

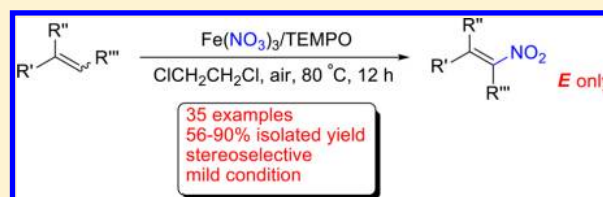
A Predictably Selective Nitration of Olefin with $\text{Fe}(\text{NO}_3)_3$ and TEMPO

Togati Naveen, Soham Maity, Upendra Sharma, and Debabrata Maiti*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, 400076, India

S Supporting Information

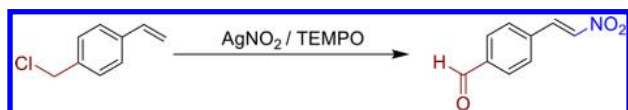
ABSTRACT: Ferric nitrate with catalytic TEMPO has been identified as a useful reagent for regio- and stereoselective nitration of a wide variety of aromatic, aliphatic, and heteroaromatic olefins. This reaction provided nitroolefins in preparatively useful yields with excellent *E*-selectivity. Due to its mild nature and operational simplicity, the present protocol is expected to find application in synthetic setup.



INTRODUCTION

Nitro compounds, particularly conjugated nitroolefins, have great importance in synthetic organic chemistry.¹ To obtain nitroolefins directly from olefins, different nitrating agents such as $\text{HNO}_3/\text{H}_2\text{SO}_4$,^{2a} $\text{NaNO}_2/\text{HgCl}_2$,^{2b} AgNO_2/I_2 ,^{2c} NO , NO_2/O_3 ,^{2e} $\text{NaNO}_2/\text{Cu}(\text{II})\text{-I}_2$,^{2f} and $\text{AgNO}_2/\text{CH}_3\text{COCl}$ ^{2g} have been employed so far.² However, these methods are often limited by a number of serious drawbacks: harsh conditions, limited scope, formation of an undesired mixture of *E/Z* isomer, among others. In this context, we recently reported an efficient nitration of olefins with silver nitrite (AgNO_2) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) where we circumvented the lack of stereoselectivity issue.³ While performing the screening of different metal nitrates as potential nitrating agents, we discovered that inexpensive ferric nitrate could provide (*E*)-nitrostyrene exclusively in 78% yield, whereas silver nitrite turned out to be the optimal reagent (99% yield). In fact, by using a reaction tube of larger volume (o.d. $\times$ *L* = 20×150 mm vs o.d. $\times$ *L* = 16×125 mm) with an appropriate stir-bar, up to 95% yield was achieved with $\text{Fe}(\text{NO}_3)_3$. Further, 1-(chloromethyl)-4-(2-nitrovinyl)benzene (Scheme 1), which failed to produce the desired nitro

Scheme 1. Undesired Nitration Product with AgNO_2 /TEMPO

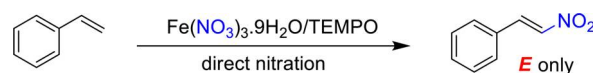


compound with AgNO_2 , remained intact under the present condition while undergoing nitration. Encouraged by these observations, we decided to explore the scope of the reaction with $\text{Fe}(\text{NO}_3)_3$ to provide an economic alternative for stereoselective olefin nitration (Scheme 2).⁴

RESULTS AND DISCUSSION

Styrene was chosen as a model substrate to discover the best reaction conditions using various nitrating agents and solvents. We found that 2 equiv of $\text{Fe}(\text{NO}_3)_3$ with 0.2 equiv of TEMPO

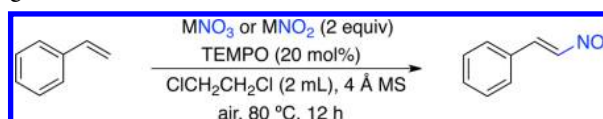
Scheme 2. Nitration of Olefins with $\text{Fe}(\text{NO}_3)_3$



in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 80°C can produce nitrostyrene in 95% yield (Table 1, entry 1).

However, lower yields were observed in the case of other metal nitrates such as $\text{Co}(\text{NO}_3)_2$ and $\text{Na}_3\text{Co}(\text{NO}_2)_6$ (Table 1, entries 3 and 4, respectively), but nitration was not observed in

Table 1. Optimization by Varying Different Nitrating Agents^a



entry	nitrating agents	GC yield (%)
1	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	95
2	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	78 ^b
3	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	37
4	$\text{Na}_3\text{Co}(\text{NO}_2)_6$	22
5	NaNO_2	0
6	AgNO_3	0
7	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0
8	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	74
9	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	57 ^c
10	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	19 ^d
11	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0 ^e

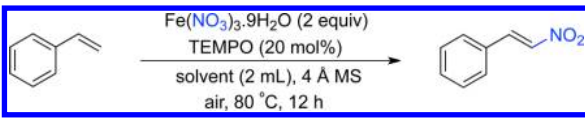
^aOlefin (0.5 mmol), nitrating agent (1 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80°C , $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2 mL), reaction carried out in borosilicate glass tubes with threaded end: o.d. $\times$ *L* = 20×150 mm.

^bReaction carried out in borosilicate glass tubes with threaded end: o.d. $\times$ *L* = 16×125 mm. ^cWithout molecular sieves. ^dWithout TEMPO. ^eDDQ, chloranil, and anthraquinone were used instead of TEMPO.

Received: March 25, 2013

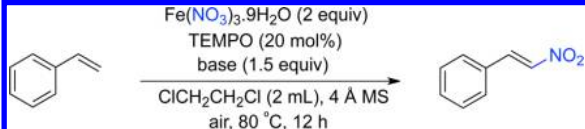
the case of NaNO_2 and AgNO_3 (Table 1, entries 5 and 6, respectively). Controlled experiments with or without TEMPO confirmed its necessity to obtain desired outcome of the reaction (Table 1, entries 1 and 10, respectively). The nature of the solvent had a significant effect on the nitration reaction as less/nonpolar solvents were found to be better compared to polar solvents (Table 2). The addition of different bases along with TEMPO was found to have a detrimental effect on the reaction outcome (Table 3).

