Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Cooperative Mn(I)-complex catalyzed transfer hydrogenation of ketones and imines

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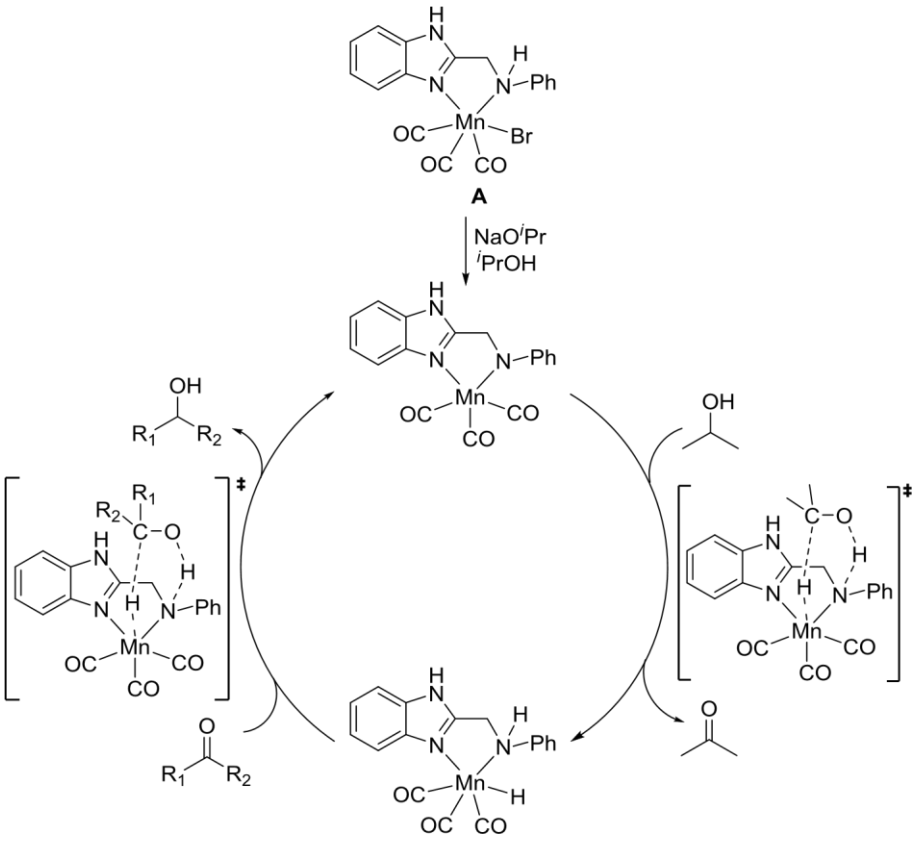
1. Proposed catalytic cycle for the transfer hydrogenation of ketones



2. Characterization of the metal complexes

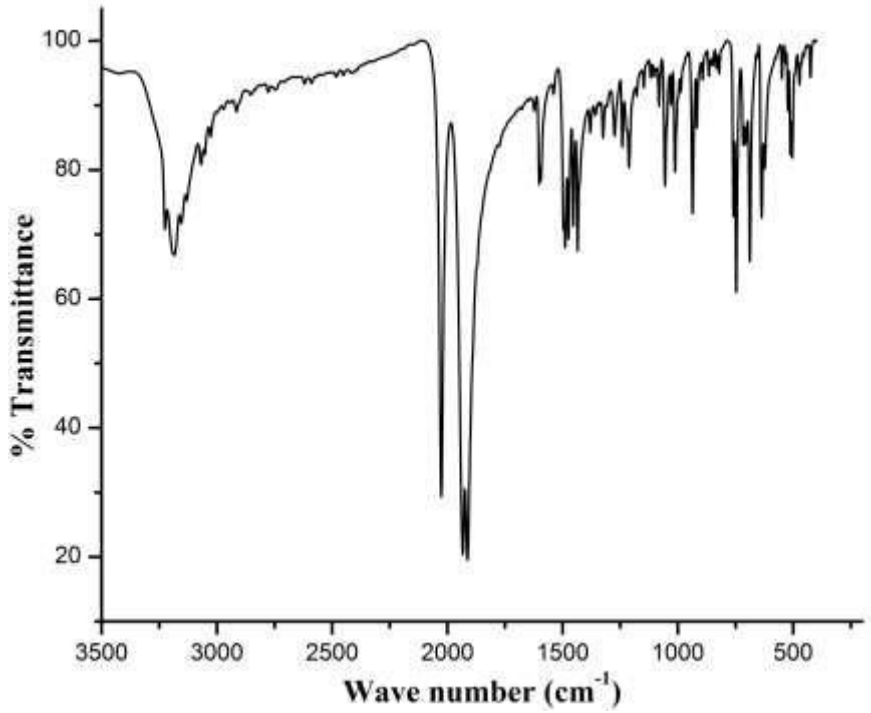


Fig. S1 FT-IR spectra of complex **A.**

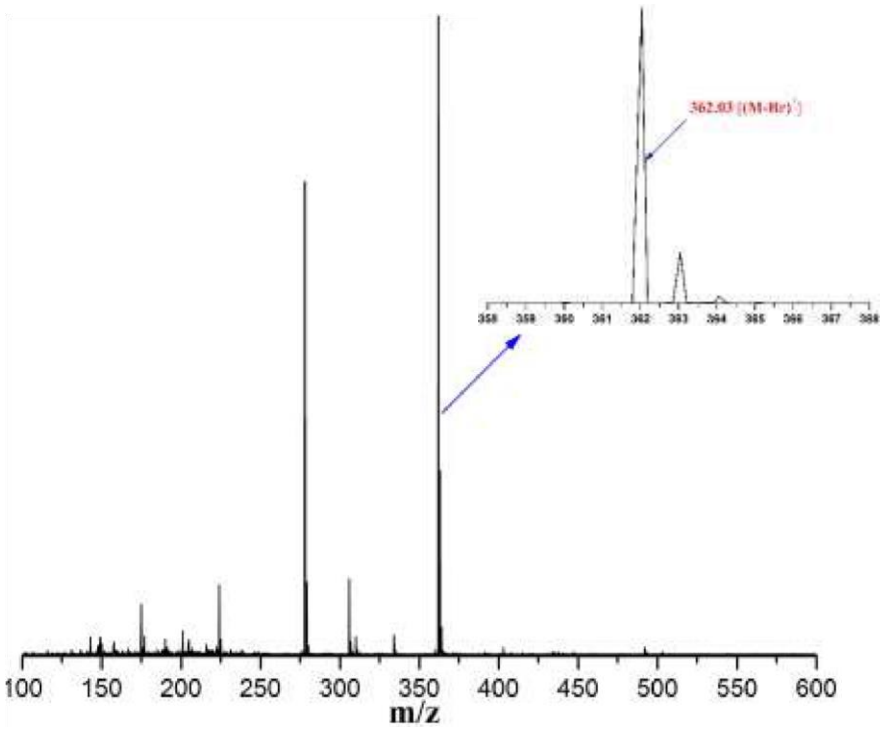


Fig. S2 ESI-MS spectra of complex **A.**

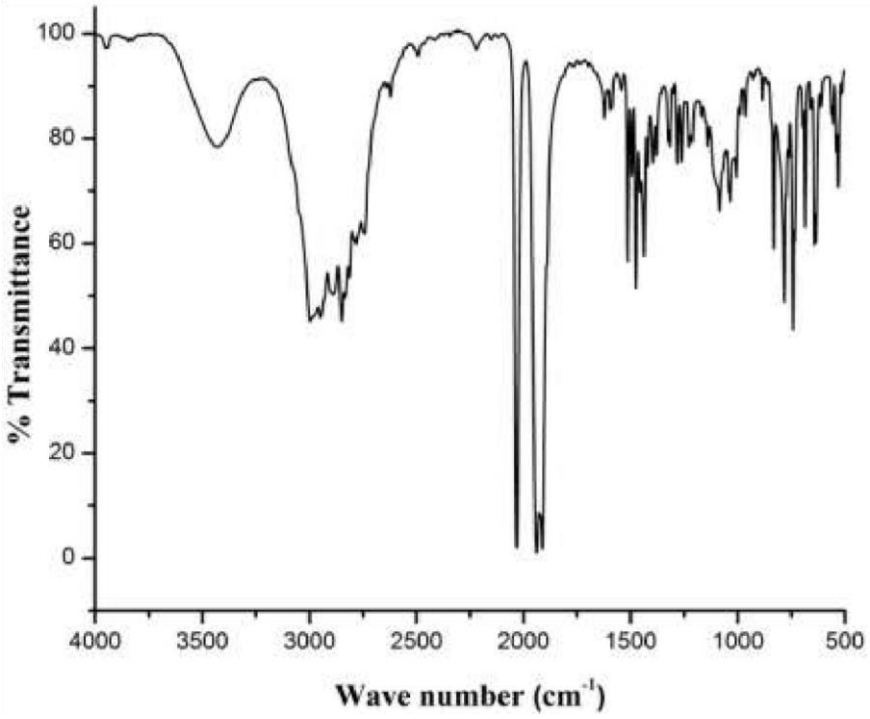


Fig. S3 FT-IR spectra of complex **B.**

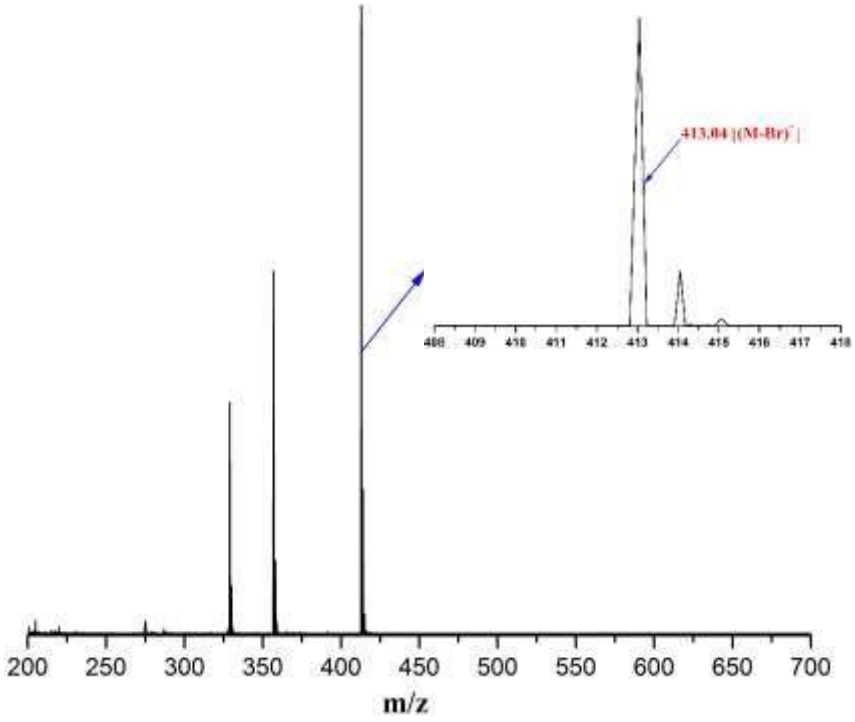


Fig. S4 ESI-MS spectra of complex **B.**

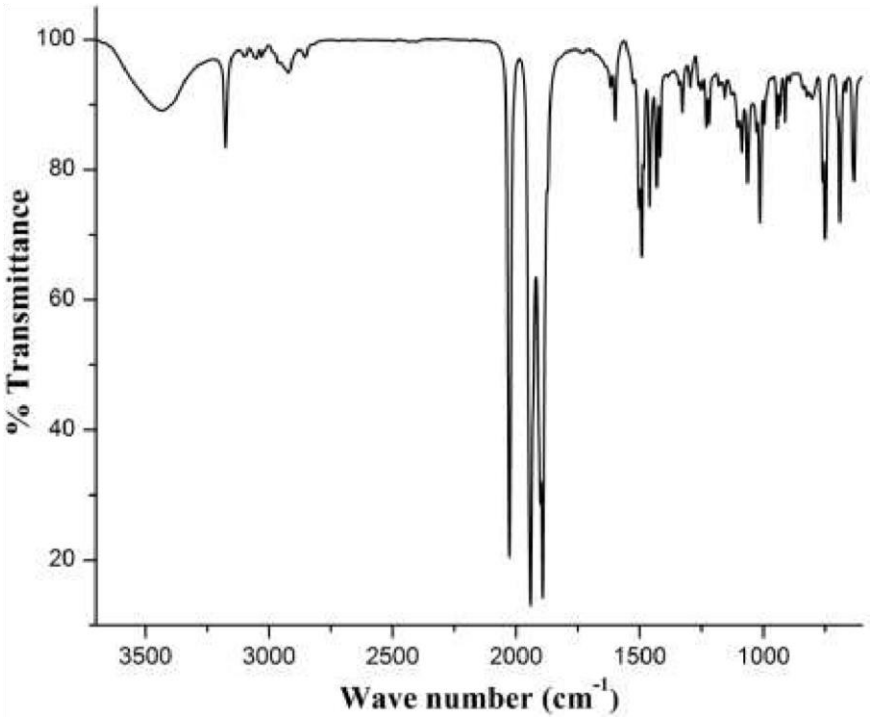


Fig. S5 IR spectra of complex **C.**

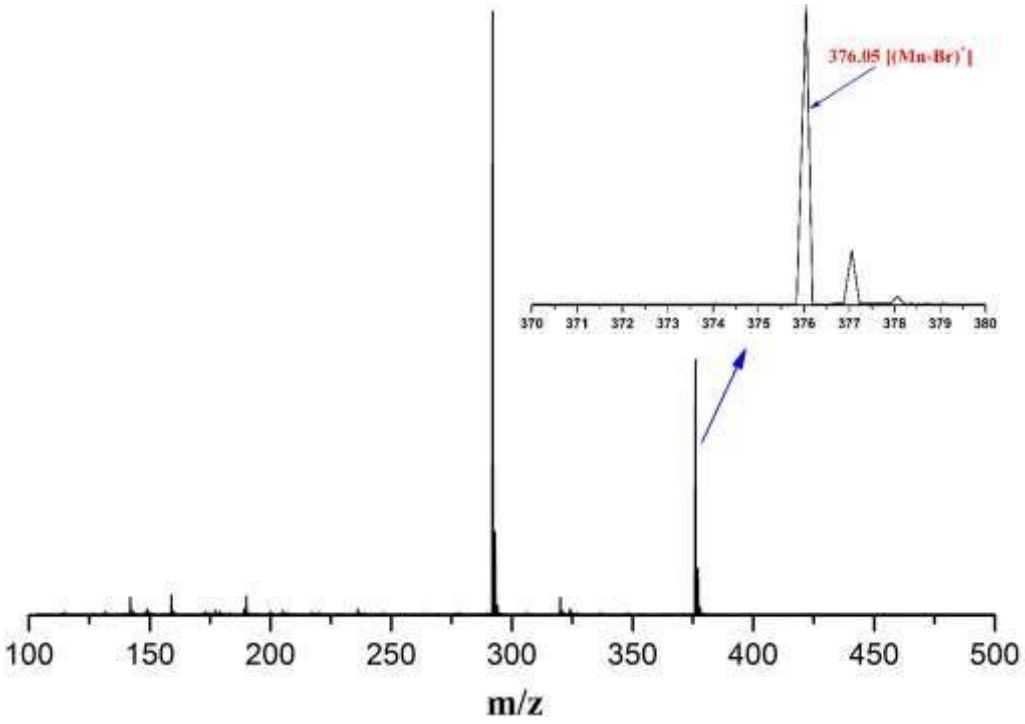


Fig. S6 ESI-MS spectra of complex **C.**

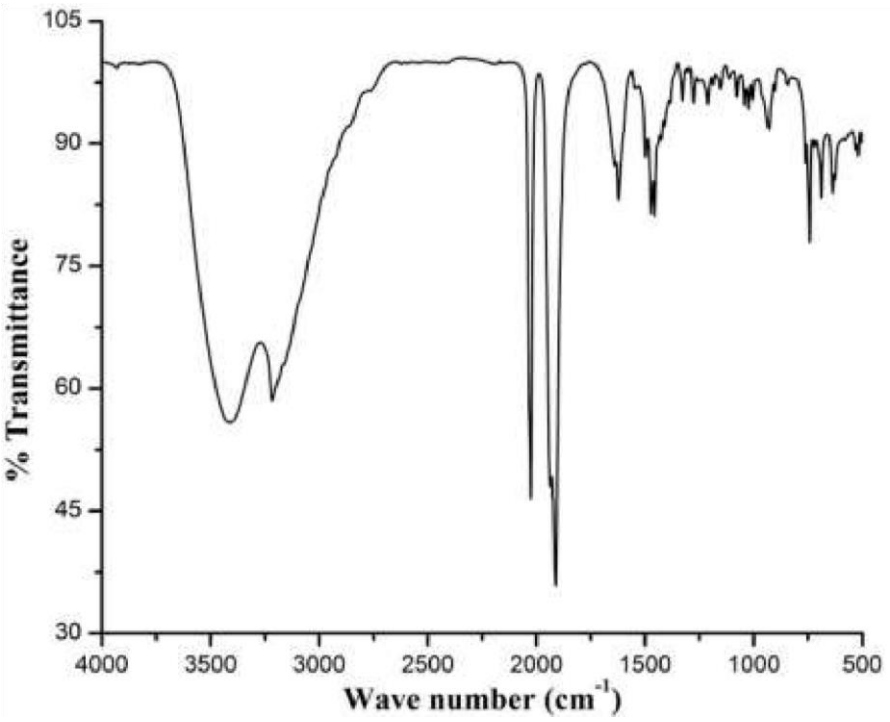


Fig. S7 FT-IR spectra of complex **D.**

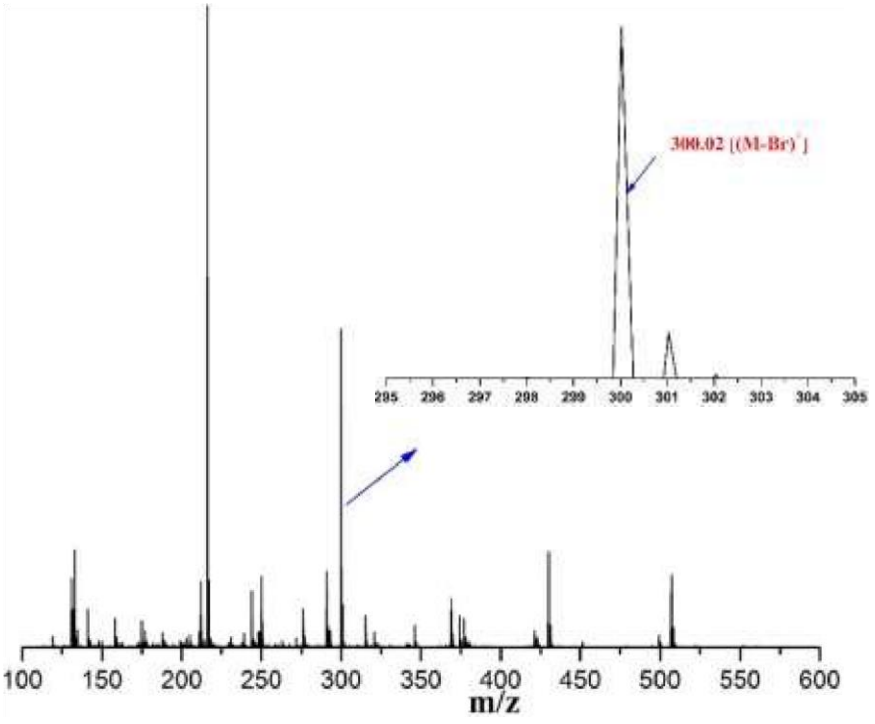


Fig. S8 ESI-MS spectra of complex **D.**

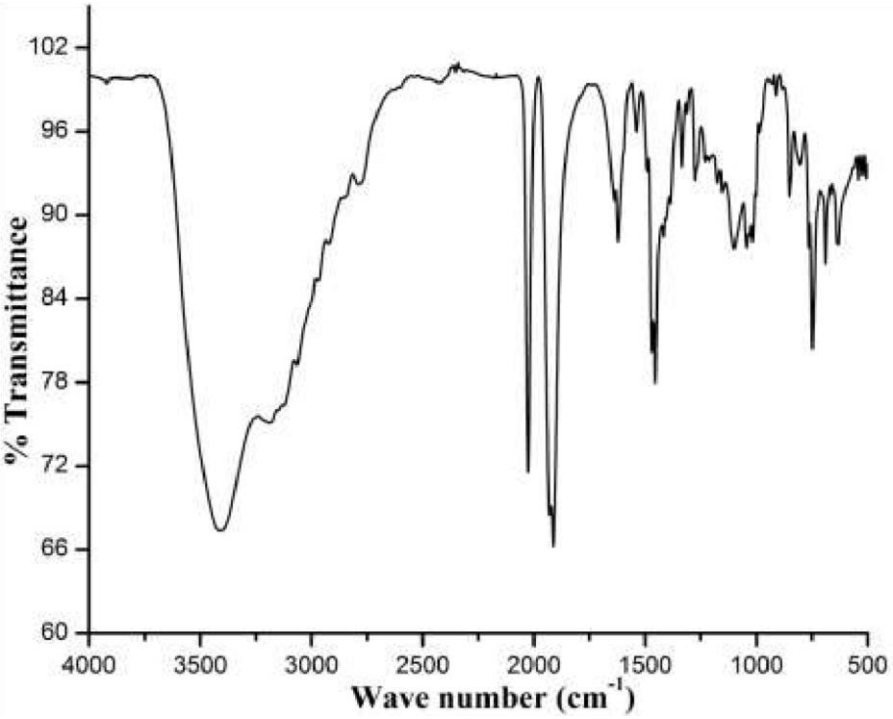


Fig. S9 FT-IR spectra of complex **E.**

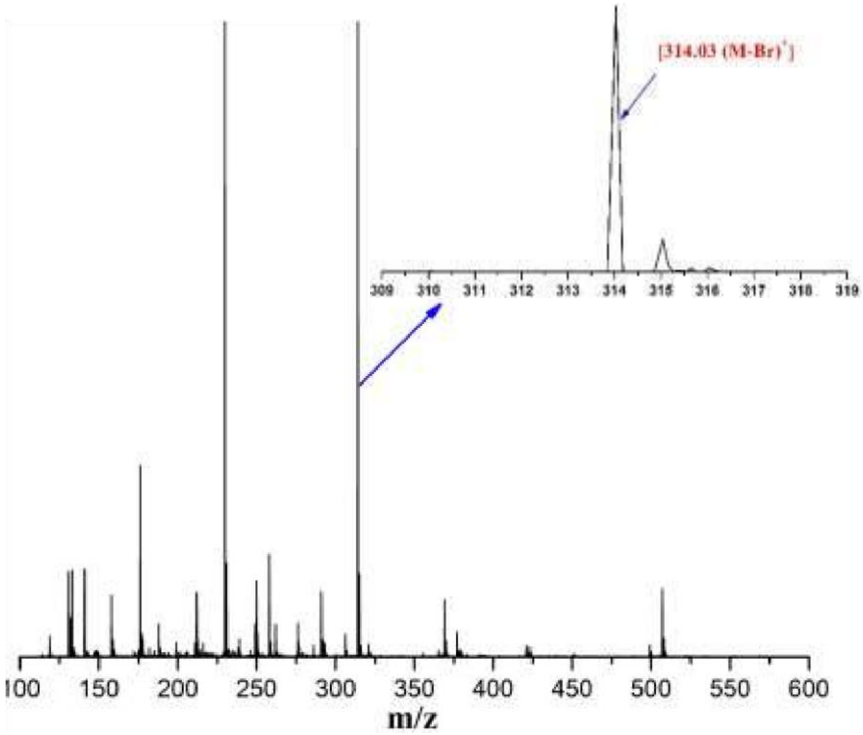


Fig. S10 ESI-MS spectra of complex **E.**

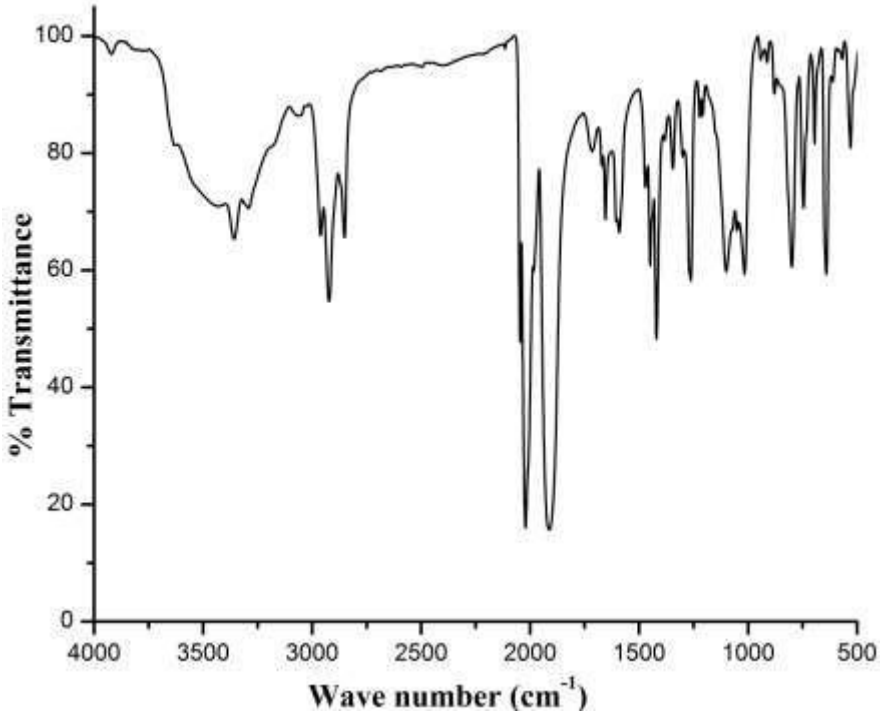


Fig. S11 FT-IR spectra of complex **F.**

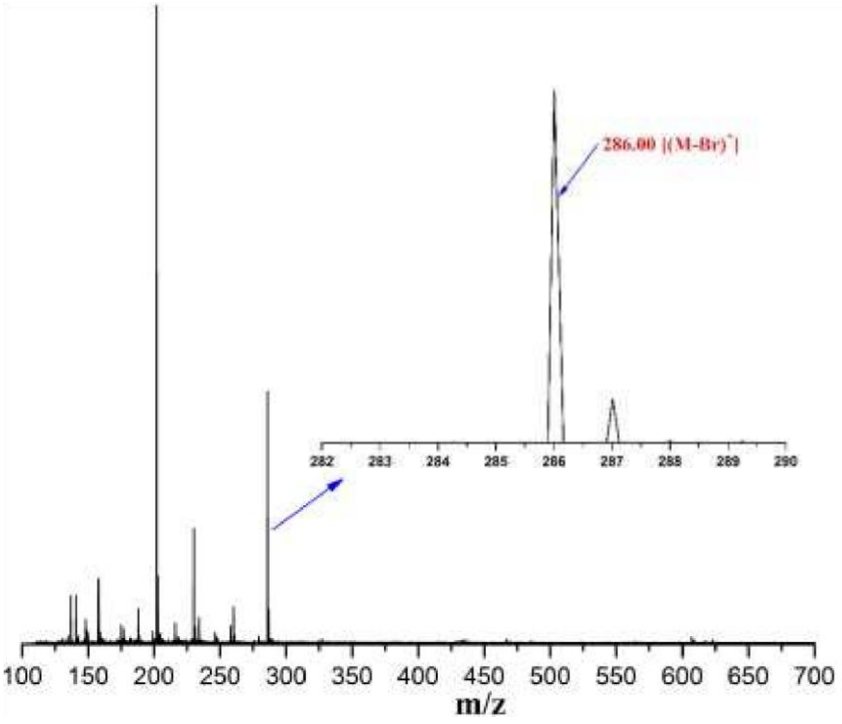
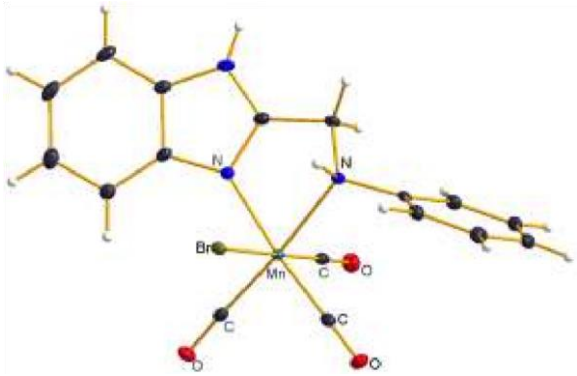


Fig. S12 ESI-MS spectra of complex **F.**

3. X-Ray crystallographic studies

Single crystal of complex **A** was obtained by slow evaporation of a saturated solution of the complex in acetone. Crystals of complex **B** were obtained by vapour diffusion of diethyl ether into a saturated solution of the complex in methanol. Single crystal X-ray data of the complexes were collected at 100 K by using a Bruker SMART APEX II CCD diffractometer and Bruker D8 Quest Single Crystal diffractometer with graphite monochromated MoKα radiation (λ =0.71073 Å). The frames were indexed, integrated and scaled using SMART and SAINT software package and the data were corrected for absorption using the SADABS program. The structures were solved and refined using WINGX, Olex2 and SHELX programs. The crystallographic figures have been generated using Diamond 3 software10 (30% probability thermal ellipsoids). The CCDC number of complexes **A** and **B** are 1878549 and 1883243.

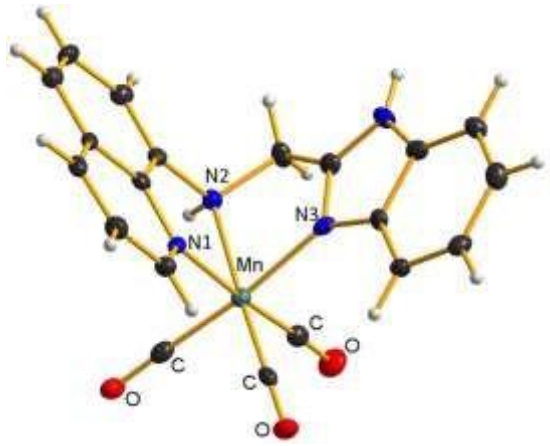


3.1 Fig. S13 Molecular structure of complex **A** (30% thermal ellipsoids).

3.2 Table S1 Crystal data and structure refinement for complex A.

Identification code	complex **A**
Empirical formula	$C_{17}H_{13}BrMnN_3O_3$
Formula weight	442.15
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	7.740(5)
b/Å	10.095(5)
c/Å	12.203(5)
α/°	108.914(5)
β/°	102.309(5)
γ/°	100.172(5)
Volume/Å^3	849.6(8)
Z	2
ρ_{calc}g/cm$_3$	1.728
μ/mm^{-1}	3.150

F(000)	440.0
Crystal size/mm^3	0.01 × 0.01 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.588 to 56.65
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16 Reflections collected 13352
Independent reflections	4206 [R_{int} = 0.0249, R_{sigma} = 0.0261]
Data/restraints/parameters	4206/0/226
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0212, wR_2 = 0.0518
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0541 Largest
diff. peak/hole / e Å^{-3}	0.37/-0.39



3.3 Fig. S14 Molecular structure of complex **B** (30% thermal ellipsoids).

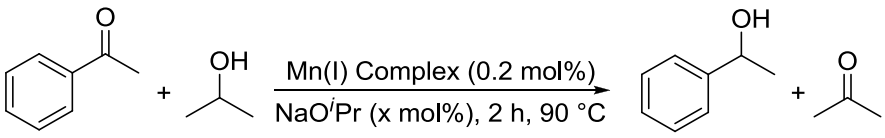
3.4 Table S2 Crystal data and structure refinement for complex B.

