Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Support Information

Rhodium(III)-Catalyzed Cascade Oxidative Annulation Reactions of Aryl Imidazolium Salts with Alkynes involving Multiple C–H Bond Activation

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Contents

^{1}H NMR data for imidazolium salts 1

1-Phenyl-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1a)

^{1}H NMR ($CDCl_3$) δ 11.79 (s, 1H), 7.78 (d, J = 7.7 Hz, 2H), 7.57 (t, J = 7.5 Hz, 3H), 7.51 (dd, J = 11.1, 3.5 Hz, 1H), 6.94 (s, 2H), 6.90 (s, 1H), 5.86 (s, 2H), 2.33 (s, 6H), 2.30 (s, 3H).

1-(4-Fluorophenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1b)

^{1}H NMR (DMSO-d_6) δ 9.79 (s, 1H), 8.31 (t, J = 1.7 Hz, 1H), 7.86 (dd, J = 9.0, 4.6 Hz, 2H), 7.75 (t, J = 1.7 Hz, 1H), 7.52 (t, J = 8.8 Hz, 2H), 6.98 (s, 2H), 5.48 (s, 2H,), 2.32 (s, 6H), 2.26 (s, 3H).

1-(4-Chlorophenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1c)

^{1}H NMR (DMSO-d_6) δ 9.83 (s, 1H), 8.35 (s, 1H), 7.86 (s, 1H), 7.76 (s, 1H), 7.75 (s, 1H), 7.72 (s, 1H), 6.98 (s, 2H), 5.47 (s, 2H), 2.31 (s, 6H), 2.26 (s, 3H).

1-(4-Bromophenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1d)

^{1}H NMR (DMSO-d_6) δ 9.84 (s, 1H), 8.35 (d, J = 1.7 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 14.3 Hz, 3H), 6.98 (s, 2H), 5.48 (s, 2H), 2.31 (s, 6H), 2.26 (s, 3H).

1-p-Tolyl-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1e)

^{1}H NMR ($CDCl_3$) δ 11.44 (s, 1H), 7.63 (d, J = 8.2 Hz, 3H), 7.31 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 6.9 Hz, 3H), 5.81 (s, 2H), 2.38 (s, 3H), 2.30 (s, 6H), 2.28 (s, 3H).

1-(4-Methoxyphenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1f)

^{1}H NMR ($CDCl_3$) δ 11.20 (s, 1H), 7.69 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.88 (s, 3H), 5.73 (s, 2H), 3.77 (s, 3H), 2.26 (d, J = 4.7 Hz, 9H).

1-(4-(Dimethylamino)phenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1g)

^{1}H NMR ($CDCl_3$) δ 11.05 (s, 1H), 7.52 (d, J = 8.1 Hz, 3H), 6.90 (s, 3H), 6.70 (d, J = 8.9 Hz, 2H), 5.77 (s, 2H), 2.96 (s, 6H), 2.28 (s, 6H), 2.27 (s, 3H).

1-(4-*tert*-Butylphenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1h)

^{1}H NMR (DMSO-d_6) δ 9.79 (s, 1H), 8.30 (s, 1H), 7.70 (d, J = 1.7 Hz, 3H), 7.64 (d, J = 8.8 Hz, 2H), 6.98 (s, 2H), 5.48 (s, 2H), 2.31 (s, 6H), 2.26 (s, 3H), 1.32 (s, 9H).

1-(4-Nitrophenyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1i)

^{1}H NMR (DMSO-d_6) δ 10.00 (s, 1H), 8.49 (d, J = 8.7 Hz, 3H), 8.12 (d, J = 9.0 Hz, 2H), 7.82 (s, 1H), 6.99 (s, 2H), 5.50 (s, 2H), 2.32 (s, 6H), 2.26 (s, 3H).

1,3-diphenylimidazolium chloride (1j)

^{1}H NMR (DMSO-d_6) δ 10.63 (s, 1H), 8.68 (s, 2H), 8.03 (dd, J = 5.5, 3.2 Hz, 4H), 7.69 (t, J = 7.7 Hz, 4H), 7.62 (t, J = 7.4 Hz, 2H).

1-Phenyl-3-(2,4,6-trimethylbenzyl)benzo[d]imidazolium bromide (1k)

^{1}H NMR (DMSO-d_6) δ 9.76 (s, 1H), 8.18 (d, J = 8.1 Hz, 1H), 7.85 – 7.66 (m, 8H), 7.01 (s, 2H), 5.78 (s, 2H), 2.34 (s, 6H), 2.28 (s, 3H).

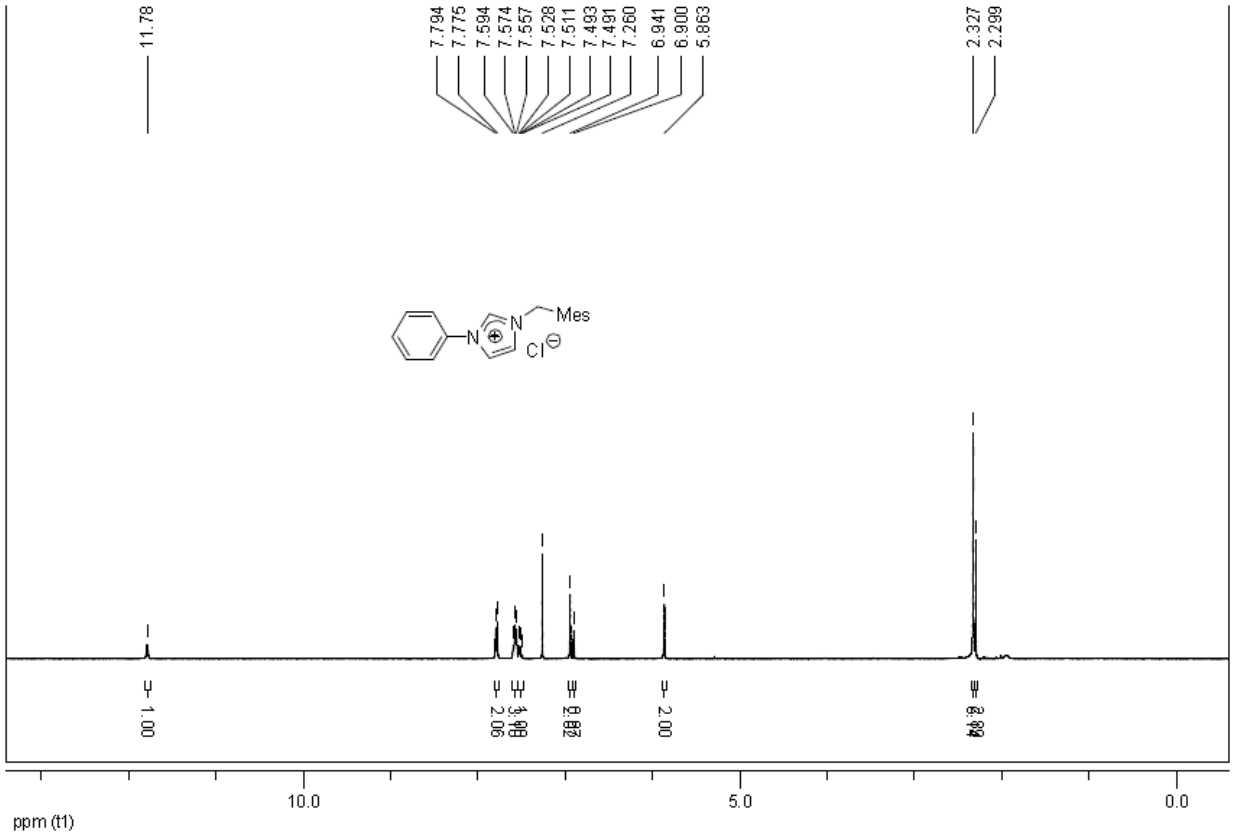
3-methyl-1-phenylimidazolium iodide (1l)

^{1}H NMR ($CDCl_3$) δ 10.37 (d, J = 23.3 Hz, 1H), 7.73 (ddd, J = 27.3, 9.5, 2.2 Hz, 4H), 7.59 – 7.48 (m, 3H), 4.25 (d, J = 6.6 Hz, 3H).

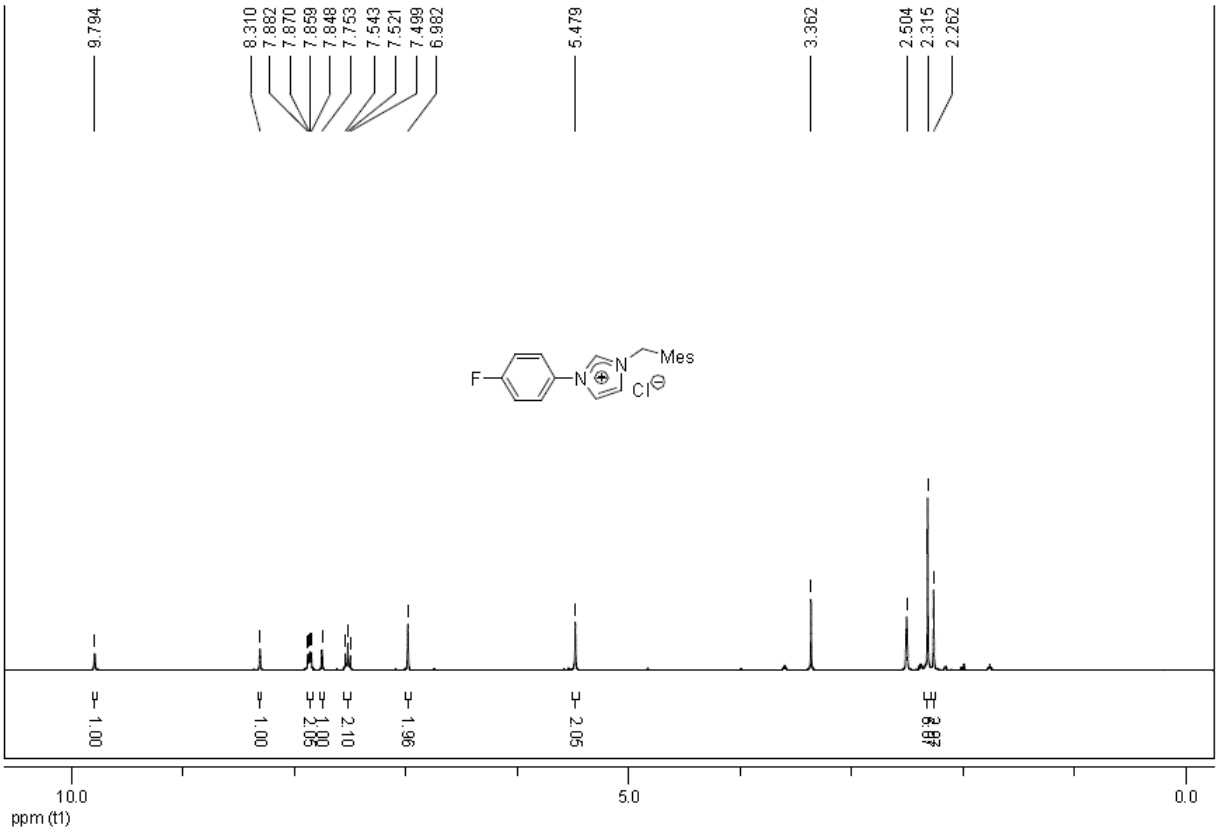
2-methyl-1-phenyl-3-(2,4,6-trimethylbenzyl)imidazolium chloride (1m)

^{1}H NMR ($CDCl_3$) δ 7.70 (dd, J = 6.1, 3.2 Hz, 2H), 7.58 – 7.53 (m, 3H), 7.27 (d, J = 2.1 Hz, 1H), 6.94 (s, 2H), 6.66 (d, J = 2.1 Hz, 1H), 5.49 (s, 2H), 2.91 (s, 3H), 2.34 (s, 6H), 2.30 (s, 3H).

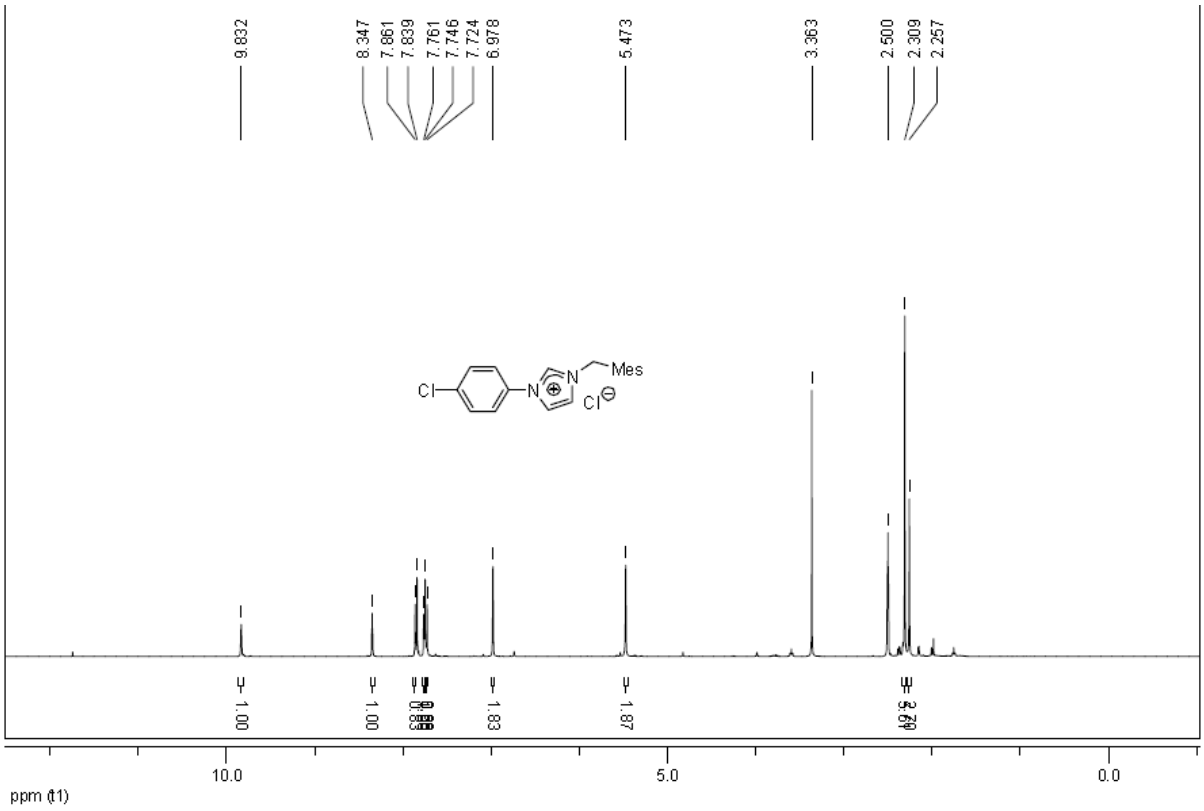
^{1}H NMR spectrum of 1a



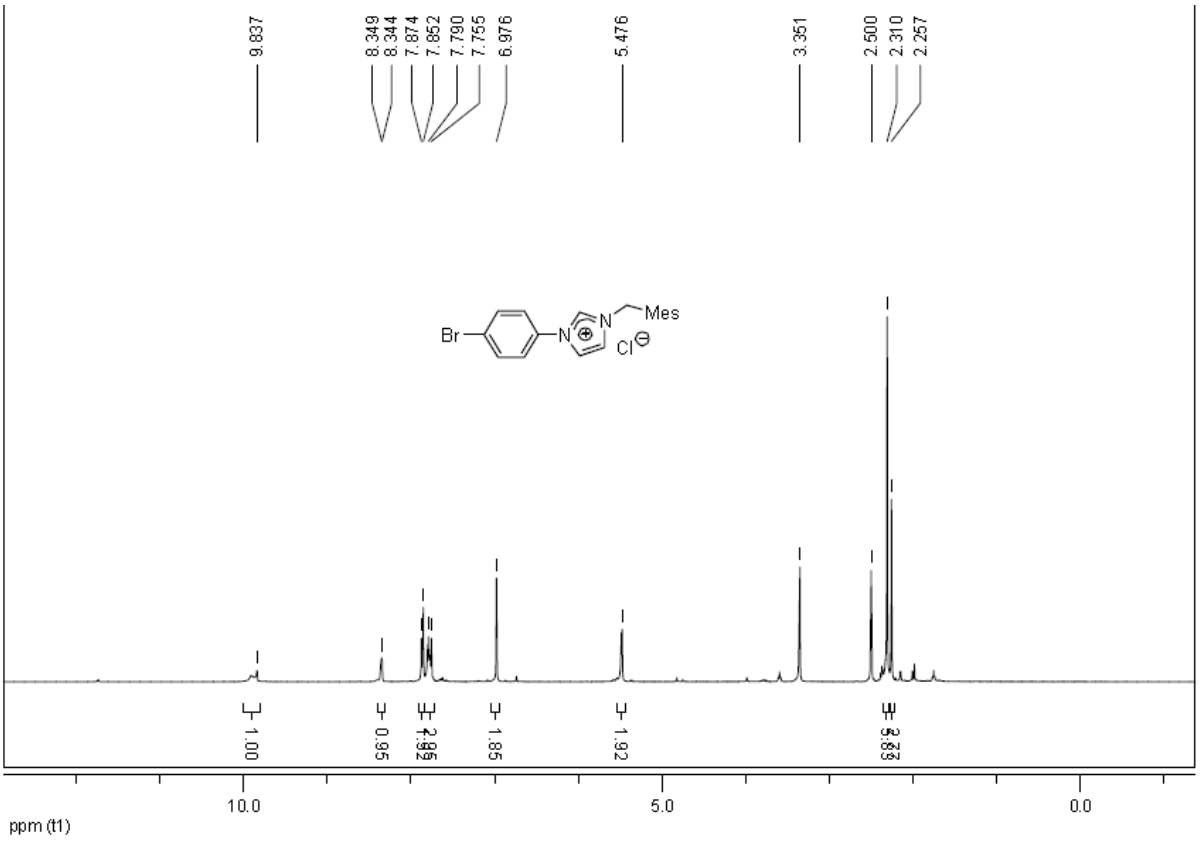
^{1}H NMR spectrum of 1b



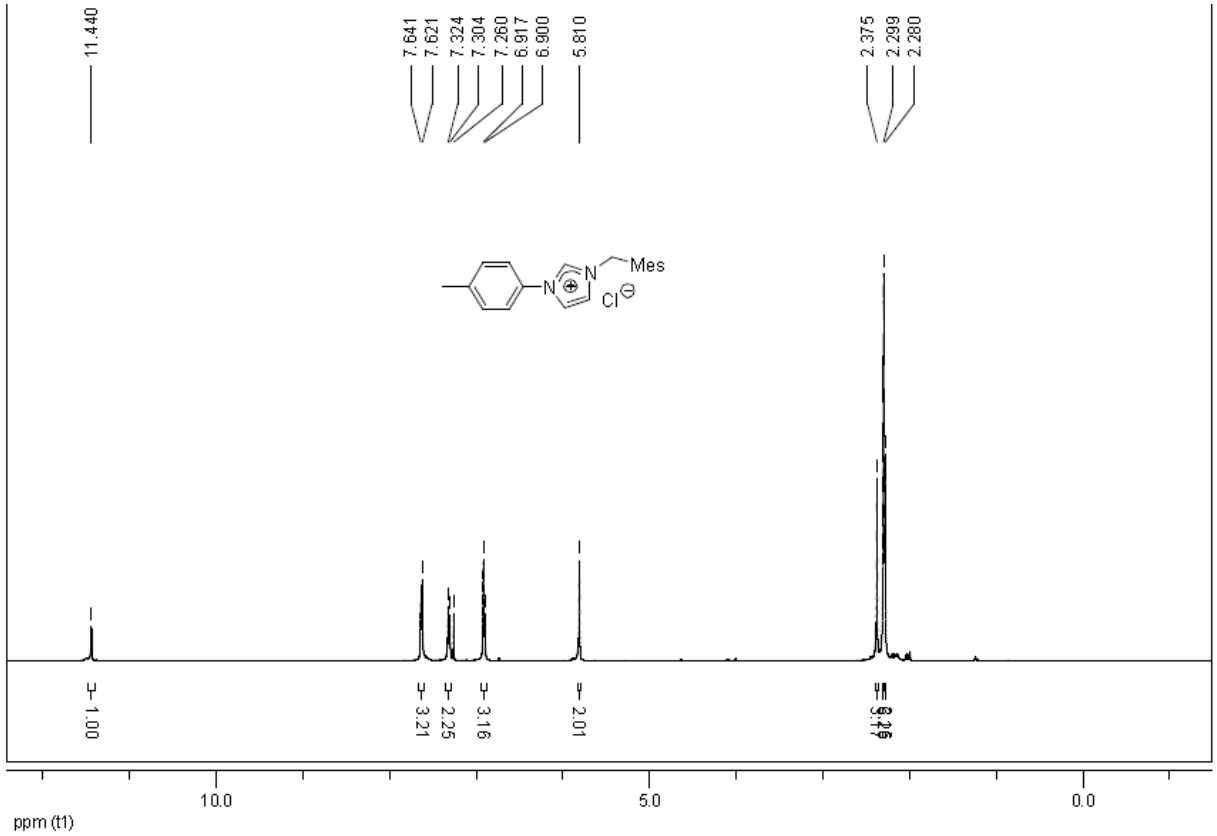
^{1}H NMR spectrum of 1c



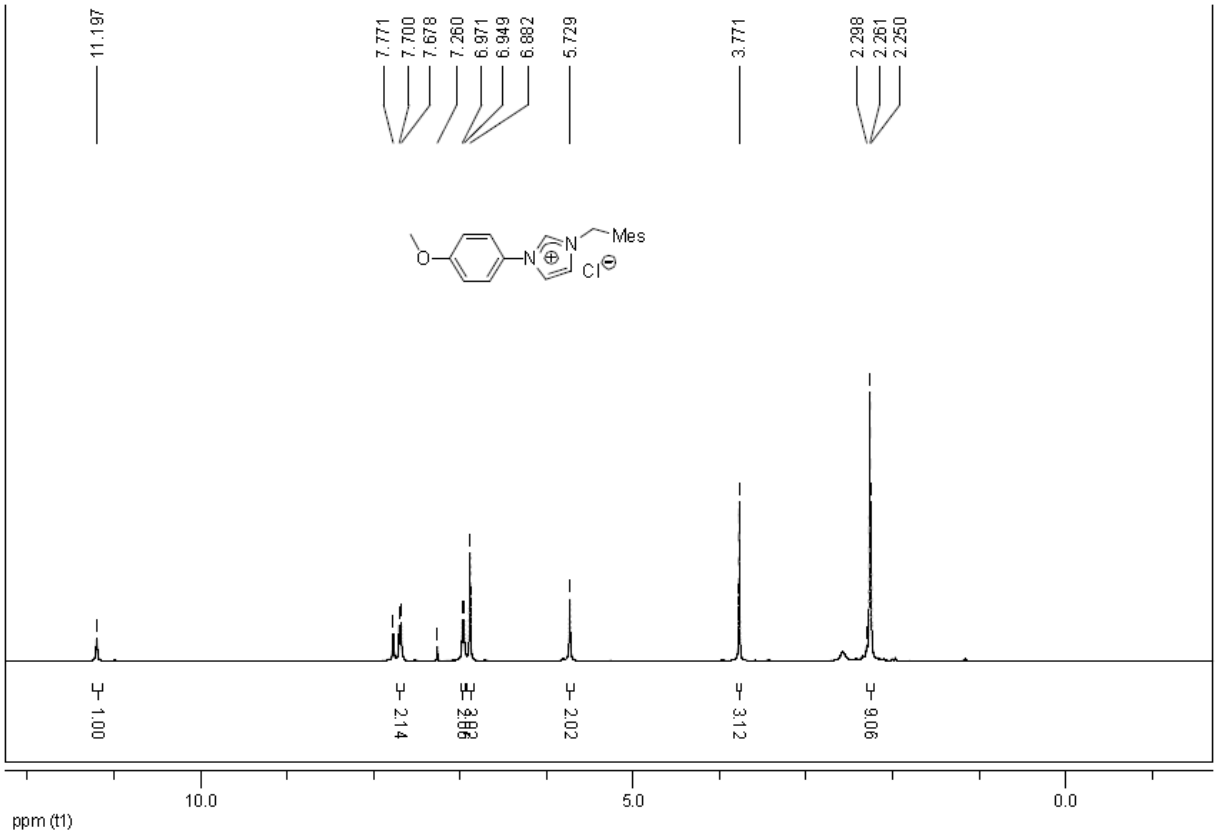
^{1}H NMR spectrum of 1d



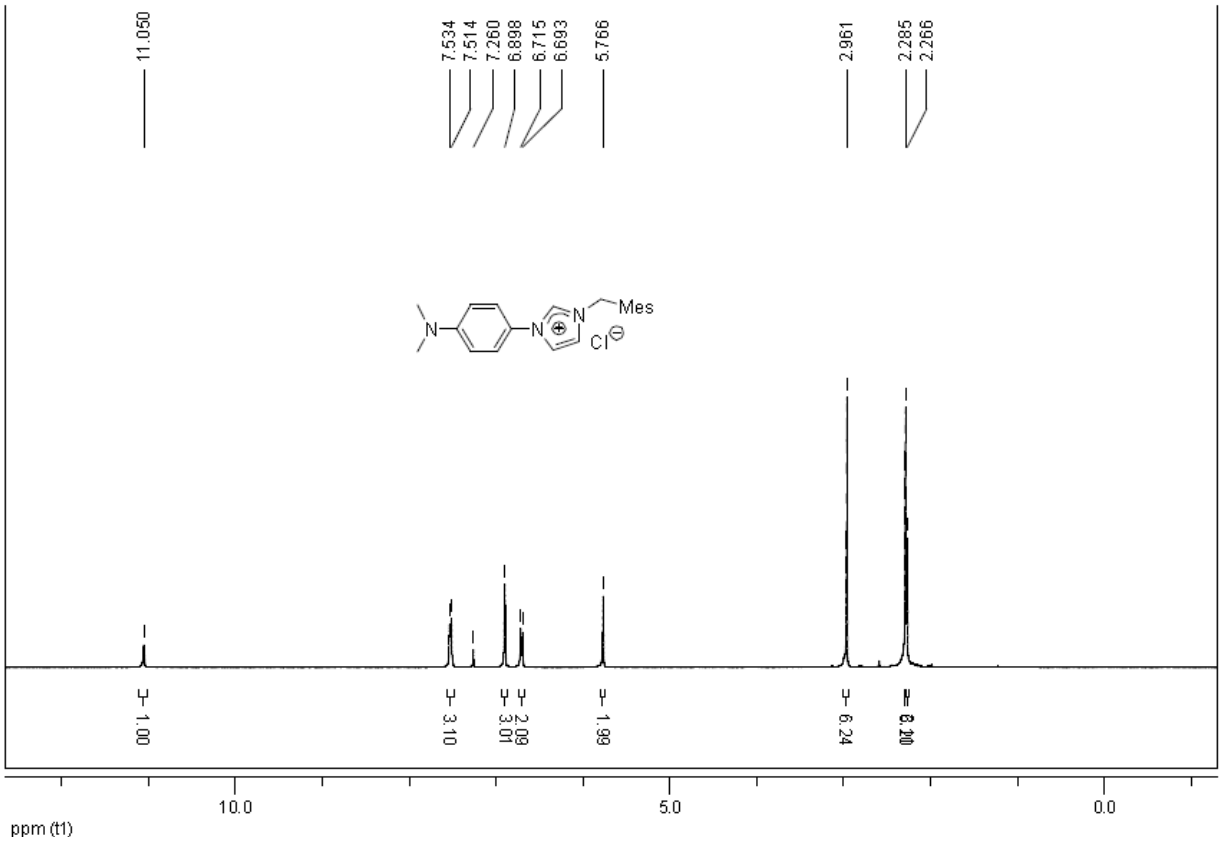
^{1}H NMR spectrum of 1e



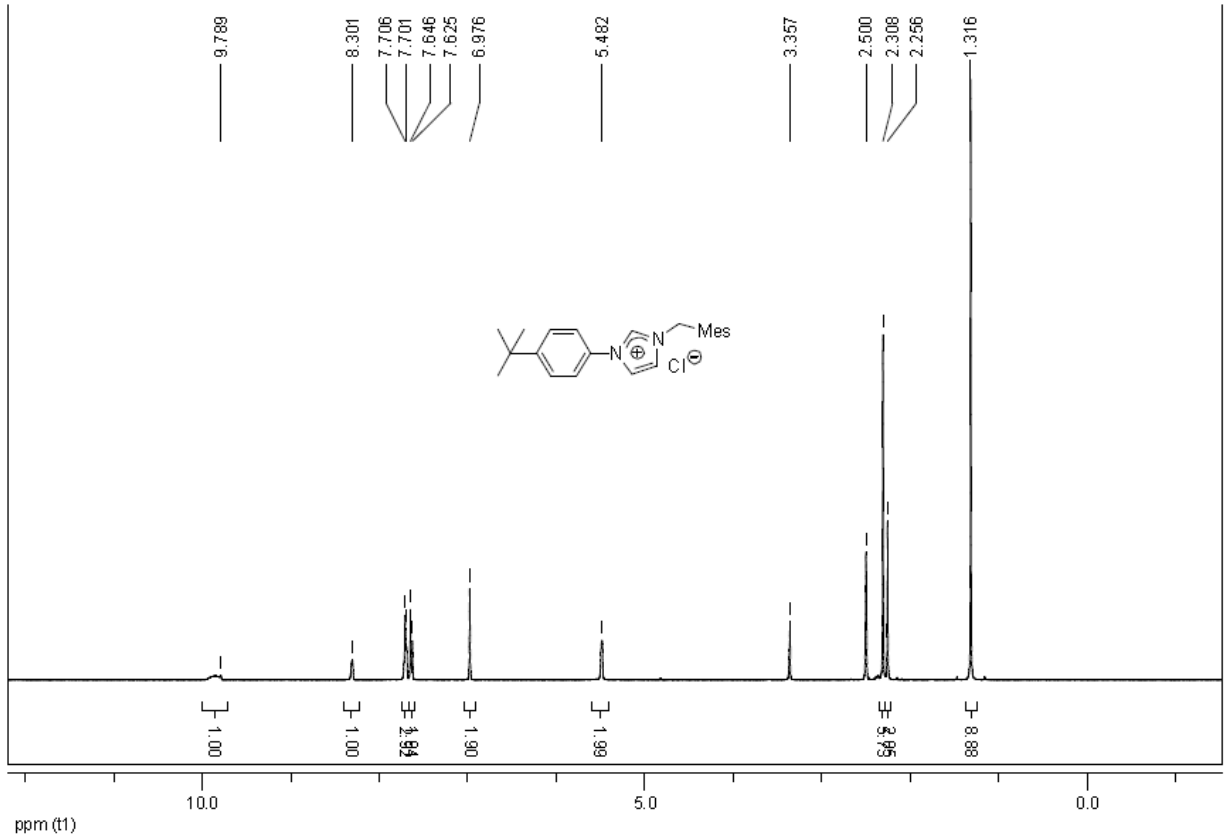
^{1}H NMR spectrum of 1f



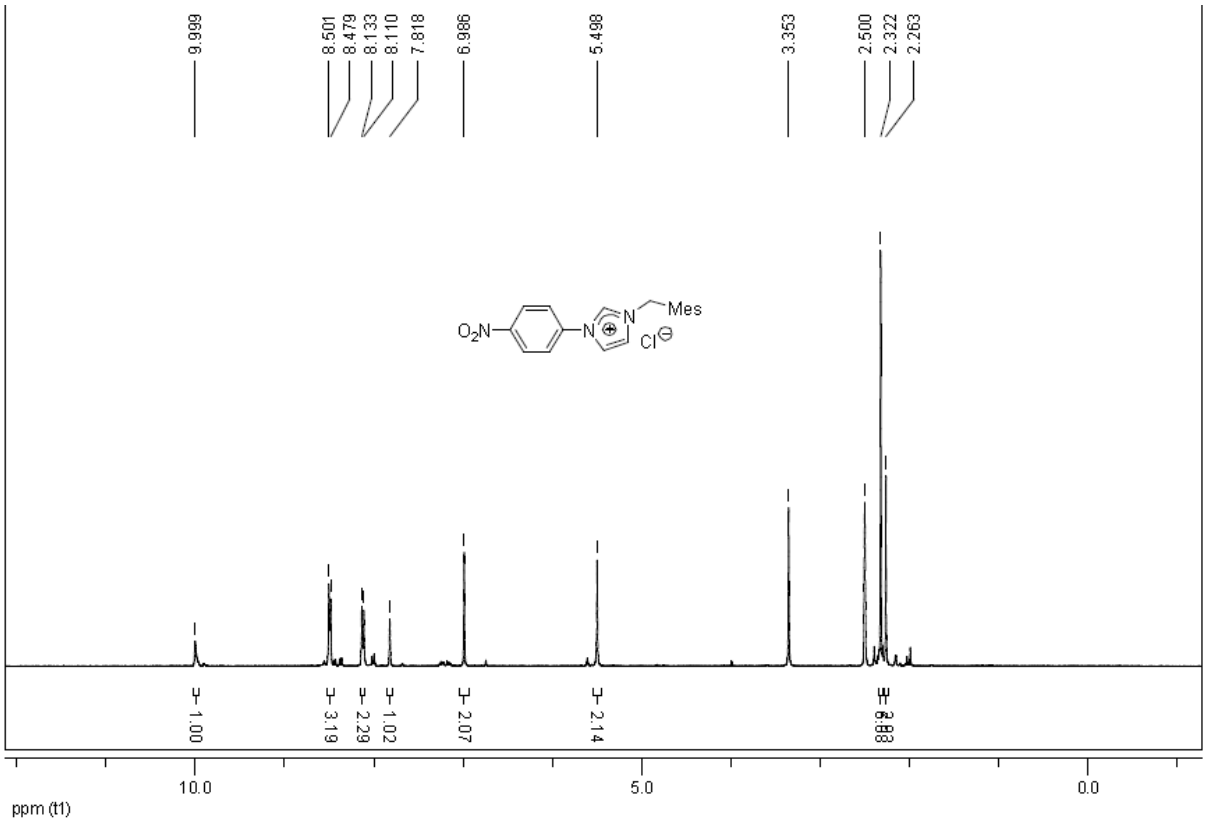
^{1}H NMR spectrum of 1g



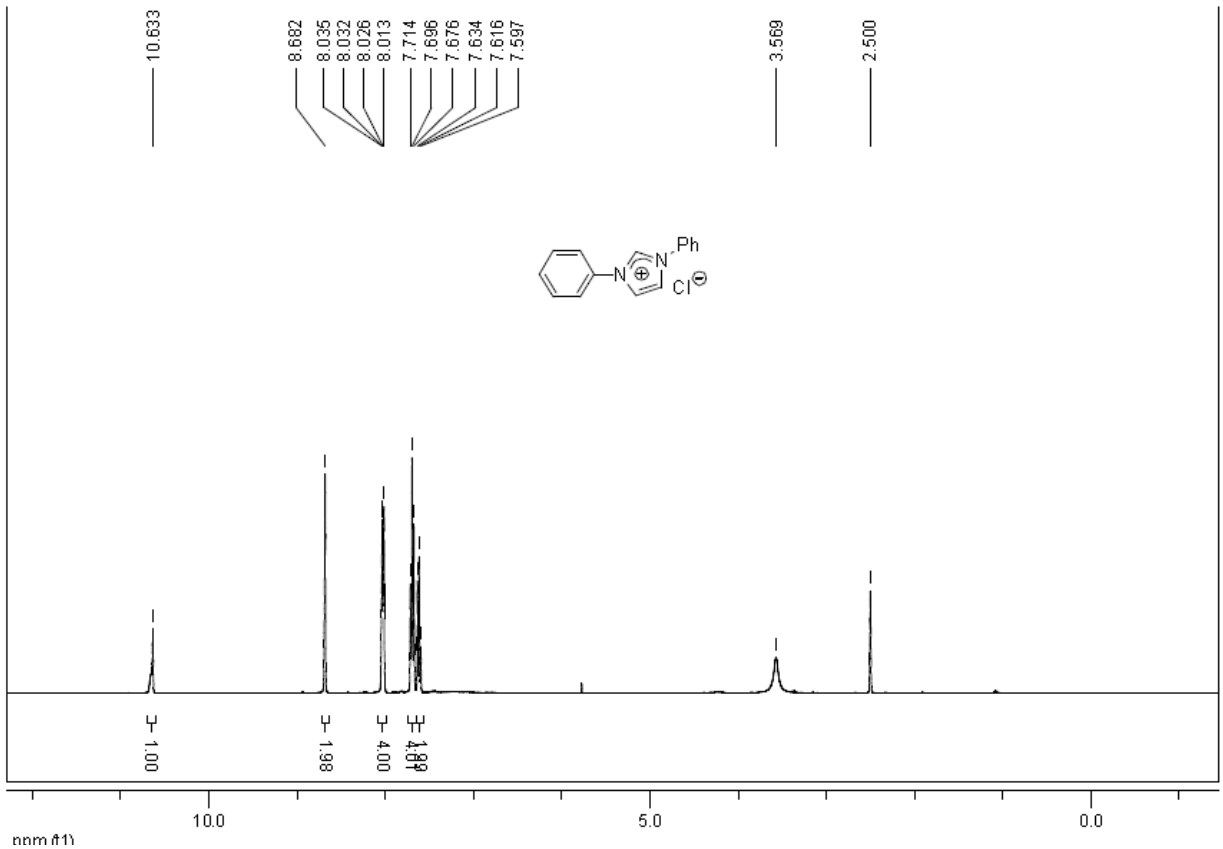
^{1}H NMR spectrum of 1h



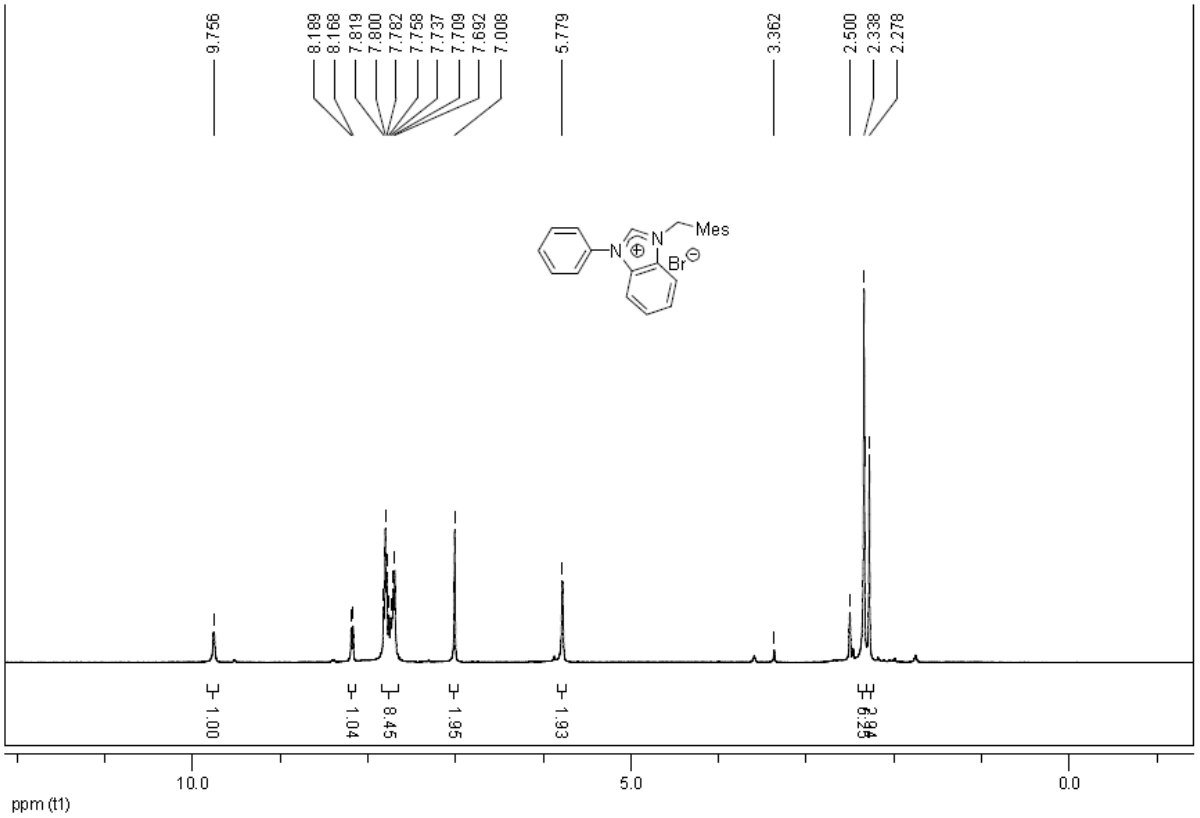
^{1}H NMR spectrum of 1i



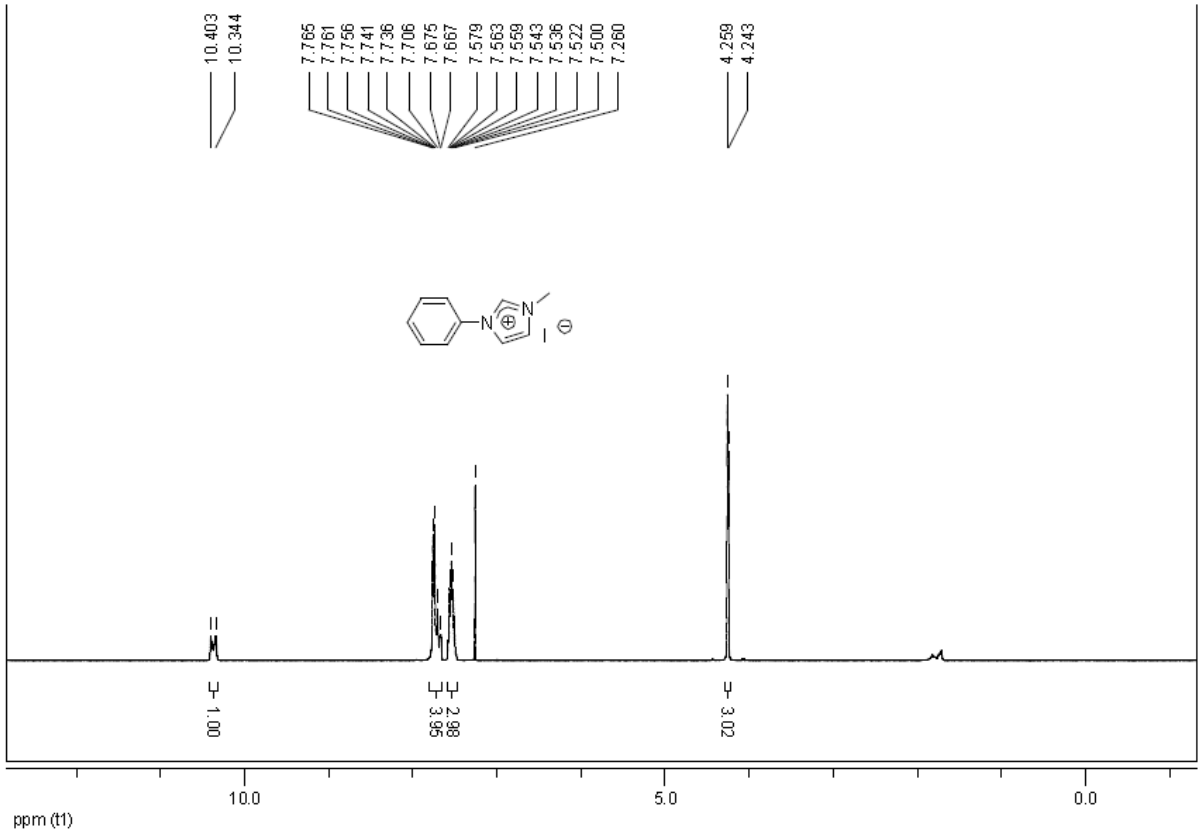
^{1}H NMR spectrum of 1j



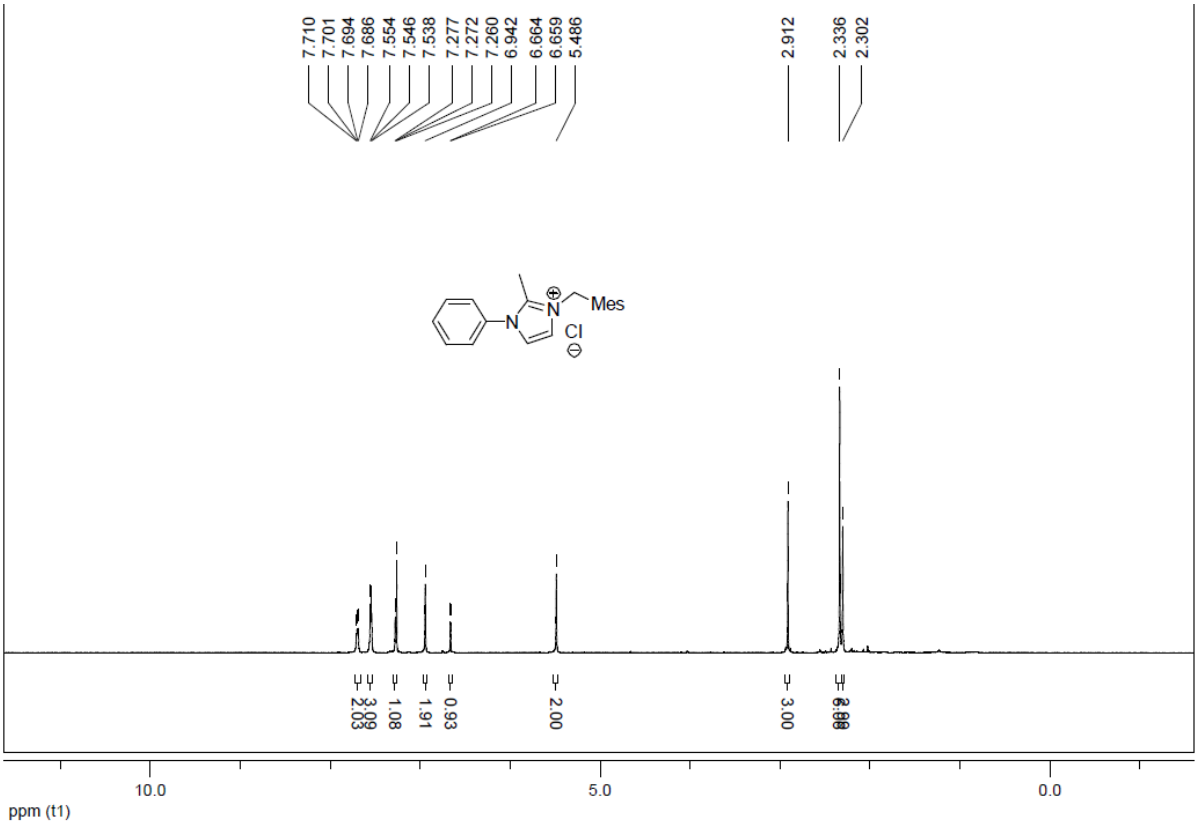
^{1}H NMR spectrum of 1k



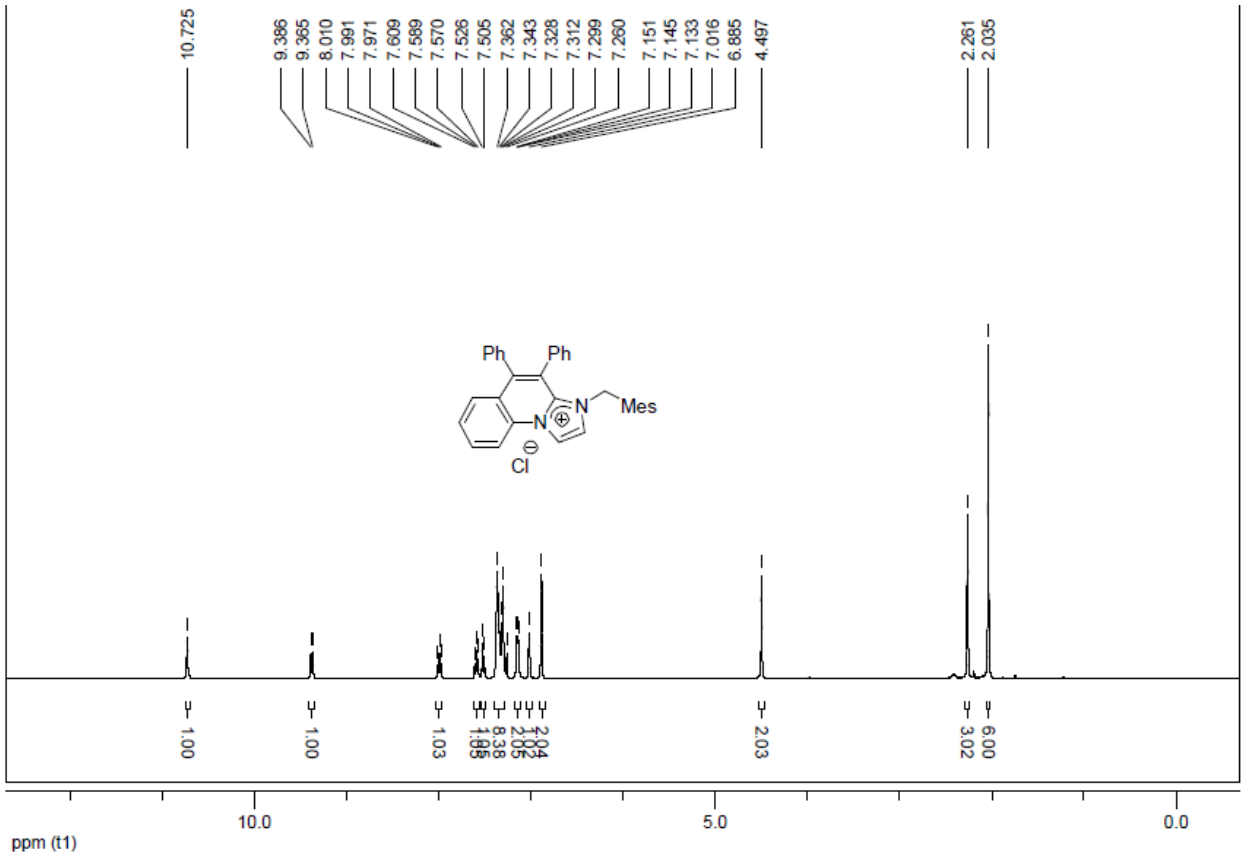
^{1}H NMR spectrum of 1l



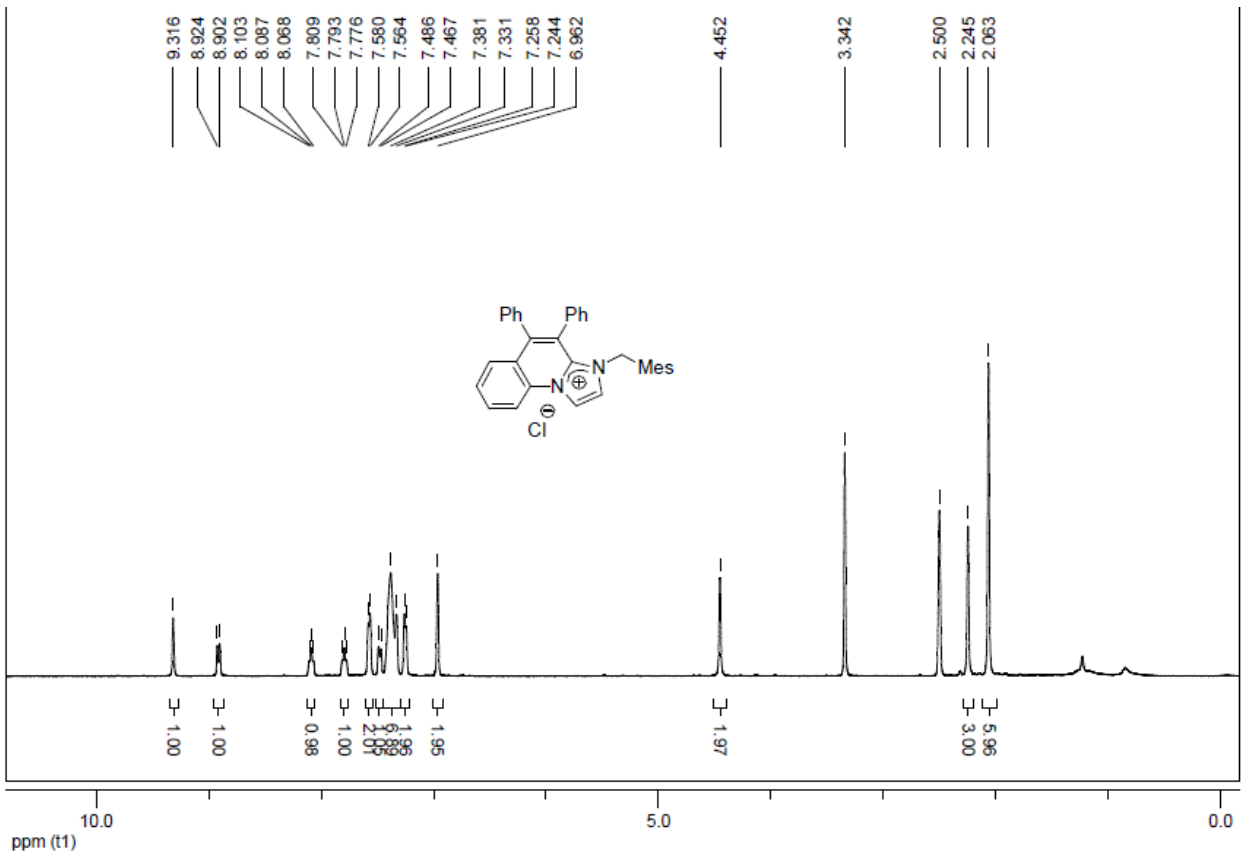
^{1}H NMR spectrum of 1m



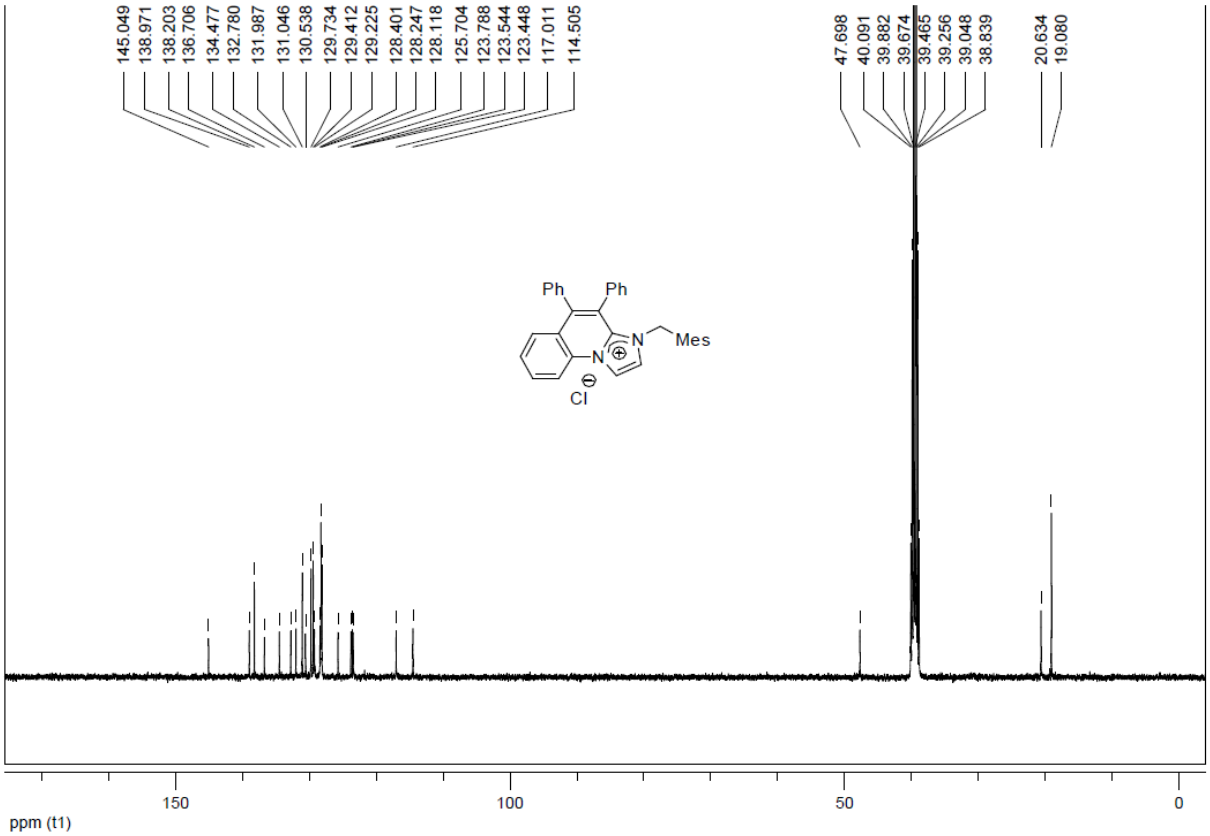
^{1}H NMR spectrum of 3aa (in $CDCl_3$)