Table 2. Optimization with Solvents^a

		
entry	solvent	GC yield (%)
1	$\text{ClCH}_2\text{CH}_2\text{Cl}$	95
2	TFT	89
3	dioxane	62
4	benzene	80
5	cyclohexane	63
6	toluene	68
7	THF	1
8	DMF	43

^aOlefin (0.5 mmol), $\text{Fe}(\text{NO}_3)_3$ (1 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80 °C, solvent (2 mL).

Table 3. Effect of Various Bases on Nitration Reaction^a

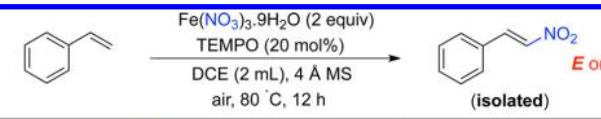
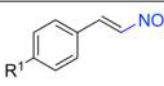
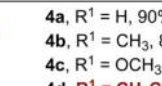
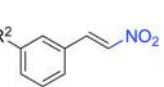
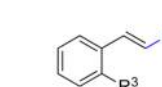
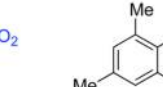
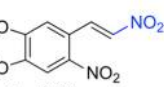
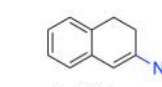
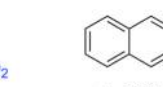
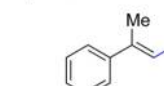
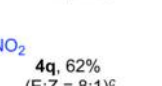
		
entry	base	GC yield (%)
1	BaCO_3	71
2	K_2CO_3	43
3	Na_2CO_3	45
4	CS_2CO_3	40
5	KO^tBu	66
6	DABCO	82
7	pyridine	65
8	DBU	22
9	K_3PO_4	66

^aOlefin (0.5 mmol), $\text{Fe}(\text{NO}_3)_3$ (1 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80 °C, $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2 mL).

Next, the scope and limitations of the reaction were investigated with the optimized reaction condition. First, we applied the present protocol on different styrene derivatives of stereoelectronic variety (Table 4). Notably, only the *E* isomer was observed in all these cases in contrast to earlier-reported methods, which provided *E/Z* mixtures.²

The electronic nature of the substituents did not have an impact on reaction outcome as both electron-donating (CH_3 , OCH_3) and electron-withdrawing (CO_2CH_3 , CN , CHO , and NO_2) substituents provided the desired nitroolefins in good to excellent yields (**4b**, **4c**, **4g–4j**). Different chloro- and bromo-substituted styrenes were tolerated as well (**4e**, **4k** and **4f**, **4l**). These halo-substituted β -nitrostyrenes are useful compounds for different cross-coupling reactions and other related transformations.

Table 4. Stereoselective Nitration of Styrenes^a

		
 4a , $\text{R}^1 = \text{H}$, 90% (95%) ^b 4b , $\text{R}^1 = \text{CH}_3$, 88% 4c , $\text{R}^1 = \text{OCH}_3$, 84% 4d , $\text{R}^1 = \text{CH}_2\text{Cl}$, 76%	 4e , $\text{R}^1 = \text{Cl}$, 85% 4f , $\text{R}^1 = \text{Br}$, 84% 4g , $\text{R}^1 = \text{COOCH}_3$, 82% 4h , $\text{R}^1 = \text{CN}$, 77%	
 4i , $\text{R}^2 = \text{CHO}$, 78% 4j , $\text{R}^2 = \text{NO}_2$, 83%	 4k , $\text{R}^3 = \text{Cl}$, 81% 4l , $\text{R}^3 = \text{Br}$, 77%	 4m , 85%
 4n , 71%	 4o , 87%	 4p , 88%
 4q , 62% <i>(E:Z = 8:1)</i> ^c	 4r , 60% <i>(E:Z = 7:1)</i> ^c	

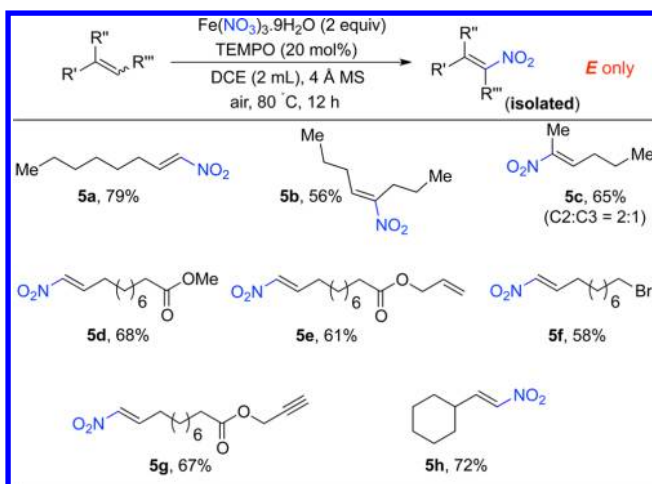
^aOlefin (0.5 mmol), $\text{Fe}(\text{NO}_3)_3$ (1 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80 °C, $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2 mL); isolated yield of the *E* isomer; reaction mixtures were analyzed by GC-MS and/or ^1H NMR to determine *E/Z* ratios. ^bGC yield. ^cYield of *E* isomer only.

A 2,4,6-trisubstituted styrene derivative afforded the corresponding nitration product in an excellent 85% yield (**4m**). Slight decreases in yield were observed in the case of α - and β -substituted styrene (as compared to styrene) probably owing to the steric effect of the methyl group adjacent to the reaction center (**4q** and **4r**). In both of these cases, a $>7:1$ *E/Z* mixture was obtained. One of the important findings of the present protocol is tolerance of the chloromethyl group, which can be otherwise easily oxidized to the corresponding aldehyde (**4d**) (Scheme 1). Notably, 3-nitro-1,2-dihydronaphthalene (**4o**) was synthesized in excellent yield. Such an internal nitroolefin is difficult to access through a traditional Henry reaction.⁵

