Supporting Information

Nickel-Catalysed *para*-CH Activation of Pyridine with Switchable Regioselective Hydroheteroarylation of Allylarenes

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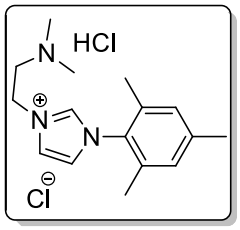
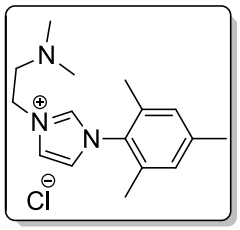
General. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk technique or in a glovebox. ^{1}H and ^{13}C NMR spectra were run a Bruker 300 MHz, or 400 MHz spectrometer using the residual proton of the deuterated solvent for reference ($CDCl_3$, ^{1}H NMR: 7.24 ppm. ^{13}C NMR: 77.2 ppm). Chemical shifts are reported in ppm (δ); coupling constants, *J*, are reported in Hz. Standard abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet. Column chromatography was performed using silica gel (spherical, 40-63 m). Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was performed with UV light (254 nm). GC analyses were performed on an Agilent Technologies 7890 GC instrument. High-resolution mass spectra were obtained with a JEOL, JMS-700 (EI or FAB+) spectrometer. High-resolution MALDI-mass spectra were conducted on an Applied Biosystems 4800 Proteomics Analyzer (Applied Biosystem, Foster City) equipped with an Nd/YAG laser (335nm) operating at a repetition rate of 200 Hz.

Chemicals. All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification in advance before use. Solvents for chromatography were reagent grade. Toluene was dried over sodium with benzophenone-ketyl intermediate as an indicator. All chemicals were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification.

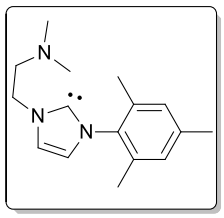


3-(2-(dimethylamino)ethyl)-1-mesityl-1*H*-imidazol-3-ium chloride hydrochloride (L2 salt·HCl): To a 1 L round bottom flask containing 2-chloro-*N*,*N*-dimethylethanamine hydrochloride (8.64g, 0.06 mol) and 1-mesityl-1*H*-imidazole (33.2g, 0.18 mol) was added acetonitrile (190mL) and the resulting mixture was then refluxed for three days. The reaction was cooled to room temperature and filtered. The solid crude was extracted with hot acetonitrile (the mixture was

filtered while the acetonitrile solution was hot). The combined filtrate was evaporated to give the pure product. Yield: 38%. ^{1}H NMR (500 MHz, D_2O): δ 9.15 (s, 1H), 7.89 (s, 1H), 7.64 (s, 1H), 7.11 (s, 2H), 4.83 (t, $^{3}J_{HH}$ = 1.8 Hz, 2H), 3.83 (t, $^{3}J_{HH}$ = 1.8 Hz, 2H), 3.00 (s, 6H), 2.30 (s, 3H), 2.01 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, D_2O):δ 141.6 (Ar), 137.3 (Ar), 134.5 (Ar), 130.6 (Ar), 129.3 (Ar), 125.0 (Ar), 123.1 (Ar), 55.4 (CH_2), 44.3 (CH_2), 43.4 (CH_3), 20.2 (CH_3), 16.4 (CH_3). HR-MS (APCI): m/z calcd. for $C_{16}H_{24}N_3Cl_2$ ([M-H]$^-$) 328.1347, found 328.1352.

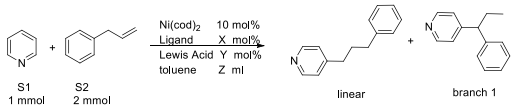


3-(2-(dimethylamino)ethyl)-1-mesityl-1*H*-imidazol-3-ium chloride (L2 salt): To a 100 mL round bottom flask containing **L2** salt·HCl (2.63 g，8 mmol) and sodium hydroxide (0.32 g，8 mmol) was added methanol (33 mL) and the solution was stirred at room temperature for 1 hour. The solution was evaporated to dryness. The resulting crude was extracted with dichloromethane (33 mL). The filtrated was dried with $MgSO_4$. After filtration, the filtrate was evaporated to dryness to give the product. Yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.38 (s, 1H), 7.99 (s, 1H), 7.05 (s, 1H), 6.98 (s, 2H), 4.85 (t, $^{3}J_{HH}$ = 1.3 Hz, 2H), 2.82 (t, $^{3}J_{HH}$ = 1.3 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 6H), 2.04 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):δ 141.5 (Ar), 139.0 (Ar), 134.5 Ar), 131.0 (Ar), 130.1 (Ar), 123.7 (Ar), 122.3 (Ar), 58.9 CH_2), 47.9 (CH_2), 45.8 (CH_3), 21.3 (CH_3), 17.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{16}H_{24}N_3$ ([M-Cl]$^+$) 258.1970, found 258.1972.



2-(3-mesityl-2,3-dihydro-1H-imidazol-1-yl)-N,N-dimethylethanamine (L2): L2 was prepared in situ by using **L2** salt and NaHMDS in the reaction. See general procedure B.

Table S1. Optimization.[a]



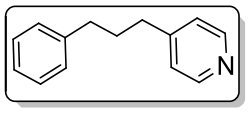
entry	eq(S1:S2)	ligand	X mol%	lewis acid	Y mol%	toluene (mL)	temperature(^{O}C)	time(hr)	yield(linear:branch1)[a]
1	1 : 2	**L1**	20%	$AlMe_3$	10%	1	80	19	0 : trace
2	1 : 2	IMes	10%	$AlMe_3$	10%	1	80	19	trace : trace
3	1 : 2	PCy_3	20%	$AlMe_3$	10%	1	80	19	no reaction
4	1 : 2	**L1**	20%	$AlMe_3$	20%	0.6	130	17	trace : 18
5	1 : 2	IMes	10%	$AlMe_3$	20%	0.6	130	17	39 : 48
6	1 : 2	PCy_3	20%	$AlMe_3$	20%	0.6	130	17	no reaction
7	1 : 2	IMes	10%	$AlMe_3$	20%	1	130	18	39 : 36
8	1 : 2	IPr	10 %	$AlMe_3$	20%	0.6	130	17	63 : trace
9	1 : 2	IPr	15%	$AlMe_3$	30%	0.4	130	17	75 : trace
10	1 : 2	PPh_3	20%	$AlMe_3$	20%	0.6	130	17	no reaction
11	1 : 2	PCy_3	10%	—	—	1	130	18	no reaction
12	1 : 2	IMes	10%	—	—	1	130	18	no reaction
13	1 : 2	**L1**	30%	$AlMe_3$	30%	0.4	130	17	trace : 40
14	1 : 2	**L1**	30%	$AlMe_3$	30%	0	130	42	5:40
15	1 : 2	**L1**	10%	$AlMe_3$	30%	1	130	18	10 : 29
16	1 : 2	**L1**	20%	$AlMe_3$	50%	0	130	18	9:38
17	1 : 2	**L1**	20%	$AlMe_3$	30%	0.4	150	18	trace : 30
18	1 : 2	**L1** salt	30%	$AlMe_3$	30%	0.4	130	18	17 : 5
19	1 : 2	**L2**	15%	$AlMe_3$	30%	0.4	130	18	41 : 20
20	1 : 3	**L2**	30%	$AlMe_3$	30%	0.4	130	18	63 : 9
21	1 : 3	**L2**	30%	$AlMe_3$	30%	0.4	130	18	40 : 12
22	1 : 3	**L2**	30%	$ZnMe_2$	30%	0.4	130	18	no reaction
23	1 : 3	**L2**	30%	$AlMe_3$	30%	1.5	130	18	50 : 9
24	0.5 : 1.5	**L2**	15%	$AlMe_3$	30%	0.3	130	18	45 : 18
25	0.5 : 1.5	**L2**	30%	$AlMe_3$	30%	0.3	130	18	55 : 15
26	0.5 : 1.5	**L2**	30%	$AlMe_3$	30%	0	130	18	60 : 8
27	0.5 : 2.5	**L2**	30%	$AlMe_3$	30%	0.3	130	18	63 : 15
28	0.5 : 2.5	**L2**	30%	$AlMe_3$	30%	0	130	18	61 : 13
29	0.5 : 1.5	**L2**	30%	$AlMe_3$	30%	0	150	18	57 : 17
30	0.5 : 2.5	**L2**	30%	$AlMe_3$	30%	0	150	18	68 : 20
31	0.5 : 2.5	**L2**	30%	$AlMe_3$	30%	DMSO(0.5)	130	18	no reaction
32	0.5 : 2.5	**L2**	30%	$AlMe_3$	30%	DMF(0.5)	130	18	no reaction
33	0.5 : 2.5	**L2**	30%	$AlMe_3$	30%	NMP(0.5)	130	18	no reaction
34	0.5 : 2.5	**L2**	30%	$AlMe_3$	50%	0.3	130	18	71 : 14
35	0.5 : 2.5	**L2**	30%	$AlMe_3$	100%	0.3	130	18	76 : 19
36	0.5 : 2.5	**L2**	60%	$AlMe_3$	50%	0.3	130	18	73 : 12
37	0.5 : 2.5	**L2**	15%	$AlMe_3$	50%	0.3	130	18	35 : 17
38	0.5 : 1.5	**L2**	30%	$AlMe_3$	50%	0.5	130	18	65 : 14
39	0.5 : 1.5	**L2**	30%	$AlMe_3$	50%	1	130	18	67 : 12
40	0.5 : 1.5	**L2**	30%	$AlMe_3$	50%	1.5	130	18	57 : 9
41	0.5 : 1.5	**L2**	30%	$AlMe_3$	50%	0	130	18	77 : 14
42	1 : 3	**L2**	30%	$AlMe_3$	50%	0	130	18	62 : 14
43	1 : 3	**L2**	30%	$AlMe_3$	100%	0	130	18	74 : 14
44	2.5 : 0.5	**L2**	30%	$AlMe_3$	100%	0.1	130	18	23 : 8

[a] Reaction condition: $Ni(COD)_2$ (10 mol%), ligand, Lewis acid, solvent, temperature, time. [b] isolated yield (%). [c] **L2** was prepared in situ by adding **L2** salt and NaHMDS. [d] NaHMDS (45 mol%).

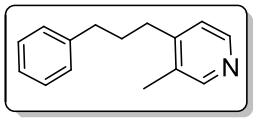
General procedure A for C-H functionalization of pyridine to afford linear product: To a vial containing $Ni(COD)_2$ (28 mg, 0.1 mmol) and IPr (32 mg, 0.1 mmol) in toluene (1 mL) was added allylbenzene (3.0 mmol). After stirring for 5 minutes, pyridine (1.0 mmol) and MAD (0.5 mL, 0.2 mmol, 0.4 M in toluene) were added into the vial in order. After the vial was screw-capped, the reaction solution was taken outside the glovebox and heated at 130 ^{o}C for 18 h. The resulting mixture was filtered through *Celite* and washed with dichloromethane. The filtrate solution was concentrated in *vacuo* to afford crude product. The crude was further purified by flash chromatography using hexane/ethyl acetate (3:1) as eluent.

General procedure B for C-H functionalization pyridine to afford branch product: To a vial containing $Ni(COD)_2$ (28 mg, 0.1 mmol), **L2** salt (88 mg, 0.3 mmol) and NaHMDS (56 mg, 0.3 mmol) was added allylbenzene (3.0 mmol). After stirring for 5 minutes, pyridine (1.0 mmol) and $AlMe_3$ (0.5 mL, 1.0 mmol, 2 M in toluene) were added into the vial in order. After the vial was screw-capped, the reaction solution was taken outside the glovebox and heated at 130 ^{o}C for 18 h. The resulting mixture was filtered through *Celite* and washed with dichloromethane. The filtrate solution was concentrated in *vacuo* to afford crude product. The crude was further purified by flash chromatography using hexane/ethyl acetate (3:1) as eluent.

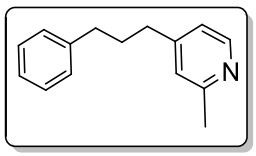
General procedure C for C-H functionalization of pyridine with styrene: To a vial containing $Ni(COD)_2$ (28 mg, 0.1 mmol) and IMes (16 mg, 0.05 mmol) in toluene (1 mL) was added styrene (3.0 mmol), pyridine (1.0 mmol), and $AlMe_3$ (0.2 mmol, 0.1 mL, 2 M in toluene) in order. After the vial was screw-capped, the reaction solution was taken outside the glovebox and heated at 130 ^{o}C for 18 h. The resulting mixture was filtered through *Celite* and washed with dichloromethane. The filtrate solution was concentrated in *vacuo* to afford crude product. The crude was further purified by flash chromatography using hexane/ethyl acetate (3:1) as eluent.



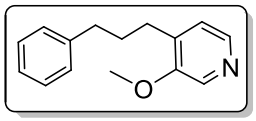
4-(3-phenylpropyl)pyridine (3aa): The reaction was performed according to the above general procedure A. Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.21-7.14 (m, 3H), 7.08 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 2.66-2.59 (m, 4H), 2.00-1.90 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 151.3 (Ar), 149.9 (Ar), 141.8 (Ar), 128.6 (Ar), 126.1 (Ar), 124.1 (Ar), 35.4 (CH_2), 34.8 (CH_2), 31.9 (CH_2). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}N$ ($[M+H]^{+}$) 198.1283, found 198.1277.



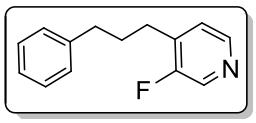
4-(3-phenylpropyl)pyridine (3ba): The reaction was performed according to the above general procedure A. Yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.29-7.24 (m, 2H), 7.19-7.14 (m, 3H), 7.03 (d, $^{3}J_{HH}$ = 1.2 Hz, 2H), 2.69-2.55 (m, 4H), 2.19 (s, 3H), 1.94-1.83 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 150.1 (Ar), 149.9 (Ar), 147.1 (Ar), 141.6 (Ar), 131.9 (Ar), 128.5 (Ar), 126.1 (Ar), 123.5 (Ar), 35.6 (CH_2), 32.0 (CH_2), 30.6 (CH_2), 16.1 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1437.



4-(3-phenylpropyl)pyridine (3ca): The reaction was performed according to the above general procedure A. Yield: 98% (linear : branch = 87 : 13). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H), 7.29-7.13 (m, 5H), 6.94 (s, 1H), 6.88 (d, $^{3}J_{HH}$ = 1.3 Hz, 2H), 2.64-2.53 (m, 4H), 2.49 (s, 3H), 1.97-1.87 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 158.3 (Ar), 151.5 (Ar), 149.1 (Ar), 141.8 (Ar), 128.5 (Ar), 126.1 (Ar), 123.5 (Ar), 121.1 (Ar), 35.4 (CH_2), 34.7 (CH_2), 31.9 (CH_2), 24.4 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1433.

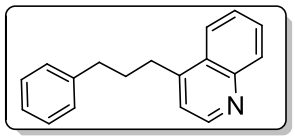


3-methoxy-4-(3-phenylpropyl)pyridine (3da): The reaction was performed according to the above general procedure A. Yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.14 (d, $^{3}J_{HH}$ = 1.2 Hz, 2H), 7.29-7.26 (m, 2H), 7.18-7.15 (m, 3H), 7.02 (d, $^{3}J_{HH}$ = 1.2 Hz, 1H), 3.87 (s, 3H), 67-2.60 (m, 4H), 1.96-1.85 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 154.1 (Ar), 142.8 (Ar), 142.1 (Ar), 139.4 (Ar), 132.9 (Ar), 128.6 (Ar), 126.0 (Ar), 124.4 (Ar), 56.0 (CH_3), 35.7 (CH_2), 30.5 (CH_2), 29.2 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1388, found 228.1387.

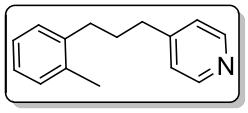


3-fluoro-4-(3-phenylpropyl)pyridine (3ja): The reaction was performed according to the above general procedure A. Yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.29 (d, $^{3}J_{HH}$ = 1.2 Hz, 2H), 7.31-7.26 (m, 2H), 7.21-7.16 (m, 3H), 7.13-7.10 (m, 1H), 2.71-2.64 (m, 4H), 2.03-1.91

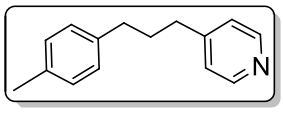
(m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 158.6 (d, $^{1}J_{FC}$ = 252.6 Hz, Ar), 145.7 (d, $^{1}J_{FC}$ = 4.8 Hz, Ar), 141.5 (s, Ar), 137.8 (d, $^{2}J_{FC}$ = 24.6 Hz, Ar), 128.5 (d, $^{3}J_{FC}$ = 4.3 Hz, Ar), 126.2 (s, Ar), 125.1 (s, Ar), 35.5 (s, CH_2), 30.8 (s, CH_2), 38.0 (s, CH_2). HR-MS (ESI): m/z calcd. for $C_{14}H_{15}NF$ ($[M+H]^+$) 216.1189, found 216.1189.



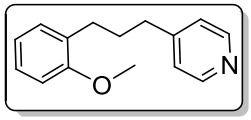
4-(3-phenylpropyl)quinoline (3la): The reaction was performed according to the above general procedure A. Yield: 80% (*para* : *meta* = 91 : 9). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (d, $^{3}J_{HH}$ = 1.1 Hz, 2H), 8.10 (d, $^{3}J_{HH}$ = 2.2 Hz, 1H), 7.94-7.91 (m, 1H), 7.70-7.65 (m, 1H), 7.54-7.48(m, 1H), 7.32-7.27 (m, 2H), 7.22-7.18 (m, 1H), 3.07 (t, $^{3}J_{HH}$ = 1.9 Hz, 2H), 2.75 (t, $^{3}J_{HH}$ = 1.9 Hz, 2H), 2.17-2.04 (m, 4H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 150.3 (Ar), 148.5 (Ar), 148.4 (Ar), 141.7 (Ar), 130.4 (Ar), 129.2 (Ar), 128.6 (Ar), 127.7 (Ar), 126.5 (Ar), 126.2 (Ar), 123.7 (Ar), 120.9 (Ar), 35.9 (CH_2), 31.7 (CH_2). HR-MS (ESI): m/z calcd. for $C_{18}H_{18}N$ ($[M+H]^+$) 248.1439, found 248.1443.



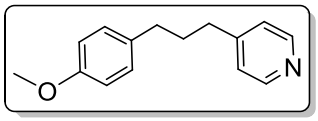
4-(3-(o-tolyl)propyl)pyridine (3ab): The reaction was performed according to the above general procedure A. Yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, $^{3}J_{HH}$ = 1.0 Hz, 2H), 7.11-7.09 (m, 6H), 2.70-2.60 (m, 4H), 2.25 (s, 3H), 1.96-1.85 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 151.3 (Ar), 149.7 (Ar), 139.8 (Ar), 135.9 (Ar), 130.3 (Ar), 128.8 (Ar), 126.1 (Ar), 126.0 (Ar), 123.9 (Ar), 35.0 (CH_2), 32.7 (CH_2), 30.6 (CH_2), 19.3 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1438.



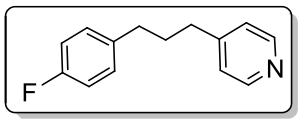
4-(3-(p-tolyl)propyl)pyridine (3ac): The reaction was performed according to the above general procedure A. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.11-7.04 (m, 6H), 2.63-2.57 (m, 4H), 2.31 (s, 3H), 1.98-1.88 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 151.4 (Ar), 149.8 (Ar), 138.6 (Ar), 135.5 (Ar), 139.2 (Ar), 128.4 (Ar), 124.0 (Ar), 34.9 (CH_2), 34.7 (CH_2), 32.0 (CH_2), 21.1 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1434.



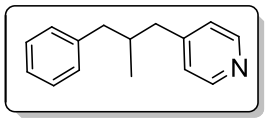
4-(3-(2-methoxyphenyl)propyl)pyridine (3ae): The reaction was performed according to the above general procedure A. Yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.20-7.17 (m, 1H), 7.11-7.08 (m, 3H), 6.89-6.81 (m, 2H), 3.79 (s, 3H), 2.67-2.60 (m, 4H), 1.96-1.86 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 157.6 (Ar), 151.7 (Ar), 149.7 (Ar), 130.2 (Ar), 130.0 (Ar), 127.4 (Ar), 124.1 (Ar), 120.5 (Ar), 110.4 (Ar), 55.3 (CH_2), 35.6 (CH_2), 30.3 (CH_2), 30.0 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1388, found 228.1382.



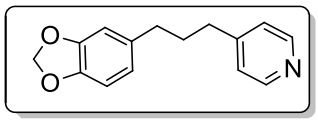
4-(3-(4-methoxyphenyl)propyl)pyridine (3af): The reaction was performed according to the above general procedure A. Yield: 23%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.09-7.04 (m, 4H), 6.84-6.80 (m, 2H), 3.77 (s, 3H), 2.63-2.55 (m, 4H), 1.96-1.86 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 157.9 (Ar), 151.3 (Ar), 149.7 (Ar), 133.7 (Ar), 129.3 (Ar), 123.9 (Ar), 113.9 (Ar), 55.3 (CH_2), 34.6 (CH_2), 34.5 (CH_2), 32.0 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1388, found 228.1388.



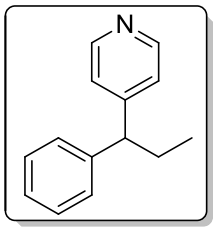
4-(3-(4-fluorophenyl)propyl)pyridine (3ah): The reaction was performed according to the above general procedure A. Yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, $^{3}J_{HH}$ = 0.8 Hz, 2H), 7.10-6.89 (m, 6H), 2.60-2.55 (m, 4H), 1.95-1.84 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 161.5 (d, $^{1}J_{FC}$ = 242.2 Hz, Ar), 151.2 (s, Ar), 149.8 (s, Ar), 137.3 (s, Ar), 129.8 (d, $^{3}J_{FC}$ = 7.7 Hz, Ar), 124.0 (s, Ar), 115.3 (d, $^{2}J_{FC}$ = 20.9 Hz, Ar), 34.6 (s, CH_2), 34.5 (s, CH_2), 32.0 (s, CH_2). HR-MS (ESI): m/z calcd. for $C_{14}H_{15}NF$ ($[M+H]^+$) 216.1189, found 216.1185.



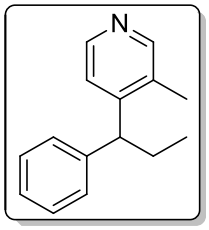
4-(2-methyl-3-phenylpropyl)pyridine (3ai): The reaction was performed according to the above general procedure A. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$ = 1.1 Hz, 2H), 7.29-7.04 (m, 7H), 2.68-2.58 (m, 2H), 2.48-2.30 (m, 2H), 2.08-2.01 (m, 1H), 0.83-0.80 (m, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 150.3 (Ar), 149.7 (Ar), 140.6 (Ar), 129.2 (Ar), 128.4 (Ar), 126.1 (Ar), 124.7 (Ar), 43.4 (CH_2), 42.5 (CH_2), 36.5 (CH_2), 19.2 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1436.



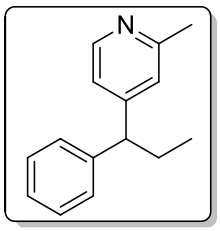
4-(3-(benzo[d][1,3]dioxol-5-yl)propyl)pyridine (3aj): The reaction was performed according to the above general procedure A. Yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 7.05 (d, $^{3}J_{HH}$ = 1.3 Hz, 2H), 6.70-6.56 (m, 3H), 5.87 (s, 2H), 2.59-2.50 (m, 4H), 1.92-1.82 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 151.2 (Ar), 149.8 (Ar), 147.7 (Ar), 145.8 (Ar), 135.5 (Ar), 124.0 (Ar), 121.2 (Ar), 108.9 (Ar), 108.2 (Ar), 100.9 (Ar), 35.1 (CH_2), 34.6 (CH_2), 32.1 (CH_2). HR-MS (ESI): m/z calcd. for $C_{15}H_{16}NO_2$ ($[M+H]^+$) 242.1181, found 242.1177.



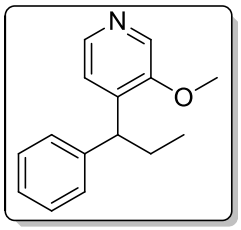
4-(1-phenylpropyl)pyridine (4aa): The reaction was performed according to the above general procedure B. Yield: 88% (branch : linear = 84 : 16). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, $^{3}J_{HH}$ = 0.9 Hz, 2H), 7.30-7.24 (m, 2H), 7.21-7.17 (m, 3H), 7.13 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 3.75 (t, $^{3}J_{HH}$ = 1.4 Hz, 1H), 2.10-2.00 (m, 2H), 0.88 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 154.1 (Ar), 150.0 (Ar), 143.3 (Ar), 128.8 (Ar), 128.1 (Ar), 126.8 (Ar), 123.5 (Ar), 52.8 (CH), 28.1 (CH_2), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}N$ ($[M+H]^+$) 198.1283, found 198.1282.



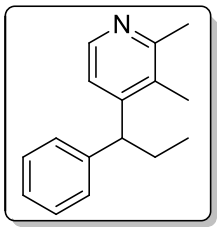
3-methyl-4-(1-phenylpropyl)pyridine (4ba): The reaction was performed according to the above general procedure B. Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, $^{3}J_{HH}$ = 1.3 Hz, 2H), 8.30 (s, 1H), 7.26-7.23 (m, 1H), 7.21-7.17 (m, 2H), 7.14-7.11 (m, 3H), 3.90 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.18 (s, 1H), 2.10-2.0 (m, 2H), 0.89 (t, $^{3}J_{HH}$ = 1.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 151.7 (Ar), 150.9 (Ar), 147.6 (Ar), 142.7 (Ar), 132.0 (Ar),128.5 (Ar), 128.2 (Ar), 126.4 (Ar), 121.4 (Ar), 48.5 (CH), 28.3 (CH_2), 16.6 (CH_3), 12.5 (CH_3). HR-MS (APCI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1443.



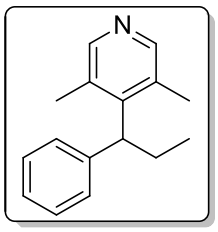
2-methyl-4-(1-phenylpropyl)pyridine (4ca): The reaction was performed according to the above general procedure B. Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, $^{3}J_{HH}$ = 1.3 Hz, 2H), 7.29-7.24 (m, 2H), 7.19-7.16 (m, 3H), 6.99 (s, 1H), 6.95 (d, $^{3}J_{HH}$ = 1.3 Hz, 2H), 3.69 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.47 (s, 1H), 2.05-2.00 (m, 2H), 0.86 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 158.3 (Ar), 154.7 (Ar), 148.9 (Ar), 143.4 (Ar), 128.7 (Ar),128.0 (Ar), 126.7 (Ar), 123.0 (Ar), 120.6 (Ar), 52.7 (CH), 28.0 (CH_2), 24.3 (CH_3), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1436.



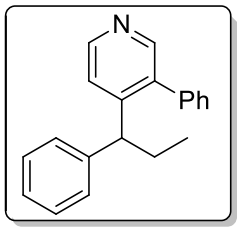
3-methoxy-4-(1-phenylpropyl)pyridine (4da): The reaction was performed according to the above general procedure B. Yield: 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, $^{3}J_{HH}$ = 1.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.25-7.23 (m, 2H), 7.22-7.13 (m, 3H), 4.24 (t, $^{3}J_{HH}$ = 2.0 Hz, 1H), 2.06-1.96 (m, 2H), 0.88 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 153.6 (Ar), 143.3 (Ar), 143.0 (Ar), 142.2 (Ar), 133.5 (Ar), 128.5 (Ar), 128.3 (Ar), 126.4 (Ar), 122.2 (Ar), 56.2 (CH), 44.8 (CH_2), 27.5 (CH_3), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1388, found 228.1383.



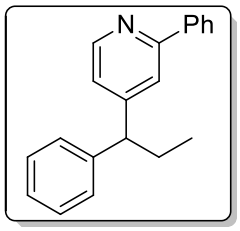
2,3-dimethyl-4-(1-phenylpropyl)pyridine (4fa): The reaction was performed according to the above general procedure B. Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H), 7.27-7.22 (m, 2H), 7.18-7.11 (m, 3H), 7.08-7.06 (m, 1H), 3.98 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.47 (s, 3H), 2.16 (s, 3H), 2.04-1.95 (m, 2H), 0.89 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 157.4 (Ar), 151.5 (Ar), 146.3 (Ar), 143.5 (Ar), 130.2 (Ar), 128.6 (Ar), 128.4 (Ar), 126.5 (Ar), 119.9 (Ar), 48.8 (CH), 28.9 (CH_3), 23.9 (CH_3), 14.4 (CH_2), 12.8 (CH_3). HR-MS (ESI): m/z calcd. for $C_{16}H_{20}N$ ($[M+H]^+$) 226.1596, found 226.1591.



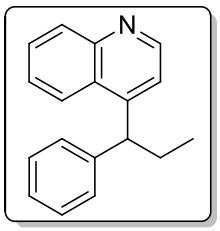
3,5-dimethyl-4-(1-phenylpropyl)pyridine (4ga): The reaction was performed according to the above general procedure B. Yield: 36% (branch : linear = 81 :19). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H,), 7.29-7.24 (m, 2H), 7.20-7.11 (m, 3H), 4.43 (m, 1H,), 2.43-2.32 (m, 1H), 2.14-2.02 (m, 7H), 0.92 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 150.1 (Ar), 142.6 (Ar), 132.1 (Ar), 128.5 (Ar), 127.4 (Ar), 126.1 (Ar), 45.5 (CH), 23.7 (CH_2), 18.0 (CH_3), 12.6 (CH_3). HR-MS (APCI): m/z calcd. for $C_{16}H_{20}N$ ([M+H]$^{+}$) 226.1596, found 226.1597.



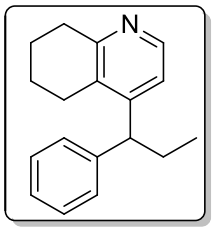
3-phenyl-4-(1-phenylpropyl)pyridine (4ha): The reaction was performed according to the above general procedure B. Yield: 54% (branch : linear = 85 : 15). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H), 8.40 (s, 1H,), 7.41-7.39 (m, 3H), 7.32 (d, $^{3}J_{HH}$ = 1.3Hz, 1H), 7.24-7.11 (m, 5H), 7.01-6.98 (m,2H), 3.95 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.04-1.94 (m, 2H), 0.78 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 151.3 (Ar), 150.6 (Ar), 149.0 (Ar), 143.6 (Ar), 138.3 (Ar), 138.1 (Ar), 129.9 (Ar), 128.6 (Ar), 128.4 (Ar), 128.0 (Ar), 127.8 (Ar), 126.5 (Ar), 122.0 (Ar), 48.0 (CH), 28.0 (CH_2), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{20}H_{20}N$ ([M+H]$^{+}$) 274.1596, found 274.1596.



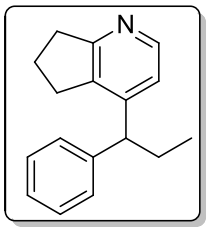
2-phenyl-4-(1-phenylpropyl)pyridine (4ia): The reaction was performed according to the above general procedure B. Yield: 36% (para : meta = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, $^{3}J_{HH}$ = 1.1 Hz, 1H), 7.57 (s, 1H,), 7.45-7.41 (m, 2H), 7.29 (s, 1H), 7.225-7.21 (m, 7H), 7.15 (s, 1H), 7.10 (s, 1H), 7.02 (s, 1H), 4.18 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.15-2.08 (m, 2H), 0.92 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). HR-MS (ESI): m/z calcd. for $C_{20}H_{20}N$ ([M+H]$^{+}$) 274.1596, found 274.1596.



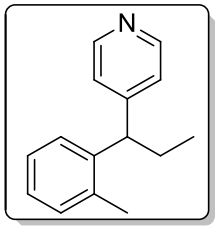
4-(1-phenylpropyl)quinoline (4la): The reaction was performed according to the above general procedure B. Yield: 28% (branch : linear = 55 : 45). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.87 (d, $^{3}J_{HH}$ = 1.1 Hz, 1H), 8.10 (d, $^{3}J_{HH}$ = 2.34 Hz, 1H), 7.92 (d, $^{3}J_{HH}$ = 2.1 Hz, 1H), 7.70-7.60 (m, 1H), 7.56-7.44 (m, 1H), 7.32-7.12 (m, 6H), 4.58 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.20-2.06 (m, 2H), 0.97 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). HR-MS (ESI): m/z calcd. for $C_{18}H_{18}N$ ($[M+H]^{+}$) 248.1439, found 248.1433.



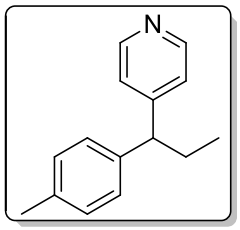
4-(1-phenylpropyl)-5,6,7,8-tetrahydroquinoline (4ma): The reaction was performed according to the above general procedure B. Yield: 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H), 7.26-7.21 (m, 2H), 7.17-7.11 (m, 3H), 7.07 (d, $^{3}J_{HH}$ = 1.3Hz, 1H), 3.91 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.90 (s, 2H), 2.83-2.71 (m, 1H), 2.54-2.45 (m, 1H), 2.03-1.94 (m, 2H), 1.81-1.70 (m, 4H), 0.89 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 157.6 (Ar), 151.8 (Ar), 146.6 (Ar), 143.2 (Ar), 130.9 (Ar), 128.9 (Ar), 128.4 (Ar), 126.5 (Ar), 119.4 (Ar), 47.8 (CH), 29.0 (CH_2), 25.6 (CH_2), 23.0 (CH_2), 22.7 (CH_2), 12.8 (CH_3). HR-MS (ESI): m/z calcd. for $C_{18}H_{22}N$ ($[M+H]^{+}$) 252.1752, found 252.1749.



