Supporting Information

Switchable Chemoselective Transfer Hydrogenations of Unsaturated Carbonyls Using Copper(I) N-donor Thiolate Clusters

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M. J. Zhang and D. W. Tan contributed equally to this work.

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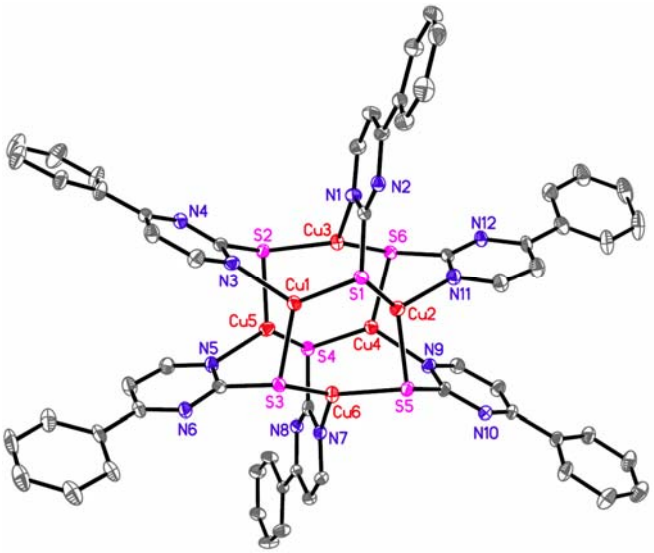


Figure S1. View of the molecular structure of **1g** with labeling scheme with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

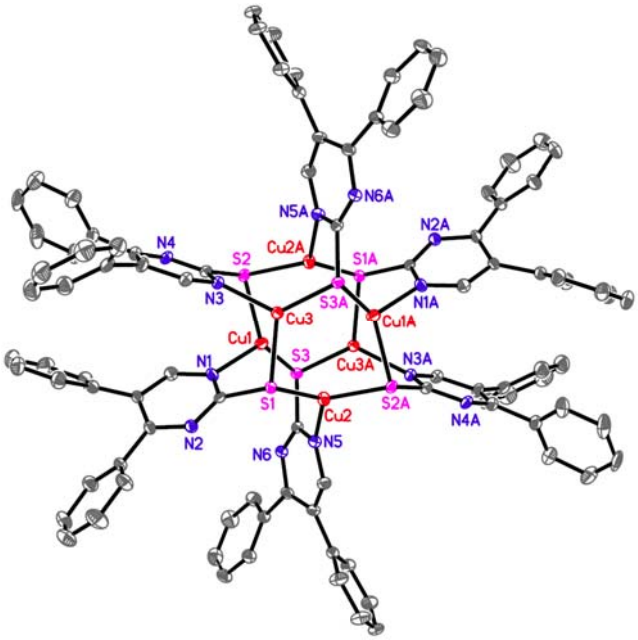


Figure S2. View of the molecular structure of **1h** with labelling scheme with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

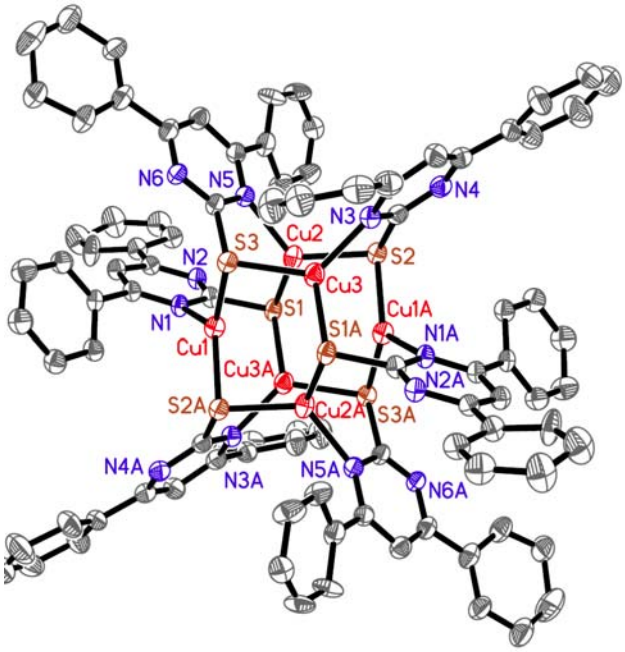
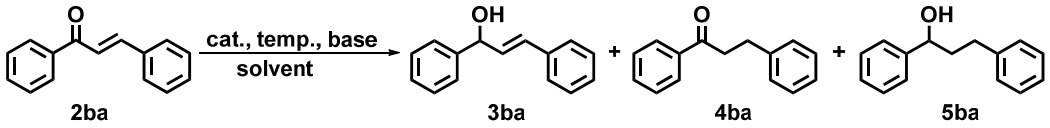


Figure S3. View of the molecular structure of **1i** with labelling scheme with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

Table S1. Optimizing reaction conditions for the transfer hydrogenation reduction of **2ba** to **4ba**.



Entry[a]	Cat.	Base (mol%)	Solvent	Temp (ºC)	Yield (%)[b]		
					3ba	**4ba**	**5ba**
1	**1d**	NaOH (20)	*i*-PrOH	100	82	4	6
2	**1d**	NaOH (50)	*i*-PrOH	100	57	23	12
3	**1d**	NaOH (100)	*i*-PrOH	100	18	64	11
4	**1d**	NaOH (200)	*i*-PrOH	100	17	66	12
5	**1a**	NaOH (100)	*i*-PrOH	100	17	61	12
6	**1b**	NaOH (100)	*i*-PrOH	100	10	74	13
7	**1c**	NaOH (100)	*i*-PrOH	100	15	62	14
8	**1e**	NaOH (100)	*i*-PrOH	100	12	60	17
9	**1f**	NaOH (100)	*i*-PrOH	100	13	63	15
10	**1g**	NaOH (100)	*i*-PrOH	100	12	59	21
11	**1h**	NaOH (100)	*i*-PrOH	100	16	66	19
12	**1i**	NaOH (100)	*i*-PrOH	100	17	61	15
13	**1b**	NaOH (100)	EtOH	90	41	54	5
14	**1b**	NaOH (100)	*n*-BuOH	120	2	89	4
15	**1b**	NaOH (100)	*n*-Pentanol	120	12	78	10
16	**1b**	NaOH (100)	BnOH	120	9	62	12
17	**1b**	KOH (100)	*n*-BuOH	120	3	91	2
18	**1b**	NaOEt (100)	*n*-BuOH	120	4	86	5
19	**1b**	KOBut (100)	*n*-BuOH	120	0	95	3
20	**1b**	NaH (100)	*n*-BuOH	120	10	78	0
21	**1b**	K_2CO_3 (100)	*n*-BuOH	120	trace	96	2
22	**1b**	K_3PO_4 (100)	*n*-BuOH	120	trace	93	4
23	**1b**	Cs_2CO_3 (100)	*n*-BuOH	120	3	81	trace
24	**1b**	LiOH (100)	*n*-BuOH	120	trace	trace	trace

[a] Reaction conditions: **2ba** (1.0 mmol), base, cat. (10 mol% of Cu), solvent (2 mL) at reserved temperature (oil bath) under N_2 for 24 h. [b] Yields determined by HPLC.

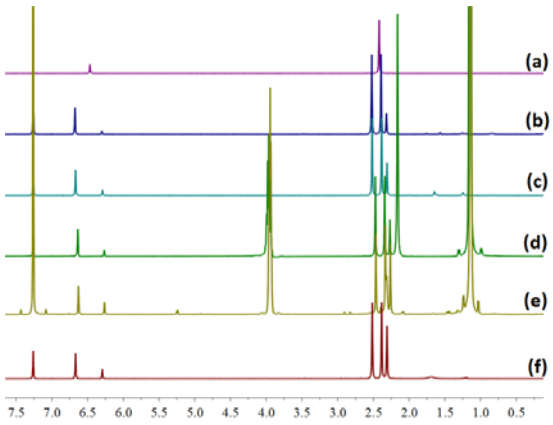


Figure S4. ^{1}H NMR spectra ($CDCl_3$) of (a) Hdmpymt, (b) **1d**, (c) **1d** + NaOH, (d) **1d** + *i*PrOH, (e) **1d** + *i*PrOH + NaOH and (f) after the reaction of **2aa** with NaOH in *i*PrOH using **1d** as a catalyst.

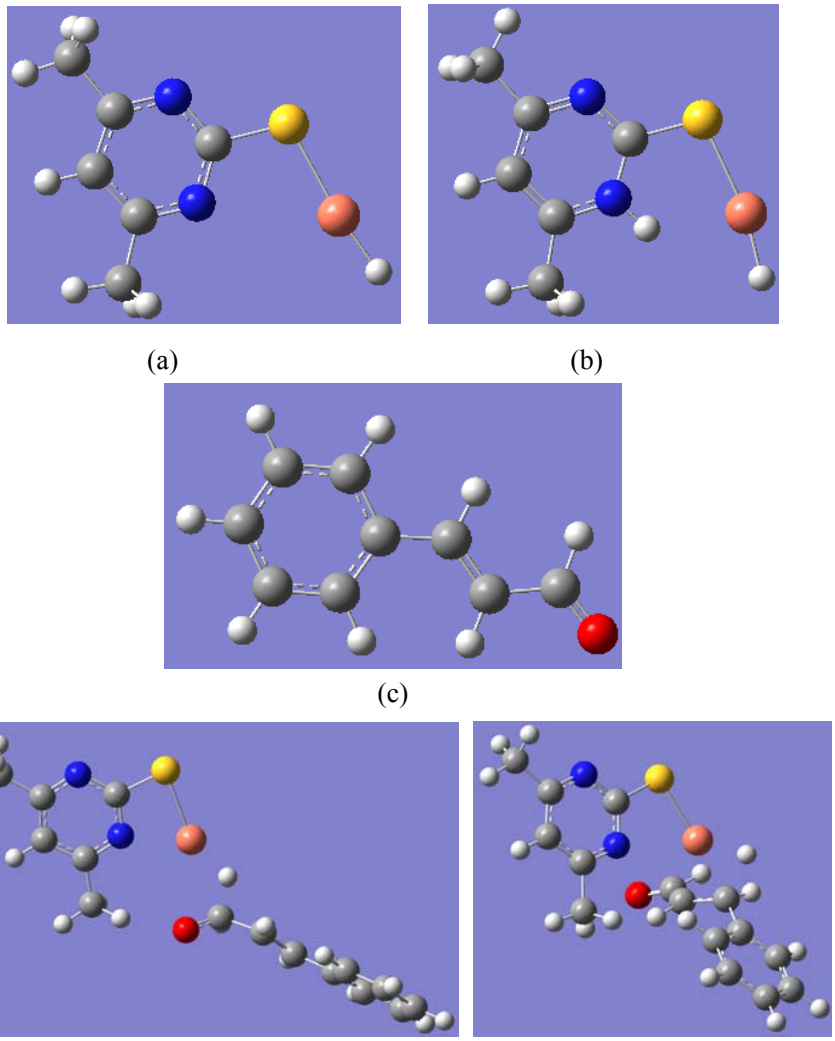


Figure S5. Optimized structures of (dmpymt)Cu-H (a), (Hdmpymt)Cu-H (b), **2aa** (c), transition state for C=O hydrogenation catalyzed by (dmpymt)Cu-H (E_a = 16.9 kcal/mol) (d) and transition state for C=C hydrogenation catalyzed by (dmpymt)Cu-H (E_a = 16.1 kcal/mol) (e)

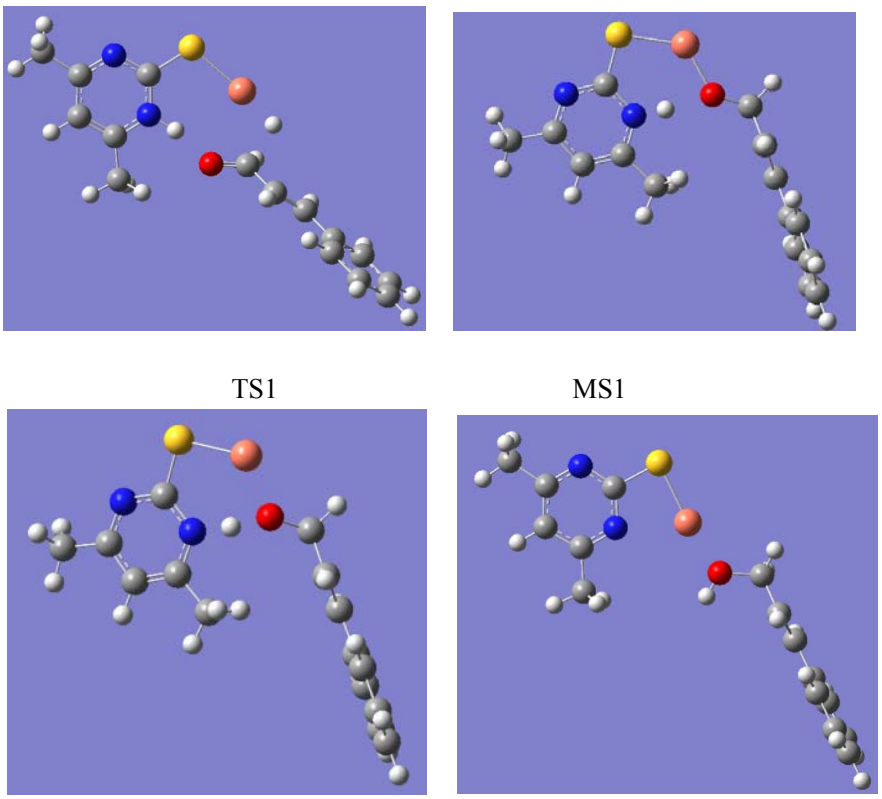
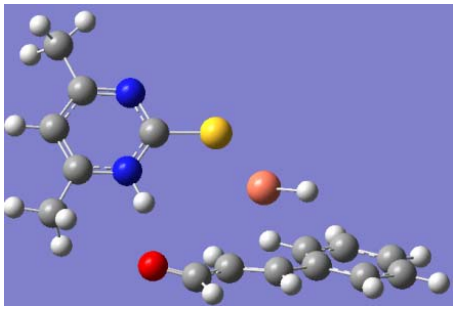
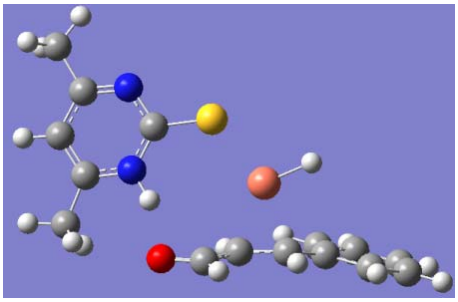


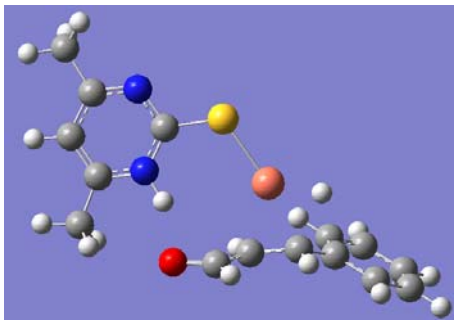
Figure S6. Optimized structures of **TS1** (E_a = 10.6 kcal/mol), **MS1** (E_a = -9.81 kcal/mol), **TS2** (E_a = -9.64 kcal/mol), **FS1** (E_a = -17.1 kcal/mol) for C=O hydrogenation catalyzed by (Hdmpymt)Cu-H.



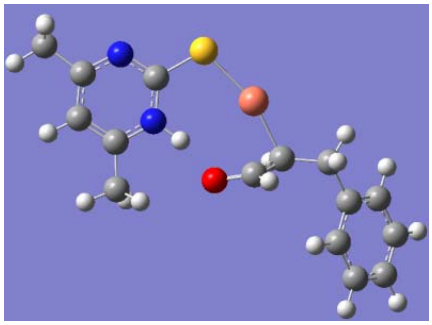
TS3



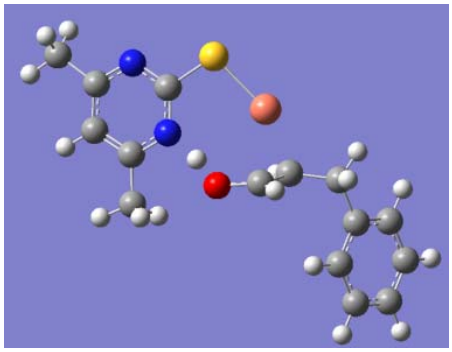
MS2



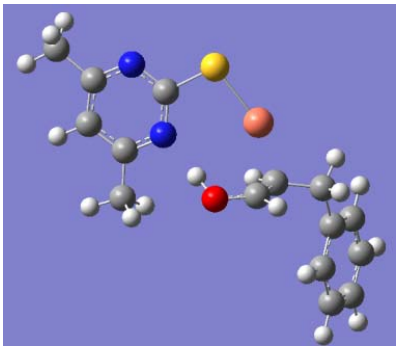
TS4



MS3



TS5



FS2

Figure S7. Optimized structures of **TS3** (E_a = 12.2 kcal/mol), **MS2** (E_a = 10 kcal/mol), **TS4** (E_a = 15.3 kcal/mol), **MS3** (E_a = -20.6 kcal/mol), **TS5** (E_a = -18.2 kcal/mol) and **FS2** (E_a = -17.5 kcal/mol) for C=C hydrogenation catalyzed by (Hdmpymt)Cu-H.

Cartesian coordinates of all DFT-optimized structures described in this work

2aa

C	-2.79953200	-0.99592700	0.00001100
C	-1.43603900	-1.27347300	0.00000200
C	-0.48559900	-0.23868300	-0.00000700
C	-0.94752400	1.08994500	-0.00000700
C	-2.30793200	1.36668800	0.00000200
C	-3.23973500	0.32578700	0.00001100
H	-3.51639400	-1.80895900	0.00001800
H	-1.09606800	-2.30394200	0.00000300
H	-0.23900400	1.90949900	-0.00001300
H	-2.64679300	2.39641000	0.00000200
H	-4.30100800	0.54656400	0.00001700
C	0.93370600	-0.58636400	-0.00001500
C	1.99486000	0.24347300	-0.00002600
H	1.14293500	-1.65564200	-0.00001300
H	1.90219700	1.32436000	-0.00002900
C	3.35763200	-0.28861100	-0.00003900
O	4.36357500	0.39161400	0.00004500
H	3.42651200	-1.39821700	0.00005400

(dmpymt)Cu-H

S	1.19524200	-1.44983100	-0.00002900
C	-0.30493400	-0.56971100	-0.00002700
C	-2.60853600	-0.62950700	-0.00006800
C	-1.43575100	1.43937800	0.00001800
C	-2.66243100	0.76751800	-0.00002500
N	-0.27706700	0.78929200	0.00001600
N	-1.45706200	-1.29299300	-0.00007000
Cu	2.84264100	0.15571900	0.00005700
H	4.04935600	1.08908900	0.00012200
H	-3.60536200	1.30189600	-0.00002700
C	-3.86444900	-1.46780100	-0.00011500
H	-3.87957300	-2.11780200	-0.87955500
H	-3.87962800	-2.11781800	0.87931200
H	-4.76575800	-0.84931900	-0.00013700
C	-1.35552200	2.94619700	0.00007900
H	-0.80199300	3.28924600	0.87839400
H	-0.80173600	3.28930400	-0.87805000
H	-2.34713100	3.40632900	-0.00004400

(Hdmpymt)Cu-H

S	1.18904300	-1.57087600	0.00000100
C	-0.26550100	-0.68981100	0.00000100

C	-2.57572000	-0.60340000	-0.00000100
C	-1.36723500	1.46248000	0.00000000
C	-2.57600100	0.81678700	0.00000000
N	-0.24800400	0.69318100	0.00000100
N	-1.46231800	-1.31677500	0.00000000
Cu	2.73427900	0.16147700	-0.00000100
H	3.48788500	1.45786600	-0.00000300
H	-3.49997800	1.37835000	-0.00000100
H	0.67958600	1.13242900	0.00000100
C	-3.87555700	-1.35424600	-0.00000100
H	-4.46915600	-1.09065200	-0.88089900
H	-3.68699500	-2.42598700	-0.00000600
H	-4.46915100	-1.09065900	0.88090300
C	-1.17735200	2.94703700	0.00000100
H	-0.61239800	3.26249600	0.88184400
H	-0.61239900	3.26249600	-0.88184300
H	-2.13970300	3.45690400	0.00000100

TS-S1

S	2.69144900	-2.36569000	-0.24629400
C	3.58786800	-0.87920700	-0.08783700
C	5.47849300	0.34537600	0.31713600
C	3.37244600	1.43973500	0.01649300
C	4.74398500	1.53056900	0.29195800
N	2.81704800	0.24696200	-0.18605000
N	4.91379500	-0.85359500	0.13203700
Cu	0.91159700	-0.80256800	-0.38782200
H	-0.64331200	-0.25993600	-0.73307700
H	5.21456300	2.49046800	0.46718600
C	-7.38101100	0.32262700	-0.66847500
C	-6.06107000	0.64537900	-0.97413100
C	-4.99576900	0.27138200	-0.13504000
C	-5.31937400	-0.44212800	1.03526300
C	-6.63567600	-0.76519000	1.34190000
C	-7.67949000	-0.38740100	0.49307100
H	-8.17789000	0.62693600	-1.33986400
H	-5.84071100	1.19892300	-1.88182200
H	-4.52767600	-0.74267700	1.71133000
H	-6.85159000	-1.31566800	2.25217500
H	-8.70562700	-0.64146100	0.73604400
C	-3.62313600	0.63648400	-0.50627400
C	-2.48781300	0.31126000	0.12881800
H	-3.53897100	1.24282200	-1.40808100
H	-2.49274800	-0.26883600	1.04868500

C	-1.10991900	0.80317800	-0.27041000
O	-0.44075200	1.38126900	0.69688800
H	-1.19863300	1.36510600	-1.23352800
C	2.46746700	2.63398600	-0.07698100
H	2.36189200	2.93201400	-1.12730300
H	1.46567100	2.37369600	0.29273600
H	2.87835600	3.48540400	0.47225900
C	6.96545800	0.34358800	0.56803000
H	7.19185300	-0.24227000	1.46337400
H	7.48334800	-0.13568600	-0.26760100
H	7.35734700	1.35511100	0.69690500

TS-S2

S	-1.75824900	-1.61379200	-1.39710500
C	-2.49372800	-0.26937600	-0.56904200
C	-4.41867300	0.84239300	0.01762700
C	-2.28583500	1.61550100	0.73930000
C	-3.67290300	1.77889600	0.73923100
N	-1.69671600	0.61455600	0.08656200
N	-3.84358500	-0.16773600	-0.62789800
Cu	0.41087400	-1.27912800	-0.80820600
H	1.73425500	-1.09100500	-1.65476600
H	-4.14698100	2.59446900	1.27203900
C	5.17172700	1.38625200	-0.46972100
C	4.45699500	0.19466700	-0.34906300
C	3.06872700	0.19778900	-0.17135500
C	2.41118100	1.43485300	-0.12158400
C	3.12183200	2.62487300	-0.23905800
C	4.50754700	2.60939700	-0.41309700
H	6.24805200	1.35650700	-0.60730500
H	4.98346300	-0.75374300	-0.39211400
H	1.33231800	1.45398300	-0.01174500
H	2.59137400	3.57113000	-0.20437100
H	5.05896400	3.53892600	-0.50828700
C	2.33757300	-1.09301300	-0.00185200
C	1.50630000	-1.27271200	1.16376900
H	2.94867100	-1.95764700	-0.24500900
H	1.10653900	-0.40810600	1.68112800
C	1.38382900	-2.54185800	1.79904400
O	0.85828800	-2.78898800	2.88963300
H	1.84636200	-3.38122600	1.22183500
C	-1.37897400	2.56741100	1.47708100
H	-0.78270300	2.02184400	2.21308100
H	-0.68073400	3.03907800	0.77988900

H	-1.94533900	3.34858900	1.98938200
C	-5.92288300	0.92213000	-0.06549300
H	-6.23705200	0.96389000	-1.11195500
H	-6.36821200	0.02213300	0.36790400
H	-6.31282300	1.79749000	0.45950900

TS1

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C	3.47638400	-0.50048100	0.11101700
C	5.30828400	0.90210700	0.21777100
C	3.15482100	1.85196500	-0.19045000
C	4.50735000	2.03922300	-0.00777900
N	2.67108200	0.58778500	-0.13154600
N	4.79920700	-0.32260100	0.27176900
Cu	0.63220600	-1.94092300	-0.04449600
H	-0.89148900	-1.65704500	-0.25377700
H	1.63199900	0.47127400	-0.26171700
C	-7.21520000	0.28529500	-0.64639900
C	-5.90617400	0.09156600	-1.07902600
C	-4.81997900	0.23209800	-0.19983300
C	-5.09372700	0.57588200	1.13607500
C	-6.39936900	0.77064800	1.56817500
C	-7.46790600	0.62643200	0.68019400
H	-8.03651200	0.16877200	-1.34467400
H	-5.71635400	-0.17544900	-2.11365300
H	-4.27993100	0.68845900	1.84253900
H	-6.58796300	1.03351600	2.60323600
H	-8.48550500	0.77762400	1.02203500
C	-3.46274400	0.01601200	-0.70989800
C	-2.30620500	0.14019400	-0.04233900
H	-3.40938600	-0.27560900	-1.75803700
H	-2.26104300	0.43793300	0.99999100
C	-0.99131200	-0.03640300	-0.69946400
O	0.00060600	0.66205600	-0.31357700
H	-1.05791800	-0.33649400	-1.75562000
C	6.79026600	1.02205300	0.42862800
H	7.02712000	0.80656700	1.47502500
H	7.31168400	0.27859500	-0.17699900
H	7.15930500	2.01913500	0.18528800
H	4.93271000	3.03237400	-0.04380700
C	2.18015400	2.95323800	-0.47091000
H	1.89688700	2.93934000	-1.52785000
H	1.26131200	2.81573500	0.10114900
H	2.62560000	3.92132800	-0.24310100

MS1

S	3.93202100	-1.26196900	0.16521700
C	3.22330100	0.31084400	0.05452900
C	3.55957000	2.59801900	0.02152000
C	1.32620100	1.76196000	-0.09706700
C	2.17429400	2.84534500	-0.05792800
N	1.86170100	0.51751700	-0.04389900
N	4.05452000	1.36848700	0.07199100
Cu	2.01088300	-2.39442500	0.10202500
H	-1.01891000	-3.22061500	-0.45044400
H	1.17448500	-0.30055500	-0.08037600
C	-6.20631900	1.25581500	-0.75868900
C	-5.06133300	0.57833900	-1.17115500
C	-4.26480700	-0.13406400	-0.25994600
C	-4.66779500	-0.15051000	1.08700200
C	-5.80919500	0.52596900	1.50073100
C	-6.58550400	1.23491300	0.58134000
H	-6.80280100	1.79719300	-1.48487400
H	-4.77521800	0.59738500	-2.21815600
H	-4.08767500	-0.70388500	1.81619400
H	-6.10020700	0.49668900	2.54520100
H	-7.47718700	1.75832000	0.90723000
C	-3.05852400	-0.81880200	-0.75085100
C	-2.12785900	-1.45826800	-0.03096500
H	-2.92381900	-0.78142900	-1.83153600
H	-2.19807100	-1.51057900	1.05358900
C	-0.91635800	-2.13435400	-0.61122500
O	0.26195600	-1.66009700	-0.00592700
H	-0.90555600	-1.98436300	-1.70413800
C	4.54677400	3.72827200	0.07867600
H	4.78508400	3.95014300	1.12457300
H	5.47466000	3.43767400	-0.41402600
H	4.15020400	4.63700200	-0.37737300
H	1.78056000	3.85172200	-0.09427900
C	-0.16232400	1.86350400	-0.21497900
H	-0.48246900	1.57052300	-1.21920000
H	-0.65873000	1.18591400	0.48157500
H	-0.49223300	2.88553400	-0.03132500

TS2

S	-3.94478800	-1.23135500	0.12917900
C	-3.16176100	0.32601000	0.03980300
C	-3.46426700	2.61379000	0.02201600
C	-1.28180900	1.71031900	-0.31221300

