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Ethylammonium Nitrate (EAN)/Tf_2O and EAN/TFAA: Ionic Liquid Based Systems for Aromatic Nitration

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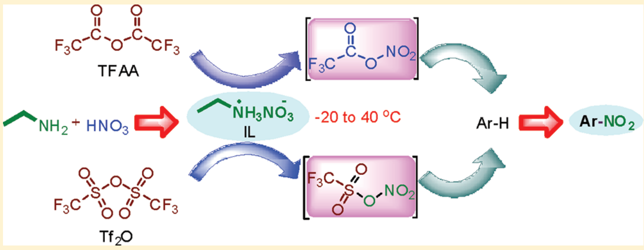
Supporting Information

ABSTRACT: Acting as in situ sources of triflyl nitrate ($TfONO_2$) and trifluoroacetyl nitrate (CF_3COONO_2), the EAN/Tf_2O and EAN/TFAA systems, generated via metathesis in the readily available ethylammonium nitrate (EAN) ionic liquid as solvent, are powerful electrophilic nitrating reagents for a wide variety of aromatic and heteroaromatic compounds. Comparative nitration experiments indicate that EAN/Tf_2O is superior to EAN/TFAA for nitration of strongly deactivated systems. Both systems exhibit low substrate selectivity (K_T/K_B = 5−10) in between values reported for covalent nitrates and preformed nitronium salts.



Nitroarenes continue to be in high demand as key intermediates in synthesis and materials chemistry and as energetic compounds. Despite its reputation as a notoriously "ungreen" reaction, electrophilic aromatic nitration is the most direct and general method for the synthesis of nitroaromatics and has firmly retained its position over the years as a fundamental transformation of great industrial importance.

The mechanistic aspects of electrophilic aromatic nitration have been very extensively studied over the years, both experimentally and computationally.[1,2] On the synthetic side, depending on the desired chemo- and regioselectivity and the reactivity of aromatic substrate, a host of nitrating systems have been developed over the years ranging from protic nitration with mixed acids and superacids, to acyl- and alkyl nitrates, metal nitrates, nitronium salts, nitryl halides, supported nitration, and transfer nitration reagents.[1] Nitration of highly deactivated arenes is particularly challenging but has been achieved in superacids.[3] The use of large quantities of protic acids, acid neutralization and disposal, problems associated with regeneration of used acids, product recovery problems stemming from solubility of nitroarenes in concentrated HNO_3, and decreased efficiency in continuous operation due to dilution of HNO_3 by the water byproduct represent some of the issues facing classical nitration methods. Most other nitration methods also suffer from practical drawbacks such as use of hazardous/toxic reagents, high cost, cumbersome workup procedures, and disposal-related issues.

In our survey study in 2001 on the use of imidazoliun ILs as solvents for electrophilic nitration of aromatics,[4] we identified the systems [NH_4NO_3/TFAA/[$HNEtPr^i_2$][CF_3COO], NH_4NO_3/TFAA/[EMIM][CF_3COO], and isoamyl nitrate/TfOH/[EMIM][OTf] as most promising for IL nitration, allowing simple product recovery and recycling of the IL. Since then, several other studies were reported demonstrating (a) the importance of the IL cation,[5a] (b) better conversions with ILs as solvent as compared to CH_2Cl_2,[5b] and (c) that nitronium ion is the nitrating species in acetyl nitrate nitration in IL.[5b] The importance of counterion was demonstrated by Earle and associates,[5c] showing that it can influence the course of the reaction. The majority of these studies employed HNO_3 or HNO_3−Ac_2O requiring additional steps for product isolation and IL recycling. The para-selective nitration of phenol and substituted phenols promoted by ultrasound was also reported by using ferric nitrate and clayfen in EAN as solvent.[6a] Nitration of simple aromatics with liquid nitrogen dioxide in caprolactam-based ILs,[6b] and with N_2O_5 in PEG-based dicationic IL,[6c] were also reported.

