Ligand-Enabled Regioselectivity in the Oxidative Cross-Coupling of Arenes with Toluenes and Cycloalkanes using Ruthenium Catalysts: Tuning the Site-selectivity from the *ortho* to *meta*-Positions

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Supporting Information

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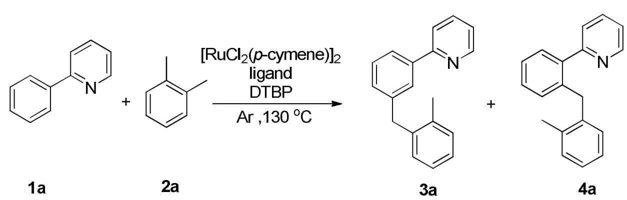
1. Reagents: Unless otherwise noted, all reagents were purchased from Acros, Alfa, Adamas and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

2. Instruments: NMR spectra were recorded on Varian Inova-400 MHz, Inova-300 MHz, Bruker DRX-400 or Bruker DRX-500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. HRMS analysis were carried out using TOF-MS instrument with EI source.

3. Optimization of reaction conditions

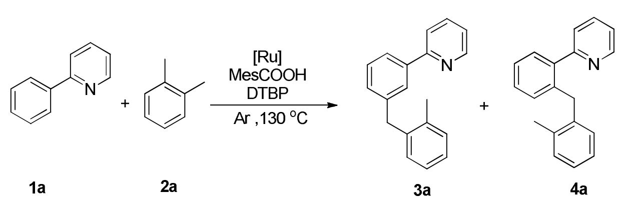
Table S1. Screening of ligand[a,b]



Entry	ligand	3a Yield (%)[b]	4a Yield (%)[b]
1	1-Ad-OH	trace	73
2	MesCOOH	trace	70
3	Piv-Val-OH	trace	64
4	PivOH	trace	56
5	2,6-Lutidine	0	0
6	PPh_3	14	41
7	CF_3COOH	trace	trace

[a]**1a** (0.2 mmol), **2a** (5 mmol), $[RuCl_2\ (p\text{-cymene})]_2$ (5 mol%), DTBP (0.8 mmol), and ligand (0.06 mmol), 130 °C, 24 h. [b]Yields were based on GC analysis using tridecane as an internal standard.

Table S2. Screening of catalyst[a,b]

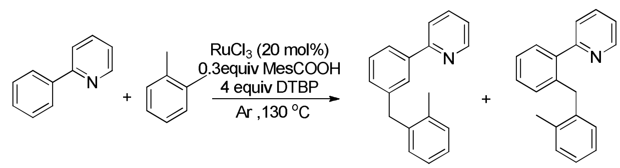


Entry	Catalyst	3a Yield (%)[b]	?4a Yield (%)[b]
1	$[RuCl_2\ (p\text{-cymene})]_2$	trace	70
2	$Ru(acac)_3$	trace	trace
3	$Ru(PPh_3)_3Cl_2$	4	70
4	$Ru(PPh_3)_3COH_2$	11	trace
5	Ru_3CO_{12}	45	7

6	Ru(2,2'-bipyridine)$_3$	0	0
7	$RuCl_3$[c]	20	trace
8	$RuCl_3$[d]	34	11

[a]**1a** (0.2 mmol), **2a** (5 mmol), [Ru] (5 mol%), DTBP (0.8 mmol), and MesCOOH (0.06 mmol), 130 ^{o}C, 24 h. [b]Yields were based on GC analysis using tridecane as an internal standard.[c]$RuCl_3$ (10 mol%), [d]$RuCl_3$ (20 mol%).

Table S3. Screening of additive[a,b]

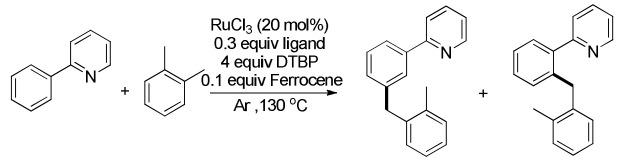


1a **2a** **3a** **4a**

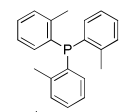
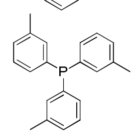
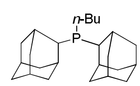
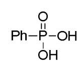
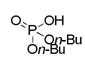
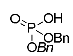
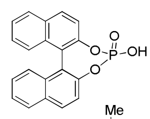
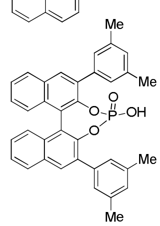
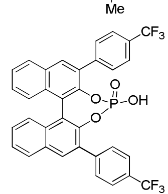
Entry	Additive	3a Yield (%)[b]	5a Yield (%)[b]
1	AgOTf	12	18
2	AgNTf	trace	trace
3	$Ag(OAc)_2$	21	trace
4	Ag_2O	8	trace
5	$Ni(OAc)_2$	29	12
6	$Mn(OAc)_2$	trace	trace
7	$Co(OAc)_3$	24	5
8	$FeBr_3$	30	13
9	$FeCl_3$	32	12
10	Ferrocene	44	16
11	$FeCl_2$	41	30
12	MnO_2	26	trace
13	$NiCl_2$	13	trace
14	CuCl	trace	trace
15	$AlCl_3$	29	11
16	Fe(II)Pc	trace	trace
17	$Fe(OTs)_3$	trace	trace
18	$Fe(OTf)_3$	trace	trace
19	$Fe(acac)_3$	17	6
20	$Fe(acac)_2$	11	trace

[a]**1a** (0.2 mmol), **2a** (5 mmol), $RuCl_3$ (20 mol%), DTBP (0.8 mmol), and MesCOOH (0.06 mmol), 130 ^{o}C, 24 h. [b]Yields were based on GC analysis using tridecane as an internal standard.

Table S4. Screening of ligand[a,b]

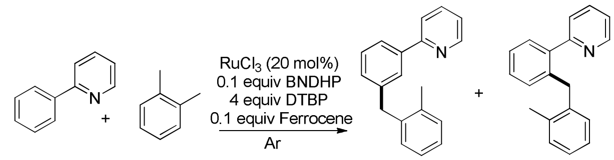


1a **2a** **3a** **4a**

Entry	Ligand	3a yield(%)[b]	4a yield(%)[b]
1	1-Ad-OH	23	19
2	Piv-val-OH	36	9
3	PPh_3	4	75
4		8	54
5		trace	trace
6		trace	trace
7		trace	trace
8		25	10
9		48	18
10[c]		83	5
11[c]		80	4
12[c]		74	5

[a]**1a** (0.2 mmol), **2a** (5 mmol), $RuCl_3$ (20 mol%), DTBP (0.8 mmol), and ligand (0.06 mmol), 130 °C, 24 h. [b]Yields were based on GC analysis using tridecane as an internal standard. [c]ligand (0.02 mmol).

Table S5. Screening of time and temperature[a,b]

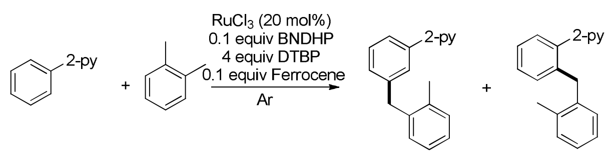


1a **2a** **3a** **4a**

Entry	T (°C)	t (h)	3a Yield (%)[b]	4a Yield (%)[b]
1	120	24	58	13
2	110	24	34	3
3	130	18	76	4
4	130	12	45	5
5	130	6	26	4

[a]**1a** (0.2 mmol), **2a** (5 mmol), $RuCl_3$ (20 mol%), DTBP (0.8 mmol), Ferrocene (0.02 mmol) and ligand (0.02 mmol). [b]Yields were based on GC analysis using tridecane as an internal standard.

Table S6. Screening of solvent[a,b]

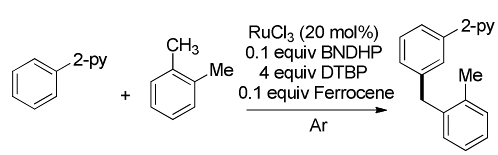


1a **2a** **3a** **4a**

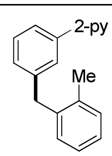
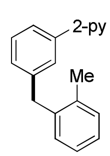
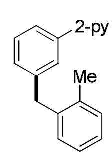
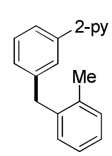
Entry	solvent	3a Yield (%)[b]	4a Yield (%)[b]
1	CH_3CN	12	trace
2	Chlorobenzene	trace	trace
3	benzene	30	trace
4	*t*-Bu-benzene	78	7

[a]**1a** (0.2 mmol), **2a** (2 mmol), $RuCl_3$ (20 mol%), DTBP (0.8 mmol) , Ferrocene (0.02 mmol) and ligand (0.02 mmol), solvent (0.5 mL), 130 °C, 36 h. [b]Yields were based on GC analysis using tridecane as an internal standard.

Table S7. Screening of solvent[a]

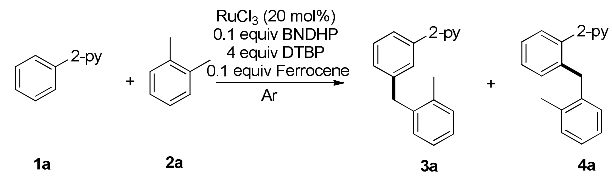


1a **2a** **3a**

			
1 equiv **2a** trace	2 equiv **2a** trace	5 equiv **2a** 21%	10 equiv **2a** 78%[b]

[a]**1a** (0.2 mmol), **2a** (2 mmol), $RuCl_3$ (20 mol%), DTBP (0.8 mmol) , Ferrocene (0.02 mmol) and ligand (0.02 mmol), solvent (0.5 mL), 130 °C, 24 h. Isolated yield. [b]36 h.

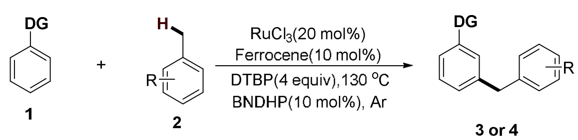
Table S8. Screening of amount of L1[a,b]



Entry	Amount of L1	3a Yield (%)[b]	4a Yield (%)[b]
1	30%	78	2
2	20%	80	6
3	10%	83	5

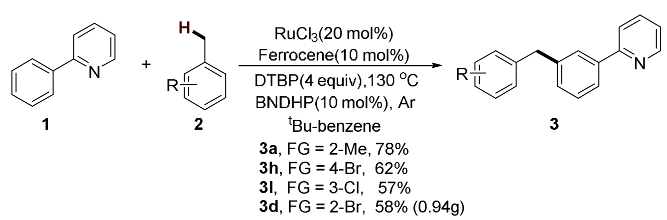
[a]**1a** (0.2 mmol), **2a** (5 mmol), $RuCl_3$ (20 mol%), DTBP (0.8 mmol), and ligand (0.06 mmol), 130 °C, 24 h. [b]Yields were based on GC analysis using tridecane as an internal standard.

4. General procedures for Ru-catalyzed *meta*-C_{Ar}-H benzylation



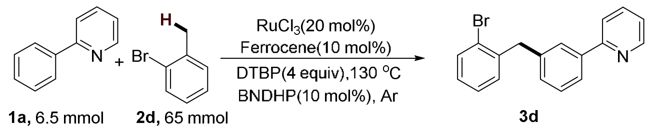
A mixture of **1** (0.2 mmol), **2** (5 mmol), $RuCl_3$ (8.3 mg, 20 mol%), Ferrocene (3.6 mg, 0.02 mmol, 0.1 equiv), BNDHP (7.0 mg, 0.02 mmol, 0.1 equiv), and DTBP (117.0 mg, 0.8 mmol, 4 equiv) in a 15 mL sealed glass vial was heated at 130 °C under argon with vigorous stirring for 24 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:100 to 1:50) to give the corresponding product.

5. General procedures for Ru-catalyzed *meta*-C_{Ar}-H benzylation with solvent



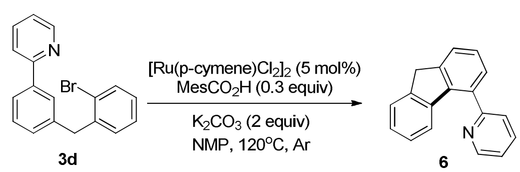
A mixture of **1a** (31.0 mg, 0.2 mmol), **2** (2 mmol, 10 equiv), $RuCl_3$ (8.3 mg, 20 mol%), Ferrocene (3.6 mg, 0.02 mmol, 0.1 equiv), BNDHP (7.0 mg, 0.02 mmol, 0.1 equiv), DTBP (117.0 mg, 0.8 mmol, 4 equiv) and *t*-Bu-benzene (0.5 mL) in a 15 mL sealed glass vial was heated at 130 °C under argon with vigorous stirring for 36 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:100 to 1:50) to give product.

6. Gram scale reaction



A mixture of **1a** (1007.5 mg, 6.5 mmol), **2k** (11117.6 mg, 65 mmol, 10 equiv), $RuCl_3$ (269.1 mg, 20 mol%), Ferrocene (117.1 mg, 0.65 mmol, 0.1 equiv), BNDHP (227.0 mg, 0.65 mmol, 0.1 equiv), DTBP (3802.0 mL, 26 mmol, 4 equiv) and *t*-Bu-benzene (10 mL) in a 50 mL schlenk tube was heated at 130 °C under argon with vigorous stirring for 36 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:100 to 1:50) to give product **3k** (0.94 g).

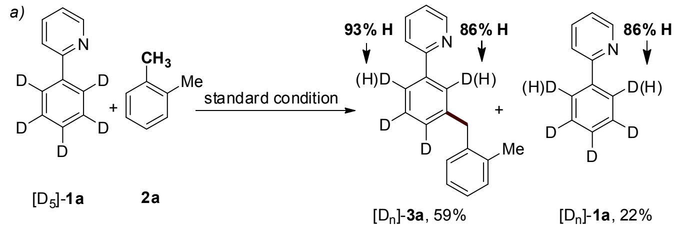
7. Procedure for preparation of 6

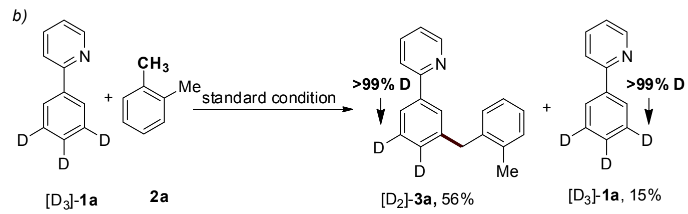


A mixture of **3k** (49.0 mg, 0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.1 mg, 5 mol%), $MesCO_2H$ (9.9 mg, 0.6 mmol, 0.3 equiv), K_2CO_3 (55.3 mg, 0.4mmol, 2 equiv) and NMP (1 mL) in a 15 mL sealed glass vial was heated at 130 °C under argon with vigorous stirring for 24 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:50) to give product **6** (27.2 mg).

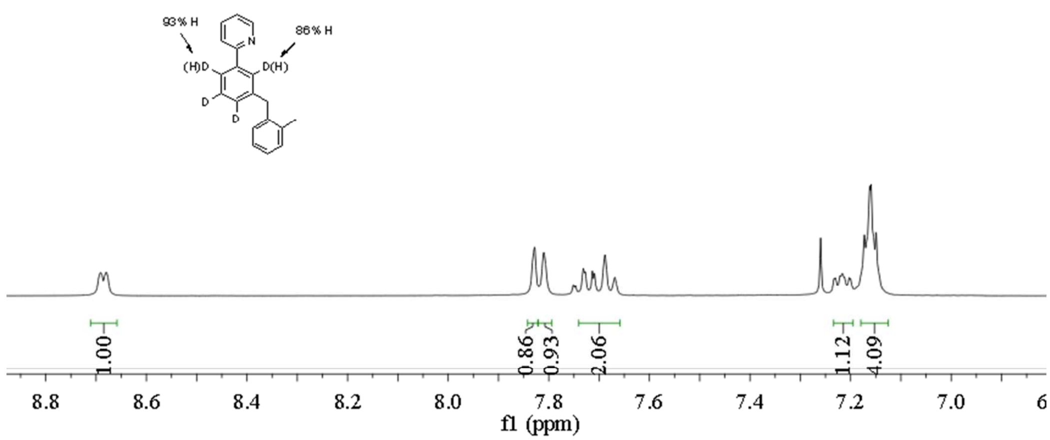
7. Preliminary Mechanistic Experiments

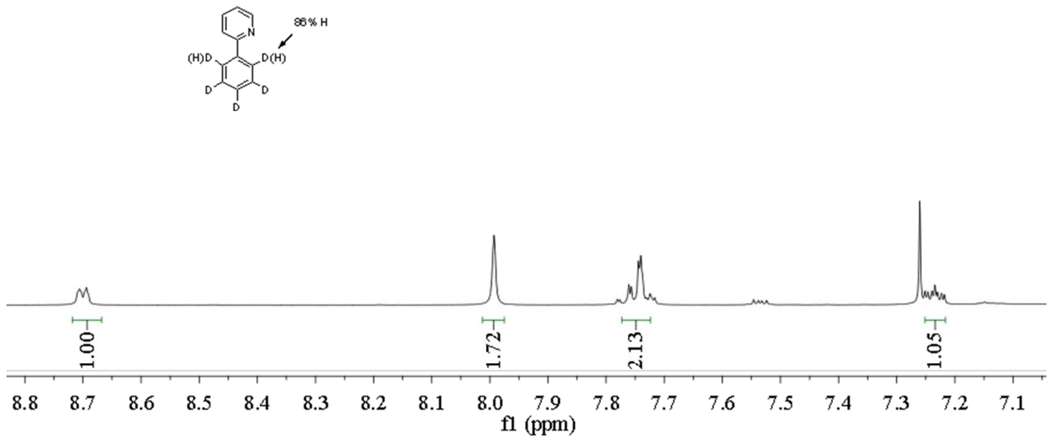
7.1 Isotopic Labelling Studies

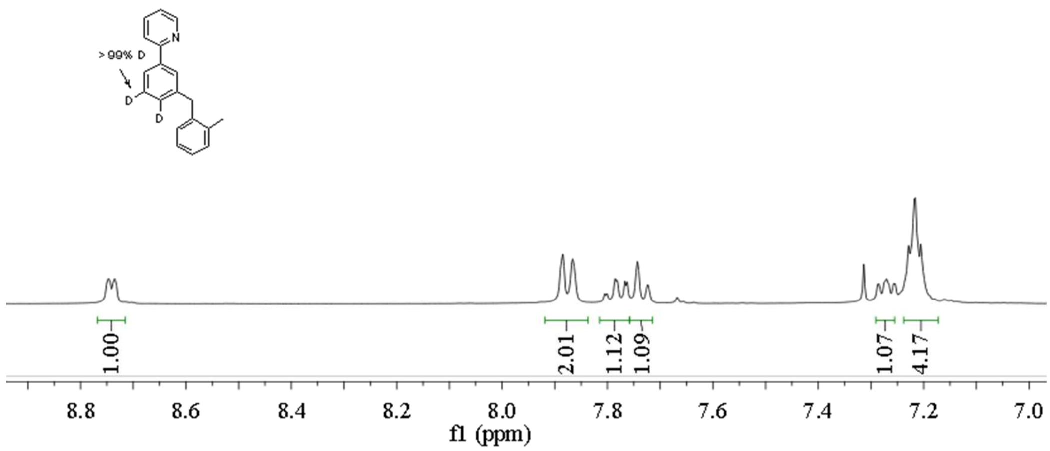




A mixture of $[D_5]$-**1a** or $[D_3]$-**1a** (31.0 mg, 0.2 mmol), **2a** (5 mmol), $RuCl_3$ (8.3 mg, 20 mol%), Ferrocene (3.6 mg, 0.02 mmol, 0.1 equiv), BNDHP (7.0 mg, 0.02 mmol, 0.1 equiv), and DTBP (117.0 mg, 0.8 mmol, 4 equiv) in a 15 mL sealed glass vial was heated at 130 ^{o}C under argon with vigorous stirring for 24 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:100 to 1:50) to give products $[D_n]$-**2a** (30.9 mg) or $[D_2]$-**1a** (29.2 mg) .

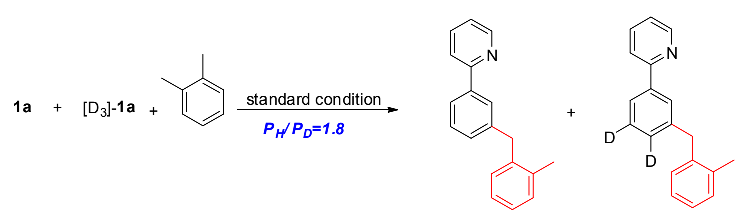






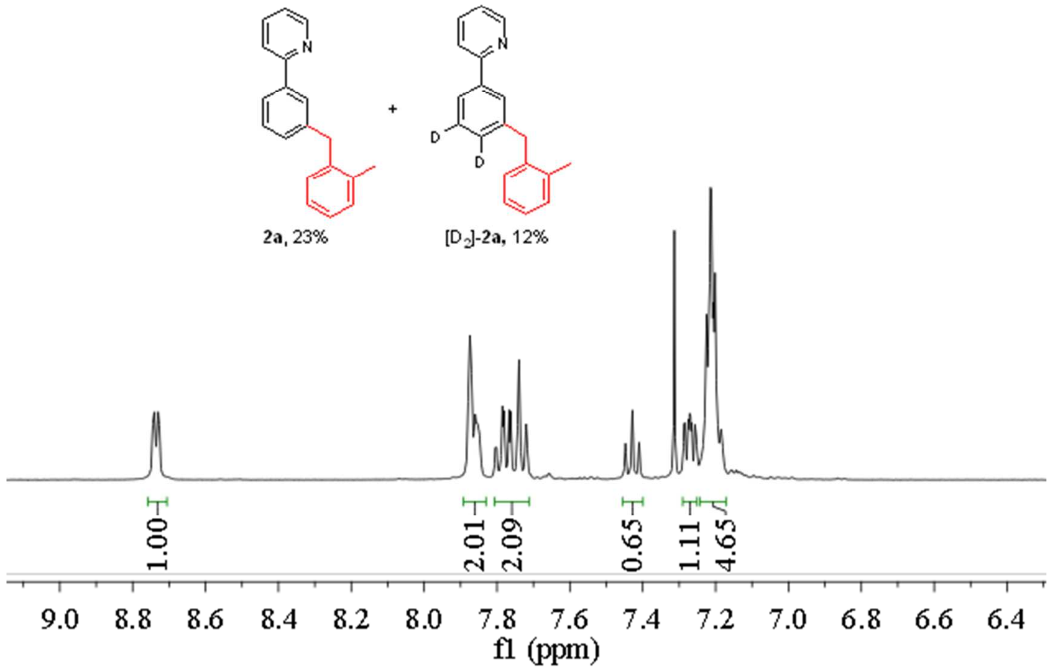
7.2 Kinetic Isotope Effect (KIE) Studies

Intermolecular Competition Reactions

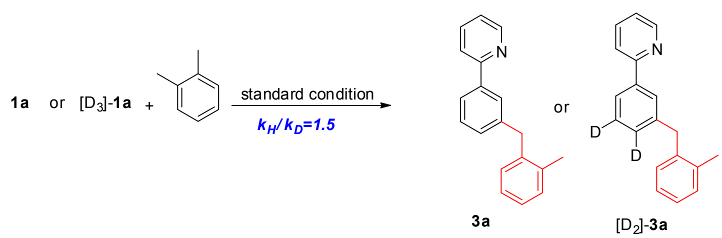


3a, 23% [D$_2$]-**3a**, 12%

A mixture of **1a** (15.5 mg, 0.1 mmol) and [D$_3$]-**1a** (15.8 mg, 0.1 mmol), **2a** (5 mmol), $RuCl_3$ (8.3 mg, 20 mol%), Ferrocene (3.6 mg, 0.02 mmol, 0.1 equiv), BNDHP (7.0 mg, 0.02 mmol, 0.1 equiv), and DTBP (117.0 mg, 0.8 mmol, 4 equiv) in a 15 mL sealed glass vial was heated at 130 ^{o}C under argon with vigorous stirring for 24 hours. The reaction mixture was cooled to room temperature, and diluted with ethyl acetate and filtered through celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (Ethyl acetate/Petroleum ether = 1:100 to 1:50) to give products **2a** and [D$_2$]-**2a** (18.2 mg) .

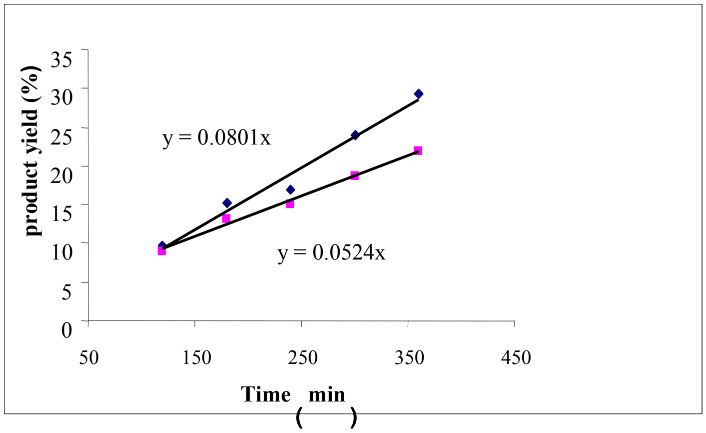


7.3 Two Parallel Reactions



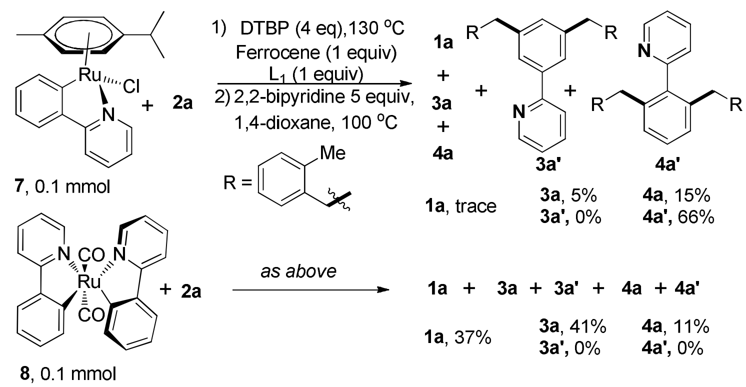
A mixture of **1a** (31.0 mg, 0.2 mmol) or [D$_3$]-**1a** (31.0 mg, 0.2 mmol), **2a** (5 mmol), $RuCl_3$ (8.3 mg, 20 mol%), Ferrocene (3.6 mg, 0.02 mmol, 0.1 equiv), BNDHP (7.0 mg, 0.02 mmol, 0.1 equiv), and DTBP (117.0 mg, 0.8 mmol, 4 equiv) in a 15 mL sealed glass vial was heated at 130 ^{o}C under argon with vigorous stirring for 24 hours. The reaction mixture was cooled to room temperature, GC analysis using tridecane as an internal standard to provide the following conversions.

Time/(min)	120	180	240	300	360
[D2]-**3a**/(%)	8.93	13.21	15.08	18.60	21.94
3a/(%)	9.65	15.18	16.95	23.97	29.29

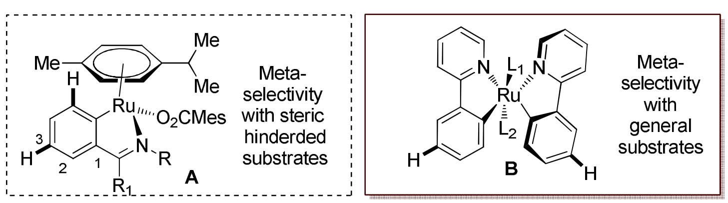


7.4 Controlled experiment

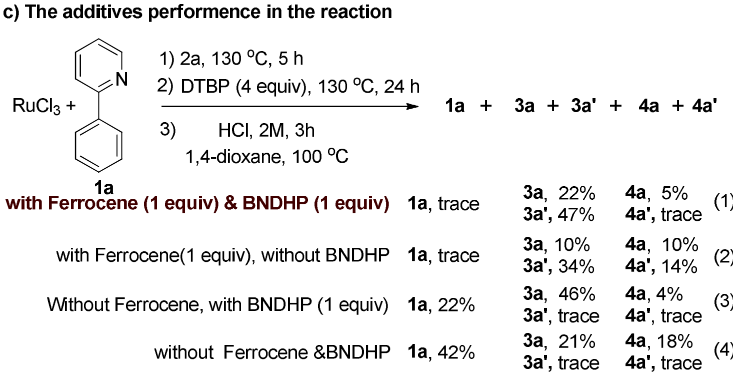
a) Regioselectivity of two types of ruthenium complex



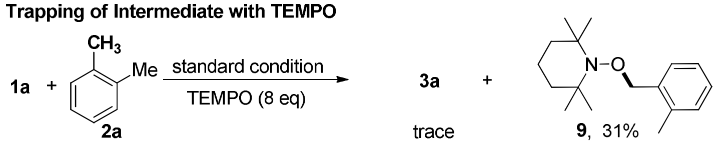
b) The ruthenium intermediate in meta-selective C-H functionalization

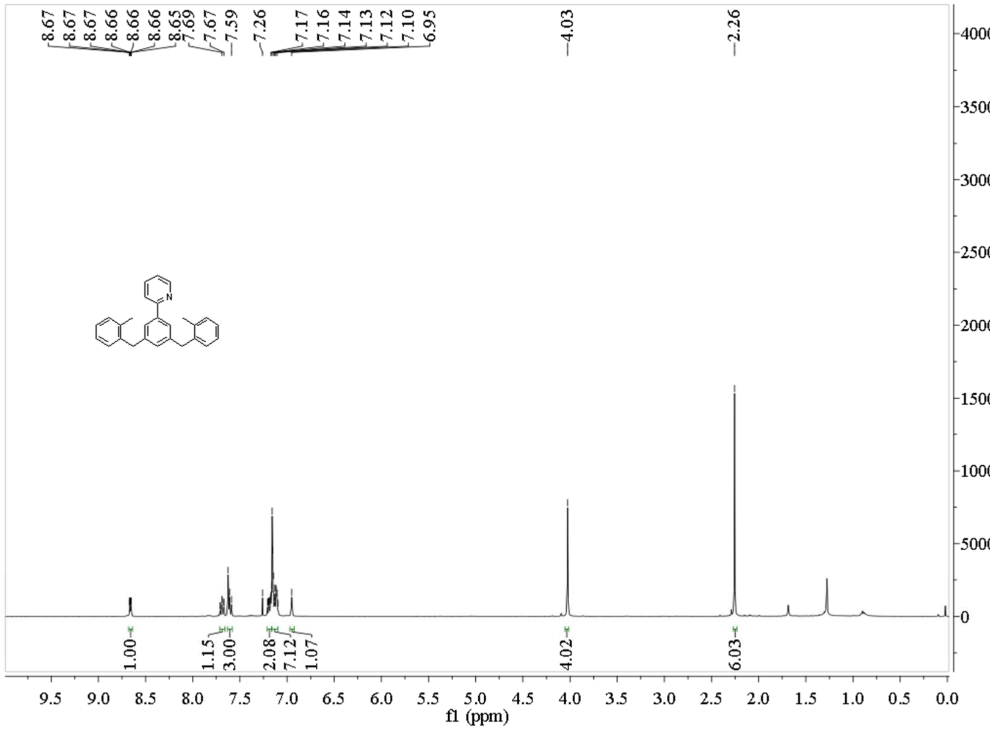


c) The additives performence in the reaction



d) Trapping of Intermediate with TEMPO

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6.03
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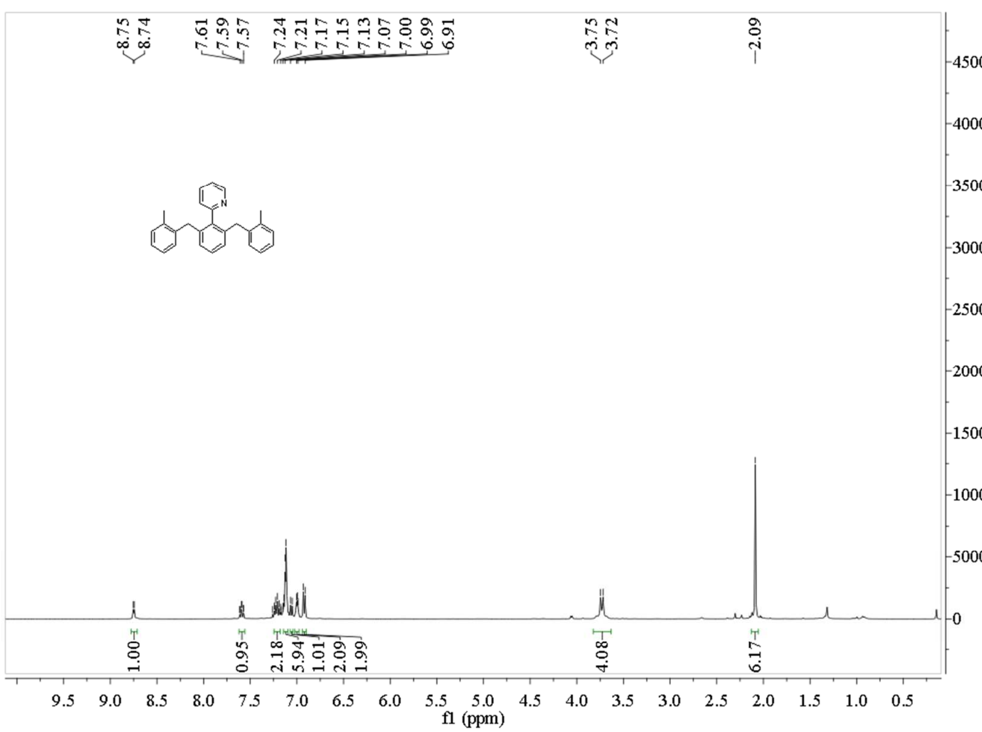
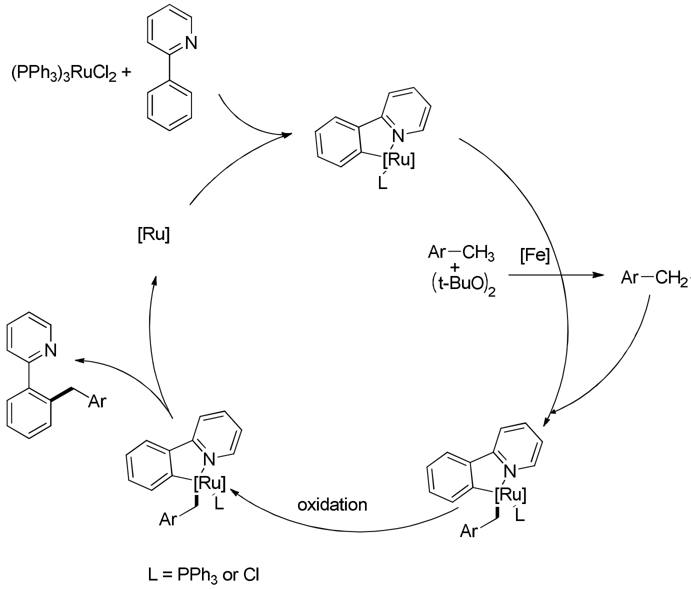
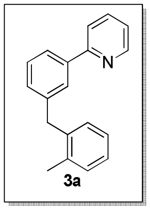

8.75
8.74
7.61
7.59
7.57
7.24
7.21
7.17
7.15
7.13
7.07
7.00
6.99
6.91
3.75
3.72
2.09
N
1.00
0.95
2.18
5.94
1.01
2.09
1.99
4.08
6.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

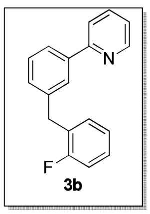
8. The plausible catalytic cycle of *ortho*-benzylation[1,2]



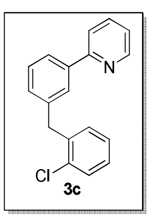
9. Spectroscopic Data of All New Compounds



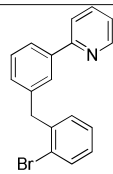
White solid; Yield (81%, 41.9 mg); R_f = 0.47 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.65 (m, 1H), 7.83 (s, 1H), 7.83-7.80 (m, 1H), 7.75 – 7.66 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.18-7.12 (m, 5H), 4.09 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.69, 149.76, 141.08, 139.67, 138.94, 136.84, 136.79, 130.43, 130.09, 129.49, 128.98, 127.60, 126.62, 126.16, 124.80, 122.19, 120.83, 39.65, 19.91. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1448.