Identification code	complex **B**
Empirical formula	$C_{20}H_{14}BrMnN_4O_3$
Formula weight	493.19
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	14.6520(13)
b/Å	29.737(3)
c/Å	10.2242(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4454.7(7)

Z	8
ρ_{calc}g/cm3	1.471
μ/mm^{-1}	2.413
F(000)	1968.0
Crystal size/mm^3	0.01 × 0.01 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.836 to 56.522
Index ranges	-19 ≤ h ≤ 19, -39 ≤ k ≤ 39, -13 ≤ l ≤ 13 Reflections collected 71212
Independent reflections	10992 [R_{int} = 0.1052, R_{sigma} = 0.0728]
Data/restraints/parameters	10992/0/523
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.1121
Final R indexes [all data]	R_1 = 0.0806, wR_2 = 0.1292
Largest diff. peak/hole / e Å^{-3}	1.37/-0.86
Flack parameter	0.048(5)

4. Optimization details

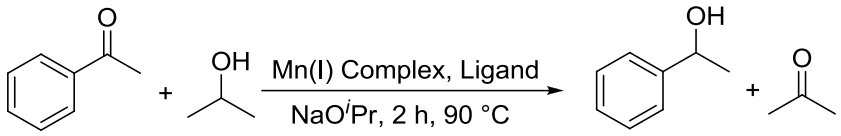
4.1 Table S3 Optimization of the amount of base and catalytic activities of the complexes **A**, **C** and **E** at lower amount of base[a]



Entry	Mn Cat. (0.2 mol%)	NaO^{i}Pr (mol%)	Yield (%)
1	**A**	20	96
2	**A**	10	92
3	**A**	6	88
4	**A**	4	87
5	**A**	3	70
6	**A**	2.4	32
7	**A**	2	< 5
8	**C**	20	52
9	**C**	4	7
10	**E**	4	4
12	-	4	n.d.

[a]Reaction conditions: acetophenone (0.5 mmol), Mn(I) complex (0.2 mol%), NaO^{i}Pr (x mol%), refluxed in ^{i}PrOH (2.5 mL) at 90 °C for 2 h, GC yields (*n*-dodecane was used as an internal standard); n.d. = not detected.

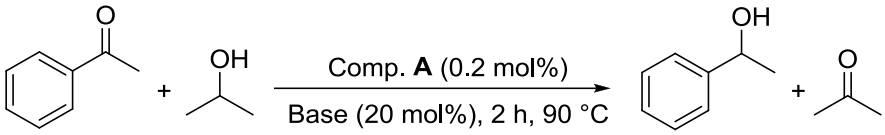
4.2 Table S4 Comparison between activities of isolated metal complexes and [$MnBr(CO)_5$ + L][a]



Entry	Mn(I) Cat. (mol%)	Ligand (mol%)	Yield (%)
1	Comp. **A** (0.2)	-	87
2	$MnBr(CO)_5$ (0.2)	L_1 (0.2)	86
3	Comp. **C** (0.2)	-	49
4	$MnBr(CO)_5$ (0.2)	L_3 (0.2)	47
5	Comp. **F** (0.2)	-	55
6	$MnBr(CO)_5$ (0.2)	L_6 (0.2)	48

[a]Reaction conditions: acetophenone (0.5 mmol), Mn(I) Cat. (0.2 mol%), ligand (0.2 mol%), NaO^{i}Pr (20 mol%), refluxed in ^{i}PrOH (2.5 mL) at 90 °C for 2 h, GC yields (*n*-dodecane was used as an internal standard).

4.3 Table S5 Optimization of different bases to test the role of counter cation in TH of ketones[a]

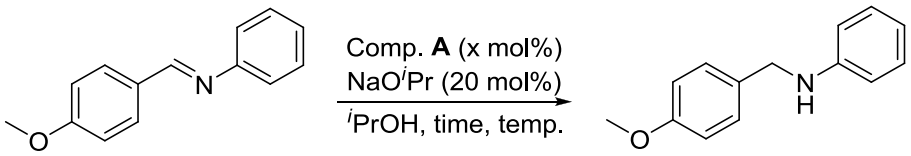


Entry	Comp. **A** (mol%)	Base (20 mol%)	Yield (%)
1	0.2	LiO^{t}Bu	84
2	0.2	NaO^{t}Bu	52
3	0.2	KO^{t}Bu	32
4	0.2	NaO^{i}Pr	96
5[b]	0.2	NaO^{i}Pr	95
6	0.2	$LiOH.H_2O$	41
7	0.2	NaOH	85
8	0.2	KOH	37
9	0.2	Li_2CO_3	n.d.

10	0.2	Na_2CO_3	n.d.
11	0.2	K_2CO_3	17

[a]Reaction conditions: acetophenone (0.5 mmol), complex **A** (0.2 mol%), base (20 mol%), refluxed in ^{i}PrOH (2.5 mL) at 90 °C for 2 h, GC yields (*n*-dodecane was used as an internal standard). [b]In presence of 1.2 equiv. 15-crown-5 ether w.r.to acetophenone; n.d. = not detected.

4.4 Table S6 Optimization of the reaction conditions for the TH of imines[a]



Entry	Comp. **A** (mol%)	Temp. (°C)	Time (h)	Yield (%)
1	10	90	24	73
2	5	100	24	84
3	5	110	24	89
4	5	120	24	100
5	5	120	18	84
6	5	120	16	62
7	5	120	12	60
8	4	120	24	79
9	-	120	24	n.d.
10[b]	5	120	24	55
11[c]	5	120	24	5

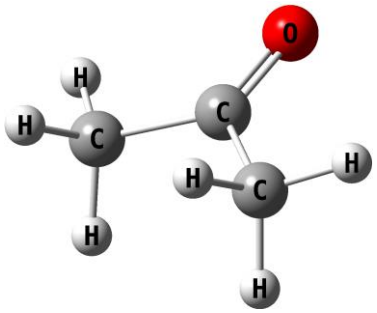
[a]Reaction conditions: substrate (0.5 mmol), Comp. **A** (x mol%), NaO^{i}Pr (20 mol%), refluxed in ^{i}PrOH (2.5 mL) at the specified time and temperature; NMR yields (using 1,3,5-trimethoxybenzene as internal standard); [b]10 mol% NaO^{i}Pr; [c]5 mol% NaO^{i}Pr; n.d. = not detected.

5. Computational studies

All the calculations were performed using the Gaussian 09 package.[1] Full geometry optimization followed by frequency calculations on the stationary points were carried out to ascertain the nature of the stationary points as minima or first order saddle point. Hybrid functional, M062X was used with the LANL2DZ basis set[2] for Mn and 6-31G** basis set[3-5] for non-metal elements. The transition states (TS) were further confirmed by performing intrinsic reaction coordinate (IRC) calculation using same method. Solvent effect was incorporated using the polarizable continuum model (PCM) with isopropanol as solvent.[6]

5.1 Cartesian coordinates and statistical thermodynamic analysis data

Acetone



SCF Done for solvent	: -193.069655
Zero-point correction	: 0.084592
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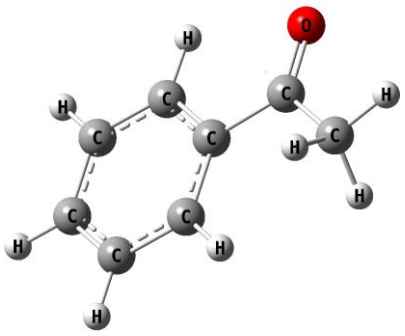
Total Thermal Energy	: -192.972308
Total Thermal Free Energy	: -193.015726

Coordinate

Atom	X	Y	Z
C	0.00014200	0.18637300	0.00000000
C	0.00014200	-0.61331400	-1.28689400
H	-0.88038300	-1.26205700	-1.32681400
H	0.00058100	0.06335600	-2.14052000
H	0.88028600	-1.26263700	-1.32657300
C	0.00014200	-0.61331400	1.28689400
H	0.88028600	-1.26263700	1.32657300

H	0.00058100	0.06335600	2.14052000
H	-0.88038300	-1.26205700	1.32681400
O	-0.00044100	1.39552500	0.00000000

Acetophenone



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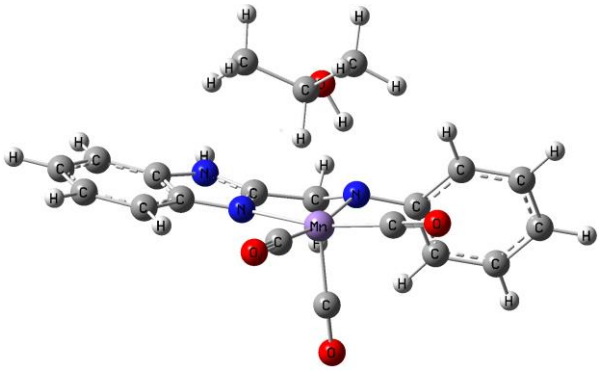
Total Thermal Energy	: -384.58189
Total Thermal Free Energy	: -384.63469

Coordinate

Atom	X	Y	Z
C	1.69496900	0.20502300	0.00007700
C	2.54614600	-1.04722200	-0.00001300
H	3.59485700	-0.75420700	0.00021500
H	2.33316800	-1.65752600	0.88269000
H	2.33339300	-1.65693600	-0.88319400
O	2.20474700	1.30601900	0.00000200
C	0.20186800	0.05609100	-0.00001200
C	-0.42596100	-1.19149300	0.00002200
C	-0.57397300	1.21909100	-0.00003200

C	-1.81507800	-1.27515600	-0.00000600
H	0.16400200	-2.10278300	0.00003000
C	-1.95968800	1.13532800	-0.00000400
H	-0.06163300	2.17558200	-0.00000100
C	-2.58147100	-0.11283600	0.00000500
H	-2.29916800	-2.24632200	-0.00003400
H	-2.55853800	2.04029400	0.00001600
H	-3.66492900	-0.17921200	0.00004200

I1_out



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Total Thermal Energy	: -1342.316851
Total Thermal Free Energy	: -1342.433285

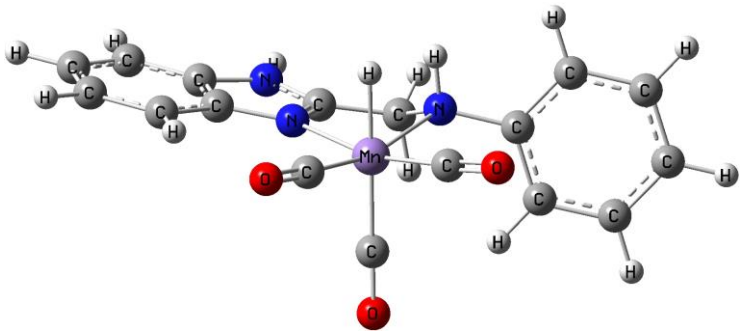
Coordinate

Atom	X	Y	Z
C	-2.73663800	-0.55748600	0.32711200

C	-3.20150600	-1.61193300	-0.47985000
C	-4.55617700	-1.83588300	-0.71383400
C	-5.44487600	-0.96251800	-0.10476200
C	-4.99545900	0.09367700	0.70660900
C	-3.64531500	0.31266800	0.93405000
C	-0.98964800	-1.60480400	-0.40738400
H	-4.89922200	-2.65045900	-1.34221500
H	-6.50994300	-1.09729400	-0.25917100
H	-5.72429000	0.75443200	1.16324900
H	-3.30682900	1.13100000	1.55862000
H	-2.01172900	-3.02705500	-1.57218700
C	0.44822500	-1.94791200	-0.58287500
H	0.68760200	-2.71686200	0.17186600
H	0.61063600	-2.41405000	-1.56812500
N	1.19295500	-0.70799900	-0.42772400
H	0.63712200	0.01677000	-1.83768600
C	2.59601500	-0.88301800	-0.42064400
C	3.38810300	0.03670600	-1.12479000
C	3.24995800	-1.91080000	0.27711400
C	4.77473600	-0.04805500	-1.11172700
H	2.88441500	0.81159000	-1.69727700
C	4.63883700	-2.00004000	0.27819700
H	2.67271100	-2.63386100	0.84608900
C	5.41179000	-1.06965900	-0.41044800
H	5.35979000	0.68044100	-1.66490800
H	5.12031800	-2.80152200	0.83080700
H	6.49408700	-1.14218600	-0.40487900
N	-1.34726200	-0.58755200	0.34532400
N	-2.05798400	-2.25995400	-0.92031200

Mn	0.28127500	0.60851200	0.86156000
C	1.79914100	1.71927500	0.94498300
C	-0.73739600	1.86883800	1.77918000
C	0.75702300	-0.33240000	2.36118100
O	2.69749900	2.41799000	0.98836700
O	1.06770600	-1.01590400	3.22129800
O	-1.35148500	2.64151600	2.35732700
C	-0.46560600	1.59929800	-1.93881700
H	-0.44107000	1.52822000	-0.81702300
O	0.01047900	0.42328900	-2.51227400
C	0.39246100	2.80368200	-2.31504300
H	0.01058500	3.72464900	-1.86298000
H	1.42529200	2.65815400	-1.98399000
H	0.39677000	2.91915300	-3.40277600
C	-1.92889200	1.78468000	-2.31097500
H	-2.50632400	0.90692100	-2.00820900
H	-2.35467900	2.67234800	-1.83394600
H	-2.01335500	1.89432600	-3.39667200

I2_out



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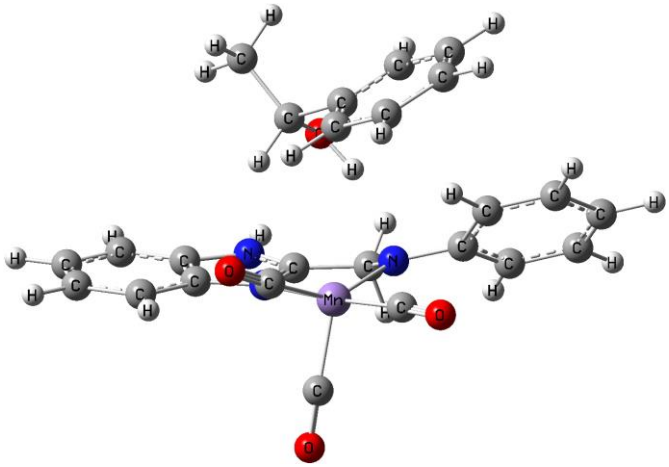
Total Electronic Energy : -1149.33630
Total Thermal Energy : -1149.306303
Total Thermal Free Energy : -1149.402488

Coordinate

Atom	X	Y	Z
C	-2.79878300	-0.32839900	-0.10208500
C	-3.23737400	-1.66852800	0.00461800
C	-4.58630900	-2.02378000	-0.02700200
C	-5.50055200	-0.98477700	-0.17157700
C	-5.07885600	0.35538700	-0.28144300
C	-3.73295800	0.70417600	-0.25000100
C	-1.02357300	-1.55099800	0.09715900
H	-4.90923900	-3.05685200	0.05629500
H	-6.56161000	-1.21255600	-0.20120500
H	-5.82528900	1.13536700	-0.39438100
H	-3.41458300	1.73526800	-0.33762300
H	-2.01540500	-3.42426500	0.21277500
C	0.42035100	-1.90963900	0.21143400
H	0.71749200	-1.93819000	1.26550100
H	0.62850800	-2.90189400	-0.21549500
N	1.19376300	-0.83806700	-0.45653800
H	0.98585300	-0.85915000	-1.45213600
C	2.62391500	-0.94766200	-0.27668000
C	3.44593700	-1.17186300	-1.38400200
C	3.19000700	-0.81478600	0.99595400
C	4.82971900	-1.25876000	-1.22179900
H	3.00645800	-1.26668000	-2.37415300

C	4.57091000	-0.92014700	1.15253400
H	2.55982400	-0.59801000	1.85205900
C	5.39615800	-1.14114400	0.04701000
H	5.46070900	-1.42238700	-2.09022800
H	5.00397300	-0.81148300	2.14240400
H	6.47194400	-1.21220700	0.17415200
N	-1.40644800	-0.29996100	-0.03714200
N	-2.07669800	-2.42192200	0.12648500
Mn	0.15441200	1.09611900	-0.14912100
C	1.60429900	2.06057000	-0.58603900
C	-0.87911100	2.54429900	-0.26155500
C	0.39733100	1.18553400	1.65289700
O	2.53553900	2.65870500	-0.92904000
O	0.56297700	1.30976200	2.79697400
O	-1.56454500	3.47271600	-0.39335600
H	-0.06166000	1.04336400	-1.73273400

I3_out



SCF Done : -1534.398756

SCF Done for solvent : -1534.414070
Zero-point correction : 0.427914
Total Electronic Energy : -1533.970842
Total Thermal Energy : -1533.926863
Total Thermal Free Energy : -1534.057252

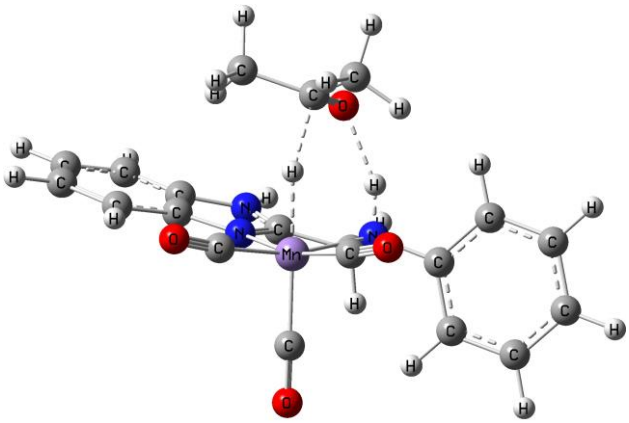
Coordinate

Atom	X	Y	Z
C	-3.17241400	-0.21869900	-0.12584400
C	-3.68319300	-0.38209700	-1.42650300
C	-4.95917700	0.04445300	-1.78579900
C	-5.71793700	0.64327300	-0.79062600
C	-5.22270800	0.80549700	0.51501200
C	-3.95109700	0.37890100	0.86712700
C	-1.62557600	-1.18004500	-1.29161300
H	-5.34276800	-0.08402100	-2.79198400
H	-6.71761400	0.99248200	-1.02542000
H	-5.85221100	1.27523600	1.26291800
H	-3.57048600	0.50384200	1.87464000
H	-2.65890800	-1.20584400	-3.12370300
C	-0.30090500	-1.78651200	-1.59285200
H	-0.41905600	-2.88302900	-1.59532800
H	0.02276100	-1.50071900	-2.60718800
N	0.61404700	-1.31124300	-0.56305800
H	0.36763000	0.45036700	-1.45370300
C	1.96424300	-1.59503900	-0.83779500
C	2.96124700	-0.74242900	-0.32924600
C	2.37920900	-2.67654200	-1.63336500
C	4.30626700	-0.98772300	-0.56531800
H	2.66319900	0.14380600	0.22510900

C	3.73069500	-2.91309400	-1.87125600
H	1.64621600	-3.35596600	-2.05587200
C	4.70583800	-2.07870900	-1.33612500
H	5.04414500	-0.30169500	-0.15943600
H	4.01892600	-3.76448700	-2.48086000
H	5.75710600	-2.26618300	-1.52665700
N	-1.88270300	-0.73087800	-0.08626000
N	-2.67266800	-1.01506000	-2.13442000
Mn	-0.21814600	-0.85053700	1.16244300
C	1.38302600	-0.95693100	2.15322900
C	-0.85414100	0.48124000	2.27039600
C	-0.99215900	-2.16256800	2.18646600
O	2.30055700	-1.02584100	2.82408400
O	-1.48352300	-3.03471100	2.73814600
O	-1.24258700	1.34035300	2.92190400
C	-0.14982000	2.22480500	-0.93597800
H	-0.81875200	1.92295400	-0.10896600
O	-0.08098200	1.19436900	-1.90157000
C	-0.74312900	3.44875700	-1.61753900
H	-1.72551200	3.20325900	-2.02925400
H	-0.84776700	4.27256100	-0.90737400
H	-0.08926600	3.76859600	-2.43386000
C	1.22654100	2.50036700	-0.35628300
C	2.34080400	2.49334200	-1.19900500
C	1.40930900	2.73458700	1.00737800
C	3.61617600	2.70506600	-0.68528700
H	2.19594500	2.28391400	-2.25476000
C	2.68709800	2.93628700	1.52656000
H	0.54641800	2.75407000	1.66832900

C	3.79372200	2.91792700	0.68081800
H	4.47579900	2.68493600	-1.34802000
H	2.81813800	3.10375200	2.59118500
H	4.78972500	3.06781800	1.08548600

TS1_out



SCF Done	: -1342.704021
SCF Done for solvent	: -1342.719534
Zero-point correction	: 0.368827
Total Electronic Energy	: -1342.335194
Total Thermal Energy	: - 1342.296431
Total Thermal Free Energy	: -1342.414757

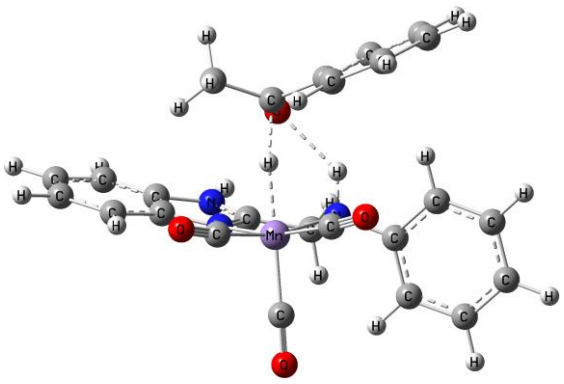
Coordinate

Atom	X	Y	Z
C	-2.76907700	-0.53909600	0.13823400
C	-3.22562600	-1.52108100	-0.76050500
C	-4.57735200	-1.70340400	-1.04730400
C	-5.46776100	-0.86243200	-0.39822300

C	-5.02559900	0.12406700	0.50250300
C	-3.68042800	0.30166900	0.78337500
C	-1.02171200	-1.54994100	-0.61299400
H	-4.91705400	-2.46193500	-1.74406300
H	-6.53014800	-0.96643200	-0.59085000
H	-5.75790500	0.76173700	0.98565600
H	-3.33948900	1.06735500	1.47043700
H	-2.02502400	-2.86461300	-1.92490700
C	0.41311400	-1.92197400	-0.78529000
H	0.68808400	-2.66941500	-0.03205000
H	0.59500900	-2.35354800	-1.77833700
N	1.19590100	-0.69670500	-0.57006600
H	0.98618600	-0.10761600	-1.39523800
C	2.61264800	-0.90772200	-0.49707000
C	3.43570300	-0.30801800	-1.44915700
C	3.17384900	-1.66671400	0.53081700
C	4.81736200	-0.45689800	-1.36645100
H	2.98042100	0.26869200	-2.25076400
C	4.55364200	-1.82351100	0.59757800
H	2.53546400	-2.11229800	1.28829400
C	5.38039000	-1.21765800	-0.34660400
H	5.45259000	0.01911100	-2.10641000
H	4.98596800	-2.41135000	1.40090800
H	6.45685900	-1.33584100	-0.28378900
N	-1.38402100	-0.58977000	0.20007100
N	-2.08020000	-2.15383600	-1.21308100
Mn	0.23274800	0.55282600	0.94141400
C	1.74995900	1.58286500	1.12678700
C	-0.78421600	1.75616800	1.86332500

C	0.56238700	-0.58492700	2.36003800
O	2.67530700	2.25658700	1.13385300
O	0.76609500	-1.26322200	3.26232500
O	-1.43900300	2.56162700	2.35393400
C	-0.29605700	1.73609100	-2.03359800
H	-0.09975700	1.57929200	-0.32223700
O	-0.04374300	0.63056400	-2.55210800
C	0.75330800	2.83517300	-2.08903400
H	0.54366200	3.64079600	-1.38351600
H	1.74210800	2.42051700	-1.88106500
H	0.75719400	3.24257100	-3.10780300
C	-1.73988300	2.18686000	-1.91873700
H	-2.37920200	1.32806200	-1.70930000
H	-1.87297300	2.94678900	-1.14691400
H	-2.03433000	2.61108800	-2.88727600

TS2_out



SCF Done : -1534.370175
SCF Done for solvent : -1534.3860035
Zero-point correction : 0.423098
Total Electronic Energy : -1533.947077

Total Thermal Energy : -1533.903935
Total Thermal Free Energy : -1534.030881

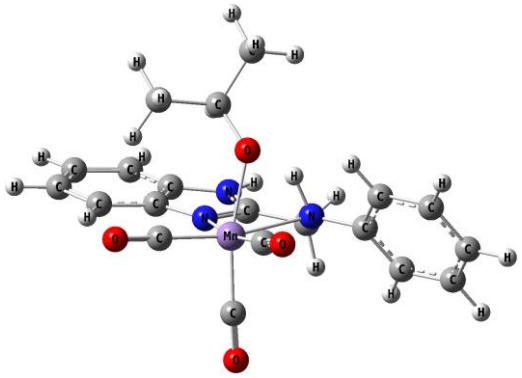
Coordinate

Atom	X	Y	Z
C	-3.19699800	-0.31996800	-0.14887400
C	-3.69399000	-0.28501700	-1.46445700
C	-4.99311400	0.11858300	-1.76402500
C	-5.79001100	0.49413400	-0.69326700
C	-5.30847700	0.46045200	0.62781500
C	-4.01605400	0.05367500	0.92039800
C	-1.59089700	-0.94863300	-1.43615300
H	-5.36235700	0.14291900	-2.78347200
H	-6.80756000	0.82100300	-0.87877500
H	-5.96587300	0.76081100	1.43651200
H	-3.64690000	0.03275100	1.93902400
H	-2.60260400	-0.68696200	-3.26297200
C	-0.24167000	-1.41548400	-1.87017300
H	-0.21679200	-2.50873600	-1.83958900
H	-0.02729200	-1.09685000	-2.89763300
N	0.73773500	-0.87339100	-0.91736800
H	0.81697500	0.12010000	-1.15595300
C	2.03494800	-1.48723200	-0.92371000
C	3.16482100	-0.66855700	-0.91009900
C	2.18327100	-2.87337300	-0.85483200
C	4.43269100	-1.23625600	-0.83877600
H	3.04511600	0.41210400	-0.93575200
C	3.45603900	-3.43150000	-0.79420000
H	1.31318600	-3.52124800	-0.81705500

C	4.58633300	-2.61845800	-0.78787700
H	5.30297200	-0.58826400	-0.82297800
H	3.56058000	-4.51026100	-0.73876800
H	5.57616800	-3.05864600	-0.73375700
N	-1.87527700	-0.74356700	-0.17492100
N	-2.64597600	-0.72025200	-2.25715100
Mn	-0.17956700	-0.68263100	1.07155600
C	1.45210100	-0.34299400	1.87192500
C	-1.07300500	-0.15913300	2.57854900
C	-0.20392500	-2.50235900	1.42034600
O	2.45080700	-0.04305000	2.34288700
O	-0.22476100	-3.62261600	1.65899100
O	-1.62168100	0.26655800	3.49224000
C	-0.28271300	2.10325700	-0.50234500
H	-0.18921600	0.95591100	0.72166600
O	-0.53804700	1.53759500	-1.58450100
C	-1.38551300	2.85561900	0.22394300
H	-2.30287200	2.26527100	0.19261700
H	-1.12852500	3.08291500	1.25954300
H	-1.55157500	3.79720800	-0.31290300
C	1.14313000	2.58652700	-0.29154300
C	1.93090500	2.76907300	-1.42937000
C	1.68632800	2.86341000	0.96542200
C	3.24734000	3.21371900	-1.31429500
H	1.49069600	2.55354200	-2.39796100
C	3.00090300	3.29743200	1.08280300
H	1.08628100	2.69246700	1.85560500
C	3.78556600	3.47309400	-0.05779500
H	3.85101300	3.35487400	-2.20578900

H	3.42105500	3.48628100	2.06551300
H	4.81272400	3.81110400	0.03663600

I1_in



SCF Done	: -1342.74305
SCF done for solvent	: -1342.75897
Zero-point correction	: 0.373074
Total Electronic Energy	: -1342.36997
Total Thermal Energy	: -1342.33114
Total Thermal Free Energy	: -1342.44885

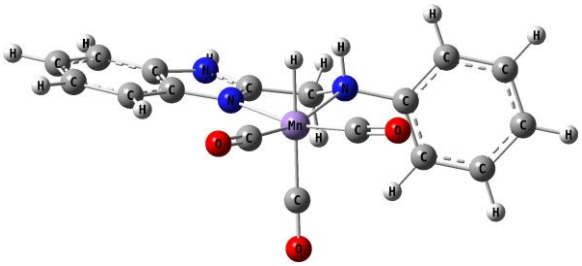
Coordinate

Atom	X	Y	Z
C	2.68474600	-0.62672800	-0.29019700
C	3.10058400	-1.83701600	0.29336800
C	4.44286600	-2.14943900	0.49996500
C	5.36807100	-1.19974300	0.09692000
C	4.96845000	0.01362400	-0.49301000
C	3.63216800	0.31801000	-0.69547800
C	0.89481200	-1.74666800	0.15373800
H	4.74935700	-3.08590400	0.95316800

H	6.42518900	-1.39692900	0.23857900
H	5.72714100	0.72682700	-0.79617500
H	3.32756500	1.25291600	-1.15220100
H	1.84810900	-3.42742400	1.00667200
C	-0.55154700	-2.11443600	0.23129800
H	-0.80622100	-2.67161200	-0.67975600
H	-0.74314700	-2.78118200	1.08567100
N	-1.30642000	-0.87454200	0.30388800
H	-0.93255600	-0.19166200	1.06601500
C	-2.72157500	-0.97529200	0.33673600
C	-3.42515600	0.00684700	1.04756200
C	-3.42898700	-1.98132000	-0.32403100
C	-4.81224900	-0.01241400	1.07516400
H	-2.85683800	0.77685500	1.56509500
C	-4.82222800	-1.99343300	-0.28413500
H	-2.90725500	-2.75314800	-0.88017000
C	-5.52112200	-1.01289600	0.41000300
H	-5.34367300	0.75794600	1.62487300
H	-5.35999700	-2.77971900	-0.80469600
H	-6.60528600	-1.02746300	0.43624200
N	1.29845700	-0.60933700	-0.35701300
N	1.92977500	-2.52623000	0.56317100
Mn	-0.26883100	0.76182500	-0.75482700
C	-1.78452300	1.88308800	-0.83300800
C	0.80337800	2.15556700	-1.32643400
C	-0.51110500	0.06461500	-2.45799900
O	-2.67513600	2.59234800	-0.83586200
O	-0.66387900	-0.42950200	-3.47810200
O	1.46027000	3.02482700	-1.67644900

O	-0.28006200	1.15830600	1.27560800
C	0.78903000	1.21570200	2.16471900
H	1.39222400	0.28075500	2.13208400
C	1.73464200	2.36957100	1.83877800
H	1.16666500	3.30560300	1.80132200
H	2.52690600	2.46695900	2.58840700
H	2.21055000	2.21682400	0.86600200
C	0.23677600	1.35642600	3.58391300
H	-0.32684900	2.29179500	3.66193600
H	-0.44832400	0.53138800	3.80267000
H	1.03279700	1.36011000	4.33584100

I2_in



SCF Done : -1149.61974
SCF Done for solvent : -1149.64181
Zero-point correction : 0.28344
Total Electronic Energy : -1149.33630
Total Thermal Energy : -1149.30630
Total Thermal Free Energy : -1149.40248

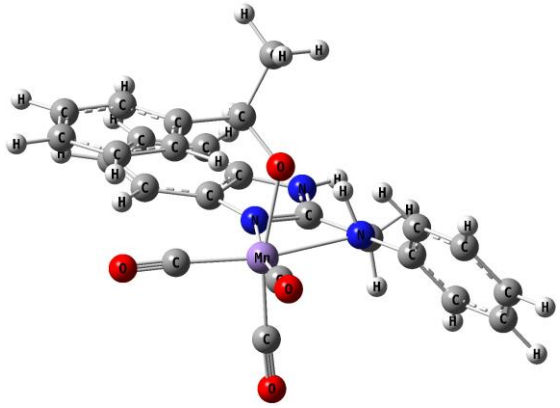
Coordinate

Atom	X	Y	Z
C	-2.79878300	-0.32839900	-0.10208500
C	-3.23737400	-1.66852800	0.00461800