In a previous study, tetraalkylammonium nitrate in combination with triflic anhydride was employed by Shackelford et al.[7a] for nitration of a selected group of substituted aromatics, heterocycles, and *N*-nitration of heterocycles[7b] in DCM as solvent. They also examined the microwave-assisted version of this reaction.[7a]

In continuation of our studies on electrophilic chemistry in ionic liquids,[8] and in relation to recent work from this laboratory utilizing EAN as solvent and reagent in tetrazole chemistry,[9] we report here on EAN/Tf_2O and EAN/TFAA systems as convenient in situ sources of triflyl nitrate ($TfONO_2$) and trifluoroacetyl nitrate (CF_3COONO_2) for facile nitration of a wide range of aromatics including strongly deactivated systems under very mild conditions, in respectable yields, and in a simple operation, with recovery and reuse of the IL.

In a survey study, we first examined the IL-mediated nitration of monosubstituted arenes with activating and deactivating substituents and compared the relative efficiency of the two systems. A summary of these results is presented in Table 1. Both systems proved to be powerful with nitration yields in the 77−100% range. Comparison of nitration outcomes for toluene in the two systems (entries 2 and 2a) shows that EAN/TFAA is both more

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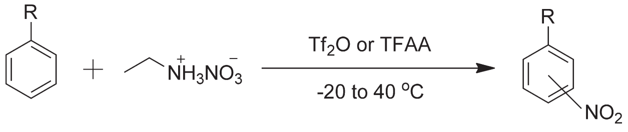
Table 1. Ionic Liquid (EAN) Mediated Nitration of Monosubstituted Arenes Promoted by Tf_2O and TFAA



1-18

entry	R	reagent	$T^{\neq}$ (°C)	time (min)	regioselectivity[a] (%)				yield[a] (%)	isolated major isomer (%)
					ortho	meta	para	dinitro		
1[4]	H[*]	Tf_2O	−15	5				(2)[b]	100 (98)[b]	98
1a	H[*]	TFAA	−15	25					100 (100)[c]	97
2[4]	CH_3	Tf_2O	−5 to rt	30	54 (56.4)[d]	trace (4.8)[d]	28 (38.8)[d]	18 (−)[d]	100[e]	
2a	CH_3	TFAA	−5 to rt	45	59	trace	41		86	38 (para)
3[6c]	CH_2CH_3	Tf_2O	−5 to rt	30	36 (47.6)[d]	2 (4)[d]	62 (48.4)[d]		100	
3a	CH_2CH_3	TFAA	−5 to rt	50	41	2	57		86	
4[10a]	$CH(CH_3)_2$	Tf_2O	−5 to rt	40	14 (25.9)[d]	3 (6.6)[d]	83 (67.5)[d]		100	
5[6a]	OH[*]	TFAA	−15 to −5	10	37		57	4	100[f]	
6[4]	OCH_3	Tf_2O[g]	0 to rt	20	20		36	44	100	
6a	OCH_3	Tf_2O	0 to rt	20	28		64	8	95	
6b	OCH_3	TFAA	0 to rt	35	37 (35)[h]		63 (65)[h]		93	59
7[4]	F	Tf_2O	0 to rt	30	8 (9.9)[c]		92 (90.1)[c]		100 (100)[c]	99 (crude isomer mixture)
8[10b]	Cl	TFAA	0 to rt	80	27		73		95	
8a	Cl	Tf_2O	0 to rt	50	24 (30)[b]	trace (0.1)[b]	76 (70)[b]		100	72
9[10b]	$N(CH_3)_2$[*]	TFAA	−20	5	28	2	30	38/2[i]	100	
10[10c]	CH_2OH	Tf_2O	0 to rt	25			100		100	
10a	CH_2OH	TFAA	0 to rt	35			100		89	
11[10c]	CH_2CN	Tf_2O	0 to rt	120	16 (16)[c]	8 (10)[c]	76 (74)[c]		100	95 (crude)
12[10d]	$CH_2CO_2CH_3$	TFAA	0 to rt	20	43 (41)[c]	12 (15)[c]	45 (44)[c]		100 (100)[c]	99 (crude)
13[10e]	$COOCH_3$	Tf_2O	−5 to rt	120		96	4		100	94
14[10e]	CN	Tf_2O	−5 to rt	8 h		100 (100)[c]			100 (100)[c]	80
15[10d]	$NHCOCH_3$	Tf_2O	−10 to 0	40			71	29	100[j]	
15a	$NHCOCH_3$	TFAA	−5 to 40	16 h			51	49	77	
16[4]	CF_3	Tf_2O	0 to rt	90	15[c] (14)[b]	83[c] (85)[b]	2[c] (1)[b]		100[c]	81 (crude)
17[10c]	$COCH_3$	Tf_2O	0 to rt	120	19	81			91	77
18[10e]	CHO	Tf_2O	0 to 40	120	27 (25.5)[c]	70 (70.9)[c]	3 (3.6)[c]		100 (100)[c]	81 (crude)

