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Synthesis of Ionic Liquid-Supported Sulfonyl Azide and Its Application in Diazotransfer Reaction

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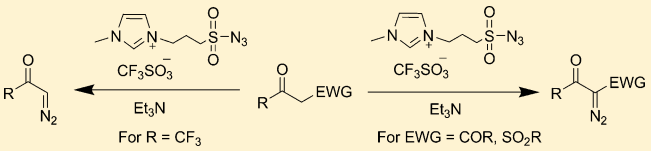
Supporting Information

ABSTRACT: The paper describes synthesis of a novel ionic liquid-supported sulfonyl azide and its applications as diazotransfer reagent of active methylene compounds as well as deformylative diazo transfer reagent. The diazo compounds were isolated in excellent yields (82−94%) and high purity. The method offers better separation of product and reagent. This method is experimentally simple and mild, and requires very short reaction time.



Diazo compounds are useful industrial and pharmaceutical reagents since they can undergo a wide variety of chemical transformations such as 1,3-dipolar cycloadditions and insertion reactions under mild conditions.[1,2] Commonly used reagents in diazotransfer reaction are methanesulfonyl azide (MsN_3),[3] *p*-tolylsulfonyl azide (TsN_3),[4] *p*-carboxybenzylsulfonyl azide (*p*-CBSA),[5] imidazole-1-sulfonyl azide (Im-SO_2N_3), trifluoromethanesulfonyl azide (TfN_3),[6] and triisopropylbenzenesulfonyl azide.[7] Unfortunately, some of these reagents are associated with purification problems due to formation of sulfonamide coproducts, and some of them decompose at higher temperature.[3] To circumvent these problems, several alternative reagents such as polymer-supported benzenesulfonyl azide (PS-SO_2N_3),[8] nonafluorobutanesulfonyl azide (NfN_3),[9] imidazole-1-sulfonyl azide hydrochloride,[10,11] oligomeric sulfonyl azide,[12] benzotriazol-1-yl-sulfonyl azide (Bt-SO_2N_3),[13] and 2-azido-1,3-dimethylimidazolinium (ADM) salts[14] have been developed. Some of these reagents such as NfN_3, ADMP have improved yield in short reaction time, and the side product is easily removed. The stability of imidazole-1-sulfonyl azide salts has been improved by changing the counterion.[11] Due to the wide importance of diazo compounds and problems associated with the safety of reagents and the separation of sulfonamides generated as side products in diazotransfer reactions, the development of novel diazotransfer reagents is of considerable interest.

Over the past few decades, ionic liquids have experienced exponential growth in research activity.[15,16] Now, ionic liquids have marched far from their reaction media status.[17] Task-specific ionic liquids have been used as alternatively supported tools,[17,18] scavengers,[19,20] catalysts,[21] and reagents[22,23] as well in combinatorial chemistry (instead of polymers) due to their unique properties. Task-specific ionic liquids with new functionalities can be synthesized for application in many fields of chemistry, especially in organic synthesis. Ramachary et al. reported ionic liquid promoted organocatalyticall selective diazotransfer reactions using some of the well-known diazo transfer reagents.[24] Use of ionic liquid as the solvent has improved the yield and the separation of products, and the solvent could be recycled.

In continuation of our interest in ionic liquid-supported reagents in organic synthesis,[18,19,23] herein we report ionic liquid-supported sulfonyl azide (**5**) as a green reagent for diazotransfer reaction under solvent-free conditions. To the best of our knowledge, this is the first report on the synthesis and application of ionic liquid-supported sulfonyl azide.

Synthesis of **5** was achieved following the reaction sequences shown in Scheme 1. Initially, the reaction of 1-methylimidazole (**1**) with 1,3-propanesultone (**2**) at 0 °C followed by reaction with trifluoromethanesulfonic acid (TfOH) at room temperature for 2 h gave **3**. Reaction of **3** with thionyl chloride under reflux conditions gave **4**, which on reaction with sodium azide afforded **5**. The structure of **5** was confirmed by IR, ^{1}H NMR, and high-resolution mass spectrometry. The IR spectrum of **5** showed a strong band for the N_3 group at 2130 cm^{-1}. The ^{1}H NMR spectrum showed a triplet and a multiplet at δ 4.28 and δ 3.80 for aliphatic protons adjacent to sulfonyl group and 1-methylimidazole, respectively. Peaks for protons of imidazole moiety were observed at δ 9.07, 7.79, and 7.65. In HRMS, the peak for m/z of [M-CF_3SO_3]$^+$ ion appeared at 230.0714, which confirmed the structure of **5**.