C	-2.10103700	2.82123900	-0.23790500
N	-1.80729000	0.47555200	-0.15004900
N	-3.97170000	1.39268100	0.14942700
Cu	-2.09543400	-2.42716100	-0.13335600
H	0.82318500	-2.91640200	0.80082400
H	-1.02620600	-0.46972100	-0.15728000
C	6.20221200	1.26041300	0.84678900
C	4.96577400	0.74122300	1.22312400
C	4.22554100	-0.08099400	0.35866200
C	4.77644700	-0.37173400	-0.90147400
C	6.00894800	0.14714000	-1.27938200
C	6.72954300	0.96724400	-0.40838700
H	6.75300700	1.89212600	1.53493700
H	4.56309700	0.97336300	2.20409000
H	4.24023600	-1.01397700	-1.59027600
H	6.41413700	-0.09223800	-2.25647600
H	7.69225300	1.36737800	-0.70538100
C	2.92098400	-0.59205300	0.80684400
C	2.04164800	-1.32024600	0.10773700
H	2.66098800	-0.33074200	1.83243000
H	2.23743600	-1.59901500	-0.92485300
C	0.73922800	-1.82964700	0.65523100
O	-0.34097400	-1.57153700	-0.23123100
H	0.55682800	-1.39517100	1.65039200
C	-4.42637500	3.75942100	0.16032800
H	-5.18746200	3.69710000	-0.62205200
H	-4.94743700	3.68907200	1.11817100
H	-3.92457600	4.72559400	0.09293300
H	-1.69389100	3.81470600	-0.36809900
C	0.19018200	1.80902400	-0.58075600
H	0.77144200	1.37542400	0.23550400
H	0.45241900	1.25028200	-1.48260100
H	0.48789600	2.84934200	-0.71009100

FS1

S	3.29889700	-2.08769700	0.01960800
C	3.91841500	-0.44864000	0.00421200
C	5.68199000	1.01236900	-0.04540800
C	3.43433200	1.81088400	0.03405200
C	4.79900800	2.09529500	-0.00804700
N	2.99136000	0.55053500	0.03924300
N	5.24412800	-0.24877500	-0.03894100
Cu	1.25497700	-1.20145800	0.09125900
H	-1.58091200	-2.43039100	0.09031300

H	-0.85088500	0.30197400	-0.06356200
C	-7.50162100	1.01449600	-0.97562400
C	-6.24268900	0.49863700	-1.27142500
C	-5.37666100	0.07005900	-0.25346200
C	-5.81574000	0.17197100	1.07772000
C	-7.07146700	0.68643800	1.37368100
C	-7.92054900	1.11049600	0.34891900
H	-8.15378700	1.33899600	-1.77841100
H	-5.92229300	0.42470400	-2.30561000
H	-5.17575400	-0.15657600	1.88805300
H	-7.39315500	0.75585100	2.40667500
H	-8.90049300	1.50953800	0.58425500
C	-4.06057300	-0.46330500	-0.62672200
C	-3.08730100	-0.89660900	0.18755500
H	-3.87880100	-0.51187500	-1.69960600
H	-3.20314300	-0.87481900	1.26743800
C	-1.79389500	-1.44063700	-0.31654100
O	-0.66956900	-0.62410800	0.13616700
H	-1.77995200	-1.50093600	-1.40840000
C	7.17340100	1.20358600	-0.09321000
H	7.63733200	0.71582500	0.76809300
H	7.58006800	0.72531000	-0.98810600
H	7.44968000	2.25950000	-0.09634500
H	5.15891600	3.11639100	-0.01150800
C	2.39434200	2.89897300	0.07267000
H	1.74613700	2.83200000	-0.80607300
H	1.76305700	2.78598200	0.95841900
H	2.84948800	3.89044300	0.09247400

TS3

S	0.71991800	-1.37293200	0.74190200
C	2.23750700	-0.82078200	0.20220000
C	4.45251200	-1.32031900	-0.25857200
C	3.71809500	0.93939200	-0.52143500
C	4.74330100	0.03123800	-0.57098100
N	2.48643500	0.49062200	-0.14952800
N	3.24888400	-1.71695700	0.11260700
Cu	-0.96495700	0.08372000	1.49346800
H	-1.94432000	0.35222000	2.63844100
H	5.73854900	0.34233700	-0.85727400
H	1.71885200	1.17357000	-0.17278400
C	-5.67624800	-0.59722500	-0.12679700
C	-4.69334100	0.31804200	0.22822300
C	-3.42391900	0.28284900	-0.37301700

C	-3.16466000	-0.70919800	-1.33486600
C	-4.14659000	-1.62661800	-1.68582700
C	-5.40591100	-1.57307500	-1.08584400
H	-6.64968900	-0.55561700	0.34808600
H	-4.89674300	1.06390100	0.98844100
H	-2.18958600	-0.77217600	-1.80220600
H	-3.93021700	-2.38867600	-2.42571500
H	-6.16906000	-2.29250100	-1.36027300
C	-2.44244700	1.30076000	-0.00045400
C	-1.22760700	1.53009100	-0.59889200
H	-2.78435700	2.02762500	0.72902700
H	-0.82657000	0.87825400	-1.36569600
C	-0.40400100	2.62119800	-0.15654800
O	0.79172100	2.75794500	-0.43578200
H	-0.89210300	3.35990600	0.50523300
C	5.53031900	-2.36346900	-0.33610500
H	6.31587600	-2.15162000	0.39655300
H	5.11136600	-3.34724100	-0.13298100
H	6.00007000	-2.36194900	-1.32418000
C	3.85824600	2.39270100	-0.84971300
H	3.17646200	2.67528500	-1.65473400
H	3.59127800	3.00905800	0.01223100
H	4.88271200	2.61392400	-1.14669000

MS2

S	-1.13826600	-1.58240400	-0.92415700
C	-2.47145300	-0.77949400	-0.21519100
C	-4.64069300	-0.93832900	0.58301000
C	-3.55425500	1.18908000	0.65223700
C	-4.66925500	0.43685800	0.91868800
N	-2.47978200	0.56275700	0.09654000
N	-3.58129600	-1.51034100	0.03812400
Cu	0.96631100	-0.56211100	-1.14452000
H	1.86279400	-1.54457800	-1.91501900
H	-5.54430800	0.89108600	1.36295600
H	-1.67420200	1.16035600	-0.13874700
C	5.86845500	-0.39301500	0.31602500
C	4.80286400	0.10543300	-0.42411900
C	3.52815300	0.24650100	0.14627000
C	3.35391700	-0.13670200	1.48600300
C	4.41877600	-0.63811700	2.22566800
C	5.68100400	-0.76846200	1.64577800
H	6.84446500	-0.49312400	-0.14521800
H	4.95152100	0.38354800	-1.46200500

H	2.38046600	-0.05317000	1.95465500
H	4.26329500	-0.93225600	3.25759300
H	6.50897000	-1.16130400	2.22474800
C	2.44760700	0.82390200	-0.66750800
C	1.23946700	1.34460600	-0.16163100
H	2.75816100	1.17178700	-1.64897700
H	0.96096600	1.22389500	0.87952300
C	0.40466800	2.19088200	-0.96194300
O	-0.70964900	2.61554400	-0.62430200
H	0.80368900	2.46153400	-1.95805100
C	-5.84134700	-1.80489500	0.83397300
H	-6.70409600	-1.43250800	0.27273600
H	-5.63108100	-2.82894100	0.53136800
H	-6.11281700	-1.78778200	1.89399400
C	-3.43423800	2.65363900	0.93704100
H	-2.66644400	2.83446600	1.69418400
H	-3.12446500	3.19850800	0.04324500
H	-4.38496500	3.04558600	1.29658600

TS4

S	-1.26399000	-1.77721700	-0.73503600
C	-2.53785500	-0.78364600	-0.14365200
C	-4.73186200	-0.70236600	0.58822300
C	-3.46428100	1.32267000	0.54258800
C	-4.64843200	0.68465300	0.82756700
N	-2.43273100	0.57403000	0.06427200
N	-3.70715400	-1.39742000	0.11633000
Cu	0.73835700	-0.75680000	-0.90796300
H	2.15878600	-1.22387900	-1.39629400
H	-5.49036600	1.24349500	1.21181300
H	-1.57978600	1.10548800	-0.19346000
C	6.03729100	-0.05418200	0.21539700
C	4.90460100	0.22549500	-0.54541900
C	3.62357000	0.13224400	0.01047100
C	3.50428600	-0.25511300	1.35126700
C	4.63378500	-0.53918500	2.11148500
C	5.90615500	-0.43807200	1.54800000
H	7.02071900	0.02646300	-0.23409400
H	5.01474800	0.51857400	-1.58437400
H	2.52283000	-0.35441400	1.80099900
H	4.52158200	-0.84467600	3.14582300
H	6.78527600	-0.66067200	2.14196600
C	2.44417900	0.48701500	-0.82475300
C	1.33966300	1.22757400	-0.27018500

H	2.70359900	0.75547700	-1.84438500
H	1.16969700	1.24250800	0.80131600
C	0.46634700	1.98222700	-1.08486900
O	-0.60792600	2.51009100	-0.71231400
H	0.76879300	2.09241400	-2.14516500
C	-5.99213000	-1.46459600	0.87930600
H	-6.87366500	-0.82285900	0.83404300
H	-6.09615800	-2.29332000	0.17904700
H	-5.93466700	-1.89005600	1.88714300
C	-3.24045300	2.78994300	0.72724800
H	-2.45624300	2.96660200	1.46781200
H	-2.88906400	3.24673800	-0.19965200
H	-4.16116800	3.26983100	1.05721800

MS3

S	-2.19445100	-2.08709500	-0.06931100
C	-3.05862400	-0.60307500	0.07681500
C	-5.09391100	0.44332300	0.39689500
C	-3.14632300	1.79087800	0.08764700
C	-4.50478100	1.71872800	0.30571300
N	-2.45422100	0.62977900	-0.02283100
N	-4.38336100	-0.67320600	0.28665600
Cu	-0.03262800	-1.49638300	-0.21198700
H	3.07472800	-2.03599500	-0.07722200
H	-5.09231000	2.62125100	0.39889400
H	-1.43021900	0.72686400	-0.24008000
C	5.61751600	1.74572800	-0.21813200
C	4.48743100	1.02890700	-0.60184400
C	4.23338500	-0.24766600	-0.08500300
C	5.14219700	-0.78065700	0.83372000
C	6.27355900	-0.06452800	1.22688800
C	6.51610600	1.20156500	0.70058100
H	5.79811000	2.73073400	-0.63502700
H	3.79228800	1.46808900	-1.31020700
H	4.96377500	-1.76943000	1.24533000
H	6.96421600	-0.49789200	1.94228200
H	7.39509400	1.76038100	1.00193800
C	3.00170200	-1.03372700	-0.50758800
C	1.68407600	-0.37437500	-0.11645400
H	3.01693000	-1.17307500	-1.59555600
H	1.59097400	-0.09372000	0.93535700
C	1.01778100	0.48550700	-1.02353300
O	0.05661100	1.27268900	-0.77061400
H	1.36418600	0.43212500	-2.07424600

C	-6.56922900	0.27760400	0.62195400
H	-7.07944800	1.23624400	0.72061800
H	-7.00663700	-0.27792600	-0.21168500
H	-6.73884100	-0.31626000	1.52349200
C	-2.37480800	3.06840300	-0.02106500
H	-1.77990800	3.22197100	0.88448700
H	-1.66819000	3.02592400	-0.85157800
H	-3.05360700	3.91213400	-0.14160800

TS5

S	-2.31290600	-2.12646600	0.04710800
C	-2.93610400	-0.49511300	0.12343100
C	-4.75755500	0.82007600	0.63782400
C	-2.72617200	1.83274300	-0.09355600
C	-4.02816600	1.98196000	0.35188100
N	-2.18688600	0.59952900	-0.21307500
N	-4.21239900	-0.38766100	0.52750200
Cu	-0.14654800	-1.72985800	-0.22629000
H	2.88325100	-1.98287600	0.50767600
H	-4.46658100	2.96538200	0.45598200
H	-1.03467700	0.59333900	-0.84837800
C	5.35764400	1.75383900	-0.33851300
C	4.28935900	0.91372400	-0.64165800
C	4.03168000	-0.22680400	0.12813400
C	4.86813600	-0.49703400	1.21473200
C	5.93690500	0.34404600	1.52553600
C	6.18613400	1.47215200	0.74825600
H	5.54394900	2.62986700	-0.95016600
H	3.64696300	1.14914400	-1.48393600
H	4.68386200	-1.37635800	1.82409400
H	6.57289000	0.11613100	2.37388900
H	7.01622500	2.12773400	0.98612600
C	2.88008000	-1.16126000	-0.21356000
C	1.52609400	-0.47147700	-0.23430300
H	3.05975100	-1.61928800	-1.19367200
H	1.24233600	0.06684000	0.67069900
C	0.92909300	-0.07796700	-1.42541200
O	-0.11219700	0.69129000	-1.58899000
H	1.38840800	-0.42406500	-2.35926500
C	-6.19227800	0.87277200	1.08104100
H	-6.54783500	1.89784500	1.19434500
H	-6.82131200	0.35609900	0.35106000
H	-6.30570300	0.34412900	2.03045500
C	-1.86524700	3.00839100	-0.46091700

H	-1.00262700	3.07521900	0.20788300
H	-1.47361200	2.90097400	-1.47438100
H	-2.43393500	3.93555200	-0.39027700

FS2

S	2.32500000	-2.11779800	-0.20693300
C	2.91869800	-0.45911200	-0.18546800
C	4.71358000	0.90900000	-0.62474100
C	2.64819900	1.82068400	0.13968800
C	3.95278000	2.03255400	-0.28695300
N	2.12840500	0.58002400	0.20496200
N	4.19461300	-0.31641800	-0.57842500
Cu	0.20078800	-1.70574000	0.22323700
H	-2.71691500	-1.85784000	-0.80716700
H	4.36553800	3.03157100	-0.34017600
H	0.72851500	0.56269700	1.22588400
C	-5.46694700	1.54193900	0.49068000
C	-4.39770800	0.68544700	0.73874000
C	-3.97588700	-0.23334600	-0.22915000
C	-4.64800200	-0.26783400	-1.45371000
C	-5.71726100	0.59127800	-1.70810100
C	-6.13082900	1.49805200	-0.73567200
H	-5.78333400	2.24359300	1.25455400
H	-3.88509000	0.73407700	1.69409900
H	-4.33526600	-0.97499100	-2.21556200
H	-6.22625600	0.54884200	-2.66463100
H	-6.96238200	2.16589800	-0.92986400
C	-2.81903200	-1.18262900	0.04642500
C	-1.51232500	-0.45465400	0.30424800
H	-3.05547800	-1.81380800	0.91053600
H	-1.16192500	0.21717400	-0.47817500
C	-0.99272100	-0.31125100	1.56723800
O	0.02722700	0.46353000	1.94879600
H	-1.47334600	-0.80930900	2.40871200
C	6.14856600	1.01774100	-1.05939400
H	6.49139800	2.05343900	-1.07944000
H	6.78442000	0.44427100	-0.37980800
H	6.26892900	0.58098400	-2.05402000
C	1.75983100	2.96391700	0.55269300
H	0.86680400	3.00246900	-0.07750500
H	1.42378900	2.84109600	1.58559500
H	2.28315700	3.91686700	0.46876100

Figure S8. The observed (red) and simulated (black) PXRD patterns for **1g**.

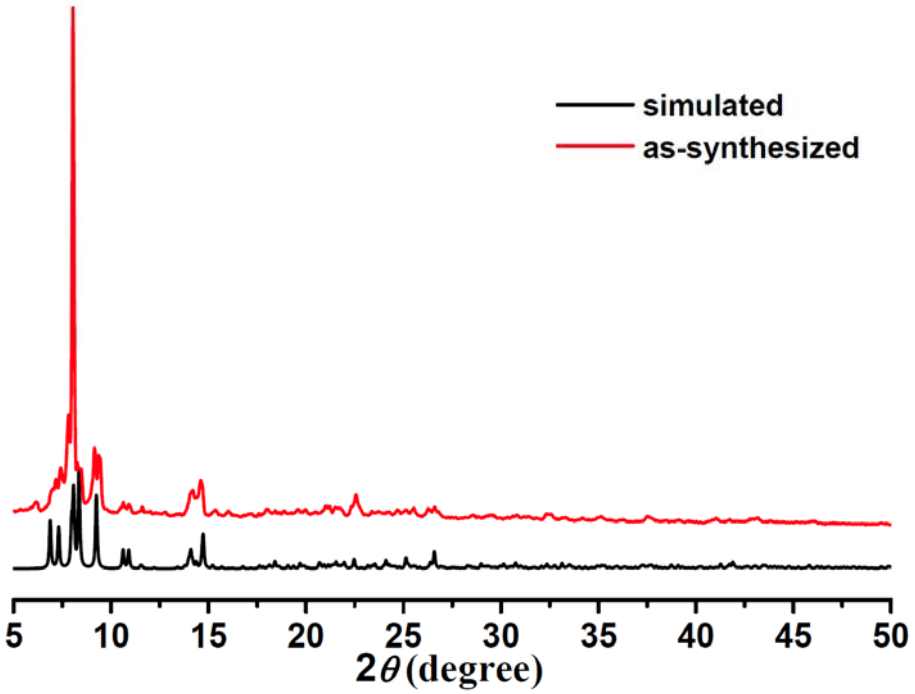


Figure S9. The observed (red) and simulated (black) PXRD patterns for **1h**.

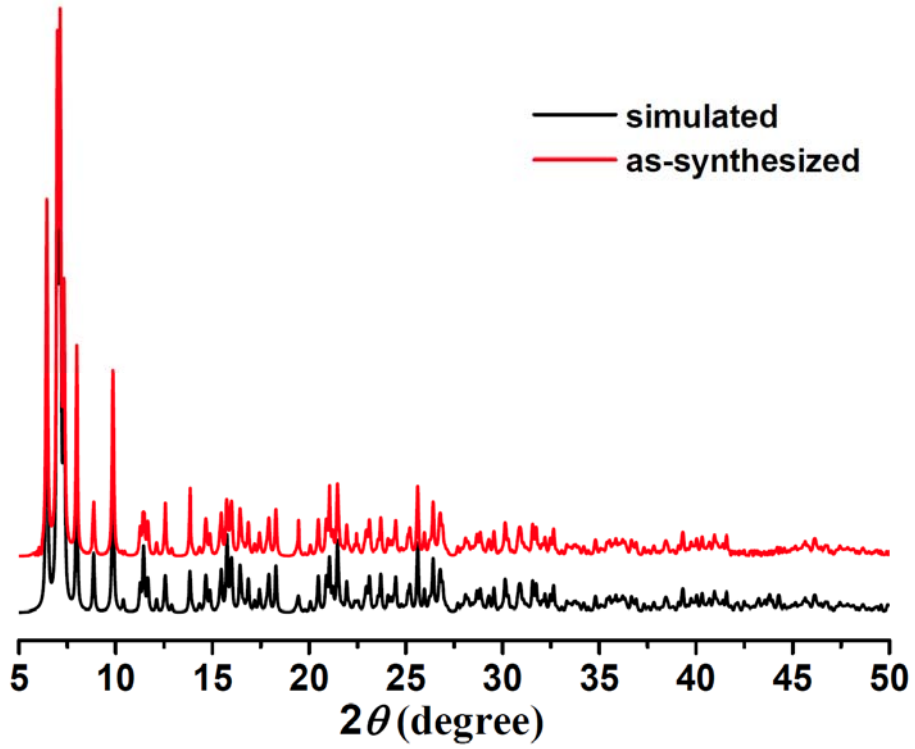


Figure S10. The observed (red) and simulated (black) PXRD patterns for **1i**.

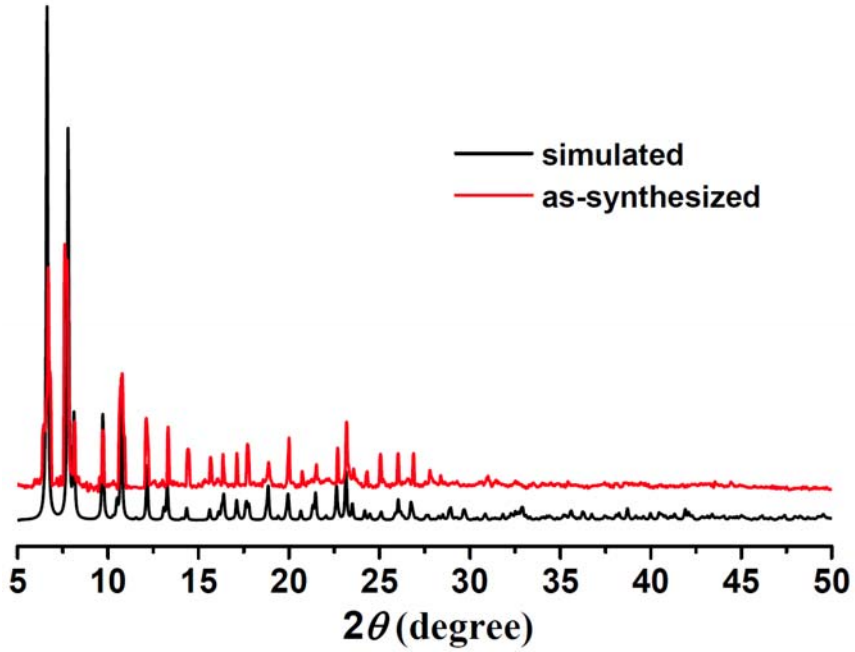


Figure S11. The ^{1}H NMR spectrum of **1g** in $CDCl_3$.

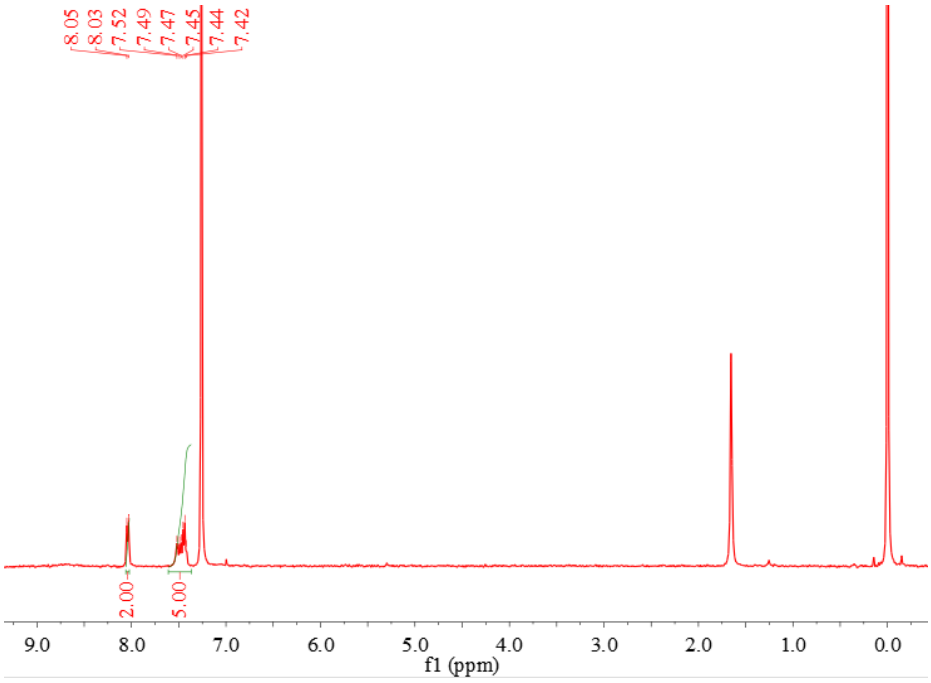


Figure S12. The ^{1}H NMR spectrum of **1h** in $CDCl_3$.

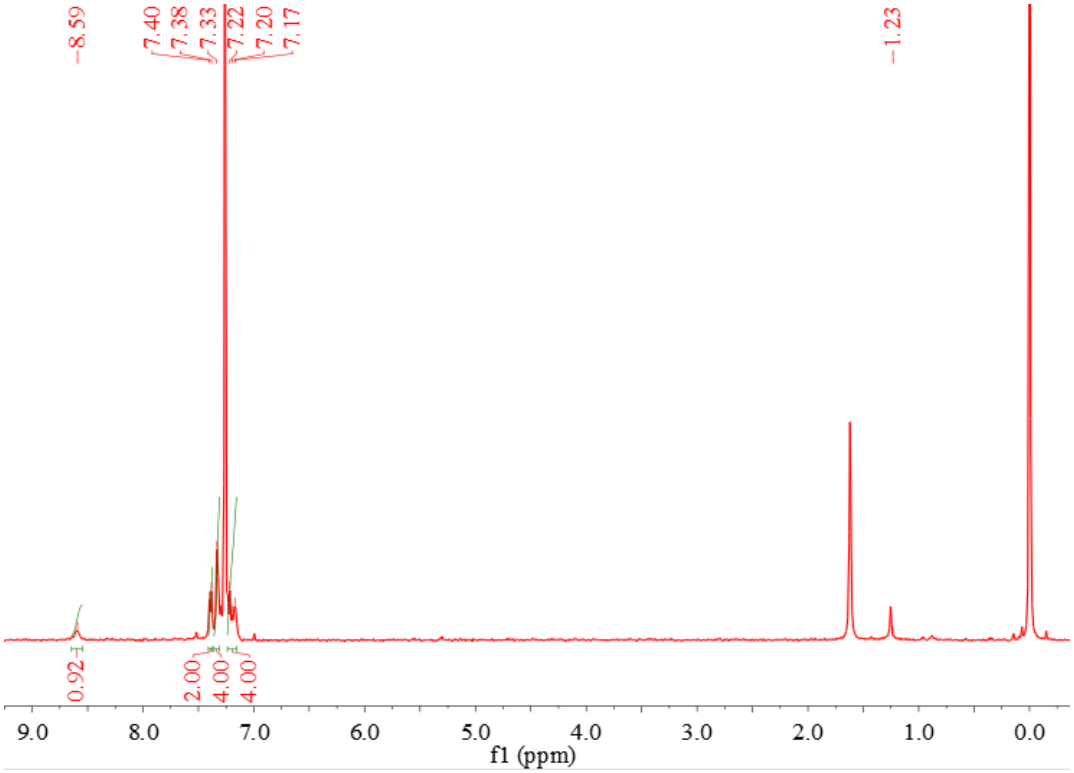
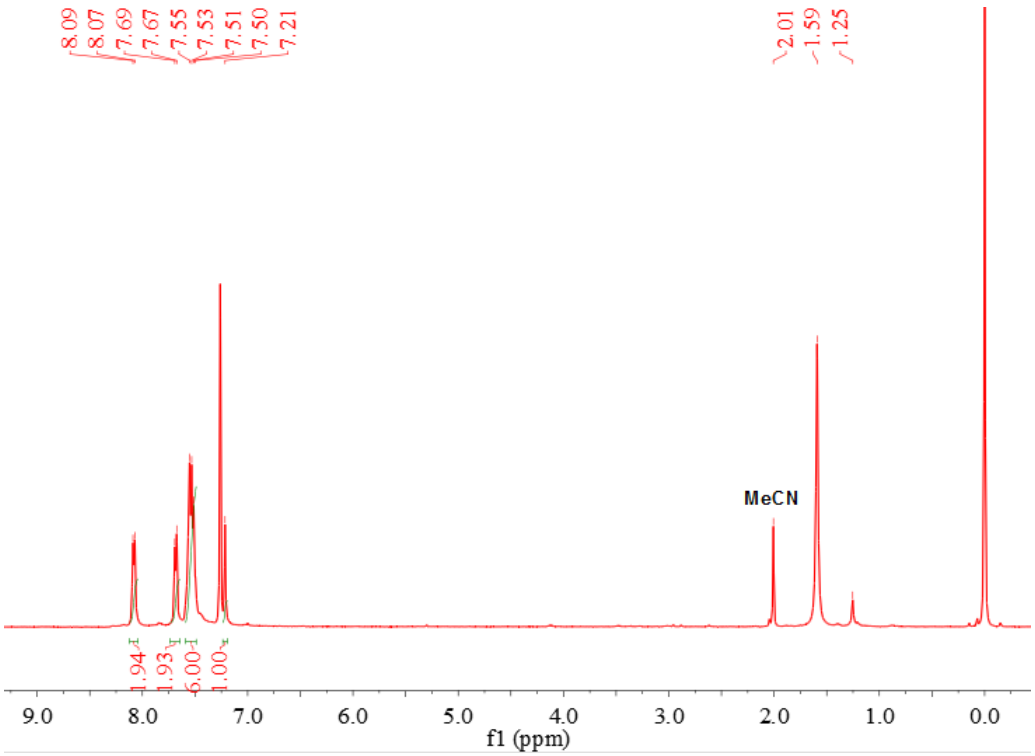
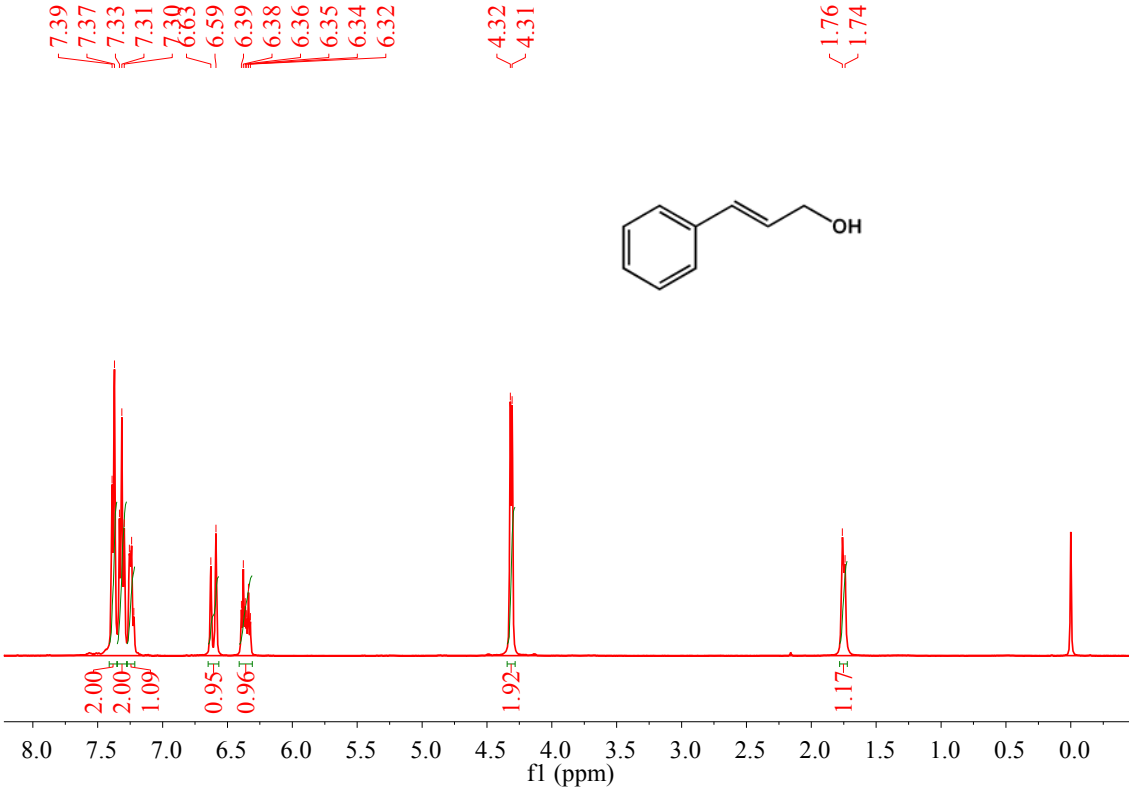


Figure S13. The ^{1}H NMR spectrum of **1i** in $CDCl_3$.



