

An Efficient and Stereoselective Nitration of Mono- and Di-Substituted Olefins with AgNO₂ and TEMPO

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Supporting Information

General Consideration:

Reagent Information. Unless otherwise stated, all reactions were carried out in screw cap reaction tubes. All the solvents were bought from Aldrich and were used as received. Silver Nitrite and TEMPO were purchased from Aldrich/Alfa Aesar and Spectrochem respectively. Molecular sieves (4Å; particle size 2–3 μ) were bought from Aldrich and were always kept in oven in small amount before use. Olefins corresponding to entries **4a**, **4c**, **4f**, **5h** and **5i** were bought from Alfa Aesar. Styrene and olefins corresponding to entries **4b**, **4d**, **4e**, **4g**, **4h**, **4j-4o**, **5a-5e** and **5g** were bought from Aldrich. Other olefins were synthesized from commercially available compounds by Wittig reaction, esterification, C-O coupling, amide synthesis etc following literature procedure. For column chromatography, silica gel (60–120 mesh or 100–200 mesh) obtained from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel 60F₂₅₄).
Analytical Information. All compounds are characterized by ¹H NMR, ¹³C NMR spectroscopy, Gas chromatography mass spectra (GC–MS) and HRMS. Copies of the ¹H NMR, ¹³C NMR can be found in the Supporting Information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. All ¹H NMR experiments are reported

in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuteriochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^1H decoupling. All GC analyses were performed on a Agilent 7890A GC system with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.) using *n*-decane as the internal standard. All GC-MS analyses were done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector). High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer. XPS measurements were performed on a V.G. Microtech Unit ESCA 3000 Spectrometer. Melting point of the compounds was determined using a Buchi B-545 melting point apparatus.

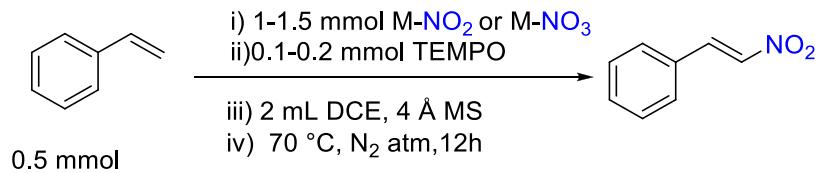
Description of Reaction Tube :



Fig. S1. Pictorial description of reaction tube for nitration of olefin: Fisherbrand Disposable Borosilicate Glass Tubes (16*125 MM) with Threaded End (Fisher Scientific Order No. 1495935A) [left]; Kimble Black Phenolic Screw Thread Closures with Open Tops (Fisher Scientific Order No. 033407E) [middle]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [right].

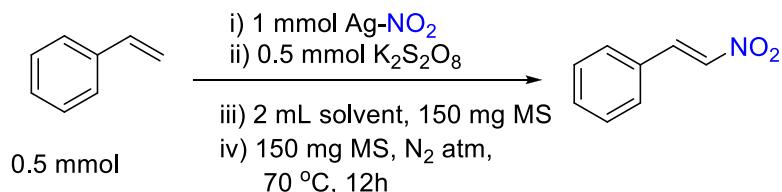
Optimization details for nitration of olefins:

Table S1: Optimization by varying different nitrating agent.



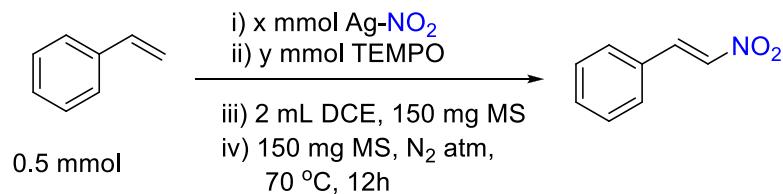
| Entry | Nitrating Agents | TEMPO (mmol) | GC Yield (%) |
|-------|--|--------------|--------------|
| 1 | AgNO_2 | 0.2 | 99 |
| 2 | AgNO_2 | 0.1 | 92 |
| 3 | $\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ | 0.1 | 78 |
| 4 | $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ | 0.1 | 74 |
| 5 | $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 0.1 | 37 |
| 6 | $\text{Na}_3\text{Co}(\text{NO}_2)_6$ | 0.1 | 22 |
| 7 | NaNO_2 | 0.1 | 0 |
| 8 | AgNO_3 | 0.1 | 0 |
| 9 | $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 0.1 | 0 |

Table S2: Optimization by varying different Solvents.



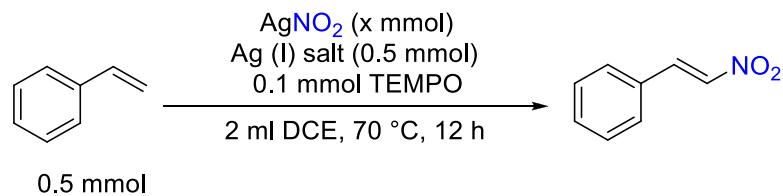
| Entry | Solvents | GC Yield (%) |
|-------|------------------|--------------|
| 1 | DCE | 46 |
| 2 | Benzene | 45 |
| 3 | DCM | 44 |
| 4 | DMSO | 43 |
| 5 | Acetonitrile | 33 |
| 6 | CHCl_3 | 29 |
| 7 | Dioxane | 12 |
| 8 | <i>p</i> -Xylene | 20 |
| 9 | <i>o</i> -Xylene | 19 |
| 10 | THF | 6 |
| 11 | DMF | 5 |
| 12 | Toluene | 15 |
| 13 | Cyclohexane | 11 |

Table S3: Optimization by varying amount of AgNO_2 and TEMPO.



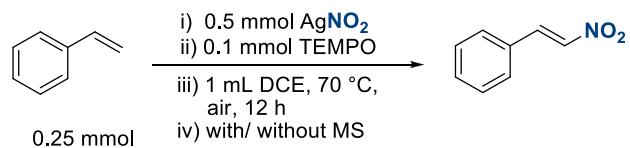
| Entry | AgNO_2 (mmol) | $\text{K}_2\text{S}_2\text{O}_8$ (mmol) | TEMPO (mmol) | GC Yield (%) |
|-------|------------------------|---|--------------|--------------|
| 1 | 1.0 | 0.5 | 0.2 | 82 |
| 2 | 1.0 | - | 0.2 | 85 |
| 3 | 1.0 | 0.5 | 0.1 | 78 |
| 4 | 1.0 | - | 0.1 | 92 |
| 5 | 1.5 | - | 0.1 | 85 |
| 6 | 1.5 | - | 0.2 | 99 |

Table S4: Screening of Ag(I) salts as oxidizing agent



| Entry | AgNO_2 (mmol) | Ag (I) salt (mmol) | Conv. | GC Yield (%) |
|-------|------------------------|--------------------------|-------|--------------|
| 1 | 1.0 | - | 99 | 93 |
| 2 | 0.5 | - | 91 | 72 |
| 3 | 0.5 | AgOAc | 94 | 89 |
| 4 | 0.5 | AgNO_3 | 98 | 91 |
| 5 | 0.5 | Ag_2CO_3 | 97 | 92 |
| 6 | 0.5 | Ag_2O | 96 | 89 |

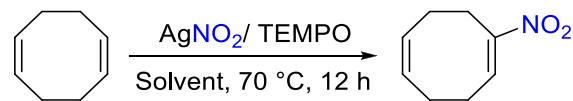
Table S5: Comparative experiments with/ without MS



| Entry | Without MS | With MS |
|-------|------------|---------|
| 1 | 80% | 83% |
| 2 | 78% | 82% |

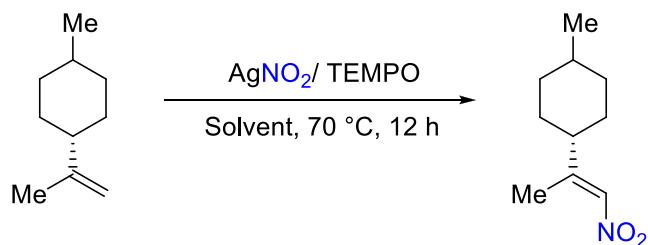
Optimization of aliphatic substrates:

Table S6: Optimization of COD by varying AgNO₂, TEMPO and Solvent



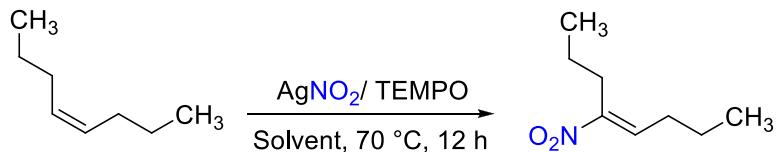
| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | Solvent | Conv. | GC Yield (%) |
|-------|--------------------------|--------------|-------------------|-------|----------------|
| 1 | 0.3 | 0.04 | Dioxane | 99 | 35 |
| 2 | 0.3 | 0.04 | EtOAc | 99 | 31 |
| 3 | 0.3 | 0.04 | CHCl ₃ | 82 | 79 |
| 4 | 0.3 | 0.04 | DCE | 97 | 45 |
| 5 | 1.5 | 0.2 | DCE | 97 | 52 |
| 6 | 2.0 | 0.2 | DCE | 96 | 56 |
| 7 | 1.5 | 1.0 | DCE | 78 | 43 |
| 8 | 2.0 | 1.0 | DCE | 78 | 20 |

Table S7: Optimization of Limonene by varying AgNO₂, TEMPO

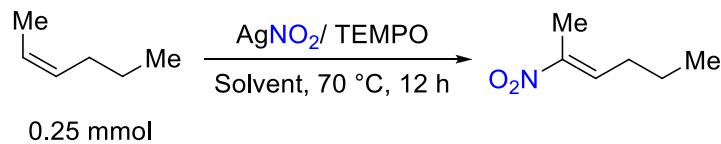


| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | Conv. | GC Yield (%) |
|-------|--------------------------|--------------|-------|----------------|
| 1 | 1.5 | 0.2 | 99 | 75 |
| 2 | 2.0 | 0.2 | 99 | 75 |
| 3 | 1.5 | 1.0 | - | 23 |
| 4 | 2.0 | 1.0 | - | 22 |

Table S8: Optimization of trans-4-octene by varying Solvent



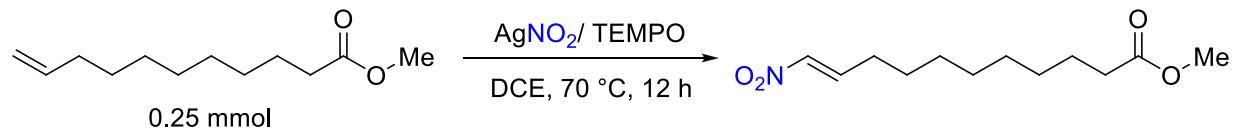
| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | Solvent | Conv. | GC Yield (%) |
|-------|--------------------------|--------------|-------------------|-------|----------------|
| 1 | 0.3 | 0.04 | Dioxane | 76 | 58 |
| 2 | 0.3 | 0.04 | EtOAc | 61 | 52 |
| 3 | 0.3 | 0.04 | CHCl ₃ | 66 | 42 |
| 4 | 0.3 | 0.04 | DCE | 97 | 58 |

Table S9: Optimization of cis-2-hexene by varying Solvent

| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | Solvent | GC Yield (%) |
|-------|--------------------------|--------------|--------------------|----------------|
| 1 | 0.75 | 0.1 | DCE | 44 |
| 2 | 1.0 | 0.1 | DCE | 56 |
| 3 | 0.75 | 0.5 | DCE | 58 |
| 4 | 1.0 | 0.5 | DCE | 74 |
| 5 | 0.75 | 0.1 | CH ₃ CN | 9 |
| 6 | 0.75 | 0.1 | CHCl ₃ | 82 |
| 7 | 0.75 | 0.1 | Dioxane | 65 |
| 8 | 0.75 | 0.1 | EtOAc | 60 |

Table S10: Optimization of 10-bromo-1-decene by varying reagents

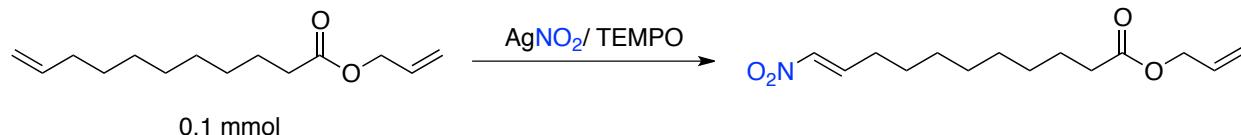
| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | Conv. | GC Yield (%) |
|-------|--------------------------|--------------|-------|----------------|
| 1 | 0.75 | 0.1 | | 55 |
| 2 | 1.0 | 0.1 | | 77 |
| 3 | 0.75 | 0.5 | | 41 |
| 8 | 0.75 | 0.5 | | 73 |

Table S11: Optimization of methyl-10-undecenoate by varying reagents

| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | GC Yield (%) |
|-------|--------------------------|--------------|----------------|
| 1 | 0.5 | 0.1 | 45 |
| 2 | 0.75 | 0.1 | 60 |

| | | | |
|----|------|------|----|
| 3 | 1.0 | 0.1 | 85 |
| 4 | 1.5 | 0.1 | 75 |
| 5 | 2.0 | 0.1 | 4 |
| 6 | 0.75 | 0.05 | 44 |
| 7 | 0.75 | 0.1 | 60 |
| 8 | 0.75 | 0.2 | 45 |
| 9 | 0.75 | 0.5 | 67 |
| 10 | 0.75 | 1.0 | 61 |
| 11 | 0.75 | 2.0 | 52 |

Table S12: Optimization of methyl-10-undecenoate by varying reagents



| Entry | AgNO ₂ (mmol) | TEMPO (mmol) | Solvent | GC Yield (%) |
|-------|--------------------------|--------------|-------------------|----------------|
| 1 | 0.2 | 0.04 | DCE | 45 |
| 2 | 0.3 | 0.04 | DCE | 51 |
| 3 | 0.4 | 0.04 | DCE | 43 |
| 4 | 0.3 | 0.08 | DCE | 37 |
| 5 | 0.3 | 0.04 | CHCl ₃ | 55 |

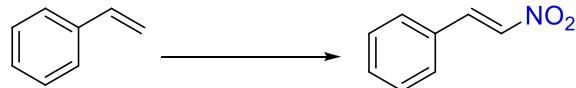
General Procedure A for nitration of olefins with AgNO₂ and TEMPO using DCE as the solvent

To an oven-dried screw cap test tube charged with a magnetic stir-bar was added AgNO₂ (3 equiv.), TEMPO (0.4 equiv.), olefin and oven-dried molecular sieves (4 Å, 150 mg). The olefin (if it was liquid) and solvent (DCE, 2 mL) were added by microliter syringe and laboratory syringe respectively. The tube was placed in a preheated oil bath at 70 °C and the reaction mixture was stirred vigorously for 12h. Then the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a celite bed filter with ethyl acetate as the washing solvent. Finally organic extract was concentrated and was purified by column chromatography using silica gel (60-120/100-200 mesh size) and PET-ether / ethyl acetate as the eluent. All the reactions were carried out for 12 h unless otherwise stated and in no condition nitration of second or less reactive olefin has been observed.