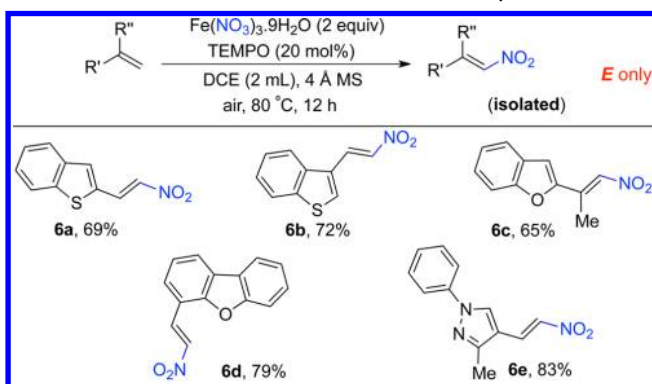
After successful nitration of styrenes, a number of aliphatic olefins were subjected to nitration (Table 5). Long chain aliphatic substrates with a terminal olefin produced the desired nitro product in good yield (**5a**). Alkenes with internal double bonds were also nitrated successfully (**5b** and **5c**). Symmetrical olefin, such as (*E*)-4-octene, produced the thermodynamically stable (*E*)-4-nitrooct-4-ene (**5b**).

To investigate the site-selectivity of nitration, we designed a substrate with two olefins embedded in different electronic environments. As expected, nitration occurred exclusively at the distal olefin, which is electron-rich, as compared to the other part, which is in the vicinity of the electron-withdrawing group and hence deactivated (**5e**). On the other hand, selective nitration at the terminal olefin was observed in the presence of a terminal alkyne (**5g**). Ester and halide functional groups on a distal position of a terminal alkene were also well-tolerated (**5d** and **5f**).

The present condition is also compatible with heterocyclic olefins (Table 6). Nitration of 2-vinylbenzothiophene and 3-vinylbenzothiophene afforded the desired product in good yield (**6a** and **6b**). Reaction of a vinyl group containing dibenzofuran proceeded smoothly to generate the nitro product with *E*-

Table 5. Regio- and Stereoselective Nitration of Aliphatic Olefins^a

^aOlefin (0.5 mmol), Fe(NO₃)₃ (1.0 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80 °C, ClCH₂CH₂Cl (2 mL); isolated yield of the *E* isomer; reaction mixtures were analyzed by GC-MS and/or ¹H NMR to determine *E/Z* ratios. ^bIsolated as *E/Z* mixture.

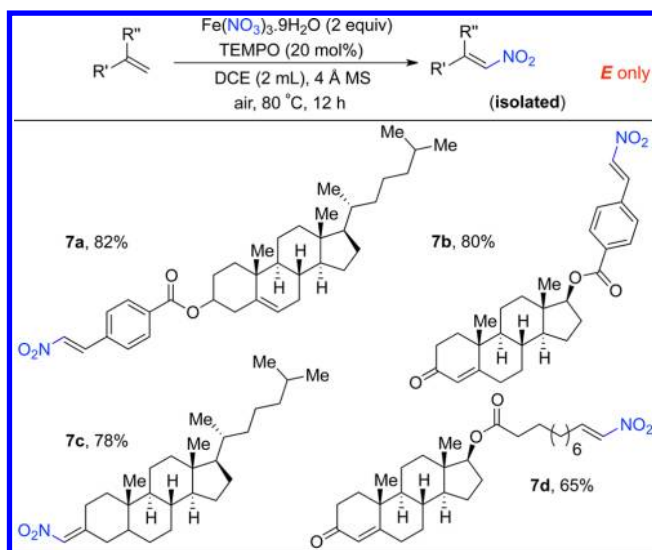
Table 6. Stereoselective Nitration of Heterocyclic Olefins^a

^aOlefin (0.5 mmol), Fe(NO₃)₃ (1.0 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80 °C, ClCH₂CH₂Cl (2 mL); isolated yield of the *E* isomer; reaction mixtures were analyzed by GC-MS and/or ¹H NMR to determine *E/Z* ratios.

stereoselectivity (6d). A vinyl pyrazole derivative provided the nitration product with an excellent 83% isolation yield (6e).

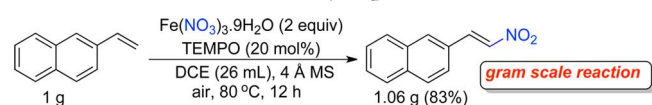
Next, we examined the applicability of this nitration protocol with steroid-derived molecules to exhibit the applicability of our method (Table 7). Substrates based on naturally occurring testosterone were nitrated in synthetically useful yield (7b and 7d). The substrate containing an *exo*-cyclic double bond was nitrated with excellent stereoselectivity (7c, 78% yield). Further, the reaction was successfully scaled-up to 1 g with 2-vinylnaphthalene (Scheme 3, yield 83%).

In an earlier study with silver nitrite, we postulated about involvement of a nitro radical. Indeed, the nitro radical (NO₂•) can be generated from Fe(NO₃)₃ under thermal conditions (Scheme 4),²¹ following which we have depicted a plausible mechanism in Scheme 4. The nitro radical would react at the less-hindered side of the olefin in order to generate a secondary or benzylic radical. This nitroalkane radical can be converted to nitroolefin via two pathways. In *path 1*, TEMPO can abstract a hydrogen radical, and in *path 2*, TEMPO may trap and oxidize a benzylic radical to generate nitroolefin stereoselectively.³

Table 7. Regio- and Stereoselective Nitration of Natural Product Derived Olefins^a

^aOlefin (0.5 mmol), Fe(NO₃)₃ (1.0 mmol), TEMPO (0.1 mmol), 4 Å MS (150 mg), 80 °C, ClCH₂CH₂Cl (2 mL); isolated yield of the *E* isomer; reaction mixtures were analyzed by GC-MS and/or ¹H NMR to determine *E/Z* ratios.