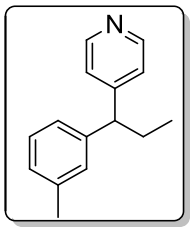
4-(1-phenylpropyl)-5,6,7,8-tetrahydroquinoline (4na): The reaction was performed according to the above general procedure B. Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, $^{3}J_{HH}$ = 1.3 Hz, 1H), 7.27-7.22 (m, 2H), 7.18-7.13 (m, 3H), 6.99 (d, $^{3}J_{HH}$ = 1.3Hz, 1H), 3.78 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.99-2.83 (m, 3H), 2.74-2.63 (m, 1H), 2.08-1.98 (m, 4H), 0.88 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 165.7 (Ar), 149.6 (Ar), 148.1 (Ar), 143.1 (Ar), 136.1 (Ar), 128.6 (Ar), 128.3 (Ar), 122.6 (Ar), 119.0 (Ar), 50.1 (CH), 34.6 (CH_2), 29.6 (CH_2), 27.9 (CH_2), 22.6 (CH_2), 12.8 (CH_3). HR-MS (ESI): m/z calcd. for $C_{17}H_{20}N$ ($[M+H]^{+}$) 238.1596, found 238.1598.



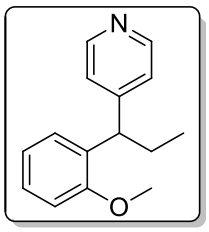
4-(1-(o-tolyl)propyl)pyridine (4ab): The reaction was performed according to the above general procedure B. Yield: 77% (branch : linear = 87 : 13). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 7.13-7.09 (m, 6H), 2.70-2.60 (m, 4H), 2.25 (s, 3H), 1.96-1.88 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 151.6 (Ar), 149.7 (Ar), 140.0 (Ar), 136.0 (Ar), 130.5 (Ar), 129.0 (Ar), 126.3 (Ar), 126.2 (Ar), 124.1 (Ar), 35.2 (CH), 32.9 (CH_2), 30.7 (CH_3), 19.4 (CH_3). HR-MS (APCI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1434.



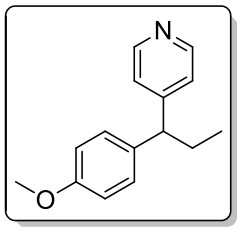
4-(1-(p-tolyl)propyl)pyridine (4ac): The reaction was performed according to the above general procedure B. Yield: 70% (branch : linear = 86 : 14). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 7.14 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.10-7.05 (m, 4H), 3.71 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.28 (s, 3H), 2.07-1.97 (m, 2H), 0.87 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 154.9 (Ar), 149.4 (Ar), 140.1 (Ar), 136.4 (Ar), 129.5 (Ar), 127.9 (Ar), 123.5 (Ar), 52.3 (CH), 28.0 (CH_3), 21.1 (CH_2), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1434.



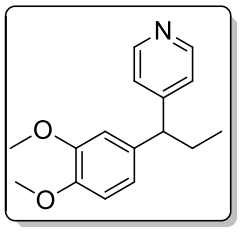
4-(1-(m-tolyl)propyl)pyridine (4ad): The reaction was performed according to the above general procedure B. Yield: 71% (branch : linear = 87 : 13). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, $^{3}J_{HH}$ = 1.2 Hz, 2H), 7.19-7.13 (m, 3H), 7.00-6.98 (m, 3H), 3.70 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.29 (s, 3H), 2.08-1.98 (m, 2H), 0.87 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 154.5 (Ar), 149.6 (Ar), 143.1 (Ar), 138.3 (Ar), 128.8 (Ar), 128.6 (Ar), 127.5 (Ar), 125.0 (Ar), 123.5 (Ar), 52.7 (CH), 28.0 (CH_3), 21.6 (CH_2), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1439.



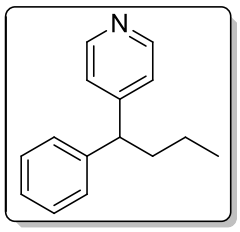
4-(1-(2-methoxyphenyl)propyl)pyridine (4ae): The reaction was performed according to the above general procedure B. Yield: 78% (branch : linear = 95 : 5). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 7.20-7.14 (m, 4H), 6.91 (t, $^{3}J_{HH}$ =1.9 Hz, 1H), 6.80 (t, $^{3}J_{HH}$ = 2.0 Hz, 1H), 4.21 (t, $^{3}J_{HH}$ = 2.0 Hz, 1H), 3.70 (s, 3H), 2.05-1.95 (m, 2H), 0.87 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 157.2 (Ar), 155.1 (Ar), 149.0 (Ar), 131.5 (Ar), 127.8 (Ar), 127.6 (Ar), 123.8 (Ar), 120.7 (Ar), 110.8 (Ar), 55.4 (CH), 44.9 (CH_3), 27.0 (CH_2), 12.6 (CH_3). HR-MS (APCI): m/z calcd. for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1388, found 228.1381.



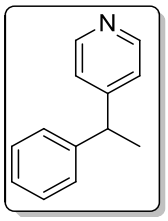
4-(1-(4-methoxyphenyl)propyl)pyridine (4af): The reaction was performed according to the above general procedure B. Yield: 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.13-7.07 (m, 4H), 6.81 (d, $^{3}J_{HH}$ = 2.2 Hz, 2H), 3.73 (s, 3H), 3.69 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.05-1.95 (m, 2H), 0.86 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 158.4 (Ar), 155.0 (Ar), 149.5 (Ar), 135.2 (Ar), 129.0 (Ar), 123.4 (Ar), 114.1 (Ar), 55.3 (CH_3), 51.9 (CH), 28.1 (CH_2), 12.7 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1388, found 228.1388.



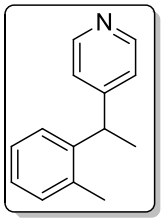
4-(1-(3,4-dimethoxyphenyl)propyl)pyridine (4ag): The reaction was performed according to the above general procedure B. Yield: 43%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$ = 1.1 Hz, 2H), 7.12 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 6.81-6.73 (m, 2H), 6.66 (s, 1H), 3.82 (d, $^{3}J_{HH}$ = 1.3 Hz, 6H), 3.69 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H), 2.07-1.97 (m, 2H), 0.88 (t, $^{3}J_{HH}$ = 1.9 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):δ 154.5 (Ar), 155.0 (Ar), 149.2 (Ar), 148.0 (Ar), 135.9 (Ar), 123.4 (Ar), 120.0 (Ar), 111.5 (Ar), 111.4 (Ar), 56.1 (CH_3), 52.3 (CH), 28.3 (CH_2), 12.8 (CH_3). HR-MS (ESI): m/z calcd. for $C_{16}H_{20}NO_2$ ($[M+H]^+$) 258.1494, found 258.1491.



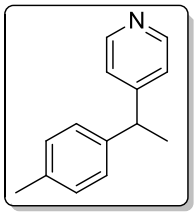
4-(1-phenylbutyl)pyridine (4am): The reaction was performed according to the above general procedure B. Yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$ = 1.0 Hz, 2H), 7.30-7.08 (m, 6H), 3.86 (t, $^{3}J_{HH}$ = 1.9 Hz, ^{1}H), 2.03-1.96 (m, 2H), 1.32-1.19 (m, 2H), 0.91 (t, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 154.4 (Ar), 150.0 (Ar), 143.5 (Ar), 128.8 (Ar), 128.1 (Ar), 126.8 (Ar), 123.5 (Ar), 50.7 (CH), 37.3 (CH_2), 21.2 (CH_2), 14.2 (CH_3). HR-MS (ESI): m/z calcd. for $C_{15}H_{18}N$ ($[M+H]^+$) 212.1439, found 212.1443.



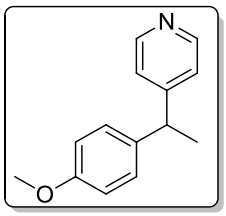
4-(1-(o-tolyl)ethyl)pyridine (6aa): The reaction was performed according to the above general procedure C. Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.32-7.10 (m, 7H), 4.13-4.06 (m, 1H), 1.62 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 155.2 (Ar), 149.9 (Ar), 144.5 (Ar), 128.8 (Ar), 127.8 (Ar),126.8 (Ar), 123.1 (Ar), 44.4 (CH), 21.2 (CH_3). HR-MS (ESI): m/z calcd. for $C_{13}H_{14}N$ ($[M+H]^+$) 184.1126, found 184.1124.



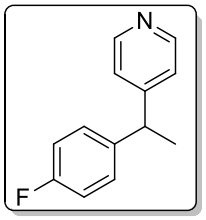
4-(1-(o-tolyl)ethyl)pyridine (6ab): The reaction was performed according to the above general procedure C. Yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H), 7.21-7.13 (m, 4H), 7.05-7.03 (m, 2H), 4.31-4.24 (m, 1H), 2.19 (s, 3H), 1.59 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 155.2 (Ar), 142.2 (Ar), 136.1 (Ar), 130.7(Ar), 126.8 (Ar),126.4 (Ar), 123.1 (Ar), 40.6 (CH), 21.4 (CH_3). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}N$ ($[M+H]^+$) 198.1283, found 198.1284.



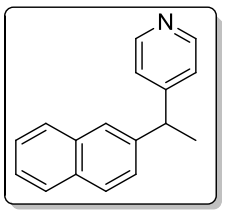
4-(1-(p-tolyl)ethyl)pyridine (6ac): The reaction was performed according to the above general procedure C. Yield: 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$=1.5 Hz, 2H), 7.12-7.05 (m, 6H), 4.09-4.02 (m, 1H), 2.30 (s, 3H), 1.60 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 155.5 (Ar), 149.8 (Ar), 149.9 (Ar), 141.5 (Ar), 136.3 (Ar), 129.4 (Ar), 127.6 (Ar), 123.0 (Ar), 43.9 (CH), 21.2 (CH_3), 21.1 (CH_3). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}N$ ($[M+H]^+$) 198.1283, found 198.1282.



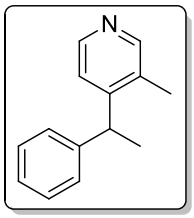
4-(1-(4-methoxyphenyl)ethyl)pyridine (6ad): The reaction was performed according to the above general procedure C. Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{HH}$= 1.3 Hz, 2H), 7.10-7.07 (m, 4H), 6.83 (d, $^{3}J_{HH}$= 2.2 Hz, 2H), 4.08-4.01 (m, 1H), 3.76 (s, 3H), 1.59 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 158.4 (Ar), 155.7 (Ar), 149.9 (Ar), 136.7 (Ar), 128.7 (Ar), 123.1 (Ar), 114.1 (Ar), 55.3 (CH_3), 43.6 (CH), 21.4 (CH_3). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}N$ ($[M+H]^+$) 214.1232, found 214.1228.



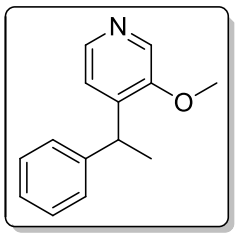
4-(1-(4-fluorophenyl)ethyl)pyridine (6ae): The reaction was performed according to the above general procedure C. Yield: 79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, $^{3}J_{HH}$= 1.5 Hz, 2H), 7.15-7.07 (m, 4H), 7.01-6.94 (m, 2H), 4.12-4.04 (m, 1H), 1.60 (d, $^{3}J_{HH}$= 1.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 161.8 (d, $^{1}J_{FC}$= 243.6 Hz, Ar), 155.1 (s, Ar), 150.1 (s, Ar), 140.3 (s, Ar), 129.2 (d, $^{3}J_{FC}$= 7.8 Hz, Ar), 123.0 (s, Ar), 115.6 (, $^{2}J_{FC}$= 21.1 Hz d, Ar), 43.7 (s, CH), 21.4 (s, CH_3). HR-MS (ESI): m/z calcd. for $C_{13}H_{13}NF$ ($[M+H]^+$) 202.1032, found 202.1037.



4-(1-(naphthalen-2-yl)ethyl)pyridine (6af): The reaction was performed according to the above general procedure C. Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 7.81-7.74 (m, 3H), 7.67 (s, 1H), 7.50-7.41 (m, 2H), 7.16 (d, $^{3}J_{HH}$ = 1.4 Hz, 2H), 4.30-4.23 (m, 1H), 1.72 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 155.1 (Ar), 150.0 (Ar), 141.9 (Ar), 133.6 (Ar), 132.5 (Ar), 128.5 (Ar), 127.9 (Ar), 127.8 (Ar), 126.5 (Ar), 126.4 (Ar), 125.9 (Ar), 123.3 (Ar), 44.5 (CH), 21.2 (CH_3). HR-MS (ESI): m/z calcd. for $C_{17}H_{16}N$ ($[M+H]^+$) 234.1283, found 234.1287.



3-methyl-4-(1-phenylethyl)pyridine (6ba): The reaction was performed according to the above general procedure C. Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, $^{3}J_{HH}$ = 1.3 Hz, 2H), 8.30 (s, 1H), 7.27-7.08 (m, 6H), 4.27-4.19 (m, 1H), 2.16 (s, 1H), 1.57 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 152.7 (Ar), 150.9 (Ar), 147.8 (Ar), 144.2 (Ar), 131.7 (Ar),128.6 (Ar), 127.7 (Ar), 126.5 (Ar), 121.5 (Ar), 40.9 (CH_3), 21.4 (CH), 16.5 (CH_3). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}N$ ($[M+H]^+$) 198.1283, found 198.1285.

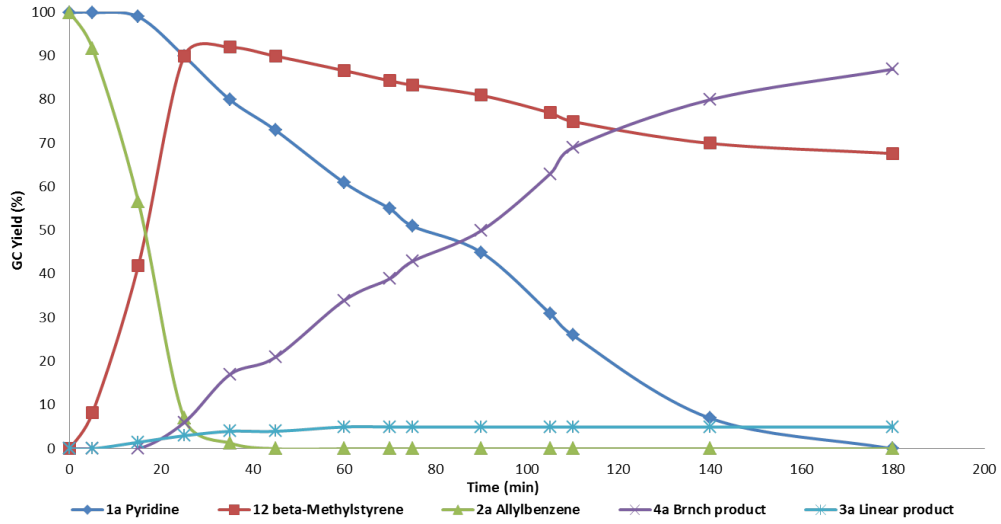


3-methoxy-4-(1-phenylethyl)pyridine (6da): The reaction was performed according to the above general procedure C. Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, $^{3}J_{HH}$ = 1.6 Hz, 2H), 7.29-7.15 (m, 5H), 7.03 (d, $^{3}J_{HH}$ = 1.2 Hz, 1H), 4.55-4.48 (m, 1H), 3.84 (s, 1H), 1.55 (d, $^{3}J_{HH}$ = 1.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):δ 153.3 (Ar), 144.5 (Ar), 143.4 (Ar), 142.9 (Ar), 133.3 (Ar),128.5 (Ar), 127.8 (Ar), 126.4 (Ar), 122.2 (Ar), 56.2 (CH_3), 37.2 (CH), 20.3 (CH_3). HR-MS (ESI): m/z calcd. for $C_{14}H_{16}NO$ ($[M+H]^+$) 214.1232, found 214.1237.

Kinetic Isotope Effect (KIE) Experiments

Intermolecular competition reactions between pyridine and d_5-pyridine with allylbenzene: To perform the KIE experiments, the target coupling product **4aa** was prepared as the standard for GC-MS analysis to afford the calibration curve involving product concentration and peak area. The intermolecular competition reactions between pyridine and d_5-pyridine with allylbenzene were examined in two separated vials. The reaction was carried out according to the general procedure A under the same conditions. After cooling down, the reaction mixture was filtered through a short pad of silica gel and washed with acetone**.** The filtrate was concentrated under reduced pressure. The resulting crude mixture was subjected and analyzed by GC. The GC yield of the product **4aa** was obtained according to the calibration curve. The ratio of the two product yields represents the KIE value (k_H/k_D = 1.1).

Figure S1. GC analysis.



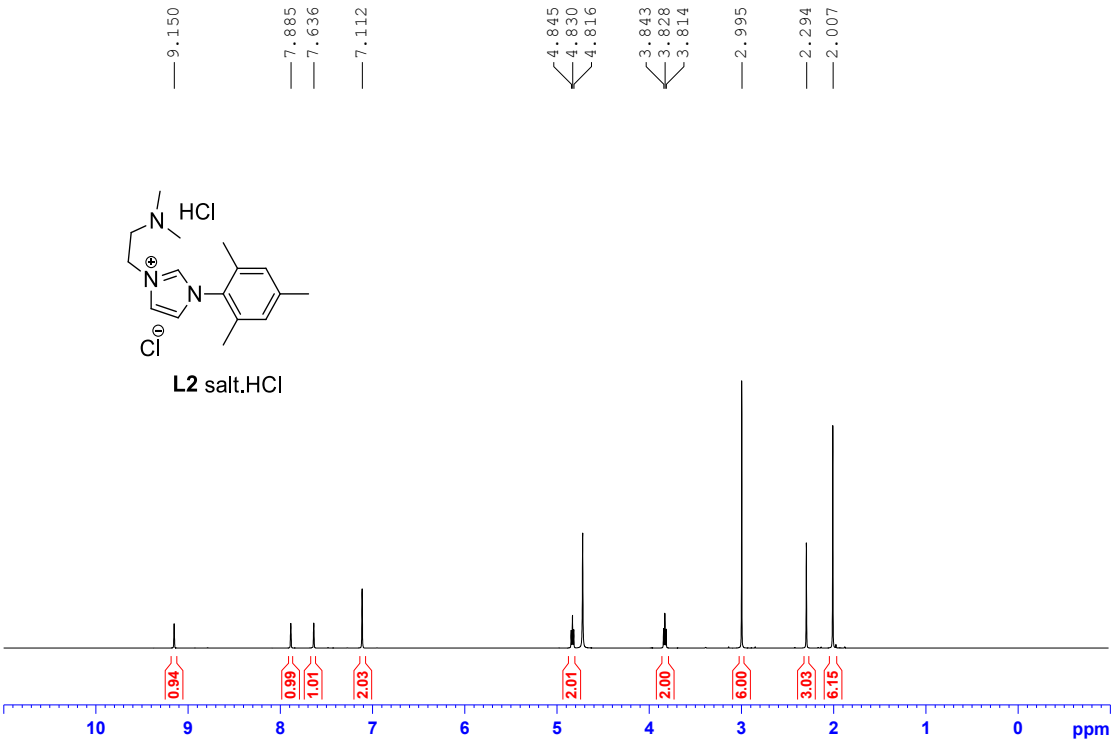


Figure 1S. ^{1}H NMR spectrum of **L2** salt • HCl.

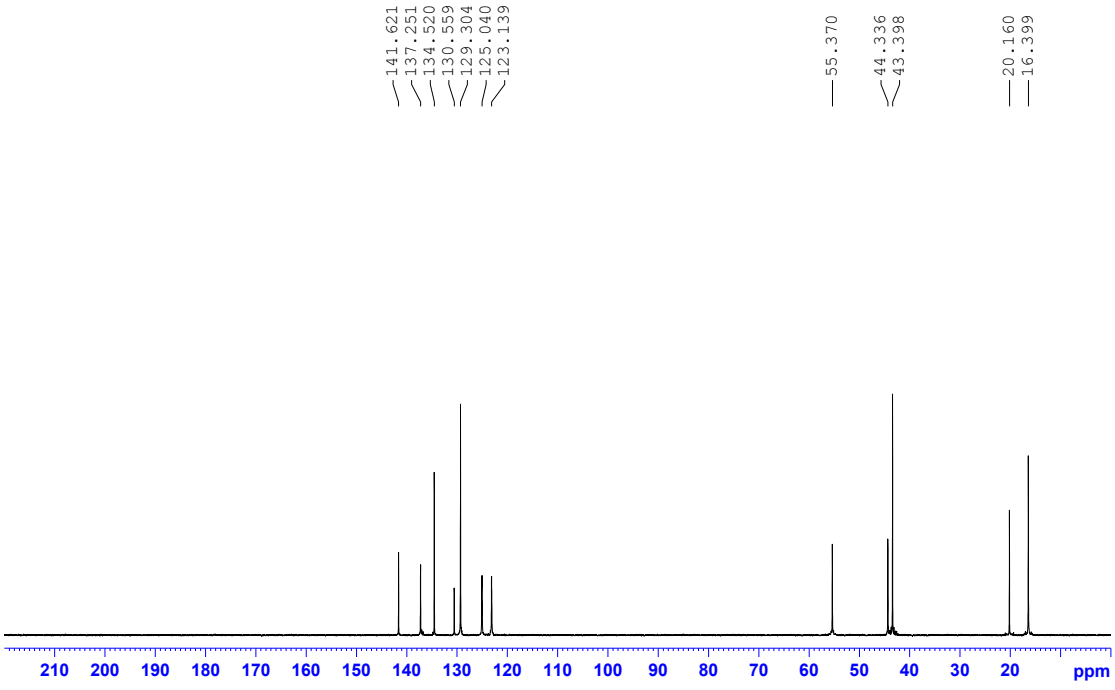


Figure 2S. ^{13}C{^{1}H} NMR spectrum of **L2** salt • HCl.

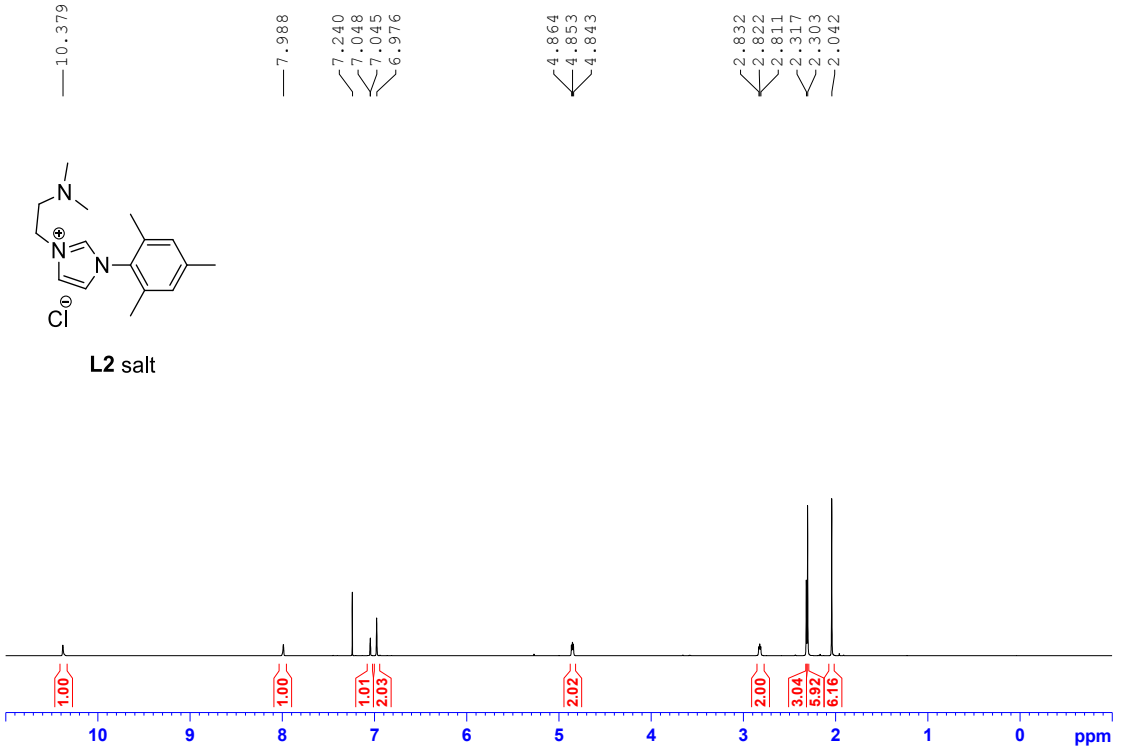


Figure 3S. ^{1}H NMR spectrum of **L2** salt.

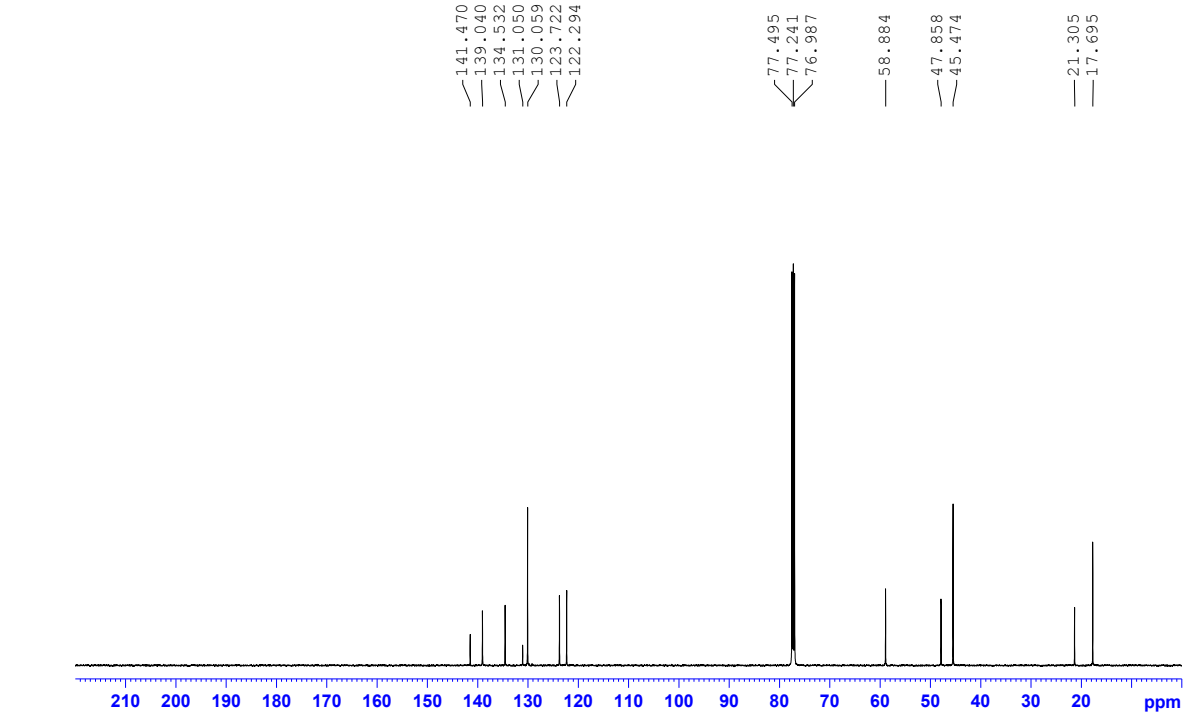


Figure 4S. ^{13}C{^{1}H} NMR spectrum of **L2** salt.

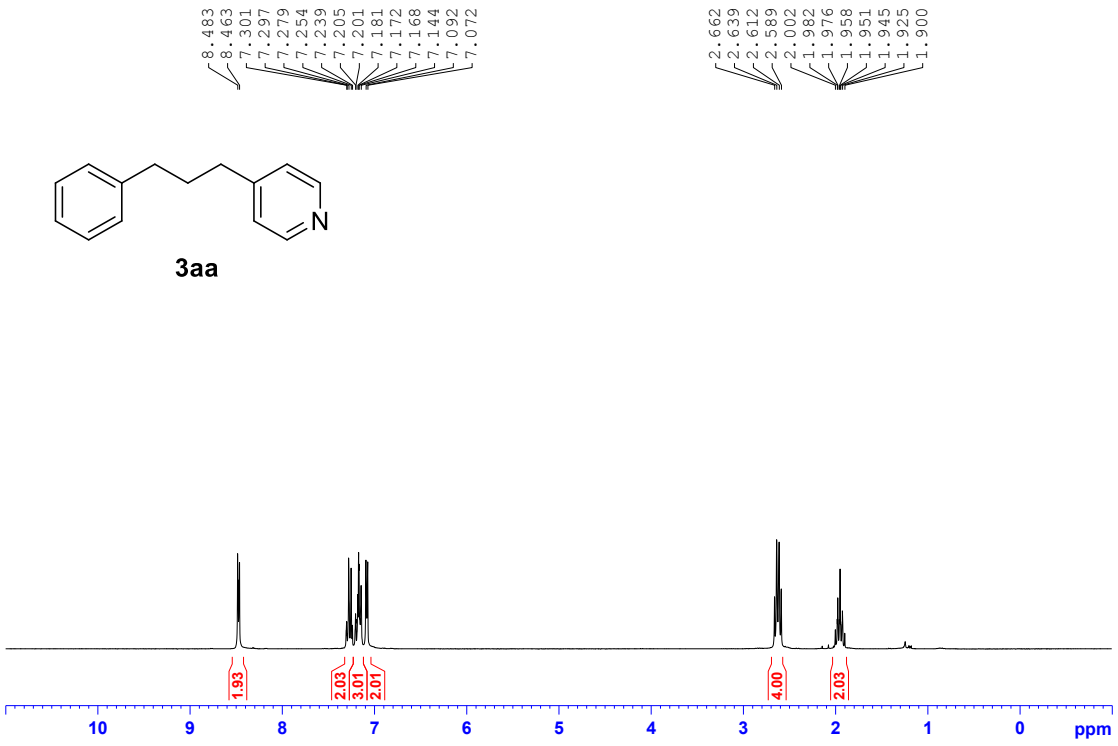


Figure 5S. ^{1}H NMR spectrum of **3aa**.

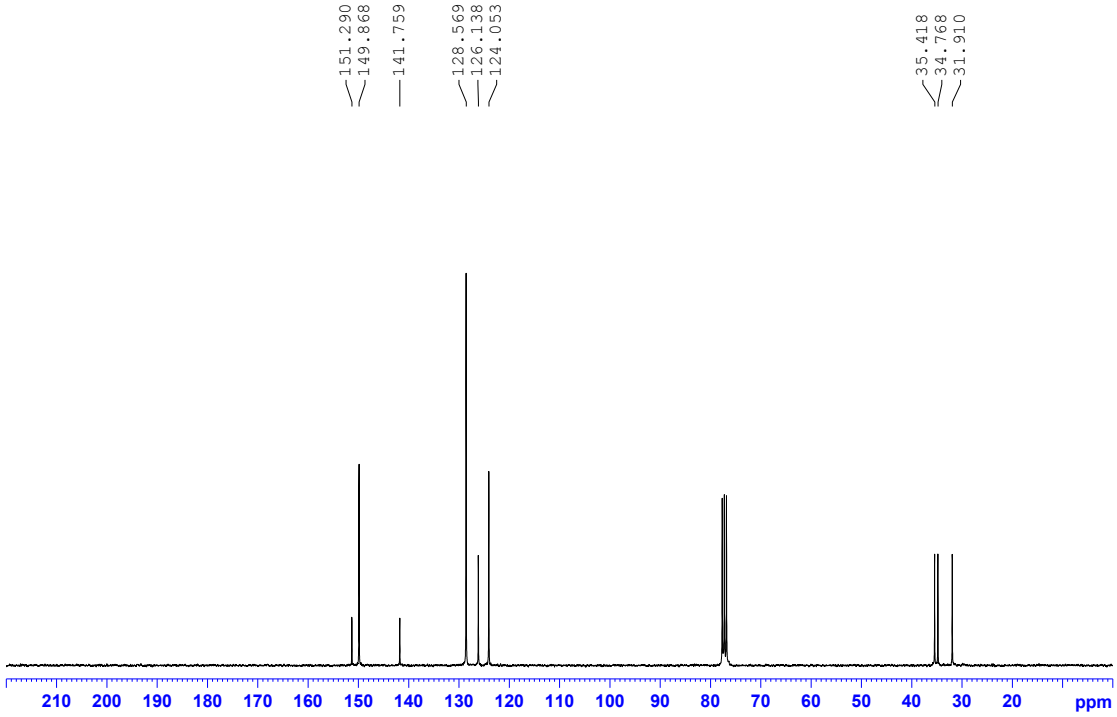


Figure 6S. ^{13}C{^{1}H} NMR spectrum of **3aa**.

