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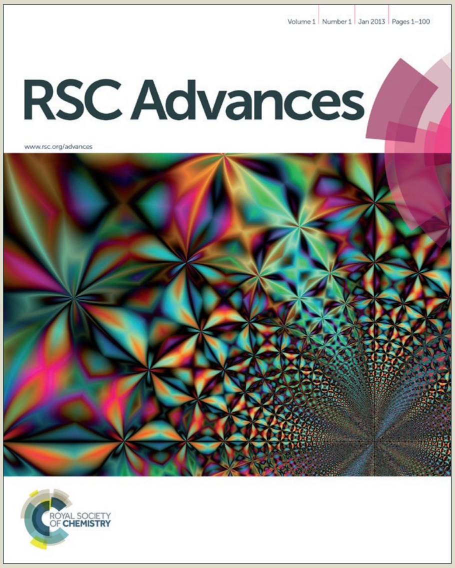

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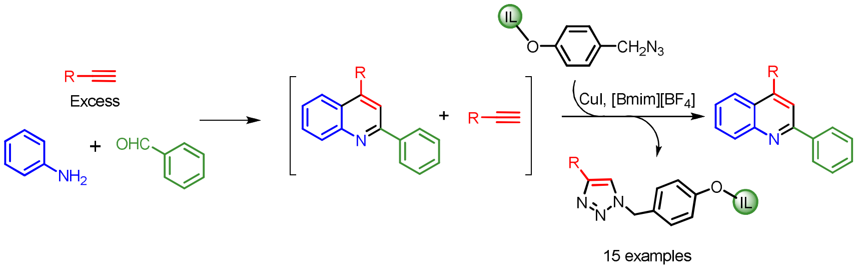
Graphical Abstract



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ARTICLE TYPE

Ionic Liquid-Supported Benzyl Azide: An Efficient Soluble Scavenger for Alkynes

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An ionic liquid scavenger functionalized with benzyl azide was synthesized and its synthetic utility was evaluated by scavenging excess alkynes in the synthesis of 2,4-disubituted quinoline *via* Povarov reaction. The ionic liquid-supported benzyl azide gave excellent efficiency in alkynes scavenging (85-100%). Purification of products without column chromatography, ease of monitoring, high loading of scavenger and shorter scavenging time are some of the advantages of this approach over solid-supported scavengers.

Introduction

Combinatorial and parallel synthetic techniques are frequently used in organic synthesis to generate library of pharmaceutically active compounds for biological screening.[1] Need for chromatographic separation of excess reagents, byproducts from the reaction mixture at each step of the synthesis of product is serious issue with these approaches. To overcome these problems, immobilized reagents and scavengers were developed as effective tools for impurity removal/product purification. Scavengers are the materials which detain excess reagent or byproduct after completion of the reaction.[2] Polymer supported scavengers were introduced as successful tools which selectively eradicated nucleophiles,[2b, 3] electrophiles,[4] dienophiles,[5] metal ions,[6] and alkynes[7] from the reaction mixture leading to pure products. Products can be purified by simply filtering the scavenged compounds and thus avoids column chromatography. These scavengers are widely used but some limitations associated with these scavengers such as slow reaction rate due to biphasic nature of the reaction mixture, requirement of large volume of the solvent to swell the polymer resin and less number of equally accessible active sites in polymer resin to capture the excess reagent led to look for newer alternatives.[8] Consequently, some new scavengers such as PEG-supported,[9] fluorous-supported,[10] silica-supported[11] and ionic liquid-supported[12] scavenger have been developed. Recently, Otvas et al. have reported iron powder as a readily available copper scavenger in continuous-flow azide–alkyne cycloaddition reaction.[13] Among these, ionic liquid-supported scavengers have received greater attention in recent years due to their homogenous reaction conditions, high loading capacity, and ease of preparation and easy monitoring of the reaction by various analytical techniques such as NMR, IR and mass spectroscopy.[14] BASIL™ is the first commercial process using ionic liquids for scavenging acids.[14a] Some ionic liquid based scavengers are depicted in figure 1. Ionic liquid [Cmmim][x] (**1**) and [2-Aemim][PF_6] (**2**) have been utilized to scavenge electrophiles like benzyl chlorides, sulfonyl chlorides, isocyanates and isothiocyanates in solution phase synthesis.[3, 15] Ionic liquid (**3**) has been used as a recyclable scavenger for CO_2 from the natural gas.[16] A diol functionalized ionic liquid (**4**) has been used as an efficient and recyclable scavenger for aldehydes[17] while ionic liquids functionalized with a Michael acceptor has been used to scavenge H_2S gas and thiols.[18] We have also demonstrated that ionic liquid-supported aldehyde (**5**) can be used as an effective scavenger for primary amine in the synthesis of secondary amines.[19] In continuation of our interest in application of ionic liquids in organic synthesis, herein, we report our finding on use of ionic liquid-supported benzyl azide as an efficient soluble scavenger for alkynes

