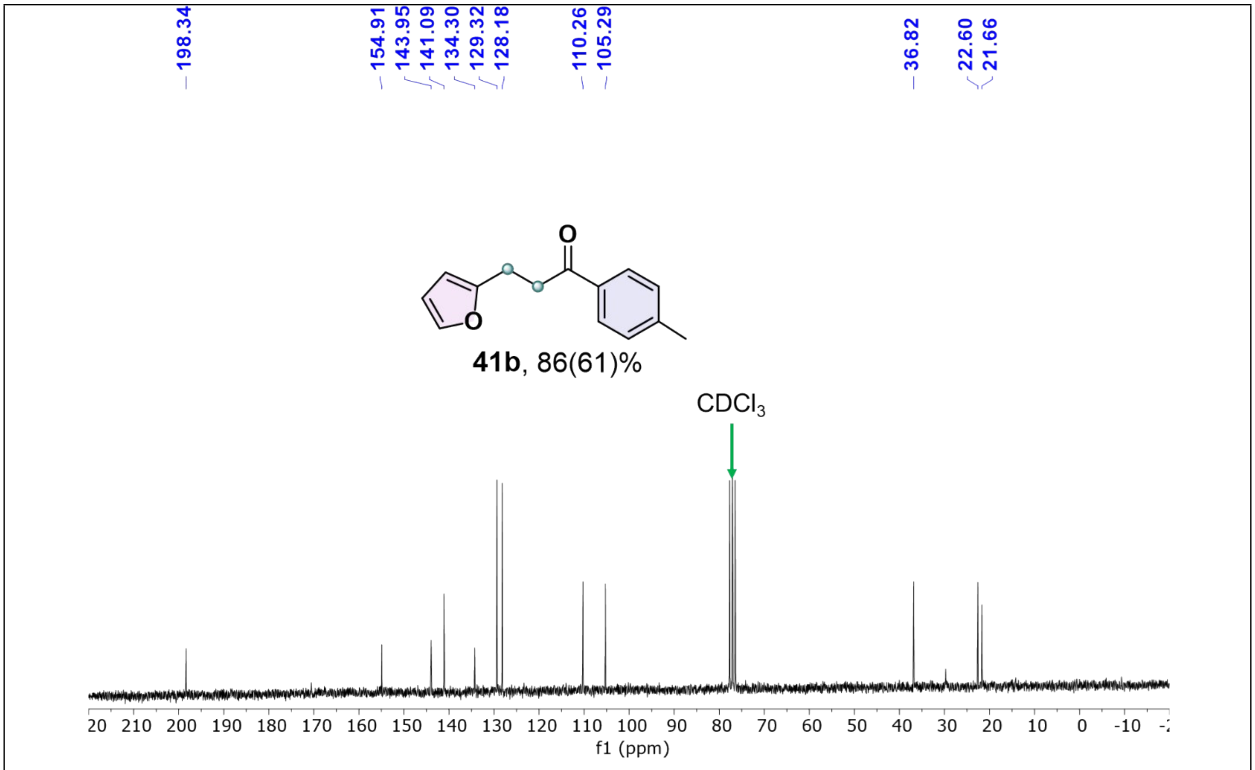


Fig. S76 $^{13}C\{^1H\}$ –NMR of **41b** in $CDCl_3$ at 298K.

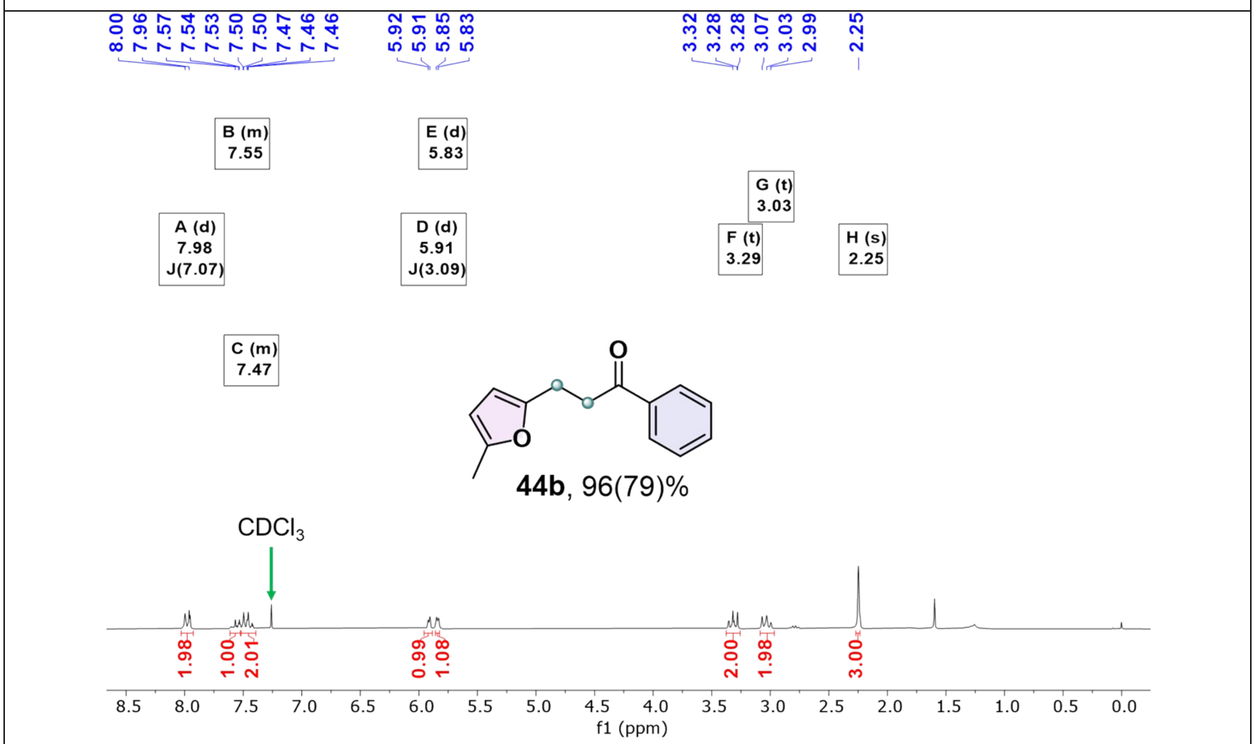


Fig. S77 ^1H–NMR of **44b** in $CDCl_3$ at 298K.

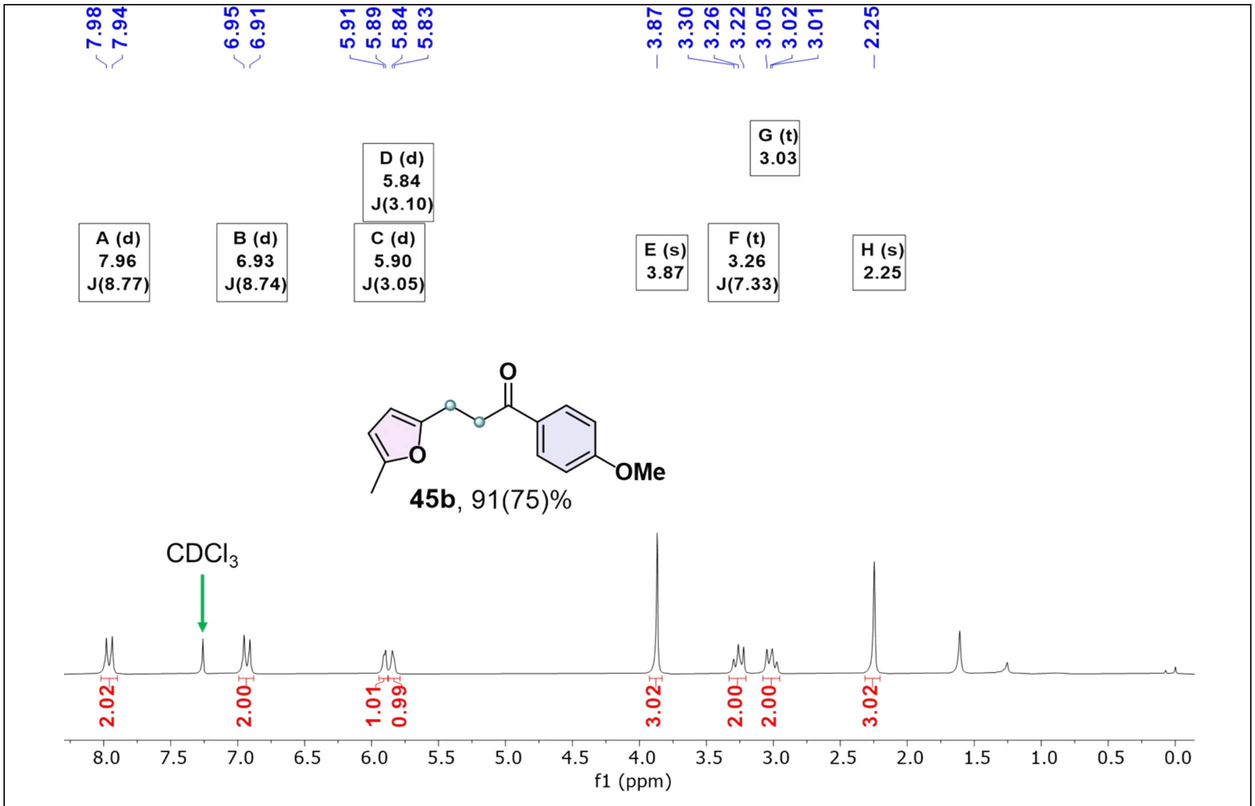


Fig. S78 ^{1}H–NMR of **45b** in $CDCl_3$ at 298K.

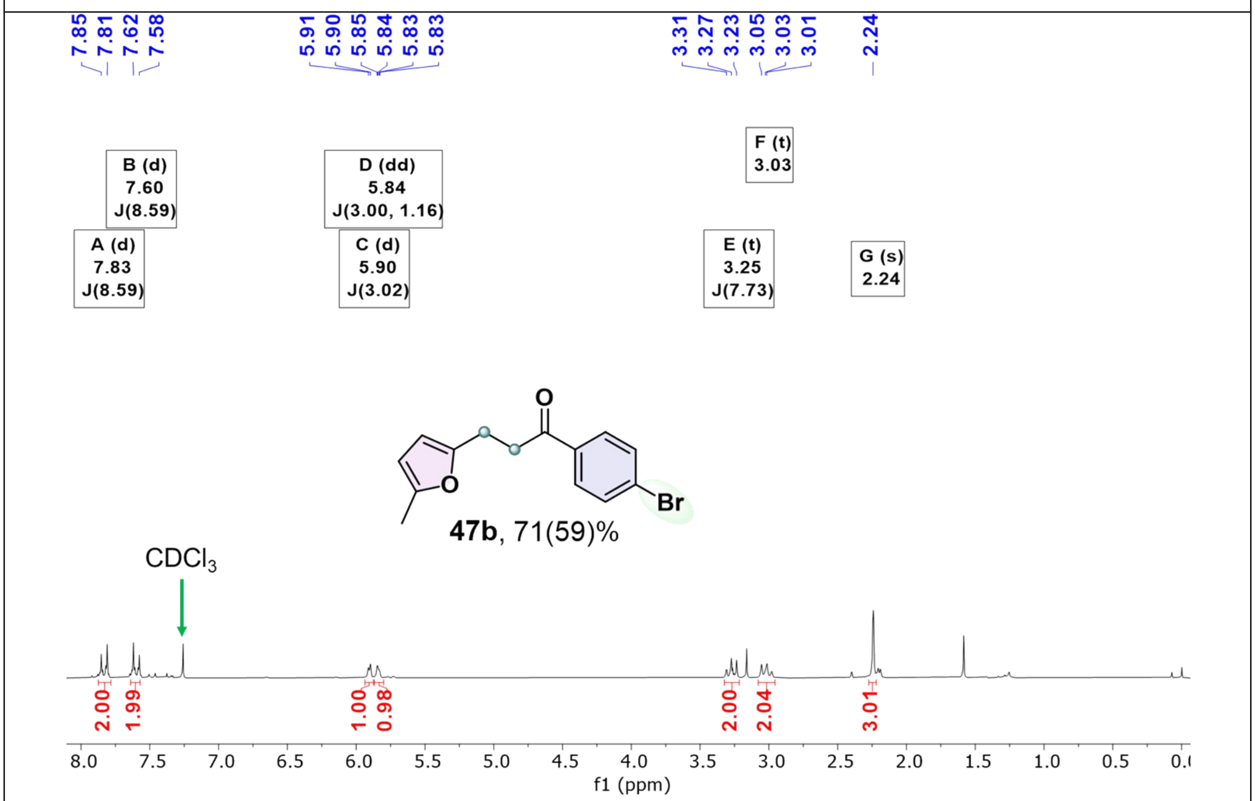


Fig. S79 ^{1}H–NMR of **47b** in $CDCl_3$ at 298K.

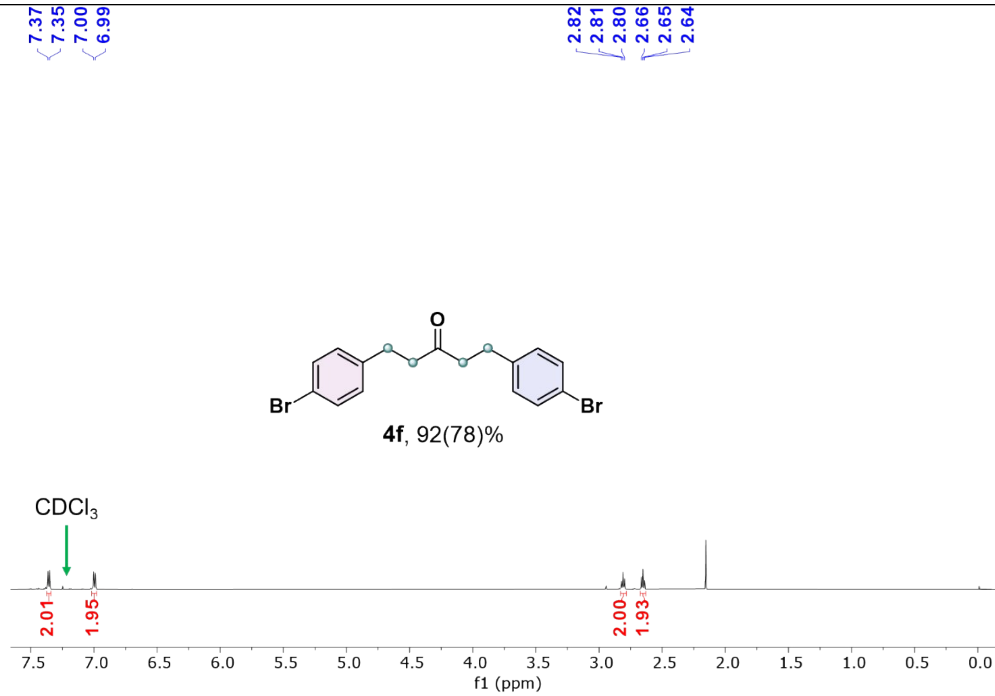


Fig. S80 ^{1}H–NMR of **4f** in $CDCl_3$ at 298K.

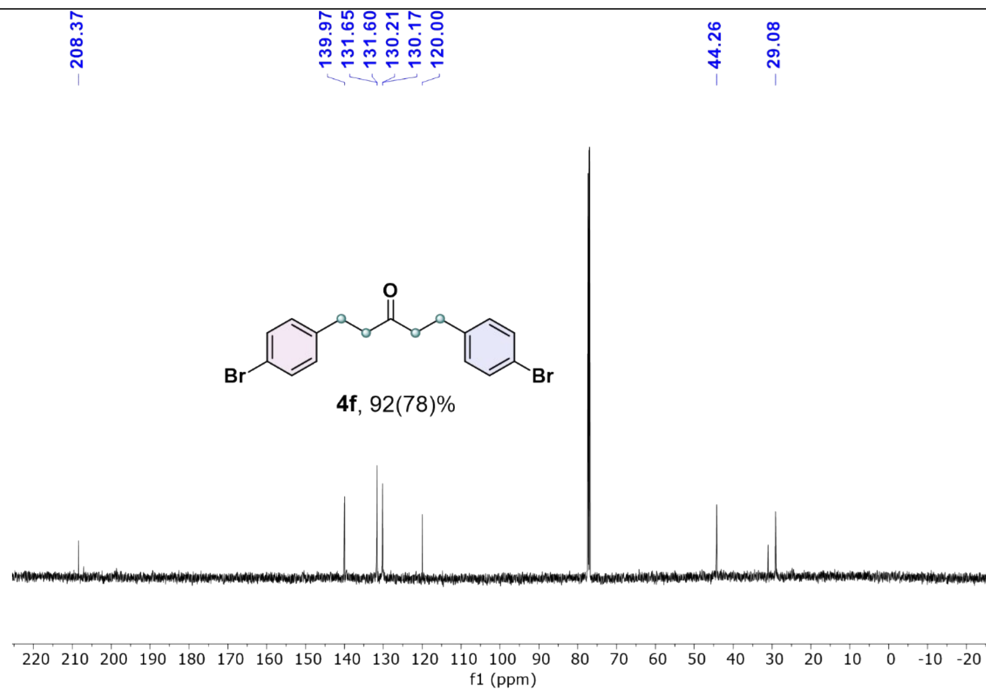


Fig. S81 ^{13}C{^{1}H} –NMR of **4f** in $CDCl_3$ at 298K.

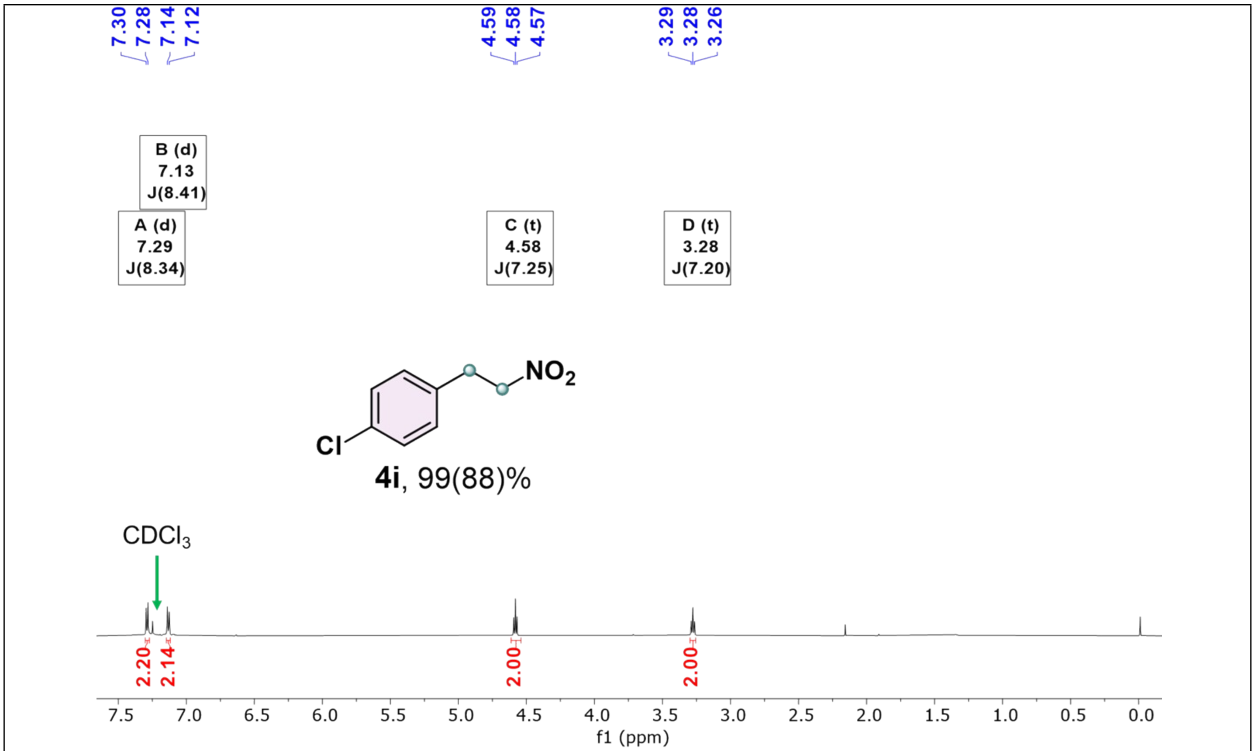


Fig. S82 ^{1}H–NMR of **4i** in $CDCl_3$ at 298K.

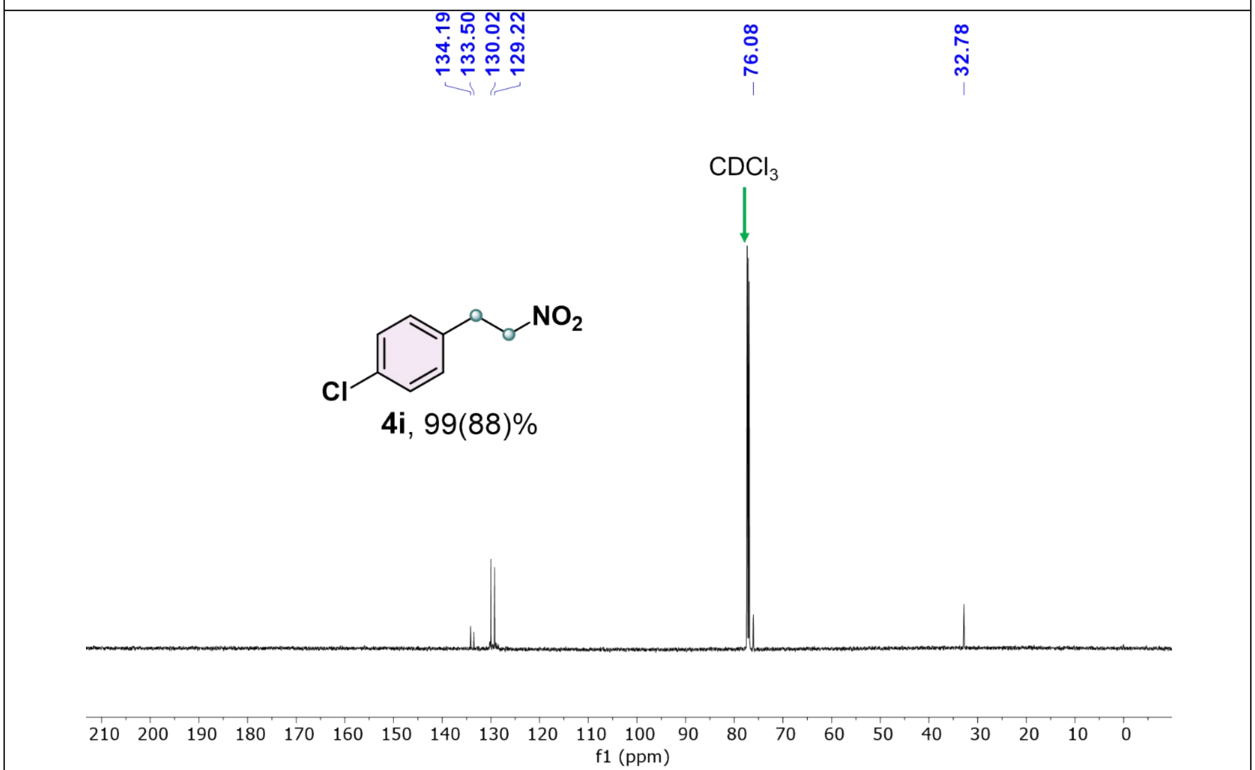


Fig. S83 $^{13}C\{^{1}H\}$ –NMR of **4i** in $CDCl_3$ at 298K.

3.2 ^{1}H NMR spectra of saturated ketones were separated and isolated through a simple evaporation and precipitation method from the reaction mixture.

General procedure for separating and isolating the catalyst and product from the reaction mixture

For the reaction, 1.5 mmol of α,β-unsaturated ketones/nitro were mixed with 1.2 mol% (12 mg) of the **Ru-1** catalyst and 30 mL of methanol in a high-pressure reactor. The mixture was stirred at room temperature (29–32°C) under 30 bar of H_2 pressure for the required reaction time. Upon completion of the reaction, the reaction mixture was distilled to recover methanol and obtain a crude solid to which diethyl ether was added to facilitate the solvent-mediated precipitation of the catalyst. The precipitated catalyst was collected by simple filtration, while the product was obtained by distillation of the diethyl ether. The purity of the catalyst and the product was confirmed using ^{1}H NMR spectroscopy.

Replacement of Diethyl Ether with Green Solvents

To recover the **Ru-1** catalyst efficiently, initial precipitation using diethyl ether proved effective. However, due to the non-green nature of diethyl ether, we investigated more sustainable alternatives, including 2-methyltetrahydrofuran (Me-THF), dimethyl carbonate, and cyclopentyl methyl ether (CPME). As shown in Fig. 84a, these greener solvents enabled only partial precipitation of the catalyst. Although the precipitates were isolated and the filtrates evaporated, residual catalyst remained in the product mixtures, indicating incomplete separation. To achieve complete catalyst recovery, diethyl ether was subsequently added to the crude solids obtained from each green solvent, which successfully precipitated the remaining **Ru-1** catalyst (Figs. 84b–84d). These observations highlight the challenges of replacing diethyl ether in catalyst recovery and the need for further exploration of effective, green alternatives.

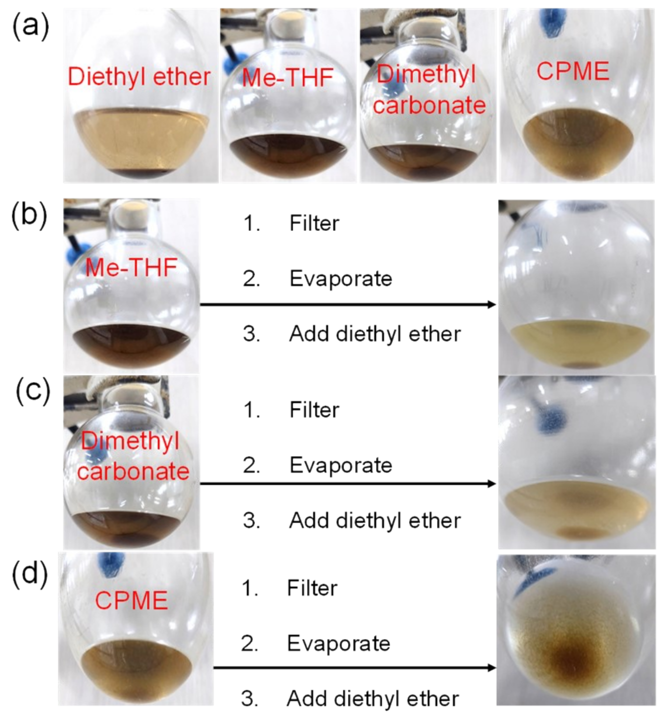


Fig. S84 Precipitation of **Ru-1** catalyst using diethyl ether, Me-THF, dimethyl carbonate, and CPME.

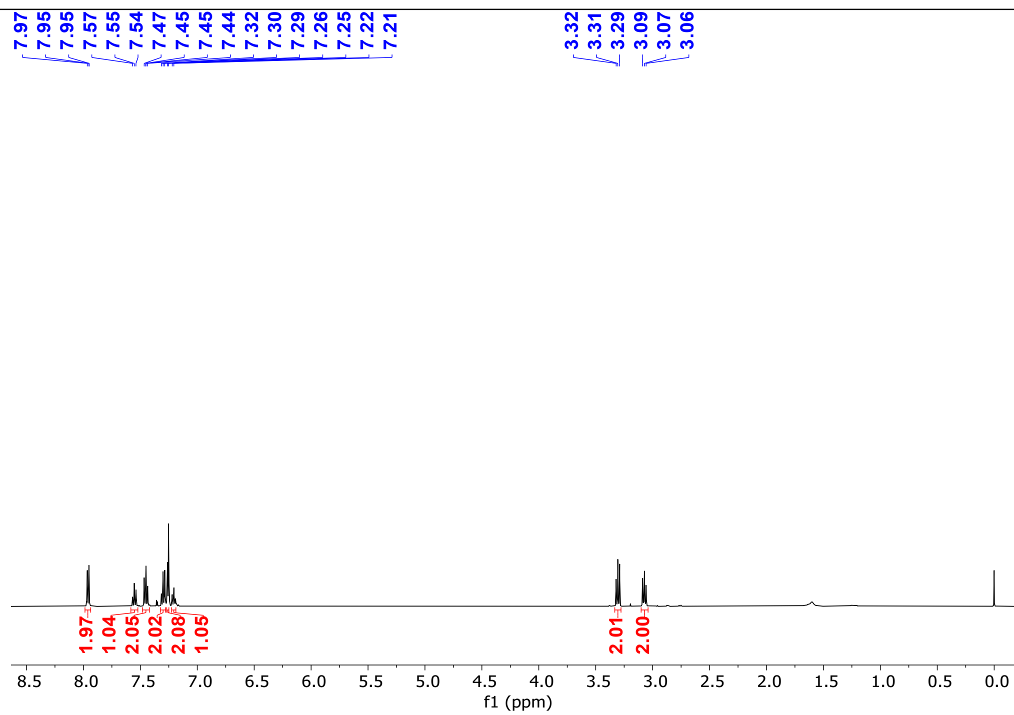


Fig. S85 ^{1}H NMR of **1b** in $CDCl_3$ at 298K.

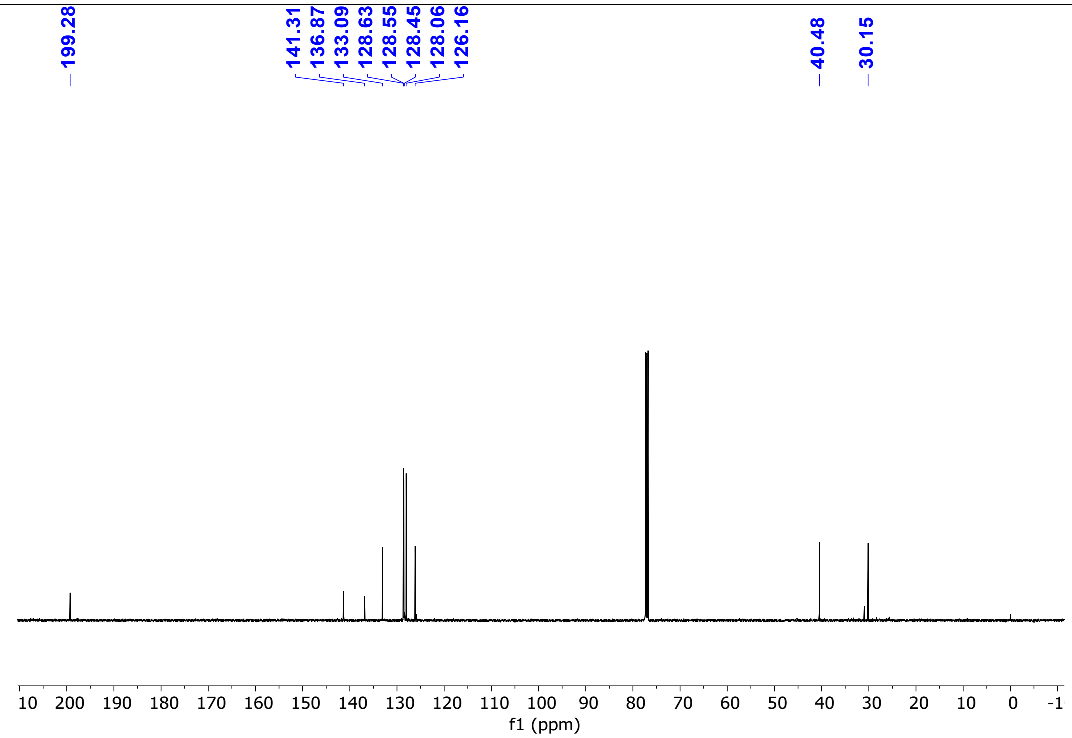


Fig. S86 ^{13}C NMR of **1b** in $CDCl_3$ at 298K.

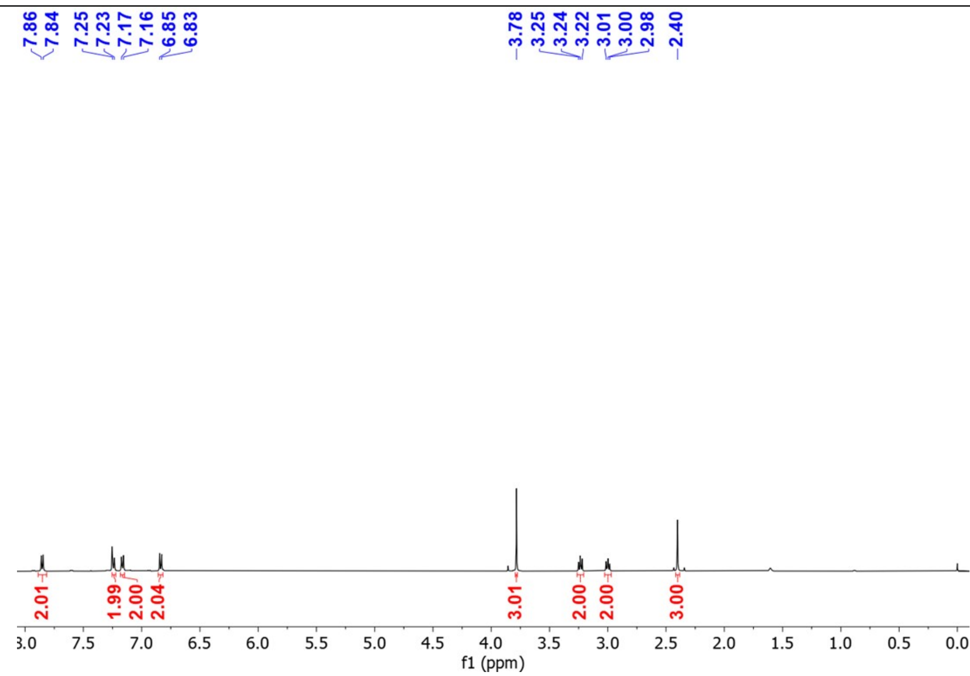


Fig. S87 ^{1}H NMR of **2b** in $CDCl_3$ at 298K.

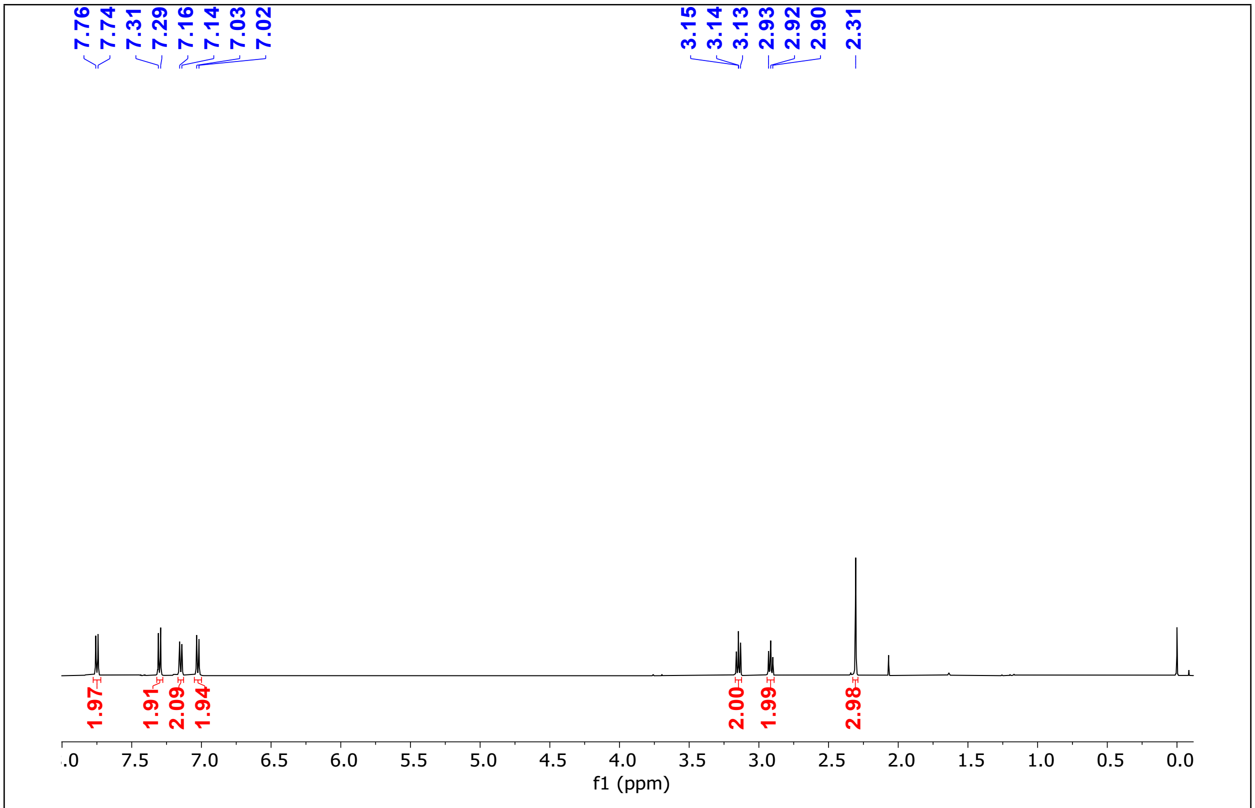


Fig. S88 ^{1}H NMR of **8b** in $CDCl_3$ at 298K.

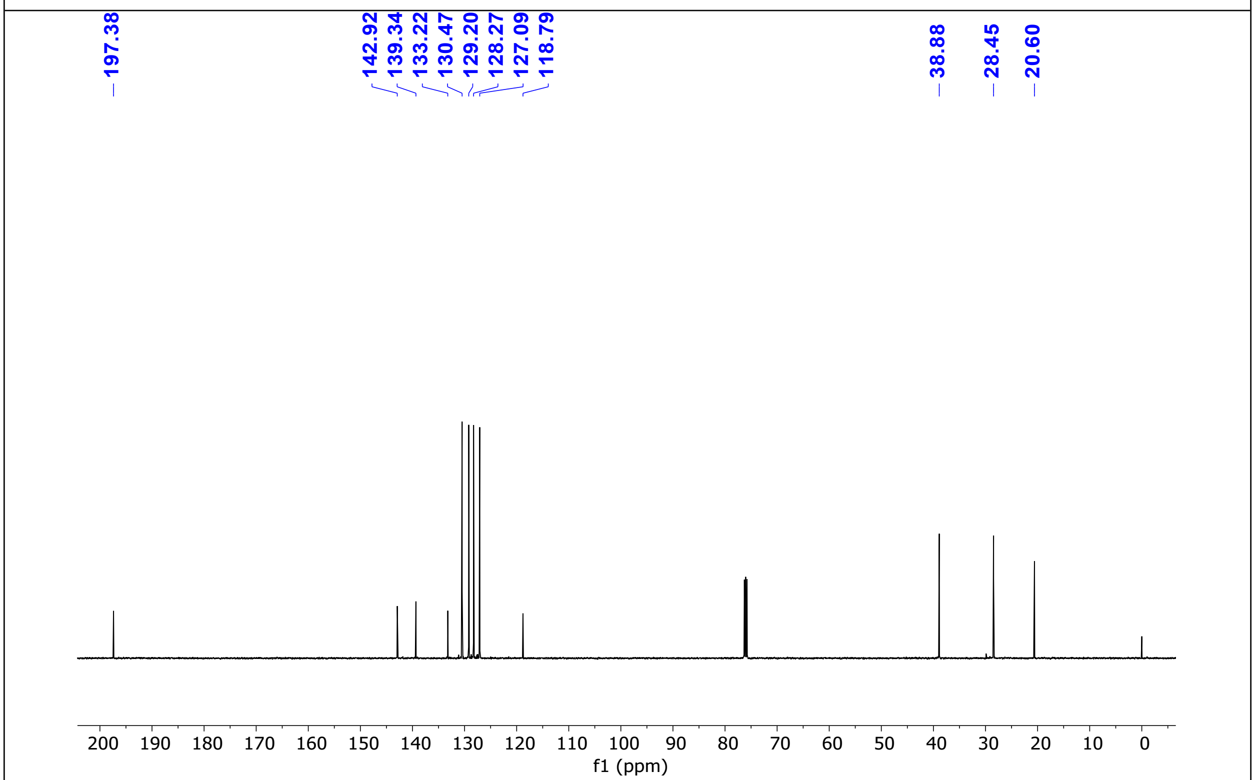


Fig.S89 ^{13}C NMR of **8b** in $CDCl_3$ at 298K.

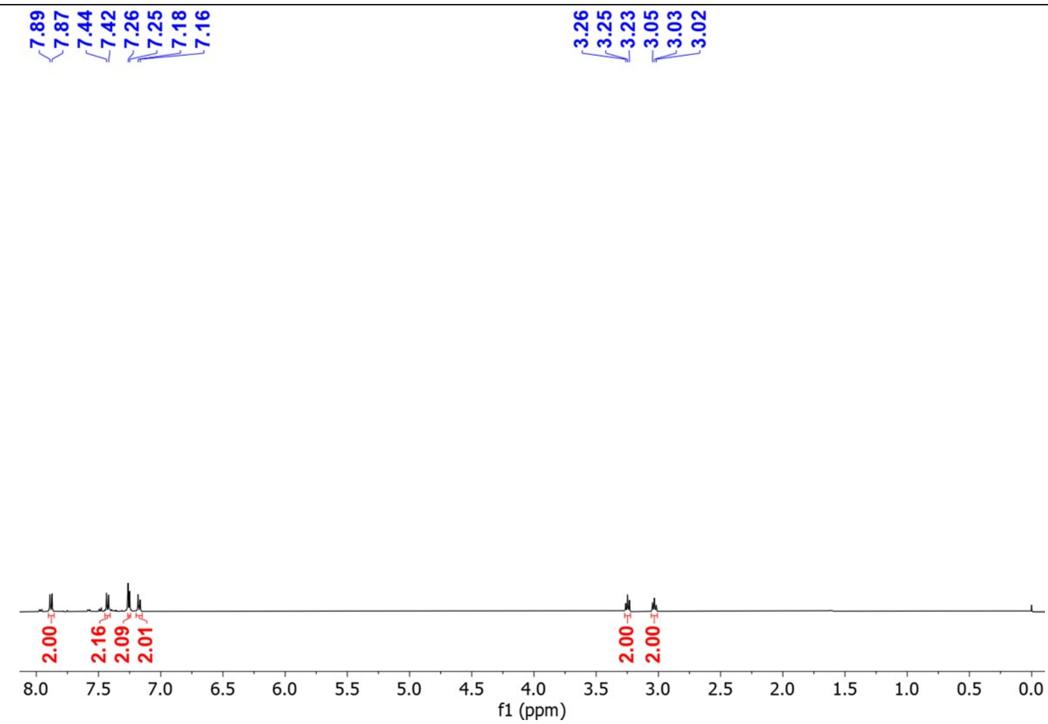


Fig. S90 ^{1}H NMR of **11b** in $CDCl_3$ at 298K.

