Supporting Information:

Radical Transfer Hydroamination with Aminated Cyclohexadienes Using Polarity Reversal Catalysis: Scope and Limitations

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Experimental Section:

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in hot dried glassware under an argon atmosphere. Tetrahydrofuran (THF) was freshly distilled from potassium under argon. Diethylether (Et₂O) was freshly distilled from K/Na under argon. Dichloromethane (CH₂Cl₂) was freshly distilled from phosphorus(V)oxide (P₂O₅). Triethylamine were distilled from CaH₂ and stored over molecular sieve 4 Å. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Fluka or Acros. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AMX 400, ARX 300. TLC was performed using Merck silica gel 60 F254 plates; detection with UV or dipping into a solution of KMnO₄ (1.5 g in 400 mL H₂O, 5 g

NaHCO₃) or a solution of Ce(SO₄)₂·xH₂O (10 g), phosphormolybdic acid hydrate (25 g), concentrated H₂SO₄ (60 mL), and H₂O (940 mL), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 μm) applying a pressure of about 0.4 bar. IR spectra were recorded on a *Bruker IFS-28* and a *Digilab FTS 4000* spectrophotometer. Mass spectra were recorded on a *Finnigan MAT 4200S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quattro LCZ* (ESI); and peaks are given in *m/z* (% of basis peak).

General Procedure (1) for the Synthesis of Enamidones from 1,3-Diketones:

A catalytic amount of an acid (p-toluenesulfonic acid; TsOH) and the amide (1.25 equiv.) was added to a stirred solution of acetylacetone (1.0 equiv.) in toluene. The mixture was heated under reflux using a Dean-Stark apparatus. After 6-8 h the reaction mixture was allowed to cool to r.t. The mixture was washed with saturated NaHCO₃ solution and water, dried over MgSO₄, concentrated under reduced pressure. The solid crude material was purified by FC (SiO₂) (pentane / *t*-butylmethylether) to afford the desired corresponding keto-amide.

***N*-((*Z*)-1-Methyl-3-oxobut-1-enyl)acetamide:** Prepared according to the general procedure (1) using acetylacetone (5.0 g, 50 mmol), acetamide (3.7 g, 63 mmol), PTSA (0.5 g) in toluene (180 ml). Purification by FC (pentane / MTBE 5:1) provided *N*-((*Z*)-1-Methyl-3-oxobut-1-enyl)acetamide as a white solid^a (5.0 g, 72 %). IR (neat) 3125br.w, 1727s, 1632s, 1576s, 1467m, 1421s, 1363s, 1246s, 1211s, 1179s, 1035s, 981s, 956s, 925w, 835m, 795s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.11 (s, 3H, CH₃), 2.12 (s, 3H, CH₃), 2.33 (d, 3H, *J* = 0.9 Hz, NHCCCH₃), 5.30 (s, br., 1H, CH-vinyl), 11.97 (s, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 21.71 (CH₃), 25.30 (CH₃), 30.39 (CH₃), 105.22 (CH), 155.22 (C), 169.65 (C), 199.57 (C). HRMS (ESI) calculated for C₇H₁₁NO₂Na ([M+Na]⁺): 164.0682. Found: 164.0683.

***N*-((*Z*)-1-Methyl-3-oxobut-1-enyl)benzamide:** Prepared according to the general procedure (1) using acetylacetone (5.0 g, 50 mmol), benzamide (9.8 g, 63 mmol), PTSA (0.5 g) in toluene (180 ml). Purification by FC (pentane / MTBE 5:1) provided *N*-((*Z*)-1-Methyl-3-oxobut-1-enyl)benzamide as a white solid^a (7.7 g, 65%). IR (neat) 3067br.w, 1688s, 1633s, 1588s, 1478s, 1432s, 1354s, 1262s, 1236s, 1195m, 1093m, 1025m, 976m, 897m, 855w cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.17 (s, 3H, COCH₃), 2.50 (d, 3H, *J* = 0.9 Hz, NHCCCH₃), 5.44 (s, 1H, CH-vinyl), 7.57-7.44 (m, 3H, CH-aromatic), 8.01-7.98 (m, 2H, CH-aromatic), 10.86 (s, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 21.96 (CH₃), 30.39 (CH₃), 106.08 (CH), 127.87 (CH), 128.79 (CH), 132.53 (CH), 133.57 (C), 156.01 (C), 165.95 (C), 199.99 (C). HRMS (ESI) calculated for C₁₂H₁₃NO₂Na ([M+Na]⁺): 226.0838. Found: 226.0825

2,6-Difluoro-*N*-((*Z*)-1-methyl-3-oxobut-1-enyl)benzamide: Prepared according to the general procedure (1) using acetylacetone (5.0 g, 50 mmol), 2,6-difluorobenzamide (9.9 g, 63 mmol), PTSA (0.5 g) in toluene (180 ml). Purification by FC (pentane / MTBE 5:1) provided 2,6-Difluoro-*N*-((*Z*)-1-methyl-3-oxobut-1-enyl)benzamide as a white solid (6.8 g, 57 %). IR (neat) 3101br.w, 1703s, 1644s, 1592s, 1481s, 1462s, 1438s, 1354s, 1276s, 1256s, 1219m, 1196s, 1112s, 1041m, 1003s, 984m, 897m, 856m, 810s, 788s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.14 (s, 3H, COCH₃), 2.50 (d, 3H, *J* = 0.9 Hz, NHCCCH₃), 5.44 (s, 1H, CH-vinyl), 7.00-6.93 (m, 2H, CH-aromatic), 7.45-7.35 (m, 1H, CH-aromatic), 11.50 (s, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 22.01 (CH₃), 30.50 (CH₃), 106.75 (CH), 112.19 (dd, *J* = 2.3 Hz, *J* = 22.9 Hz, CH), 114.26 (t, *J* = 19.1 Hz, C), 132.44 (t, *J* = 10.3 Hz, CH), 154.14 (C), 159.53 (C), 159.96 (dd, *J* = 6.3 Hz, *J* = 254.0 Hz, C), 199.83 (C). HRMS (ESI) calculated for C₁₂H₁₁F₂NO₂Na ([M+Na]⁺): 262.0650. Found: 262.0643.

4-Methoxy-*N*-((*Z*)-1-methyl-3-oxobut-1-enyl)benzamide: Prepared according to the general procedure (1) using acetylacetone (5.0 g, 50 mmol), 4-methoxybenzamide (9.4 g, 63 mmol), PTSA (0.5 g) in toluene (180 ml). Purification by FC (pentane / MTBE 5:1) provided 4-Methoxy-*N*-((*Z*)-1-methyl-3-oxobut-1-enyl)benzamide as a white solid (7.8 g, 67 %). IR (neat) 3055br.w, 3001m, 1681s, 1640s, 1598s, 1574s, 1480s, 1437s, 1354s, 1250s, 1184s, 1123s, 1102s, 1027s, 980m, 898w, 863s, 758s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.18 (s, 3H, COCH₃), 2.50 (d, *J* = 0.9 Hz, NHCCCH₃), 3.85 (s, 3H, OCH₃), 5.42 (s, br., 1H, CH-vinyl), 6.97-6.94 (m, 2H, CH-aromatic), 8.00-7.97 (m, 2H, CH-aromatic), 10.91 (s, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 21.96 (CH₃), 30.34 (CH₃), 55.42 (CH₃), 105.66 (CH), 114.00 (CH), 125.87 (C), 129.95 (CH), 156.41 (C), 163.04 (C), 165.45 (C), 199.87 (C). HRMS (ESI) calculated for C₁₃H₁₅NO₃Na ([M+Na]⁺): 256.0944. Found: 256.0945.

1-((*Z*)-1-Methyl-3-oxobut-1-enyl)pyrrolidin-2-one: Prepared according to the general procedure (1) using acetylacetone (5.0 g, 50 mmol), 2-pyrrolidinone (4.4 g, 63 mmol), PTSA (0.5 g), toluene (180 ml). Purification by FC (pentane / MTBE 1:2) provided 1-((*Z*)-1-Methyl-3-oxobut-1-enyl)pyrrolidin-2-one as a white solid^a (2.9 g, 35 %). IR (neat) 2971br.w, 2891w, 1711s, 1665s, 1567s, 1461w, 1419m, 1366s, 1313s, 1179s, 1124m, 1029m, 961m, 843w, 815s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.07-1.98 (m, 2H, CH₂), 2.17 (s, 3H, COCH₃), 2.52 (t, 2H, *J* = 8.1 Hz, COCH₂), 2.59 (s, 3H, NCCCH₃), 3.66 (t, 2H, *J* = 7.0 Hz, NCH₂), 6.14 (s, 1H, CH-vinyl). ¹³C NMR (75 MHz, CDCl₃) δ 16.51 (CH₃), 17.56 (CH₂), 32.58 (CH₃), 33.21 (CH₂), 48.58 (CH₂), 110.52 (CH), 152.03 (C), 175.40 (C), 198.27 (C). HRMS (ESI) calculated for C₉H₁₃NO₂Na ([M+Na]⁺): 190.0838. Found: 190.0835.

General Procedure (2) for the Synthesis of the Different Dienes:

A flame dried 100 ml flask was charged with methyltriphenylphosphonium bromide (1.5-3.0 equiv.) in dry THF at 0 °C under argon. To the stirred suspension, *n*-BuLi (0.95 equiv. 1.6 M solution in hexane) was added dropwise. After complete addition of *n*-BuLi reaction temperature was maintained at 0 °C for 30 min. and then allowed to warm up to r.t. Stirring was continued for another 1 h. The red solution was then cooled down to 0 °C. A solution of the ketone in dry THF was added dropwise to the stirred red solution. The whole reaction mixture was kept at 0 °C for another 30 min. Finally the reaction mixture was allowed to warm up to r.t. and was stirred for 12 h. The reaction was quenched with 30 ml of saturated NH₄Cl solution. The aqueous phase was extracted with Et₂O (3 × 25 ml). The combined organic layers were washed with brine (50 ml), dried over MgSO₄, and concentrated under reduced pressure. Purification by FC (SiO₂) (pentane / *t*-butylmethylether) afforded the desired diene. Compounds **7a** and **7b** were prepared according to a literature procedure^b. For the synthesis of **7c** see the preparation of compound **8c** below.

***N*-((*Z*)-1,3-Dimethylbuta-1,3-dienyl)acetamide (7d):** Prepared according to the general procedure (2) using methyltriphenylphosphonium bromide (6.3 g, 18 mmol), *n*-BuLi (10.5 ml of a 1.6 M solution in hexane, 16.8 mmol), *N*-((*Z*)-1-methyl-3-oxobut-1-enyl)acetamide (1.0 g, 7.1 mmol), dry THF (35 ml). Purification by FC (pentane / MTBE 5:1) provided **7d** as low melting pale yellow solid (0.46 g, 47 %). IR (neat) 3417br.m, 1651s, 1526m, 1439w, 1375m, 1283m, 1044m, 888w cm⁻¹. ¹H NMR (400 MHz, DMSO) δ 1.84 (s, 3H, CH₃), 1.86 (s, 3H, CH₃), 1.91 (s, 3H, CH₃), 4.84 (s, 1H, CH-vinyl), 4.87 (s, 1H, CH-vinyl), 5.52 (s, 1H, CH-vinyl), 8.85 (s, br., 1H, NH). ¹³C NMR (100 MHz, DMSO) δ 21.58 (CH₃), 22.39 (CH₃), 22.91 (CH₃), 115.61 (CH₂), 121.98 (CH), 132.42 (C), 140.22 (C), 168.14 (C). HRMS (ESI) calculated for C₈H₁₃NONa ([M+Na]⁺): 162.0889. Found: 162.0902.

***N*-((*Z*)-1,3-Dimethylbuta-1,3-dienyl)benzamide (7e):** Prepared according to the general procedure (2) using methyltriphenylphosphonium bromide (5.2 g, 15 mmol), *n*-BuLi (8.7 ml of a 1.6 M solution in hexane, 14 mmol), *N*-((*Z*)-1-methyl-3-oxobut-1-enyl)benzamide (1.0 g, 4.9 mmol), dry THF (30 ml).

Purification by FC (pentane / MTBE 10:1) provided **7e** as low melting white solid (0.45 g, 45 %). IR (neat) 3250br.m, 2968w, 1663w, 1634s, 1602m, 1578m, 1518s, 1486s, 1433w, 1372m, 1291s, 1185w, 1076w, 1040m, 931m, 889s, 865w, 801m cm⁻¹. ¹H NMR (400 MHz, DMSO) δ 1.85 (s, 3H, CH₃), 2.01 (s, 3H, CH₃), 4.85 (s, 1H, CH-vinyl), 4.92 (s, 1H, CH-vinyl), 5.79 (s, 1H, CH-vinyl), 7.56-7.44 (m, 3H, CH-aromatic), 7.89-7.87 (m, 2H, CH-aromatic), 9.36 (s, br., 1H, NH). ¹³C NMR (100 MHz, DMSO) δ 21.37 (CH₃), 22.62 (CH₃), 116.04 (CH₂), 124.38 (CH), 127.23 (CH), 128.23 (CH), 131.26 (CH), 132.13 (C), 134.14 (C), 140.48 (C), 164.78 (C). HRMS (ESI) calculated for C₁₃H₁₅NONa ([M+Na]⁺): 224.1046. Found: 224.1045.

