Supplementary Material for Chemical Communications

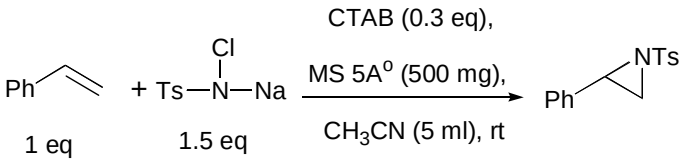
Supplementary data

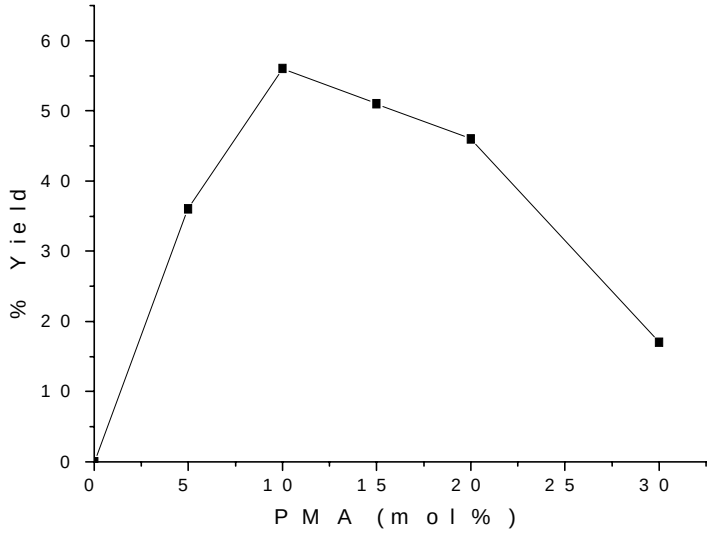
Heteropoly acid as a novel nitrene transfer agent: A facile and practical aziridination of olefins with Chloramine-T

G. D. Kishore Kumar and Sundarababu Baskaran*

Department of chemistry, Indian Institute of Technology Madras, Chennai, India, 600 036.

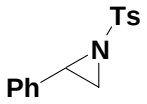
a) % of Yield Vs mol % PMA





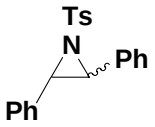
b) Experimental procedure for aziridination of olefin:

To a mixture of anhydrous PMA (0.1 eq), CTAB (0.3 eq), anhydrous Chloramine-T (1.5 eq), powdered MS 5 Å (500 mg per mmol) in dry CH_3CN (5 ml) is treated with olefin (1 eq) at room temperature under N_2 atmosphere. Then the reaction mixture is filtered and washed with CH_3CN. The combined filtrate is concentrated under reduced pressure and purified by column chromatography over silica gel to give pure product.



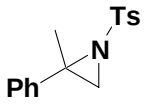
N-(p-Tolysulfonyl)-2-phenylaziridine:

IR (KBr): 2998, 1578, 1491, 1456, 1382, 1321, 1190, 1158, 1091, 912, 812, 777, 752, 710, 662, 579, 550 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.30 (m, 7H), 3.79 (dd, *J* = 7.1 and 4.5 Hz, 1H), 3.00 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.41 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 144.6, 135.0, 134.9, 129.7, 128.5, 128.3, 127.9, 126.5, 41.0, 35.9, 21.6; MS (EI, 70 eV): m/z 274 (M^++1, 0.1), 155 (25), 91 (100).



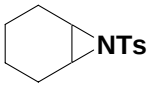
***cis* and *trans* N-(p-Tolysulfonyl)-2,3-diphenylaziridine(1 : 1.3):**

IR (KBr): 1598, 1494, 1452, 1401, 1337, 1321, 1244, 1152, 1084, 1028, 899, 803, 764, 688, 582, 534 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.95, (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.32 (m, 10H), 7.11 – 7.03 (m, 10H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.26 (s, CH_{trans}- aziridine) 4.22 (s, 2H, CH_{cis} –aziridine), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 143.8, 136.9, 132.9, 129.3, 129.2, 128.6, 128.3, 128.2, 127.5, 127.4, 50.3, 50.2, 50.2, 21.4; MS (EI, 70 eV): m/z 260 (M^+-C_7H_5, 0.02), 194 (100), 155 (4), 116 (16), 91 (25).



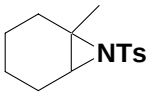
N-(p-Tolysulfonyl)-2-methyl-2-phenylaziridine:

IR (KBr): 1534, 1312, 1260, 1158, 1078, 1030, 960, 931, 841, 809, 736, 659, 579, 530, cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.24 (m, 7H), 2.96 (s, CH- aziridine, 1H), 2.52 (s, CH- aziridine, 1H), 2.42 (s, 3H), 2.00 (s, 3H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 144.1, 141.0, 137.7, 129.4, 128.8, 127.7, 127.5, 126.5, 51.8, 41.8, 21.6, 20.9.



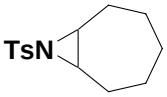
N-(p-Tolysulfonyl)-7-azabicyclo[4.1.0]heptane:

IR ($CHCl_3$): 2944, 2864, 1596, 1491, 1443, 1398, 1312, 1148, 1091, 972, 912, 899, 898, 825, 630, 576 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 2.97 (m, 2H), 2.44 (s, 3H), 1.77 – 1.80 (m, 4H), 1.36 – 1.41 (m, 2H), 1.20 – 1.25 (m, 2H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 143.9, 135.8, 129.5, 127.5, 39.7, 22.7, 21.5, 19.3; MS (EI, 70 eV): m/z 251 (M^+, 0.2), 155 (4), 96 (100), 91 (30).



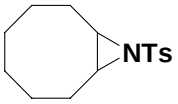
N-(p-Tolysulfonyl)-1-methyl-7-azabicyclo[4.1.0]heptane:

IR ($CHCl_3$): 2960, 2864, 1600, 1446, 1404, 1305, 1145, 1091, 1004, 976, 944, 902 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.98 (d, *J* = 5.3 Hz, 1H), 2.35 (s, 3H), 1.97 (ddd, *J* = 14.4, 5.1 and 4.9 Hz, 1H), 1.73 – 1.70 (m, 1H), 1.64 (s, 3H), 1.49 – 1.41 (m, 3H), 1.41 – 1.21 (m, 2H), 1.20 – 1.00 (m, 1H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 143.3, 139.0, 129.4, 126.9, 51.2, 47.3, 32.1, 22.8, 21.5, 20.5, 19.8, 19.5; MS (EI, 70 eV): m/z 266 (M^++1, 0.07), 155 (2.1), 110 (100), 91 (96).



