Supporting Information

Synthesis of unsymmetrical imidazolium salts by direct quaternization of *N*-substituted imidazoles using arylboronic acids

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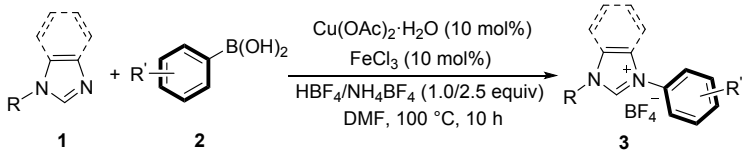
I. General Remarks

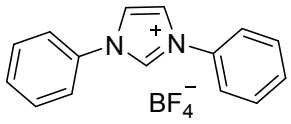
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. CuI was washed with THF using a Soxhlet extractor prior to use. Reactions were carried out under ambient atmosphere unless otherwise specified. All the known *N*-arylimidazole derivatives,[1-3] *N*-mesitylimidazole,[4] N-(2,6-diisopropylphenyl)imidazole,[5] *N*-*tert*-butylimidazole[5] and (R)-1-(1-phenylethyl)-1*H*-imidazole[6] were synthesized according to the literature procedures. NMR spectra were obtained on a Bruker AMX-400. The ^{1}H NMR (400 MHz) chemical shifts were reported relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm; The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected. The optical rotation was obtained on an Autopol® V instrument and reported as: $[\alpha]_D^t$ (c g/100 mL, in CH_2Cl_2).

II. General procedure for the direct quaternization of *N*-Substituted Imidazoles with arylboronic acids

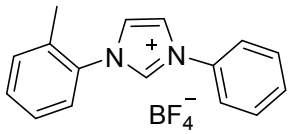


A Schlenck tube with a magnetic stir bar was charged with a *N*-substituted imidazole (0.25 mmol, 1.0 equiv), an arylboronic acid (0.375 mmol, 1.5 equiv), $Cu(OAc)_2 \cdot H_2O$ (5 mg, 10 mol%), $FeCl_3$ (4 mg, 10 mol%), HBF_4 (40 μL, 0.25 mmol, 1.0 equiv, 40% wt in aqueous solution), NH_4BF_4 (66 mg, 2.5 equiv) and DMF (1 mL). The reaction mixture was stirred at 100 °C for 10 h in an oil bath and then cooled down to room temperature. The solvent was removed under reduced pressure, and the residue was passed through a silica gel column eluted with dichloromethane/methanol (v/v, 70/1−20/1) to afford the desired product.

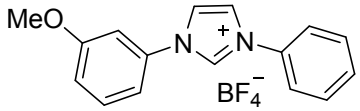
III. Characterization data of the products



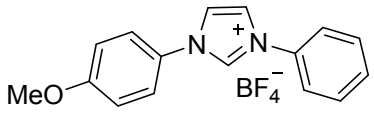
1,3-Diphenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3aa).[7] A white solid (71 mg, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.64 (t, J = 7.4 Hz, 2H), 7.72 (t, J = 7.8 Hz, 4H), 7.93 (d, J = 7.6 Hz, 4H), 8.58 (d, J = 1.2 Hz, 2H), 10.34 (t, J = 1.6 Hz, 1H) ppm.



3-Phenyl-1-o-tolyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ba or 3ab).[7] A gray solid (66 mg, 81% yield; **3ab**: 25 mg, 31% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.33 (s, 3H), 7.52−7.74 (m, 7H), 7.91 (d, J = 8.0 Hz, 2H), 8.35 (t, J = 1.6 Hz, 1H), 8.59 (t, J = 1.8 Hz, 1H), 10.11 (s, 1H) ppm.

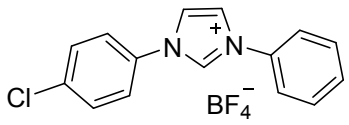


1-(3-Methoxyphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ca or 3ac).[7] **A** gray solid (**3ca**: 59 mg, 70% yield; **3ac**: 55 mg, 65% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.89 (s, 3H), 7.21 (dd, J = 8.4, 2.4 Hz, 1H), 7.50 (dd, J = 8.0, 2.0 Hz, 1H), 7.55 (t, J = 2.2 Hz, 1H), 7.61−7.66 (m, 2H), 7.73 (t, J = 7.6 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H), 8.59 (t, J = 1.8, 1H), 8.61 (t, J = 1.8, 1H), 10.34 (t, J = 1.6, 1H) ppm.

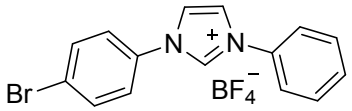


1-(4-Methoxyphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3da or 3ad).[7] **A** gray solid (**3da**: 60 mg, 71% yield; **3ad**: 59 mg, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.87 (s, 3H), 7.25 (d, J = 6.4 Hz, 2H), 7.63 (br, 1H), 7.71 (br, 2H), 7.84 (d, J = 6.4 Hz, 2H), 7.91 (d, J = 4.8 Hz, 2H), 8.49 (s, 1H), 8.54 (s, 1H),

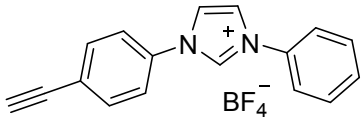
10.25 (s, 1H) ppm.



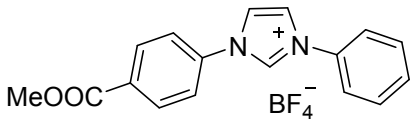
1-(4-Chlorophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ea).[7] A gray solid (57 mg, 67% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.64 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 7.8 Hz, 2H), 7.83 (d, J = 9.2 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 8.58 (s, 2H), 10.36 (s, 1H) ppm.



