

Supporting information

I₂-Catalyzed Diamination of Acetyl-compounds to Achieve Multi-substituted Imidazoles

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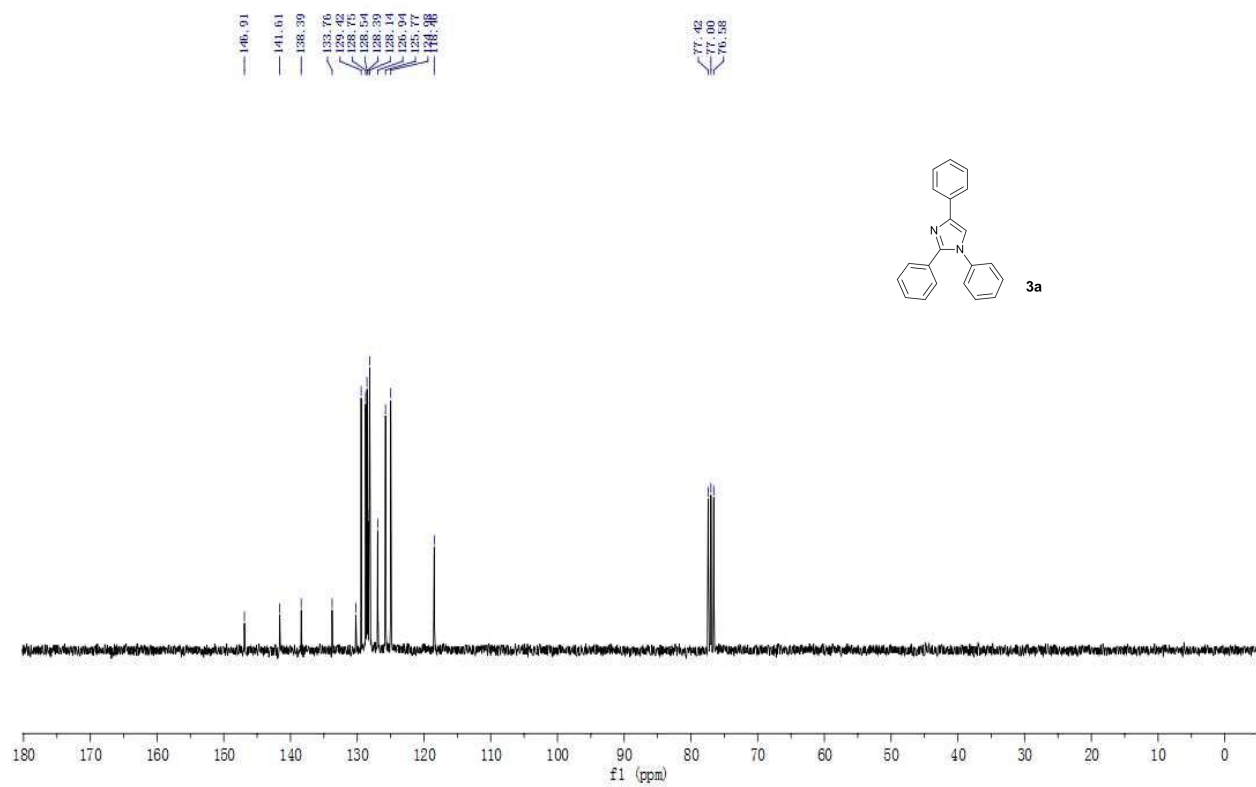
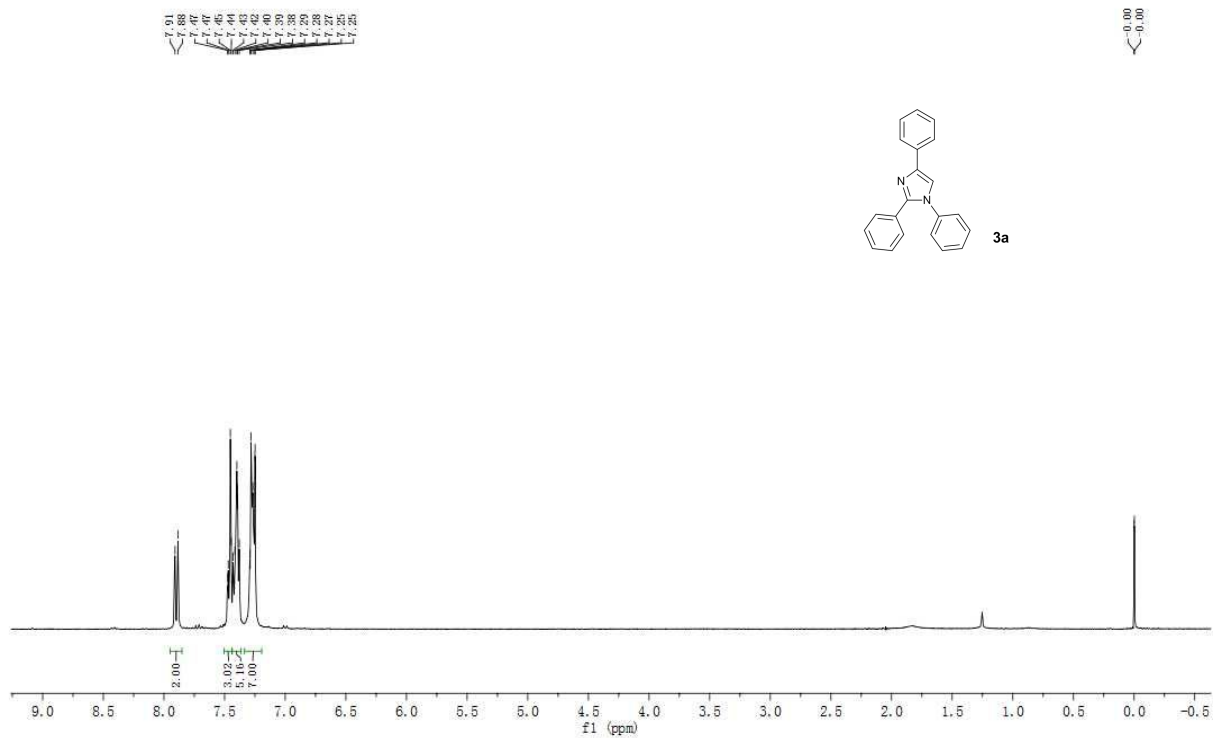
^cState Key Laboratory of Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China

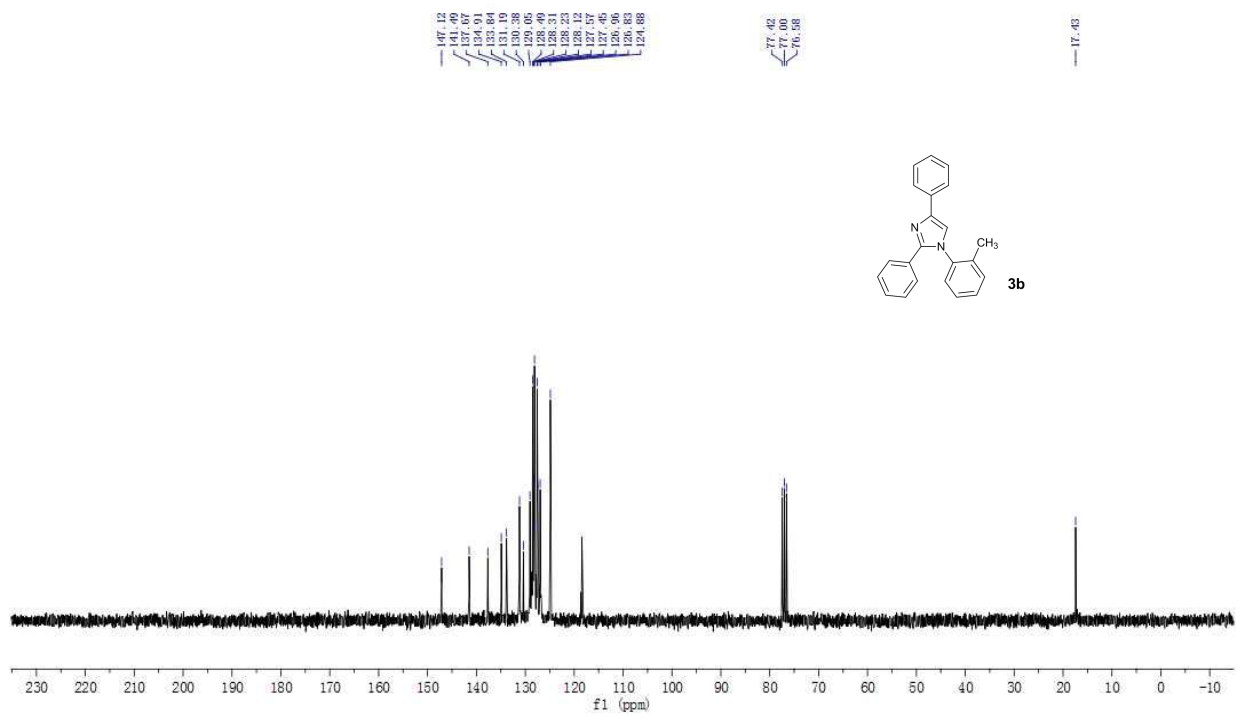
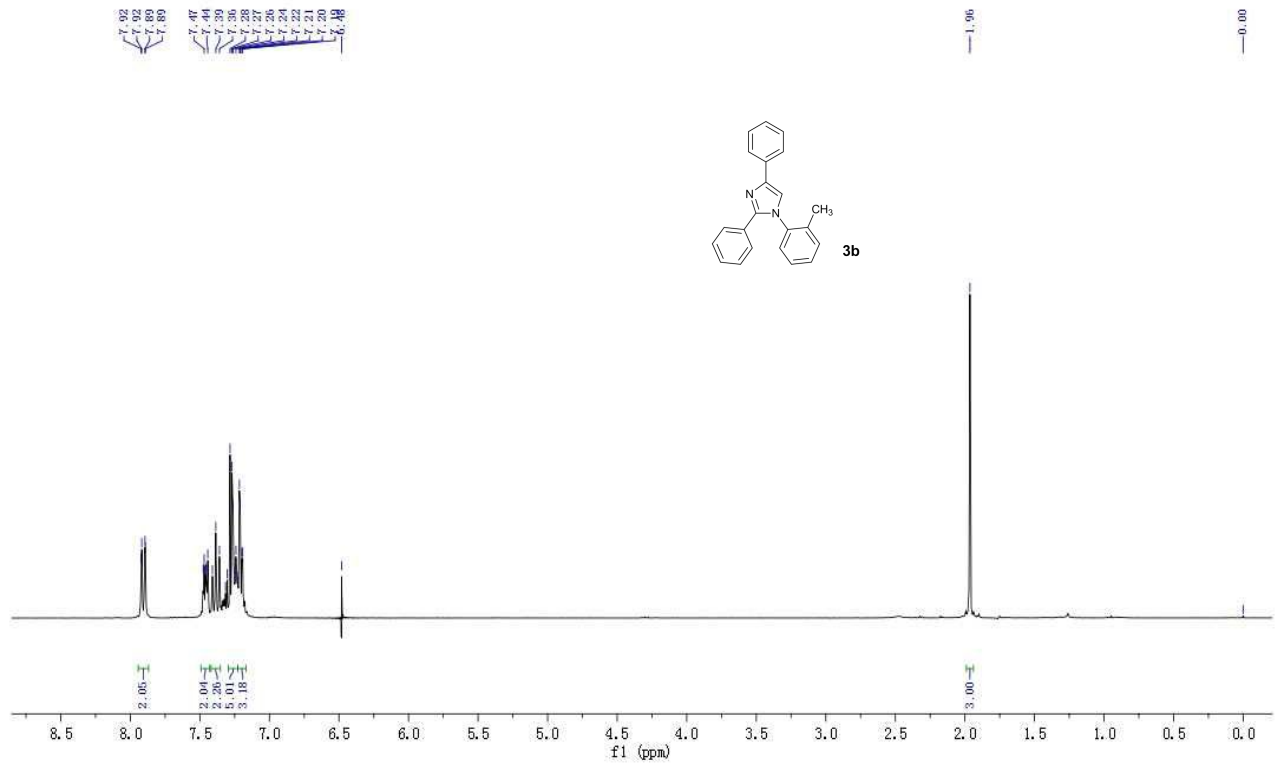
E-mail: chbh@lzu.edu.cn.