N-(p-Tolysulfonyl)-7-azabicyclo[5.1.0]octane:

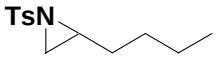
IR ($CHCl_3$): 2944, 1593, 1491, 1446, 1318, 1155, 1084, 960, 928, 860, 563 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 2.86 (m, 2H), 2.35 (s, 3H), 1.74 – 1.75 (m, 4H), 1.49 – 1.07 (m, 6H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 145.5, 137.4, 130.8, 129.0, 45.7, 32.5, 29.5, 26.7, 23.1; MS (EI, 70 eV): m/z 265 (M^+, 1.4), 155 (6.7), 110 (100), 91 (39), 55 (74).



N-(p-Tolysulfonyl)-7-azabicyclo[6.1.0]nonane:

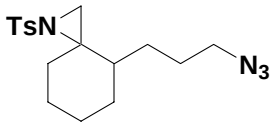
IR (KBr): 2944, 2848, 1596, 1449, 1424, 1315, 1152, 1091, 1008, 985, 931, 931, 870, 720, 662, 569, 540 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 2.79 – 2.76 (m, 2H), 1.99 – 2.02 (m, 2H), 1.27 – 1.60 (m, 10H); ^{13}C

NMR [100 MHz, $CDCl_3$] δ144.1, 135.8, 129.6, 127.5, 43.9, 26.3, 25.6, 24.9, 21.6; MS (EI, 70 eV): m/z 280 (M^++1, 1.1), 155(40), 124 (8), 91 (100).



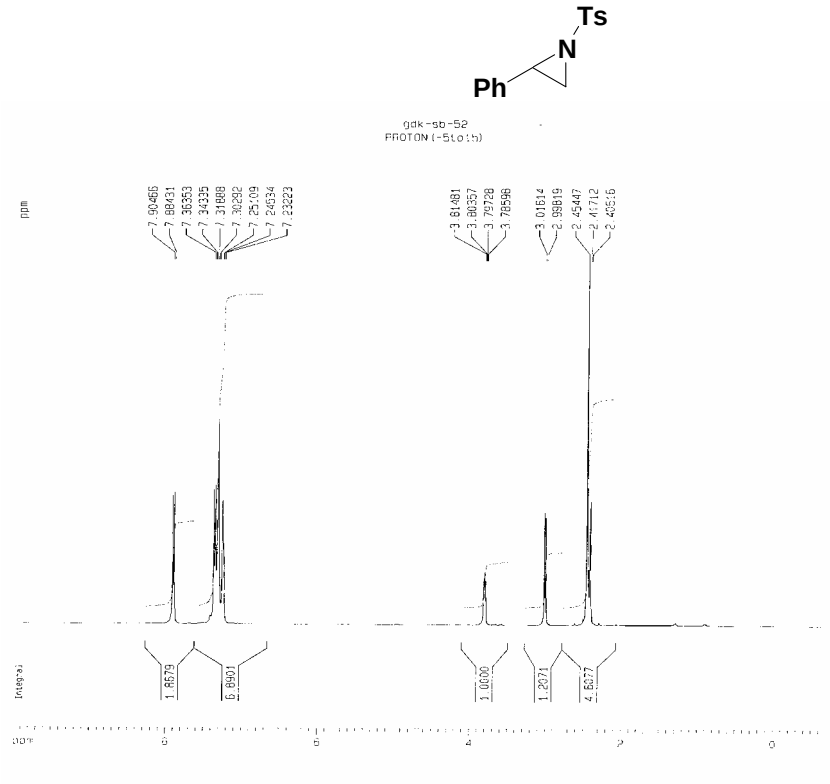
N-(p-Tolysulfonyl)-2-n-butylaziridine:

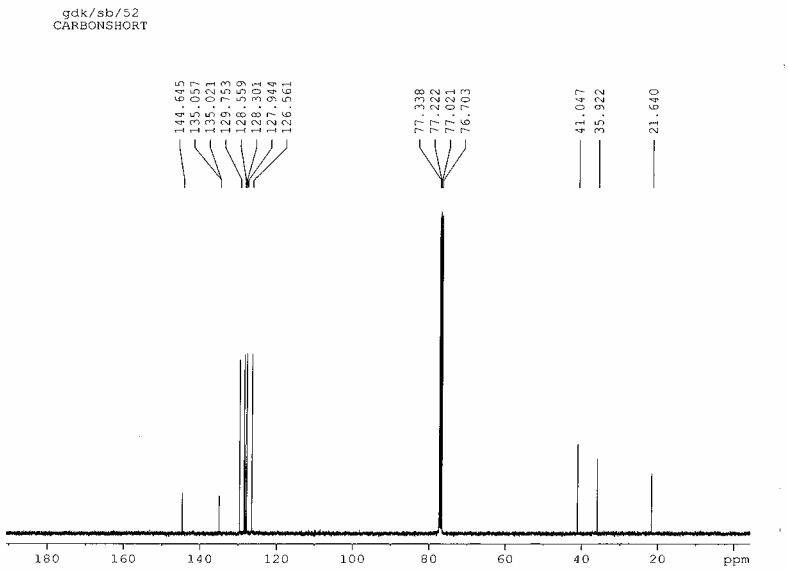
IR (neat): 2944, 1593, 1459, 1318, 1232, 1158, 1088, 921, 860, 809, 710, 659, 569 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.69 – 2.75 (m, 1H), 2.61 (d, *J* = 7.0 Hz, 1H), 2.44 (s, 3H), 1.05 (d, *J* = 4.6 Hz, 1H), 1.50 – 1.56 (m, 1H), 1.38 – 1.18 (m, 5H), 0.8 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR [100 MHz, $CDCl_3$] δ144.3, 135.2, 129.5, 127.9, 40.4, 33.7, 30.9, 28.8, 22.0, 21.5, 13.8; MS (EI, 70 eV): m/z 253 (M^+ 1.5), 155 (18), 98 (100), 91 (88).