The differential scanning calorimetry (DSC) experiment showed that the exothermic decomposition temperature of pure ionic liquid-supported sulfonyl azide (**5**) is above 150 °C (Figure 1) with an initiation temperature of 159.69 °C and end point at 213.72 °C. Therefore, it should work without any problem below 100 °C. We recommend the use of **5** well below its decomposition temperature, preferably at room temperature. It is worth mentioning that **5** has not shown any sign of decomposition or loss of reactivity even after storing for one month at room temperature.

After successfully synthesizing **5**, we studied its reaction as diazotransfer reagent for active methylene compounds (Scheme

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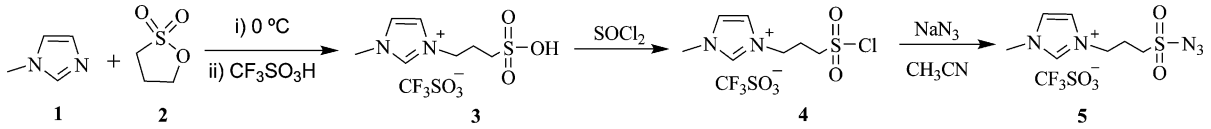
Scheme 1. Synthesis of Ionic Liquid-Supported Sulfonyl Azide (5)



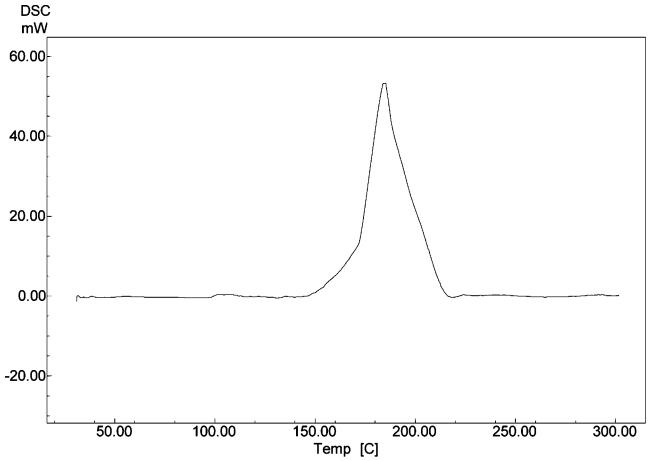
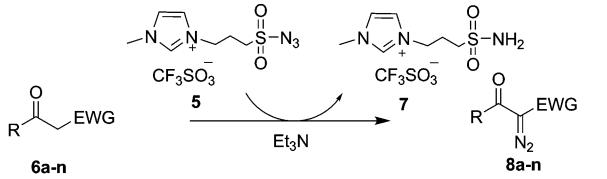


Figure 1. DSC curve for pure ionic liquid-supported sulfonyl azide (**5**).

2). Reaction of dimedone (**6h**) with **5** was taken as model reaction to optimize the reaction conditions. In our initial studies, we investigated the effect of different solvents. It was observed that the best yield of **8h** (94%) was obtained under solvent-free conditions. Among different solvents studied, the maximum yield of **8h** was obtained in ethanol (92%), whereas good to moderate yield of **8h** was obtained in other solvents such as acetonitrile (70%), ionic liquid [bmim][BF_4] (65%), THF (60%), and toluene (35%). No product formation was observed in water.

Scheme 2. Diazotransfer to Active Methylene Compounds Using 5



	R	EWG		R	EWG		R	EWG
a	C_6H_5	$COCH_3$	f	CH_3	$COCH_3$	k	4-ClC_6H_4	4-$CH_3C_6H_4SO_2$
b	C_6H_5	$CO_2C_2H_5$	g	-COC_6H_4CO-		l	4-$CH_3C_6H_4$	4-$CH_3C_6H_4SO_2$
c	CH_3	$CO_2C_2H_5$	h	-$CH_2C(CH_3)_2CH_2CO$-		m	4-$OCH_3C_6H_4$	4-$CH_3C_6H_4SO_2$
d	OC_2H_5	$CO_2C_2H_5$	i	-$CH_2CH_2CH_2CO$-		n	OC_2H_5	$C_6H_5SO_2$
e	CH_3	CO_2CH_3	j	-$N(CH_3)CON(CH_3)CO$-				

To assess the scope of **5** as diazotransfer reagent, structurally diverse 1,3-diketones, β-ketoester, and 1,3-diesters were reacted with **5** under the optimized reaction conditions to afford corresponding diazo compounds in excellent yields (Table 1). There was no appreciable difference in the yield and rate of reaction with different substrates. All the synthesized diazo compounds were well-characterized by ^{1}H NMR and ^{13}C NMR (see Supporting Information).