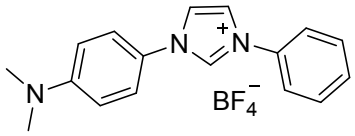
1-(2-Bromophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3fa or 3ah).[7] A white solid (**3fa**: 63 mg, 66% yield; **3ah**: 77 mg, 80% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.65 (t, J = 7.4 Hz, 1H), 7.73 (t, J = 7.8 Hz, 2H), 7.89−7.93 (m, 4H), 7.97 (d, J = 8.8 Hz, 2H), 8.588 (s, 1H), 8.59 (s, 1H), 10.36 (s, 1H) ppm.



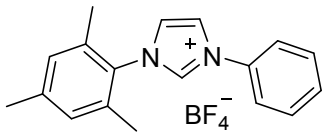
1-(4-Ethynylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ga).[7] A yellow solid (47 mg, 57% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.46 (s, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 8.59 (s, 1H), 8.61 (s, 1H), 10.38 (s, 1H) ppm.



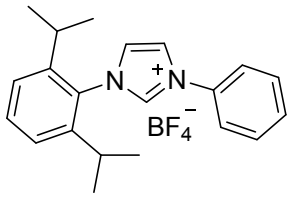
1-(4-(Methoxycarbonyl)phenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ha).[7] A yellow solid (82 mg, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.92 (s, 3H), 7.64 (t, J = 7.4 Hz, 1H), 7.73 (t, J = 7.6 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 8.27 (d, J = 8.8 Hz, 2H), 8.61 (t, J = 1.8 Hz, 1H), 8.67 (t, J = 1.8 Hz, 1H), 10.47 (s, 1H) ppm.



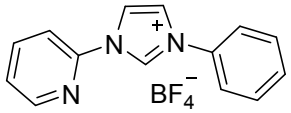
1-[4-(Dimethylamino)phenyl]-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ia).[7] A yellow solid (57 mg, 65% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.01 (s, 6H), 6.92 (d, J = 9.2 Hz, 2H), 7. 60−7. 64 (m, 1H), 7. 68−7. 72 (m, 4H), 7.91 (d, J = 8.0 Hz, 2H), 8.44 (t, J = 2.0 Hz, 1H), 8.51 (t, J = 1.8 Hz, 1H), 10.17 (t, J = 1.6 Hz, 1H) ppm.



1-Mesityl-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ja).[7] A gray solid (58 mg, 66% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.13 (s, 6H), 2.35 (s, 3H), 7.19 (s, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.71 (t, J = 7.6 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 8.20 (t, J = 1.6 Hz, 1H), 8.65 (t, J = 1.8 Hz, 1H), 10.03 (t, J = 1.4 Hz, 1H) ppm.

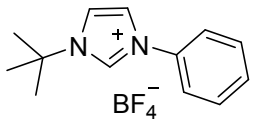


1-(2,6-Diisopropylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ka).[7] A gray solid (48 mg, 49% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.17 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H), 2.42−2.47 (m, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.62−7.74 (m, 4H), 7.91 (d, J = 8.0 Hz, 2H), 8.37 (s, 1H), 8.71 (s, 1H), 10.24 (s, 1H) ppm.

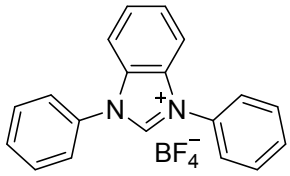


3-Phenyl-1-(pyridin-2-yl)-1*H*-imidazol-3-ium Tetrafluoroborate (3la).[7] A gray solid (58 mg, 75% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.63−7.66 (m, 1H), 7.69−7.72 (m, 3H), 7.94 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.4 Hz, 1H), 8.28 (td, J = 7.8, 2.0 Hz, 1H), 8.58 (t, J = 2.0 Hz, 1H), 8.71−8.72 (m, 1H), 8.76 (t, J = 2.0 Hz, 1H),

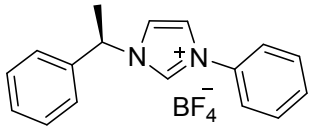
10.59 (t, J = 1.6 Hz, 1H) ppm.



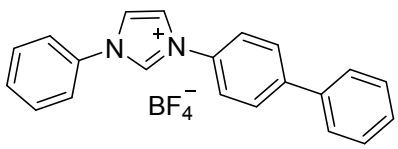
1-*tert*-Butyl-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ma).[7] A gray solid (65 mg, 91% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.66 (s, 9H), 7.59 (t, J = 7.2 Hz, 1H), 7.67 (t, J = 7.8 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 8.28 (t, J = 2.0 Hz, 1H), 8.38 (t, J = 1.8 Hz, 1H), 9.69 (t, J = 1.6 Hz, 1H) ppm.



1,3-Diphenyl-1*H*-benzo[*d*]imidazol-3-ium Tetrafluoroborate (3na).[7] A gray solid (41 mg, 46% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.74−7.83 (m, 8H), 7.93−7.98 (m, 6H), 10.58 (s, 1H) ppm.

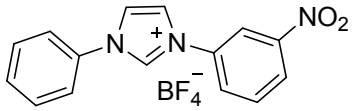


(*R*)-3-Phenyl-1-(1-phenylethyl)-1*H*-imidazol-3-ium Tetrafluoroborate (3oa). A gray semisolid (76 mg, 90% yield). $[\alpha]_D^{12.7}$ = +36.3 (c = 3.01, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (d, J = 6.8 Hz, 3H), 5.91 (q, J = 6.8 Hz, 1H), 7.34−7.39 (m, 3H), 7.43−7.48 (m, 6H),7.60 (d, J = 6.8 Hz, 2H), 7.66 (s, 1H), 9.33 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 60.6, 121.7, 121.8, 122.1, 127.3, 129.6, 129.7, 130.4, 130.6, 133.5, 134.5, 137.6 ppm. HRMS (ESI): calcd for $C_{15}H_{12}N_3O_2^+$ ([M−BF_4^-]$^+$) 249.1386, found 249.1395.