Colorless oil; Yield (63%, 33.1 mg); R_f = 0.44 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70-8.67 (m, 1H), 7.89 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.27 (m, 4H), 7.09 – 7.00 (m, 2H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.11(J_{C-F}=244 Hz),157.60, 149.78, 140.16(J_{C-F}=71 Hz), 136.85, 131.19 (J_{C-F}=4), 129.62, 129.08, 128.11 (J_{C-F}=8 Hz), 127.64, 125.07, 124.25 (J_{C-F}=3 Hz), 122.23, 120.84, 115.67, 115.35, 115.46 (J_{C-F}=11 Hz), 34.96. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.75.HRMS Calcd for $C_{18}H_{14}FN$ [M+H$^+$]: 264.1189; Found: 264.1179

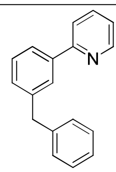


Colorless oil; Yield (59%, 32.9 mg); R_f = 0.43 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.65 (m, 1H), 7.88 (s, 1H), 7.92 – 7.79 (m, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.78 – 7.66 (m, 2H), 7.77 – 7.64 (m, 2H), 7.45 – 7.28 (m, 2H), 7.43 – 7.37 (m, 2H), 7.27 – 7.12 (m, 6H), 7.24 – 7.15 (m, 5H), 4.20 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.58, 149.77, 140.18, 139.77, 138.70, 136.85, 134.36, 131.18, 129.74, 129.05, 127.01, 125.09, 122.23, 120.83, 39.36. HRMS Calcd for $C_{18}H_{14}ClN$ [M+H$^+$]: 280.0893; Found: 280.0898.



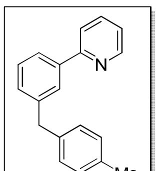
3d

Pale yellow oil; Yield (61%, 39.4 mg); R_f = 0.40 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.66 (m, 1H), 7.88 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.57-7.59 (m, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.25 – 7.16 (m, 4H), 7.12 – 7.05 (m, 1H), 4.21 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 149.79, 140.40, 140.15, 139.78, 136.84, 132.98, 131.25, 129.78, 129.06, 128.07, 127.85, 127.65, 125.10, 125.03, 122.23, 120.81, 41.92. HRMS Calcd for $C_{18}H_{14}BrN$ [M+H$^+$]: 324.0386; Found: 324.0386.



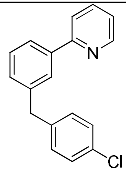
3e

Colorless oil; Yield (70%, 34.3 mg); R_f = 0.51 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.65 (m, 1H), 7.88 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.32 – 7.16 (m, 8H), 4.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.66, 149.78, 141.78, 141.15, 139.76, 136.83, 129.77, 129.10, 129.03, 128.62, 127.73, 126.24, 124.90, 122.21, 120.82, 42.13. HRMS Calcd for $C_{18}H_{15}N$ [M+H$^+$]: 246.1283; Found: 246.1282.



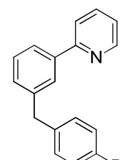
3f

Colorless oil; Yield (63%, 38.8 mg); R_f = 0.50 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.65 (m, 1H), 7.89 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.16-7.09 (m, 4H), 4.05 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.65, 149.71, 142.06, 139.67, 138.08, 136.79, 135.68, 129.68, 129.28, 128.98, 128.94, 127.64, 124.80, 122.15, 120.80, 41.68, 21.12. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1447.



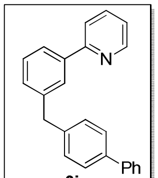
3g

Pale yellow oil; Yield (71%, 39.6 mg); R_f = 0.43 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70-8.67 (m 1H), 7.85 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.13 (m, 6H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48, 149.78, 141.23, 139.86, 139.60, 136.88, 132.06, 130.42, 129.65, 129.12, 128.72, 127.66, 125.07, 122.29, 120.82, 41.42. HRMS Calcd for $C_{18}H_{14}ClN$ [M+H$^+$]: 280.0893; Found: 280.0896.



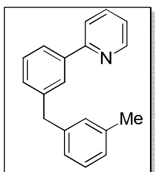
3h

Yellow oil; Yield (61%, 39.5 mg); R_f = 0.40 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.7 Hz, 1H), 7.84 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.76-7.67 (m, 2H), 7.43 – 7.37 (m, 3H), 7.24-7.18 (m, 2H), 7.09-7.11 (m, 2H), 4.02 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.49, 149.79, 141.15, 140.14, 139.87, 136.91, 131.69, 130.85, 129.67, 129.14, 127.68, 125.10, 122.31, 120.85, 120.13, 41.49. HRMS Calcd for $C_{18}H_{14}BrN$ [M+H$^+$]: 324.0388; Found: 324.0384.



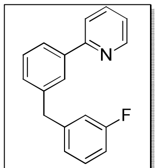
3i

White solid; Yield (71%, 45.5 mg); R_f = 0.52 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.68 (m, 1H), 7.92 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.60 – 7.56 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 3H), 7.35 – 7.27 (m, 4H), 7.20-7.24 (m, 1H), 4.13 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.62, 149.77, 141.68, 141.11, 140.28, 139.80, 139.19, 136.86, 129.80, 129.49, 129.09, 128.84, 127.76, 127.37, 127.20, 127.14, 124.97, 122.23, 120.85, 41.77. HRMS Calcd for $C_{24}H_{19}N$ [M+H$^+$]: 322.1596; Found: 322.1589.



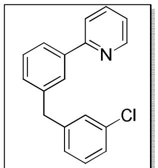
3j

Pale yellow oil; Yield (73%, 37.8 mg); R_f = 0.46 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.6 Hz, 1H), 7.88 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.15 (m, 3H), 7.07 – 6.99 (m, 3H), 4.05 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.68, 149.74, 141.91, 141.06, 139.70, 138.19, 136.84, 129.87, 129.77, 129.00, 128.49, 127.72, 127.00, 126.13, 124.86, 122.19, 120.85, 42.09, 21.54. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1449.



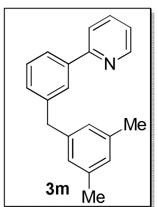
3k

Pale yellow oil; Yield (51%, 32.1 mg); R_f = 0.41 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.3 Hz, 1H), 7.87 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.77-7.67 (m, 2H), 7.46 – 7.36 (m, 1H), 7.26 – 7.19 (m, 3H), 7.01 (d, J = 7.6 Hz, 1H), 6.95 – 6.85 (m, 2H), 4.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.11 (J_{C-F}=244 Hz), 157.49, 149.79, 143.69 (J_{C-F}=4 Hz), 140.96, 139.88, 136.88, 130.00 (J_{C-F}=9 Hz),129.72, 129.14, 127.73, 125.13, 124.71(J_{C-F}=3 Hz), 122.29, 120.83, 115.94 (J_{C-F}=21 Hz), 113.17 (J_{C-F}=21 Hz), 41.80 (J_{C-F}=2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.46. HRMS Calcd for $C_{18}H_{14}FN$ [M+H$^+$]: 264.1189; Found: 264.1177.



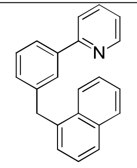
3l

Pale yellow oil; Yield (66%, 36.8 mg); R_f = 0.42 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.6 Hz, 1H), 7.86 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.77-7.68 (m, 2H), 7.41 (t, J = 7.7 Hz, 1H), 7.25 – 7.16 (m, 5H), 7.11 (d, J = 7.3 Hz, 1H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50, 149.79, 144.26, 143.18, 140.89, 139.90, 136.92, 134.41, 129.86, 129.75, 129.18, 127.74, 127.29, 126.50, 125.18, 122.32, 120.87, 41.40. HRMS Calcd for $C_{18}H_{14}ClN$ [M+H$^+$]: 280.0893; Found: 280.0900.



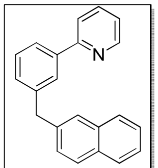
3m

White solid; Yield (85%, 46.4 mg); R_f = 0.52 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.7 Hz, 1H), 7.86 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.19 - 7.25 (m, 2H), 6.85 (s, 3H), 3.99 (s, 2H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.75, 149.77, 142.04, 141.04, 139.70, 138.09, 136.84, 129.80, 129.00, 127.91, 127.73, 126.94, 124.84, 122.19, 120.87, 42.04, 21.42. HRMS Calcd for $C_{20}H_{19}N$ [M+H$^+$]: 274.1596; Found: 274.1600.



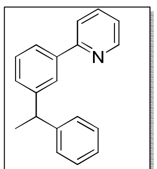
3n

White solid; Yield (63%, 32.6 mg); R_f = 0.51 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.3 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.95 (s, 1H), 7.89 – 7.85 (m, 1H), 7.82 - 7.76 (m, 2H), 7.73 – 7.64 (m, 2H), 7.49 – 7.40 (m, 3H), 7.35 (dd, *J* = 7.3, 3.9 Hz, 2H), 7.21 (t, *J* = 5.8 Hz, 2H), 4.56 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 149.78, 141.22, 139.85, 139.59, 136.86, 132.04, 130.41, 129.64, 129.11, 128.71, 127.64, 125.06, 122.27, 120.79, 41.41. HRMS Calcd for $C_{22}H_{17}N$ [M+H$^+$]: 296.1439; Found: 296.1425.



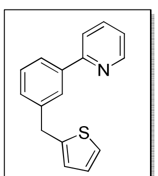
3o

White solid; Yield (59%, 42,7 mg); R_f = 0.49 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.67 (m, 1H), 7.94 (s, 1H), 7.86-7.76 (m, 4H), 7.74 – 7.67 (m, 3H), 7.48 – 7.35 (m, 4H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.23-7.19 (m, 1H), 4.25 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 149.72, 141.63, 139.76, 138.61, 136.82, 133.72, 132.21, 129.85, 129.05, 128.23, 127.79, 127.75, 127.73, 127.69, 127.28, 126.08, 125.47, 124.97, 122.20, 120.82, 42.28. HRMS Calcd for $C_{22}H_{17}N$ [M+H$^+$]: 296.1439; Found: 296.1443.



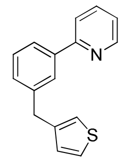
3p

White solid; Yield (79%, 40.9 mg); R_f = 0.53 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.67 (m, 1H), 7.89 (s, 1H), 7.80 – 7.75 (m, 1H), 7.73 -7.66 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.21 – 7.14 (m, 2H), 4.28 – 4.22 (m, 1H), 1.69 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.80, 149.77, 147.04, 146.36, 139.65, 136.81, 128.94, 128.52, 128.43, 127.81, 126.48, 126.19, 124.88, 122.16, 120.86, 45.02, 22.05. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1433.



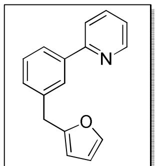
3q

Yellow oil; Yield (49%, 24.5 mg); R_f = 0.39 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.5 Hz, 1H), 7.91 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.24-7.21 (m, 1H), 7.15 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.85 – 6.80 (m, 1H), 4.25 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52, 149.78, 144.02, 141.09, 139.81, 136.90, 129.41, 129.13, 127.40, 126.98, 125.42, 125.29, 124.14, 122.28, 120.86, 36.25. HRMS Calcd for $C_{16}H_{13}NS$ [M+H$^+$]: 252.0847; Found:252.0855.



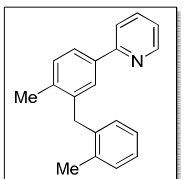
3r

Yellow oil; Yield (33%,16.5 mg); R_f = 0.40 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, 1H), 7.88 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 19.2, 7.4 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.19 (m, 3H), 6.95 (d, *J* = 5.6 Hz, 2H), 4.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.64, 149.80, 141.51, 141.30, 139.79, 136.87, 129.58, 129.06, 128.60, 127.55, 125.80, 124.98, 122.24, 121.50, 120.83, 36.76. HRMS Calcd for $C_{16}H_{13}NS$ [M+H$^+$]: 252.0847; Found:252.0867.



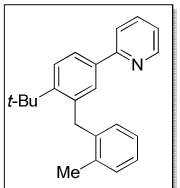
3s

Yellow oil; Yield (45%, 26.7 mg); R_f = 0.41 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 1H), 7.90 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 1.3 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.24-7.21 (m, 1H), 6.30 (dd, *J* = 2.9, 2.0 Hz, 1H), 6.04 (d, *J* = 3.1 Hz, 1H), 4.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52, 154.56, 149.77, 141.66, 139.79, 138.82, 136.85, 129.49, 129.06, 127.51, 125.29, 122.25, 120.80, 110.40, 106.48, 34.68. HRMS Calcd for $C_{16}H_{13}NO$ [M+H$^+$]: 236.1075; Found:236.1077.



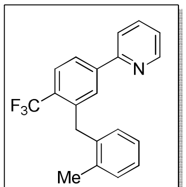
5a

Yellow oil; Yield (76%, 41.5 mg); R_f = 0.48 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.71-7.66 (m, 1H), 7.61 (s, 1H), 7.61 – 7.58 (m, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.20-7.07 (m, 4H), 6.87 (d, *J* = 7.4 Hz, 1H), 4.00 (s, 2H), 2.33 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.66, 149.68, 138.88, 138.43, 138.01, 137.42, 136.76, 136.53, 130.82, 130.13, 128.85, 128.25, 126.30, 126.18, 125.05, 121.88, 120.48, 36.97, 19.84, 19.55. HRMS Calcd for $C_{20}H_{19}N$ [M+H$^+$]: 274.1596; Found:274.1602.



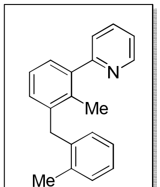
5b

Yellow oil; Yield (43%, 27.0 mg); R_f = 0.46 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.1 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.65 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.58 (d, *J* = 5.5 Hz, 1H), 7.57 (s, 1H), 7.56 (d, *J* = 2.6 Hz, 1H), 7.20 – 7.09 (m, 3H), 7.06 (d, *J* = 6.7 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 4.30 (s, 2H), 2.35 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.35, 149.67, 149.48, 140.38, 138.63, 137.08, 136.72, 136.30, 131.18, 129.90, 129.39, 127.13, 126.08, 126.05, 124.80, 121.92, 120.48, 38.37, 36.03, 31.73, 20.07. HRMS Calcd for $C_{23}H_{25}N$ [M+H$^+$]: 316.2065; Found:316.2070.



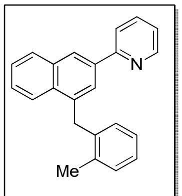
5c

Yellow oil; Yield (57%, 37.3 mg); R_f = 0.44 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.70 (m, 1H), 7.73-7.68 (m, 1H), 7.59 – 7.53 (m, 2H), 7.34 (s, 1H), 7.32 – 7.27 (m, 2H), 7.12 – 7.07 (m, 3H), 6.89 (d, *J* = 6.8 Hz, 1H), 4.10 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.68, 149.53, 144.15, 139.45, 138.25, 136.56, 136.48, 130.80, 130.48, 130.43, 130.33, 130.29, 130.15, 129.64, 126.95 (J_{C-F}=5 Hz), 126.63, 126.19, 124.05, 132.26 (J_{C-F}=6 Hz),, 122.51, 36.67, 19.70. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55. HRMS Calcd for $C_{20}H_{16}F_3N$ [M+H$^+$]: 328.1313; Found:328.1318.



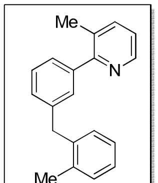
5d

Yellow oil; Yield (54%, 29.4 mg); R_f = 0.45 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.6 Hz, 1H), 7.74-7.70 (m, 1H), 7.31 – 7.26 (m, H), 7.24 – 7.16 (m, 3H), 7.15 – 7.05 (m, 3H), 7.03 – 6.98 (m, 1H), 6.89 (d, *J* = 7.3 Hz, 1H), 3.73 (s, 2H), 2.12 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 149.81, 140.60, 139.08, 138.30, 136.60, 136.21, 136.04, 130.02, 128.11, 128.07, 126.86, 126.18, 125.91, 124.69, 121.81, 37.06, 20.39, 19.68. HRMS Calcd for $C_{20}H_{19}N$ [M+H$^+$]: 274.1596; Found:274.1600.



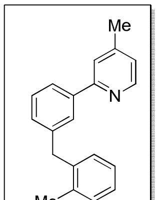
5f

Yellow oil; Yield (47%, 29.9 mg); R_f = 0.36 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.7 Hz, 1H), 8.50 (s, 1H), 8.08 – 7.96 (m, 2H), 7.87 (s, 1H), 7.83 – 7.78 (m, 2H), 7.60 – 7.51 (m, 2H), 7.31 – 7.25 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 4.53 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 149.88, 138.61, 136.92, 136.91, 136.45, 134.17, 132.72, 130.17, 129.73, 129.35, 126.81, 126.42, 126.24, 126.20, 125.73, 125.67, 124.21, 122.24, 120.95, 36.57, 19.94. HRMS Calcd for $C_{23}H_{19}N$ [M+H$^+$]: 310.1596; Found:.310.1588



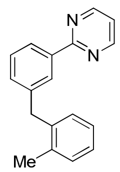
5g

Yellow oil; Yield (51%, 27.8 mg); R_f = 0.40 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.85 (s, 1H), 7.82 (s, 1H), 7.64-7.57 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 5.1, 4.1 Hz, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 4.13 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.02, 150.17, 140.99, 139.68, 139.00, 137.39, 136.78, 131.67, 130.40, 130.08, 129.12, 128.92, 127.40, 126.58, 126.14, 124.57, 120.29, 39.65, 19.91, 18.30. HRMS Calcd for $C_{20}H_{19}N$ [M+H$^+$]: 274.1596; Found: 274.1604.



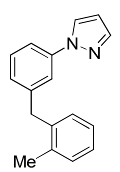
5h

Yellow oil; Yield (56%, 30.6 mg); R_f = 0.41 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.0 Hz, 1H), 7.87 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.55 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.14 (m, 5H), 7.10 (d, *J* = 4.9 Hz, 1H), 4.13 (s, 2H), 2.46 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.59, 149.51, 147.86, 140.99, 139.79, 139.02, 136.79, 130.41, 130.07, 129.36, 128.93, 127.70, 126.59, 126.15, 124.84, 123.24, 121.82, 39.66, 21.37, 19.92. HRMS Calcd for $C_{20}H_{19}N$ [M+H$^+$]: 274.1596; Found:274.1605.



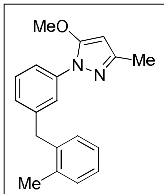
5i

Yellow oil; Yield (74%, 38.8 mg); R_f = 0.43 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.30 (s, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.22 – 7.12 (m, 6H), 4.09 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.00, 157.37, 141.01, 138.98, 137.84, 136.78, 131.31, 130.44, 130.09, 128.91, 128.84, 126.62, 126.18, 126.08, 119.19, 39.65, 19.93. HRMS Calcd for $C_{18}H_{16}N_2$ [M+H$^+$]: 261.1392; Found:261.1393.



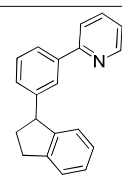
5j

Yellow oil; Yield (55%, 27.3 mg); R_f = 0.39 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.71 (s, 1H), 7.51 (s, 2H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.14 – 7.17 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.44 (s, 1H), 4.05 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.29, 141.14, 140.47, 138.41, 136.77, 130.55, 130.11, 129.56, 127.00, 126.97, 126.84, 126.26, 119.84, 117.08, 107.63, 39.56, 19.88. HRMS Calcd for $C_{17}H_{16}N$ [M+H$^+$]: 249.1392; Found:249.1387.



5k

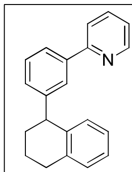
Yellow oil; Yield (53%, 30.9 mg); R_f = 0.42 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.48 (s, 1H), 7.26 - 7.30 (m, 1H), 7.18 – 7.10 (m, 4H), 6.95 (d, *J* = 7.5 Hz, 1H), 5.48 (s, 1H), 4.02 (s, 2H), 3.87 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.92, 148.78, 141.39, 138.86, 138.74, 136.82, 130.39, 130.13, 128.89, 126.63, 126.40, 126.13, 122.55, 119.70, 85.89, 58.84, 39.51, 19.85, 14.72. HRMS Calcd for $C_{19}H_{20}N_2O$ [M+H$^+$]: 293.1654; Found:293.1685.



3u

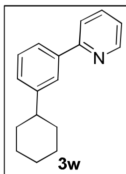
Pale yellow oil; Yield (59%, 31.9 mg); R_f = 0.52 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.73 – 8.67 (m, 1H), 7.91 (s, 1H), 7.89 – 7.82 (m, 1H), 7.76 – 7.69 (m, 2H), 7.43 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.24-7.19 (m, 3H), 7.15 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 4.47 (t, J = 8.4 Hz, 1H), 3.14 – 2.96 (m, 2H), 2.68 – 2.60 (m, 1H), 2.20 – 2.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.00, 148.55, 146.73, 146.41, 144.52, 138.17, 129.49, 129.28, 127.23, 126.75, 126.55, 125.41, 125.05, 124.53, 122.49, 121.50, 51.87, 36.73, 32.01. HRMS Calcd for $C_{20}H_{17}N$ [M+H$^+$]: 272.1439; Found: 272.1436.



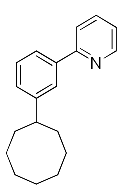
3v

Pale yellow oil; Yield (70%, 39.9 mg); R_f = 0.51 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.6 Hz, 1H), 7.83 (s, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.75-7.68 (m, 2H), 7.38 (t, J = 7.7 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.17 – 7.08 (m, 3H), 7.06 – 7.00 (m, 1H), 6.89 (d, J = 7.7 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.04 – 2.81 (m, 2H), 2.28 – 2.14 (m, 1H), 2.02 – 1.88 (m, 2H), 1.83-1.76 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.81, 149.78, 148.20, 139.58, 139.44, 137.74, 136.82, 130.33, 129.68, 129.13, 128.83, 127.60, 126.08, 125.84, 124.83, 122.16, 120.88, 45.99, 33.49, 29.97, 21.36. HRMS Calcd for $C_{21}H_{19}N$ [M+H$^+$]: 276.1388; Found: 286.1593.



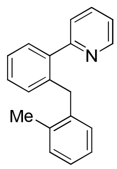
3w

yellow oil; Yield (53%, 41.9 mg); R_f = 0.49 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.69 (m, 1H), 7.87 (s, 1H), 7.78 – 7.75 (m, 1H), 7.74 – 7.72 (m, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.26 - 7.28 (m, 2H), 7.23-7.20 (m, 1H), 2.64-2.67 (m, 1H), 1.98 – 1.83 (m, 4H), 1.79 – 1.74 (m, 1H), 1.55 – 1.38 (m, 4H), 1.33-1.26 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 149.77, 148.79, 139.51, 136.79, 128.81, 127.64, 125.76, 124.57, 122.09, 120.82, 44.90, 34.60, 27.07, 26.30. HRMS Calcd for $C_{17}H_{19}N$ [M+H$^+$]: 238.1596; Found: 238.1595.



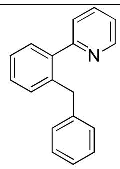
3x

yellow oil; Yield (61%, 28.9 mg); R_f = 0.46 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70-8.69 (m, 1H), 7.85 (s, 1H), 7.76 – 7.71 (m, 3H), 7.38 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 2.2 Hz, 1H), 7.23 – 7.19 (m, 1H), 2.93 – 2.83 (m, 1H), 1.94 – 1.75 (m, 7H), 1.59 - 1.68 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 151.23, 149.74, 139.47, 136.77, 128.82, 127.70, 125.86, 124.24, 122.06, 120.81, 44.92, 34.95, 27.00, 26.56, 26.22. HRMS Calcd for $C_{19}H_{23}N$ [M+H$^+$]: 266.1909; Found: 266.1915.



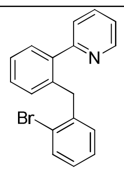
4a

Yellow oil; Yield (80%, 41.4 mg); R_f = 0.45 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, 1H), 7.70-7.66 (m, 1H), 7.44 – 7.40 (m, 1H), 7.34 – 7.28 (m, 3H), 7.25 – 7.20 (m, 1H), 7.10 – 7.02 (m, 5H), 6.98 – 6.92 (m, 1H), 4.06 (s, 2H), 2.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.05, 149.30, 140.79, 139.40, 138.22, 136.64, 136.31, 130.13, 130.09, 129.91, 129.88, 128.58, 126.33, 126.25, 125.98, 124.18, 121.88, 36.74, 19.73. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found:260.1429.



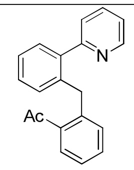
4b

Yellow oil; Yield (80%, 38.7 mg); R_f = 0.49 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.69 (m, 1H), 7.68-7.64 (m, 1H), 7.41-7.36 (m, 1H), 7.35-7.31 (m, 2H), 7.28 – 7.22 (m, 3H), 7.16 – 7.18 (m, 2H), 7.12 (dd, *J* = 6.1, 3.8 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.05, 149.20, 141.41, 140.76, 138.93, 136.28, 130.76, 129.98, 128.98, 128.55, 128.29, 126.45, 125.83, 124.33, 121.85, 38.91. HRMS Calcd for $C_{18}H_{15}N$ [M+H$^+$]: 246.1283; Found:246.1293.



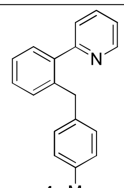
4c

Yellow oil; Yield (87%, 56.2 mg); R_f = 0.38 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.1 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.54 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.49 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.29 – 7.25 (m, 1H), 7.22 – 7.15 (m, 2H), 7.06 (dd, *J* = 16.4, 7.8 Hz, 2H), 4.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 149.79, 140.40, 140.15, 139.78, 136.84, 132.98, 131.25, 129.78, 129.06, 128.07, 127.85, 127.65, 125.10, 125.03, 122.23, 120.81, 41.92. HRMS Calcd for $C_{18}H_{14}BrN$ [M+H$^+$]: 324.0386; Found: 324.0384.



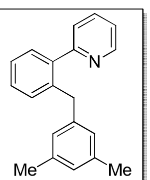
4d

Yellow oil; Yield (56%, 32.1 mg); R_f = 0.33 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 7.68-7.63 (m, 2H), 7.55 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.27 (m, 6H), 7.24 – 7.17 (m, 4H), 7.06-7.00 (m, 3H), 4.37 (s, 2H), 2.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.43, 157.61, 149.69, 141.46, 140.53, 139.55, 138.39, 136.77, 131.87, 131.54, 129.93, 129.09, 128.86, 127.88, 126.31, 124.79, 122.11, 120.76, 39.34, 29.89. HRMS Calcd for $C_{20}H_{17}NO$ [M+H$^+$]: 288.1388; Found: 288.1395.



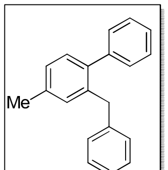
4e

Yellow oil; Yield (71%, 36.7 mg); R_f = 0.48 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 4.2 Hz, 1H), 7.74-7.70 (m, 1H), 7.46 – 7.41 (m, 1H), 7.39 – 7.32 (m, 3H), 7.28 (dd, J = 7.3, 5.1 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.9 Hz, 2H), 4.13 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.11, 149.27, 140.74, 139.18, 138.37, 136.29, 135.32, 130.70, 129.98, 129.05, 128.89, 128.57, 126.38, 124.39, 121.86, 38.44, 21.11. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1436.



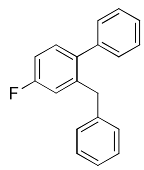
4f

Yellow oil; Yield (74%, 40.4 mg); R_f = 0.50 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 7.69-7.65 (m, 1H), 7.39 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.33 – 7.22 (m, 5H), 6.76 (s, 1H), 6.58 (s, 2H), 4.04 (s, 2H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.13, 149.26, 141.22, 140.74, 139.15, 137.72, 136.20, 130.69, 129.91, 128.53, 127.53, 126.90, 126.33, 124.44, 121.81, 38.74, 21.36. HRMS Calcd for $C_{20}H_{19}N$ [M+H$^+$]: 274.1596; Found: 274.1602.



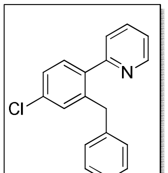
4g

Yellow oil; Yield (58%, 30.0 mg); R_f = 0.45 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.65 (m, 1H), 7.66-7.62 (m, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.21-7.17 (m, 3H), 7.12 (t, *J* = 6.2 Hz, 2H), 7.07 (s, 1H), 7.00 (d, *J* = 6.9 Hz, 2H), 4.12 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.12, 149.16, 141.59, 138.67, 138.27, 138.01, 136.20, 131.48, 129.97, 128.95, 128.26, 127.22, 125.76, 124.34, 121.63, 38.82, 21.35. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1430.



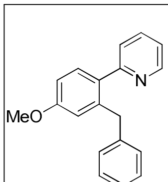
4h

Yellow oil; Yield (78%,41.0 mg); R_f = 0.42 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.1 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.25 – 7.13 (m, 5H), 6.99 (t, *J* = 6.6 Hz, 3H), 6.91 (d, *J* = 9.8 Hz, 1H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.91 (J_{C-F}= 246 Hz), 159.20, 149.37, 141.79 (J_{C-F}= 8 Hz), 140.58, 136.89, 136.31 (J_{C-F}= 33 Hz), 131.75 (J_{C-F}= 8 Hz), 129.10, 128.55, 126.24, 124.47, 122.09, 117.34 (J_{C-F}= 11 Hz), 113.43 (J_{C-F}= 21 Hz), 39.02. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.71. HRMS Calcd for $C_{18}H_{14}FN$ [M+H$^+$]: 264.1189; Found: 264.1178.



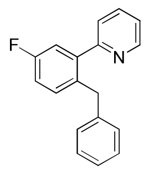
4i

Yellow oil; Yield (64%, 35.7 mg); R_f = 0.40 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.1 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.31 – 7.26 (m, 1H), 7.21 – 7.24 (m, 3H), 7.14 – 7.20 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 4.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99, 149.39, 141.06, 140.50, 139.21, 136.47, 134.39, 131.36, 130.61, 128.99, 128.92, 128.48, 126.65, 126.17, 124.31, 122.16, 38.79. HRMS Calcd for $C_{18}H_{14}ClN$ [M+H$^+$]: 280.0893; Found: 280.0890.



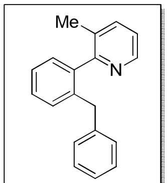
4j

Yellow oil; Yield (80%, 44.0 mg); R_f = 0.41 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.63 (m, 1H), 7.66-7.61 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.2 – 7.11 (m, 4H), 7.01 (t, *J* = 6.9 Hz, 2H), 6.85 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 4.13 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.84, 159.73, 149.19, 141.23, 140.54, 136.25, 133.63, 131.34, 128.98, 128.34, 125.90, 124.37, 121.53, 116.44, 111.63, 55.38, 39.13. HRMS Calcd for $C_{19}H_{17}NO$ [M+H$^+$]: 276.1388; Found: 276.1390.



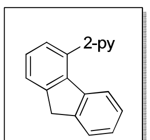
4k

Yellow oil; Yield (65%, 34.1 mg); R_f = 0.39 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 4.2 Hz, 1H), 7.72-7.68 (m, 1H), 7.39-7.34 m, 1H), 7.33 – 7.29 (m, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.24 – 7.14 (m, 4H), 7.01 (d, J = 7.3 Hz, 2H), 4.25 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89, 160.45, 158.76 (J_{C-F} =3 Hz), 149.33, 142.99 (J_{C-F} =4 Hz), 140.49, 136.40, 128.30 (J_{C-F} =1 Hz), 128.26, 127.83 (J_{C-F}=9 Hz), 126.37 (J_{C-F} =16 Hz), 125.86, 125.77 (J_{C-F} =2 Hz), 124.34, 122.27, 115.62, 115.39, 31.26 (J_{C-F} =4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.38. HRMS Calcd for $C_{18}H_{14}FN$ [M+H$^+$]: 264.1189; Found: 264.1186.



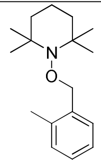
4l

Yellow oil; Yield (81%, 41.9 mg); R_f = 0.37 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 1.4 Hz, 1H), 7.48 (dd, J = 8.2, 1.9 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.32 – 7.29 (m, 2H), 7.23 (d, J = 2.6 Hz, 1H), 7.18 (d, J = 7.7 Hz, 3H), 7.13 (t, J = 4.9 Hz, 1H), 7.00 (d, J = 7.3 Hz, 2H), 4.13 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.18, 149.62, 141.52, 140.71, 138.91, 136.84, 131.26, 130.69, 130.00, 129.01, 128.36, 128.29, 126.40, 125.82, 123.78, 38.87, 18.31. HRMS Calcd for $C_{19}H_{17}N$ [M+H$^+$]: 260.1439; Found: 260.1448.



6

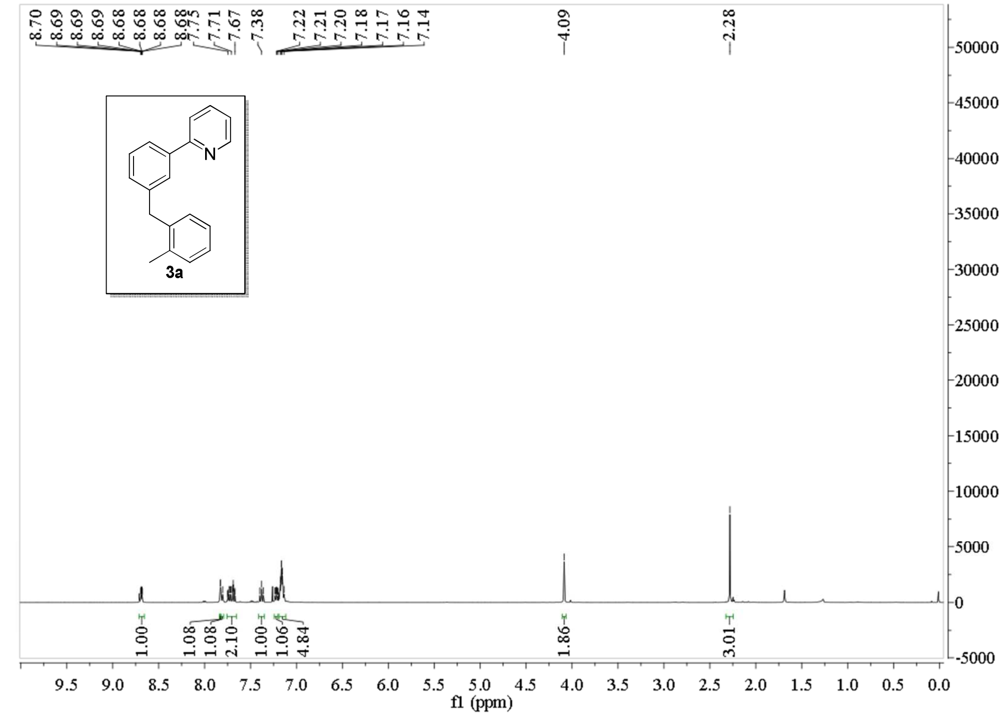
yellow oil; Yield (56%, 27.2 mg); R_f = 0.30 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 4.2 Hz, 1H), 7.86-7.81 (m, 1H), 7.57 – 7.73 (m, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.23 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 3.94 (d, J = 18.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72, 149.76, 144.40, 143.98, 141.18, 138.91, 136.64, 136.58, 128.57, 126.72, 126.50, 126.36, 125.01, 124.93, 124.39, 123.04, 122.58, 37.16. HRMS Calcd for $C_{18}H_{13}N$ [M+H$^+$]: 244.1126; Found: 244.1115.