α-Diazo-β-ketosulfones have been employed as carbene source in intramolecular cyclopropanation, insertion reactions. Recently, Kumar and Namboothiri has utilized α-diazo-β-ketosulfone for the synthesis of sulfonylpyrazoles by reacting with nitroalkenes.[25] To further broaden the scope of our reagent **5**, we explored the reaction of β-ketosulfones. As expected, the reaction went very smooth in a short time with excellent yield (82−87%) to give corresponding diazo derivatives of β-ketosulfones (Table 1, entries k−n). It is worth mentioning that β-ketosulfones have been reported as poor substrates with several diazotransfer reagents such as Im-SO_2N_3·HCl[10] and Bt-SO_2N_3[13] (Table 2, entries 7,8).

The reactivity and stability of **5** was compared with other traditional diazotransfer reagents (Table 2). As is apparent from Table 1 and Table 2, higher yields of diazo products were obtained with **5** in shorter reaction time under optimized reaction conditions in comparison to other traditional reagents such as oligomeric-SO_2N_3, PS-SO_2N_3, *p*-CBSA, Im-SO_2N_3·HCl, ADMP, and Bt-SO_2N_3 on similar substrates. Presset et al.[26] reported that TsN_3 is a better reagent for multigram scale than other reagents such as MsN_3, Im-SO_2N_3·HCl, ADMC, and *p*-CBSA. However, it becomes very difficult to remove tosylamide generated during the reaction, and repetitive column chromatography first over silica gel and then over basic alumina is required. We can overcome this problem by using **5**. Simple extraction with a hexane−ethyl acetate mixture followed by a water wash gave pure product, except in the case of **8g**, where purification was performed over a silica-gel column. Comparing the DSC experimental data with some of the traditional diazotransfer reagents, it was observed that the initiation temperature at which decomposition started in DSC for **5** (159 °C) was higher or comparable to these diazotransfer reagents (Table 2). Only for AMDP was the initiation temperature at which decomposition started in DSC (200 °C) higher than that for **5**.

Encouraged by these results, we then decided to investigate the suitability of **5** for synthesis of diazo compounds from acetophenone. The reaction did not work under these conditions, and we recovered the acetophenone. We also screened this reaction using different strong bases such as sodium hydride and potassium *tert*-butoxide instead of triethylamine but did not get the desired product. It is also reported that diazotransfer to the simple carbonyl compound usually fails when the methylene group is linked to a single carbonyl group only.[27] The diazo derivative of such compounds can be prepared by employing the deacylating diazotransfer strategy.[28] We studied the use of **5** for detrifluoroacetylative diazo group transfer for commercially available 4,4,4-trifluoro-1-phenylbutane-1,3-dione (**6o**) and 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione (**6p**) (Scheme 3). Treating 1 equiv of **6o** and **6p** with **5** in the presence of triethyl amine under the above conditions gave corresponding α-diazo derivatives **8o** and **8p** in 82% and 80%, respectively.

In conclusion, we have developed a green method for diazotransfer reaction using a novel ionic liquid-supported sulfonyl azide under solvent free conditions. Different diazo compounds were synthesized from active methylene compounds in excellent yield (82−94%) and high purity. The reagent is versatile and can be used for detrifluoroacetylative

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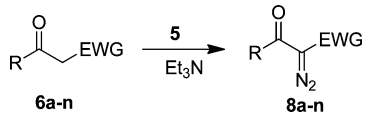
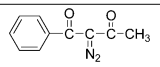
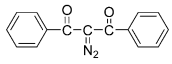
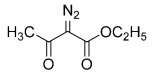
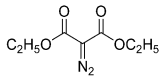
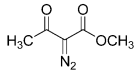
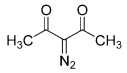
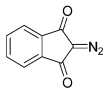
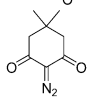
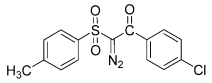
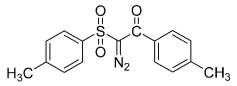
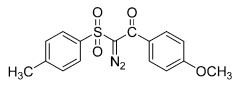
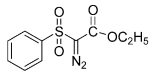
Table 1. Synthesis of Diazo Compounds Using 5