[≠] Temperature range refers to initial temperature followed by gradual/slow warming up to indicated final temp. [*] Caution: "vigorous reaction". [a] Determined by GC−MS (entries **1**/**1a**, **3a**, and **14** by GC). [b] Classical nitration (HNO_3 and TfOH).[10f] [c] By NMR. [d] Classical nitration (HNO_3 and H_2SO_4).[1a] [e] For recycled ionic liquid (representative case): 43.3 (ortho), 1.4 (meta), 34.4 (para), 20.9 (dinitro). [f] 2% of quinone was also formed (by GC−MS). [g] 1.3 mol ratio of Tf_2O was used. [h] Classical nitration (HNO_3).[5c] [i] Trinitro. [j] When the reaction was carried out at 5 °C to rt the product distribution was 34 (para) and 66 (dinitro) after 100 min.

chemoselective (no dinitration) and more regioselective (more *o*-nitrotoluene isomer), while giving slightly lower overall yield relative to EAN/Tf_2O.

No significant difference is observed for ethylbenzene, except for somewhat lower conversion with EAN/TFAA. For nitration of cumene (with EAN/Tf_2O), para selectivity is notably higher as compared to the mixed acid nitration. Given the potency of these systems, nitration of activated systems such as dimethylaniline (DMA) and phenol are highly exothermic and should be performed with care at lower temperatures. With DMA, dinitration is competitive. Significant amounts of dinitration were also observed in nitration of acetanilide. Quantitative or near-quantitative nitration yields were observed at or below rt for deactivated systems such as trifluoromethylbenzene, benzonitrile, and benzaldehyde, with isomer distributions close to those reported in mixed acid nitration (see Table 1).

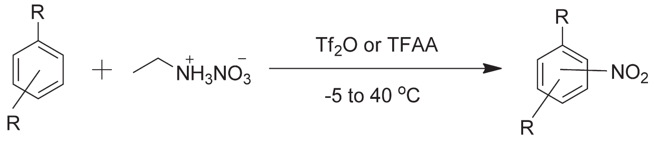
Table 2. Comparison of Substrate Selectivity in Various Nitrating Systems

nitration system	K_T/K_B
nitronium salts	~2[a]
EAN/Tf_2O	9.8[b]
EAN/TFAA	5.2[b]
HNO_3−HOAC	24[a]
CF_3COONO_2	28[a]
HNO_3/Tf_2O	36[a]