C	-4.58630900	-2.02378000	-0.02700200
C	-5.50055200	-0.98477700	-0.17157700
C	-5.07885600	0.35538700	-0.28144300
C	-3.73295800	0.70417600	-0.25000100
C	-1.02357300	-1.55099800	0.09715900
H	-4.90923900	-3.05685200	0.05629500
H	-6.56161000	-1.21255600	-0.20120500
H	-5.82528900	1.13536700	-0.39438100
H	-3.41458300	1.73526800	-0.33762300
H	-2.01540500	-3.42426500	0.21277500
C	0.42035100	-1.90963900	0.21143400
H	0.71749200	-1.93819000	1.26550100
H	0.62850800	-2.90189400	-0.21549500
N	1.19376300	-0.83806700	-0.45653800
H	0.98585300	-0.85915000	-1.45213600
C	2.62391500	-0.94766200	-0.27668000
C	3.44593700	-1.17186300	-1.38400200
C	3.19000700	-0.81478600	0.99595400
C	4.82971900	-1.25876000	-1.22179900
H	3.00645800	-1.26668000	-2.37415300
C	4.57091000	-0.92014700	1.15253400
H	2.55982400	-0.59801000	1.85205900
C	5.39615800	-1.14114400	0.04701000
H	5.46070900	-1.42238700	-2.09022800
H	5.00397300	-0.81148300	2.14240400
H	6.47194400	-1.21220700	0.17415200
N	-1.40644800	-0.29996100	-0.03714200
N	-2.07669800	-2.42192200	0.12648500
Mn	0.15441200	1.09611900	-0.14912100

C	1.60429900	2.06057000	-0.58603900
C	-0.87911100	2.54429900	-0.26155500
C	0.39733100	1.18553400	1.65289700
O	2.53553900	2.65870500	-0.92904000
O	0.56297700	1.30976200	2.79697400
O	-1.56454500	3.47271600	-0.39335600
H	-0.06166000	1.04336400	-1.73273400

I3_in



SCF Done : -1534.41266
SCF Done for solvent : -1534.43000
Zero-point correction : 0.427452
Total Electronic Energy : -1533.98521
Total Thermal Energy : -1533.94178
Total Thermal Free Energy : -1534.069614

Coordinate

Atom	X	Y	Z
C	1.87865800	2.00290400	0.15294400
C	1.88780100	3.25864600	-0.47995000
C	3.06226900	3.97339200	-0.70981200

C	4.24019900	3.38005600	-0.28393900
C	4.24663000	2.12039900	0.34365100
C	3.07601700	1.41429800	0.57018200
C	-0.17027700	2.46008200	-0.34085100
H	3.05730100	4.94060100	-1.20040000
H	5.18058100	3.89690600	-0.44226800
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C	-4.34832300	1.25213900	-0.03093500
C	-4.86392000	-1.23647300	-1.16925900
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C	1.31564700	-3.17611200	-0.54331300
C	4.03951700	-2.71412900	-0.22132800
H	3.67896500	-0.84875600	-1.24231700
C	2.10910500	-4.11961200	0.09999200
H	0.24560600	-3.32631000	-0.66084900
C	3.47370600	-3.88753200	0.26958600
H	5.10188500	-2.52835400	-0.09254400
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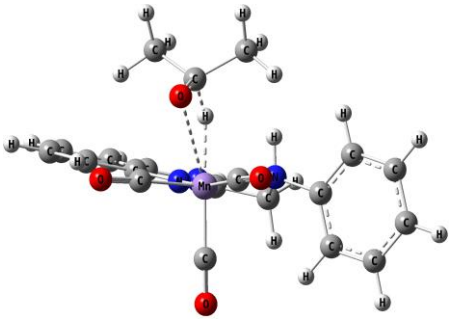
TS1_in



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C	-3.70518300	0.31651900	0.50133100
C	-1.09536000	-1.82617100	-0.52444200
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H	-1.51880000	3.69277000	-2.27314500
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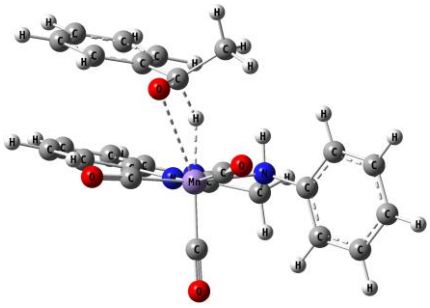
TS2_in



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H	1.34820000	-0.18464400	-1.50940900
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C	3.74567100	0.33308300	-1.65923300
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C	5.12176800	0.53665900	-1.66215100
H	3.09414400	0.96728300	-2.25598600
C	5.39382500	-1.26761800	-0.09497200
H	3.59399500	-2.22228000	0.58329200
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H	5.54232500	1.32682400	-2.27504700
H	6.03057900	-1.89017300	0.52485500
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O	-1.03974800	1.54012000	2.90362300
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C	-0.34905800	2.43287100	-0.52125000
H	0.15108500	1.19167200	-0.34646400
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H	0.04467400	3.69698300	-2.21690200
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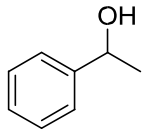
6. Characterization of the products

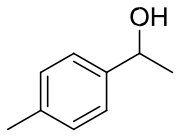
6.1 Characterization data for the alcohols

1-Phenylethanol (**5a**):[7]



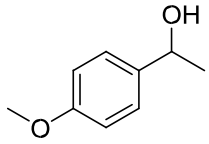
52.0 mg; 85% isolated yield; faint yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-7.34 (m, 4H), 7.32-7.25 (m, 1H), 4.86 (q, $J_{H,H}$ = 6.2 Hz, 1H), 2.36 (brs, 1H), 1.48 (d, $J_{H,H}$ = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 145.94, 128.57, 127.53, 125.51, 70.51, 25.25. **GCMS (M^+):** 122.1.

1-*p*-Tolylethanol (**5b**):[7]



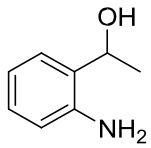
49.5 mg; 73% isolated yield; pale yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.27 (d, $J_{H,H}$ = 8 Hz, 2H), 7.16 (d, $J_{H,H}$ = 8 Hz, 2H), 4.85 (q, $J_{H,H}$ = 4 Hz, 1H), 2.34 (s, 3H), 1.95 (s, 1H), 1.47 (d, $J_{H,H}$ = 4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 143.02, 137.26, 129.29, 125.50, 70.36, 25.21, 21.23. **GC-MS (M^+):** 136.1.

1-(4-Methoxyphenyl)ethanol (**5d**):[8]



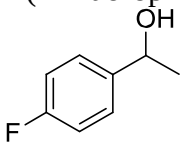
53.0 mg; 70% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.27 (t, $J_{H,H}$ = 8.7 Hz, 2H), 6.86 (d, $J_{H,H}$ = 8.6 Hz, 2H), 4.82 (q, $J_{H,H}$ = 6.5 Hz, 1H), 3.78 (s, 3H), 2.08 (brs, 1H), 1.45 (d, $J_{H,H}$ = 6.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 159.07, 138.18, 126.79, 113.96, 70.03, 55.40, 25.13. **GC-MS (M^+):** 152.1.

1-(2-Aminophenyl)ethanol (**5f**):[9]



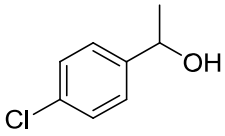
50.7 mg; 74% isolated yield; pale yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.09-7.05 (m, 2H), 6.71 (t, $J_{H,H}$ = 5.9 Hz, 1H), 6.64 (d, $J_{H,H}$ = 6.1 Hz, 1H), 4.88 (brs, 1H), 1.55 (d, $J_{H,H}$ = 3.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 145.24, 128.63, 126.64, 118.31, 116.87, 69.72, 21.70. **GC-MS (M^+):** 137.1.

1-(4-Fluorophenyl)ethanol (**5g**):[7]



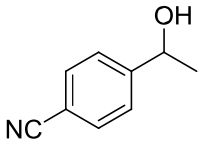
56.1 mg; 80% isolated yield; faint pink liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.33-7.30 (m, 2H), 7.03-6.99 (m, 2H), 4.86 (q, $J_{H,H}$ = 6.5 Hz, 1H), 1.94 (brs, 1H), 1.46 (d, $J_{H,H}$ = 6.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 163.22, 161.27, 141.64, 127.19, 115.41, 69.92, 25.44. **GCMS (M^+):** 140.0.

1-(4-Chlorophenyl)ethanol (**5h**):[8]



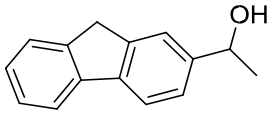
69.7 mg; 89% isolated yield; pale yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.29-7.25 (m, 4H), 4.88-4.83 (m, 1H), 1.97 (brs, 1H), 1.45 (d, $J_{H,H}$ = 6.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 144.38, 133.19, 128.74, 126.95, 69.88, 25.41. **GC-MS (M^+):** 156.0.

4-(1-Hydroxyethyl)benzonitrile (**5k**):[7]



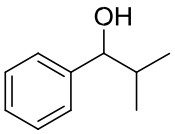
52.2 mg; 71% isolated yield; brown liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.59-7.55 (m, 2H), 7.45-7.42 (m, 2H), 4.92-4.87 (m, 1H), 2.71 (brs, 1H), 1.45-1.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 151.36, 132.28, 126.08, 118.90, 110.73, 69.48, 25.35. **GC-MS (M^+):** 147.1.

1-(9*H*-Fluoren-2-yl)ethanol (**5m**):[8]

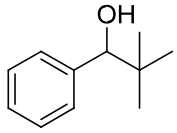


78.6 mg; 75% isolated yield; white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75 (t, $J_{H,H}$ = 8 Hz, 2H), 7.54 (t, $J_{H,H}$ = 8 Hz, 2H), 7.37-7.35 (m, 2H), 7.31-7.27 (m, 1H), 4.98 (q, $J_{H,H}$ = 4 Hz, 1H), 3.88 (s, 2H), 1.84 (s, 1H), 1.55 (d, $J_{H,H}$ = 4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 144.58, 143.70, 143.45, 141.50, 141.26, 126.84, 126.74, 125.12, 124.28, 122.16, 119.93, 119.92, 70.77, 36.98, 25.41. **GC-MS (M^+):** 210.1.

2-Methyl-1-phenylpropan-1-ol (**5n**):[10]

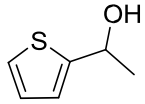


61.6 mg; 82% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-7.25 (m, 5H), 4.32 (d, $J_{H,H}$ = 6.9 Hz, 1H), 2.18 (s, 1H), 1.98-1.91 (m, 1H), 0.99 (dd, $J_{H,H}$ = 6.7 Hz, $J_{H,H}$ = 0.6 Hz, 3H), 0.79 (dd, $J_{H,H}$ = 6.7 Hz, $J_{H,H}$ = 0.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 143.76, 128.25, 127.47, 126.70, 80.09, 35.33, 19.08, 18.40. **GC-MS (M^+):** 150.5. 2,2-Dimethyl-1-phenylpropan-1-ol (**5o**) :[11]



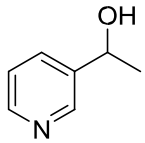
62.4 mg; 76% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ =7.32-7.25 (m, 4H), 4.38 (s, 1H), 2.02 (brs, 1H), 0.93 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 142.34, 127.75, 127.67, 127.38, 82.49, 35.73, 26.07. **GC-MS (M^+):** 164.2.

1-(Thiophen-2-yl)ethanol (**5r**):[12]



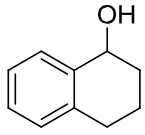
26.9 mg; 42% isolated yield; faint yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.29-7.27 (m, 1H), 7.16 (d, $J_{H,H}$ = 2.6 Hz, 1H), 7.08 (dd, $J_{H,H}$ = 4.9 Hz, $J_{H,H}$ = 1 Hz, 1H), 4.93 (q, $J_{H,H}$ = 6.4 Hz, 1H), 2.25 (brs, 1H), 1.50 (d, $J_{H,H}$ = 6.4 Hz, 3H) . **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 147.41, 126.20, 125.71, 120.22, 66.60, 24.53. **GC-MS (M^+):** 128.0.

1-(Pyridine-3-yl)ethanol (**5s**):[8]



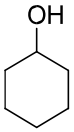
49.3 mg; 80% isolated yield; yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.48 (d, $J_{H,H}$ = 3.4 Hz, 1H), 8.41 (s, 1H), 7.71 (d, $J_{H,H}$ = 7.8 Hz, 1H), 4.90 (qd, $J_{H,H}$ = 6.4 Hz, $J_{H,H}$ = 3.8 Hz, 1H), 1.48 (dd, $J_{H,H}$ = 6.4 Hz, $J_{H,H}$ = 2.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 148.49, 147.32, 141.56, 133.57, 123.72, 67.93, 25.34. **GC-MS (M^+):** 123.1.

1,2,3,4-Tetrahydronaphthalen-1-ol (**6a**):[8]

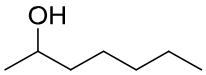


41.5 mg; 56% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.43-7.41 (m, 1H), 7.20-7.18 (m, 2H), 7.11-7.08 (m, 1H), 4.77 (t, $J_{H,H}$ = 8 Hz, 1H), 2.86-2.68 (m, 2H), 1.99-1.72 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 138.92, 137.28, 129.19, 128.82, 127.75, 126.34, 68.31, 32.41, 29.39, 18.93. **GC-MS (M^+):** 148.1.

Cyclohexanol (**6b**):[8]

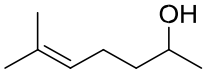


31.0 mg; 62% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.60-3.53 (m, 1H), 1.94 (s, 1H), 1.87-1.83 (m, 2H), 1.71-1.68 (m, 2H), 1.53-1.48 (m, 1H), 1.27-1.20 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 70.31, 35.53, 25.48, 24.19. **GC-MS (M^+):** 100.1. Heptan-2-ol (**6d**):[8]

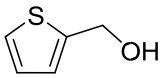


48.8 mg; 84% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.81-3.74 (m, 1H), 1.46-1.27 (m, 8H), 1.17 (d, $J_{H,H}$ = 6.2 Hz, 3H), 0.87 (t, $J_{H,H}$ = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 76.87, 68.31, 39.48, 32.01, 25.60, 23.60, 22.79, 14.17. **GC-MS (M^+):** 116.1.

6-Methylhept-5-en-2-ol (**6g**):[8]

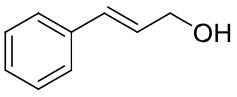


48.1 mg; 75% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 5.12-5.09 (m, 1H), 3.78 (q, $J_{H,H}$ = 6.2 Hz, 1H), 2.08-2.01 (m, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 1.48-1.42 (m, 2H), 1.16 (d, $J_{H,H}$ = 6.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 132.20, 124.20, 68.08, 39.33, 25.87, 24.64, 23.60, 17.82. **GC-MS (M^+):** 128.1. Thiophen-2-ylmethanol (**7f**):[13]



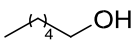
50.2 mg; 88% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.27-7.26 (m, 1H), 7.00-6.96 (m, 2H), 4.80 (s, 2H), 2.07 (brs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 144.00, 126.93, 125.67, 125.56, 60.01. **GC-MS (M^+):** 114.0.

3-Phenylprop-2-en-1-ol (**7g**):[7]



58.3 mg; 87% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.38 (d, $J_{H,H}$ = 7.5 Hz, 2H), 7.31 (t, $J_{H,H}$ = 7.3 Hz, 2H), 7.24-7.23(m, 1H), 6.61 (d, $J_{H,H}$ = 15.9 Hz, 1H), 6.39-6.33 (m, 1H), 4.32 (d, $J_{H,H}$ = 5.9 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 136.90, 130.80, 128.62, 127.21, 126.14, 61.50. **GC-MS (M^+):** 134.1.

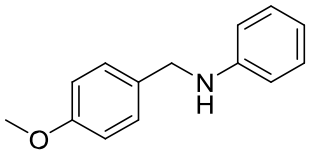
1-Hexanol (**7h**):[14]



18.0 mg; 60% isolated yield; colourless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.61 (t, $J_{H,H}$ = 6.6 Hz, 2H), 1.57-1.50 (m, 3H), 1.36-1.24 (m, 6H), 0.87 (t, $J_{H,H}$ = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 63.10, 32.82, 31.71, 25.49, 22.70, 14.09. **GC-MS (M^+):** 60.1.

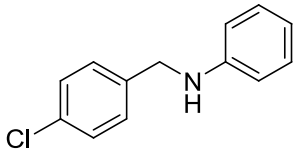
6.2 Characterization data for the amines:

N-(4-Methoxybenzyl)aniline (**8a**):[15]



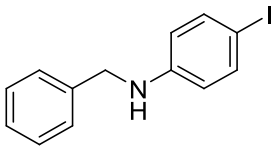
101.0 mg; 95% isolated yield; light yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.38-7.36 (d, $J_{H,H}$ = 8.7 Hz, 2H), 7.29-7.24 (m, 2H), 6.97 (d, $J_{H,H}$ = 8.6 Hz, 2H), 6.81 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.71 (d, $J_{H,H}$ = 8.0 Hz, 2H), 4.31 (s, 2H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 158.87, 148.25, 131.46, 129.28, 128.82, 117.50, 114.05, 112.88, 56.27, 47.76. **GC-MS (M^+):** 213.1.

N-(4-Chlorobenzyl)aniline (**8b**):[16]



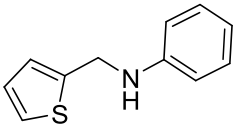
91.4 mg; 84% isolated yield; yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.30 (s, 3H), 7.17 (t, $J_{H,H}$ = 8 Hz, 2H), 6.73 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.61 (d, $J_{H,H}$ = 8.1 Hz, 2H), 4.31 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 147.92, 138.09, 129.39, 128.84, 128.78, 117.90, 112.98, 47.70. **GC-MS (M^+):** 217.1.

N-Benzyl-4-iodoaniline (**8c**):[17]



131.0 mg; 85% isolated yield; light brown oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ =7.32-7.25 (m, 7H), 6.31-6.29 (m, 2H), 4.18 (s, 2H), 3.88 (brs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 147.63, 138.85, 137.77, 128.73, 128.61, 128.30, 127.39, 115.10, 47.98. **GC-MS (M^+):** 309.0.

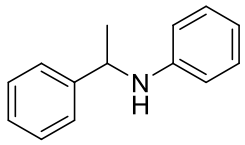
N-(Thiophen-2-ylmethyl)aniline (**8d**):[16]



64.0 mg; 63% isolated yield; yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.24-7.20 (m, 3H), 7.05-6.99 (m, 2H), 6.79 (t, $J_{H,H}$ = 8.0 Hz, 1H), 6.72-6.69 (m, 2H), 4.53 (s, 2H), 3.86 (brs, 1H).

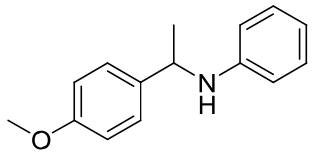
^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.68, 143.03, 129.40, 126.98, 125.17, 124.72, 118.22, 113.29, 76.87, 43.60. **GC-MS (M^+):** 189.1.

N-(1-Phenylethyl)aniline (**8e**):[18]



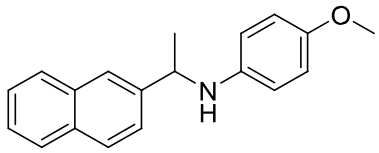
88.8 mg; 90% isolated yield; light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.41-7.33 (m, 4H), 7.28-7.24 (m, 1H), 7.14-7.10 (m, 2H), 6.68 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.56-6.53 (m, 2H), 4.52 (q, $J_{H,H}$ = 6.7 Hz, 1H), 1.54 (d, $J_{H,H}$ = 6.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 147.95, 146.17, 128.66, 128.31, 126.41, 125.90, 115.54, 112.76, 52.05, 24.76. **GC-MS (M^+):** 197.1.

4-Methoxy-N-(1-(4-methoxyphenyl)ethyl)aniline (**8f**):[18]



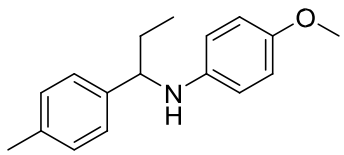
79.5 mg; 70% isolated yield; yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.33 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.17-7.13 (m, 2H), 6.91 (d, $J_{H,H}$ = 8.0 Hz, 2H), 6.71-6.68 (m, 1H), 6.57 (d, $J_{H,H}$ = 8.0 Hz, 2H), 4.50 (q, $J_{H,H}$ = 4.0 Hz, 1H), 3.82 (s, 3H), 1.54 (d, $J_{H,H}$ = 4.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 158.58, 147.44, 137.35, 129.21, 127.02, 117.30, 114.11, 113.45, 55.34, 52.95, 25.12. **GC-MS (M^+):** 227.1.

4-Methoxy-N-(1-(naphthalen-2-yl)ethyl)aniline (**8g**):[18]



77.7 mg; 56% isolated yield; white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.85 (d, $J_{H,H}$ = 7.0 Hz, 4H), 7.55-7.46 (m, 3H), 6.72 (d, $J_{H,H}$ = 8.8 Hz, 2H), 6.55 (d, $J_{H,H}$ = 8.8 Hz, 2H), 4.60 (q, $J_{H,H}$ = 6.7 Hz, 1H), 3.70 (s, 3H), 1.60 (d, $J_{H,H}$ = 3.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 152.14, 128.57, 127.95, 127.80, 126.11, 125.61, 124.60, 114.91, 114.81, 55.83, 54.66, 25.23. **GC-MS (M^+):** 277.1.

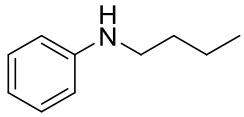
4-Methoxy-N-(1-phenylpropyl)aniline (**8h**):[19]



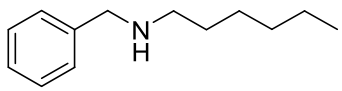
72.4 mg; 60% isolated yield; light brown oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.26 (d, $J_{H,H}$ = 7.9 Hz, 2H), 7.16 (d, $J_{H,H}$ = 7.9 Hz, 2H), 6.73 d, $J_{H,H}$ = 9.0 Hz, 2H), 6.52 (d, $J_{H,H}$ = 9.0 Hz, 2H), 4.16 (t, $J_{H,H}$ = 6.6 Hz, 1H), 3.72 (s, 3H), 2.36 (s, 3H), 1.90-1.77 (m, 2H), 0.98 (t, $J_{H,H}$ =

7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 151.89, 141.98, 141.20, 136.43, 129.29, 126.57, 114.87, 114.63, 60.42, 55.86, 31.79, 21.26, 11.01. **GC-MS (M^+):** 255.2.

N-Butylaniline (**8i**):[20]

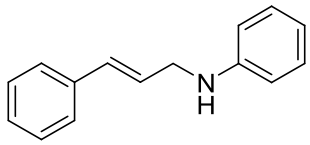


49.2 mg; 66% isolated yield; light brown oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.19-7.14 (m, 2H), 6.71-6.66 (m, 1H), 6.62-6.59 (m, 2H), 3.11 (t, $J_{H,H}$ = 7.1 Hz, 2H), 1.64-1.56 (m, 2H), 1.471.38 (m, 2H), 0.95 (t, $J_{H,H}$ = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 148.57, 129.39, 117.34, 112.93, 43.91, 31.79, 20.47, 14.09. **GC-MS (M^+):** 149.3. N-Benzylhexan-1-amine (**8j**):[21]



62.2 mg; 65% isolated yield; light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.32-7.23 (m, 4H), 3.78 9S, 2H), 2.62 (t, JH,H = 7.2 Hz, 2H), 1.94 (brs, 1H), 1.53-1.47 (m, 2H), 1.33-1.25 (m, 6H), 0.89-0.86 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 140.07, 128.49, 128.32, 127.07, 53.99, 49.43, 31.84, 29.93, 27.10, 22.70, 14.14. **GC-MS (M^+):** 191.3.

N-Cinnamylimine (**8k**):[22]



83.7 mg; 80% isolated yield; yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.41-7.32 (m, 4H), 7.28-7.20 (m, 3H), 6.78-6.63 (m, 4H), 6.39-6.33 (m, 1H), 3.96 (d, $J_{H,H}$ = 5.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 148.15, 136.97, 131.62, 129.40, 128.70, 127.65, 127.15, 126.45, 117.75, 113.17, 46.33. **GC-MS (M^+):** 209.3.

7. Copies of ^{1}H and ^{13}C NMR spectra

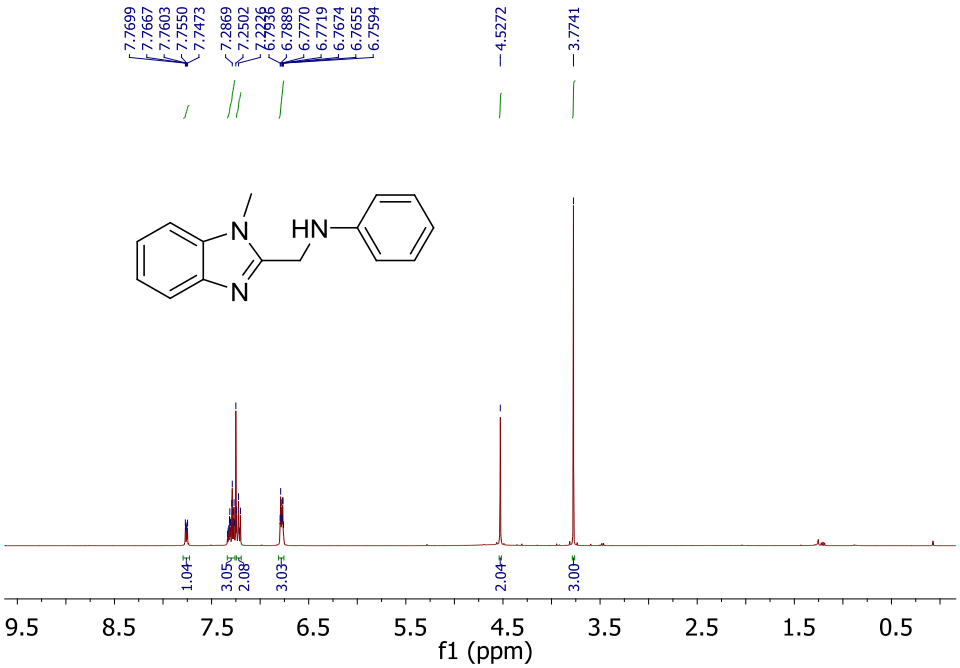


Fig. S15 ^{1}H NMR Spectrum of ligand **L3** in $CDCl_3$ (400 MHz).

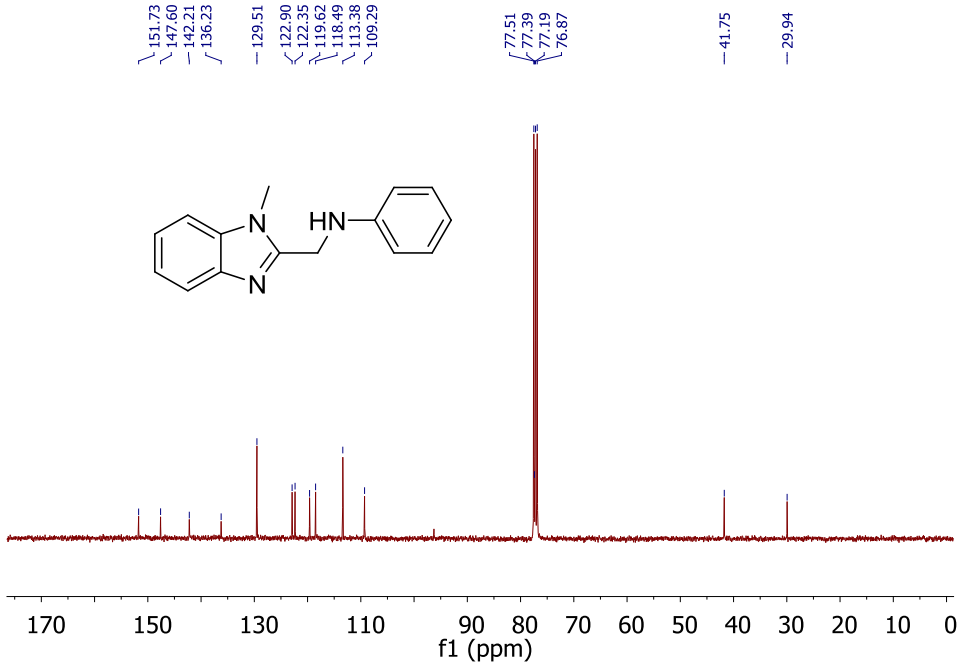


Fig. S16 ^{13}C NMR Spectrum of ligand **L3** in $CDCl_3$ (100 MHz).

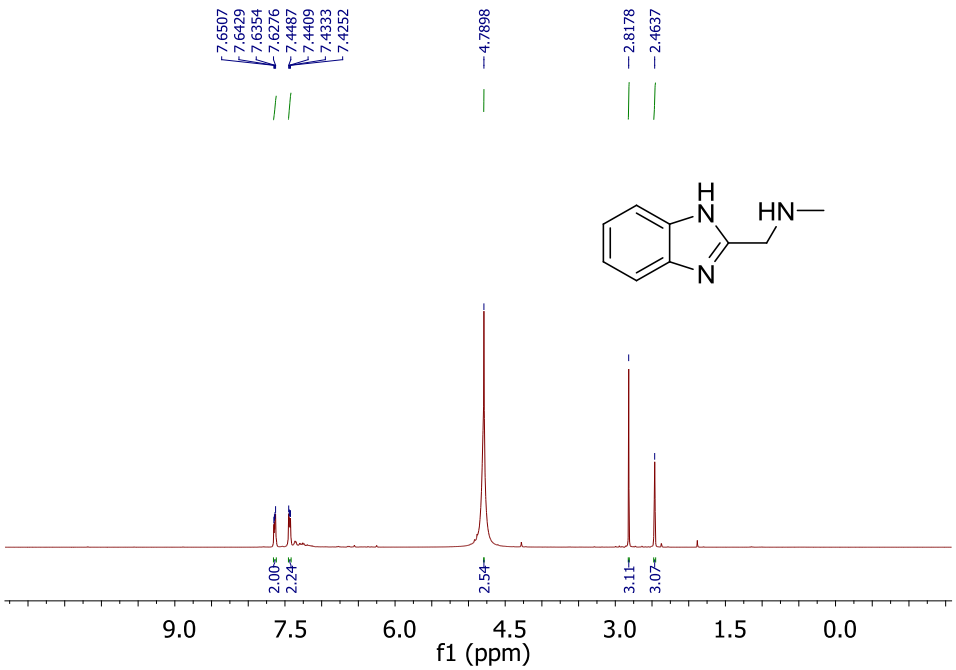


Fig. S17 ^{1}H NMR Spectrum of ligand **L4** in D_2O (400 MHz).

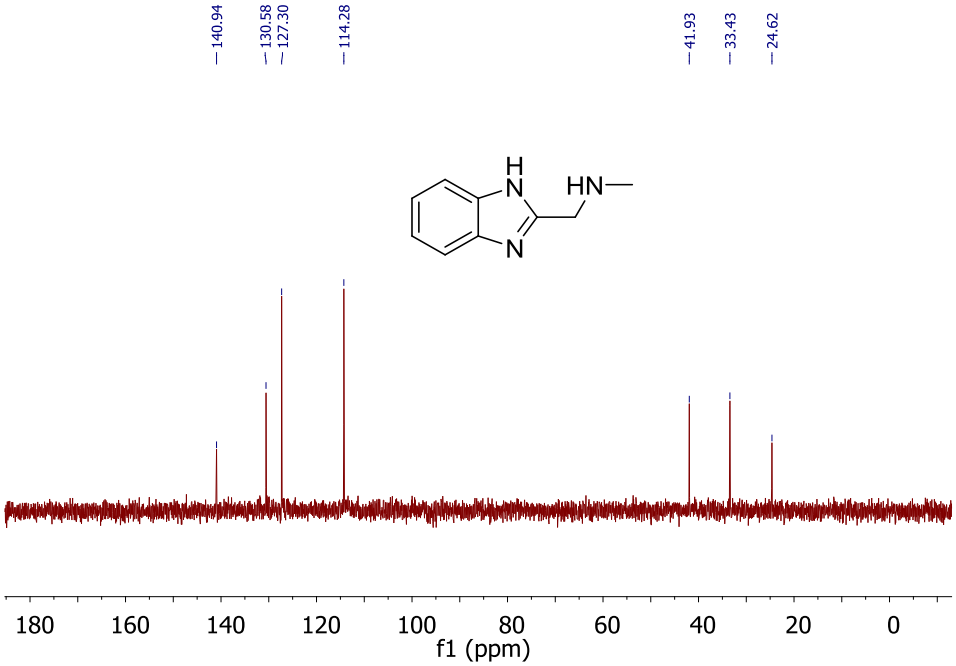


Fig. S18 ^{13}C NMR Spectrum of ligand **L4** in D_2O (100 MHz).