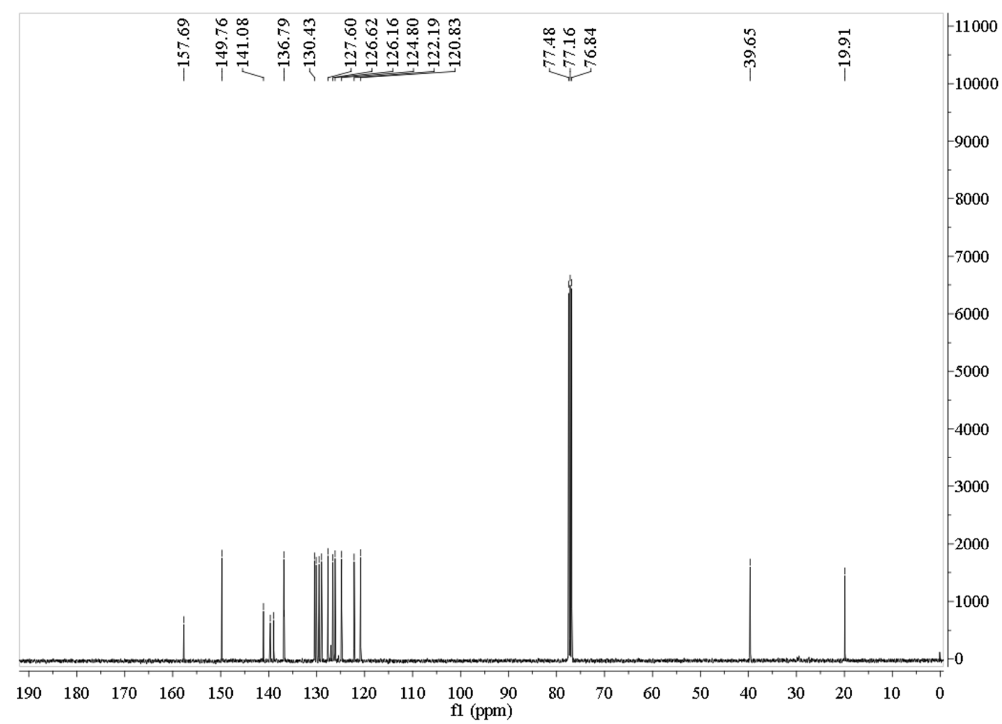


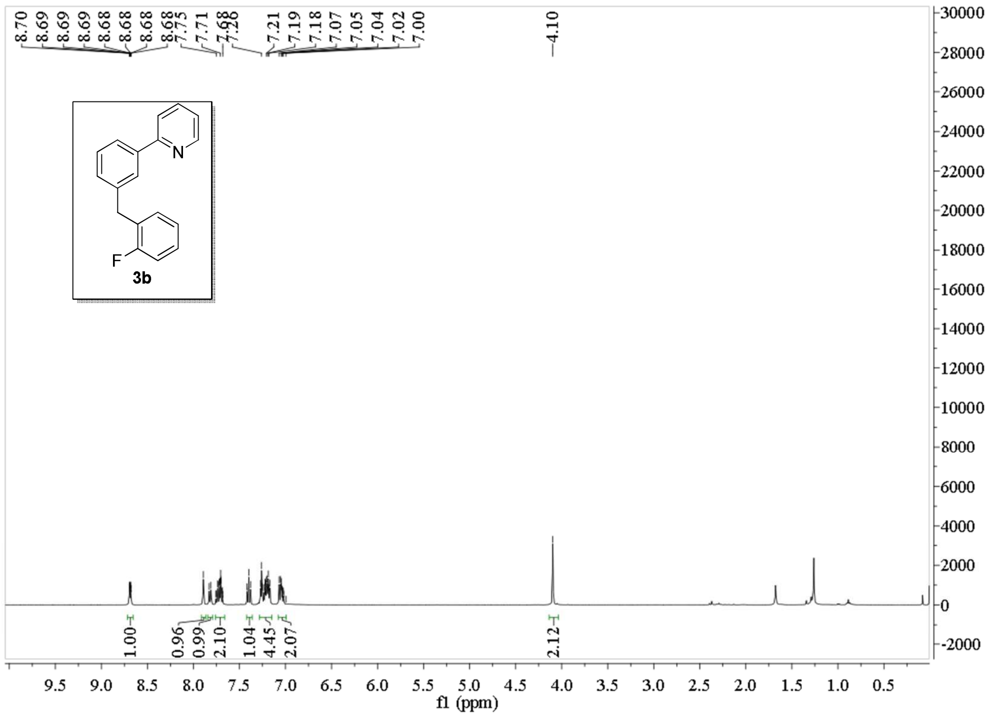
9

White solid; Yield (31%, 129.4 mg); R_f = 0.65 (petroleum ester/ethyl acetate, 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 4.6 Hz, 1H), 7.18 (dd, *J* = 14.4, 10.3 Hz, 3H), 4.82 (s, 2H), 2.31 (s, 3H), 1.63 – 1.44 (m, 4H), 1.35 (d, *J* = 10.9 Hz, 1H), 1.25 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.86, 135.85, 129.99, 127.89, 127.26, 125.83, 76.96, 60.08, 39.89, 33.21, 20.46, 19.37, 17.27. HRMS data for the desired product were in agreement with the previously reported literature data[3].

10. ^{1}HCMR and ^{13}C NMR spectra



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7.04
7.02
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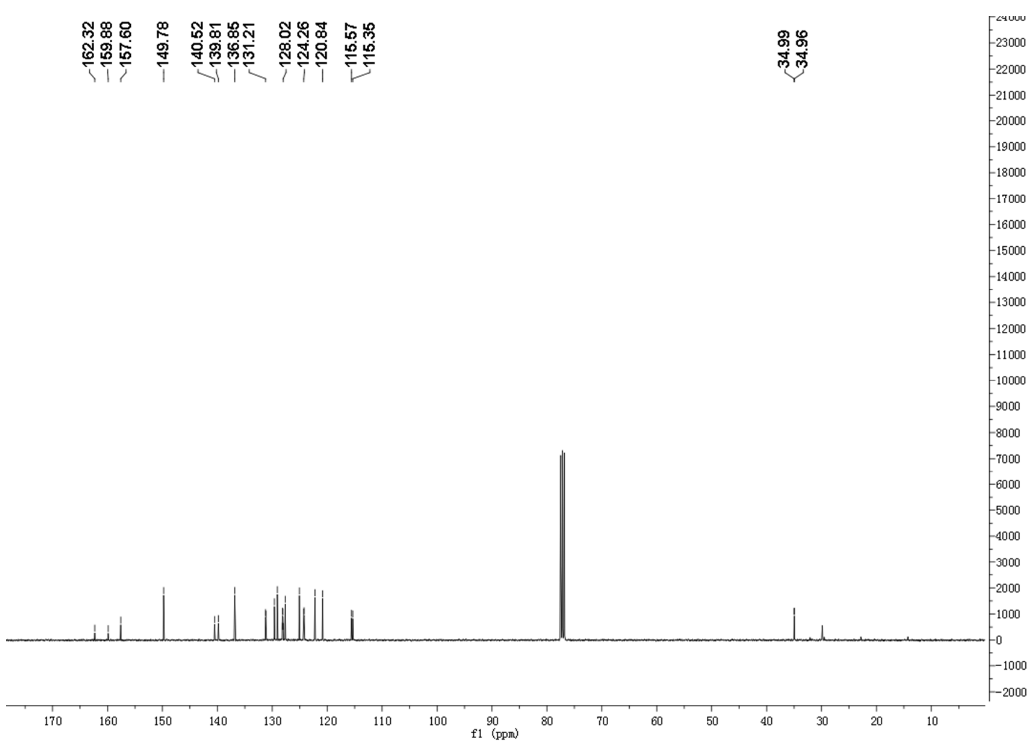
f1 (ppm)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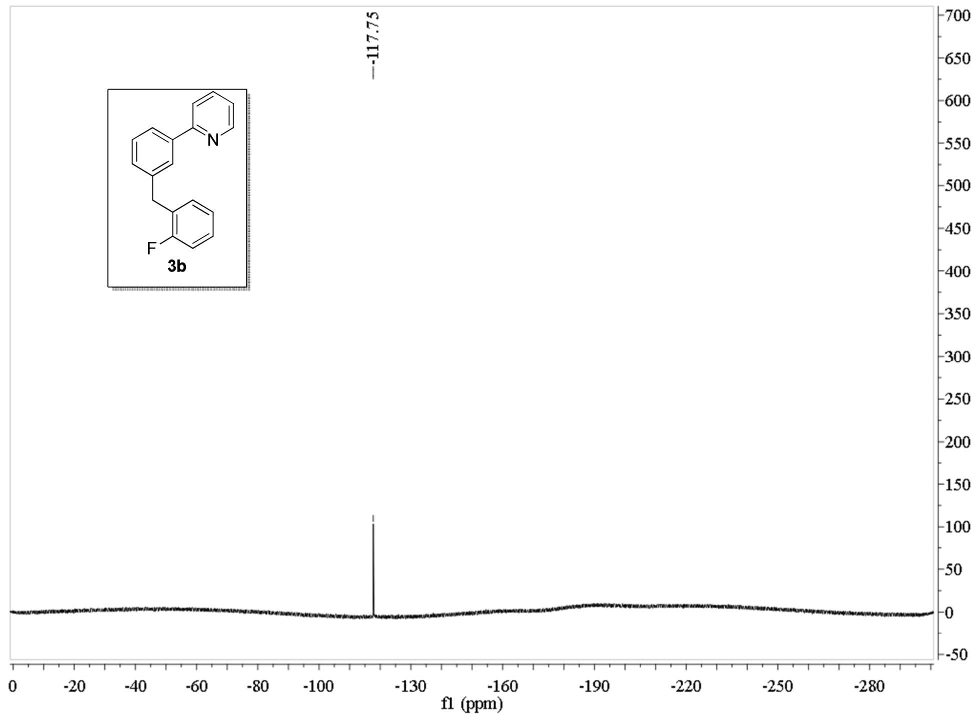
f1 (ppm)



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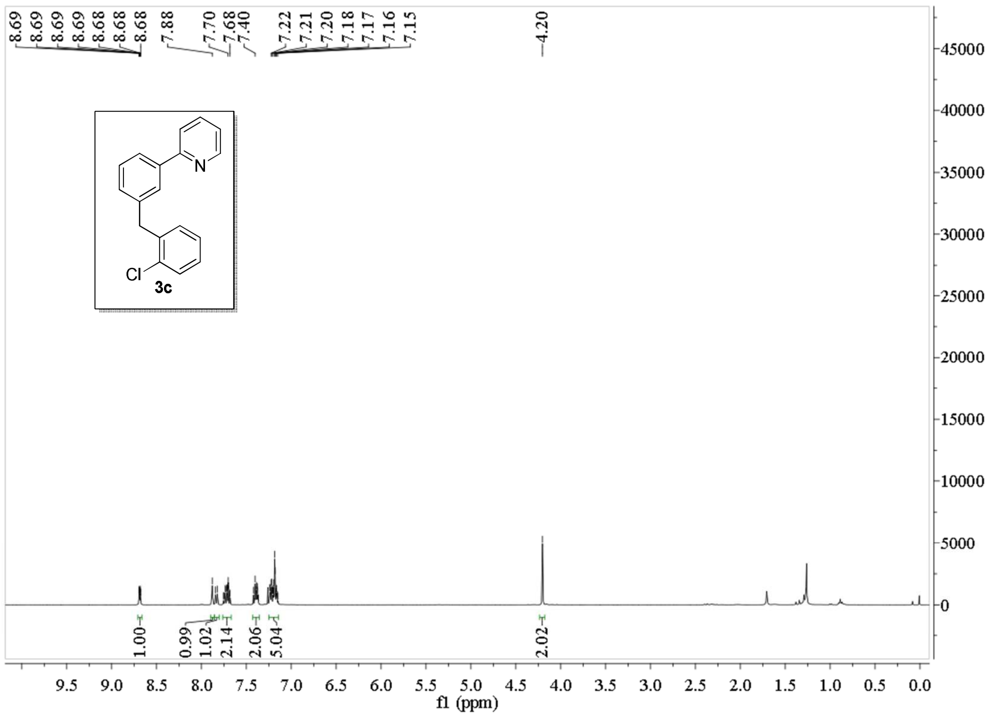
f1 (ppm)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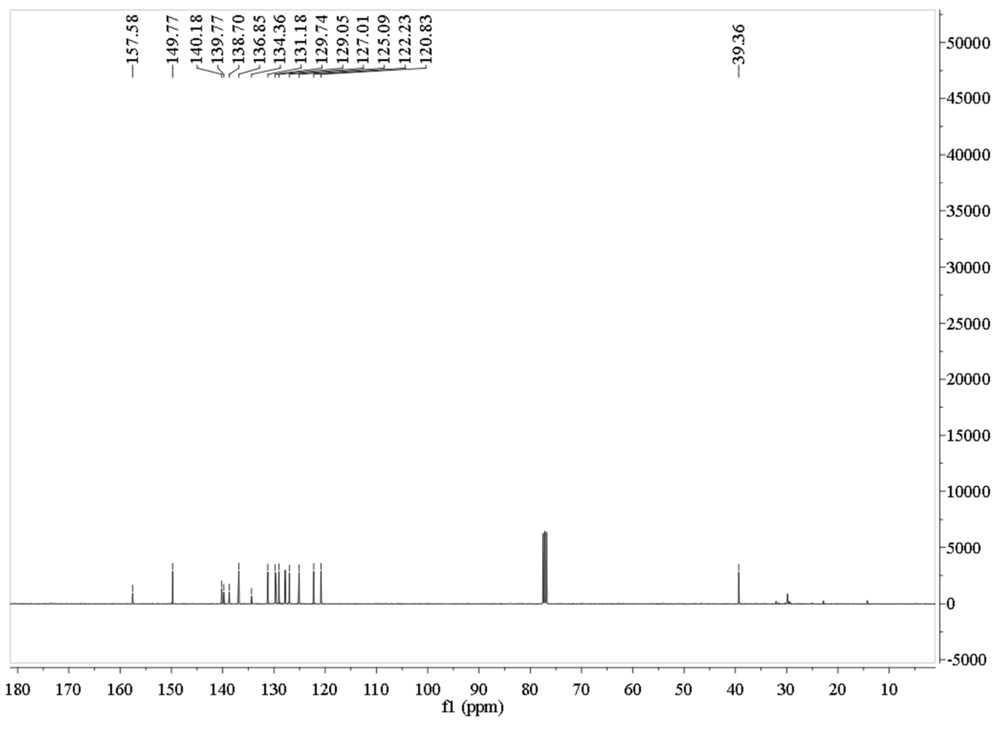
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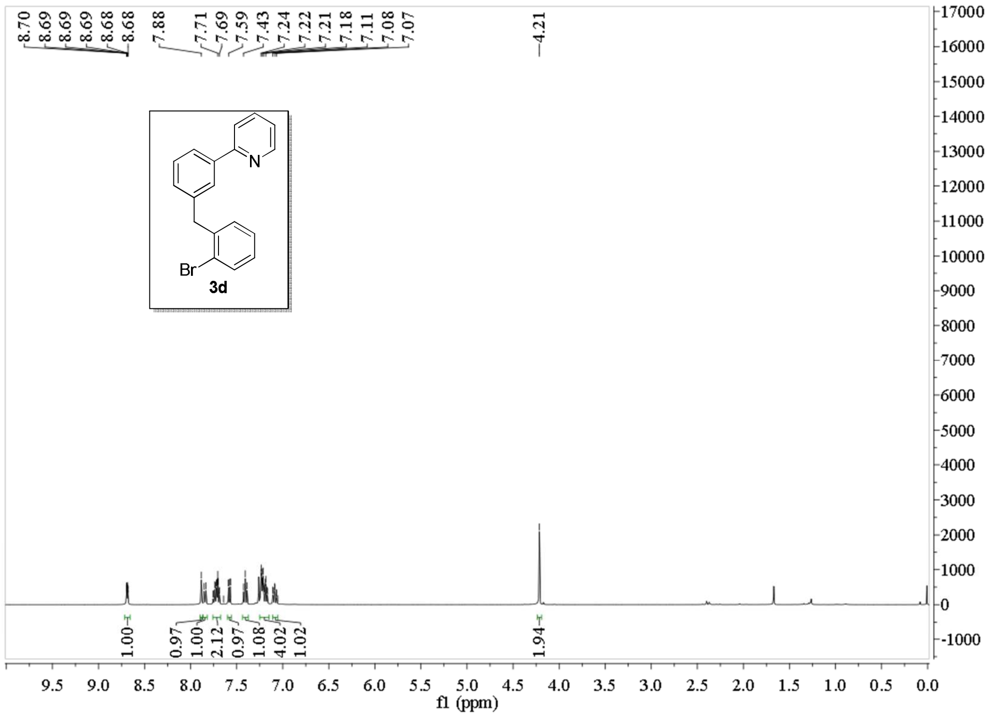
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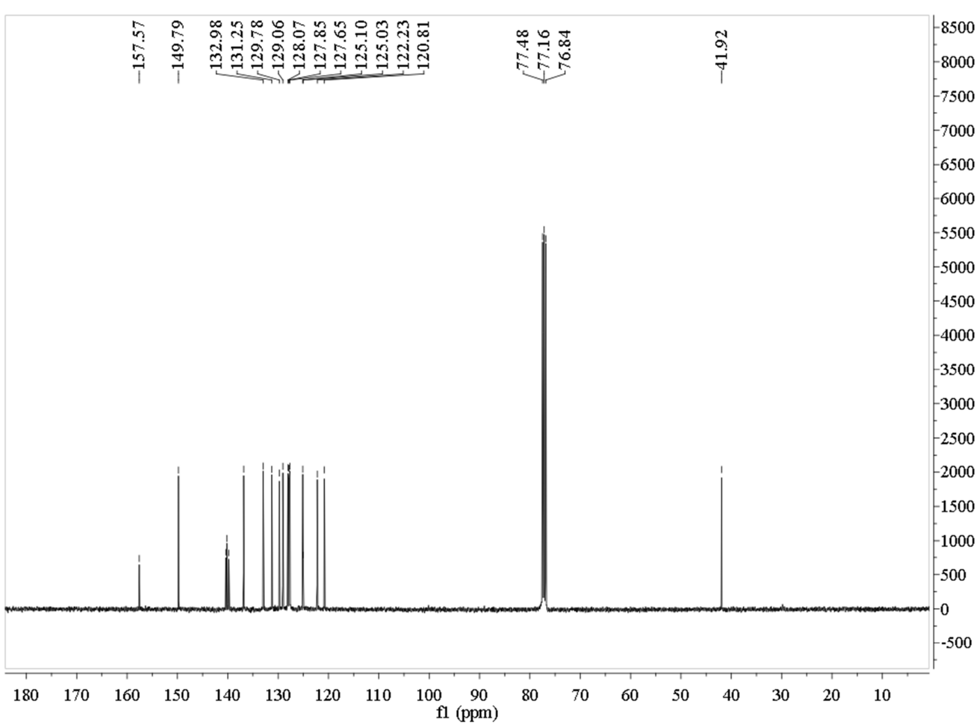
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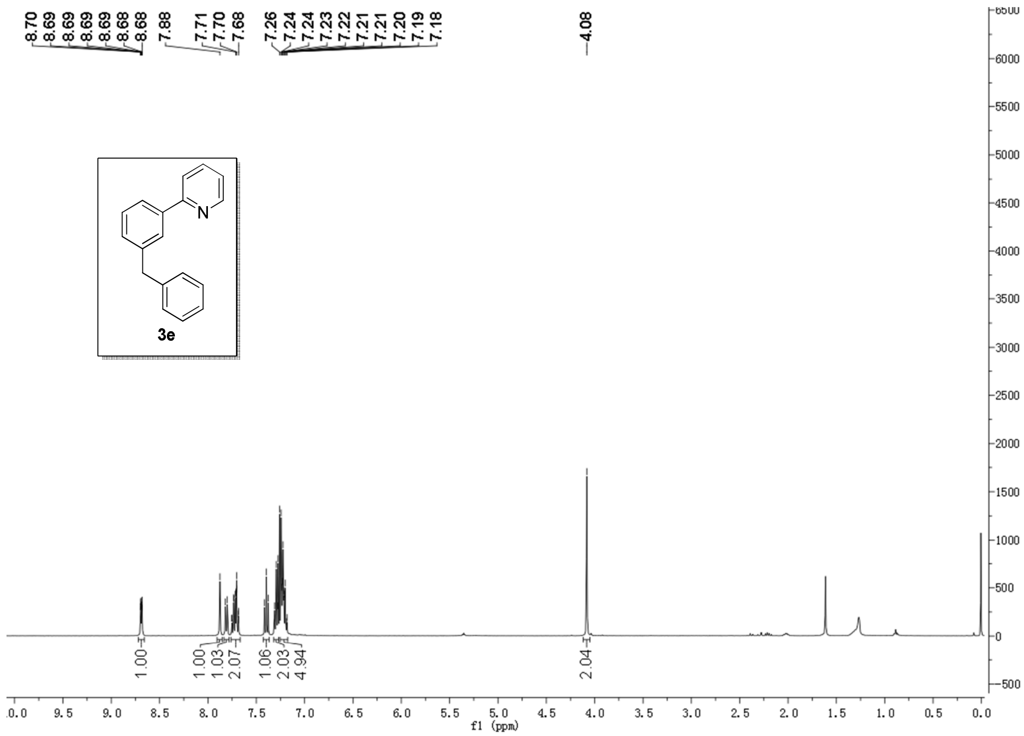
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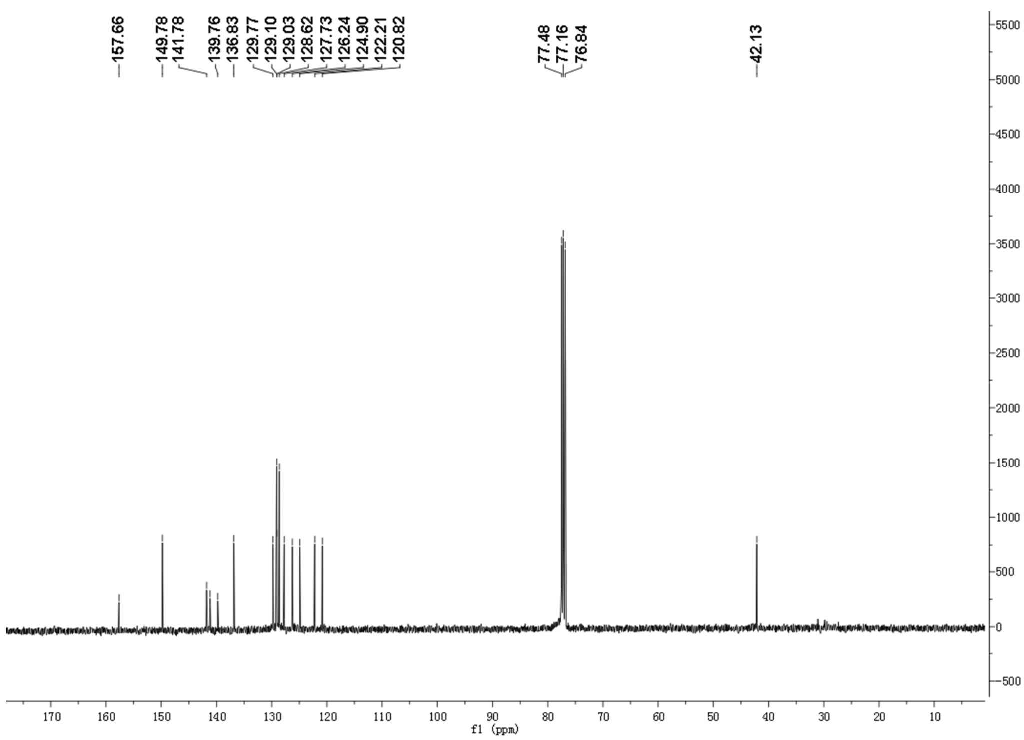
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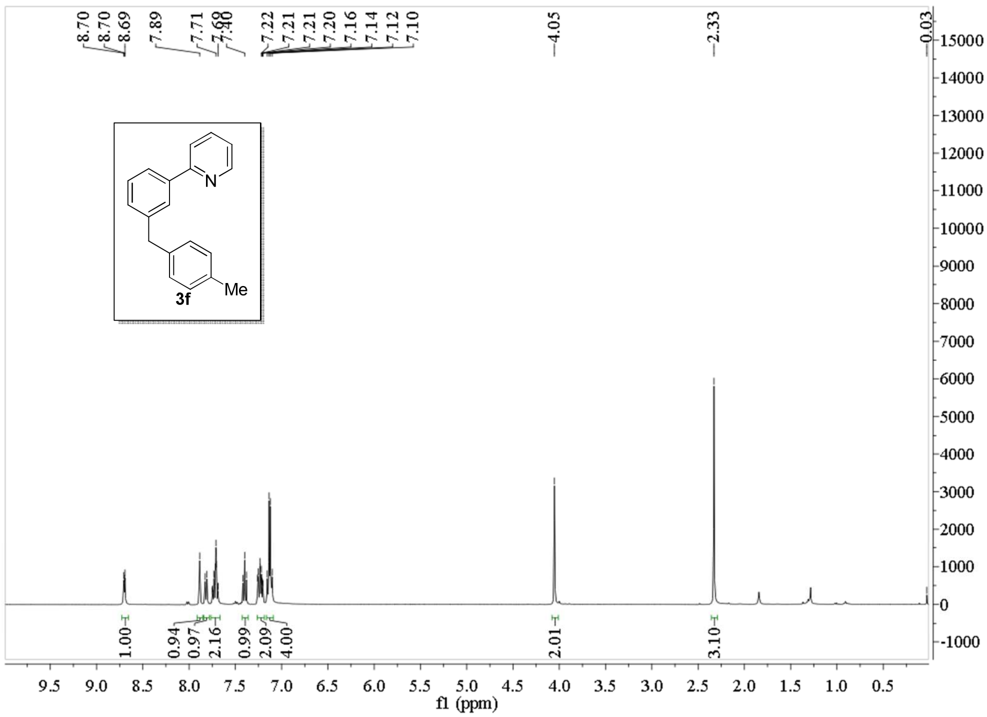

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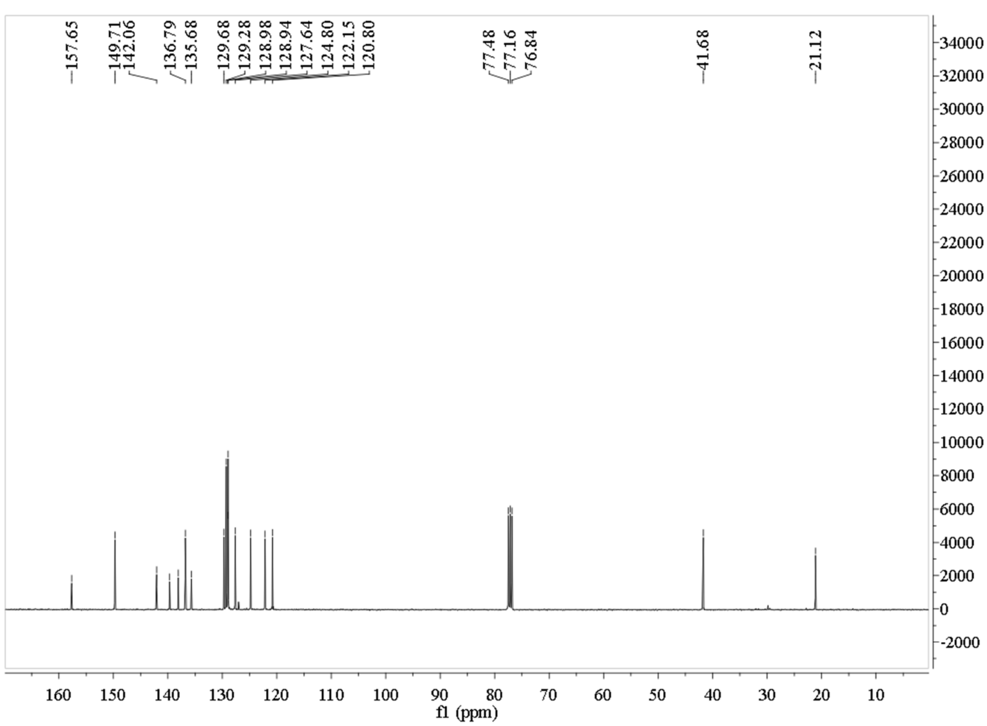

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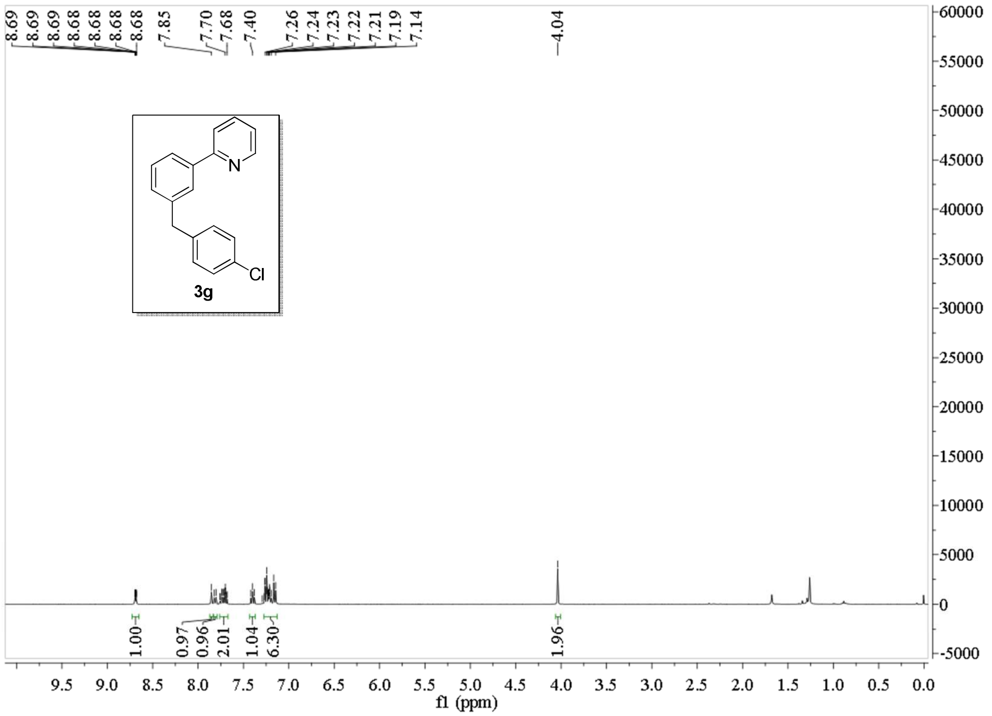
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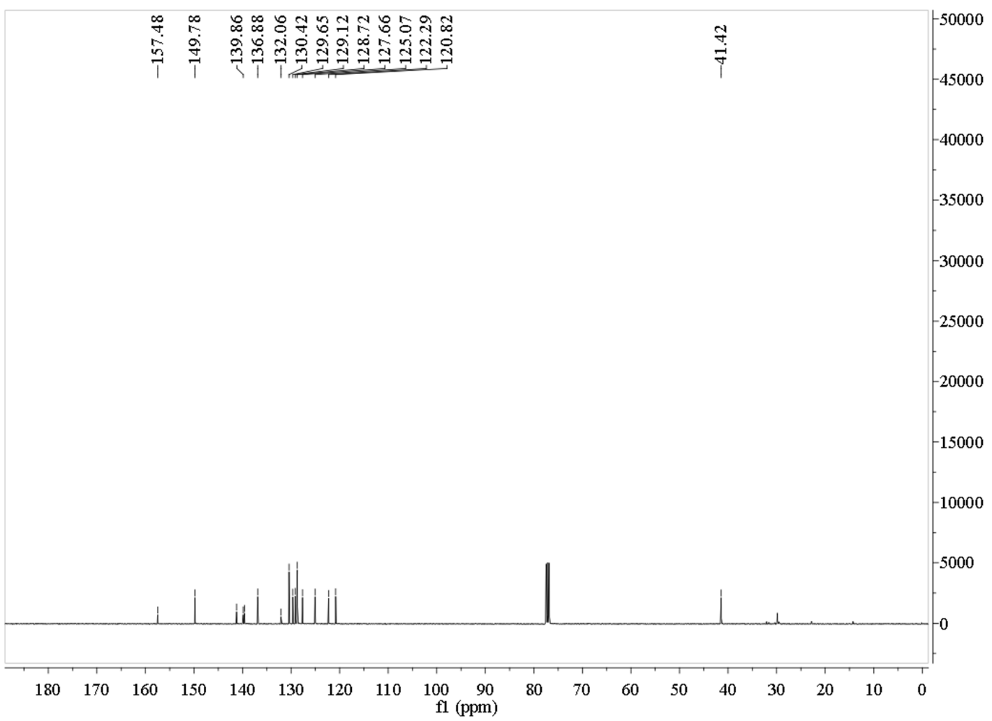
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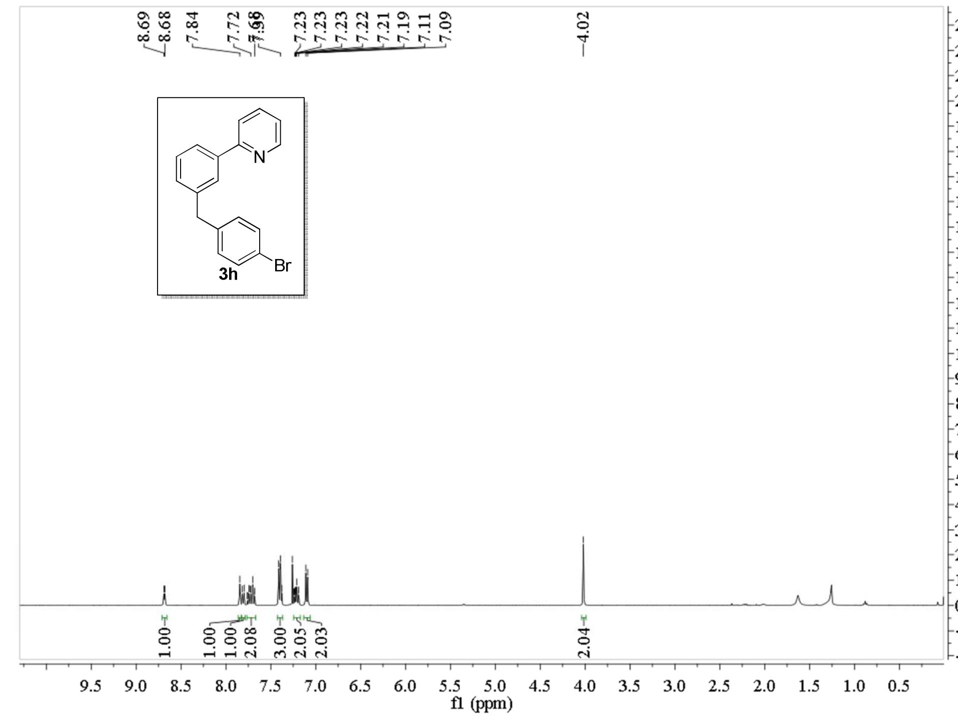
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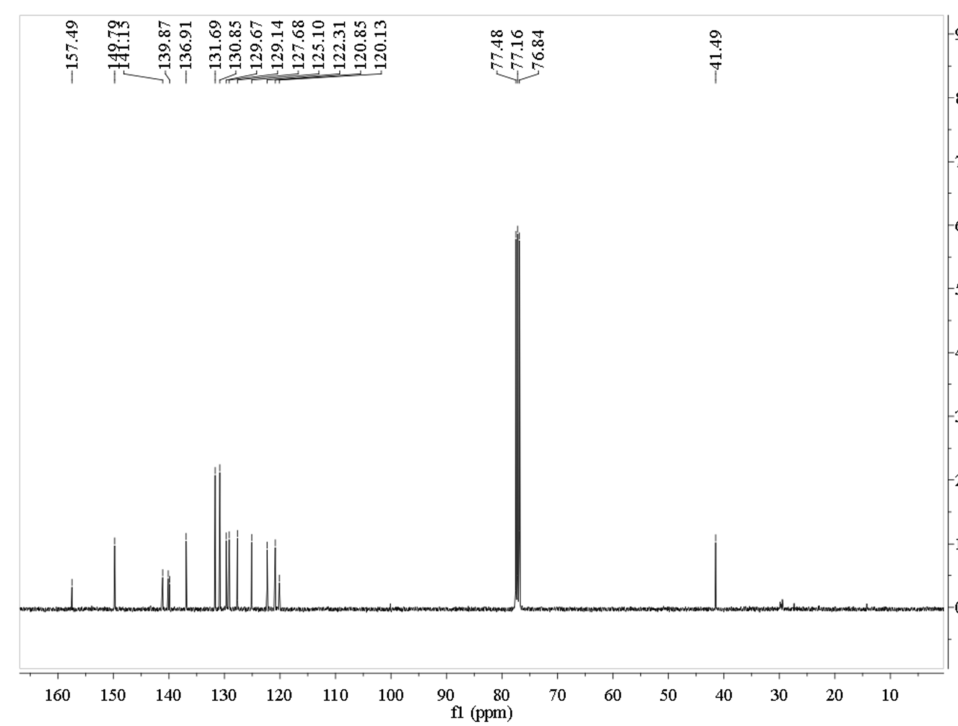
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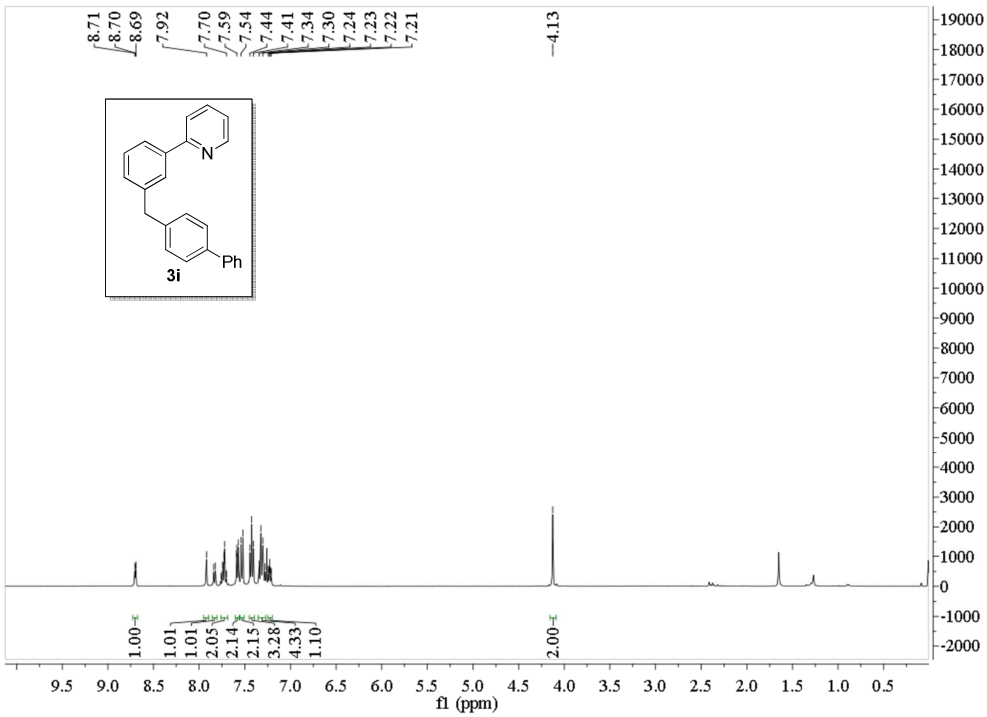