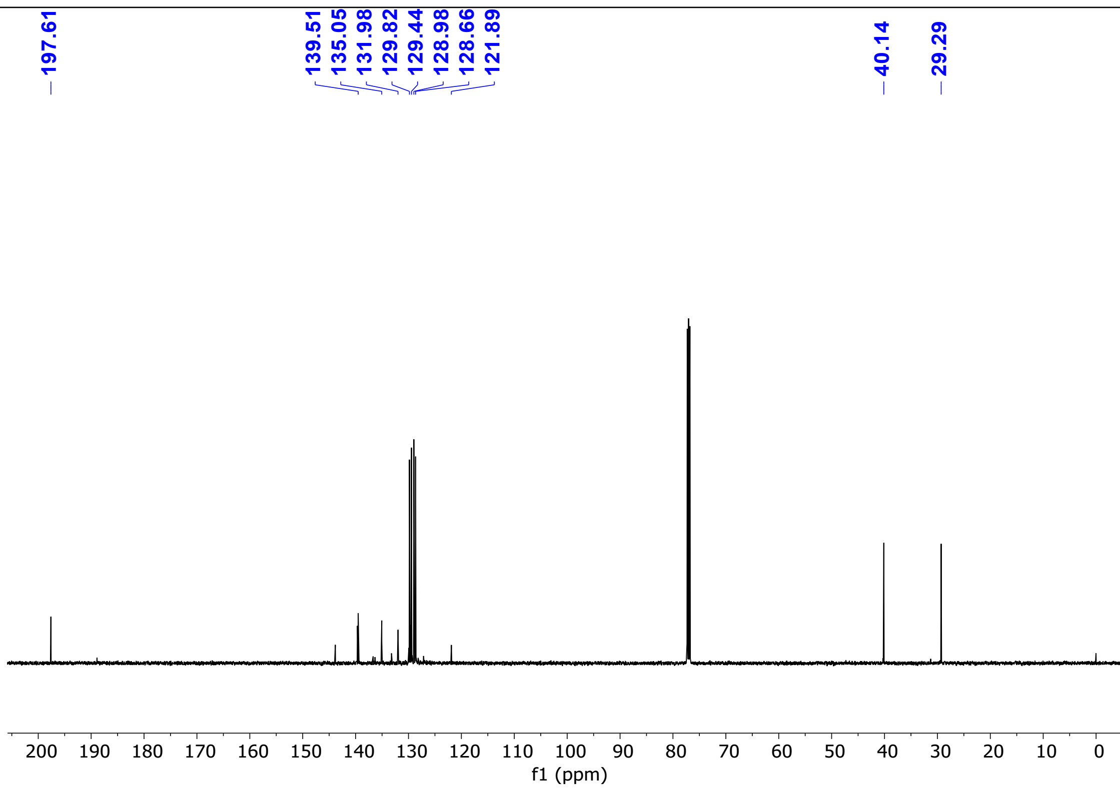


Fig. S91 ^{13}C NMR of **11b** in $CDCl_3$ at 298K.

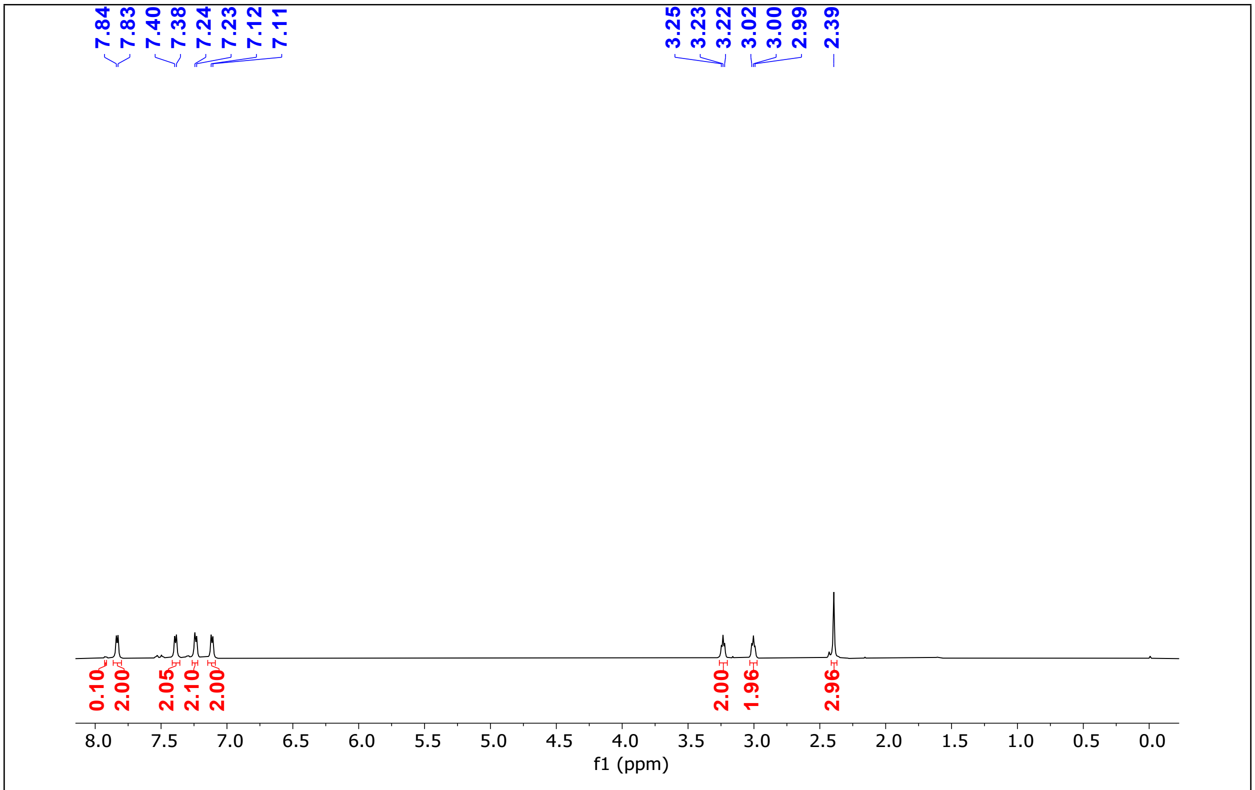


Fig. S92 ^{1}H NMR of **14b** in $CDCl_3$ at 298K.

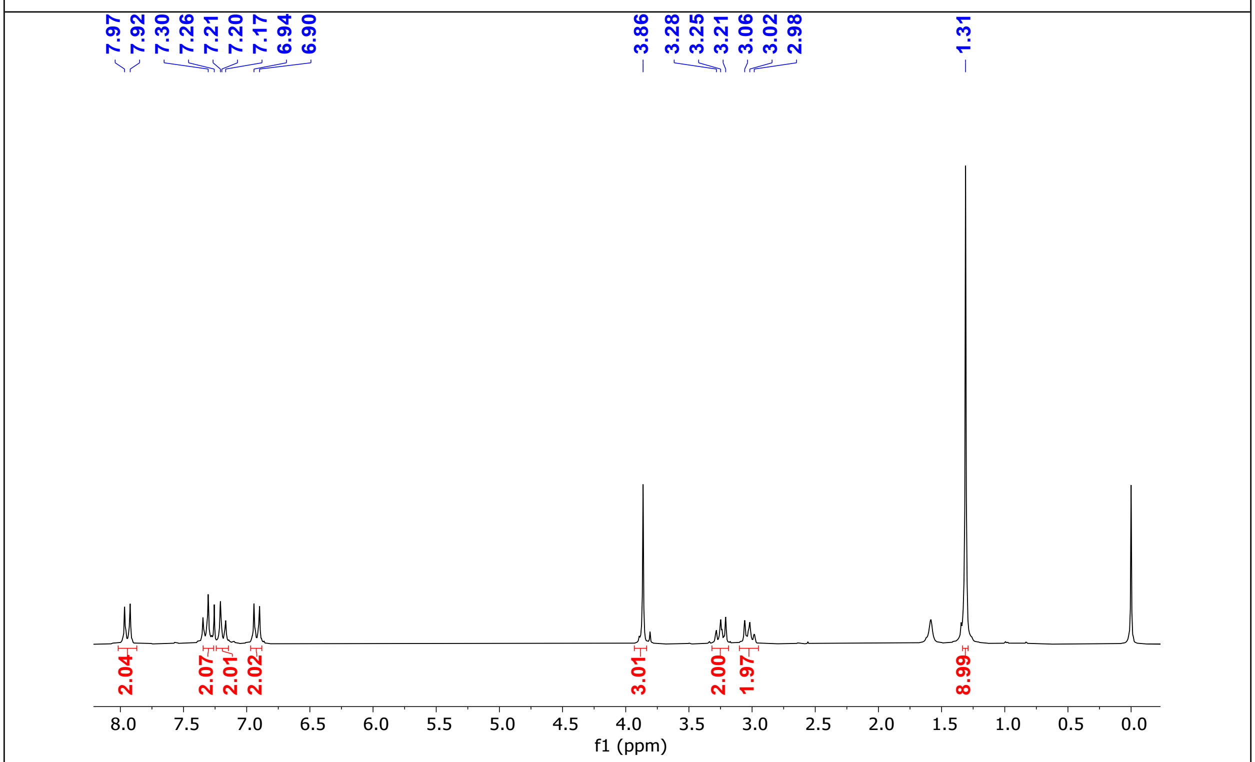


Fig. S93 ^{1}H NMR of **15b** in $CDCl_3$ at 298K.

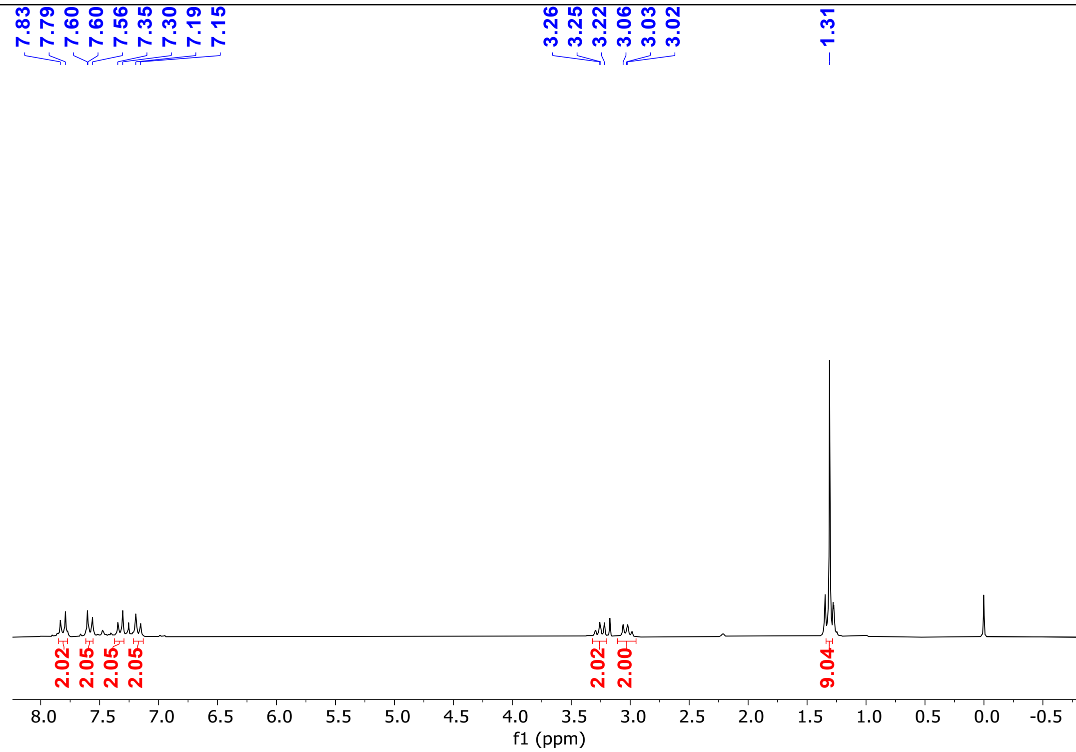


Fig. S94 ^{1}H NMR of **16b** in $CDCl_3$ at 298K.

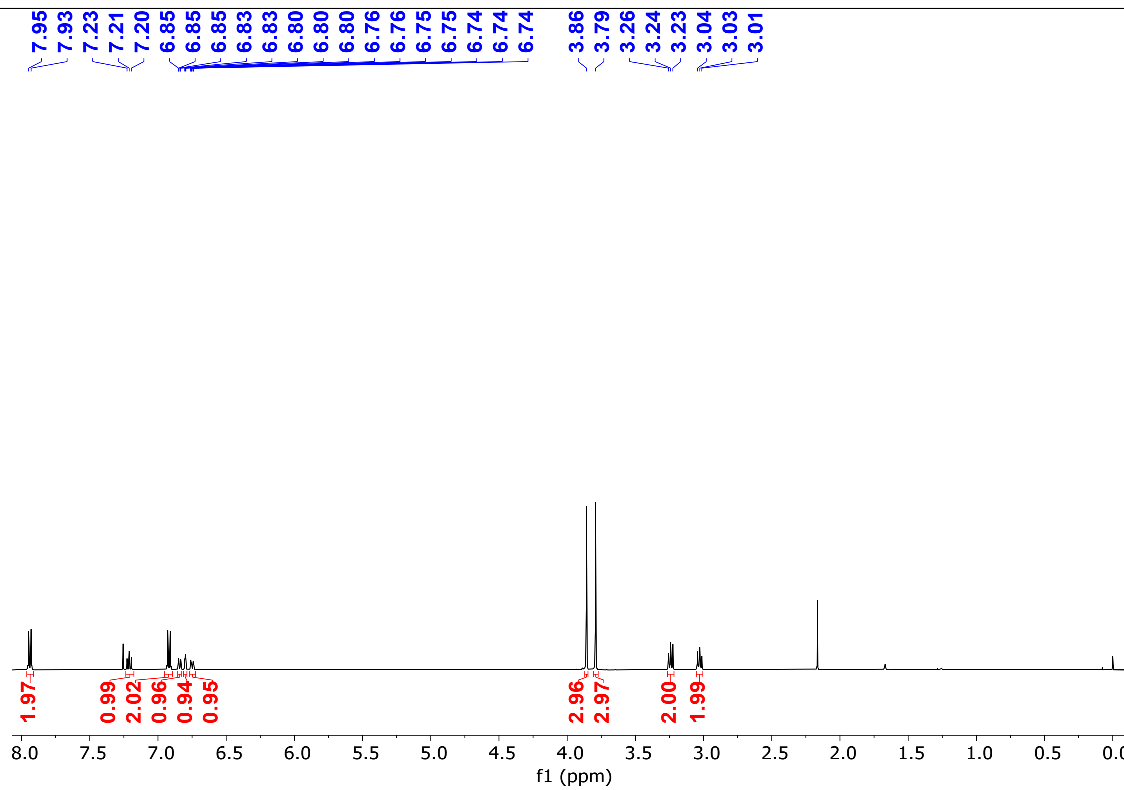


Fig. S95 ^{1}H NMR of **17b** in $CDCl_3$ at 298K.

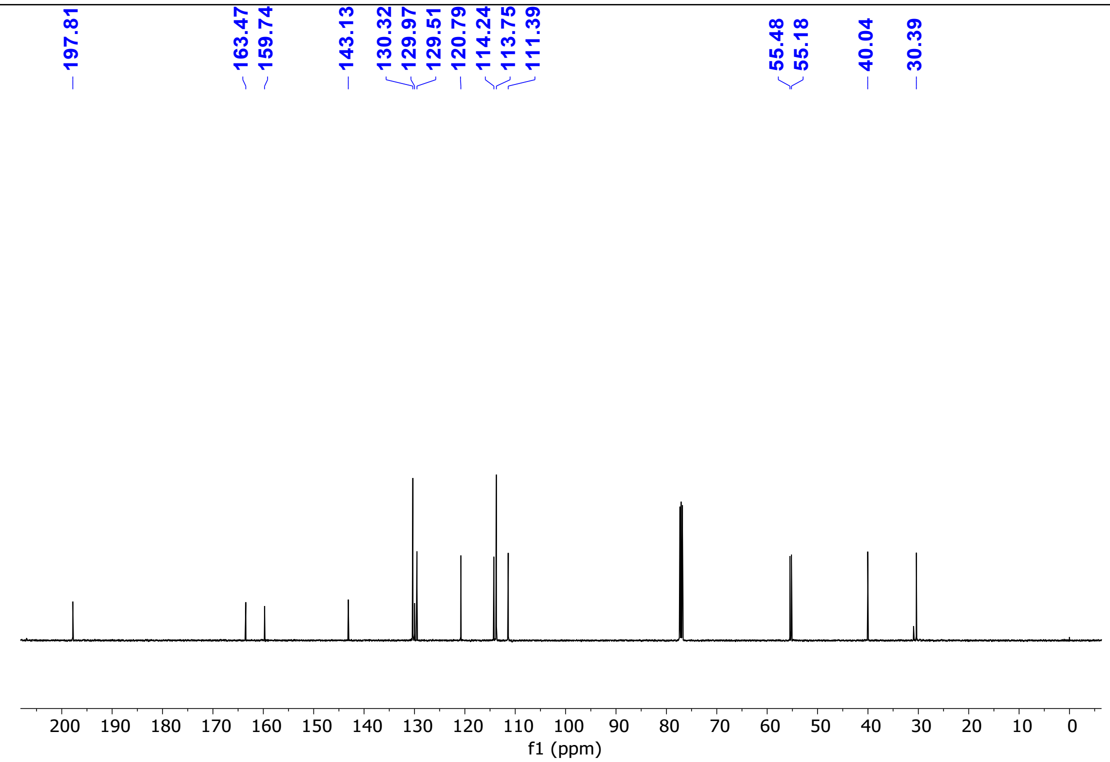


Fig. S96 ^{13}C NMR of **17b** in $CDCl_3$ at 298K.

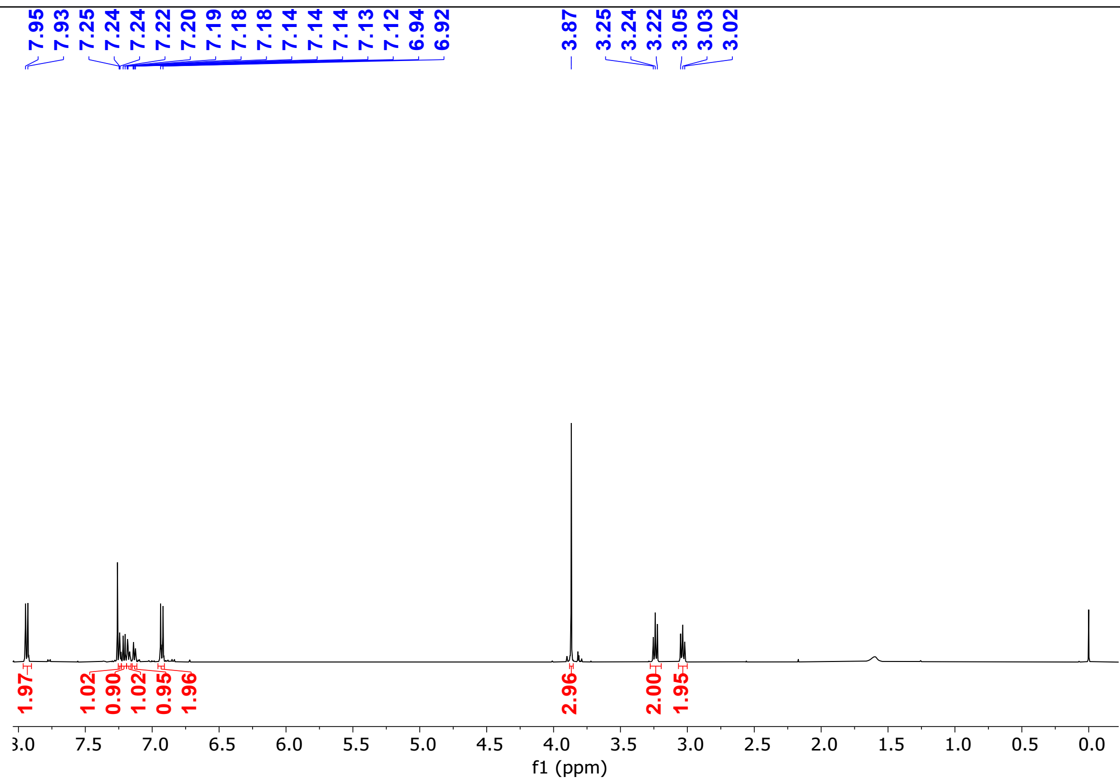


Fig. S97 ^{1}H NMR of **19b** in $CDCl_3$ at 298K.

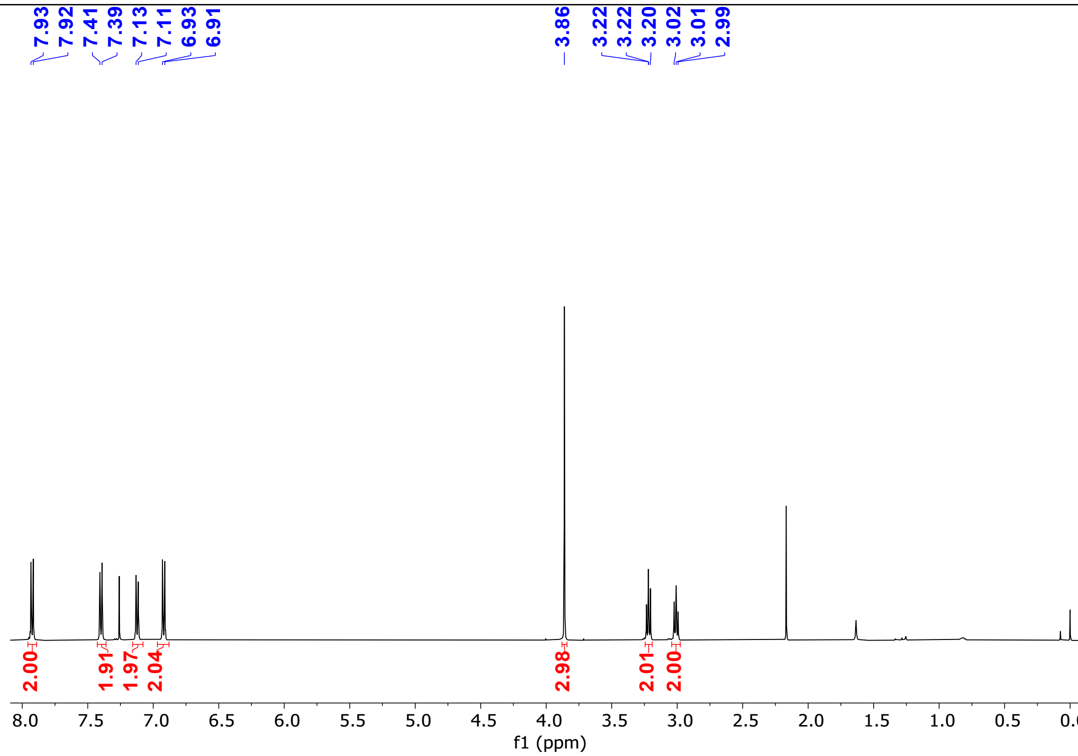


Fig. S98 ^{1}H NMR of **20b** in $CDCl_3$ at 298K.

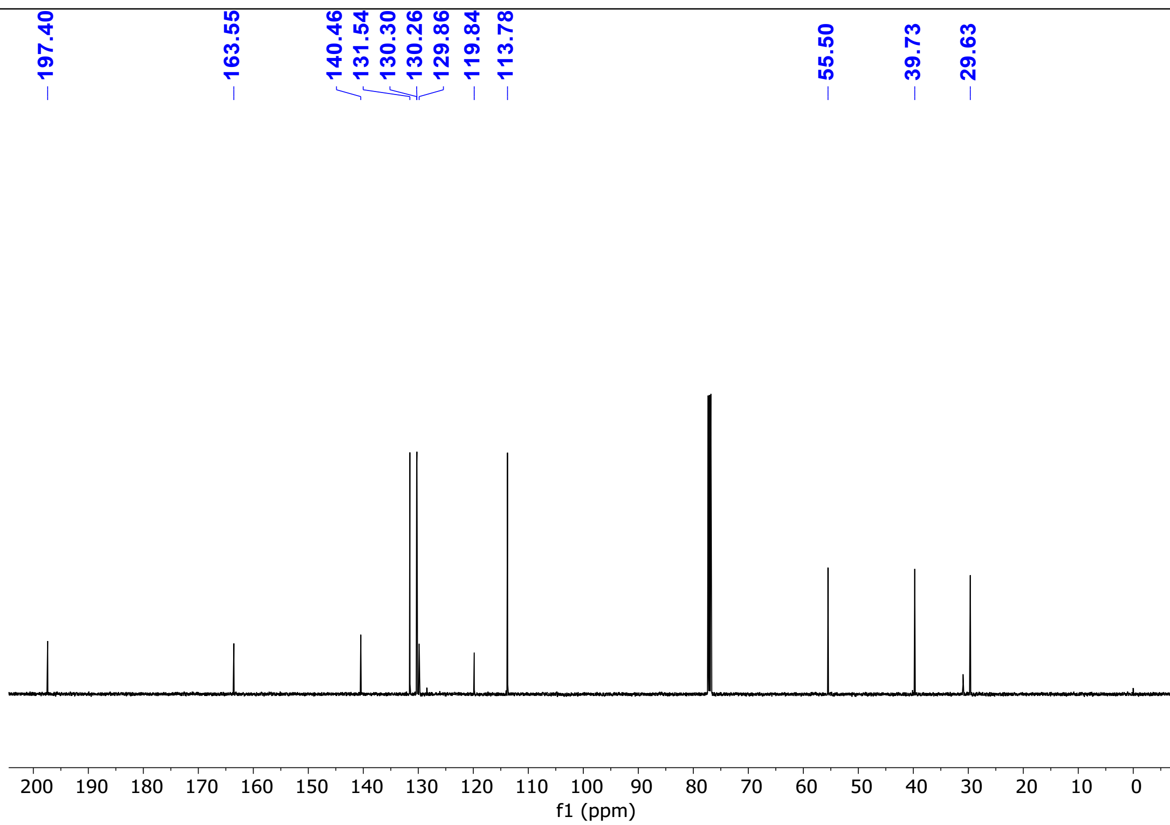


Fig. S99 ^{13}C NMR of **20b** in $CDCl_3$ at 298K.

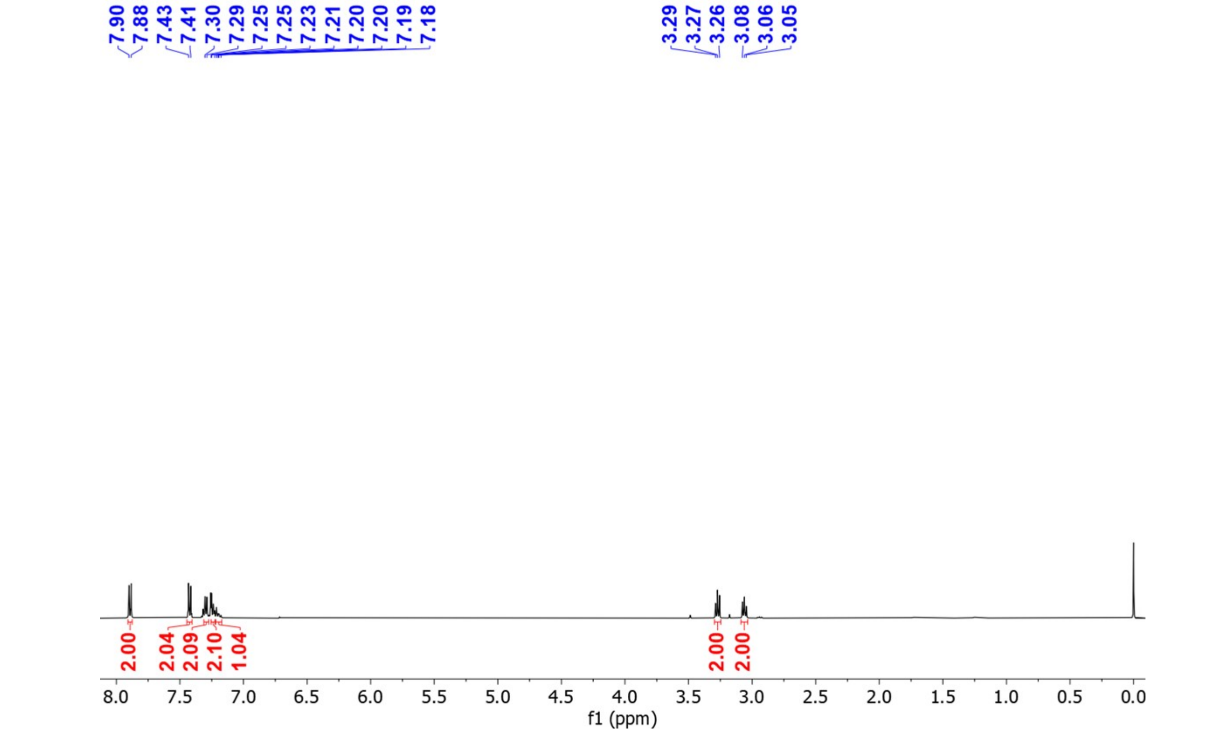


Fig. S100 ^{1}H NMR of **23b** in $CDCl_3$ at 298K.

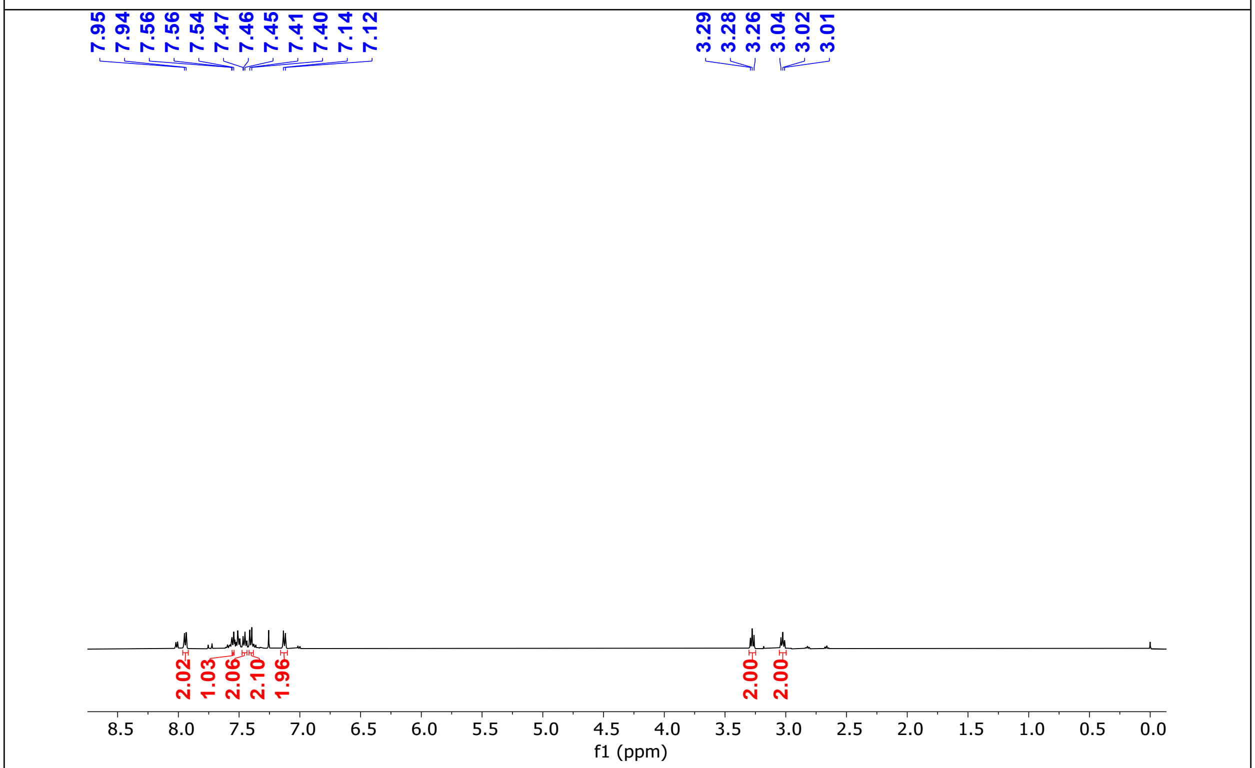


Fig. S101 ^{1}H NMR of **25b** in $CDCl_3$ at 298K.

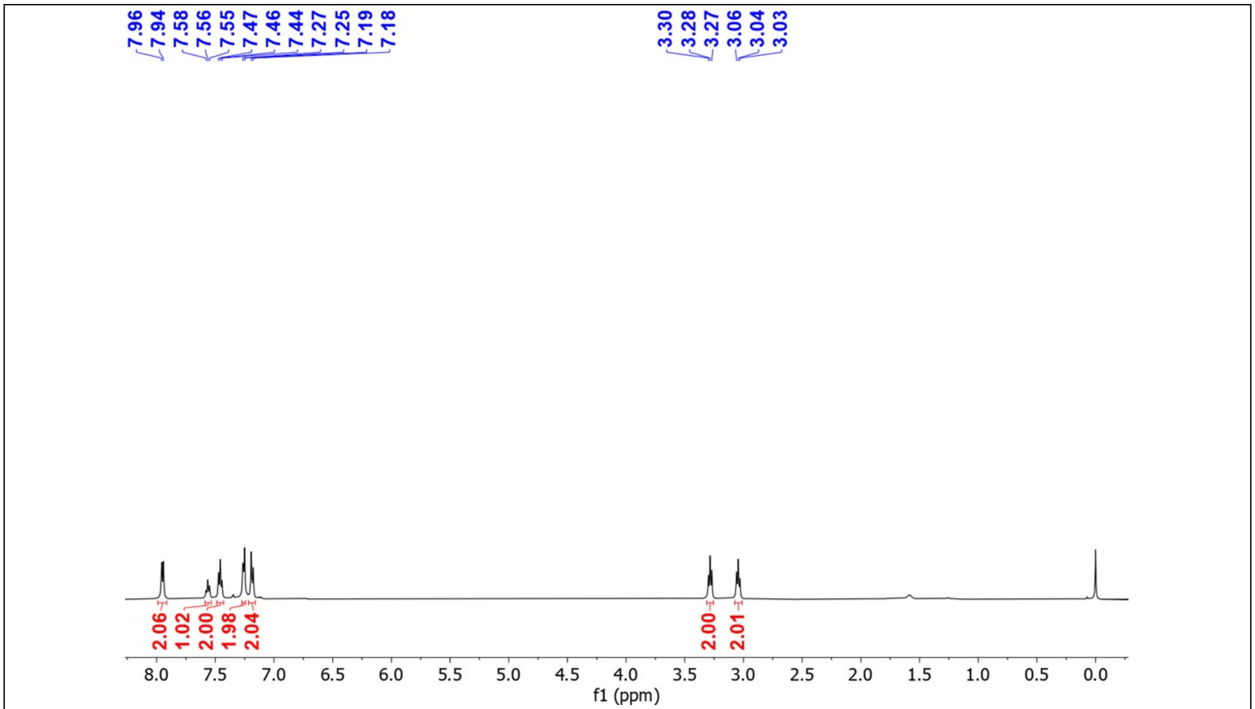
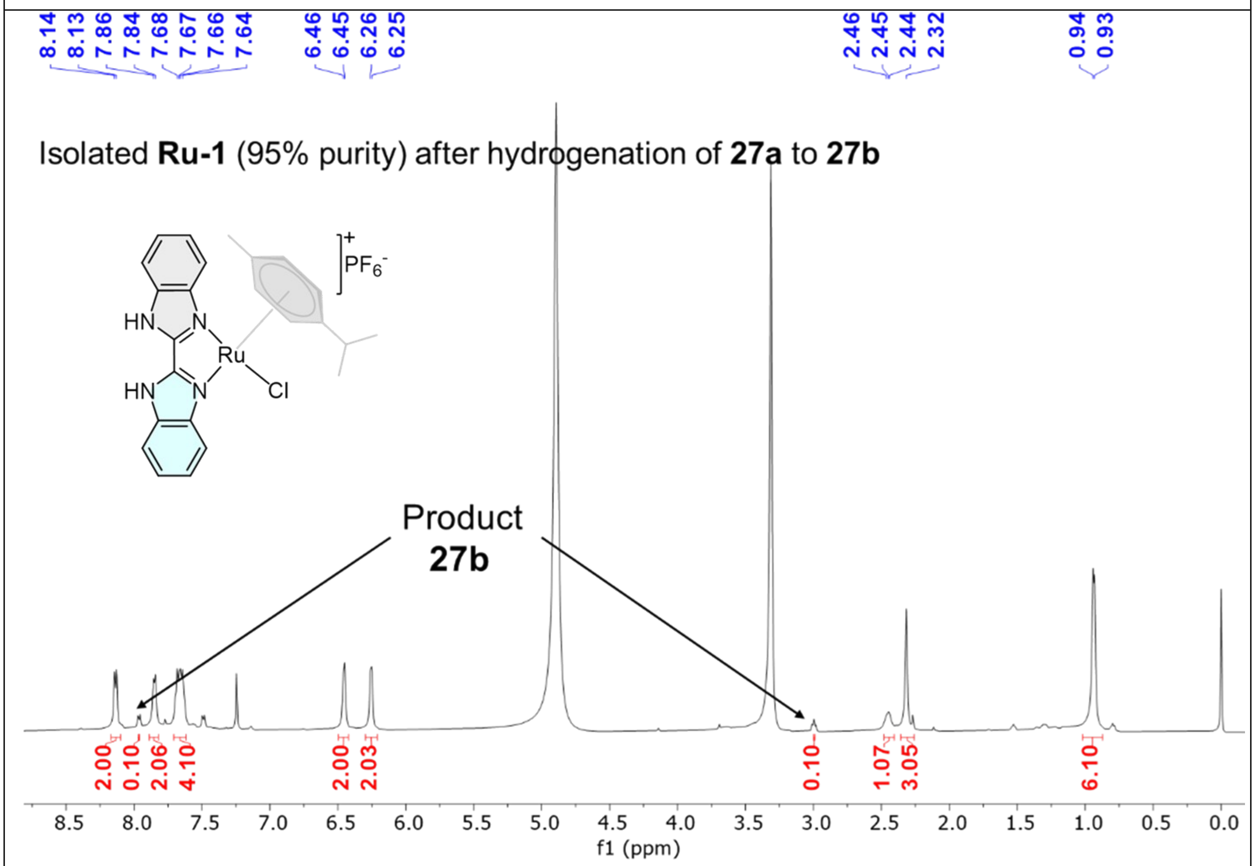


Fig. S102 ^{1}H NMR of **27b** in $CDCl_3$ at 298K.



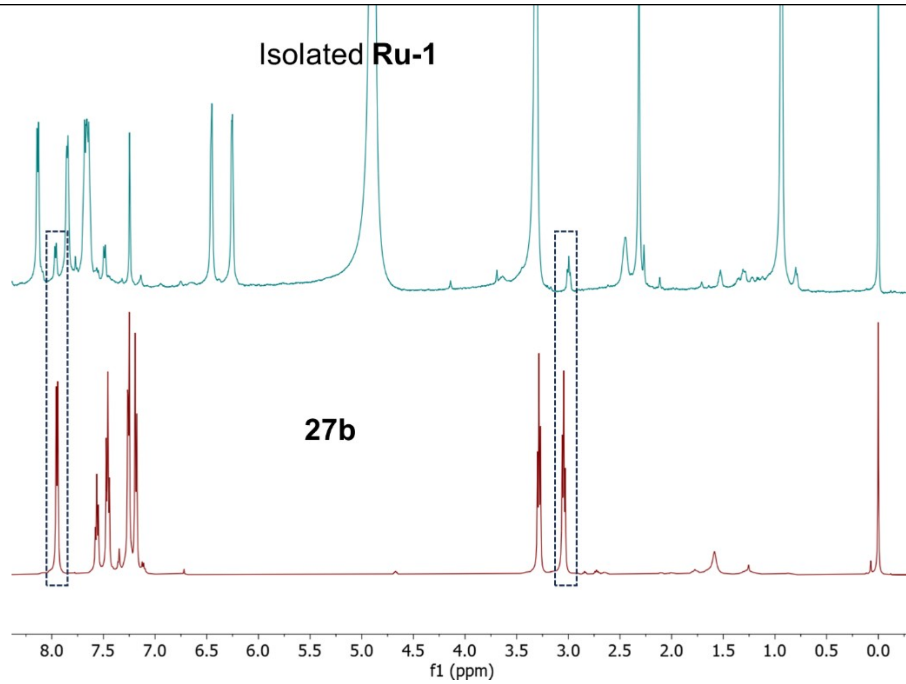


Fig. S103 ^{1}H NMR of recovered **Ru-1** (95% purity) after hydrogenation of **27a** to **27b**

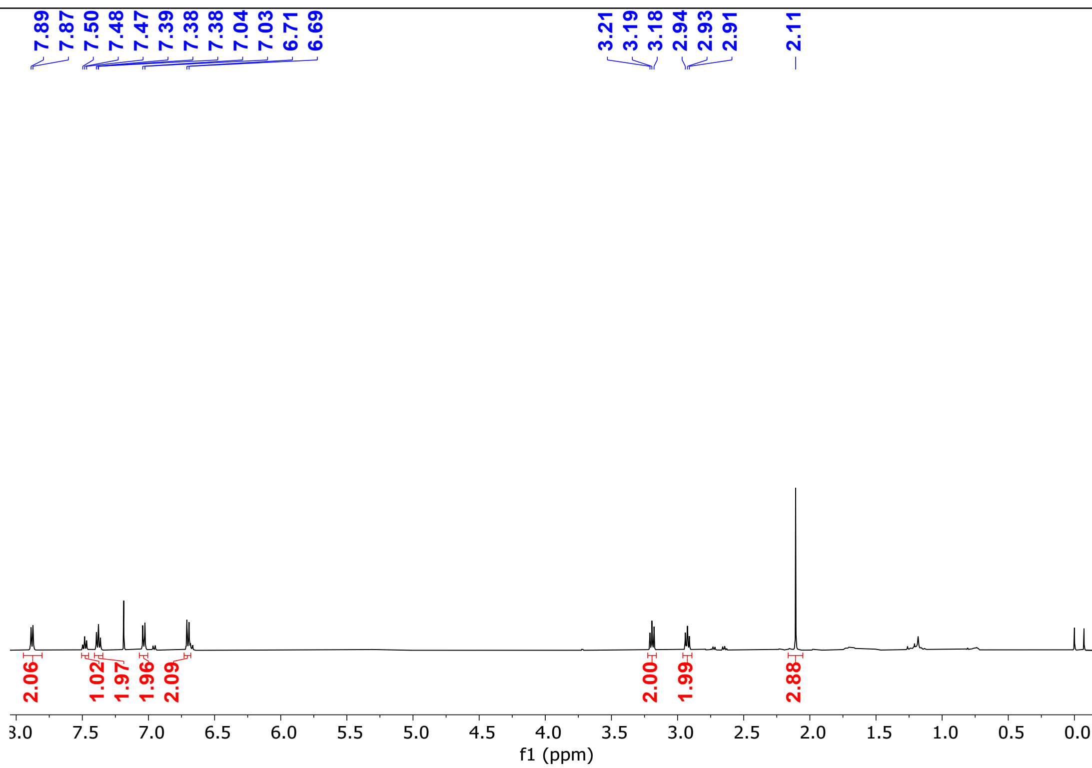


Fig. S104 ^{1}H NMR of **28b** in $CDCl_3$ at 298K.