Entry	R	EWG	Product	Time (Min.)	Yield (%)[a]
a	C_6H_5	$COCH_3$		2	88
b	C_6H_5	COC_6H_5		2	85
c	CH_3	$CO_2C_2H_5$		3	89
d	C_2H_5O	$CO_2C_2H_5$		3	87
e	CH_3	CO_2CH_3		3	90
f	CH_3	$COCH_3$		3	89
g	-CO- C_6H_4- CO-			2	87[b]
h	$CH_2C(CH_3)_2CH_2CO$			2	94
i	$CH_2CH_2CH_2CO$			2	94
j	$CH_3NCON(CH_3)CO$			2	91
k	4-ClC_6H_4	4-$CH_3C_6H_4SO_2$		4	82
l	4-$CH_3C_6H_4$	4-$CH_3C_6H_4SO_2$		4	87
m	4-$OCH_3C_6H_4$	4-$CH_3C_6H_4SO_2$		4	83
n	C_2H_5O	$C_6H_5SO_2$		5	84

[a]Isolated yields. [b]Product purified by column chromatography over silica-gel.

diazotransfer as well. The method offers better and simple purification and high purity of product.

EXPERIMENTAL SECTION

Procedure for Synthesis of Ionic Liquid-Supported Sulfonic acid (3). Ionic liquid-supported sulfonic acid (**3**) was prepared according to earlier procedures with slight modifications. Propane sultone (1 equiv) was added dropwise to 1-methylimidazole (1 equiv) at 0 °C. The resulting solution was stirred at room temperature until a solid was obtained. After completion of the reaction, the product was washed with toluene (3 × 15 mL) and finally with diethyl ether (3 × 15 mL) to remove unreacted starting materials. The compound was dried under reduced pressure to get the zwitterionic form. Trifluoromethane sulfonic acid (1.1 mmol) was added dropwise to zwitter ion at 0 °C. The solution was stirred at 40 °C after completion of the addition until a thick liquid was obtained. The resulting liquid was washed with diethyl ether to remove excess of triflic acid. The compound was dried under reduced pressure to give **3** as a thick liquid in 98% yield.

Procedure for Synthesis of Ionic Liquid-Supported Sulfonyl Chloride (4). Thionyl chloride ($SOCl_2$) (3 equiv) was added dropwise to the ionic liquid sulfonic acid **3** (1 equiv) at 0 °C. The resulting mixture was stirred at room temperature for 8 h and finally heated up to 80 °C for 2 h. The excess of thionyl chloride was removed by rotatory evaporator under reduced pressure with nitrogen atmosphere to get ionic liquid sulfonyl chloride **4** as a thick yellow liquid in 96% yield.

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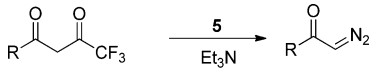
Table 2. Comparison of Stability and Yield for Selected Substrates with Other Reagents

S. no.	reagent	stability (°C)[c,d]	substrate	product	time (h)	yield (%)[a,b]
1	Oligomeric-SO_2N_3	–[e]	**6h**	**8h**	0.5	75[12]
2	NfN_3	120	**6a**	**8a**	0.25	89[9]
3	PS-SO_2N_3	130	**6d**	**8d**	16	63[8]
4	*p*-CBSA	–[f]	**6d**	**8d**	16	76[5]
5	Im-SO_2N_3·HCl	~85	**6d**	**8d**	16	65[10]
6	ADMP	200	**6g**	**8g**	0.15	78[14]
7	Bt-SO_2N_3	85	**6n**	**8n**	14	56[13]
8	Im-SO_2N_3·HCl	85	**6n**	**8n**	48	–[10]

[a]Yields are as reported in the literature. [b]Yields for **8a**, **8d**, **8g**, **8h**, and **8n** using **5** are 94%, 87%, 87%, 94%, and 84%, respectively (Table 1). [c]Initiation temperature at which decomposition started in DSC. [d]For reagent **5**, initiation temperature is 159 °C. [e]Slowly decomposes at room temperature. [f]Stable at room temperature after two days.