Scheme 3. Nitration of 2-Vinylnaphthalene in Gram Scale



CONCLUSION

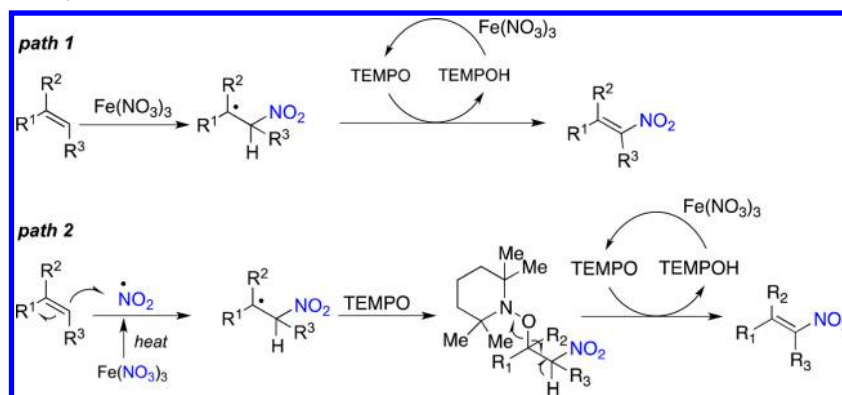
In conclusion, an efficient method for nitration of olefin has been developed by using inexpensive ferric nitrate and TEMPO. A wide range of olefins including aromatic, aliphatic, heteroaromatic, and steroid-derived molecules were studied, and nitration occurred in excellent yields. The present method exhibited an excellent *E*-selectivity for all the observed cases. This economical alternative is expected to complement our previous approaches^{3,13} to generate nitroolefins stereoselectively in everyday synthetic setup.

EXPERIMENTAL SECTION

General Procedures. All solvents, ferric nitrate, TEMPO, and molecular sieves (4 Å; particle size 2–3 μm) were purchased from commercial sources. All isolated compounds were characterized on the basis of ¹H NMR and ¹³C NMR spectroscopic data, gas chromatography mass spectra (GC-MS), and HRMS data. All ¹H and ¹³C NMR data were reported in parts per million relative to tetramethylsilane (δ = 0) and were measured relative to the signals for residual chloroform (7.26 ppm for ¹H and 77.23 ppm for ¹³C) in the deuterated solvent. All GC analyses were performed on a GC system with an FID detector using a J & W DB-1 column (10 m, 0.1 mm i.d.). As the internal standard, *n*-decane was used. All GC-MS analysis was done on a GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

General Procedure for the Synthesis of Nitroolefins. Olefin (1 mmol), Fe(NO₃)₃·9H₂O (1 mmol, 404 mg), TEMPO (0.1 mmol, 16 mg), and molecular sieves (4 Å, 150 mg) were added to an oven-dried screw cap test tube (borosilicate glass tubes with threaded end; o.d. × L = 20 × 150 mm) which was already charged with a magnetic stir-bar. To start, olefin (if it was liquid) and solvent (ClCH₂CH₂Cl, 2 mL) were added by microliter and laboratory syringe, respectively. The tube was placed in a preheated oil bath at 80 °C, and the reaction

Scheme 4. Proposed Pathways for Stereoselective Nitration



mixture was stirred vigorously for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature and filtered through a Celite bed with ethyl acetate as the washing solvent. Finally, organic extract was concentrated and purified by column chromatography using silica gel (60–120/100–200 mesh size) and petroleum ether/ethyl acetate as the eluent.

Procedure for the Synthesis of Nitroolefins in Gram Scale.

To an oven-dried round-bottom (250 mL) flask, which was already charged with a magnetic stir-bar, were added 2-vinylnaphthalene (6.4 mmol, 1.00 g), Fe(NO₃)₃·9H₂O (12.8 mmol, 5.17 g), TEMPO (1.28 mmol, 0.20 g), and molecular sieves (4 Å, 960 mg), and the solvent (ClCH₂CH₂Cl, 26 mL). The flask was then sealed with a rubber septum, placed in a preheated oil bath at 80 °C, and the reaction mixture was stirred vigorously for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature and filtered through a Celite bed with ethyl acetate as the washing solvent. Finally, organic extract was concentrated and purified by column chromatography using silica gel (100–200 mesh size) and PET-ether/ethyl acetate as the eluent.

(*E*)-β-Nitrostyrene (Table 4, Entry 4a) (Known Compound^{2h,3}): Crystalline yellow solid (67 mg, 90%), mp 57–58 °C, GC-MS (*m/z*) 149.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43–7.51 (m, 3H), 7.54–7.57 (m, 2H), 7.57–7.61 (d, *J* = 13.7 Hz, 1H), 7.99–8.04 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 129.3, 129.6, 130.2, 132.3, 137.3, 139.3.

(*E*)-1-Methyl-4-(2-nitrovinyl)benzene (Table 4, Entry 4b) (Known Compound^{2h,3}): Yellow solid (72 mg, 88%), mp 106–107 °C, GC-MS (*m/z*) 163.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 2.36–2.49 (s, 3H), 7.25–7.30 (d, *J* = 2.5 Hz, 2H), 7.44–7.47 (d, *J* = 8.2 Hz, 2H), 7.56–7.60 (d, *J* = 13.7 Hz, 1H), 7.98–8.02 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 21.8, 127.4, 129.3, 130.3, 136.4, 139.3, 143.3.

(*E*)-1-Methoxy-4-(2-nitrovinyl)benzene (Table 4, Entry 4c) (Known Compound^{2h,3}): Yellow solid (75 mg, 84%), GC-MS (*m/z*) 179.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 3.87 (s, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.49–7.55 (m, 3H), 7.98 (d, *J* = 13.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 55.7, 115.1, 122.7, 131.3, 135.2, 139.2, 163.1.

(*E*)-1-(Chloromethyl)-4-(2-nitrovinyl)benzene (Table 4, Entry 4d): Yellow solid (75 mg, 76%); ¹H NMR (400 MHz, CHCl₃) δ (ppm) 4.61 (s, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.53–7.61 (m, 3H), 7.99 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 45.4, 129.6, 129.7, 130.2, 137.6, 138.4, 141.7; ESI-MS calcd for C₉H₈ClNO₂ 220.01, found 219.91. Anal. Calcd for C₉H₈ClNO₂: C, 54.70; H, 4.08; N, 7.09. Found: C, 54.84; H, 3.93; N, 7.30.

(*E*)-1-Chloro-4-(2-nitrovinyl)benzene (Table 4, Entry 4e) (Known Compound^{2h,3}): Crystalline light yellow solid (78 mg, 85%), mp 113–114 °C, GC-MS (*m/z*) 183.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.40–7.47 (m, 2H), 7.46–7.53 (m, 2H), 7.56 (d, *J* = 13.7 Hz, 1H), 7.96 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 128.7, 129.9, 130.4, 137.6, 137.9, 138.5.