The ^{1}H and ^{13}C NMR spectra of products

Figure S14. The ^{1}H and ^{13}C NMR spectra for cinnamic alcohol (***3aa***).



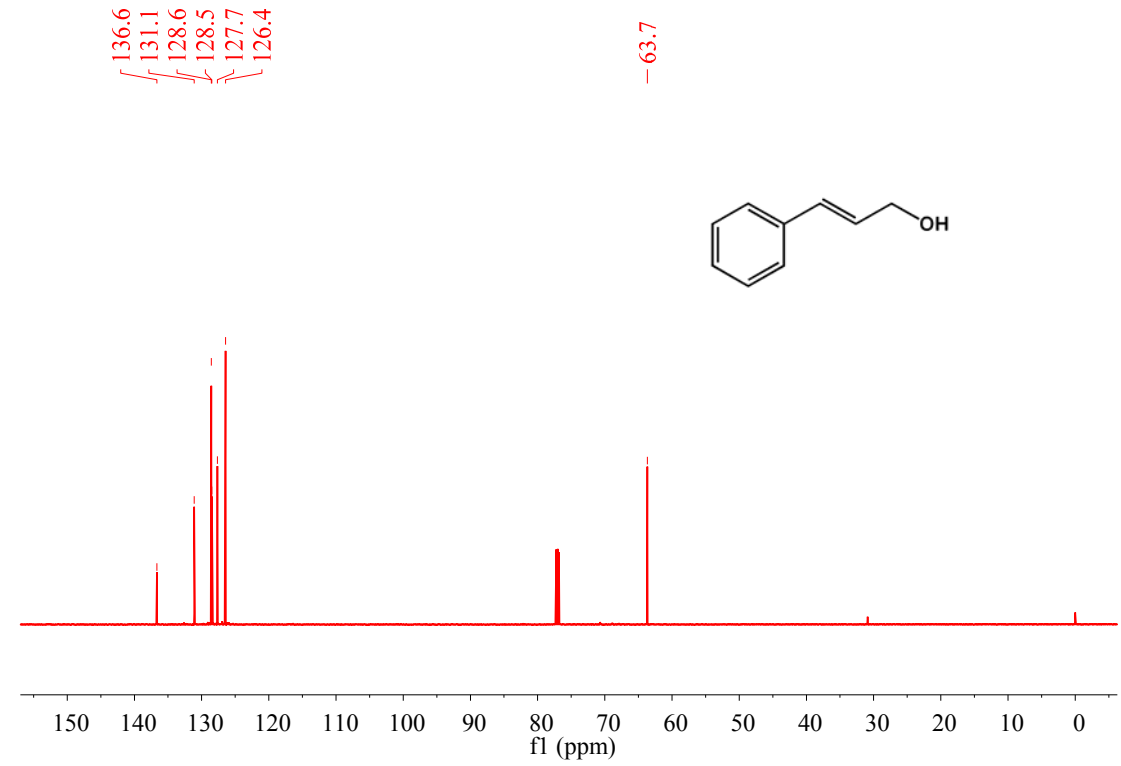


Figure S15. The ^{1}H and ^{13}C NMR spectra for 4-methoxycinnamic alcohol (***3ab***).

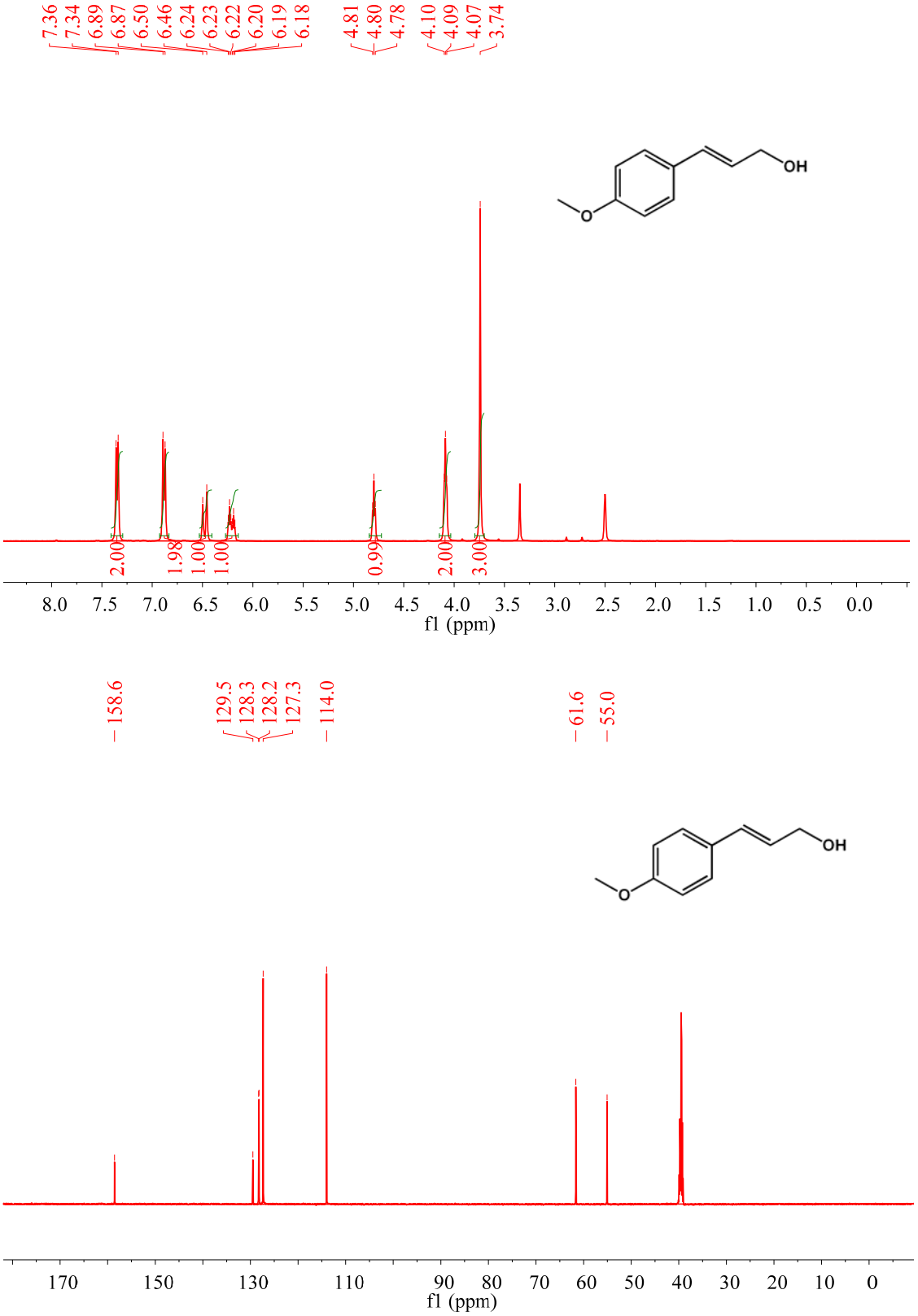


Figure S16. The ^{1}H and ^{13}C NMR spectra for 4-nitrocinnamic alcohol (***3ac***).

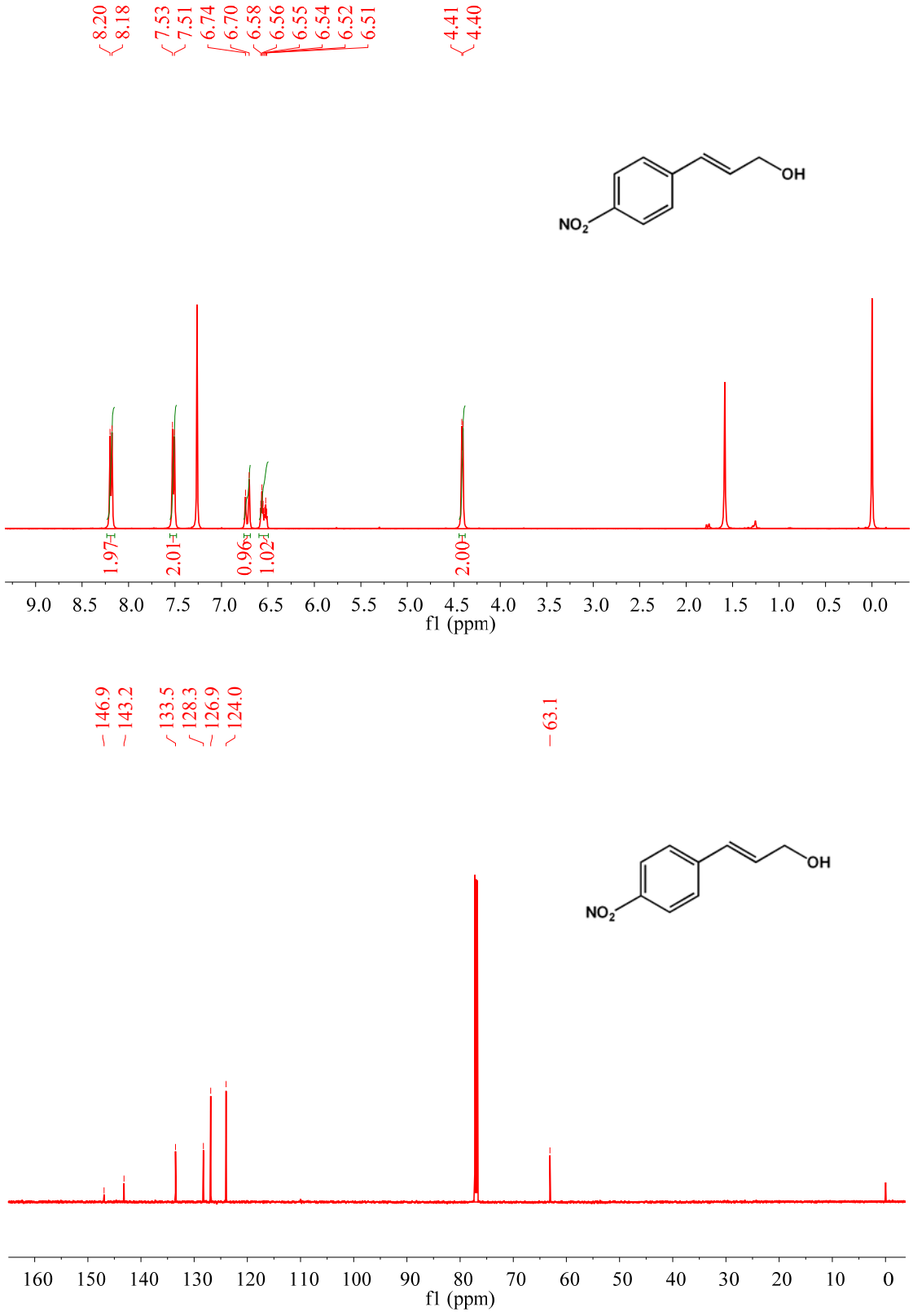


Figure S17. The ^{1}H and ^{13}C NMR spectra for α-methylcinnamic alcohol (***3ad***).

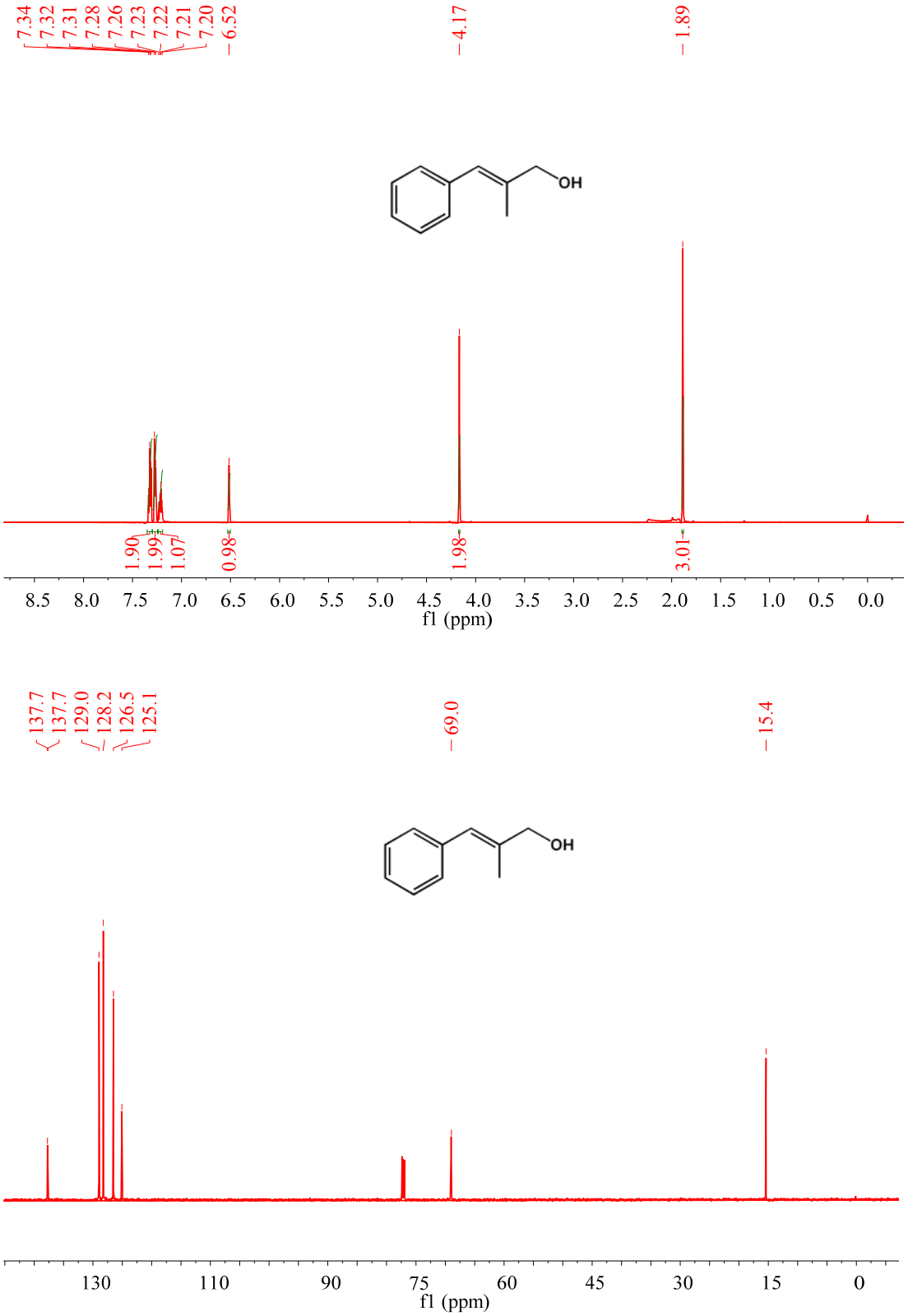


Figure S18. The ^{1}H and ^{13}C NMR spectra for α-amylcinnamic alcohol (***3ae***).

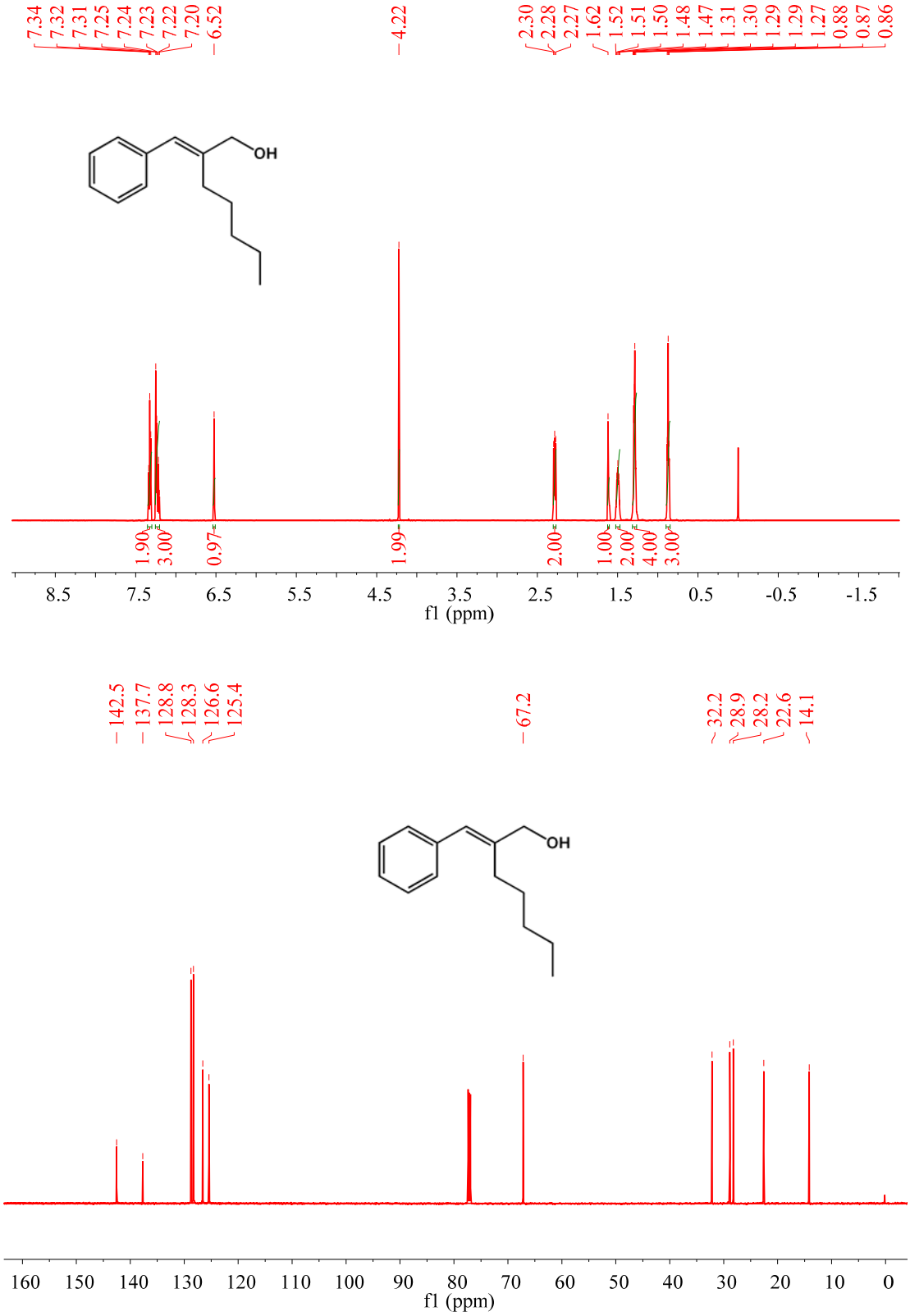


Figure S19. The ^{1}H and ^{13}C NMR spectra for (E)-3-(furan-2-yl)prop-2-en-1-ol (***3af***).

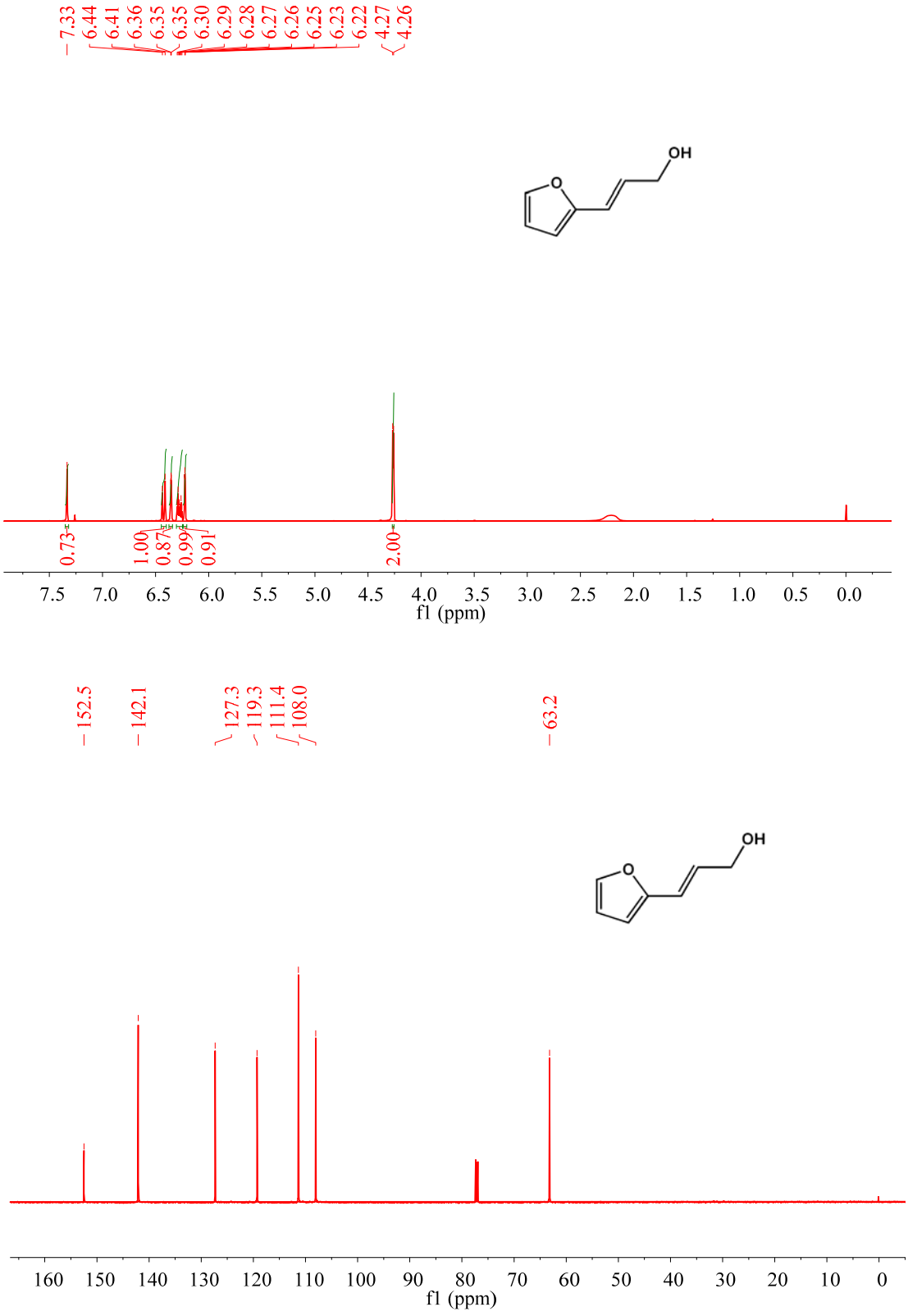


Figure S20. The ^{1}H and ^{13}C NMR spectra for (E)-hept-2-en-1-ol (***3ag***).