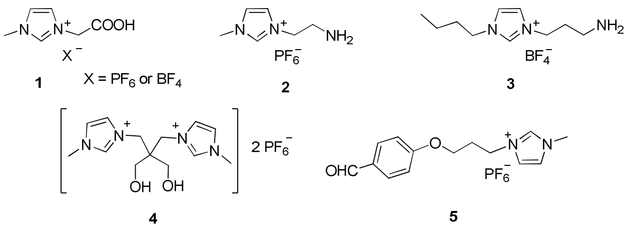
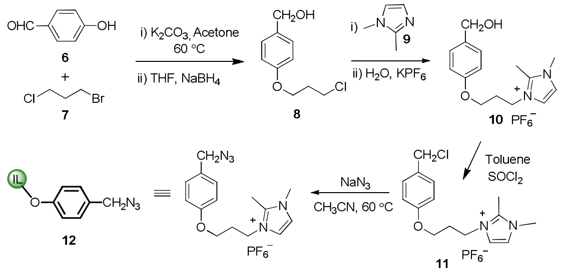


Fig. 1: Structure of some ionic liquid based scavengers

In continuation to our interest towards ionic liquid-supported reagents in organic synthesis,[12a, 19-20] herein we report the synthesis of novel imidazolium salt-supported Mukaiyama reagent (2-chloropyridinium salt) and its application in amide bond formation. To the best of our knowledge this is the first report of the synthesis of an imidazolium salt-supported Mukaiyama reagents.

Result and discussion

The ionic liquid-supported benzyl azide (**12**) was synthesized from 4-hydroxybezaldehyde (**6**) as shown in scheme 1. Initially, reaction of **6** with 3-chloro-1-bromopropane (**7**) followed by reduction with sodium borohydride gave (**8**) in 86% yield. Quaternization of 1,2-dimethylimidazole (**9**) with **8** followed by anion exchange resulted in the formation of ionic liquid-supported benzyl alcohol (**10**).[21] Reaction of **10** with sulfonyl chloride gave ionic liquid-supported benzyl chloride (**11**) in 93% yield. Finally, substitution of chloro group with azide in **11** resulted in the formation of ionic liquid-supported benzyl azide (**12**) in 92% yield. The structure of **12** was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopic analysis. The IR spectra of **12** showed the characteristic band for azide group at 2106 cm^{-1} along with peaks at 1612 and 1427 cm^{-1} for C=N and C=C stretching, respectively. In the ^{1}H NMR spectra of **12**, a singlet at 4.36 ppm for benzylic protons and doublets at 7.67 and 7.62 ppm for imidazolium proton were observed along with other protons. Similarly, a characteristic peak for benzylic carbon appeared at 53.6 ppm in the ^{13}C NMR spectrum of **12** along with peaks for other carbons.



Scheme 1: Synthesis of ionic liquid-supported benzyl azide **12**

The differential scanning calorimetric (DSC) analysis of **12** displayed that it was thermally stable up to 230 °C with melting point of 92 °C (Fig. 2).[20b, 22] It is worth to mention that we did not observe any decomposition or loss in reactivity of **12** even after storage for one month at room temperature.

