Supporting Information:

DMF as amine source: iron-catalyzed cyclization of 2*H*-azirines to imidazoles

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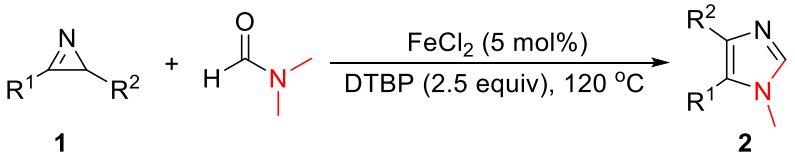
CONTENTS

1. General Information

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points were determined with a digital melting point measuring instrument. All products were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. The 2*H*-azirines were in all cases prepared from the corresponding ketoxime acetates according to following literature:

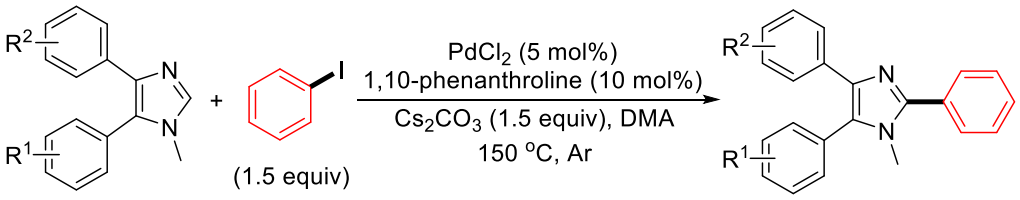
M.-N. Zhao, W. Zhang, X.-C. Wang, Y. Zhang, D.-S. Yang and Z.-H. Guan, *Org. Biomol. Chem.*, 2018, **16**, 4333-4337.

2. Typical Procedure for Cycloaddition of 2*H*-Azirines and *N*,*N*-Dimethylformamide



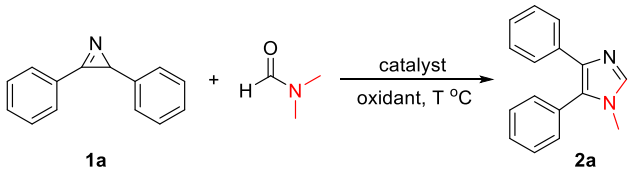
In a 25 mL round bottom flask, the 2*H*-azirines **1** (0.2 mmol), $FeCl_2$ (5 mol %, 1.27 mg) and DTBP (0.5 mmol, 73 mg) were stirred in *N*,*N*-dimethylformamide (2 mL) at 120 °C. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (25 mL) and washed with H_2O (20 mL). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding imidazoles **2** with petroleum ether/ethyl acetate (v/v = 2:1) as the eluent.

3. Synthesis of 1-Methyl-2,4,5-Triaryl-1*H*-Imidazoles from 1-Methyl-4,5-Diaryl-1*H*-Imidazoles and Aryl Iodides



In a 25 mL round bottom flask, the 1-methyl-4,5-diaryl-1*H*-imidazoles **2** (0.2 mmol), iodobenzene (0.3 mmol), $PdCl_2$ (5 mol%, 1.8 mg), 1,10-phenanthroline (10 mol%, 3.6 mg) and Cs_2CO_3 (0.3 mmol) were stirred in *N*,*N*-dimethylacetamide (1 mL) at 150 °C in argon. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, the resultant mixture poured into H_2O (20 mL) and extracted with EtOAc (25 mL). After the solvent was evaporated under vacuum, the crude product was purified by column chromatography on silica gel to afford the corresponding 1-methyl-2,4,5-triaryl-1*H*-imidazoles **3** with petroleum ether/ethyl acetate (v/v = 10:1) as the eluent.

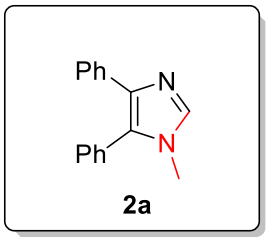
4. Optimization of the reaction conditions[a]



Entry	Catalyst	Oxidant	T (°C)	Yield (%)
1[b]	[M]		120	0
2	$FeCl_2$		120	33
3	$Fe(acac)_2$		120	27
4	$Fe(OTf)_2$		120	22
5[c]	$FeCl_2$	CHP	120	41
6	$FeCl_2$	$K_2S_2O_8$	120	trace
7	$FeCl_2$	$PhI(OAc)_2$	120	33
8	$FeCl_2$	TBHP	120	32
9	**$FeCl_2$**	**DTBP**	**120**	**68**
10	$FeCl_2$	DTBP	110	32
11	$FeCl_2$	DTBP	100	35
12	$FeCl_2$	DTBP	130	44
13	$FeCl_2$	DTBP	140	42
14	$FeCl_3$	DTBP	120	47
15	$Fe(acac)_3$	DTBP	120	49
16	$Fe(OTf)_3$	DTBP	120	50
17	$Fe_2(SO_4)_3$	DTBP	120	41

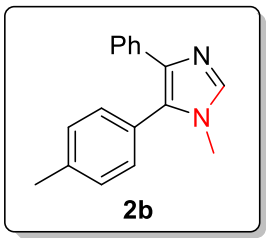
[a] Reaction condition: **1a** (0.2 mmol), DMF (2 mL), catalyst (5 mol%), oxidant (0.5 mmol), 12 h. [b] $Cu(OAc)_2$, CuI, $CuCl_2$, $[(C_6H_5)_3P]_3RhCl$, $C_8H_{12}Cl_2Ru$ or $C_{20}H_{28}Cl_4Ru_2$ were screened. [C] CHP = Cumyl Hydroperoxide.

5. Spectroscopic Data for Imidazoles



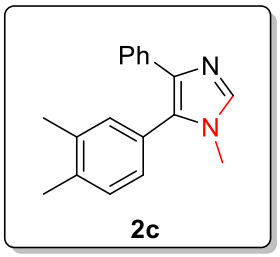
2a

2a: Yield 68% (31.8 mg); Yellow solid; mp 141-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.49-7.43 (m, 5H), 7.34-7.31 (m, 2H), 7.22-7.11 (m, 3H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.4, 134.6, 130.6, 130.6, 128.9, 128.9, 128.5, 128.0, 126.6, 126.2, 32.1. HRMS Calcd (ESI) m/z for $C_{16}H_{14}N_2$: $[M+Na]^+$ 257.1049. Found: 257.1054.



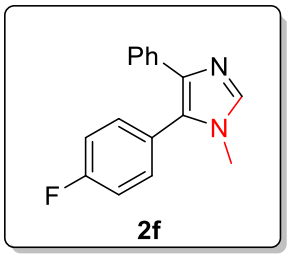
2b

2b: Yield 53% (26.3 mg); Yellow solid; mp 113-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.51-7.48 (m, 2H), 7.26-7.18 (m, 6H), 7.15-7.11 (m, 1H), 3.46 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.0, 137.3, 134.7, 130.5, 129.7, 128.8, 128.1, 127.5, 126.5, 126.2, 32.1, 21.3. HRMS Calcd (ESI) m/z for $C_{17}H_{16}N_2$: $[M+H]^+$ 249.1386. Found: 249.1389.



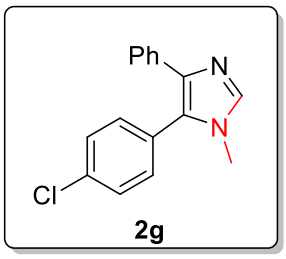
2c

2c: Yield 50% (26.2 mg); Yellow solid; mp 110-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 3H), 7.15-7.04 (m, 3H), 3.46 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.2, 137.1, 134.8, 131.6, 130.7, 130.2, 128.9, 128.1, 128.0, 128.0, 126.4, 126.1, 32.1, 19.8, 19.7. HRMS Calcd (ESI) m/z for $C_{18}H_{18}N_2$: $[M+Na]^+$ 285.1362. Found: 285.1365.



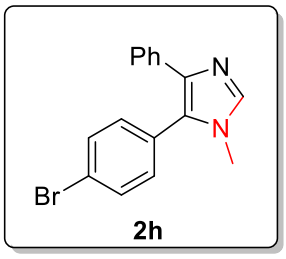
2f

2f: Yield 50% (25.2 mg); Yellow solid; mp 142-143 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.45-7.43 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 2H), 7.17-7.13 (m, 3H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.7, 138.3, 137.6, 134.1, 132.6 (d, J_{CF} = 8.0 Hz), 128.2, 126.7, 126.6, 126.4 (d, J_{CF} = 3.0 Hz), 116.3 (d, J_{CF} = 21.0 Hz), 32.2 (s). HRMS Calcd (ESI) m/z for $C_{16}H_{13}FN_2$: $[M+H]^+$ 253.1136. Found: 253.1136.



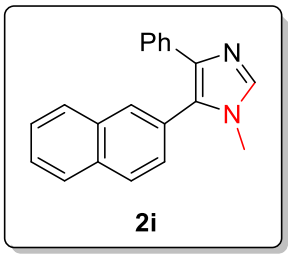
2g

2g: Yield 52% (27.9 mg); Yellow solid; mp 154-156 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.46-7.42 (m, 4H), 7.28-7.16 (m, 5H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.7, 134.7, 134.2, 131.9, 129.3, 129.0, 128.2, 127.6, 126.7, 126.6, 32.2. HRMS Calcd (ESI) m/z for $C_{16}H_{13}ClN_2$: $[M+H]^+$ 269.0840. Found: 269.0849.



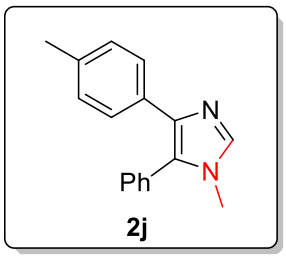
2h

2h: Yield 47% (29.3 mg); Yellow solid; mp 152-154 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 3H), 7.47-7.45 (m, 2H), 7.25-7.14 (m, 5H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.8, 134.3, 132.3, 132.2, 129.5, 128.2, 127.5, 126.7, 126.6, 122.9, 32.2. HRMS Calcd (ESI) m/z for $C_{16}H_{13}BrN_2$: $[M+H]^+$ 313.0335. Found: 313.0340.



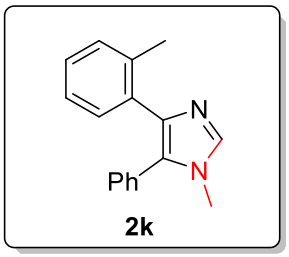
2i

2i: Yield 44% (25.0 mg); Brown solid; mp 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.84-7.82 (m, 2H), 7.62 (s, 1H), 7.57-7.50 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.18-7.11 (m, 3H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.6, 134.6, 133.4, 133.1, 129.9, 128.7, 128.1, 128.1, 128.1, 127.8, 126.7, 126.7, 126.5, 126.4, 32.3. HRMS Calcd (ESI) m/z for $C_{20}H_{16}N_2$: $[M+H]^+$ 285.1386. Found: 285.1391.



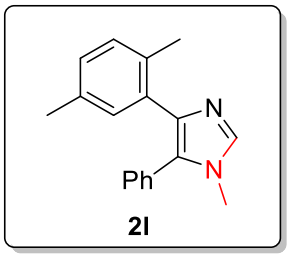
2j

2j: Yield 51% (25.3 mg); Yellow solid; mp 106-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.45-7.43 (m, 3H), 7.38-7.32 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.48 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.3, 135.9, 131.8, 130.7, 130.7, 129.7, 128.9, 128.8, 128.5, 126.5, 32.2, 21.1. HRMS Calcd (ESI) m/z for $C_{17}H_{16}N_2$: $[M+Na]^+$ 271.1206. Found: 271.1205.



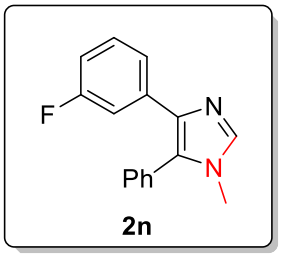
2k

2k: Yield 35% (17.4 mg); Yellow solid; mp 49-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.34-7.28 (m, 3H), 7.20-7.11 (m, 5H), 7.09-7.05 (m, 1H), 3.64 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.0, 137.3, 134.7, 130.5, 129.7, 128.9, 128.9, 128.8, 128.1, 127.5, 126.5, 126.2, 32.1, 21.3. HRMS Calcd (ESI) m/z for $C_{17}H_{16}N_2$: $[M+Na]^+$ 271.1206. Found: 271.1206.



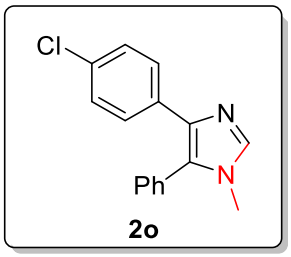
2l

2l: Yield 45% (23.6 mg); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.33-7.27 (m, 3H), 7.17-7.15 (m, 2H), 7.10 (s, 1H), 6.99-6.94 (m, 2H), 3.63 (s, 3H), 2.23 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.5, 134.5, 134.0, 133.5, 131.5, 130.2, 129.9, 129.6, 128.5, 128.0, 127.6, 125.4, 32.7, 20.8, 19.6. HRMS Calcd (ESI) m/z for $C_{18}H_{18}N_2$: $[M+Na]^+$ 285.1362. Found: 285.1359.



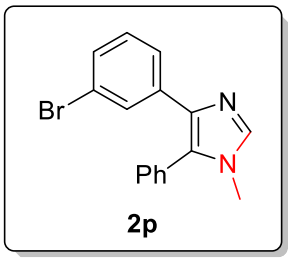
2n

2n: Yield 78% (39.3 mg); Yellow solid; mp 90-91 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.48-7.45 (m, 3H), 7.34-7.31 (m, 2H), 7.25-7.19 (m, 2H), 7.16-7.10 (m, 1H), 6.84-6.79 (m, 1H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 137.4, 136.9 (d, J_{CF} = 2.0 Hz), 136.8 (d, J_{CF} = 9.0 Hz), 130.5, 130.1, 129.5 (d, J_{CF} = 9.0 Hz), 129.1, 128.9, 122.0 (d, J_{CF} = 2.0 Hz), 113.3, 113.1 (d, J_{CF} = 3.0 Hz), 112.9, 32.12. HRMS Calcd (ESI) m/z for $C_{16}H_{13}FN_2$: $[M+Na]^+$ 275.0955. Found: 275.0966.



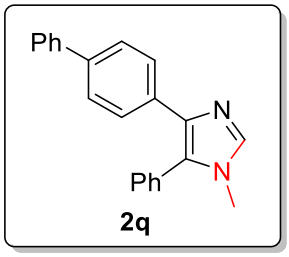
2o

2o: Yield 56% (30.0 mg); Yellow solid; mp 64-65 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.46 (dd, J = 8.0, 4.0 Hz, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.32-7.30 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 137.1, 133.0, 132.1, 130.6, 130.2, 129.1, 128.9, 128.3, 127.9, 32.2. HRMS Calcd (ESI) m/z for $C_{16}H_{13}ClN_2$: $[M+H]^+$ 269.0840. Found: 269.0846.



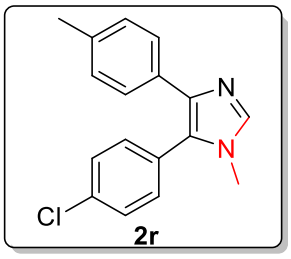
2p

2p: Yield 63% (39.3 mg); Yellow solid; mp 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 4.0 Hz, 1H), 7.56 (s, 1H), 7.48-7.45 (m, 3H), 7.33-7.29 (m, 3H), 7.24 (m, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.8, 136.8, 130.6, 130.1, 129.6, 129.5, 129.2, 129.1, 128.9, 124.9, 122.4, 32.2. HRMS Calcd (ESI) m/z for $C_{16}H_{13}BrN_2$: $[M+Na]^+$ 335.0154. Found: 335.0151.



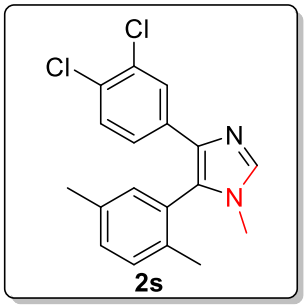
2q

2q: Yield 35% (21.7 mg); Yellow solid; mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 4H), 7.47-7.44 (m, 5H), 7.40-7.36 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 3.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 138.9, 137.5, 133.7, 131.0, 130.7, 130.6, 128.7, 128.6, 128.2, 127.6, 127.0, 126.9, 126.9, 126.8, 126.8, 32.2. HRMS Calcd (ESI) m/z for $C_{22}H_{18}N_2$: $[M+Na]^+$ 333.1362. Found: 333.1362.



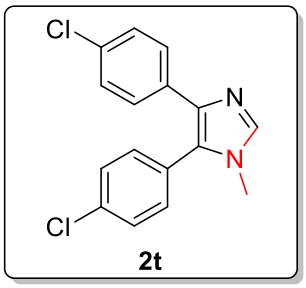
2r

2r: Yield 34% (19.2 mg); Yellow solid; mp 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.43-7.41 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.48 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.7, 136.3, 134.7, 132.0, 131.3, 129.3, 129.1, 129.0, 127.2, 126.7, 32.2, 21.1. HRMS Calcd (ESI) m/z for $C_{17}H_{15}ClN_2$: $[M+Na]^+$ 305.0816. Found: 305.0811.



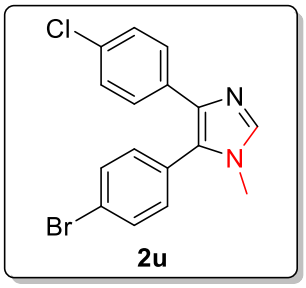
2s

2s: Yield 35% (23.1 mg); Yellow solid; mp 45-46 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.58 (s, 1H), 7.24-7.19 (m, 3H), 7.15 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.03 (s, 1H), 3.36 (s, 3H), 2.36 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.3, 135.6, 135.3, 135.1, 132.3, 131.4, 130.7, 130.5, 130.1, 129.6, 129.3, 129.1, 127.3, 124.4. HRMS Calcd (ESI) m/z for $C_{18}H_{16}Cl_2N_2$: $[M+Na]^+$ 353.0583. Found: 353.0588.



2t

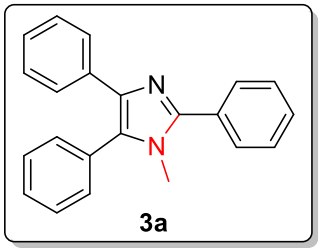
2t: Yield 57% (34.4 mg); Yellow solid; mp 150-151 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.0, 132.7, 132.3, 131.9, 131.2, 129.5, 128.6, 128.5, 128.4, 127.9, 32.2. HRMS Calcd (ESI) m/z for $C_{16}H_{12}Cl_2N_2$: $[M+H]^+$ 303.0450. Found: 303.0457.



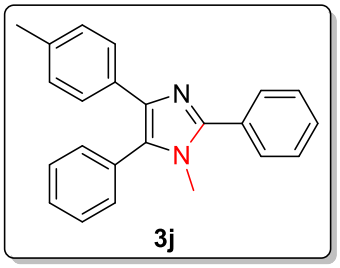
2u

2u: Yield 60% (41.5 mg); Yellow solid; mp 144-145 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.20-7.18 (m, 4H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 132.8, 132.4, 132.4, 132.4, 132.1, 129.2, 128.4, 127.9, 123.2, 32.2. HRMS Calcd (ESI) m/z for $C_{16}H_{12}BrClN_2$: $[M+H]^+$

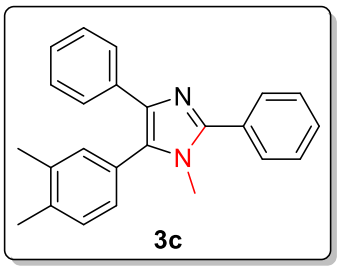
346.9945. Found: 346.9954.



3a: Yield 82% (51.1 mg); White solid; mp 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52-7.41 (m, 8H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 1H), 3.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.75, 137.64, 134.60, 131.13, 130.82, 130.35, 128.93, 128.52, 127.95, 126.84, 126.18, 33.01. HRMS Calcd (ESI) m/z for $C_{22}H_{18}N_2$: $[M+Na]^+$ 333.1362. Found: 333.1356.

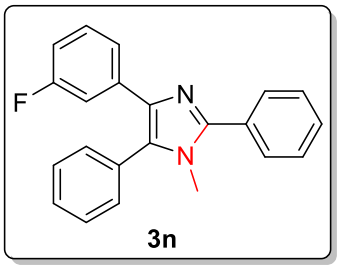


3j: Yield 63% (40.8 mg); Yellow solid; mp 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.51-7.41 (m, 10H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.50 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.73, 137.81, 135.84, 131.74, 131.36, 130.89, 130.00, 129.73, 129.17, 128.34, 126.86, 33.09, 21.13. HRMS Calcd (ESI) m/z for $C_{23}H_{20}N_2$: $[M+H]^+$ 325.1699. Found: 325.1702.



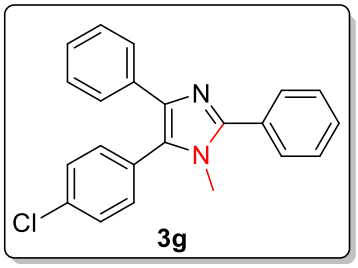
3c: Yield 60% (51.1 mg); Yellow solid; mp 87-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.51-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.24-7.19 (m, 4H), 7.15-7.14 (m, 2H), 3.49 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.56, 137.44, 137.01, 134.72, 131.78, 130.98, 130.65, 130.23, 129.05, 128.49, 127.97, 126.83, 126.12, 33.04, 19.72. HRMS Calcd

(ESI) m/z for $C_{24}H_{22}N_2$: $[M+Na]^+$ 361.1675. Found: 361.1676.



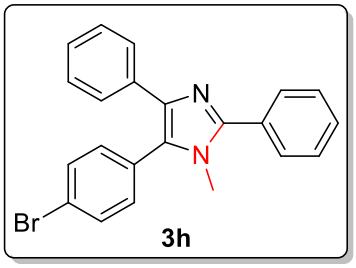
3n

3n: Yield 61% (40.0 mg); Yellow solid; mp 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.52-7.40 (m, 8H), 7.31-7.28 (m, 2H), 7.17-7.12 (m, 1H), 6.85-6.80 (m, 1H), 3.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 147.9, 137.0 (d, *J* =8.0 Hz), 136.5 (d, *J* = 3.0 Hz), 130.9, 130.8, 130.8, 129.4, 129.3, 129.1, 129.0, 128.9 (d, *J* = 2.0 Hz), 128.6, 122.3 (d, *J* = 3.0 Hz), 113.6 (d, *J* = 22.0 Hz), 113.1 (d, *J* = 21.0 Hz), 33.1. HRMS Calcd (ESI) m/z for $C_{22}H_{17}FN_2$: $[M+Na]^+$ 351.1268. Found: 351.1264.



3g

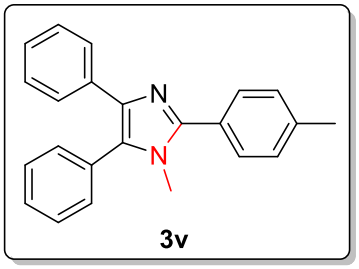
3g: Yield 70% (48.2 mg); White solid; mp 166-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.55-7.44 (m, 7H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19-7.15 (m, 1H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.25, 138.16, 134.67, 134.28, 132.15, 130.69, 129.90, 129.62, 129.35, 128.97, 128.58, 128.15, 127.06, 126.55, 33.15. HRMS Calcd (ESI) m/z for $C_{22}H_{17}ClN_2$: $[M+Na]^+$ 367.0973. Found: 361.0972.



3h

3h: Yield 62% (48.1 mg); Yellow solid; mp 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.51-7.40 (m, 6H), 7.24-7.13 (m,

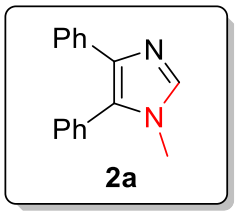
4H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.30, 138.14, 134.20, 132.35, 130.86, 129.98, 128.99, 128.57, 128.16, 127.10, 126.59, 122.88, 33.17. HRMS Calcd (ESI) m/z for $C_{22}H_{17}BrN_2$: $[M+H]^+$ 389.0648. Found: 389.0651.

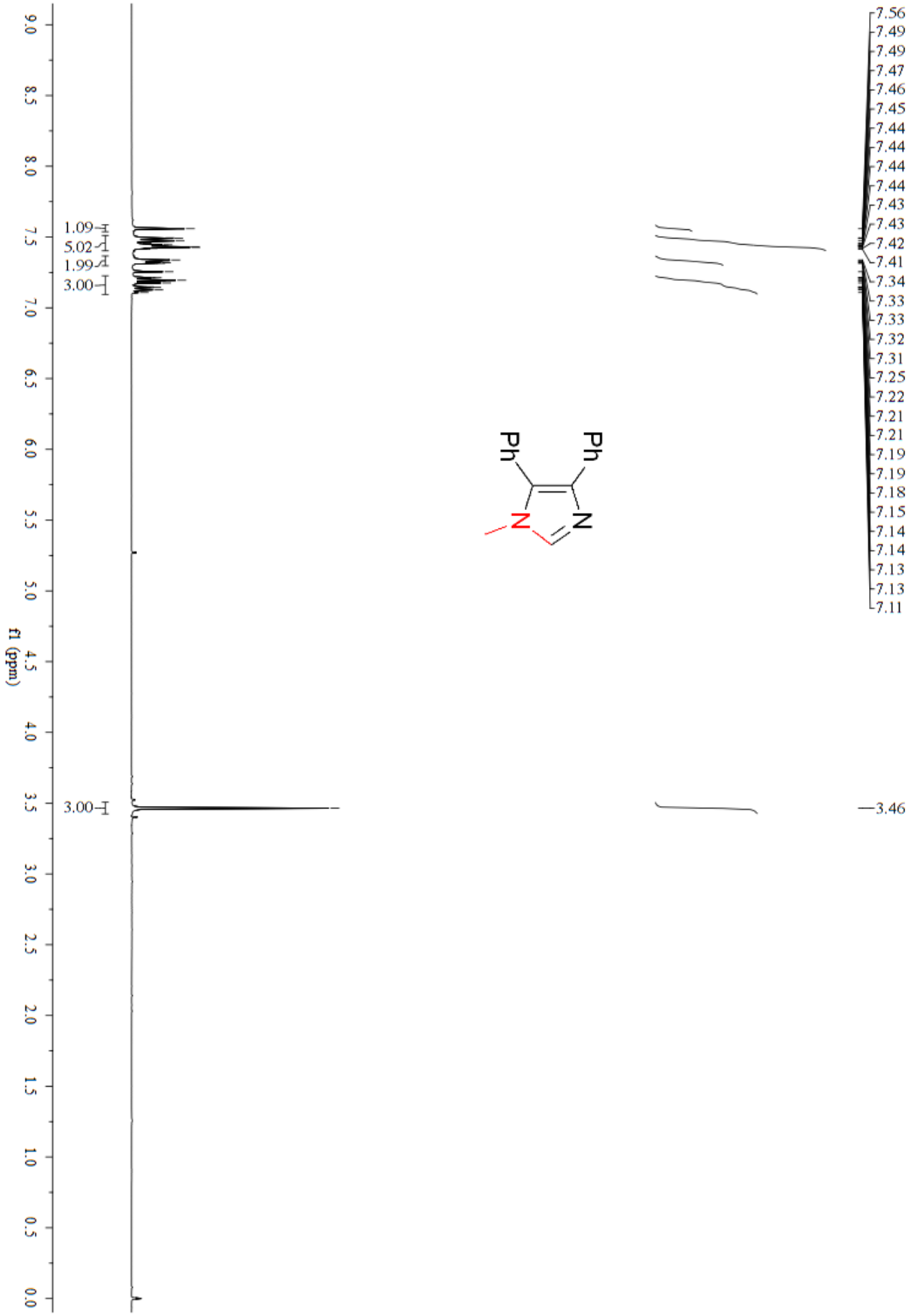


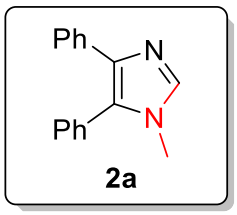
3v

3v: Yield 65% (42.1 mg); Yellow solid; mp 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51-7.38 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (m, 3H), 3.49 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.97, 138.64, 137.56, 134.67, 131.28, 130.84, 130.24, 129.20, 128.93, 128.45, 128.01, 126.93, 126.20, 33.08, 21.33. HRMS Calcd (ESI) m/z for $C_{23}H_{20}N_2$: $[M+Na]^+$ 347.1516. Found: 347.1516.