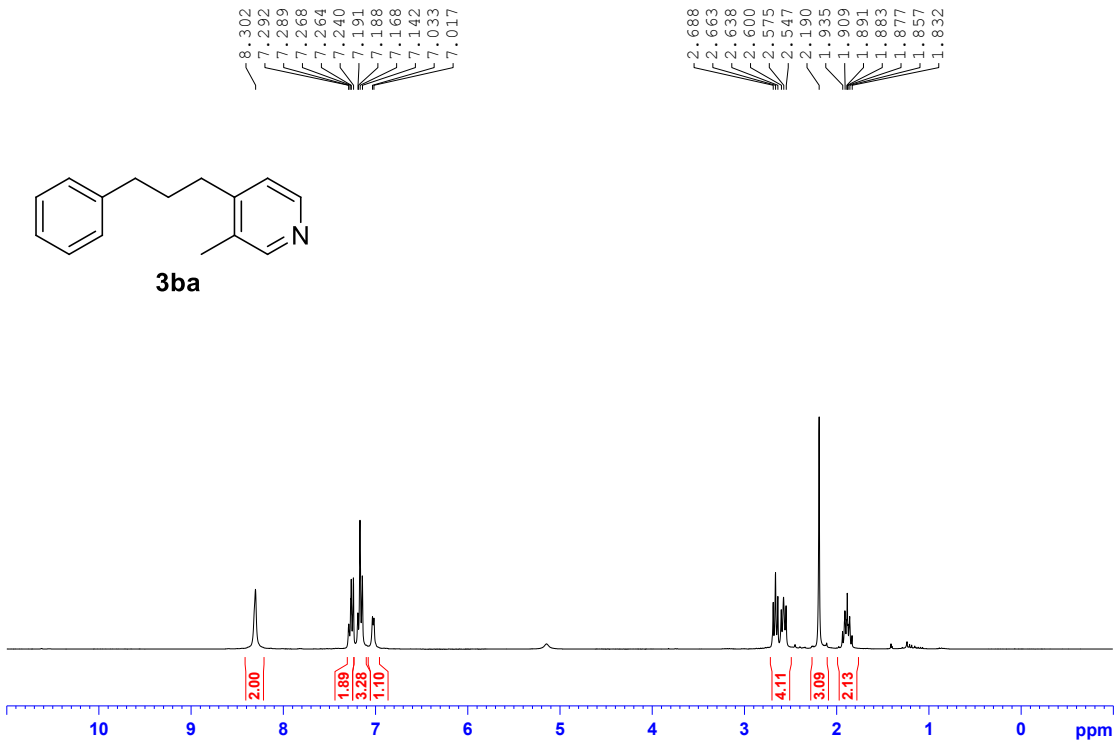


Figure 7S. ^{1}H NMR spectrum of **3ba**.

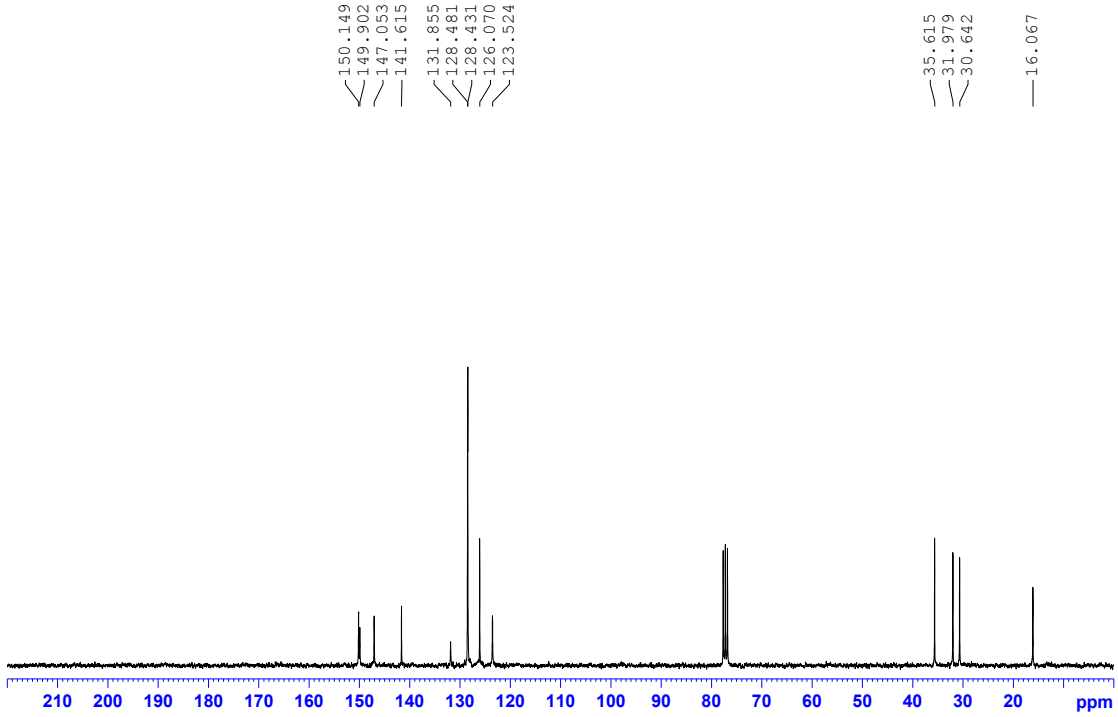


Figure 8S. ^{13}C{^{1}H} NMR spectrum of **3ba**.

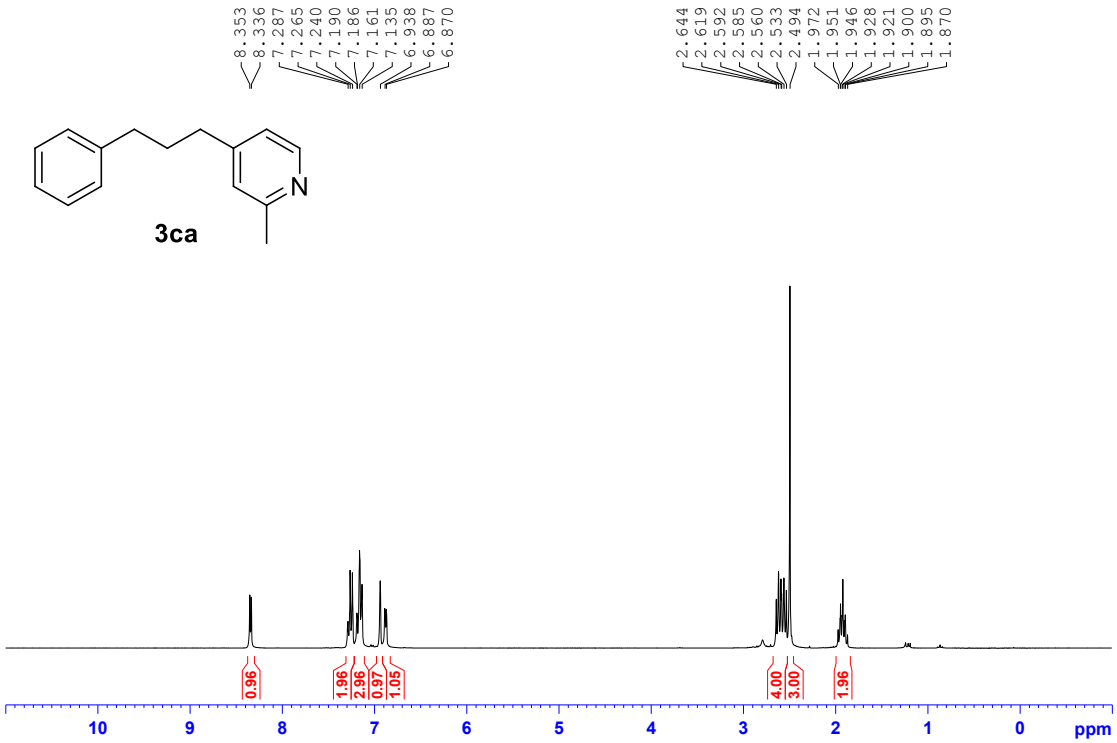


Figure 9S. ^{1}H NMR spectrum of **3ca**.

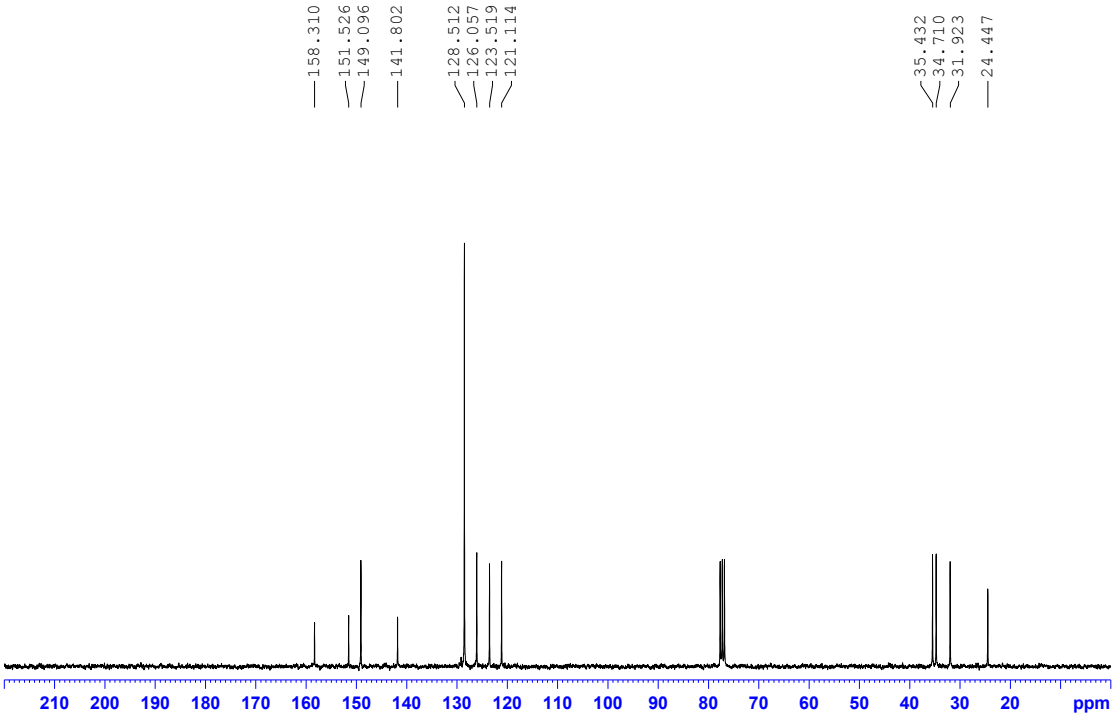


Figure 10S. ^{13}C{^{1}H} NMR spectrum of **3ca**.

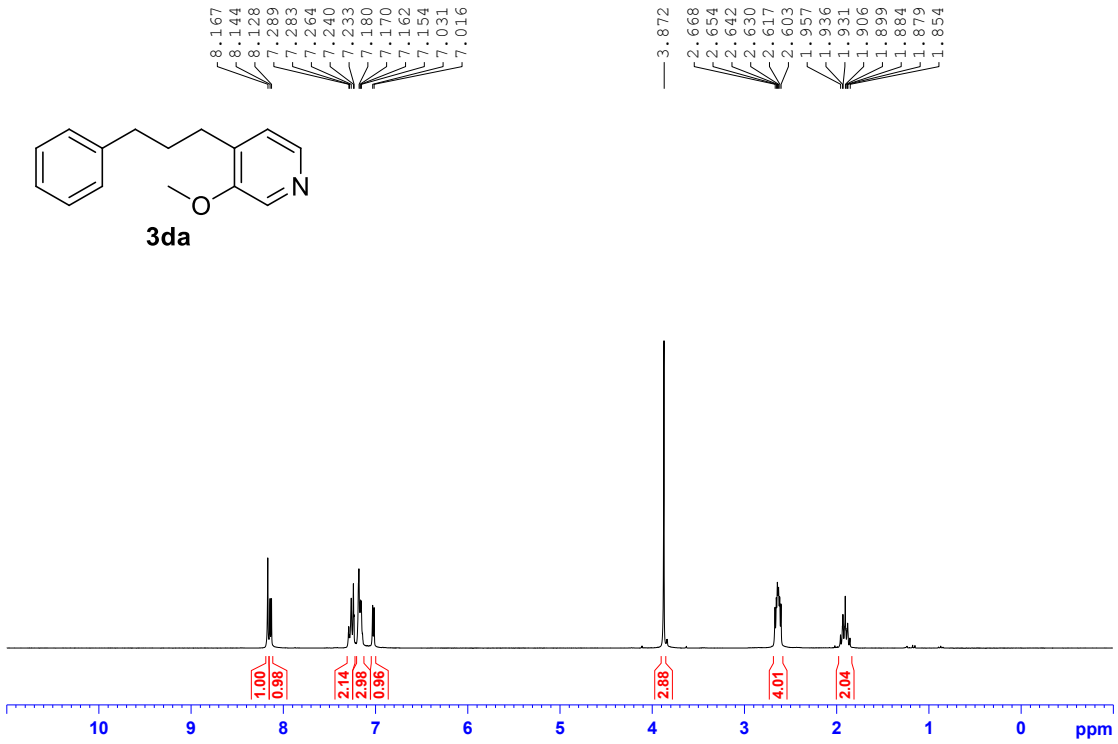


Figure 11S. ^{1}H NMR spectrum of **3da**.

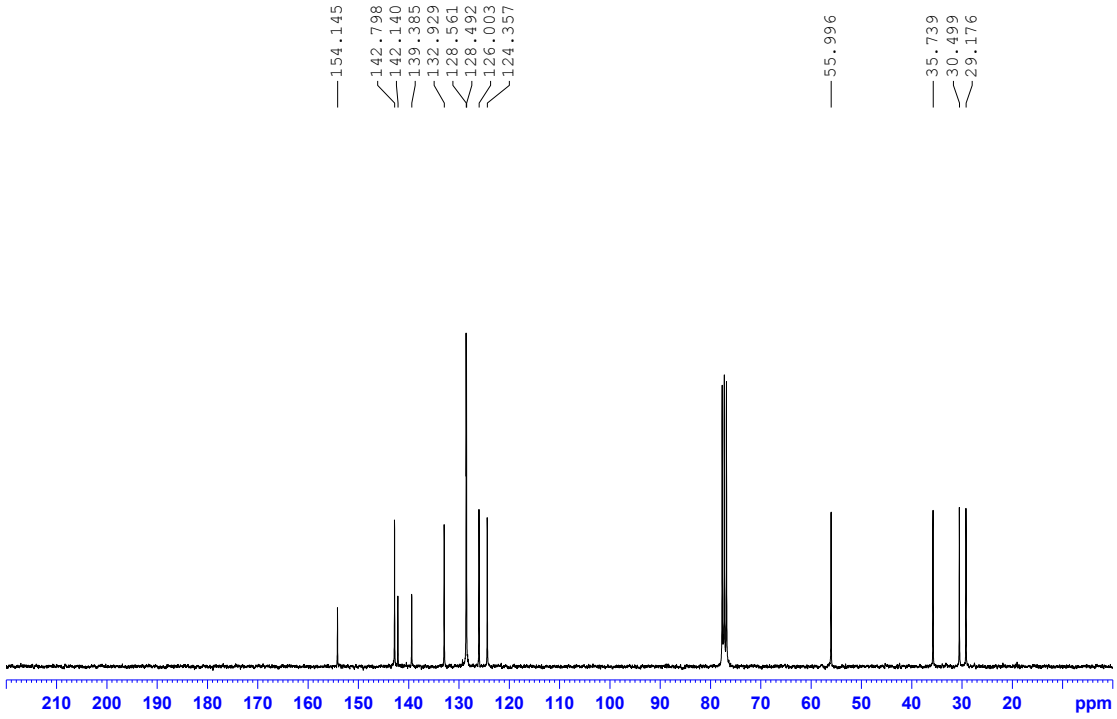


Figure 12S. ^{13}C{^{1}H} NMR spectrum of **3da**.

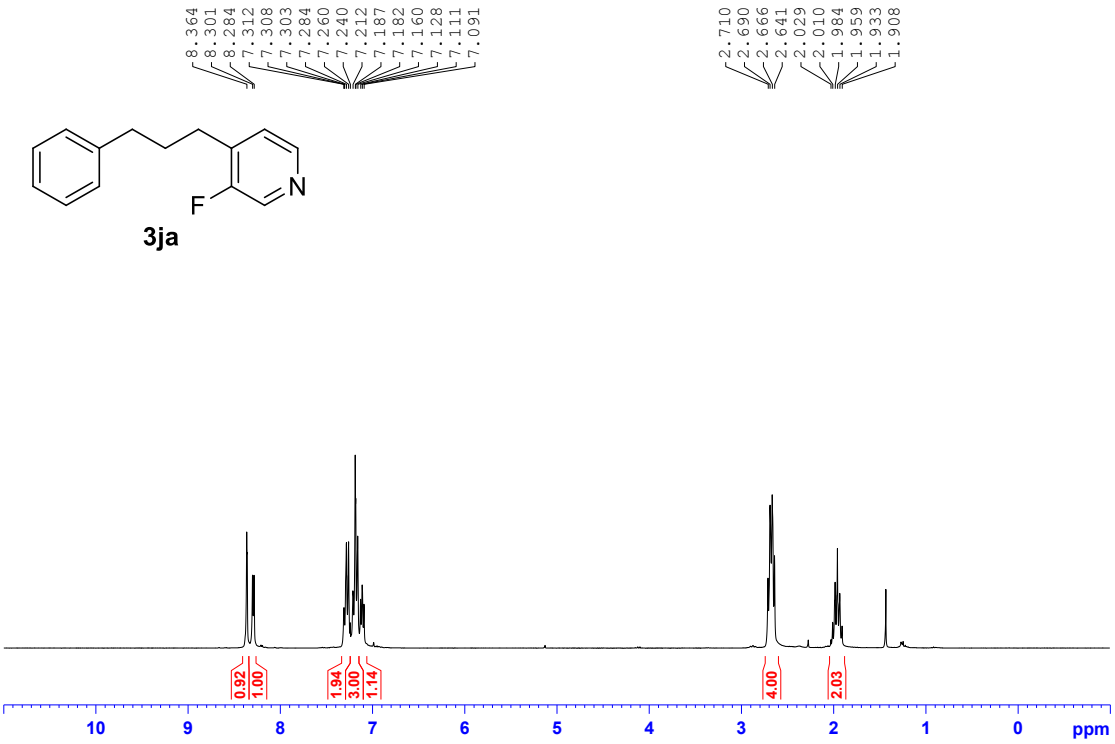


Figure 13S. ^{1}H NMR spectrum of **3ja**.

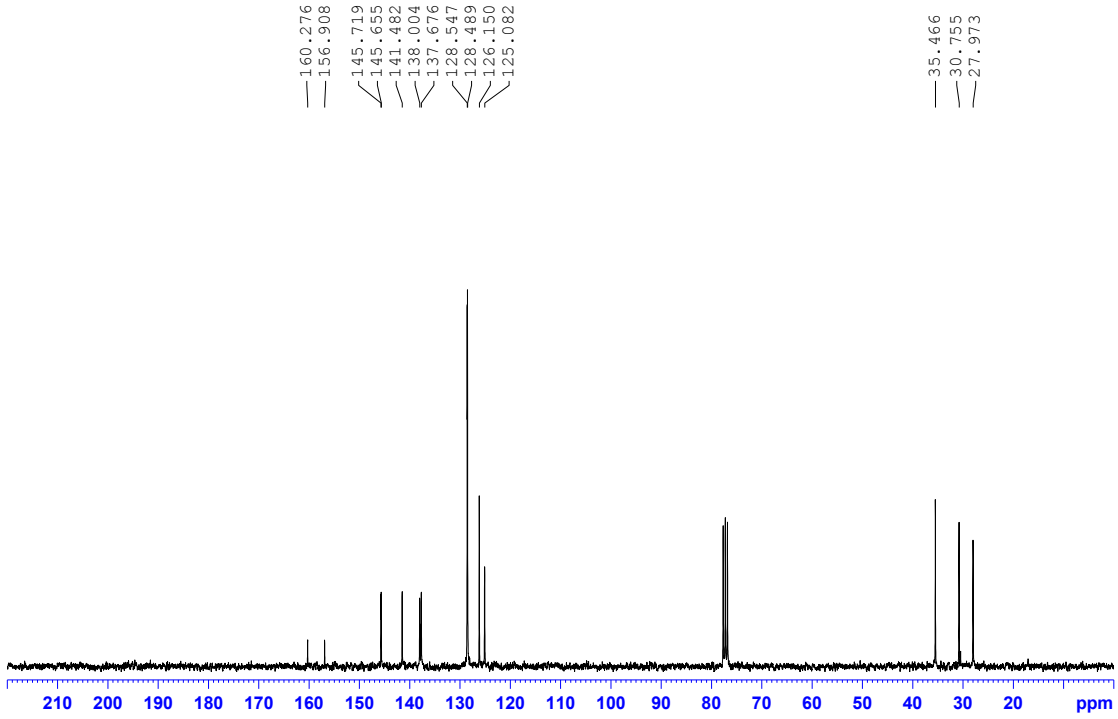


Figure 14S. ^{13}C{^{1}H} NMR spectrum of **3ja**.

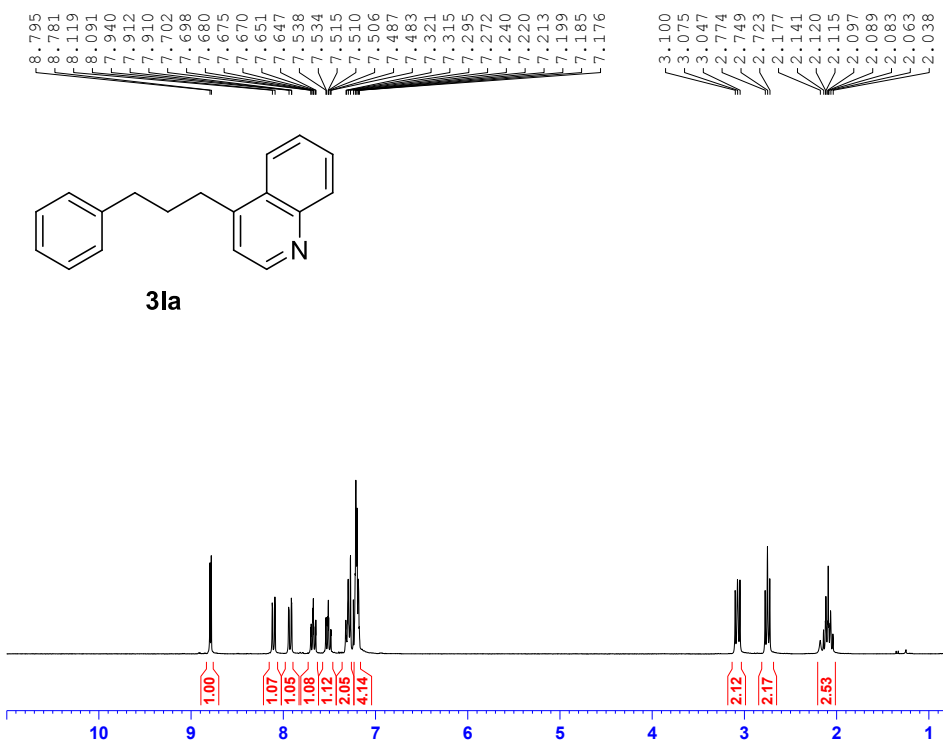


Figure 15S. ^{1}H NMR spectrum of **3la**.

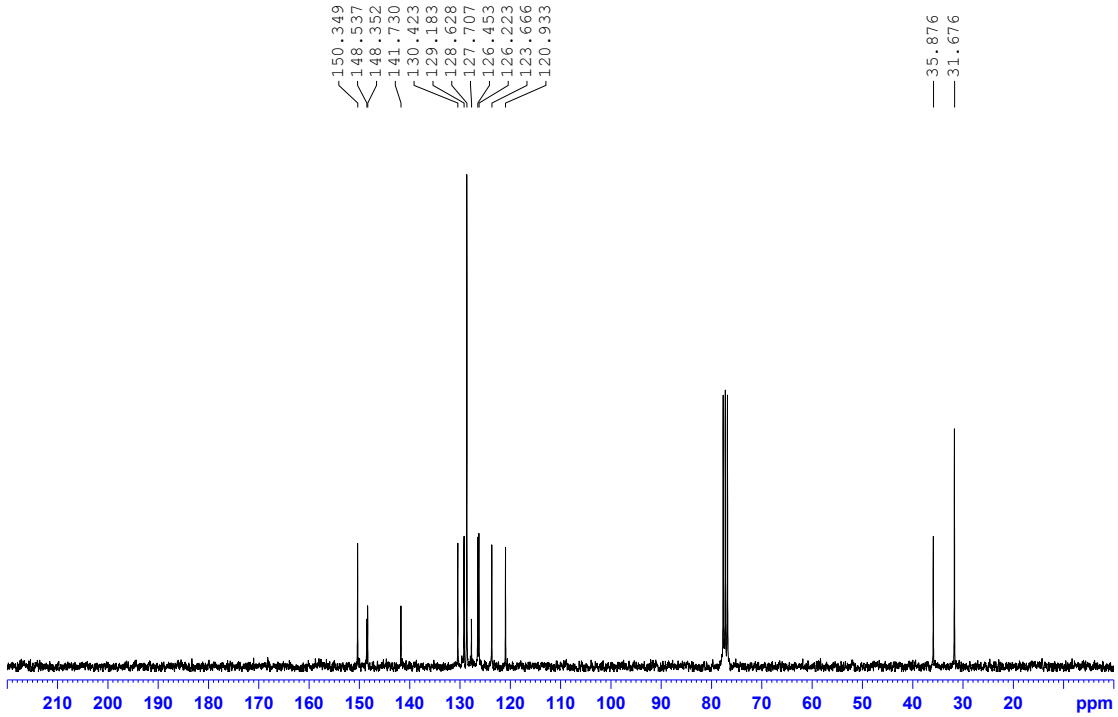


Figure 16S. ^{13}C{^{1}H} NMR spectrum of **3la**.

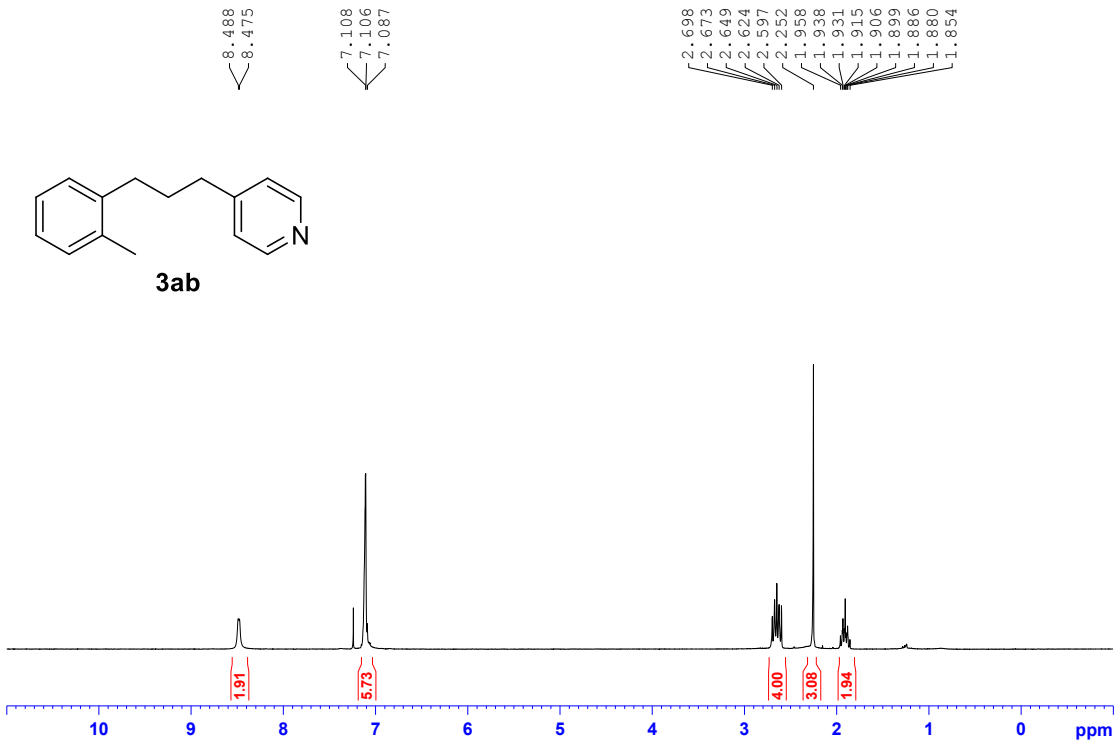


Figure 17S. ^{1}H NMR spectrum of **3ab**.

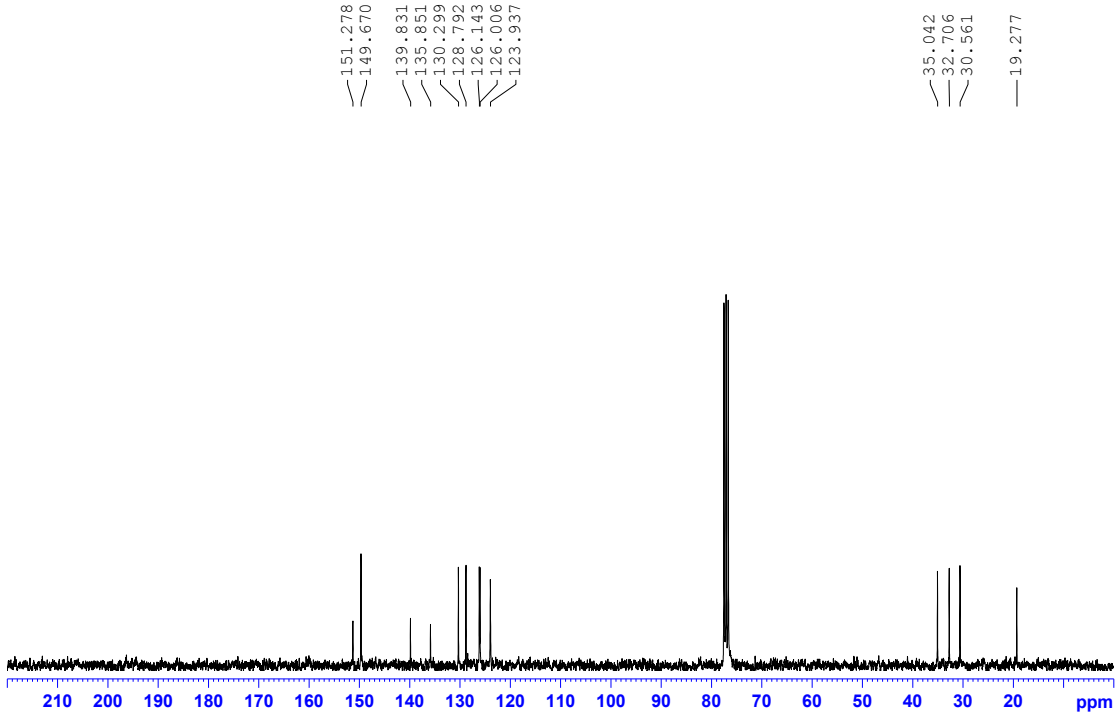


Figure 18S. ^{13}C{^{1}H} NMR spectrum of **3ab**.

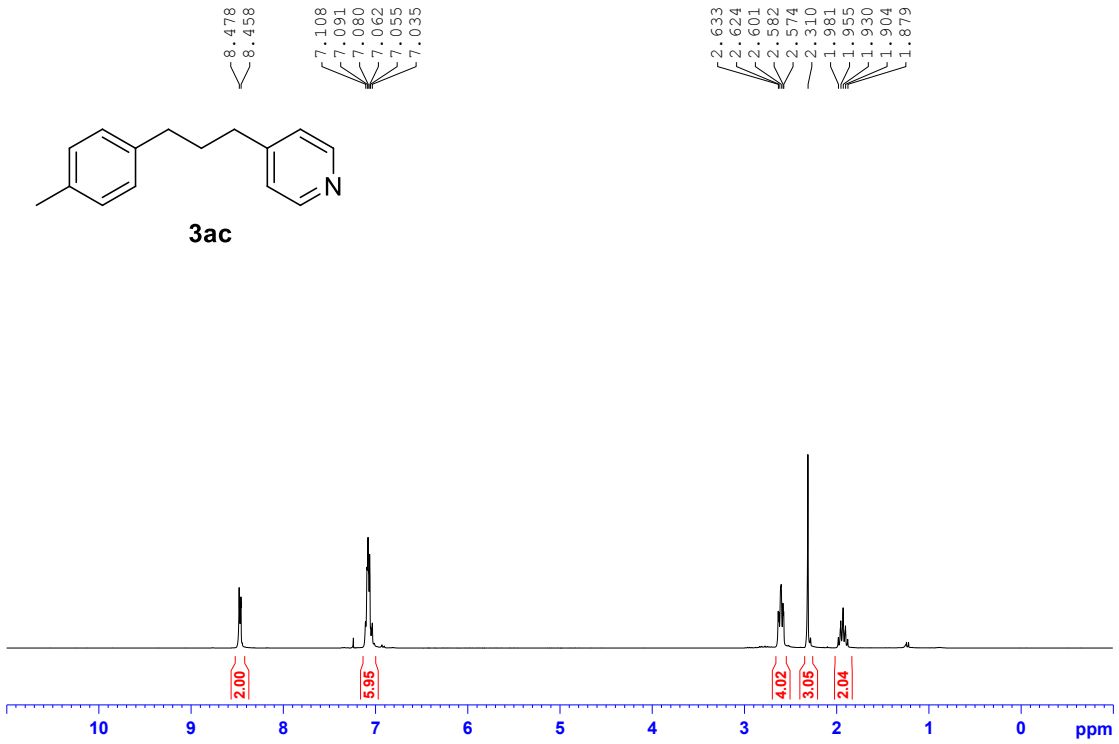


Figure 19S. ^{1}H NMR spectrum of **3ac**.