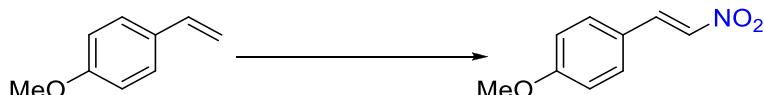
General Procedure B for synthesis of olefins from corresponding aldehydes and ketones by Wittig reaction

To an oven-dried two neck round bottom flask (100 mL) charged with a magnetic stir-bar was added Wittig salt (methyl)triphenylphosphonium iodide (3 mmol, approximately 1200 mg). Then the RB flask was fitted with a reflux condenser which was attached with a nitrogen balloon through a two way glass take-off. Under nitrogen atmosphere, 15-20 mL solvent (dry benzene) was added with a laboratory syringe and the system was kept in ice bath. Approximately, 700-800 mg of potassium *tert*-butoxide was added quickly and the system was allowed to come to room temperature and was refluxed for one hour. Formation of the ylide can be visibly observed by its persistent yellow color. After refluxing, the system was again allowed to come to room temperature and kept in an ice bath, followed by drop wise addition of the substrate dissolved in dry benzene. Then the system was kept in room temperature for 4-6 hours, and progress of the reaction was monitored by TLC and GC-MS analysis. Upon completion, the reaction was quenched by saturated solution of ammonium chloride and the organic layer was extracted with ethyl acetate several times. The organic layer was dried over oven-dried anhydrous sodium sulfate and evaporated under reduced pressure. The crude reaction mixture was purified with silica gel column chromatography (60-120 mesh) with PET-ether/ethyl acetate as the eluent.

Characteristic Data of Synthesized Nitroolefins:

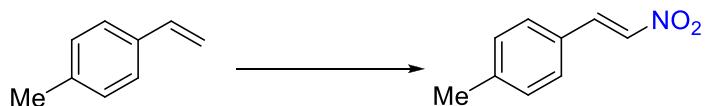


(E)-β-Nitrostyrene.¹ Nitration was done by general procedure A with styrene (0.5 mmol, 57 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); crystalline yellow solid; isolated yield: 95% (71 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 7.41 – 7.48 (m, 2H), 7.48 – 7.52 (m, 1H), 7.52 – 7.56 (m, 2H), 7.56 – 7.64 (dd, J = 13.7, 1.1 Hz, 1H), 7.95 – 8.05 (dd, J = 13.7, 1.8 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 129.29, 129.53, 130.17, 132.30, 137.22, 139.23. GC-MS (m/z): 149.1 [M]⁺. m. p. 57–58 °C.

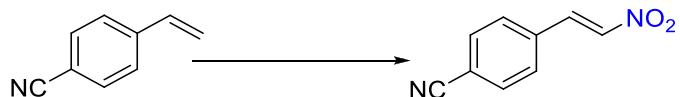


(E)-1-methoxy-4-(2-nitroviny)benzene (Scheme 4, 4a).² Nitration was done by general procedure A with 4-methoxystyrene (0.5 mmol, 67 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); crystalline yellow solid; isolated yield: 85% (76 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 3.52 – 4.21 (s, 3H), 6.83 – 7.00 (d, J = 8.8 Hz, 2H), 7.43 –

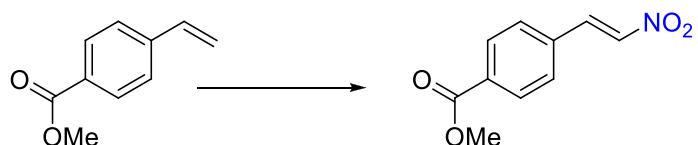
7.47 (d, $J = 2.0$ Hz, 1H), 7.47 – 7.50 (m, 1H), 7.50 – 7.54 (s, 1H), 7.85 – 8.01 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 55.59, 114.97, 122.54, 131.28, 135.00, 139.13, 163.02. GC-MS (m/z): 179.1 [M] $^+$.



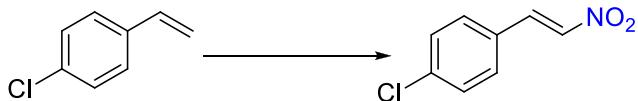
(E)-1-methyl-4-(2-nitrovinyl)benzene (Scheme 4, 4b).² Nitration was done by general procedure A with 4-methylstyrene (0.5 mmol, 66 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); yellow solid; isolated yield: 96% (78 mg). ^1H NMR (400 MHz, Chloroform-d) δ 2.32 – 2.56 (s, 3H), 7.17 – 7.37 (m, 2H), 7.37 – 7.52 (m, 2H), 7.52 – 7.68 (d, $J = 13.7$ Hz, 1H), 7.92 – 8.07 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 21.84, 127.41, 129.36, 130.30, 136.41, 139.35, 143.29. GC-MS (m/z): 163.1 [M] $^+$. m. p. 106–107 °C.



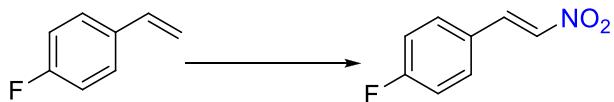
(E)-4-(2-nitrovinyl)benzonitrile (Scheme 4, 4c).³ Nitration was done by general procedure A with 4-vinylbenzonitrile (0.5 mmol, 65 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (10:90 v/v); light yellow solid; isolated yield: 81% (71 mg). ^1H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.65 (d, $J = 13.8$ Hz, 1H), 7.65 – 7.71 (m, 2H), 7.71 – 7.81 (m, 2H), 7.95 – 8.05 (d, $J = 13.7$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 115.38, 118.00, 129.59, 133.21, 134.52, 136.77, 139.63. GC-MS (m/z): 174.1 [M] $^+$. m. p. 186–187 °C.



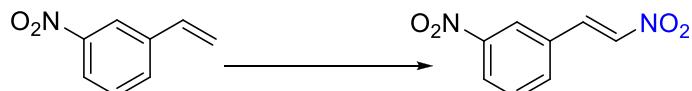
(E)-methyl 4-(2-nitrovinyl)benzoate (Scheme 4, 4d).⁴ Nitration was done by general procedure A with methyl 4-vinylbenzoate (0.5 mmol, 66 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (5:95 v/v); yellow solid; isolated yield: 86% (89 mg). ^1H NMR (400 MHz, Chloroform-d) δ 3.30 – 4.47 (s, 3H), 7.60 – 7.62 (s, 1H), 7.62 – 7.65 (m, 2H), 7.97 – 8.06 (d, $J = 13.7$ Hz, 1H), 8.06 – 8.14 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 52.71, 129.16, 130.64, 133.19, 134.35, 137.77, 138.85, 166.17. GC-MS (m/z): 207.1 [M] $^+$. m. p. 176–178 °C.



(E)-1-chloro-4-(2-nitrovinyl)benzene (Scheme 4, 4e).² Nitration was done by general procedure A with 1-chloro-4-vinylbenzene (0.5 mmol, 63 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); crystalline light yellowish solid; isolated yield: 97% (89 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 7.38 – 7.45 (m, 2H), 7.45 – 7.53 (m, 2H), 7.53 – 7.64 (d, J = 13.7 Hz, 1H), 7.90 – 8.01 (d, J = 13.7 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 128.65, 129.87, 130.42, 137.53, 137.85, 138.43, 77.51, 77.20, 76.88. GC-MS (m/z): 183.1 [M] $^+$. m. p. 113–114 °C.



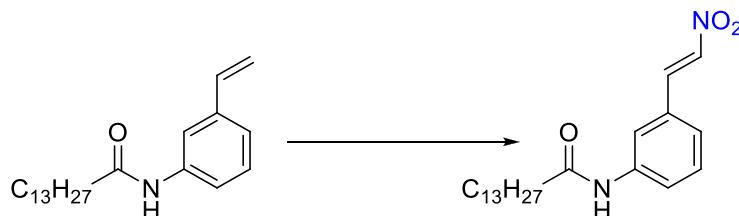
(E)-1-fluoro-4-(2-nitrovinyl)benzene (Scheme 4, 4f).² Nitration was done by general procedure A with 1-fluoro-4-vinylbenzene (0.5 mmol, 65 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); light yellow solid; isolated yield: 95% (79 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 7.09 – 7.21 (m, 2H), 7.51 – 7.55 (m, 1H), 7.55 – 7.60 (m, 2H), 7.88 – 8.22 (d, J = 13.7 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 116.90, 117.12, 131.53, 137.04, 138.04, 166.41. GC-MS (m/z): 167.1 [M] $^+$. m. p. 102–103 °C.



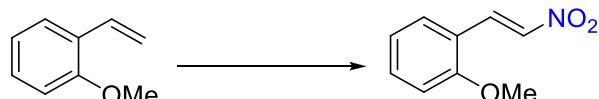
(E)-1-nitro-3-(2-nitrovinyl)benzene (Scheme 4, 4g).⁵ Nitration was done by general procedure A with 1-nitro-3-vinylbenzene (0.5 mmol, 70 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (3:97 v/v); isolated yield: 88% (86 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 7.65 – 7.70 (m, 1H), 7.70 – 7.72 (d, J = 3.4 Hz, 1H), 7.85 – 7.93 (dt, J = 7.9, 1.4, 1.4 Hz, 1H), 7.98 – 8.13 (d, J = 13.7 Hz, 1H), 8.30 – 8.39 (ddd, J = 8.2, 2.2, 1.0 Hz, 1H), 8.39 – 8.47 (dt, J = 2.2, 1.1, 1.1 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 123.65, 126.36, 130.79, 131.96, 134.67, 136.46, 139.42, 148.92. GC-MS (m/z): 194.1 [M] $^+$. m. p. 125–126 °C.



(E)-3-(2-nitroviny)benzaldehyde (Scheme 4, 4h). Nitration was done by general procedure A with 3-vinylbenzaldehyde (0.5 mmol, 64 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (10:90 v/v); light yellow solid; isolated yield: 82% (73 mg). ^1H NMR (400 MHz, Chloroform-d) δ 7.67 (m, 1H), 7.70–7.71 (d, J = 4 Hz 1H), 7.83 (dt, J = 8.0, 4 Hz, 1H), 7.87 – 7.95 (dt, J = 8.0, 4 Hz, 1H), 8.09 (d, J = 12 Hz, 1H), 10.08 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 129.73, 130.39, 131.26, 133.01, 134.54, 137.31, 137.60, 138.54, 191.26. GC-MS (m/z): 177.1 [M] $^+$. m. p. 91–92 $^{\circ}\text{C}$.

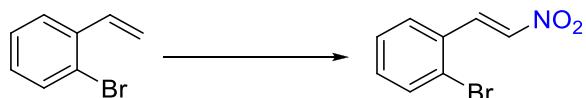


(E)-N-(3-(2-nitroviny)phenyl)tetradecanamide (Scheme 4, 4i). Nitration was done by general procedure A with *N*-(3-vinylphenyl)tetradecanamide (0.25 mmol, 80 mg), 4.8 equiv AgNO_2 and 0.6 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (20:80 v/v); crystalline light creamy solid; isolated yield: 75% (70 mg). ^1H NMR (400 MHz, Chloroform-d) δ 0.80 – 0.95 (m, 3H), 1.07 – 1.54 (s, 20H), 1.68 – 1.80 (p, J = 7.6, 7.6, 7.5, 7.5 Hz, 2H), 2.31 – 2.44 (m, 2H), 7.27 – 7.29 (t, J = 1.3, 1.3 Hz, 1H), 7.30 – 7.34 (s, 1H), 7.35 – 7.43 (t, J = 7.9, 7.9 Hz, 1H), 7.46 – 7.54 (dd, J = 2.2, 1.1 Hz, 1H), 7.55 – 7.63 (d, J = 13.7 Hz, 1H), 7.91 – 8.00 (d, J = 13.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 14.34, 22.90, 25.71, 29.47, 29.57, 29.59, 29.69, 29.83, 29.86, 29.89, 32.13, 37.99, 119.93, 123.16, 125.12, 130.14, 131.12, 137.76, 138.96, 139.21, 172.03. HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{35}\text{N}_2\text{O}_3$: 375.2648, found: 375.2630. m. p. 121–122 $^{\circ}\text{C}$.

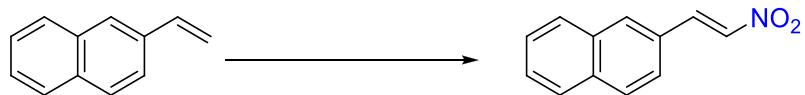


(E)-1-methoxy-2-(2-nitroviny)benzene (Scheme 4, 4j).² Nitration was done by general procedure A with 2-methoxystyrene (0.5 mmol, 66 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (3:97 v/v); yellow solid; isolated yield: 85% (76 mg). ^1H NMR (400 MHz, Chloroform-d) δ 3.47 – 4.33 (s, 3H), 6.88 – 7.09 (m, 2H), 7.36 – 7.53 (m, 2H), 7.77 –

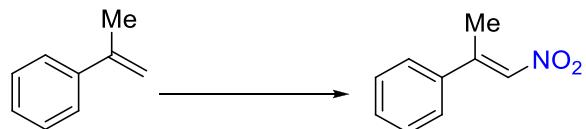
7.99 (d, $J = 13.6$ Hz, 1H), 8.07 – 8.19 (d, $J = 13.5$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 55.75, 111.47, 119.18, 121.20, 132.60, 133.61, 135.65, 138.32, 159.60. GC-MS (m/z): 179.1 [M] $^+$. m. p. 84 °C.



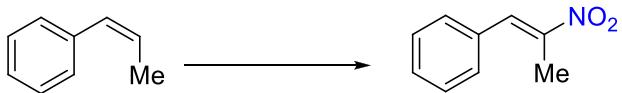
(E)-1-bromo-2-(2-nitrovinyl)benzene (Scheme 4, 4k).⁶ Nitration was done by general procedure A with 1-bromo-2-vinylbenzene (0.5 mmol, 65 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (3:97 v/v); crystalline light yellowish solid; isolated yield: 92% (104 mg). ^1H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.45 (m, 2H), 7.50 – 7.56 (d, $J = 13.6$ Hz, 1H), 7.56 – 7.60 (m, 1H), 7.63 – 7.75 (m, 1H), 8.33 – 8.45 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 126.53, 128.27, 128.63, 130.43, 133.15, 134.16, 137.78, 138.95. GC-MS (m/z): 228.1 [M] $^+$. m. p. 88–89 °C.



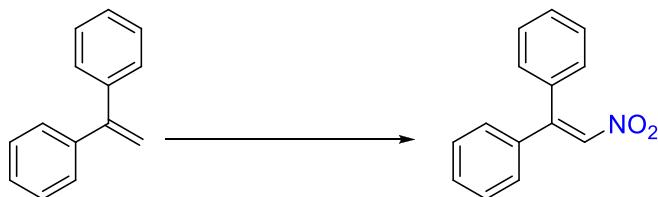
(E)-2-(2-nitrovinyl)naphthalene (Scheme 4, 4l).⁷ Nitration was done by general procedure A with 2-vinylnaphthalene (0.5 mmol, 77 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (3:97 v/v); yellowish solid; isolated yield: 88% (88 mg). ^1H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.63 (tdd, $J = 11.1, 11.1, 6.4, 1.7$ Hz, 3H), 7.63 – 7.76 (dd, $J = 13.6, 4.0$ Hz, 1H), 7.76 – 7.92 (m, 3H), 7.92 – 8.04 (d, $J = 6.6$ Hz, 1H), 8.04 – 8.18 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 76.91, 77.23, 77.54, 123.41, 127.40, 127.62, 128.06, 128.53, 128.96, 129.45, 132.45, 133.22, 135.00, 137.19, 139.35. GC-MS (m/z): 199.1 [M] $^+$. m. p. 128–130 °C.