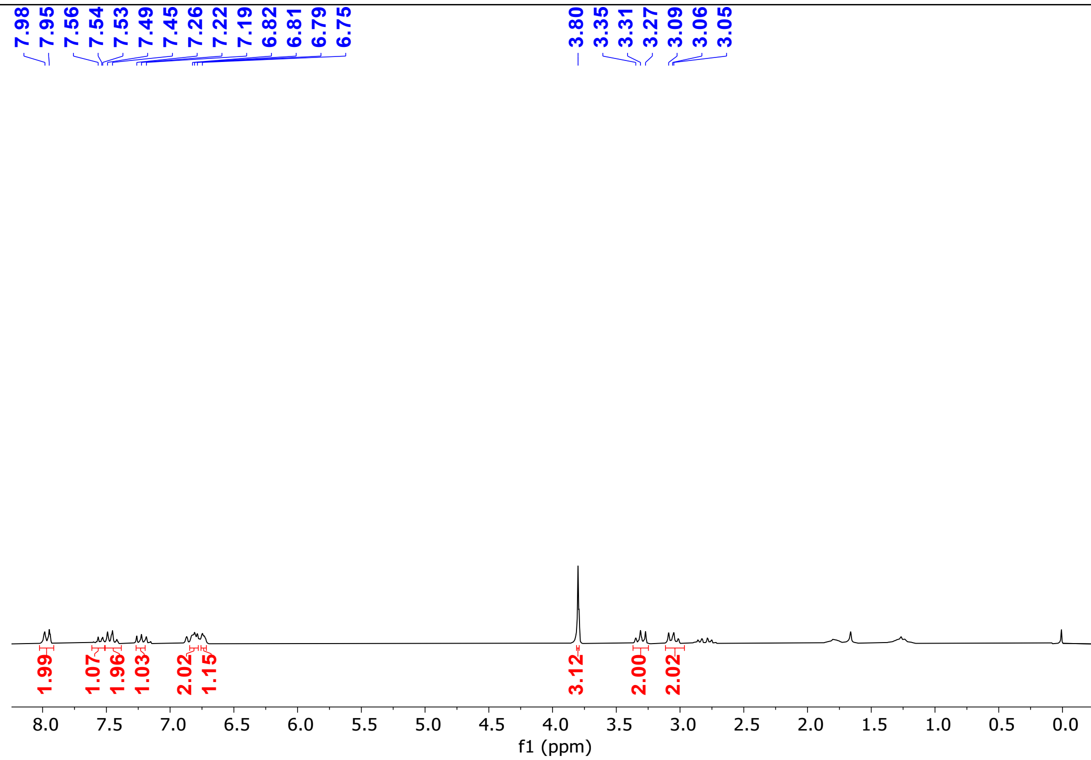


Fig. S105 ^{1}H NMR of **30b** in $CDCl_3$ at 298K.

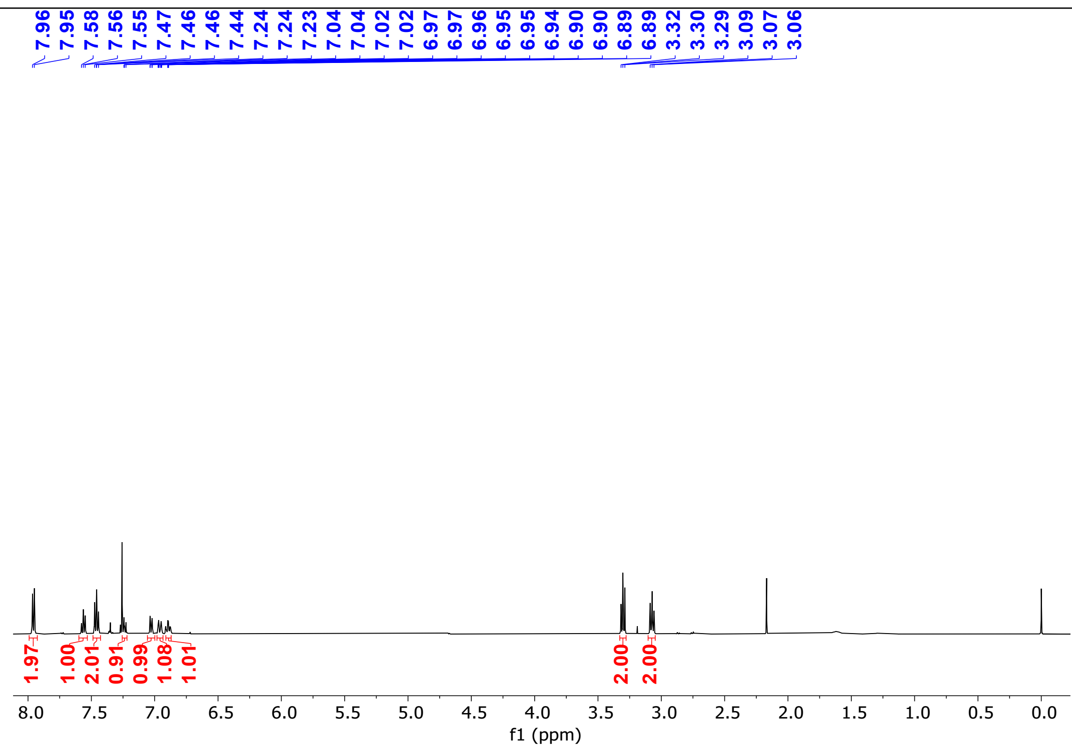


Fig. S106 ^{1}H NMR of **31b** in $CDCl_3$ at 298K.

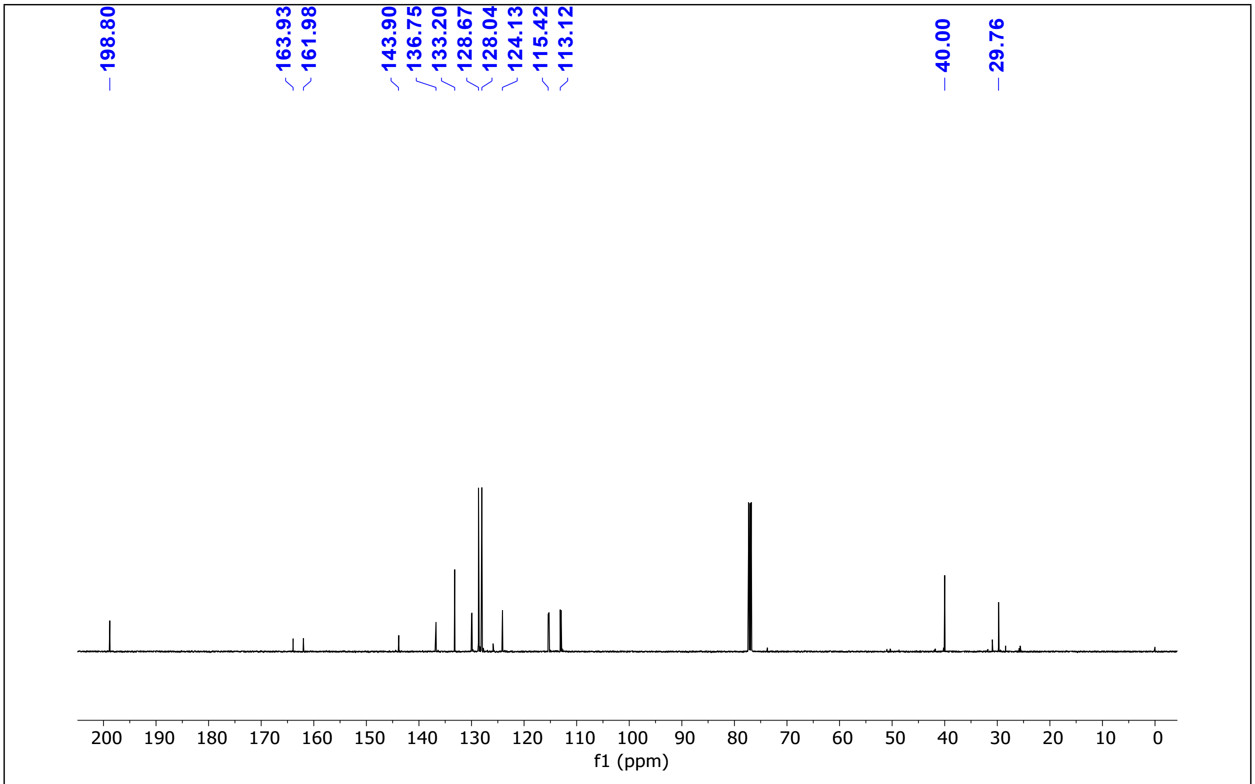


Fig. S107 ^{13}C NMR of **31b** in $CDCl_3$ at 298K.

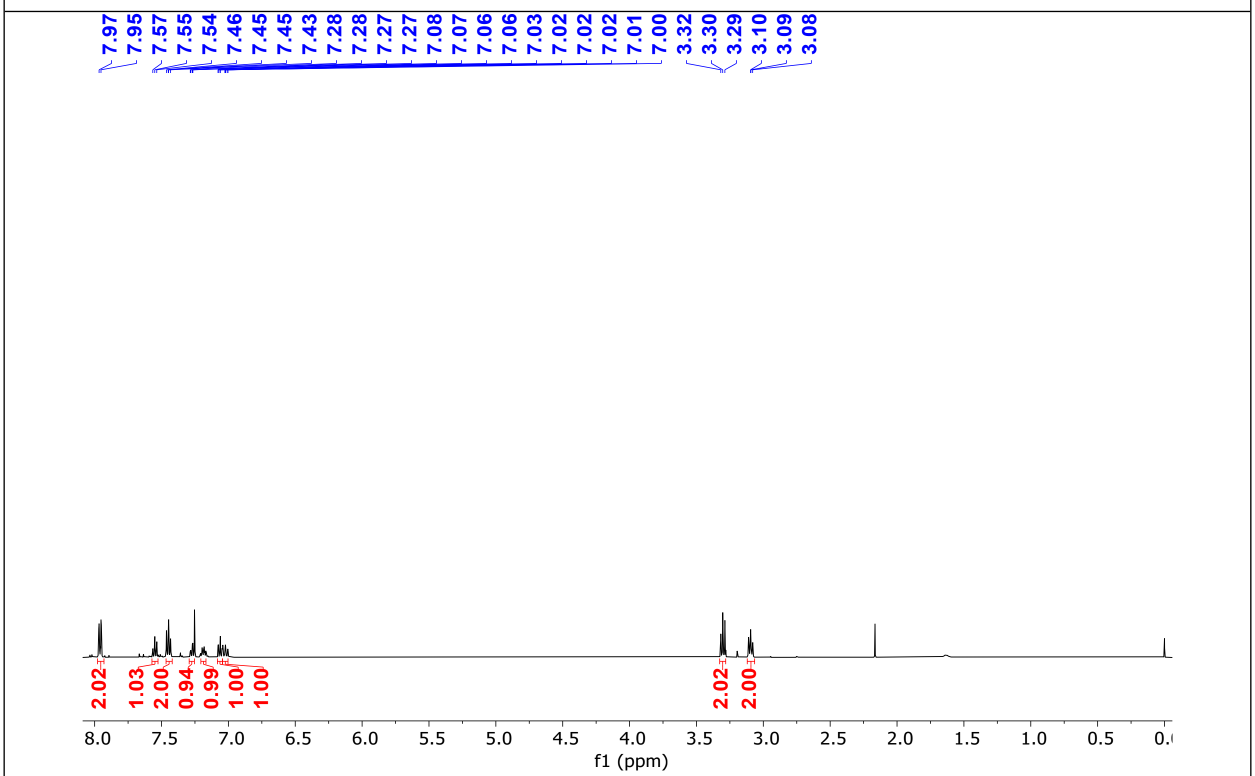


Fig. S108 ^{1}H NMR of **33b** in $CDCl_3$ at 298K.

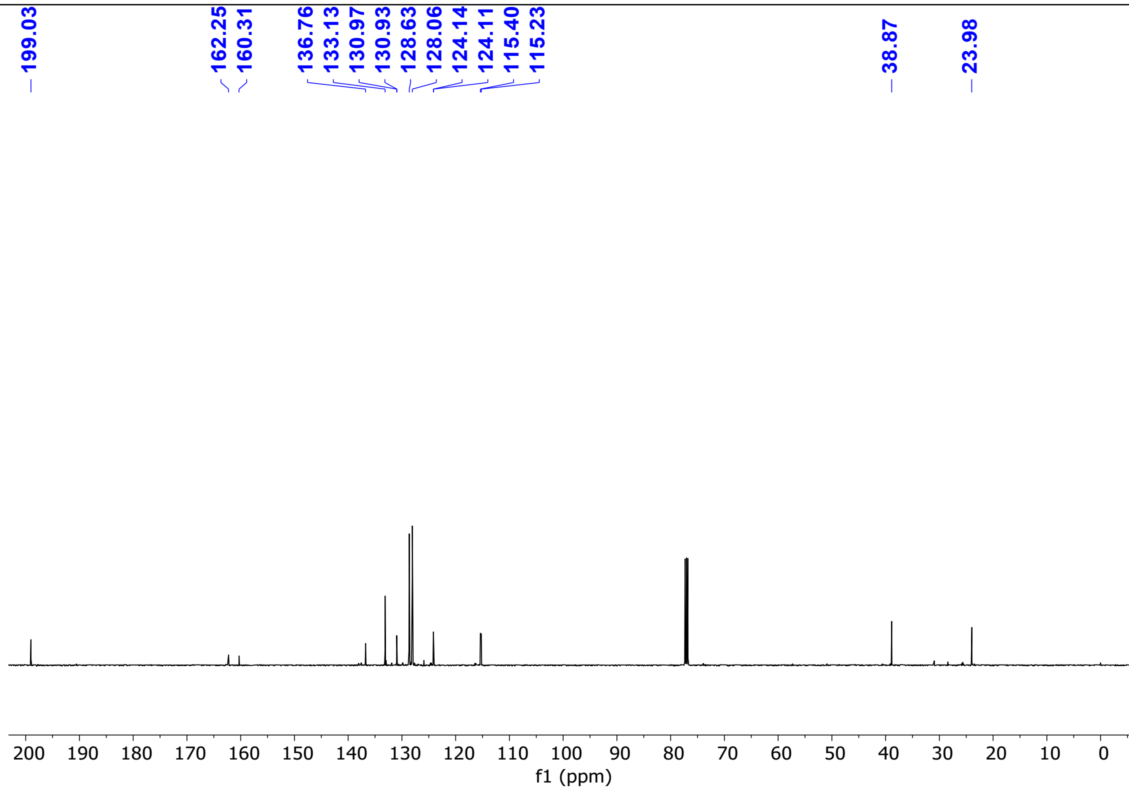


Fig. S109 ^{13}C NMR of **33b** in $CDCl_3$ at 298K.

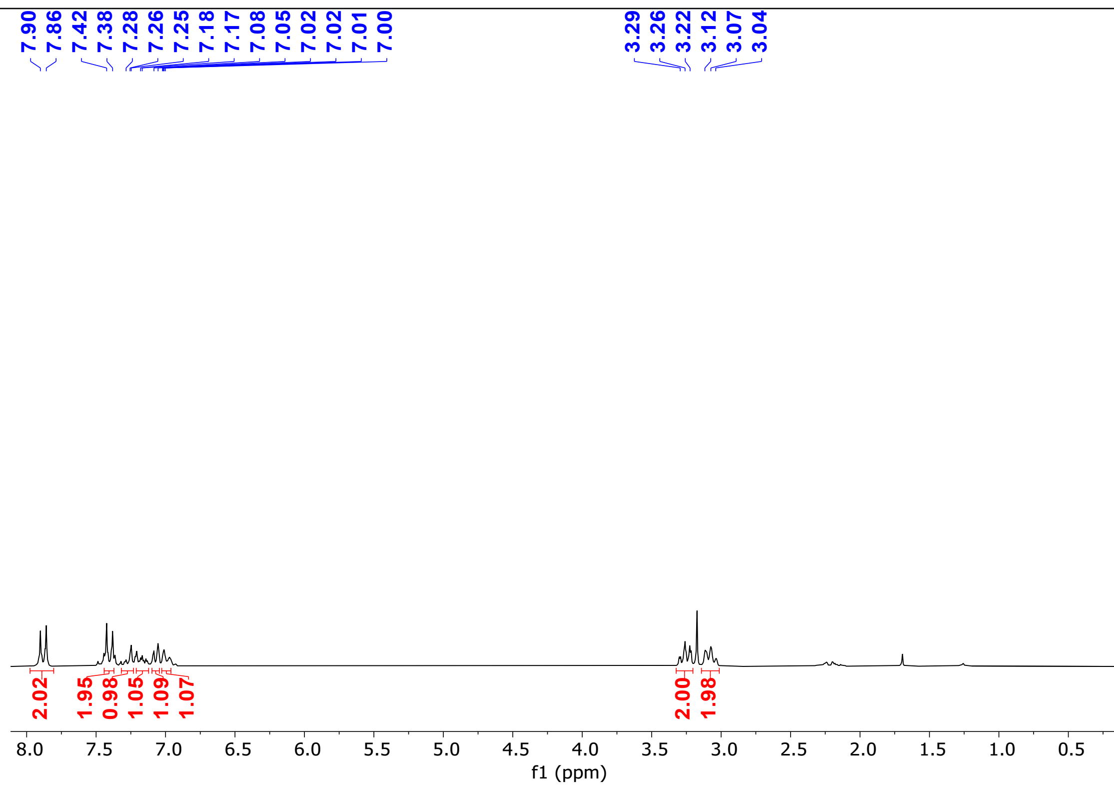


Fig. S110 ^{1}H NMR of **34b** in $CDCl_3$ at 298K.

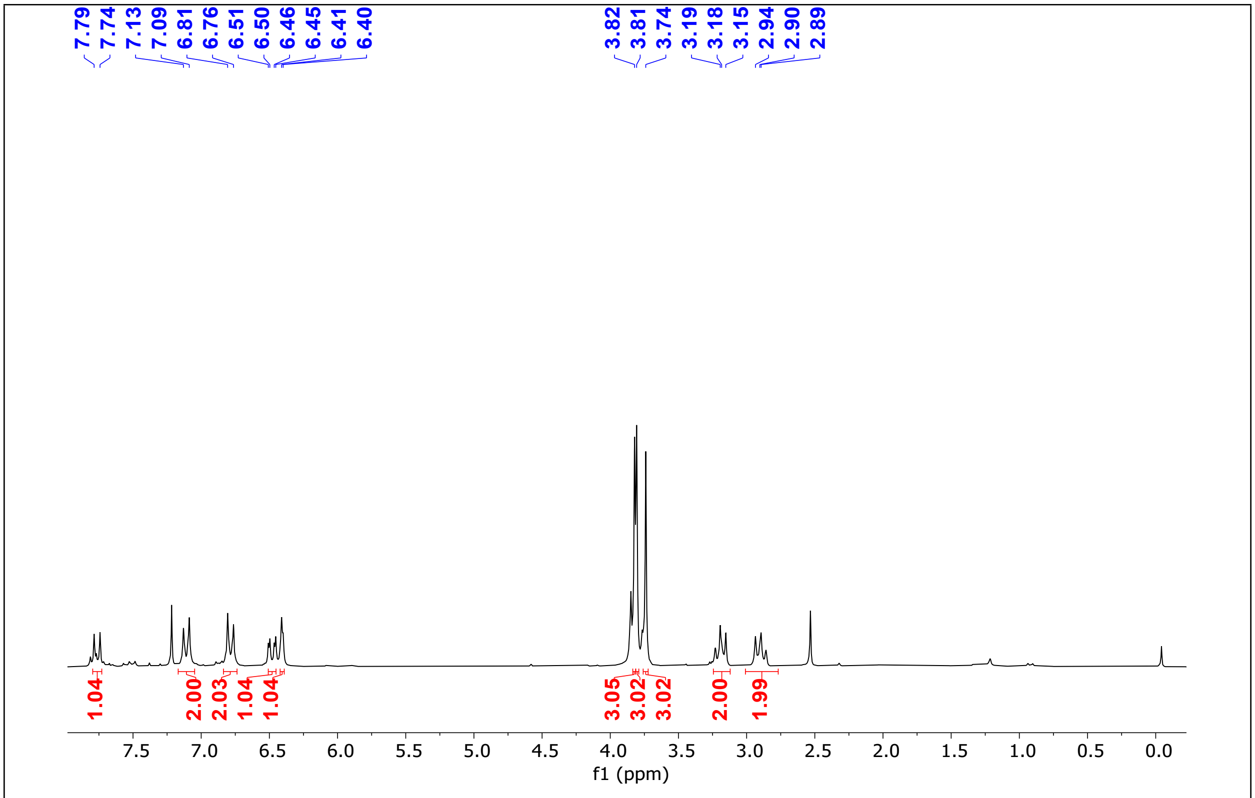


Fig. S111 ^{1}H NMR of **35b** in $CDCl_3$ at 298K.

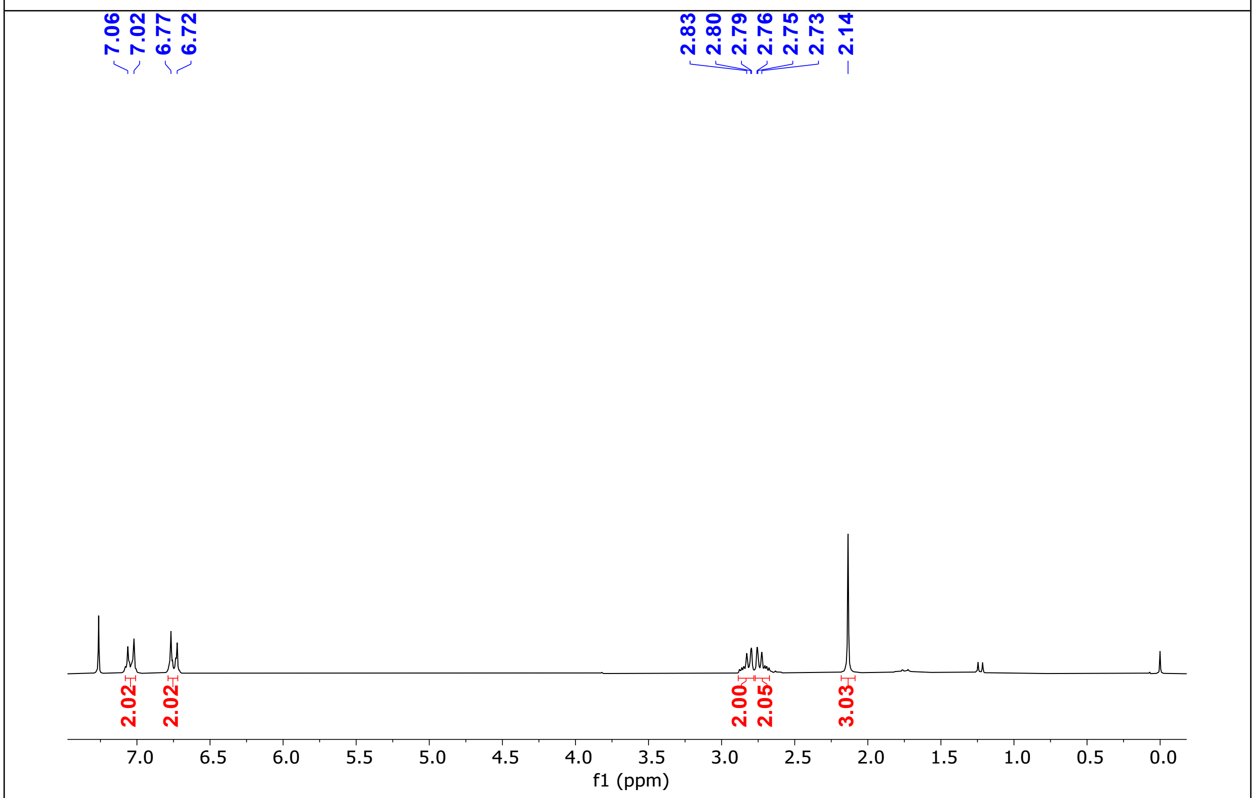


Fig. S112 ^{1}H NMR of **37b** in $CDCl_3$ at 298K.

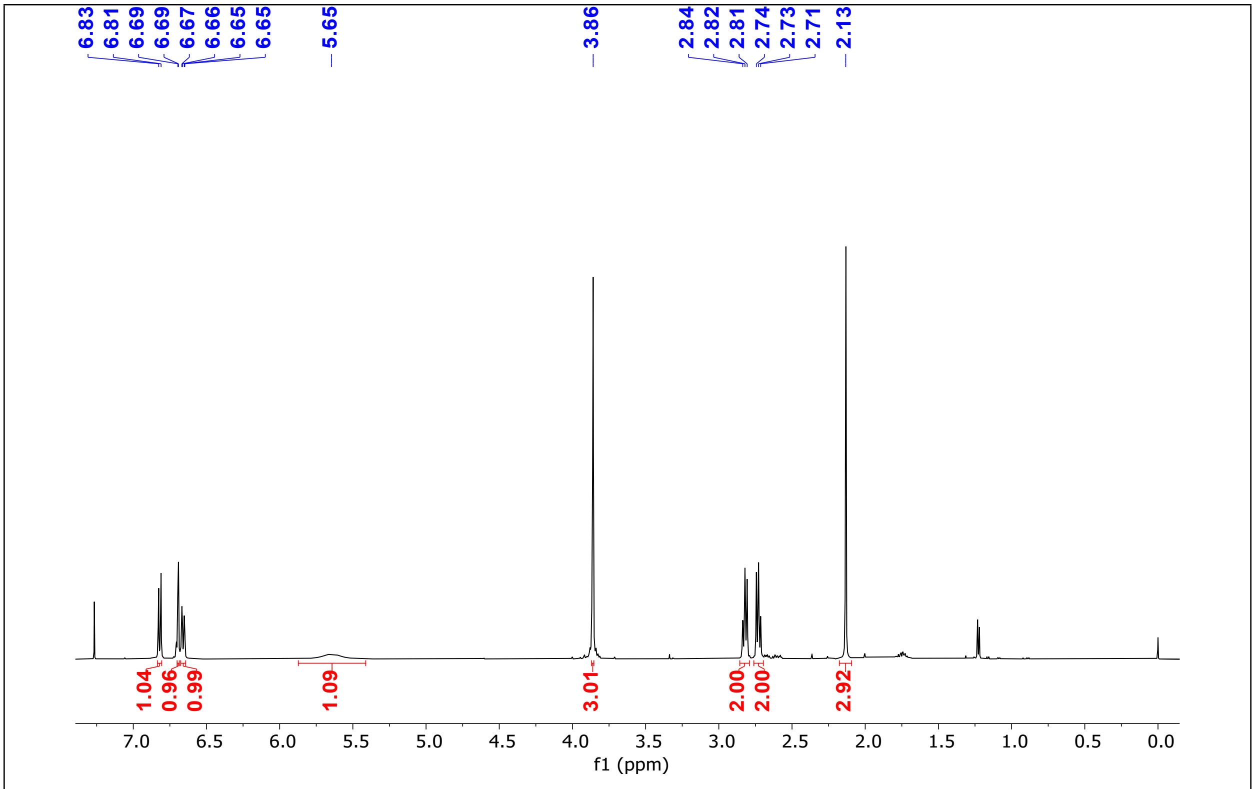


Fig. S113 ^{1}H NMR of **38b** in $CDCl_3$ at 298K.

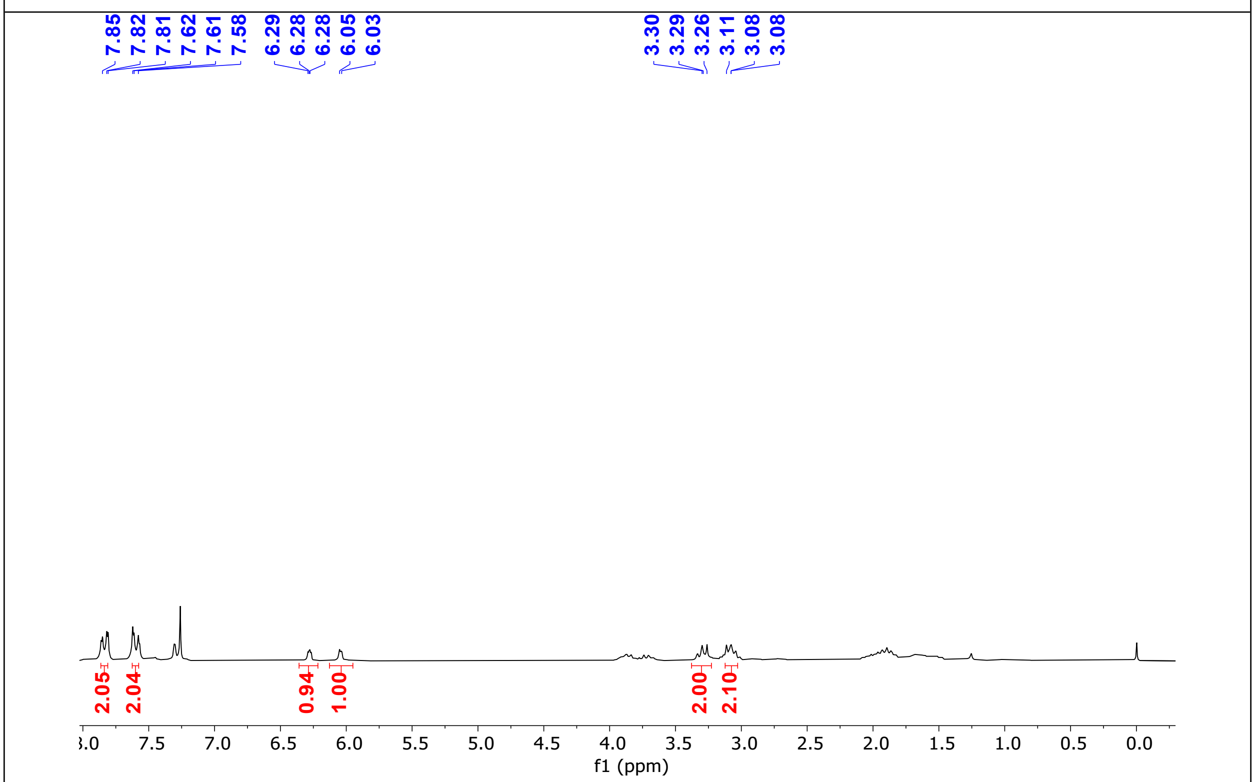


Fig. S114 ^{1}H NMR of **42b** in $CDCl_3$ at 298K.

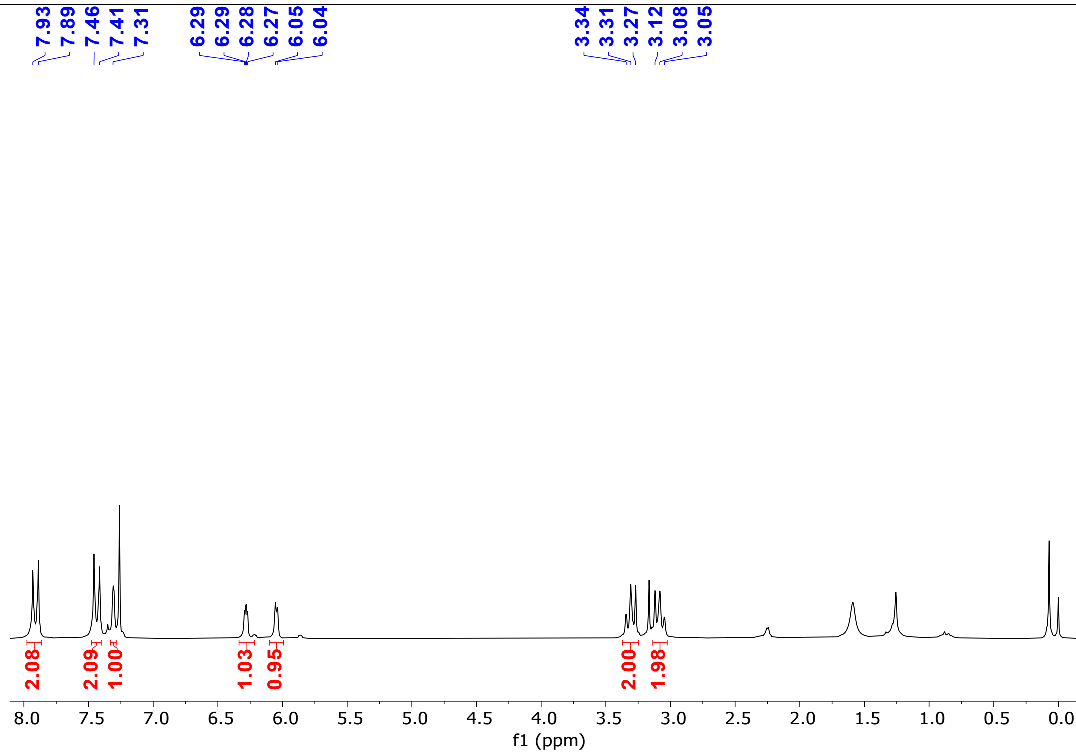


Fig. S115 ^{1}H NMR of **43b** in $CDCl_3$ at 298K.

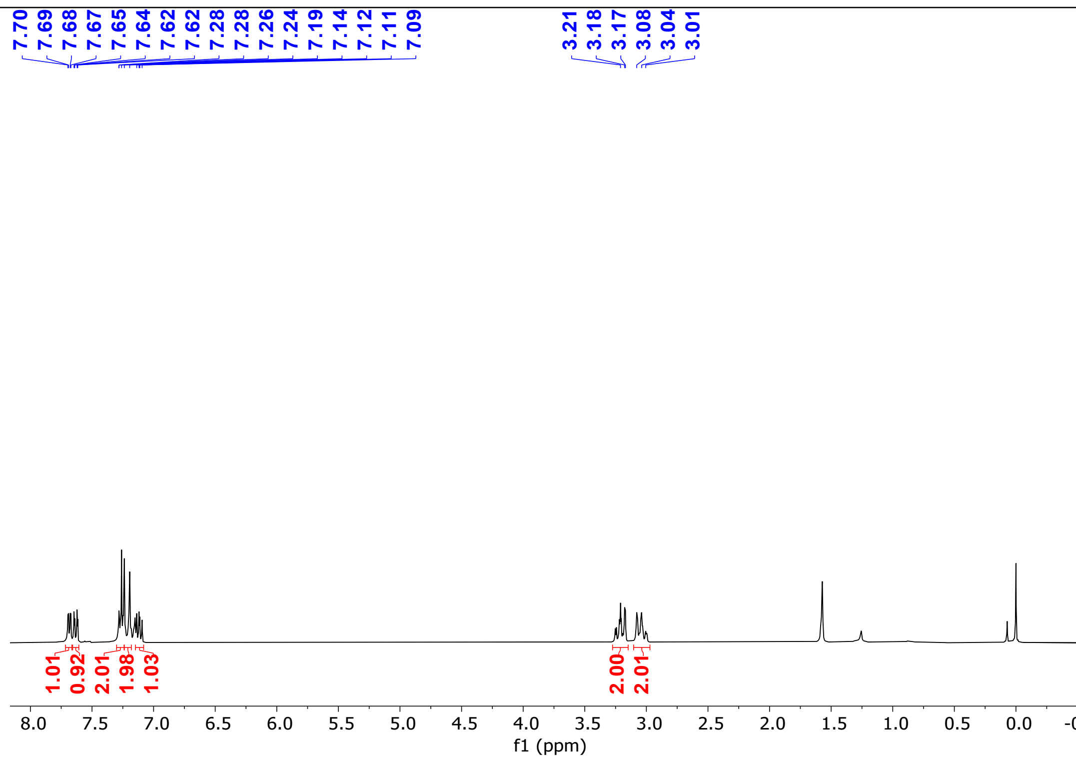


Fig. S116 ^{1}H NMR of **48b** in $CDCl_3$ at 298K.

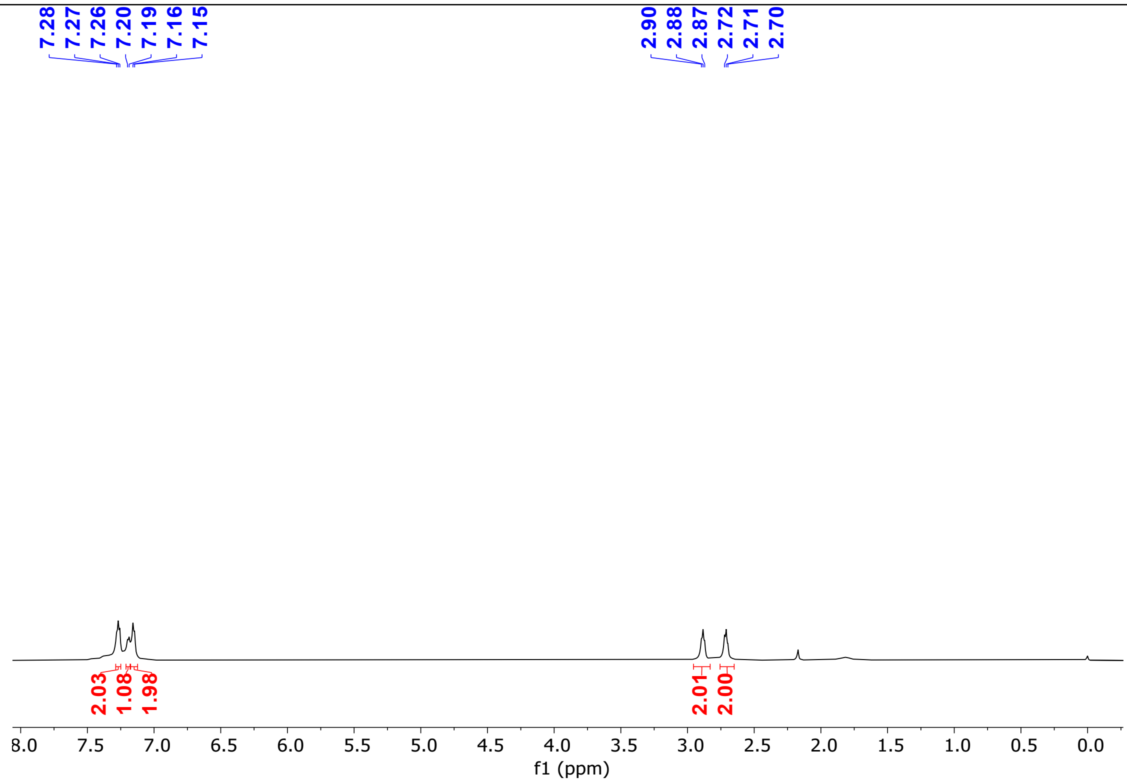


Fig. S117 ^1H NMR of **1f** in $CDCl_3$ at 298K.

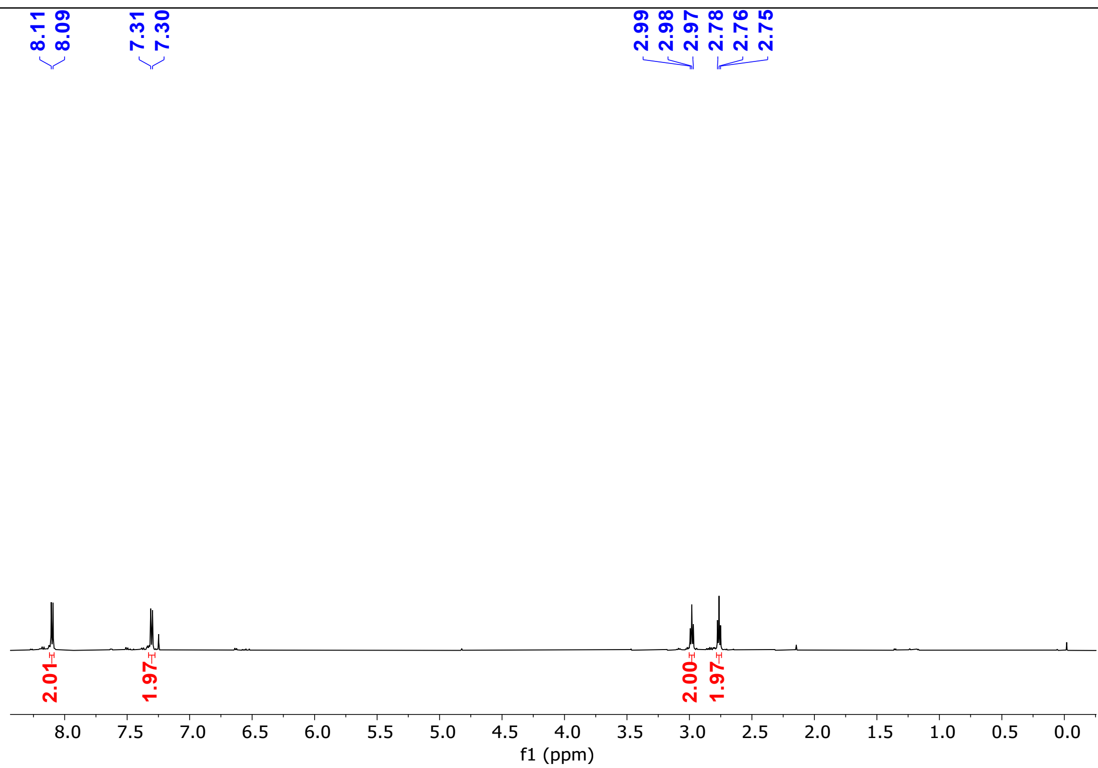


Fig. S118 ^1H NMR of **3f** in $CDCl_3$ at 298K.

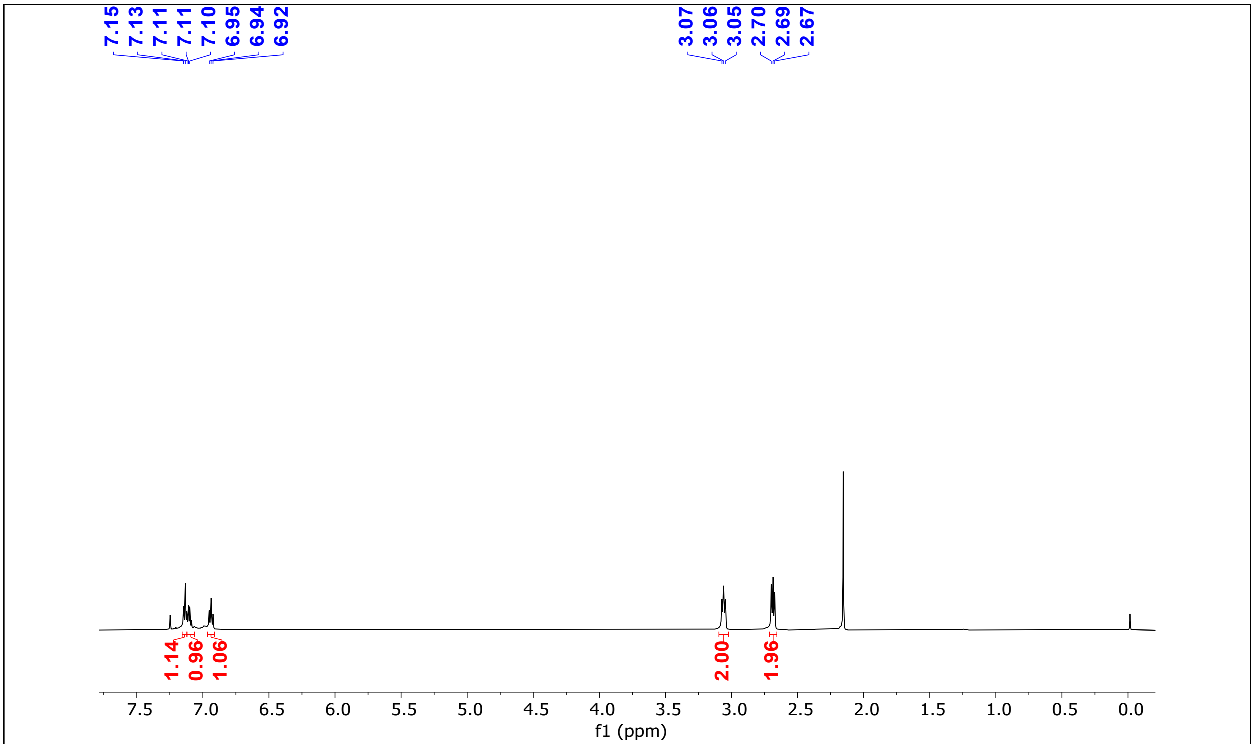


Fig. S119 ^{1}H NMR of **5f** in $CDCl_3$ at 298K.

