Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Aryl Fluoride Functionalized graphene oxides for the application of excellent room temperature ammonia sensitivity/selectivity

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1. General procedure for the synthesis of aryl propargyl ethers (Ar1, Ar2 and Ar3)

Aryl propargyl ethers has been prepared through Williamson ether synthesis, [1] in which propargyl bromide (1.2 equiv) was added to 1 equivalent three separate suspensions of 2, 4, 6-trimethylphenol, 3, 4, 6 –triflurophenol, 2, 4-diflurophenol dissolved and also K_2CO_3 (1.5 mmol) in dry DMF (10 mL). The reaction mixtures were stirred at room temperature and continuously monitored using TLC until the completion of reaction. Afterwards, the reaction mixtures were quenched with 10 mL of distilled water and extracted with ethyl acetate (4 x 25 mL). The extracted organic layers were washed with brine solution (4 x 15 mL) and Na_2SO_4. The crude products were purified by column chromatography using silica gel. Then the samples were dried in vacuum to get aryl propargyl ethers, namely, Ar-1, Ar-2 and Ar3 with the yield of 74%, 60% and 65%, respectively. The corresponding ^{1}HNMR and ^{13}CNMR spectra of the aryl propargyl ethers (Ar-1, Ar-2 and Ar3) is given below

(i) 2, 4, 6-Trimethyl-2-(2-propyn-1-yloxy)benzene (Ar1).

^{1}HNMR (Fig.S1(a)) (400 MHz, $CDCl_3$): δ 6.80 (d, *J*=8.6 Hz, 2H, Ar-H), 4.69 (d, *J*=2.4 Hz, 2H, O-CH_2), 2.34 (s, 3H, CH3), 3.32 (t, *J*=2.4 Hz, 1H, CH); ^{13}C NMR (Fig.S1(b)) (100 MHz, $CDCl_3$): δ 154.7, 121.9, 130.5, 131, 57.5, 16.0, 21.9, 78.7, 76.4.

