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A facile synthesis of novel triazabicyclic molecules as potential bicyclic templates for pharmaceutical ligands by the ring opening metathesis-cross metathesis of triazatricyclo[3.2.1.$0^{2,6}$]dec-8-ene-3,5-diones

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Novel multifunctional triazabicyclic molecules are synthesized in excellent yields by the ring opening metathesis-cross metathesis of triazatricyclo [3.2.1.$0^{2,6}$]dec-8-ene-3,5-diones with various terminal olefins. The rigid synthesized molecules can be used as potential bicyclic templates for a number of pharmaceutically important ligands.

Keywords: Ring opening metathesis-cross metathesis, Grubb's catalyst, 1,2,4-triazoline–3,5-diones, triazabicyclic molecules

The development of rigid multivalent scaffolds with well defined structures is of great interest in pharmaceutical chemistry[1], in which the azabicyclic scaffolds have been known to serve as conformationally fixed surrogates of peptide turn secondary structures[2]. Recently, there is lot of interest in their synthesis as constituents of azabicyclo alkane amino acids that restrain the back bone and side chain geometry of native proteins. These bicyclic aminoacids act as valuable building blocks for constructing conformationally rigid surrogates of peptide structures that have served to probe protein chemistry and biology[2c]. An azabicyclic scaffold should be formed with stereocontrol and the ability to attach functional groups on to different positions of the heterocycle in order to mimic the side chains of common aminoacids.

F. Diederich and co-workers have shown that rigid diazabicyclic and tricyclic molecules, acts as scaffolds for potent inhibitors of thrombin (**Figure 1**, ref. 3). Michael Kahn and co-workers have shown that the secondary structure motifs such as β-turns and α-helices on rigid bicyclic templates could meet the requirement of dipeptide mimetic and can be used as novel therapeutic agents[4]. These ligands possess bicyclic or tricyclic core structures with attached side chains in order to reach the binding pockets present in the active site of enzyme. The performance of these agents in clinical setting is to be answered using ligands based on already developed scaffolds or new scaffolds. As part of the program on the development of potential scaffolds for novel therapeutic agents, the design and synthesis of a series of triazabicyclic molecules utilizing the ring opening metathesis-cross metathesis (ROM-CM) reaction was undertaken and the preliminary results of the investigation are described in this paper.

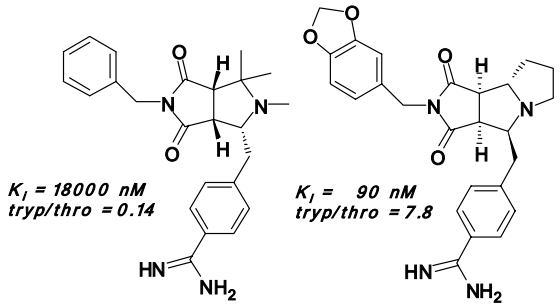


Figure 1 — Bicyclic molecules as scaffolds for potent inhibitors of thrombin

Developments in transition metal catalysed olefin metathesis had a dramatic impact in the field of chemical synthesis[5]. Among the various metathetical-based processes, the ring opening metathesis/cross metathesis (ROM-CM) reactions of norbornene analogs have received significant attention because of the ease with which these substrates undergo ROM-CM reactions leading to highly substituted five membered rings[6]. ROM-CM reactions offer unique

and efficient pathways for the synthesis of versatile organic molecules[7]. Amir H. Hoveyda and co-workers have reported an efficient and highly enantioselective ROM-CM reactions of oxabicyclic olefins leading to a wide range of 2,6-disubstituted pyrans[8], building blocks found in numerous biologically significant molecules. Recently, Jon D. Rainier and co-workers have utilized this reaction for the synthesis of highly substituted furans and pyrroles[9]. Winkler and co-workers have shown that tri- and penta heterocyclic molecules can be prepared from substituted oxanorbornenes *via* metathesis reaction[10].

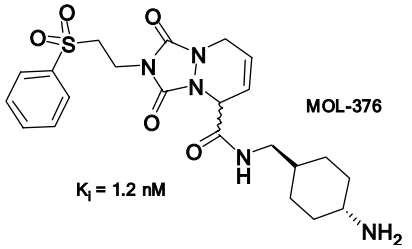


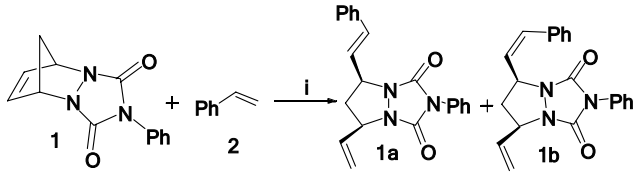
Figure 2 — Triazabicyclic molecule in peptidomimetics

The impetus to undertake the work reported in this paper came from the reports by Michael Kahn and co-workers[4,11]. Their work showed the ability of triazabicyclic molecules (**Figure 2**) in the synthesis of compounds that mimic secondary structure of proteins, especially potent and selective inhibitors of serine proteases. Although these inhibitors were potent and selective, their synthesis did not allow for the rapid introduction of diverse functionality. This prompted us to synthesize the triazabicyclic molecule from the azatricyclic olefin **1**. A survey of literature showed that there is no report on the ROM-CM of azatricyclic olefins from 4-substituted-1,2,4-triazoline-3,5-diones.

Results and Discussion

The experiments started with the ring opening metathesis-cross metathesis of 4-phenyl-2,4,6-triazatricyclo [3.2.1.0 ^{2,6}] dec-8-ene-3,5-dione **1** with styrene **2** in presence of first generation Grubbs' catalyst, which afforded the highly substituted triazabicyclic molecules **1a** and **1b** in 97% yield. The compound was isolated as a mixture of stereo isomers (*E* : *Z* = 2:1). The reaction is illustrated in **Scheme I**.