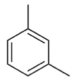
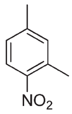
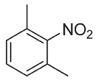
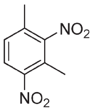
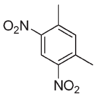
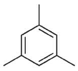
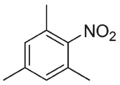
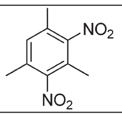
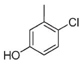
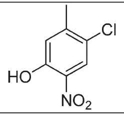
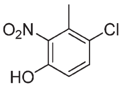
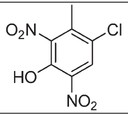
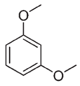
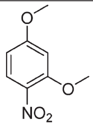
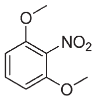
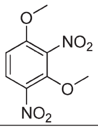
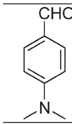
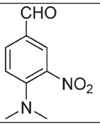
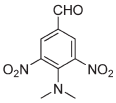
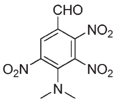
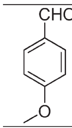
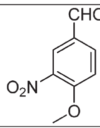
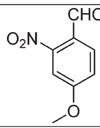
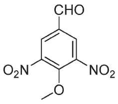
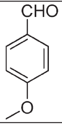
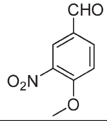
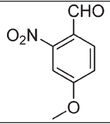
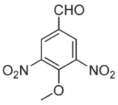
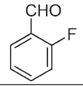
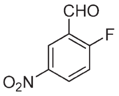
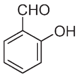
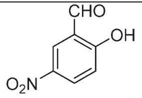
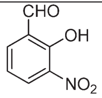
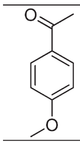
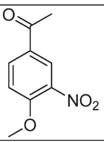
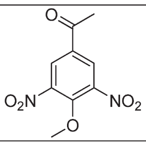
[a] Taken from refs 1c and 12. [b] This work (determined by GC).

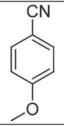
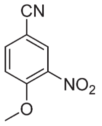
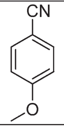
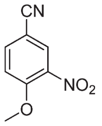
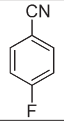
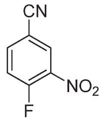
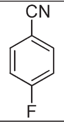
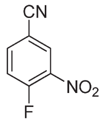
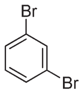
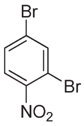
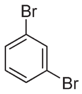
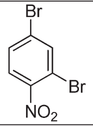
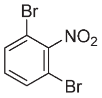
Substrate selectivity (K_T/K_B) was measured for EAN/Tf_2O and EAN/TFAA systems at 0 °C with a short reaction time (15 min) and is compared with other systems in Table 2. The observed

Table 3. Ionic Liquid (EAN) Mediated Nitration of Multiply Substituted Arenes Promoted by Tf_2O and TFAA



19-30

Arene /Entry	Reagent	Temp (°C)[≠]	Time (min)	% Nitro products[a]					Yield (%)[a]	Isolated yield (%)
	TFAA	-5 to rt	70						99	-
19[13a]				83	11	2	4			
	Tf_2O	0 to rt	20						100	-
20[4]				96	4					
	TFAA	-5 to 0	10						100	67 (major isomer)
21[13b]				71	11	18				
	Tf_2O	-5 to rt	30						100	-
22[7a]				88	trace	12				
	TFAA	-10 to -5	10					X[b]	100	-
23*[13c]				43	43	4				
	Tf_2O	0 to rt	40					X[c]	95	84 (major isomer)
24[10b]				89	5	6				
	TFAA	0 to rt	100						66	-
24a				95	3	2				
	Tf_2O	0 to 30	4 hrs						100	97
25[13d]										
	Tf_2O	0 to rt	30						100 (100)[d]	98 (crude)
26[13e]				58 (51)	42 (49)					
	Tf_2O	0 to rt	20					X[e]	100	74 (major isomer)
27[13f]				80	20					

 **28**	Tf_2O	-5 to 0	15		100	98
 **28a**	TFAA	-5 to rt	60		99	94
 **29**	Tf_2O	0 to 40	4 hrs		97 (95.7)[d]	89
 **29a**	TFAA	0 to 40	7 hrs		17	-
 **30**	Tf_2O	0 to 35	80		100	88
 **30a**[13g]	TFAA	0 to 40	3 hrs	 91  9	14	-

≠ Temperature range refers to initial temperature followed by gradual/slow warming up to indicated final temperature. * Caution: "vigorous reaction". [a] Determined by GC−MS. [b] Other mono- (2%) and disubstituted (8%) products. [c] Traces of other mono- and disubstituted products. [d] By NMR. [e] Traces of other mononitrated products.

selectivity is in between values reported for nitronium ion and covalent nitrates and implies possible dissociation of the in situ formed triflyl nitrate and trifluoroacetyl nitrate in the IL to the nitronium ion,[11] in line with the finding reported by Dal and Lancaster[5b] for acetyl nitrate in [bmpy][OTf] and [bmpy][NTf_2].