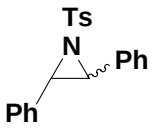


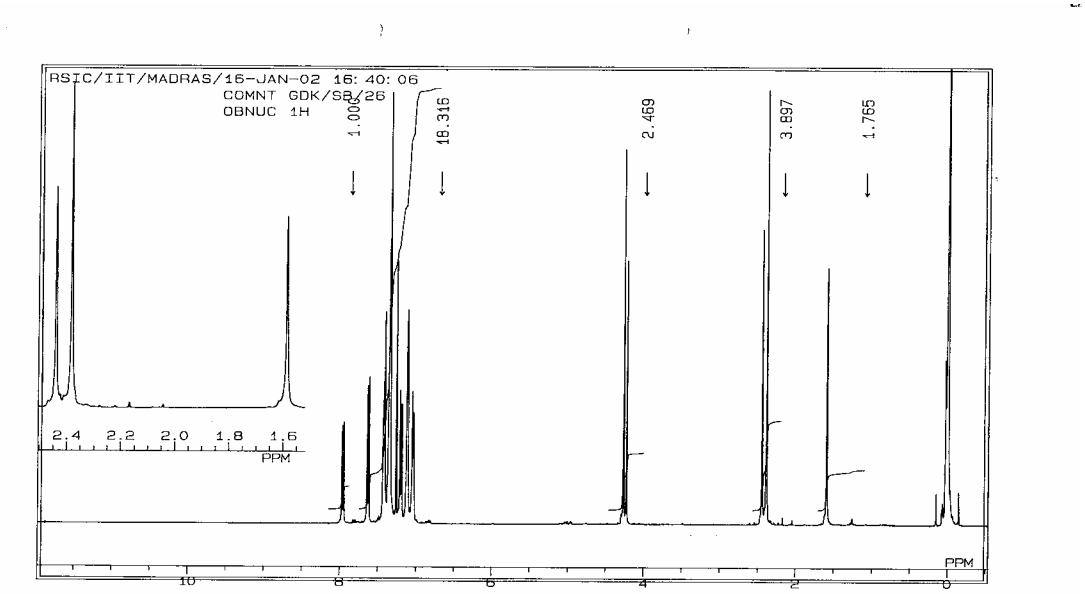
4-(3-Azido-propyl)-1-(p-tolylsulfonyl)-1-aza-spiro[2.5]octane:

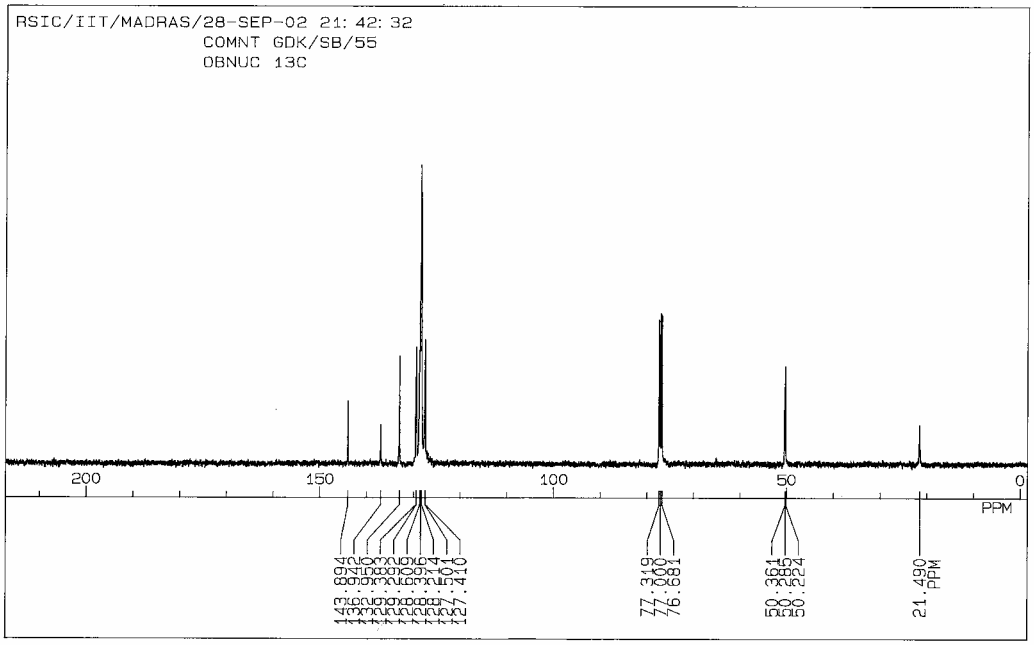
IR (neat): 2944, 2096, 1596, 1446, 1312, 1158, 1094, 972, 819, 720, 560 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.15 (m, 2H), 2.40 (s, 1H), 2.35 (s, 3H), 2.20 (s, 1H), 1.18 – 1.88 (m, 13H); ^{13}C NMR [100 MHz, $CDCl_3$] δ 143.6, 138.1, 129.4, 127.2, 56.7, 51.4, 40.8 38.1, 30.1, 29.7, 26.3, 25.6, 22.8, 21.5; (EI, 70 eV): m/z 253 (M^+-N_2, 3), 306 (62), 165 (100).