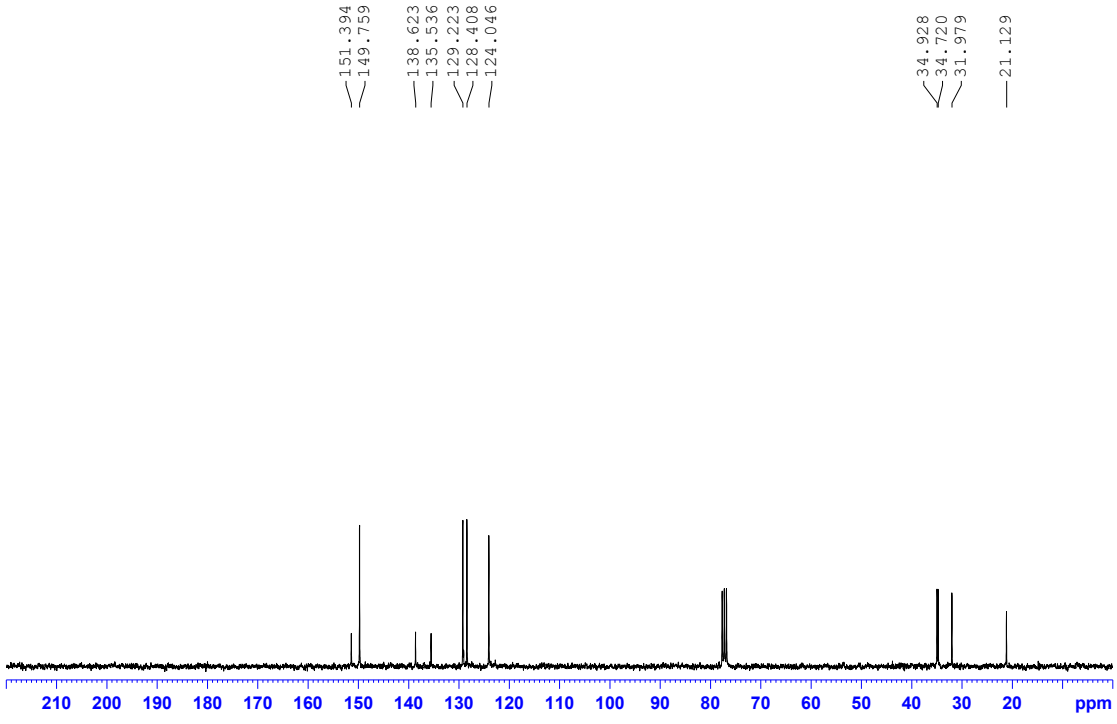


Figure 20S. ^{13}C{^{1}H} NMR spectrum of **3ac**.

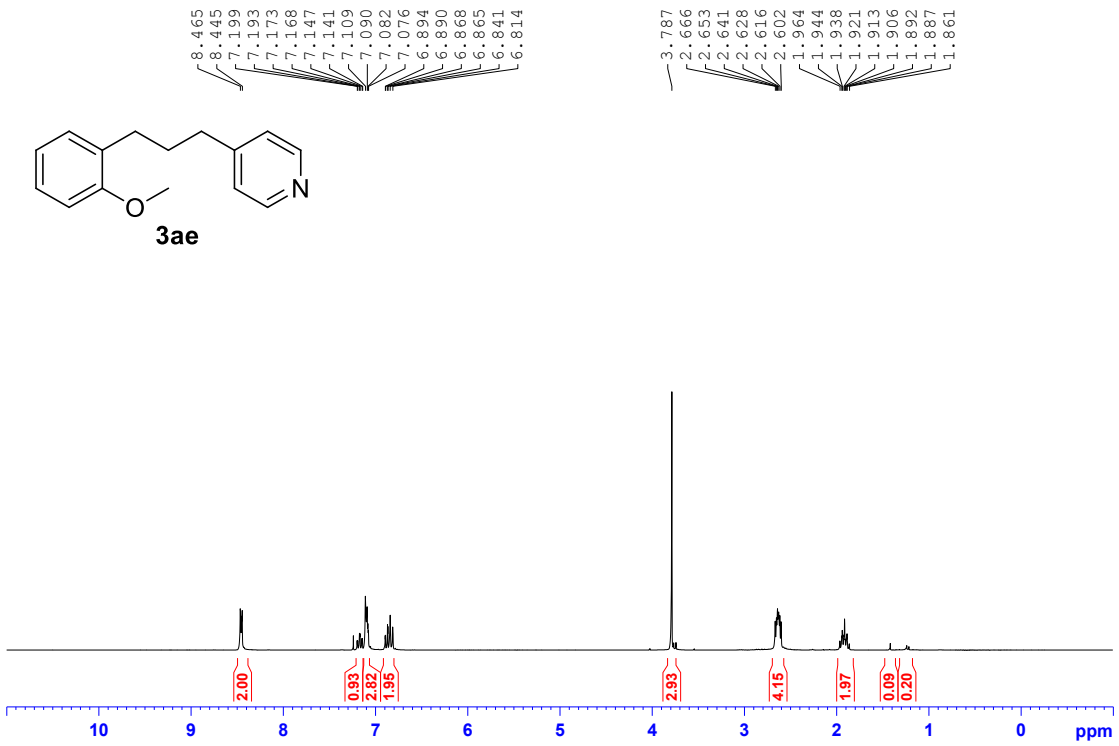


Figure 21S. ^{1}H NMR spectrum of **3ae**.

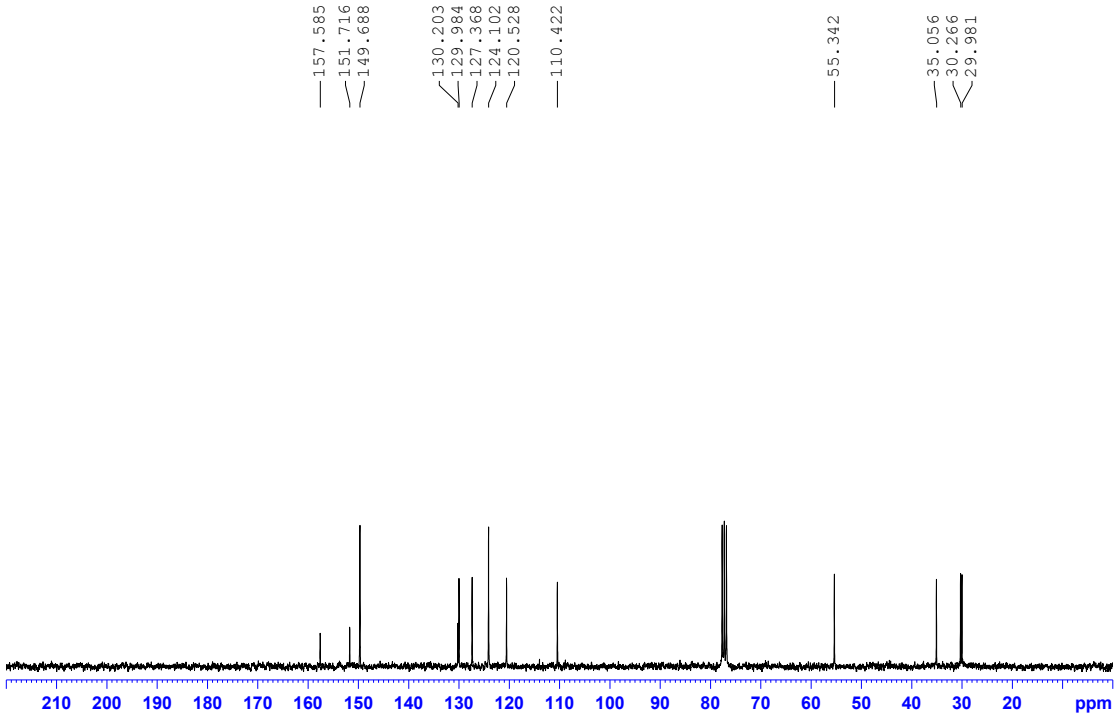


Figure 22S. ^{13}C{^{1}H} NMR spectrum of **3ae**.

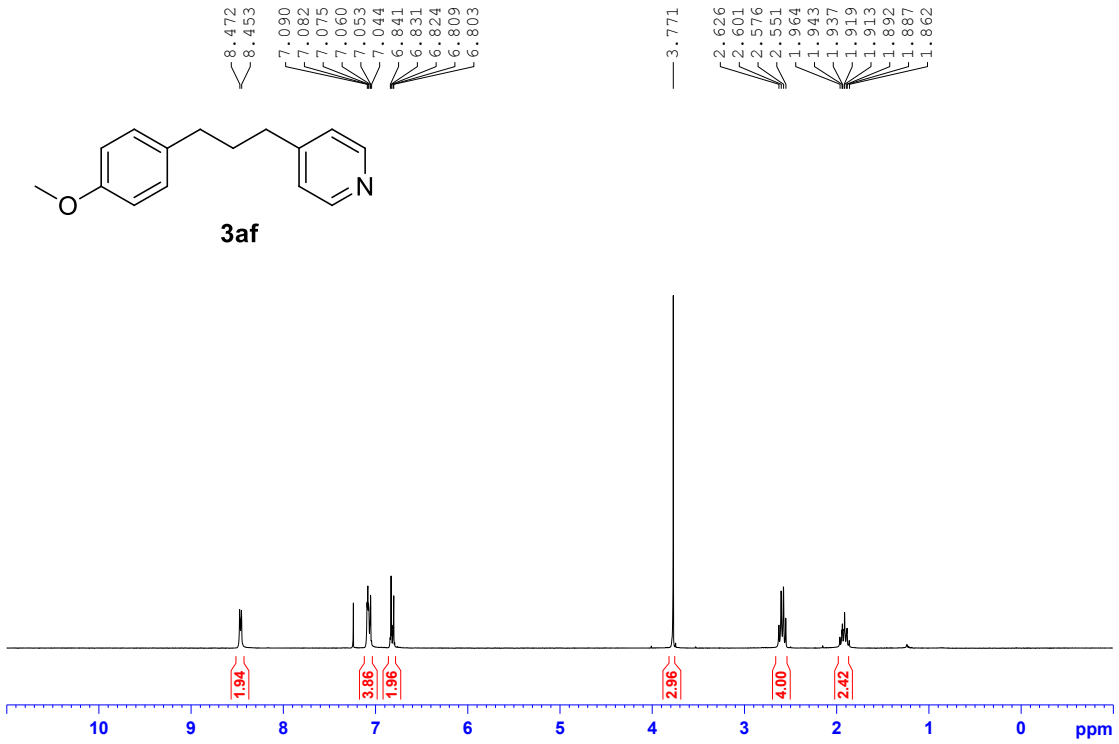


Figure 23S. ^{1}H NMR spectrum of **3af**.

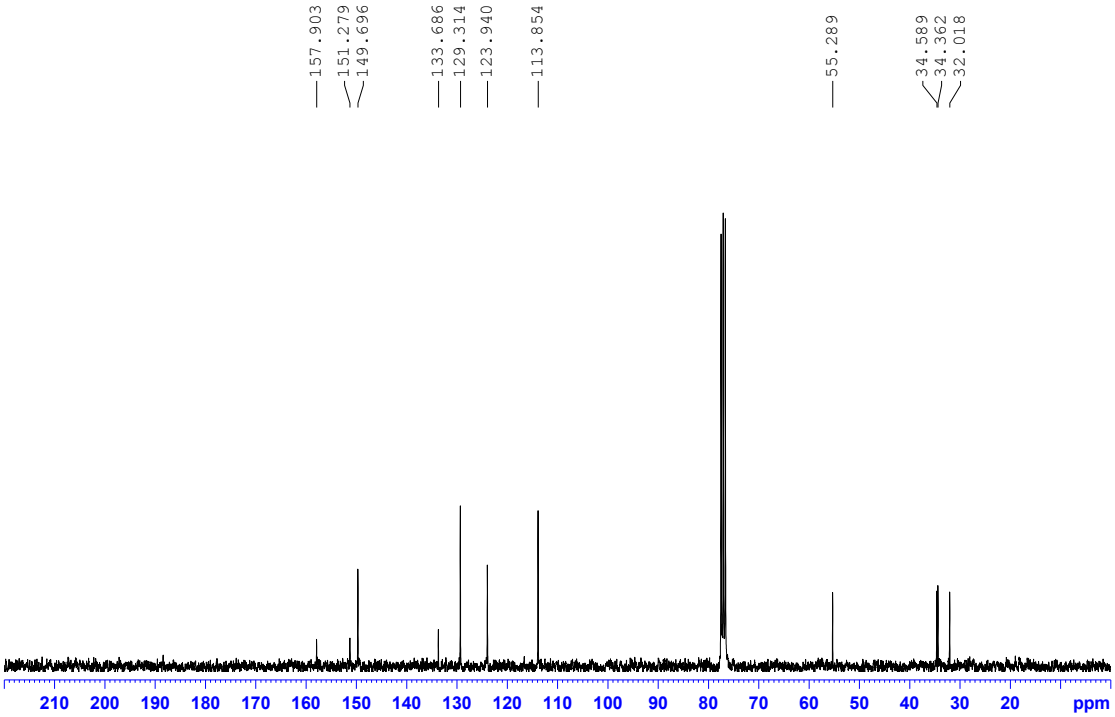


Figure 24S. ^{13}C{^{1}H} NMR spectrum of **3af**.

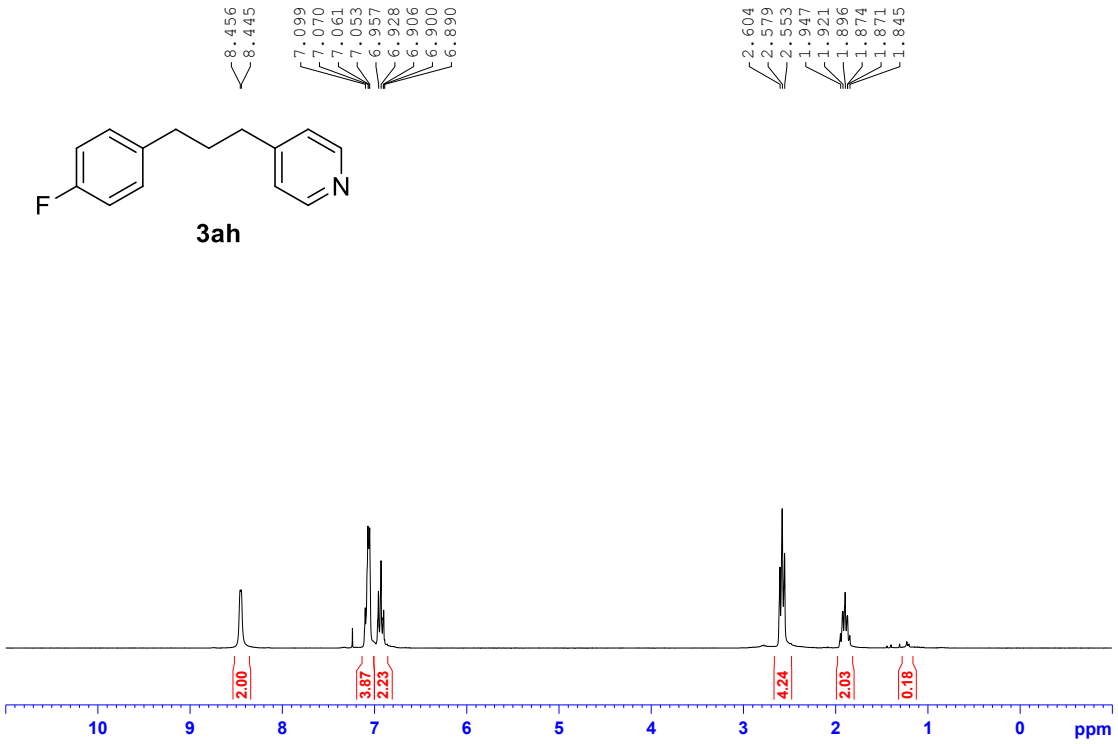


Figure 25S. ^{1}H NMR spectrum of **3ah**.

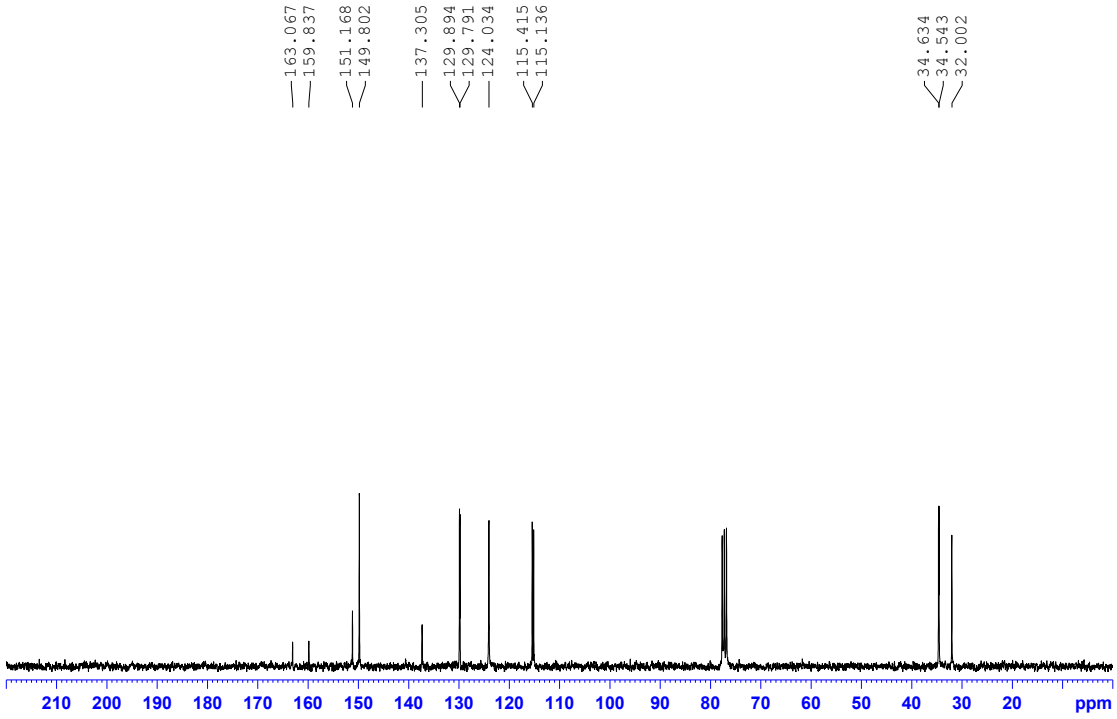


Figure 26S. ^{13}C{^{1}H} NMR spectrum of **3ah**.

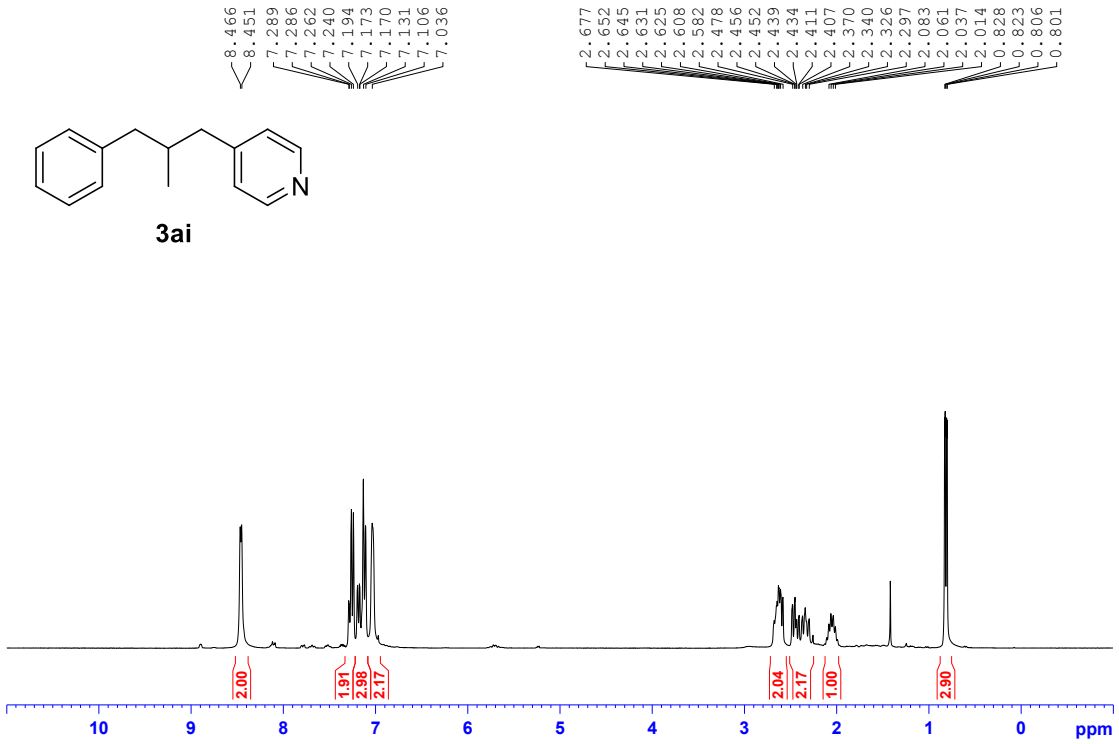


Figure 27S. ^{1}H NMR spectrum of **3ai**.

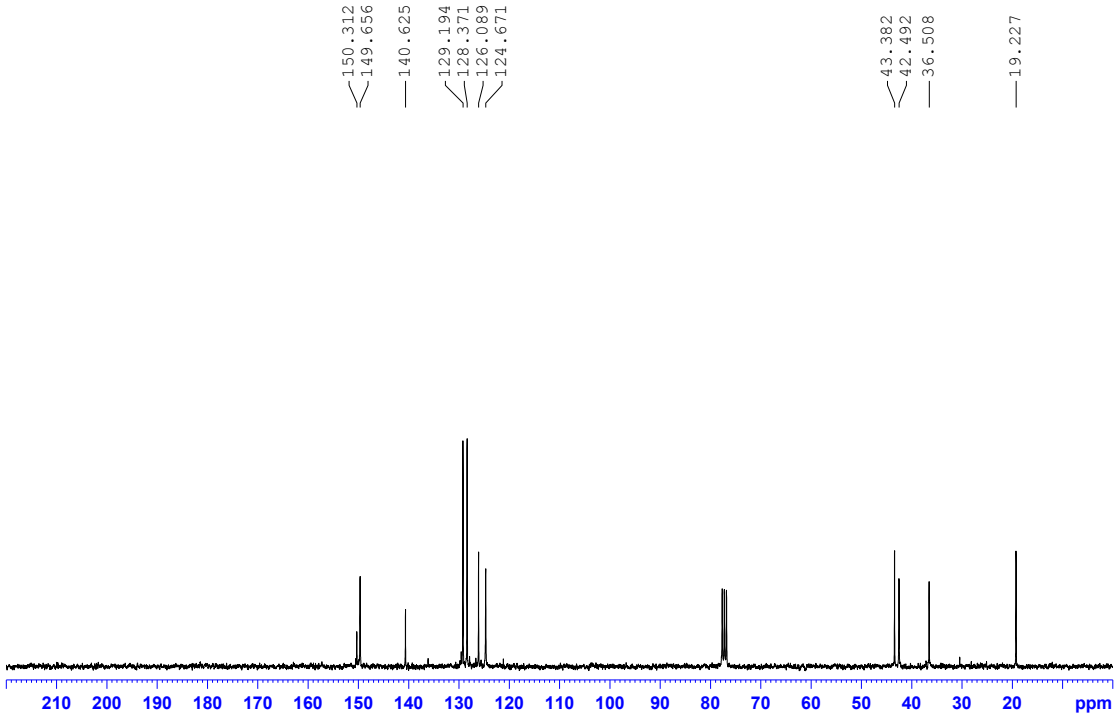


Figure 28S. ^{13}C{^{1}H} NMR spectrum of **3ai**.

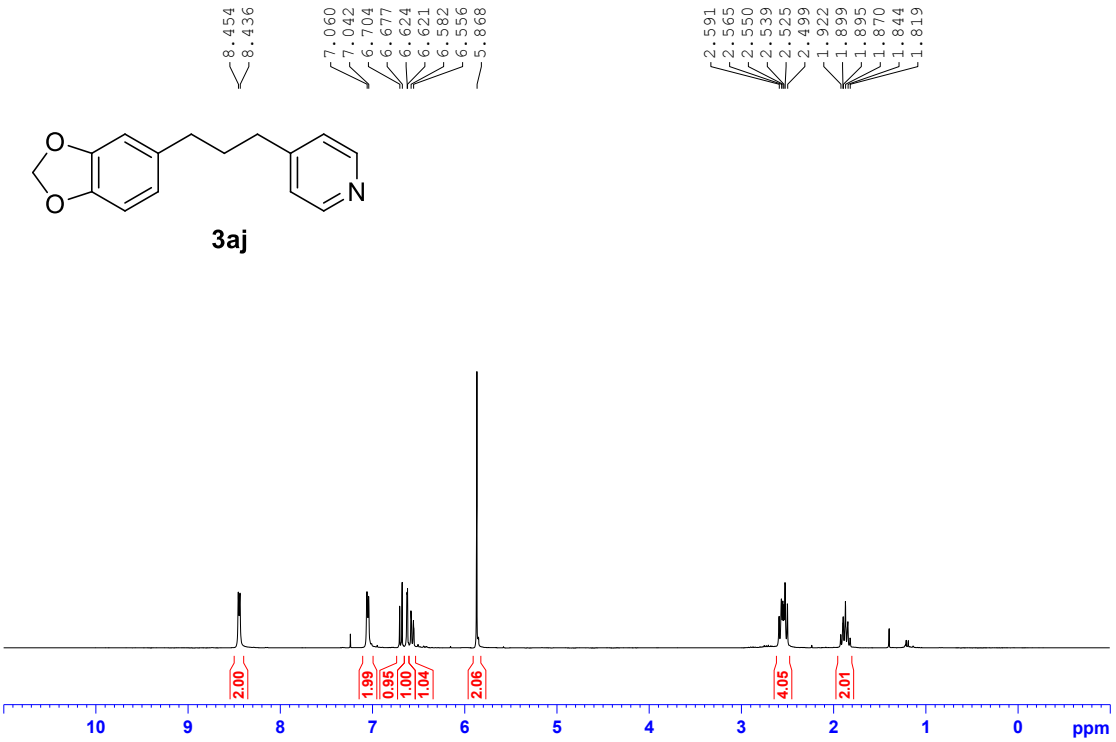


Figure 29S. ^{1}H NMR spectrum of **3aj**.

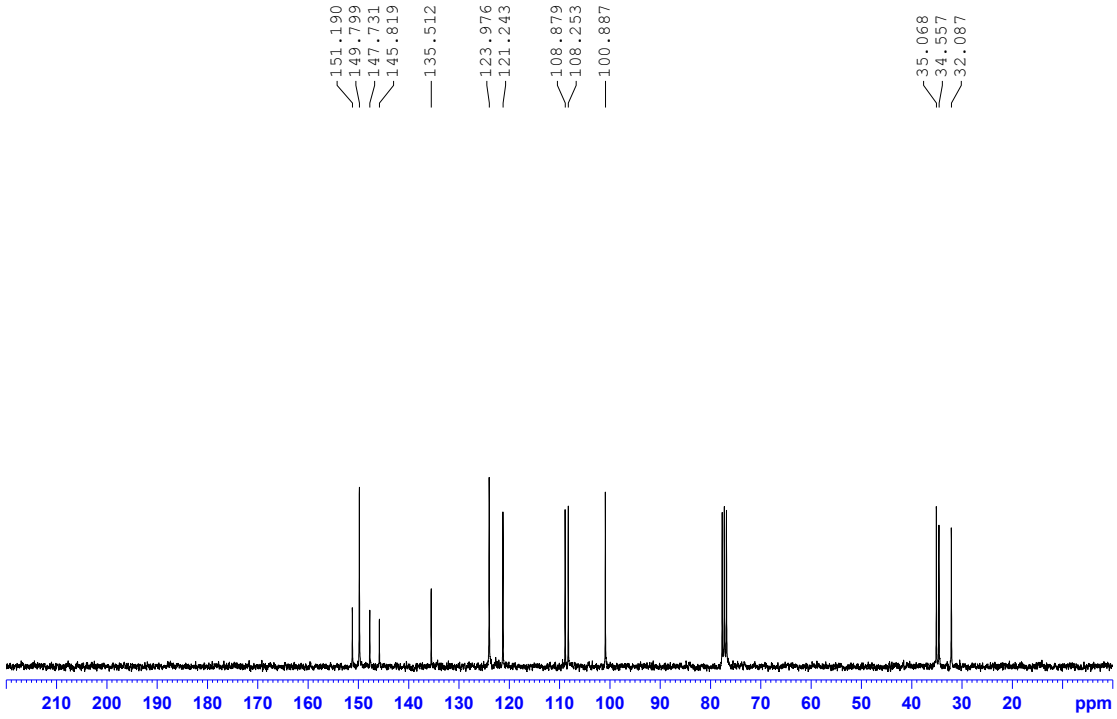


Figure 30S. ^{13}C{^{1}H} NMR spectrum of **3aj**.

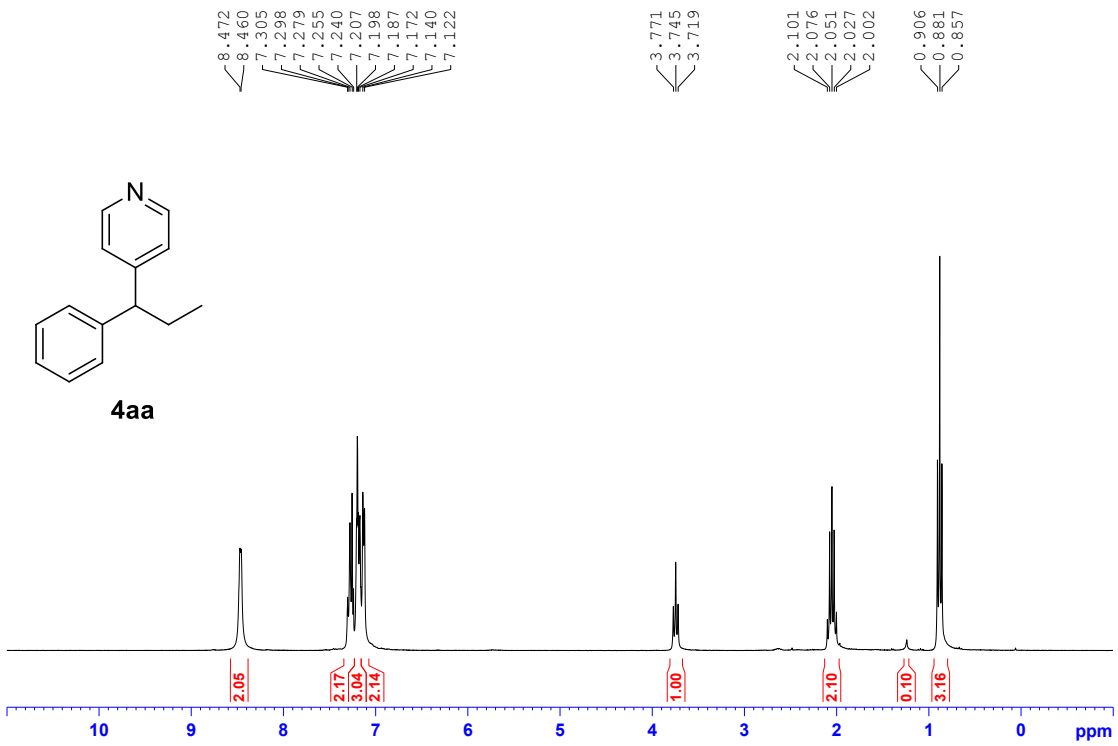


Figure 31S. ^{1}H NMR spectrum of **4aa**.

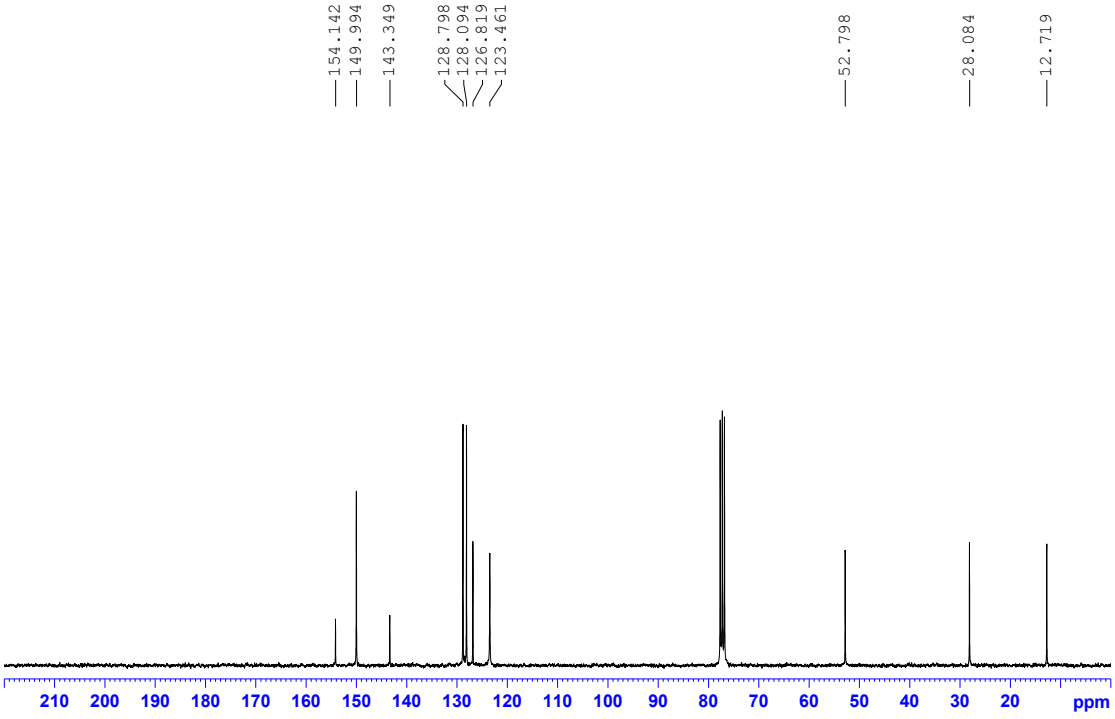


Figure 32S. ^{13}C{^{1}H} NMR spectrum of **4aa**.

