Supporting information

Catalytic utility of bimetallic (pincer) PNN based nickel complex in the synthesis of quinolines and α-alkylation of ketones

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Table of content

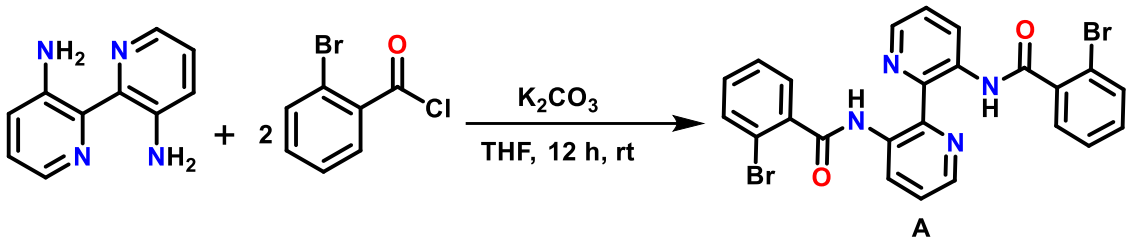
Crystal structure determination of compounds A,1, and 2.

Single crystals of all compounds 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. The structures were solved using Olex2 1.5[1] with the ShelXT[2] structure solution program using intrinsic phasing and refined with the SHELXL[3] refinement package using least-squares minimization. All nonhydrogen 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 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 S2. The disordered solvent present in the voids of structure **2** could not be identified as a known solvent; therefore, it was SQUEEZED using PLATON. This analysis revealed 850 electrons and a volume of 3762 Å^3. The provided chemical formula and other crystallographic data do not account for the unknown solvent molecules. Reflections with error/esd greater than 10 were excluded to improve the refinement of the data. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 2386216-2386218.

Table S1 Crystallographic information of compounds **A**, **1** and **2**.

	A	**1**	**2**
Formula	$C_{24}H_{16}N_4O_2Br_2$	$C_{48}H_{36}N_4O_2P_2$	$C_{48}H_{34}Cl_2N_4Ni_2O_2P_2$
Formula Weight	552.23	762.75	949.05
Crystal System	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	$P2_1/n$	Pbca
a, Å	7.4221(6)	9.147(2)	17.2416(6)
b, Å	9.7208(8)	13.350(3)	16.0245(4)
c, Å	15.3202(14)	16.012(4)	39.9762(10)
α, deg	75.512(3)	90	90
β, deg	84.689(3)	91.037(8)	90
γ, deg	82.270(3)	90	90
V, $Å^3$	1058.46(16)	1954.9(8)	11044.9(5)
Z	2	2	8
$\rho_{calc,\ m}$g cm^{-3}	1.733	1.296	1.141
μ (MoK\a), mm^{-1}	3.860	0.157	0.872
F (000)	548.0	796.0	3888.0
crystal size, mm	0.126 × 0.042 × 0.036	0.568 × 0.062 × 0.045	0.186 × 0.055 × 0.045
T (K)	150	150	111.15
2θ range, deg	4.356 to 67.452	3.972 to 49.996	3.616 to 49.996
Total no. reflns	69069	39433	96802
No.of indep reflns	69069	3434	9716
on F^2	1.036	1.126	1.041
R_1	0.0504	0.0541	0.0363
wR_2	0.1287	0.1341	0.0788

Synthesis of [2,2′-{C_5H_3N-3- N(H)C(O)-C_6H_4-Br-o}$_2$] (A)



Scheme S1 Synthesis of **A**.

[2,2'-bipyridine]-3,3'-diamine (0.05g, 2.684 mmol) and K_2CO_3 (1.113 g, 8.054 mmol) in THF were stirred under an inert atmosphere for 30 minutes. The solution of 2-bromobenzoylchloride (1.308 g, 5.906 mmol) in THF was added slowly into it and stirred for 12 hours at room temperature. After removing the solvent under vacuo, the residue was redissolved in 5 mL DMF and washed with 12 mL HCl (5% v/v) and 15 mL K_2CO_3 (10% w/v), respectively. The residue was recovered by filtration and washed with deionized water until pH 7.0 and dried under vacuo. Single crystals of **A** suitable for X-ray analysis were obtained by slow diffusion of petroleum ether into the dichloromethane solution of **A**. Yield 1.26 g (85%). Mp >275 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.10 (s, 2H), 9.41 – 9.31 (m, 2H), 8.19 (dd, J = 4.6, 1.6 Hz, 2H), 7.80 – 7.62 (m, 4H), 7.51 – 7.32 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 142.0, 140.8, 138.5, 136.7, 134.0, 131.6, 130.0, 129.2, 127.6, 124.2, 119.8. HRMS (ESI) Calcd for $C_{24}H_{17}N_4O_2Br_2$ ($[M+H]^+$): 552.9703; found: 552.9703. FT-IR (KBr disk, cm^{-1}): 3055 m (ν_{NH}) 2871 m, 1668 s (ν_{CO}), 1567 s, 1509 s, 1437 s, 1304 s. Anal. Calcd for $C_{24}H_{16}N_4O_2Br_2$: C, 52.20; H, 2.92; N, 10.15. Found: C, 51.98; H, 2.72; N, 10.01.

The representative cyclic voltammogram along with the differential pulse voltammogram of compound **1** and **2** are given in Fig. S1. The voltammogram of compound **1** showed two irreversible oxidation potential and one irreversible reduction potential at 0.89 V, 1.25 V, and -1.89 V respectively, whereas compound **2** showed one irreversible oxidation potential and irreversible reduction potential at 1.49 V and -1.28 V, respectively. This lower oxidation potential means that compound **1** is more readily oxidized, which supports the stability and formation of metal complex **2**.

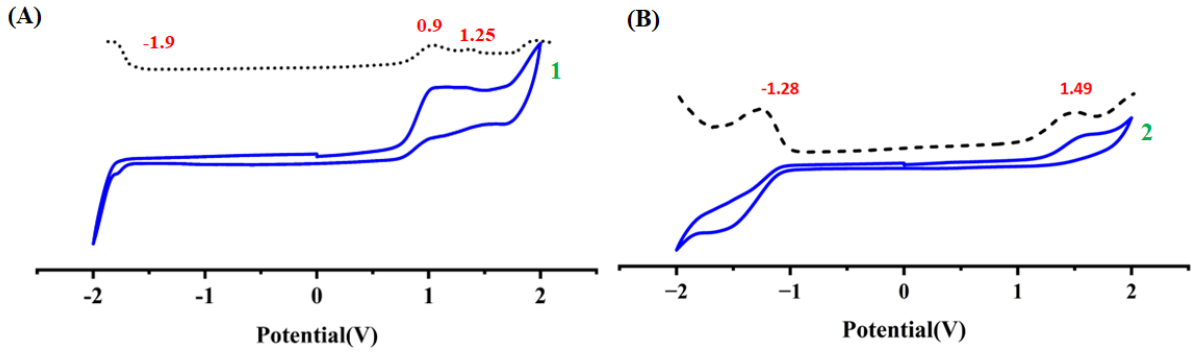


Fig. S1 Cyclic voltammogram of (A) compound **1** and (B) compound **2** recorded using polarographic convention in dichloromethane containing supporting electrolyte (0.1 M TBAP) and the analyte (10^{-3} M) at scan rates of 50 mVs^{-1} at 25 °C. Saturated calomel electrode (SCE), glassy carbon and platinum wire were used as the reference electrode, working electrode and auxiliary electrode, respectively. For plotting CV starting at 0 V, the polarographic convention has been followed.

NMR, HRMS and IR spectra

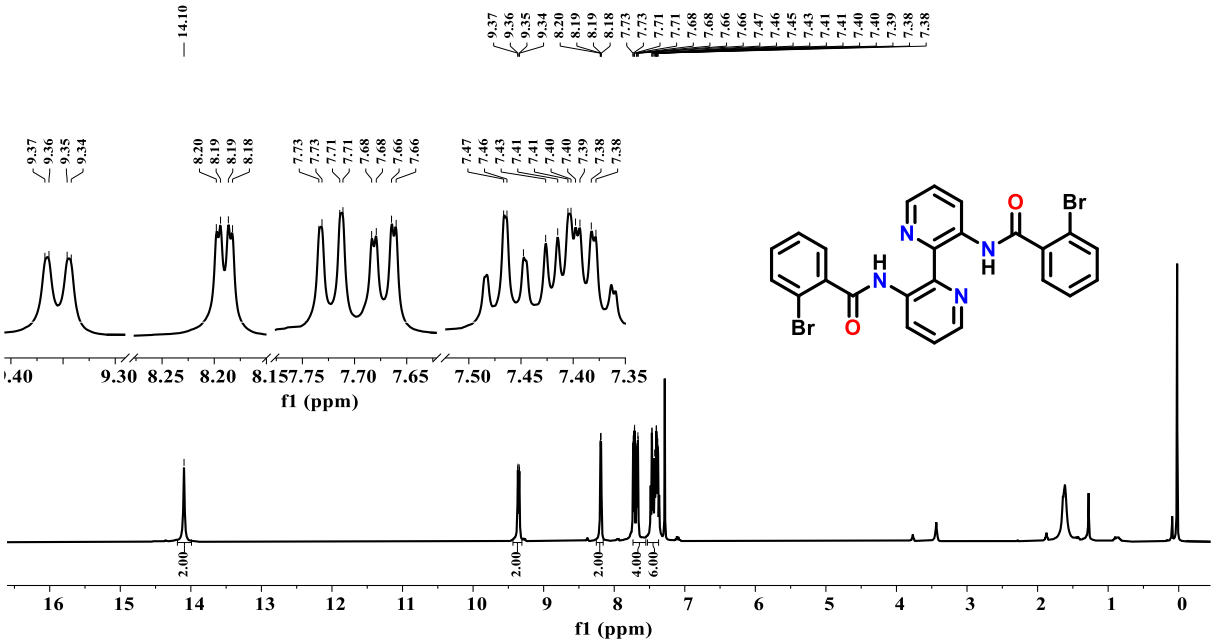


Fig. S2 ^{1}H NMR spectrum of **A** in $CDCl_3$ (400 MHz).

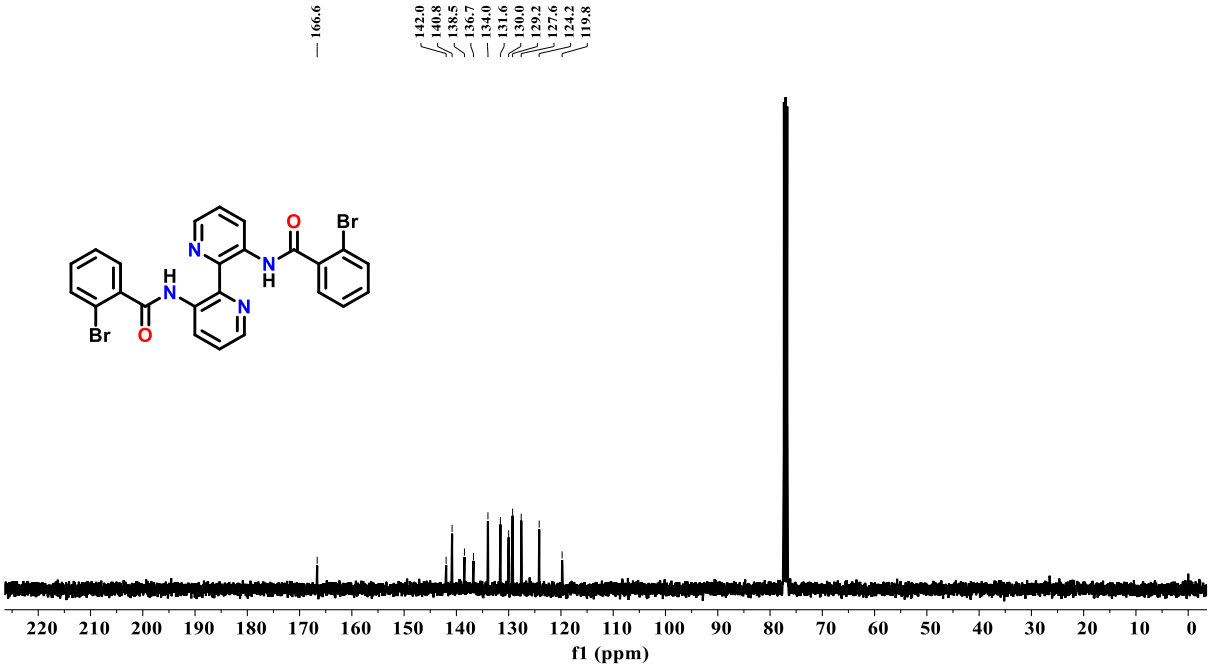


Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of **A** in $CDCl_3$ (101 MHz).

Sample Information

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Inj. Vol. (ul)	0.3	**IRM Status**	Success
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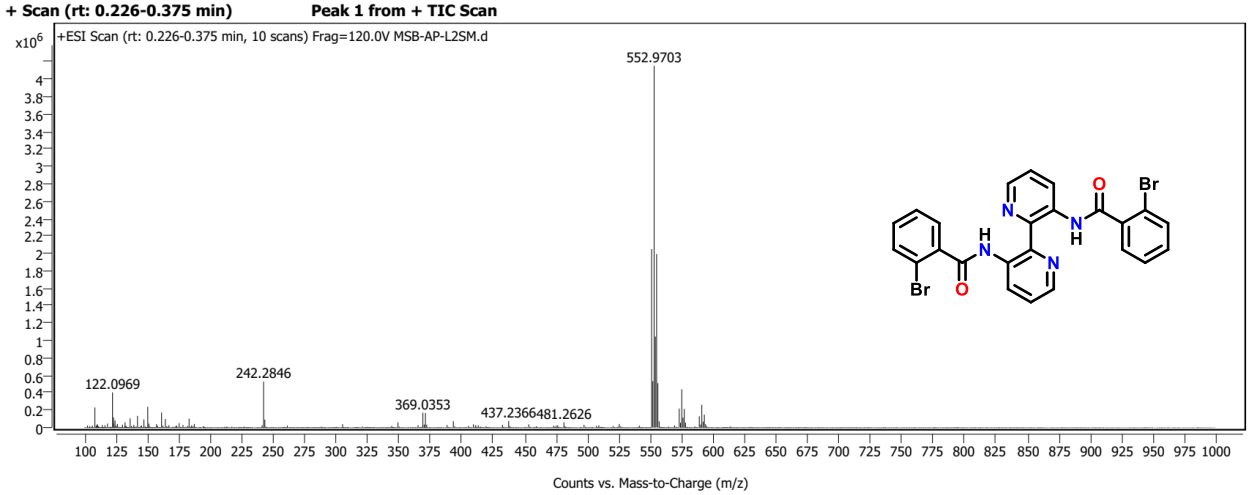
Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.226-0.375 min) **Peak 1 from + TIC Scan**

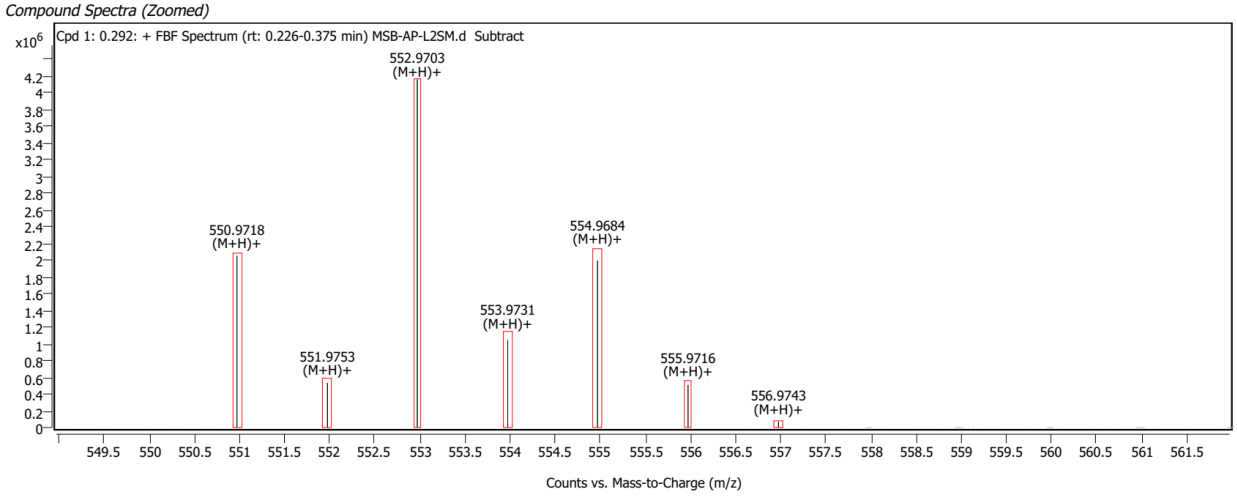


Compound Details

Cpd. 1: C24 H16 Br2 N4 O2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C24 H16 Br2 N4 O2	552.9703	552.970346376488	0.789629619816878	1.43578419231392	98.14

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Fig. S4 HRMS spectrum of **A**.

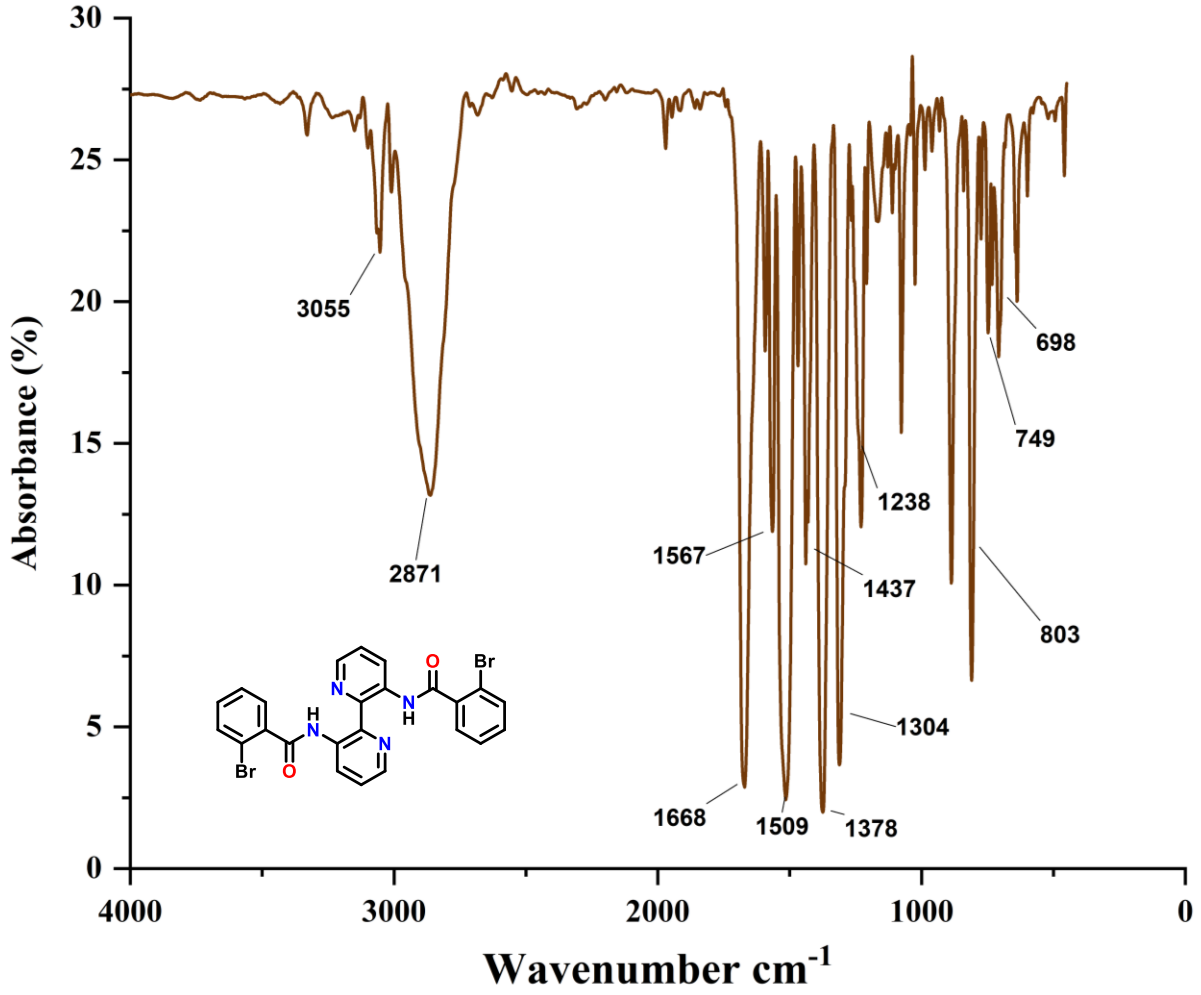


Fig. S5 FT-IR spectrum of **A**.

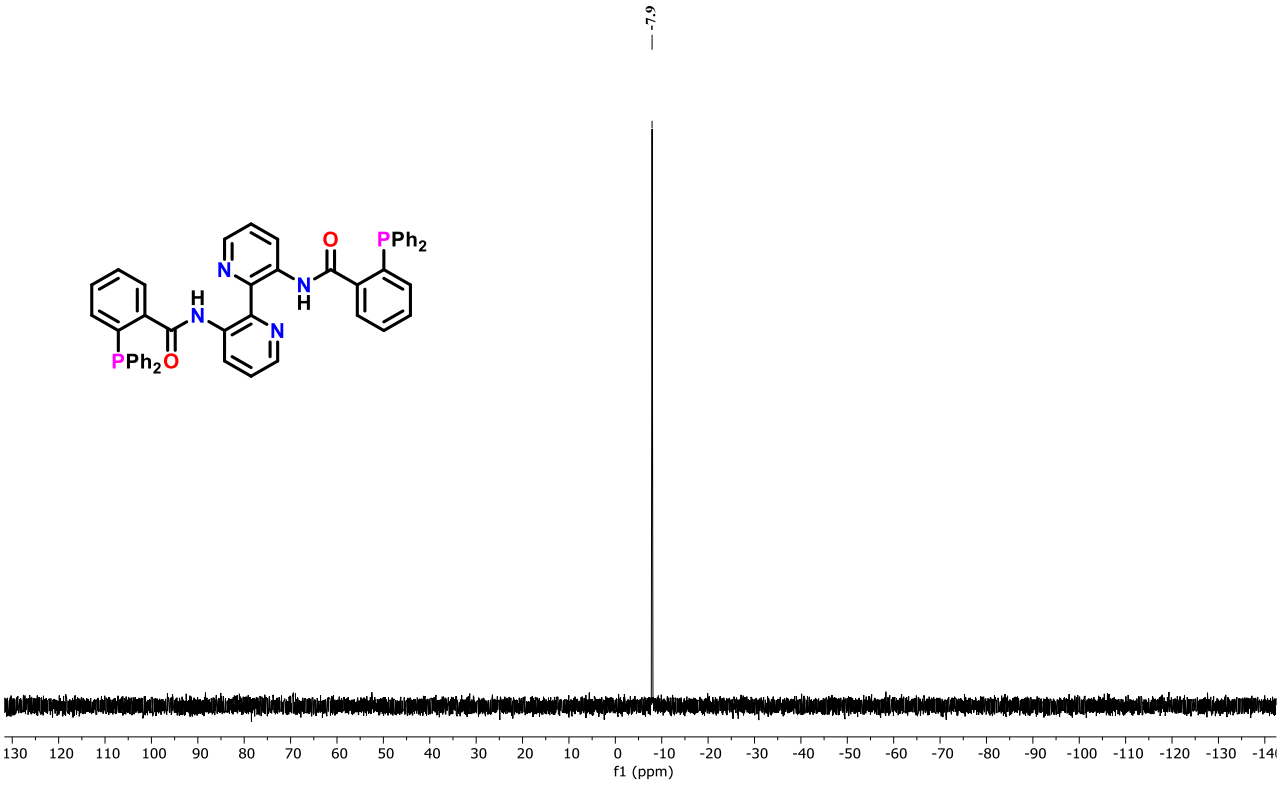


Fig. S6 $^{31}P\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (202 MHz).

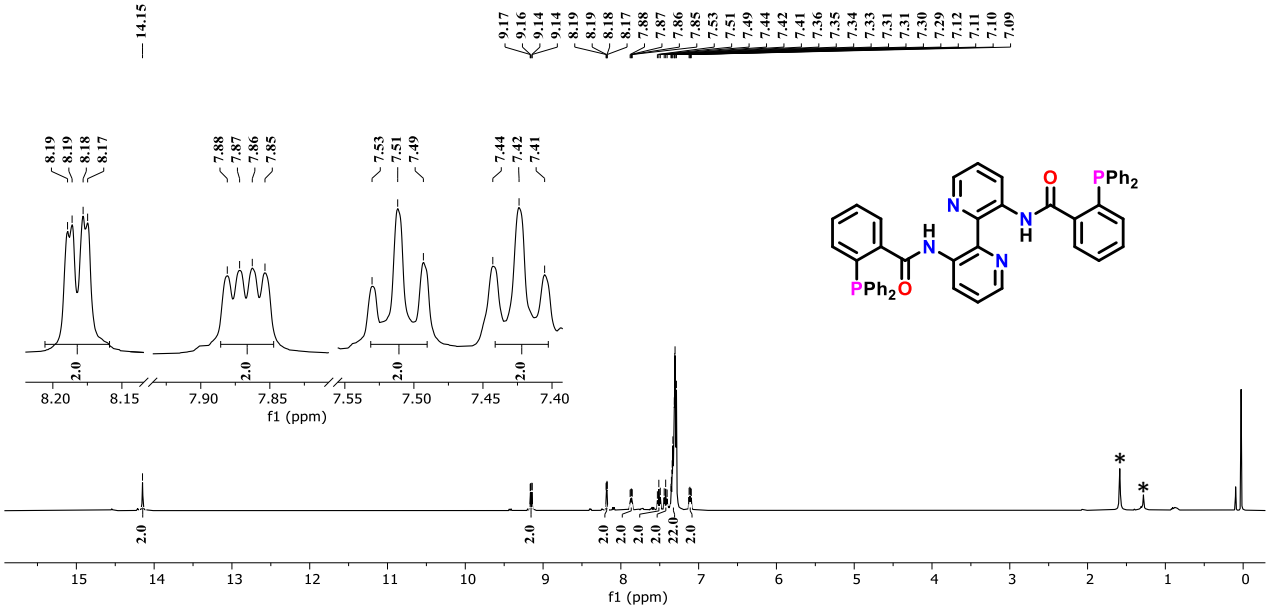


Fig. S7 ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz). Asterisk indicates the residual solvent peak.

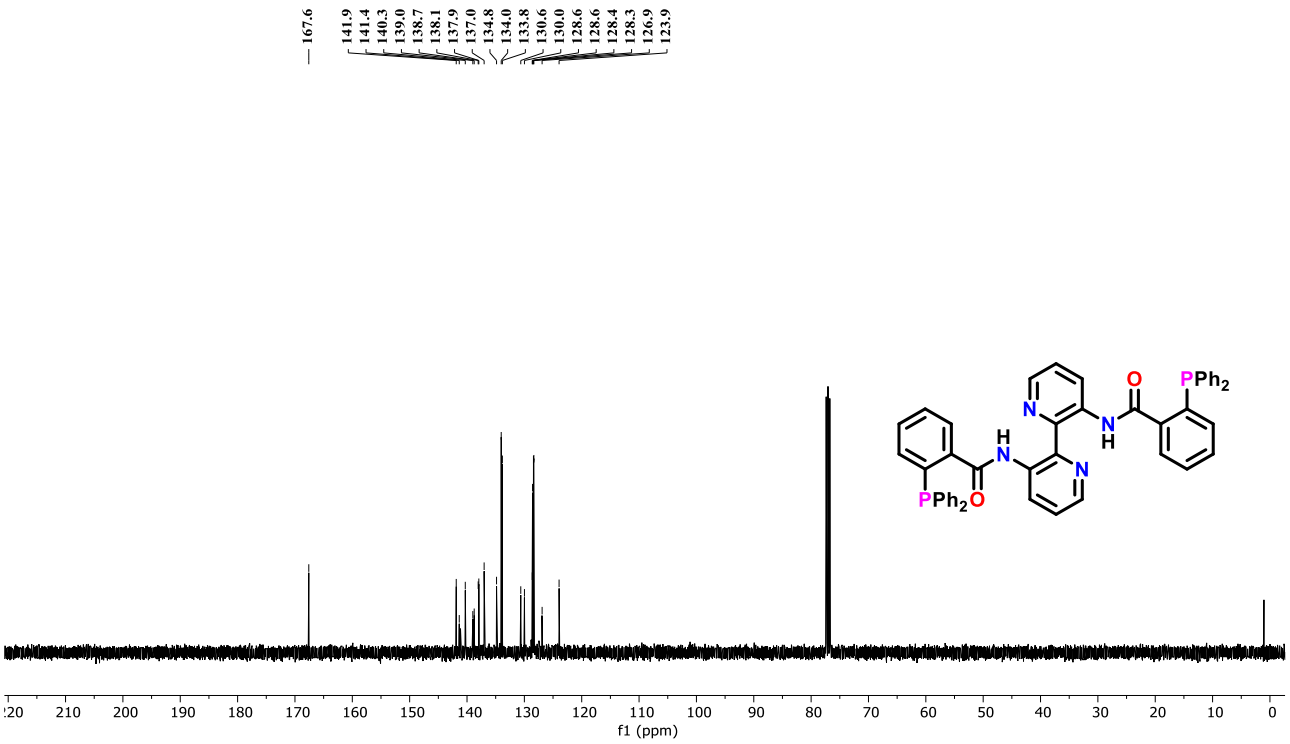


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (101 MHz).

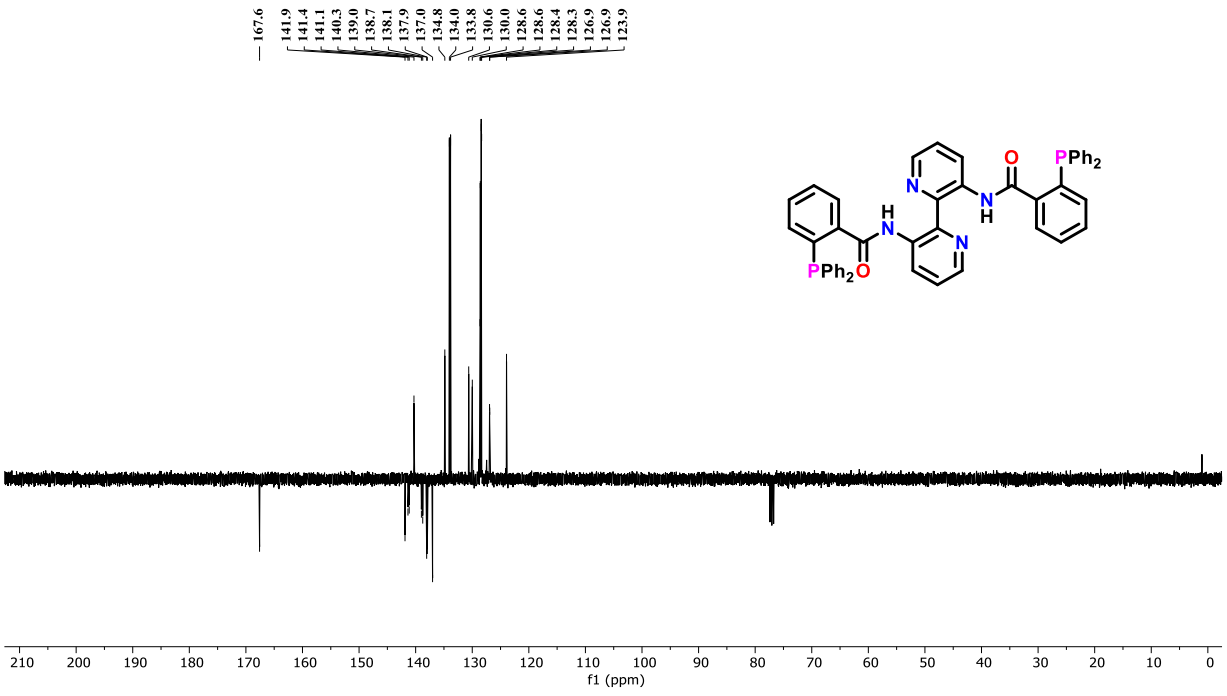


Fig. S9 APT NMR spectrum of **1** in $CDCl_3$ (101 MHz).

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Sample Information

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Inj. Vol. (ul)	0.3	**IRM Status**	Success
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Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

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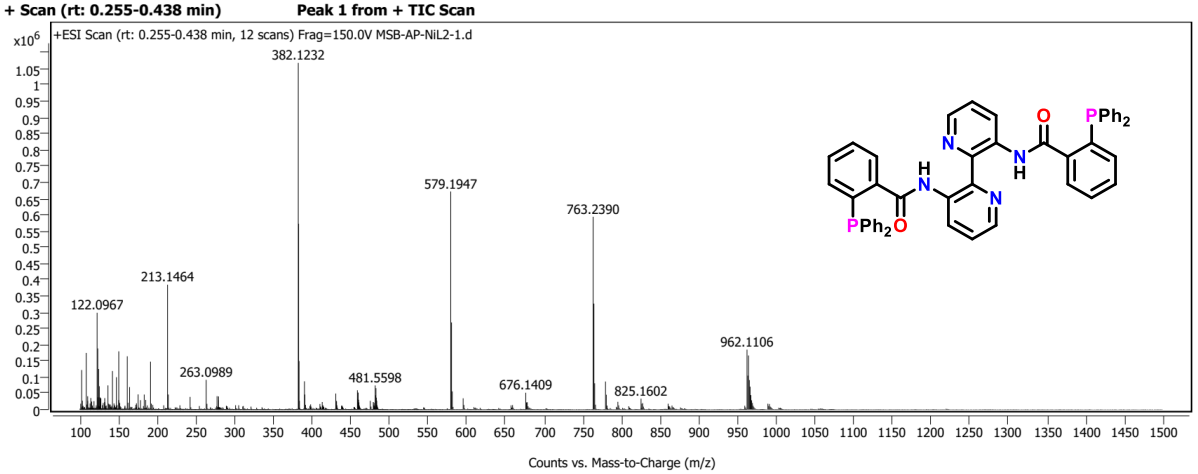
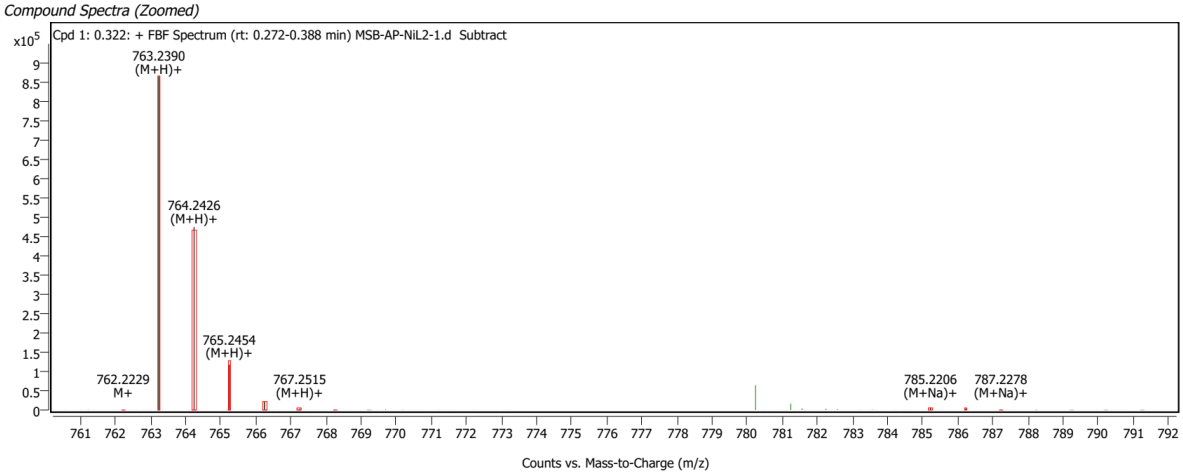


Compound Details

Cpd. 1: C48 H36 N4 O2 P2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C48 H36 N4 O2 P2	763.2390	763.238979384372	0.500192351410078	0.656221174584468	99.19

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Fig. S10 HRMS spectrum of **1**.

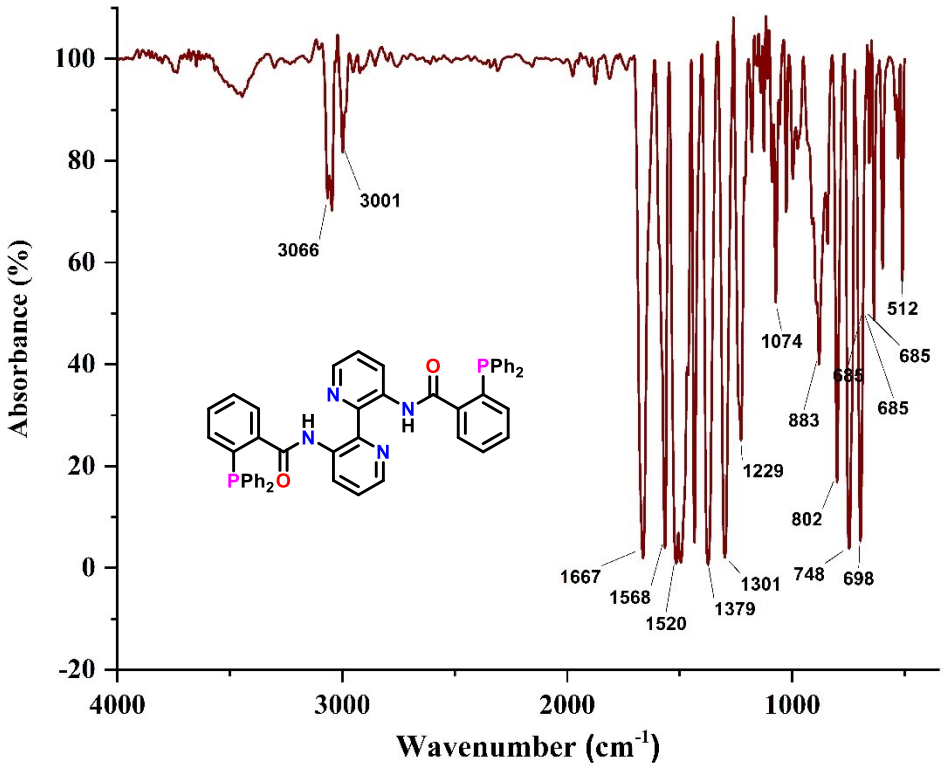


Fig. S11 FT-IR spectrum of **1**.