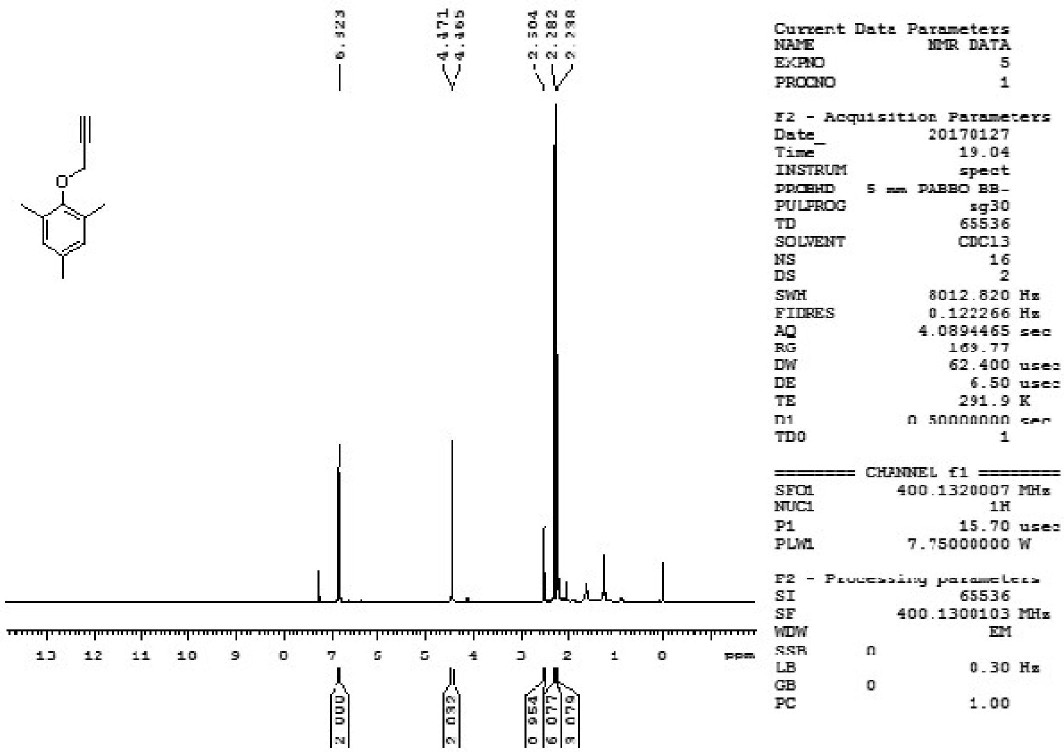

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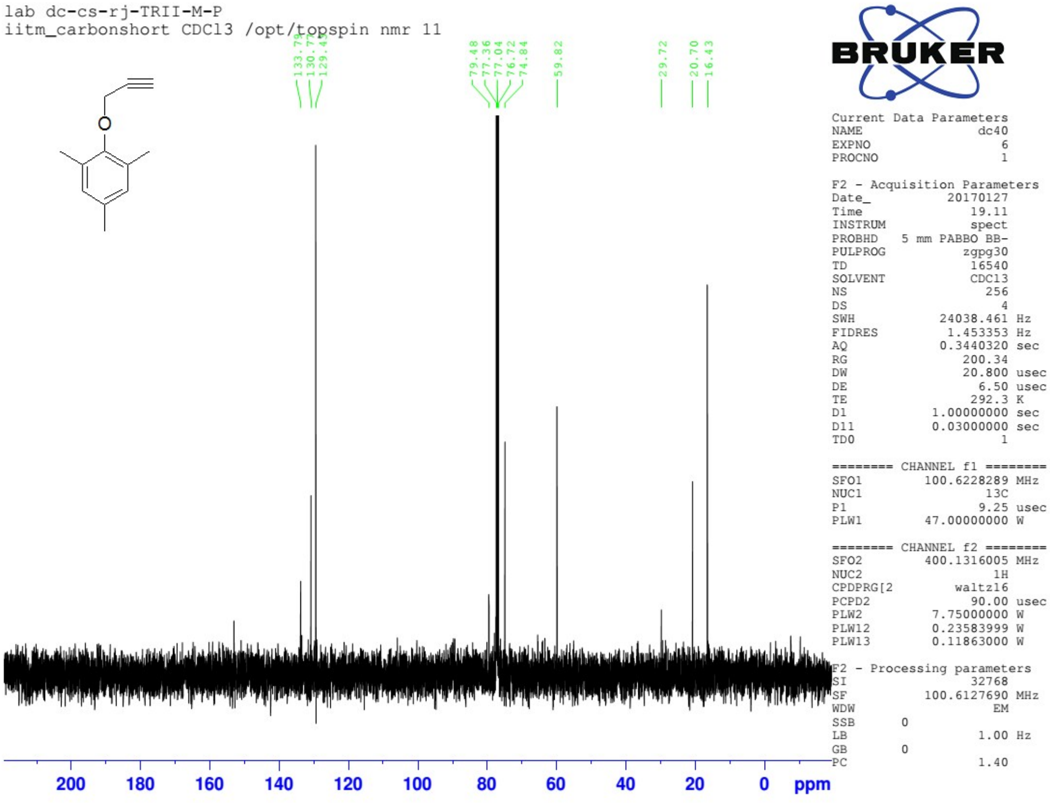
Figure. S1(a). ^{1}H NMR spectrum of 2, 4, 6-Trimethyl- 2-(2- propyn-1- yloxy)benzene (Ar1).



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BRUKER

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F2 - Processing parameters
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Figure. S1(b). ^{13}C NMR spectrum of 2, 4, 6-Trimethyl- 2-(2- propyn-1- yloxy)benzene (Ar1)

(ii). 1, 2-difluoro-3-(2-propyn-1-yloxy)benzene (Ar2)

^{1}H NMR (Fig. S2(a)) (400 MHz, CDCl3):δ 7.09 (d, J=8.6 Hz, 2H, Ar-H), 6.74 (d, J=8.6 Hz, 2H, Ar-H), 6.72 (d, J=8.6 Hz, 2H, Ar-H) 4.69 (d, J=2.4 Hz, 2H, O-CH$_2$), 3.32 (s, J=2.4 Hz, 1H CH);^{13}C NMR (Fig.S2(b)) (100 MHz, CDCl3): δ 144.2, 150.5, 151.5, 109, 110.2, 125.6, 56.9, 78.7,76.4.