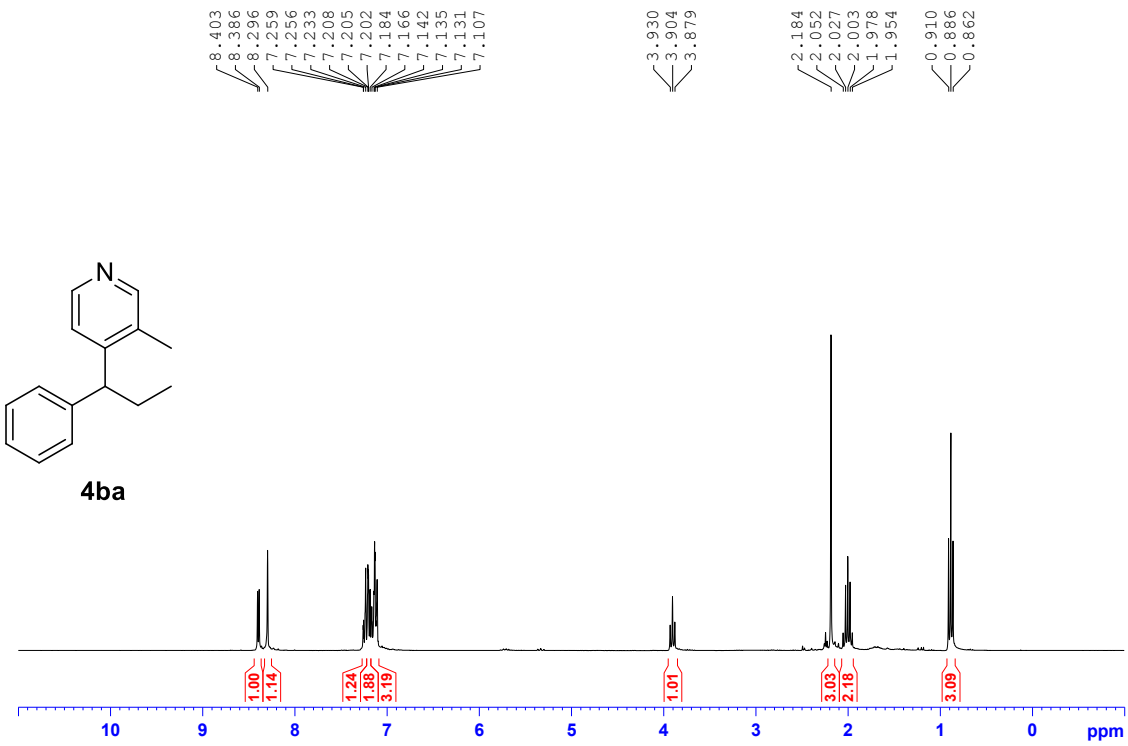


Figure 33S. ^{1}H NMR spectrum of **4ba**.

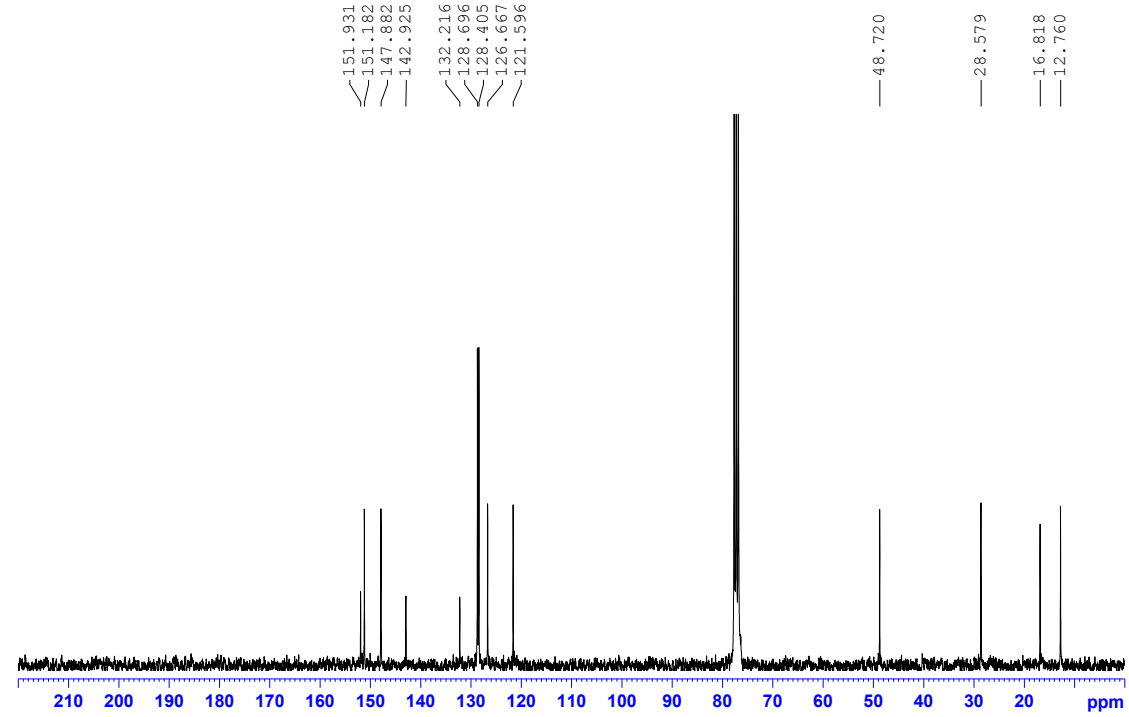


Figure 34S. ^{13}C{^{1}H} NMR spectrum of **4ba**.

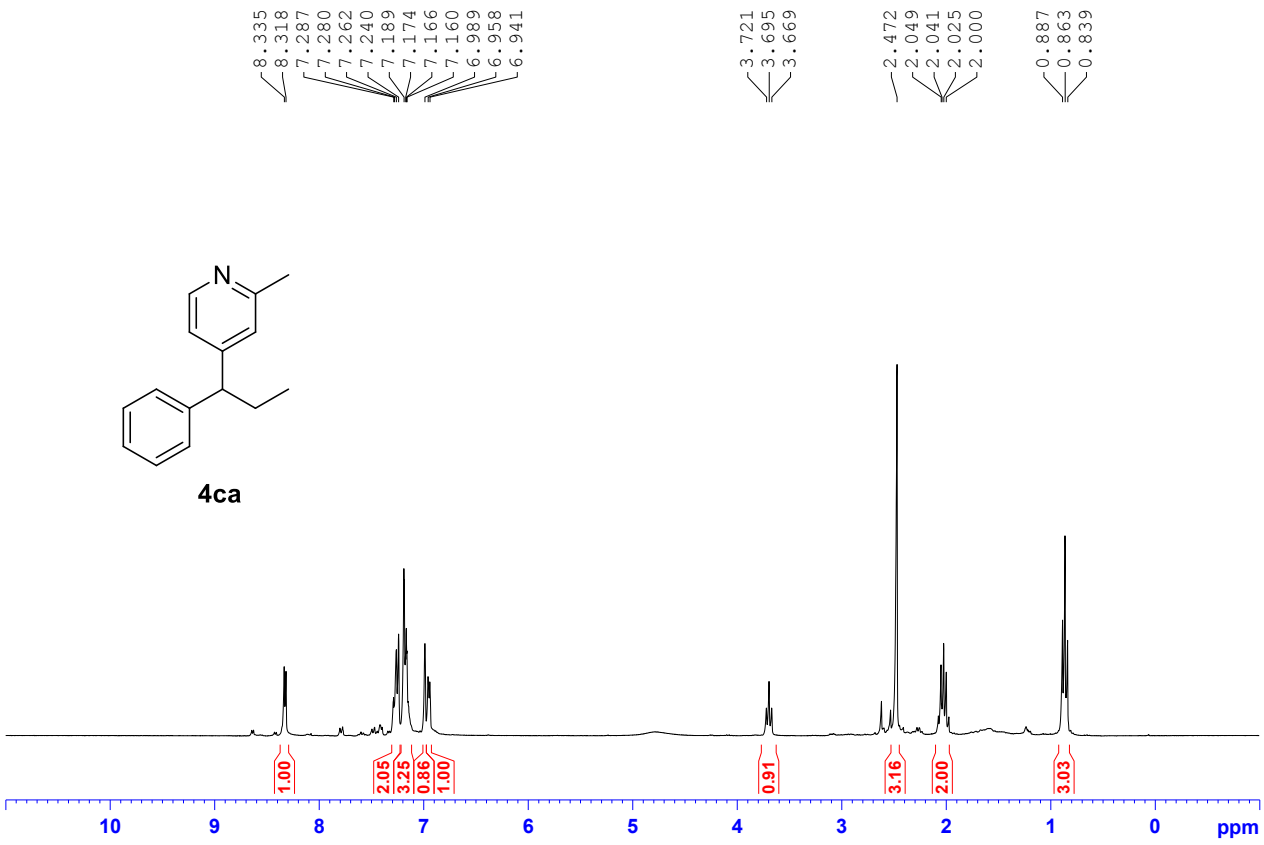


Figure 35S. ^{1}H NMR spectrum of **4ca**.

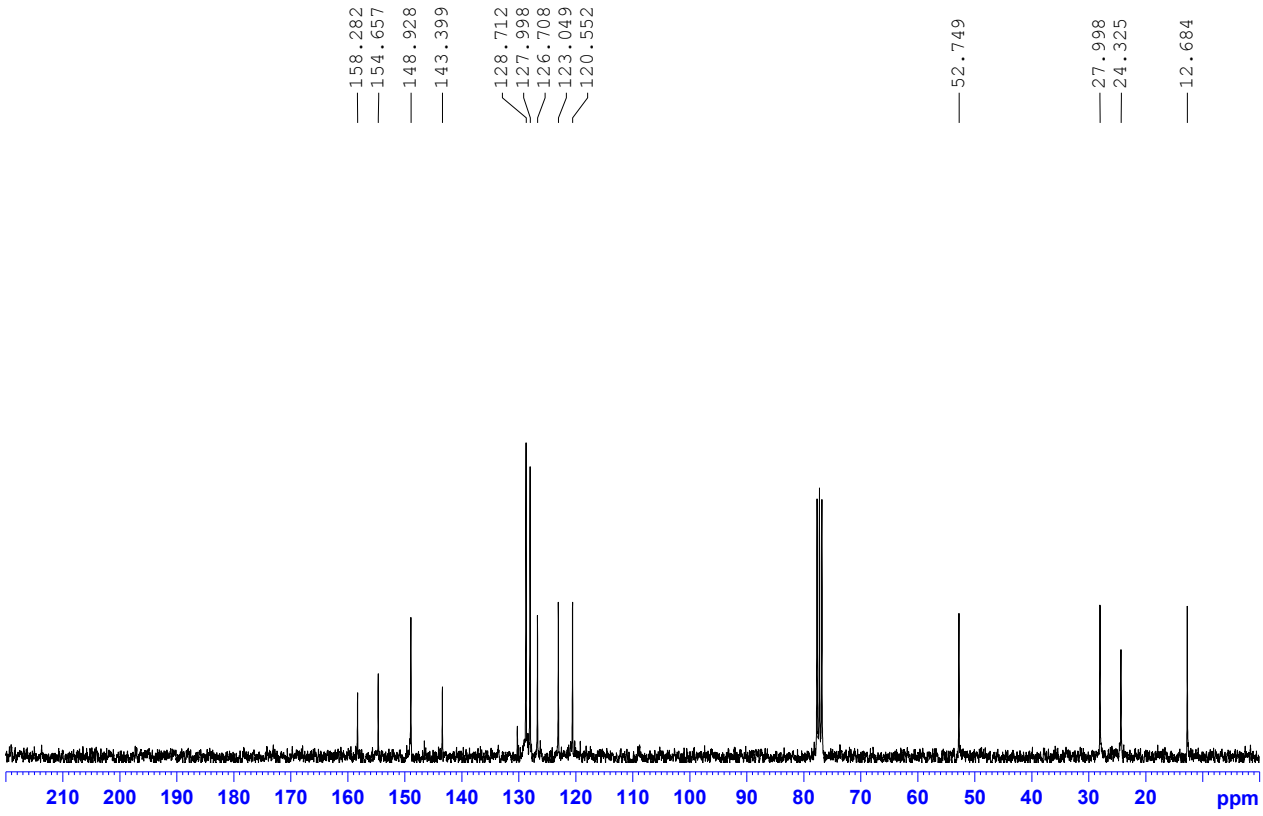


Figure 36S. ^{13}C{^{1}H} NMR spectrum of **4ca**.

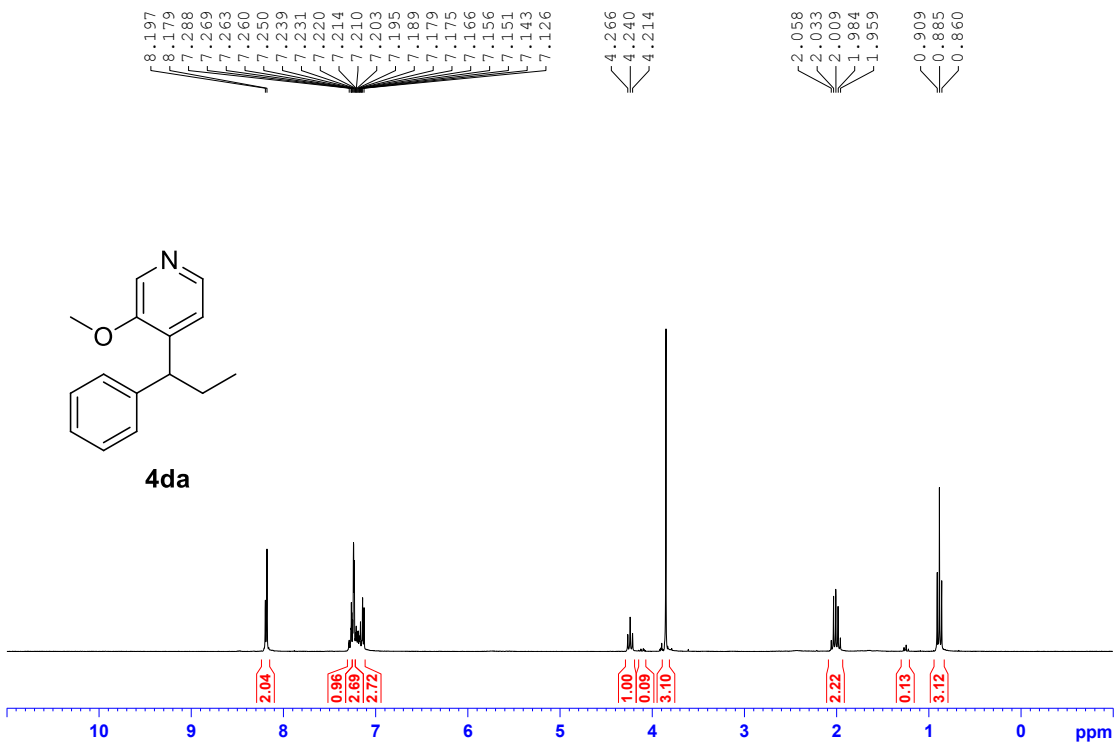


Figure 37S. ^{1}H NMR spectrum of **4da**.

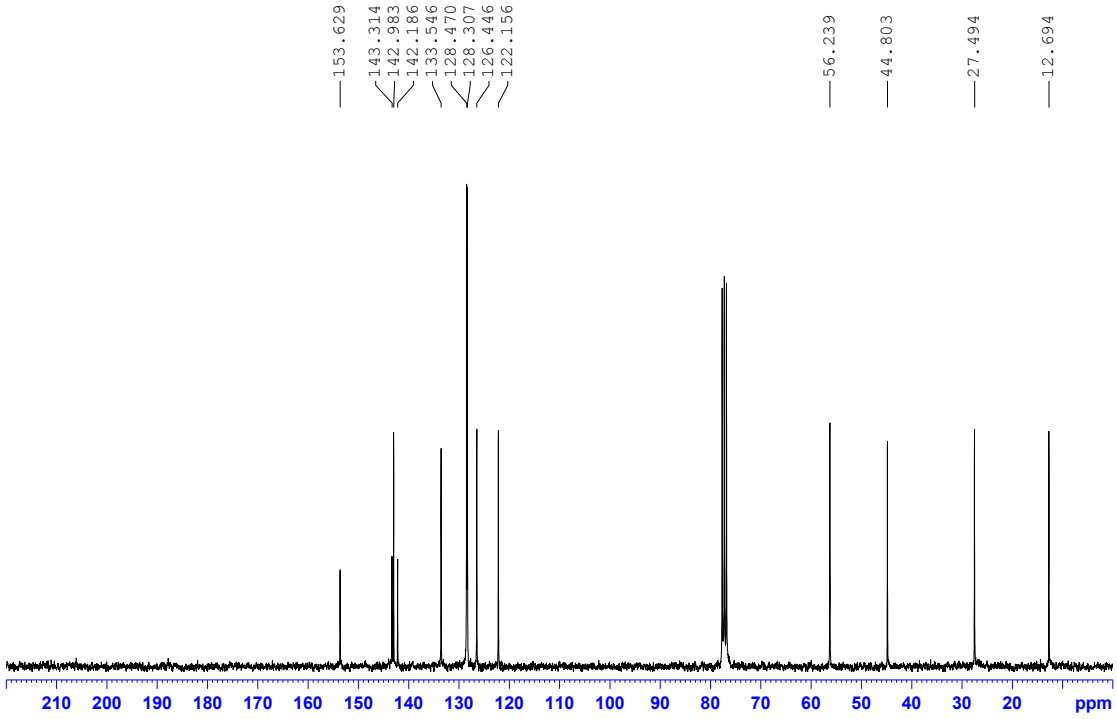


Figure 38S. ^{13}C{^{1}H} NMR spectrum of **4da**.

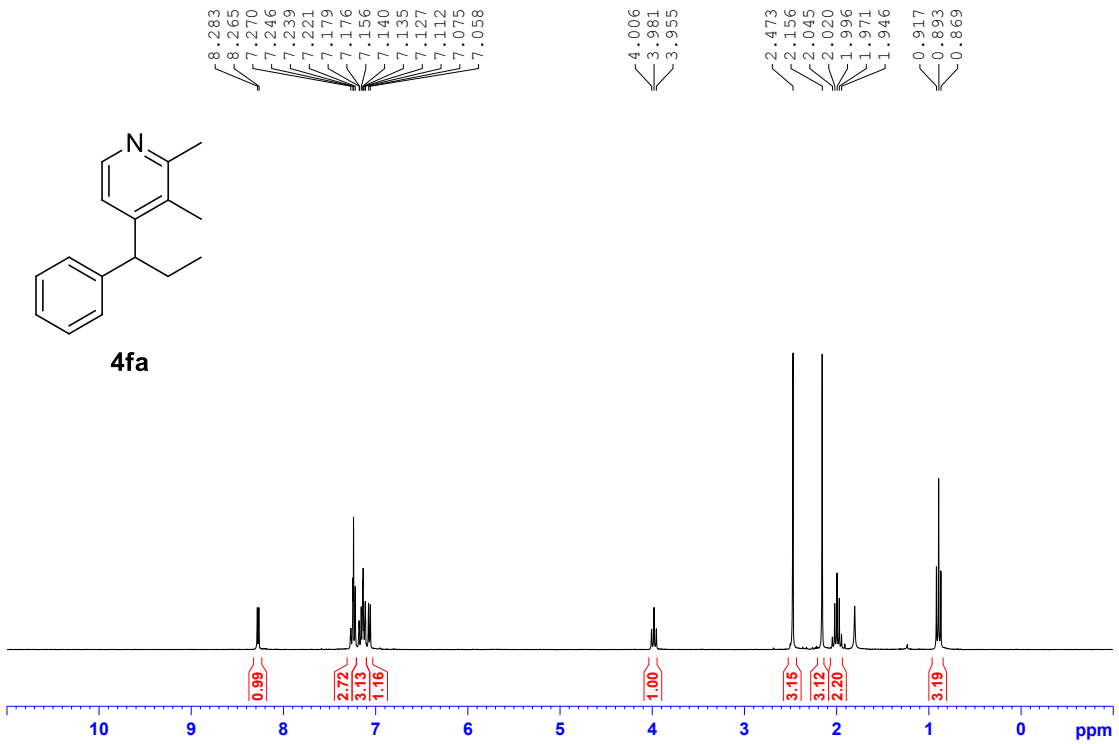


Figure 39S. ^{1}H NMR spectrum of **4fa**.

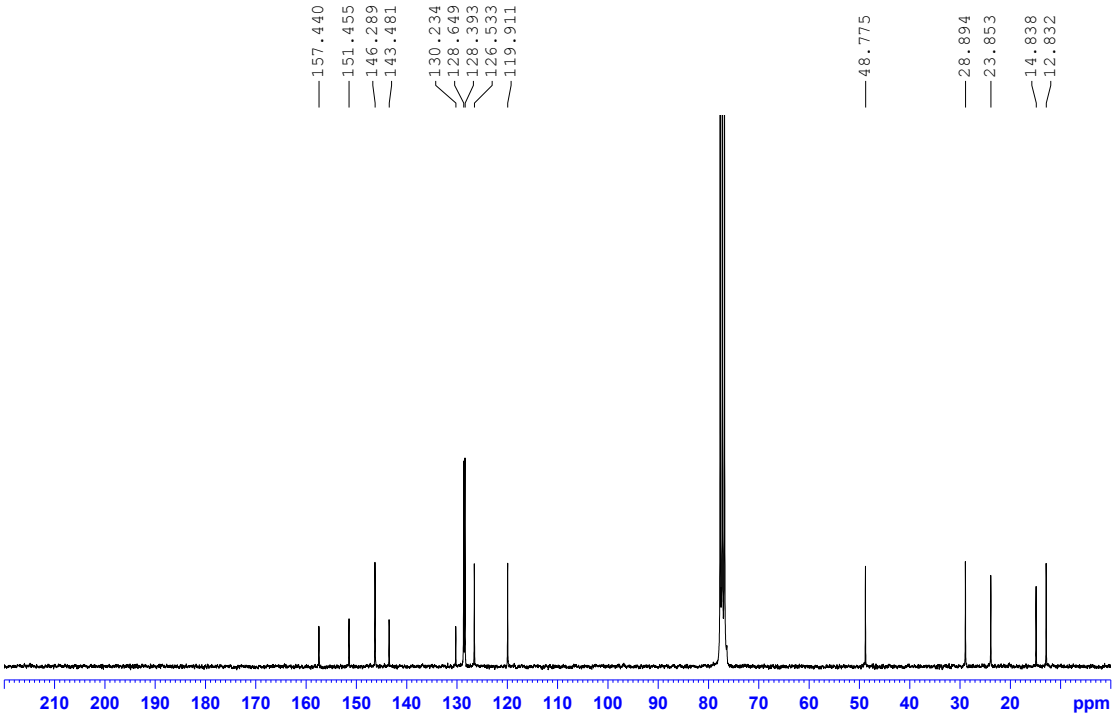


Figure 40S. ^{13}C{^{1}H} NMR spectrum of **4fa**.

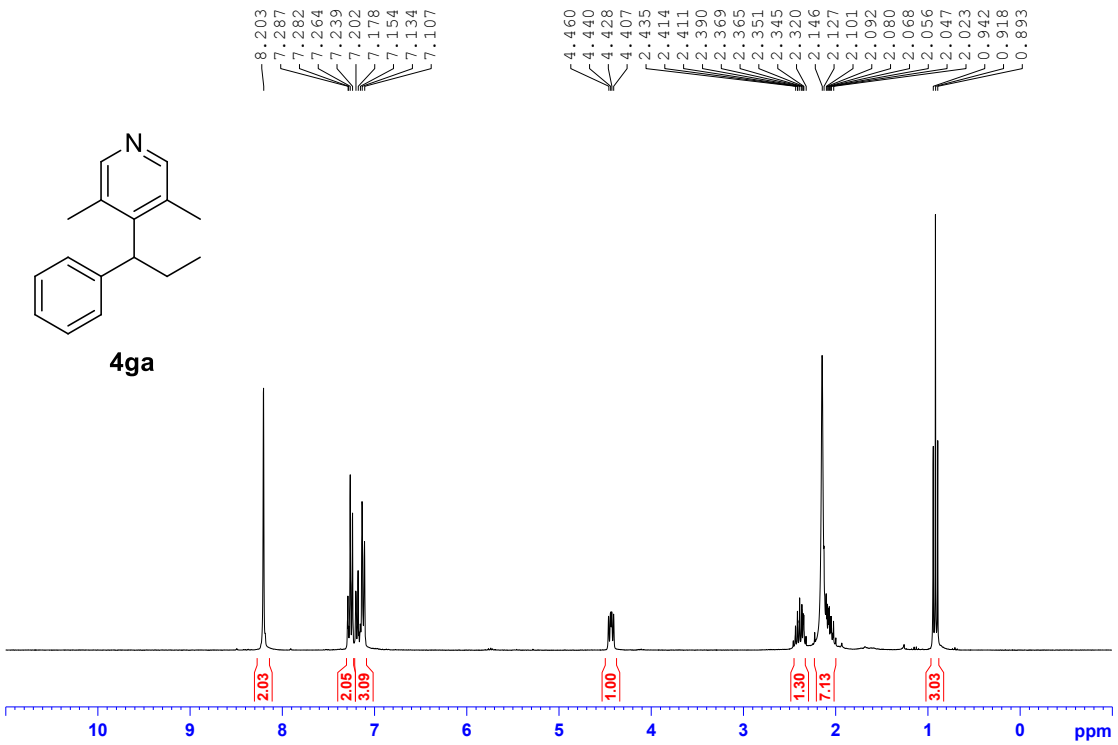


Figure 41S. ^{1}H NMR spectrum of **4ga**.

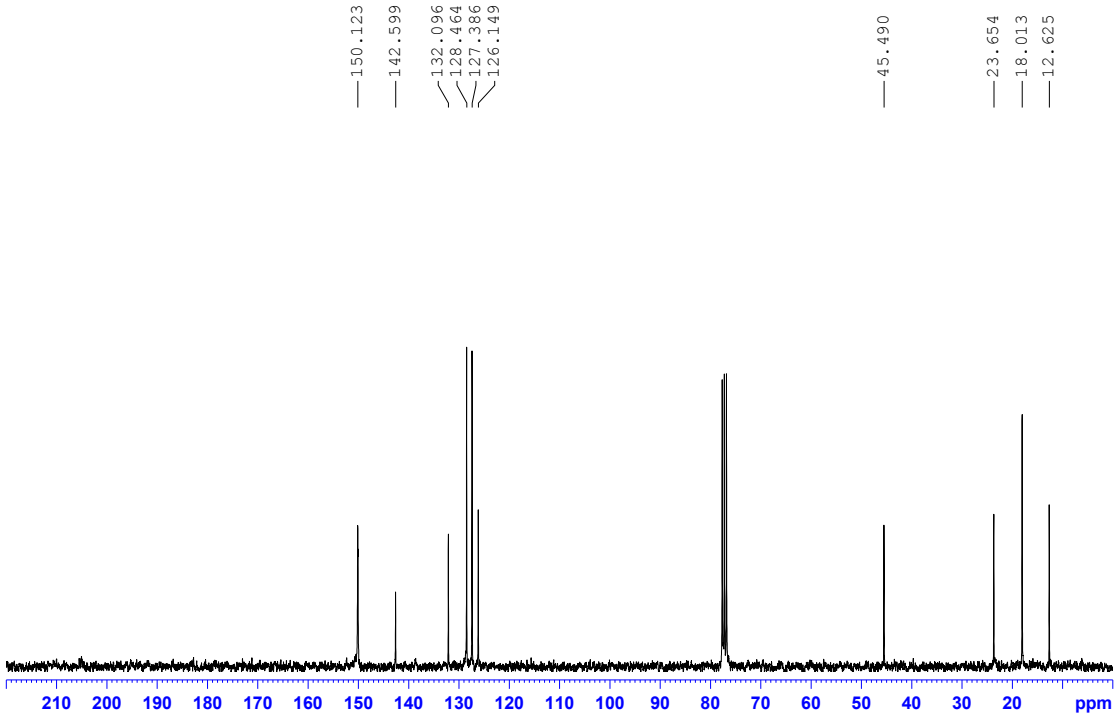


Figure 42S. ^{13}C{^{1}H} NMR spectrum of **4ga**.

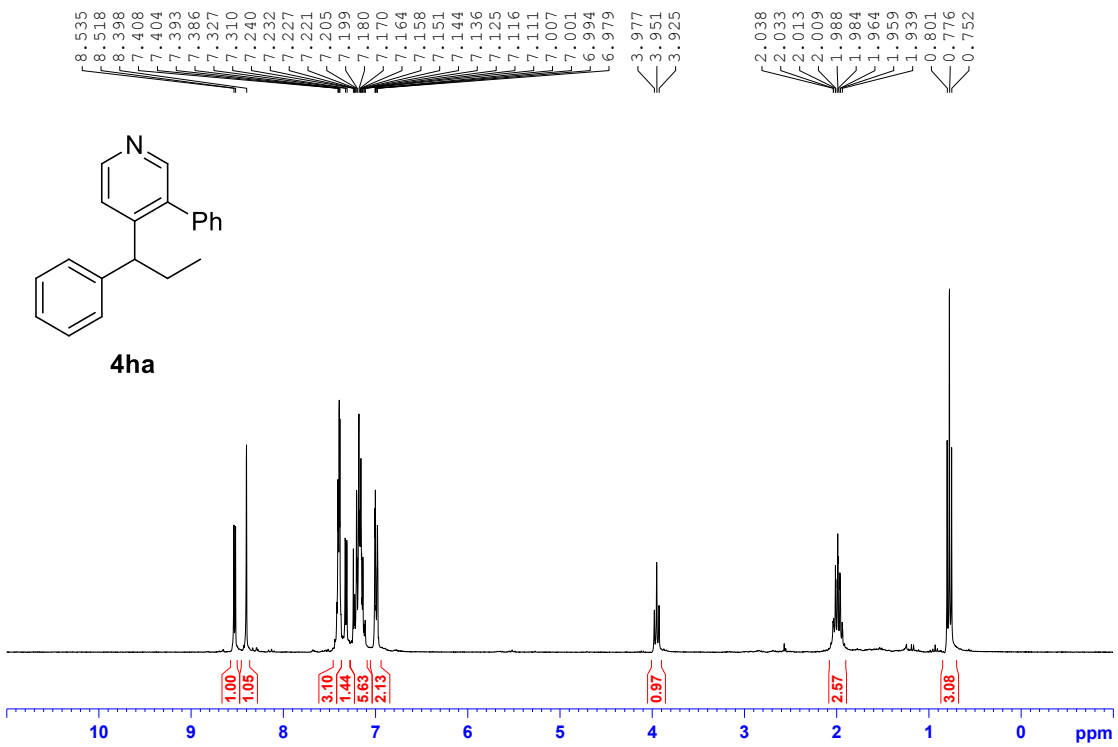


Figure 43S. ^{1}H NMR spectrum of **4ha**.

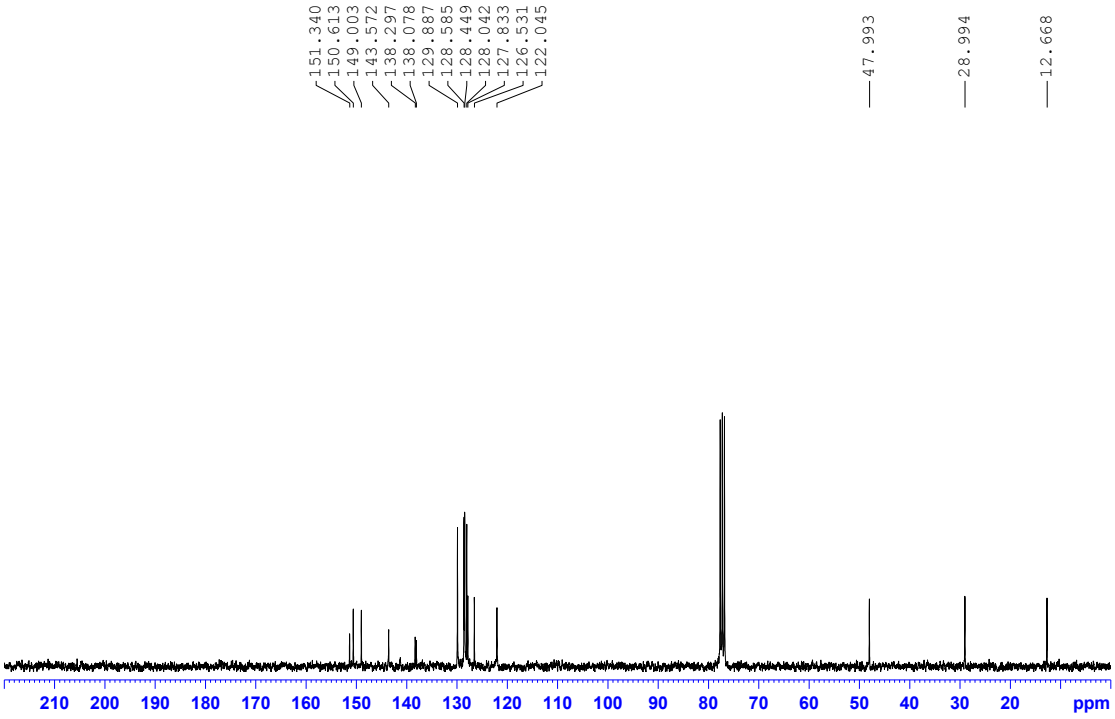


Figure 44S. ^{13}C{^{1}H} NMR spectrum of **4ha**.