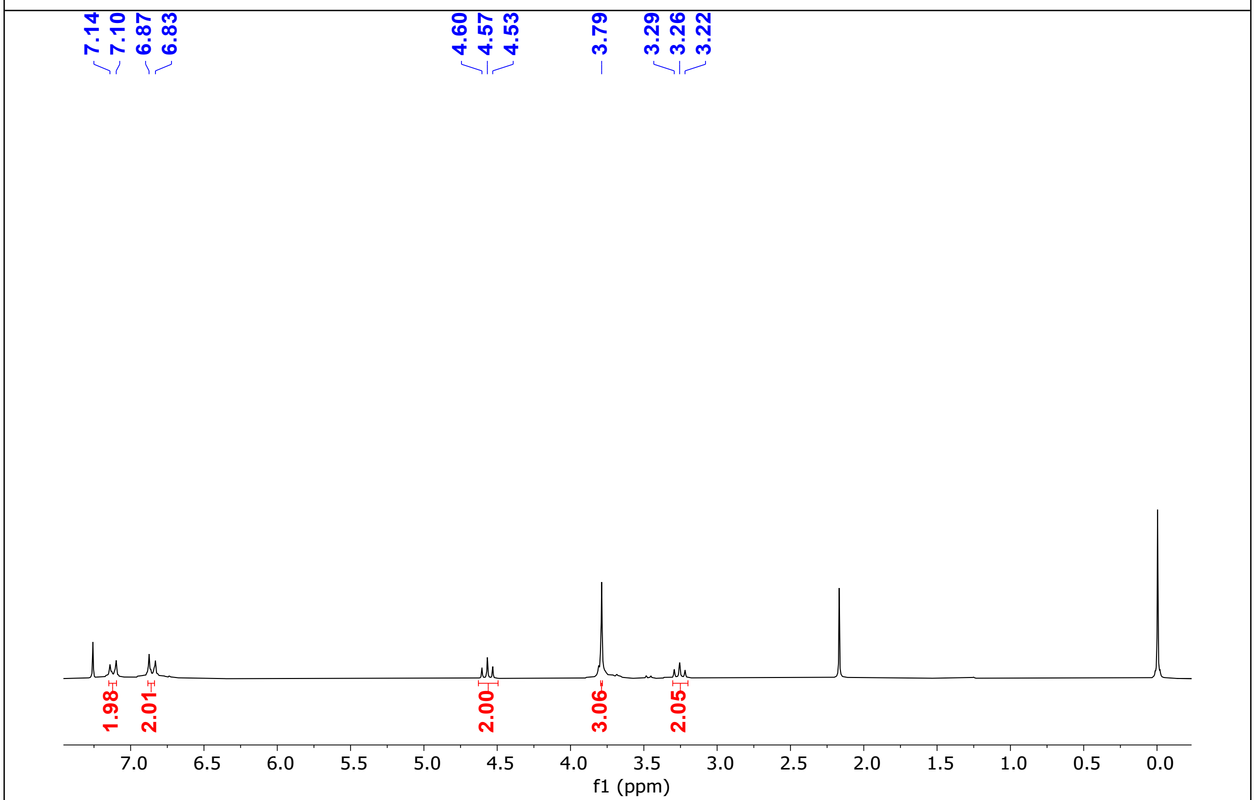


Fig. S120 ^{1}H NMR of **1i** in $CDCl_3$ at 298K.

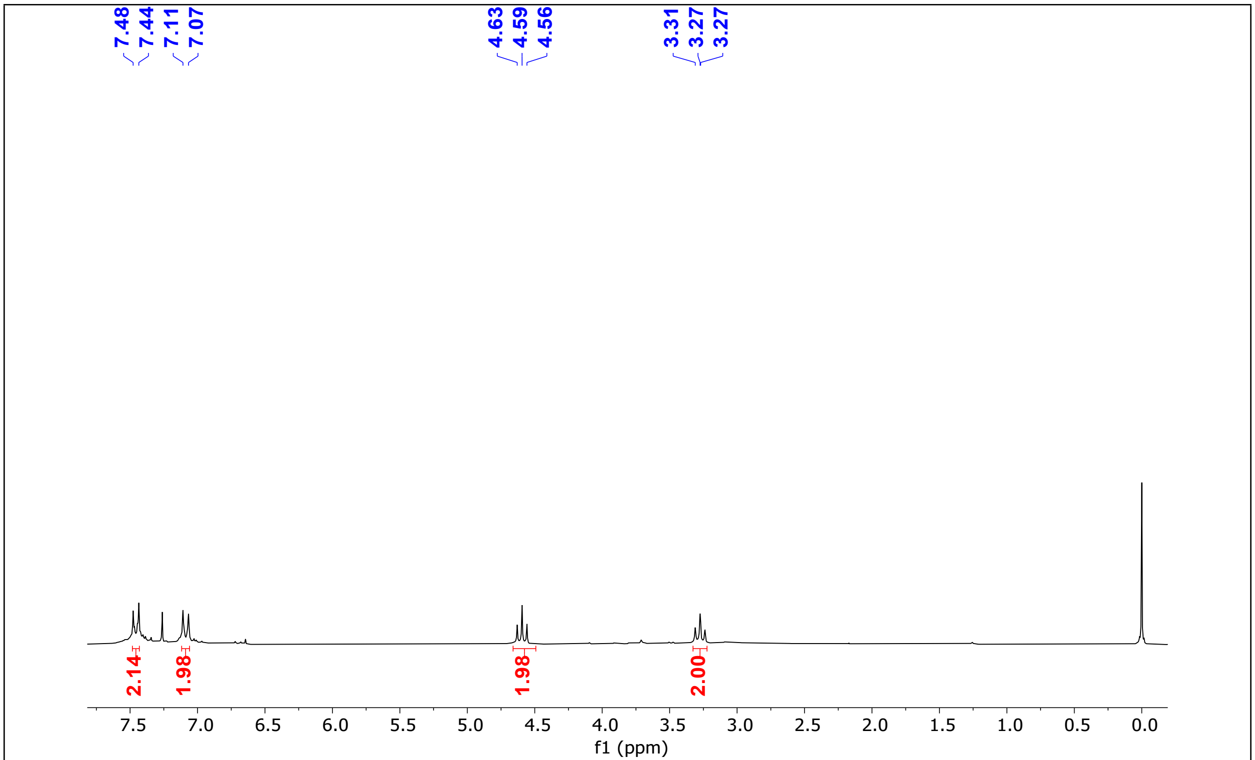


Fig. S121 ^{1}H NMR of **3i** in $CDCl_3$ at 298K.

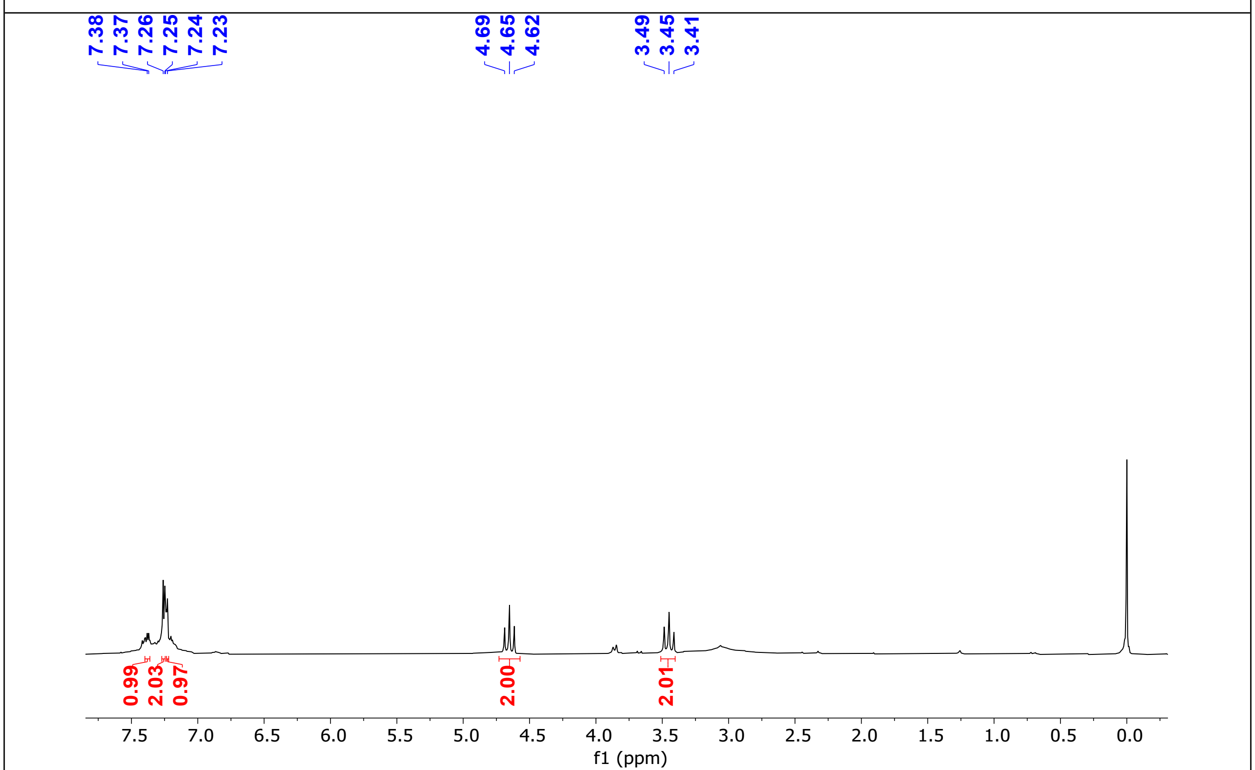


Fig. S122 ^{1}H NMR of **7i** in $CDCl_3$ at 298K.

3.3 In situ [1]H NMR/GC-MS Spectra for catalytic hydrogenation of αβ-unsaturated ketones/nitro to saturated ketones/nitro.

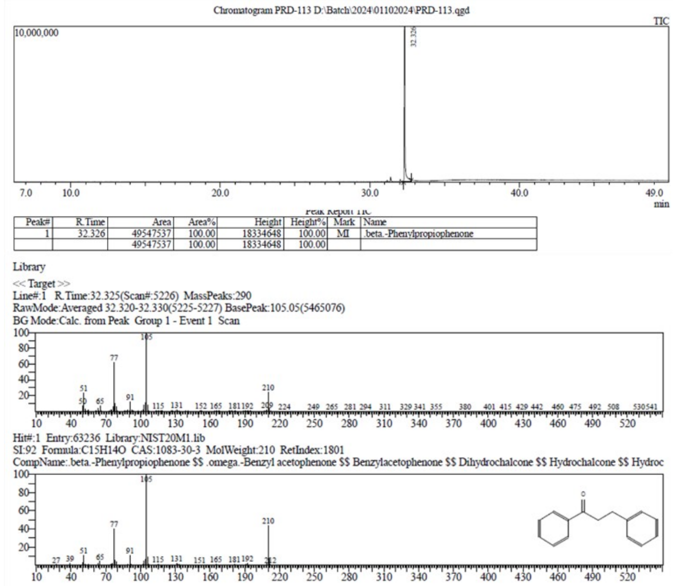


Fig. S123 GC-MS spectra of **1b** in ethyl acetate.

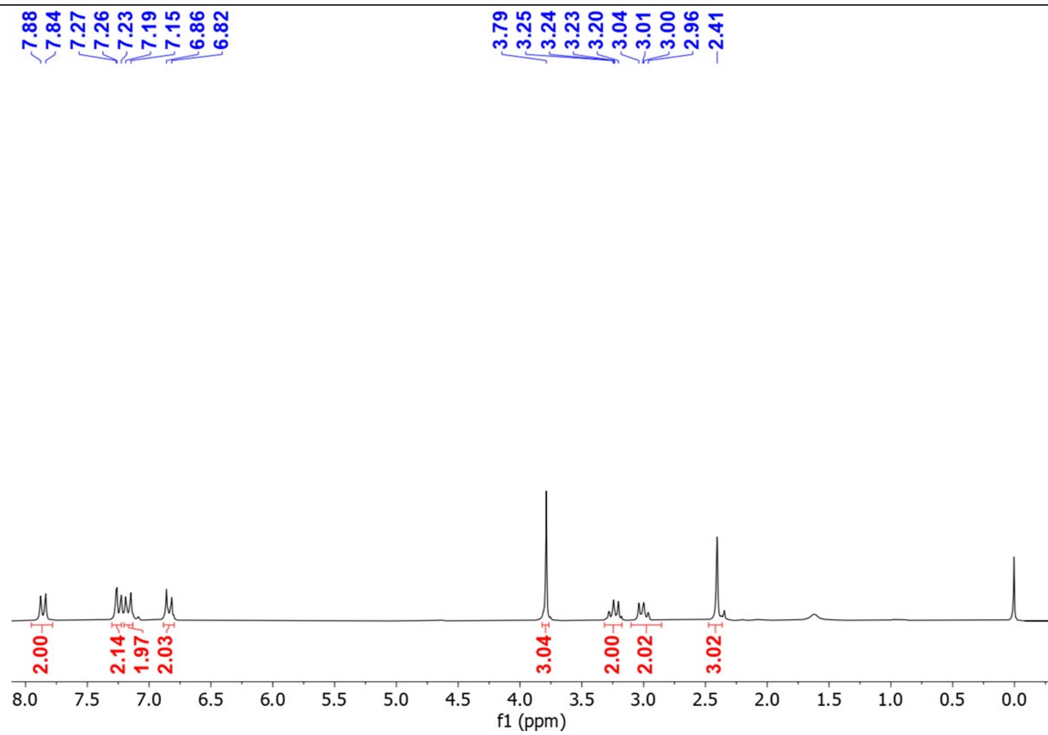


Fig. S124 In situ ^{1}H NMR of **2b** in $CDCl_3$ at 298K.

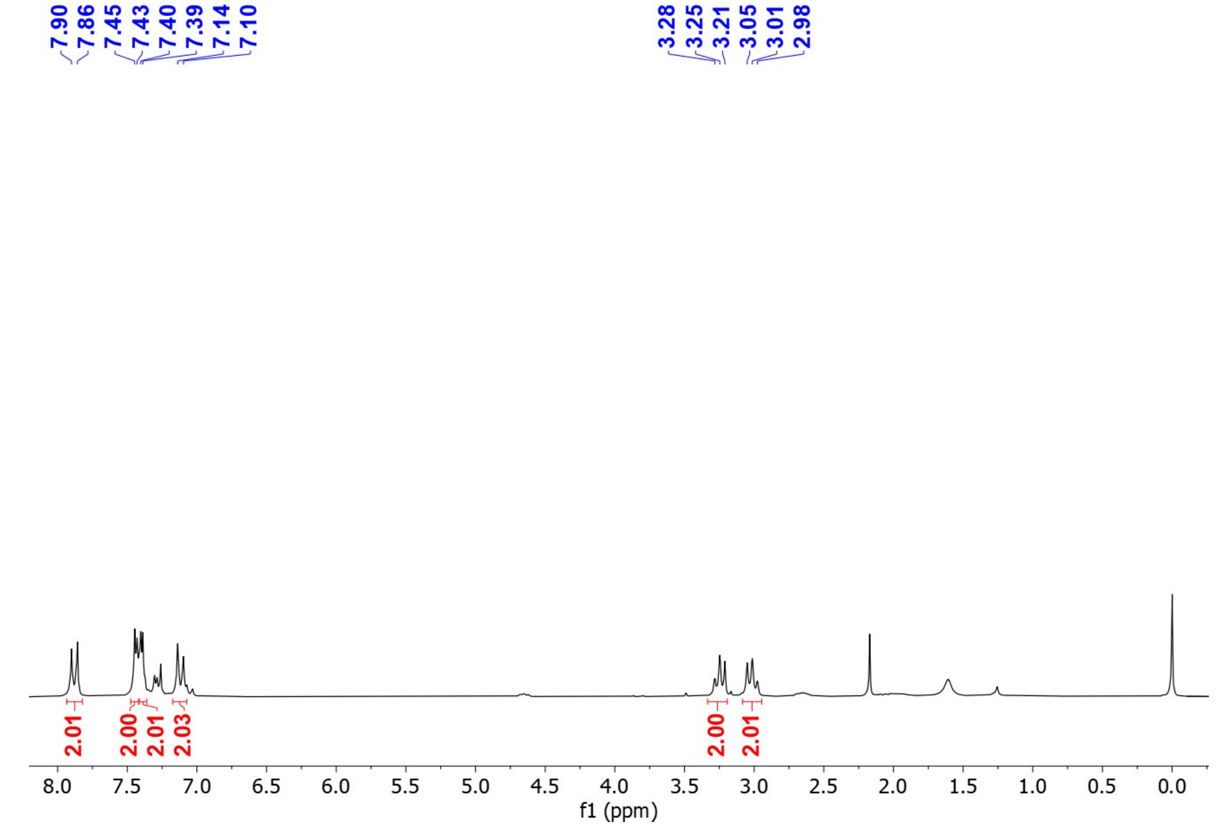


Fig. S125 In–situ ^{1}H NMR of **3b** in $CDCl_3$ at 298K.

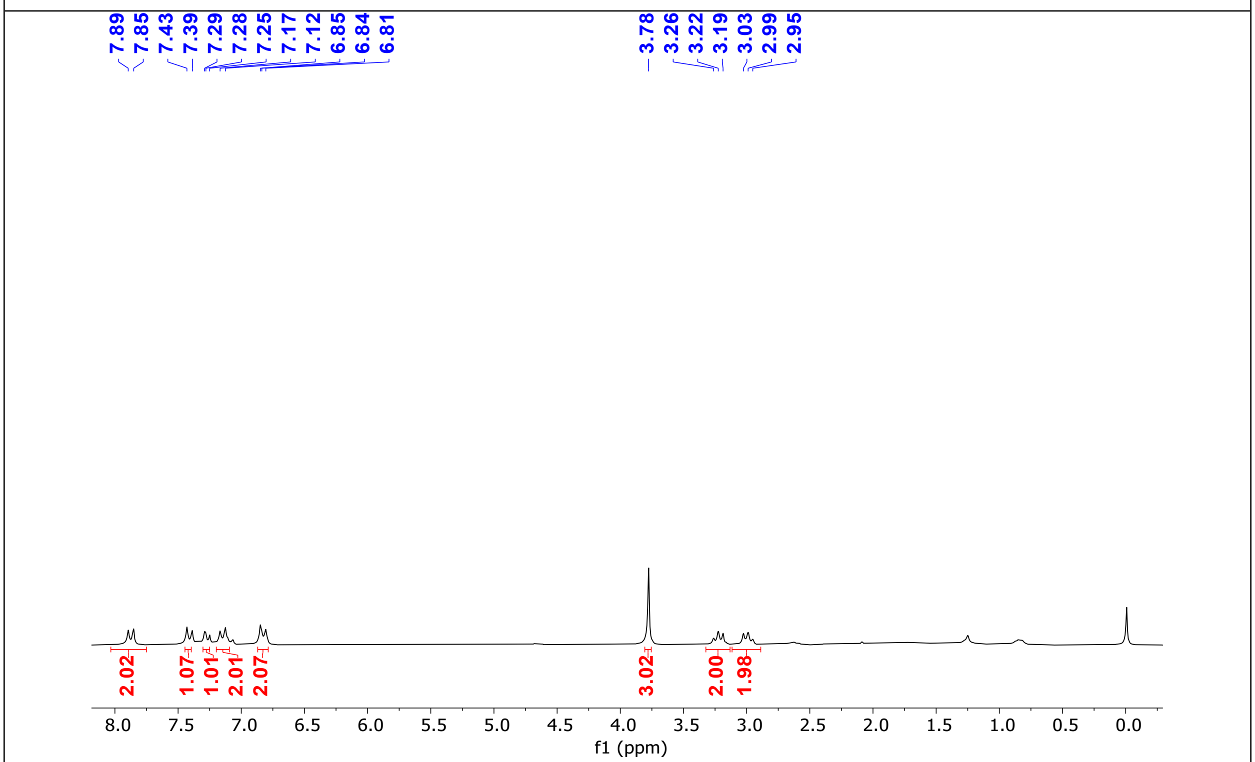


Fig. S126 In–situ ^{1}H NMR of **4b** in $CDCl_3$ at 298K.

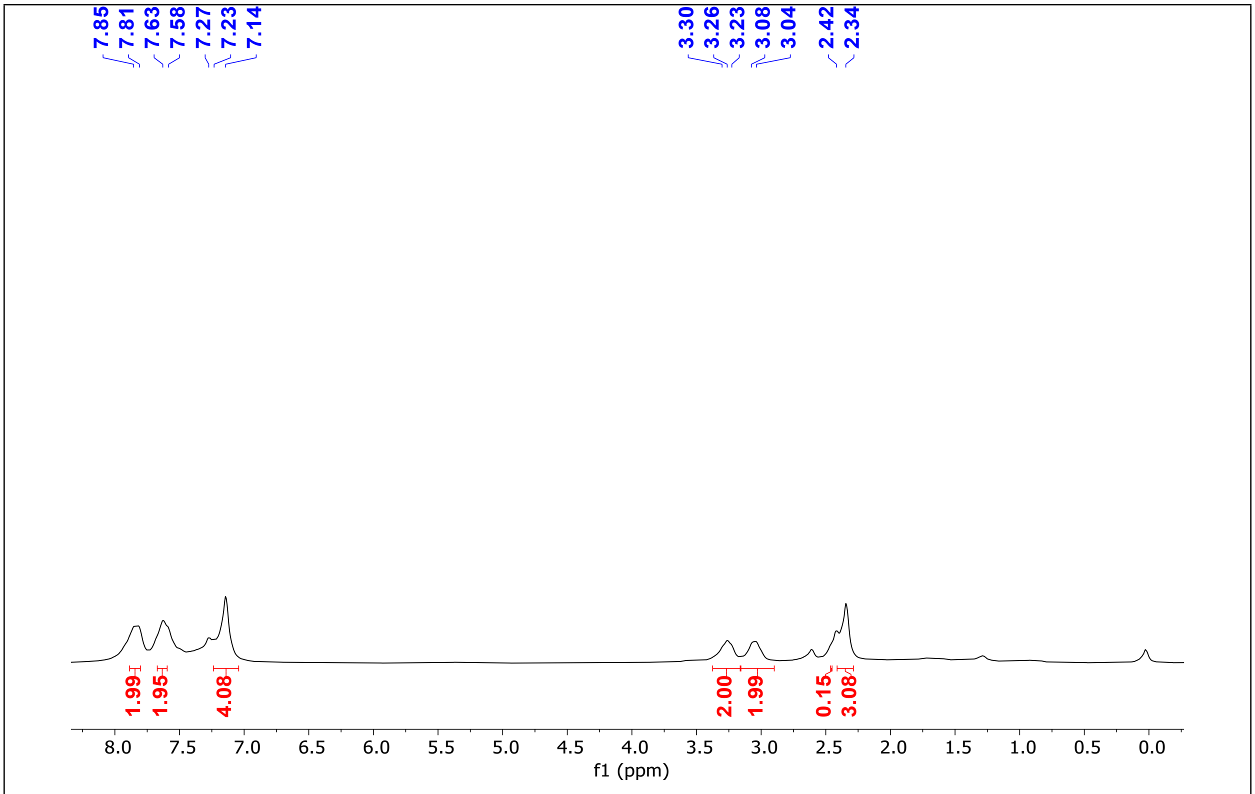


Fig. S127 In–situ [1]H NMR of **5b** in $CDCl_3$ at 298K.

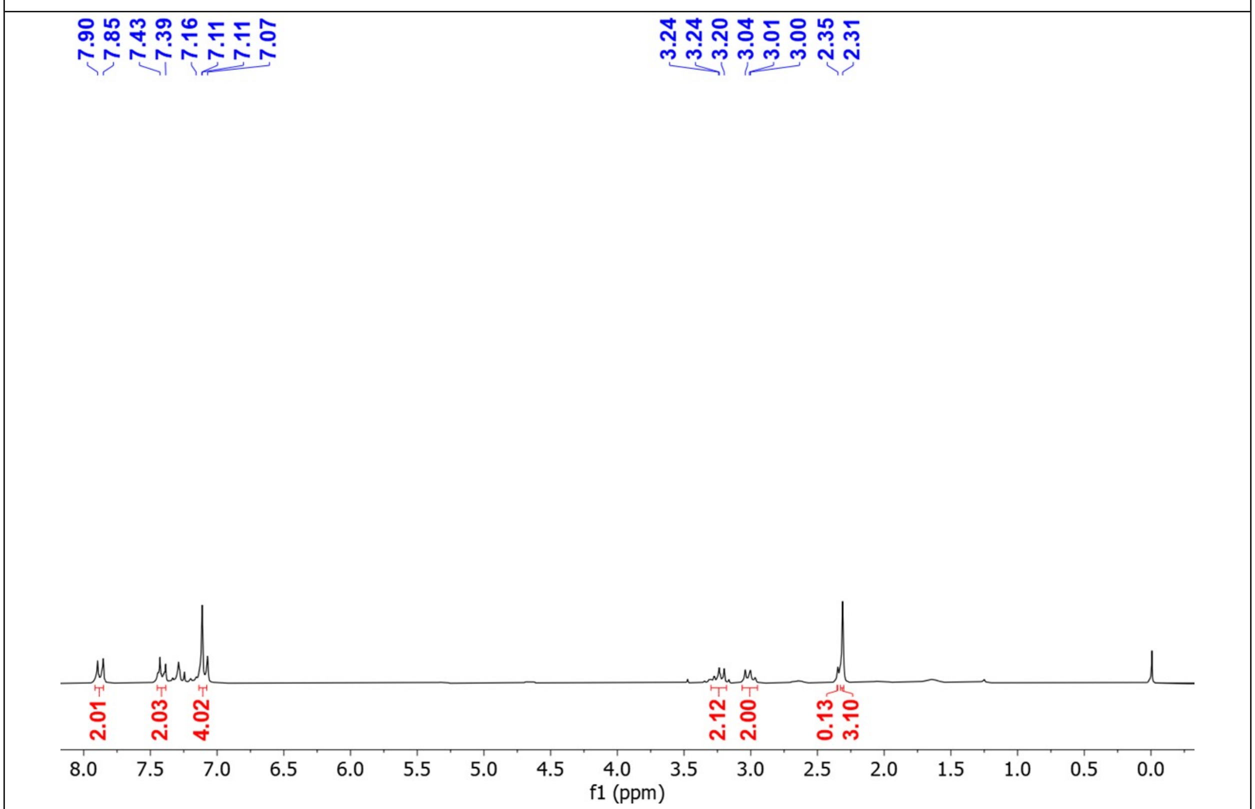


Fig. S128 In–situ [1]H NMR of **6b** in $CDCl_3$ at 298K.

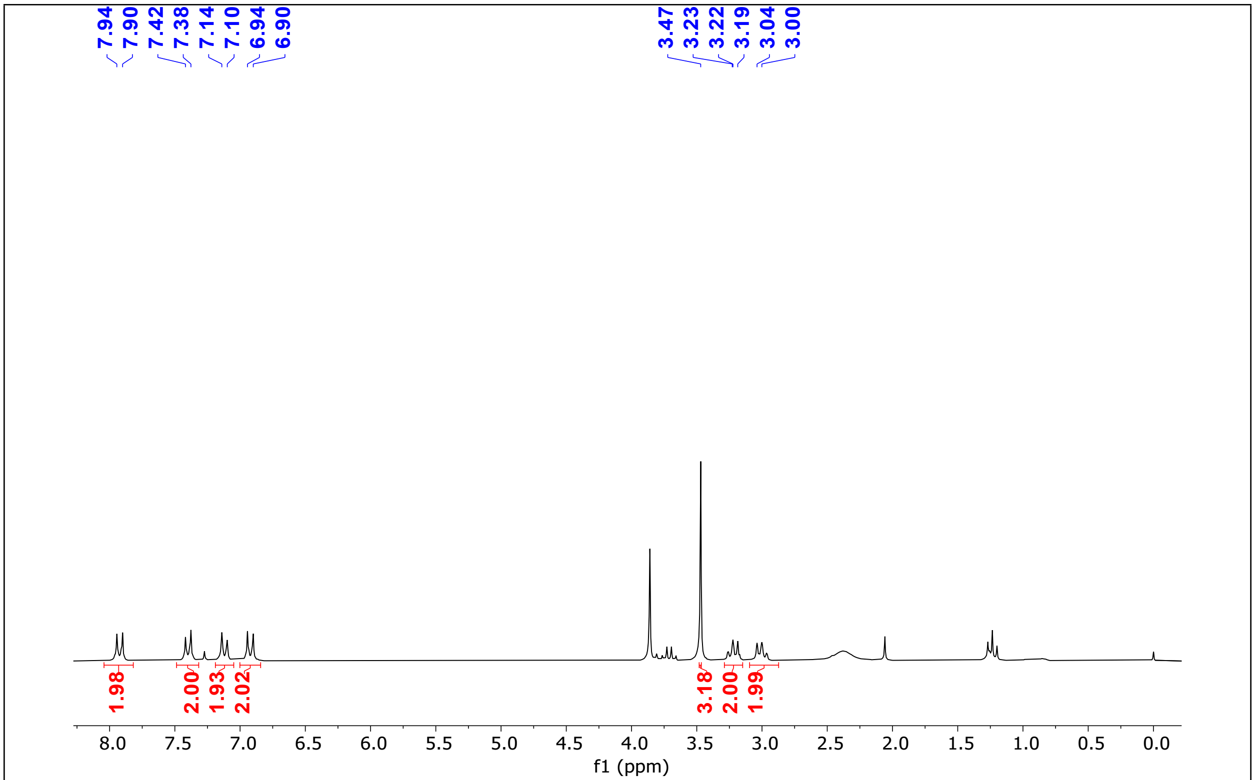


Fig. S129 In–situ ^{1}H NMR of **7b** in $CDCl_3$ at 298K.

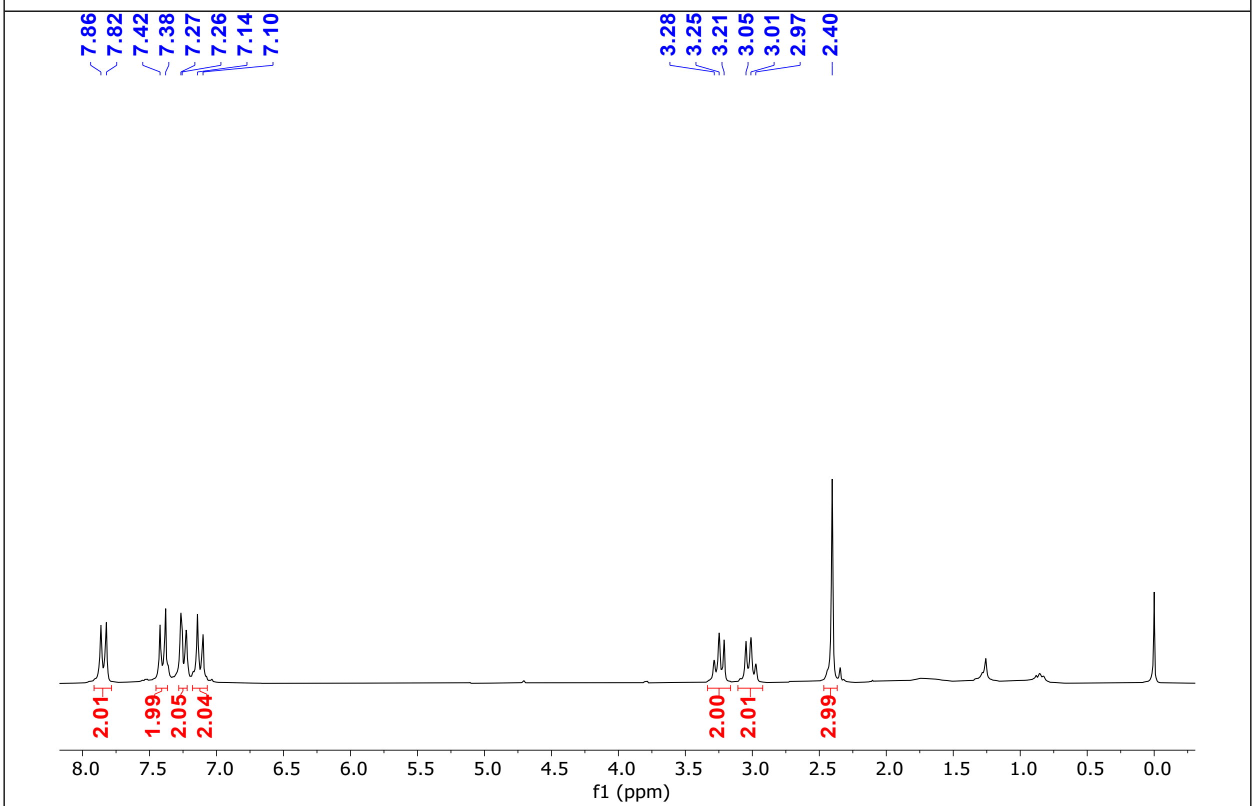


Fig. S130 In–situ ^{1}H NMR of **8b** in $CDCl_3$ at 298K.

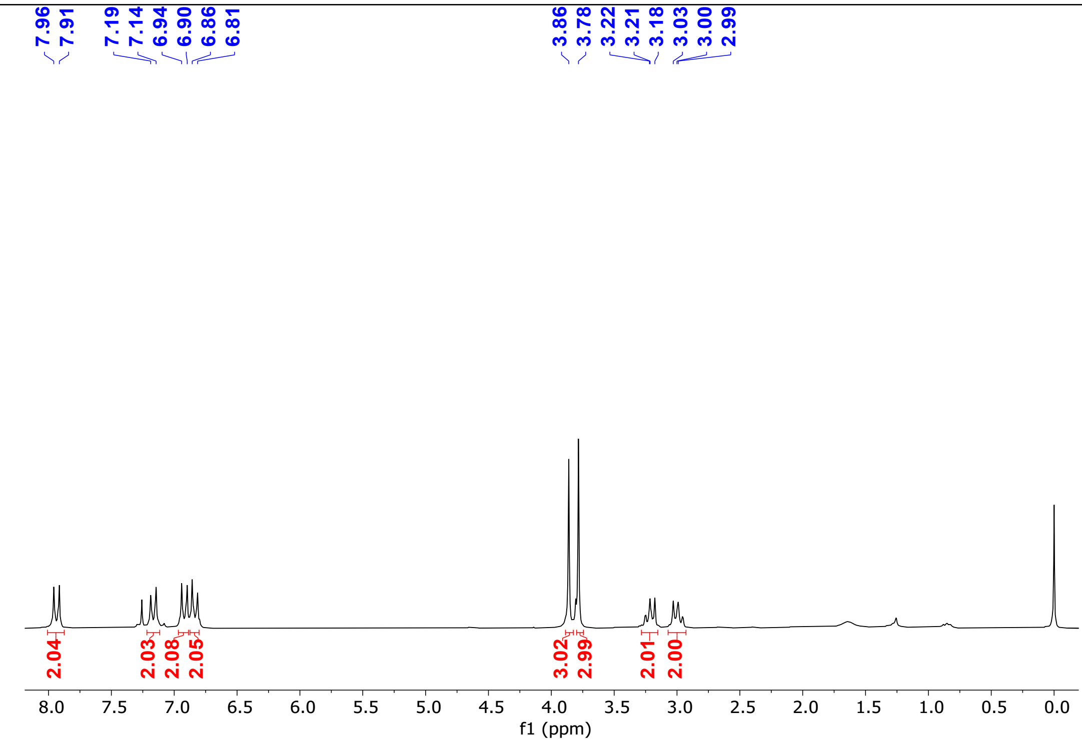


Fig. S131 In–situ [1]H NMR of **9b** in $CDCl_3$ at 298K.

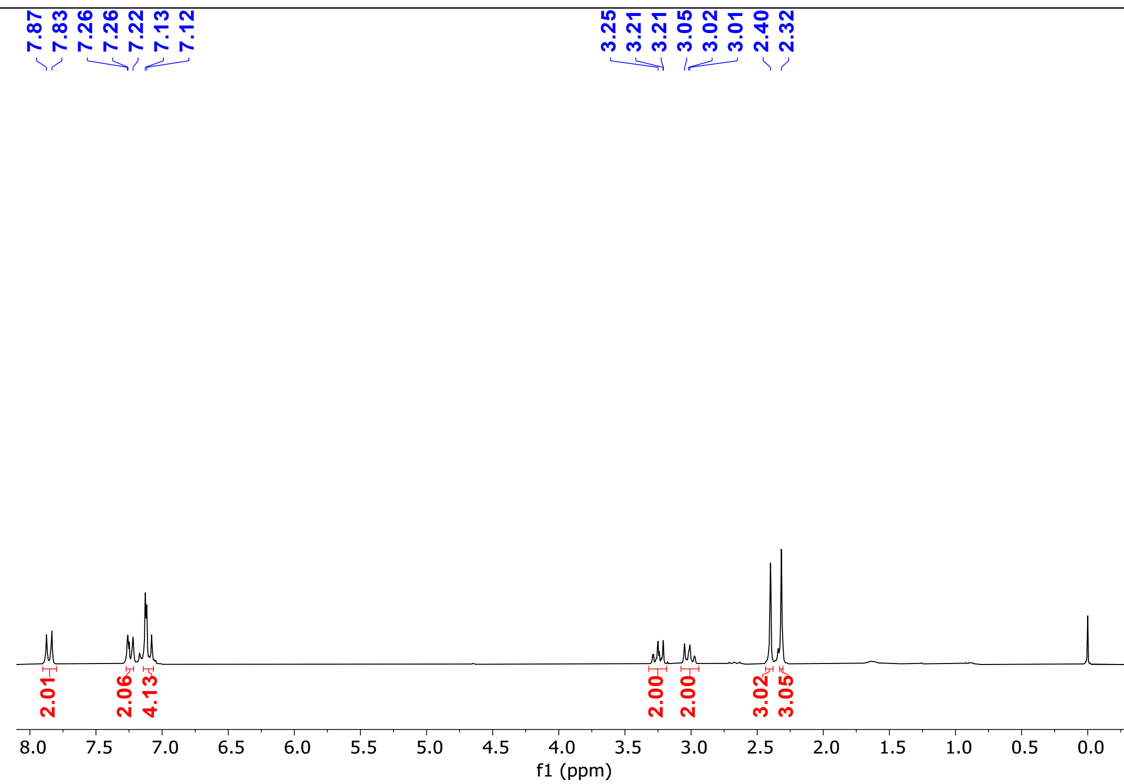


Fig. S132 In–situ [1]H NMR of **10b** in $CDCl_3$ at 298K.

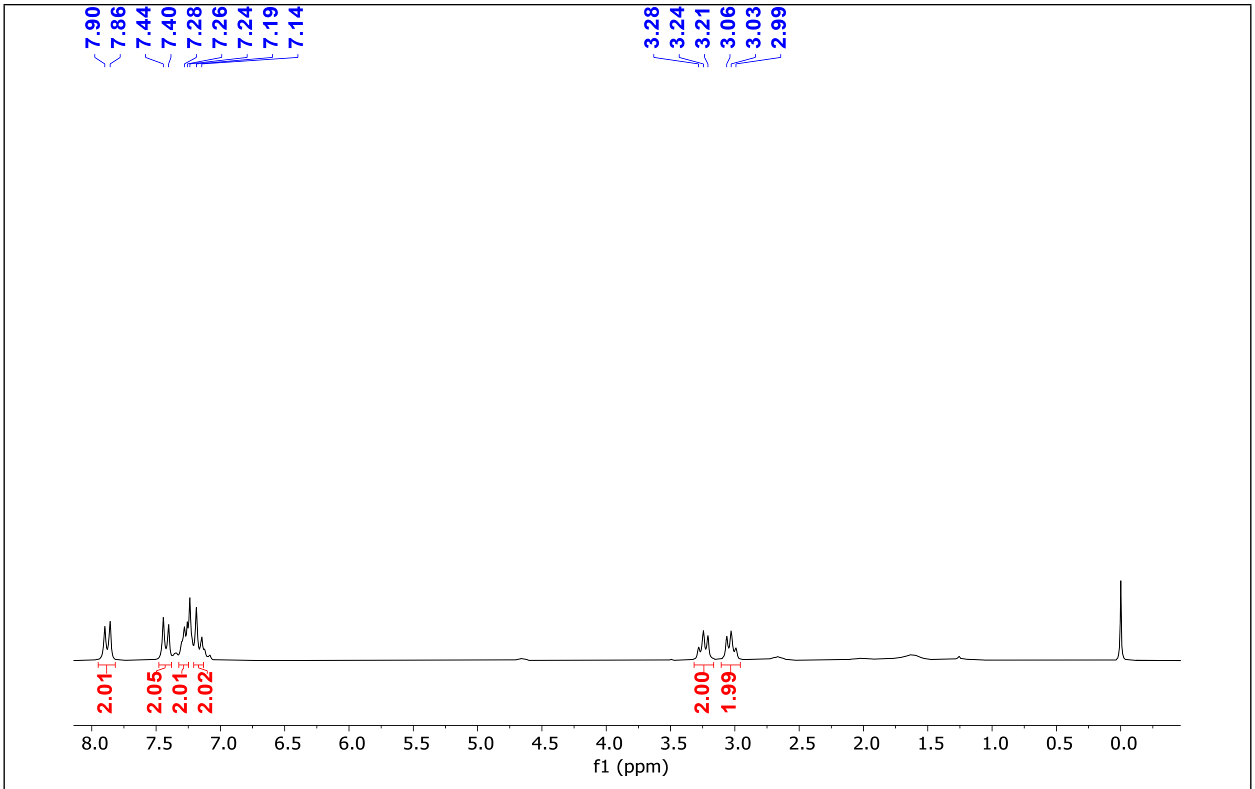


Fig. S133 In–situ [1]H NMR of **11b** in $CDCl_3$ at 298K.

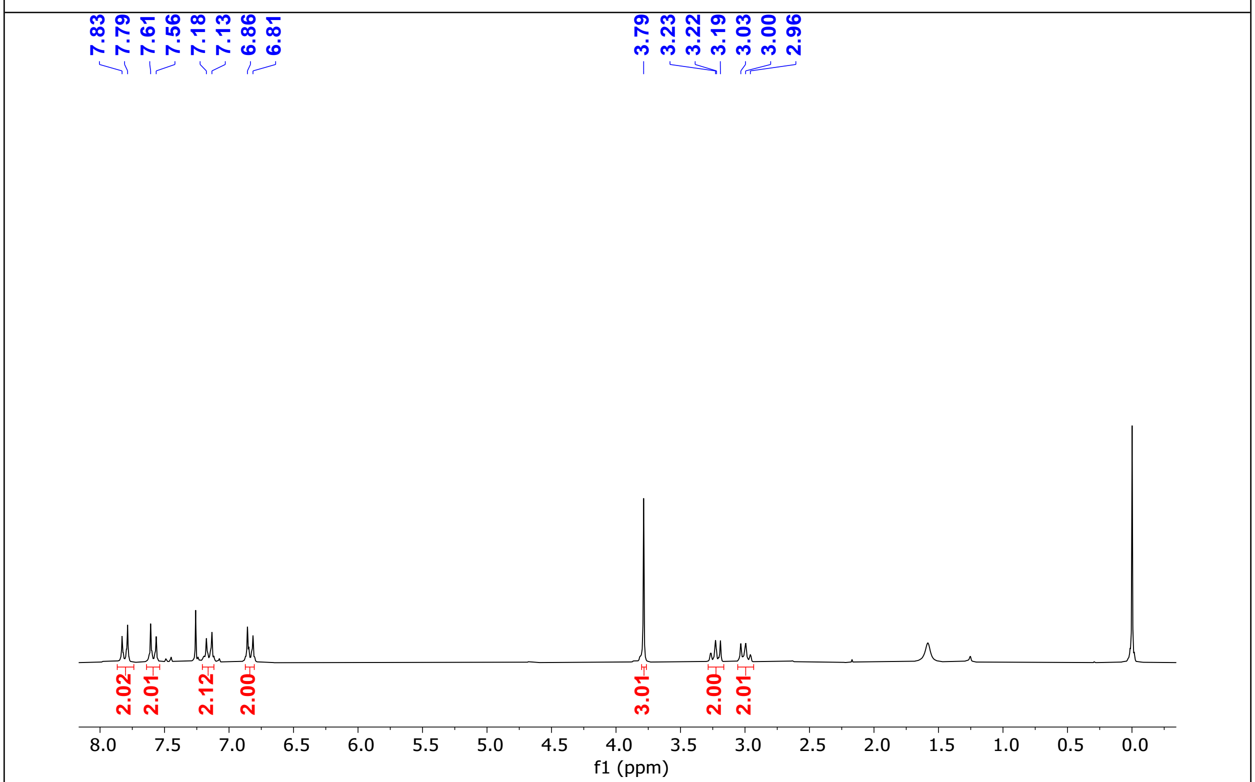


Fig. S134 In–situ [1]H NMR of **12b** in $CDCl_3$ at 298K.