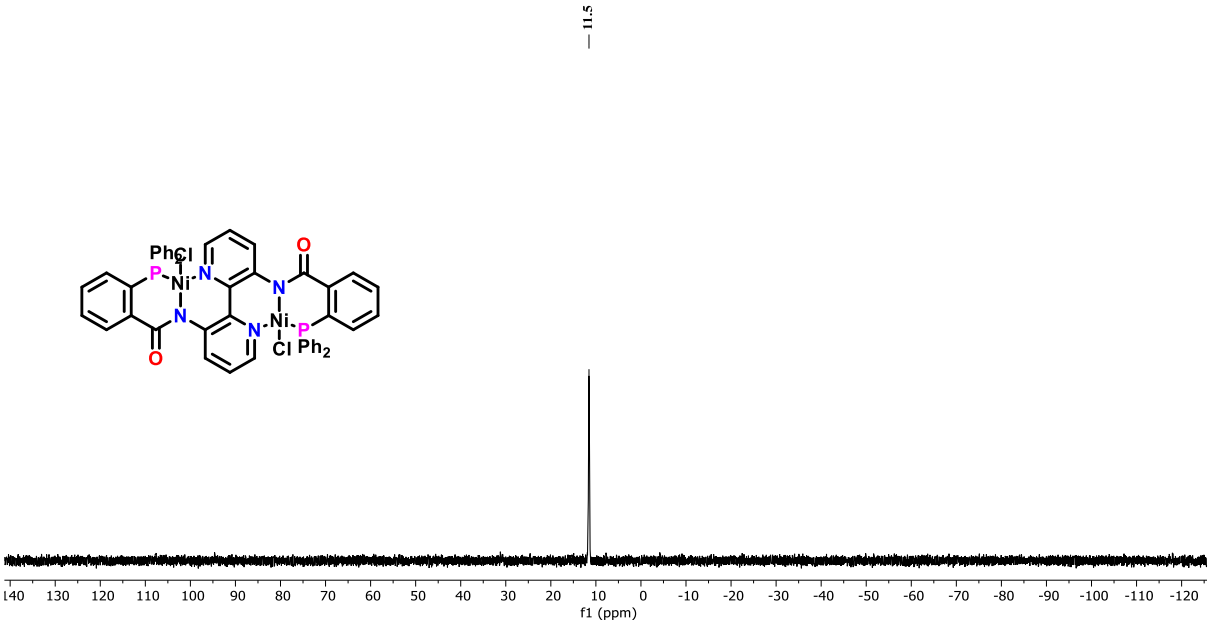


Fig. S12 $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (202 MHz).

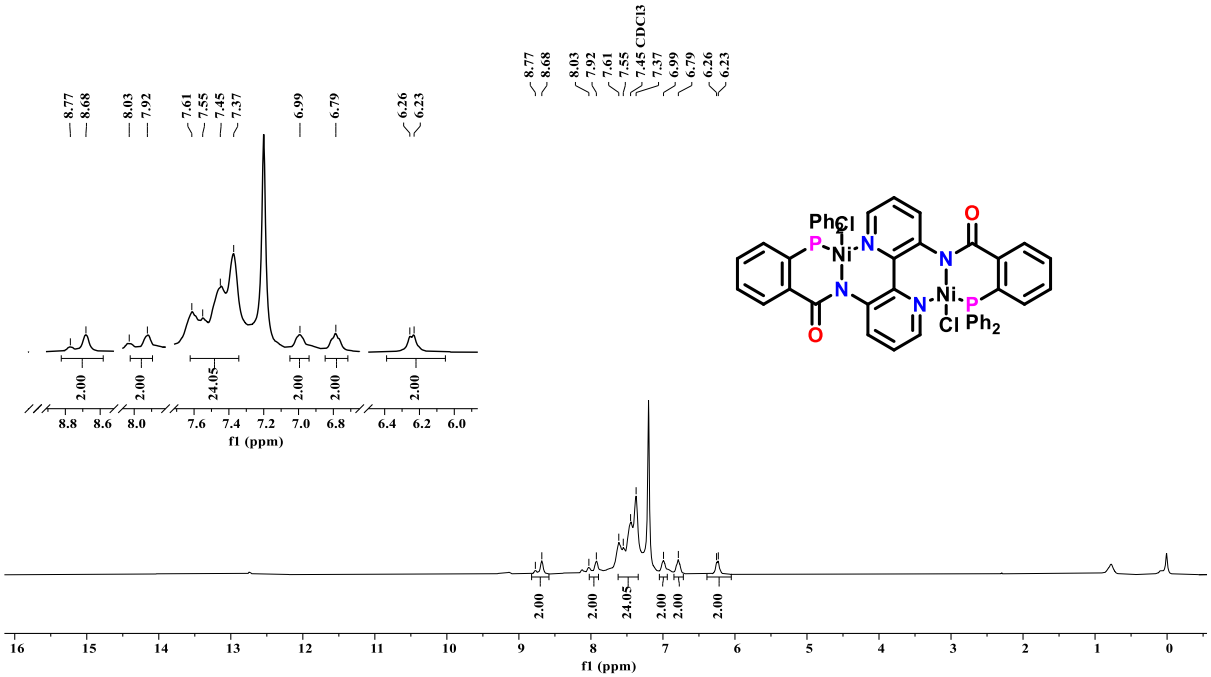


Fig. S13 ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz).

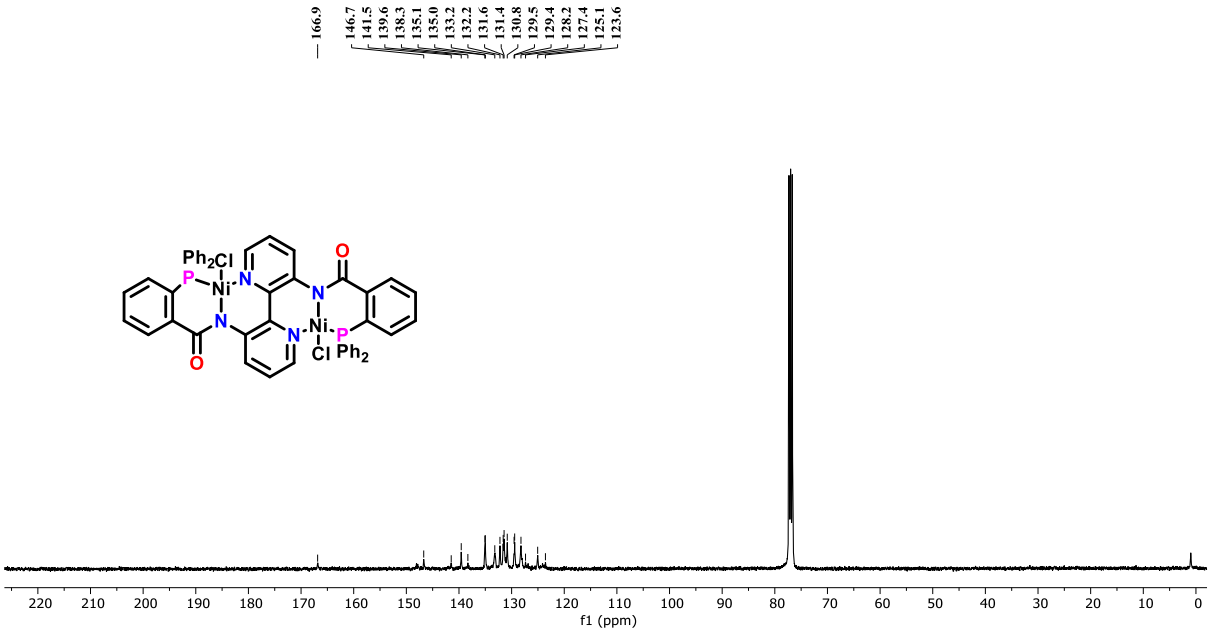


Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (101 MHz).

Department of Chemistry I.I.T. (B)

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Sample Information

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Inj. Vol. (ul)	0.5	**IRM Status**	Success
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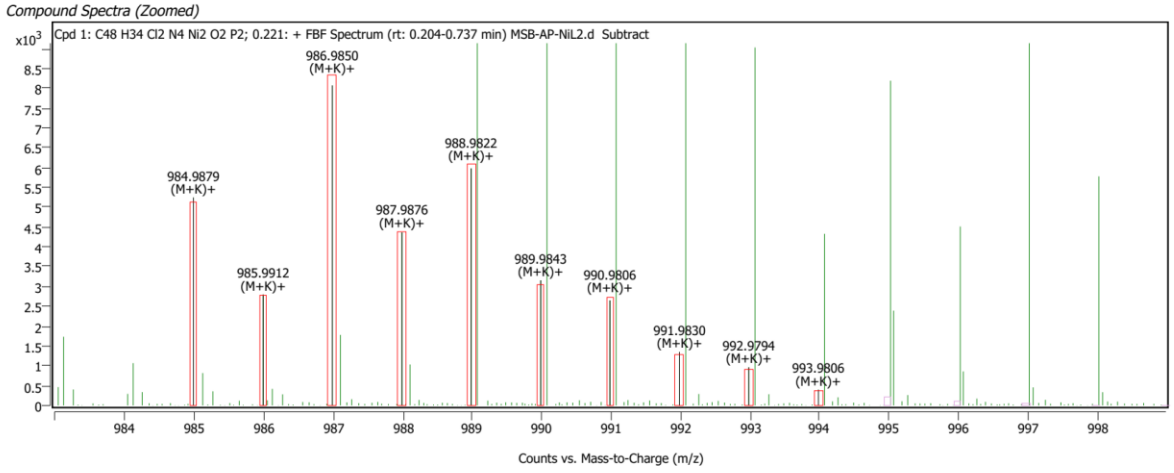
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C48 H34 Cl2 N4 Ni2 O2 P2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C48 H34 Cl2 N4 Ni2 O2 P2	986.9850	986.984957635703	0.702212846249495	0.742277967476326	99.08

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Fig. S15 HRMS spectrum of **2**.

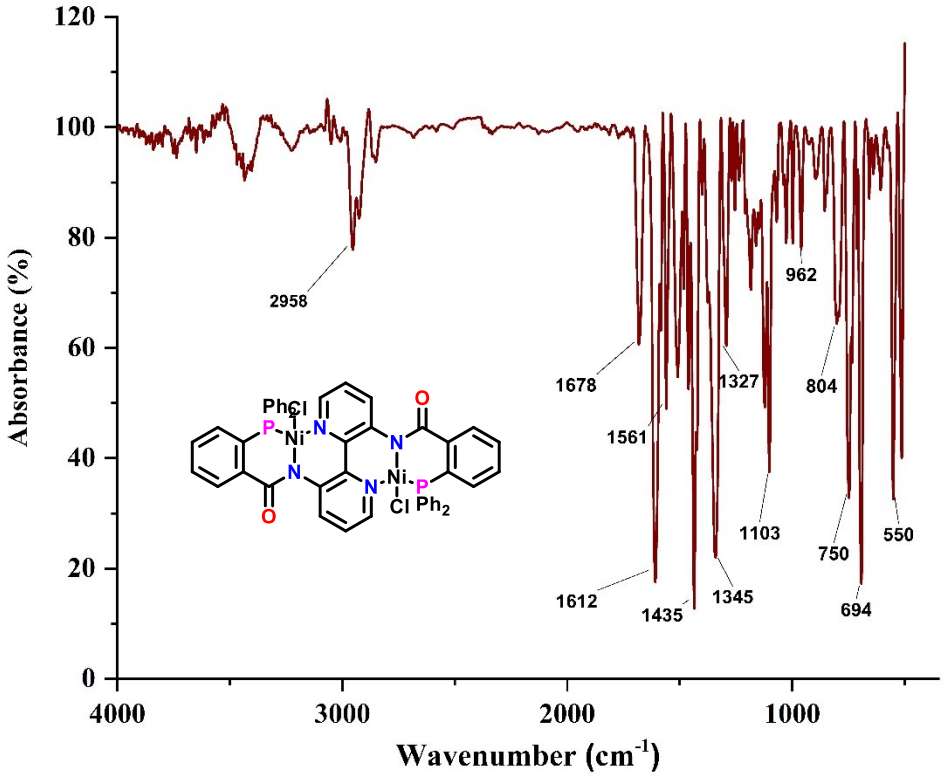


Fig. S16 FT-IR spectrum of **2**.

Controlled Experiments

Evolution of H_2 gas

In an oven-dried catalytic tube, the mixture of 2-aminobenzyl alcohol **2a** (3 mmol), catalyst-**2** (0.5 mol%), and K^{t}OBu (1 equiv) was taken in toluene (1 mL). The tube was sealed with a septum cap, evacuated, and filled with inert gas. The tube was then placed in an oil bath and heated at 110 °C. After 3.5 hours, gas was taken by syringe, and GC analysis was done, which showed peak of H_2 which indicates the evolution of H_2 gas during the reaction. After 6 h of reaction time GC-MS of the reaction mixture was taken which showed the formation of the 2-aminobenzaldehyde.

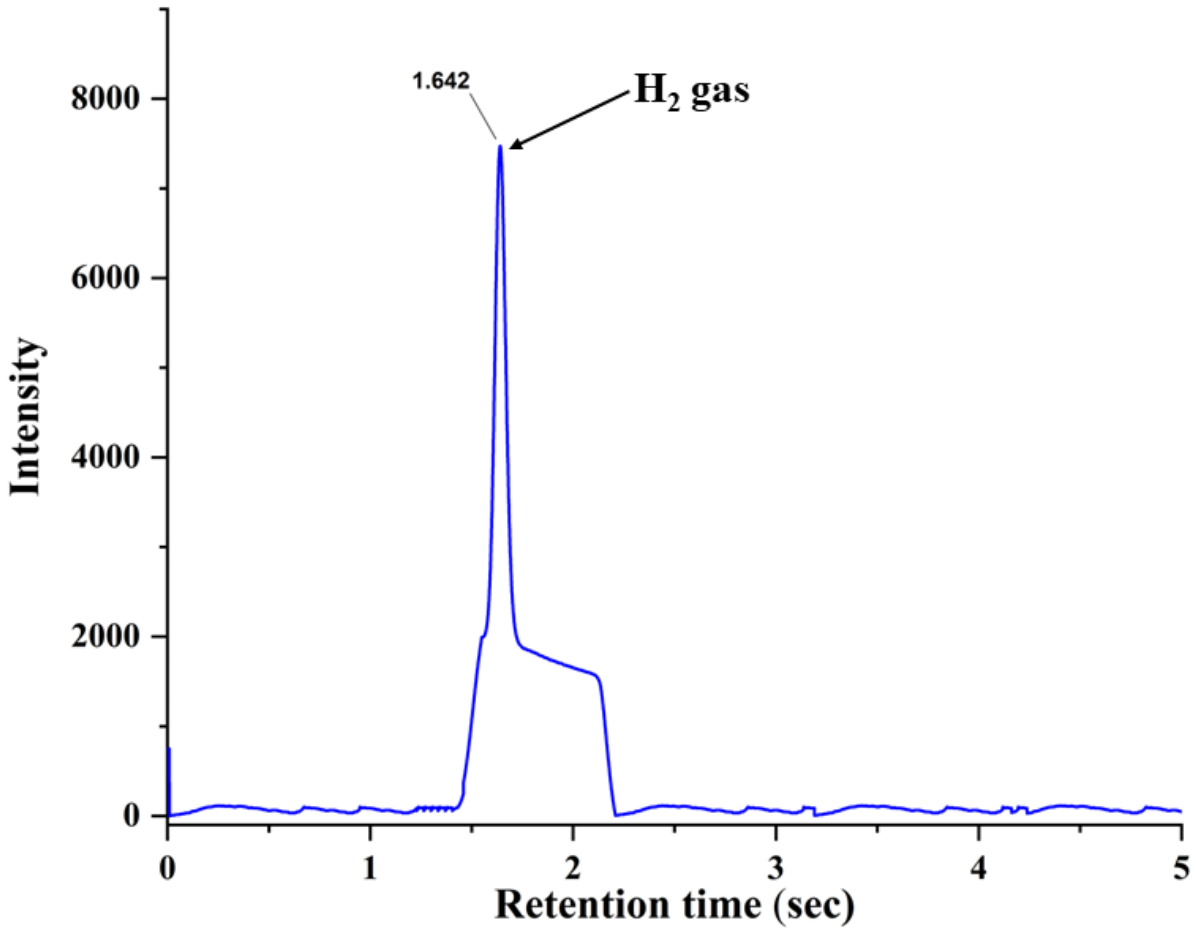
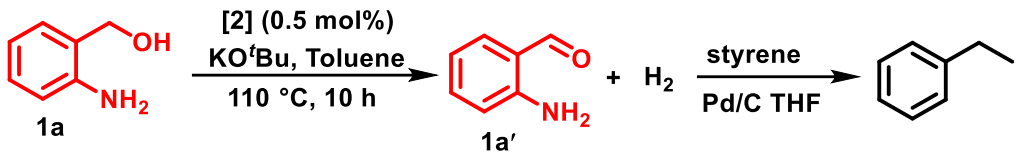


Fig. S17 Evidence of H_2 evolution from the independent reaction after 1.5 h.

Hydrogenation of styrene by evolved hydrogen:

In a H-shaped catalytic tube, mixture of 2-aminobenzyl alcohol (**1a**) (2.0 mmol), **2** (0.5 mol%), KO^{t}Bu (1.0 eqiuv), and toluene (2 mL) was taken in one catalytic tube and styrene (1.0 mmol), Pd/C (10 mol%) and THF with a magnetic stirrer were placed in second catalytic tube. The tubes were capped with a Teflon screw cap, evacuated, and filled with nitrogen. The first tube was then placed in an oil bath and heated at 110 °C for 10 h and put the second tube at room temperature. 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.

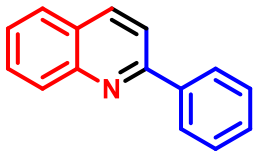
Detectin of Ni-H Intermediate:

Procedure A: In an oven dried catalytic tube mixture of 2-aminobenzyl alcohol (0.5 mmol) Acetophenone (0.55 mmol), **Ni2** (0.5 mol%) and KO^{t}Bu (1.0 equiv) was taken in toluene. The reaction mixture was degassed and purged with nitrogen gas and then subjected to heat at 110 °C for 2 hour. After that aliquot was taken and HRMS analysis was carried out, which showed a peak at 901.0193 corresponds to Nickel hydride [{PNNNiH}$_2$+Na]$^+$ species.

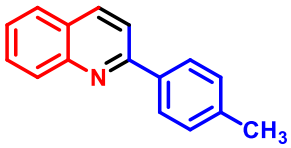
Procedure B: To an oven-dried J. Young NMR tube were added 2-aminobenzyl alcohol (0.2 mmol) [**2**] (0.5 mol%) and C_6D_6 (0.4 mL) in the glove-box. Heat the reaction mixture and take NMR readings at different time intervals; however, despite multiple attempts at various temperatures, no successful peak corresponding to the Ni-hydride was observed (Fig. 96 and 97).

Procedure C: Under an argon atmosphere, a suspension of compound **2** (30 mg, 0.03 mmol) and $LiAlH_4$ (48 mg, 0.63 mmol) in 15 mL of toluene was stirred at room temperature for 24 h. The resulting mixture was filtered through Celite pad, giving an orange solution. The solvent was removed under vacuum, and the residue was rinsed with chilled (0 °C) deoxygenated methanol(0.6 mL × 2). In the ^{1}H NMR spectrum, peaks corresponding to complex **2** were observed, and no peaks corresponding to Ni-hydride were detected.

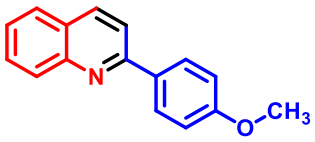
NMR spectral data of catalytic products



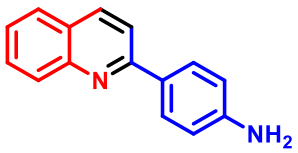
2-Phenylquinoline (3a)[4] Purified by column chromatography on silica gel using petroleum ether as eluent 98% (90 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.19 (m, 4H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.53 – 7.48 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.4, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0. HRMS (ESI) Calcd for $C_{15}H_{11}N$ ($[M+H]^+$): 206.0964; found: 206.0694.



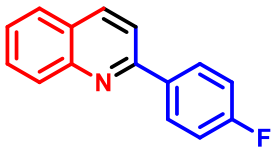
2-(4-Tolyl)quinoline (3b)[4] Purified by column chromatography on silica gel using petroleum ether and 2% ethyl acetate as eluents, 94 % (92 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (td, *J* = 9.0, 0.9 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.90 – 7.82 (m, 2H), 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 148.3, 139.4, 136.9, 136.6, 129.6, 129.5, 127.4, 127.1, 126.7, 126.5, 126.1, 118.9, 21.4. HRMS (ESI) Calcd for $C_{16}H_{13}N$ ($[M+H]^+$): 220.1120; found: 220.1121.



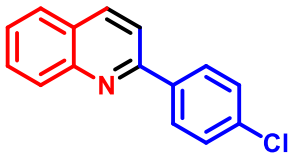
2-(4-Methoxyphenyl)quinoline (3c)[4] Purified by column chromatography on silica gel using petroleum ether and 5% ethyl acetate as eluents, 93 % (98 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 4H), 7.83 (dd, *J* = 10.0, 8.4 Hz, 2H), 7.74 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 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. HRMS (ESI) Calcd for $C_{16}H_{13}NO$ ($[M+H]^+$): 236.1069; found: 236.1069.



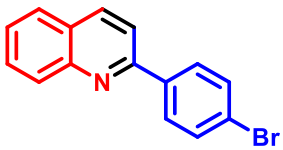
2-(4-Aminophenyl)quinoline (3d)[5] Purified by column chromatography on silica gel using petroleum ether and 10 % ethyl acetate as eluents, 89 % (88 mg) yielded as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 2H), 8.08 – 8.03 (m, 2H), 7.85 – 7.79 (m, 2H), 7.71 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 148.3, 147.8, 136.5, 129.9, 129.4, 129.4, 128.8, 127.4, 126.8, 125.6, 118.4, 115.1. HRMS (ESI) Calcd for $C_{15}H_{12}N_2$ ($[M+H]^+$): 221.1073; found: 221.1072.



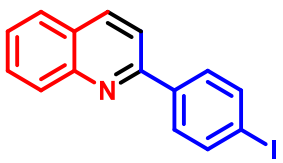
2-(4-Fluorophenyl)quinoline (**3e**)[4] Purified by column chromatography on silica gel using petroleum ether and 8% ethyl acetate as eluents, 89 % (89 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.12 (m, 4H), 7.85 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.28 – 7.21 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 162.6, 156.3, 148.2, 136.9, 129.8, 129.7, 129.5, 129.4, 127.5, 126.4, 118.7, 115.9, 115.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.. HRMS (ESI) Calcd for $C_{15}H_{10}NF$ ($[M+H]^+$): 224.0872; found: 224.0871.



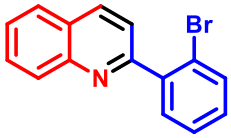
2-(4-Chlorophenyl)quinoline (**3f**)[6] Purified by column chromatography on silica gel using petroleum ether and 5% ethyl acetate as eluents, 91 % (98 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddt, *J* = 16.6, 8.4, 1.0 Hz, 2H), 8.17 – 8.12 (m, 2H), 7.84 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.76 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.61 – 7.48 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 148.2, 138.0, 136.9, 135.6, 129.9, 129.7, 129.0, 128.84, 127.5, 127.2, 126.5, 118.6. HRMS (ESI) Calcd for $C_{15}H_{10}NCl$ ($[M+H]^+$): 240.0574; found: 240.0574.



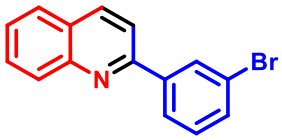
2-(4-Bromophenyl)quinoline (**3g**)[6] Purified by column chromatography on silica gel using petroleum ether and 8% ethyl acetate as eluents, 92 % (117 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 8.09 – 8.04 (m, 2H), 7.84 (ddd, *J* = 8.6, 2.9, 1.1 Hz, 2H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.56 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 148.2, 138.5, 137.0, 132.0, 129.8, 129.7, 129.1, 127.5, 127.2, 126.5, 123.9, 118.5. HRMS (ESI) Calcd for $C_{15}H_{10}NBr$ ($[M+H]^+$): 284.0069; found: 284.0068.



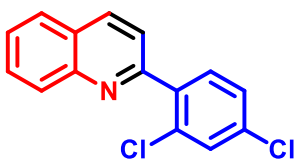
2-(4-Iodophenyl)quinoline (**3h**)[6] Purified by column chromatography on silica gel using petroleum ether and 10% ethyl acetate as eluents, 91 % (135 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 2H), 7.95 – 7.85 (m, 4H), 7.85 – 7.80 (m, 2H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 148.3, 139.1, 137.9, 136.9, 129.8, 129.7, 129.2, 127.5, 127.3, 126.6, 118.5, 95.9. HRMS (ESI) Calcd for $C_{15}H_{10}NI$ ($[M+H]^+$): 331.9930; found: 331.9931.



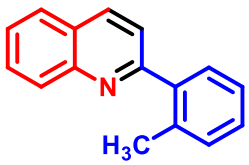
2-(2-Bromophenyl)quinoline (**3i**)[7] Purified by column chromatography on silica gel using petroleum ether and 5% ethyl acetate as eluents, 92 % (117 mg) yielded as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.24 – 8.18 (m, 3H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.76 (s, 1H), 7.57 (dt, *J* = 8.0, 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 148.2, 139.6, 136.9, 129.8, 129.6, 129.5, 129.4, 128.9, 127.6, 127.5, 127.2, 126.4, 119.0, 115.7. HRMS (ESI) Calcd for $C_{15}H_{10}NBr$ ($[M+H]^+$): 284.0069; found: 284.0069.



2-(3-Bromophenyl)quinoline (**3j**)[8] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 83 % (106 mg) yielded as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (t, *J* = 1.9 Hz, 1H), 8.25 (dd, *J* = 8.6, 0.8 Hz, 1H), 8.20 (dq, *J* = 8.4, 0.9 Hz, 1H), 8.10 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.77 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.41 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 148.2, 141.7, 137.1, 132.2, 130.7, 130.3, 129.9, 129.8, 127.5, 127.4, 126.7, 126.0, 123.2, 118.7. HRMS (ESI) Calcd for $C_{15}H_{10}NBr$ ($[M+H]^+$): 284.0069; found: 284.0069.

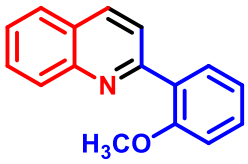


2-(2,4-Dichlorophenyl)quinoline (**3k**)[9] Purified by column chromatography on silica gel using petroleum ether and 15% ethyl acetate as eluents, 92 % (113 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.16 (dq, *J* = 8.5, 1.0 Hz, 1H), 7.87 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.59 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 8.3, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 148.1, 138.2, 135.9, 135.2, 133.1, 132.7, 129.9, 129.9, 129.7, 127.5, 127.6, 127.2, 126.9, 122.5. HRMS (ESI) Calcd for $C_{15}H_9NCl_2$ ($[M+H]^+$): 274.0184; found: 274.0185.

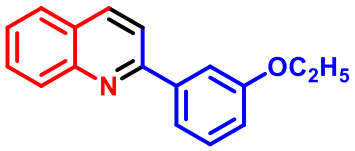


2-(2-Methylphenyl)quinoline (**3l**)[8] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 87 % (86 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.87 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.38 – 7.32 (m, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 147.9, 140.8, 136.1, 136.0, 130.9,

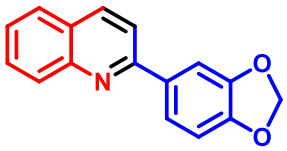
129.8, 129.7, 129.6, 128.6, 127.6, 126.8, 126.5, 126.1, 122.4, 20.4. HRMS (ESI) Calcd for $C_{16}H_{13}N$ ($[M+H]^+$): 220.1120; found: 220.1121.



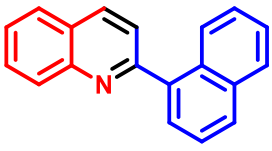
2-(2-Methoxyphenyl)quinoline (3m)[10] Purified by column chromatography on silica gel using petroleum ether and 10% ethyl acetate as eluents, 93 % (98 mg) yielded as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.15 (m, 2H), 7.93 – 7.84 (m, 3H), 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.2, 7.4, 1.8 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.06 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 157.1, 148.3, 135.2, 131.5, 130.4, 129.7, 129.6, 129.3, 127.4, 127.1, 126.2, 123.5, 121.3, 111.5, 55.6. HRMS (ESI) Calcd for $C_{16}H_{13}NO$ ($[M+H]^+$): 236.1069; found: 236.1068.



2-(3-Ethoxyphenyl)quinoline (3n) Purified by column chromatography on silica gel using petroleum ether and 10% ethyl acetate as eluents, 88 % (99 mg) yielded as white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.5, 4.8 Hz, 2H), 7.88 – 7.80 (m, 2H), 7.78 – 7.69 (m, 3H), 7.53 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.02 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 157.2, 148.2, 141.1, 136.8, 129.8, 129.7, 129.7, 127.5, 127.3, 126.3, 119.9, 119.1, 115.8, 113.5, 63.6, 14.9. HRMS (ESI) Calcd for $C_{17}H_{17}N$ ($[M+H]^+$): 250.1231; found: 250.1231.

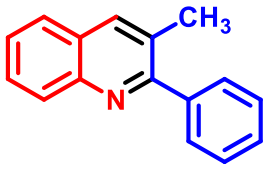


2-(Benzodioxol-5-yl)quinoline (3o)[11] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 81 % (91 mg) yielded as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 7.83 – 7.77 (m, 3H), 7.75 – 7.67 (m, 2H), 7.52 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 148.9, 148.4, 148.2, 136.7, 134.2, 129.7, 129.6, 127.4, 127.0, 126.0, 121.8, 118.6, 108.5, 107.9, 101.4. HRMS (ESI) Calcd for $C_{16}H_{11}NO_2$ ($[M+H]^+$): 250.0862; found: 250.0861.

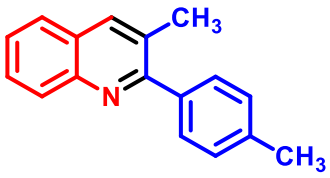


2-Naphthylquinoline (3p)[7] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 84 % (96 mg) yielded as brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 15.8, 8.3 Hz, 2H), 8.20 – 8.15 (m, 1H), 8.01 – 7.92

(m, 3H), 7.82 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.64 (dd, J = 8.2, 7.1 Hz, 2H), 7.57 – 7.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 148.1, 138.7, 136.3, 134.0, 131.3, 129.8, 129.7, 129.2, 128.4, 127.8, 127.6, 127.0, 126.6, 126.0, 125.7, 125.4, 123.3, 116.0. HRMS (ESI) Calcd for $C_{19}H_{13}N$ ($[M+H]^+$): 256.1120; found: 256.1121.

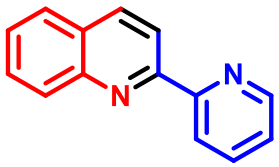


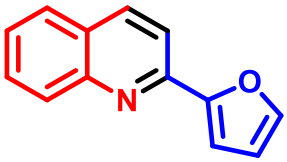
3-Methyl-2-phenylquinoline (3r)[10] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 84 % (83 mg) yielded as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 1H), 8.05 (s, 1H), 7.81 (dd, J = 8.2, 1.4 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.64 – 7.61 (m, 2H), 7.56 – 7.50 (m, 3H), 7.49 – 7.45 (m, 1H), 7.36 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 146.6, 140.9, 136.8, 129.3, 128.9, 128.8, 128.3, 128.2, 127.6, 126.7, 126.4, 125.9, 20.6. HRMS (ESI) Calcd for $C_{16}H_{13}N$ ($[M+H]^+$): 220.1120; found: 220.1119.



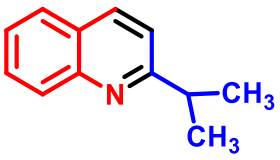
2-(4-Methylphenyl)-3-methylquinoline (3s)[12] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 83 % (87 mg) yielded as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dq, J = 8.5, 0.9 Hz, 1H), 8.03 – 8.01 (m, 1H), 7.79 (dd, J = 8.1, 1.5 Hz, 1H), 7.68 (ddd, J = 8.5, 6.9, 1.6 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.35 – 7.31 (m, 2H), 2.50 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 146.7, 138.0, 136.7, 129.3, 129.0, 128.9, 128.8, 128.7, 127.6, 126.7, 126.3, 125.9, 21.4, 20.7. HRMS (ESI) Calcd for $C_{17}H_{16}N$ ($[M+H]^+$): 235.1355; found: 235.1356.

2-(2-Pyridyl)quinoline (3t)[6] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 99 % (75 mg) yielded as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.68 (dt, J = 8.0, 1.1 Hz, 1H), 8.59 (d, J = 8.6 Hz, 1H), 8.31 (dd, J = 8.7, 1.0 Hz, 1H), 8.21 (dq, J = 8.5, 0.9 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.76 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H), 7.57 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.38 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 156.2, 149.2, 147.9, 136.9, 136.8, 129.8, 129.6, 128.3, 127.6, 126.8, 124.0, 121.9, 118.9. HRMS (ESI) Calcd for $C_{14}H_{10}N_2$ ($[M+H]^+$): 207.0916; found: 207.0916.

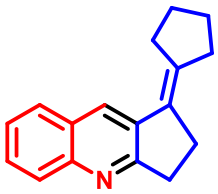




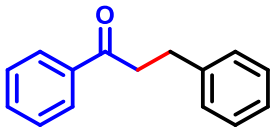
2-(2-Furyl)quinoline (**3u**)[7] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 82 % (76 mg) yielded as brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 2H), 7.86 – 7.79 (m, 2H), 7.75 – 7.71 (m, 1H), 7.66 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.24 (s, 1H), 6.62 (dd, *J* = 3.4, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 149.0, 148.1, 144.1, 136.7, 129.9, 129.4, 127.6, 127.2, 126.2, 117.5, 112.2, 110.1. HRMS (ESI) Calcd for $C_{13}H_9NO$ ($[M+H]^+$): 196.0756; found: 196.0756.



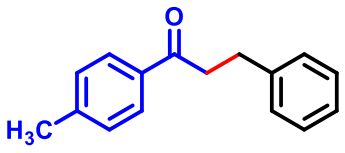
2-isopropylquinoline (**3v**)[7] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (65 mg) yielded as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 7.80 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 3.30 (h, *J* = 7.0 Hz, 1H), 1.43 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 147.7, 136.5, 129.3, 128.9, 127.5, 126.9, 125.7, 119.2, 37.3, 22.6. HRMS (ESI) Calcd for $C_{12}H_{13}N$ ($[M+H]^+$): 172.1120; found: 172.1121.



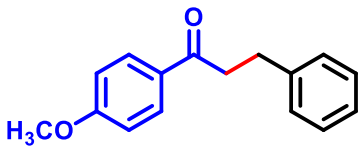
1-cyclopentylidene-2,3-dihydro-1H-cyclopenta[b]quinoline (**3w**) Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 68 % (72 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.85 (q, *J* = 1.3 Hz, 1H), 7.69 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.42 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 3.21 – 3.12 (m, 4H), 2.81 (ddt, *J* = 10.1, 5.1, 2.6 Hz, 2H), 2.45 (tt, *J* = 7.1, 2.0 Hz, 2H), 1.88 – 1.77 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 148.4, 146.6, 138.4, 130.0, 129.8, 129.4, 127.9, 127.1, 126.8, 125.1, 33.9, 32.7, 28.8, 27.5, 27.3, 25.8. HRMS (ESI) Calcd for $C_{17}H_{17}N$ ($[M+H]^+$): 236.1436; found: 236.1436.



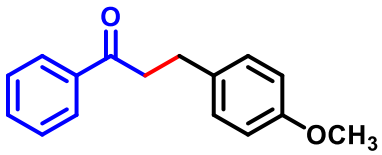
1,3-diphenylpropan-1-one (**5a**)[13] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 96 % (100 mg) yielded as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.24 (m, 5H), 3.37 – 3.31 (m, 2H), 3.12 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 199.3, 141.3, 136.9, 133.1, 128.6, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2. HRMS (ESI) Calcd for $C_{15}H_{14}O$ ($[M+H]^+$): 211.1117; found: 211.1116.



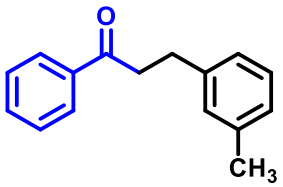
3-phenyl-1-(p-tolyl)propan-1-one (5b)[14] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 97 % (108 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.33 – 7.21 (m, 7H), 3.30 – 3.24 (m, 2H), 3.09 – 3.03 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 198.9, 143.8, 141.4, 134.4, 129.3, 128.5, 128.4, 128.2, 126.1, 40.4, 30.2, 21.6. HRMS (ESI) Calcd for $C_{16}H_{16}O$ ($[M+H]^+$): 225.1273; found: 225.1272.



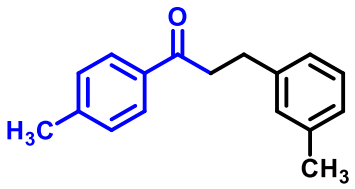
1-(4-methoxyphenyl)-3-phenylpropan-1-one (5c)[13] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 94 % (112 mg) yielded a yellow solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.98 (d, J = 8.9 Hz, 2H), 7.35 – 7.22 (m, 5H), 6.95 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.28 (dd, J = 8.7, 6.9 Hz, 2H), 3.09 (dd, J = 8.6, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 197.9, 163.5, 141.5, 130.3, 129.9, 128.5, 128.4, 126.1, 113.7, 55.5, 40.1, 30.3. HRMS (ESI) Calcd for $C_{16}H_{16}O_2$ ($[M+H]^+$): 241.1223; found: 241.1122.