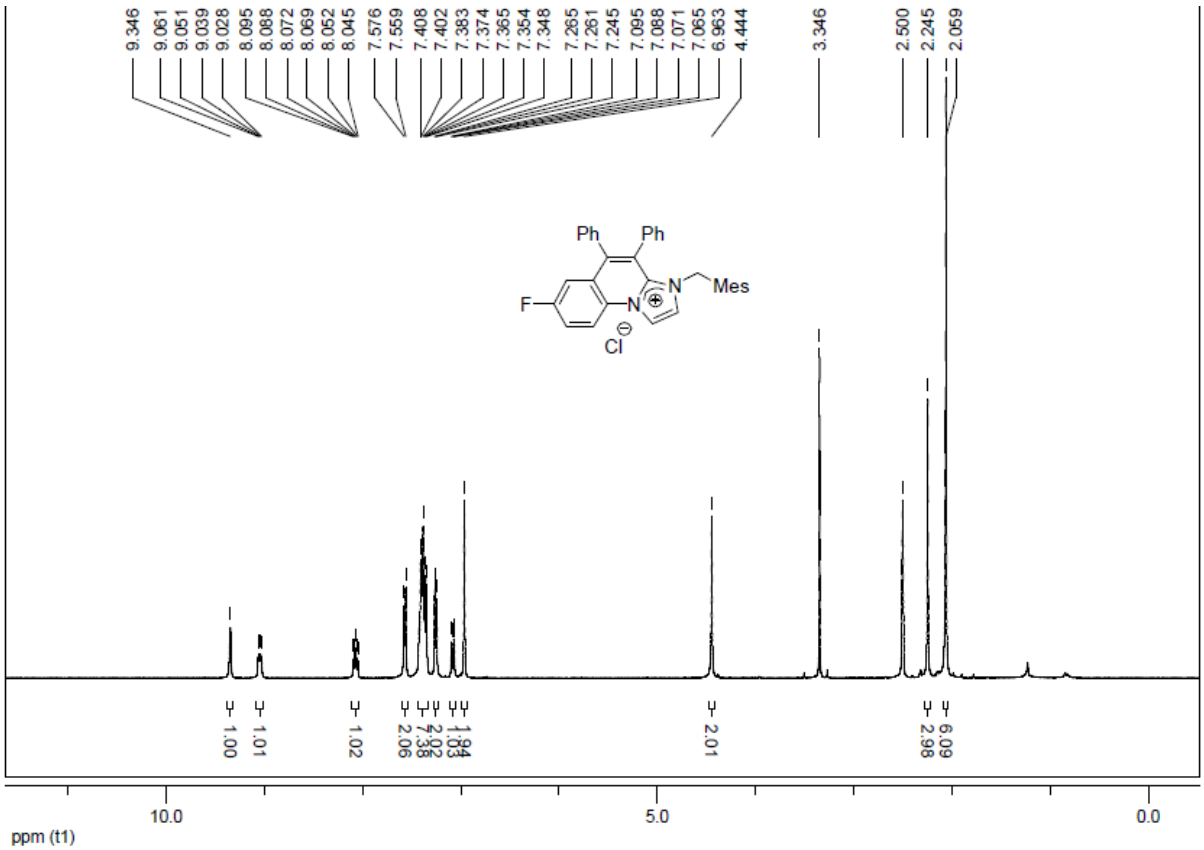
^{1}H NMR spectrum of 3aa (in DMSO-d_6)