(E)-(1-nitroprop-1-en-2-yl)benzene (Scheme 4, 4m).⁸ Nitration was done by general procedure A with prop-1-en-2-ylbenzene (0.5 mmol, 65 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); yellow solid; isolated yield: 84% (69 mg). ^1H NMR (400 MHz, Chloroform-d) δ 2.29 – 3.07 (d, $J = 1.5$ Hz, 3H), 7.29 – 7.33 (q, $J = 1.4, 1.4, 1.4$ Hz, 1H), 7.41 – 7.49 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-d) δ 18.77, 127.00, 129.19, 130.55, 136.47, 138.43, 150.19. GC-MS (m/z): 163.1 [M] $^+$.



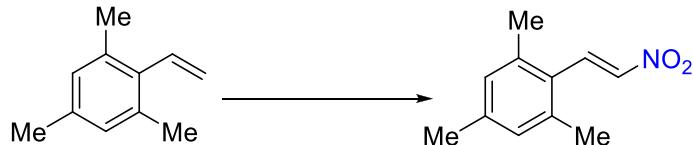
(Z)-(2-nitroprop-1-enyl)benzene (Scheme 4, 4n).⁸ Nitration was done by general procedure A with (Z)-prop-1-enylbenzene (0.5 mmol, 65 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (3:97 v/v); yellow liquid; isolated yield: 66% (54 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 2.42 – 2.51 (d, J = 1.1 Hz, 3H), 7.37 – 7.52 (m, 5H), 8.05 – 8.15 (m, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 14.25, 128.16, 129.10, 130.12, 132.61, 133.76, 147.94. GC-MS (m/z): 163.1 [M]⁺. HRMS (ESI): calcd. for $\text{C}_9\text{H}_{10}\text{NO}_2$: 164.0712, found: 164.0713.



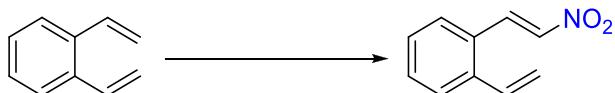
(2-nitroethene-1,1-diyldibenzene (Scheme 4, 4o).¹ Nitration was done by general procedure A with ethene-1,1-diyldibenzene as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); yellow liquid; isolated yield: 85% (95 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 7.19 – 7.25 (m, 2H), 7.27 – 7.32 (m, 2H), 7.36 – 7.40 (m, 1H), 7.40 – 7.50 (m, 6H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 128.68, 128.98, 129.06, 129.10, 129.50, 131.09, 134.57, 135.71, 137.26, 150.68. GC-MS (m/z): 225.1 [M]⁺.



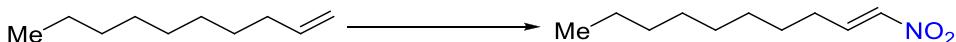
(E)-5-nitro-6-(2-nitrovinyl)benzo[d][1,3]dioxole (Scheme 4, 4p).⁹ Nitration was done by general procedure A with 5-nitro-6-vinylbenzo[d][1,3]dioxole (0.5 mmol, 96 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (30:70 v/v); yellowish solid; isolated yield: 70% (83 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 6.15 – 6.30 (s, 2H), 6.88 – 6.98 (s, 1H), 7.31 – 7.43 (d, J = 13.4 Hz, 1H), 7.61 – 7.69 (s, 1H), 8.41 – 8.63 (d, J = 13.4 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 104.13, 106.61, 107.79, 122.51, 135.90, 139.41, 143.75, 150.56, 152.59. GC-MS (m/z): 238.1 [M]⁺. m. p. 110–111 °C. HRMS (ESI): calcd. for $\text{C}_9\text{H}_7\text{N}_2\text{O}_6$: 239.0304, found: 239.0307.



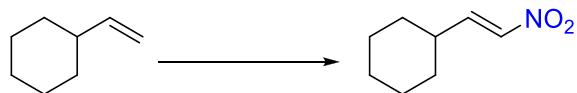
(E)-1,3,5-trimethyl-2-(2-nitroviny)benzene (Scheme 4, 4q). Nitration was done by general procedure A with 1,3,5-trimethyl-2-vinylbenzene (0.5 mmol, 80 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether; yellowish solid; isolated yield: 93% (89 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 2.25 – 2.35 (s, 3H), 2.35 – 2.47 (s, 6H), 6.83 – 7.06 (s, 2H), 7.28 – 7.39 (d, J = 13.9 Hz, 1H), 8.22 – 8.35 (d, J = 13.9 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 21.42, 21.75, 125.95, 130.09, 136.79, 138.67, 139.88, 141.07. GC-MS (m/z): 191.1 [M] $^+$. m. p. 123–124 $^{\circ}\text{C}$.



(E)-1-(2-nitroviny)-2-vinylbenzene (Scheme 4, 4r). Nitration was done by general procedure A with 1,2-divinylbenzene (0.23 mmol, 30 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; yellowish oil; isolated yield: 70% (30 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 5.48 – 5.58 (dd, J = 11.0, 1.0 Hz, 1H), 5.62 – 5.71 (dd, J = 17.3, 1.0 Hz, 1H), 6.98 – 7.07 (dd, J = 17.3, 11.0 Hz, 1H), 7.30 – 7.40 (td, J = 7.5, 7.5, 1.4 Hz, 1H), 7.42 – 7.59 (m, 4H), 8.28 – 8.42 (d, J = 13.5 Hz, 1H). GC-MS (m/z): 175.1 [M] $^+$.



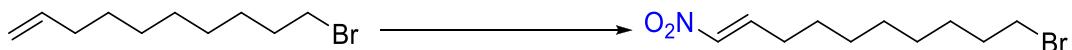
(E)-1-nitrodec-1-ene (Scheme 5, 5a).¹⁰ Nitration was done by general procedure A with dec-1-ene (0.5 mmol, 94 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); reddish orange liquid; isolated yield: 95% (88 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 0.81 – 0.95 (h, J = 3.5, 3.5, 3.5, 3.4, 3.4 Hz, 5H), 1.20 – 1.39 (m, 8H), 1.46 – 1.60 (dq, J = 14.9, 7.5, 7.2, 7.2 Hz, 2H), 2.22 – 2.31 (qd, J = 7.6, 7.6, 7.5, 1.6 Hz, 2H), 6.94 – 7.02 (dt, J = 13.4, 1.6, 1.6 Hz, 1H), 7.22 – 7.34 (m, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 14.24, 22.79, 27.87, 28.62, 29.25, 29.37, 31.94, 139.68, 143.04. HRMS (ESI): calcd. for $\text{C}_{10}\text{H}_{20}\text{NO}_2$: 186.1494, found: 186.1501.



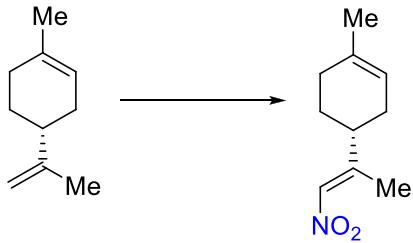
(E)-(2-nitrovinyl)cyclohexane (Scheme 5, 5b).² Nitration was done by general procedure A with vinylcyclohexane (0.5 mmol, 68 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether; orange liquid; isolated yield: 90% (70 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 1.1–1.3 (m, 6H), 1.74–1.83 (m, 4H), 2.2–2.3 (m, 1H), 6.89 – 6.94 (m, 1H), 7.20 (m, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 25.59, 25.75, 31.56, 37.70, 138.39, 147.49.



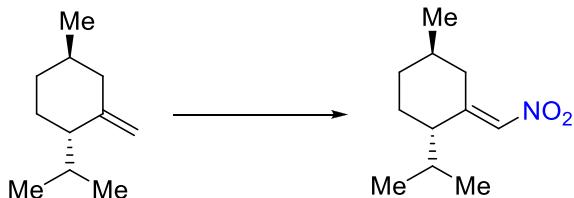
(E)-methyl 11-nitoundec-10-enoate (Scheme 5, 5c). Nitration was done by general procedure A using 4 equiv. AgNO_2 with methyl undec-10-enoate (0.5 mmol, 112 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); orange liquid; isolated yield: 80% (97 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 1.22 – 1.42 (m, 14H), 1.57 – 1.75 (m, 4H), 2.11 – 2.47 (m, 5H), 2.49 – 2.67 (m, 1H), 3.57 – 3.79 (s, 3H), 6.87 – 7.14 (dt, J = 13.4, 1.5, 1.5 Hz, 1H), 7.14 – 7.38 (dt, J = 13.3, 7.4, 7.4 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 24.83, 27.06, 27.66, 28.39, 28.78, 28.99, 30.04, 33.98, 51.42, 116.84, 139.56, 142.75, 174.20. GC-MS (m/z): 212.1 [M]⁺. From GC-MS analysis of reaction mixture, it was observed that 20% starting material left unreacted.



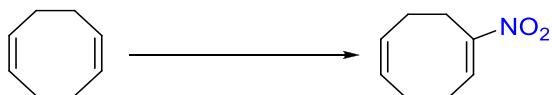
(E)-10-bromo-1-nitrodec-1-ene (Scheme 5, 5d). Nitration was done by General Procedure A using 4 equiv. AgNO_2 with 10-bromo dec-1-ene (0.5 mmol, 100 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (5:95 v/v); yellow liquid; isolated yield: 75% (99 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 1.37 – 1.46 (s, 4H), 1.58 – 1.62 (s, 4H), 1.78 – 1.89 (m, 5H), 2.23 – 2.30 (qd, J = 7.5, 7.5, 7.4, 1.6 Hz, 2H), 3.37 – 3.44 (t, J = 6.8, 6.8 Hz, 2H), 6.90 – 7.05 (dt, J = 13.4, 1.6, 1.6 Hz, 1H), 7.14 – 7.39 (dt, J = 13.4, 7.4, 7.4 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 27.86, 28.24, 28.62, 28.75, 29.16, 29.25, 32.89, 34.15, 139.77, 142.93.



(R,E)-1-methyl-4-(1-nitroprop-1-en-2-yl)cyclohex-1-ene (Scheme 5, 5e). Nitration was done by general procedure A with ((R)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene (0.5 mmol, 85 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); light yellowish liquid; isolated yield: 69% (62 mg). $^1\text{H NMR}$ (400 MHz, Chloroform-d) δ 1.63 – 1.68 (tq, J = 1.7, 1.7, 1.0, 0.9, 0.9 Hz, 5H), 1.69 – 1.76 (m, 1H), 1.82 – 1.86 (d, J = 1.4 Hz, 1H), 1.90 – 2.17 (m, 3H), 2.20 – 2.24 (d, J = 1.4 Hz, 3H), 5.36 – 5.43 (dtd, J = 4.8, 2.4, 2.4, 1.3 Hz, 1H), 6.95 – 6.98 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-d) δ 17.21, 23.54, 27.01, 29.95, 30.02, 42.24, 119.35, 134.30, 135.16, 157.27. HRMS (ESI): calcd. for $\text{C}_{10}\text{H}_{16}\text{NO}_2$: 182.1181, found: 182.1173.

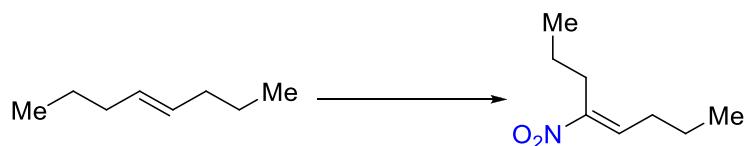


(1S,4R,E)-1-isopropyl-4-methyl-2-(nitromethylene)cyclohexane (Scheme 5, 5f). Nitration was done by general procedure A with (1S,4R)-1-isopropyl-4-methyl-2-methylenecyclohexane (0.5 mmol, 76 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); light yellowish liquid; isolated yield: 35% (30 mg). $^1\text{H NMR}$ (400 MHz, Chloroform-d) δ 0.74 – 1.12 (m, 9H), 1.13 – 2.23 (m, 7H), 2.45 – 2.63 (dd, J = 13.1, 7.3 Hz, 1H), 2.77 – 3.08 (ddt, J = 13.0, 4.7, 0.9, 0.9 Hz, 1H), 6.82 – 7.00 (q, J = 1.0, 1.0, 1.0 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-d) δ 19.83, 20.29, 21.86, 27.20, 27.49, 30.79, 33.58, 34.75, 50.66, 123.22, 133.93, 157.26. HRMS (ESI): calcd. for $\text{C}_{11}\text{H}_{20}\text{NO}_2$: 198.1494, found: 198.1503.



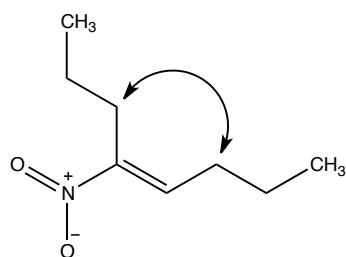
(1E,5Z)-1-nitrocycloocta-1,5-diene (Scheme 5, 5g). Nitration was done by general procedure A using CHCl_3 as the solvent with (1Z,5Z)-cycloocta-1,5-diene (0.5 mmol, 54 μ L) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh

60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); reddish orange liquid; isolated yield: 76% (58 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 2.40 – 2.55 (dtdd, J = 12.2, 6.1, 6.1, 3.0, 1.2 Hz, 4H), 2.55 – 2.68 (q, J = 6.4, 6.3, 6.3 Hz, 2H), 2.95 – 3.10 (m, 2H), 5.47 – 5.63 (m, 2H), 7.29 – 7.40 (t, J = 6.3, 6.3 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 25.81, 26.47, 26.86, 27.23, 127.83, 128.78, 135.41, 151.68. HRMS (ESI): calcd. for $\text{C}_8\text{H}_{12}\text{NO}_2$: 154.0868, found: 154.0867.

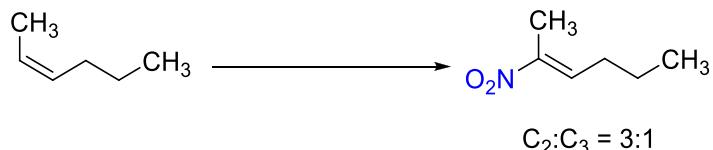


(E)-4-nitrooct-4-ene (Scheme 5, 5h).¹¹ Nitration was done by general procedure A with trans-4-octene (0.5 mmol, 56 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: petroleum ether; yellowish liquid; isolated yield: 51% (40 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 0.75 – 1.04 (m, 7H), 1.43 – 1.65 (ddt, J = 14.7, 7.3, 3.5, 3.5 Hz, 3H), 2.13 – 2.29 (q, J = 7.6, 7.6, 7.6 Hz, 2H), 2.44 – 2.66 (m, 2H), 7.00 – 7.18 (t, J = 7.9, 7.9 Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-d) δ 13.78, 13.99, 14.27, 21.39, 22.04, 22.84, 28.35, 30.13, 31.78, 136.55, 151.90. HRMS (ESI): calcd. for $\text{C}_8\text{H}_{15}\text{NO}_2\text{Na}$: 180.1000, found: 180.0999.

E-stereochemistry is determined based upon NOESY correlations between CH_2 -3 and CH_2 -6.

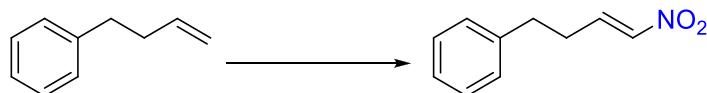


Selective NOESY correlation of **5h**.