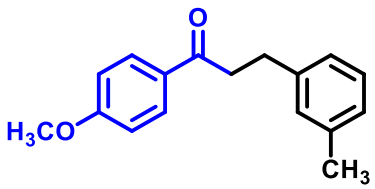
3-(4-methoxyphenyl)-1-phenylpropan-1-one (5d)[15] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 91 % (109 mg) yielded a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.01 – 7.96 (m, 2H), 7.60 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.89 – 6.85 (m, 2H), 3.82 (s, 3H), 3.32 – 3.28 (m, 2H), 3.04 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 199.4, 158.0, 136.9, 133.3, 133.1, 129.4, 128.6, 128.1, 113.9, 55.3, 40.7, 29.3. HRMS (ESI) Calcd for $C_{16}H_{16}O_2$ ($[M+H]^+$): 241.1225; found: 241.1225.



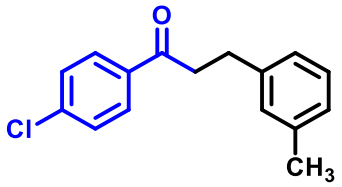
1-phenyl-3-(m-tolyl)propan-1-one (5e)[16] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 93 % (104 mg) yielded a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.03 – 7.97 (m, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 – 7.03 (m, 3H), 3.33 (dd, J = 8.7, 6.9 Hz, 2H), 3.07 (dd, J = 8.6, 6.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 199.3, 141.3, 138.1, 136.9, 133.1, 129.3, 128.6, 128.5, 128.1, 126.9, 125.4, 40.6, 30.1, 21.4. HRMS (ESI) Calcd for $C_{16}H_{16}O$ ($[M+H]^+$): 225.1281; found: 225.1281.



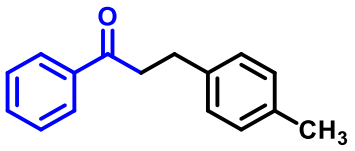
3-(m-tolyl)-1-(p-tolyl)propan-1-one (5f)[17] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 98 % (117 mg) yielded a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.92 – 7.87 (m, 2H), 7.27 (p, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.03 (m, 3H), 3.29 (dd, *J* = 8.9, 6.7 Hz, 2H), 3.07 – 3.02 (m, 2H), 2.43 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 199.0, 143.8, 141.4, 138.1, 134.4, 129.3, 129.2, 128.4, 128.2, 126.9, 125.4, 40.5, 30.2, 21.6, 21.4. HRMS (ESI) Calcd for $C_{17}H_{18}O$ ([M+H]$^+$): 239.1441; found: 239.1141.



1-(4-methoxyphenyl)-3-(m-tolyl)propan-1-one (5g)[18] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 96 % (122 mg) yielded a yellowish oil. ^{1}H NMR (400 MHz, CDCl3) δ 8.01 – 7.95 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.01 (m, 3H), 6.97 – 6.93 (m, 2H), 3.89 (s, 3H), 3.31 – 3.22 (m, 2H), 3.09 – 3.00 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 197.9, 163.4, 141.4, 138.1, 130.3, 129.9, 129.3, 128.4, 126.8, 125.4, 113.7, 55.5, 40.2, 30.3, 21.4. HRMS (ESI) Calcd for $C_{16}H_{16}O_2$ ([M+H]$^+$): 241.1223; found: 239.1222.

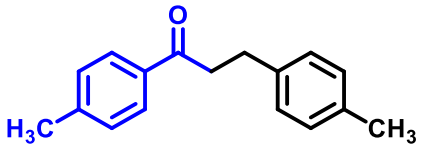


3-(m-tolyl)-1-(p-tolyl)propan-1-one (5h)[17] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 89 % (115 mg) yielded a pale orange solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.94 – 7.90 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.07 (dd, *J* = 10.8, 4.8 Hz, 3H), 3.31 – 3.26 (m, 2H), 3.05 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 198.1, 141.0, 139.5, 138.2, 135.2, 129.5, 129.2, 128.9, 128.5, 126.9, 125.4, 40.5, 29.9, 21.4. HRMS (ESI) Calcd for $C_{16}H_{15}OCl$ ([M+H]$^+$): 259.0885; found: 259.0885.

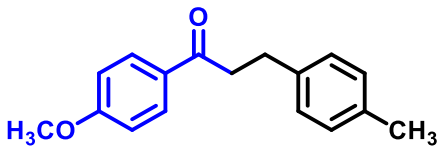


1-phenyl-3-(p-tolyl)propan-1-one (5i)[13] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 95 % (106 mg) yielded a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.02 – 7.95 (m, 2H), 7.58 (tt, *J* = 6.8, 1.3 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.15 (q, *J* = 8.1 Hz, 4H), 3.34 – 3.28 (m, 2H), 3.10 – 3.02 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 199.4, 138.2, 136.9,

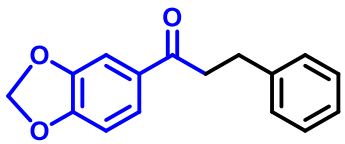
135.6, 133.0, 129.2, 128.6, 128.3, 128.1, 40.6, 29.7, 21.0. HRMS (ESI) Calcd for $C_{16}H_{16}O$ ($[M+H]^+$): 225.1272; found: 225.1272.



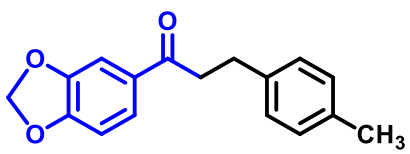
1,3-di-p-tolylpropan-1-one (**5j**)[17] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 98 % (116 mg) yielded a yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.92 – 7.86 (m, 2H), 7.26 (t, *J* = 0.7 Hz, 2H), 7.15 (q, *J* = 8.1 Hz, 4H), 3.31 – 3.25 (m, 2H), 3.07 – 3.02 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 199.1, 143.8, 138.3, 135.6, 134.4, 129.3, 129.2, 128.3, 128.1, 40.5, 29.8, 21.6, 21.0. HRMS (ESI) Calcd for $C_{17}H_{18}O$ ($[M+H]^+$): 239.1437; found: 239.1437.



1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (**5k**)[18] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 95 % (120 mg) yielded a yellowish liquid. ^{1}H NMR (500 MHz, CDCl3) δ 8.03 – 7.91 (m, 2H), 7.25 – 7.07 (m, 4H), 6.99 – 6.91 (m, 2H), 3.89 (s, 3H), 3.26 (t, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 197.9, 163.4, 138.4, 135.6, 130.3, 130.0, 129.2, 128.3, 55.5, 40.3, 29.9, 21.0. HRMS (ESI) Calcd for $C_{17}H_{18}O_2$ ($[M+H]^+$): 255.1379; found: 255.1379.

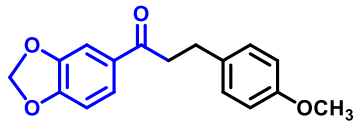


1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one (**5l**)[14] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 94 % (119 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.30 (s, 1H), 7.27 – 7.21 (m, 3H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H), 3.22 (t, *J* = 7.8 Hz, 2H), 3.08 – 3.01 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 197.3, 148.2, 141.3, 131.7, 129.0, 128.5, 128.4, 126.1, 124.3, 107.9, 107.9, 101.8, 40.2, 30.4. HRMS (ESI) Calcd for $C_{16}H_{14}O_3$ ($[M+H]^+$): 255.1021; found: 255.1020.

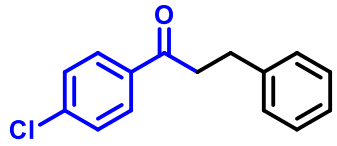


1-(benzo[d][1,3]dioxol-5-yl)-3-(p-tolyl)propan-1-one (**5m**) Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 96 % (128 mg) yielded a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.58 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.18 – 7.12 (m, 4H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.06 (s, 2H), 3.25 – 3.20 (m, 2H), 3.06 – 3.01 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 197.4, 151.7, 148.2, 138.2, 135.6, 131.8, 129.2, 128.3, 124.3, 107.9,

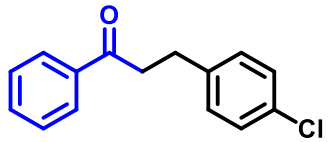
107.9, 101.8, 40.4, 29.9, 21.0. HRMS (ESI) Calcd for $C_{17}H_{16}O_3$ ([M+H]$^+$): 269.1172; found: 269.1172.



1-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propan-1-one (**5n**) Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 95 % (135 mg) yielded a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.57 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.86 (dd, *J* = 8.5, 2.8 Hz, 3H), 6.06 (s, 2H), 3.81 (s, 3H), 3.24 – 3.18 (m, 2H), 3.04 – 2.97 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 197.5, 157.9, 151.7, 148.2, 133.4, 131.8, 129.3, 124.3, 113.9, 107.9, 107.9, 101.8, 55.3, 40.5, 29.5. HRMS (ESI) Calcd for $C_{17}H_{16}O_4$ ([M+H]$^+$): 285.1122; found: 285.1122.



1-(4-chlorophenyl)-3-phenylpropan-1-one (**5o**)[13] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 88 % (107 mg) yielded a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.95 – 7.88 (m, 2H), 7.47 – 7.42 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 3.33 – 3.27 (m, 2H), 3.11 – 3.06 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 198.0, 141.1, 139.5, 135.2, 129.5, 128.9, 128.6, 128.4, 126.2, 40.4, 30.1. HRMS (ESI) Calcd for $C_{15}H_{13}OCl$ ([M+H]$^+$): 245.2737; found: 245.0736.



3-(4-chlorophenyl)-1-phenylpropan-1-one (**5p**)[13] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (104 mg) yielded a colorless liquid. ^{1}H NMR (500 MHz, CDCl3) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.22 (s, 2H), 3.31 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 198.9, 139.8, 136.7, 133.2, 131.9, 129.9, 128.7, 128.6, 128.0, 77.3, 77.0, 76.8, 40.2, 29.4. HRMS (ESI) Calcd for $C_{15}H_{13}OCl$ ([M+H]$^+$): 245.2737; found: 245.0736.

NMR specta of catalytic products

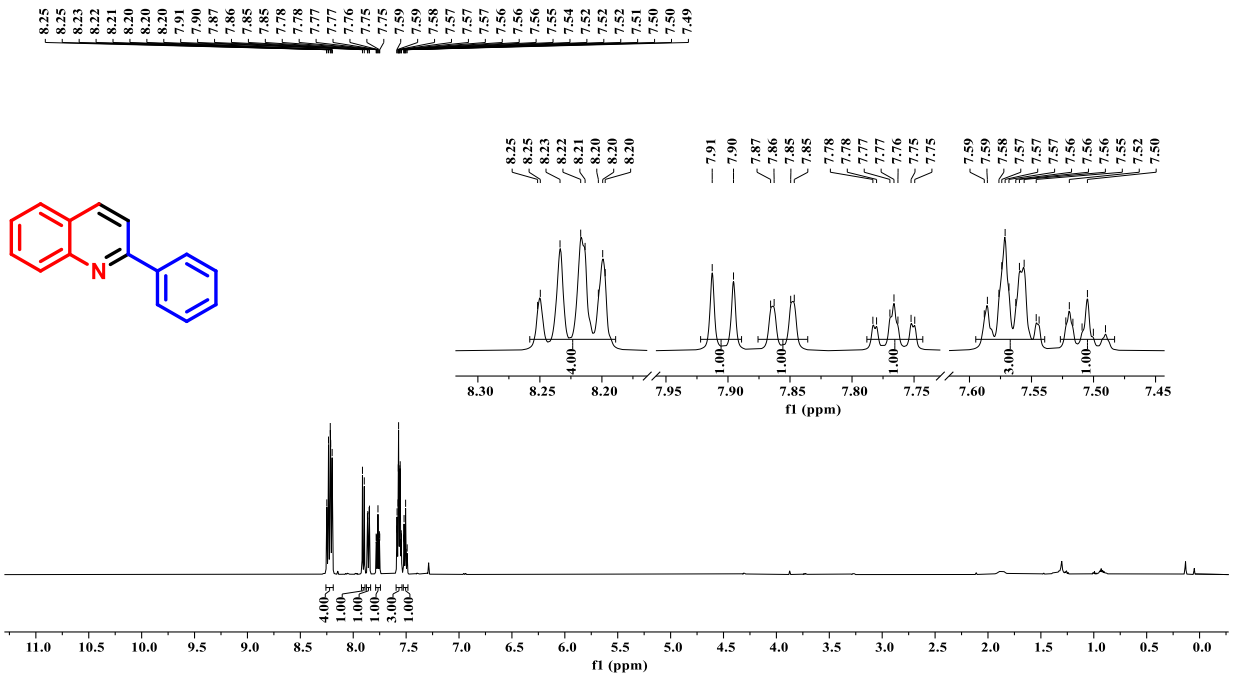


Fig. S18 ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz).

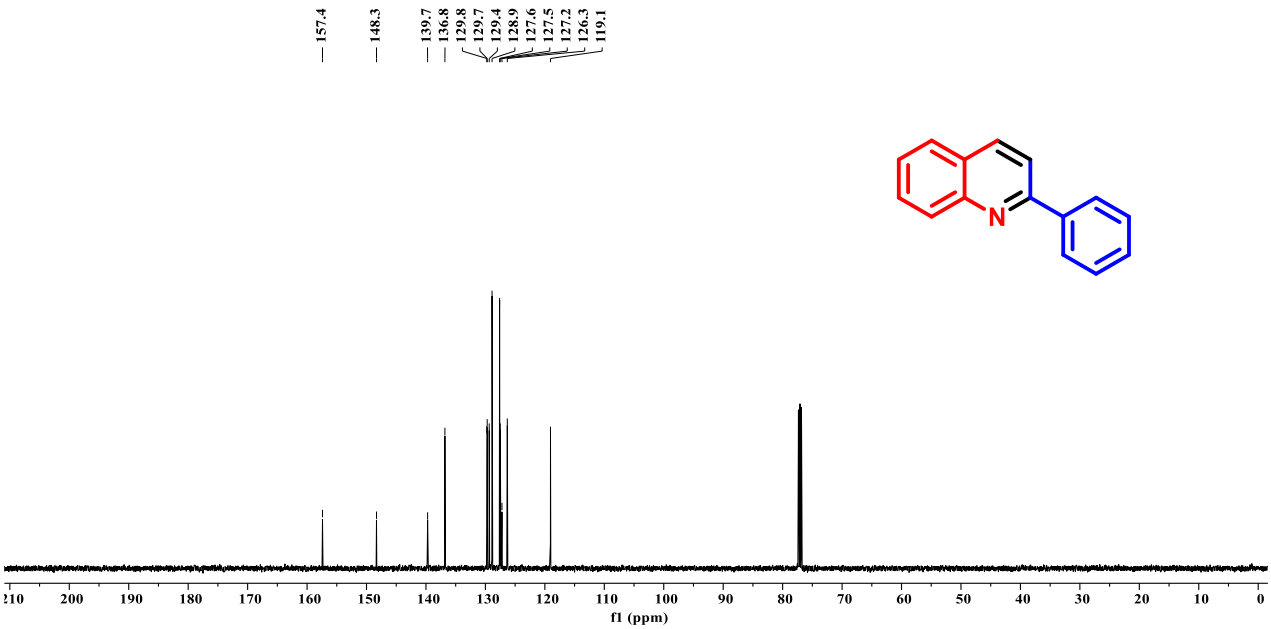


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$ (126 MHz).

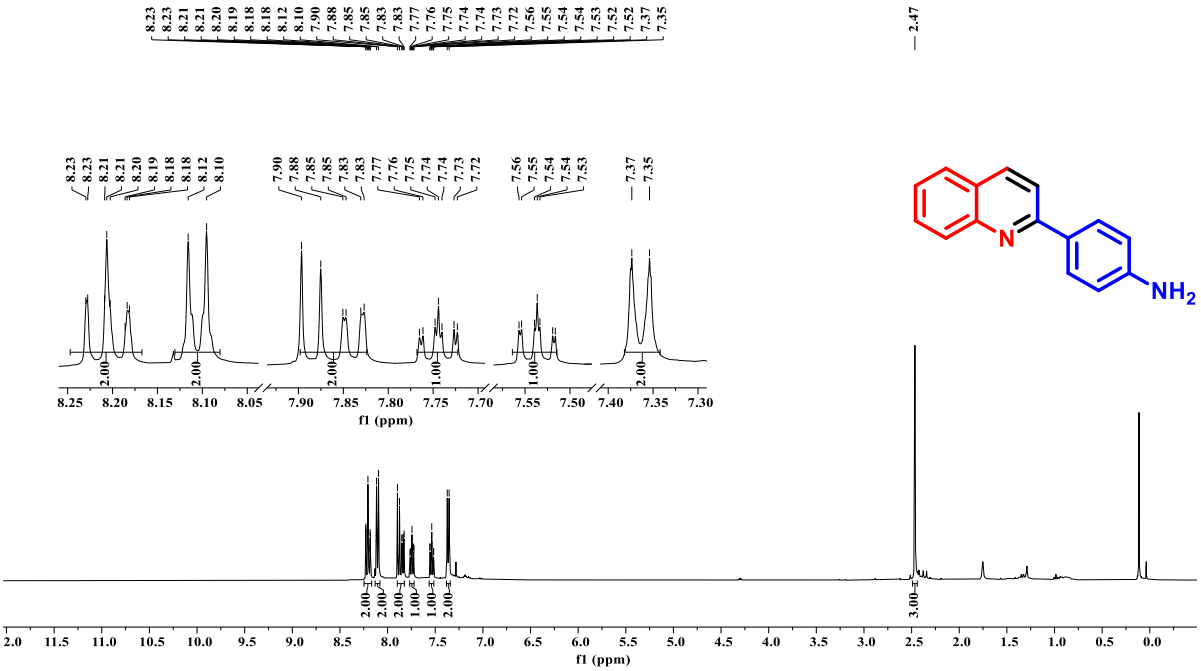


Fig. S20 ^{1}H NMR spectrum of **3b** in $CDCl_3$ (400 MHz).

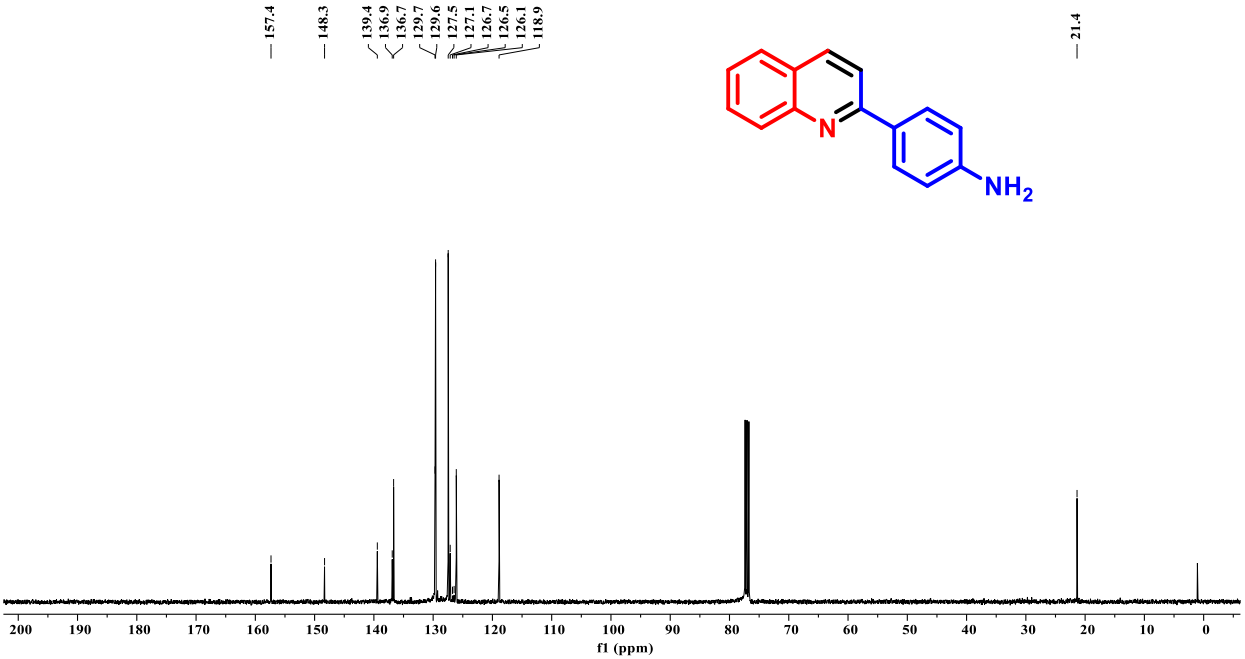


Fig. S21 ^{13}C{^{1}H} NMR spectrum of **3b** in $CDCl_3$ (101 MHz).

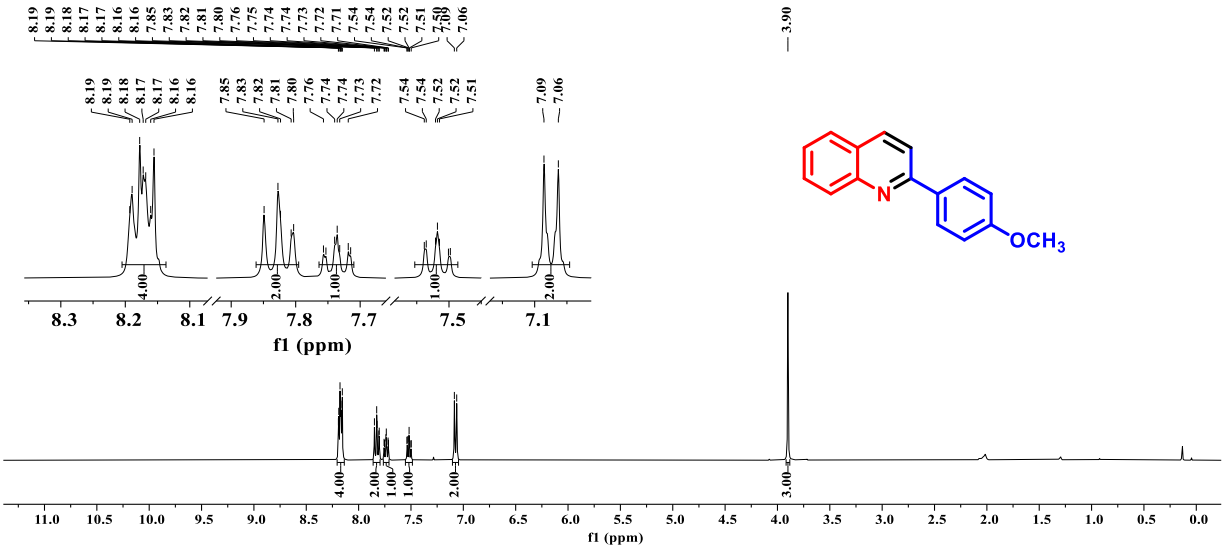


Fig. S22 ^{1}H NMR spectrum of **3c** in $CDCl_3$ (400 MHz).

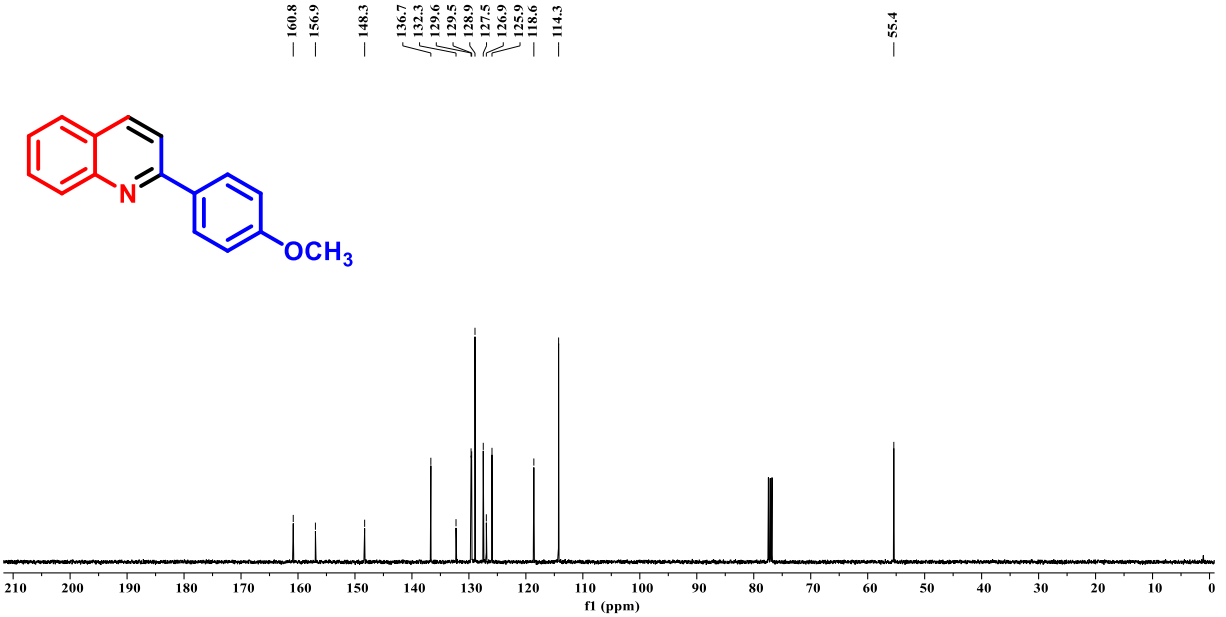


Fig. S23 ^{13}C{^{1}H} NMR spectrum of **3c** in $CDCl_3$ (101 MHz).

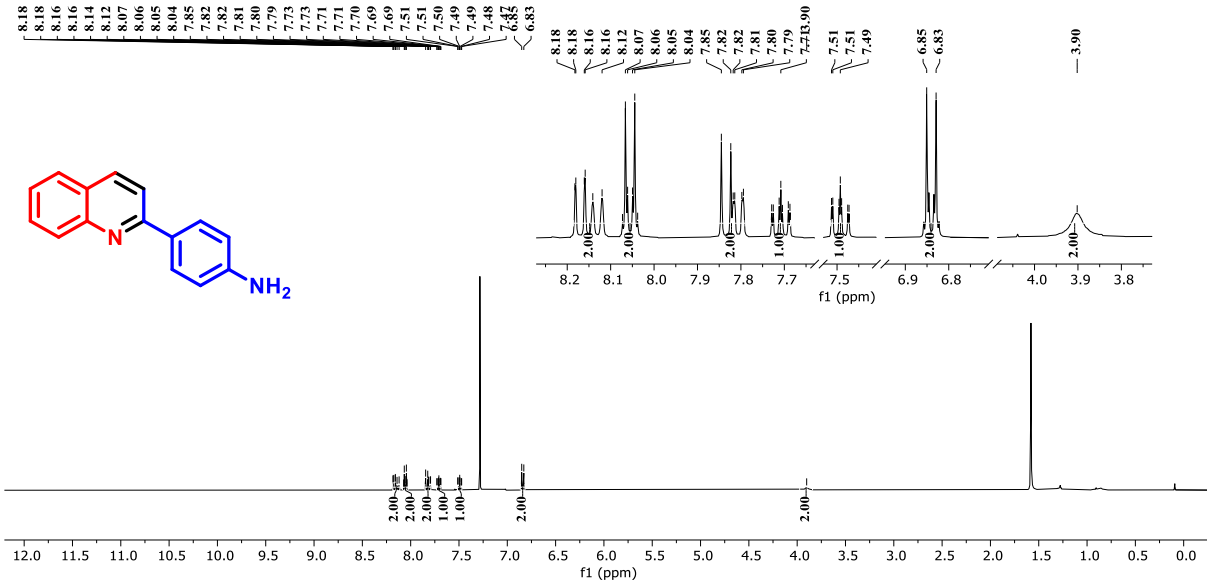


Fig. S24 ^{1}H NMR spectrum of **3d** in $CDCl_3$ (400 MHz).

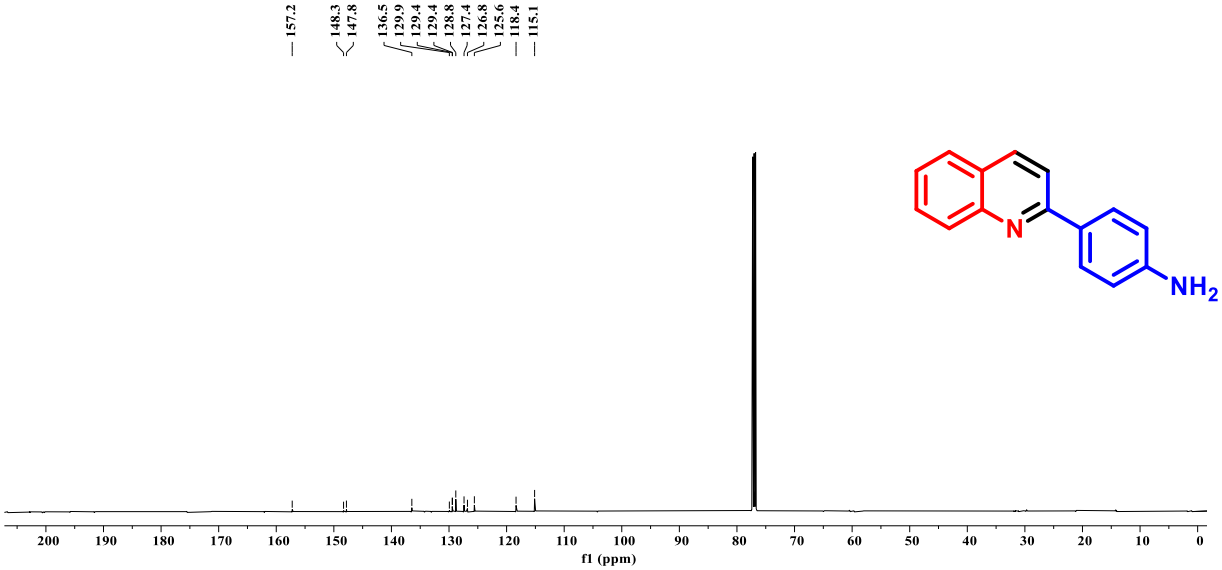


Fig. S25 $^{13}C\{^{1}H\}$ NMR spectrum of **3d** in $CDCl_3$ (126 MHz).

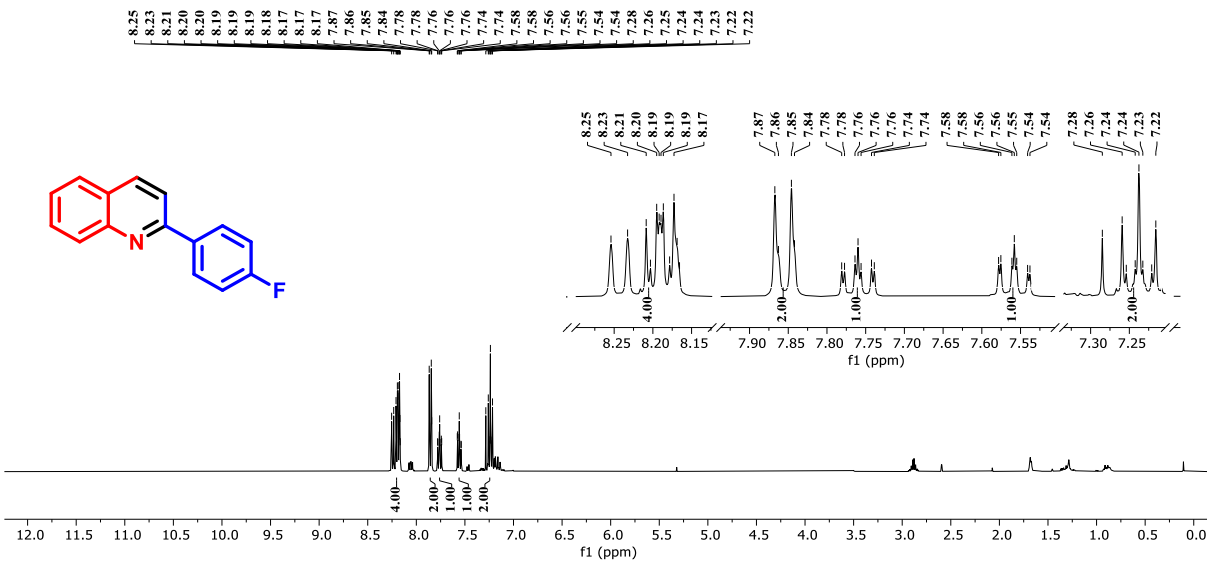


Fig. S26 ^{1}H NMR spectrum of **3e** in $CDCl_3$ (400 MHz).

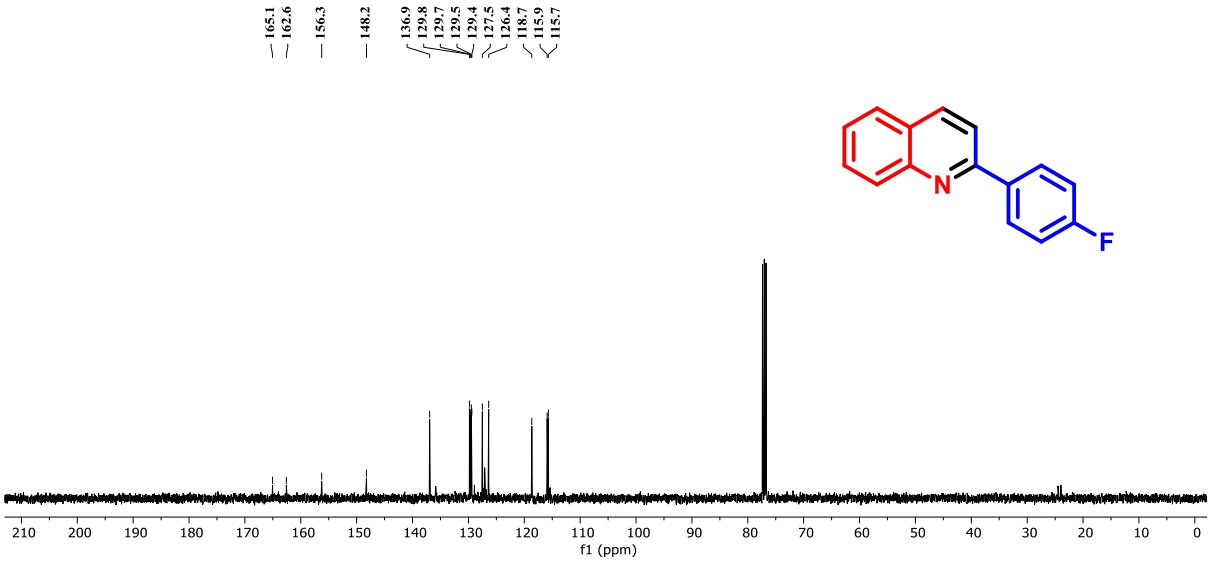


Fig. S27 ^{13}C{^{1}H} NMR spectrum of **3e** in $CDCl_3$ (101 MHz).

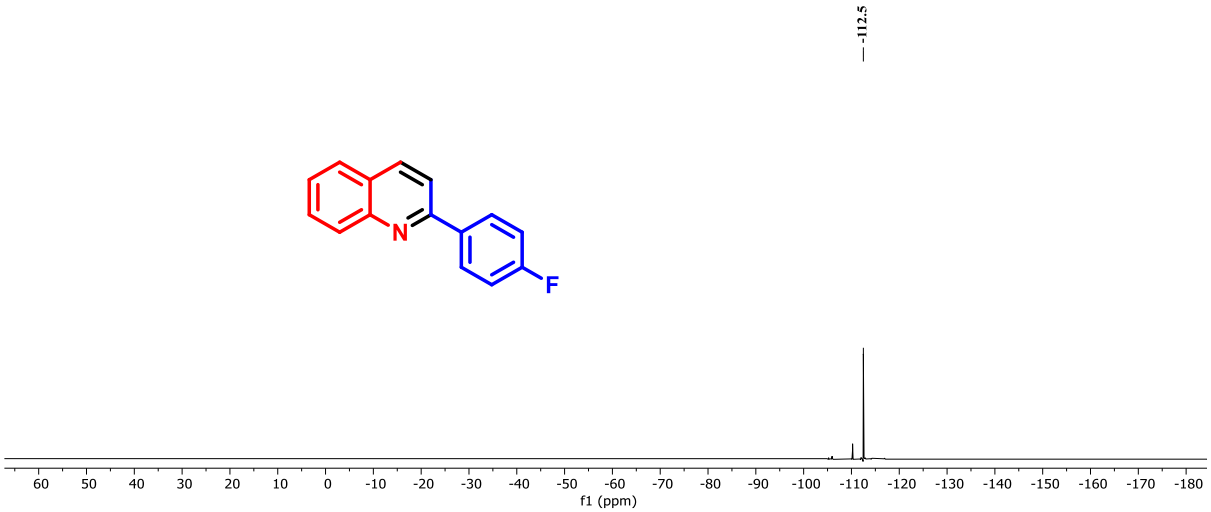


Fig. S28 ^{19}F{^{1}H} NMR spectrum of **3e** in CDCl3 (376 MHz).