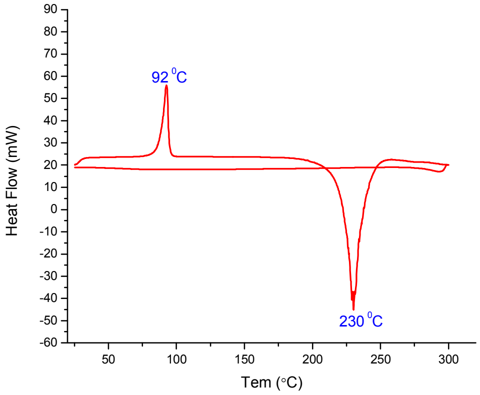
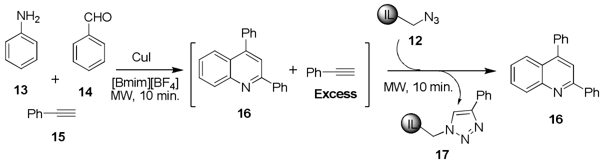


Fig. 2: DSC analysis of ionic liquid-supported benzyl azide **12**.

Next, to study the efficacy of **12** as a scavenger, the Povarov reaction between aniline (**13**), benzaldehyde (**14**), and phenylacetylene (**15**) was selected as model reaction. Initially, mixture of **13** (1.0 mmol), **14** (1.0 mmol), **15** (2.0 mmol) and CuI (10 mol %) in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]), was irradiated under microwave at 80 °C for 10 min. (Scheme 2).[23] After completion of the reaction, **12** was added to scavenge excess of **15** and reaction mixture was again irradiated for 10 min at 40 °C, 40W and 250 psi. On complete scavenging of excess **15**, the product 2,4-diphenylquinoline (**16**) was extracted in ethyl acetate/ hexane (1: 1, *v/v*) mixture leaving behind scavenged **15** in [Bmim][BF$_4$] as ionic liquid-supported triazole (**17**). Capturing of **15** by **12** was monitored by IR and HPLC analysis. Figure 3 shows an overlap of IR spectra of the reaction mixture before reaction (black), after reaction (red) and after treating with **12** (blue). Vanishing of the peak at 2106 cm^{-1} for carbon-carbon triple bond stretching on treating the reaction mixture with **12** indicated complete scavenging of **15**. The purity of the product was analyzed by HPLC analysis (Supporting info, Fig. S1) and it was found that after scavenging the reaction mixture with **12** for 10 min. the purity of the product was more than 95%. Similarly, excess alkyne was trapped using **12** for Povrov reaction of 3-methyl-, 4-methyl- and 4-*tert*-butylpheylacetylene with benzaldehyde and aniline. The HPLC analysis showed that the product was moe than 95% pure after treating the reaction mixture with 12 (Supporting info, Fig. S2-S4).



Scheme 2: Scavenging of excess alkyne using **12** in Povarov reaction

To further understand the scope of alkyne scavenging using **12**, it was allowed to react with different type of pure alkynes under similar conditions. The results for capturing of different alkyne using **12** are shown in Table 1. Aliphatic alkynes, aromatic alkynes as well as heterocyclic alkynes were effectively scavenged under these conditions. In general, the scavenging ability of **12** was not much affected by electronic effects on aryl ring of aromatic alkynes. However, internal alkynes remained as such and they could not be scavenged under these conditions. The scavenged products (**17**) were characterized by ^{1}H and ^{13}C NMR analysis (see supporting information). It is important to note that these ionic liquid-supported triazoles can be cleaved to give corresponding 1,2,3-triazoles.[24]

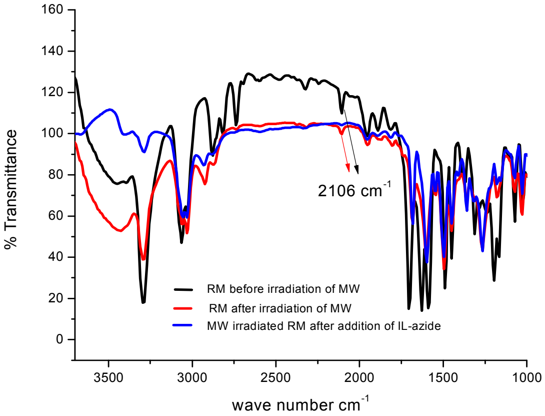
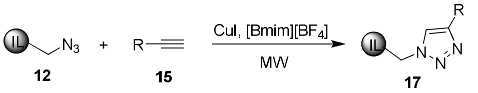


Fig. 3: IR spectra of reaction mixture before & after MW irradiation and after treating with **12**.

Table 1: Scavenging of different alkynes using **12**.



