Supplementary Material (ESI) for Green Chemistry

Polyethylene glycol as a non-ionic liquid solvent for Michael addition reaction of amines to conjugated alkenes

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Experimental

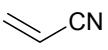
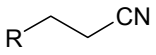
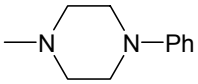
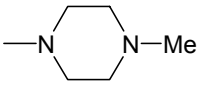
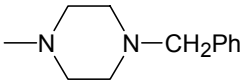
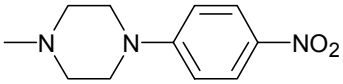
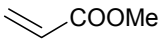
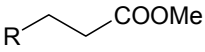
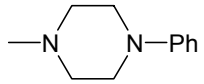
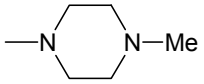
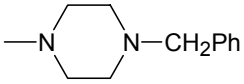
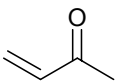
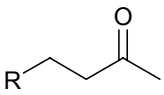
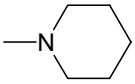
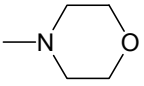
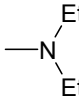
1. General

All reagents used were AR grade. THF was distilled from sodium/benzophenone prior to use. Melting points were determined using a Thomas Hoover melting point apparatus and are uncorrected. ^{1}H (300 MHz) and ^{13}C NMR (75MHz) spectra were recorded on a Bruker 300 NMR spectrometer in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as internal references) unless otherwise stated. MS were recorded on Agluent 1100 ES-MS Karlsrhue Germany. Column chromatography was performed on silica gel (230-400 mesh). Microanalyses were obtained with an Elemental Analysensysteme GmbH VarioEL V3.00 element analyser. The reactions were monitored by Thin Layer chromatography (TLC) using aluminium sheets with silica gel 60 F_{254} (Merck). All of the reactions were carried out under nitrogen atmosphere.

2. General procedure for the aza-Michael reaction of amines with electron deficient alkenes in PEG

A mixture of amine (1mmol), alkene (1.5 mmol) and PEG 400 (2.5 g) was placed in 20 mL round-bottomed flask. The reaction mixture was stirred at room temperature until the reaction was complete. The reaction mixture was extracted with dry ether, the extract dried and concentrated under reduced pressure and resulting crude product was purified by silica column chromatography using ethyl acetate and hexane as an eluent to obtain the adduct in excellent yield. The recovered PEG can be reused for a number of cycles without significant loss of activity.

Table 1 The aza-Michael reaction of amines with electron deficient alkenes in PEG.

Entry	Unsaturated alkenes	Product	Time (h)	Yield (%)[b]
				
1		a R = 	35 min	99
2		b R = 	45 min	98
3		c R = 	45 min	99
4		d R = 	45 min	99
				
5		a R = 	30 min	99
6		b R = 	45 min	98
7		c R = 	35 min	99
				
8		a R = 	35 min	99
9		b R = 	35 min	99
10		c R = 	35 min	99

[b]Isolated yield by GC.