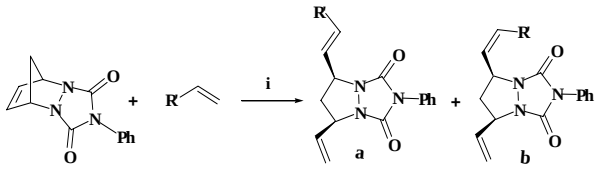
The IR spectrum of **1a** and **1b** showed characteristic absorption of carbonyl group at 1711 cm^{-1}. The ^{1}H NMR spectrum of compound **1b** showed a doublet at δ 6.73 (d, *J* = 11.4 Hz) for α proton and a doublet of doublet at δ 5.84 (dd, J_1 = 9.3 Hz, J_2 = 11.4 Hz) for β proton of phenyl (ethenyl) group, indicating the *cis* coupling. The methine proton of the carbon bearing phenyl (ethenyl) group resonated as quartet at δ = 4.99 ppm. The ^{1}H NMR spectrum of compound **1a** showed α and β protons of phenyl (ethenyl) group as doublet at δ 6.73 (d, *J* = 15.7 Hz) and doublet of doublet at δ 6.22 (dd, J_1 = 6.6 Hz, J_2 = 15.8 Hz) respectively, indicating *trans* coupling. Noted that the downfield absorption of β proton and up field absorption at δ = 4.75 ppm of the methine proton of carbon bearing the phenyl (ethenyl) group of compound **1a** also differentiate it from compound **1b**. The HOMO and HETERO COSY analysis were also in good agreement with the proposed structures. Finally the structure was confirmed by HRMS, (*m/z* = 345.1467). Similar reactivity was observed in the reaction of 4-phenyl-2,4,6-triazatricyclo [3.2.1.0^{2,6}] dec-8-ene-3,5-dione **1** with other terminal olefins. The details of the results are in **Table I**.



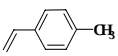
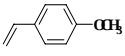
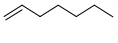
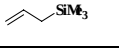
i = [Cl_2 (Cy_3P)$_2$ Ru =CHPh], CH_2Cl_2 , r.t, 2 hr, 97%.

Scheme I

Table I—ROMCM of 4-Phenyl-2,4,6-triazatricyclo[3.2.1.0^{26}] dec-8-ene-3,5-diones with various olefins

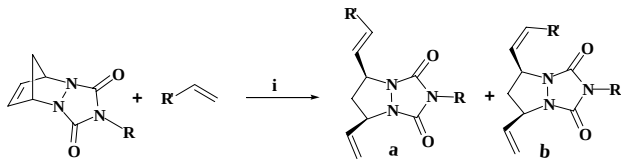


i = [Cl_2 (Cy_3P)$_2$ Ru =CHPh], CH_2Cl_2 , r.t, 2 hr

Entry	Olefin	Products (E:Z)	Yield (%)
1		1a + 1b (2:1)	97
2		2a + 2b (2:1)	96
3		3a + 3b (1.7:1)	93
4		4a + 4b (1.5:1)	94
5		5a + 5b (1.9:1)	85

Other *N*-substituted triazatricyclo[3.2.1.$0^{2,6}$]dec-8-ene-3,5-diones also afforded separable mixture of *E* and *Z* isomers under the same reaction conditions with a number of terminal olefins. The results are summarized in **Table II**.

Table II- RCM: CM of 4- Substituted- 2,4,6- triazatricyclo [3.2.1.$0^{2,6}$] dec- 8- ene- 3,5- diones



i = $[Cl_2(Cy_3P)_2Ru{=}CHPh]$, CH_2Cl_2, r.t, 2 hr

Entry	R	R'	Products (E:Z)	Yield(%)
1	Bn	Ph	6a + 6b(2.3:1)	95
2	Bn		7a + 7b(1.6:1)	98
3	Bn	$SiMe_3$	8a + 8b(1.4:1)	83
4	Cy	Ph	9a + 9b(3.7:1)	95
5	Cy		10a + 10b(1.8:1)	98
6	Cy	$SiMe_3$	11a + 11b(2.2:1)	92
7	(*p*- NO_2)Ph	Ph	12a + 12b(1.7:1)	98
8	(*p*- Cl)Bn	Ph	13a + 13b(1.3:1)	98
9	(*p*- OMe)Bn	Ph	14a + 14b (2.1:1)	99
10	(*p*- CH_3)Bn	Ph	15a + 15b (1.4:1)	99

Experimental Section

All reactions were conducted in oven-dried glasswares. Solvents used for the experiments were distilled and dried as specified. All other reagents were purchased from local supplier. All reactions were monitored by TLC (Silica gel 60 F_{254}, 0.25 mm, Merck), visualization was effected with UV and/or by developing in iodine or by staining with Enholm-Yellow solution. Chromatography refers to open column chromatography on silica gel (100-200 mesh). NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz respectively on a Brucker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer; absorptions are reported in cm^{-1}. Mass spectra were recorded using JEOL JMS 600H mass spectrometer. Abbreviations used in ^{1}H NMR are s-singlet, d-doublet, t-triplet, q-quartet, dd-doublet of a doublet and m-multiplet.