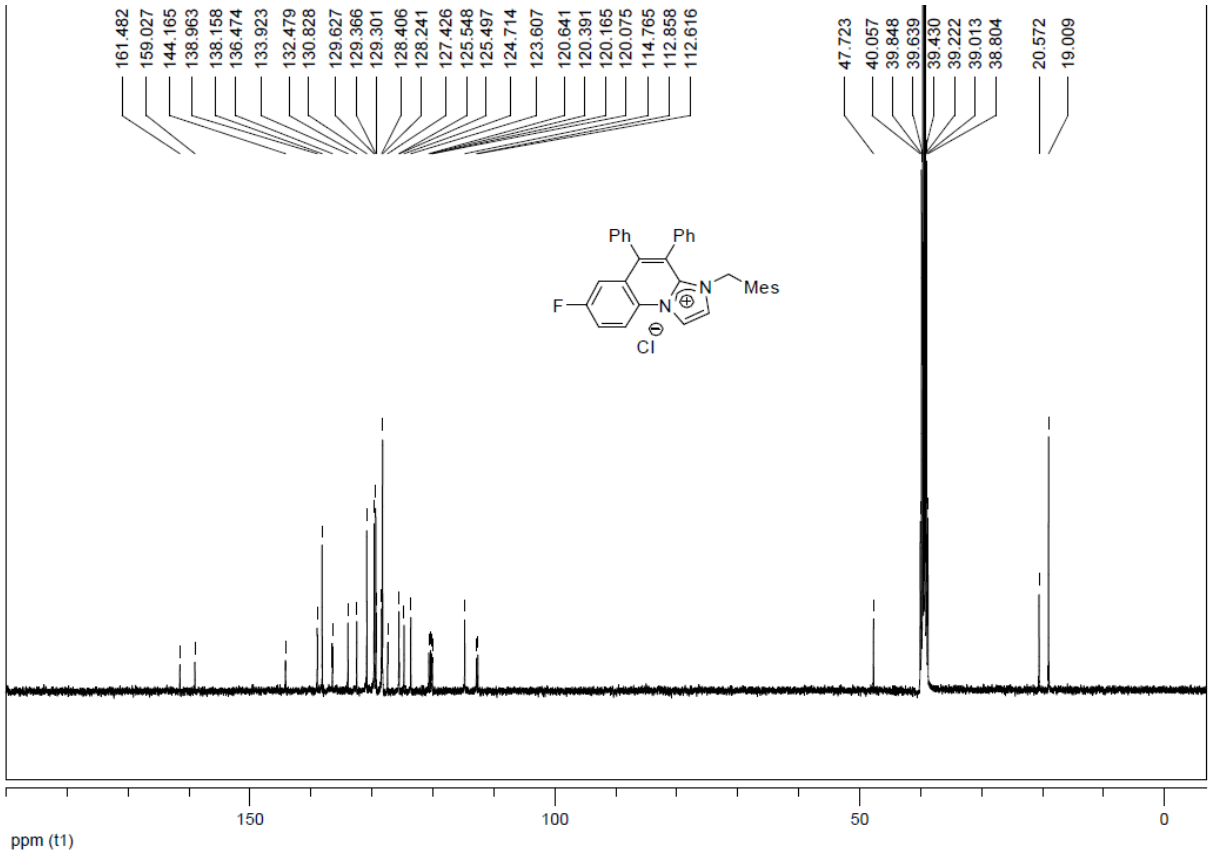
^{13}C NMR spectrum of 3aa



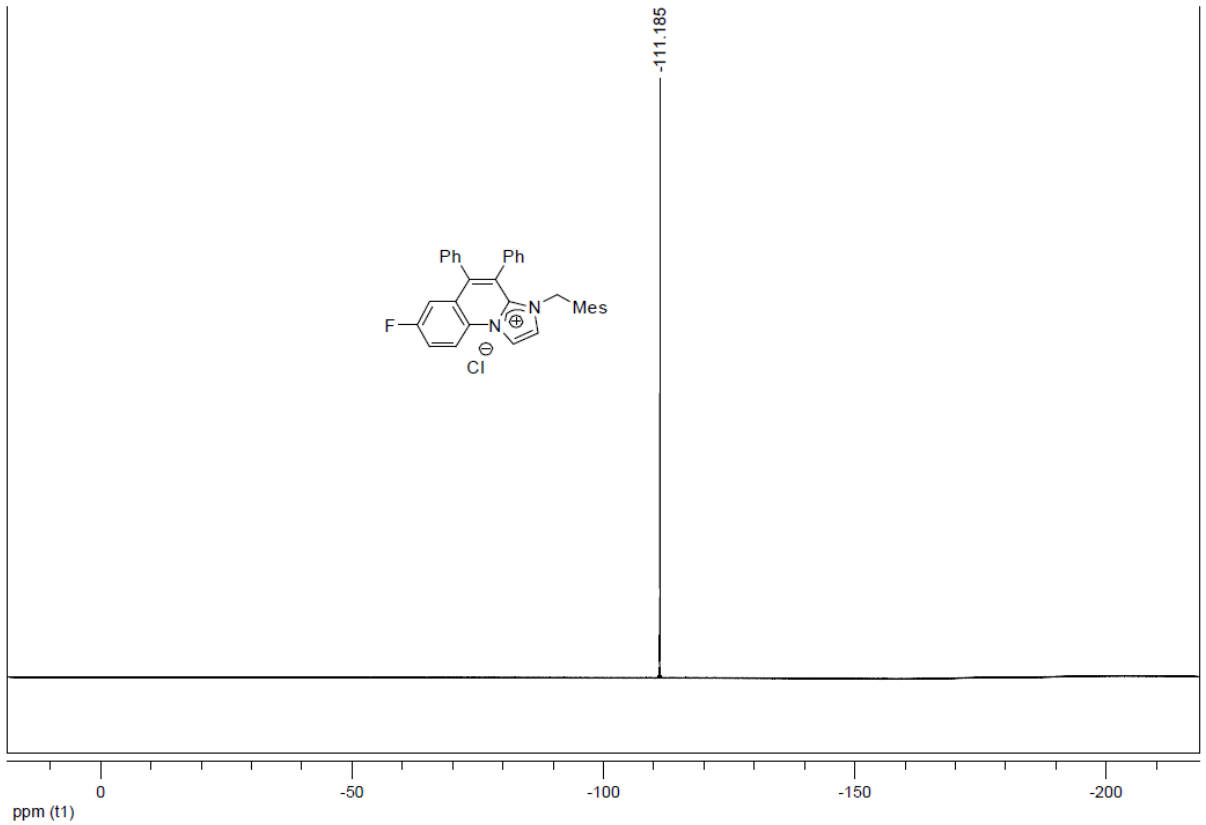
^{1}H NMR spectrum of 3ba



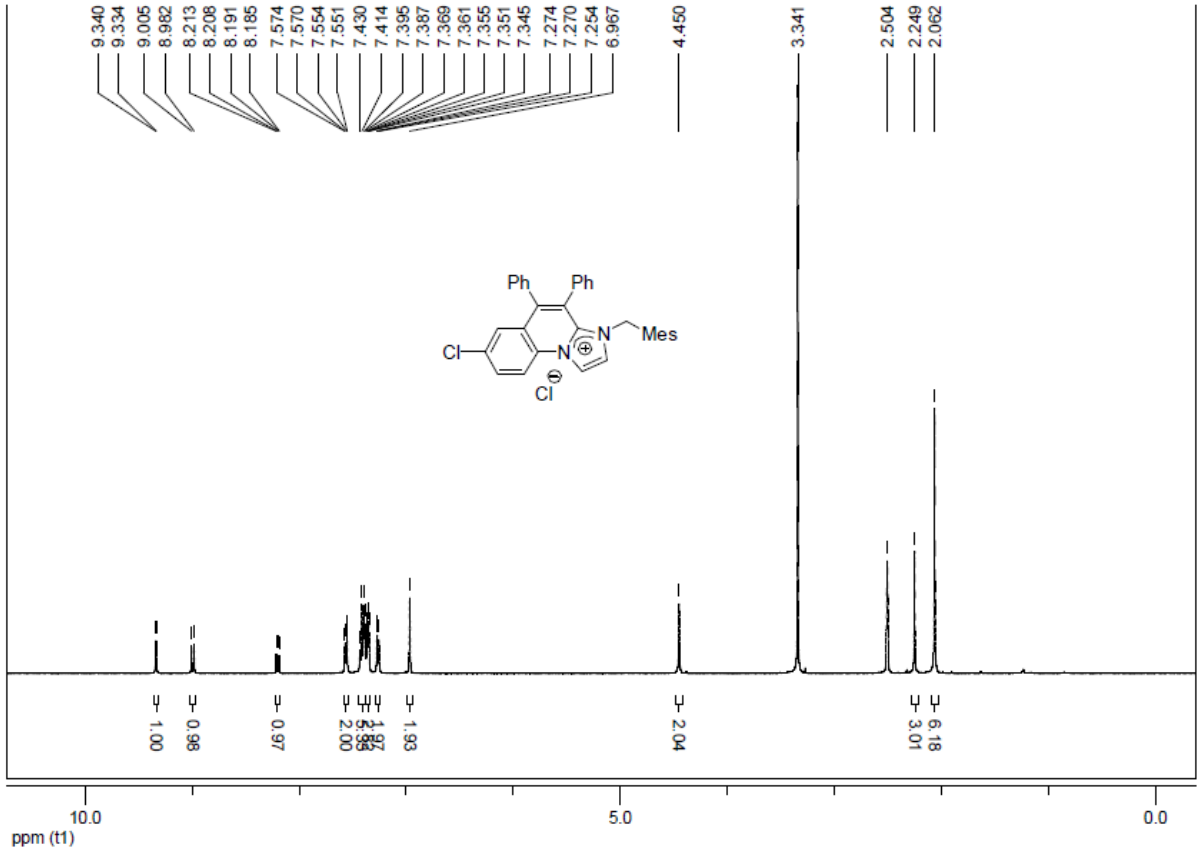
^{13}C NMR spectrum of 3ba



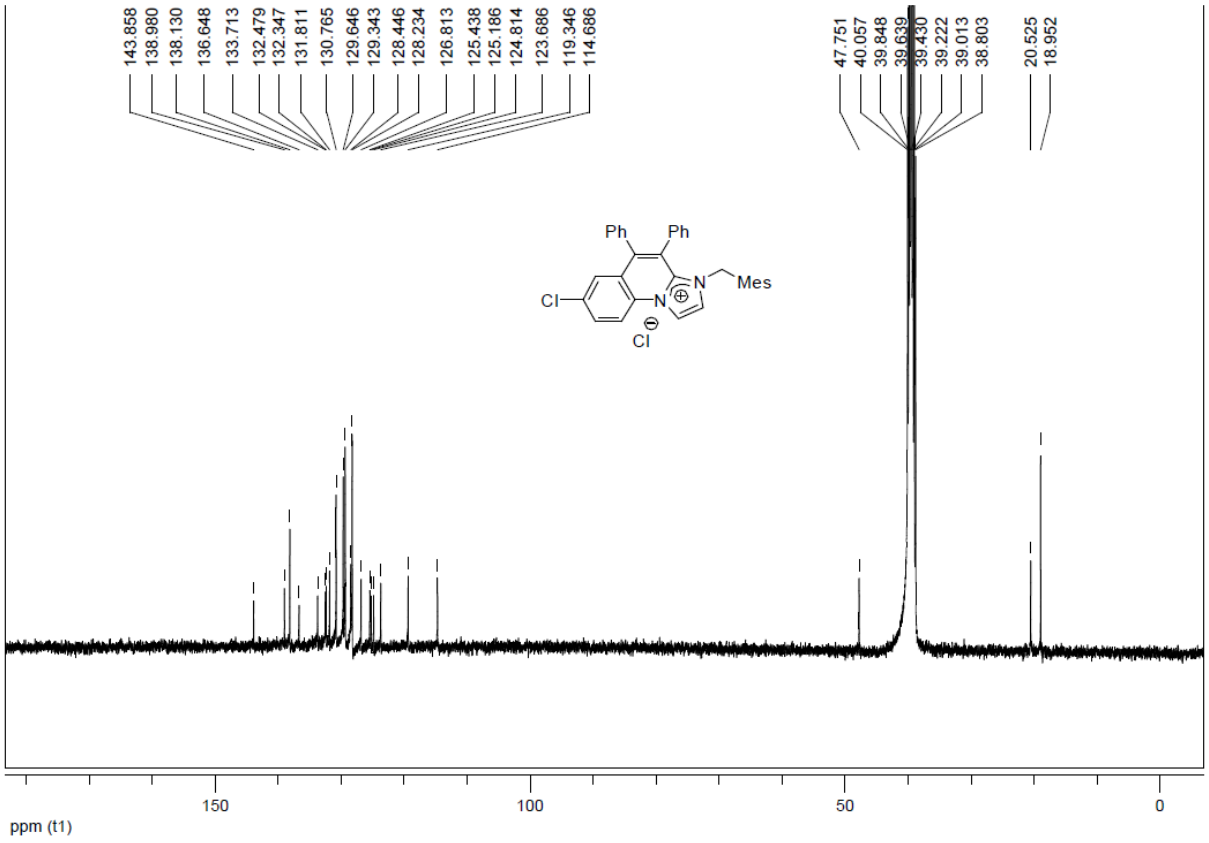
^{19}F NMR spectrum of 3ba



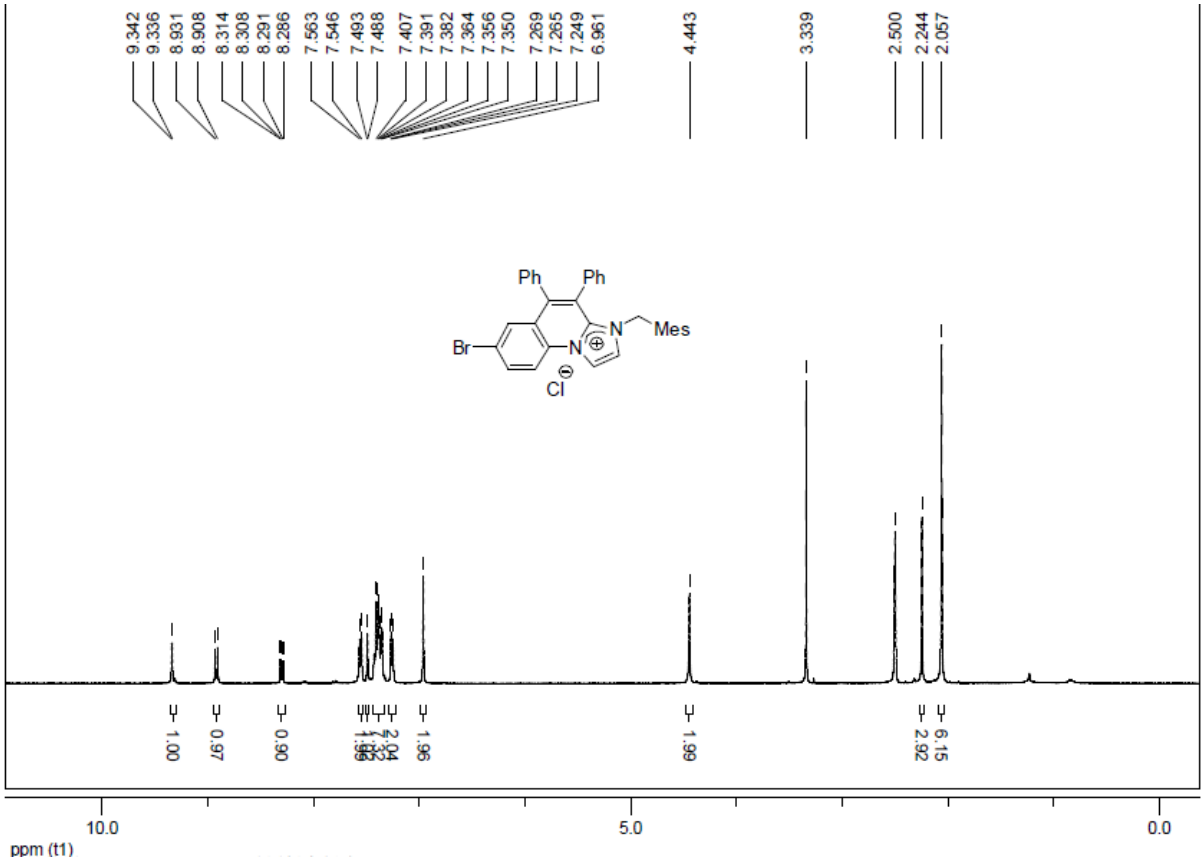
^{1}H NMR spectrum of 3ca



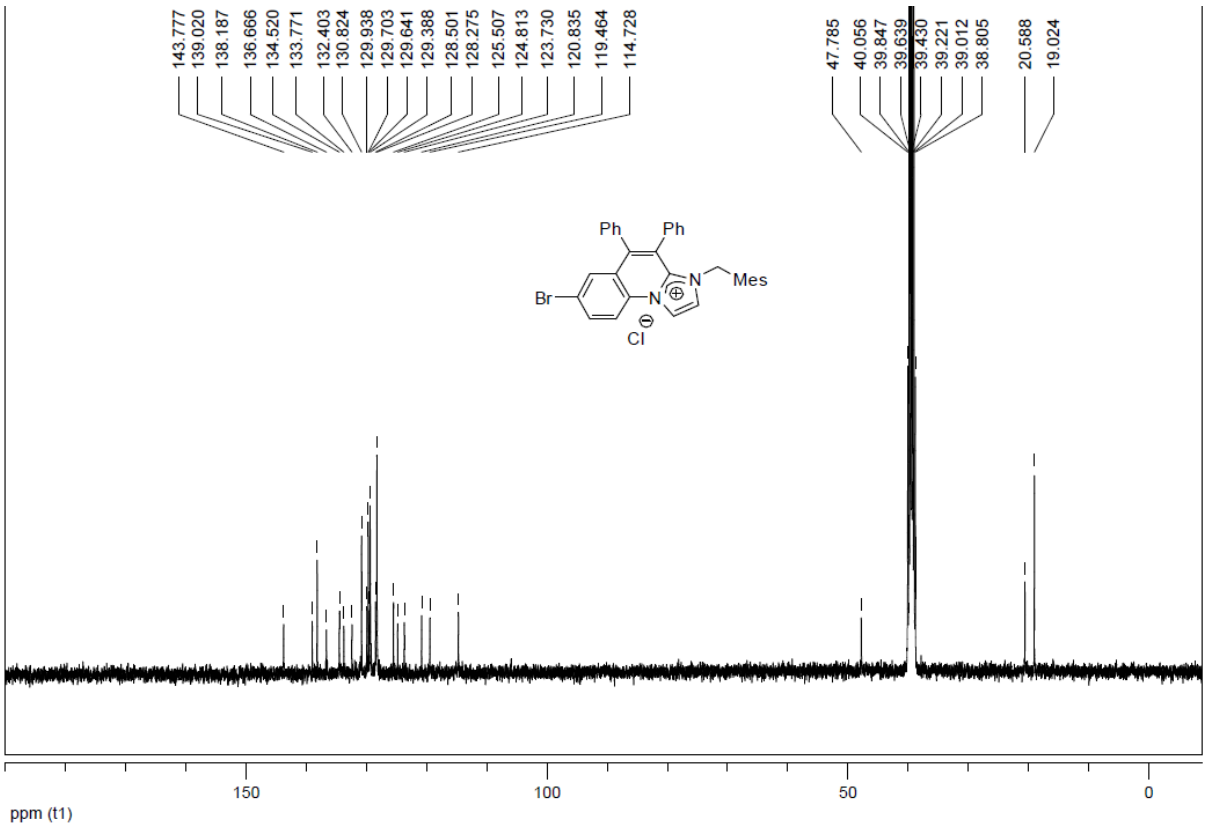
^{13}C NMR spectrum of 3ca



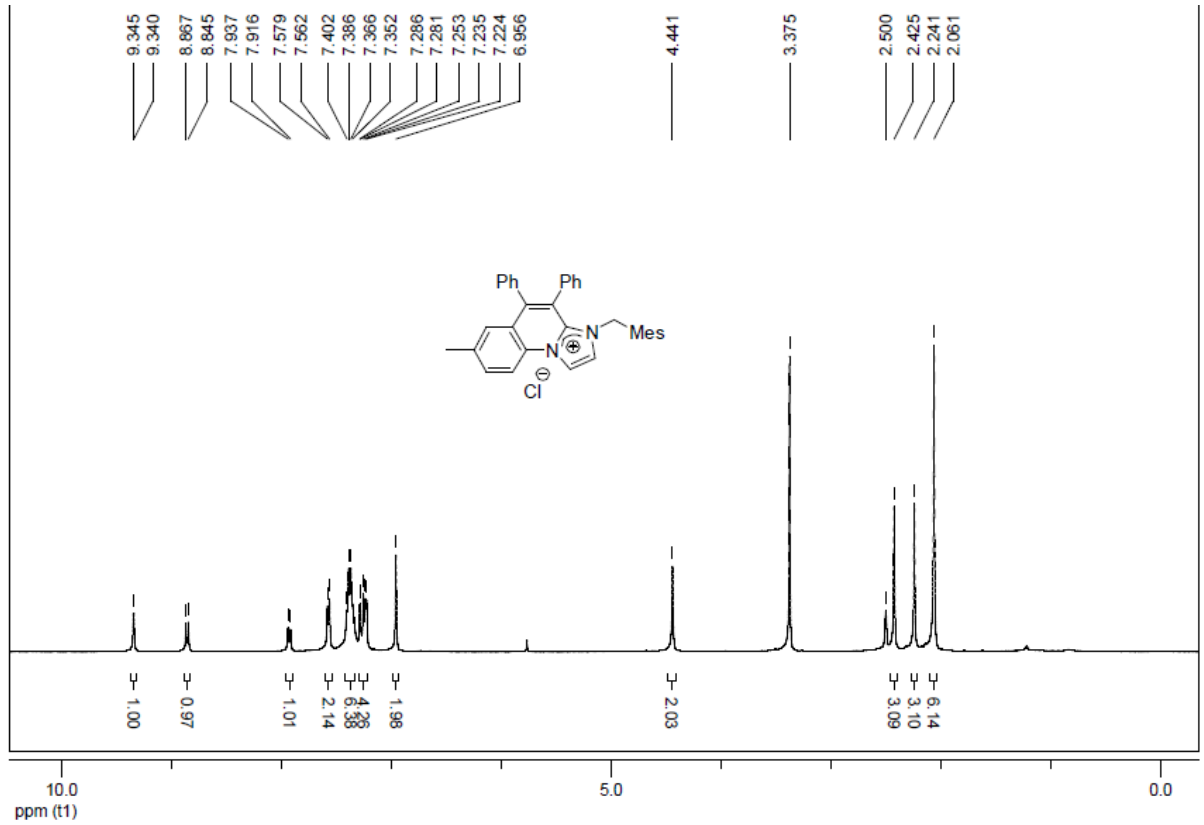
^{1}H NMR spectrum of 3da



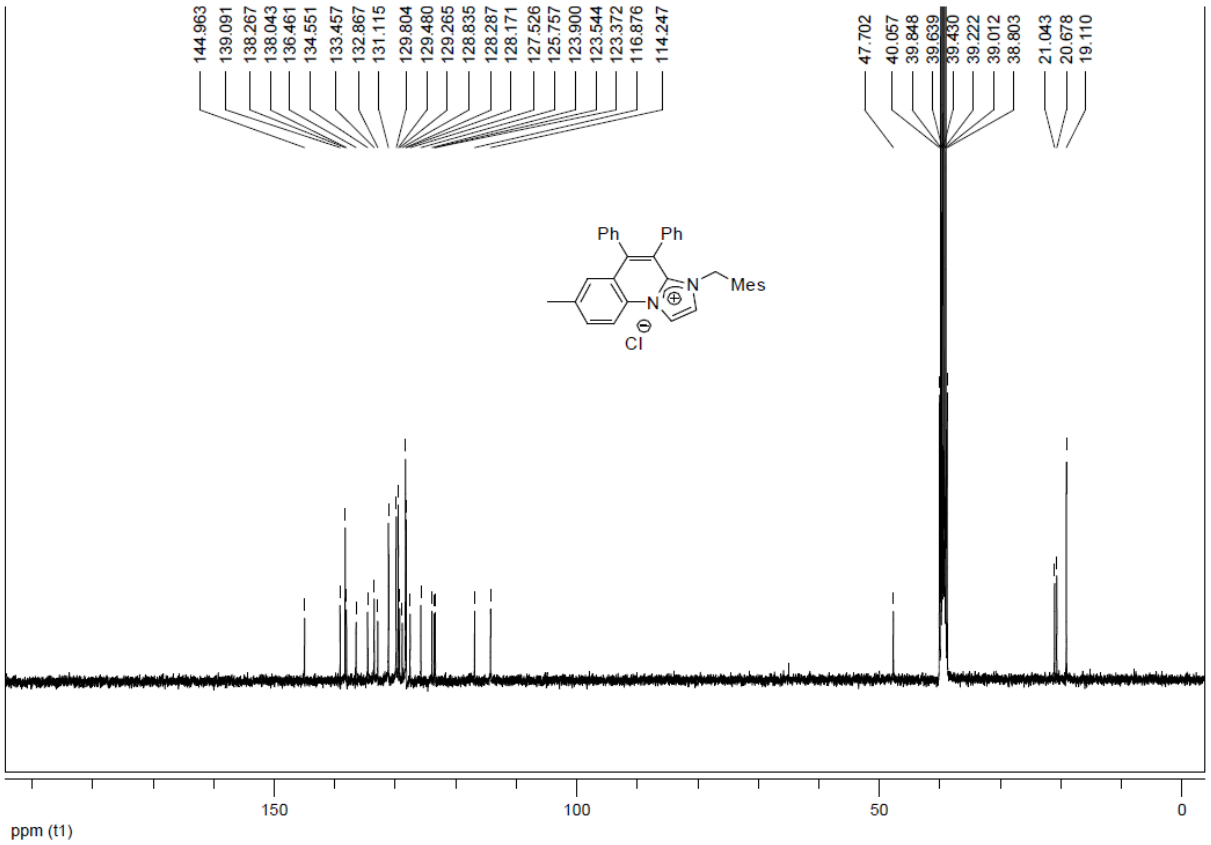
^{13}C NMR spectrum of 3da



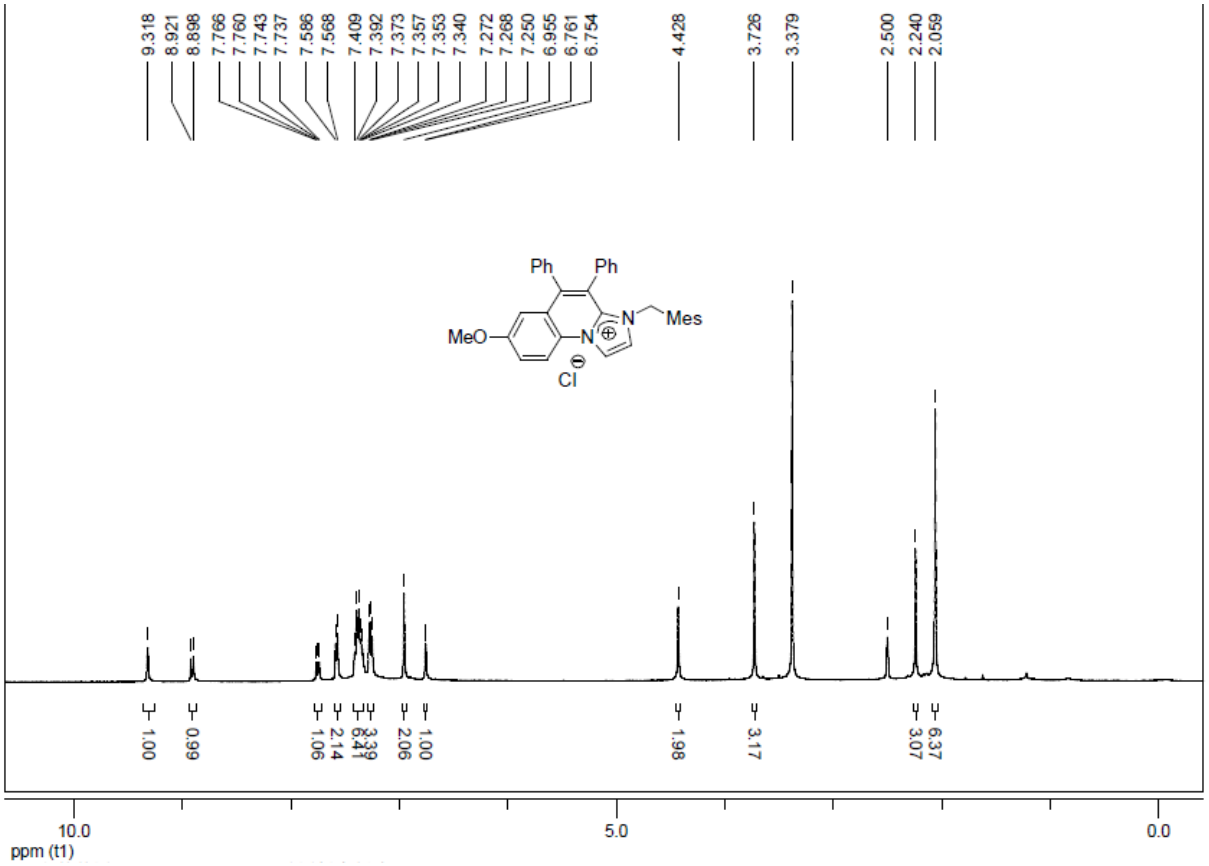
^{1}H NMR spectrum of 3ea



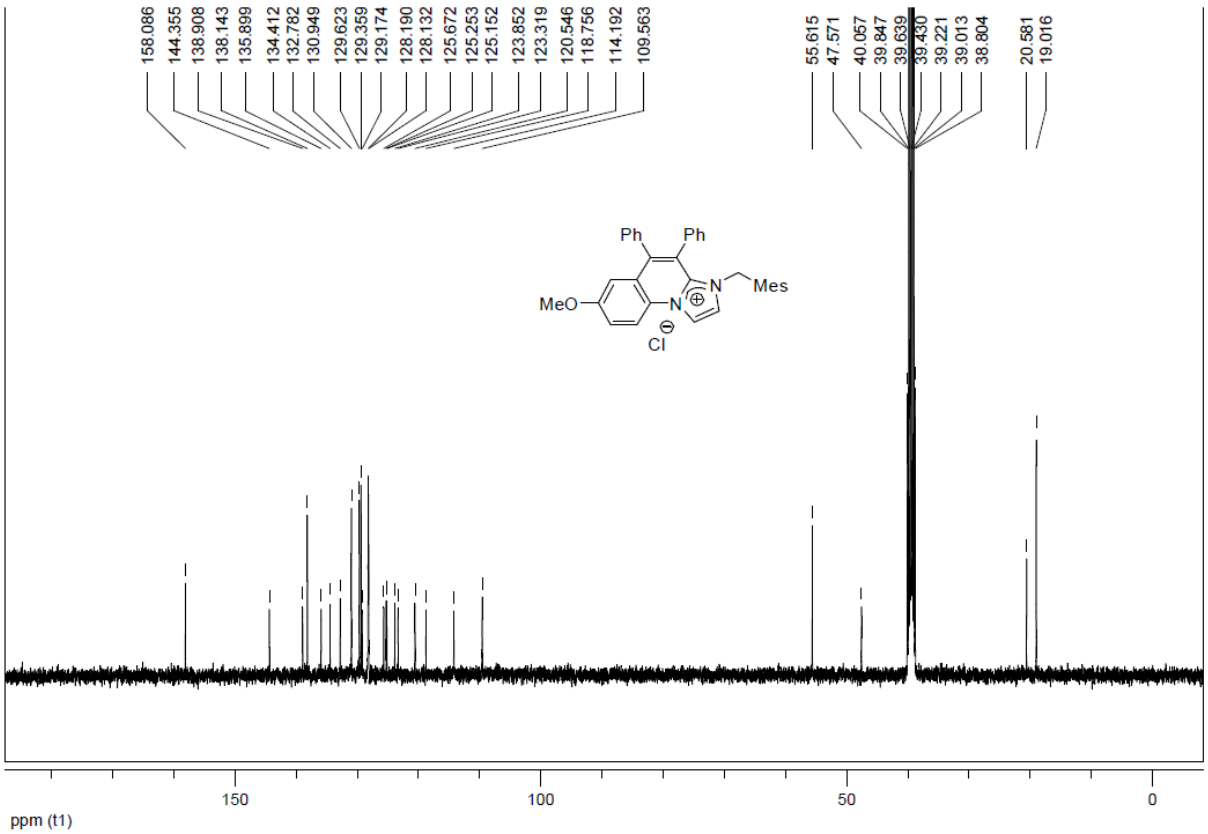
^{13}C NMR spectrum of 3ea



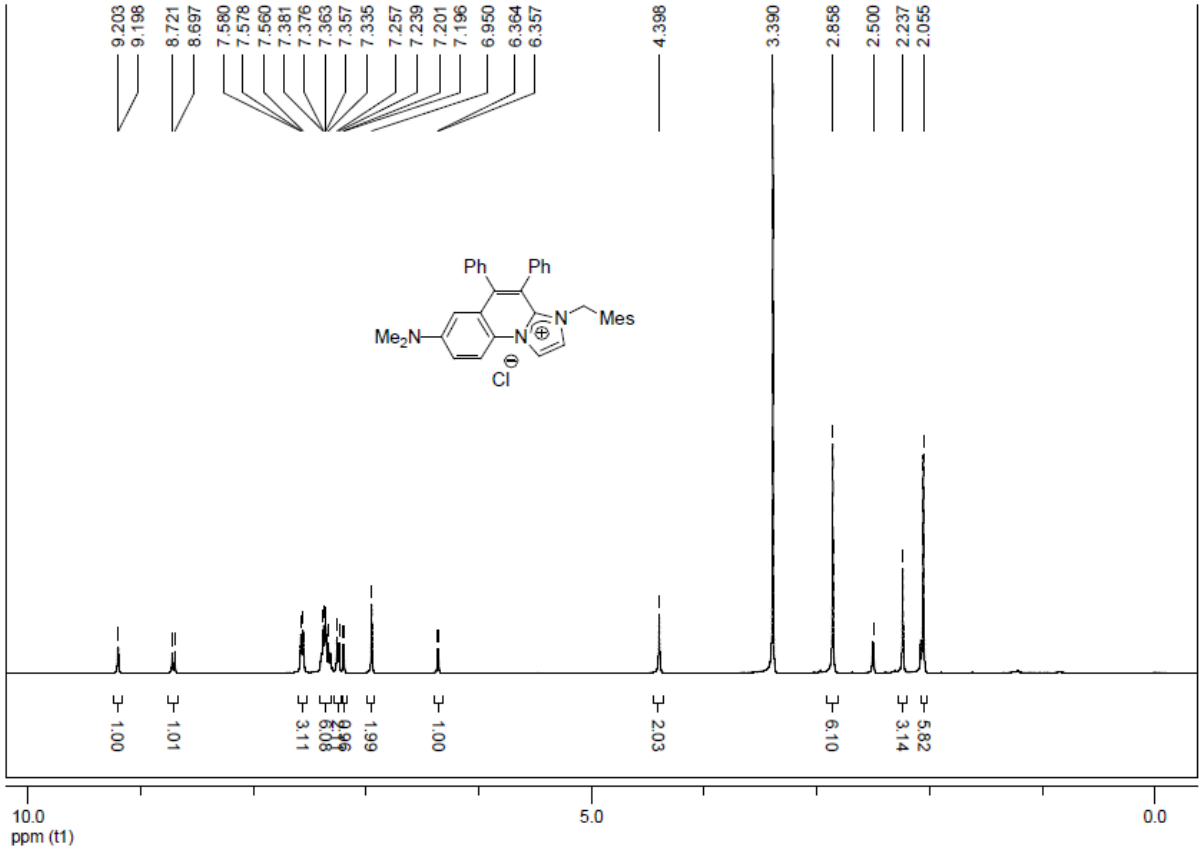
^{1}H NMR spectrum of 3fa



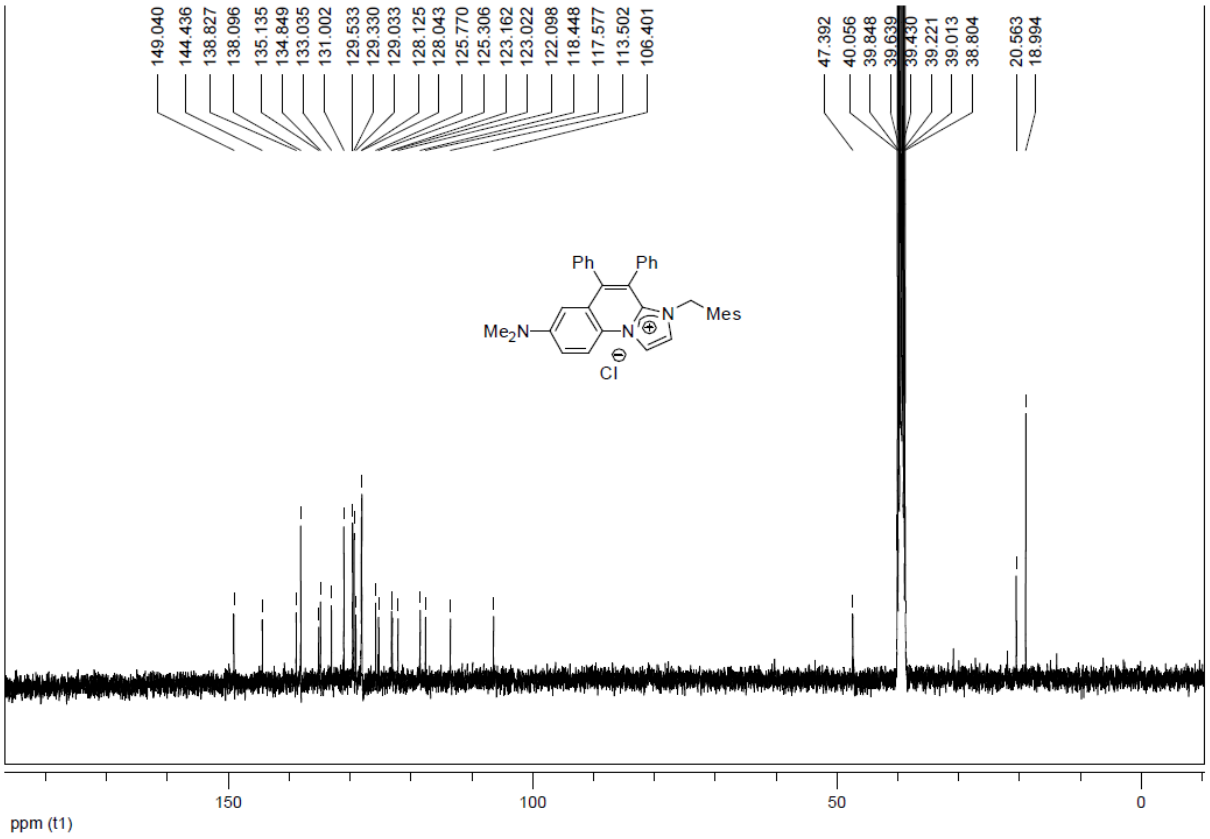
^{13}C NMR spectrum of 3fa



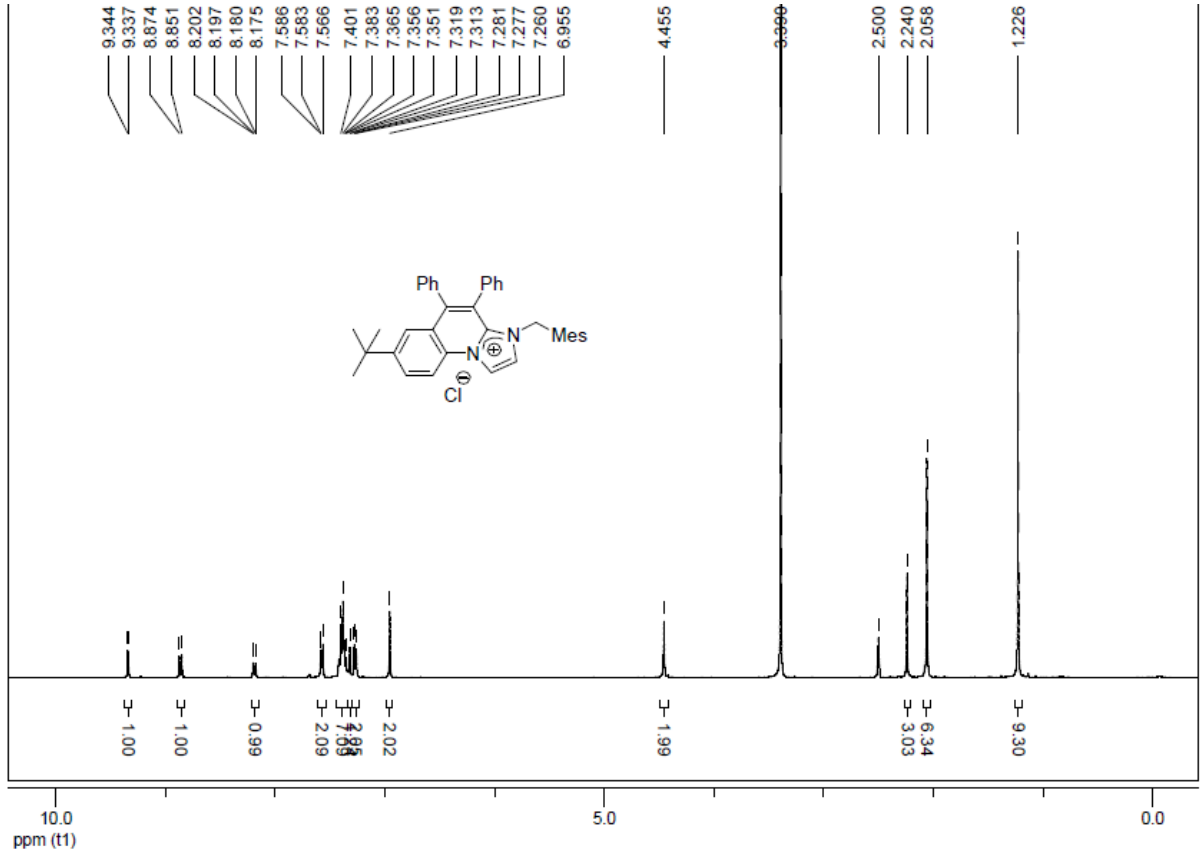
^{1}H NMR spectrum of 3ga



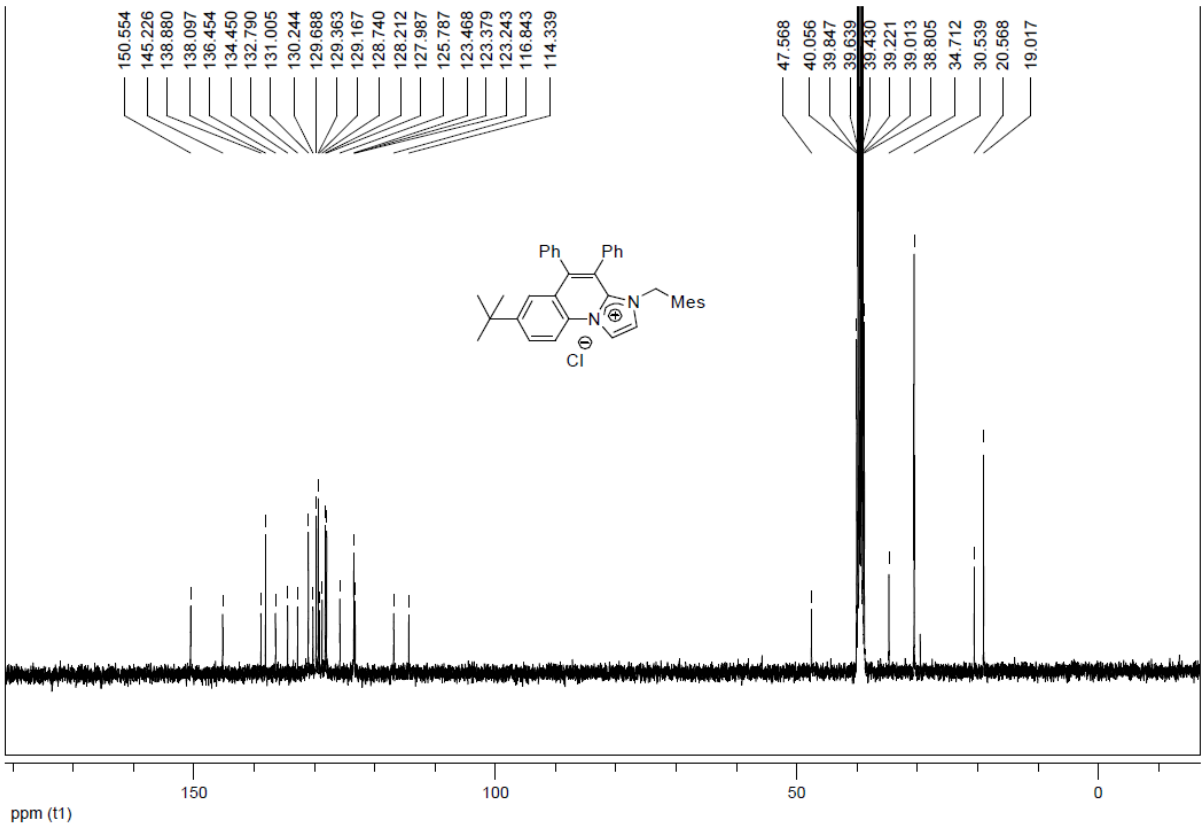
^{13}C NMR spectrum of 3ga



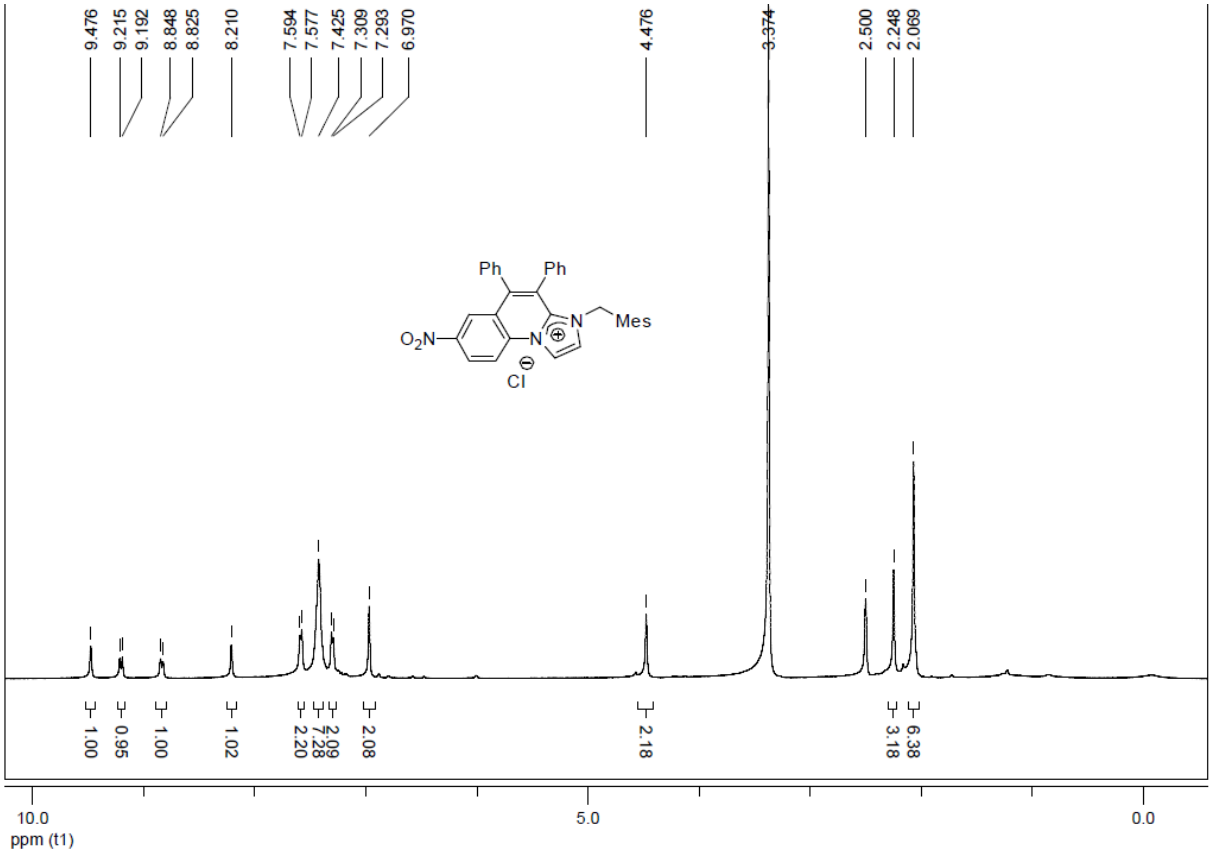
^{1}H NMR spectrum of 3ha



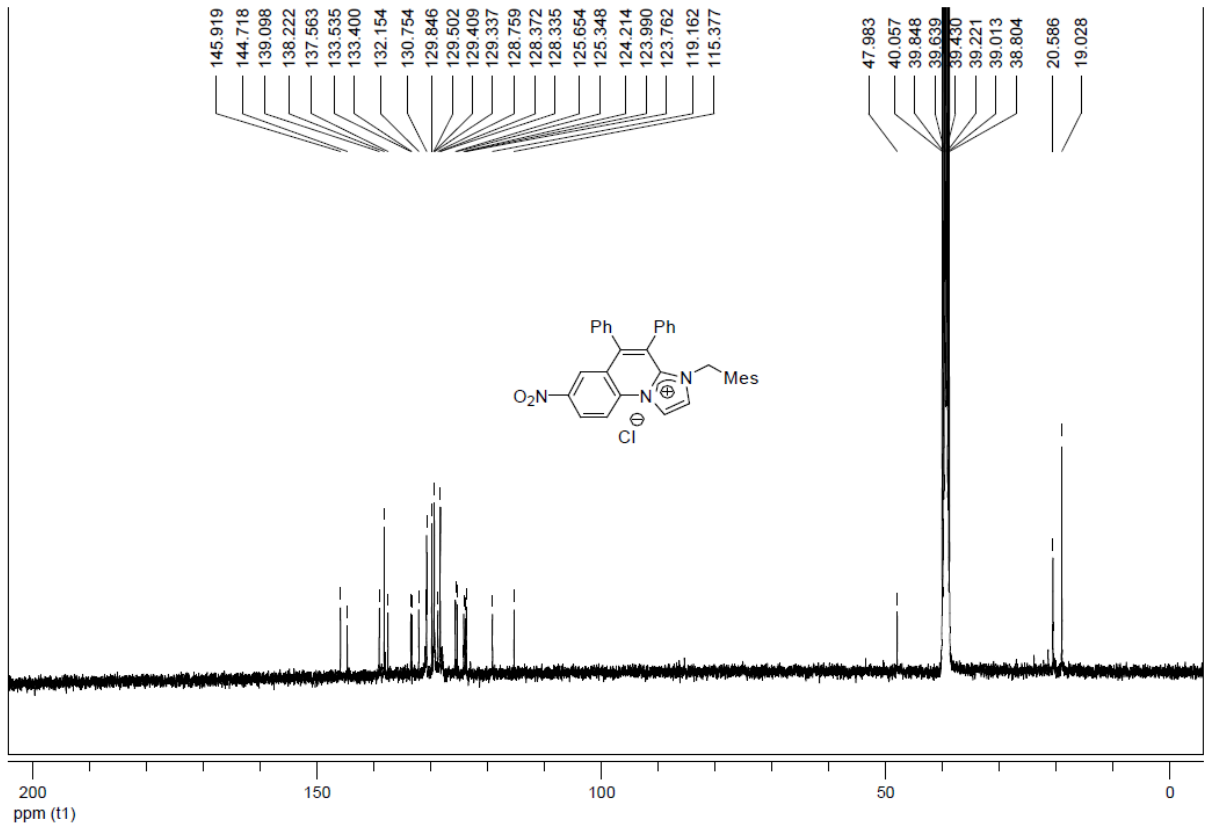
^{13}C NMR spectrum of 3ha



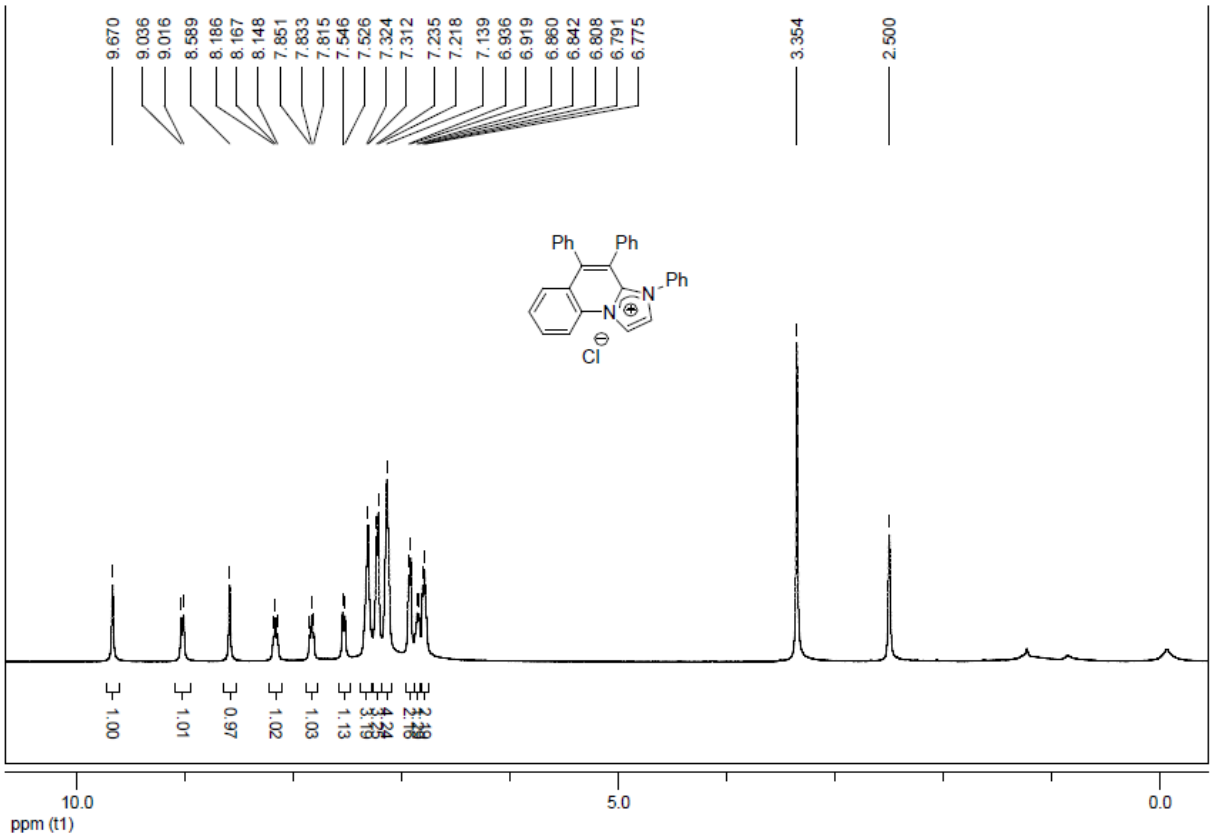
^{1}H NMR spectrum of 3ia



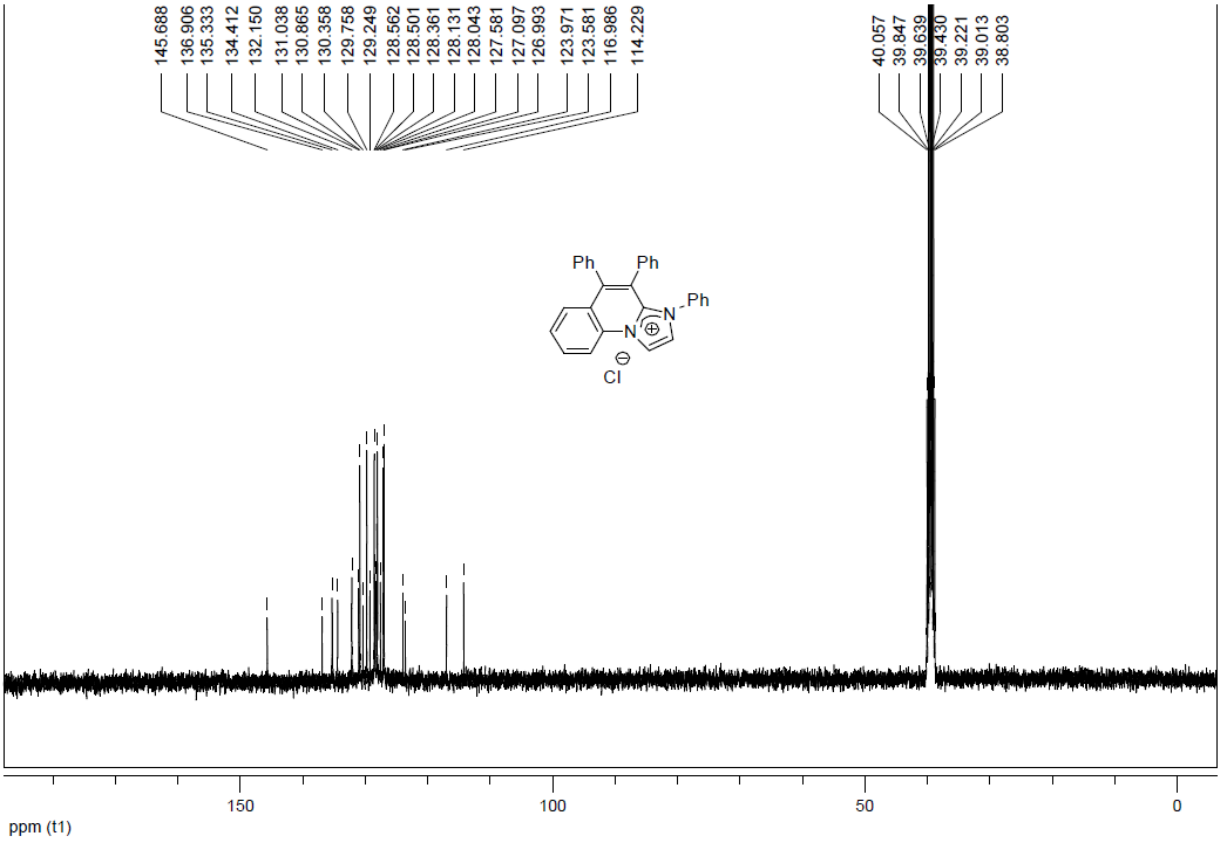
^{13}C NMR spectrum of 3ia



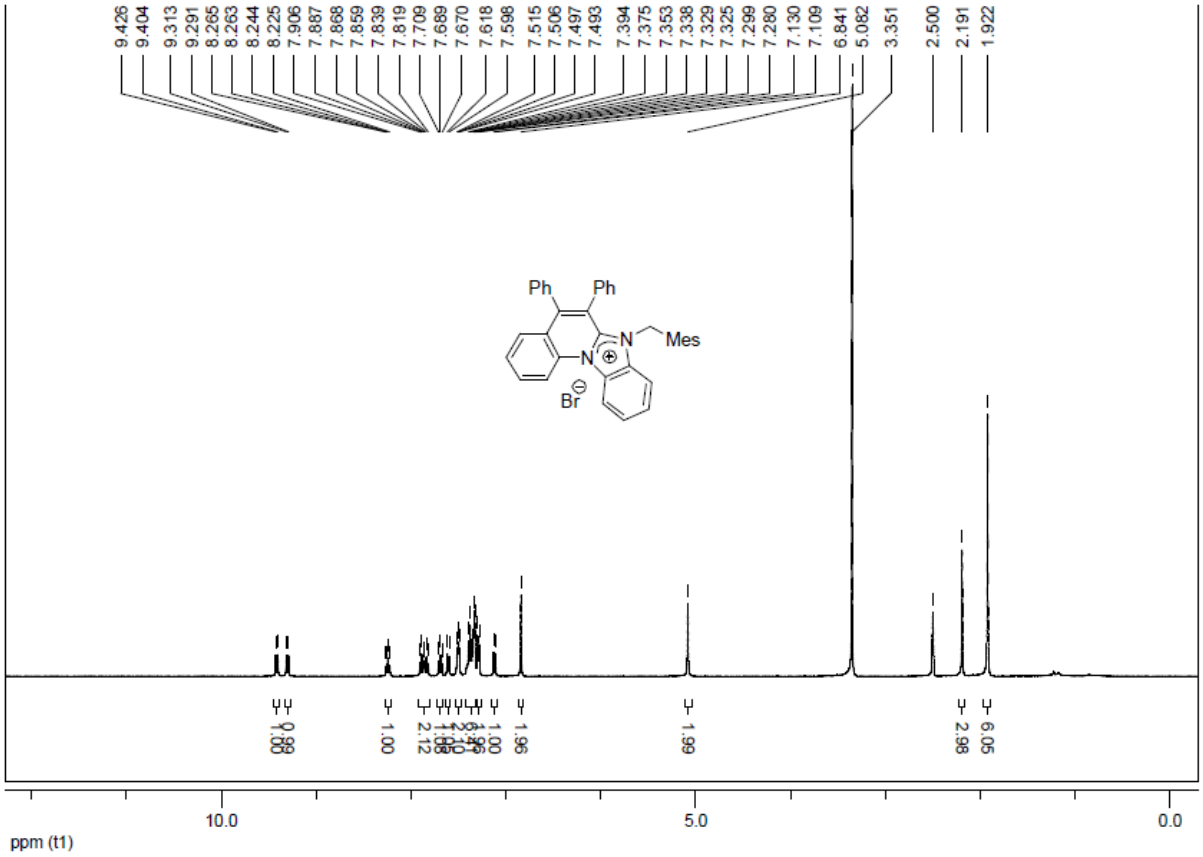
^{1}H NMR spectrum of 3ja



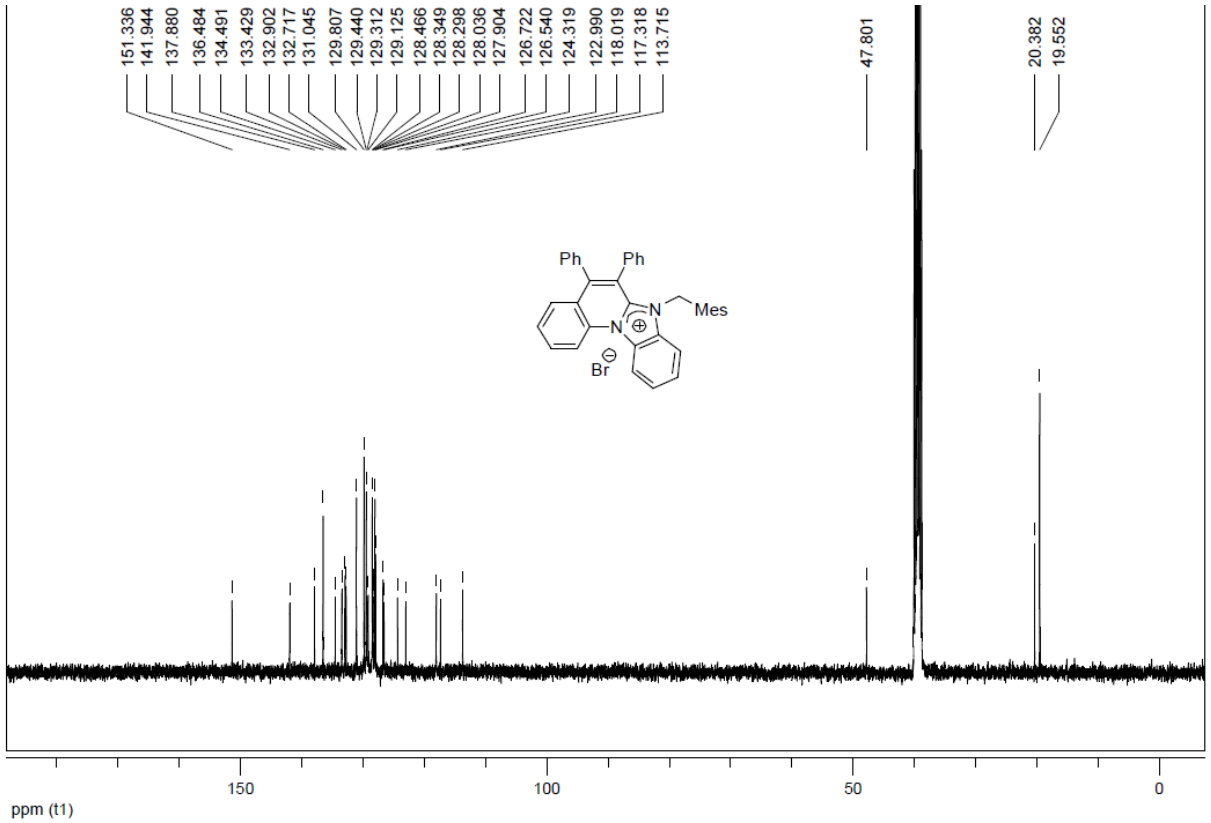
^{13}C NMR spectrum of 3ja



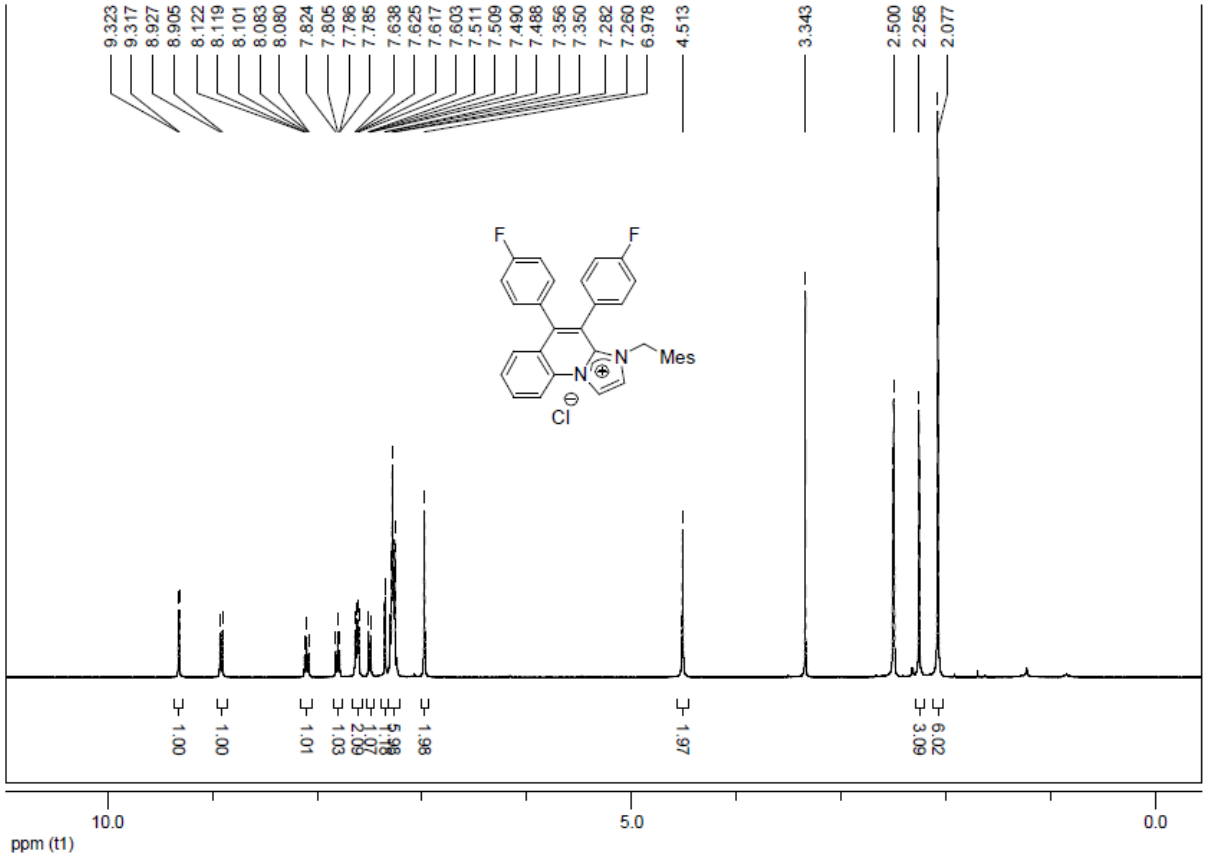
^{1}H NMR spectrum of 3ka