Entry	R	Time (min.)	Product	Conversion[b]	% Yield[c]
1	C_6H_5	10	**17a**	90	65
2	$3\text{-}CH_3C_6H_4$	10	**17b**	100	88
3	$4\text{-}CH_3C_6H_4$	10	**17c**	92	75
4	$4\text{-}C_2H_5C_6H_4$	15	**17d**	85	64
5	$4\text{-}C(CH_3)_3C_6H_4$	15	**17e**	98	79
6	$4\text{-}OCH_3C_6H_4$	15	**17f**	92	65
7	$3,4\text{-}(OCH_3)_2C_6H_3$	10	**17g**	100	94
8	$4\text{-}OC_7H_7C_6H_4$	10	**17h**	95	76
9	$2\text{-}CHOC_6H_4$	10	**17i**	100	82
10	$4\text{-}COCH_3C_6H_4$	10	**17j**	100	89
11	$4\text{-}FC_6H_4$	15	**17k**	94	67
12	$\text{-}CH_2(CH_2)_2C_6H_5$	10	**17l**	99	89
13	$\text{-}C_3H_7$	15	**17m**	91	63
14	$\text{-}C_{10}H_7$	10	**17n**	100	85
15	$\text{-}C_{14}H_{11}N_2$	10	**17o**	100	94

[a]Reaction conditions: **15** (1.0 mmol), CuI (10 mol%), **12** (1.0 mmol) and [Bmim][BF$_4$] (3 ml), microwave irradiation at 40 °C, 40 W and 250 psi, [b]Based on HPLC-analysis, [c]Isoalted yield of **17**.

Experimental

General

The NMR spectra were recorded on 300 MHz, 400 MHz and 500 MHz spectrometers using $CDCl_3$ and DMSO-d_6 as solvents. The chemical shifts were expressed in ppm. The IR spectra were recorded on ABB Bomen MB3000 FTIR spectrophotometer. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica-coated aluminum plates (60-F_{254}) using UV light as visualizing agent. All the chemicals and reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

General procedure for the synthesis of imidazolium-supported benzyl alcohol (10):

A round bottom flask containing 1,2-dimethylimidazole (2.87 g, 30 mmol) and (4-(3-chloropropoxy)phenyl)methanol[21] (6.00 g, 30 mmol) was heated at 110 °C for 3 h. A thick viscous liquid was obtained which was washed with ethyl acetate (3 × 20 mL) to remove unreacted starting materials. After washing 8.56 g (96%) of pure chloride salt was obtained. Ion metathesis of chloride with hexafluorophosphate was performed using aqueous potassium hexafluorophosphate solution (20 mL, 6.37 g, 35 mmol) at room temperature for 1 h. After filtrating solid precipitate, the filtrate was washed with water and dried in vacuum to get pure **10**.

Yield: 97%; White solid; mp 115 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.65 (d, J = 2.0 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.23 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.05 (t, J = 5.6 Hz, 1H), 4.41 (d, J = 5.6 Hz, 2H), 4.29 (t, J = 6.8 Hz, 2H), 3.97 (t, J = 5.9 Hz, 2H), 3.73 (s, 3H), 2.55 (s, 3H), 2.19 (p, J = 6.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.4, 144.9, 135.3, 128.4, 122.8, 121.4, 114.4, 64.5, 62.9, 45.3, 35.1, 29.1, 9.5

General procedure for the synthesis of ionic liquid-supported benzyl chloride (11): Thionyl chloride (1.61ml, 22.15mmol) was added dropwise to the suspension of ionic liquid supported benzyl alcohol (3gm, 7.38mmol) in DCM at 0 °C. The reaction mixture was allowed to stir at room temperature till complete consumption of ionic liquid supported benzyl alcohol (2 h). After completion of reaction, excess of thionyl chloride was removed on rotatory-evaporator to obtain white solid as product (2.90 g, 93%).

General procedure for the synthesis of ionic liquid-supported benzyl azide (12): Ionic liquid supported benzyl chloride (2.90gm, 6.82mmol) and sodium azide (0.533gm, 8.19mmol) were dissolved in acetonitrile (15ml). The reaction mixture was heated at 60 °C for 12 h and then cooled to room temperature. The resulting mixture was filtered by simple filtration method to remove NaCl formed. The filtrate was concentrated under high vacuum to get white solid as product (2.70 g, 92%).