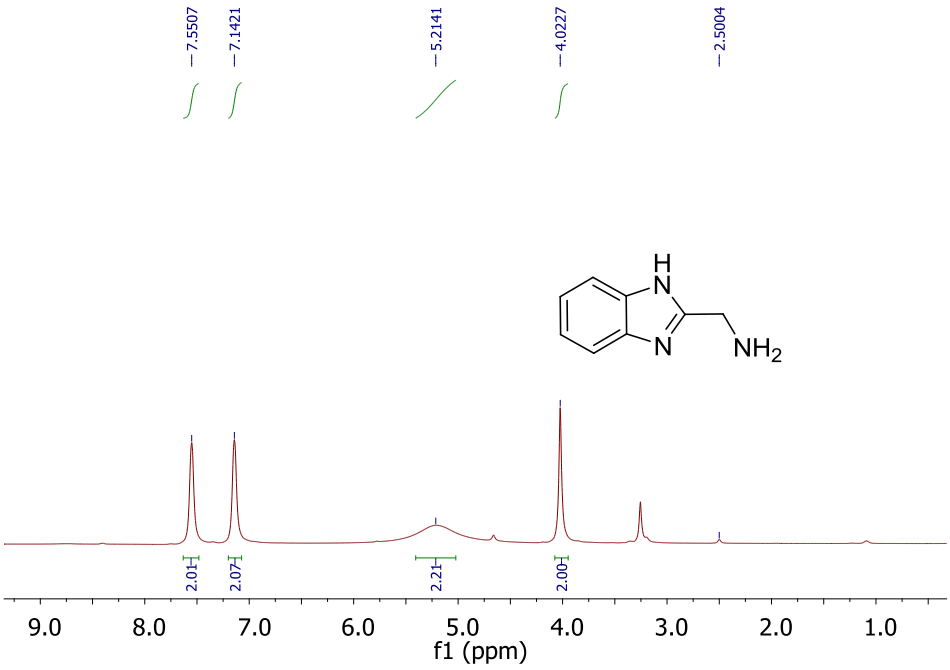


Fig. S19 [1]H NMR Spectrum of ligand **L6** in DMSO-D_6 (400 MHz).

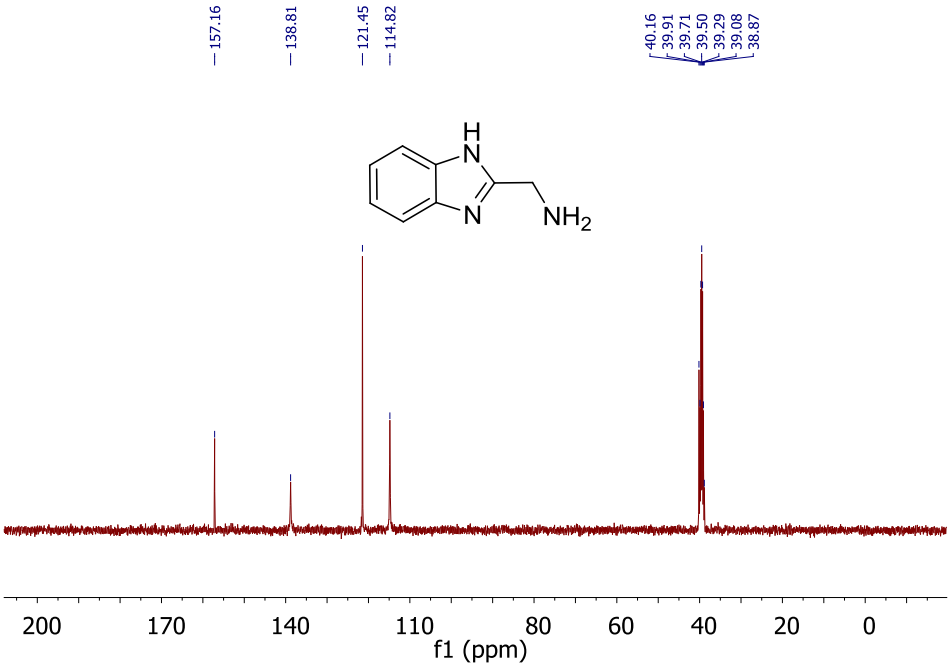


Fig. S20 [13]C NMR Spectrum of ligand **L6** in DMSO-D_6 (100 MHz).

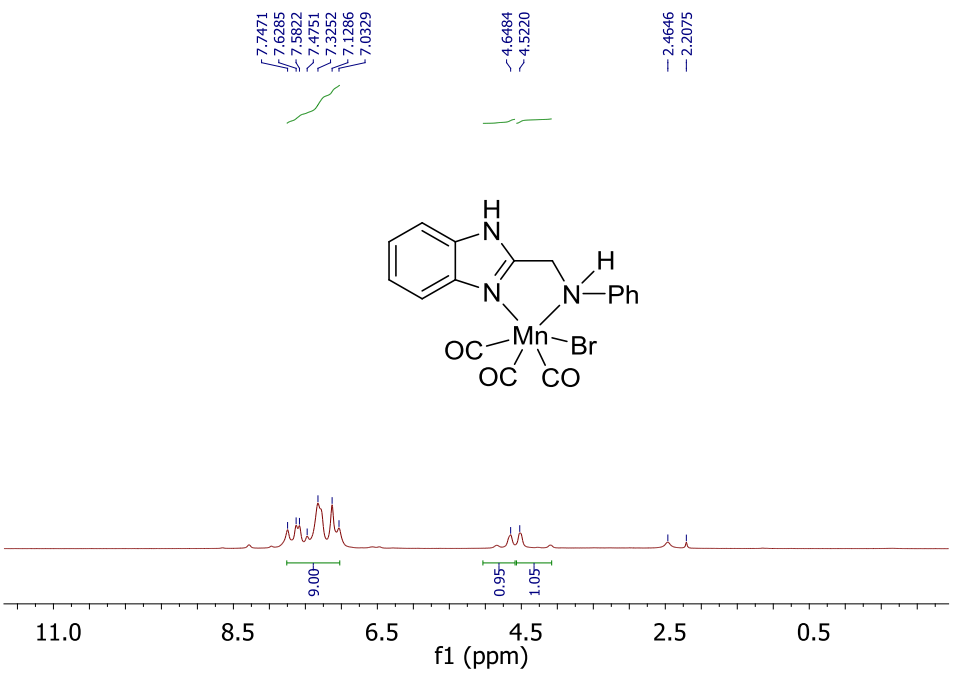


Fig. S21 ^{1}H NMR Spectrum of complex **A** in DMSO-D_6 (500 MHz).

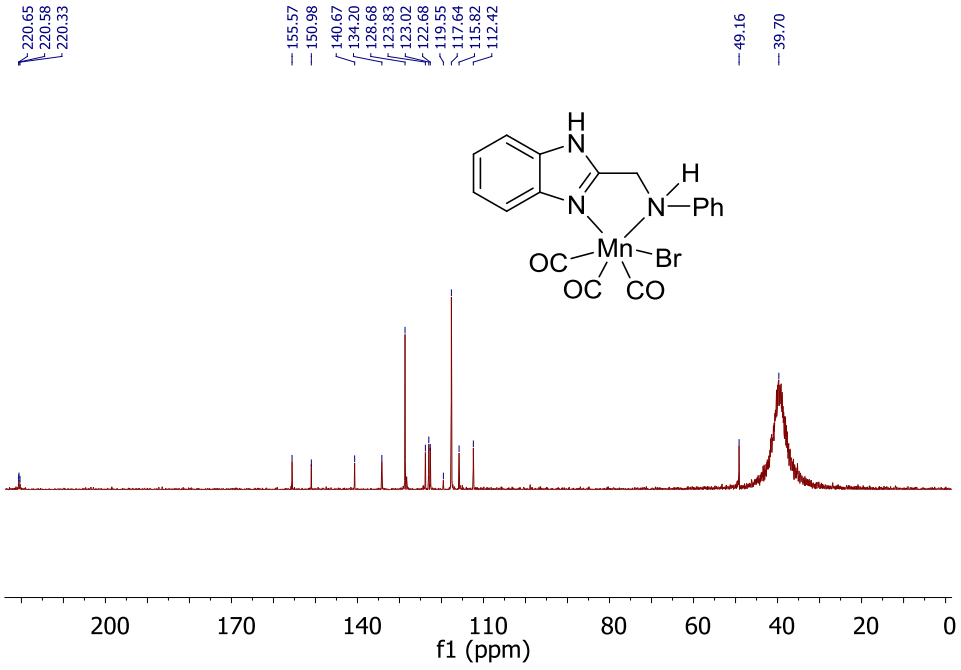


Fig. S22 ^{13}C NMR Spectrum of complex **A** in DMSO-D_6 (125 MHz).

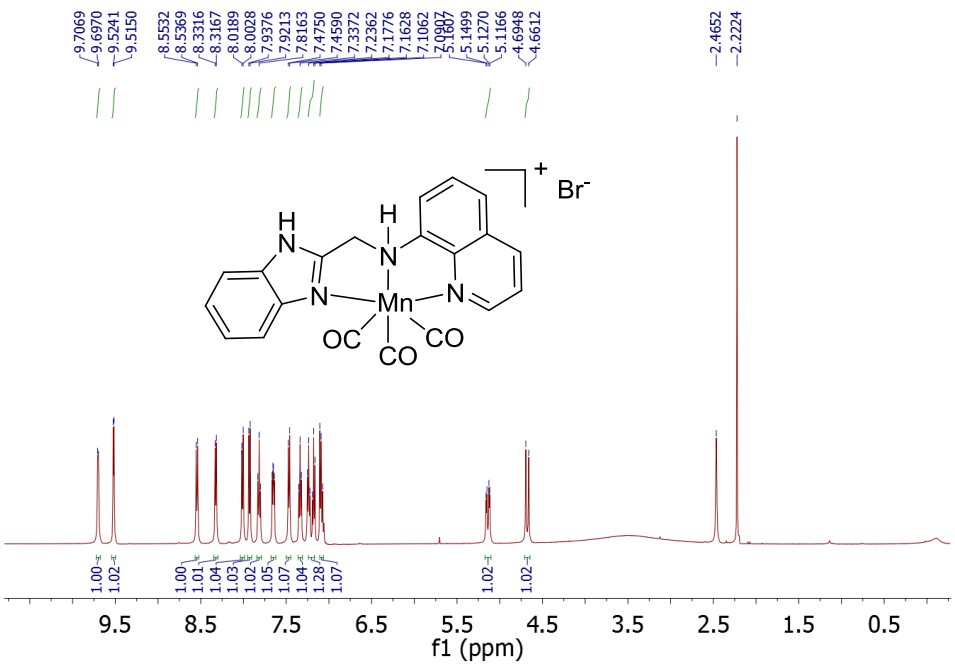


Fig. S23 ^{1}H NMR Spectrum of complex **B** in DMSO-D_6 (500 MHz).

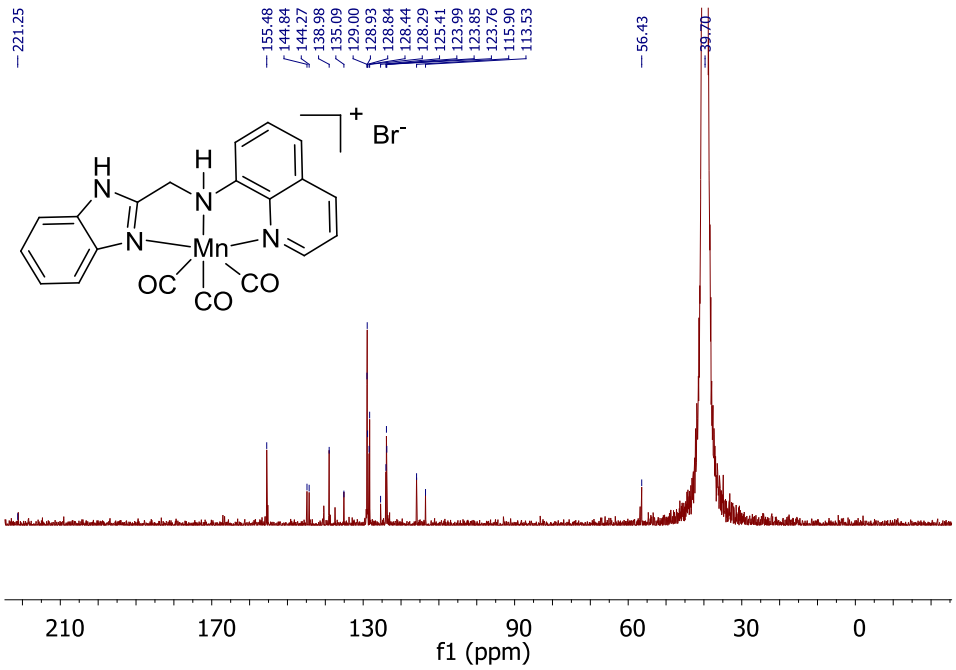


Fig. S24 ^{13}C NMR Spectrum of complex **B** in DMSO-D_6 (125 MHz).

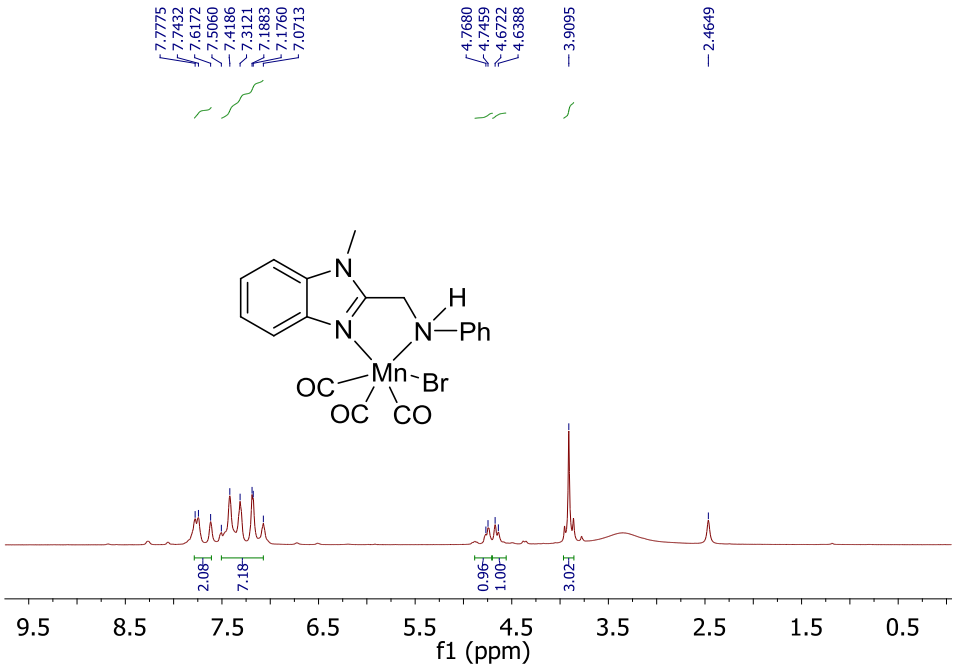


Fig. S25 ^{1}H NMR Spectrum of complex **C** in DMSO-D_6 (500 MHz).

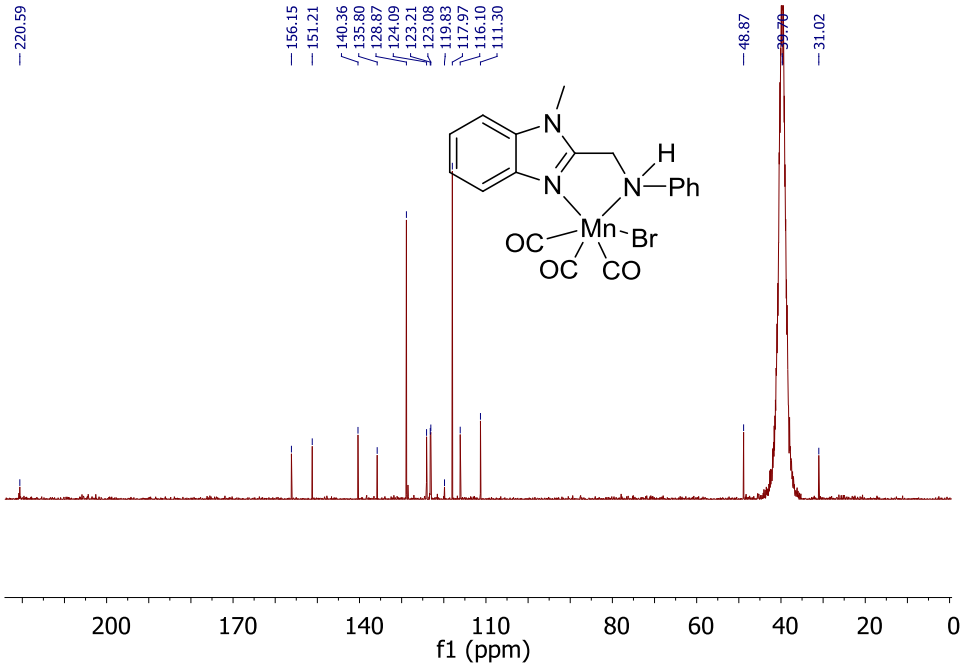


Fig. S26 ^{13}C NMR Spectrum of complex **C** in DMSO-D_6 (125 MHz).

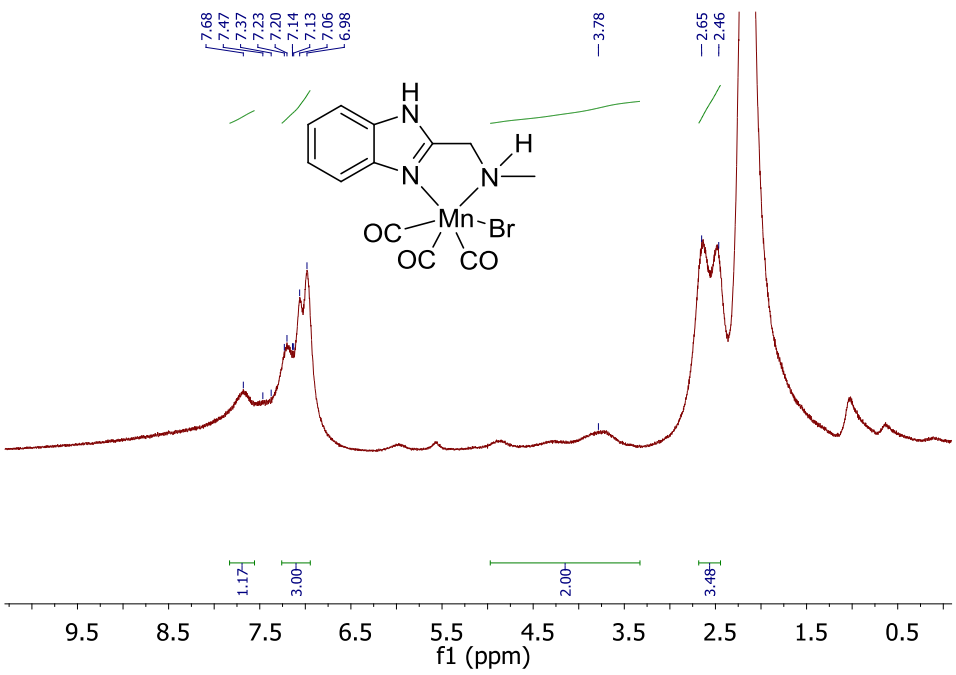


Fig. S27 ^{1}H NMR Spectrum of complex **D** in DMSO-D_6 (500 MHz).

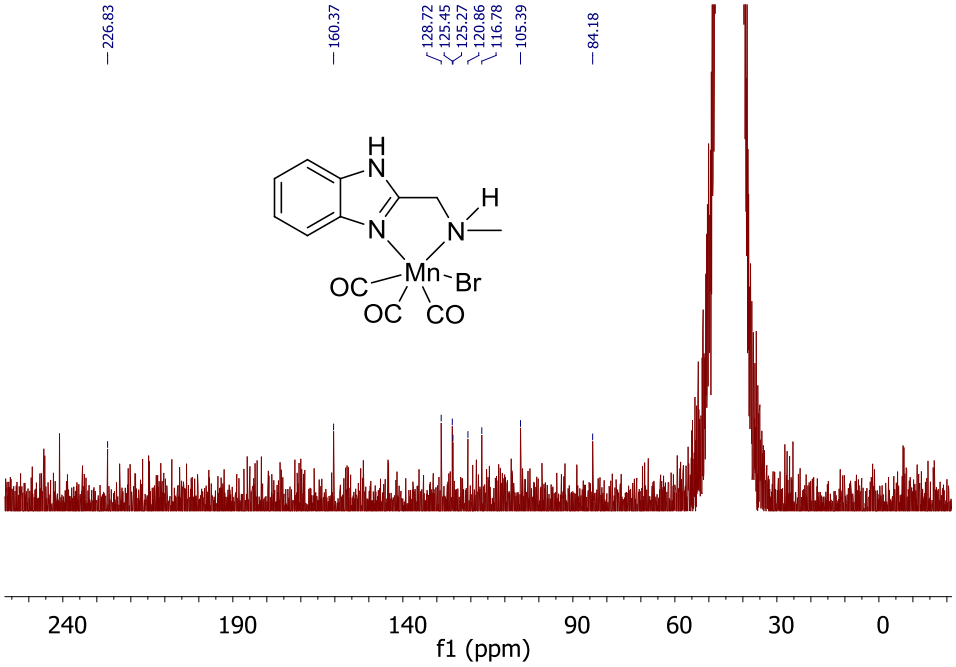


Fig. S28 ^{13}C NMR Spectrum of complex **D** in DMSO-D_6 (125 MHz).

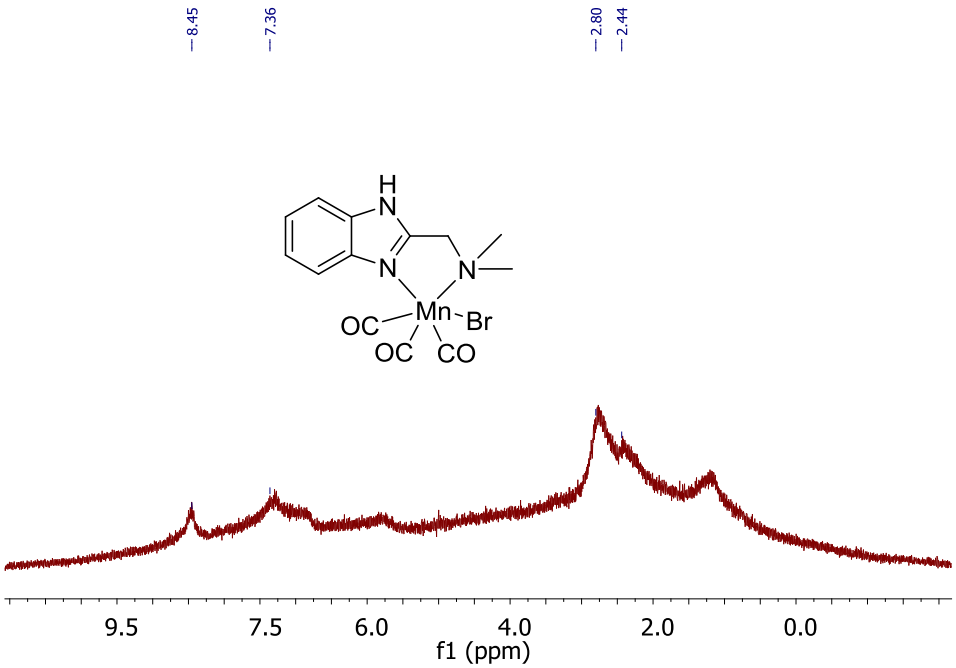


Fig. S29 ^{1}H NMR Spectrum of complex **E** in DMSO-D_6 (500 MHz).

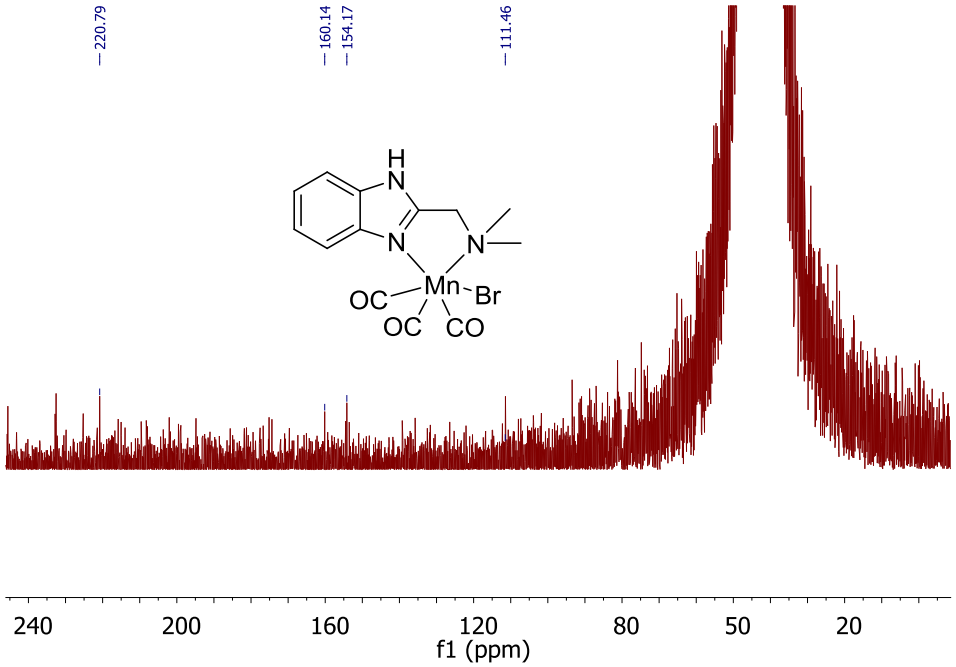


Fig. S30 ^{13}C NMR Spectrum of complex **E** in DMSO-D_6 (125 MHz).

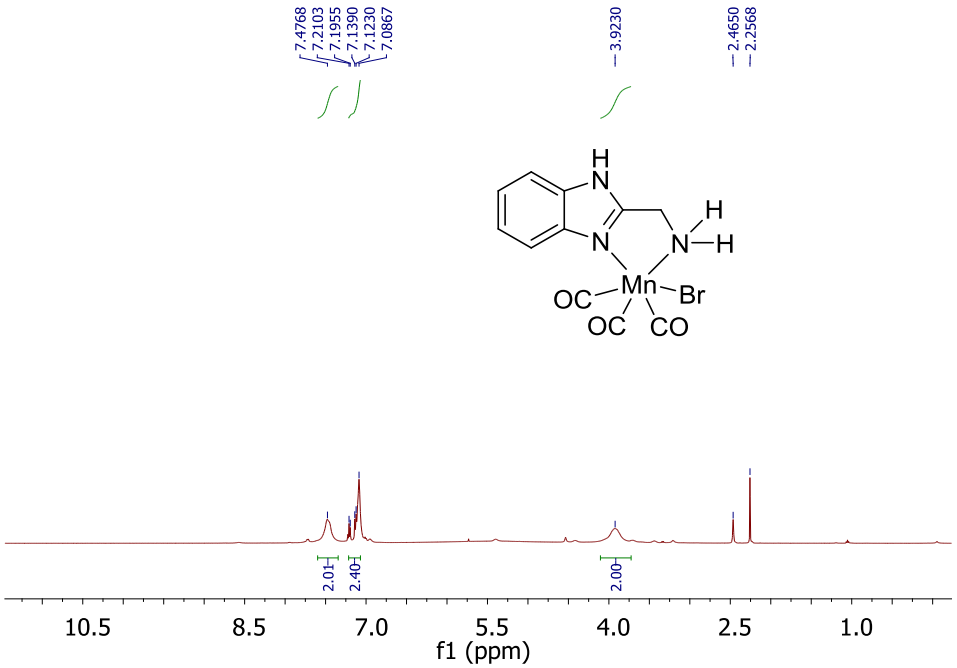


Fig. S31 ^{1}H NMR Spectrum of complex **F** in DMSO-D_6 (500 MHz).

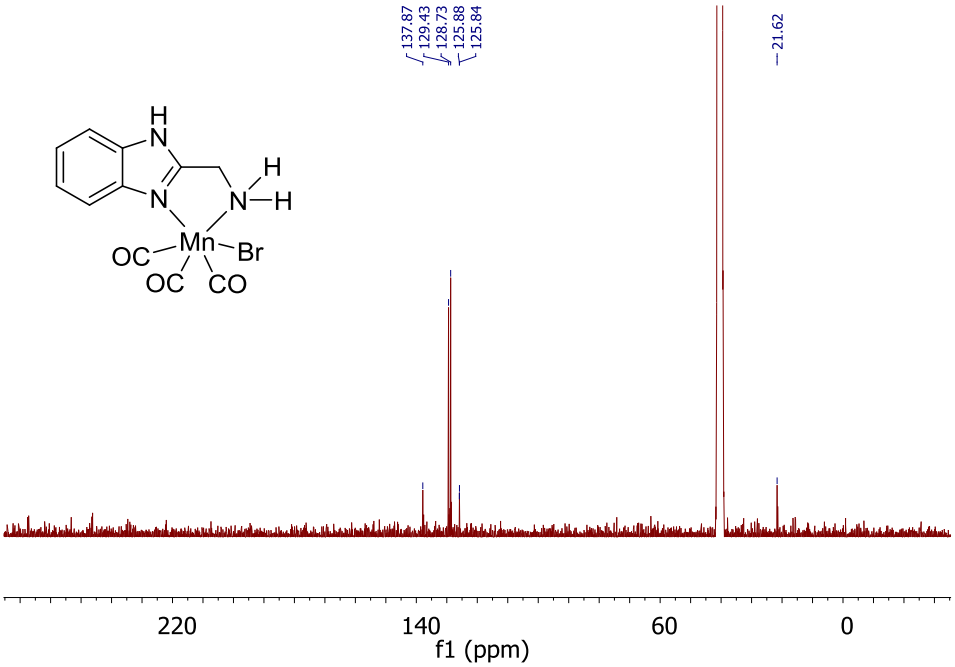


Fig. S32 ^{13}C NMR Spectrum of complex **F** in DMSO-D_6 (125 MHz).