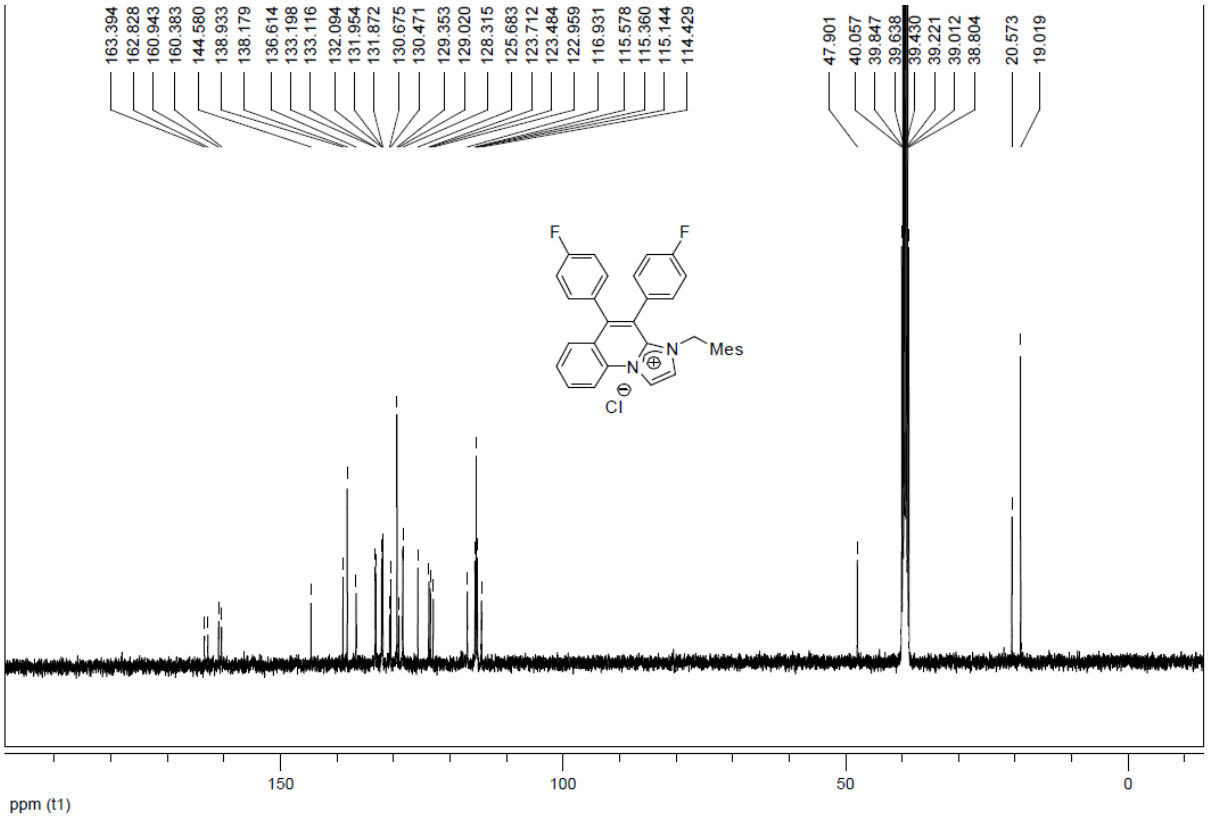
^{13}C NMR spectrum of 3ka



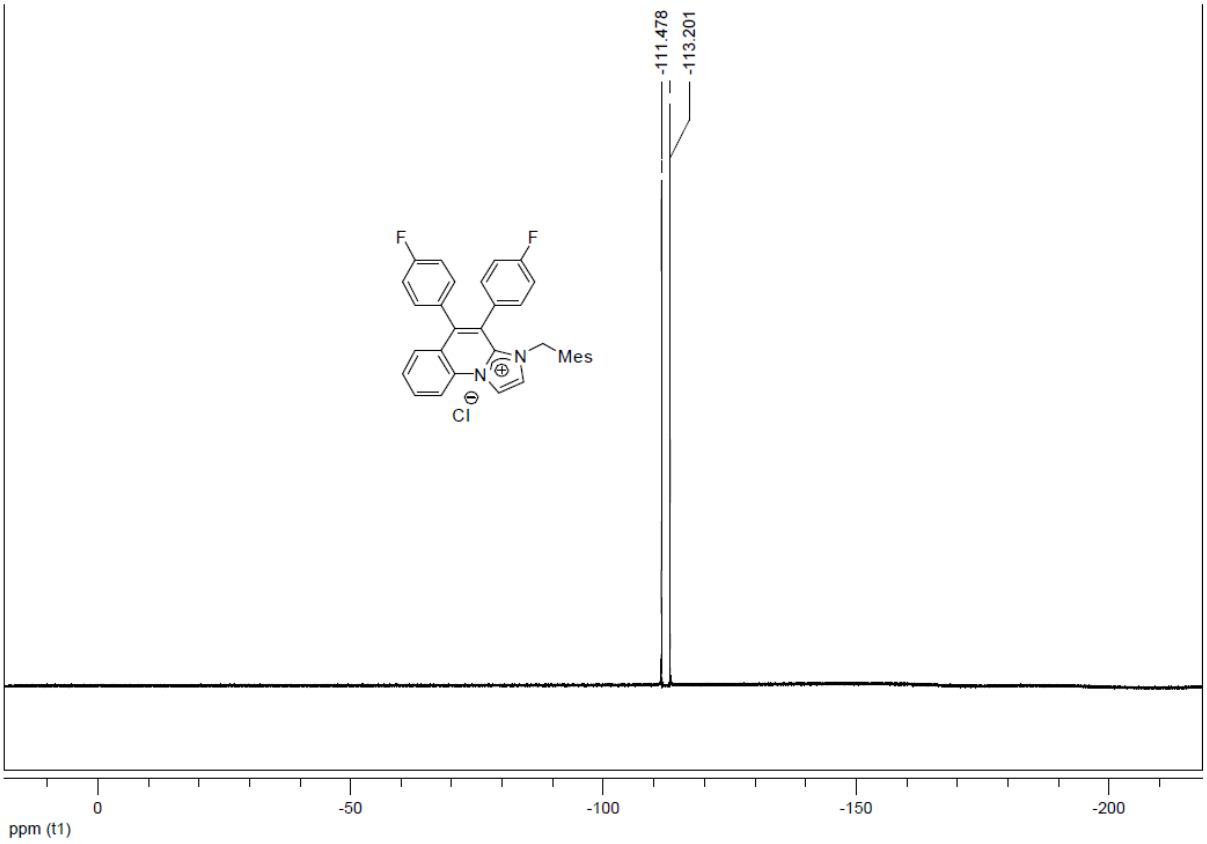
^{1}H NMR spectrum of 3ab



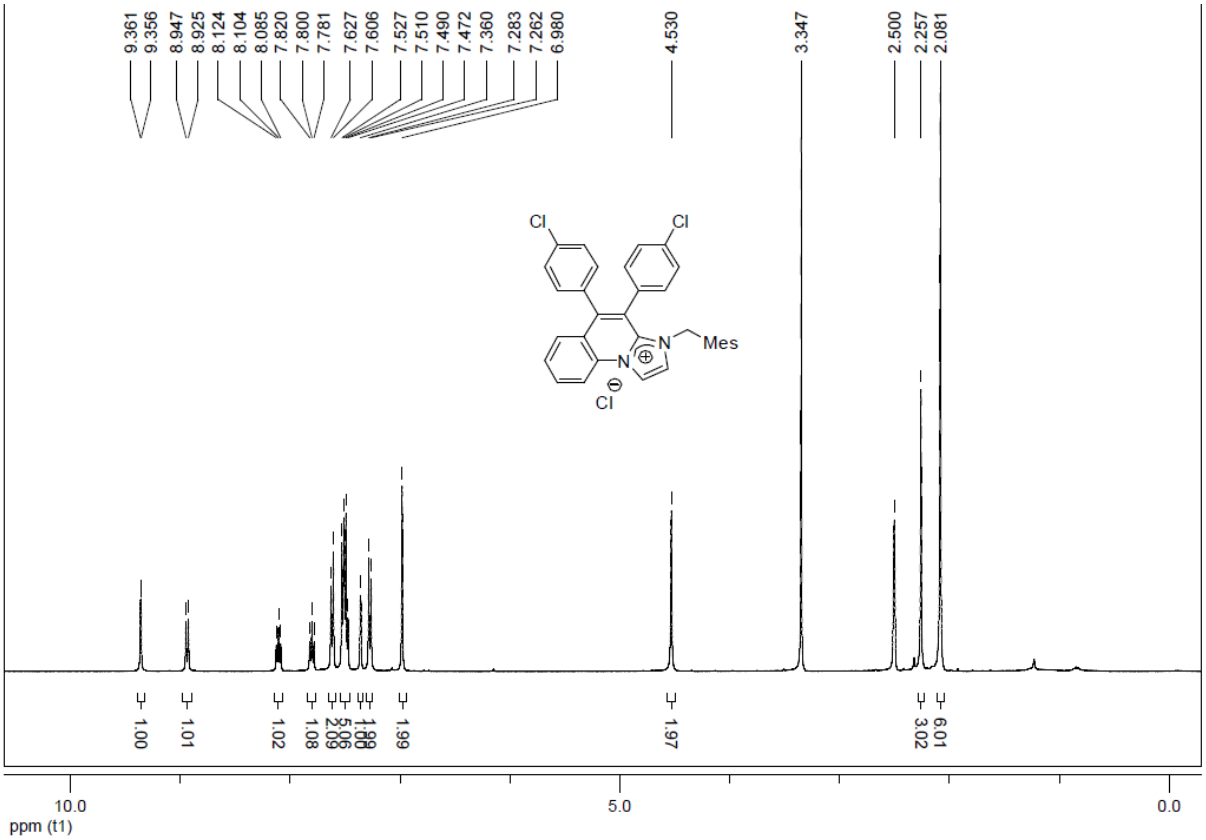
^{13}C NMR spectrum of 3ab



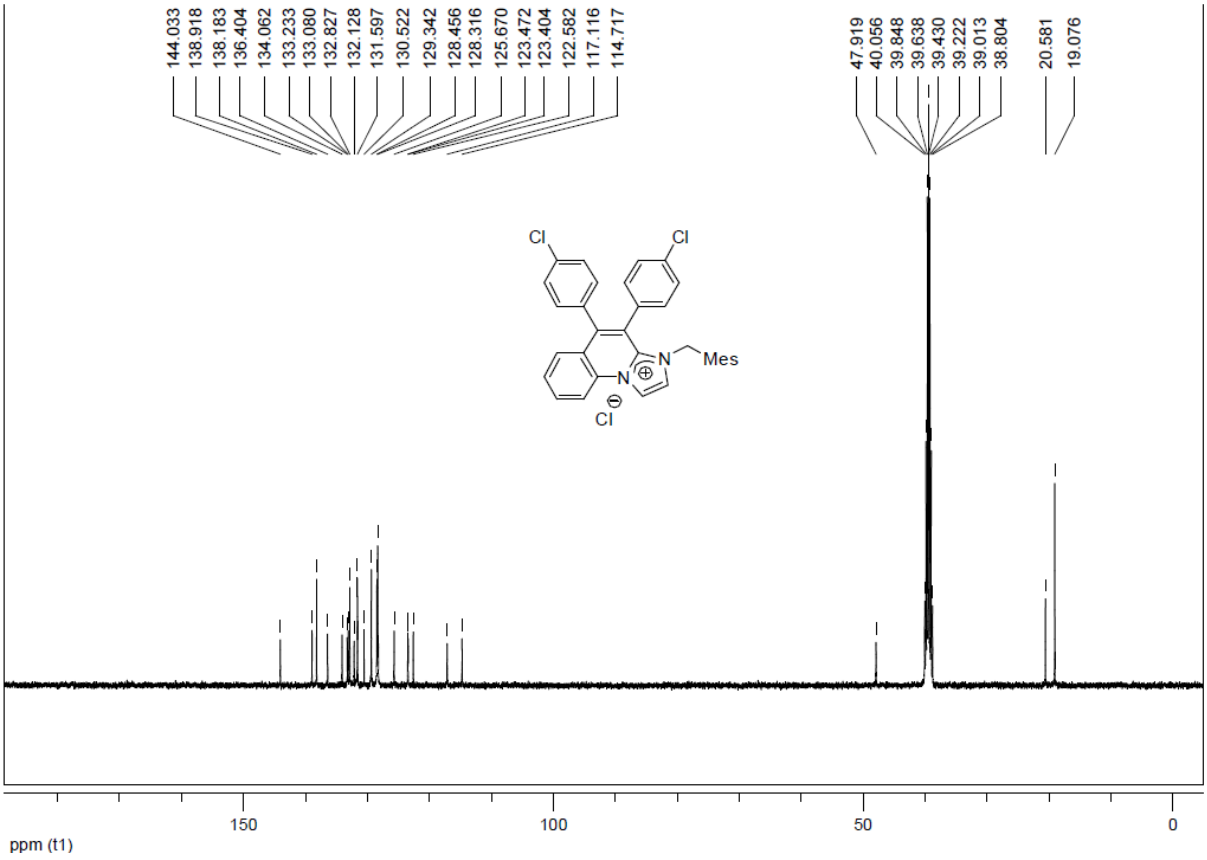
^{19}F NMR spectrum of 3ab



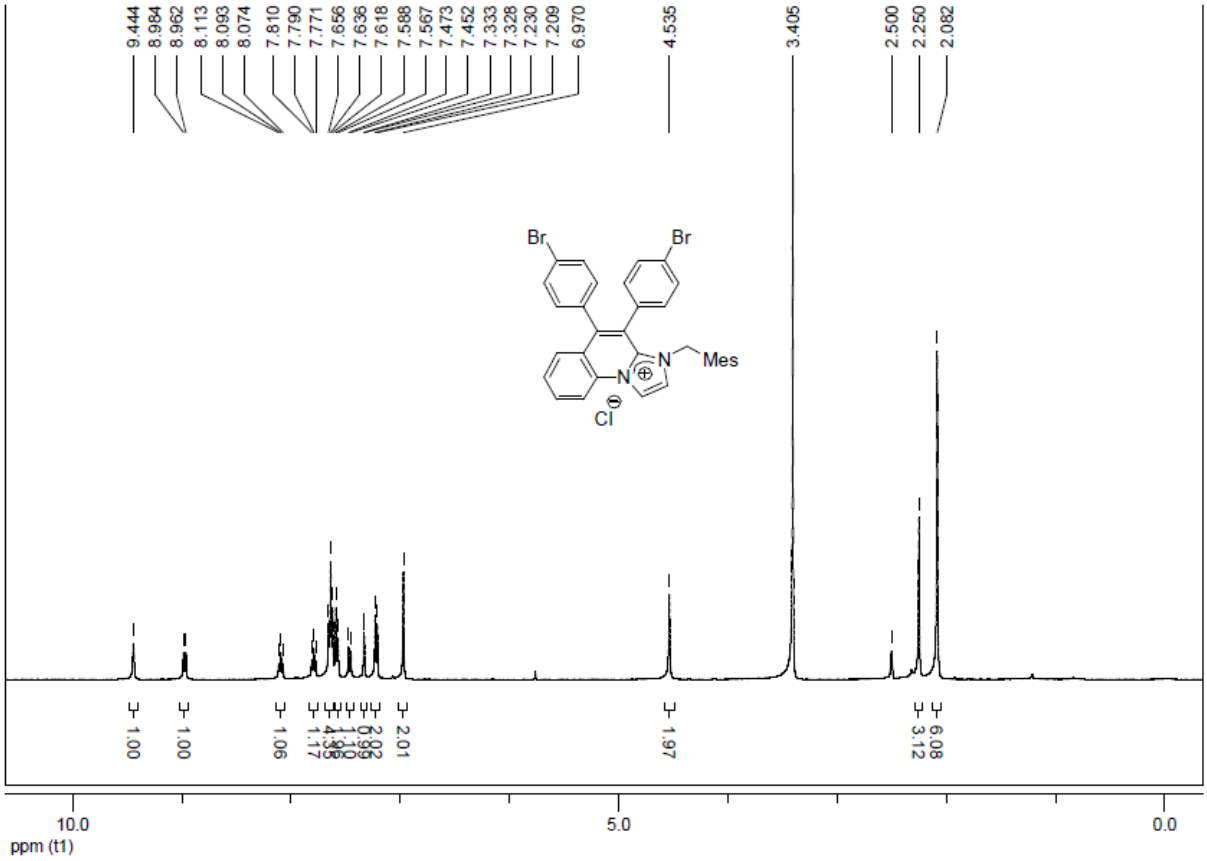
^{1}H NMR spectrum of 3ac



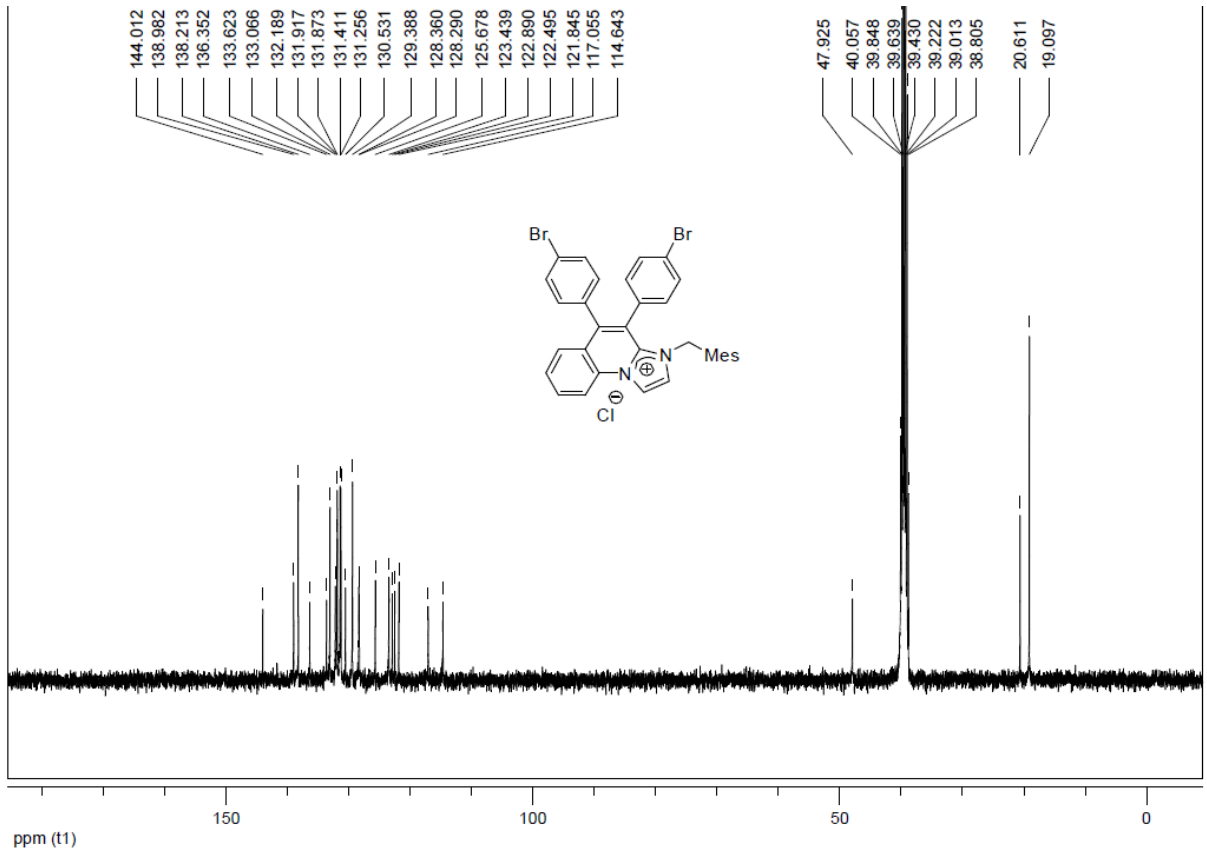
^{13}C NMR spectrum of 3ac



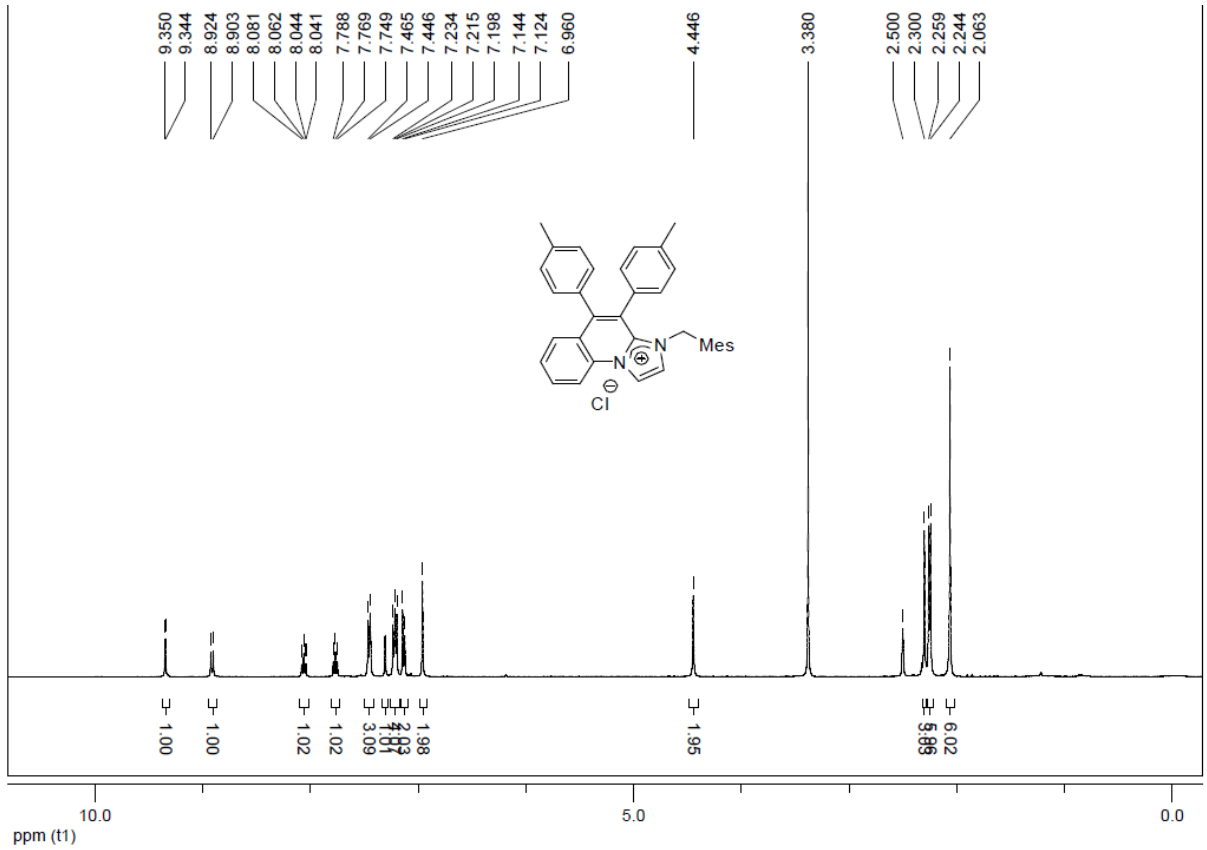
^{1}H NMR spectrum of 3ad



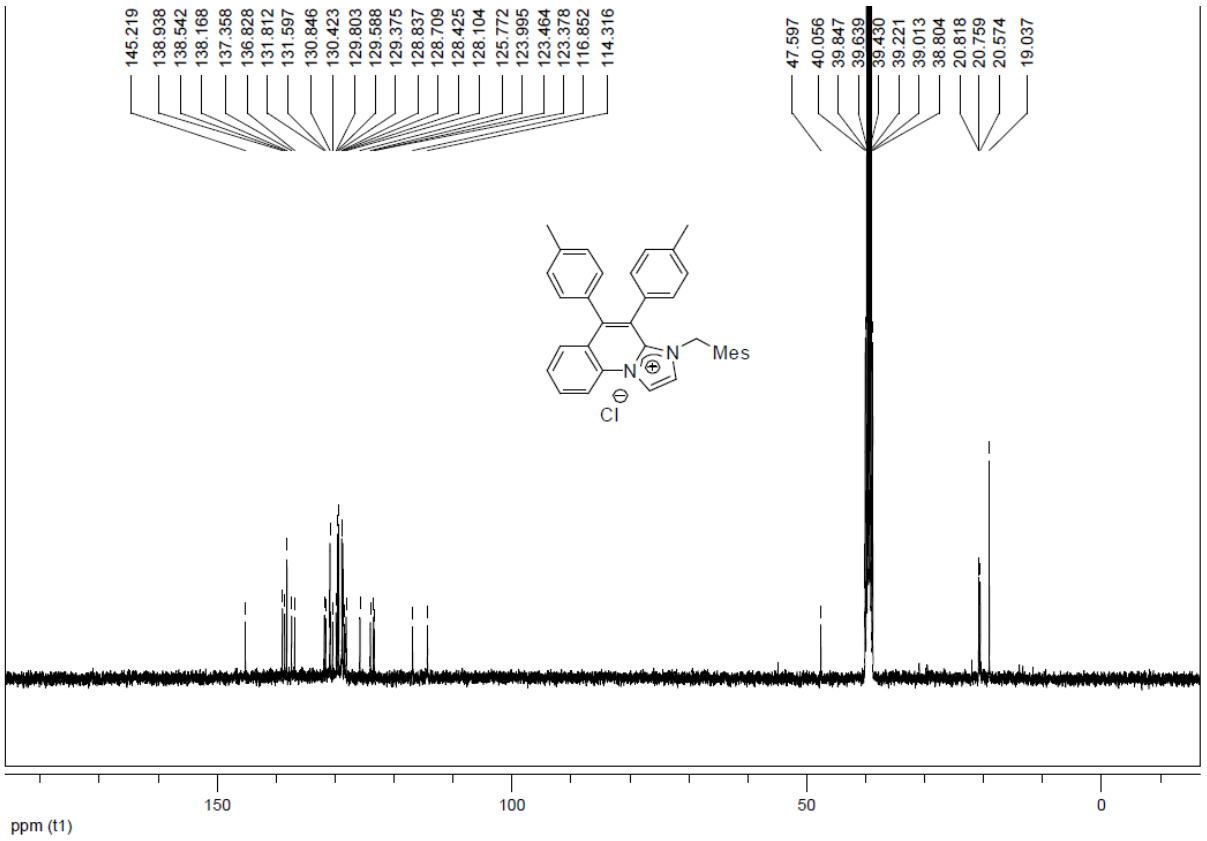
^{13}C NMR spectrum of 3ad



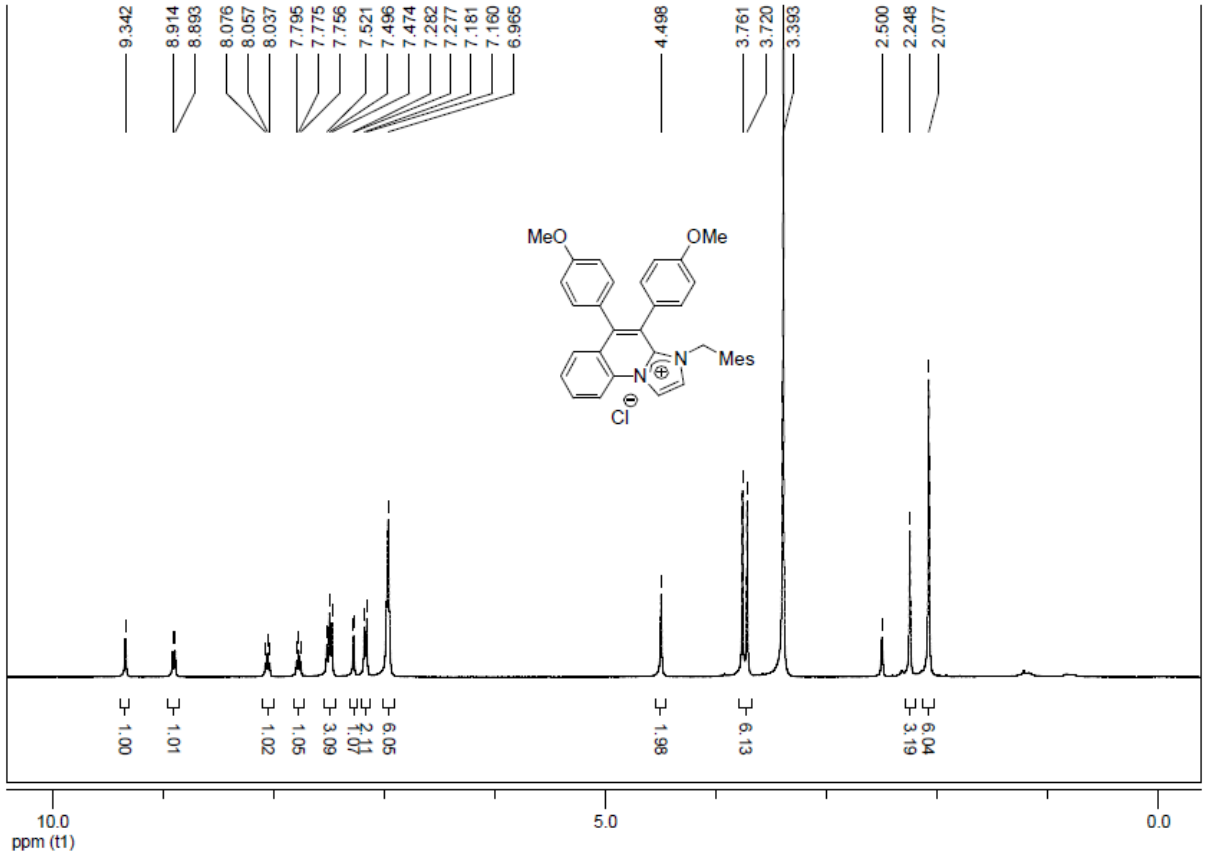
^{1}H NMR spectrum of 3ae



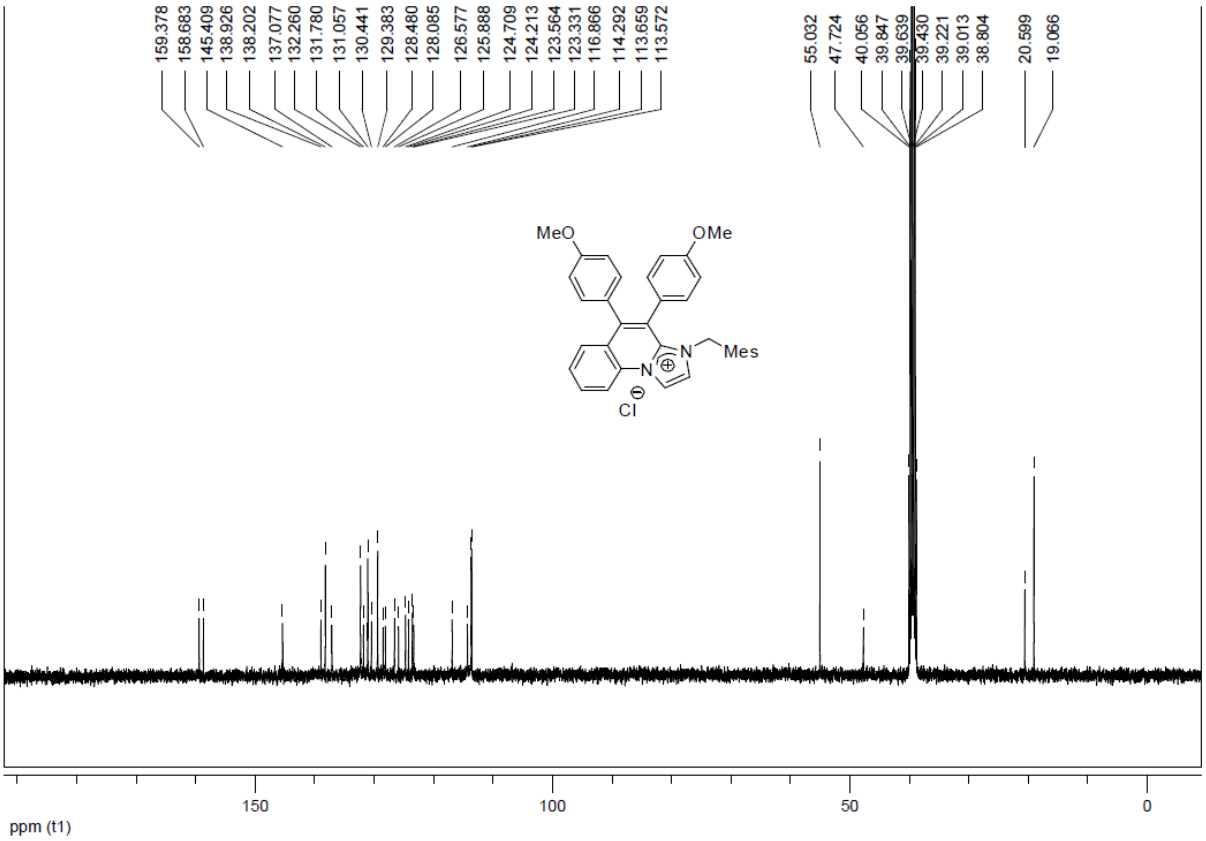
^{13}C NMR spectrum of 3ae



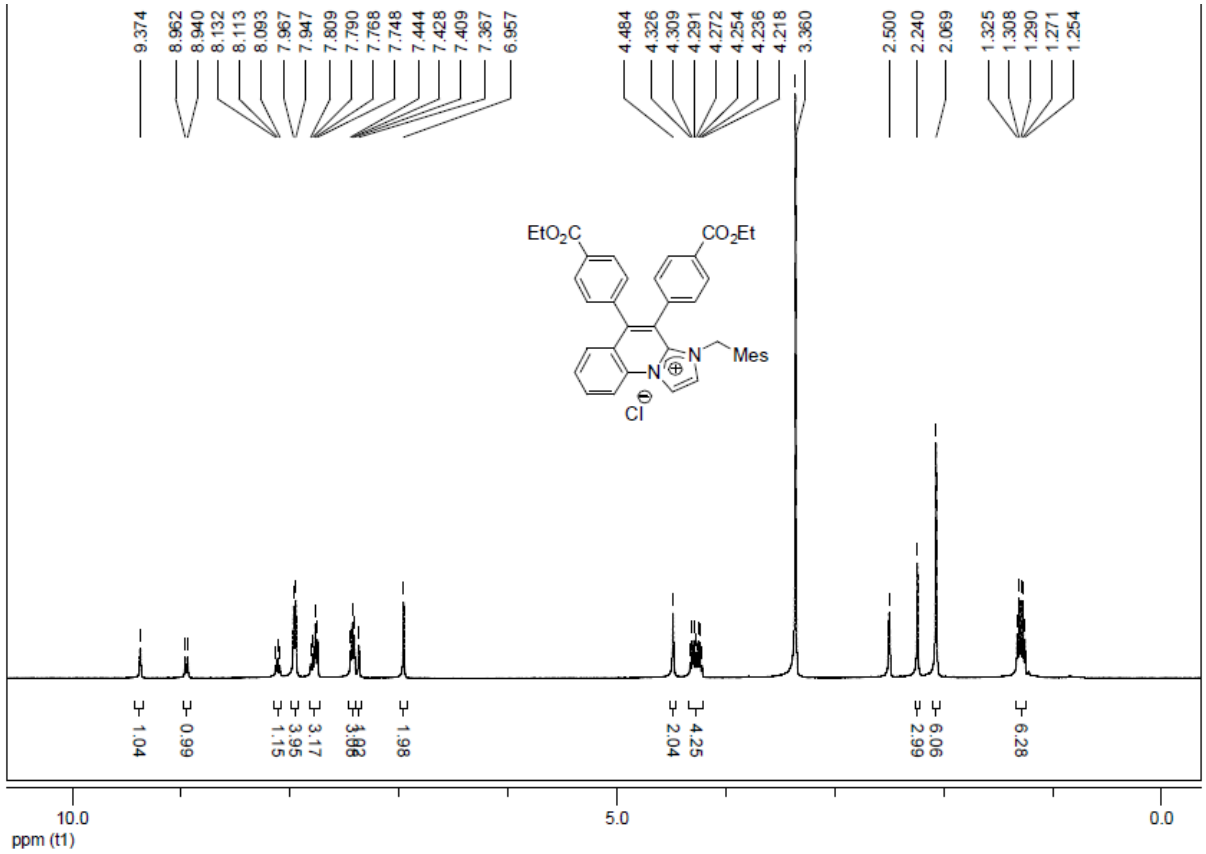
^{1}H NMR spectrum of 3af



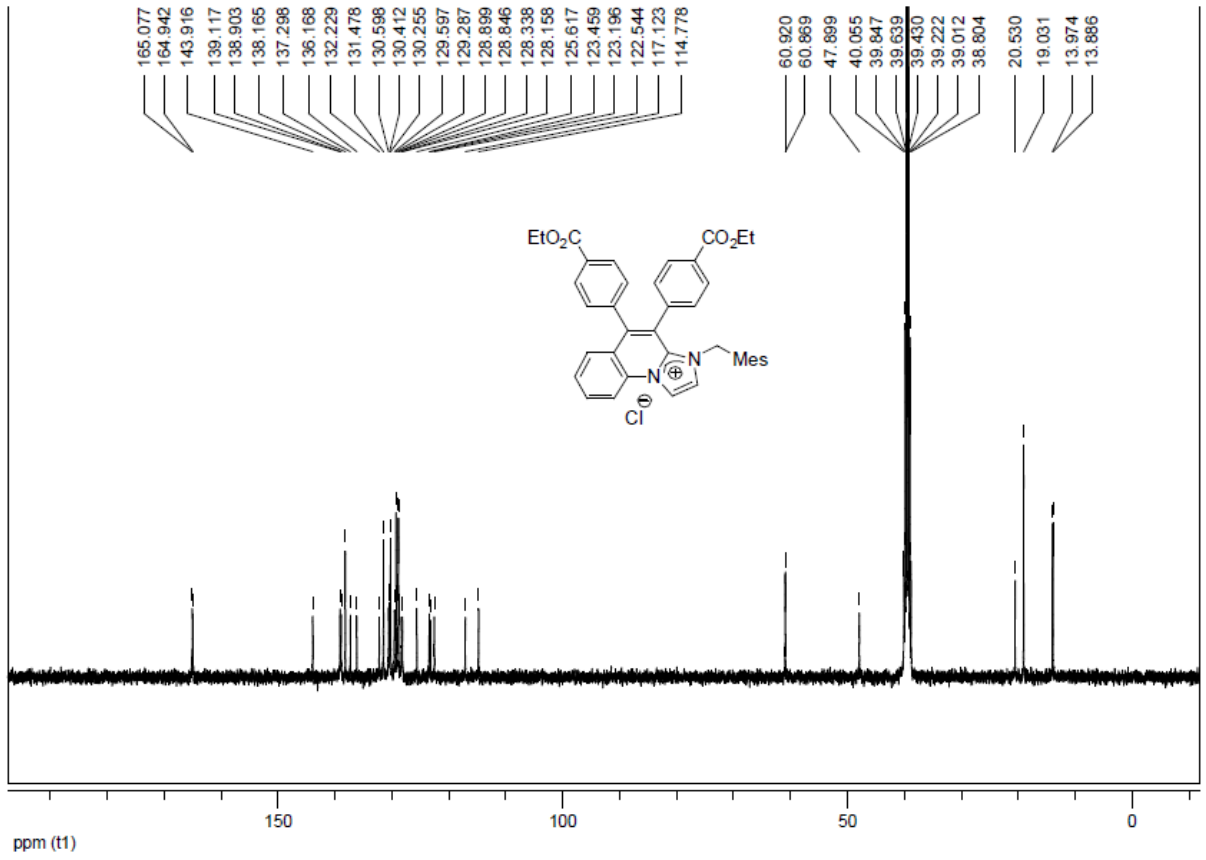
^{13}C NMR spectrum of 3af



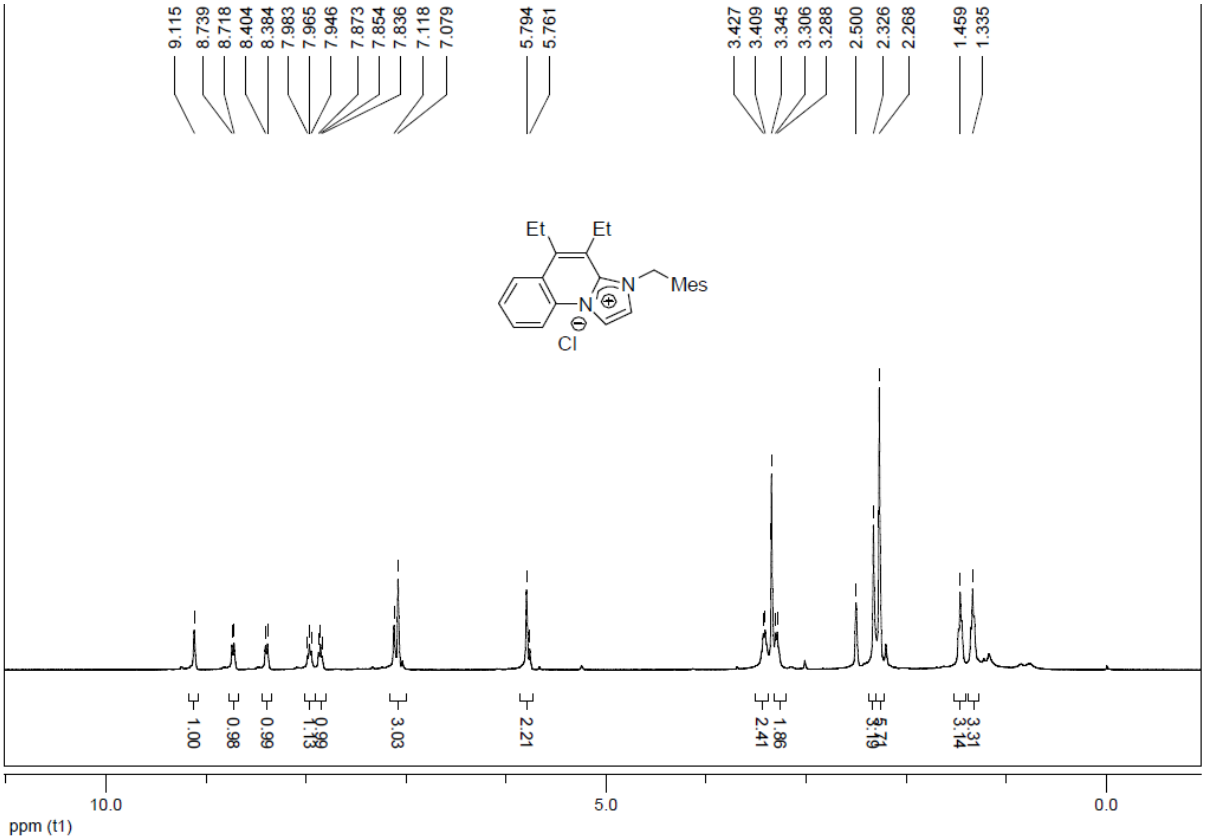
^{1}H NMR spectrum of 3ag



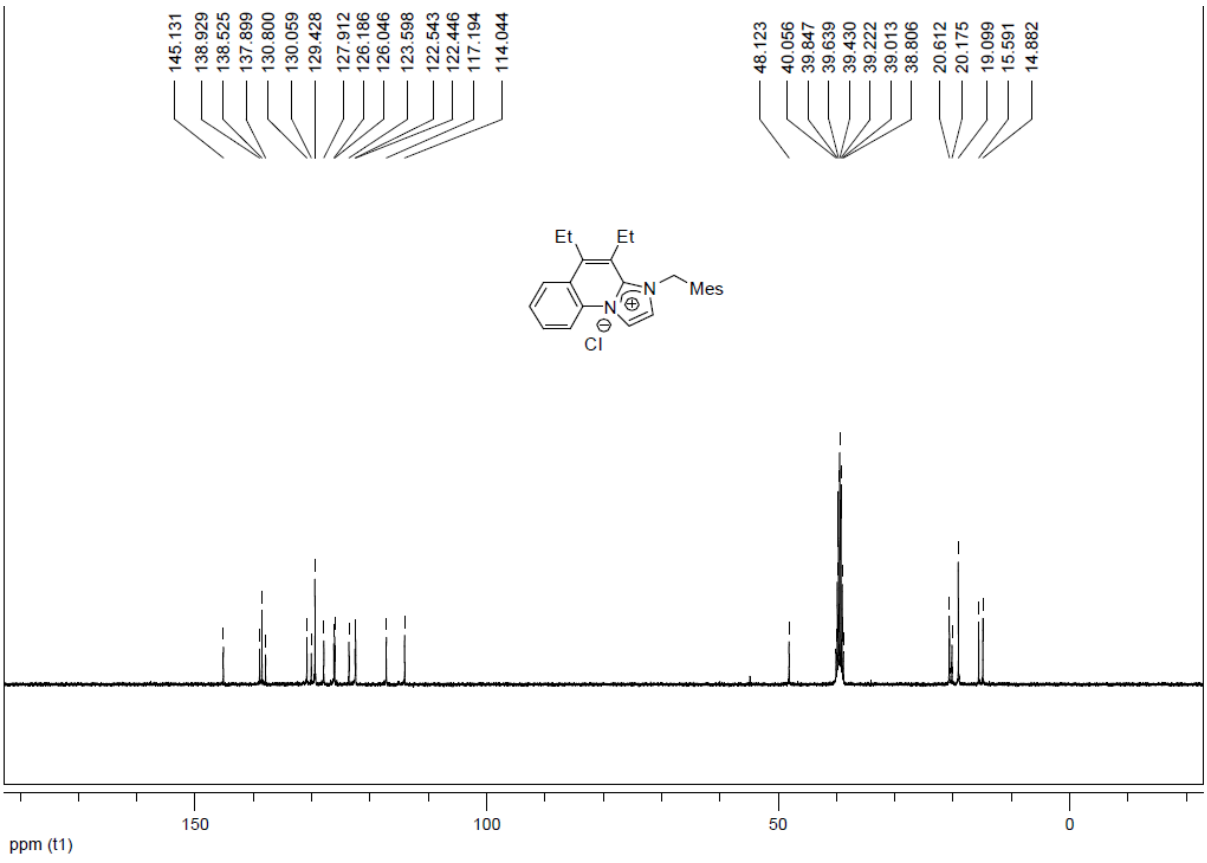
^{13}C NMR spectrum of 3ag



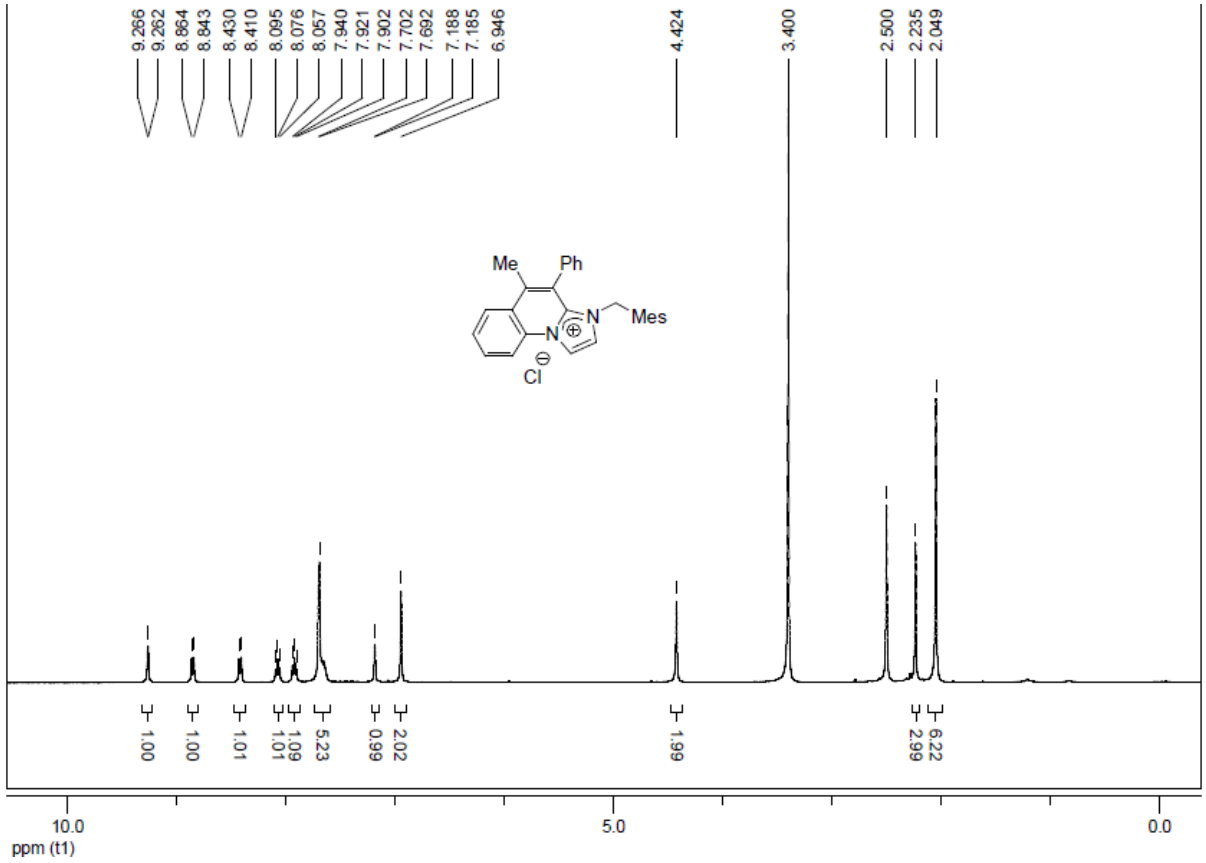
^{1}H NMR spectrum of 3ah



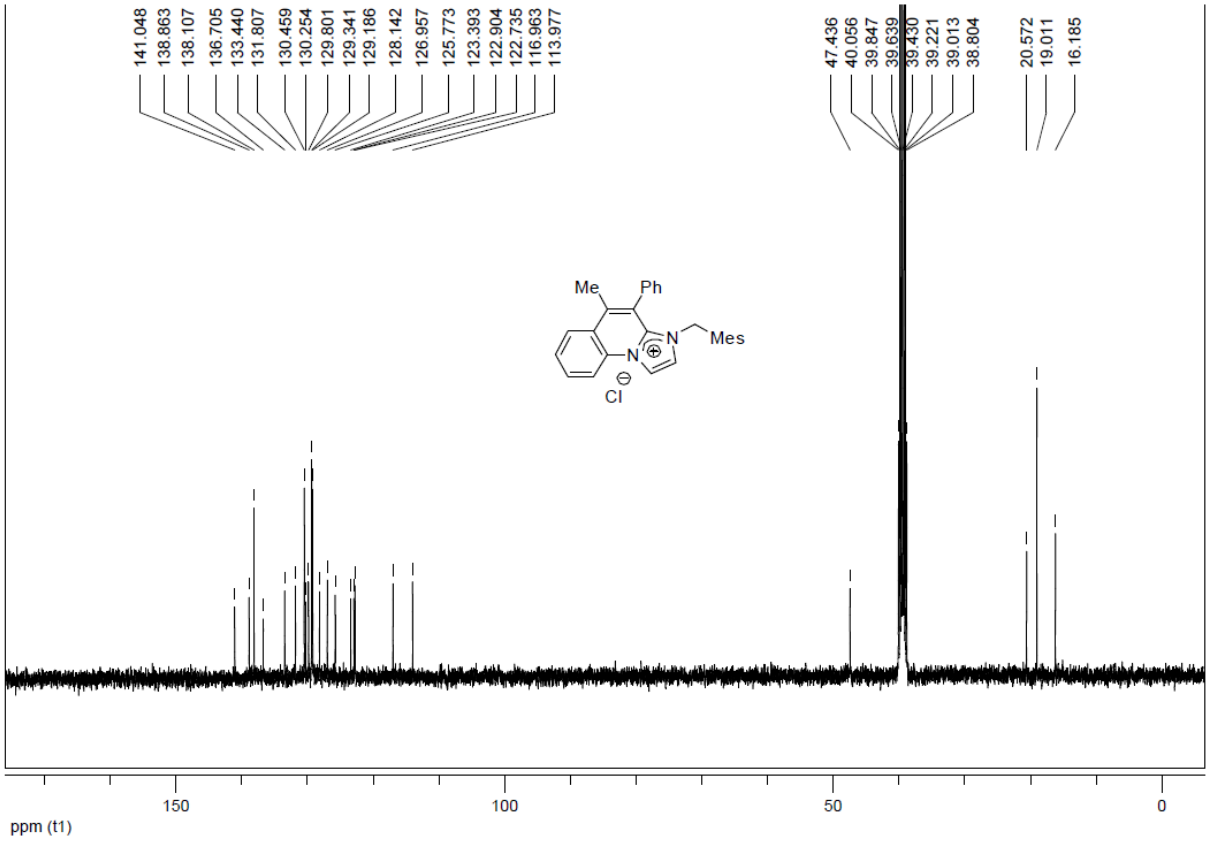
^{13}C NMR spectrum of 3ah



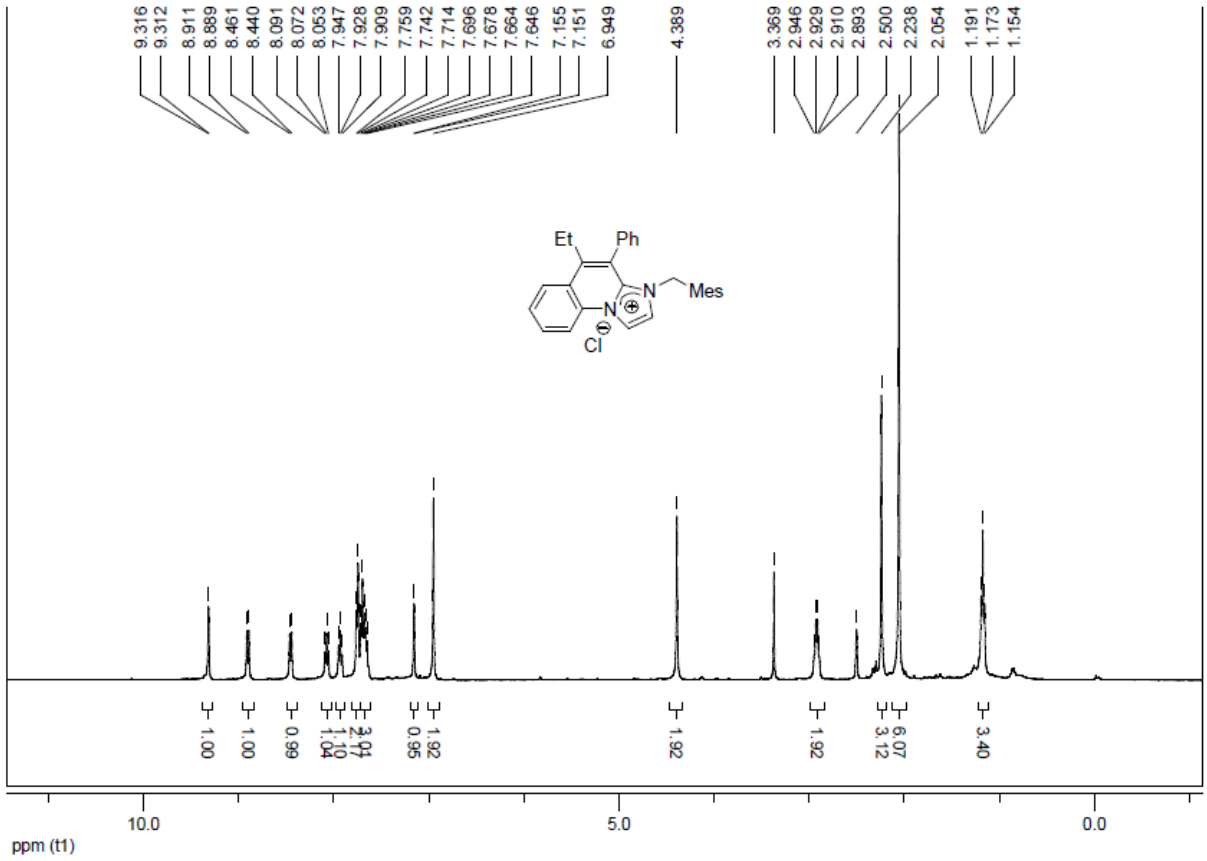
^{1}H NMR spectrum of 3ai



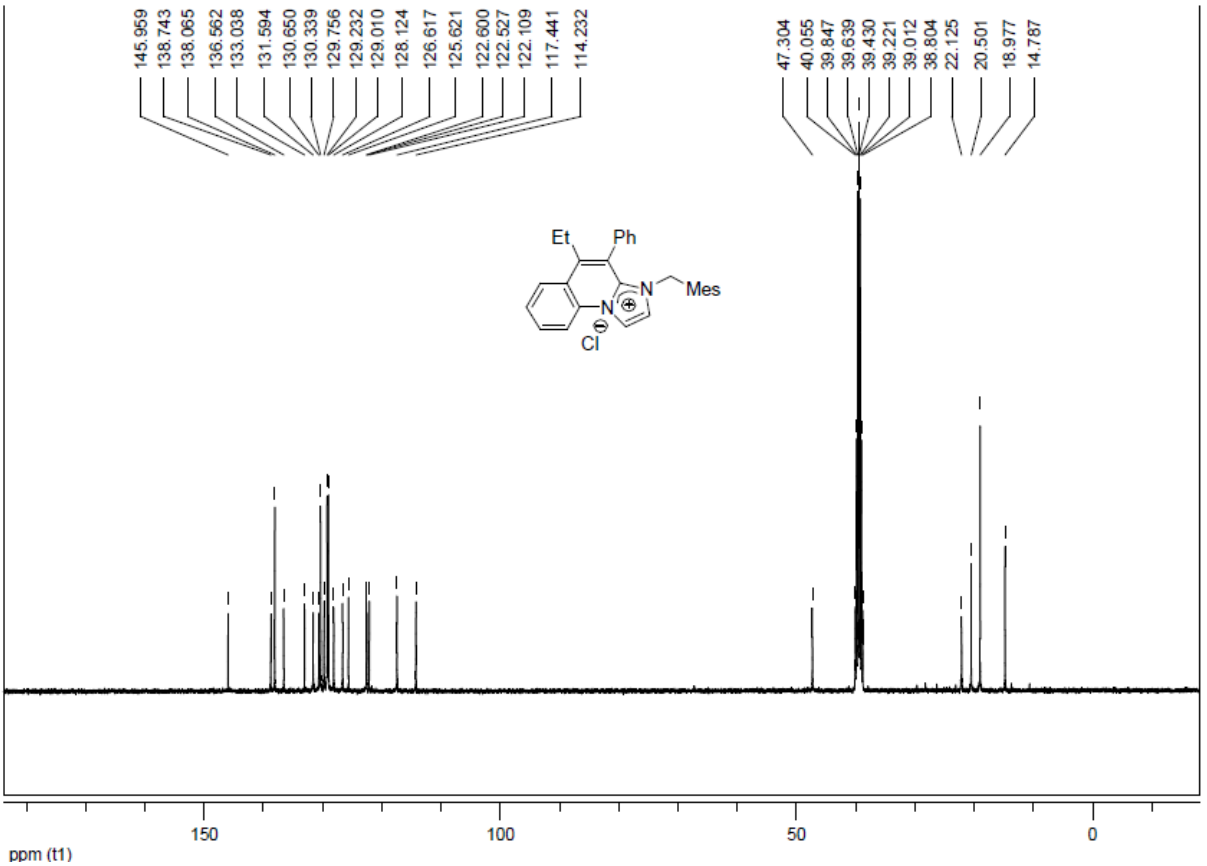
^{13}C NMR spectrum of 3ai



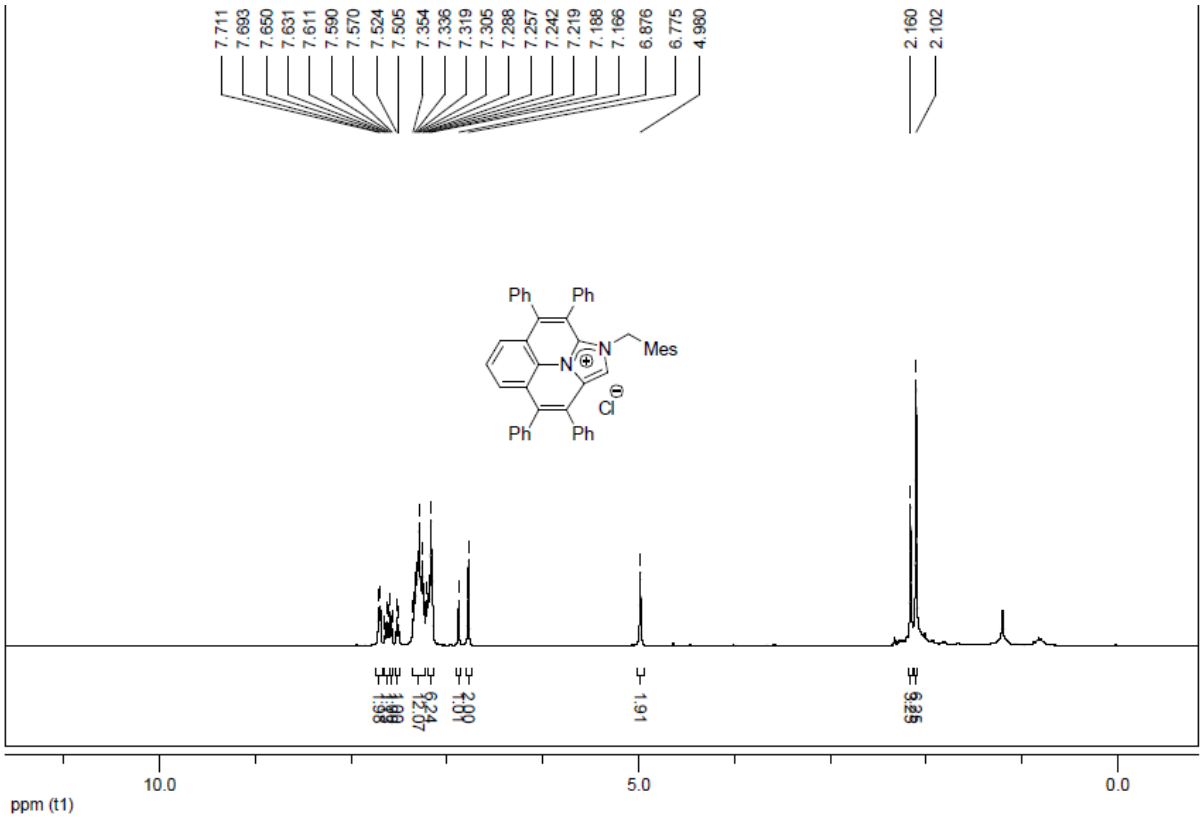
^{1}H NMR spectrum of 3aj



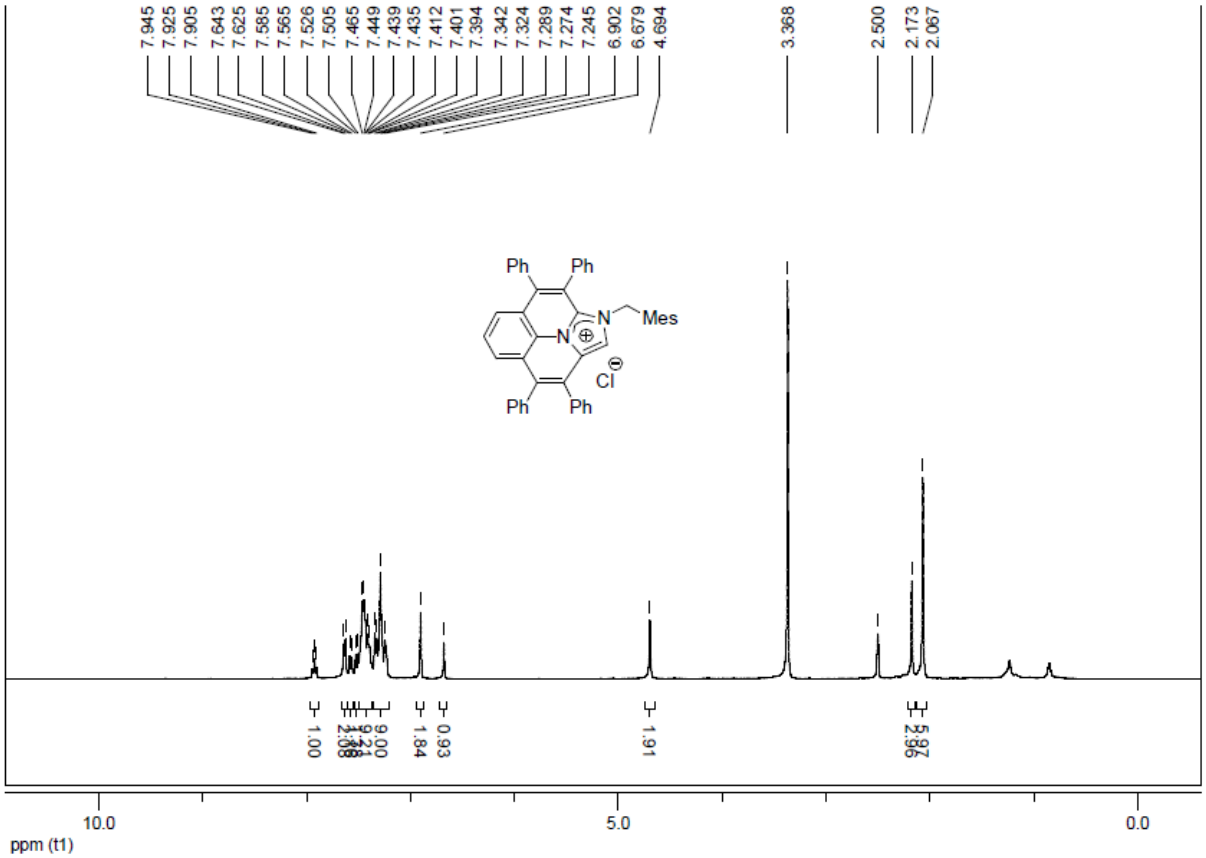
^{13}C NMR spectrum of 3aj



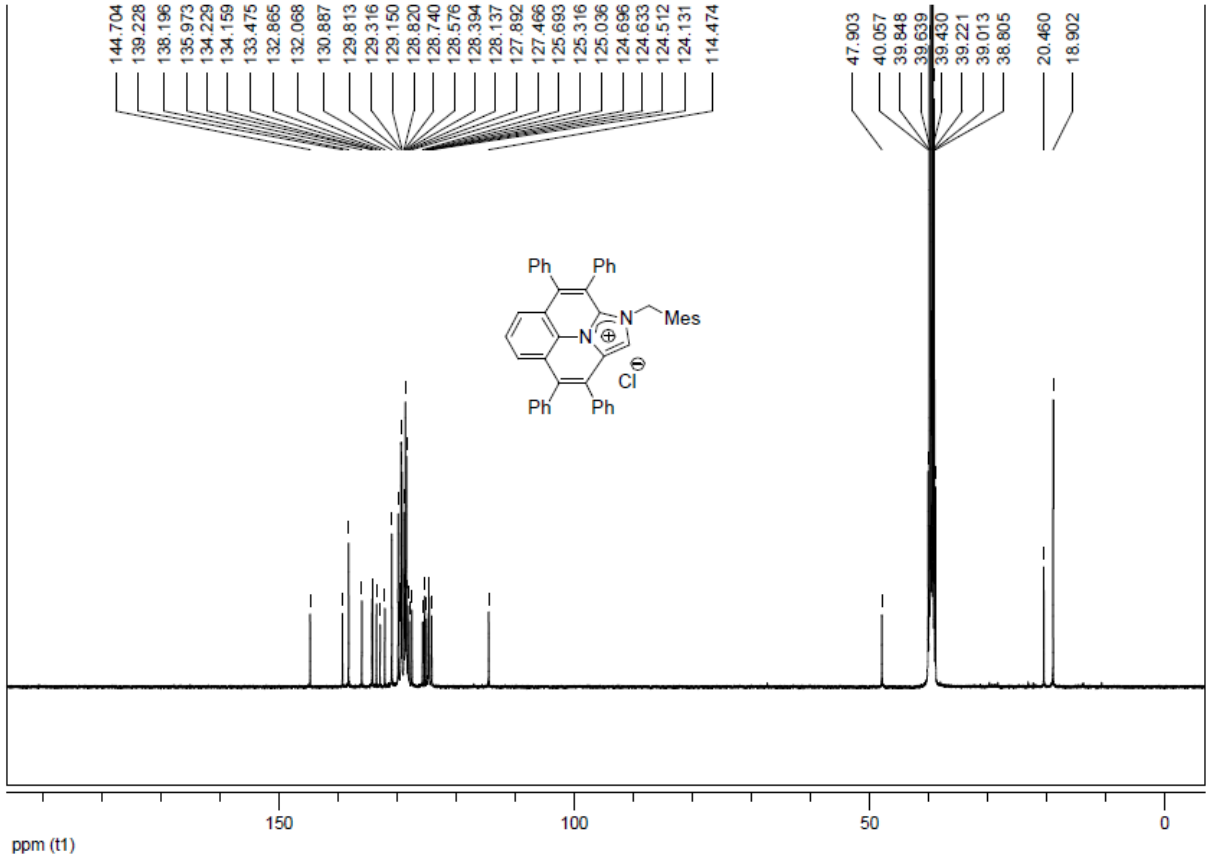
^{1}H NMR spectrum of 4aa (in $CDCl_3$)