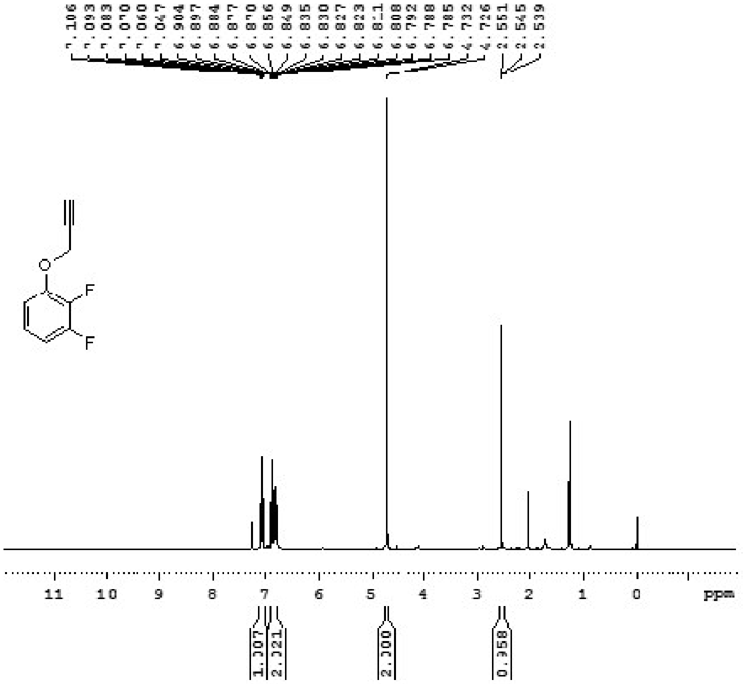

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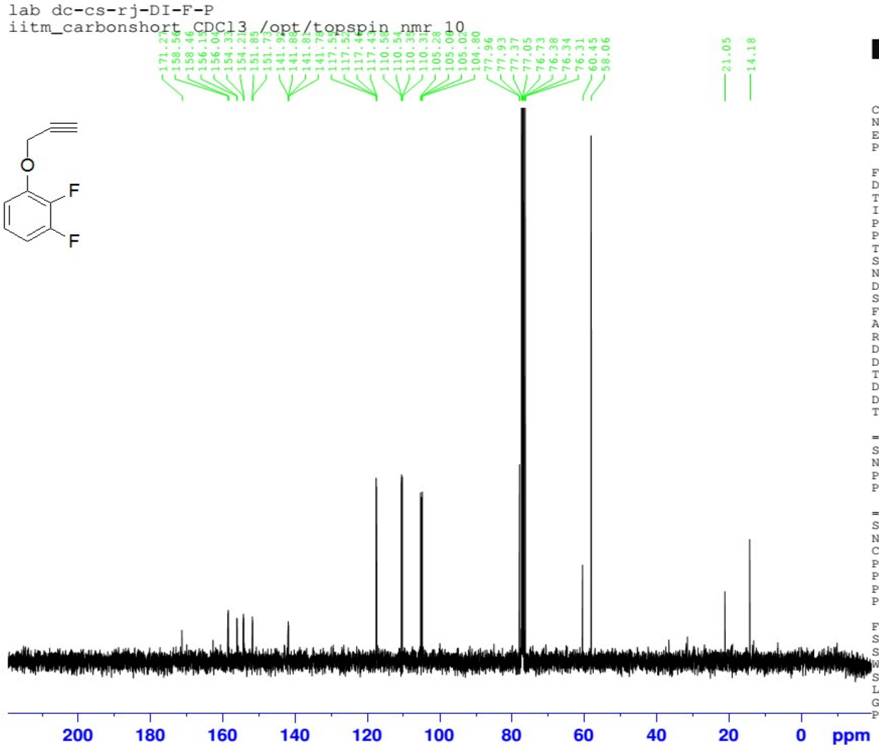
Figure. S2(a). ^{1}H NMR spectrum of 1, 2-difluoro- 3-(2- propyn-1- yloxy)benzene (Ar2).



BRUKER

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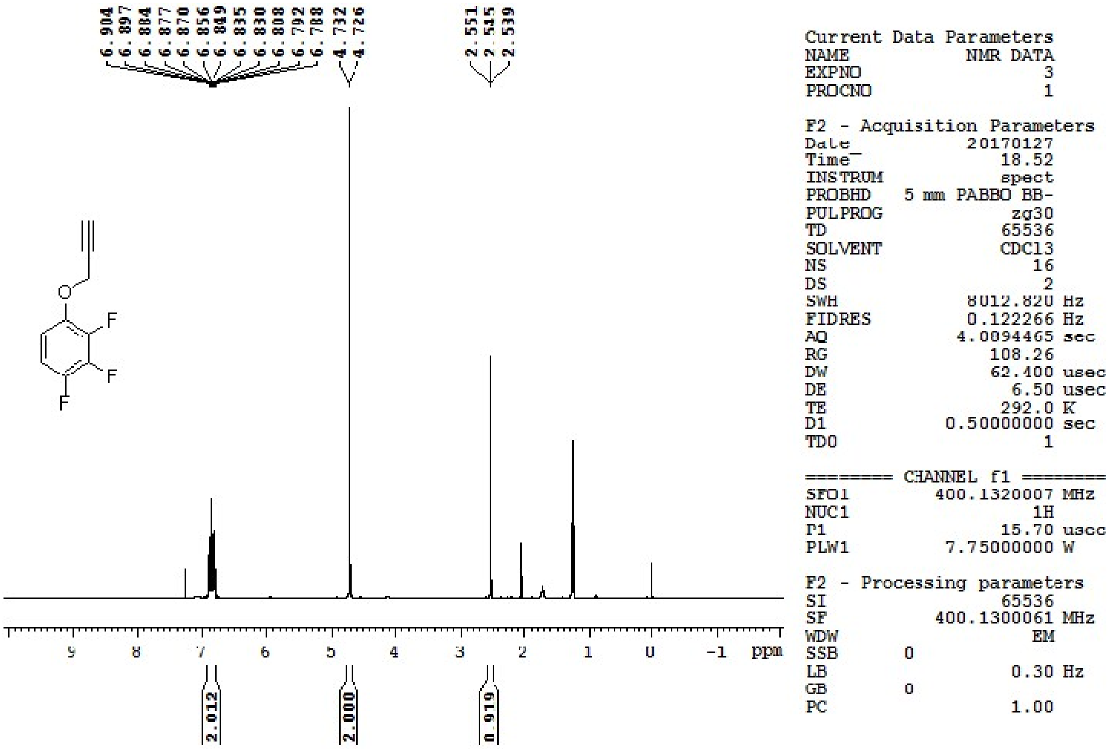
Figure. S2(b). ^{13} CNMR spectrum of 1, 2-difluoro- 3-(2- propyn-1- yloxy)benzene (Ar2).