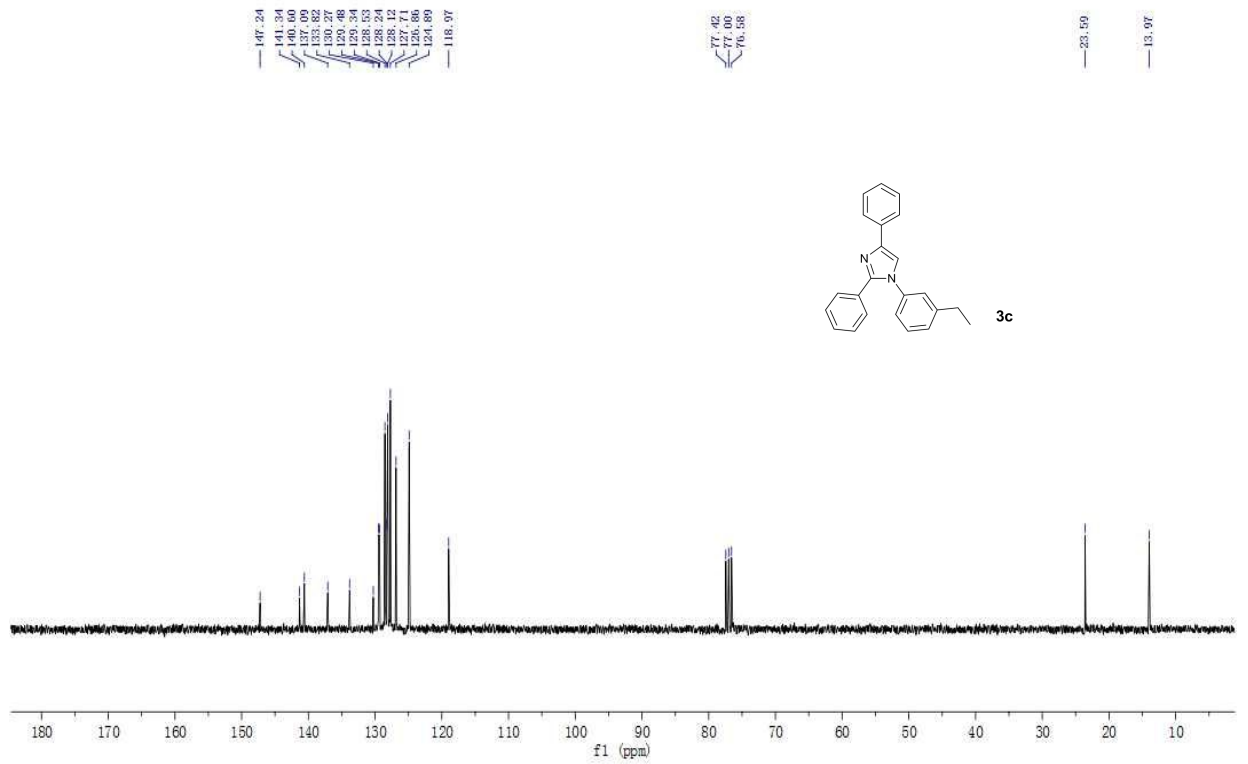
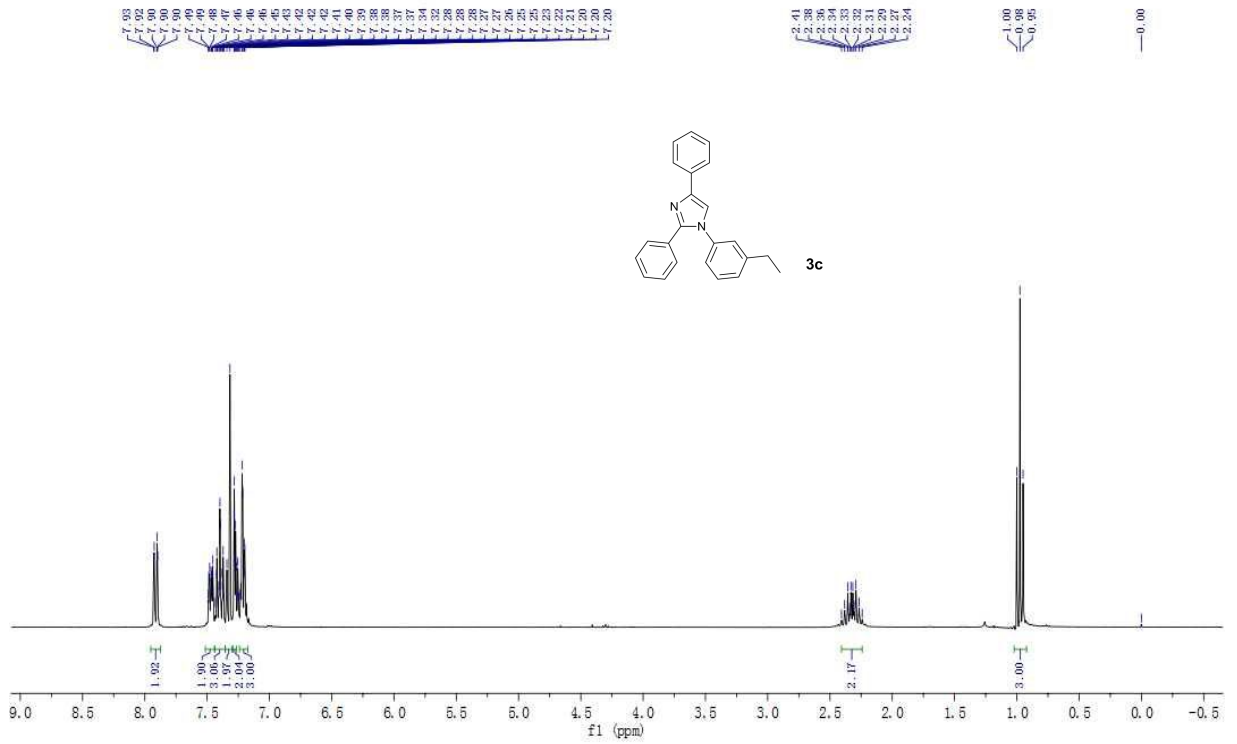
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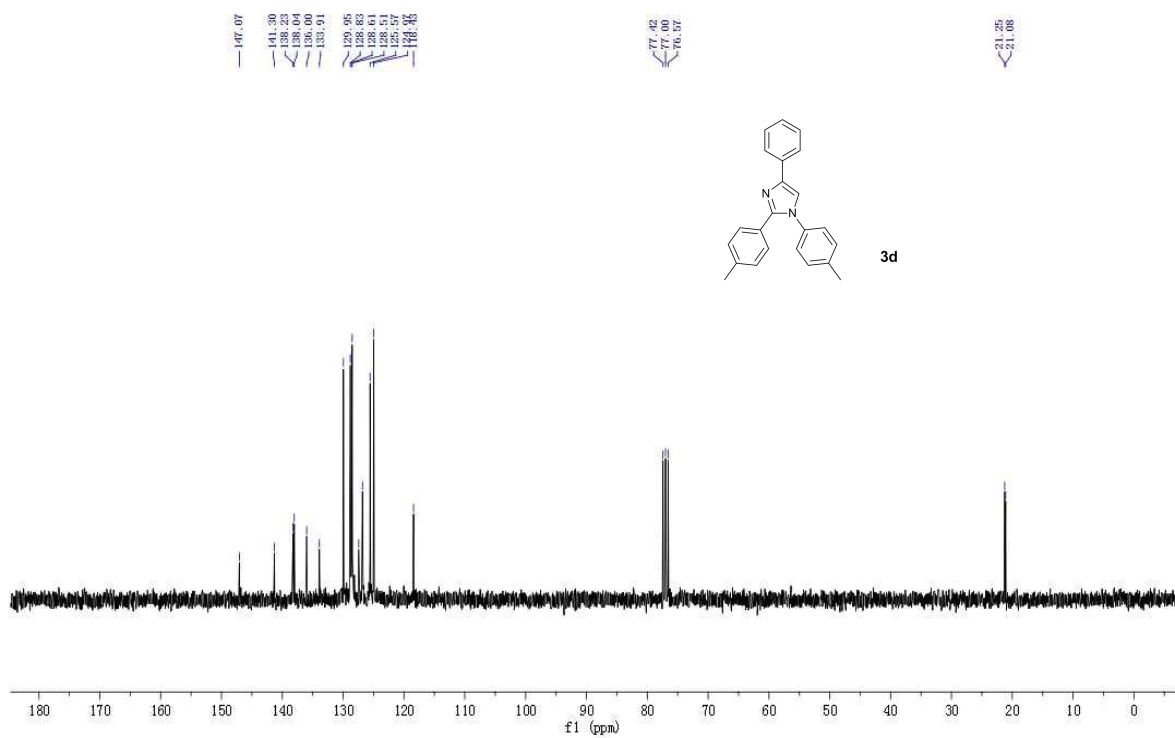
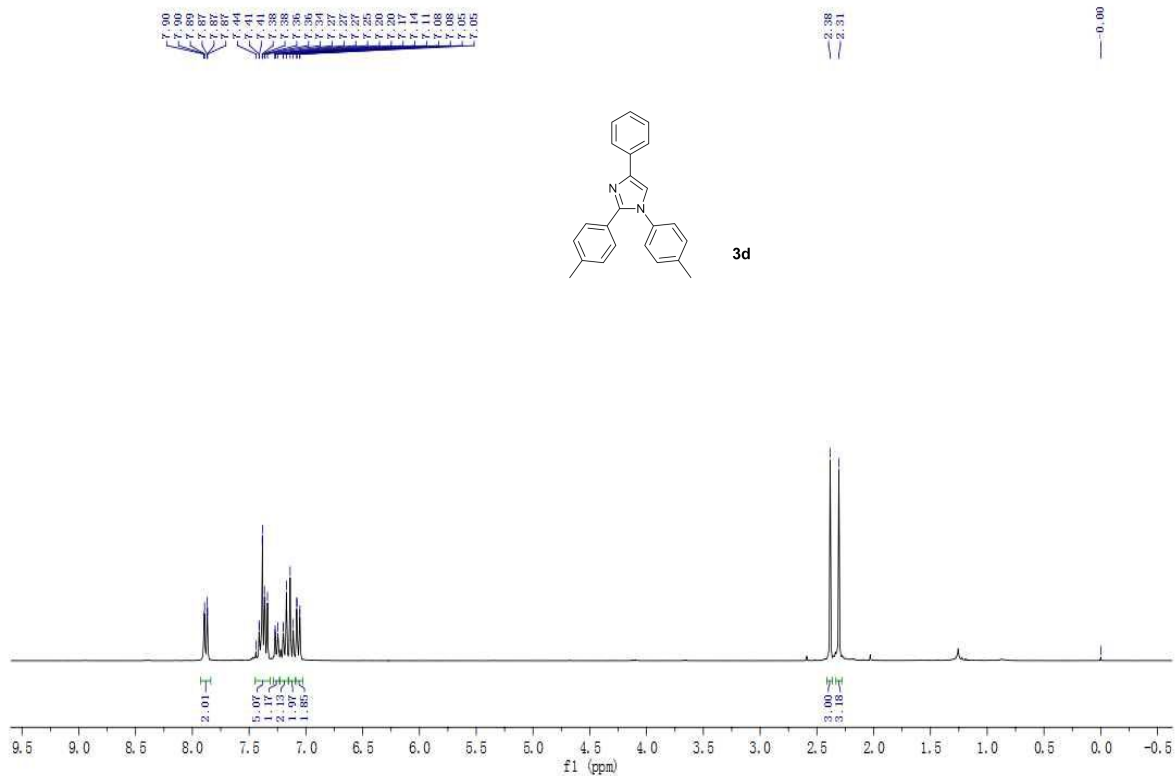
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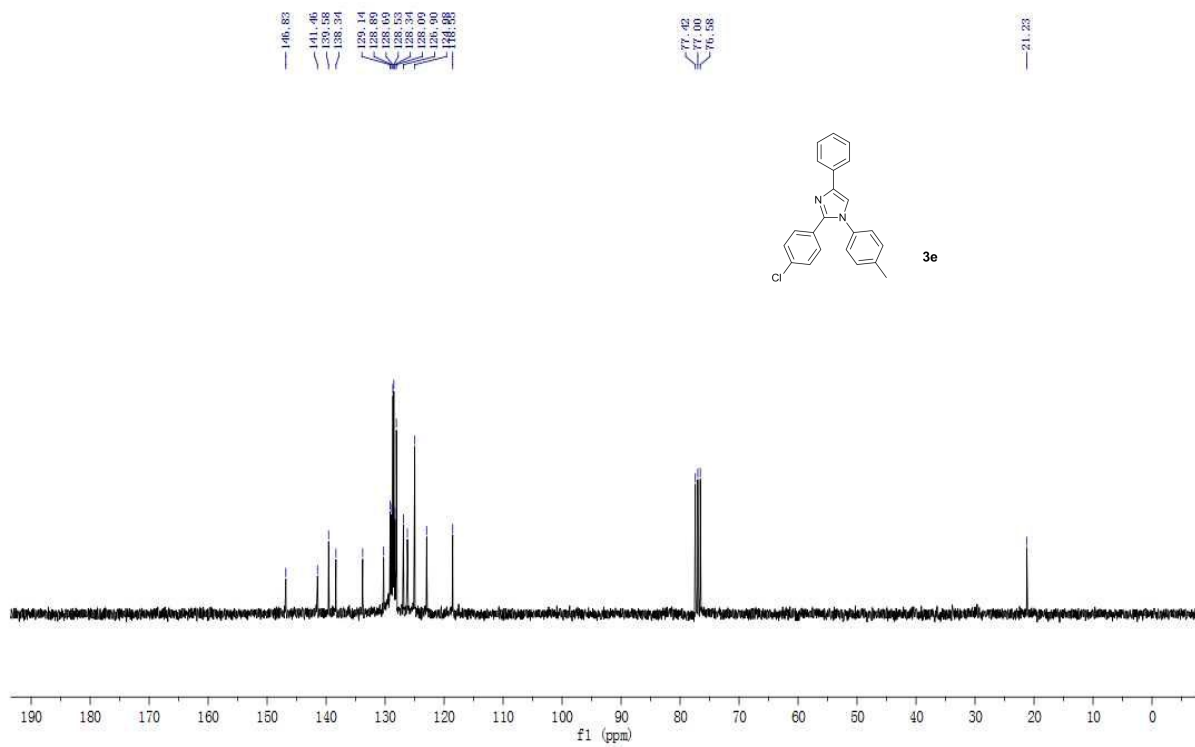
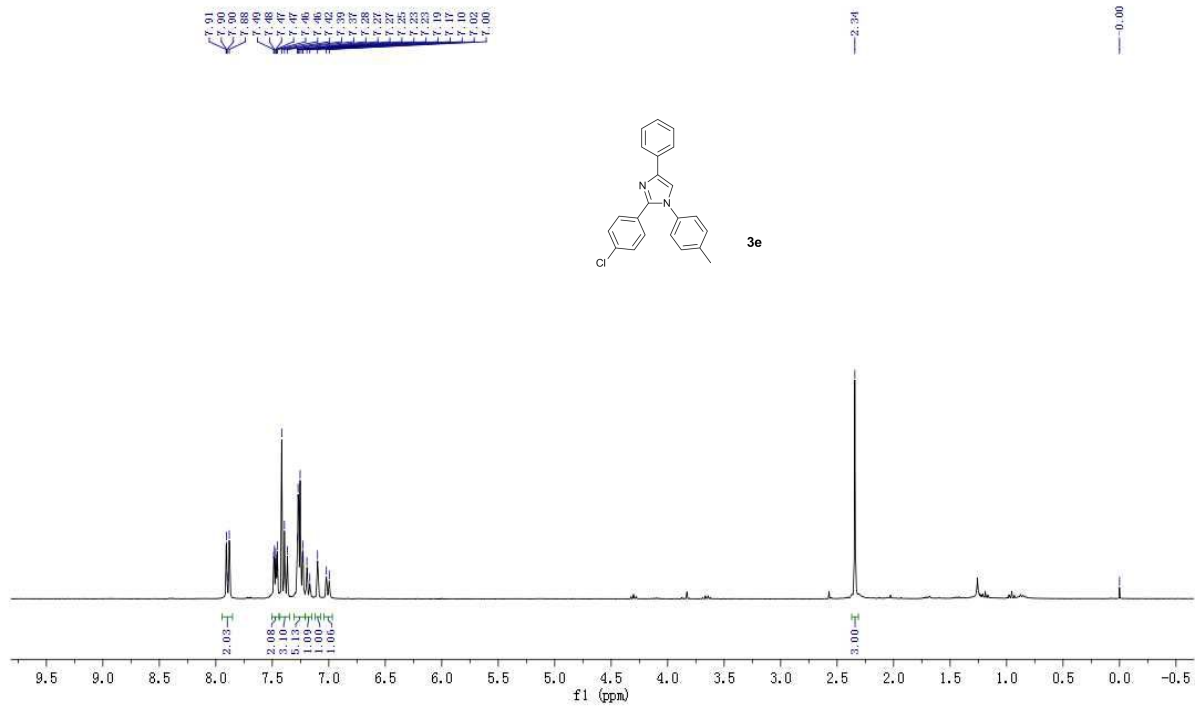
1) ^1H and ^{13}C NMR spectra of the products





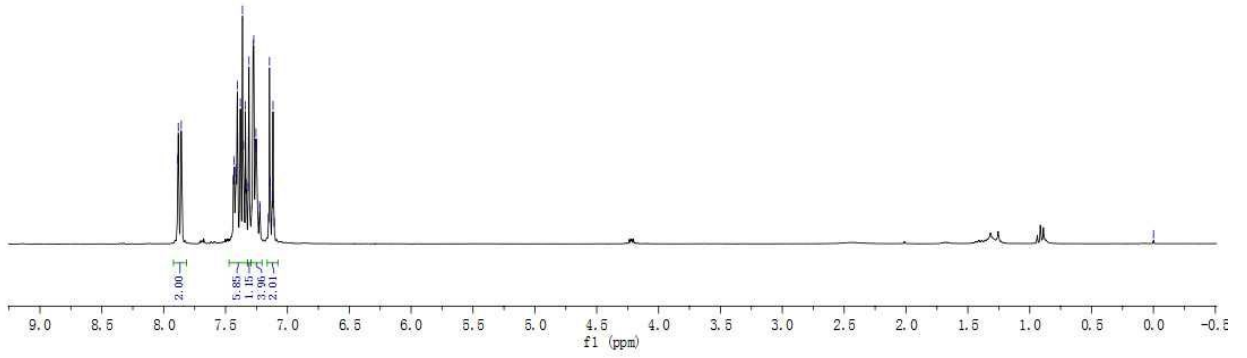
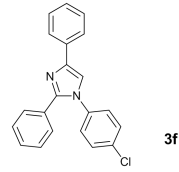