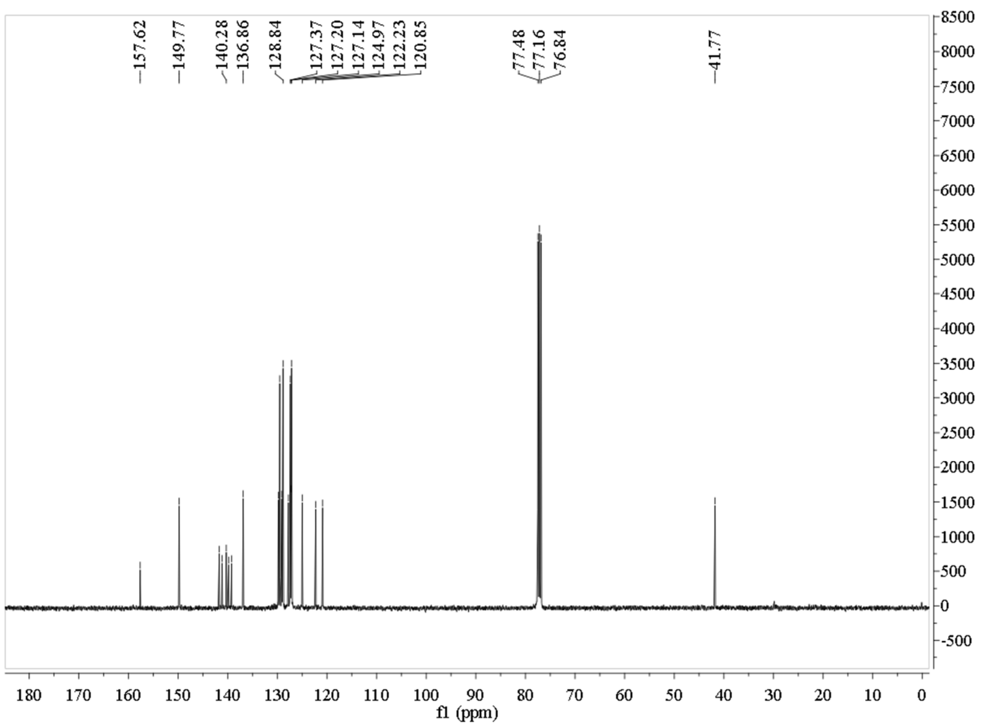

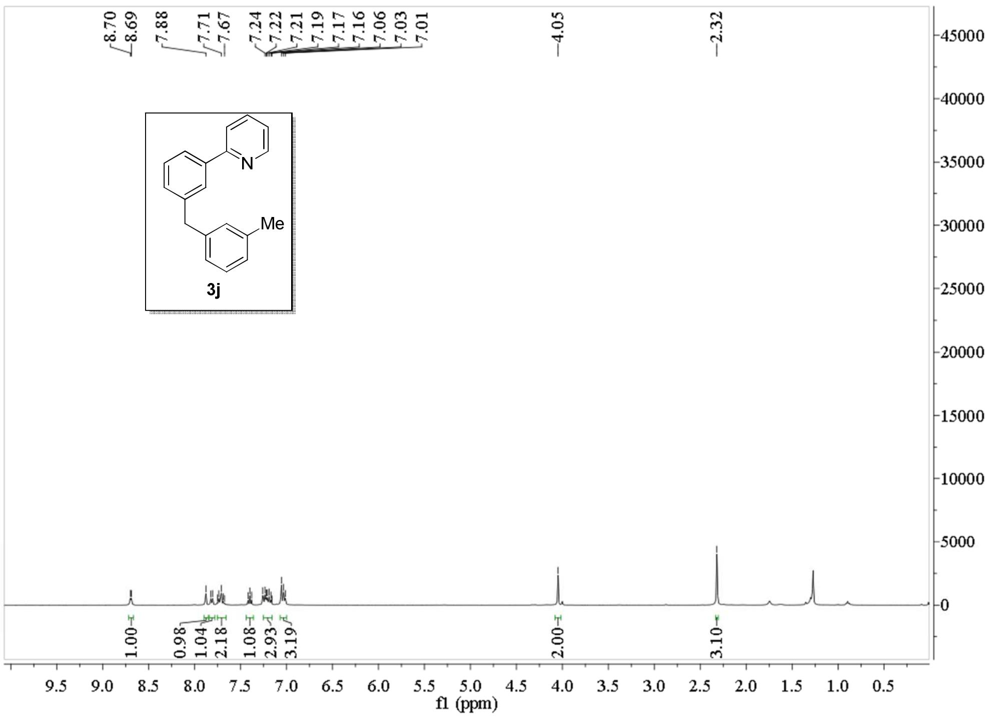
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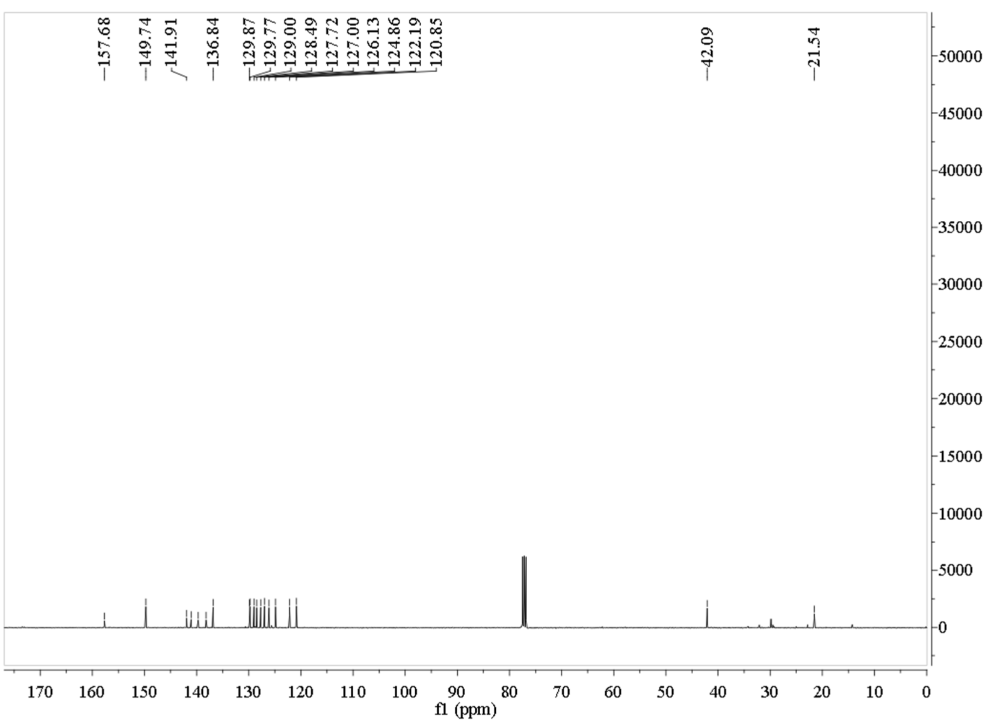
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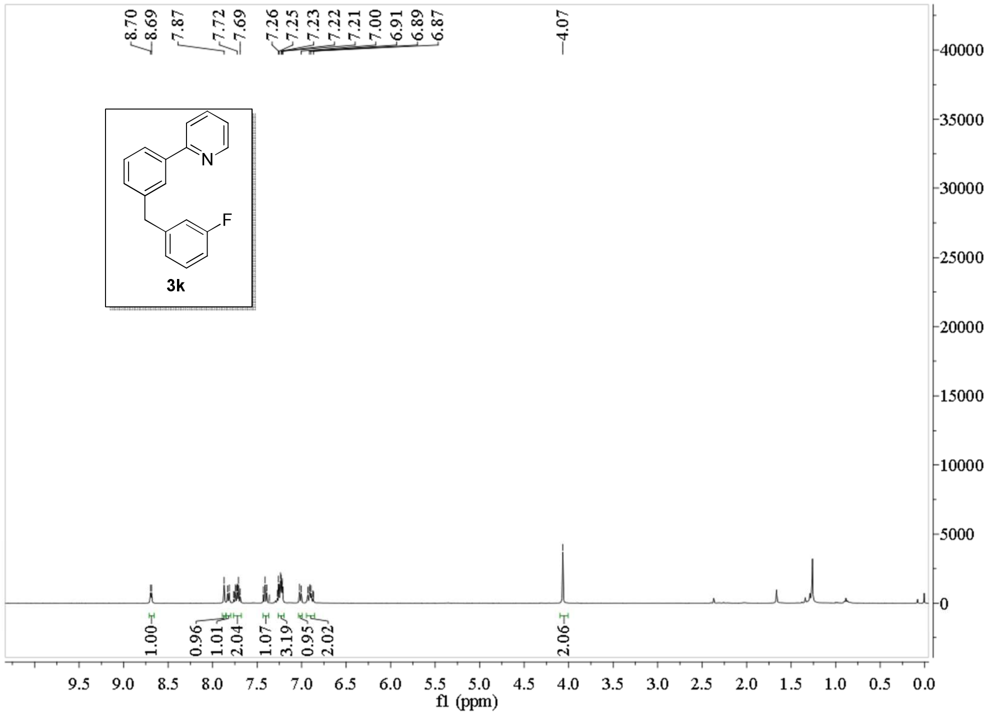
21.54
f1 (ppm)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6.89
6.87
4.07
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1.07
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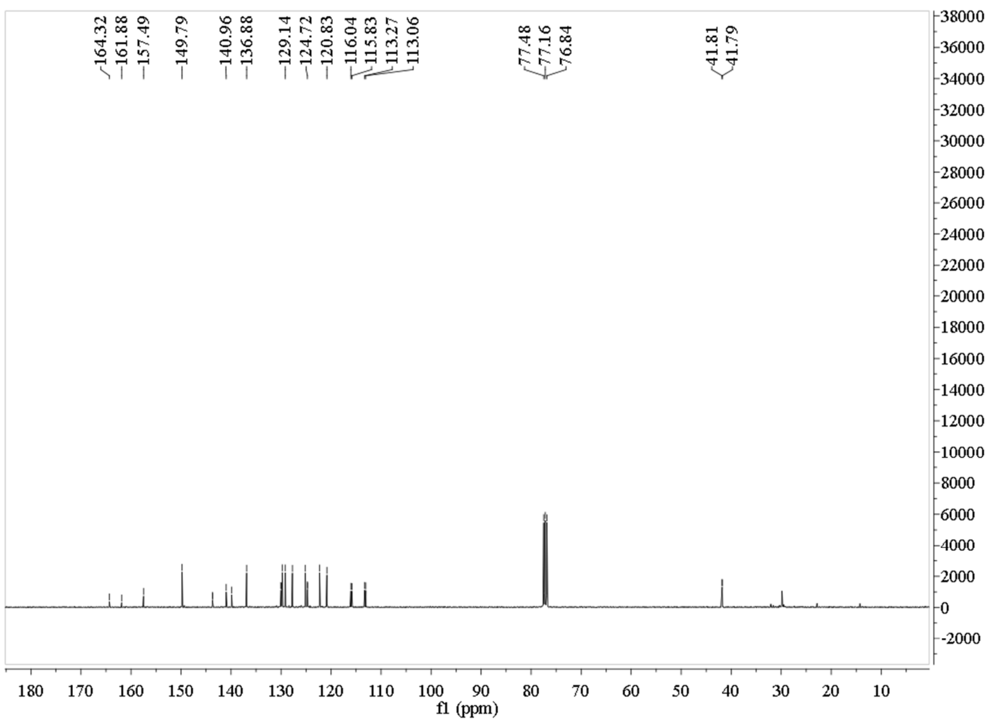
2.02
2.06
f1 (ppm)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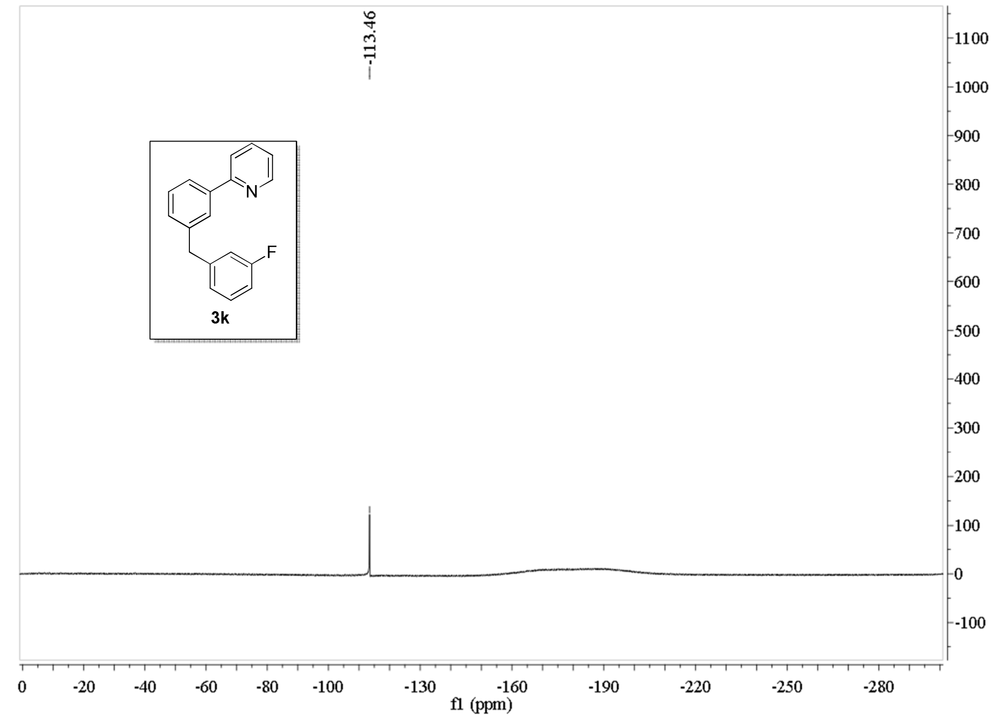
f1 (ppm)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-220
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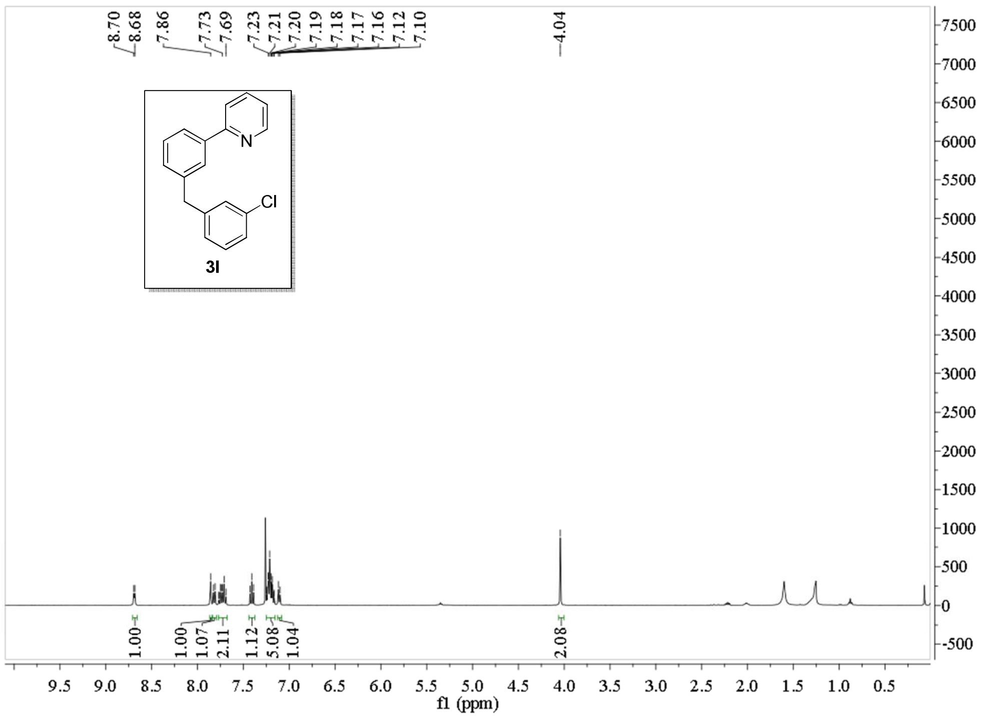
-280
f1 (ppm)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7.12
7.10
4.04
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1.00
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1.04
2.08
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7000
6500
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4500
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3500
3000
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1000
500
0
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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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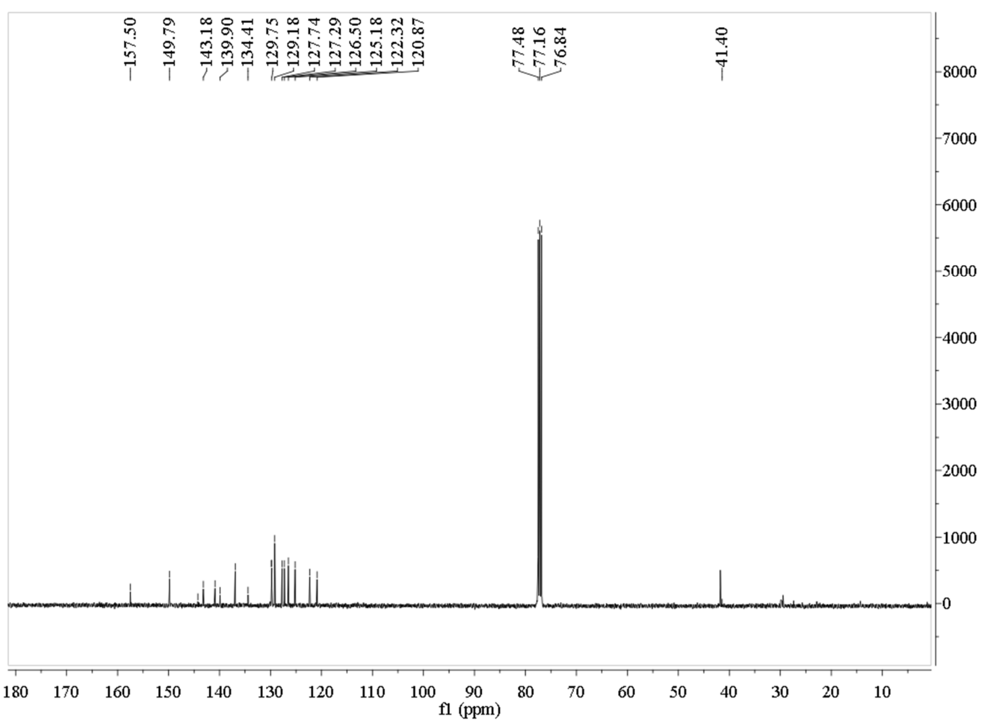
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77.48
77.16
76.84
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5000
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3000
2000
1000
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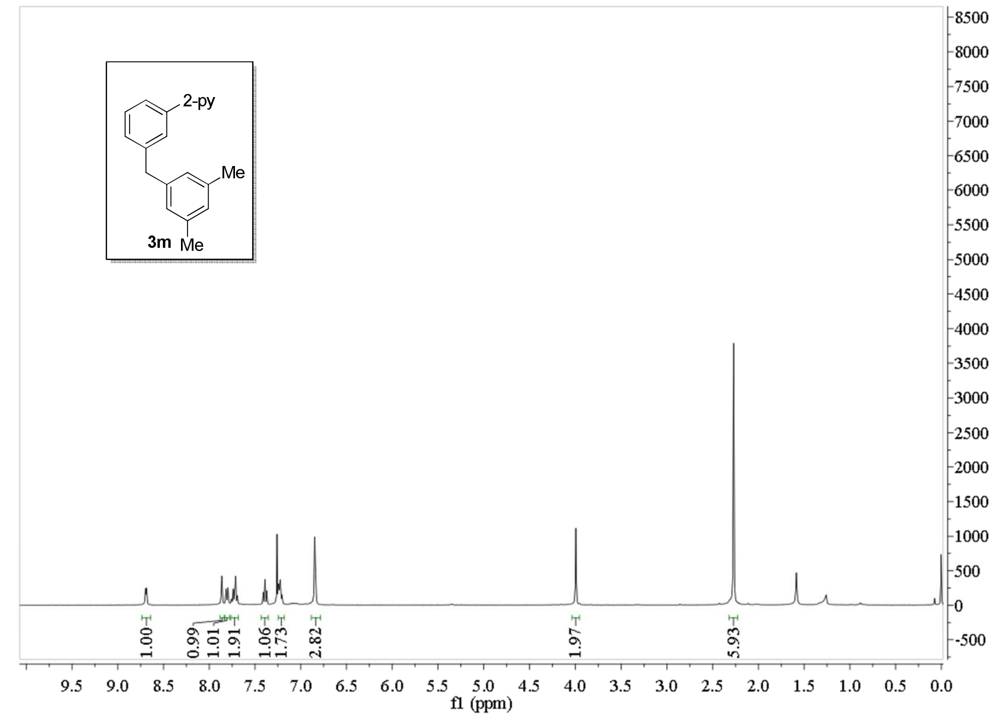
f1 (ppm)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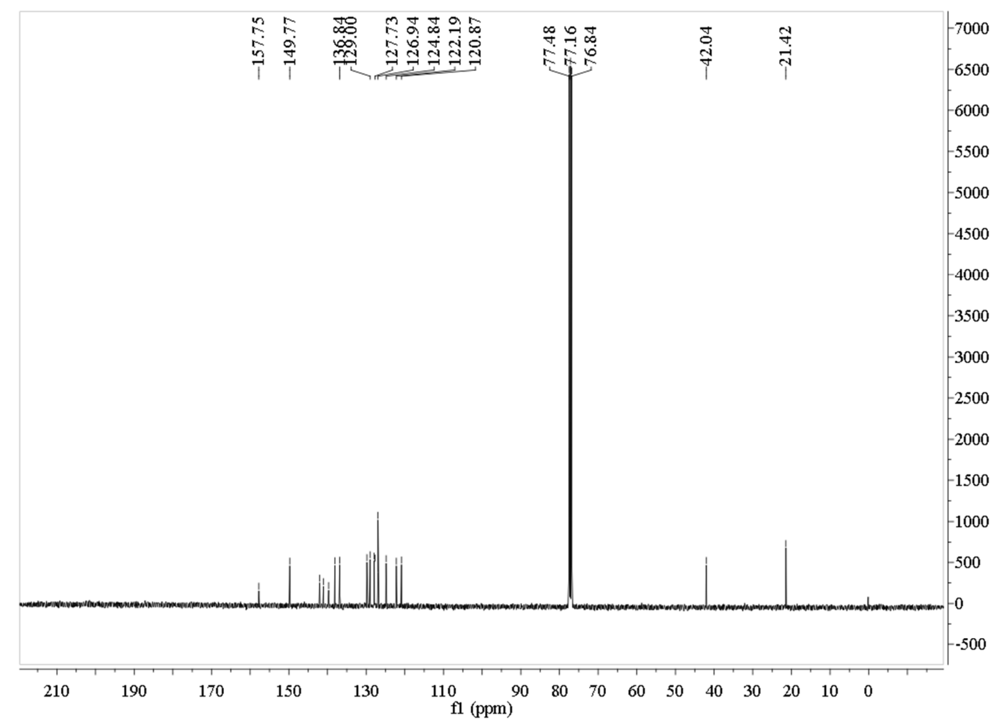
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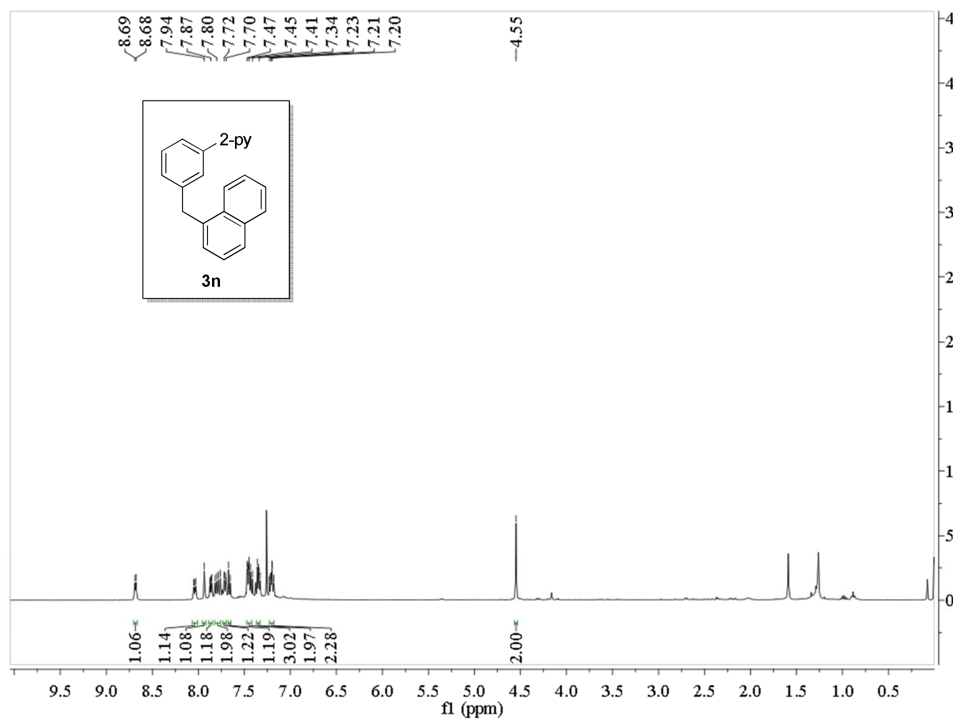
f1 (ppm)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7.20
4.55
2-py
3n
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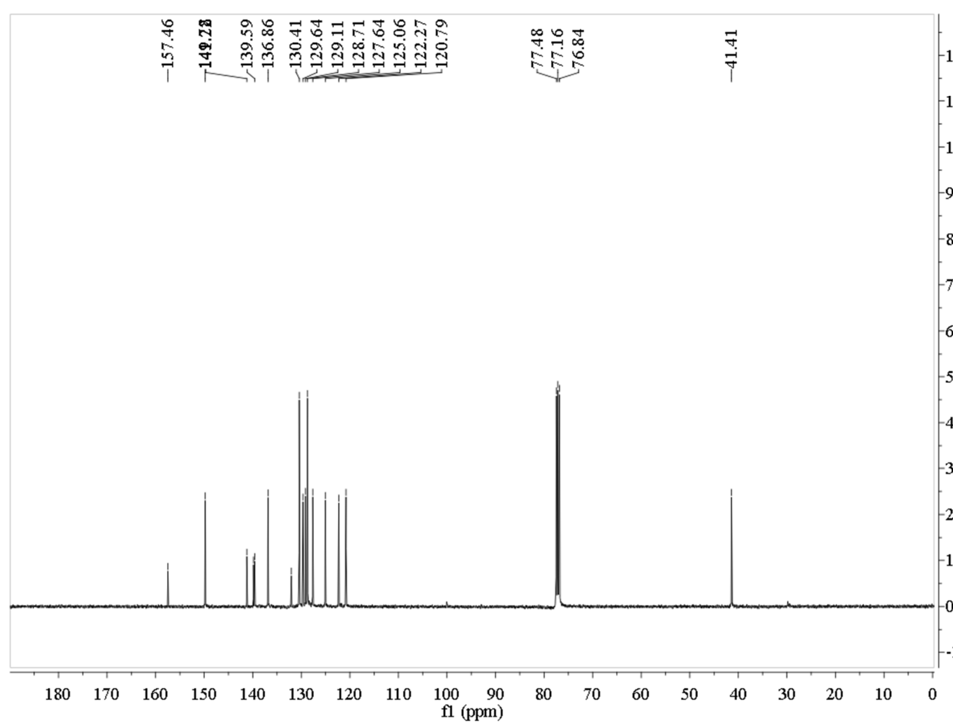
f1 (ppm)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41.41
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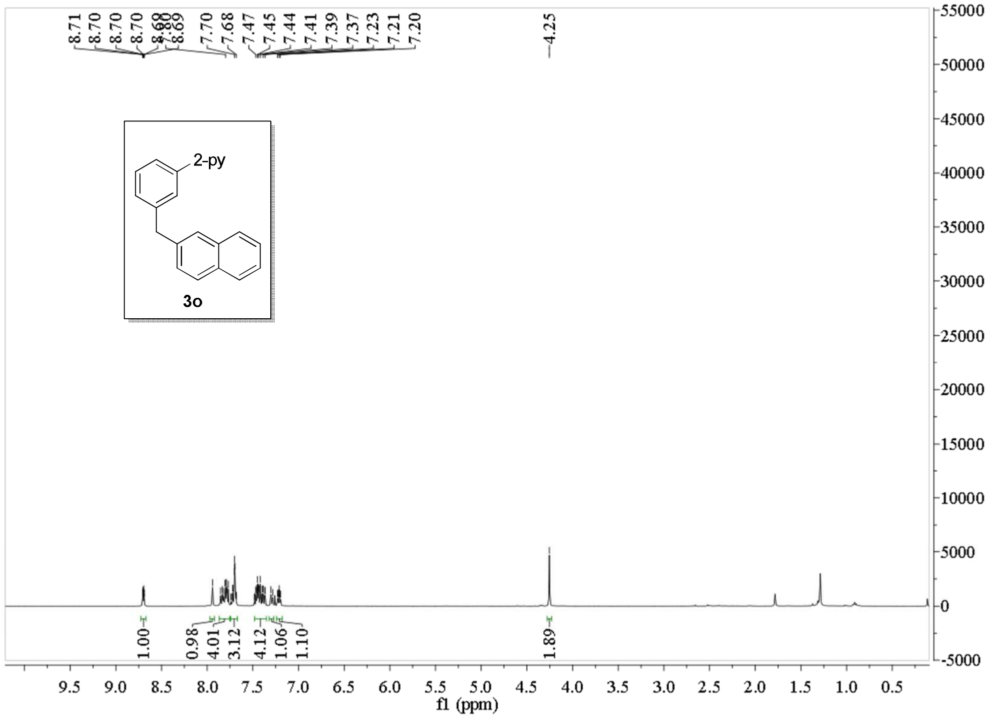
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7.23
7.21
7.20
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1.89
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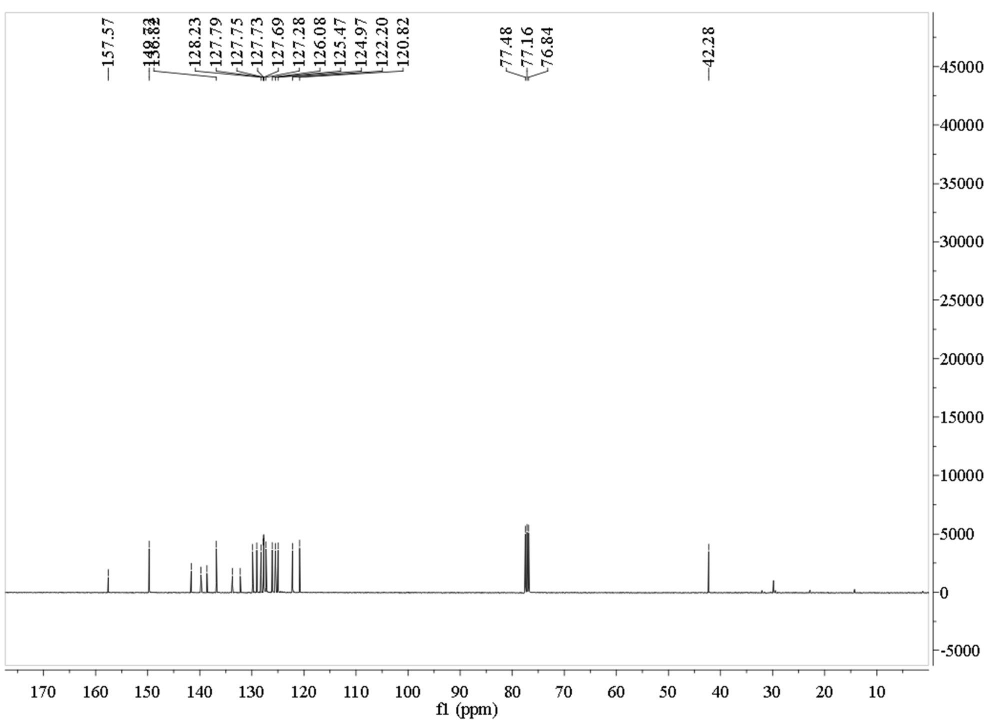
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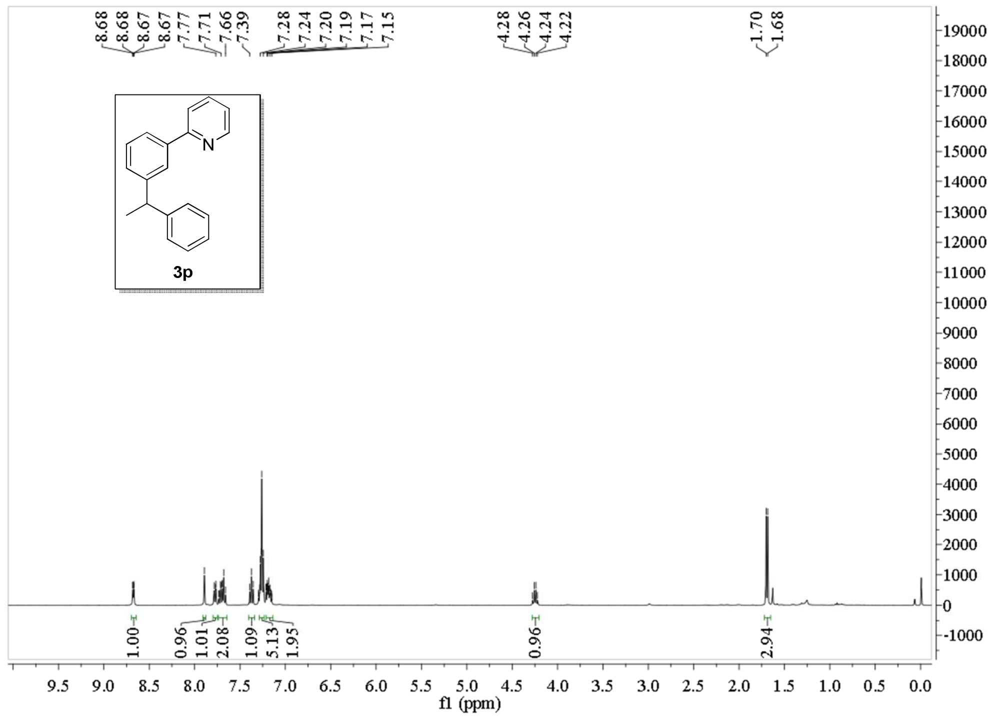
42.28
f1 (ppm)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4.26
4.24
4.22
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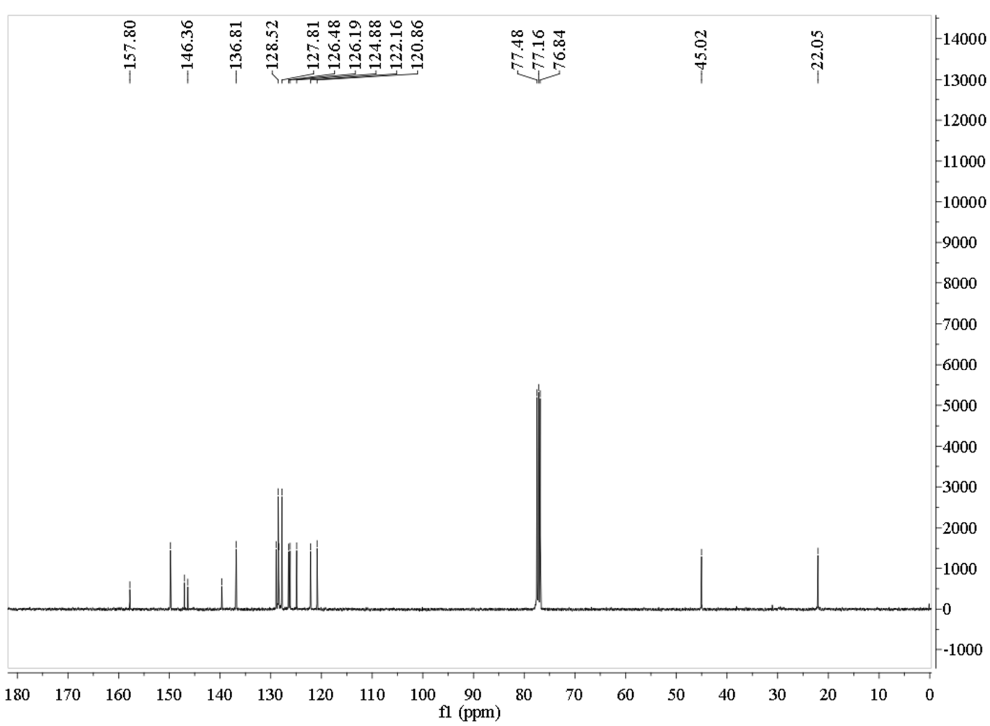
f1 (ppm)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22.05
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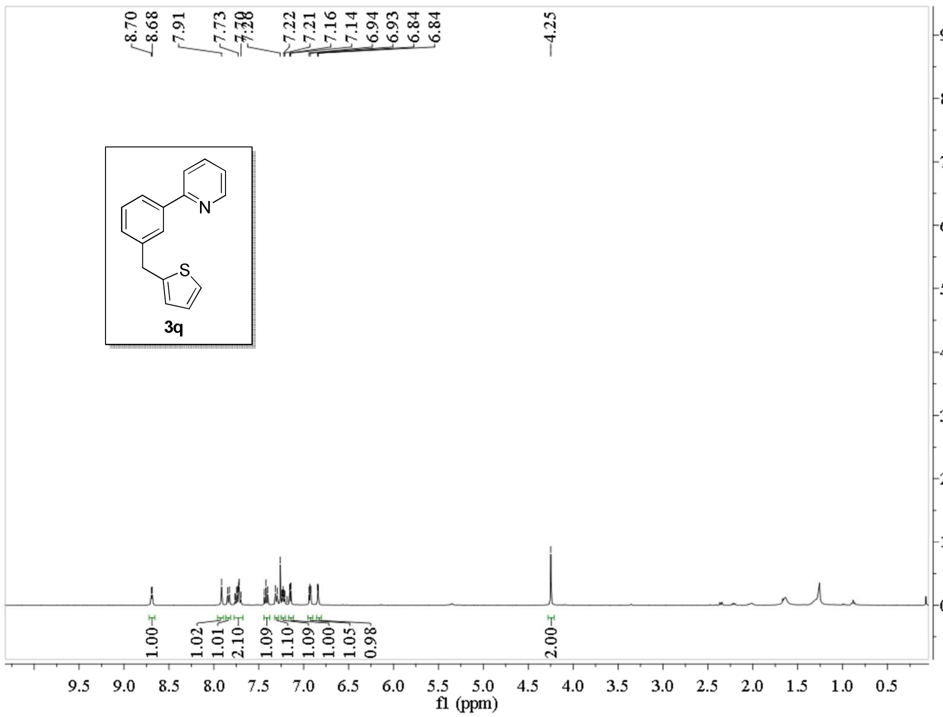
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S
3q
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2.00
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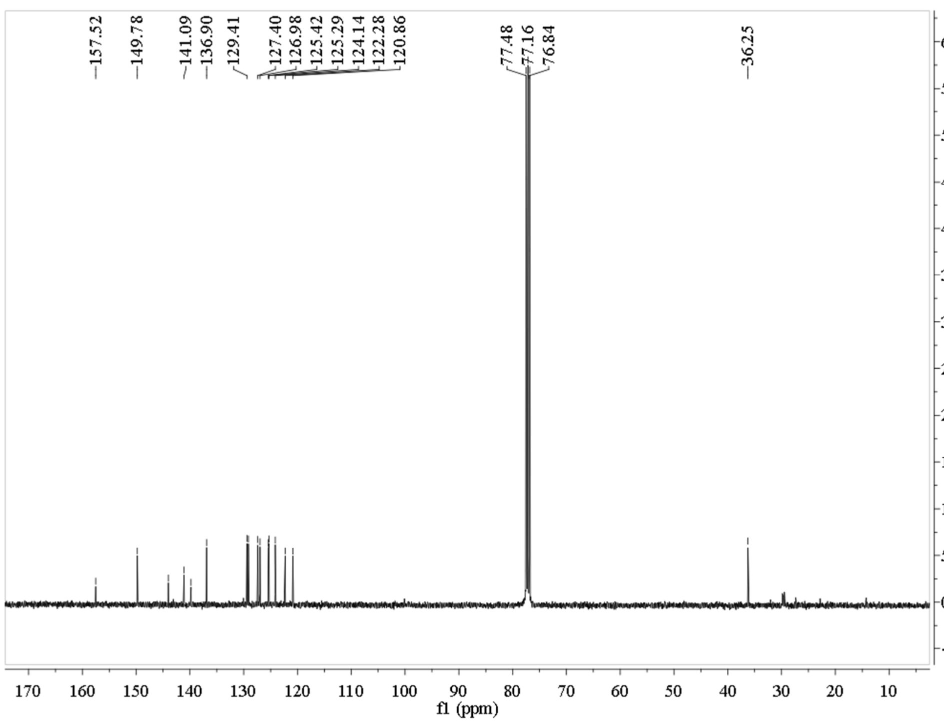
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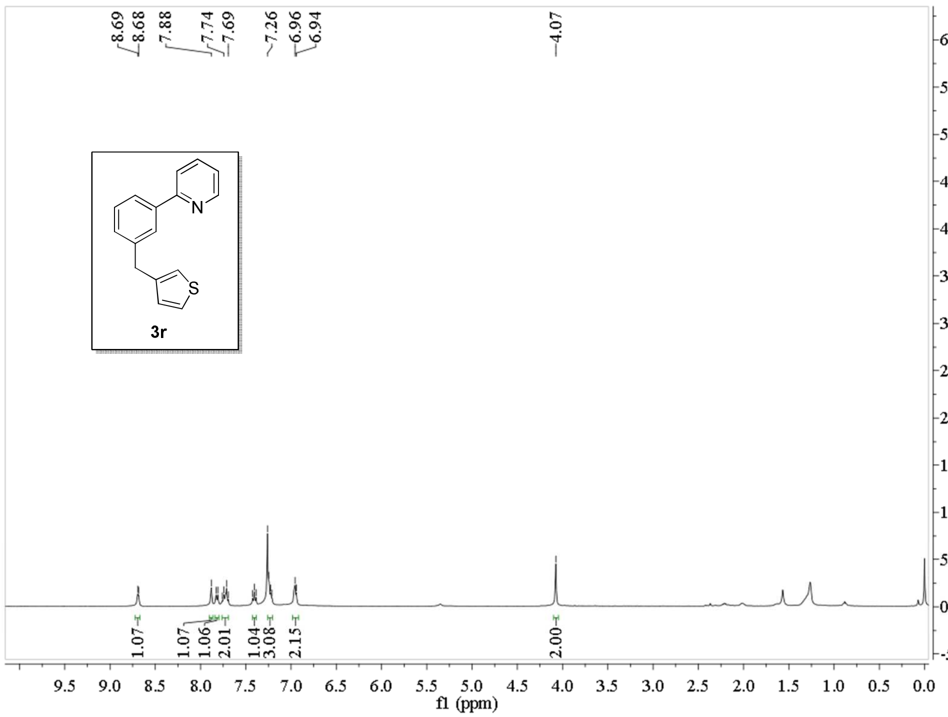
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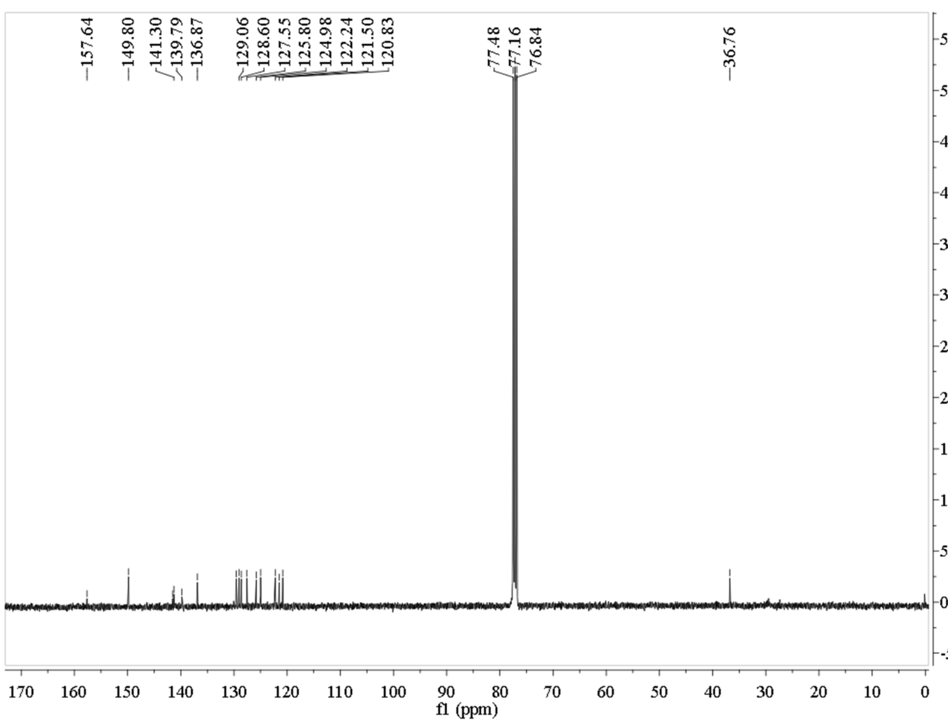
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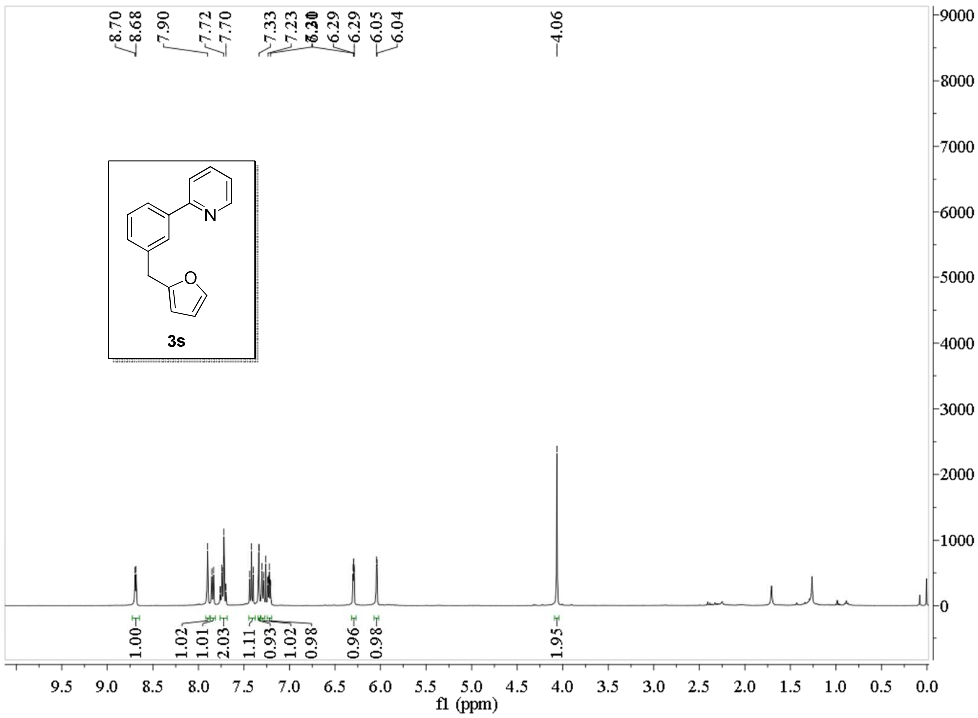
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3s
N
O
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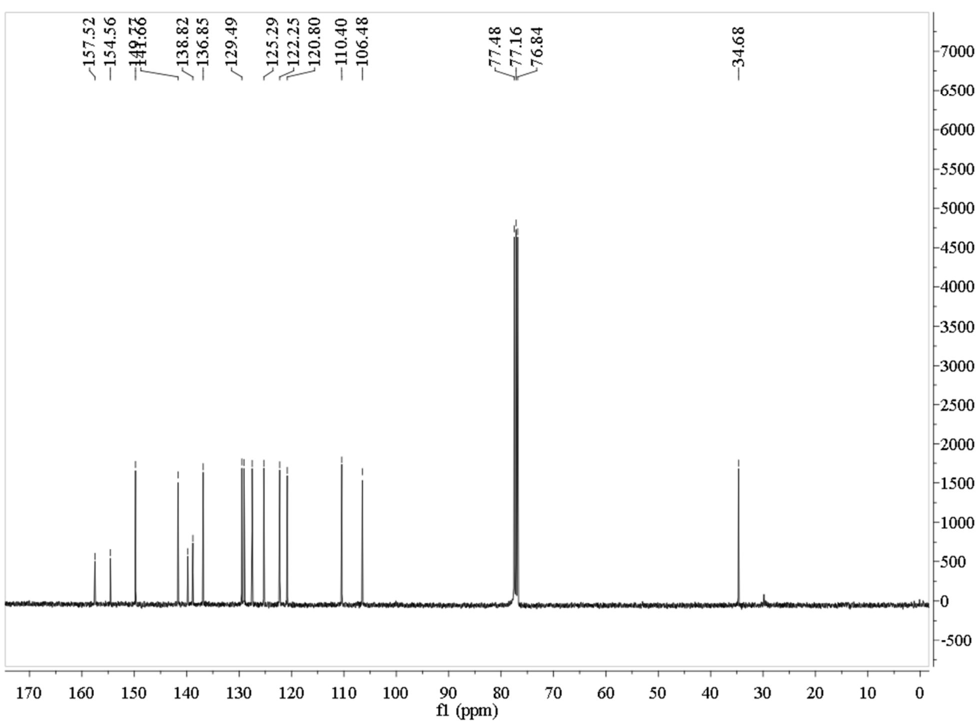
f1 (ppm)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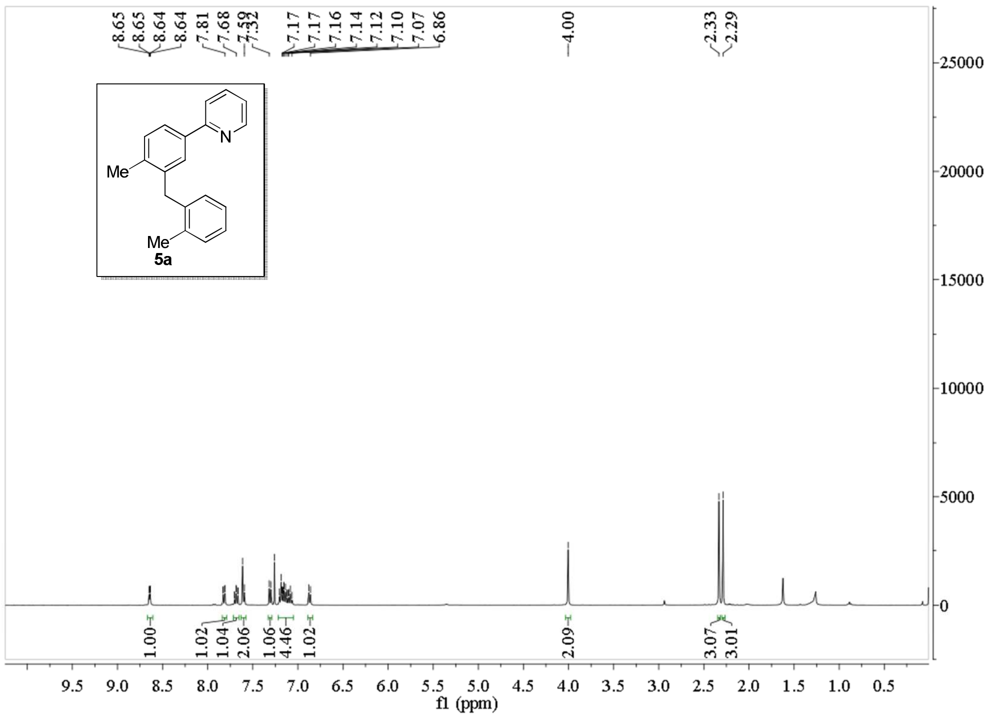