(iii). 1,2,3-trifluoro-4-(2-propyn-1-yloxy)benzene (Ar3)

^{1}HNMR (Fig.S3(a)) (400 MHz, $CDCl_3$): δ 6.80 (d, *J*=8.6 Hz, 2H, Ar-H), 6.72 (d, *J*=8.6 Hz, 2H, Ar-H), 4.68 (d, *J*=2.4 Hz, 2H, O-CH_2), 3.32 (s, *J*=2.4 Hz, 1H, CH); ^{13}C NMR (Fig.S3(b)) (100 MHz, $CDCl_3$): δ 141.1, 143.4, 145.8, 146.7, 113.7, 56.9, 78.7, 76.4.



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F2 - Processing parameters
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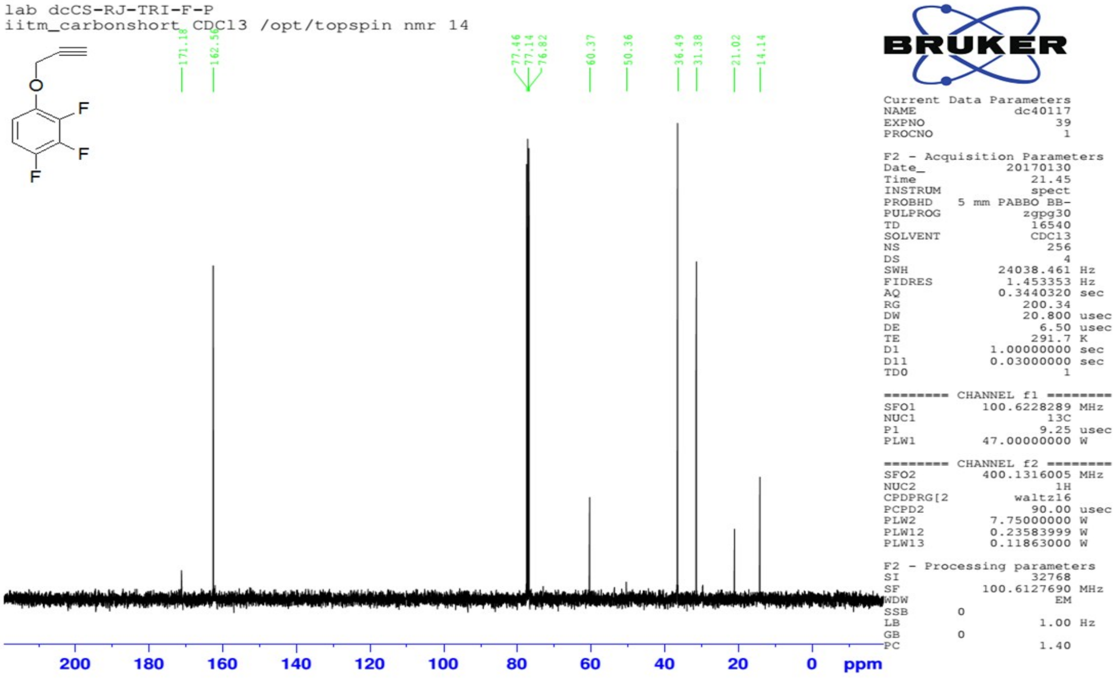
Figure. S3(a). ^{1}H NMR spectrum of 1,2,3-trifluoro- 4-(2- propyn-1- yloxy)benzene (Ar3).



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PLW12        0.23583999 W
PLW13        0.11863000 W

F2 - Processing parameters
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Figure. S3(b). ^{13} C NMR spectrum of 1,2,3-trifluoro- 4-(2- propyn-1- yloxy)benzene (Ar3) .

2. Synthesis of 3-azidopropan-1-amine.

The 3-azidopropan-1-amine was synthesized by dissolving a mixture of 3-cholropropylamine hydrochloride (14.84 mmol) and sodium azide (44.5 mmol) in 50 ml water and stirred at 80 ^{O}C for 23 hours. [2] Approximately, two third of the solvent was dried under vacuum and then cooled below 10 ^{O}C in an ice bath. The mixture of 20 ml diethyl ether and KOH solution (33.6 mmol) were added slowly to the mixture at 10 ^{O}C. Afterwards, the organic layer was extracted twice using diethyl ether and washed and filtered using Na_2SO_4. The sample was then dried under vacuum and subjected for FT- IR and Mass spectroscopy analysis for confirmation (Fig.S4(a) and S4(b)).