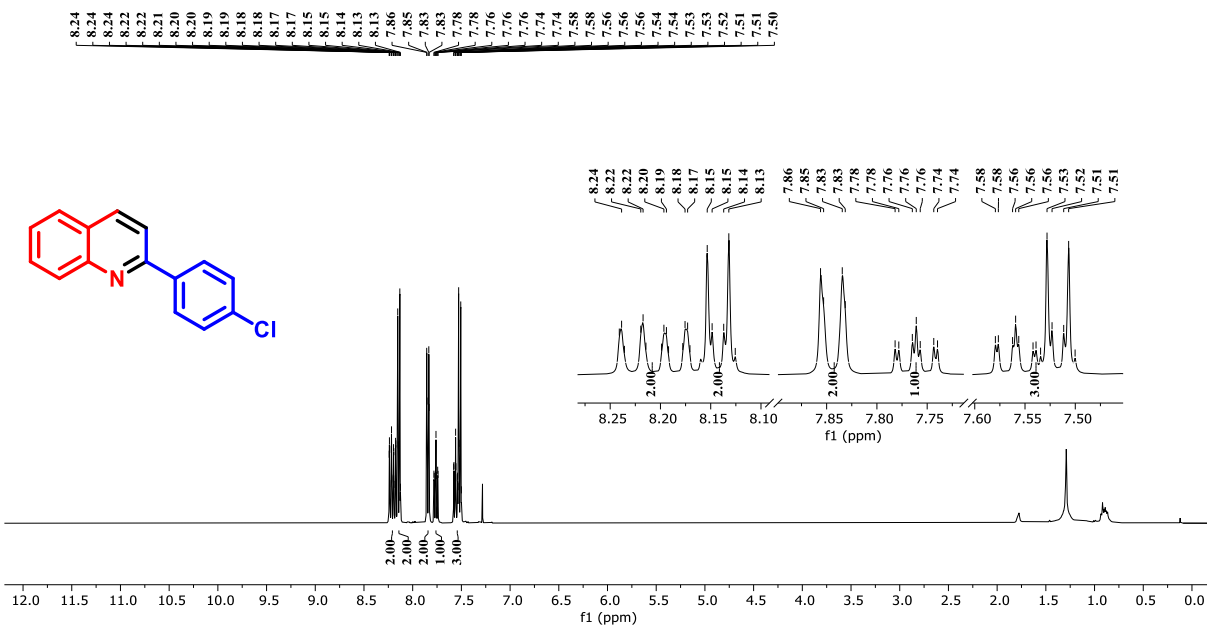


Fig. S29 ^{1}H NMR spectrum of **3f** in $CDCl_3$ (400 MHz).

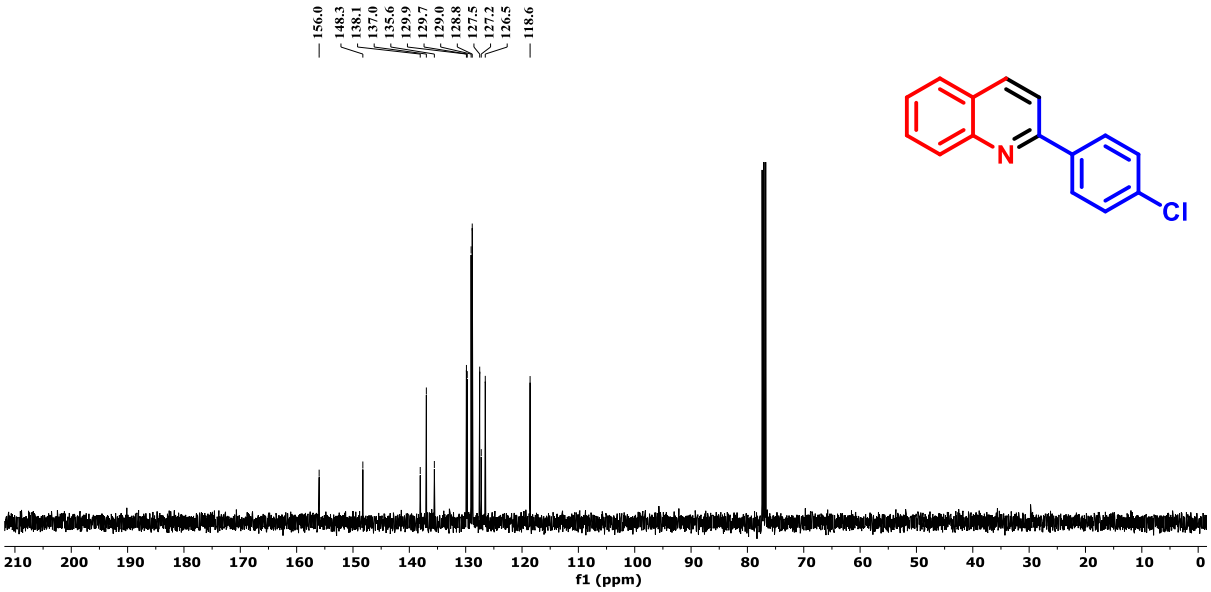


Fig. S30 $^{13}C\{^{1}H\}$ NMR spectrum of **3f** in $CDCl_3$ (101 MHz).

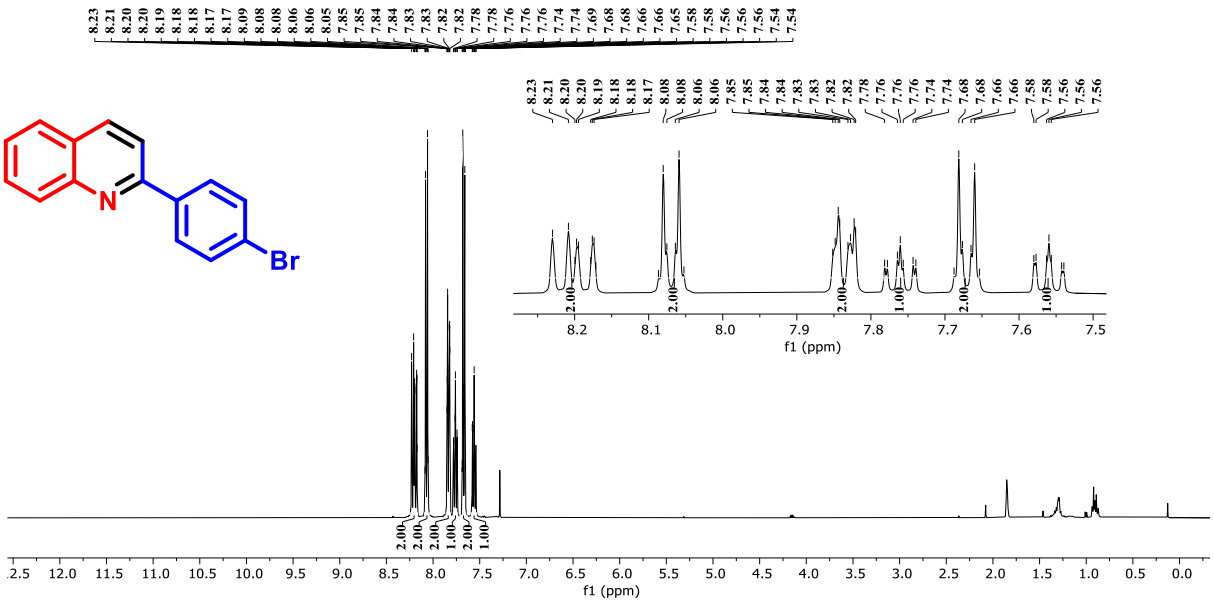


Fig. S31 ^{1}H NMR spectrum of **3g** in $CDCl_3$ (400 MHz).

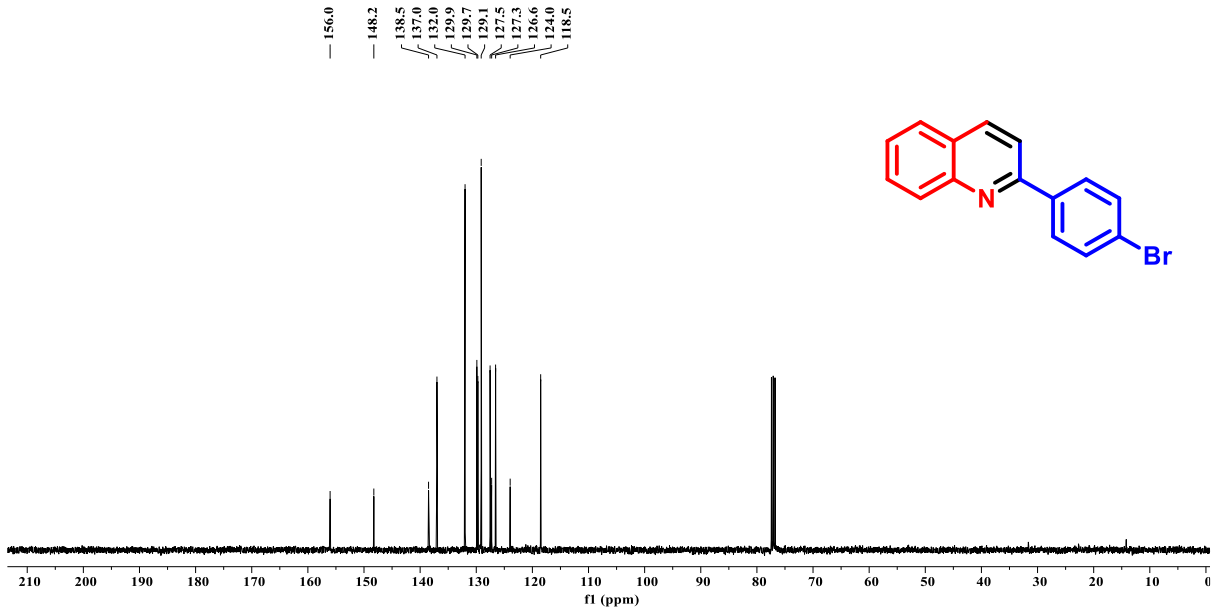


Fig. S32 $^{13}C\{^{1}H\}$ NMR spectrum of **3g** in $CDCl_3$ (101 MHz).

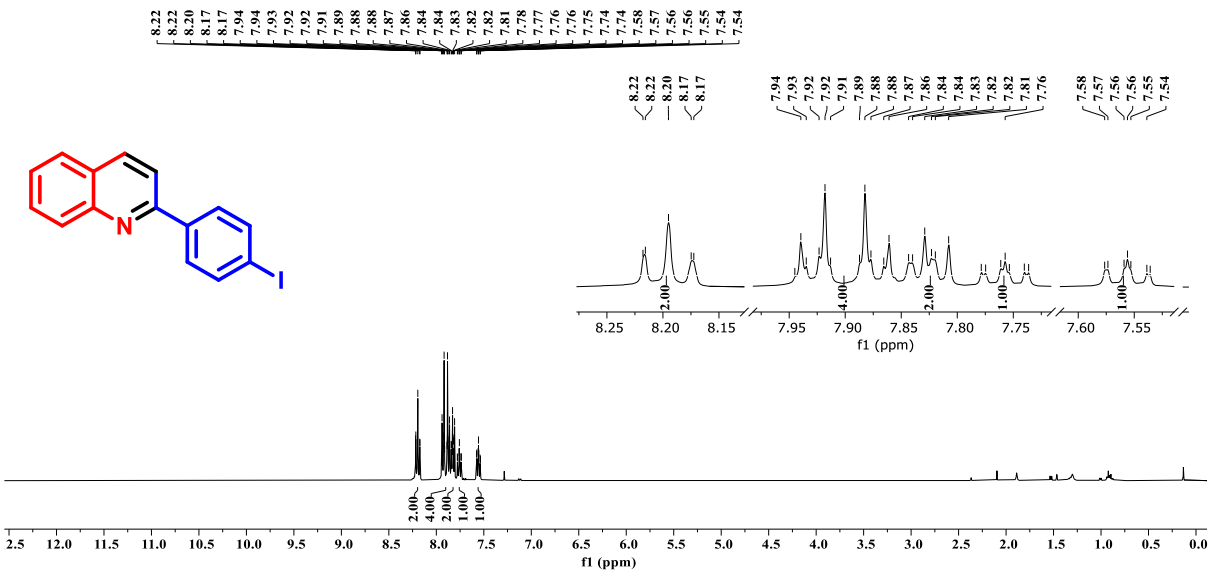


Fig. S33 ^{1}H NMR spectrum of **3h** in $CDCl_3$ (400 MHz).

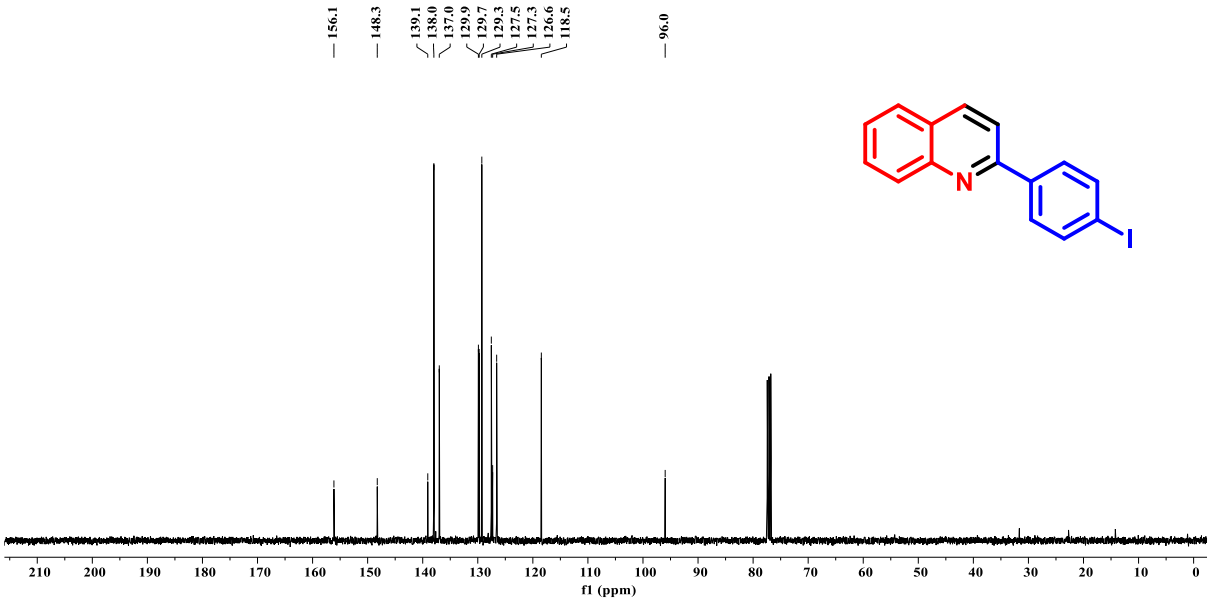


Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of **3h** in $CDCl_3$ (101 MHz).

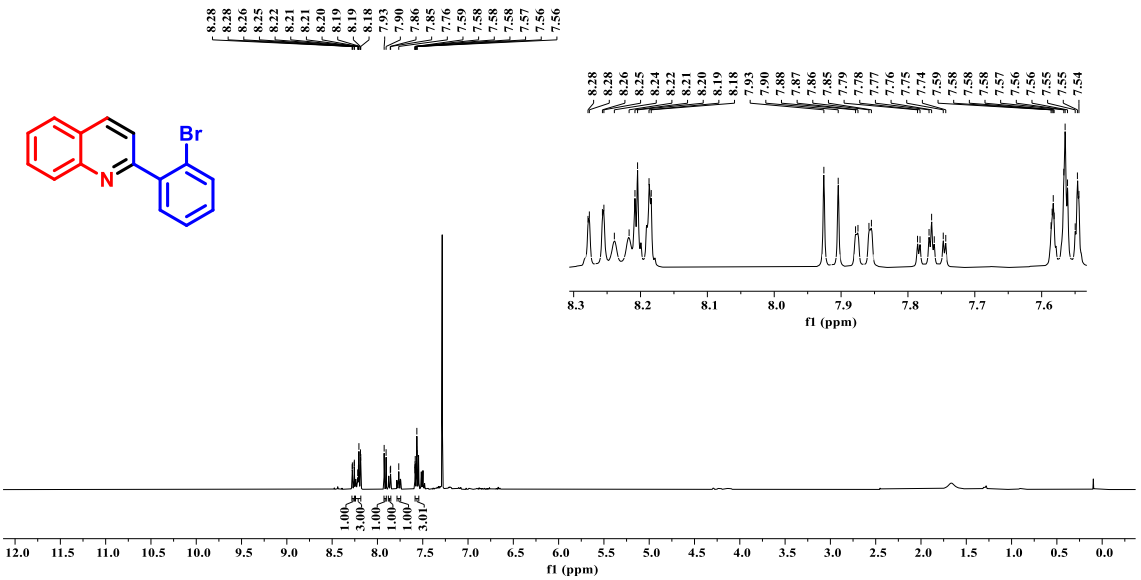


Fig. S35 ^{1}H NMR spectrum of **3i** in $CDCl_3$ (400 MHz).

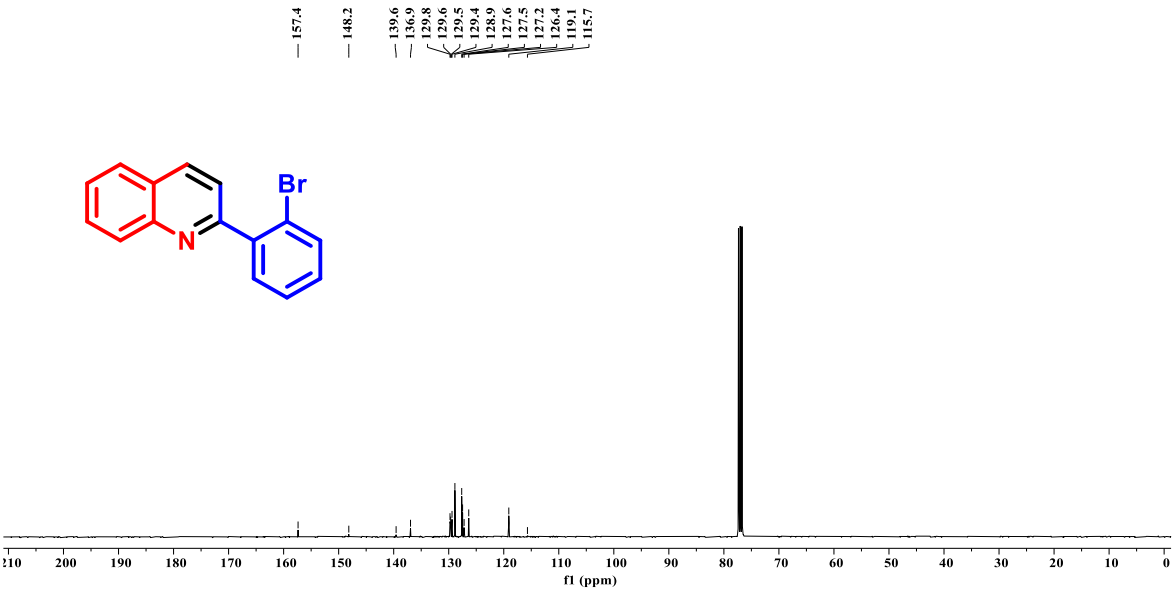


Fig. S36 $^{13}C\{^{1}H\}$ NMR spectrum of **3i** in $CDCl_3$ (101 MHz).

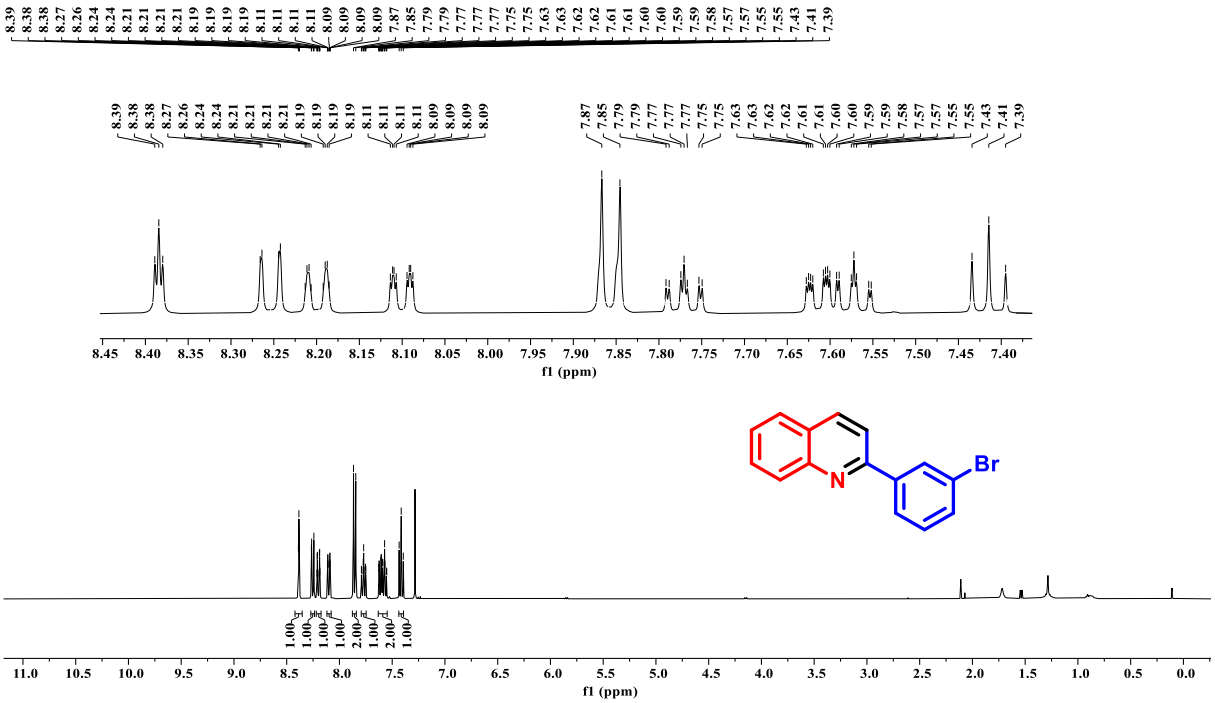


Fig. S37 ^{1}H NMR spectrum of **3j** in $CDCl_3$ (400 MHz).

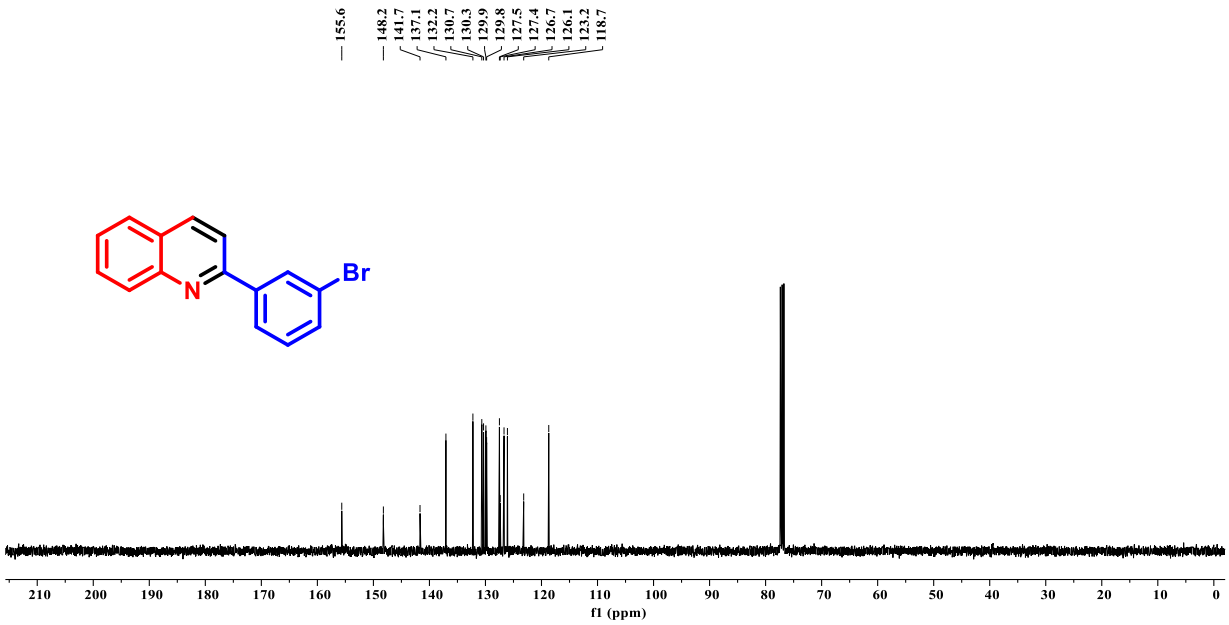


Fig. S38 ^{13}C{^{1}H} NMR spectrum of **3j** in $CDCl_3$ (101 MHz).

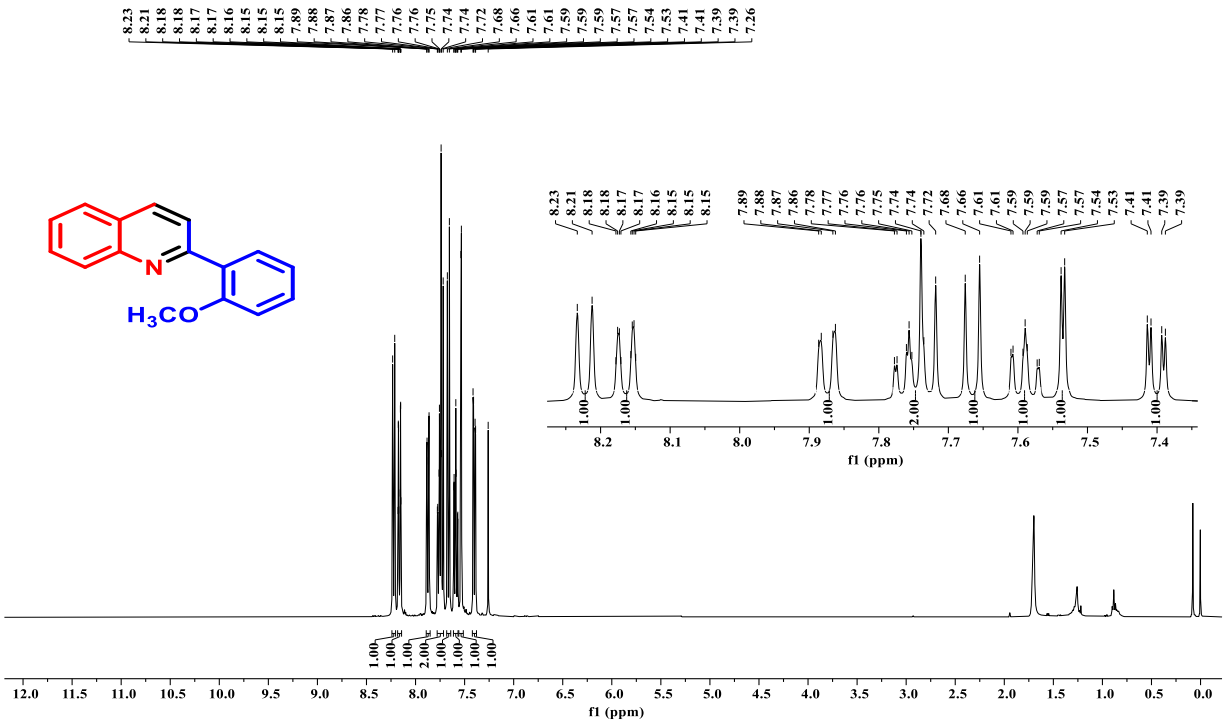


Fig. S39 ^{1}H NMR spectrum of **3k** in $CDCl_3$ (400 MHz).

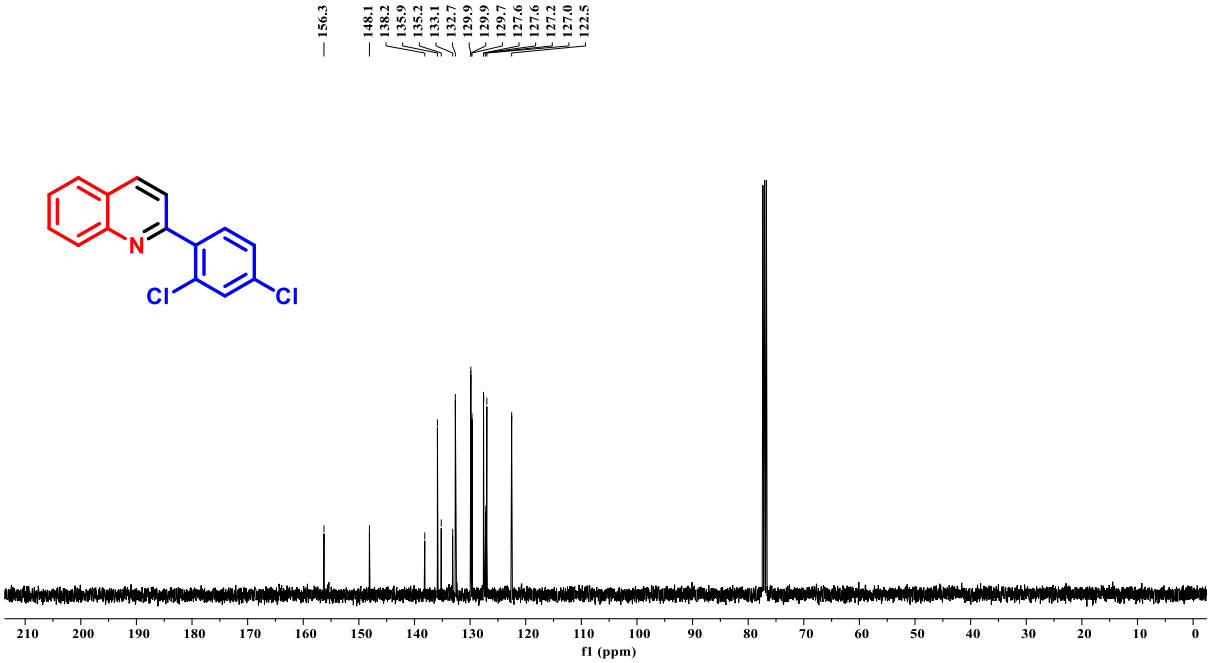


Fig. S40 $^{13}C\{^{1}H\}$ NMR spectrum of **3k** in $CDCl_3$ (101 MHz).

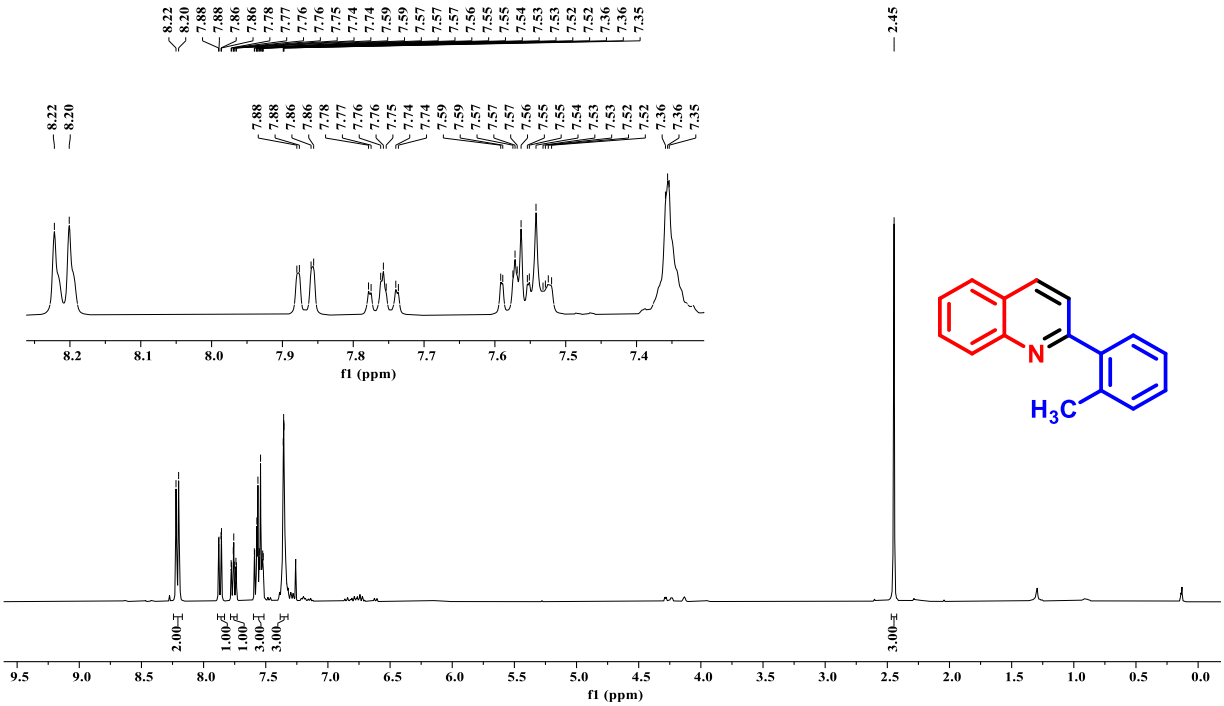


Fig. S41 ^{1}H NMR spectrum of **3l** in $CDCl_3$ (400 MHz).

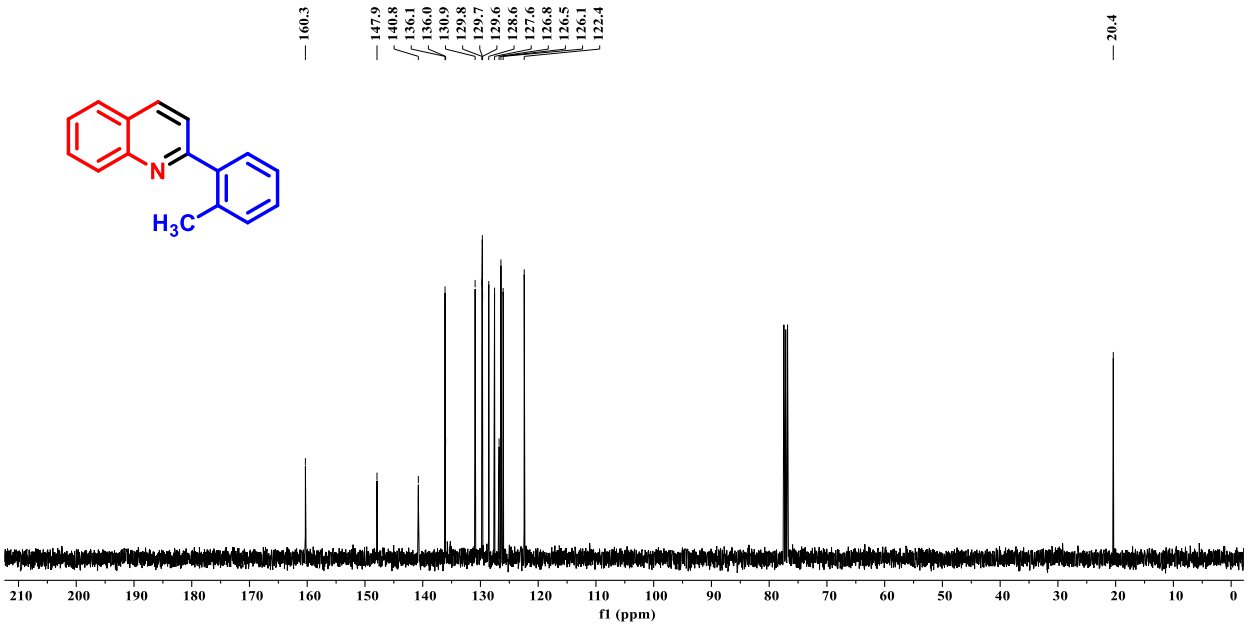


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum of **3l** in $CDCl_3$ (101 MHz).

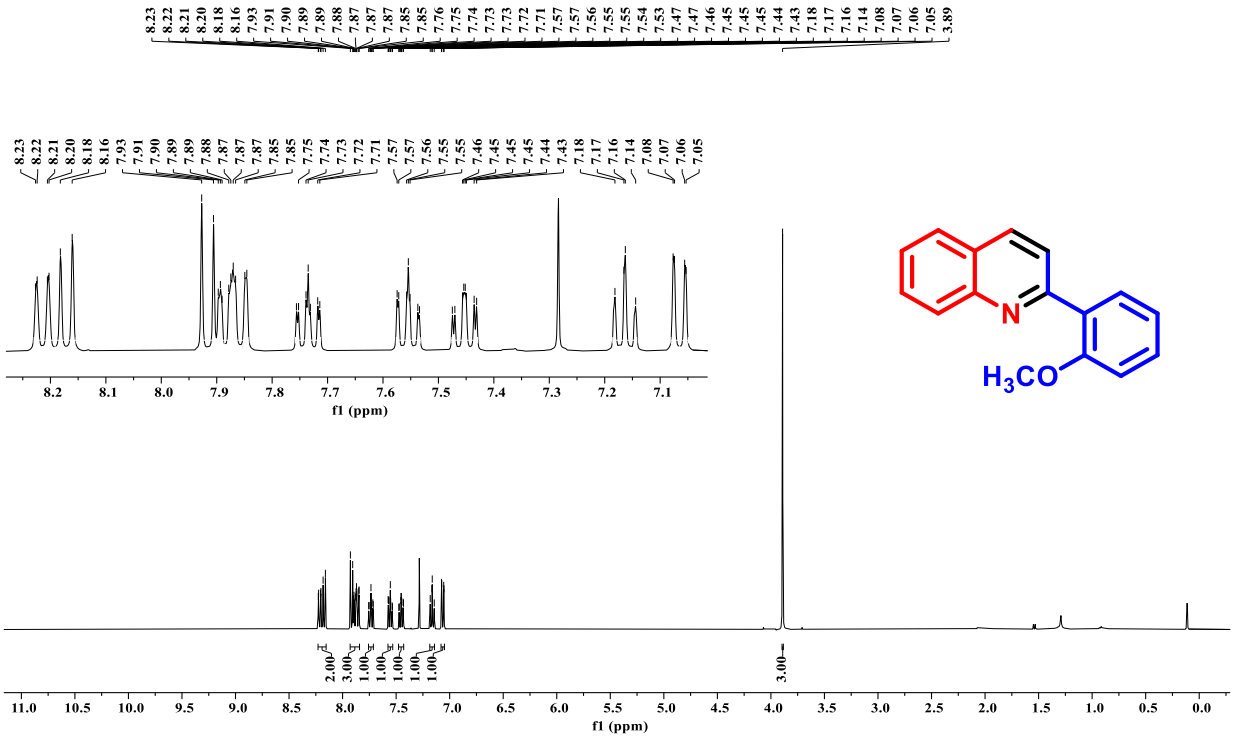


Fig. S43 ^{1}H NMR spectrum of **3m** in $CDCl_3$ (400 MHz).

