Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Catalytic utility of PNN based Mn^{I} pincer complexes in the synthesis of quinolines and transfer hydrogenation of carbonyl derivatives

Manali A. Mohite, Sonu Sheokand, Dipanjan Mondal, and Maravanji S. Balakrishna*

Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India.

*Author to whom correspondence should be addressed. E-mail: krishna@chem.iitb.ac.in, msb_krishna@iitb.ac.in (M. S. Balakrishna); Fax: +91-22-5172-3480/2576-7152

Table of content

Crystal structure determination of complexes **2 – 4**	S2-S3
Crystallographic information for complexes **2 – 5**	S3
NMR and HRMS spectra of complexes	S4-S16
Controlled experiments of reaction mechanism	S17-S21
NMR spectra of catalytic products	S22-S88
References	S89

Crystal structure determination of complexes.

Single crystals of all complexes were mounted on a Cryoloop with a drop of paratone oil and positioned in the cold nitrogen stream on a Bruker D8 Venture diffractometer. The data collections were performed at 100 K to 150 K using Bruker D8 Venture diffractometer with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å) with the ω-scan technique. The data were reduced using CrysalisPro Red 171.41_64.93a software.[1] The structures were solved using Olex2 1.5[2] with the ShelXT[3] structure solution program using intrinsic phasing and refined with SHELXL[3] refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. The given chemical formula and other crystal data do not take into account the unknown solvent molecule(s). The reflections with error/esd more than 10 were excluded in order to avoid problems related to better refinement of the data. The data completeness is more than 99.8% in most of the cases, which is enough to guarantee a very good refinement of data. The details of X-ray structural determinations are given in Tables S1. Crystallographic data for the structures reported in this paper have been deposited with the

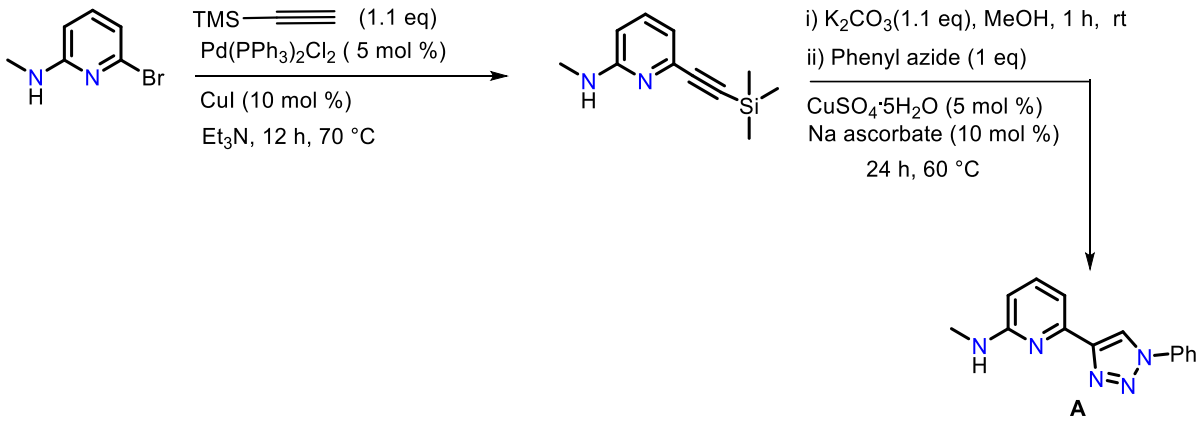
Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 23018662-2301864

Table S1 Crystallographic information of compound **2-4**

Identification code	**2**	**3**	**4**
Formula	$C_{30}H_{24}BrMnN_5O_3P$	$C_{29}H_{24}BrMnN_5O_2P$	$C_{30}H_{24}MnN_5O_3PBF_4$
Formula weight	668.36	640.35	675.26
Temperature/K	150.00	150.15	293
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/c$	P-1
a/Å	8.7605(18)	18.7073(13)	8.9264(3)
b/Å	10.686(2)	8.3671(6)	13.0268(3)
c/Å	16.726(4)	18.4670(11)	13.0647(3)
α/°	98.226(9)	90	90.870(2)
β/°	97.121(7)	110.297(2)	102.085(2)
γ/°	101.652(7)	90	94.427(2)
Volume/$Å^3$	1498.9(6)	2711.1(3)	1480.33(7)
Z	2	4	2
$\rho_{calc}g/cm^3$	1.481	1.569	1.515
μ/mm^{-1}	1.866	2.057	0.567
F(000)	676.0	1296.0	688.0
Crystal size/mm^3	0.095 × 0.072 × 0.056	0.215 × 0.065 × 0.045	0.095 × 0.072 × 0.052
2θ range, deg	4.292 to 50.758	4.644 to 56.964	3.138 to 72.064
Total no of reflection	42104	25461	62836
Independent reflections	5342 [R_{int} = 0.0606]	6820 [R_{int} = 0.0498]	10908 [R_{int} = 0.0544]
Goodness-of-fit on F^2	1.061	1.072	1.038
R_1	0.0727	0.0603	0.0544
WR_2	0.2206	0.1700	0.1357

Synthesis of [2,6-(Me)HNC$_5$H$_3$N(C$_2$HN$_3$C$_6$H$_5$)] (A)

Synthesis of compound **A** was achieved through a multistep process involving Sonagashira coupling of 6-bromo-N-methylpyridine-2-amine with trimethylsilyl acetylene in dry Et_3N to afford protected acetylene; which was deprotected by treatment with MeOH/K_2CO_3. Later acetylene derivative was treated with phenyl azide under click condition [$CuSO_4 \cdot 5H_2O$ and sodium ascorbate] to yield triazole derivative **A**.[5] The formation of **A** was confirmed by ^{1}H and $^{13}C\{^1H\}$c NMR spectroscopy. In the ^{1}H NMR spectrum of **A**, triazolic proton showed a singlet at 8.48 ppm and CH_3 protons appeared as a doublet at 2.95 ppm, possibly due to the coupling with NH proton ($^2J_{H\text{-}H}$ = 8 Hz).



Scheme S1. Synthesis of **A**.

Synthesis of compound [2,6-(Me)HNC$_5$H$_3$N(C$_2$HN$_3$C$_6$H$_5$)] (A)

Compound **A** was obtained by the combination of two-name reactions respectively. First 6-Bromo-N-methyl pyridine-2-amine (1000 mg, 5.34 mmol) was treated with trimethylsilyl acetylene (0.84ml, 5.88 mmol) in presence of $PdCl_2(PPh_3)_2$ (188 mg, 5 mol %) and CuI (102 mg, 10 mol %) in triethylamine at 60°C. The reaction mixture was stirred at room temperature for 12 h and after completion, the solution was passed through a neutral alumina pad. Then the solvent was evaporated using a rota-evaporator and the trimethylsilyl acetylene deprotected with the help of potassium carbonate in MeOH (20 mL). Deprotection was monitored with the

help of TLC, after 1 h the deprotection was complete, added 20 mL H_2O. After that click reaction was performed with the help of phenyl azide (700 mg, 5.88 mmol), $CuSO_4.5H_2O$ (66.84 mg, 5 mmol%), and Na ascorbate (106 mg, 10 mmol%) respectively. The reaction mixture was stirred at 60°C for 24 h. Compound A was purified with help of column chromatography (1:1, pet ether: ethyl acetate). Yield 71% (953 mg). ^{1}H NMR (400 MHz, $CDCl_3$ δ 8.48 (s, 1H), 7.79 (d, J = 7.9 Hz, 2H), 7.52 (q, J = 7.2 Hz, 4H), 7.42 (t, J = 8.1 Hz, 1H), 6.38 (d, J = 7.3 Hz, 1H), 4.71 (br, 1H), 2.96 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.48, 149.63, 148.04, 138.38, 137.21, 129.82, 128.77, 120.56, 119.79, 109.58, 105.94, 29.17.

NMR, HRMS and IR spectra

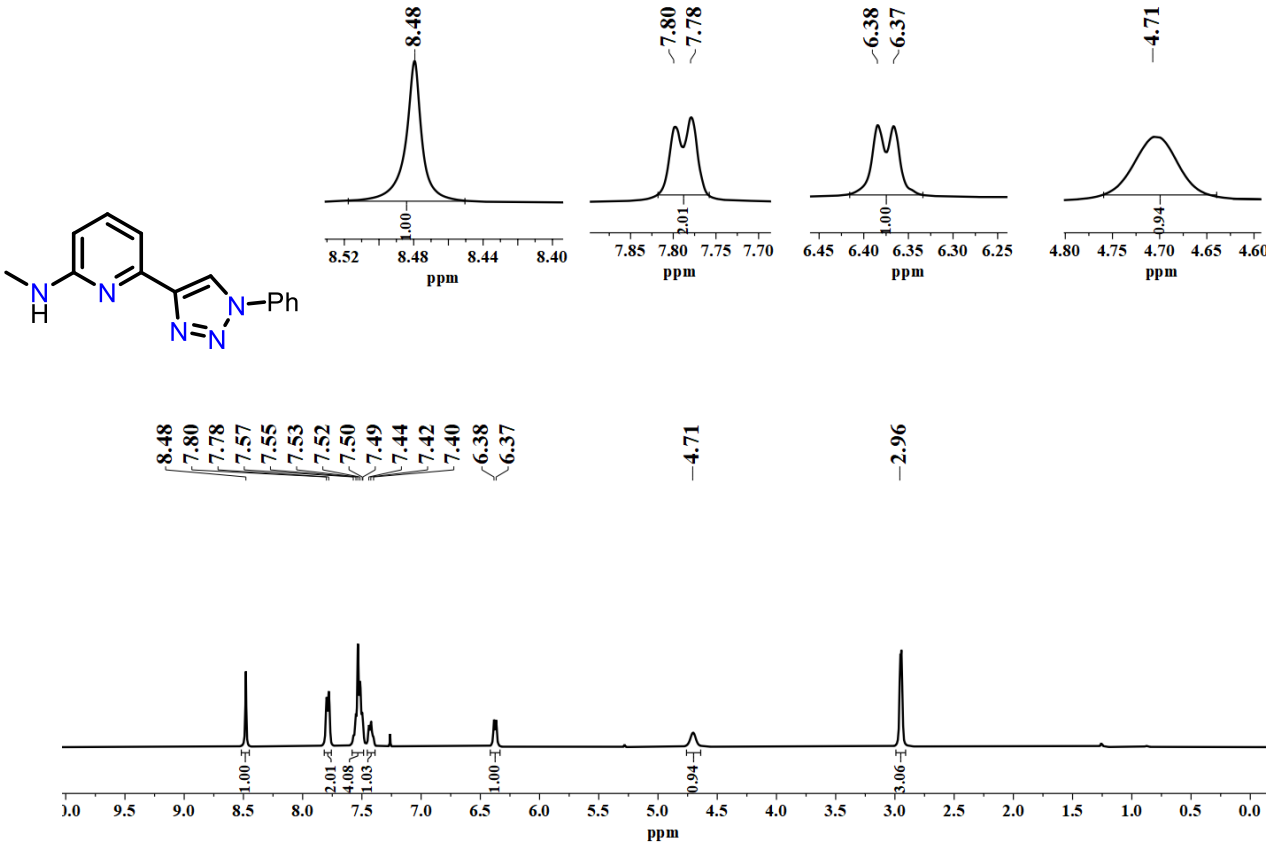


Fig. S1. ^{1}H NMR spectrum of **A** in $CDCl_3$ (400 MHz).

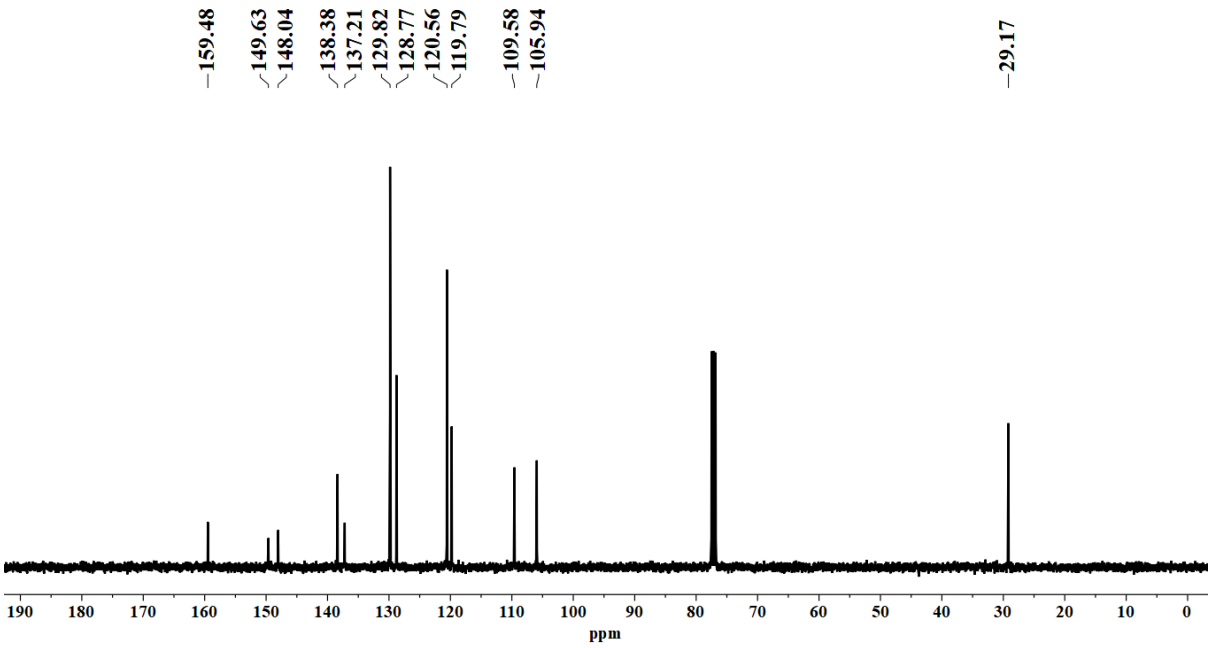


Fig. S2. ^{13}C NMR spectrum of **A** in $CDCl_3$ (101 MHz).

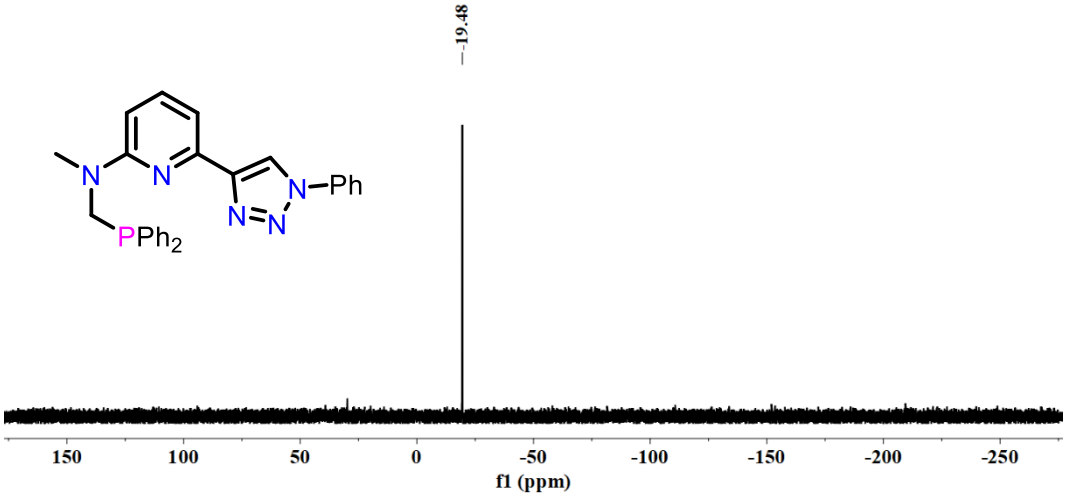


Fig. S3. ^{31}P NMR spectrum of **1** in $CDCl_3$ (162 MHz).

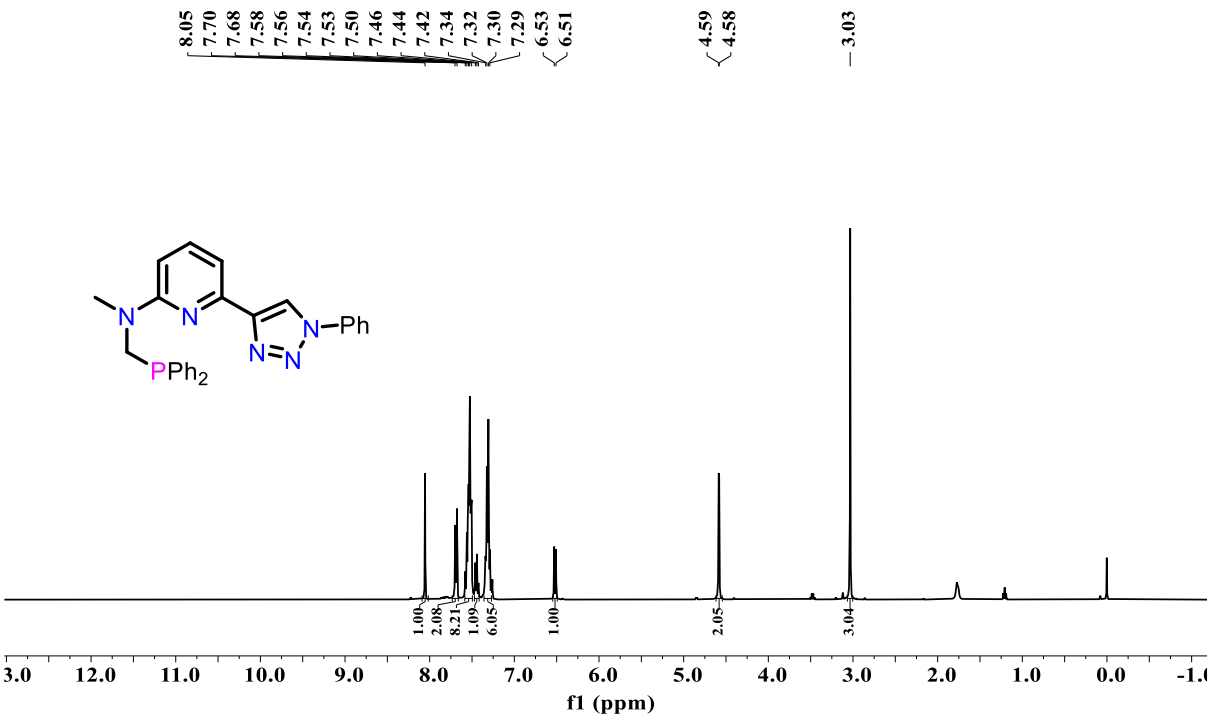


Fig. S4. ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz).

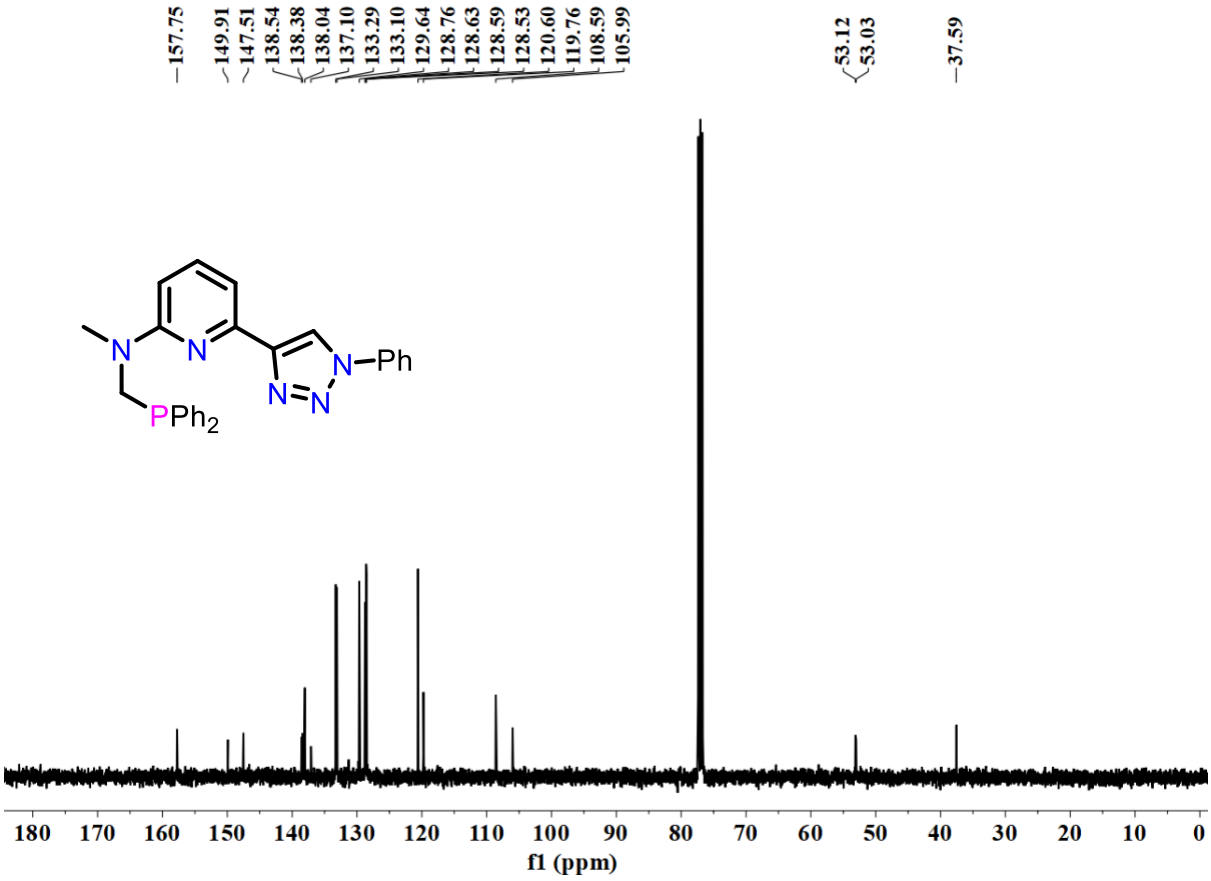


Fig. S5. ^{13}C NMR spectrum of **1** in $CDCl_3$ (101 MHz).

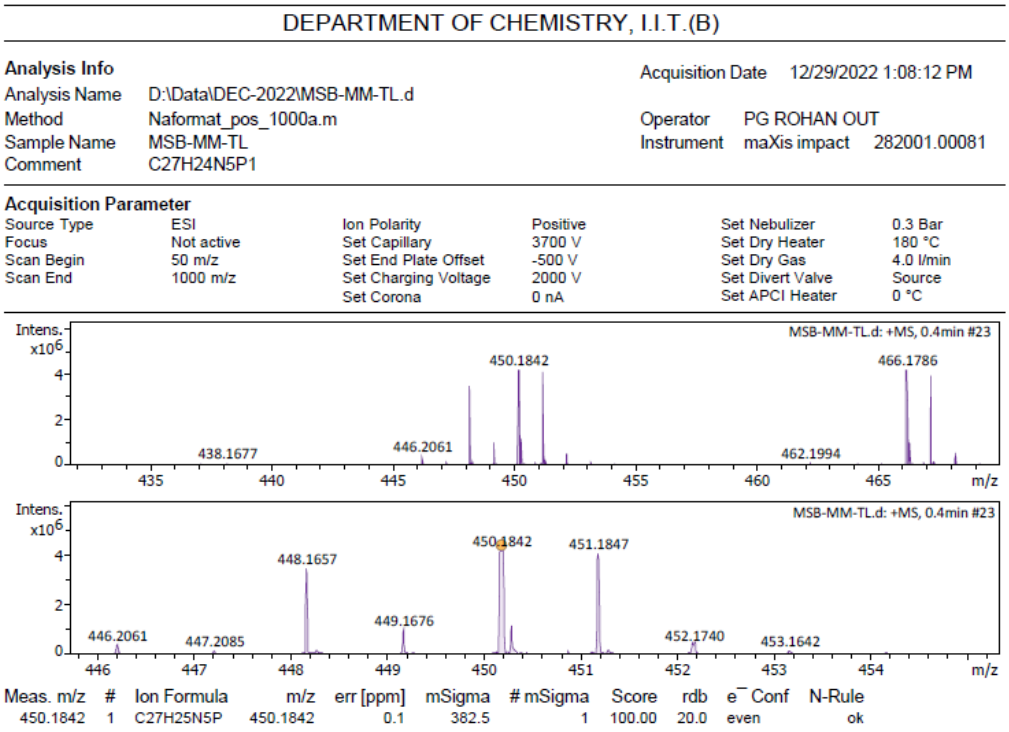


Fig. S6. HRMS spectrum of **1**.

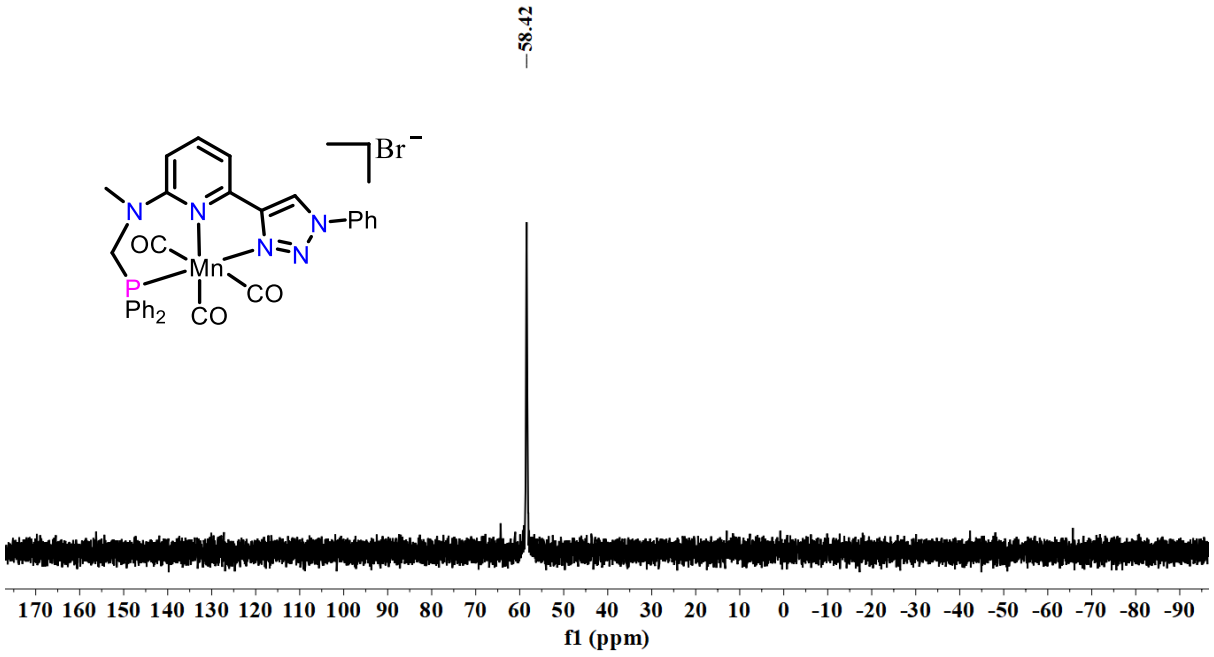


Fig. S7. ^{31}P NMR spectrum of **2** in $CDCl_3$ (162 MHz).

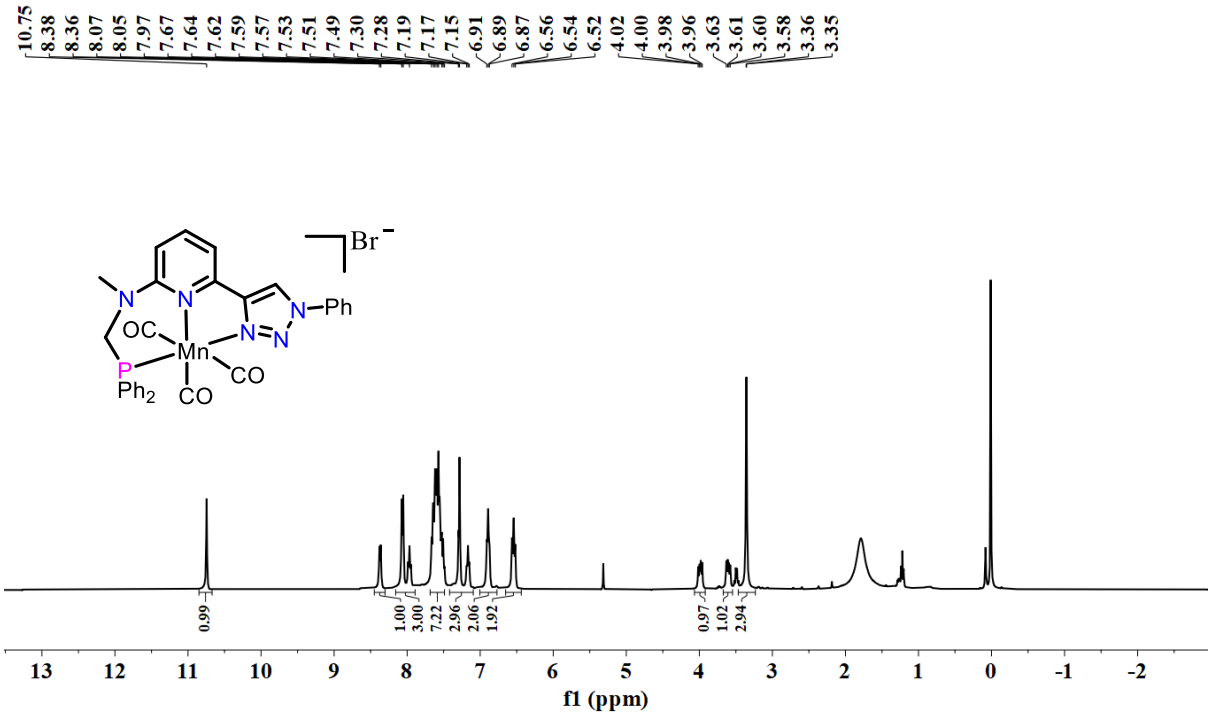


Fig. S8. ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz).

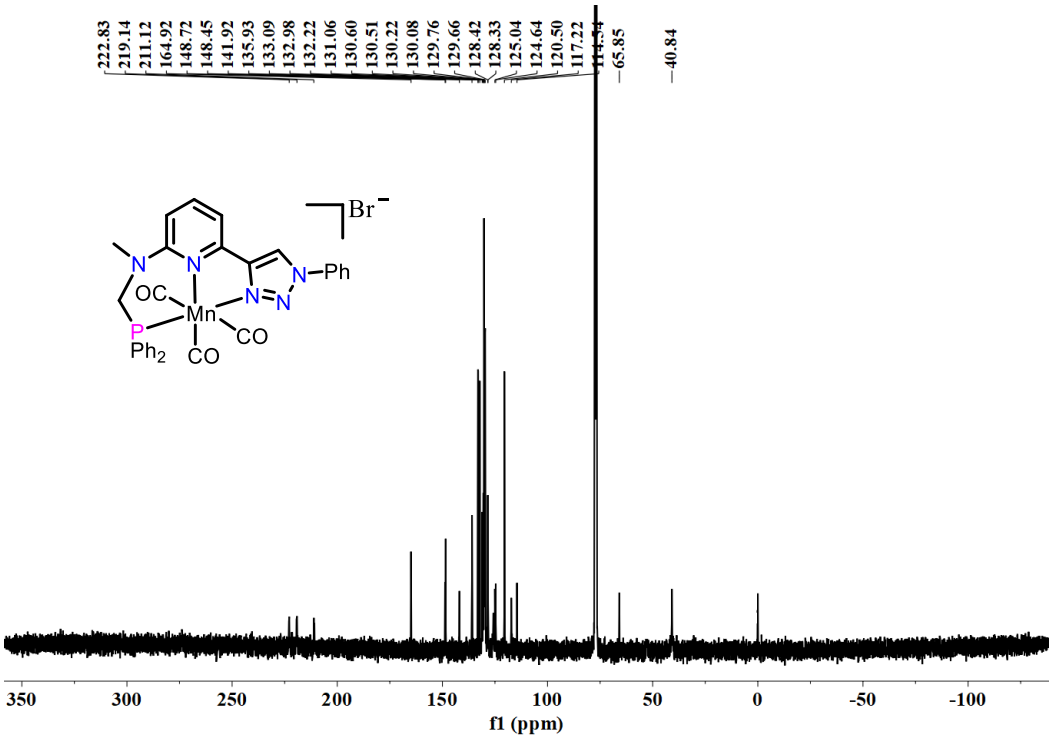


Fig.S9. ^{13}C NMR spectrum of **2** in $CDCl_3$ (101 MHz).

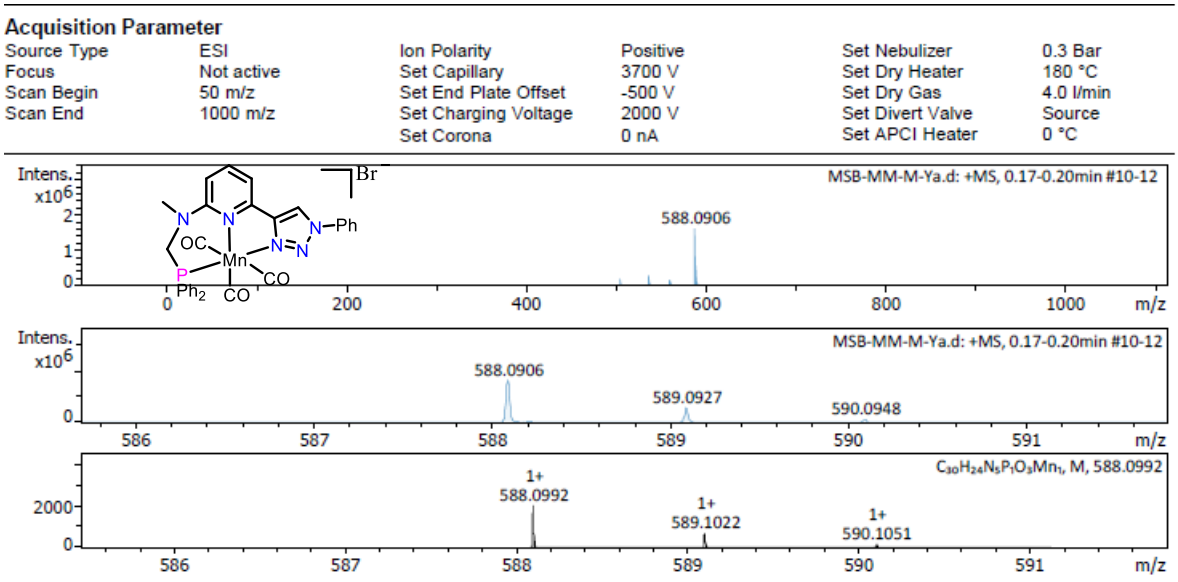


Fig. S10. HRMS spectrum of **2**.

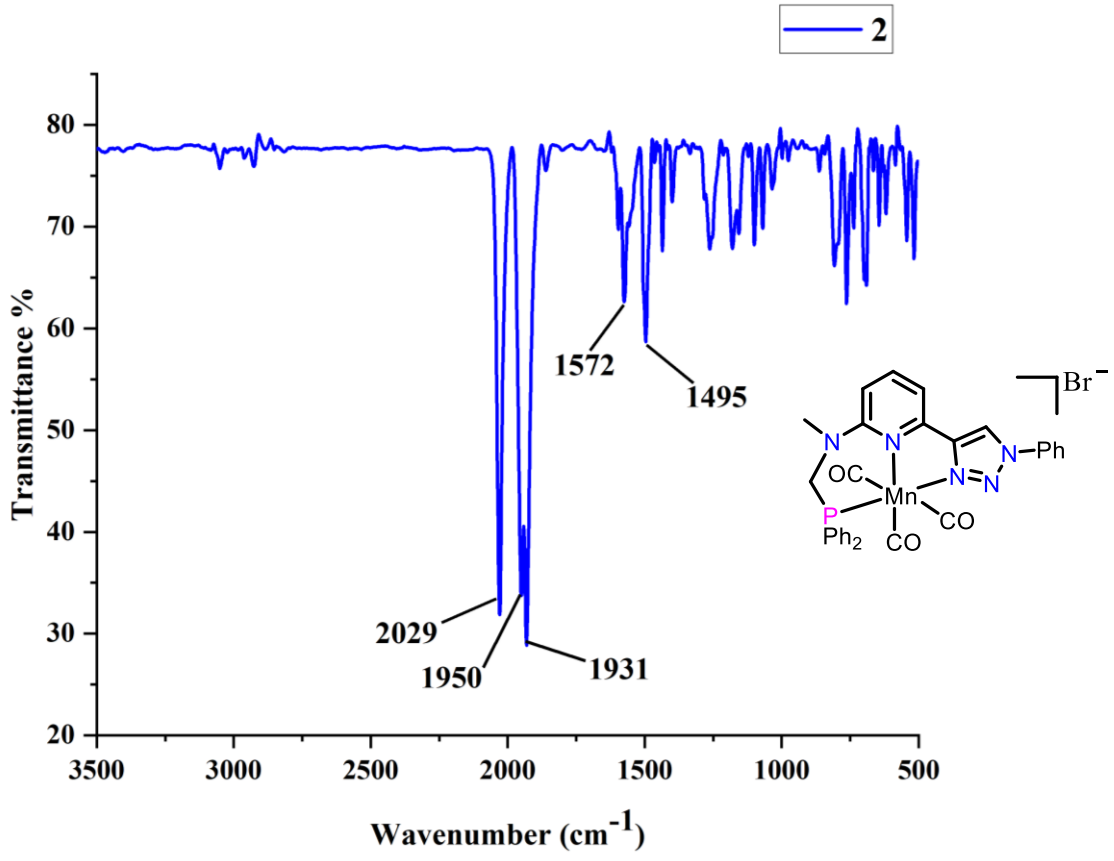


Fig. S11. IR spectrum of **2**.

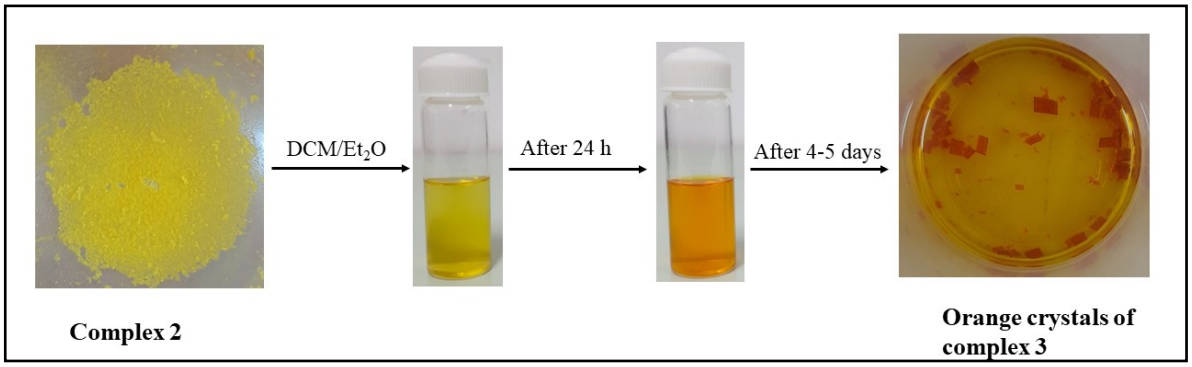


Fig. S12. Conversion of complex **2** into **3** in solution.

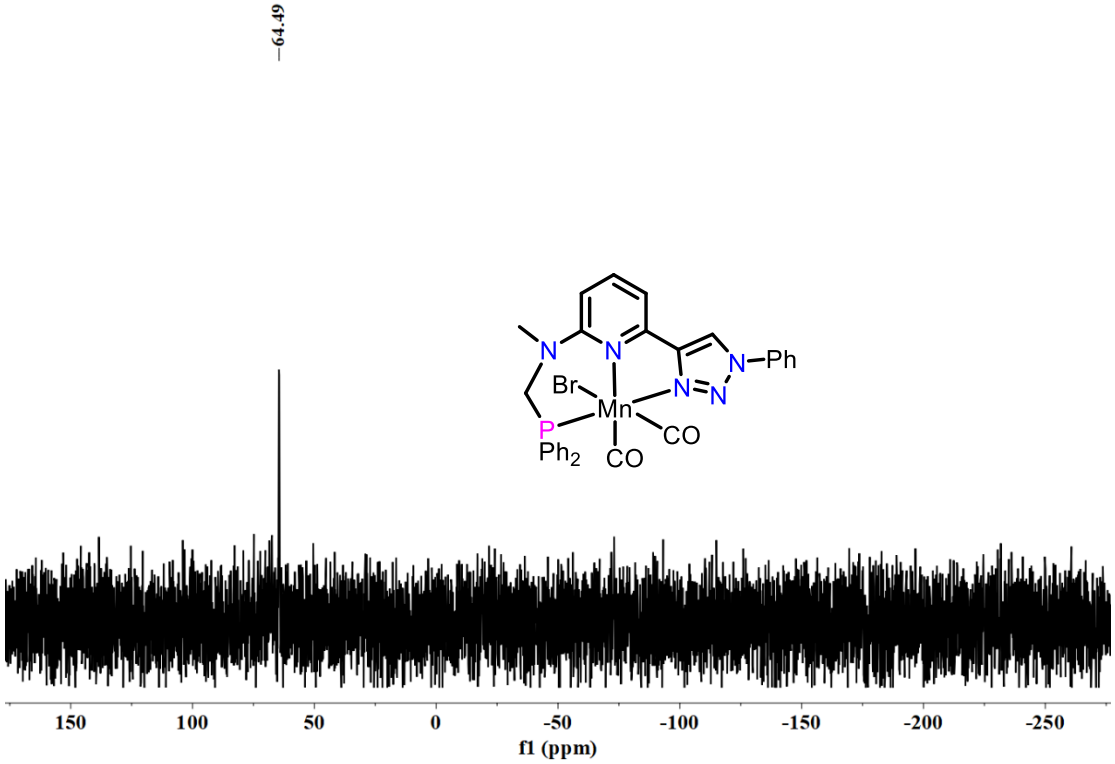


Fig. S13. ^{31}P NMR spectrum of **3** in DMSO-d_6 (162 MHz).

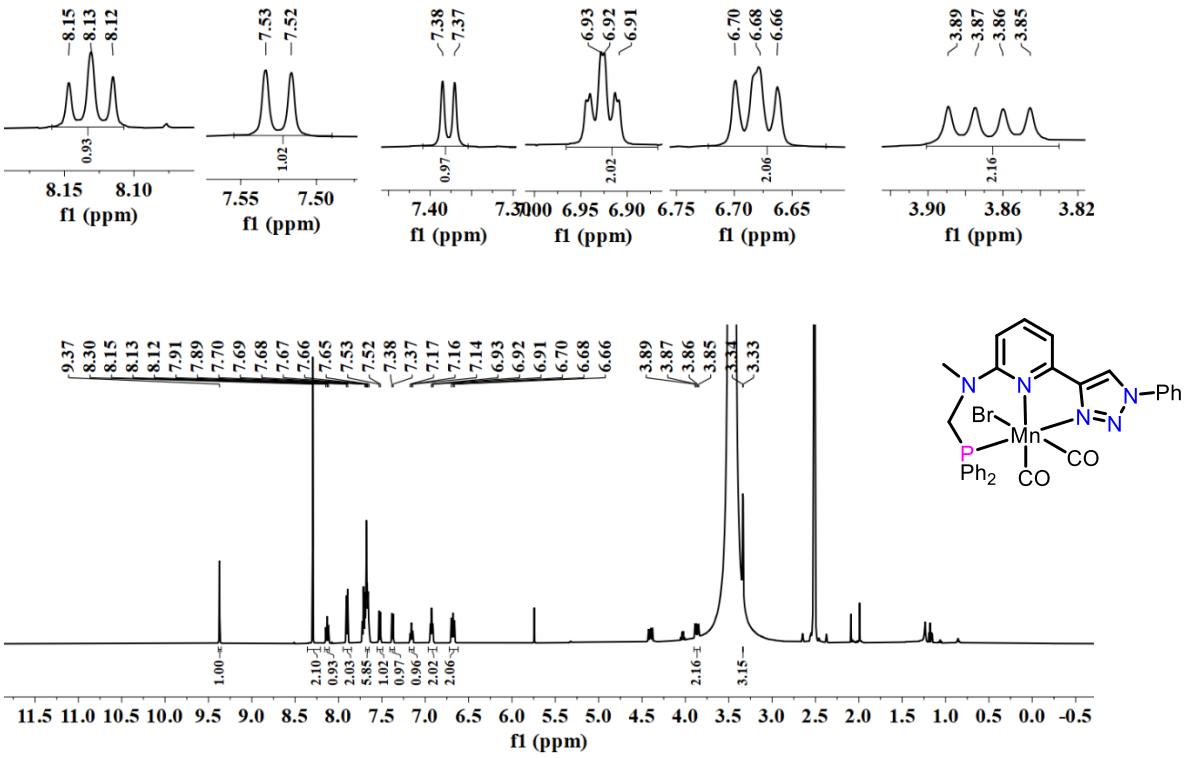


Fig. S14. ^{1}H NMR spectrum of **3** in DMSO-d_6 (400 MHz).

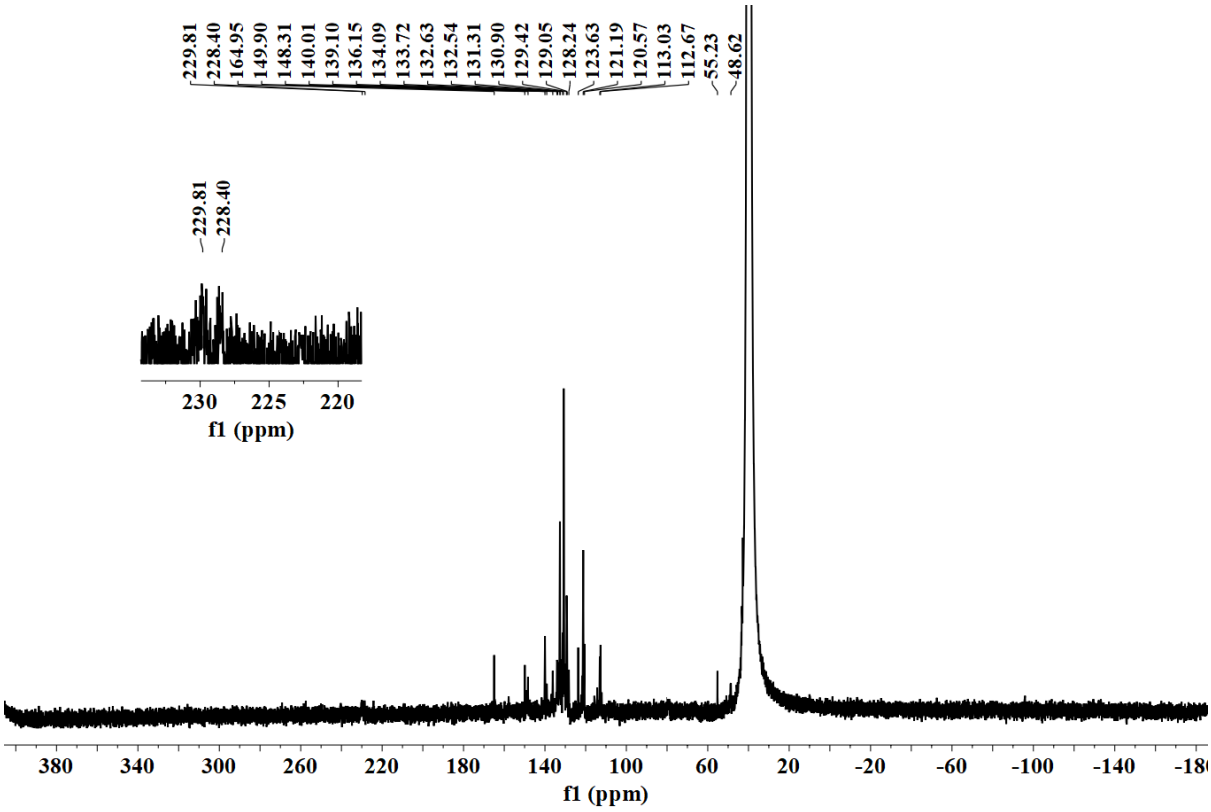


Fig. S15. ^{13}C NMR spectrum of **3** in DMSO-d_6 (101 MHz).

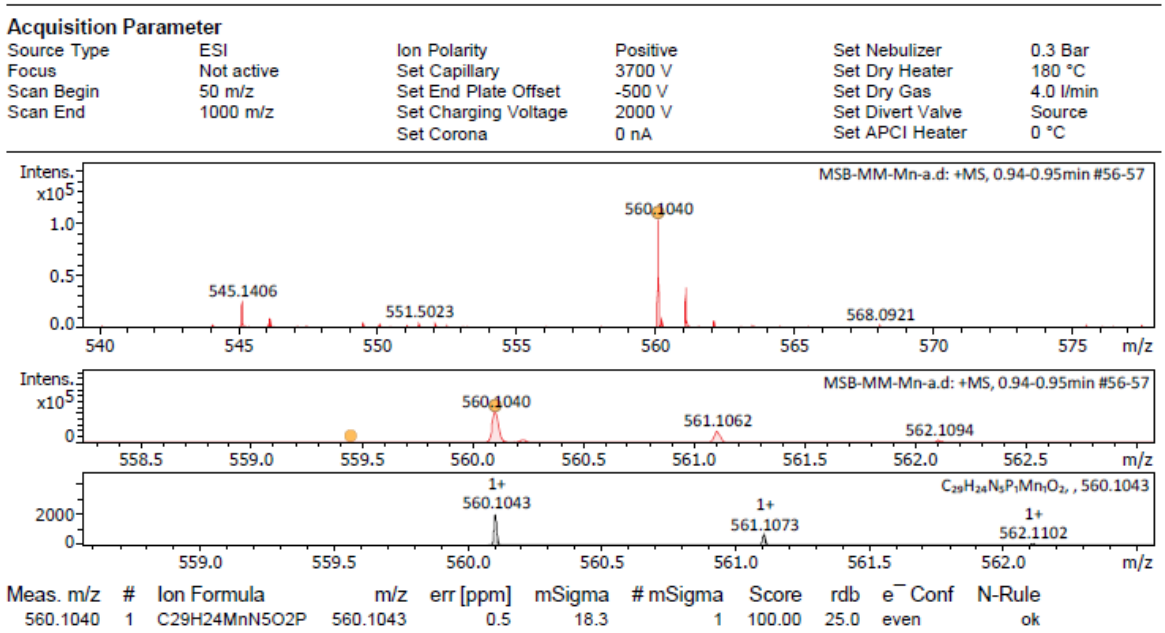


Fig. S16. HRMS spectrum of **3**.

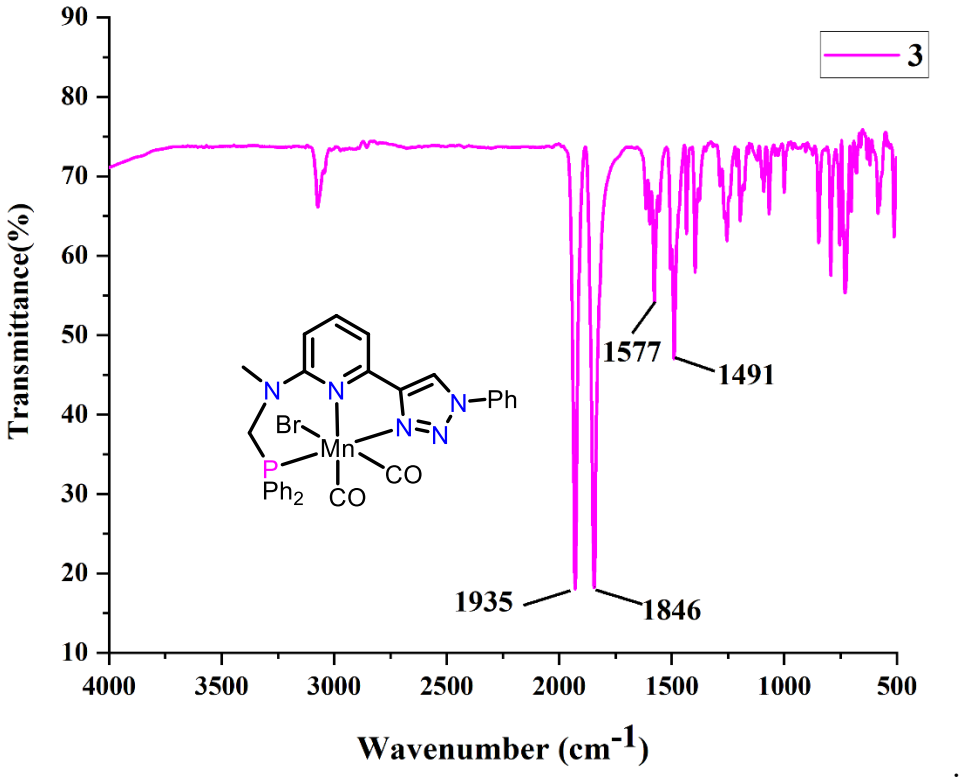


Fig. S17. IR spectrum of **3**.