N-((Z)-1,3-Dimethylbuta-1,3-dienyl)-2,6-difluorobenzamide (7f): Prepared according to the general procedure (2) using methyltriphenylphosphonium bromide (3.7 g, 10 mmol), *n*-BuLi (5.9 ml of a 1.6 M solution in hexane, 9.5 mmol), 2,6-difluoro-*N*-((Z)-1-methyl-3-oxobut-1-enyl)benzamide (1.0 g, 4.1 mmol), dry THF (21 ml). Purification by FC (pentane / MTBE 10:1) provided **7f** as a low melting white solid (0.44 g, 44 %). IR (neat) 3206br.w, 2978w, 2934w, 1646s, 1623s, 1590w, 1518m, 1466s, 1377w, 1304m, 1269w, 1237s, 1195w, 1007s, 889m, 791s, 761m cm⁻¹. ¹H NMR (400 MHz, DMSO) δ 1.89 (s, 3H, CH₃), 2.02 (s, 3H, CH₃), 4.88 (s, 1H, CH-vinyl), 4.94 (s, 1H, CH-vinyl), 5.73 (s, 1H, CH-vinyl), 7.19-7.15 (m, 2H, CH-aromatic), 7.55-7.48 (m, 1H, CH-aromatic), 9.75 (s, br., 1H, NH). ¹³C NMR (100 MHz, MDSO) δ 21.18 (CH₃), 22.12 (CH₃), 111.73 (*dd*, *J*₁ = 5.3 Hz, *J*₂ = 19.1 Hz, CH), 115.41 (*t*, *J* = 23.3 Hz, C), 116.39 (CH₂), 124.29 (CH), 130.74 (C), 131.44 (*t*, *J* = 9.76 Hz, CH), 139.95 (C), 158.42 (C), 158.66 (*dd*, *J*₁ = 8.1 Hz, *J*₂ = 247.9 Hz, C). HRMS (ESI) calculated for C₁₃H₁₃F₂NONa ([M+Na]⁺): 260.0857. Found: 260.0855.

N-((Z)-1,3-Dimethylbuta-1,3-dienyl)-4-methoxybenzamide (7g): Prepared according to the general procedure (2) using methyltriphenylphosphonium bromide (3.8 g, 11 mmol), *n*-BuLi (6.3 ml of a 1.6 M solution in hexane, 10 mmol), 4-methoxy-*N*-((Z)-1-methyl-3-oxobut-1-enyl)benzamide (1.0 g, 4.3 mmol), dry THF (22 ml). Purification by FC (pentane / MTBE 6:1) provided **7g** as a low melting white solid (0.4 g, 40 %). IR (neat) 3287br.m, 2984w, 2944w, 1631s, 1603s, 1522m, 1487s, 1459w, 1440m, 1374m, 1314m, 1254s, 1182s, 1123w, 1027s, 929s, 889s, 840s, 766s cm⁻¹. ¹H NMR (400 MHz, DMSO) δ 1.83 (s, 3H, CH₃), 2.00 (s, 3H, CH₃), 3.80 (s, 3H, OCH₃), 4.83 (s, 1H, CH-vinyl), 4.91 (br., 1H, CH-vinyl), 5.75 (s, 1H, CH-vinyl), 7.00 (*d*, 2H, *J* = 8.9 Hz, CH-aromatic), 7.87 (*d*, 2H, *J* = 8.9 Hz, CH-aromatic), 9.20 (s, br., 1H, NH). ¹³C NMR (100 MHz, DMSO) δ 21.45 (CH₃), 22.75 (CH₃), 55.31 (CH₃), 113.51 (CH), 115.97 (CH₂), 124.08 (CH), 126.37 (C), 129.19 (CH), 132.44 (C), 140.60 (C), 161.67 (C), 164.36 (C). HRMS (ESI) calculated for C₁₄H₁₇NO₂Na ([M+Na]⁺): 254.1151. Found: 254.1143.

General Procedure (3) for the Synthesis of the Hydroamination Reagents:

A solution of 3-nitro-acrylic acid methyl ester in benzene was added dropwise at 0 °C under argon to a stirred solution of diene in dry benzene. The reaction temperature was maintained for another 1 h at 0 °C then allowed to warm up to r.t. where stirring was continued for 18 h. The reaction mixture was cooled to 0 °C and DBU was added dropwise and the mixture was stirred for 1 h at 0 °C. Stirring was continued at r.t. for another 18 h. under argon. Brine was added and the reaction mixture was extracted with Et₂O (3x). The combined organic layers were washed with water and finally with brine. The organic phase was dried over MgSO₄ and concentrated under reduced pressure. Purification by FC (SiO₂) (pentane/*tert*-butyl-methylether) provided the desired hydroamination reagent.

3-Acetylamino-3,5-dimethylcyclohexa-1,4-dienecarboxylic acid methyl ester (8d): Prepared according to the general procedure (3) using *N*-((Z)-1,3-dimethylbuta-1,3-dienyl)acetamide (**7d**) (0.50 g,

3.6 mmol), 3-nitroacrylic acid methyl ester (0.71 g, 5.4 mmol) and DBU (1.0 g, 6.5 mmol) in benzene (5 ml). Purification by FC (pentane / MTBE 5:1) provided **8d** as a pale yellow viscous liquid which was solidified upon standing at low temperature (0.55 g, 69 %). IR (neat) 3475br.w, 2970m, 1719s, 1683s, 1438m, 1301s, 1259s, 1177m, 1073m, 997w, 934m, 852m, 745s cm⁻¹. ¹H NMR (300 MHz, C₆D₆) δ 1.37 (s, 3H, CH₃), 1.53 (s, 3H, CH₃), 1.54 (s, 3H, CH₃), 2.93-2.63 (m, 2H, CH₂), 3.41 (s, 3H, CO₂CH₃), 5.30 (s, 1H, CH-vinyl), 5.36 (s, br., 1H, NH), 7.27 (s, br., 1H, CH-vinyl). ¹³C NMR (75 MHz, C₆D₆) δ 22.55 (CH₃), 23.64 (CH₃), 27.88 (CH₃), 30.99 (CH₂), 51.29 (CH₃), 53.22 (C), 124.54 (CH), 132.47 (C), 139.96 (CH), 167.08 (C), 168.75 (C). HRMS (ESI) calculated for C₁₂H₁₇NO₃Na ([M+Na]⁺): 246.1101. Found: 246.1091.

3-Benzoylamino-3,5-dimethylcyclohexa-1,4-dienecarboxylic acid methyl ester (8e): Prepared according to the general procedure (**3**) using *N*-((*Z*)-1,3-Dimethylbuta-1,3-dienyl)benzamide (**7e**) (2.50 g, 12.4 mmol), 3-nitro-acrylic acid methyl ester (2.7 g, 21 mmol) and DBU (4.1 g, 27 mmol) in benzene (20 ml). Purification by FC (pentane / MTBE 5:1) provided **8e** as a pale yellow viscous liquid which was solidified upon standing at low temperature (2.3 g, 66 %). IR (neat) 3235br.m, 3056w, 2948w, 1717s, 1688w, 1636s, 1531s, 1493w, 1441m, 1350w, 1312s, 1290s, 1256s, 1191s, 1143w, 1087w, 1068s, 987w, 927m, 831m, 748m cm⁻¹. ¹H NMR (400 MHz, C₆D₆) δ 1.49 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 2.95-2.67 (m, 2H, CH₂), 3.39 (s, 3H, CO₂CH₃), 5.41-5.4 (m, 1H, CH-vinyl), 5.88 (s, br., 1H, NH), 7.09-6.98 (m, 3H, CH-aromatic), 7.42-7.41 (m, 1H, CH-vinyl), 7.63-7.60 (m, 2H, CH-aromatic). ¹³C NMR (100 MHz, C₆D₆) δ 22.60 (CH₃), 27.93 (CH₃), 31.08 (CH₂), 51.27 (CH₃), 53.62 (C), 124.35 (CH), 127.34 (CH), 128.46 (CH), 131.08 (CH), 132.99 (C), 135.90 (CH), 139.66 (C), 166.04 (C), 167.02 (C). HRMS (ESI) calculated for C₁₇H₁₉NO₃Na ([M+Na]⁺): 308.1257. Found: 308.1255.

3-(2,6-Difluorobenzoylamino)-3,5-dimethylcyclohexa-1,4-dienecarboxylic acid methyl ester (8f): Prepared according to the general procedure (**3**) (for the *Diels-Alder* reaction, the reaction mixture was heated at 60 °C for 6 h and complete consumption of the diene was confirmed by TLC) using *N*-((*Z*)-1,3-dimethylbuta-1,3-dienyl)-2,6-difluorobenzamide (**7f**) (0.80 g, 3.4 mmol), 3-nitro-acrylic acid methyl ester (0.65 g, 4.9 mmol), and DBU (1.1 g, 7.2 mmol) in benzene (10 ml). Purification by FC (pentane / MTBE 3:1) provided **8f** as a colourless oil (0.68 g, 63 %). IR (neat) 3285br.m, 2953w, 1718s, 1658s, 1624s, 1590m, 1532s, 1567s, 1259s, 1195w, 1072m, 1008s, 793s, 744m cm⁻¹. ¹H NMR (400 MHz, C₆D₆) δ 1.42 (s, 3H, CH₃), 1.48 (s, 3H, CH₃), 2.90-2.61 (m, 2H, CH₂), 3.35 (s, 3H, CO₂CH₃), 5.38-5.37 (m, 1H, CH-vinyl), 5.61 (s, br., 1H, NH), 6.40-6.34 (m, 2H, CH-aromatic), 6.61-6.53 (m, 1H, CH-aromatic), 7.32-7.31 (m, 1H, CH-vinyl). ¹³C NMR (100 MHz, C₆D₆) δ 22.50 (CH₃), 27.95 (CH₃), 30.97 (CH₂), 51.27 (CH₃), 54.36 (C), 111.84-111.59 (m, CH), 116.11 (t, *J* = 21.8 Hz, C), 123.85 (CH), 128.62 (C), 131.01 (t, *J* = 9.9 Hz, CH), 133.23 (C), 139.0 (CH), 160.12 (dd, *J*₁ = 7.0 Hz, *J*₂ = 250.4 Hz, C), 166.9 (C). HRMS (ESI) calculated for C₁₇H₁₇F₂NO₃Na ([M+Na]⁺): 344.1069. Found: 344.1077.

3-(4-Methoxybenzoylamino)-3,5-dimethylcyclohexa-1,4-dienecarboxylic acid methyl ester (8g): Prepared according to the general procedure (**3**) using *N*-((*Z*)-1,3-dimethylbuta-1,3-dienyl)-4-methoxybenzamide (**7g**) (1.0 g, 4.3 mmol), 3-nitro-acrylic acid methyl ester (0.85 g, 6.5 mmol), and DBU (1.4 g, 9.5 mmol) in benzene (10 ml). Purification by FC (pentane / MTBE 5:1) provided **8g** as a white solid (0.54 g, 40 %). IR (neat) 3276br.m, 2988w, 2947w, 1709s, 1692m, 1632s, 1606s, 1534m, 1503s, 1440s, 1350m, 1315m, 1257s, 1179s, 1128m, 1093m, 1068m, 1031s, 927m, 846s, 771m, 747s cm⁻¹. ¹H NMR (400 MHz, C₆D₆) δ 1.52 (s, 6H, CH₃), 2.99-2.69 (m, 2H, CH₂), 3.18 (s, 3H, OCH₃), 3.39 (s, 3H, CO₂CH₃), 5.42 (s, 1H, CH-vinyl), 5.62 (s, br., 1H, NH), 6.60 (d, 2H, *J* = 8.8 Hz, CH-aromatic), 7.49-7.48 (m, 1H, CH-vinyl), 7.59 (d, 2H, *J* = 8.8 Hz, CH-aromatic). ¹³C NMR (100 MHz, C₆D₆) δ 22.61 (CH₃), 27.96 (CH₃), 31.13 (CH₂), 51.24 (CH₃), 53.53 (C), 54.80 (CH₃), 113.81 (CH), 124.52 (CH), 129.12 (CH), 132.98 (C), 139.79 (CH), 162.31 (C), 165.49 (C), 167.03 (C). HRMS (ESI) calculated for C₁₈H₂₁NO₄Na ([M+Na]⁺): 338.1363. Found: 338.1361.

