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Supporting Information

A DFT Study on the Formation of Heterocycles Formation via Iodine(III)-Promoted Ring Expansion Reactions

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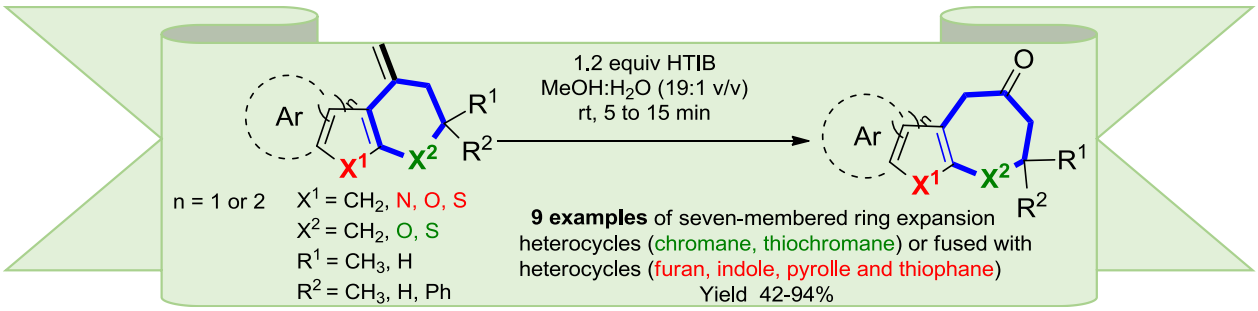
†In memory of Professor Luiz F. Silva Jr (1971-2017) for his numerous contributions to hypervalent iodine chemistry



Experimental

Known compounds were characterized by ^{1}H NMR, ^{13}C NMR and melting point (for solids) and compared with literature data. All novel compounds were characterized by ^{1}H NMR,^{13}C NMR, IR, HRMS and melting point (for solids). All Wittig reactions have been performed in septum-sealed flasks under nitrogen atmosphere. Progress of the reactions was monitored by TLC analysis. The chromatographic analyses were performed by thin layer (TLC) employing silica gel plates (Merck Type 60 F_{254} on aluminum), with detection by UV light (254 nm) and stained with phosphomolybdic acid solution, vanillin, $KMnO_4$ solution or *p*-anisaldehyde. Chromatographic purifications were carried out by flash column chromatography using 200-400 mesh silica gel. The reagents and solvents have been treated and/or dried, when necessary, according to the usual methods.

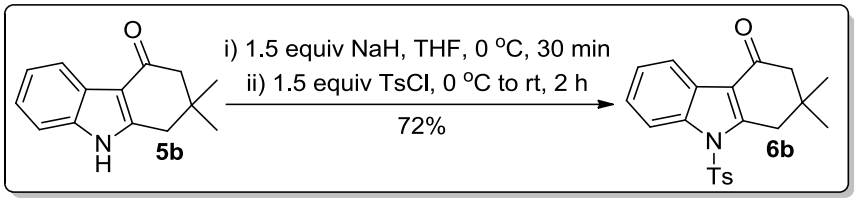
Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) in Hertz. Standard and peak multiplicities are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quintet; br s, broad singlet; and m, multiplet. The samples were prepared using $CDCl_3$ as solvent.

Bruker Avance-III 300 NMR and Bruker Avance-III 500 NMR instruments were used to record the proton and 13-C NMR spectra using detruded solvent of $CDCl_3$. For the IR analysis of the compound, Perkin Elmer 1750-FT equipment was used. Similarly, for the MS spectrometer, Bruker Daltonics microTOF electrospray was used while Perkin Elmer 2400 Series II for the elemental analysis have been used.

Compounds **7h** and **7j** were prepared according to literature procedures.[2]

4.1. *N*-Protection[1,2]

4.1.1. **2,2-Dimethyl-9-tosyl-1,2,3,9-tetrahydro-*4H*-carbazol-4-one** (**6b**).