Details of a typical experimental procedure: To a solution of 4-phenyl-2, 4, 6-triazatricyclo [3.2.1.$0^{2,6}$] dec-8-ene-3,5-dione **1** (50 mg, 0.21 mmole), and styrene **2** (44 mg, 0.42 mmole) in dichloromethane (5 mL), first generation Grubbs' catalyst (8 mg, 5 mole%) was added under nitrogen atmosphere. The reaction mixture was stirred for 2 hr at room temperature and the reaction was monitored by TLC. When the reaction was complete, the mixture was diluted with water (20 mL) and extracted using dichloromethane (3 × 20 mL). The combined organic layers were washed with saturated brine and dried over anhydrous sodium sulphate. The crude product obtained was purified by silica gel column chromatography to afford the products **1a** and **1b** (*E* and *Z* isomers) as light brown viscous liquids (*E:Z* = 2:1) in 97% yield.

8-[(Phenyl)ethenyl]-3-phenyl-6-vinyl-1,3, 5-triaza-bicyclo[3.3.$0^{1,5}$]octane-2,4-dione

***E* isomer 1a**: Light brown viscous liquid, R_f: 0.42 (35% EtOAc-hexane). IR (Neat): 2925, 2854, 1769, 1711, 1598, 1500, 1406, 1277, 1176, 1124, 965, 929, 751, 692, 497 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.20 (m, 10H), 6.73 (d, J = 15.7 Hz, 1H), 6.22 (dd, J_1 = 6.6 Hz, J_2 = 15.8 Hz, 1H), 6.00-5.89 (m, 1H), 5.47 (d, J = 17.1 Hz, 1H), 5.31 (d, J = 10.3 Hz, 1H), 4.75 (q, 1H), 4.60 (q, 1H), 2.88-2.78 (m, 1H), 2.40 - 2.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 153.2, 135.8, 134.9, 133.3, 129.0, 128.6, 128.2, 127.9, 126.7, 125.8, 125.3, 118.3, 59.3, 59.2, 41.6; HRMS (EI): *m/z* Calcd. for $C_{21}H_{19}N_3O_2$: 345.1477. Found: 345.1467.

***Z* isomer 1b**: Light brown viscous liquid, R_f: 0.62 (35% EtOAc-hexane). IR (Neat): 2926, 2855, 1768, 1711, 1598, 1498, 1405, 1277, 1177, 1124, 1029, 985, 928, 759, 695, 642, 499 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52-7.25 (m, 10H), 6.73 (d, J = 11.4 Hz, 1H), 6.01-5.90 (m, 1H), 5.84 (dd, J_1 = 9.3 Hz, J_2 =11.4 Hz, 1H), 5.48 (d, J = 17 Hz, 1H), 5.34 (d, J = 10.2 Hz, 1H), 4.99 (q, 1H), 4.53 (q, 1H), 2.82-2.73 (m, 1H), 2.23-2.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 153.0, 135.7, 134.6, 133.1, 129.0, 128.7, 128.6, 128.5, 127.8, 127.6, 125.3, 118.5, 59.2, 55.1, 42.2; HRMS (EI): *m/z* Calcd. for $C_{21}H_{19}N_3O_2$: 345.1477. Found: 345.1467.

8-[2-(4-Methylphenyl)ethenyl]-3-phenyl-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 2a**: Light brown viscous liquid, R_f: 0.45 (35% EtOAc-hexane). IR (Neat): 2923, 1768, 1711, 1599, 1502, 1405, 1276, 1179, 1124, 966, 800, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.08 (m, 9H), 6.68 (d, J = 15.5 Hz, 1H), 6.14 (dd, J_1 = 15.7 Hz, J_2 = 6.7 Hz, 1H), 5.97-5.86 (m, 1H), 5.43 (d, J = 17.2 Hz, 1H), 5.28 (d = 10.1 Hz, 1H), 4.67 (q, 1H), 4.53 (q, 1H), 2.79-2.70 (m, 1H), 2.32 (s, 3H), 2.25- 2.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6, 153.5, 137.9, 137.8, 135.0, 133.2, 133.1, 132.0, 129.2, 129.0, 127.7, 126.5, 125.1, 124.9, 124.8, 118.1, 59.3, 59.2, 41.6, 21.2; HRMS (EI): *m/z* Calcd. for $C_{22}H_{21}N_3O_2$: 359.1634. Found: 359.1650.

***Z* isomer 2b:** Light brown viscous liquid, R_f: 0.60 (35% EtOAc-hexane). IR (Neat): 2924, 1768, 1710, 1597, 1502, 1405, 1124, 759, 688, 500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.06 (m, 9H), 6.62 (d, J = 11.4 Hz, 1H), 5.94-5.85 (m, 1H), 5.70 (dd, J_1 = 9.3 Hz , J_2 = 11.3 Hz, 1H), 5.41 (d, J = 17 Hz, 1H), 5.27 (d, J = 10.2 Hz, 1H), 4.94 (q, 1H), 4.43 (q, 1H), 2.73-2.66 (m, 1H), 2.28 (s, 3H), 2.22-2.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 153.0, 137.3, 134.7, 133.1, 132.9, 131.9, 129.2, 128.8, 128.7, 128.1, 127.8, 125.2, 118.5, 59.2, 55.3, 42.3, 21.3; HRMS (EI): *m/z* Calcd. for $C_{22}H_{21}N_3O_2$: 359.1634. Found: 359.1645.