Scheme 3. Detrifluoroacetylative Diazotransfer



6o-p **8o-p**

6o R = C_6H_5
6p R = 2-C_4H_3S

Procedure for Synthesis of Ionic Liquid-Supported Sulfonyl Azide (5). Ionic liquid-supported sulfonyl chloride (**4**, 30 mmol) was dissolved in acetonitrile and then treated with NaN_3 (36 mmol). The resulting solution was stirred for 12 h at 60 °C. The reaction mixture was filtered to remove sodium salts. The organic layers concentrated to give a crude product, which was then washed with DCM and ethyl acetate mixture (4 × 50 mL, 1: 1 v/v) to purify the ionic liquid. Finally, the ionic liquid-supported sulfonyl azide (**5**) was dried under reduced pressure.

*Ionic Liquid-Supported Sulfonyl Azide (**5**).* Thick pale yellow liquid; IR (neat) ν_{max} 2145 (diazo), 1366, 1257, 1157, 1034 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 9.06 (s, 1H), 7.75 (s, 1H), 7.69 (s, 1H), 4.28 (t, J = 6.9 Hz, 2H), 3.83 (s, 2H), 3.80 (d, J = 7.6 Hz, 2H), 2.36–2.28 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 137.9, 124.2, 122.6, 122.4, 119.8, 52.2, 47.1, 36.2, 24.3; HRMS (ESI-qTOF) Calcd for $C_7H_{12}N_5O_2S^+$ 230.0706; Found 230.0714 $[M\text{-}CF_3SO_3]^+$.

General Procedure for Diazotransfer Using Ionic Liquid-Supported Sulfonyl Azide (5). (CAUTION: *Although we never had any accident while using* **5**, *it may be explosive.*) Triethyl amine (1.5 mmol) was added to the mixture of active methylene compound (1 mmol) and ionic liquid-supported sulfonyl azide (**5**) (1.2 mmol). The resulting mixture was stirred at room temperature for the time indicated in Table 2. The progress of reaction was monitored by TLC. After completion of reaction, the product was extracted with hexane/ethyl acetate mixture (4 × 10 mL, 1: 1 v/v) and washed with water. The organic layers were combined, dried with anhydrous sodium sulfate, and concentrated to give crude product. In the case of **8g**, purification was performed over silica-gel column. The side product ionic liquid-supported sulfonylamide (**7**) does not dissolve in organic layer and thus can be easily removed. Physical and spectral data of synthesized diazo compounds are given below.

*2-Diazo-1-phenyl-butane-1,3-dione (**8a**).* White solid (165 mg, 88%); mp 62–63 °C (Lit.[29] 60–62 °C); IR (neat) ν_{max} 2177 (diazo), 1651 (C═O), 1059, 752, 642 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, J = 5.5, 4.0 Hz, 2H), 7.61–7.55 (m, 1H), 7.53–7.47 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 185.1, 137.3, 132.7, 128.9, 127.3, 29.2.

*2-Diazo-1,3-diphenylpropane-1,3-dione (**8b**).* Solid (212.6 mg, 85%); mp 106–109 °C (Lit.[5] 107–109 °C); IR (neat) ν_{max} 2119 (diazo), 1643, 1317, 1176 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 4H), 7.44 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4, 136.9, 132.6, 128.3, 128.3.

*2-Diazo-3-oxo-butyric Acid Ethyl Ester (**8c**).* Pale yellow liquid[29] (139 mg, 89%); IR (neat) ν_{max} 2136 (diazo), 1720 (–C═O), 1658 (O–C═O), 1319, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.29 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 161.6, 61.6, 28.3, 14.5.

*2-Diazomalonic Acid Diethyl Ester (**8d**).* Yellow liquid[29] (162 mg, 87%); IR (neat) ν_{max} 2144 (diazo), 1720, 1373, 1319, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.29 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 61.7, 14.5.

*2-Diazo-3-oxo-butyric Acid Methyl Ester (**8e**).* Yellow liquid[30] (128 mg, 90%); IR (neat) ν_{max} 2142 (diazo), 1687, 1365, 752, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 161.8, 52.2, 28.2.