3,5-Dimethyl-3-(2-oxopyrrolidin-1-yl)cyclohexa-1,4-dienecarboxylic acid methyl ester (8h): Prepared using 1-((*Z*)-1,3-Dimethylbuta-1,3-dienyl)pyrrolidin-2-one, which was prepared according to

the general procedure (**2**) using methyltriphenylphosphonium bromide (3.2 g, 8.9 mmol), *n*-BuLi (5.2 ml of a 1.6 M solution in hexane, 8.4 mmol), 1-((*Z*)-1-Methyl-3-oxobut-1-enyl)pyrrolidin-2-one (1.0 g, 6.0 mmol), dry THF (20 ml). Purification by FC (pentane / MTBE 1:2) provided 1-((*Z*)-1,3-Dimethylbuta-1,3-dienyl)pyrrolidin-2-one as colourless oil (0.54 g, 55%). IR (neat) 3368br.*m*, 2978*m*, 1682*s*, 1461*w*, 1414*m*, 1291*s*, 1073*w*, 994*m*, 840*w* cm⁻¹. ¹H NMR (400 MHz, C₆D₆) δ 1.23-1.13 (*m*, 2H, CH₂), 1.75 (*s*, 3H, CH₃), 2.01-1.97 (*m*, 2H, COCH₂), 2.37-2.35 (*m*, 3H, CH₃), 2.84-2.79 (*m*, 2H, NCH₂), 4.87 (*s*, 1H, CH-vinyl), 4.99 (*s*, 1H, CH-vinyl), 5.48 (*s*, 1H, CH-vinyl). ¹³C NMR (100 MHz, C₆D₆) δ 16.95 (CH₃), 17.99 (CH₂), 24.26 (CH₃), 32.65 (CH₂), 48.61 (CH₂), 114.87 (CH₂), 118.00 (CH), 136.99 (C), 140.74 (C), 173.04 (C). HRMS (ESI) calculated for C₁₀H₁₅NONa ([M+Na]⁺): 188.1046. Found: 188.1037.

1-((*Z*)-1,3-Dimethylbuta-1,3-dienyl)pyrrolidin-2-one (1.1 g, 6.6 mmol), 3-nitroacrylic acid methyl ester (1.3 g, 9.9 mmol), and DBU (2.2 g, 14 mmol) in benzene (10 ml) according to the general procedure (**3**). Purification by FC (pentane / MTBE 1:2) provided **8h** as a colourless oil (1.1 g, 67 %). IR (neat) 3288br.*m*, 2970*w*, 1720*s*, 1658*s*, 1538*s*, 1438*s*, 1372*s*, 1258*s*, 1195*m*, 1127*w*, 1071*m*, 932*w*, 849*w*, 752*m* cm⁻¹. ¹H NMR (300 MHz, C₆D₆) δ 1.21-1.11 (*m*, 2H, CH₂), 1.48-1.47 (*m*, 3H, NCCCH₃), 1.75 (*s*, 3H, CH₃-vinyl), 1.98-1.92 (*m*, 2H, COCH₂), 2.83-2.60 (*m*, 4H, NCH₂ and CH₂-allyl), 3.39 (*s*, 3H, CO₂CH₃), 5.43-5.40 (*m*, 1H, CH-vinyl), 7.30-7.28 (*m*, 1H, CH-vinyl). ¹³C NMR (75 MHz, C₆D₆) δ 18.10 (CH₂), 22.53 (CH₃), 26.86 (CH₃), 30.72 (CH₂), 32.73 (CH₂), 45.90 (CH₂), 51.31 (CH₃), 56.34 (C), 123.61 (CH), 132.12 (C), 139.04 (CH), 166.88 (C), 174.47 (C). HRMS (ESI) calculated for C₁₄H₁₉NO₃Na ([M+Na]⁺): 272.1257. Found 272.1250.

3-(3-*tert*-Butylureido)-3,5-dimethylcyclohexa-1,4-dienecarboxylic acid methyl ester (8c): To a solution of 2,4-dimethylpenta-2,4-dienoic acid (0.5 g, 4 mmol) in acetone (10 ml) Et₃N (0.90 ml, 6.35 mmol) was added. After cooling to 0 °C a solution of ethyl chloroformate (0.64 g, 6.0 mmol) in acetone (5 mL) was added dropwise. The mixture was stirred for 30 min at 0 °C and a solution of NaN₃ (0.36 g, 5.6 mmol) in water (2 ml) was added slowly (0 °C). After stirring for 2 h at 0 °C the reaction mixture was poured onto ice-water and extracted with CH₂Cl₂ (3x). The combined organic layers were dried over MgSO₄ and 90 % of the solvent was removed under reduced pressure. Purification by FC (pentane / MTBE 15:1) provided the desired azide^b.

A solution of the azide in dry toluene (10 ml) was heated under reflux for 3 h under argon. The solution was cooled to 0 °C and a solution of *tert*-butylamine (0.19 g, 2.7 mmol) in dry toluene (5 ml) was added dropwise. The mixture was heated to reflux for 1 h and then allowed to stir at r.t. over night. A white solid powder was precipitated. The solvent was removed under reduced pressure at r.t. and the solid was used directly for the next step without purification.

To a stirred suspension of the 1-*tert*-Butyl-3-((*Z*)-1,3-dimethylbuta-1,3-dienyl)urea (**7c**) (0.4 g, 2 mmol) in benzene (15 ml) a solution of 3-nitro-acrylic acid methyl ester (0.4 g, 3 mmol) in benzene was added dropwise at 0 °C under argon. The reaction mixture was kept at 0 °C for 1 h and was then allowed to warm to r.t. After stirring at r.t. for 12 h the solution was cooled at 0 °C and DBU (0.46 g, 3.0 mmol) was added dropwise. The reaction temperature was maintained for another 1 h at 0 °C and then allowed to warm up to r.t where stirring was continued for 18 h. Brine was added and the reaction mixture was extracted with Et₂O (3x). The combined organic layers were washed with water, dried over MgSO₄, concentrated under reduced pressure. Purification by FC (pentane / MTBE 1:2) provided **8c** as a white solid powder (0.38 g, 66 %). IR (neat) 3344br.*m*, 2967*w*, 2933*w*, 1712*s*, 1687*w*, 1635*s*, 1553*s*, 1449*m*, 1437*m*, 1360*w*, 1258*s*, 1255*s*, 1220*m*, 1193*m*, 1141*s*, 1074*s*, 1063*m*, 986*w*, 929*m*, 834*w*, 777*w*, 742*s* cm⁻¹. ¹H NMR (300 MHz, DMSO) δ 1.15 (*s*, 9H, C(CH₃)₃), 1.26 (*s*, 3H, CH₃), 1.71 (*s*, 3H, CH₃-vinyl), 2.75-2.57 (*m*, 2H, CH₂), 3.68 (*s*, 3H, CO₂CH₃), 5.31 (*s*, 1H, CH-vinyl), 5.46 (*s*, 1H, NH), 5.79 (*s*, 1H, NH), 6.91-6.90 (*m*, 1H, CH-vinyl). ¹³C NMR (75 MHz, DMSO) δ 22.26 (CH₃), 28.39 (CH₃), 29.24 (CH₃), 29.96 (CH₂), 48.92 (C), 51.12 (C), 51.59 (CH₃), 125.12 (CH), 125.76 (C), 130.14

(C), 142.18 (CH), 156.26 (C), 166.66 (C). HRMS (ESI) calculated for $C_{15}H_{24}N_2O_3Na$ ($[M+Na]^+$): 303.1679. Found: 303.1672.

General Procedure (4) for the Hydroamination of Norbornene with Different Reagents and for the Hydroamination of Different Olefins with Reagent 8a:

A mixture of the hydroamination reagent (1 equiv.), the olefin (2.5 to 6.0 equiv.), di-*tert*-butyl-peroxide (DTBP) (0.5 equiv.) and thiophenol (0.15 to 0.20 equiv.) in dry benzene was placed in a sealed tube under argon. The reaction mixture was heated in the sealed tube under argon at 140 °C (oil bath temperature) for 18 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. Purification by FC (SiO_2) afforded the desired hydroamination product.

Octylcarbamic acid methyl ester (9a): Prepared according to the general procedure (4) using reagent **8a** (0.10 g, 0.41 mmol), 1-octene (0.18 g, 1.6 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (7.0 mg, 0.06 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **9a** as a low melting white solid with another regio-isomer in 1:7 ratio (ratio was determined by 1H NMR spectroscopy) (40 mg, 51 % (combined yield of both isomers)). Physical data of the major isomer is given. IR (neat) 3335br.*m*, 2927s, 2856m, 1703s, 1538s, 1465m, 1262s, 1146w, 776s cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.87 (*t*, 3H, J = 6.8 Hz, CH_3), 1.30-1.26 (*m*, 10H, CH_2), 1.49-1.44 (*m*, 2H, $NHCH_2CH_2$), 3.15-3.14 (*m*, 2H, $NHCH_2$), 3.65 (*s*, 3H, CO_2CH_3), 4.65 (*s*, br., 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02 (CH_3), 22.60 (CH_2), 26.71 (CH_2), 29.17 (CH_2), 29.21 (CH_2), 30.01 (CH_2), 31.76 (CH_2), 41.14 (CH_2), 51.94 (CH_3), 157.06 (C). HRMS (ESI) calculated for $C_{10}H_{21}NO_2Na$ ($[M+Na]^+$): 210.1465. Found: 210.1466.

Bicyclo[2.2.1]hept-2-yl-carbamic acid methyl ester (10a): Prepared according to the general procedure (4) using reagent **8a** (0.10 g, 0.41 mmol), norbornene (98 mg, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (7.0 mg, 0.06 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **10a** as a white solid^b (40 mg, 57 %). IR (neat) 3322br. *m*, 2952s, 2872m, 1689s, 1535s, 1451m, 1365w, 1304m, 1252s, 1190m, 1071s, 1009m, 779m, 631s cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 1.29-1.03 (*m*, 5H, CH_3), 1.53-1.35 (*m*, 2H, CH_2), 1.77-1.69 (*m*, 1H, CH_2), 2.17 (*s*, br., 1H, CH), 2.21 (*s*, br., 1H, CH), 3.46 (*s*, br, 1H, $NHCH$), 3.61 (*s*, 3H, CH_3), 4.54 (*s*, br, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.29 (CH_2), 28.09 (CH_2), 35.20 (CH_2), 35.61 (CH), 42.51 (CH_2), 51.79 (CH), 54.31 (CH_3), 156.09 (C). HRMS (ESI) calculated for $C_9H_{15}NO_2Na$ ($[M+Na]^+$): 192.0995. Found: 192.0997.

Bicyclo[2.2.1]hept-2-yl-carbamic acid *tert*-butyl ester (10b): Prepared according to the general procedure (4) using reagent **8b** (0.10 g, 0.35 mmol), norbornene (84 mg, 0.90 mmol), DTBP (26 mg, 0.17 mmol) and thiophenol (6.0 mg, 0.05 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **10b** as a white solid^b (42 mg, 56 %). IR (neat) 3352br. *m*, 2955m, 2874w, 1680s, 1519s, 1452w, 1365m, 1248s, 1162s, 1066s, 997 *m*, 780w cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 1.41 (*s*, 9H, CH_3), 1.54-1.03 (*m*, 7H, CH_2), 1.76-1.68 (*m*, 1H, CH_2), 2.16 (*s*, br., 1H, CH), 2.21 (*s*, br., 1H, CH), 3.41 (*s*, br., 1H, $NHCH$), 4.33 (*s*, br., 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.39 (CH_2), 28.15 (CH_2), 28.46 (CH_3), 35.25 (CH_2), 35.61 (CH), 40.48 (CH_2), 42.56 (CH), 54.05 (CH), 79.02 (C), 155.23 (C). HRMS (ESI) calculated for $C_{12}H_{21}NO_2Na$ ($[M+Na]^+$): 234.1470. Found: 234.1465.

1-Bicyclo[2.2.1]hept-2-yl-3-*tert*-butyl-urea (10c): Prepared according to the general procedure (4) using reagent **8c** (0.10 g, 0.36 mmol), norbornene (84 mg, 0.90 mmol), DTBP (26 mg, 0.17 mmol) and thiophenol (6.0 mg, 0.05 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-

butylmethylether 3:1) provided **10c** as a white solid (6 mg, 8 %). IR (neat) 3323br.m, 2954s, 2870m, 1624s, 1558s, 1475w, 1450m, 1389m, 1360m, 1306m, 1278m, 1216s, 1181w, 1136m, 837w, 775w cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.20-1.00 (m, 4H, CH₂), 1.27 (s, 9H, C(CH₃)₃), 1.48-1.32 (m, 3H, CHH, CH₂), 1.70-1.63 (m, 1H, CHH), 2.10 (s, br., 1H, CH), 2.17 (s, br., 1H, CH), 3.43-3.40 (m, 1H, NHCH), 4.95 (s, br., 2H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 26.43 (CH₂), 28.17 (CH₂), 29.53 (CH₃), 35.20 (CH₂), 35.54 (CH), 40.56 (CH₂), 42.72 (CH), 49.95 (C), 53.20 (CH), 157.55 (C). HRMS (ESI) calculated for C₁₂H₂₂N₂ONa ([M+Na]⁺): 233.1624. Found: 233.1622.