To a round bottom flask, **5b** (0.639 g, 3.00 mmol) and NaH (0.180 g, 6.0 mmol, 60% dispersion in mineral oil) was added in THF (10 mL) at 0 °C. After 30 minutes TsCl (0.857 g 4.50 mmol) was added to the reaction mixture. The solution was allowed to rt and stirred for 2 h. The reaction mixture was quenched with distilled H_2O (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure.

Purification: The residue was purified by flash column chromatography (50% EtOAc in hexanes).

Yield: 72% (0.792 g, 2.16 mmol).

Sample appearance: Light brown solid.

Milting Point: 171-172 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.13 (6H, s), 2.37 (3H, s), 2.44 (2H, s), 3.22 (2H, s), 7.26 (2H, d, *J* = 8.1 Hz), 7.34 (2H, t, *J* = 3.9 Hz), 7.74 (2H, d, *J* = 8.4 Hz), 8.14-8.17 (1H, m), 8.20-8.24 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.8, 28.7, 35.3, 38.5, 52.0, 114.1, 117.1, 121.9, 125.1, 125.4, 125.7, 126.7, 130.3, 135.7, 136.4, 146.0, 150.0 194.9.

HRMS [ESI(+)] calcd. for $[C_{21}H_{21}NO_3SH]^+$ 368.1320, found 368.1311.

IR (film): 3339, 3059, 2959, 1669, 1597, 1559, 1450, 1408, 1176, 917, 813, 751, 665 cm^{-1}.

Figure S1: ^{1}H NMR of 2,2-Dimethyl-9-tosyl-1,2,3,9-tetrahydro-*4H*-carbazol-4-one (**6b**).