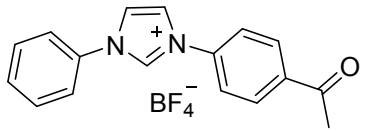


3-([1,1'-Biphenyl]-4-yl)-1-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ae). A gray solid (62 mg, 65% yield). M.p.: 169-171 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.45 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.74 (t, J

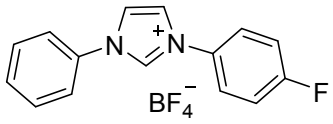
= 7.8 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H), 8.03 (s, 4H), 8.61 (t, J = 2.0 Hz, 1H), 8.65 (t, J = 1.8 Hz, 1H), 10. 41 (t, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 121.9, 122.0, 122.1, 122.5, 127.0, 128.3, 128.4, 129.2, 130.1, 130.2, 133.9, 134.5, 134.7, 138.4, 141.7 ppm. HRMS (ESI): calcd for $C_{21}H_{17}N_2^+$ ([M−BF_4^-]$^+$) 297.1386, found 297.1380.



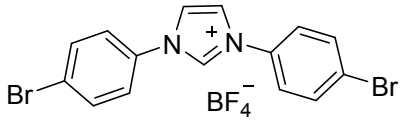
3-(3-Nitrophenyl)-1-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3af). A brown solid (63 mg, 72% yield). M.p.: 176-178 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.66 (t, J = 7.2 Hz, 1H), 7.74 (t, J = 7.6 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 8.03 (t, J = 8.4 Hz, 1H), 8.39 (dd, J = 8.4, 2.4 Hz, 1H), 8.49 (dd, J = 8.4, 1.6 Hz, 1H), 8.63 (t, J = 1.8 Hz, 1H), 8.72 (t, J = 2.0 Hz, 1H), 8.89 (t, J = 2.2 Hz, 1H), 10. 54 (t, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 117.6, 122.01, 122.02, 122.2, 124.7, 128.6, 130.26, 130.30, 131.8, 134.6, 135.5, 135.6, 148.5 ppm. HRMS (ESI): calcd for $C_{15}H_{12}N_3O_2^+$ ([M−BF_4^-]$^+$) 266.0924, found 266.0926.



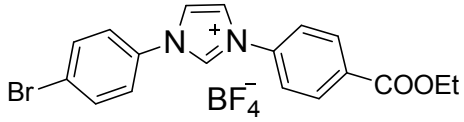
3-(4-Acetylphenyl)-1-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ag).[7] A yellow solid (51 mg, 57% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.68 (s, 3H), 7.65 (t, J = 7.4 Hz, 1H), 7.73 (t, J = 7.8 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 8.27 (d, J = 8.8 Hz, 2H), 8.62 (t, J = 2.0 Hz, 1H), 8.69 (t, J = 2.0 Hz, 1H), 10. 47 (t, J = 1.6 Hz, 1H) ppm.



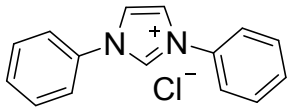
3-(4-Fluorophenyl)-1-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ah).[7] A white solid (64 mg, 73% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.59−7.64 (m, 3H), 7.73 (t, J = 7.8 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.95−7.98 (m, 2H), 8.54 (t, J = 1.8 Hz, 1H), 8.58 (t, J = 1.8 Hz, 1H), 10.32 (t, J = 1.6 Hz, 1H) ppm.



1,3-Bis(4-bromophenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (3fi).[7] A gray solid (50 mg, 43% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.88 (d, J = 8.4 Hz, 4H), 7.96 (d, J = 8.8 Hz, 4H), 8.58 (d, J = 1.6 Hz, 2H), 10.41 (d, J = 1.6 Hz, 1H) ppm.



1-(4-Bromophenyl)-3-(4-(ethoxycarbonyl)phenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (3fj). A gray solid (50 mg, 44% yield). M.p.: 198-200 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.37 (s, 3H), 4.38 (d, J = 6.4 Hz, 2H), 7.91 (br, 2H), 7.96 (br, 2H), 8.08 (d, J = 7.6 Hz, 2H), 8.26 (d, J = 7.2 Hz, 2H), 8.61 (s, 1H), 8.67 (s, 1H), 10.49 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.2, 61.4, 121.8, 122.15, 122.19, 123.2, 124.2, 131.1, 133.1, 133.9, 135.3, 138.0, 138.9, 164.7 ppm. HRMS (ESI): calcd for $C_{15}H_{12}N_3O_2^+$ ([M−BF_4^-]$^+$) 371.0390, found 371.0390.