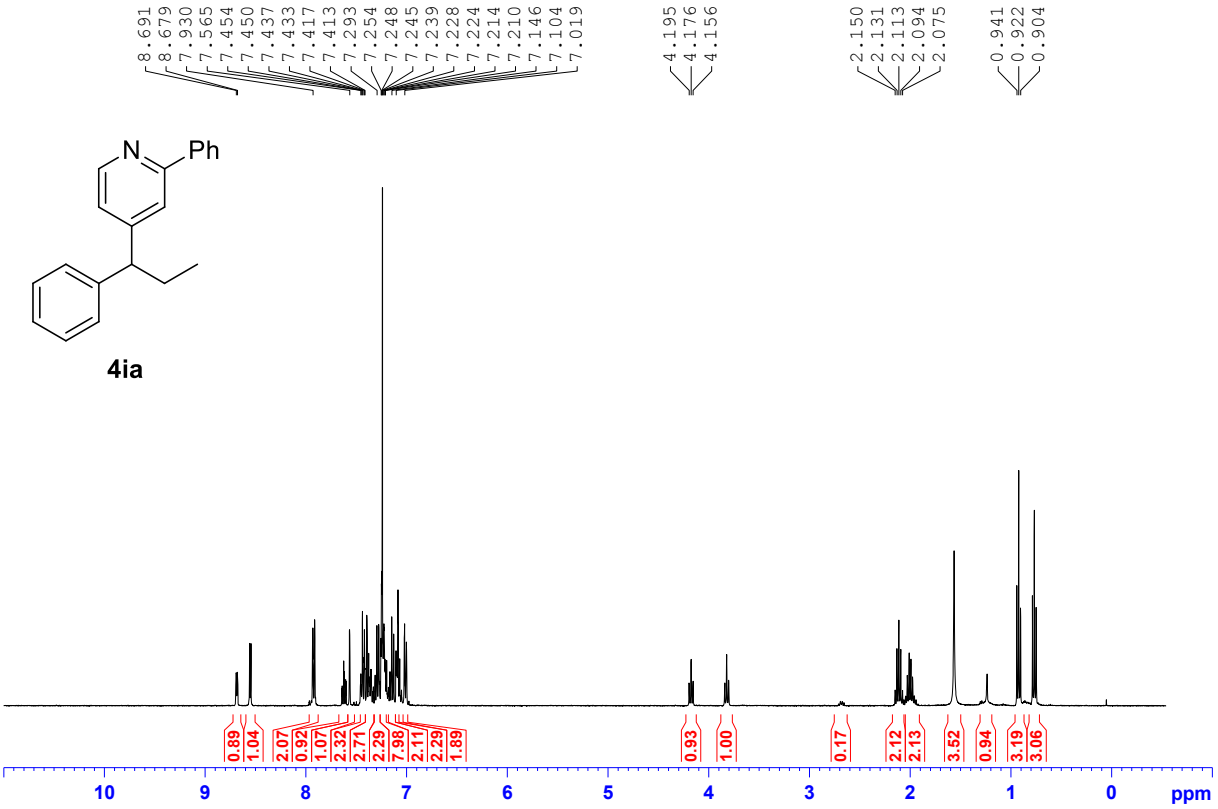


Figure 45S. ^{1}H NMR spectrum of **4ia**.

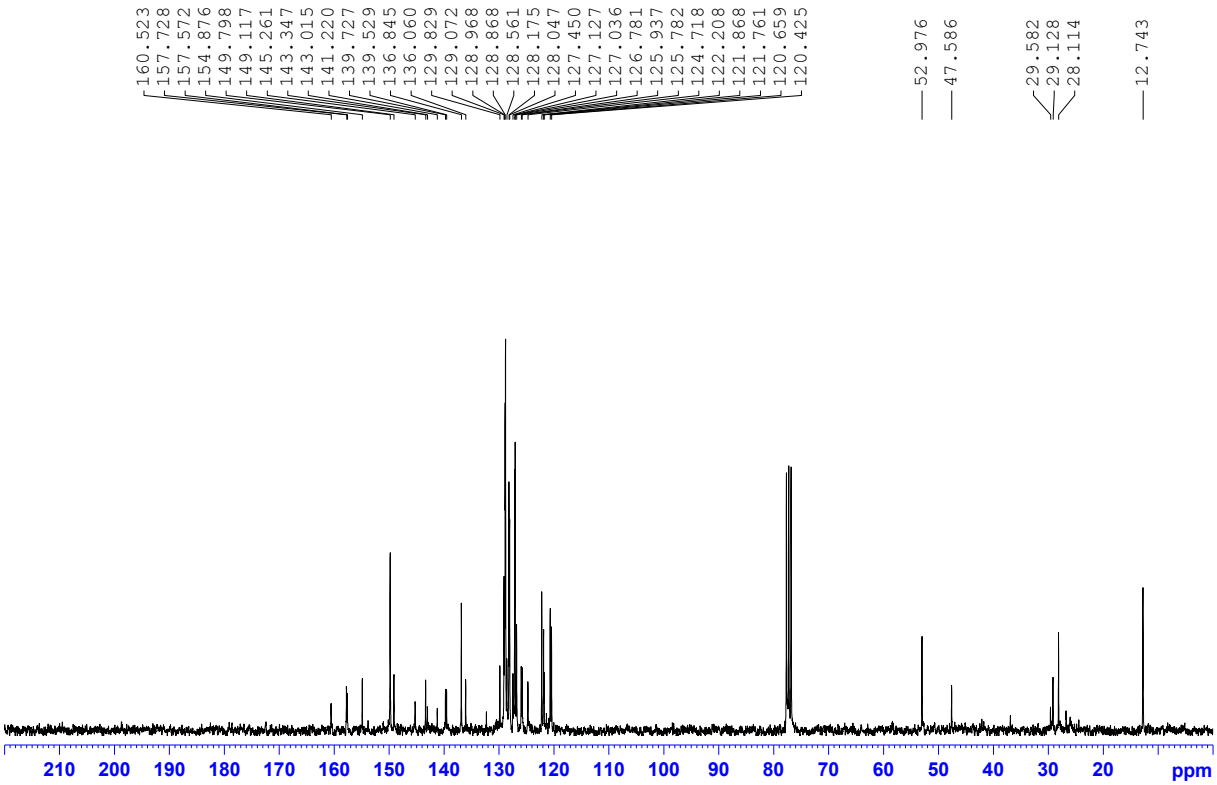


Figure 46S. ^{13}C{^{1}H} NMR spectrum of **4ia**.

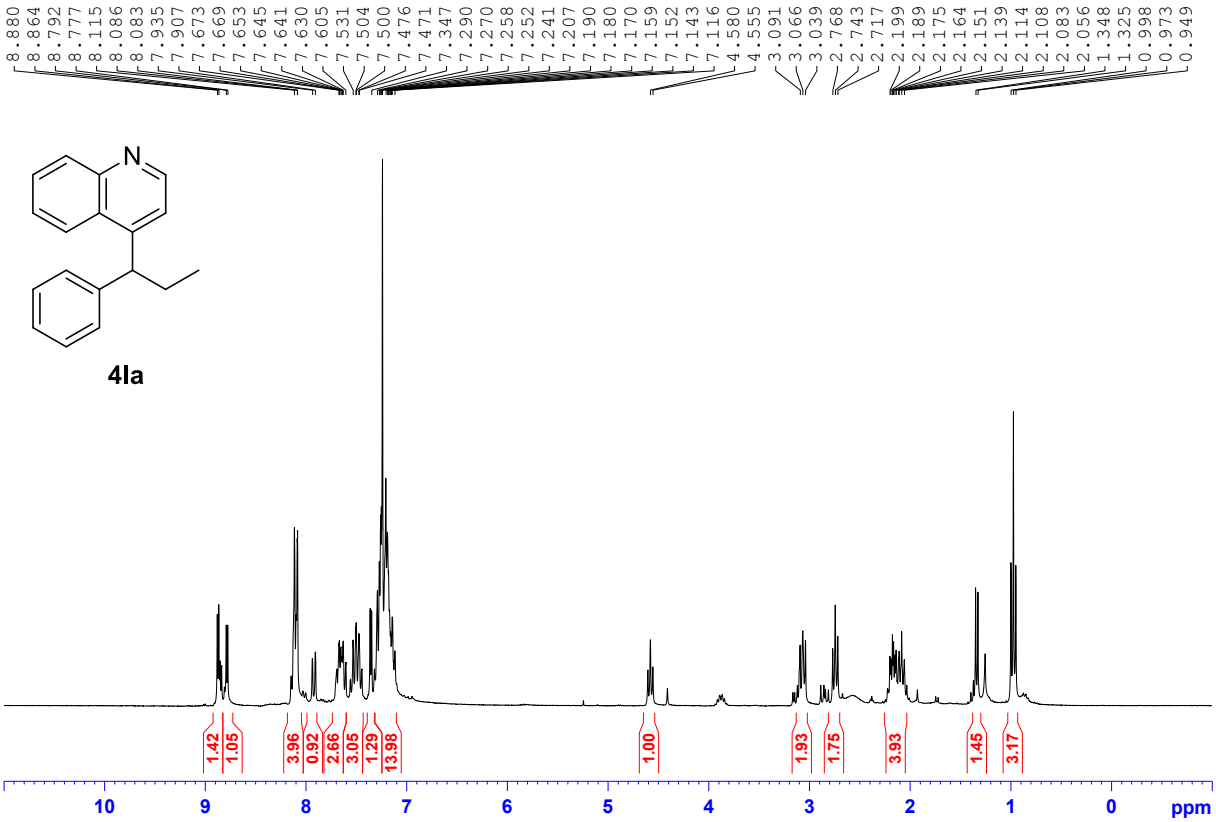


Figure 47S. ^{1}H NMR spectrum of **4la**.

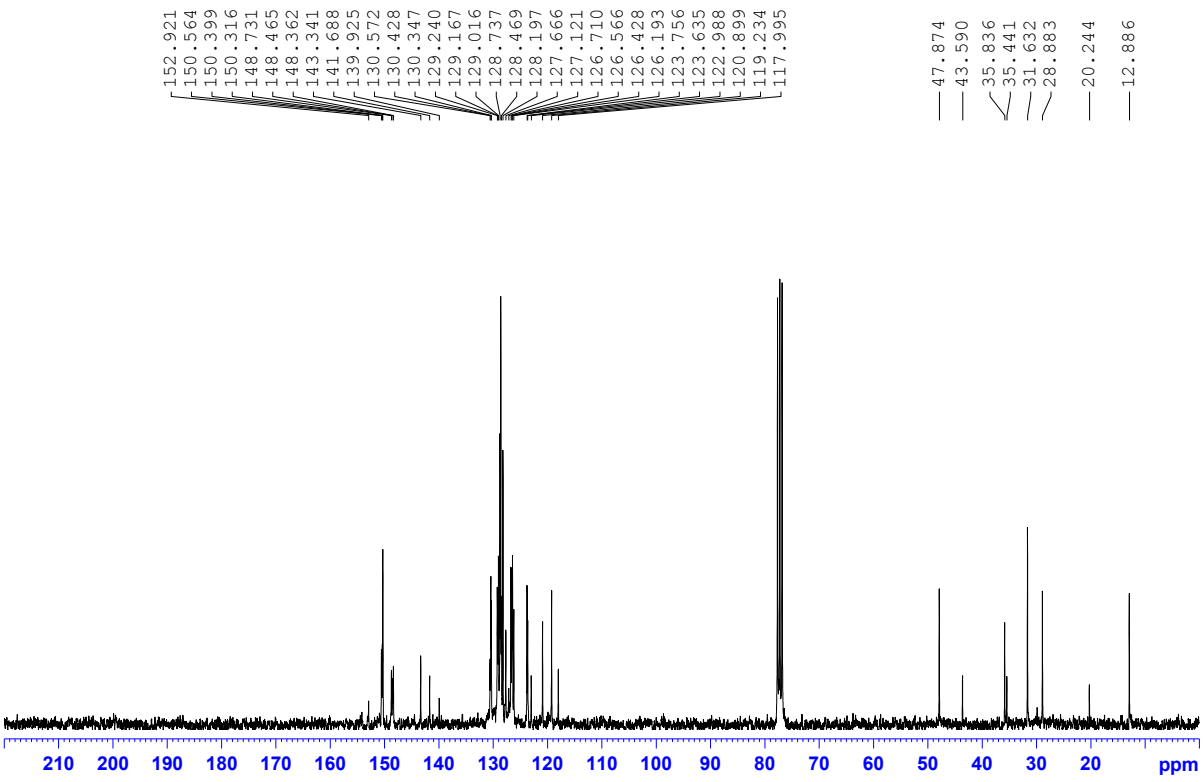


Figure 48S. ^{13}C{^{1}H} NMR spectrum of **4la**.

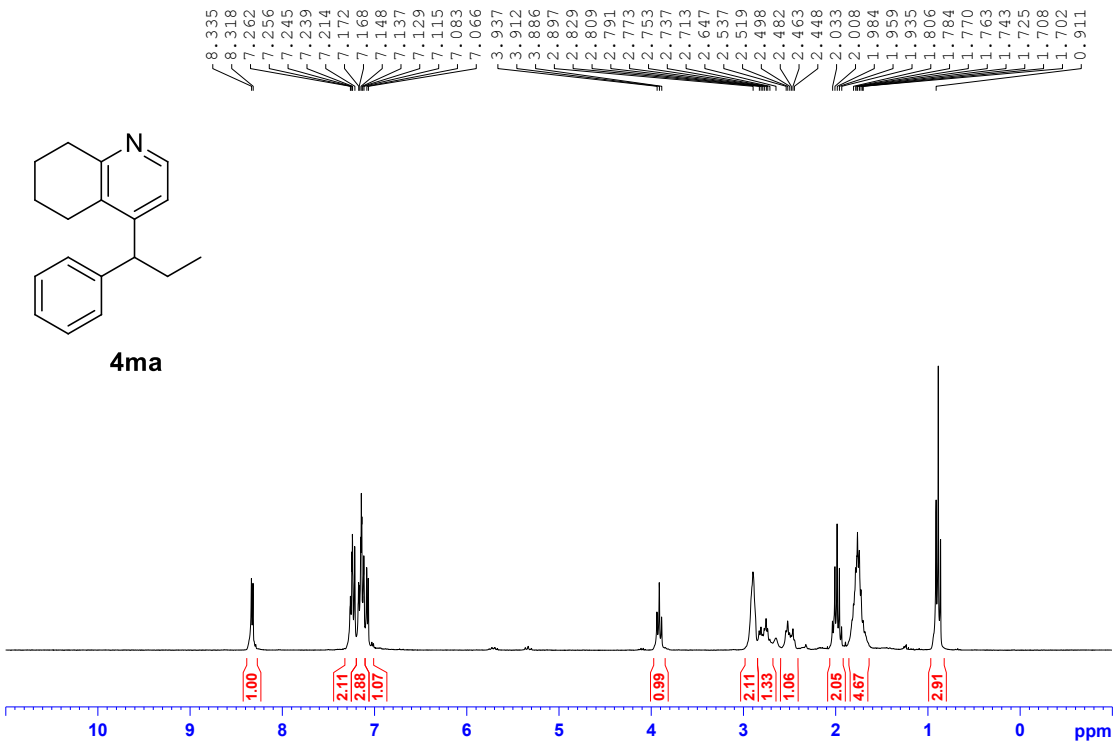


Figure 49S. ^{1}H NMR spectrum of **4ma**.

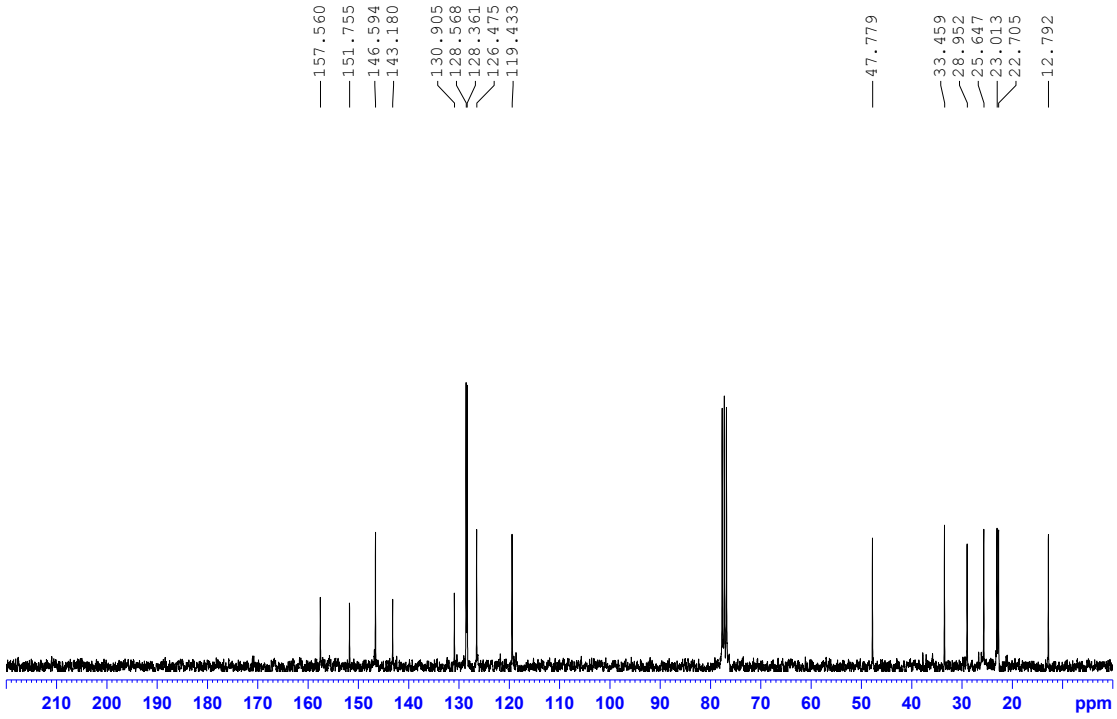


Figure 50S. ^{13}C{^{1}H} NMR spectrum of **4ma**.

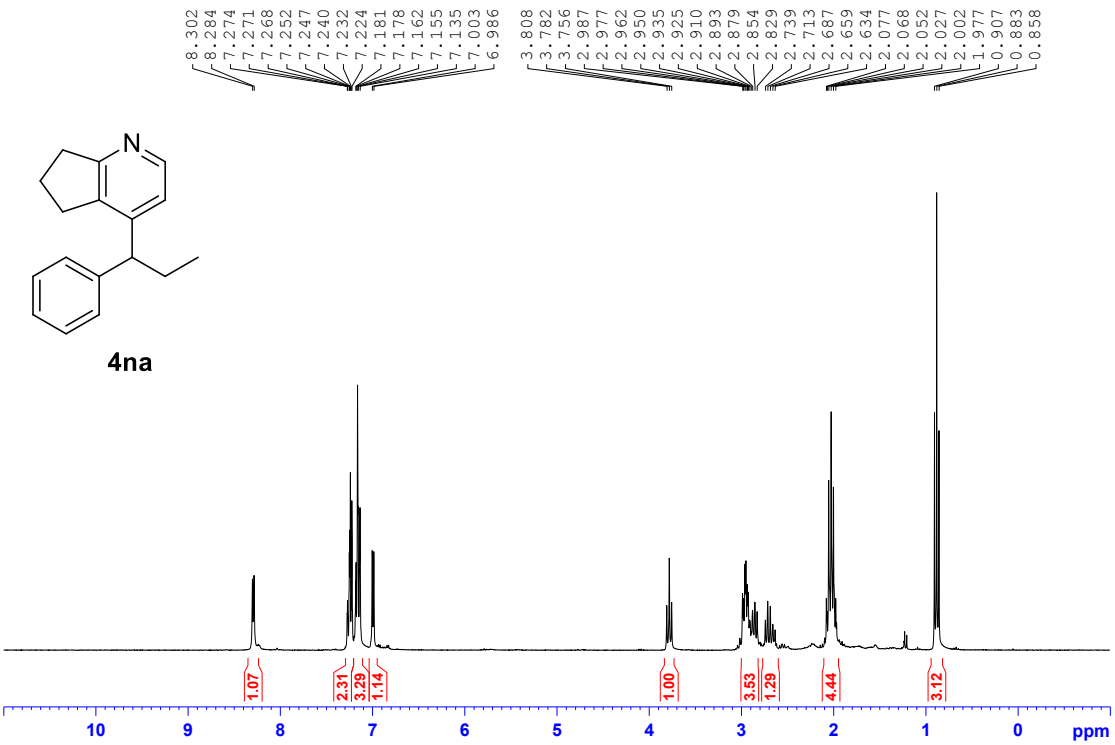


Figure 51S. ^{1}H NMR spectrum of **4na**.

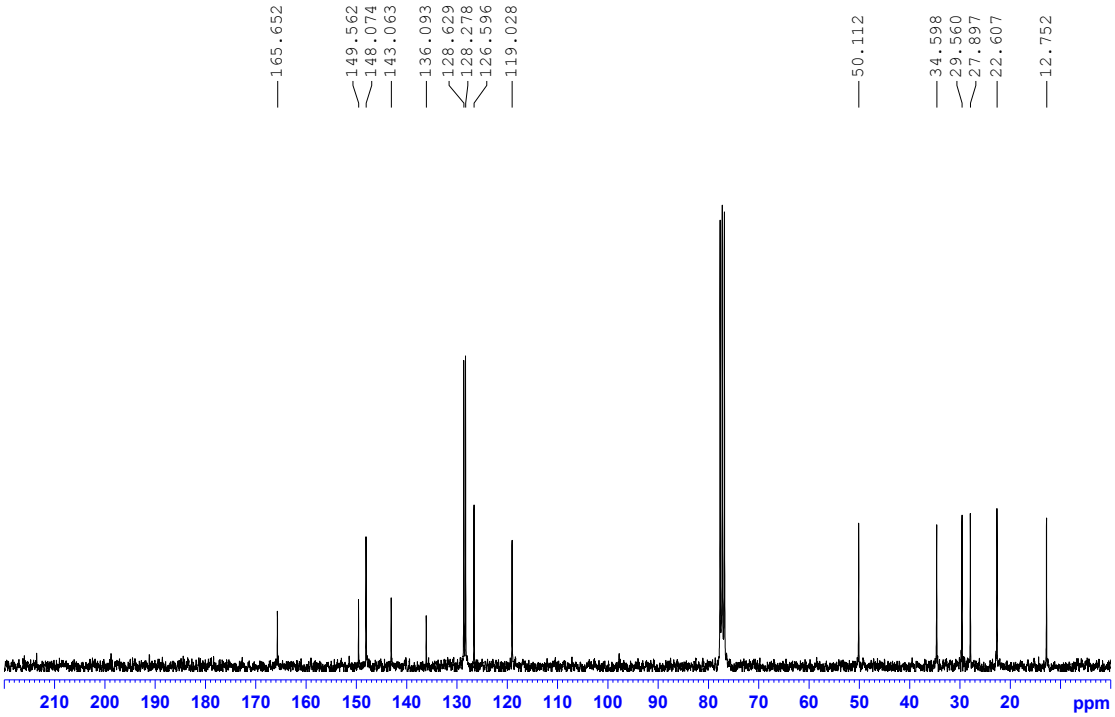


Figure 52S. ^{13}C{^{1}H} NMR spectrum of **4na**.

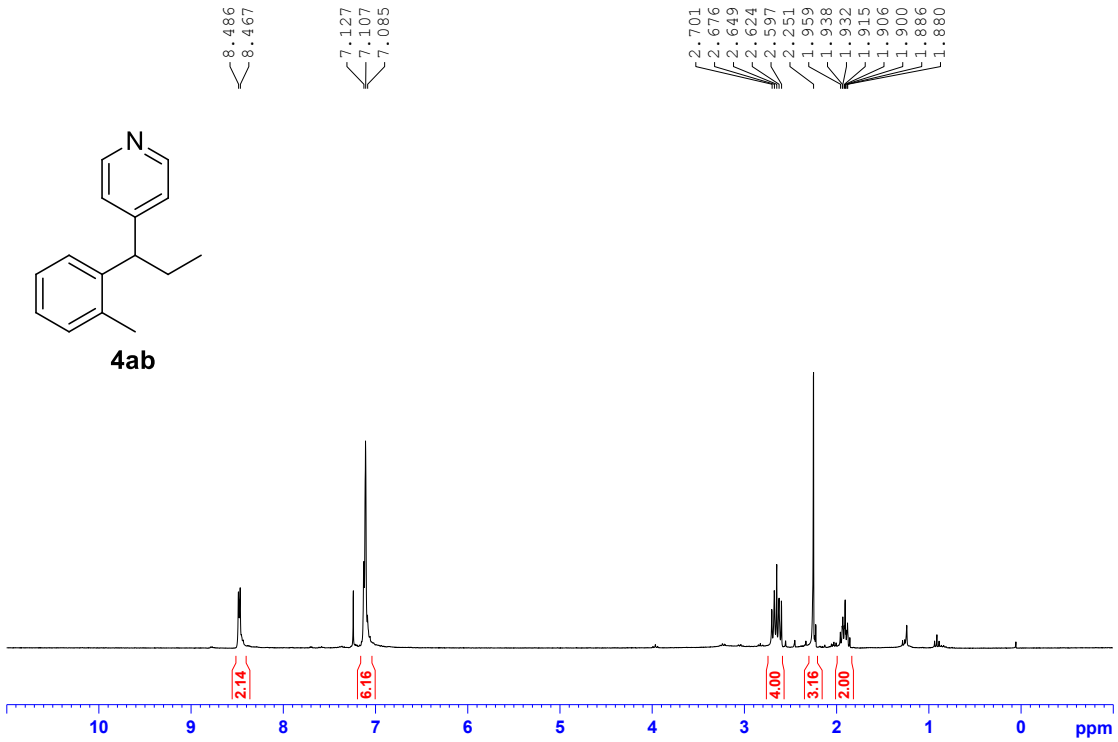


Figure 53S. ^{1}H NMR spectrum of **4ab**.

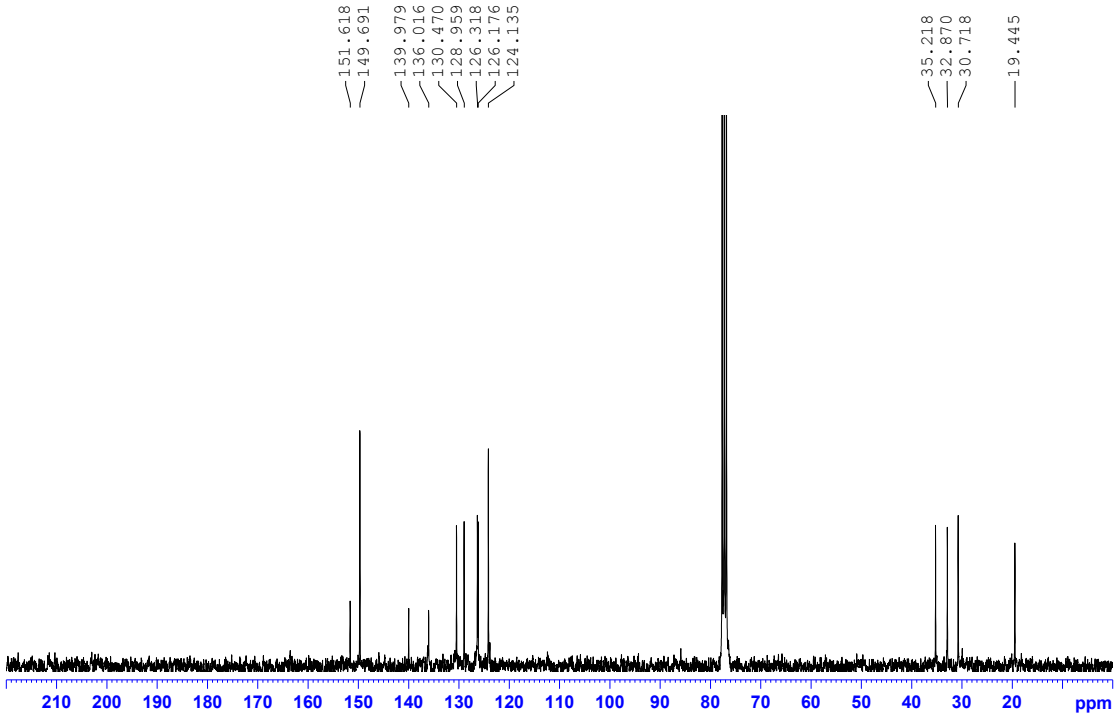


Figure 54S. ^{13}C{^{1}H} NMR spectrum of **4ab**.

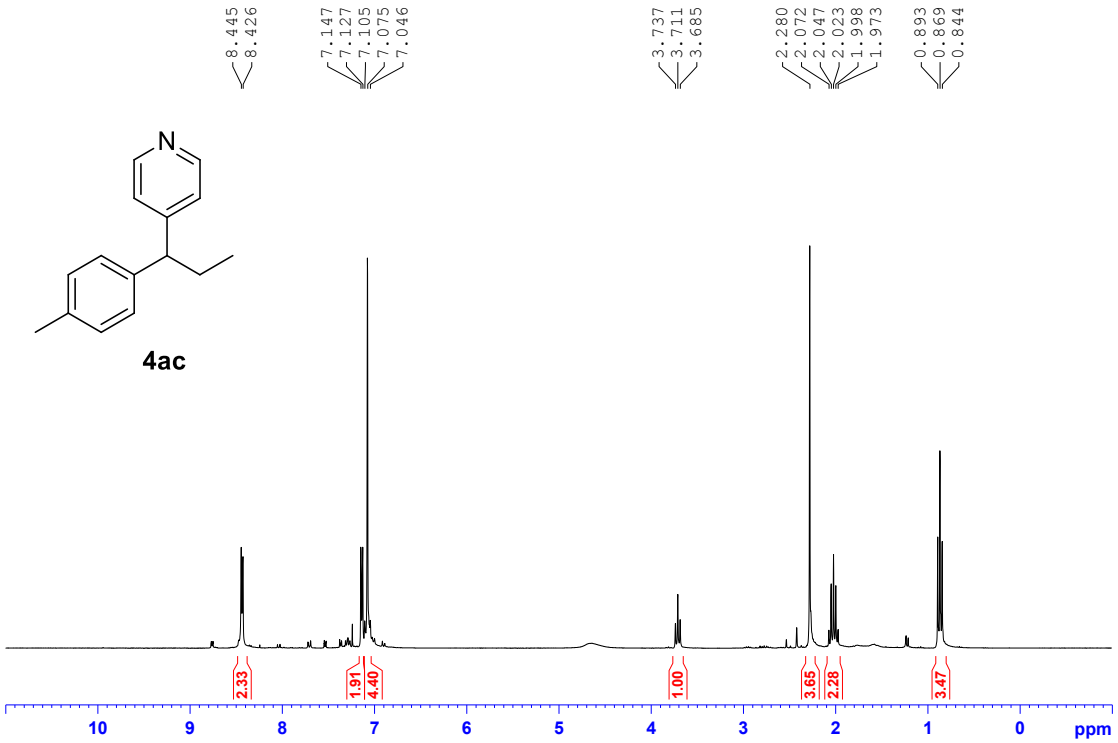


Figure 55S. ^{1}H NMR spectrum of **4ac**.

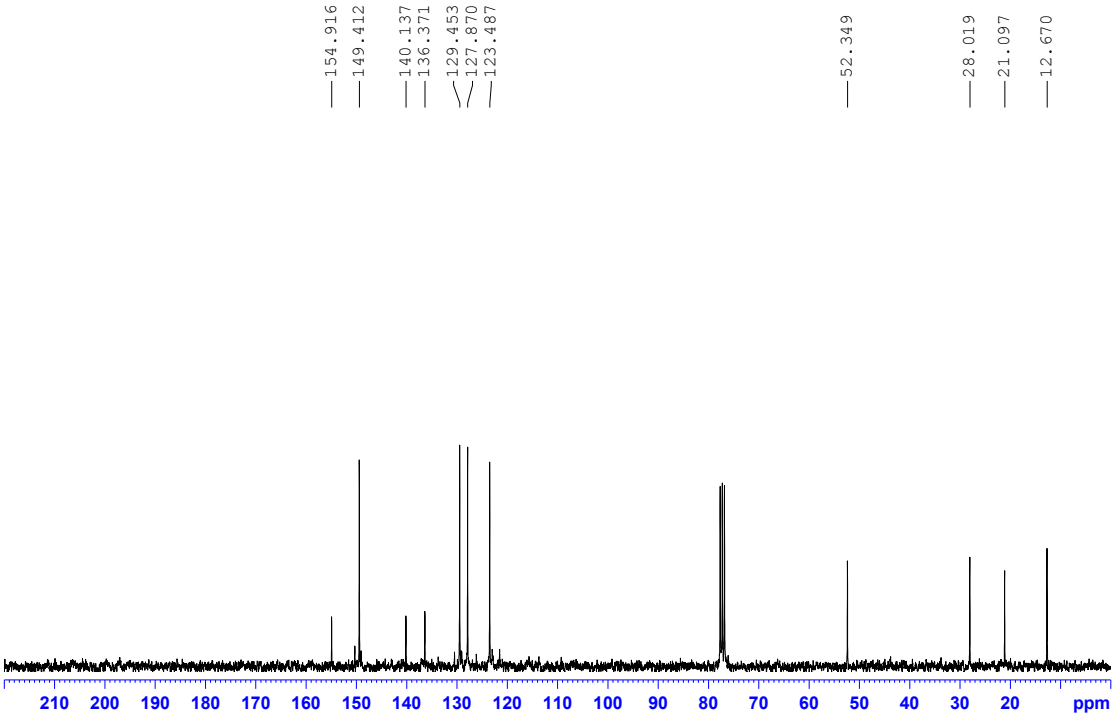


Figure 56S. ^{13}C{^{1}H} NMR spectrum of **4ac**.