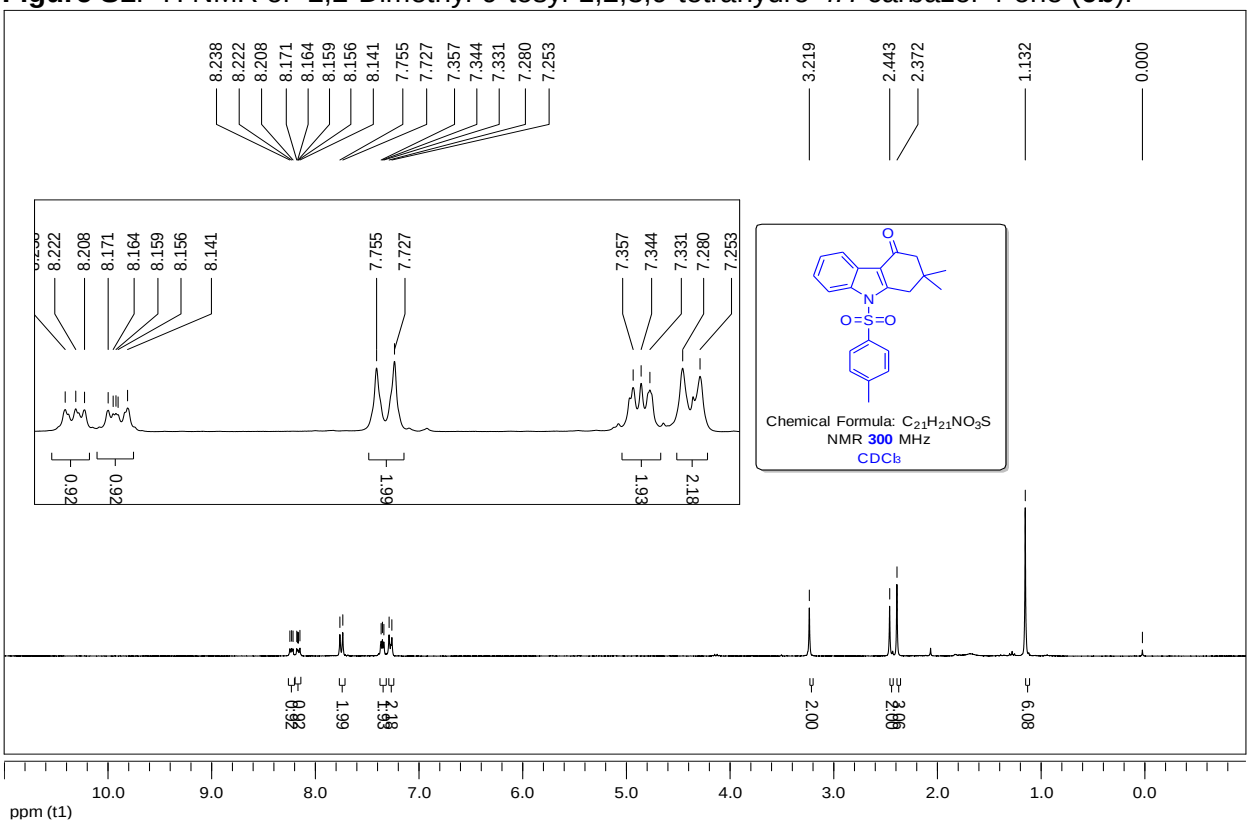
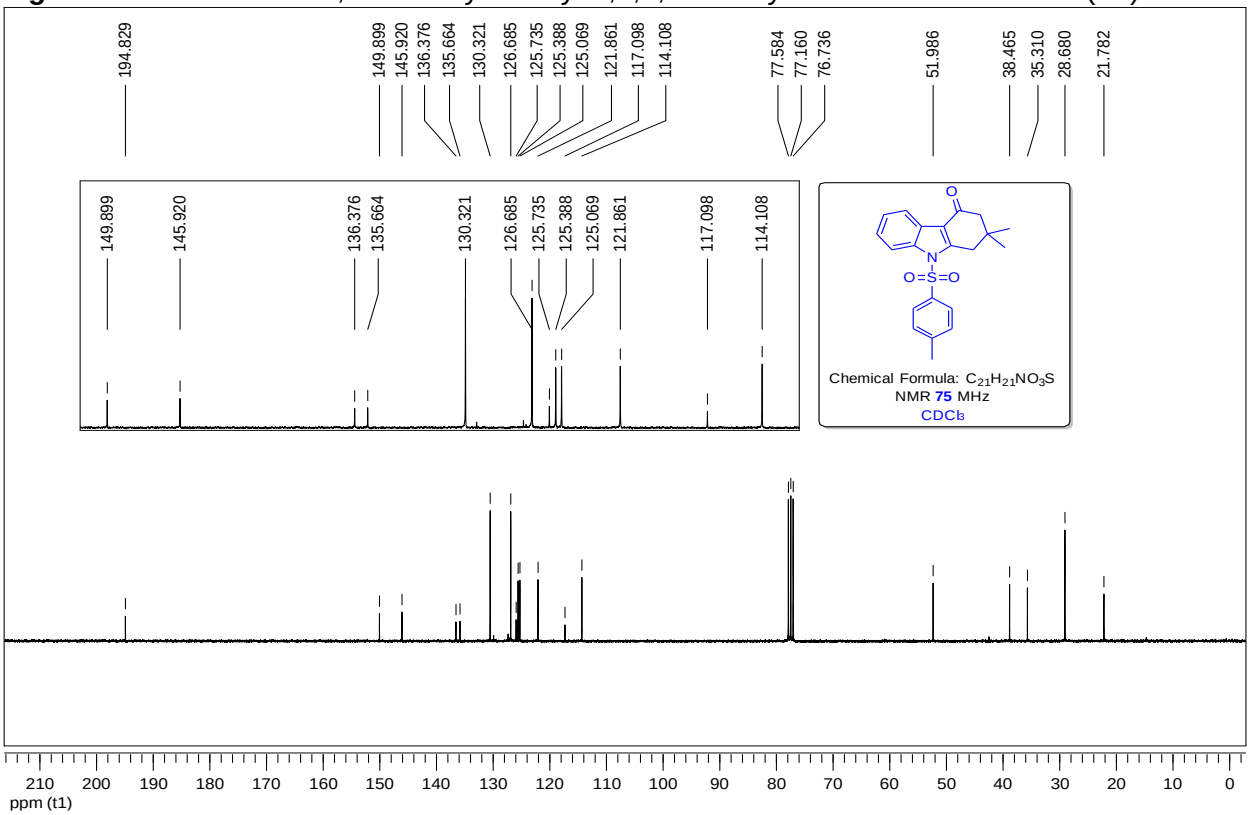
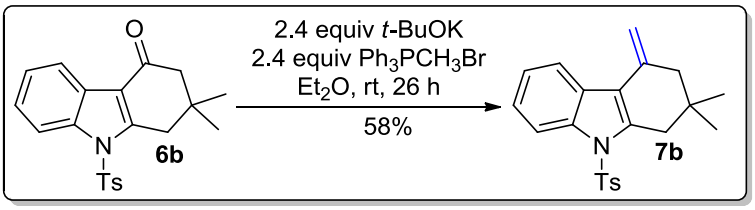