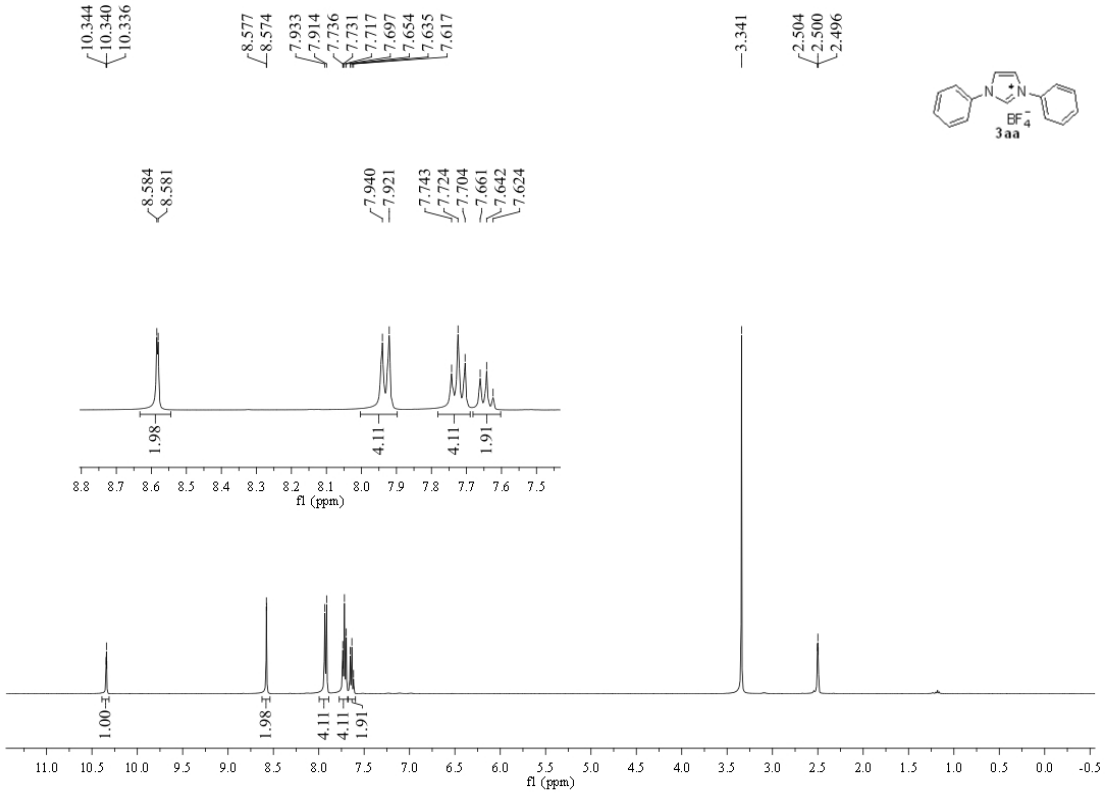
1,3-Diphenyl-1*H*-imidazol-3-ium chloride (3aa'). 3aa' was prepared by following a modified procedure.[8] A mixture of about 5 g Dowex® 1×4-50 anion exchange resin in the chloride form and 5 mL water was packed in a column. 1,3-Diphenyl-1H-imidazol-3-ium tetrafluoroborate **3aa** (77 mg) was dissolved in 5 mL methanol and 2 mL water. The solution was passed through the column and the resin was then washed with methanol/water. The solution obtained was concentrated and run through a short silica gel column (3 cm) with methanol. Vacuum concentration of the collected methanol solution afforded the diphenylimidazolium chloride salt **3aa'** as a gray solid (60 mg, 94% yield). ^{1}H NMR (400 MHz, DMSO-d_6): 7.63 (t, J = 7.2 Hz, 2H), 7.71 (t, J = 7.8 Hz, 4H), 7.99 (d, J = 8.0 Hz, 4H), 8.65 (d, J = 0.8 Hz, 2H), 10.54 (s, 1H) ppm.

IV. References

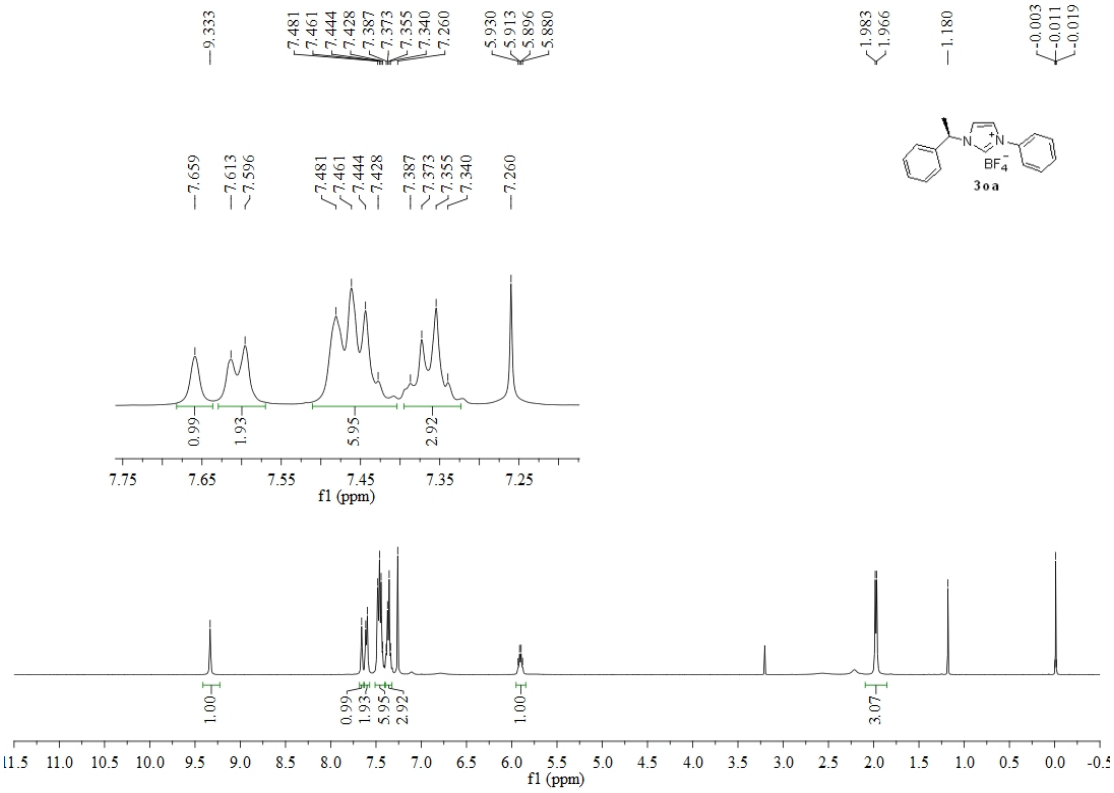
1. L. Zhu, L. Cheng, Y. Zhang, R. Xie and J. You, *J. Org. Chem*., 2007, **72**, 2737.
2. L. Zhu, P. Guo, G. Li, J. Lan, R. Xie and J. You, *J. Org. Chem*., 2007, **72**, 8535.
3. L. Zhu, G. Li, L. Luo, P. Guo, J. Lan and J. You, *J. Org. Chem*., 2009, **74**, 2200.
4. D. –H. Lee, J. –H. Kim, B. –H. Jun, H. Kang, J. Park and Y. –S. Lee, *Org. Lett*., 2008, **10**, 1609.
5. M. C. Perry, X. Cui, M. T. Powell, D. –R. Hou, J. H. Reibenspies and K. Burgess, *J. Am. Chem. Soc*., 2003, **125**, 113.
6. D. Brissy, M. Skander , P. Retailleau, G. Frison and A. Marinetti, *Organometallics*, 2009, **28**, 140.
7. T. Lv, Z. Wang, J. You, J. Lan and G. Gao, *J. Org. Chem*., 2013, **78**, 5723.
8. E. M. Higgins, J. A. Sherwood, A. G. Lindsay, J. Armstrong, R. S. Massey, R. W. Alder and A. C. O'Donoghue, *Chem. Commun*., 2011, **47**, 1559.