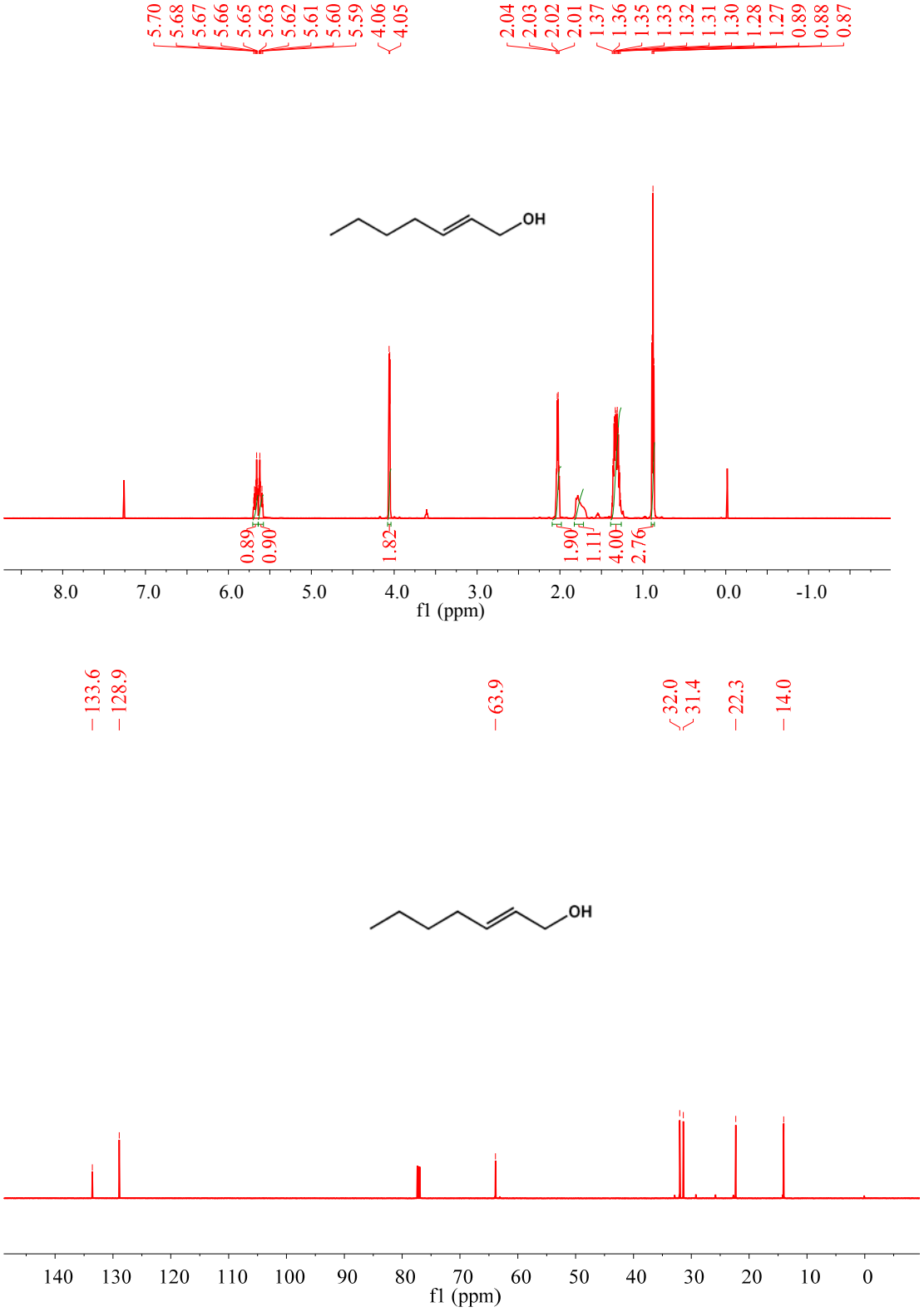


Figure S21. The ^{1}H and ^{13}C NMR spectra for (E)-2-methylpent-2-en-1-ol (***3ah***).

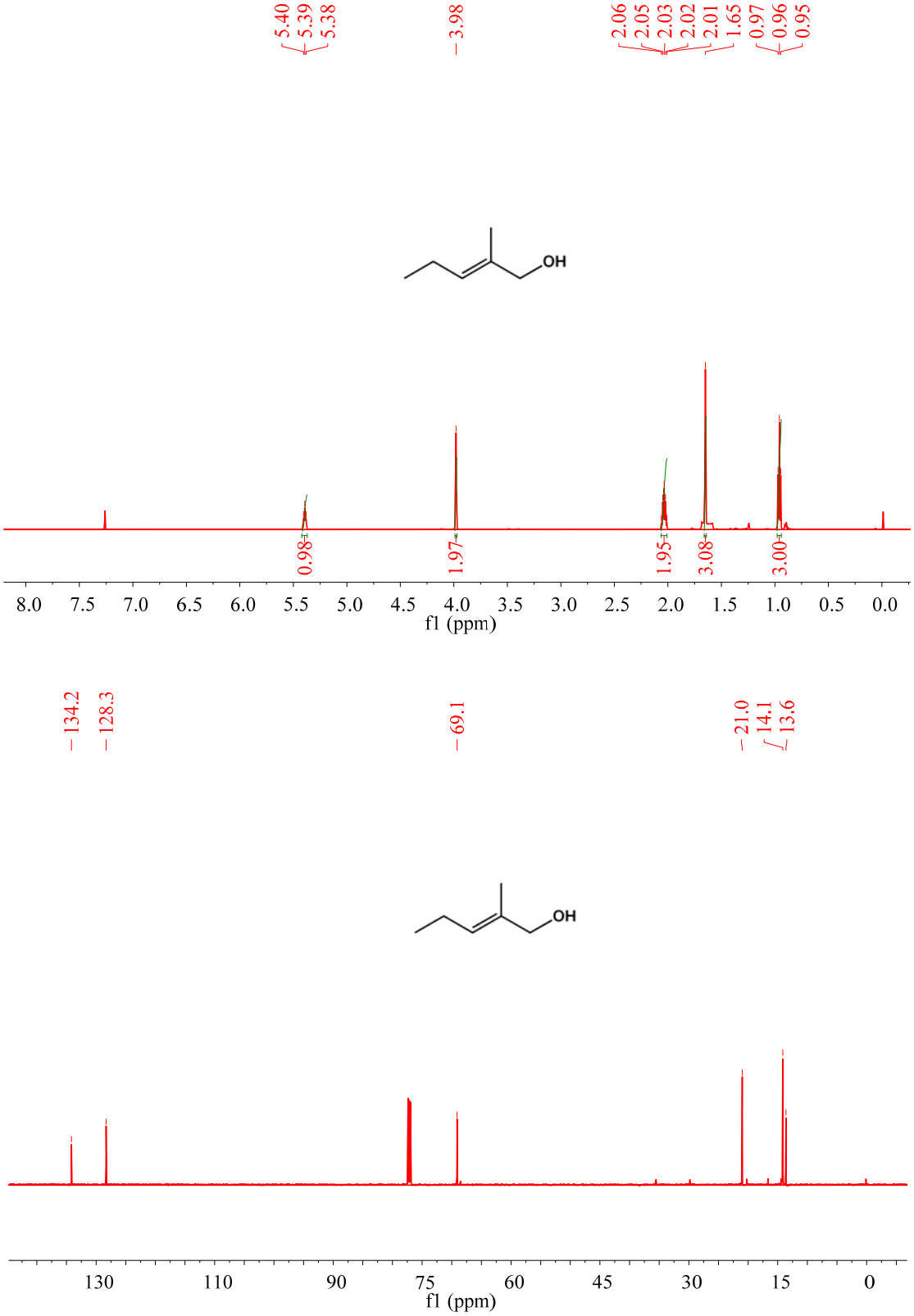


Figure S22. The ^{1}H and ^{13}C NMR spectra for 2-furfurylalcohol (***3ai***).

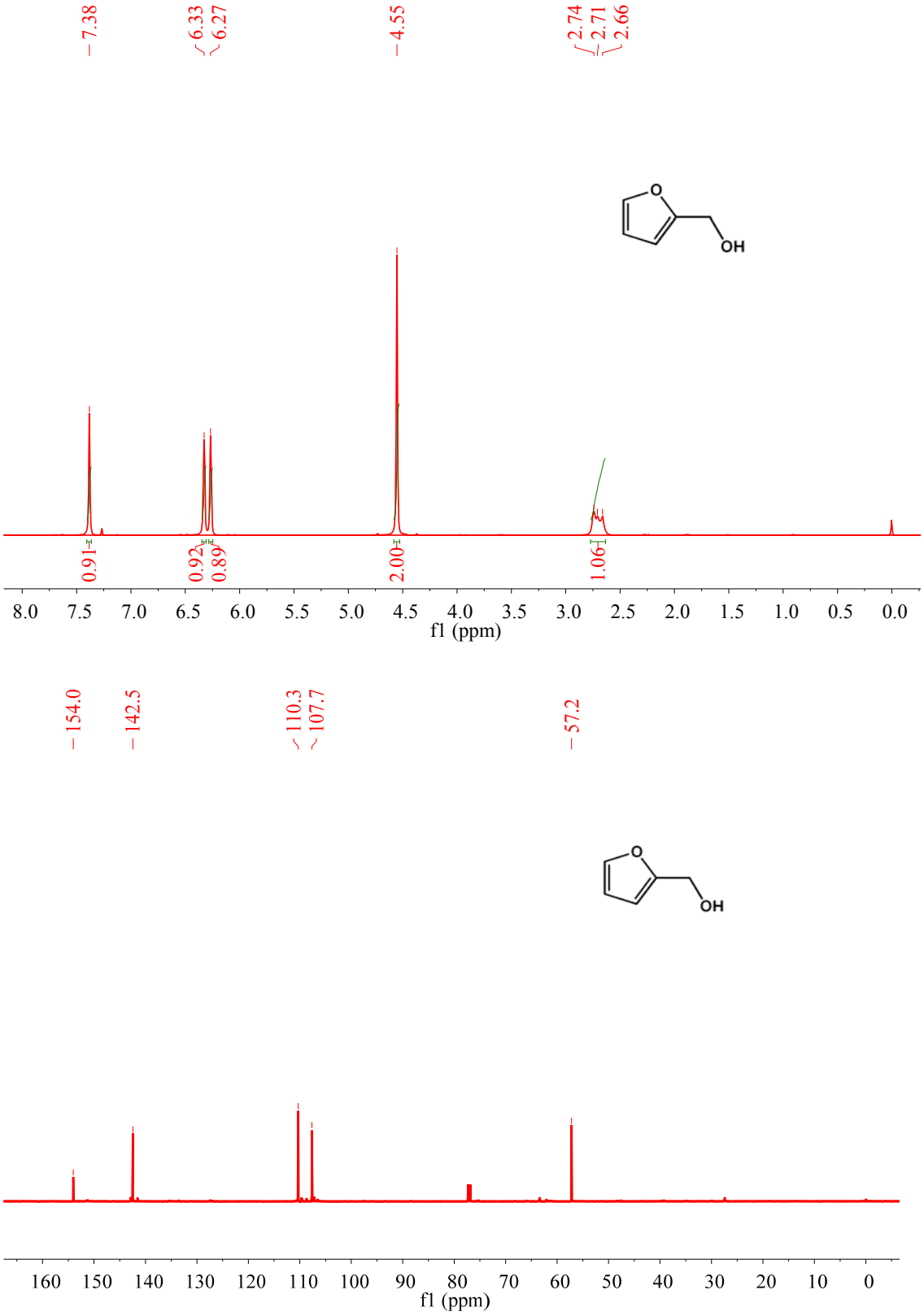
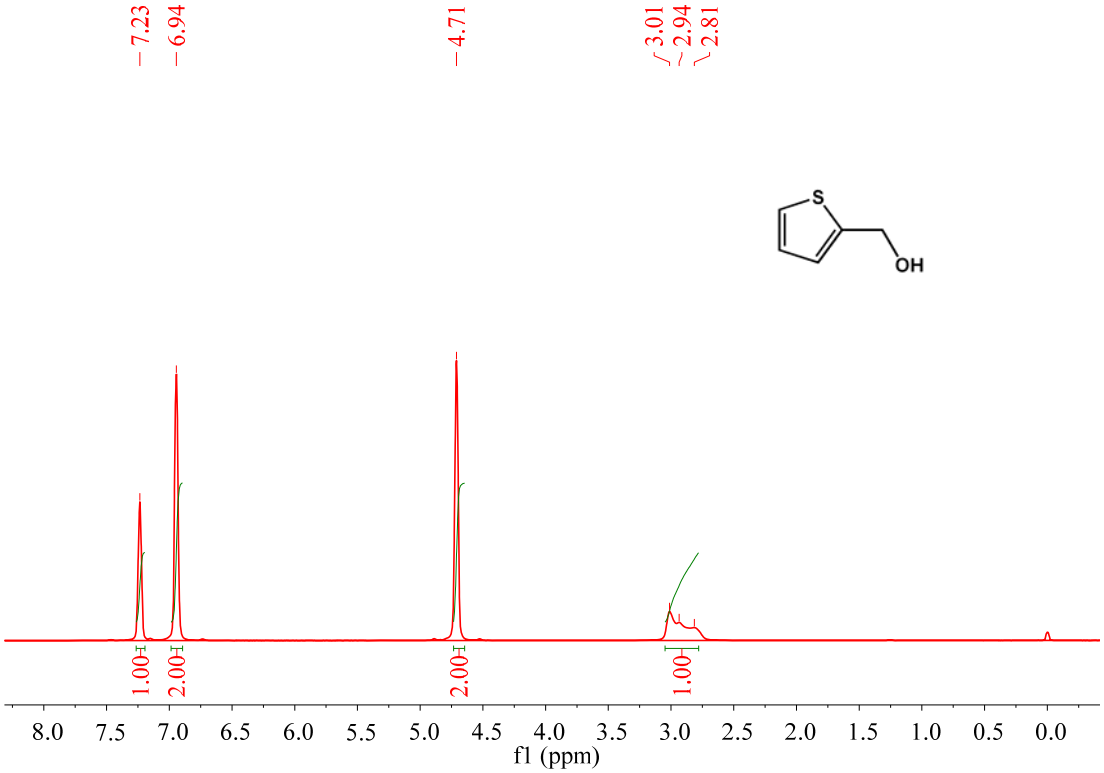


Figure S23. The ^{1}H and ^{13}C NMR spectra for thiophen-2-ylmethanol (***3aj***).



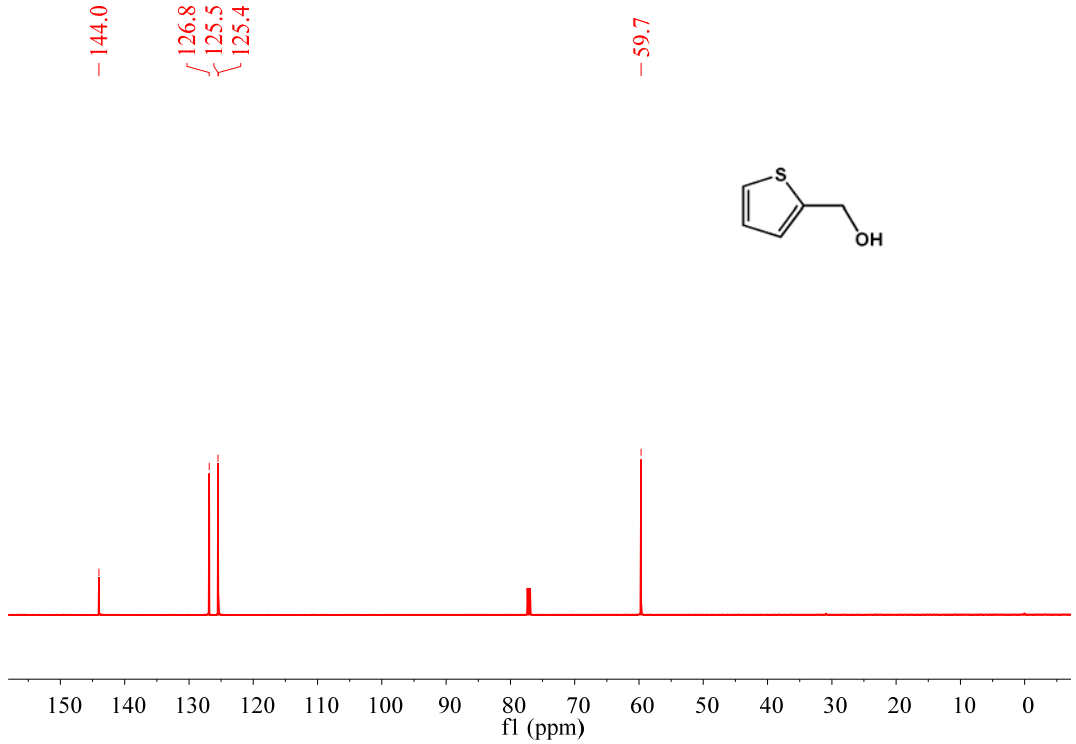
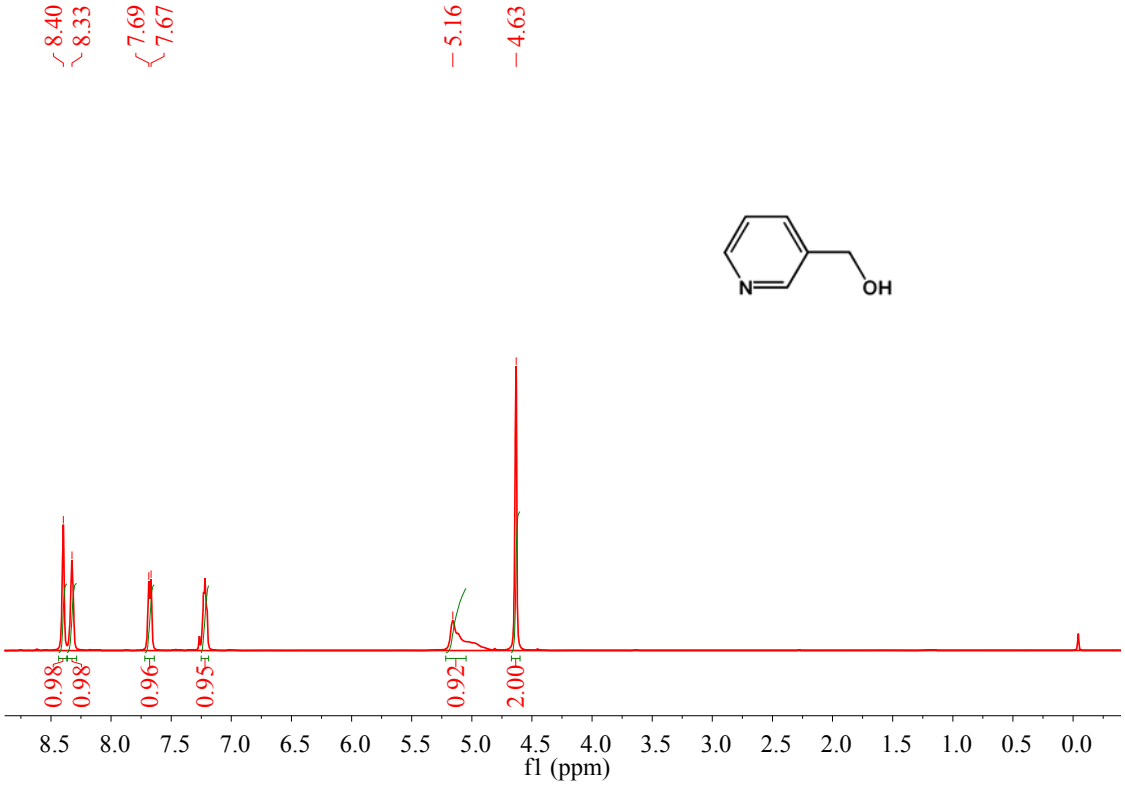


Figure S24. The ^{1}H and ^{13}C NMR spectra for 3-pyridylmethanol (***3ak***).



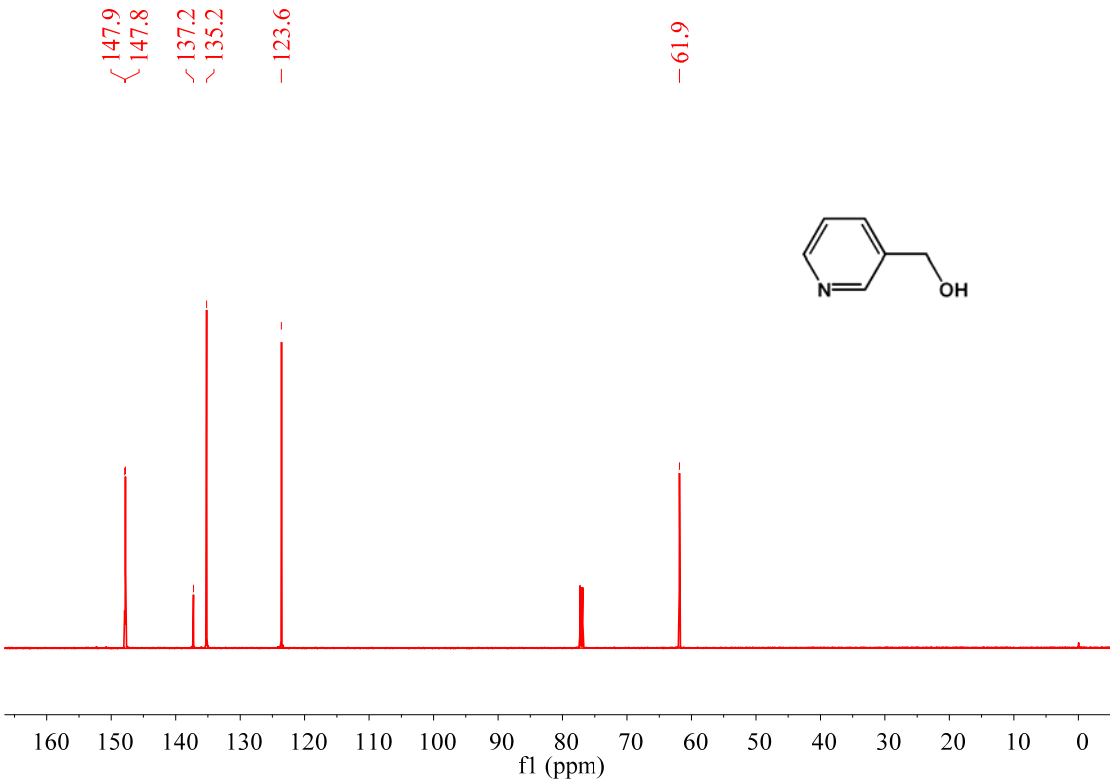


Figure S25. The ^{1}H and ^{13}C NMR spectra for 4-phenylbut-3-en-2-ol (***3al***).

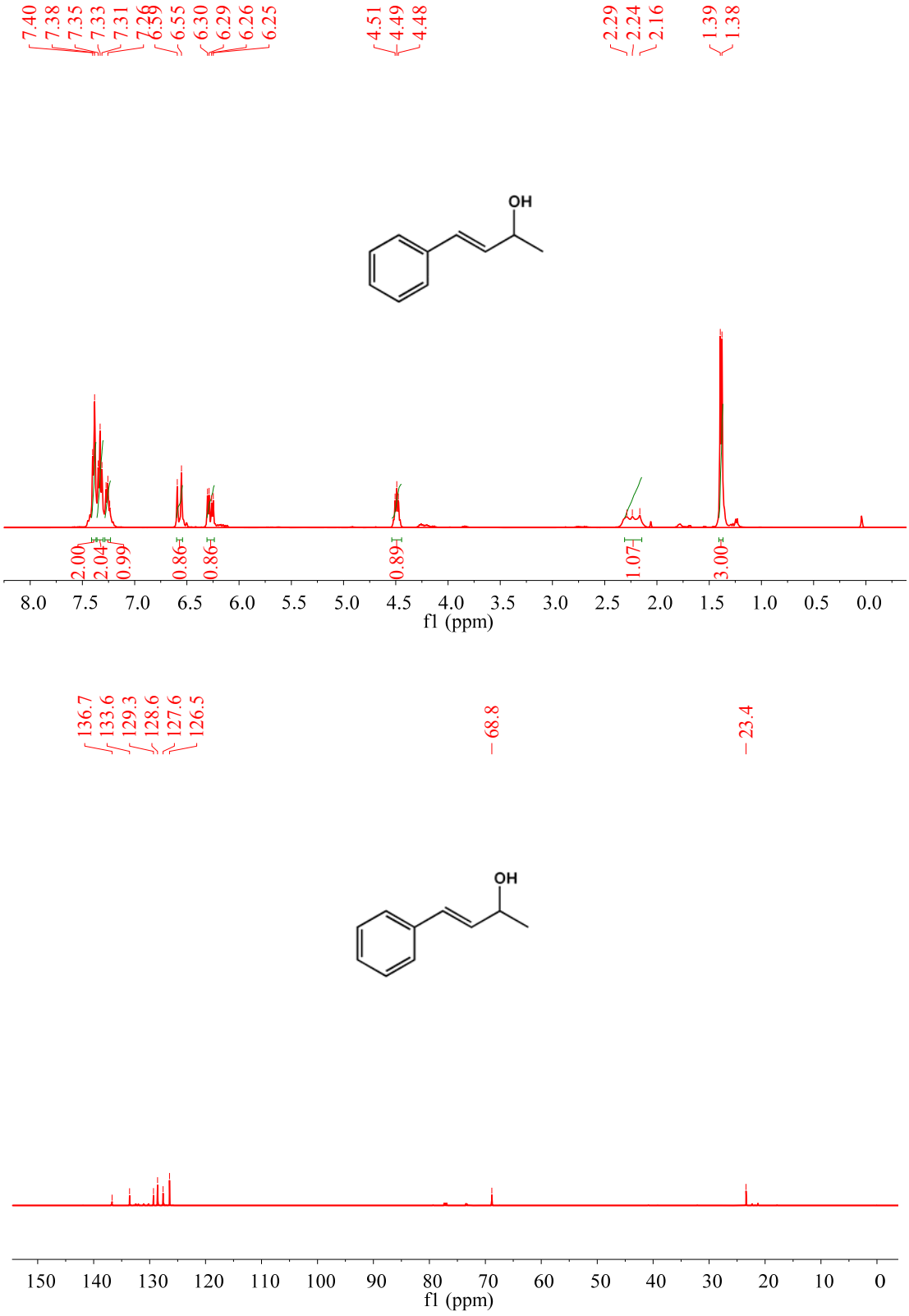
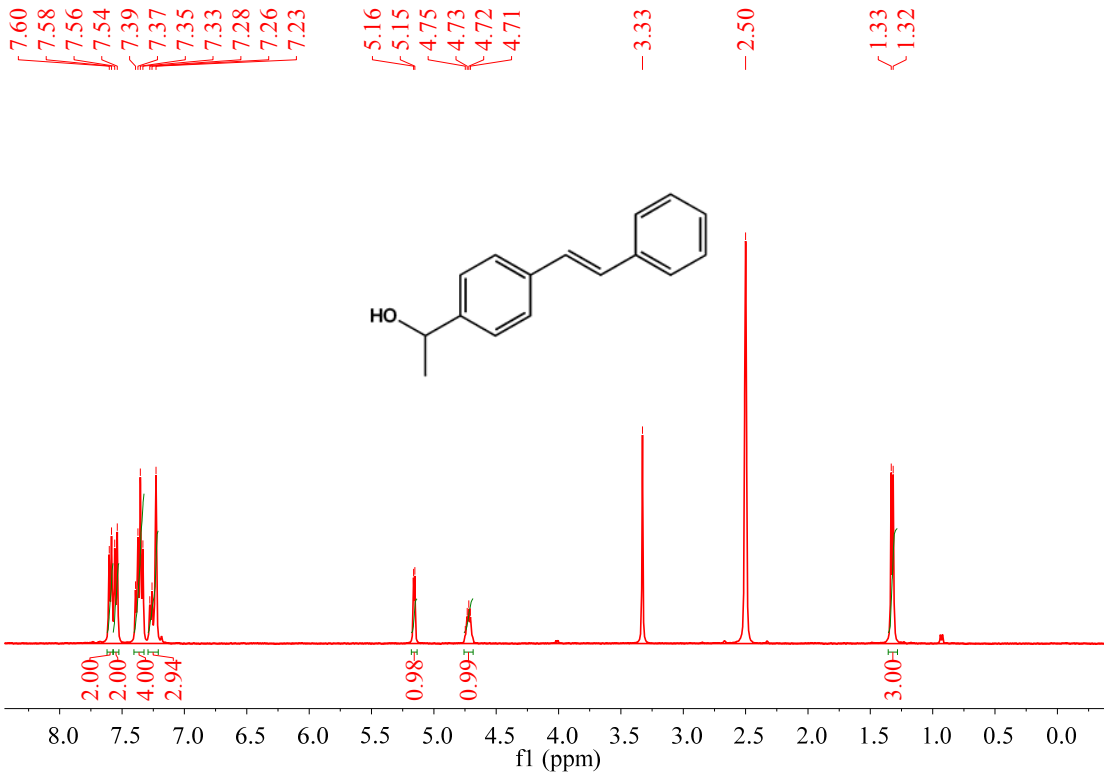


Figure S26. The ^{1}H and ^{13}C NMR spectra for 1-(4-styrylphenyl)ethan-1-ol (***3am***).