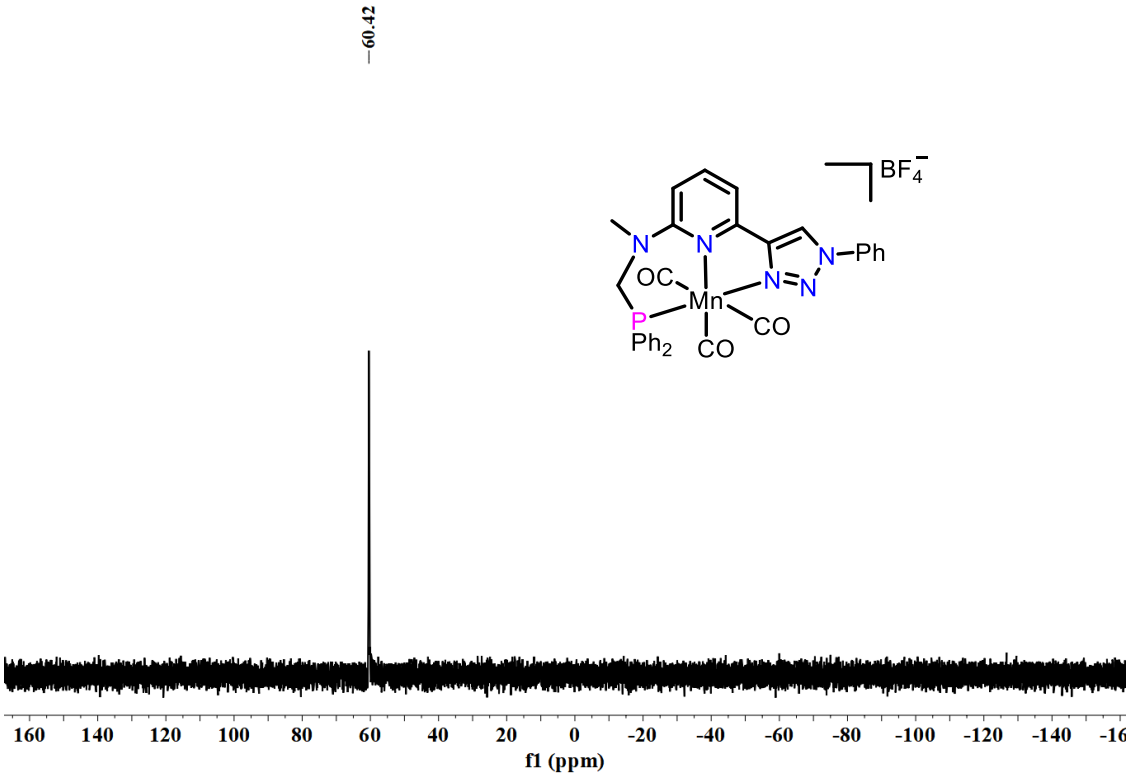


Fig.S18. ^{31}P NMR spectrum of **4** in DMSO-d_6 (162MHz).

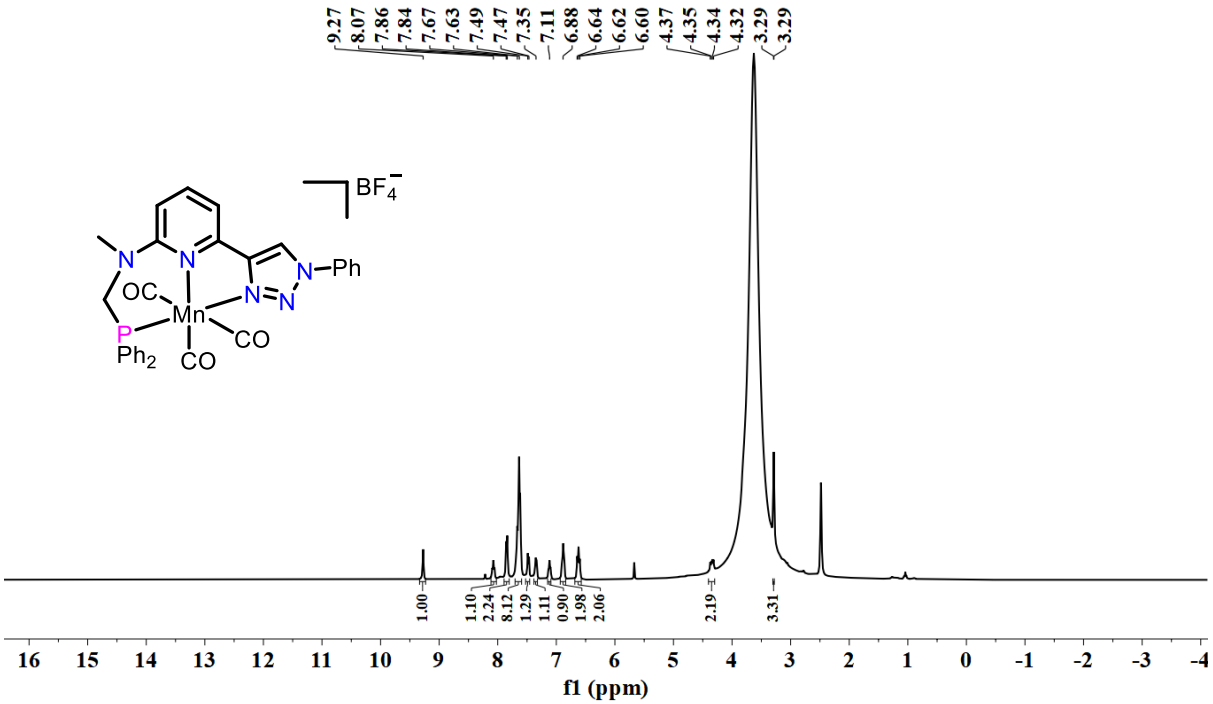


Fig. S19. ^{1}H NMR spectrum of **4** in DMSO-d_6 (400 MHz).

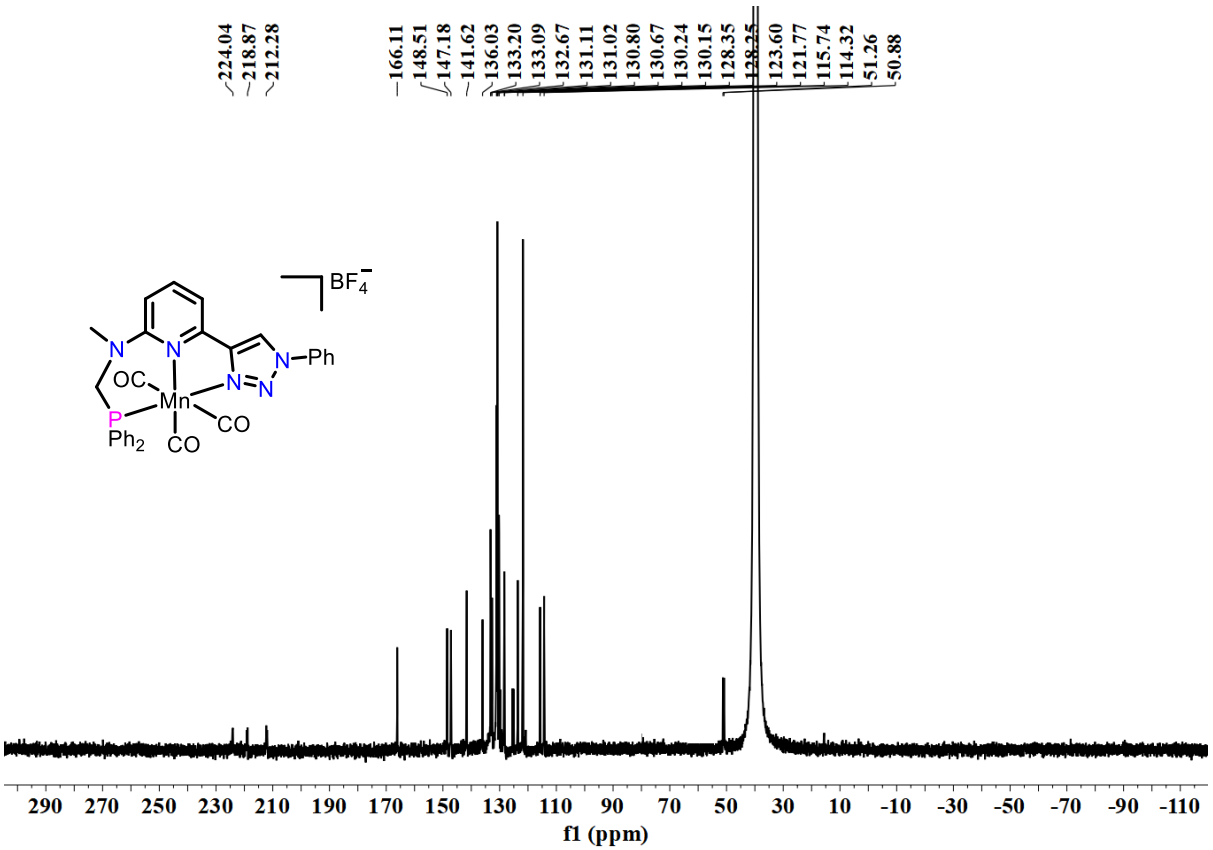


Fig. S20. ^{13}C NMR spectrum of **4** in DMSO-d_6 (101 MHz).

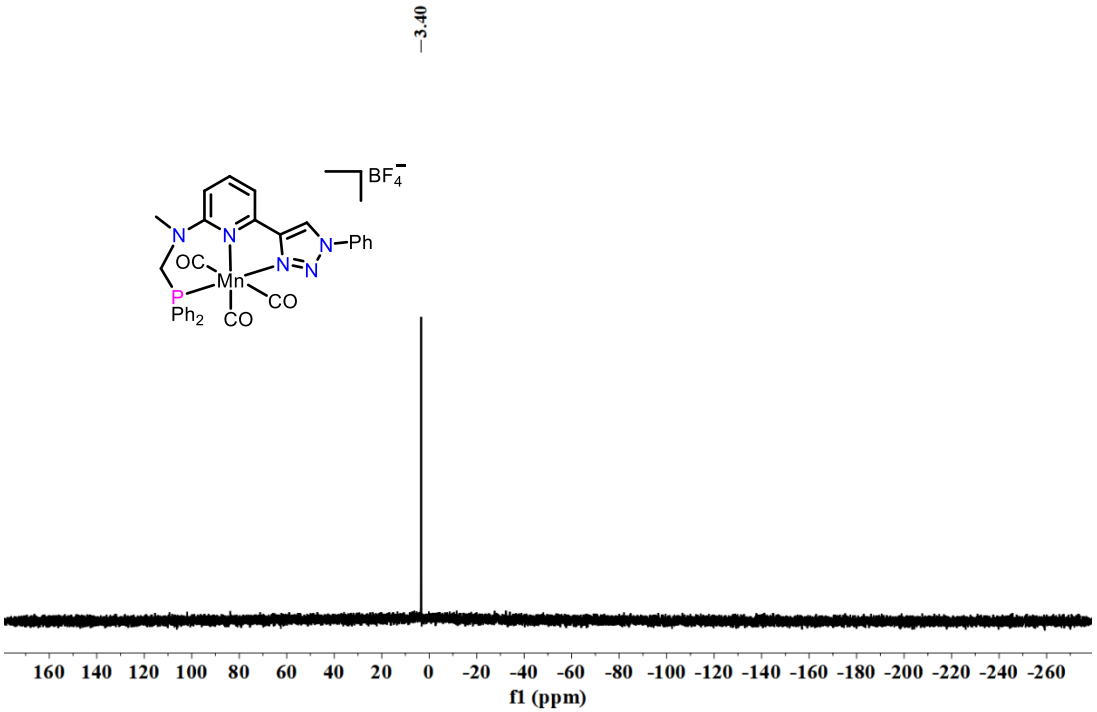


Fig. S21. ^{11}B NMR spectrum of **4** in DMSO-d_6 (128 MHz).

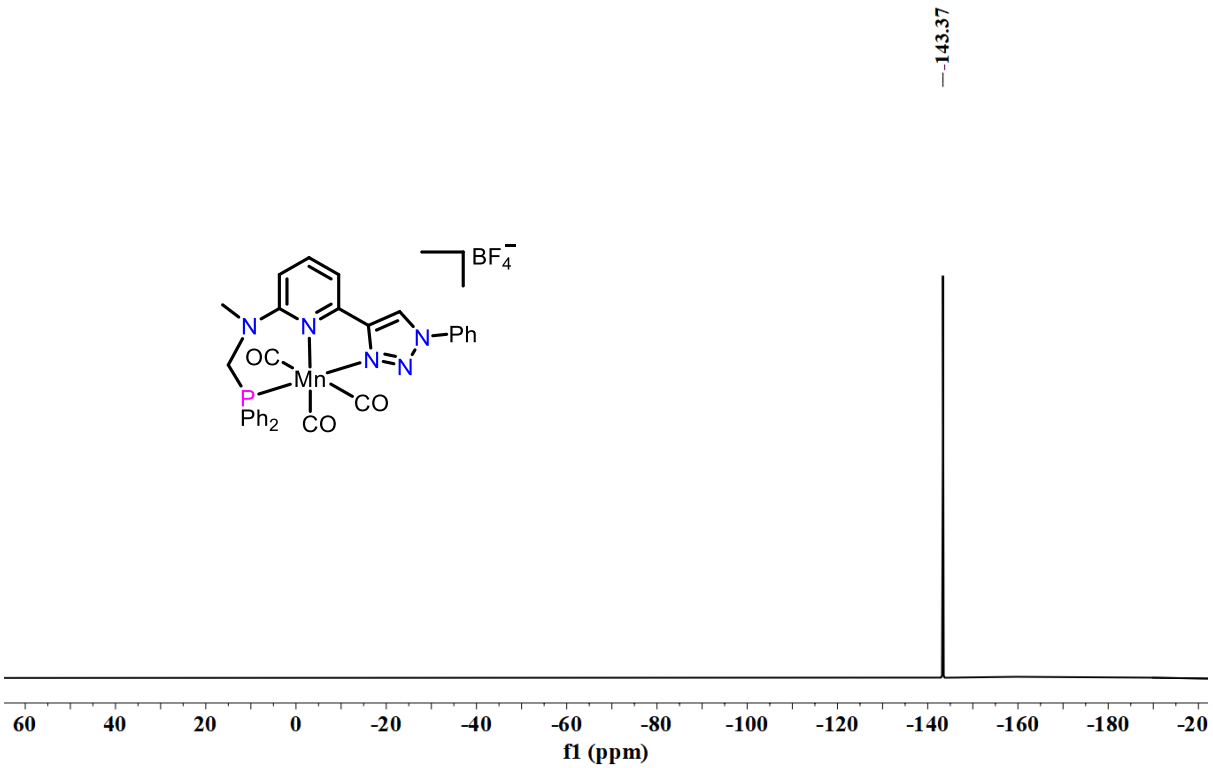


Fig. S22. $^{19}F\{^{1}H\}$. NMR spectrum of **4** in DMSO-d_6 (376 MHz)

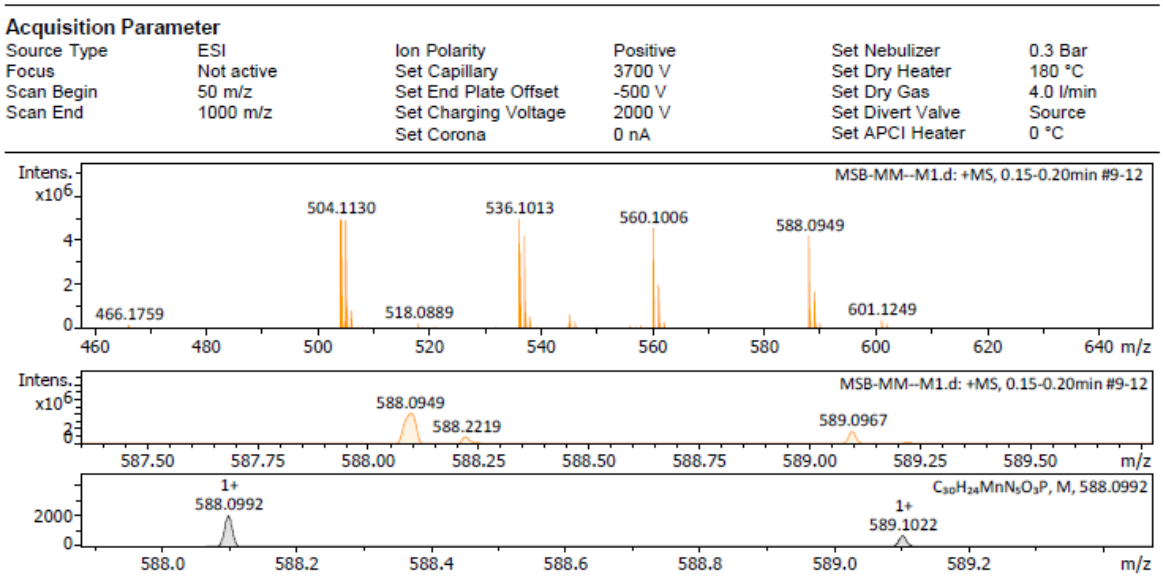


Fig.S23. HRMS spectrum of **4**.

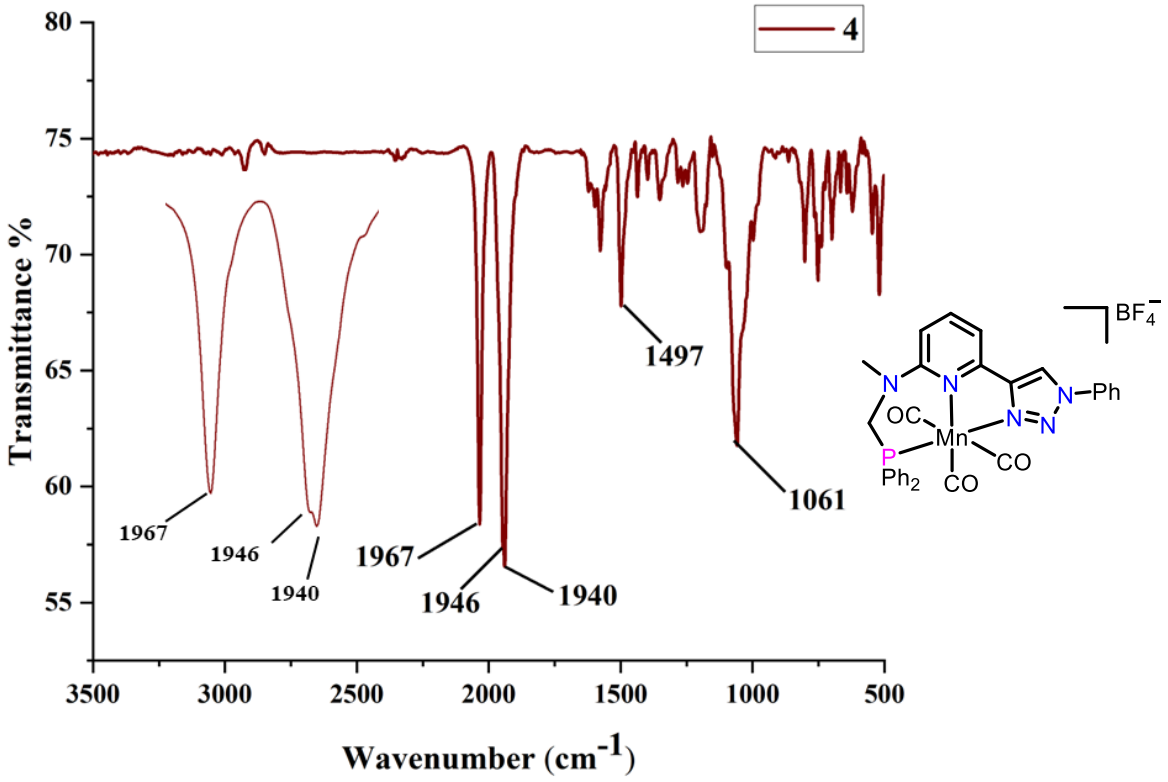
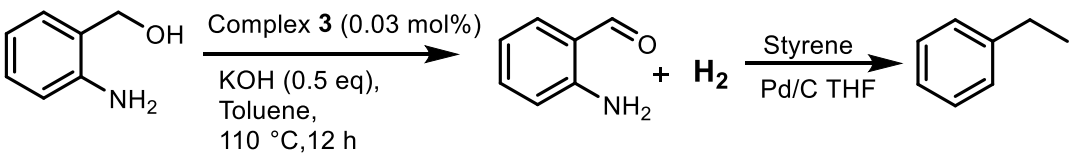


Fig. S24. IR spectrum of **4**.

Controlled experiments

Hydrogenation of styrene by evolved hydrogen

In a catalytic tube, mixture 2-aminobenzyl alcohol (2 mmol), **3** (0.03 mol%) and KOH (0.5 eqiuv) was taken in toluene, catalytic tube connected to another catalytic tube in which styrene (1.0 mmol) and catalytic amount of Pd/C were placed in THF with a magnetic stirrer. The tube was capped with a Teflon screw cap, evacuated, and filled with nitrogen. The tube was then placed in an oil bath and heated at 110 °C for 12 h. GC-MS analysis of the reaction mixture present in the second catalytic tube containing styrene revealed the conversion of styrene to ethylbenzene.



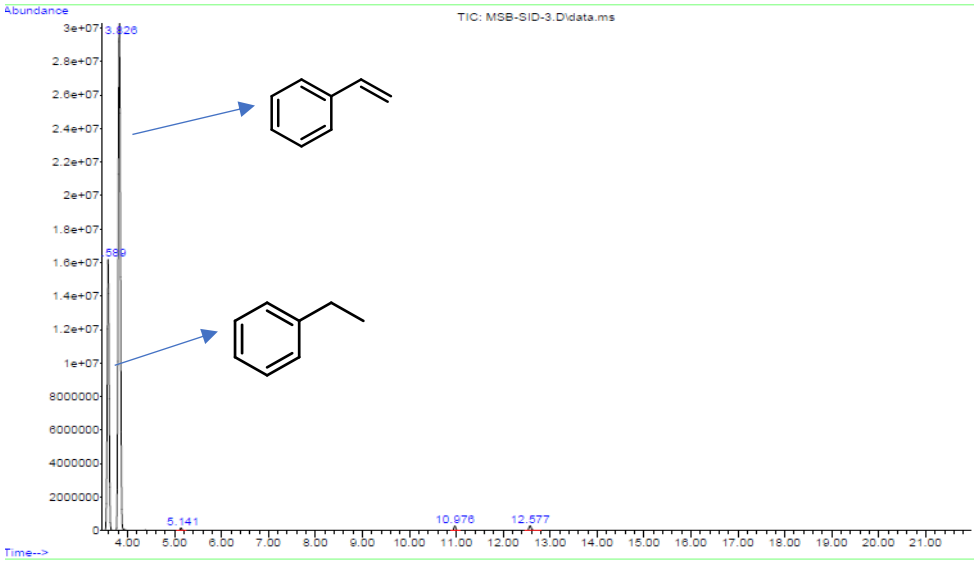
Scheme S2. Control experiments in the presence of external hydrogen acceptor.

A

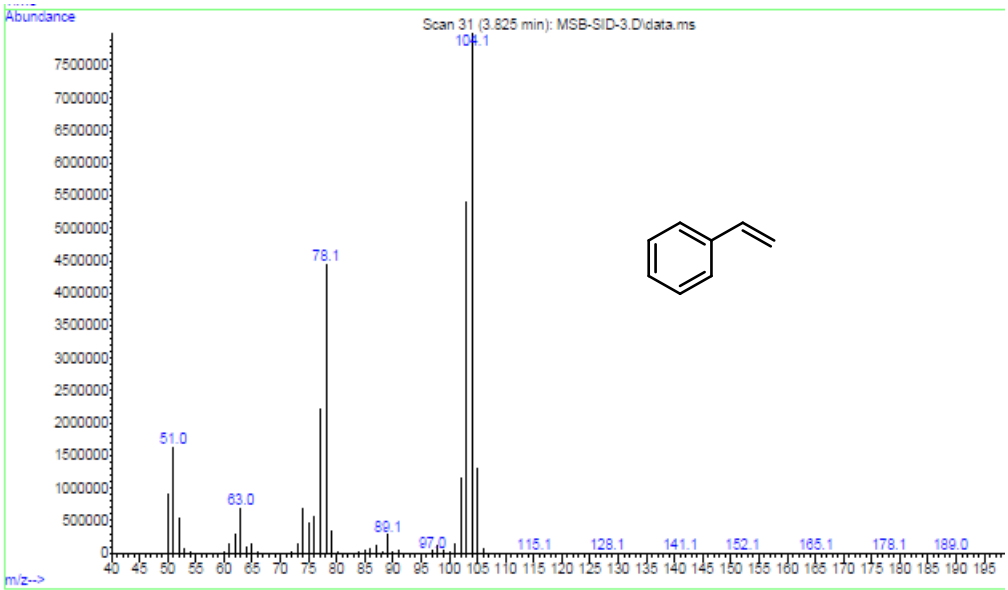
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.589	4	12	24	BV	15828843	486301602	45.83%	30.997%
2	3.826	24	31	35	VB	30761633	1061119538	100.00%	67.636%
3	5.141	132	139	147	BB	146108	3677661	0.35%	0.234%
4	10.976	612	618	628	BB	265384	7521319	0.71%	0.479%
5	12.577	741	750	768	BB	271105	10252006	0.97%	0.653%

Sum of corrected areas: 1568872126

CM2023.M Sun Jul 30 13:36:29 2023



B



C

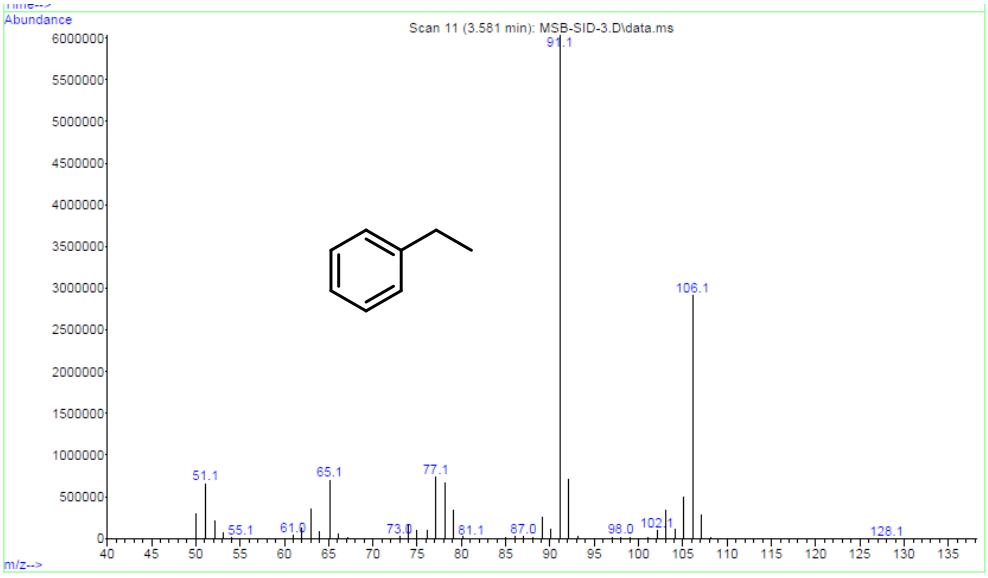
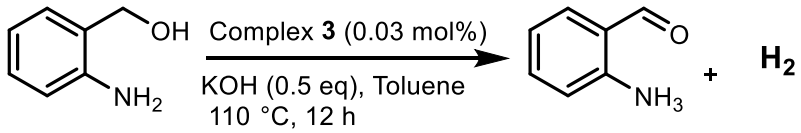


Fig.S25. (A) GC-MS spectrum of the reaction mixture of scheme S1 (**B**) GC-MS mass distribution for Styrene (**C**) GC-MS mass distribution for ethylbenzene.

Evolution of H_2 gas

In a catalytic tube mixture 2-aminobenzyl alcohol (2 mmol), **3** (0.03 mol%) and KOH (0.5 equiv) was taken in toluene taken. The tube was capped with a Teflon screw cap, evacuated, and filled with nitrogen. The tube was then placed in an oil bath and heated at 110 °C. After 2 h gas was taken by syringe and GC analysis was done, which showed peak of H_2 indicates evolution of H_2 gas during reaction. After 8 h of reaction GC-MS of reaction mixture was taken which showed formation of aldehyde.



Scheme S3. Control experiment to check evolution of H_2.

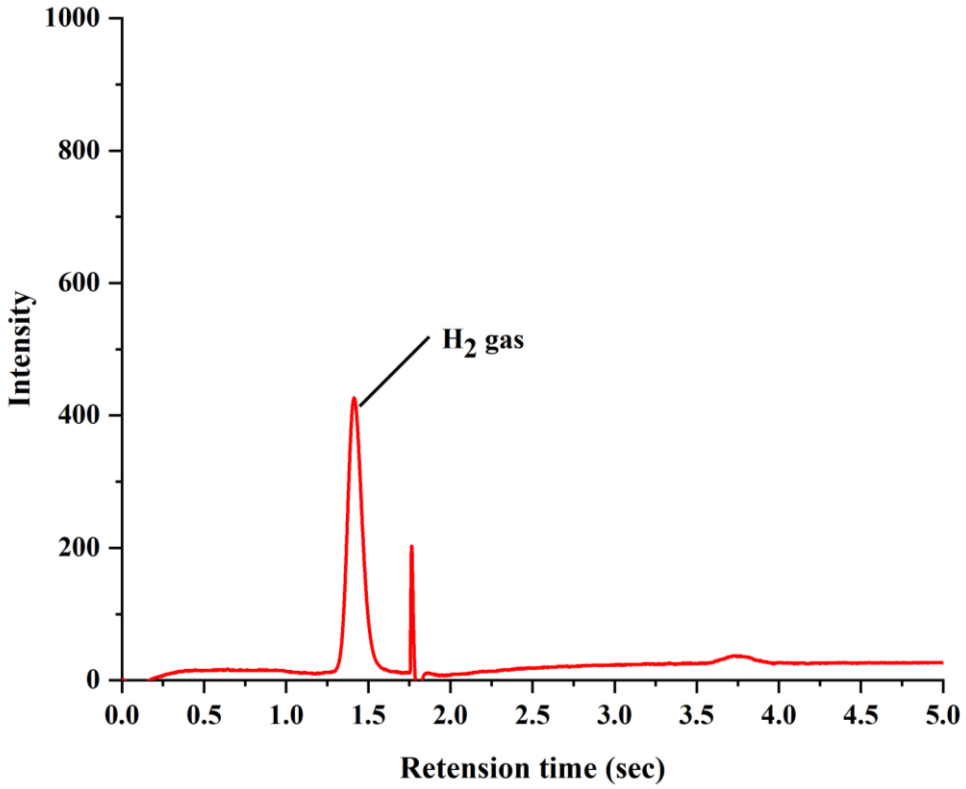


Fig.S26. Evidence of H_2 evolution from the independent reaction after 2 h.

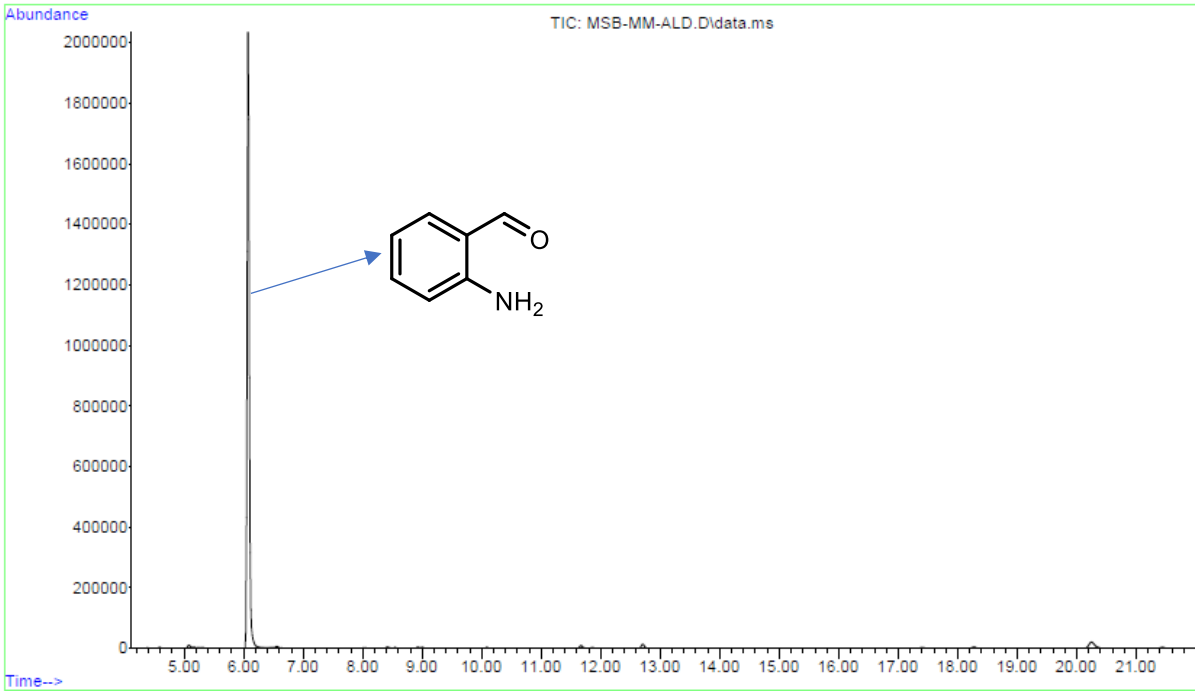


Fig. S27. Formation of aldehyde from the independent reaction.

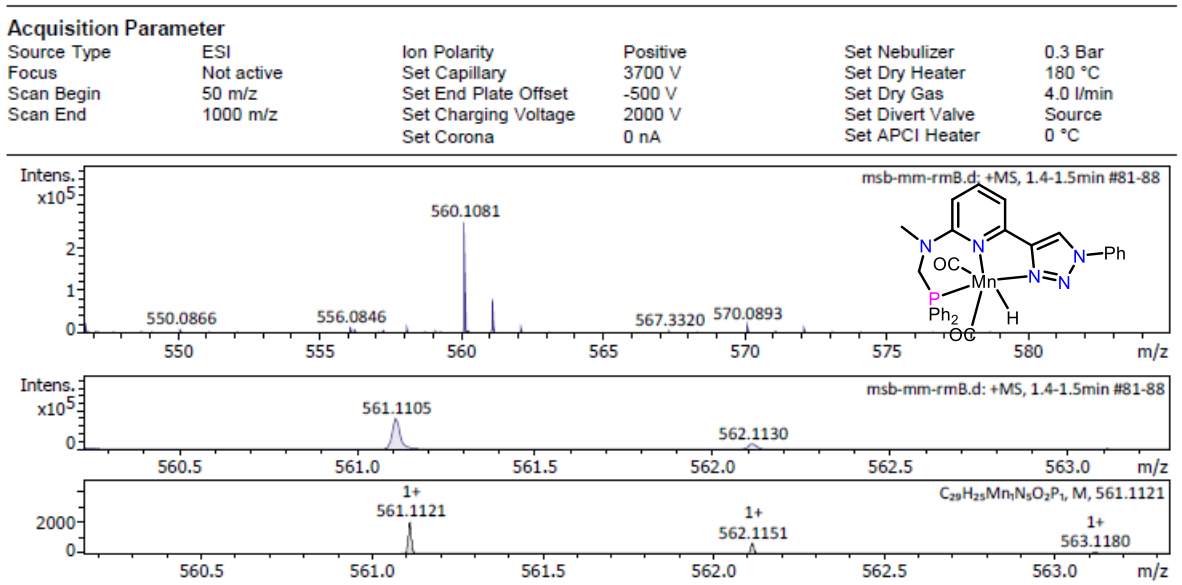
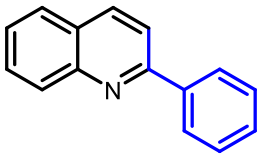


Fig.S28. HRMS spectrum of manganese hydride intermediate II.

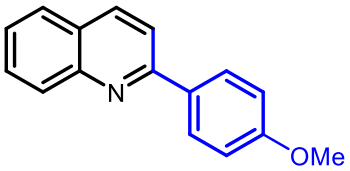
General procedure for synthesis of quinolines from 2-amino benzyl alcohol

In a catalytic tube, 2-aminobenzyl alcohol (1 mmol), ketone (1.1 mmol), complex **3** (0.03mol %), and KOH (1 equiv) in toluene (2 mL) were taken. The reaction mixture was degassed and purged with nitrogen gas for a few minutes to create a N_2 atmosphere. The reaction mixture was then heated at 120 °C in a preheated oil bath for 8 h followed by cooling to room temperature. Then the reaction mixture was diluted with water (2 mL) and extracted with ethyl acetate (3 × 4 mL). The resultant organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Final products were purified by silica gel column chromatography (60-120 mesh size) using petroleum ether /ethyl acetate as eluent.

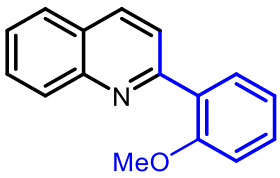
NMR spectral data of catalytic products



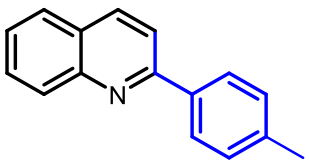
2-phenylquinoline (**1a**)[4] 98% (201 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (t, J = 8.8 Hz, 4H), 7.87 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.54 (q, J = 6.9 Hz, 3H), 7.49 (d, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.4, 139.8, 136.9, 129.8, 129.7, 129.4, 128.9, 127.7, 127.6, 127.3, 126.4, 119.1.



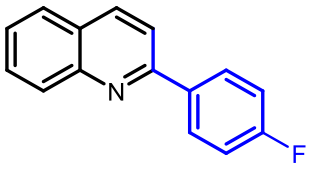
2-(4-methoxyphenyl)quinoline (**2a**)[4] 95% (223 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.10 (m, 4H), 7.79 (t, J = 8.0 Hz, 2H), 7.75 – 7.68 (m, 1H), 7.52 – 7.46 (m, 1H), 7.05 (d, J = 6.7 Hz, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.9, 156.9, 148.3, 136.7, 132.3, 129.6, 129.5, 128.9, 127.5, 126.9, 125.9, 118.6, 114.3, 55.4.



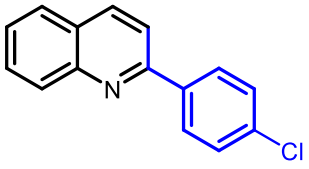
2-(2-methoxyphenyl)quinoline (**3a**)[5] 96% (225 mg) yielded as Colourless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 10.4 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.92 – 7.81 (m, 3H), 7.71 (dd, J = 9.2, 6.2 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.46 – 7.39 (m, 1H), 7.18 – 7.12 (m, 1H), 7.04 (d, J = 9.5 Hz, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.2, 157.2, 148.4, 135.1, 131.5, 130.4, 129.8, 129.7, 129.3, 127.4, 127 .1, 126. 2, 123.5, 121.3, 111.5, 55.7.



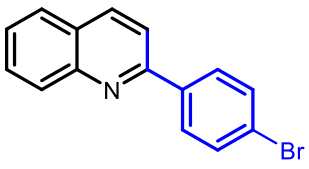
2-(p-tolyl)quinoline (**4a**)[5] 93% (203 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.17 (m, 2H), 8.13 (d, J = 6.3 Hz, 2H), 7.90 – 7.80 (m, 2H), 7.79 – 7.73 (m, 1H), 7.58 – 7.51 (m, 1H), 7.38 (d, J = 8.6 Hz, 2H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.4, 148.4, 139.4, 136.9, 136.7, 129.7, 129.6, 127.5, 127.2, 126.1, 118.9, 21.4.



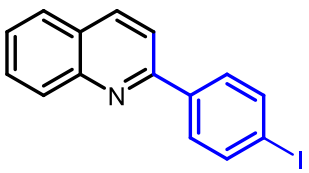
2-(4-fluorophenyl)quinoline (**5a**)[4] 84% (187 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.12 (m, 4H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.78 – 7.70 (m, 1H), 7.57 – 7.50 (m, 1H), 7.25 – 7.17 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.1, 162.6, 156.3, 148.2, 136.9, 135.9, 135.8, 129.8, 129.7, 129.5, 129.4, 127.5, 127.1, 126.4, 118.7, 115.9, 115.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.47.



2-(4-chlorophenyl)quinoline (**6a**)[6] 88% (210 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 – 8.14 (m, 2H), 8.12 (d, *J* = 6.6 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.77 – 7.71 (m, 1H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.51 – 7.46 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 156.0, 148.3, 138.1, 137.0, 135.6, 129.9, 129.7, 129.0, 128.8, 127.5, 127.2, 126.5, 118.6.

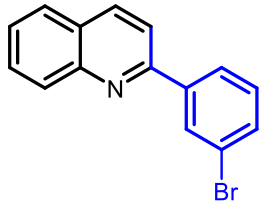


2-(4-bromophenyl)quinoline (**7a**)[6] 90% (255 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 6.4 Hz, 2H), 7.82 – 7.71 (m, 3H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 156.0, 148.2, 138.5, 137.0, 132.0, 129.9, 129.7, 129.1, 127.5, 127.3, 126.6, 124.0, 118.5.

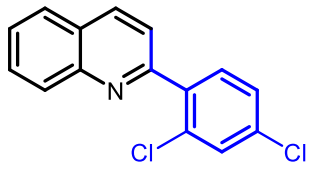


2-(4-idophenyl)quinoline (**8a**)[6] 92% (304 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (dd, *J* = 17.8, 8.0 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.88 – 7.79 (m, 4H), 7.76 – 7.71

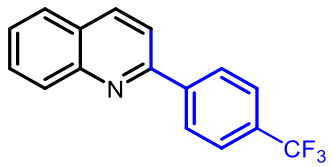
(m, 1H), 7.56 – 7.51 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 156.2, 148.3, 139.1, 138.0, 137.0, 129.9, 129.7, 129.3, 127.5, 127.3, 126.5, 118.5, 95.9.



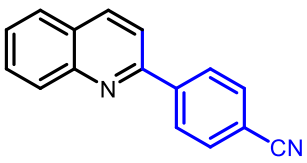
2-(3-bromophenyl)quinoline (**9a**)[4] 81% (229 mg) yielded as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 1.8 Hz, 1H), 8.25 – 8.15 (m, 2H), 8.07 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.72 (m, 1H), 7.62 – 7.52 (m, 2H), 7.39 (t, *J* = 7.9 Hz, 1H). $^{13}C\{^{1}H\}$MR (101 MHz, $CDCl_3$): δ 155.6, 148.2, 141.7, 137.0, 132.2, 130.7, 130.3, 129.9, 129.8, 127.5, 127.4, 126.7, 126.1, 123.2, 118.7.



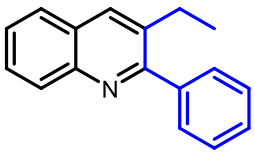
2-(2,4-dichlorophenyl)quinoline (**10a**) 94% (257 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 15.3, 8.4 Hz, 2H), 7.86 (d, *J* = 6.4 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.39 (dd, *J* = 8.3, 2.1 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 156.3, 148.1, 138.2, 135.9, 135.2, 133.1, 132.7, 129.9, 129.7, 127.6, 127.5, 127.2, 127.0, 122.5.



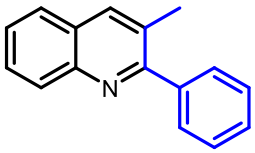
2-(4-(trifluoromethyl)phenyl)quinoline (**11a**)[7] 80% (218 mg) yielded as white solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 – 8.14 (m, 4H), 7.84 (dd, *J* = 8.3, 3.7 Hz, 2H), 7.76 (t, *J* = 8.1 Hz, 3H), 7.60 – 7.53 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 155.6, 148.3, 142.9, 137.1, 131.2, 130.9, 130.0, 129.9, 127.8, 127.6, 127.5, 126.9, 125.8, 125.8, 125.7, 125.7, 123.0, 118.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49.



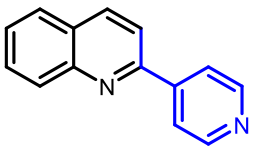
4-(quinolin-2-yl)benzonitrile (**12a**)[8] 84% (193 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.25 (m, 3H), 8.18 (d, *J* = 7.4 Hz, 1H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.83 – 7.75 (m, 3H), 7.59 (t, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 154.9, 148.3, 143.7, 137.3, 132.6, 130.2, 129.9, 128.1, 127.7, 127.6, 127.2, 118.9, 118.7, 112.8.



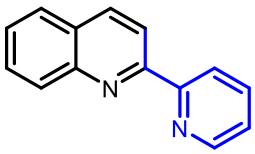
3-ethyl-2-phenylquinoline (**13a**) 89% (207 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.6 Hz, 1H), 8.08 (s, 1H), 7.84 (d, *J* = 9.9 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.60 – 7.46 (m, 6H), 2.86 – 2.80 (m, 2H), 1.22 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.7, 146.4, 140.9, 135.3, 135.0, 129.3, 128.8, 128.8, 128.3, 128.1, 127.8, 127.0, 126.4, 26.1, 14.8.



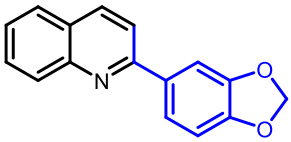
3-methyl-2-phenylquinoline (**14a**)[5] 88% (192 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.6 Hz, 1H), 8.00 (s, 1H), 7.78 (d, *J* = 9.9 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.60 (d, *J* = 9.6 Hz, 2H), 7.49 (td, *J* = 15.3, 7.0 Hz, 4H), 2.46 (d, *J* = 1.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.6, 146.7, 140.9, 136.8, 129.3, 129.4, 128.9, 128.8, 128.4, 128.2, 127.6, 126.8, 126.5, 20.7.



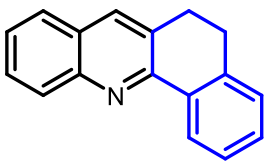
2-(pyridin-4-yl)quinoline (**15a**)[6] 79% (162 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 5.9 Hz, 2H), 8.29 – 8.13 (m, 2H), 8.03 (d, *J* = 6.2 Hz, 2H), 7.85 (dd, *J* = 10.1, 8.3 Hz, 2H), 7.75 (t, *J* = 8.5 Hz, 1H), 7.60 – 7.52 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 154.4, 150.5, 148.3, 146.6, 137.3, 130.0, 130.0, 127.7, 127.6, 127.24, 121.7, 118.4.



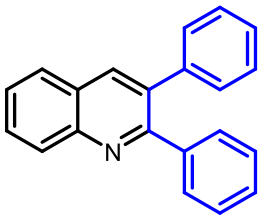
2-(pyridin-2-yl)quinoline (**16a**)[6] 75% (154 mg) yielded as colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (d, *J* = 5.5 Hz, 1H), 8.66 (d, *J* = 7.9 Hz, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.79 (m, 2H), 7.73 (t, *J* = 6.9 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.39 – 7.32 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 156.4, 156.19, 149.2, 148.0, 137.0, 136.8, 129.8, 129.6, 128.3, 127., 126.8, 124.1, 121.9, 119.0.



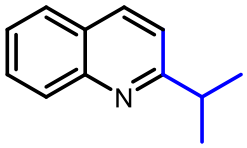
2-(benzo[d][1,3]dioxol-5-yl)quinoline (**17a**)[5] 83% (206 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (t, *J* = 7.9 Hz, 2H), 7.82 – 7.74 (m, 3H), 7.73 – 7.69 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 156.7, 148.9, 148., 148.2, 136.7, 134.2, 129.66, 129.6, 127.4, 127.0 126.1, 121.8, 118.6, 108.5, 107.94, 101.4.



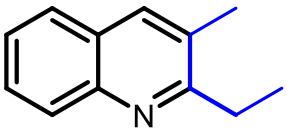
5,6-dihydrobenzo[c]acridine (**18a**)[6] 85% (196 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 7.7 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 7.80 – 7.59 (m, 2H), 7.53 – 7.36 (m, 3H), 7.29 (d, *J* = 7.4 Hz, 1H), 3.17 – 2.96 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.4, 147.7, 139.5, 134.8, 133.7, 130.6, 129.7, 129.5, 128.7, 128.0, 128.0, 127.4, 127.0, 126.1, 126.1, 28.9, 28.4.



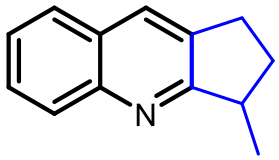
2,3-diphenylquinoline (**19a**)[9] 87% (244 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.20 (m, 2H), 7.90 (d, J = 10.0 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.60 (t, J = 6.9 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.35 – 7.27 (m, 8H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.5, 147.3, 140.4, 140.0, 137.6, 134.6, 130.1, 129.8, 129.7, 129.5, 128.3, 128.1, 128.0, 127.5, 127.3, 127.2, 126.8.



2-isopropylquinoline (**20a**)[10] 89% (152 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.03 (m, 2H), 7.77 (d, J = 6.3 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.47 (t, J = 8.1 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 3.28 (dq, J = 13.9, 7.0 Hz, 1H), 1.40 (d, J = 6.8 Hz, 6H). ^{13}C{^{1}H} (101 MHz, $CDCl_3$): δ 167.7, 147.7, 136.4, 129.3, 129.0, 127.5, 127.0, 125.7, 119.2, 37.3, 22.6.



2-ethyl-3-methylquinoline (**21a**) 93% (159 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 9.3 Hz, 1H), 7.81 (s, 1H), 7.68 (d, J = 9.7 Hz, 1H), 7.60 (t, J = 6.9 Hz, 1H), 7.47 – 7.40 (m, 1H), 2.99 (q, J = 7.5 Hz, 2H), 2.47 (s, 3H), 1.37 (t, J = 7.5 Hz, 3H).^{13}C{^{1}H} (101 MHz, $CDCl_3$): δ 163.3, 146.7, 135.8, 129.4, 128.5, 128.3, 127.3, 126.7, 125.61, 29.5, 19.13, 12.9.



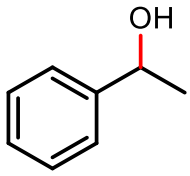
3-methyl-2,3-dihydro-1H-cyclopenta[b]quinoline (**22a**) 88% (156 mg) yielded as colourless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.4 Hz, 1H), 7.89 (s, 1H), 7.75 (d, J = 9.8 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.50 – 7.44 (m, 1H), 3.35 (h, J = 7.0 Hz, 1H), 3.15 – 3.05 (m, 1H), 3.05 – 2.95 (m, 1H), 2.52 – 2.40 (m, 1H), 1.79 (dq, J = 12.5, 8.2 Hz, 1H), 1.48 (d, J = 7.0 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 171.00, 147.7, 135.4, 130.4, 128.8, 128.2, 127.5, 127.4, 125.5, 40.4, 32.9, 28.7, 18.6.

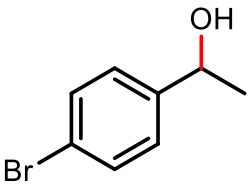
General procedure of transfer hydrogenation of ketones.

In a catalytic tube, Ketone (1 mmol), complex **3** (0.5mol %), and KOH (1 equiv) in isopropanol (2 mL) were taken. The reaction mixture was degassed and purged with nitrogen gas for a few minutes to create a N_2 atmosphere. The reaction mixture was then heated at 80 °C in a preheated oil bath for 6 h followed by cooling to room temperature. Then the reaction mixture was diluted with water (2 mL) and extracted with ethyl acetate (3 × 4 mL). The resultant organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Final products were purified by silica gel column chromatography (60-120 mesh size) using petroleum ether /ethyl acetate as eluent.

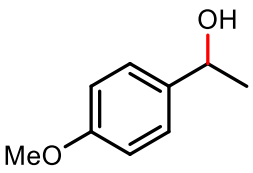
NMR Spectral data of ketones



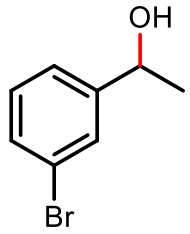
1-phenylethan-1-ol (**2b**)[11] Yield 97% (108.8 mg) yielded as Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 4.6, 2.4 Hz, 4H), 7.34 – 7.26 (m, 1H), 4.95 – 4.76 (m, 1H), 1.55 – 1.46 (m, 3H).$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 145.9, 128.5, 127.4, 125.5, 70.3, 25.2.