8-[2-(4-Methoxyphenyl)ethenyl]-3-phenyl -6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}] octane-2,4-dione

***E* isomer 3a**: Light brown viscous liquid, R_f: 0.36 (35% EtOAc-hexane). IR (Neat): 2919, 1769, 1703, 1508, 1458, 1246, 1173, 1027, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.24 (m, 7H), 6.81 (d, J = 8.7 Hz, 2H), 6.56 (d, J = 15.7 Hz, 1H), 6.03 (dd, J_1 = 6.8 Hz, J_2 =15.7 Hz, 1H), 5.95-5.84 (m, 1H), 5.41 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.5 Hz, 1H), 4.64 (q, 1H), 4.49 (q, 1H), 3.75 (s, 3H), 2.76-2.66 (m, 1H), 2.22-2.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 153.4, 134.9, 132.6, 131.9, 128.8, 128.4, 127.8, 127.7, 125.1, 123.5, 118.0, 113.9, 59.2, 59.2, 41.5; MS (FAB): *m/z* Calcd. for $C_{22}H_{21}N_3O_3$[M+1]: 376.42. Found: 376.85.

***Z* isomer 3b**: Light brown viscous liquid, R_f: 0.48 (35% EtOAc-hexane). IR (Neat): 2917, 2365, 2845, 1761, 1706, 1509, 1408, 1256, 1126, 1030, 760, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.25 (m, 7H), 6.87 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 11.4 Hz, 1H), 6.01-5.90 (m, 1H), 5.73 (dd, J_1 = 9.3 Hz, J_2 = 11.5 Hz, 1H), 5.50 (d, J = 17.0 Hz, 1H), 5.35 (d, J = 10.4 Hz, 1H), 5.03 (q, 1H), 4.56 (q, 1H), 3.8 (s, 3H), 2.83-2.74 (m, 1H), 2.28-2.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 153.2, 134.7, 132.7, 131.9, 130.1, 128.9, 128.2, 127.8, 127.4, 125.2, 118.4, 114.0, 59.2, 55.3, 42.2; MS(FAB): *m/z* Calcd. for $C_{22}H_{21}N_3O_3$ [M+1]: 376.42. Found: 376.74.

8-[Hept-1-enyl]-3-phenyl-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 4a**: Brown viscous liquid, R_f : 0.49 (35% EtOAc-hexane). IR (Neat): 2926, 2856, 1770, 1712, 1502, 1402, 1275, 1123, 983, 761, 689, 496 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52-7.15 (m, 5H), 5.98-5.78 (m, 2H), 5.54-5.42 (m, 2H), 5.29 (d, J = 10.2 Hz, 1H), 4.55-4.47 (m, 2H), 2.77-2.68 (m, 1H), 2.21-2.03 (m, 3H), 1.41-1.28 (m, 6H), 0.90-0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 153.4, 135.5, 135.0, 132.0, 128.9, 127.8, 126.5, 125.3, 118.2, 59.3, 59.1, 41.7, 32.1, 31.4, 28.5, 22.5, 14.1; HRMS (EI): *m/z* Calcd. for $C_{20}H_{25}N_3O_2$: 339.1947. Found: 339.1973.

***Z* isomer 4b**: Brown viscous liquid, R_f: 0.60 (35% EtOAc-Hexane). IR (Neat): 2927, 2856, 1770, 1713, 1502, 1403, 1274, 1177, 1124, 1029, 983, 762, 690, 641, 495 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.15 (m, 5H), 6.00-5.86 (m, 1H), 5.70-5.61(m, 1H), 5.53-5.51 (m, 2H), 5.31 (d, J = 10.2 Hz, 1H), 4.82 (q, 1H), 4.53 (q, 1H), 2.78-2.65 (m, 1H), 2.26-2.05 (m, 3H), 1.46-1.25 (m, 6H), 0.89-0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4, 153.4, 135.2, 135.0, 134.8, 131.9, 128.9, 127.8, 126.4, 125.2, 118.3, 59.3, 59.3, 54.5, 41.9, 31.5, 29.7, 27.6, 22.5, 14.0; HRMS (EI): *m/z* Calcd. for $C_{20}H_{25}N_3O_2$: 339.1947. Found: 339.1970.

3-Phenyl-8-[(3-trimethylsilyl)propenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 5a**: White viscous liquid, R_f: 0.48 (35% EtOAc-hexane); IR (Neat): 2966, 2357, 1778, 1712, 1551, 1504, 1400, 1249, 1121, 856, 764, 689 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.13 (m, 5H), 5.96 –5.73 (m, 2H), 5.45-5.26 (m, 3H), 4.52-4.42 (m, 2H), 2.75-2.61 (m, 1H), 2.19-2.07 (m, 1H), 1.56-1.48 (m, 2H), -0.003 (m, 9H); ^{13}C NMR (75MHz, $CDCl_3$): δ 153.4, 153.3, 135.0, 132.6, 132.0, 128.9, 127.8, 125.4, 124.7, 124.7, 118.2, 59.9, 59.2, 42.2, 23.1, -1.8; MS(FAB): *m/z* Calcd. for $C_{19}H_{25}N_3O_2Si$ [M+1]: 356.21. Found: 356.29.

***Z* isomer 5b**: White viscous liquid, R_f: 0.59 (35% EtOAc-hexane). IR (Neat): 2959, 2366, 1769, 1712, 1503, 1402, 1249, 1174, 1121, 855, 689, 495 cm^{-1}; ^{1}H

NMR (300 MHz, $CDCl_3$): δ 7.48-7.20 (m, 5H), 5.96-5.85 (m, 1H), 5.66 (m, 1H), 5.47-5.27 (m, 3H), 4.77 (q, 1H), 4.52 (q, 1H), 2.74-2.65 (m, 1H), 2.15-2.06 (m, 1H), 1.80-1.67 (m, 1H), 1.57-1.51 (m, 1H), -0.20 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 153.4, 134.9, 131.5, 128.9, 127.8, 125.4, 124.2, 118.2, 59.3, 54.4, 41.9, 19.3, -1.7; MS(FAB): *m/z* Calcd. for $C_{19}H_{25}N_3O_2Si$ [M+1]: 356.21. Found: 356.27.