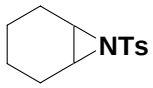


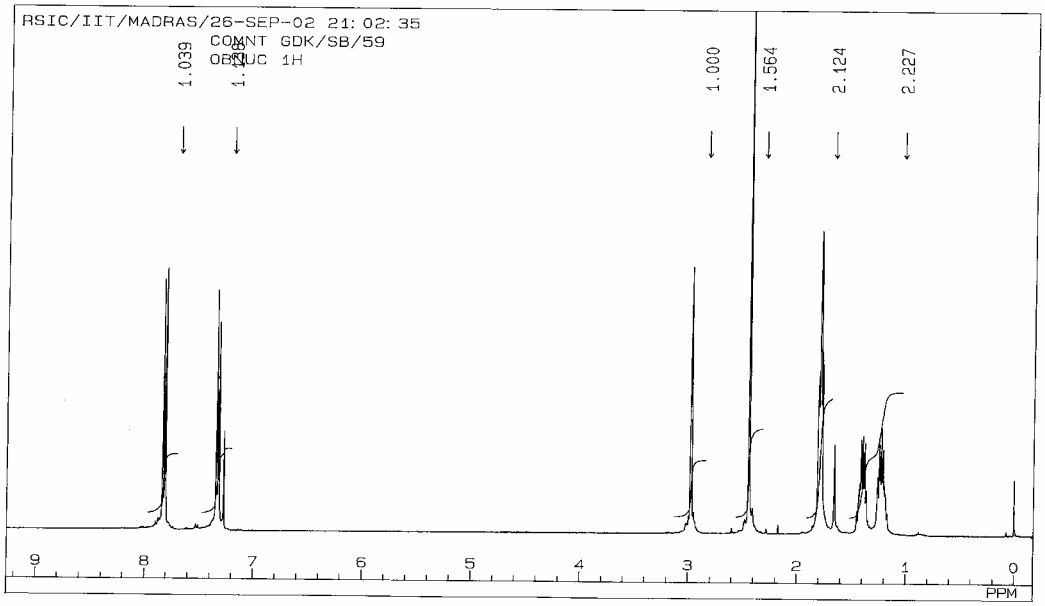


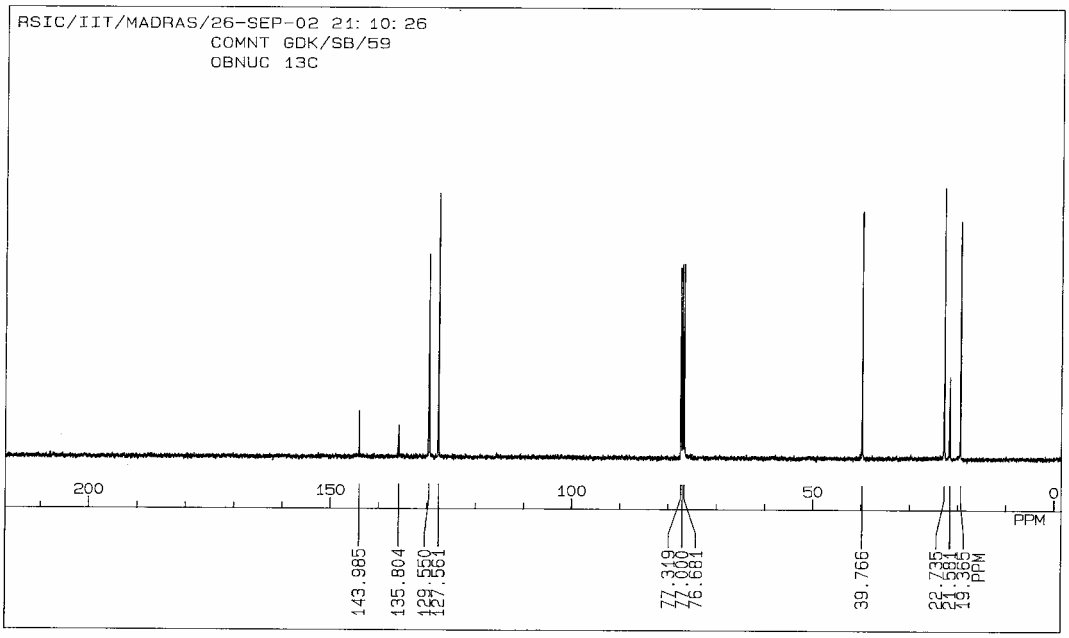


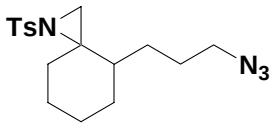


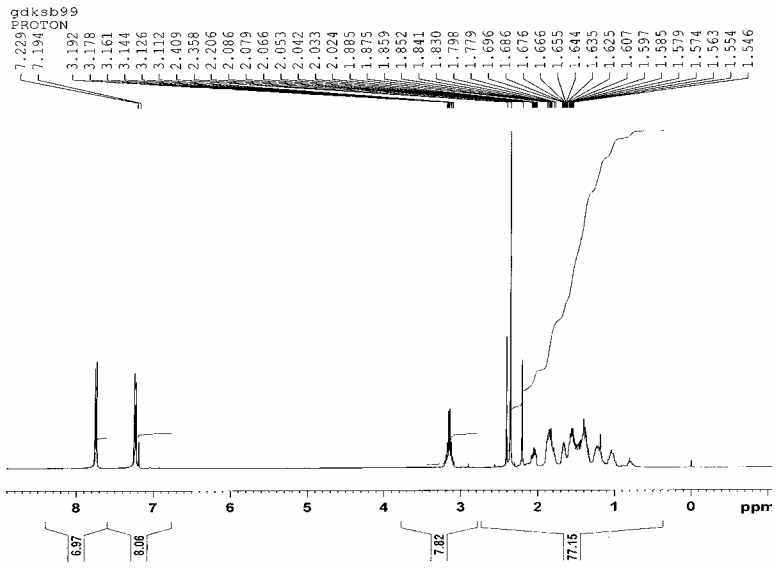
Supplementary Material for Chemical Communications