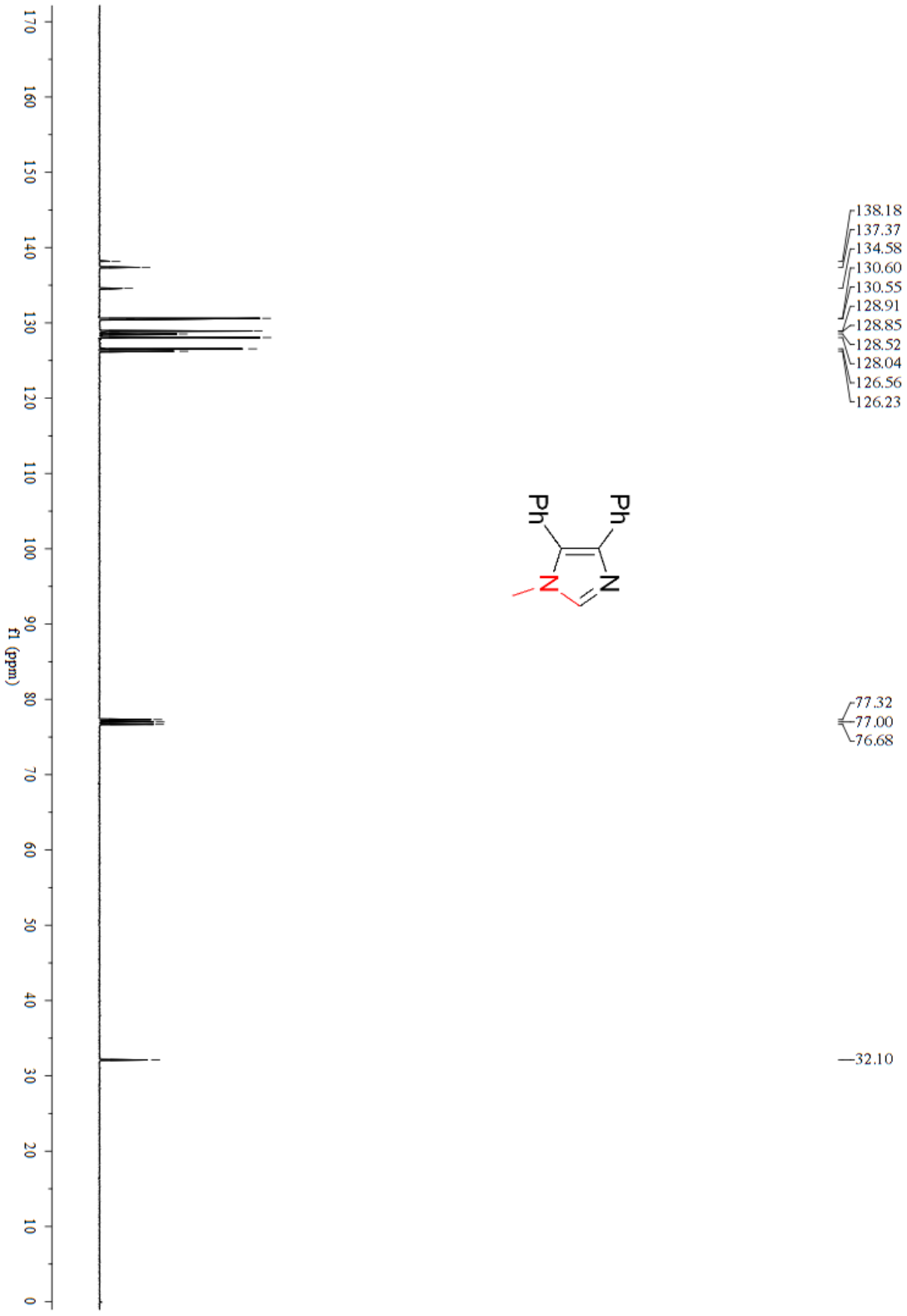
6. Appendix (Copies of ^{1}H and ^{13}C NMR Spectra)






Ph
N
Ph
N

2a


f1 (ppm)
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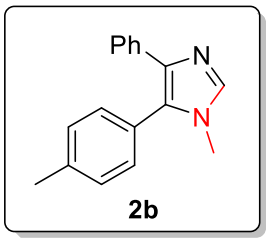
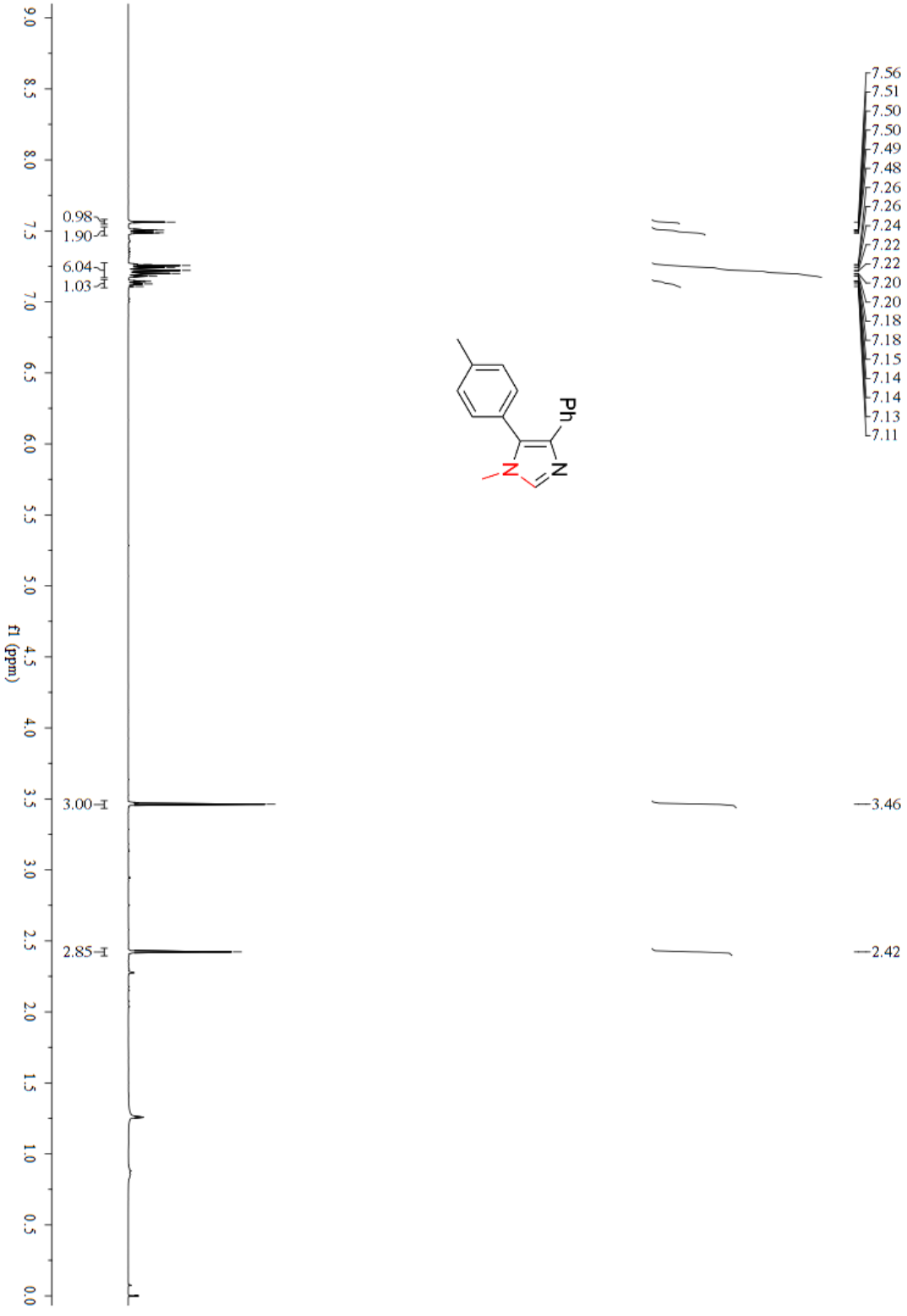
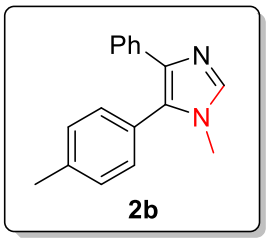
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
138.18
137.37
134.58
130.60
130.55
128.91
128.85
128.52
128.04
126.56
126.23
77.32
77.00
76.68
32.10
Ph
Ph
N
N

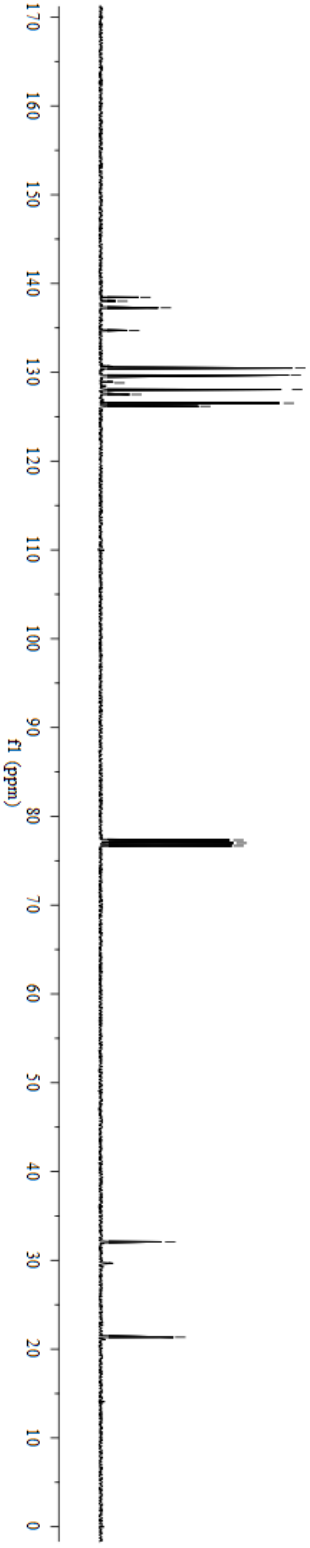

Ph
N
N

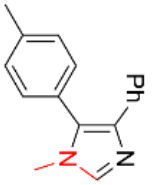
2b


0.98
1.90
6.04
1.03
3.00
2.85
f1 (ppm)
7.56
7.51
7.50
7.50
7.49
7.48
7.26
7.26
7.24
7.22
7.22
7.20
7.20
7.18
7.18
7.15
7.14
7.14
7.13
7.11
3.46
2.42
Ph
N
N



2b



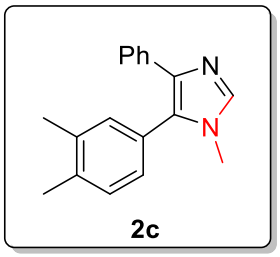


138.45
138.02
137.26
134.72
130.48
129.68
128.81
128.05
127.51
126.52
126.18

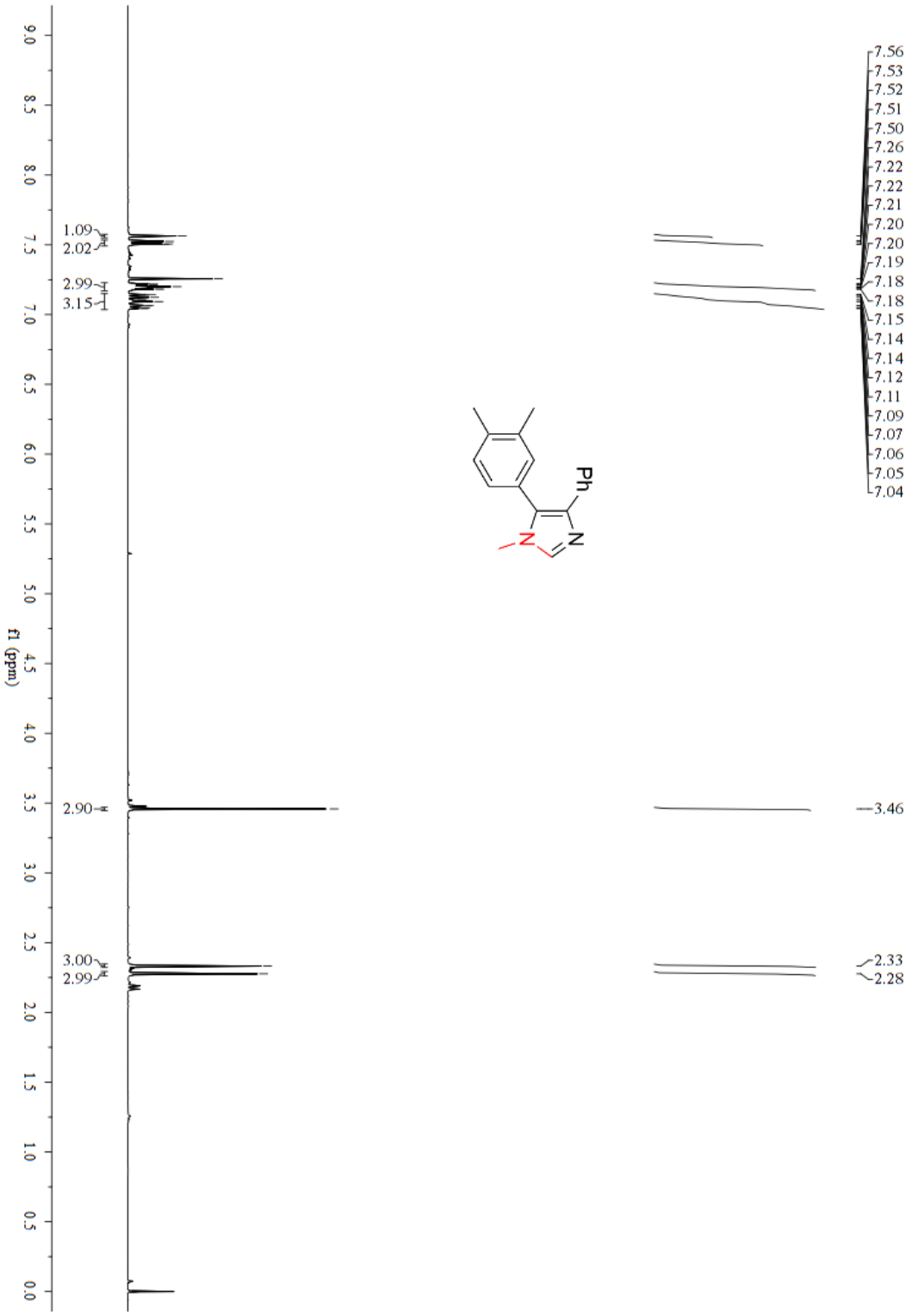
77.32
77.00
76.68

32.09

21.34


Ph
N
N

2c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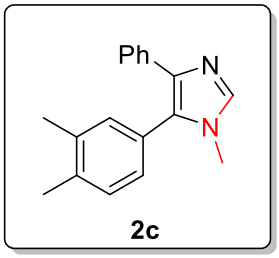
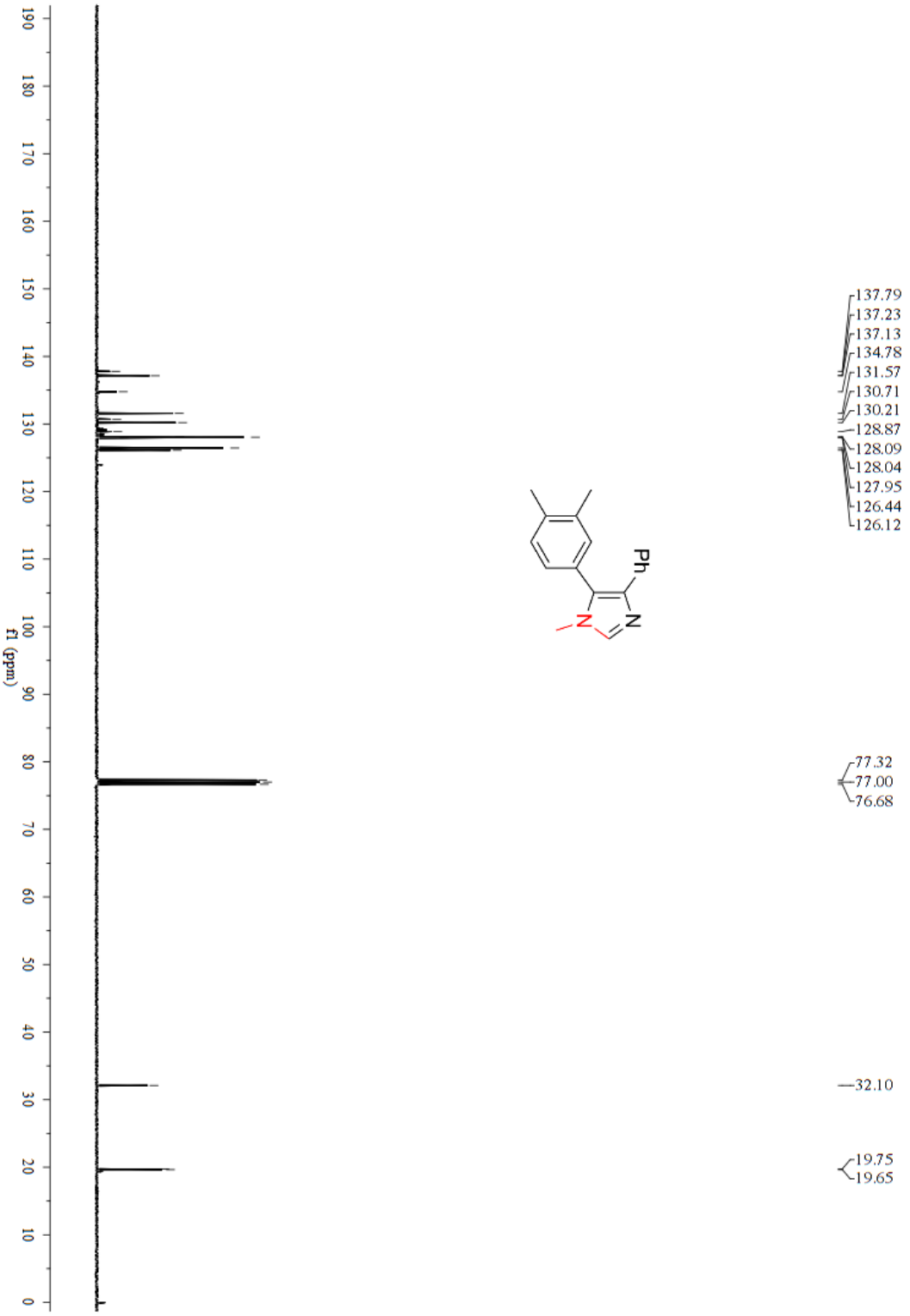
2.02
2.99
3.15
2.90
3.00
2.99
7.56
7.53
7.52
7.51
7.50
7.26
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.15
7.14
7.14
7.12
7.11
7.09
7.07
7.06
7.05
7.04
3.46
2.33
2.28
Ph
N
N


Ph
N
N

2c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130.21
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128.09
128.04
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126.44
126.12
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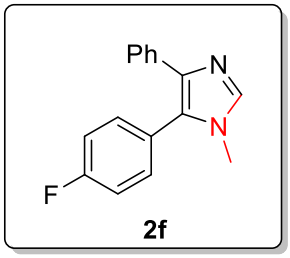
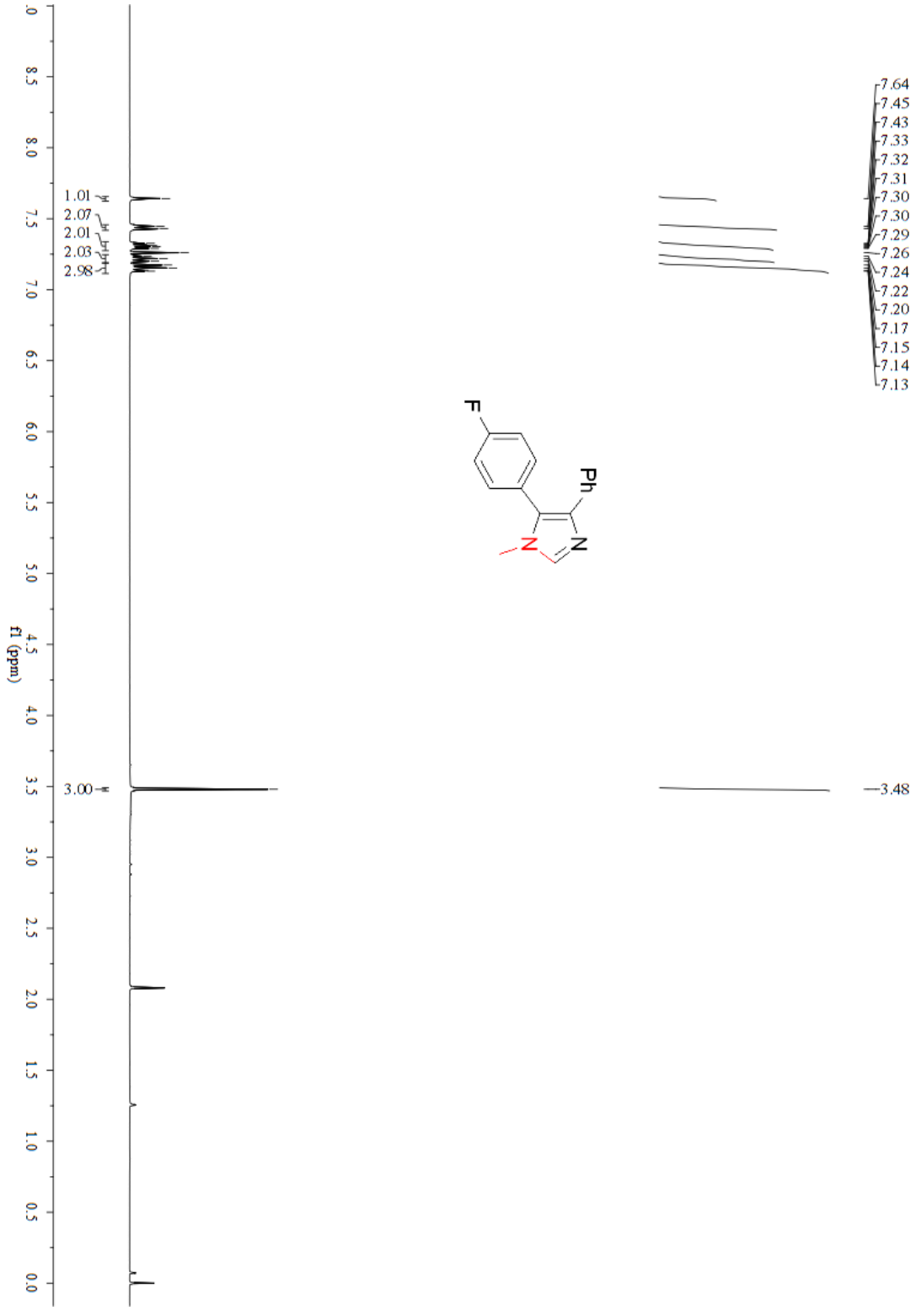
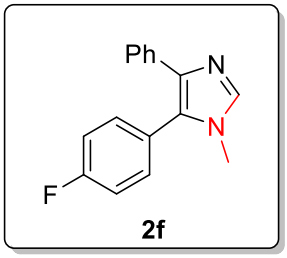
77.00
76.68
32.10
19.75
19.65
Ph
N
N

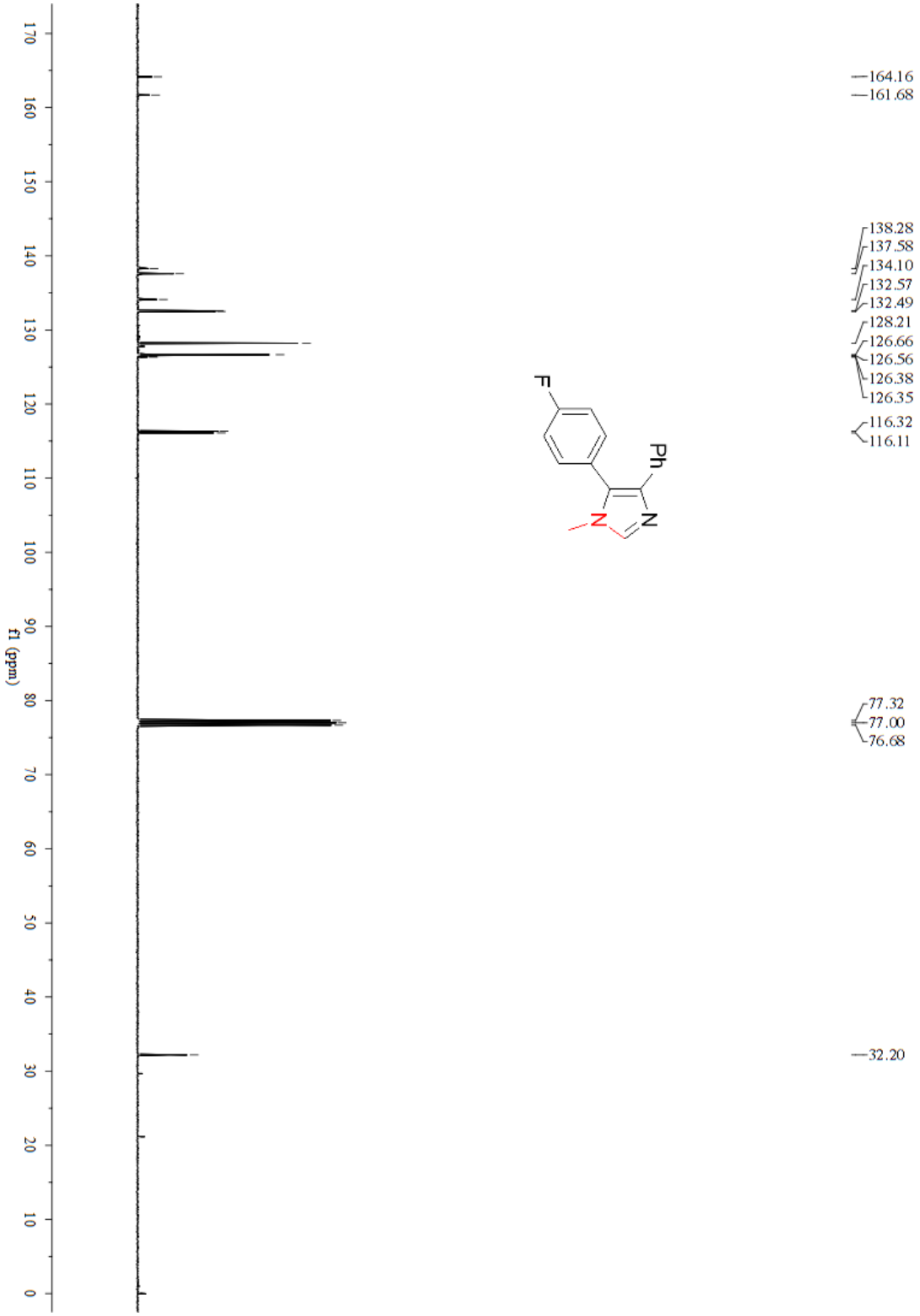

Ph
N
N
F

2f


1.01
2.07
2.01
2.03
2.98
3.00
7.64
7.45
7.43
7.33
7.32
7.31
7.30
7.30
7.29
7.26
7.24
7.22
7.20
7.17
7.15
7.14
7.13
3.48
f1 (ppm)