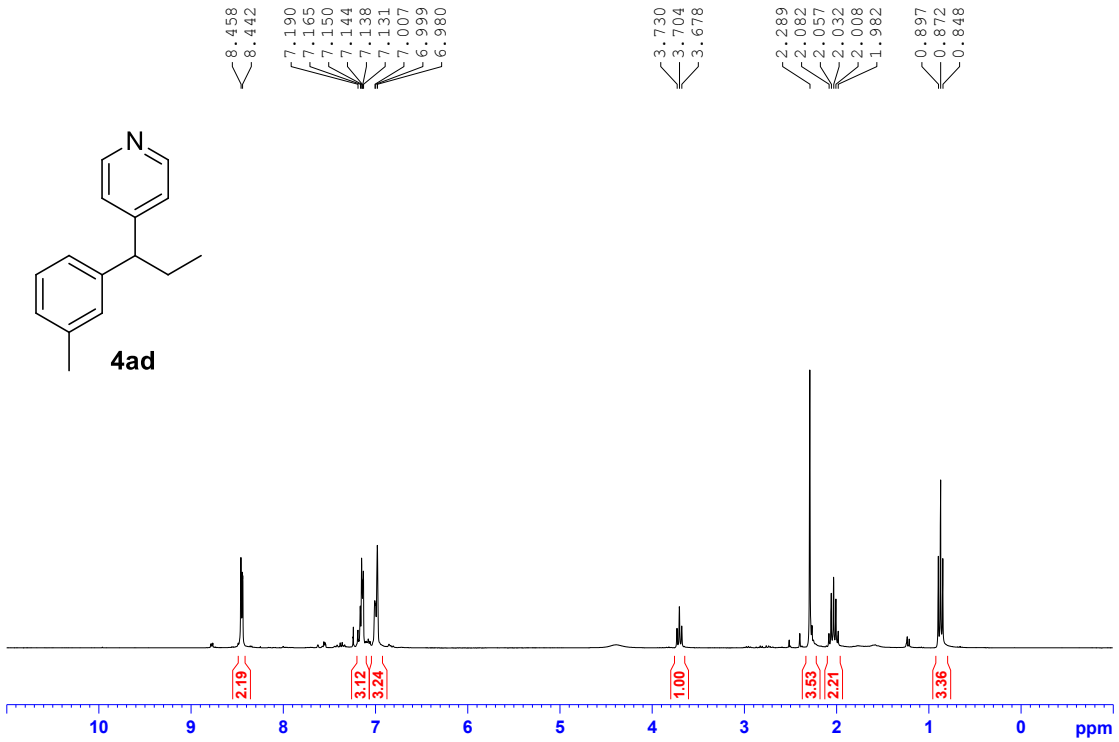


Figure 57S. ^{1}H NMR spectrum of **4ad**.

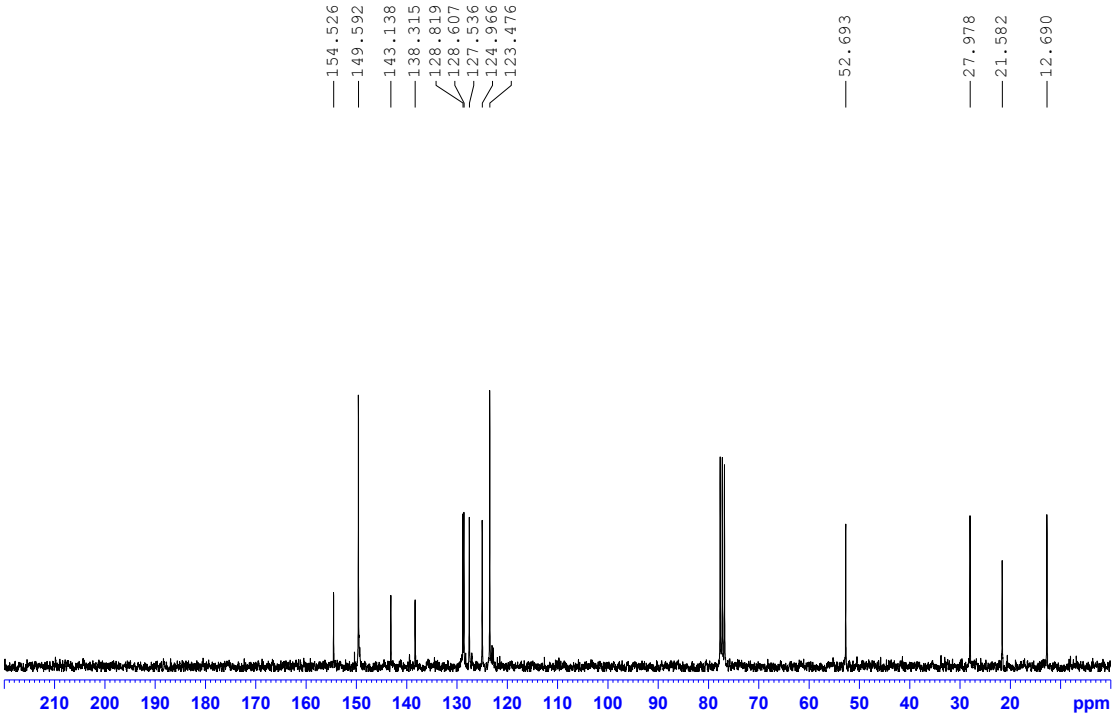


Figure 58S. ^{13}C{^{1}H} NMR spectrum of **4ad**.

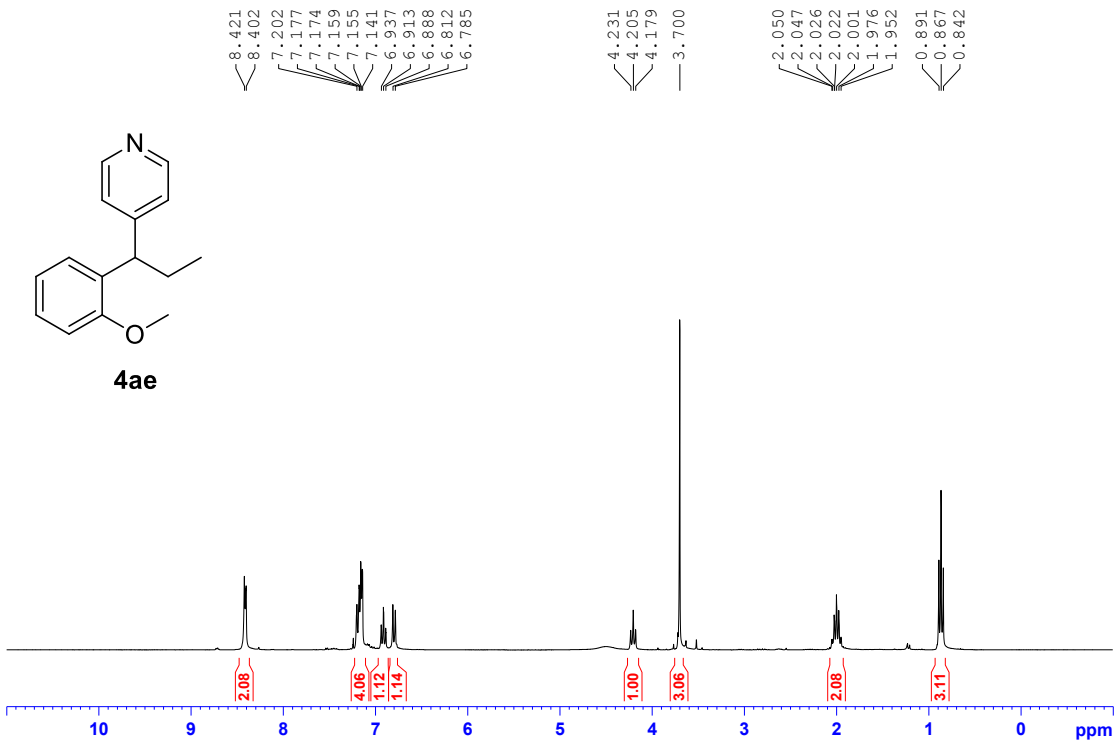


Figure 59S. ^{1}H NMR spectrum of **4ae**.

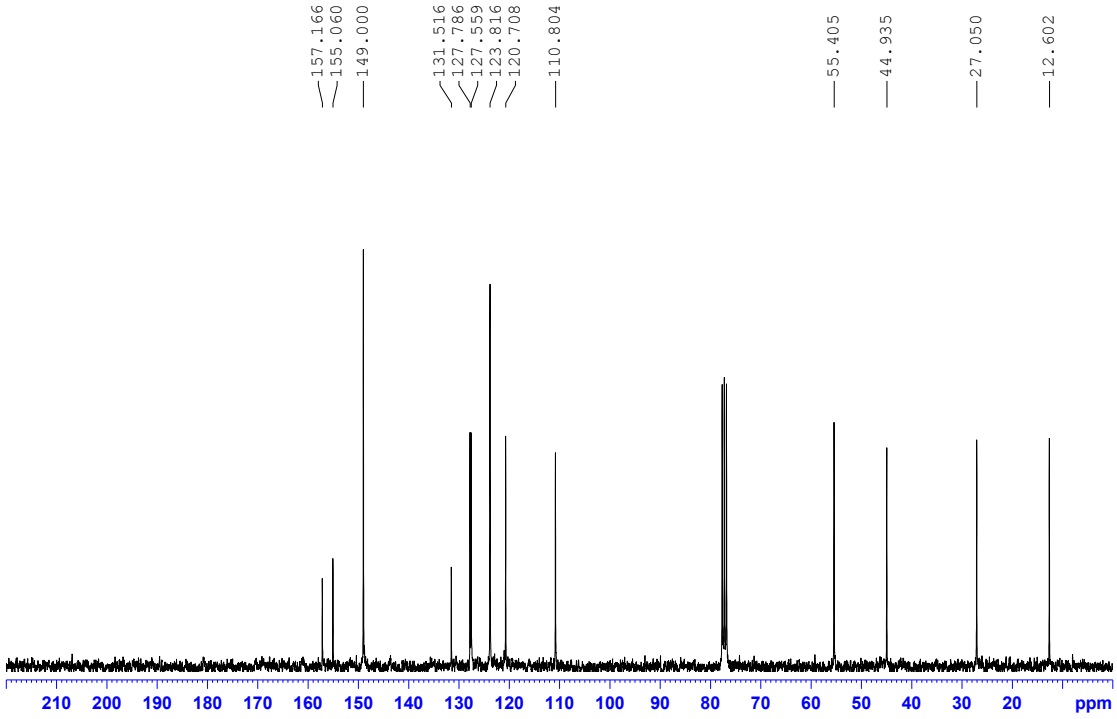


Figure 60S. ^{13}C{^{1}H} NMR spectrum of **4ae**.

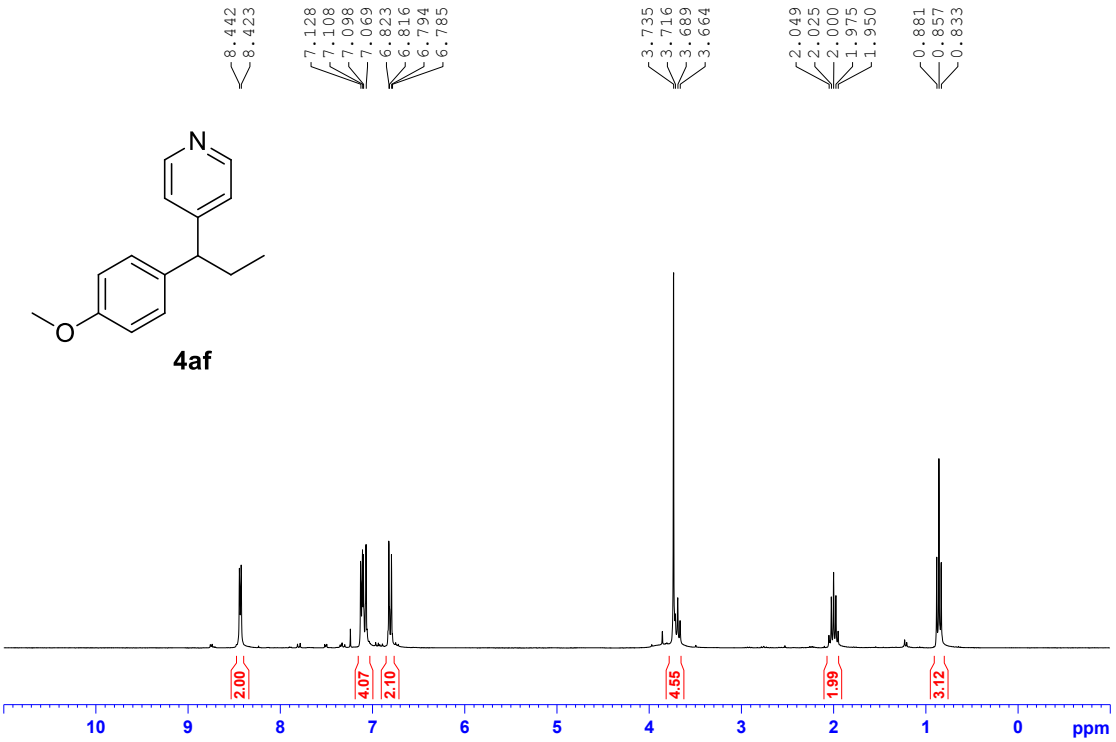


Figure 61S. ^{1}H NMR spectrum of **4af**.

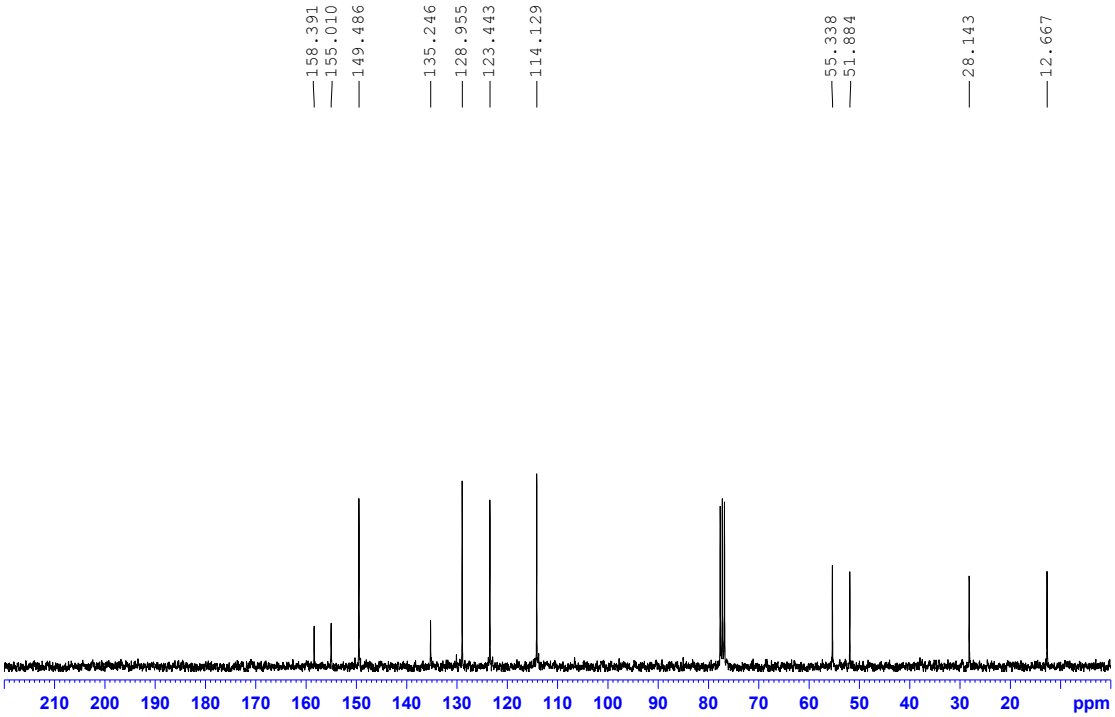


Figure 62S. ^{13}C{^{1}H} NMR spectrum of **4af**.

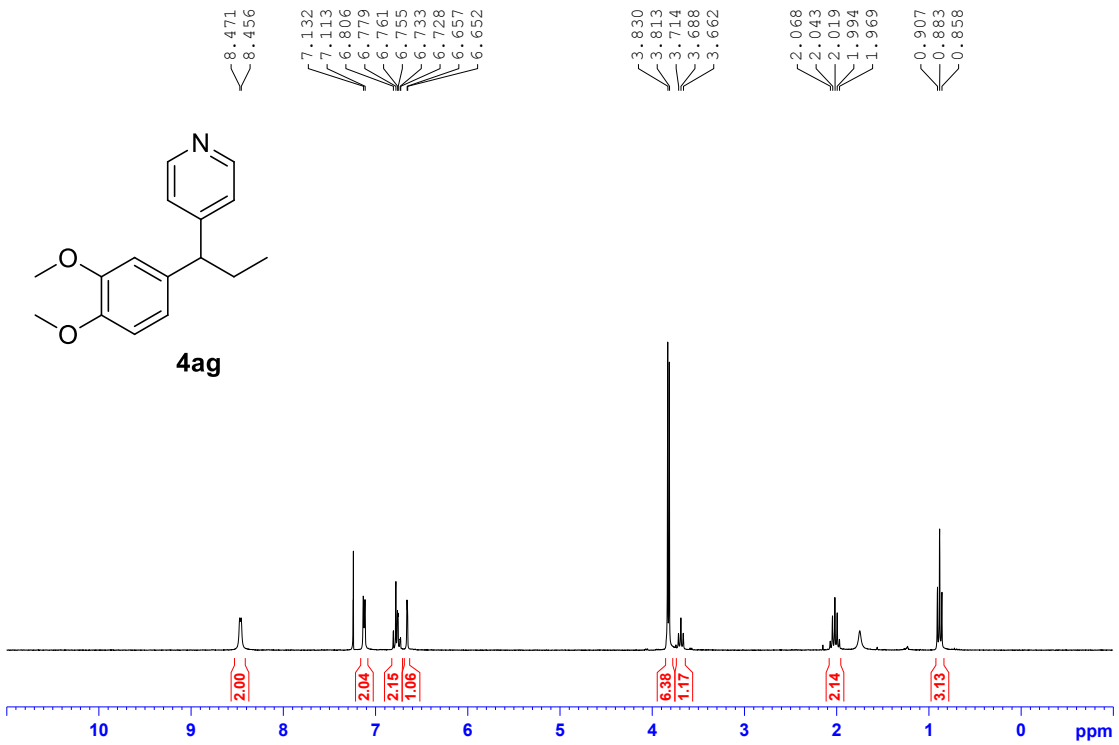


Figure 63S. ^{1}H NMR spectrum of **4ag**.

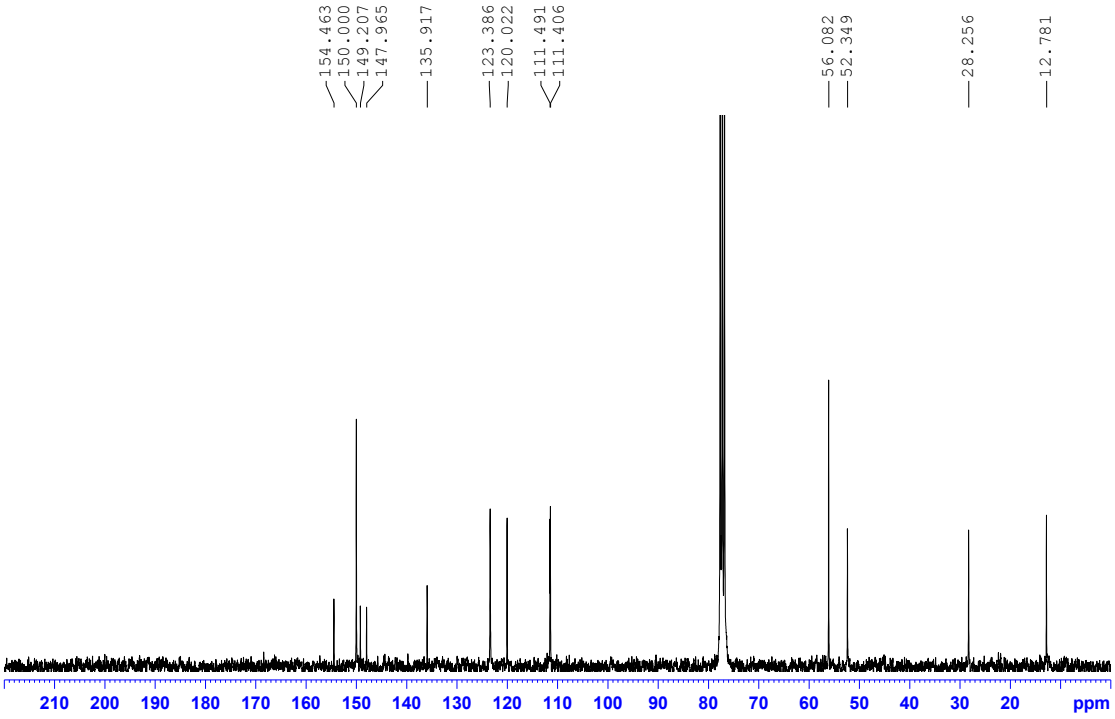


Figure 64S. ^{13}C{^{1}H} NMR spectrum of **4ag**.

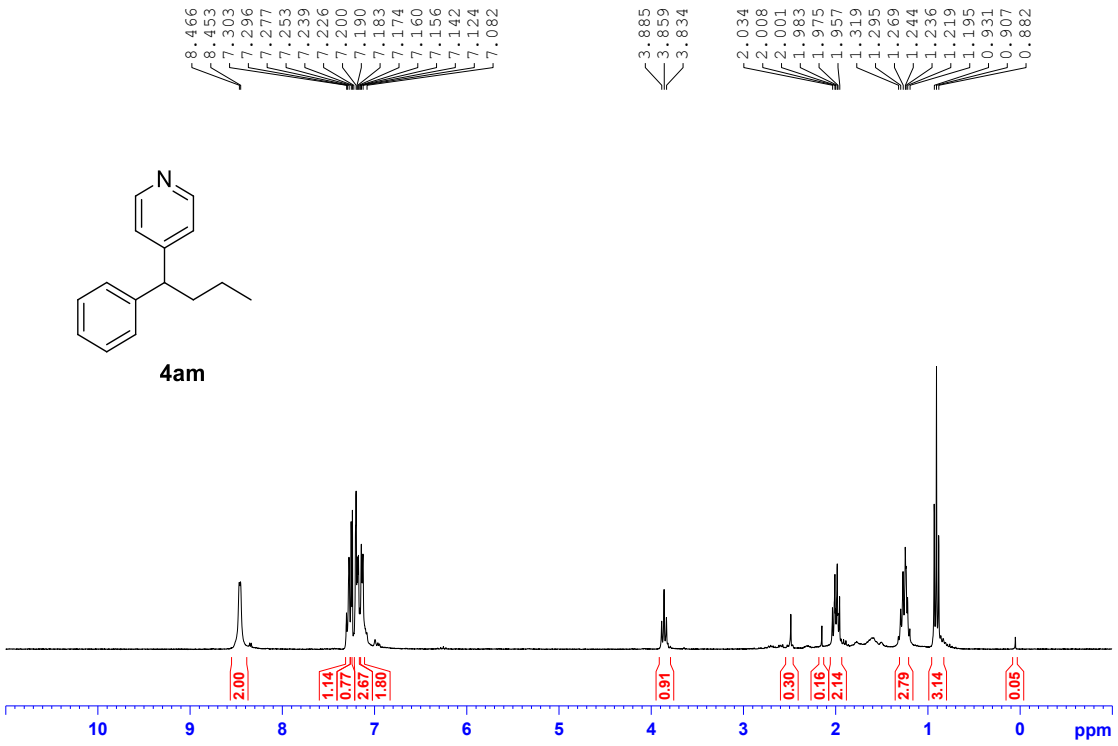


Figure 65S. ^{1}H NMR spectrum of **4am**.

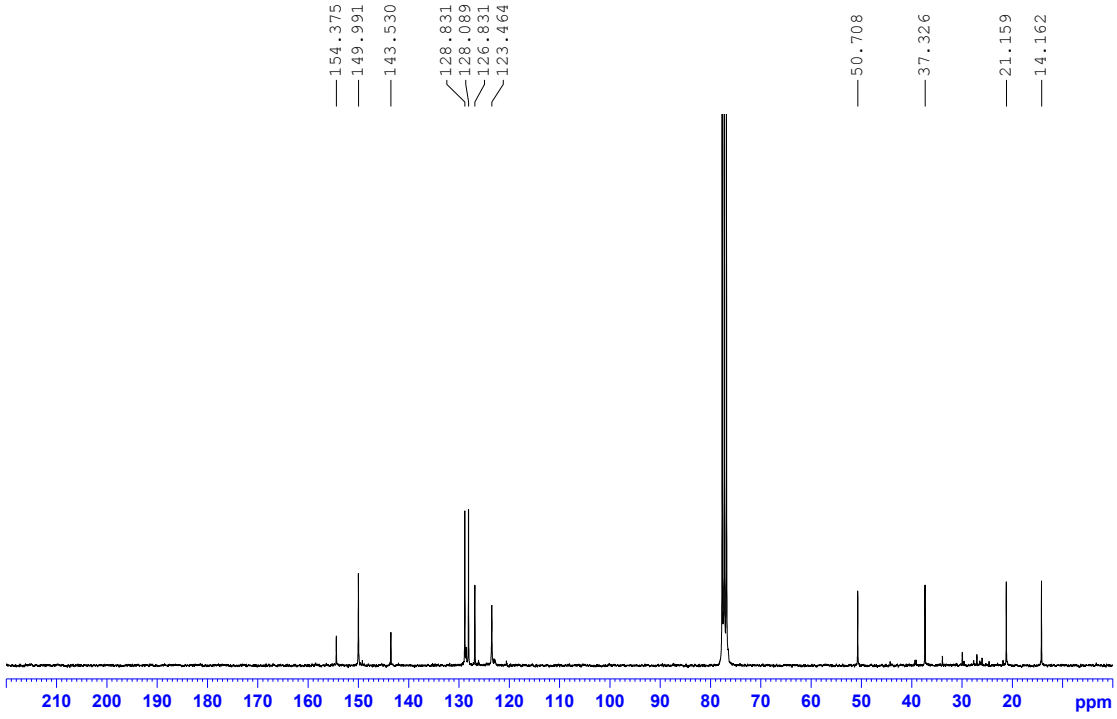


Figure 66S. ^{13}C{^{1}H} NMR spectrum of **4am**.

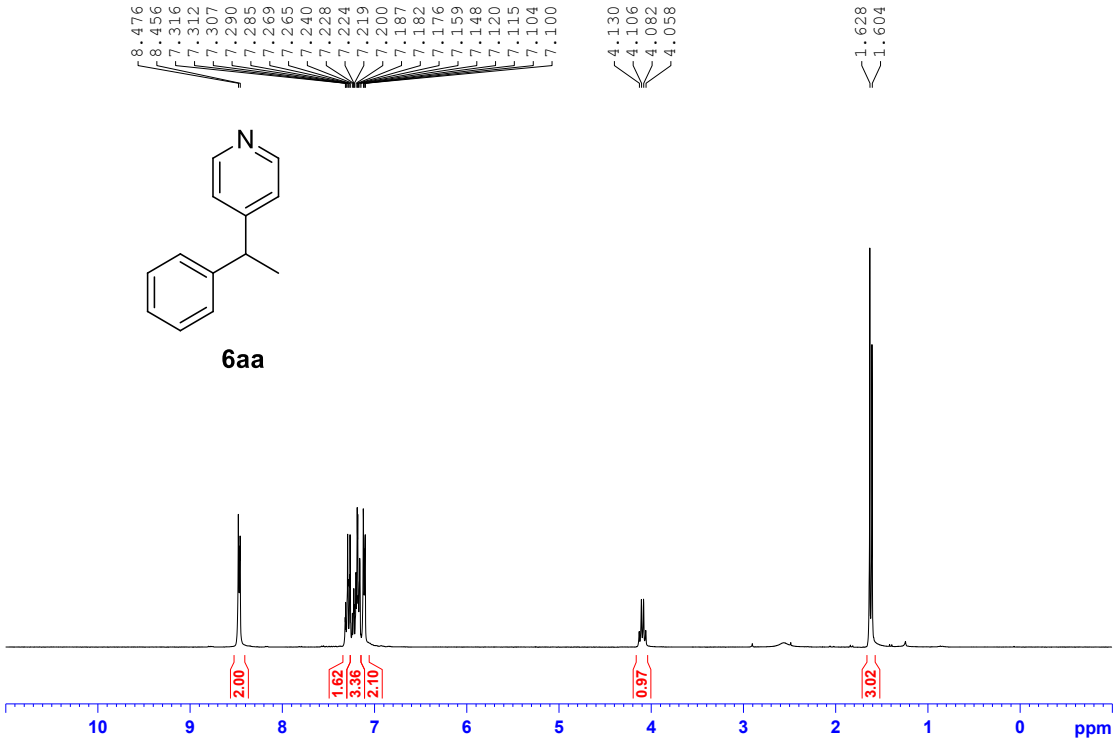


Figure 67S. ^{1}H NMR spectrum of **6aa**.

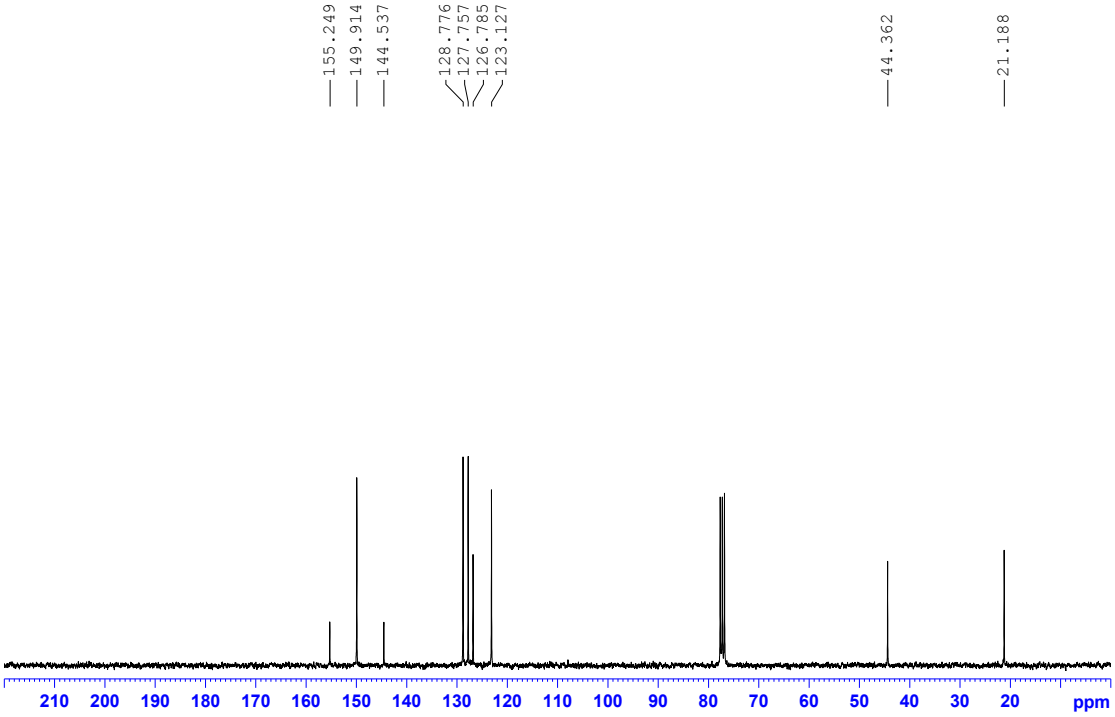


Figure 68S. ^{13}C{^{1}H} NMR spectrum of **6aa**.

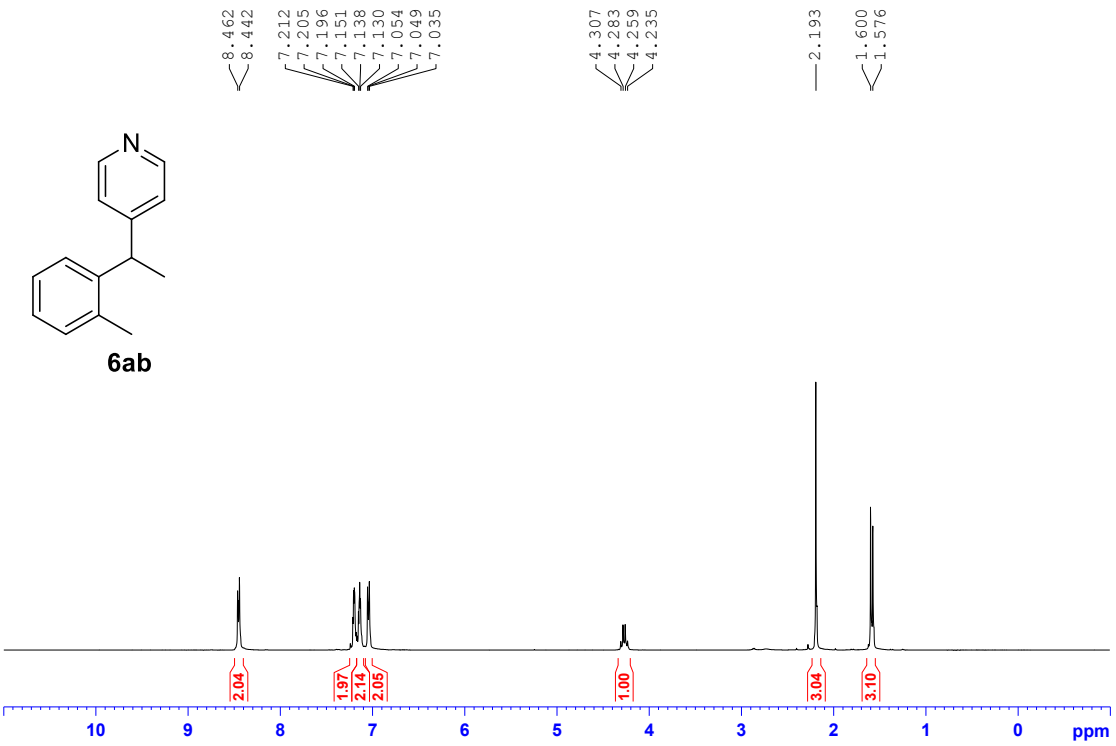


Figure 69S. ^{1}H NMR spectrum of **6ab**.