N-Bicyclo[2.2.1]hept-2-yl-acetamide (10d): Prepared according to the general procedure (4) using reagent **8d** (0.10 g, 0.45 mmol), norbornene (0.10 g, 1.1 mmol), DTBP (32 mg, 0.22 mmol) and thiophenol (7.4 mg, 0.06 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **10d** as a white solid^c (28 mg, 41 %). IR (neat) 3274br.m, 3078w, 2955s, 2870m, 1638s, 1550s, 1478w, 1440m, 1373m, 1311m, 1290m, 1159w, 1112w, 1039w, 728m cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.32-1.07 (m, 5H, CH₂, CHH), 1.53-1.39 (m, 2H, CH₂), 1.81-1.75 (m, 1H, CHH), 1.94 (s, 3H, COCH₃), 2.19-2.18 (br., 1H, CH), 2.26 (s, br., 1H, CH), 3.72-3.68 (m, 1H, NHCH), 5.60 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 23.32 (CH₃), 26.46 (CH₂), 28.09 (CH₂), 35.54 (CH₂), 35.68 (CH), 40.40 (CH₂), 42.31 (CH), 52.92 (CH), 169.27 (C). HRMS (ESI) calculated for C₉H₁₅NONa ([M+Na]⁺): 176.1046. Found 176.1048.

N-Bicyclo[2.2.1]hept-2-yl-benzamide (10e): Prepared according to the general procedure (4) using reagent **8e** (0.10 g, 0.35 mmol), norbornene (82 mg, 0.87 mmol), DTBP (25 mg, 0.17 mmol) and thiophenol (6.0 mg, 0.05 mmol) in dry benzene (0.9 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **10e** as a white solid^d (10 mg, 13 %). IR (neat) 3296br.m, 2958m, 2946s, 2873w, 1628s, 1580m, 1529s, 1490m, 1451m, 1365w, 1313s, 1294m, 1223w, 1181w, 1097m, 1028m, 891w, 836m, 803m, 767w cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.58-1.09 (m, 7H, CH₂, CHH), 1.89-1.81 (m, 1H, CHH), 2.30-2.27 (m, 2H, CH), 3.91-3.85 (m, 1H, NHCH), 6.17 (s, br., 1H, NH), 7.47-7.34 (m, 3H, CH-aromatic), 7.75-7.71 (m, 2H, CH-aromatic). ¹³C NMR (75 MHz, CDCl₃) δ 26.43 (CH₂), 28.07 (CH₂), 35.58 (CH₂), 35.67 (CH), 40.30 (CH₂), 42.33 (CH), 53.28 (CH), 126.78 (CH), 128.35 (CH), 131.13 (CH), 134.78 (C), 166.83 (C). HRMS (ESI) calculated for C₁₄H₁₇NONa ([M+Na]⁺): 238.1202. Found: 238.1201.

N-Bicyclo[2.2.1]hept-2-yl-2,6-difluorobenzamide (10f): Prepared according to the general procedure (4) using reagent **8f** (0.1 g, 0.3 mmol), norbornene (73 mg, 0.80 mmol), DTBP (23 mg, 0.15 mmol) and thiophenol (5.0 mg, 0.05 mmol) in dry benzene (0.8 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **10f** as a white solid (12 mg, 15 %). IR (neat) 3285br.m, 2976w, 2956m, 2873w, 1640s, 1626s, 1593m, 1546s, 1465s, 1313s, 1292m, 1234m, 1091w, 1002s, 933w, 791s, 763m cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.36-1.09 (m, 5H, CH₂, CHH), 1.59-1.40 (m, 2H, CH₂), 1.89-1.81 (m, 1H, CH₂, CHH), 2.32-2.28 (m, 2H, CH), 3.92-3.86 (m, 1H, NHCH), 5.98 (s, br., 1H, NH) 6.92-6.84 (m, 2H, CH-aromatic), 7.35-7.25 (m, 1H, CH-aromatic). ¹³C NMR (75 MHz, CDCl₃) δ 26.37 (CH₂), 28.07 (CH₂), 35.55 (CH₂), 35.68 (CH), 40.19 (CH₂), 42.26 (CH), 53.38 (CH), 111.79 (d, *J* = 25.2 Hz, CH), 114.58 (t, *J* = 20.0 Hz, C), 131.28 (t, *J* = 10.2 Hz, CH), 159.42 (C), 159.84 (dd, *J*₁ = 7.1 Hz, *J*₂ = 251.9 Hz, C). HRMS (ESI) calculated for C₁₄H₁₅F₂NONa ([M+Na]⁺): 274.1014. Found: 274.1004.

N-Bicyclo[2.2.1]hept-2-yl-4-methoxybenzamide (10g): Prepared according to the general procedure (4) using reagent **8g** (0.1 g, 0.3 mmol), norbornene (75 mg, 0.80 mmol), DTBP (23 mg, 0.15 mmol) and thiophenol (5.0 mg, 0.05 mmol) in dry benzene (0.8 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **10g** as a white solid (7 mg, 9 %). IR (neat) 3296br.m, 2955s, 2870m, 1622s, 1606s, 1546m, 1502s, 1364w, 1311m, 1249s, 1174s, 1097w, 1031s, 938w, 842s, 769s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.57-1.09 (m, 7H, CH₂, CHH), 1.88-1.80 (m, 1H, CHH), 2.29-2.28 (m, 2H, CH), 3.80 (s, 3H, OCH₃), 3.90-3.85 (m, 1H, NHCH), 6.07 (s, br., 1H, NH), 6.86 (d, 2H, *J* = 9.0, CH-aromatic), 7.69 (d, 2H, *J* = 9.0, CH-aromatic). ¹³C NMR (75 MHz, CDCl₃) δ 26.45 (CH₂), 28.09 (CH₂), 35.59 (CH₂), 35.67 (CH), 40.38 (CH₂), 42.36 (CH), 53.23 (CH), 55.29 (CH₃), 113.52 (CH), 127.05 (C),

128.56 (CH), 131.98 (C), 161.87 (C). HRMS (ESI) calculated for $C_{15}H_{19}NO_2Na$ ($[M+Na]^+$): 268.1308. Found: 268.1298.

1-Bicyclo[2.2.1]hept-2-yl-pyrrolidin-2-one (10h): Prepared according to the general procedure (4) using reagent **8h** (0.1 g, 0.4 mmol), norbornene (94 mg, 1.0 mmol), DTBP (29 mg, 0.20 mmol) and thiophenol (6.0 mg, 0.05 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 1:2) provided **10h** as a colourless oil (16 mg, 22 %). IR (neat) 3453br.w, 2954s, 2871m, 1976s, 1492w, 1495w, 1423m, 1287s, 1228s, 1048w, 877w, 734w cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.21-1.12 (m, 2H, CH_2), 1.50-1.29 (m, 5H, CH_2 , CHH), 1.73-1.67 (m, 1H, CHH), 2.03-1.87 (m, 2H, CH_2), 2.16 (s, br., 1H, CH), 2.29 (s, br., 1H, CH), 2.35 (t, 2H, J = 8.5 Hz, $COCH_2$), 3.43-3.31 (m, 2H, NCH_2), 4.05-4.01 (m, 1H, NHCH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.06 (CH_2), 27.66 (CH_2), 28.45 (CH_2), 31.38 (CH_2), 36.05 (CH), 36.78 (CH_2), 36.95 (CH_2), 40.36 (CH), 44.17 (CH_2), 54.30 (CH), 174.65 (C). HRMS (ESI) calculated for $C_{11}H_{17}NONa$ ($[M+Na]^+$): 202.1202. Found: 202.1189.

Cyclopentylcarbamic acid methyl ester (11): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), cyclopentene (0.11 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 8:1) provided **11** as a white solid (43 mg, 48 %). IR (neat) 3326br.s, 2958s, 2872m, 1722s, 1538s, 1454m, 1360m, 1252m, 1106m, 1050m, 780s cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.39-1.31 (m, 2H, CH_2), 1.67-1.50 (m, 4H, CH_2), 1.95-1.87 (m, 2H, CH_2), 3.62 (s, 3H, CO_2CH_3), 3.94-3.89 (m, 1H, NHCH), 4.68 (s, br., 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.43 (CH_2), 33.20 (CH_2), 51.79 (CH), 52.79 (CH_3), 156.57 (C). HRMS (ESI) calculated for $C_7H_{13}NO_2Na$ ($[M+Na]^+$): 166.0838. Found: 166.0837.

Cyclohexylcarbamic acid methyl ester (12): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), cyclohexene (0.13 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 8:1) provided **12** as a white solid (50 mg, 51 %). IR (neat) 3345s, 2942s, 2851m, 1639s, 1530s, 1451w, 1317m, 1277m, 1250m, 1229s, 1054s cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.17-1.04 (m, 3H, CH_2 , CHH), 1.35-1.24 (m, 2H, CH_2), 1.68-1.52 (m, 3H, CH_2 , CHH), 1.90-1.86 (m, 2H, CH_2), 3.44-3.43 (m, 1H, NHCH), 3.61 (s, 3H, CO_2CH_3), 6.64 (s, br., 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.72 (CH_2), 25.43 (CH_2), 33.37 (CH_2), 49.82 (CH), 51.71 (CH_3), 156.19 (C). HRMS (ESI) calculated for $C_8H_{15}NO_2Na$ ($[M+Na]^+$): 180.1000. Found: 180.1017.

Cyclododecylcarbamic acid methyl ester (13): Prepared according to the general procedure (4) using reagent **8a** (0.1 g, 0.4 mmol), cyclododecene (0.42 g, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (7.0 mg, 0.06 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **13** as a white solid (42 mg, 42 %). IR (neat) 3349br. s, 2932s, 2856m, 1694s, 1530s, 1459m, 1233w, 1123w, 1071w cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.67-1.18 (m, 22H, CH_2), 3.64 (s, 3H, CO_2CH_3), 3.74 (s, br., 1H NHCH), 4.48 (s, br., 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.39 (CH_2), 23.40 (CH_2), 23.54 (CH_2), 23.66 (CH_2), 23.90 (CH_2), 30.63 (CH_2), 47.86 (CH), 51.78 (CH_3), 156.53 (C). HRMS (ESI) calculated for $C_{14}H_{27}NO_2Na$ ($[M+Na]^+$): 264.1934. Found: 264.1942.

(2-Methylnonyl)carbamic acid methyl ester (14): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 2-methyl-1-nonene (0.26 g, 1.9 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 8:1) provided **14** as a colourless oil (62 mg, 46 %). IR (neat) 3339br.m, 2925s, 2859w, 1708s, 1537s, 1460m, 1257s cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.91-0.80 (m, 6H, CH_3), 1.37-0.98 (m, 12H, CH_2), 1.63-1.49 (m, 1H, CH), 2.98-2.89 (m, 1H, NHCHH), 3.13-3.05 (m, 1H, NHCHH), 3.64 (s, 3H, CO_2CH_3), 4.71 (s, br., 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07 (CH_3), 17.43 (CH_3), 22.63 (CH_2), 26.85 (CH_2), 29.25 (CH_2), 29.79 (CH_2), 31.82 (CH_2), 33.55 (CH_2), 34.15 (CH), 47.05 (CH_2),

51.96 (CH₃), 157.16 (C). HRMS (ESI) calculated for C₁₂H₂₅NO₂Na ([M+Na]⁺): 238.1778. Found: 238.1762.

Cyclohexylmethylcarbamic acid methyl ester (15): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), methylene-cyclohexane (0.38 g, 1.9 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **15** as colourless oil which was solidified upon stand at low temperature (88 mg, 51 %). IR (neat) 3336br.m, 2924s, 2825m, 1705s, 1538s, 1449m, 1254s cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.93-0.84 (m, 2H, CH₂), 1.26-1.07 (m, 3H, CH₂), 1.41 (s, br., 1H, CH), 1.82-1.62 (m, 5H, CH₂), 2.99 (s, br., 2H, NHCH₂), 3.64 (s, 3H, CO₂CH₃), 4.74 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 25.77 (CH₂), 26.38 (CH₂), 30.62 (CH₂), 38.24 (CH), 47.32 (CH₂), 51.92 (CH₃), 157.18 (C). HRMS (ESI) calculated for C₉H₁₇NO₂Na ([M+Na]⁺): 194.1151. Found: 194.1145.

[5-(*tert*-Butyldimethylsilanyloxy)pentyl]carbamic acid methyl ester (16a): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), *tert*-butyl-dimethyl-pent-4-enyloxy-silane (0.38 g, 1.9 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **16a** as a colourless oil with another regioisomer in 1:10 ratio (ratio was determined by ¹H NMR spectroscopy) (88 mg, 51 % (combined yield of both isomers)). Physical data of the major isomer is given. IR (neat) 3342br.m, 2932m, 2858w, 1706s, 1535m, 1463w, 1253s, 1099s, 835s, 776s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.02 (s, 6H, SiCH₃), 0.95 (s, 9H, C(CH₃)₃), 1.18-1.06 (m, 4H, CH₂), 1.38-1.28 (m, 2H, CH₂), 2.94-2.86 (m, 2H, NHCH₂), 3.42-3.37 (m, 2H, OCH₂), 3.44 (s, 3H, CO₂CH₃), 4.12 (s, br., 1H, NH). ¹³C (75 MHz, CDCl₃) δ -5.17 (CH₃), 18.49 (C), 23.16 (CH₂), 26.14 (CH₃), 30.02 (CH₂), 32.70 (CH₂), 41.12 (CH₂), 51.59 (CH₃), 63.02 (CH₂), 156.84 (C). HRMS (ESI) calculated for C₁₃H₂₉NO₃SiNa ([M+Na]⁺): 298.1809. Found: 298.1804.