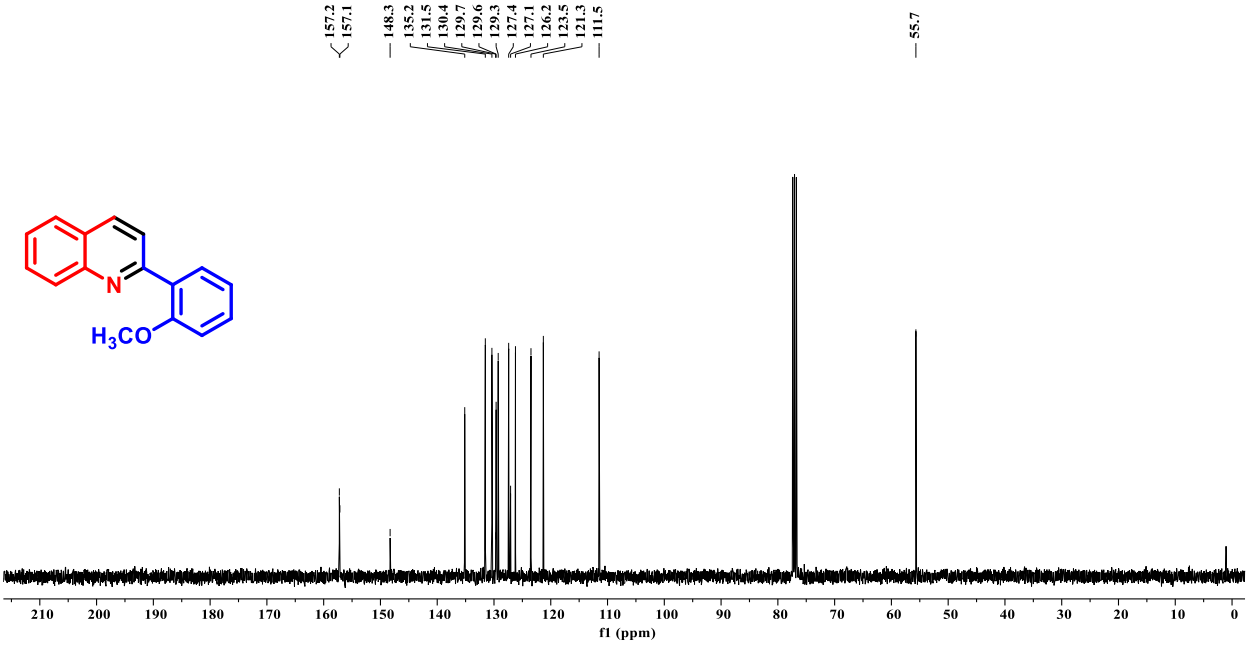


Fig. S44 $^{13}C\{^{1}H\}$ NMR spectrum of **3m** in $CDCl_3$ (101 MHz).

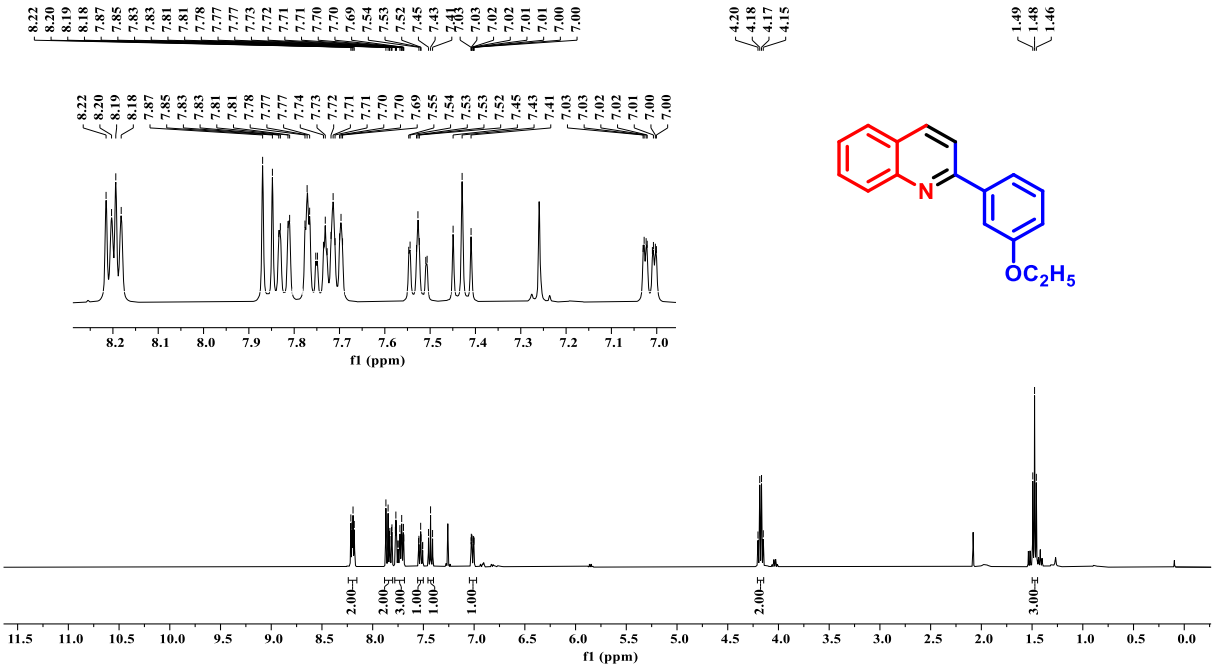


Fig. S45 ^{1}H NMR spectrum of **3n** in $CDCl_3$ (400 MHz).

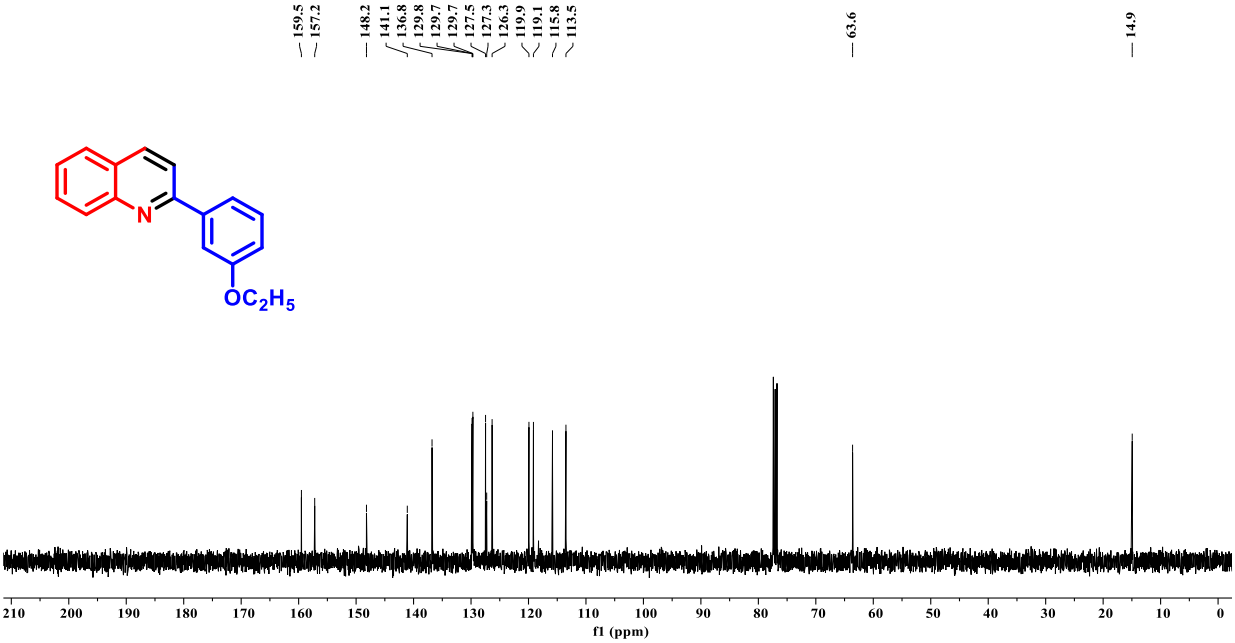


Fig. S46 $^{13}C\{^{1}H\}$ NMR spectrum of **3n** in $CDCl_3$ (101 MHz).

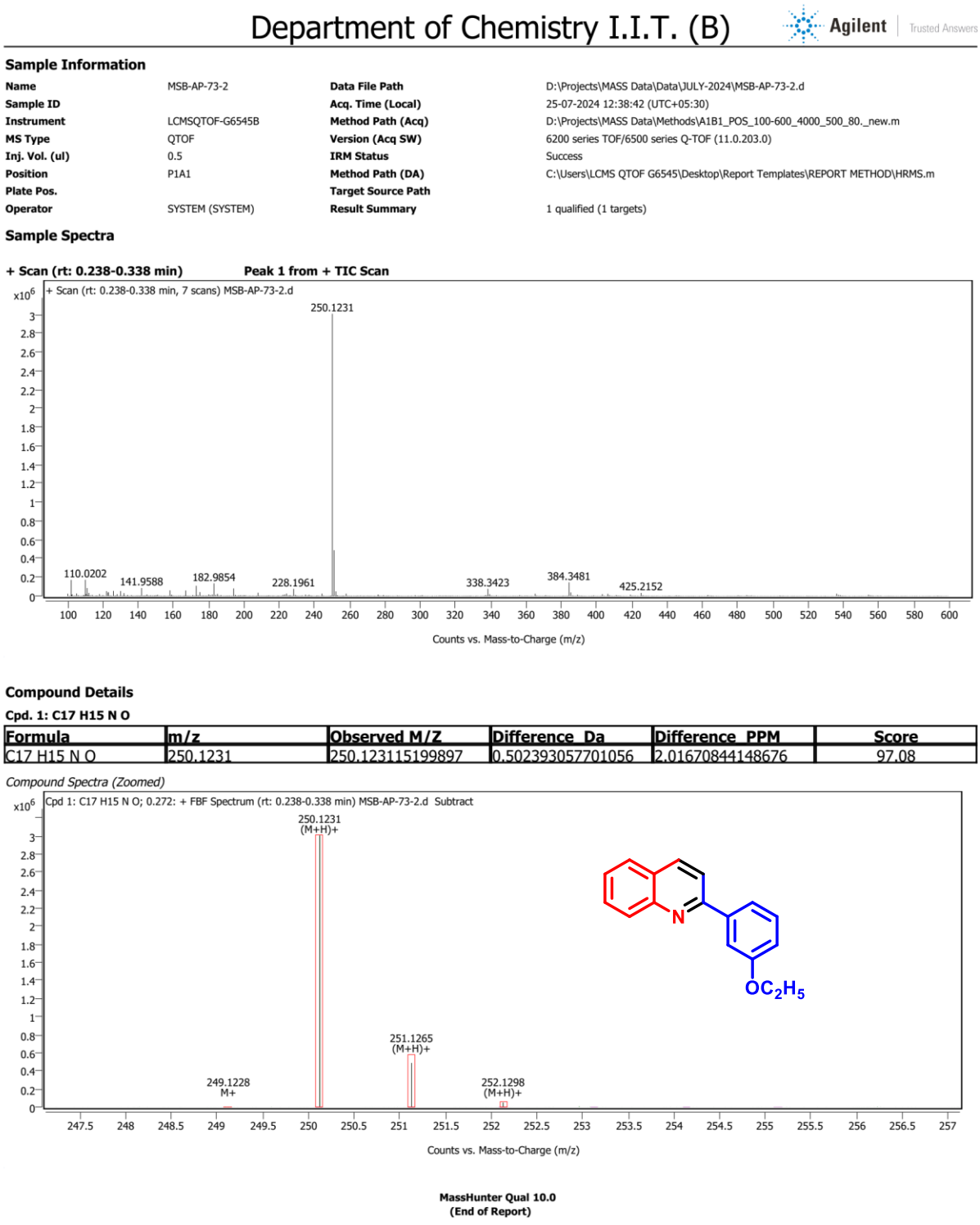


Fig. S47 HRMS spectrum of **3n**.

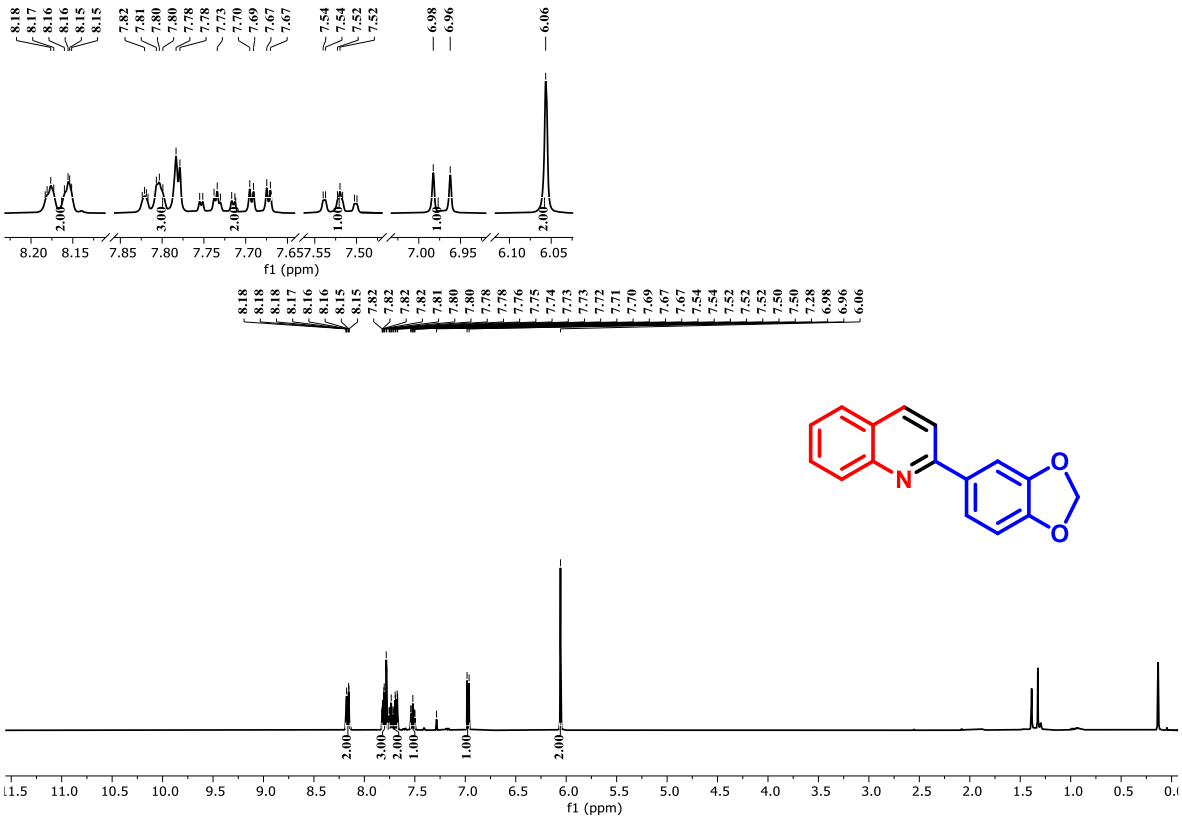


Fig. S48 ^{1}H NMR spectrum of **3o** in $CDCl_3$ (400 MHz).

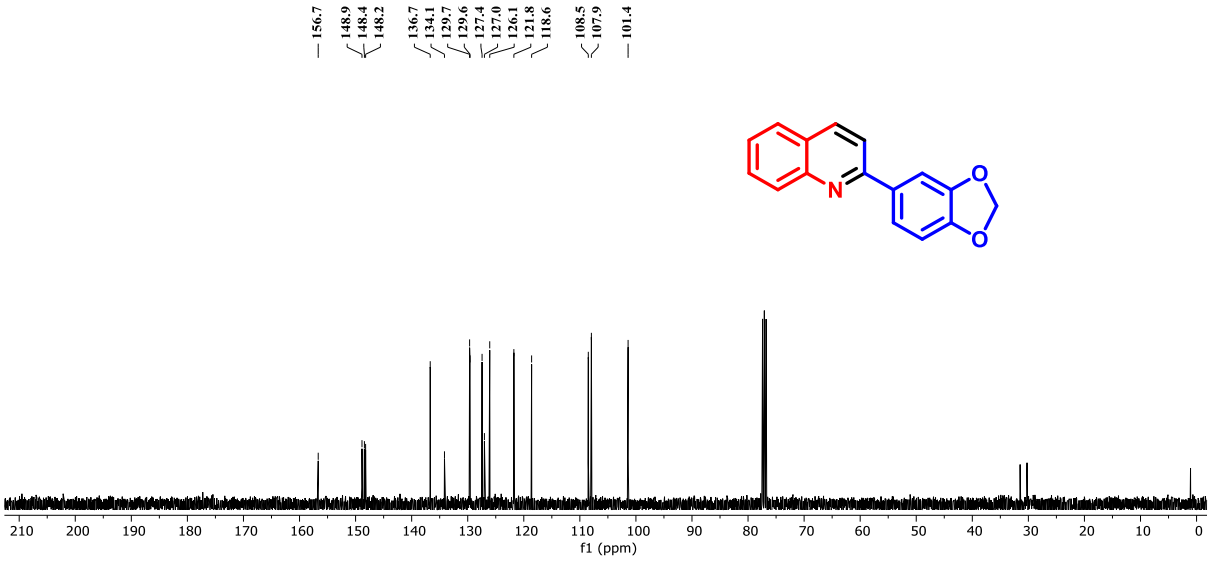


Fig. S49 $^{13}C\{^{1}H\}$ NMR spectrum of **3o** in $CDCl_3$ (101 MHz).

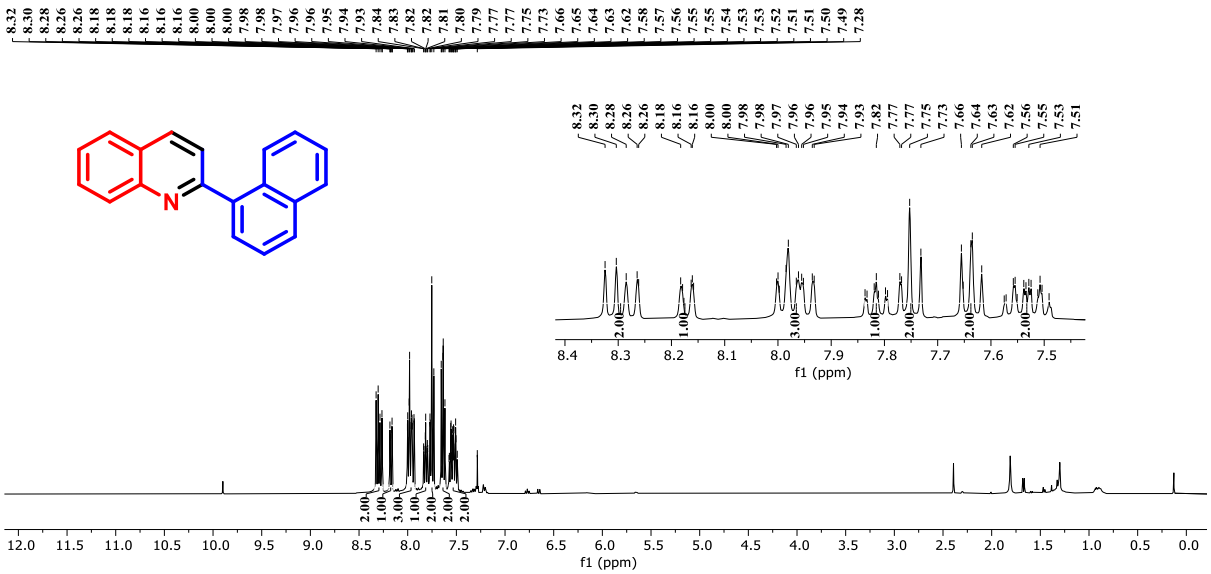


Fig. S50 ^{1}H NMR spectrum of **3p** in $CDCl_3$ (400 MHz).

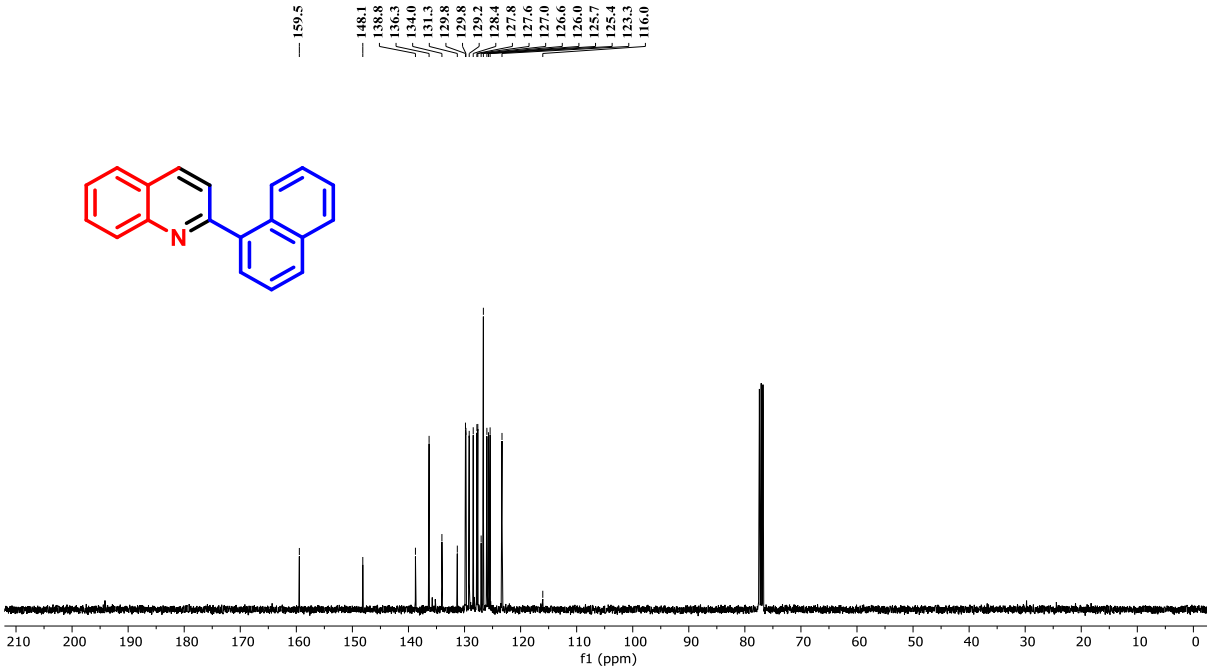


Fig. S51 $^{13}C\{^{1}H\}$ NMR spectrum of **3p** in $CDCl_3$ (101 MHz).

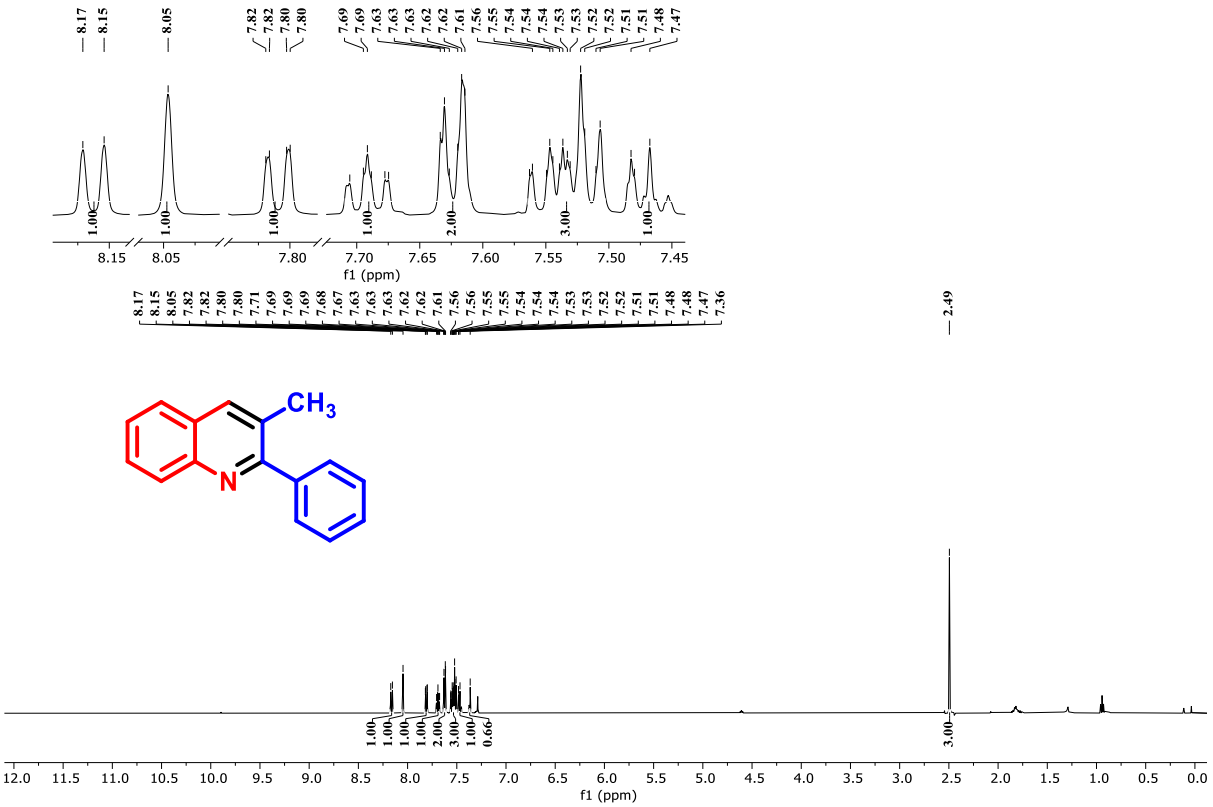


Fig. S52 ^{1}H NMR spectrum of **3r** in $CDCl_3$ (500 MHz).

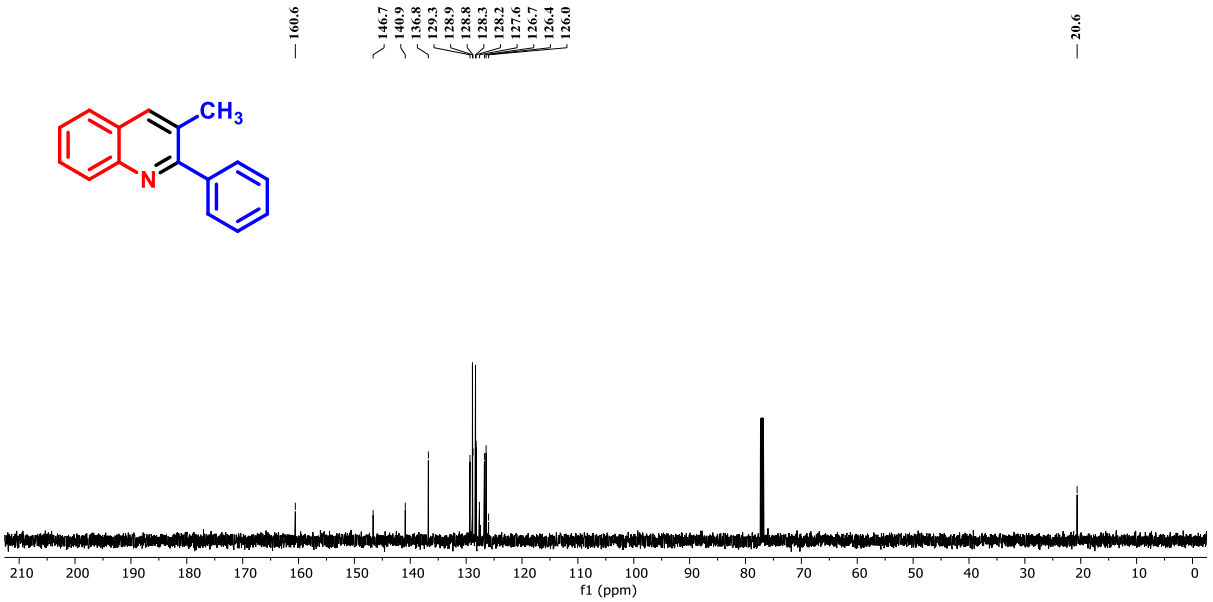


Fig. S53 $^{13}C\{^{1}H\}$ NMR spectrum of **3r** in $CDCl_3$ (126 MHz).

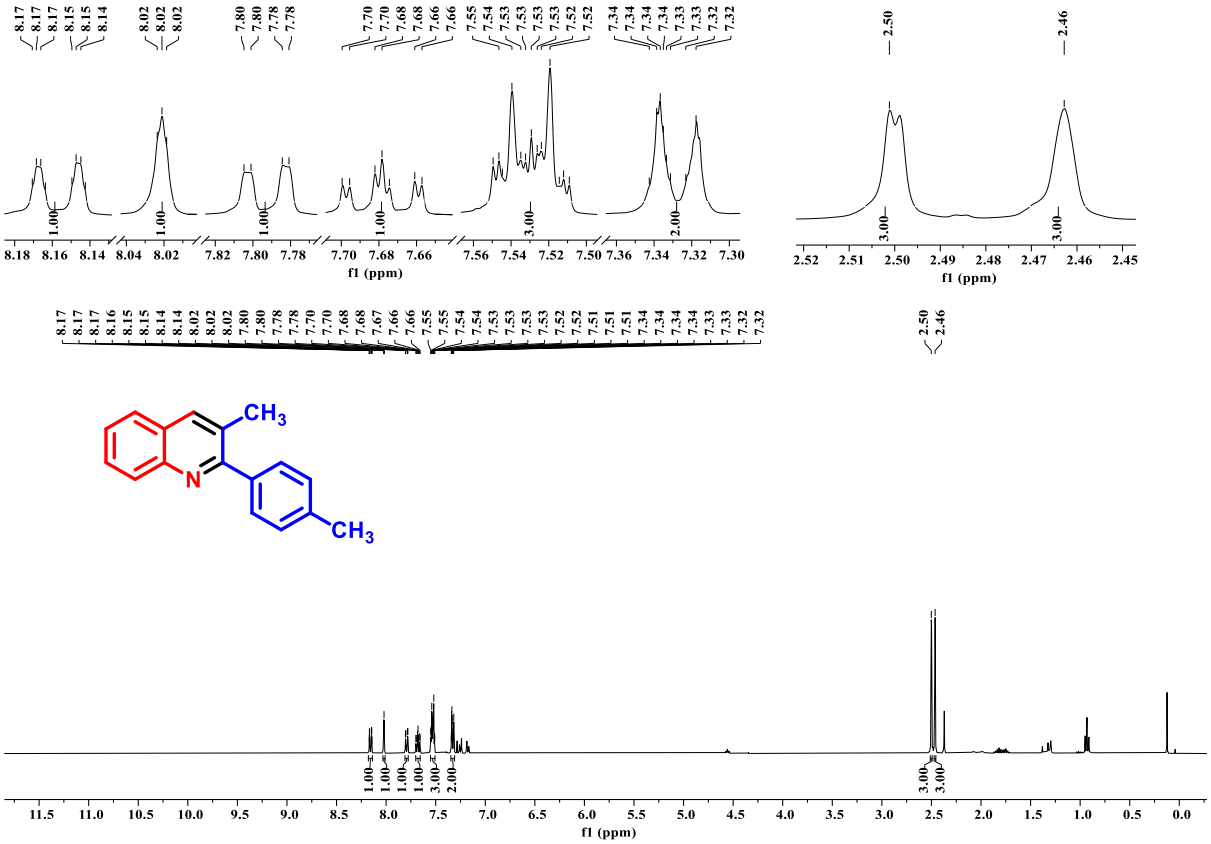


Fig. S54 ^{1}H NMR spectrum of **3s** in $CDCl_3$ (400 MHz).

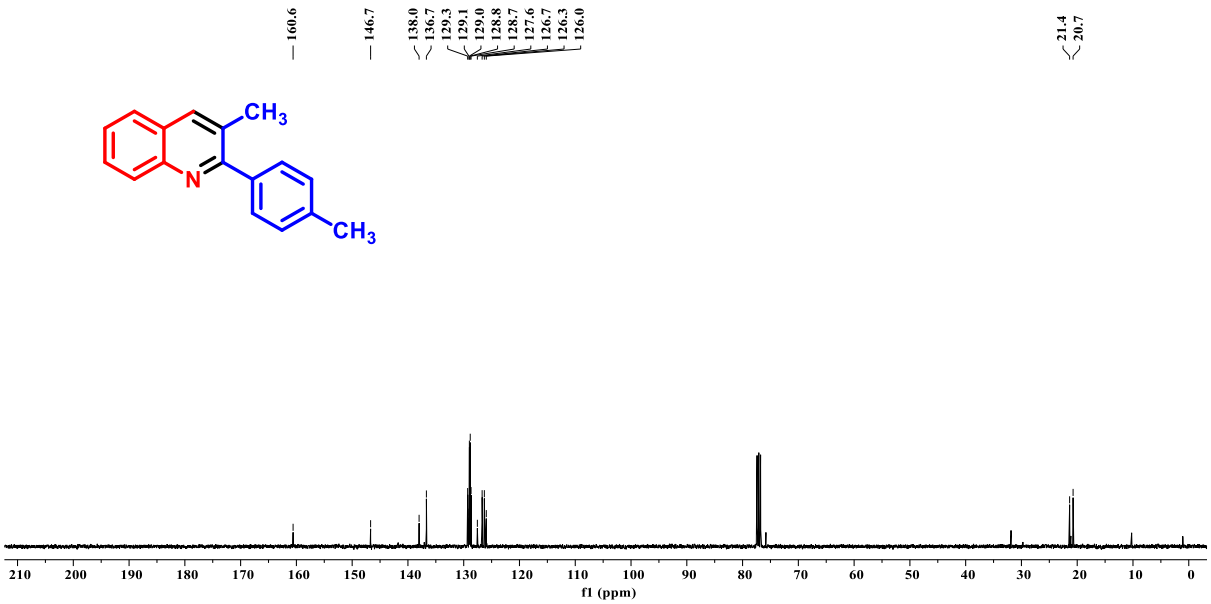


Fig. S55 $^{13}C\{^{1}H\}$ NMR spectrum of **3s** in $CDCl_3$ (101 MHz).

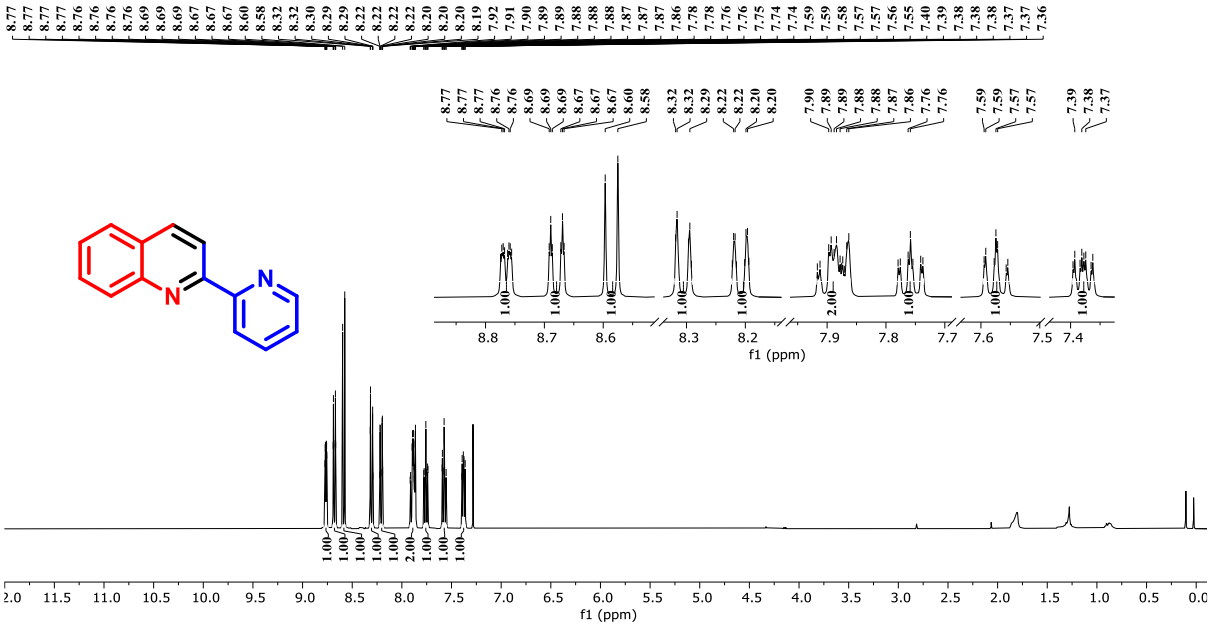


Fig. S56 ^{1}H NMR spectrum of **3t** in $CDCl_3$ (400 MHz).

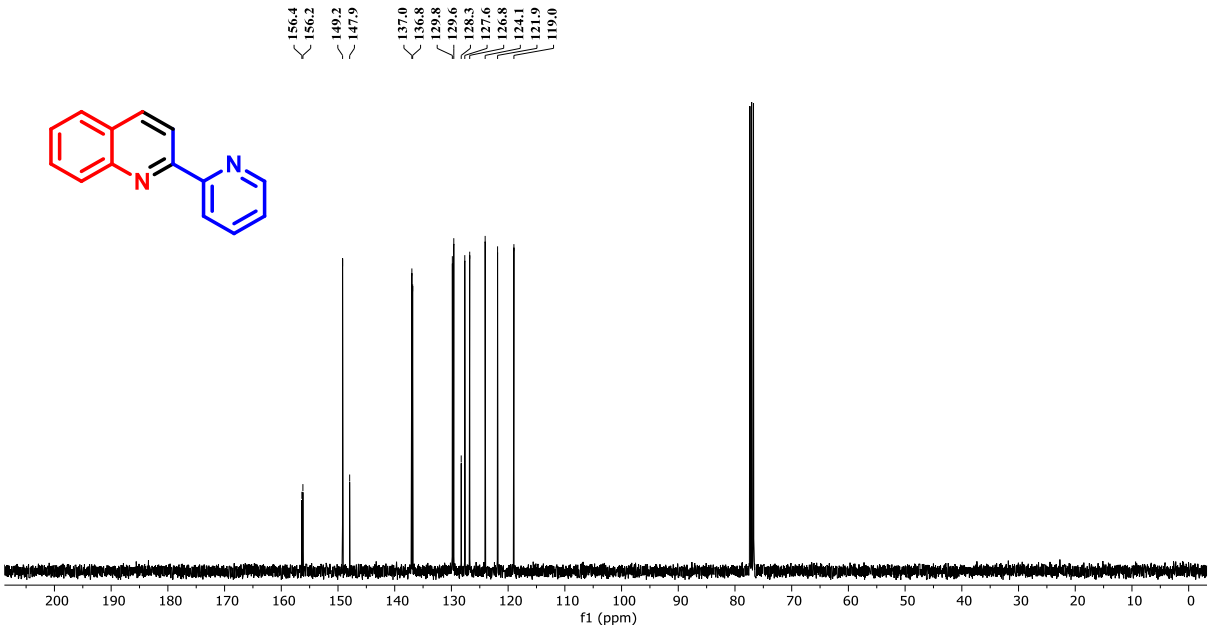


Fig. S57 $^{13}C\{^{1}H\}$ NMR spectrum of **3t** in $CDCl_3$ (101 MHz).