V. Copies of ^{1}H and ^{13}C NMR spectra

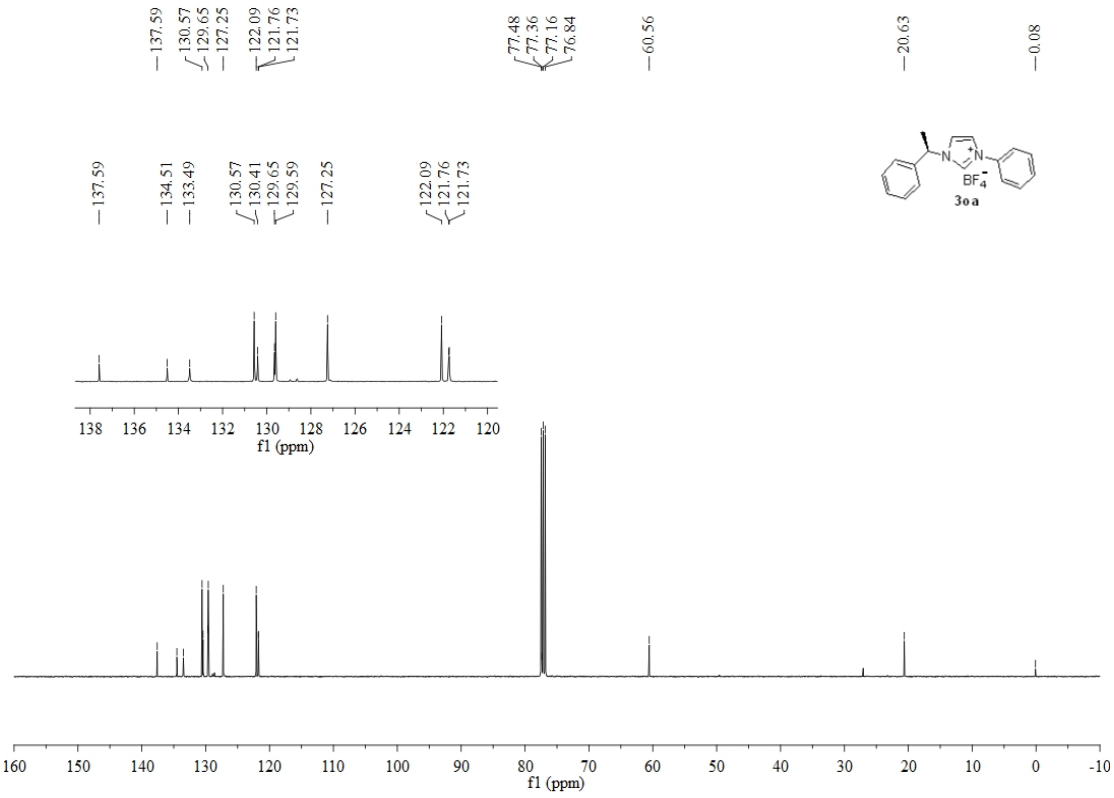
^{1}H NMR of 3aa in DMSO



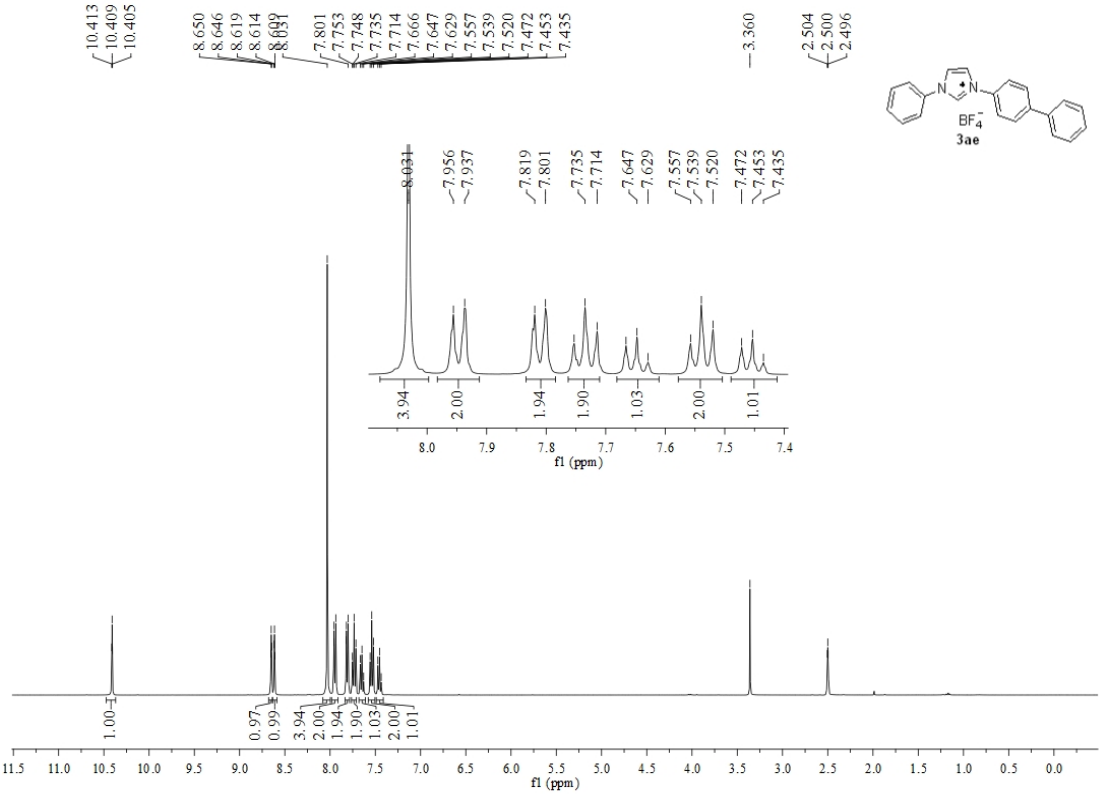