3-Benzyl-8-[(phenyl)ethenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 6a**: Light brown viscous liquid, R_f: 0.35 (35% EtOAc-hexane). IR (Neat): 2934, 1769, 1710, 1436, 1410, 1358, 1117, 1065, 965, 750, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.25 (m, 10H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.18-6.13 (m, 1H), 5.96-5.85 (m, 1H), 5.44 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 4.63 (s, 2H), 4.62-4.59 (m, 2H), 4.47-4.37 (m, 1H), 2.80-2.72 (m, 1H), 2.29-2.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 154.8, 135.8, 135.7, 135.0, 133.3, 129.2, 128.9, 128.7, 128.6, 128.2, 128.1, 126.7, 125.8, 118.4, 59.4, 59.1, 43.2, 41.9; MS (FAB): *m/z* Calcd. for $C_{22}H_{21}N_3O_2$[M+1]: 360.16. Found: 360.11.

***Z* isomer 6b**: Light brown viscous liquid, R_f: 0.49 (35% EtOAc-hexane); IR (Neat): 2922, 2851, 2366, 1771, 1710, 1443, 1236, 1122, 1076, 926, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.18 (m, 10H), 6.71 (d, *J* = 11.5 Hz, 1H), 5.95-5.84 (m, 1H), 5.74 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.31(d, *J* = 10.0 Hz, 1H), 4.86 (q, 1H), 4.61 (s, 2H), 4.39 (q, 1H), 2.75-2.66 (m, 1H), 2.24-2.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.5, 154.4, 135.7, 134.7, 133.1, 128.9, 128.7, 128.6, 128.0, 127.6, 118.5, 59.1, 55.0, 43.1, 42.5; MS(FAB): *m/z* Calcd. for $C_{22}H_{21}N_3O_2$[M+1]: 360.16. Found: 360.14.

3-Benzyl-8-[hept-1-enyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

E isomer 7a: Light brown viscous liquid, R_f: 0.53 (35% EtOAc-hexane). IR (Neat) : 2926, 2855, 2364, 2331, 1770, 1716, 1440, 1414, 1355, 1112, 1073, 928, 756, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.23 (m, 5H), 5.93-5.75 (m, 2H), 5.50- 5.25 (m, 3H), 4.60 (s, 2H), 4.39-4.30 (m, 2H), 2.74-2.61 (m, 1H), 2.27-2.01 (m, 3H), 1.40-1.26 (m, 6H), 1.00-0.96 (m, 1H), 0.90-0.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 154.5, 135.7, 135.3, 135.0, 128.8, 128.6, 127.9, 126.6, 118.1, 59.2, 59.1, 43.0, 42.0, 32.1, 30.1, 29.1, 22.5, 14.1; MS(FAB): *m/z* Calcd. for $C_{21}H_{27}N_3O_2$ [M+1]: 354.46. Found: 354.26.

***Z* isomer 7b**: Light brown viscous liquid, R_f: 0.59 (35% EtOAc-hexane). IR (Neat) : 2926, 2855, 2364, 1770, 1716, 1440, 1414, 1355, 1233, 1120, 1073, 929, 755, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.26 (m, 5H), 5.93-5.74 (m, 1H), 5.66-5.58 (m, 1H), 5.47-5.39 (m, 2H), 5.28 (d, *J* = 10.1 Hz, 1H), 4.68-4.61 (m, 1H), 4.59 (s, 2H), 4.43-4.29 (m, 1H), 2.71-2.62 (m, 1H), 2.32-2.02 (m, 3H), 1.40-1.25 (m, 6H), 0.93-0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 154.7, 135.7, 135.2, 135.0, 134.8, 128.9, 128.7, 128.0, 126.8, 126.6, 118.3, 59.2, 59.0, 54.4, 43.0, 42.1, 32.1, 31.4, 29.0, 22.6, 14.1; MS(FAB): *m/z* Calcd. for $C_{21}H_{27}N_3O_2$ [M+1]: 354.46. Found: 354.10.

3-Benzyl-8-[(3-trimethylsilyl)propenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 8a**: White viscous liquid, R_f: 0.54 (35% EtOAc-hexane). IR (Neat): 2958, 2931, 1761, 1711, 1440, 1409, 1354, 1246, 1142, 957, 848, 749, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.41-7.17 (m, 5H), 5.91-5.73 (m, 2H), 5.42-5.24 (m, 3H), 4.59 (s, 2H), 4.38-4.28 (m, 2H), 2.65-2.61 (m, 1H), 2.14-2.07 (m,1H), 1.57-1.51 (m, 2H), -0.02 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ154.8, 151.7, 135.8, 135.0, 132.6, 132.4, 128.9, 128.7, 128.0, 125.3, 124.8, 118.2, 59.7, 59.2, 43.0, 42.4, 23.0, -1.84; MS(FAB): *m/z* Calcd. for $C_{20}H_{27}N_3O_2Si$[M+1]: 370.19. Found: 370.14.