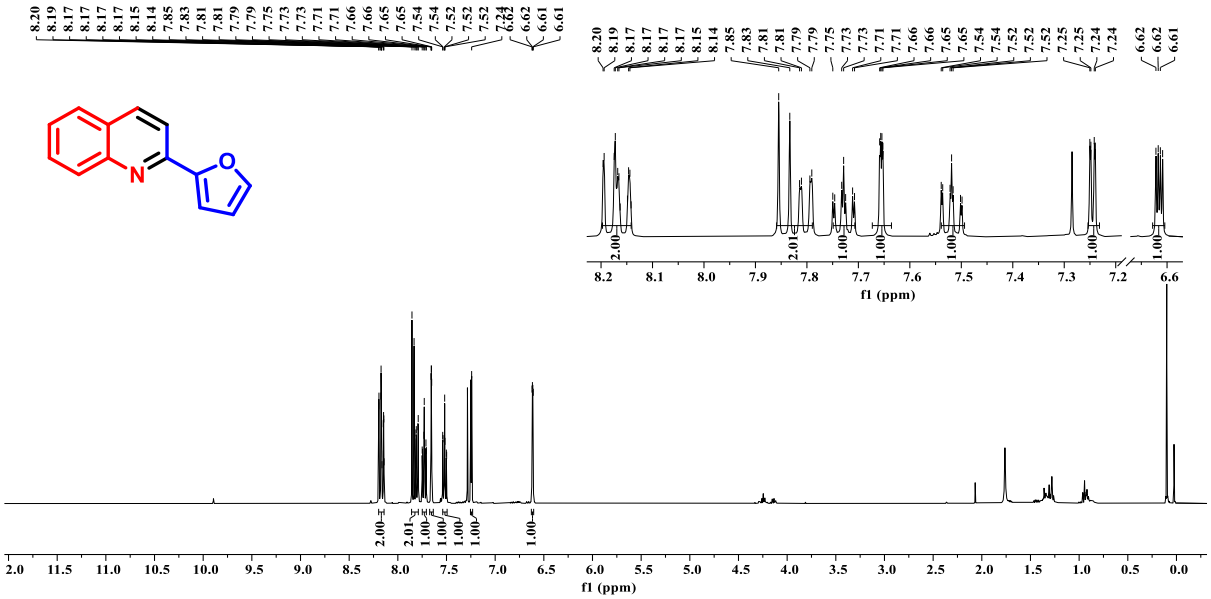


Fig. S58 ^{1}H NMR spectrum of **3u** in $CDCl_3$ (400 MHz).

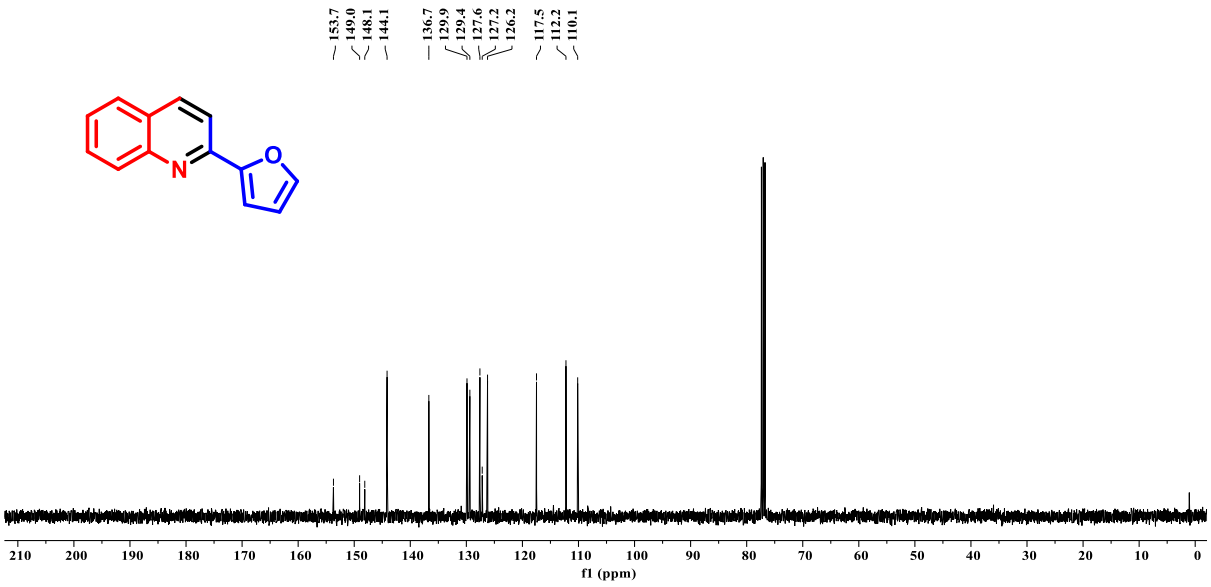


Fig. S59 $^{13}C\{^{1}H\}$ NMR spectrum of **3u** in $CDCl_3$ (101 MHz).

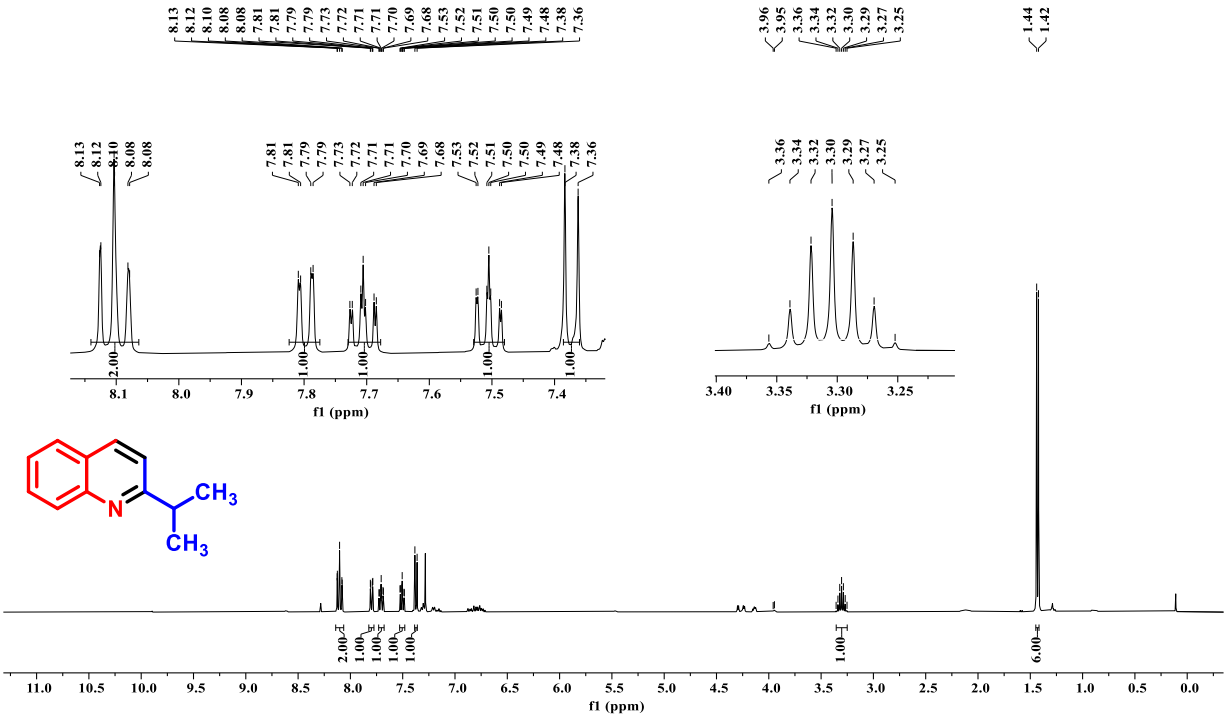


Fig. S60 ^{1}H NMR spectrum of **3v** in $CDCl_3$ (400 MHz).

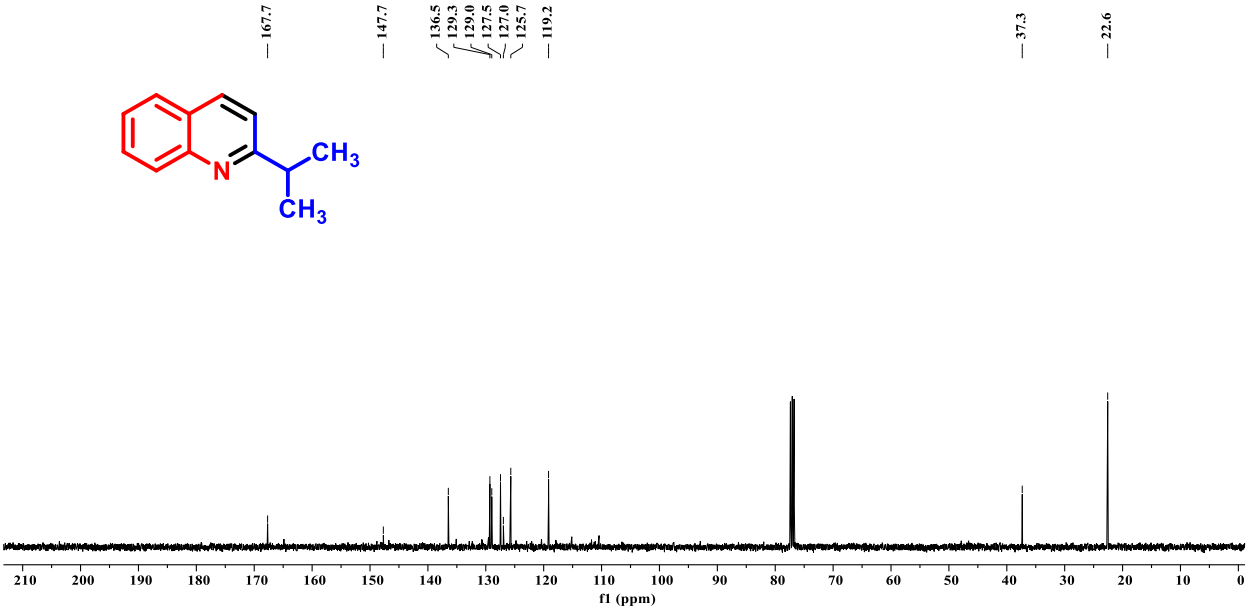


Fig. S61 ^{13}C{^{1}H} NMR spectrum of **3v** in $CDCl_3$ (101 MHz).

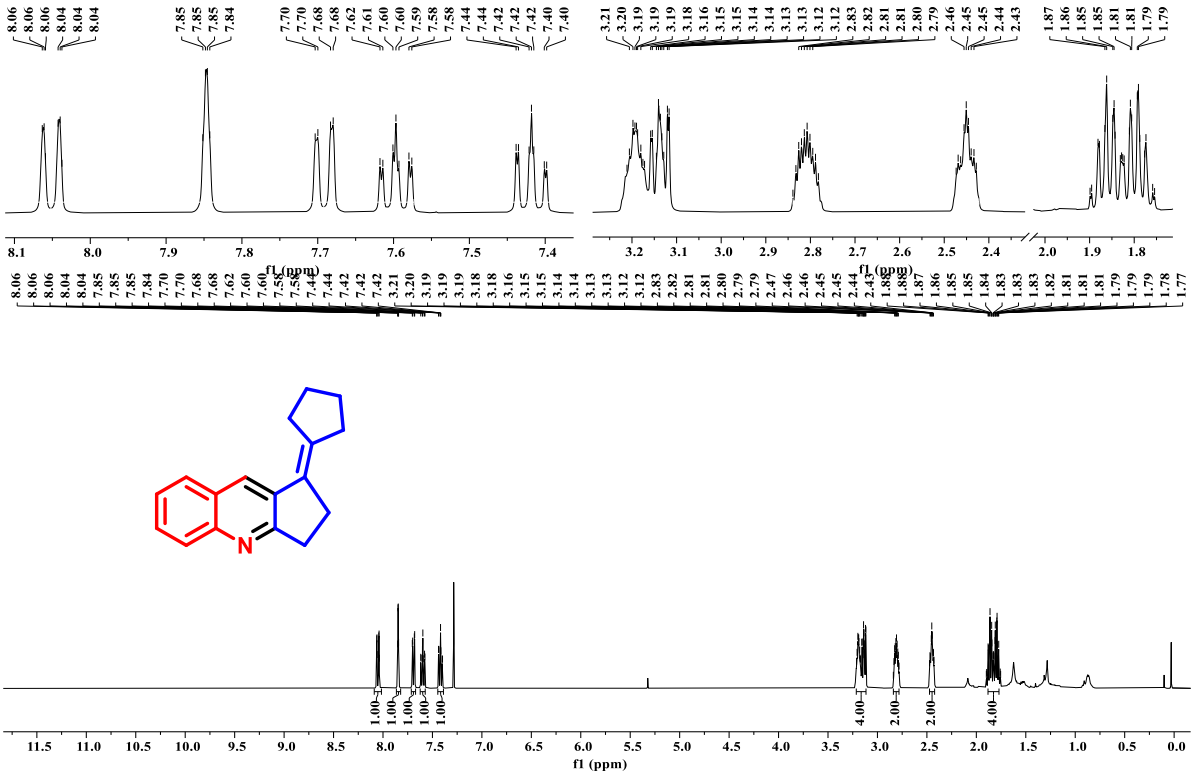


Fig. S62 ^{1}H NMR spectrum of **3w** in $CDCl_3$ (400 MHz).

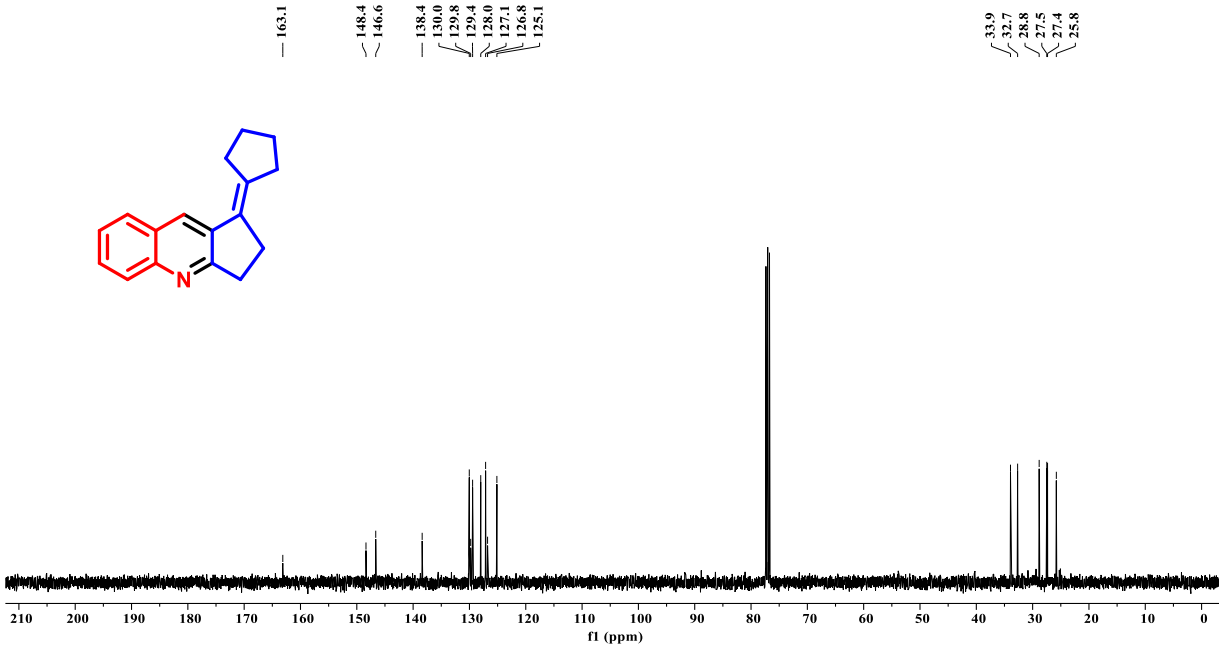


Fig. S63 $^{13}C\{^{1}H\}$ NMR spectrum of **3w** in $CDCl_3$ (101 MHz).

Department of Chemistry I.I.T. (B)

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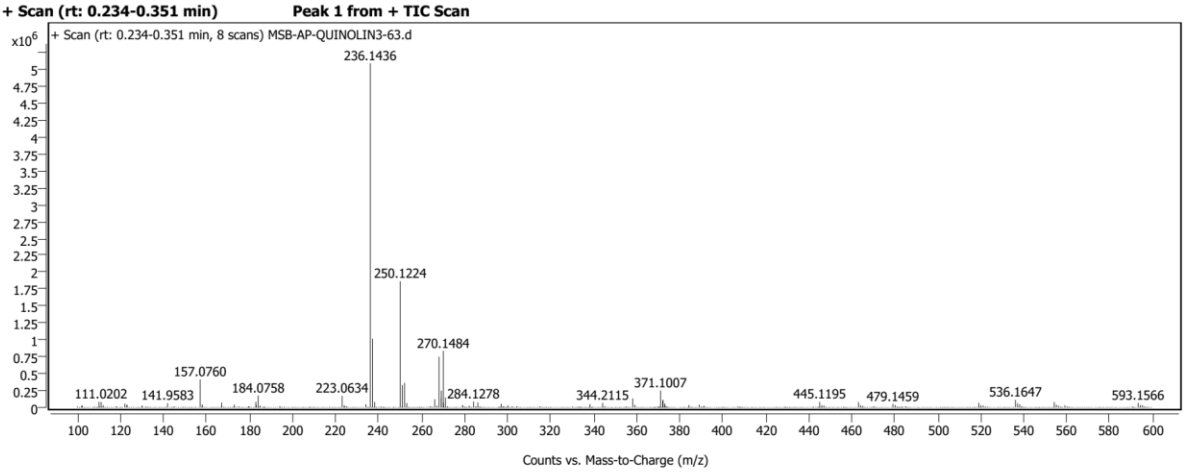
Sample Information

Name	MSB-AP-QUINOLIN3-63	**Data File Path**	D:\Projects\MASS Data\Data\JULY-2024\MSB-AP-QUINOLIN3-63.d
Sample ID		**Acq. Time (Local)**	02-07-2024 17:20:13 (UTC+05:30)
Instrument	LCMSQTOF-G6545B	**Method Path (Acq)**	D:\Projects\MASS Data\Methods\A1B1_POS_100-600_4000_500_80._new.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.203.0)
Inj. Vol. (ul)	0.5	**IRM Status**	Success
Position	P1A1	**Method Path (DA)**	C:\Users\LCMS QTOF G6545\Desktop\Report Templates\REPORT METHOD\HRMS.m
Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.234-0.351 min) **Peak 1 from + TIC Scan**

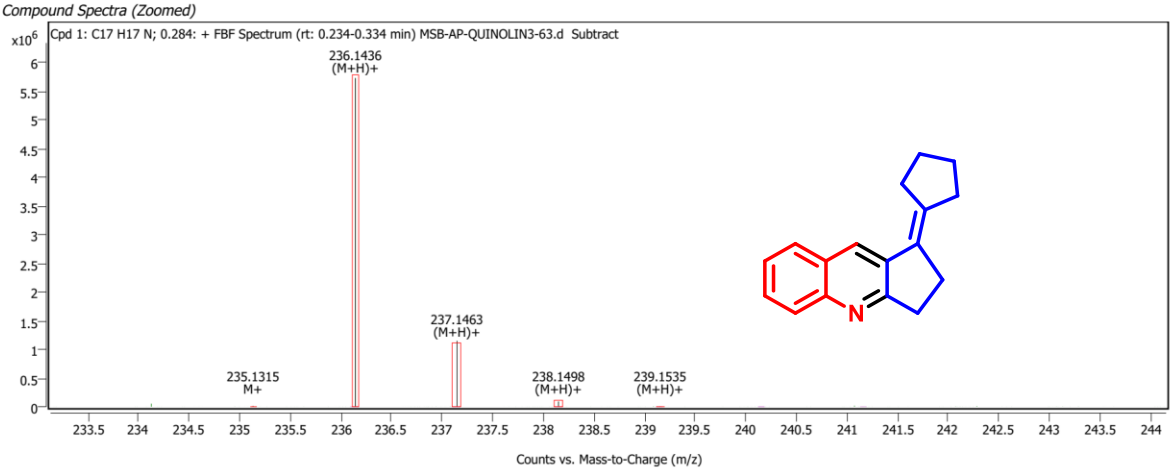


Compound Details

Cpd. 1: C17 H17 N

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C17 H17 N	236.1436	236.143622937519	0.137440141372736	0.584513146369025	99.00

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Fig. S64 HRMS spectrum of **3w**.

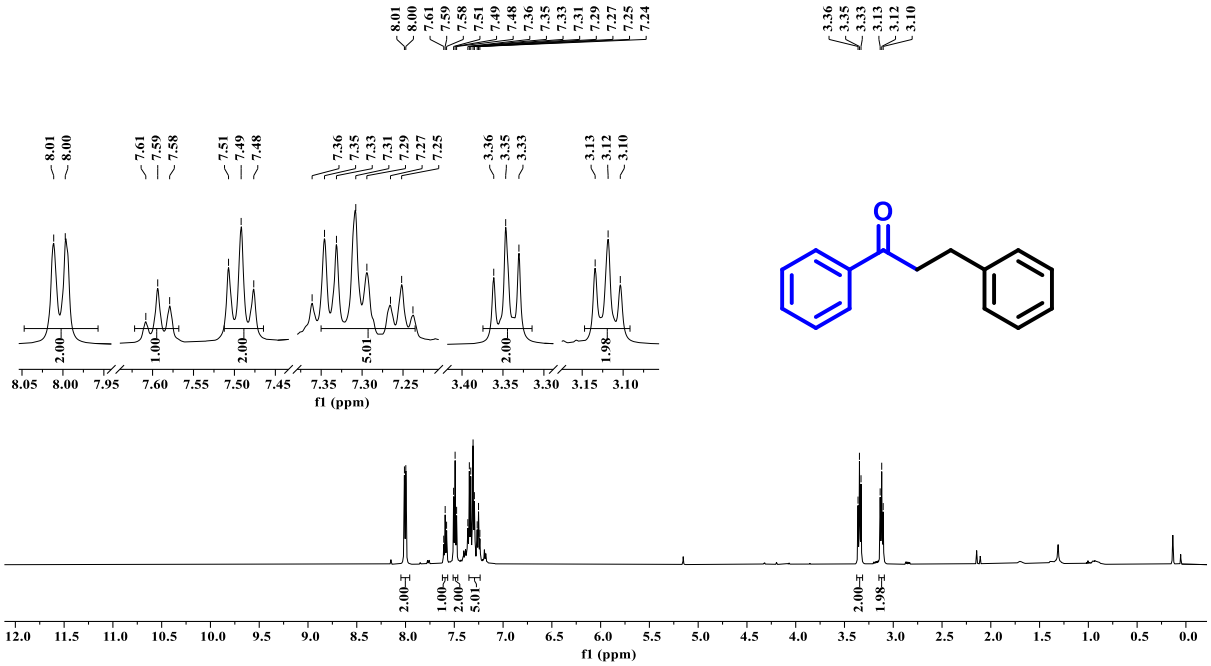


Fig. S65 ^{1}H NMR spectrum of **5a** in $CDCl_3$ (500 MHz).

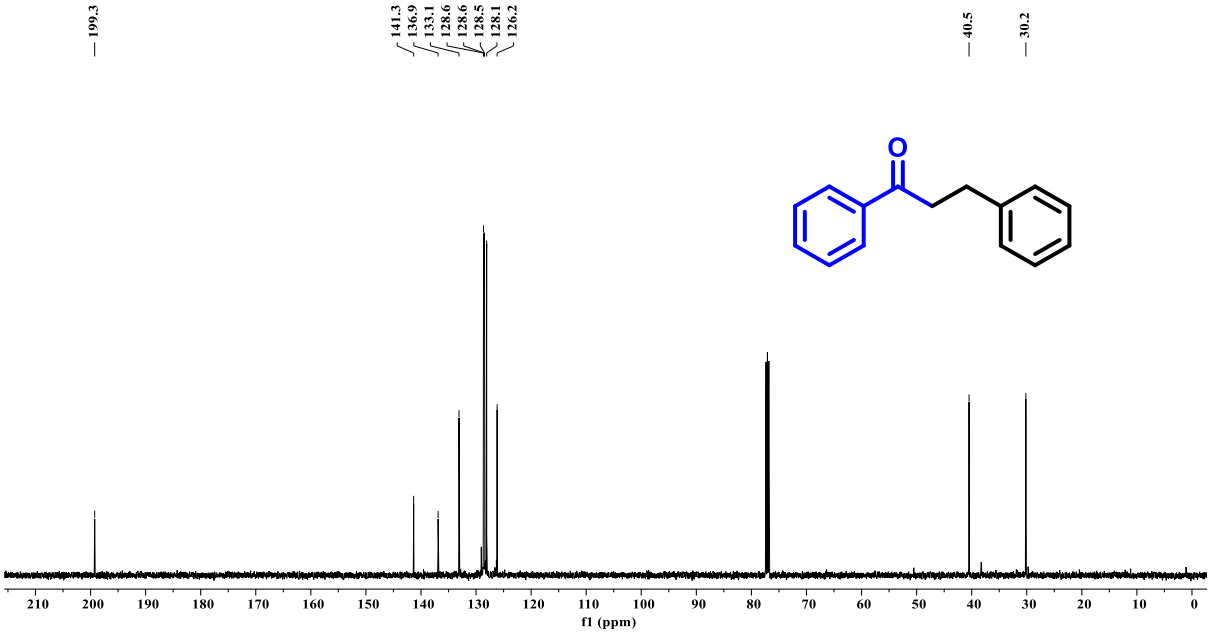


Fig. S66 $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ (126 MHz).

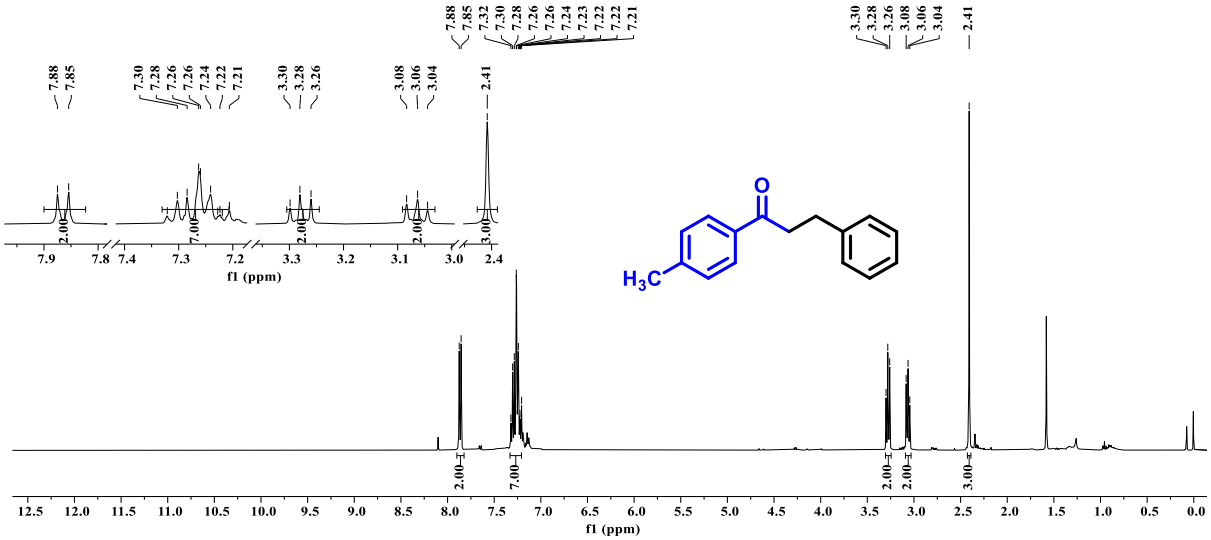


Fig. S67 ^{1}H NMR spectrum of **5b** in $CDCl_3$ (400 MHz).

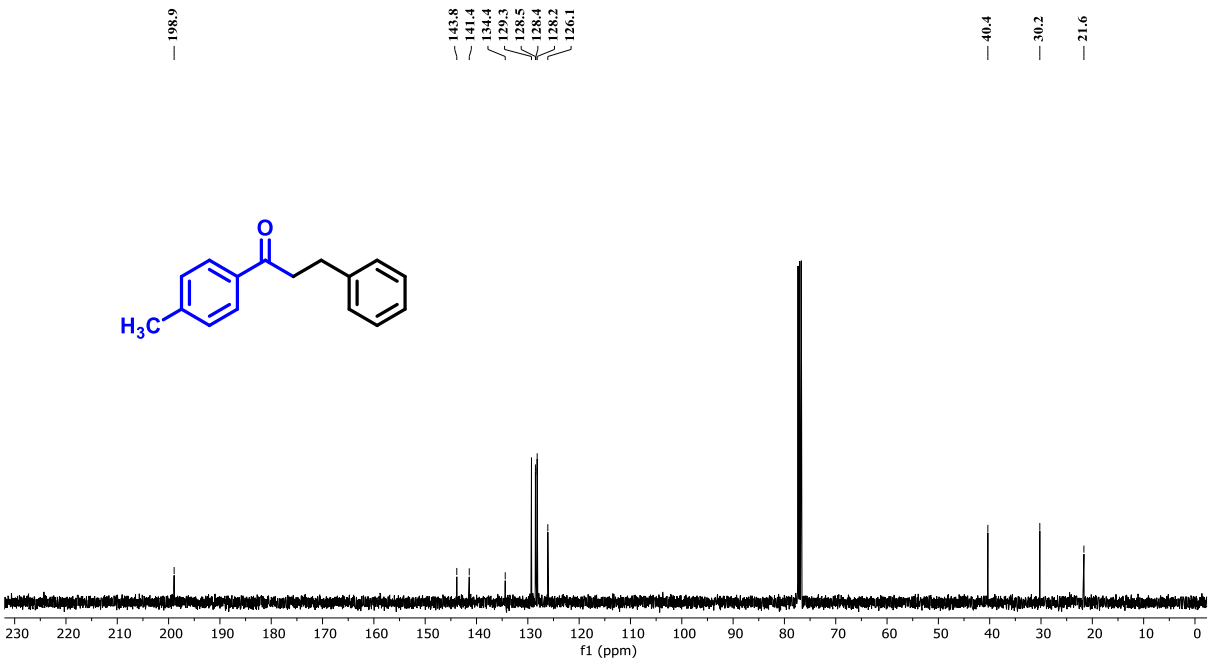


Fig. S68 $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$ (101 MHz).

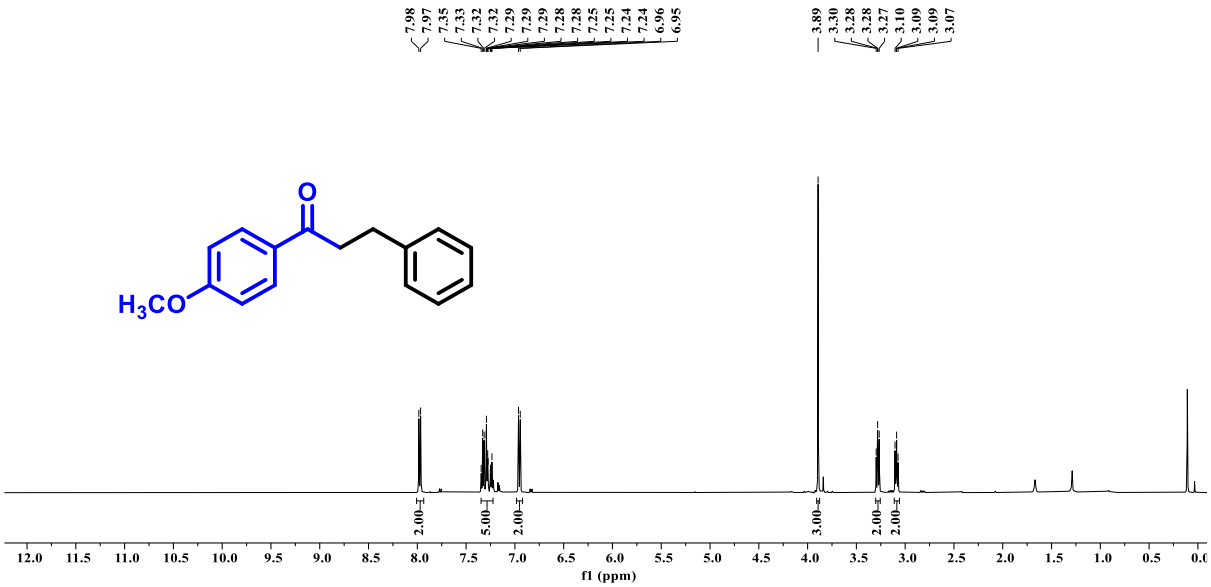


Fig. S69 ^{1}H NMR spectrum of **5c** in $CDCl_3$ (500 MHz).

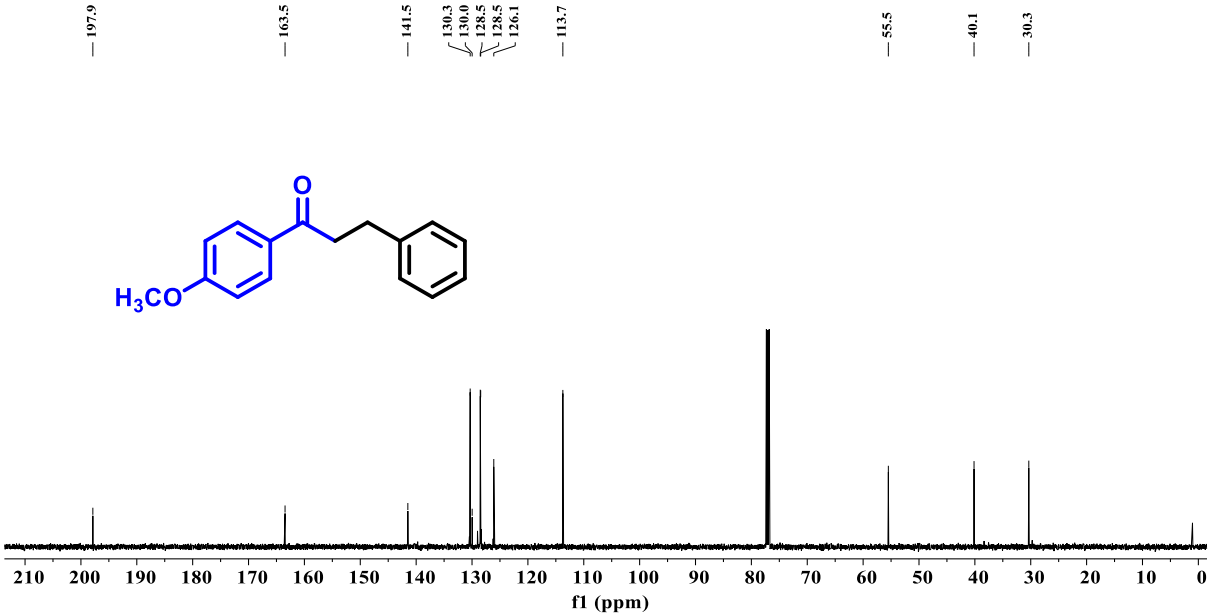


Fig. S70 ^{13}C{^{1}H} NMR spectrum of **5c** in $CDCl_3$ (126 MHz).