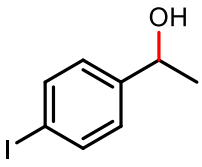
1-(4-bromophenyl)ethan-1-ol (**2b**)[11] 93% (187mg) yielded as Yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.84 (q, J = 6.4 Hz, 1H), 2.11 (s, 1H), 1.45 (d, J = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 144.8, 131.6, 127.2, 121.2, 69.8, 25.3.



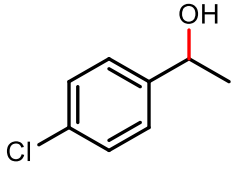
1-(4-methoxyphenyl)ethan-1-ol (**3b)** 83% (126 mg) yielded as Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.88 (q, *J* = 6.5 Hz, 1H), 2.35 (s, 3H), 1.77 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 142.9, 137.2, 129.2, 125.4, 70.3, 25.1, 21.1.



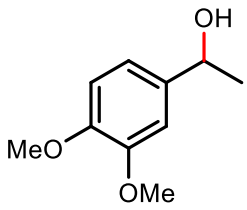
1-(3-bromophenyl)ethan-1-ol **(4b)**[12] 91% (182 mg) yielded as yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 4.88 (q, *J* = 6.4 Hz, 1H), 1.85 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 148.1, 130.5, 130.1, 128.6, 124.0, 122.6, 69.8, 25.3.



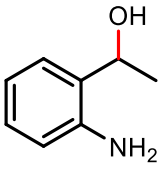
1-(4-iodophenyl)ethan-1-ol (**5b)**[11] 86% (213 mg) yielded a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 1.86 (s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.5, 137.6, 127.4, 92.7, 69.9, 25.3.



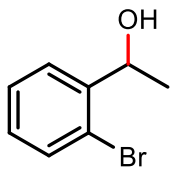
1-(4-chlorophenyl)ethan-1-ol (**6b)**[11] 90% (141 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 4H), 4.85 (q, *J* = 6.6 Hz, 1H), 2.00 (s, 1H), 1.44 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.27, 133.1, 128.6, 128.6, 126.8, 69.7, 25.3.



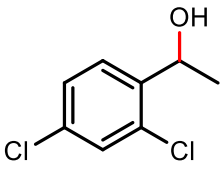
1-(3,4-dimethoxyphenyl)ethan-1-ol (**7b**)[11] 82% (149 mg) yielded as colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, *J* = 2.1 Hz, 1H), 6.87 (dd, *J* = 7.9, 2.3 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 4.82 (q, *J* = 6.5 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.03 (s, 1H), 1.46 (d, *J* = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.1, 148.3, 138.6, 117.5, 111.0, 108.7, 108.7, 70.2, 55.9, 55.9, 25.1.



1-(2-aminophenyl)ethan-1-ol (**8b**)[11] 75% (102 mg) yielded as Yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.02 (m, 2H), 6.82 – 6.62 (m, 2H), 4.94 (q, *J* = 6.6 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.2, 128.6, 128.3, 126.5, 118.1, 116.6, 69.7, 21.5.

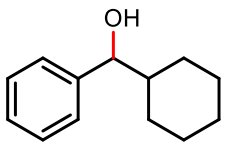


1-(2-bromophenyl)ethan-1-ol (**9b**) 90% (181 mg) yielded a White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.82 (q, *J* = 6.4 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H) ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 148.2, 130.6, 130.2, 128.7, 124.1, 122.7, 69.8, 25.3.

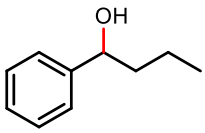


1-(2,4-dichlorophenyl)ethan-1-ol (**10b**)[12] 87% (166 mg) yielded a Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.51 (dd, *J* = 8.4, 4.5 Hz, 1H), 7.35 -7.34(d, *J* = 2.2 Hz, 1H), 7.29-7.26 (m, 1H), 5.27 – 5.20 (m,

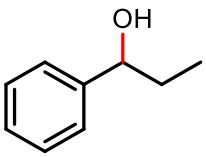
1H), 1.46 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 141.8, 133.5, 132.2, 129.2, 127.6, 127.5, 66.7, 23.7.



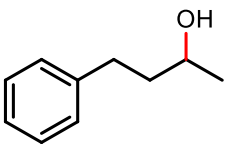
cyclohexyl(phenyl)methanol (**11b)** 83% (158 mg) yielded a Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.20 (m, 5H), 4.31 (d, J = 7.3 Hz, 1H), 1.99 – 1.91 (m, 2H), 1.73 (dd, J = 11.9, 4.2 Hz, 1H), 1.66 – 1.55 (m, 3H), 1.38 – 1.31 (m, 1H), 1.16 – 1.08 (m, 2H), 1.00 (dd, J = 12.1, 4.2 Hz, 1H), 0.94 – 0.84 (m, 1H). ^{13}C $\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 143.7, 128.3, 127.5, 126.6, 79.5, 45.1, 29.4, 29.0, 26.5, 26.2, 26.1.



1-phenylbutan-1-ol (**12b)** 81% (122 mg) yielded a Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.15 (m, 5H), 4.58 (d, J = 5.5 Hz, 1H), 1.75 – 1.58 (m, 2H), 1.38 – 1.21 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C $\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 145.0, 128.6, 127.5, 126.0, 74.4, 41.3, 19.1, 14.1.

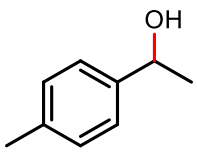


1-phenylpropan-1-ol (**13b)**[13] 80% (109 mg) yielded a Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.26 (m, 5H), 4.61 (t, J = 6.6 Hz, 1H), 1.88 – 1.74 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H). ^{13}C $\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 144.7, 128.5, 127.6, 126.1, 76.1, 32.0, 10.3.

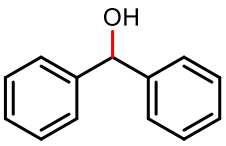


4-phenylbutan-2-ol (**14b)**[4] 78% (117 mg) yielded as Colourless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.3 Hz, 2H), 7.21 (dd, J = 7.7, 3.3 Hz, 3H), 3.84 (h, J = 6.1 Hz, 1H), 2.84 – 2.61 (m, 2H), 1.83 – 1.74 (m, 2H), 1.24

(d, J = 6.2 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)1: δ 142.2, 128.5, 125.9, 67.6, 41.0, 32.2, 23.7.



1-(p-tolyl)ethan-1-ol (**15b**)[12] 87% (109 mg) yielded as White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 4.96 (q, J = 6.5 Hz, 1H), 2.43 (s, 3H), 1.57 (d, J = 6.4 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 143.0, 137.3, 129.3, 125.5, 70.4, 25.2, 21.2.

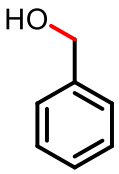


diphenylmethanol (**16b**)[11] 92% (169 mg) yielded as White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dt, J = 15.0, 7.5 Hz, 8H), 7.30 (t, J = 7.1 Hz, 2H), 5.87 (s, 1H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 143.8, 128.5, 127.6, 126.6, 76. 3.

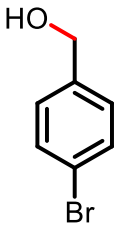
General procedure of transfer hydrogenation of ketones.

In a catalytic tube, Aldehyde (1 mmol), complex **3** (0.5mol %), and KOH (1 equiv) in isopropanol (2 mL) were taken. The reaction mixture was degassed and purged with nitrogen gas for a few minutes to create a N_2 atmosphere. The reaction mixture was then heated at 80 °C in a preheated oil bath for 6 h followed by cooling to room temperature. Then the reaction mixture was diluted with water (2 mL) and extracted with ethyl acetate (3 × 4 mL). The resultant organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Final products were purified by silica gel column chromatography (60-120 mesh size) using petroleum ether /ethyl acetate as eluent.

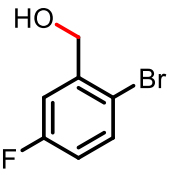
NMR spectral data of catalytic products of transfer hydrogenation of aldehyde



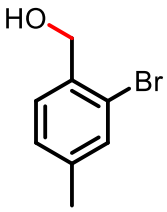
phenylmethanol (**1c**)[13] 94% (101 mg) yielded as colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 4.6 Hz, 4H), 7.30 (dq, J = 9.0, 4.5 Hz, 1H), 4.69 (s, 2H). $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$): δ 141.0, 128.6, 127.6, 127.0, 65.3, 65.3.



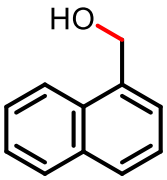
(4-bromophenyl)methanol (**2c**)[13] 91% (170 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 4.67 (s, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 139.8, 131.6, 128.6, 121.5, 64.6.



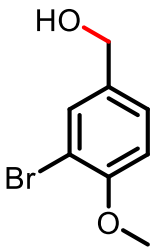
(2-bromo-5-fluorophenyl)methanol (**3c)** 87% (178 mg) yielded as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, J = 8.7, 5.1 Hz, 1H), 7.31 – 7.23 (m, 1H), 6.88 (td, J = 8.3, 2.9 Hz, 1H), 4.72 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 163.6, 161.1, 142.1, 133.7, 133.6, 116.0, 115.6, 64.5.



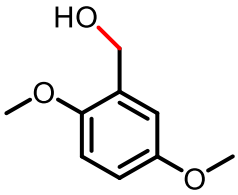
(2-bromo-4-methylphenyl)methanol (**4c)** 81% (163 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 5.7 Hz, 1H), 4.72 (s, 2H), 2.35 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 139.4, 136.7, 133.1, 129.0, 128.4, 122.6, 65.0, 20.8.



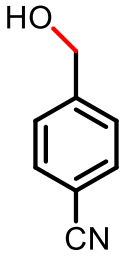
naphthalen-1-ylmethanol (**5c)** 85% (134 mg) yielded as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 9.1 Hz, 1H), 7.94 – 7.82 (m, 2H), 7.62 – 7.52 (m, 3H), 7.51 – 7.45 (m, 1H), 5.17 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 136.39, 133., 131.4, 128.7, 128.6, 126.4, 125.9, 125.4, 125.4, 123.7, 63.7.



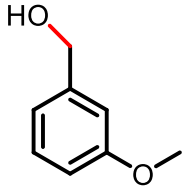
(3-bromo-4-methoxyphenyl)methanol **(6c)** 87% (189 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_{3:}$) δ 7.58 (d, *J* = 12.4 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.64 (s, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.3, 134.6, 132.2, 127.4, 111.9, 111.6, 64.2, 56.3.



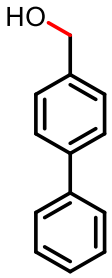
(2,5-dimethoxyphenyl)methanol **(7c)** 88% (148 mg) yielded as yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* = 2.6 Hz, 1H), 6.80 – 6.76 (m, 2H), 4.65 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.6, 151.5, 130.1, 114.8, 113.0, 111.1, 62.0, 55.8.



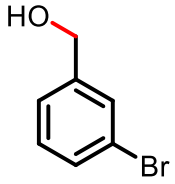
4-(hydroxymethyl)benzonitrile **(8c)** 78% (104 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.75 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.5, 132.3, 127.0, 118.9, 111.0, 64.1.



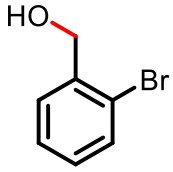
(3-methoxyphenyl)methanol **(9c)**[13] 79% (109 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 5.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 4.65 (s, 2H), 3.80 (s, 3H) ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.8, 142.6, 129.6, 119.1, 113. 4, 112.26, 65.2, 55.2.



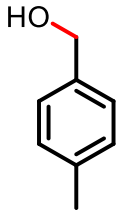
[1,1'-biphenyl]-4-ylmethanol **(10c)** 84% (154 mg) yielded as colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.60 (m, 4H), 7.50 – 7.44 (m, 4H), 7.41 – 7.35 (m, 1H), 4.77 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 140.8, 140.7, 139.9, 128.8, 127.5, 127.4, 127.1, 65.2.



3-bromophenyl)methanol **(11c)** 93% (187 mg) yielded as colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.44 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 4.63 (s, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 143.1, 130.6, 130.1, 129.9, 125.4, 122.6, 64.4.



2-bromophenyl)methanol **(12c)** 89% (166 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 9.3 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.17 (t, J = 8.6 Hz, 1H), 4.72 (s, 2H) $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 139.8, 132.6, 129.1, 128.8, 127.7, 122.5, 64.9.



p-tolylmethanol **(13c)**[13] 84% (102 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 4.65 (s, 2H), 2.35 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 137.9, 137.4, 129.3, 127.13, 65.3, 21.2.

NMR spectra of catalytic products

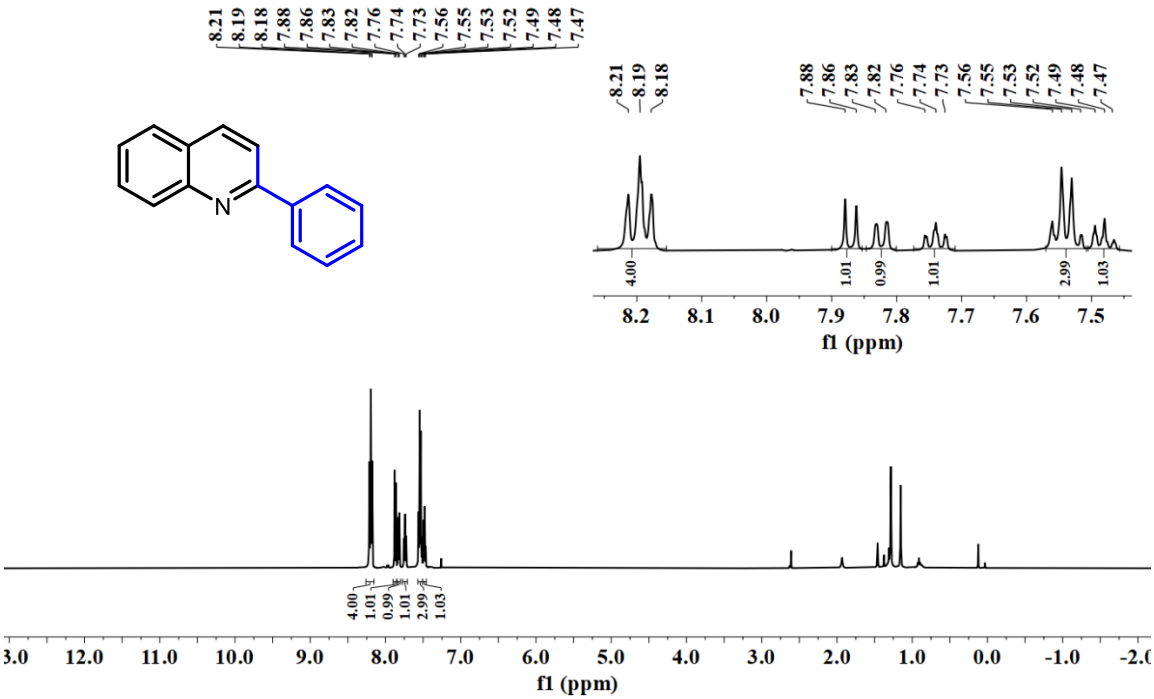


Fig. S29. ^{1}H NMR spectrum of **1a** in $CDCl_3$ (500 MHz).

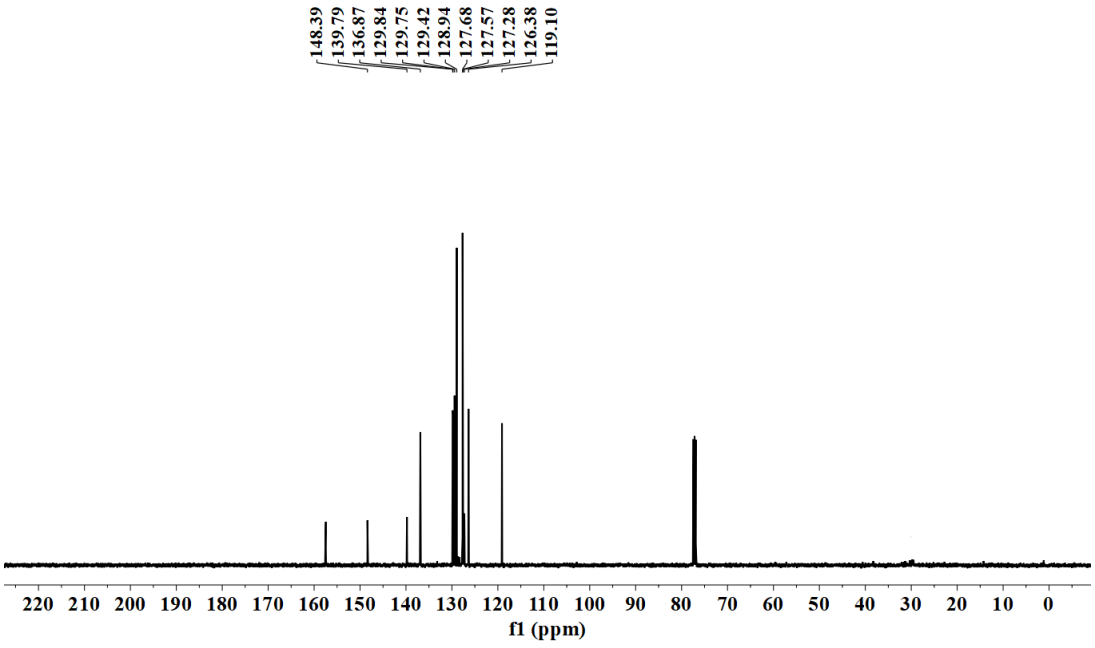


Fig. S30. ^{13}C{^{1}H} NMR spectrum of **1a** in $CDCl_3$ (126 MHz).

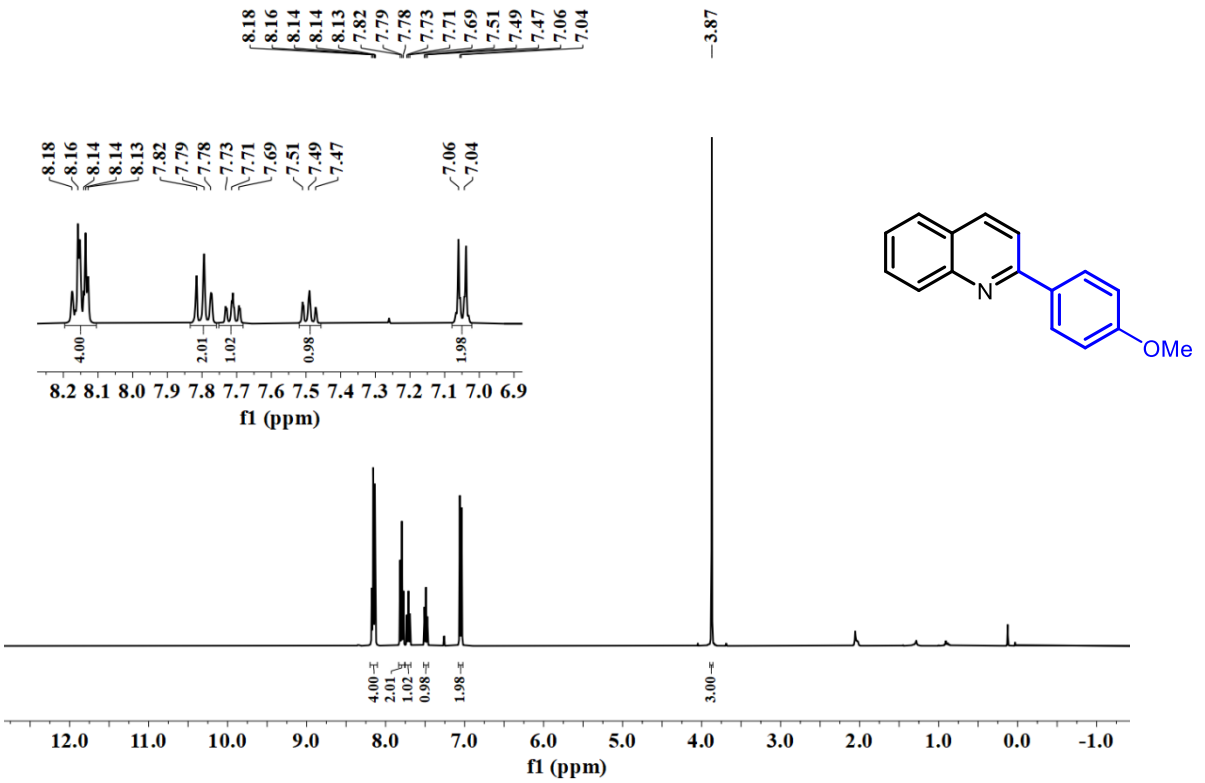


Fig. S31. ^{1}H NMR spectrum of **2a** in $CDCl_3$ (400 MHz).

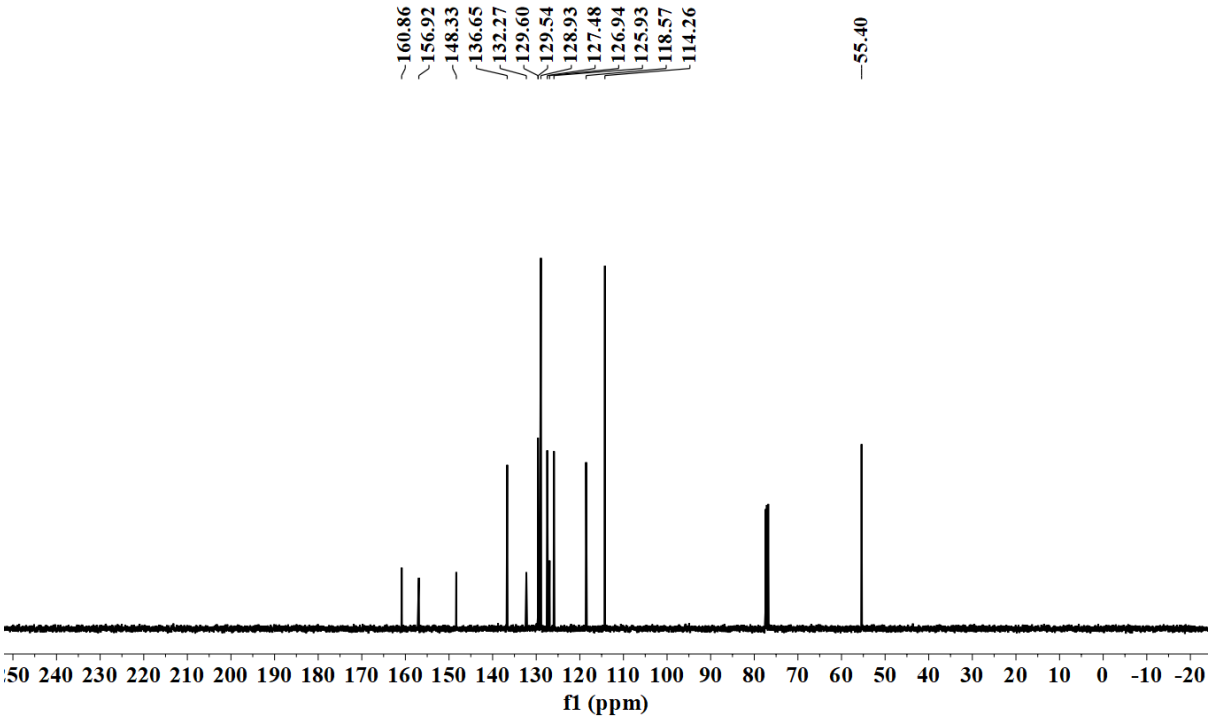


Fig. S32. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$ (101 MHz).

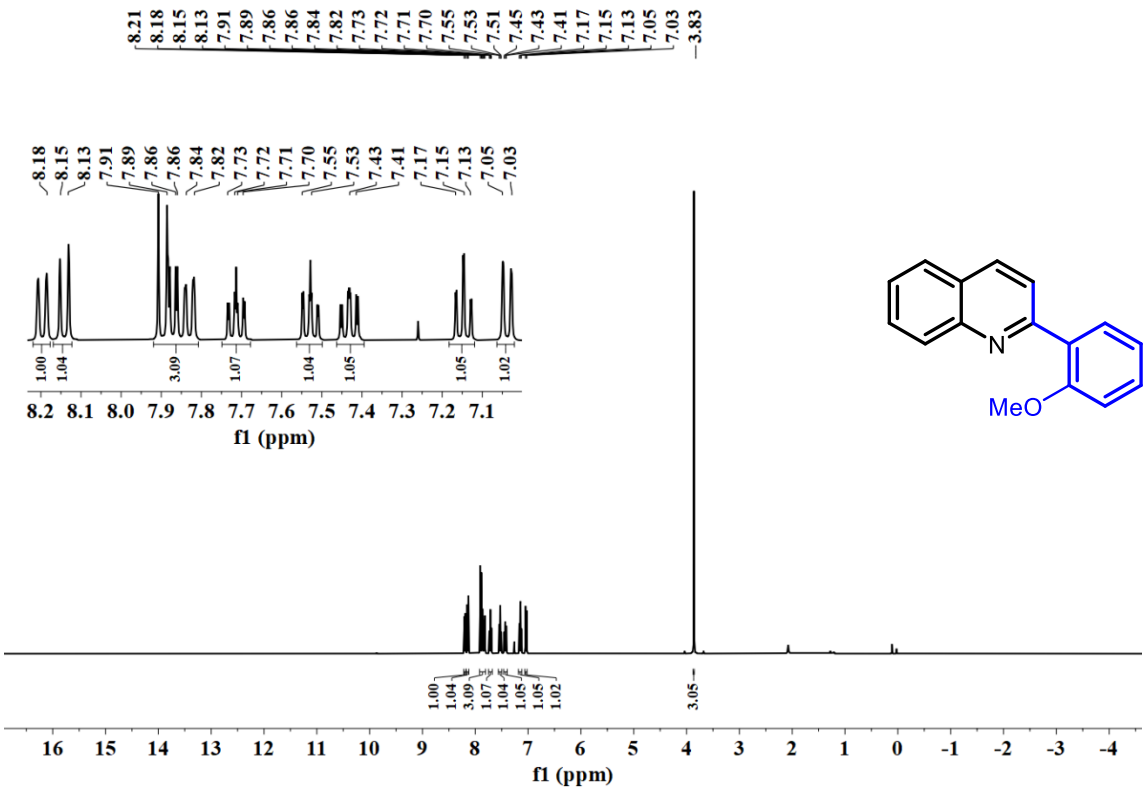


Fig. S33. ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz).

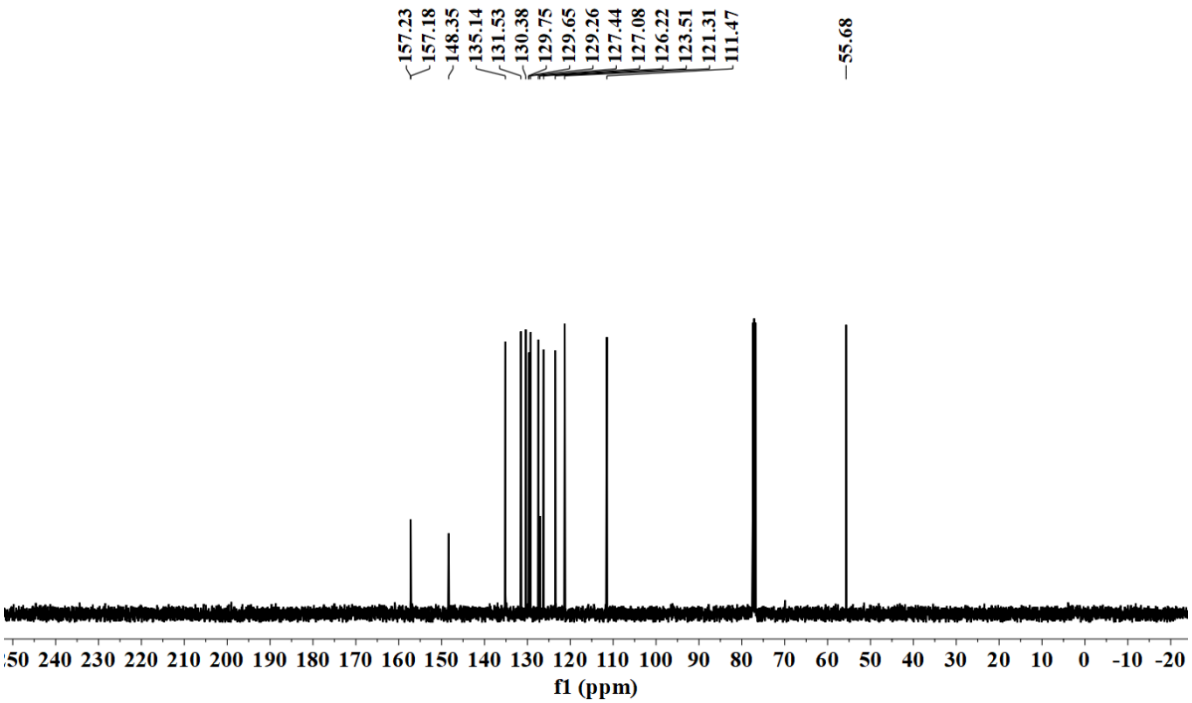


Fig. S34. ^{13}C{^{1}H} NMR spectrum of **3a** in $CDCl_3$ (101 MHz).

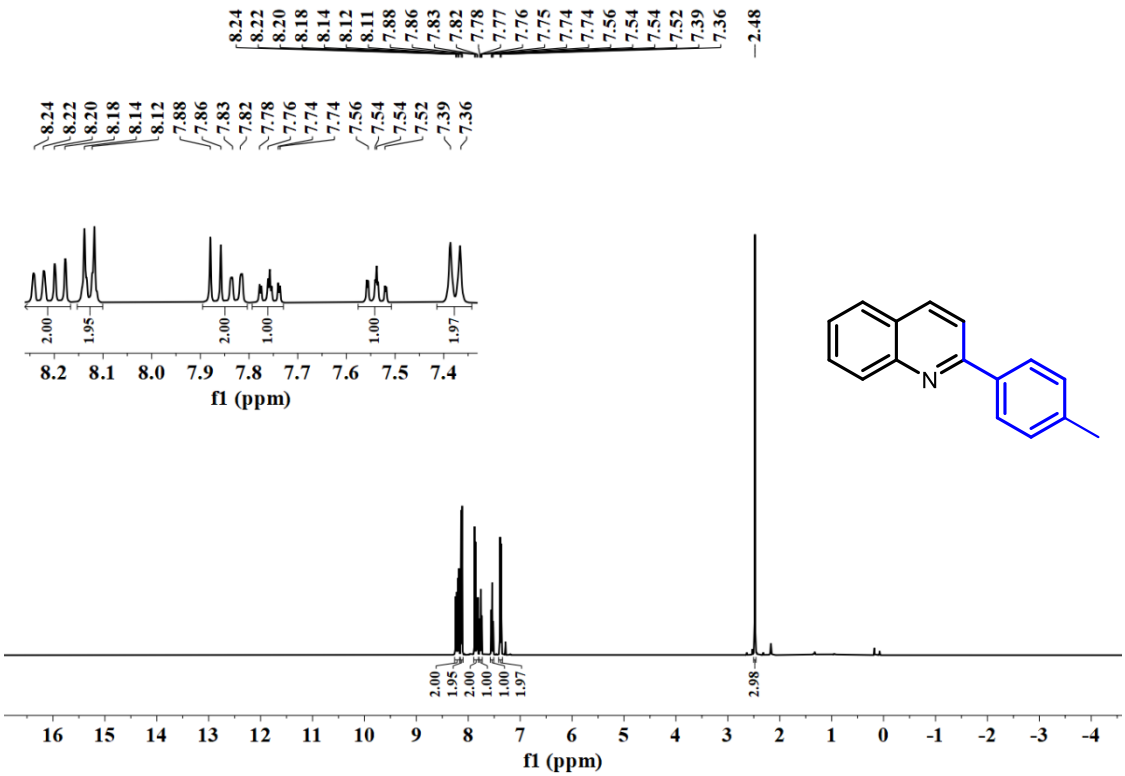


Fig. S35. ^{1}H NMR spectrum of **4a** in $CDCl_3$ (400 MHz).

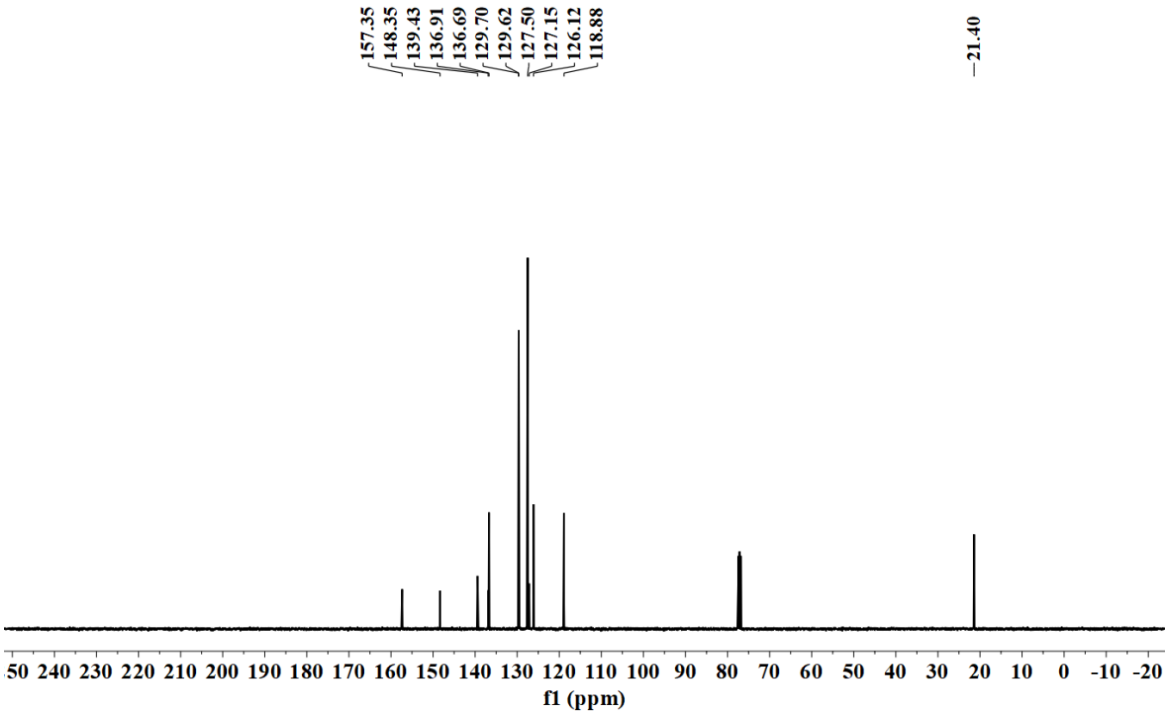


Fig. S36. ^{13}C{^{1}H} NMR spectrum of **4a** in $CDCl_3$ (101 MHz).

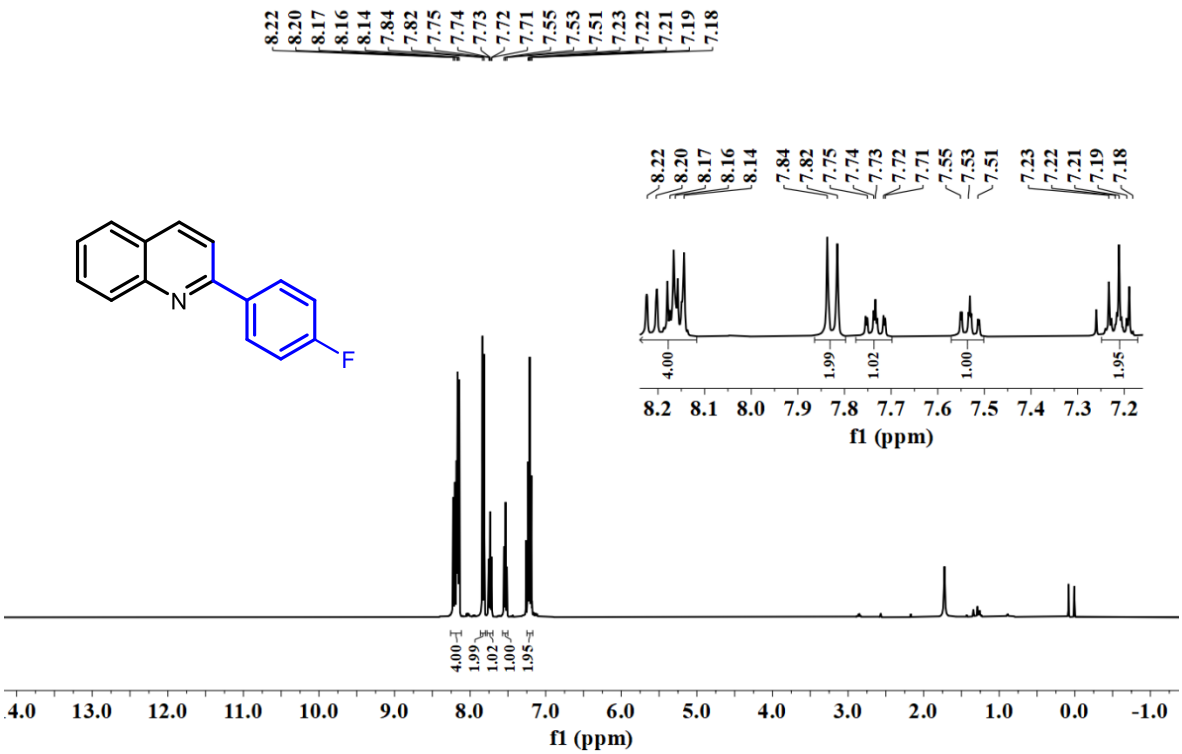


Fig. S37. ^{1}H NMR spectrum of **5a** in $CDCl_3$ (400 MHz).

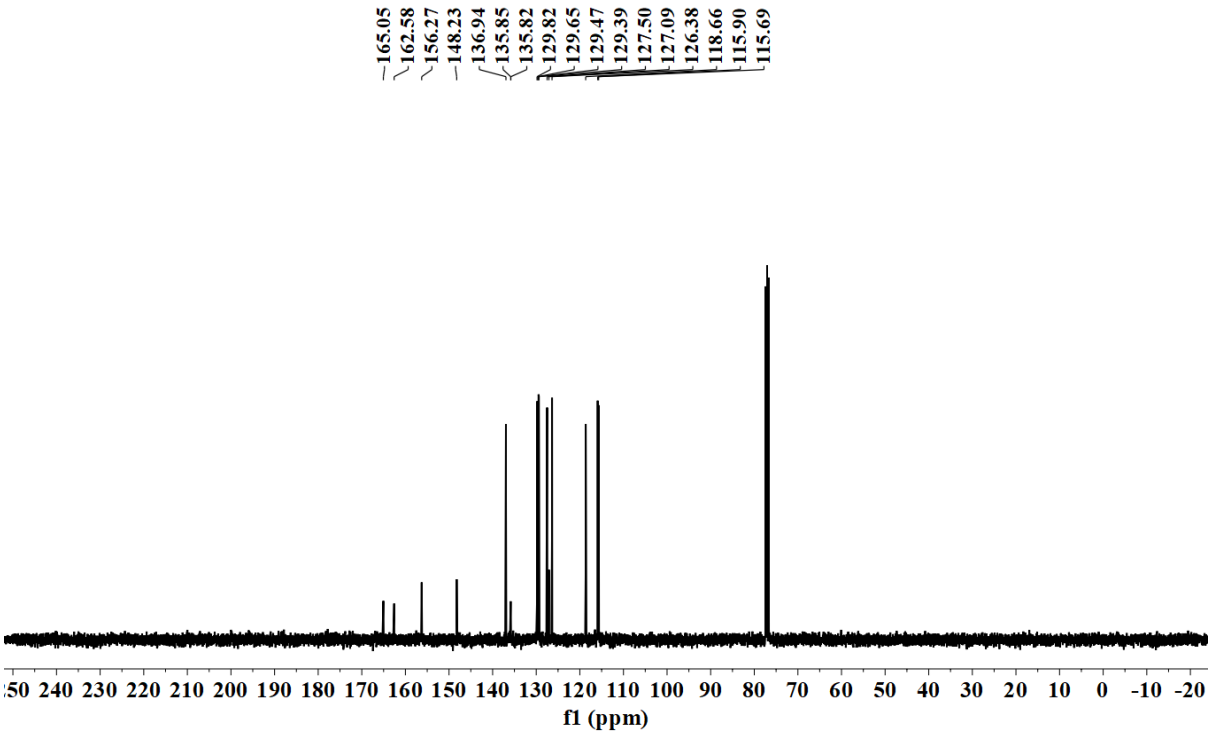


Fig. S38. ^{13}C{^{1}H} NMR spectrum of **5a** in $CDCl_3$ (101 MHz).

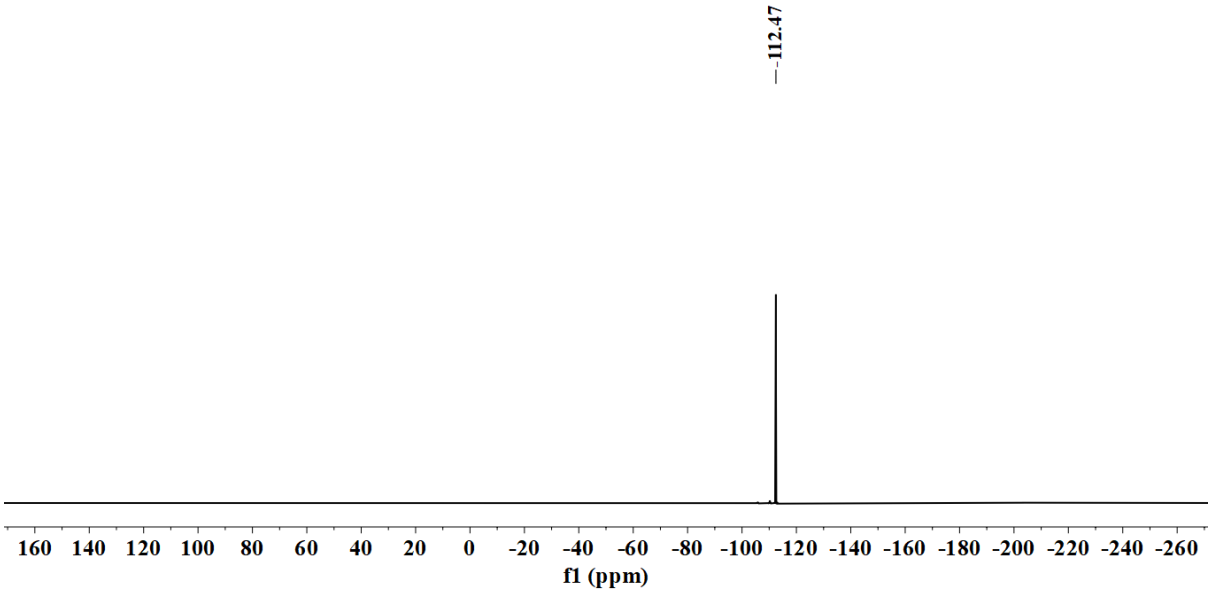


Fig. S39. $^{19}F\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ (376 MHz).

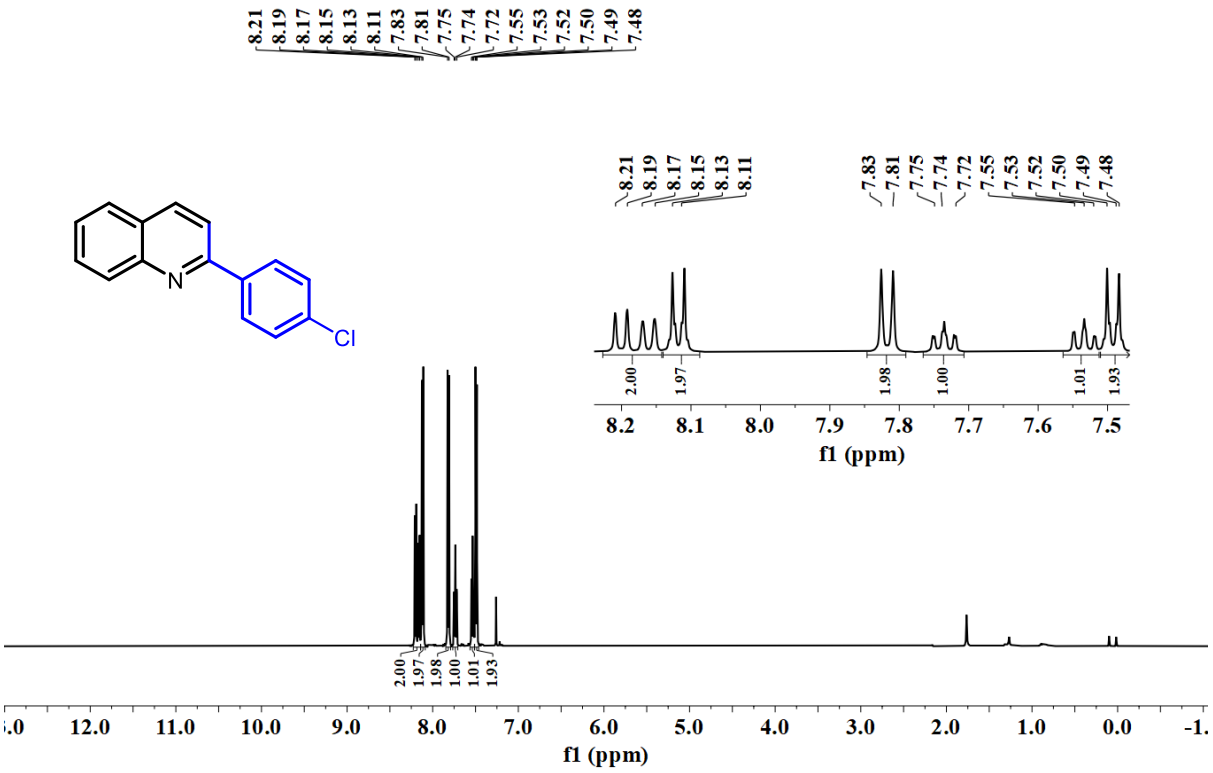


Fig.. S40. ^{1}H NMR spectrum of **6a** in $CDCl_3$ (400 MHz).

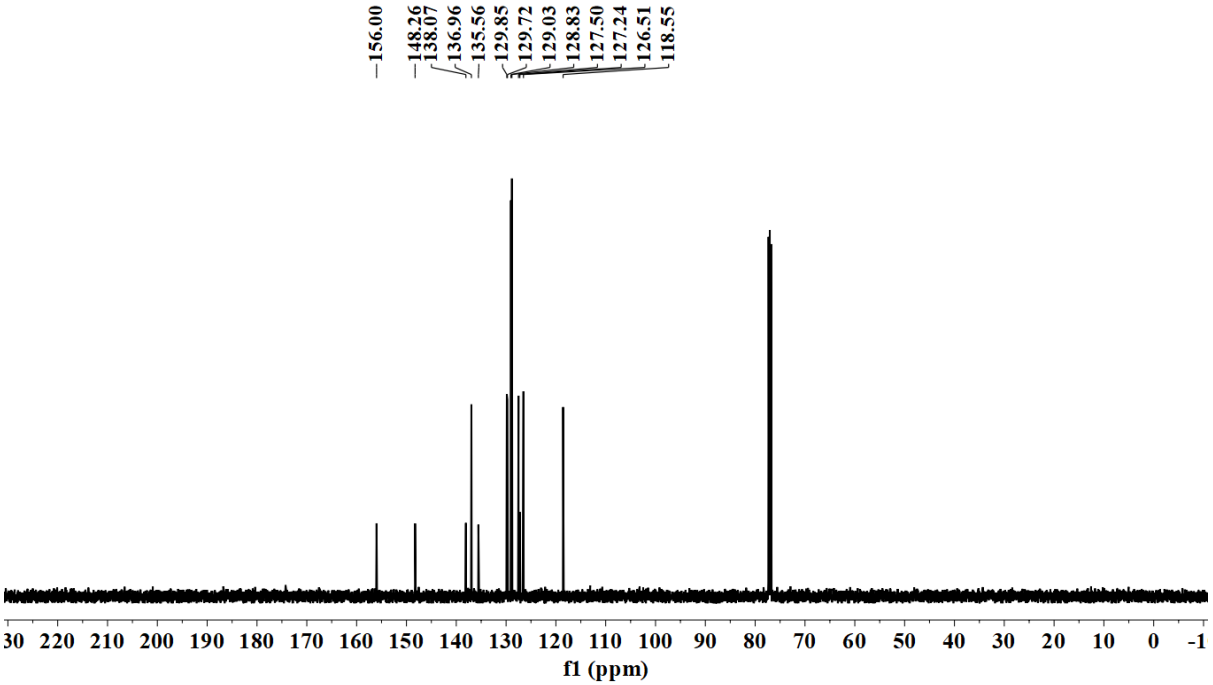


Fig. S41. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$ (101 MHz).

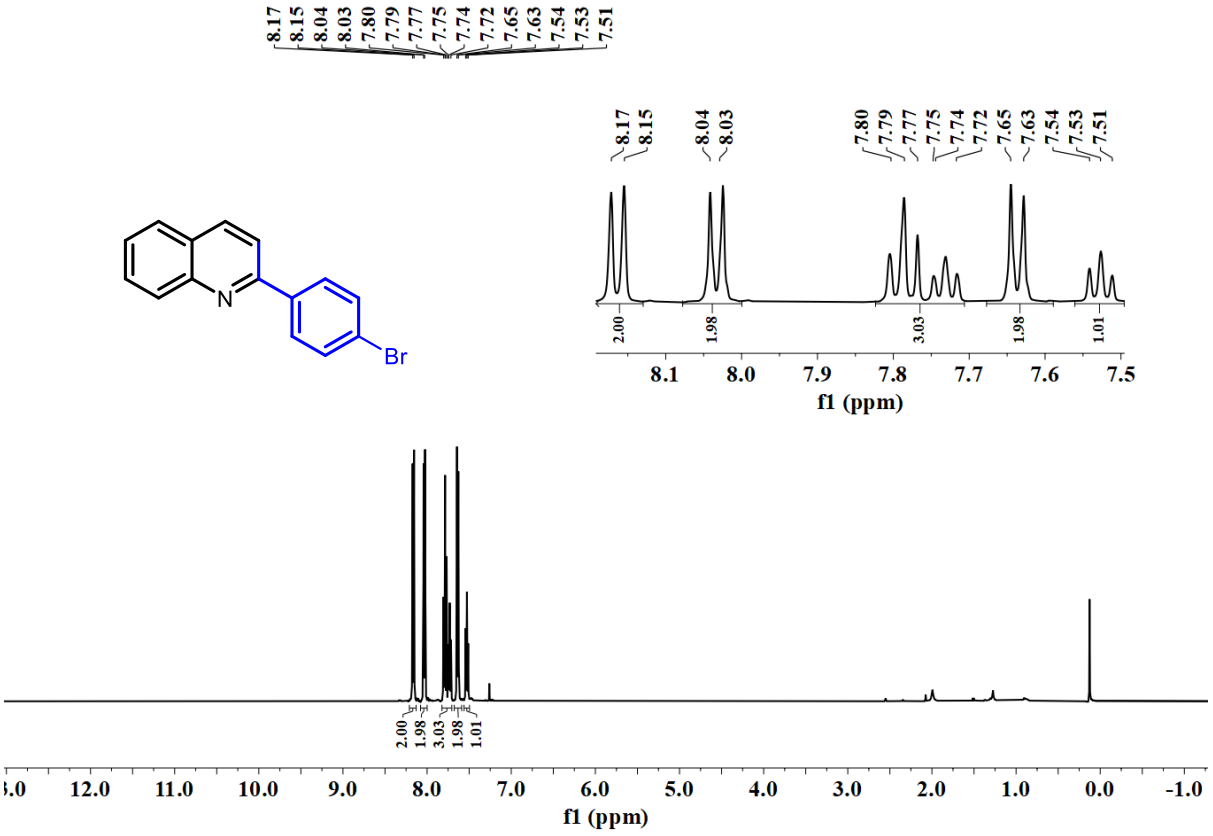


Fig. S42. ^{1}H NMR spectrum of **7a** in $CDCl_3$ (500 MHz).