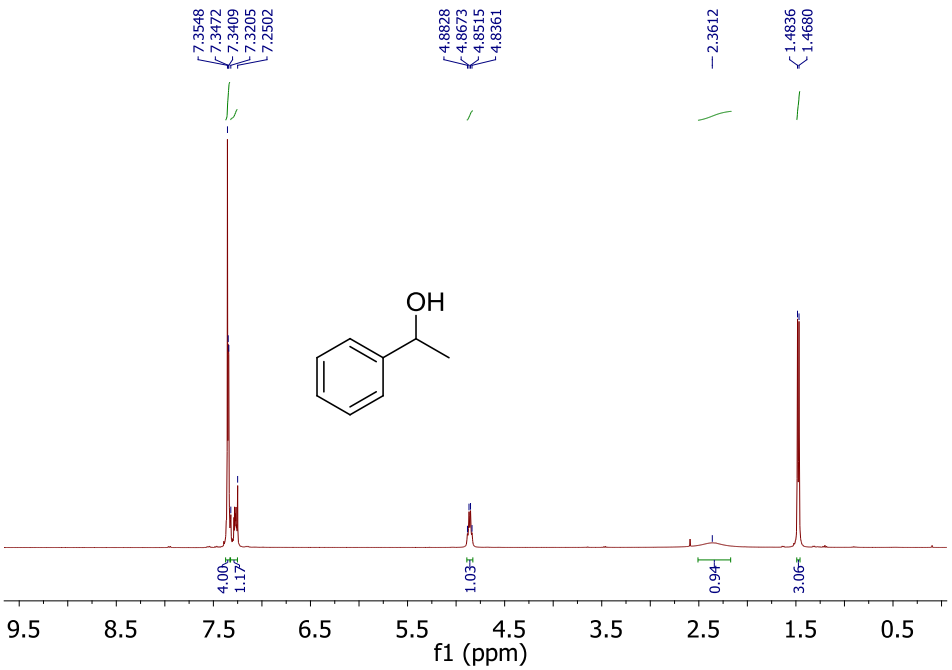


Fig. S33 ^{1}H NMR Spectrum of **5a** in $CDCl_3$ (400 MHz).

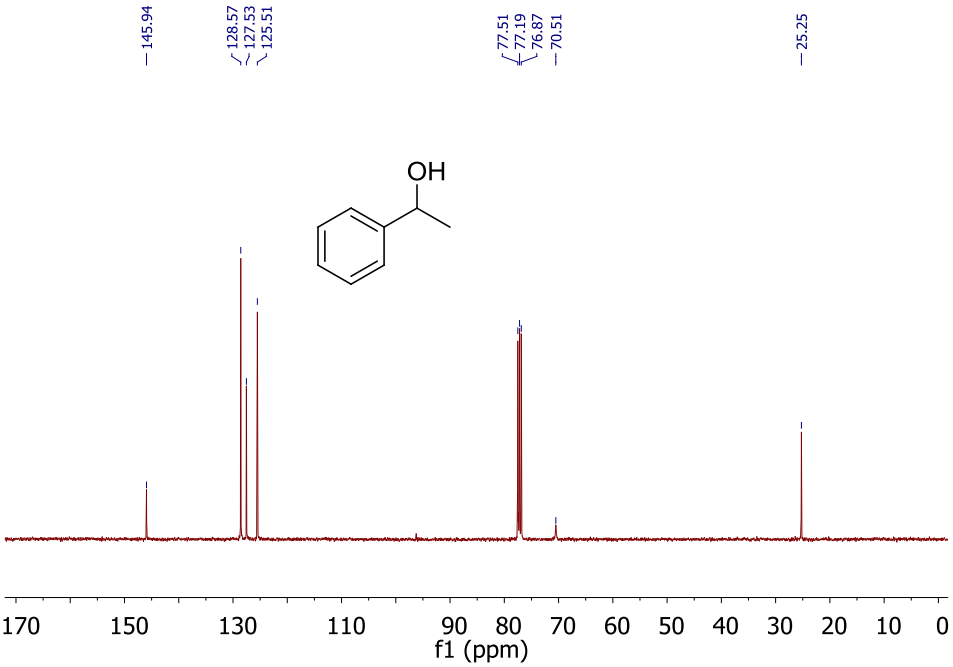


Fig. S34 ^{13}C NMR Spectrum of **5a** in $CDCl_3$ (100 MHz).

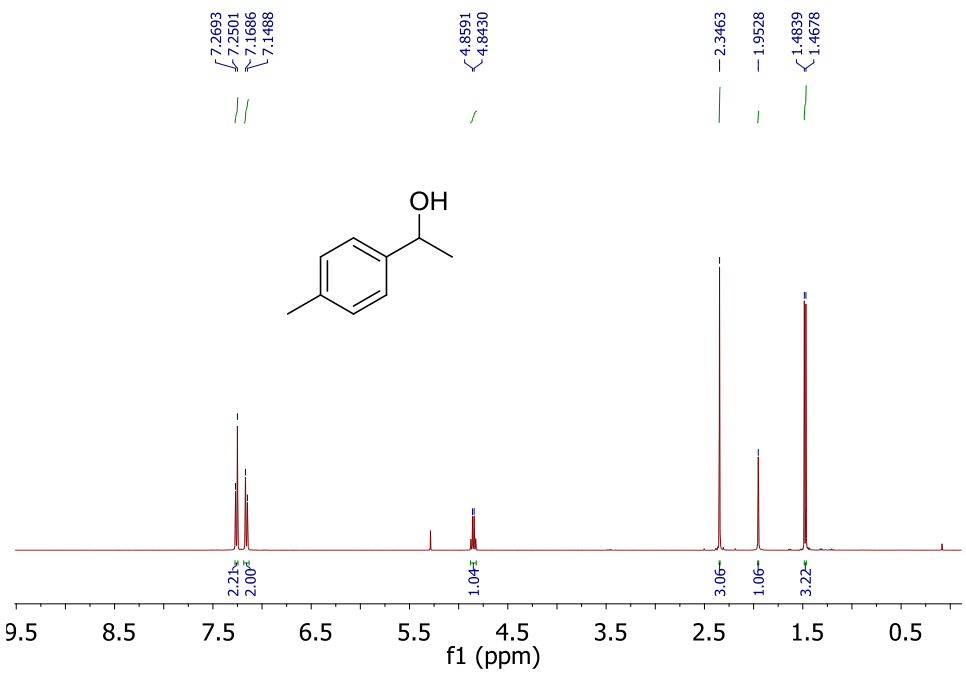


Fig. S35 ^{1}H NMR Spectrum of **5b** in $CDCl_3$ (400 MHz).

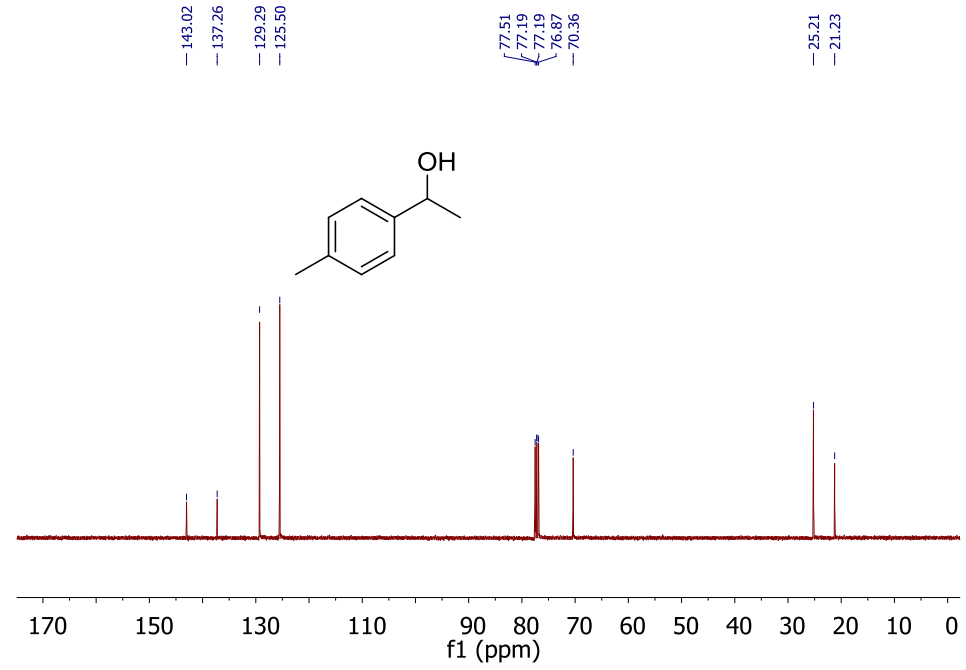


Fig. S36 ^{13}C NMR Spectrum of **5b** in $CDCl_3$ (100 MHz).

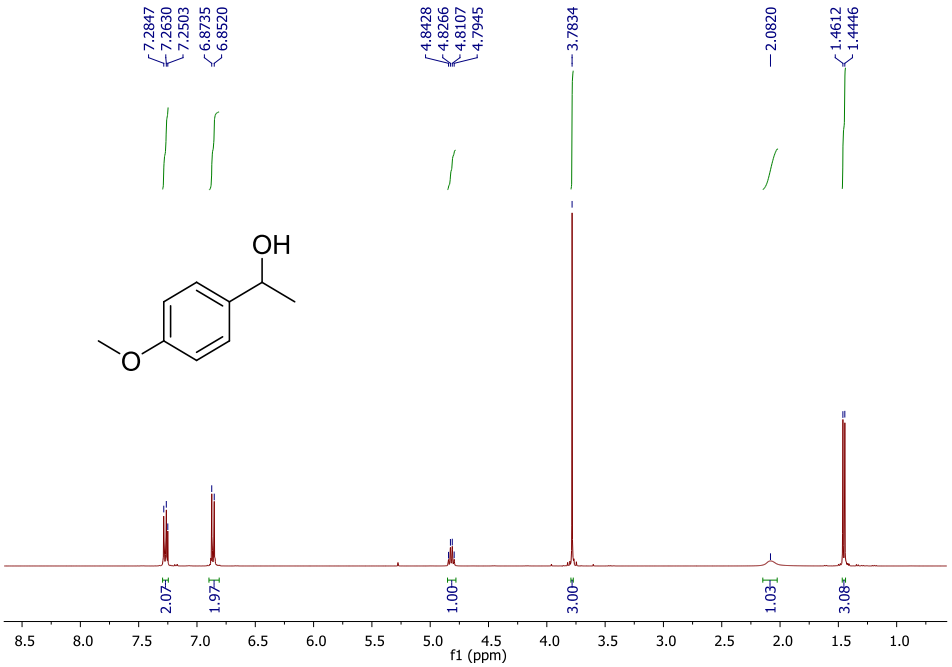


Fig. S37 ^{1}H NMR Spectrum of **5d** in $CDCl_3$ (400 MHz).

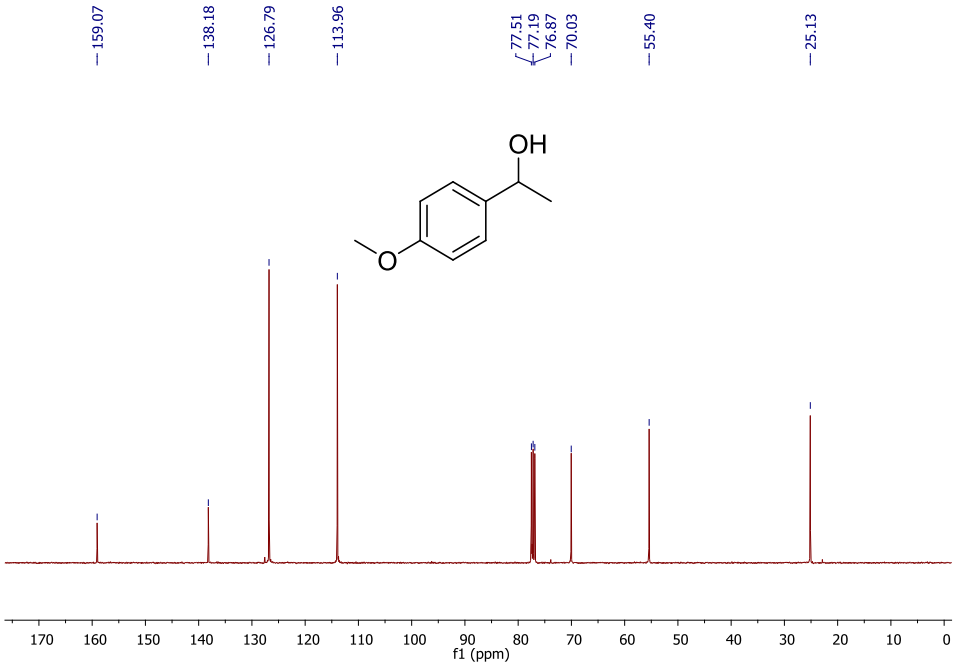


Fig. S38 ^{13}C NMR Spectrum of **5d** in $CDCl_3$ (100 MHz).

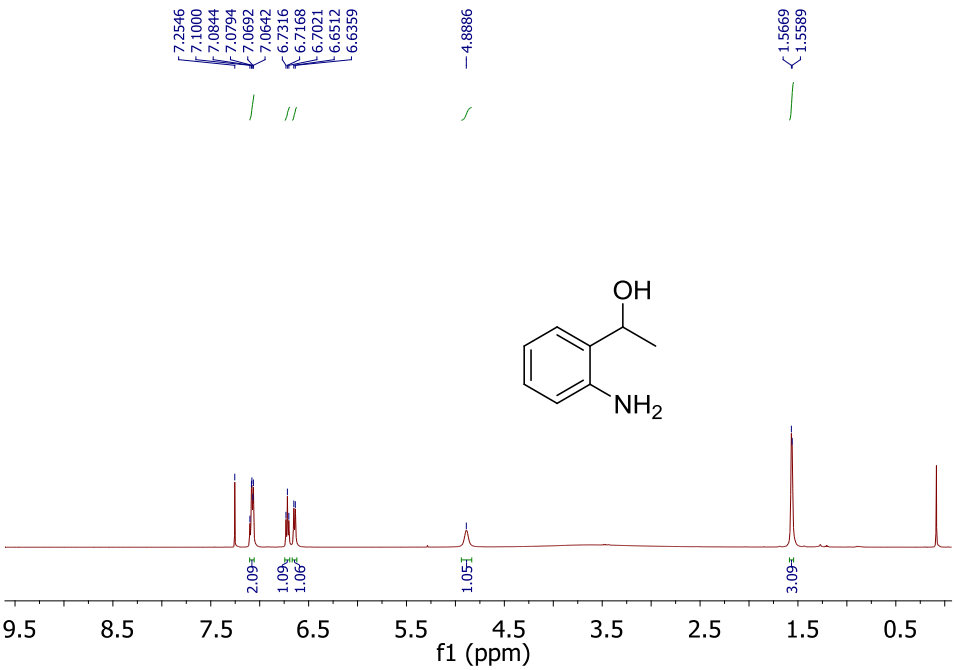


Fig. S39 ^{1}H NMR Spectrum of **5f** in $CDCl_3$ (400 MHz).

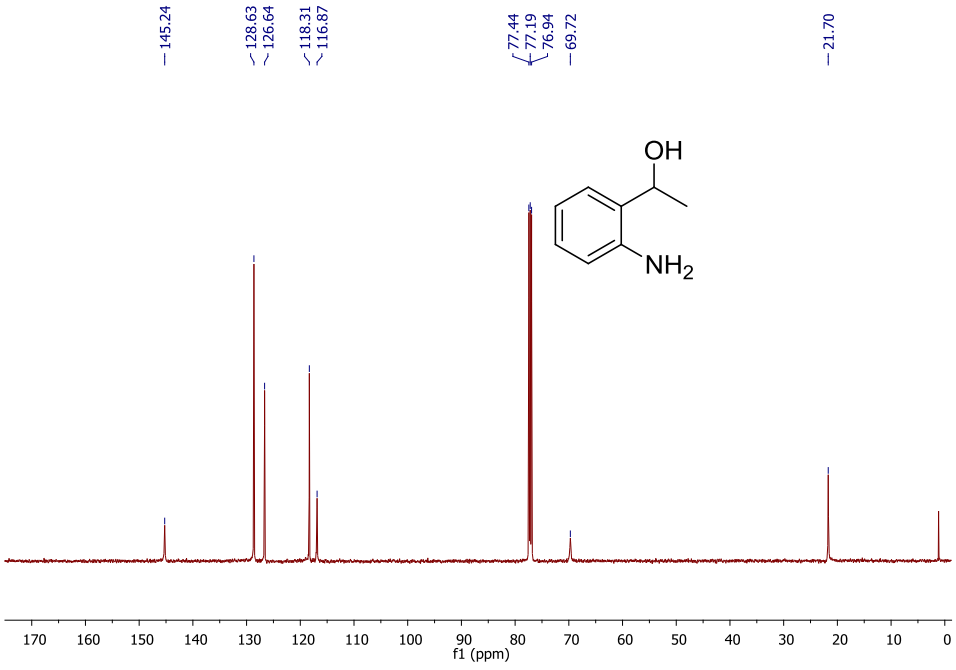


Fig. S40 ^{13}C NMR Spectrum of **5f** in $CDCl_3$ (100 MHz).

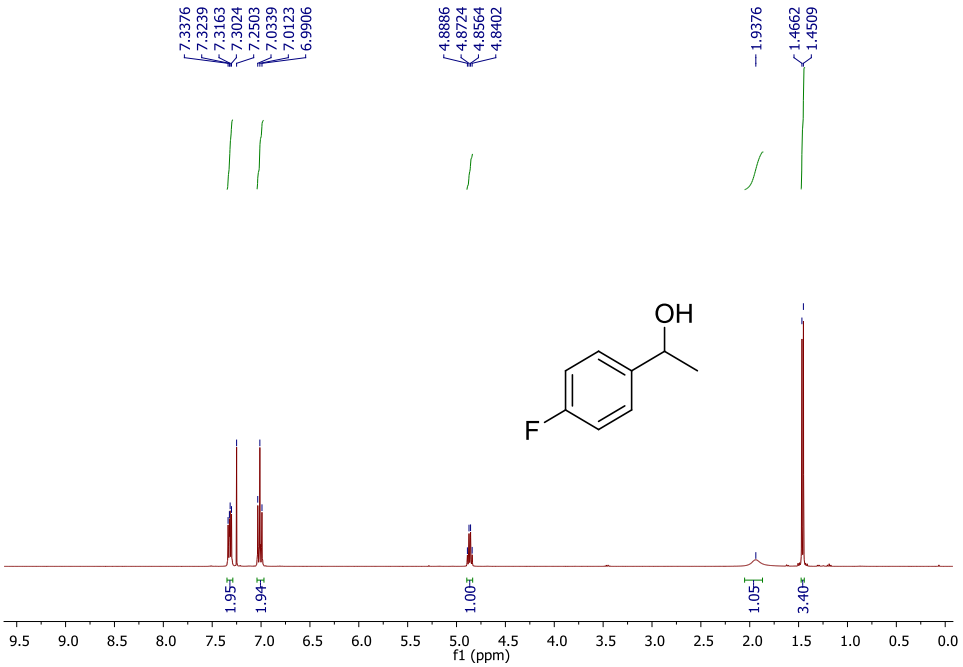


Fig. S41 ^{1}H NMR Spectrum of **5g** in $CDCl_3$ (400 MHz).

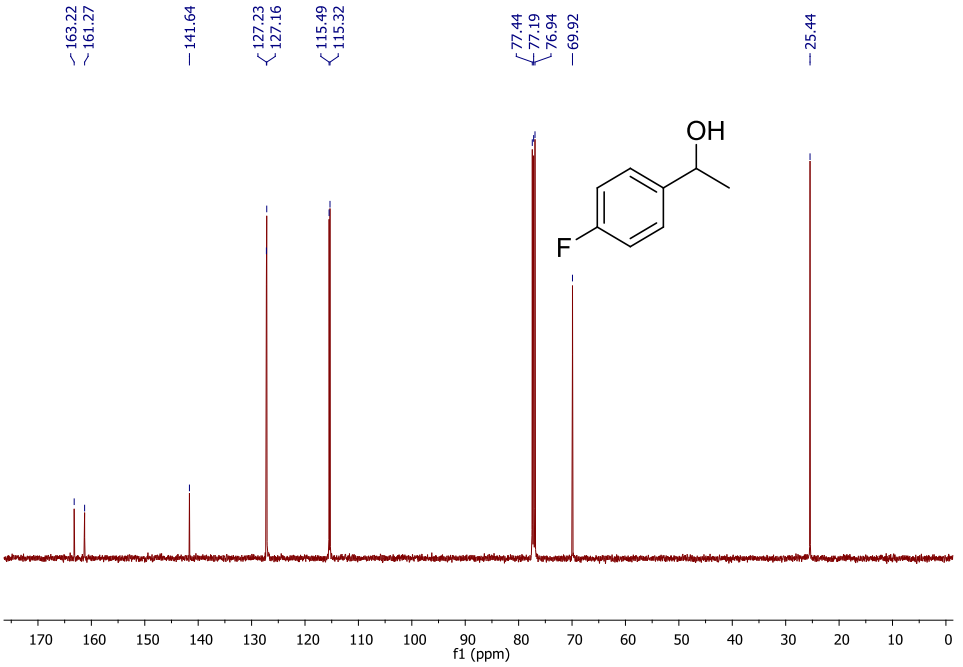


Fig. S42 ^{13}C NMR Spectrum of **5g** in $CDCl_3$ (100 MHz).

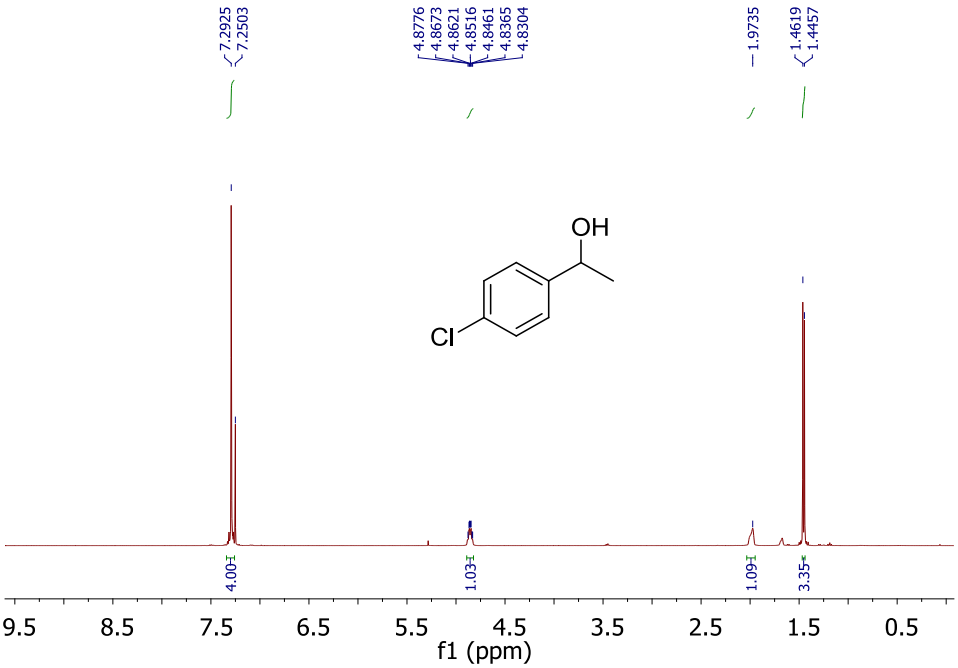


Fig. S43 ^{1}H NMR Spectrum of **5h** in $CDCl_3$ (400 MHz).

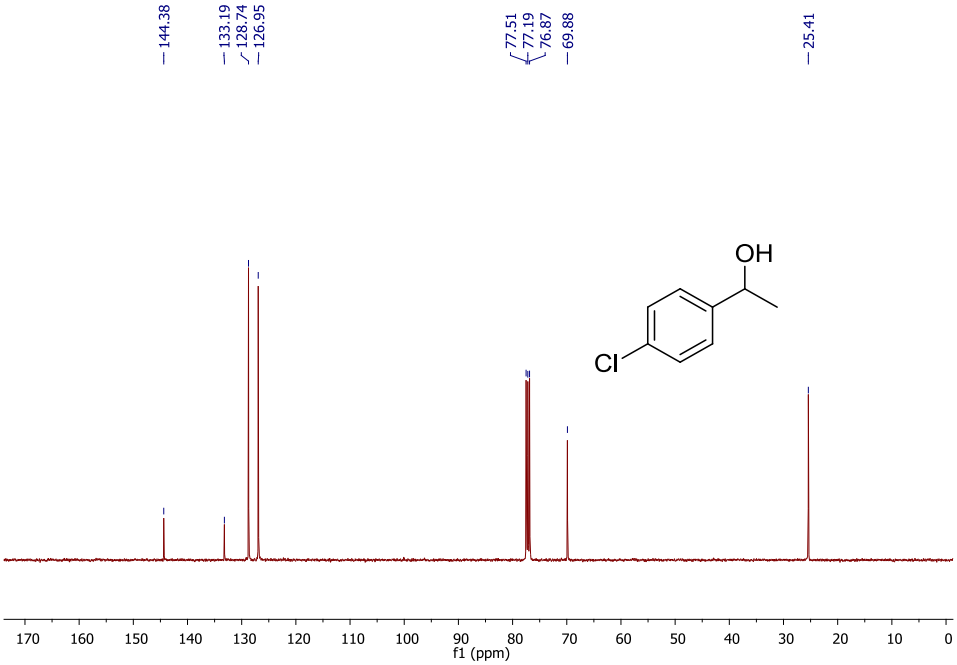


Fig. S44 ^{13}C NMR Spectrum of **5h** in $CDCl_3$ (100 MHz).

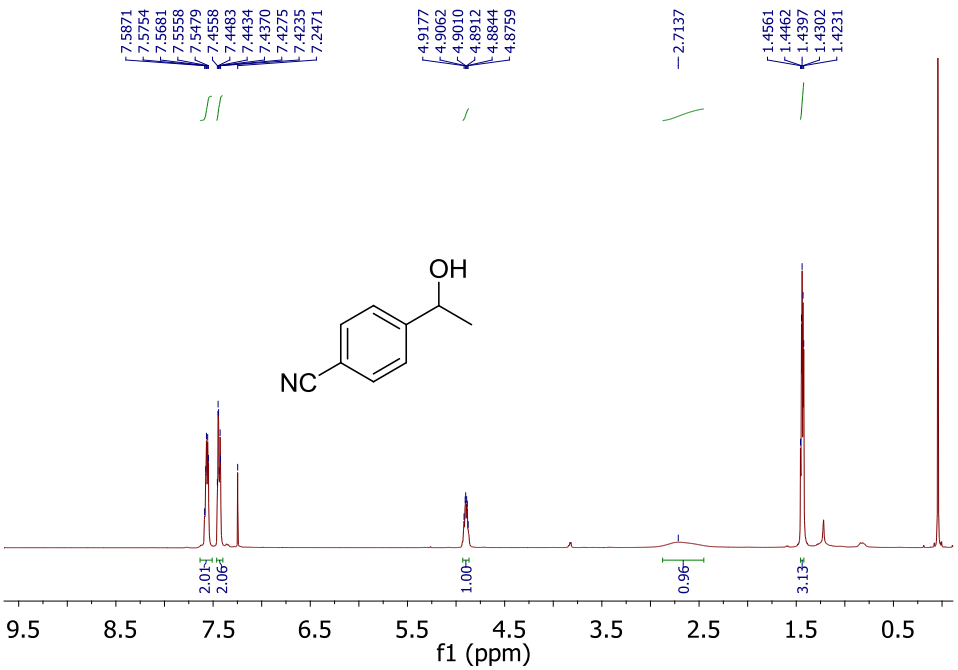


Fig. S45 ^{1}H NMR Spectrum of **5k** in $CDCl_3$ (400 MHz).

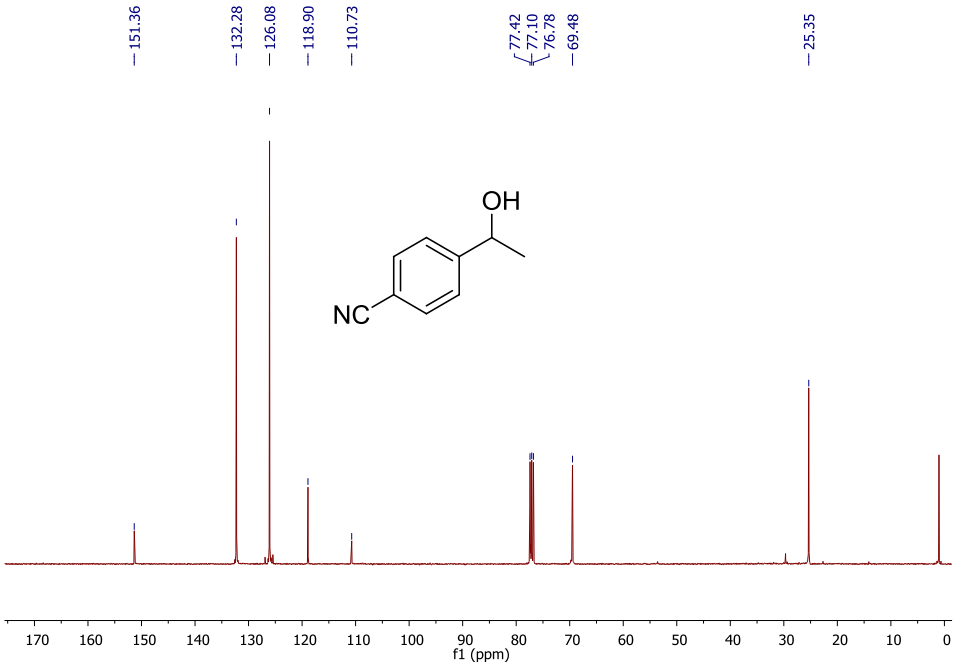


Fig. S46 ^{13}C NMR Spectrum of **5k** in $CDCl_3$ (100 MHz).

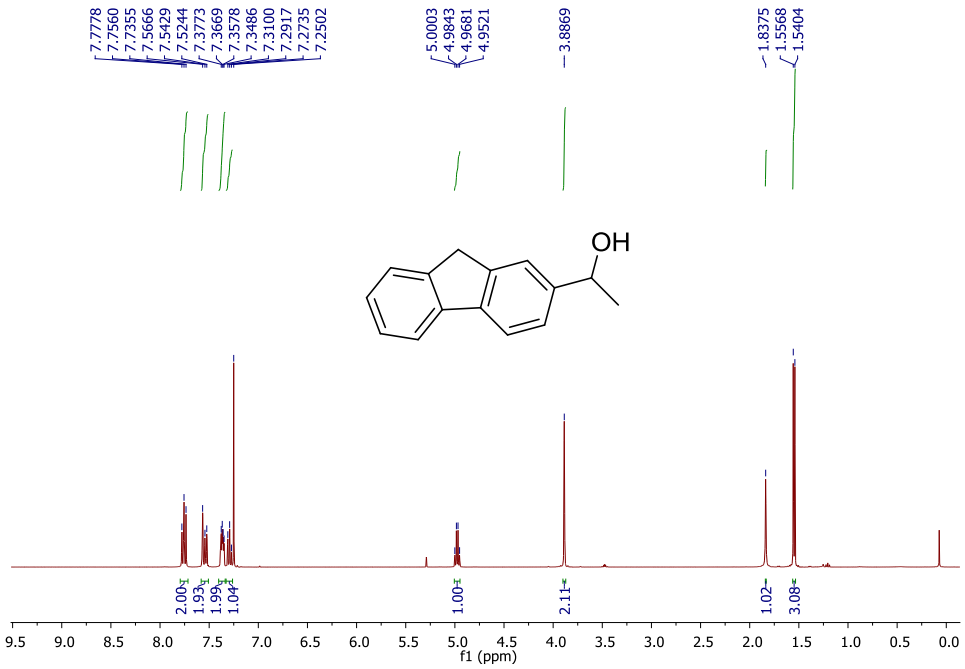


Fig. S47 ^{1}H NMR Spectrum of **5m** in $CDCl_3$ (400 MHz).