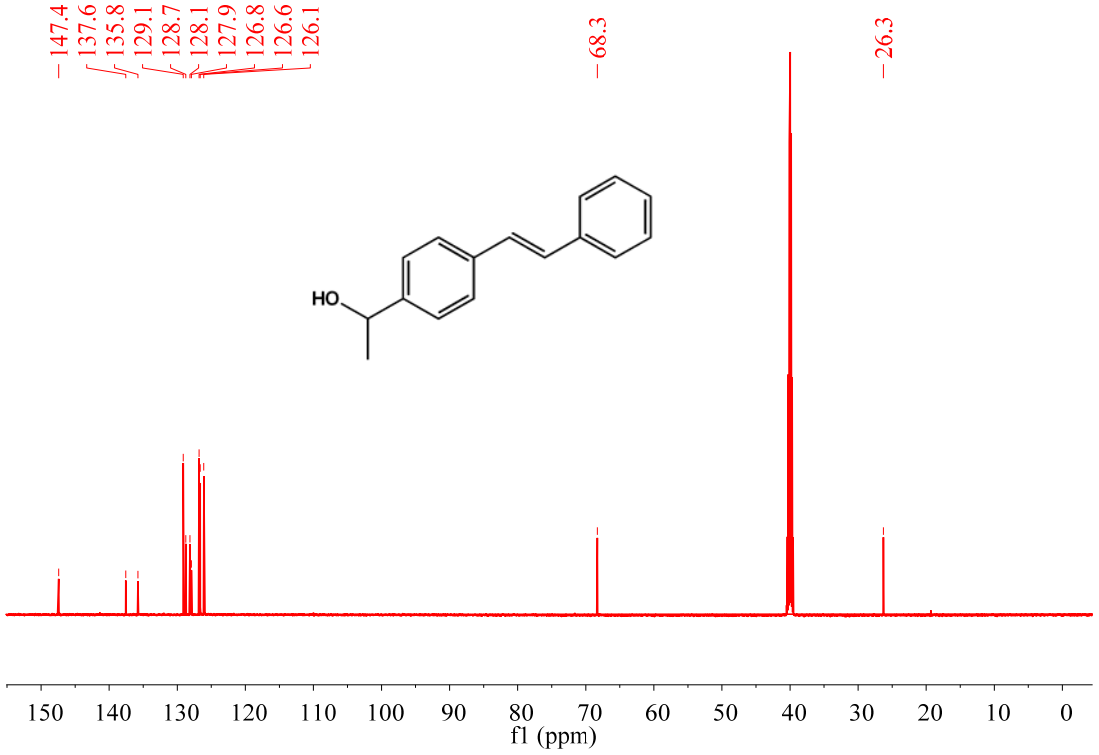


Figure S27. The ^{1}H and ^{13}C NMR spectra for 1-penten-3-ol (***3an***).

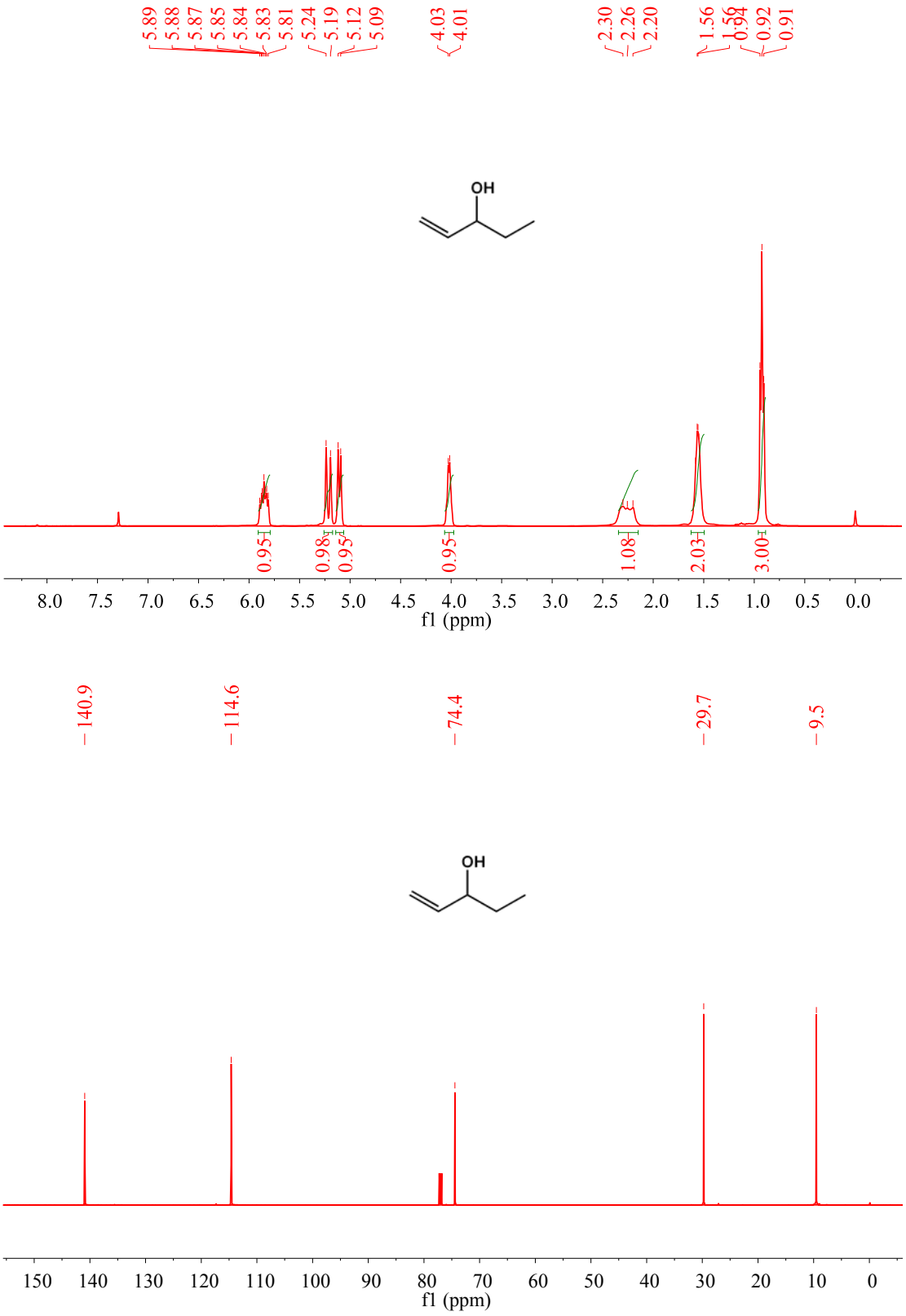


Figure S28. The ^{1}H and ^{13}C NMR spectra for hex-5-en-2-ol (***3ao***).

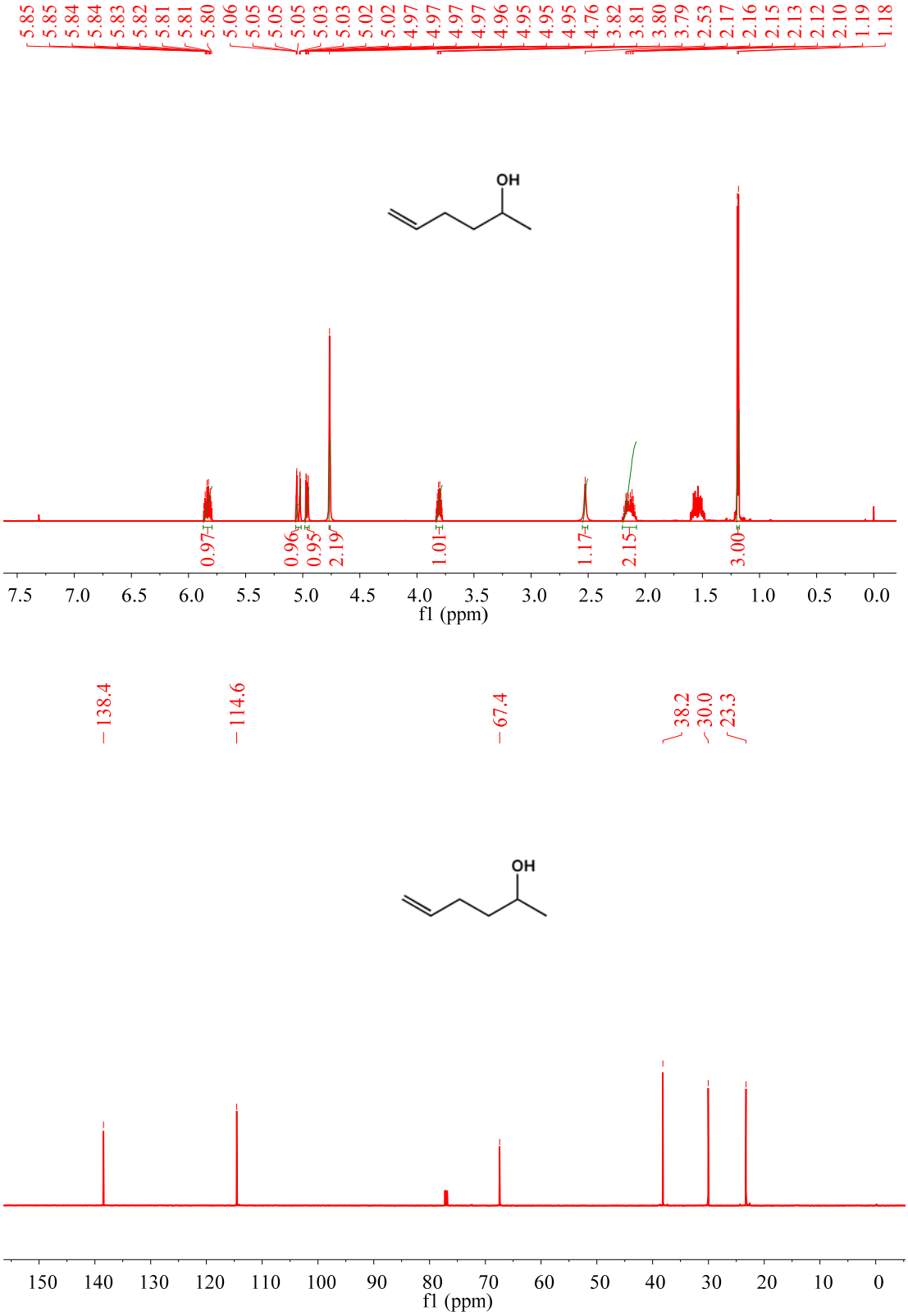


Figure S29. The ^{1}H and ^{13}C NMR spectra for 6-methylhept-5-en-2-ol (***3ap***).

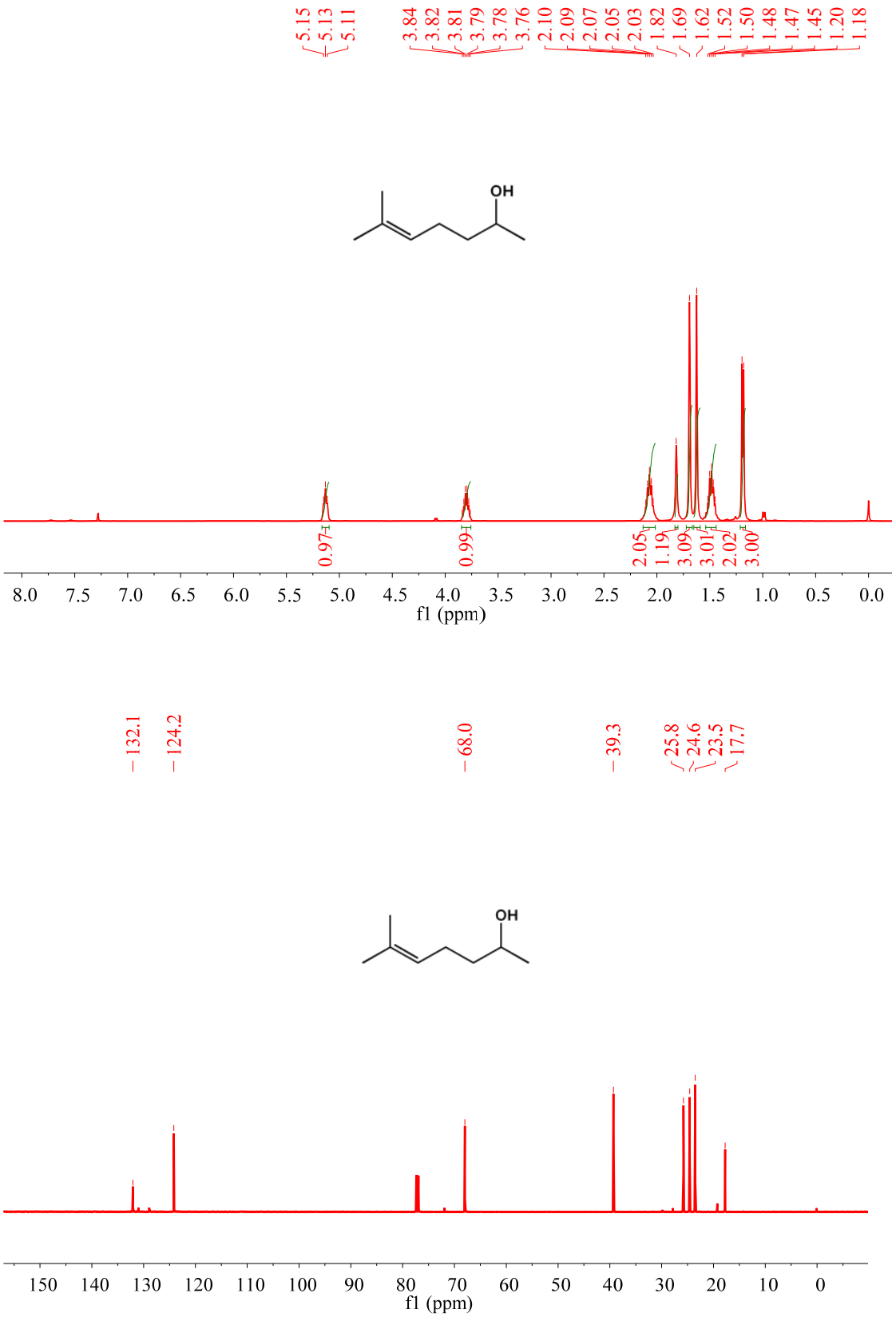


Figure S30. The ^{1}H and ^{13}C NMR spectra for 1,3-diphenylprop-2-en-1-ol (***3ba***).

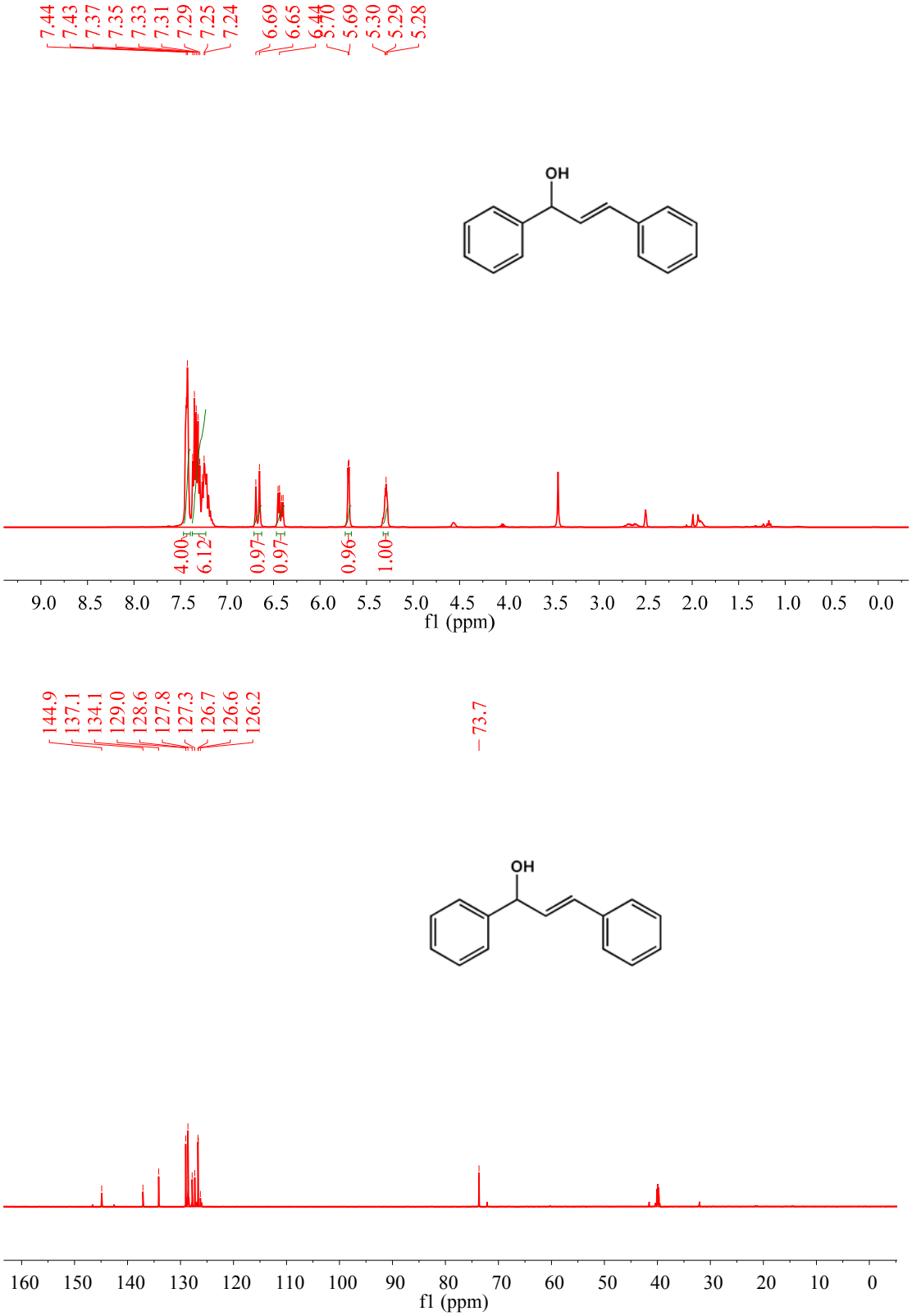


Figure S31. The ^{1}H and ^{13}C NMR spectra for 3-(4-chlorophenyl)-1-phenylprop-2-en-1-ol (***3bb***).

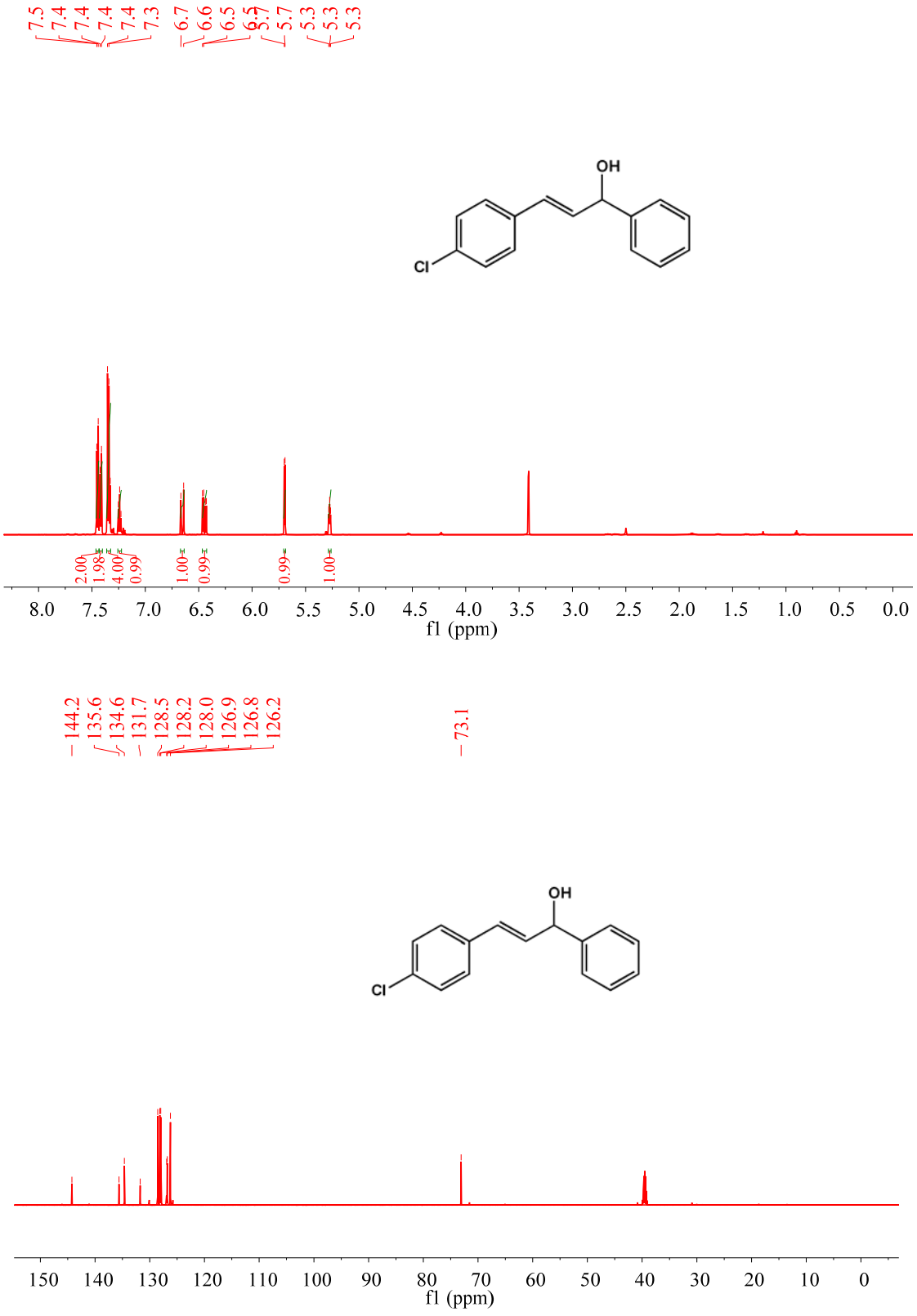


Figure S32. The ^{1}H and ^{13}C NMR spectra for 1-(naphthalen-2-yl)-3-phenylprop-2-en-1-ol (***3ca***).

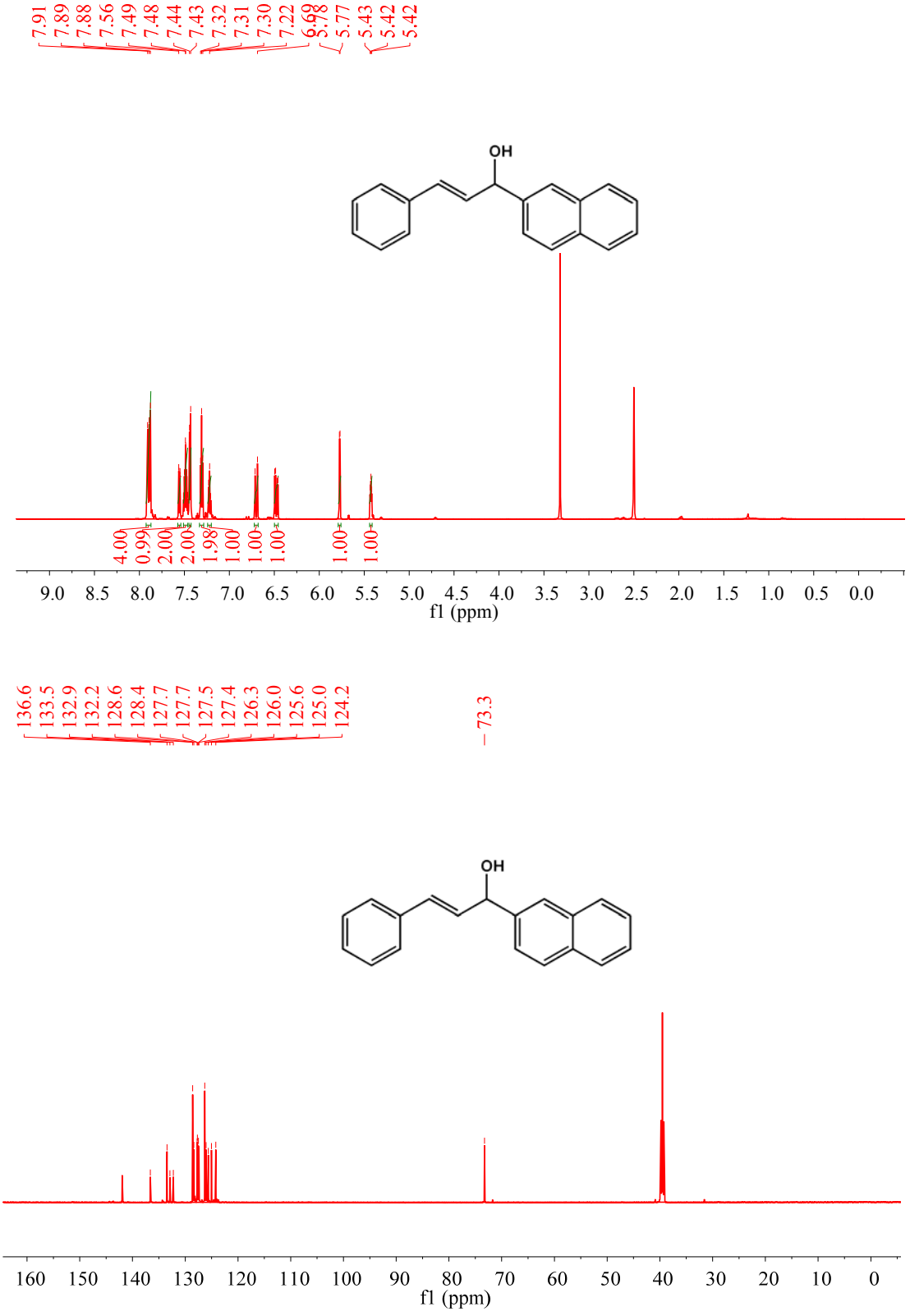
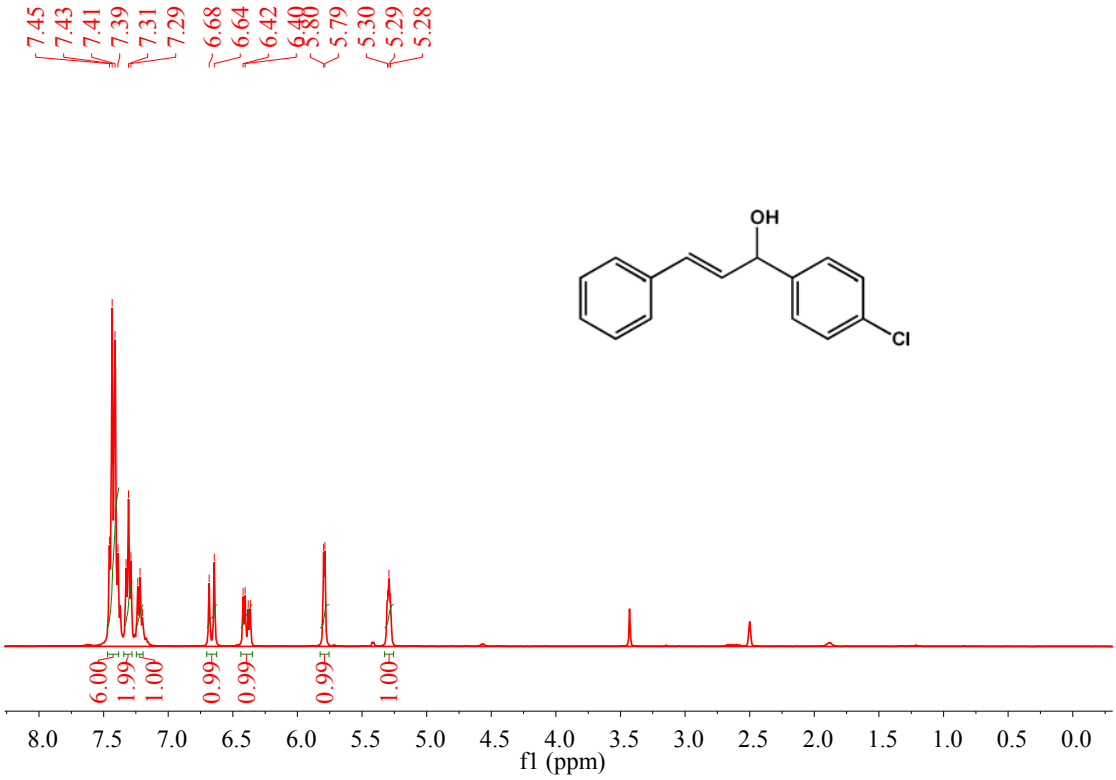


Figure S33. The ^{1}H and ^{13}C NMR spectra for 3-(4-chlorophenyl)-1-phenylprop-2-en-1-ol (***3cb***).