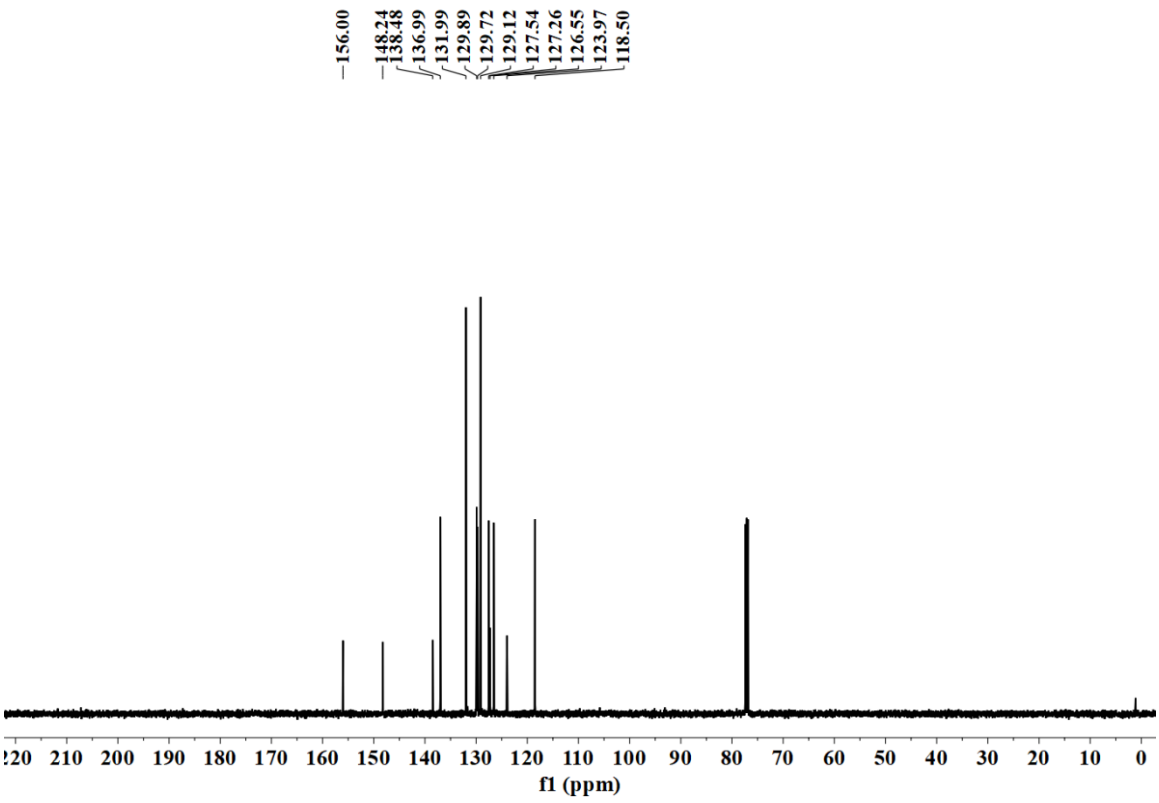


Fig. S43. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$ (126 MHz).

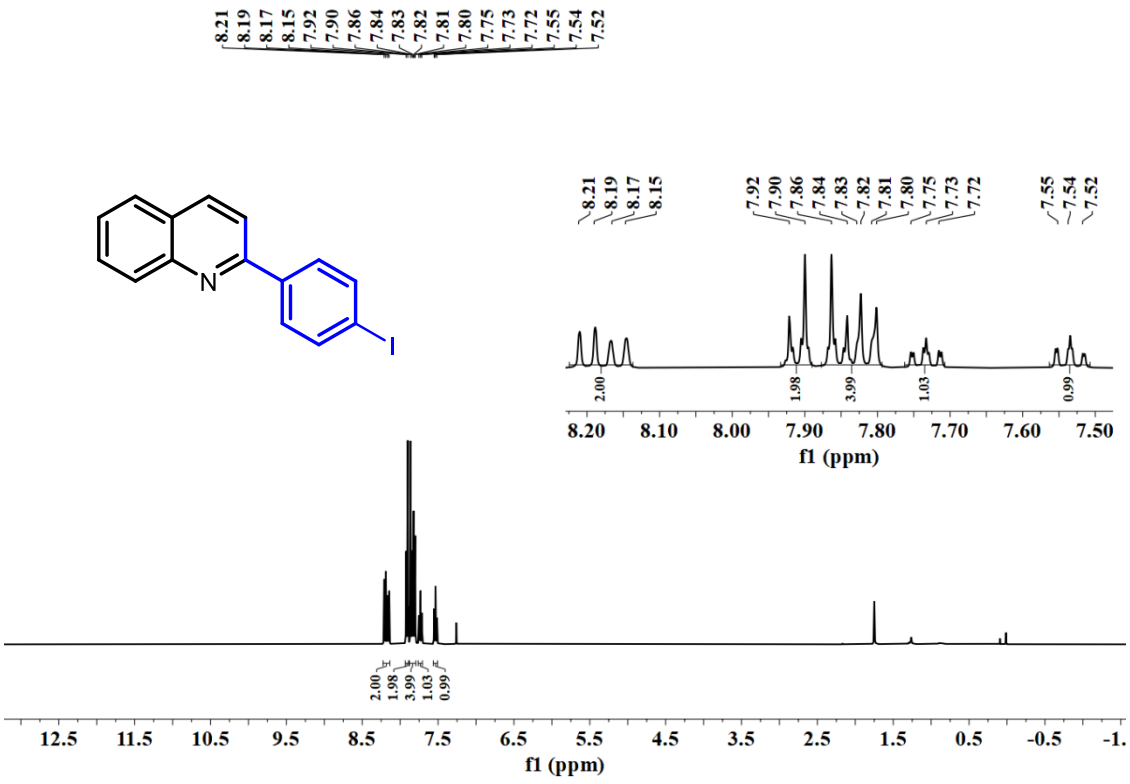


Fig. S44. ^{1}H NMR spectrum of **8a** in $CDCl_3$ (400 MHz).

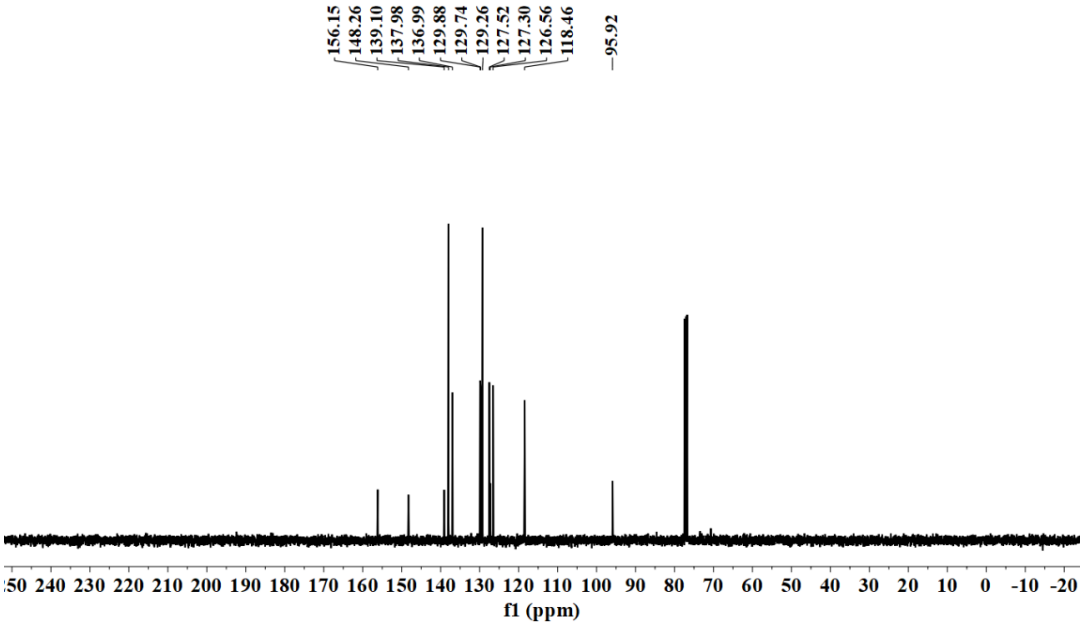


Fig. S45. $^{13}C\{^{1}H\}$ NMR spectrum of **8a** in $CDCl_3$ (101 MHz).

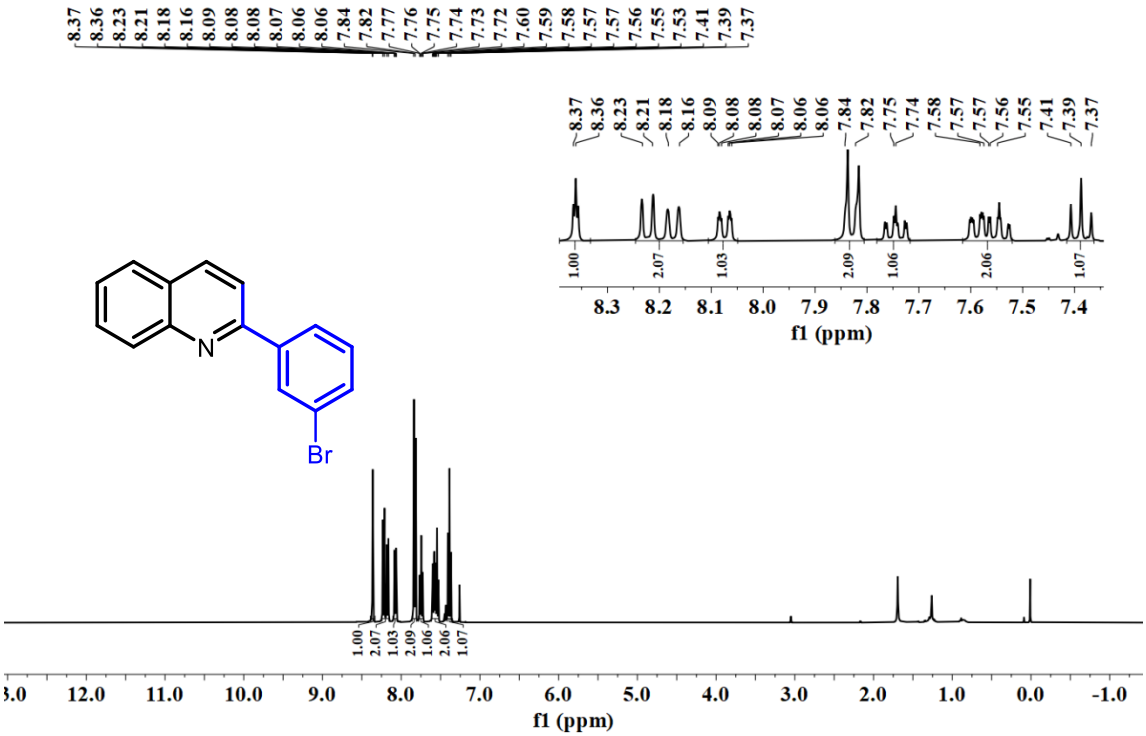


Fig. S46. ^{1}H NMR spectrum of **9a** in $CDCl_3$ (400 MHz).

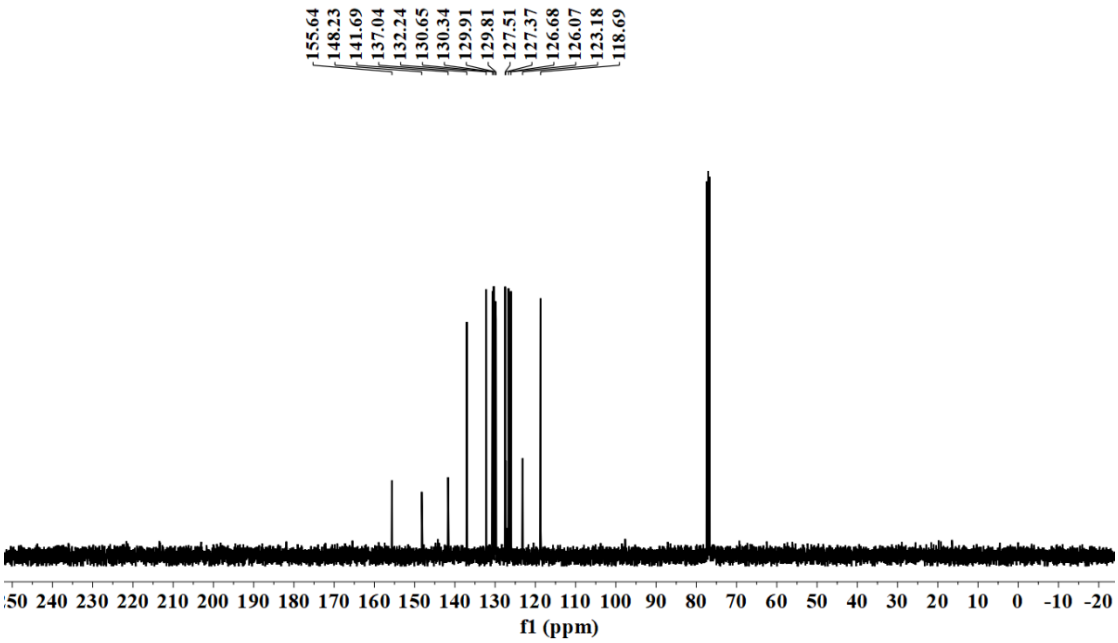


Fig. S47. $^{13}C\{^{1}H\}$ NMR spectrum of **9a** in $CDCl_3$ (101 MHz).

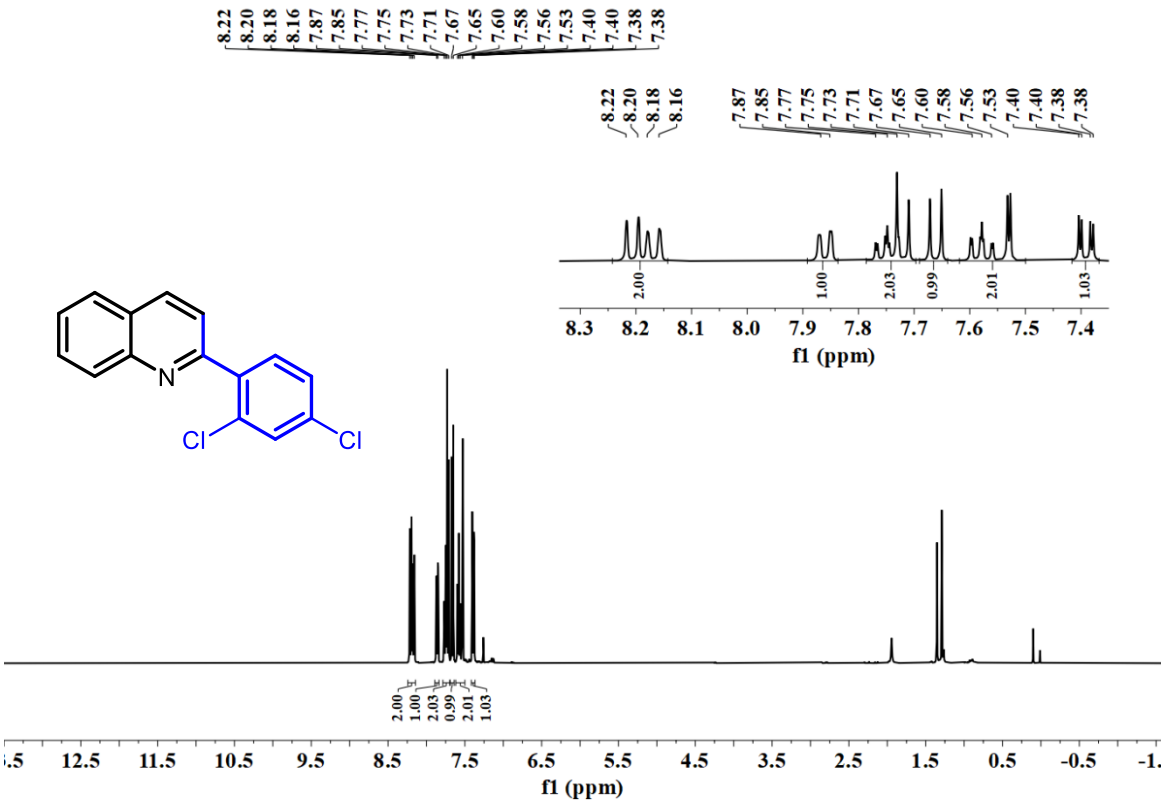


Fig. S48. ^{1}H NMR spectrum of **10a** in $CDCl_3$ (400 MHz).

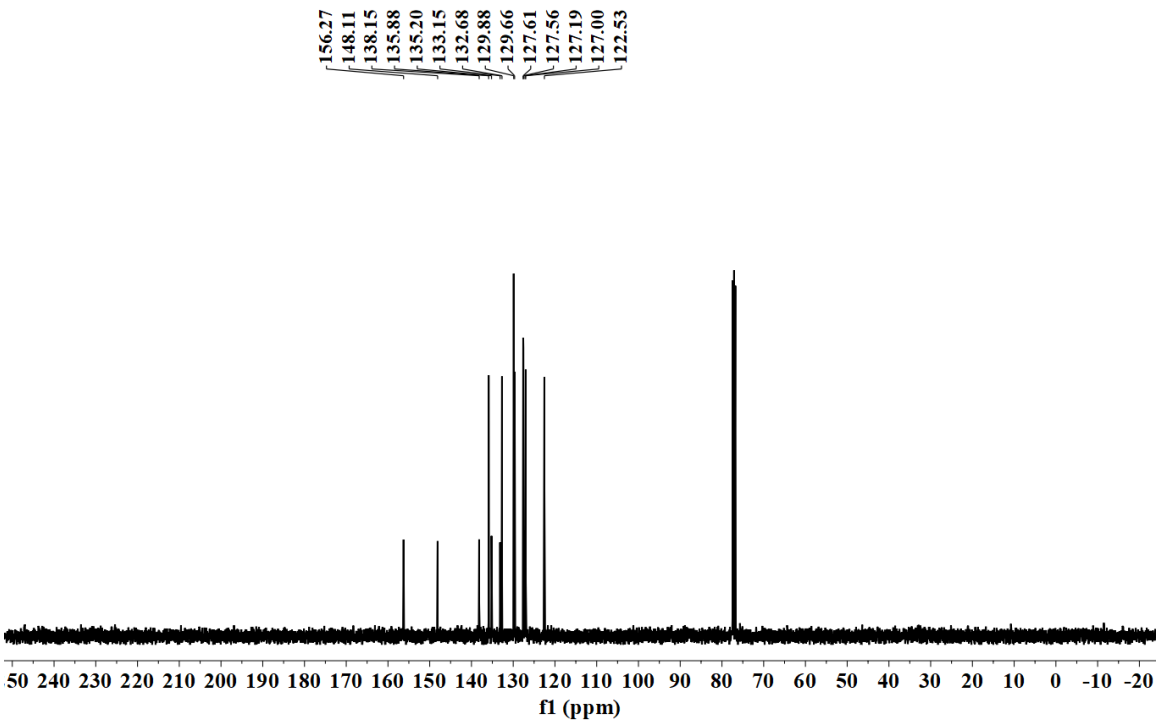


Fig. S49. $^{13}C\{^{1}H\}$ NMR spectrum of **10a** in $CDCl_3$ (101 MHz).

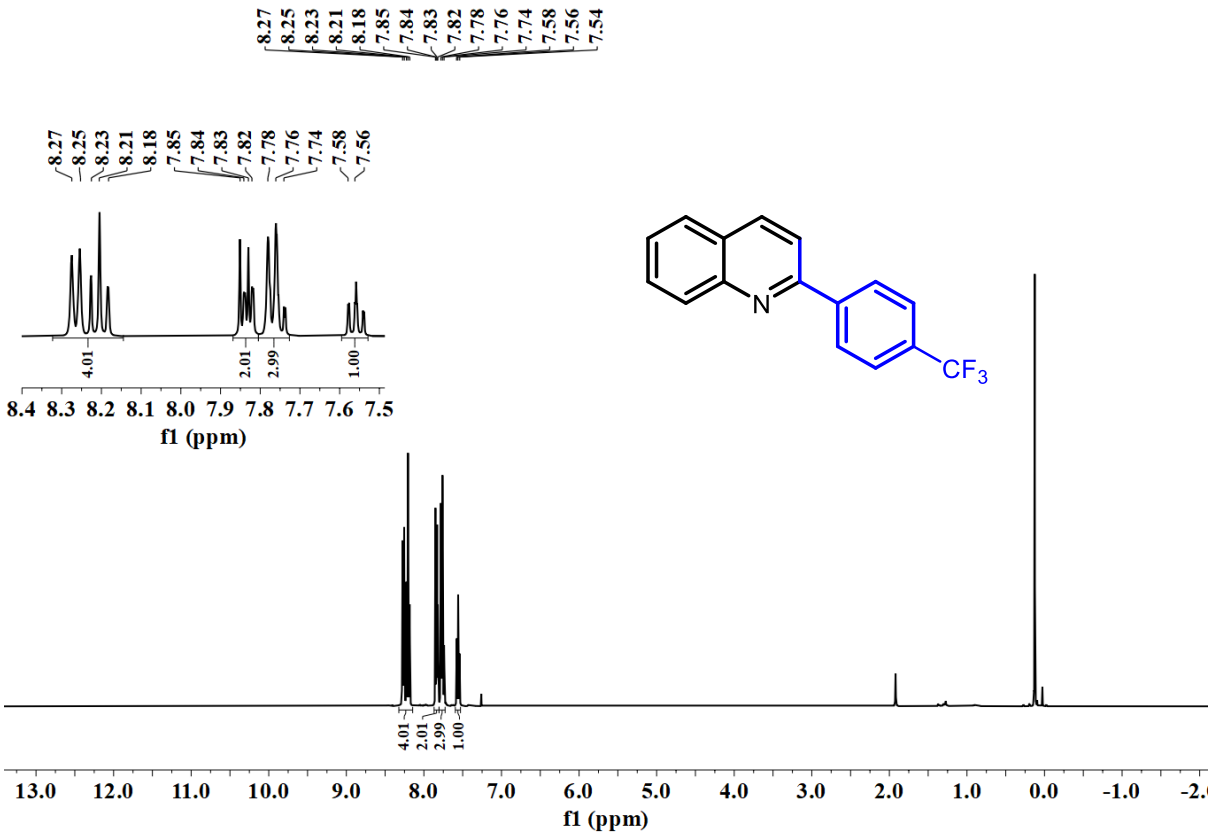


Fig. S50. ^{1}H NMR spectrum of **11a** in $CDCl_3$ (400 MHz).

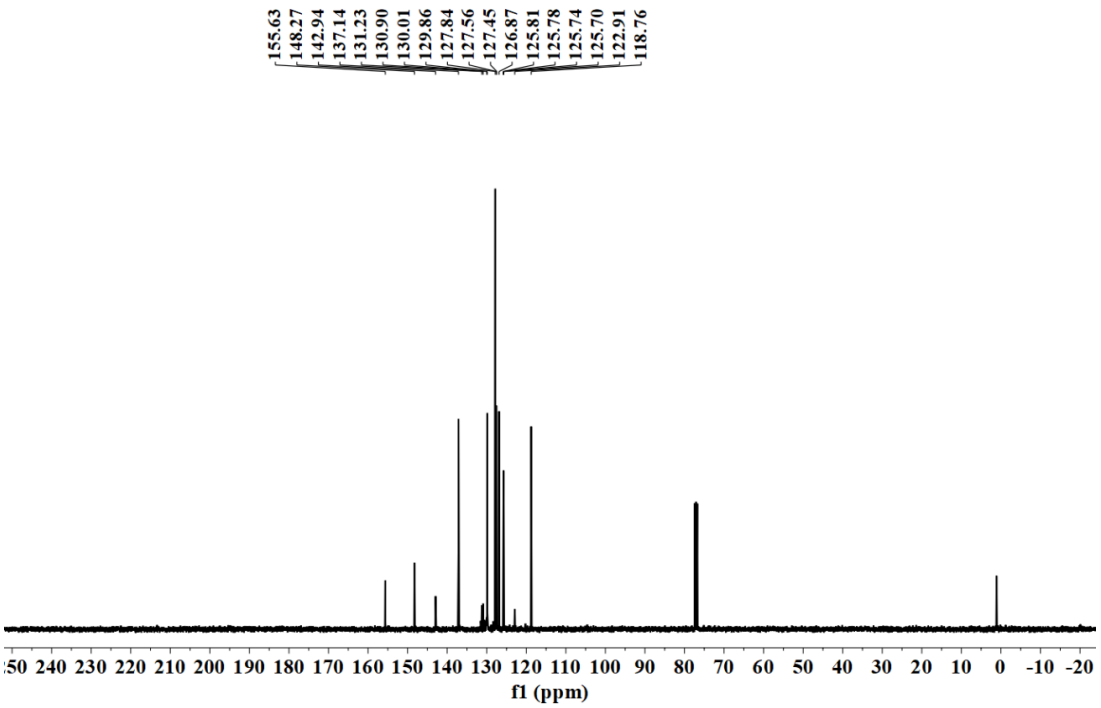


Fig. S51. $^{13}C\{^{1}H\}$ NMR spectrum of **11a** in $CDCl_3$ (101 MHz).

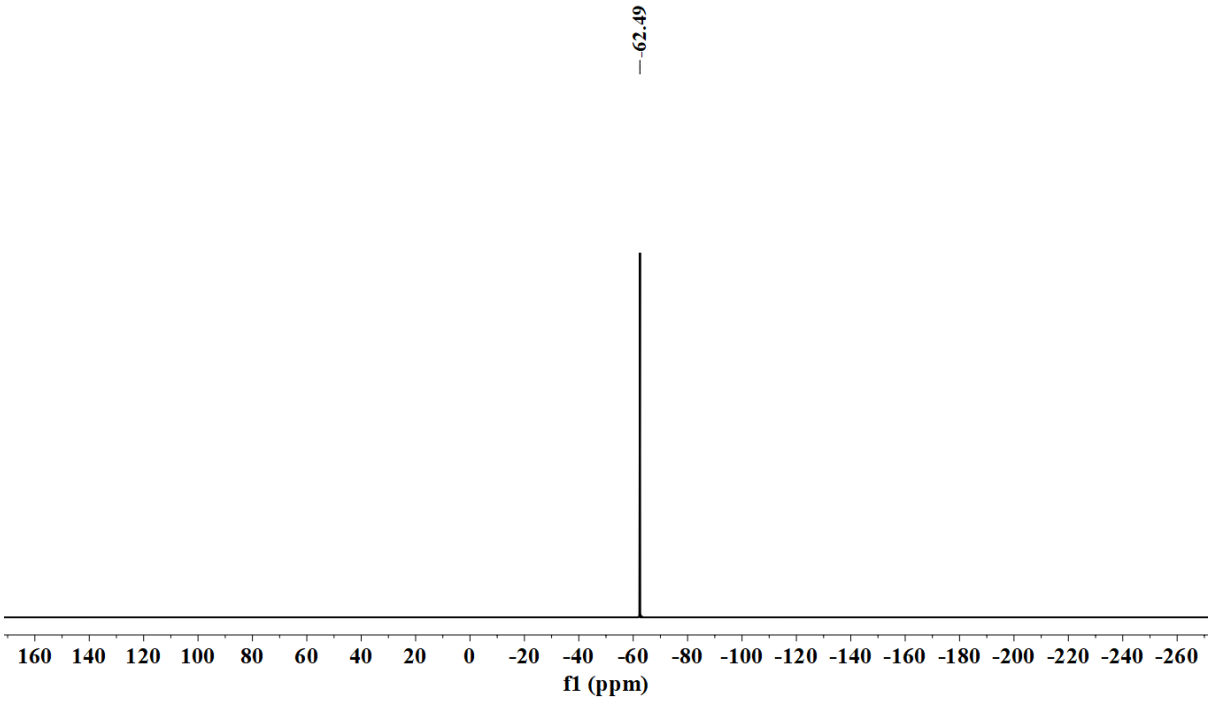


Fig. S52. $^{19}F\{^{1}H\}$ NMR spectrum of **11a** in $CDCl_3$ (376 MHz).

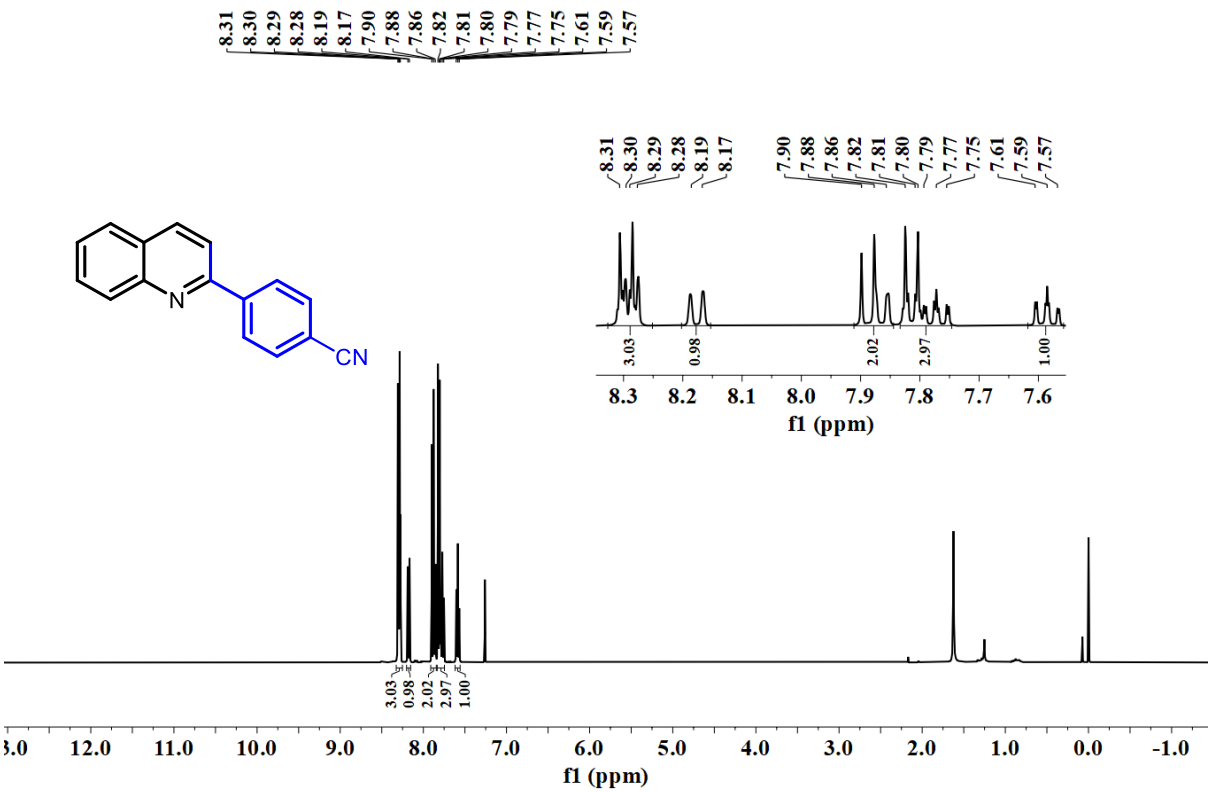


Fig. S53. ^{1}H NMR spectrum of **12a** in $CDCl_3$ (400 MHz).

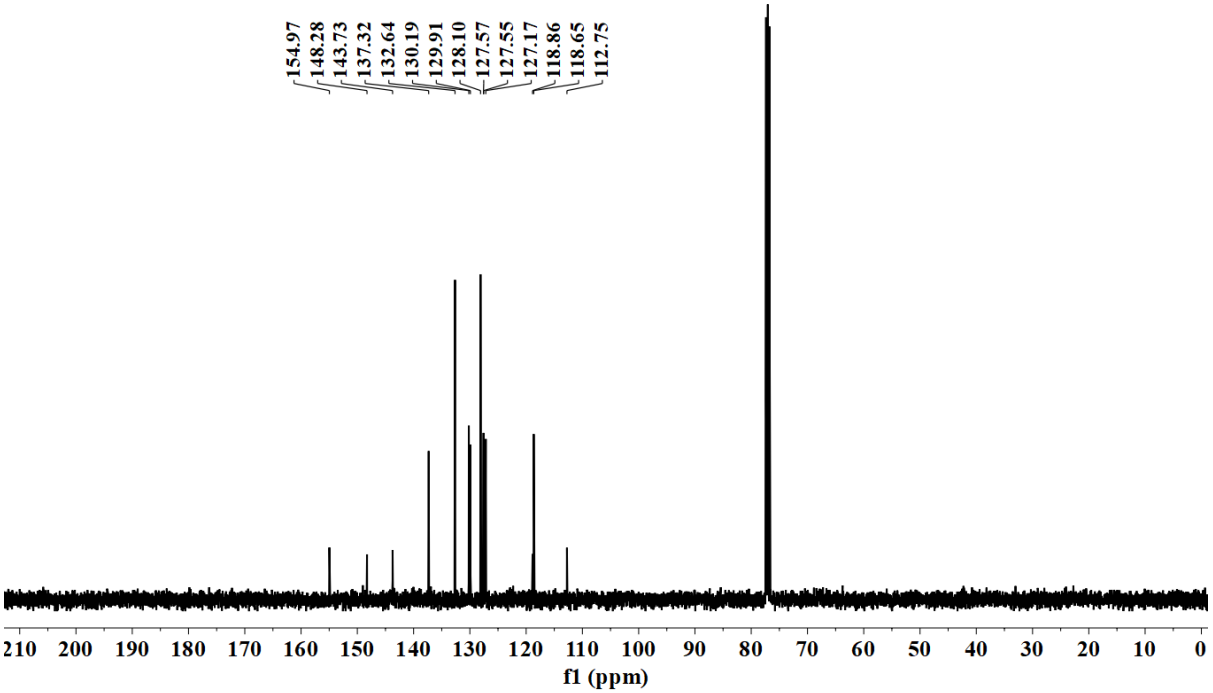


Fig. S54. $^{13}C\{^{1}H\}$ NMR spectrum of **12a** in $CDCl_3$ (101 MHz).

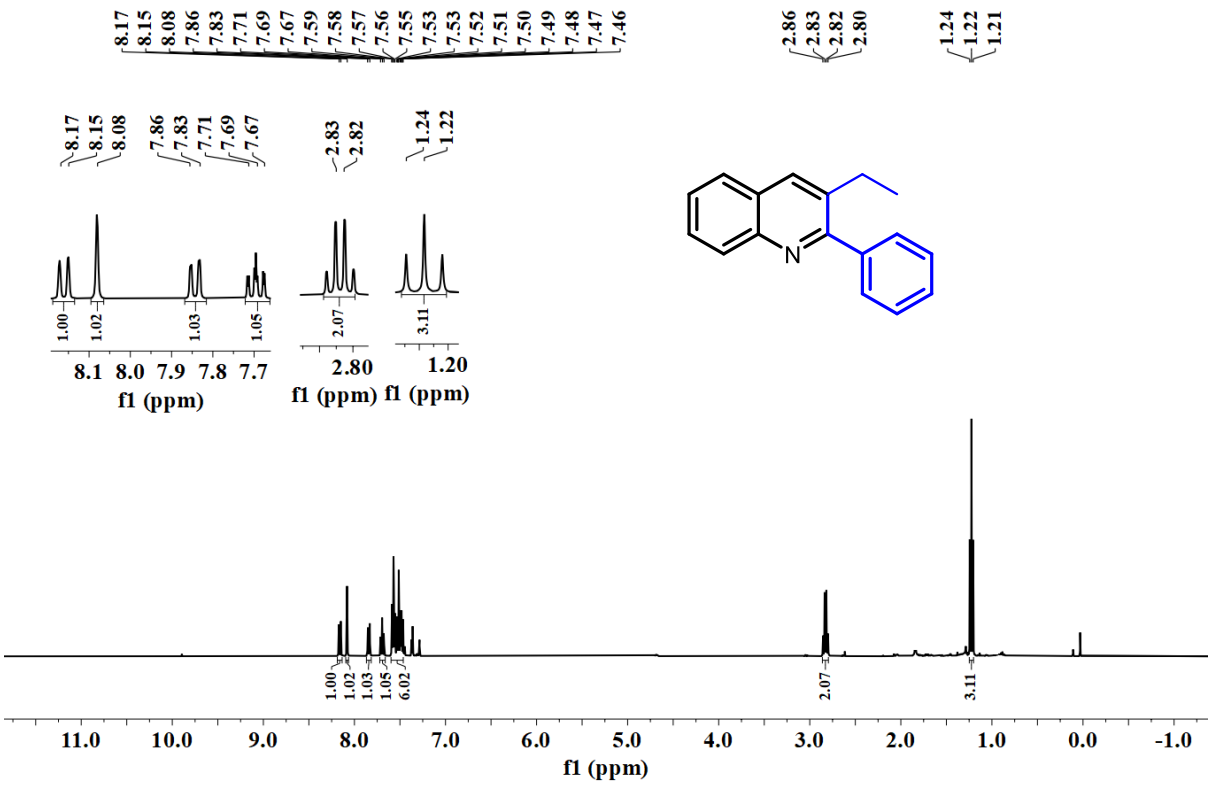


Fig. S55. ^{1}H NMR spectrum of **13a** in $CDCl_3$ (500 MHz).

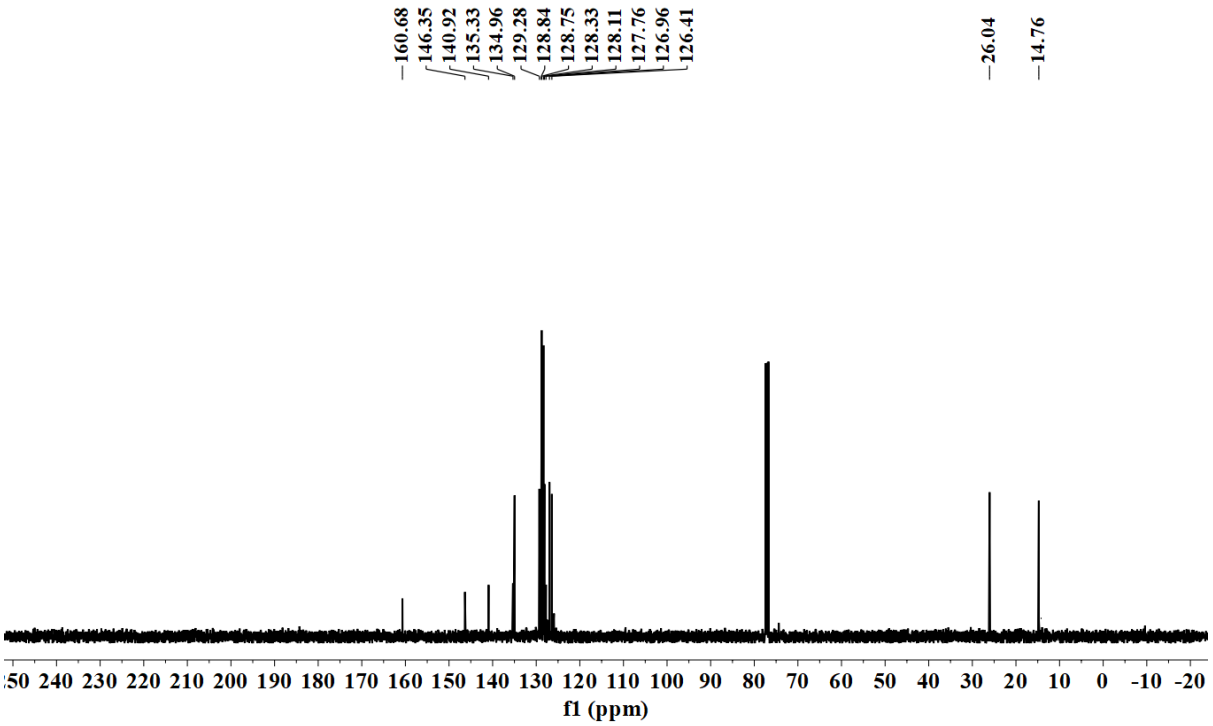


Fig. S56. $^{13}C\{^{1}H\}$ NMR spectrum of **13a** in $CDCl_3$ (101 MHz).

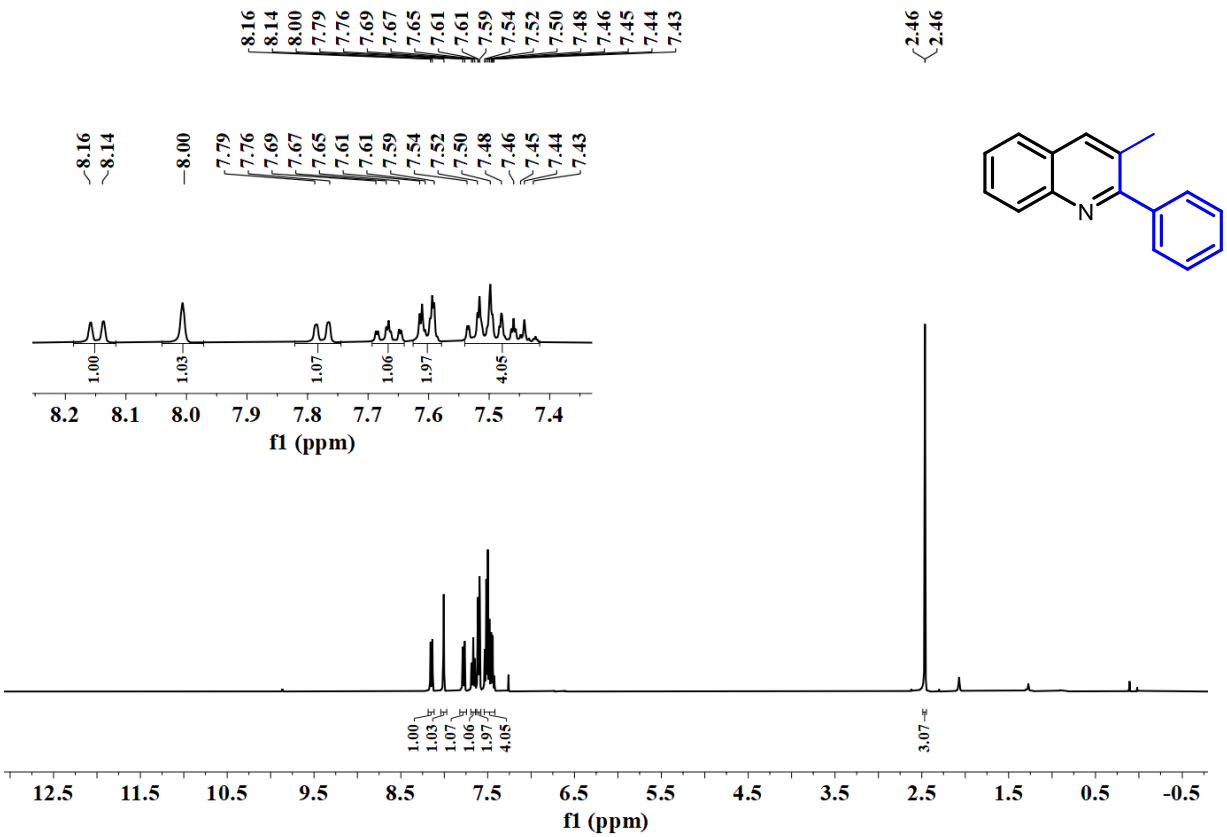


Fig. S57. ^{1}H NMR spectrum of **14a** in $CDCl_3$ (400 MHz).

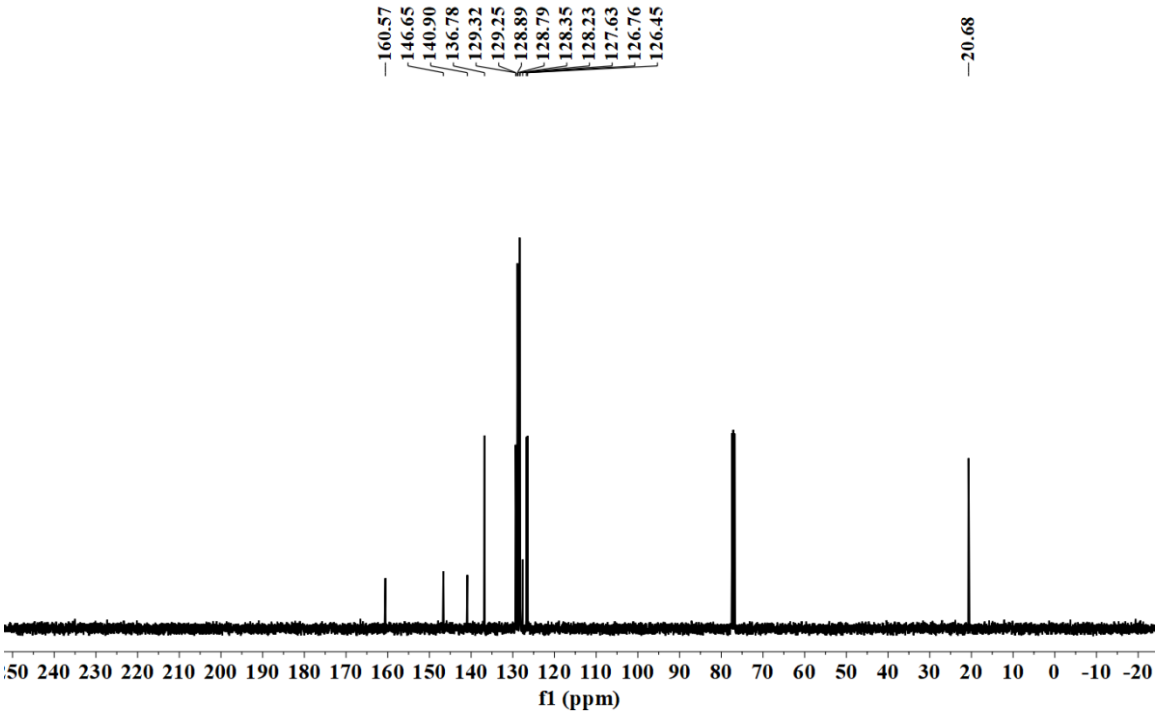


Fig. S58. $^{13}C\{^{1}H\}$ NMR spectrum of **14a** in $CDCl_3$ (101 MHz).

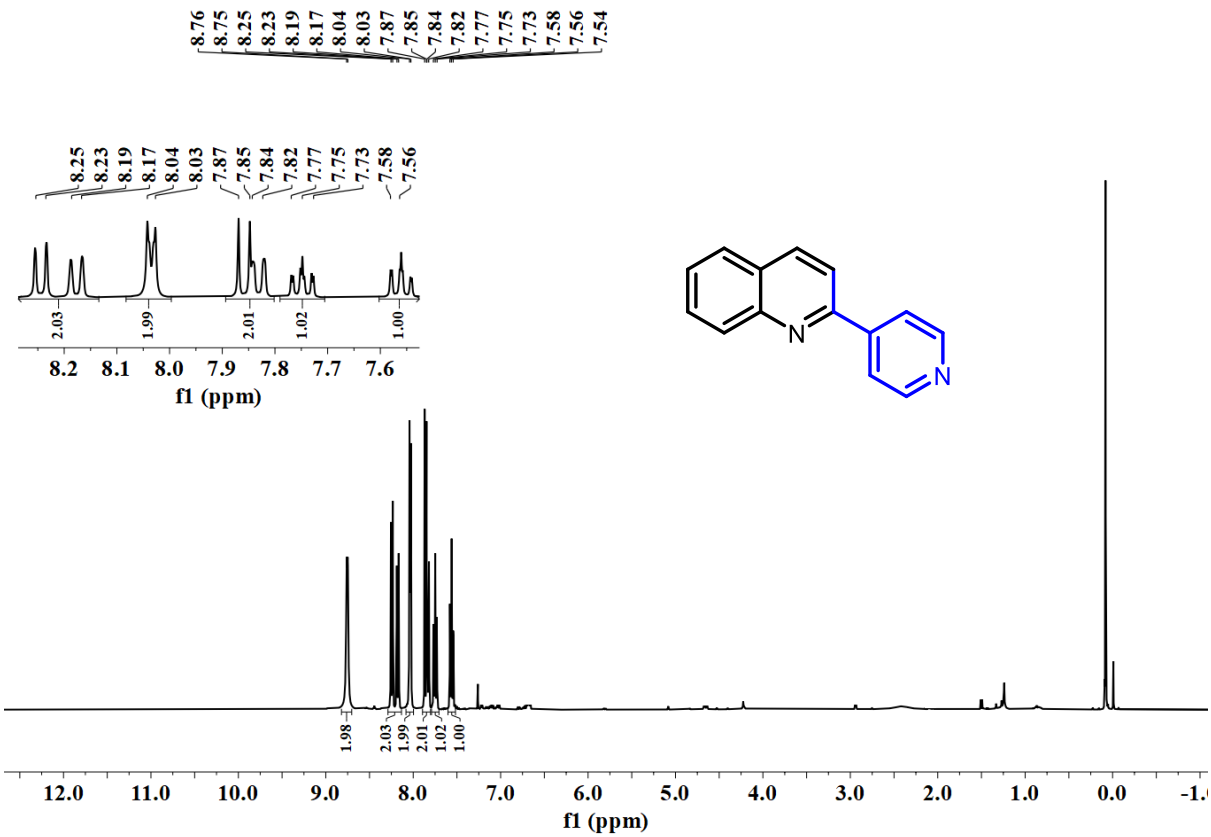


Fig. S59. ^{1}H NMR spectrum of **15a** in $CDCl_3$ (400 MHz).

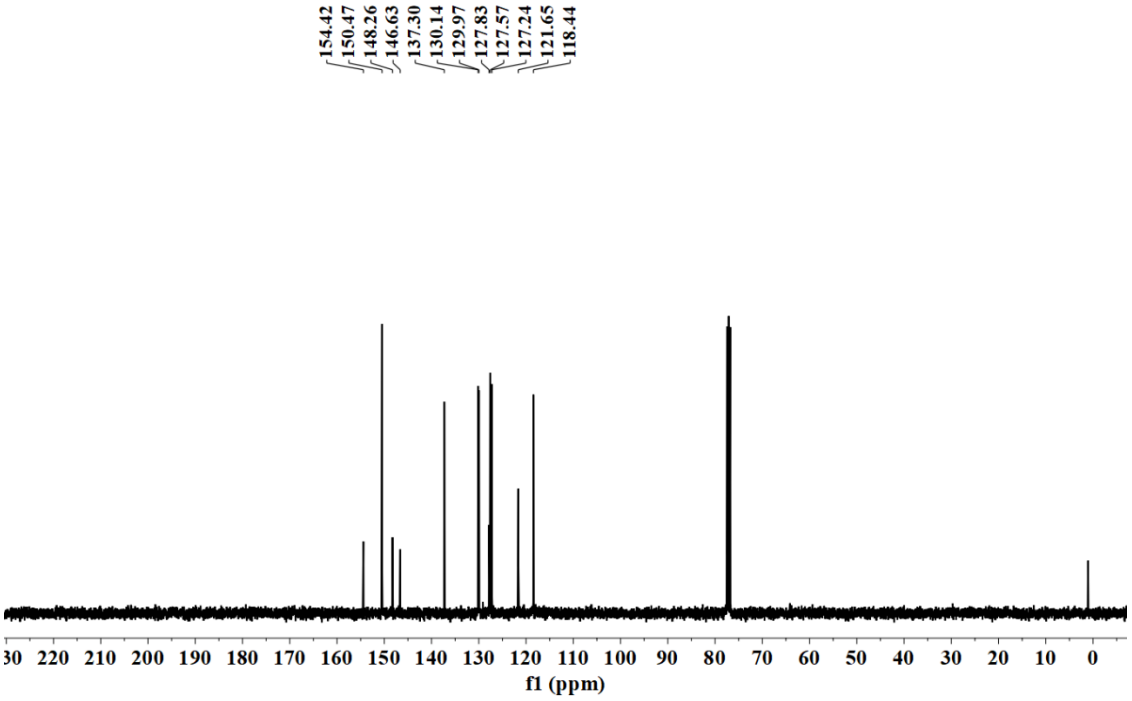


Fig. S60. $^{13}C\{^{1}H\}$ NMR spectrum of **15a** in $CDCl_3$ (101 MHz).