Ph
N
N
F

2f


f1 (ppm)
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132.49
128.21
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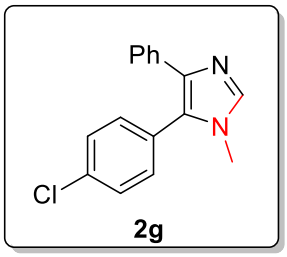
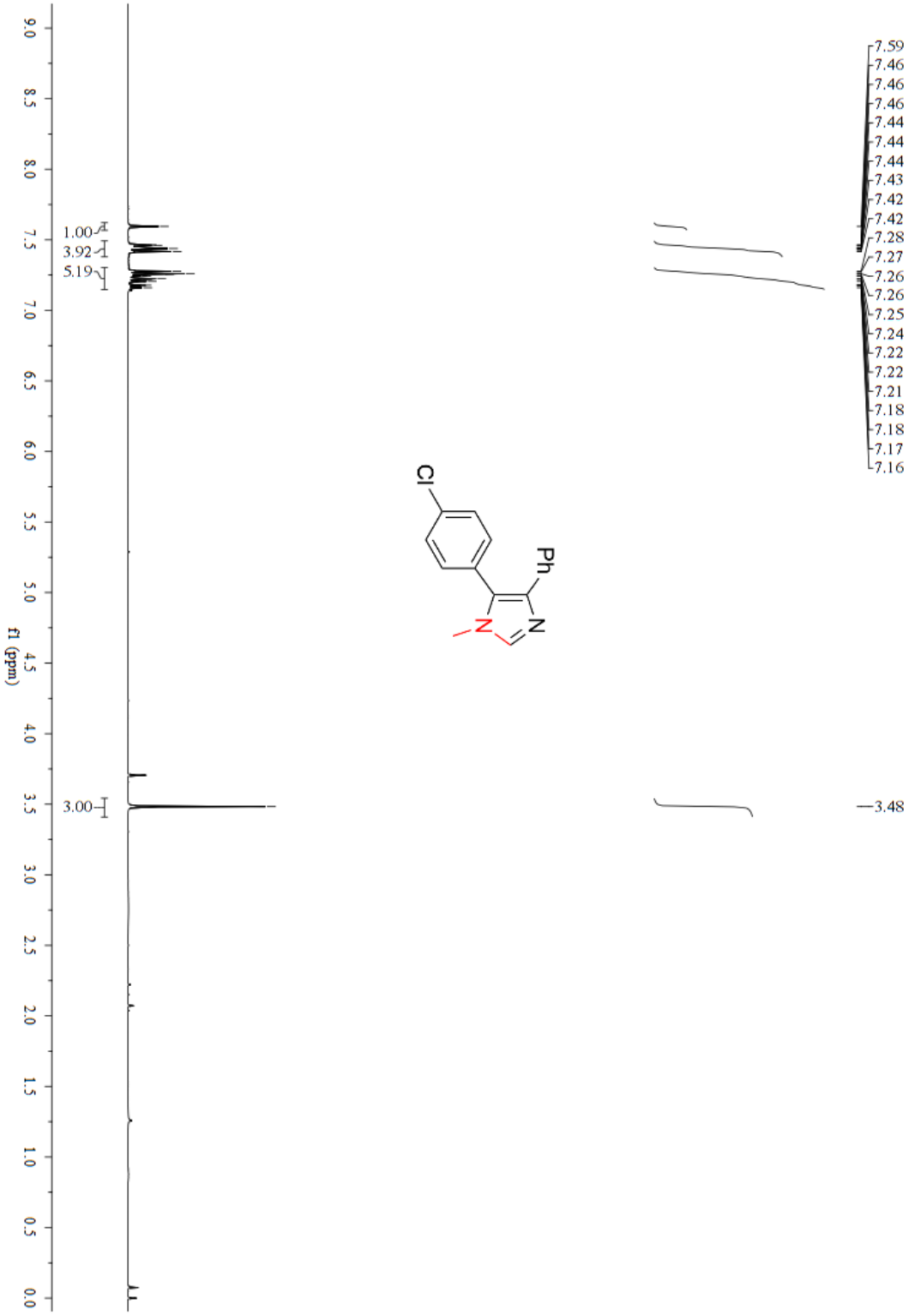
126.56
126.38
126.35
116.32
116.11
77.32
77.00
76.68
32.20
F
Ph
N
N


Ph
N
N
Cl

2g


7.59
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7.46
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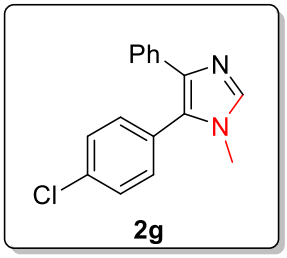
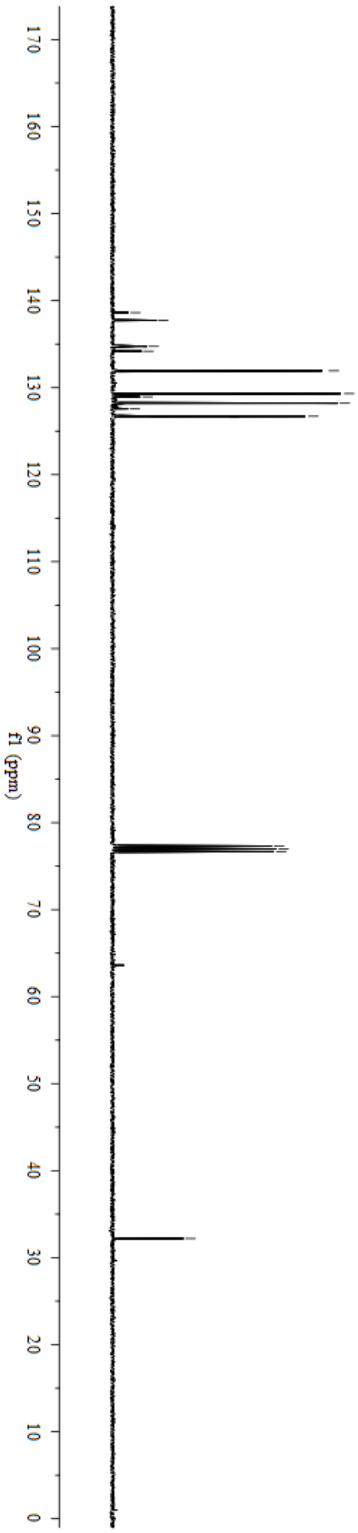
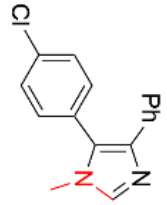
7.44
7.44
7.43
7.42
7.42
7.28
7.27
7.26
7.26
7.25
7.24
7.22
7.22
7.21
7.18
7.18
7.17
7.16
1.00
3.92
5.19
3.00
3.48
Cl
Ph
N
N
f1 (ppm)



2g

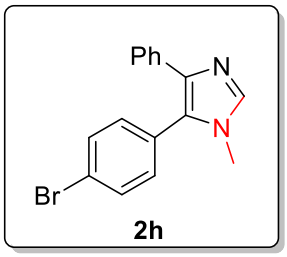




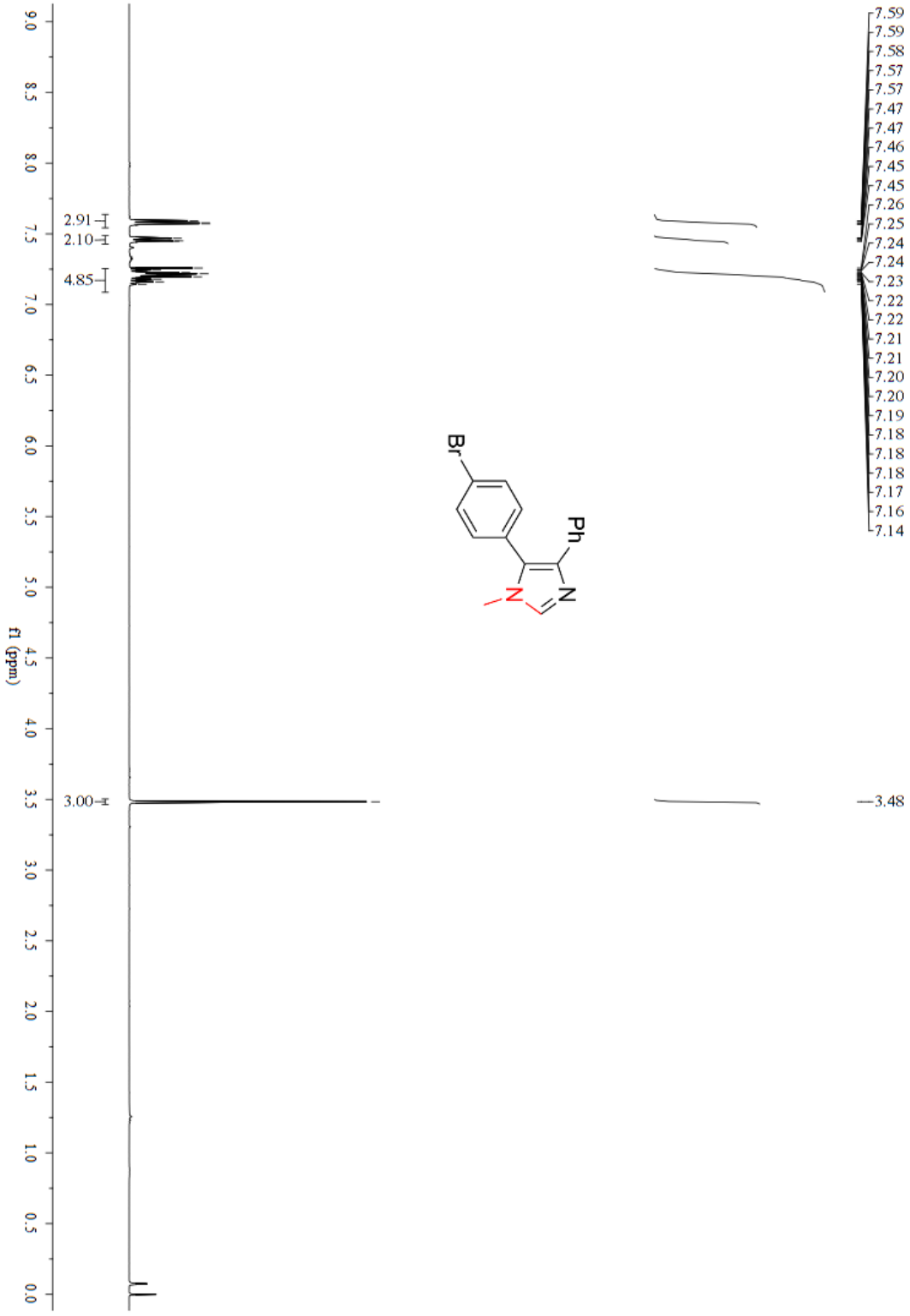
138.62
137.73
134.74
134.19
131.94
129.32
128.95
128.21
127.55
126.71
126.57

77.32
77.00
76.68

32.21


Ph
N
N
Br

2h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7.58
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7.57
7.47
7.47
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7.45
7.45
7.26
7.25
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7.24
7.23
7.22
7.22
7.21
7.21
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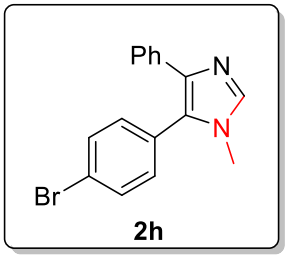
7.20
7.19
7.18
7.18
7.18
7.17
7.16
7.14
f1 (ppm)


Ph
N
N
Br

2h


f1 (ppm)
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132.27
132.22
129.51
128.21
127.54
126.71
126.56
122.92
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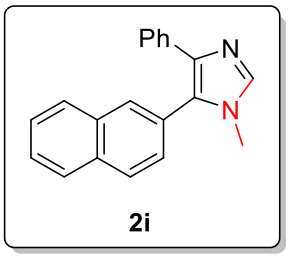
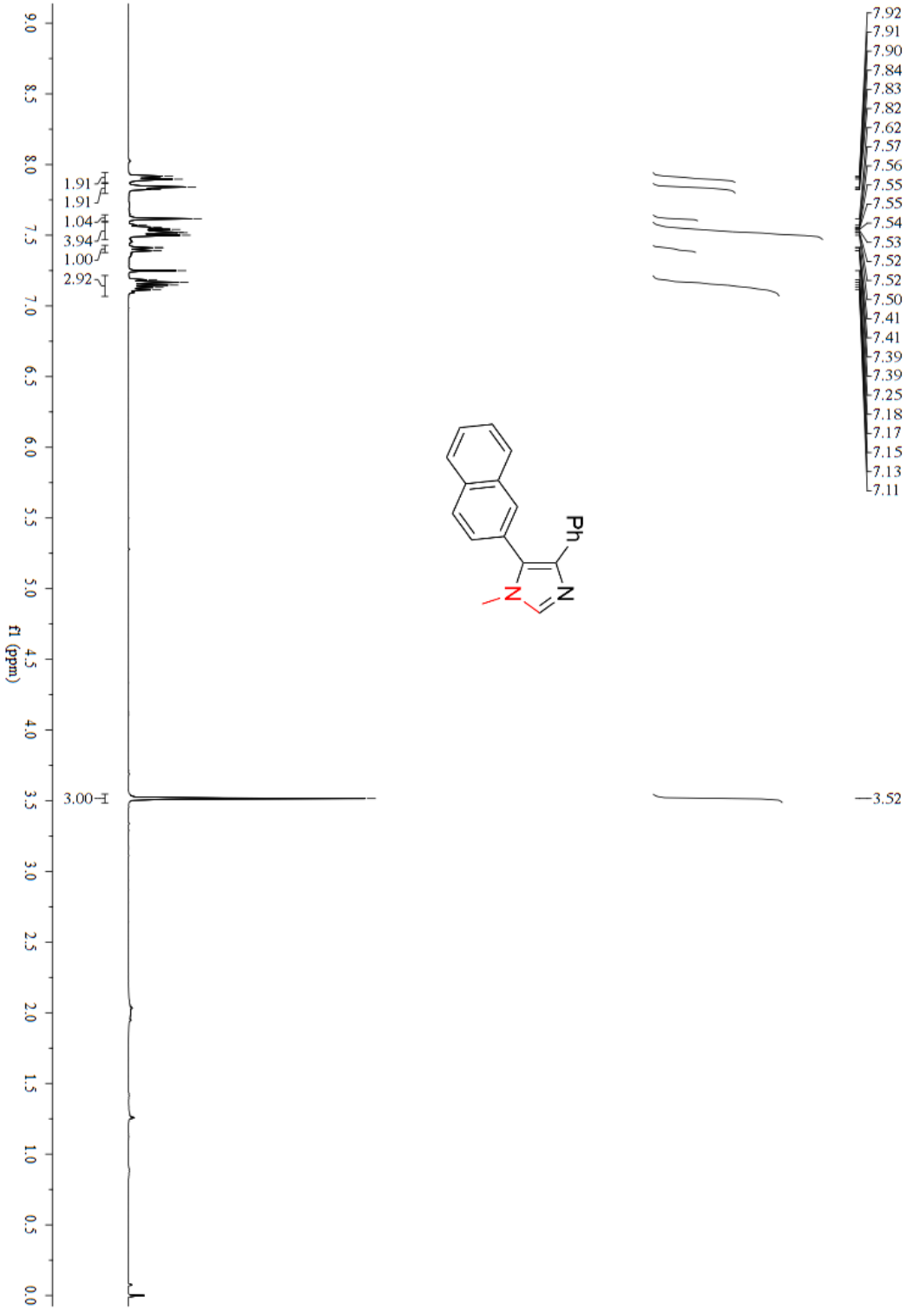
77.00
76.68
32.20
Br
Ph
N
N


Ph
N
N

2i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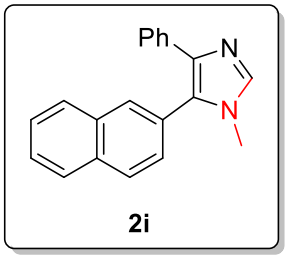
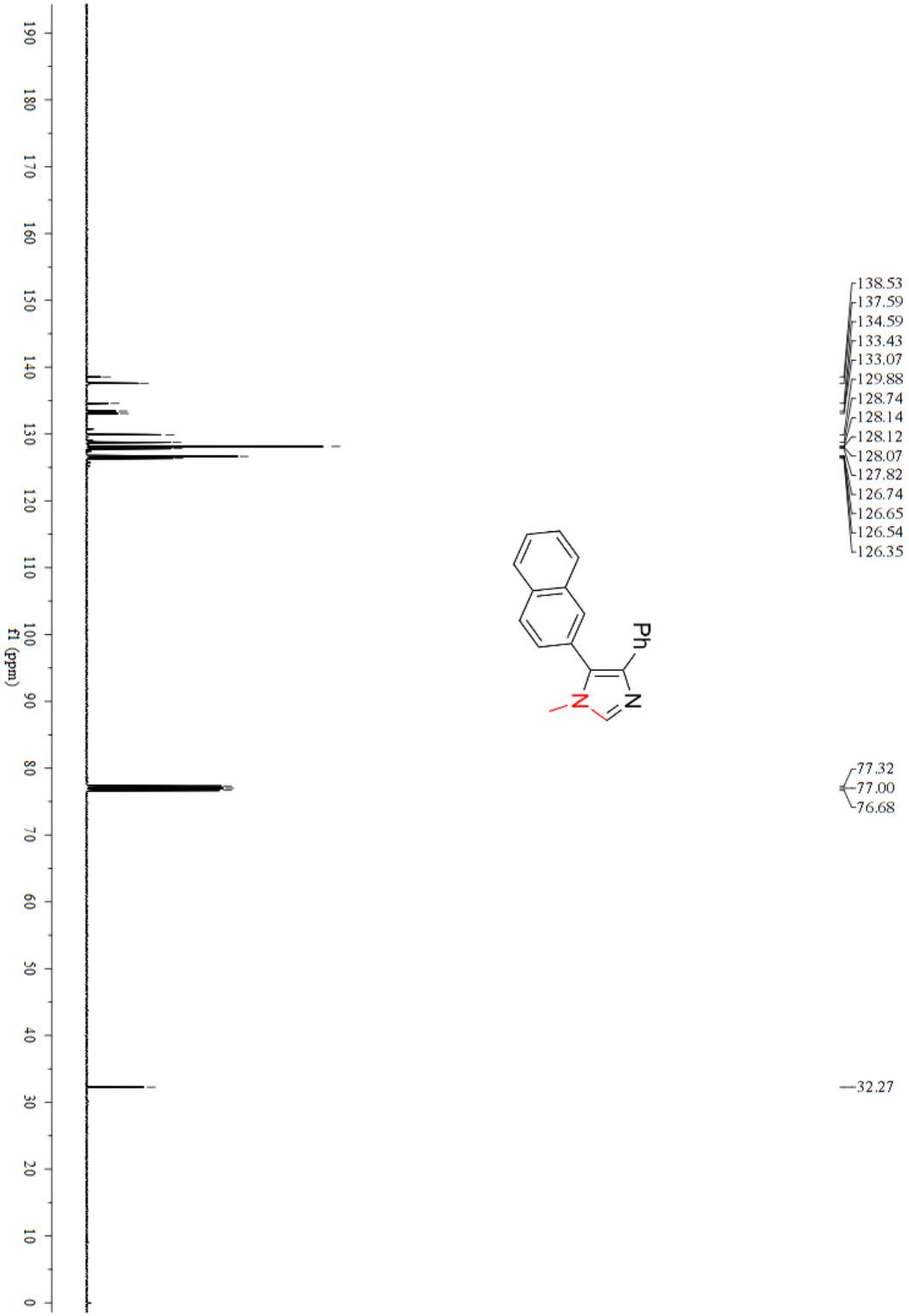
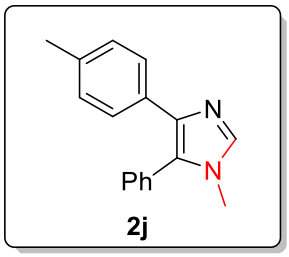
1.04
3.94
1.00
2.92
3.00
3.52
7.92
7.91
7.90
7.84
7.83
7.82
7.62
7.57
7.56
7.55
7.55
7.54
7.53
7.52
7.52
7.50
7.41
7.41
7.39
7.39
7.25
7.18
7.17
7.15
7.13
7.11
Ph
N
N
f1 (ppm)

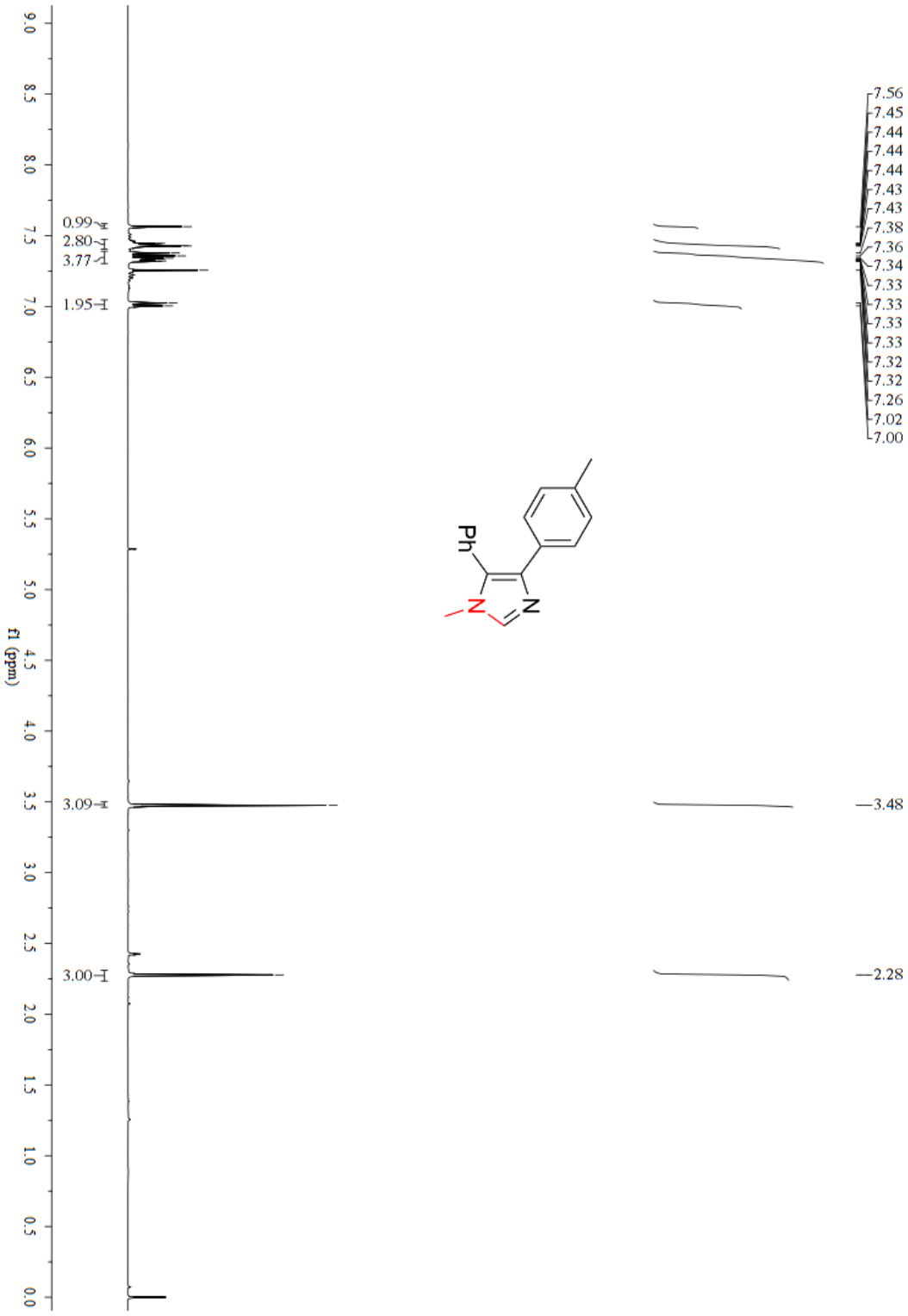

Ph
N
N

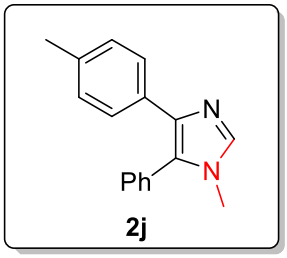
2i


f1 (ppm)
138.53
137.59
134.59
133.43
133.07
129.88
128.74
128.14
128.12
128.07
127.82
126.74
126.65
126.54
126.35
77.32
77.00
76.68
32.27
Ph
N
N