3. Spectral characterization of Entry 4 in Table 1: ^{1}HNMR of 3-[4-(4-Nitro-phenyl)-piperazin-1-yl]-propanitrile

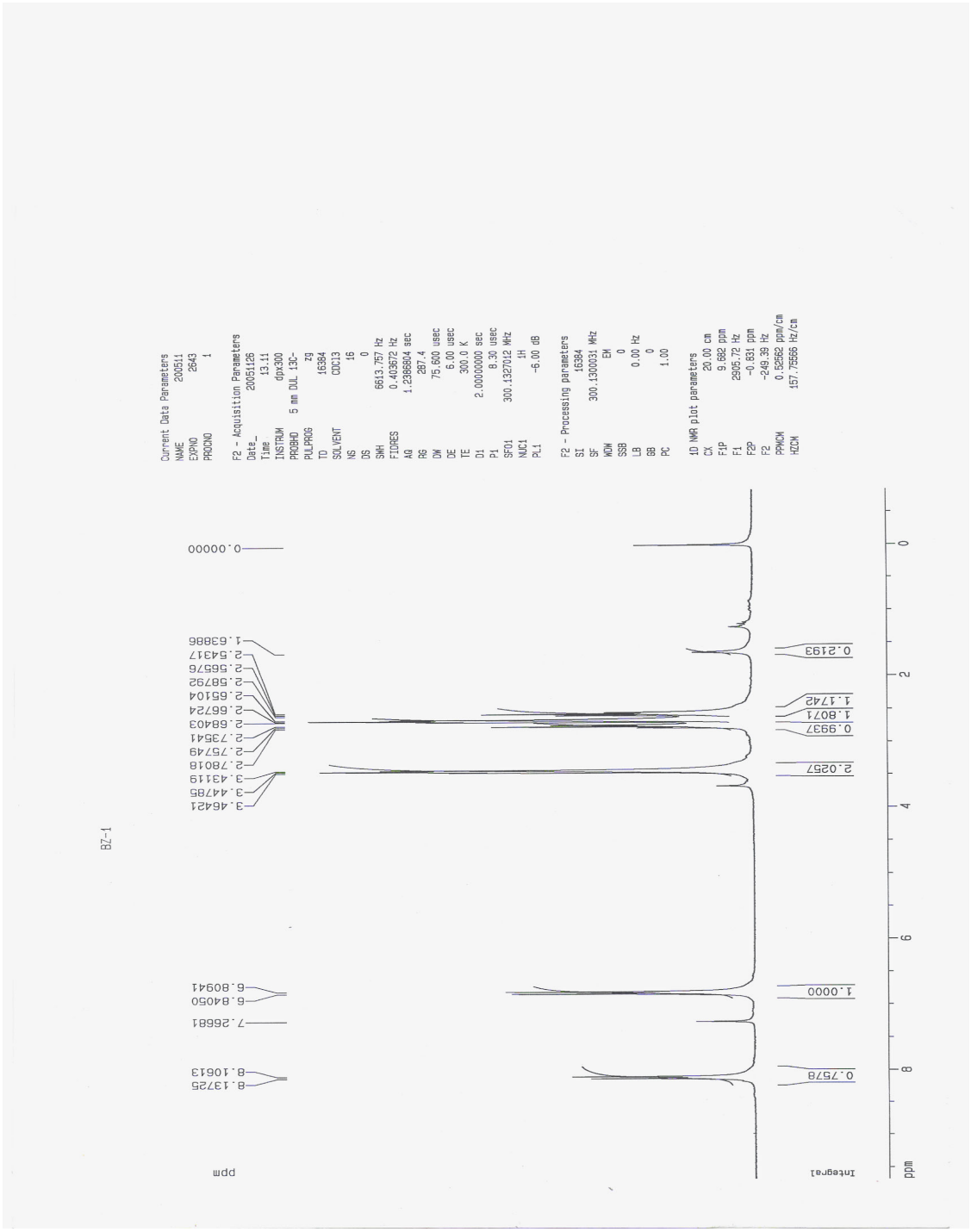
^{1}HNMR δ (ppm, 300MHz) 8.12 (d, *J*= 9Hz, 2H), 6.83 (d, *J*= 9Hz, 2H), 3.44 (t, *J*= 5Hz, 4H), 2.75 (t, *J*= 7Hz, 2H), 2.66 (t, *J*= 5Hz, 4H), 2.56 (t, *J*= 7Hz, 2H).