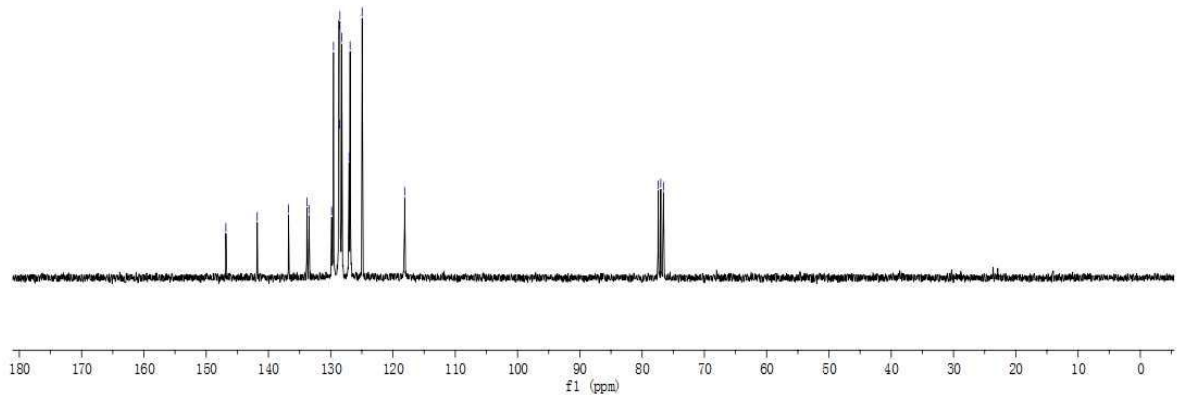
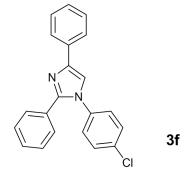
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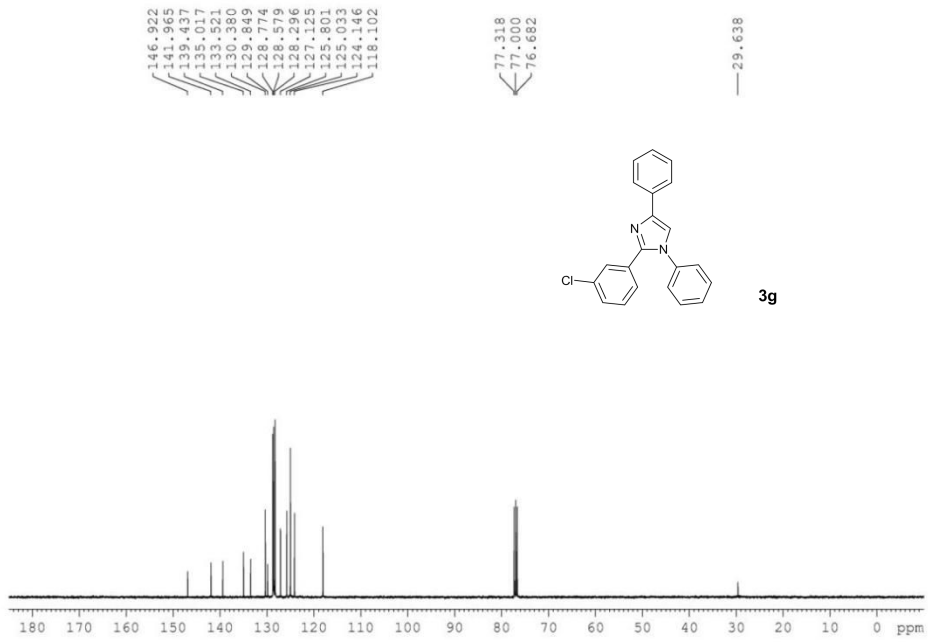
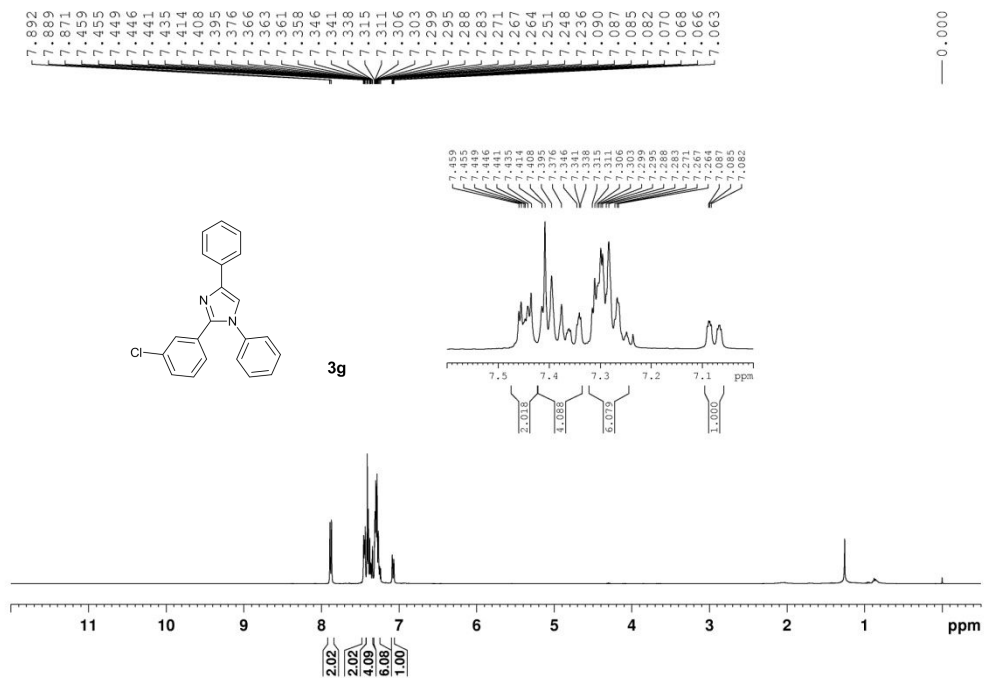
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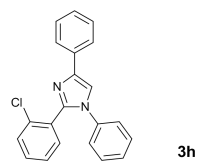
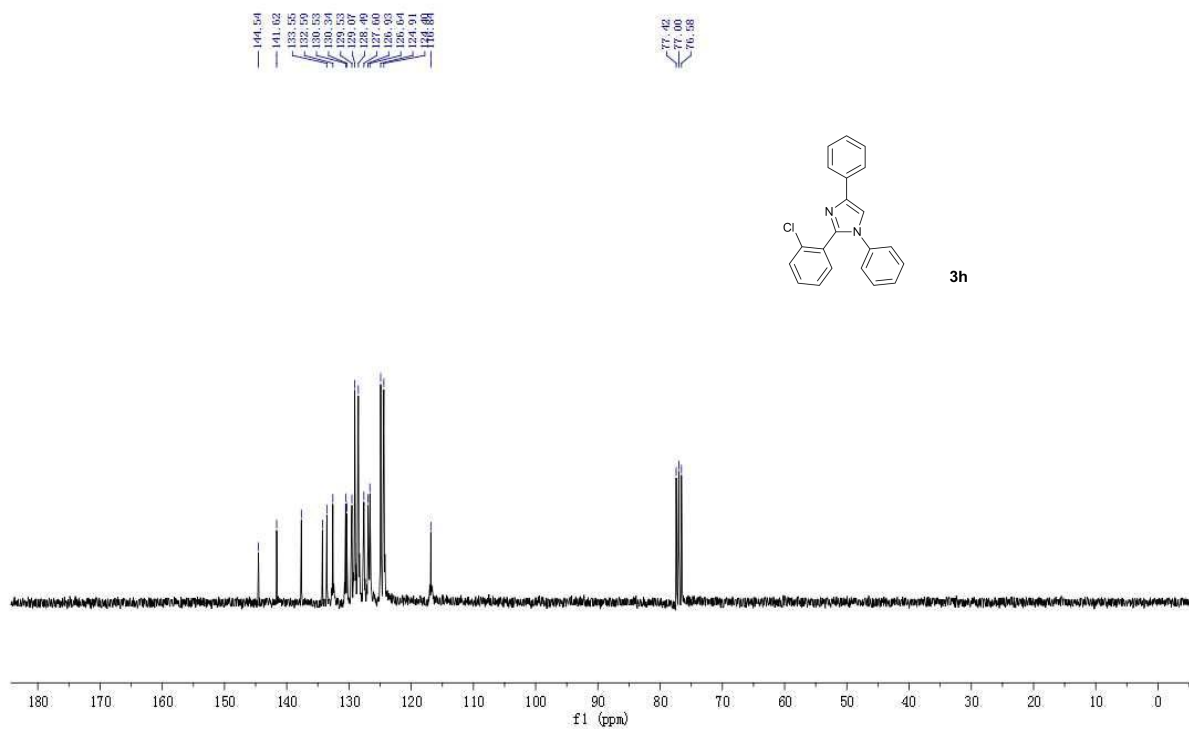
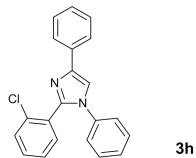
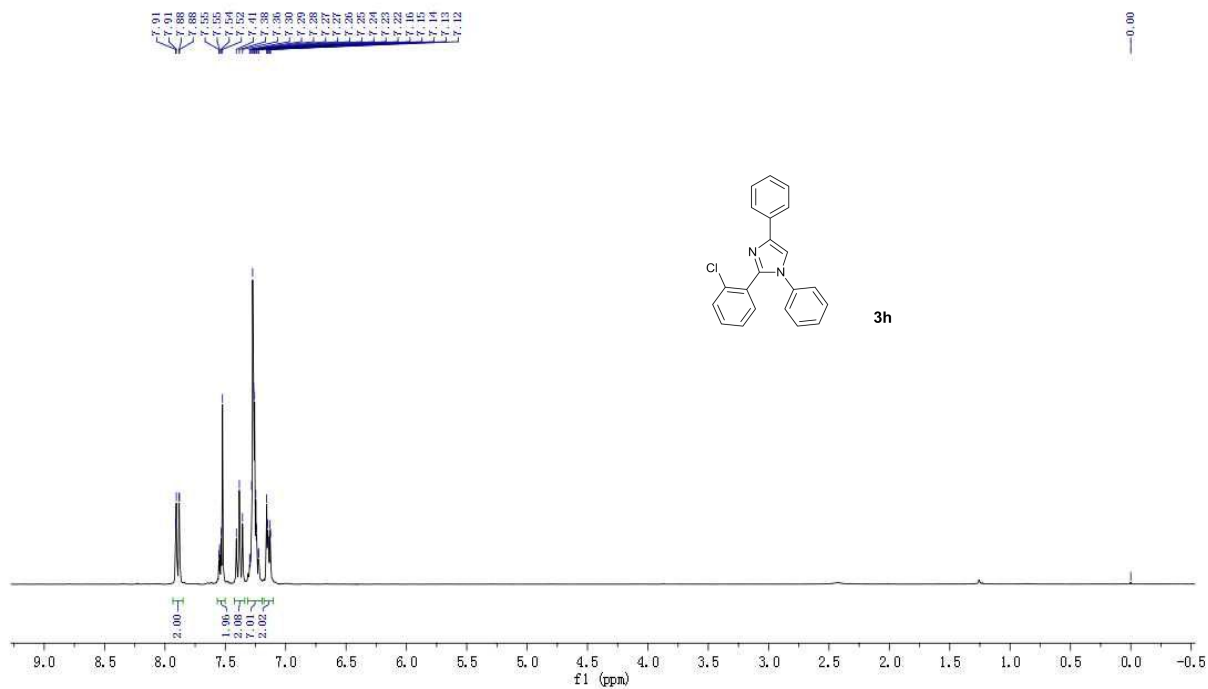