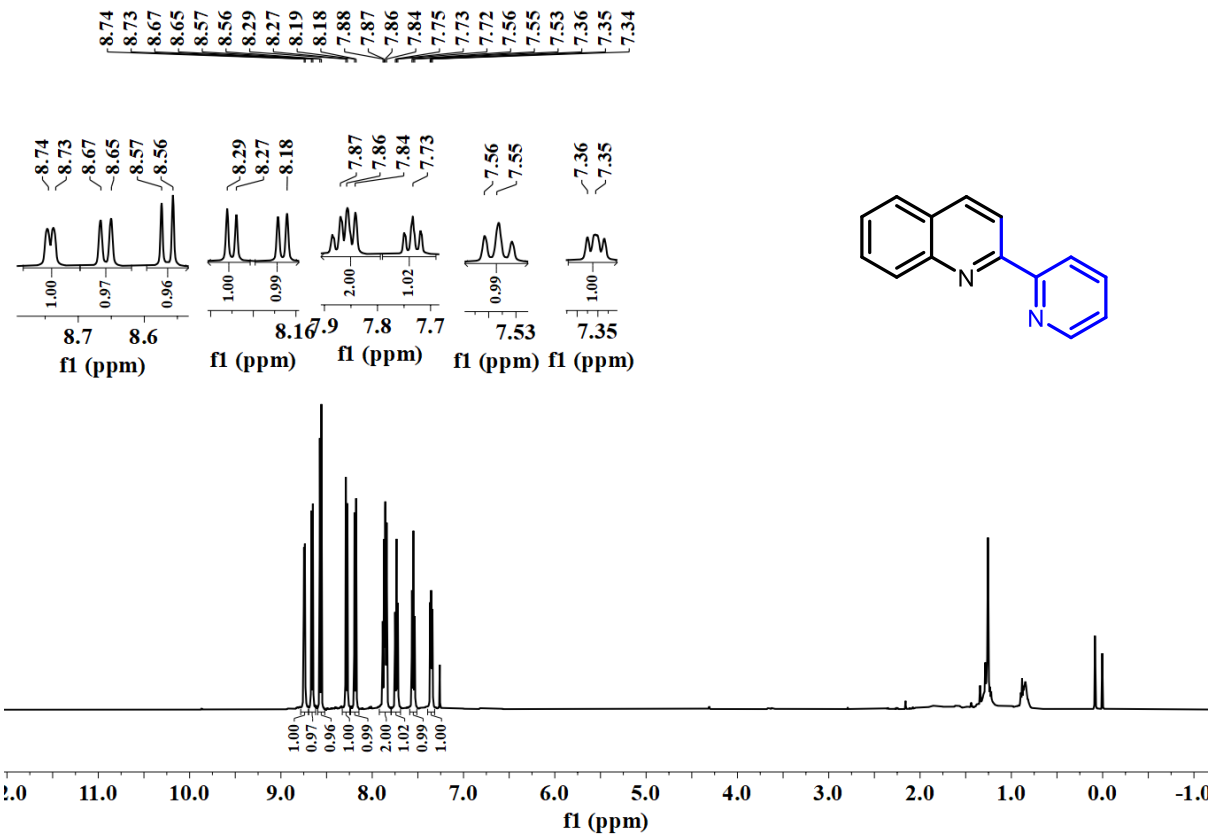


Fig. S61. ^{1}H NMR spectrum of **16a** in $CDCl_3$ (500 MHz).

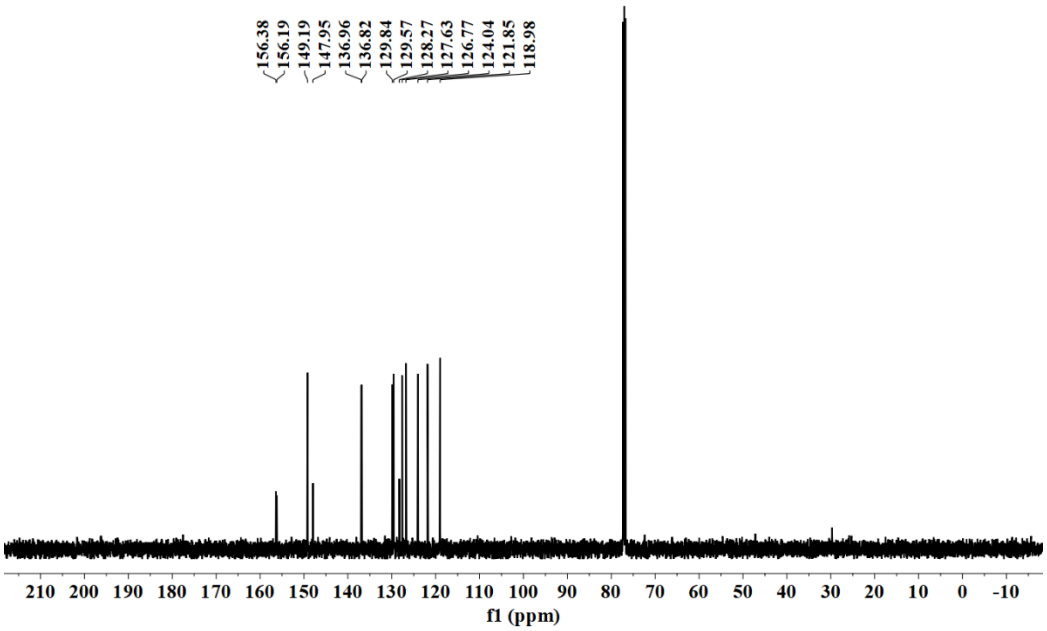


Fig. S62. $^{13}C\{^{1}H\}$ NMR spectrum of **16a** in $CDCl_3$ (126 MHz).

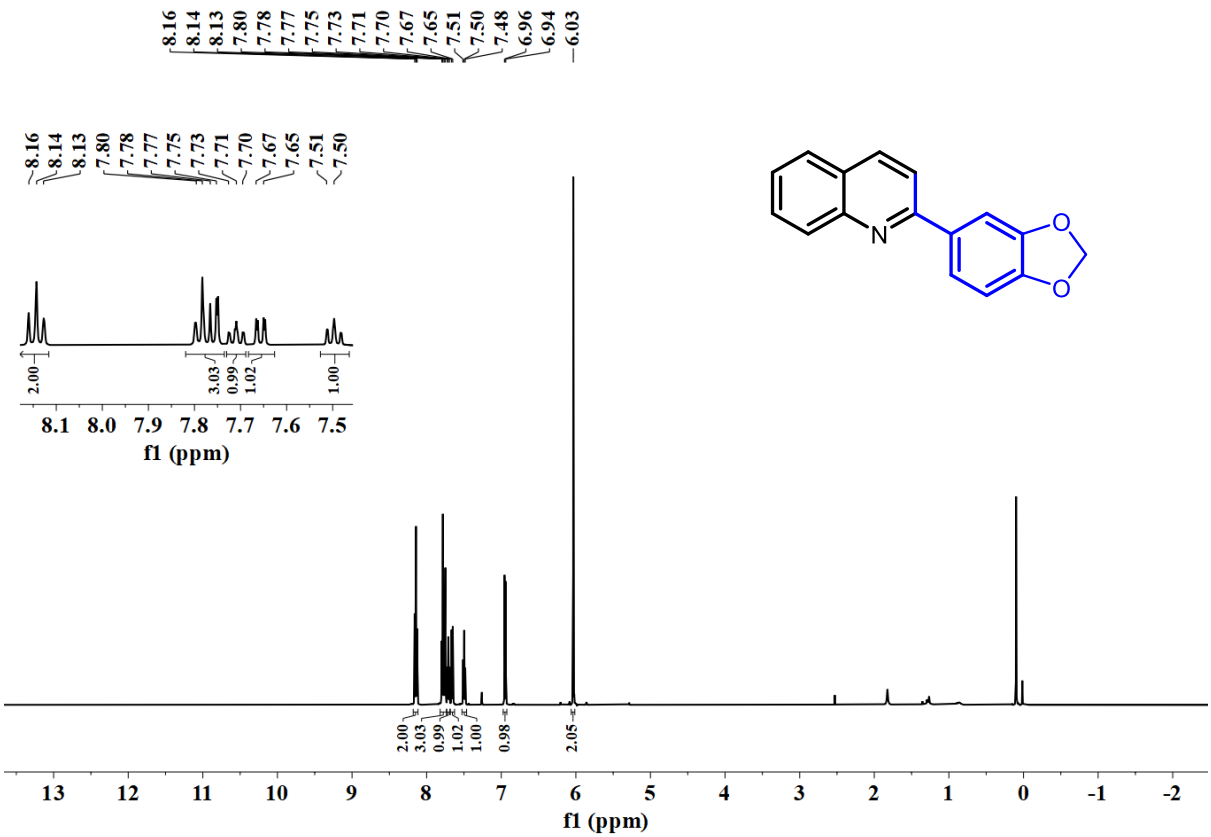


Fig. S63. ^{1}H NMR spectrum of **17a** in $CDCl_3$ (500 MHz).

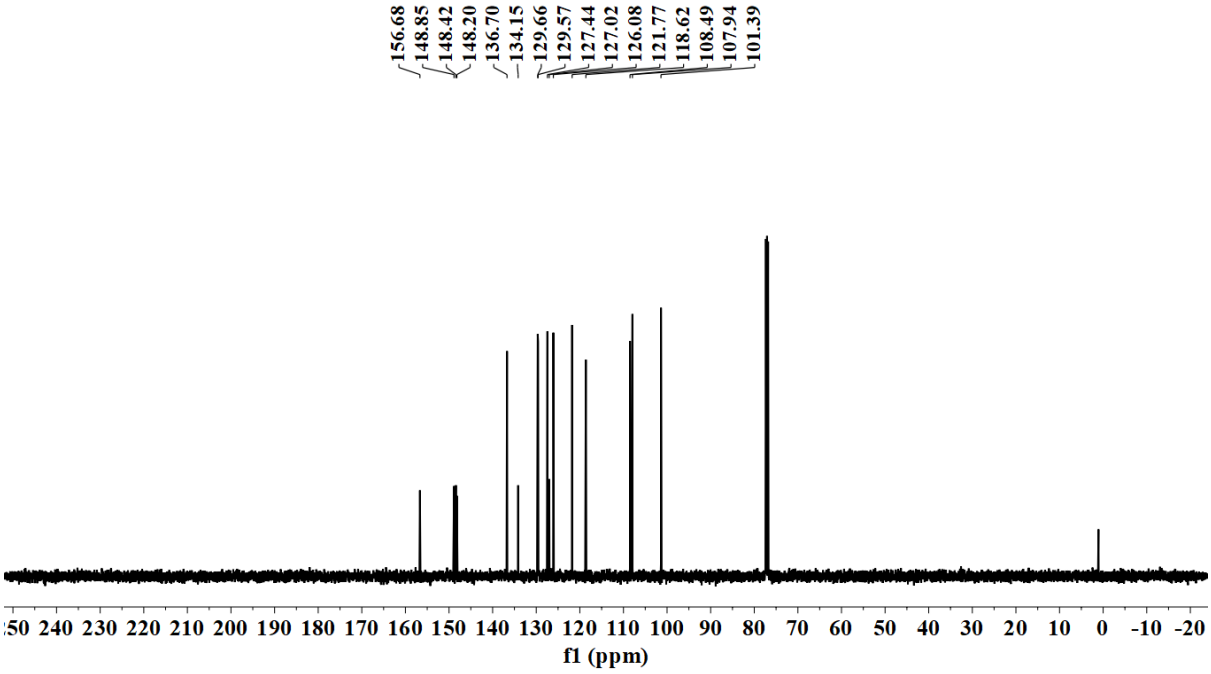


Fig. S64. $^{13}C\{^{1}H\}$ NMR spectrum of **17a** in $CDCl_3$ (126 MHz).

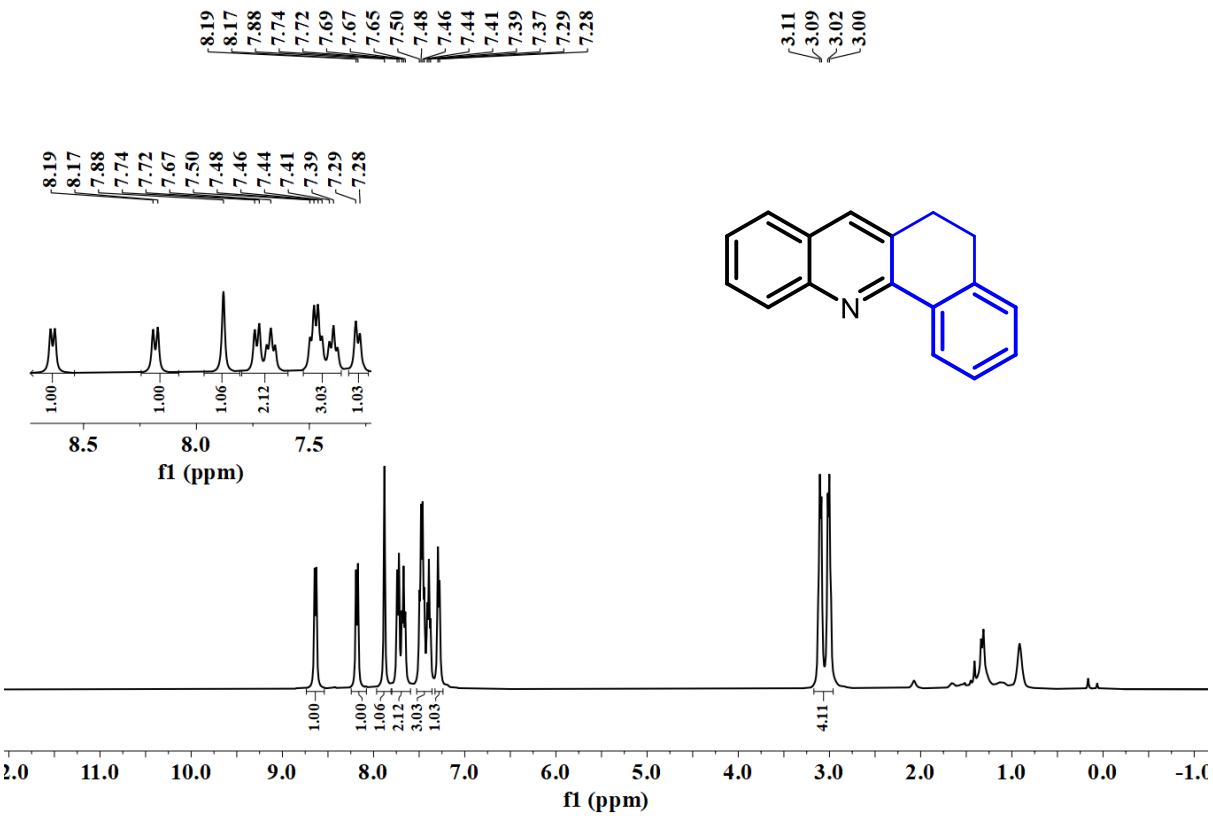


Fig. S65. ^{1}H NMR spectrum of **18a** in $CDCl_3$ (400 MHz).

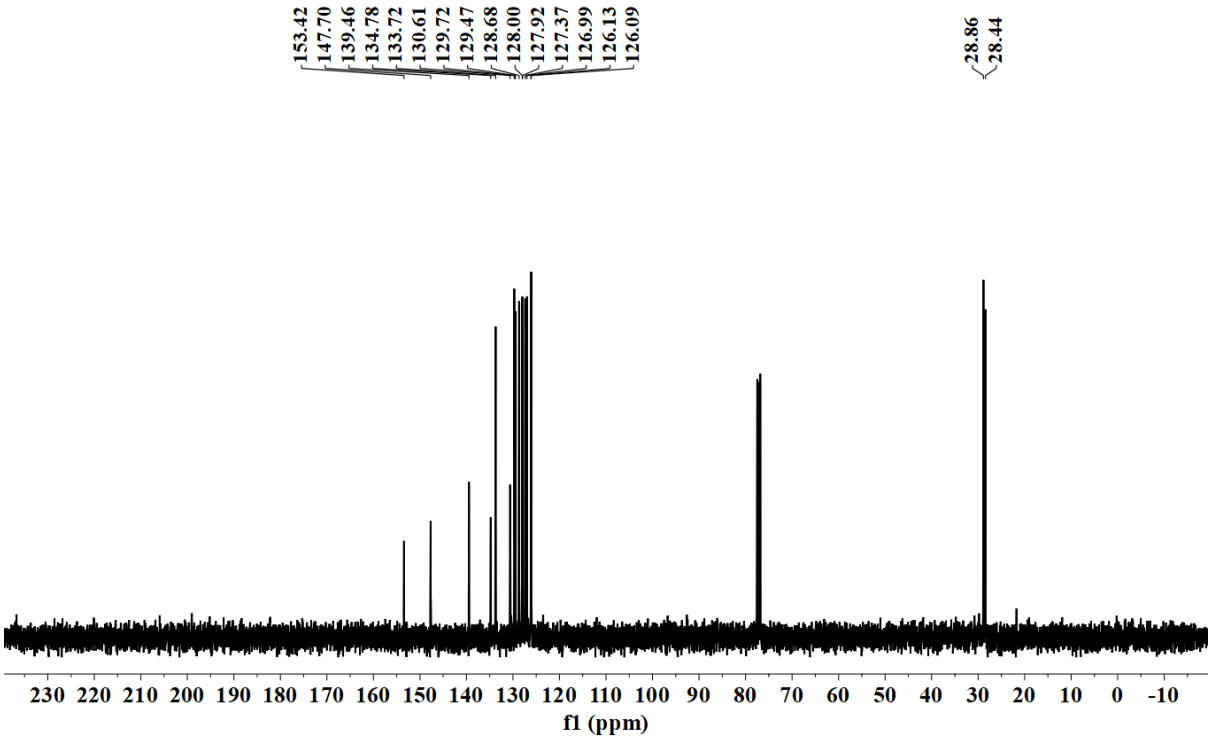


Fig. S66. ^{13}C{^{1}H} NMR spectrum of **18a** in $CDCl_3$ (101 MHz).

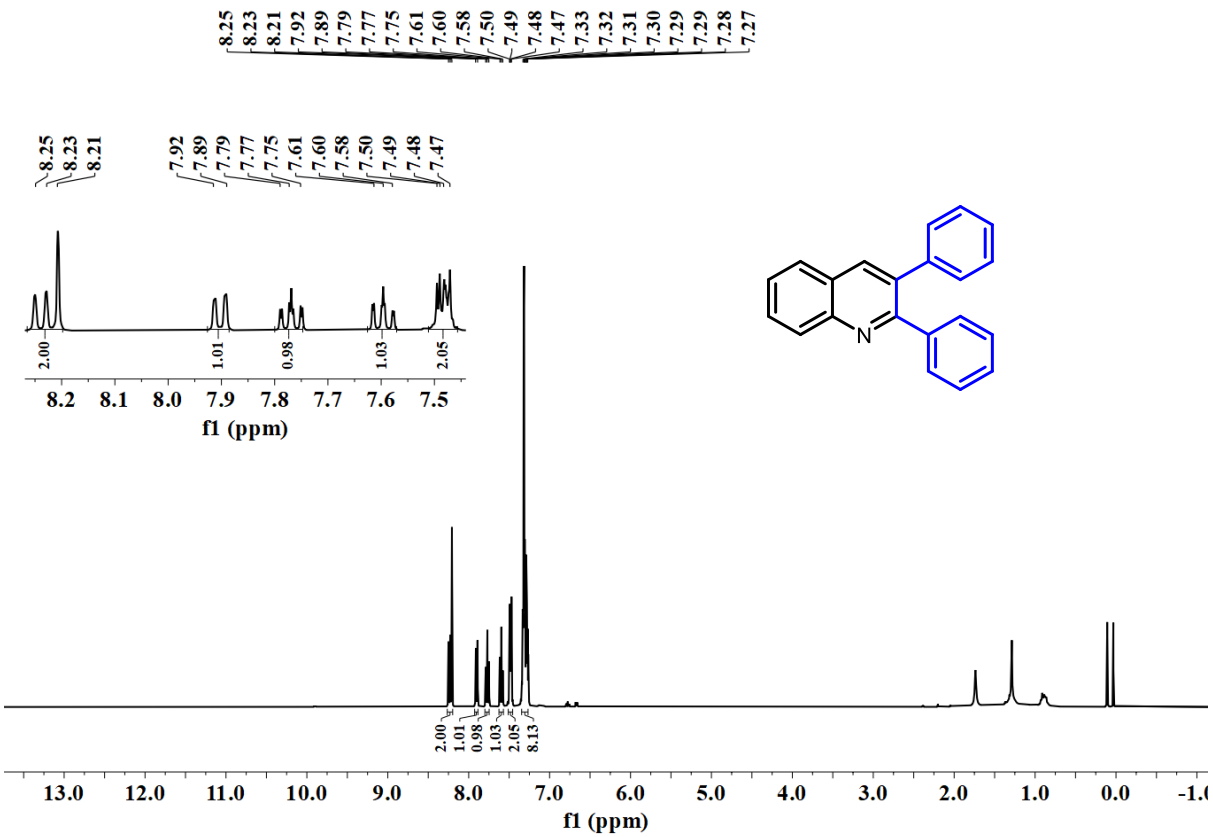


Fig. S67. ^{1}H NMR spectrum of **19a** in $CDCl_3$ (400 MHz).

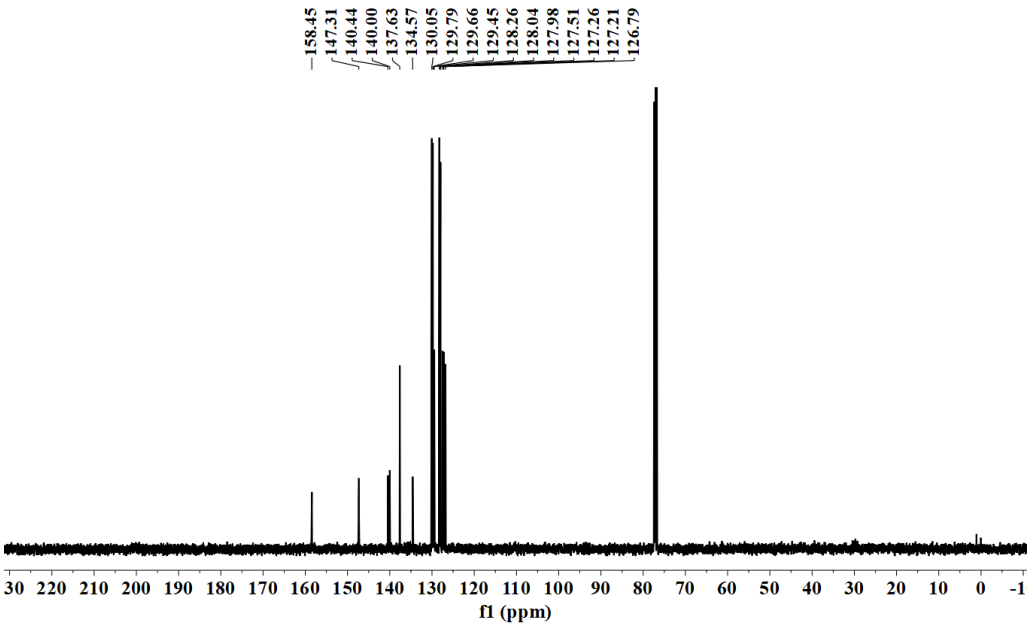


Fig. S68. $^{13}C\{^{1}H\}$ NMR spectrum of **19a** in $CDCl_3$ (101 MHz).

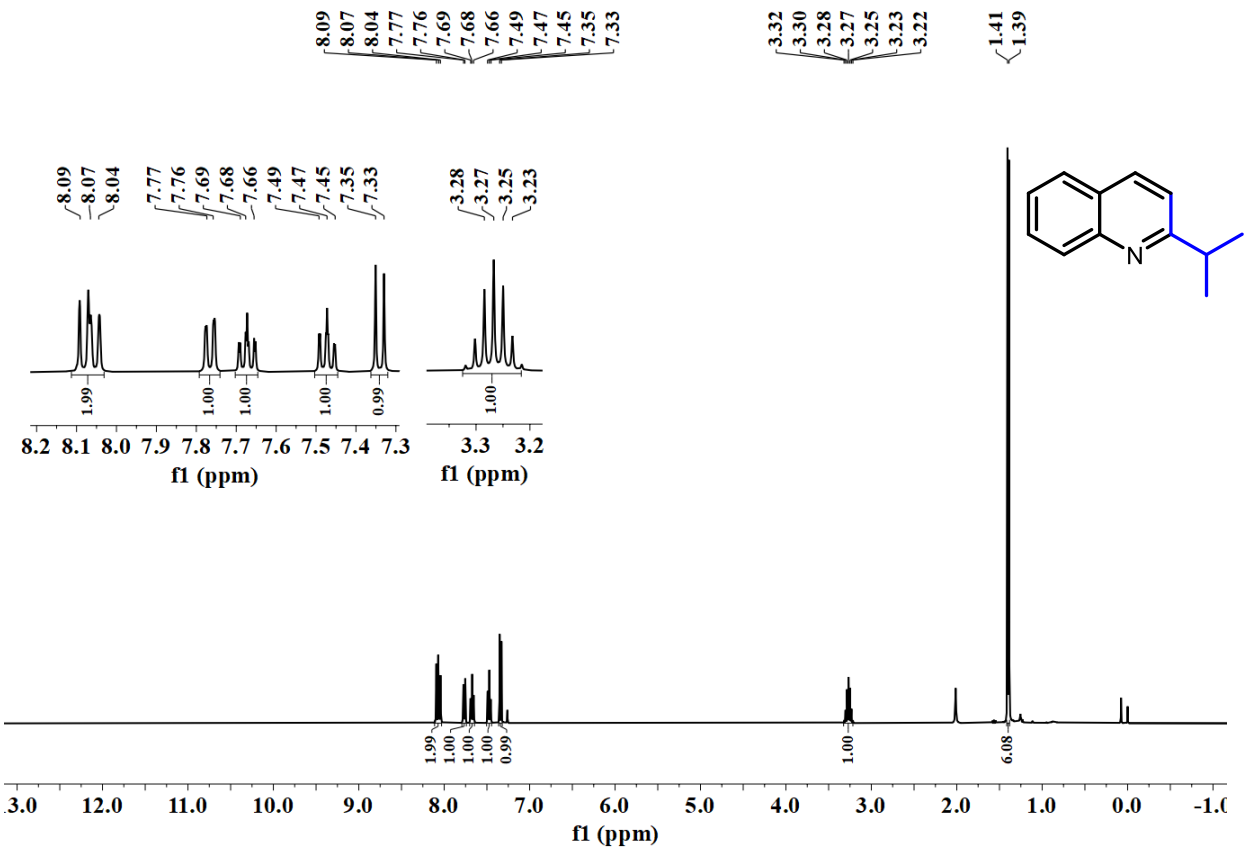


Fig. S69. ^{1}H NMR spectrum of **20a** in $CDCl_3$ (400 MHz).

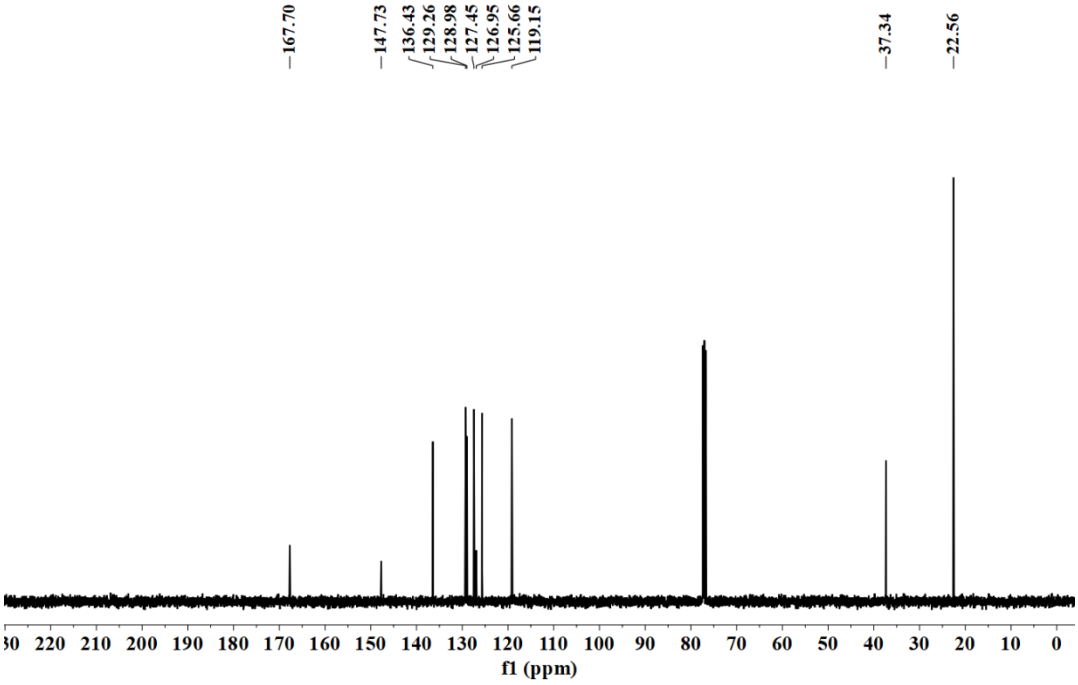


Fig. S70. $^{13}C\{^{1}H\}$ NMR spectrum of **20a** in $CDCl_3$ (101 MHz).

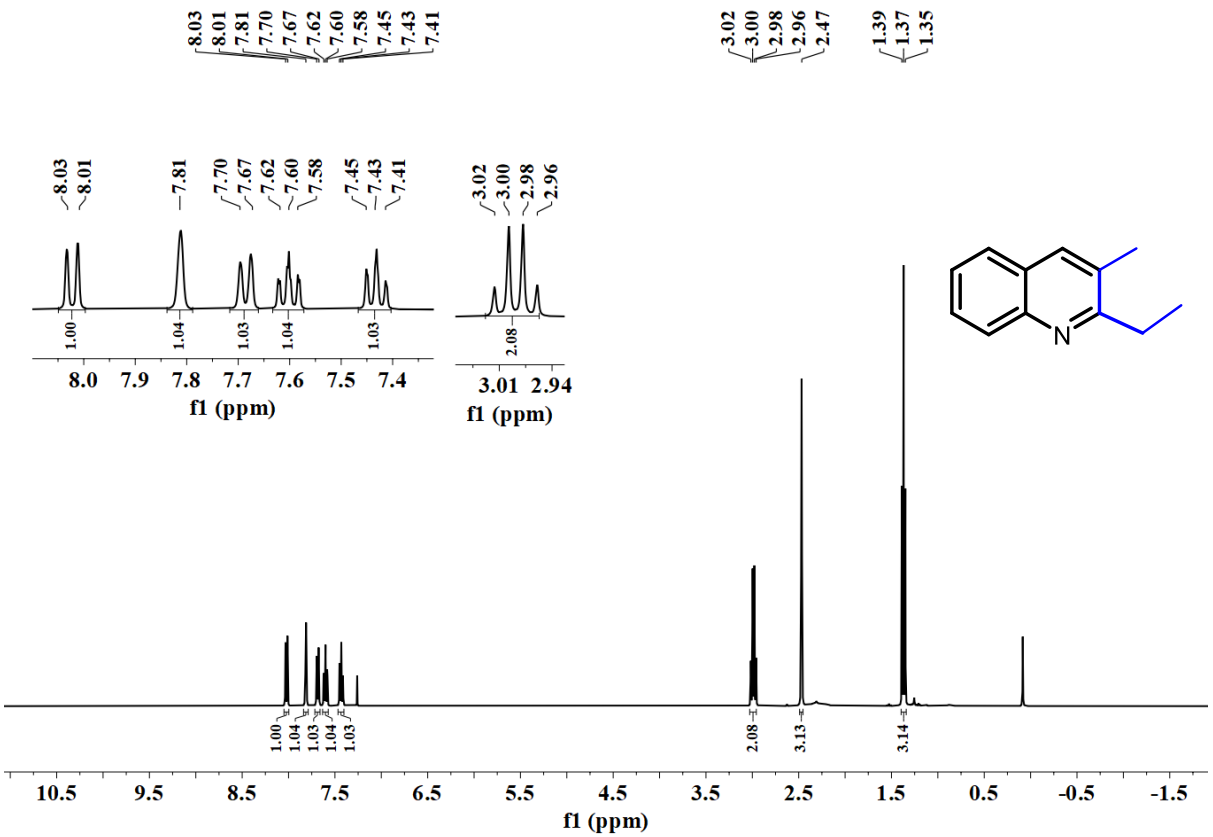


Fig. S71. ^{1}H NMR spectrum of **21a** in $CDCl_3$ (400 MHz).

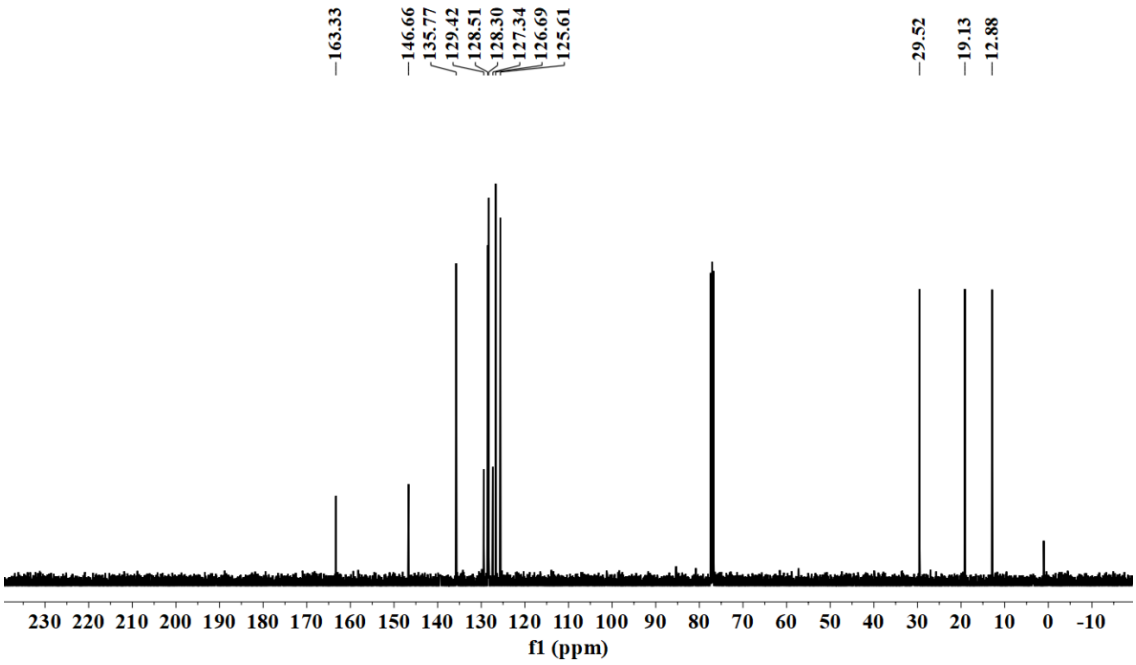


Fig. S72. $^{13}C\{^{1}H\}$ NMR spectrum of **21a** in $CDCl_3$ (101 MHz).

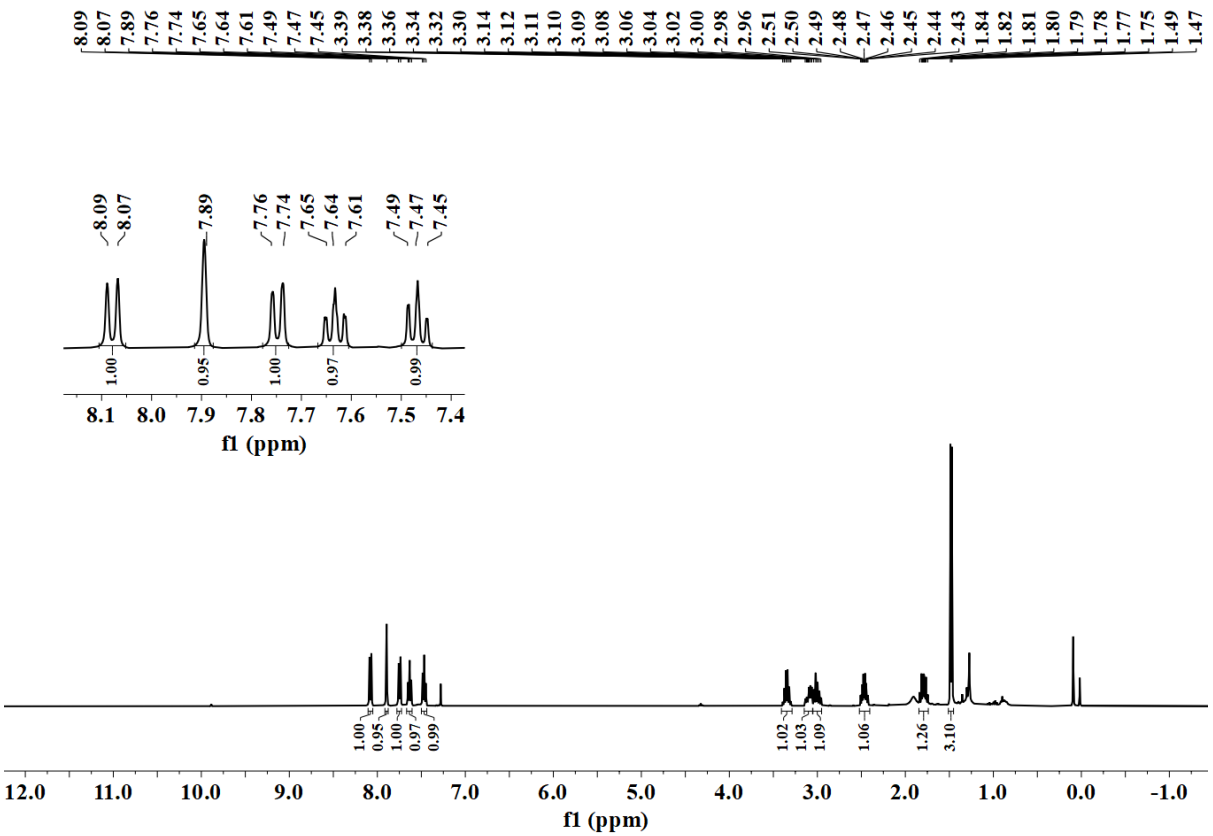


Fig. S73. ^{1}H NMR spectrum of **212a** in $CDCl_3$ (400 MHz).

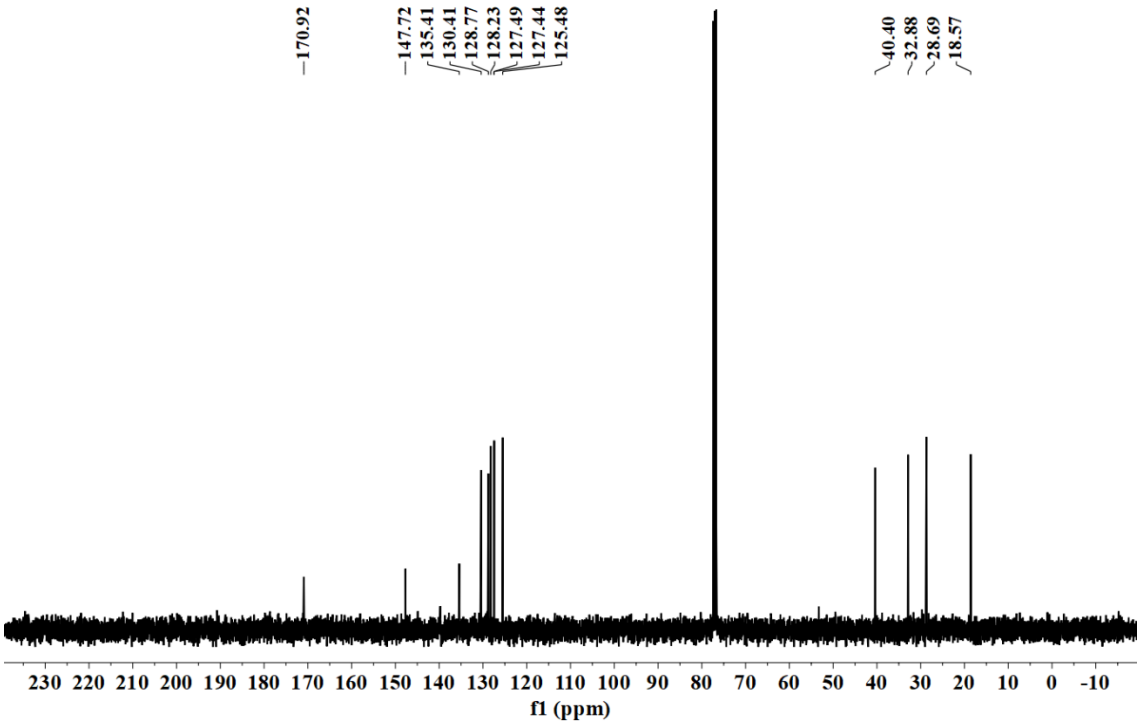


Fig. S74. $^{13}C\{^{1}H\}$ NMR spectrum of **22a** in $CDCl_3$ (101 MHz).

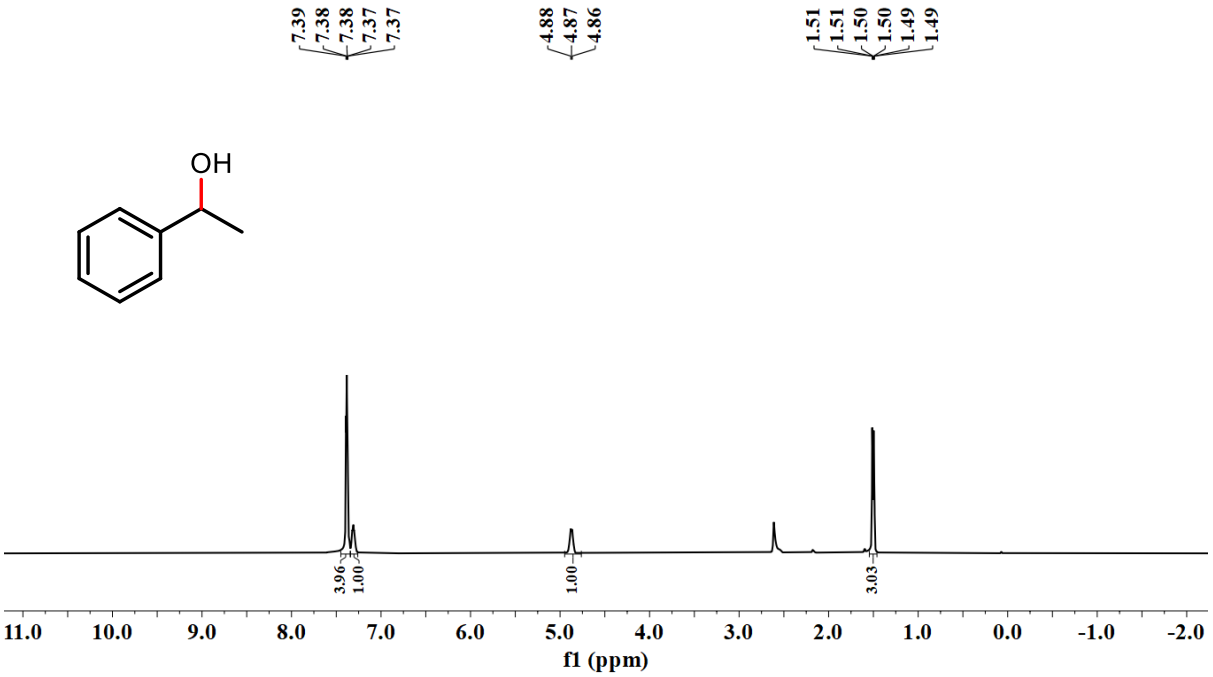


Fig. S75. ^{1}H NMR spectrum of **1b** in $CDCl_3$ (400 MHz).

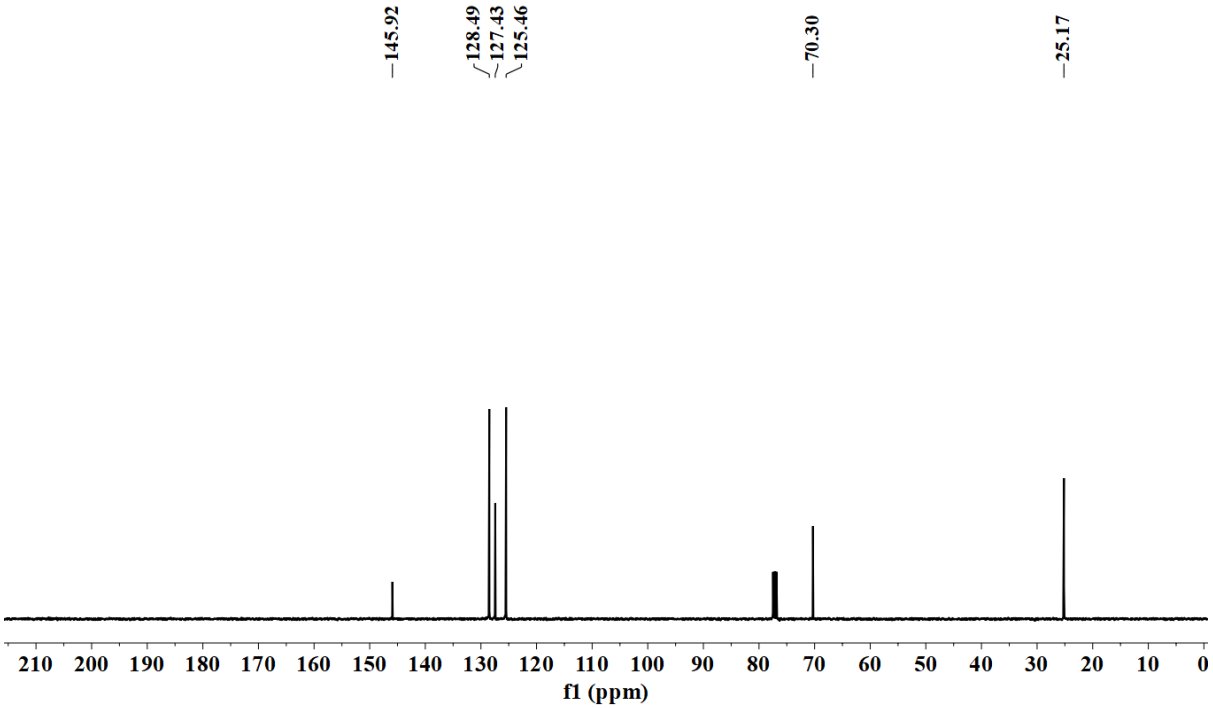


Fig. S76. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in $CDCl_3$ (101 MHz).

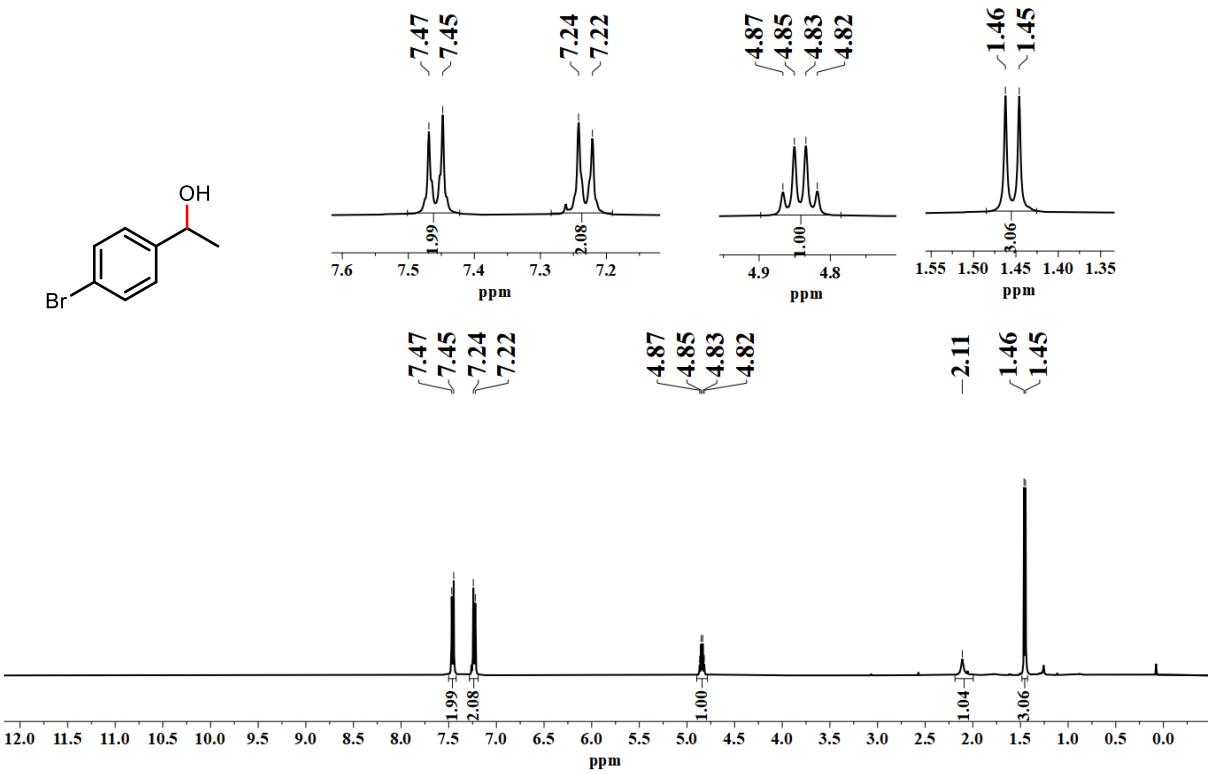


Fig. S77. ^{1}H NMR spectrum of **2b** in $CDCl_3$ (400 MHz).

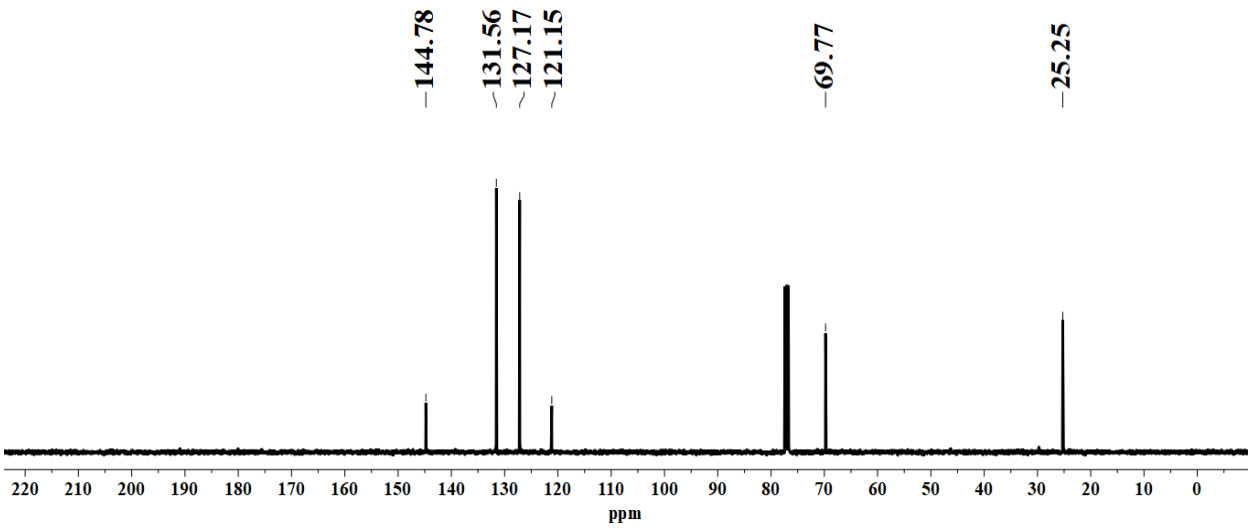


Fig. S78. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$ (101 MHz).

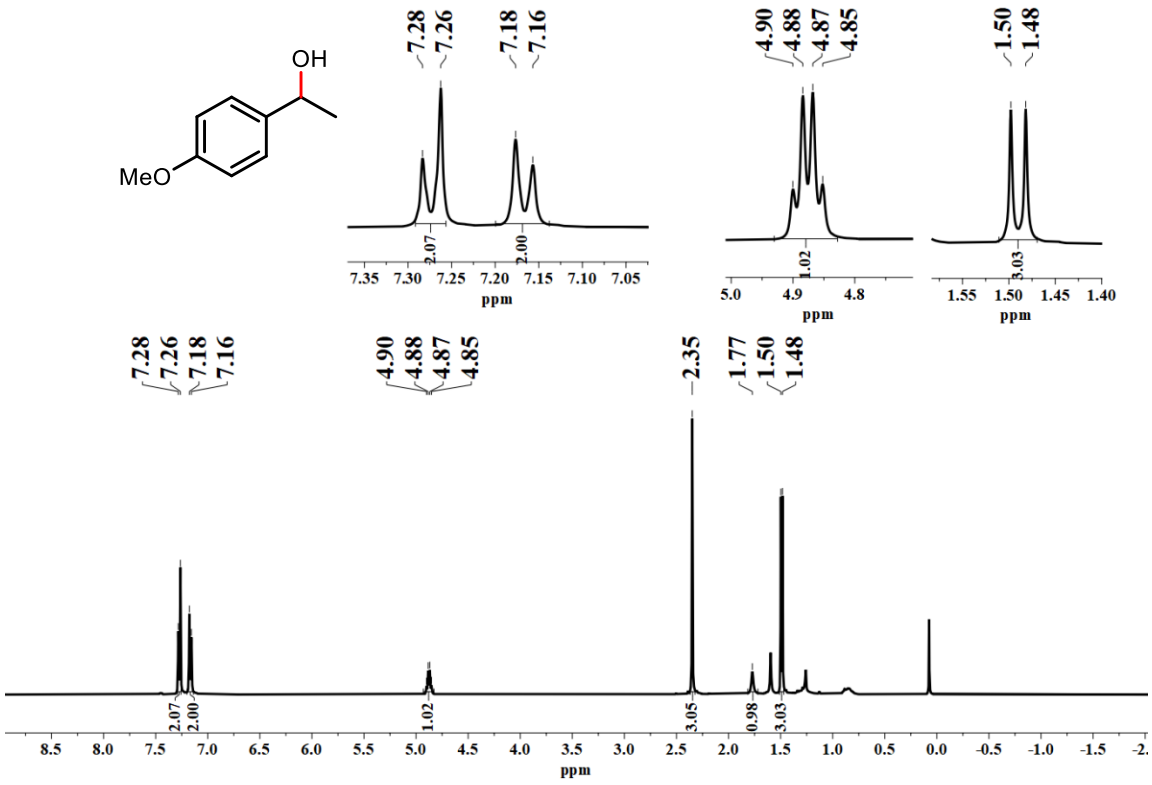


Fig. S79. ^{1}H NMR spectrum of **3b** in $CDCl_3$ (400 MHz).