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Me
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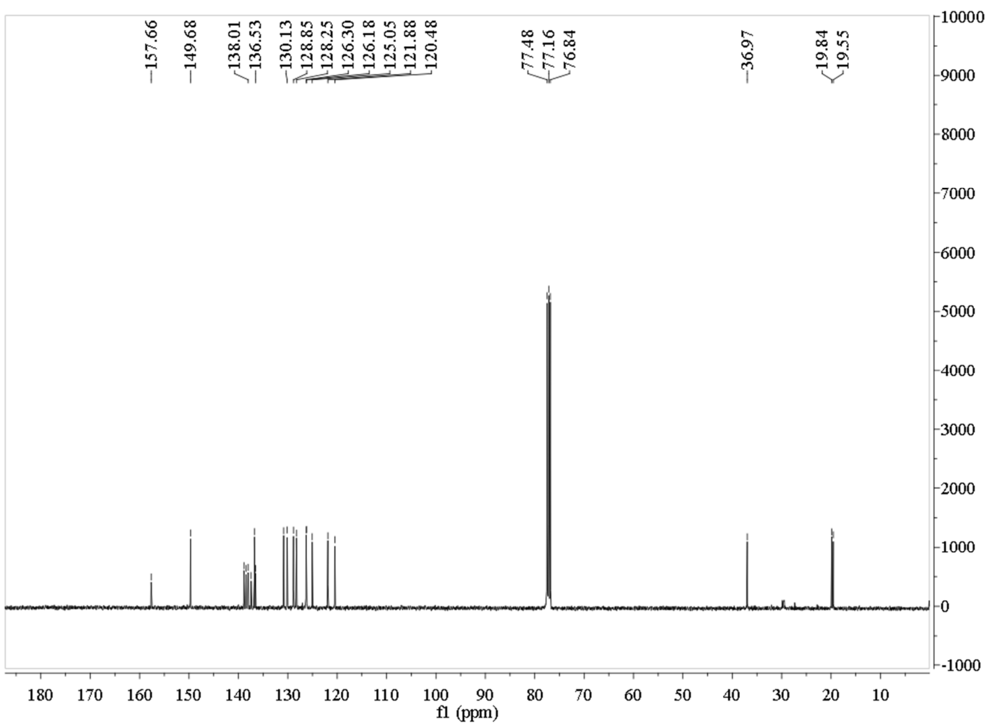