(*E*)-1-Bromo-4-(2-nitrovinyl)benzene (Table 4, Entry 4f) (Known Compound^{2h}): Light yellow solid (96 mg, 84%); ¹H NMR (400 MHz,

CDCl₃) δ (ppm) 7.39–7.44 (m, 2H), 7.57 (d, *J* = 10.3 Hz, 1H), 7.60 (dd, *J* = 4.8, 1.7 Hz, 2H), 7.94 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 127.0, 129.1, 130.5, 132.9, 137.6, 138.0.

(*E*)-Methyl 4-(2-nitrovinyl)benzoate (Table 4, Entry 4g) (Known Compound^{3,7}): Light yellow solid (85 mg, 82%), mp 176–178 °C, GC-MS (*m/z*) 207.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.30–7.38 (td, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.39–7.45 (td, *J* = 8.0, 7.7, 1.7 Hz, 1H), 7.46–7.51 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.56–7.61 (m, 2H), 8.36–8.40 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 52.7, 129.1, 130.6, 133.2, 134.3, 137.7, 138.8, 166.2.

(*E*)-4-(2-Nitrovinyl)benzonitrile (Table 4, Entry 4h) (Known Compound^{3,6}): Light yellow solid (67 mg, 77%), mp 186–187 °C, GC-MS (*m/z*) 174.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.62 (d, *J* = 13.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.72–7.80 (m, 2H), 7.99 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 115.3, 117.9, 129.5, 133.1, 134.4, 136.7, 139.6.

(*E*)-3-(2-Nitrovinyl)benzaldehyde (Table 4, Entry 4i) (Known Compound³): Light yellow solid (69 mg, 78%), mp 91–92 °C, GC-MS (*m/z*) 177.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.62–7.70 (m, 2H), 7.78–7.85 (m, 1H), 7.97–8.10 (m, 3H), 10.06 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 129.7, 130.4, 131.2, 133.0, 134.5, 137.3, 137.6, 138.5, 191.2.

(*E*)-1-Nitro-3-(2-nitrovinyl)benzene (Table 4, Entry 4j) (Known Compound^{3,8}): Light yellow solid (81 mg, 83%), mp 125–126 °C, GC-MS (*m/z*) 194.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.66–7.72 (m, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 13.8 Hz, 1H), 8.34–8.37 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.43 (t, *J* = 2.0, 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 123.6, 126.3, 130.8, 131.9, 134.6, 136.4, 139.4, 148.9.

(*E*)-1-Chloro-2-(2-nitrovinyl)benzene (Table 4, Entry 4k) (Known Compound^{2h}): Yellow liquid (74 mg, 81%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.30–7.36 (td, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.39–7.45 (td, *J* = 8.0, 7.7, 1.7 Hz, 1H), 7.46–7.50 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.56–7.61 (m, 2H), 8.38 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 127.6, 128.6, 128.7, 130.8, 133.0, 135.2, 136.1, 138.9.

(*E*)-1-Bromo-2-(2-nitrovinyl)benzene (Table 4, Entry 4l) (Known Compound^{3,9}): Crystalline light yellow solid (88 mg, 77%), mp 88–89 °C, GC-MS (*m/z*) 228.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.31–7.40 (dtd, *J* = 19.3, 7.5, 7.5, 1.6 Hz, 2H), 7.50–7.59 (m, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 8.35–8.39 (dd, *J* = 13.7, 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 126.4, 128.2, 128.6, 130.4, 133.1, 134.1, 137.7, 138.9.

(*E*)-1,3,5-tri-Methyl-2-(2-nitrovinyl)benzene (Table 4, Entry 4m) (Known Compound³): Yellow solid (81 mg, 85%), mp 123–124 °C, GC-MS (*m/z*) 191.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 2.31 (s, 3H), 2.38 (s, 6H), 6.95 (s, 2H), 7.24–7.34 (m, 1H), 8.26 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 21.3, 21.7, 125.8, 130.0, 136.7, 138.6, 139.8, 141.0.

(*E*)-5-Nitro-6-(2-nitrovinyl)benzo[d][1,3]dioxole (Table 4, Entry 4n) (Known Compound³): Yellow solid (85 mg, 71%), mp 110–111 °C, GC-MS (*m/z*) 238.1 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.14 (s, 2H), 6.85 (s, 1H), 7.28 (d, *J* = 13.5 Hz, 1H), 7.57 (s,

1H), 8.42 (d, $J = 13.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 100.1, 104.1, 106.6, 107.8, 122.5, 135.8, 139.4, 150.5, 152.5.

3-Nitro-1,2-dihydronaphthalene (Table 4, Entry 4o) (Known Compound¹⁰): Greenish yellow liquid (76.2, 87%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 2.94–2.97 (m, 2H), 2.98–2.99 (t, $J = 1.3$, 1.3 Hz, 1H), 3.02–3.03 (t, $J = 1.1$, 1.1 Hz, 2H), 7.28–7.31 (m, 2H), 7.31–7.34 (dd, $J = 4.6$, 1.7 Hz, 1H), 7.34–7.37 (dd, $J = 7.3$, 1.8 Hz, 1H), 7.78–7.90 (d, $J = 1.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 22.5, 28.0, 127.4, 128.06, 130.2, 130.3, 131.4, 131.7, 136.5, 148.0.

(E)-2-(2-Nitrovinyl)naphthalene (Table 4, Entry 4p) (Known Compound^{2,c,j}): Yellow solid (88 mg, 88%), mp 128–130 °C, GC-MS (m/z) 199.1 [$\text{M}]^+$; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.54–7.62 (m, 3H), 7.70 (d, $J = 13.6$ Hz, 1H), 7.86–7.91 (m, 3H), 8.01–8.02 (m, 1H), 8.16 (d, $J = 13.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 123.5, 127.4, 127.7, 128.1, 128.6, 129.0, 129.5, 132.5, 133.3, 135.1, 137.3, 139.4.

(E)-1-(1-Nitroprop-1-en-2-yl)benzene (Table 4, Entry 4q) (Known Compound^{3,11}): Yellow liquid (51 mg, 62%), GC-MS (m/z) 163.1 [$\text{M}]^+$; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 2.65 (d, $J = 1.5$ Hz, 3H), 7.31 (q, $J = 1.5$, 1.4, 1.4 Hz, 1H), 7.45 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 18.8, 127.0, 129.2, 130.5, 136.5, 138.4, 150.2.