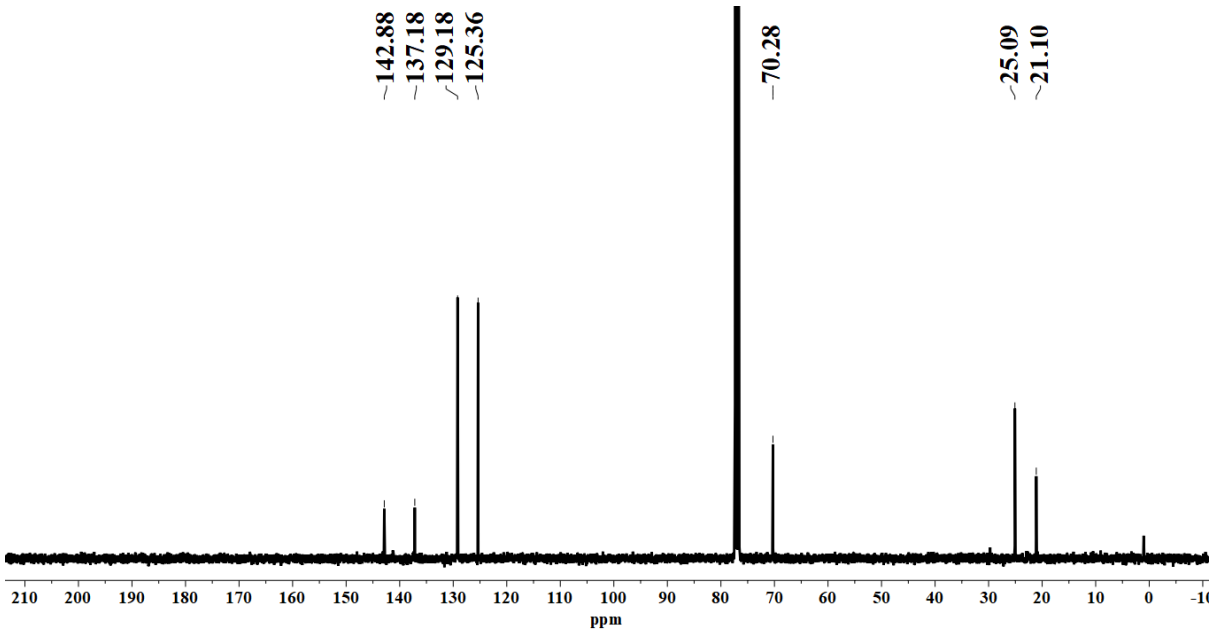


Fig. S80. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$ (101 MHz).

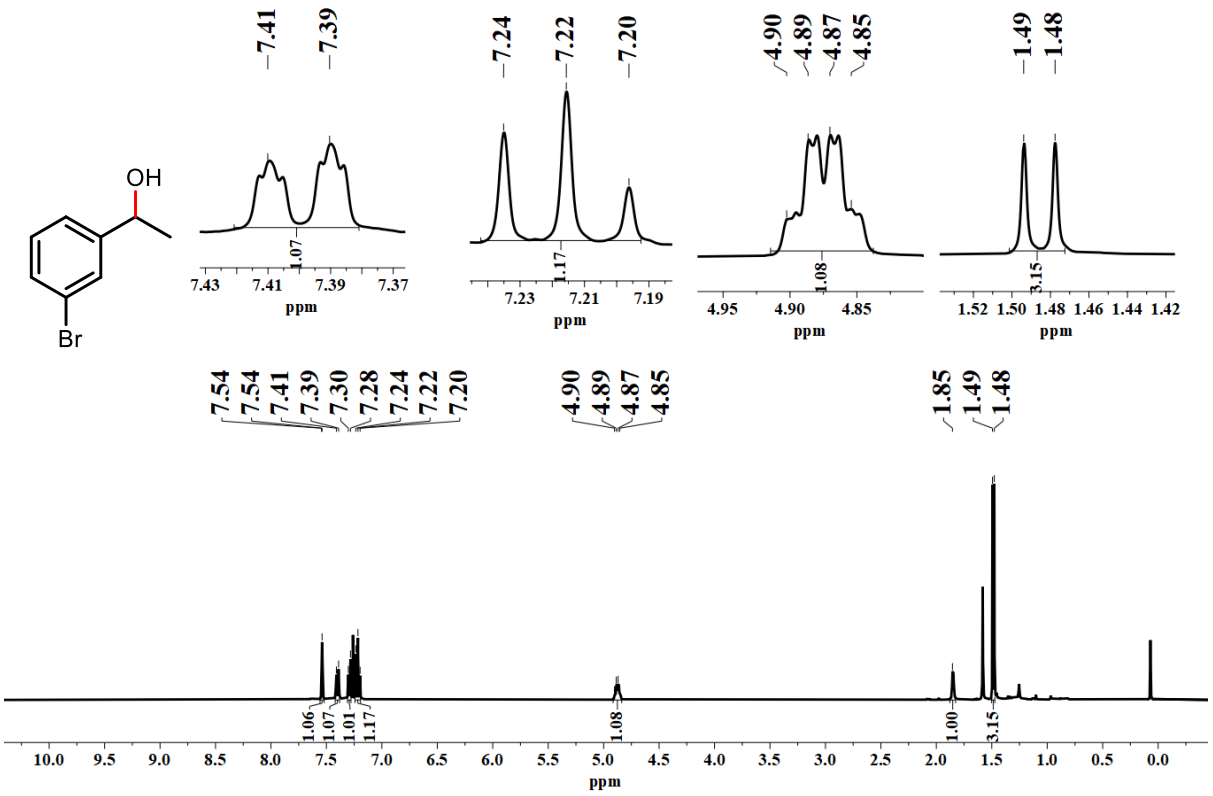


Fig. S81. ^{1}H NMR spectrum of **4b** in $CDCl_3$ (400 MHz).

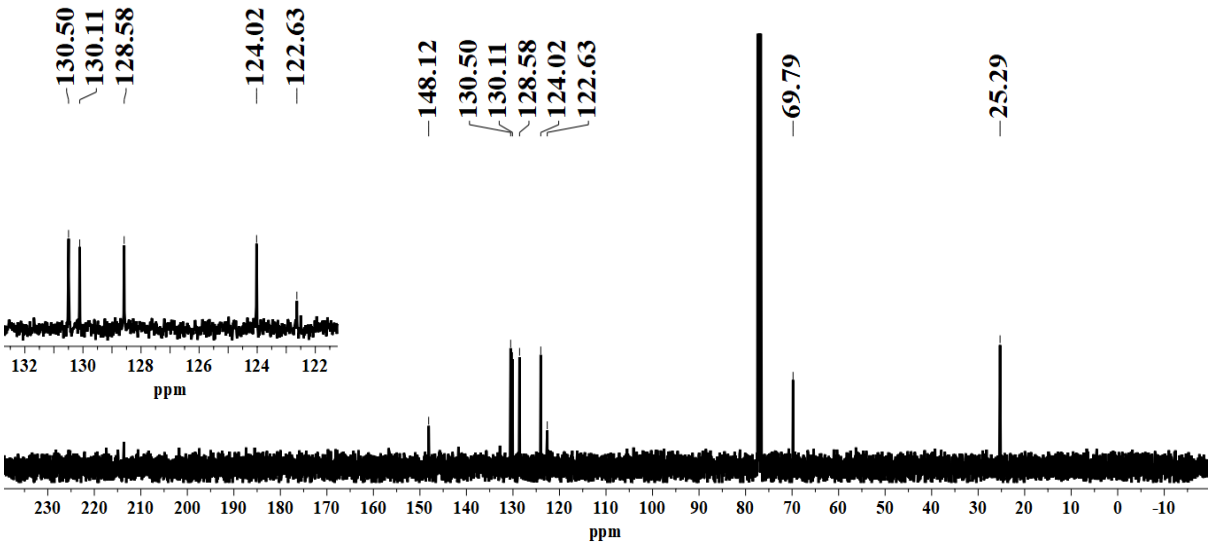


Fig. S82. ^{13}C{^{1}H} NMR spectrum of **4b** in $CDCl_3$ (101 MHz).

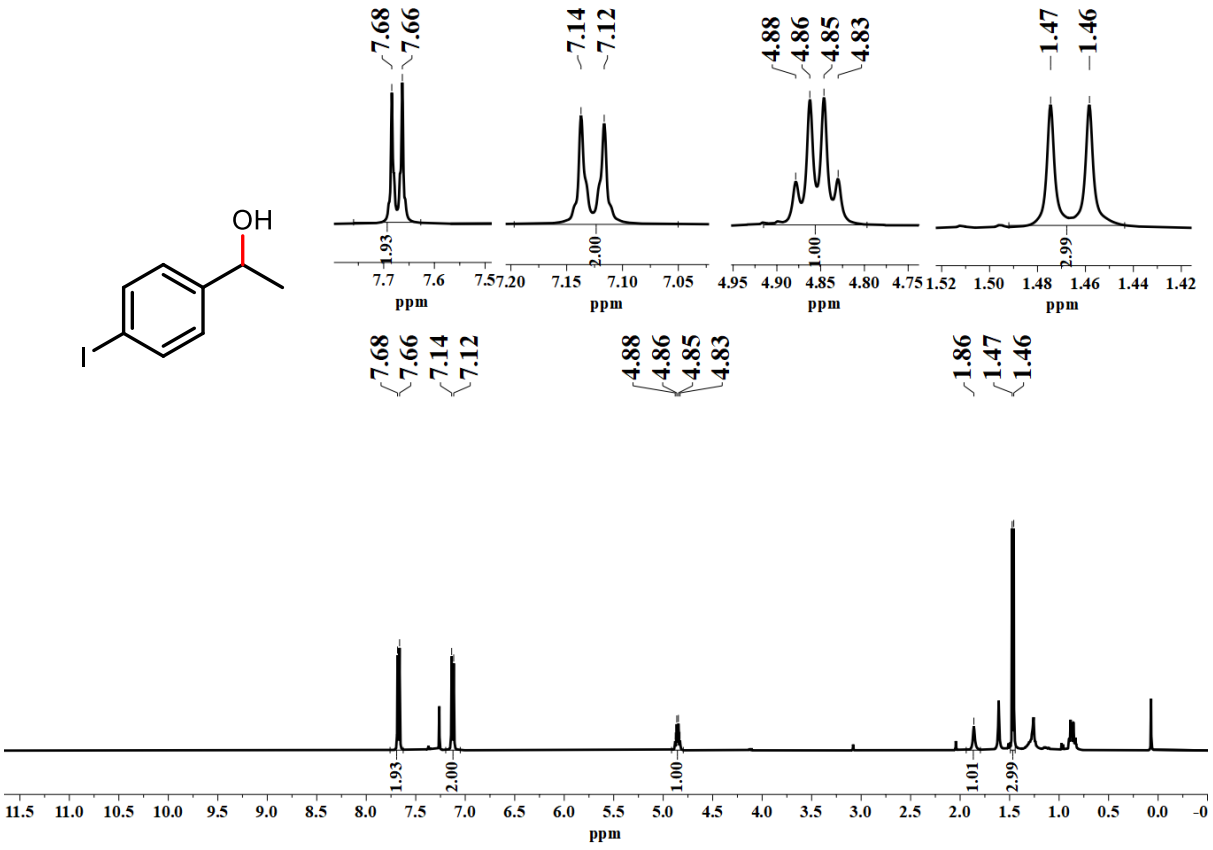


Fig. S83. ^{1}H NMR spectrum of **5b** in $CDCl_3$ (400 MHz).

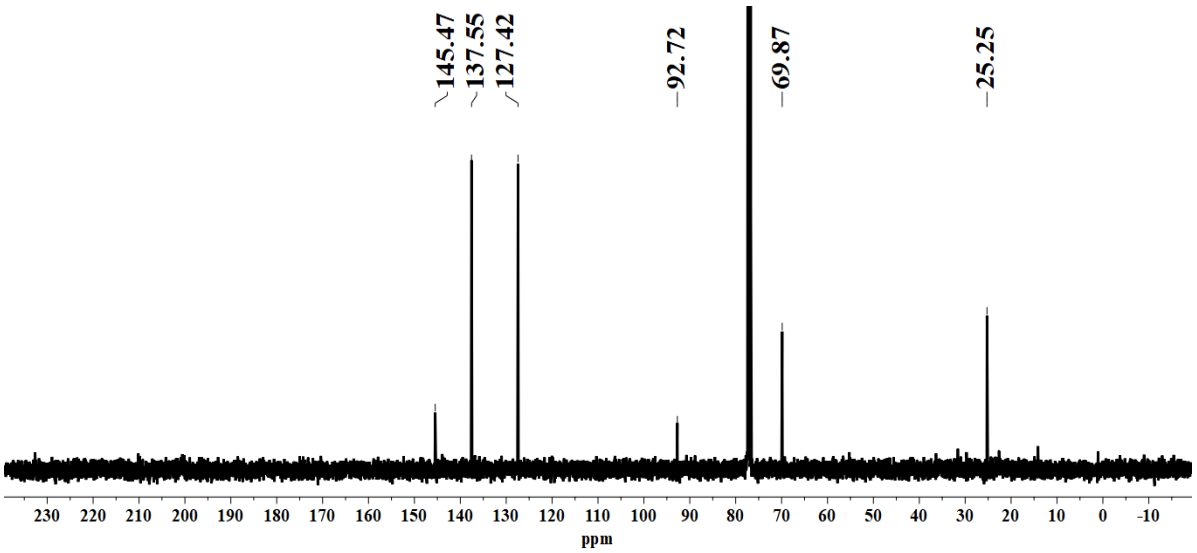


Fig. S84. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$ (101 MHz).

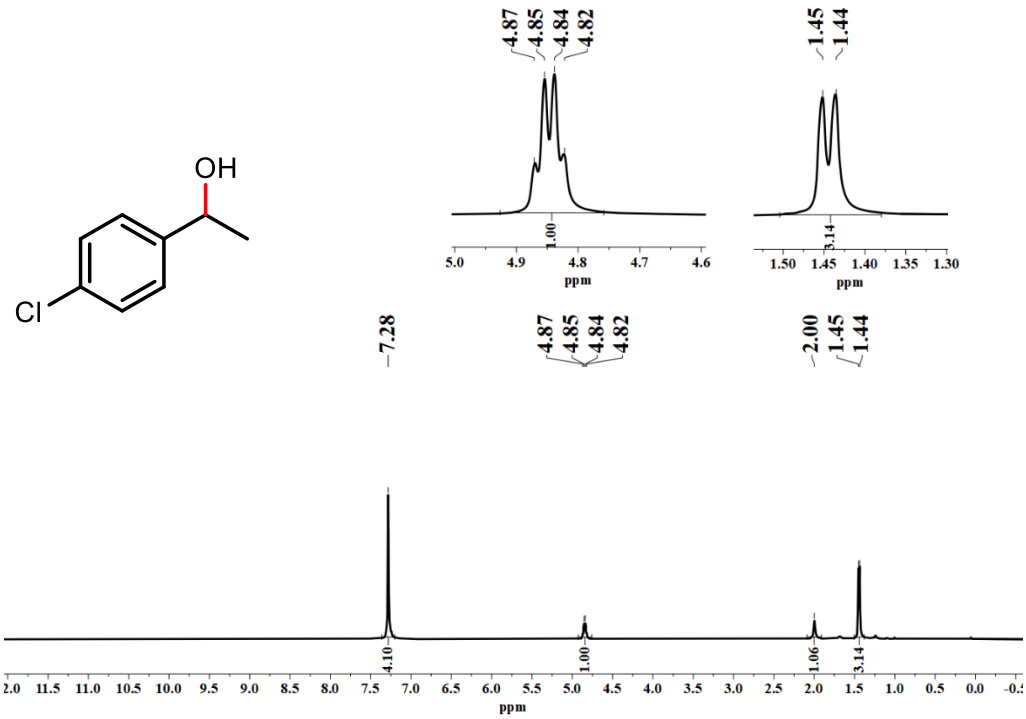


Fig. S85. ^{1}H NMR spectrum of **6b** in $CDCl_3$ (400 MHz).

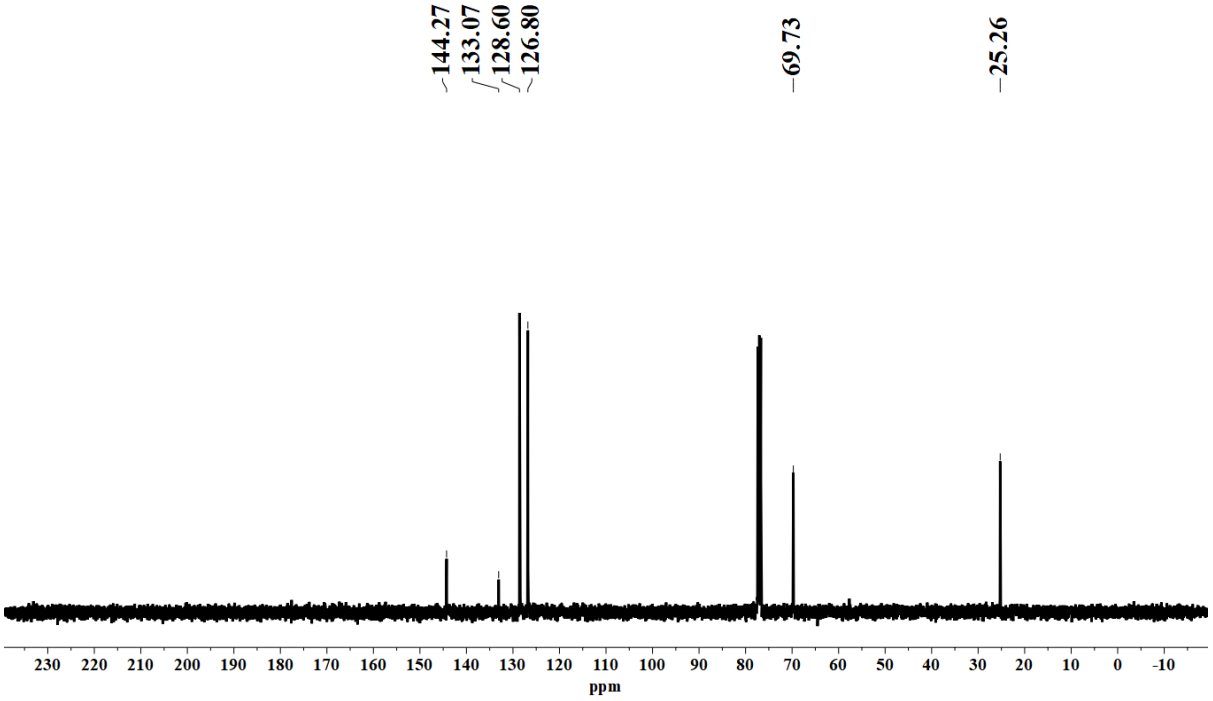


Fig. S86. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** in $CDCl_3$ (101 MHz).

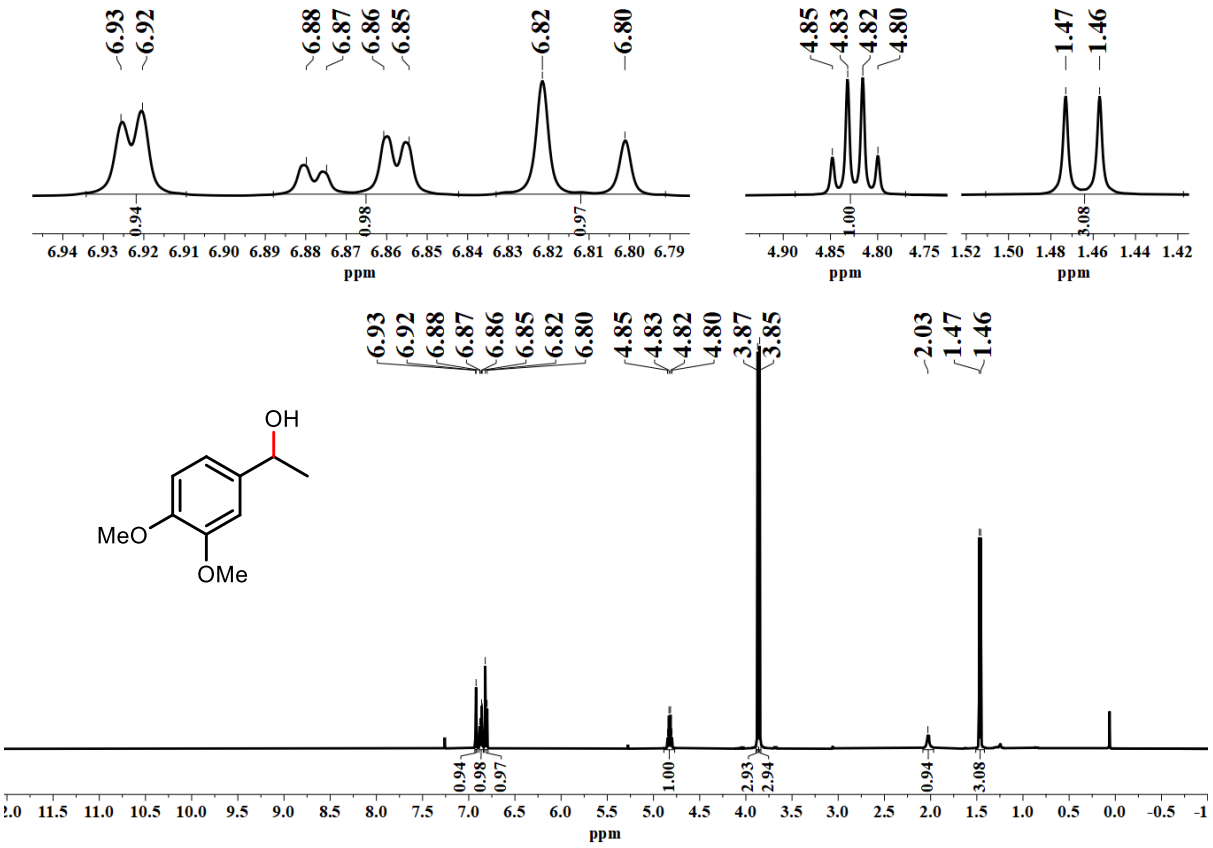


Fig. S87. ^{1}H NMR spectrum of **7b** in $CDCl_3$ (400 MHz).

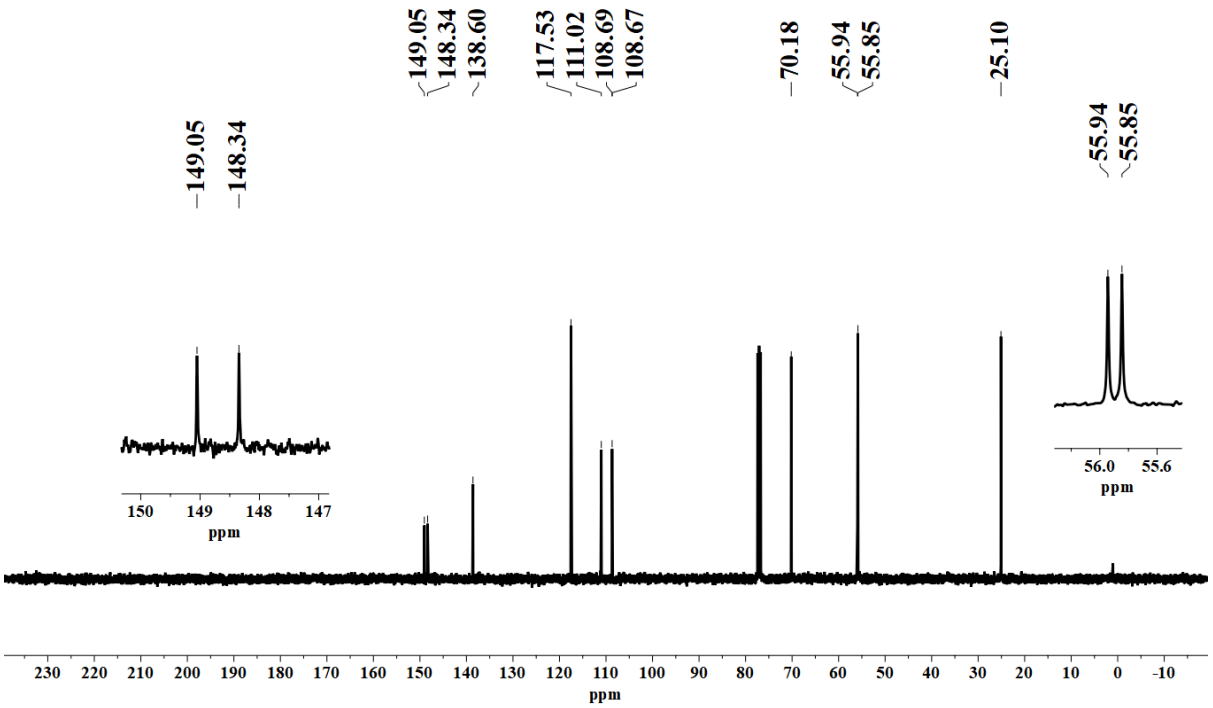


Fig. S88. $^{13}C\{^{1}H\}$ NMR spectrum of **7b** in $CDCl_3$ (101 MHz).

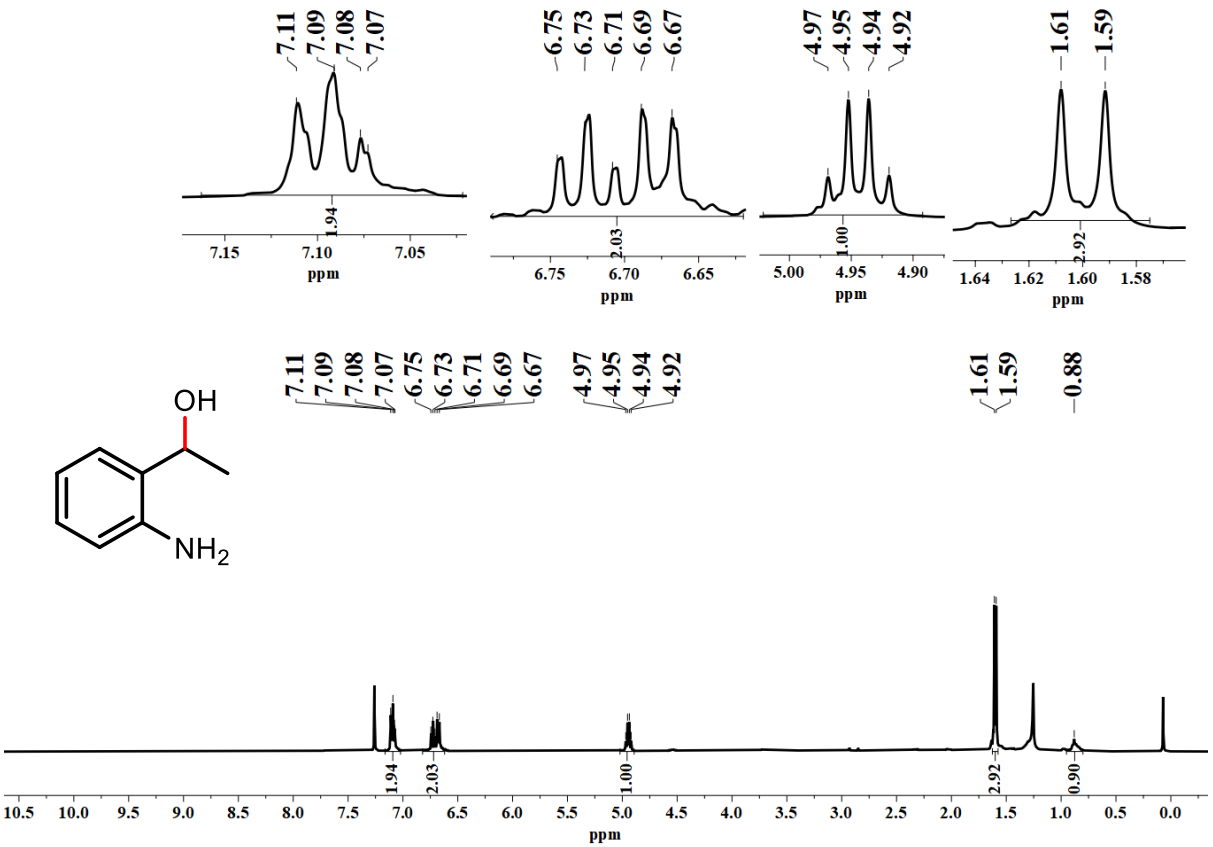


Fig. S89. ^{1}H NMR spectrum of **8b** in $CDCl_3$ (400 MHz).

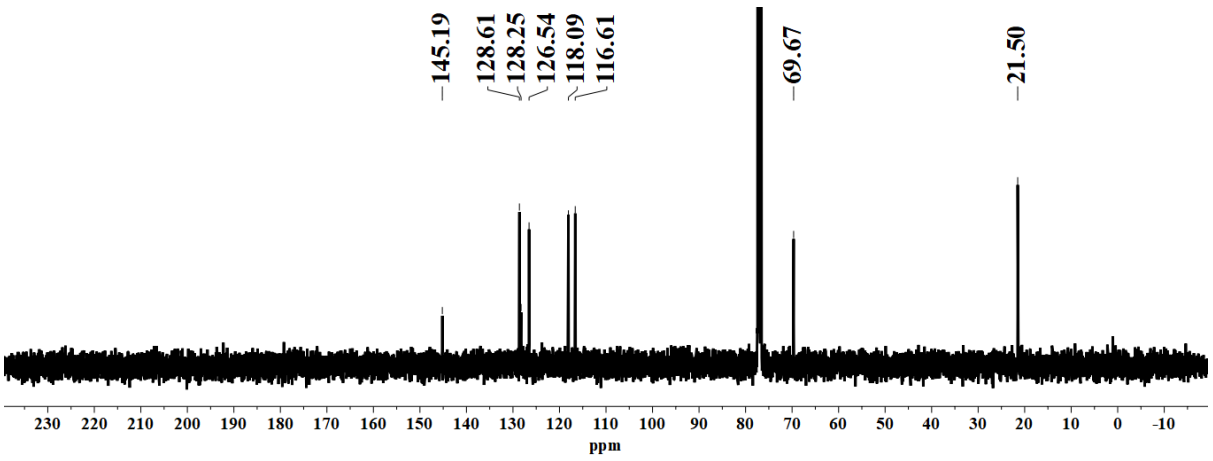


Fig. S90. $^{13}C\{^{1}H\}$ NMR spectrum of **8b** in $CDCl_3$ (101 MHz).

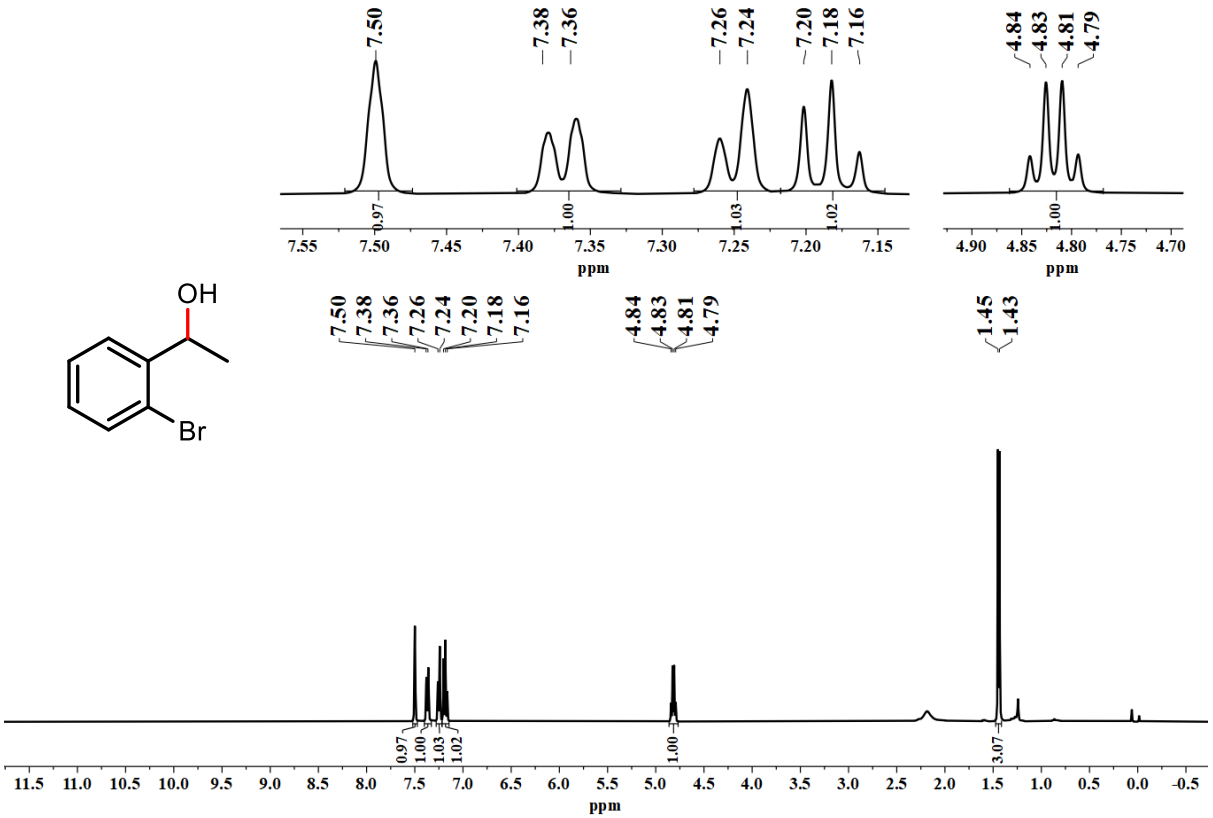


Fig. S91. ^{1}H NMR spectrum of **9b** in $CDCl_3$ (400 MHz).

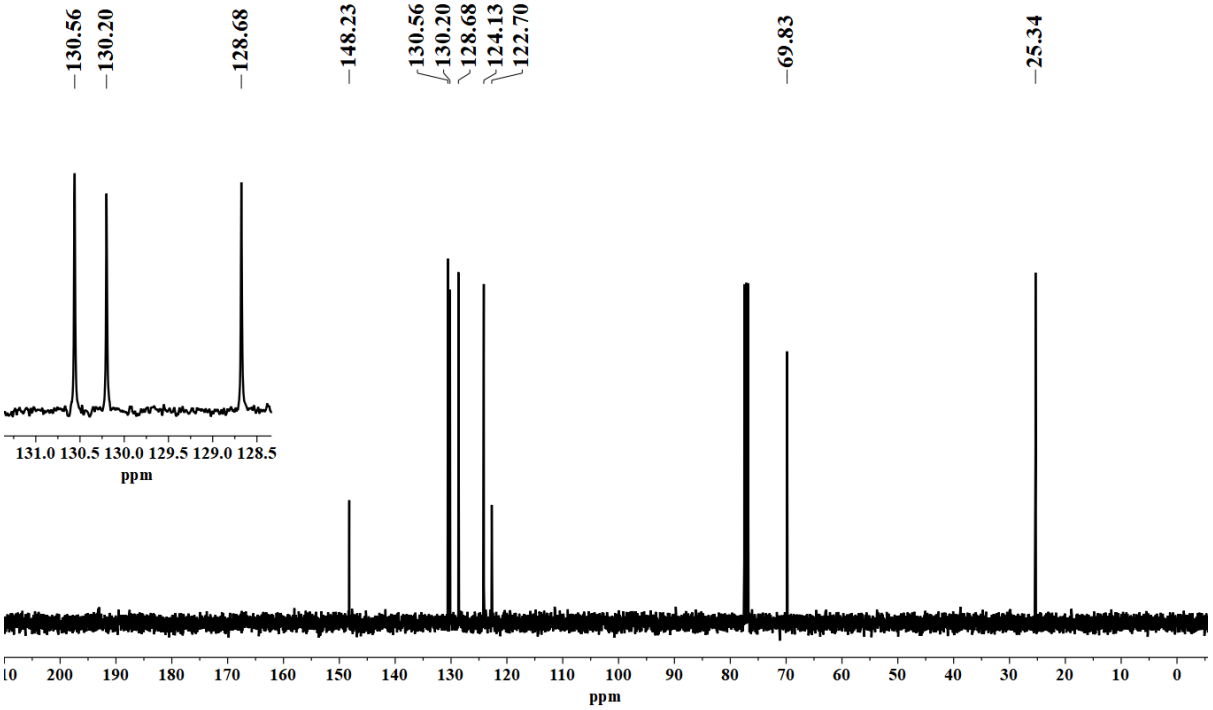


Fig. S92. $^{13}C\{^{1}H\}$ NMR spectrum of **9b** in $CDCl_3$ (101 MHz).

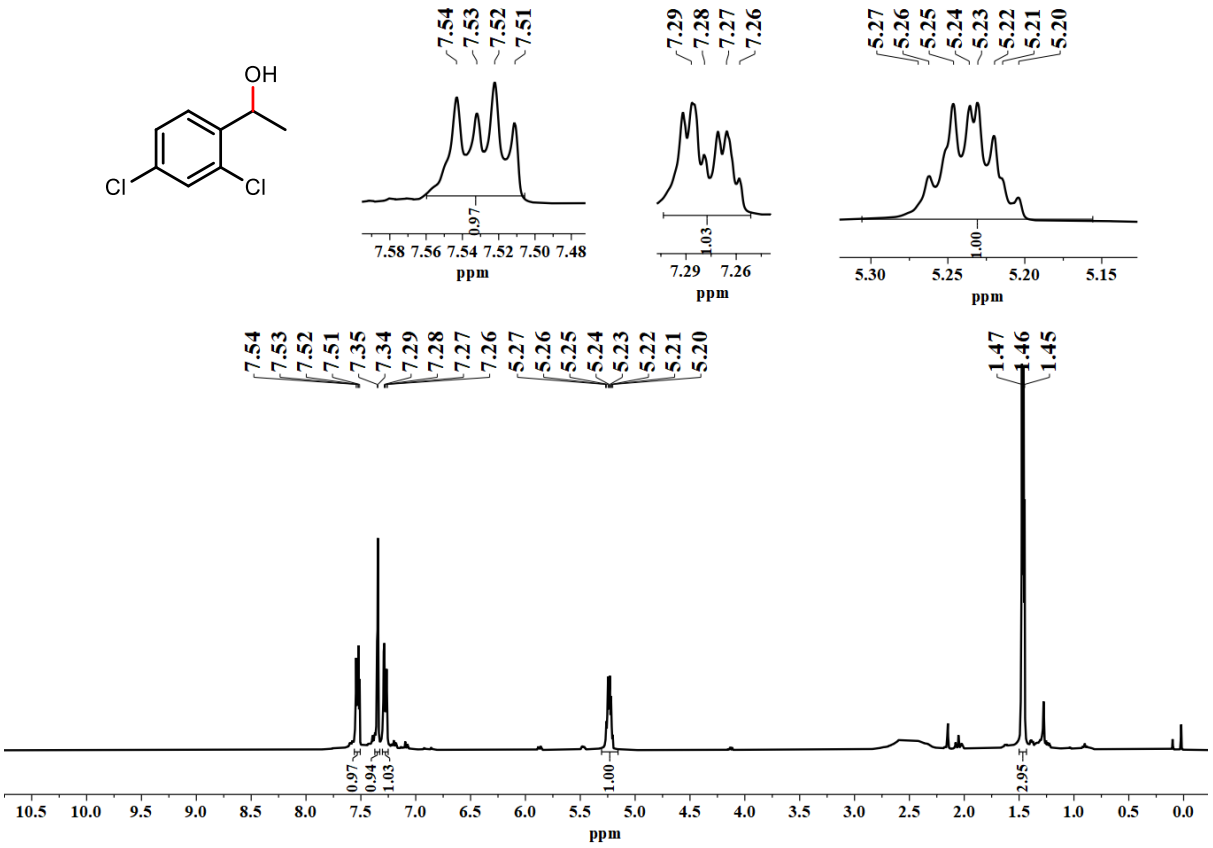


Fig. S93. ^{1}H NMR spectrum of **10b** in $CDCl_3$ (400 MHz).

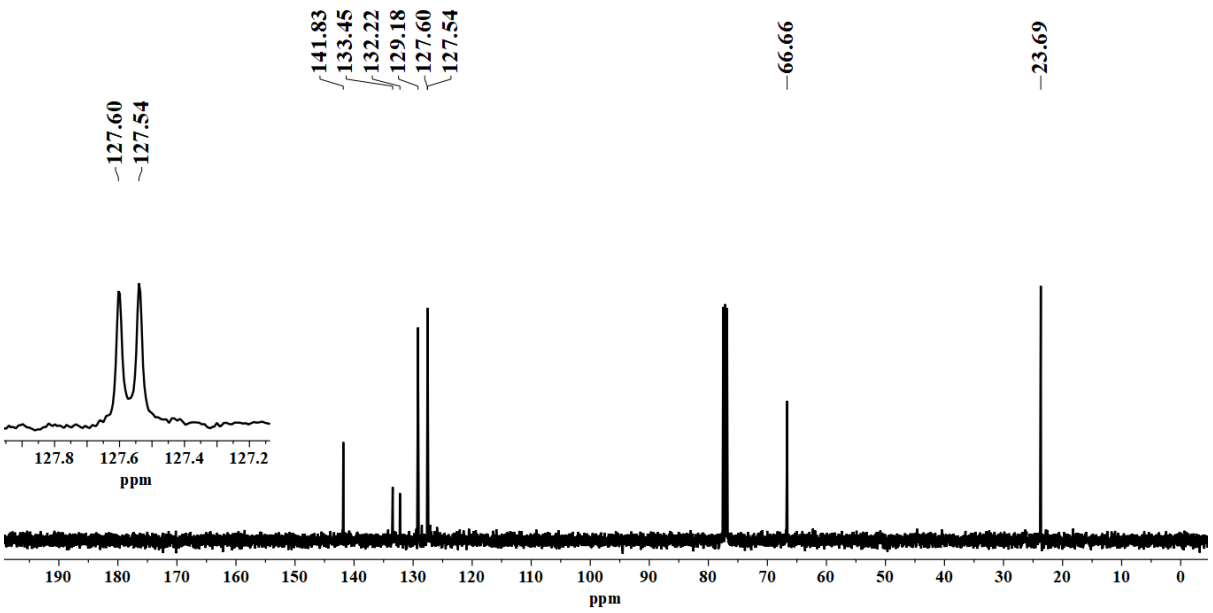


Fig. S94. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$ (101 MHz).

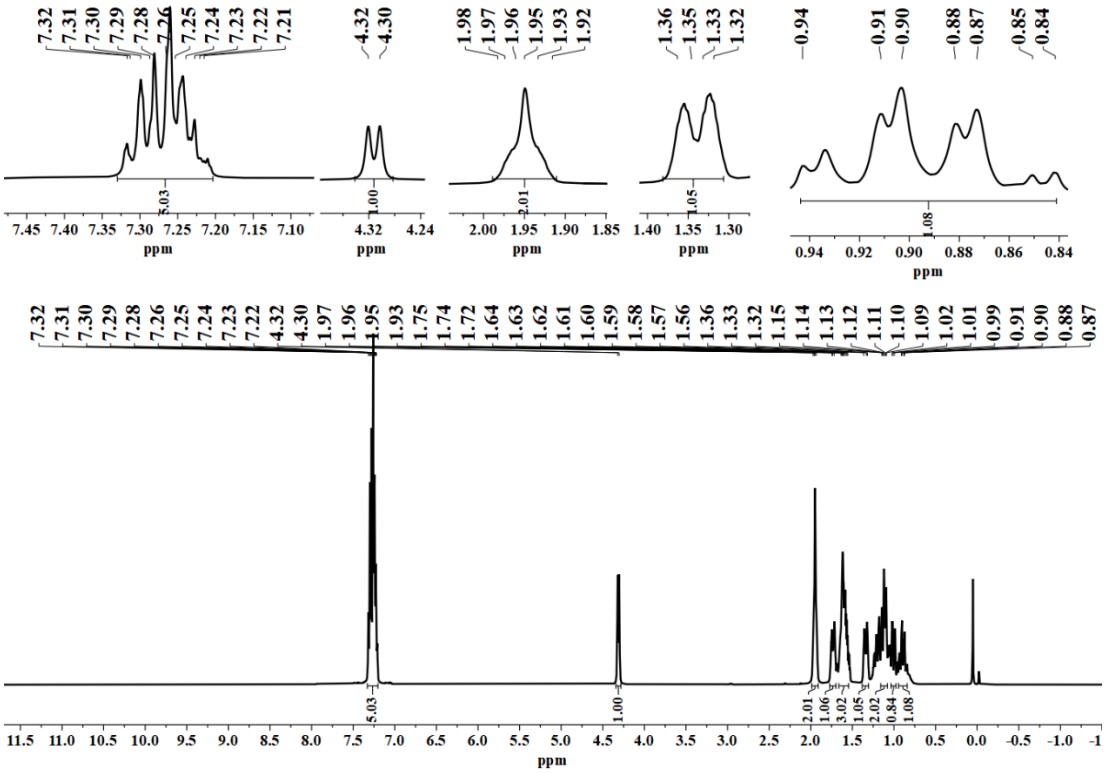


Fig. S95. ^{1}H NMR spectrum of **11b** in $CDCl_3$ (400 MHz).

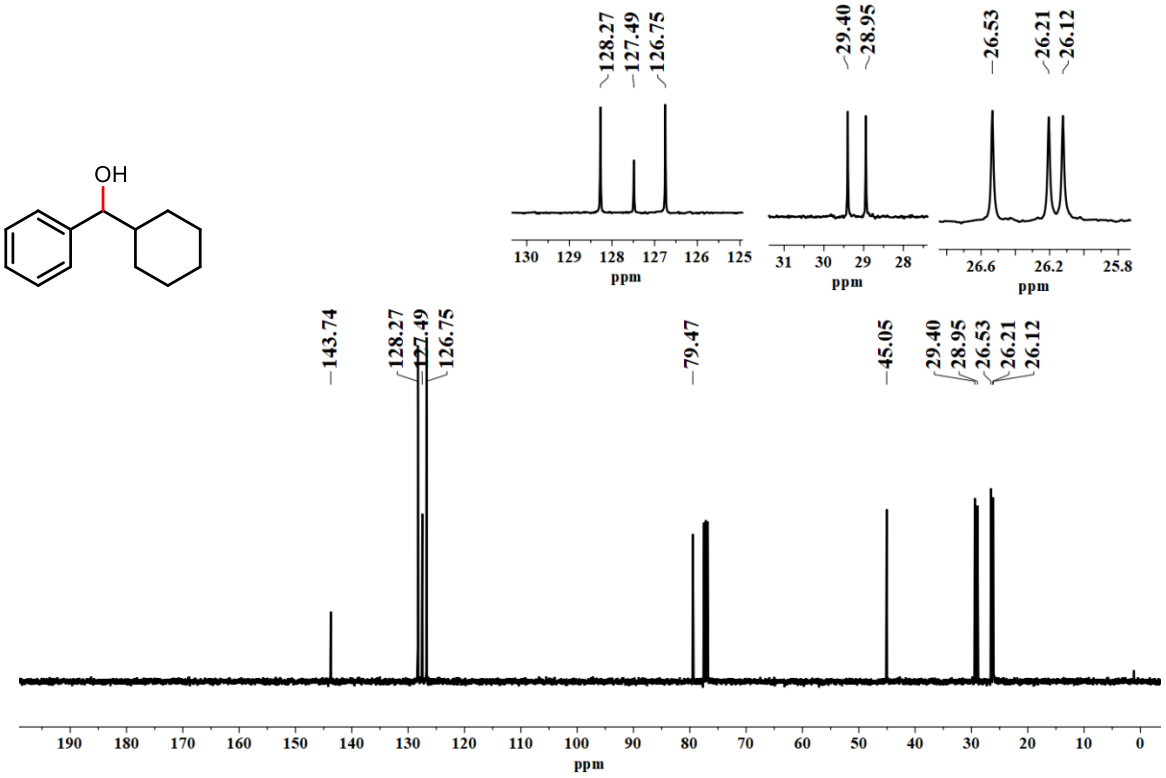


Fig. S96. $^{13}C\{^{1}H\}$ NMR spectrum of **11b** in $CDCl_3$ (101 MHz).

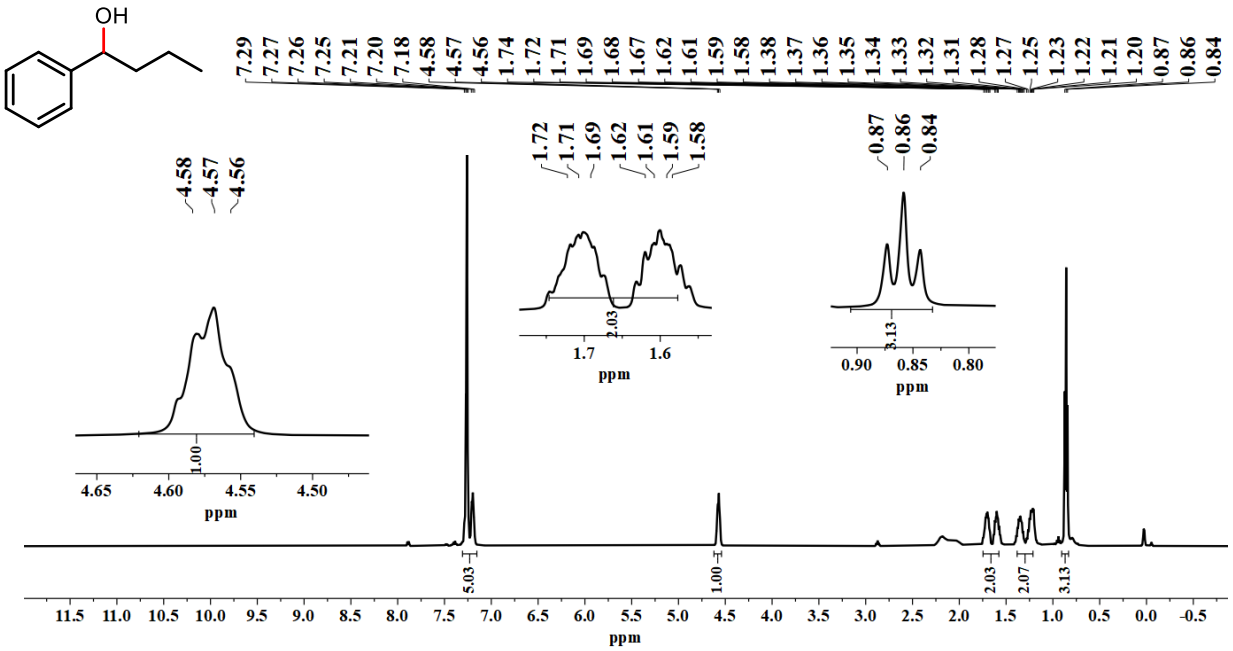


Fig. S97. ^{1}H NMR spectrum of **12b** in $CDCl_3$ (500 MHz).