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19.55
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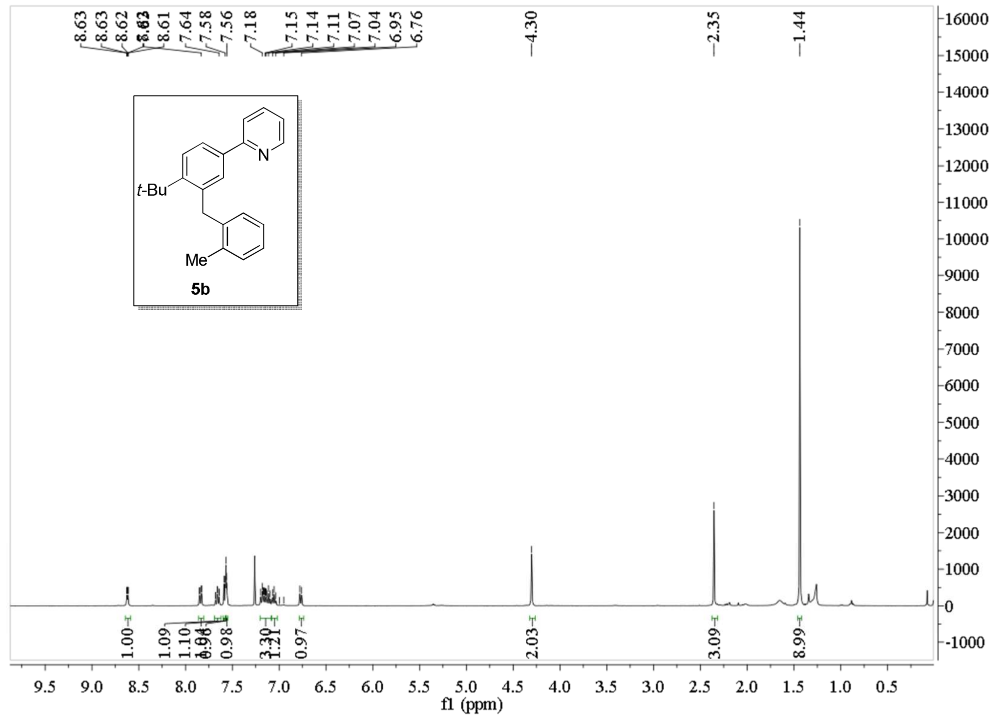
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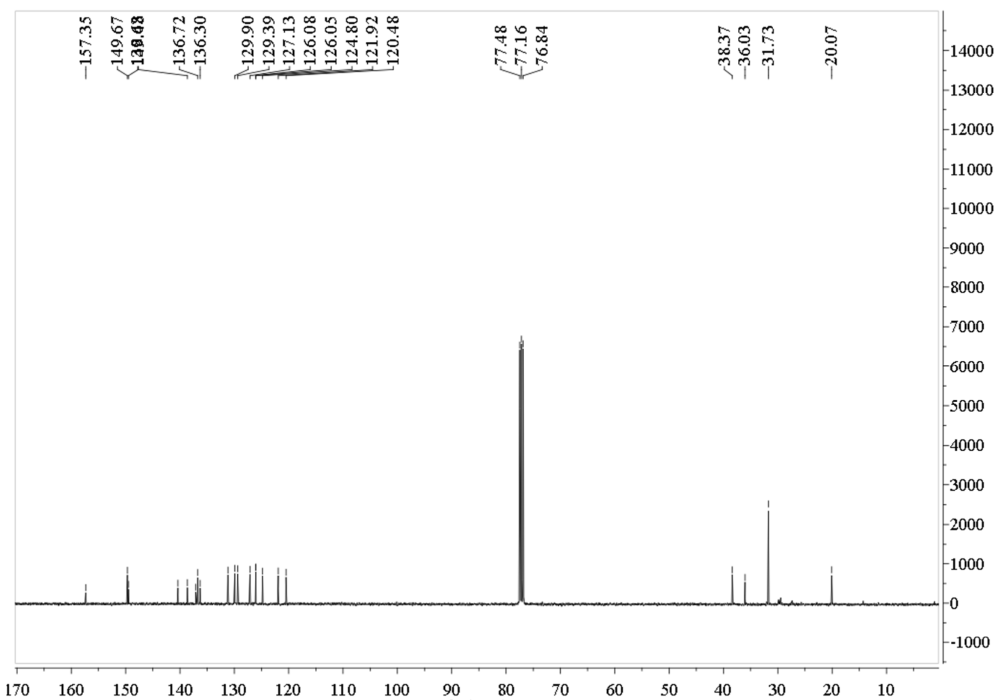
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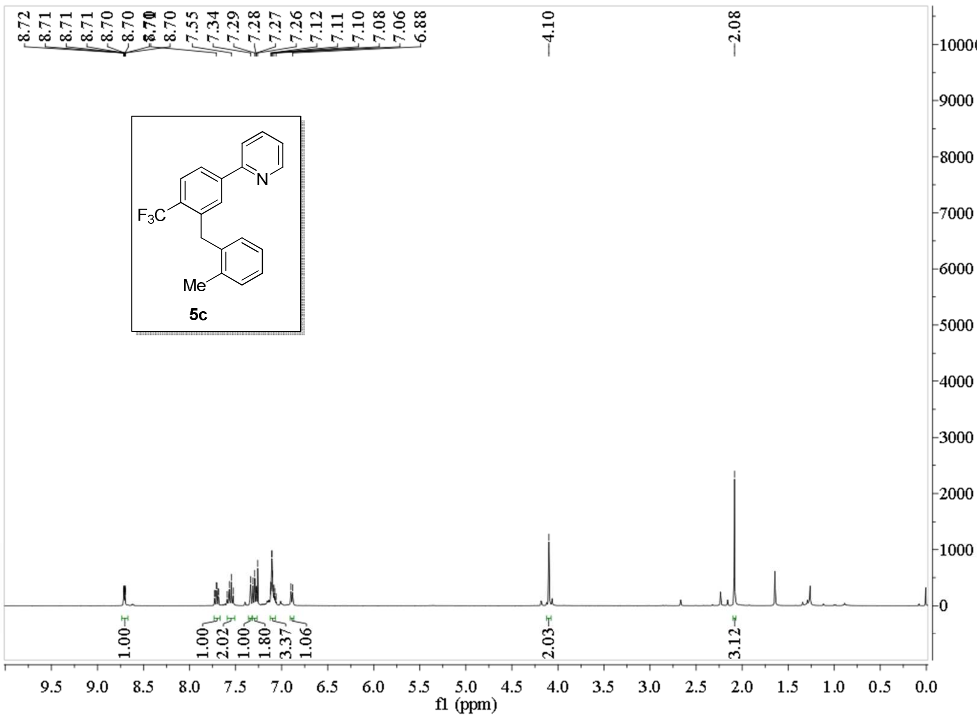
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Me
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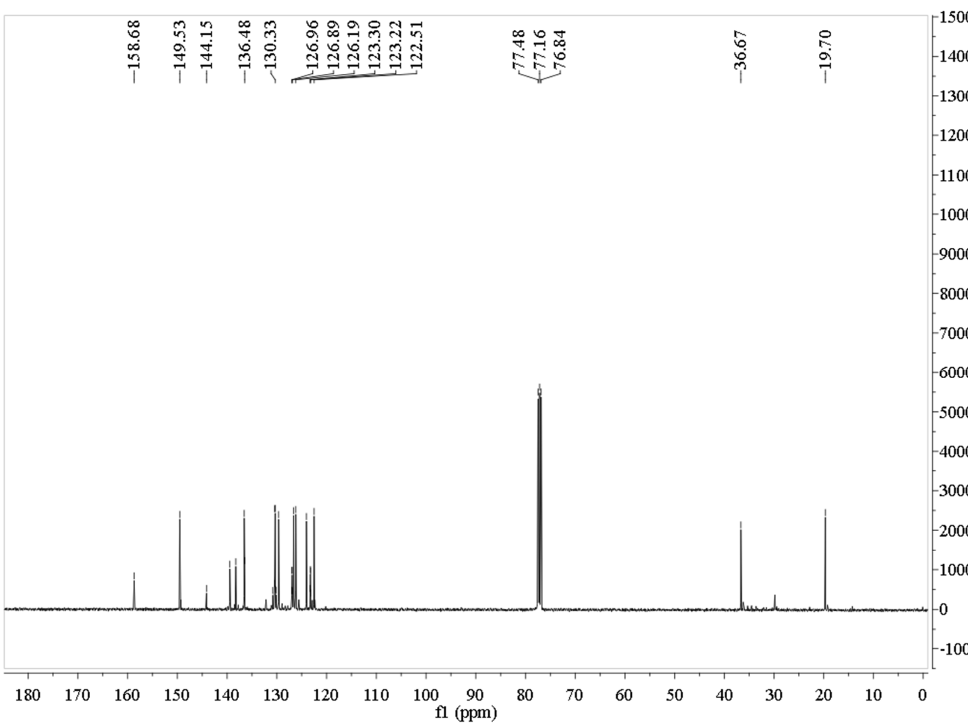
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19.70
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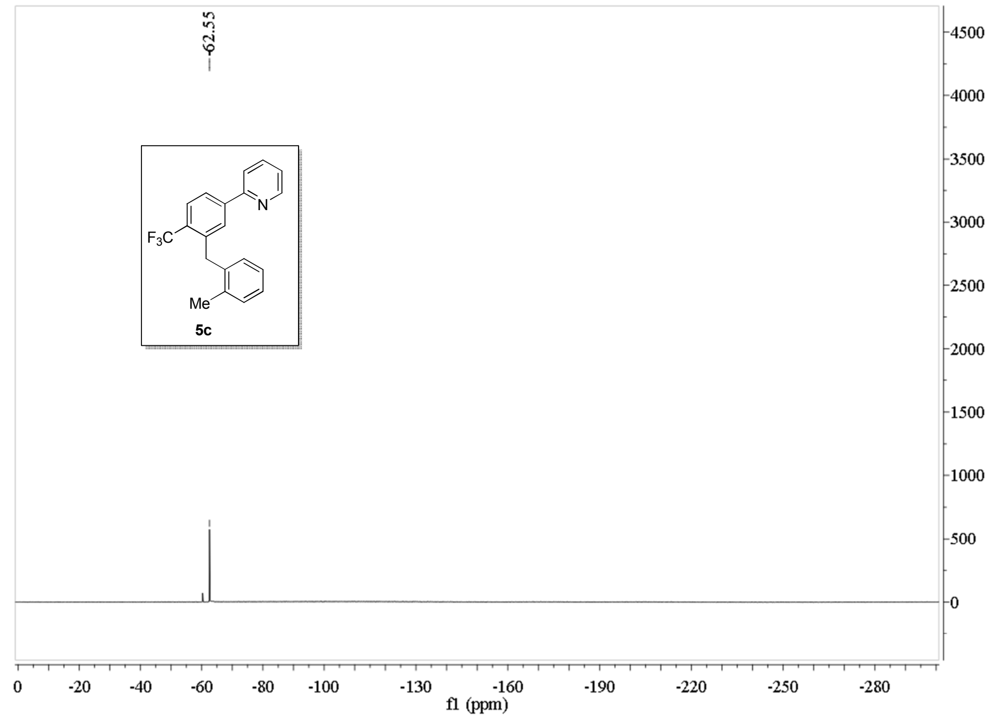
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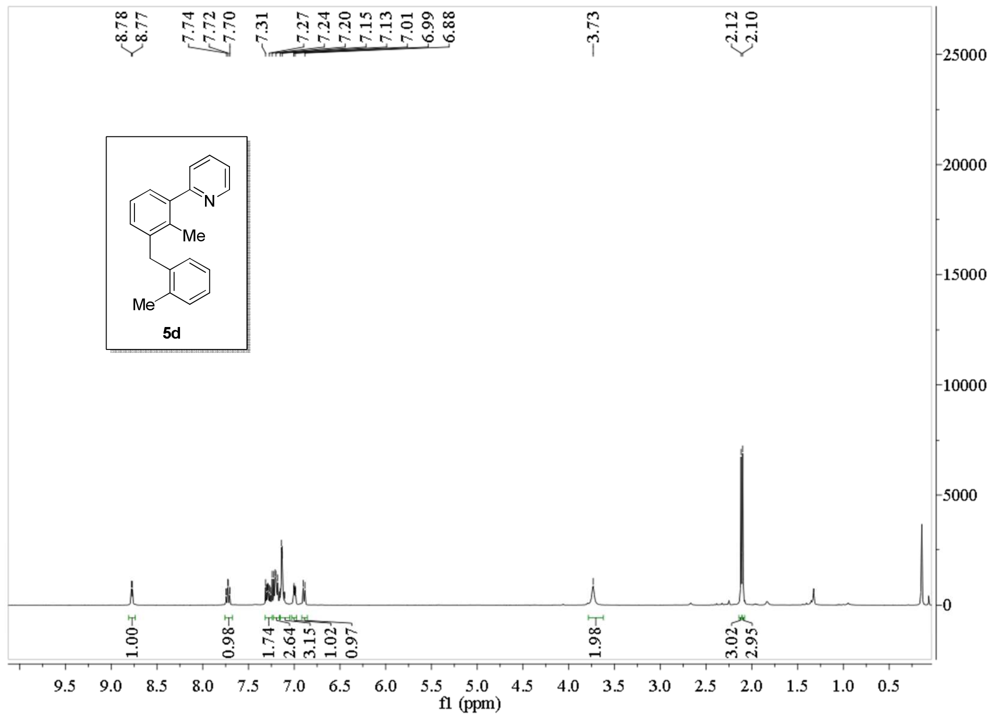
-250
-280
f1 (ppm)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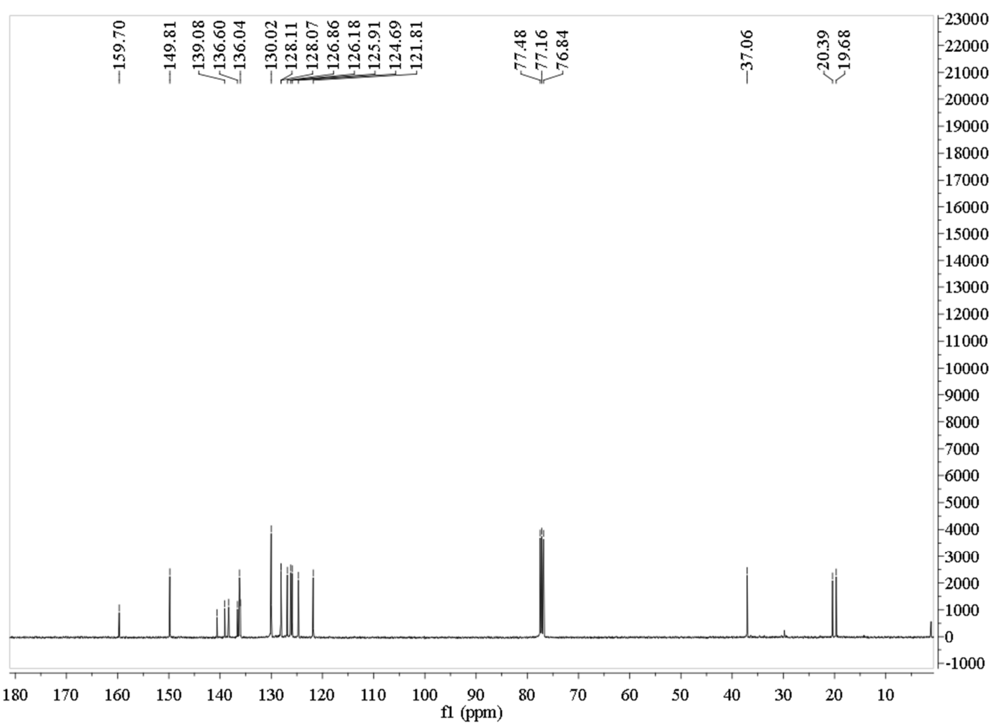
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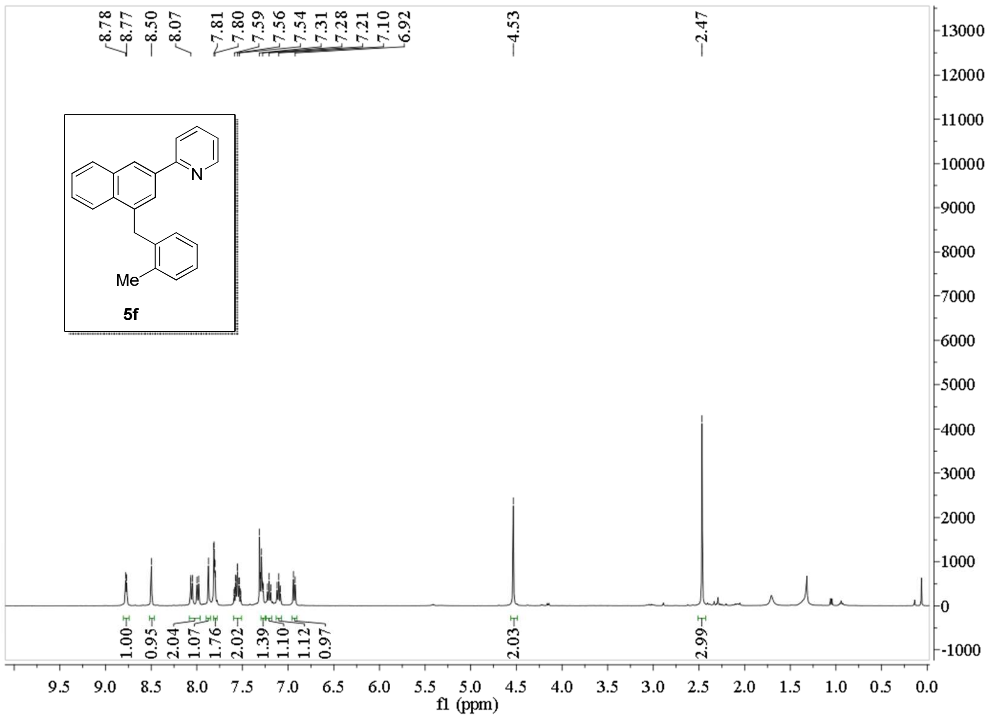
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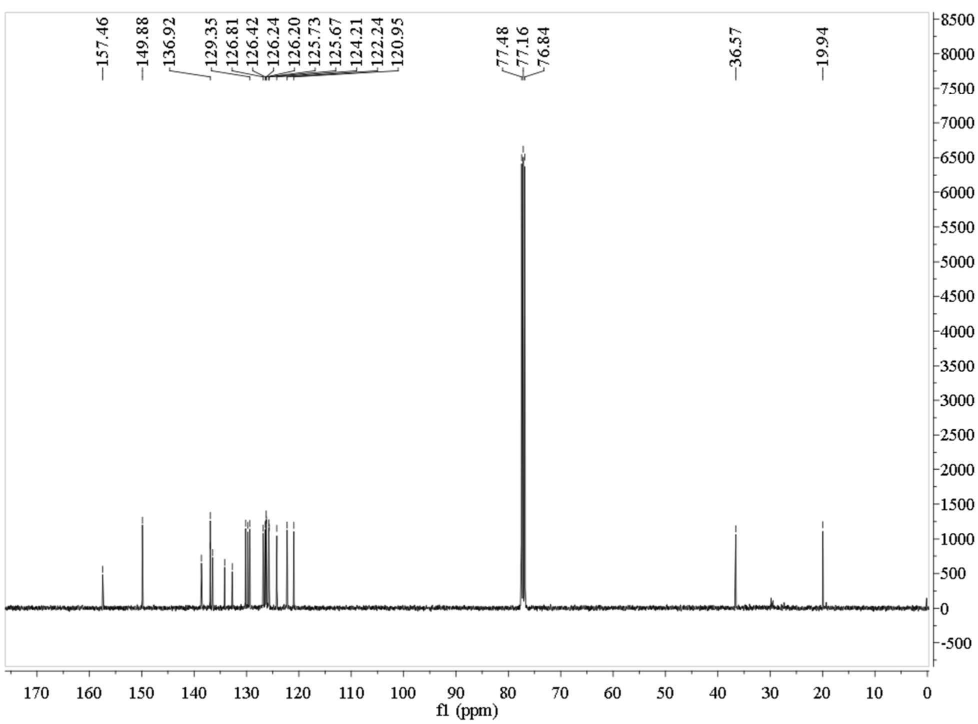
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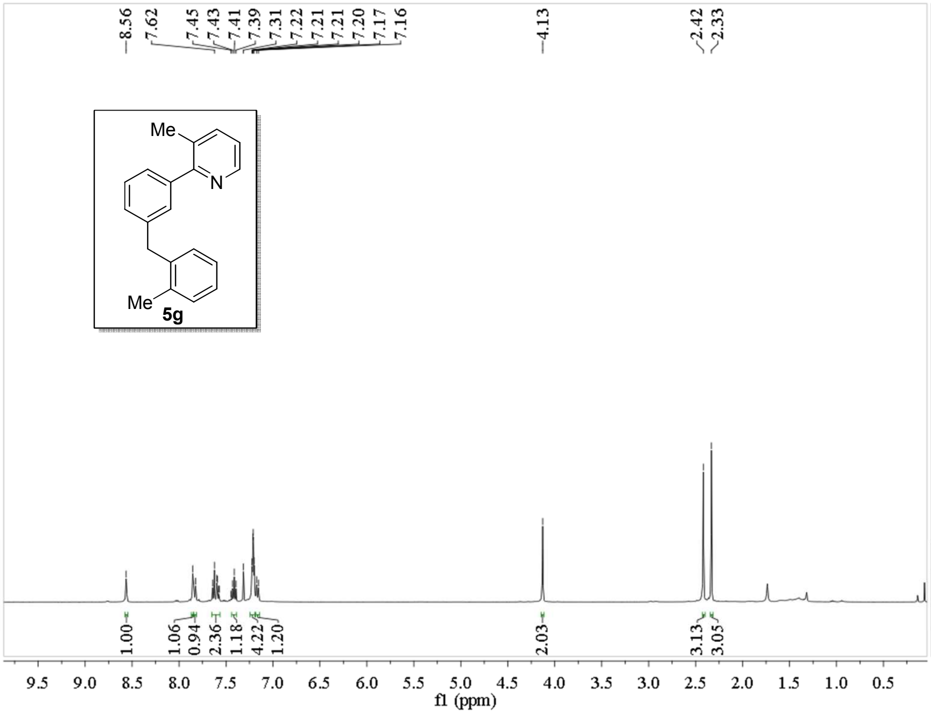
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3.05
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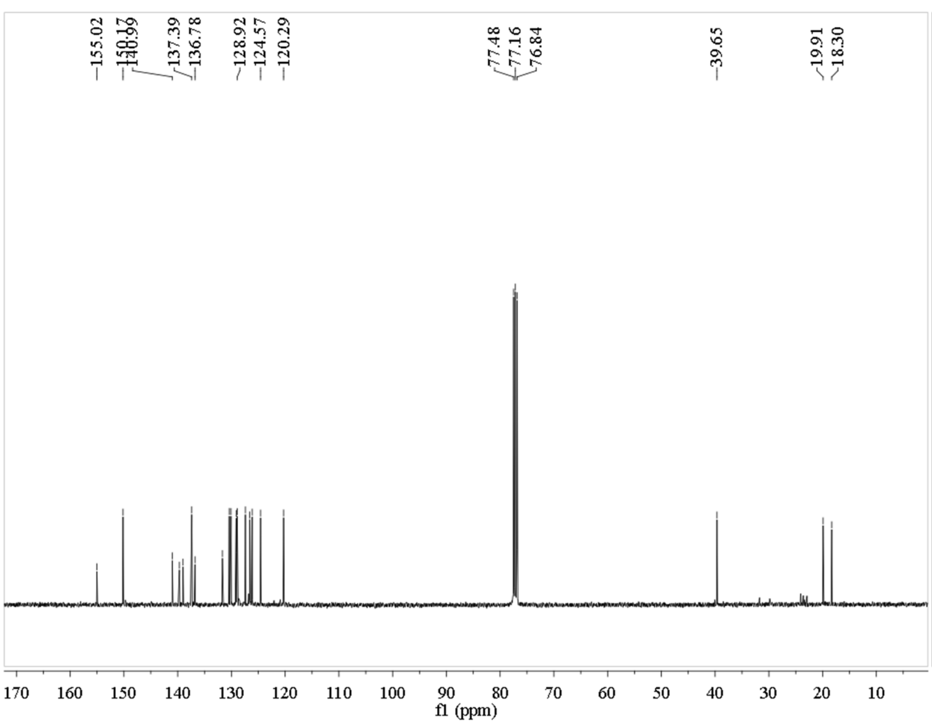
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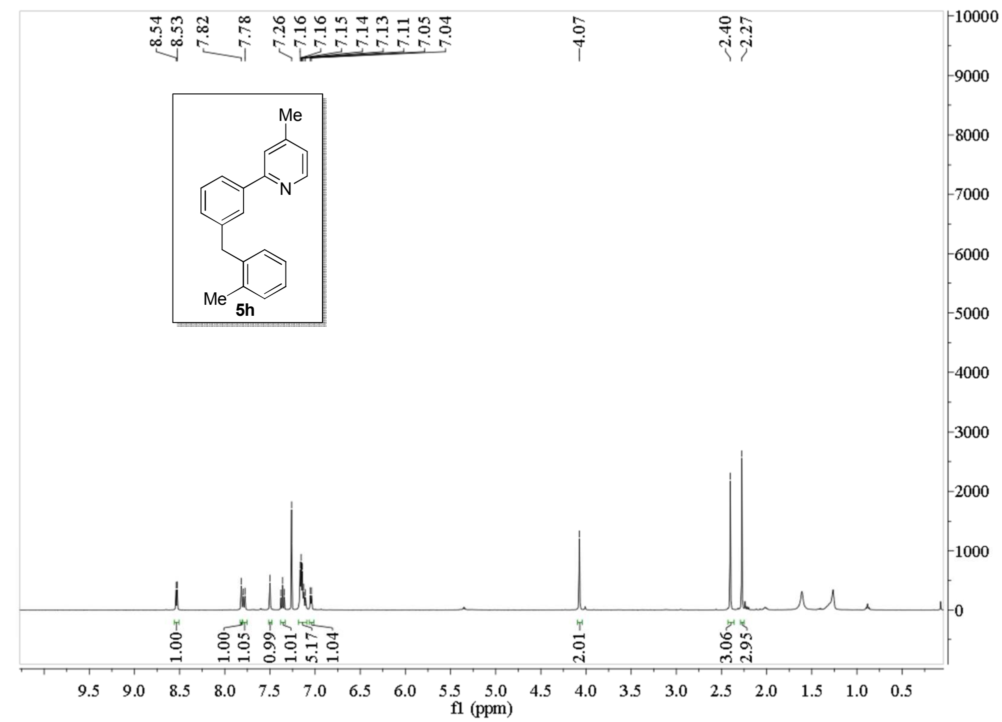
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2.27
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Me
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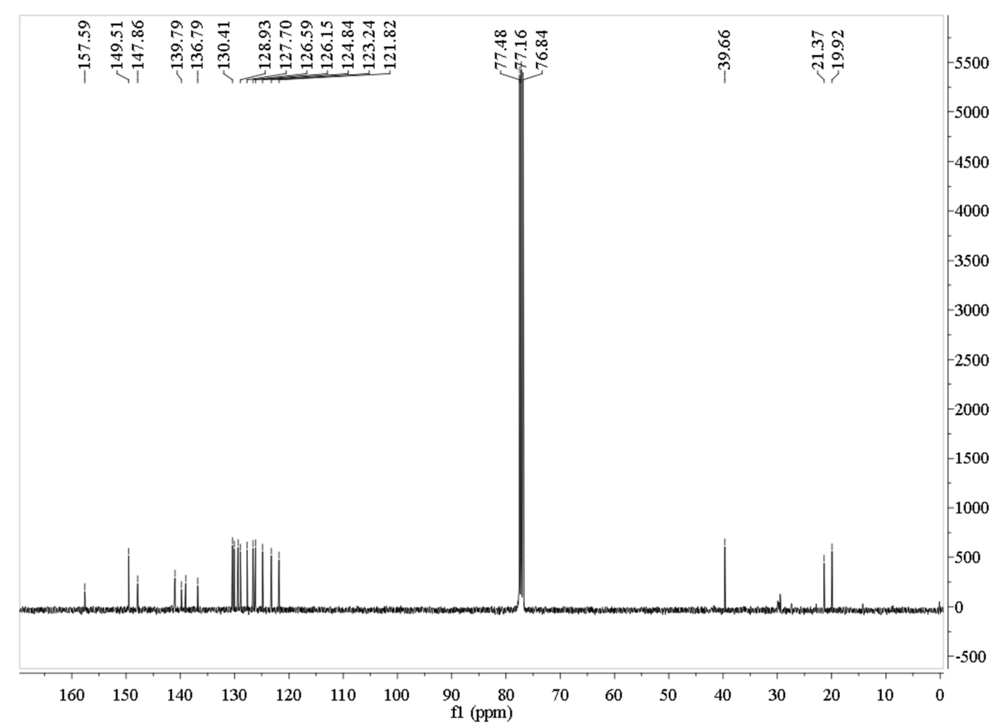
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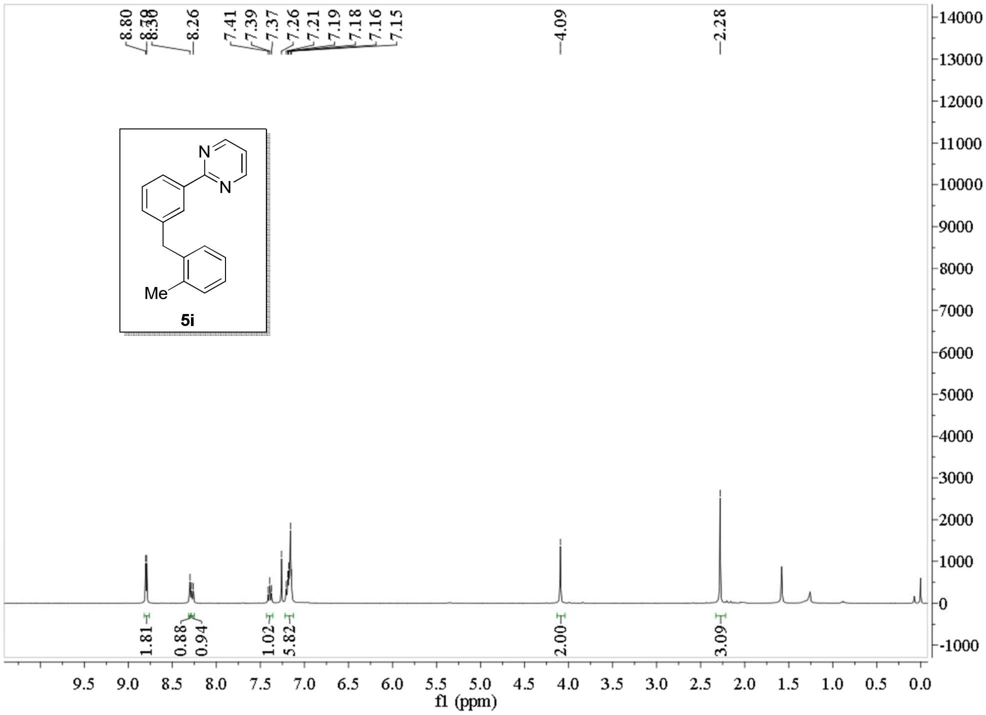
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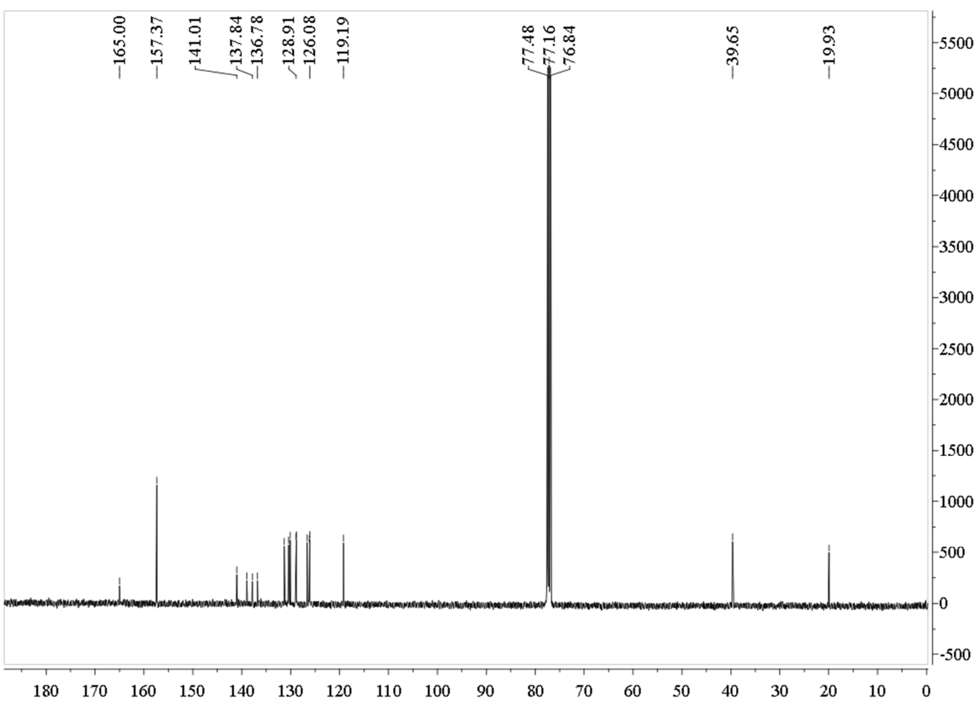
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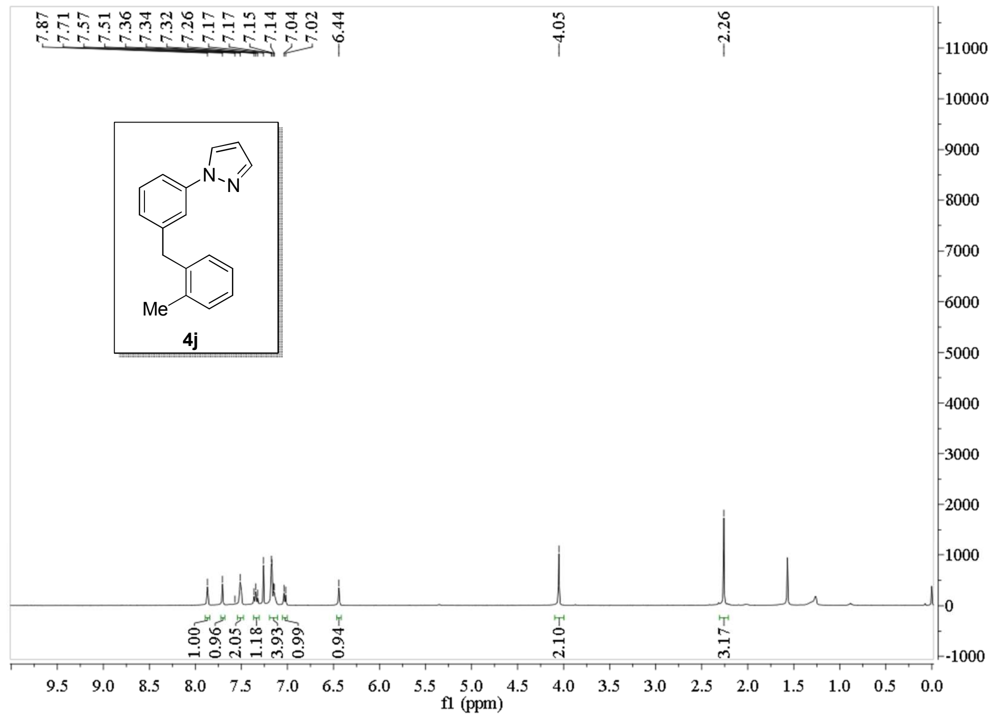
f1 (ppm)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2.26
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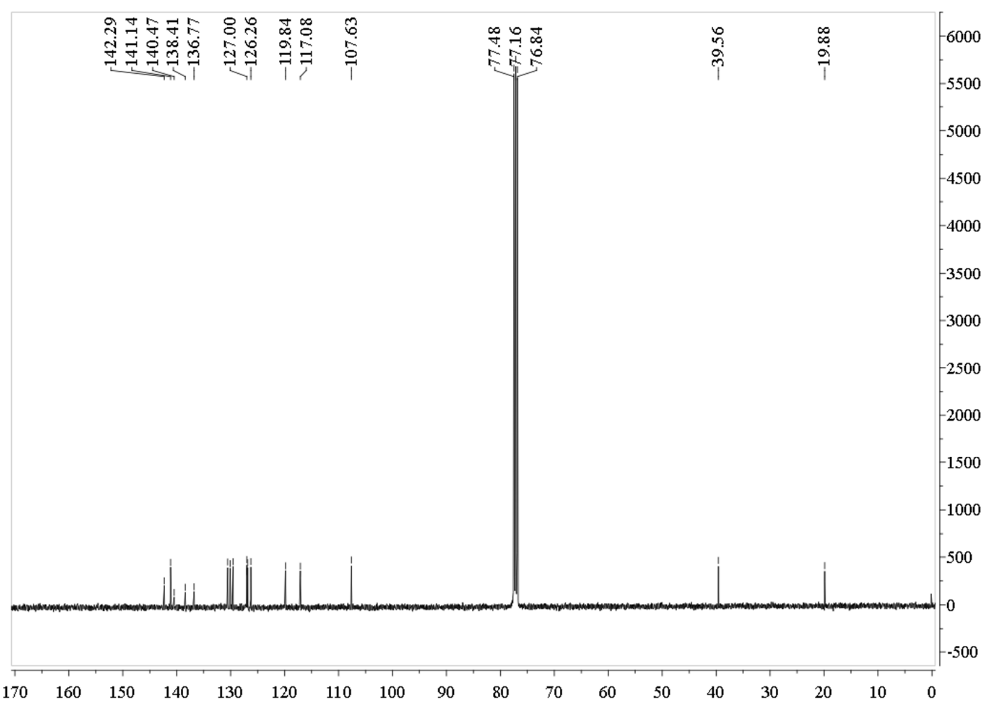
f1 (ppm)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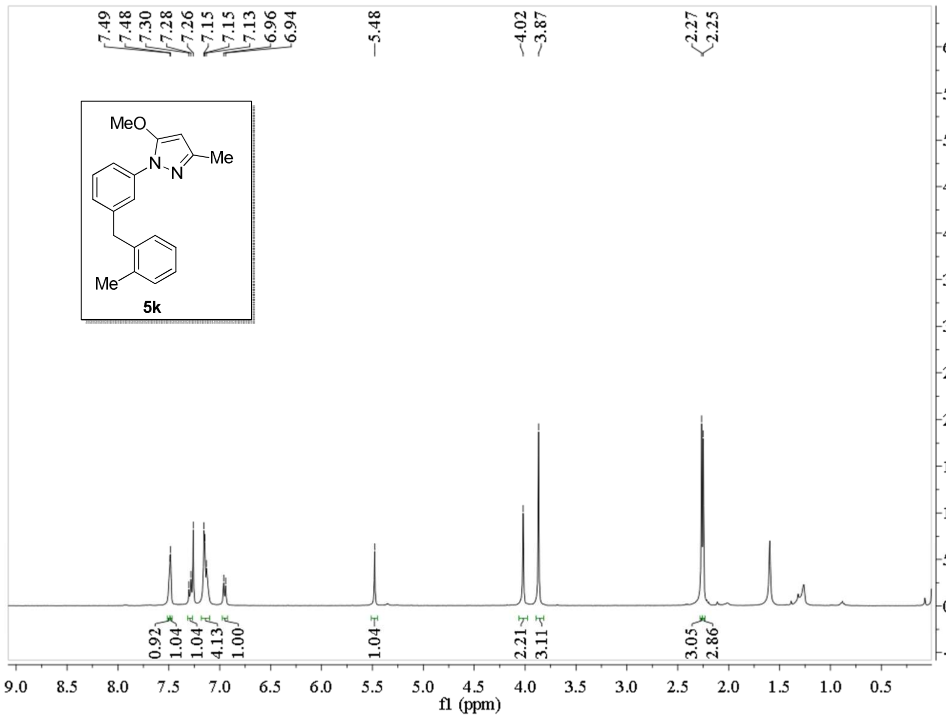
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2.25
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Me
Me
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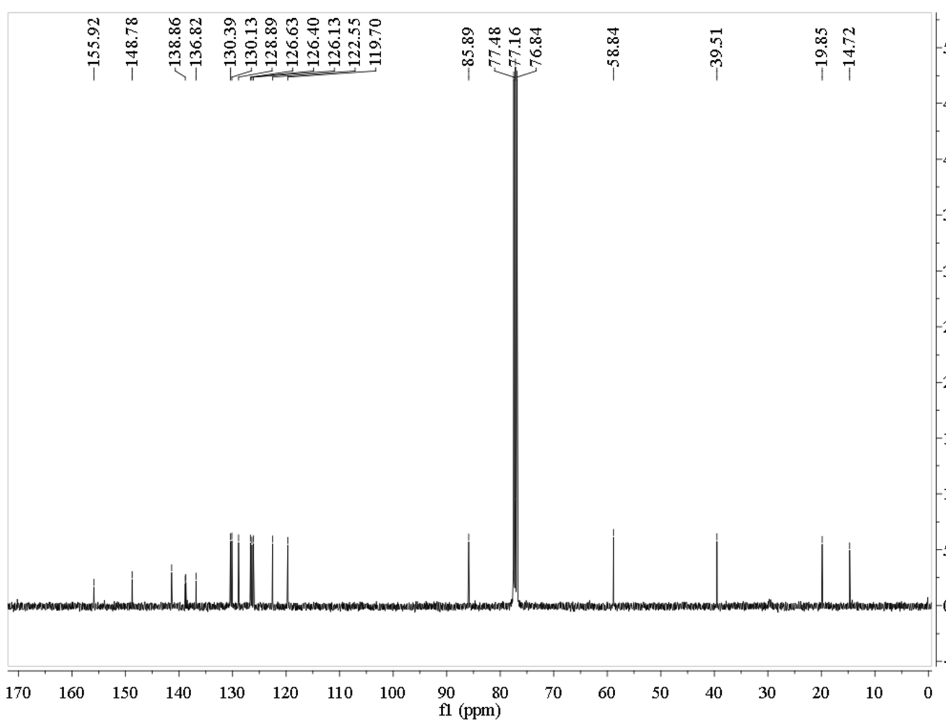
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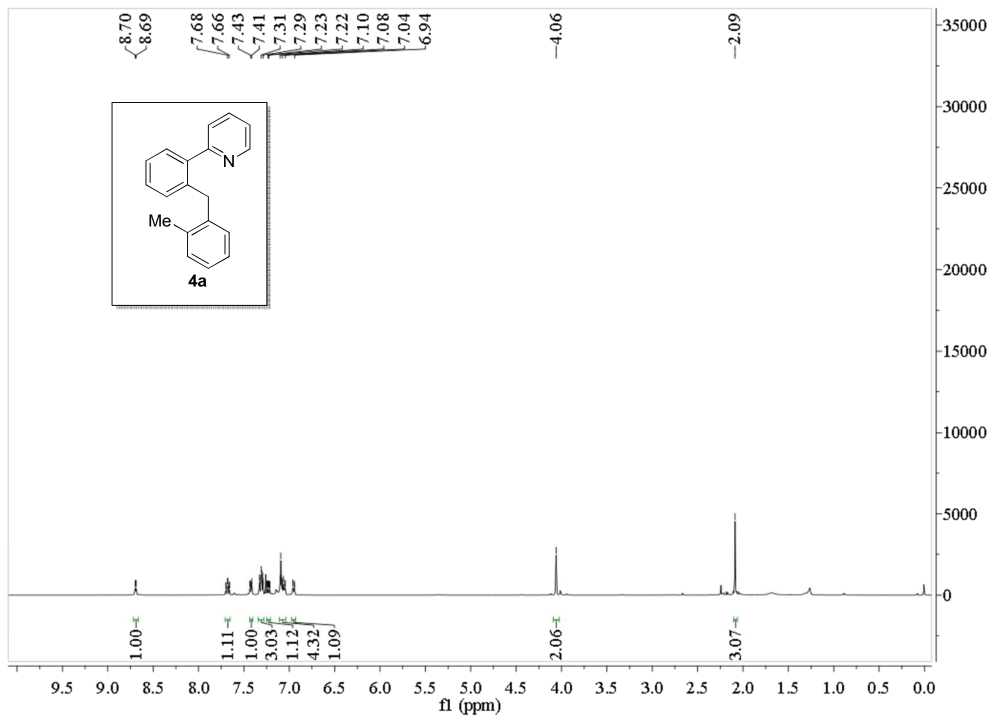
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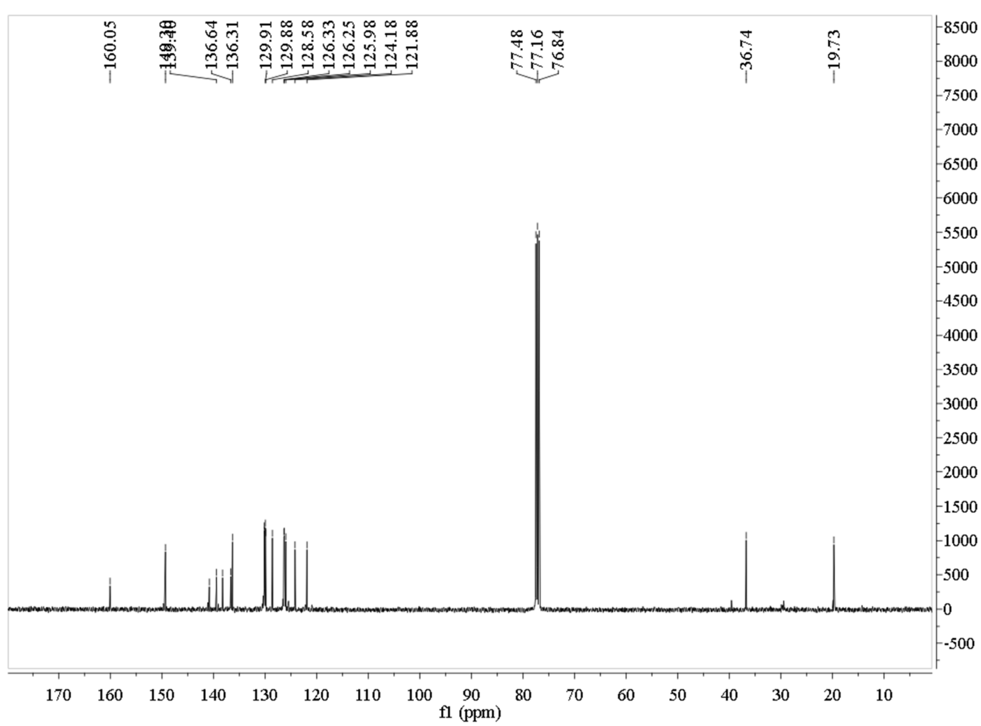
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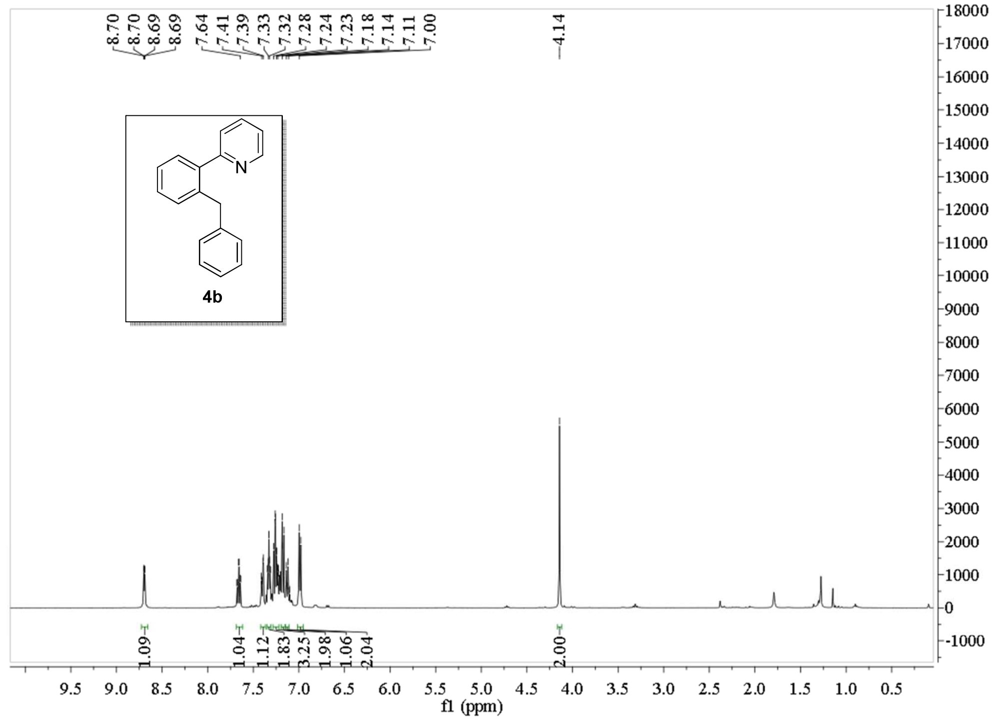
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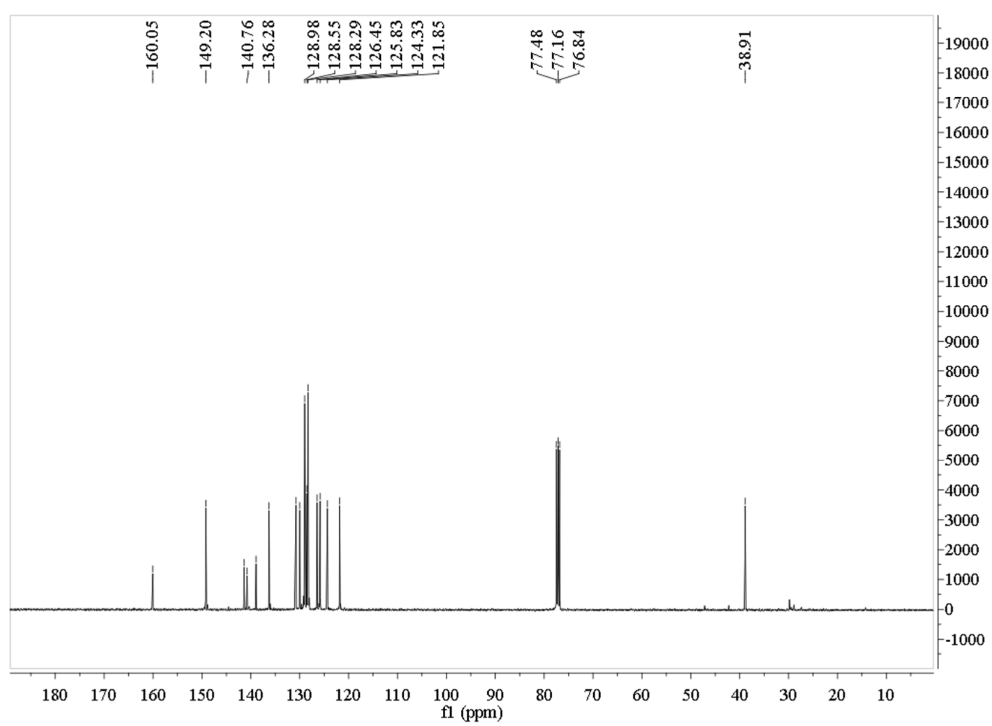
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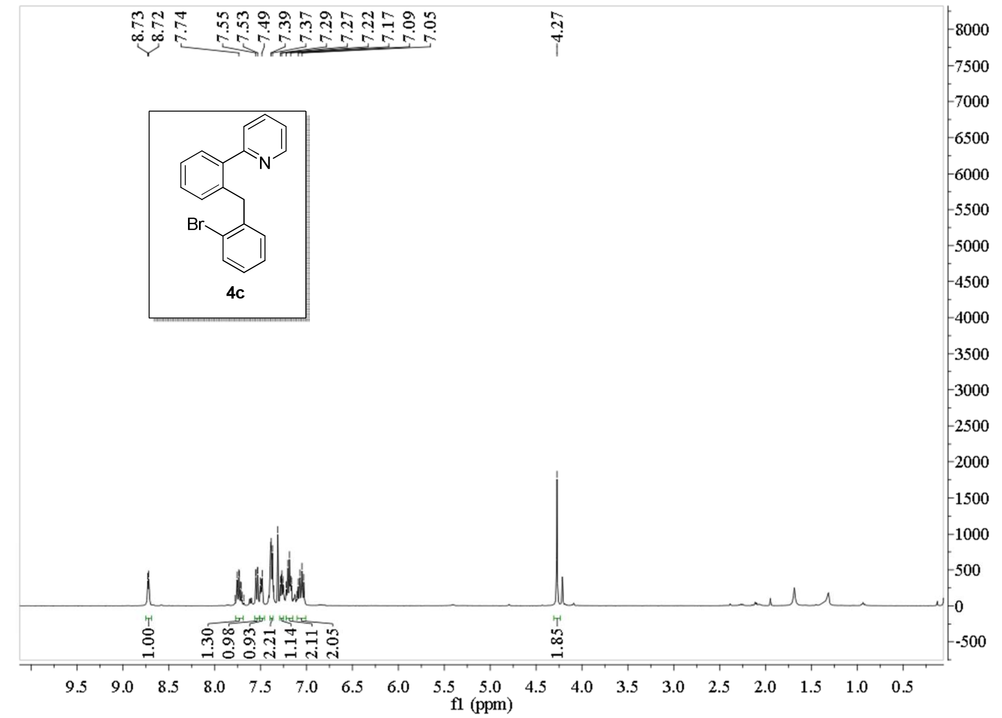
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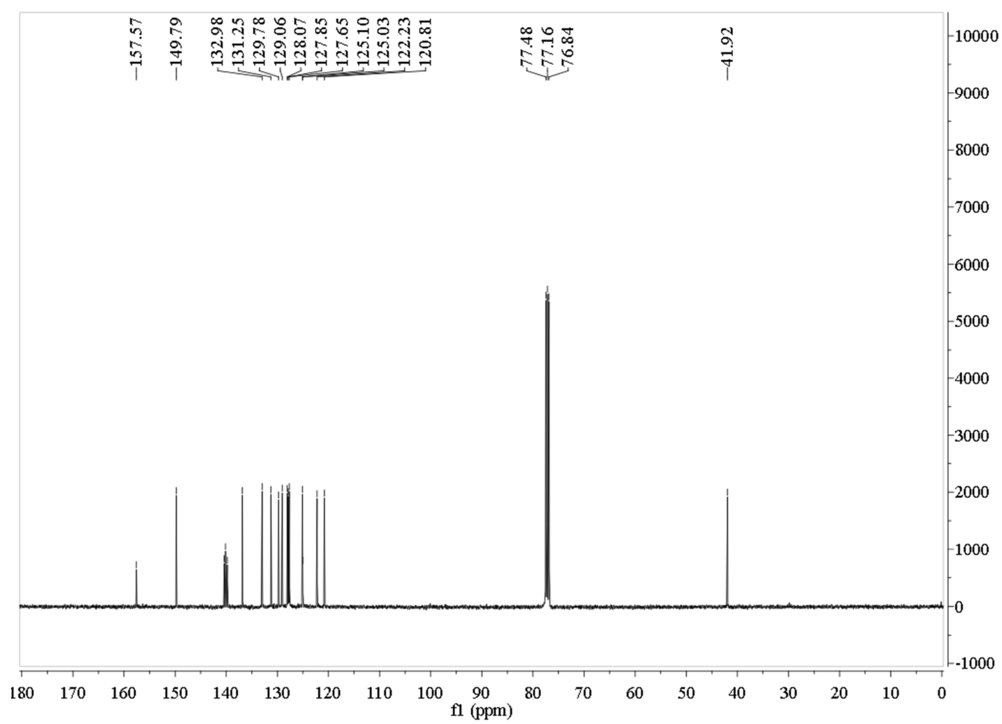
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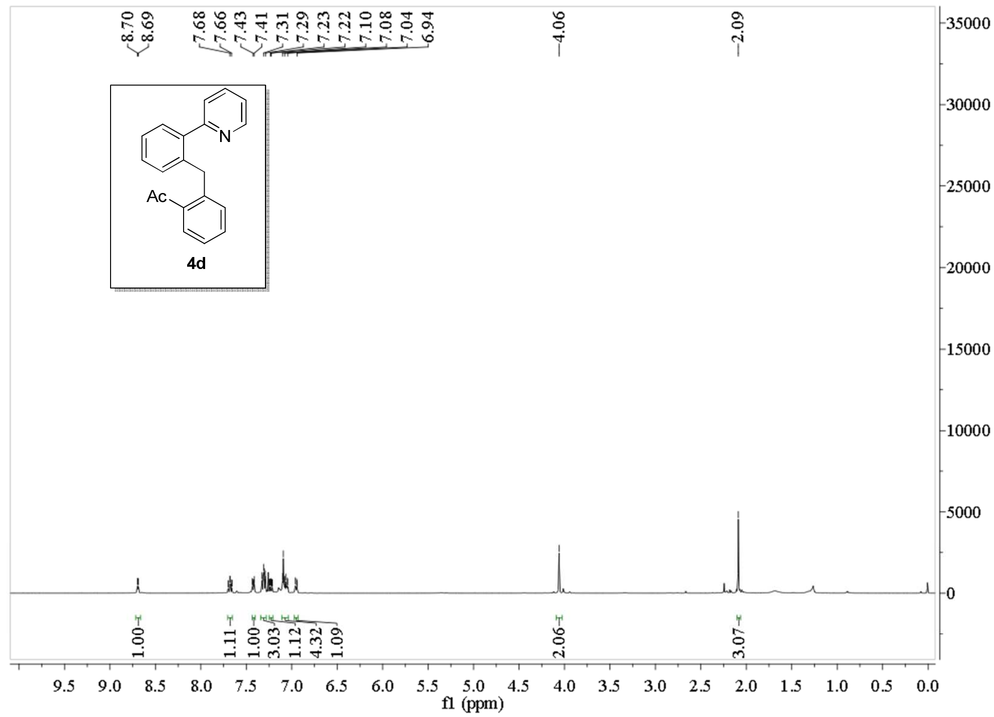