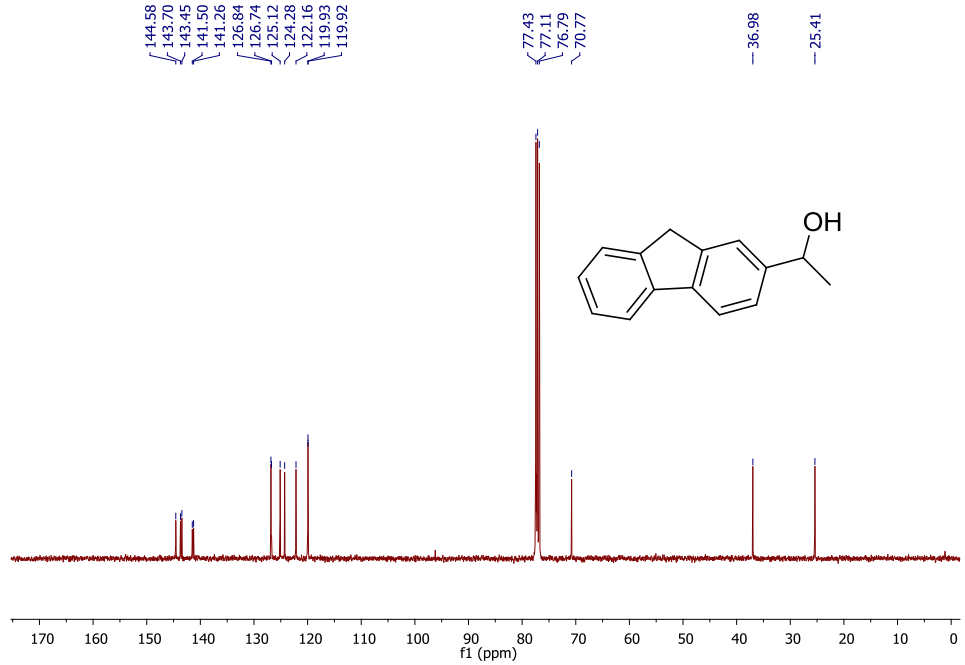


Fig. S48 ^{13}C NMR Spectrum of **5m** in $CDCl_3$ (100 MHz).

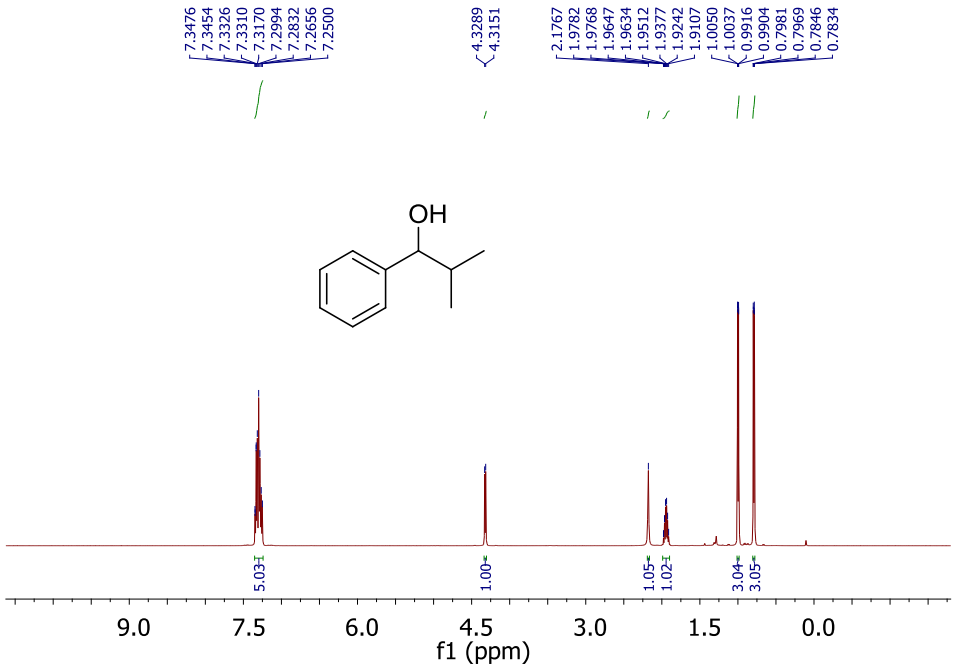


Fig. S49 ^{1}H NMR Spectrum of **5n** in $CDCl_3$ (400 MHz).

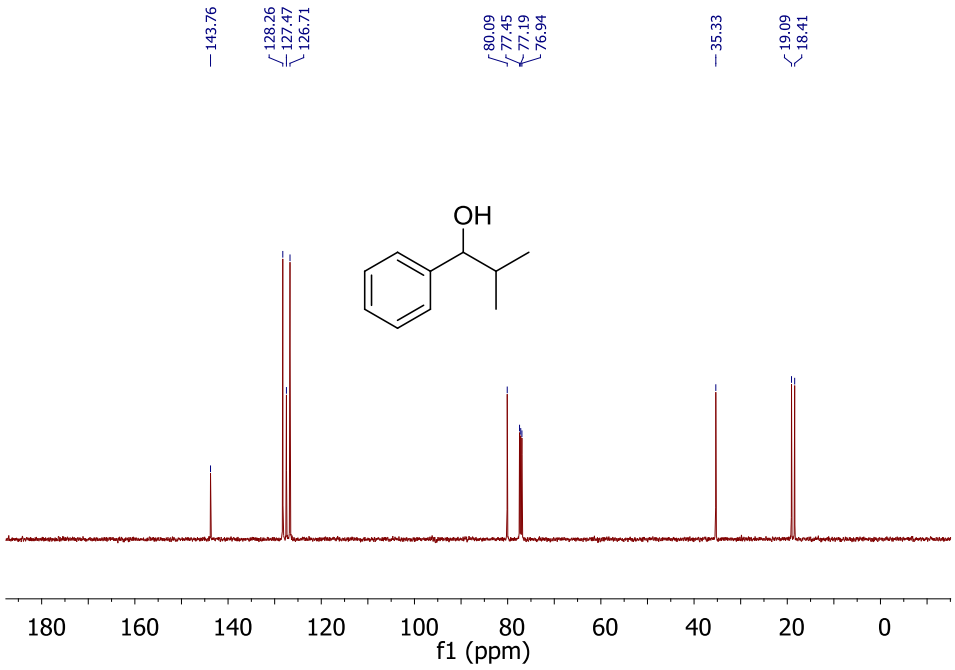


Fig. S50 ^{13}C NMR Spectrum of **5n** in $CDCl_3$ (100 MHz).

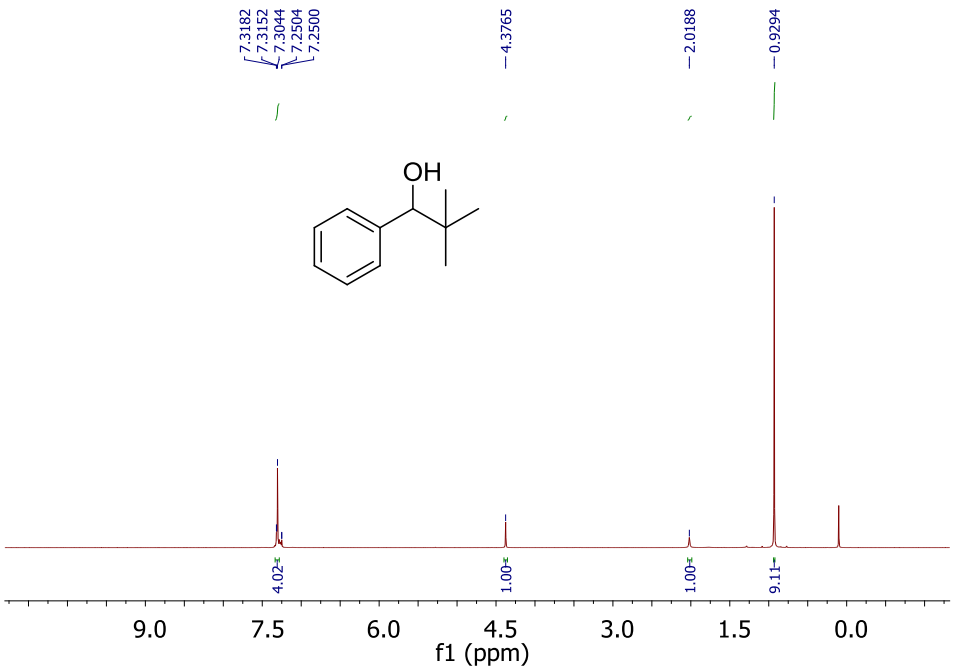


Fig. S51 ^{1}H NMR Spectrum of **5o** in $CDCl_3$ (400 MHz).

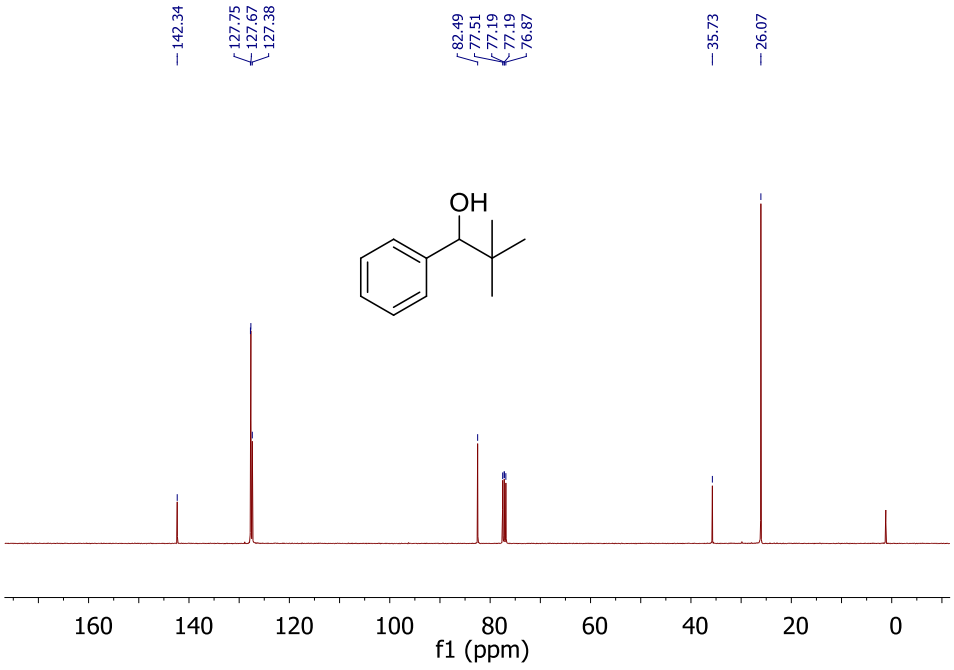


Fig. S52 ^{13}C NMR Spectrum of **5o** in $CDCl_3$ (100 MHz).

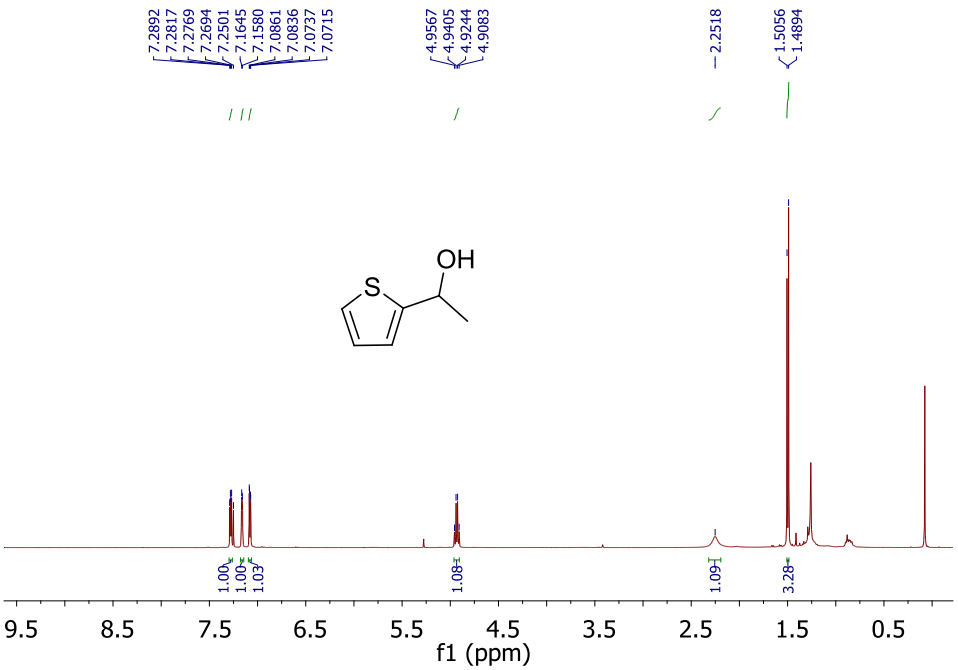


Fig. S53 ^{1}H NMR Spectrum of **5r** in $CDCl_3$ (400 MHz).

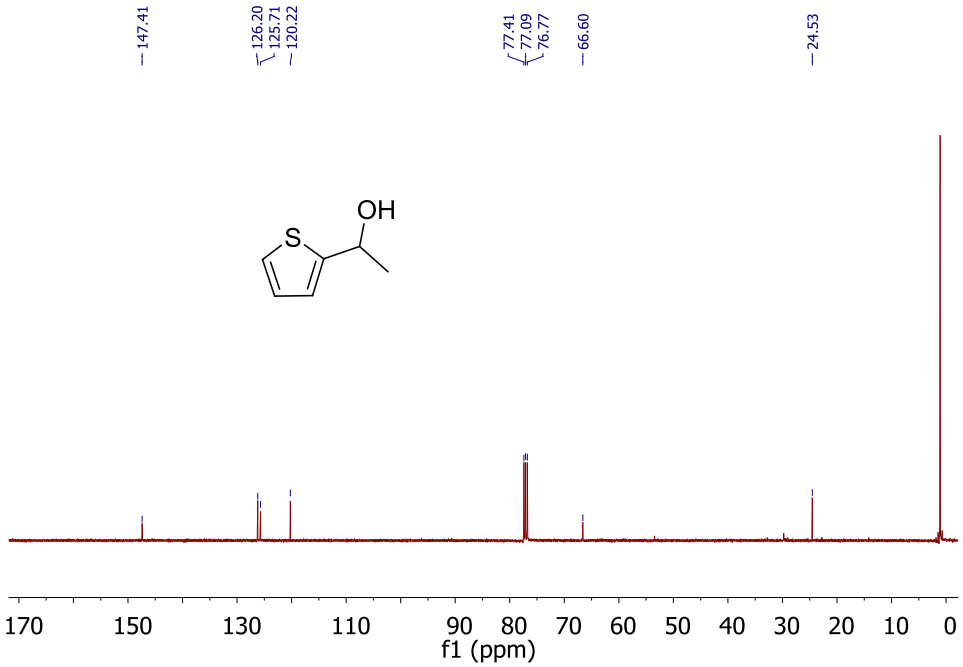


Fig. S54 ^{13}C NMR Spectrum of **5r** in $CDCl_3$ (100 MHz).

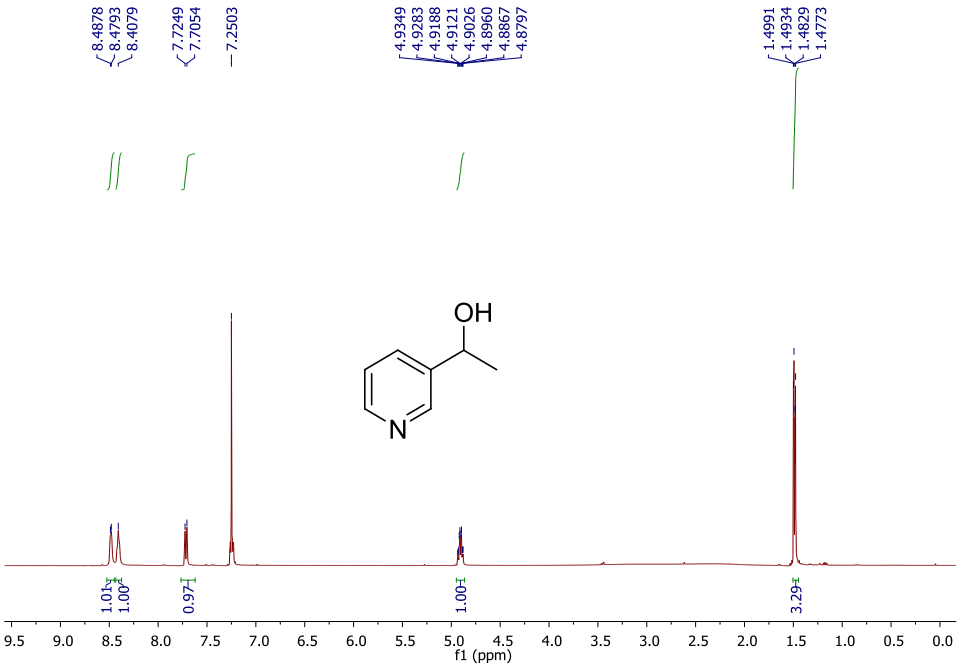


Fig. S55 ^{1}H NMR Spectrum of **5s** in $CDCl_3$ (400 MHz).

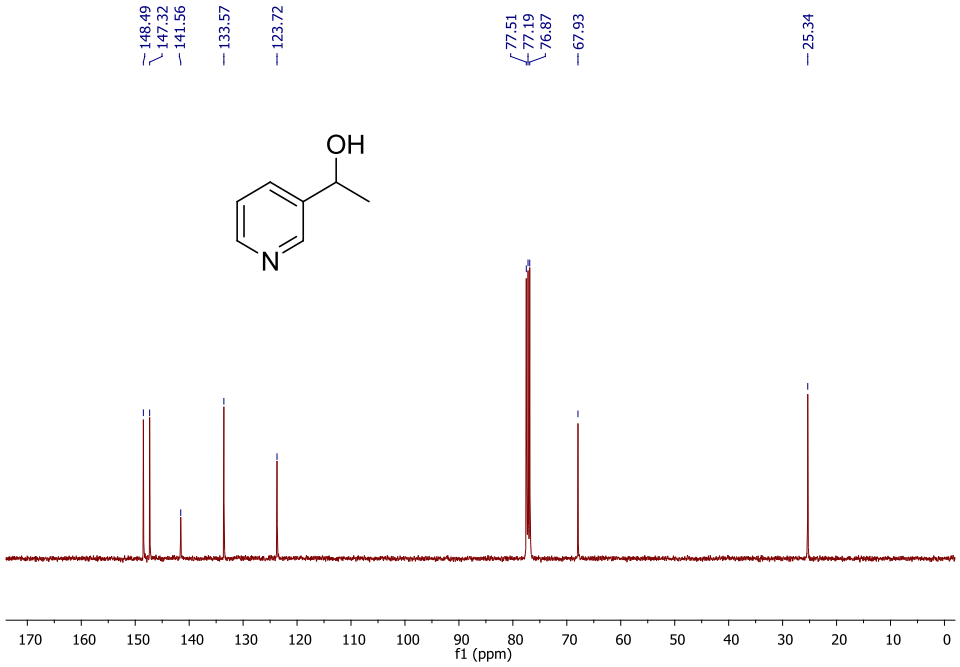


Fig. S56 ^{13}C NMR Spectrum of **5s** in $CDCl_3$ (100 MHz).

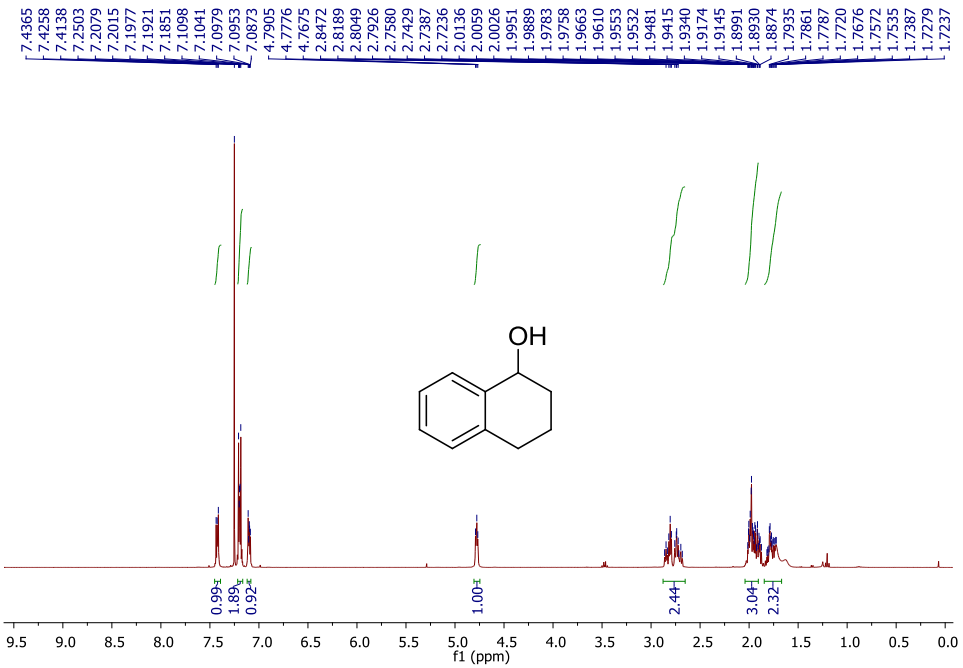


Fig. S57 ^{1}H NMR Spectrum of **6a** in $CDCl_3$ (400 MHz).

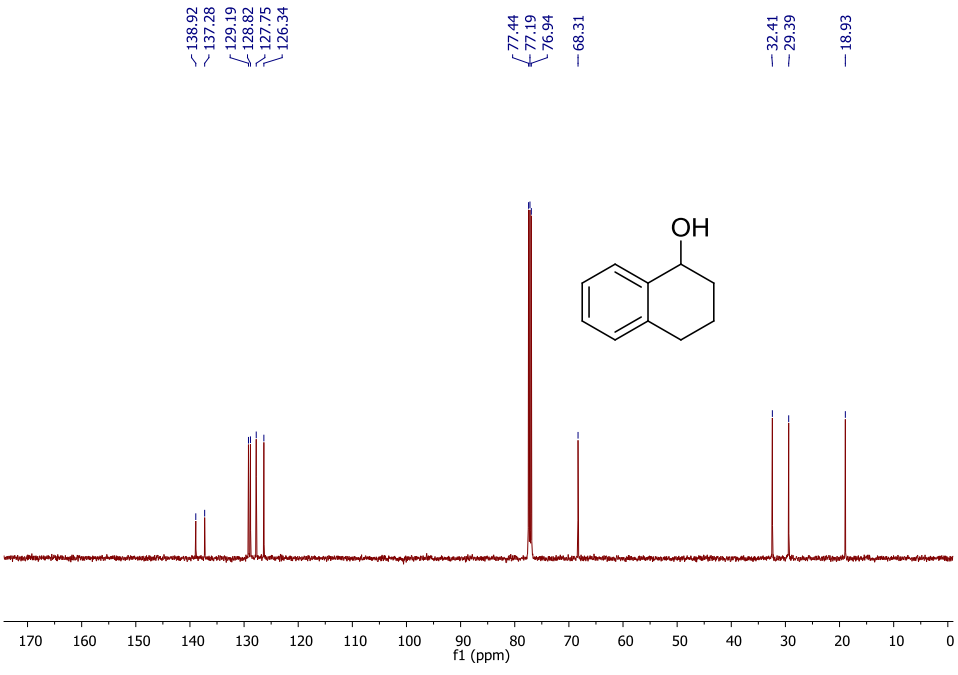


Fig. S58 ^{13}C NMR Spectrum of **6a** in $CDCl_3$ (100 MHz).

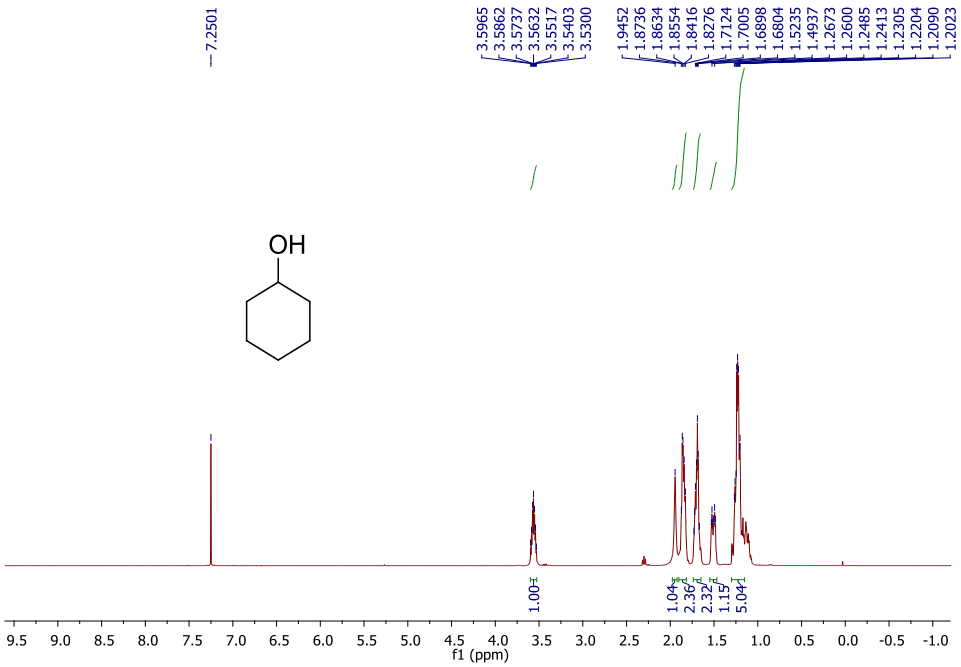


Fig. S59 ^{1}H NMR Spectrum of **6b** in $CDCl_3$ (400 MHz).

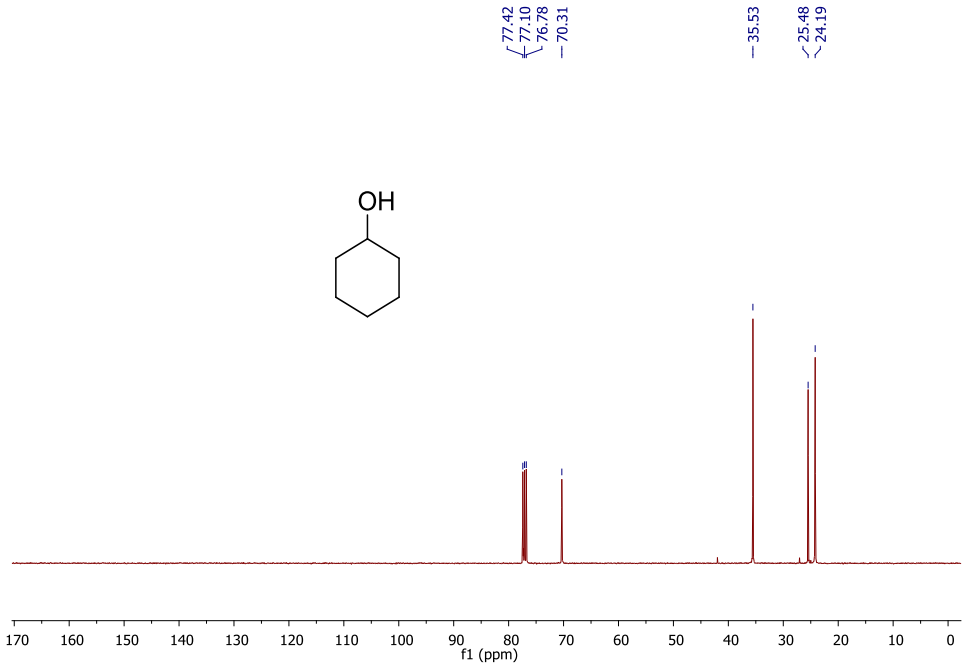


Fig. S60 ^{13}C NMR Spectrum of **6b** in $CDCl_3$ (100 MHz).

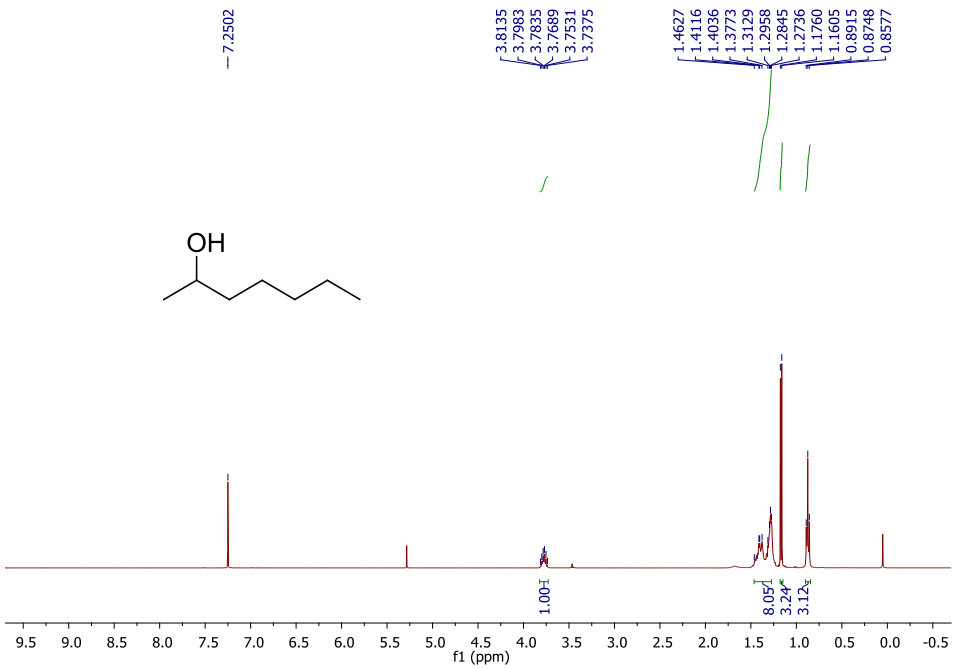


Fig. S61 ^{1}H NMR Spectrum of **6d** in $CDCl_3$ (400 MHz).

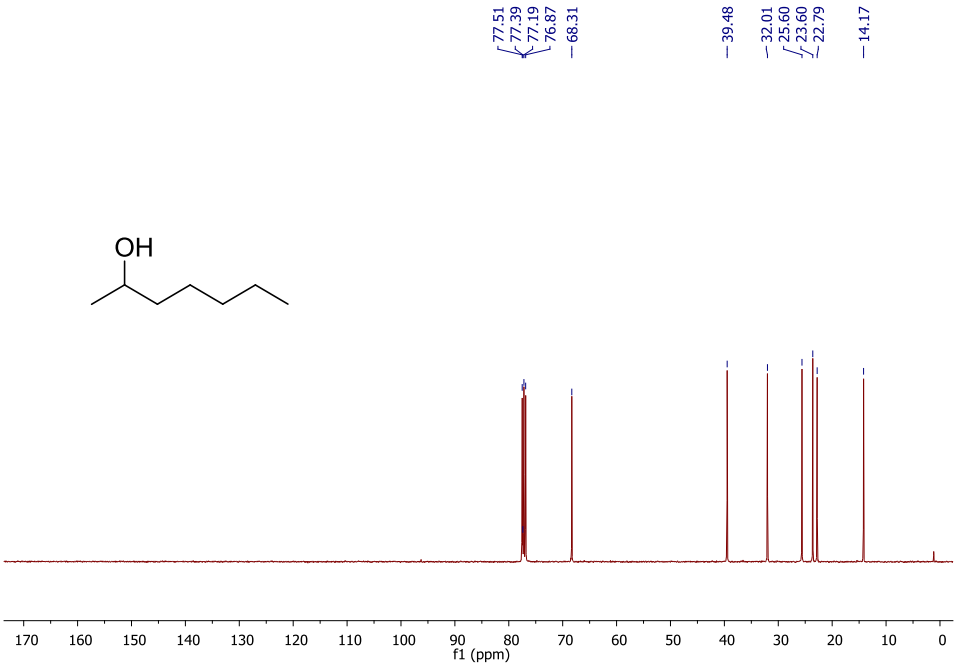


Fig. S62 ^{13}C NMR Spectrum of **6d** in $CDCl_3$ (100 MHz).