***Z* isomer 8b**: White viscous liquid, R_f: 0.58 (35% EtOAc-hexane). IR (Neat): 2964, 2913, 1769, 1702, 1415, 1351, 1249, 856, 752, 699, 493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.40-7.23 (m, 5H), 5.91-5.80 (m, 1H), 5.63 (q, 1H), 5.43-5.24 (m, 3H), 4.67-4.58 (m, 3H), 4.37 (q, 1H), 2.65-2.56 (m, 1H), 2.10-2.00 (m, 1H), 1.57-1.49 (m, 2H), 0.02 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ154.2, 154.0, 134.9, 131.2, 128.9, 128.7, 128.0, 124.2, 118.3, 59.2, 54.1, 43.1, 42.1, 19.3, -1.7; MS(FAB): *m/z* Calcd. for $C_{20}H_{27}N_3O_2$ Si[M+1]: 370.19. Found: 370.23

3-Cyclohexyl-8-[phenylethenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 9a**: Light brown viscous liquid, R_f: 0.40 (35% EtOAc-hexane). IR (Neat): 2938, 2850, 2371, 1758, 1707, 1418, 1382, 1104, 965, 748 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ7.55-7.22 (m, 5H), 6.69 (d, *J* = 15.7 Hz, 1H), 6.17 (dd, J_1 = 6.7 Hz, J_2 = 15.8 Hz, 1H), 5.96-5.85 (m, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.60 (q, 1H), 4.46 (q ,1H), 3.93-3.76 (m, 1H), 2.81-2.71 (m, 1H), 2.27-2.07 (m, 3H), 1.85-1.18 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$):

δ155.4, 155.0, 135.9, 135.2, 133.1, 129.0, 128.6, 128.4, 128.1, 126.7, 126.2, 118.1, 59.2, 59.1, 52.3, 41.7, 29.7, 29.4, 25.8, 25.0; MS(FAB): *m/z* Calcd. for $C_{21}H_{25}N_3O_2$ [M+1] : 351.19. Found: 351.08.

***Z* isomer 9b**: Light brown viscous liquid, R_f: 0.49 (35% EtOAc-hexane). IR (Neat): 2940, 2851, 2401, 1760, 1710, 1121, 958, 751 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ7.39-7.26 (m, 5H), 6.70 (d, *J* = 11.45 Hz, 1H), 5.97-5.86 (m, 1H), 5.76 (t, *J* = 10.3 Hz, 1H), 5.45 (d, *J* = 16.9 Hz, 1H), 5.31 (d, *J* = 10.2 Hz , 1H), 4.86 (q, 1H), 4.38 (q, 1H), 3.83-3.74 (m, 1H), 2.76-2.67 (m, 1H), 2.24-2.04 (m, 3H), 1.83-1.16 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$):δ154.8, 154.4, 135.9, 135.0, 132.7, 129.1, 128.8, 128.5, 127.5, 118.3, 59.1, 54.9, 52.2, 42.2, 29.7, 29.4, 29.3, 25.8, 25.0; MS (FAB): *m/z* Calcd. for $C_{21}H_{25}N_3O_2$[M+1]: 351.19. Found: 351.35.

3-Cyclohexyl-8-[hept-1-enyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 10a**: Light brown viscous liquid, R_f: 0.52 (35% EtOAc-hexane). IR (Neat): 2923, 2852, 2344, 1764, 1708, 1551, 1399, 1104, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ5.94-5.76 (m, 2H), 5.51-5.37 (m, 2H), 5.28 (d, *J* = 10.6 Hz, 1H), 4.41-4.32 (m, 2H), 3.81-3.73 (m, 1H), 2.71-2.62 (m, 1H), 2.16-2.05 (m, 5H), 1.84-1.65 (m, 6H), 1.42-1.25 (m, 8H), 0.91-0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ155.2, 154.9, 135.3, 135.2, 126.8, 118.0, 59.2, 59.1, 52.1, 41.8, 32.8, 32.1, 31.4, 29.4, 28.5, 25.8, 25.0, 22.5, 14.1; MS(FAB): *m/z* Calcd. for $C_{20}H_{31}N_3O_2$[M+1]: 346.48. Found: 346.64.

***Z* isomer 10b**: Light brown viscous liquid, R_f: 0.66 (35% EtOAc-hexane). IR (Neat): 2942, 2846, 2350, 1769, 1702, 1543, 1404, 1111, 769 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ5.95-5.84 (m, 1H), 5.66-5.58 (m, 1H), 5.48-5.40 (m, 2H), 5.29 (d, *J* = 10.2 Hz, 1H), 4.69 (q, 1H), 4.39 (q, 1H), 3.81-3.73 (m, 1H), 2.70-2.62 (m, 1H), 2.16-2.06 (m, 5H), 1.84-1.61 (m, 6H), 1.41-1.22 (m, 8H), 0.90 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ155.1, 155.3, 135.1, 134.6, 126.9, 118.1, 59.2, 54.3, 52.1, 41.9, 31.5, 29.7, 29.4, 29.4, 29.1, 27.6, 25.8, 25.0, 22.5, 14.1; MS(FAB): *m/z* Calcd. for $C_{20}H_{31}N_3O_2$[M+1]: 346.48. Found: 346.26.

3-Cyclohexyl-8-[(3-trimethylsilyl) propenyl]-6-vinyl-1,3,5-iazabicyclo [3.3.0^{1,5}]octane-2,4-dione

***E* isomer 11a**: Light brown viscous liquid, R_f: 0.56 (35% EtOAc-hexane). IR (Neat): 2951, 2927, 2351, 1769, 1702, 1547, 1421, 1242, 854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ5.92-5.72 (m, 2H), 5.41-5.23 (m, 3H), 4.36-4.26 (m, 2H), 3.83-3.69 (m, 1H), 2.67-2.58 (m, 1H), 2.14-2.03 (m, 3H), 1.82-1.54 (m, 8H), 1.31-1.11 (m, 2H), 0.002 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ155.2, 155.0, 135.3, 132.1, 125.0, 117.9, 59.7, 59.1, 52.0, 42.2, 29.4, 29.3, 25.8, 25.0, 22.9, -1.90; MS(FAB): *m/z* Calcd. for $C_{19}H_{31}N_3O_2Si$ [M+1]: 362.21. Found: 362.45.