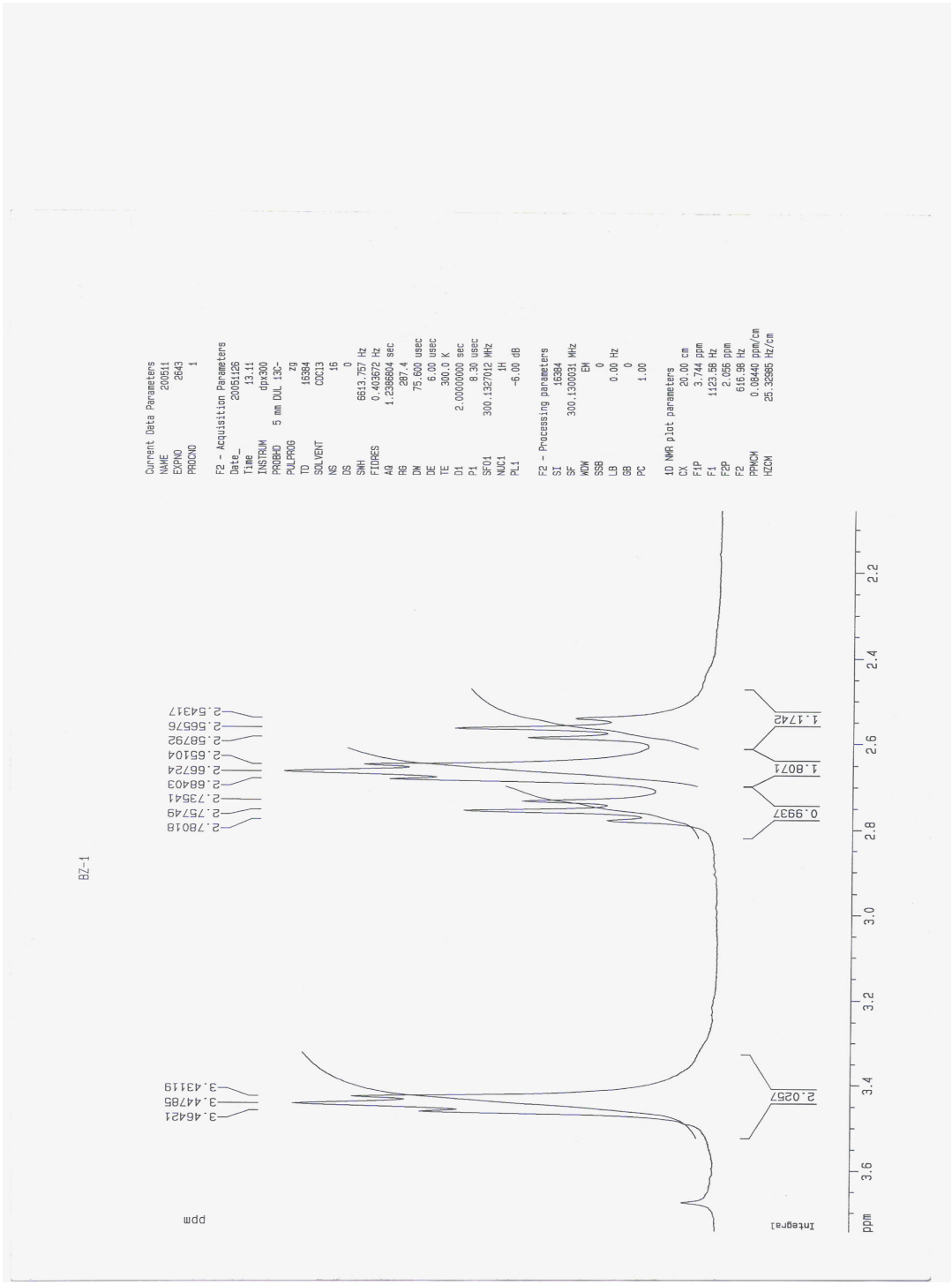
^{13}CNMR δ (ppm, 75MHz) 141.3, 132.4, 125.9, 114.2, 113.2, 51.3, 50.6, 46.6, 45.9.

TOF MS (m/z) 261.6 (M+1).