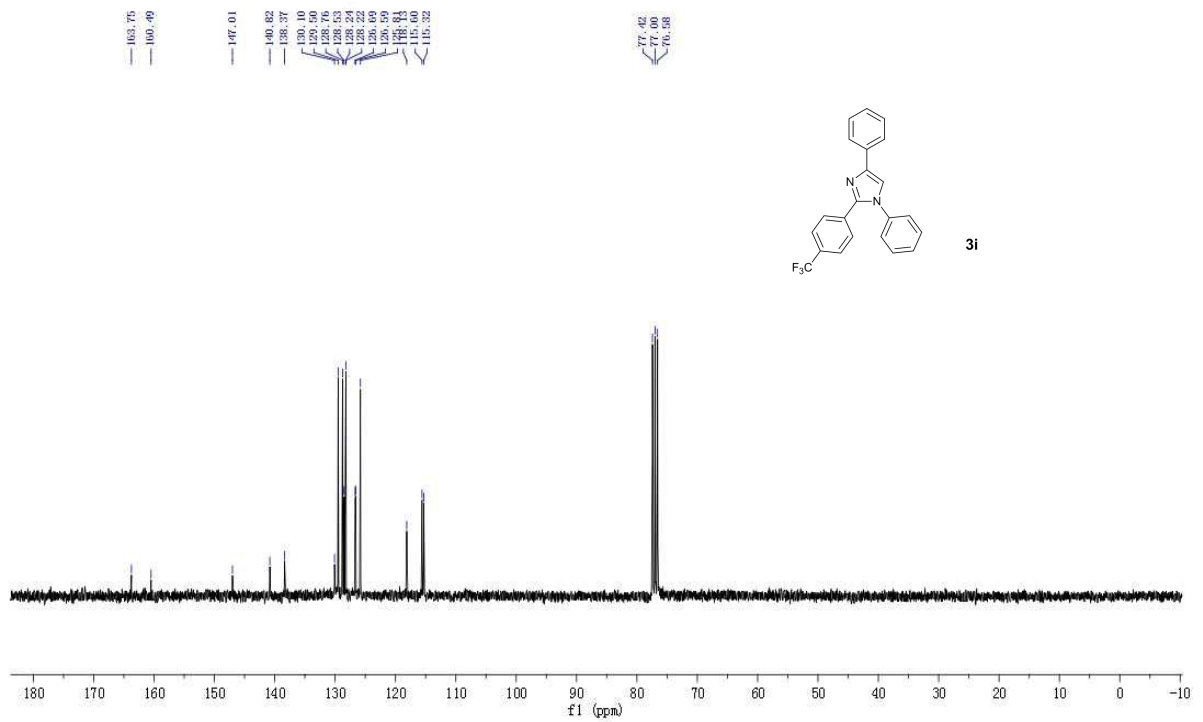
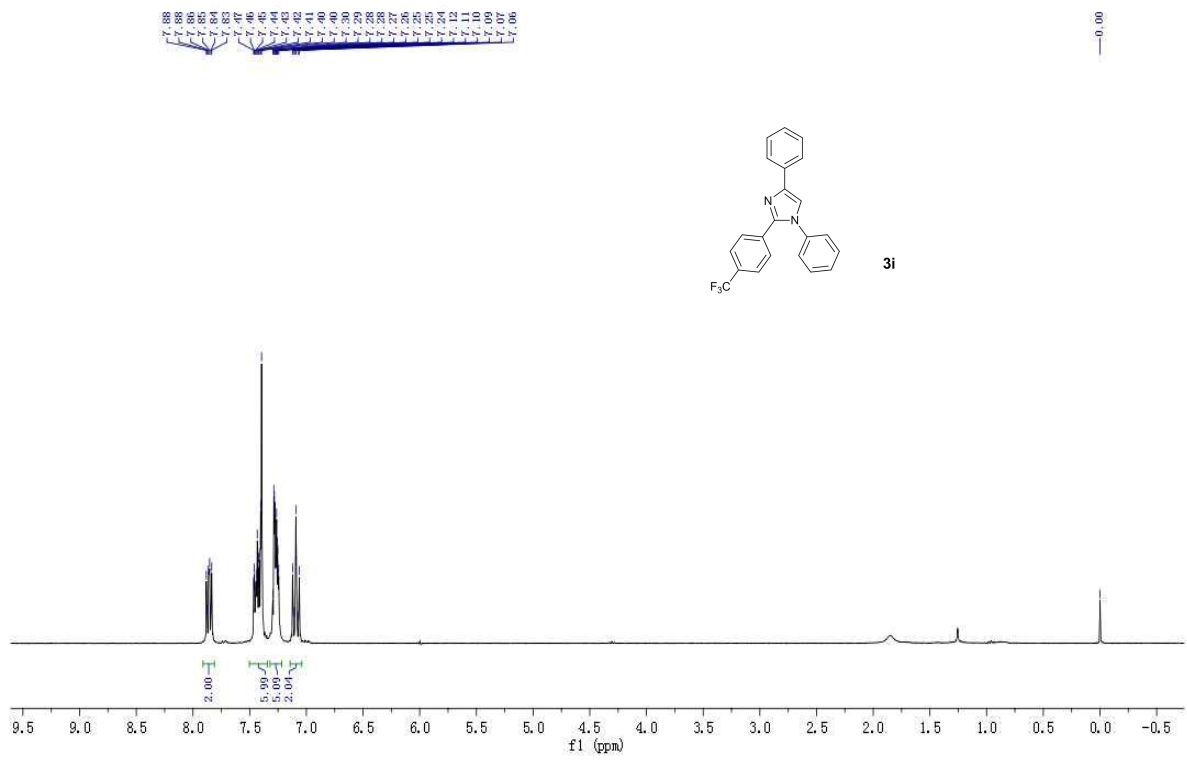
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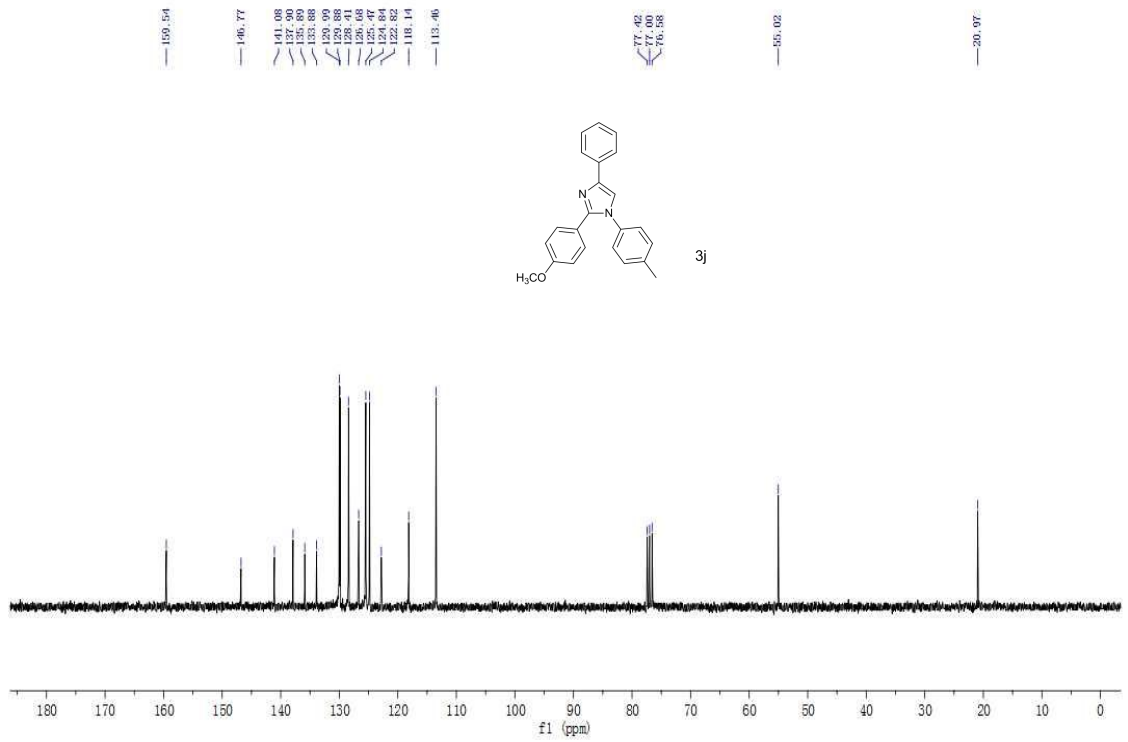
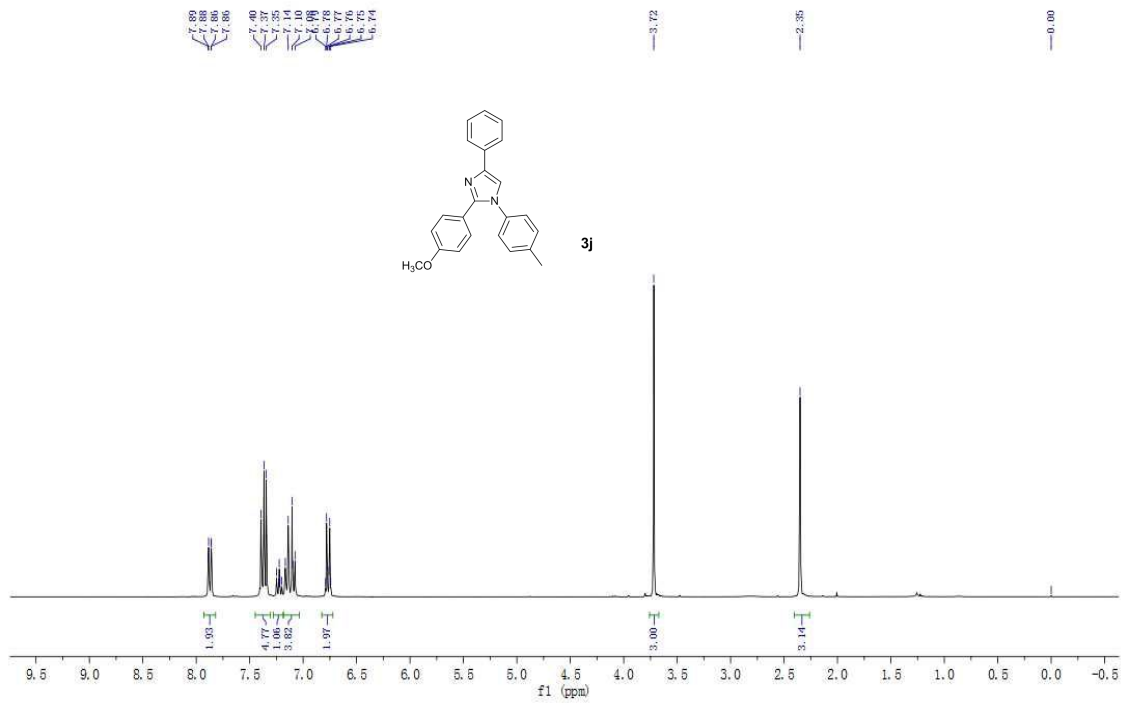
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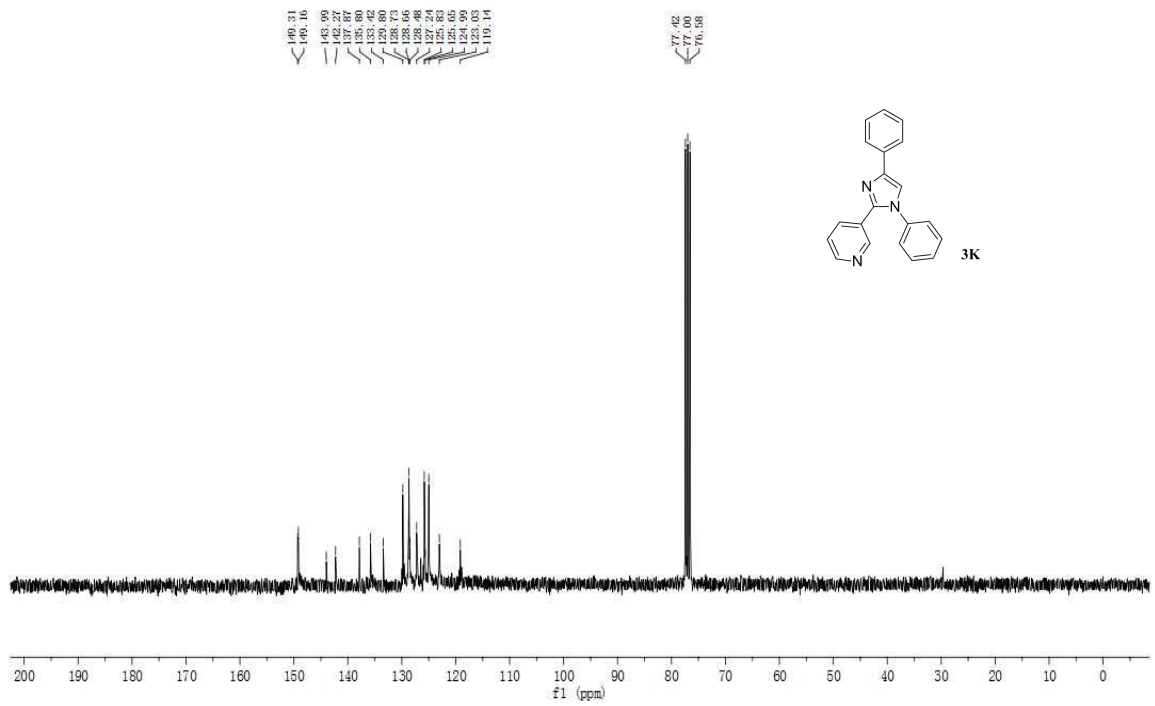
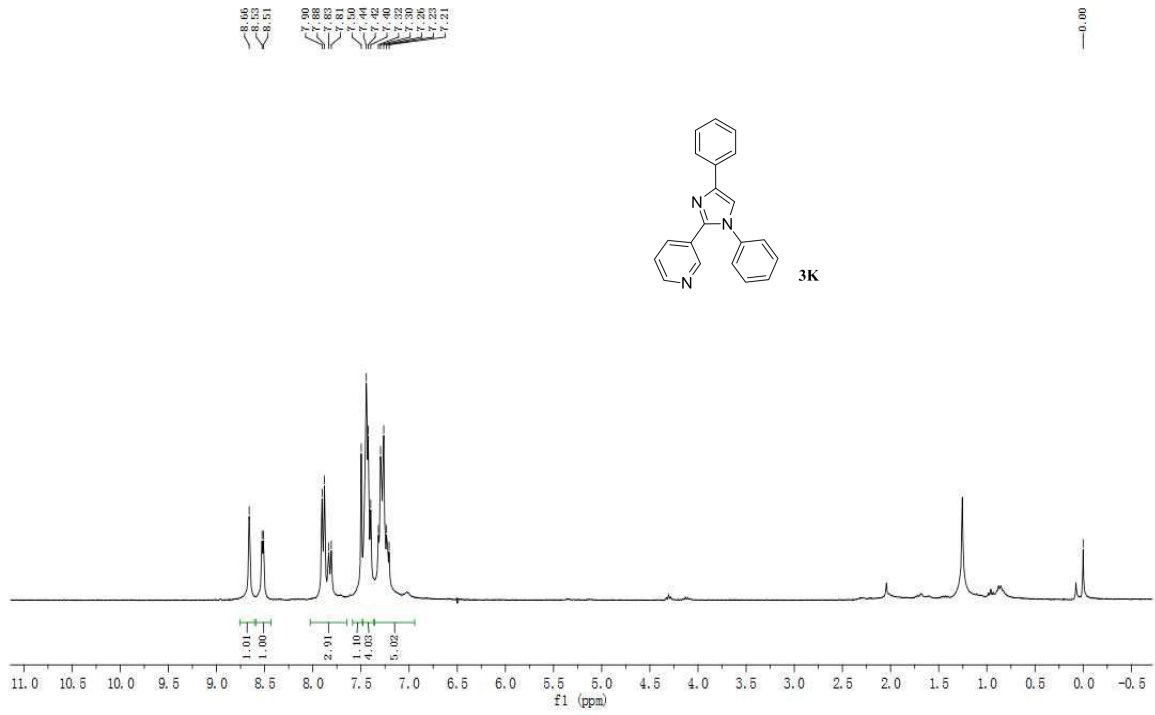


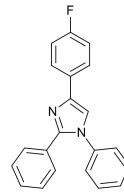
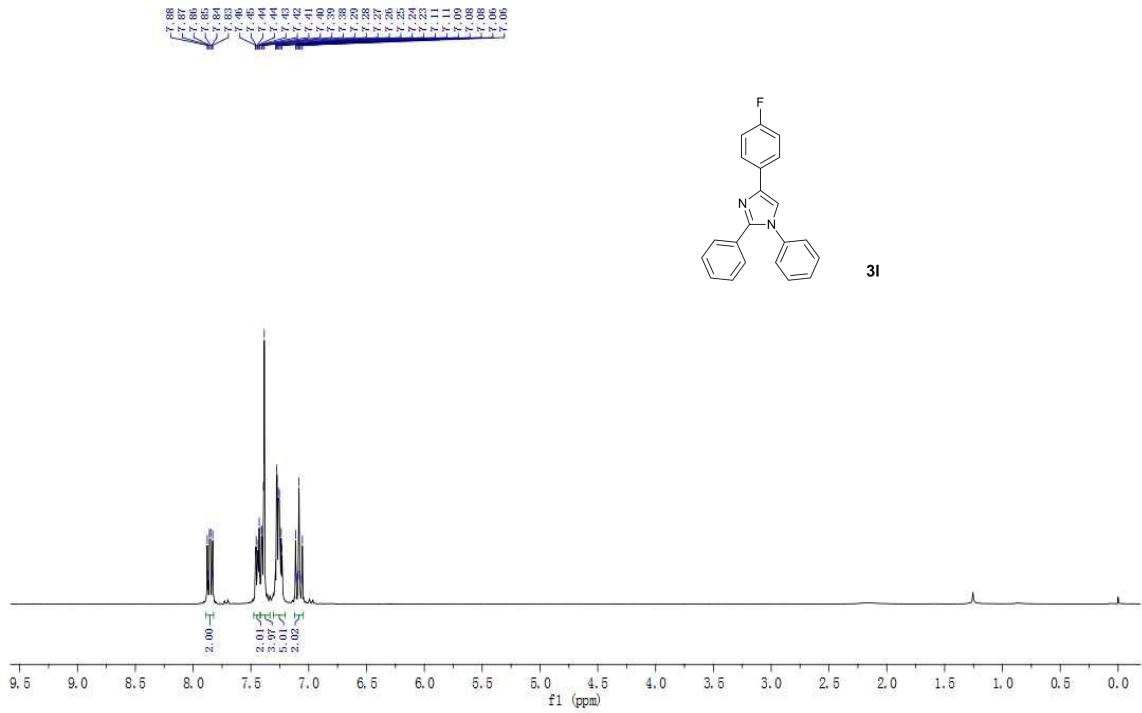




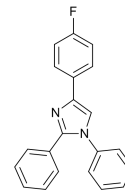
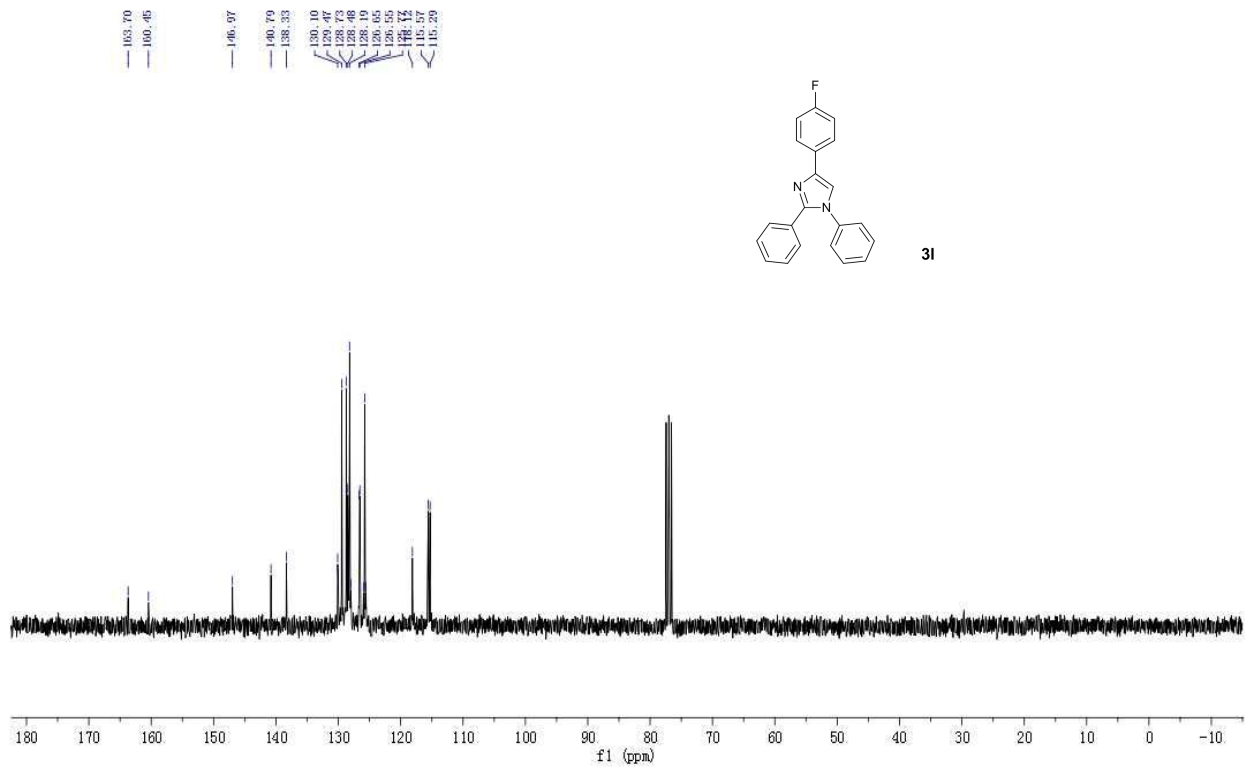