Yield 92%; White solid; mp 95-97 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.67 (d, J = 2.1 Hz, 1H), 7.61 (d, J = 2.1 Hz, 1H), 7.31 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 4.36 (s, 2H), 4.28 (d, J = 6.9 Hz, 2H), 4.00 (d, J = 6.0 Hz, 2H), 3.74 (s, 3H), 2.55 (s, 3H), 2.20 (p, J = 6.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4, 144.9, 130.5, 128.2, 122.8, 121.4, 115.0, 64.6, 53.6, 45.2, 35.1, 29.1, 9.5

Experimental procedure for scavenging alkyne using ionic liquid-supported benzyl azide 12: In microwave vial, a mixture of benzaldehyde (1.0 mmol), aniline (1.0 mmol), phenylacetylene (2.0 mmol) and CuI (10 mol %) in [Bmim]BF$_4$ (3 ml) was irradiated in close vessel at 80 °C, 50W, 250psi for 10min. The reaction was monitored by TLC. IL-benzyl azide (**12**) (1.0 mmol) was added in same reaction mixture after complete consumption of benzaldehyde and aniline. The resulting mixture was again irradiated in microwave for 10 min at 40 °C, 40W, 250psi to remove excess of alkyne. Organic phase was separated by simple extraction by ethyl acetate/ hexane (1: 1, *v/v*) mixture leaving ionic liquid-supported triazole in [Bmim][BF$_4$] at bottom of vial. To isolate IL-triazole we added H_2O to reaction mixture, [Bmim][BF$_4$] dissolved in H_2O, leaving behind IL-triazole at the bottom of microwave vial. The resulting mixture was washed with toluene (3 × 5 mL) to remove H_2O to obtain the desired compound.

Physical and spectroscopic data for 17a-o

17a: Yield 60%; Green solid; mp 98-101 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 8.60 (s, 1H), 7.82 (d, J = 7.4 Hz, 2H), 7.61 (d, J = 13.7 Hz, 2H), 7.43 (t, J = 7.1 Hz, 2H), 7.33 (d, J = 7.5 Hz, 3H), 6.92 (d, J = 7.8 Hz, 2H), 5.55 (s, 2H), 4.26 (t, J = 6.2 Hz, 2H), 3.97 (t, J = 4.8 Hz, 2H), 3.71 (s, 3H), 2.52 (s, 3H), 2.19-2.13 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4, 147.0, 144.9, 131.1, 130.0, 129.3, 128.7, 128.3, 125.5, 122.8, 121.7, 121.4, 115.1, 64.6, 52.9, 45.2, 35.1, 29.0, 9.5

17b: Yield 84%; Brown liquid; ^1H NMR (300 MHz, DMSO-d_6) δ 8.58 (s, 1H), 7.71 – 7.56 (m, 5H), 7.34 (d, J = 8.1 Hz, 3H), 7.14 (d, J = 7.1 Hz, 1H), 6.93 (d, J = 7.9 Hz, 2H), 5.55 (s, 2H), 4.28 (t, J = 6.1 Hz, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 2.54 (s, 3H), 2.35 (s, 3H), 2.24 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4, 144.9, 138.4, 131.0, 130.0, 129.5, 129.4, 129.2, 128.9, 128.7, 126.1, 122.8, 122.7, 121.7, 121.3, 115.1, 64.6, 53.0, 46.2, 45.2, 35.1, 29.0, 21.4, 9.5

17c: Yield 70%;White solid; mp 136-140 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 13.6 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 6.93 (d, J = 7.8 Hz, 2H), 5.55 (s, 2H), 4.28 (s, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 2.54 (s, 3H), 2.32 (s, 3H), 2.19 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4, 147.1, 144.9, 137.6, 130.0, 129.8, 128.7, 128.3, 125.5, 122.8, 121.4, 121.3, 115.1, 64.6, 52.9, 45.2, 35.1, 29.0, 21.2, 9.5

17d: Yield 59%; Colorless solid; mp 100-104 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 1.9 Hz, 1H), 7.46 (d, J = 1.8 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 5.53 (s, 2H), 4.33 (t, J = 6.8 Hz, 2H), 4.00 (t, J = 5.6 Hz, 2H), 3.79 (s, 3H), 2.65 (q, J = 7.6 Hz, 2H), 2.59 (s, 3H), 2.32 – 2.23 (m, 2H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.0, 144.0, 143.9, 129.6, 128.1, 127.9, 125.3, 122.6, 121.1, 120.1, 114.6, 63.7, 53.1, 45.2, 34.9, 28.8, 28.3, 15.4, 9.2