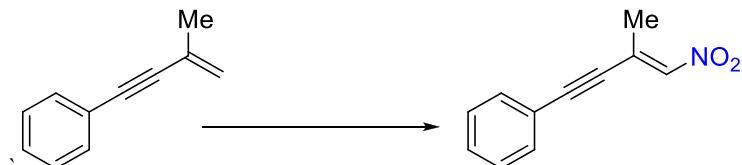


(E)-2-nitrohex-2-ene (Scheme 5, 5i). Nitration was done by general procedure A using CHCl_3 as the solvent with cis-2-hexene (0.5 mmol, 63 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: petroleum ether; light yellowish liquid; isolated yield (mixture of regioisomers): 76% (50 mg). **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 0.78 – 0.90 (m, 3H), 0.90 – 1.01 (dt, J = 10.3, 7.4, 7.4 Hz,

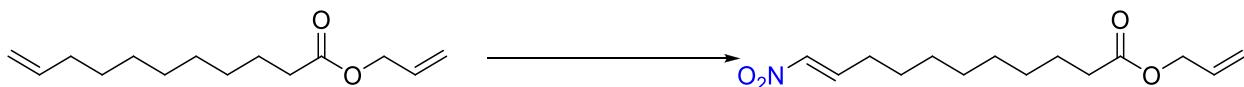
3H), 1.16 – 1.36 (m, 3H), 1.46 – 1.60 (h, J = 7.3, 7.3, 7.3, 7.3, 7.3 Hz, 2H), 1.84 – 1.92 (d, J = 7.4 Hz, 1H), 2.12 – 2.17 (d, J = 1.2 Hz, 2H), 2.17 – 2.25 (q, J = 7.8, 7.5, 7.5 Hz, 1H), 2.52 – 2.62 (t, J = 7.5, 7.5 Hz, 1H), 7.08 – 7.15 (td, J = 7.9, 7.9, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 12.69, 13.74, 13.96, 14.31, 21.17, 21.85, 22.85, 25.46, 27.09, 28.01, 30.23, 31.78, 34.84, 131.84, 132.31, 136.42, 137.44.



(E)-(4-nitrobut-3-enyl)benzene (Scheme 5, 5j).⁷ Nitration was done by general procedure A with but-3-enylbenzene (0.5 mmol, 66 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/petroleum ether (1:99 v/v); dark reddish orange liquid; isolated yield: 53% (47 mg). ^1H NMR (400 MHz, Chloroform-d) δ 2.45 – 2.55 (qd, J = 7.5, 7.2, 7.2, 1.6 Hz, 2H), 2.70 – 2.78 (t, J = 7.5, 7.5 Hz, 2H), 6.79 – 6.96 (dt, J = 13.4, 1.6, 1.6 Hz, 1H), 7.08 – 7.13 (m, 2H), 7.13 – 7.20 (m, 2H), 7.20 – 7.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 30.13, 33.93, 126.63, 128.35, 128.74, 139.68, 139.99, 141.56. GC-MS (m/z): 177.1 [M]⁺.

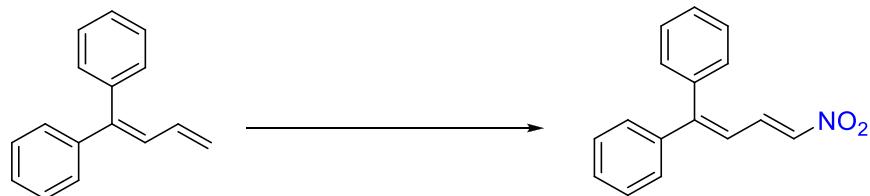


(E)-(3-methyl-4-nitrobut-3-en-1-ynyl)benzene (Scheme 5, 5k). Nitration was done by general procedure A with (3-methylbut-3-en-1-ynyl)benzene (0.35 mmol, 50 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: petroleum ether; orange-yellow liquid; isolated yield: 30% (20 mg). ^1H NMR (400 MHz, Chloroform-d) δ 2.35 – 2.73 (d, J = 1.6 Hz, 3H), 7.32 – 7.34 (q, J = 1.6, 1.5, 1.5 Hz, 1H), 7.35 – 7.45 (m, 3H), 7.46 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 20.29, 87.54, 100.02, 121.46, 128.83, 130.25, 132.33, 133.60, 141.34. GC-MS (m/z): 175.1 [M]⁺. HRMS (ESI): calcd. for $\text{C}_{11}\text{H}_{10}\text{NO}_2$: 188.0712, found: 188.0713.

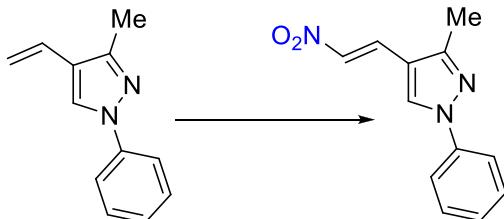


(E)-allyl 11-nitroundec-10-enoate (Scheme 5, 5l). Nitration was done by general procedure A with allyl undec-10-enoate (0.5 mmol, 127 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/petroleum ether (2:98 v/v); light yellow liquid; isolated yield: 48% (64 mg). ^1H NMR (400 MHz, Chloroform-d) δ 1.18 – 1.35 (m, 10H), 1.53 – 1.65 (ddd, J = 16.0, 8.2, 4.1 Hz, 2H),

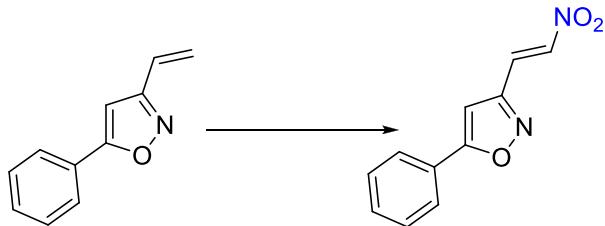
2.18 – 2.25 (qd, J = 7.5, 7.5, 7.4, 1.6 Hz, 2H), 2.25 – 2.31 (td, J = 7.6, 7.6, 3.8 Hz, 2H), 4.50 – 4.56 (dt, J = 5.7, 1.4, 1.4 Hz, 2H), 5.15 – 5.22 (dq, J = 10.4, 1.3, 1.3, 1.3 Hz, 1H), 5.23 – 5.31 (dq, J = 17.2, 1.5, 1.5, 1.5 Hz, 1H), 5.78 – 5.96 (ddt, J = 17.3, 10.4, 5.8, 5.8 Hz, 1H), 6.89 – 6.98 (dt, J = 13.4, 1.6, 1.6 Hz, 1H), 7.18 – 7.25 (m, 1H), 8.20 – 8.41 (s, 0H). ^{13}C NMR (101 MHz, Chloroform-d) δ 25.00, 27.83, 28.57, 29.15, 29.18, 29.19, 34.33, 39.65, 65.09, 76.91, 77.23, 77.55, 118.22, 132.46, 139.73, 142.91, 173.57. About 30% starting material was recovered after reaction.



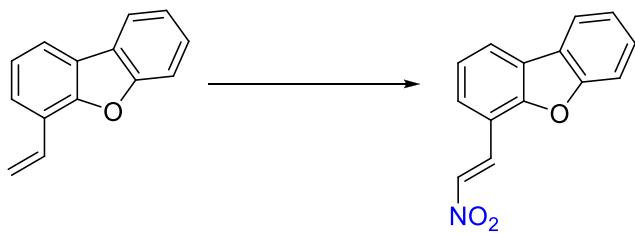
(E)-(4-nitrobuta-1,3-diene-1,1-diyldibenzene (Scheme 5, 5m).¹² Nitration was done by general procedure A with buta-1,3-diene-1,1-diyldibenzene (0.5 mmol, 103 μL) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: petroleum ether; dark orange liquid; isolated yield: 10% (12 mg). ^1H NMR (400 MHz, Chloroform-d) δ 6.73 – 6.85 (m, 1H), 7.16 – 7.23 (m, 2H), 7.28 – 7.40 (m, 6H), 7.42 – 7.49 (dd, J = 5.0, 1.8 Hz, 3H), 7.63 – 7.74 (dd, J = 13.0, 12.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 119.71, 128.68, 128.75, 128.79, 129.40, 129.96, 130.56, 137.29, 137.82, 139.65, 140.73, 157.34. GC-MS (m/z): 251.1 [M] $^+$.



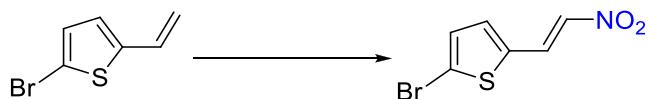
(E)-3-methyl-4-(2-nitrovinyl)-1-phenyl-1H-pyrazole (Scheme 6, 6a). Nitration was done by general procedure A with 3-methyl-1-phenyl-4-vinyl-1H-pyrazole (0.5 mmol, 92 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (6:94 v/v); yellow solid; isolated yield: 90% (100 mg). ^1H NMR (400 MHz, Chloroform-d) δ 2.46 – 2.52 (s, 3H), 7.30 – 7.40 (m, 1H), 7.44 – 7.53 (m, 3H), 7.62 – 7.72 (m, 2H), 7.98 – 8.09 (dd, J = 13.7, 0.5 Hz, 1H), 8.12 – 8.20 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 13.51, 113.63, 119.50, 127.74, 129.00, 129.88, 130.20, 135.13, 139.17, 151.47. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_2$: 230.0930, found: 230.0923. m. p. 143–144 $^{\circ}\text{C}$.



(E)-3-(2-nitrovinyl)-5-phenylisoxazole (Scheme 6, 6b). Nitration was done by general procedure A with 5-phenyl-3-vinylisoxazole (0.5 mmol, 86 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (6:94 v/v); creamy solid; isolated yield: 80% (87 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 6.68 – 6.77 (s, 1H), 7.43 – 7.58 (m, 3H), 7.63 – 7.74 (d, J = 13.8 Hz, 1H), 7.75 – 7.89 (m, 2H), 7.95 – 8.07 (d, J = 13.8 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 97.69, 126.18, 126.60, 129.45, 130.33, 131.29, 142.19, 156.44, 172.13. HRMS (ESI): calcd. for $C_{11}H_9N_2O_3$: 217.0613, found: 217.0615. m. p. 186–187 °C.

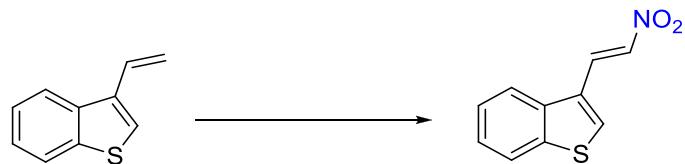


(E)-4-(2-nitrovinyl)dibenzo[b,d]furan (Scheme 6, 6c). Nitration was done by general procedure A with 4-vinyldibenzo[b,d]furan (0.5 mmol, 97 μ L, d=1 taken) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (0.2:99.8 v/v); greenish yellow solid; isolated yield: 76% (90 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 7.35 – 7.46 (m, 2H), 7.49 – 7.57 (dtd, J = 7.2, 4.4, 4.1, 1.3 Hz, 2H), 7.61 – 7.68 (dt, J = 8.3, 0.9, 0.9 Hz, 1H), 7.91 – 7.99 (m, 1H), 7.99 – 8.10 (dd, J = 7.7, 1.2 Hz, 1H), 8.09 – 8.21 (d, J = 13.6 Hz, 1H), 8.24 – 8.36 (d, J = 13.7 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 76.91, 77.23, 77.54, 112.18, 115.47, 121.06, 123.24, 123.60, 123.86, 124.48, 125.52, 128.27, 130.66, 134.36, 139.91, 154.44, 156.21. HRMS (ESI): calcd. for $C_{14}H_{10}NO_3$: 240.0661, found: 240.0668. m. p. 123–124 °C.

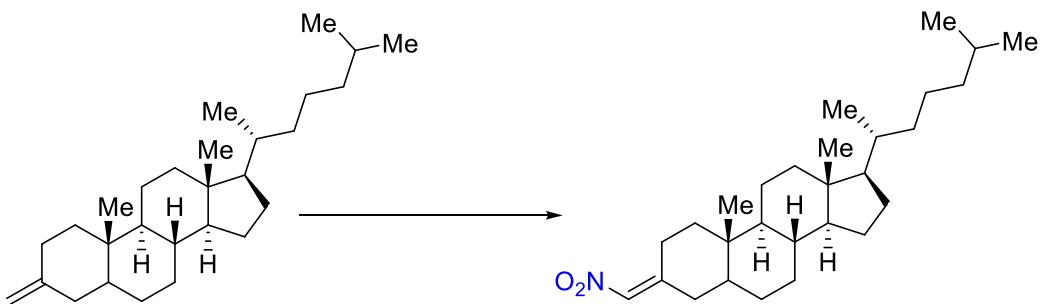


(E)-2-bromo-5-(2-nitrovinyl)thiophene (Scheme 6, 6d). Nitration was done by general procedure A with 2-bromo-5-vinylthiophene (0.16 mmol, 30 μ L, d=1 taken), 3.75 equiv $AgNO_2$ and 0.625 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (0.5:99.5 v/v);

dark golden yellow solid; isolated yield: 81% (30 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 7.09 – 7.15 (d, J = 3.9 Hz, 1H), 7.17 – 7.23 (dq, J = 4.0, 0.6, 0.6, 0.6 Hz, 1H), 7.33 – 7.42 (d, J = 13.4 Hz, 1H), 7.98 – 8.07 (dd, J = 13.4, 0.6 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 119.82, 131.32, 132.07, 135.29, 135.38, 135.60. HRMS (ESI): calcd. for C₆H₅NO₂SBr: 233.9224, found: 233.9224.

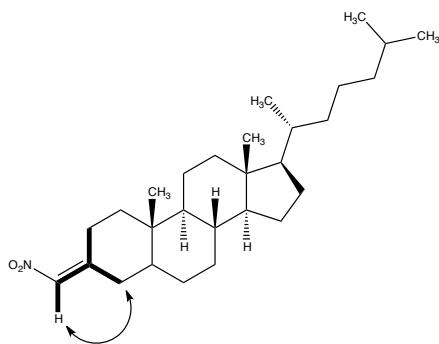


(E)-3-(2-nitroviny)benzo[b]thiophene (Scheme 6, 6e). Nitration was done by general procedure A with 3-vinylbenzo[b]thiophene (0.5 mmol, 80 μ L, d=1 taken) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (0.5:99.5 v/v); dark orange solid; isolated yield: 59% (60 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 7.40 – 7.55 (m, 2H), 7.65 – 7.76 (d, J = 13.7 Hz, 1H), 7.85 – 7.95 (m, 3H), 8.18 – 8.29 (dd, J = 13.7, 0.7 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 122.06, 123.39, 125.75, 125.79, 127.12, 131.10, 133.09, 136.45, 136.68, 140.54. HRMS (ESI): calcd. for C₁₀H₈NO₂S: 206.0276, found: 206.0279. m. p. 112–113 °C.