***Z* isomer 11b**: Light brown viscous liquid, R_f: 0.60 (35% EtOAc-hexane). IR (Neat): 2934, 2862, 2364, 2332, 1763, 1707, 1558, 1414, 1382, 1248, 1104, 856, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ5.91-5.80 (m, 1H), 5.62 (m, 1H), 5.42-5.23 (m, 3H), 4.63 (q, 1H), 4.37 (q, 1H), 3.77-3.69 (m, 1H), 2.62-2.58 (m, 1H), 2.13-2.01 (m, 3H), 1.81-1.51 (m, 8H), 1.25-1.10 (m, 2H), 0.0003 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ155.1, 155.0, 135.2, 130.9, 124.6, 118.0, 59.2, 54.0, 52.1, 41.8, 29.4, 29.3, 25.8, 25.0, 19.2, -1.7; MS(FAB): *m/z* Calcd. for $C_{19}H_{31}N_3O_2Si$[M+1]: 362.21. Found: 362.81.

3-[4-Nitrophenyl]-8-[phenylethenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 12a**: Light brown viscous liquid, R_f: 0.49 (60% EtOAc-hexane); IR (Neat): 2929, 1774, 1700, 1596, 1513, 1388, 1119, 854, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ8.33 (d, *J* = 9.09 Hz, 2H), 7.95 (d, *J* = 9.1 Hz, 2H), 7.42-7.28 (m, 5H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, J_1 = 6.8 Hz, J_2 = 15.7 Hz, 1H), 6.05-5.94 (m, 1H), 5.53 (d, *J* = 17.0 Hz, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 4.82 (q, 1H), 4.68 (q, 1H), 2.99-2.90 (m, 1H), 2.43-2.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ151.8, 151.4, 145.4, 137.8, 136.9, 135.5, 134.0, 128.7, 128.3, 128.0, 124.9, 124.3, 119.0, 59.9, 59.1, 42.6; MS(FAB): *m/z* Calcd. for $C_{21}H_{18}N_40_4$ [M+1]: 391.13. Found: 391.30.

***Z* isomer 12b**: Light brown viscous Liquid, R_f: 0.55 (60% EtOAc-hexane); IR (Neat): 2919, 2364, 1774, 1704, 1602, 1521, 1391, 1121, 963, 856 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ8.31 (d, *J* = 9.1 Hz, 2H), 7.92 (d, *J* = 9.1 Hz, 2H), 7.40-7.30 (m, 5H), 6.81 (d, *J* = 11.4 Hz, 1H), 6.04-5.93 (m, 1H), 5.82 (dd, J_1 = 9.4, J_2 = 11.4 Hz, 1H), 5.52 (d, *J* = 16.9 Hz, 1H), 5.45 (d, *J* = 10.2 Hz, 1H), 5.05 (q, 1H), 4.58 (q, 1H), 2.88-2.82 (m, 1H), 2.37-2.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ151.6, 151.4, 146.2, 137.9, 135.6, 134.1, 133.8, 128.8, 128.6, 127.8, 124.5, 124.3, 119.1, 59.3, 55.2, 42.3; MS(FAB): *m/z* Calcd. for $C_{21}H_{18}N_40_4$ [M+1]: 391.13. Found: 391.26.

3-(4-Chlorobenzyl)-8-[(phenyl)ethenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 13a**: Pale yellow viscous liquid, R_f: 0.59 (60% EtOAc-hexane); IR (Neat): 2926, 1767, 1708, 1493, 1443, 1414, 1354, 1096, 924, 763, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.40-7.24 (m, 9H), 6.68 (d, J = 15.7 Hz, 1H), 6.15 (dd, J_1 = 6.8 Hz, J_2 = 15.8 Hz, 1H), 5.95-5.83 (m, 1H), 5.43 (d, J = 17.0 Hz, 1H), 5.29 (d, J = 10.2 Hz, 1H), 4.59 (m, 3H), 4.45 (q, 1H), 2.81-2.72 (m, 1H), 2.29-2.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ155.1, 154.8, 135.9, 135.7, 133.9, 129.7, 129.0, 128.8, 128.7, 128.5, 128.2, 126.9, 125.9, 118.4, 59.4, 59.2, 42.3, 42.0; HRMS [EI]: *m/z* Calcd. for $C_{22}H_{20}Cl\,N_3O_2$: 393.1244. Found: 393.1256.

***Z* isomer 13b**: Pale yellow viscous liquid, R_f: 0.63 (60% EtOAc-hexane). IR (Neat): 2927, 2853, 1768, 1709, 1490, 1441, 1412, 1354, 1242, 1094, 966, 924, 751, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.40-7.25 (m, 9H), 6.71 (d, J = 11.4 Hz, 1H), 5.94-5.83 (m, 1H), 5.73 (dd, J_1= 9.4 Hz, J_2 = 11.2 Hz, 1H), 5.43 (d, J = 17.0 Hz, 1H), 5.31 (d, J = 10.2 Hz, 1H), 4.83 (q, 1H), 4.56 (s, 2H), 4.46-4.34 (m, 1H), 2.81-2.66 (m, 1H), 2.35-2.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ154.5, 154.5, 135.7, 134.6, 133.3, 129.0, 128.8, 128.5, 128.0, 127.7, 118.8, 59.1, 55.1, 43.2, 42.6; HRMS [EI]: *m/z* Calcd. for $C_{22}H_{20}Cl\,N_3O_2$: 393.1244. Found: 393.1248.