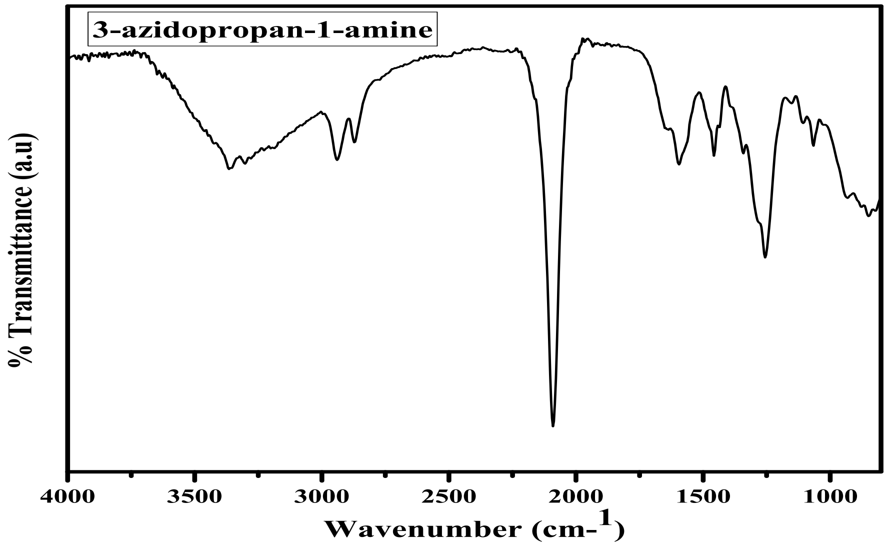

Figure. S4(a). FTIR spectra of 3-azidopropan-1-amine

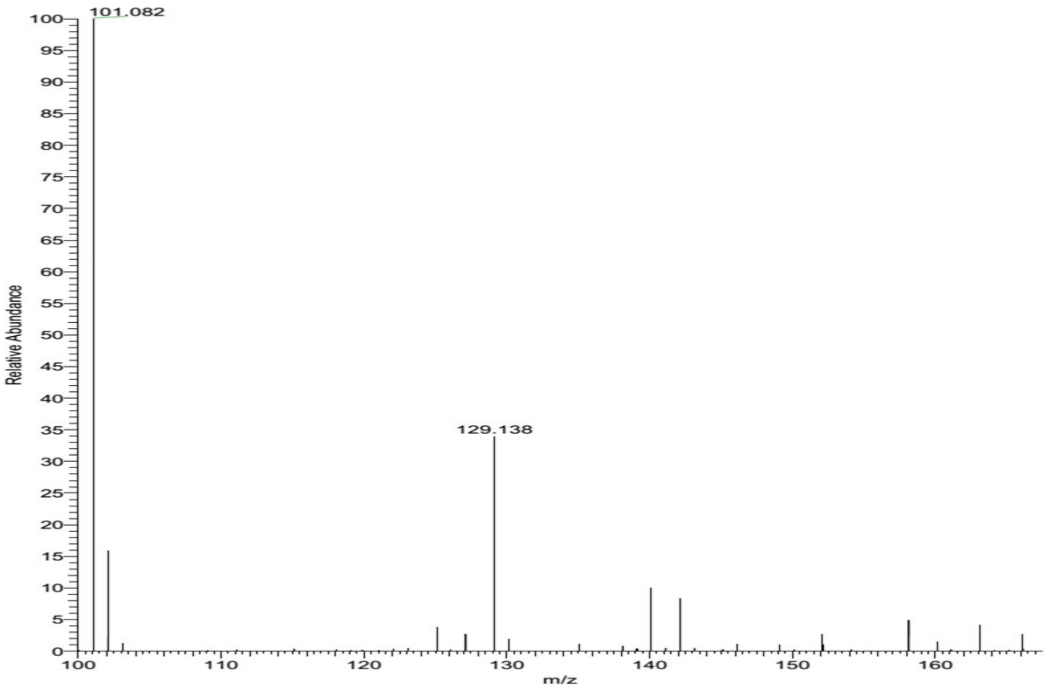

Figure. S4(b). Mass spectra of 3-azidopropan-1-amine

3. Solid state^{13}C NMR measurement for GO-Ar1.

The detailed synthesis procedure for GO-Ar is given in the Experimental section of the manuscript. Among different GO-Ar samples (GO-Ar1, GO-Ar2 and GO-Ar3), we have confirmed the clik-functionalization of Ar on terminal azide GO (GO-N_3) in GO-Ar1 using solid state ^{13}C NMR. The corresponding NMR spectra of GO-Ar1 is shown in Fig.S5. The peaks corresponding to phenolic moieties are identified at δ 160 ppm. The peaks observed between δ 120 to 134 ppm and between δ 10 to 90 ppm corresponds to 1, 2, 3-triazoles [3] and methyl groups present in phenols, respectively.