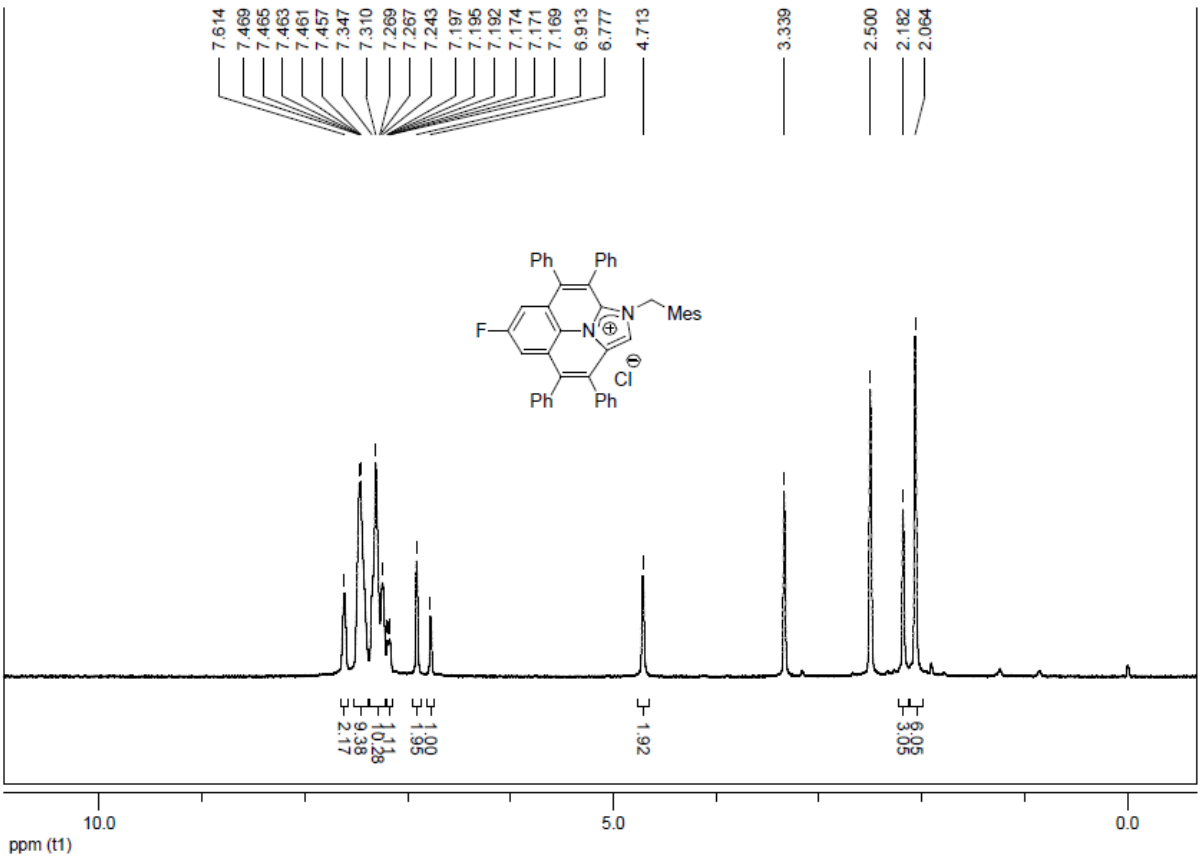
^{1}H NMR spectrum of 4aa (in DMSO-d_6)