Figure S2: ^{13}C NMR of 2,2-Dimethyl-9-tosyl-1,2,3,9-tetrahydro-*4H*-carbazol-4-one (**6b**).



4.2. Wittig Olefination

4.2.1. **2,2-Dimethyl-4-methylene-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazole** (**7b**)**.**



Under nitrogen atmosphere, *t*-BuOK (0.220 g, 1.96 mmol) was added to a stirred mixture of Ph_3PCH_3Br (pre-dried in vacuum oven for 5-6 h) (0.700 g, 1.96 mmol) in anhydrous Et_2O (10 mL). The resulting yellow mixture was allowed to stir for 2 h. After which **6b** (0.300 g, 0.817 mmol) dissolved in anhydrous Et_2O/THF (5 mL, 1:1 v/v) was added dropwise to the above reaction mixture. The reaction was monitored by TLC for the consumption of the starting material. The reaction mixture was quenched with distilled H_2O and extracted with EtOAc (3 x 15 mL). The combine organic layers were washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure.

Purification: The residue was purified by flash column chromatography (20% Et_2O in hexane).
Yield: 58% (0.173 g, 0.474 mmol).
Sample appearance: Colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.01 (6H, s), 2.23 (2H, s), 2.33 (3H, s), 2.96 (2H, s), 5.05 (1H, s), 5.56 (1H, s), 7.18 (2H, d, *J* = 8.1 Hz), 7.26-7.29 (2H, m), 7.63 (2H, d, *J* = 8.1 Hz), 7.79 (1H, m), 8.21 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.7, 28.3, 32.0, 39.1, 47.1, 109,7, 114.8, 117.5, 120.4, 124.0, 124.2, 126.5, 127.7, 130.0, 136.2, 137.2, 137,7, 138.3, 144.9.
HRMS [ESI(+)] calcd. for $[C_{22}H_{23}NO_2SNa]^+$ 388.1347, found 388.1358.
IR (film): 3102, 2956, 2926, 1736, 1633, 1597, 1451, 1225, 1178, 975, 811, 771, 666, 585, 541 cm^{-1}

Figure S3: ^{1}H NMR of 2,2-Dimethyl-4-methylene-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazole (**7b**)**.**