In the next phase of the study a survey of nitration of multiply substituted arenes was conducted.

The results are summarized in Table 3. Comparative nitration experiments performed with *p*-methoxybenzaldehye, *p*-methoxybenzonitrile, *p*-fluorobenzonitrile, and *m*-dibromobenzene show that EAN/Tf_2O is a superior reagent for strongly deactivated systems.

Nitration of nitroarenes (Table 4) provided a more rigorous test of the relative efficiency of the two systems. Nitration yields for nitrobenzene with EAN/Tf_2O and EAN/TFAA were approximately 82:2, respectively. EAN/Tf_2O nitrates *p*-chloronitrobenzene in 90% yield, whereas EAN/TFAA did not react (0 to 40 °C). Nitration yields for *p*-nitroanisole and *p*-nitrotoluene with EAN/Tf_2O and EAN/TFAA were 100:87 and 100:30, respectively. The observed yields for the deactivated systems (Tables 1 and 4) compare favorably with those obtained in mixed acid systems and in superacids.

Attempted nitration of the more highly deactivated arenes, namely 1,2,4,5-tetrafluorobenzene, *m*-bromoacetophenone, *m*-nitroacetophenone, pentafluorobenzene, and hexafluorobiphenyl, with the EAN/Tf_2O system in the temperature range −5 to +45 °C resulted in no reaction.

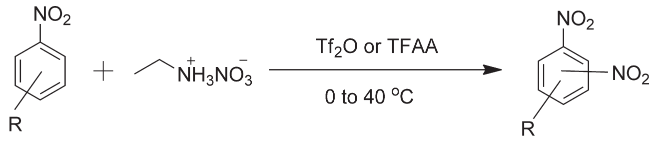
The efficacy of the EAN/Tf_2O system for nitration of deactivated heteroaromatics was shown by nitration of 2-acetylfuran, 2-acetylthiophene, and thiophene-2-carbaldehyde as representative cases (Table 5). With the thiophenes, a mixture of 4-nitro and 5-nitro isomers was obtained in excellent yields.

In summary, combination of high potency, high regio- and chemoselectivity, mild reaction conditions, ready availability of the reagents, simple workup procedure, and reuse and recycling make this an all-around excellent nitration method with good potential for wide application.

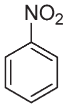
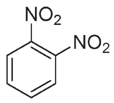
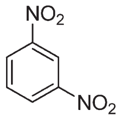
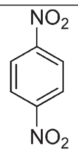
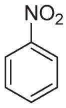
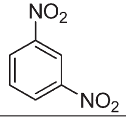
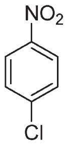
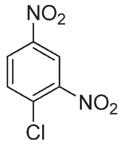
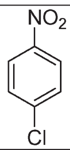
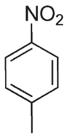
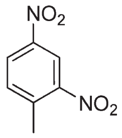
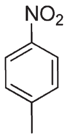
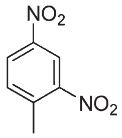
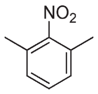
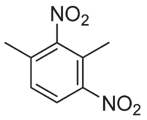
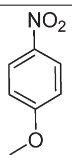
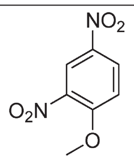
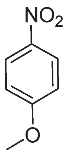
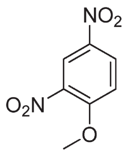
■ EXPERIMENTAL SECTION