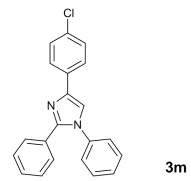
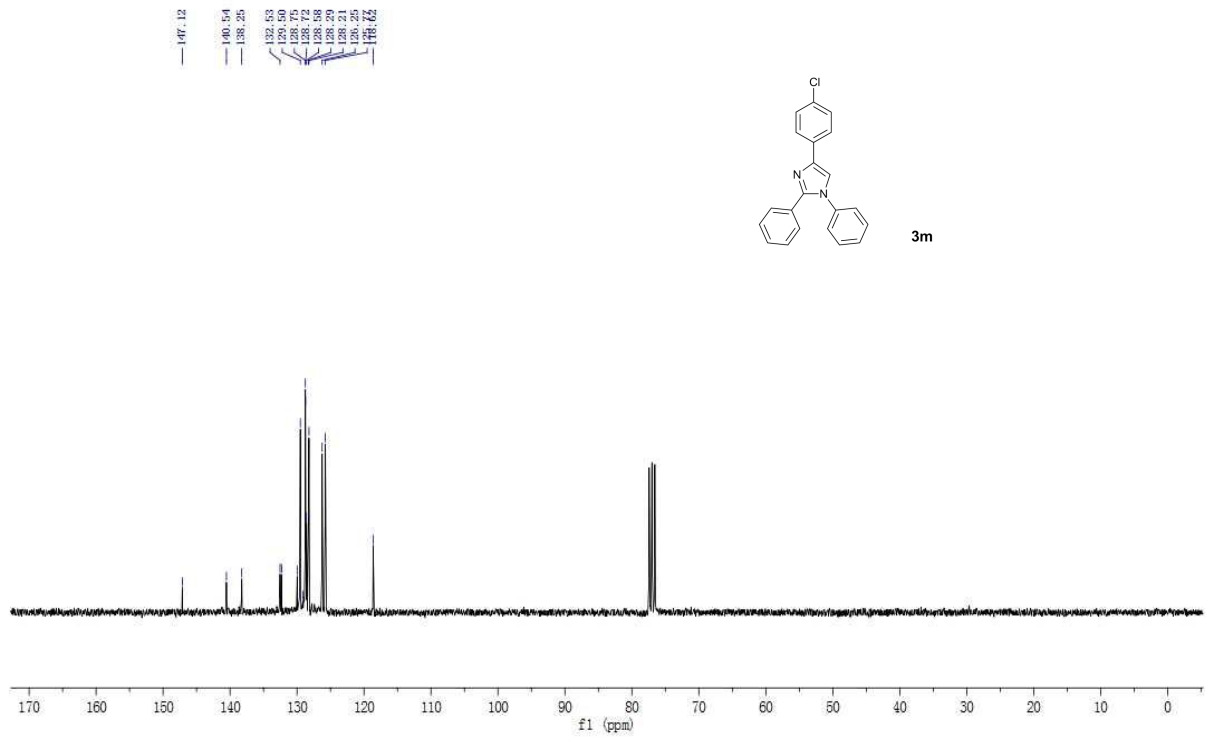
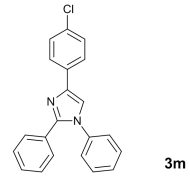
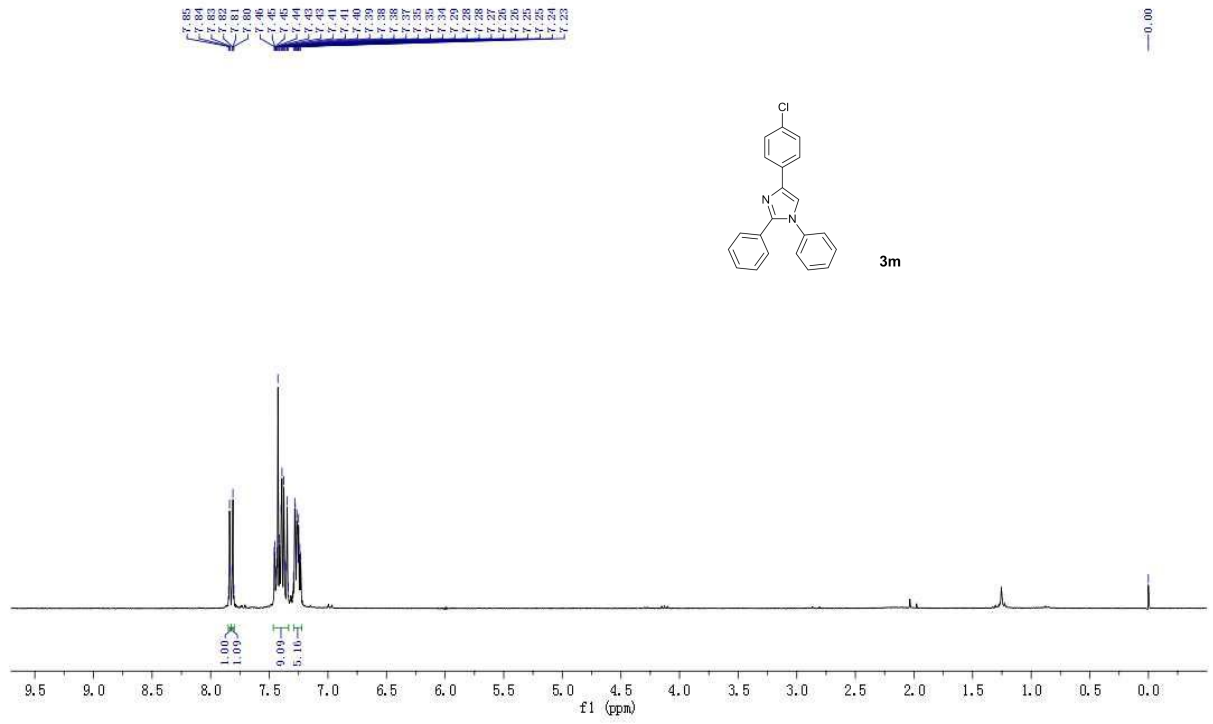


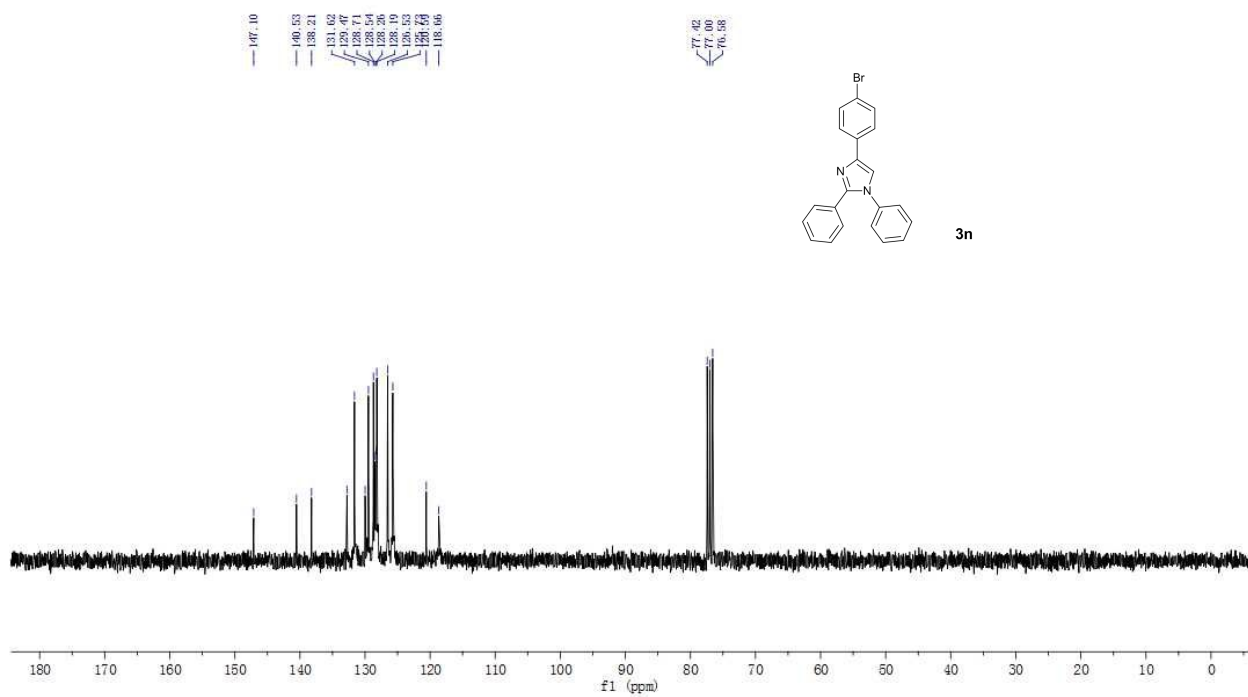
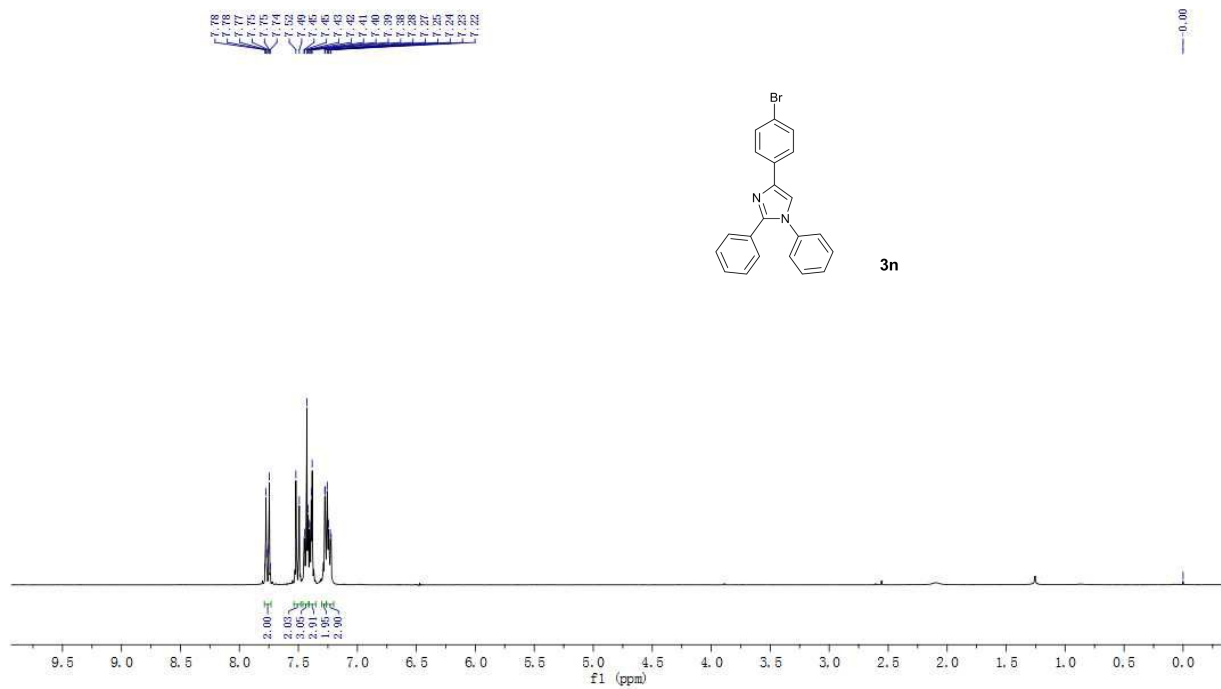