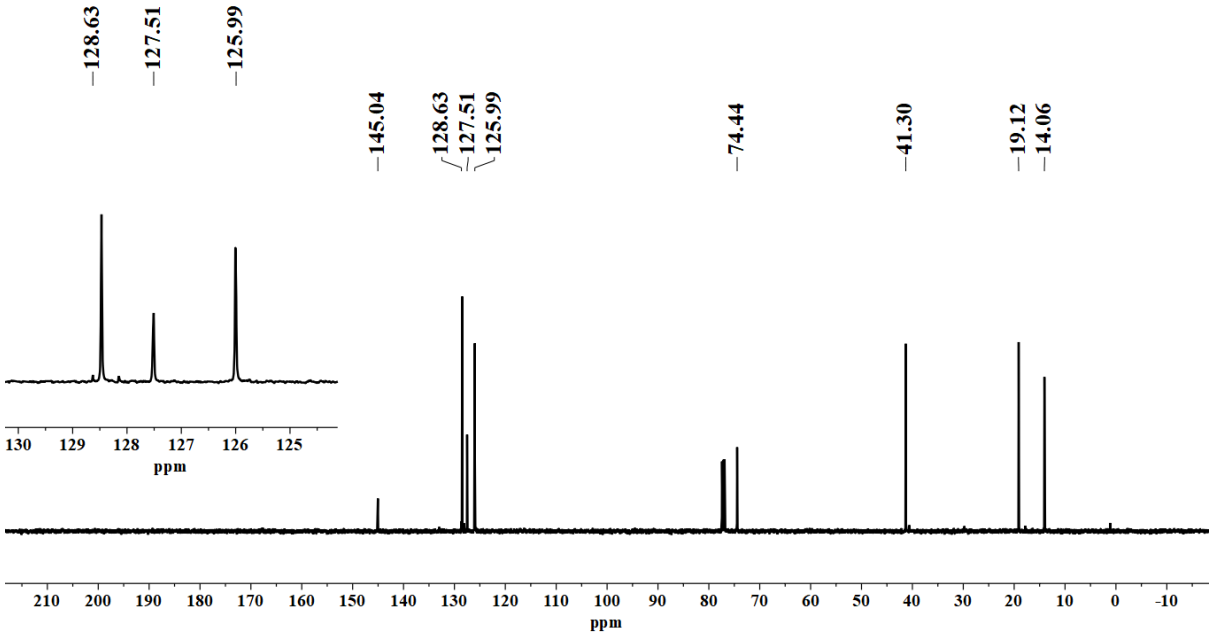


Fig. S98. ^{13}C{^{1}H} NMR spectrum of **12b** in $CDCl_3$ (126 MHz).

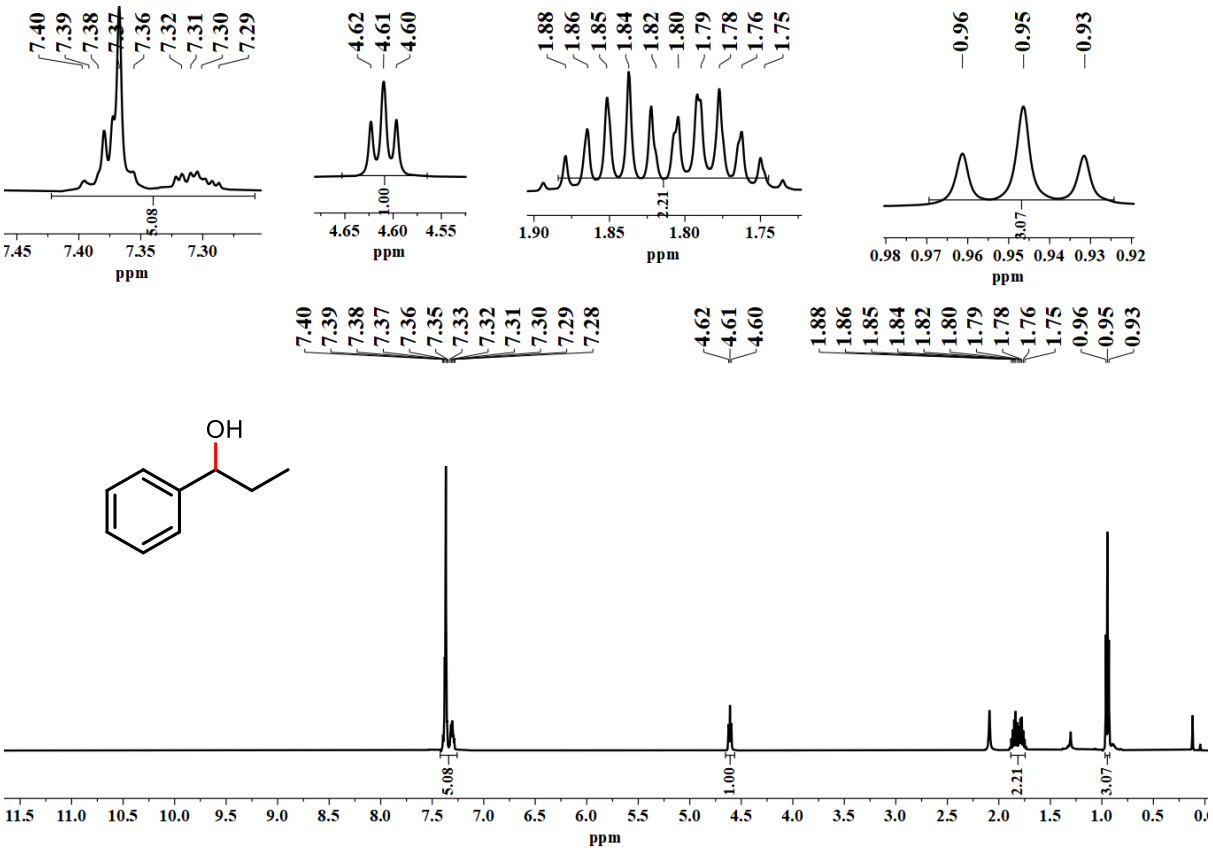


Fig. S99. ^{1}H NMR spectrum of **13b** in $CDCl_3$ (500 MHz).

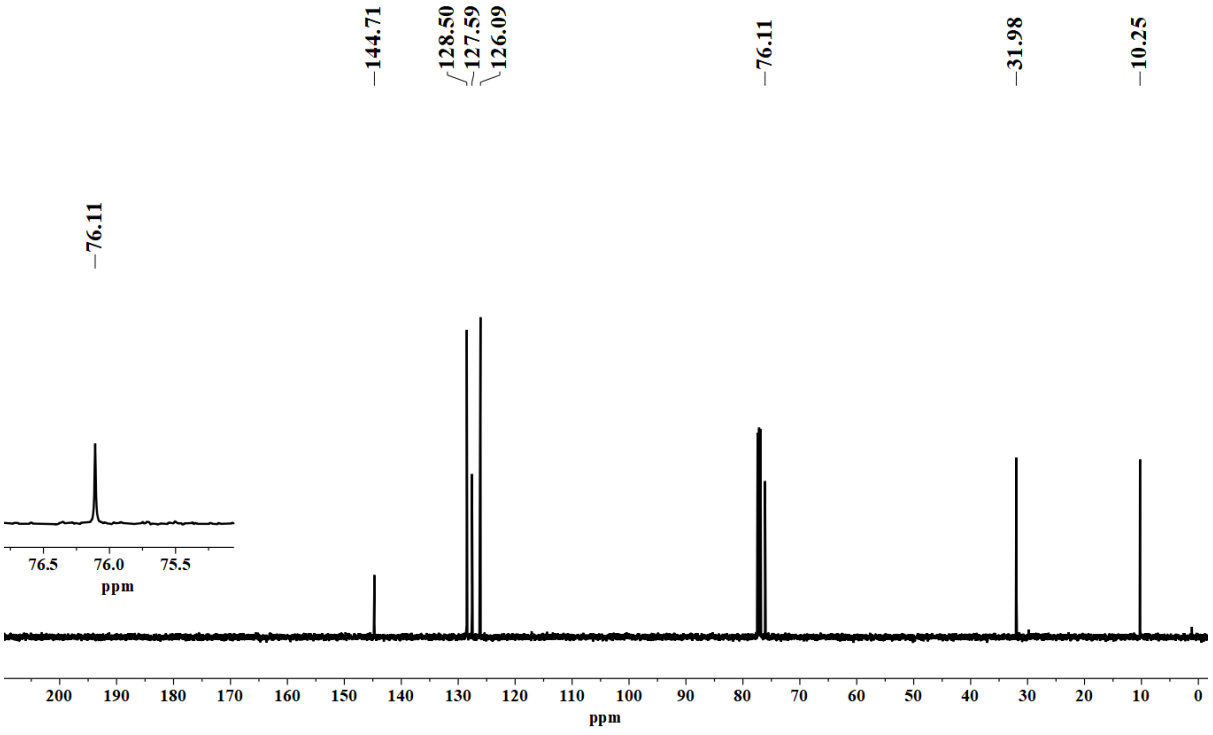


Fig. S100. $^{13}C\{^{1}H\}$ NMR spectrum of **13b** in $CDCl_3$ (126 MHz).

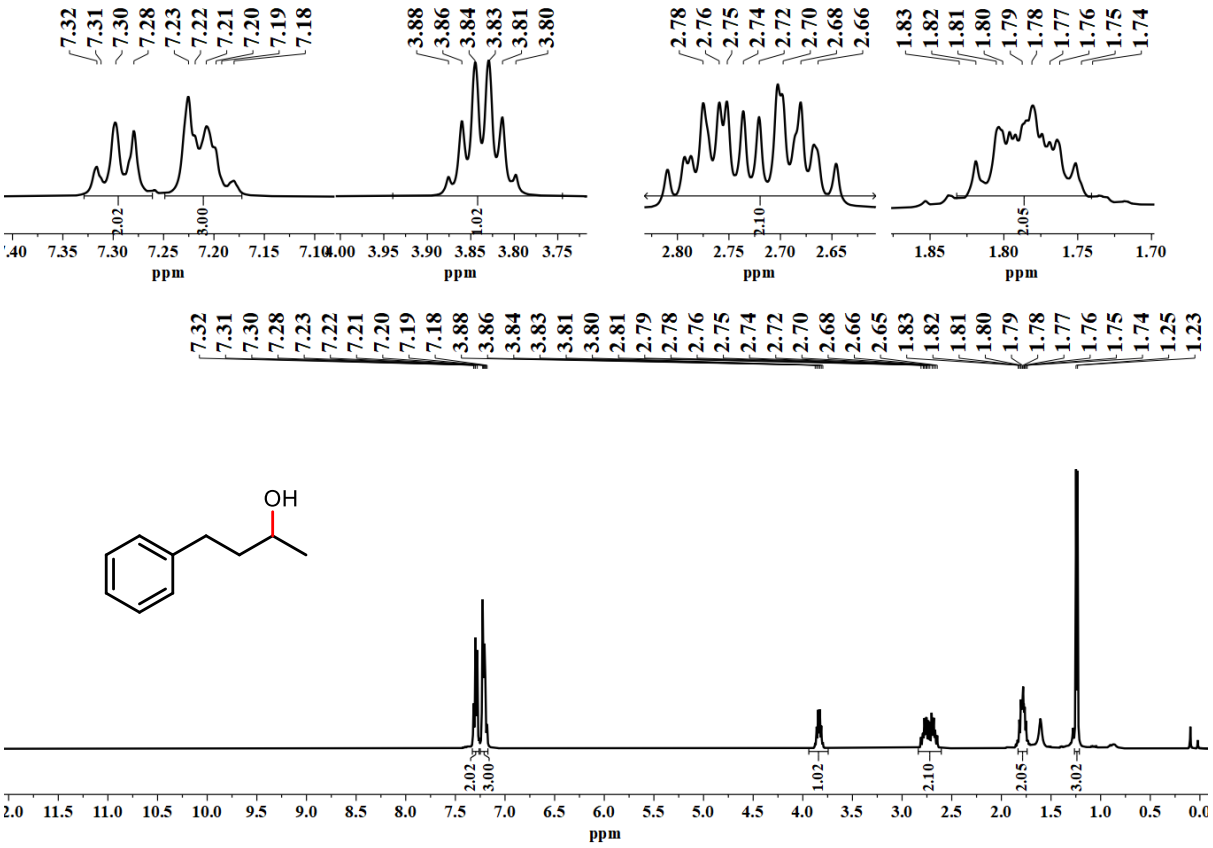


Fig. S101. ^{1}H NMR spectrum of **14b** in $CDCl_3$ (400 MHz).

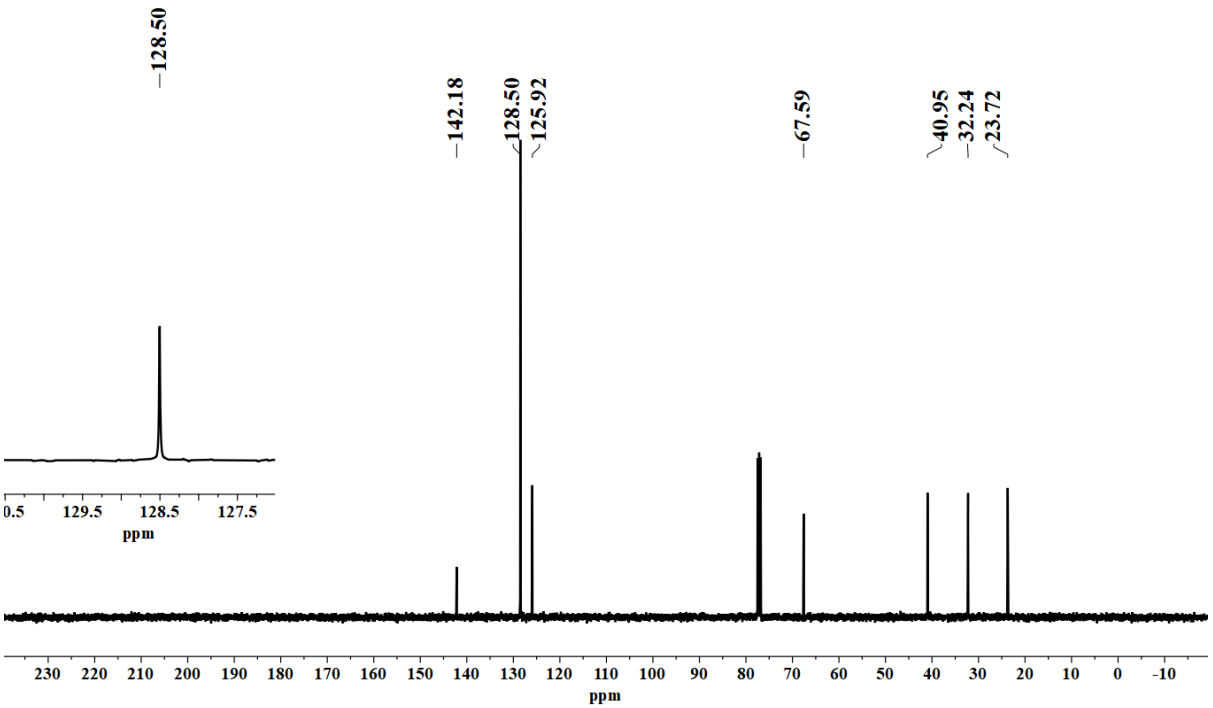


Fig. S102. $^{13}C\{^{1}H\}$ NMR spectrum of **14b** in $CDCl_3$ (101 MHz).

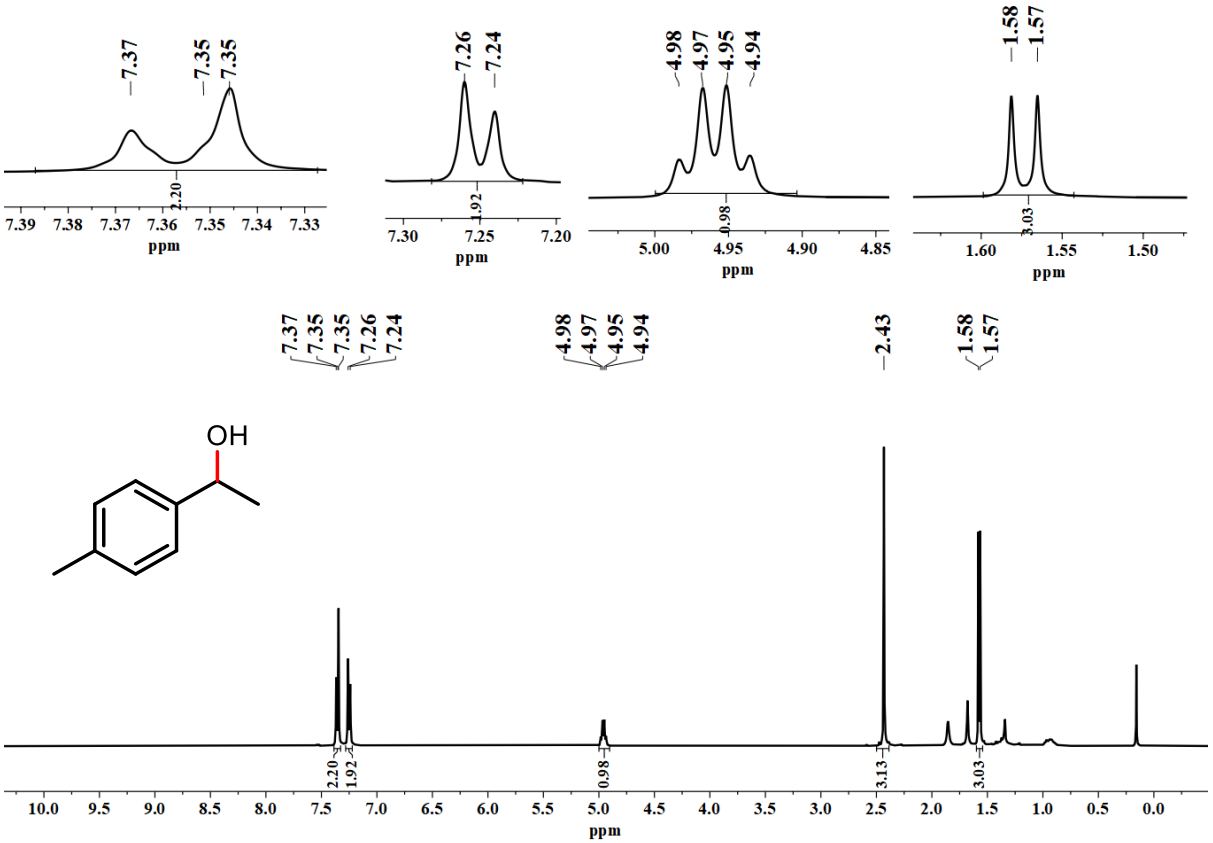


Fig. S103. ^{1}H NMR spectrum of **15b** in $CDCl_3$ (400 MHz).

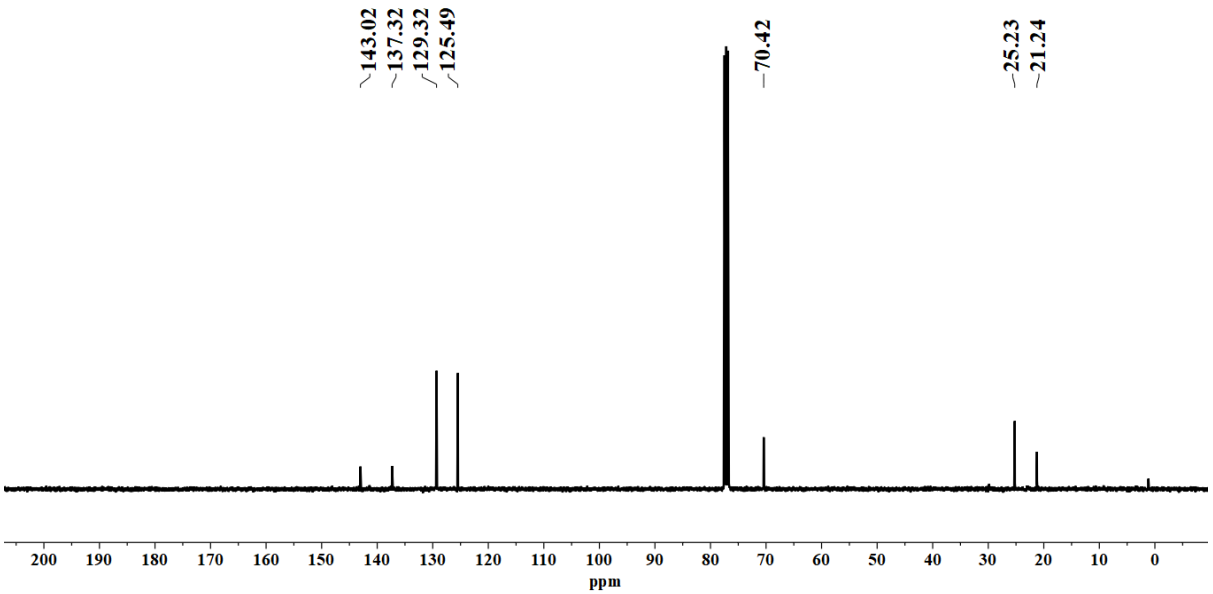


Fig. S104. $^{13}C\{^{1}H\}$ NMR spectrum of **15b** in $CDCl_3$ (101 MHz).

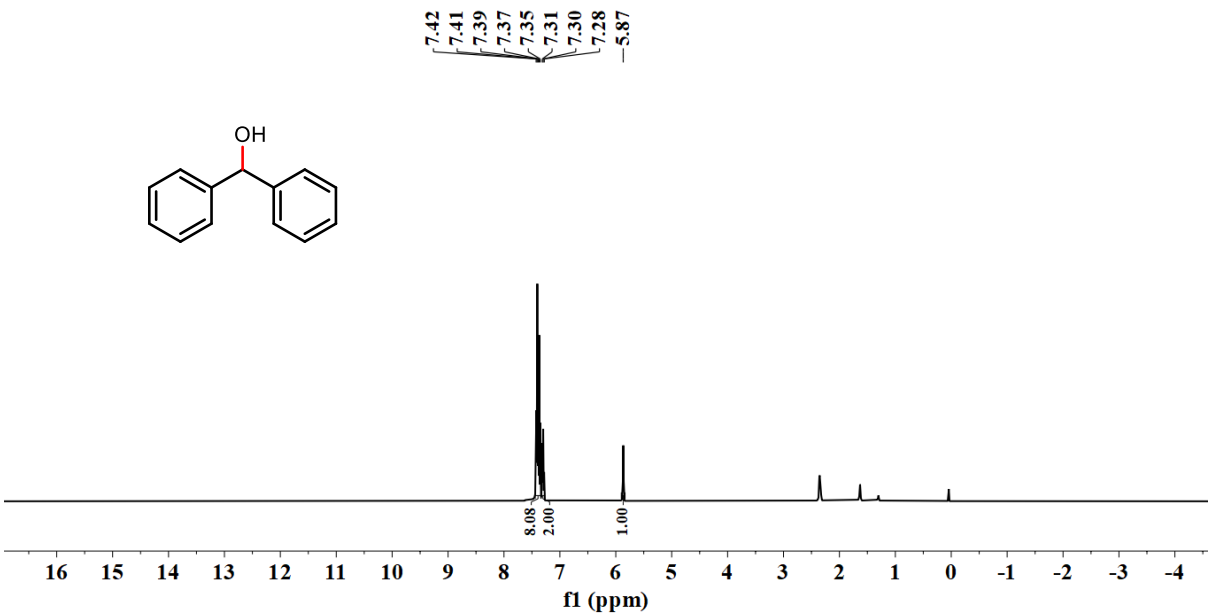


Fig. S105. ^{1}H NMR spectrum of **16b**in $CDCl_3$ (400 MHz).

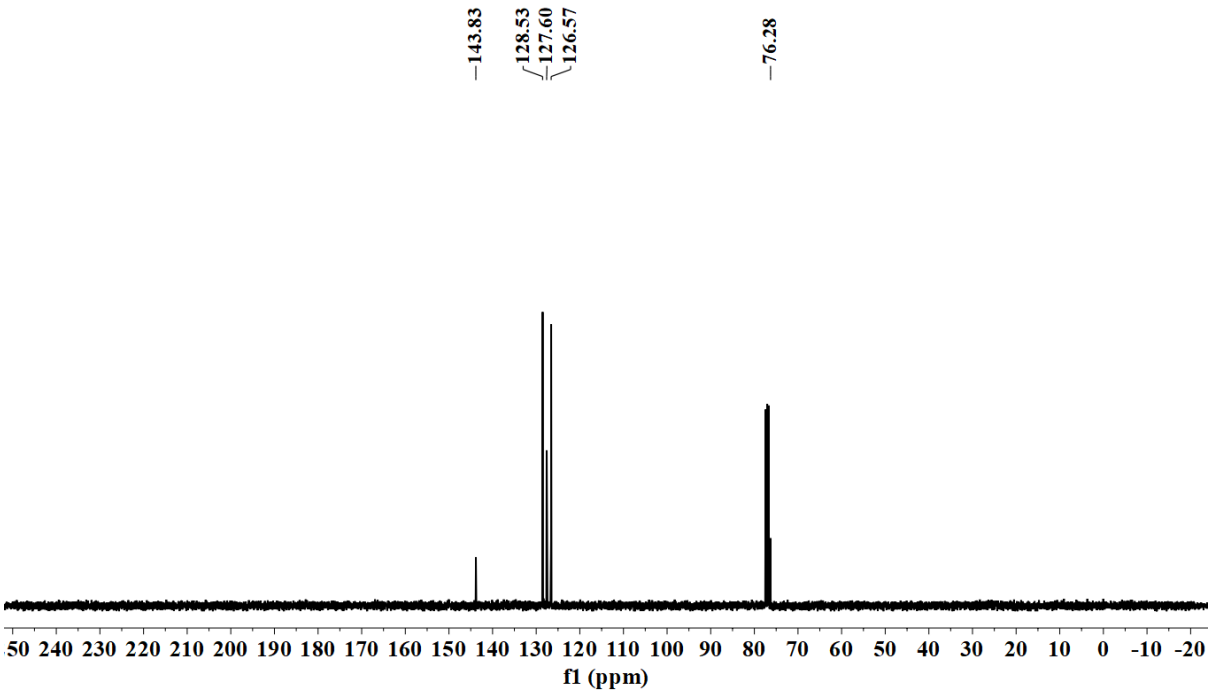


Fig. S106. $^{13}C\{^{1}H\}$ NMR spectrum of **16b** in $CDCl_3$ (101 MHz).

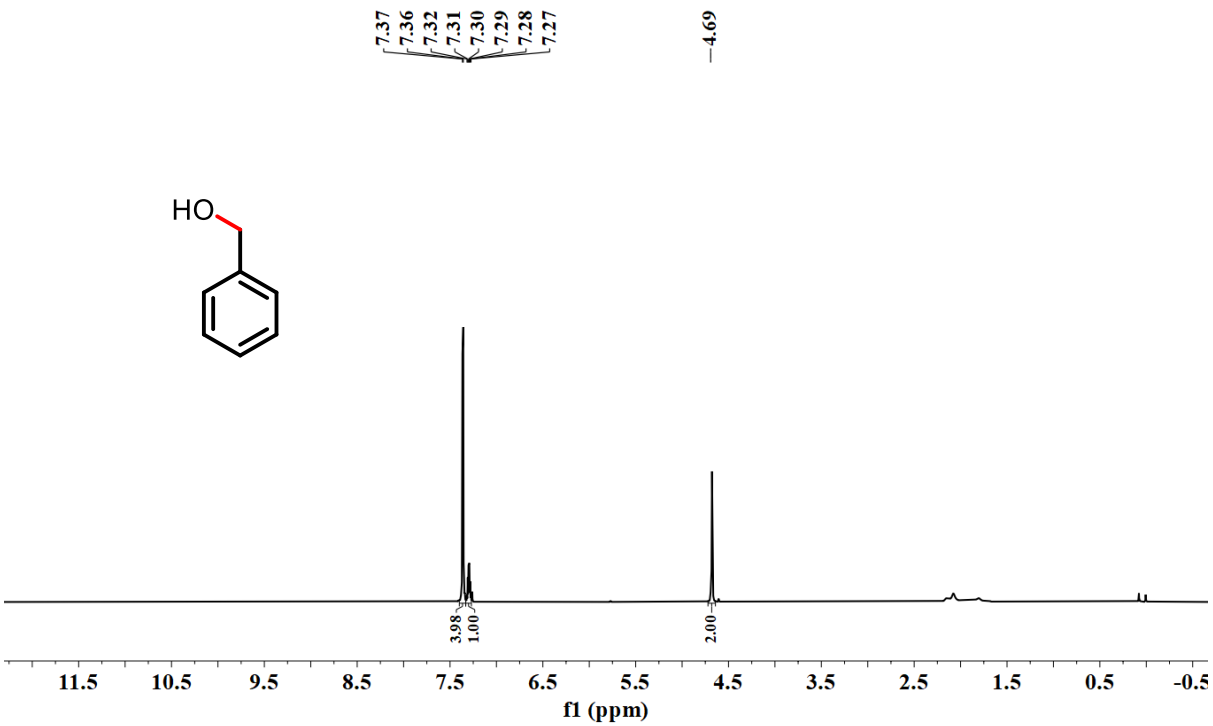


Fig. S107. ^{1}H NMR spectrum of **1c** in $CDCl_3$ (500 MHz).

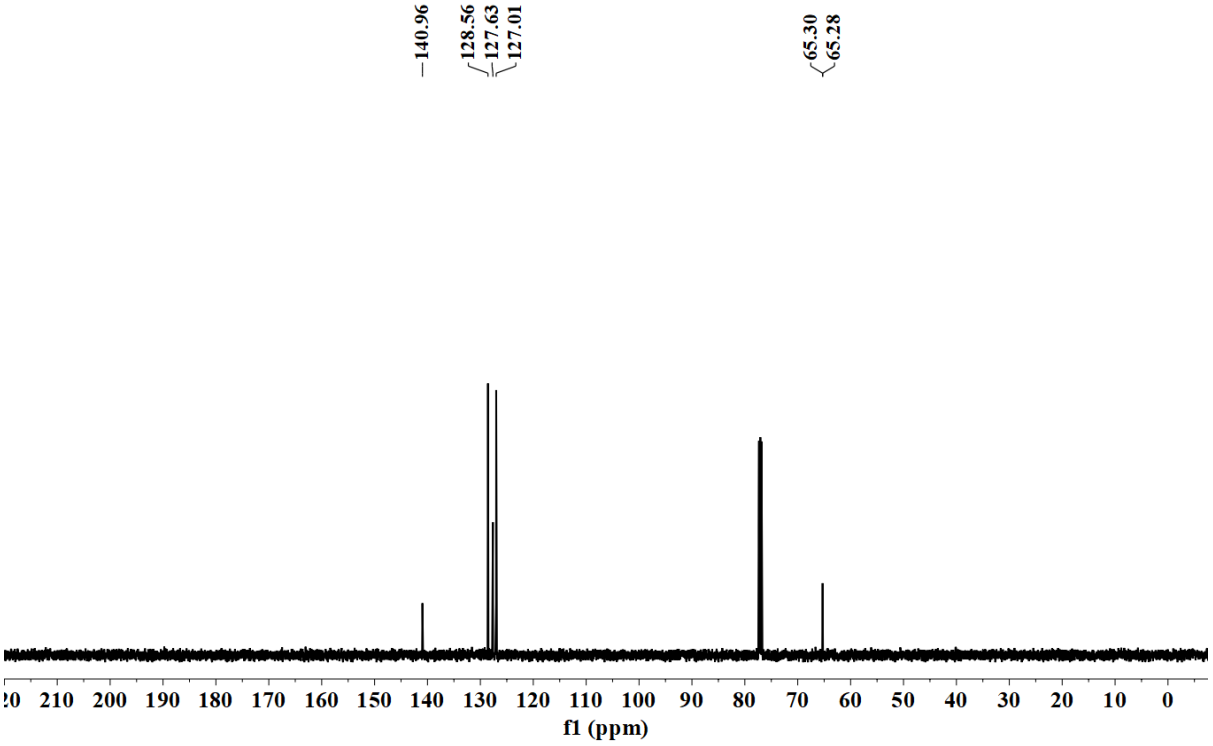


Fig. S108. $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in $CDCl_3$ (126 MHz).

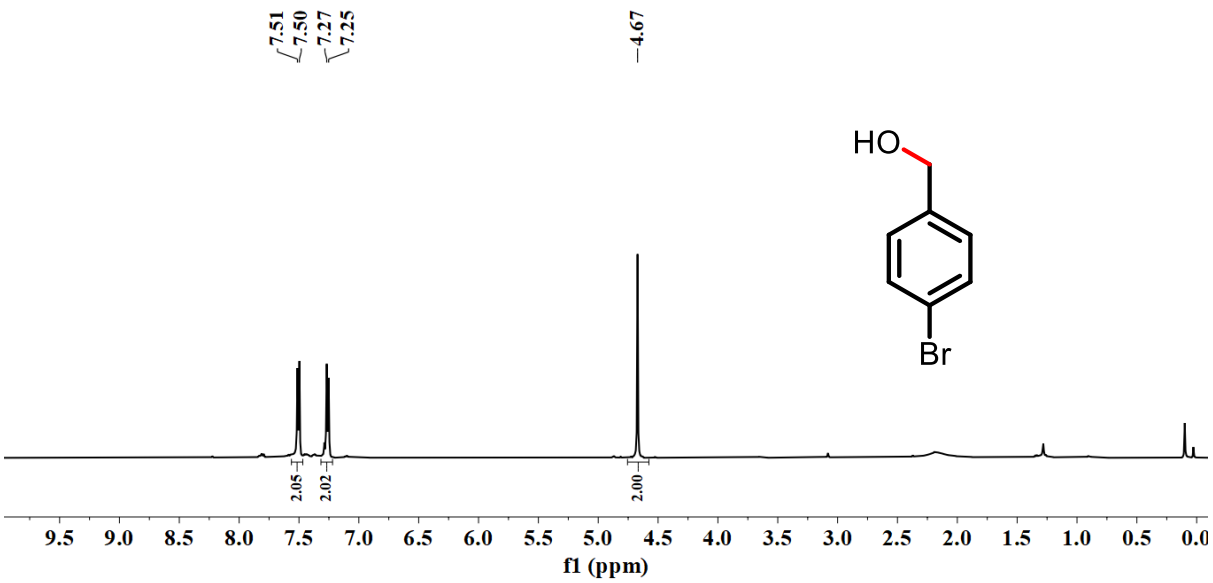


Fig. S109. ^{1}H NMR spectrum of **2c** in $CDCl_3$ (500 MHz).

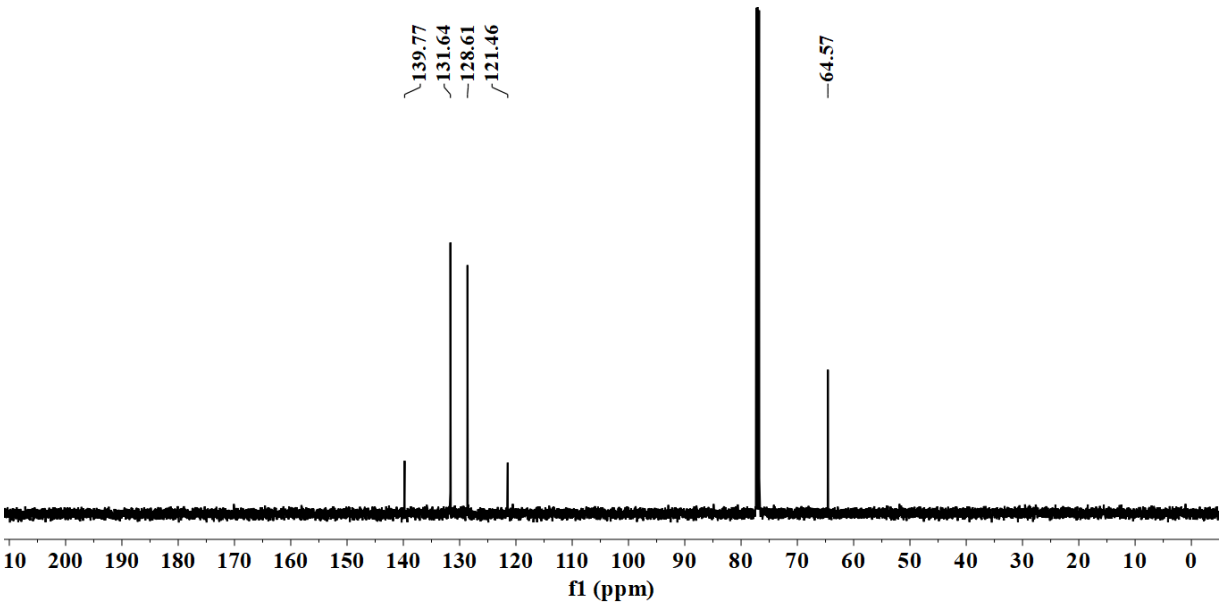


Fig. S110. $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in $CDCl_3$ (126 MHz).

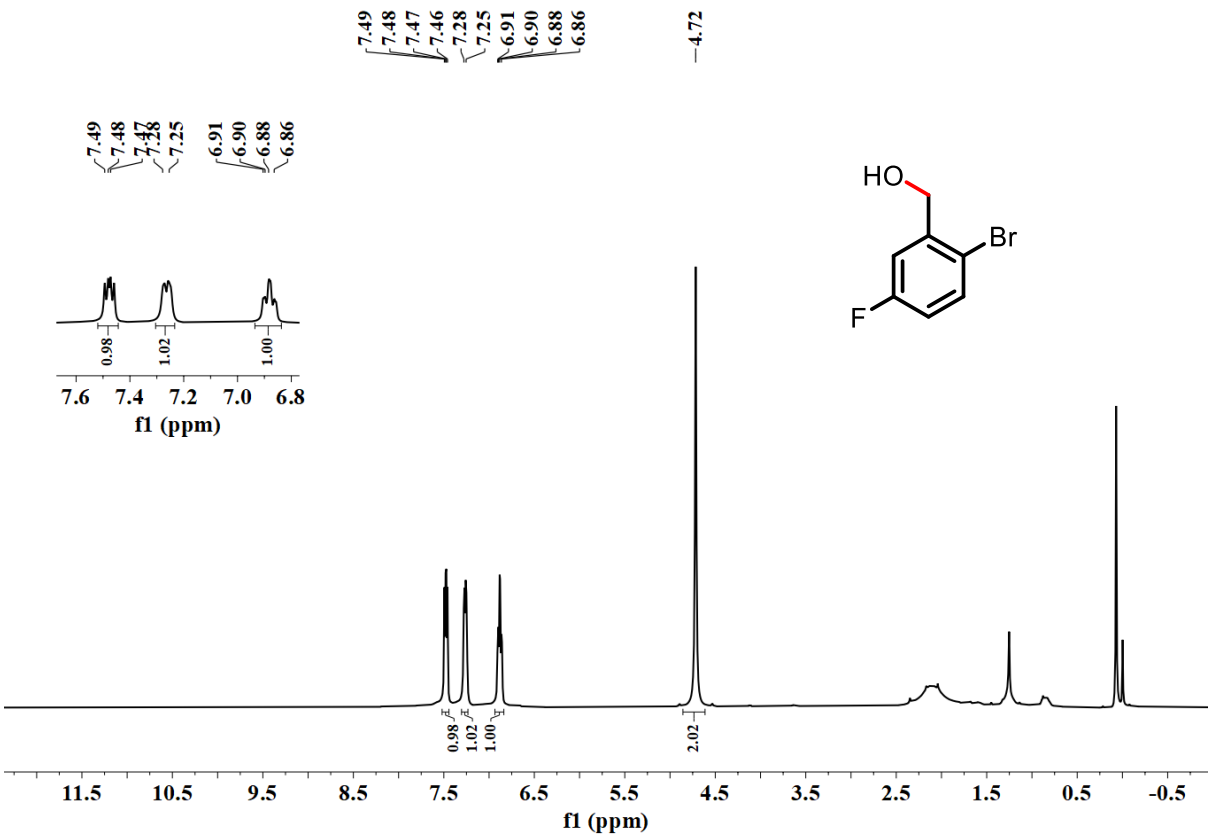


Fig. S111. ^{1}H NMR spectrum of **3c** in $CDCl_3$ (400 MHz).

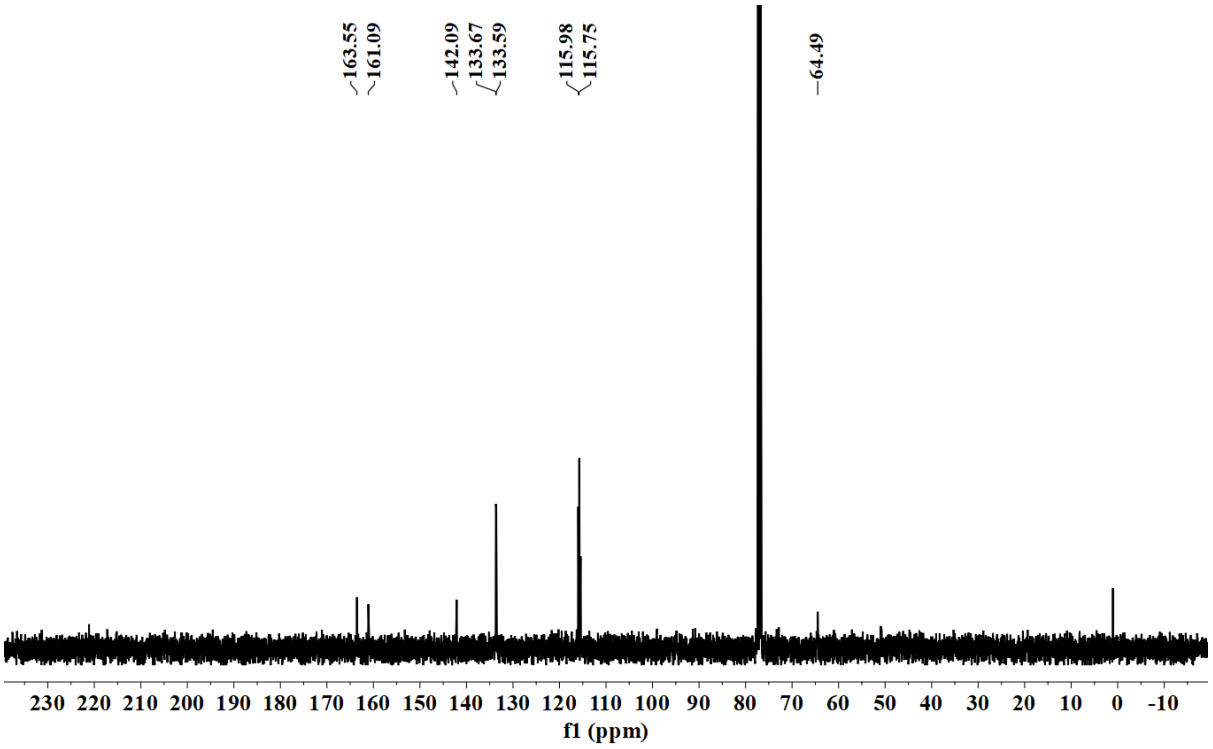


Fig. S112. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in $CDCl_3$ (101 MHz).

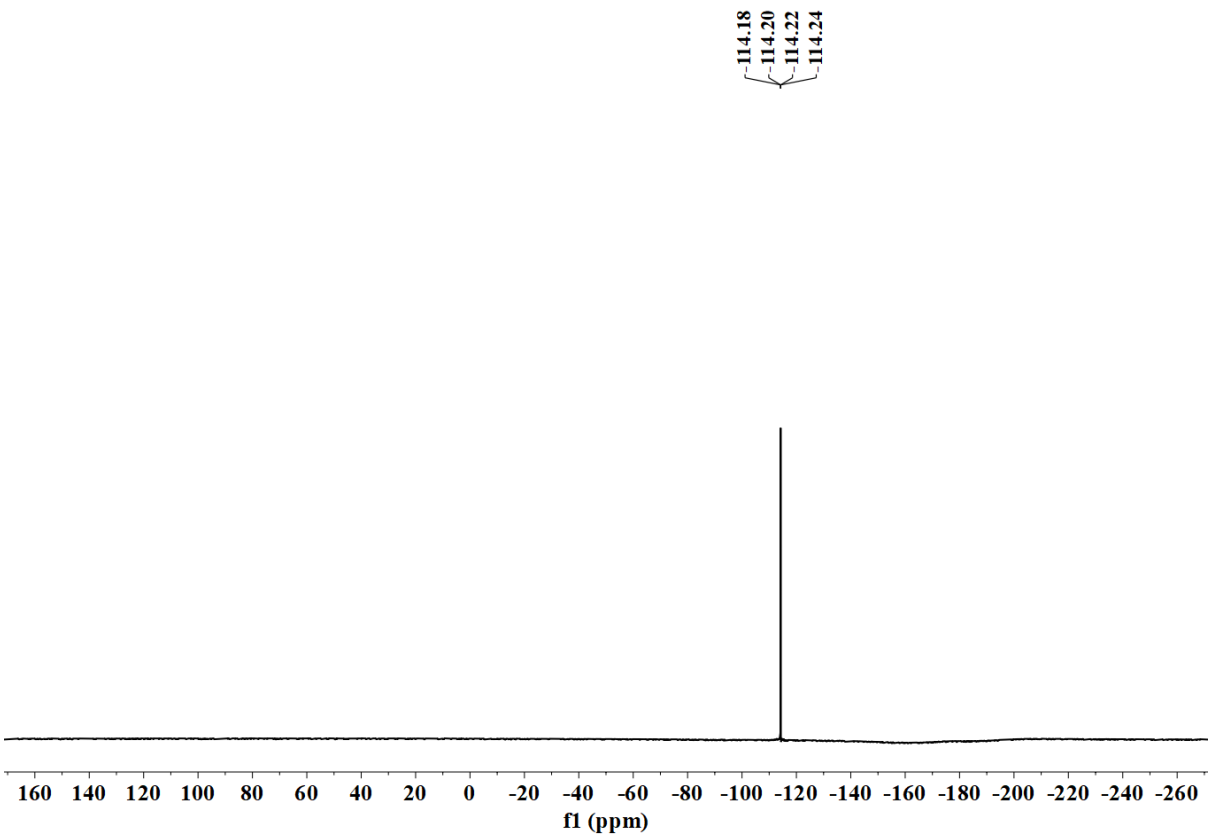


Fig. S113. $^{19}F\{^{1}H\}$ NMR spectrum of **3c** in $CDCl_3$ (376 MHz).

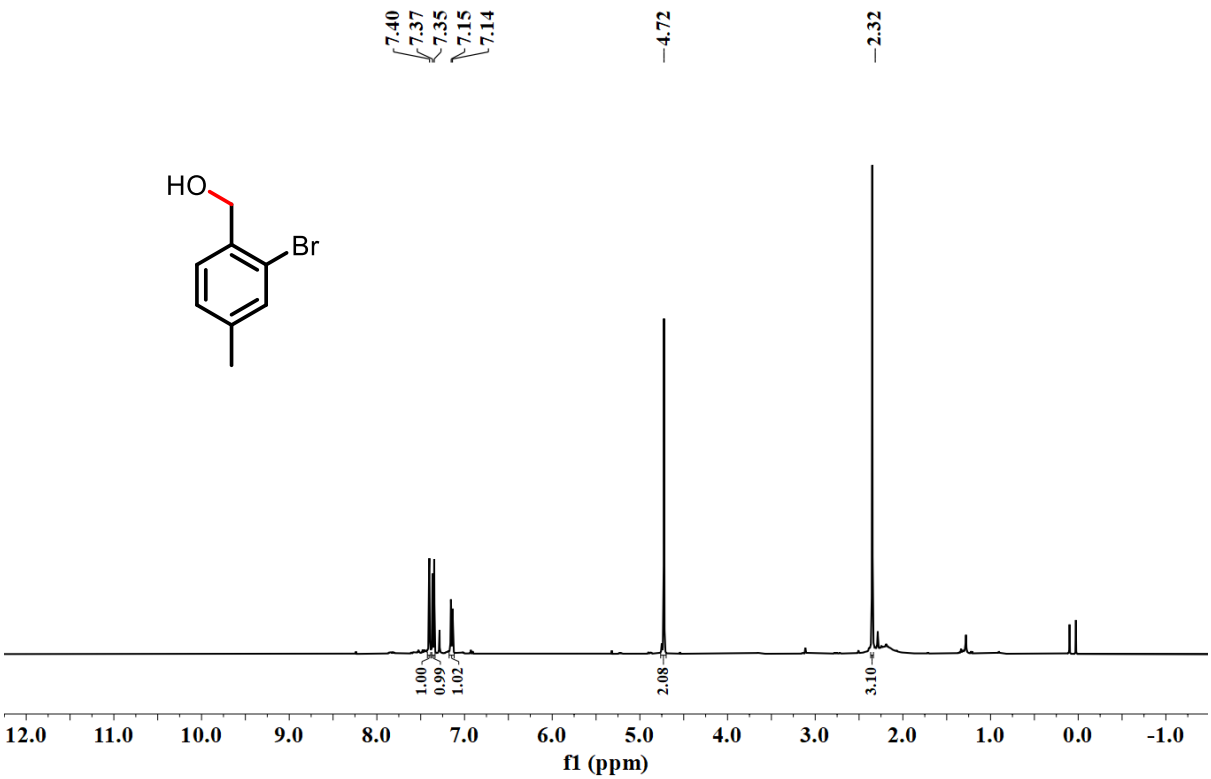


Fig. S114. ^{1}H NMR spectrum of **4c** in $CDCl_3$ (400 MHz).

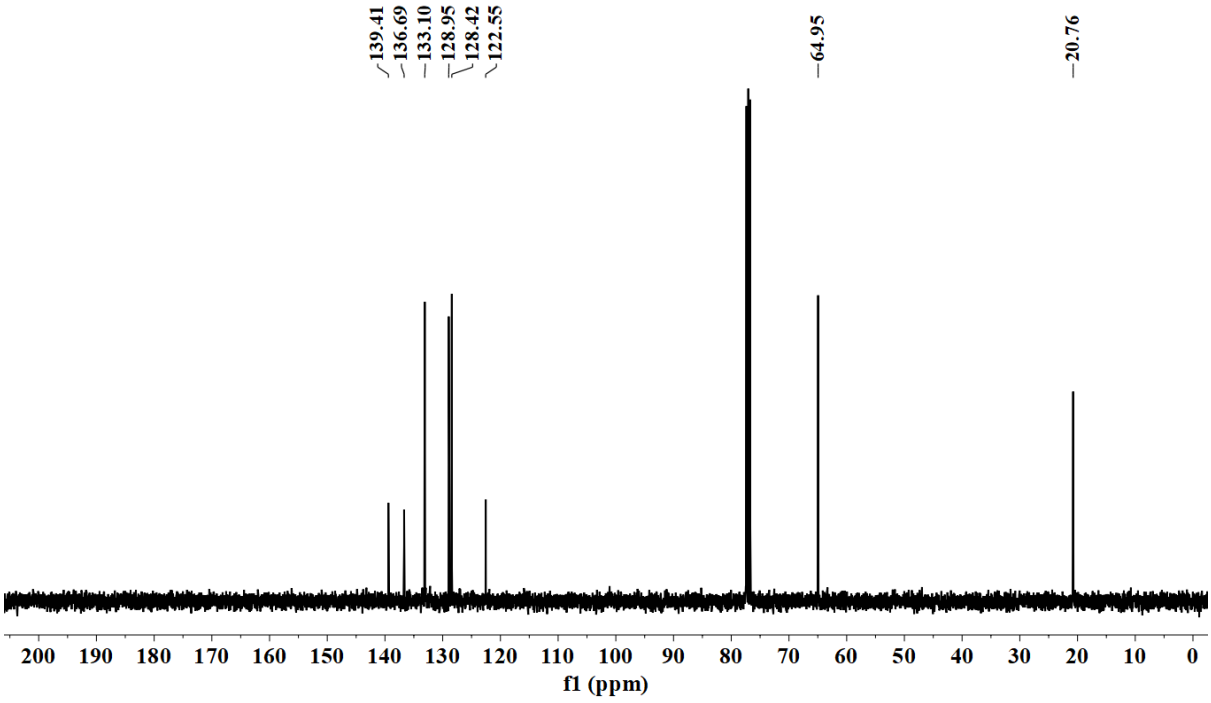


Fig. S115. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in $CDCl_3$ (101 MHz).