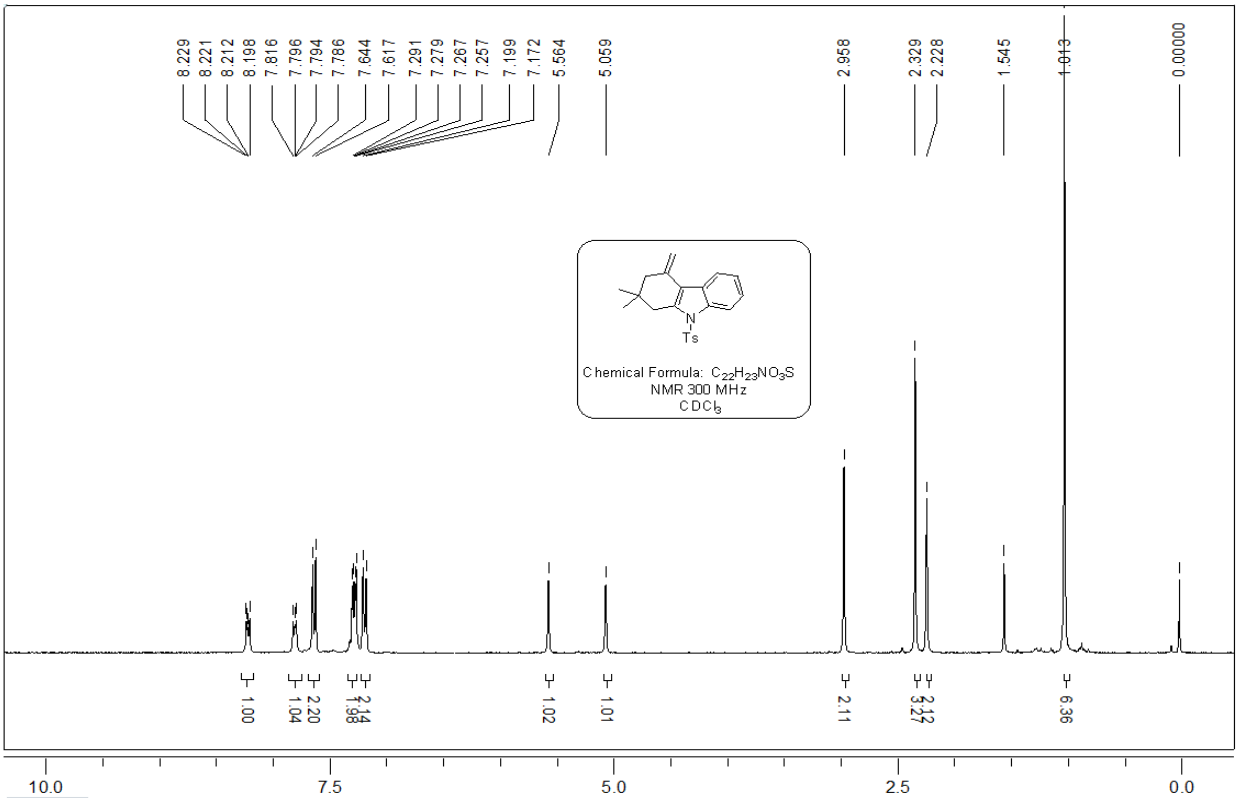
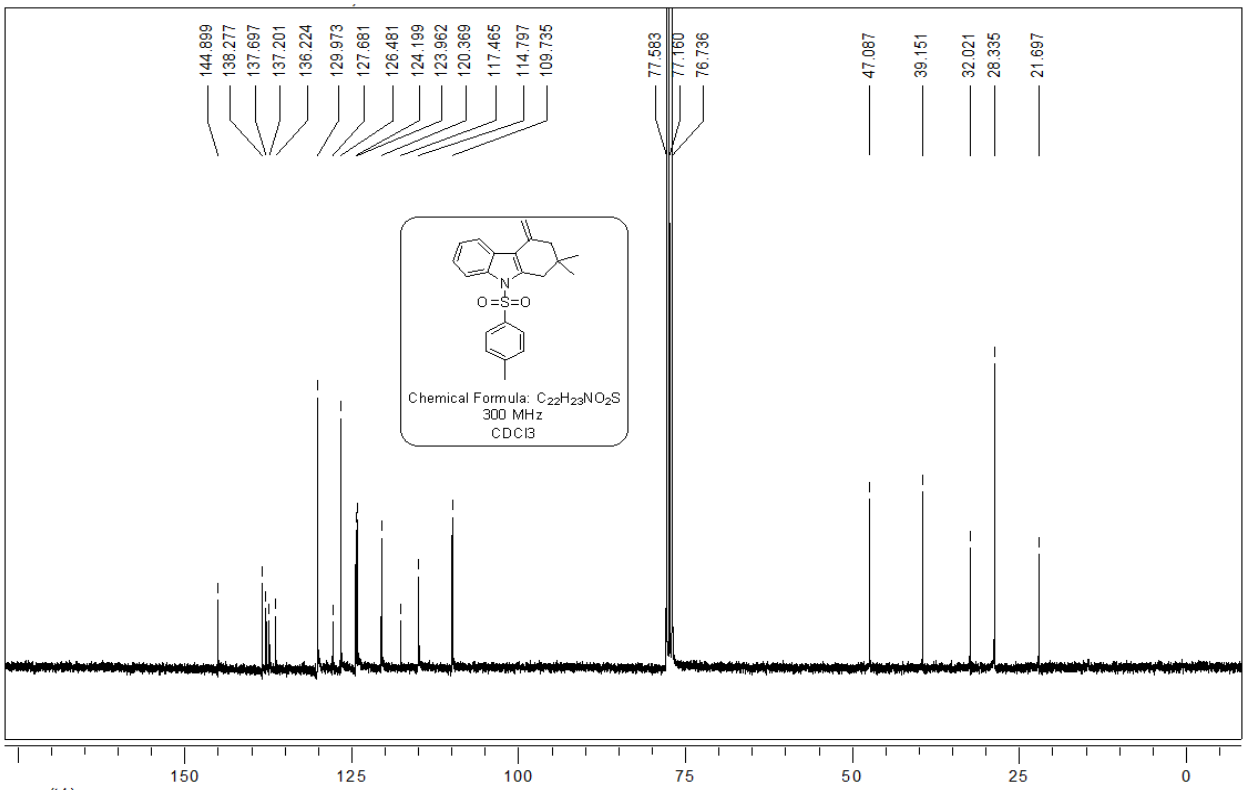
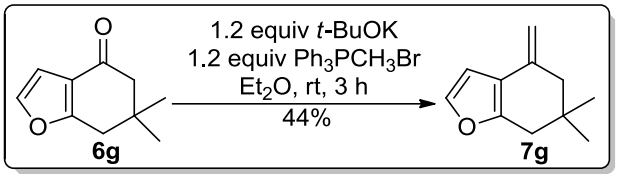