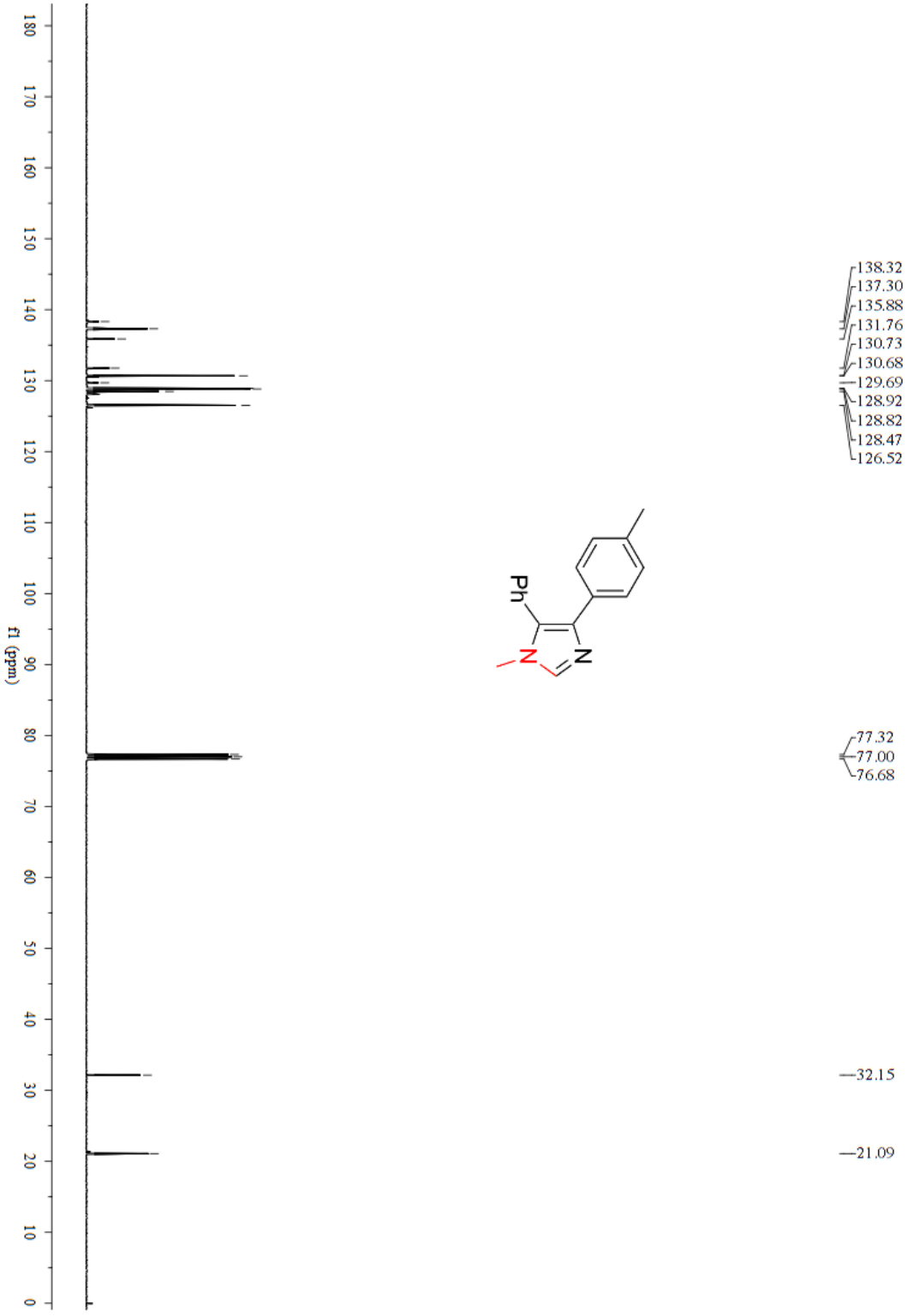

N
Ph
N

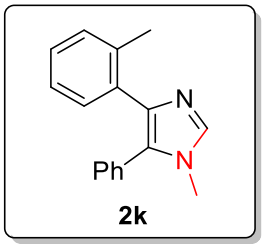
2j


0.99
2.80
3.77
1.95
3.09
3.00
3.48
2.28
7.56
7.45
7.44
7.44
7.44
7.43
7.43
7.38
7.36
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.26
7.02
7.00
Ph
N
N
f1 (ppm)

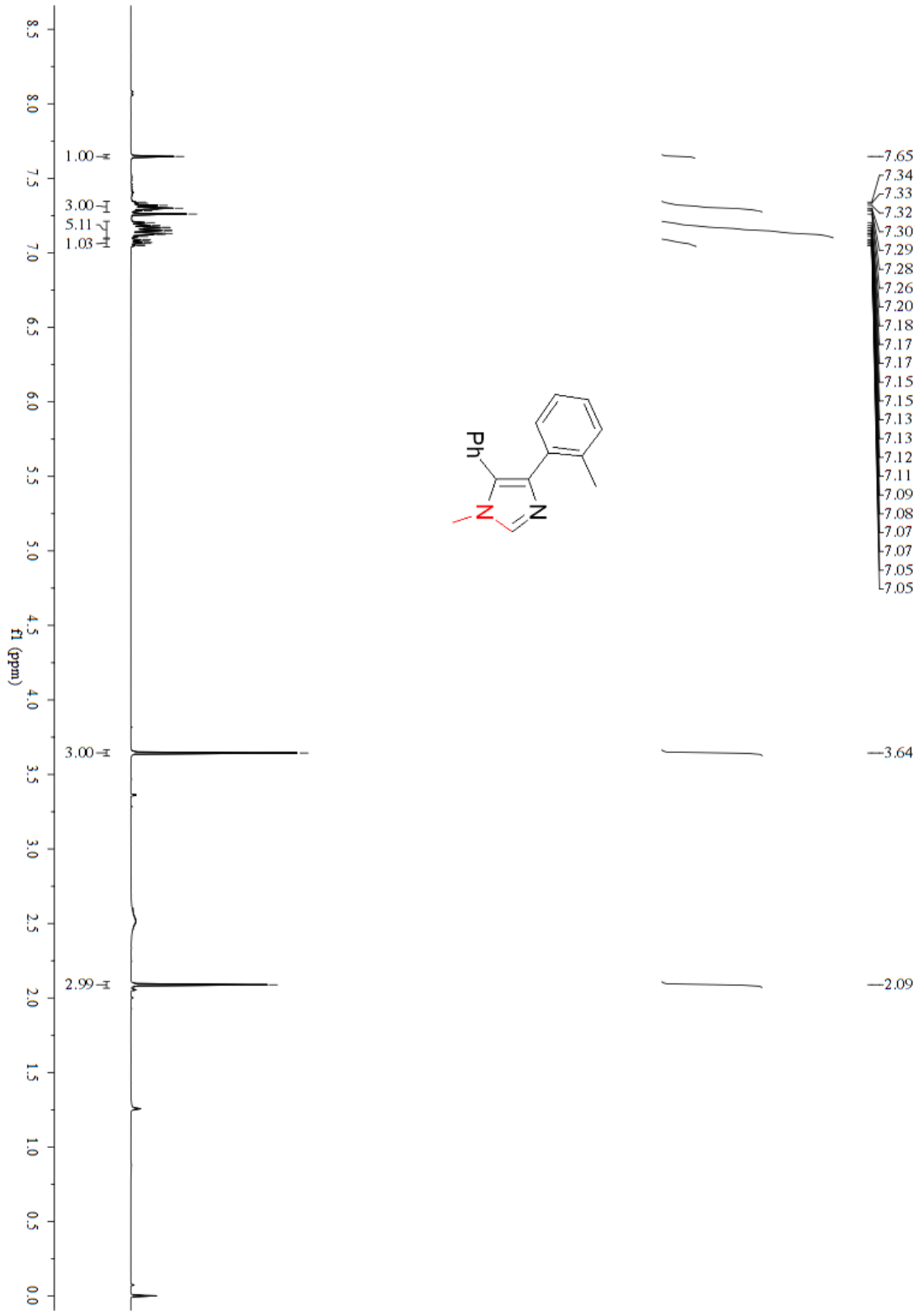

N
Ph
N

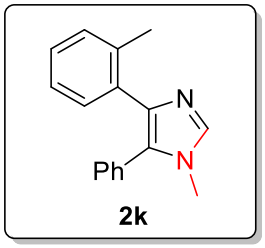
2j


f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
138.32
137.30
135.88
131.76
130.73
130.68
129.69
128.92
128.82
128.47
126.52
77.32
77.00
76.68
32.15
21.09
Ph
N
N

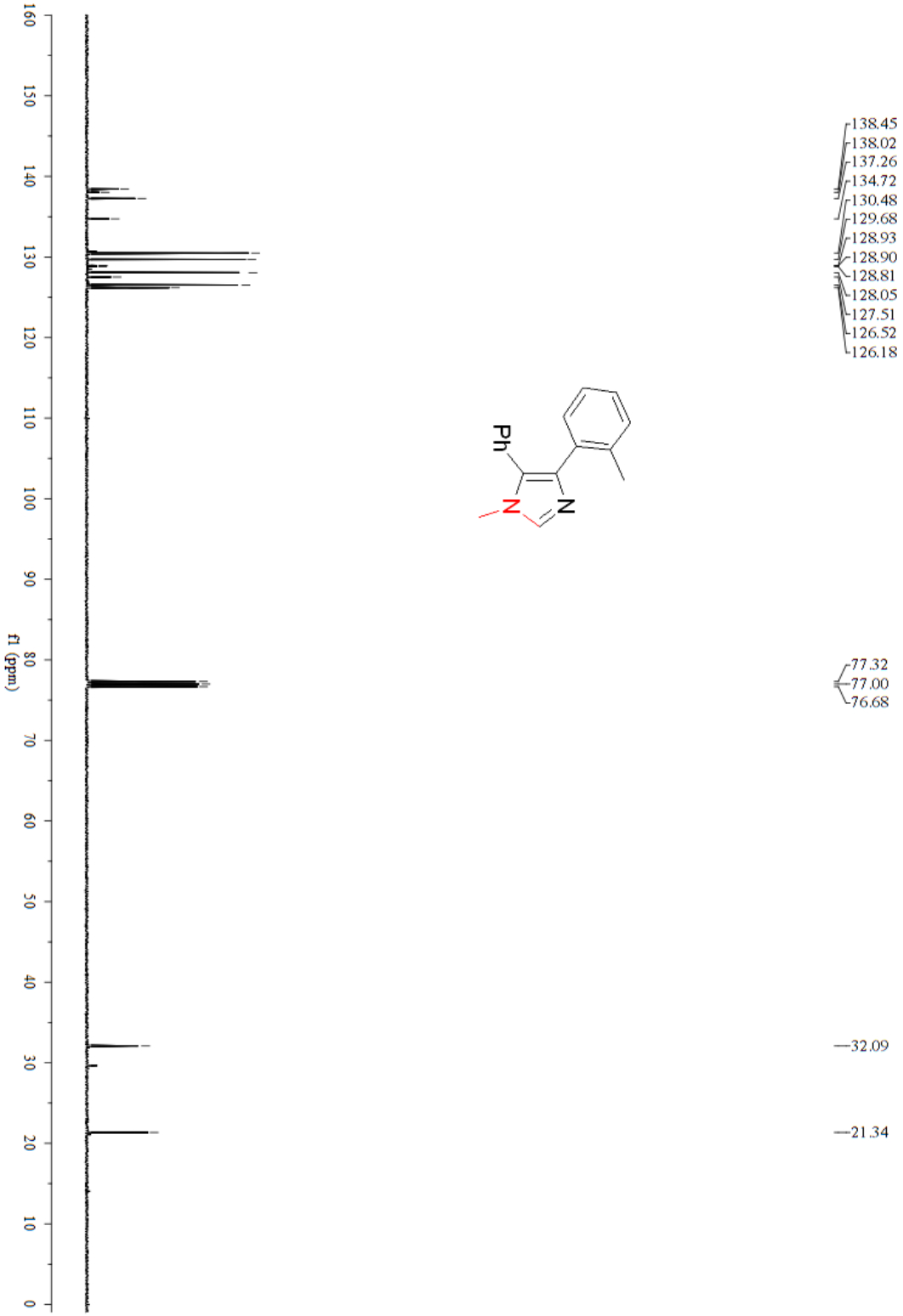

N
Ph
N

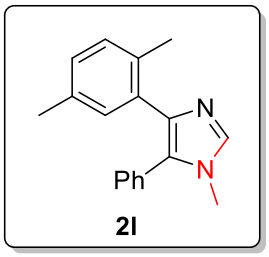
2k


1.00
3.00
5.11
1.03
3.00
2.99
f1 (ppm)
7.65
7.34
7.33
7.32
7.30
7.29
7.28
7.26
7.20
7.18
7.17
7.17
7.15
7.15
7.13
7.13
7.12
7.11
7.09
7.08
7.07
7.07
7.05
7.05
3.64
2.09
Ph
N
N

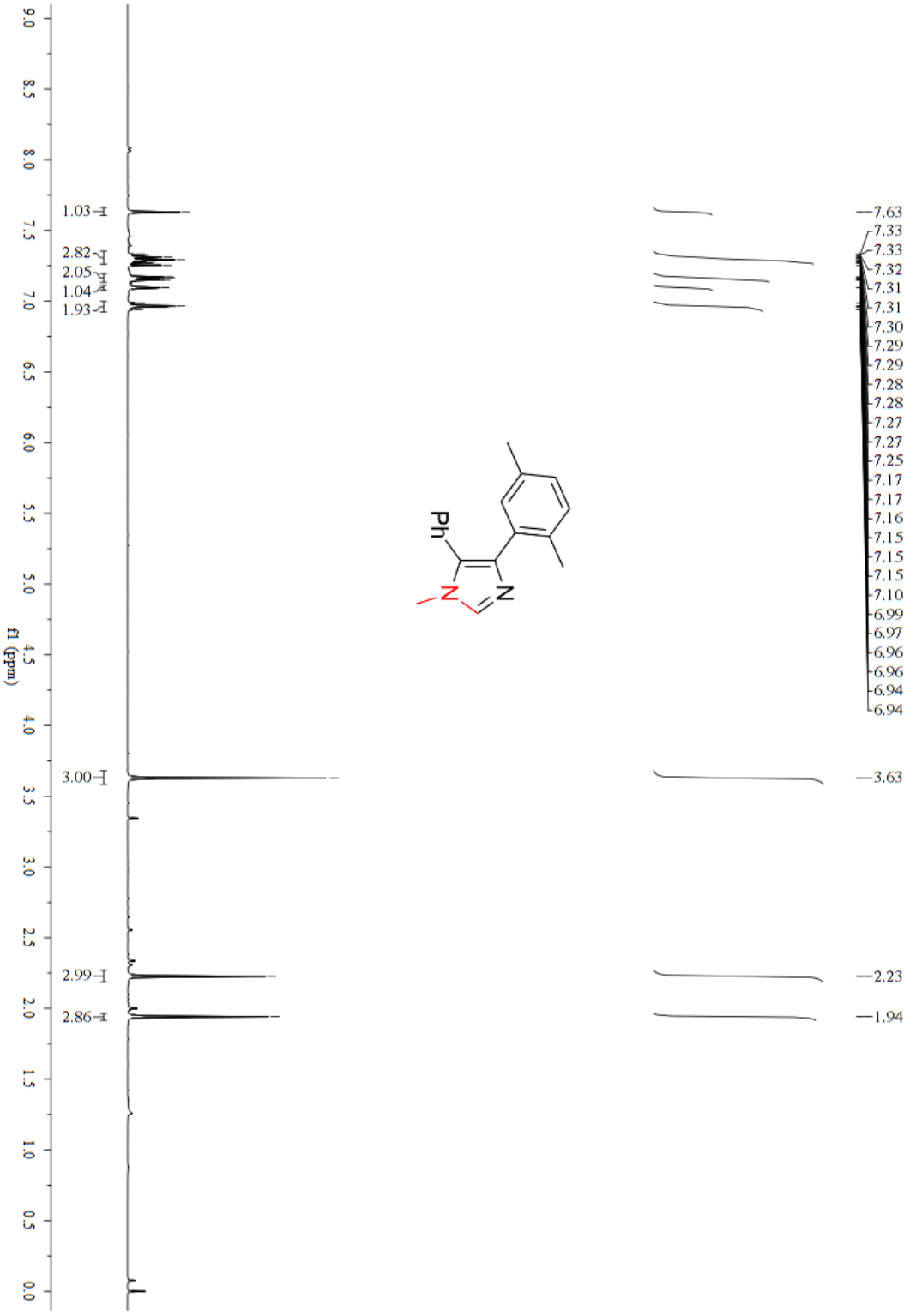

N
Ph
N

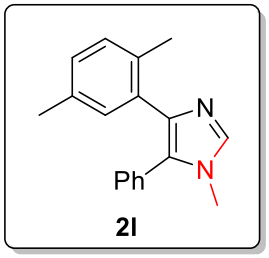
2k


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
138.45
138.02
137.26
134.72
130.48
129.68
128.93
128.90
128.81
128.05
127.51
126.52
126.18
77.32
77.00
76.68
32.09
21.34
Ph
N
N

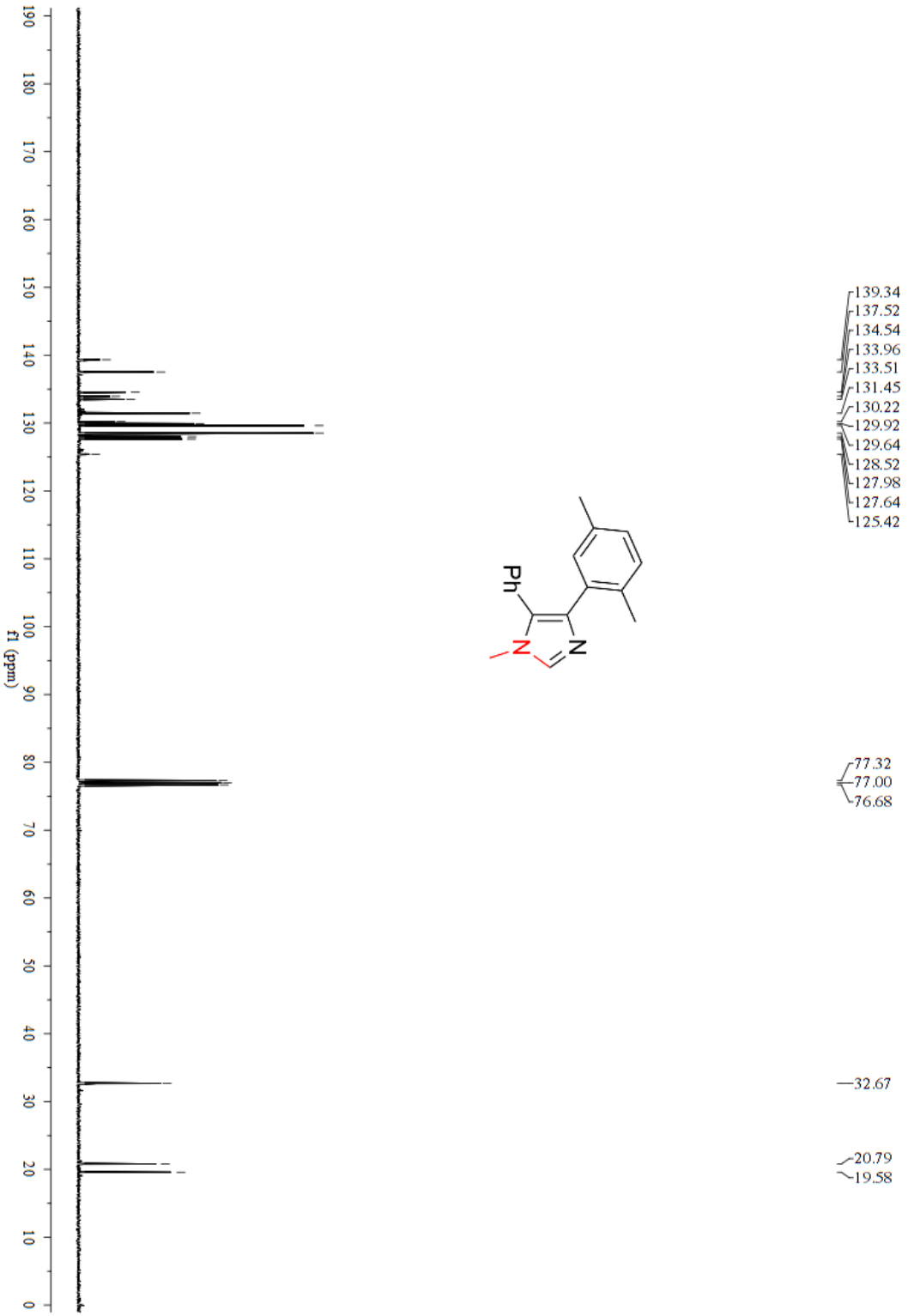

N
Ph
N

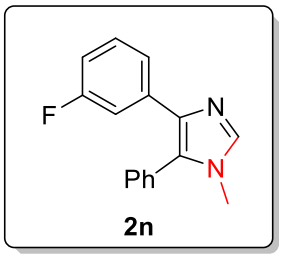
2l


f1 (ppm)
1.03
2.82
2.05
1.04
1.93
3.00
2.99
2.86
7.63
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.25
7.17
7.17
7.16
7.15
7.15
7.15
7.10
6.99
6.97
6.96
6.96
6.94
6.94
3.63
2.23
1.94
Ph
N
N

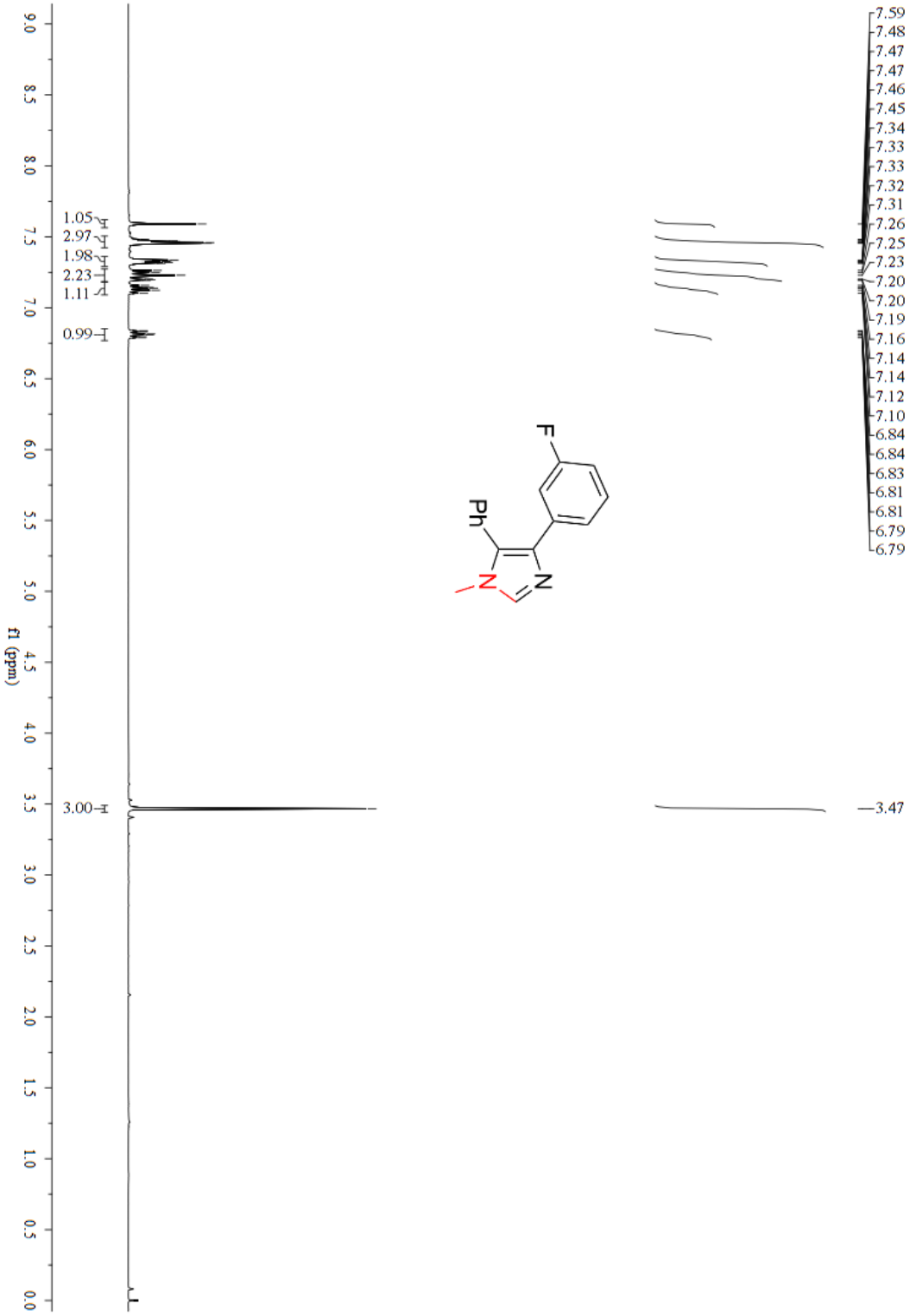

N
Ph
N

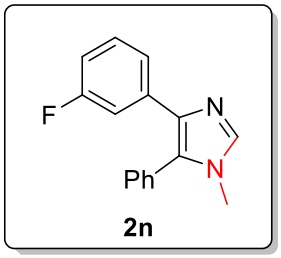
2l


f1 (ppm)
139.34
137.52
134.54
133.96
133.51
131.45
130.22
129.92
129.64
128.52
127.98
127.64
125.42
77.32
77.00
76.68
32.67
20.79
19.58
Ph
N
N