(Z)-2-(2-Nitroprop-1-enyl)benzene (Table 4, Entry 4r) (Known Compound^{3,11}): Yellow liquid (49 mg, 60%), GC-MS (m/z) 163.1 [$\text{M}]^+$; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 2.45–2.48 (d, $J = 1.1$ Hz, 3H), 7.42–7.47 (m, 5H), 8.10–8.11 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 14.2, 128.1, 129.1, 130.1, 130.1, 132.6, 133.7.

(E)-1-Nitrooct-1-ene (Table 5, Entry 5a) (Known Compound^{3,12}): Yellow liquid (62 mg, 79%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.86–0.92 (m, 3H), 1.21–1.39 (m, 6H), 1.46–1.56 (m, 2H), 2.23–2.30 (qd, $J = 7.5$, 7.5, 7.4, 1.6 Hz, 2H), 6.96–7.01 (dt, $J = 13.4$, 1.6, 1.6 Hz, 1H), 7.24–7.32 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 14.2, 22.6, 27.8, 28.6, 28.9, 31.6, 139.7, 143.0.

(E)-4-Nitrooct-4-ene (Table 5, Entry 5b) (Known Compound^{3,12}): Yellow liquid (44 mg, 56%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.91–1.00 (dt, $J = 13.2$, 7.4, 7.4 Hz, 6H), 1.23–1.26 (s, 1H), 1.49–1.57 (ddt, $J = 11.5$, 7.5, 3.9, 3.9 Hz, 3H), 2.17–2.25 (q, $J = 7.6$, 7.6, 7.6 Hz, 2H), 2.53–2.60 (m, 2H), 7.07–7.13 (t, $J = 8.0$, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 13.8, 14.0, 21.4, 22.0, 28.3, 30.1, 76.9, 77.2, 77.5, 100.1, 136.6.

(E)-2-Nitrohex-2-ene (Table 5, Entry 5c) (Known Compound³): Yellow liquid (42 mg, 65%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.92–1.00 (dt, $J = 10.2$, 7.4, 7.4 Hz, 3H), 1.24–1.27 (d, $J = 9.0$ Hz, 0H), 1.49–1.60 (td, $J = 14.8$, 14.8, 7.4 Hz, 3H), 1.87–1.90 (dt, $J = 7.4$, 0.7, 0.7 Hz, 1H), 2.15–2.24 (m, 4H), 2.54–2.60 (m, 1H), 7.11–7.23 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 12.7, 13.7, 14.0, 21.1, 21.8, 28.0, 30.2, 131.8, 136.4.

(E)-Methyl-11-nitroundec-10-enoate (Table 5, Entry 5d) (Known Compound³): Light yellow liquid (83 mg, 68%), GC-MS (m/z) 212.1 [$\text{M}]^+$; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.29–1.36 (m, 9H), 1.46–1.63 (m, 4H), 2.22–2.32 (m, 4H), 3.66 (s, 3H), 6.95–6.99 (dt, $J = 13.4$, 1.6, 1.6 Hz, 1H), 7.23–7.30 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 24.9, 27.8, 28.5, 29.1, 29.1, 29.1, 29.1, 34.1, 51.6, 139.7, 142.9, 174.3.

(E)-3-Nitroallyl-undec-10-enoate (Table 5, Entry 5e) (Known Compound³): Light yellow liquid (82 mg, 61%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.24–1.66 (m, 12H), 2.21–2.38 (m, 3H), 4.55–4.60 (d, $J = 5.7$ Hz, 1H), 5.20–5.37 (m, 1H), 5.85–6.00 (ddt, $J = 17.2$, 10.4, 5.7, 5.7 Hz, 1H), 6.95–7.01 (m, 1H), 7.23–7.33 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 25.0, 27.9, 28.6, 29.2, 29.2, 29.2, 29.9, 34.4, 65.1, 118.3, 132.5, 139.7, 142.9, 173.6.

(E)-10-Bromo-1-nitrodec-1-ene (Table 5, Entry 5f) (Known Compound³): Yellow liquid (77 mg, 58%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.24–1.35 (m, 7H), 1.35–1.44 (m, 2H), 1.49 (p, $J = 7.5$, 7.5, 7.3, 7.3 Hz, 2H), 1.74–1.90 (m, 2H), 2.17–2.31 (qd, $J = 7.4$, 7.4, 7.4, 1.5 Hz, 2H), 3.38 (t, $J = 6.8$, 6.8 Hz, 2H), 6.88–7.03 (dd, $J = 13.4$, 1.5 Hz, 1H), 7.17–7.34 (dt, $J = 13.7$, 7.4, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 27.8, 28.2, 28.6, 28.7, 29.1, 29.2, 32.9, 34.1, 139.7, 142.9.

(E)-Prop-2-yn-1-yl 11-nitroundec-10-enoate (Table 5, Entry 5g): Yellow liquid (89.5 mg, 67%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.28–1.37 (m, 9H), 1.47–1.70 (m, 5H), 2.24–2.31 (qd, $J = 7.4$, 7.4, 1.5 Hz, 2H), 2.32–2.39 (t, $J = 7.5$, 7.5 Hz, 2H), 2.47–2.50 (t, $J = 2.5$, 2.5 Hz, 1H), 4.64–4.70 (d, $J = 2.5$ Hz, 2H), 6.95–7.04 (m, 1H), 7.22–7.34 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 24.7, 27.7, 28.4, 28.9, 29.0, 29.0, 33.9, 51.8, 74.8, 77.8, 139.6, 142.8, 172.9; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_4$ 290.1368, found 290.1360.

(E)-2-(2-Nitrovinyl)cyclohexane (Table 5, Entry 5h) (Known Compound^{3,6}): Yellow liquid 56 mg, 72%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.14–1.40 (m, 5H), 1.57–1.59 (s, 2H), 1.68–1.75 (dddd, $J = 11.7$, 5.0, 3.2, 1.6 Hz, 1H), 1.78–1.84 (m, 2H), 2.20–2.31 (ddtd, $J = 11.0$, 7.4, 3.9, 3.5, 1.3 Hz, 1H), 6.91–6.96 (dd, $J = 13.5$, 1.4 Hz, 1H), 7.20–7.26 (dd, $J = 13.5$, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 25.6, 25.8, 31.6, 37.7, 138.4, 147.5.