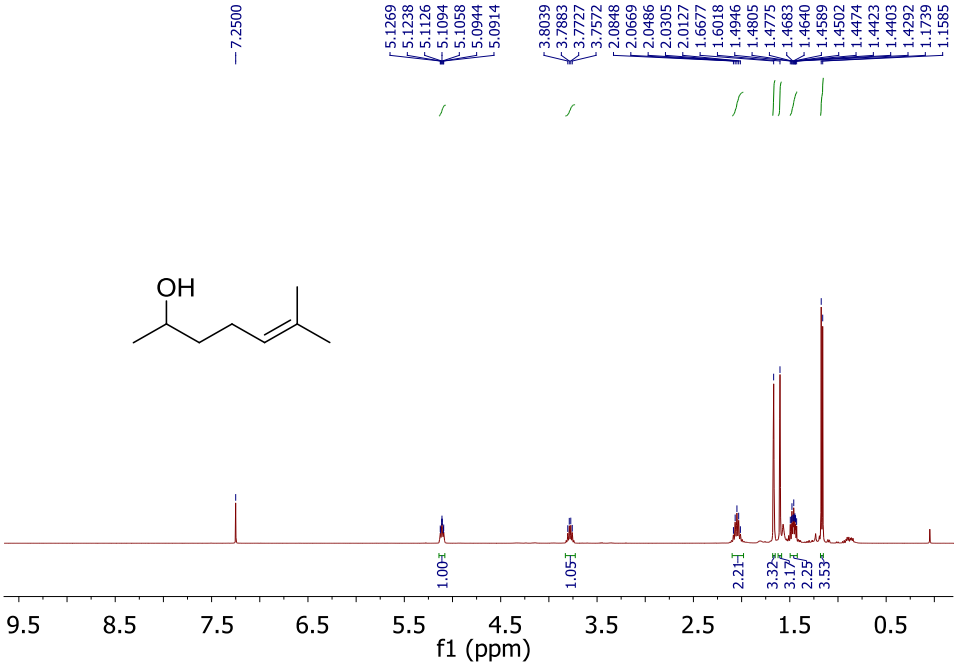


Fig. S63 ^{1}H NMR Spectrum of **6g** in $CDCl_3$ (400 MHz).

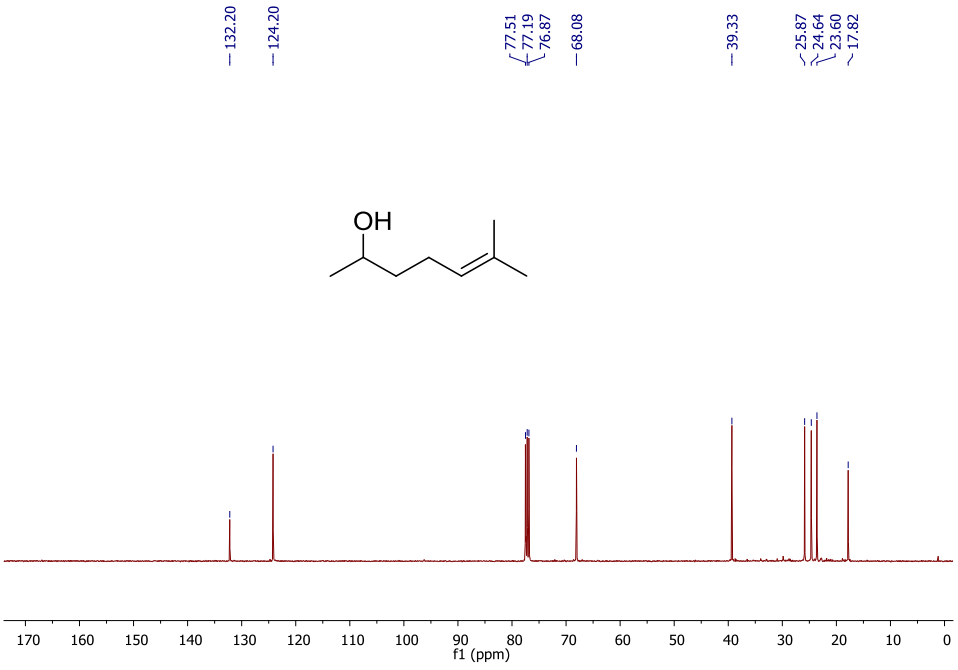


Fig. S64 ^{13}C NMR Spectrum of **6g** in $CDCl_3$ (100 MHz).

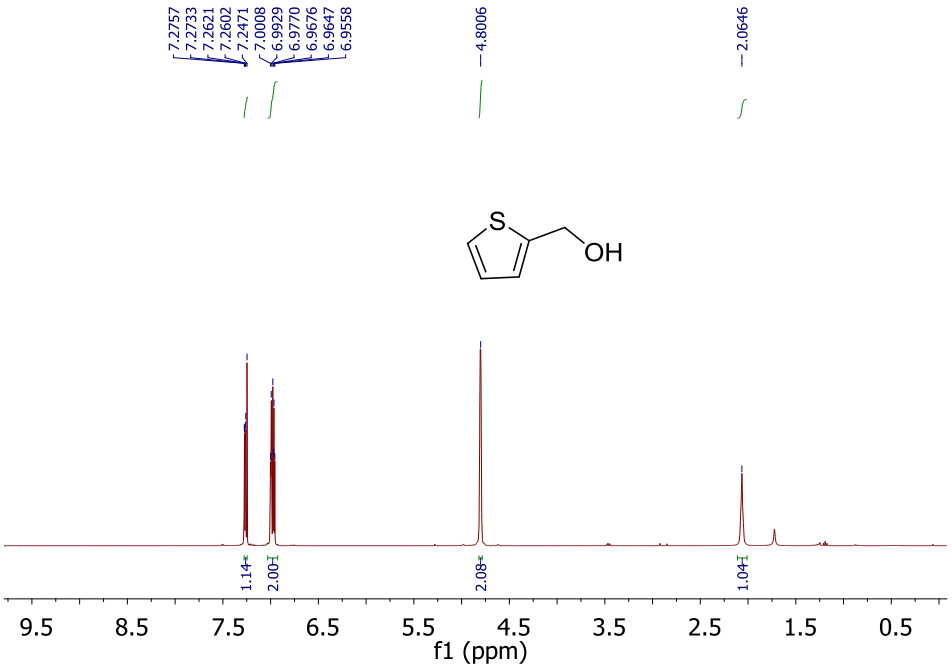


Fig. S65 ^{1}H NMR Spectrum of **7f** in $CDCl_3$ (400 MHz).

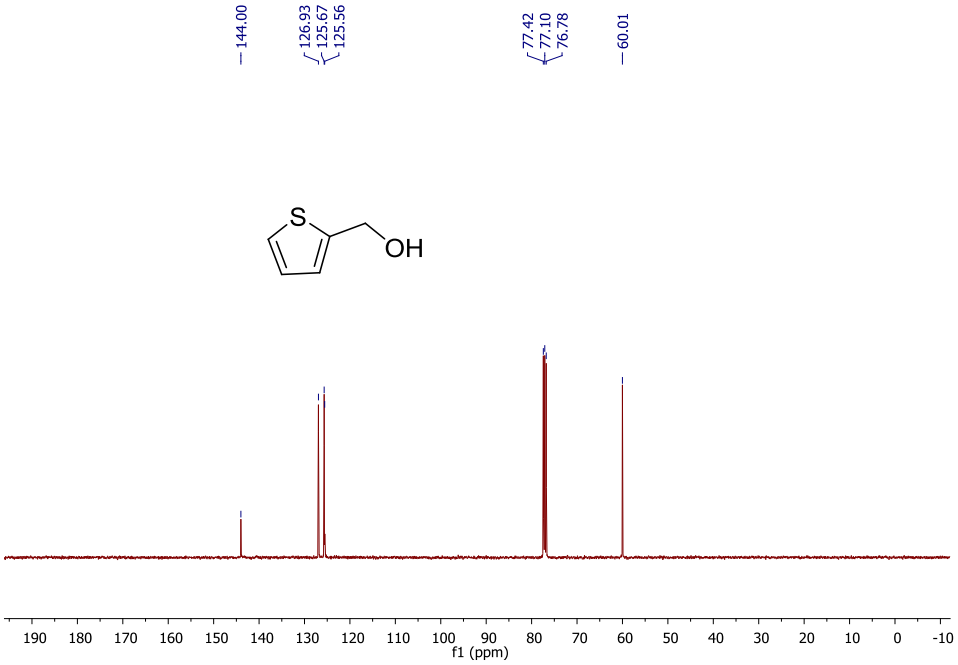


Fig. S66 ^{13}C NMR Spectrum of **7f** in $CDCl_3$ (100 MHz).

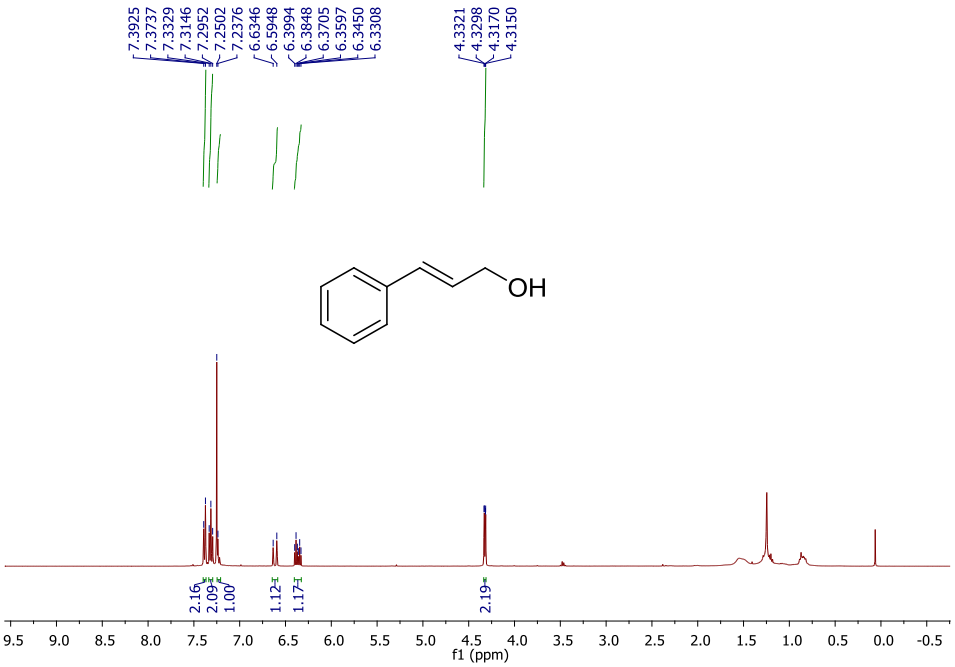


Fig. S67 ^{1}H NMR Spectrum of **7g** in $CDCl_3$ (400 MHz).

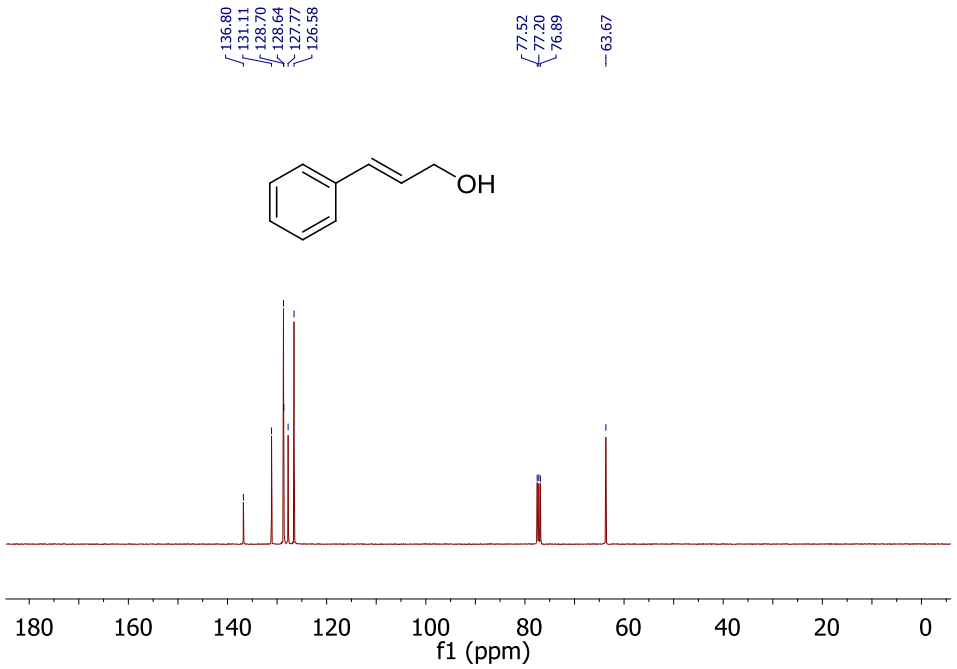


Fig. S68 ^{13}C NMR Spectrum of **7g** in $CDCl_3$ (100 MHz).

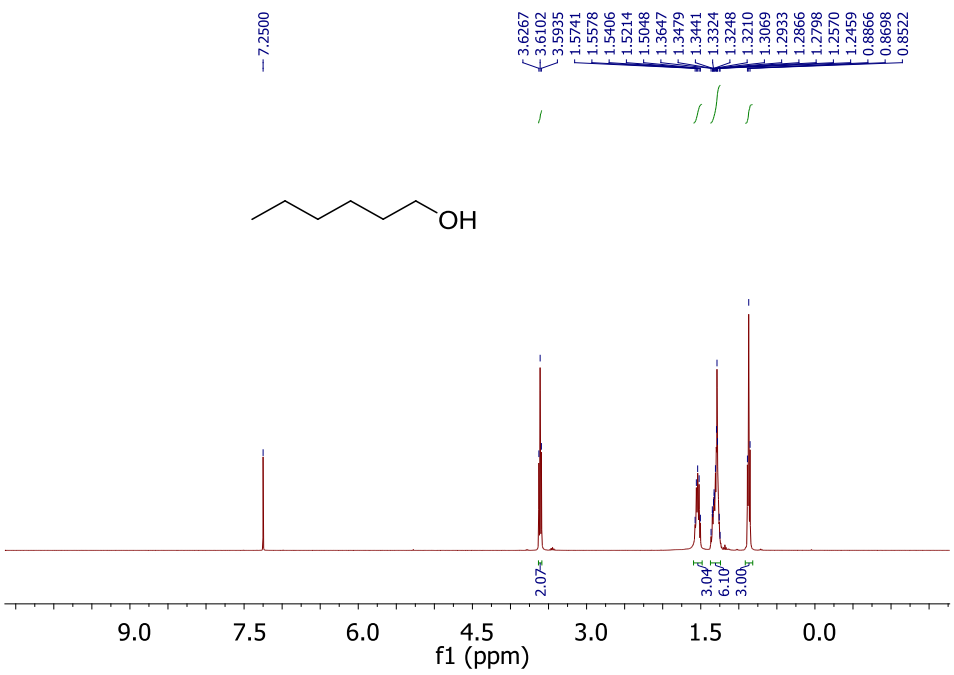


Fig. S69 ^{1}H NMR Spectrum of **7h** in $CDCl_3$ (400 MHz).

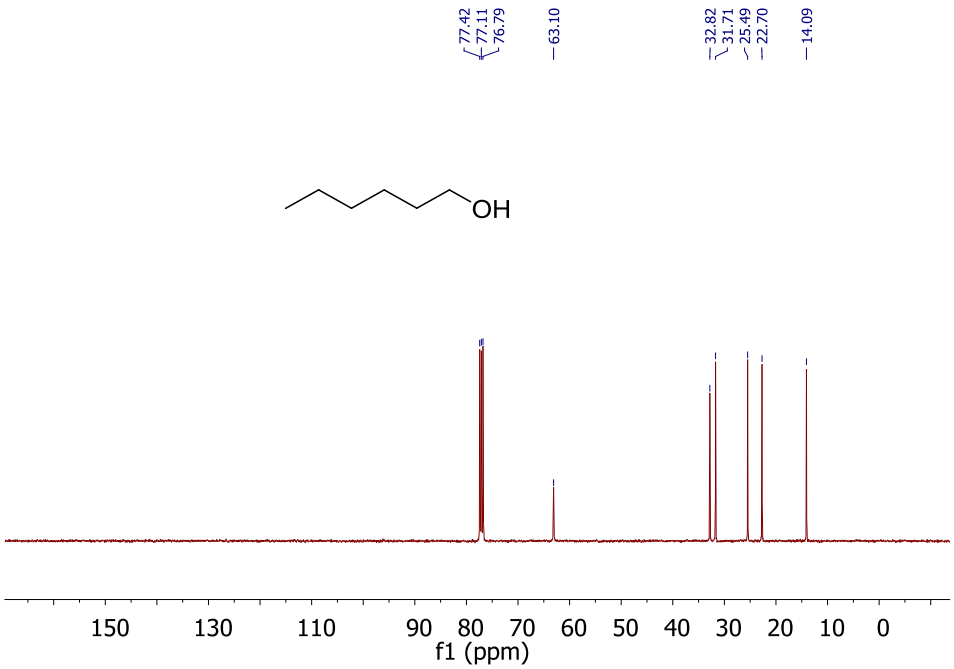


Fig. S70 ^{13}C NMR Spectrum of **7h** in $CDCl_3$ (100 MHz).

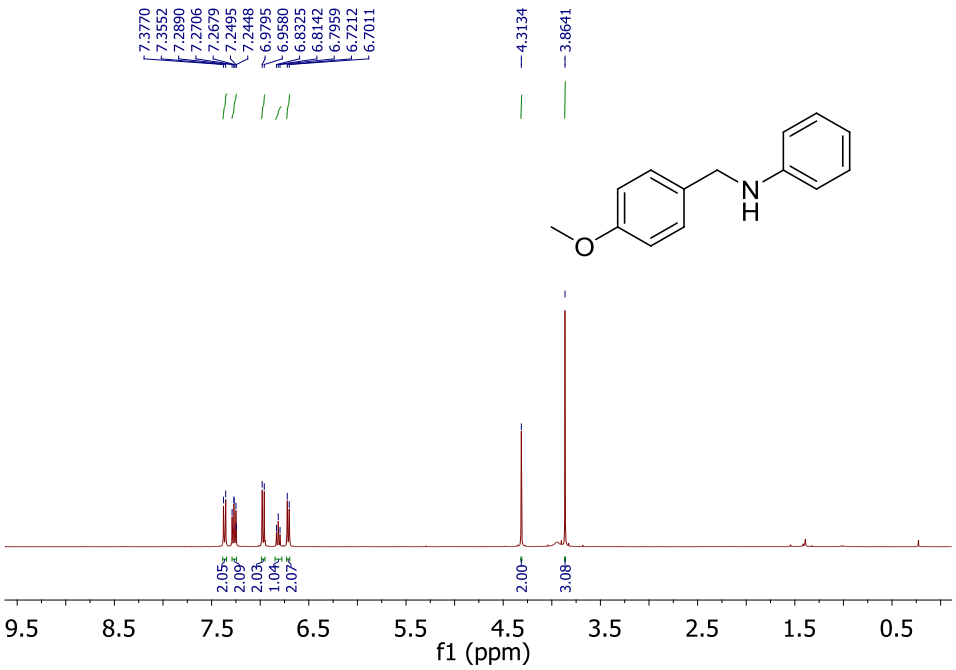


Fig. S71 ^{1}H NMR Spectrum of **8a** in $CDCl_3$ (400 MHz).

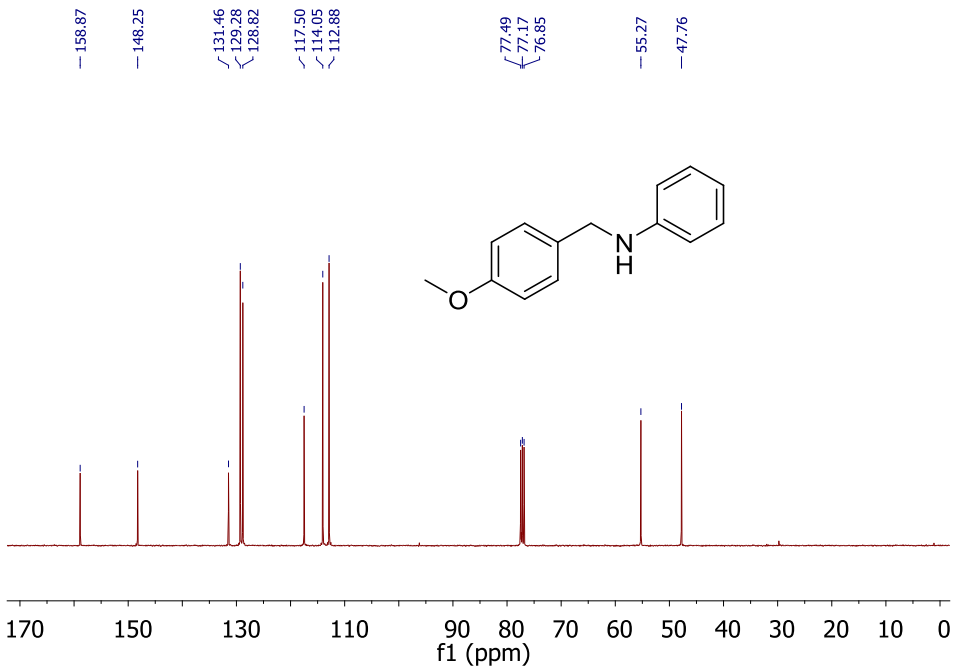


Fig. S72 ^{13}C NMR Spectrum of **8a** in $CDCl_3$ (100 MHz).

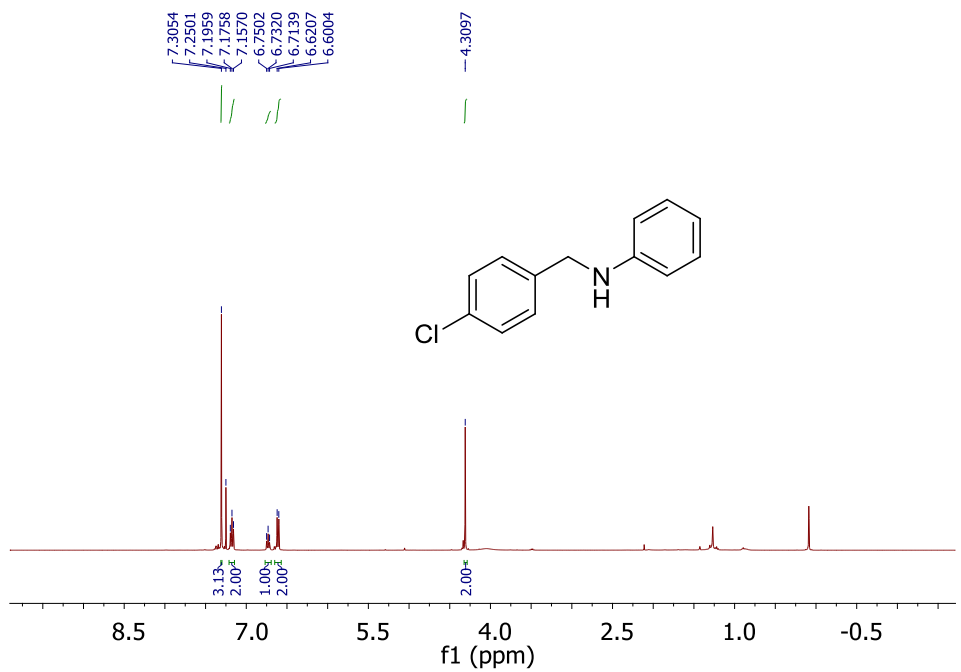


Fig. S73 ^{1}H NMR Spectrum of **8b** in $CDCl_3$ (400 MHz).

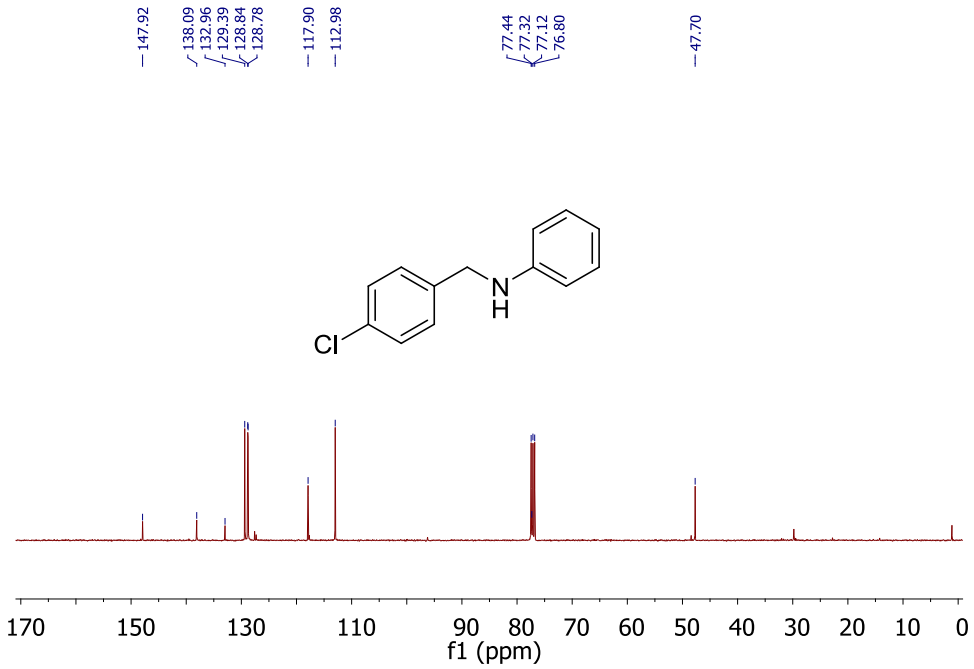


Fig. S74 ^{13}C NMR Spectrum of **8b** in $CDCl_3$ (100 MHz).

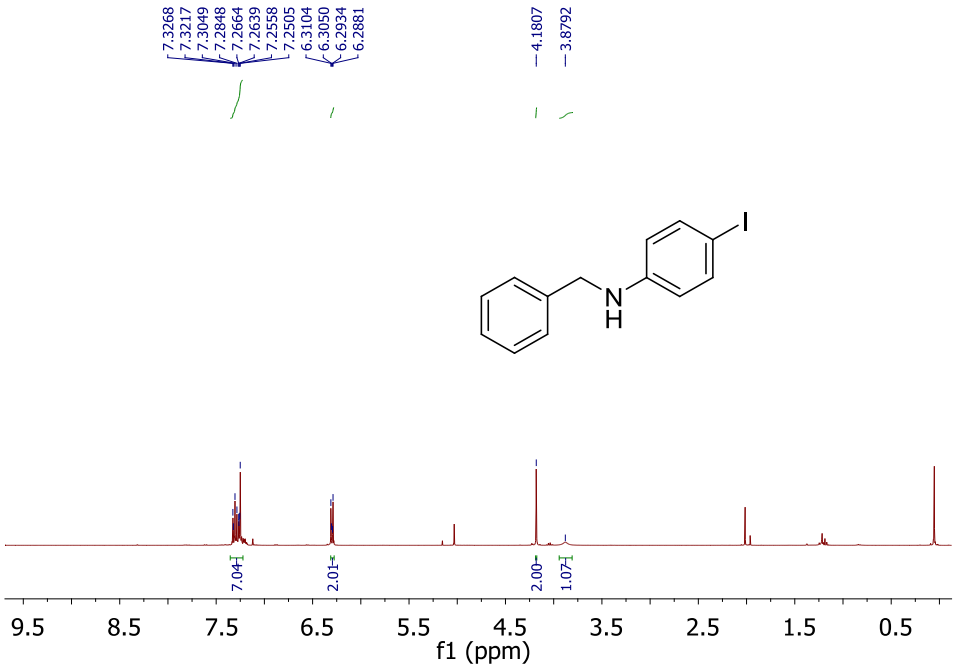


Fig. S75 ^{1}H NMR Spectrum of **8c** in $CDCl_3$ (400 MHz).

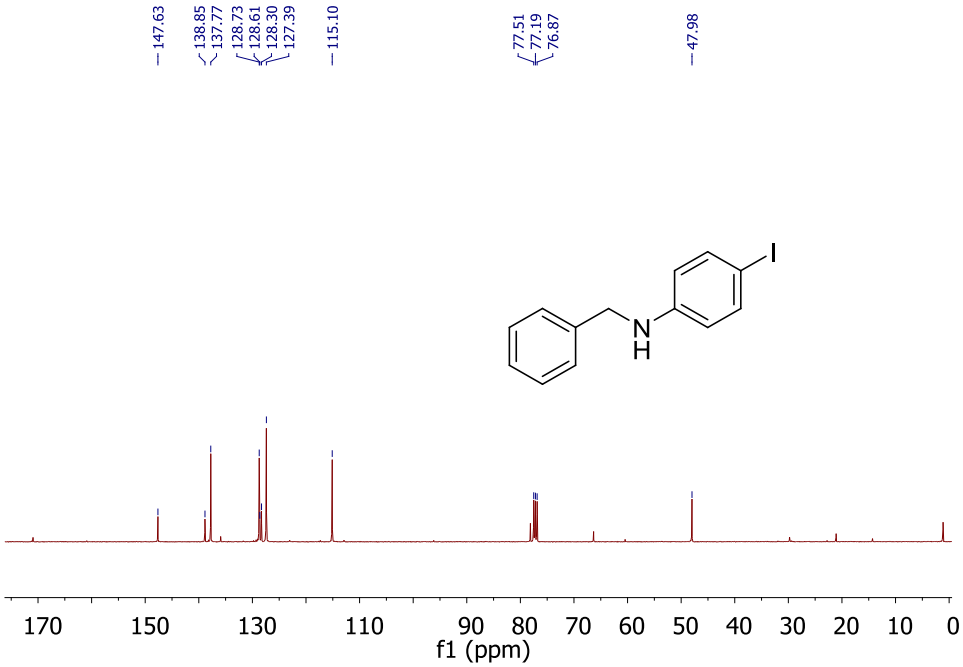


Fig. S76 ^{13}C NMR Spectrum of **8c** in $CDCl_3$ (100 MHz).

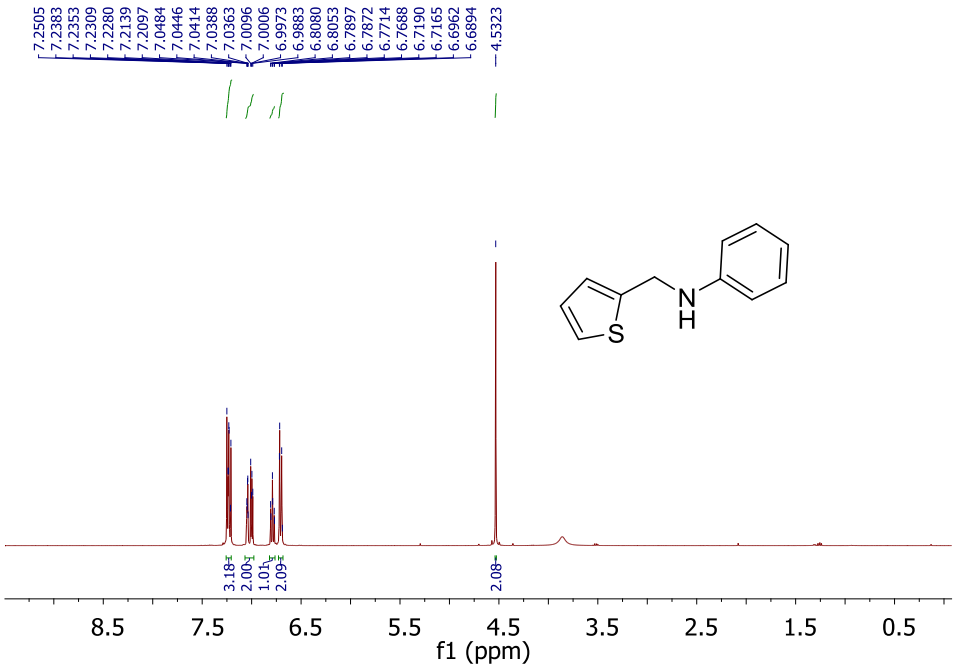


Fig. S77 ^{1}H NMR Spectrum of **8d** in $CDCl_3$ (400 MHz).