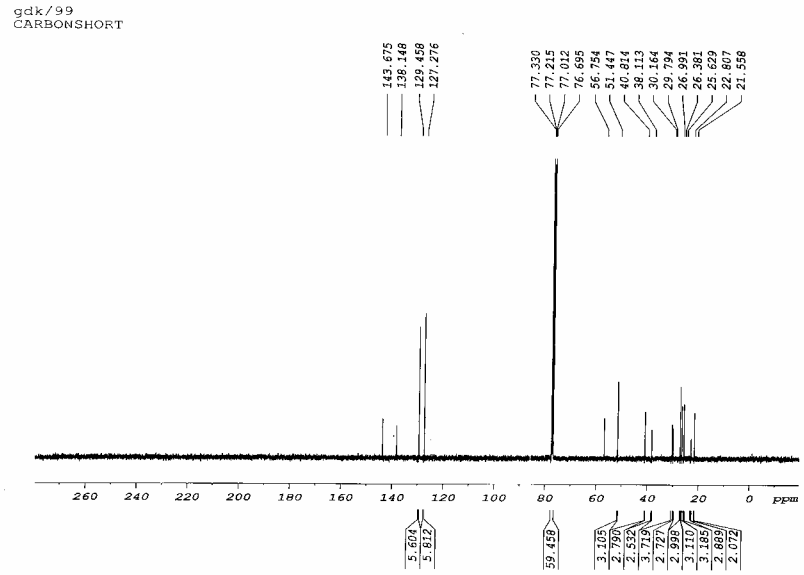


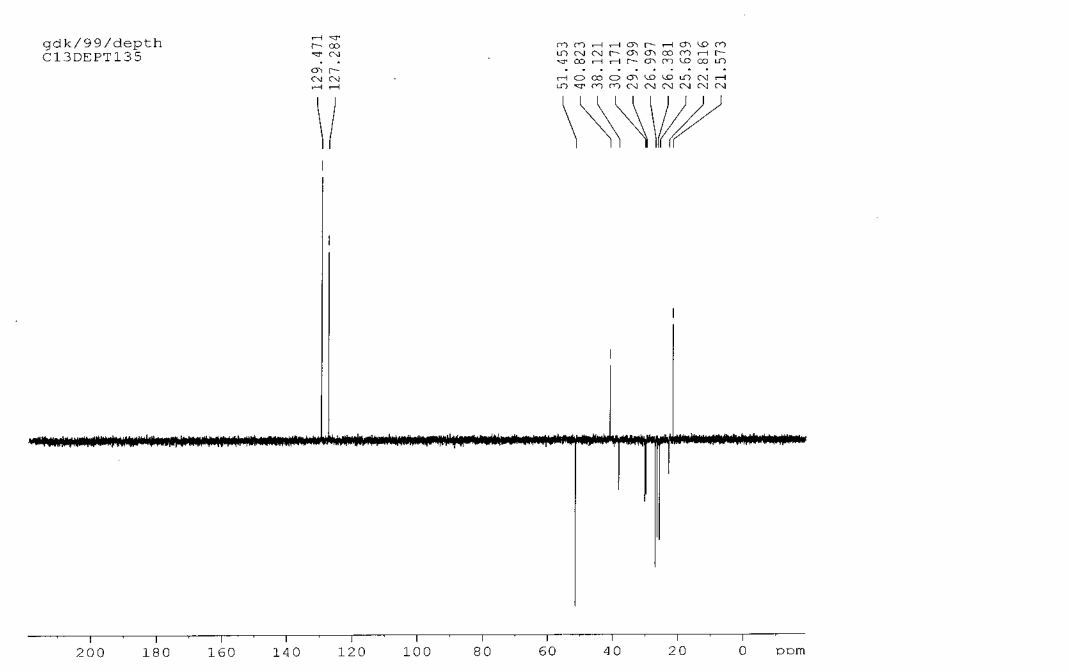


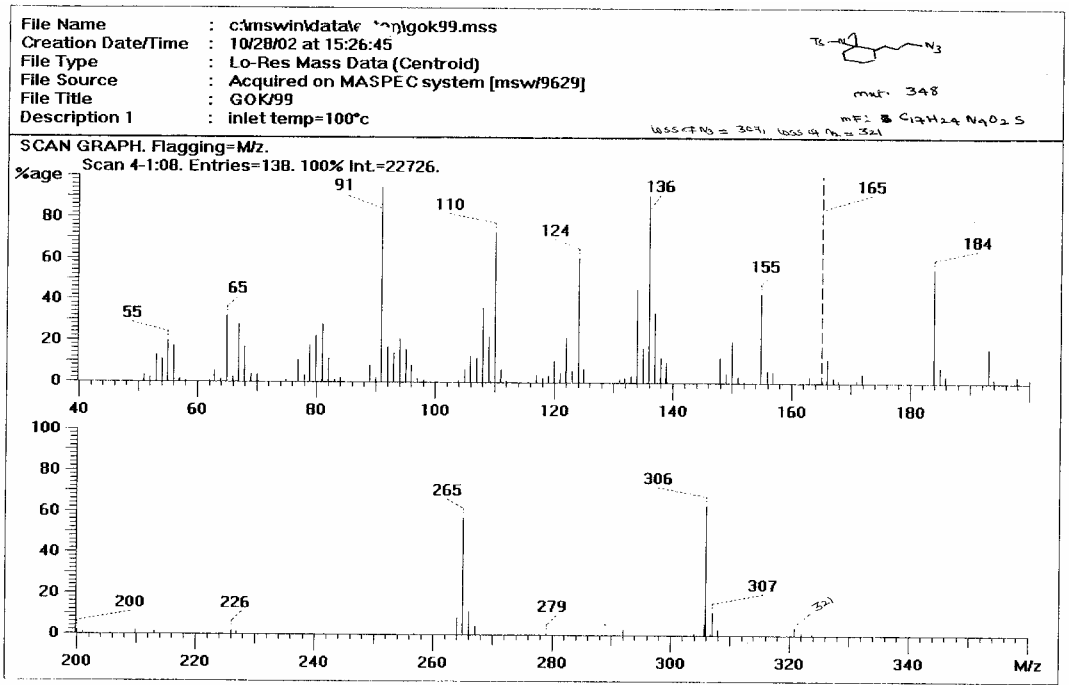


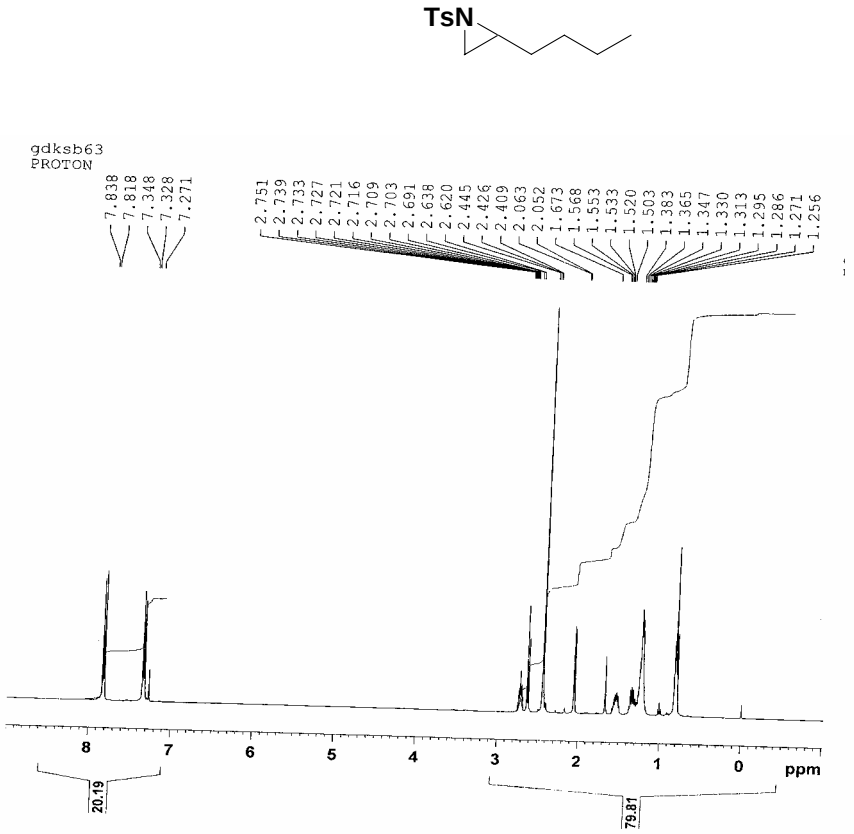


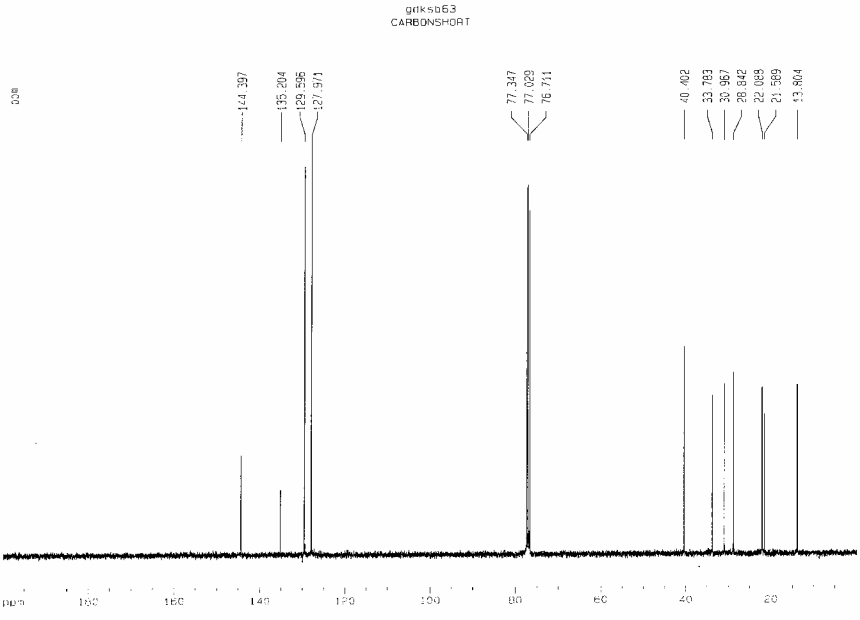