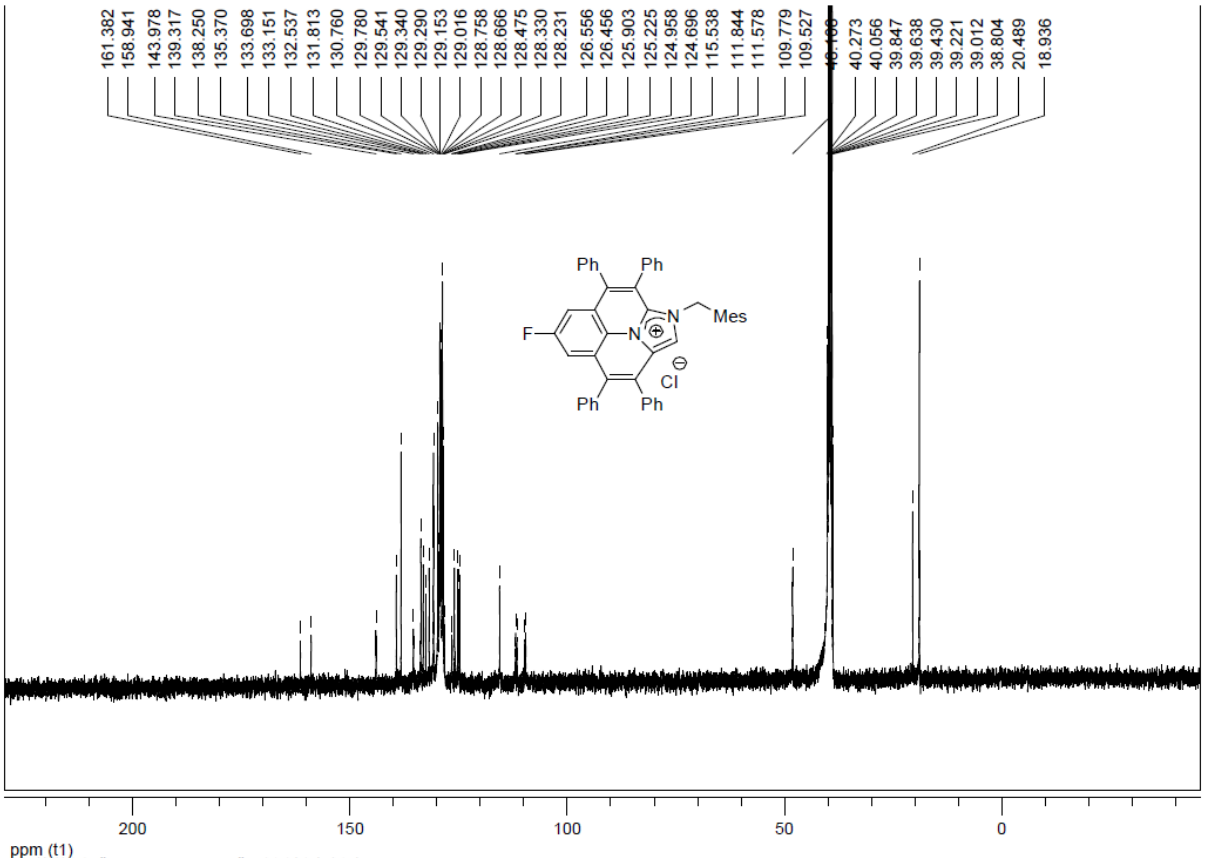
^{13}C NMR spectrum of 4aa



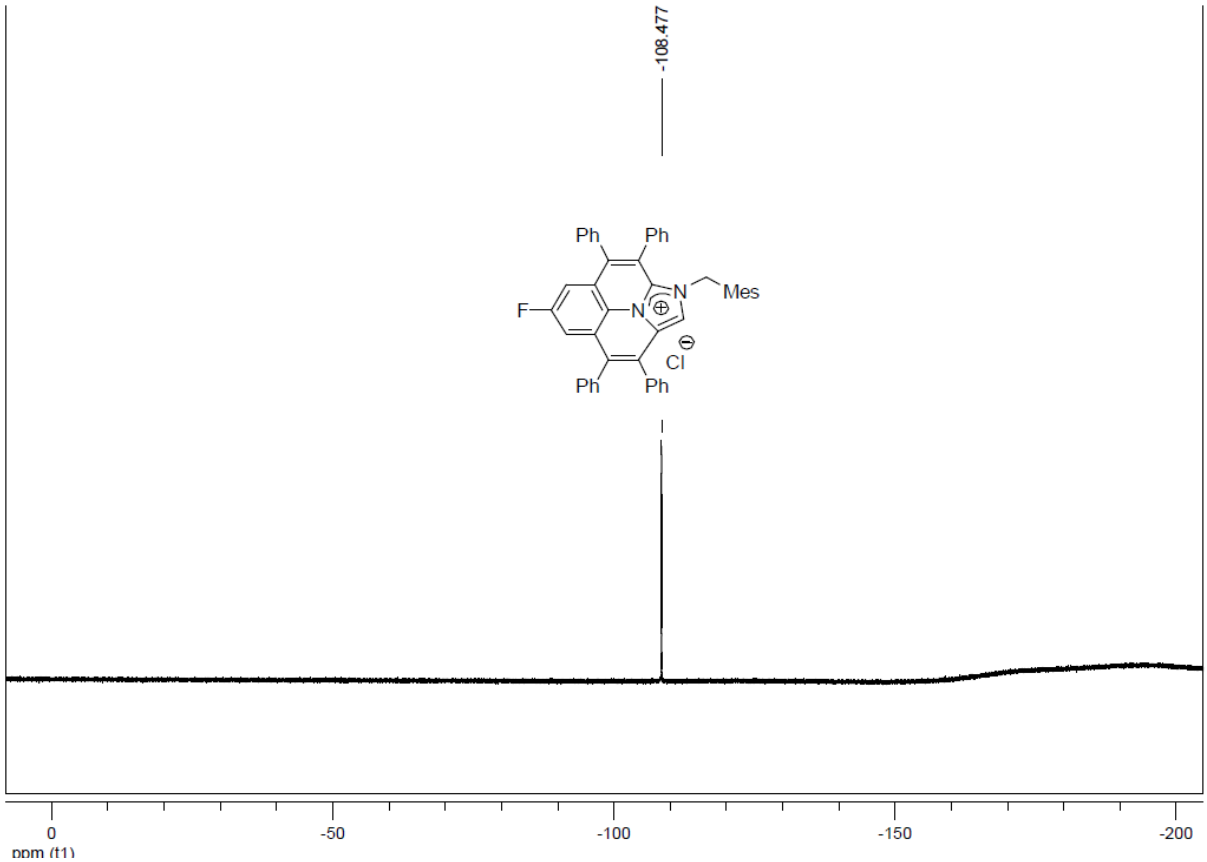
^{1}H NMR spectrum of 4ba



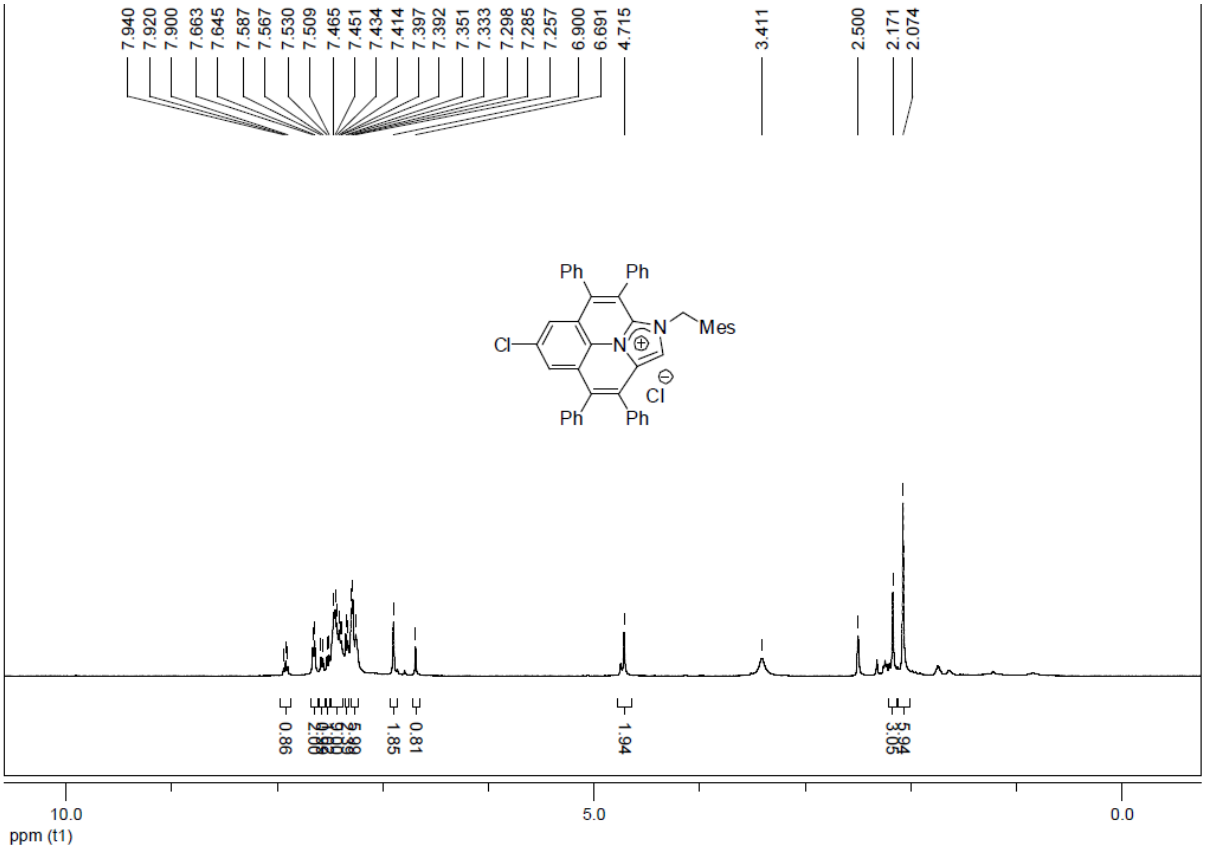
^{13}C NMR spectrum of 4ba



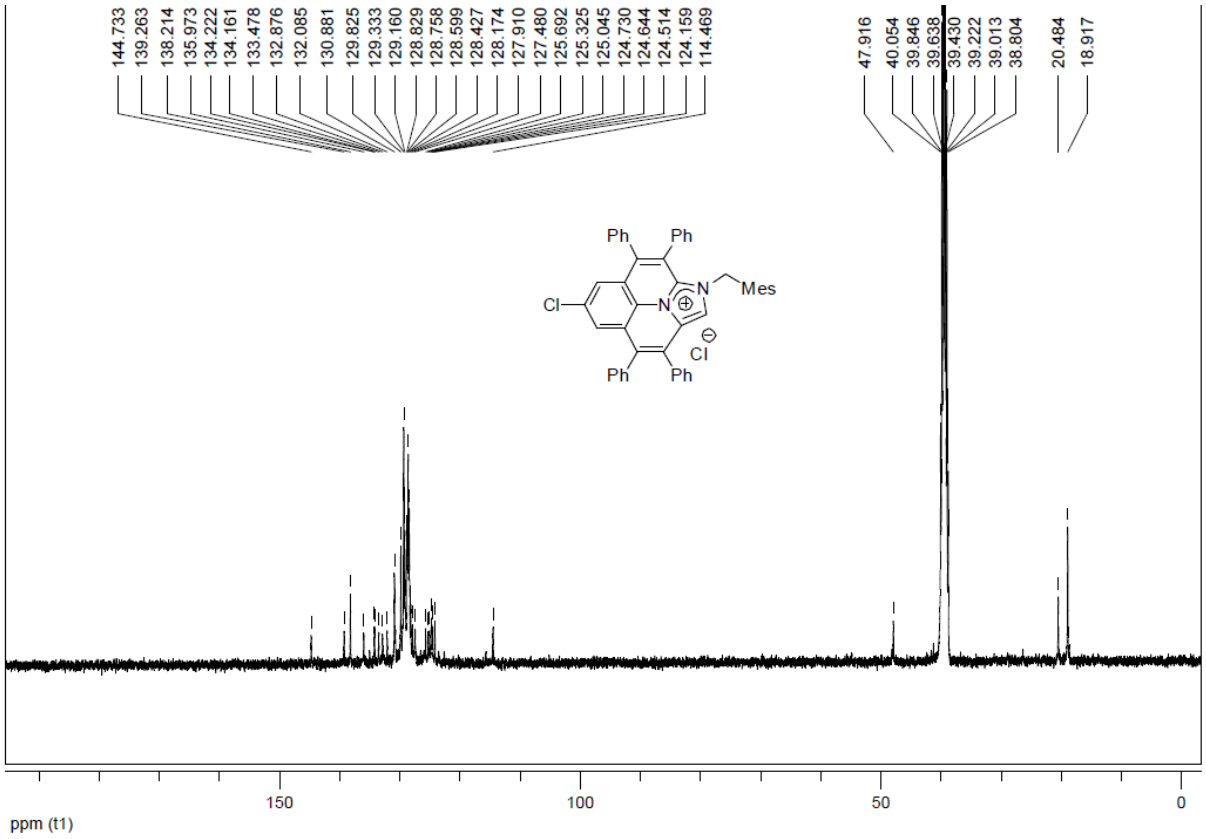
^{19}F NMR spectrum of 4ba



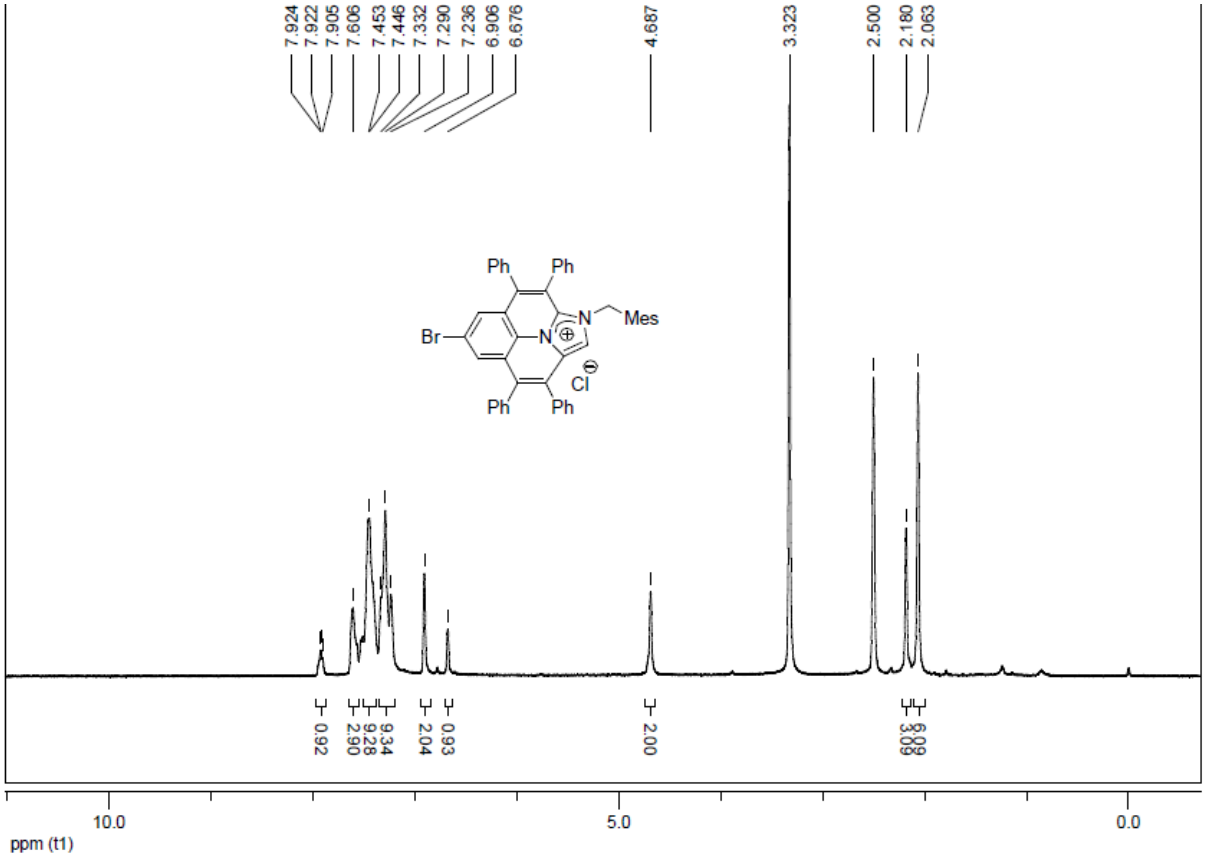
^{1}H NMR spectrum of 4ca



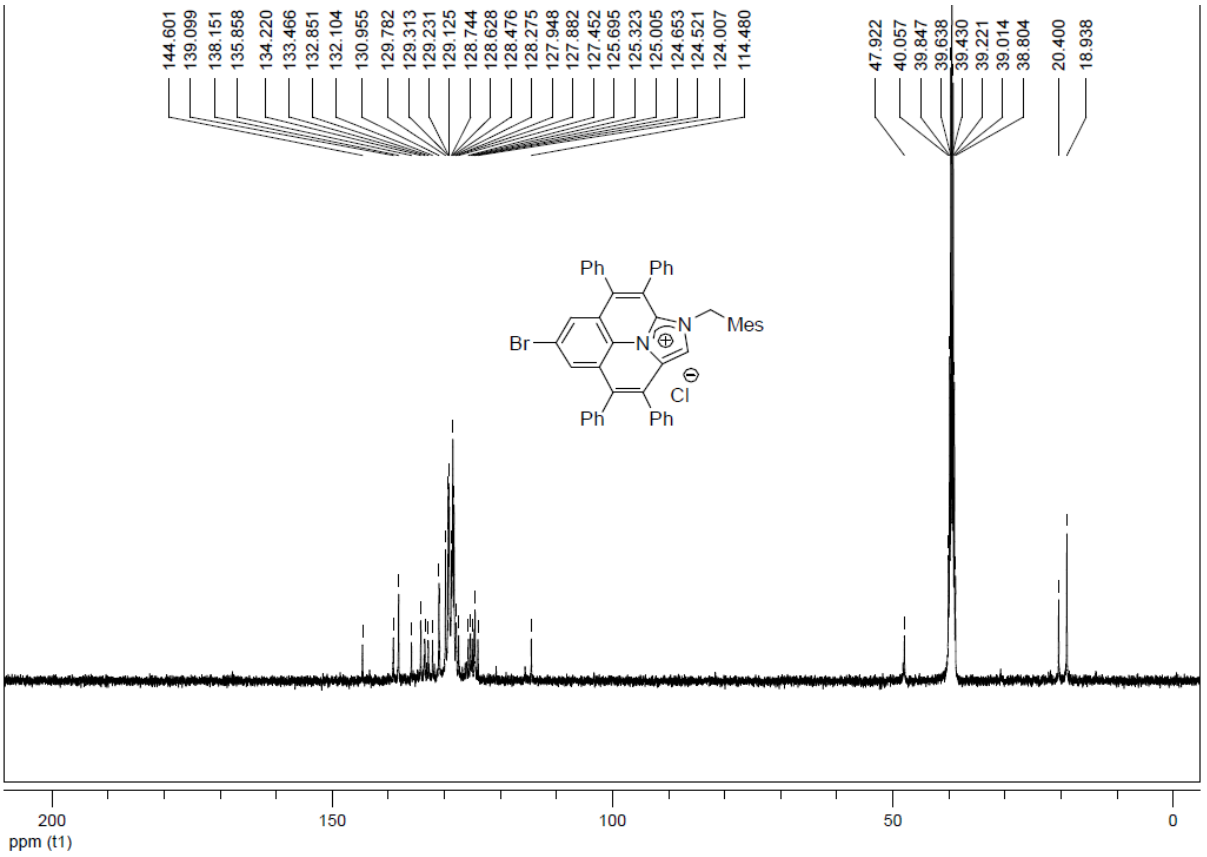
^{13}C NMR spectrum of 4ca



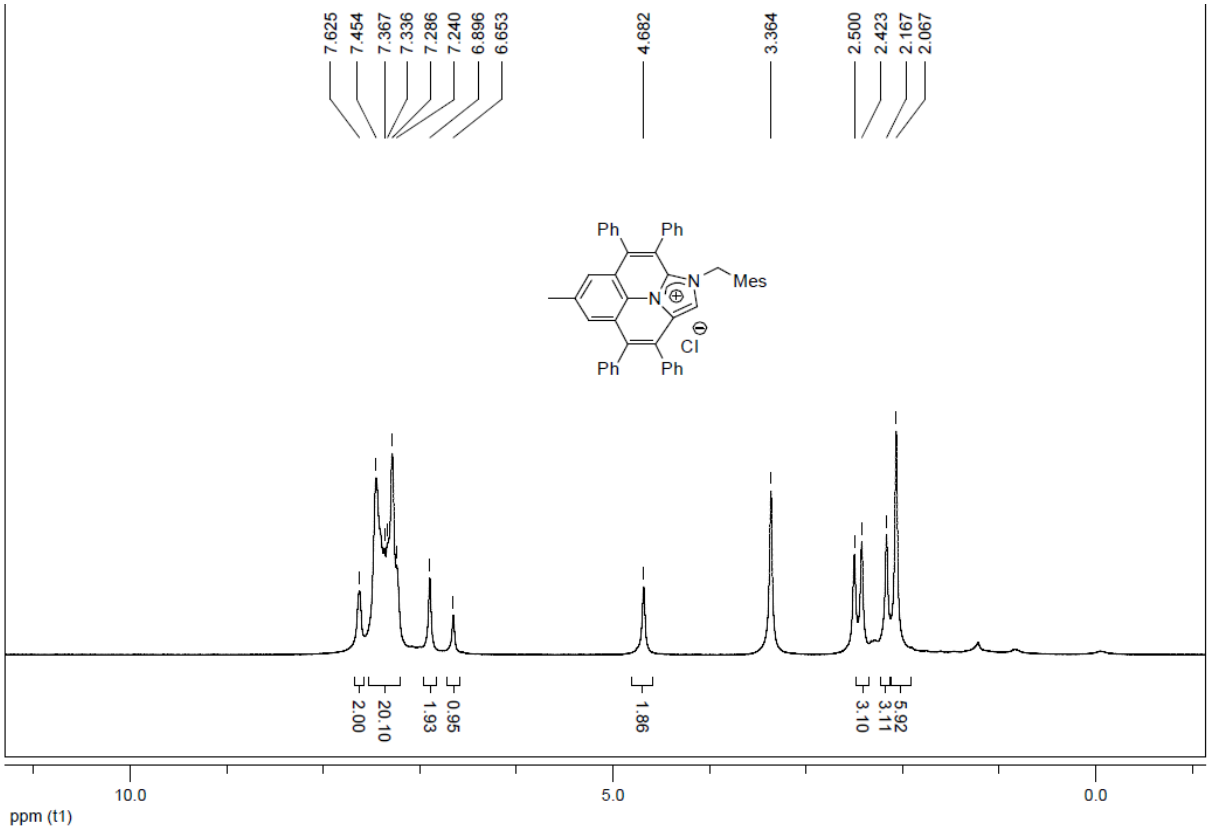
^{1}H NMR spectrum of 4da



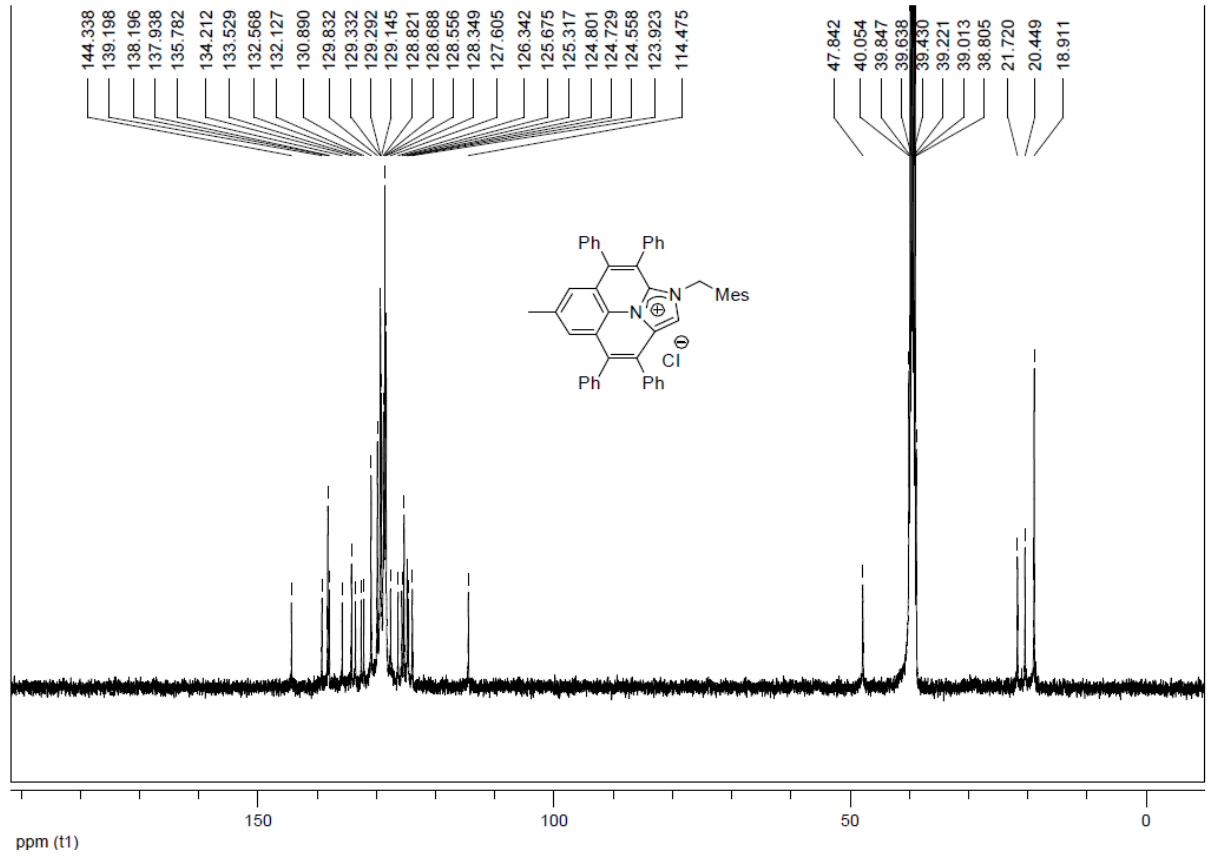
^{13}C NMR spectrum of 4da



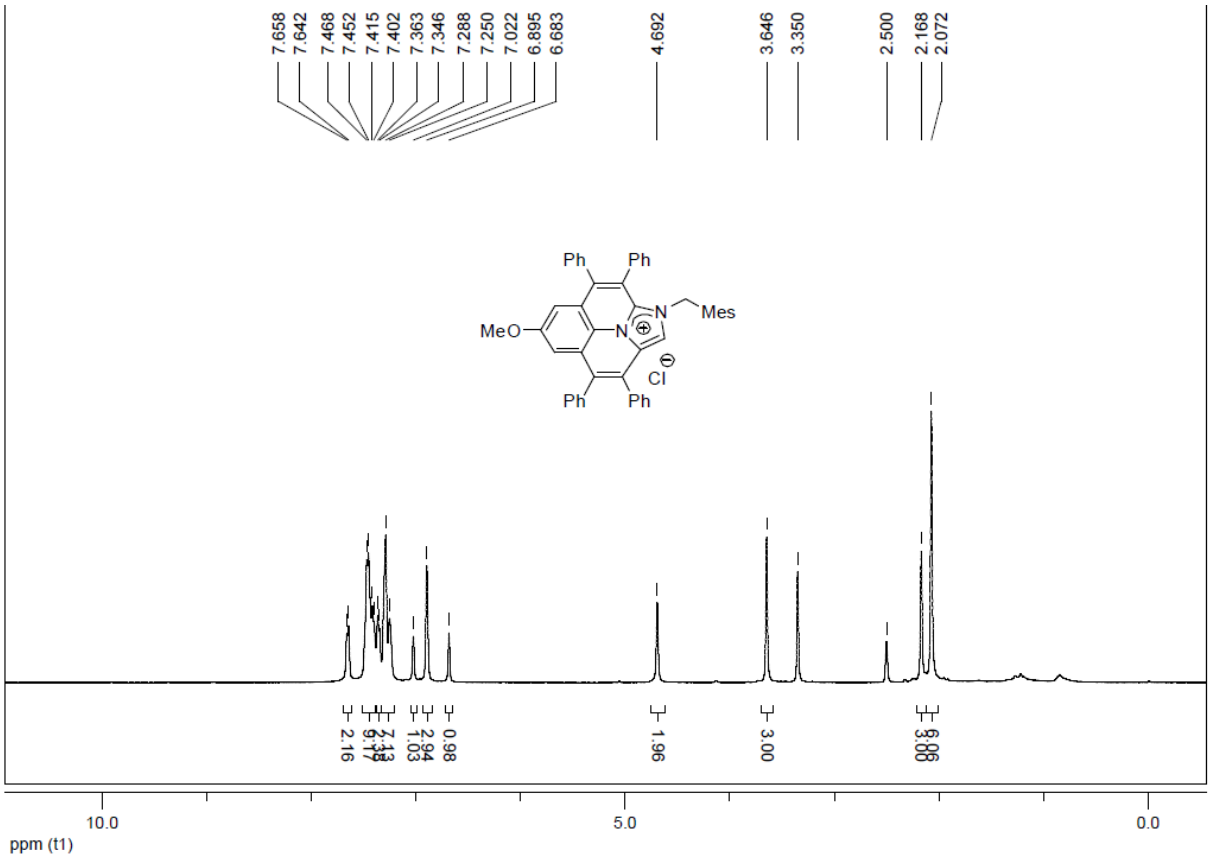
^{1}H NMR spectrum of 4ea



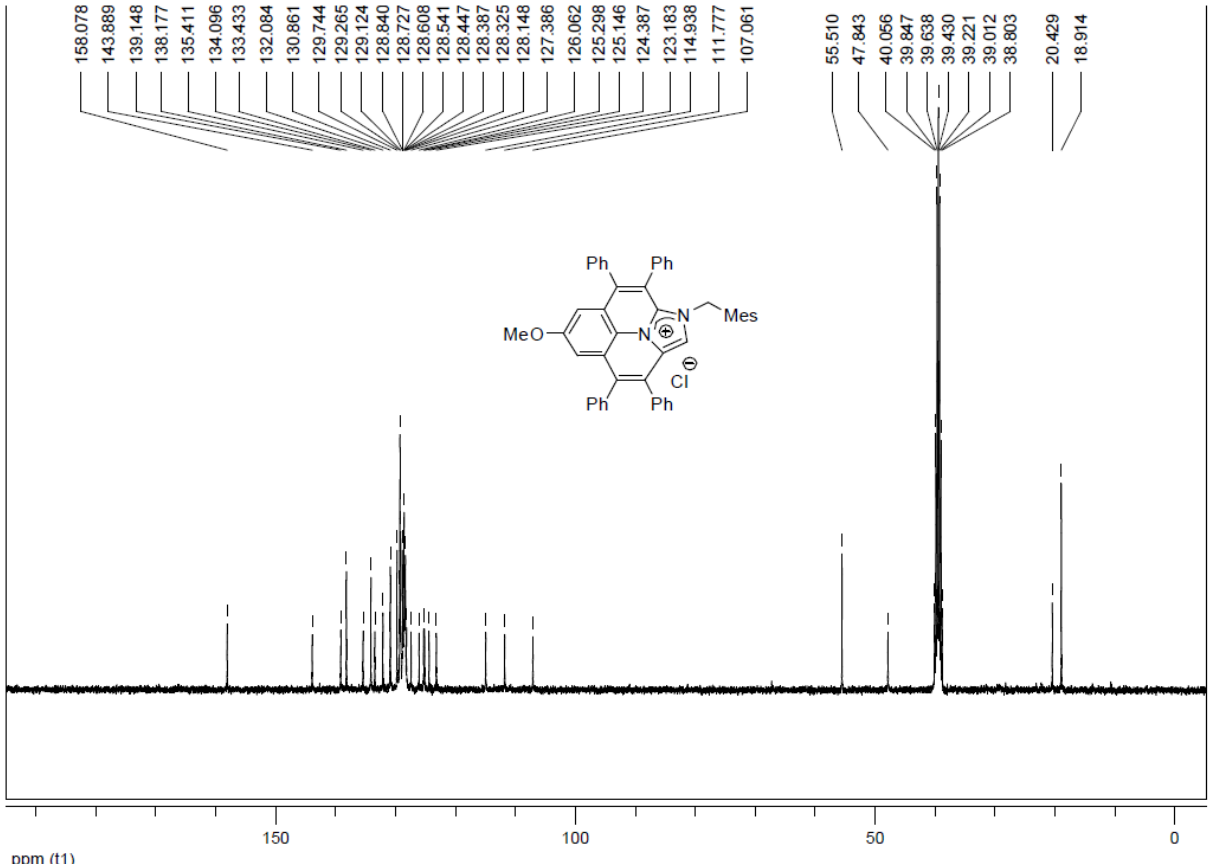
^{13}C NMR spectrum of 4ea



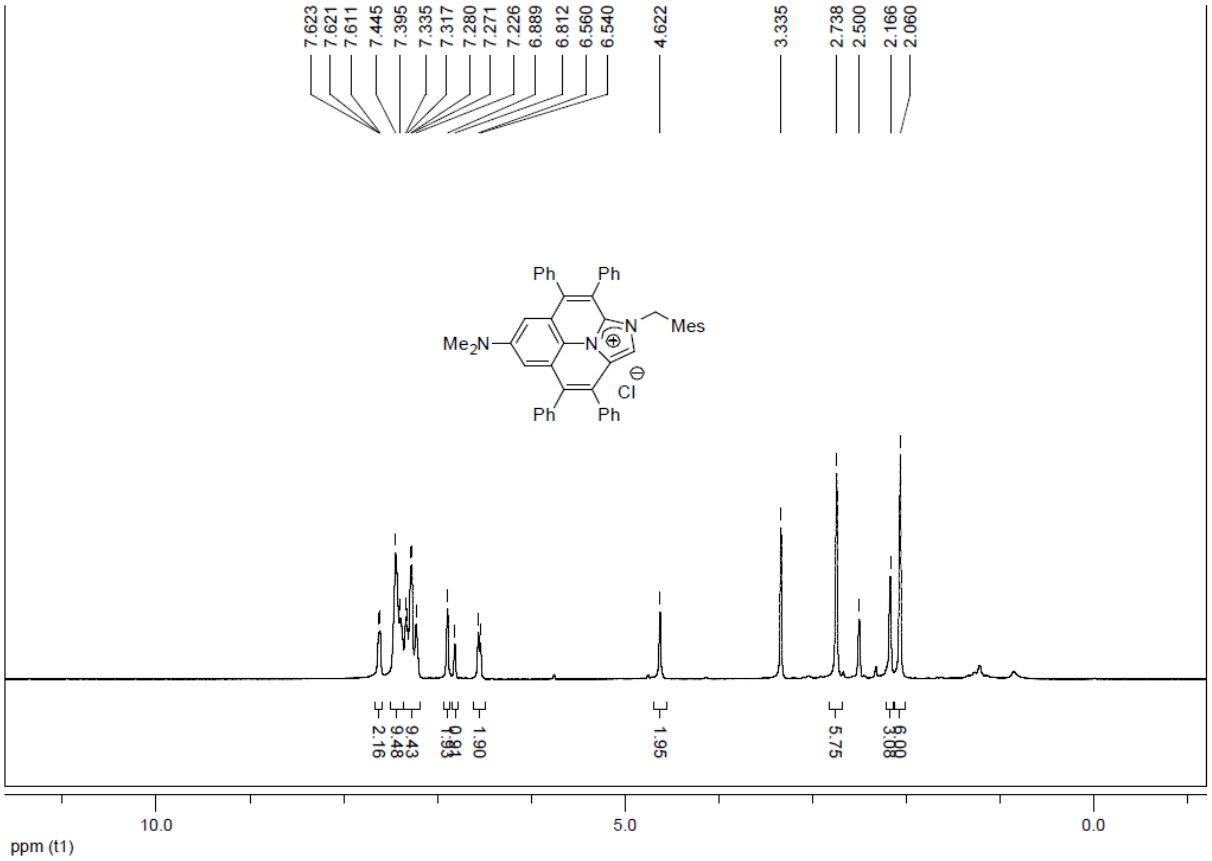
^{1}H NMR spectrum of 4fa



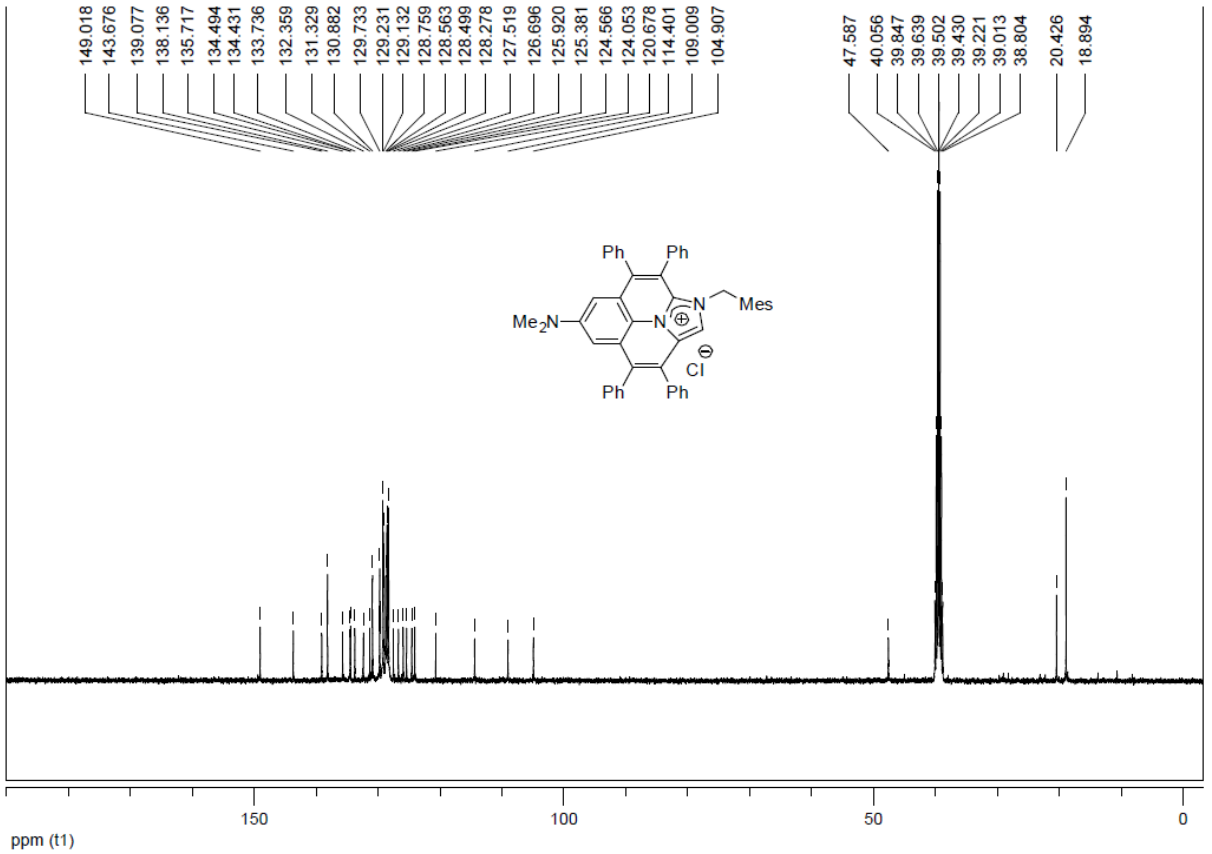
^{13}C NMR spectrum of 4fa



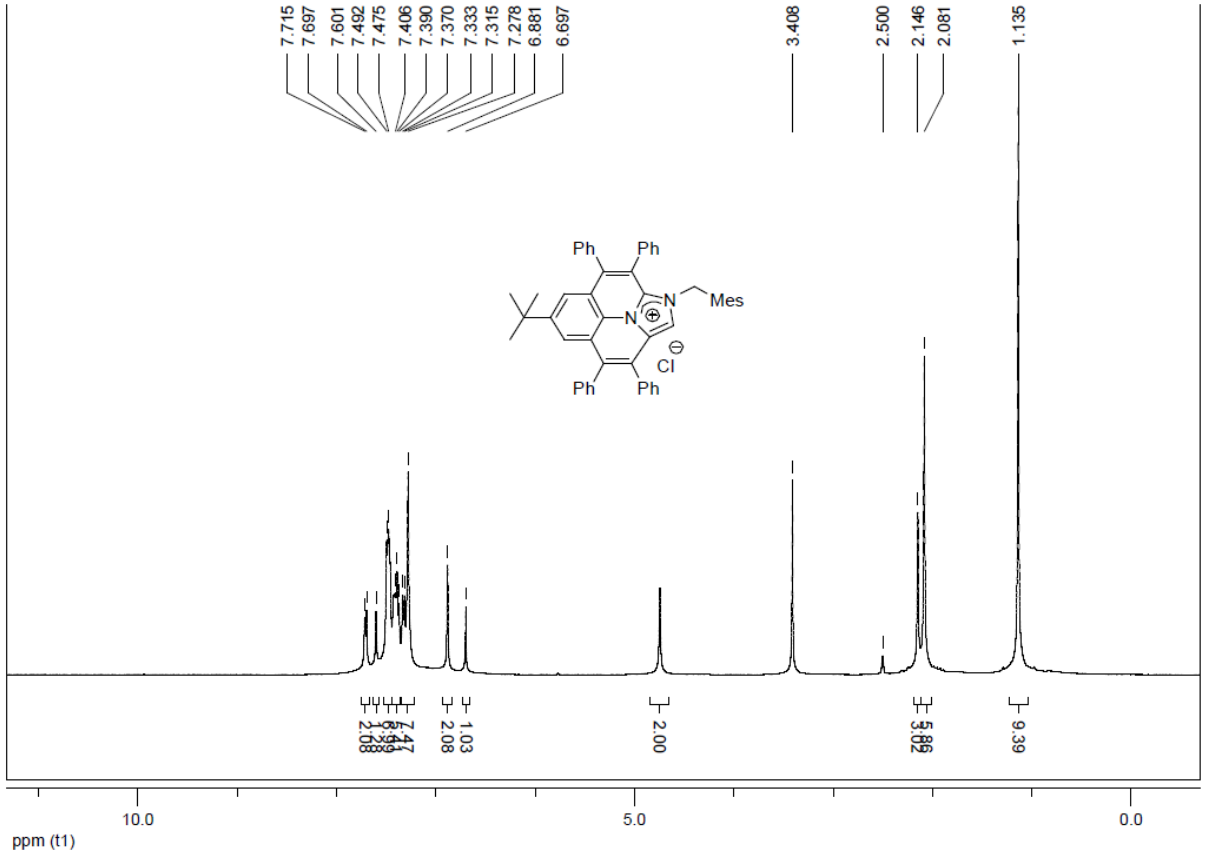
^{1}H NMR spectrum of 4ga



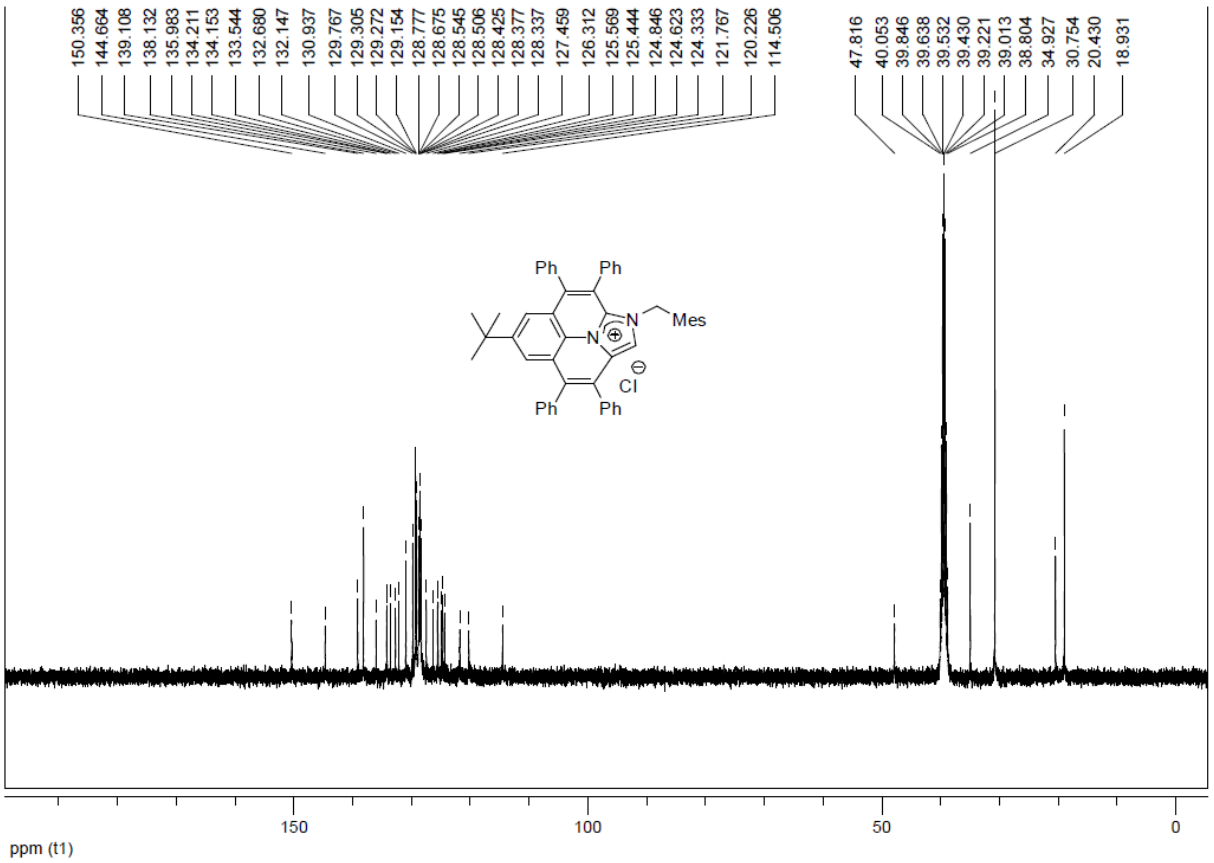
^{13}C NMR spectrum of 4ga



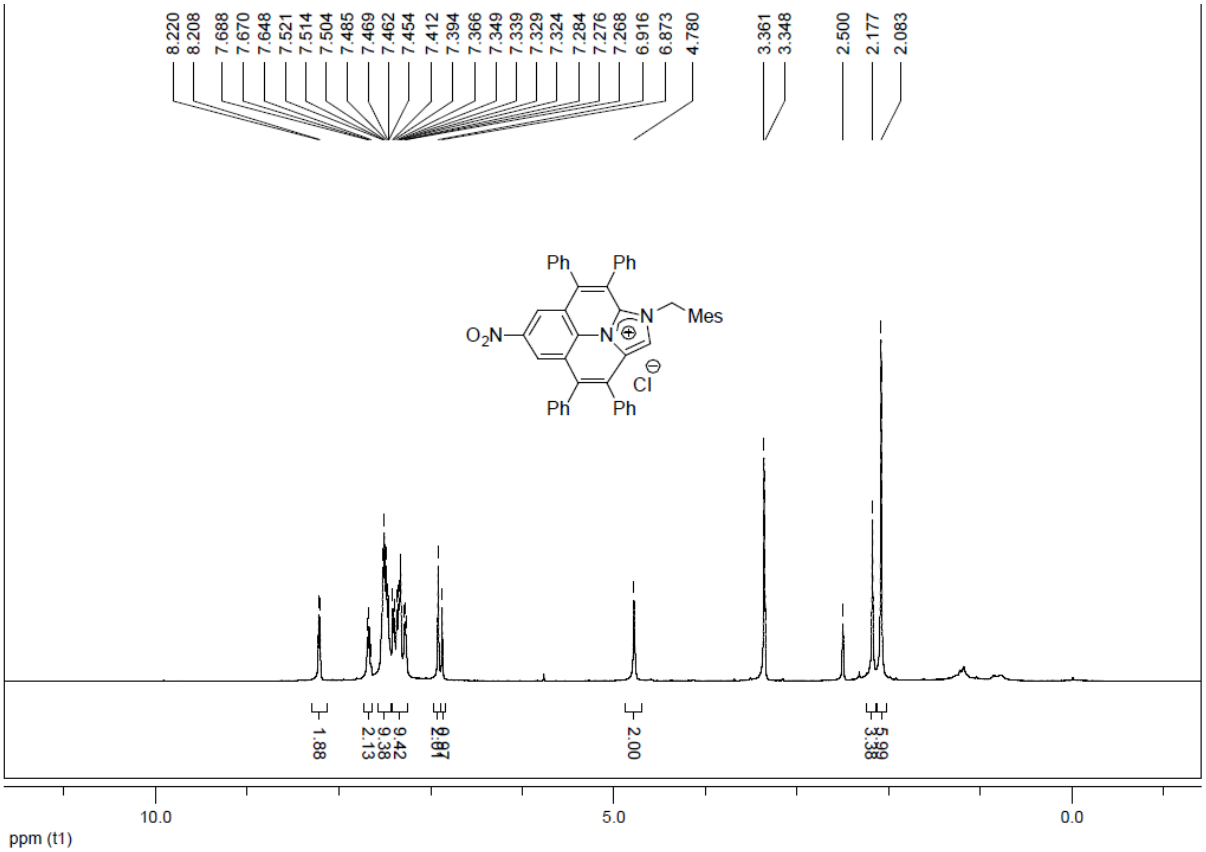
^{1}H NMR spectrum of 4ha



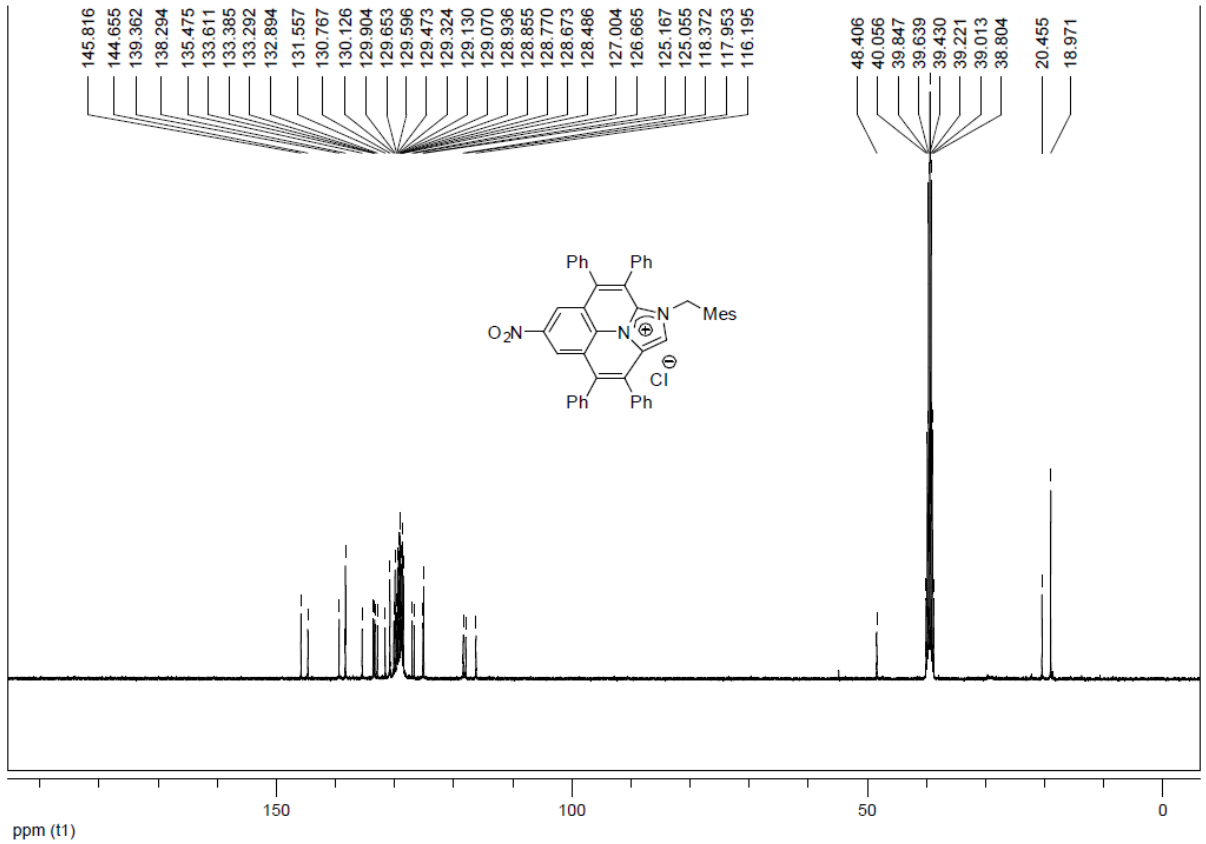
^{13}C NMR spectrum of 4ha



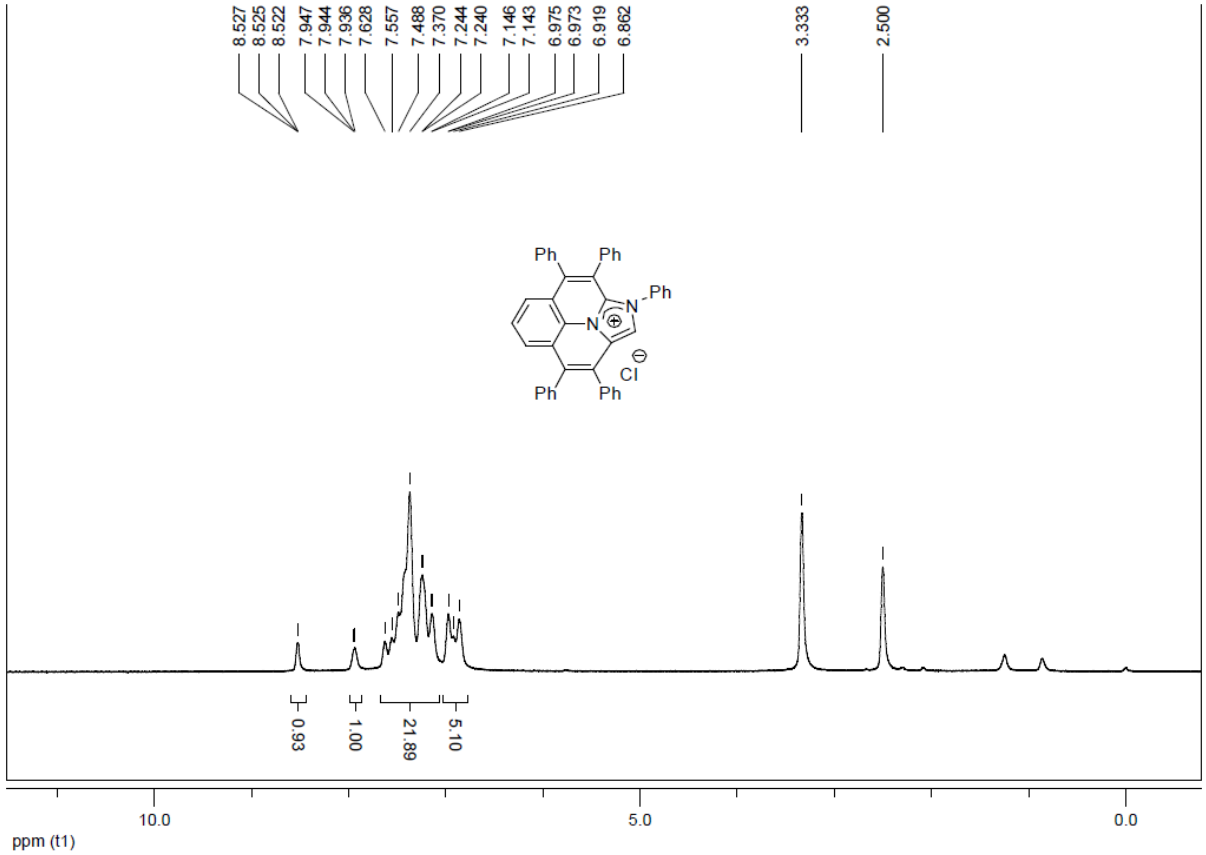
^{1}H NMR spectrum of 4ia



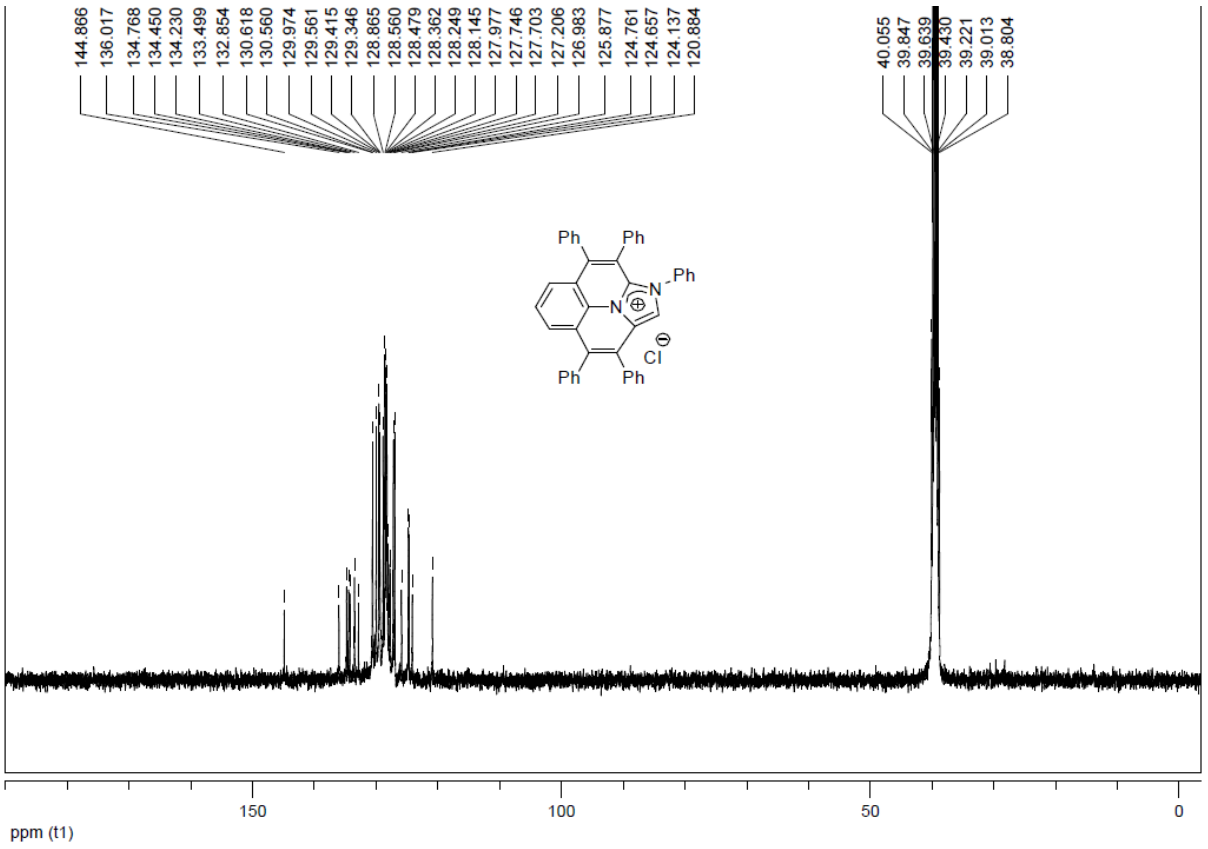
^{13}C NMR spectrum of 4ia



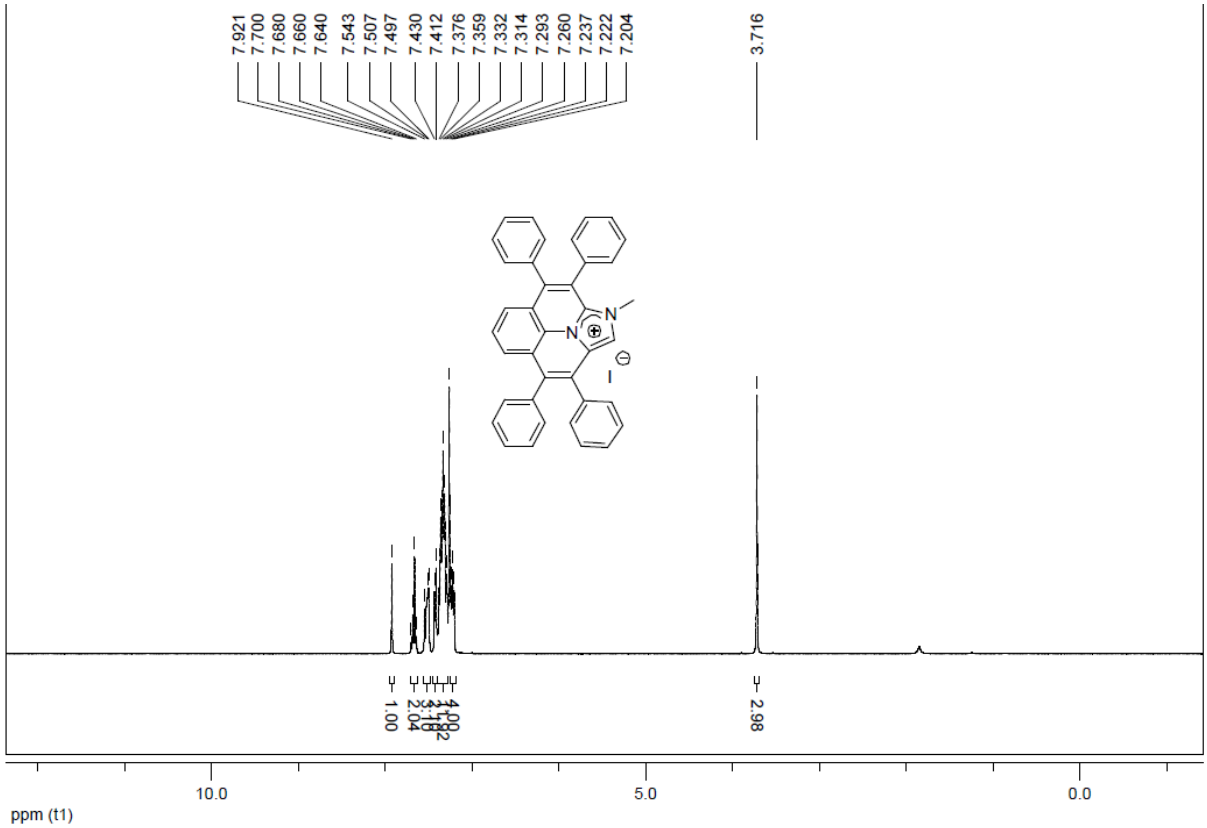
^{1}H NMR spectrum of 4ja



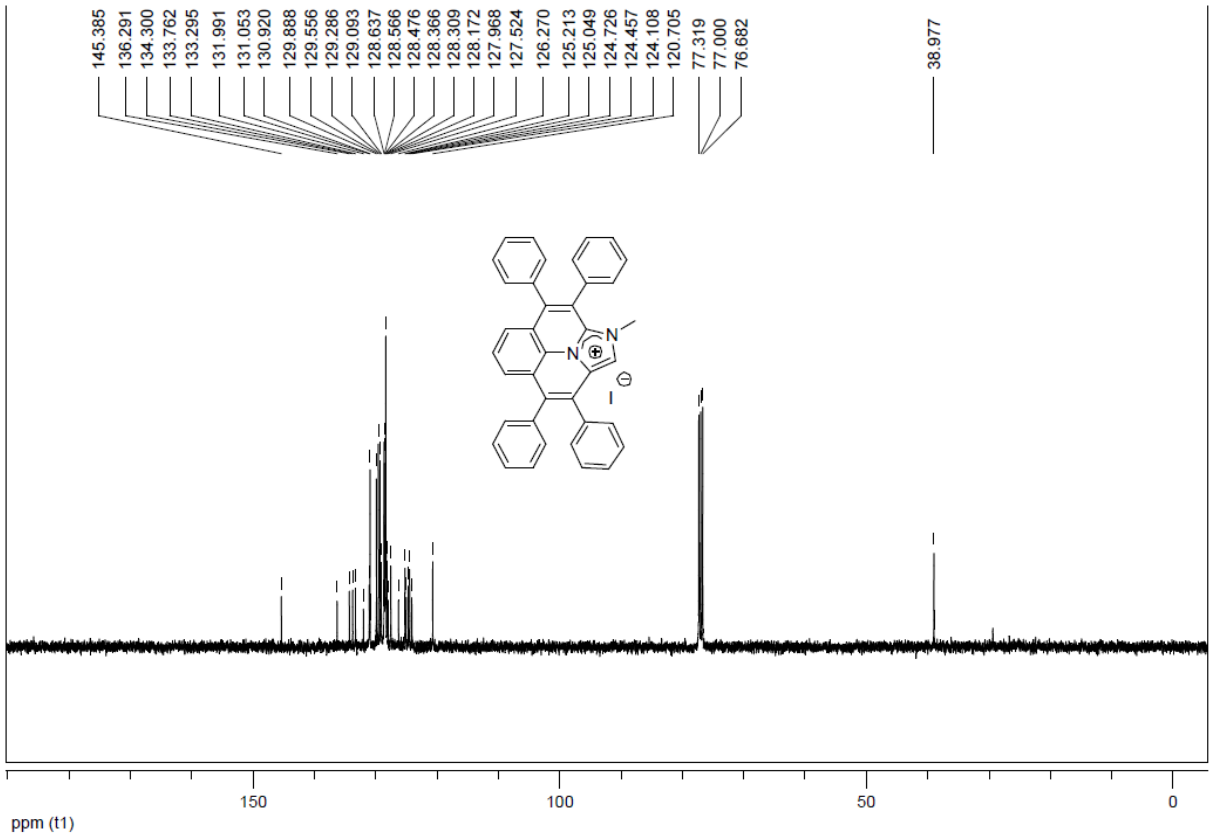
^{13}C NMR spectrum of 4ja



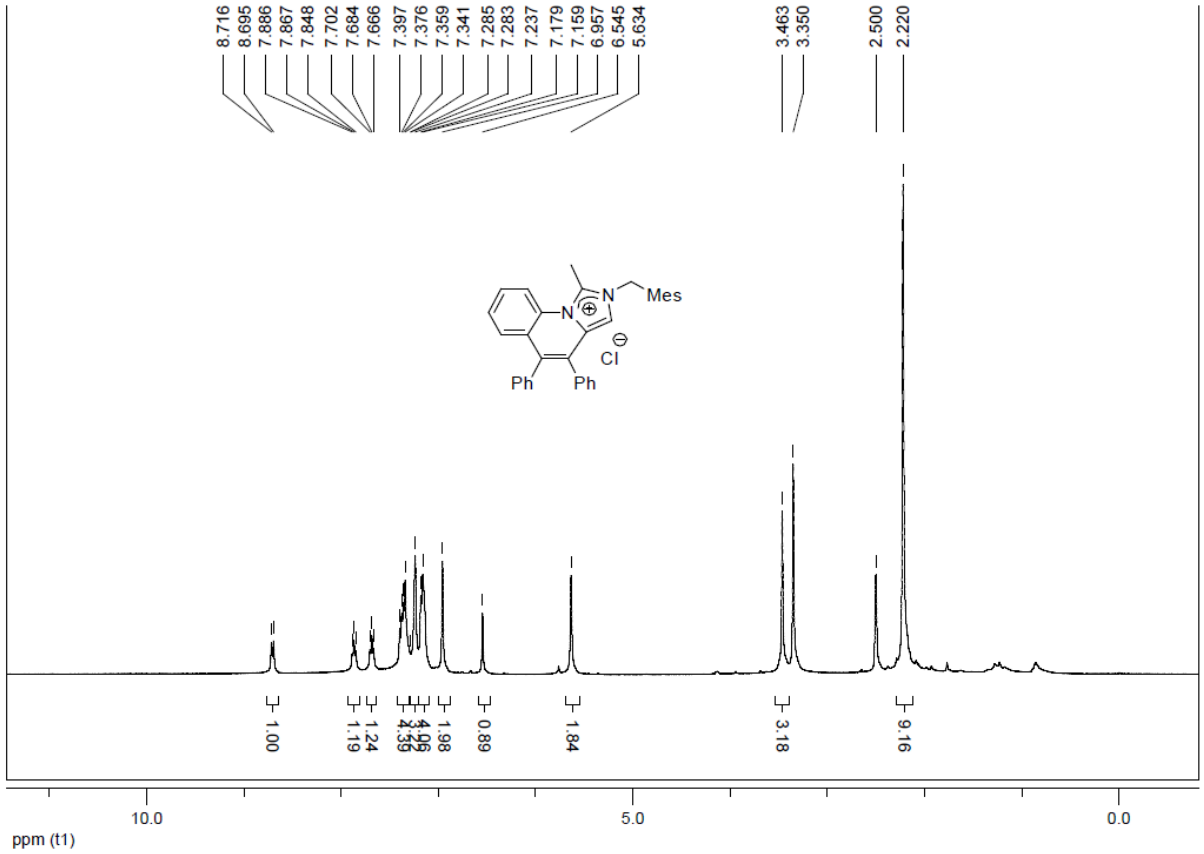
^{1}H NMR spectrum of 4la



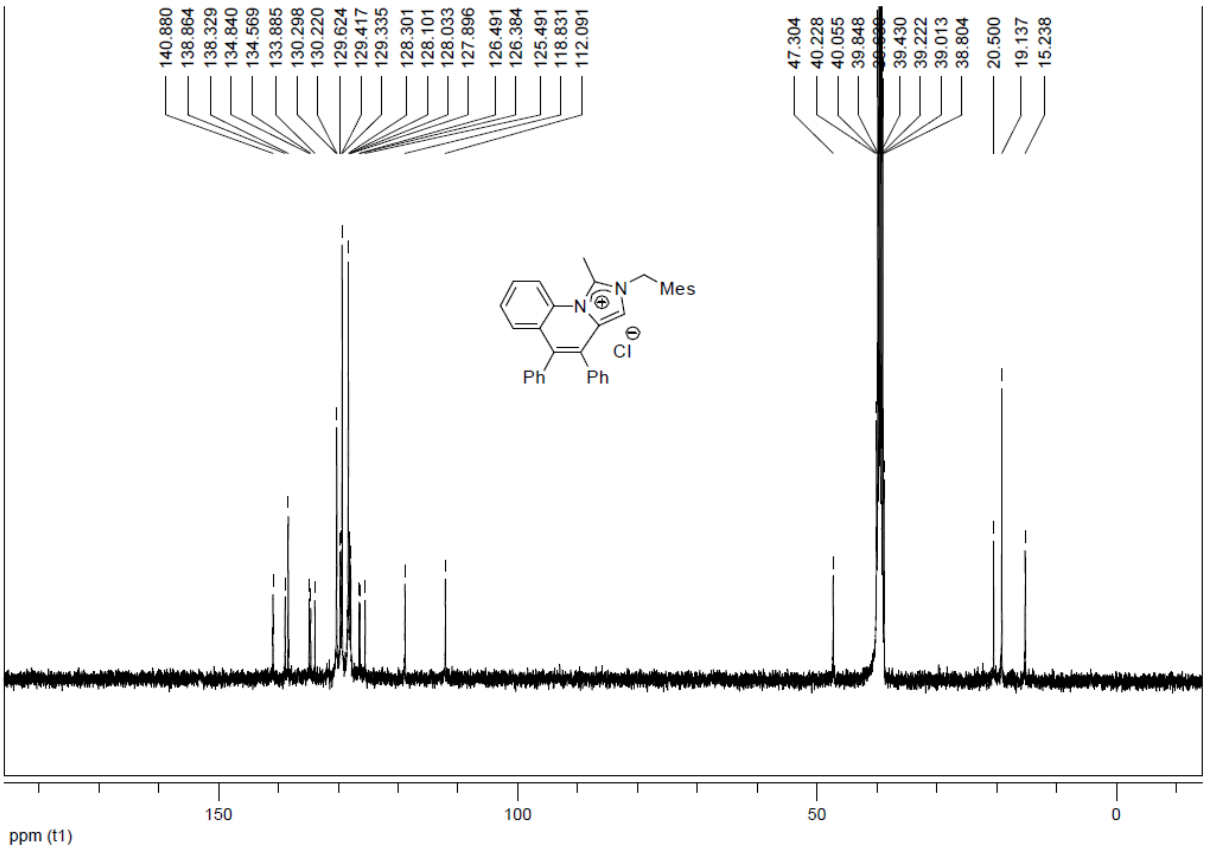
^{13}C NMR spectrum of 4la



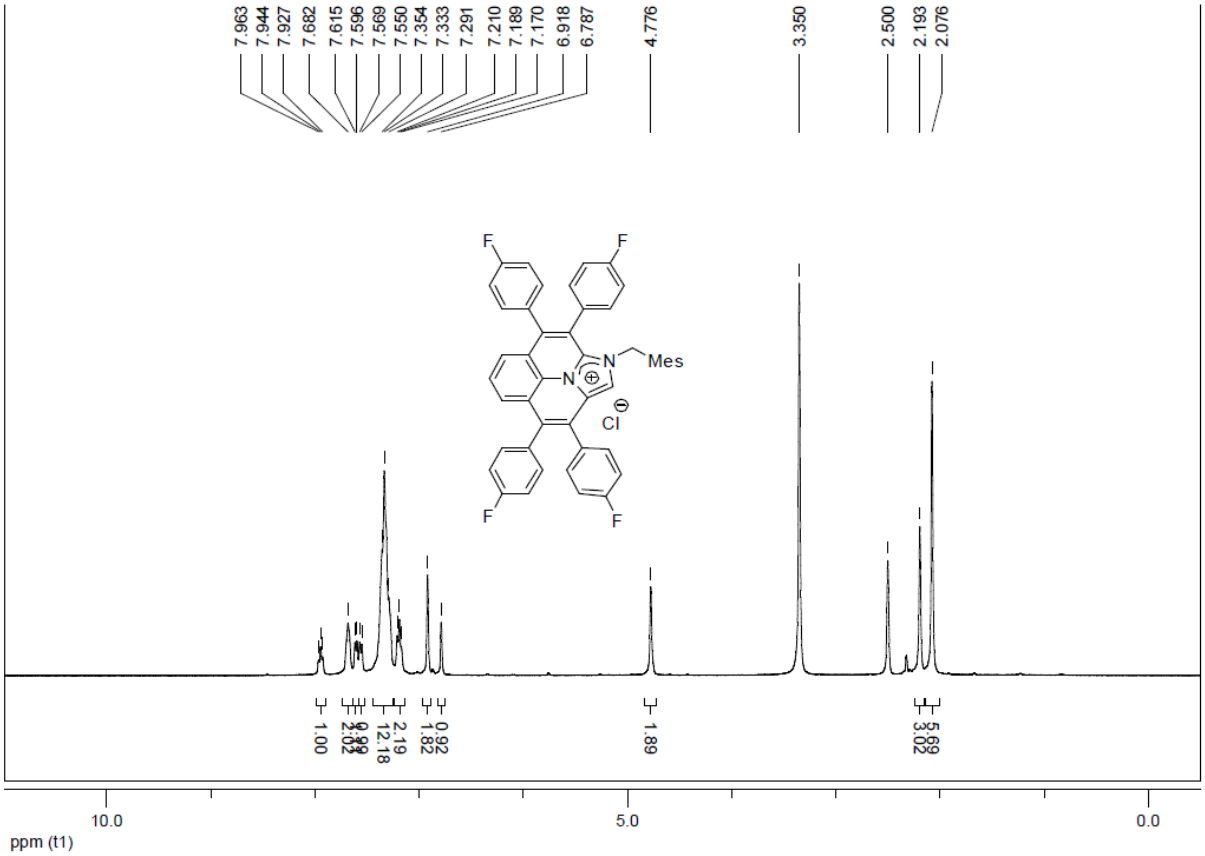