General Methods. The reagents employed were of high purity commercial samples which were used without further purification. Reactions were carried out in small Schlenk tubes. Column chromatography was performed on silica gel (200−400 mesh). Melting points were

Table 4. Ionic Liquid (EAN) Mediated Nitration of Nitroarenes Promoted by Tf_2O and TFAA

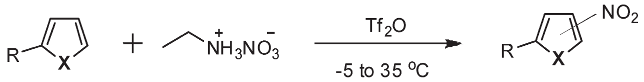


31-35

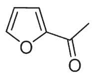
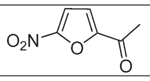
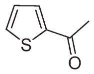
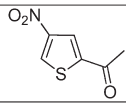
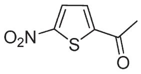
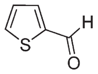
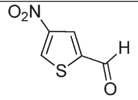
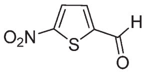
Entry	Arene	Reagent	Temp (°C)≠	Time (min)	% Isomer distribution[a]			Yield (%)[a]	Isolated yield (%)
31[10c]		Tf_2O	0 to 40	5.5 hrs	 6 (10)[b]	 92 (87)[b]	 2 (2)[b]	82[c]	71 (crude)
31a		TFAA	0 to 40	5.5 hrs	- -	 2	- -	2	-
32[14a]		Tf_2O	0 to 40	9 hrs				90 (94.8)[d]	78
32a		TFAA	0 to 40	12 hrs		No reaction		-	-
33[10d]		Tf_2O	0 to 35	4 hrs				100	98
33a		TFAA	0 to 35	8 hrs				29	-
34		Tf_2O	0 to rt	25				100	97
35[14b]		Tf_2O	0 to rt	25				100	98
35a		TFAA	0 to 35	3 hrs				88	-

≠ Temperature range refers to initial temperature followed by gradual/slow warming to indicated final temp. [a] Determined by GC−MS. [b] Classical nitration (HNO_3 and TfOH).[10f] [c] Isomer distribution was ascertained from the NMR of solid products obtained as crude, but the total yield is based on GC−MS. [d] By NMR.

Table 5. Ionic Liquid (EAN) Mediated Nitration of Thiophene and Furan Heterocycles Promoted by Tf_2O



36-38

Entry	Arene (I)/Entry	Reagent	Temp (°C)[≠]	Time (min)	% Nitro products[a]	Yield (%)[a]	Isolated crude yield (%)
36[14c]		Tf_2O	-5 to 35	5 hrs	 100	74	57 (single product)
37[14d]		Tf_2O	-5 to 0	30	  61[b] 39[b]	100[b]	98
38[14e]		Tf_2O	-5 to 0	75	  60[b] 40[b]	100[b]	97

[≠] Temperature range refers to initial temperature followed by gradual/slow warming up to indicated final temperature. [a] Determined by GC−MS. [b] By NMR.

recorded in open-capillaries and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 500 MHz NMR instrument. Chemical shifts were referenced to internal solvent signals: ^1H at 7.26 ppm/^{13}C at 77.16 ppm. The ^{19}F NMR spectra were referenced relative to external $CFCl_3$. ^{15}N NMR spectra were recorded at 50.66 MHz as neat or using CD_3CN and CD_3COCD_3 as solvents. ^{15}N NMR chemical shift values were referenced to external nitromethane (neat). GC analyses employed a split/splitless injector, a capillary RTX-5 column, and FID detection. GC−MS analyses were performed in the EI mode. The total ion chromatogram (TIC) acquired by GC−MS was used for peak area integration.