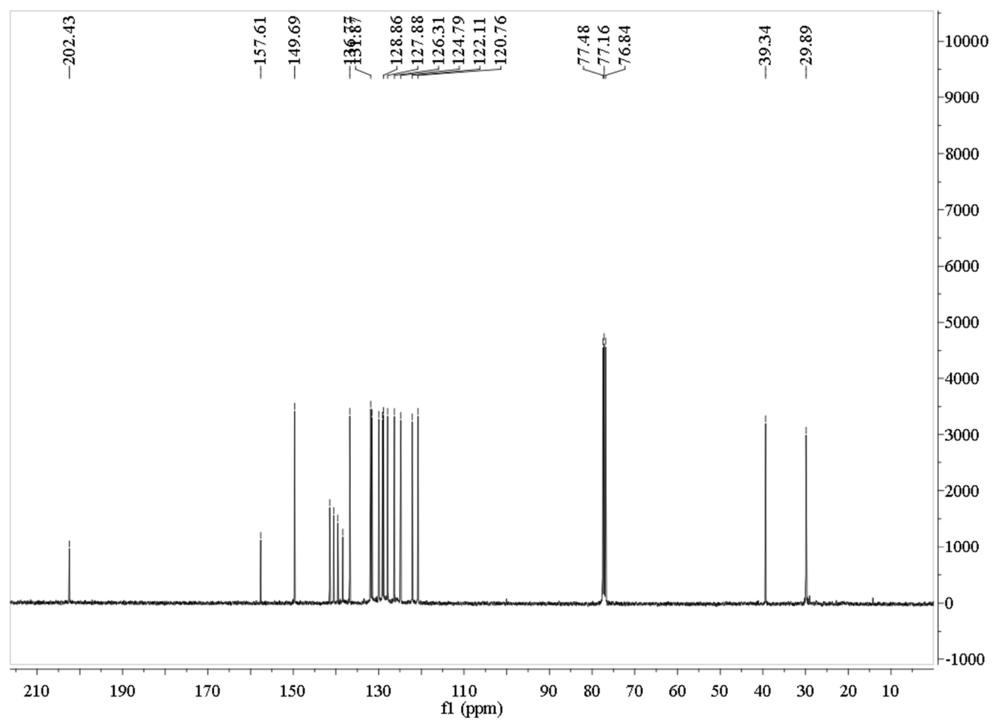

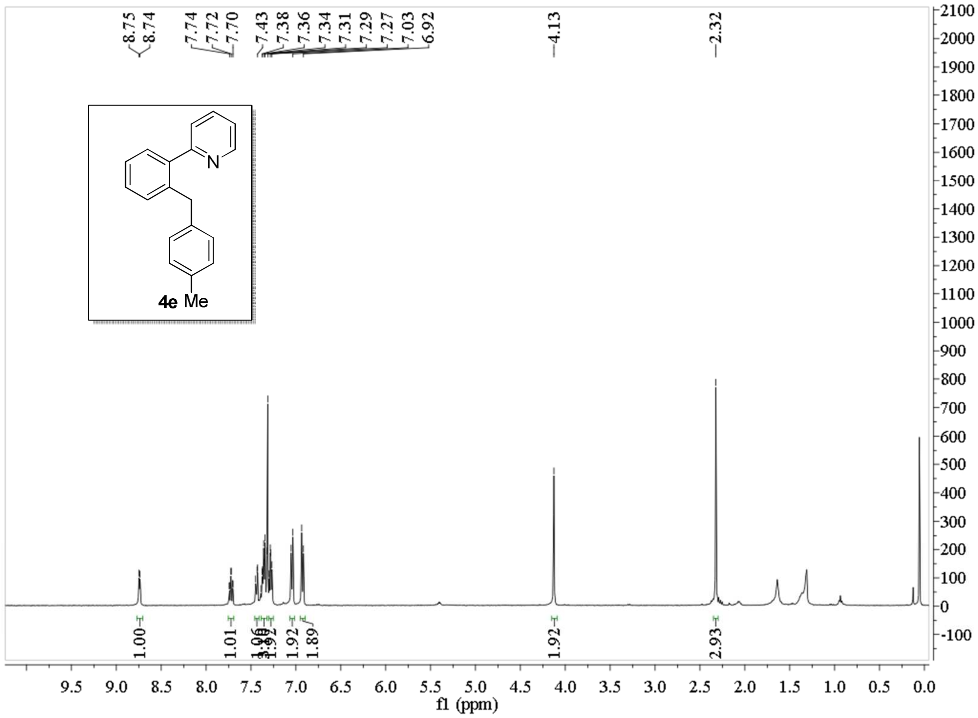
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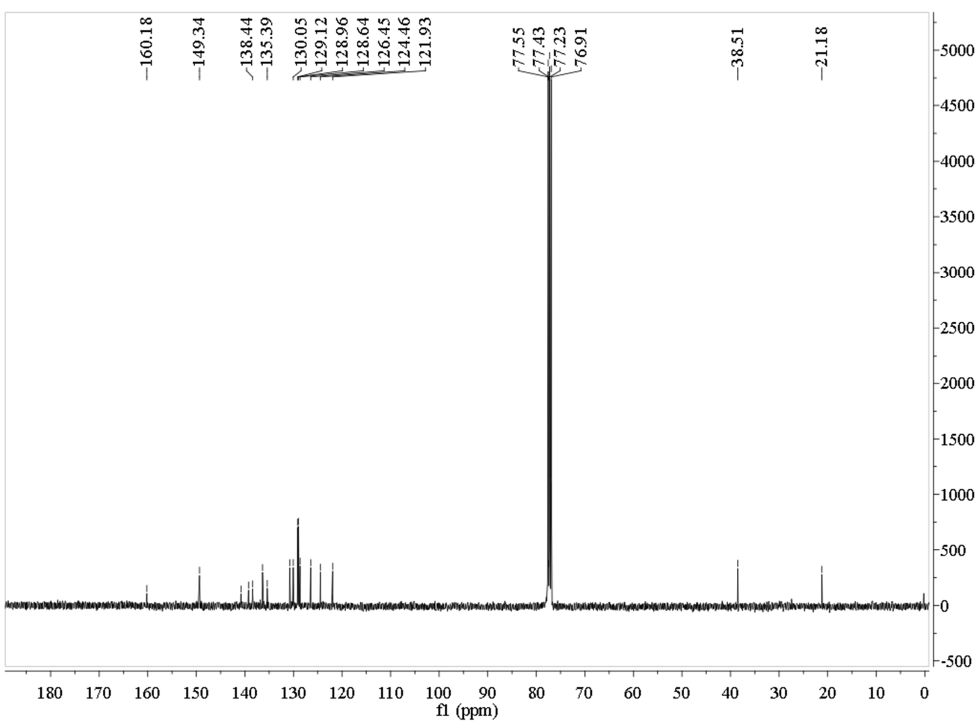
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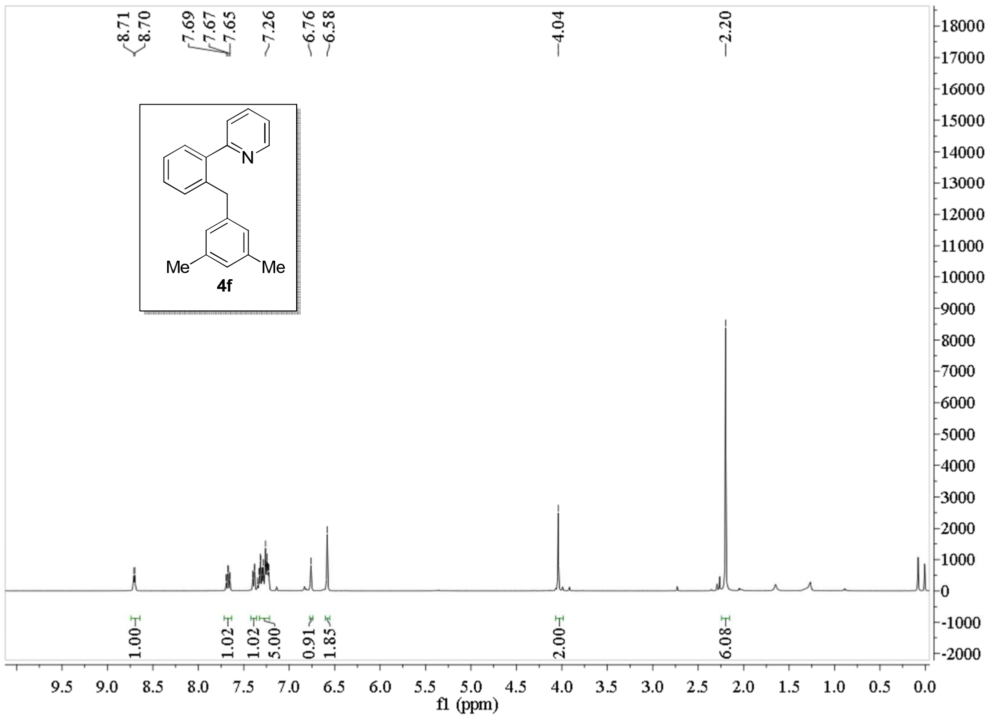
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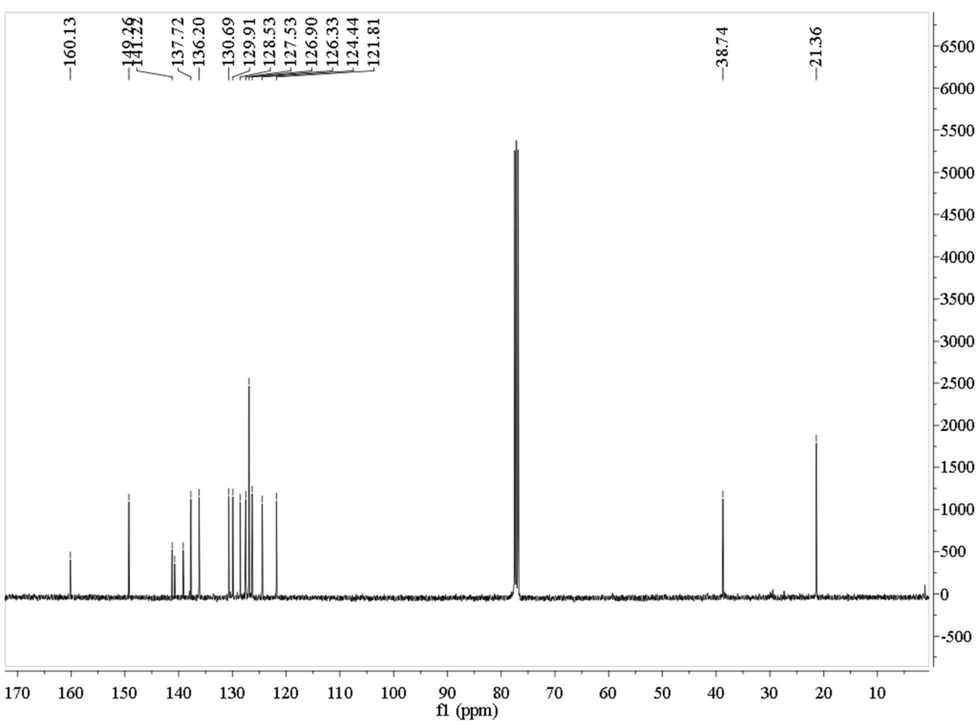
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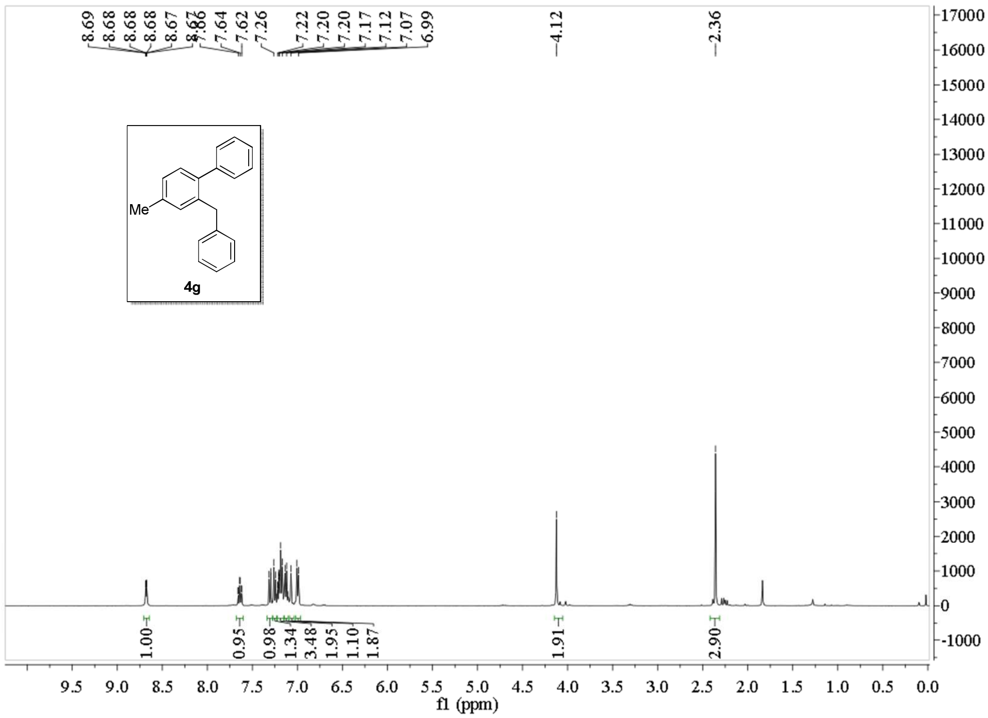
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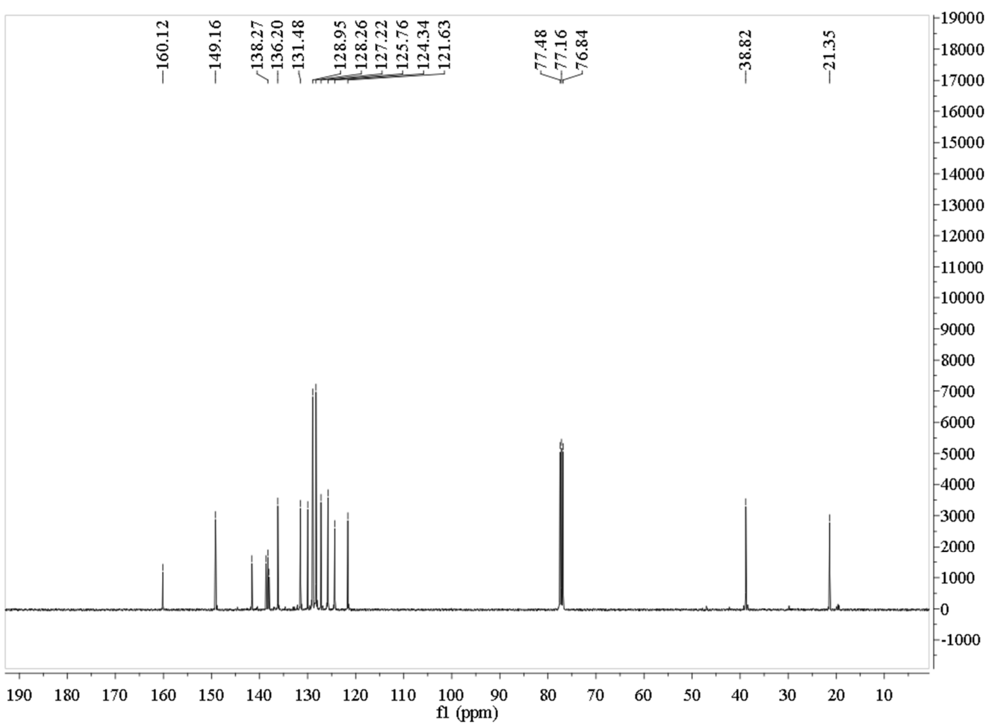
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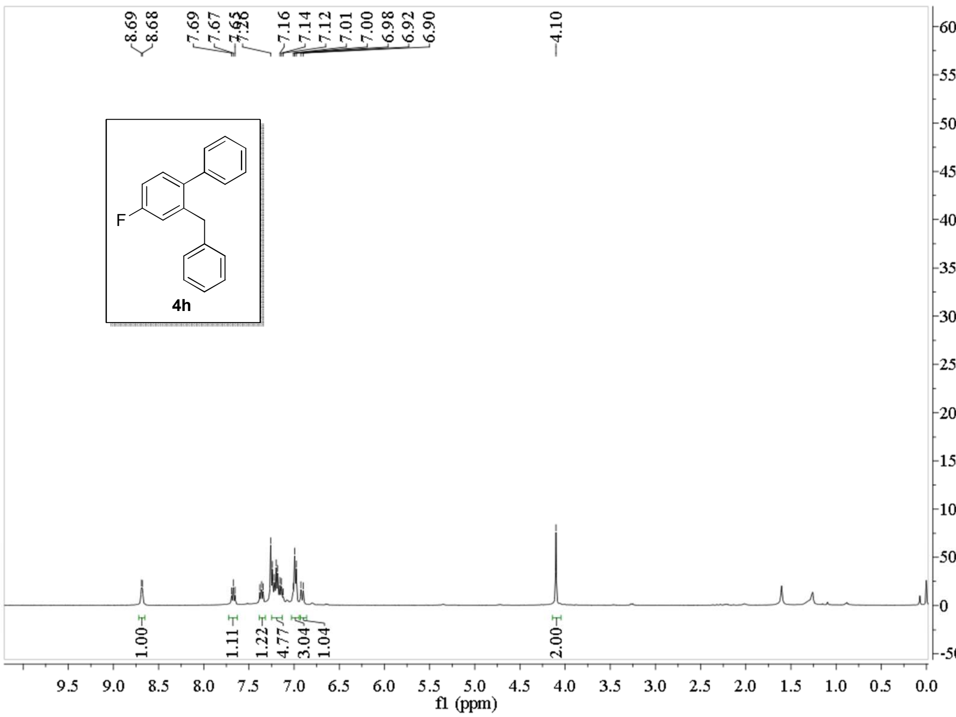
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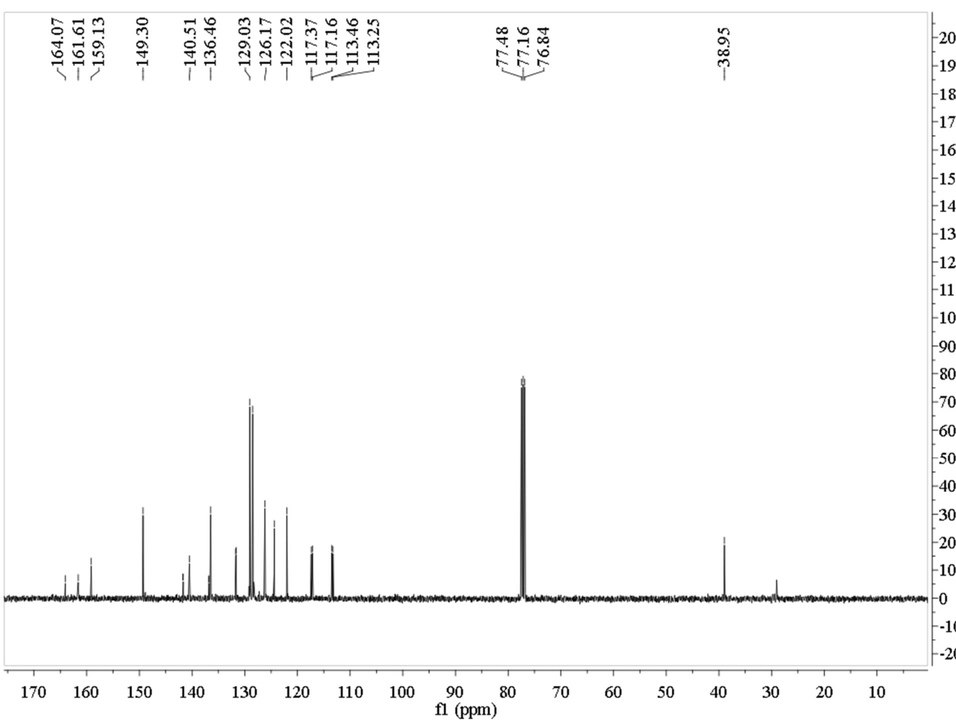
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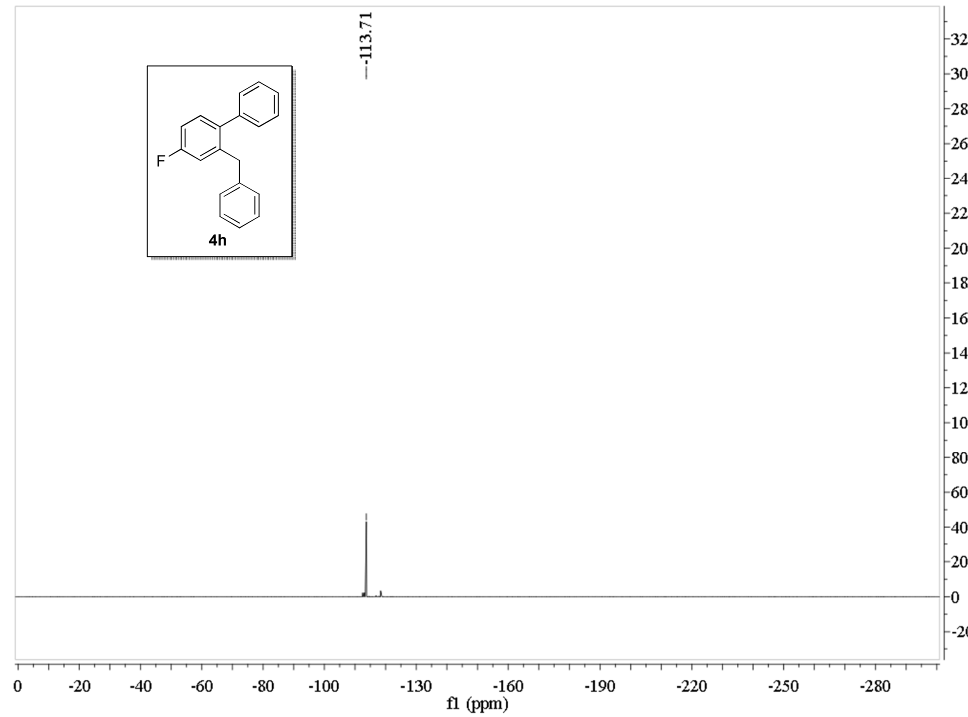
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2000
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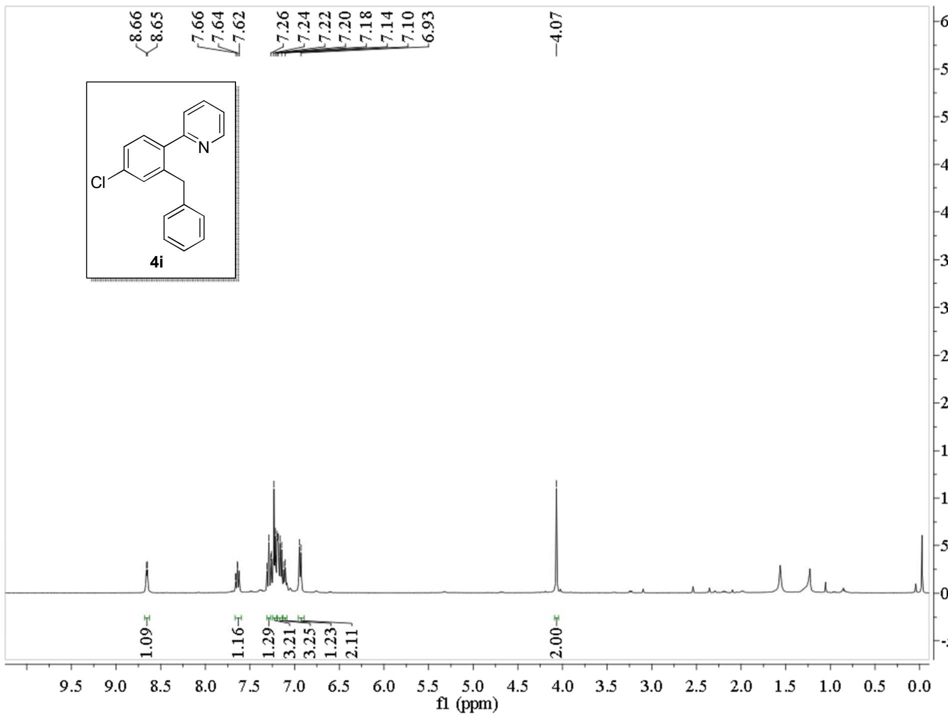
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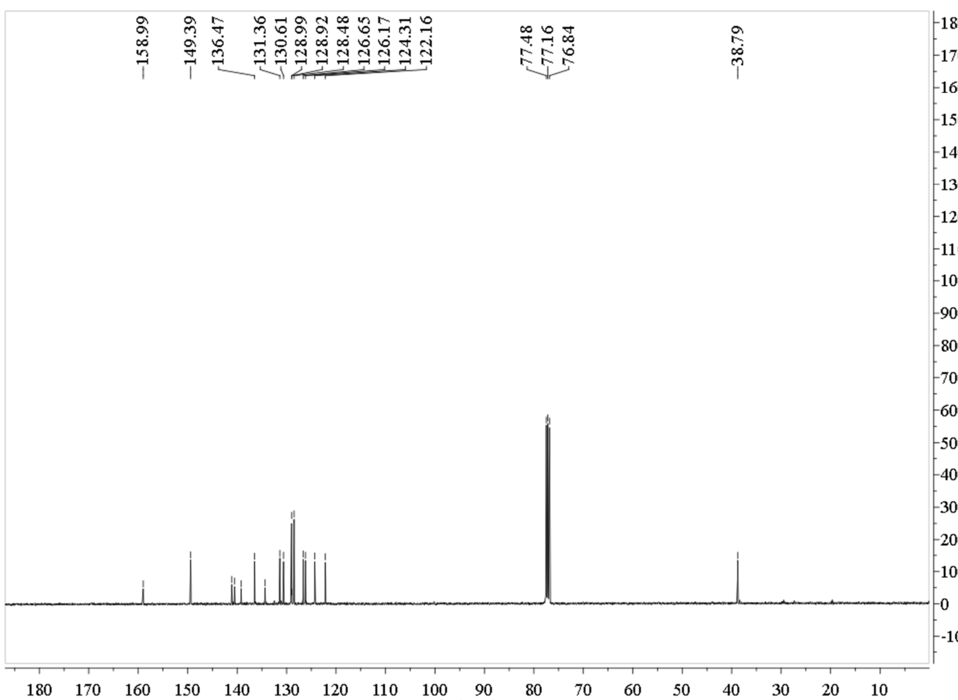
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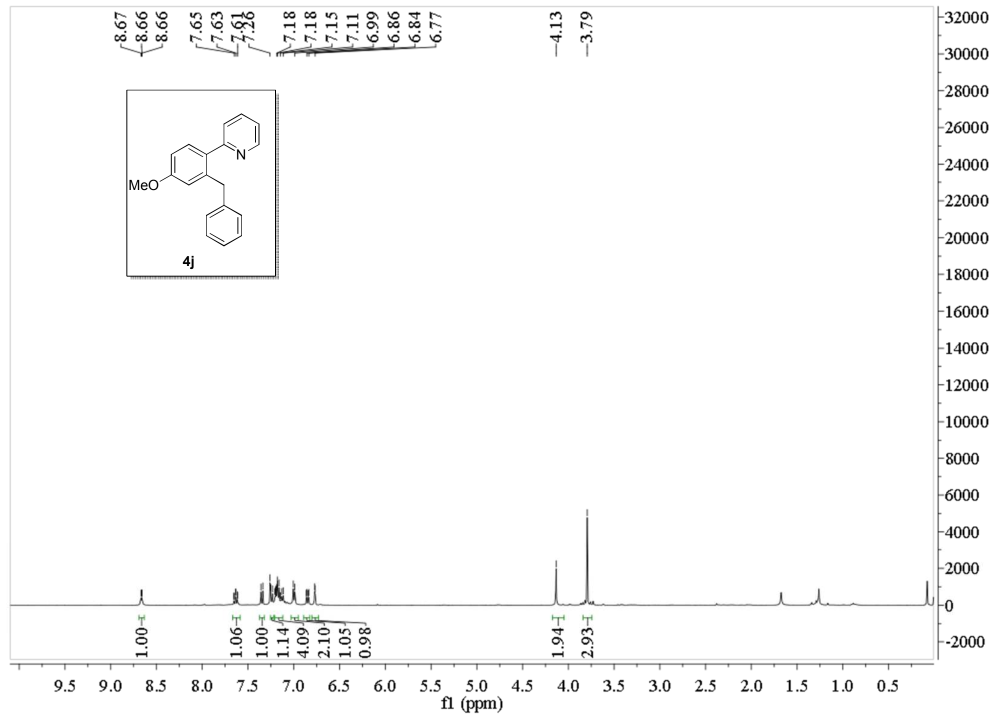
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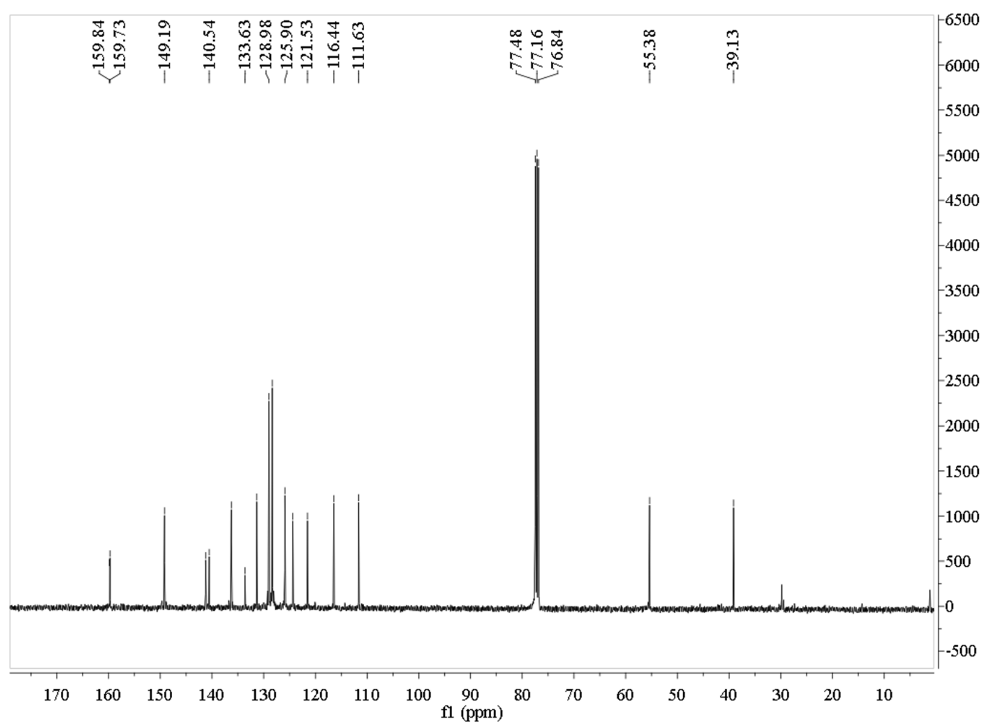
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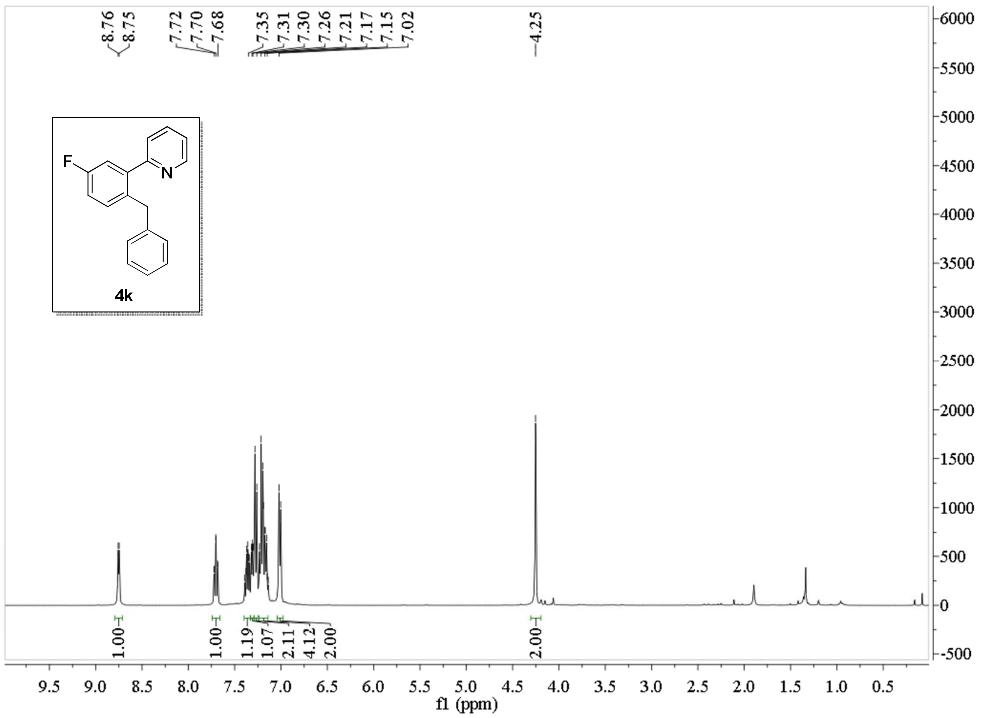
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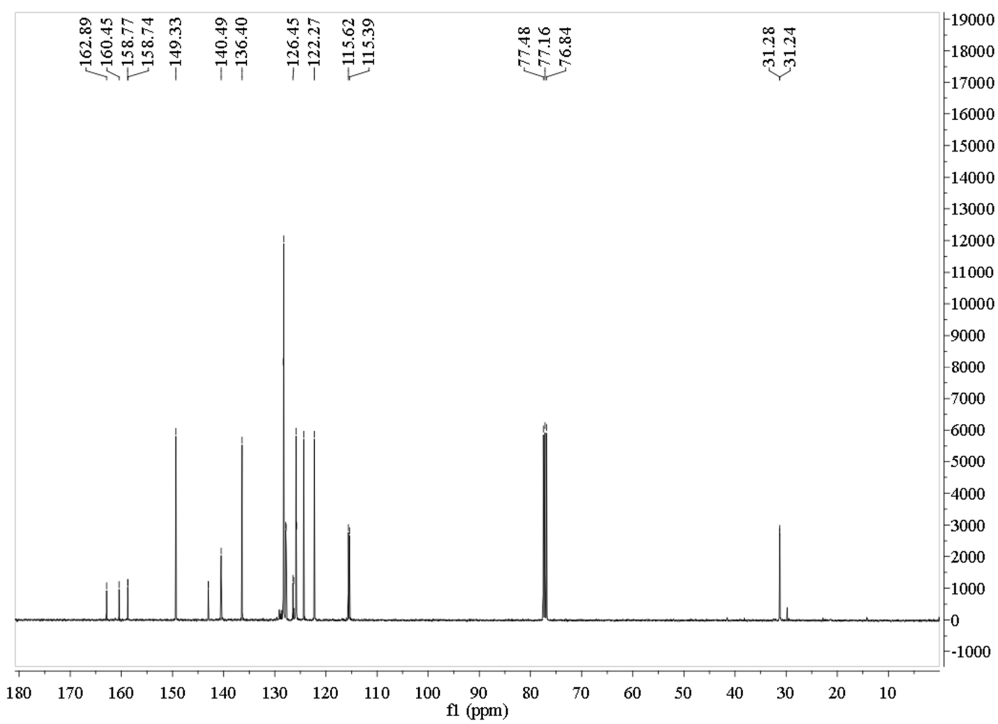
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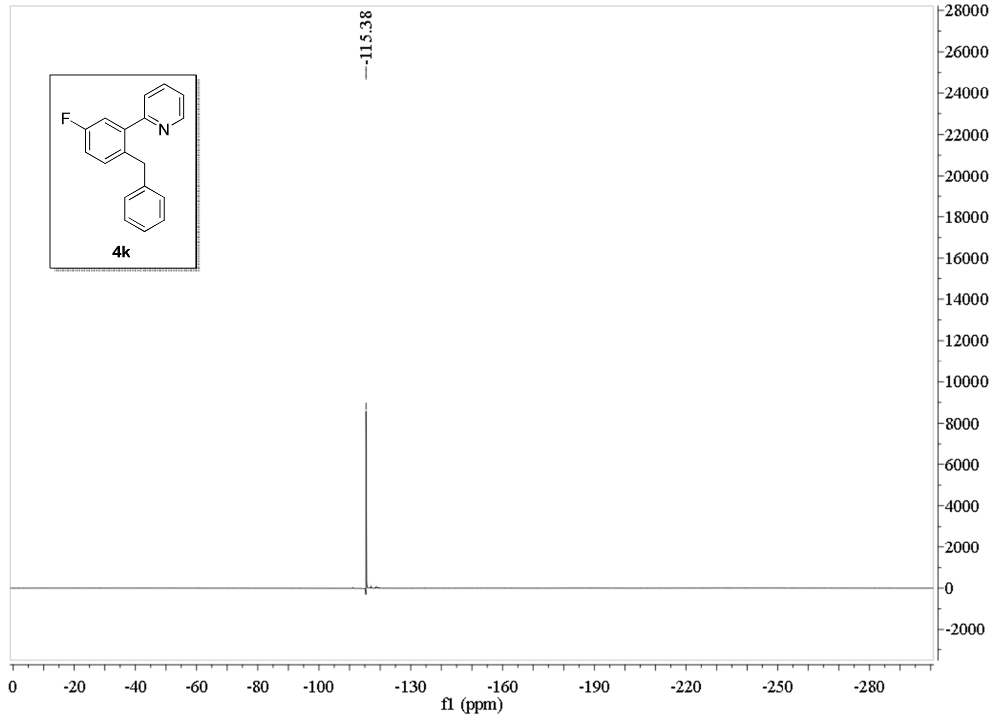
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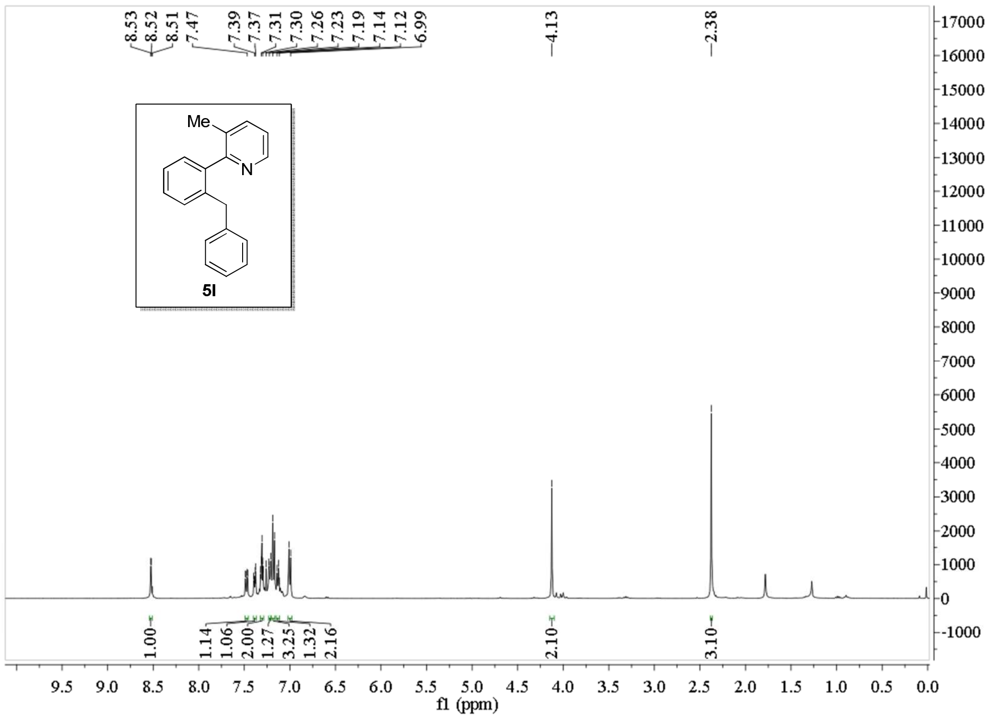
f1 (ppm)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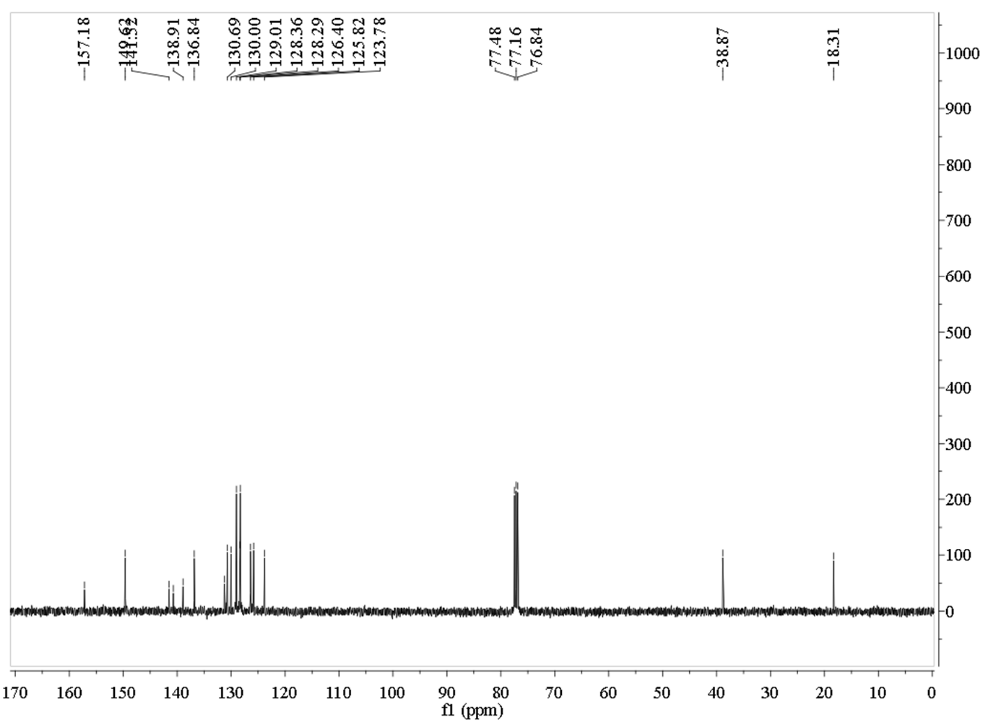
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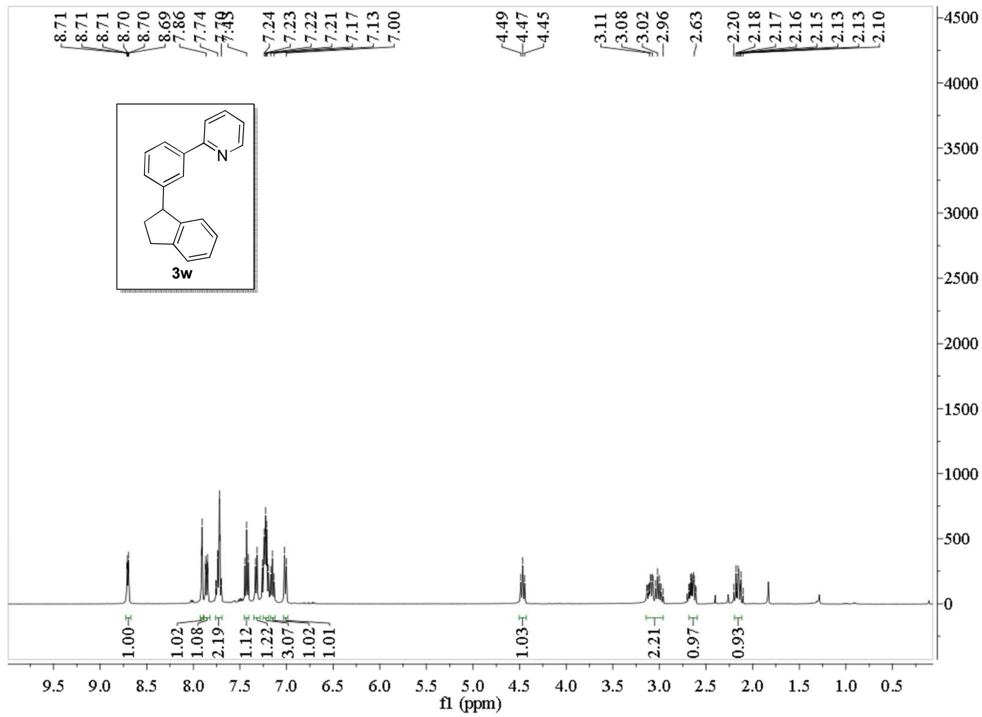
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3.11 3.08 3.02 2.96
2.63
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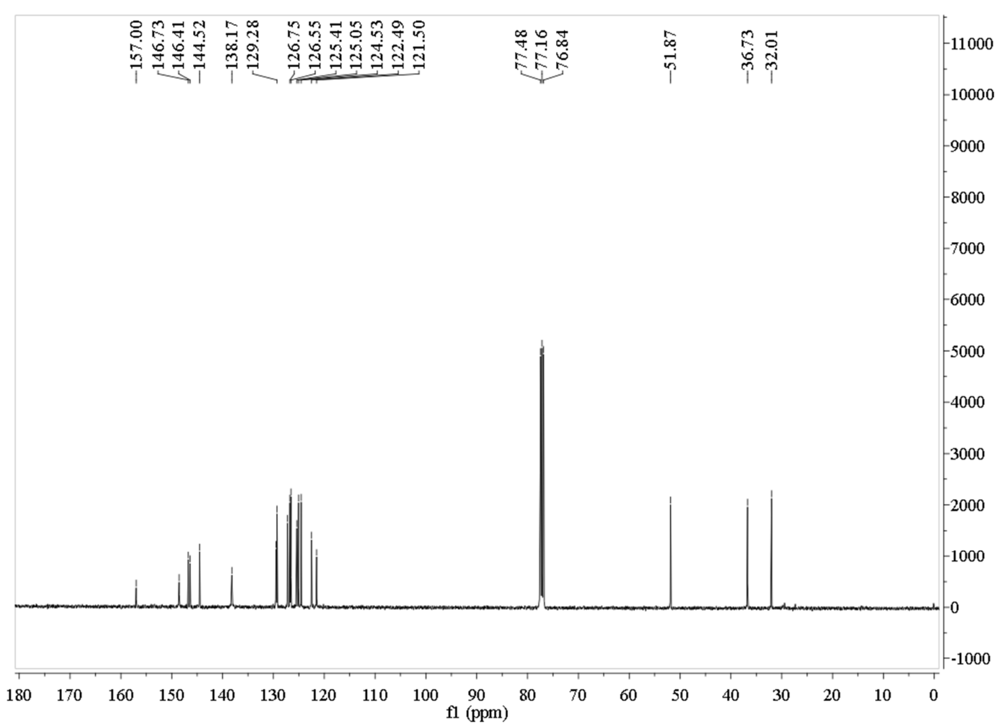
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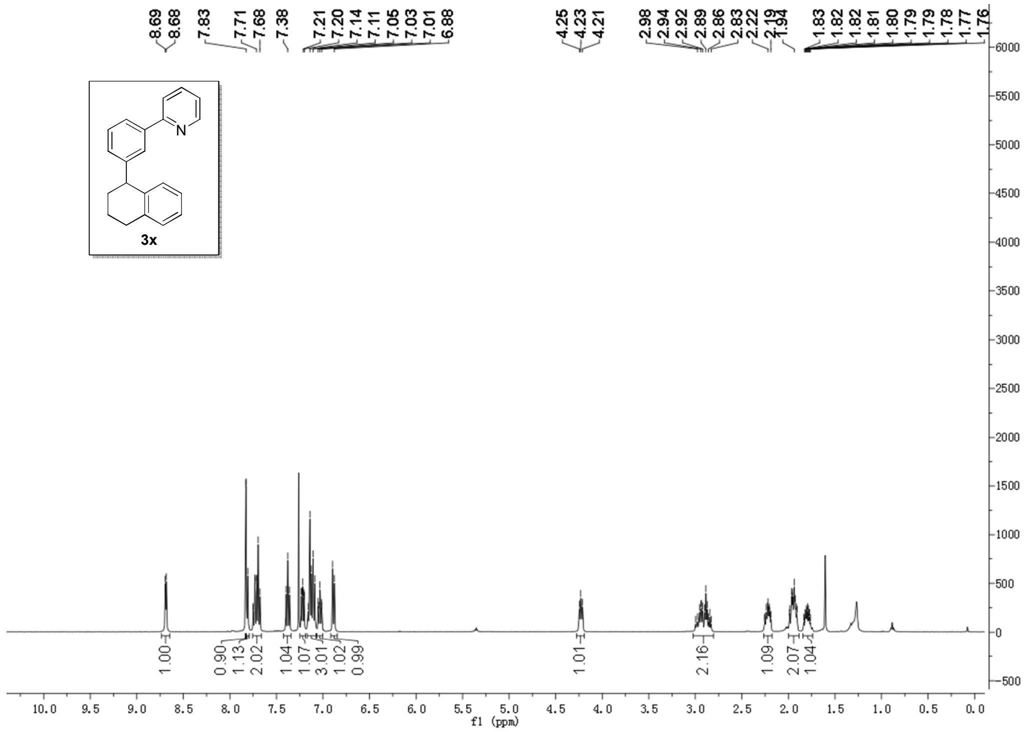
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1.94
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1.76
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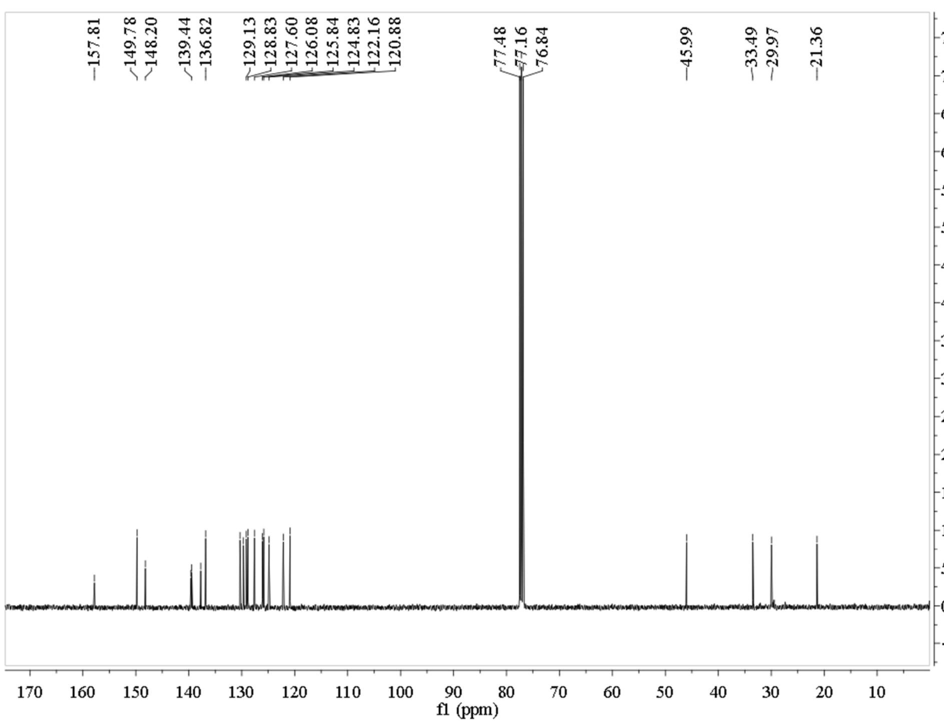
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21.36
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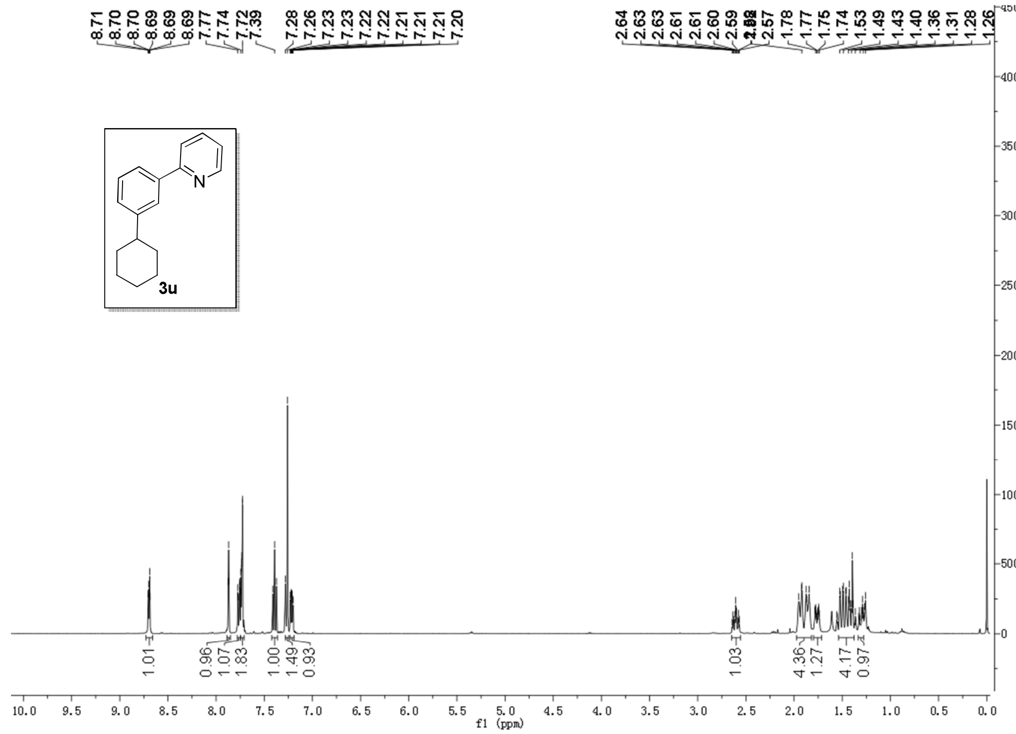
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2.64 2.63 2.63 2.61 2.61 2.60 2.59 2.57 1.78 1.77 1.75 1.74 1.53 1.49 1.43 1.40 1.36 1.31 1.28 1.26
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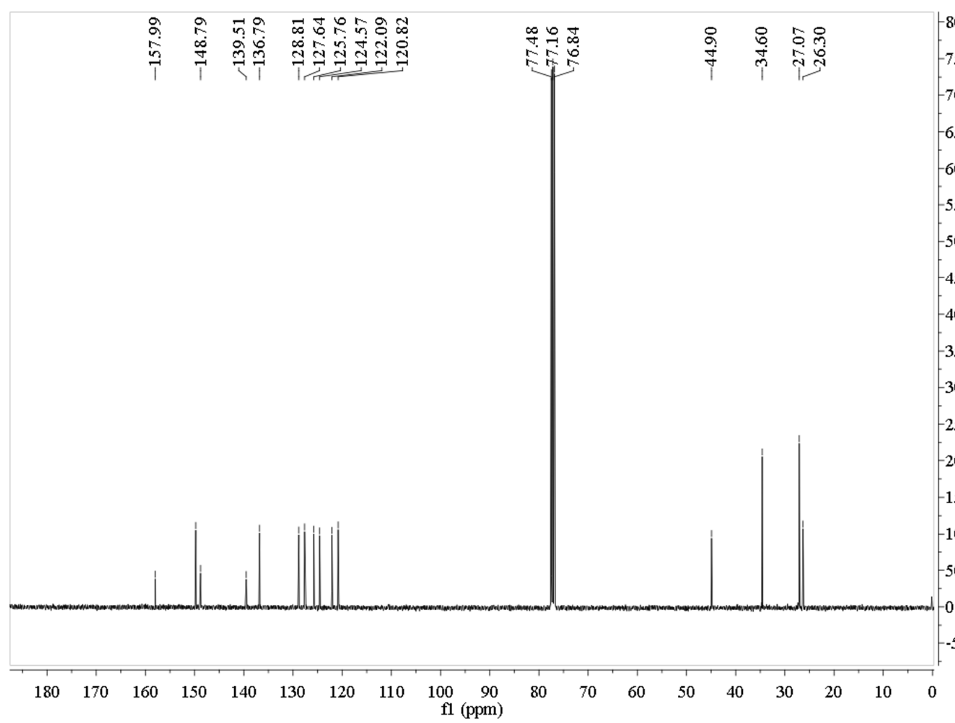
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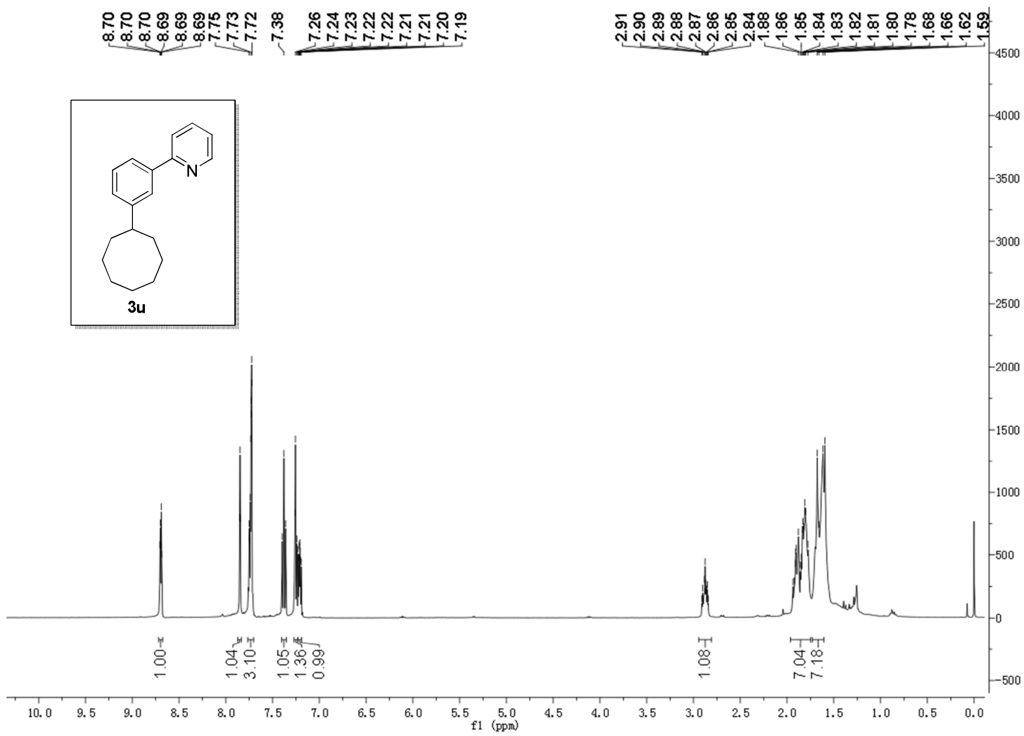