^{1}H NMR spectrum of 4ma



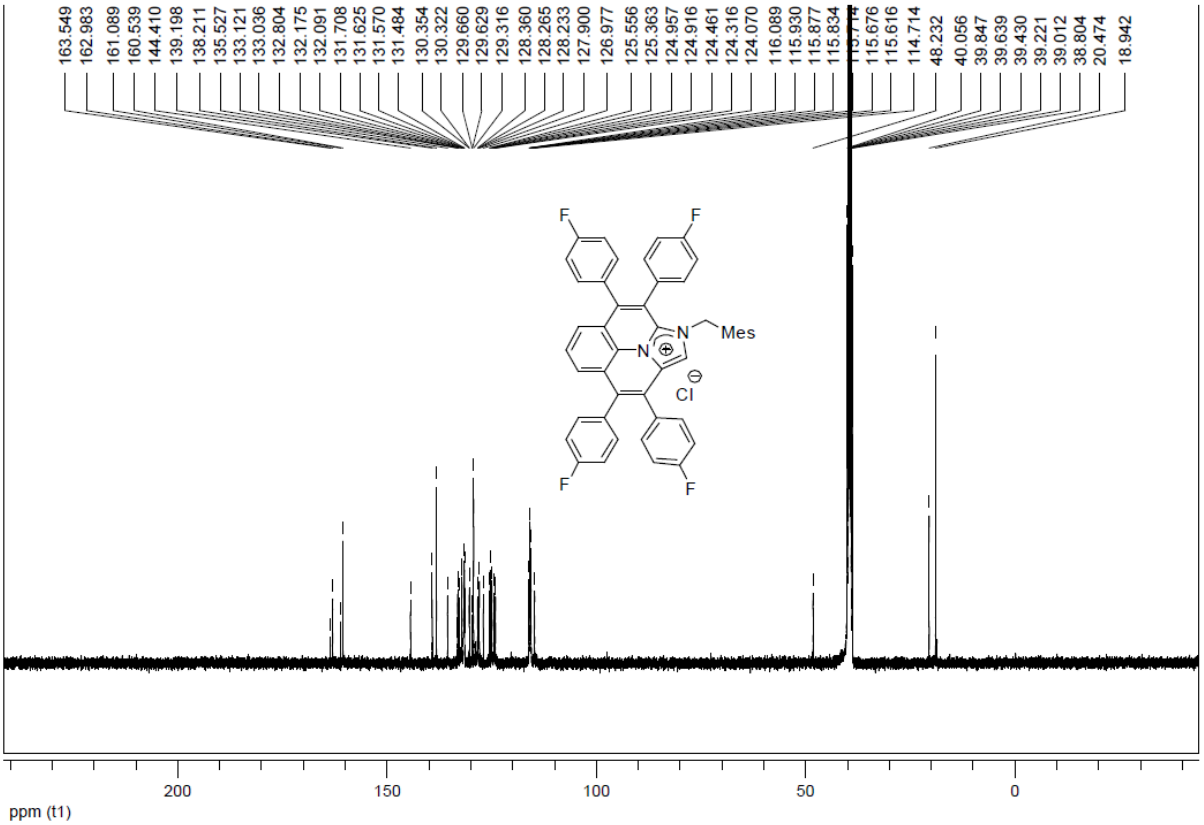
^{13}C NMR spectrum of 4ma



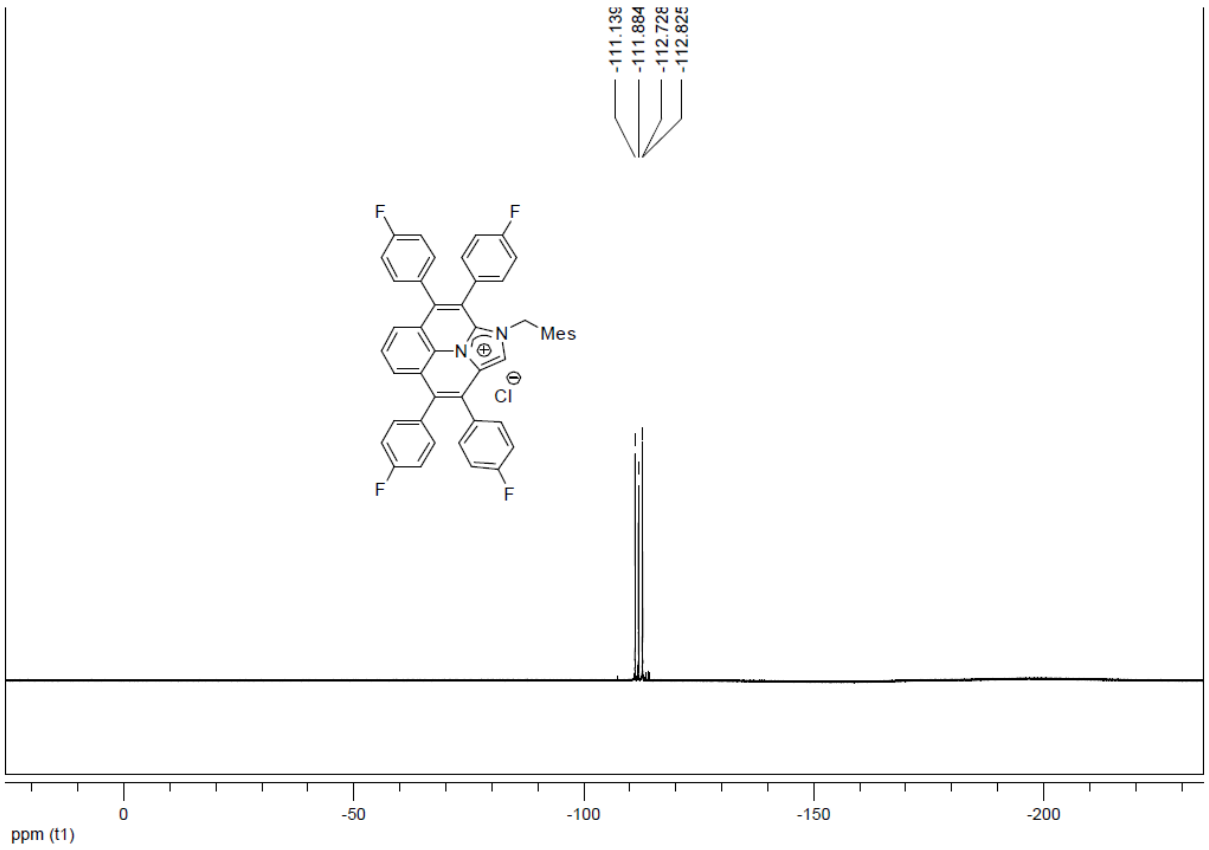
^{1}H NMR spectrum of 4ab



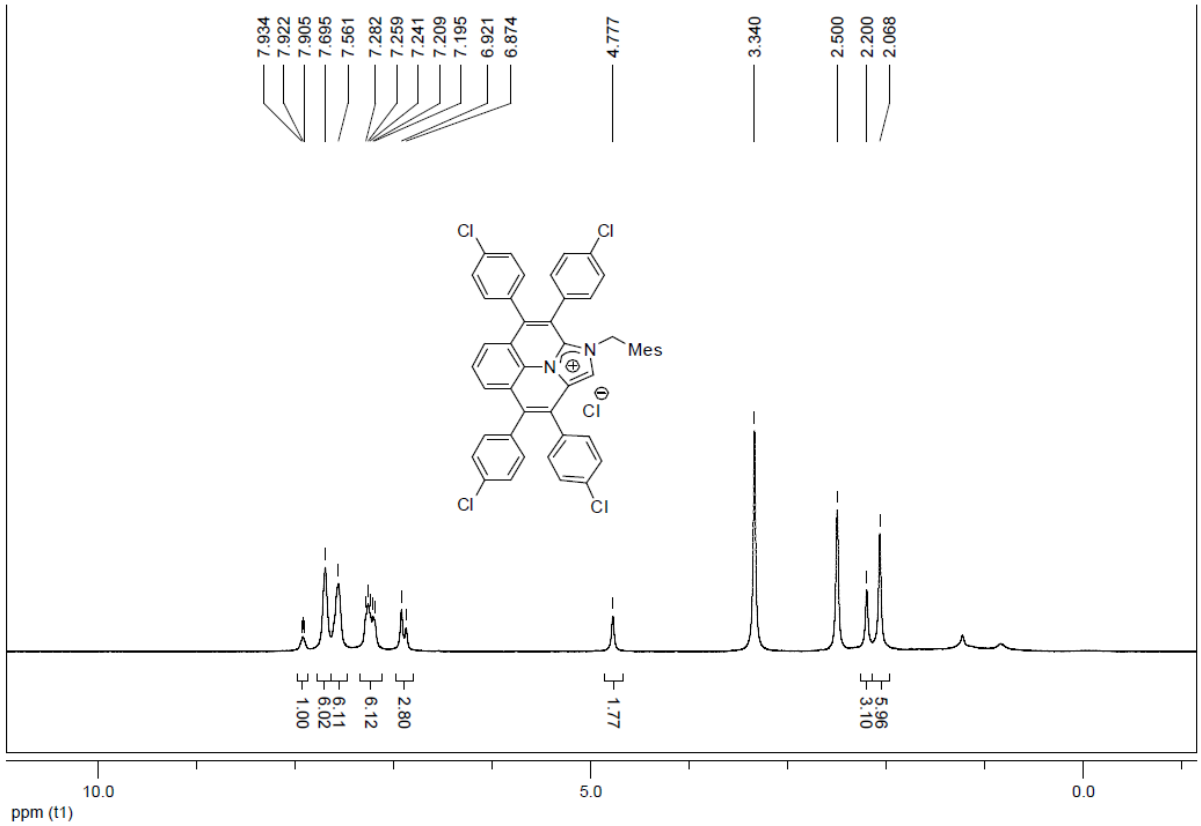
^{13}C NMR spectrum of 4ab



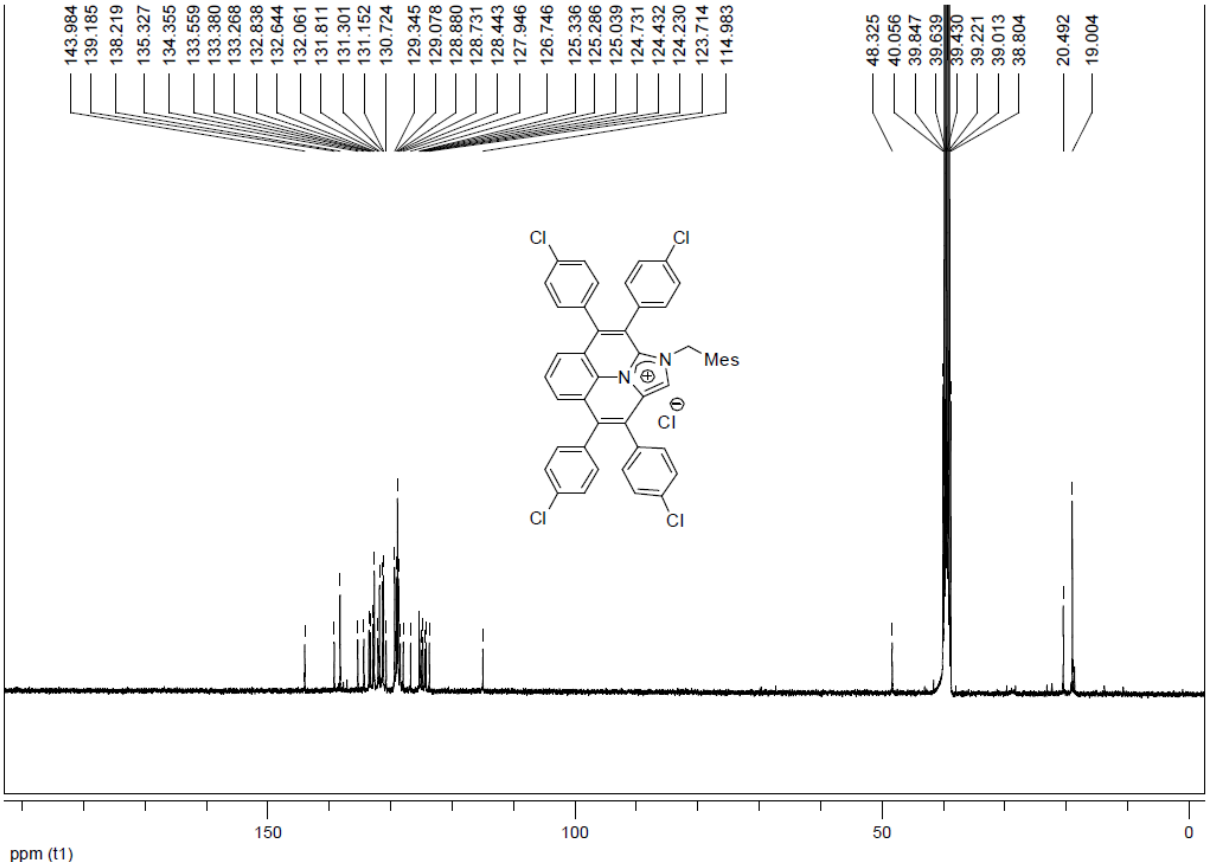
^{19}F NMR spectrum of 4ab



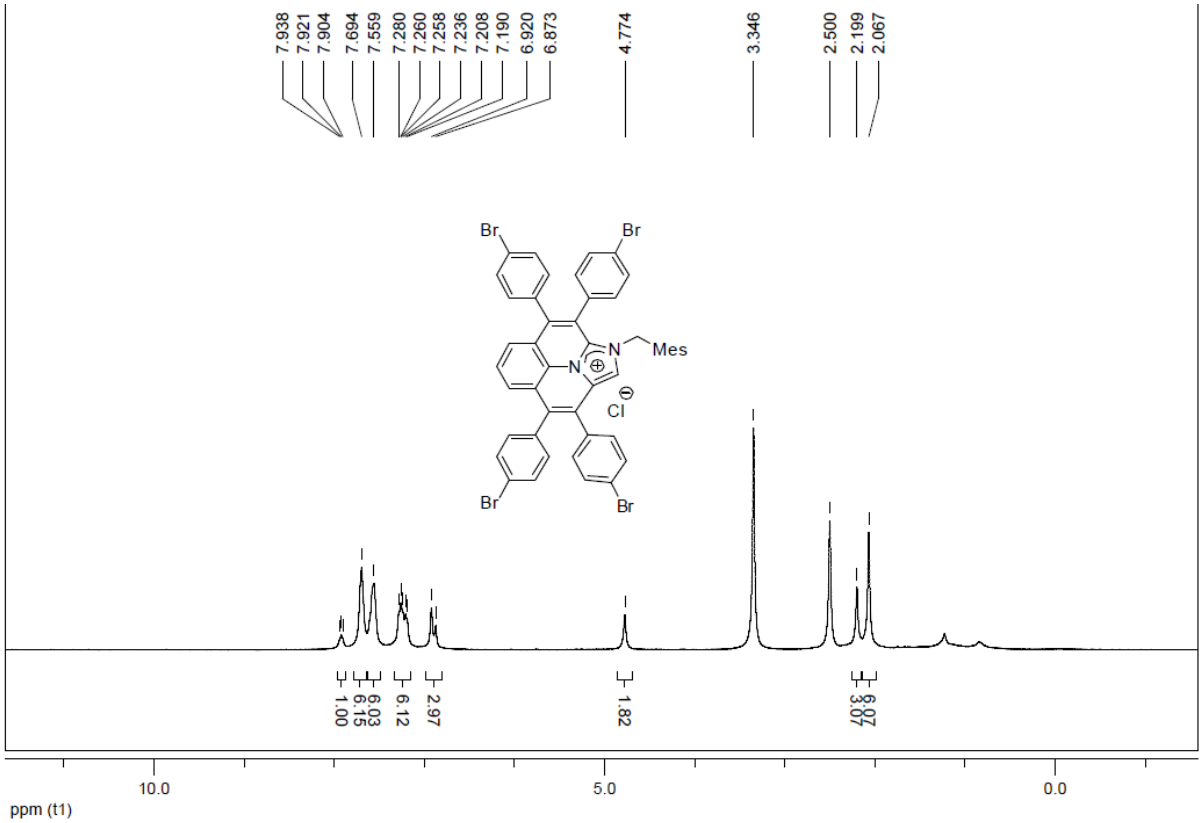
^{1}H NMR spectrum of 4ac



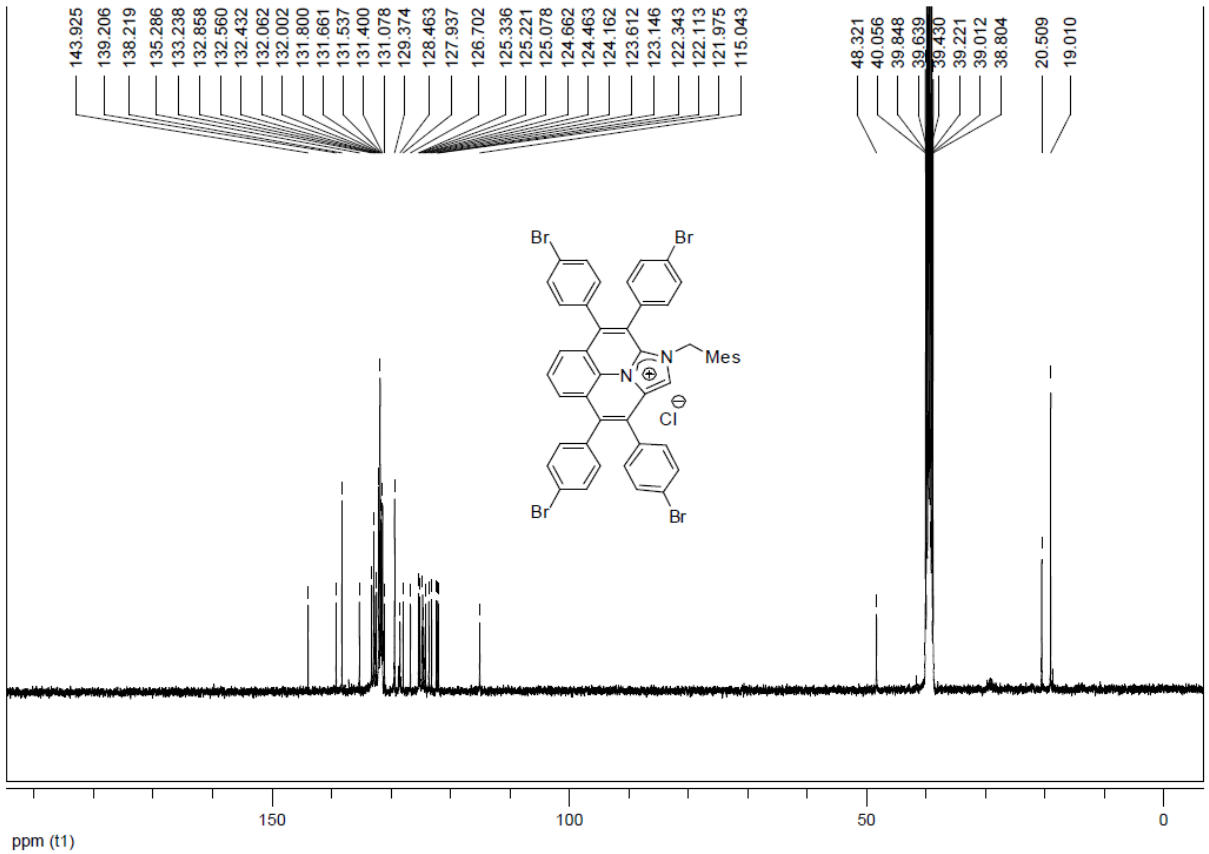
^{13}C NMR spectrum of 4ac



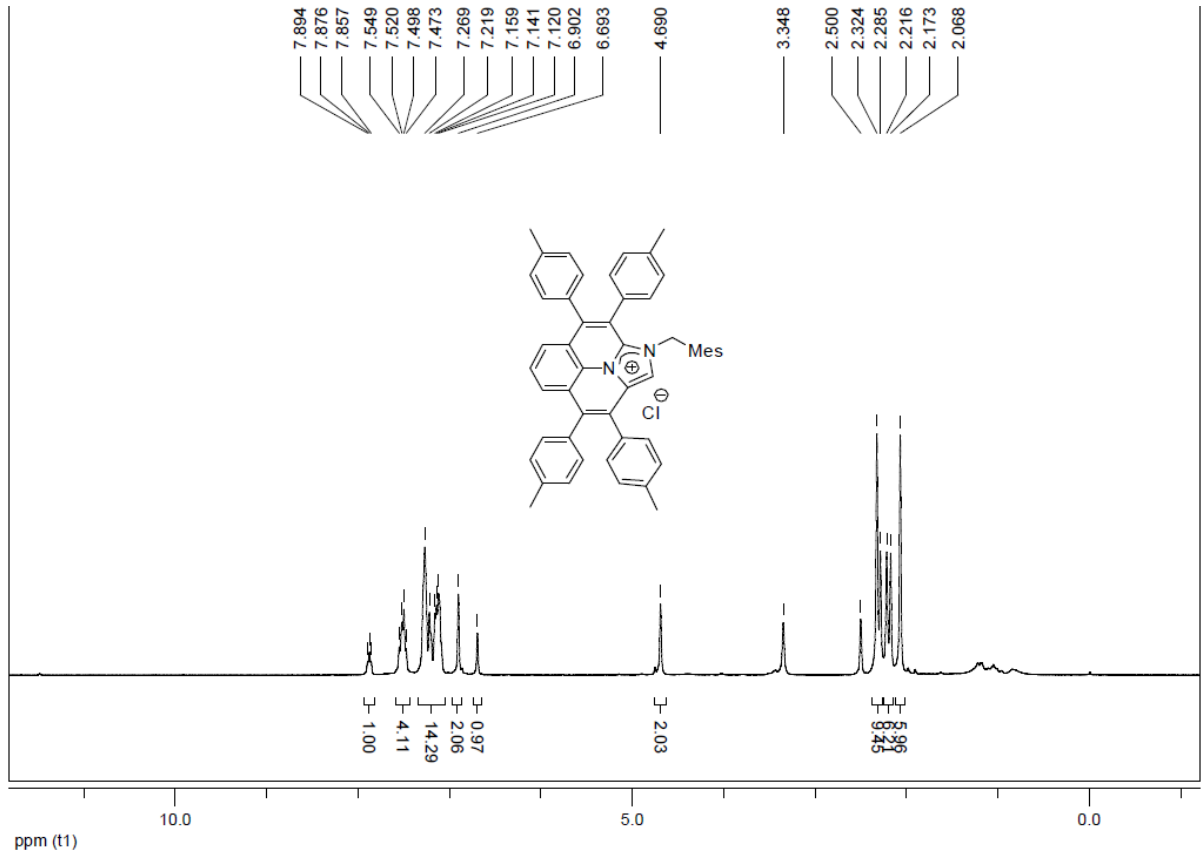
^{1}H NMR spectrum of 4ad



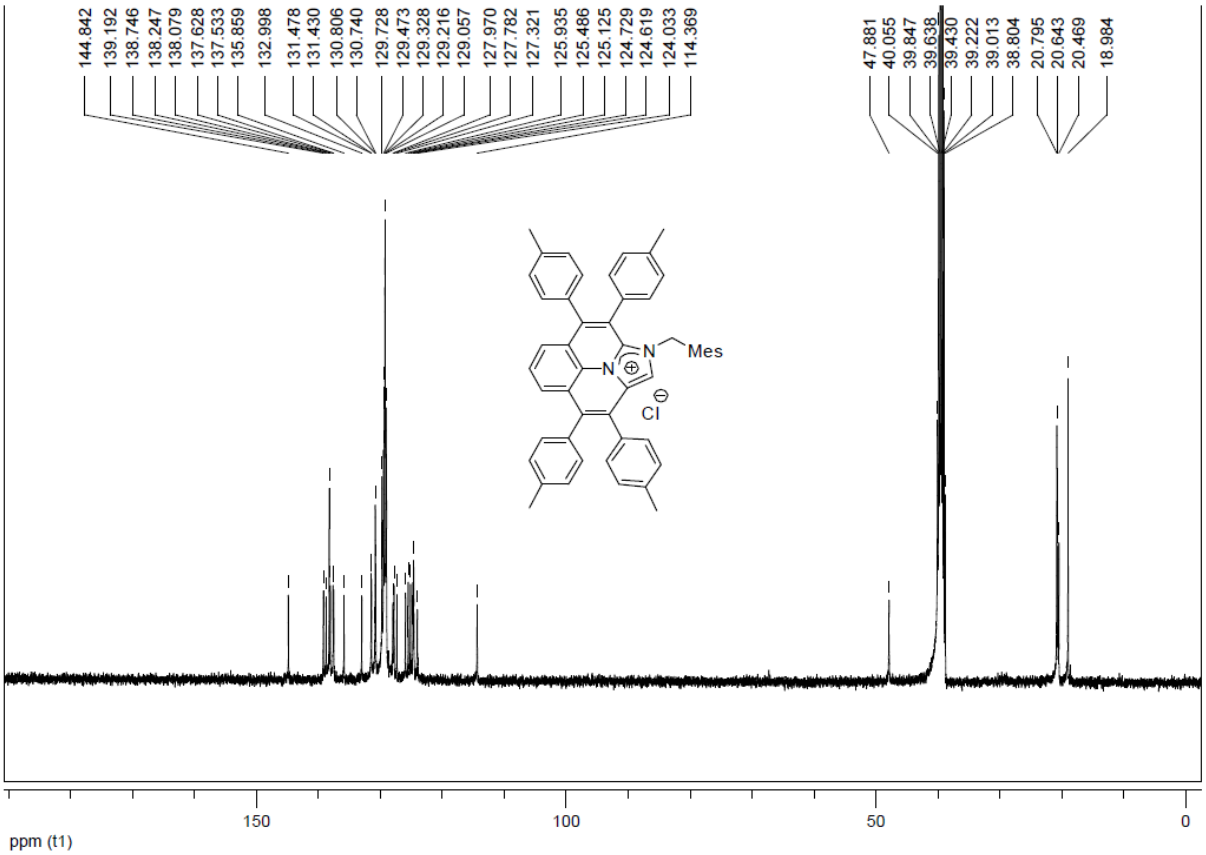
^{13}C NMR spectrum of 4ad



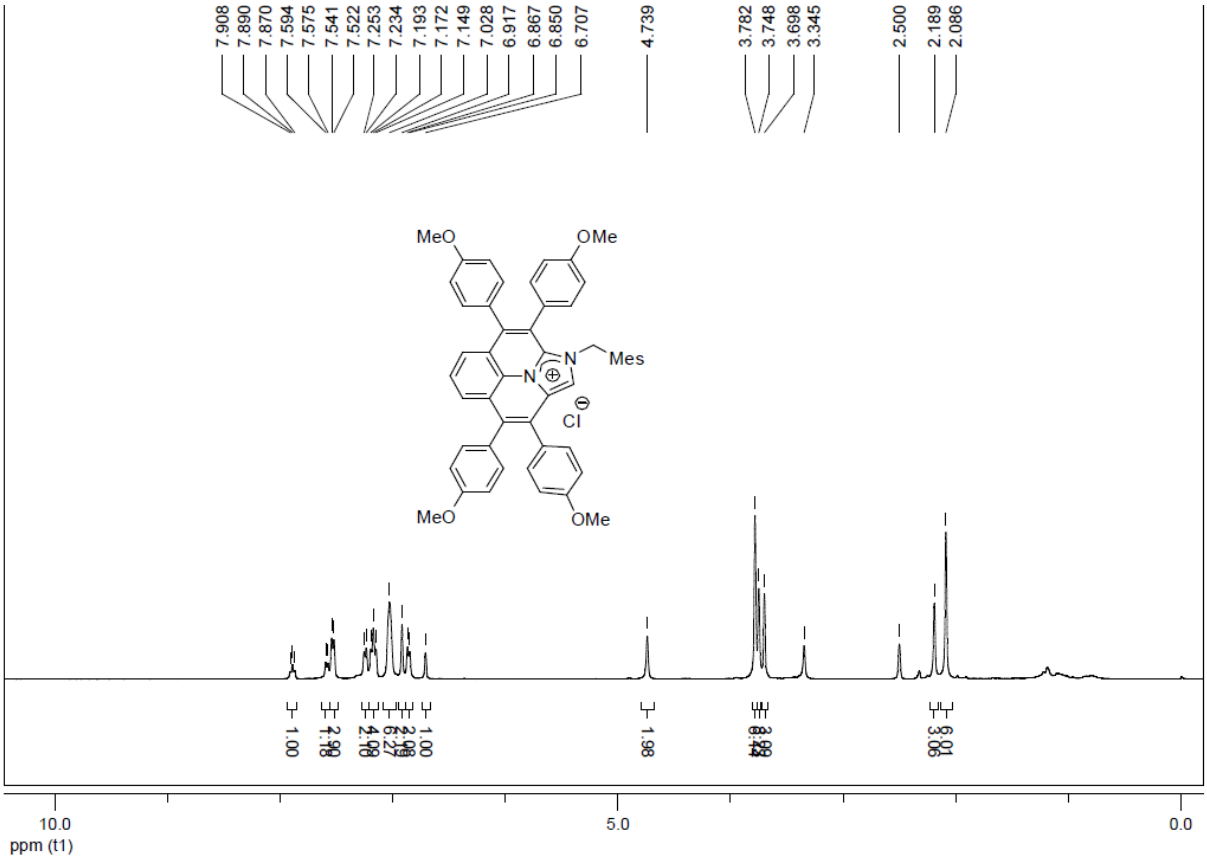
^{1}H NMR spectrum of 4ae



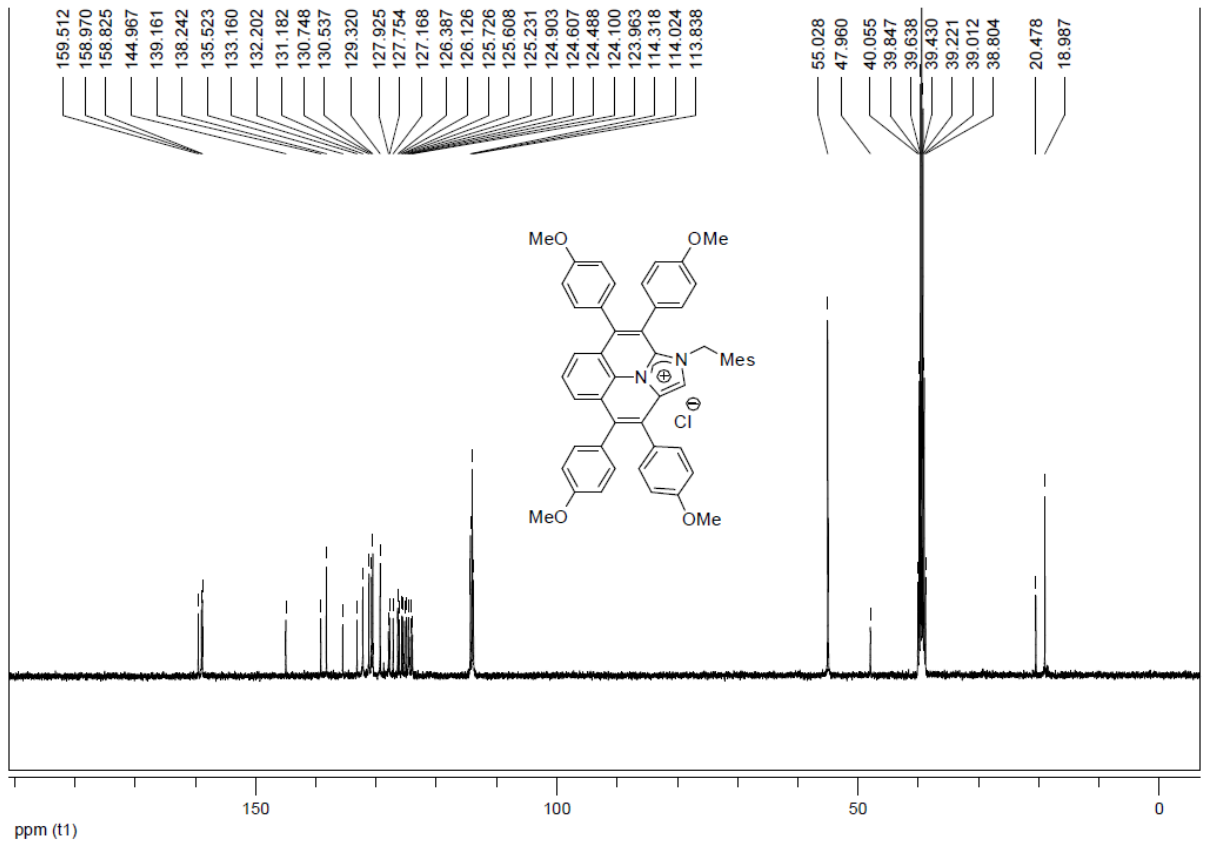
^{13}C NMR spectrum of 4ae



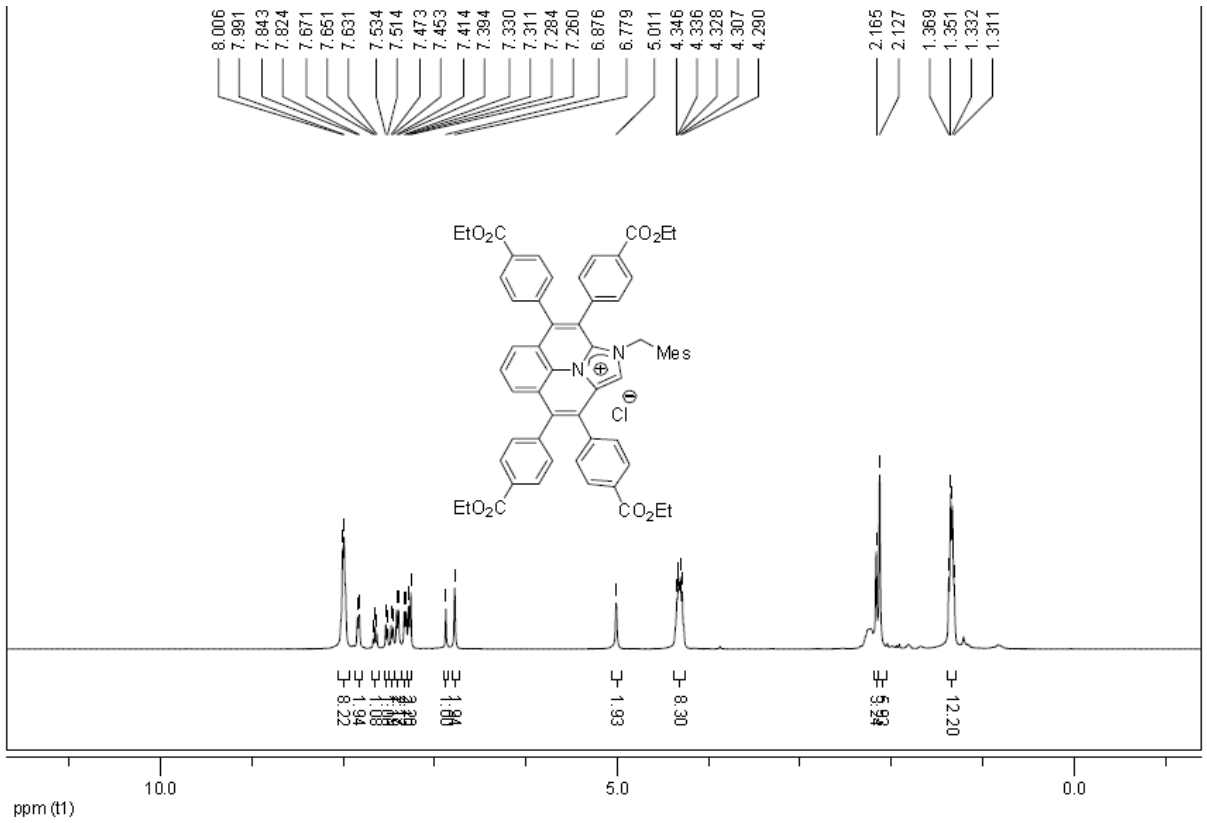
^{1}H NMR spectrum of 4af



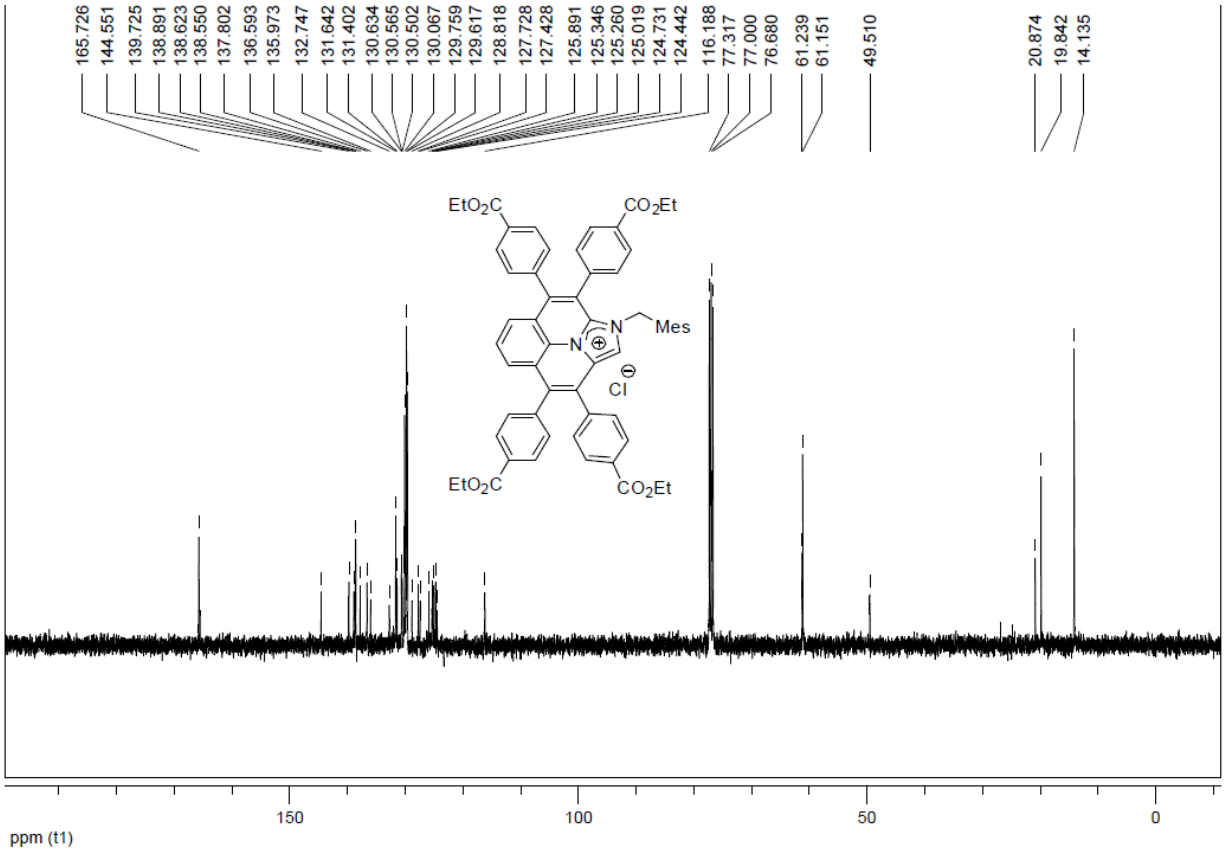
^{13}C NMR spectrum of 4af



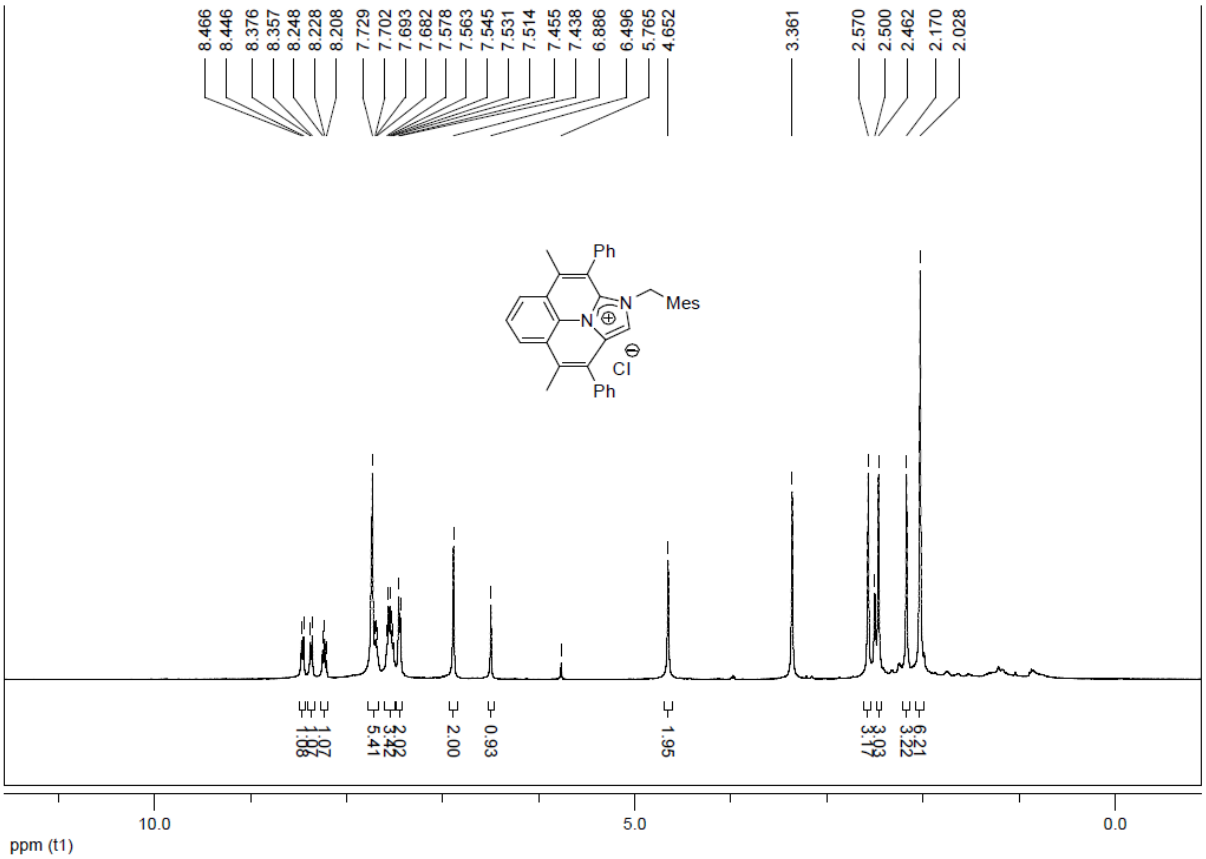
^{1}H NMR spectrum of 4ag



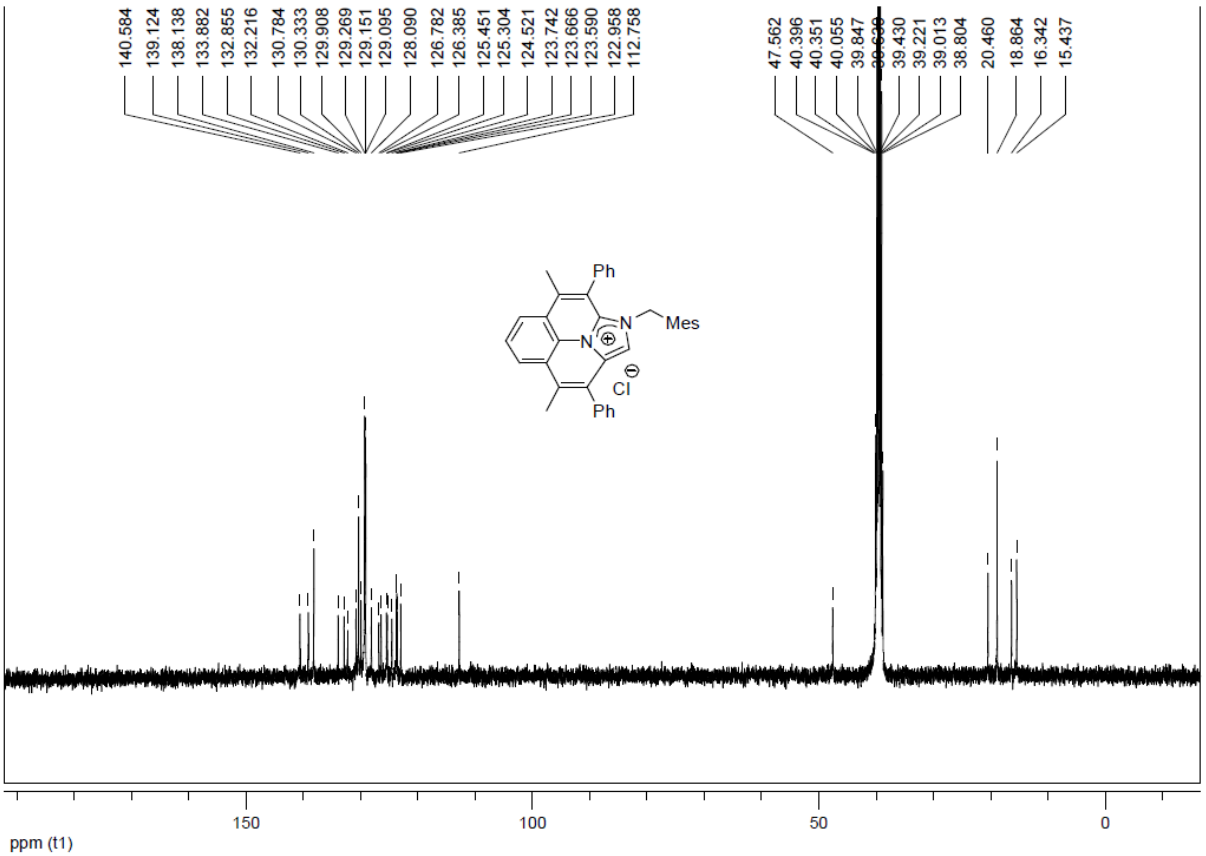
^{13}C NMR spectrum of 4ag



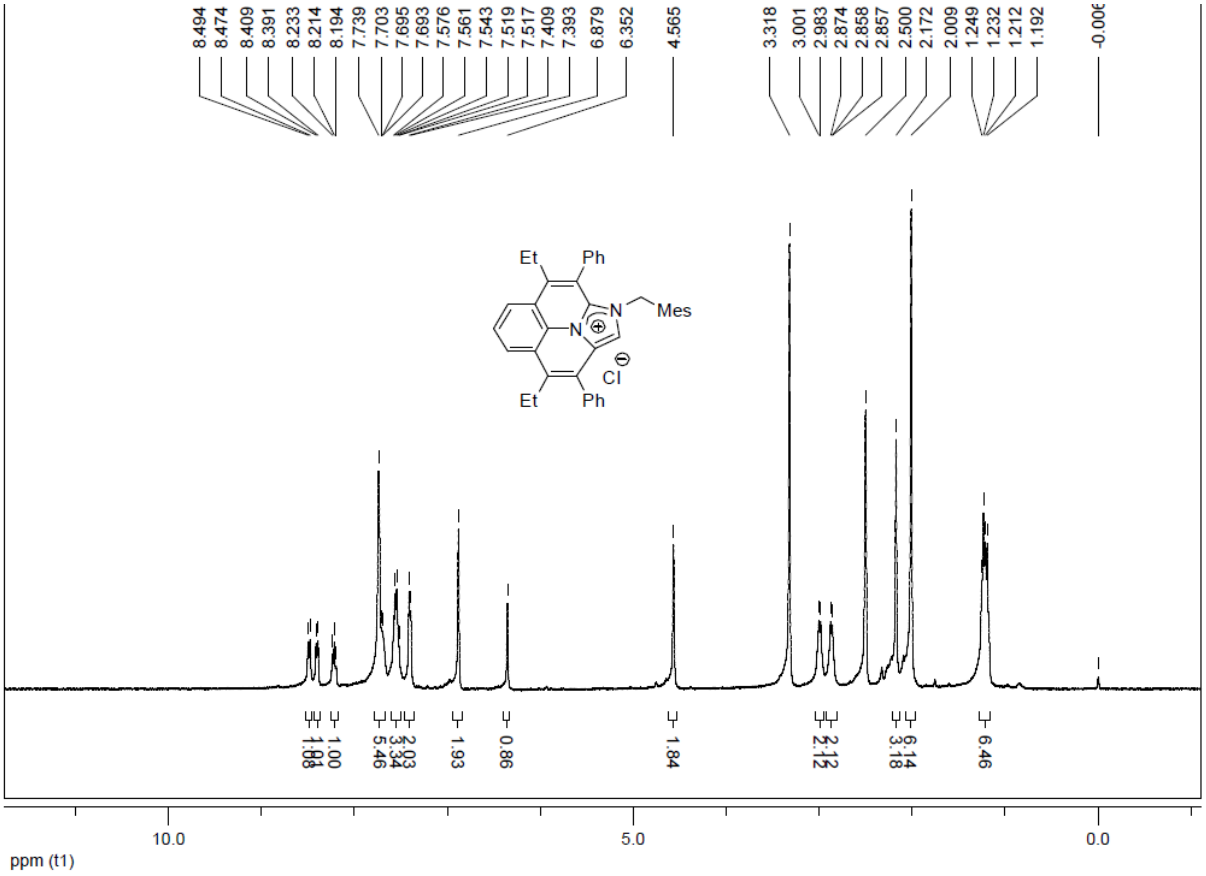
^{1}H NMR spectrum of 4ai



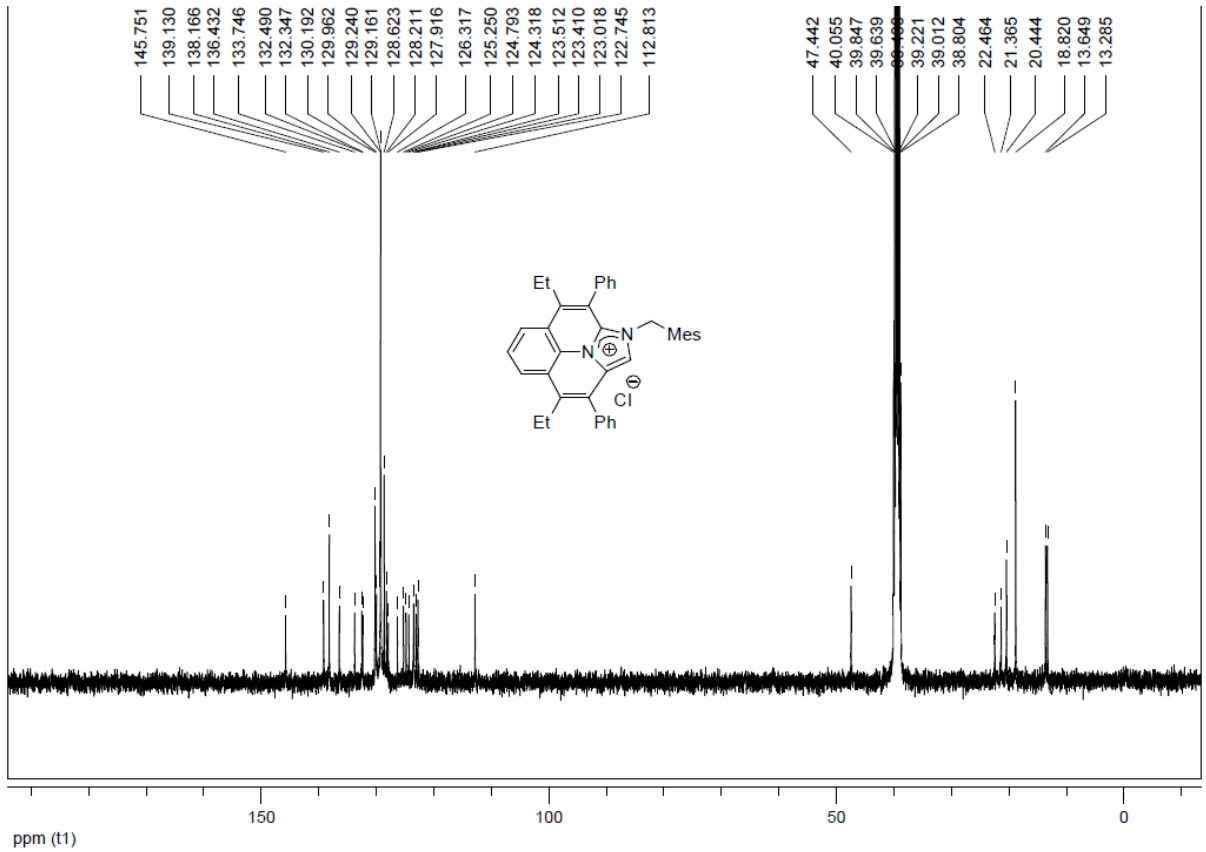
^{13}C NMR spectrum of 4ai



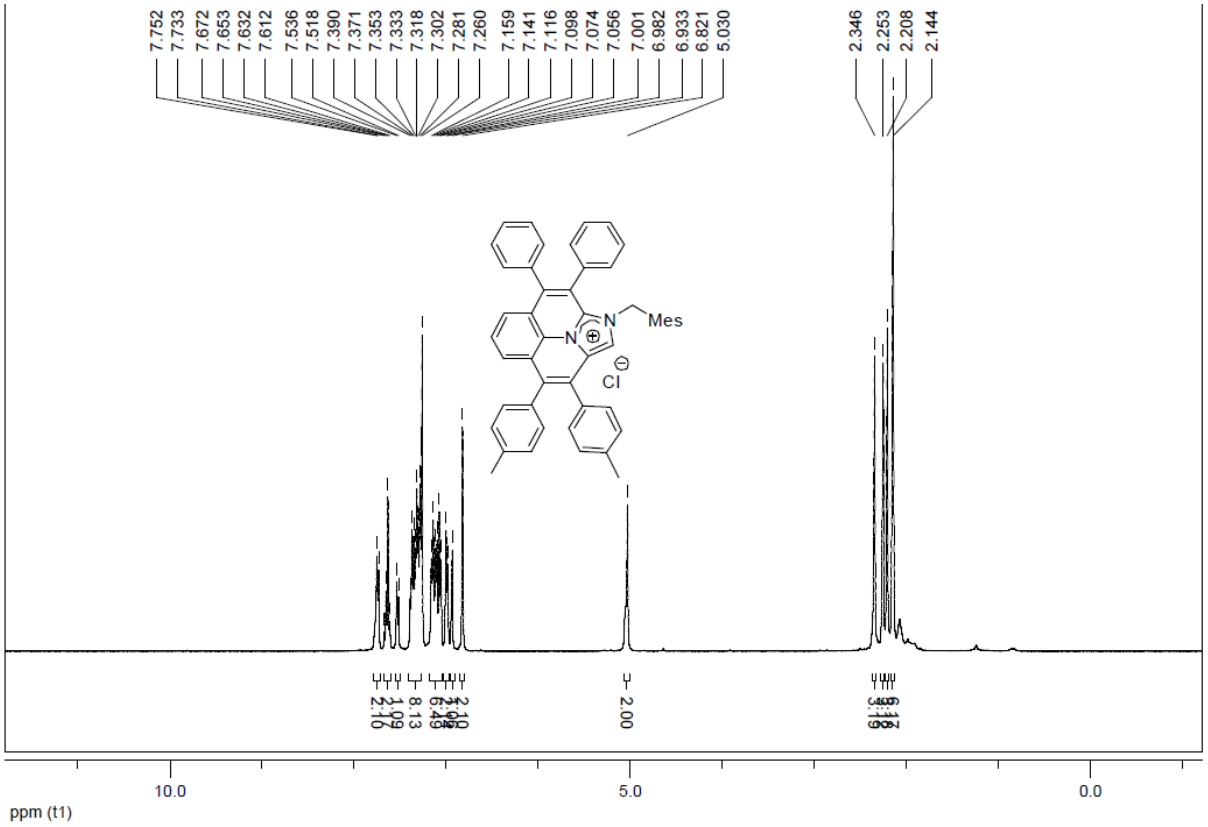
^{1}H NMR spectrum of 4aj



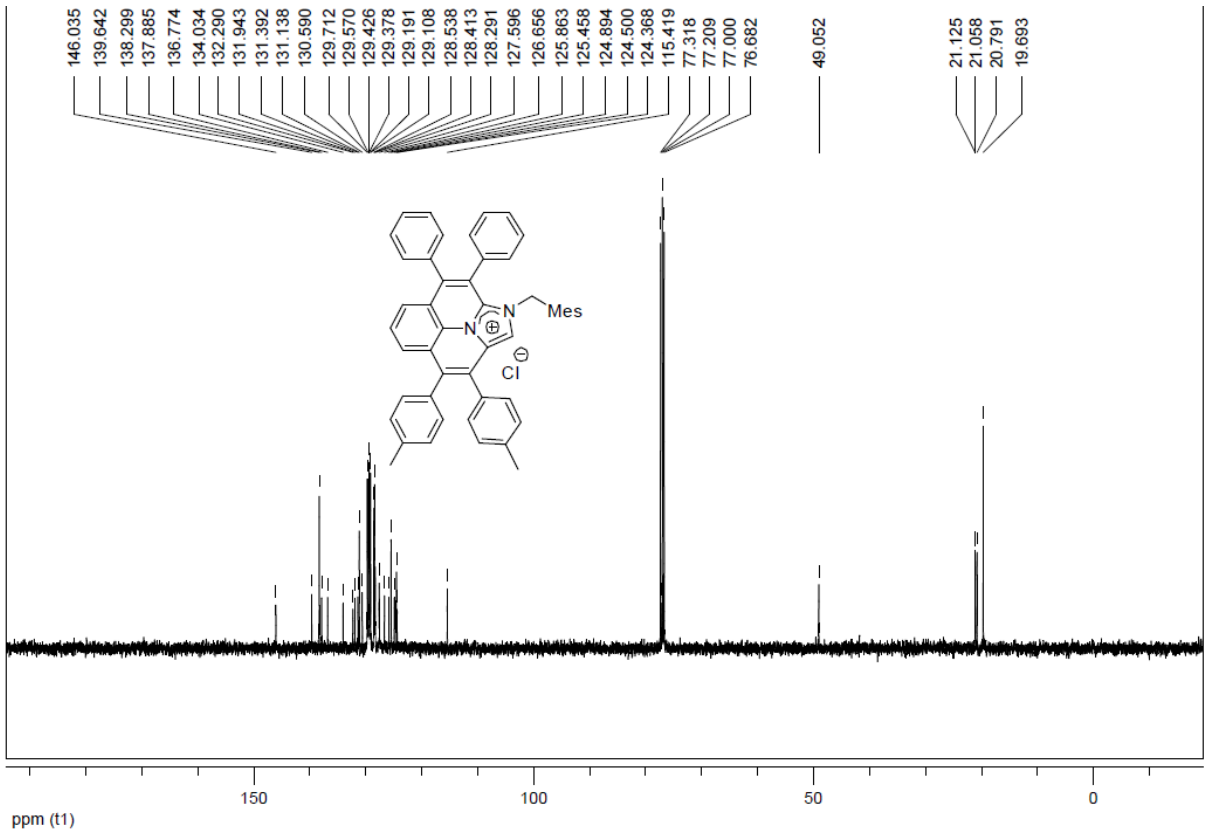
^{13}C NMR spectrum of 4aj



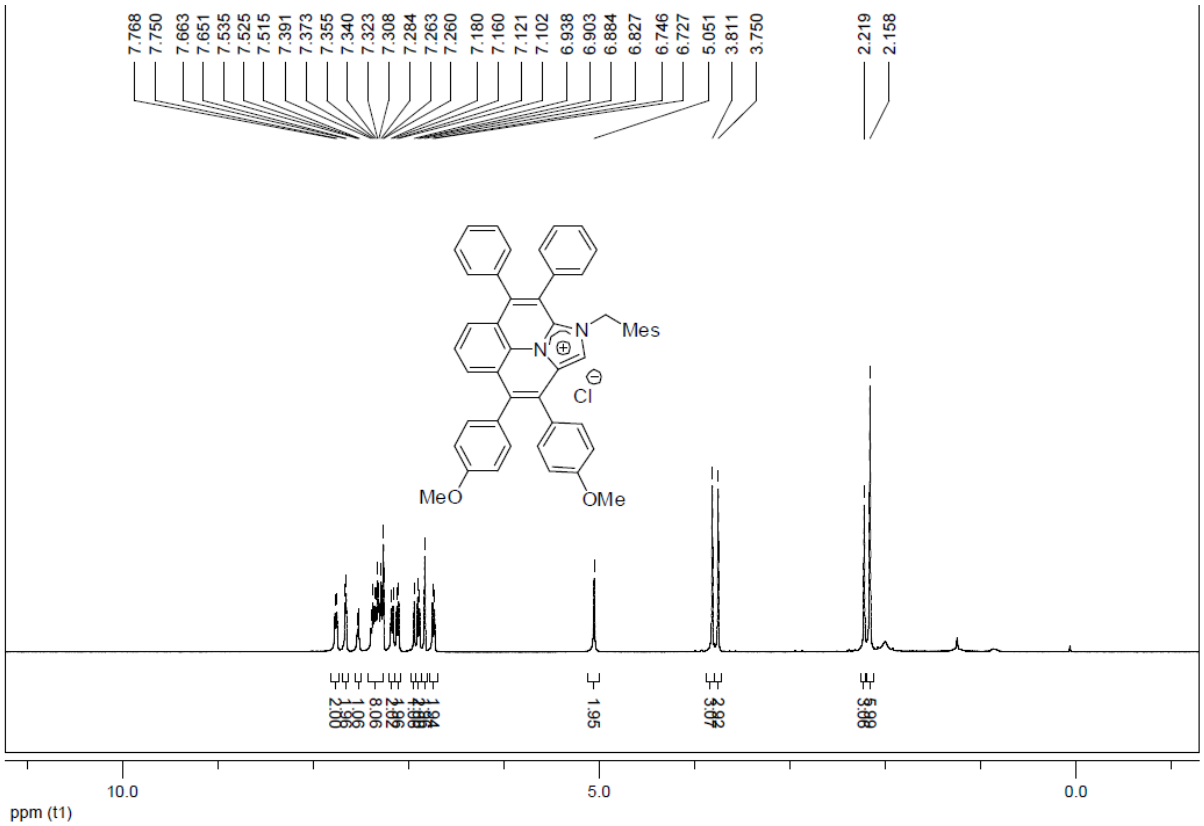
^{1}H NMR spectrum of 4ae’



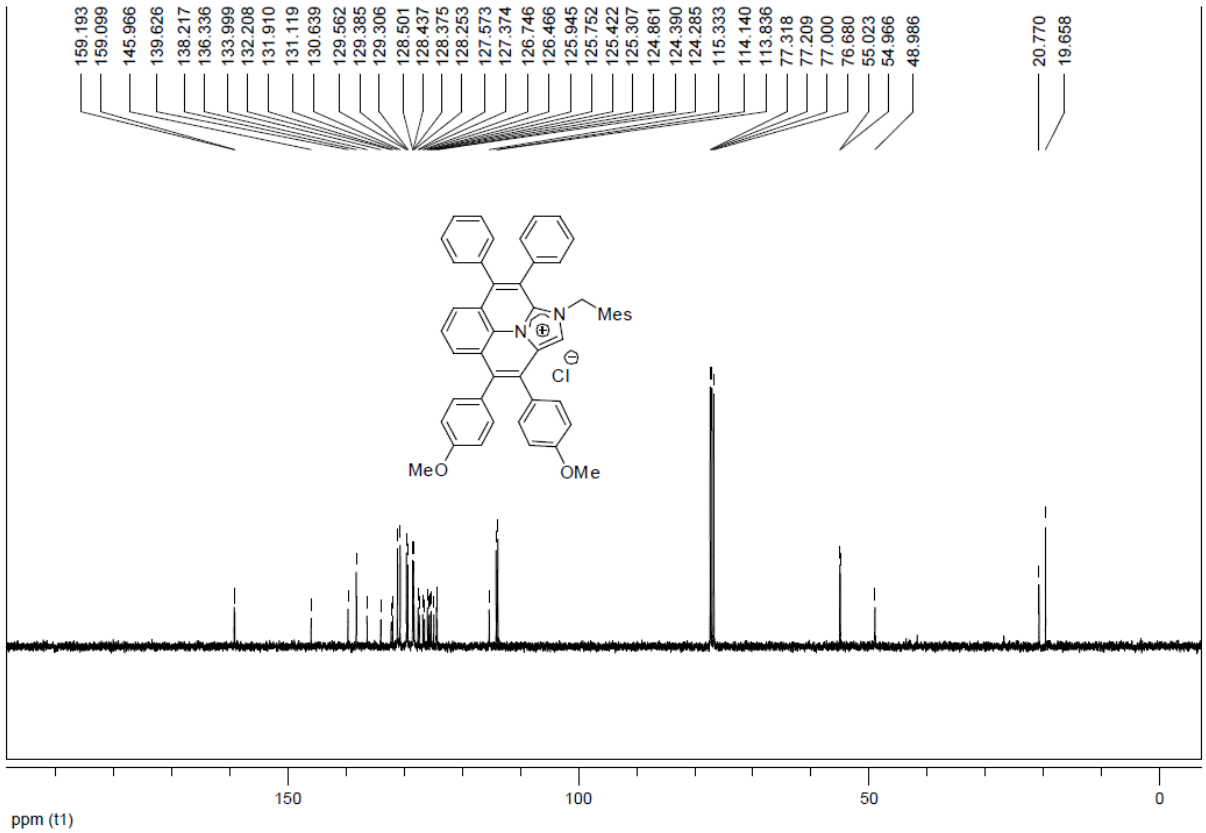
^{13}C NMR spectrum of 4ae’



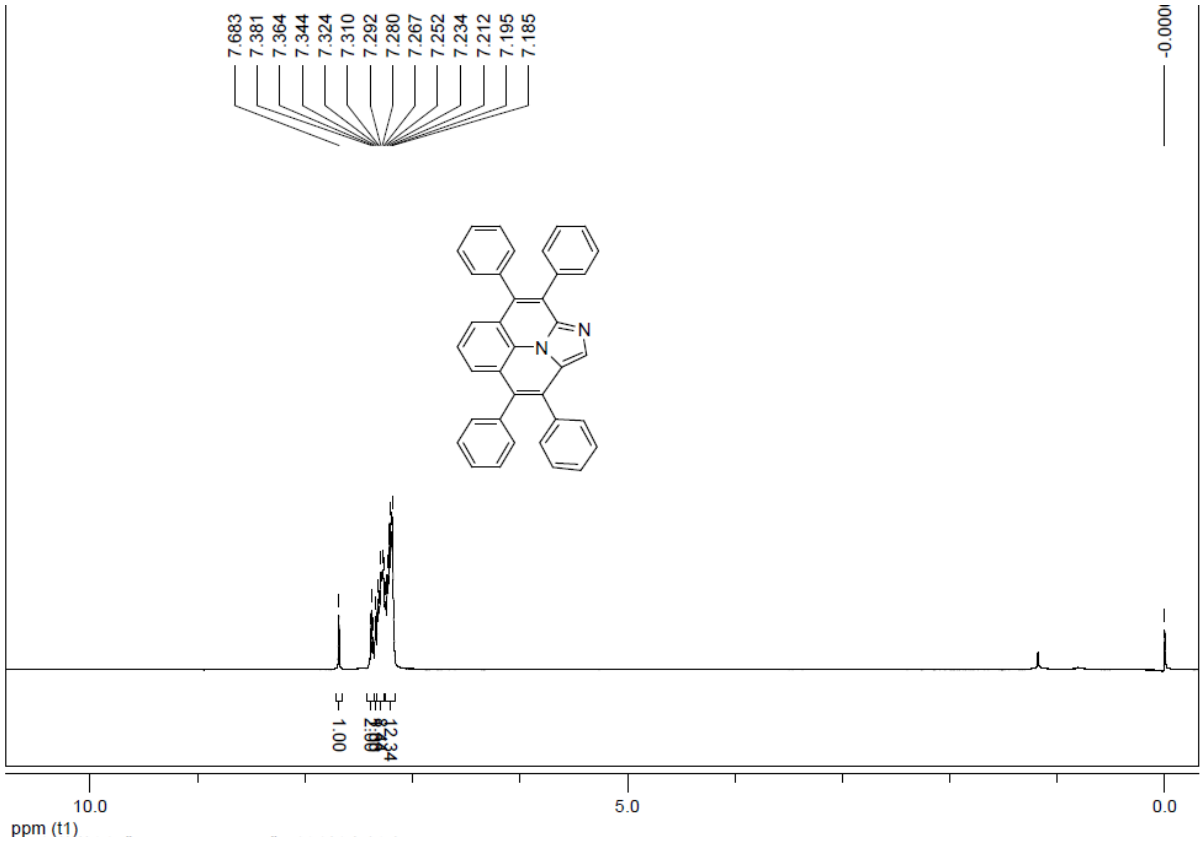
^{1}H NMR spectrum of 4af’



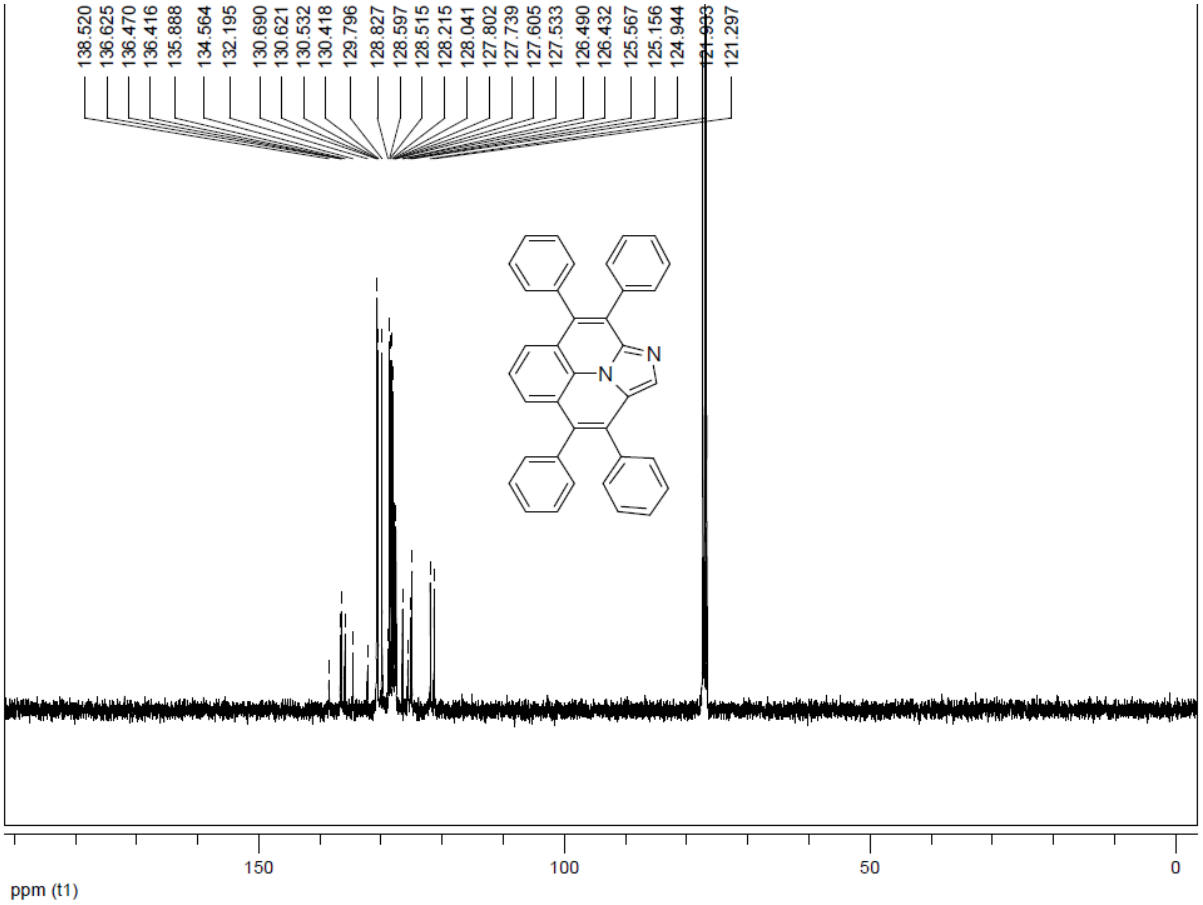
^{13}C NMR spectrum of 4af’