(10-Hydroxydecyl)carbamic acid methyl ester (17a): Prepared according to the general procedure (4) using reagent **8a** (0.1 g, 0.4 mmol), dec-9-en-1-ol (0.16 g, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (7.0 mg, 0.08 mmol) in dry benzene (1 ml) Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **17a** as white solid with another regioisomer in 1:10 ratio (ratio was determined by ¹H NMR spectroscopy) (44 mg, 46 % (combined yield of both isomers)). Physical data of the major isomer is given. IR (neat) 3349br.s, 2923s, 2852s, 1689s, 1531s, 1462m, 1354w, 1278m, 1254s, 1055s, 1012m cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.48-1.12 (m, 16H, CH₂), 3.05-3.02 (m, 2H, NHCH₂), 3.51 (t, 2H, *J* = 6.6 Hz, OCH₂), 3.54 (s, 3H, CO₂CH₃), 4.53 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 25.69 (CH₂), 26.66 (CH₂), 29.18 (CH₂), 29.33 (CH₂), 29.38 (CH₂), 29.44 (CH₂), 29.99 (CH₂), 32.77 (CH₂), 41.11 (CH₂), 51.98 (CH₃), 63.02 (CH₂), 157.07 (C). HRMS (ESI) calculated for C₁₂H₂₅NO₃Na ([M+Na]⁺): 254.1727. Found: 254.1724.

[1-(*tert*-Butyldimethylsilanyloxymethyl)2-methyl-propyl]carbamic acid methyl ester (18): Prepared according to the general procedure (4) using reagent **8a** (0.1 g, 0.4 mmol), *tert*-butyl-dimethyl-(3-methyl-but-2-enyloxy)-silane (0.21 g, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (9.0 mg, 0.08 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **18** as colourless oil (47 mg, 41 %). IR (neat) 3333br.w, 2958s, 1705s, 1536s, 1465m, 1255s, 1102m, 837s, 777s cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.04 (s, 6H, SiCH₃), 0.88 (s, 9H, SiC(CH₃)₃), 0.94-0.90 (m, 6H, CH(CH₃)₂), 1.92-1.82 (m, 1H, CH(CH₃)₂), 3.41 (s, br., 1H, CHH), 3.59-3.55 (dd, 1H, *J*₁ = 4.2 Hz, *J*₂ = 10.1 Hz, CHH), 3.71-3.63 (m, 4H, CO₂CH₃, CHOTBS), 4.82 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ -5.54 (CH₃), 18.20 (C), 18.63 (CH), 25.82 (CH₃), 29.05 (CH₃), 51.96 (CH₃), 57.61 (CH), 63.04 (CH₂), 157.00 (C). HRMS (ESI) calculated for C₁₃H₂₉NO₃SiNa ([M+Na]⁺): 298.1809. Found: 298.1798.

Acetic acid 3-methoxycarbonylaminopropyl ester (19): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), acetic acid allyl ester (0.19 g, 1.9 mmol), DTBP (46 mg, 0.31

mmol) and thiophenol (7.0 mg, 0.06 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 1:1) provided **19** as a colourless oil (57 mg, 52 %). IR (neat) 3355br.*m*, 2956*m*, 1733*s*, 1534*s*, 1451*w*, 1368*m*, 1243*s*, 1043*m*, 779*w* cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.85-1.77 (*m*, 2H, CH₂), 2.04 (*s*, 3H, COCH₃), 3.26-3.20 (*m*, 2H, NHCH₂), 3.64 (*s*, 3H, CO₂CH₃), 4.11 (*t*, 2H, *J* = 6.1 Hz, CH₂OAc), 4.94 (*s*, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 20.88 (CH₃), 28.97 (CH₂), 37.80 (CH₂), 52.02 (CH₃), 61.76 (CH₂), 157.00 (C), 171.15 (C). HRMS (ESI) calculated for C₇H₁₃NO₄Na ([M+Na]⁺): 198.0737. Found: 198.0734.

(3-*iso*-Propyloxysilanylpropyl)carbamic acid methyl ester (20): Prepared according to the general procedure (**4**) using reagent **8a** (0.15 g, 0.62 mmol), allyltriisopropoxysilane (0.39 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **20** as a colourless oil (93 mg, 46 %). IR (neat) 3344br.*m*, 2973*s*, 1708*s*, 1533*s*, 1377*m*, 1251*m*, 1173*m*, 1122*s*, 1039*s*, 886*m*, 776*m* cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 0.65-0.59 (*m*, 2H, SiCH₂), 1.27 (*d*, 18H, *J* = 6.1 Hz, CH(CH₃)₂), 1.76-1.66 (*m*, 2H, CH₂), 3.24-3.17 (*m*, 2H, NHCH₂), 3.56 (*s*, 3H, CO₂CH₃), 4.28 (sept., 1H, *J* = 6.1 Hz, CH(CH₃)₂), 4.77 (*s*, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 9.46 (CH₂), 24.01 (CH₂), 25.75 (CH₃), 43.78 (CH₂), 51.54 (CH₃), 65.17 (CH), 156.94 (C). HRMS (ESI) calculated for C₁₄H₃₁NO₅SiNa ([M+Na]⁺): 344.1864. Found: 344.1860.

(3-Methoxycarbonylaminopropyl)phosphonic acid dimethyl ester (21): Prepared according to the general procedure (**4**) using reagent **8a** (0.1 g, 0.4 mmol), allyl-phosphonic acid dimethyl ester (0.16 g, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (7.0 mg, 0.06 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **21** as a colourless oil (30 mg, 32 %). IR (neat) 3417br.*m*, 2956*w*, 1708*s*, 1541*m*, 1455*w*, 1255*s*, 1036*s*, 823*w* cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.85-1.71 (*m*, 4H, CH₂), 3.22 (*s*, br., 2H, NHCH₂), 3.64 (*s*, 3H, CO₂CH₃), 3.70 (*s*, 3H, OCH₃), 3.73 (*s*, 3H, OCH₃), 5.11 (*s*, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 21.93 (*d*, *J* = 142.5 Hz, CH₂), 22.98 (*d*, *J* = 4.9 Hz, CH₂), 41.16 (*d*, *J* = 16.4 Hz, CH₂), 52.03 (CH₃), 52.35 (*d*, *J* = 6.6 Hz, CH₃), 157.09 (C). HRMS (ESI) calculated for C₇H₁₆NO₅PNa ([M+Na]⁺): 248.0658. Found: 248.0639.

2-(3-Methoxycarbonylaminopropyl)malonic acid diethyl ester (22): Prepared according to the general procedure (**4**) using reagent **8a** (0.15 g, 0.62 mmol), 2-allyl-malonic acid diethyl ester (0.37 g, 1.9 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **22** as a colourless oil (68 mg, 40 %). IR (neat) 3386br.*w*, 2982*m*, 1728*s*, 1532*m*, 1450*w*, 1371*w*, 1254*s*, 1029*m* cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.24 (*t*, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃), 1.57-1.45 (*m*, 2H, CH₂), 1.93-1.85 (*m*, 2H, CH₂), 3.20-3.14 (*m*, 2H, NHCH₂), 3.30 (*t*, 1H, *J* = 7.4 Hz, CH(CO₂Et)₂), 3.63 (*s*, 3H, CO₂CH₃), 4.20-4.13 (*dq*, 4H, *J*₁ = 0.9 Hz, *J*₂ = 7.1 Hz, CO₂CH₂CH₃), 4.82 (*s*, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 14.00 (CH₃), 25.72 (CH₂), 27.60 (CH₂), 40.42 (CH₂), 51.49 (CH), 51.97 (CH₃), 61.39 (CH₂), 156.97 (C), 169.20 (C). HRMS (ESI) calculated for C₁₂H₂₁NO₆Na ([M+Na]⁺): 298.1261. Found: 298.1260.

(2-Phenyl-propyl)carbamic acid methyl ester (23): Prepared according to the general procedure (**4**) using reagent **8a** (0.1 mg, 0.4 mmol), β-methylstyrene (0.12 mg, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (7.0 mg, 0.06 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **23** as a colourless oil (39 mg, 48 %). IR (neat) 3336br.*m*, 2963*m*, 1704*s*, 1527*s*, 1259*s*, 1010*m*, 762*m*, 700*s* cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.27 (*d*, 3H, *J* = 7.2 Hz, CH₃), 2.98-2.83 (*m*, 1H, CH-benzylic), 3.27-3.19 (*m*, 1H, NHCHH), 3.51-3.38 (*m*, 1H, NHCHH), 3.62 (*s*, 3H, CO₂CH₃), 4.59 (*s*, br., 1H, NH), 7.26-7.18 (*m*, 3H, CH-aromatic), 7.35-7.30 (*m*, 2H, CH-aromatic). ¹³C NMR (75 MHz, CDCl₃) δ 19.09 (CH₃), 40.04 (CH), 47.69 (CH₂), 52.00 (CH₃), 126.65 (CH), 127.15 (CH), 128.64 (CH), 143.91 (C), 156.95 (C). HRMS (ESI) calculated for C₁₁H₁₅NO₂Na ([M+Na]⁺): 216.0995. Found: 216.0985.

[2-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]carbamic acid methyl ester (24): Prepared according to the general procedure (4) using reagent **8a** (0.1 g, 0.4 mmol), *tert*-butyl-dimethyl-(1-phenyl-vinyloxy)-silane (0.34 g, 0.80 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (9.0 mg, 0.08 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 5:1) provided **24** as a colourless oil (90 mg, 70 %). IR (neat) 3356br. *m*, 2954s, 2857m, 1716s, 1518s, 1468m, 1257s, 1098s, 1007w, 836s, 778s, 701s cm⁻¹. ¹H NMR (300 MHz, C₆D₆) δ -0.12 (s, 3H, SiCH₃), 0.02 (s, 3H, SiCH₃), 0.91 (s, 9H, SiC(CH₃)₃), 3.13-3.02 (m, 1H, NHCHH), 3.39-3.33 (m, 1H, NHCHH), 3.44 (s, 3H, CO₂CH₃), 4.57 (s, br., 1H, NH), 4.79-4.75 (m, 1H, CHOTBS), 7.12-7.01 (m, 3H, CH-aromatic), 7.23-7.18 (m, 2H, CH-aromatic). ¹³C NMR (75 MHz, CDCl₃) δ -5.13 (CH₃), -4.77 (CH₃), 18.15 (C), 25.76 (CH₂), 49.36 (CH₃), 52.09(CH), 73.69 (CH), 125.95 (CH), 127.55 (CH), 128.23 (CH), 142.11 (C), 156.98 (C). HRMS (ESI) calculated for C₁₆H₂₇NO₃SiNa ([M+Na]⁺): 332.1652. Found: 332.1646.

[2-(4-Bromophenyl)-2-(*tert*-butyldimethylsilanyloxy)ethyl]carbamic acid methyl ester (25): Prepared according to the general procedure (4) using reagent **8a** (0.1 g, 0.4 mmol), [1-(4-bromophenyl)-vinyloxy]-*tert*-butyl-dimethyl-silane (0.33 g, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (9.0 mg, 0.08 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **25** as a colourless oil (100 mg, 62%). IR (neat) 3357 br.*m*, 2954m, 2857w, 1715s, 1517m, 1258s, 1092s, 1009m, 836s, 777s cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ -0.10 (s, 3H, SiCH₃), 0.03 (s, 3H, SiCH₃), 0.07 (s, 9H, SiC(CH₃)₃), 3.17-3.10 (m, 1H, NHCHH), 3.42-3.36 (m, 1H, NHCHH), 3.65 (s, 3H, CO₂CH₃), 4.75-4.72 (m, 1H, CHOTBS), 4.90 (s, br, 1H, NH), 7.20 (d, 2H, *J* = 8.4 Hz, CH-aromatic), 7.45 (d, 2H, *J* = 8.4 Hz, CH-aromatic). ¹³C NMR (100 MHz, CDCl₃) δ -5.11 (CH₃), -4.77 (CH₃), 18.13 (C), 25.74 (CH₃), 49.27 (CH₂), 52.13 (CH₃), 73.16 (CH), 121.42 (C), 127.69 (CH), 131.43 (CH), 141.29 (C), 156.96 (C). HRMS (ESI) calculated for C₁₆H₂₆BrNO₃SiNa ([M+Na]⁺): 412.0739. Found: 412.0734.