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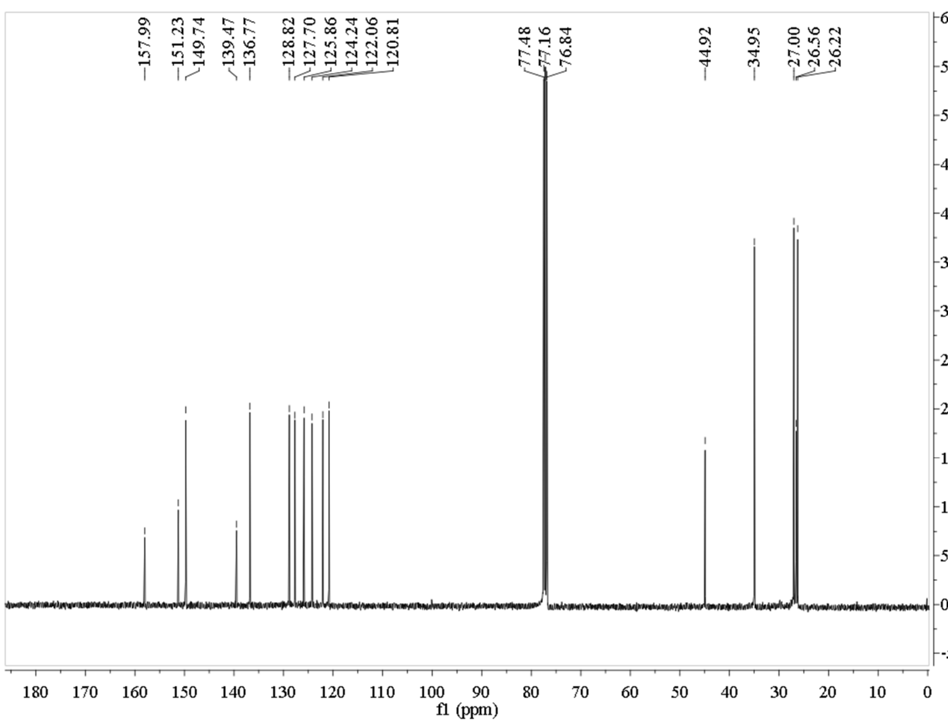
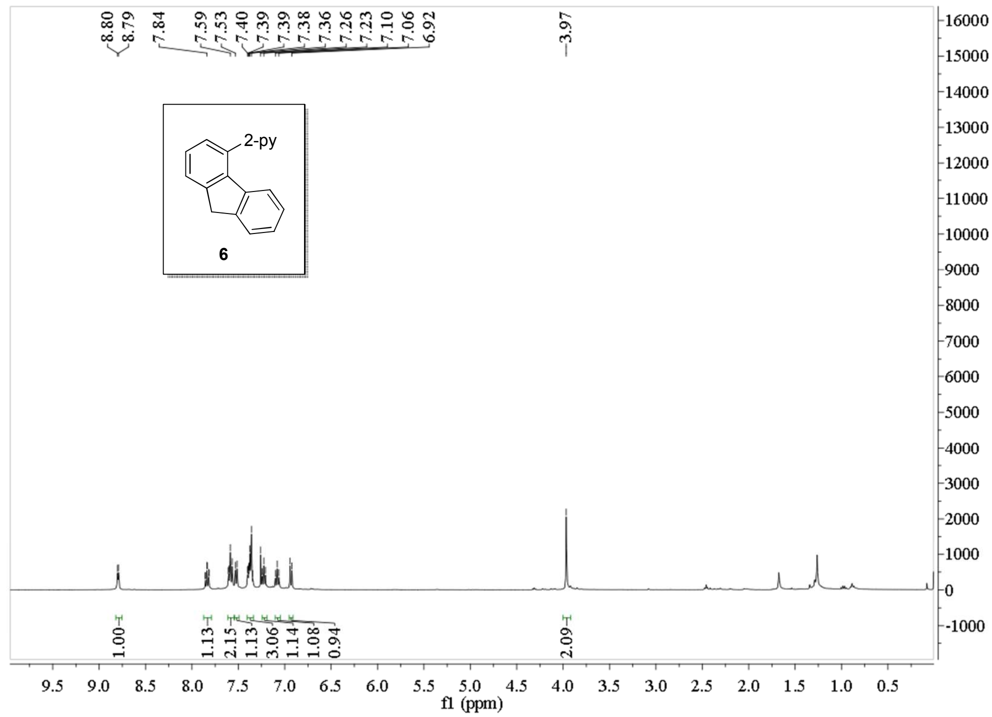
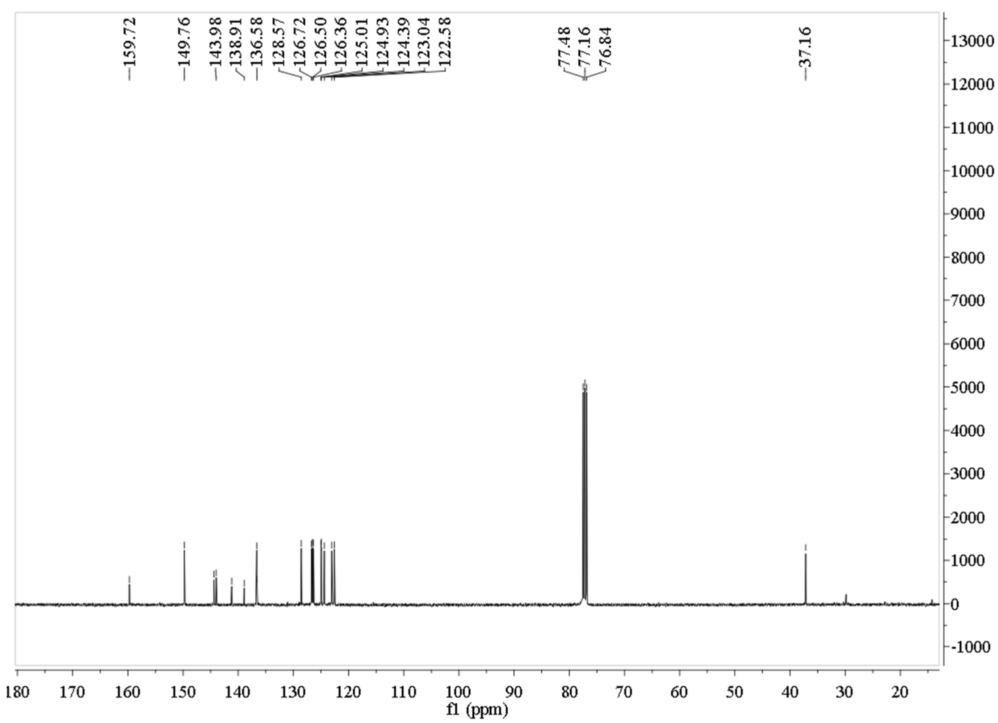
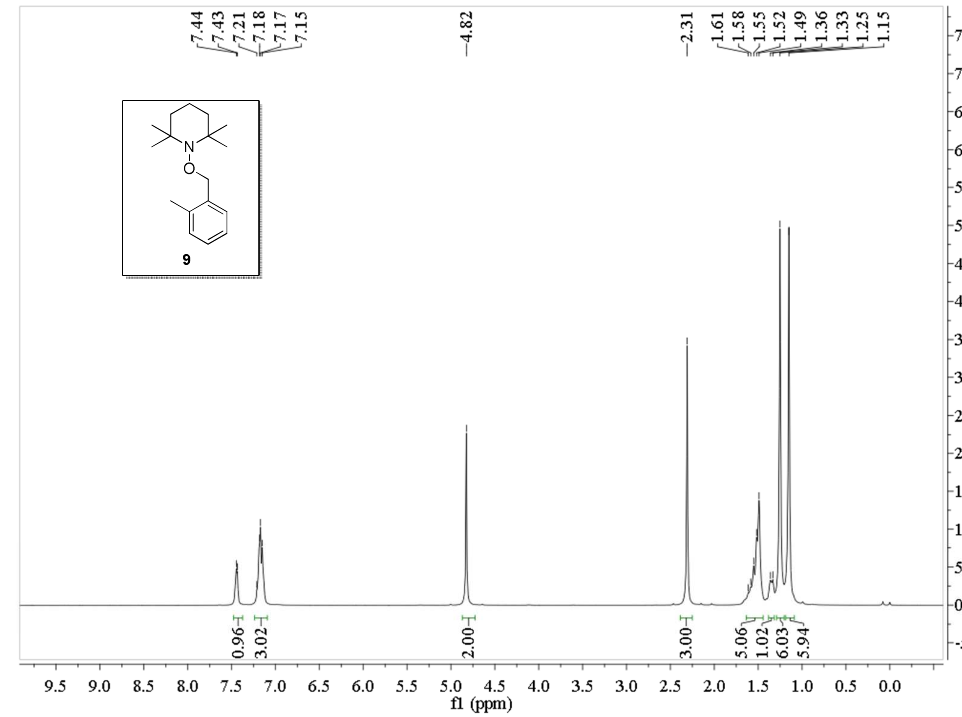
7.18
f1 (ppm)

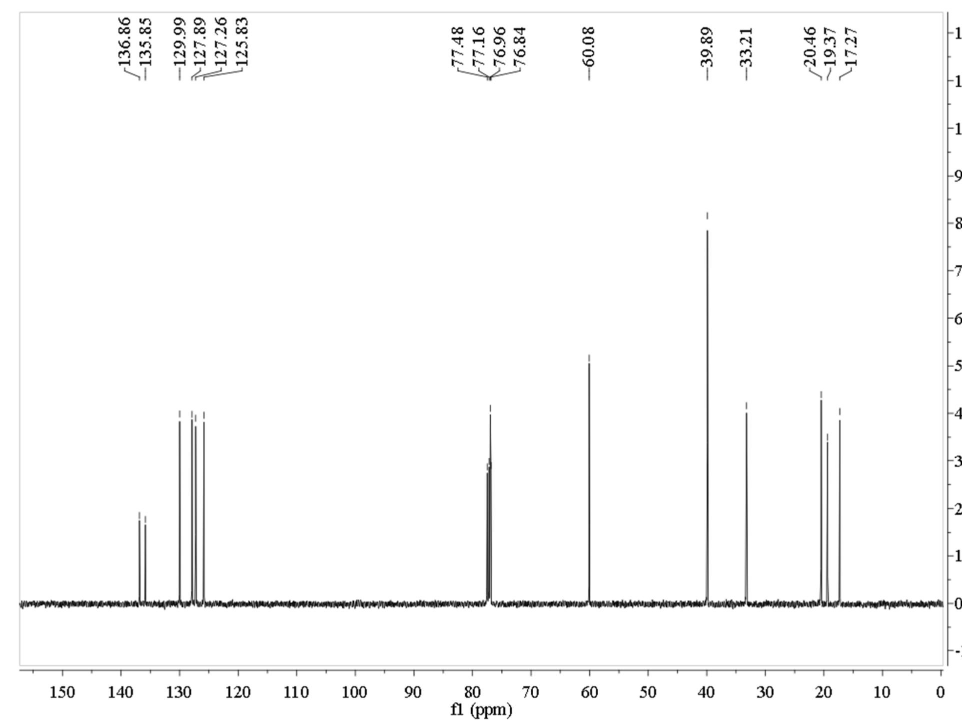


157.99
151.23
149.74
139.47
136.77
128.82
127.70
125.86
124.24
122.06
120.81
77.48
77.16
76.84
44.92
34.95
27.00
26.56
26.22
f1 (ppm)


8.80
8.79
7.84
7.59
7.53
7.40
7.39
7.39
7.38
7.36
7.26
7.23
7.10
7.06
6.92
3.97
2-py
6
1.00
1.13
2.15
1.13
3.06
1.14
1.08
0.94
2.09
f1 (ppm)


159.72
149.76
143.98
138.91
136.58
128.57
126.72
126.50
126.36
125.01
124.93
124.39
123.04
122.58
77.48
77.16
76.84
37.16
f1 (ppm)





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