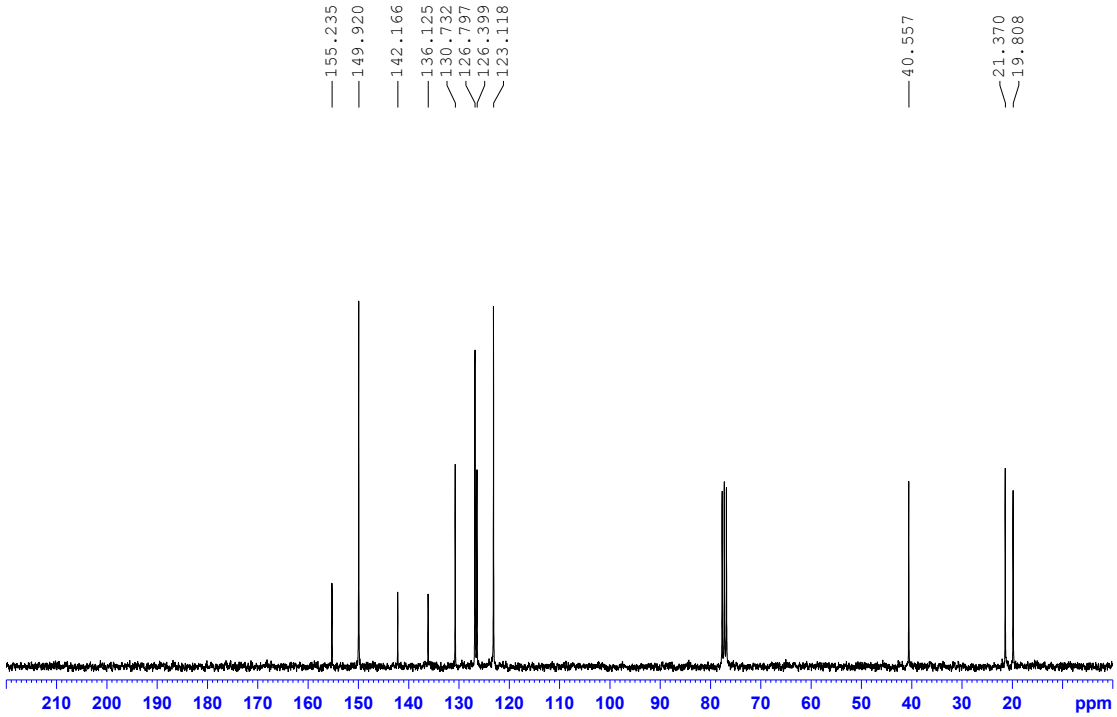


Figure 70S. ^{13}C{^{1}H} NMR spectrum of **6ab**.

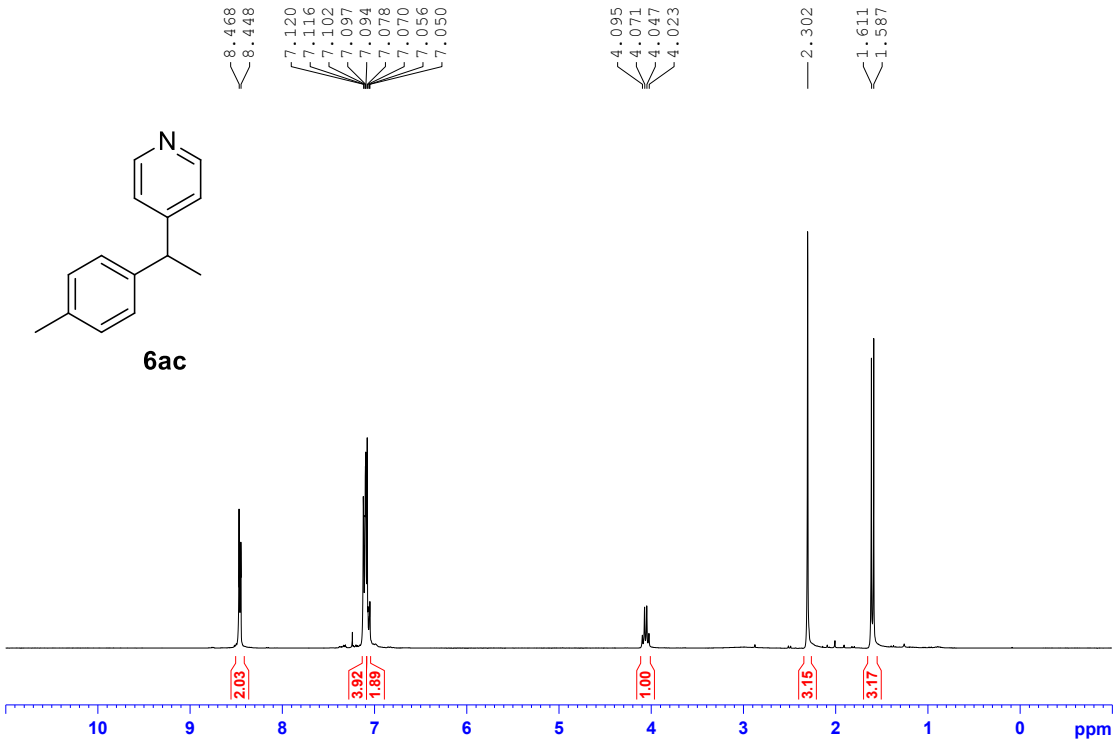


Figure 71S. ^{1}H NMR spectrum of **6ac**.

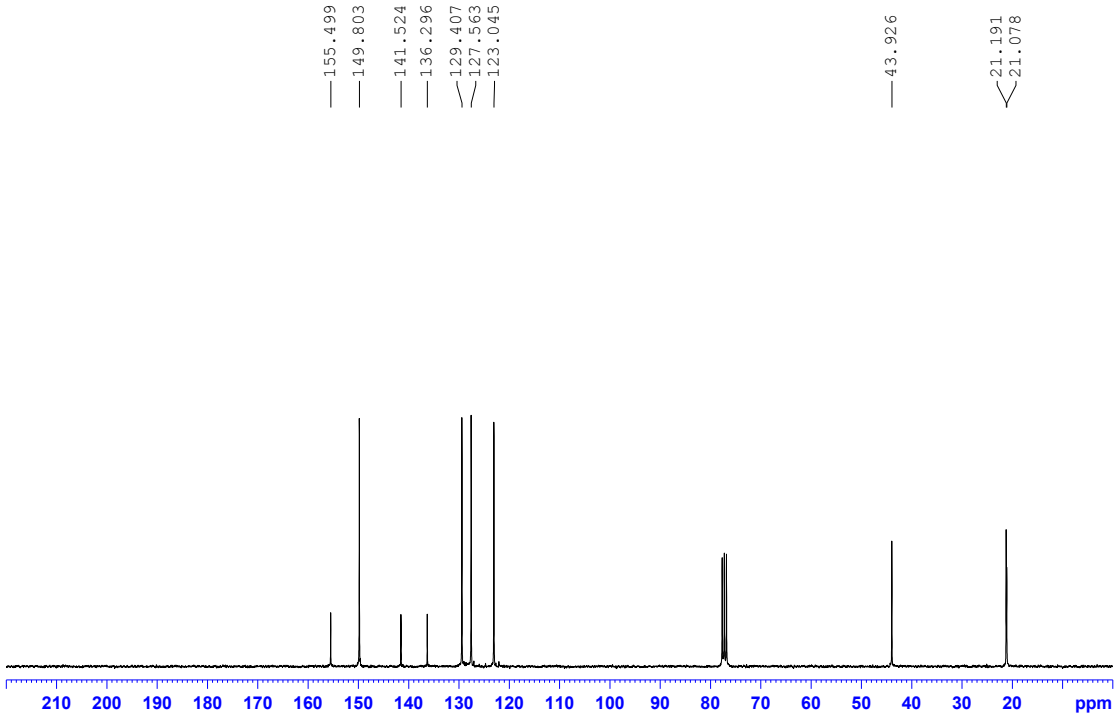


Figure 72S. ^{13}C{^{1}H} NMR spectrum of **6ac**.

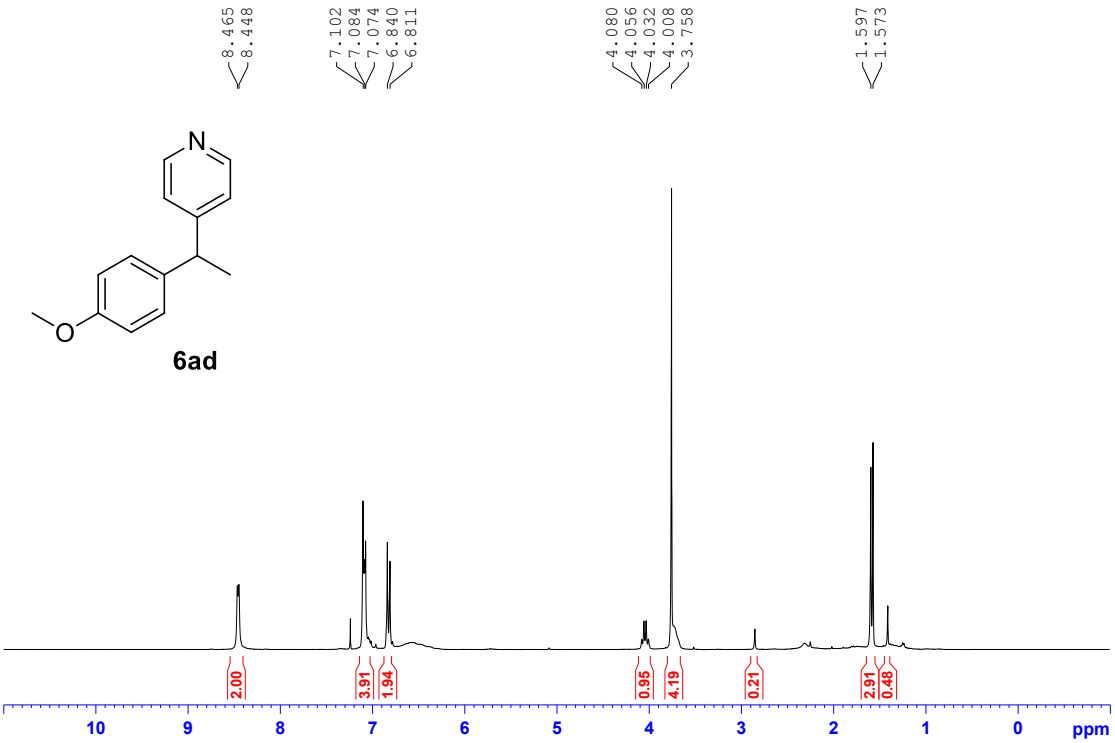


Figure 73S. ^{1}H NMR spectrum of **6ad**.

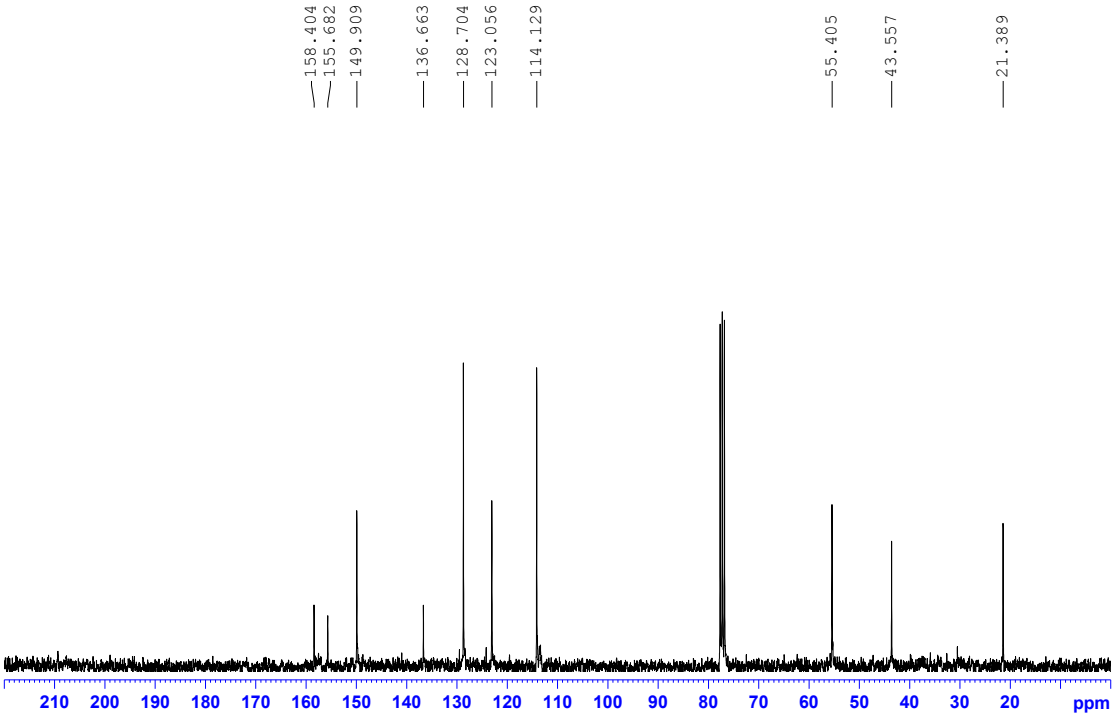


Figure 74S. ^{13}C{^{1}H} NMR spectrum of **6ad**.

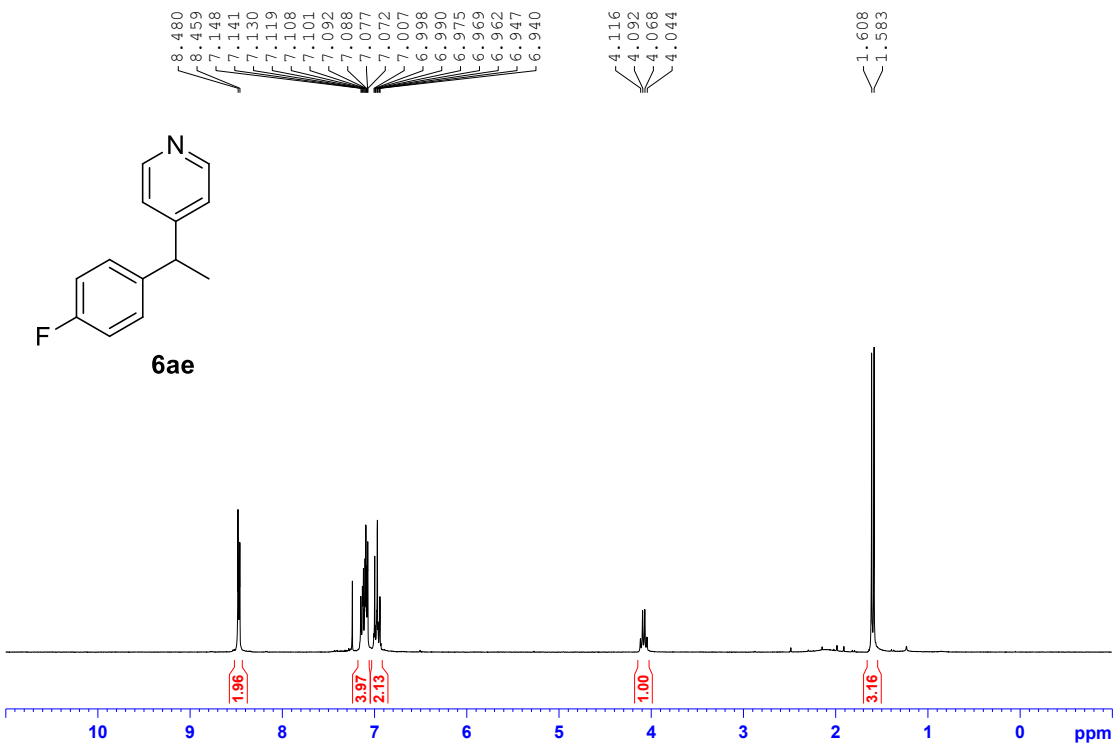


Figure 75S. ^{1}H NMR spectrum of **6ae**.

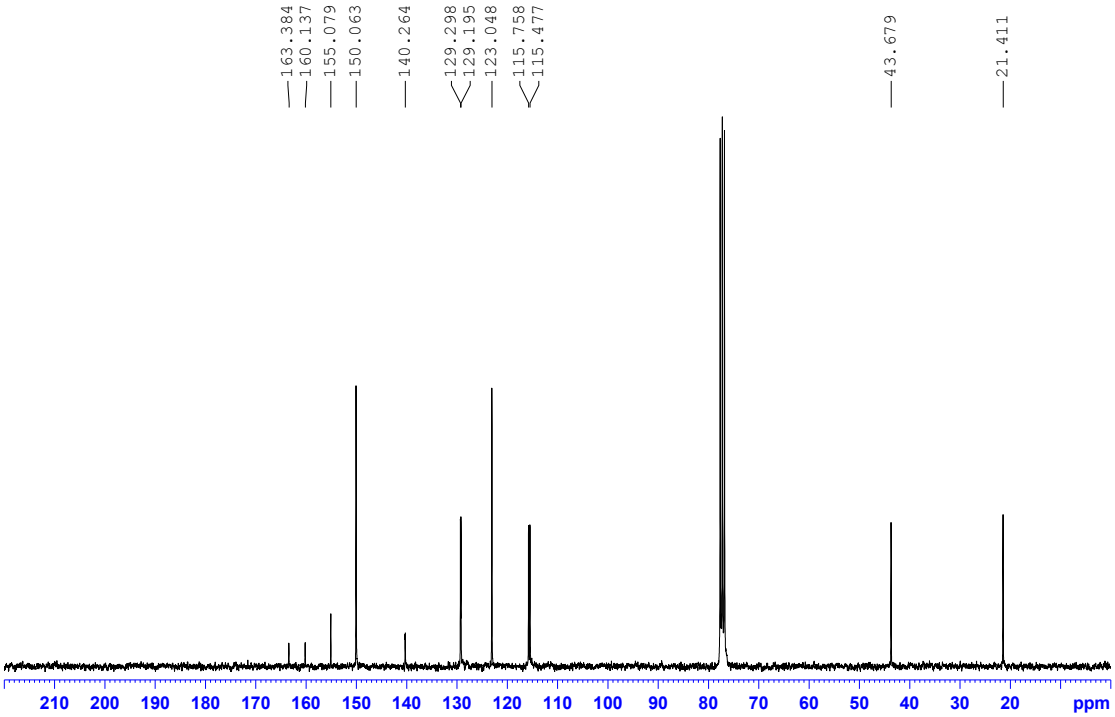


Figure 76S. ^{13}C{^{1}H} NMR spectrum of **6ae**.

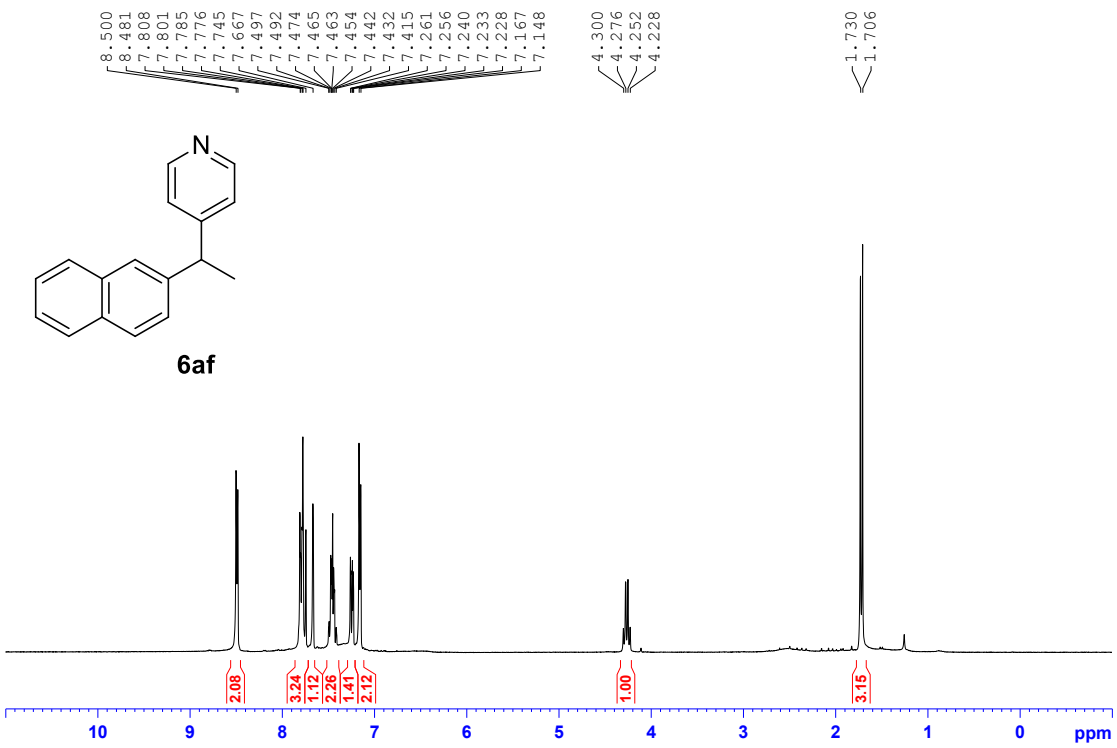


Figure 77S. ^{1}H NMR spectrum of **6af**.

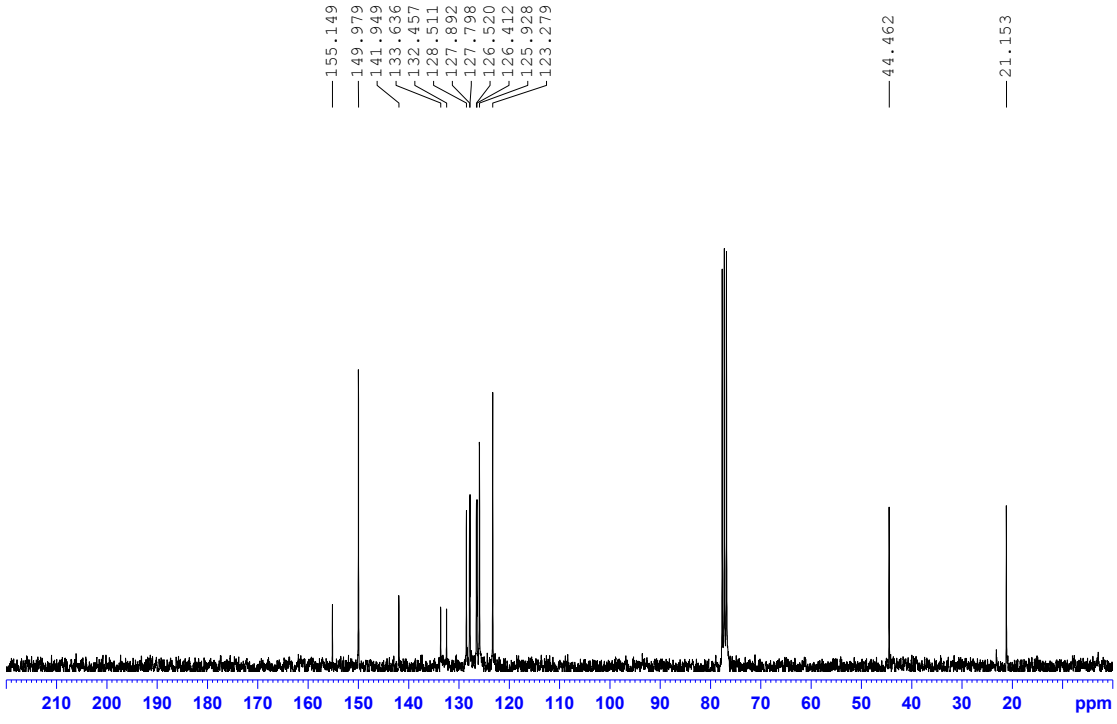


Figure 78S. ^{13}C{^{1}H} NMR spectrum of **6af**.

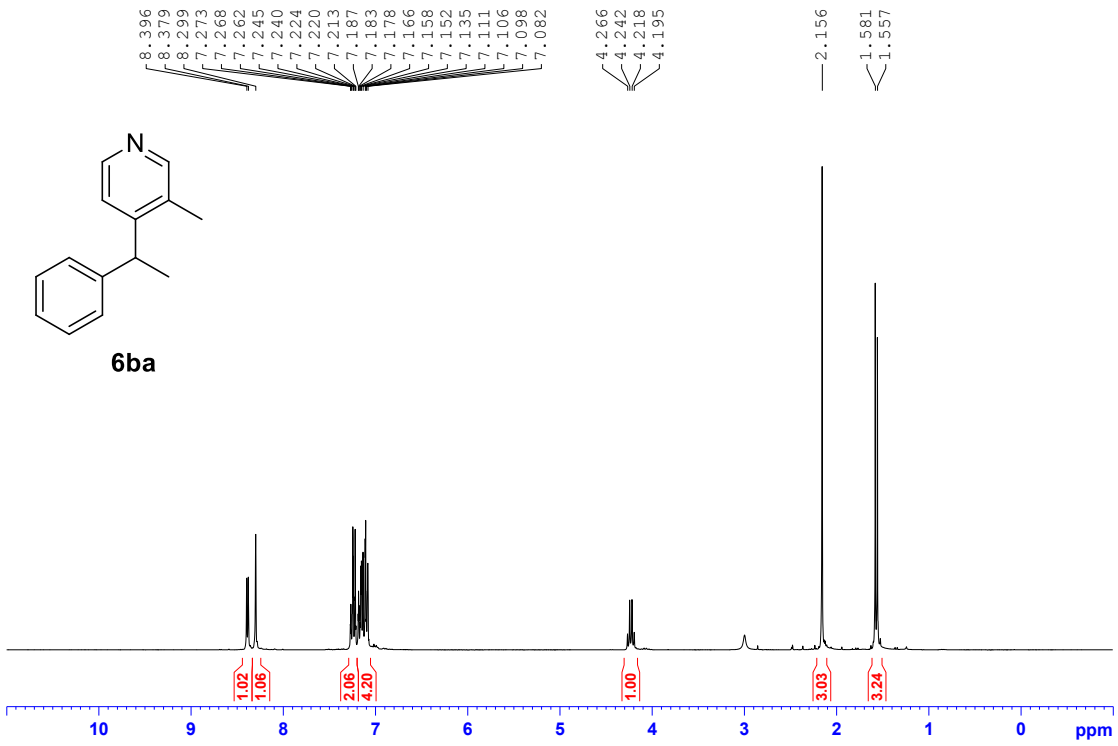


Figure 79S. ^{1}H NMR spectrum of **6ba**.

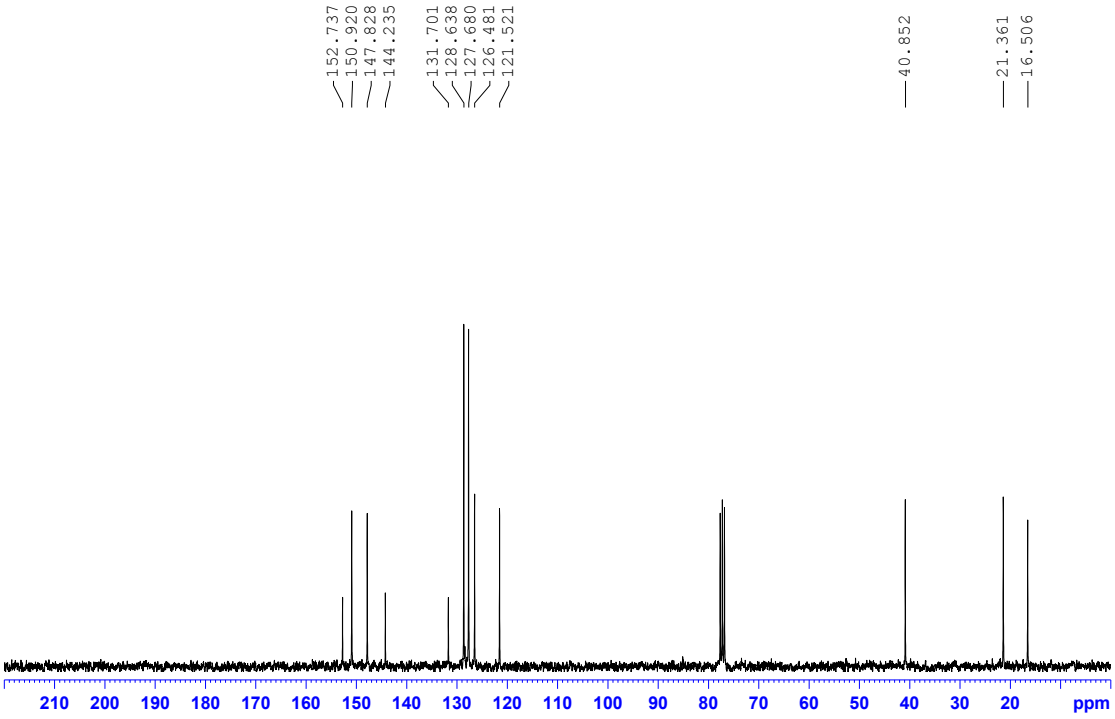


Figure 80S. ^{13}C{^{1}H} NMR spectrum of **6ba**.

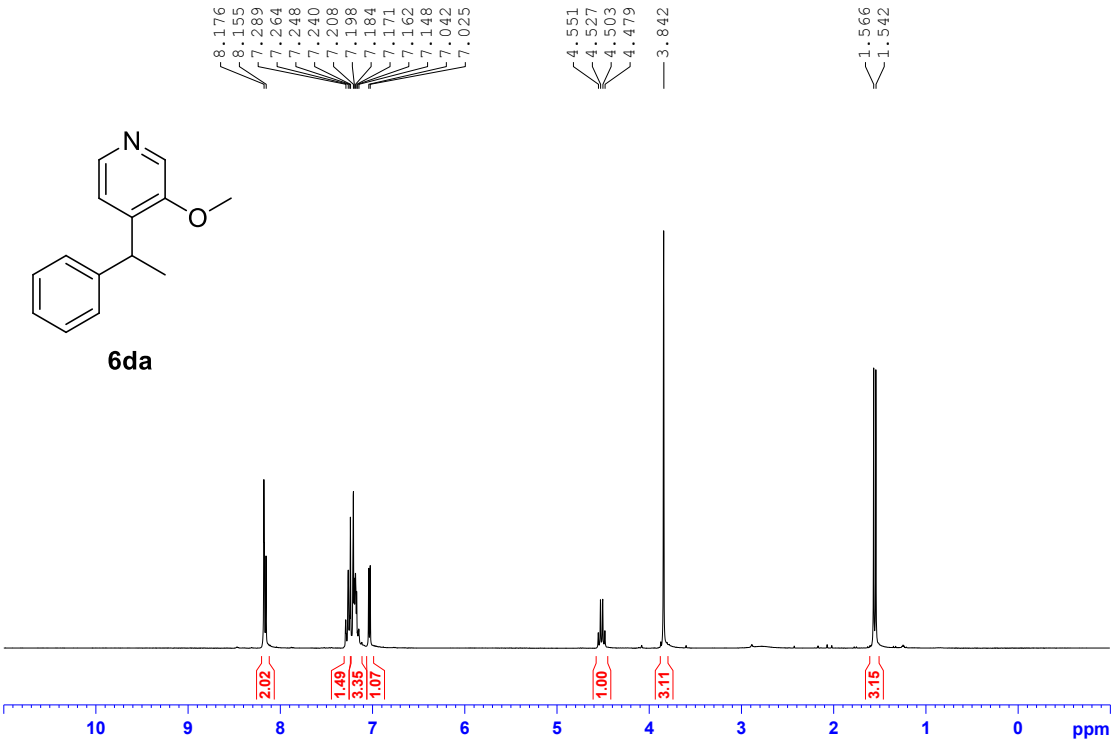


Figure 81S. ^{1}H NMR spectrum of **6da**.

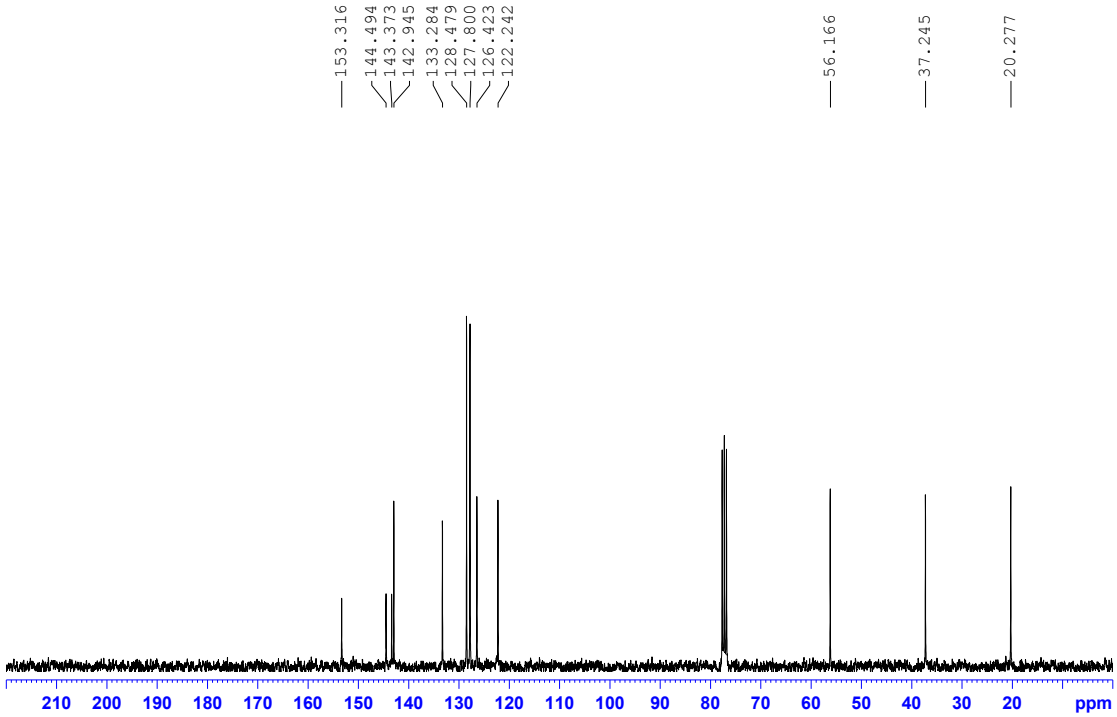


Figure 82S. ^{13}C{^{1}H} NMR spectrum of **6da**.