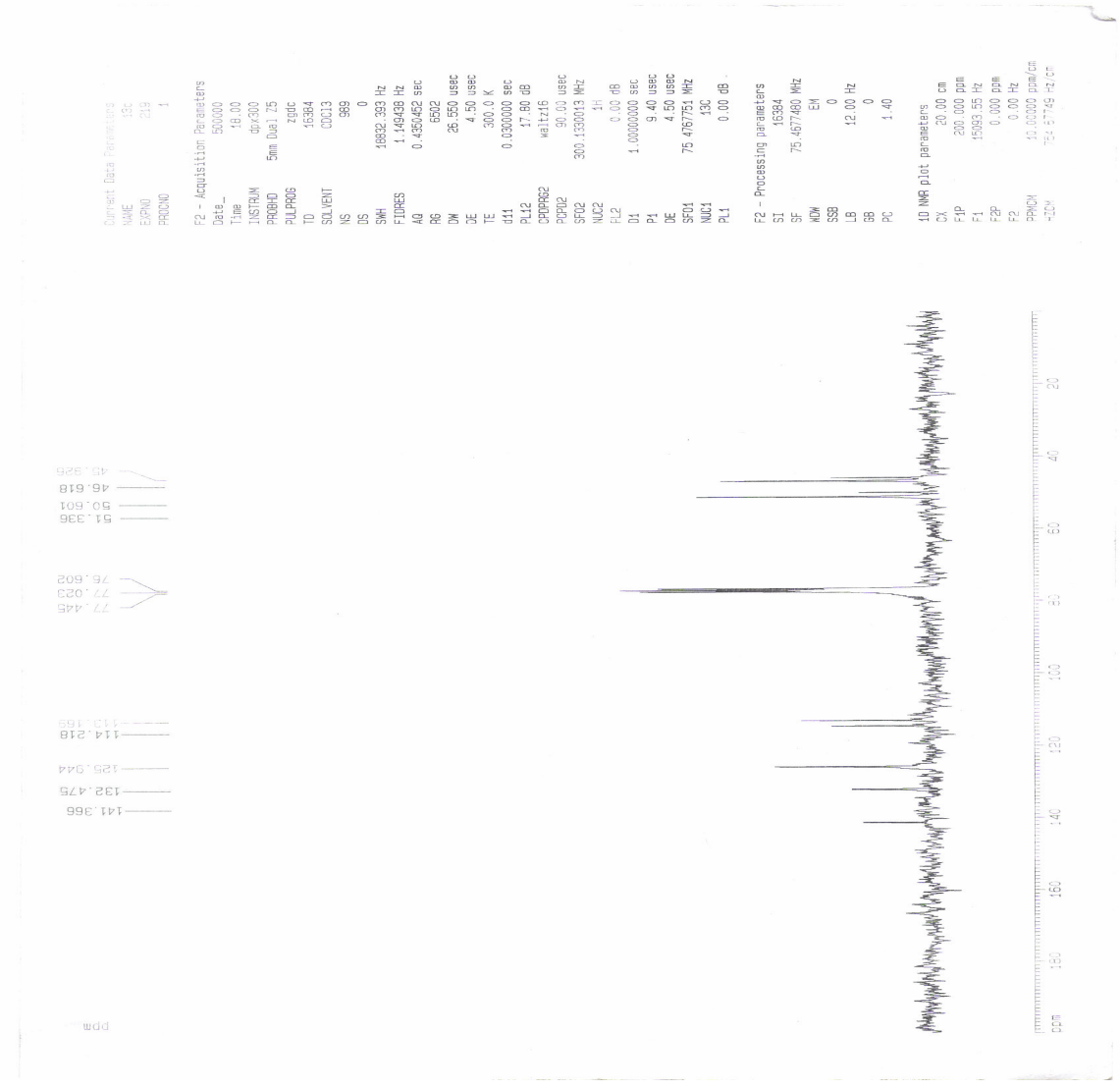
IR (ν, cm^{-1}) 2245.41 (CN), 1328.72 (NO_2).