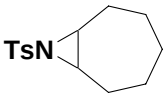


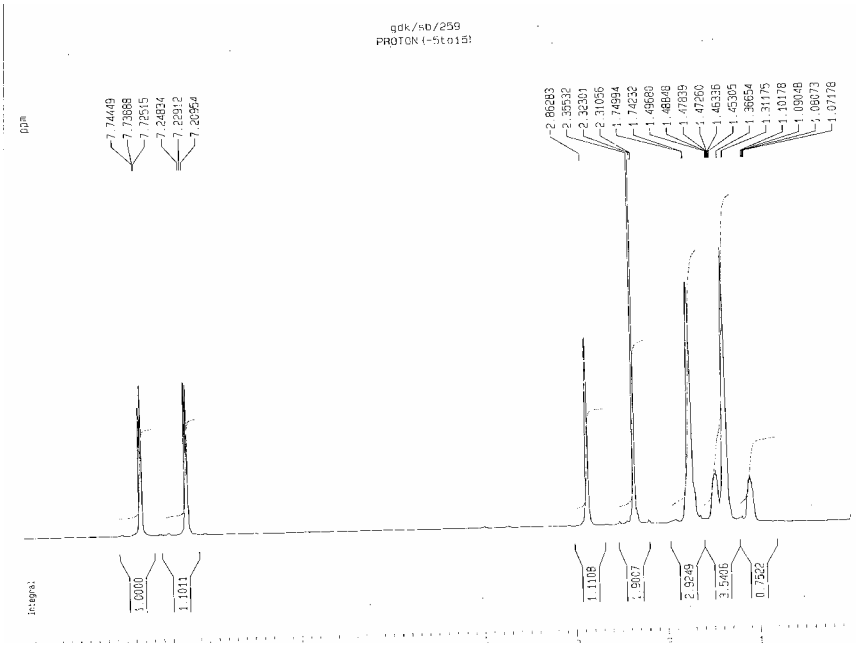


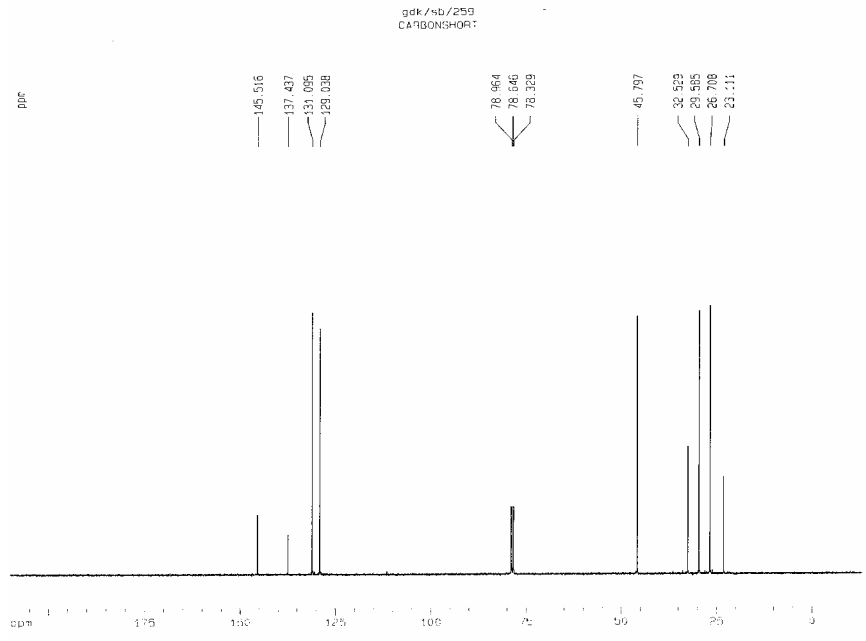


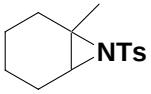