Figure S4: ^{13}C NMR of 2,2-Dimethyl-4-methylene-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazole (**7b**)**.**



4.2.2. **6,6-Dimethyl-4-methylene-4,5,6,7-tetrahydrobenzofuran** (**7g**).



The reaction was performed following the general protocol **4.2.1**, but using *t*-BuOK (0.134 g, 1.2 mmol), Ph_3PCH_3Br (0.428 g, 1.2 mmol) and **6g** (0.164 g, 1.00 mmol) in anhydrous Et_2O (8 mL).
Purification: The residue was purified by flash column chromatography (10% EtOAc in hexanes).
Yield: 44% (0. 071 g, 0.44 mmol).
Sample appearance: Colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.00 (6H, s), 2.18 (2H, s), 2.48 (2H, s), 4.79 (1H, s), 5.04 (1H, s), 6.47 (1H, d, *J* = 2.0 Hz), 7.25 (1H, d, *J* = 2.0 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 28.3, 32.7, 37.4, 45.7, 106.3, 106.4, 118.4, 137.5, 141.5, 153.0.
Elemental Analysis: calcd. for $C_{11}H_{14}O$ - C, 81.44; H, 8.70; found: C, 81.17; H, 8.28.
IR (film): 3067, 2929, 2836, 1583, 1462, 1462, 1437, 1327, 1252, 1073, 726, 719 cm^{-1}.