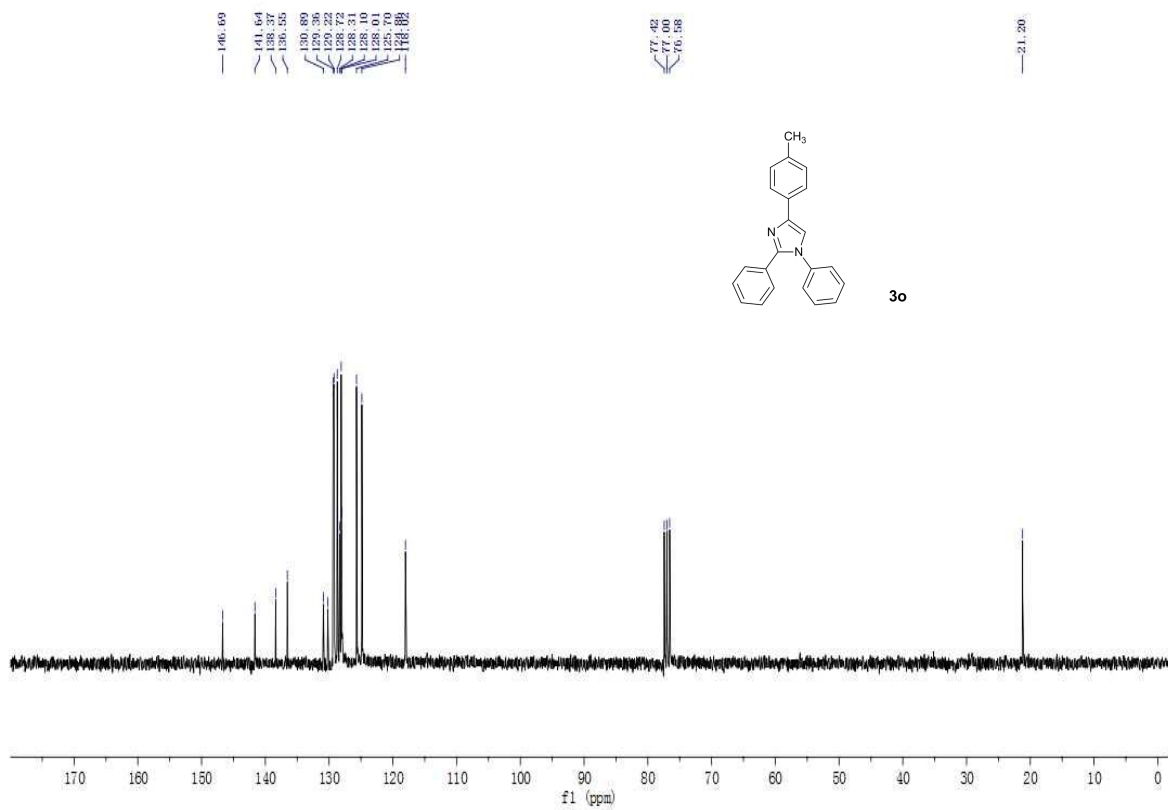
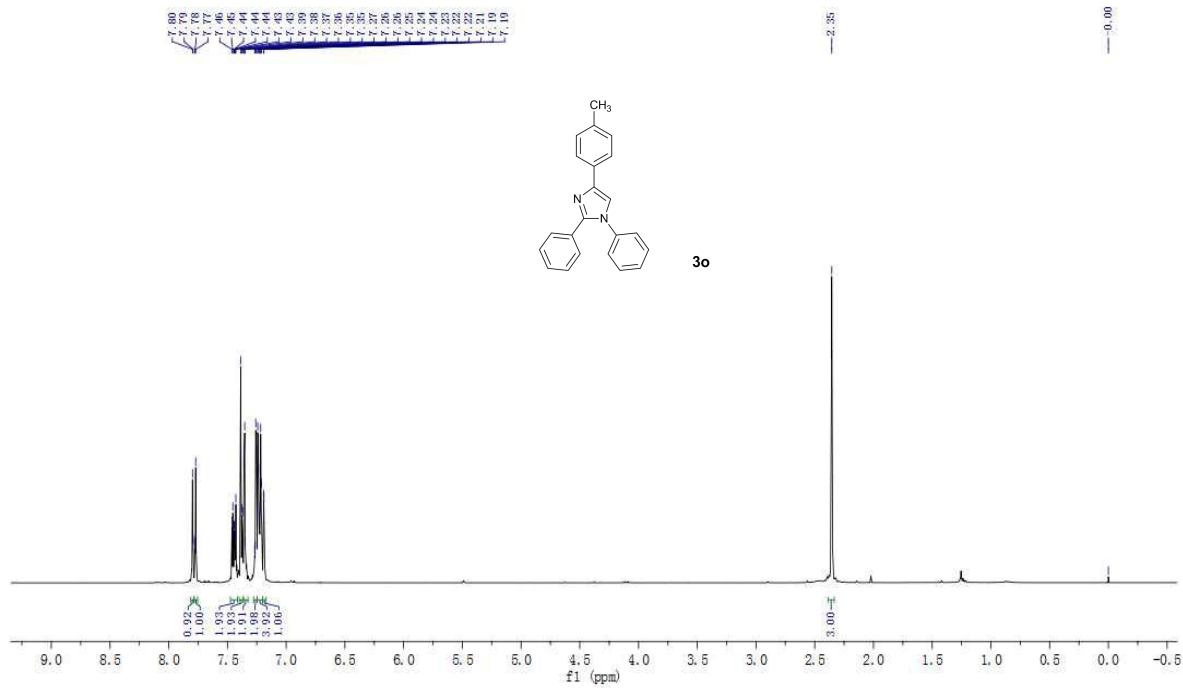
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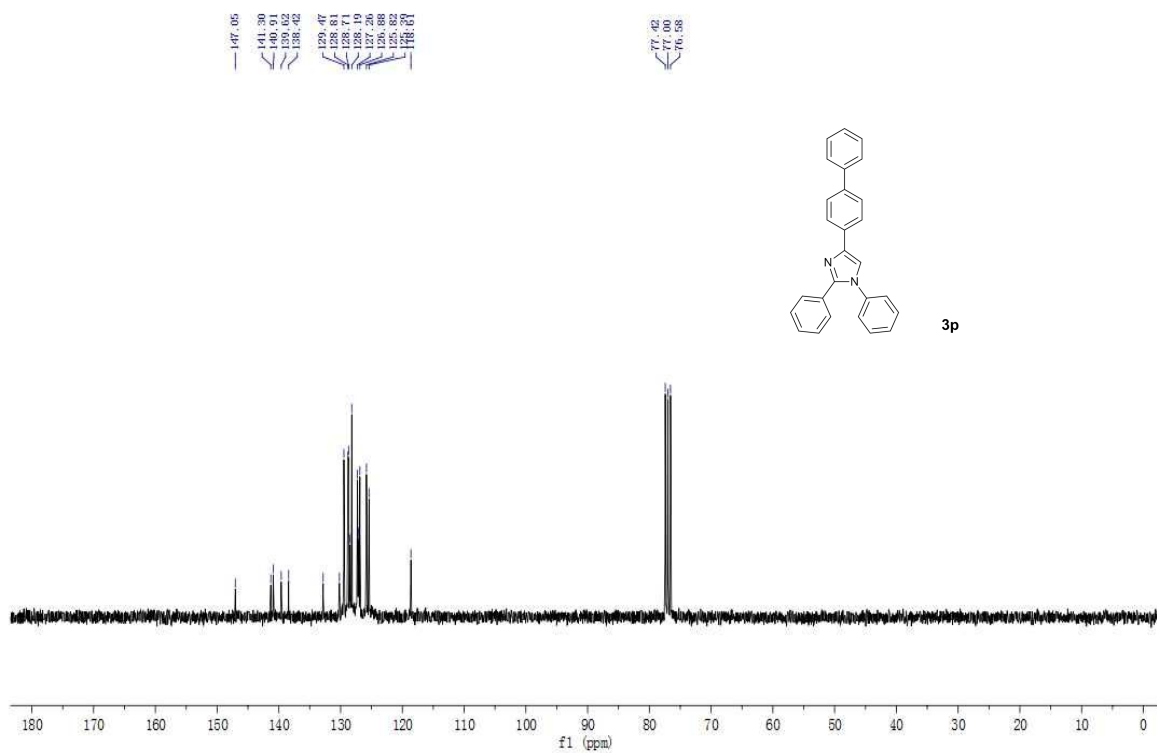
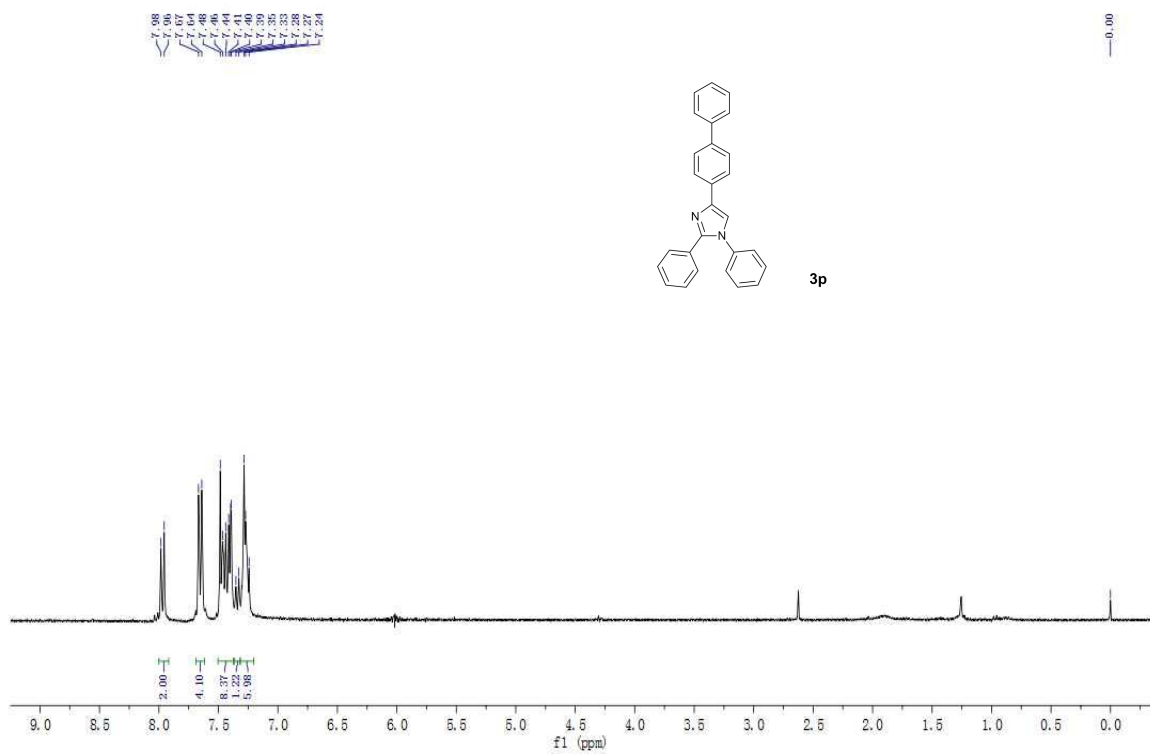


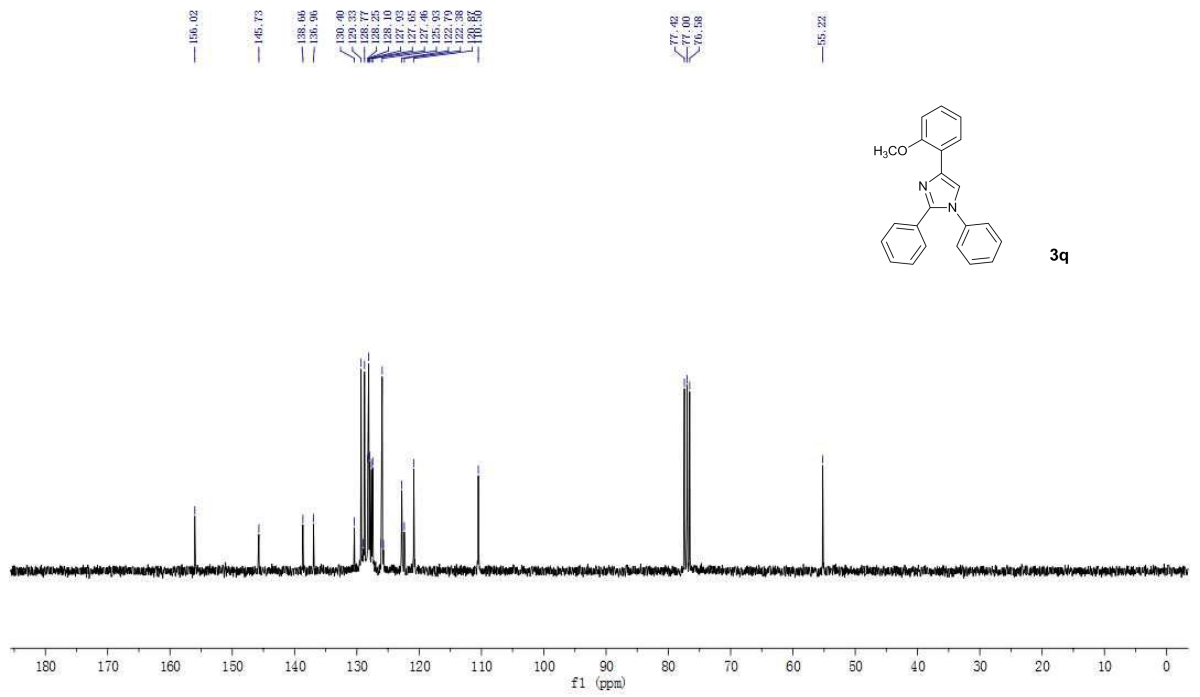
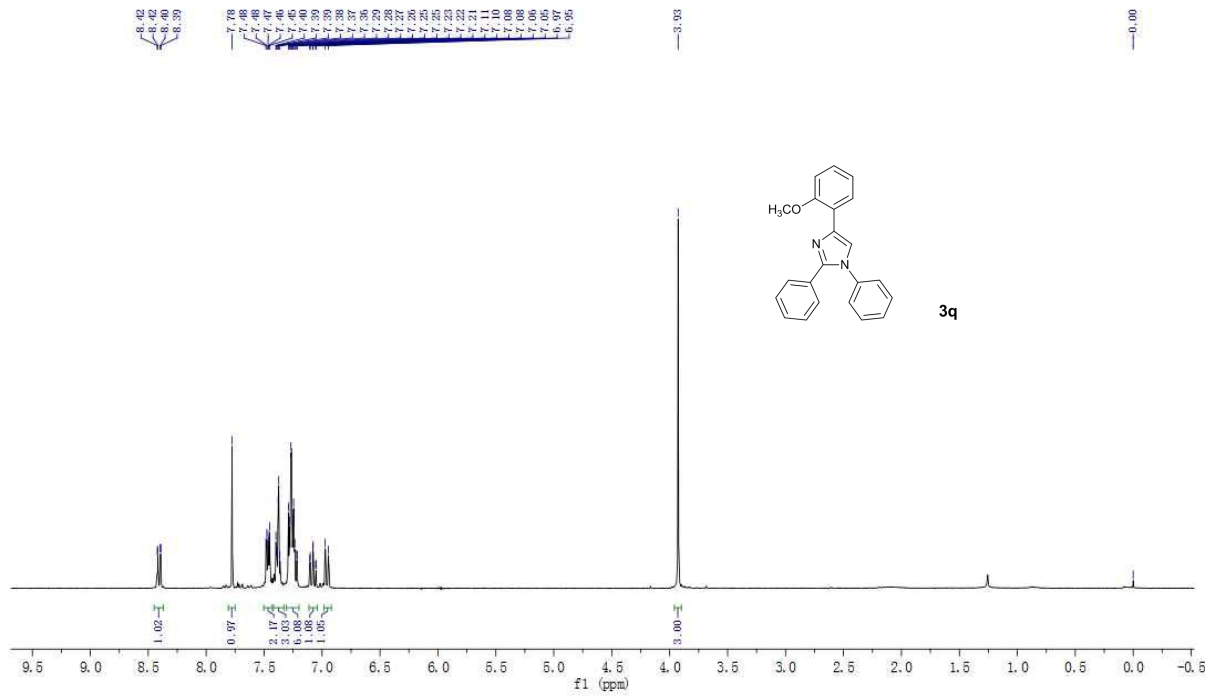
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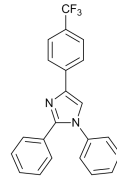




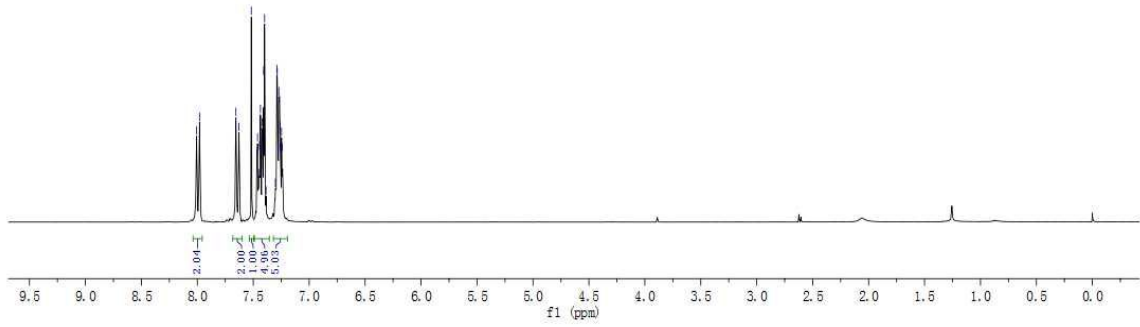




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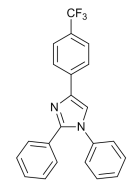


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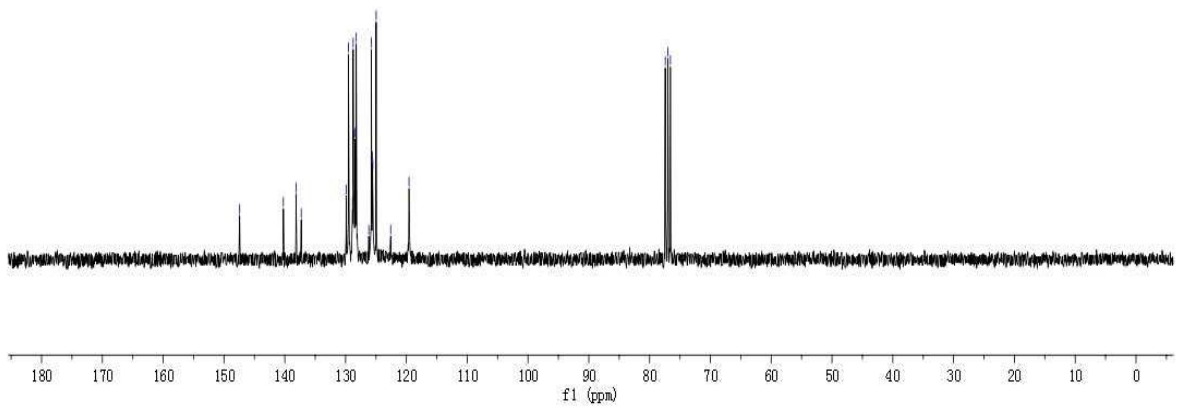