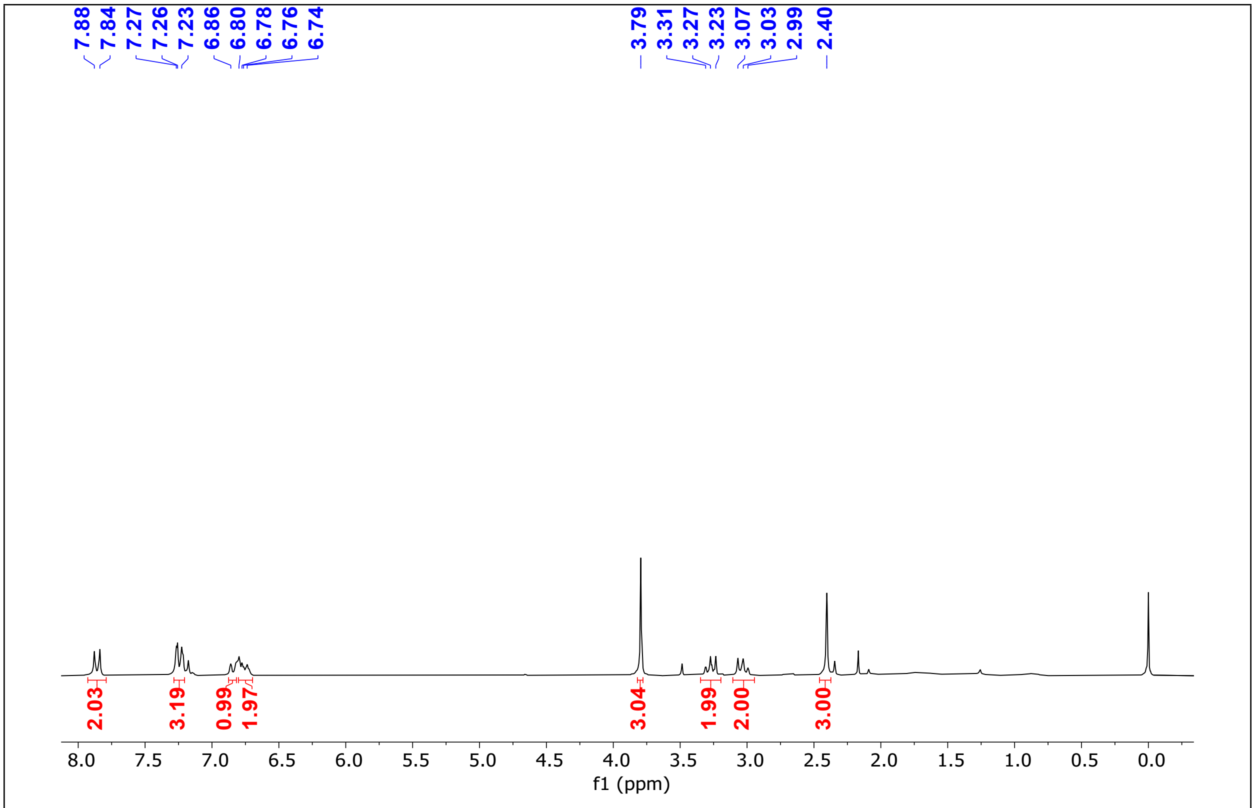


Fig. S135 In–situ ^{1}H NMR of **13b** in $CDCl_3$ at 298K.

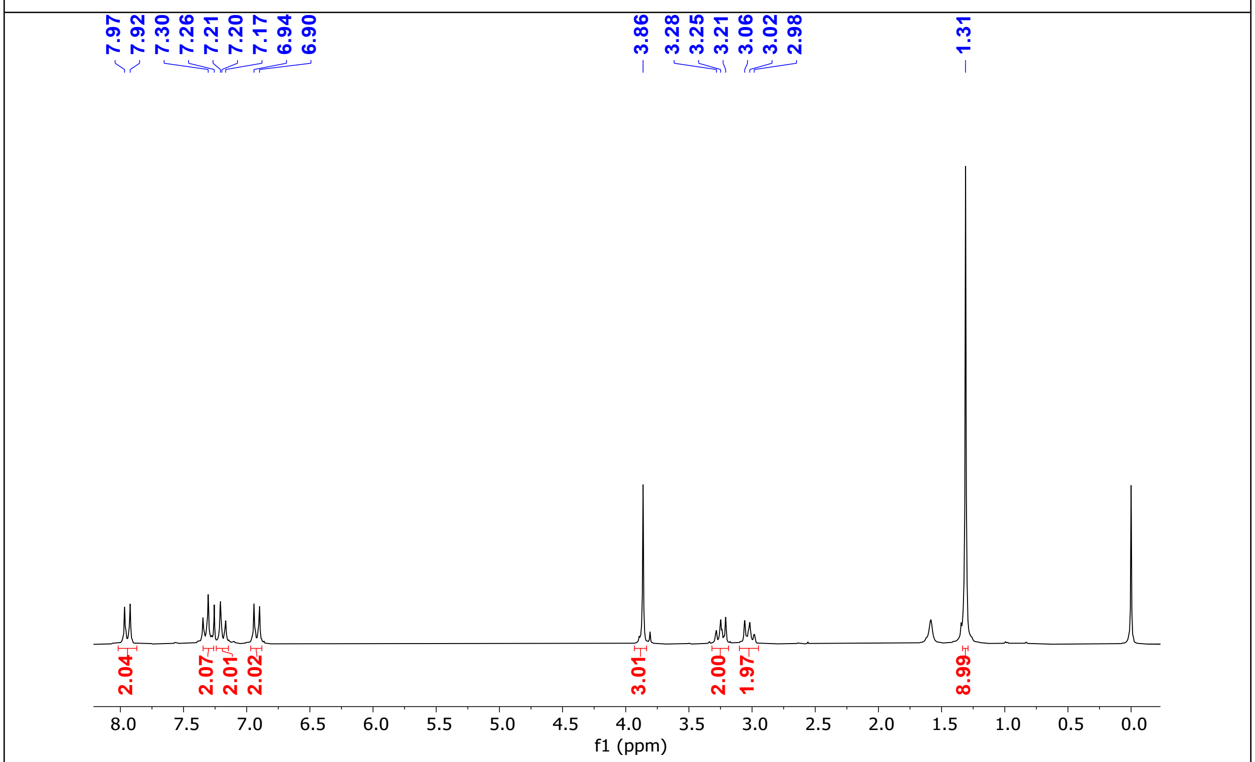


Fig. S136 In–situ ^{1}H NMR of **15b** in $CDCl_3$ at 298K.

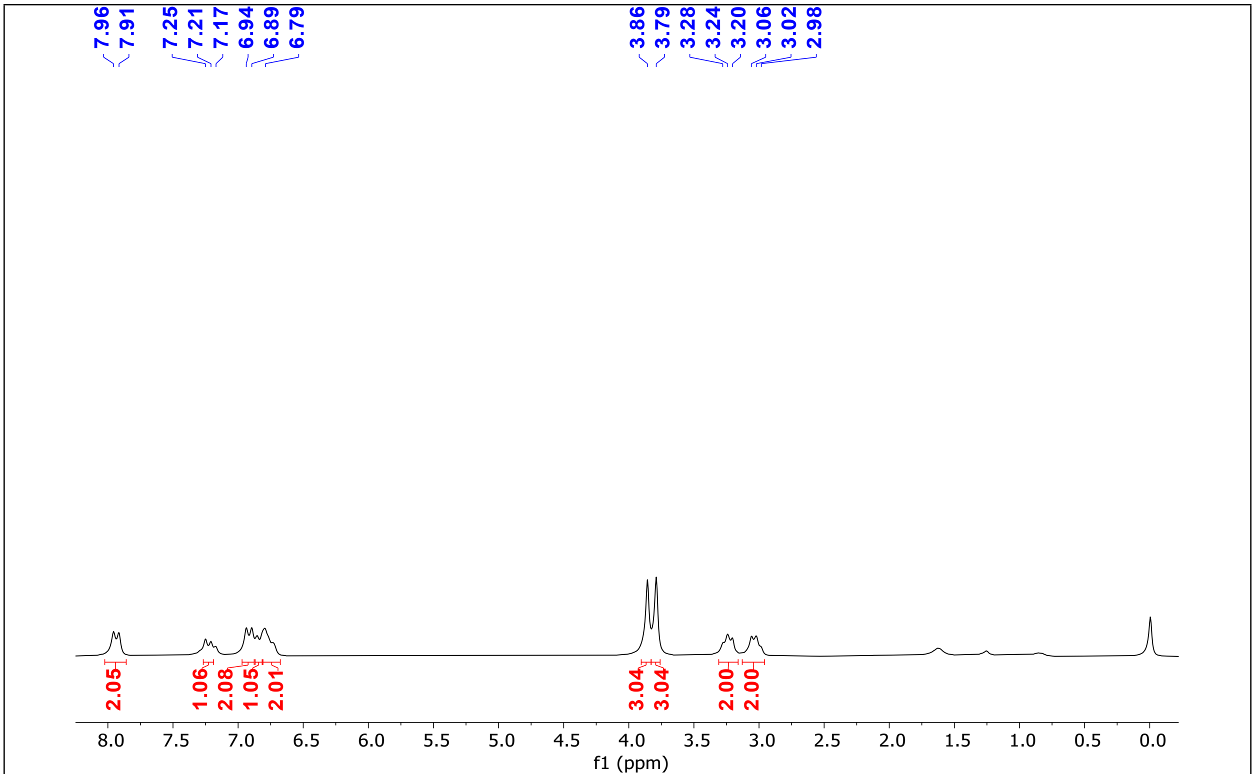


Fig. S137 In–situ ^{1}H NMR of **17b** in $CDCl_3$ at 298K.

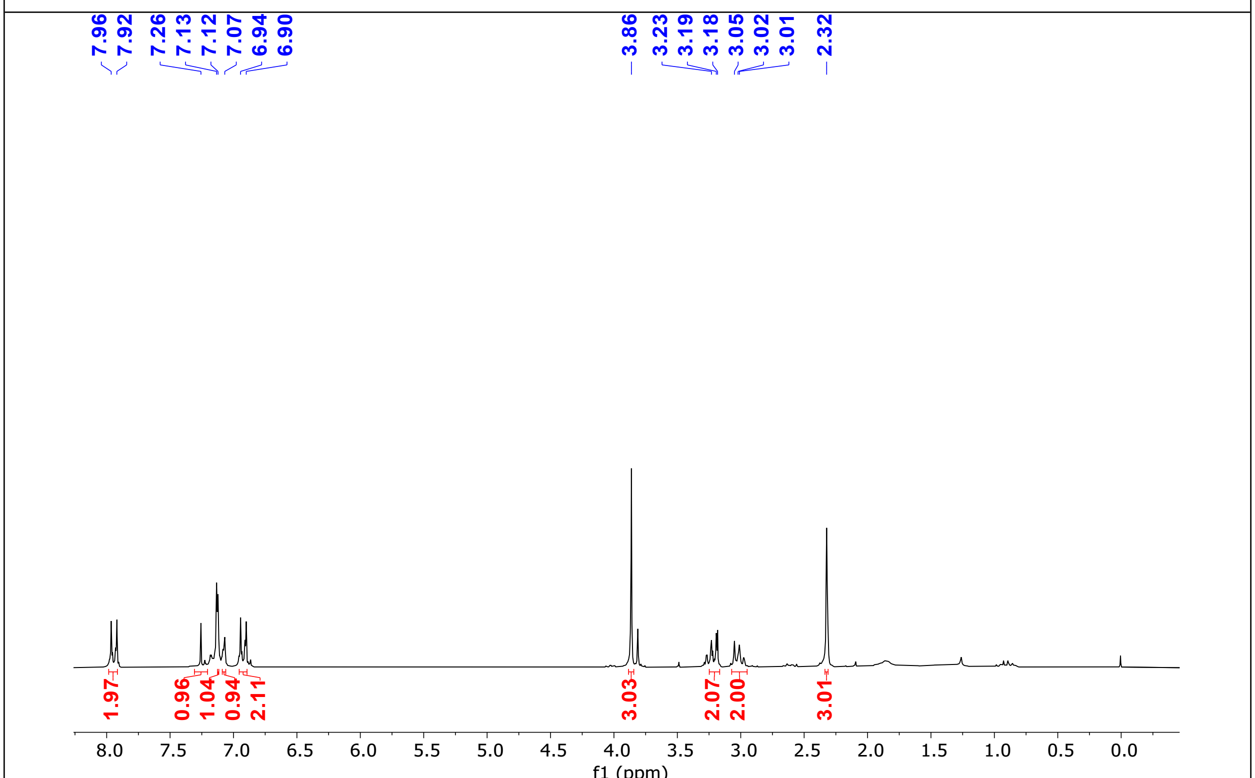


Fig. S138 In–situ ^{1}H NMR of **18b** in $CDCl_3$ at 298K.

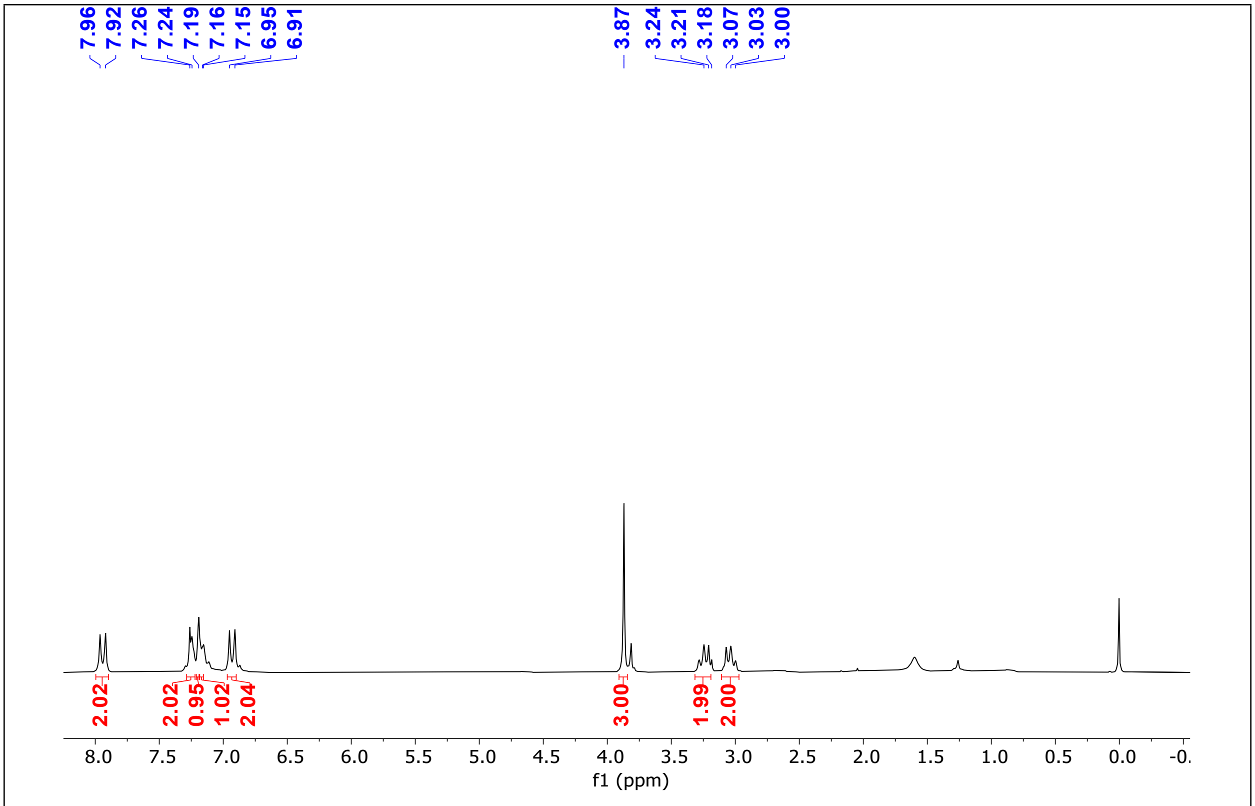


Fig. S139 In–situ ¹H NMR of **19b** in $CDCl_3$ at 298K.

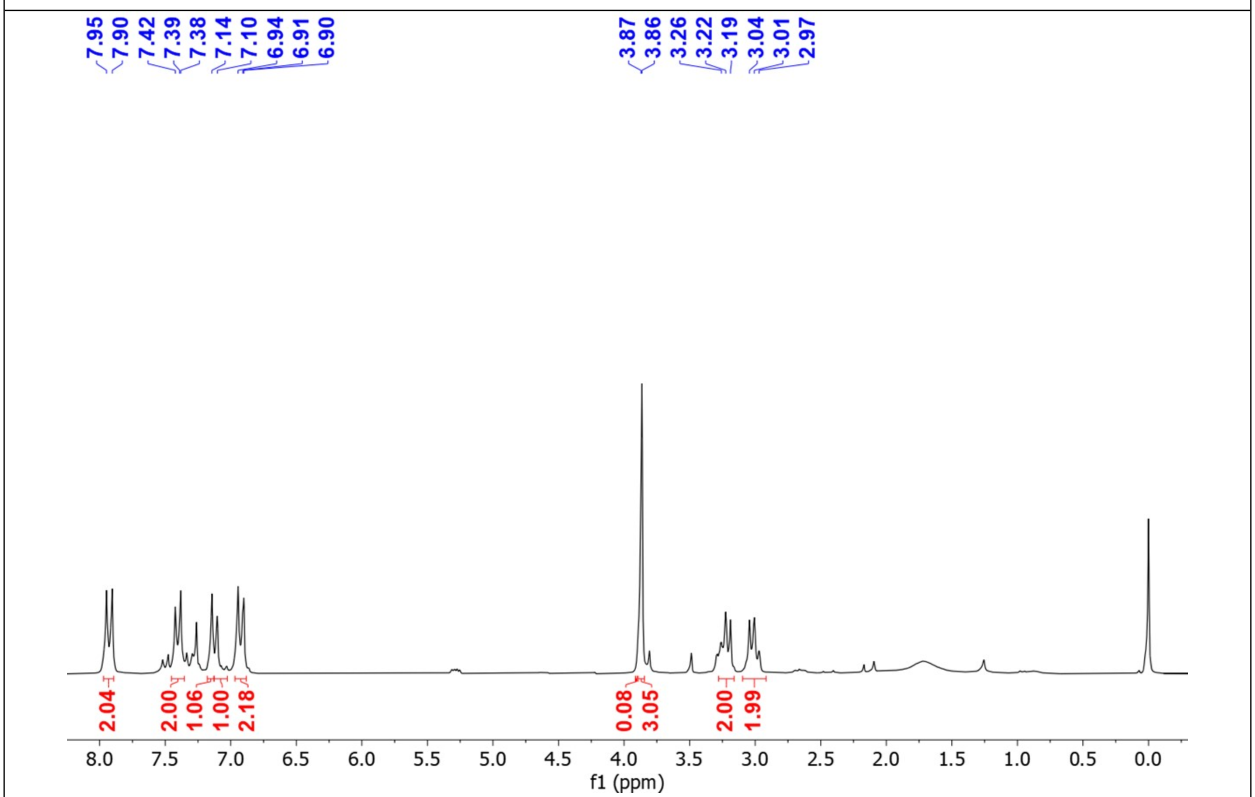


Fig. S140 In–situ ¹H NMR of **20b** in $CDCl_3$ at 298K.

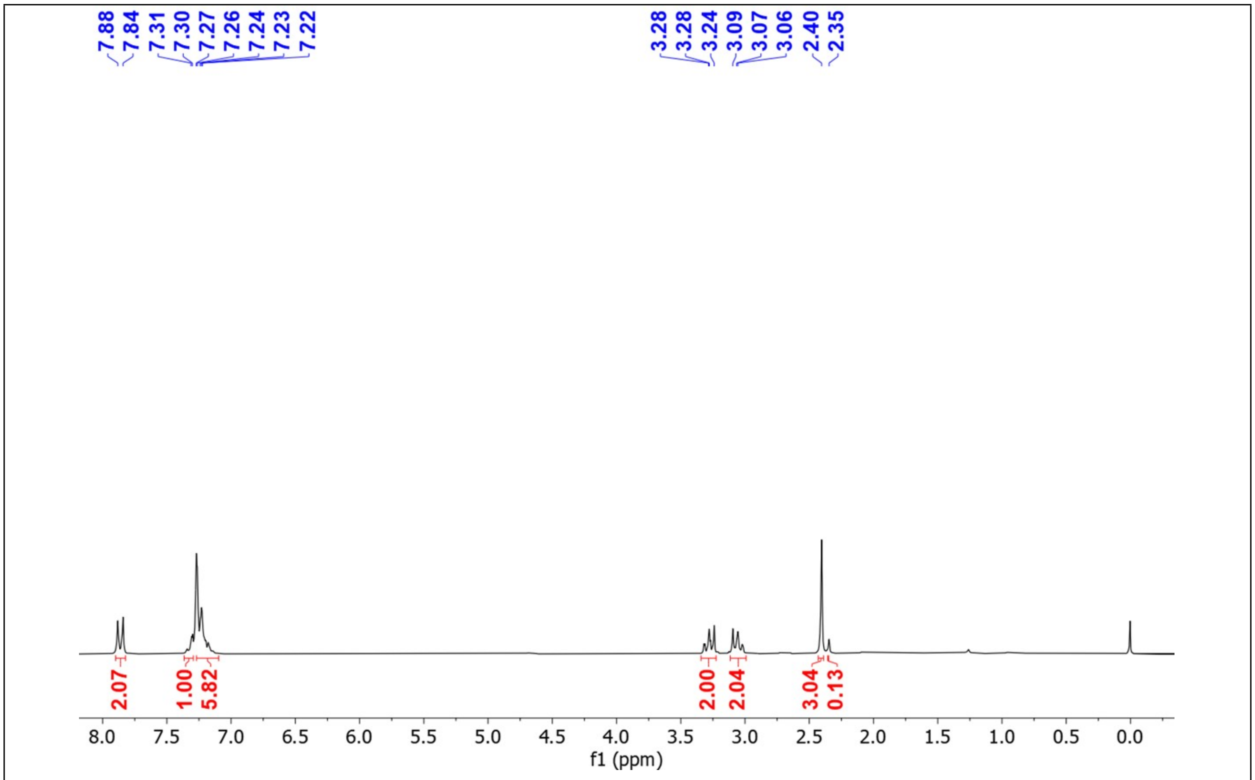


Fig. S141 In–situ ^{1}H NMR of **21b** in $CDCl_3$ at 298K.

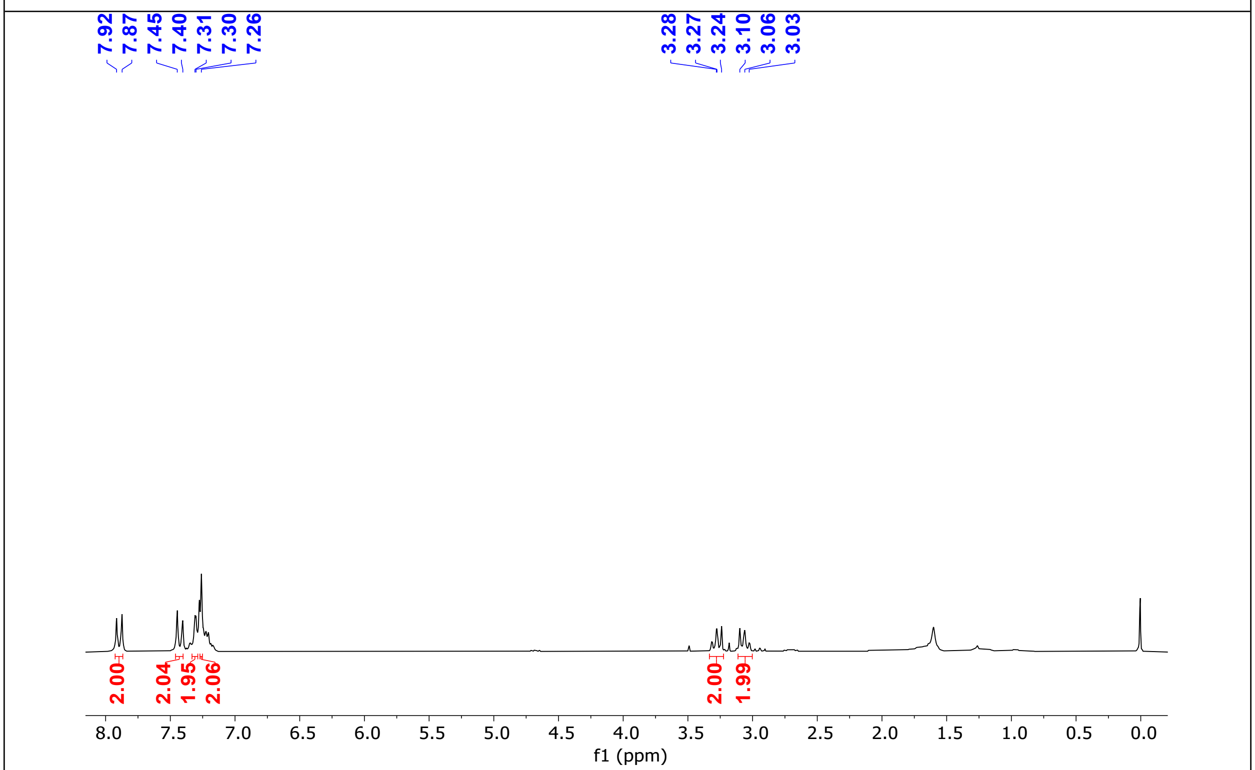


Fig. S142 In–situ ^{1}H NMR of **23b** in $CDCl_3$ at 298K.

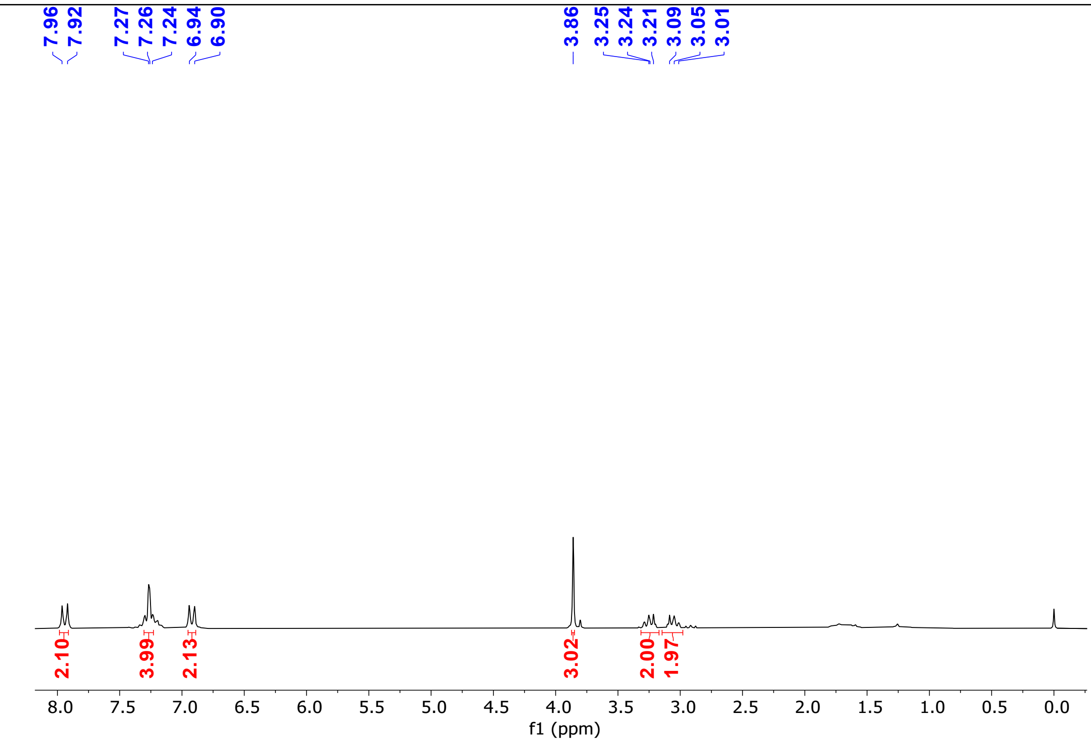


Fig. S143 In–situ ^{1}H NMR of **24b** in $CDCl_3$ at 298K.

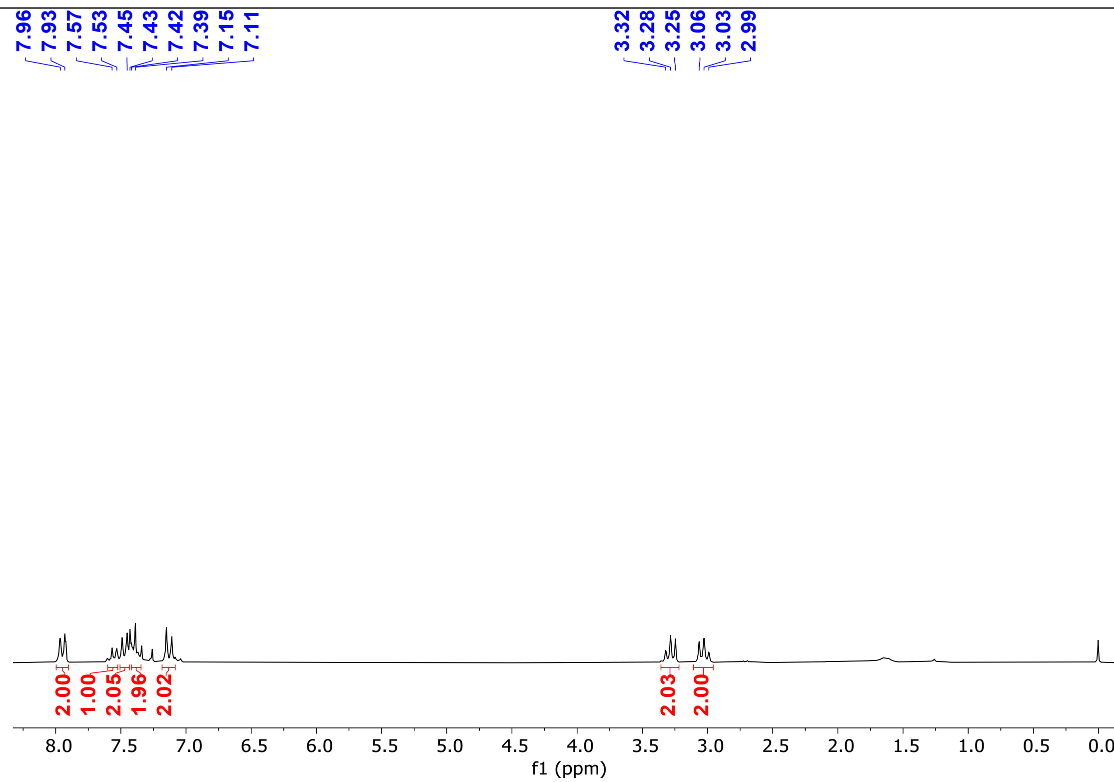


Fig. S144 In–situ ^{1}H NMR of **25b** in $CDCl_3$ at 298K.

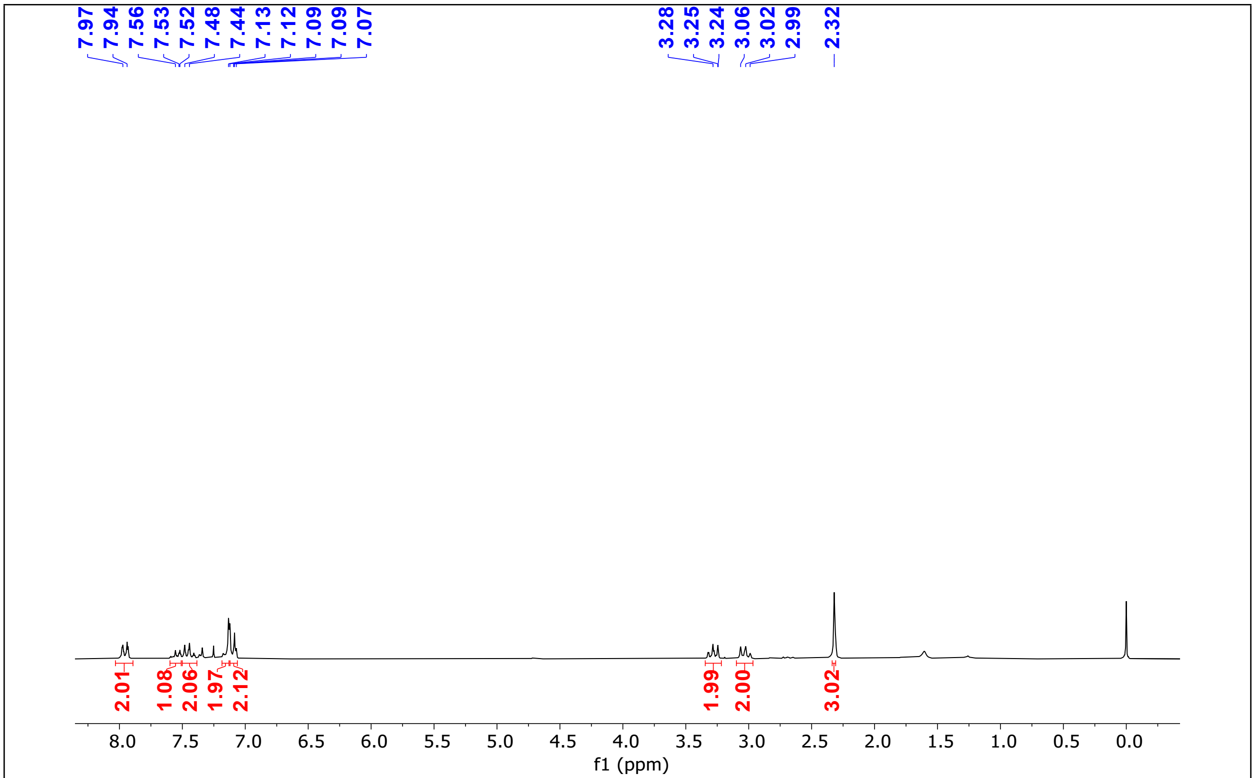


Fig. S145 In–situ ¹H NMR of **26b** in $CDCl_3$ at 298K.

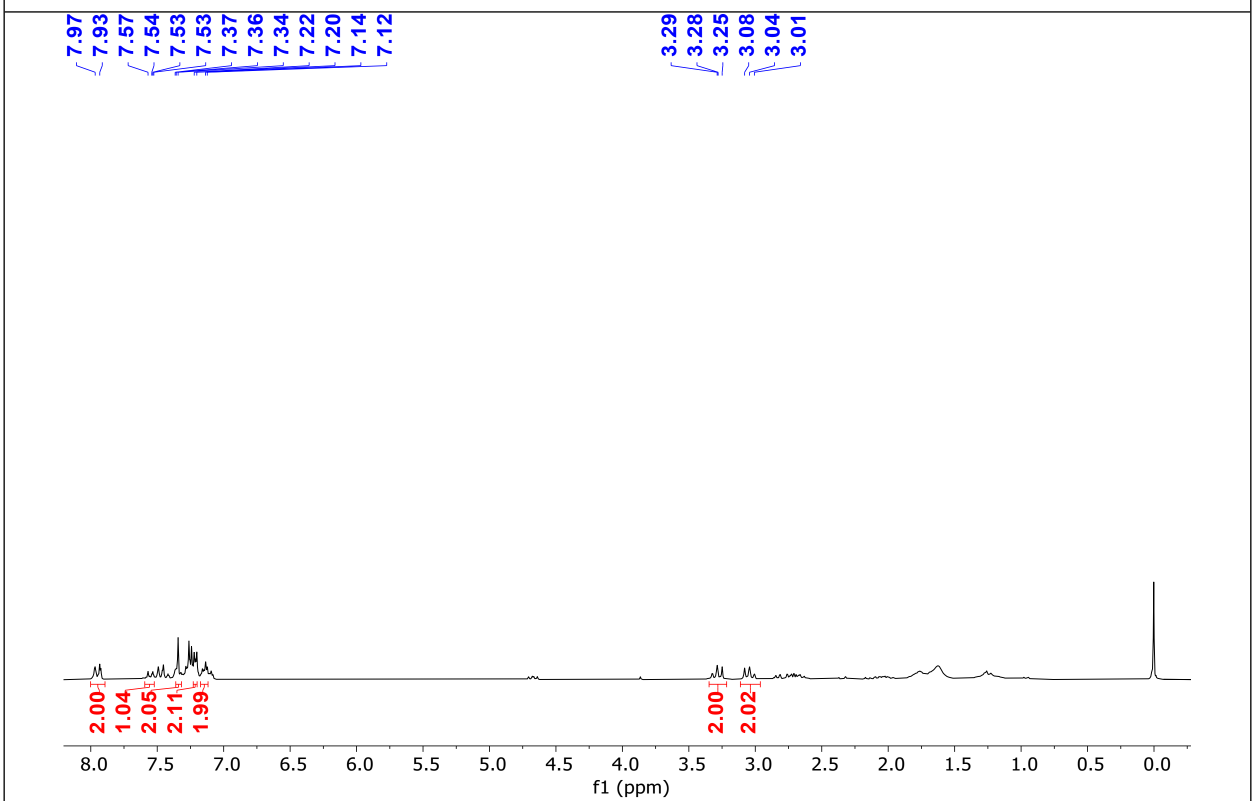


Fig. S146 In–situ ¹H NMR of **27b** in $CDCl_3$ at 298K.

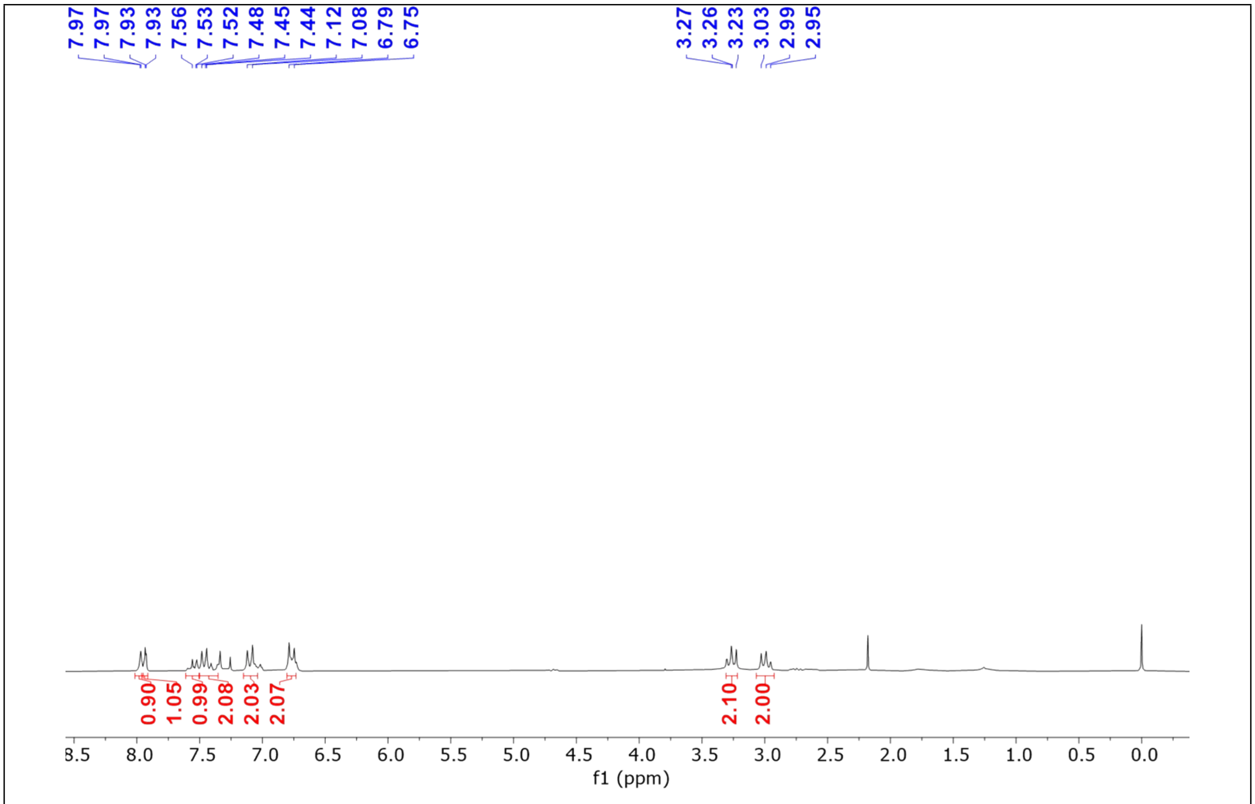


Fig. S147 In–situ ^{1}H NMR of **28b** in $CDCl_3$ at 298K.

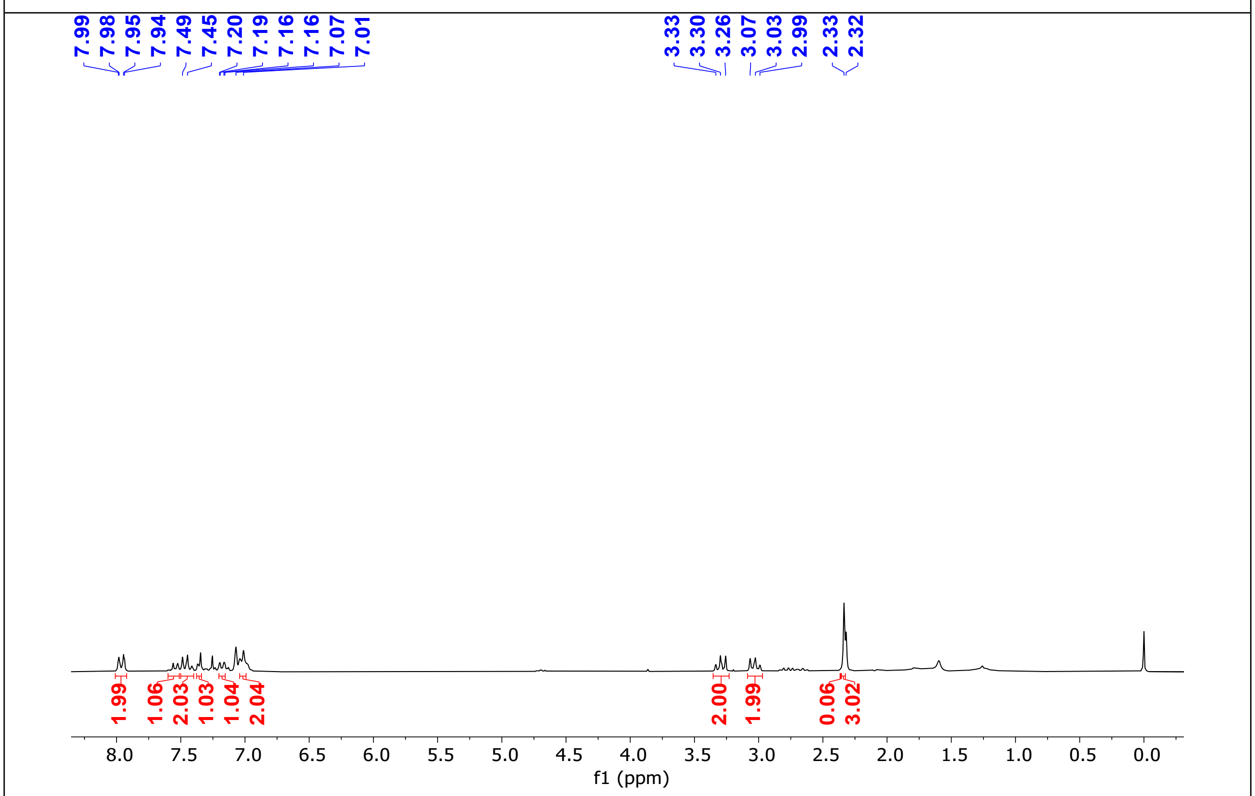


Fig. S148 In–situ ^{1}H NMR of **29b** in $CDCl_3$ at 298K.