^{1}H NMR of 3oa in $CDCl_3$



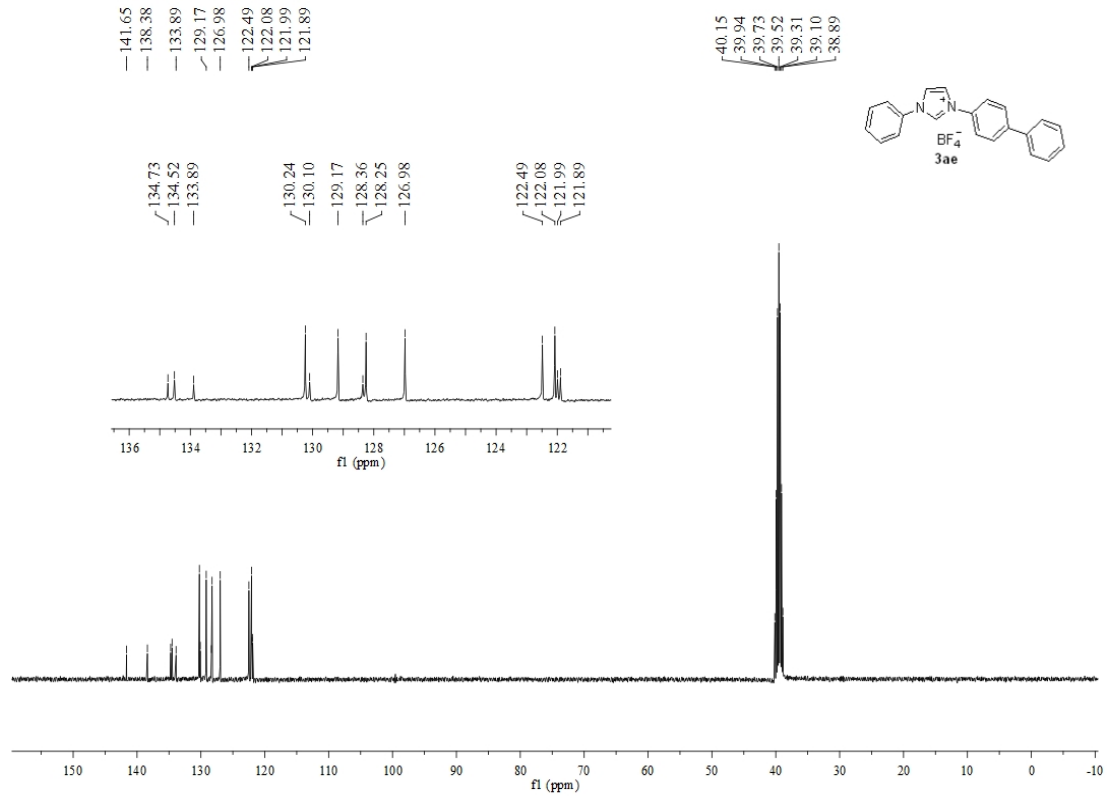
^{13}C NMR of 3oa in $CDCl_3$



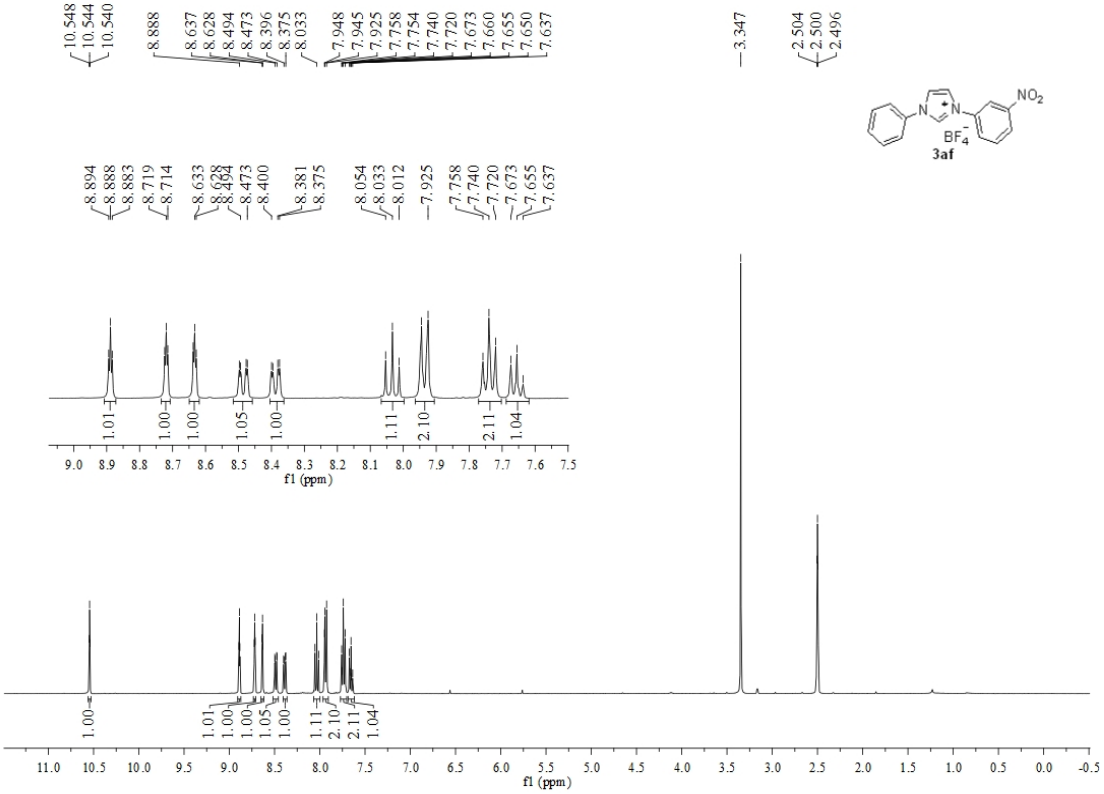