17e: Yield 74%; Light yellow solid; mp 82-86 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (s, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 1.9 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 5.43 (s, 2H), 4.17 (t, J = 7.2 Hz, 2H), 3.88 (t, J = 5.3 Hz, 2H), 3.62 (s, 3H), 2.43 (s, 3H), 2.22 – 2.12 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.2, 151.3, 144.0, 129.7, 127.7, 127.6, 127.5, 125.7, 125.3, 122.4, 120.8, 114.8, 63.5, 53.5, 45.2, 34.9, 34.6, 31.2, 28.7, 8.9

17f: Yield 45%; Green solid; mp 67-70 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.49 (s, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 18.2 Hz, 2H), 7.33 (d, J = 7.3 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 6.93 (d, J = 7.3 Hz, 2H), 5.54 (s, 2H), 4.28 (s, 2H), 3.98 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 2.54 (s, 3H), 2.19 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.4, 158.4, 147.0, 144.9, 130.0, 128.8, 126.9, 123.7, 122.8, 121.4, 120.8, 115.1, 114.7, 64.6, 55.6, 52.9, 45.2, 35.1, 29.0, 9.5

17g: Yield 94%; Yellow solid; mp 80-84 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.51 (s, 1H), 7.60 (d, J = 13.6 Hz, 2H), 7.39 (s, 1H), 7.31 (d, J = 7.2 Hz, 3H), 6.99 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 6.8 Hz, 2H), 5.53 (s, 2H), 4.26 (s, 2H), 3.97 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 2.52 (s, 3H), 2.17 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4, 149.4, 149.0, 144.9, 130.0, 128.8, 123.8, 123.4, 122.8, 121.4, 121.0, 117.9, 115.1, 112.4, 109.2, 64.6, 55.9, 52.9, 45.2, 35.1, 29.0, 9.5

17h: Yield 68%; Brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (s, 1H), 7.75 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 18.2 Hz, 2H), 7.45 (d, J = 6.7 Hz, 2H), 7.39 (t, J = 6.8 Hz, 2H), 7.32 (d, J = 7.5 Hz, 3H), 7.07 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 5.53 (s, 2H), 5.12 (s, 2H), 4.26 (t, J = 6.1 Hz, 2H), 3.97 (s, 2H), 3.71 (s, 3H), 2.53 (s, 3H), 2.23 – 2.13 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.5, 158.4, 144.9, 137.4, 130.0, 128.9, 128.8, 128.3, 128.1, 126.9, 123.9, 122.8, 121.4, 120.9, 118.5, 115.6, 115.1, 69.7, 64.6, 52.9, 45.2, 35.1, 29.0, 9.5

17i: Yield 88%; Brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 1H), 8.73 (s, 1H), 7.89 (d, J = 4.2 Hz, 1H), 7.76 (s, 2H), 7.70 – 7.52 (m, 3H), 7.38 (d, J = 5.9 Hz, 2H), 6.94 (d, J = 5.5 Hz, 2H), 5.62 (s, 2H), 4.28 (s, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 2.54 (s, 3H), 2.19 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 192.8, 158.5, 144.9, 134.4, 133.8, 133.4, 130.2, 130.0, 129.5, 128.9, 128.5, 128.1, 125.0, 122.8, 121.4, 115.1, 64.6, 53.1, 45.2, 35.1, 29.0, 9.5

17j: Yield 85%; Light yellow solid; mp 180-184 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.78 (s, 1H), 8.01 (d, J = 7.8 Hz, 4H), 7.62 (d, J = 18.5 Hz, 2H), 7.36 (d, J = 4.8 Hz, 2H), 6.94 (d, J = 4.6 Hz, 2H), 5.59 (s, 2H), 4.28 (s, 2H), 3.99 (s, 2H), 3.73 (s, 3H), 2.60 (s, 3H), 2.54 (s, 3H), 2.19 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 197.8, 158.5, 146.0, 144.9, 136.3, 135.4, 130.1, 129.4, 128.5, 125.5, 123.0, 122.8, 121.4, 115.1, 64.6, 53.1, 45.2, 35.1, 29.0, 27.1, 9.5.