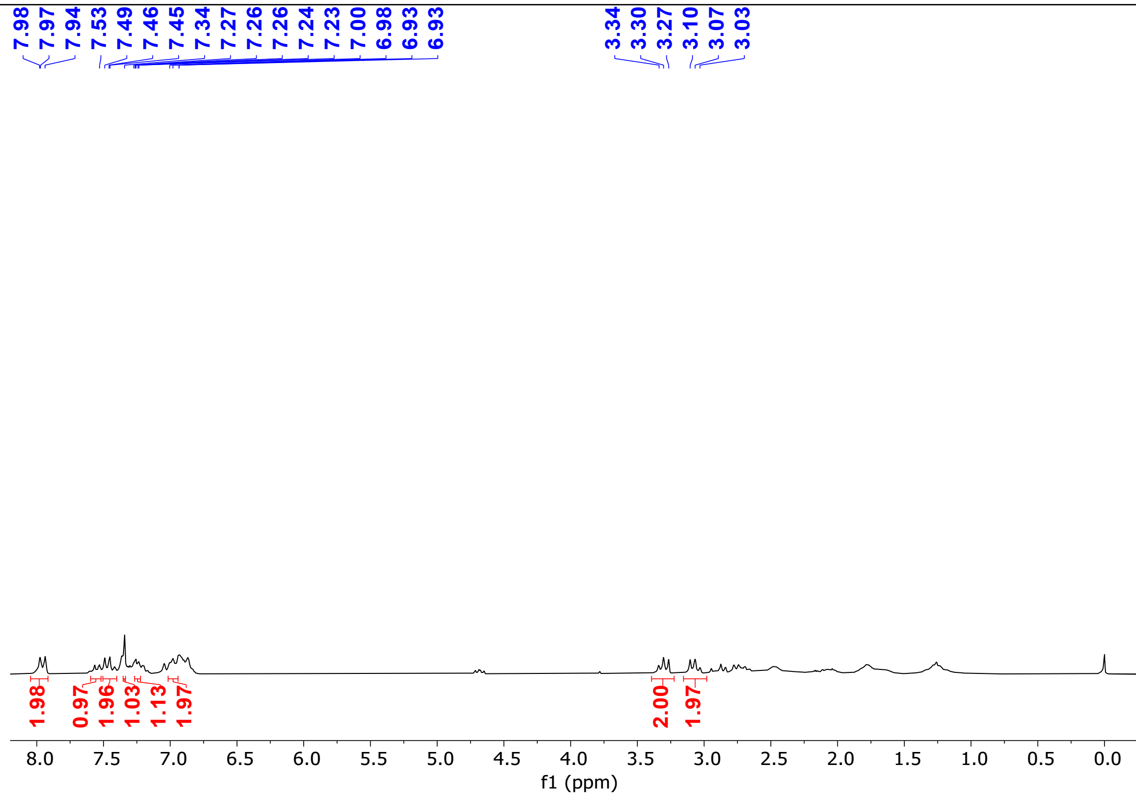


Fig. S149 In–situ ^{1}H NMR of **31b** in $CDCl_3$ at 298K.

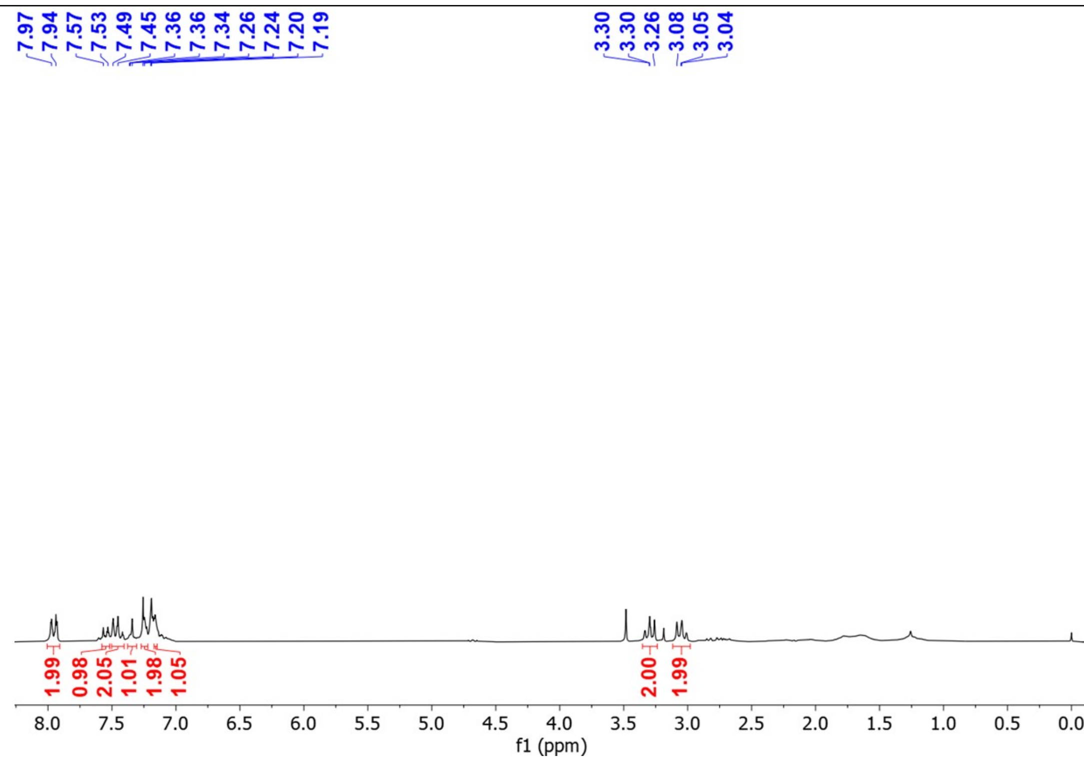


Fig. S150 In–situ ^{1}H NMR of **32b** in $CDCl_3$ at 298K.

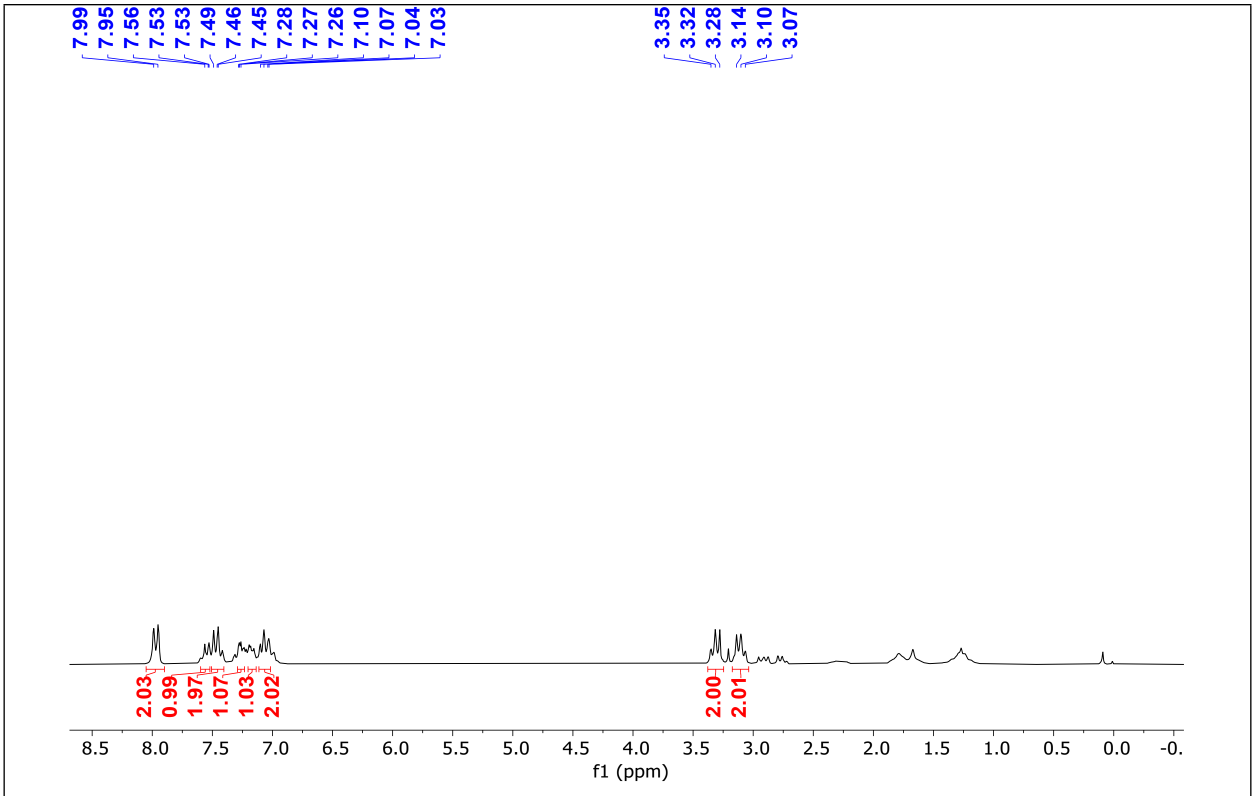


Fig. S151 In–situ ^{1}H NMR of **33b** in $CDCl_3$ at 298K.

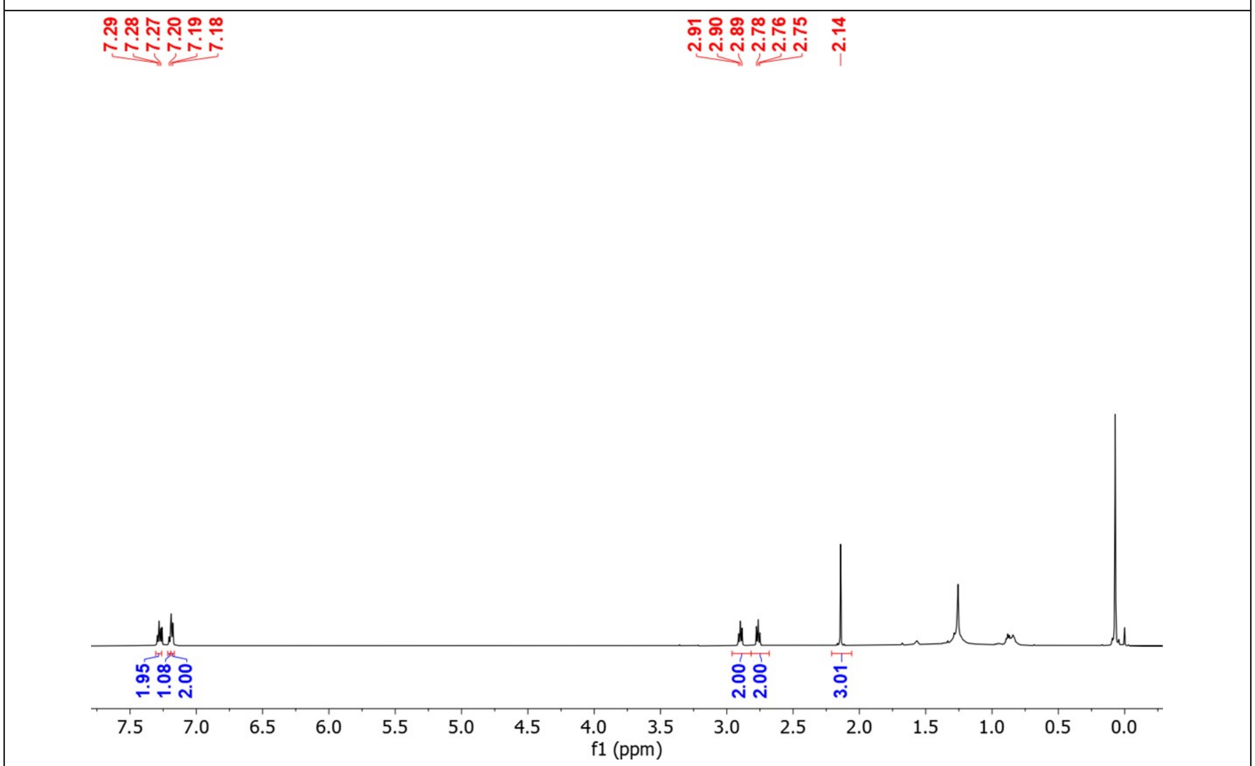


Fig. S152 In–situ ^{1}H NMR of **36b** in $CDCl_3$ at 298K.

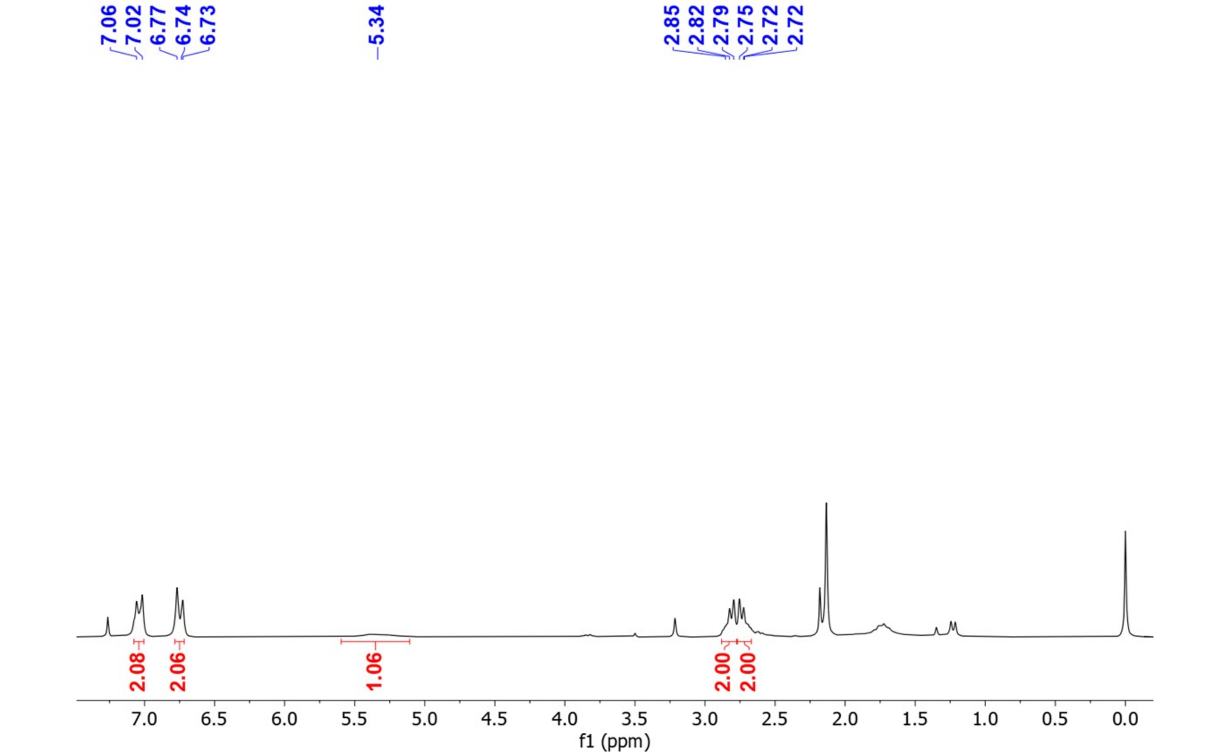


Fig. S153 In–situ ^{1}H NMR of **37b** in $CDCl_3$ at 298K.

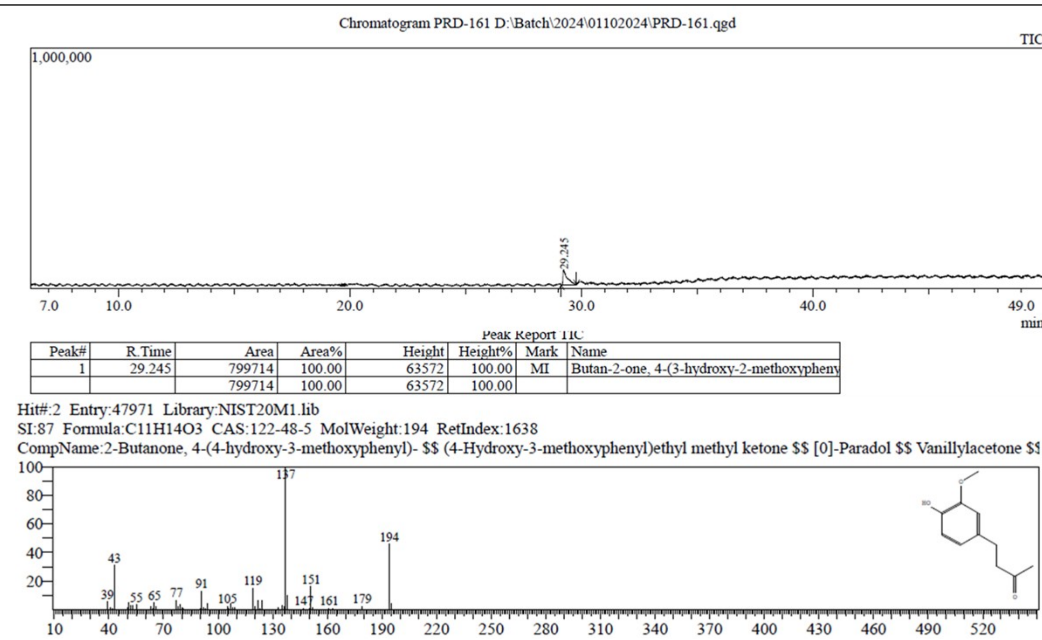


Fig. S154 GC-MS spectra of **38b** in ethyl acetate.

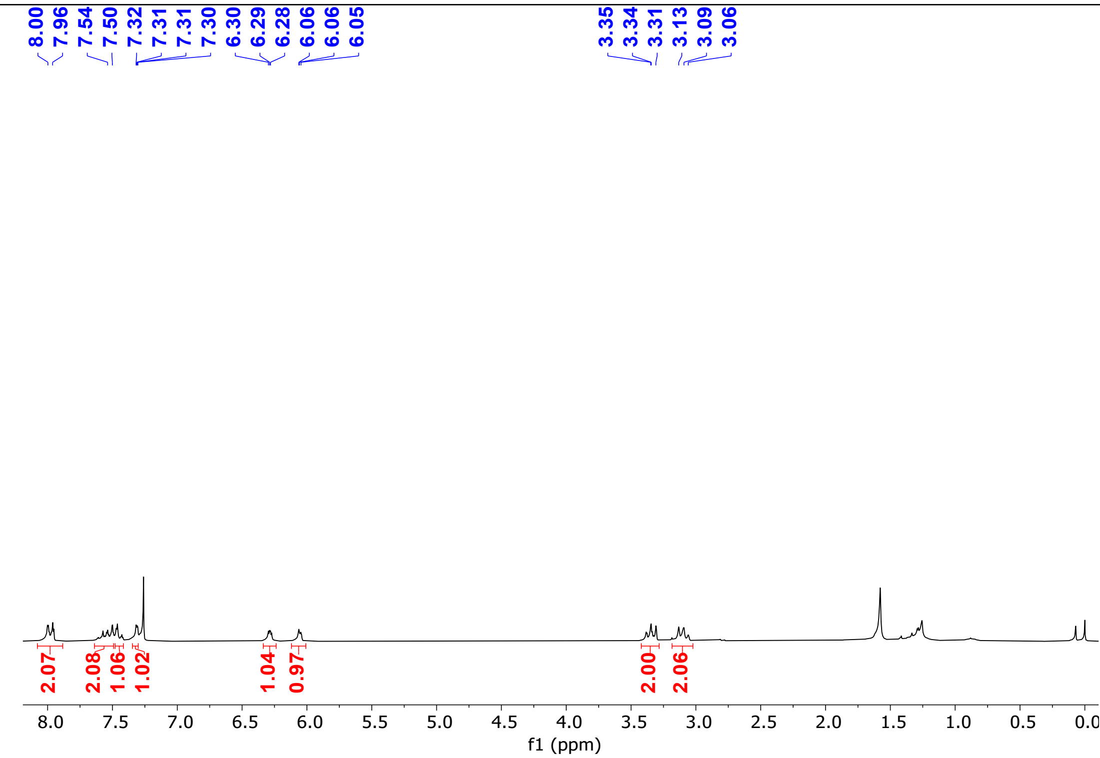


Fig. S155 In–situ ^{1}H NMR of **39b** in $CDCl_3$ at 298K.

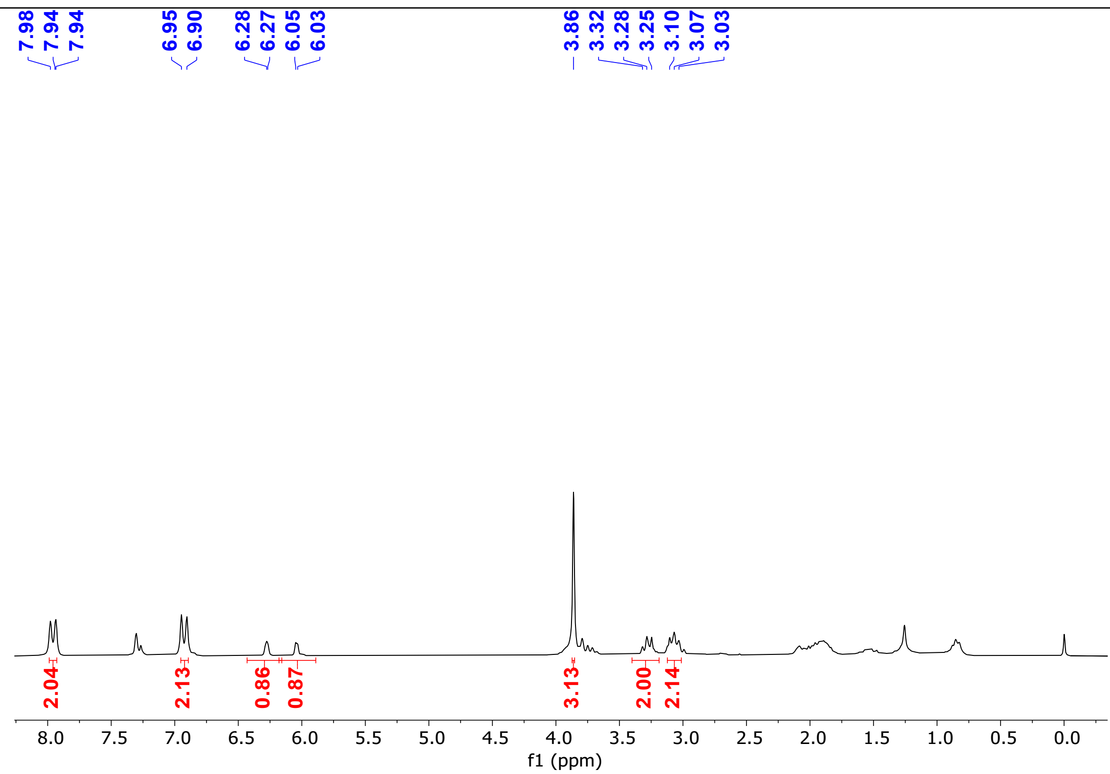


Fig. S156 In–situ ^{1}H NMR of **40b** in $CDCl_3$ at 298K.

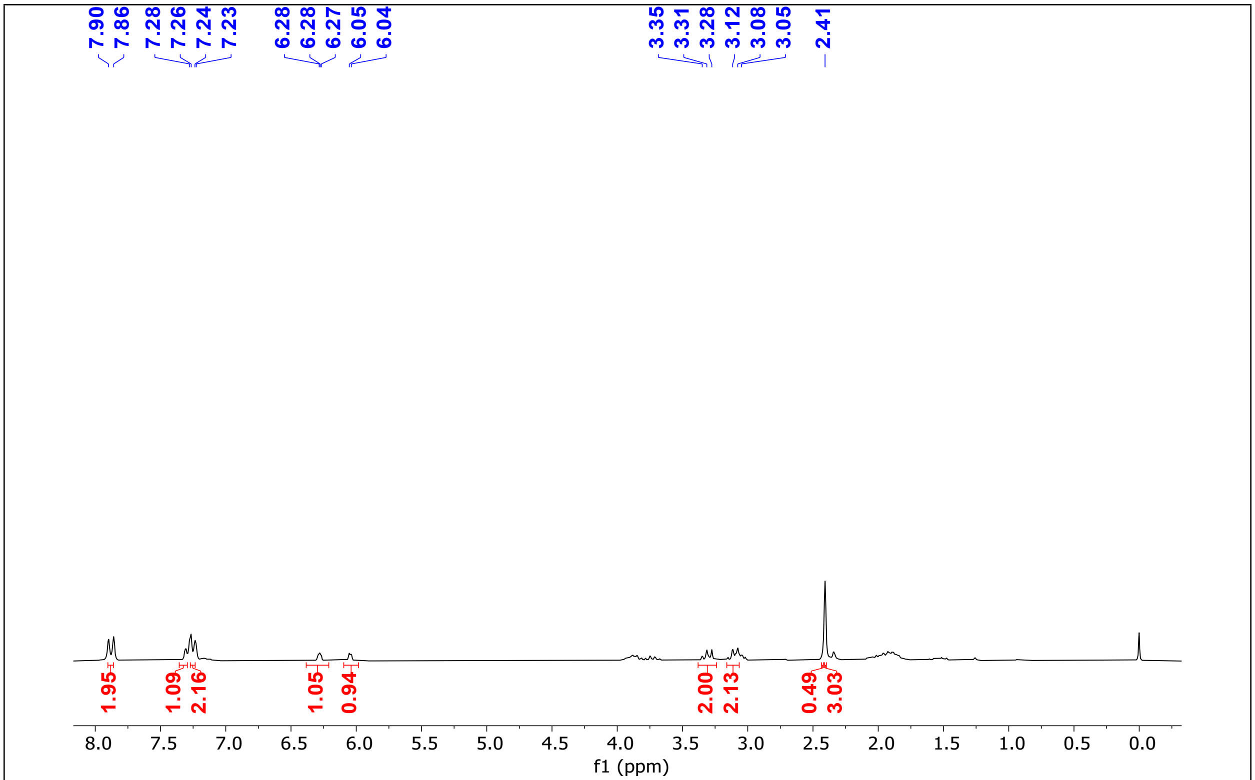


Fig. S157 In–situ [1]H NMR of **41b** in $CDCl_3$ at 298K.

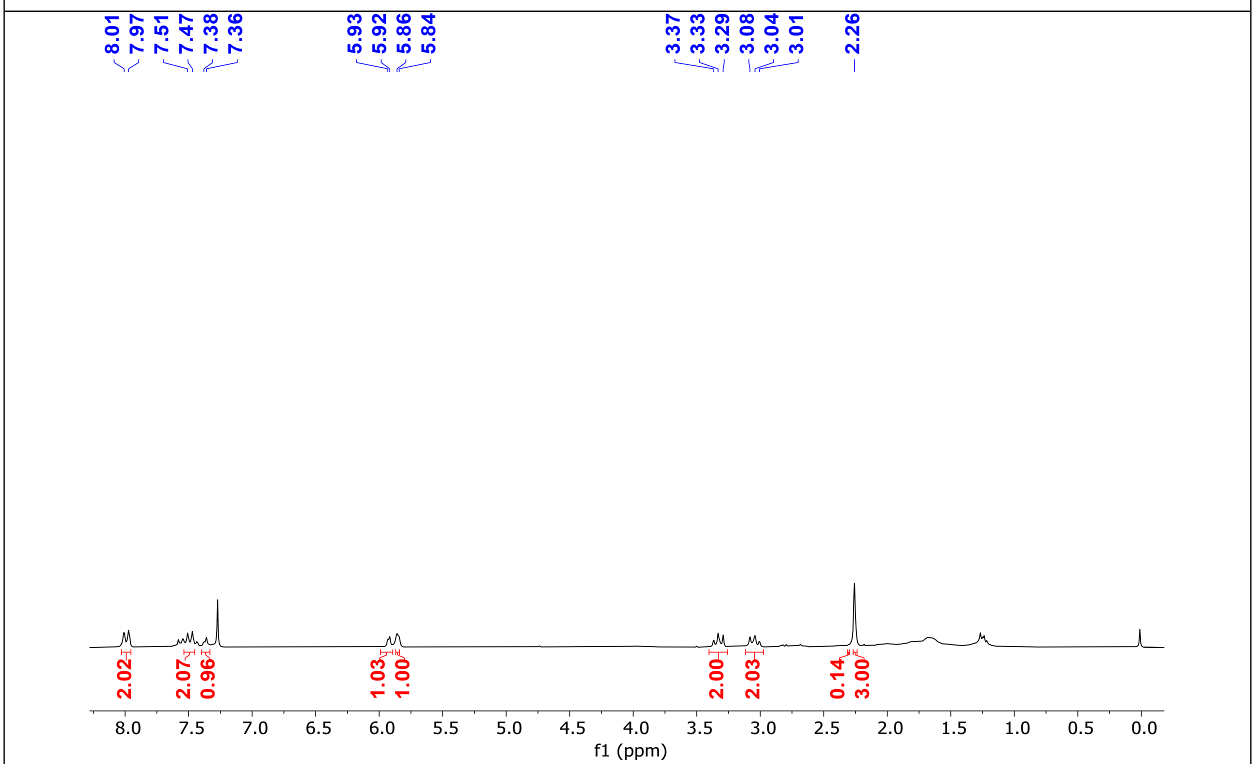


Fig. S158 In–situ [1]H NMR of **44b** in $CDCl_3$ at 298K.

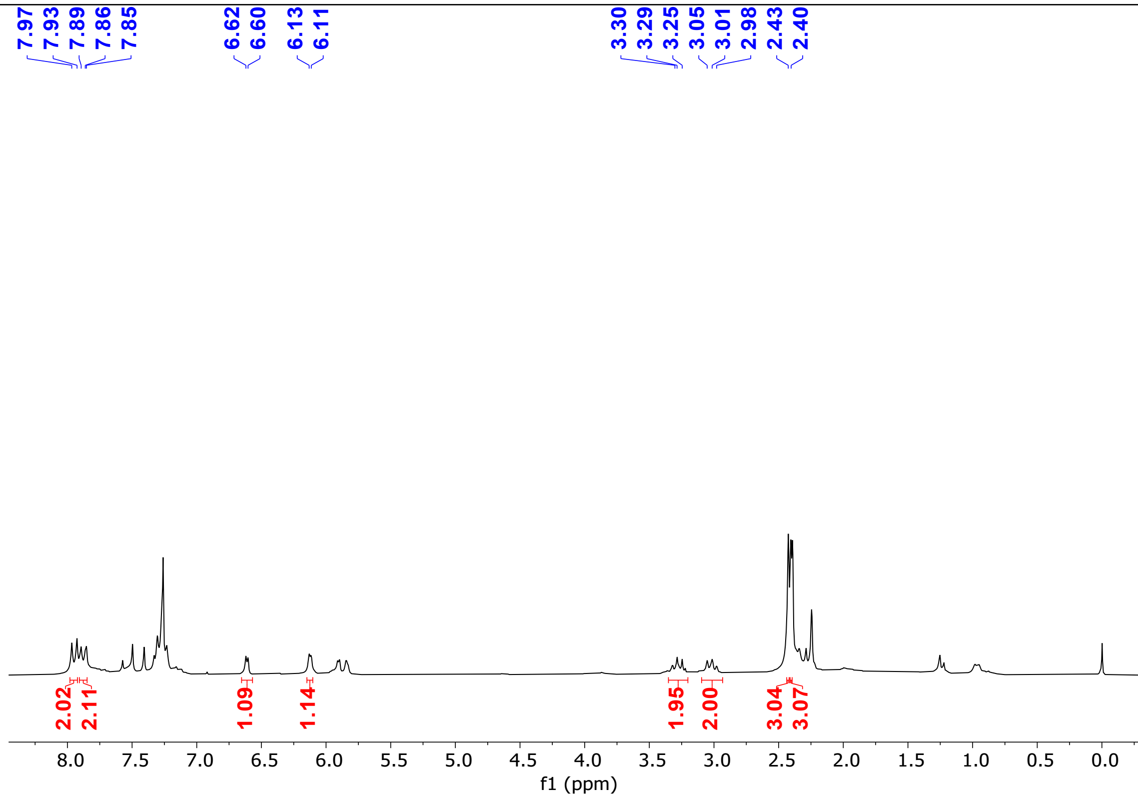


Fig. S159 In–situ ^{1}H NMR of **46b** in $CDCl_3$ at 298K.

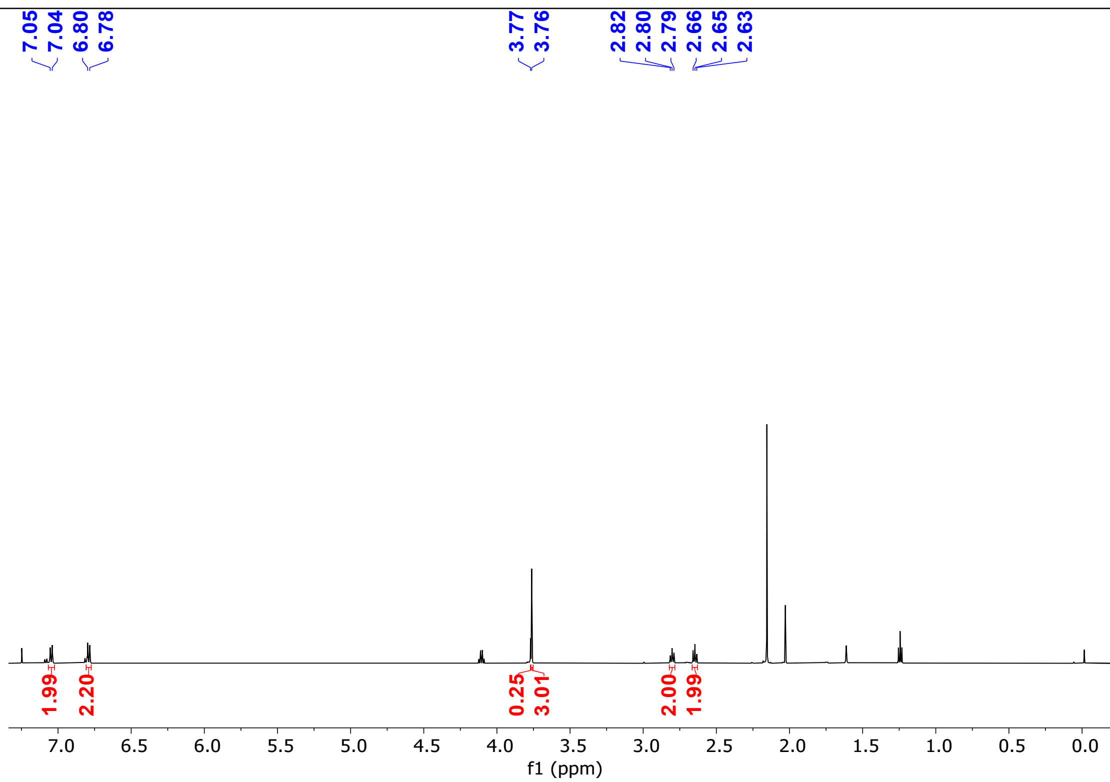


Fig. S160 In–situ ^{1}H NMR of **2f** in $CDCl_3$ at 298K.

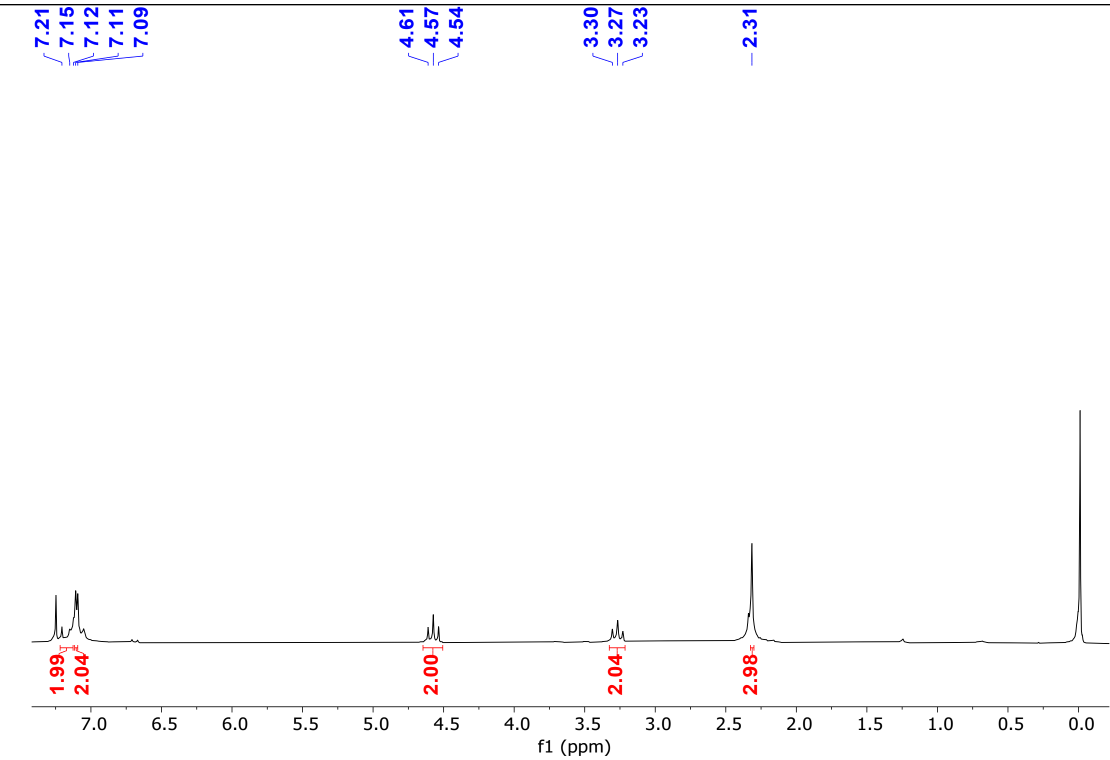


Fig. S161 In–situ ^{1}H NMR of **2i** in $CDCl_3$ at 298K.

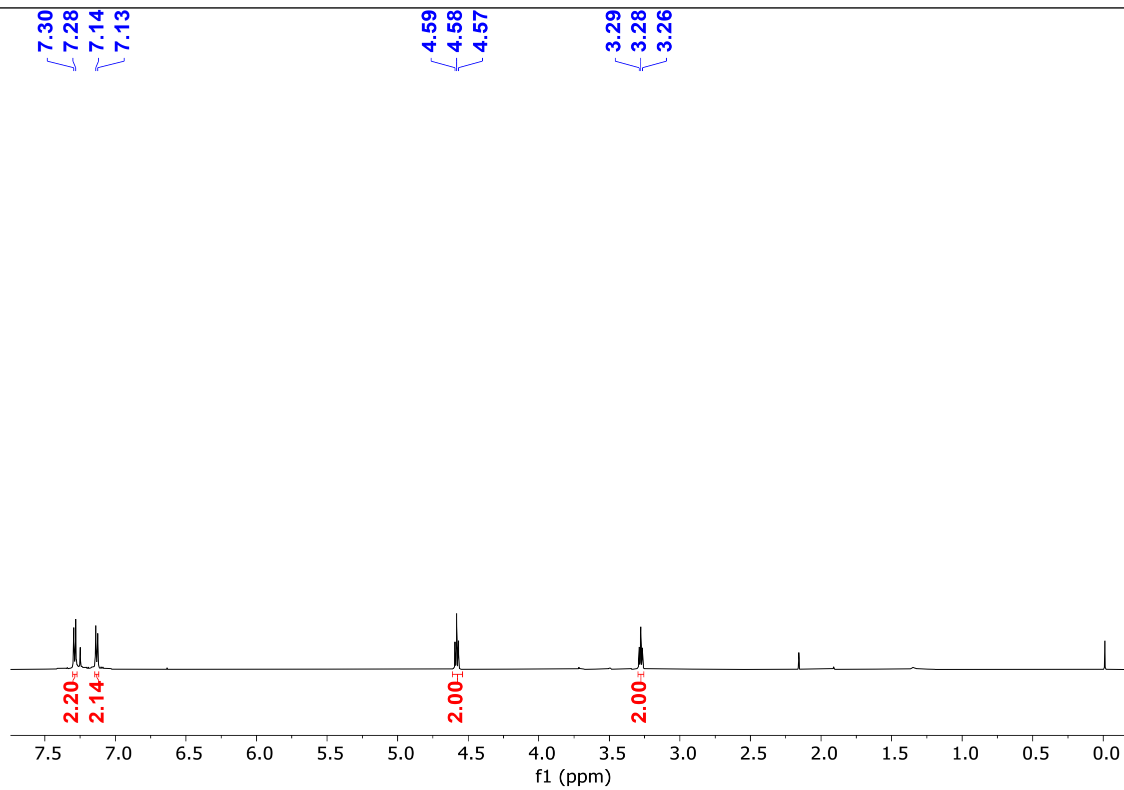


Fig. S162 In–situ ^{1}H NMR of **4i** in $CDCl_3$ at 298K.

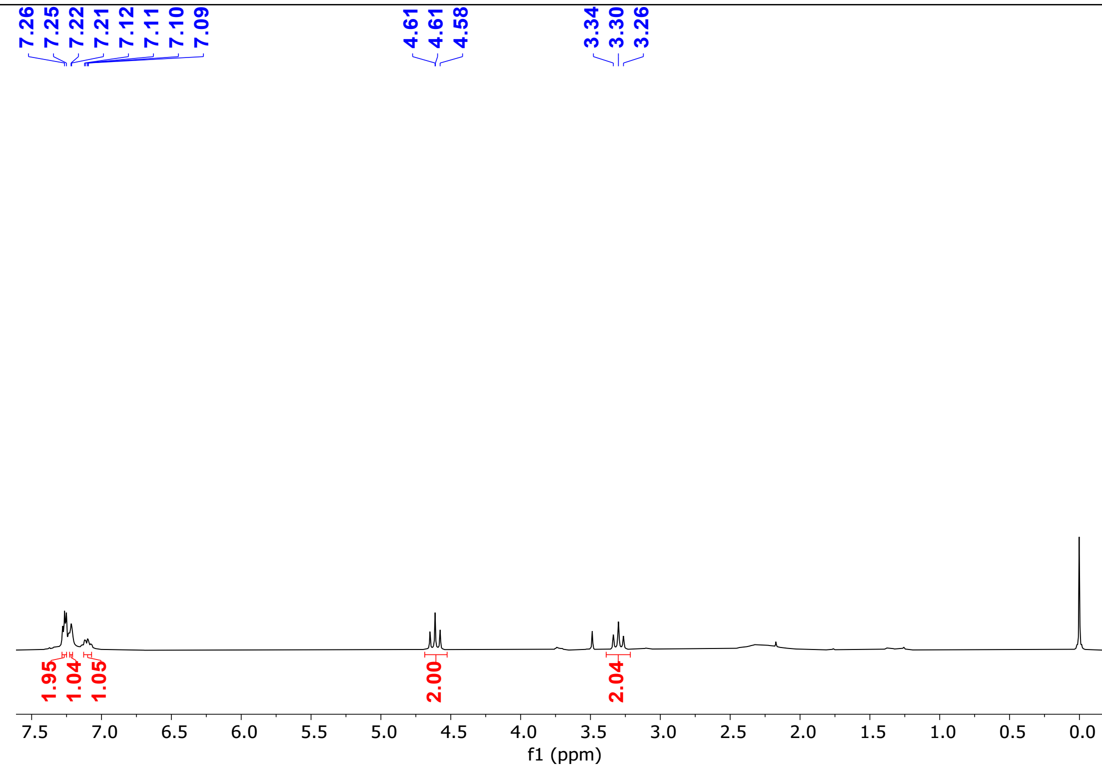


Fig. S163 In–situ ^{1}H NMR of **5i** in $CDCl_3$ at 298K.