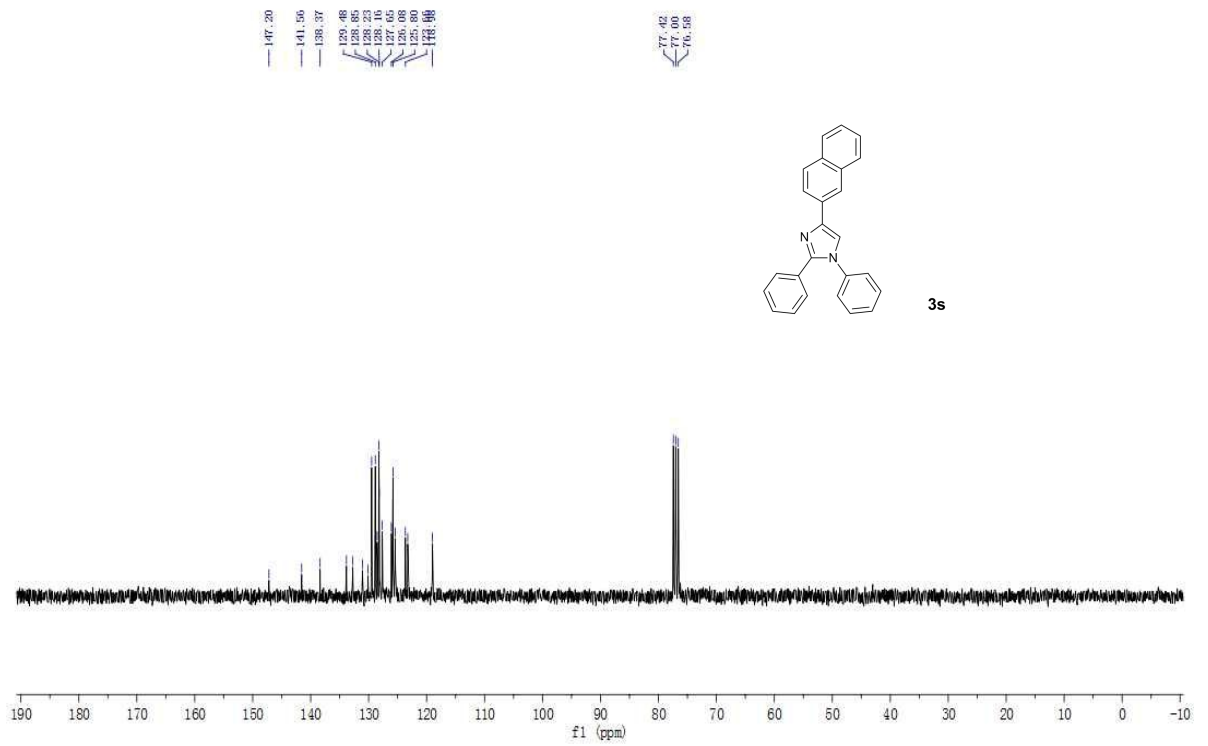
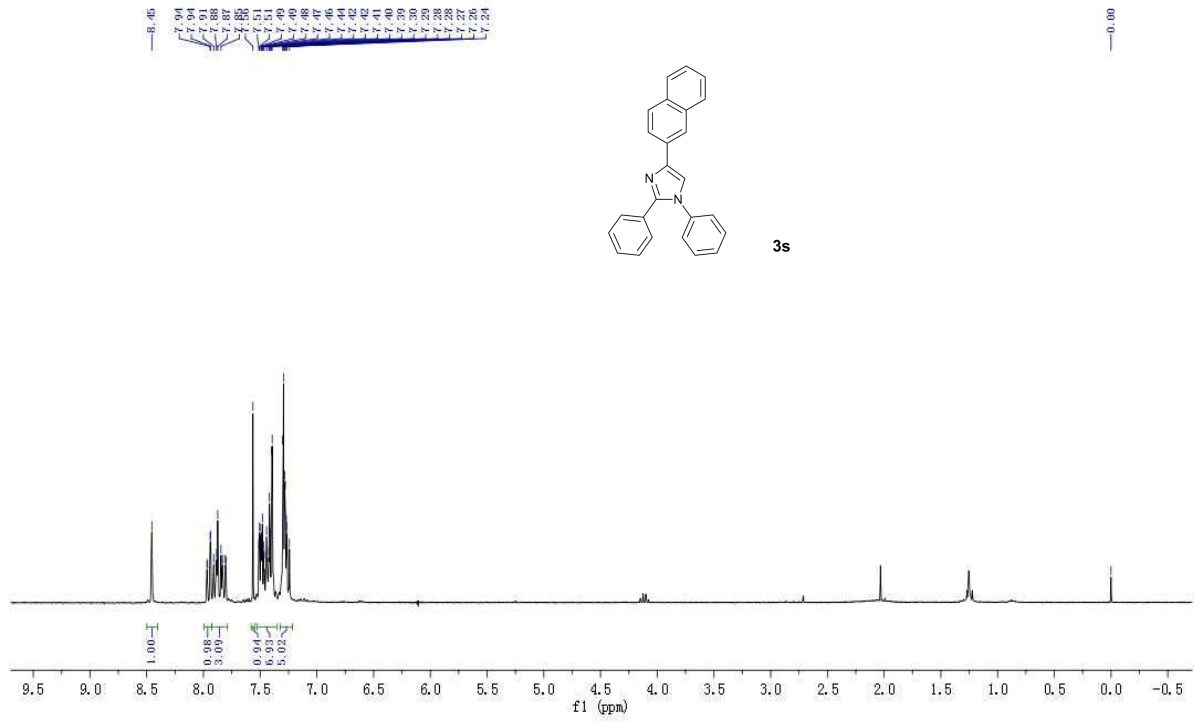
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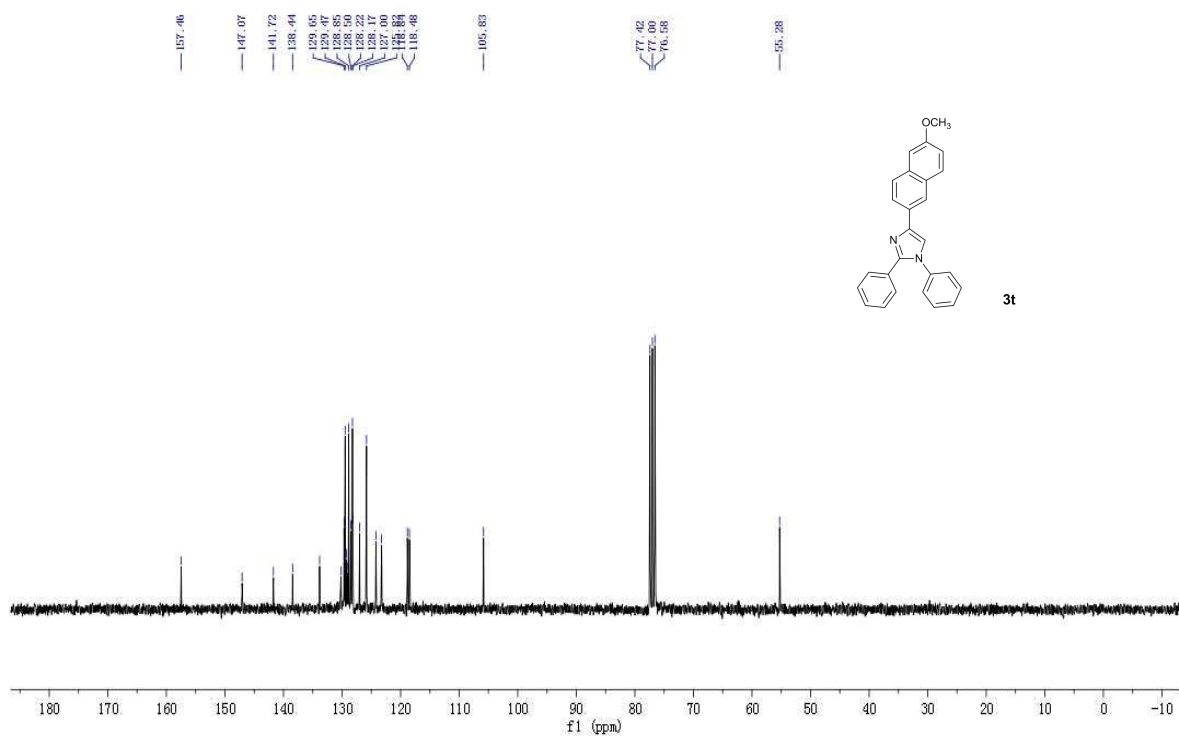
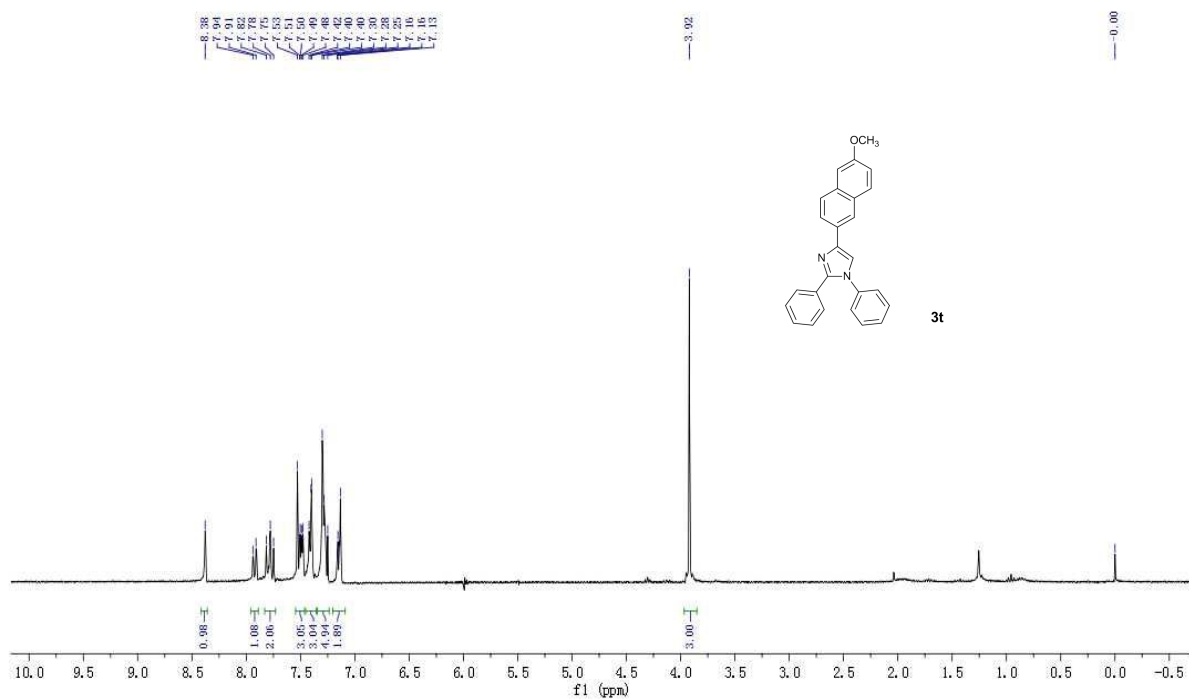
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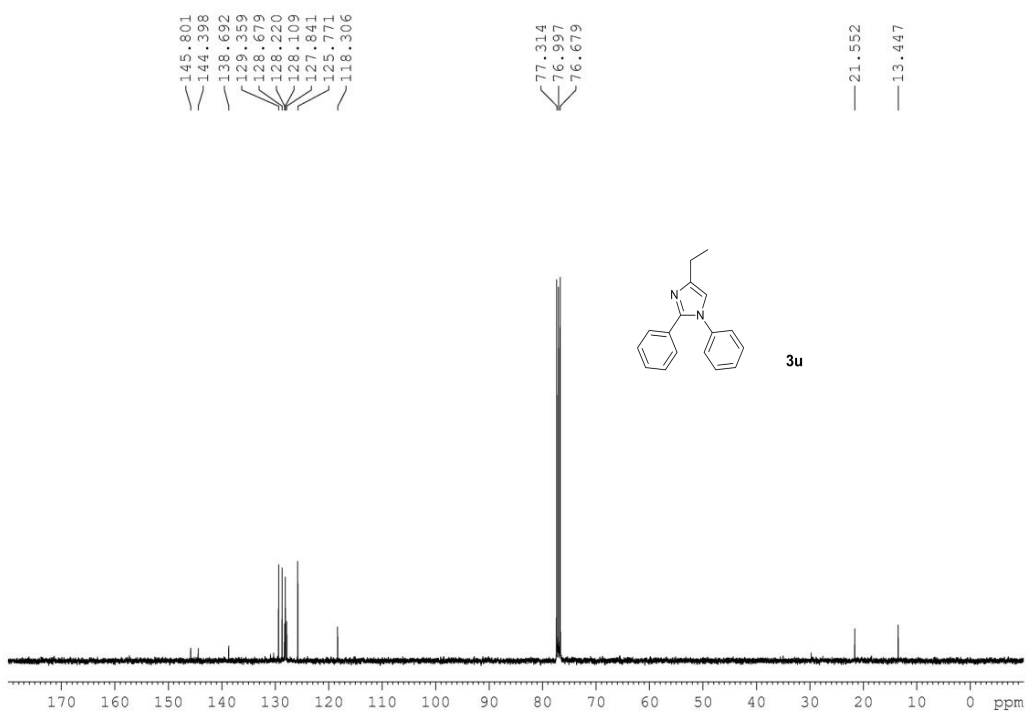
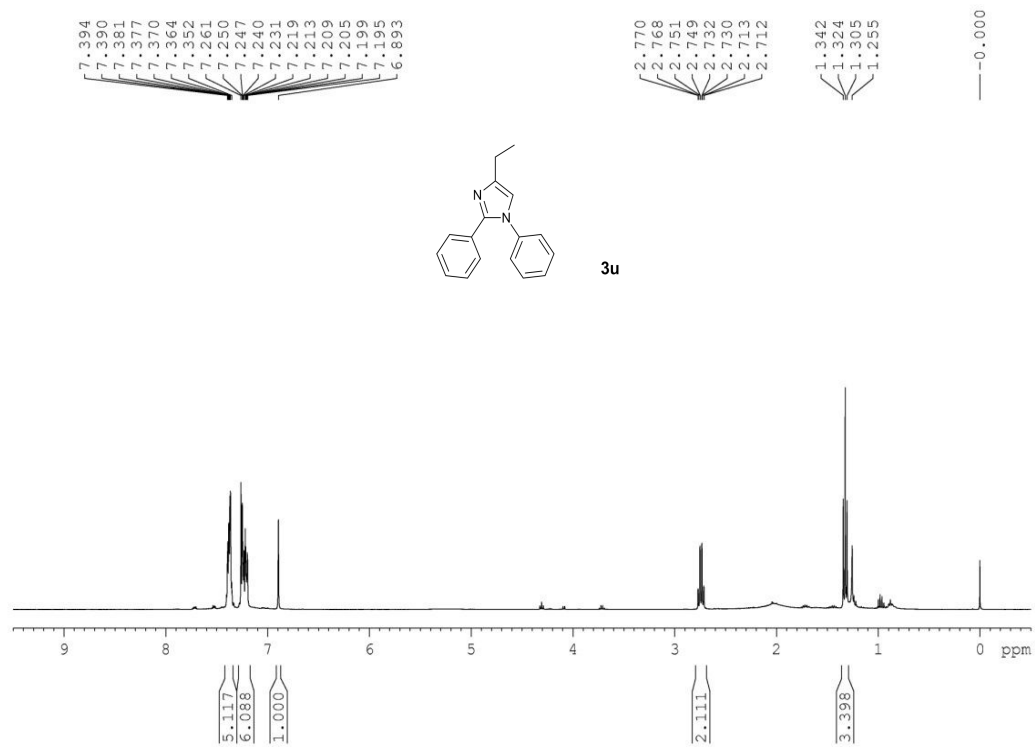