(E)-2-(2-Nitrovinyl)benzo[b]thiophene (Table 6, Entry 6a): Greenish yellow solid (71 mg, 69%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.54–1.63 (s, 1H), 7.39–7.52 (m, 3H), 7.68–7.70 (s, 1H), 7.82–7.85 (m, 1H), 8.20–8.26 (dd, $J = 13.3$, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 122.8, 125.2, 125.6, 127.7, 132.9, 133.2, 133.8, 137.2, 139.3, 141.27; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{NO}_2\text{S}$ 206.0276, found 206.0282.

(E)-3-(2-Nitrovinyl)benzo[b]thiophene (Table 6, Entry 6b) (Known Compound³): Greenish yellow solid (74 mg, 72%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.46–7.56 (m, 2H), 7.76 (d, $J = 12.0$ Hz, 1H), 7.92–7.98 (m, 3H), 8.29 (d, $J = 12.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 122.2, 123.5, 125.9, 127.2, 131.3, 133.1, 136.6, 136.8, 140.7.

(E)-2-(1-Nitroprop-1-en-2-yl)benzofuran (Table 6, Entry 6c): Yellow solid (66 mg, 65%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 2.64 (d, $J = 1.4$ Hz, 3H), 7.26 (s, 1H), 7.24–7.33 (m, 1H), 7.40–7.44 (ddd, $J = 8.4$, 7.2, 1.3 Hz, 1H), 7.48–7.51 (dd, $J = 8.4$, 1.0 Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 1.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 14.9, 111.7, 112.3, 122.1, 123.9, 127.7, 128.1, 135.1, 136.6, 152.3, 155.6; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{10}\text{NO}_3$ 204.0661, found 204.0652.

(E)-4-(2-Nitrovinyl)dibenzo[b,d]furan (Table 6, Entry 6d) (Known Compound³): Light yellow solid (94.4 mg, 79%), mp 123–124 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.39–7.44 (tdd, $J = 7.7$, 7.7, 2.6, 0.8 Hz, 2H), 7.51–7.57 (m, 2H), 7.65–7.68 (dd, $J = 8.3$, 0.9 Hz, 1H), 7.96–7.99 (m, 1H), 8.04–8.07 (dt, $J = 7.7$, 0.9, 0.9 Hz, 1H), 8.15–8.20 (dd, $J = 13.7$, 0.9 Hz, 1H), 8.30–8.35 (dd, $J = 13.6$, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 112.2, 115.5, 121.1, 123.2, 123.6, 123.8, 124.5, 125.5, 128.3, 130.7, 134.4, 139.9, 154.5, 156.2; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{10}\text{NO}_3$ 240.0661, found 240.0668.

(E)-3-Methyl-4-(2-nitrovinyl)-1-phenyl-1H-pyrazole (Table 6, Entry 6e) (Known Compound³): Greenish yellow solid (95 mg, 83%), mp 143–144 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 2.40–2.54 (s, 2H), 7.32–7.37 (td, $J = 7.5$, 7.3, 1.2 Hz, 1H), 7.44–7.50 (m, 3H), 7.64–7.69 (dd, $J = 8.7$, 1.1 Hz, 2H), 8.00–8.04 (d, $J = 13.7$ Hz, 1H), 8.15–8.16 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 122.8, 125.2, 125.6, 127.7, 132.9, 133.2, 133.8, 137.2, 139.3, 141.2; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_2$ 230.0930, found 230.0923.

(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((E)-2-nitrovinyl)benzoate (Table 7, Entry 7a): Bright yellowish solid (230 mg, 82%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.68–0.70 (s, 2H), 0.84–2.07 (m, 21H), 2.39–2.57 (d, $J = 7.7$ Hz, 1H), 4.79–4.99 (tdd, $J = 9.2$, 9.2, 7.6, 4.5 Hz, 1H), 5.37–5.50 (m, 1H), 7.60–7.65 (m, 2H), 8.00–8.05 (d, $J = 13.8$ Hz, 1H), 8.09–8.13 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 12.0, 18.9, 19.5, 21.2, 22.7, 23.0, 24.0, 24.5, 28.0, 28.2, 28.4, 32.0, 32.1, 36.0, 36.4, 36.8, 37.2, 38.3, 39.7, 39.9, 42.5, 50.2, 56.3, 56.8, 75.48, 123.2, 129.1, 130.6, 133.9, 134.1, 137.9, 138.7, 139.6, 159.8, 165.4; ESI-MS calcd for $\text{C}_{36}\text{H}_{51}\text{NO}_4$ 561.38, found 561.39 and 562.41.

(8R,9S,10R,13S,14S,17S)-10,13-Di-methyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl-4-((E)-2-nitrovinyl)benzoate (Table 7, Entry 7b) (Known Compound³): Light yellow solid (185 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.95–1.32 (m, 9H), 1.38–1.50 (m, 2H),

1.57–1.80 (m, 6H), 1.84–1.92 (m, 2H), 2.00–2.07 (m, 1H), 2.26–2.48 (m, 4H), 4.04–4.20 (d, $J = 7.1$ Hz, 1H), 4.83–4.91 (dd, $J = 9.2$, 7.7 Hz, 1H), 5.72–5.76 (m, 1H), 7.61–7.65 (m, 3H), 8.01–8.04 (d, $J = 13.8$ Hz, 1H), 8.09–8.11 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 12.5, 17.6, 20.7, 23.8, 27.8, 31.6, 32.9, 34.1, 35.6, 35.9, 36.9, 38.8, 43.1, 50.4, 53.8, 83.7, 124.2, 129.1, 130.5, 133.7, 134.2, 137.8, 138.8, 165.5, 170.9, 199.6.