4 *Mechanistic experiments*

4.1 Deuterium labelling experiment

For this, 0.25 mmol of **1a** substrate was mixed with 1.2 mol% of the **Ru-1** catalyst in mixture of THF and CD_3OD (THF:CD_3OD = 10:1 mL) in a high-pressure reactor. The mixture was stirred at room temperature (29–32°C) under 20 bar of H_2 pressure for 18 h. Upon completion of the reaction, the volatile components were removed under high vacuum to yield the crude product, which was analyzed using ^{1}H NMR spectroscopy with unreacted substrates serving as the internal standard to check the incorporation of deuterium from methanol into the product.

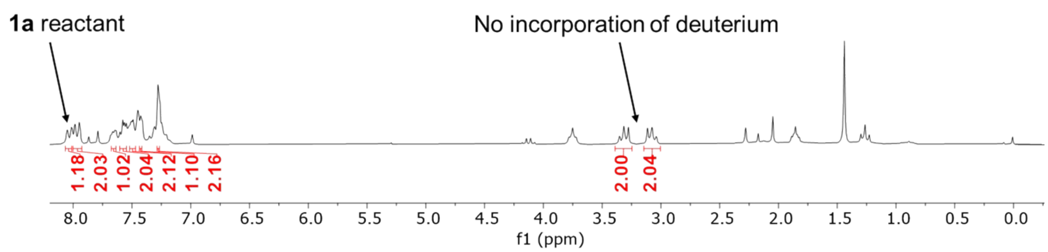


Fig. S164 ^{1}H NMR of deuterium exchange study in $CDCl_3$ at 298K.

4.2 ^{1}H NMR titration

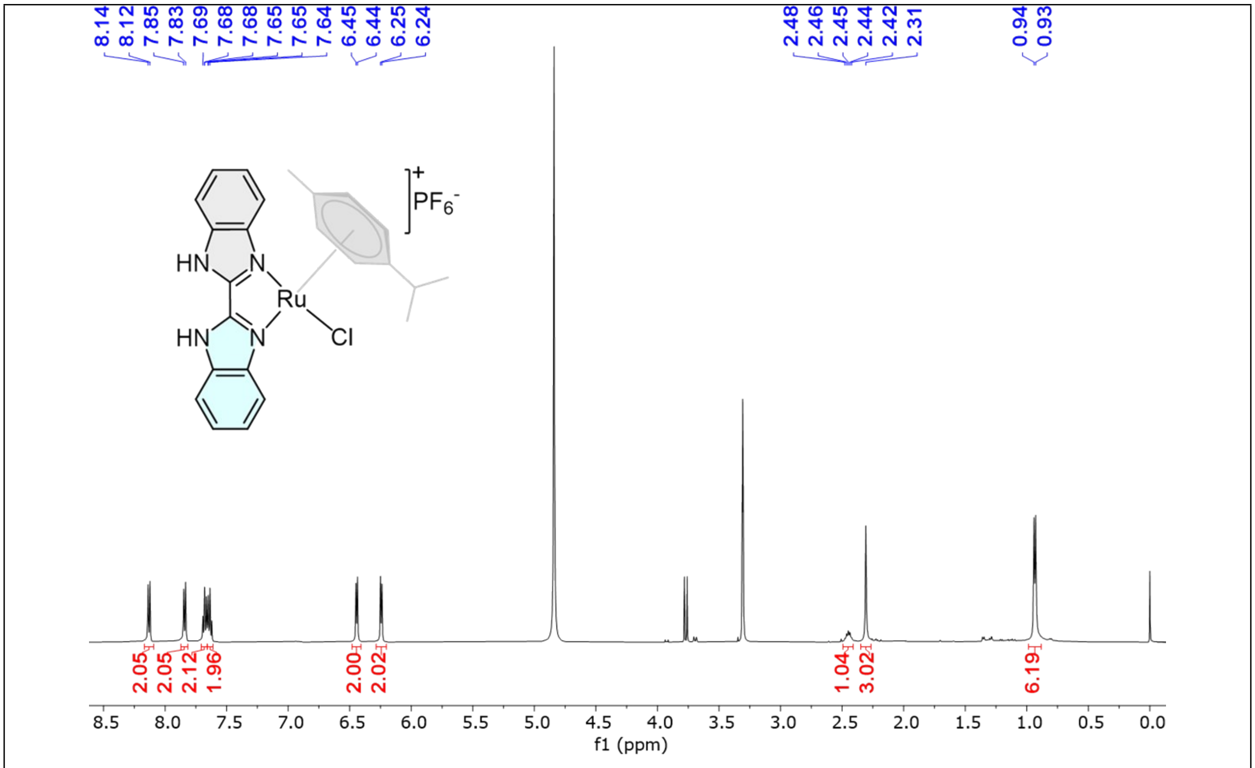


Fig. S165 ^{1}H NMR of **Ru-1** in CD_3OD at 298K.

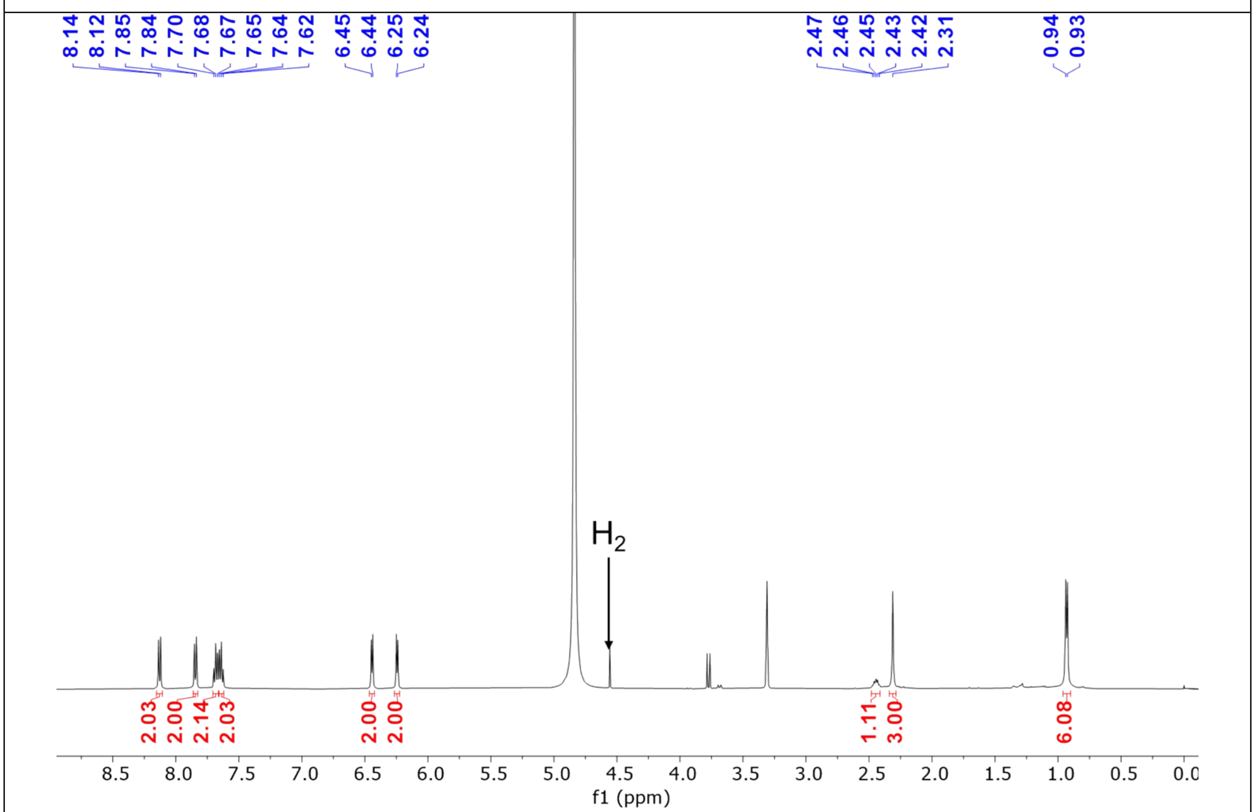


Fig. S166 ^{1}H NMR of **Ru-1** purged with H_2 in CD_3OD at 298K.

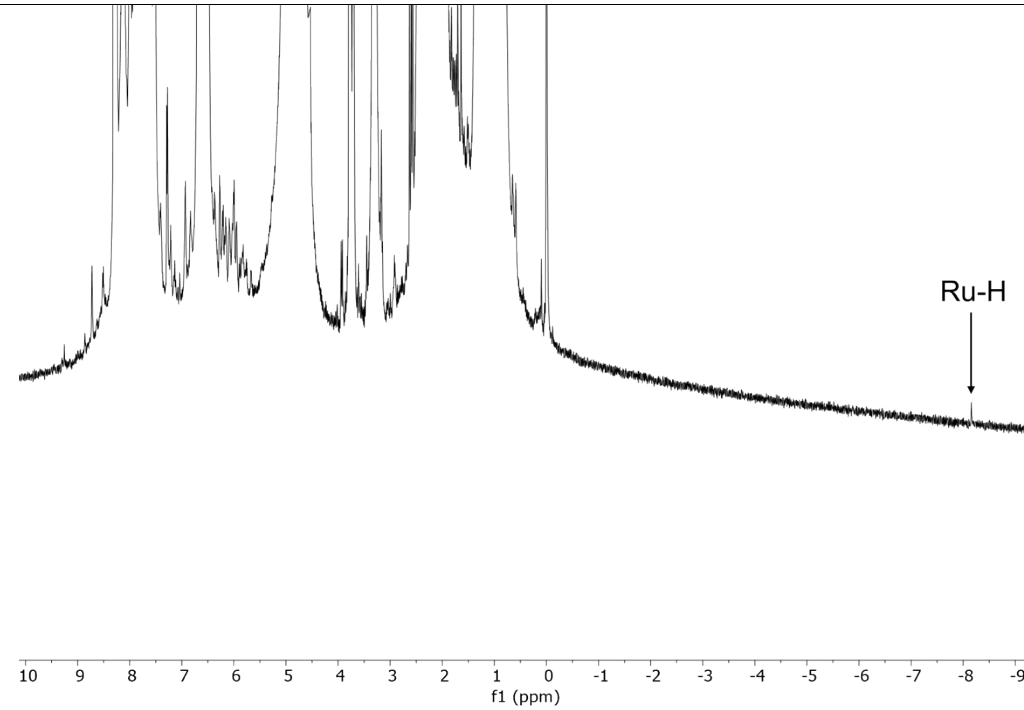
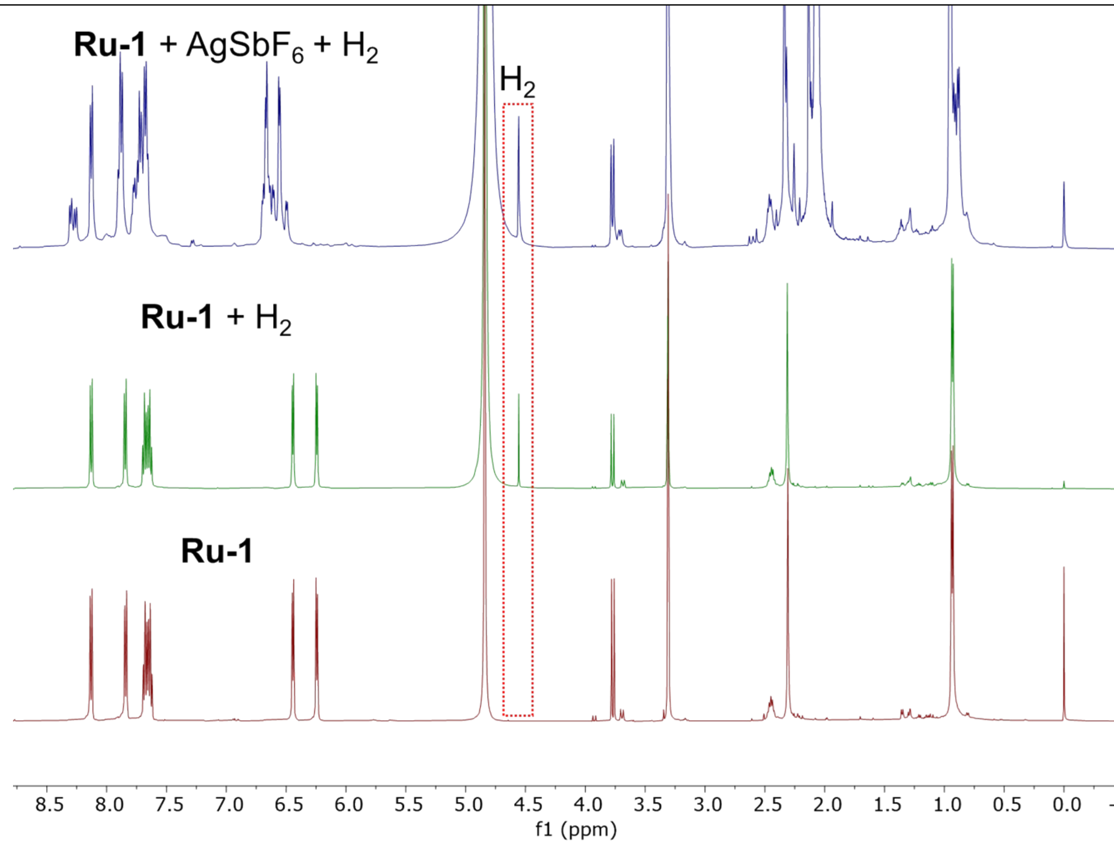


Fig. S167 ^{1}H NMR of **Ru-1** + AgSbF6 purged with H_2 for Ru-H in CD_3OD at 298K.



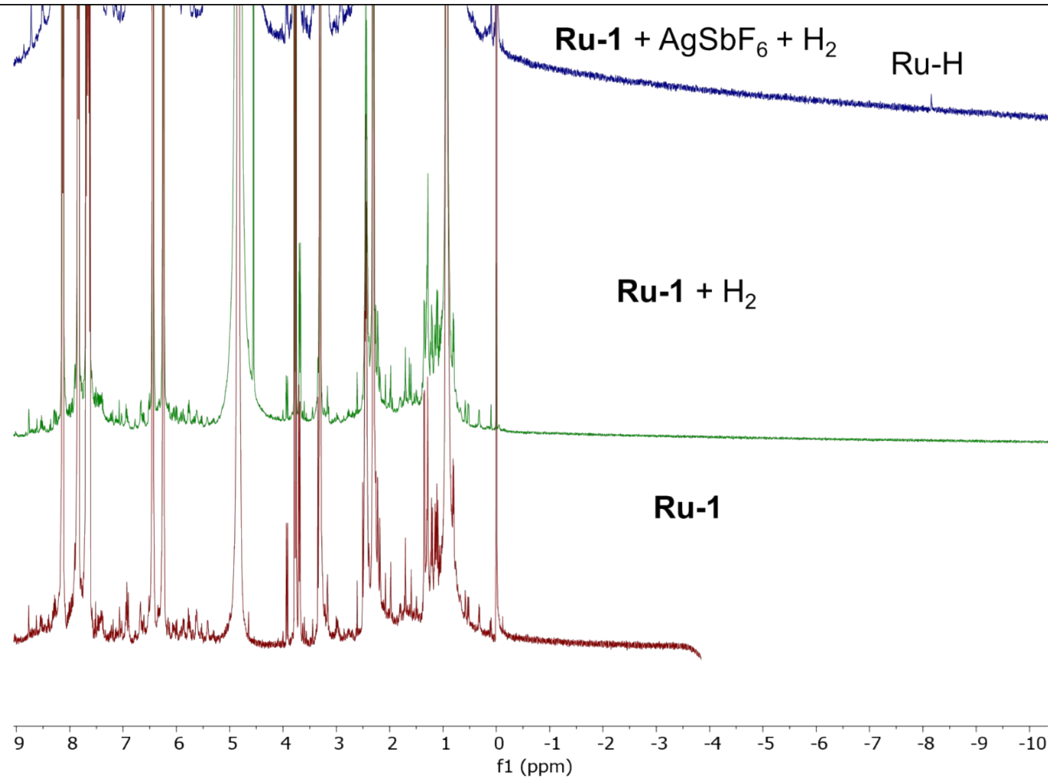


Fig. S168 ^{1}H NMR-titration stacked spectra in CD_3OD at 298K.

5 Large-scale reactions

For the scalability experiments, the variable concentrations (2.5 mM or 5 mM) of α,β-unsaturated ketones (**1a** or **2a**, or **37a**) were mixed with **Ru-1** (0.6 mol%) catalyst in methanol (20-50 mL) in a high-pressure reactor. The mixture was stirred at room temperature (29–32°C) under H_2 pressure (20-30 bar) for the required reaction time. Upon completion of the reaction, the methanol was removed under a high vacuum to yield the crude product, to which diethyl ether was added to precipitate the catalyst. Furthermore, filtration separates the catalyst and product, and further evaporation of diethyl ether to obtain the corresponding saturated ketone (**1b** or **2b**, or **37b**). The Conversion of the reaction was measured through GC-MS analysis.

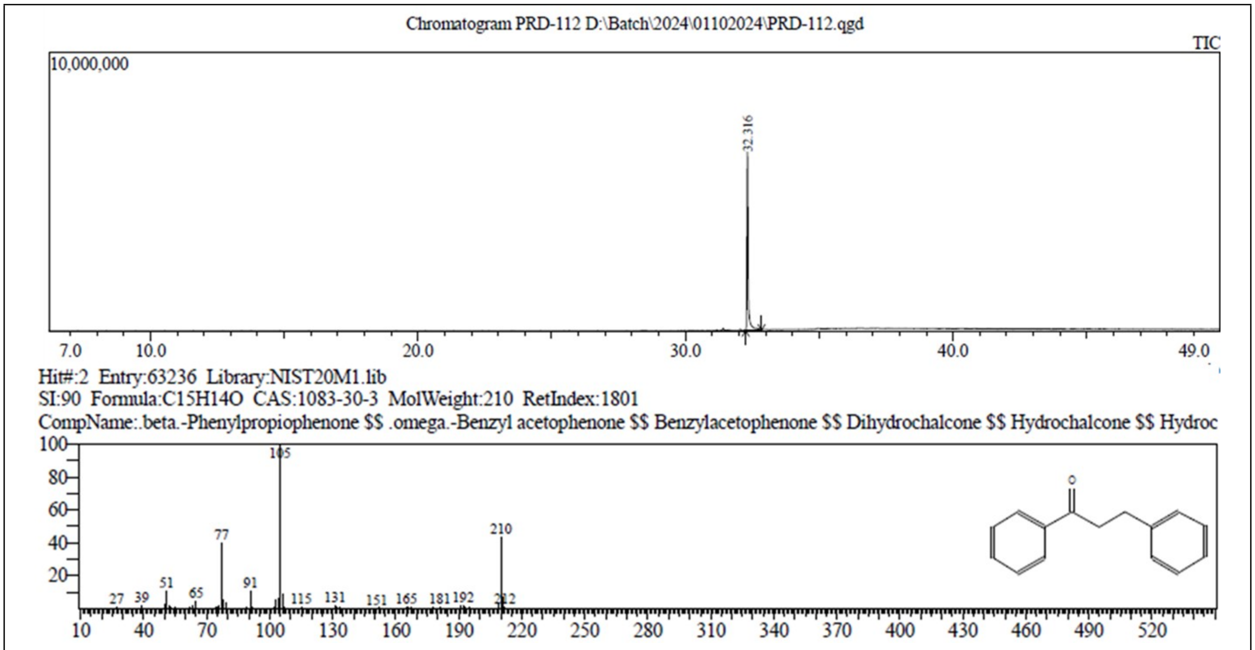


Fig. S169 GC-MS spectra of 2.5 mM **1a** hydrogenation in ethyl acetate.

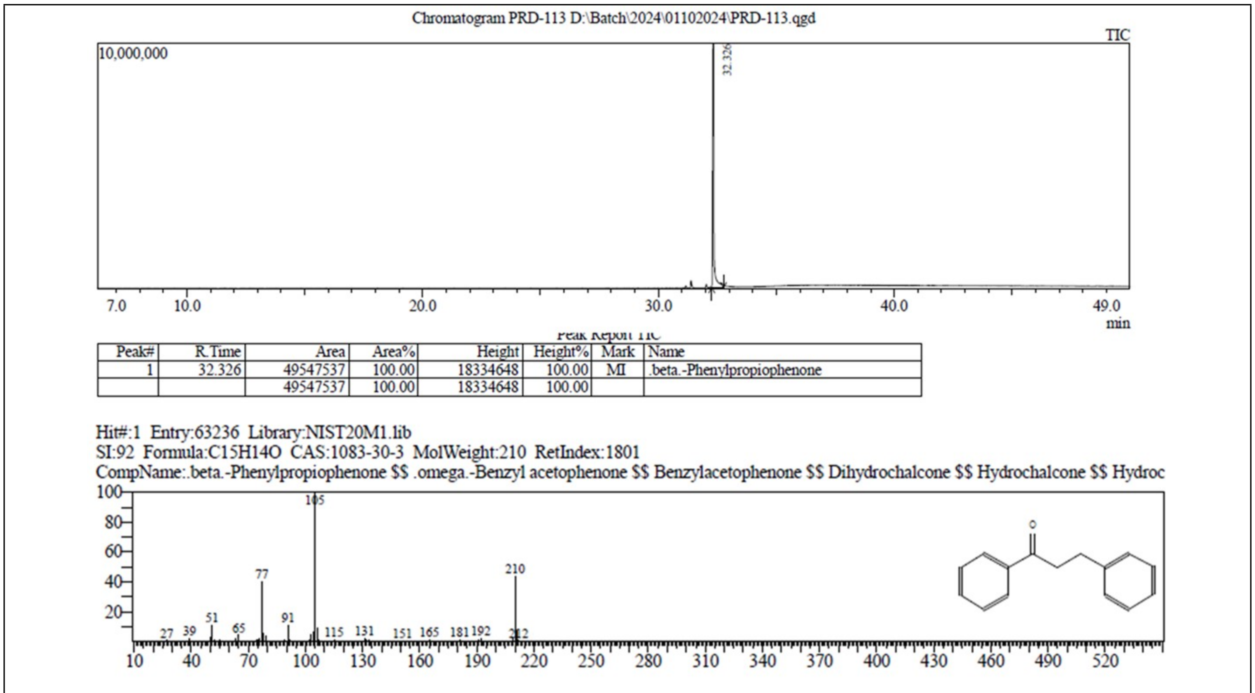


Fig. S170 GC-MS spectra of 5 mM **1a** hydrogenation in ethyl acetate.

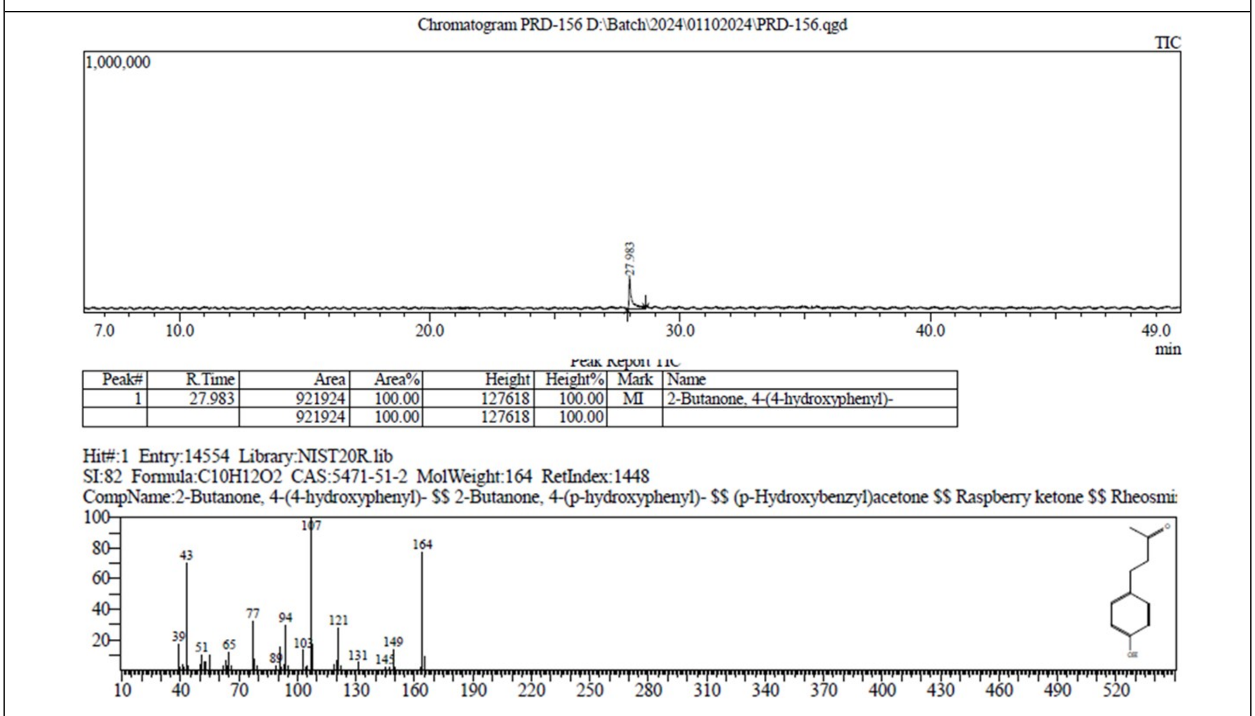
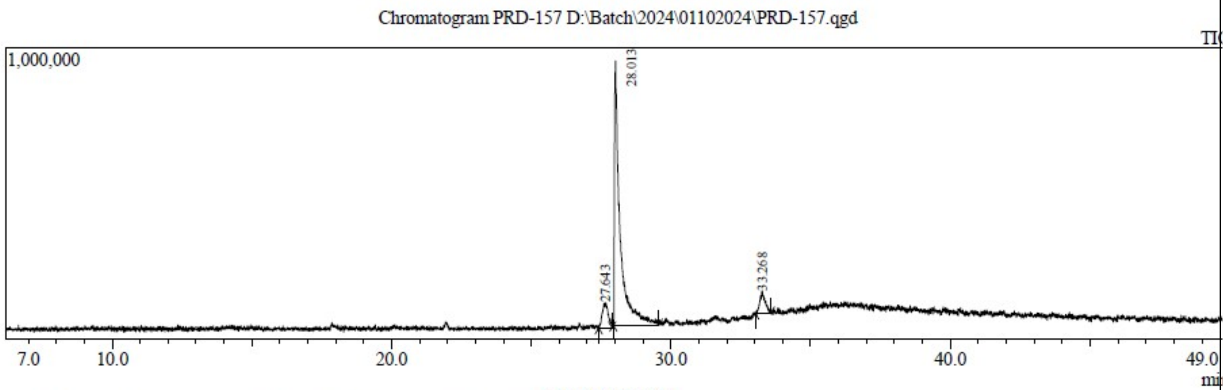


Fig. S171 GC-MS spectra of 2.5 mM **37a** hydrogenation in ethyl acetate.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Mark	Name
1	27.643	1267062	8.67	86893	8.09	MI	2-Methyl-1-phenyl-1-butanol
2	28.013	12404193	84.85	909502	84.71	MI	2-Butanone, 4-(4-hydroxyphenyl)-
3	33.268	947579	6.48	77216	7.19	MI	Benzene, (1-methoxypropyl)-
		14618834	100.00	1073611	100.00		

Hit#:1 Entry:14554 Library:NIST20R.lib
SI:83 Formula:C10H12O2 CAS:5471-51-2 MolWeight:164 RetIndex:1448
CompName:2-Butanone, 4-(4-hydroxyphenyl)- $$ 2-Butanone, 4-(p-hydroxyphenyl)- $$ (p-Hydroxybenzyl)acetone $$ Raspberry ketone $$ Rheosm

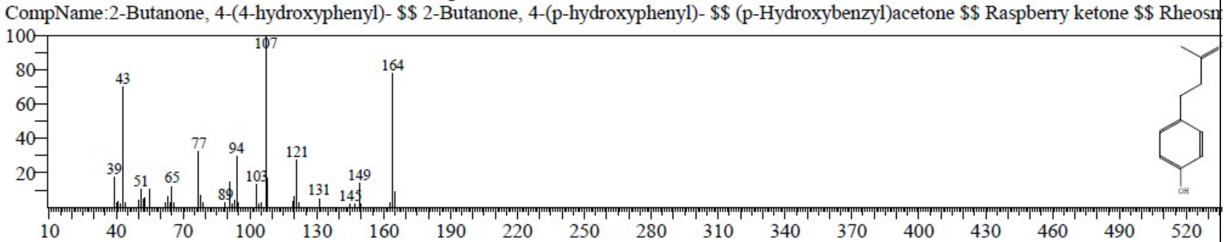


Fig. S172 GC-MS spectra of 5 mM **37a** hydrogenation in ethyl acetate.

6. Reusability study

For the catalyst reusability studies, the hydrogenation of substrate **1a** (0.25 mmol, 52 mg) was carried out using 1.2 mol% (2 mg) of **Ru-1** catalyst in 30 mL methanol under 20 bar H_2 pressure at ambient temperature (29–32 °C) for 2 hours in a high-pressure reactor. Upon completion of the first reaction cycle, 100 µL of the reaction mixture was withdrawn and analyzed by GC-MS to determine conversion. Subsequently, the reactor was recharged with a fresh batch of substrate 1a (0.25 mmol, 52 mg) and 20 bar H_2 pressure without adding additional **Ru-1** catalyst. This process was repeated for each subsequent cycle using the same catalyst batch. The **Ru-1** catalyst was successfully reused for 16 consecutive cycles, consistently delivering good to excellent conversions across all runs. The conversion for each cycle was quantified using GC-MS, confirming the robustness and sustained activity of the catalyst under the reaction conditions. These results highlight the reusability of **Ru-1**, demonstrating its potential for practical and scalable applications in homogeneous hydrogenation processes.

7. *Representative ^{1}H and ^{13}C spectra of α,β-unsaturated ketone substrates*

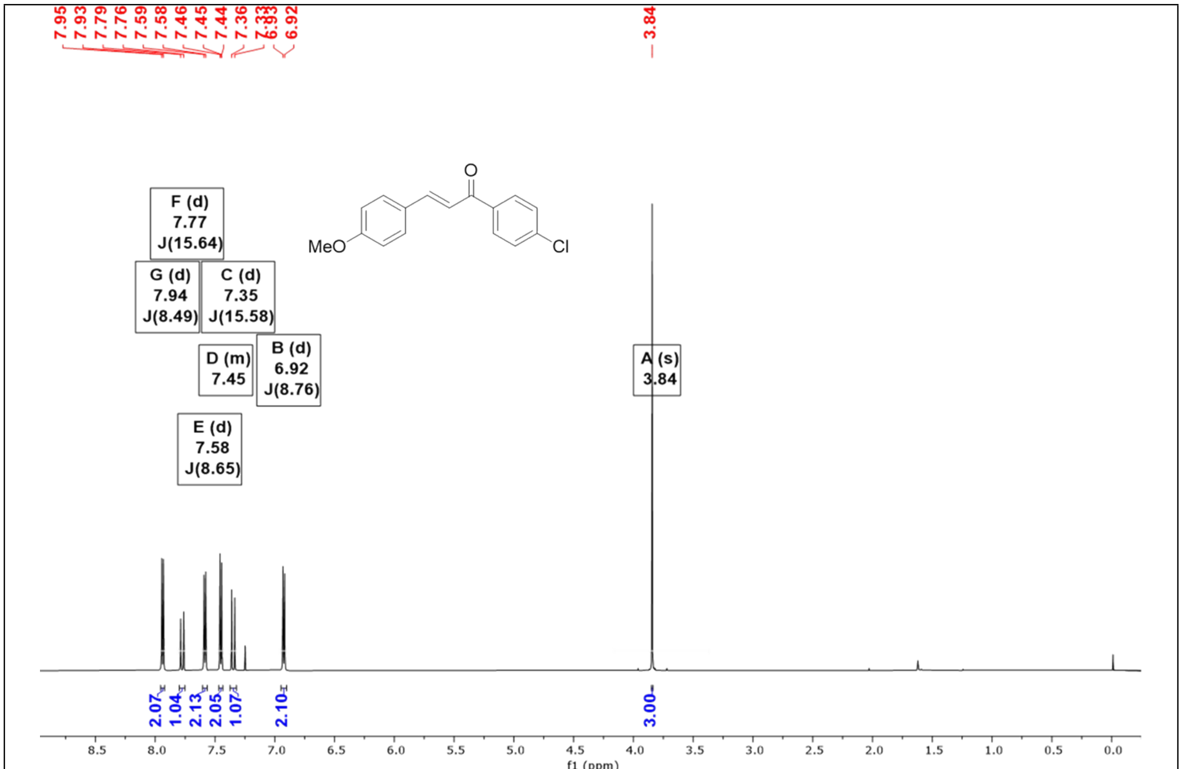


Fig. S173 ^{1}H NMR spectra of **4a** in $CDCl_3$ at 298 K.

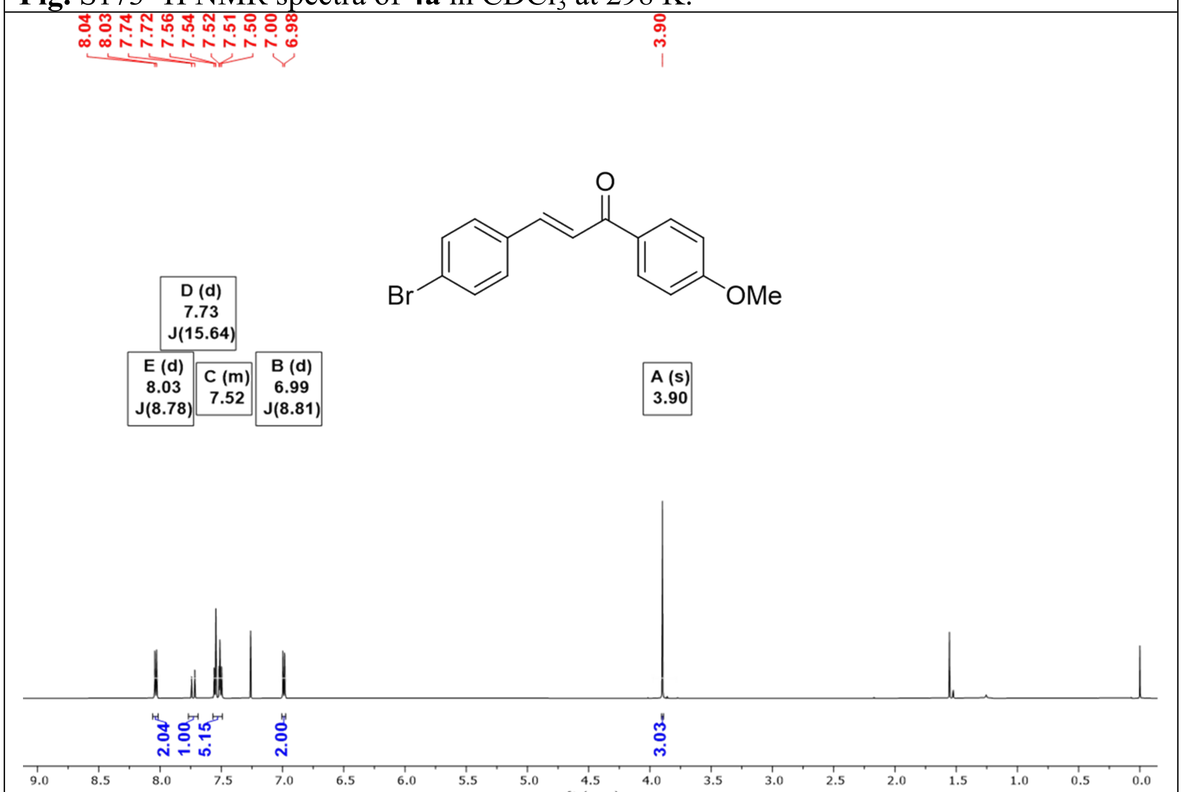


Fig. S174 ^{1}H NMR spectra of **7a** in $CDCl_3$ at 298 K.

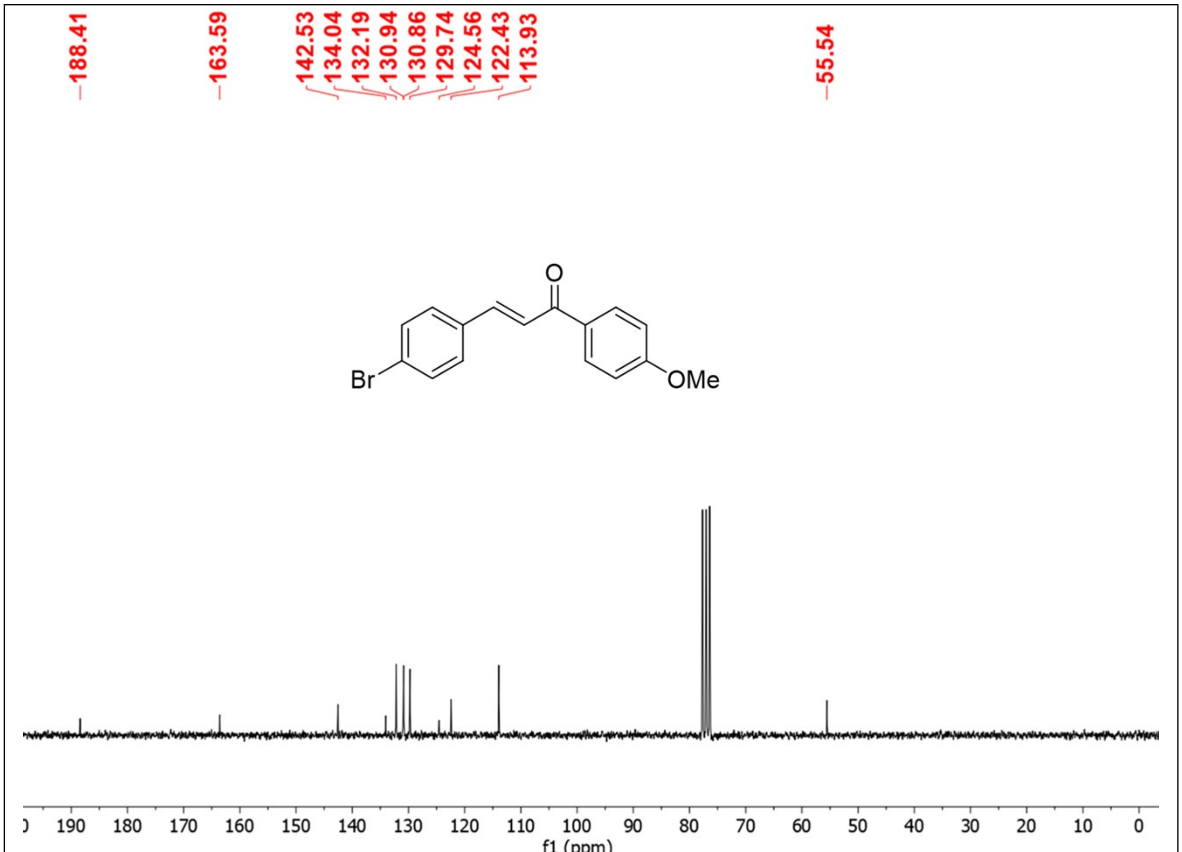


Fig. S175 $^{13}C\{^{1}H\}$ –NMR of **7a** in $CDCl_3$ at 298K.

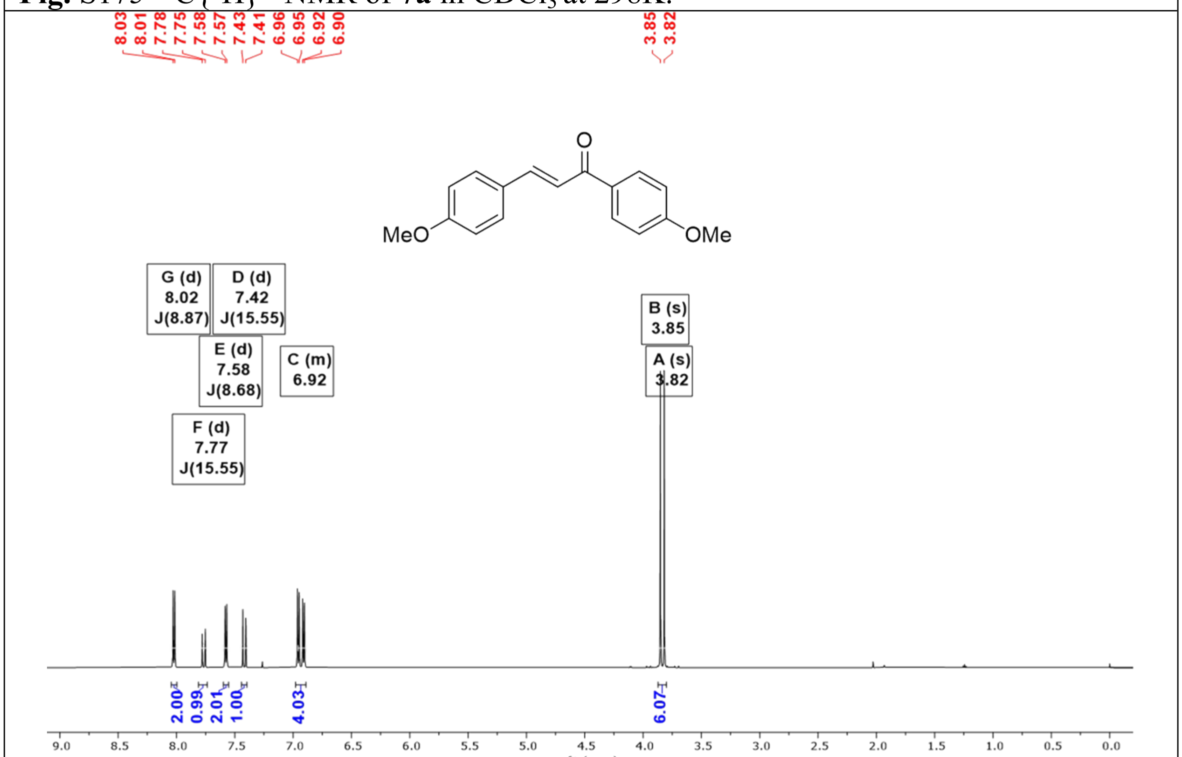


Fig. S176 ^{1}H NMR spectra of **9a** in $CDCl_3$ at 298 K.