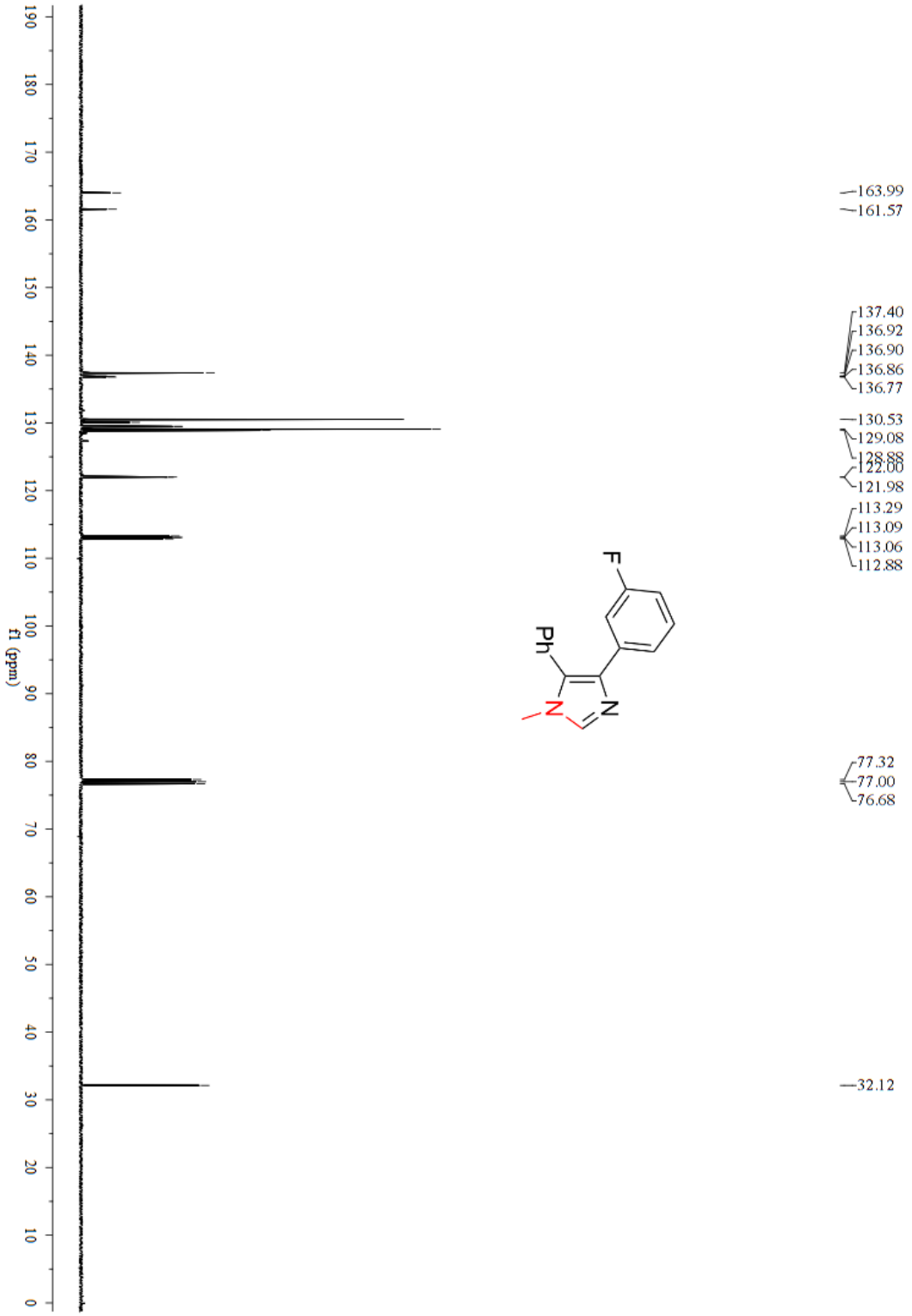

F
N
Ph
N

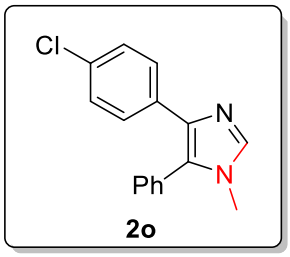
2n


f1 (ppm)
1.05
2.97
1.98
2.23
1.11
0.99
3.00
3.47
7.59
7.48
7.47
7.47
7.46
7.45
7.34
7.33
7.33
7.32
7.31
7.26
7.25
7.23
7.20
7.20
7.19
7.16
7.14
7.14
7.12
7.10
6.84
6.84
6.83
6.81
6.81
6.79
6.79
F
Ph
N
N

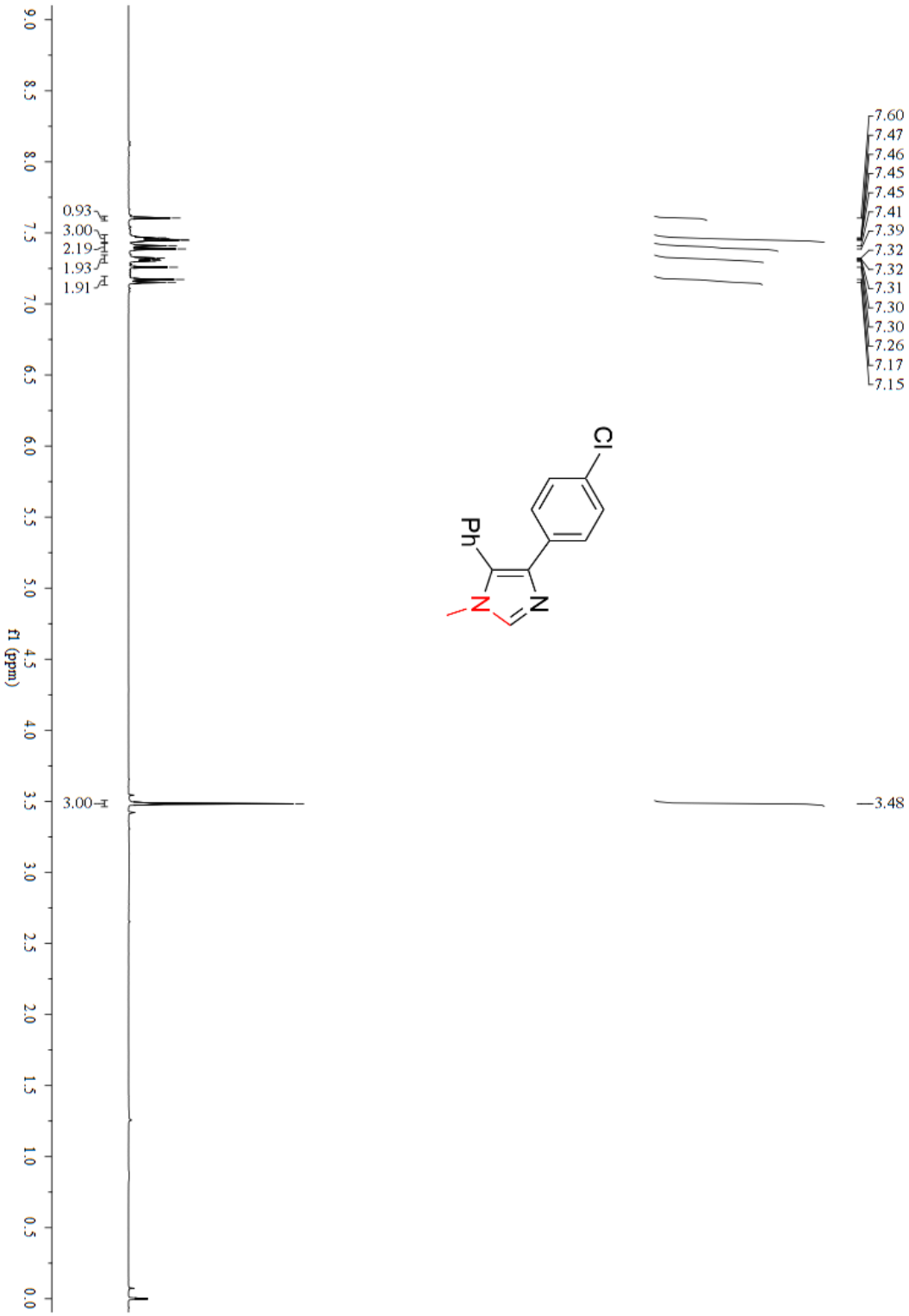

F
N
Ph
N

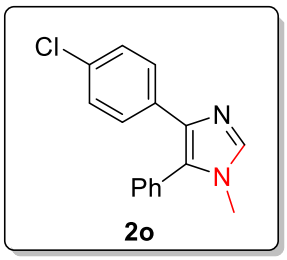
2n


f1 (ppm)
163.99
161.57
137.40
136.92
136.90
136.86
136.77
130.53
129.08
128.88
122.00
121.98
113.29
113.09
113.06
112.88
77.32
77.00
76.68
32.12
F
Ph
N
N

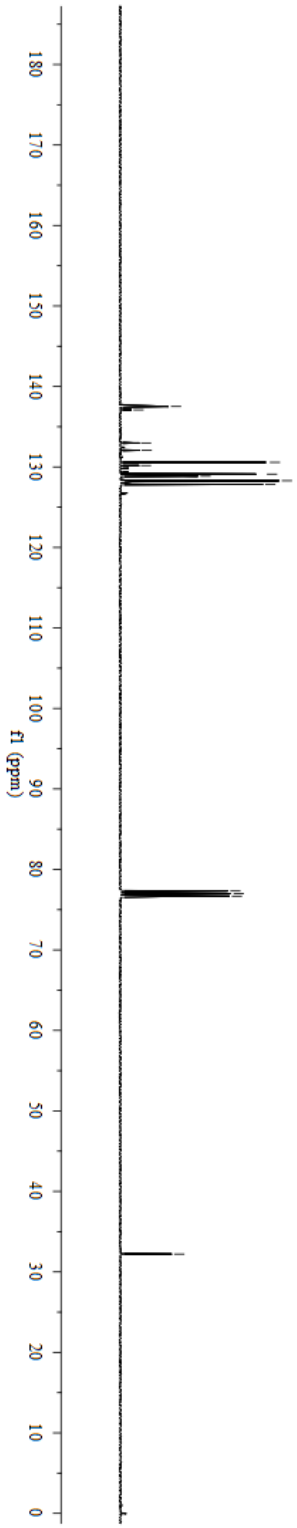

Cl
N
Ph
N

2o

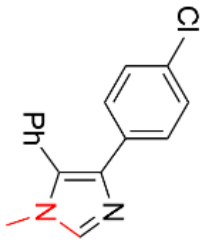

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.93
3.00
2.19
1.93
1.91
3.00
7.60
7.47
7.46
7.45
7.45
7.41
7.39
7.32
7.32
7.31
7.30
7.30
7.26
7.17
7.15
3.48
Cl
Ph
N
N



2o

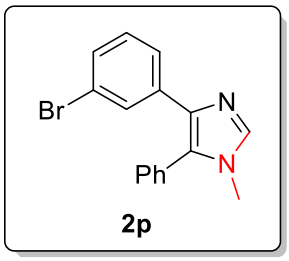


137.51
137.10
132.98
132.07
130.57
130.18
129.11
128.85
128.29
127.85

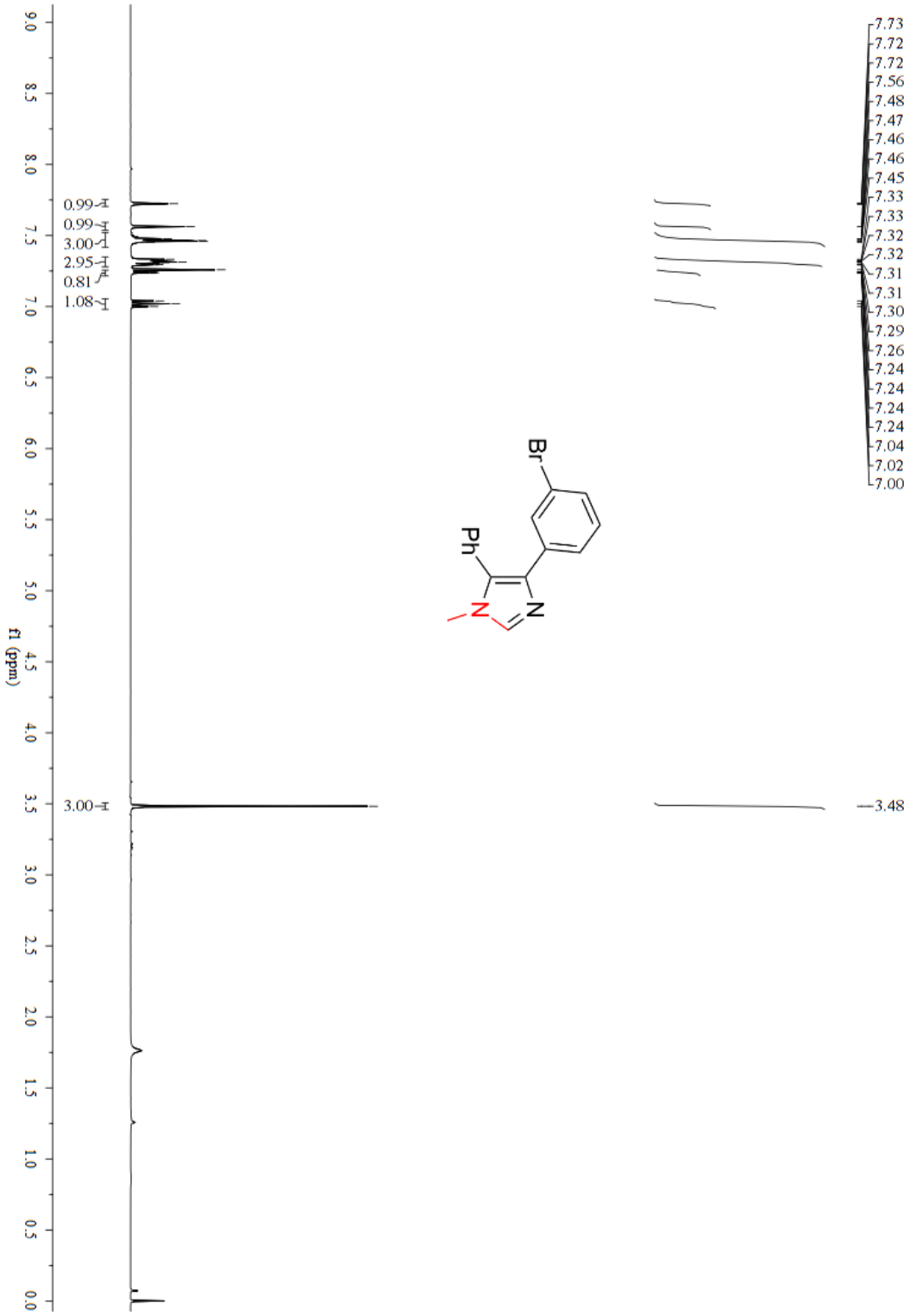


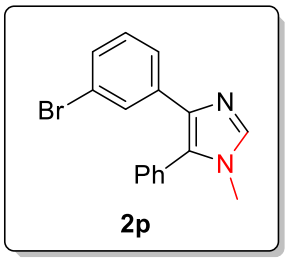
77.32
77.00
76.68

32.21

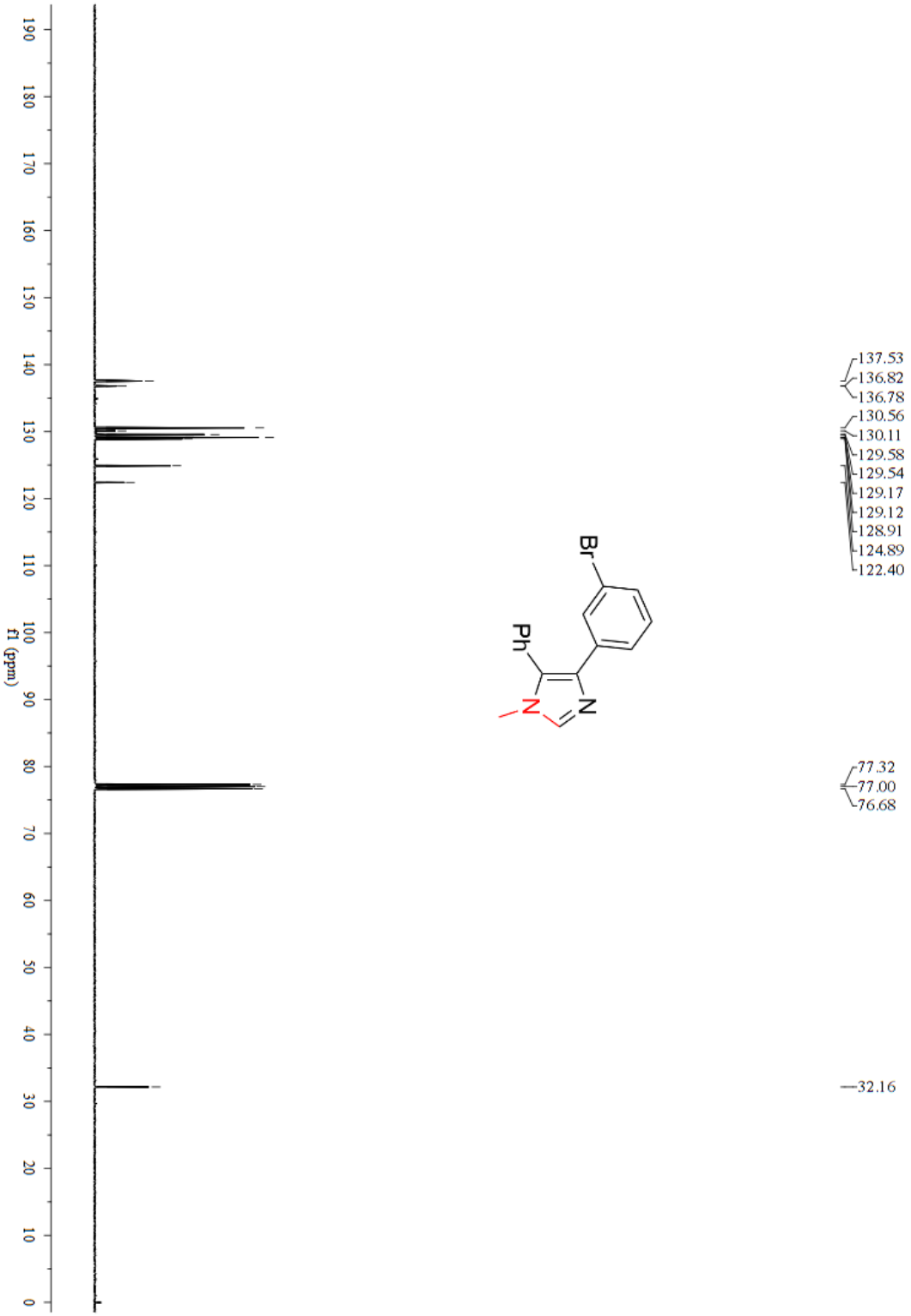

Br
N
Ph
N

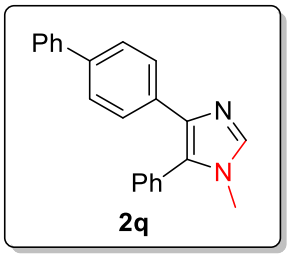
2p


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
0.0
f1 (ppm)
0.99
0.99
3.00
2.95
0.81
1.08
3.00
7.73
7.72
7.72
7.56
7.48
7.47
7.46
7.46
7.45
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26
7.24
7.24
7.24
7.24
7.04
7.02
7.00
3.48
Br
Ph
N
N

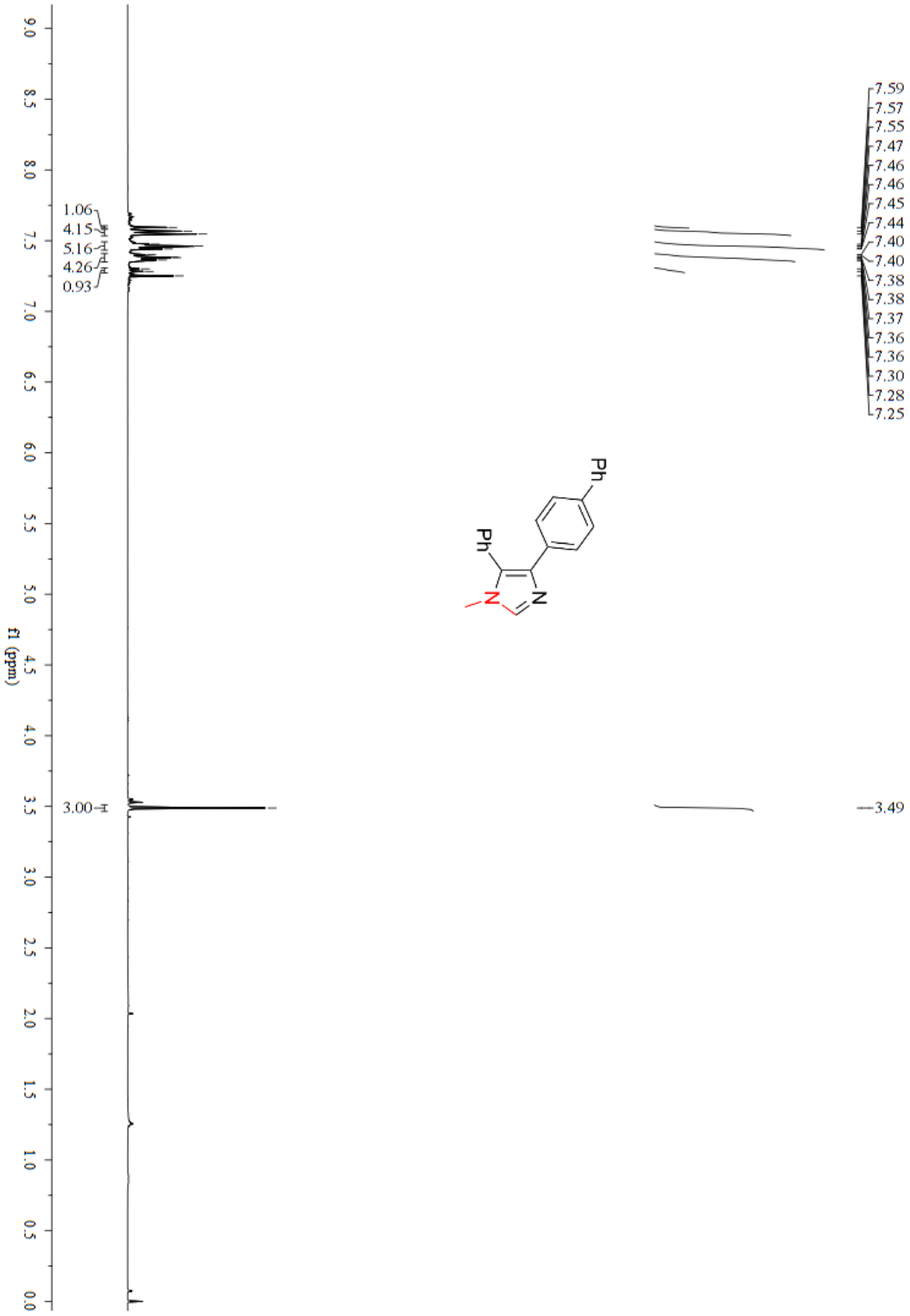

Br
N
Ph
N

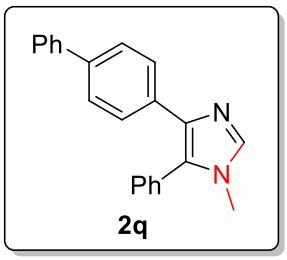
2p


f1 (ppm)
137.53
136.82
136.78
130.56
130.11
129.58
129.54
129.17
129.12
128.91
124.89
122.40
77.32
77.00
76.68
32.16
Br
Ph
N
N

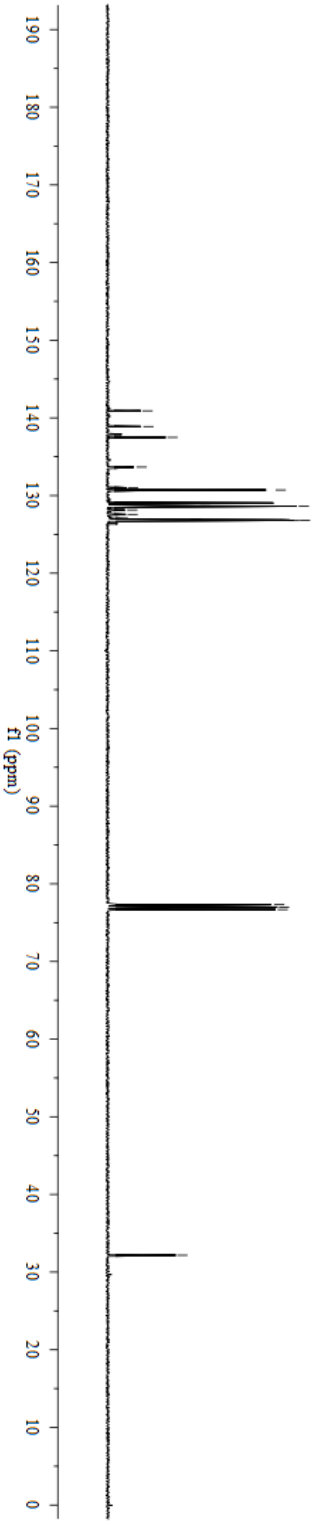

Ph
N
Ph
N

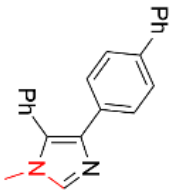
2q


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
0.0
f1 (ppm)
1.06
4.15
5.16
4.26
0.93
3.00
7.59
7.57
7.55
7.47
7.46
7.46
7.45
7.44
7.40
7.40
7.38
7.38
7.37
7.36
7.36
7.30
7.28
7.25
3.49
Ph
Ph
N
N



2q

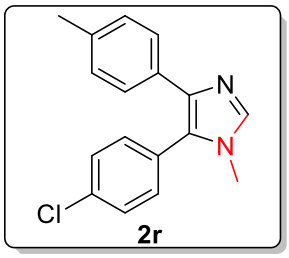




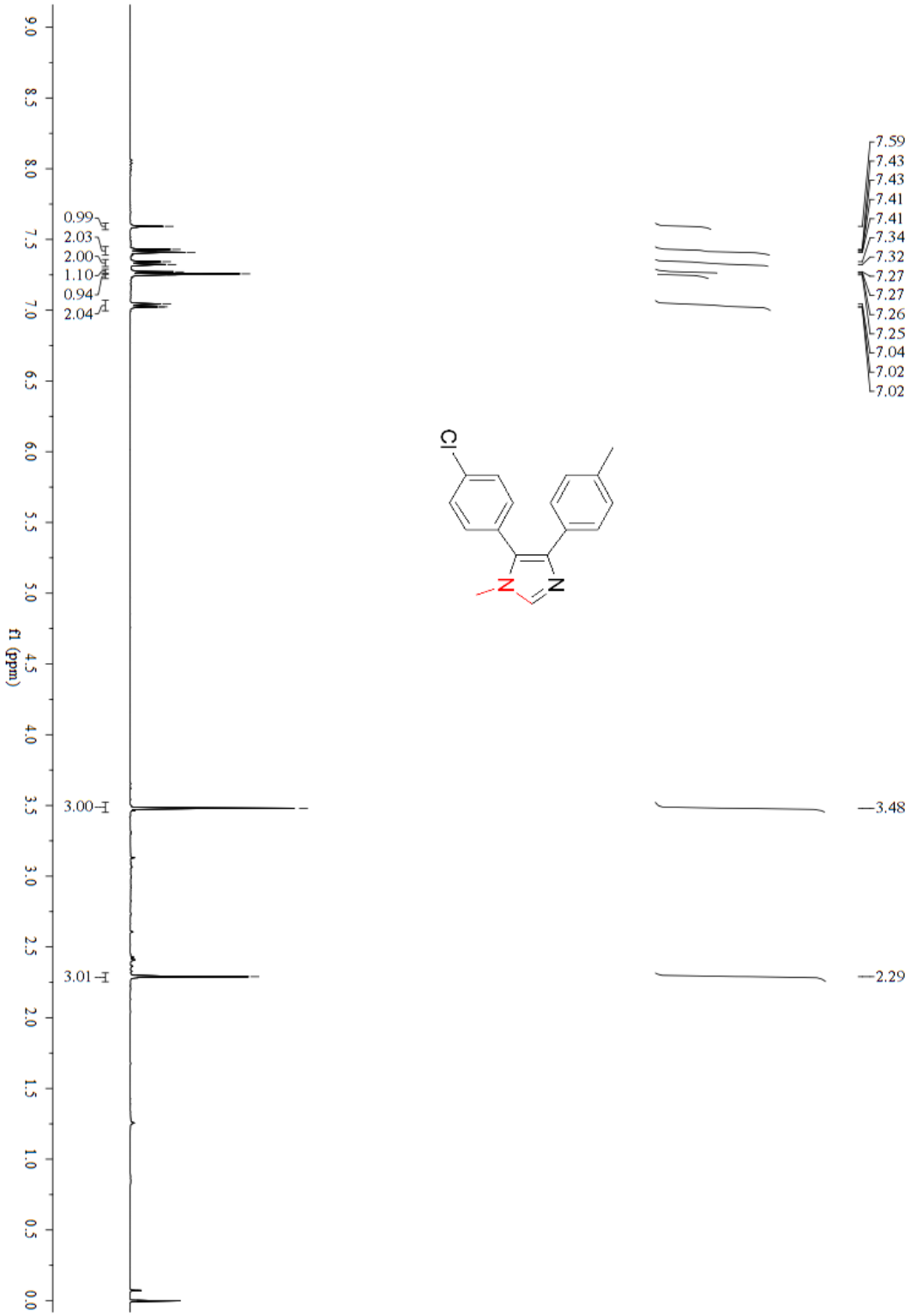
140.91
138.88
137.48
133.66
131.01
130.71
130.61
128.67
128.62
128.15
127.57
126.96
126.87
126.81
126.78