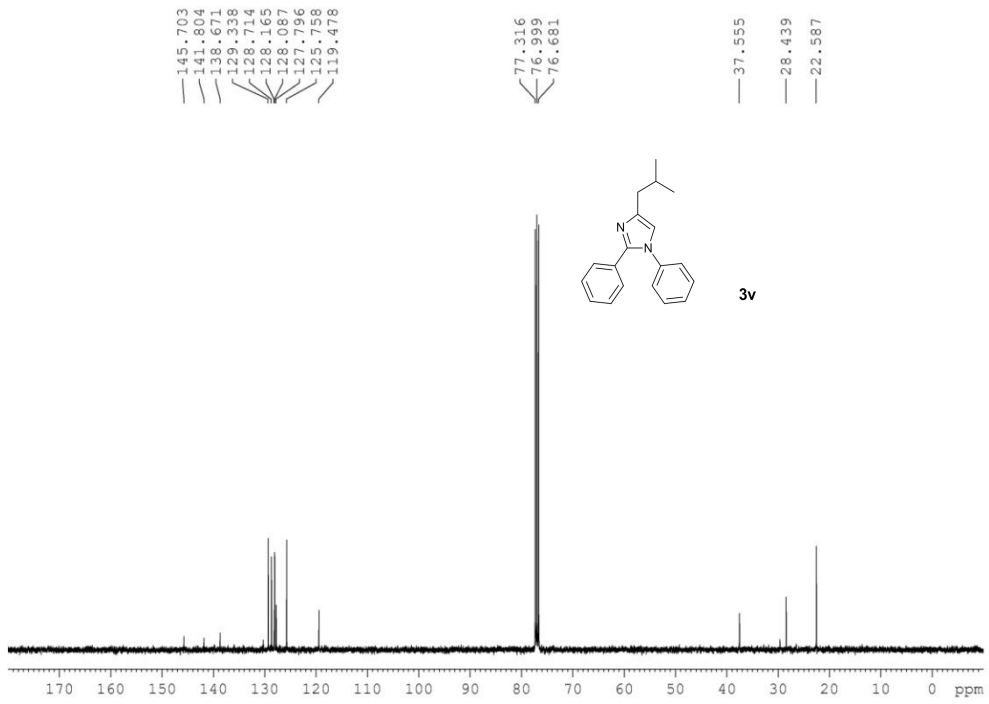
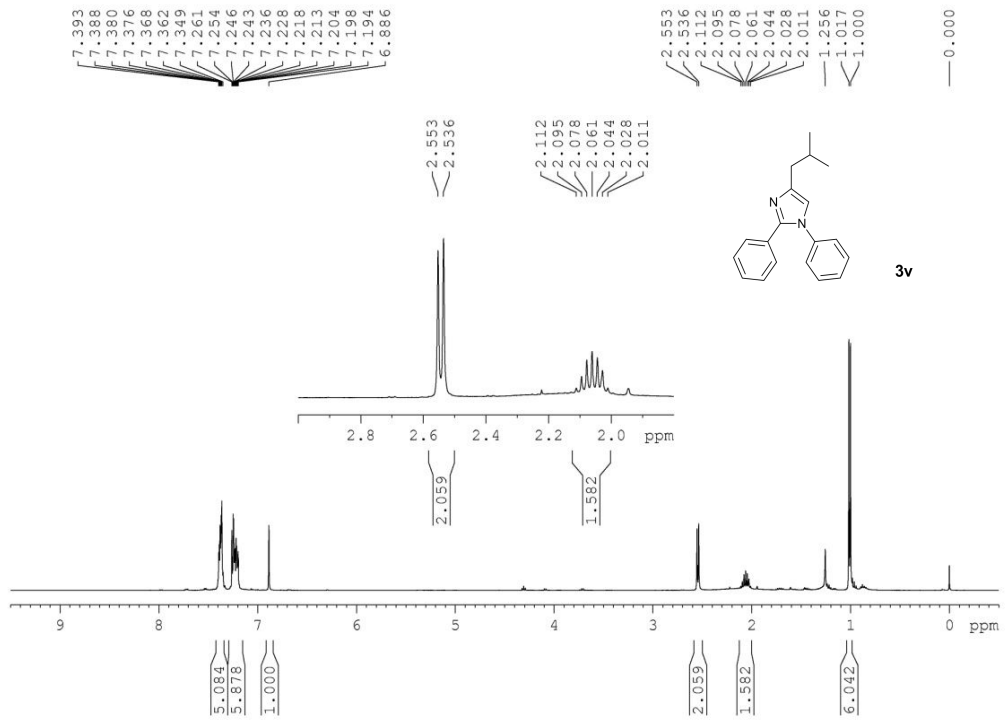
3r











2) Spectra data of the compounds

2.1

1,2,4-triphenyl-1H-imidazole 3a. 0.2 mmol, 50 mg, 85%; Light yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.46 (dd, *J* = 7.1, 2.0 Hz, 3H), 7.44 – 7.36 (m, 5H), 7.34 – 7.19 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 141.6, 138.4, 133.8, 129.4, 128.8, 128.5, 128.4, 128.1, 126.9, 125.7, 124.9, 118.5.

2.2

2,4-diphenyl-1-(o-tolyl)-1H-imidazole 3b. 0.2 mmol, 54 mg, 88%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 5H), 7.23 – 7.17 (m, 3H), 1.96 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 147.1, 141.5, 137.7, 134.9, 133.8, 131.2, 130.4, 129.1, 128.7, 128.3, 128.2, 128.0, 127.6, 127.2, 126.9, 126.8, 124.9, 17.4.

2.3

1-(3-ethylphenyl)-2,4-diphenyl-1H-imidazole 3c. 0.2 mmol, 52 mg, 81%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.47 (ddd, *J* = 4.2, 2.7, 0.9 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 2.33 (tt, *J* = 12.2, 7.4 Hz, 2H), 0.98 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 163.7, 147.3, 141.4, 140.6, 137.2, 133.9, 130.3, 129.5, 129.4, 128.6, 128.3, 128.2, 127.8, 126.9, 125.0, 119.0, 23.6, 14.0.

2.4

4-phenyl-1,2-di-p-tolyl-1H-imidazole 3d. 0.2 mmol, 59 mg, 92%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.93 – 7.84 (m, 2H), 7.45 – 7.32 (m, 5H), 7.26 (dd, *J* = 4.6, 3.4 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.07 (dd, *J* = 7.9, 0.6 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 147.0, 141.3, 138.2, 138.0, 136.0, 133.9, 130.0, 128.8, 128.6, 128.5, 127.4, 126.8, 125.6, 125.0, 118.4, 21.2, 21.0.

2.5

2-(4-chlorophenyl)-4-phenyl-1-(p-tolyl)-1H-imidazole 3e. 0.2 mmol, 65 mg, 95%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.90 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.35 (m, 3H), 7.31 – 7.21 (m, 5H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.10 (s, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 146.8, 141.5, 139.6, 138.3, 133.8, 130.2, 129.4, 129.1, 128.9, 128.7, 128.5, 128.3, 128.1, 126.9, 126.2, 125.0, 123.0, 118.6, 21.2.

2.6

1-(4-chlorophenyl)-2,4-diphenyl-1H-imidazole 3f. 0.2 mmol, 62 mg, 94%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.87 (d, *J* = 1.4 Hz, 1H), 7.87 – 7.83 (d, *J* = 0.8 Hz, 1H), 7.46 – 7.44 (d, *J* = 2.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.39 (s, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.23 (m, 5H), 7.20 – 7.17 (m, 1H), 7.17 – 7.14 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 147.2, 142.1, 137.1, 134.2, 133.8, 130.1, 130.0, 129.1, 128.9, 128.8, 128.6, 127.4, 127.2, 125.3, 118.4.

2.7

2-(3-chlorophenyl)-1,4-diphenyl-1H-imidazole 3g. 0.2 mmol, 55 mg, 83%; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.69 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.33 (m, 4H), 7.32 – 7.25 (m, 6H), 7.09 – 7.08 (t, *J* = 1.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 142.0, 139.4, 135.0, 133.5, 130.4, 129.8, 128.8, 128.6, 128.3, 127.1, 125.8, 125.0, 124.1, 118.1.

2.8

2-(2-chlorophenyl)-1,4-diphenyl-1H-imidazole 3h. 0.2 mmol, 54 mg, 82%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.89 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.20 (m, 7H), 7.18 – 7.10 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 145.0, 142.0, 134.8, 133.2, 131.2,

130.1, 129.6, 129.0, 128.2, 127.6, 127.2, 125.5, 125.0, 117.4.

2.9

1,4-diphenyl-2-(4-(trifluoromethyl)phenyl)-1H-imidazole 3i. 0.2 mmol, 45 mg, 62%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.90 – 7.81 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.50 – 7.35 (m, 6H), 7.31 – 7.22 (m, 5H), 7.15 – 7.03 (t, *J* = 8.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 163.8, 160.5, 147.1, 140.8, 138.4, 130.1, 130.0, 129.5, 128.8, 128.5, 128.2, 126.7, 126.6, 125.8, 118.1, 115.6, 115.3.

2.10

2-(4-methoxyphenyl)-4-phenyl-1-(p-tolyl)-1H-imidazole 3j. 0.2 mmol, 45 mg, 62%; Light yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.87 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.45 – 7.31 (m, 5H), 7.28 – 7.19 (m, 1H), 7.19 – 7.03 (m, 4H), 6.82 – 6.72 (m, 2H), 3.72 (s, 3H), 2.35 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 159.6, 146.8, 141.0, 137.9, 135.9, 133.9, 130.0, 129.9, 128.4, 126.8, 125.5, 124.8, 122.8, 118.3, 113.4, 55.0, 21.0.

2.11

3-(1,4-diphenyl-1H-imidazol-2-yl)pyridine 3k. 0.2 mmol, 30.9mg, 52%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 8.66 (s, 1H), 8.52 (d, *J* = 4.0 Hz, 1H), 7.86 (dd, *J* = 21.0, 7.7 Hz, 3H), 7.50 (s, 1H), 7.48-7.37 (m, 4H), 7.36 -6.94 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 149.3, 149.1, 144.0, 142.3, 137.9, 135.8, 133.4, 129.8, 128.7, 128.6, 128.6, 127.2, 125.8, 125.6, 125.0, 123.0, 119.1.

2.12

4-(4-fluorophenyl)-1,2-diphenyl-1H-imidazole 3l. 0.2 mmol, 43 mg, 69%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.89 – 7.82 (m, 2H), 7.44 (dt, *J* = 4.6, 1.8 Hz, 2H), 7.40 (dd, *J* = 5.3, 2.0 Hz, 4H), 7.26 (dq, *J* = 6.7, 2.4 Hz, 5H), 7.12 – 7.05 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 160.9, 147.0, 140.8, 138.4, 130.0, 129.5, 128.8, 128.6, 128.3, 128.2, 126.8, 126.7, 125.8, 118.2, 115.6, 115.4.

2.13

4-(4-chlorophenyl)-1,2-diphenyl-1H-imidazole 3m. 0.2 mmol, 55 mg, 84%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.85 – 7.79 (m, 2H), 7.51 – 7.32 (m, 9H), 7.29 – 7.22 (ddt, *J* = 6.5, 5.4, 2.7 Hz, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 147.1, 140.5, 138.3, 133.0, 132.5, 132.3, 130.0, 129.5, 129.1, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 127.4, 126.3, 125.8, 118.6.

2.14

4-(4-bromophenyl)-1,2-diphenyl-1H-imidazole 3n. 0.2 mmol, 72 mg, 96%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.79 – 7.73 (m, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.44 (dd, *J* = 7.5, 2.2 Hz, 3H), 7.40 (dd, *J* = 5.1, 1.7 Hz, 3H), 7.27 (d, *J* = 1.5 Hz, 2H), 7.24 (dd, *J* = 7.0, 2.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 147.1, 140.5, 138.2, 132.7, 131.7, 129.9, 129.5, 128.8, 128.6, 128.3, 128.2, 126.6, 125.8, 120.7, 118.7.

2.15

1,2-diphenyl-4-(p-tolyl)-1H-imidazole 3o. 0.2 mmol, 47 mg, 77%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.60 – 7.53 (m, 2H), 7.15 (dt, *J* = 4.6, 1.8 Hz, 2H), 7.11 (dd, *J* = 5.3, 2.0 Hz, 4H), 6.97 (dq, *J* = 6.7, 2.4 Hz, 5H), 6.83 – 6.75 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 146.8, 141.7, 138.5, 136.7, 130.9, 130.2, 129.4, 129.3, 128.8, 128.4, 128.2, 128.1, 125.8, 125.0, 118.1, 21.2.

2.16

4-([1,1'-biphenyl]-4-yl)-1,2-diphenyl-1H-imidazole 3p. 0.2 mmol, 66 mg, 89%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.92 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.76 (d, *J* = 8.2 Hz, 4H), 7.51 – 7.43 (m, 4H), 7.40 – 7.36 (dd, *J* = 10.0, 8.3 Hz, 4H), 7.34 – 7.18 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 147.1, 141.3, 140.9, 139.6, 138.4, 132.8, 130.2, 129.5, 128.8, 128.7, 128.5, 128.2, 127.3, 127.1, 126.9, 125.8, 125.4, 118.6.

2.17

4-(2-methoxyphenyl)-1,2-diphenyl-1H-imidazole 3q. 0.2 mmol, 51 mg, 79%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 8.41 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.78 (s, 1H), 7.50 – 7.43 (m, 2H), 7.38 (dt, *J* = 7.3, 2.4 Hz, 3H), 7.31 – 7.20 (m, 6H), 7.08 (td, *J* = 7.6, 1.1 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 3.93 (s, 3H). δ 156.2, 145.9, 138.8, 137.1, 129.5, 128.9, 128.4, 128.2, 128.1, 127.8, 127.6, 126.1, 122.9, 122.5, 121.0, 110.6, 110.0, 55.4.

2.18

1,2-diphenyl-4-(4-(trifluoromethyl)phenyl)-1H-imidazole 3r. 0.2 mmol, 36 mg, 50%; Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.52 (s, 1H), 7.49 – 7.36 (m, 5H), 7.27 (ddt, *J* = 6.2, 4.9, 3.1 Hz, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 147.7, 140.5, 138.4, 137.6, 130.4, 130.2, 129.8, 129.2, 129.0, 128.9, 128.8, 128.7, 128.5, 128.0, 127.0, 126.4, 126.1, 125.9, 125.8, 125.3, 124.1, 129.8.

2.19

4-(naphthalen-2-yl)-1,2-diphenyl-1H-imidazole 3s. 0.2 mmol, 61 mg, 88%; White solid; mp 196-198 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 4H), 7.50 – 7.38 (m, 8H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.20 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 146.8, 141.1, 138.0, 133.4, 132.3, 130.6, 129.7, 129.1, 128.4, 128.1, 127.8, 127.7, 127.2, 125.7, 125.4, 125.0, 123.2, 122.8, 118.6, 109.4. HRMS (ESI): *m/z* calcd for C₂₅H₁₉N₂ (M + H)⁺ 347.1543; found, 347.1547.

2.20

4-(6-methoxynaphthalen-2-yl)-1,2-diphenyl-1H-imidazole 3t. 0.2 mmol, 64 mg, 86%; Yellow solid; mp 186-189 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.38 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.55 – 7.46 (m, 3H), 7.45 – 7.36 (m, 3H), 7.35 – 7.24 (m, 5H), 7.20 – 7.09 (m, 2H), 3.92 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 157.5, 147.1, 141.7, 138.5, 133.8, 130.2, 129.7, 129.5, 129.3, 129.0, 128.9, 128.5, 128.2, 128.1, 127.0, 125.8, 124.2, 123.2, 118.8, 118.5, 105.8, 55.3. HRMS (ESI): *m/z* calcd for C₂₆H₂₁N₂O (M + H)⁺ 377.1649; found, 377.1648.

2.21

4-ethyl-1,2-diphenyl-1H-imidazole 3u. 0.2 mmol, 46 mg, 93%; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.35 (m, 5H), 7.27 – 7.18 (m, 6H), 6.89 (s, 1H), 2.78 – 2.70 (m, 2H), 1.35 – 1.25 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 144.4, 138.7, 129.4, 128.7, 128.2, 128.1, 127.8, 125.8, 118.3, 21.6, 13.5. HRMS (ESI): *m/z* calcd for C₁₇H₁₇N₂ (M + H)⁺ 249.1386; found, 249.1383.

2.22

4-isobutyl-1,2-diphenyl-1H-imidazole 3v. 0.2 mmol, 53 mg, 95%; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.36 (m, 5H), 7.35 – 7.17 (m, 6H), 6.89 (s, 1H), 2.56 – 2.52 (d, *J* = 6.8 Hz, 2H), 2.16 – 2.00 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 141.8, 138.7, 129.3, 128.7, 128.2, 128.1, 127.8, 125.8, 119.5, 37.6, 28.4, 22.6. HRMS (ESI): *m/z* calcd for C₁₉H₂₁N₂ (M + H)⁺ 277.1699; found, 277.1698.