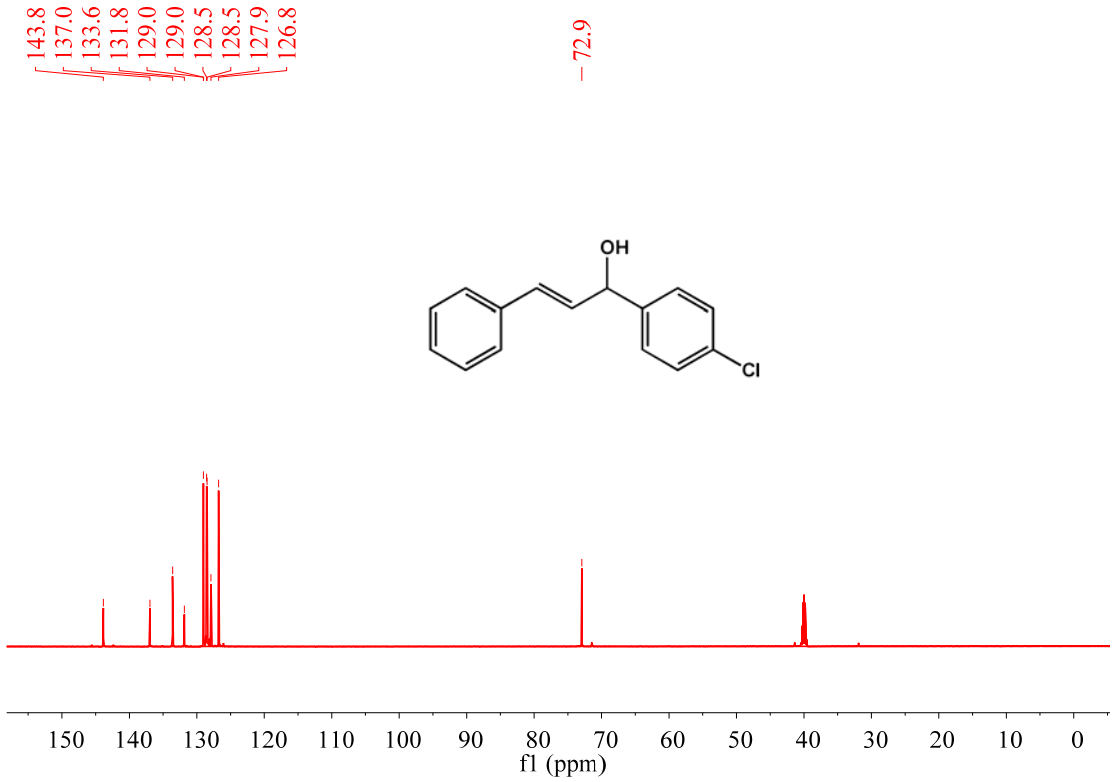


Figure S34. The ^{1}H and ^{13}C NMR spectra for 3-(4-nitrophenyl)-1-phenylprop-2-en-1-ol (***3cc***).

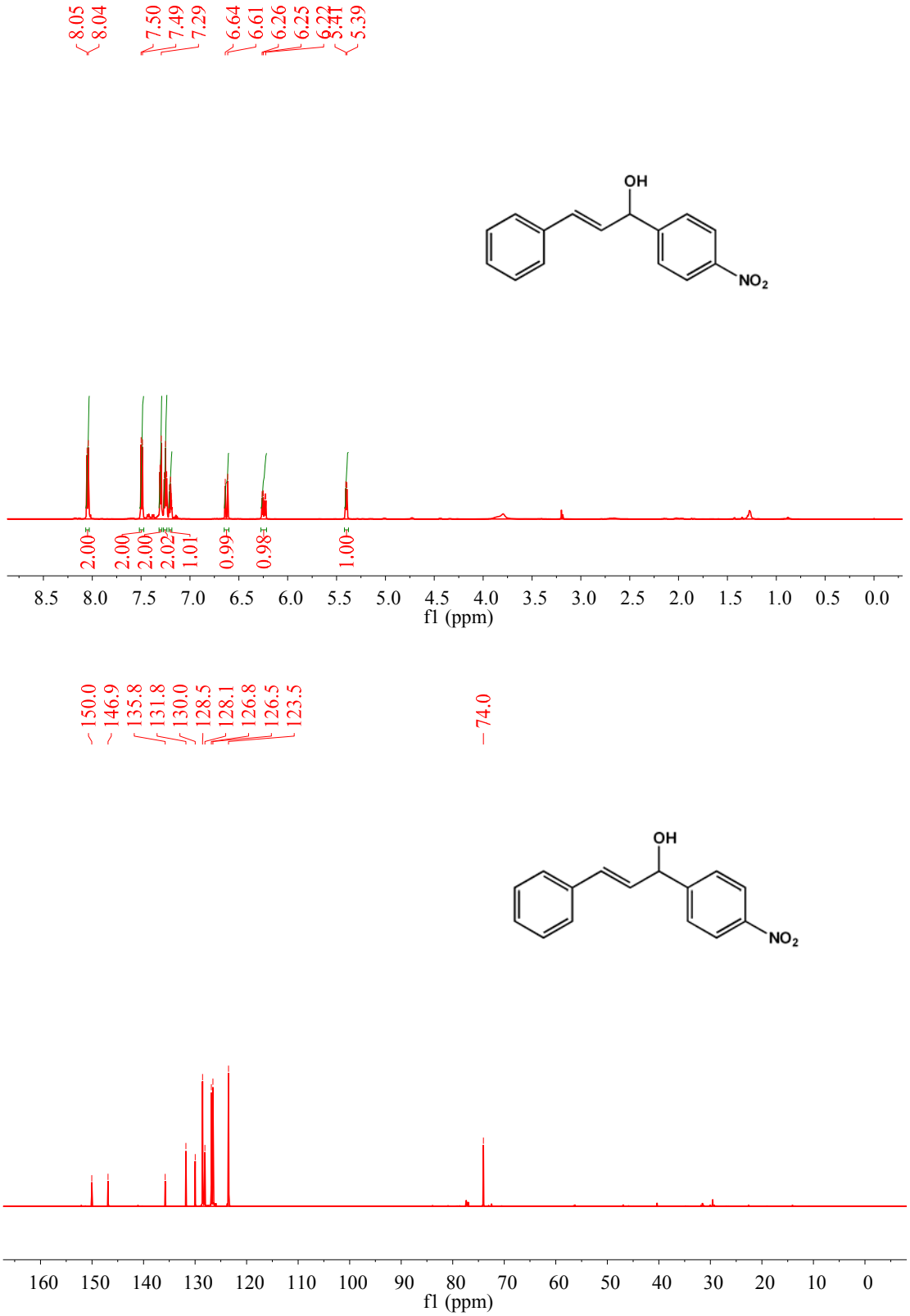


Figure S35. The ^{1}H and ^{13}C NMR spectra for 1,3-diphenylpropan-1-one (***4ba***).

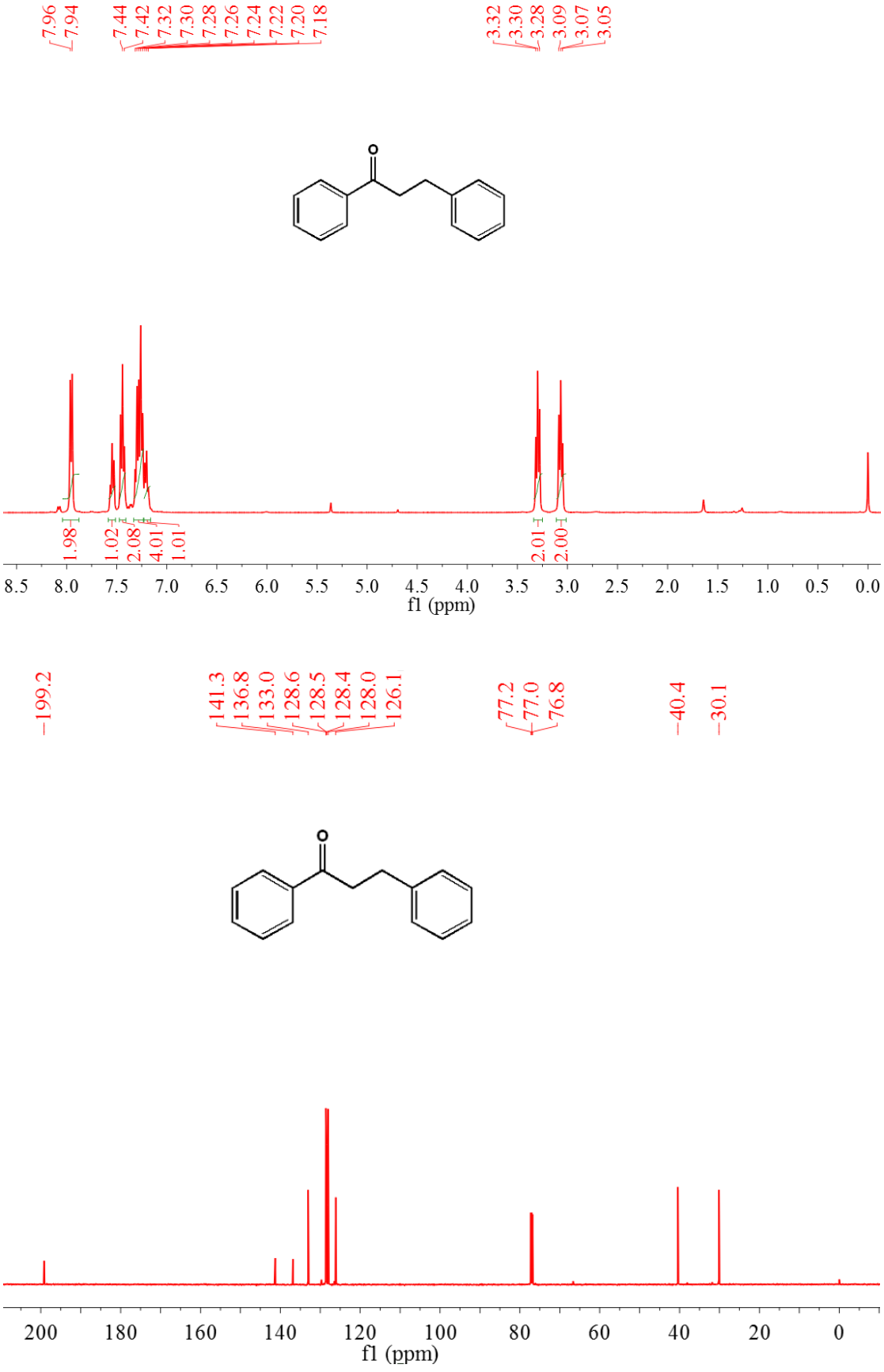


Figure S36. The ^{1}H and ^{13}C NMR spectra for 3-(4-chlorophenyl)-1-phenylpropan-1-one (***4bb***).

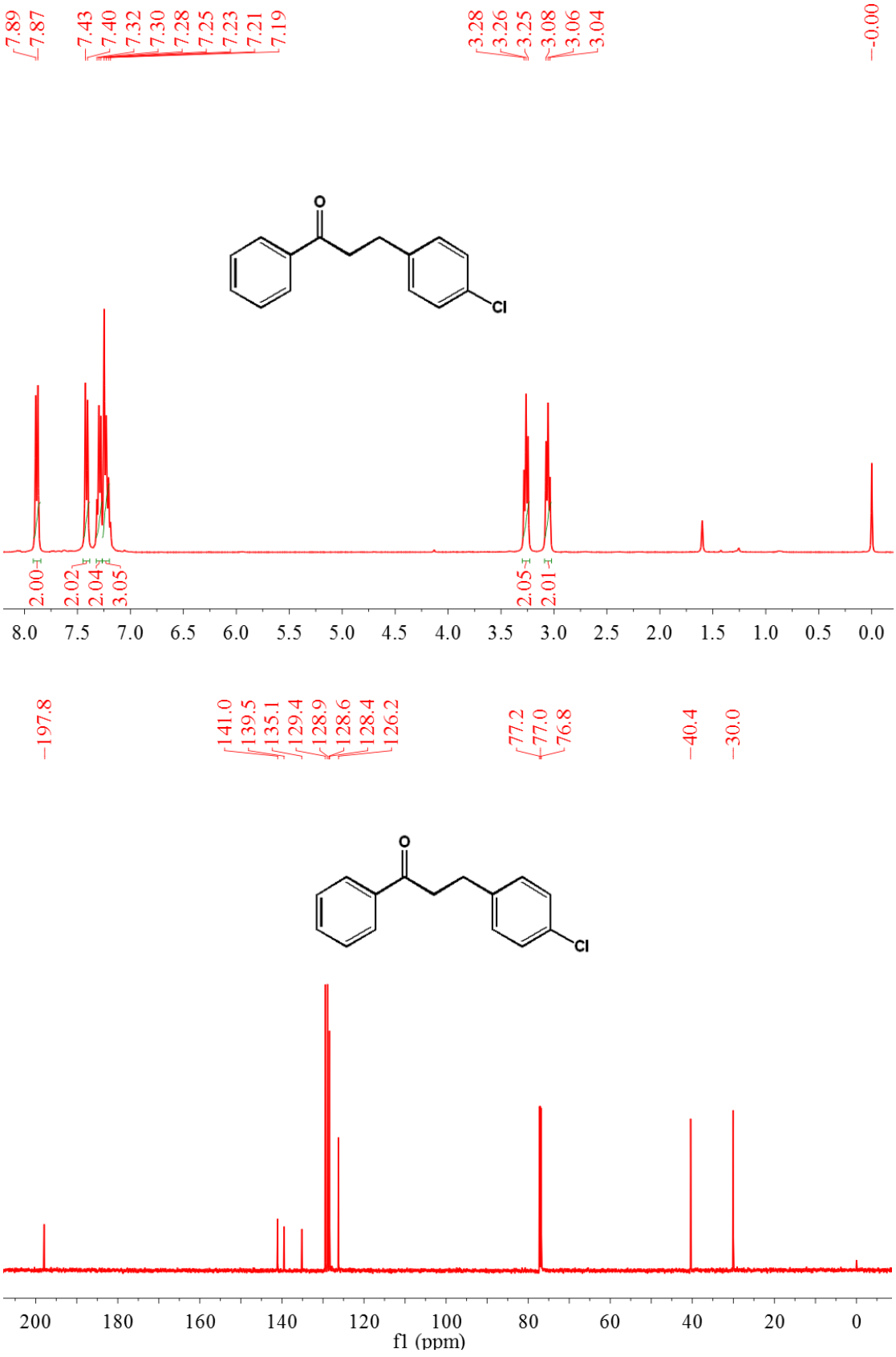
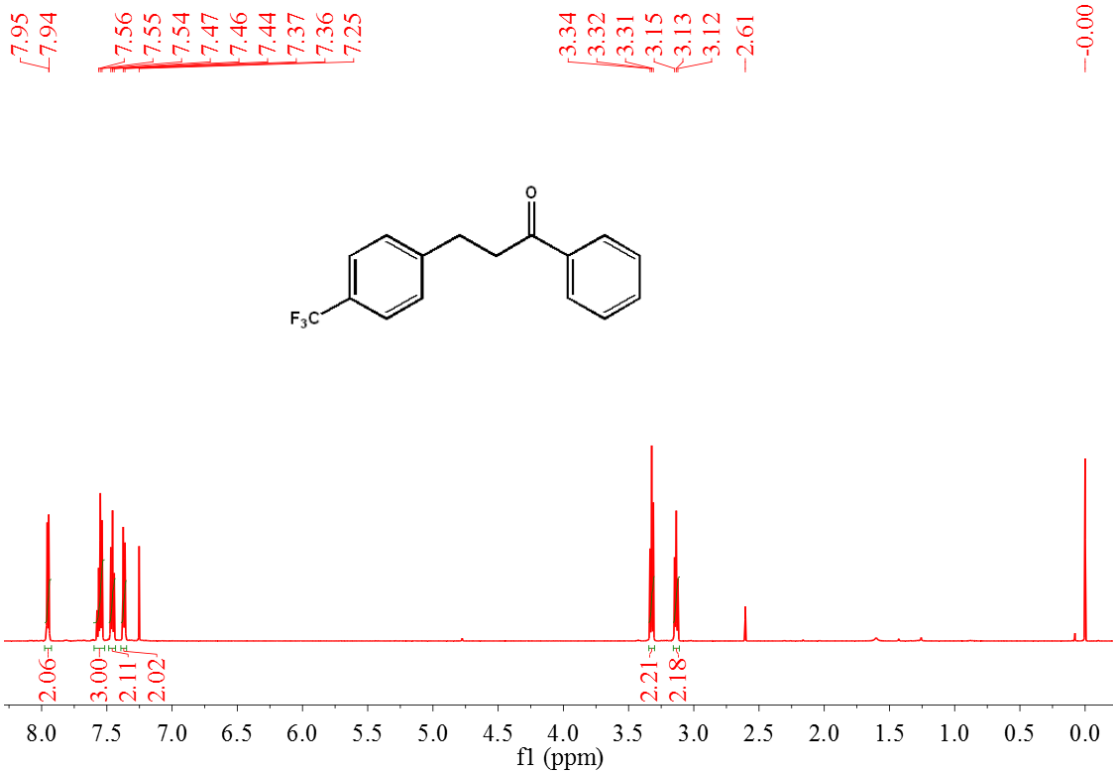


Figure S37. The ^{1}H and ^{13}C NMR spectra for 3-(4-bromophenyl)-1-phenylpropan-1-one (***4bc***).

Figure S38. The ^{1}H and ^{13}C NMR spectra for 1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (***4bd***).



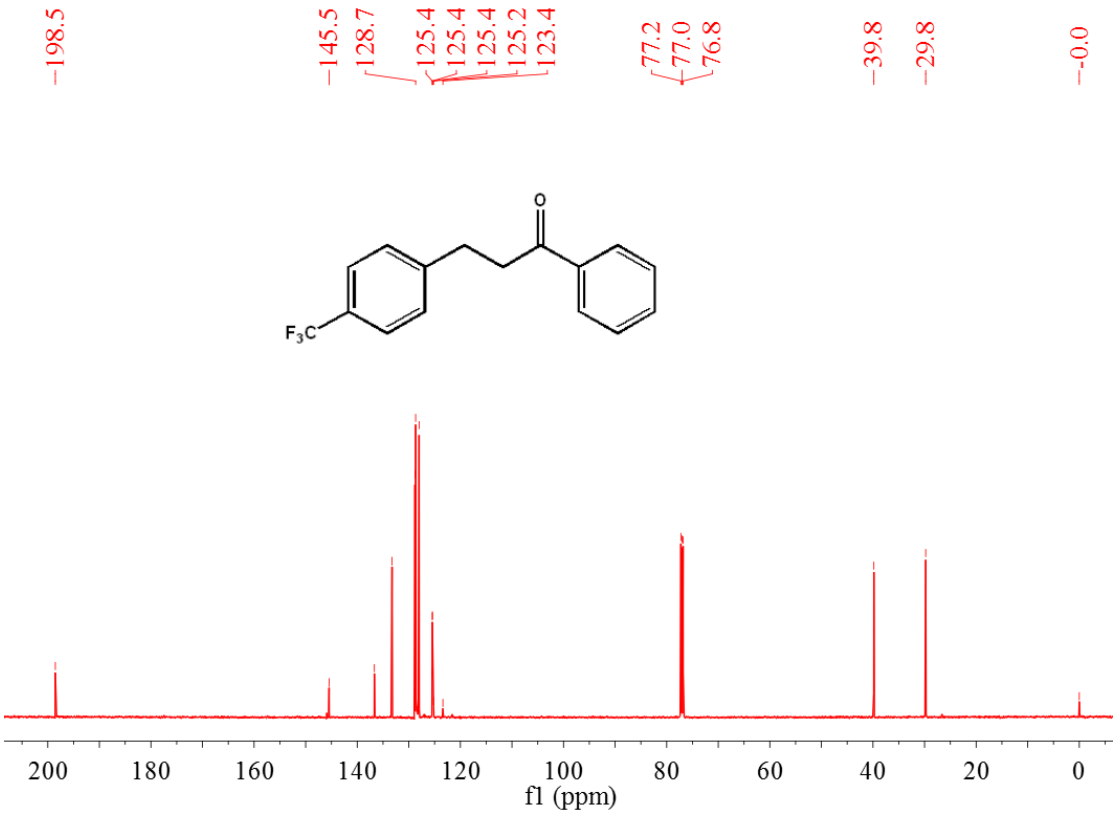


Figure S39. The ^{1}H and ^{13}C NMR spectra for 1-phenyl-3-(p-tolyl)propan-1-one (***4be***).

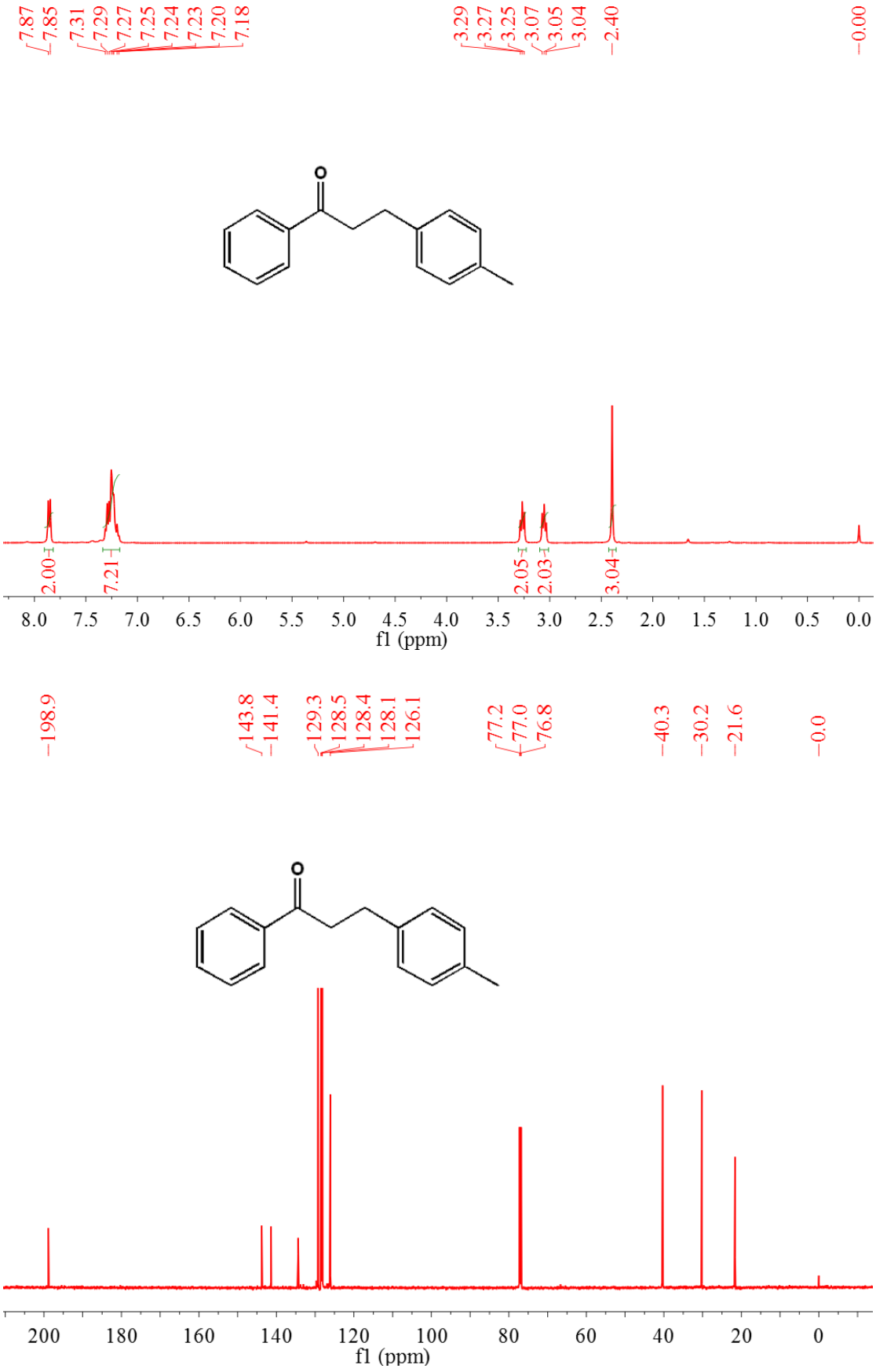
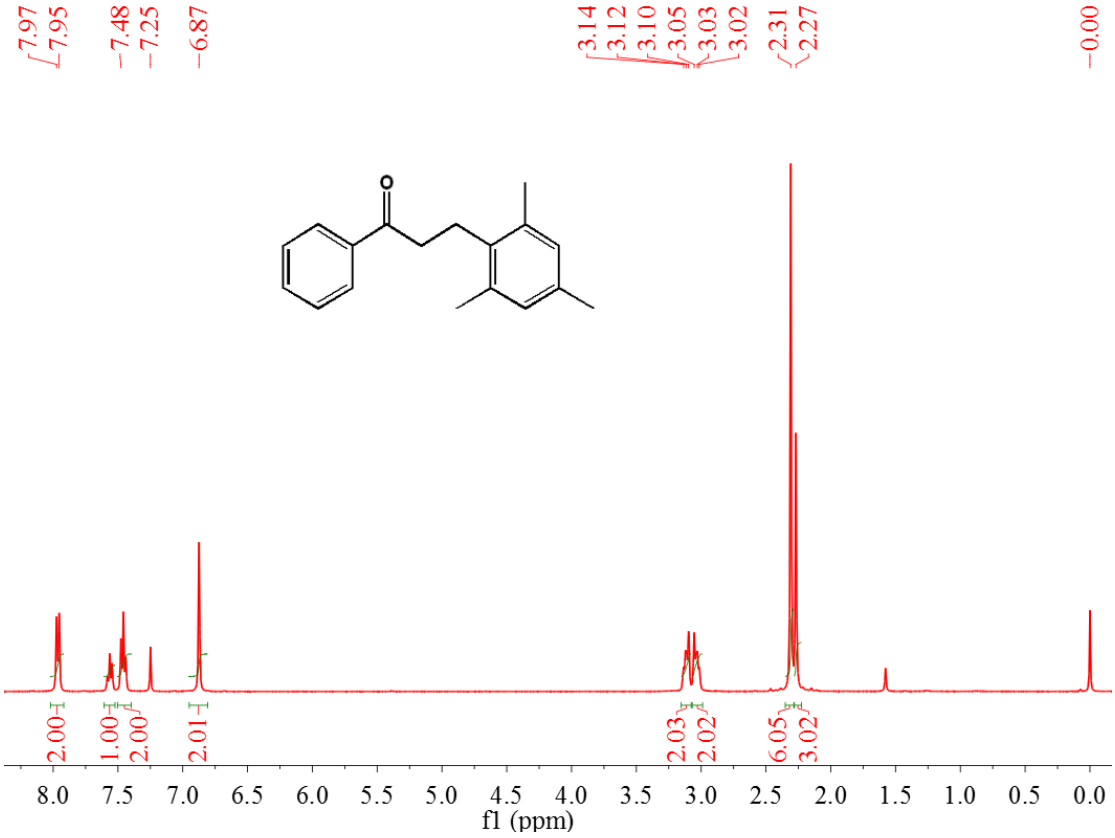


Figure S40. The ^{1}H and ^{13}C NMR spectra for 3-mesityl-1-phenylpropan-1-one (***4bf***).