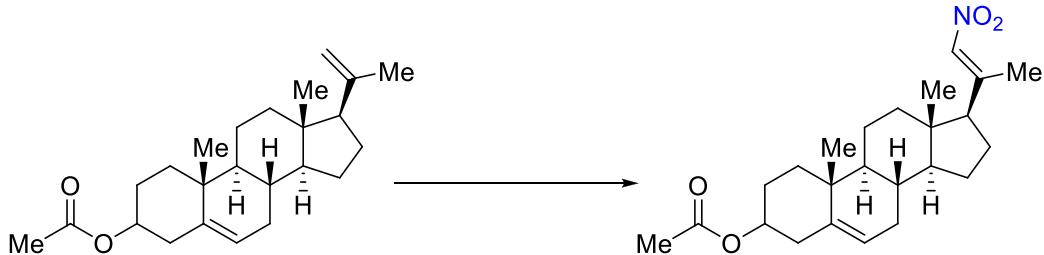
(8R,9S,10S,13R,14S,17R,E)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(nitromethylene)hexadecahydro-1H-cyclopenta[a]phenanthrene (Scheme 7, 7a). Nitration was done by general procedure A with (8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3-methylene-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (0.4 mmol, 154 mg), 3 equiv AgNO₂ and 0.5 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (0.5:99.5 v/v); creamy white solid; isolated yield: 93% (160 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 0.54 – 0.78 (m, 6H), 0.78 – 1.20 (m, 25H), 1.20 – 1.41 (m, 4H), 1.42 – 1.63 (m, 3H), 1.63 – 1.74 (dq, J = 13.2, 3.6, 3.4, 3.4 Hz, 1H), 1.74 – 2.04 (m, 4H), 2.04 – 2.27 (m, 2H), 2.27 – 2.46 (m, 1H), 6.80 – 7.00 (q, J = 1.8, 1.8, 1.8 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 12.08, 12.29, 18.87, 21.39, 22.78, 23.04, 24.03, 24.38, 28.23, 28.42, 29.13, 31.50, 32.06,

35.54, 35.99, 36.35, 36.84, 39.31, 39.71, 39.89, 40.09, 42.79, 48.32, 54.27, 56.42, 56.50, 132.16, 156.18. HRMS (ESI): calcd. for $C_{28}H_{48}NO_2$: 430.3685, found: 430.3676. m. p. 80-81 °C.



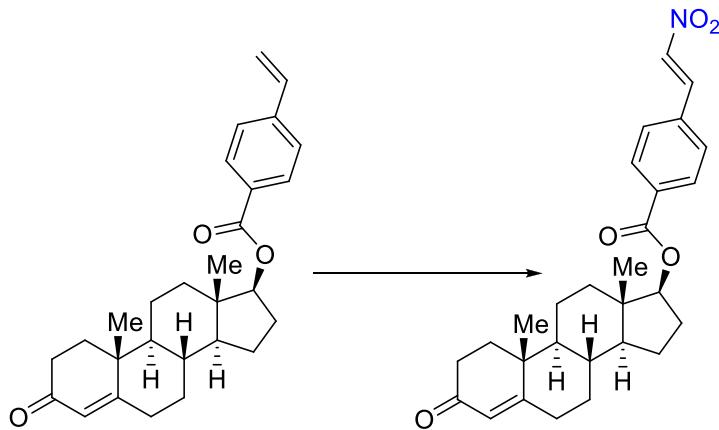
Selective COSY (bold lines) and NOESY correlations (arrow) of **7a**.

The structure of compound (**7a**) was established with the help of HRMS, one-dimensional (1H NMR and ^{13}C NMR), and two-dimensional (HSQC, COSY and NOESY) NMR spectral data. COSY spectrum revealed that the olefinic proton (δ_H 6.90) is coupled through allylic (four-bond) coupling to the two methylene groups at C-2 and C-4 (δ_H 2.40-1.90). NOESY spectrum displayed cross peaks (shown by two-headed arrow) between the olefinic proton (δ_H 6.90) and H-4 (δ_H 2.19 and 1.90, δ_C 36.8), suggesting that it is an *E*-isomer.

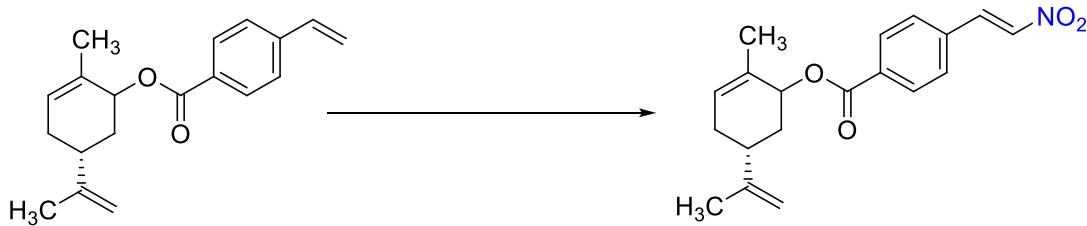


(8S,9S,10R,13S,14S,17S)-10,13-dimethyl-17-((E)-1-nitroprop-1-en-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (Scheme 7, 7b). Nitration was done by general procedure A with (*8S,9S,10R,13S,14S,17R*)-10,13-dimethyl-17-(prop-1-en-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (0.14 mmol, 50 mg), 3.2 equiv $AgNO_2$ and 0.7 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (20:80 v/v); creamy white solid; isolated yield: 40% (20 mg). 1H NMR (400 MHz, Chloroform-d) δ 0.43 – 0.75 (d, J = 15.0 Hz, 2H), 0.77 – 1.08 (m, 4H), 1.08 – 1.37 (m, 4H), 1.37 – 1.67 (m, 3H), 1.67 – 1.95 (m, 3H), 1.95 – 2.16 (m, 3H), 2.16 – 2.43 (dd, J = 31.4, 3.4 Hz, 4H), 4.51 – 4.71 (m, 1H), 5.33 – 5.44 (dd, J = 4.7, 2.3 Hz, 1H), 6.94 – 7.06 (t, J = 1.3, 1.3 Hz, 1H), 7.22 – 7.31 (d, J = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 13.30,

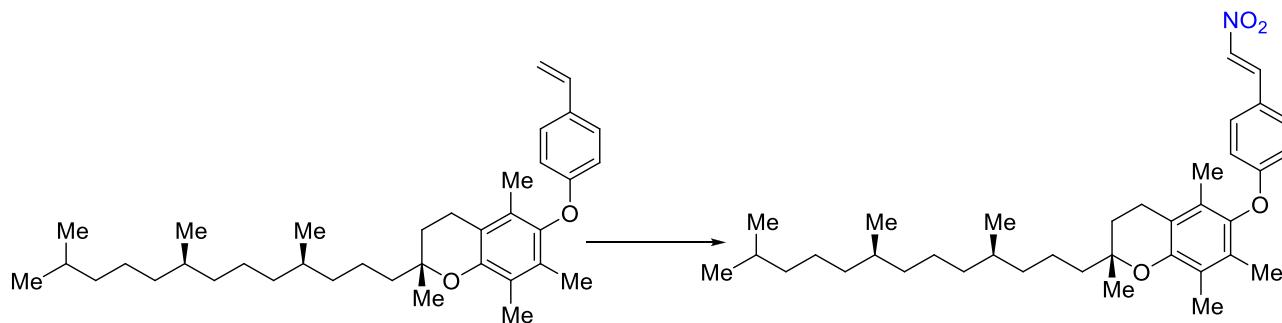
19.48, 20.37, 21.08, 21.60, 24.44, 24.94, 27.86, 31.81, 32.25, 36.76, 37.12, 38.21, 38.51, 45.46, 50.11, 56.63, 58.43, 73.96, 122.34, 136.46, 139.90, 153.81, 170.73. HRMS (ESI): calcd. for C₂₄H₃₆NO₄: 402.2644, found: 402.2635.



(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 4-((*E*)-2-nitrovinyl)benzoate (Scheme 7, 7c). Nitration was done by general procedure A with (8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 4-vinylbenzoate (0.3 mmol, 125 mg), 3.3 equiv AgNO₂ and 0.5 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (30:70 v/v); light yellowish solid; isolated yield: 82% (110 mg). ¹H NMR (400 MHz, Chloroform-d) δ 0.91 – 1.10 (m, 5H), 1.10 – 1.35 (m, 4H), 1.35 – 1.53 (m, 2H), 1.53 – 1.81 (m, 6H), 1.81 – 1.96 (m, 2H), 1.97 – 2.09 (m, 1H), 2.23 – 2.51 (m, 4H), 4.02 – 4.23 (q, *J* = 7.1, 7.1, 7.1 Hz, 1H), 4.78 – 4.96 (dd, *J* = 9.2, 7.7 Hz, 1H), 5.64 – 5.82 (m, 1H), 7.48 – 7.54 (d, *J* = 8.0 Hz, 0H), 7.59 – 7.66 (m, 3H), 7.72 – 7.76 (d, *J* = 8.7 Hz, 0H), 7.99 – 8.05 (d, *J* = 13.9 Hz, 1H), 8.07 – 8.12 (m, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 12.54, 17.63, 20.75, 23.81, 27.86, 31.69, 32.93, 34.13, 35.64, 35.92, 36.93, 38.82, 43.16, 50.48, 53.89, 83.77, 124.21, 129.16, 130.60, 133.72, 134.29, 137.81, 138.82, 165.56, 171.02, 199.66. HRMS (ESI): calcd. for C₂₈H₃₄NO₅: 464.2437, found: 464.2423. m. p. above 200 °C.

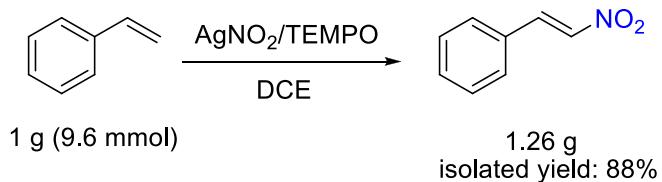


(5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enyl 4-((*E*)-2-nitrovinyl)benzoate (Scheme 7, 7d). Nitration was done by general procedure A with (5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enyl 4-vinylbenzoate (0.25 mmol, 71 μ L), 3 equiv AgNO_2 and 0.4 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 100–200). Eluent: ethyl acetate/ petroleum ether (0.5:99.5 v/v); isolated yield: 67% (55 mg). ^1H NMR (400 MHz, Chloroform-d) δ 1.61 – 1.91 (d, J = 13.3 Hz, 7H), 1.91 – 2.26 (m, 2H), 2.26 – 2.58 (dd, J = 45.0, 23.3, 11.7, 4.9 Hz, 2H), 4.72 – 4.88 (m, 1H), 5.51 – 5.67 (m, 1H), 5.70 – 5.83 (q, J = 6.0, 6.0, 5.1 Hz, 1H), 5.83 – 5.96 (m, 1H), 7.62 – 7.82 (d, J = 9.0 Hz, 3H), 8.03 – 8.13 (d, J = 13.1 Hz, 1H), 8.14 – 8.25 (d, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 18.57, 20.44, 30.49, 33.24, 35.55, 39.72, 71.54, 108.93, 126.00, 127.95, 128.57, 130.07, 132.11, 133.14, 133.62, 137.23, 138.29, 148.05, 164.82. HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{22}\text{NO}_4$: 328.1549, found: 328.1541.



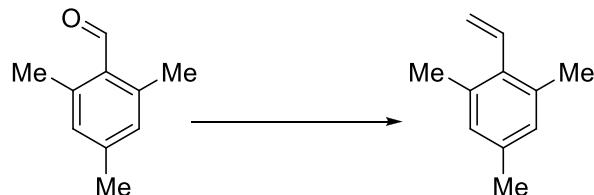
(*R*)-2,5,7,8-tetramethyl-6-(4-((*E*)-2-nitrovinyl)phenoxy)-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman (Scheme 7, 7e).¹³ Nitration was done by general procedure A with (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-6-(4-vinylphenoxy)chroman (0.2 mmol, 110 mg), 5 equiv AgNO_2 and 1 equiv TEMPO. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (0.5:99.5 v/v); bright yellowish solid; isolated yield: 90% (100 mg). ^1H NMR (400 MHz, Chloroform-d) δ 0.76 – 0.99 (m, 17H), 0.99 – 1.20 (m, 3H), 1.20 – 1.48 (m, 12H), 1.48 – 1.74 (m, 3H), 1.74 – 1.92 (m, 2H), 1.92 – 2.06 (d, J = 14.6 Hz, 7H), 2.06 – 2.17 (s, 3H), 2.56 – 2.69 (t, J = 6.9, 6.9 Hz, 2H), 6.79 – 6.86 (d, J = 8.8 Hz, 2H), 7.42 – 7.49 (d, J = 8.7 Hz, 2H), 7.49 – 7.55 (d, J = 13.6 Hz, 1H), 7.93 – 8.02 (d, J = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 12.04, 12.15, 13.02, 19.82, 19.88, 19.95, 20.81, 21.22, 22.83, 22.92, 24.04, 24.64, 25.01, 28.17, 31.32, 31.37, 32.85, 32.99, 37.48, 37.53, 37.58, 37.65, 37.74, 39.55, 40.16,

115.99, 118.27, 123.06, 123.78, 126.00, 127.84, 131.51, 135.20, 139.22, 142.95, 149.35, 162.56. HRMS (ESI): calcd. for $C_{37}H_{56}NO_4$: 578.4209, found: 578.4196.

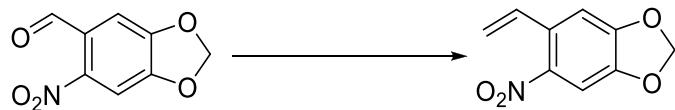


Gram scale reaction with styrene: To an oven dried two-neck round bottom flask fitted with a reflux condenser were added styrene (1 g), silver nitrite (3 g), tempo (0.6 g) and molecular sieves. After addition of about 30 mL dry DCE, it was kept in a pre-heated oil bath at 70 °C for 12 hours. After completion of the reaction, as detected by TLC analysis, reaction mixture was cooled to room temperature, filtered through a celite bed funnel, and purified by silica gel column chromatography (60-120 mesh). Crystalline yellow solid; isolated yield: 88% (1.26 g).

Characteristic data of starting materials prepared:

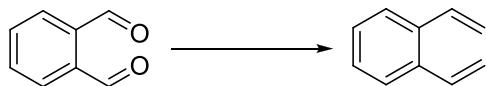


1,3,5-trimethyl-2-vinylbenzene. Reaction was done following General procedure B with 2,4,6-trimethylbenzaldehyde (2 mmol, 294 μ L) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; colorless liquid; isolated yield: 62% (180 mg). **^1H NMR** (400 MHz, Chloroform-d) δ 2.25 – 2.44 (d, J = 4.0 Hz, 9H), 5.25 – 5.35 (dd, J = 18.0, 2.1 Hz, 1H), 5.52 – 5.60 (dd, J = 11.5, 2.1 Hz, 1H), 6.66 – 6.79 (dd, J = 17.9, 11.5 Hz, 1H), 6.90 – 6.95 (d, J = 1.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 21.01, 21.13, 119.24, 128.71, 134.98, 135.20, 135.88, 136.34.

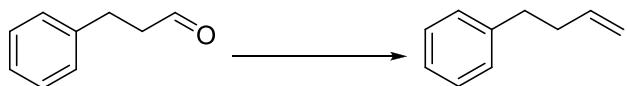


5-nitro-6-vinylbenzo[*d*][1,3]dioxole. Reaction was done following General procedure B with 6-nitrobenzo[*d*][1,3]dioxole-5-carbaldehyde (2 mmol, 390 mg) as the substrate. Pure olefin

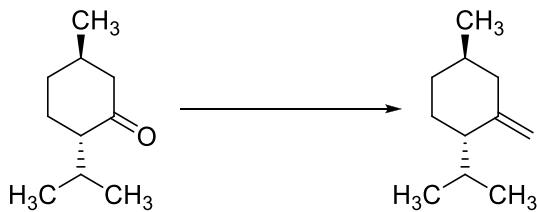
product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate / petroleum ether (3:97 v/v); yellow solid. **¹H NMR** (400 MHz, Chloroform-d) δ 5.41–5.44 (dd, J = 10.0, 4 Hz, 1H), 5.60–5.65 (dd, J = 10.0, 4.0 Hz, 1H), 6.12 (s, 2H), 6.98 (s, 1H) 7.16–7.27 (m, 1H) 7.48 (s, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 103.15, 105.38, 107.30, 118.07, 130.97, 133.35, 142.07, 147.63, 152.09.