[2-(*tert*-Butyldimethylsilanyloxy)-2-(3,4-dimethoxyphenyl)ethyl]carbamic acid methyl ester (26): Prepared according to the general procedure (4) using reagent **8a** (0.1 g, 0.4 mmol), *tert*-butyl-[1-(3,4-dimethoxy-phenyl)-vinyloxy]-dimethyl-silane (0.31 mg, 1.0 mmol), DTBP (30 mg, 0.20 mmol) and thiophenol (9.0 mg, 0.08 mmol) in dry benzene (1 ml). Purification by FC (pentane / *tert*-butylmethylether 10:1) provided **26** as a colourless oil (81 mg, 53 %). IR (neat) 3390br.*m*, 2943s, 1717s, 1515s, 1461m, 1260s, 1148m, 1092s, 1026m, 834s, 775m cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ -0.21 (s, 3H, SiCH₃), -0.07 (s, 3H, SiCH₃), 0.77 (s, 9H, SiC(CH₃)₃), 3.07-3.00 (m, 1H, NHCHH), 3.35-3.28 (m, 1H, NHCHH), 3.55 (s, 3H, CO₂CH₃), 3.75 (s, 6H, OCH₃), 4.61-4.58 (m, 1H, CHOTBS), 4.79 (s, br., 1H, NH), 6.76-6.68 (m, 3H, CH-aromatic). ¹³C NMR (100 MHz, CDCl₃) δ -5.12 (CH₃), -4.74 (CH₃), 18.15 (C), 25.75 (CH₃), 49.45 (CH₂), 52.04 (CH₃), 55.80 (CH₃), 55.85 (CH₃), 73.49 (CH), 109.07 (CH), 110.89 (CH), 118.19 (CH), 134.86 (C), 148.38 (C), 148.89 (C), 156.97 (C). HRMS (ESI) calculated for C₁₈H₃₁NO₅SiNa ([M+Na]⁺): 392.1864. Found: 392.1853.

(2-*tert*-Butoxyethyl)carbamic acid methyl ester (27): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 2-methyl-2-vinyloxy-propane (0.16 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **27** as a colourless oil (58 mg, 53 %). IR (neat) 3342br.*m*, 2975s, 1715s, 1534s, 1363s, 1257s, 1195s, 1091s, 779m cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.16 (s, 9H, C(CH₃)₃), 3.31-3.29 (m, 2H, NHCH₂), 3.40 (t, 2H, *J* = 5.1 Hz, OCH₂), 3.65 (s, 3H, CO₂CH₃), 5.03 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 27.48 (CH₃), 41.64 (CH₂), 52.02 (CH₃), 60.58 (CH₂), 73.05 (C), 157.09 (C). HRMS (ESI) calculated for C₈H₁₇NO₃Na ([M+Na]⁺): 198.1101. Found: 198.1093.

(2-Butoxyethyl)carbamic acid methyl ester (28): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 1-vinyloxy-butane (0.19 mg, 1.9 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 6:1) provided **28** as a colourless oil (56 mg, 51 %). IR (neat) 3340br.*m*, 2958s, 2870s,

1713s, 1537s, 1464m, 1370w, 1260s, 1194w, 1118s, 1030w, 779s cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, 3H, *J* = 7.3 Hz, CH₃), 1.41-1.30 (m, 2H, CH₂), 1.57-1.50 (m, 2H, CH₂), 3.36-3.34 (m, 2H, NHCH₂), 3.41 (t, 2H, *J* = 6.6 Hz, OCH₂), 3.46 (t, 2H, *J* = 5.1 Hz, OCH₂), 3.66 (s, 3H, CO₂CH₃), 5.03 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 13.85 (CH₃), 19.27 (CH₂), 31.69 (CH₂), 41.00 (CH₂), 52.03 (CH₃), 69.46 (CH₂), 70.96 (CH₂), 157.06 (C). HRMS (ESI) calculated for C₈H₁₇NO₃Na ([M+Na]⁺): 198.1101. Found: 198.1103.

Tetrahydropyran-3-yl)carbamic acid methyl ester (29a): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 3,4-dihydro-2H-pyran (0.13 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml) Purification by FC (pentane / *tert*-butylmethylether 1:1) provided **29a** as a low melting white solid with another regio isomer in 1:4 ratio (ratio was determined by ¹H NMR spectroscopy) (60 mg, 60 % (combined yield of both isomers)). Physical data of the major isomer is given. IR (neat) 3317br.m, 2949s, 2852m, 1711s, 1536s, 1454w, 1307m, 1243s, 1093 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.60-1.51 (m, 2H, CH₂), 1.77-1.68 (m, 1H, CHH), 1.89-1.83 (m, 1H, CHH), 3.40-3.38 (m, 1H, NHCH), 3.78-3.60 (m, 7H, CO₂CH₃, OCH₂), 5.03 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 23.09 (CH₂), 28.85 (CH₂), 46.45 (CH), 51.93 (CH₃), 68.02 (CH₂), 71.41 (CH₂), 156.29 (C). HRMS (ESI) calculated for C₇H₁₃NO₃Na ([M+Na]⁺): 182.0788. Found: 182.0784.

[2-(Acetylmethylamino)ethyl]carbamic acid methyl ester (30): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), *N*-methyl-*N*-vinyl-acetamide (0.16 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / acetone 1:1) provided **30** as a colourless oil (60 mg, 55 %). IR (neat) 3321br.m, 2949w, 1710s, 1627s, 1538m, 1269s, 1148w, 1019m, 779w cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.02 (s, 3H, COCH₃, rotamer-1), 2.03 (s, 3H, COCH₃, rotamer-2), 2.87 (s, 3H, NCH₃, rotamer-2), 2.98 (s, 3H, NCH₃, rotamer-1), 3.32-3.21 (m, 2H, CH₂), 3.45-3.36 (m, 2H, CH₂), 3.57 (s, 3H, CO₂CH₃, rotamer-1), 3.60 (s, 3H, CO₂CH₃, rotamer-2), 5.51 (s, br., 1H, NH, rotamer-1), 5.74 (s, br., 1H, NH, rotamer-2). ¹³C.NMR (75 MHz, CDCl₃) δ 20.96 (CH₃, rotamer-2), 21.63 (CH₃, rotamer-1), 33.16 (CH₃, rotamer-2), 36.61 (CH₃, rotamer-1), 38.84 (CH₂, rotamer-2), 39.16 (CH₂, rotamer-1), 46.97 (CH₂, rotamer-1), 49.92 (CH₂, rotamer-2), 51.88 (CH₃, rotamer-1), 52.07 (CH₃, rotamer-2), 157.18 (C, rotamer-2), 157.26 (C, rotamer-1), 170.93 (C, rotamer-2), 171.69 (C, rotamer-1). HRMS (ESI) calculated for C₇H₁₄N₂O₃Na ([M+Na]⁺): 197.0897. Found: 197.0889.

[2-(2-Oxopyrrolidin-1-yl)-ethyl]carbamic acid methyl ester (31): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 1-vinyl-pyrrolidin-2-one (0.17 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (10 mg, 0.09 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / acetone 1:1) provided **31** as a low melting solid (64 mg, 55 %). IR (neat) 3322br.m, 2952m, 1705s, 1666s, 1538s, 1466m, 1267s, 1195w, 1148w, 1023m, 779w cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 2.04-1.97 (m, 2H, CH₂), 2.35 (t, 2H, *J* = 8.1 Hz, COCH₂), 3.39-3.32 (m, 4H, NCH₂CH₂NH), 3.43 (t, 2H, *J* = 7.2 Hz, NCH₂), 3.62 (s, 3H, CO₂CH₃), 5.29 (s, br., 1H, NH). ¹³C NMR (100 MHz, CDCl₃) δ 18.02 (CH₂), 30.80 (CH₂), 39.11 (CH₂), 42.46 (CH₂), 47.64 (CH₂), 52.03 (CH₃), 157.24 (C), 176.04 (C). HRMS (ESI) calculated for C₈H₁₄N₂O₃Na ([M+Na]⁺): 209.0897. Found: 209.0896.

[2-(2-Oxoperhydroazepin-1-yl)ethyl]carbamic acid methyl ester (32): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 1-vinyl-perhydro-azepin-2-one (0.26 g, 1.9 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / acetone 1:1) provided **32** as a colourless oil (69 mg, 52 % yield). IR (neat) 3318br.m, 2932s, 1713s, 1629s, 1536m, 1355w, 1260s, 1197s, 1147m, 1083w, 1008m, 979m, 921m, 779m, 730s cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.73-1.56 (m, 6H, CH₂), 2.50-2.47 (m, 2H, COCH₂), 3.36-3.21 (m, 4H, NCH₂CH₂NH), 3.47 (t, 2H, *J* = 6.1 Hz, NCH₂), 3.60 (s, 3H, CO₂CH₃), 5.43 (s, br., 1H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 23.24 (CH₂), 28.39 (CH₂), 29.80 (CH₂), 36.97 (CH₂), 40.02

(CH₂), 47.69 (CH₂), 50.25 (CH₂), 51.94 (CH₃), 157.27 (C), 177.00 (C). HRMS (ESI) calculated for C₁₀H₁₈N₂O₃Na ([M+Na]⁺): 237.1210. Found: 237.1211.

[2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)ethyl]carbamic acid methyl ester (33): Prepared according to the general procedure (4) using reagent **8a** (0.15 g, 0.62 mmol), 2-vinyl-isoindole-1,3-dione (0.22 g, 1.6 mmol), DTBP (46 mg, 0.31 mmol) and thiophenol (14 mg, 0.12 mmol) in dry benzene (1.5 ml). Purification by FC (pentane / *tert*-butylmethylether 1:1) provided **33** as a white solid (78 mg, 50 %). IR (neat) 3375br *m*, 2949*m*, 1772*s*, 1708*s*, 1531*s*, 1434*m*, 1396*s*, 1254*s*, 1191*m*, 1009*s*, 721*s* cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 3.52-3.40 (*m*, 2H, CH₂), 3.59 (*s*, 3H, CO₂CH₃), 3.88-3.78 (*m*, 2H, CH₂), 5.14 (*s*, br., 1H, NH), 7.73-7.67 (*m*, 2H, CH-aromatic), 7.86-7.78 (*m*, 2H, CH-aromatic). ¹³C NMR (75 MHz, CDCl₃), 37.71 (CH₂), 40.27 (CH₂), 52.15 (CH₃), 123.32 (CH), 131.84 (C), 134.04 (CH), 157.02 (C), 168.42 (C). HRMS (ESI) calculated for C₁₂H₁₂N₂O₄Na ([M+Na]⁺): 271.0689. Found: 271.0685.

References.

- a. Ohta, S.; Sumino, M.; Sasaki, T.; Yamagami, N. *Heterocycles* **1989**, *29*, 1455.
- b. Kemper, J.; Studer, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 4914.
- c. Berson, J. A.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4094.
- d. Newton, M. G; Pantaleo, N. S.; Kirbawy, S.; Allinger, N. L. *J. Am. Chem. Soc* **1978**, *100*, 2176.

Table S1: Optimized ground state and transition structures of the fragmentation reaction of **34a-e** and **35a-e** (PBE/TZVPP): Electronic energies in a.u. and cartesian coordinates in a.u. (bohr).

[CH₃·]
 E = -39.78918275198 a.u.
 Cartesian Coordinates in a.u. (bohr):
 c 0.000000 0.000000 -0.000000
 h 2.052774 0.000000 0.000002
 h -1.026387 1.777755 0.000002
 h -1.026387 -1.777755 0.000002
 =====

[**34a**] X = CH₃
 E = -311.1062877810 a.u.
 Cartesian Coordinates in a.u. (bohr):
 c 0.012643 -0.004153 2.353521
 c 2.597811 -0.001371 2.310002
 c 3.951994 0.000922 0.000000
 c 2.597811 -0.001371 -2.310002
 c 0.012643 -0.004153 -2.353521
 c -1.590911 -0.000441 0.000000
 c -3.326841 -2.370128 0.000000
 h -0.995080 -0.007618 4.157086
 h 3.642239 -0.003755 4.090057
 h 6.010717 0.002613 0.000000
 h 3.642239 -0.003755 -4.090057
 h -0.995080 -0.007618 -4.157086
 h -2.199895 -4.111327 0.000000
 h -4.545584 -2.374386 -1.684314
 h -4.545584 -2.374386 1.684314
 c -3.313135 2.379397 0.000000
 h -4.531698 2.390930 1.684428
 h -4.531698 2.390930 -1.684428
 h -2.175785 4.113836 0.000000
 =====

[**34a-TS**] X = CH₃
 E = -311.0731823859 a.u.
 Cartesian Coordinates in a.u. (bohr):
 c 0.075470 -1.047530 0.997799
 c 1.894349 -3.007258 0.639734
 c 4.237732 -2.508778 -0.424966
 c 4.931537 -0.027167 -1.046197
 c 3.266365 1.961720 -0.501034
 c 0.919850 1.477533 0.563646
 c -2.098846 -1.583149 -2.597272
 c -2.147337 -1.500842 2.744035
 h 1.381233 -4.941262 1.146233
 h 5.560329 -4.056934 -0.753115
 h 6.775023 0.359118 -1.881283
 h 3.829931 3.907478 -0.888605
 h -0.352846 3.039835 1.010616
 h -0.585897 -1.268091 -3.954074
 h -3.522294 -0.103505 -2.437706
 h -2.764777 -3.520442 -2.386376
 h -2.946024 -3.398242 2.489400
 h -3.658172 -0.113401 2.435242
 h -1.535954 -1.335447 4.726591
 =====

[SiH₃·] X = SiH₃
 E = -291.0688264893 a.u.
 Cartesian Coordinates in a.u. (bohr):
 si 0.000000 0.000000 -0.000002