*3-Diazo-2,4-pentanedione (**8f**).* Colorless liquid[29] (112 mg, 89%); IR (neat) ν_{max} 2140 (diazo), 1687, 1365, 752, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 28.5.

*2-Diazoindan-1,3-dione (**8g**).* Solid (150 mg, 87%); mp 146–149 °C (Lit.[31] 148–149 °C); IR (neat) ν_{max} 2121 (diazo), 1697, 1357, 1095, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 2H), 7.77–7.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 137.3, 135.0, 122.9.

*2-Diazo-5,5-dimethylcyclohexane-1,3-dione (**8h**).* Yellow solid (156 mg, 94%); mp 103–106 °C (Lit.[12] 105–107 °C); IR (neat) ν_{max} 2138, 1738, 1693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 4H), 1.12 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 50.5, 31.1, 28.4.

*2-Diazocyclohexane-1,3-dione (**8i**).* Yellow solid (130 mg, 94%); mp 47–49 °C (Lit.[26] 48–49 °C); IR (neat) ν_{max} 2136, 1737, 1695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.58–2.53 (m, 4H), 2.08–1.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 37.0, 18.7.

*5-Diazo-1,3-dimethylpyrimidine-2,4,6-trione (**8j**).* Yellow solid (166 mg, 91%); mp 141–145 °C (Lit.[32] 158 °C solvent isopropanol); IR (neat) ν_{max} 2156 (diazo), 1650, 1303, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.34 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 150.5, 28.6.

*2-Diazo-1-(4-chlorophenyl)-2-tosylethanone (**8k**).* Solid (274 mg, 82%); mp 125–127 °C (Lit.[33] 134 °C); IR (neat) ν_{max} 2104 (diazo), 1680 (C═O), 1381, 1286, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.6, 145.6, 139.4, 138.5, 138.2, 129.8, 129.2, 129.0, 128.2, 21.7.

*2-Diazo-1-(4-tolyl)-2-tosylethanone (**8l**).* Solid (273 mg, 87%); mp 120–123 °C; IR (neat) ν_{max} 2124 (diazo), 1675 (C═O), 1361, 1276 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 145.3, 144.0, 138.7, 133.7, 129.7, 129.5, 128.2, 127.6, 21.7, 21.6. HRMS (ESI-qTOF) Calcd for $C_{16}H_{15}N_2O_3S^+$ 315.0798; Found 315.0803 $[M + H]^+$.

*2-Diazo-1-(4-methoxyphenyl)-2-tosylethanone (**8m**).* Pale yellow solid (274 mg, 83%); mp 141–145 °C (Lit.[33] 124 °C); IR (neat) ν_{max} 2121 (diazo), 1633 (C═O), 1208, 1024, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.61–7.54 (m, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.95–6.88 (m, 2H), 3.85 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 163.5, 145.3, 138.7, 129.9, 129.7, 128.4, 128.2, 114.1, 55.6, 21.7.

*Ethyl 2-Diazo-2-(phenylsulfonyl)acetate (**8n**).* Yellow solid (213 mg, 84%); mp 48–49 °C (Lit.[13] 52–54 °C); IR (neat) ν_{max} 2129 (diazo), 1727 (C═O), 1371, 1286, 1072 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 4.25–4.18 (q, J = 14.1 Hz, 2H), 1.27 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 141.7, 134.1, 129.2, 127.9, 62.4, 14.2.

*2-Diazo-1-(phenyl)ethanone (**8o**).* Yellow liquid (120 mg, 82%); (Lit.[34] 27–28 °C); IR (neat) ν_{max} 2106 (diazo), 1725, 1371, 1228,

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1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79−7.72 (m, 2H), 7.57−7.50 (m, 1H), 7.43 (dd, J = 6.8, 4.5 Hz, 2H), 5.93 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4, 136.6, 132.7, 128.7, 126.7, 54.2.

*2-Diazo-1-(2-thienyl)ethanone (**8p**).* Solid (122.7 mg, 80%); mp 61−64 °C (Lit.[35] 60 °C); IR (neat) ν_{max} 2108 (diazo), 1705, 1415, 1259, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 5.0, 1.1 Hz, 1H), 7.50 (dd, J = 3.8, 1.1 Hz, 1H), 7.11 (dd, J = 4.9, 3.8 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 142.5, 132.2, 129.0, 128.0, 54.3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H NMR, ^{13}C NMR, and mass spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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