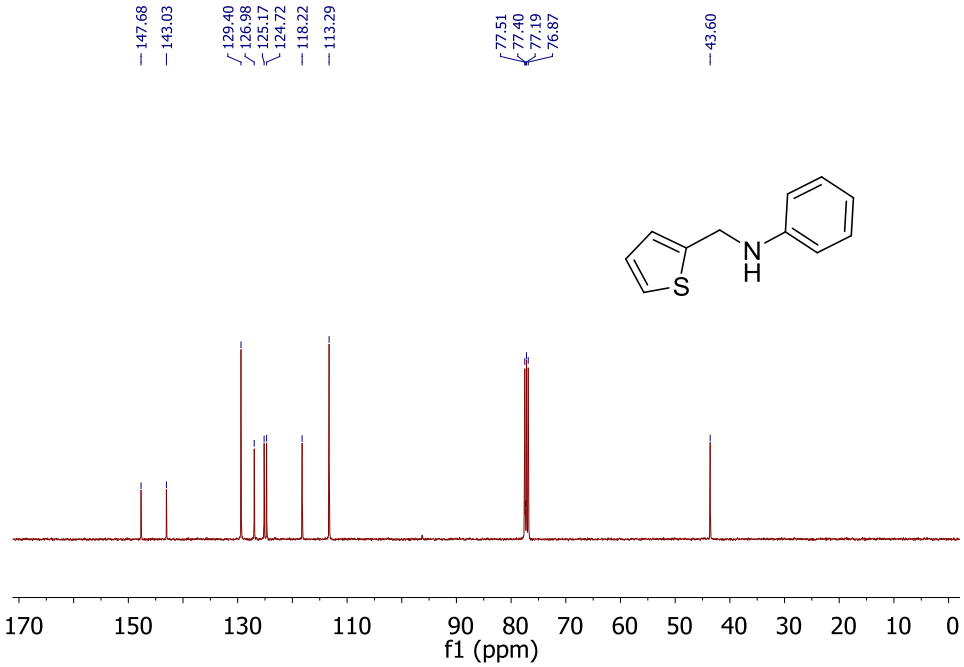


Fig. S78 ^{13}C NMR Spectrum of **8d** in $CDCl_3$ (100 MHz).

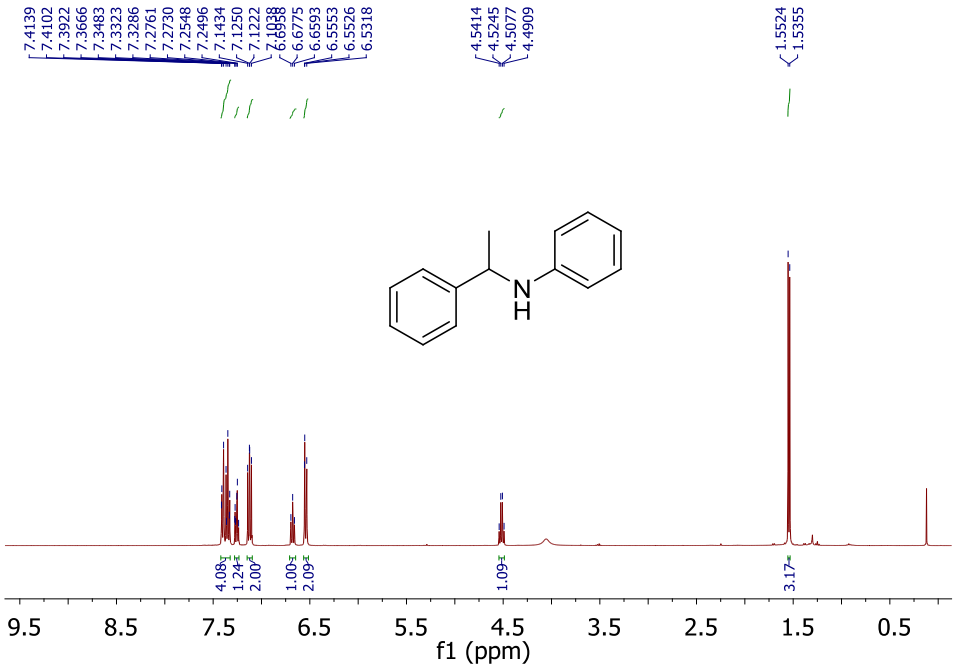


Fig. S79 ^{1}H NMR Spectrum of **8e** in $CDCl_3$ (400 MHz).

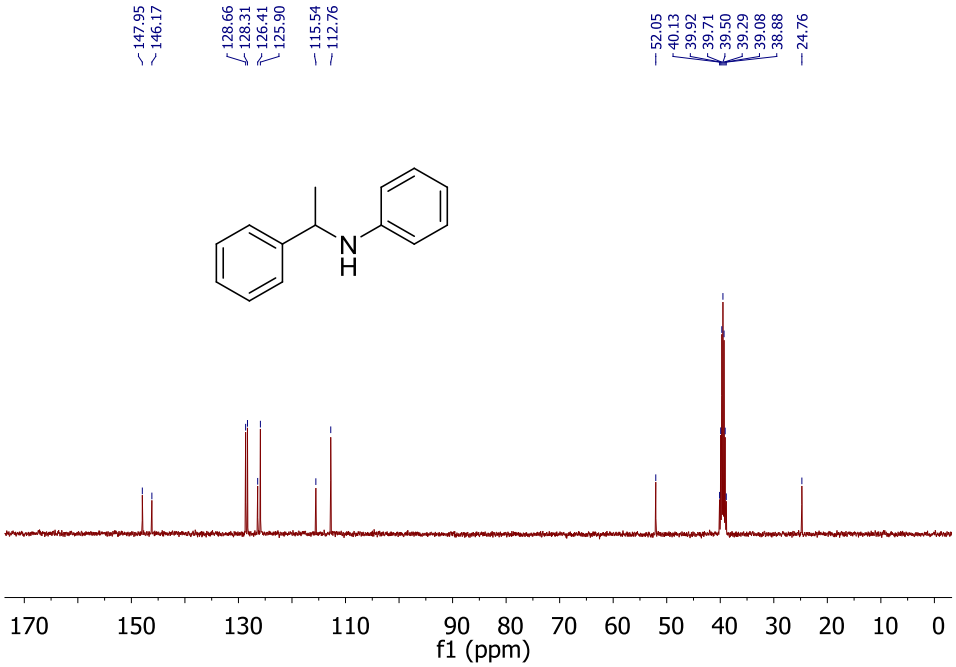


Fig. S80 ^{13}C NMR Spectrum of **8e** in $CDCl_3$ (100 MHz).

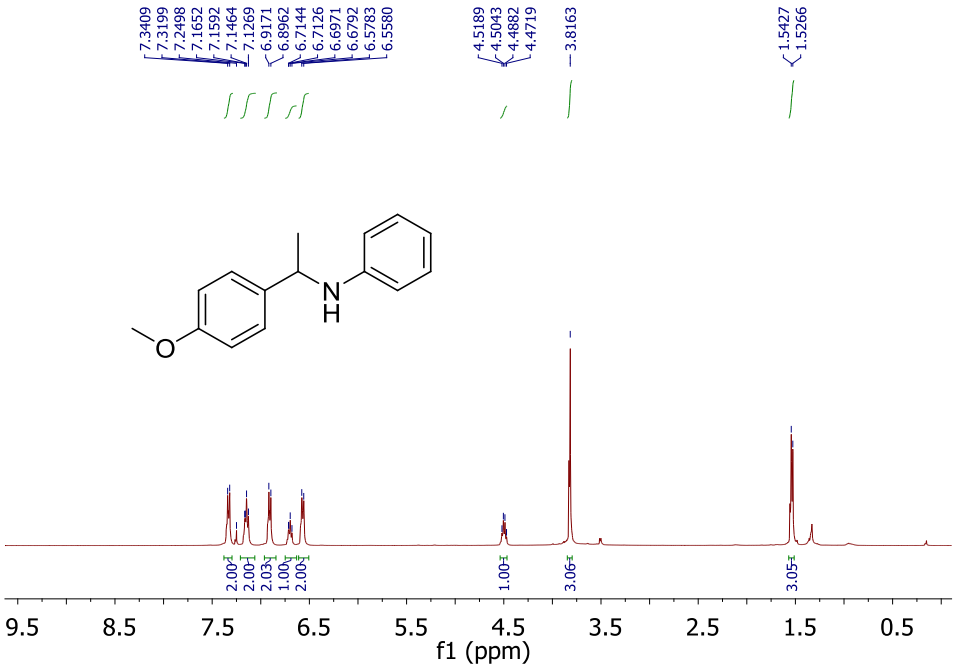


Fig. S81 ^{1}H NMR Spectrum of **8f** in $CDCl_3$ (400 MHz).

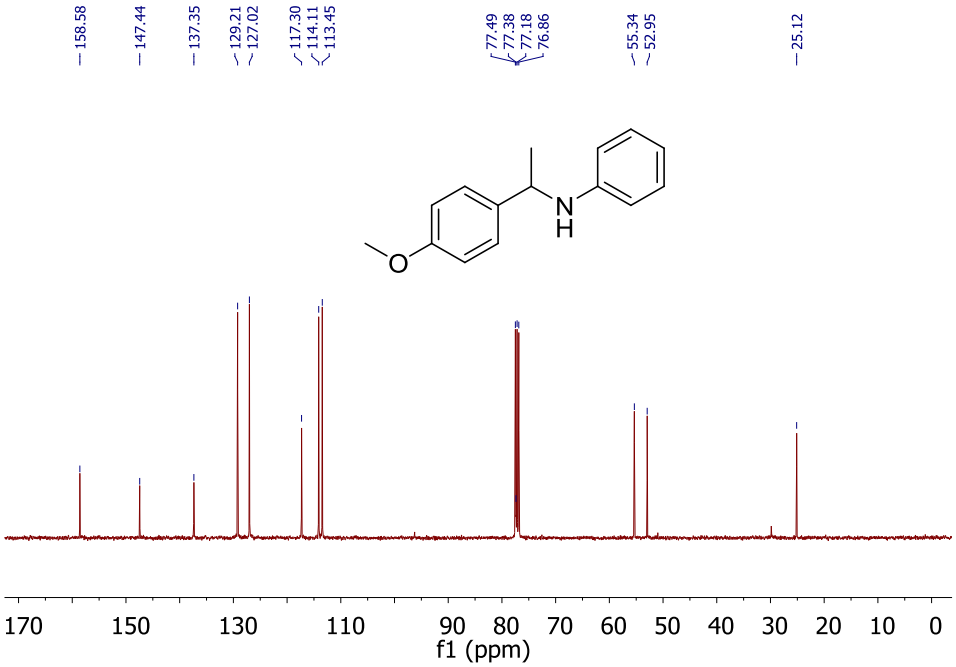


Fig. S82 ^{13}C NMR Spectrum of **8f** in $CDCl_3$ (100 MHz).

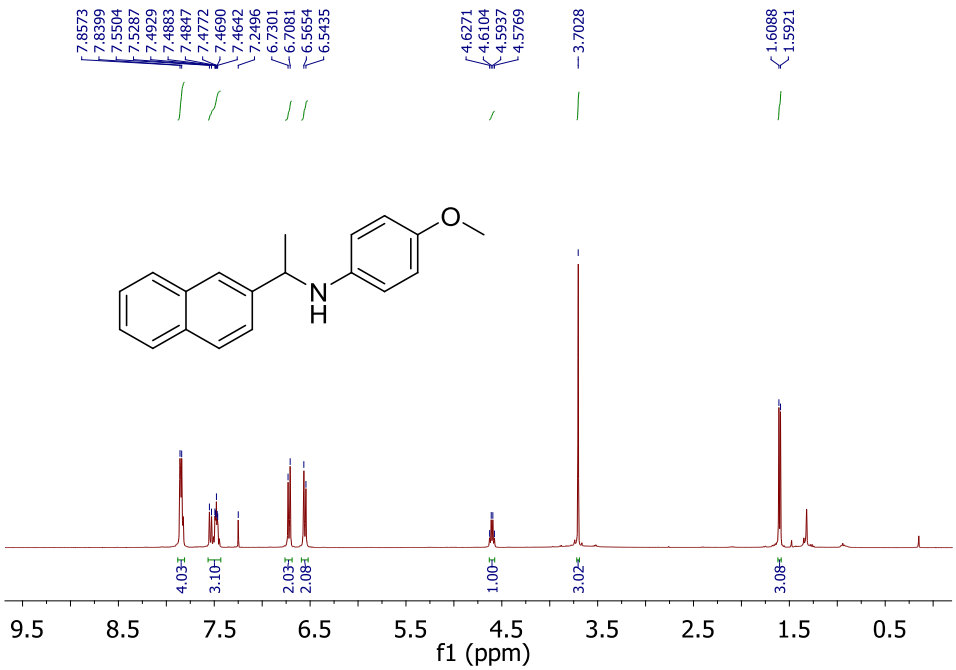


Fig. S83 ^{1}H NMR Spectrum of **8g** in $CDCl_3$ (400 MHz).

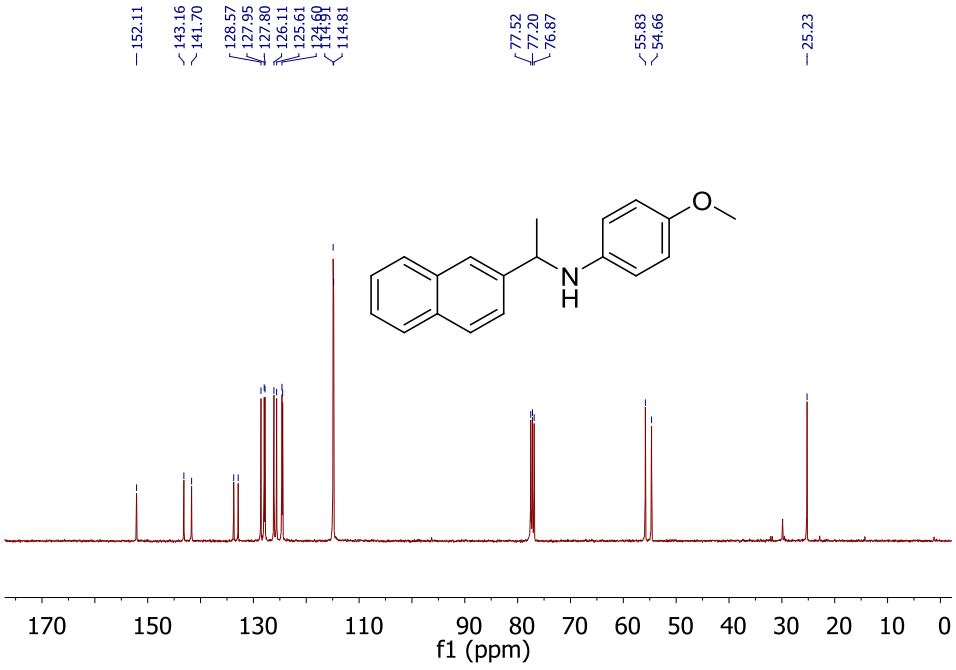


Fig. S84 ^{13}C NMR Spectrum of **8g** in $CDCl_3$ (100 MHz).

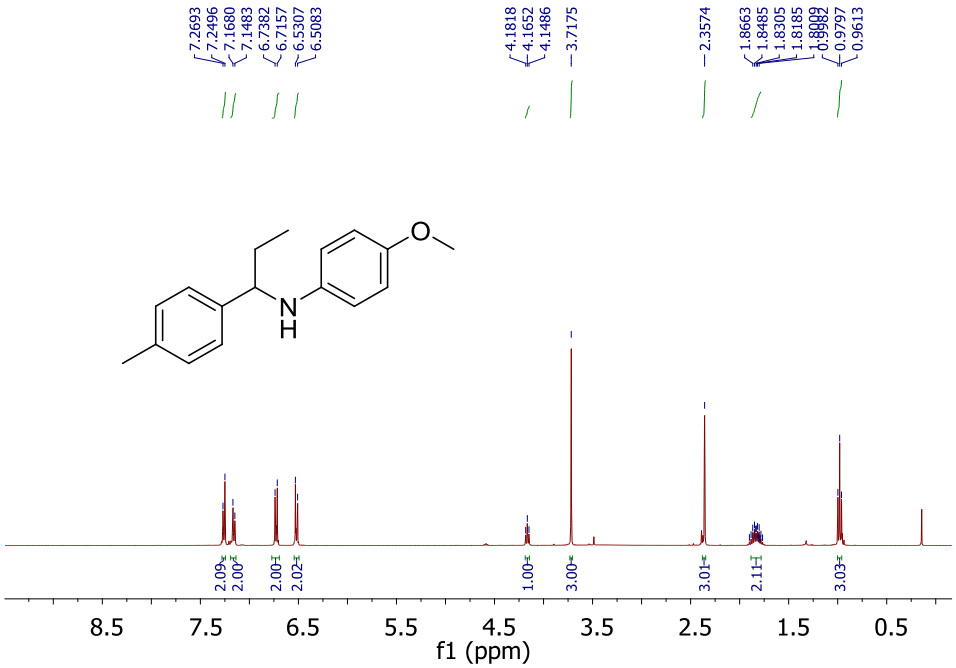


Fig. S85 ^{1}H NMR Spectrum of **8h** in $CDCl_3$ (400 MHz).

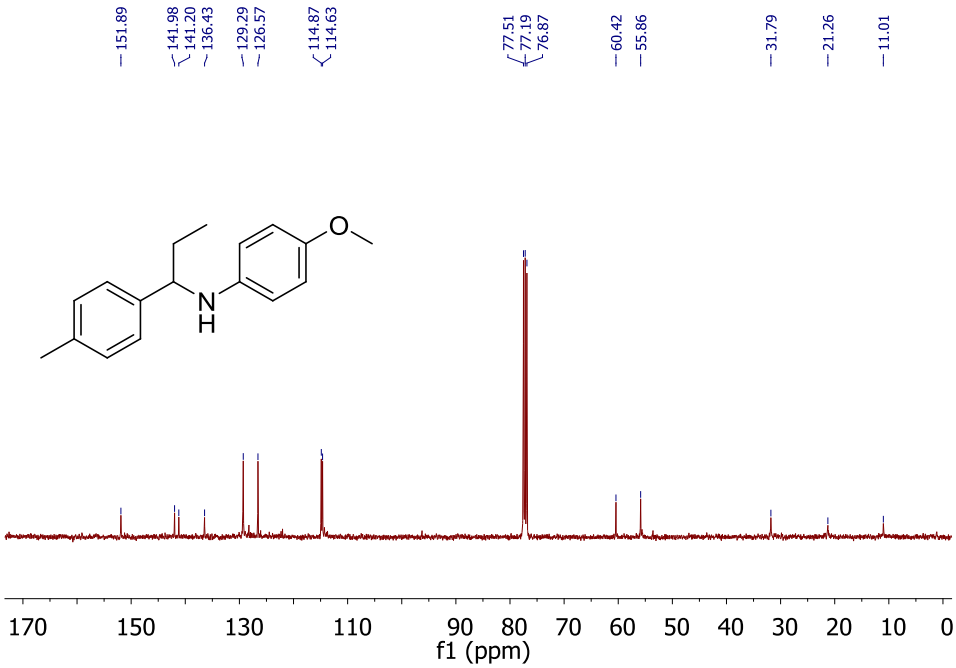


Fig. S86 ^{13}C NMR Spectrum of **8h** in $CDCl_3$ (100 MHz).

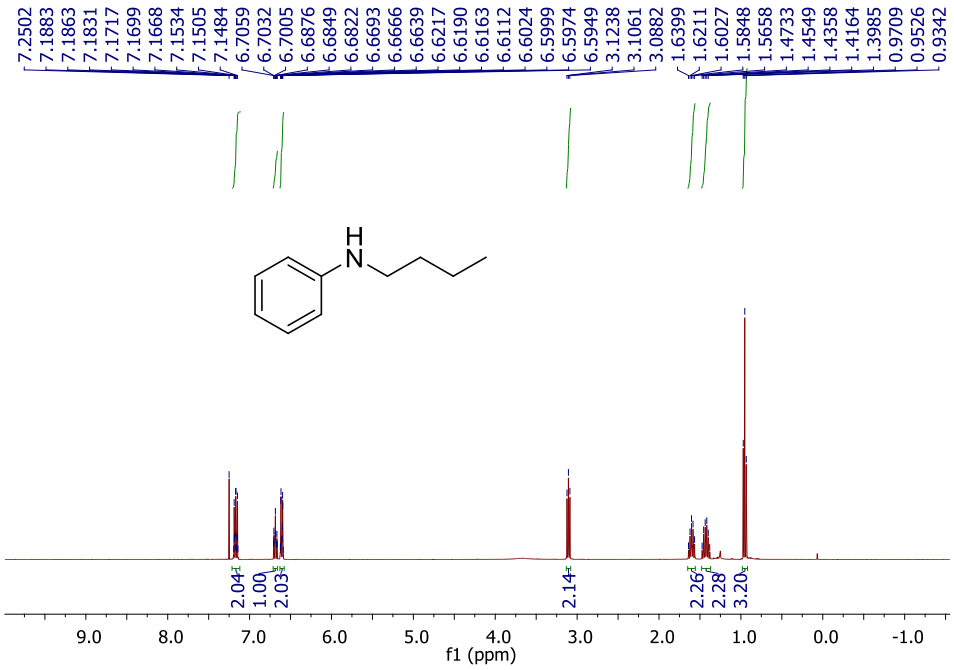


Fig. S87 ^{1}H NMR Spectrum of **8i** in $CDCl_3$ (400 MHz).

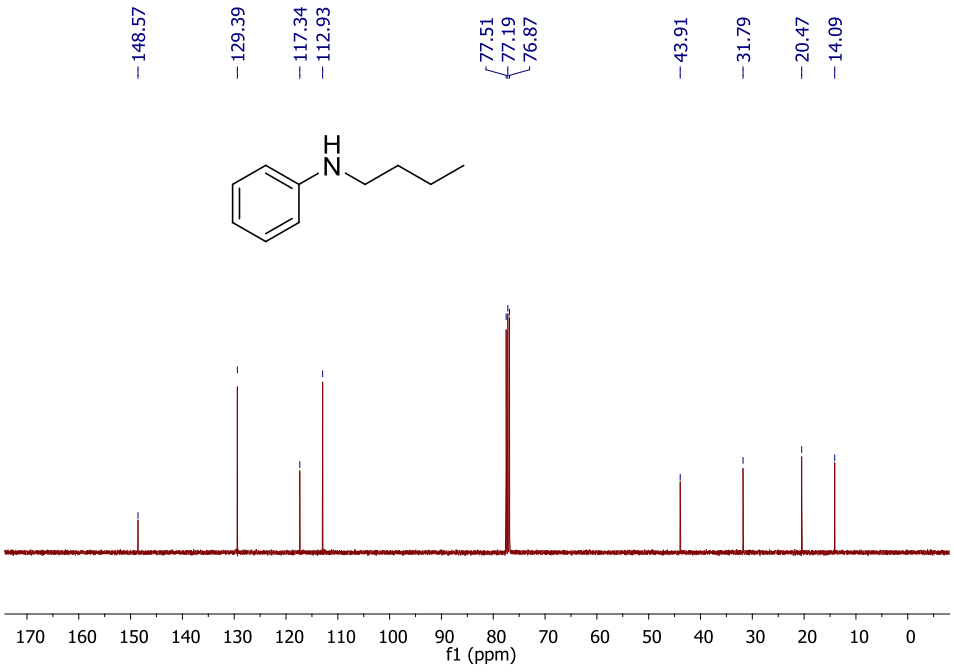


Fig. S88 ^{13}C NMR Spectrum of **8i** in $CDCl_3$ (100 MHz).

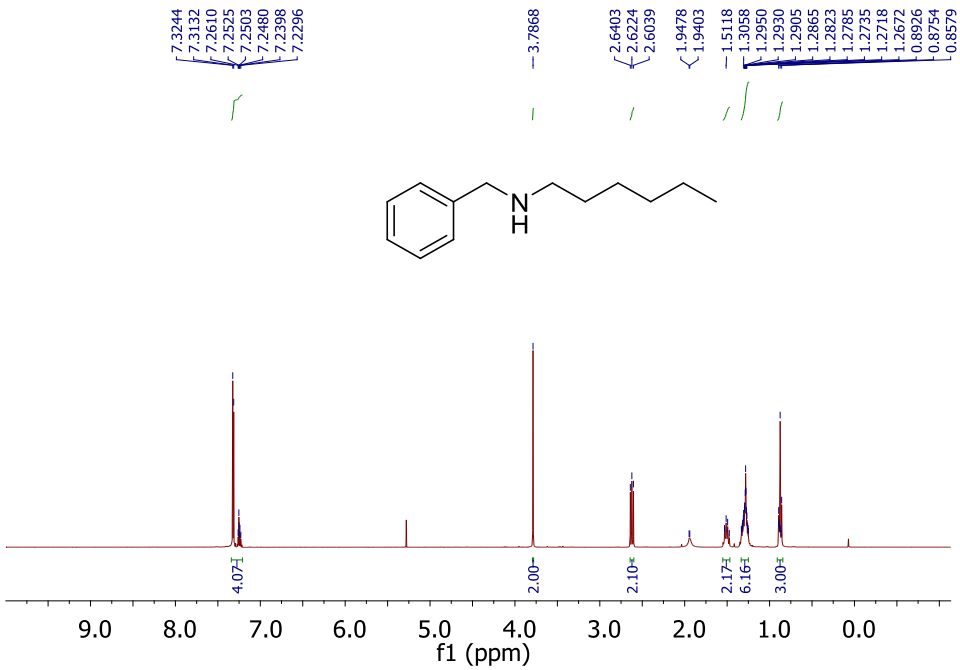


Fig. S89 ^{1}H NMR Spectrum of **8j** in $CDCl_3$ (400 MHz).

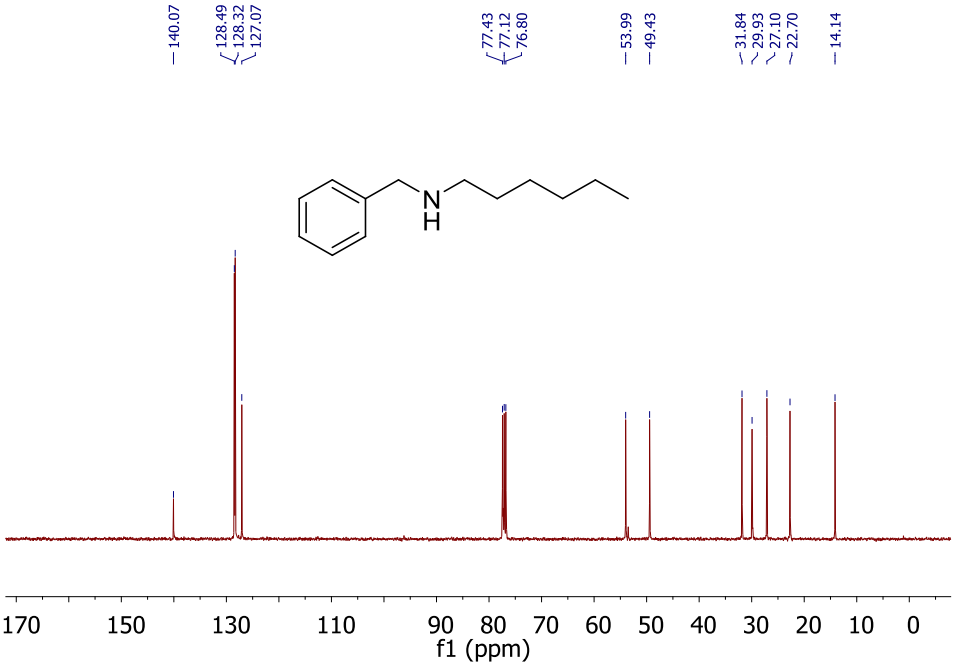


Fig. S90 ^{13}C NMR Spectrum of **8j** in $CDCl_3$ (100 MHz).

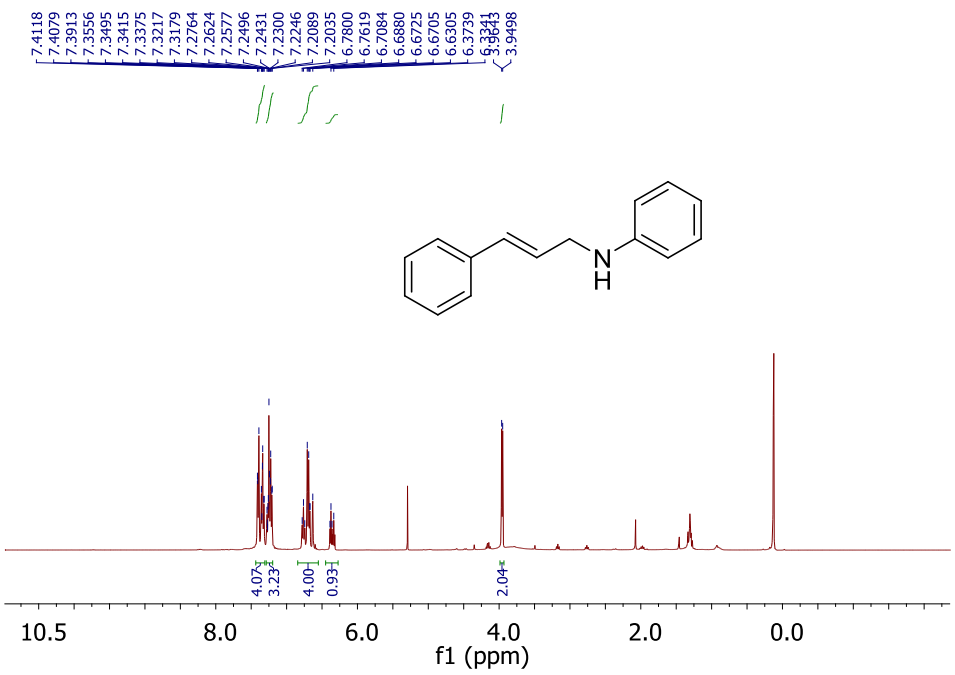


Fig. S91 ^{1}H NMR Spectrum of **8k** in $CDCl_3$ (400 MHz).

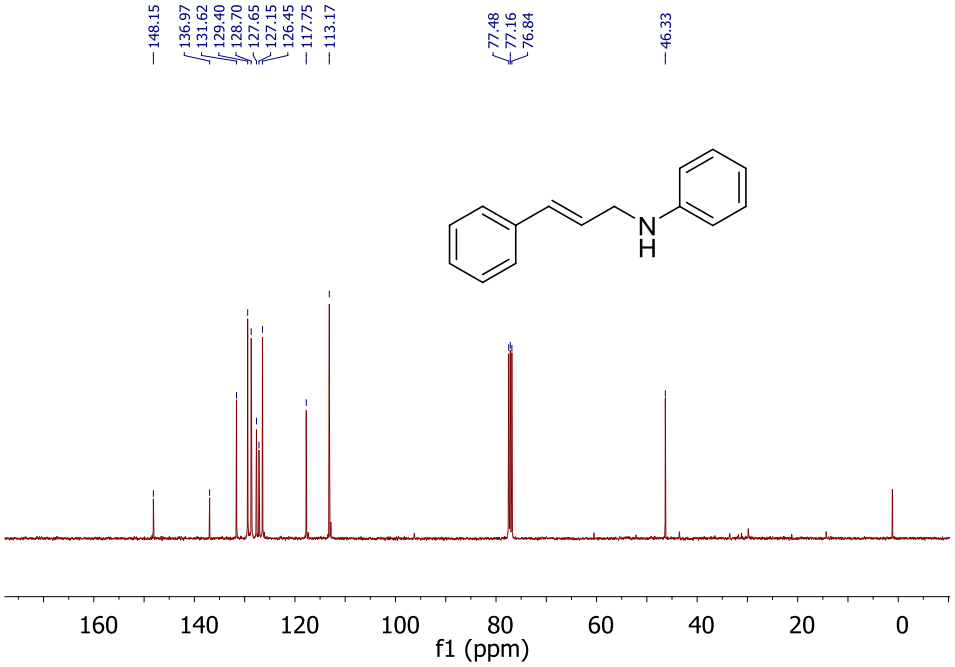


Fig. S92 ^{13}C NMR Spectrum of **8k** in $CDCl_3$ (100 MHz).

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