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h      2.802970      0.000000      0.000014
h     -1.401485      2.427443      0.000014
h     -1.401485     -2.427443      0.000014
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[34b] X = SiH3
E = -562.3785829147 a.u.
Cartesian Coordinates in a.u. (bohr):
c     -0.592490     -0.630324     -2.360892
c     -3.035556      0.240151     -2.300776
c     -4.284667      0.731963      0.012497
c     -3.038487      0.151998      2.306654
c     -0.596371     -0.722858      2.335528
c      0.948768     -0.944029     -0.017037
c      2.668149     -3.298727     -0.061713
h      0.320100     -1.050203     -4.164115
h     -4.050116      0.516941     -4.076187
h     -6.221215      1.428220      0.024625
h     -4.056139      0.357112      4.089977
h      0.313442     -1.214489      4.121944
h      1.508181     -5.024536     -0.099059
h      3.883822     -3.376873      1.621149
h      3.890863     -3.309453     -1.741335
si     3.149391      2.031325      0.038996
h      4.781851      2.048496     -2.282803
h      4.812165      1.942750      2.337980
h      1.565724      4.368421      0.102920
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[34b-TS] X = SiH3
E = -562.3644689436 a.u.
Cartesian Coordinates in a.u. (bohr):
c     -0.463525     -0.768301     -2.319353
c     -2.806970      0.409694     -2.283398
c     -3.987607      0.992547      0.016765
c     -2.816765      0.292688      2.289355
c     -0.473327     -0.885275      2.275209
c      0.870279     -1.294660     -0.031133
c      3.066628     -3.134918     -0.072987
h      0.428617     -1.240559     -4.119099
h     -3.747065      0.860003     -4.062683
h     -5.825785      1.921534      0.036556
h     -3.764749      0.651536      4.085186
h      0.411318     -1.448597      4.052329
h      2.337388     -5.086475     -0.123428
h      4.256497     -2.950479      1.615969
h      4.263294     -2.866166     -1.745780
si     3.378184      2.778825      0.058391
h      4.936045      3.243896     -2.275297
h      4.989657      3.167928      2.370217
h      1.191490      4.571928      0.113656
=====

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[NH₂·] X = NH₂
 E = -55.83100569658 a.u.
 Cartesian Coordinates in a.u. (bohr):
 n 0.000000 0.000000 0.155248
 h 1.523510 0.000000 -1.078657
 h -1.523510 0.000000 -1.078657
 =====

[**34c**] X = NH₂
 E = -327.1485060255 a.u.
 Cartesian Coordinates in a.u. (bohr):
 c -0.030921 -0.073887 -2.354191
 c -2.620411 -0.033232 -2.317154
 c -3.963397 -0.024611 -0.004398
 c -2.609481 -0.026642 2.308299
 c -0.025181 -0.022053 2.357962
 c 1.571407 -0.016958 0.000243
 n 3.187246 2.306685 0.084404
 c 3.404099 -2.287912 0.033053
 h 0.988948 -0.098088 -4.151725
 h -3.668397 -0.009470 -4.094736
 h -6.022427 -0.000253 0.000634
 h -3.657255 -0.018289 4.086064
 h 1.004765 0.028899 4.144770
 h 2.046316 3.859160 -0.085445
 h 4.352908 2.321134 -1.462561
 h 2.359514 -4.078316 0.056348
 h 4.622103 -2.182738 1.711087
 h 4.612097 -2.260388 -1.661079
 =====

[**34c**-TS] X = NH₂
 E = -327.1246566284 a.u.
 Cartesian Coordinates in a.u. (bohr):
 c -0.325468 -0.412688 -2.216197
 c -2.866339 0.256457 -2.261819
 c -4.205608 0.563831 -0.003098
 c -2.971977 0.154429 2.313206
 c -0.443231 -0.516056 2.375574
 c 1.020711 -0.697643 0.108726
 n 2.738835 2.901499 0.147395
 c 3.482268 -2.140846 0.150119
 h 0.692676 -0.717269 -3.986266
 h -3.823072 0.510892 -4.070555
 h -6.200708 1.077475 -0.038531
 h -4.024114 0.332883 4.077891
 h 0.496823 -0.856365 4.179601
 h 1.145927 3.964805 0.527075
 h 2.955871 3.142898 -1.780006
 h 3.104466 -4.187359 0.150436
 h 4.582471 -1.671118 1.840723
 h 4.640469 -1.705825 -1.514275
 =====

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[·NH(CO)CH3] X = NHAc
E = -208.3809462348 a.u.
Cartesian Coordinates in a.u. (bohr):
n    1.518971    2.036848   -0.068445
c    0.046249   -0.006966    0.076654
h    3.331860    1.728394    0.560335
o    1.163224   -2.107515   -0.029107
c   -2.771536    0.226900    0.002667
h   -3.346455    2.163608    0.463226
h   -3.461663   -0.253682   -1.896327
h   -3.620011   -1.110682    1.340681
=====

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[34d] X = NHAc
E = -479.6892744028 a.u.
Cartesian Coordinates in a.u. (bohr):
c    4.802671   -1.297318   -1.470744
c    2.486388   -2.247899   -0.832481
c    0.537129   -0.761096    0.629503
c    1.469730    1.868675    1.235146
c    3.800339    2.741875    0.532023
c    5.518538    1.196562   -0.813530
c   -0.049260   -2.240601    3.083719
n   -1.735887   -0.636312   -1.061257
c   -4.167783    0.244647   -0.735635
o   -5.553053    0.474241   -2.589431
c   -5.135659    0.831008    1.897823
h    0.175826    3.099427    2.267280
h    4.341128    4.674928    1.008284
h    7.365549    1.923934   -1.358261
h    6.127135   -2.486621   -2.513407
h    1.951029   -4.172898   -1.349749
h   -1.308032   -0.776994   -2.933241
h    1.713453   -2.538838    4.134349
h   -0.871317   -4.090307    2.618823
h   -1.358694   -1.214374    4.317715
h   -5.526550   -0.929789    2.927369
h   -3.805860    1.948327    3.029388
h   -6.907586    1.875701    1.686042
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[**34d**-TS] X = NHAc
 E = -479.6709995128 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	-3.227053	1.305619	-1.225780
c	-1.035910	1.362317	0.389852
c	-0.784316	-0.721901	2.119272
c	-2.369941	-2.799271	2.001904
c	-4.369838	-2.867866	0.262779
c	-4.796483	-0.780679	-1.324578
c	0.014628	3.912142	1.129236
n	1.559572	0.446152	-2.299333
c	3.707255	-0.954239	-2.088079
c	5.319149	-0.697312	0.256450
o	4.414377	-2.289901	-3.888101
h	0.724371	-0.654903	3.523065
h	-2.082344	-4.377817	3.296305
h	-5.614752	-4.506720	0.176140
h	-6.403198	-0.789911	-2.616752
h	-3.591034	2.940163	-2.430827
h	0.487030	-0.202493	-3.778971
h	-1.238403	4.801173	2.532326
h	0.150866	5.162018	-0.517049
h	1.897314	3.746023	1.979966
h	7.304682	-0.529524	-0.313497
h	4.788837	0.926529	1.425297
h	5.145191	-2.429600	1.390376

=====

[·NH(CO)OCH₃] X = NHMOC
 E = -283.5653042733 a.u.
 Cartesian Coordinates in a.u. (bohr):

n	3.104683	1.293684	-0.124433
c	0.909034	-0.057438	0.055557
h	4.414108	0.570488	1.116473
o	0.942003	-2.390297	-0.022870
o	-1.189899	1.363600	0.035650
c	-3.533118	-0.040980	-0.014364
h	-3.724764	-1.054445	-1.812760
h	-5.021985	1.378438	0.182749
h	-3.606002	-1.402046	1.548945

=====

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[34e] X = NHMOC
E = -554.8798220048 a.u.
Cartesian Coordinates in a.u. (bohr):
c   5.686956    0.221034   -1.475703
c   3.439793   -0.885160   -2.109782
c   1.199567   -0.976784   -0.346830
c   1.726973    0.395716    2.100643
c   4.005592    1.495235    2.634024
c   6.032704    1.423895    0.890441
c   0.562360   -3.784798    0.177788
n  -0.931998    0.256570   -1.745510
c  -3.374577    0.711011   -1.003688
o  -4.840880    2.056068   -2.174464
h   0.175413    0.466480    3.454755
h   4.262682    2.459319    4.440104
h   7.834556    2.306608    1.351251
h   7.246507    0.179388   -2.825686
h   3.194374   -1.812498   -3.937891
h  -0.390924    1.445193   -3.150972
h   2.194088   -4.710371    1.061861
h   0.127703   -4.751772   -1.608082
h  -1.068630   -3.943735    1.442972
o  -3.998393   -0.544696    1.168922
c  -6.580224   -0.183113    1.945333
h  -7.888928   -0.862001    0.486744
h  -6.965798    1.821796    2.310058
h  -6.790505   -1.290621    3.680275
=====

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[34e-TS] X = NHMOC
E = -554.8599261059 a.u.
Cartesian Coordinates in a.u. (bohr):
c  -3.242916    1.422516   -1.064656
c  -0.917365    1.208094    0.323427
c  -0.619119   -1.031368    1.828632
c  -2.363898   -2.983370    1.737935
c  -4.538487   -2.768287    0.241033
c  -4.966641   -0.538573   -1.143594
c   0.444299    3.597199    1.077424
n   1.396102    0.213973   -2.673435
c   3.623968   -1.058625   -2.358081
o   4.440584   -2.668782   -3.824946
h   1.062473   -1.189799    3.009576
h  -2.050535   -4.686975    2.855425
h  -5.908066   -4.305939    0.173134
h  -6.690784   -0.342134   -2.257263
h  -3.594789    3.162788   -2.114020
h   0.217927   -0.866453   -3.763865
h  -0.533664    4.467618    2.694731
h   0.460765    4.956952   -0.486008
h   2.399896    3.198362    1.626914
o   4.973439   -0.203047   -0.326712
c   7.428944   -1.335576   -0.058998
h   8.639042   -0.858754   -1.675383
h   7.284355   -3.401230    0.078176
h   8.214757   -0.546295    1.685140
=====

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[toluene]
E = -271.2971380777 a.u.
Cartesian Coordinates in a.u. (bohr):
c   -4.650094    0.003524    0.000000
h   -5.410490    1.933233    0.000000
h   -5.402813   -0.978585    1.670842
h   -5.402813   -0.978585   -1.670842
c   -1.802104    0.008578    0.000000
c   -0.444650   -2.270659    0.000000
c    2.191436   -2.282766    0.000000
c    3.530236   -0.005740    0.000000
c    2.206682    2.274936    0.000000
c   -0.434324    2.275531    0.000000
h   -1.473298   -4.060804    0.000000
h    3.207193   -4.077350    0.000000
h    5.591416   -0.012514    0.000000
h    3.230478    4.064848    0.000000
h   -1.455792    4.069192    0.000000
=====