1,2-divinylbenzene. Reaction was done following General procedure B with phthalaldehyde (2 mmol, 268 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; colorless liquid. **¹H NMR** (400 MHz, Chloroform-d) δ 5.32 – 5.44 (dd, J = 11.0, 1.4 Hz, 2H), 5.61 – 5.76 (dd, J = 17.4, 1.4 Hz, 2H), 6.98 – 7.16 (dd, J = 17.4, 10.9 Hz, 2H), 7.27 – 7.36 (m, 2H), 7.45 – 7.57 (dd, J = 5.7, 3.5 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 116.53, 126.44, 127.99, 134.99, 136.23.

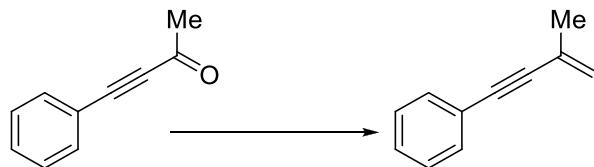


but-3-enylbenzene. Reaction was done following General procedure B with 3-phenylpropanal (2 mmol, 300 μ L) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; yellow liquid; isolated yield: 50% (150 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 2.38 (m, 2H), 2.72 (m, 2H), 5.00 (m, 2H), 5.80–5.90 (m, 1H), 7.15–7.20 (m, 3H), 7.21–7.30 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 35.59, 35.74, 115.11, 126.00, 128.49, 128.63, 138.30, 142.06.

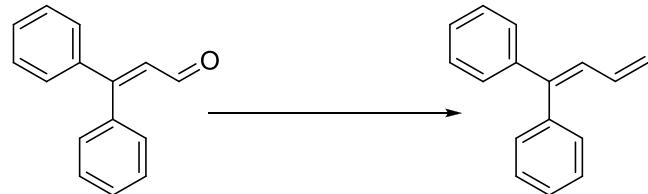


(1S,4R)-1-isopropyl-4-methyl-2-methylenecyclohexane. Reaction was done following General procedure B with (2S,5R)-2-isopropyl-5-methylcyclohexanone (5 mmol, 860 μ L) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; colorless liquid. **¹H NMR** (400 MHz, Chloroform-d) δ 0.87 – 0.90 (s, 1H), 0.90 – 0.92 (d, J = 1.7 Hz, 3H), 0.92 – 0.94 (d, J = 1.7 Hz, 3H), 0.94 – 0.97 (s, 2H), 1.02 – 1.44 (m, 2H), 1.47 – 1.63 (m, 1H), 1.63 – 1.74 (m, 2H), 1.74 – 1.88 (m, 2H), 1.88 – 2.15 (dq, J = 13.3, 6.6, 6.6 Hz, 1H), 2.16 – 2.45 (m, 1H), 4.53 – 4.66 (d,

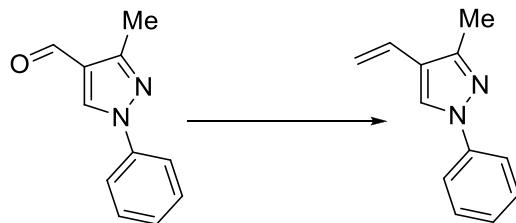
$J = 1.9$ Hz, 1H), 4.66 – 4.87 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 19.23, 21.62, 22.34, 27.31, 27.61, 33.64, 34.24, 44.66, 49.62, 106.36, 151.28.



(3-methylbut-3-en-1-ynyl)benzene. Reaction was done following General procedure B with 4-phenylbut-3-yn-2-one (2 mmol, 280 μL) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether. ^1H NMR (400 MHz, Chloroform-d) δ 1.72 – 2.41 (m, 3H), 5.29 – 5.34 (m, 1H), 5.39 – 5.44 (dd, $J = 2.1, 1.0$ Hz, 1H), 7.28 – 7.38 (dd, $J = 5.1, 2.0$ Hz, 3H), 7.42 – 7.50 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 23.71, 76.91, 77.23, 77.54, 88.57, 90.75, 122.15, 123.44, 127.04, 128.33, 128.46, 131.76.

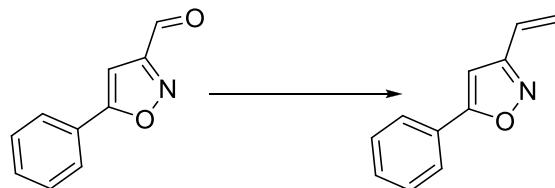


buta-1,3-diene-1,1-diylidobenzene. Reaction was done following General procedure B with 3,3-diphenylacrylaldehyde (1 mmol, 208 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; Colorless dense liquid. ^1H NMR (400 MHz, Chloroform-d) δ 5.14 – 5.21 (m, 1H), 5.39 – 5.50 (m, 1H), 6.42 – 6.58 (dd, $J = 16.9, 11.1, 10.1, 1.0$ Hz, 1H), 6.71 – 6.82 (d, $J = 11.0$ Hz, 1H), 7.20 – 7.39 (m, 6H), 7.37 – 7.49 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 118.81, 127.58, 127.69, 127.77, 128.35, 128.38, 128.70, 130.60, 135.14, 139.82, 142.26, 143.31.

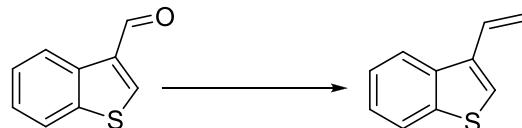


3-methyl-1-phenyl-4-vinyl-1H-pyrazole. Reaction was done following General procedure B with 3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde (2 mmol, 372 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/petroleum ether (10:90 v/v); yellowish liquid; isolated yield: 81%

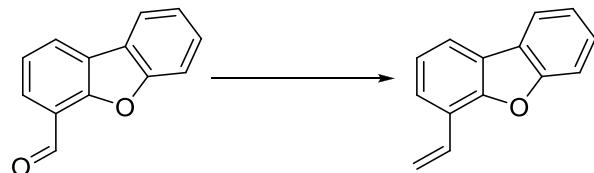
(300 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 2.35 – 2.46 (d, J = 0.5 Hz, 3H), 5.08 – 5.25 (dd, J = 11.2, 1.4 Hz, 1H), 5.42 – 5.55 (dd, J = 17.8, 1.4 Hz, 1H), 6.50 – 6.64 (ddd, J = 17.7, 11.2, 0.7 Hz, 1H), 7.18 – 7.29 (m, 1H), 7.34 – 7.48 (m, 2H), 7.54 – 7.74 (m, 2H), 7.82 – 7.97 (s, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 12.96, 113.03, 118.72, 120.67, 124.56, 126.09, 126.76, 129.43, 139.92, 148.74.



5-phenyl-3-vinylisoxazole. Reaction was done following General procedure B with 5-phenylisoxazole-3-carbaldehyde (1.5 mmol, 259 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; creamy solid; isolated yield: 43% (110 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 5.46 – 5.79 (dd, J = 11.0, 0.9 Hz, 1H), 5.79 – 6.20 (dd, J = 17.8, 0.9 Hz, 1H), 6.56 – 6.72 (s, 1H), 6.72 – 6.93 (dd, J = 17.8, 11.0 Hz, 1H), 7.33 – 7.56 (m, 3H), 7.69 – 7.87 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 96.32, 121.65, 125.39, 125.88, 127.41, 129.07, 130.30, 162.45, 169.87.

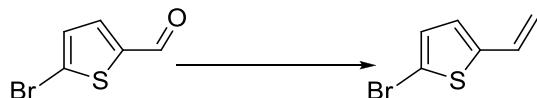


3-vinylbenzo[b]thiophene. Reaction was done following General procedure B with benzo[b]thiophene-3-carbaldehyde (1.5 mmol, 243 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; yellowish liquid; isolated yield: 62% (150 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 5.34 – 5.50 (dd, J = 11.1, 1.3 Hz, 1H), 5.75 – 5.93 (dd, J = 17.6, 1.3 Hz, 1H), 6.93 – 7.10 (ddd, J = 17.6, 11.1, 0.8 Hz, 1H), 7.32 – 7.59 (m, 3H), 7.81 – 8.08 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 115.75, 122.11, 122.44, 123.04, 124.44, 124.62, 129.37, 134.70, 137.79, 140.63.

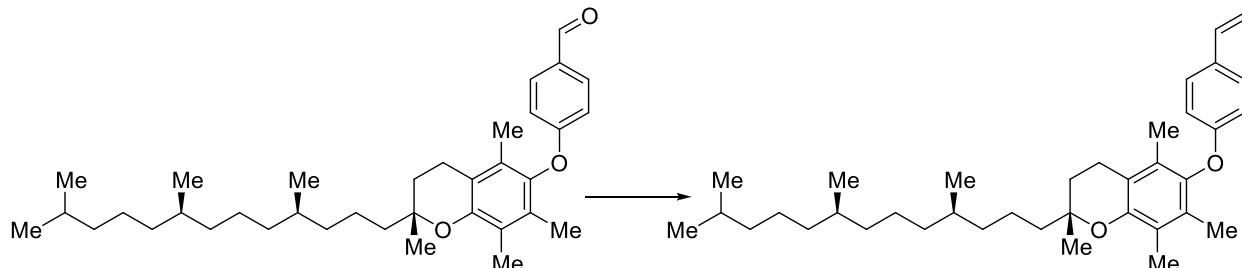


4-vinyldibenzo[b,d]furan. Reaction was done following General procedure B with dibenzo[b,d]furan-4-carbaldehyde (1.4 mmol, 273 mg) as the substrate. Pure olefin product was

isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; colorless liquid. **¹H NMR** (400 MHz, Chloroform-d) δ 5.50 – 5.69 (dt, J = 11.2, 1.1, 1.1 Hz, 1H), 6.19 – 6.44 (dt, J = 17.8, 1.1, 1.1 Hz, 1H), 7.06 – 7.21 (m, 1H), 7.29 – 7.43 (m, 2H), 7.43 – 7.58 (m, 2H), 7.58 – 7.73 (dq, J = 8.3, 0.7, 0.7, 0.7 Hz, 1H), 7.81 – 7.91 (dd, J = 7.7, 1.2 Hz, 1H), 7.91 – 8.06 (ddd, J = 7.7, 1.4, 0.7 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 111.96, 117.64, 119.95, 120.86, 122.77, 122.98, 123.01, 124.22, 124.79, 125.51, 127.36, 131.50, 153.89, 156.32.

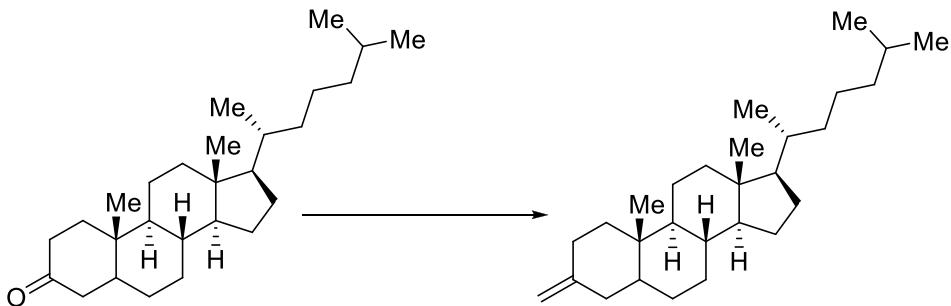


2-bromo-5-vinylthiophene. Reaction was done following General procedure B with 5-bromothiophene-2-carbaldehyde (0.26 mmol, 50 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; yellowish liquid; isolated yield: 83% (40 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 5.09 – 5.20 (m, 1H), 5.41 – 5.54 (m, 1H), 6.63 – 6.78 (m, 2H), 6.85 – 6.99 (d, J = 3.8 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 111.43, 113.95, 126.25, 129.57, 130.36, 144.82.

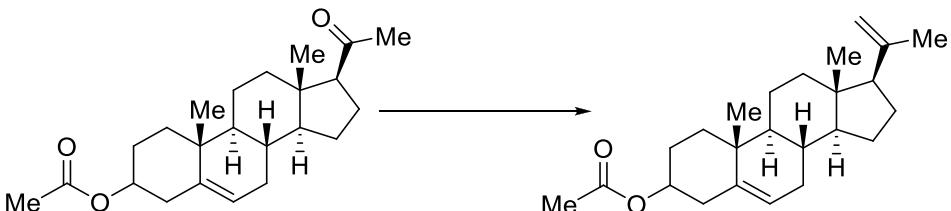


(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)-6-(4-vinylphenoxy)chroman.

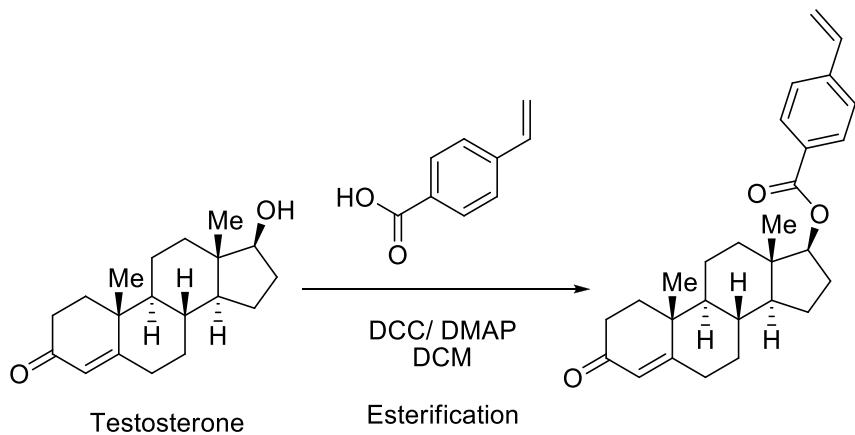
Reaction was done following General procedure B with 4-((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yloxy)benzaldehyde (0.75 mmol, 400 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; colorless liquid; isolated yield: 53% (210 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 0.74 – 0.98 (dd, J = 7.9, 6.5 Hz, 1H), 0.98 – 1.18 (dddd, J = 24.9, 12.1, 7.1, 3.4 Hz, 3H), 1.18 – 1.36 (m, 9H), 1.36 – 1.57 (m, 3H), 1.58 – 1.71 (s, 3H), 1.71 – 1.91 (m, 2H), 1.92 – 2.07 (d, J = 16.2 Hz, 6H), 2.07 – 2.21 (s, 3H), 2.52 – 2.70 (t, J = 6.8, 6.8 Hz, 2H), 4.99 – 5.25 (dd, J = 10.8, 1.0 Hz, 1H), 5.51 – 5.70 (dd, J = 17.6, 1.0 Hz, 1H), 6.59 – 6.67 (m, 1H), 6.67 – 6.74 (d, J = 8.7 Hz, 2H), 7.27 – 7.32 (d, J = 8.7 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 12.03, 12.20, 13.07, 14.41, 19.83, 19.90, 19.97, 20.83, 21.25, 22.85, 22.94, 24.07, 24.66, 25.03, 28.20, 31.49, 32.89, 33.01, 37.50, 37.57, 37.61, 37.68, 37.78, 39.58, 40.17, 53.62, 60.60, 75.22, 111.72, 114.92, 118.06, 123.46, 126.42, 127.64, 128.34, 130.79, 136.43, 143.51, 148.93, 158.86.