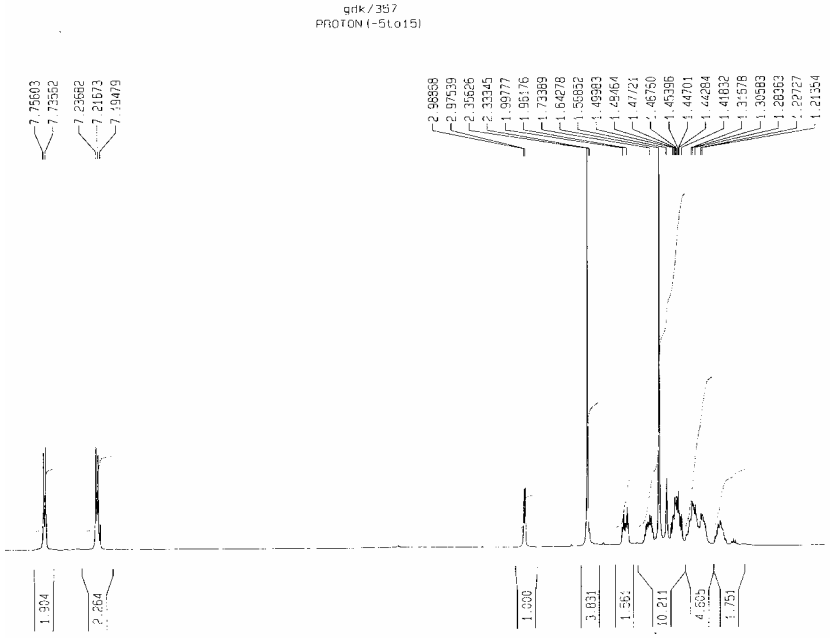


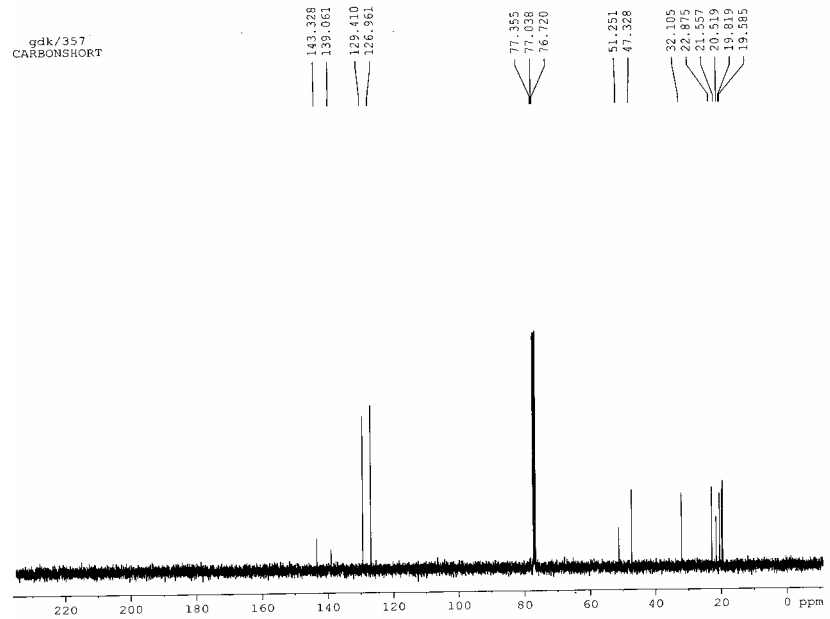




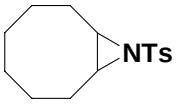


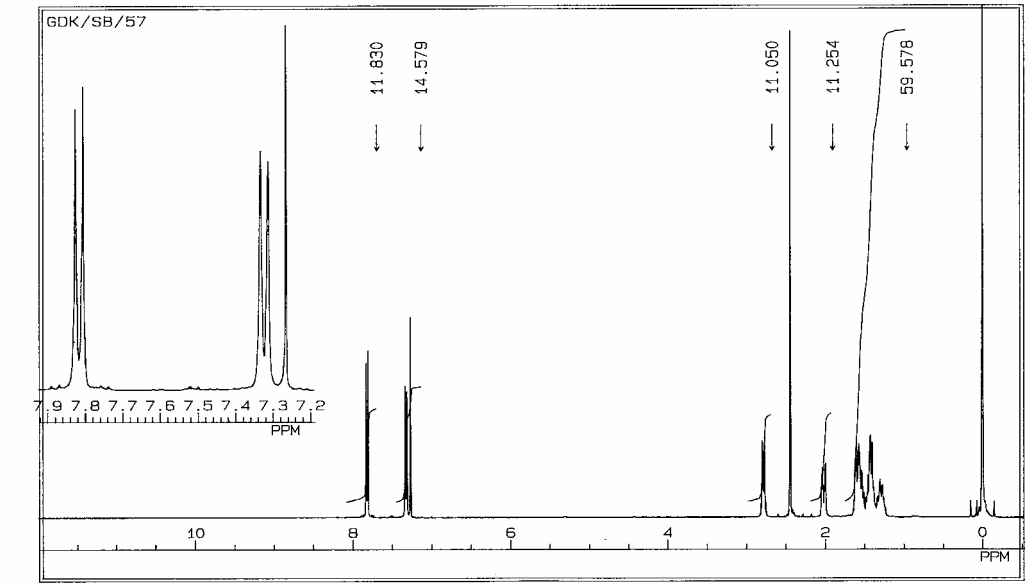


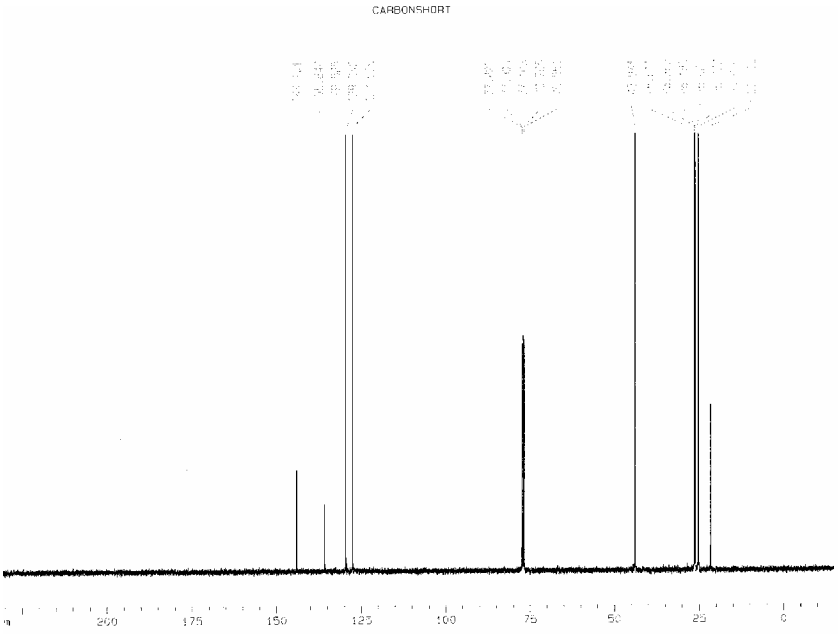