3-(4-Methoxy benzyl)-8-[(phenyl)ethenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 14a**: Dark brown viscous liquid, R_f: 0.48 (60% EtOAc-hexane); IR (Neat): 2931, 1766, 1706, 1610, 1515, 1440, 1353, 1246, 1178, 1099, 1032, 960, 822, 746, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.40-7.23 (m, 7H), 6.82 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 15.8 Hz, 1H), 6.15 (t, J = 6.7 Hz, 1H), 5.94- 5.82 (m, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.27 (d, J = 10.2 Hz, 1H), 4.53-4.57 (m, 3H), 4.42 (q, 1H), 3.77 (s, 3H), 2.77-2.68 (m, 1H), 2.25-2.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ159.5, 153.4, 134.7, 133.6, 131.4, 128.8, 128.1, 127.2, 126.2, 125.4, 123.5, 117.9, 113.8, 59.2, 59.2, 55.6, 41.5; HRMS [EI]: *m/z* Calcd. for $C_{23}H_{23}N_3O_3$: 389.1739. Found: 389.1725.

***Z* isomer 14b**: Light yellow brownish viscous liquid, R_f: 0.60 (60% EtOAc-hexane). IR (Neat): 2928, 1765, 1713, 1514, 1442, 1352, 1247, 1176, 1101, 1030, 917, 771, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.37-7.26 (m, 7H), 6.82 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 11.5 Hz, 1H), 5.94-5.83 (m, 1H), 5.73 (dd, J_1 = 11.0 Hz, J_2 = 9.6 Hz, 1H), 5.43 (d, J =17.1 Hz, 1H), 5.30 (d, J = 10.2 Hz , 1H), 4.83 (q, 1H), 4.55 (s, 2H), 4.36 (q, 1H), 3.77 (s, 3H), 2.67-2.71 (m, 1H), 2.22-2.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ158.3, 153.3, 134.7, 132.7, 131.9, 130.1, 128.9, 128.2, 127.8, 127.5, 125.1, 118.1, 112.1, 58.7, 55.2, 55.0, 42.2; HRMS [EI]: *m/z* Calcd. for $C_{23}H_{23}N_3O_3$: 389.1739. Found: 389.1729.

3-(4-Methyl benzyl)-8-[(phenyl)ethenyl]-6-vinyl-1,3,5-triazabicyclo[3.3.0^{1,5}]octane-2,4-dione

***E* isomer 15a**: Dark brown viscous liquid, R_f: 0.54 (60% EtOAc-hexane); IR (Neat): 2928, 1770, 1711, 1451, 1414, 1355, 1106, 968, 924, 754, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.34-7.24 (m, 7H), 7.12 (d, J = 7.7 Hz, 2H), 6.67 (d, J = 15.8 Hz, 1H), 6.16 (t, J = 6.7 Hz, 1H), 5.95-5.84 (m, 1H), 5.43 (d, J =17.0 Hz, 1H), 5.28 (d, J =10.2 Hz, 1H), 4.55-4.59 (m, 3H), 4.45 (q, 1H), 2.79-2.70 (m, 1H), 2.33 (s, 3H), 2.27-2.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ153.7, 154.6, 137.8, 135.5, 133.7, 133.1, 131.4, 129.3, 128.2, 127.5, 126.3, 125.1, 124.8, 124.8, 118.1, 59.3, 59.2, 55.4, 42.0, 20.2; HRMS [EI]: *m/z* Calcd. for $C_{23}H_{23}N_3O_3$: 373.1790. Found: 373.1782.

***Z* isomer 15b**: Light brownish yellow viscous liquid, R_f: 0.65 (60% EtOAc-hexane); IR (Neat): 2927, 1761, 1706, 1442, 1408, 1350, 1232, 1098, 989, 918, 775, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.37-7.26 (m, 7H), 7.10 (d, J = 7.8 Hz, 2H), 6.70 (d, J = 11.5 Hz , 1H), 5.94-5.84 (m, 1H), 5.73 (t, J = 9.3 Hz, 1H), 5.43 (d, J = 17.0 Hz , 1H), 5.30 (d, J = 10.2 Hz, 1H), 4.84 (q, 1H), 4.57 (s, 2H), 4.37 (q, 1H), 2.74-2.65 (m, 1H), 2.33 (s, 3H), 2.20-2.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ153.3, 153.0, 137.4, 134.7, 133.1, 132.9, 131.9, 129.2, 128.8, 128.7, 128.1, 127.8, 125.2, 118.5, 59.3, 59.1, 55.3, 42.3, 21.3; HRMS [EI]: *m/z* Calcd. for $C_{23}H_{23}N_3O_3$: 373.1790. Found: 373.1783.

Conclusion

In conclusion, a facile synthesis of multifunctional triazabicyclic molecules utilizing the ring opening metathesis-cross metathesis of tricyclic olefins prepared from cyclopentadiene and various substituted triazoline-3,5-diones is described. The present synthetic methodology involves simple reaction steps leading to highly functionalized triazabicyclic substrates. The rigid synthesized molecules can be used as potential bicyclic templates for a number of pharmaceutically important ligands. The recognition groups or molecules can be grafted

on to these promising scaffolds at three different points *via* phenyl (ethenyl)-, vinyl- and the nitrogen atom of the urazole ring. Further work to explore the potential of these molecules is in progress and will be reported in due course.

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