^{1}H NMR of 3ae in DMSO



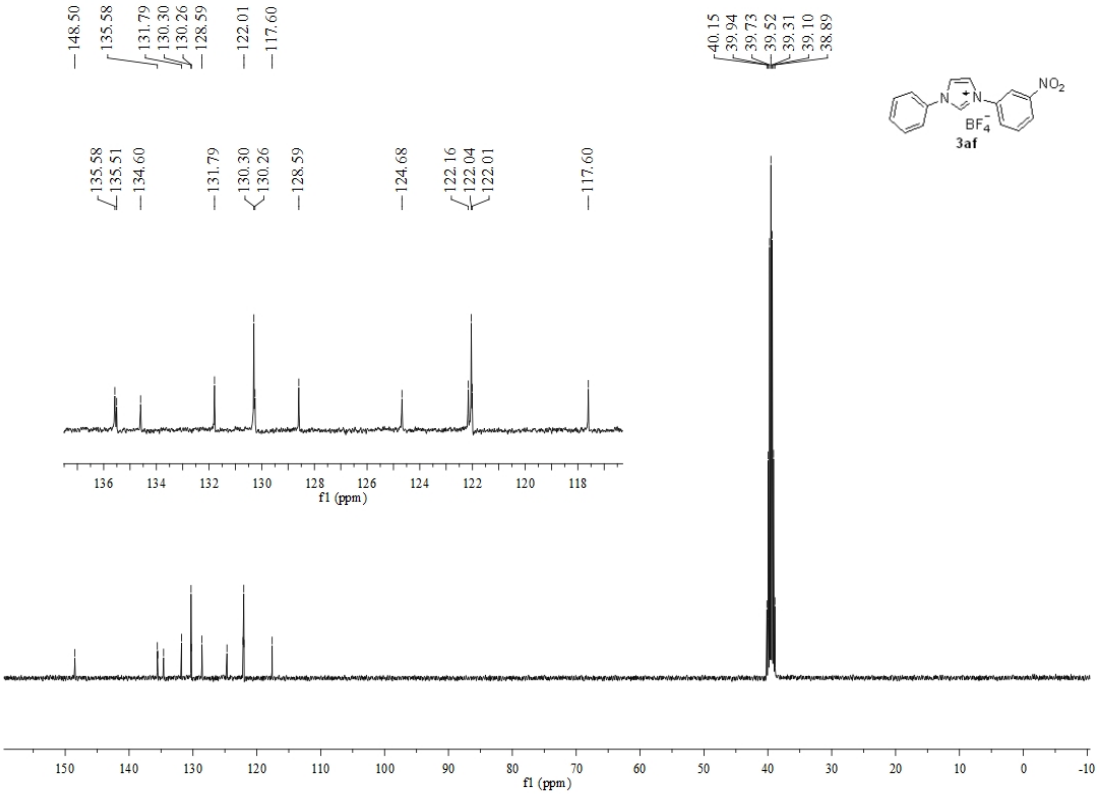
^{13}C NMR of 3ae in DMSO



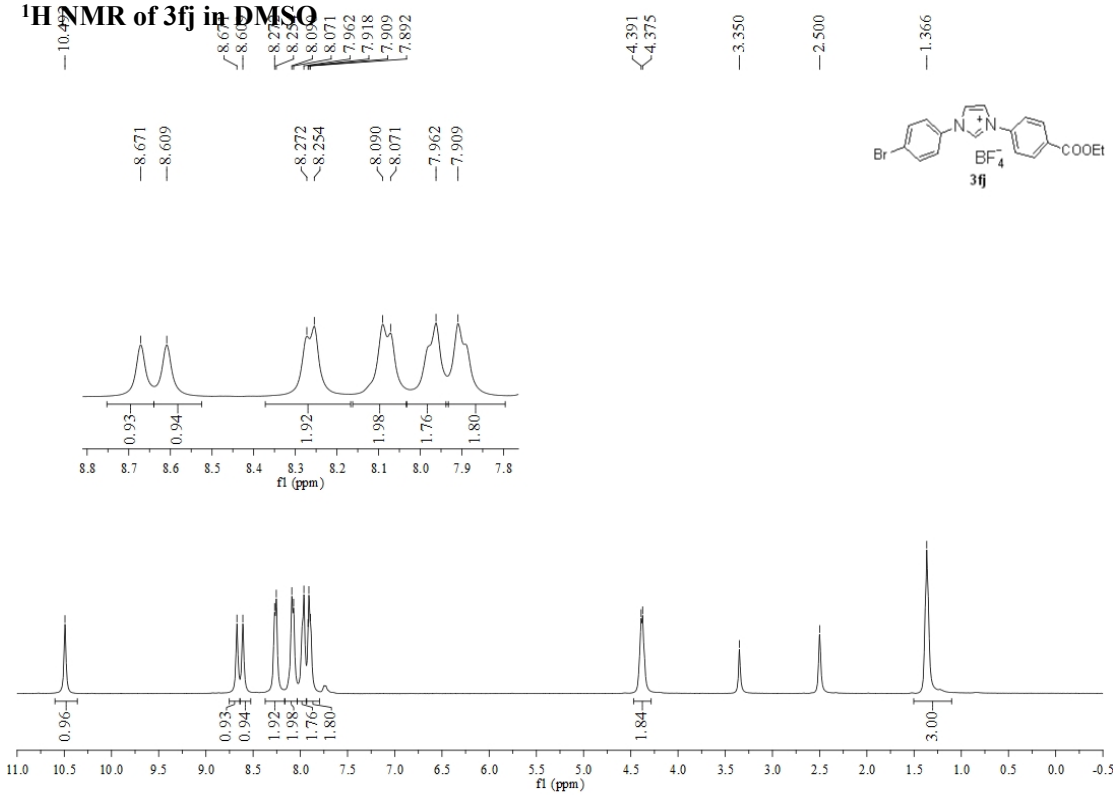
^{1}H NMR of 3af in DMSO