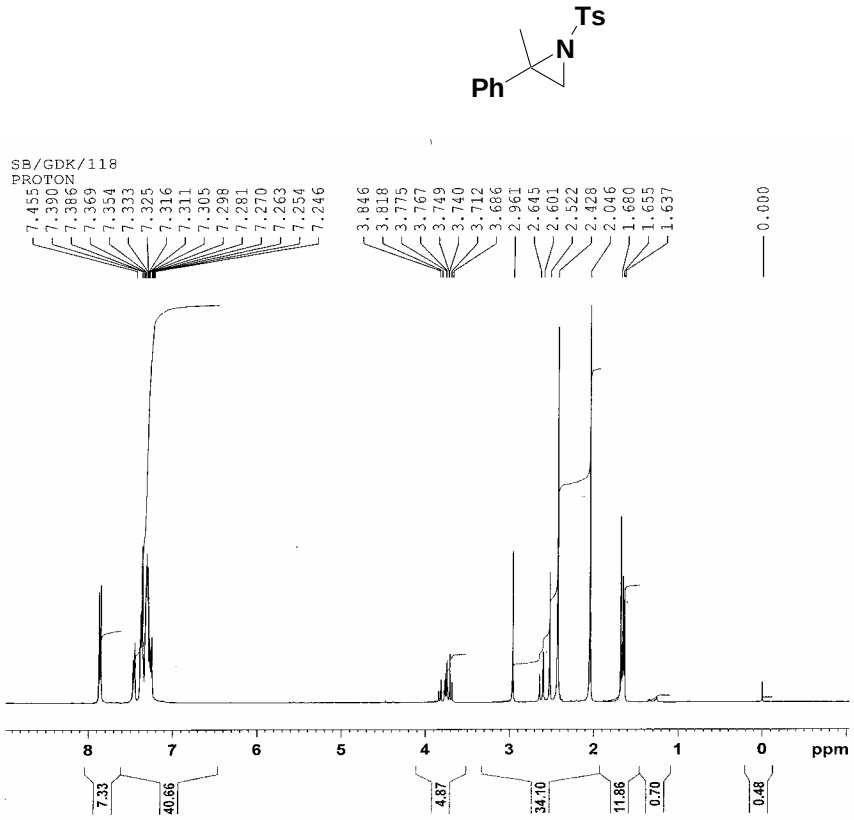


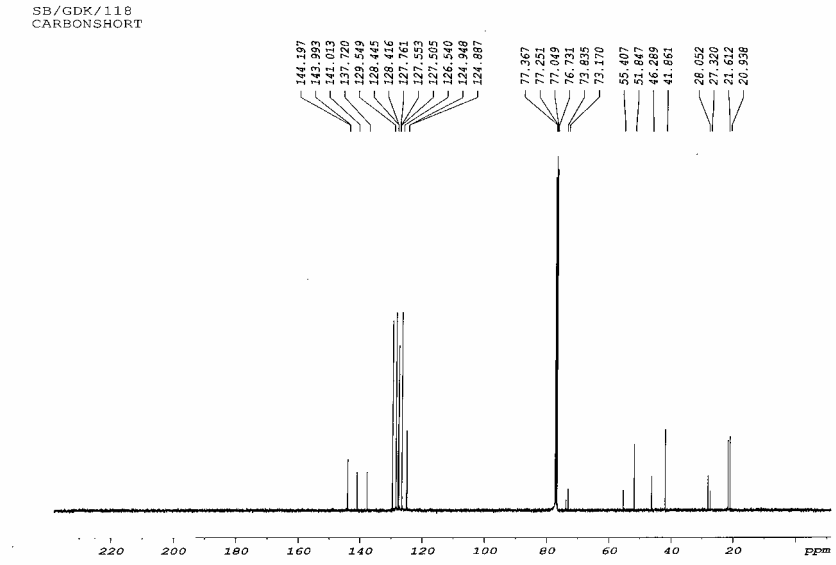
Supplementary Material for Chemical Communications











Supplementary Material for Chemical Communications