Preparation of Ethylammonium Nitrate $[EtNH_3][NO_3]$. This was prepared according to the reported procedures.[9,15]

General Procedure. The desired aromatic compound (1 mmol) was added to EAN (typically 5 mmol for nitration of liquid substrates and ∼10 mmol for nitration of solids) under nitrogen at room temperature and stirred for a few minutes. Tf_2O (triflic anhydride) or TFAA (trifluoroacetic anhydride) (1 mmol) was added slowly with stirring while the reaction mixture was kept at low temperature (as mentioned in Tables 1 and 3−5). The progress of the reaction was monitored by GC and/or GC−MS. The reaction mixture was extracted three to four times with dry ether, chloroform−hexane mixture (1:2), or ethyl acetate−hexane mixture (2:6). The combined extracts were washed with bicarbonate solution (8%) and brine and dried over $MgSO_4$. Removal of solvents under reduced pressure gave the crude product. Isomer distributions were determined by GC, GC−MS, and/or by ^1H NMR. In selected cases, the major product(s) were isolated and purified by column chromatography (4:1 ethyl acetate/hexane). To obtain optimal conversions in nitration of deactivated arenes, it is imperative that EAN, Tf_2O, and TFAA are dry and fresh (substantially lower yields or no reaction were observed with older reagents in bottles/flasks that had been repeatedly opened!).

Recycling of the Ionic Liquid. This was accomplished by drying under a nitrogen stream followed by heating in an oil bath at 75−80 °C for about 3−4 h under vacuum. The recycled IL can be used successfully without significant loss in the yields. Since EAN is used in large excess, the presence of ethylammonium triflate (formed via in situ metathesis) does not interfere with the recycling and reuse of the IL over several cycles.

Substrate Selectivity Measurements. In a typical reaction, benzene and toluene (precisely 1:1 ratio; 1 mmol each) were added to EAN ionic liquid (5 mmol) under nitrogen and stirred for a few minutes. Tf_2O or TFAA (1 mmol) was added slowly with efficient stirring, while the reaction mixture was kept at 0 °C. After 15 min, the reaction mixture was extracted with dry Et_2O. Following the usual workup, the isomer distribution and substrate selectivity were determined by GC in duplicate runs. The reported values are an average of three GC runs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. NMR analysis and other characterization data for the nitro products as well as copies of GC, GC−MS, and ^1H, ^{13}C and ^{19}F NMR spectra of the nitro products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) In an effort to shed light on the nature of intermediates in EAN/TFAA and EAN/Tf_2O nitrating systems, we employed natural abundance ^{15}N NMR. Using neat $MeNO_2$ as an external reference, the ^{15}N NMR spectrum of neat EAN exhibited two resonances at −346.8 (for NO_3^-) and −4.3 ppm (for $EtNH_3^+$). Addition of 1 equiv of TFAA to 2.5 equiv of EAN gave a homogeneous solution that exhibited three ^{15}N signals at −346.7, −39.6, and −8.7 ppm. The ^{15}N signal observed at −39.6 (~340 ppm from ammonia) is indicative of a covalent CF_3COO-NO_2 species (see ref 12). The reported value for a nitronium species is considerably more shielded (~250 ppm from ammonia). The slight ^{15}N upfield shift of the $EtNH_3^+$ signal likely stems from in situ metathesis, forming mixed counterions (NO_3^- and OTf^-). The EAN/Tf_2O system behaved differently: similar addition of Tf_2O to ice-cooled EAN gave a precipitate after mixing. The ^{15}N NMR of the liquid portion (in CD_3CN) exhibited two resonances at −346.4 and −8.9 ppm, similar to those detected in the EAN/TFAA system, but an additional signal attributable to $TfONO_2$ or NO_2^+ was not detectable at natural abundance. The ^1H NMR [1.24 (t, 3H, $J = 7.25$ Hz), 3.03−3.11 (m, 2H), 7.27 (brs, 3H)] and the ^{19}F NMR [−79.33 ppm (s)] corroborated the presence of $EtNH_3^+$/OTf^- ions. The solid portion was insoluble in CD_3CN but dissolved in acetone-d_6 (evolution of a yellow gas was noted while adding acetone-d_6). Its ^1H [1.25 (t, 3H, $J = 7.25$ Hz), 3.04−3.10 (m, 2H), 6.98 (brs, 3H)] and ^{19}F [−79.38 (s)] NMR spectra were compatible with [$EtNH_3$][OTf] salt formed via metathesis.

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