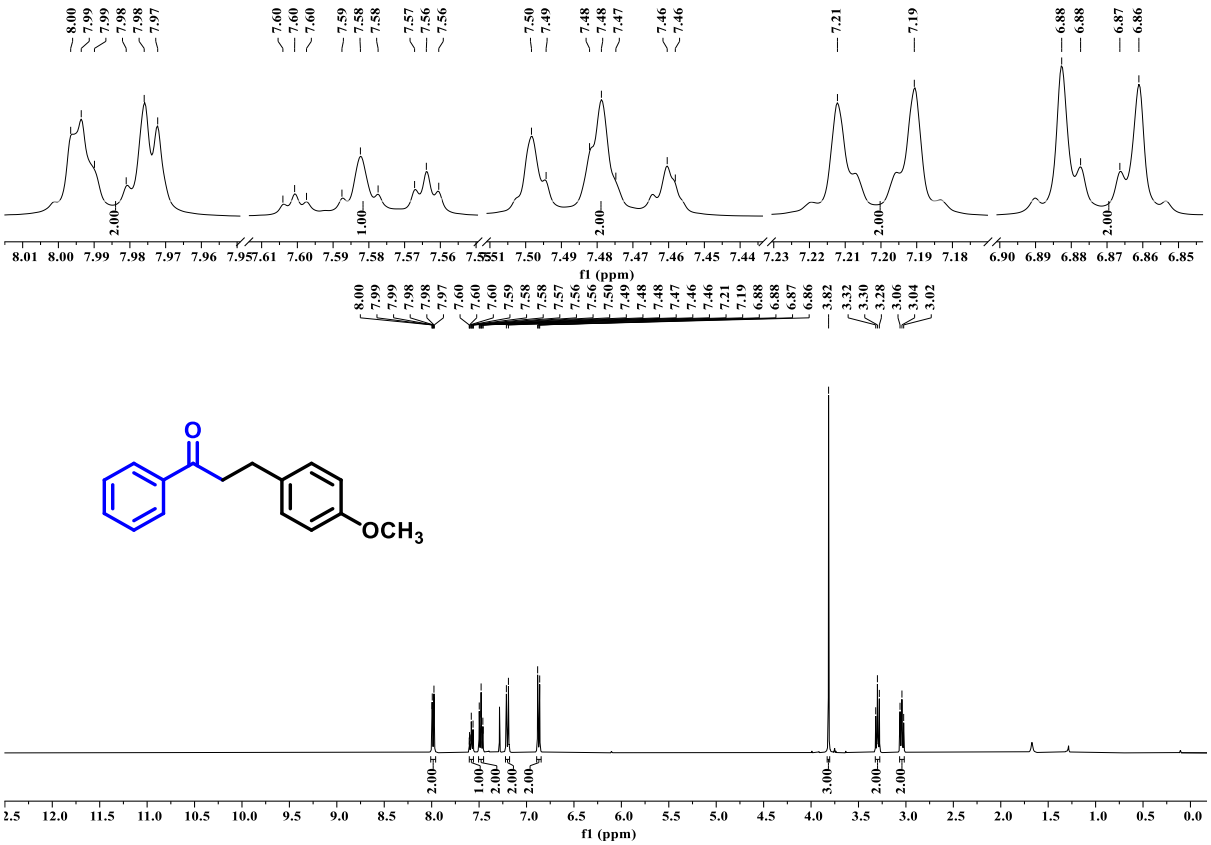


Fig. S71 ^{1}H NMR spectrum of **5d** in $CDCl_3$ (400 MHz).

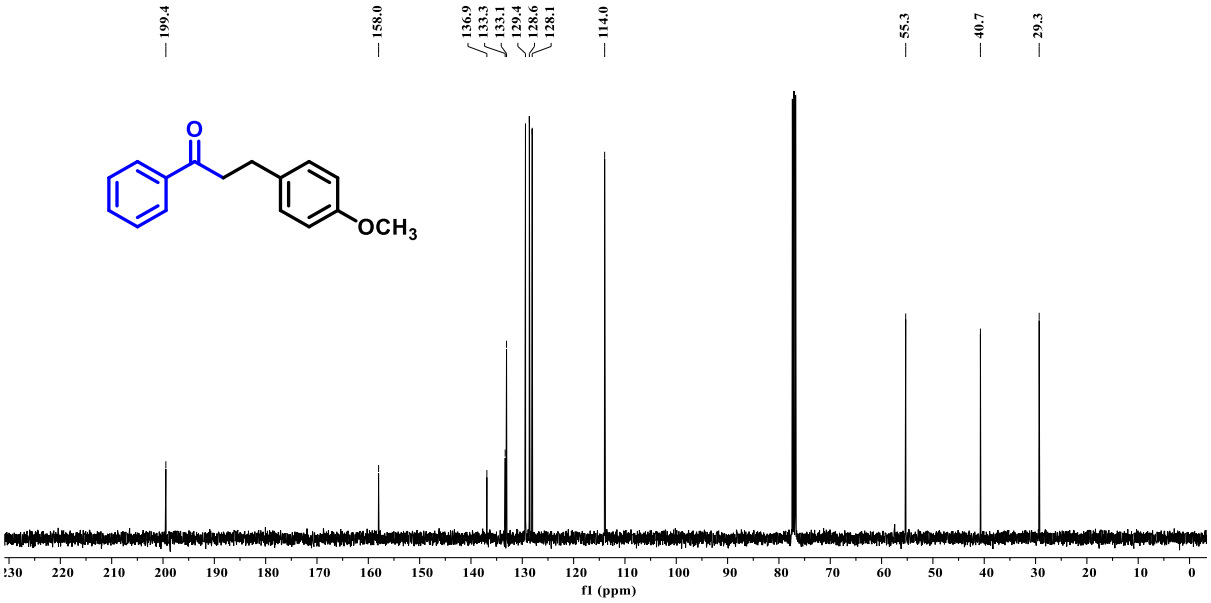


Fig. S72 ^{13}C{^{1}H} NMR spectrum of **5d** in $CDCl_3$ (101 MHz).

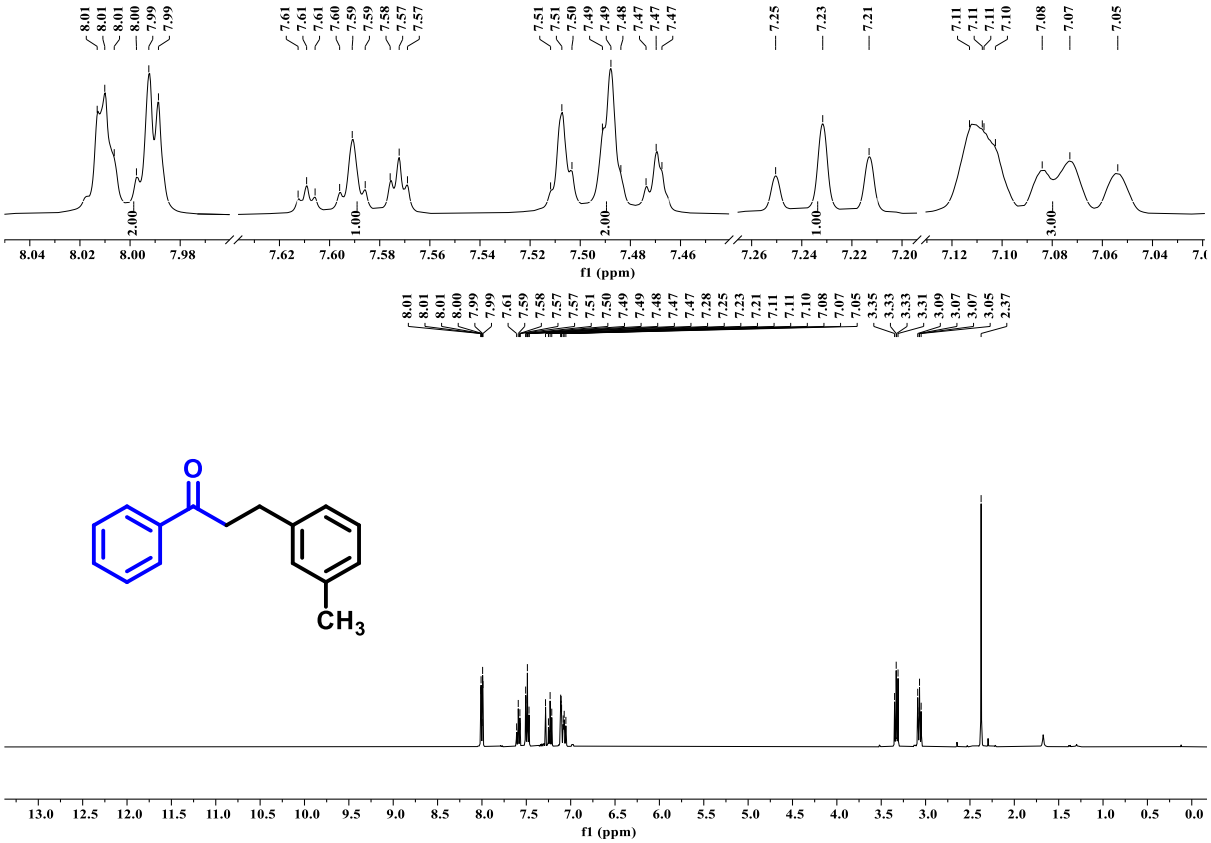


Fig. S73 ^{1}H NMR spectrum of **5e** in $CDCl_3$ (400 MHz).

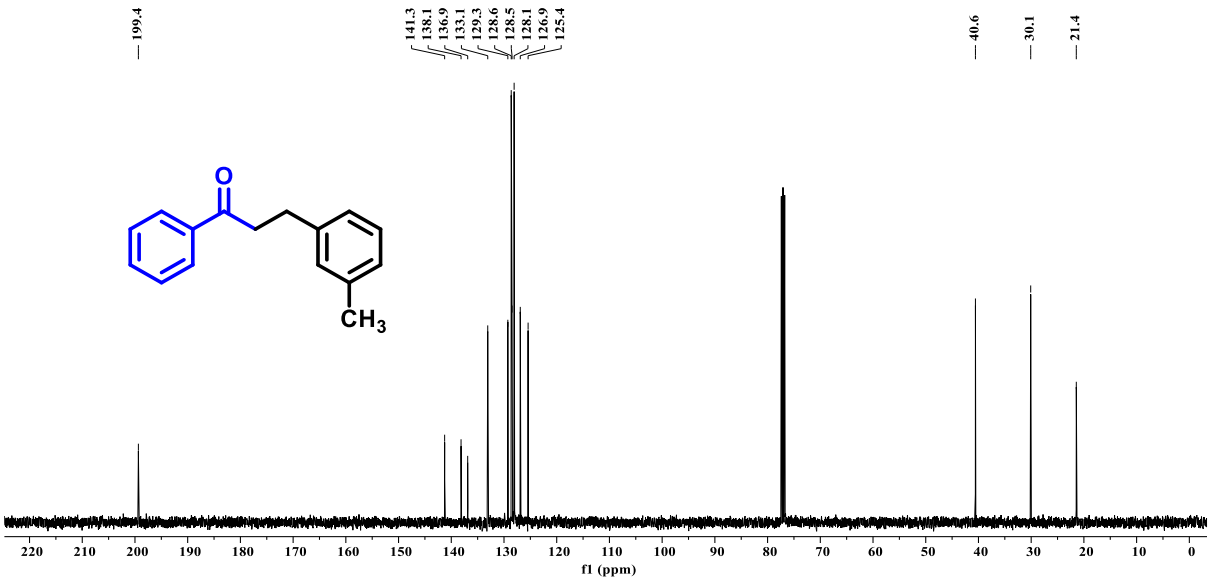


Fig. S74 $^{13}C\{^{1}H\}$ NMR spectrum of **5e** in $CDCl_3$ (101 MHz).

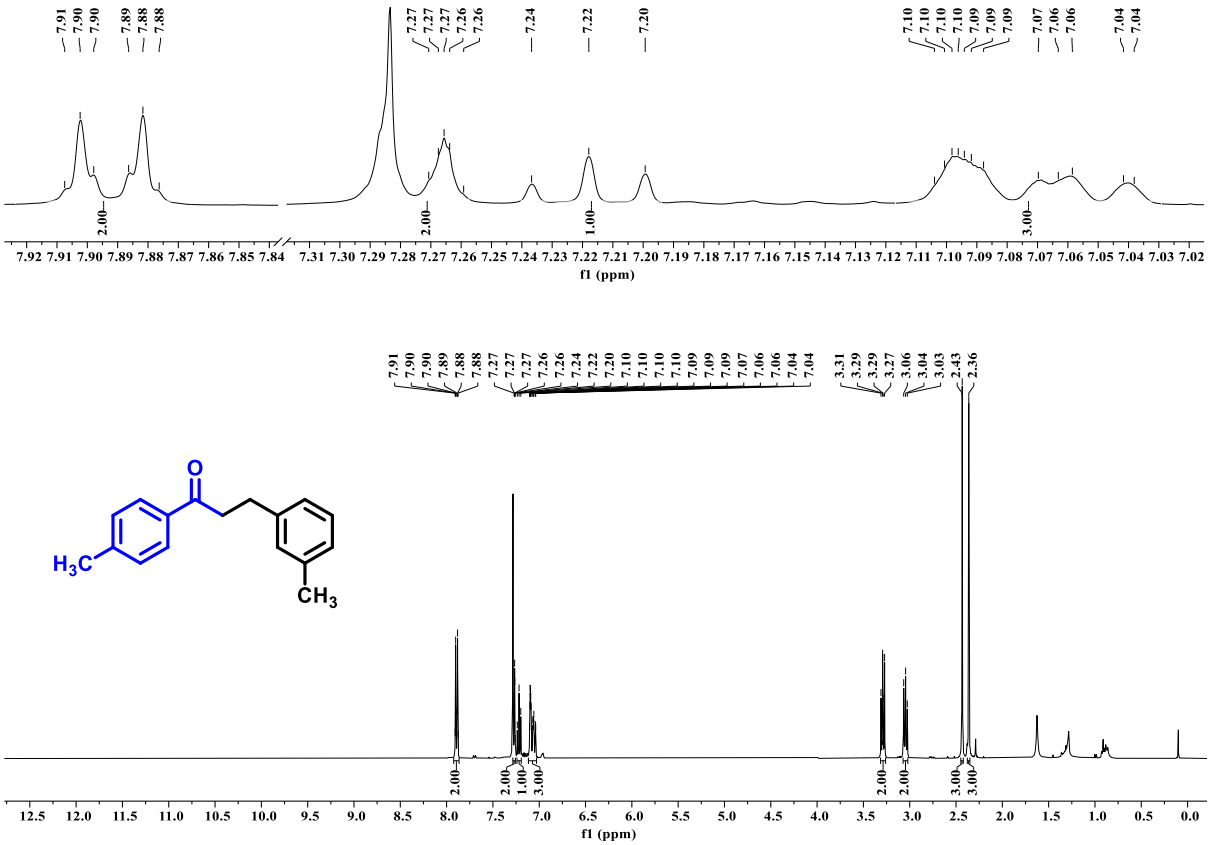


Fig. S75 ^{1}H NMR spectrum of **5f** in $CDCl_3$ (400 MHz).

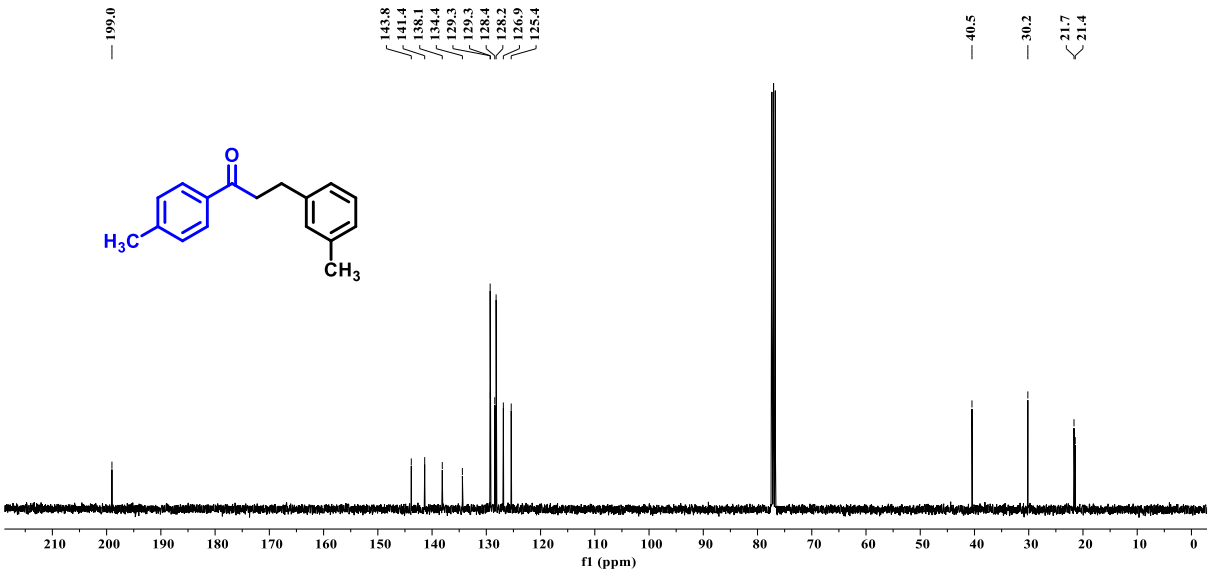


Fig. S76 $^{13}C\{^{1}H\}$ NMR spectrum of **5f** in $CDCl_3$ (101 MHz).

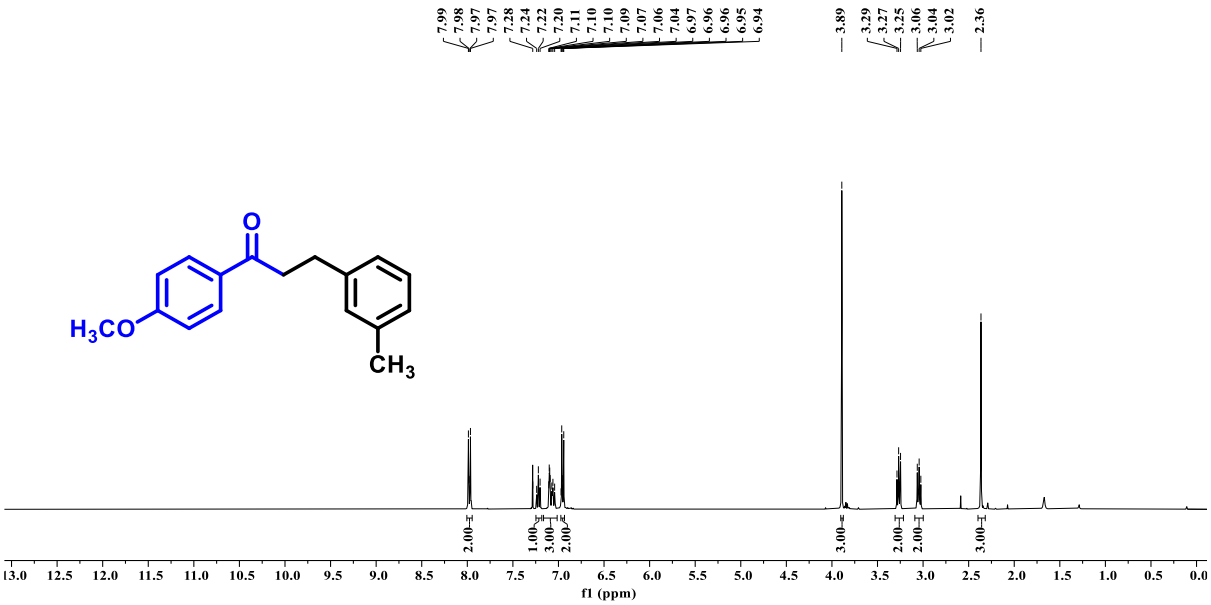


Fig. S77 ^{1}H NMR spectrum of **5g** in $CDCl_3$ (400 MHz).

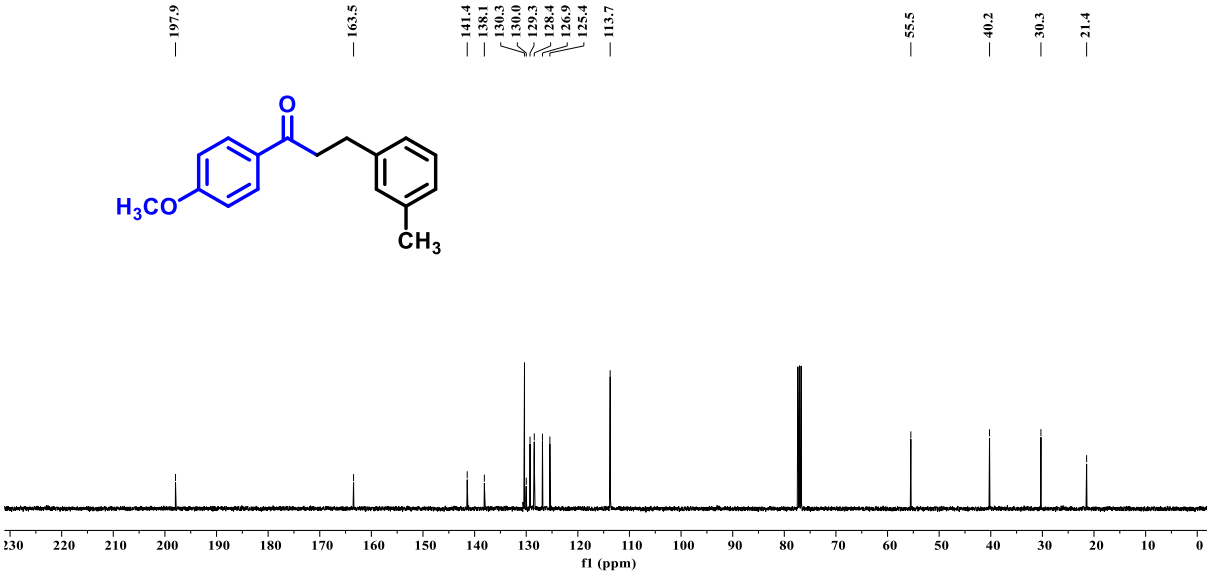


Fig. S78 $^{13}C\{^{1}H\}$ NMR spectrum of **5g** in $CDCl_3$ (101 MHz).

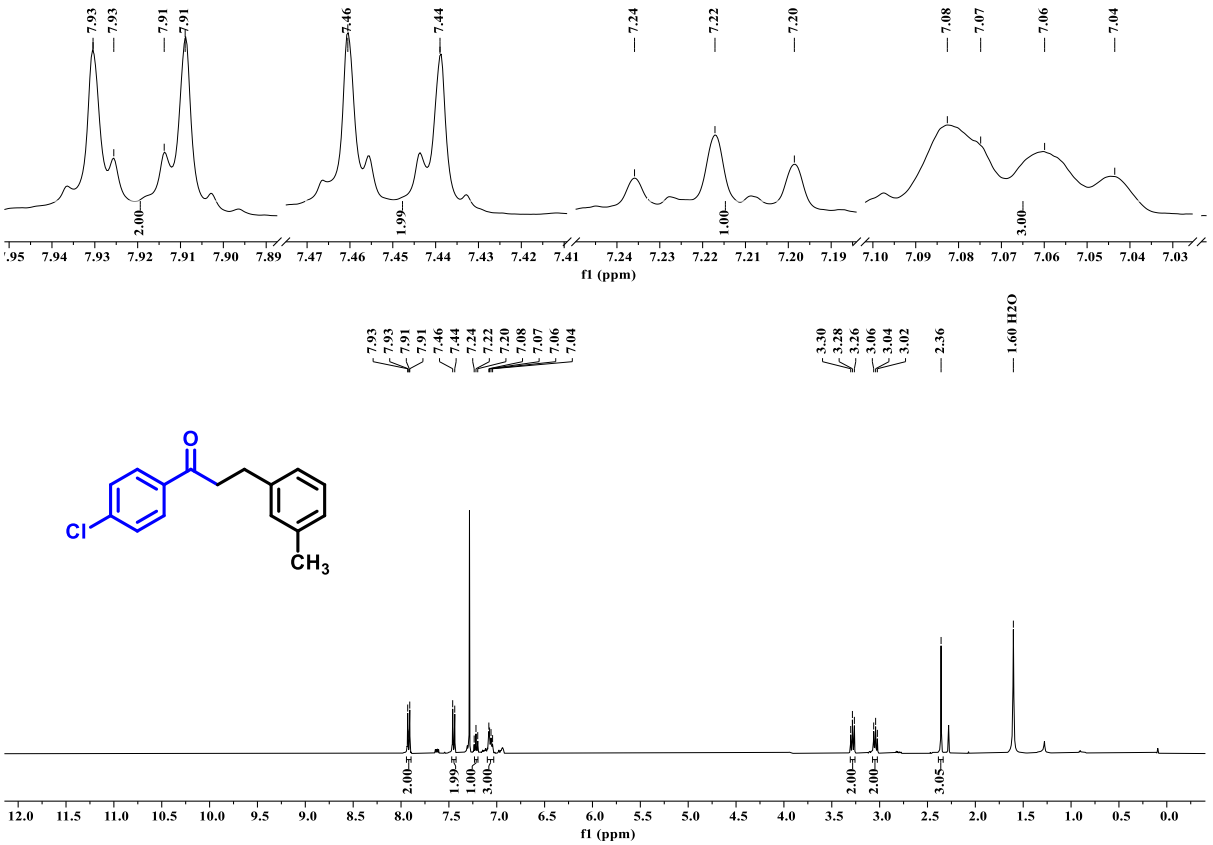


Fig. S79 ^{1}H NMR spectrum of **5h** in $CDCl_3$ (400 MHz).

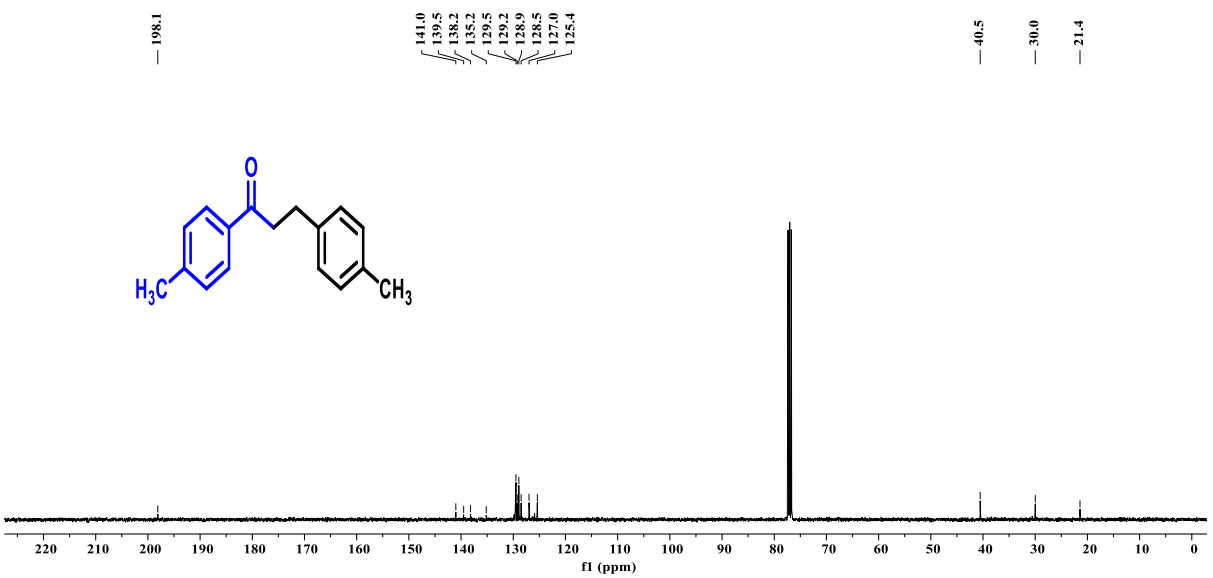


Fig. S80 ^{13}C{^{1}H} NMR spectrum of **5h** in $CDCl_3$ (101 MHz).

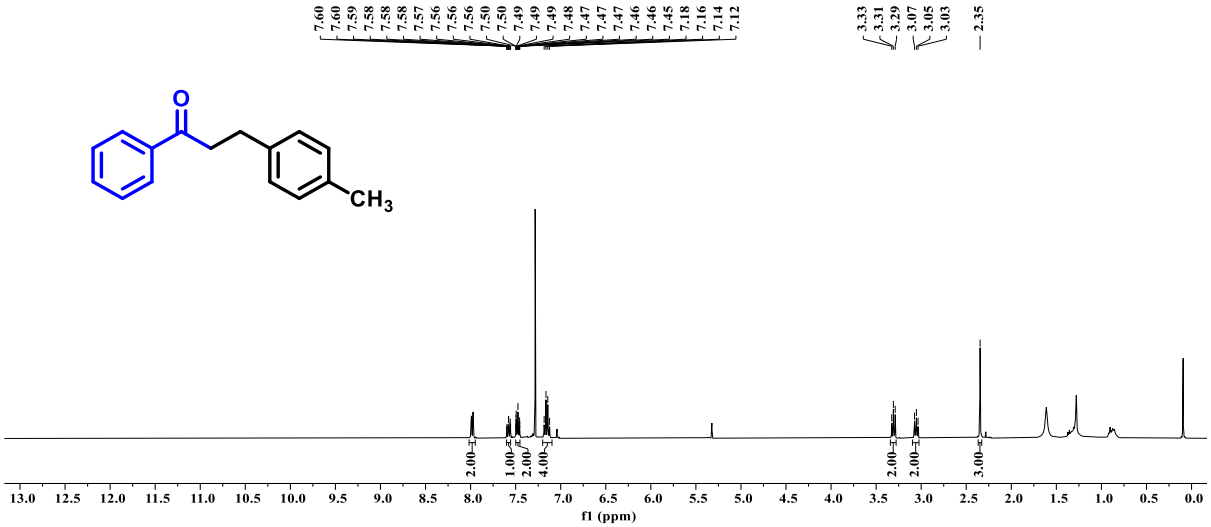


Fig. S81 ^{1}H NMR spectrum of **5i** in $CDCl_3$ (400 MHz).

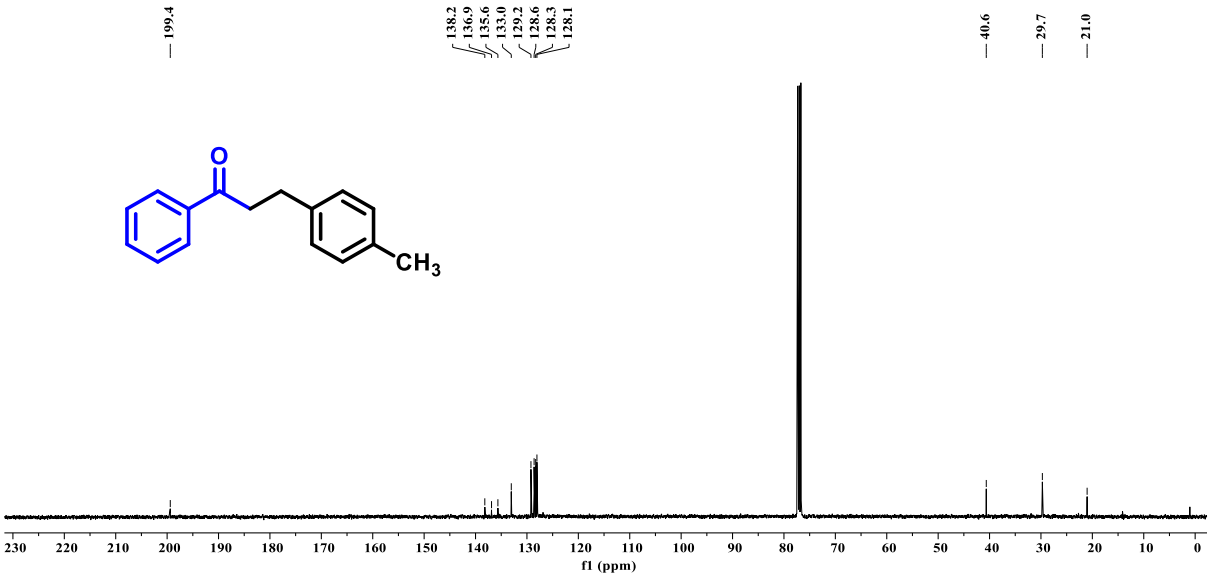


Fig. S82 ^{13}C{^{1}H} NMR spectrum of **5i** in $CDCl_3$ (101 MHz).

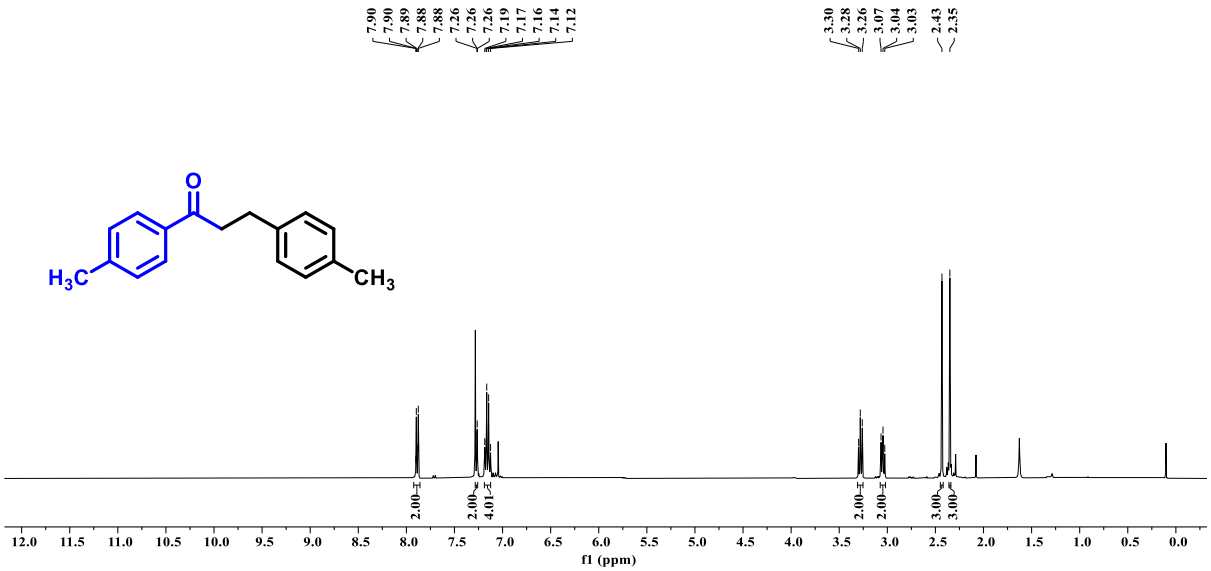


Fig. S83 ^{1}H NMR spectrum of **5j** in $CDCl_3$ (400 MHz).

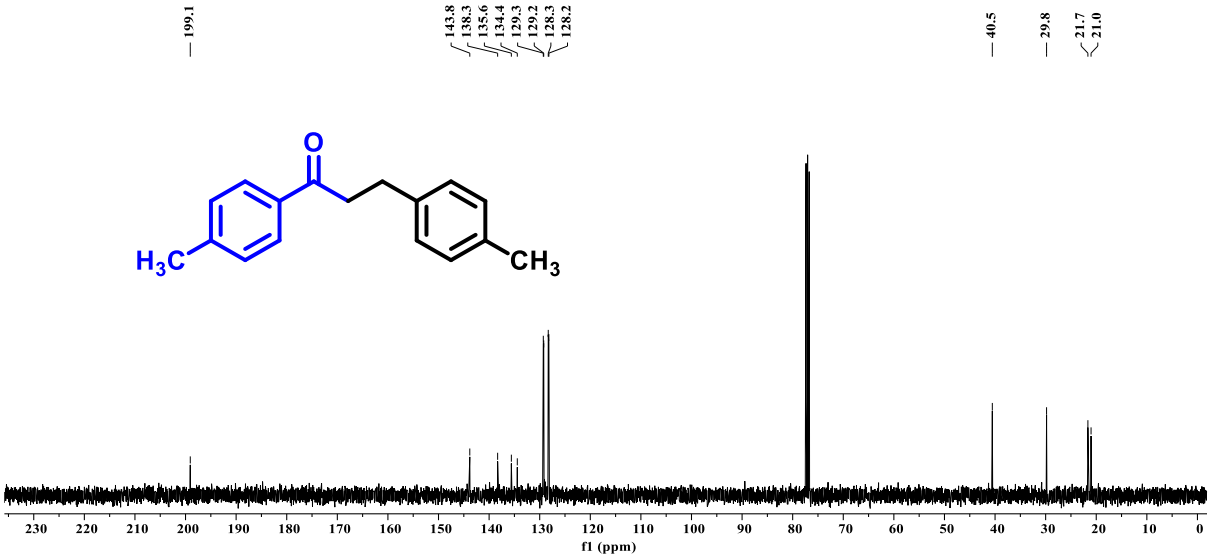


Fig. S84 $^{13}C\{^{1}H\}$ NMR spectrum of **5j** in $CDCl_3$ (101 MHz).

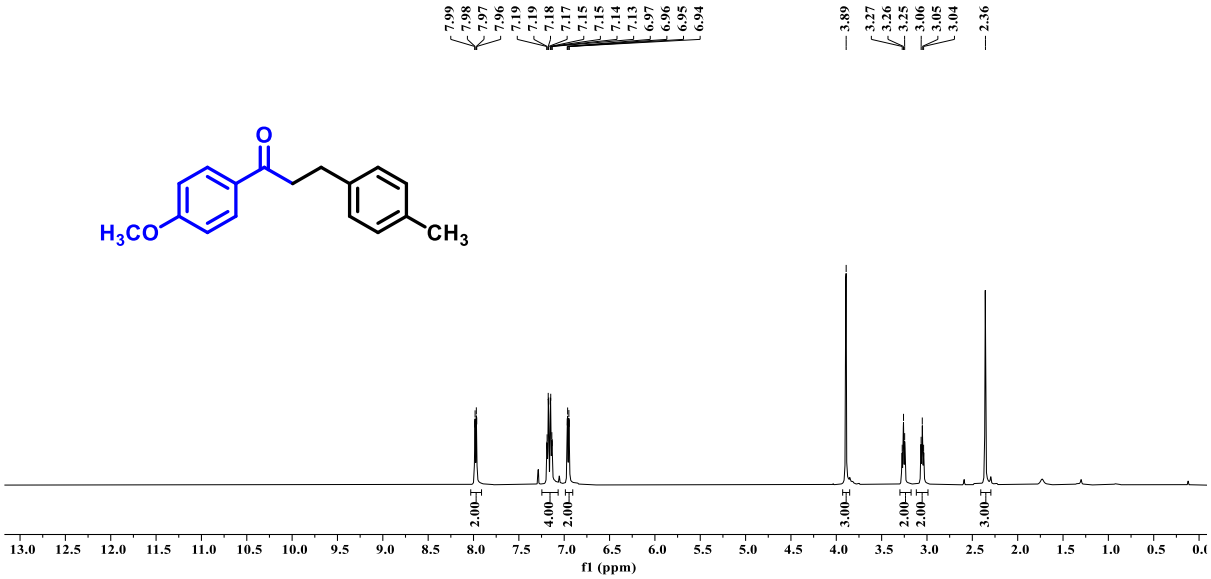


Fig. S85 ^{1}H NMR spectrum of **5k** in $CDCl_3$ (500 MHz).