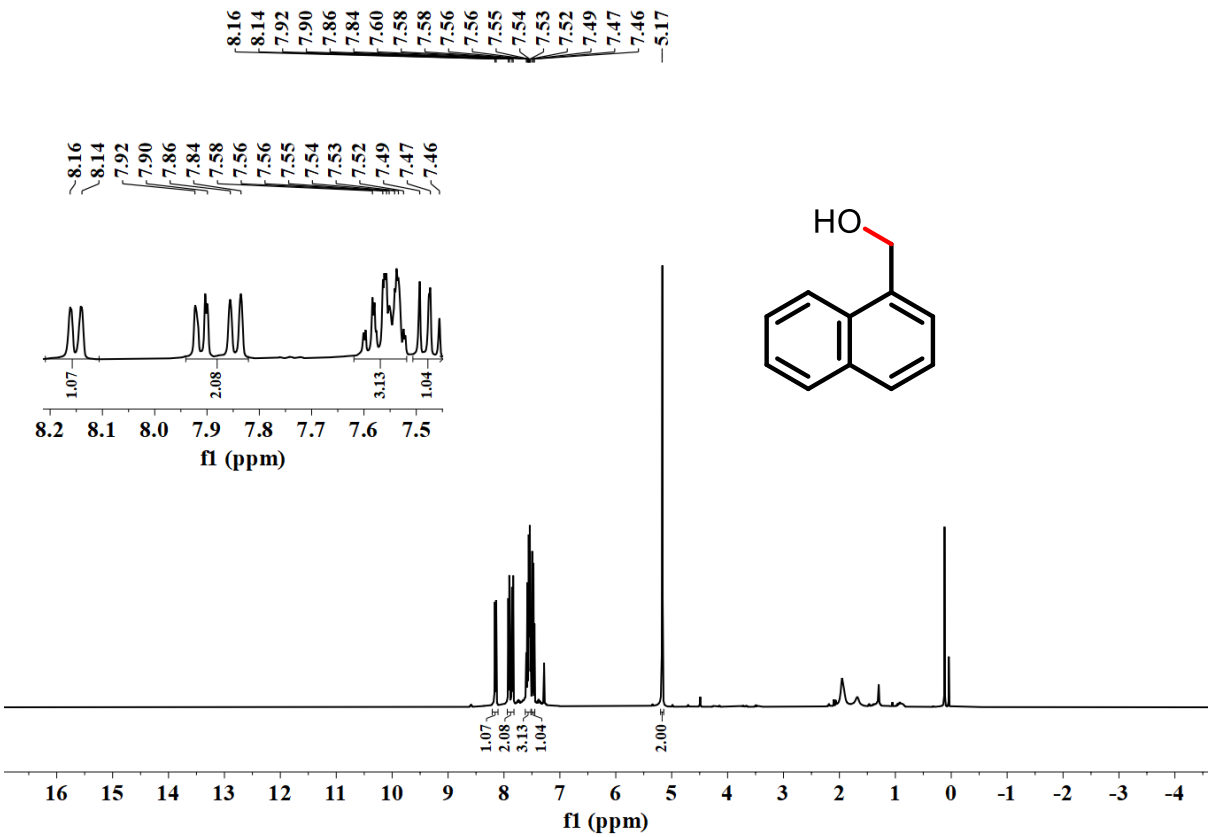


Fig. S116. ^{1}H NMR spectrum of **5c** in $CDCl_3$ (400 MHz).

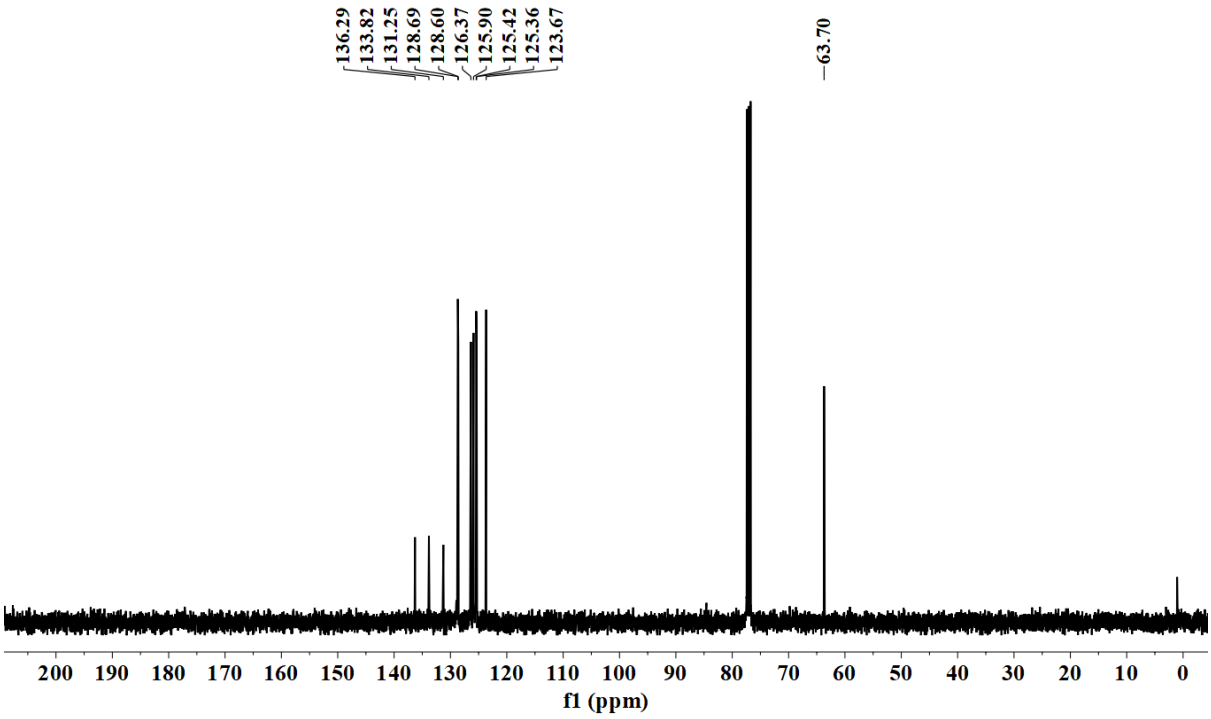


Fig. S117. $^{13}C\{^{1}H\}$ NMR spectrum of **5c** in $CDCl_3$ (101 MHz).

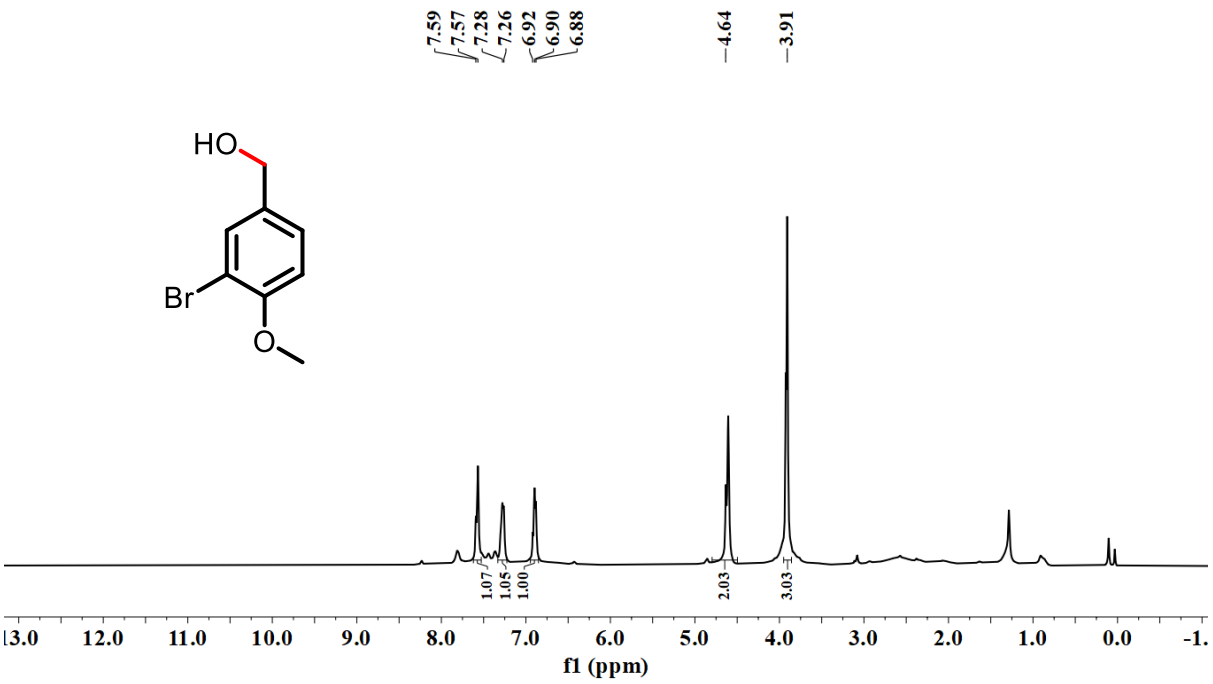


Fig. S118. ^{1}H NMR spectrum of **6c** in $CDCl_3$ (500 MHz).

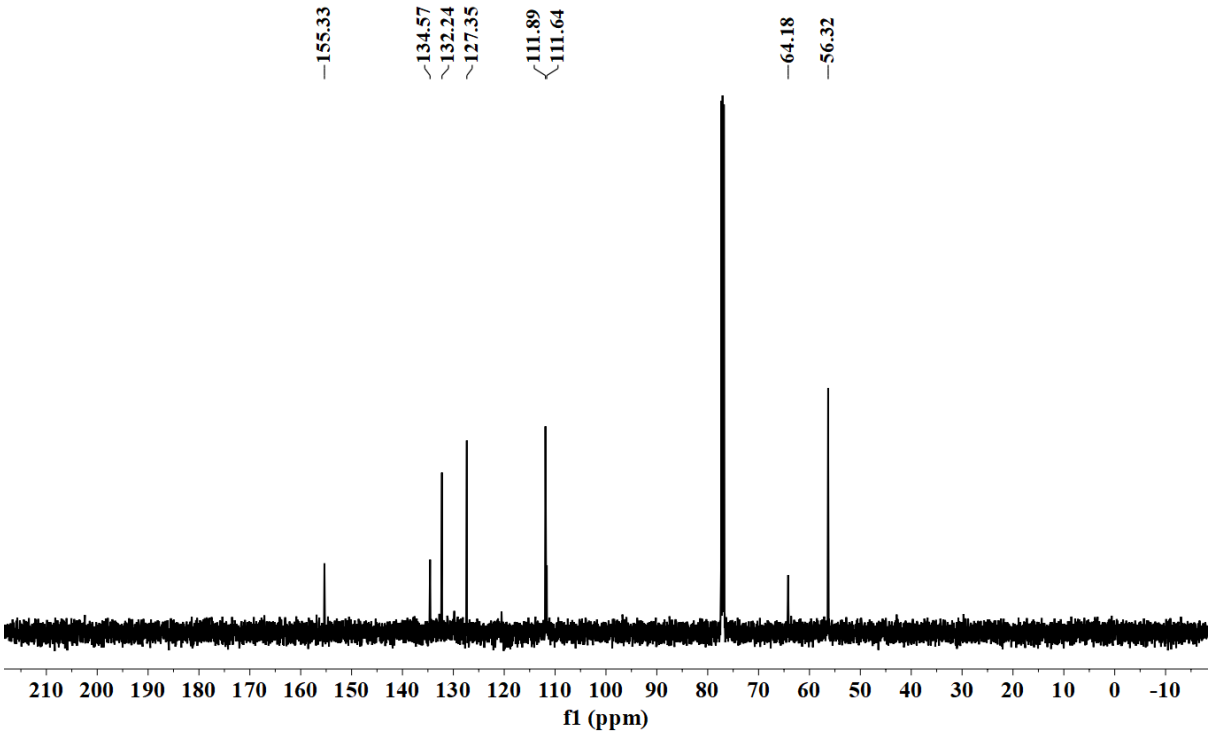


Fig. S119. $^{13}C\{^{1}H\}$ NMR spectrum of **6c** in $CDCl_3$ (126 MHz).

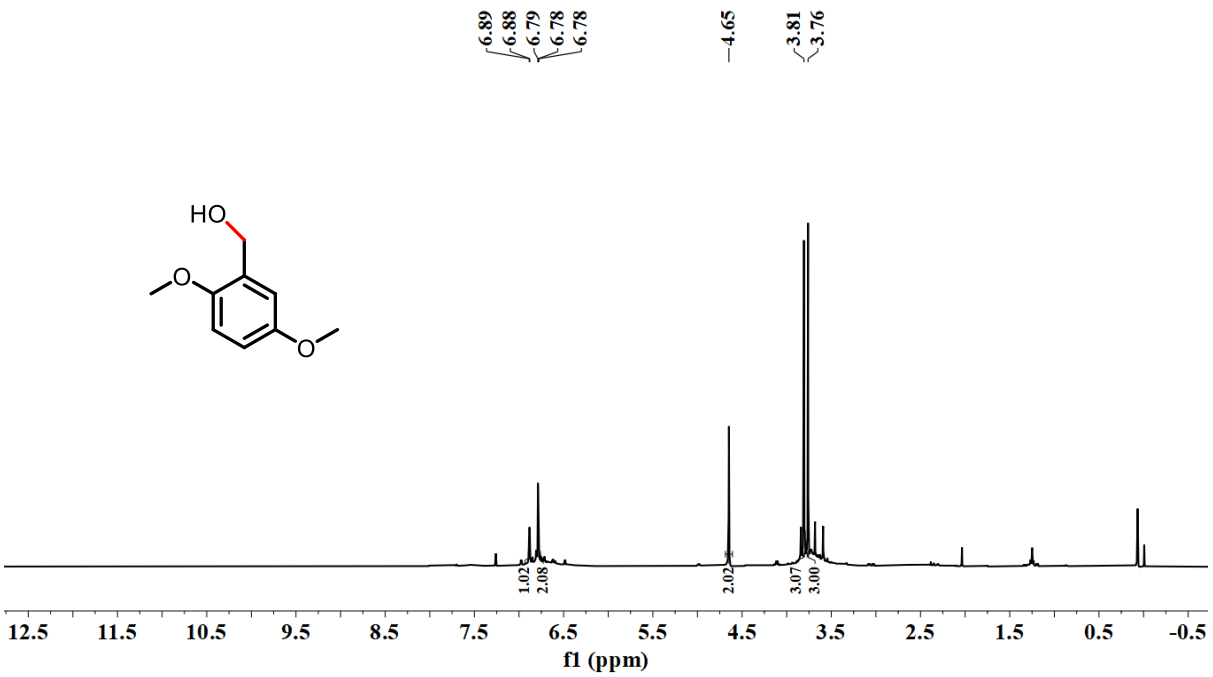


Fig. S120. ^{1}H NMR spectrum of **7c** in $CDCl_3$ (400 MHz).

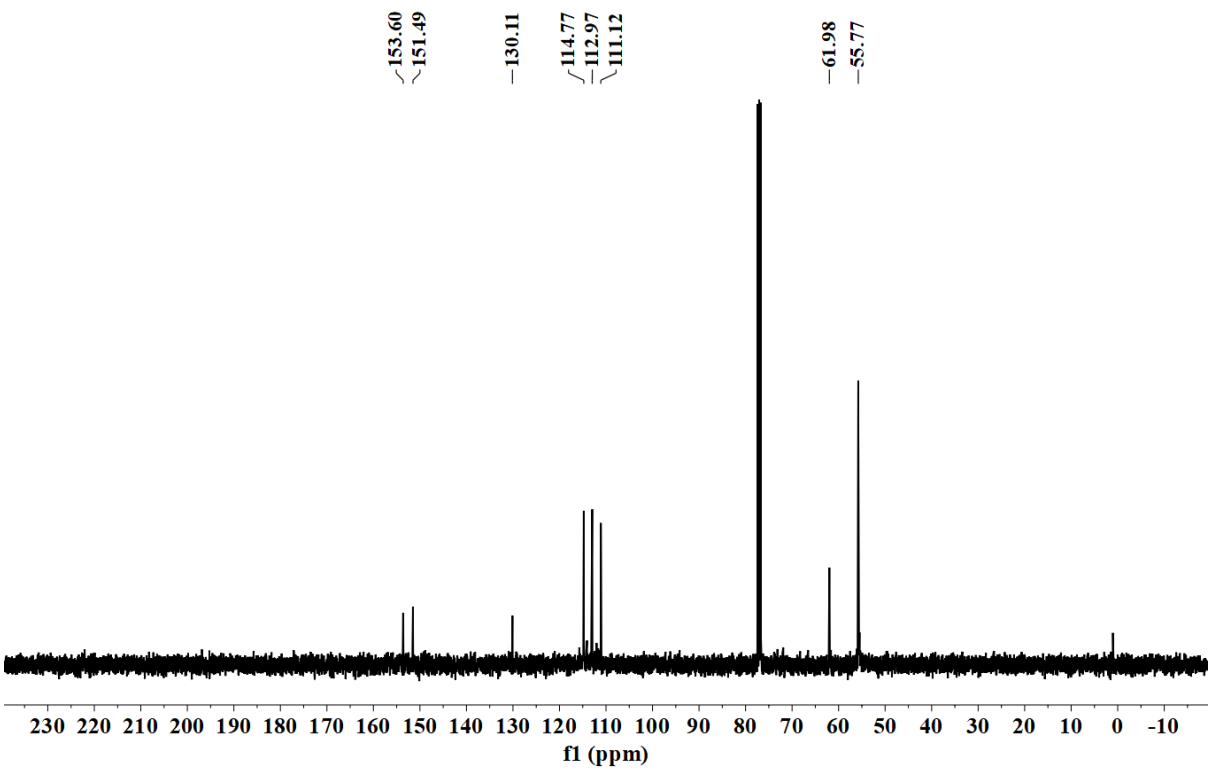


Fig. S121. $^{13}C\{^{1}H\}$ NMR spectrum of **7c** in $CDCl_3$ (101 MHz).

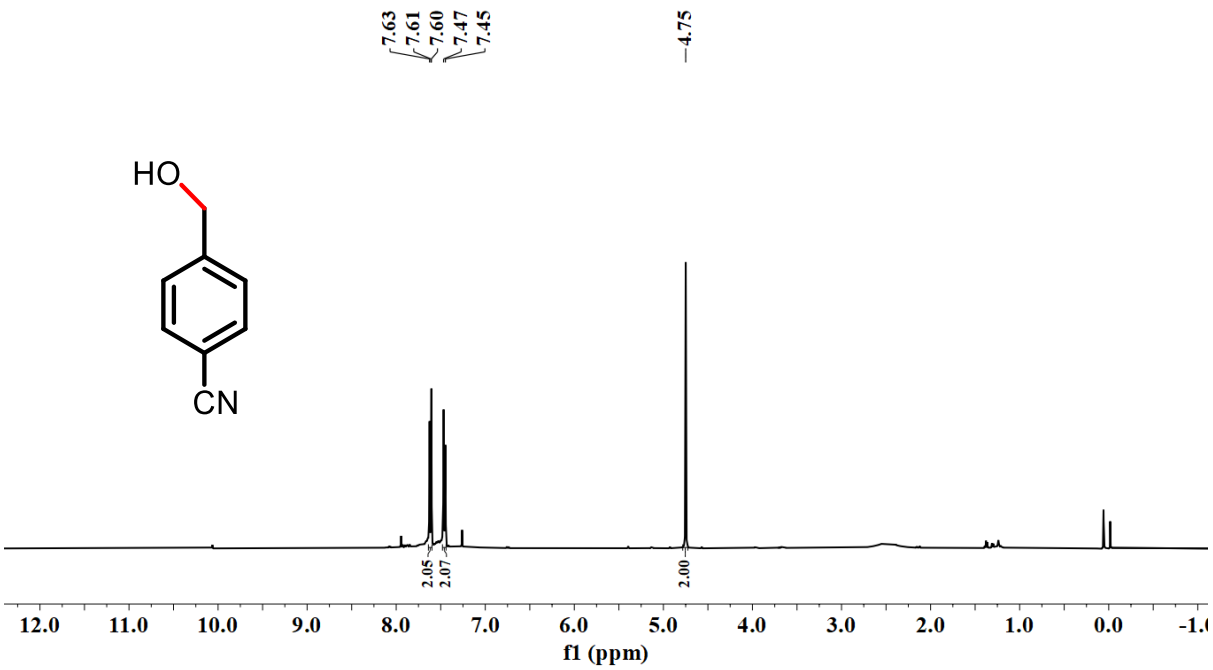


Fig. S122. ^{1}H NMR spectrum of **8c** in $CDCl_3$ (400 MHz).

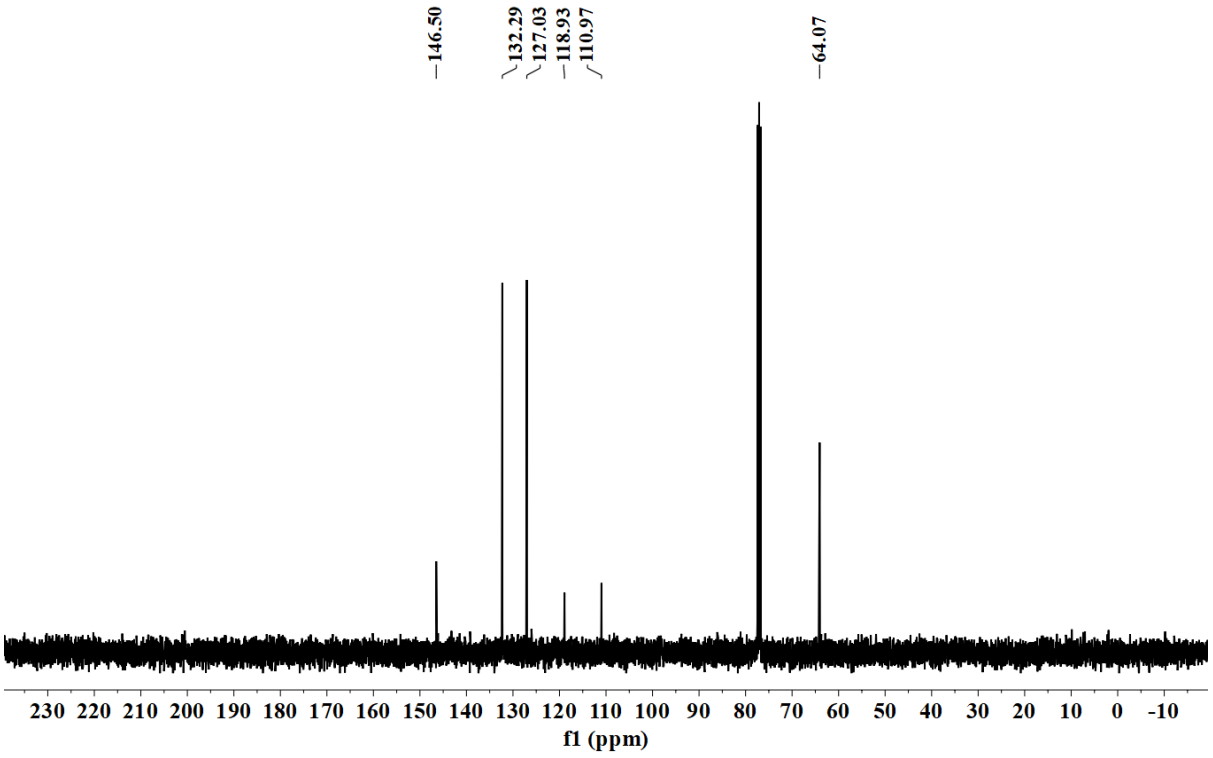


Fig. S123. $^{13}C\{^{1}H\}$ NMR spectrum of **8c** in $CDCl_3$ (101 MHz).

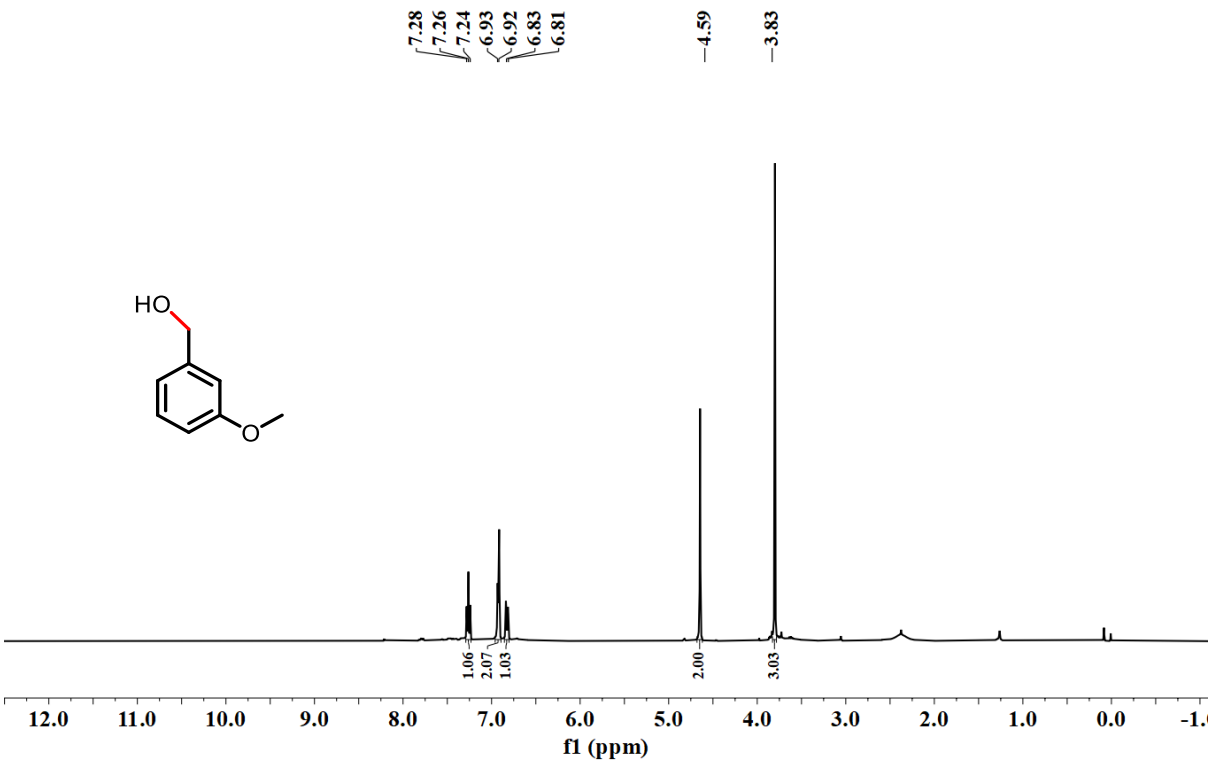


Fig. S124. ^{1}H NMR spectrum of **9c** in $CDCl_3$ (400 MHz).

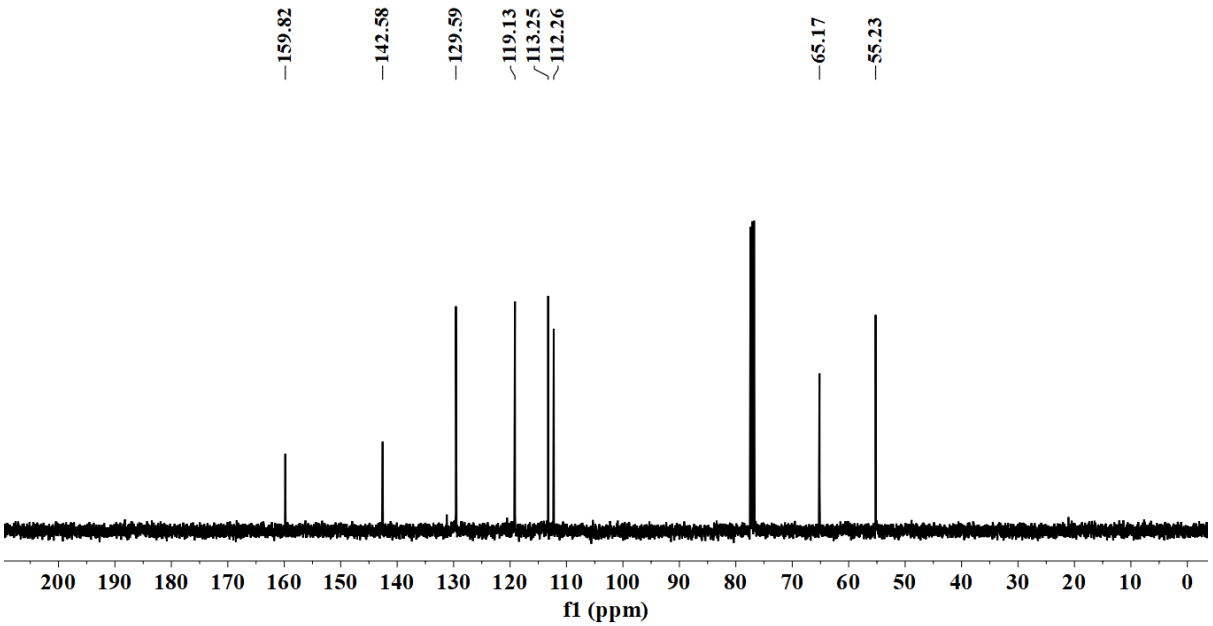


Fig. S125. $^{13}C\{^{1}H\}$ NMR spectrum of **9c** in $CDCl_3$ (101 MHz).

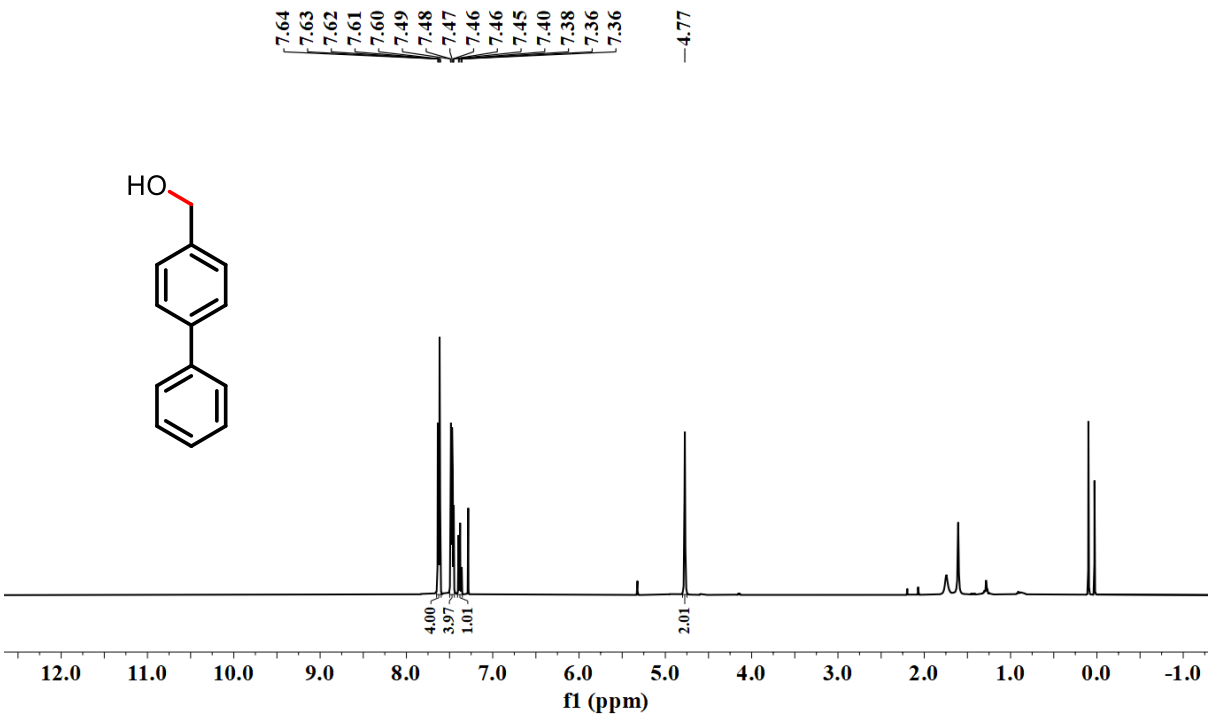


Fig. S126. ^{1}H NMR spectrum of **10c** in $CDCl_3$ (400 MHz).

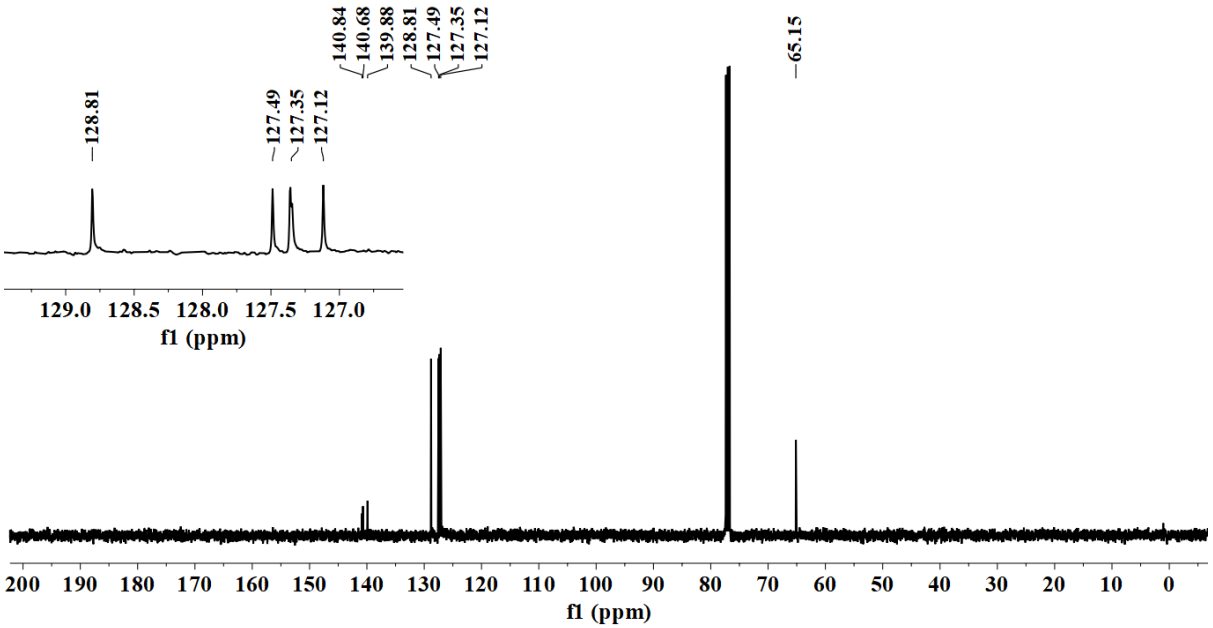


Fig. S127. $^{13}C\{^{1}H\}$ NMR spectrum of **10c** in $CDCl_3$ (101 MHz).

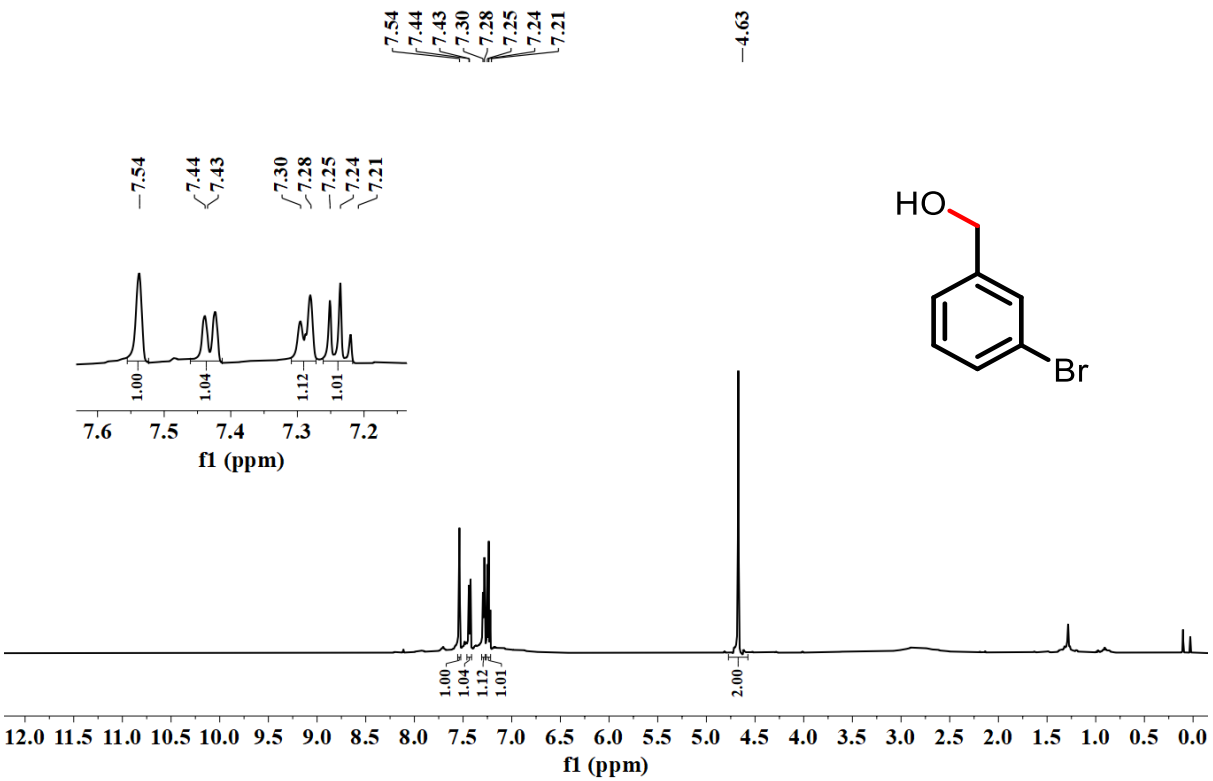


Fig. S128. ^{1}H NMR spectrum of **11c** in $CDCl_3$ (500 MHz).

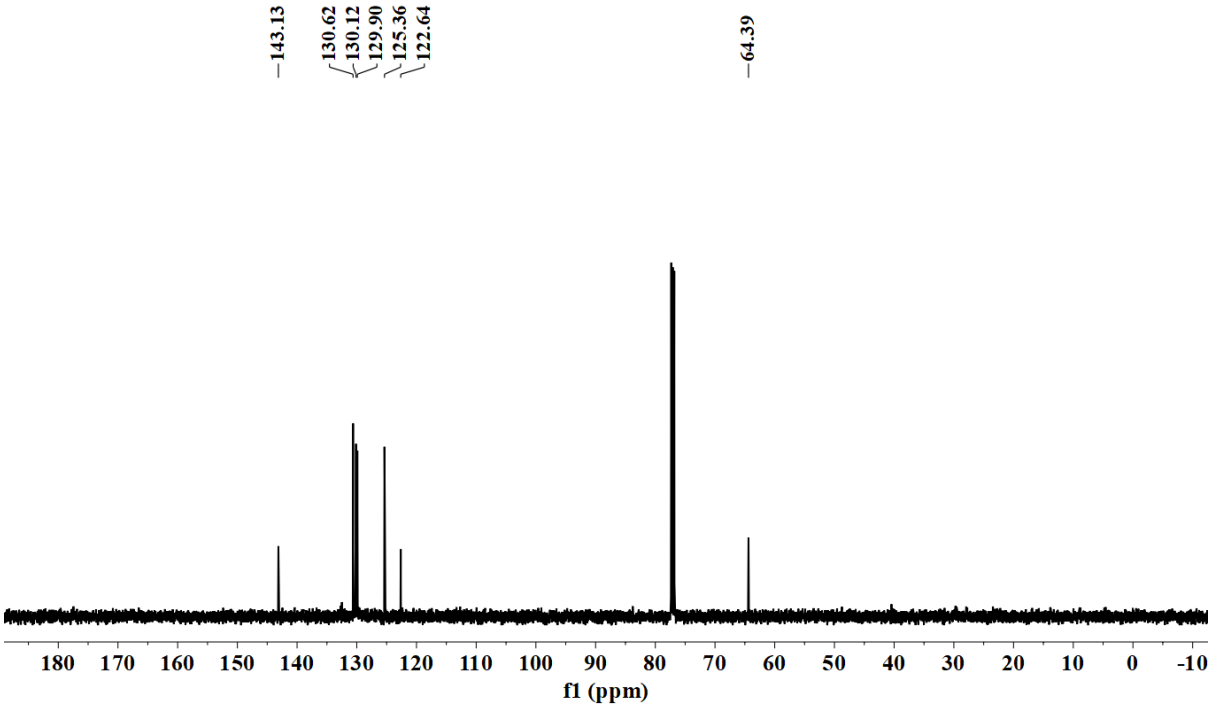


Fig. S129. $^{13}C\{^{1}H\}$ NMR spectrum of **11c** in $CDCl_3$ (126 MHz).

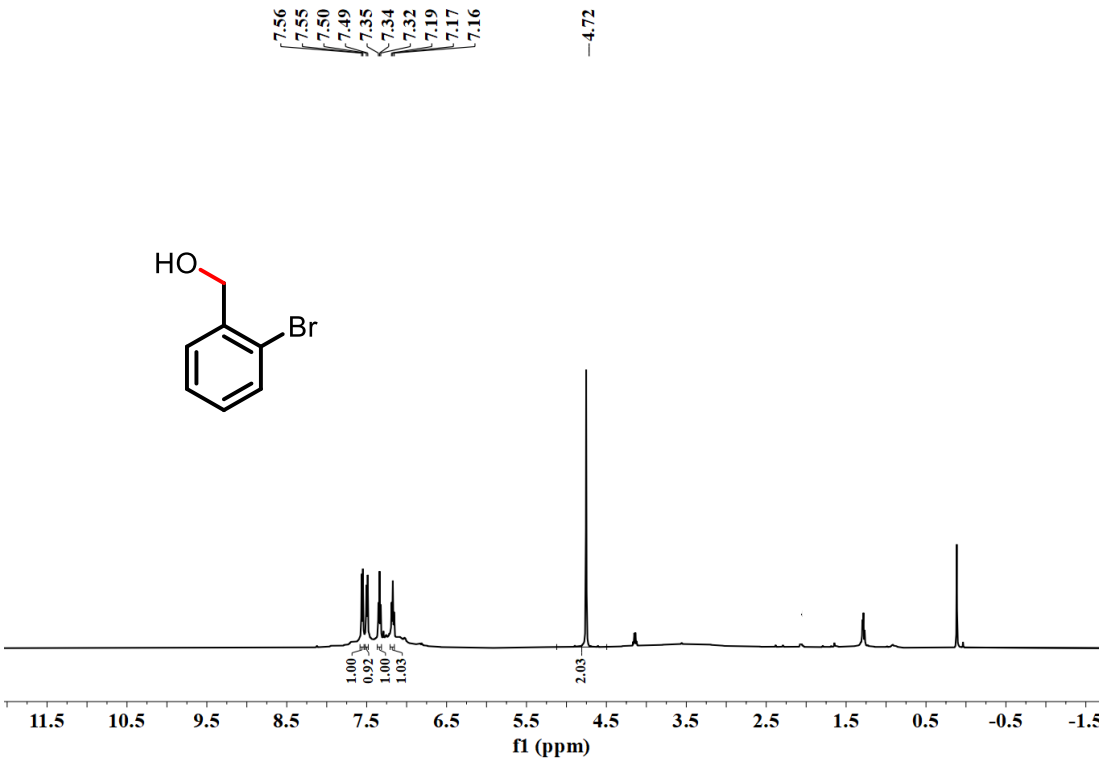


Fig. S130. ^{1}H NMR spectrum of **12c** in $CDCl_3$ (500 MHz).

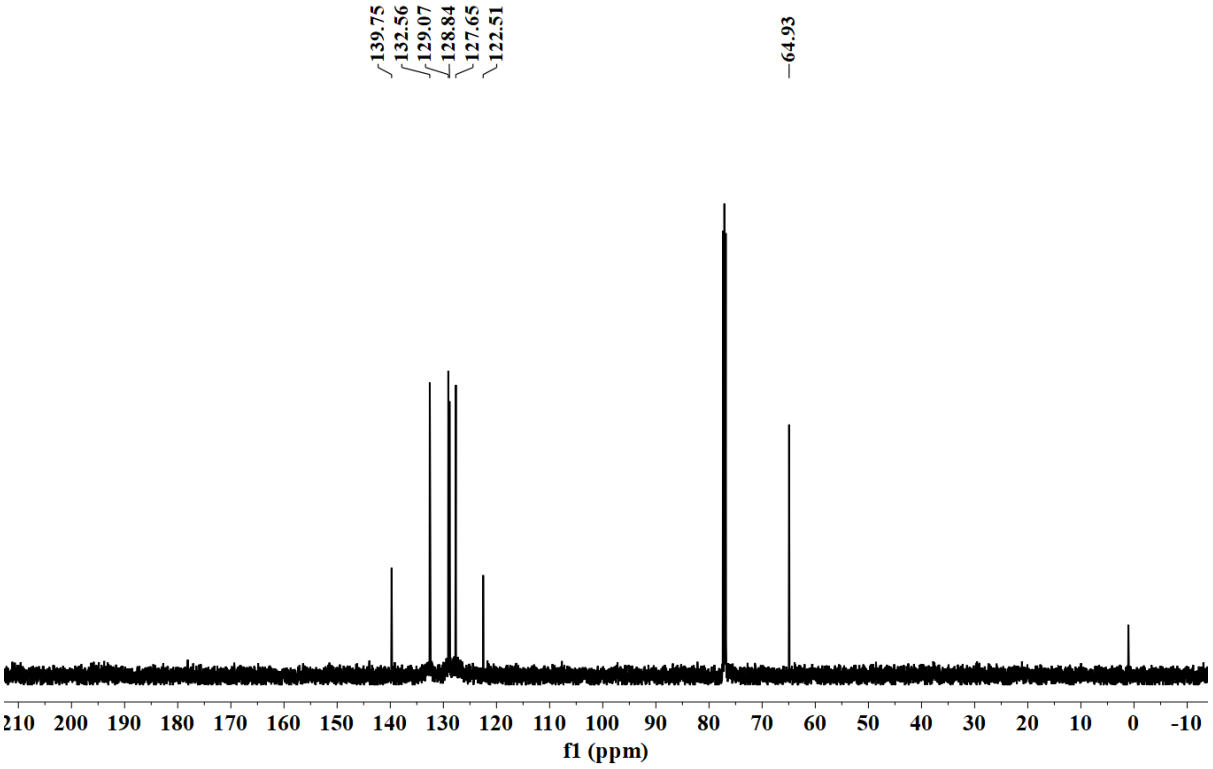


Fig. S131. $^{13}C\{^{1}H\}$ NMR spectrum of **12c** in $CDCl_3$ (126 MHz).

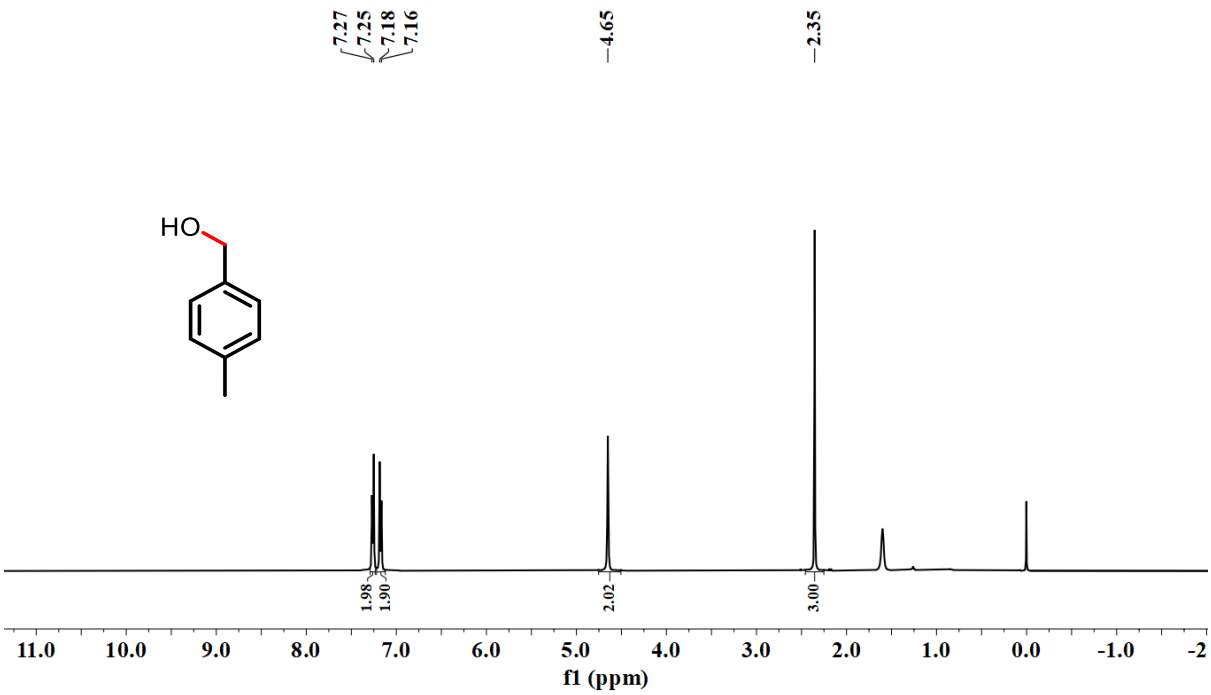


Fig. S132. ^{1}H NMR spectrum of **13c** in $CDCl_3$ (400 MHz).

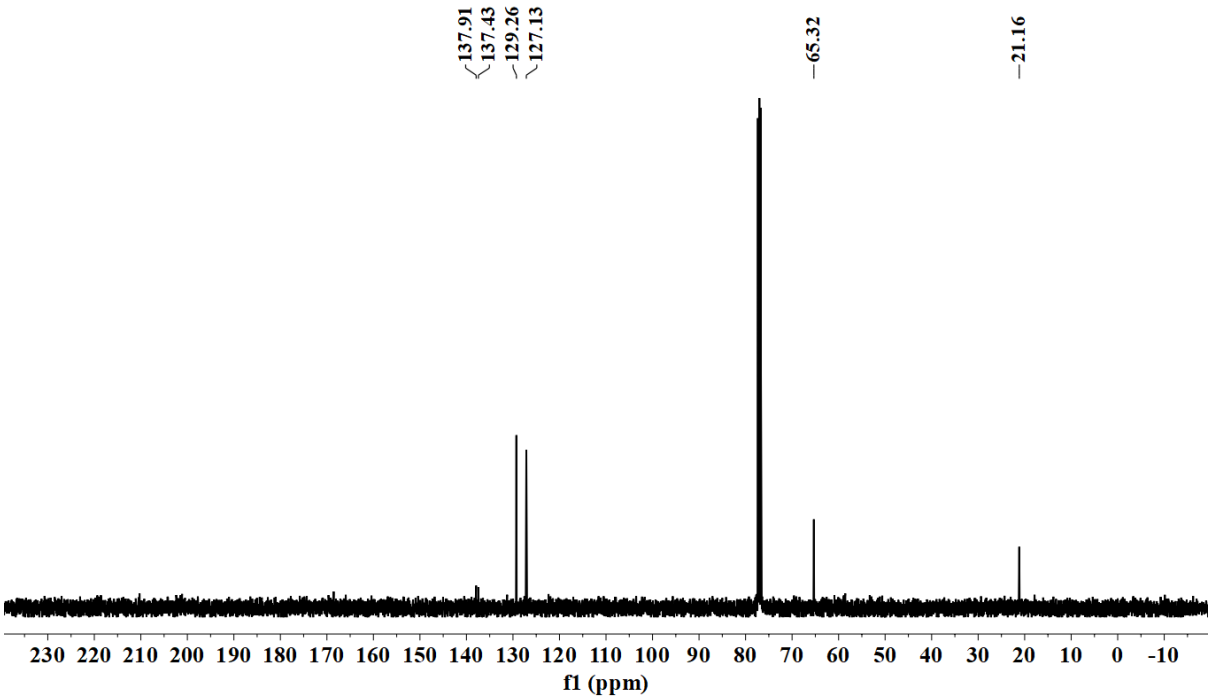


Fig. S133. $^{13}C\{^{1}H\}$ NMR spectrum of **13c** in $CDCl_3$ (101 MHz).

References:

1. Z. Li, C. Brouwer and C. He, *Chem. Rev.*, 2008, **108**, 3239-3265.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
3. G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.
4. C. Zhang, B. Hu, D. Chen and H. Xia, *Organometallics*, 2019, **38**, 3218-3226.
5. S. Nandi, I. Borthakur, K. Ganguli and S. Kundu, *Organometallics*, 2023, **42**, 1793-1802.
6. A. Maji, A. Singh, N. Singh and K. Ghosh, *ChemCatChem* 2020, **12**, 3108-3125.
7. K. Patra, A. Bhattacherya, C. Li, J. K. Bera and H. S. Soo, *ACS Catal.*, 2022, **12**, 15168-15180.
8. A. Maji, S. Gupta, M. Maji and S. Kundu, *J. Org. Chem.*, 2022, **87**, 8351-8367.
9. J. Das, K. Singh, M. Vellakkaran and D. Banerjee, *Org. Lett.*, 2018, **20**, 5587-5591.
10. D. Bhattacharyya, P. Adhikari, K. Deori and A. Das, *Catal. Sci. Technol.*, 2022, **12**, 5695-5702.
11. P. K. Namdeo, S. Sheokand, B. S. Kote, L. Radhakrishna, H. S. Kunchur, P. Saini, S. Ramakrishnan and M. S. Balakrishna, *Dalton Trans.*, 2022, **51**, 6795-6808.
12. S. Yadav, P. Vijayan, S. Yadav and R. Gupta, *Dalton Trans.*, 2021, **50**, 3269-3279.
13. M. Segizbayev, Ö. Öztopçu, D. Hayrapetyan, D. Shakhman, K. A. Lyssenko and A. Y. Khalimon, *Dalton Trans.*, 2020, **49**, 11950-11957.