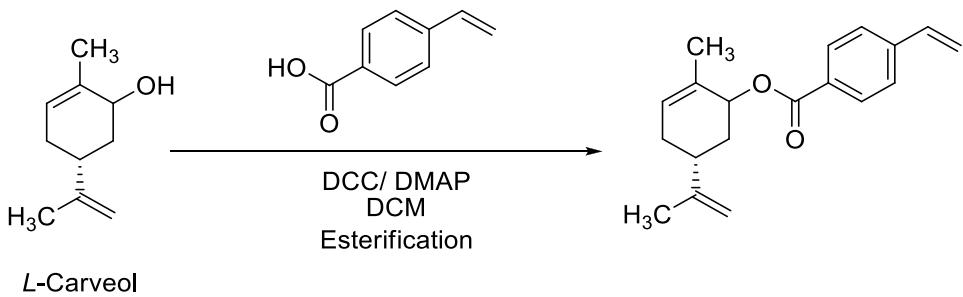
(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3-methylene-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene. Reaction was done following General procedure B with cholestan-3-one (1 mmol, 386 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; crystalline white solid; isolated yield: 55% (210 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 0.57 – 0.74 (s, 5H), 0.74 – 0.93 (m, 14H), 0.93 – 1.20 (m, 10H), 1.20 – 1.43 (m, 5H), 1.43 – 1.61 (m, 3H), 1.61 – 1.72 (dtd, J = 12.8, 3.9, 3.8, 2.7 Hz, 2H), 1.72 – 1.92 (m, 3H), 1.92 – 2.08 (m, 2H), 2.08 – 2.25 (m, 2H), 4.22 – 4.87 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 12.00, 12.30, 18.89, 21.35, 22.80, 23.06, 24.05, 24.44, 28.24, 28.48, 29.13, 31.25, 32.22, 35.69, 36.03, 36.19, 36.39, 38.18, 39.74, 40.06, 40.27, 42.80, 48.29, 54.58, 56.47, 56.70, 106.16, 150.41. HRMS (ESI): calcd. for C₂₈H₄₈Na: 407.3654, found: 407.3651.



(8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-dimethyl-17-(prop-1-en-2-yl)2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate. Reaction was done following General procedure B with pregnenolone acetate (0.5 mmol, 179 mg) as the substrate. Pure olefin product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: petroleum ether; crystalline white solid; **¹H NMR** (400 MHz, Chloroform-d) δ 0.50 – 0.63 (s, 3H), 0.91 – 1.04 (s, 4H), 1.04 – 1.32 (m, 4H), 1.32 – 1.50 (m, 2H), 1.50 – 1.61 (m, 2H), 1.61 – 1.80 (m, 5H), 1.80 – 1.93 (m, 3H), 1.93 – 2.13 (s, 4H), 2.24 – 2.39 (m, 2H), 4.52 – 4.67 (dddd, J = 14.6, 11.3, 5.6, 4.0 Hz, 1H), 4.67 – 4.76 (dt, J = 2.0, 1.0, 1.0 Hz, 1H), 4.80 – 4.89 (ddd, J = 2.3, 1.4, 0.8 Hz, 1H), 5.31 – 5.44 (dq, J = 4.7, 1.8, 1.5, 1.5 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-d) δ 12.87, 19.53, 21.26, 21.63, 24.43, 24.85, 25.59, 27.95, 31.99, 32.37, 36.82, 37.20, 38.30, 38.81, 43.27, 50.36, 56.61, 57.40, 74.12, 110.90, 122.73, 139.86, 145.77, 170.70.

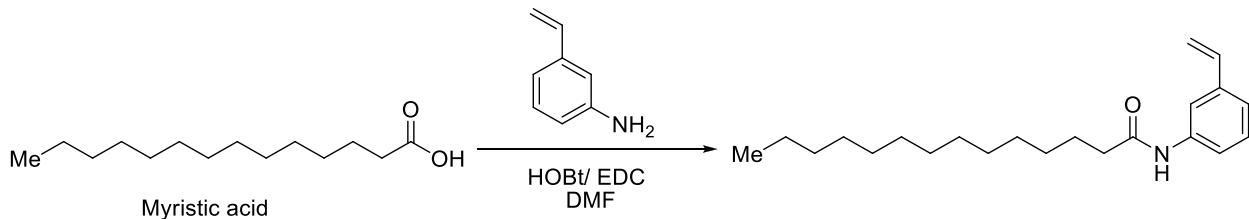


(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 4-vinylbenzoate. 4-vinylbenzoic acid (1 mmol, 148 mg), testosterone (1 mmol, 288 mg), DCC (1.2 mmol, 247 mg), DMAP (1.2 mmol, 146 mg) and DCM (10 mL) were taken in a round bottom flask and stirred at room temperature for overnight. The crude reaction mixture was purified through column chromatography (100-200 mesh); Eluent: ethyl acetate/petroleum ether (15:85 v/v); white solid; isolated yield 38% (160 mg). **¹H NMR** (400 MHz, Chloroform-d) δ 0.90 – 1.33 (m, 10H), 1.34 – 1.50 (m, 2H), 1.51 – 1.78 (m, 5H), 1.78 – 1.95 (m, 3H), 1.95 – 2.17 (ddd, J = 13.4, 5.0, 3.2 Hz, 1H), 2.17 – 2.54 (m, 4H), 4.76 – 4.91 (dd, J = 9.1, 7.6 Hz, 1H), 5.30 – 5.45 (d, J = 11.0 Hz, 1H), 5.69 – 5.78 (m, 1H), 5.79 – 5.92 (d, J = 17.6 Hz, 1H), 6.63 – 6.85 (dd, J = 17.6, 10.9 Hz, 1H), 7.35 – 7.58 (m, 2H), 7.84 – 8.11 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-d) δ 12.46, 17.57, 20.71, 23.78, 27.84, 31.66, 32.92, 34.09, 35.59, 35.85, 36.89, 38.78, 43.05, 50.44, 53.86, 83.10, 116.62, 124.11, 126.25, 129.89, 129.98, 136.17, 142.01, 166.40, 171.18, 199.68.

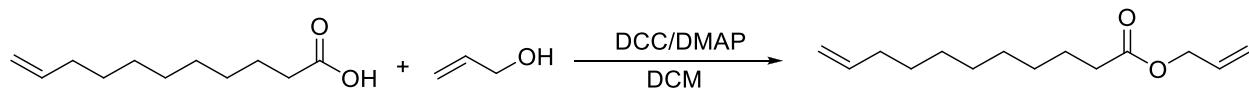


(5R)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enyl 4-vinylbenzoate. 4-vinylbenzoic acid (1 mmol, 148 mg), *L*-carveol (1 mmol, 152 μ L), DCC (1.2 mmol, 247 mg), DMAP (1.2 mmol, 146 mg) and DCM (10 mL) were taken in a round bottom flask and stirred at room temperature for overnight. The crude reaction mixture was purified through column chromatography (60-120 mesh); Eluent: ethyl acetate/petroleum ether (1:99 v/v); **$^1\text{H NMR}$** (400 MHz, Chloroform-d) δ 1.61 – 1.82 (m, 7H), 1.85 – 2.20 (m, 2H), 2.20 – 2.55 (m, 2H), 4.66 – 4.81 (m, 1H), 5.33 – 5.45

(dt, $J = 10.9, 1.0, 1.0$ Hz, 1H), 5.44 – 5.57 (dt, $J = 3.8, 1.6, 1.6$ Hz, 1H), 5.61 – 5.75 (m, 1H), 5.76 – 5.82 (dt, $J = 5.5, 1.9, 1.9$ Hz, 1H), 5.82 – 5.91 (ddd, $J = 17.6, 1.8, 0.8$ Hz, 1H), 6.61 – 6.89 (dd, $J = 17.6, 10.9$ Hz, 1H), 7.12 – 7.34 (s, 0H), 7.34 – 7.60 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.90 – 8.17 (m, 2H).



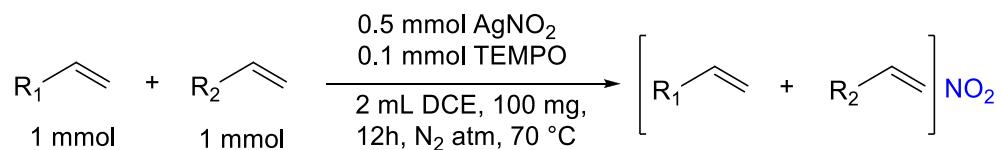
N-(3-vinylphenyl)tetradecanamide.¹⁴ tetradecanoic acid (Myristic acid) (1 mmol, 228 μ L) was taken in round bottom flask, 5 mL DMF was added to it and was stirred at 0 °C. HOBT (1.1 mmol, 140 mg), EDC (1.1 mmol, 160 mg) was added to it and stirred at 0 °C for 15 mins and then for 30 mins at room temperature. 3-vinylaniline (1 mmol, 113 μ L) was added to it and reaction mixture was stirred at room temperature for overnight. The mixture was diluted with brine solution and extracted with ethyl acetate. Organic part was dried over Na_2SO_4 and concentrated at reduced pressure and product was purified through a silica gel column (mesh 60–120). White Solid; ¹H NMR (400 MHz, Chloroform-d) δ 0.84 – 0.91 (d, $J = 6.7$ Hz, 3H), 1.19 – 1.27 (s, 18H), 1.52 – 1.65 (m, 1H), 1.65 – 1.79 (p, $J = 7.6, 7.6, 7.5, 7.5$ Hz, 2H), 2.10 – 2.59 (td, $J = 7.6, 7.6, 3.7$ Hz, 3H), 5.06 – 5.38 (d, $J = 11.0$ Hz, 1H), 5.63 – 5.86 (dd, $J = 17.5, 0.9$ Hz, 1H), 6.49 – 6.81 (dd, $J = 17.6, 10.9$ Hz, 1H), 7.09 – 7.18 (dt, $J = 7.7, 1.3, 1.3$ Hz, 1H), 7.18 – 7.25 (m, 2H), 7.31 – 7.42 (m, 1H), 7.54 – 7.65 (t, $J = 1.9, 1.9$ Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 14.33, 22.90, 24.94, 25.84, 29.29, 29.48, 29.57, 29.65, 29.70, 29.89, 32.13, 34.12, 38.07, 114.64, 117.72, 119.36, 122.31, 129.29, 136.67, 138.41, 138.67, 171.80.



allyl undec-10-enoate. 10-undecenoic acid (1 mmol), allyl alcohol (1 mmol), DCC (1.2 mmol, 247 mg), DMAP (1.2 mmol, 146 mg) and DCM (10 mL) were taken in a round bottom flask and stirred at room temperature for overnight. The crude reaction mixture was purified through column chromatography (100-200 mesh); Eluent: ethyl acetate/petroleum ether (2:98 v/v); colorless liquid. ¹H NMR (400 MHz, Chloroform-d) δ 1.19 – 1.44 (m, 10H), 1.56 – 1.66 (t, $J = 7.3, 7.3$ Hz, 2H), 1.97 – 2.08 (tdd, $J = 8.1, 8.1, 6.0, 1.5$ Hz, 2H), 2.27 – 2.37 (t, $J = 7.6, 7.6$ Hz, 2H), 4.53 – 4.59 (dt, $J = 5.7, 1.5, 1.5$ Hz, 2H), 4.88 – 4.94 (ddd, $J = 10.2, 2.3, 1.2$ Hz, 1H), 4.94 – 5.03 (dt, $J = 17.1, 1.8, 1.8$ Hz, 1H), 5.18 – 5.25 (dt, $J = 10.4, 1.4, 1.4$ Hz, 1H), 5.25 – 5.35 (m, 1H), 5.73 – 5.85 (ddt, $J = 16.9, 10.2, 6.7, 6.7$ Hz, 1H), 5.85 – 5.97 (ddt, $J = 17.4, 10.4, 5.7, 5.7$ Hz, 1H).

Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 25.11, 29.06, 29.22, 29.29, 29.37, 29.45, 33.97, 34.43, 65.09, 114.32, 118.22, 132.51, 139.32, 173.67.

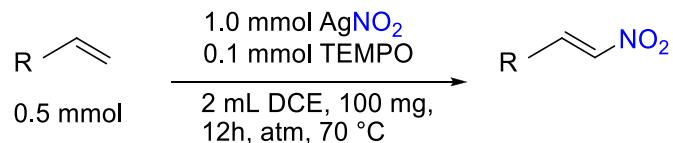
Competition experiment 1: Olefins are nitrated selectively or preferentially based on slight difference in steric and electronic environment



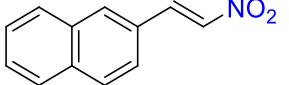
| | Olefin 1 | Olefin 2 | Result |
|---|----------|----------|------------------------------------|
| 1 | | | Only styrene nitrated |
| 2 | | | Only styrene nitrated |
| 3 | | | Only terminal double bond nitrated |

Results are based on ^1H NMR analysis of the crude reaction mixture.

Comparison under nitrogen and in air:



| | Product | GC yield (Under Air) | GC yield (Under N_2) |
|---|---------|----------------------|--------------------------------|
| 1 | | 81 | 83 |
| 2 | | 57 | 52 |
| 3 | | 72 | 75 |

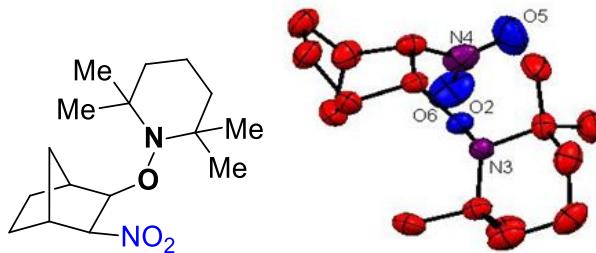
| | | | |
|---|---|----|----|
| 4 |  | 73 | 75 |
|---|---|----|----|

X-ray crystallographic Data:

General Data Collection and Refinement Procedures:

The single crystal data was collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda=0.71073$ Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystal of the C₃₂H₅₆N₄O₆ reported in the paper was mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Crystals were flash frozen to 293(2) K in a liquid nitrogen cooled stream of nitrogen.

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In this case frame widths of 0.5° was judged to be appropriate and full hemispheres of data were collected using the Bruker SMART¹⁵ software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to re-determine unit cell parameters for data integration and to check for rotational twinning using CELL_NOW.¹⁶ In no data collection was evidence for crystal decay encountered. Following exhaustive review of the collected frames the resolution of the dataset was judged. Data was integrated using Bruker SAINT¹⁷ software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data was subsequently corrected for absorption by the program SADABS.¹⁸ The space group determinations and test for merohedral twinning was carried out using XPREP.¹⁷ In this case, the highest possible space group was chosen. The structure was solved by direct method and refined using the SHELXTL 97¹⁹ software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times Ueq of the attached C atoms. In some cases modeling of electron density within the voids of the frameworks did not lead to identification of recognizable solvent molecules in these structures, probably due to the highly disordered contents of the large pores in the frameworks. The ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise.