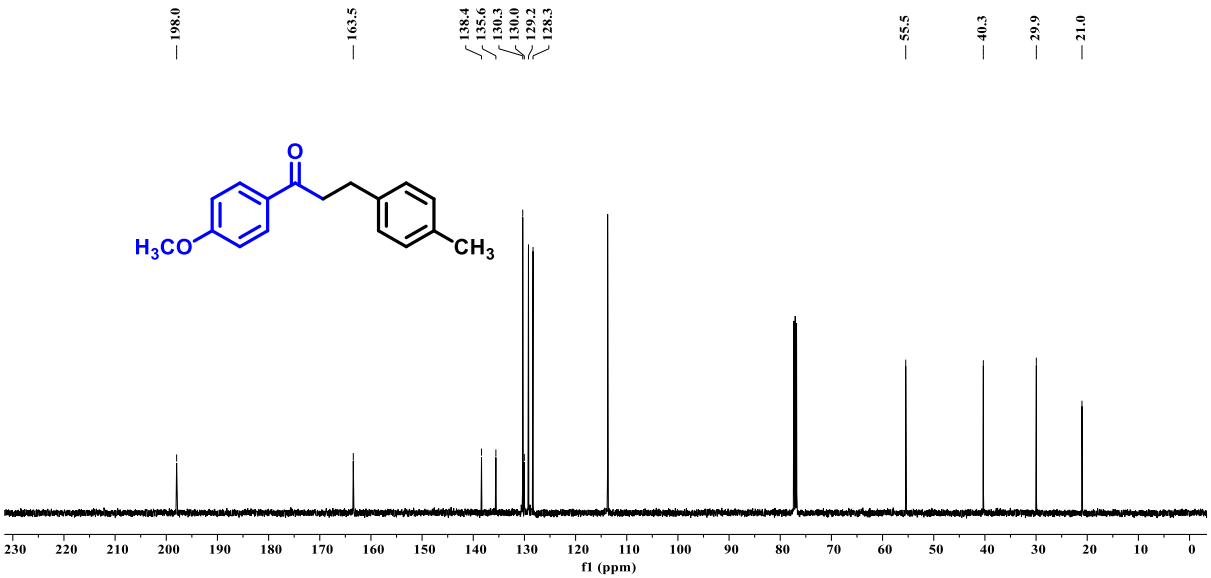


Fig. S86 $^{13}C\{^{1}H\}$ NMR spectrum of **5k** in $CDCl_3$ (126 MHz).

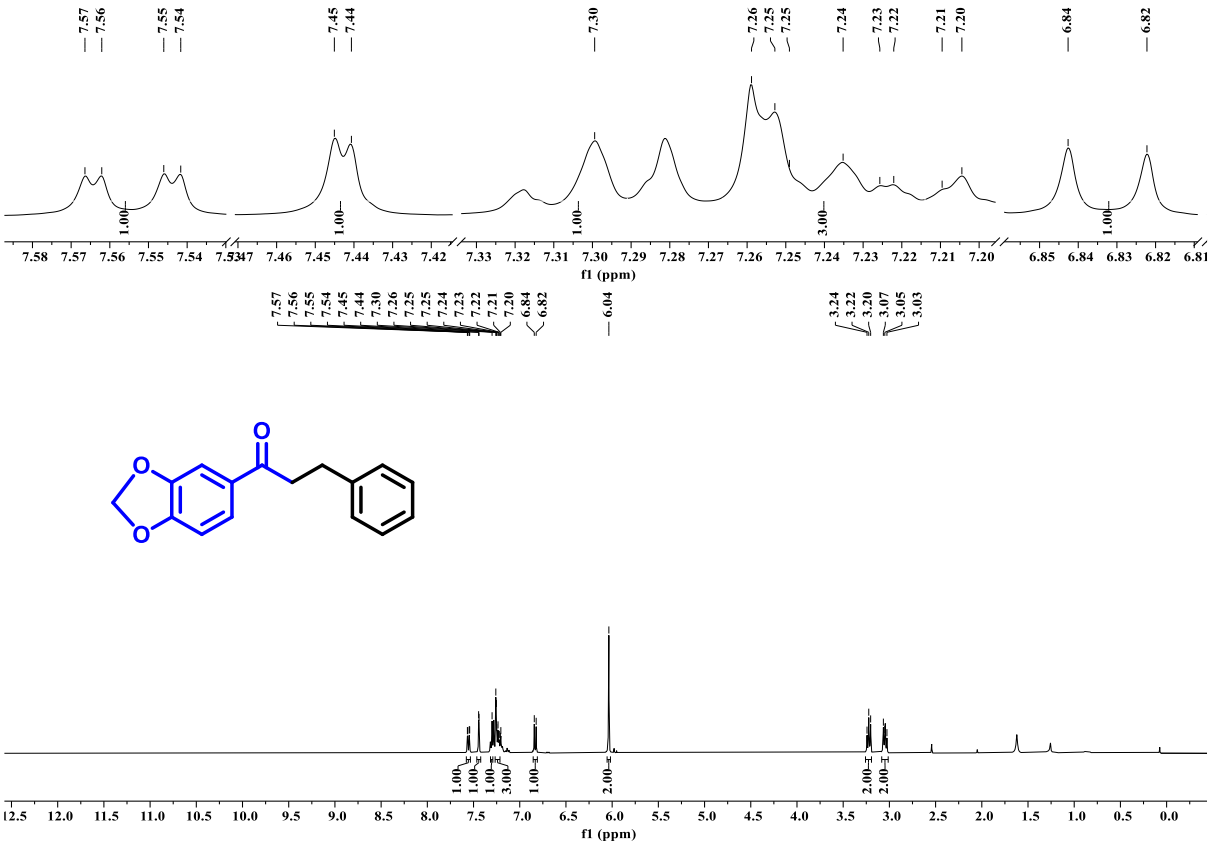


Fig. S87 ^{1}H NMR spectrum of **5l** in $CDCl_3$ (400 MHz).

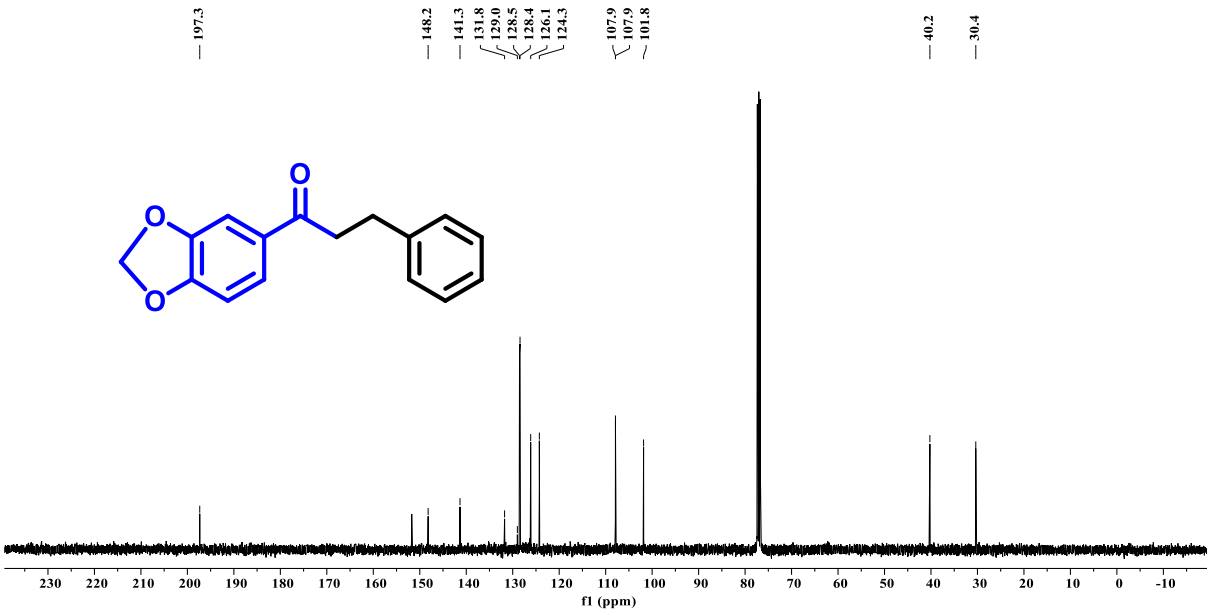


Fig. S88 $^{13}C\{^{1}H\}$ NMR spectrum of **5l** in $CDCl_3$ (101 MHz).

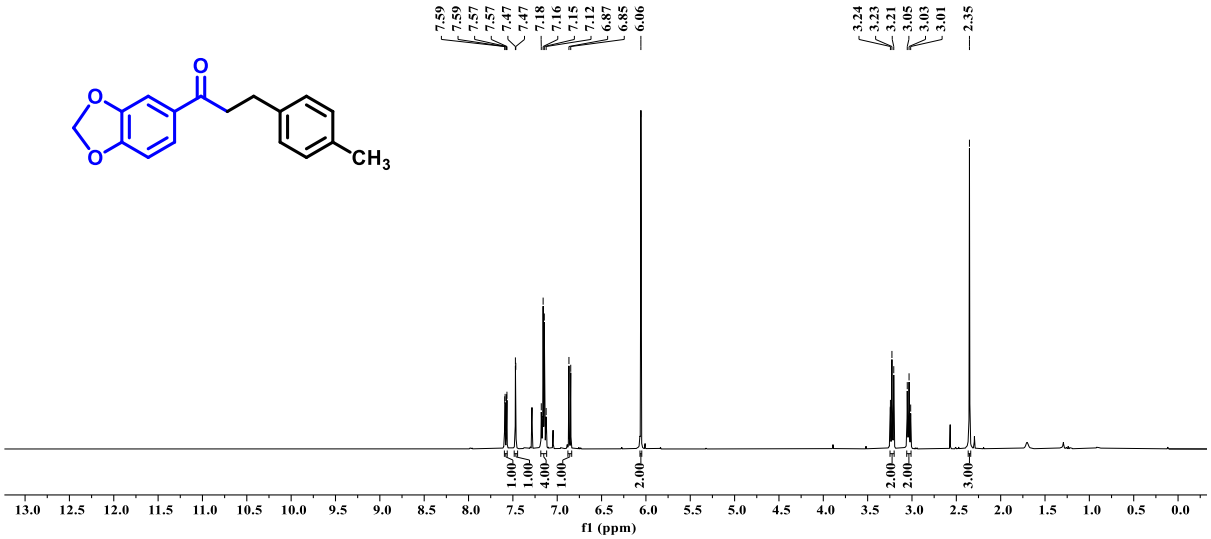


Fig. S89 ^{1}H NMR spectrum of **5m** in $CDCl_3$ (400 MHz).

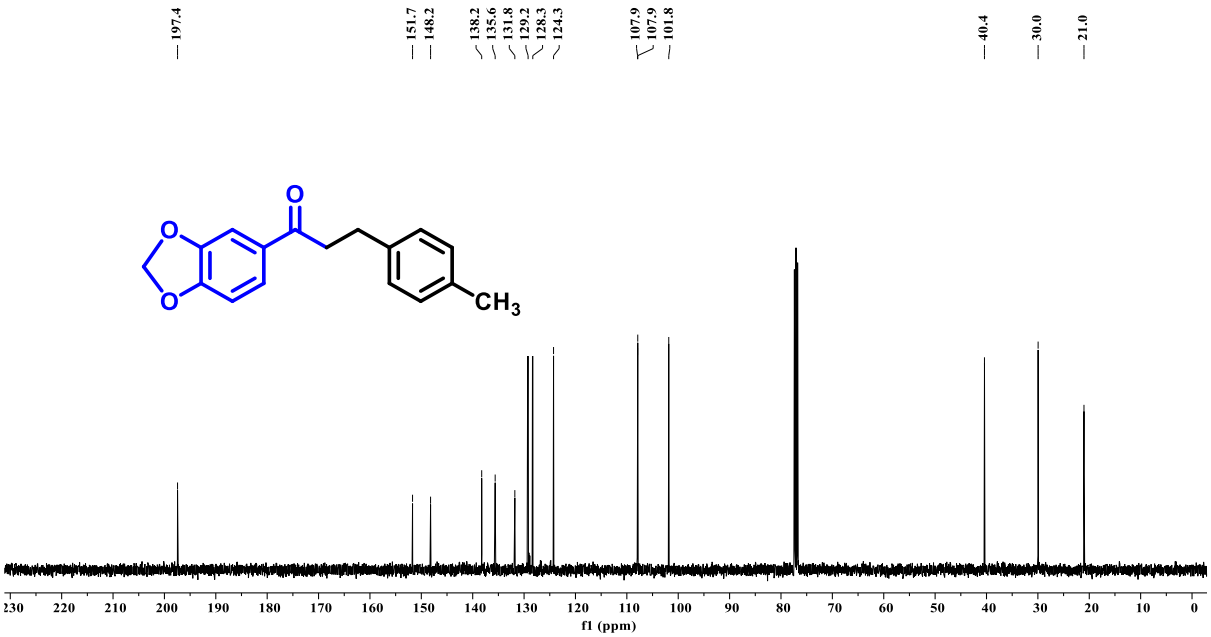


Fig. S90 $^{13}C\{^{1}H\}$ NMR spectrum of **5m** in $CDCl_3$ (101 MHz).

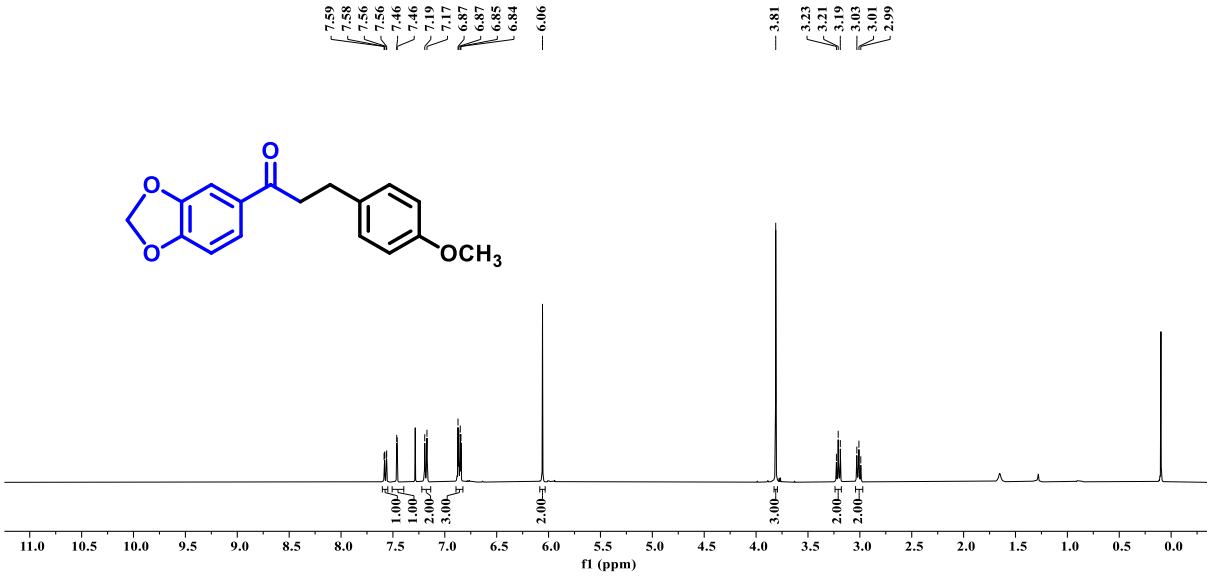


Fig. S91 ^{1}H NMR spectrum of **5n** in $CDCl_3$ (400 MHz).

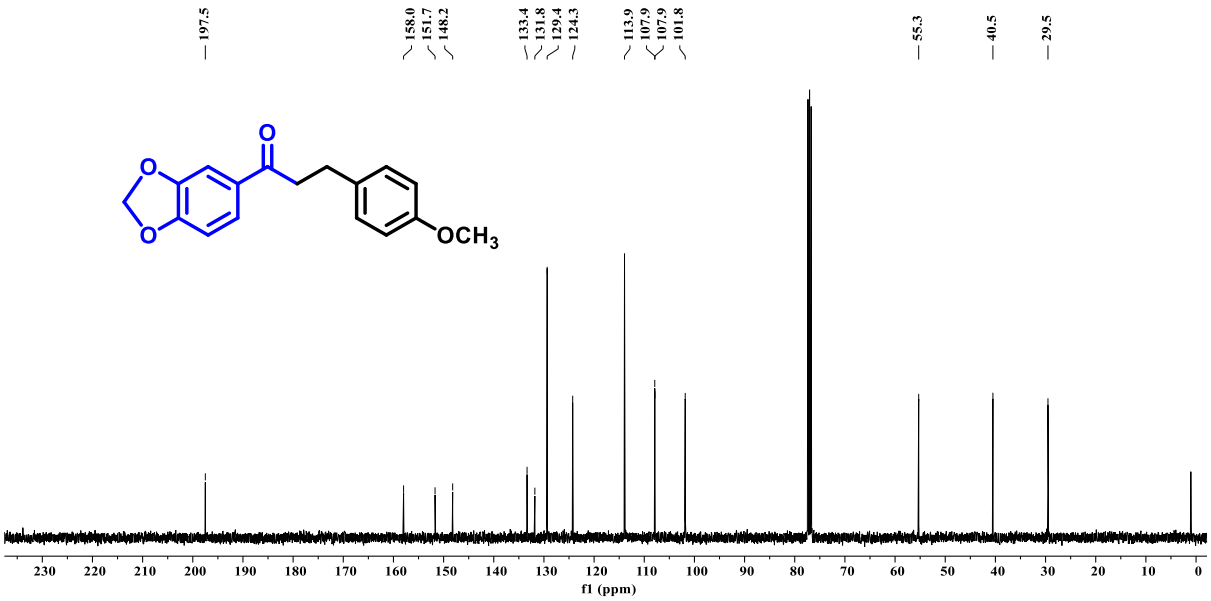


Fig. S92 ^{13}C{^{1}H} NMR spectrum of **5n** in $CDCl_3$ (101 MHz).

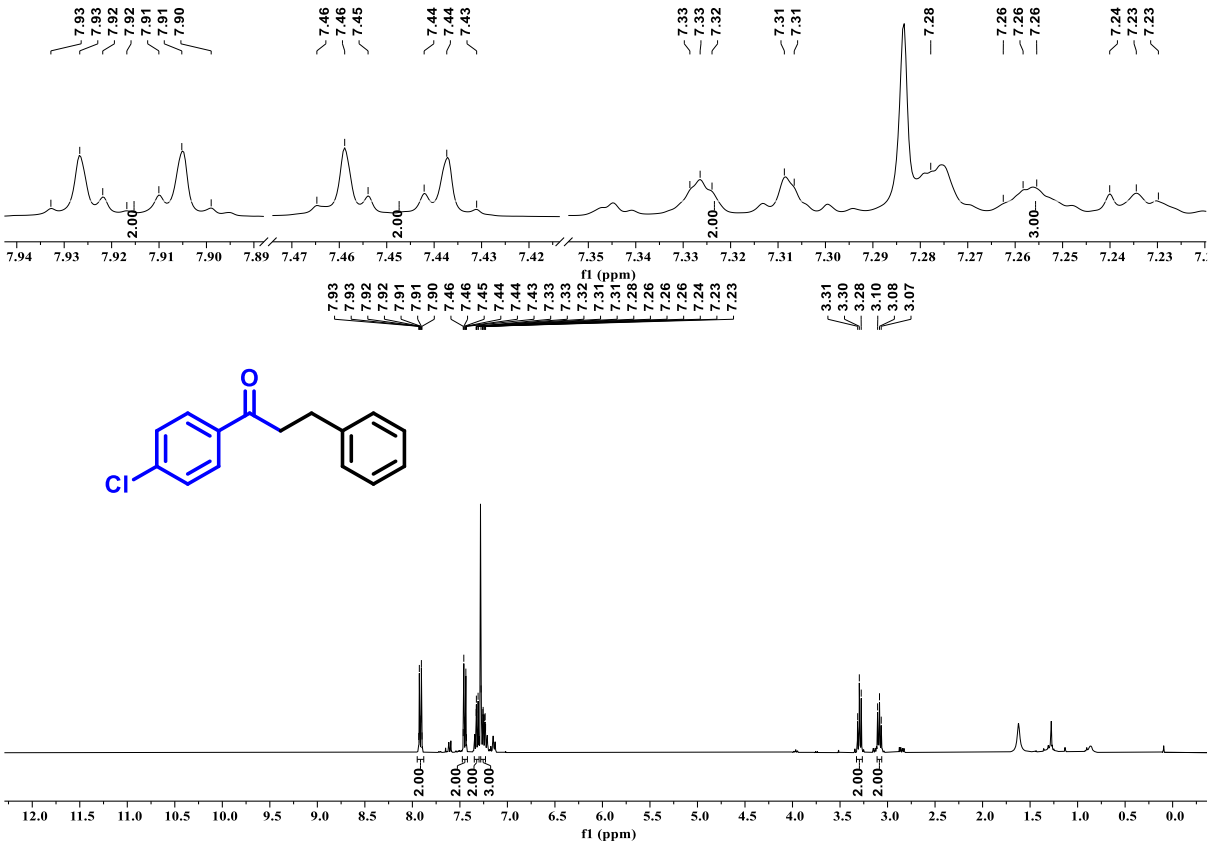


Fig. S93 ^{1}H NMR spectrum of **5o** in $CDCl_3$ (400 MHz).

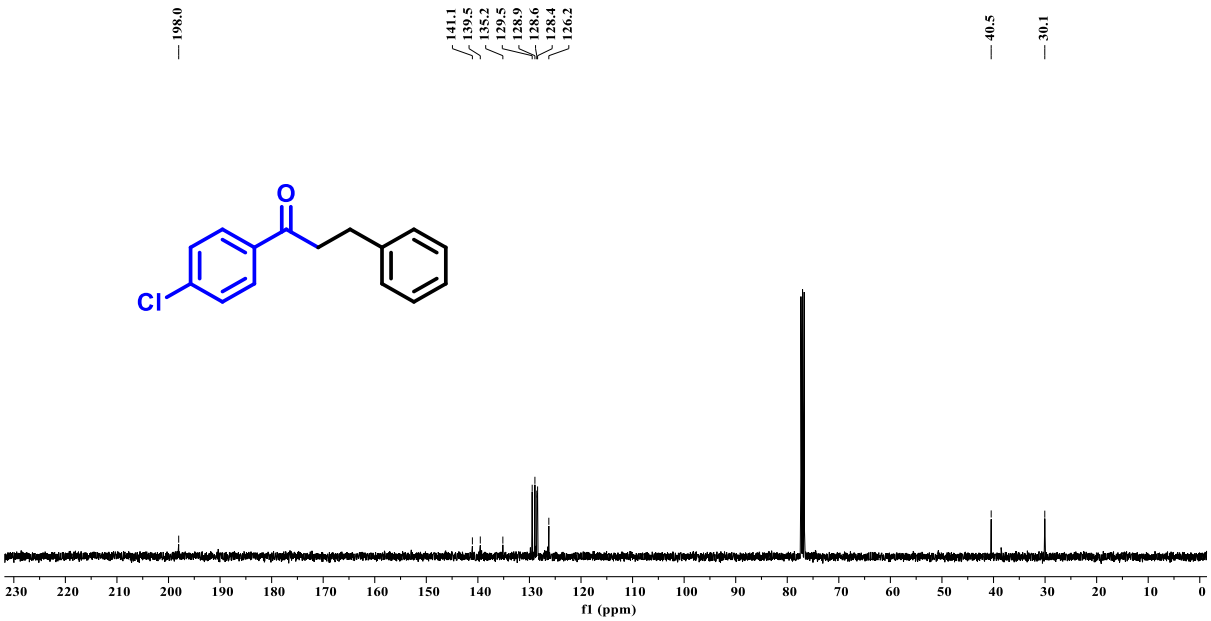


Fig. S94 $^{13}C\{^{1}H\}$ NMR spectrum of **5o** in $CDCl_3$ (101 MHz).

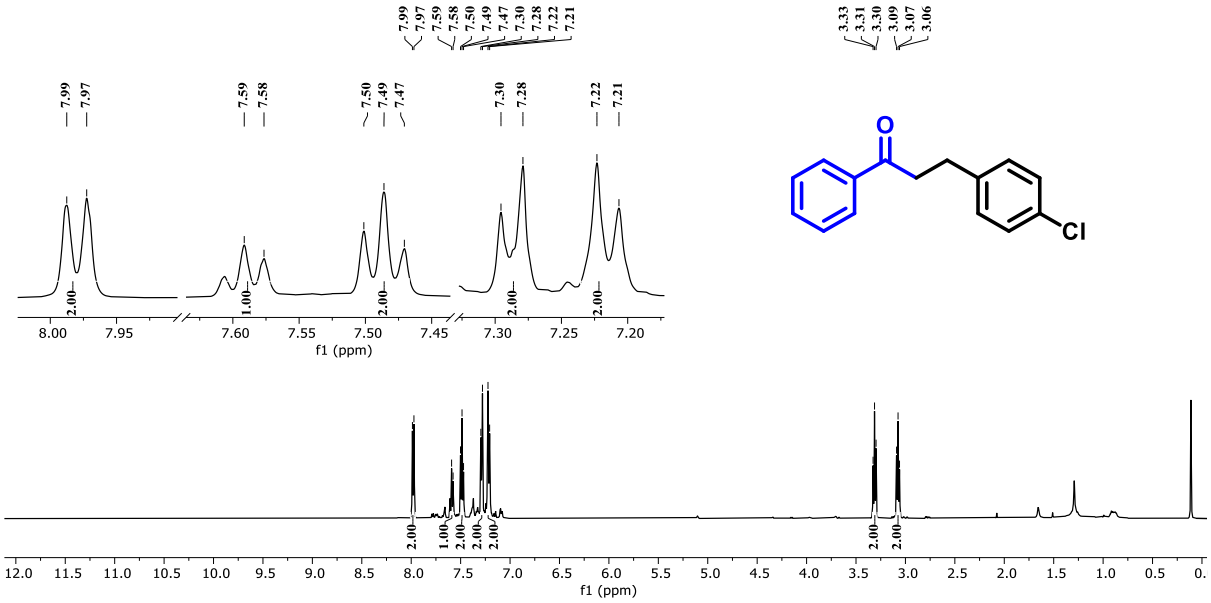


Fig. S95 ^{1}H NMR spectrum of **5p** in $CDCl_3$ (500 MHz).

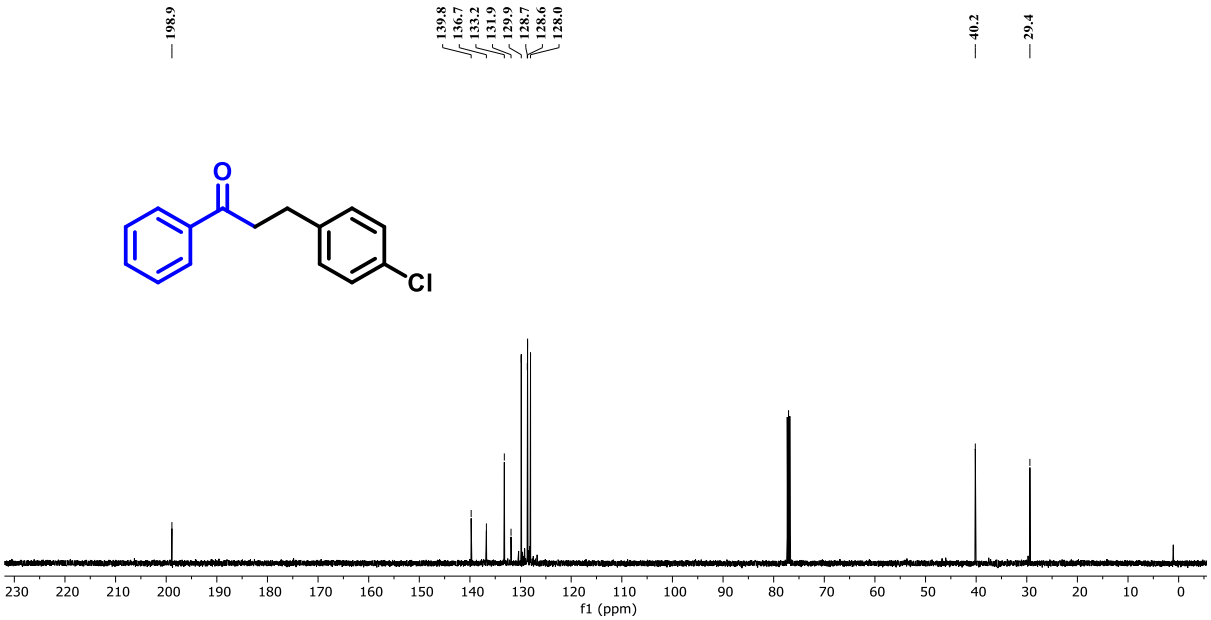


Fig. S96 $^{13}C\{^{1}H\}$ NMR spectrum of **5p** in $CDCl_3$ (126 MHz).

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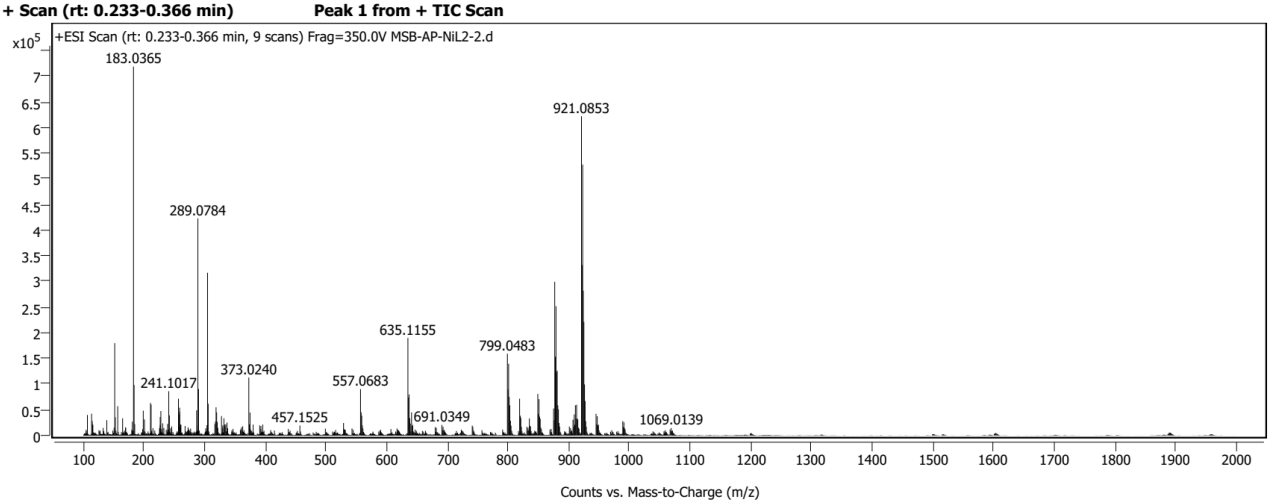
Sample Information

Name	MSB-AP-NiL2-2	**Data File Path**	X:\Projects\MASS Data\Data\MSB-AP-NiL2-2.d
Sample ID		**Acq. Time (Local)**	12/29/2023 7:59:43 PM (UTC+05:30)
Instrument	LCMSQTOF-G6545B	**Method Path (Acq)**	D:\Projects\MASS Data\Methods\A1B1_POS_100-2000_4000_2000_350_HIGH MASS.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.203.0)
Inj. Vol. (ul)	0.5	**IRM Status**	Success
Position	P2-E4	**Method Path (DA)**	D:\MassHunter\Report Templates\REPORT METHOD\HRMS_IITB.m
Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.233-0.366 min) **Peak 1 from + TIC Scan**

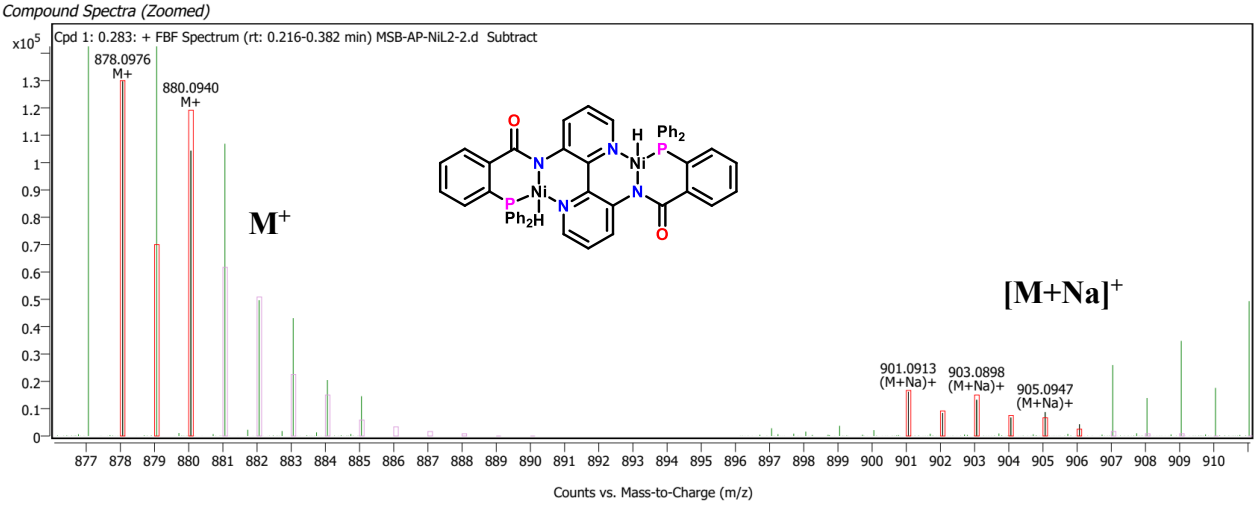


Compound Details

Cpd. 1: C48 H36 N4 Ni2 O2 P2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C48 H36 N4 Ni2 O2 P2	901.0913	901.091328766957	-2.91737806719539	-3.32236792348117	78.51

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Fig. S97 HRMS spectrum of the Ni-Hydride intermediate (**C**).

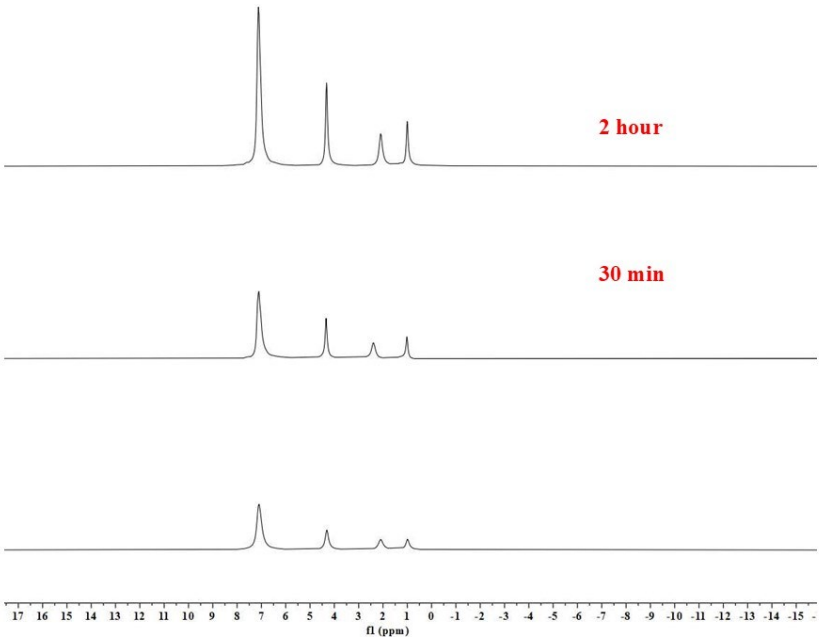


Fig. S98 Satck ^{1}H NMR spectrum of reaction mixture in $CDCl_3$ (400 MHz).

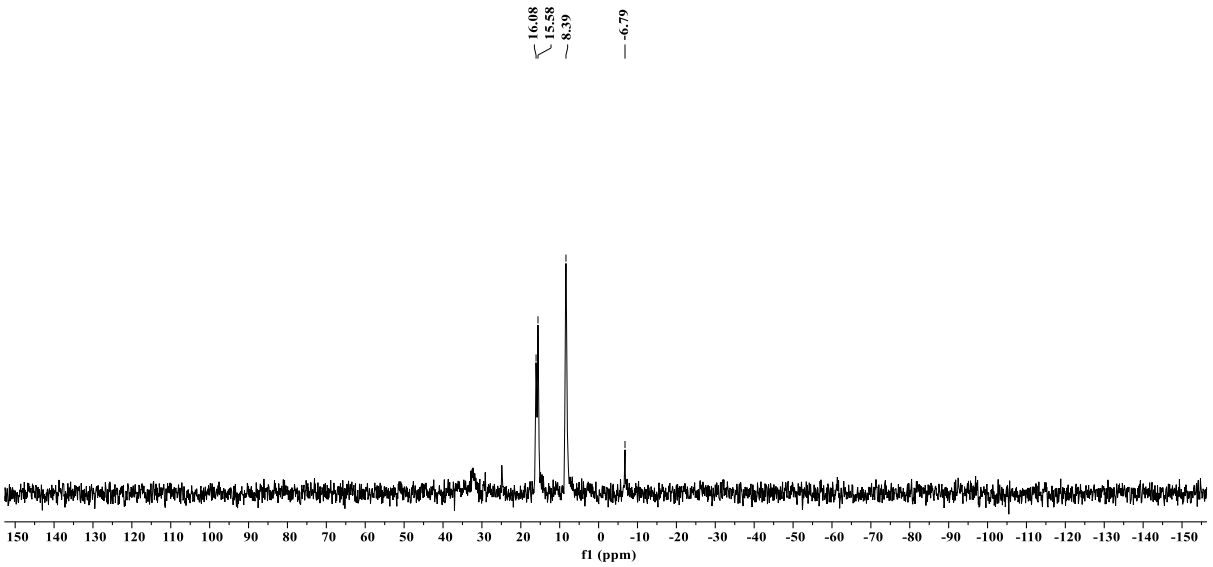


Fig. S99 $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture in $CDCl_3$ (202 MHz).

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