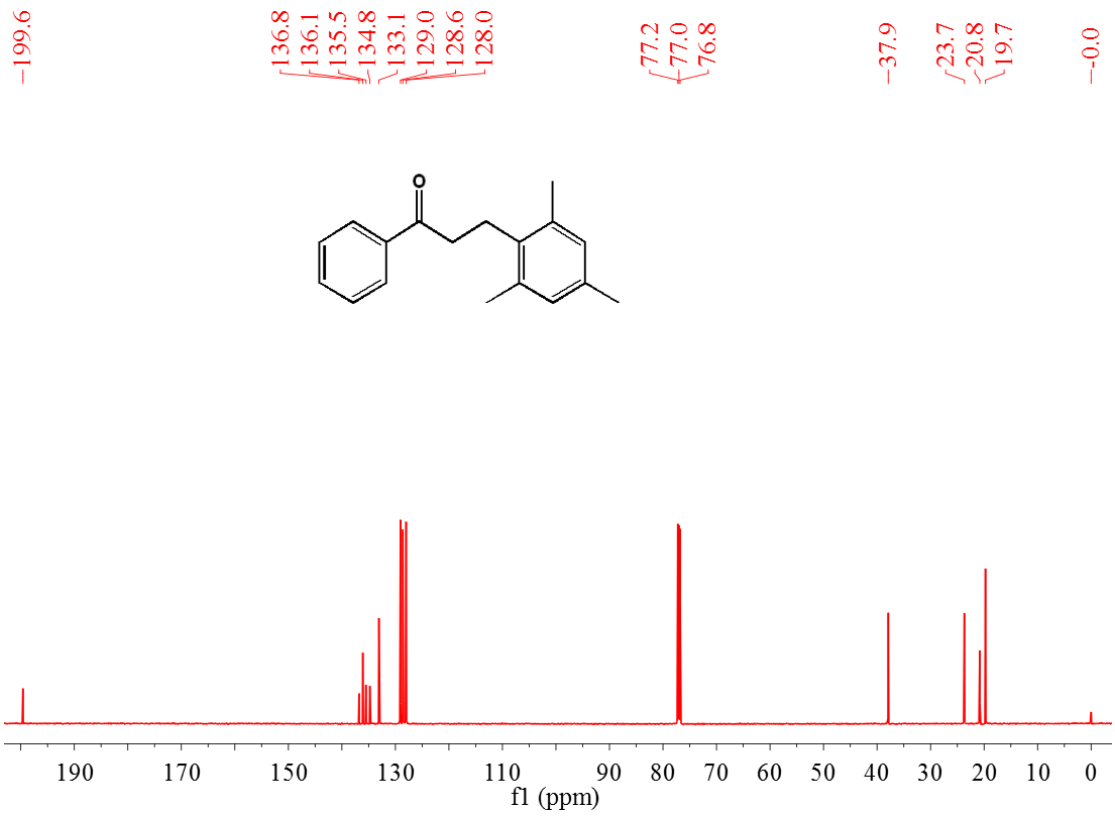
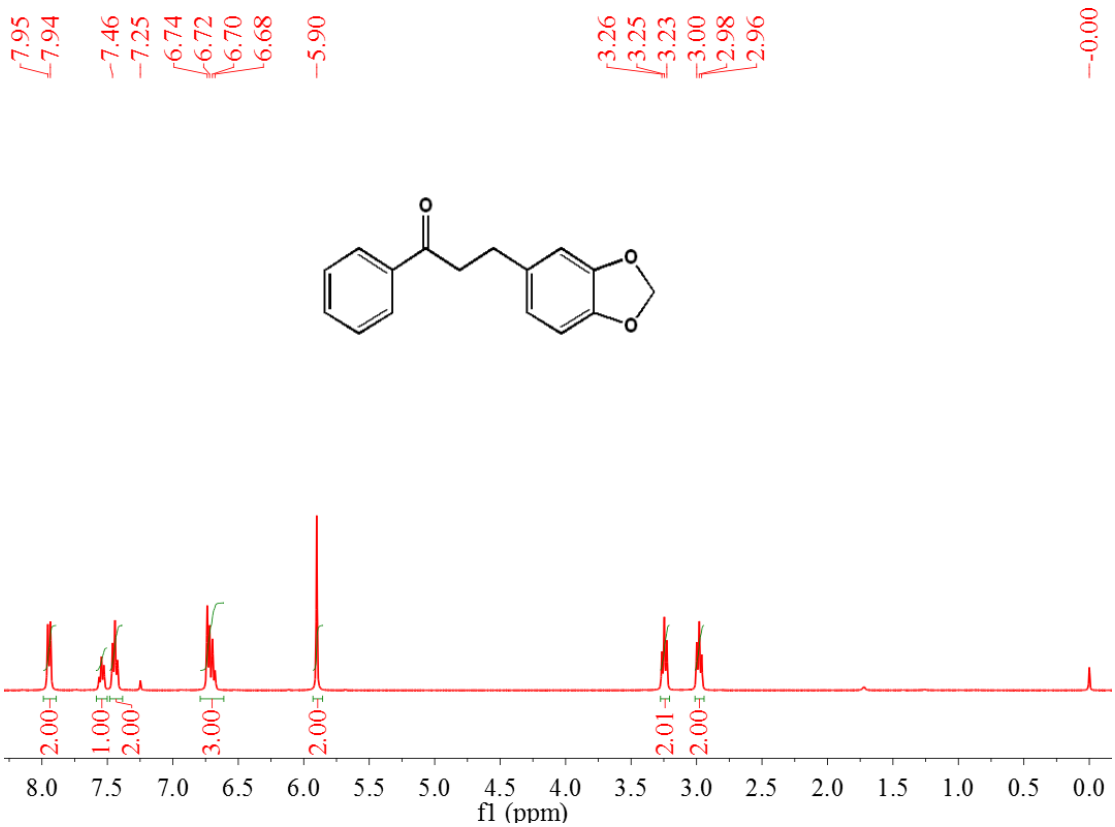


Figure S41. The ^{1}H and ^{13}C NMR spectra for 3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-one (***4bg***).



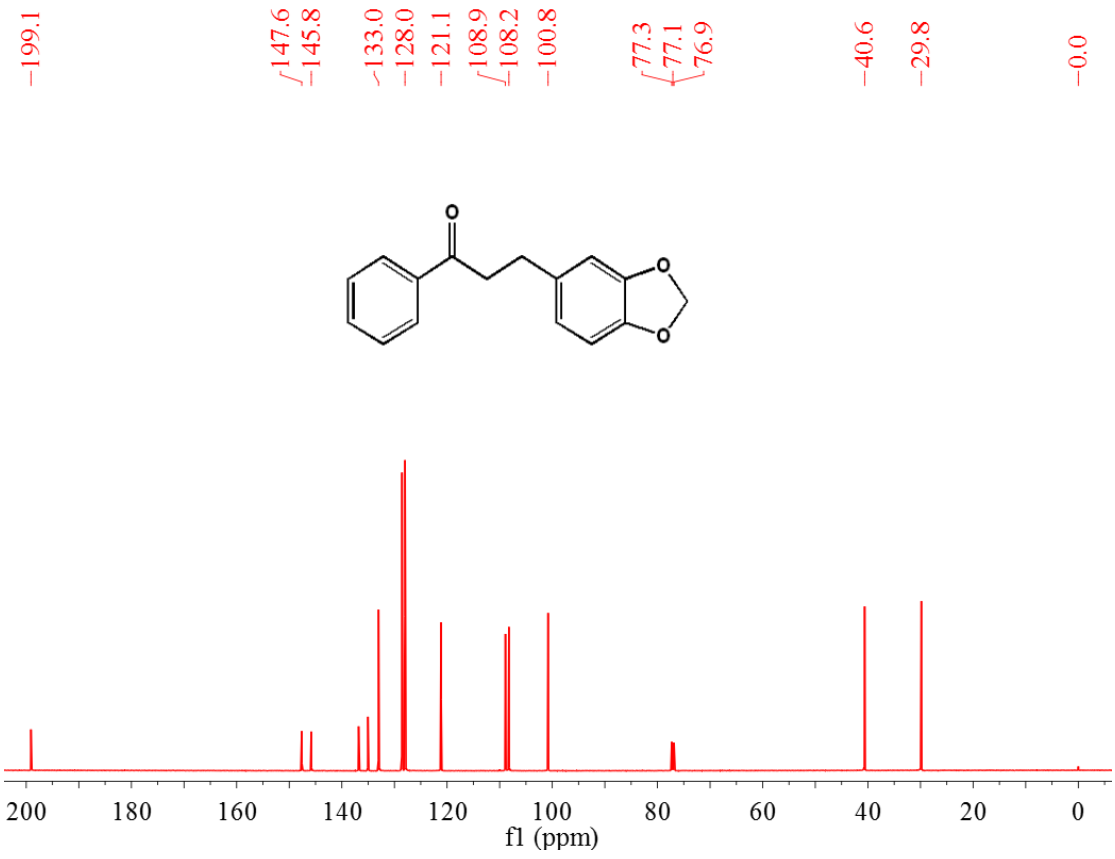


Figure S42. The ^{1}H and ^{13}C NMR spectra for 1-phenyl-3-(pyridin-3-yl)propan-1-one (***4bh***).

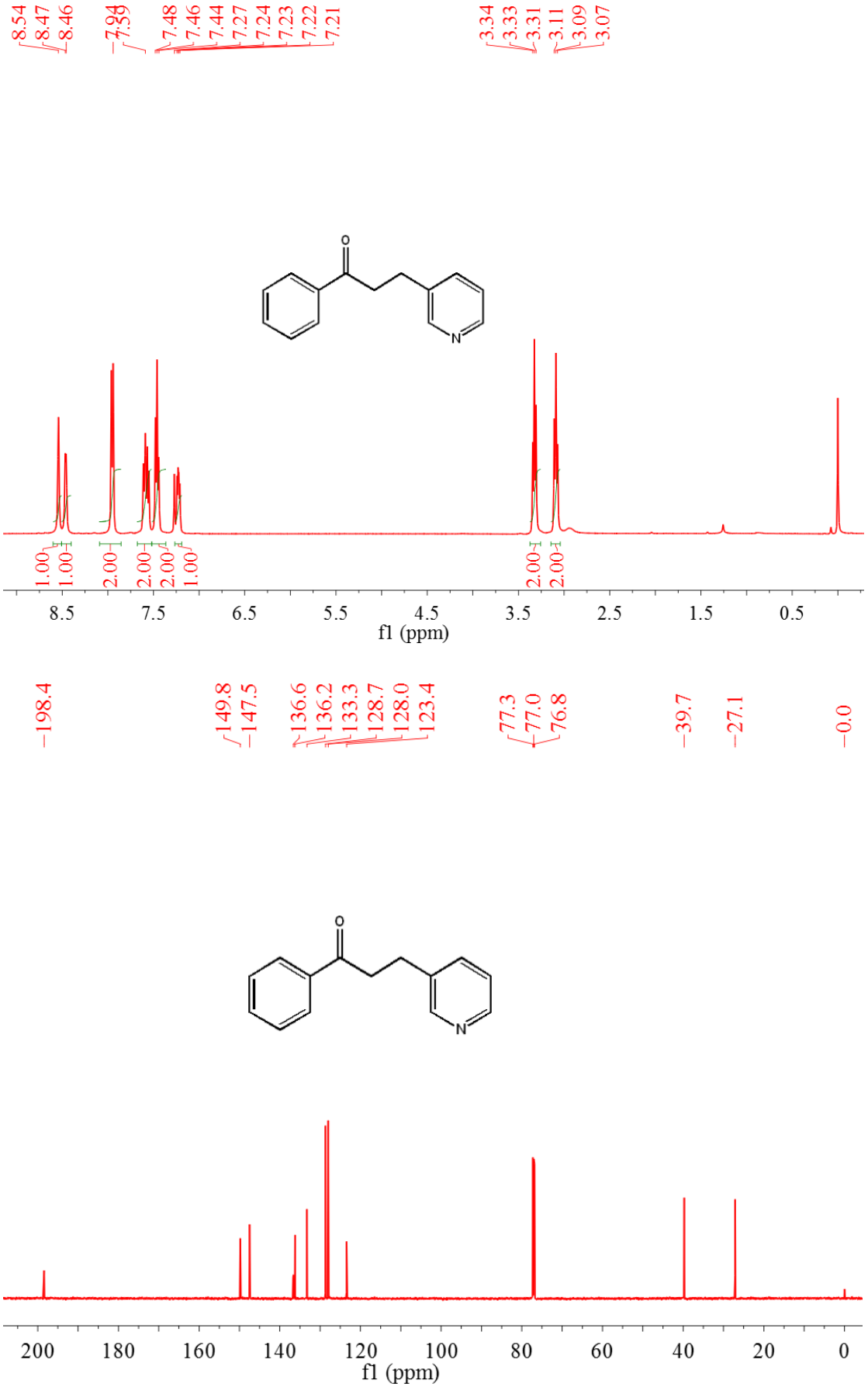


Figure S43. The ^{1}H and ^{13}C NMR spectra for 1-(naphthalen-2-yl)-3-phenylpropan-1-one (***4ca***).

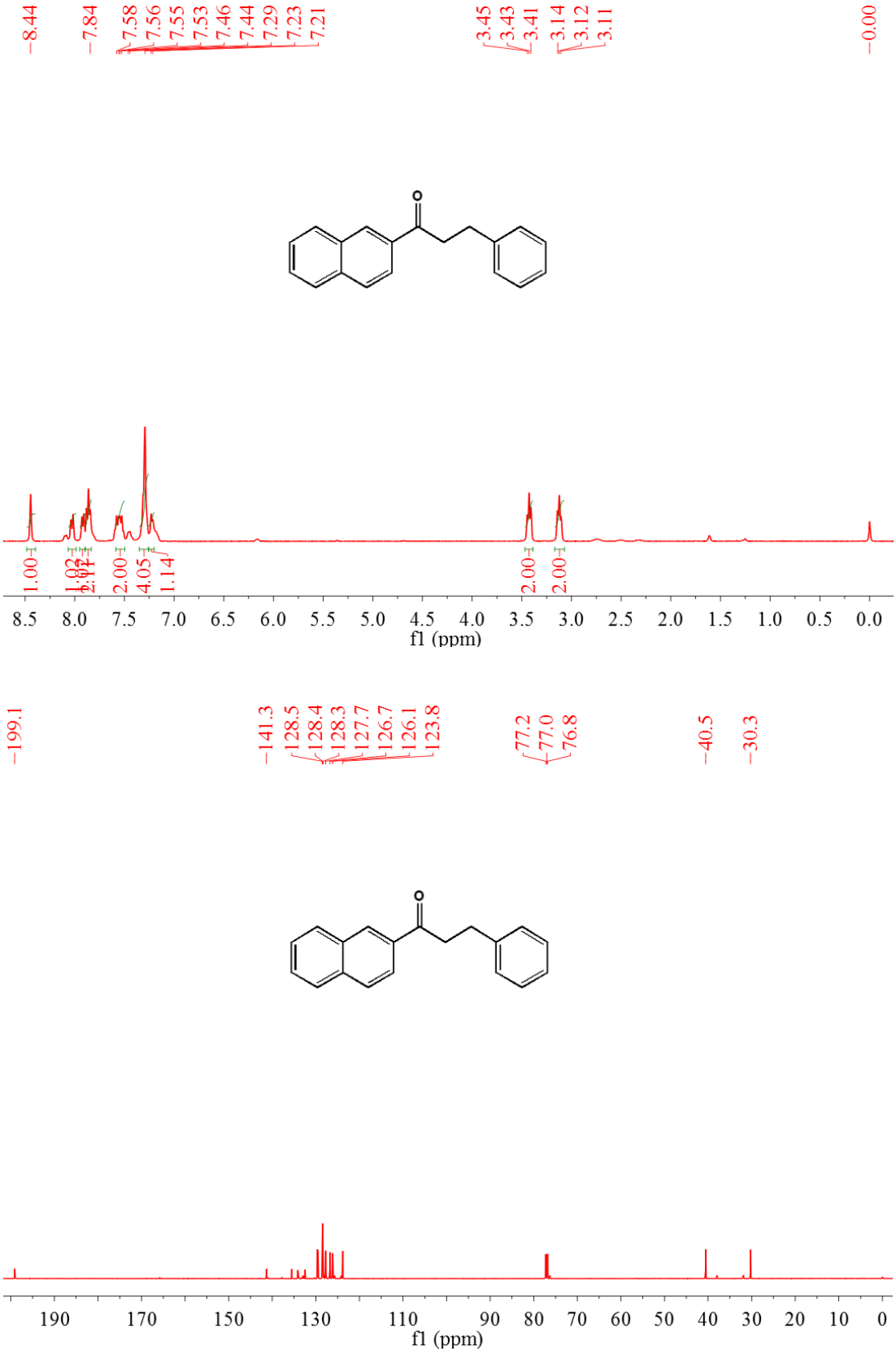


Figure S44. The ^{1}H and ^{13}C NMR spectra for 1-(4-chlorophenyl)-3-phenylpropan-1-one (***4cb***).

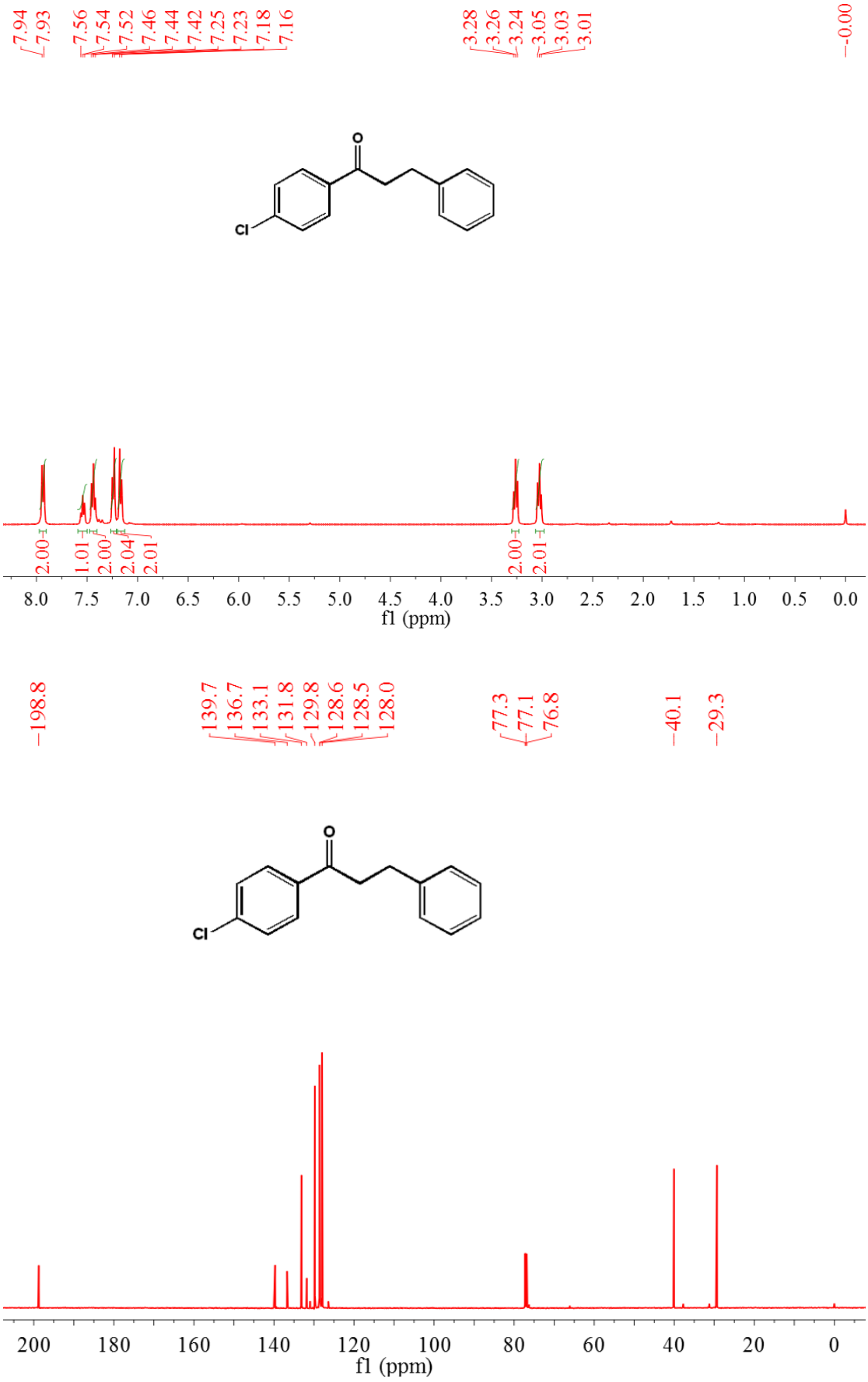


Figure S45. The ^{1}H and ^{13}C NMR spectra for 1-(4-bromophenyl)-3-phenylpropan-1-one (***4cc***).

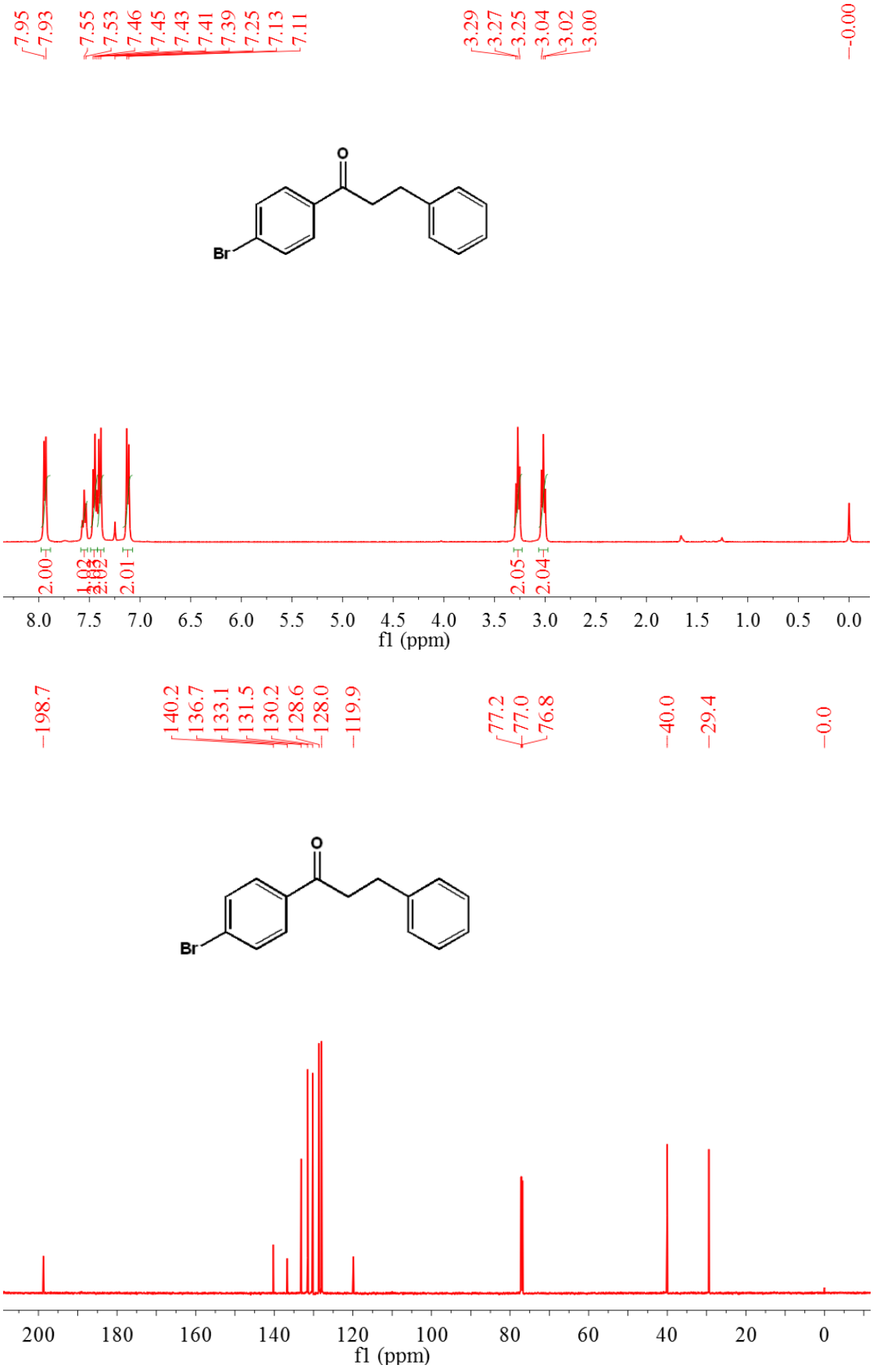


Figure S46. The ^{1}H and ^{13}C NMR spectra for 3-phenyl-1-(*p*-tolyl)propan-1-one (***4cd***).

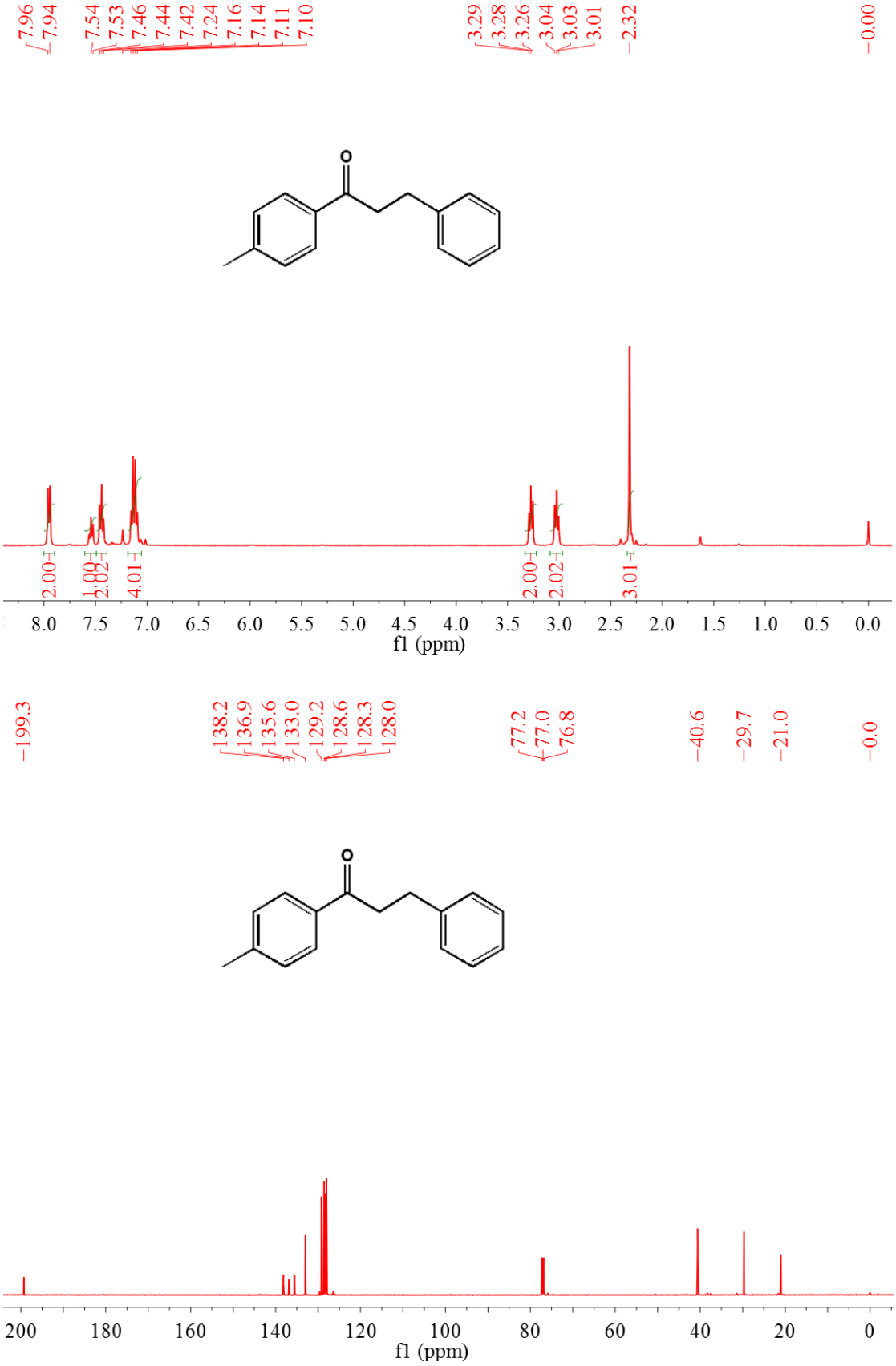
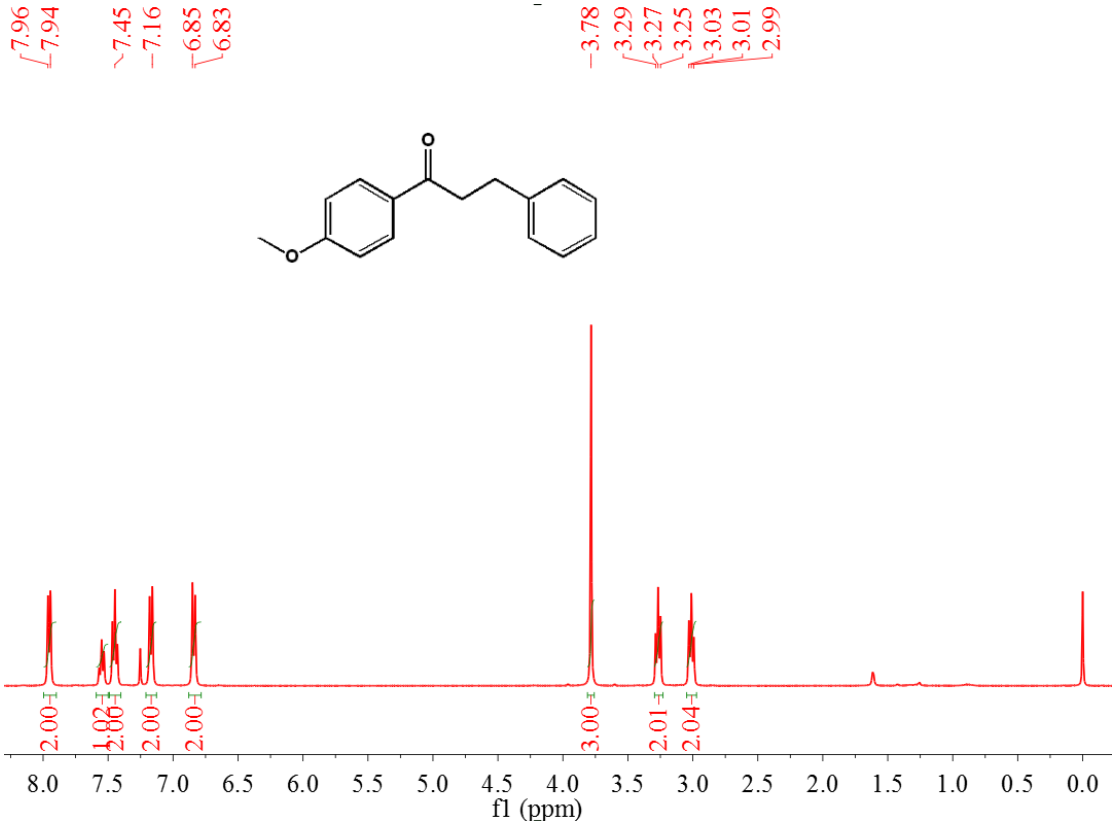


Figure S47. The ^{1}H and ^{13}C NMR spectra for 1-(4-methoxyphenyl)-3-phenylpropan-1-one (***4ce***).