ORTEP diagram of C₁₆H₂₈N₂O₃

Summary of crystallographic data for C₁₆H₂₈N₂O₃:

| | |
|--|----------------|
| Crystal | C16 H28 N2 O3 |
| Color | Colourless |
| Crystal description | Plate |
| Cell formula units Z | 4 |
| Cell volume | 1037.60(7) |
| Size | 0.25×0.20×0.14 |
| Chemical formula weight | 296.40 |
| Crystal System | Orthorhombic |
| Space Group | P 21 1 1 |
| Cell length a | 8.0513(4) |
| Cell length b | 10.4170(6) |
| Cell length c | 19.4576(10) |
| Cell angle alpha | 90.00 |
| Cell angle beta | 90.00 |
| Cell angle gamma | 90.00 |
| V, Å ³ /ρ _{calc} , gcm ⁻¹ | 1631.92 (15) |
| Temp, K/λ, Å | 293(2) |
| Z/μ mm ⁻¹ | 4 |
| 2θ _{max} [°] | 29.08 |

| | |
|--------------------|--------|
| Unique Reflections | 3254 |
| R factor all | 0.0658 |
| crystal_F_000 | 648.0 |

$$^aR1 = \sum \left| \left| F_o \right| - \left| F_c \right| \right| / \sum \left| F_o \right| ; wR^2 = \{ \sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2] \}^{1/2}$$

Selected Bond Distances:

| Bond | Length (Å) | Bond | Length (Å) |
|----------|------------|----------|------------|
| O1 C11 | 1.432(4) | C17 H17B | 0.9700 |
| O1 N2 | 1.463(3) | C19 C24 | 1.535(6) |
| N2 C23 | 1.502(5) | C19 C29 | 1.532(6) |
| N2 C8 | 1.504(4) | C19 H19A | 0.9700 |
| C7 N1 | 1.505(5) | C19 H19B | 0.9700 |
| C7 C32 | 1.510(6) | C20 C23 | 1.531(6) |
| C7 C11 | 1.564(5) | C20 H20A | 0.9600 |
| C7 H7 | 0.9800 | C20 H20B | 0.9600 |
| C8 C34 | 1.529(5) | C20 H20C | 0.9600 |
| C8 C17 | 1.524(5) | C23 C25 | 1.530(6) |
| C8 C39 | 1.534(6) | C24 C27 | 1.509(6) |
| C11 C24 | 1.529(6) | C24 H24 | 0.9800 |
| C11 H11 | 0.9800 | C25 H25A | 0.9600 |
| C14 C38 | 1.503(6) | C25 H25B | 0.9600 |
| C14 C23 | 1.539(5) | C25 H25C | 0.9600 |
| C14 H14A | 0.9700 | C27 C32 | 1.522(6) |

| | | | |
|----------|----------|----------|----------|
| C14 H14B | 0.9700 | C27 H27A | 0.9700 |
| N1 O4 | 1.206(6) | C27 H27B | 0.9700 |
| N1 O3 | 1.208(5) | C29 C32 | 1.541(6) |
| C17 C38 | 1.509(7) | C29 H29A | 0.9700 |
| C17 H17A | 0.9700 | C29 H29B | 0.9700 |

Selected Bond angles:

| Bond | Angle (deg) | Bond | Angle (deg) |
|-------------|--------------------|----------------|--------------------|
| C11 O1 N2 | 111.7(2) | C42 C15 H15B | 108.8 |
| O1 N2 C23 | 107.2(3) | C5 C15 H15B | 108.8 |
| O1 N2 C8 | 105.3(2) | H15A C15 H15B | 107.7 |
| C23 N2 C8 | 117.2(3) | C9 C22 H22A | 109.5 |
| N1 C7 C32 | 113.8(3) | C9 C22 H22B | 109.5 |
| N1 C7 C11 | 111.4(3) | H22A C22 H22 B | 109.5 |
| C32 C7 C11 | 104.4(3) | C9 C22 H22C | 109.5 |
| N1 C7 H7 | 109.0 | H22A C22 H22C | 109.5 |
| C32 C7 H7 | 109.0 | H22B C22 H22C | 109.5 |
| C11 C7 H7 | 109.0 | C9 C26 H26A | 109.5 |
| N2 C8 C34 | 115.5(3) | C9 C26 H26B | 109.5 |
| N2 C8 C17 | 107.2(3) | H26A C26 H26B | 109.5 |
| C34 C8 C17 | 111.1(3) | C9 C26 H26C | 109.5 |
| N2 C8 C39 | 107.2(3) | H26A C26 H26C | 109.5 |
| C34 C8 C39 | 108.6(4) | H26B C26 H26C | 109.5 |
| C17 C8 C39 | 106.8(4) | C30 C28 C31 | 101.2(4) |

| | | | |
|-------------|----------|----------------------|----------|
| O1 C11 C24 | 114.8(3) | C30 C28 C13 106.1(3) | 106.1(3) |
| O1 C11 C7 | 107.5(3) | C31 C28 C13 | 102.2(3) |
| C24 C11 C7 | 100.8(3) | C30 C28 H28 | 115.2 |
| O1 C11 H11 | 111.1 | C31 C28 H28 | 115.2 |
| C24 C11 H11 | 111.1 | C13 C28 H28 | 115.2 |

Experimental details for TEMPO-alkane-NO₂

Nitration of norbornene was attempted following general procedure A with 0.5 mmol substrate, 3 equiv. AgNO₂ and 0.4 equiv. TEMPO in DCE solvent. Pure nitrated product was isolated with silica gel column chromatography (60-120 mesh). Isolated yield: 60%; White solid. Single crystal of the compound was obtained in CHCl₃ solvent. ¹H NMR (400 MHz, Chloroform-d) δ 0.92 – 1.21 (m, 13H), 1.24 – 1.32 (m, 2H), 1.34 – 1.48 (dddd, J = 8.4, 6.6, 4.3, 2.2 Hz, 6H), 1.63 – 1.75 (m, 1H), 1.82 – 1.92 (dddd, J = 12.5, 8.7, 3.5, 1.7 Hz, 2H), 2.52 – 2.62 (d, J = 4.8 Hz, 1H), 2.71 – 2.77 (td, J = 4.4, 4.3, 1.7 Hz, 1H), 4.36 – 4.48 (t, J = 2.7, 2.7 Hz, 1H), 4.81 – 4.91 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 17.27, 20.02, 20.28, 20.57, 27.75, 33.47, 34.30, 34.64, 40.03, 40.27, 40.63, 45.83, 59.82, 59.93, 89.81, 94.82.

X-ray photoelectron spectroscopy for determining the oxidation state of silver:

We have carried out X-ray photoelectron spectroscopy (XPS) which showed formation of Ag(0) from the reaction mixture (Figure S2).

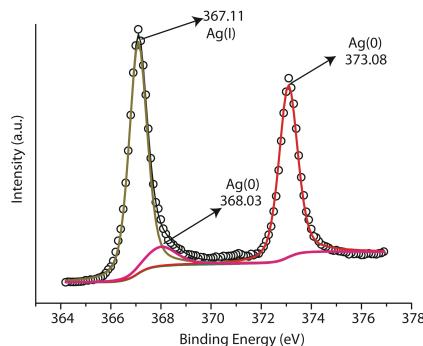


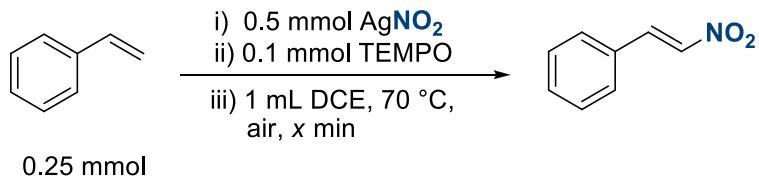
Figure S2: The deconvoluted XPS spectra of Ag3d shows peaks around 368.03 eV and 373.08 eV which are assigned for Ag(0) and the peak around 367.11 eV is for Ag(I), respectively.

Experimental details for kinetic study.

We have carried out a series of experiments in order to obtain the rate of reactions with respect to TEMPO. We plotted $\log(\text{Rate})$ vs. $\log(\text{TEMPO})$. The slope of this plot revealed a partial order with respect to TEMPO (assuming differential rate law to be multiplicative).

Using steady state analysis, it can be shown that both the suggested mechanisms (Scheme 8) are kinetically equivalent and have a partial order with respect to TEMPO undefined. In two extreme limits, the rate equation $[\text{Rate} = (k_2 k_1 C_{\text{olefin}} C_{\text{TEMPO}} C_{\text{AgNO}_2}) / (k_{-1} + k_2 C_{\text{TEMPO}})]$ gets modified to yield a partial order of 1 and 0. The $\log(\text{Rate})$ vs. $\log(\text{TEMPO})$ has been fitted to mean graph with an overall partial order of 0.4 conforming to the aforesaid limits.

A. Determination of time range for further kinetic study with styrene



| Entry | Duration (min) | Conversion (%) | GC Yield (%) |
|-------|----------------|----------------|--------------|
| 1 | 5 | 14 | 3 |
| 2 | 10 | 22 | 13 |
| 3 | 15 | 46 | 31 |
| 4 | 20 | 73 | 55 |
| 5 | 25 | 77 | 58 |
| 6 | 30 | 90 | 73 |
| 7 | 35 | 95 | 77 |
| 8 | 40 | 92 | 76 |

B. 1. Observation of yield of product in different time interval with varying TEMPO loading

Substrate styrene was taken in excess (2 mmol) in presence of 0.25 equiv. AgNO_2 . With different TEMPO loading GC- yields of the product were determined with *n*-decane as the internal standard w.r.t. nitrating agent (AgNO_2). To unravel the kinetic dependence of the designed reaction on the concentration of TEMPO we have used data for different run with varying amount of the catalyst (ranging from 0.025 mmol to 0.15 mmol). Assuming the differential rate law to be of multiplicative form and to linearize the kinetic equation employed, we have used the concentration of the reactant in large excess so as to suppress their temporal variation for a given run. We have used the method of initial slope for evaluating the partial

order with respect to the catalyst. Owing to the initial induction phase in the kinetic profile we have used the slope (rate) corresponding to 6 min for each of the TEMPO loading.

For clarity and simplicity a representative plot involving only four of the aforesaid TEMPO concentrations has been shown (Figure S3). Using steady state analysis, it can be shown that both the suggested mechanisms (Scheme 8 in manuscript) are kinetically equivalent and have a partial order with respect to TEMPO undefined. In two extreme limits, the rate equation [Rate = $(k_2 k_1 C_{\text{olefin}} C_{\text{TEMPO}} C_{\text{AgNO}_2}) / (k_{-1} + k_2 C_{\text{TEMPO}})$] gets modified to yield order (w.r.t. TEMPO) of 1 and 0. The log(Rate) vs. log(TEMPO) has been fitted to mean graph with an overall partial order of 0.4 conforming to the aforesaid limits.



1. TEMPO loading = 0.025 mmol

| Entry | Time (min) | GC Yield (%) |
|-------|------------|--------------|
| 1 | 3 | 0 |
| 2 | 6 | 2 |
| 3 | 10 | 14 |
| 4 | 15 | 28 |
| 5 | 20 | 33 |
| 6 | 30 | 49 |
| 7 | 40 | 54 |

2. TEMPO loading = 0.05 mmol

| Entry | Time (min) | GC Yield (%) |
|-------|------------|--------------|
| 1 | 3 | 0 |
| 2 | 6 | 3 |
| 3 | 10 | 18 |
| 4 | 15 | 31 |
| 5 | 20 | 42 |
| 6 | 30 | 49 |
| 7 | 40 | 56 |

3. TEMPO loading = 0.075 mmol

| Entry | Time (min) | GC Yield (%) |
|-------|------------|--------------|
| 1 | 3 | 0 |
| 2 | 6 | 3 |
| 3 | 10 | 26 |
| 4 | 15 | 49 |
| 5 | 20 | 54 |
| 6 | 30 | 55 |
| 7 | 40 | 56 |

4. TEMPO loading = 0.1 mmol

| Entry | Time (min) | GC Yield (%) |
|-------|------------|--------------|
| 1 | 3 | 0 |
| 2 | 6 | 8 |
| 3 | 10 | 25 |
| 4 | 15 | 44 |
| 5 | 20 | 48 |
| 6 | 30 | 58 |
| 7 | 40 | 57 |

5. TEMPO loading = 0.125 mmol

| Entry | Time (min) | GC Yield (%) |
|-------|------------|--------------|
| 1 | 3 | 0 |
| 2 | 6 | 5 |
| 3 | 10 | 30 |
| 4 | 15 | 48 |
| 5 | 20 | 54 |
| 6 | 30 | 56 |
| 7 | 40 | 57 |

Data for plotting log(Rate) vs. log(TEMPO) [The slope would yield the partial order w.r.t. TEMPO]

| log(rate) | log(TEMPO) |
|-----------|------------|
| 0.267 | -1.602 |
| 0.449 | -1.432 |

| | |
|-------|--------|
| 0.374 | -1.301 |
| 0.488 | -1.125 |
| 0.489 | -1.000 |
| 0.544 | -0.951 |
| 0.605 | -0.903 |
| 0.586 | -0.863 |
| 0.694 | -0.823 |

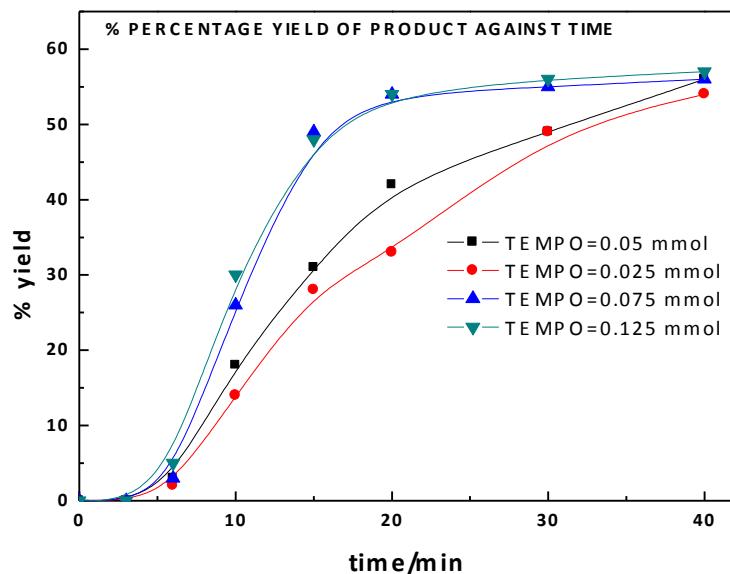


Figure S3: Variation of yield with respect to time with different TEMPO loading

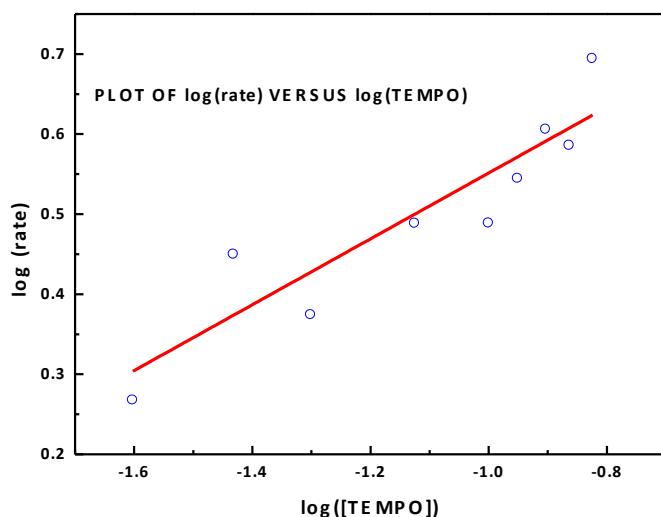


Figure S4: Plot of $\log(\text{Rate})$ vs $\log(\text{TEMPO})$. The partial order obtained with respect to TEMPO is 0.4.

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