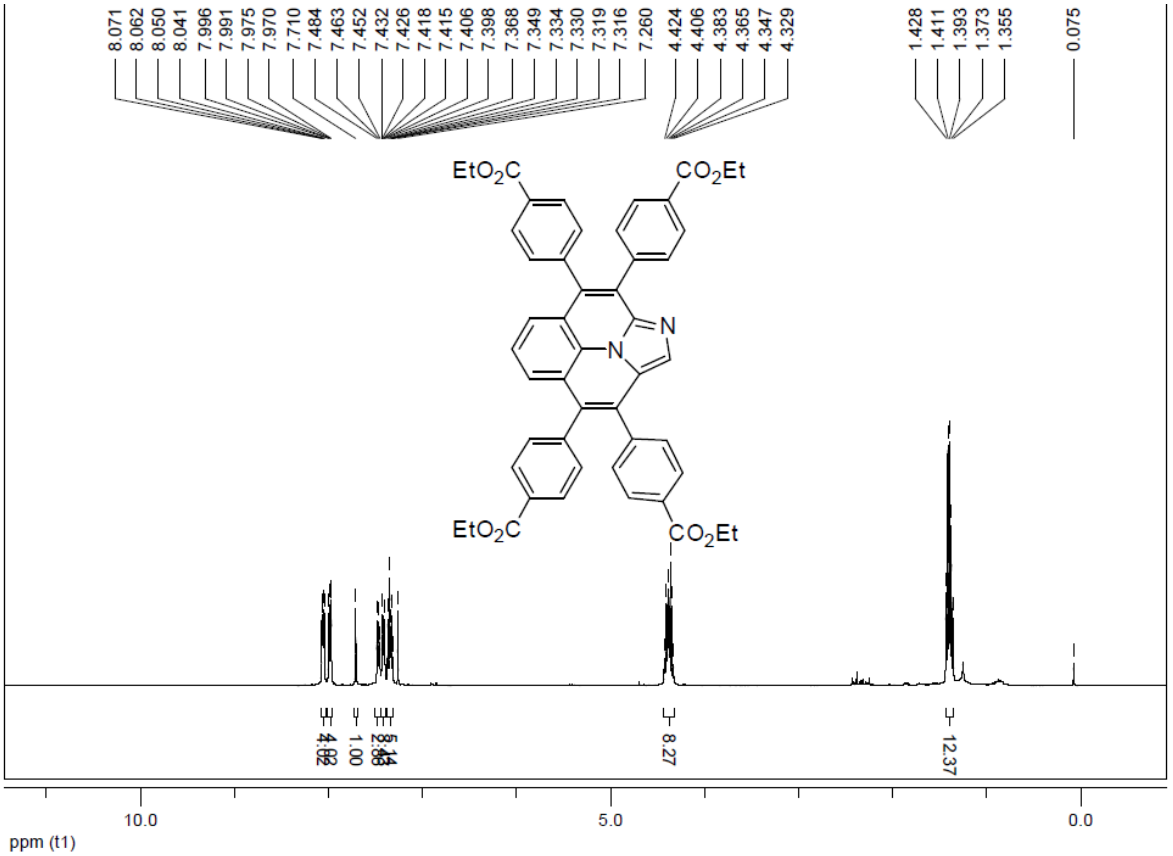
^{1}H NMR spectrum of 5aa



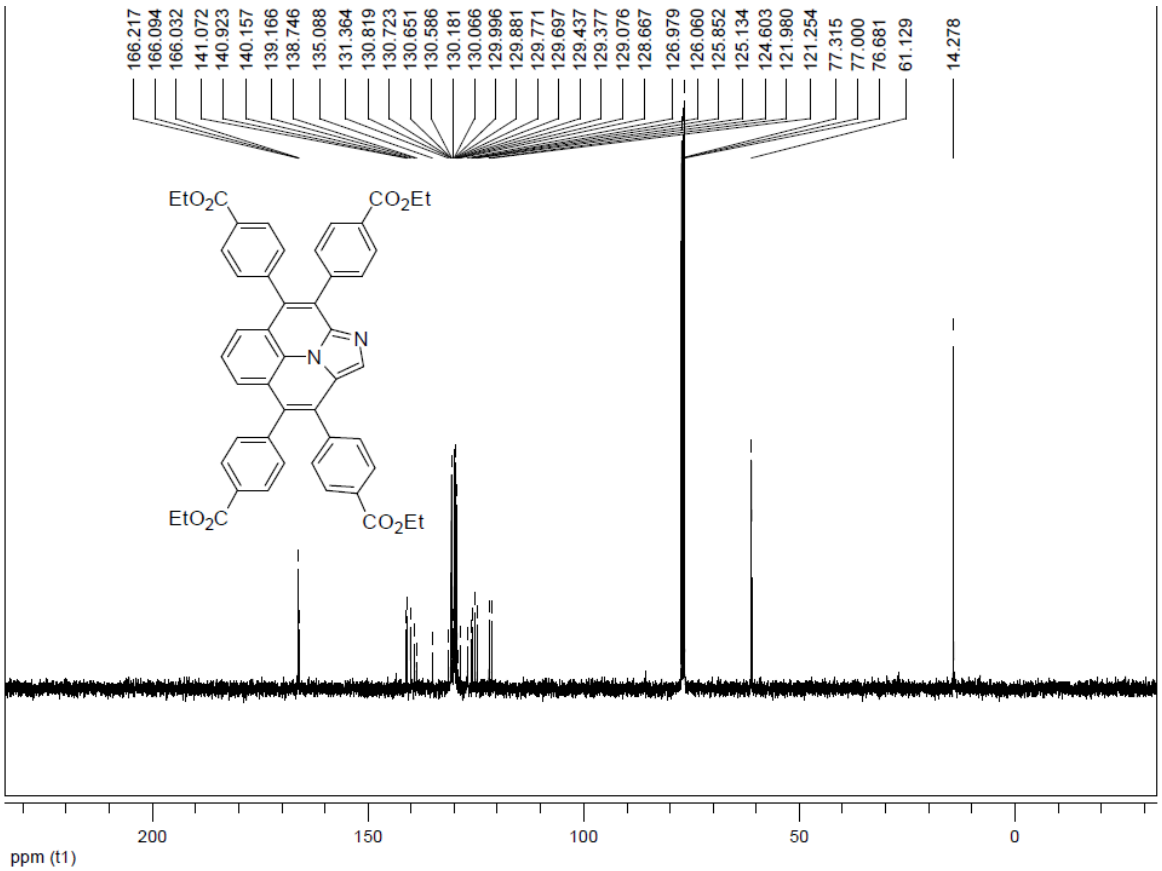
^{13}C NMR spectrum of 5aa



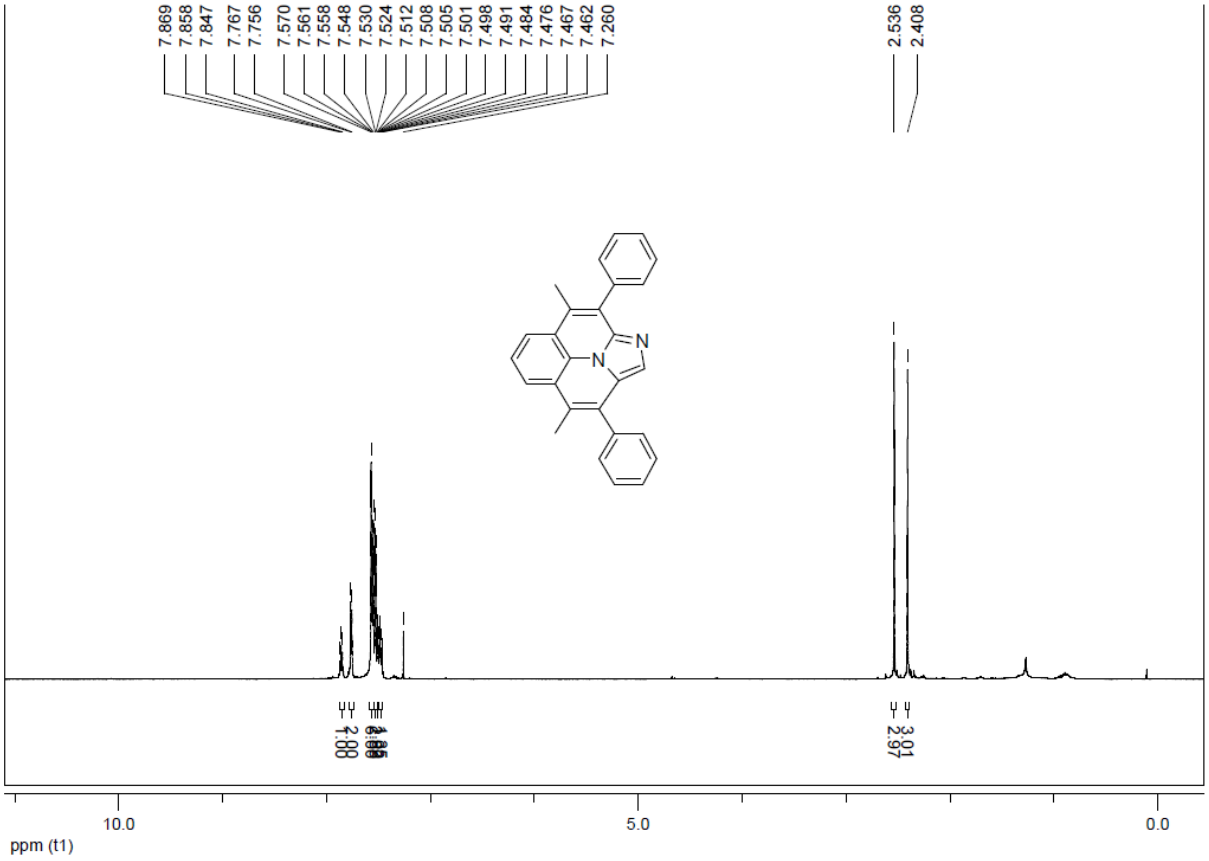
^{1}H NMR spectrum of 5ag



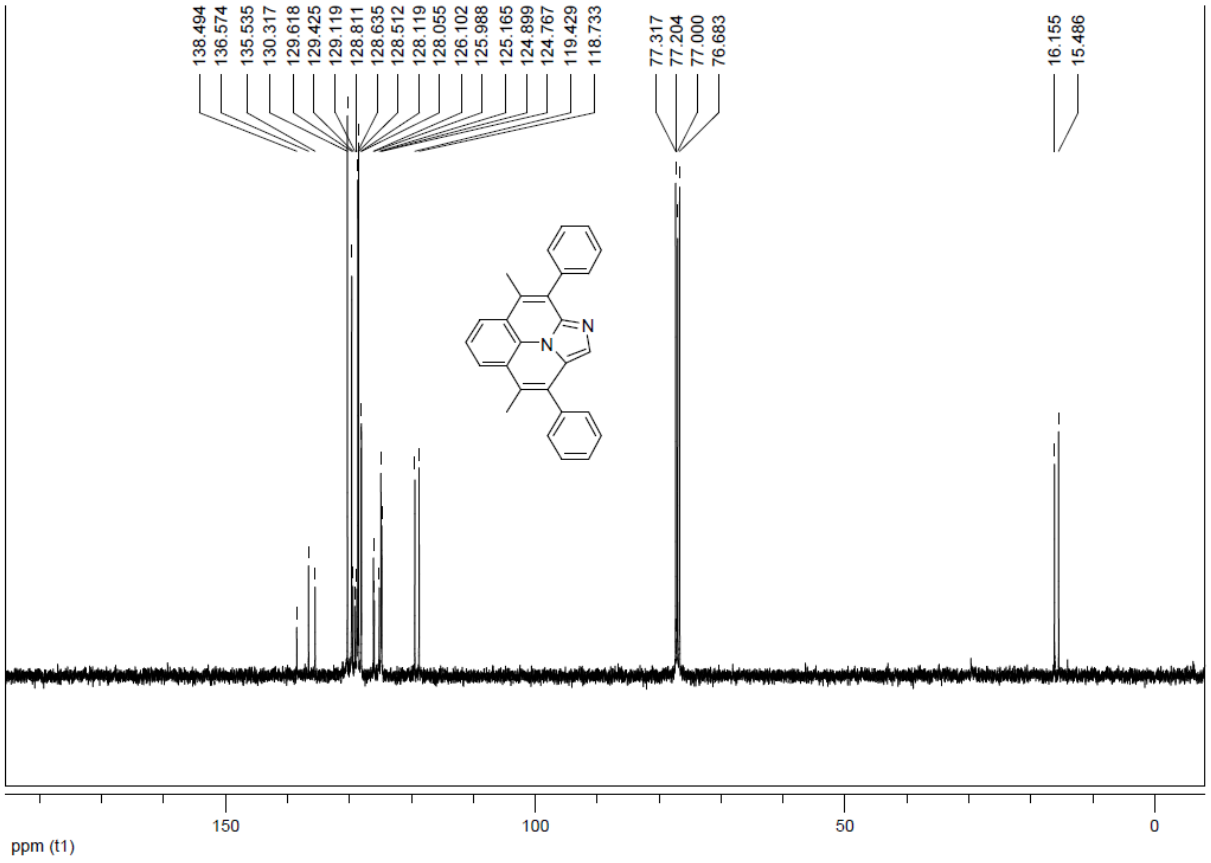
^{13}C NMR spectrum of 5ag



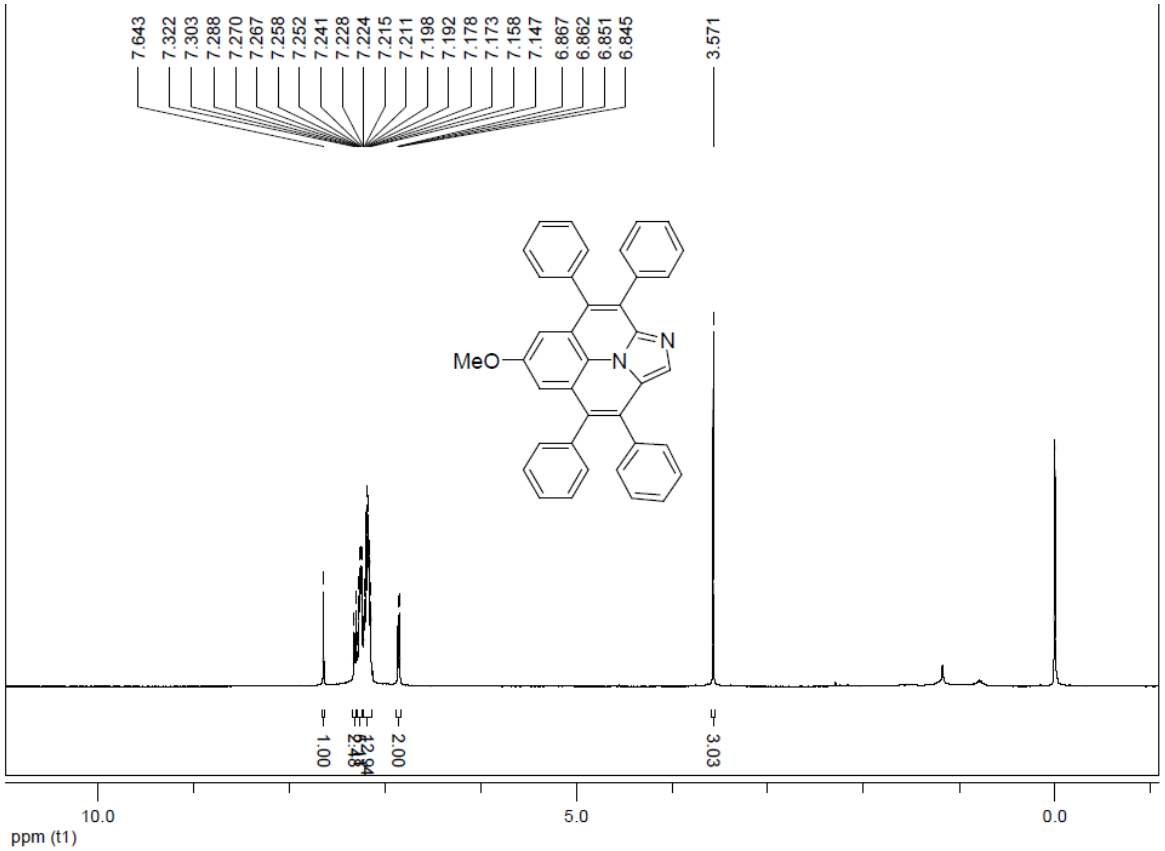
^{1}H NMR spectrum of 5ai



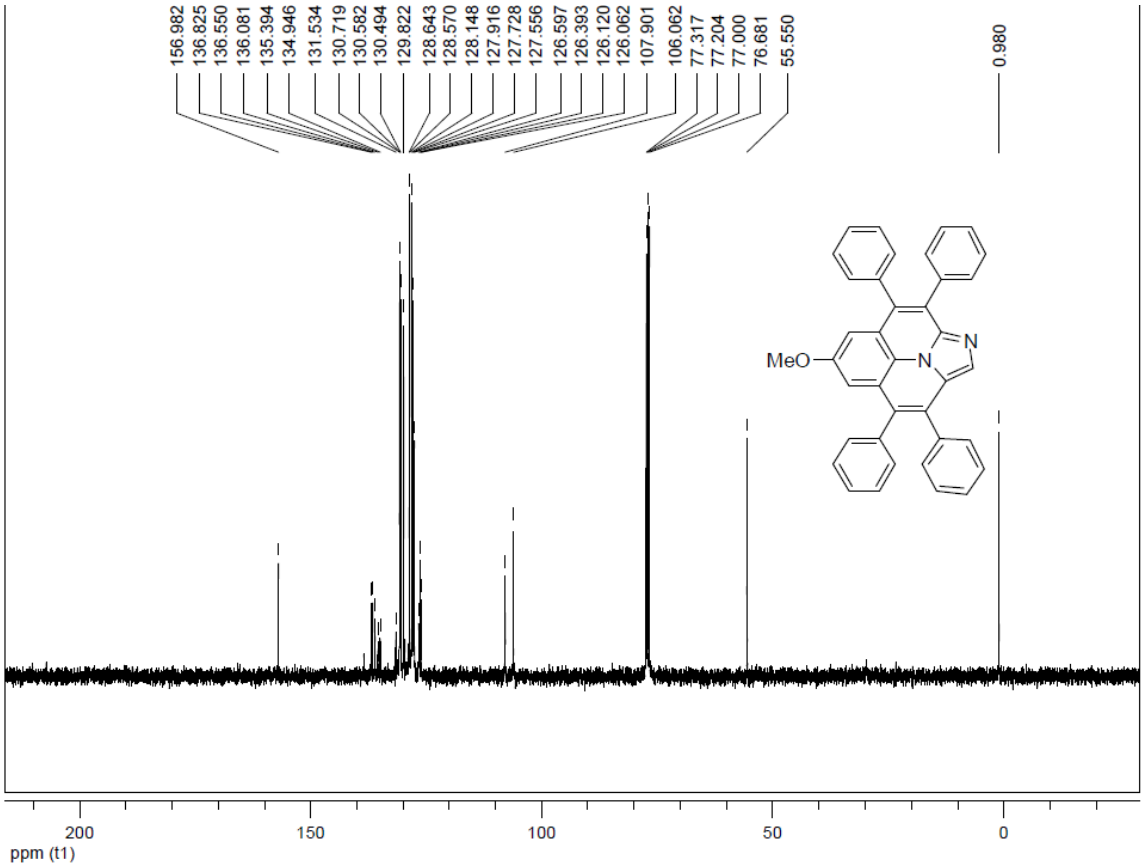
^{13}C NMR spectrum of 5ai



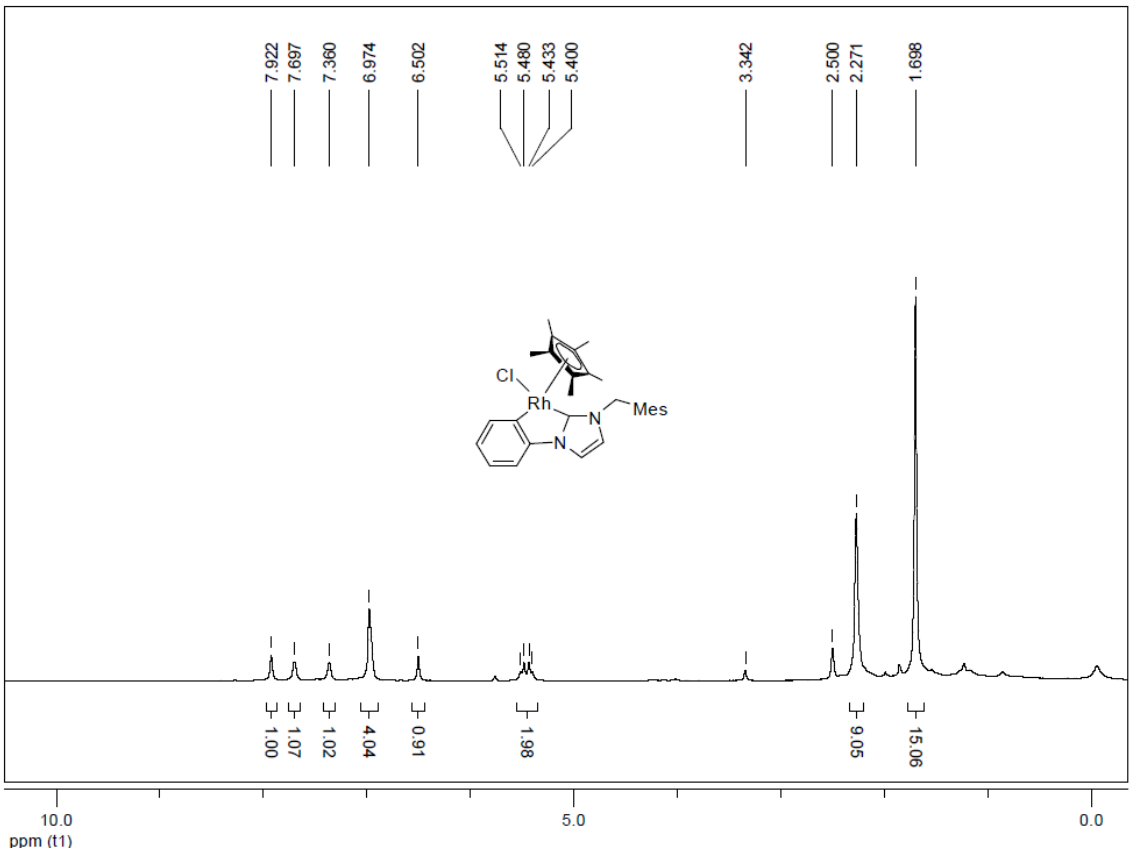
^{1}H NMR spectrum of 5fa



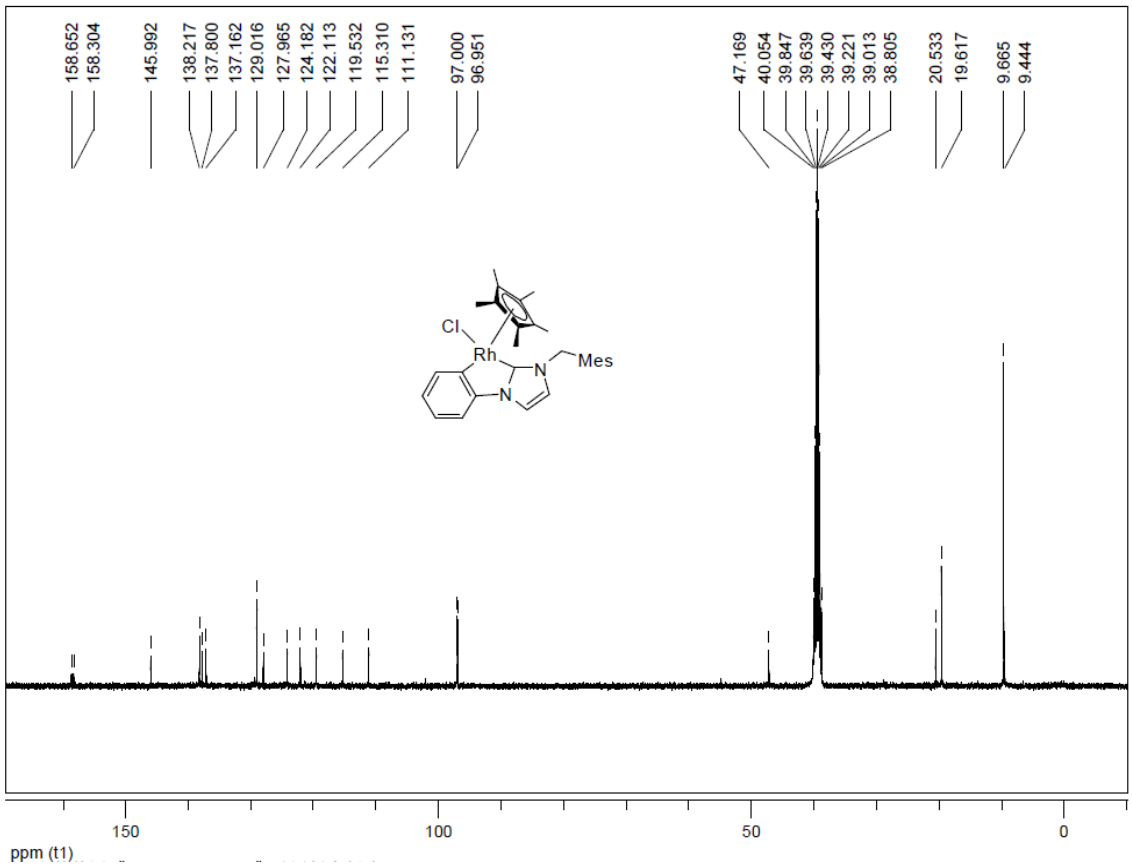
^{13}C NMR spectrum of 5fa



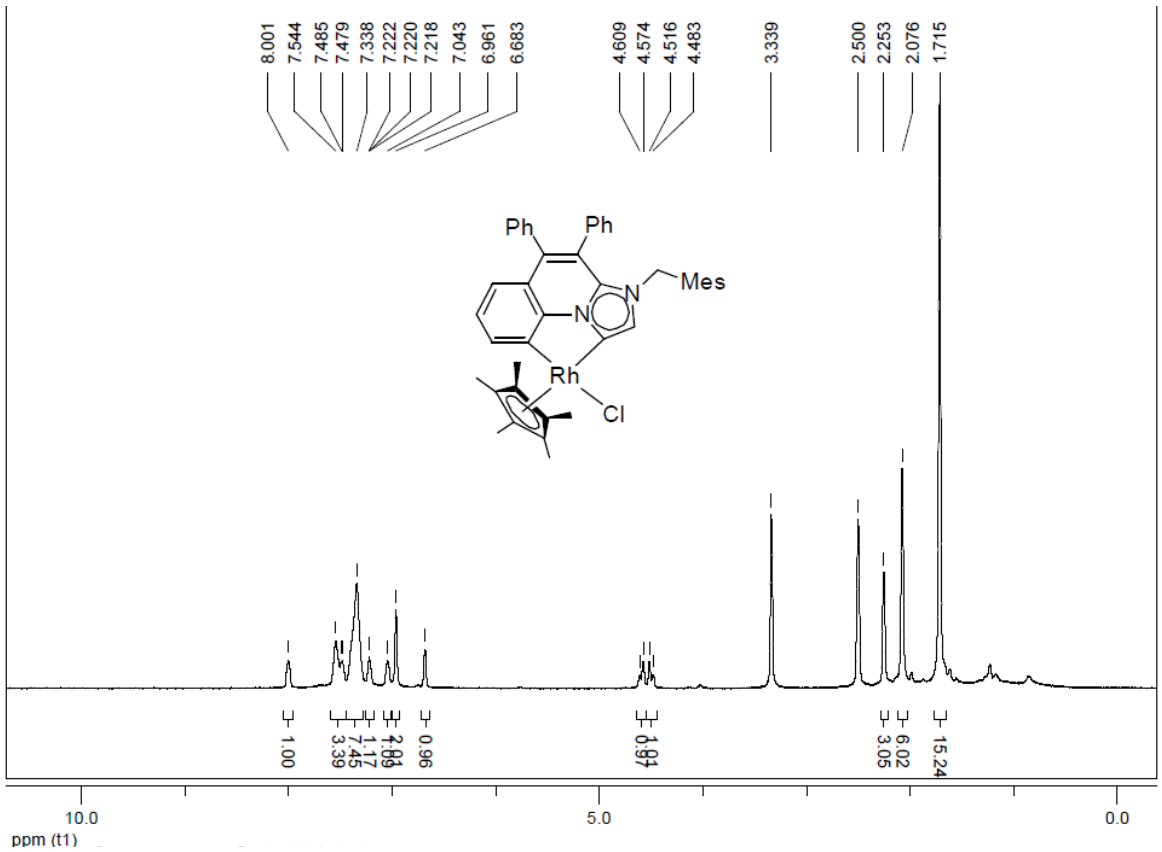
^{1}H NMR spectrum of intermediate A



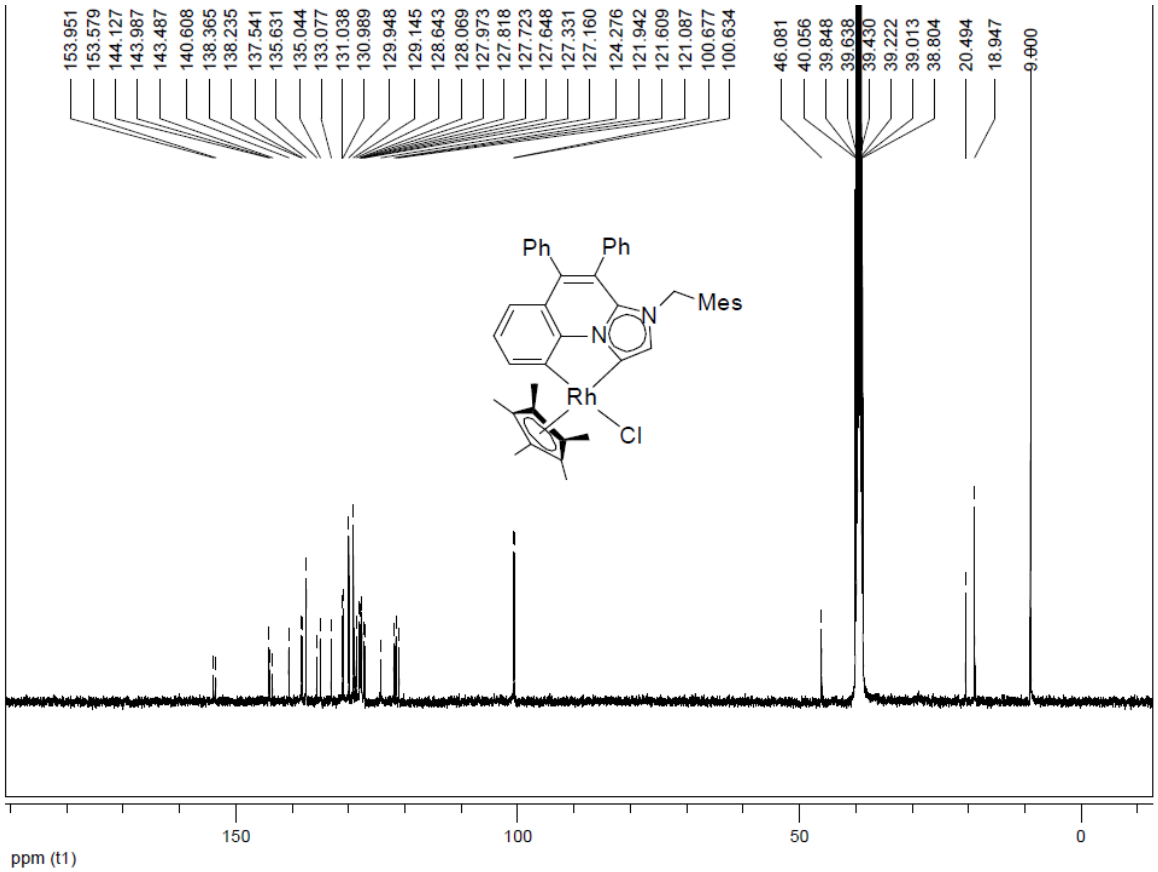
^{13}C NMR spectrum of intermediate A



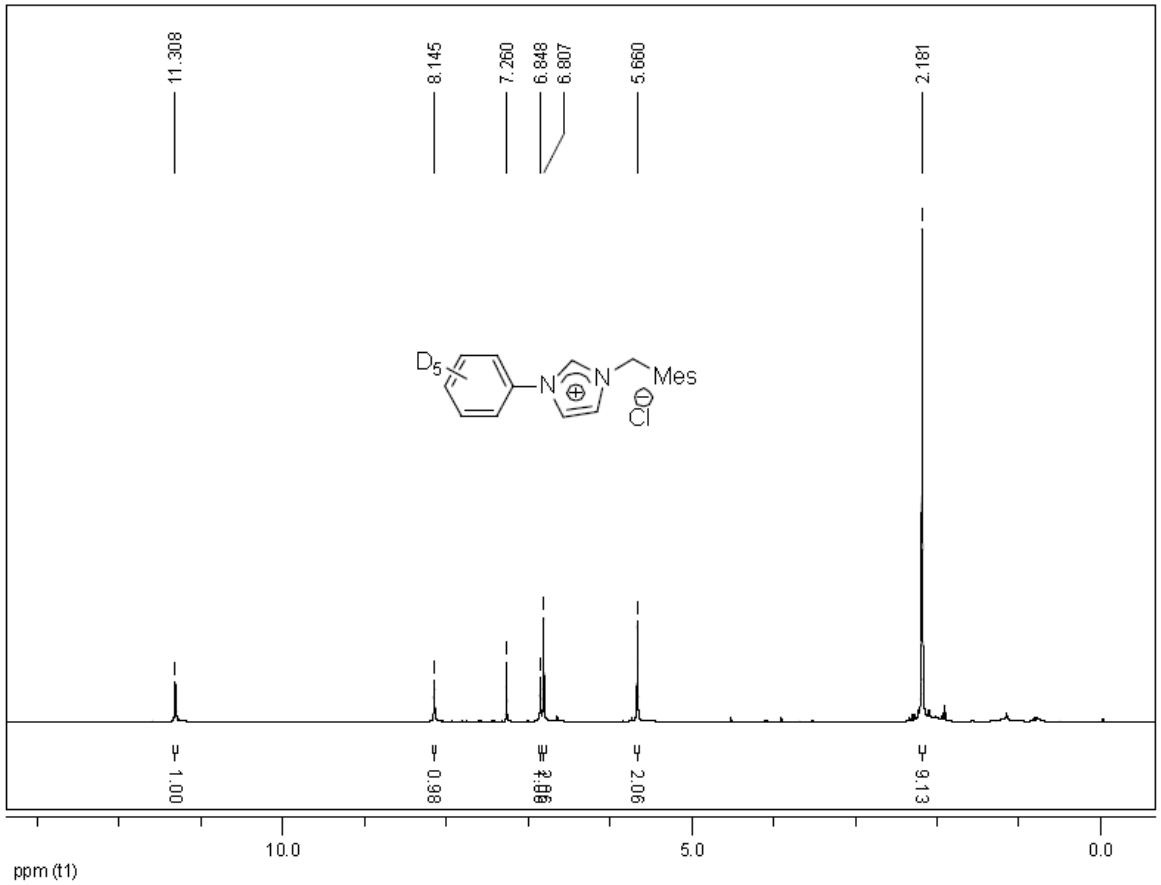
^{1}H NMR spectrum of intermediate B



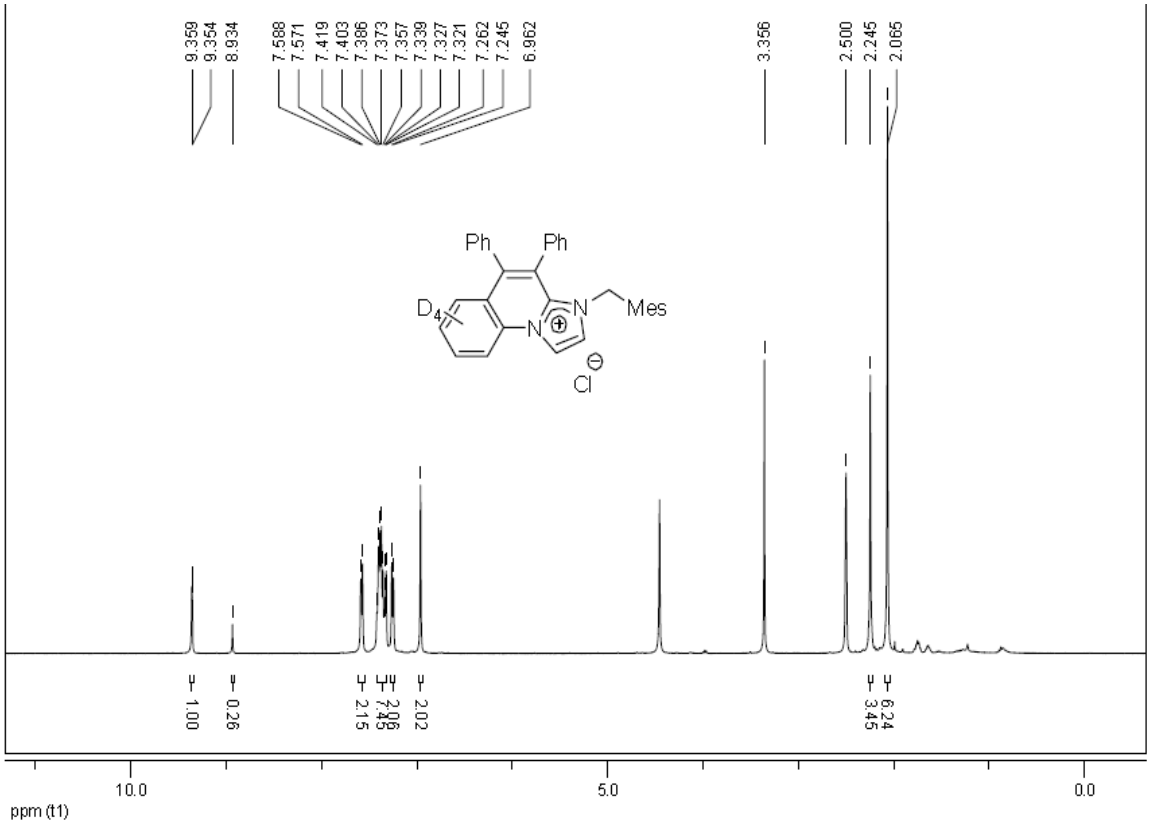
^{13}C NMR spectrum of intermediate B



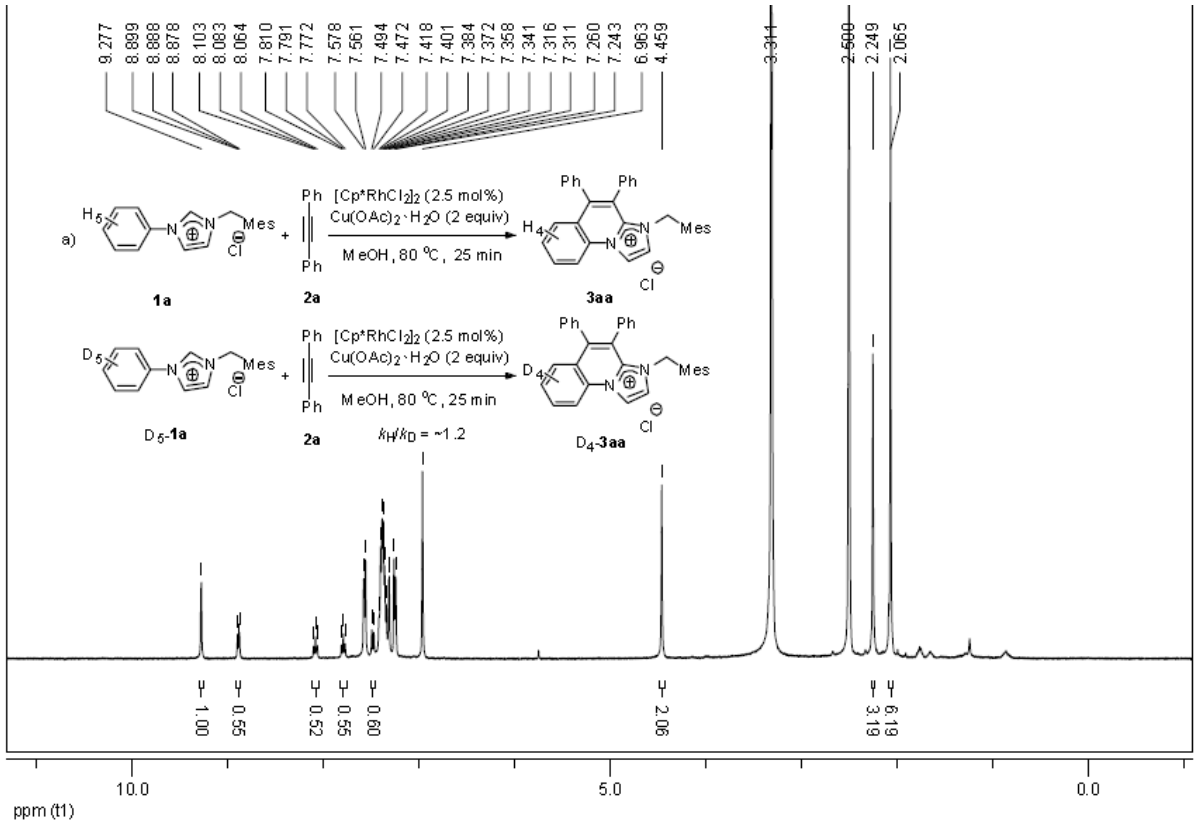
^{1}H NMR spectrum of 1a-d_5

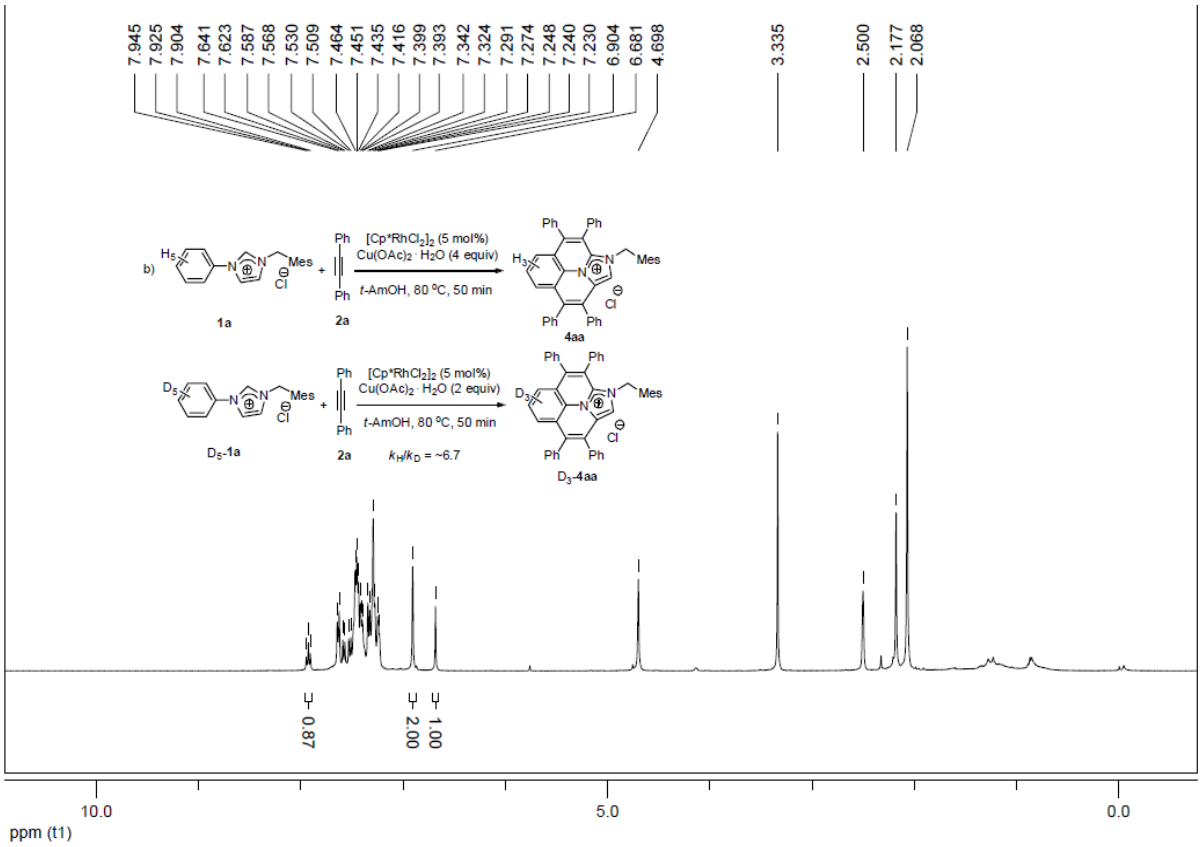


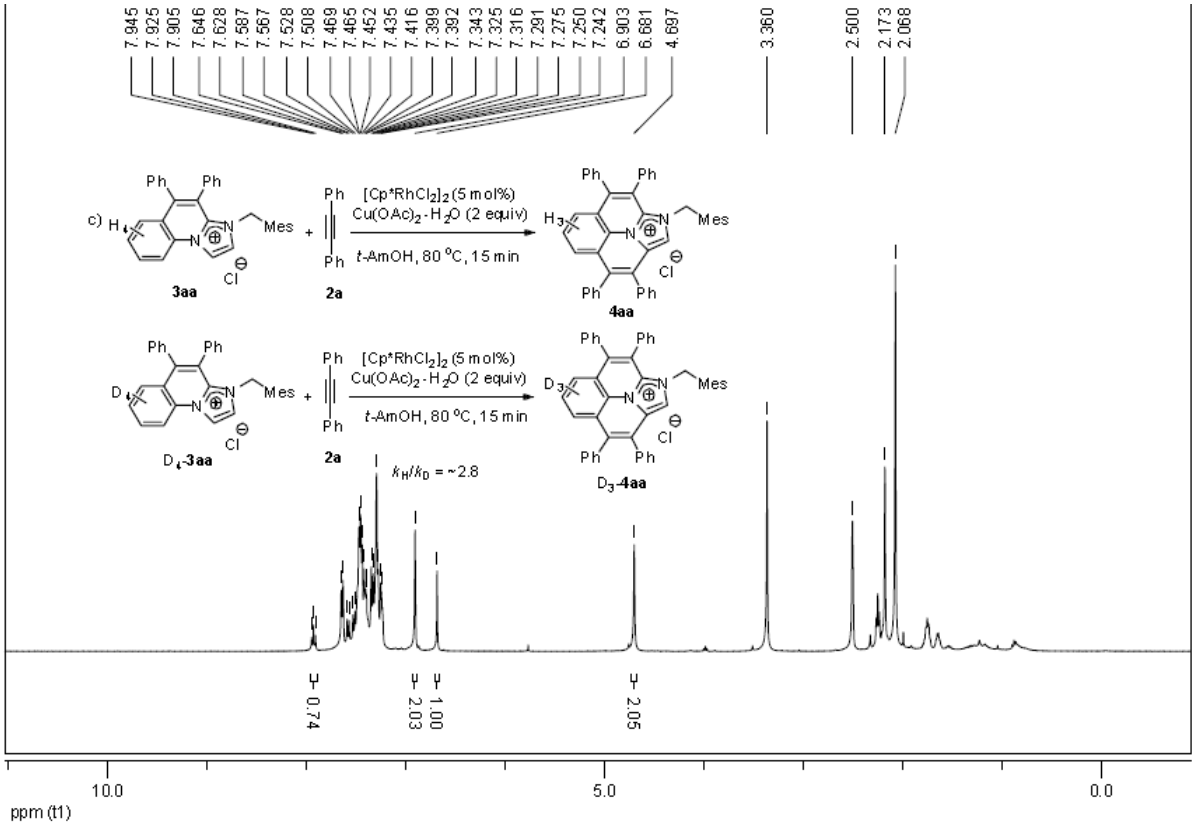
^{1}H NMR spectrum of 3aa-d_4



KIE experiments.






7.945
7.925
7.905
7.646
7.628
7.587
7.567
7.528
7.508
7.469
7.465
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7.435
7.416
7.399
7.392
7.343
7.325
7.316
7.291
7.275
7.250
7.242
6.903
6.681
4.697
3.360
2.500
2.173
2.068
c)
3aa
2a
[Cp*RhCl2]2 (5 mol%)
Cu(OAc)2·H2O (2 equiv)
t-AmOH, 80 °C, 15 min
4aa
D4-3aa
D3-4aa
kH/kD = ~2.8
0.74
2.03
1.00
2.05
10.0
5.0
0.0
ppm (t1)