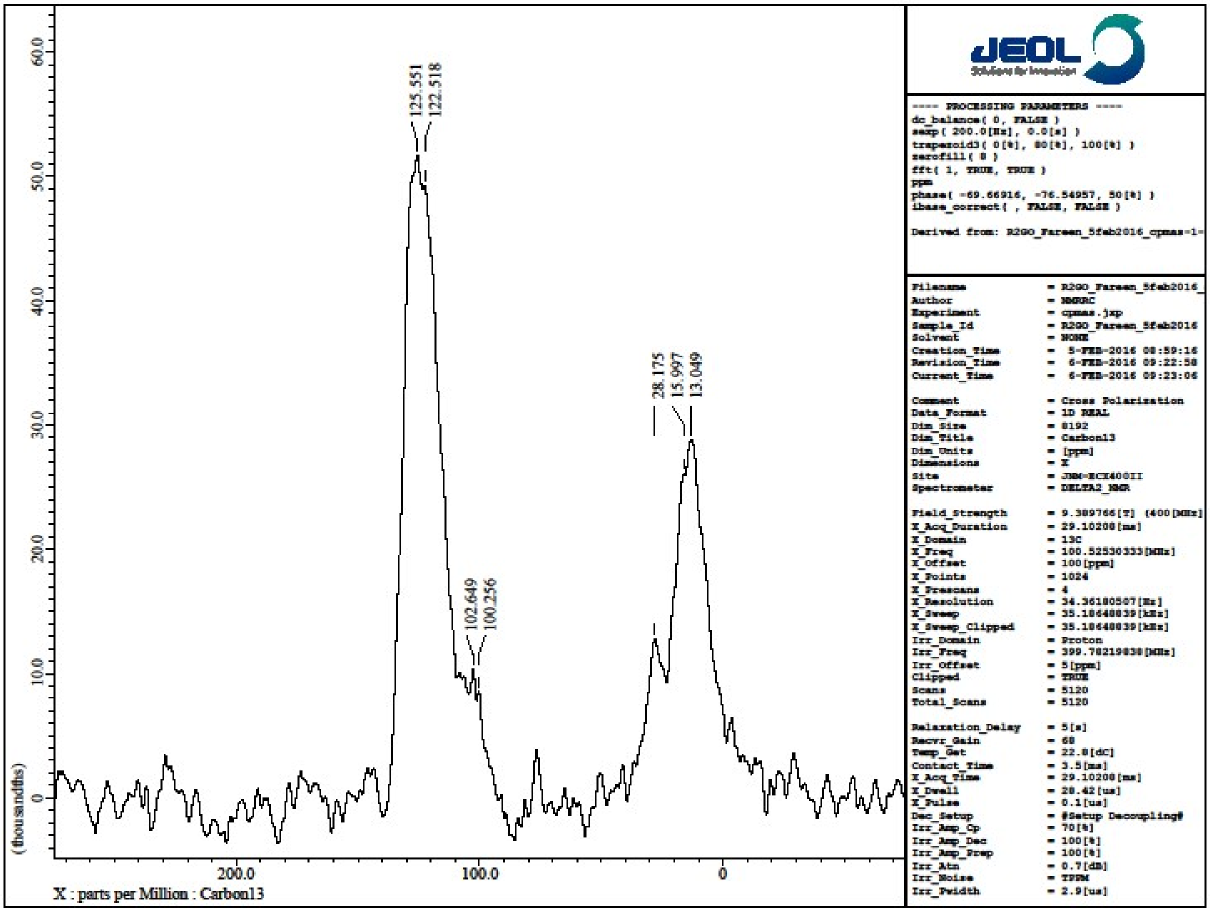

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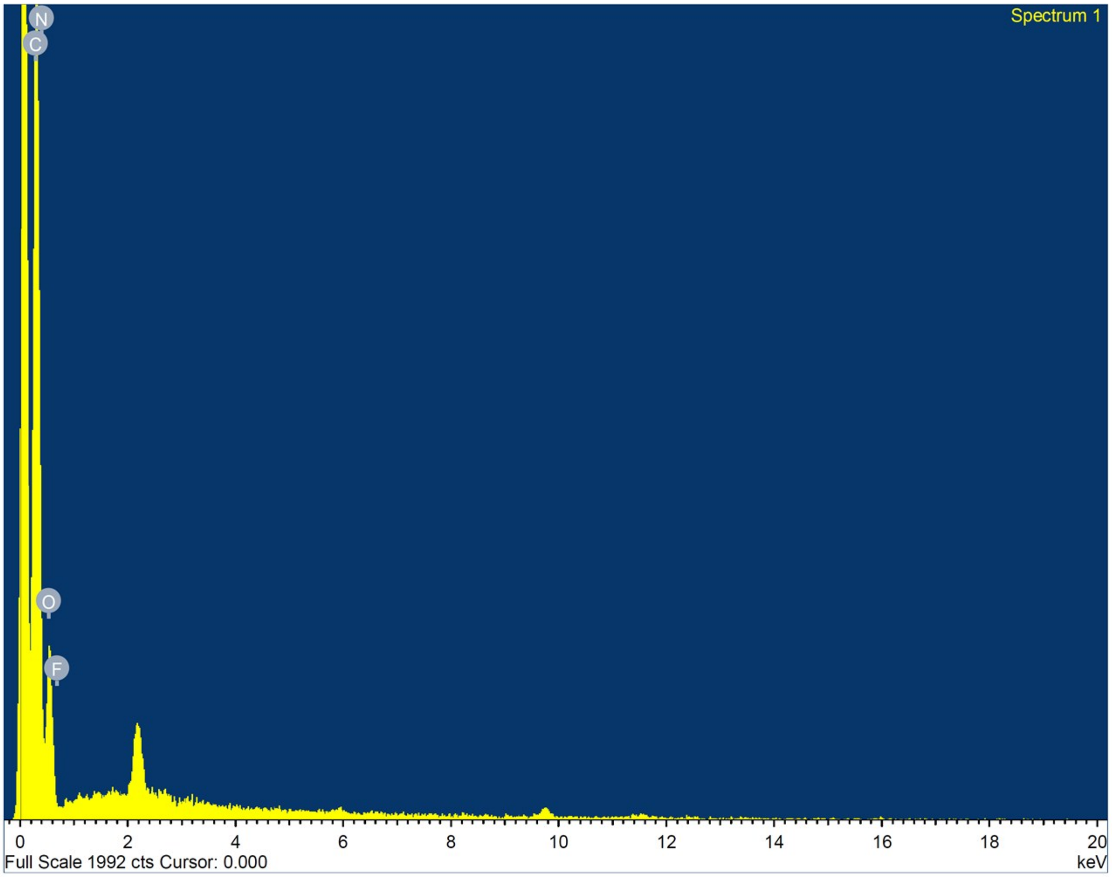
Figure. S5. ^{13}C NMR Spectrum of GO-Ar1.