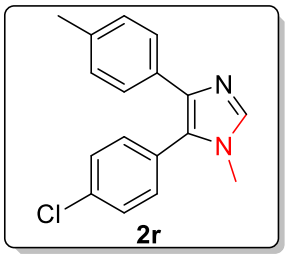
77.32
77.00
76.68

32.17

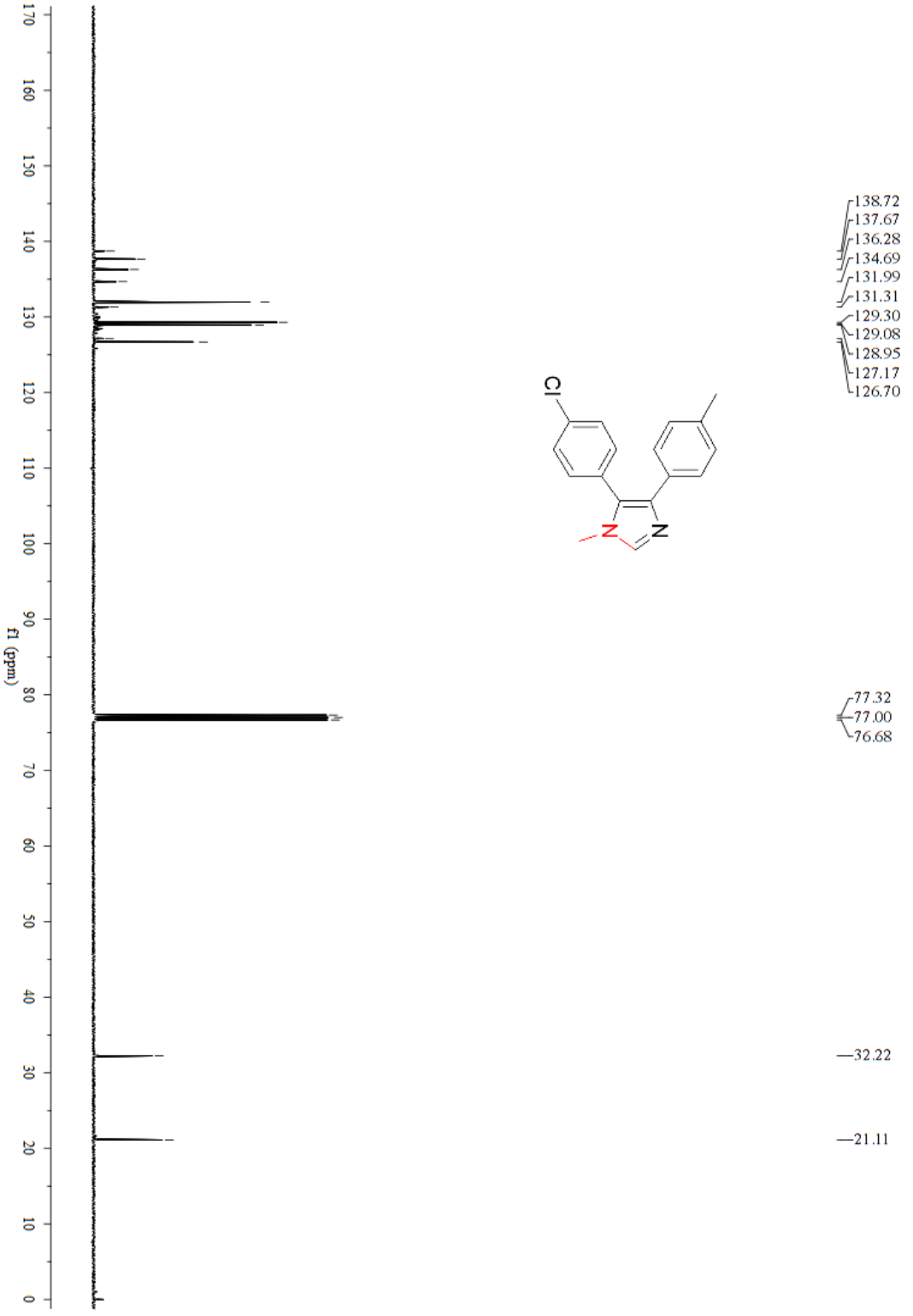

N
N
Cl

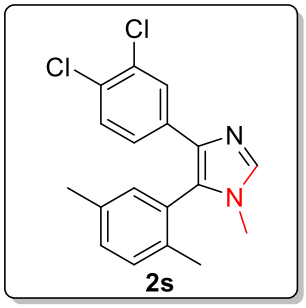
2r


0.99
2.03
2.00
1.10
0.94
2.04
3.00
3.01
7.59
7.43
7.43
7.41
7.41
7.34
7.32
7.27
7.27
7.26
7.25
7.04
7.02
7.02
3.48
2.29
Cl
N
N
f1 (ppm)

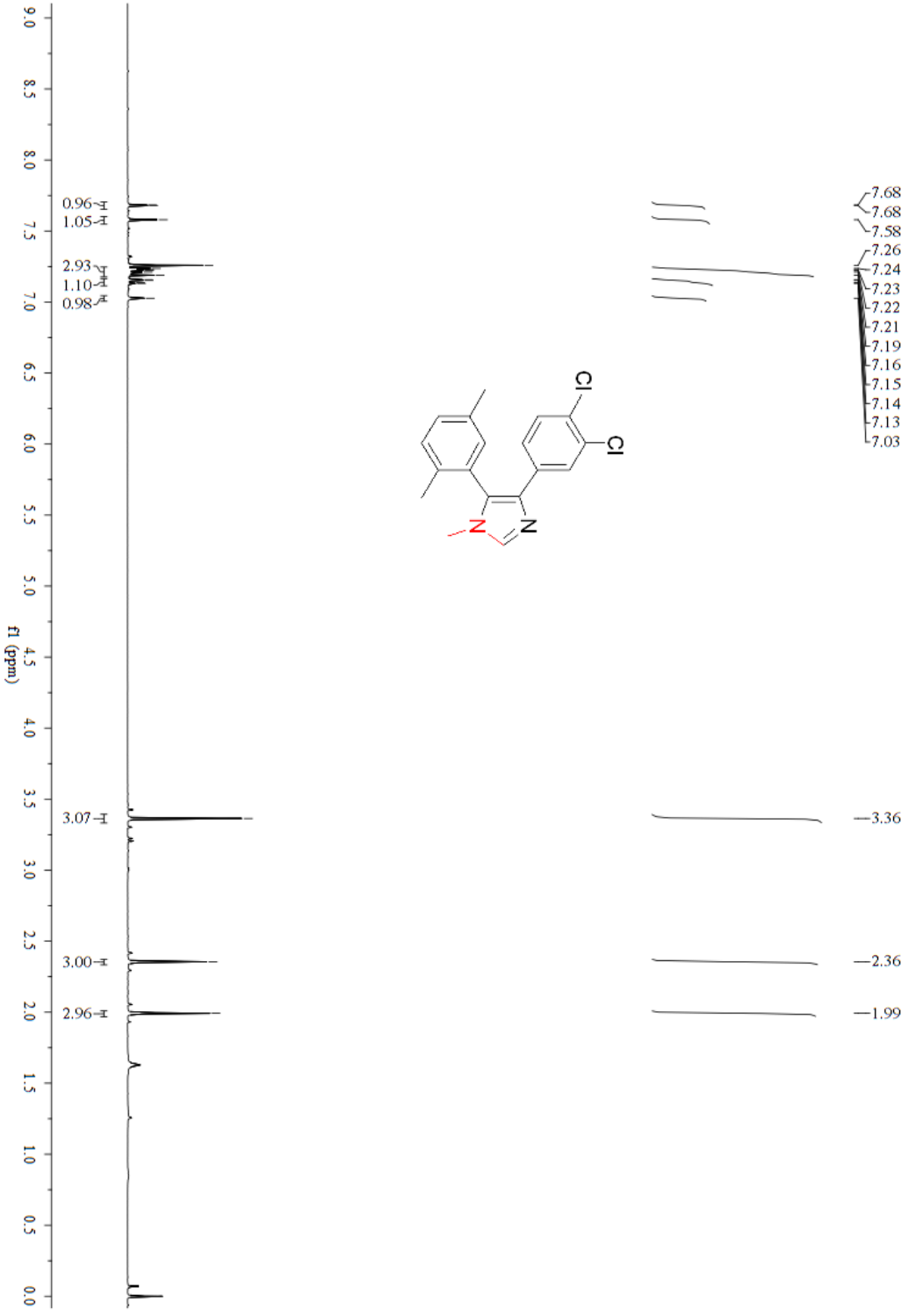

N
N
Cl

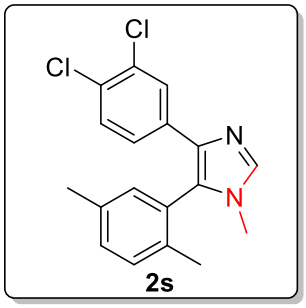
2r


f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl
N
N
138.72
137.67
136.28
134.69
131.99
131.31
129.30
129.08
128.95
127.17
126.70
77.32
77.00
76.68
32.22
21.11

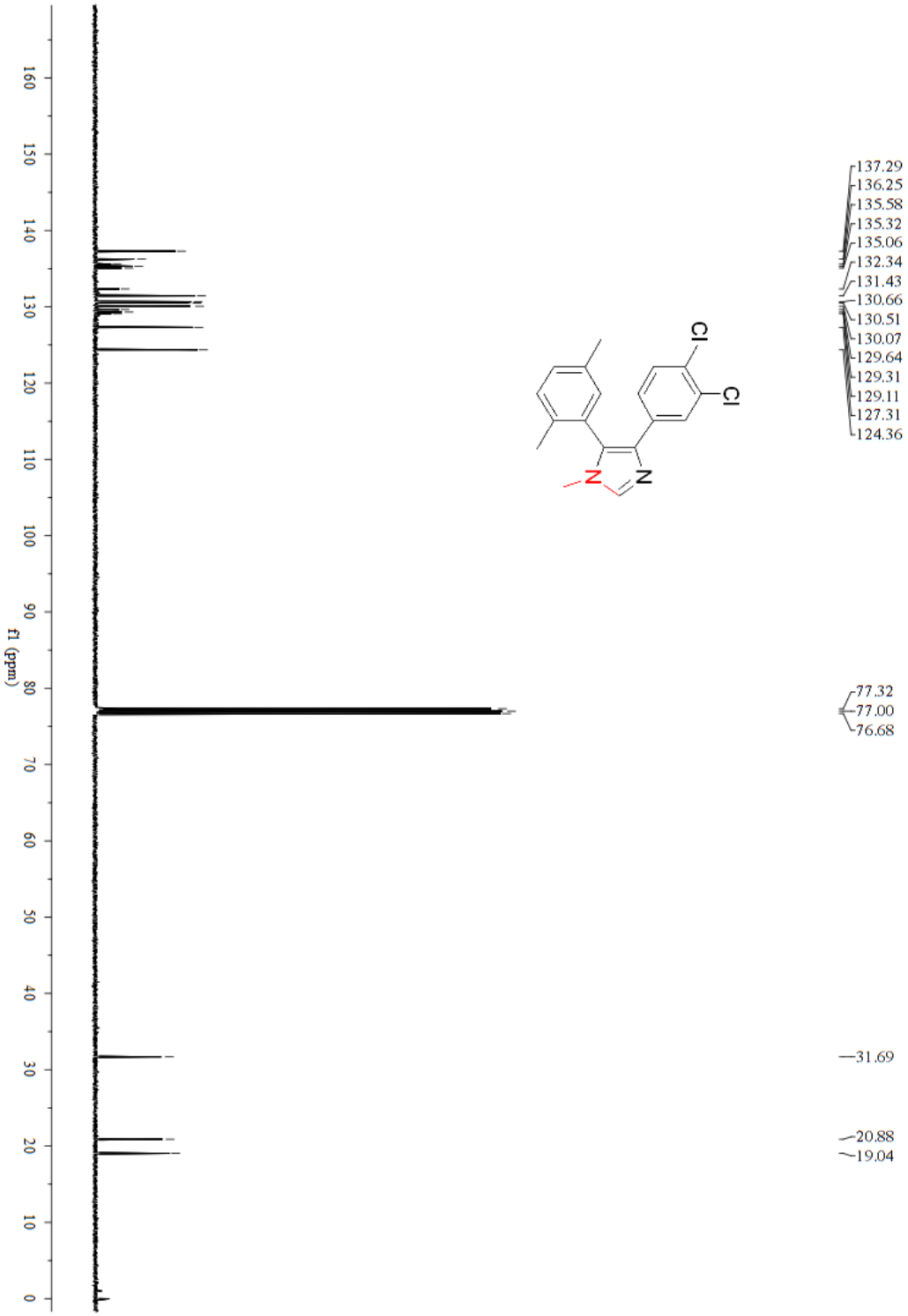

Cl
Cl
N
N

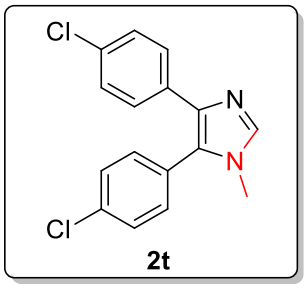
2s

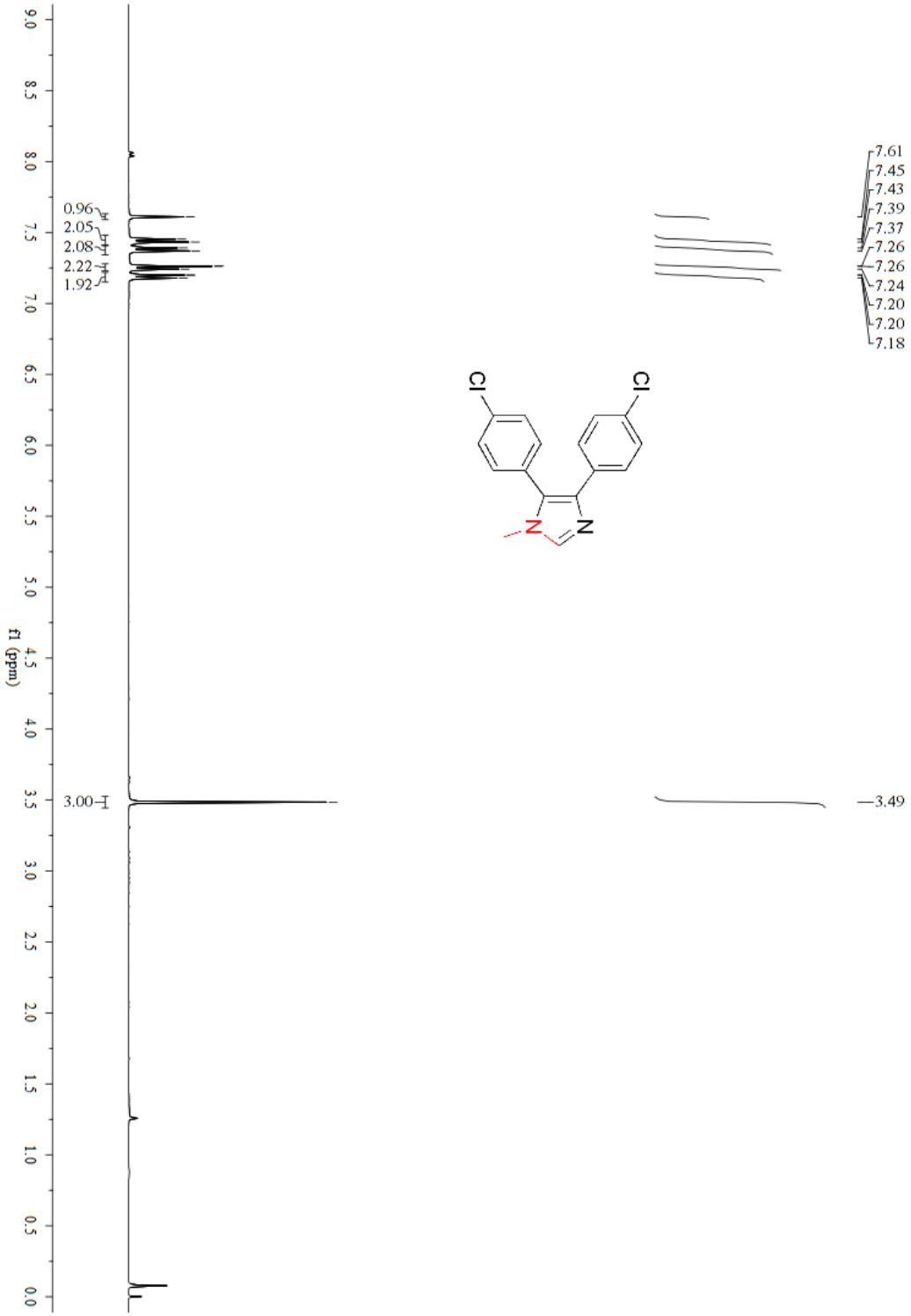

f1 (ppm)
0.96
1.05
2.93
1.10
0.98
3.07
3.00
2.96
7.68
7.68
7.58
7.26
7.24
7.23
7.22
7.21
7.19
7.16
7.15
7.14
7.13
7.03
3.36
2.36
1.99
Cl
Cl
N
N

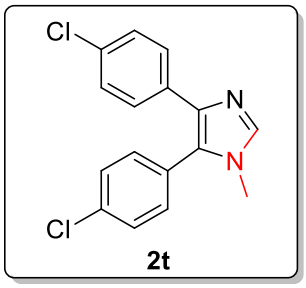

Cl
Cl
N
N

2s

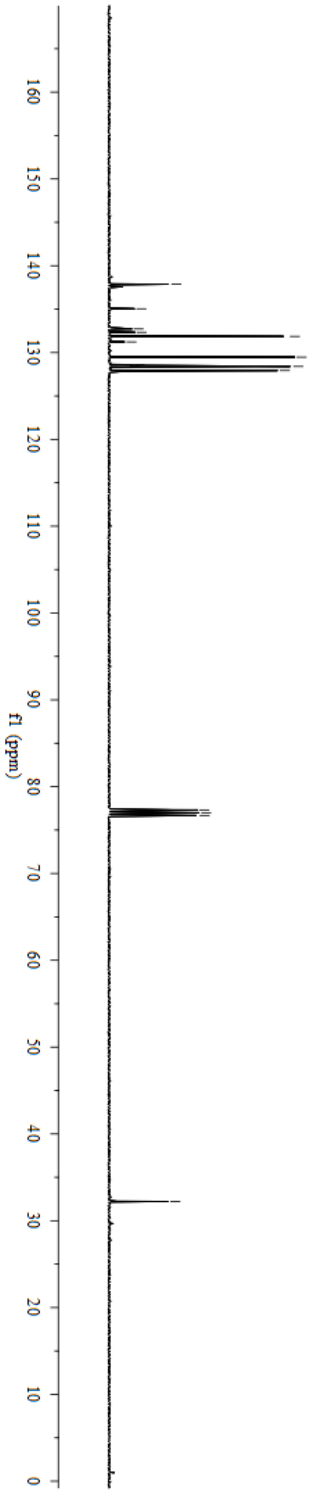

f1 (ppm)
137.29
136.25
135.58
135.32
135.06
132.34
131.43
130.66
130.51
130.07
129.64
129.31
129.11
127.31
124.36
77.32
77.00
76.68
31.69
20.88
19.04

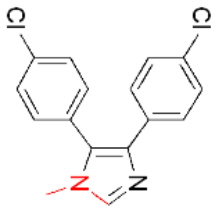

Cl
N
N
Cl
2t


0.96
2.05
2.08
2.22
1.92
3.00
3.49
7.61
7.45
7.43
7.39
7.37
7.26
7.26
7.24
7.20
7.20
7.18
Cl
Cl
N
N
f1 (ppm)



2t

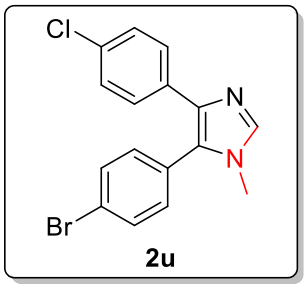




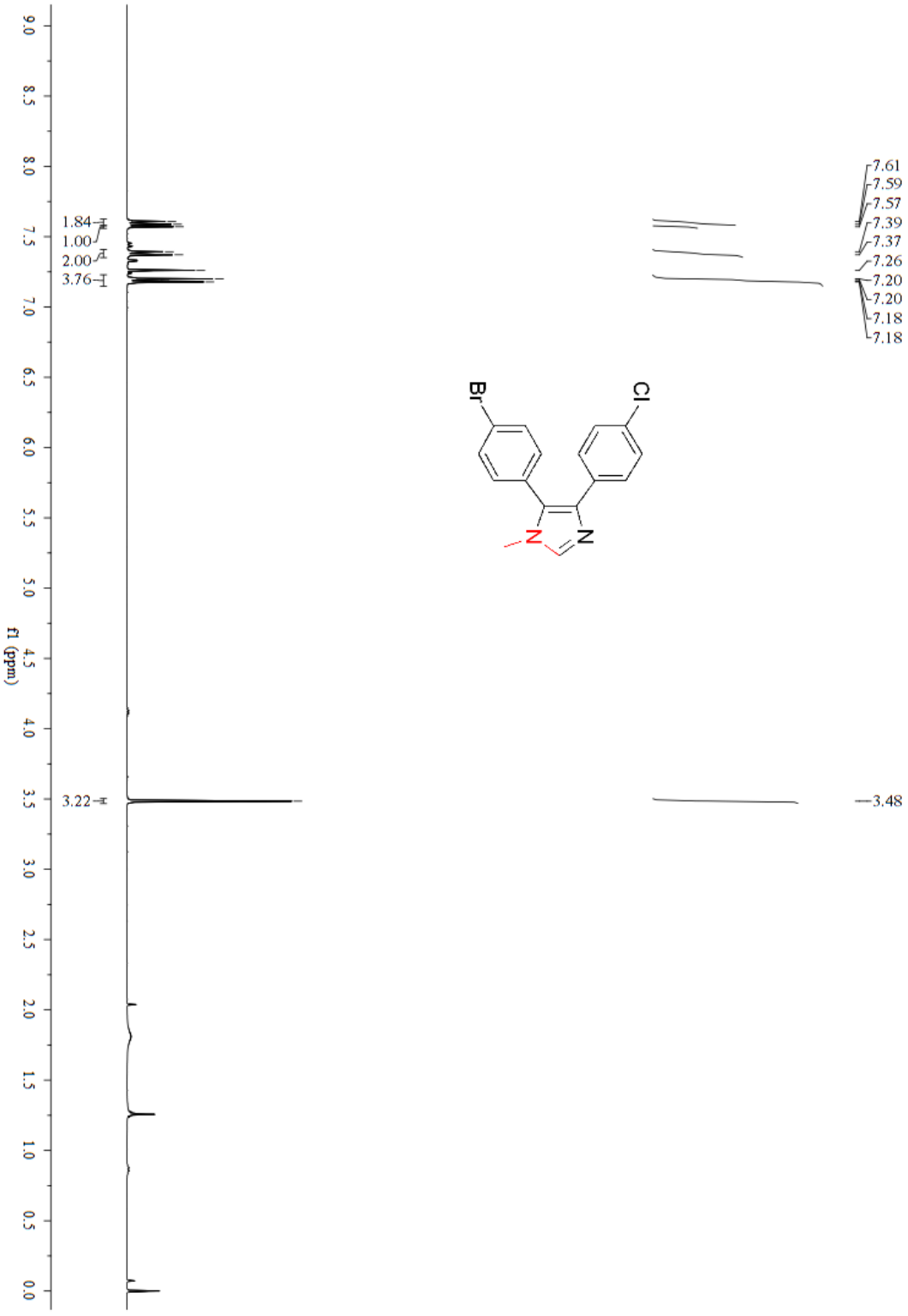
137.87
135.04
132.72
132.33
131.86
131.23
129.47
128.62
128.46
128.40
127.93

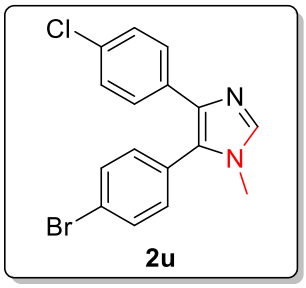
77.32
77.00
76.68

32.23

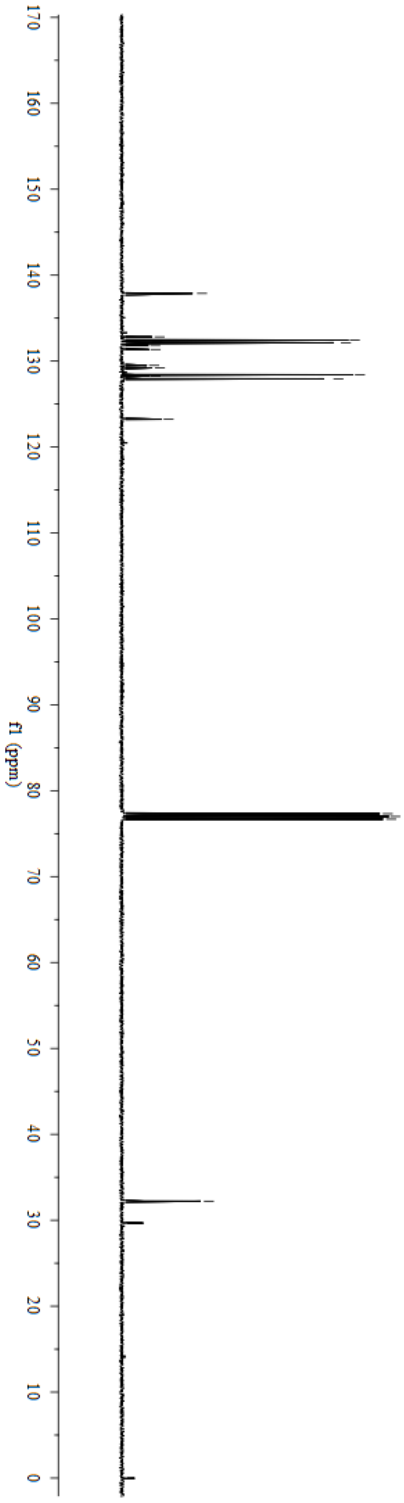

Cl
N
N
Br

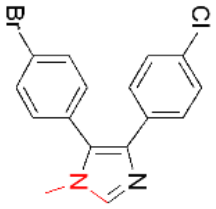
2u


1.84
1.00
2.00
3.76
3.22
3.48
7.61
7.59
7.57
7.39
7.37
7.26
7.20
7.20
7.18
7.18
Br
Cl
N
N
f1 (ppm)