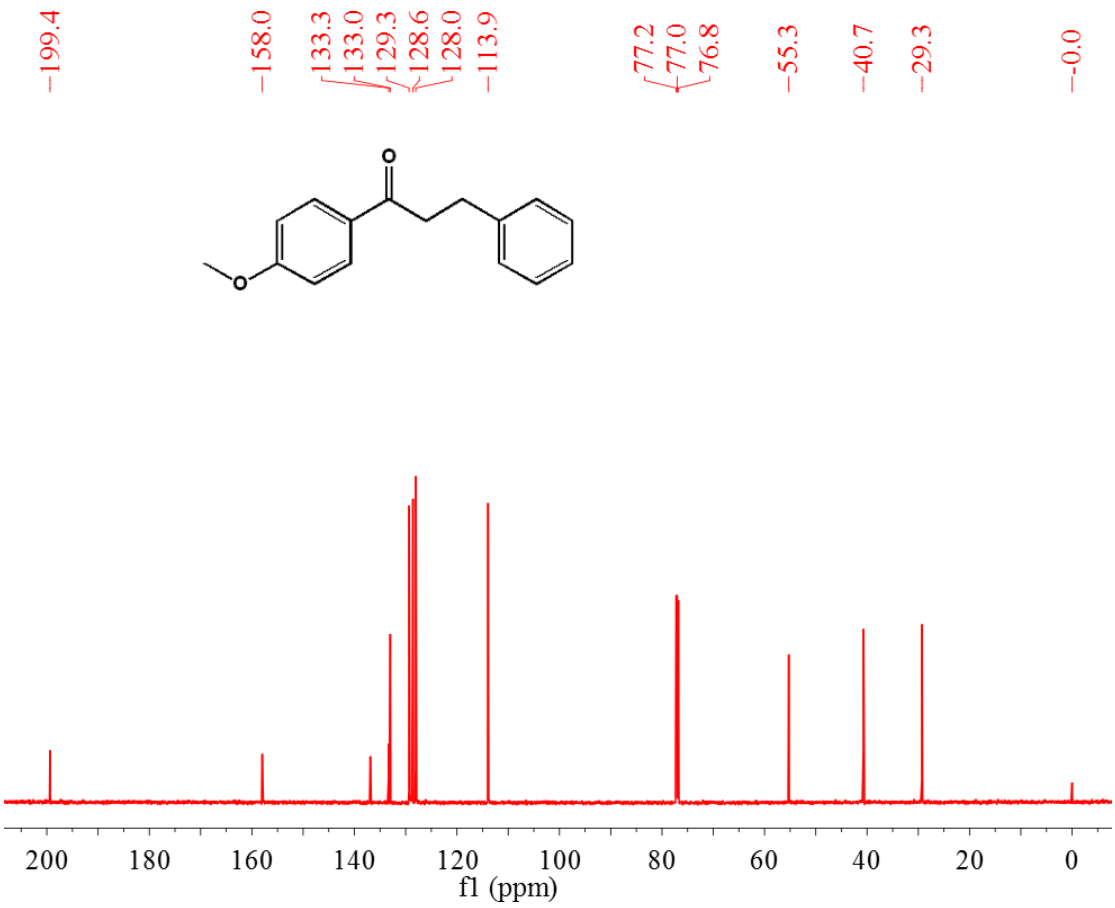


Figure S48. The ^{1}H and ^{13}C NMR spectra for 1-(2-methoxyphenyl)-3-phenylpropan-1-one (***4cf***).

Figure S49. The ^{1}H and ^{13}C NMR spectra for 1-(3-methoxyphenyl)-3-phenylpropan-1-one (***4cg***).

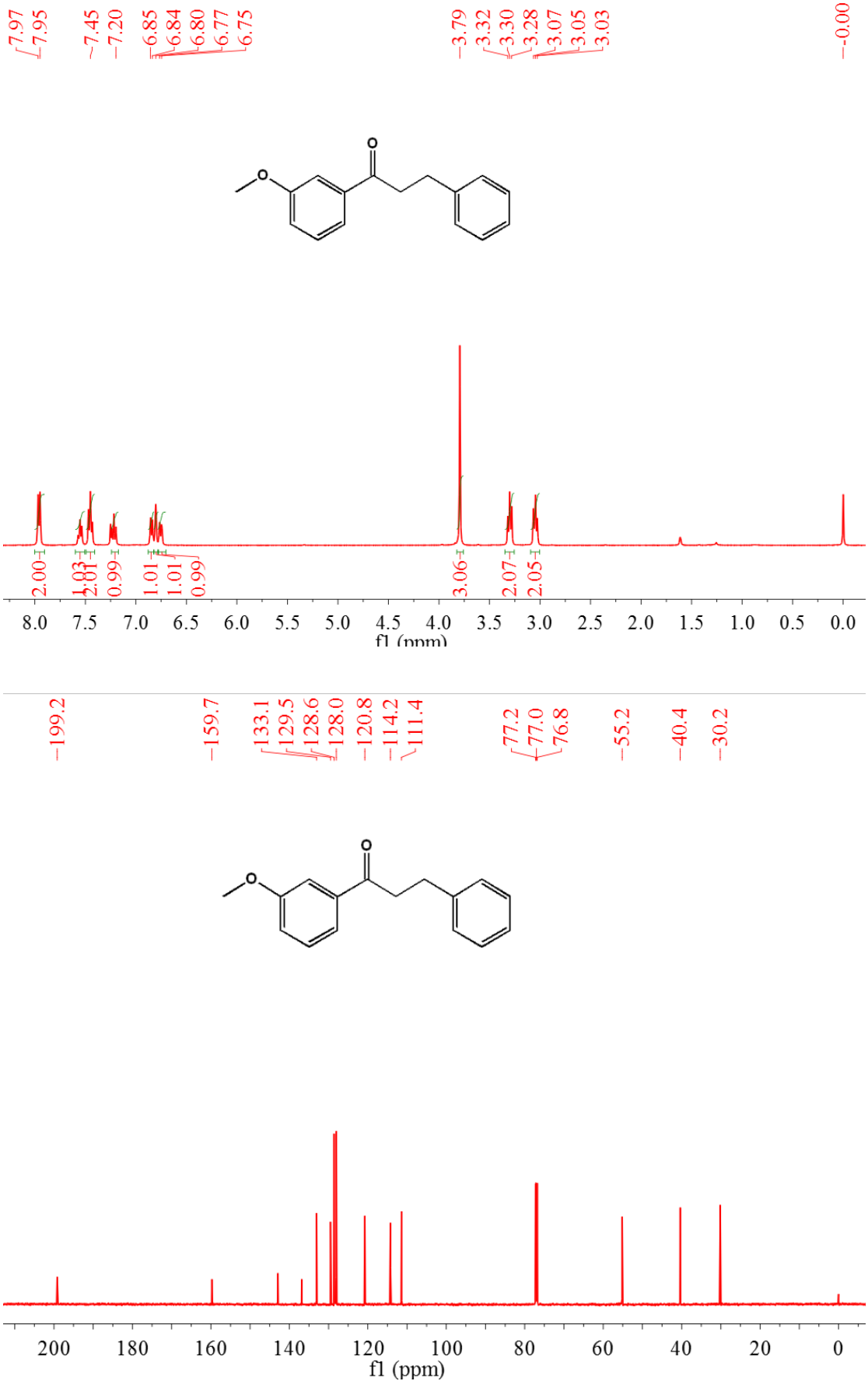


Figure S50. The ^{1}H and ^{13}C NMR spectra for 3-phenyl-1-(thiophen-2-yl)propan-1-one (***4ch***).

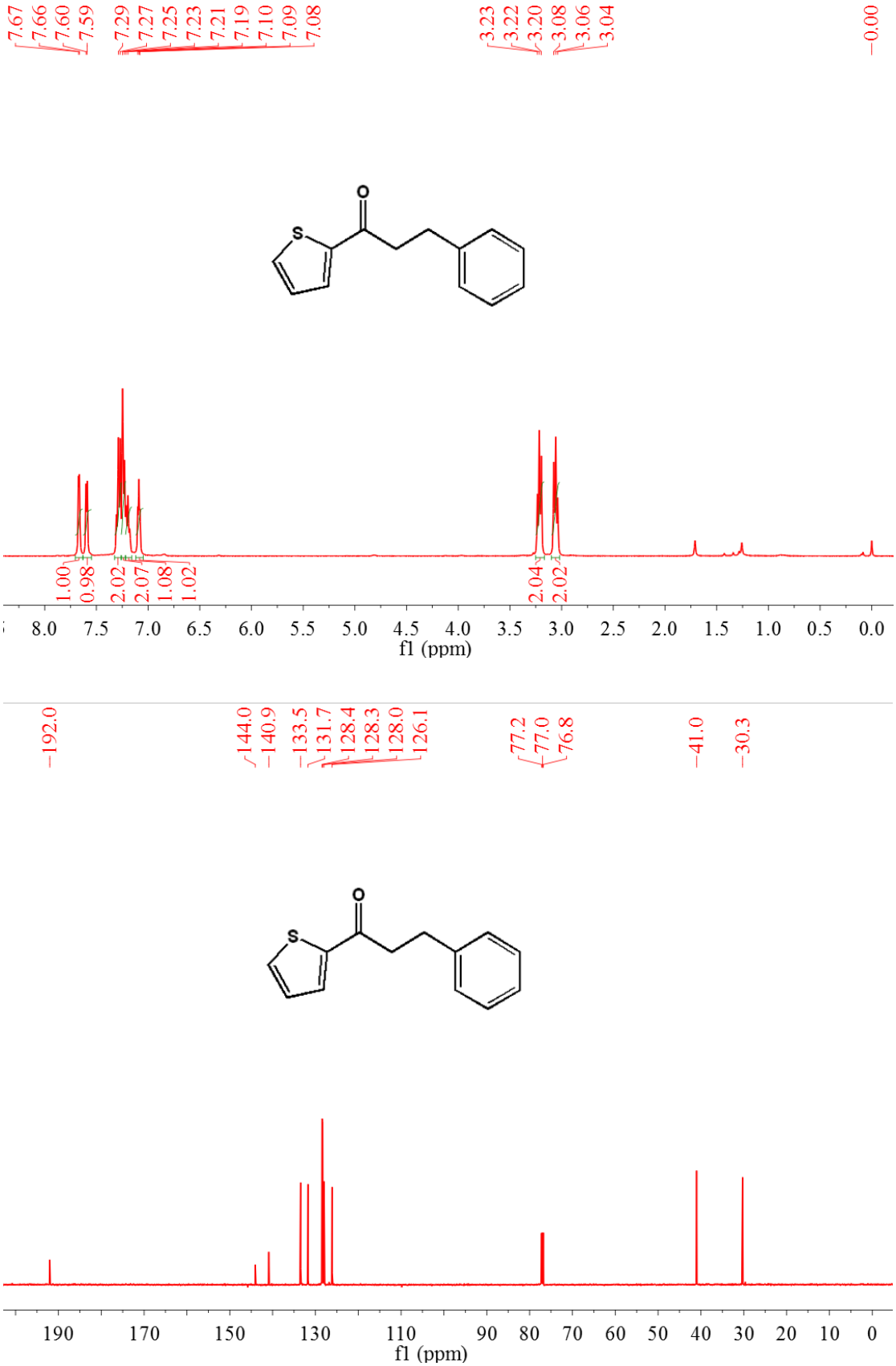


Figure S51. The ^{1}H and ^{13}C NMR spectra for 3-phenyl-1-(pyridin-3-yl)propan-1-one (***4ci***).

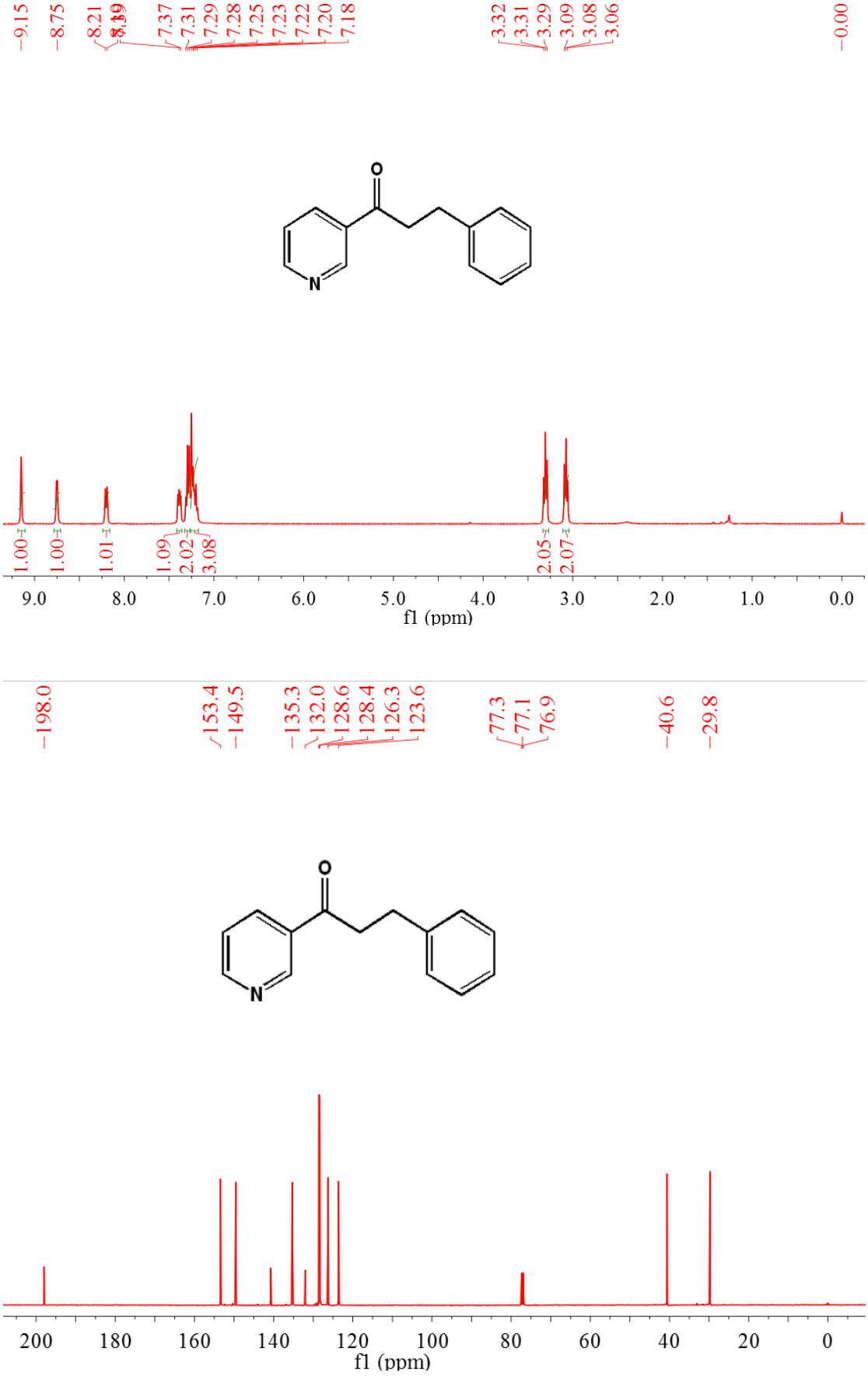


Figure S52. The ^{1}H and ^{13}C NMR spectra for 1-phenyldecan-1-one (***4cj***).

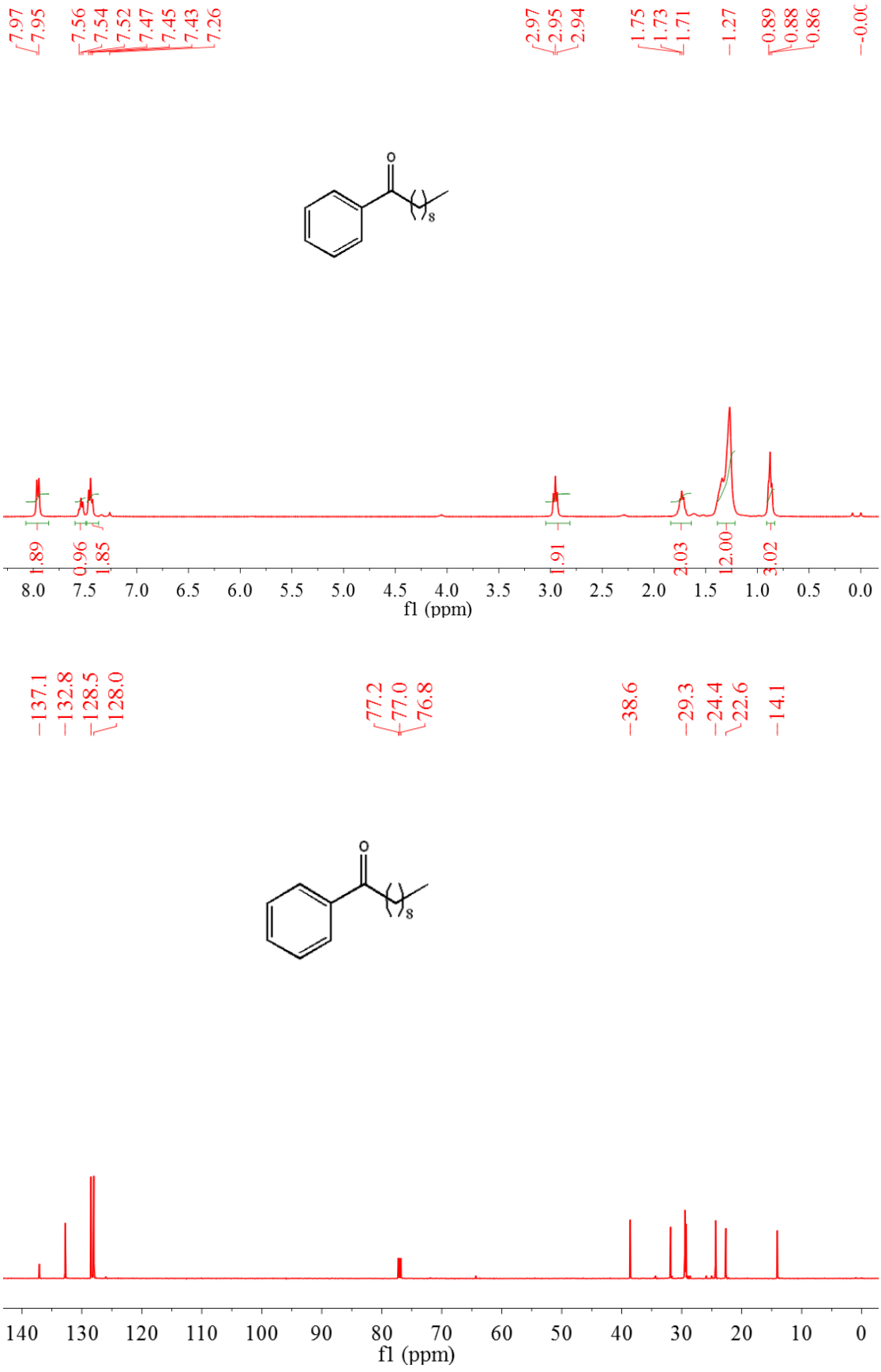
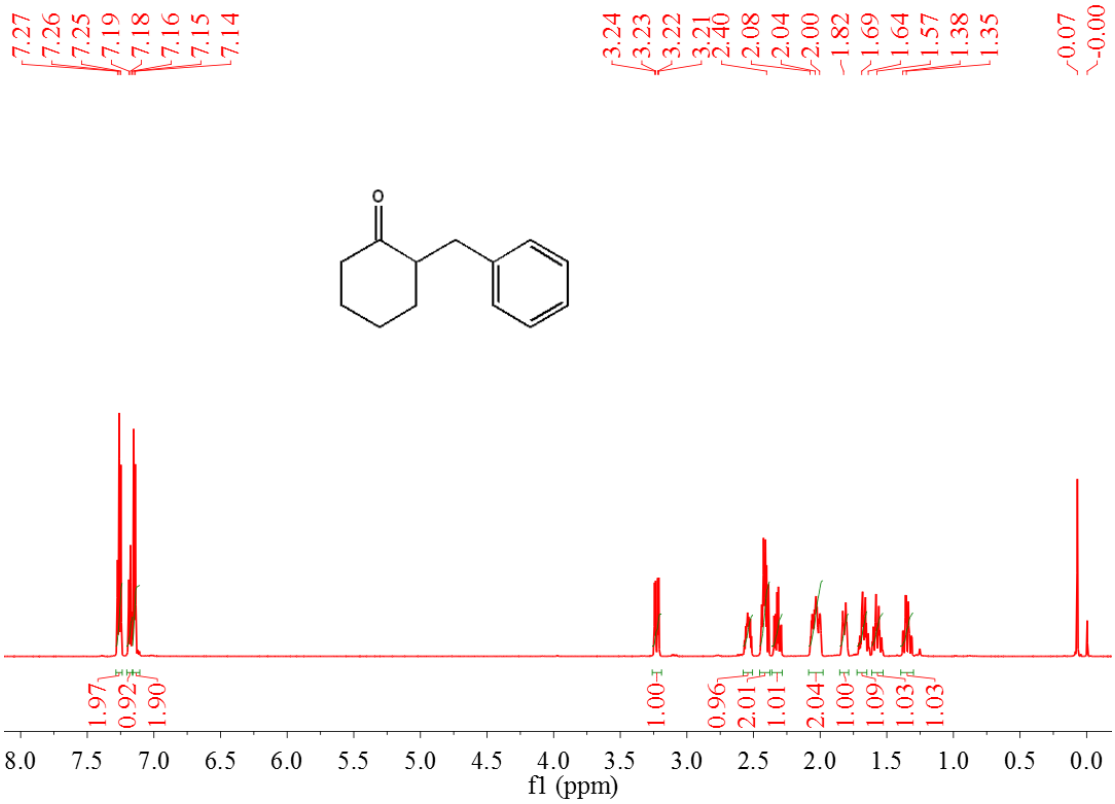


Figure S53. The ^{1}H and ^{13}C NMR spectra for 2-benzylcyclohexan-1-one (***4ck***).



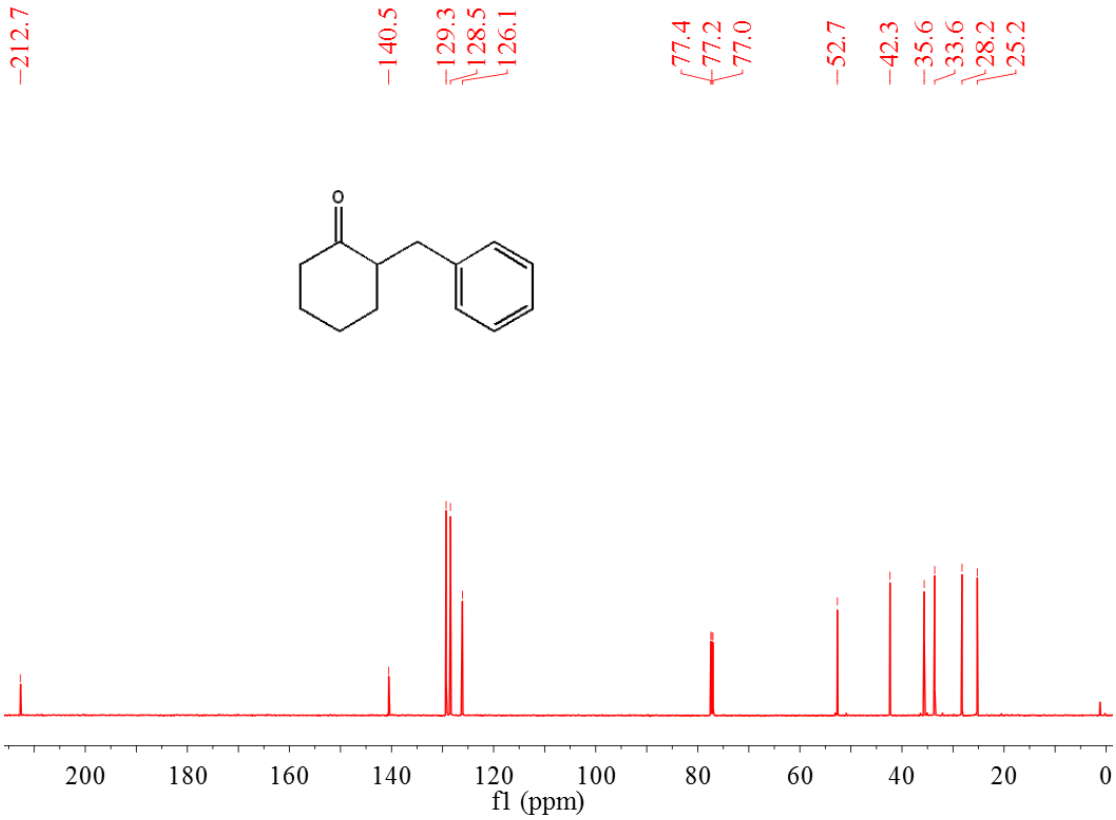


Figure S54. The ^{1}H and ^{13}C NMR spectra for 3-phenylpropanal (***4aa***).