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[3-Methoxycarbonyl-5-methyl-toluene]
E = -538.3010126599 a.u.
Cartesian Coordinates in a.u. (bohr):
c   -5.187780   -4.119079   -0.007761
h   -6.626410   -2.625827   -0.001322
h   -5.508078   -5.321957    1.657369
h   -5.506448   -5.306172   -1.684490
c   -2.557984   -3.026028   -0.001472
c   -0.437938   -4.619454   -0.013446
c    2.034829   -3.675283   -0.012099
c    2.373478   -1.053467   -0.011146
c    0.292026    0.578100    0.000763
c   -2.166570   -0.414709    0.007793
h   -0.726138   -6.666370   -0.030631
h    4.263604   -0.230284   -0.026213
h   -3.777878    0.867438    0.010767
c    4.273122   -5.434894    0.031429
h    5.893146   -4.623288   -0.979637
h    3.817182   -7.267155   -0.829523
h    4.889922   -5.804147    1.984514
c    0.803677    3.348468   -0.006601
o    2.901080    4.300256   -0.031606
o   -1.361662    4.741970    0.019961
c   -0.975098    7.434854    0.015887
h   -2.867133    8.266651    0.089080
h    0.017061    8.027039   -1.707211
h    0.145242    8.015200    1.662245
=====

```

[35a] X = CH₃
E = -578.1097454938 a.u.
Cartesian Coordinates in a.u. (bohr):

c	0.223062	1.855451	-0.001262
c	-0.923903	-0.473685	0.000183
c	0.528611	-2.729782	0.000902
c	3.211115	-2.621585	-0.001262
c	4.396577	-0.317174	-0.002568
c	3.042672	2.184794	0.000217
c	3.831729	3.728606	-2.372585
h	-0.926311	3.566758	-0.001901
c	-3.734474	-0.761507	0.000696
h	-0.461165	-4.535212	0.002250
c	4.695630	-5.053264	-0.002798
h	6.462894	-0.236491	-0.004243
h	3.310877	2.727746	-4.112814
h	5.888178	4.032886	-2.379298
h	2.898701	5.586117	-2.374711
c	3.829383	3.721374	2.378757
h	2.894183	5.577777	2.387002
h	5.885496	4.027934	2.387024
h	3.309161	2.713809	4.115286
h	6.738488	-4.696184	-0.003248
h	4.239686	-6.205036	1.666933
h	4.238703	-6.203556	-1.673286
o	-4.961984	1.499534	-0.002826
o	-4.838840	-2.782073	0.003950
c	-7.676145	1.316096	-0.002056
h	-8.362511	3.267044	-0.005901
h	-8.341477	0.303223	-1.685788
h	-8.340925	0.310102	1.686020

=====

[35a-TS] X = CH₃
E = -578.0769424239 a.u.
Cartesian Coordinates in a.u. (bohr):

c	0.051254	-1.130847	0.853969
c	1.813470	-3.090213	0.315540
c	4.161790	-2.533902	-0.737379
c	4.880830	-0.008607	-1.144920
c	3.286997	1.984560	-0.413379
c	0.945010	1.405334	0.634572
c	-2.154034	-1.375353	-2.748225
c	-2.164581	-1.680138	2.582445
h	1.284980	-5.050470	0.660101
h	6.731540	0.361789	-1.972448
h	-0.296958	2.940585	1.242469
h	-0.658029	-0.991240	-4.106321
h	-3.534969	0.121935	-2.444830
h	-2.865165	-3.306534	-2.676214
h	-2.987479	-3.544936	2.199727
h	-3.659743	-0.256067	2.385658
h	-1.535675	-1.662772	4.566060
c	4.122399	4.686826	-0.747419
h	2.785234	6.007936	0.129321
h	4.271095	5.177343	-2.762975
h	5.995241	5.006479	0.093182
c	6.010694	-4.542235	-1.441341
o	8.079911	-4.154146	-2.375176
o	5.134089	-6.907943	-0.925460
c	6.853088	-8.916816	-1.564566
h	7.278772	-8.896805	-3.594774
h	5.881097	-10.665403	-1.040079
h	8.629279	-8.722745	-0.510486

=====

[35b] X = SiH₃
 E = -829.3821310741 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	-1.144953	-0.802418	-3.933696
c	-3.241614	-0.156366	-2.536200
c	-2.995401	0.276680	0.098827
c	-0.643922	-0.136016	1.319724
c	1.479055	-0.788554	-0.039646
c	1.457789	-0.906382	-2.846520
c	3.089837	-3.066376	-3.931018
h	-1.339175	-1.184746	-5.954484
h	-4.622843	0.797142	1.246303
h	3.253697	-1.163852	0.936937
h	2.277389	-4.905192	-3.399440
h	5.033003	-2.984610	-3.201655
h	3.174058	-2.976344	-6.004520
si	3.022006	2.286956	-3.892015
h	3.056851	2.412357	-6.726392
h	5.684989	2.420606	-2.920580
h	1.518258	4.441411	-2.858622
c	-5.808800	0.057083	-3.747652
h	-5.750841	-0.461312	-5.754620
h	-6.530783	2.002345	-3.604977
h	-7.189100	-1.169653	-2.794091
c	-0.593255	0.113937	4.133098
o	-2.419189	0.659479	5.424643
o	1.738391	-0.331037	5.124985
c	1.875709	-0.124479	7.834461
h	0.565788	-1.455467	8.737288
h	1.397057	1.799726	8.444529
h	3.832637	-0.578395	8.325619

=====

[35b-TS] X = SiH₃
 E = -829.3681024604 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	-0.474543	-0.802647	-2.186624
c	-2.797353	0.441892	-2.269499
c	-3.950877	1.141505	0.012962
c	-2.822888	0.526995	2.343887
c	-0.496936	-0.696847	2.408952
c	0.835769	-1.244077	0.131775
c	2.983272	-3.142969	0.184656
h	0.418470	-1.398321	-3.950915
h	-5.771035	2.106706	0.029493
h	0.349873	-1.193470	4.219187
h	2.203349	-5.074928	0.166363
h	4.140239	-2.942513	1.893966
h	4.221189	-2.950687	-1.468693
si	3.418733	2.727834	-0.113044
h	4.605143	2.562173	-2.687247
h	5.373191	3.574000	1.779173
h	1.282695	4.581668	-0.152798
c	-4.052314	1.027560	-4.755898
h	-3.263772	-0.120017	-6.293398
h	-3.782598	3.027181	-5.263048
h	-6.098583	0.690363	-4.667683
c	-4.230016	1.208886	4.691714
o	-6.290194	2.235769	4.729055
o	-2.950966	0.555038	6.826019
c	-4.232839	1.165300	9.147872
h	-6.061623	0.191786	9.249795
h	-4.556513	3.209444	9.286477
h	-2.976888	0.521012	10.659069

=====

[**35c**] X = NH₂
 E = -594.1507179010 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	-4.372653	-0.344835	-0.074983
c	-3.176204	-2.658227	-0.033967
c	-0.507568	-2.740377	-0.028794
c	0.943341	-0.473918	-0.023307
c	-0.205908	1.850064	-0.012757
c	-3.029895	2.160053	-0.014255
n	-3.701296	3.637025	2.303917
c	-3.833111	3.803579	-2.290303
h	-6.439786	-0.257424	-0.108789
c	-4.678551	-5.086657	0.000559
h	0.495663	-4.538321	-0.013885
c	3.752782	-0.759802	-0.008010
h	0.909820	3.579496	0.045056
h	-3.388414	2.533613	3.860554
h	-5.598058	4.025818	2.282335
h	-3.315428	2.892289	-4.078499
h	-2.915415	5.662264	-2.175843
h	-5.895180	4.082043	-2.275222
h	-3.429976	-6.742047	-0.004407
h	-5.883552	-5.204264	1.689576
h	-5.926266	-5.225321	-1.655215
o	4.977392	1.500498	-0.009914
o	4.856543	-2.781927	0.003201
c	7.692229	1.320799	0.008944
h	8.374908	3.272867	0.008646
h	8.346994	0.317033	1.702072
h	8.369569	0.308313	-1.670067

=====

[**35c**-TS] X = NH₂
 E = -594.1278797498 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	-0.364597	-0.497571	-2.144194
c	-2.896651	0.233105	-2.284124
c	-4.205309	0.680370	-0.028790
c	-3.003220	0.368768	2.327636
c	-0.479926	-0.351182	2.445721
c	0.972458	-0.677671	0.193599
n	2.764040	2.868495	0.079818
c	3.399761	-2.175811	0.313661
h	0.657431	-0.936201	-3.886494
h	-6.190871	1.232202	-0.045858
h	0.431246	-0.619582	4.271617
h	1.204663	4.000707	0.394544
h	2.998223	2.999991	-1.856518
h	2.973074	-4.210345	0.403971
h	4.502144	-1.655175	1.987370
h	4.574731	-1.843485	-1.362565
c	-4.189037	0.542427	-4.802876
h	-3.328413	-0.669918	-6.250740
h	-4.046618	2.506854	-5.475297
h	-6.207733	0.079687	-4.679531
c	-4.561672	0.794027	4.641565
o	-6.783757	1.399464	4.628073
o	-3.221306	0.431235	6.804783
c	-4.638247	0.813274	9.096679
h	-6.239942	-0.501387	9.192240
h	-5.362058	2.754805	9.191739
h	-3.305676	0.454609	10.636660

=====

[**35d**] X = NHAc

E = -746.6919894066 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	2.663074	0.526045	0.045523
c	0.738628	-1.061004	0.764109
c	-1.939676	-0.164919	1.126058
c	-2.213060	2.610059	0.532609
c	-0.261173	4.143591	-0.213128
c	2.209007	3.121722	-0.440092
c	-2.667883	-0.704003	3.909950
n	-3.493727	-1.716898	-0.666506
c	-6.060724	-1.998426	-1.036562
o	-6.819583	-3.110057	-2.932016
c	-7.903396	-1.016354	0.926438
h	-4.112281	3.401195	0.705507
h	3.795457	4.300275	-1.018908
h	1.102792	-3.055484	1.127262
h	-2.517492	-2.307940	-2.217492
h	-1.289237	0.209792	5.160501
h	-2.646678	-2.748894	4.270531
h	-4.541610	0.044820	4.377984
h	-7.854372	-2.205669	2.627903
h	-7.511310	0.937090	1.501423
h	-9.796917	-1.122727	0.102539
c	-0.685359	6.896112	-0.809519
h	-0.185874	7.313199	-2.783787
h	0.506214	8.108597	0.386547
h	-2.663980	7.442132	-0.516687
c	5.321745	-0.389579	-0.266773
o	7.090364	0.949541	-0.879607
o	5.558133	-2.901679	0.207558
c	8.084061	-3.880306	-0.076806
h	9.374959	-2.961122	1.261382
h	8.776801	-3.559091	-2.004886
h	7.939962	-5.904281	0.321164

=====

[35d-TS1b] X = NHAc
 E = -746.6739213818 a.u.
 Cartesian Coordinates in a.u. (bohr):

c	2.200123	1.618782	0.132175
c	0.768890	2.981684	-1.594179
c	-1.805982	2.297656	-2.126369
c	-2.666356	-0.044254	-1.046530
c	-1.246899	-1.414732	0.682603
c	1.191918	-0.551307	1.294402
c	-2.928421	3.160451	-4.607525
c	-2.262962	-3.792048	1.873347
c	4.851485	2.333062	0.797155
o	5.603871	4.486911	-0.380393
c	8.148533	5.269872	0.195794
o	6.200921	1.139251	2.229275
n	-3.438166	4.920093	0.160717
c	-5.576050	4.728026	1.578761
o	-5.723377	5.864648	3.630502
c	-7.823725	3.309039	0.531870
h	-4.531742	-0.737311	-1.594004
h	2.371918	-1.574316	2.639387
h	1.573267	4.631818	-2.526612
h	-1.979996	5.598534	1.244348
h	-2.156800	2.008720	-6.158885
h	-2.474519	5.147824	-4.972951
h	-4.990134	2.947533	-4.626635
h	-9.539485	4.410040	0.903731
h	-7.662040	2.932284	-1.497234
h	-8.016303	1.502091	1.539449
h	-4.084282	-4.337191	1.045656
h	-2.542630	-3.533155	3.917378

h	-0.940860	-5.376688	1.636713
h	8.357043	5.623456	2.228582
h	8.448834	7.007643	-0.883313
h	9.505751	3.808286	-0.372499

=====

[35e] X = NHMOC

E = -821.8825482138 a.u.

Cartesian Coordinates in a.u. (bohr):

c	3.313376	-0.034857	0.511388
c	1.403800	-0.697504	-1.117572
c	-1.280398	-1.078705	-0.255920
c	-1.603688	-0.495709	2.515382
c	0.335885	0.196486	4.088119
c	2.825476	0.406127	3.108916
c	-2.011314	-3.862267	-0.806585
n	-2.848818	0.666294	-1.841291
c	-5.408305	1.090025	-1.818890
o	-6.425823	2.835677	-2.934464
h	-3.523752	-0.665299	3.249790
h	4.401645	0.939894	4.322020
h	1.794683	-1.028693	-3.113054
h	-1.899211	2.163788	-2.574618
h	-0.742662	-5.129609	0.234871
h	-1.830088	-4.248579	-2.838699
h	-3.962811	-4.232982	-0.221840
o	-6.693488	-0.683511	-0.446551
c	-9.393388	-0.342012	-0.462634
h	-10.137418	-0.462115	-2.394540
h	-9.906667	1.499980	0.339948
h	-10.145805	-1.877898	0.701435
c	-0.122130	0.754654	6.844001
h	0.374041	2.722218	7.296304
h	1.052232	-0.460046	8.054829
h	-2.108079	0.455633	7.358542
c	5.987980	0.264442	-0.359012
o	7.743611	0.836469	1.015080
o	6.258161	-0.171692	-2.875618
c	8.801930	0.096750	-3.809210
h	8.691977	-0.304115	-5.834657
h	10.069963	-1.245306	-2.864217
h	9.499935	2.021792	-3.479519

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[35e-TS] X = NHMOC

E = -821.8628398110 a.u.

Cartesian Coordinates in a.u. (bohr):

c	-1.792363	1.923558	-0.385970
c	0.531341	1.740453	0.999036
c	0.862949	-0.483910	2.516163
c	-0.821794	-2.500435	2.460458
c	-2.996693	-2.292458	0.952490
c	-3.485508	-0.079227	-0.447002
c	1.848784	4.154122	1.758817
n	2.840885	0.818470	-2.014866
c	5.079974	-0.435805	-1.701384
o	5.915507	-2.026420	-3.178632
h	2.546532	-0.593675	3.703500
h	-4.373852	-3.823501	0.862235
h	-2.190344	3.646783	-1.439046
h	1.683816	-0.258932	-3.130642
h	0.861412	4.996187	3.385159
h	1.830755	5.520465	0.201671
h	3.814205	3.790441	2.297263
o	6.413709	0.414901	0.341485
c	8.880112	-0.695439	0.607818

h	10.089406	-0.194573	-1.001683
h	8.755369	-2.763350	0.729330
h	9.653124	0.088857	2.359811
c	-0.340958	-4.863735	3.972424
h	0.238409	-6.428346	2.730697
h	-2.051606	-5.480415	4.974783
h	1.165738	-4.576381	5.367982
c	-5.894251	0.016297	-1.920220
o	-7.461210	-1.669563	-1.961828
o	-6.150738	2.211429	-3.226211
c	-8.445371	2.409548	-4.680221
h	-8.359751	4.260775	-5.596829
h	-10.104599	2.278711	-3.442752
h	-8.542991	0.895170	-6.093835

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