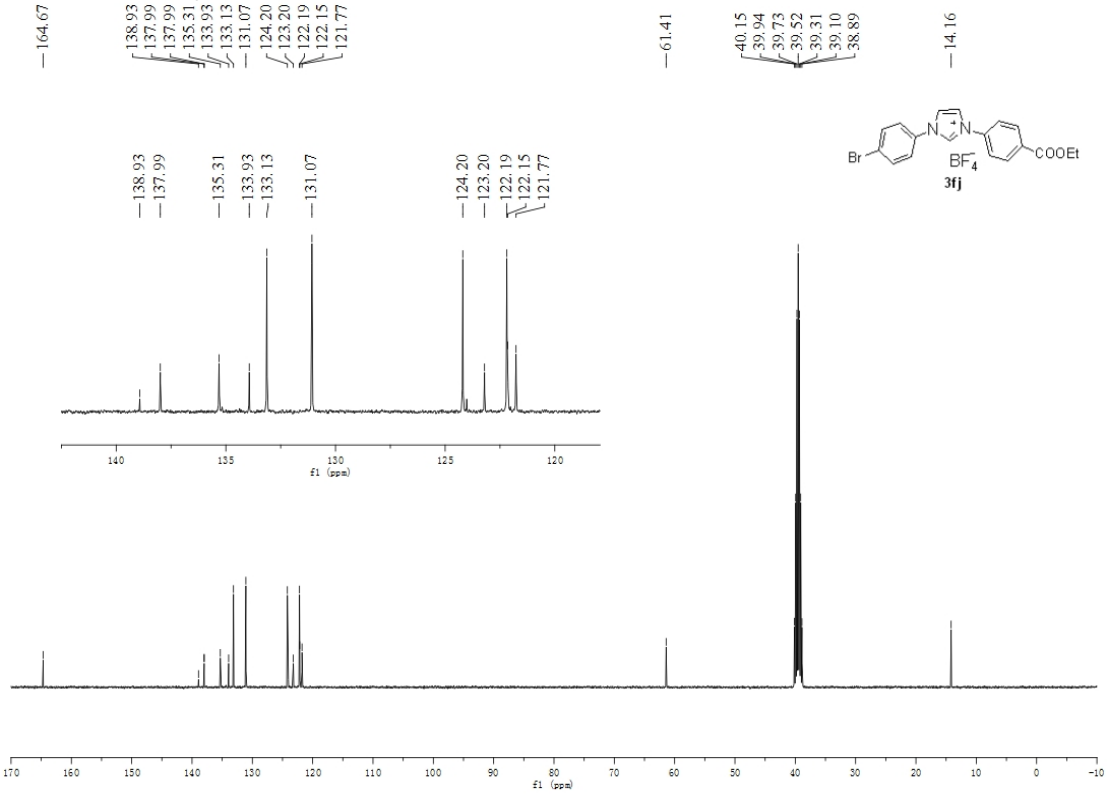
^{13}C NMR of 3af in DMSO



^{1}H NMR of 3fj in DMSO



^{13}C NMR of 3fj in DMSO



^{1}H NMR 3aa' in DMSO