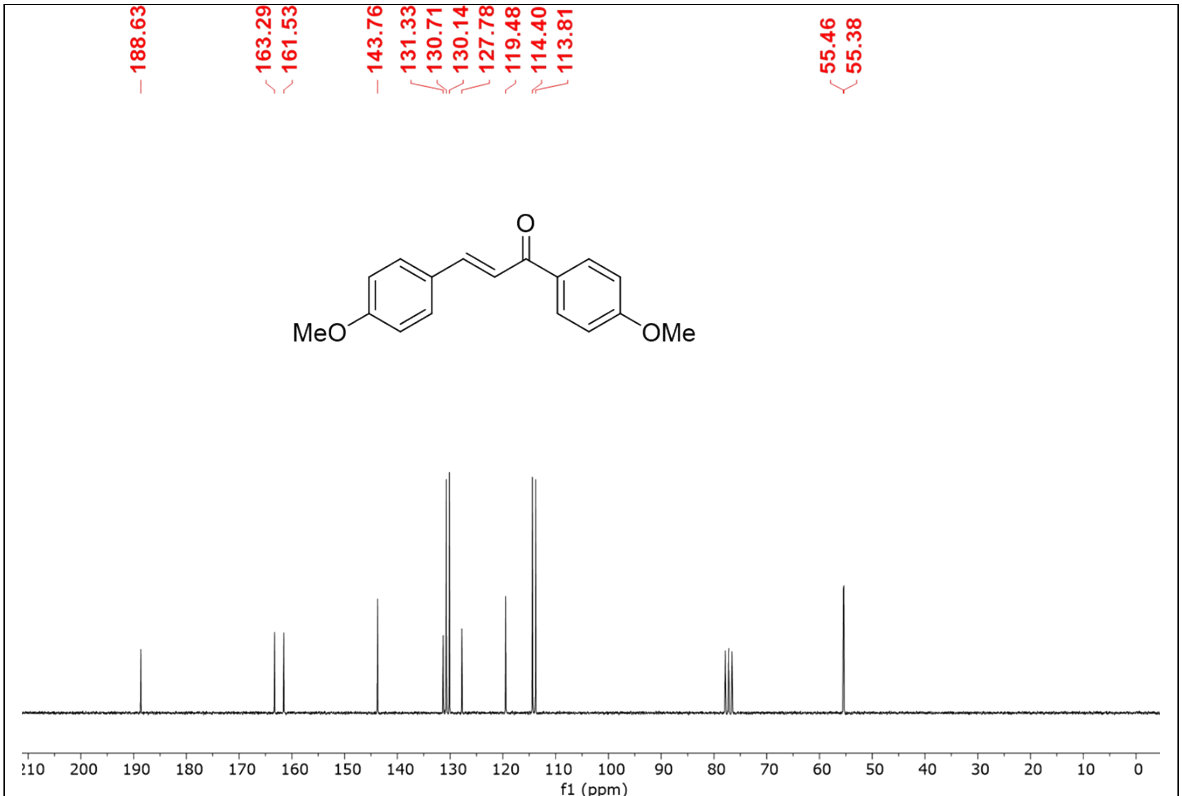


Fig. S177 $^{13}C\{^{1}H\}$ –NMR of **9a** in $CDCl_3$ at 298K.

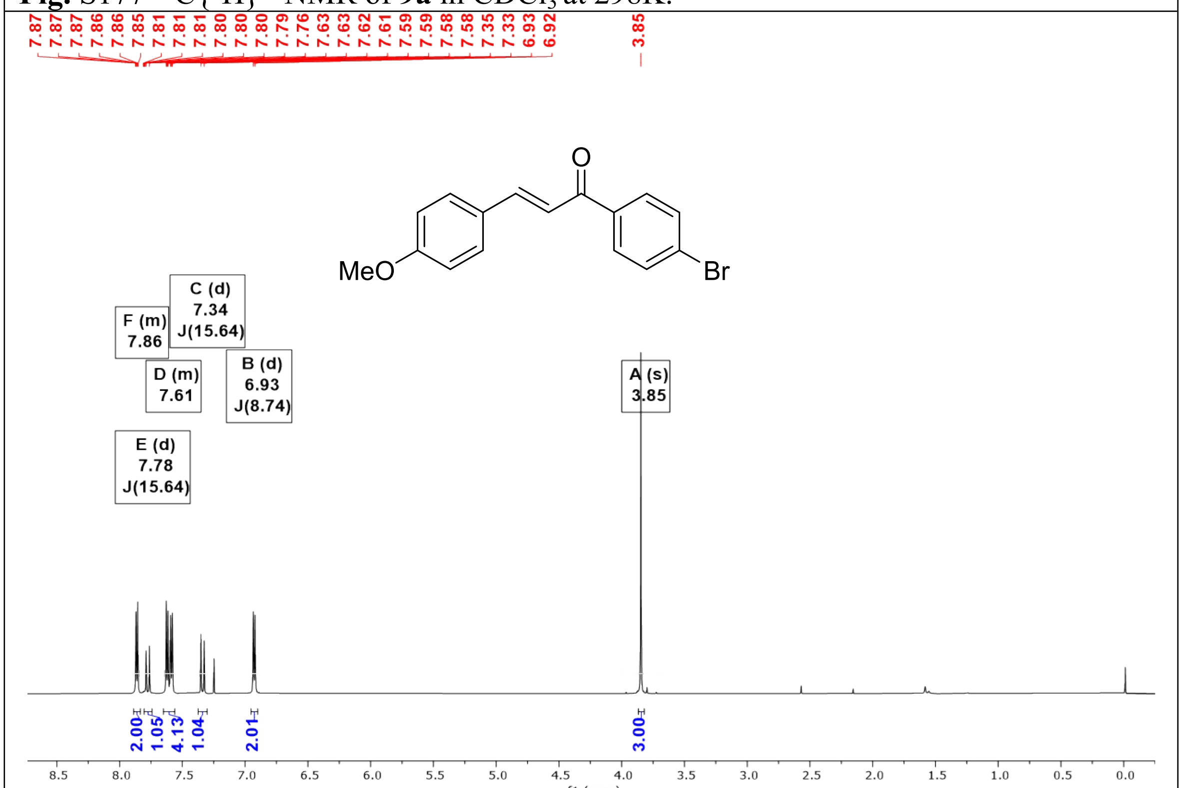


Fig. S178 ^{1}H NMR spectra of **12a** in $CDCl_3$ at 298 K.

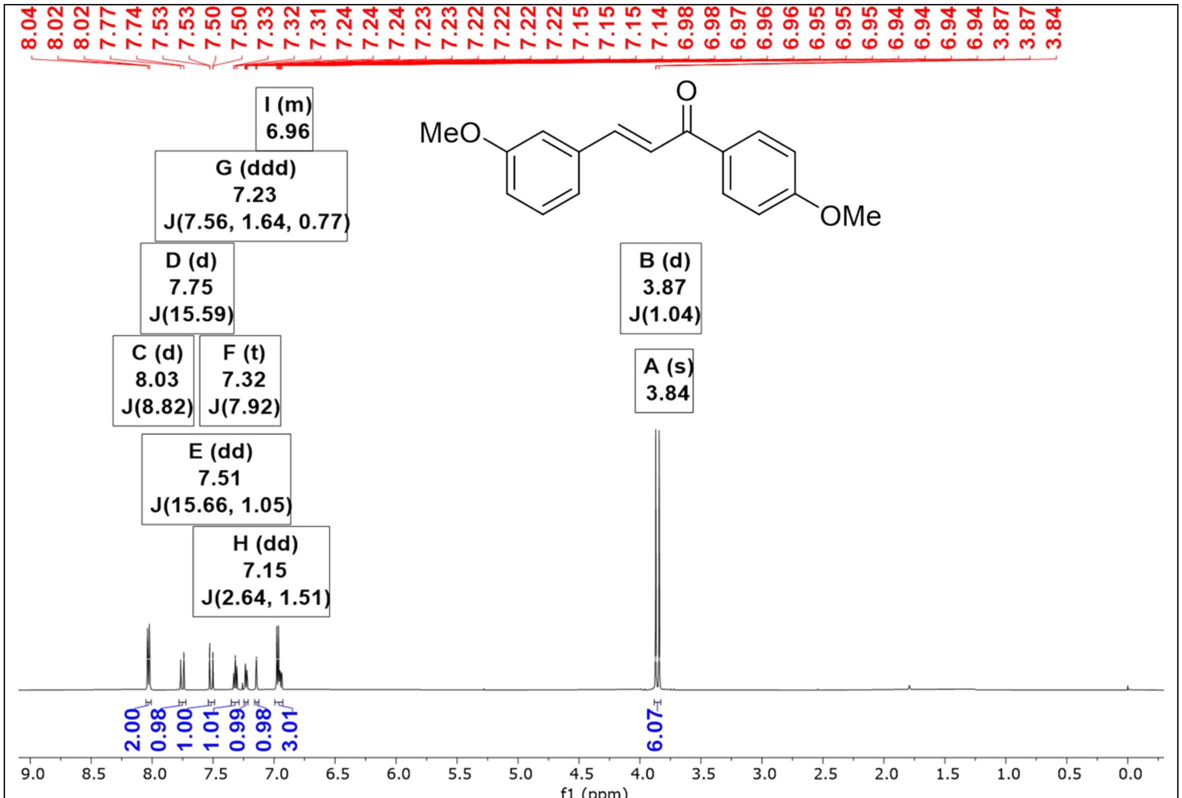


Fig. S179 ^{1}H NMR spectra of **17a** in $CDCl_3$ at 298 K.

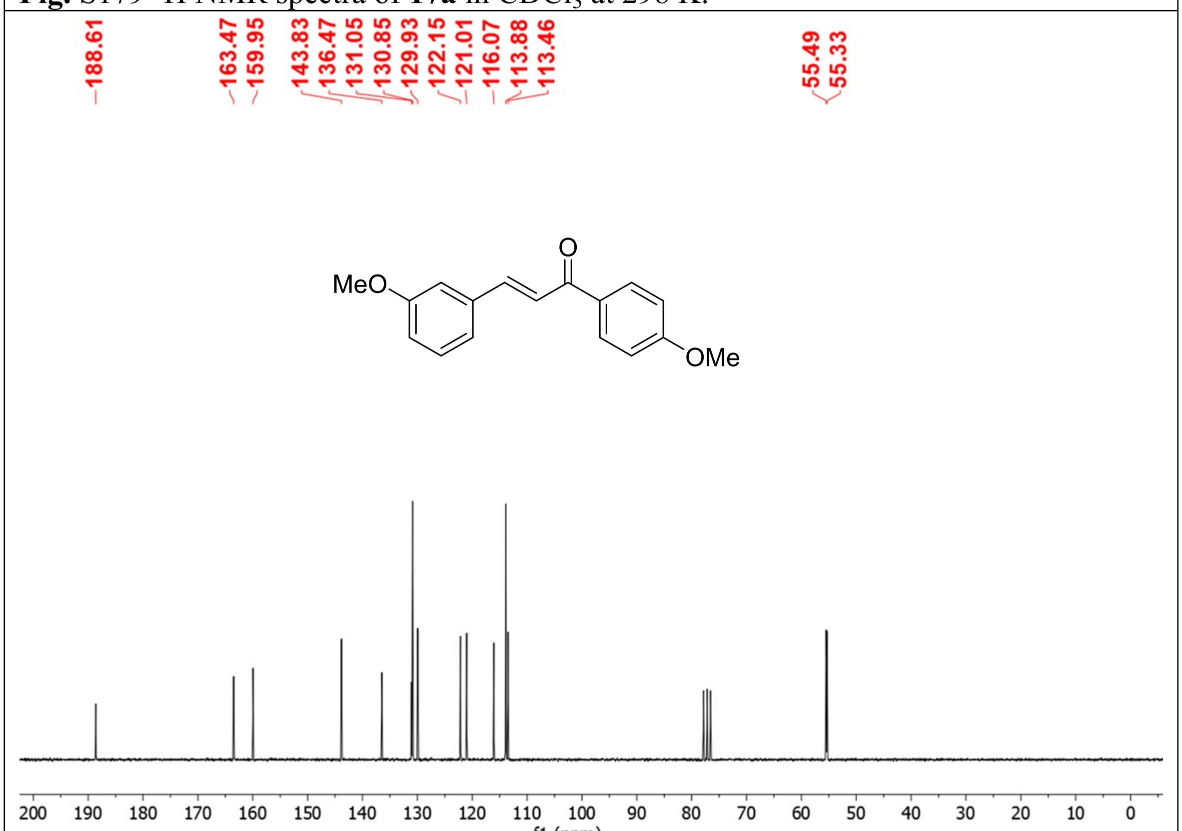


Fig. S180 $^{13}C\{^{1}H\}$ –NMR of **17a** in $CDCl_3$ at 298K.

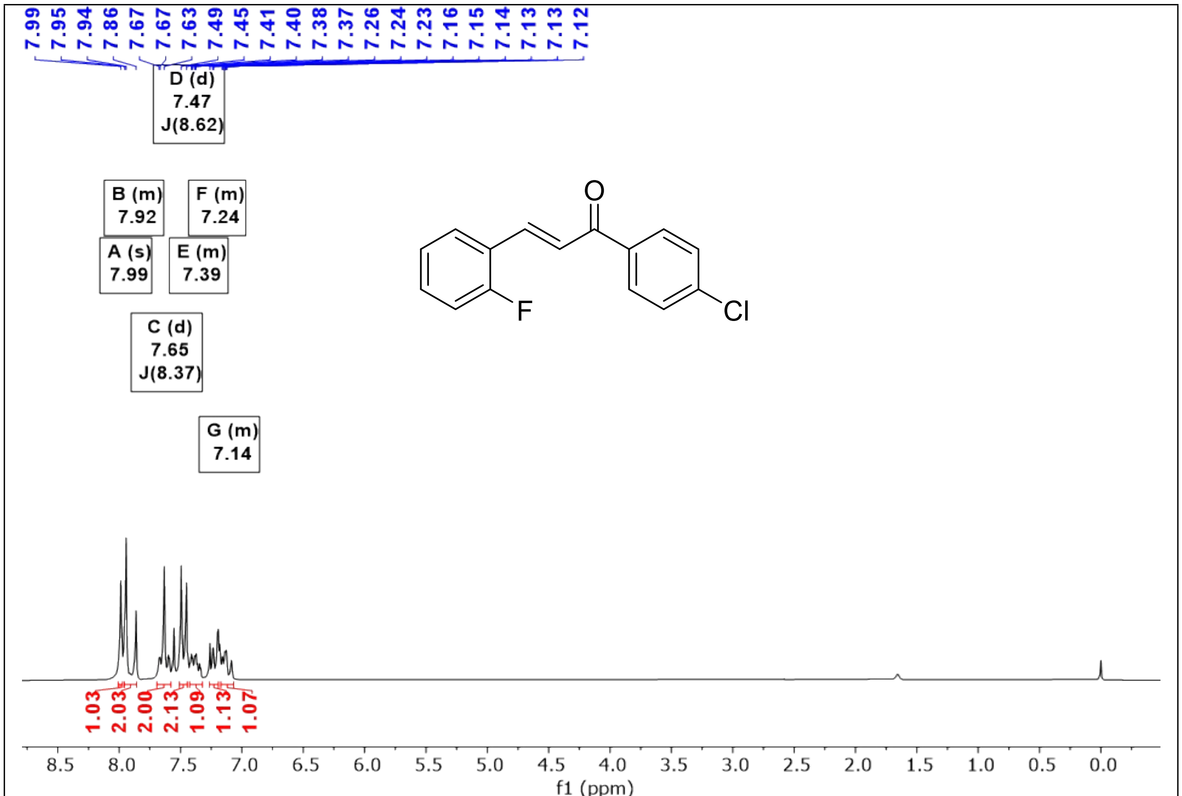


Fig. S181 ^{1}H NMR spectra of **34a** in $CDCl_3$ at 298 K.

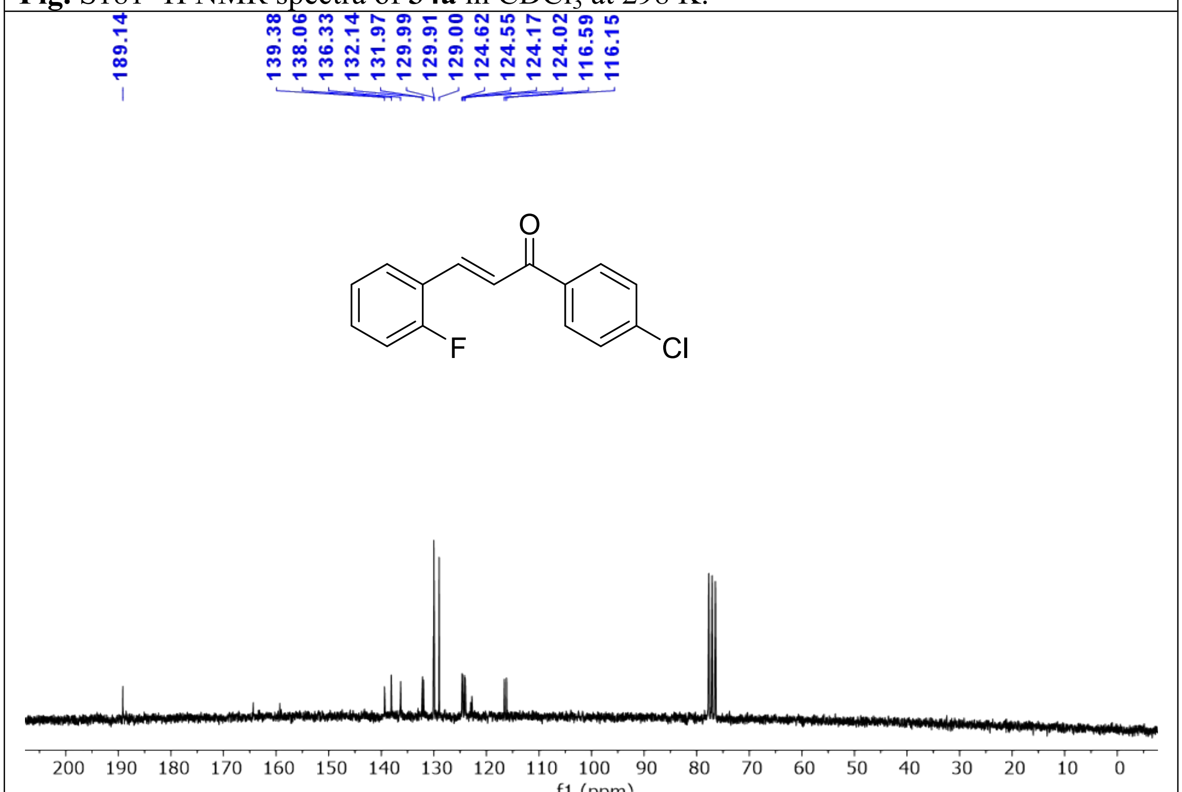


Fig. S182 $^{13}C\{^1H\}$ –NMR of **34a** in $CDCl_3$ at 298K.

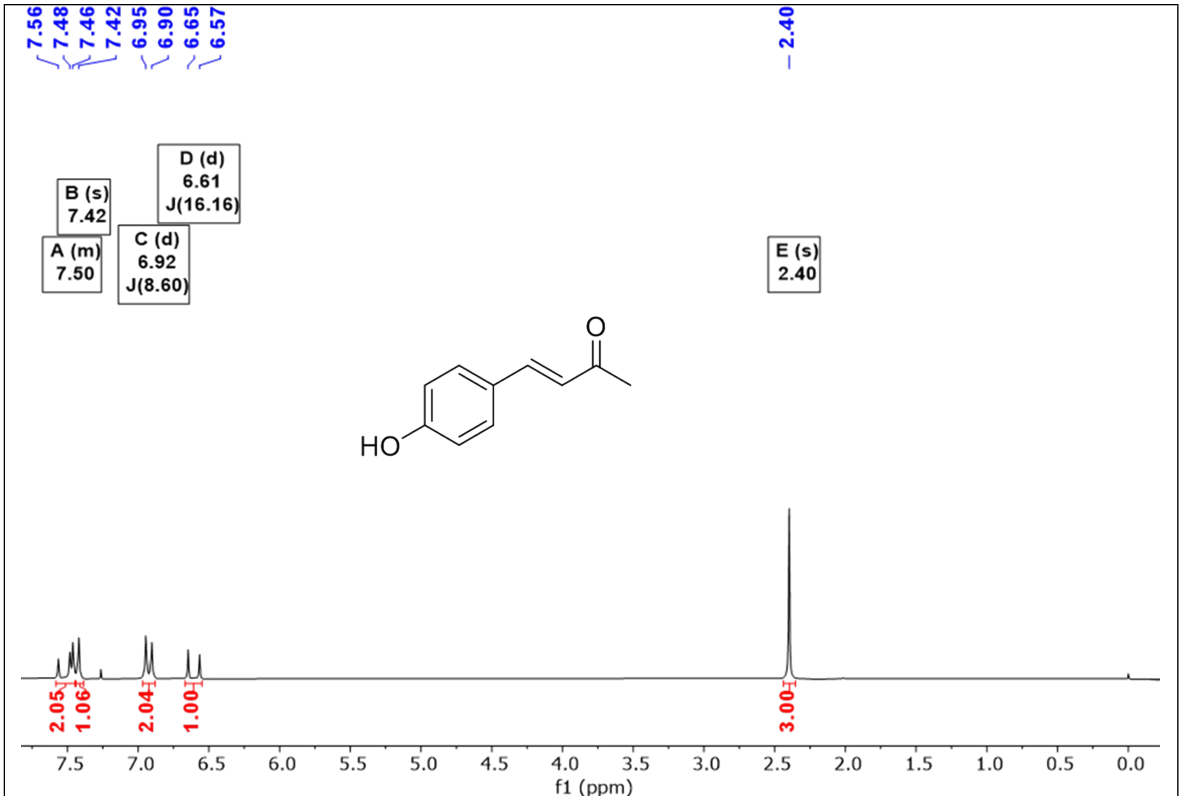


Fig. S183 ^{1}H NMR spectra of **37a** in $CDCl_3$ at 298 K.

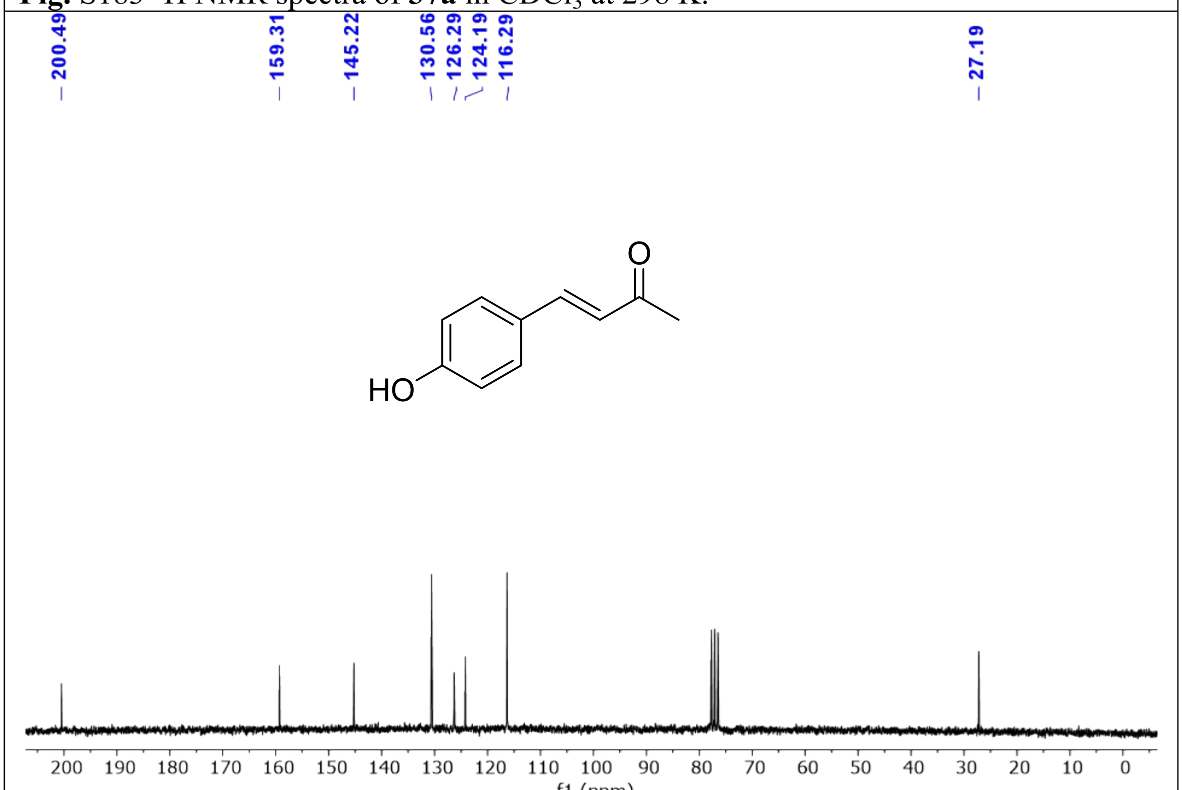


Fig. S184 $^{13}C\{^{1}H\}$ –NMR of **37a** in $CDCl_3$ at 298K.

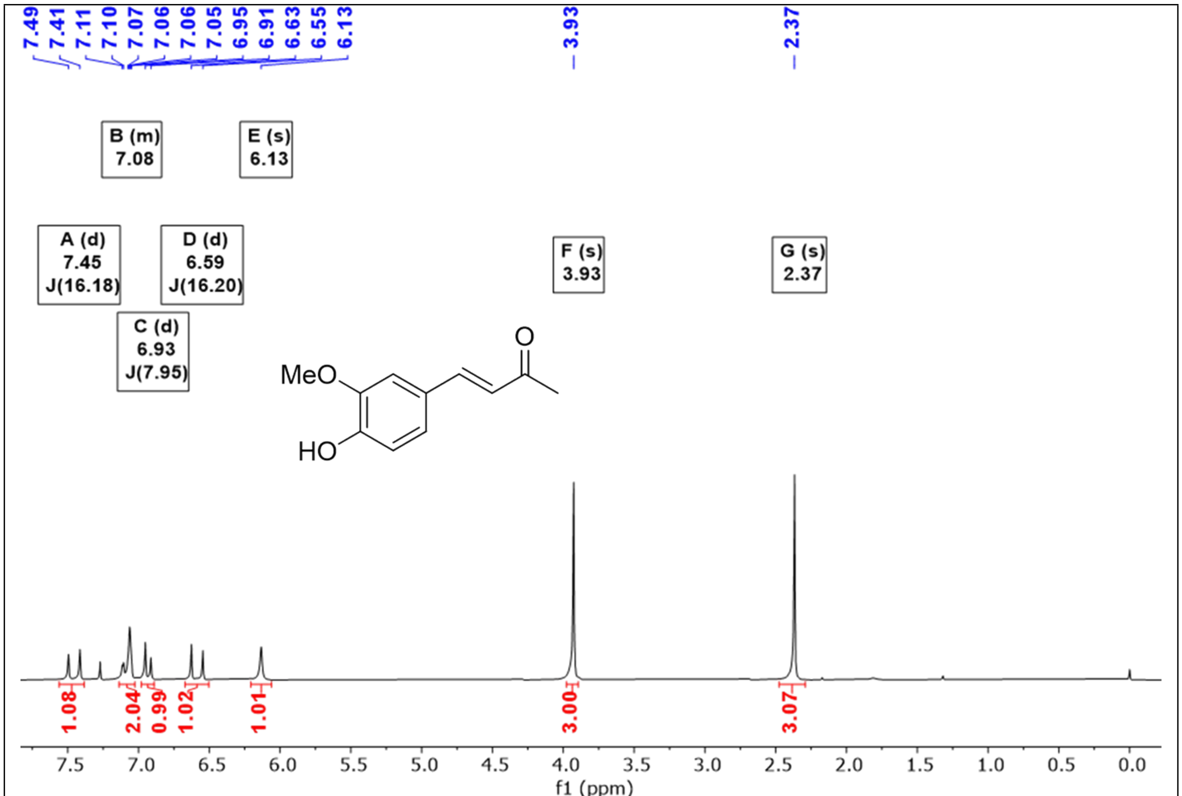


Fig. S185 ^{1}H NMR spectra of **38a** in $CDCl_3$ at 298 K.

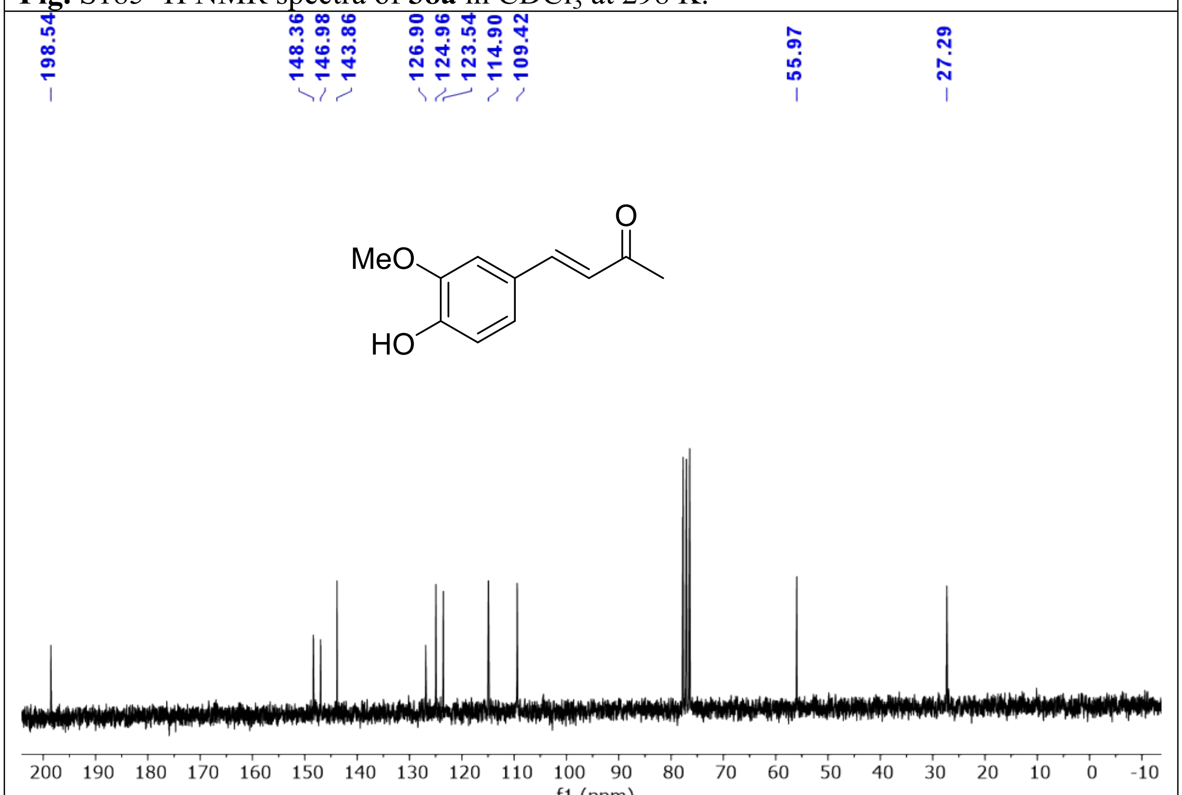


Fig. S186 $^{13}C\{^{1}H\}$–NMR of **38a** in $CDCl_3$ at 298K.

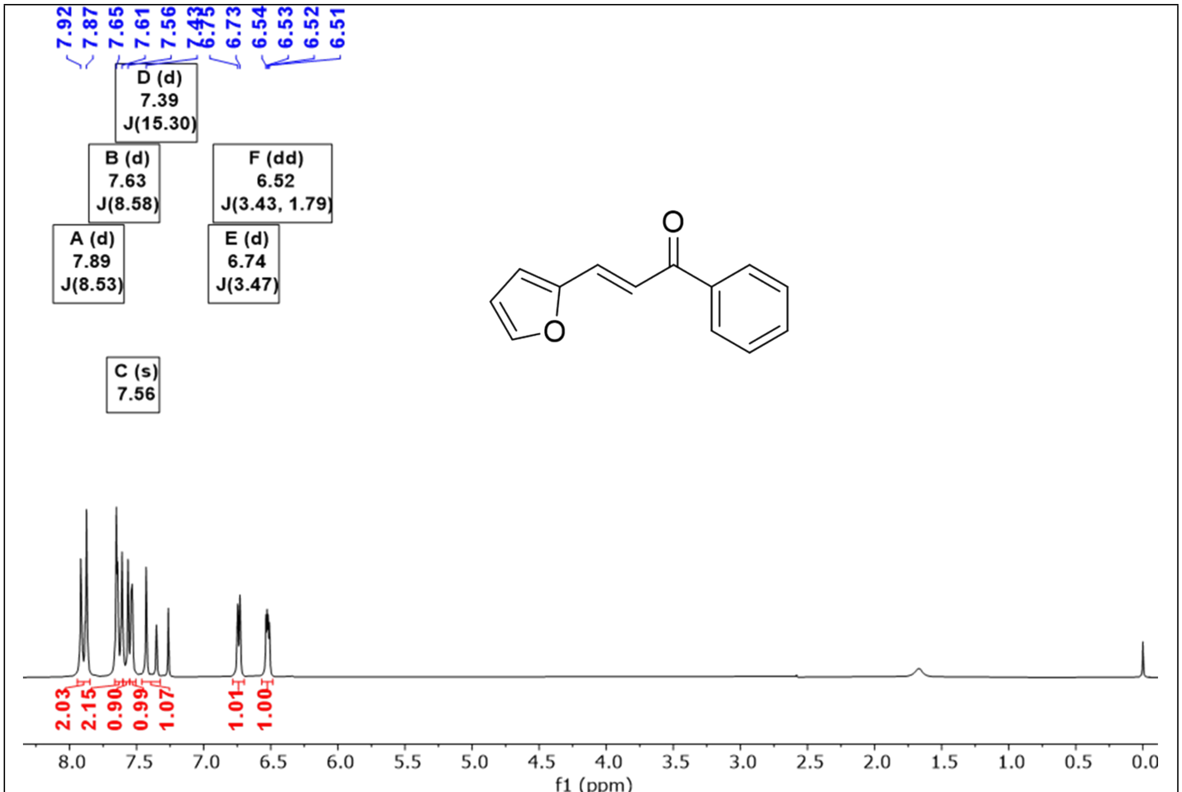


Fig. S187 ^{1}H NMR spectra of **39a** in $CDCl_3$ at 298 K.

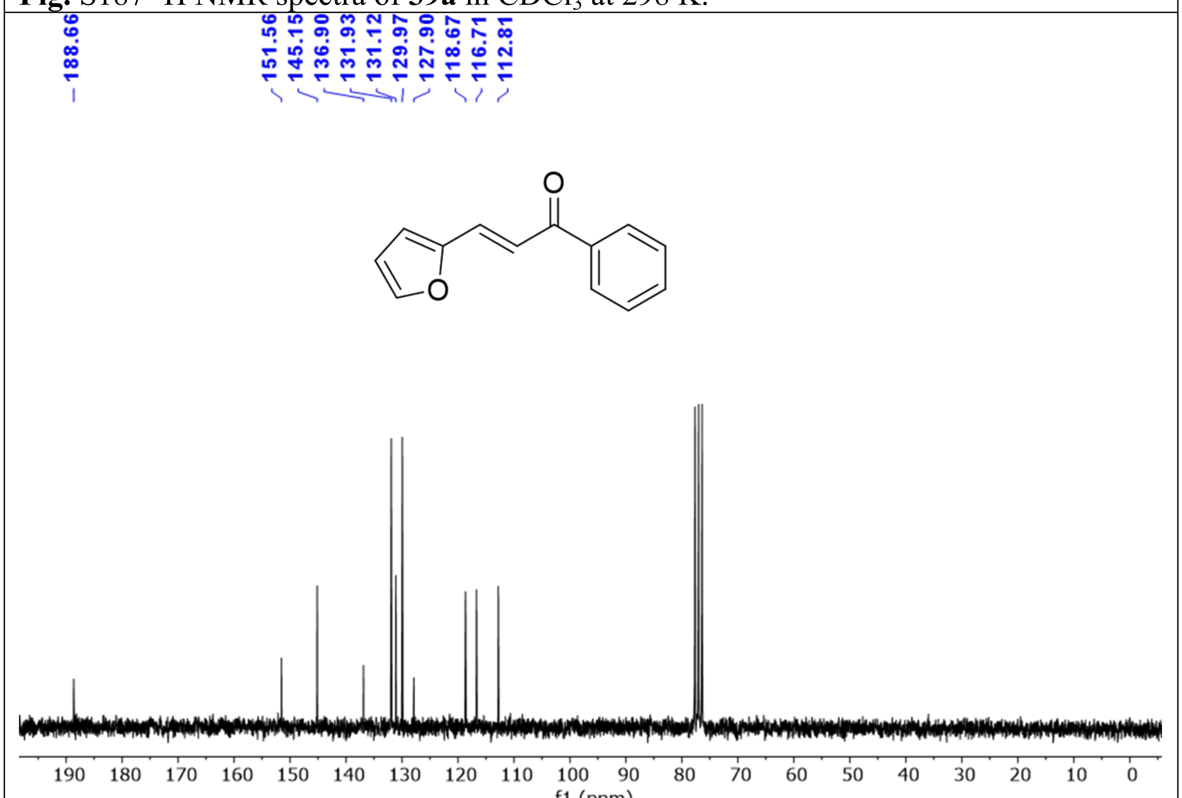


Fig. S188 ^{13}C{^{1}H} –NMR of **39a** in $CDCl_3$ at 298K.

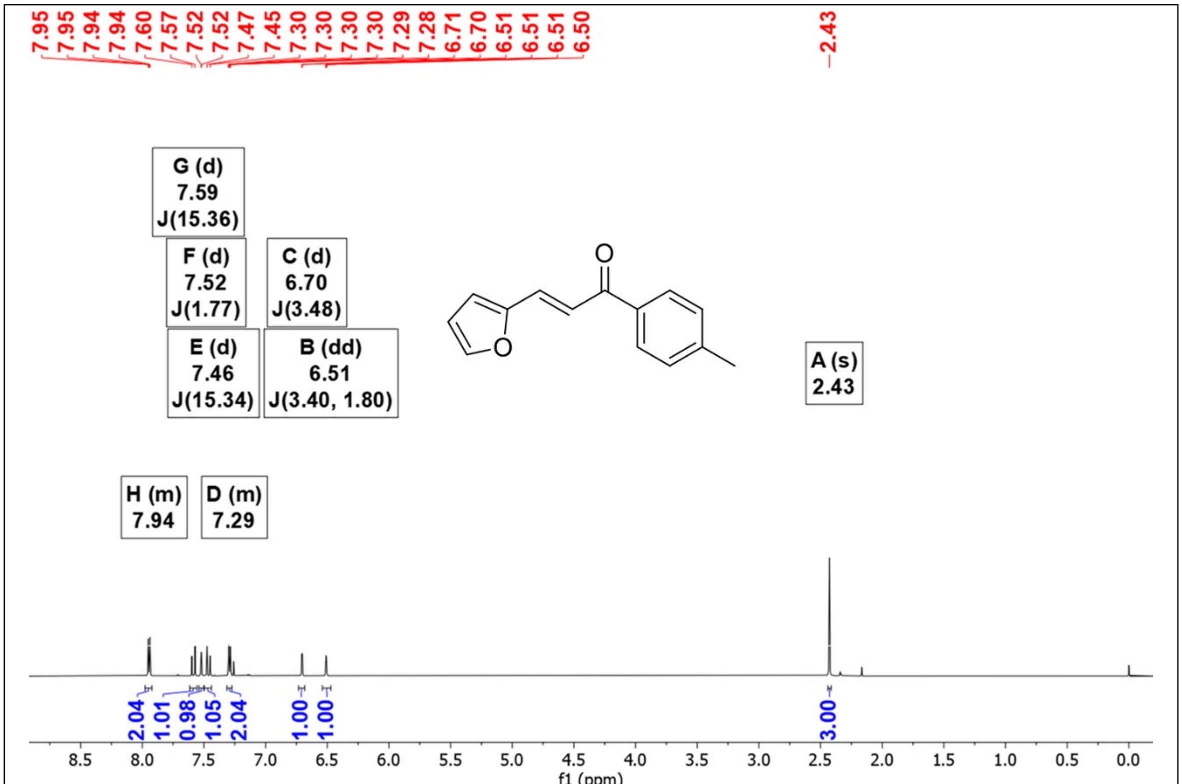


Fig. S189 ^{1}H NMR spectra of **41a** in $CDCl_3$ at 298 K.

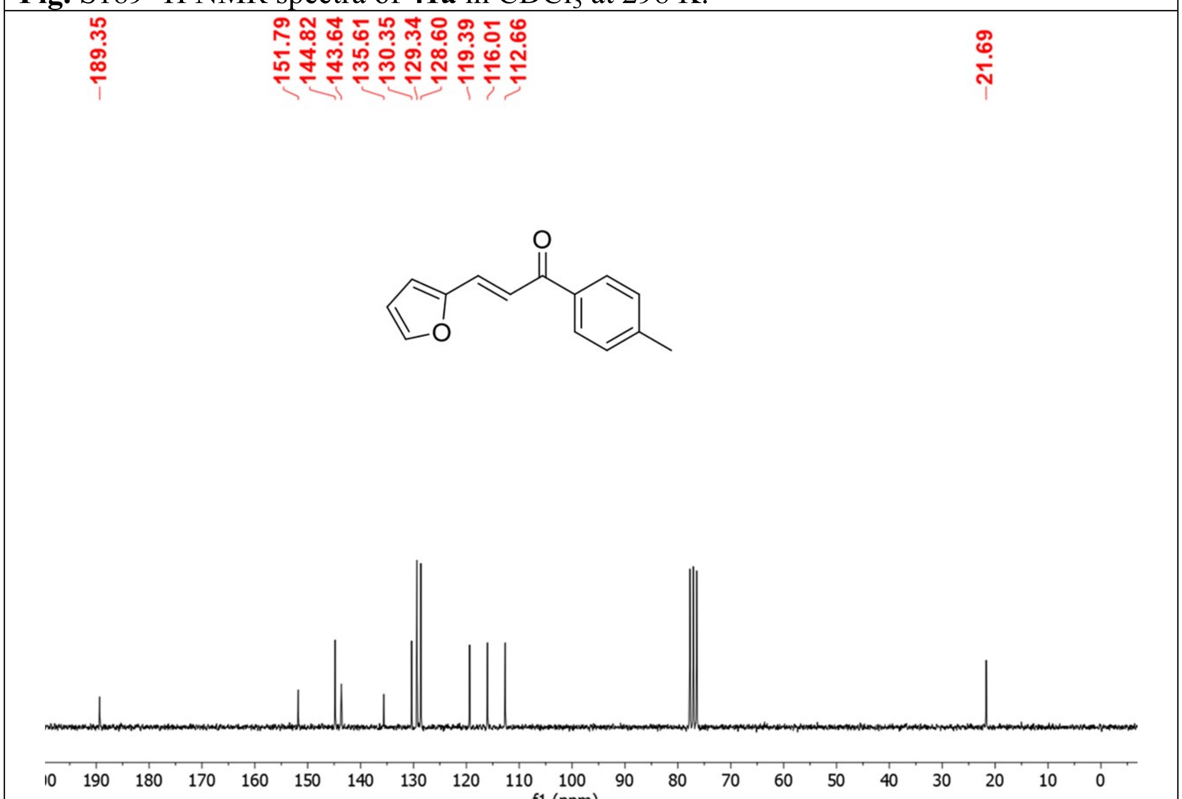


Fig. S190 ^{13}C{^{1}H} –NMR of **41a** in $CDCl_3$ at 298K.