17k: Yield 60%; Brown liquid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.60 (s, 1H), 7.88 (s, 2H), 7.62 (d, J = 13.2 Hz, 2H), 7.41 – 7.20 (m, 4H), 6.93 (d, J = 6.7 Hz, 2H), 5.56 (s, 2H), 4.28 (s, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 2.54 (s, 3H), 2.18 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4, 156.9, 146.2, 144.9, 130.0, 128.6, 127.7, 127.5, 122.8, 121.7, 121.4, 116.4, 116.1, 115.8, 115.1, 64.6, 53.0, 45.2, 35.1, 29.0, 9.5

17l: Yield 84%; Light yellow solid; mp 124-126 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 (s, 1H), 7.51 – 7.41 (m, 2H), 7.26 (d, J = 6.6 Hz, 4H), 7.17 (s, 3H), 6.87 (d, J = 6.6 Hz, 2H), 5.46 (s, 2H), 4.36 (t, J = 6.5 Hz, 2H), 4.00 (d, J = 4.7 Hz, 2H), 3.82 (s, 3H), 2.66 (s, 4H), 2.62 (s, 3H), 2.29 (d, J = 4.2 Hz, 2H), 1.98 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.0, 143.9, 141.6, 129.5, 128.2, 128.1, 127.8, 125.6, 122.6, 121.1, 114.5, 63.6, 53.1, 45.2, 35.0, 35.0, 30.8, 28.8, 25.1, 9.2

17m: Yield 55%;Yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (s, 1H), 7.64 (d, J = 2.0 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 5.45 (s, 2H), 4.28 (t, J = 6.8 Hz, 2H), 3.97 (t, J = 5.9 Hz, 2H), 3.72 (s, 3H), 2.56 (d, J = 3.8 Hz, 2H), 2.54 (s, 3H), 2.23 – 2.13 (m, 2H), 1.58 (dd, J = 14.4, 7.2 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.3, 144.9, 129.9, 129.0, 122.8, 121.4, 115.0, 64.6, 52.6, 45.2, 35.1, 29.0, 27.5, 22.6, 14.0, 9.5

17n: Yield 82%; Light yellow solid; mp 84-86 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.40 (s, 1H), 8.07 (s, 1H), 7.89 (d, J = 3.1 Hz, 2H), 7.72 (s, 1H), 7.52 (d, J = 2.6 Hz, 3H), 7.37 (d, J = 2.7 Hz, 4H), 6.90 (d, J = 3.5 Hz, 2H), 5.62 (s, 2H), 4.33 (d, J = 3.3 Hz, 2H), 3.99 (d, J = 2.9 Hz, 2H), 3.79 (s, 3H), 2.59 (s, 3H), 2.28 (d, J = 1.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.8, 140.2, 139.7, 138.5, 135.6, 134.6, 133.6, 133.1, 132.4, 131.8, 131.4, 130.8, 130.1, 127.6, 126.0, 119.5, 68.3, 58.3, 50.2, 39.9, 33.7, 14.1

17o: Yield 88%; Brown solid; mp 150-153 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 8.67 (s, 1H), 8.45 (s, 1H), 7.90 (d, J = 4.3 Hz, 2H), 7.75 (d, J = 3.9 Hz, 2H), 7.62 (d, J = 16.9 Hz, 2H), 7.36 (s, 2H), 7.25 (s, 2H), 6.95 (s, 2H), 5.60 (s, 2H), 4.27 (s, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 3.36 (s, 3H), 2.32 (s, 3H), 2.18 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.4, 144.8, 144.2, 144.1, 137.7, 130.1, 129.7, 128.5, 125.8, 123.7, 123.5, 122.8, 121.8, 121.3, 116.8, 115.1, 64.6, 53.1, 45.2, 35.1, 29.0, 21.3, 9.5

Conclusion

In summary, we have described the synthesis of ionic liquid-supported benzyl azide and explored its application as a soluble scavenger to scavenge alkynes. Purification of the reaction product without column chromatography, requirement of lesser amount of scavenger and rapid scavenging process, ease in monitoring progress of the reaction are some of the advantages of this approach over analogous polymer-supported scavenger.

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Notes

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