^{1}HNMR of 3-[4-(4-Nitro-phenyl)-piperazin-1-yl]-propanitrile

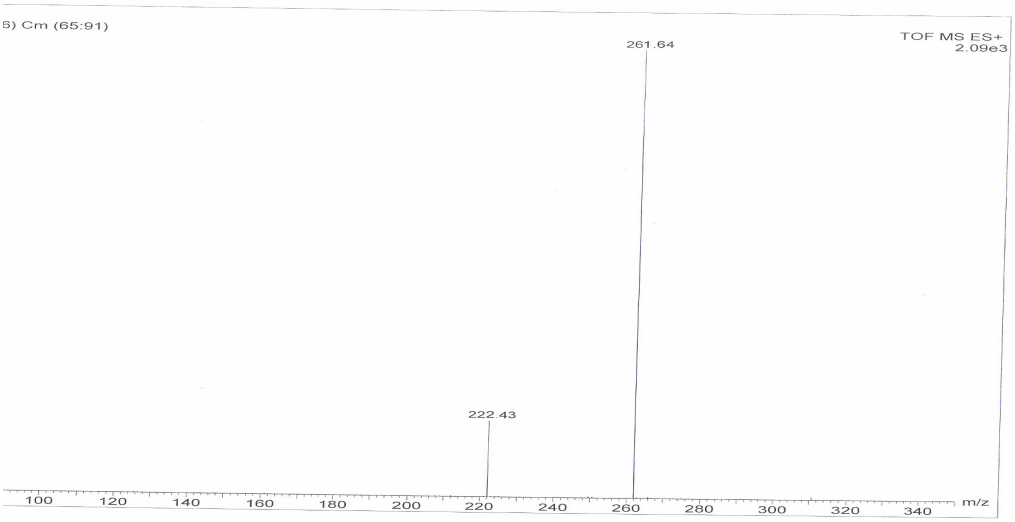




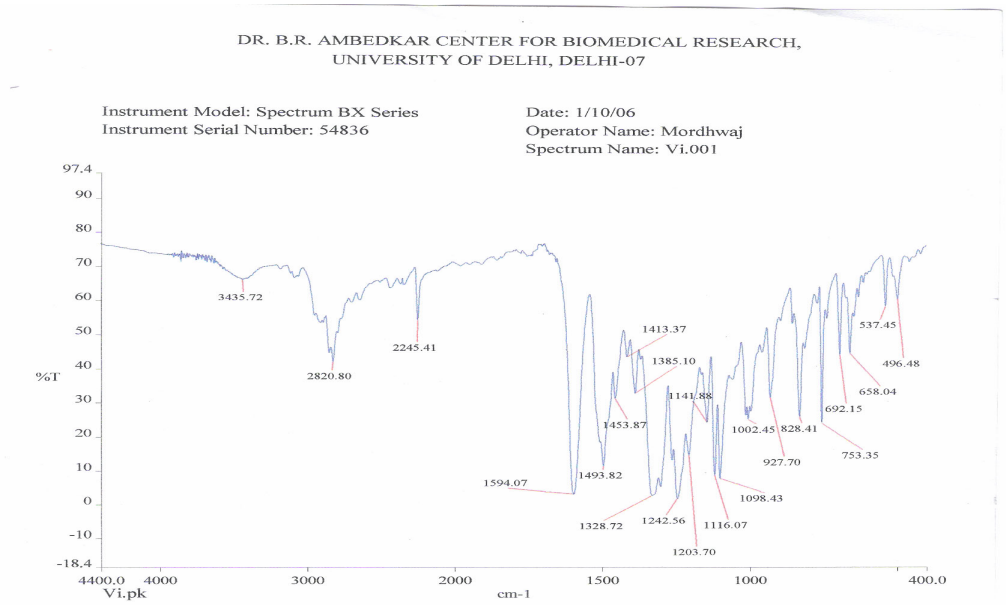
^{13}C NMR of 3-[4-(4-Nitro-phenyl)-piperazin-1-yl]-propanitrile



Mass spectra of 3-[4-(4-Nitro-phenyl)-piperazin-1-yl]-propanitrile



IR Spectra of 3-[4-(4-Nitro-phenyl)-piperazin-1-yl]-propanitrile



Vi.001 4001 4400.00 400.00 2.04 76.98 4.00 %T 16 4.00

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1453.87 31.57 1413.37 43.67 1385.10 32.99 1328.72 2.83 1242.56 2.02
1203.70 14.73 1141.88 24.35 1116.07 8.87 1098.43 7.91 1002.45 25.21
927.70 31.83 828.41 25.97 753.35 24.16 692.15 44.38 658.04 44.85
537.45 58.71 496.48 61.05