2u

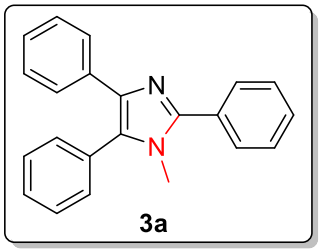




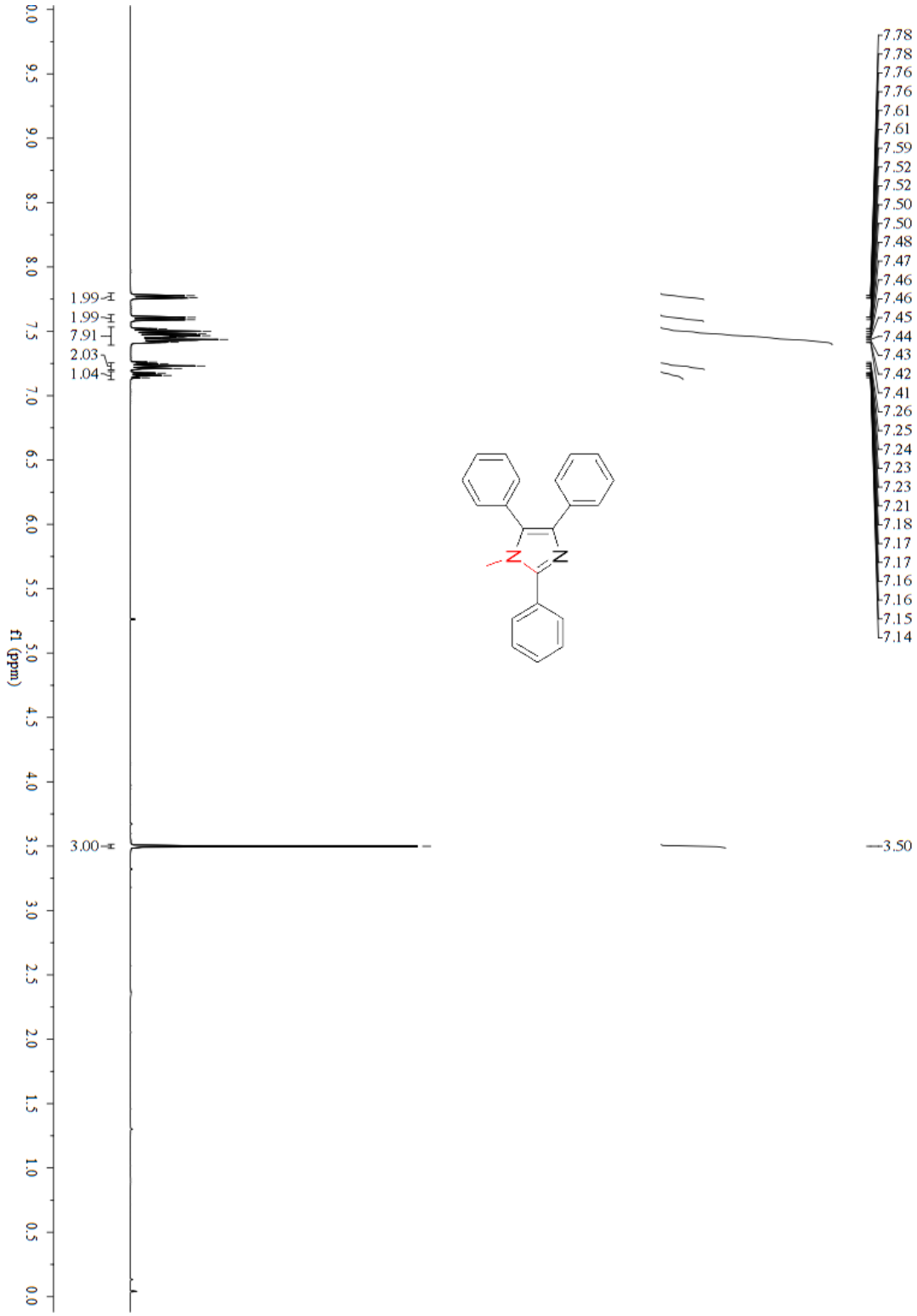
137.88
132.82
132.44
132.35
132.14
131.86
131.35
129.49
129.20
128.42
128.24
127.94
123.22

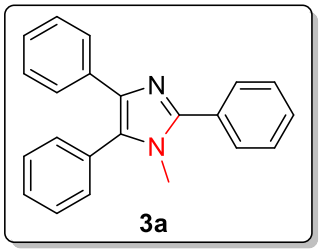
77.32
77.00
76.68

32.22

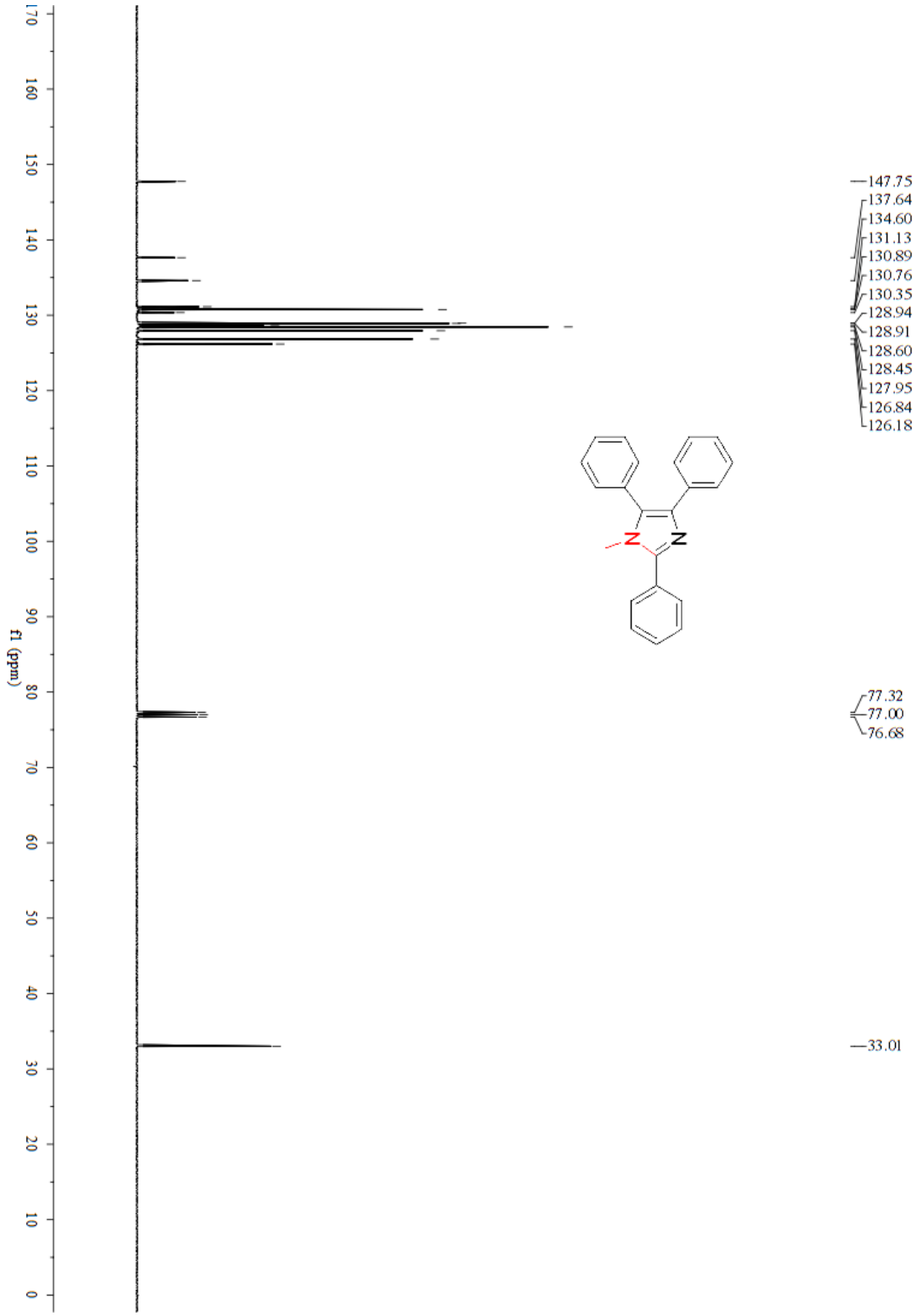

N
N

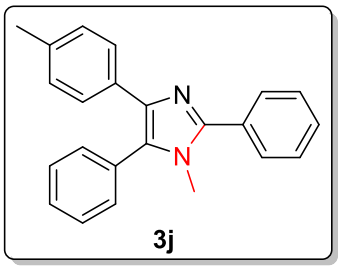
3a


1.99
1.99
7.91
2.03
1.04
3.00
f1 (ppm)
7.78
7.78
7.76
7.76
7.61
7.61
7.59
7.52
7.52
7.50
7.50
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.42
7.41
7.26
7.25
7.24
7.23
7.23
7.21
7.18
7.17
7.17
7.16
7.16
7.15
7.14
3.50

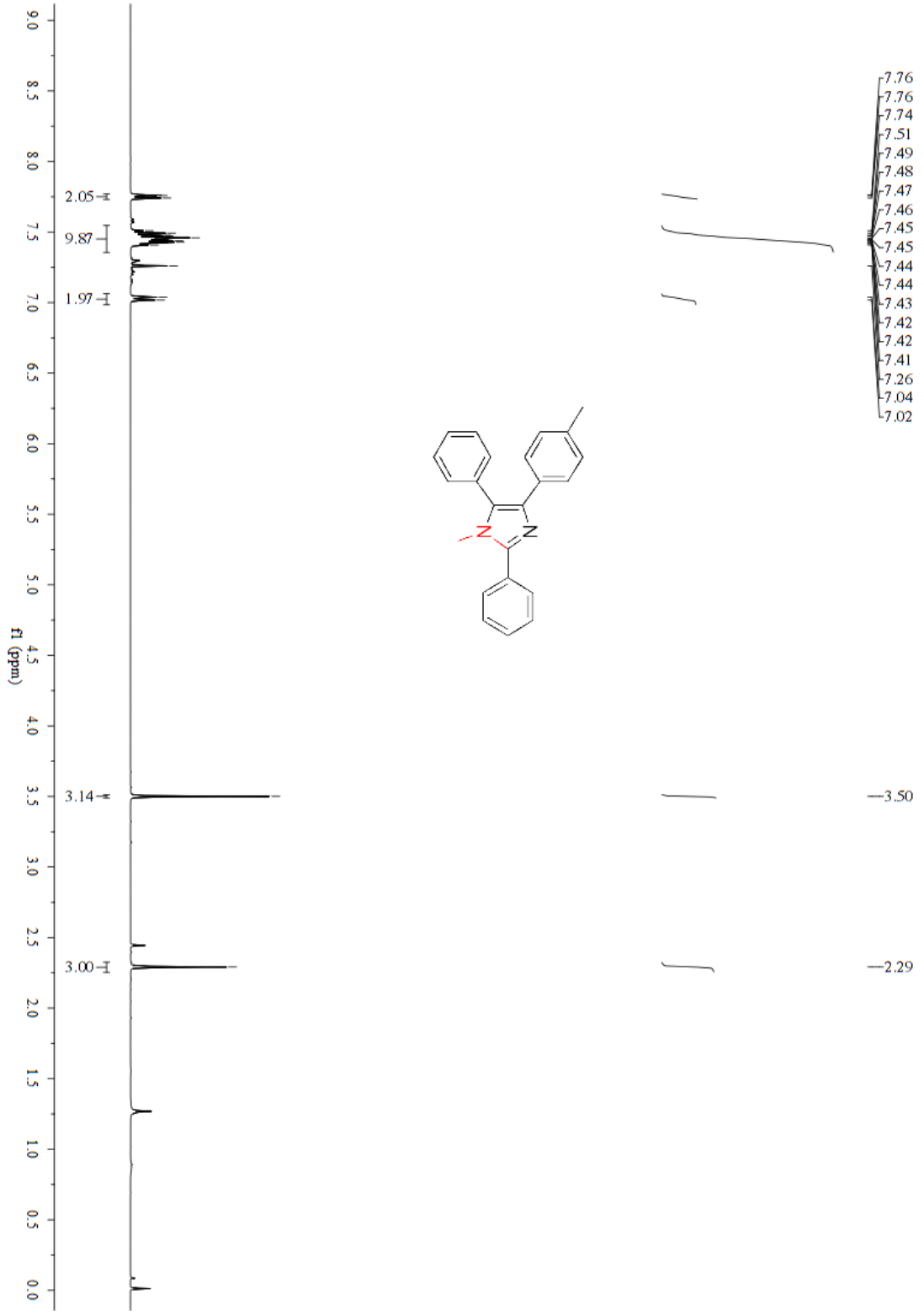

N
N

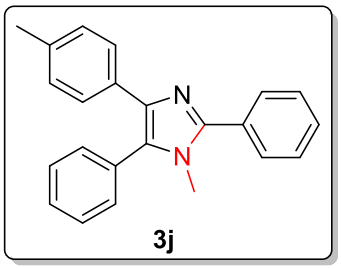
3a


f1 (ppm)
147.75
137.64
134.60
131.13
130.89
130.76
130.35
128.94
128.91
128.60
128.45
127.95
126.84
126.18
77.32
77.00
76.68
33.01

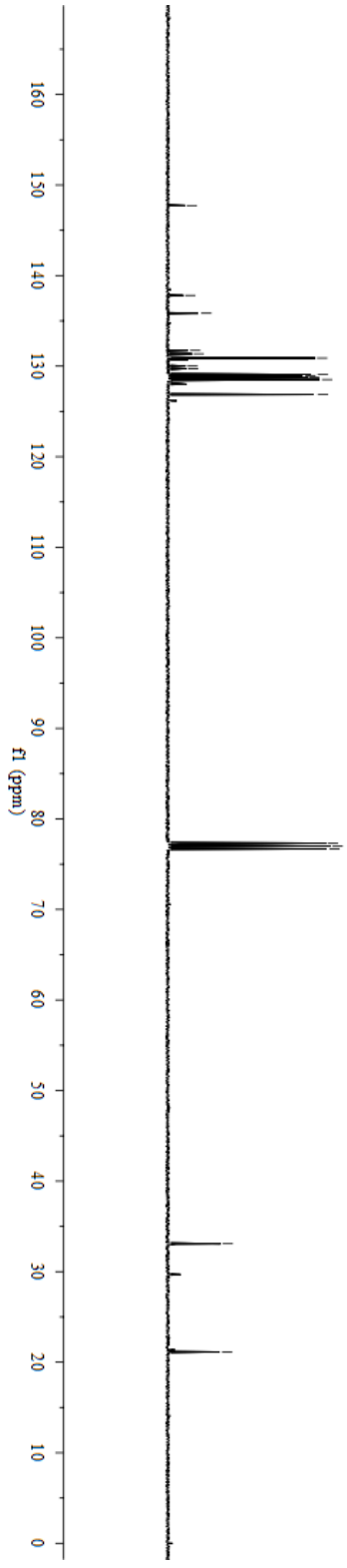

N
N

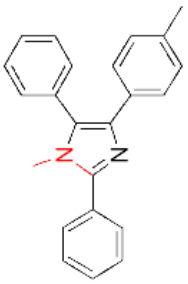
3j


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
0.0
f1 (ppm)
2.05
9.87
1.97
3.14
3.00
7.76
7.76
7.74
7.51
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.26
7.04
7.02
3.50
2.29
N
N



3j



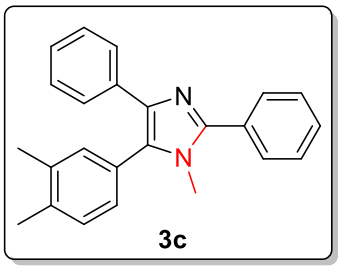


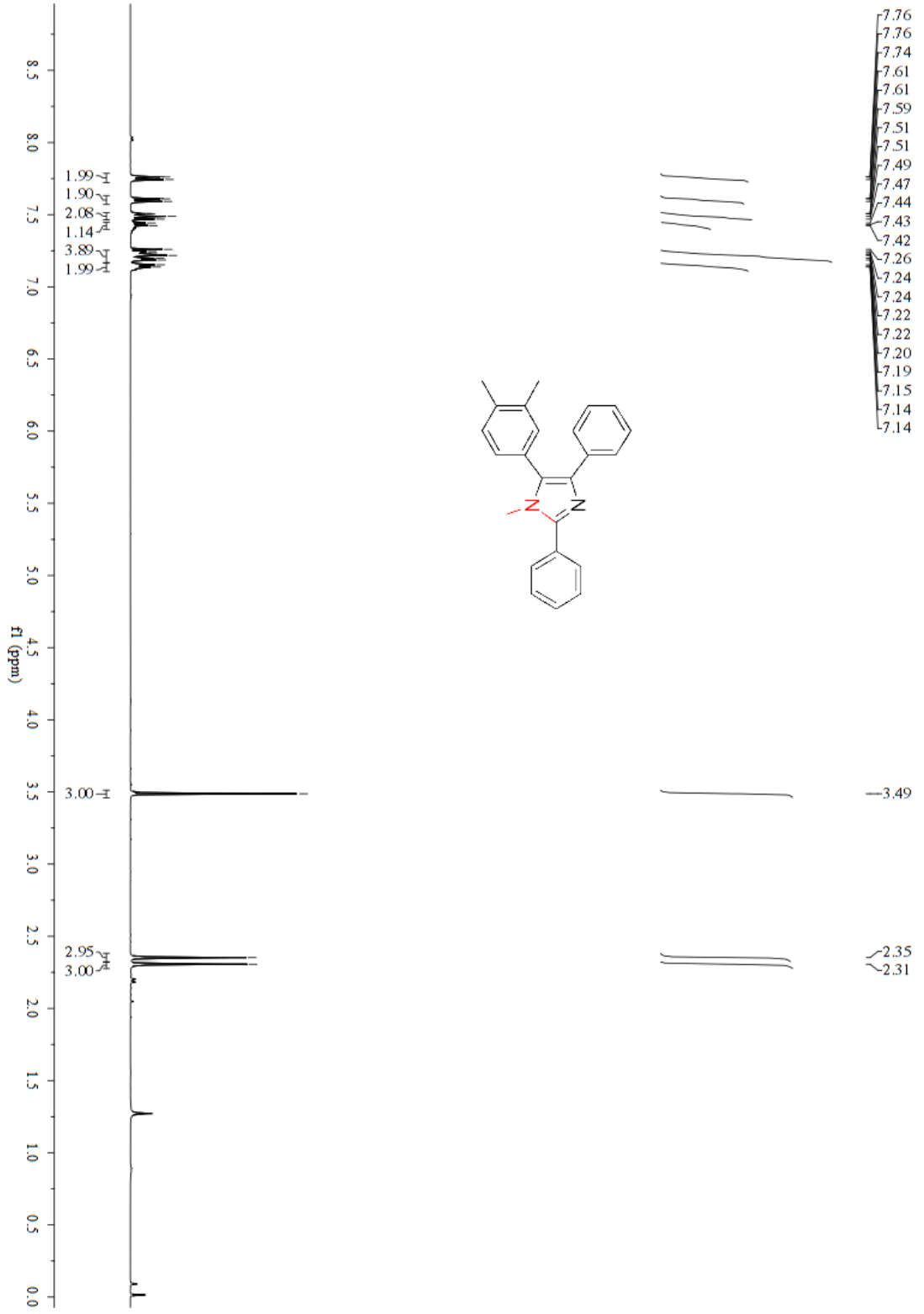
147.73
137.81
135.84
131.74
131.36
130.89
130.00
129.73
129.07
128.95
128.76
128.66
128.51
128.44
126.86

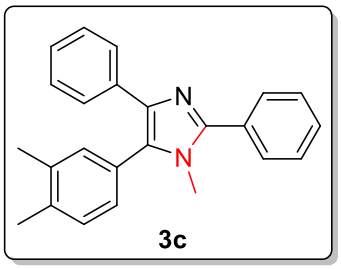
77.32
77.00
76.68

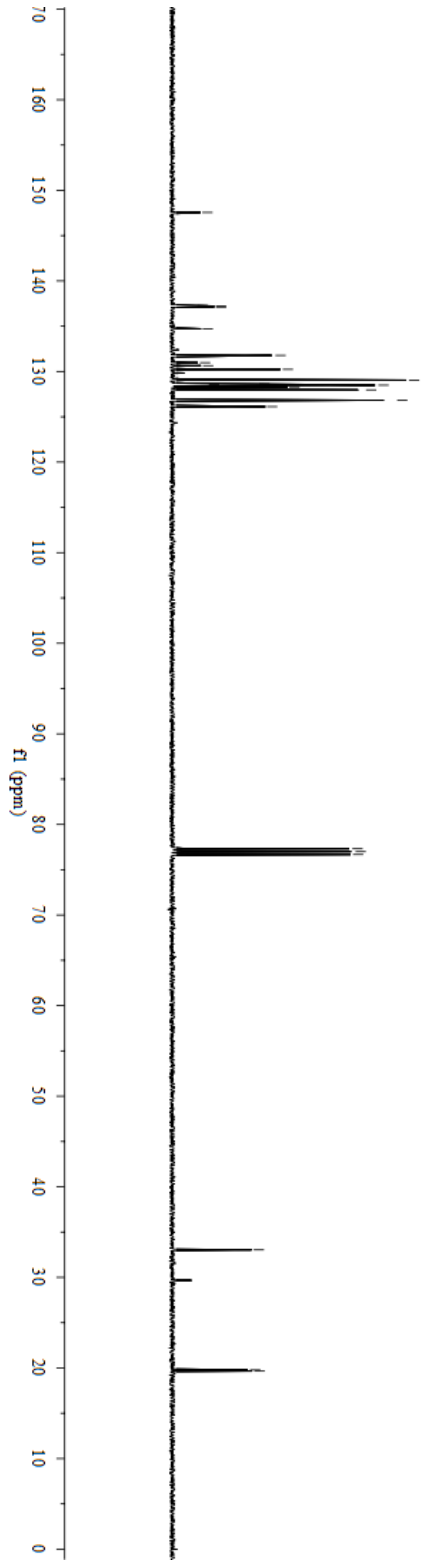
33.09

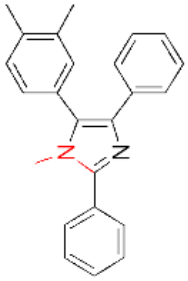
21.13


N
N
3c


7.76
7.76
7.74
7.61
7.61
7.59
7.51
7.51
7.49
7.47
7.44
7.43
7.42
7.26
7.24
7.24
7.22
7.22
7.20
7.19
7.15
7.14
7.14
3.49
2.35
2.31
1.99
1.90
2.08
1.14
3.89
1.99
3.00
2.95
3.00
f1 (ppm)





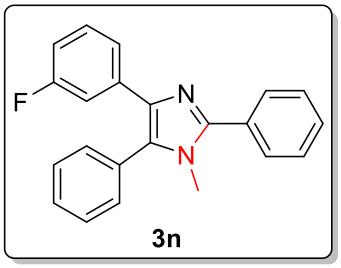


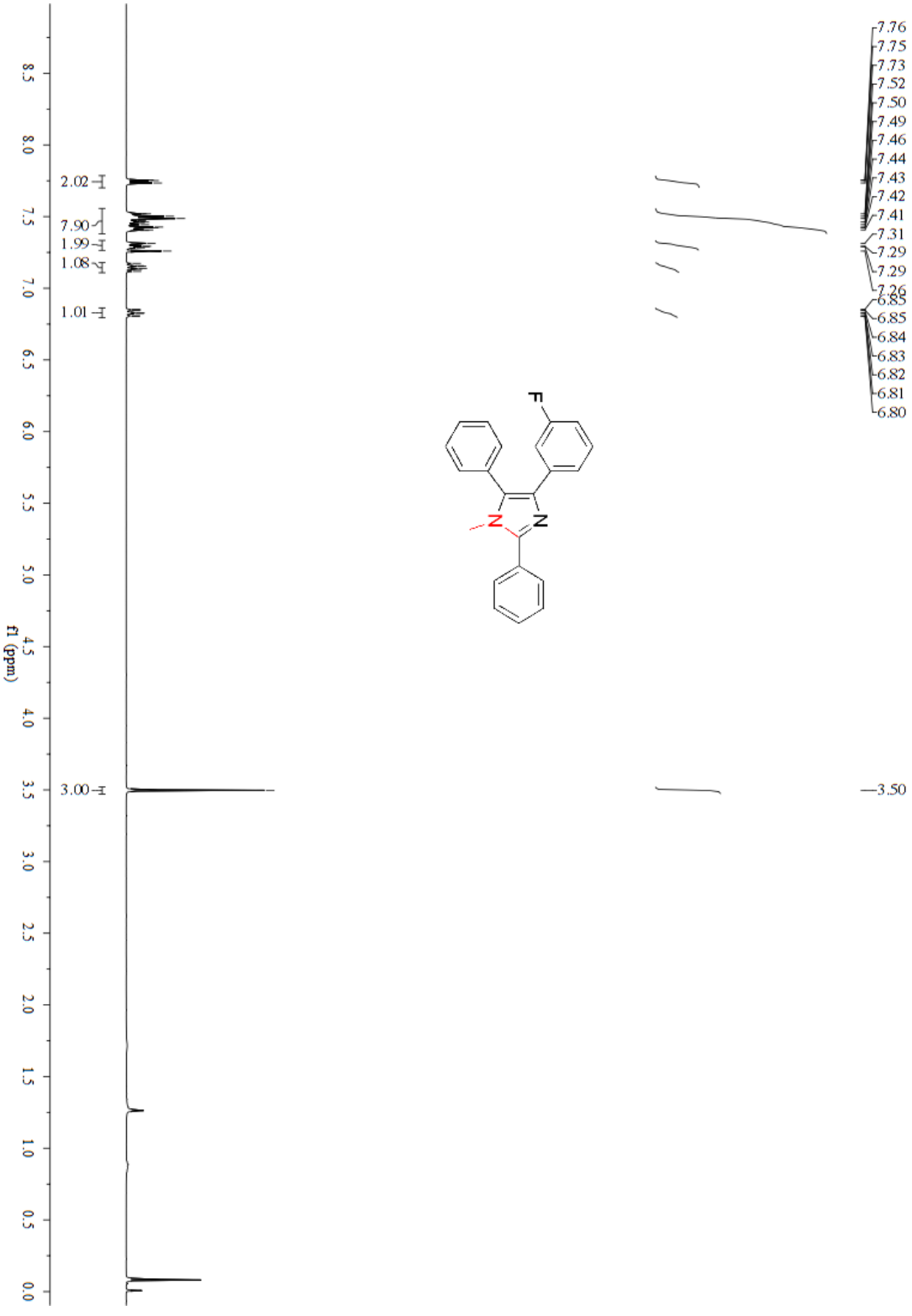
147.56
137.29
137.23
137.11
134.72
131.78
130.98
130.65
130.23
129.05
128.63
128.56
128.49
128.30
127.97
126.83
126.12