4. EDAX Spectral analysis of GO-Ar1, GO-Ar2 and GO-Ar3.

The existence of fluorine in the Ar functionalized GO (GO-Ar1, GO-Ar2 and GO-Ar3) has been confirmed from the EDAX spectra taken along with scanning microscope image. The corresponding EDAX spectra of GO-Ar1, GO-Ar2 and GO-Ar3 are shown in Fig.S6(a), S6(b) and S6(c). It has been observed that GO-Ar2 and GO-Ar3 has fluorine spectra with the atomic percentage of 3.18 and 3.98, respectively. However, GO-Ar1 doesn’t show any spectral peaks corresponding to fluorine, as it has no fluorine compound according to the synthesis scheme.



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O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM

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O K	27.38	0.2949	24.43	1.52	20.84
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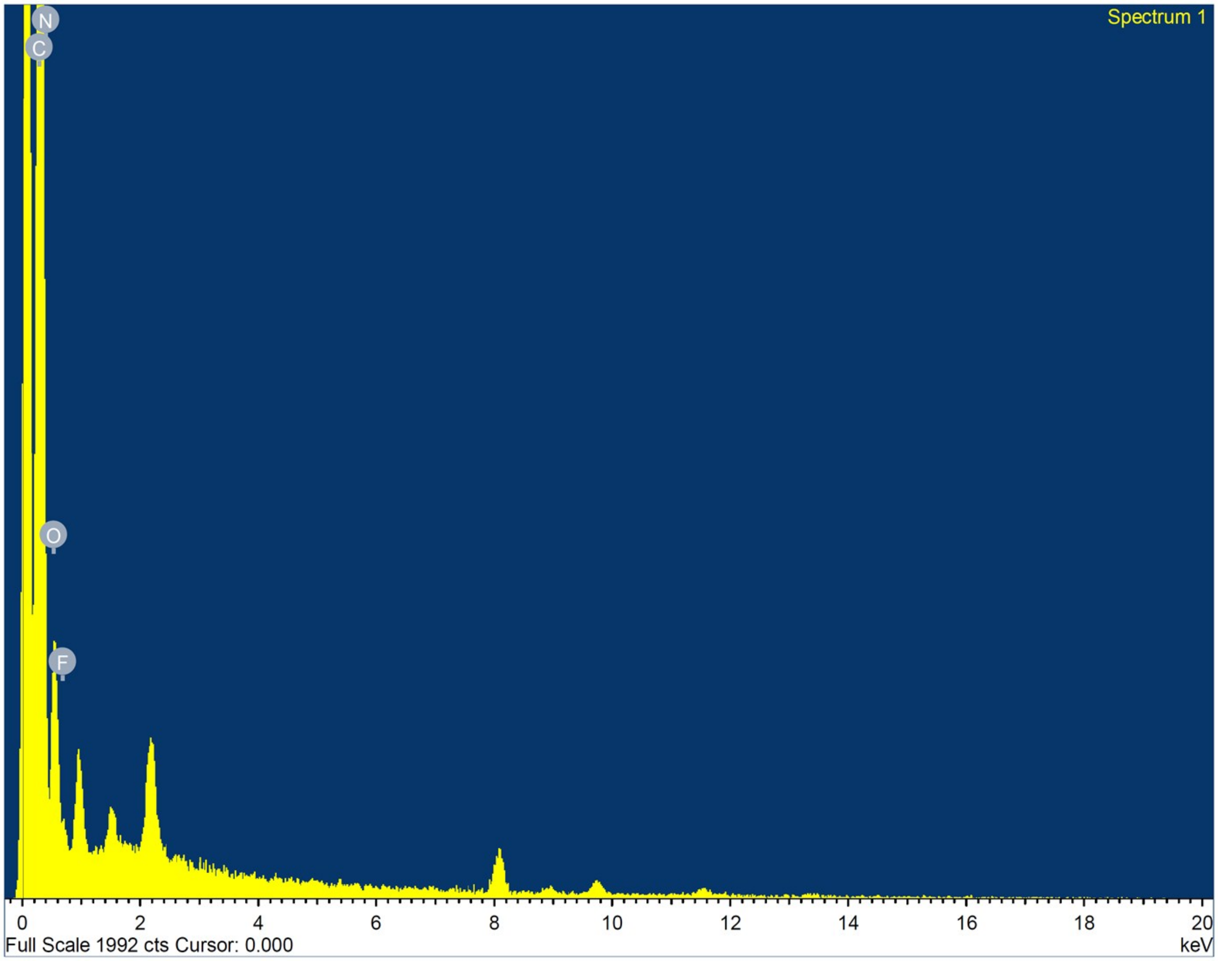
Totals			100.00		

Figure. S6(a). EDAX spectra of GO-Ar1.