(8R,9S,10S,13R,14S,17R,E)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-3-(nitromethylene)hexadecahydro-1H-cyclopenta[a]phenanthrene (Table 7, Entry 7c) (Known Compound³): Creamy white solid (168 mg, 78%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.64–0.75 (d, $J = 30.0$ Hz, 6H), 0.84–0.94 (m, 15H), 0.95–1.21 (m, 7H), 1.20–1.42 (m, 8H), 1.47–1.62 (m, 2H), 1.65–2.01 (m, 5H), 2.08–2.27 (m, 1H), 2.28–2.40 (m, 1H), 4.73–4.87 (s, 1H), 6.82–6.96 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 18.9, 21.4, 22.7, 23.0, 24.0, 24.4, 28.2, 28.4, 30.3, 31.5, 32.0, 32.1, 35.5, 36.0, 36.3, 39.3, 39.7, 40.0, 42.7, 47.3, 48.3, 54.2, 54.3, 56.4, 56.5, 132.4, 156.1.

(E)-(8R,9S,10R,13S,14S,17S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 11-nitroundec-10-enoate (Table 7, Entry 7d): Light yellow liquid (162 mg, 65%); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.79–1.24 (m, 11H), 1.24–1.44 (m, 10H), 1.44–1.89 (m, 6H), 1.99–2.06 (m, 1H), 2.12–2.48 (m, 9H), 4.56–4.65 (dd, $J = 9.2$, 7.8 Hz, 1H), 5.71–5.75 (m, 1H), 6.96–7.01 (dt, $J = 13.4$, 1.6, 1.6 Hz, 1H), 7.08–7.15 (m, 1H), 7.22–7.34 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 12.2, 17.5, 20.6, 23.6, 25.17, 27.6, 27.8, 28.6, 29.1, 29.2, 31.6, 32.9, 34.1, 34.6, 35.5, 35.8, 36.8, 38.7, 42.6, 50.3, 53.8, 82.3, 124.1, 139.7, 142.9, 171.2, 173.9, 199.6; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{45}\text{NNaO}_5$ 522.3190, found 522.3186.

■ ASSOCIATED CONTENT

● Supporting Information

Figures of ^1H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dmaiti@iitb.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This activity is supported by DST, India. Financial support received from CSIR-India (fellowship to T.N. and S.M.) and DST-India (fellowship to U.S. under Fast Track Scheme) is gratefully acknowledged.

■ REFERENCES

- (1) (a) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2001. (b) Feuer, H.; Nielsen, A. T. *Nitro Compounds*; VCH Publishers, Inc.: New York, 1990. (c) Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, 86, 751. (d) Rosini, G.; Ballini, R. *Synthesis* **1988**, 833. (e) Tamura, R.; Kamimura, A.; Ono, N. *Synthesis* **1991**, 423. (f) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, U.K., 1990. (g) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press: Oxford, U.K., 1992. (h) Ballini, R.; Bosica, G.; Fiorini, D.; Palmieri, A.; Petrini, M. *Chem. Rev.* **2005**, 105, 933.
- (2) (a) Tinsley, S. W. *J. Org. Chem.* **1961**, 26, 4723. (b) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, 100, 6294. (c) Sy, W. W.; By, A. W. *Tetrahedron Lett.* **1985**, 26, 1193. (d) Mukaiyama, T.; Hata, E.; Yamada, T. *Chem. Lett.* **1995**, 505. (e) Suzuki, H.; Mori, T. *J. Org. Chem.* **1997**, 62, 6498. (f) Campos, P. J.; Garcia, B.; Rodriguez, M. A. *Tetrahedron Lett.* **2000**, 41, 979. (g) Kancharla, P. K.; Reddy, Y. S.; Dharuman, S.; Vankar, Y. D. *J. Org. Chem.* **2011**, 76, 5832. (h) Jovel, I.

Prateptongkum, S.; Jackstell, R.; Vogl, N.; Weckbecker, C.; Beller, M. *Adv. Synth. Catal.* **2008**, 350, 2493. (i) Taniguchi, T.; Fujii, T.; Ishibashi, H. *J. Org. Chem.* **2010**, 75, 8126.

(3) Maity, S.; Manna, S.; Rana, S.; Naveen, T.; Mallick, A.; Maiti, D. *J. Am. Chem. Soc.* **2013**, 3355.

(4) (a) Bolm, C.; Legros, J.; Paith, J. L.; Zani, L. *Chem. Rev.* **2004**, 104, 6217. (b) Sherry, B. D.; Furstner, A. *Acc. Chem. Res.* **2008**, 41, 1500. (c) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem.* **2008**, 120, 3363; *Angew. Chem., Int. Ed.* **2008**, 47, 3317. (d) Correa, A.; Mancho, O. G.; Bolm, C. *Chem. Soc. Rev.* **2008**, 37, 1108. (e) Morris, R. H. *Chem. Soc. Rev.* **2009**, 38, 2282.

(5) (a) Kurti, L.; Czako, B. *Strategic Applications of Named Reactions in Organic Synthesis*; Elsevier Academic Press: Philadelphia, PA, 2005. (b) Fioravanti, S.; Pellacani, L.; Tardella, P. A.; Vergari, M. C. *Org. Lett.* **2008**, 10, 1449.

(6) Yoshida, M.; Kitamikado, N.; Ikehara, H.; Hara, S. *J. Org. Chem.* **2011**, 76, 2305.

(7) Campos, P. J.; Garcia, B.; Rodriguez, M. A. *Tetrahedron Lett.* **2000**, 41, 979.

(8) Neelakandeswari, N.; Sangami, G.; Emayavaramban, P.; Karvembu, R.; Dharmaraj, N.; Kim, H. Y. *Tetrahedron Lett.* **2012**, 53, 2980.

(9) Chang, C.-F.; Huang, C.-Y.; Huang, Y.-C.; Lin, K.-Y.; Lee, Y.-J.; Wang, C. J. *Synth. Commun.* **2010**, 40, 3452.

(10) Sreekumar, R.; Padmakumar, R.; Rugmini. *Tetrahedron Lett.* **1998**, 39, 2696.

(11) Fryszkowska, A.; Fisher, K.; Gardiner, J. M.; Stephens, G. M. *J. Org. Chem.* **2008**, 73, 4295.

(12) Motokura, K.; Tomita, M.; Tada, M.; Iwasawa, Y. *Chem.—Eur. J.* **2008**, 14, 4017.

(13) Manna, S.; Jana, S.; Saboo, T.; Maji, A.; Maiti, D. *Chem. Commun.* **2013**, 49, 5286.