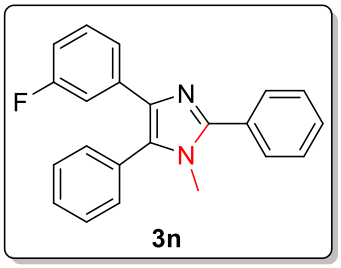
77.32
77.00
76.68

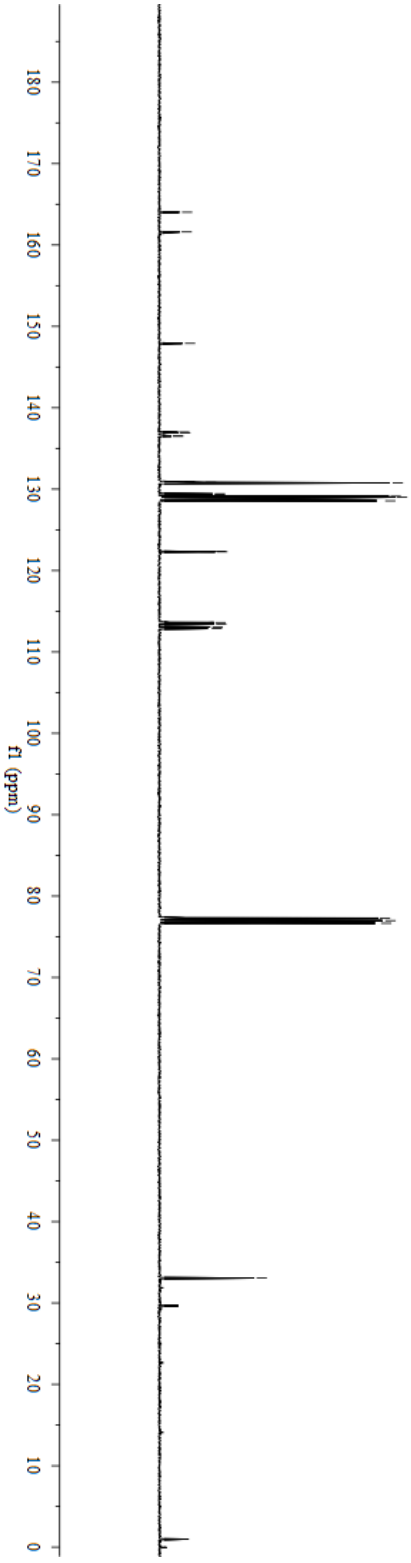
33.04

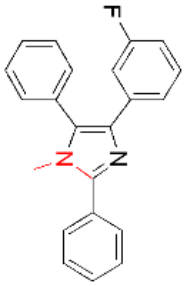
19.78
19.66


F
N
N
3n

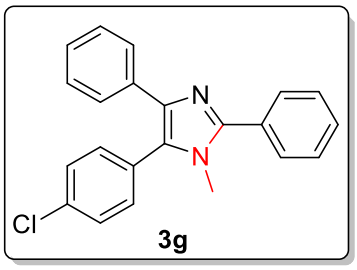

2.02
7.90
1.99
1.08
1.01
3.00
3.50
7.76
7.75
7.73
7.52
7.50
7.49
7.46
7.44
7.43
7.42
7.41
7.31
7.29
7.29
7.26
6.85
6.85
6.84
6.83
6.82
6.81
6.80
F
N
N
f1 (ppm)



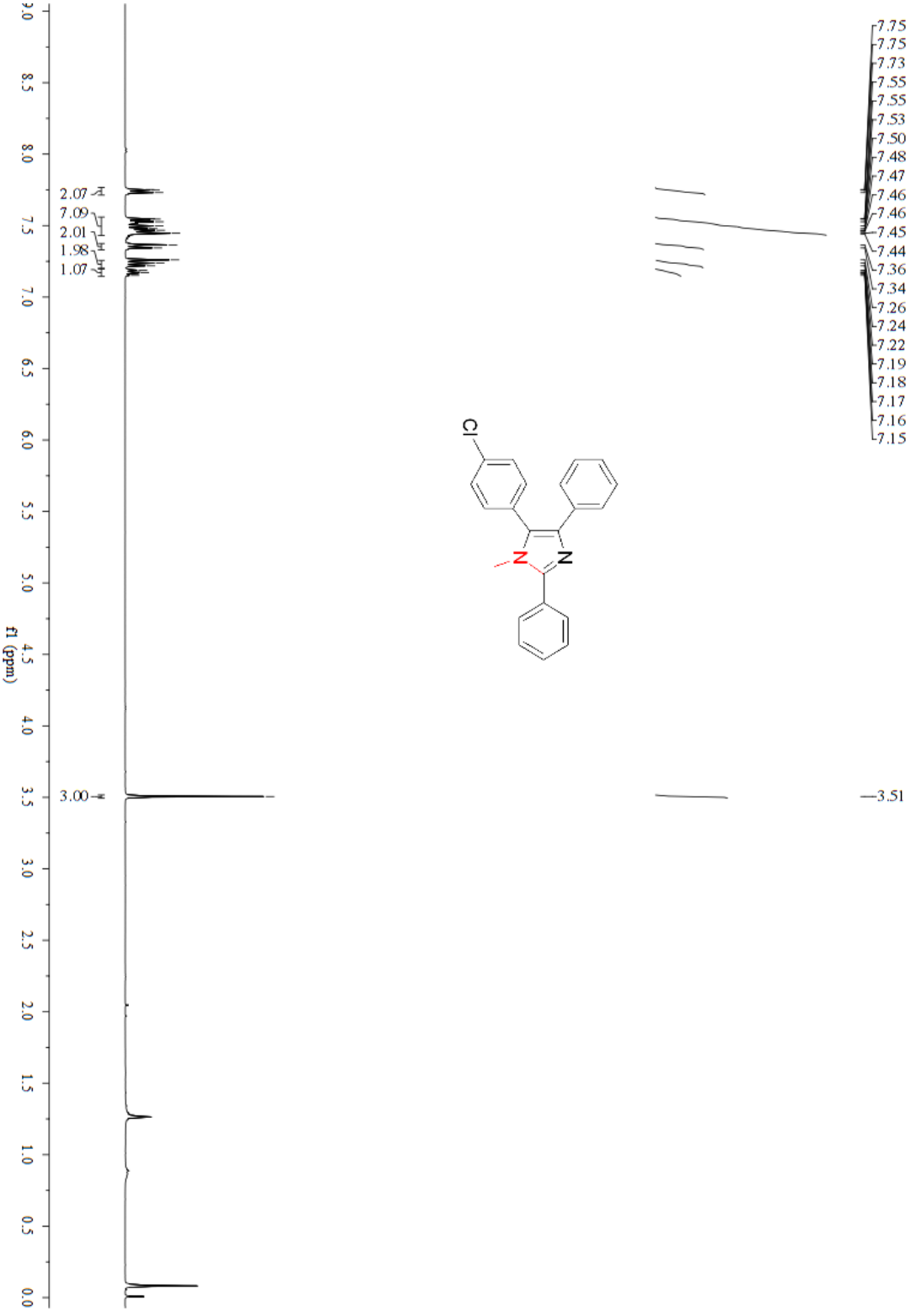


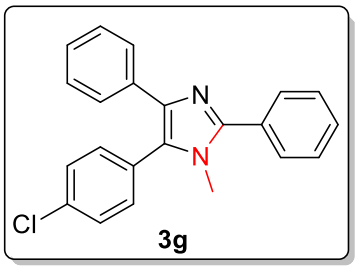


164.02
161.60
147.91
137.01
136.92
136.53
136.50
130.77
129.13
129.00
122.33
122.30
113.61
113.39
113.07
112.86
77.30
76.98
76.66
33.07

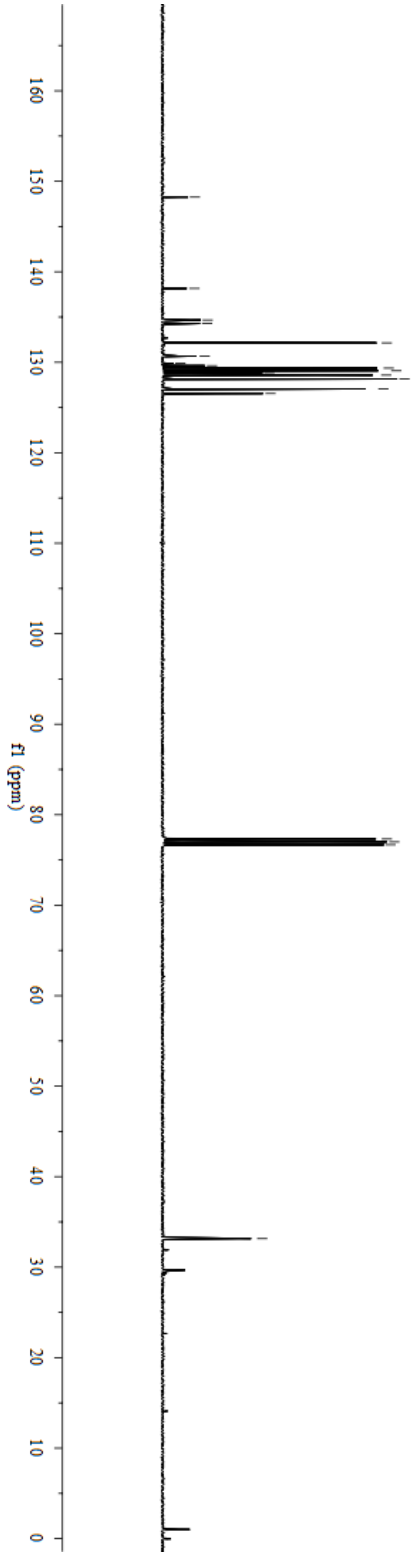

N
N
Cl

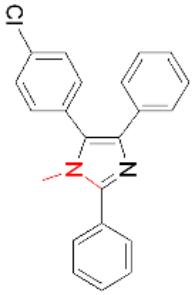
3g


2.07
7.09
2.01
1.98
1.07
3.00
3.51
7.75
7.75
7.73
7.55
7.55
7.53
7.50
7.48
7.47
7.46
7.46
7.45
7.44
7.36
7.34
7.26
7.24
7.22
7.19
7.18
7.17
7.16
7.15
Cl
N
f1 (ppm)



3g

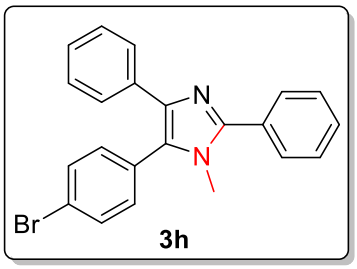




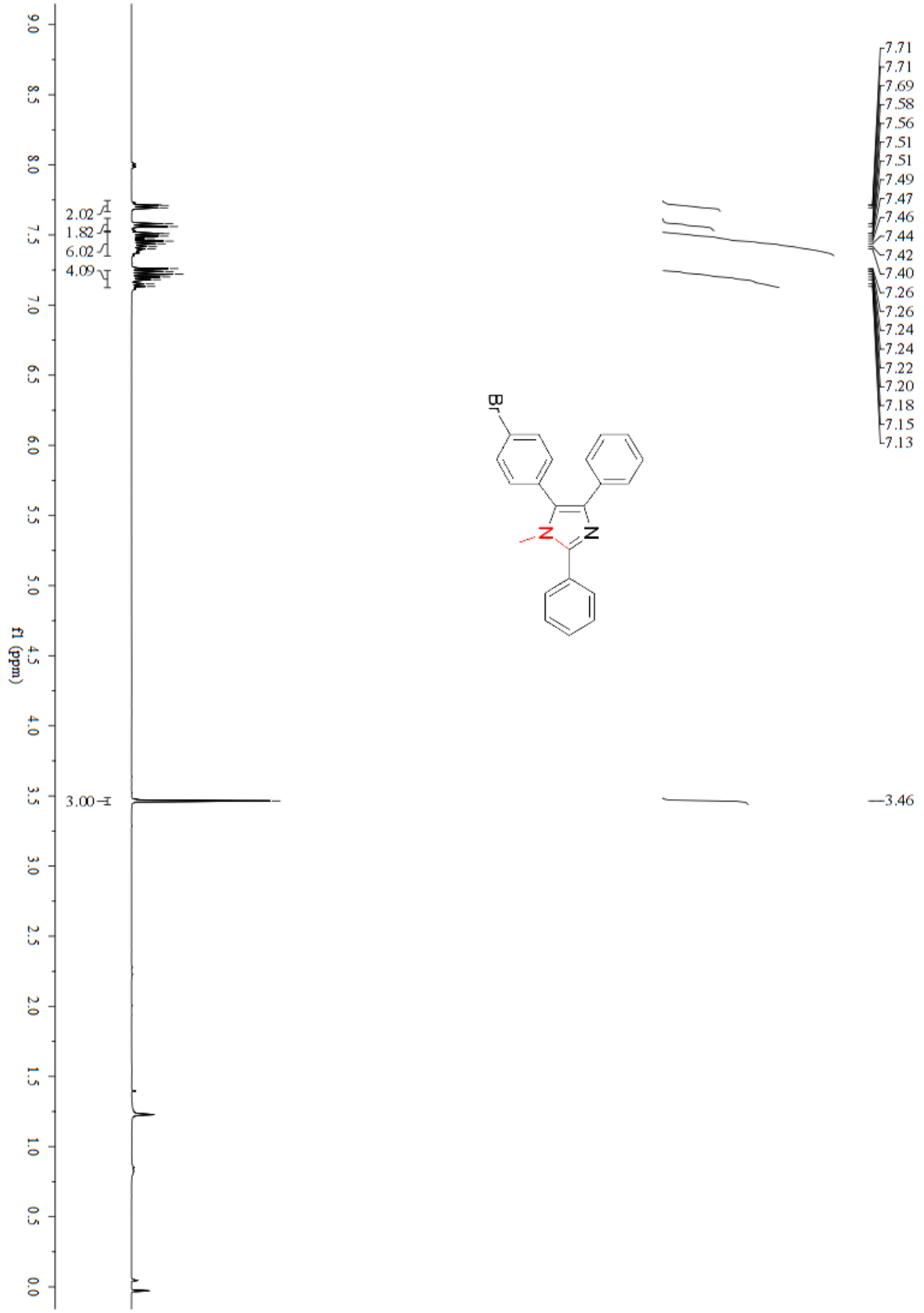
148.25
138.16
134.67
134.28
132.15
130.69
129.90
129.62
129.35
129.06
128.88
128.58
128.15
127.06
126.55

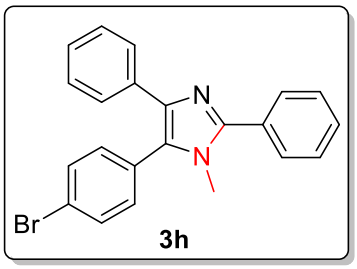
77.32
77.00
76.68

33.15

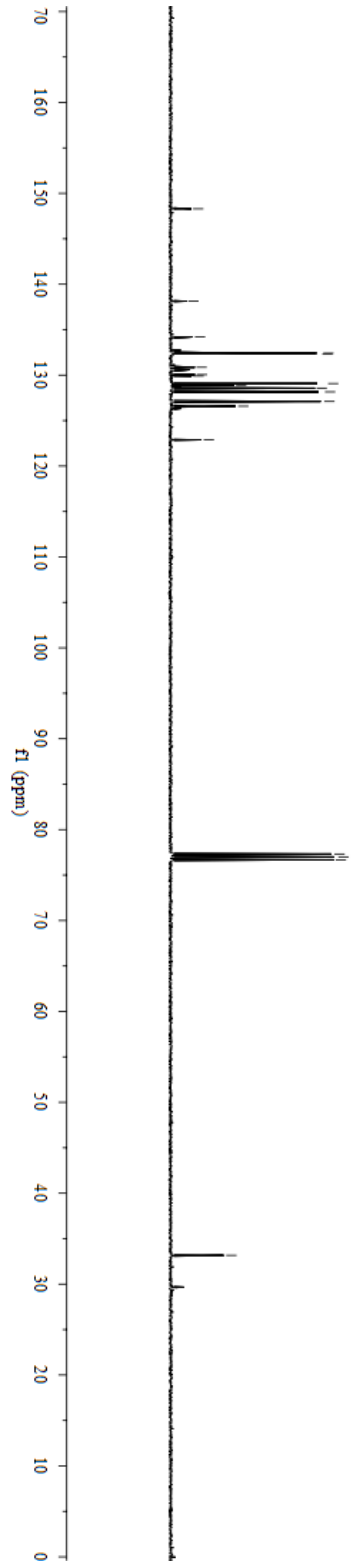

N
N
Br

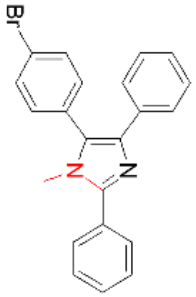
3h


2.02
1.82
6.02
4.09
3.00
f1 (ppm)
7.71
7.71
7.69
7.58
7.56
7.51
7.51
7.49
7.47
7.46
7.44
7.42
7.40
7.26
7.26
7.24
7.24
7.22
7.20
7.18
7.15
7.13
3.46
Br
N
N



3h

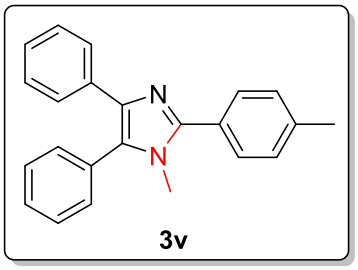




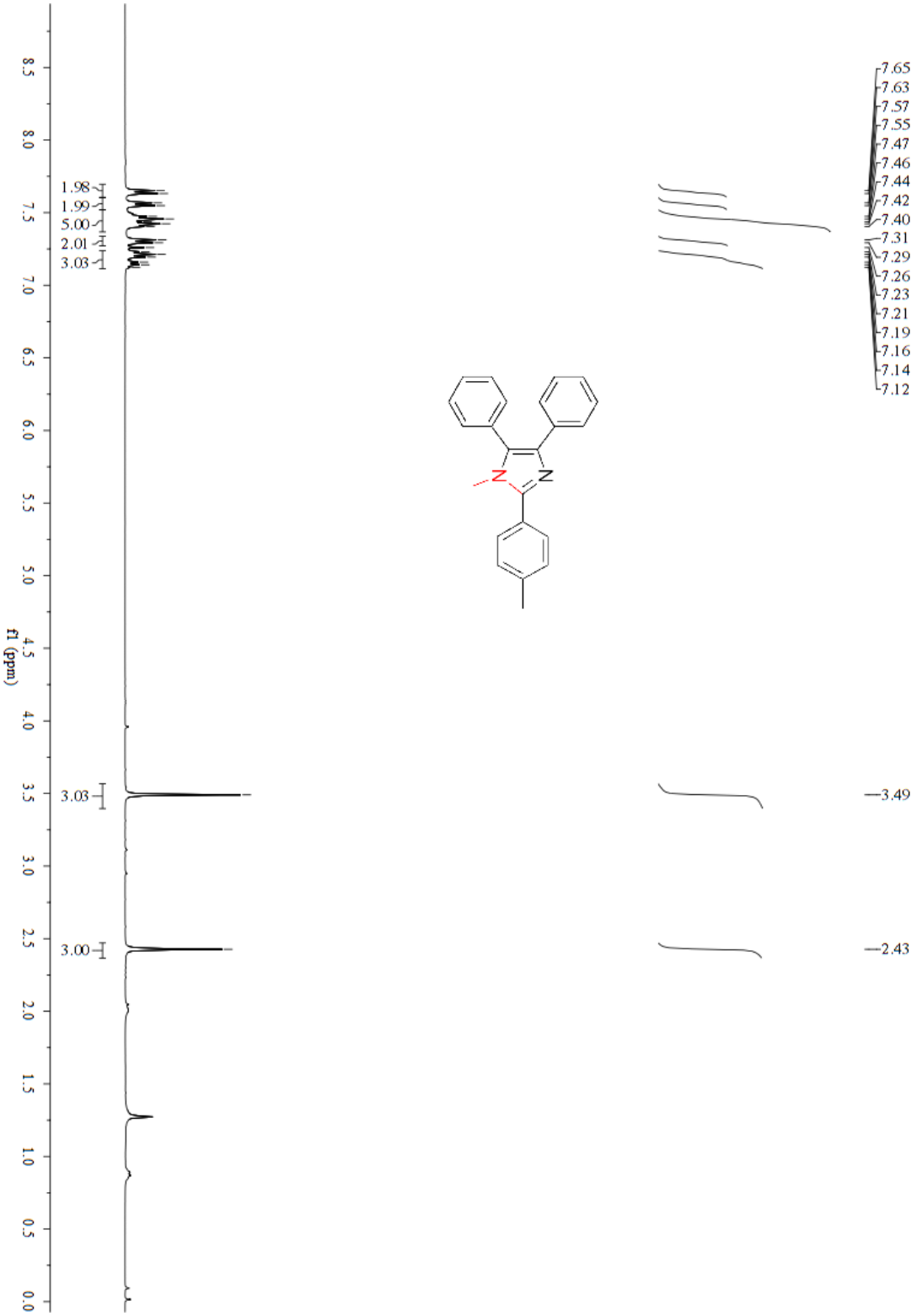
148.30
138.14
134.20
132.41
132.30
130.86
130.06
129.91
129.07
128.90
128.57
128.16
127.10
126.59
122.88

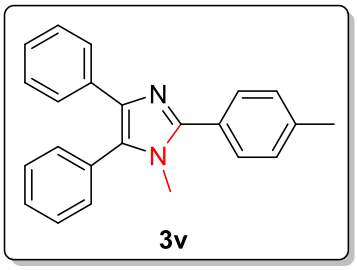
77.32
77.00
76.68

33.17

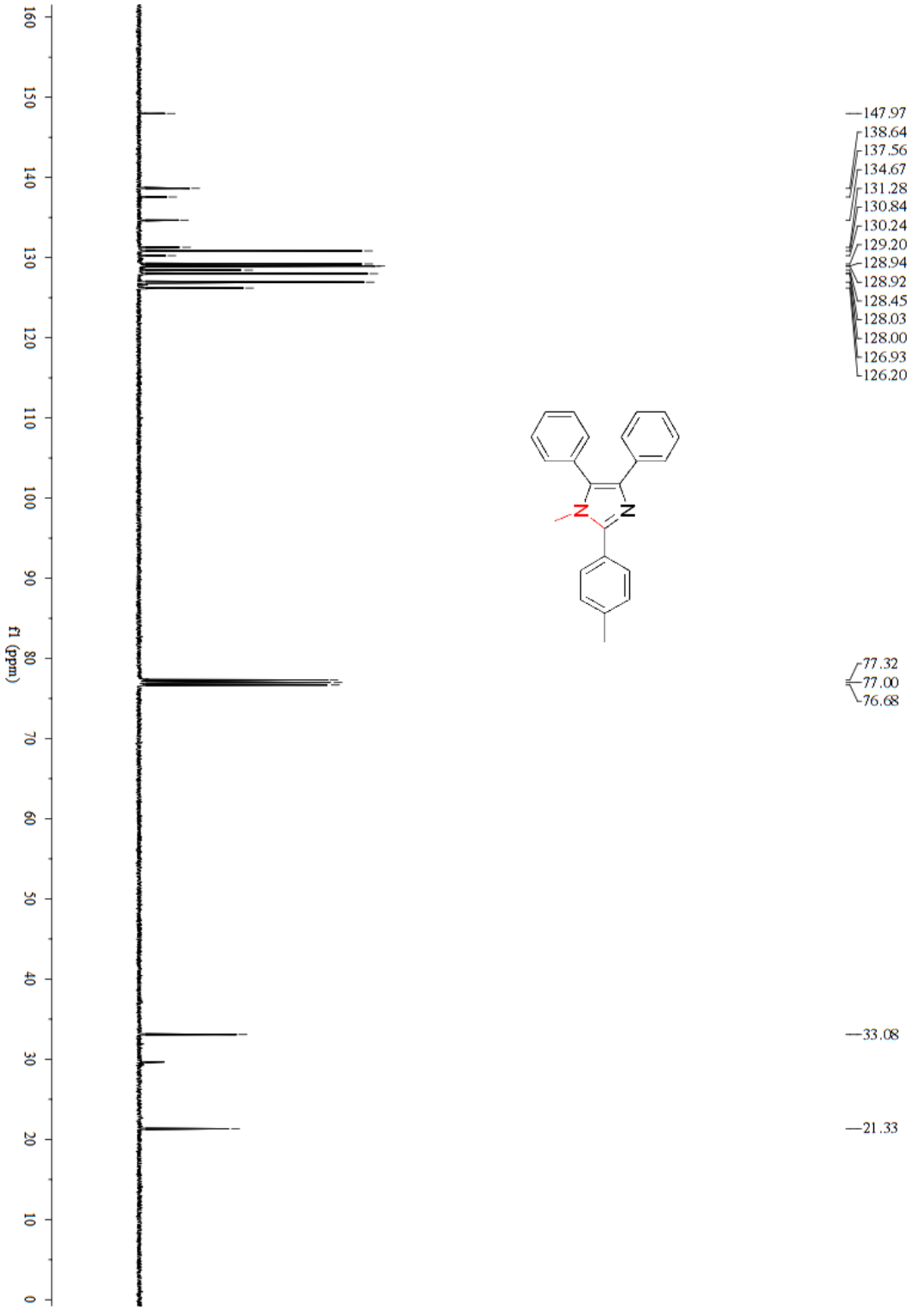

N
N

3v


1.98
1.99
5.00
2.01
3.03
3.03
3.00
f1 (ppm)
7.65
7.63
7.57
7.55
7.47
7.46
7.44
7.42
7.40
7.31
7.29
7.26
7.23
7.21
7.19
7.16
7.14
7.12
3.49
2.43


N
N

3v


f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
147.97
138.64
137.56
134.67
131.28
130.84
130.24
129.20
128.94
128.92
128.45
128.03
128.00
126.93
126.20
77.32
77.00
76.68
33.08
21.33