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N K	39.43	0.1604	40.23	1.60	39.59
O K	41.32	0.3048	22.19	1.07	19.12
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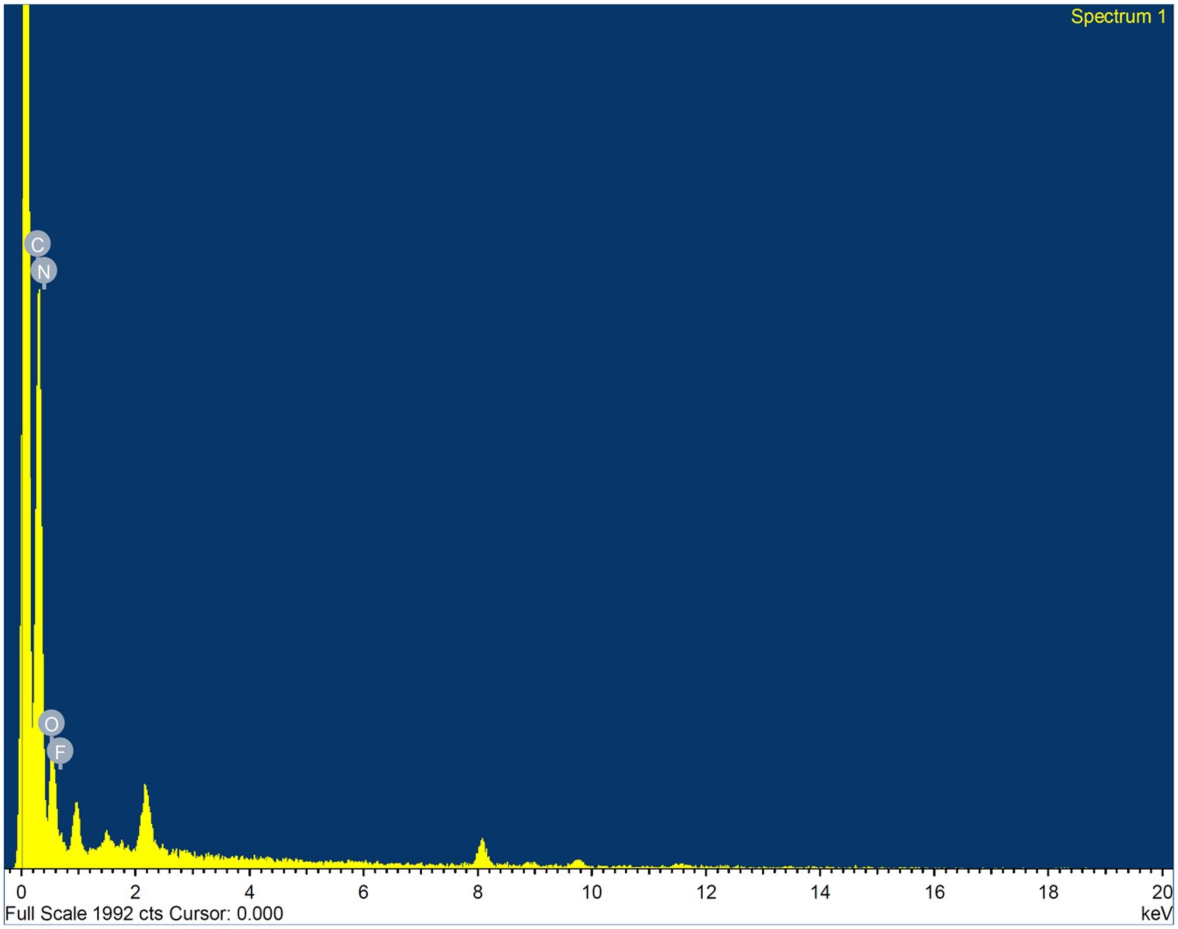
Totals			100.00		

Figure. S6(b). EDAX spectra of GO-Ar2.



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F K              2.33     0.1641     5.44     0.83     3.98

Totals                             100.00
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Figure. S6(c). EDAX spectra of GO-Ar3.

4. References

1 A. Kamble, R. Kamble, S. Dodamani, S. Jalalpure, V. Rasal, M. Kumbar, S. Joshi and S. Dixit, *Archives of pharmacal research*, 2017, **40**, 444-457.

2 S. Sulthana, T. Banerjee, J. Kallu, S. R. Vuppala, B. Heckert, S. Naz, T. Shelby, O. Yambem and S. Santra, *Molecular pharmaceutics*, 2017, **14**, 875-884.

3 Y.-S. Ye, Y.-N. Chen, J.-S. Wang, J. Rick, Y.-J. Huang, F.-C. Chang and B.-J. Hwang, *Chemistry of Materials*, 2012, **24**, 2987-2997.