Figure S5: ^{1}H NMR of 6,6-Dimethyl-4-methylene-4,5,6,7-tetrahydrobenzofuran (**7g**).

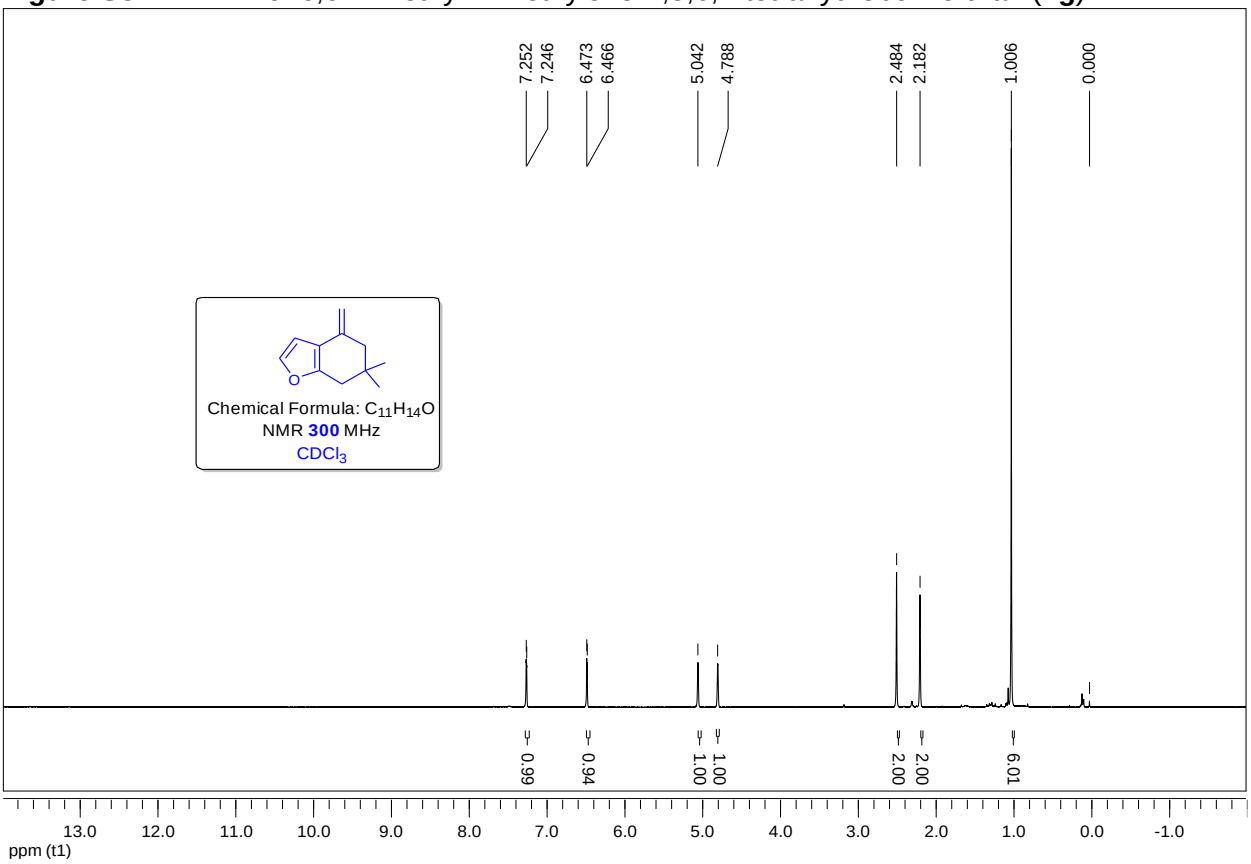
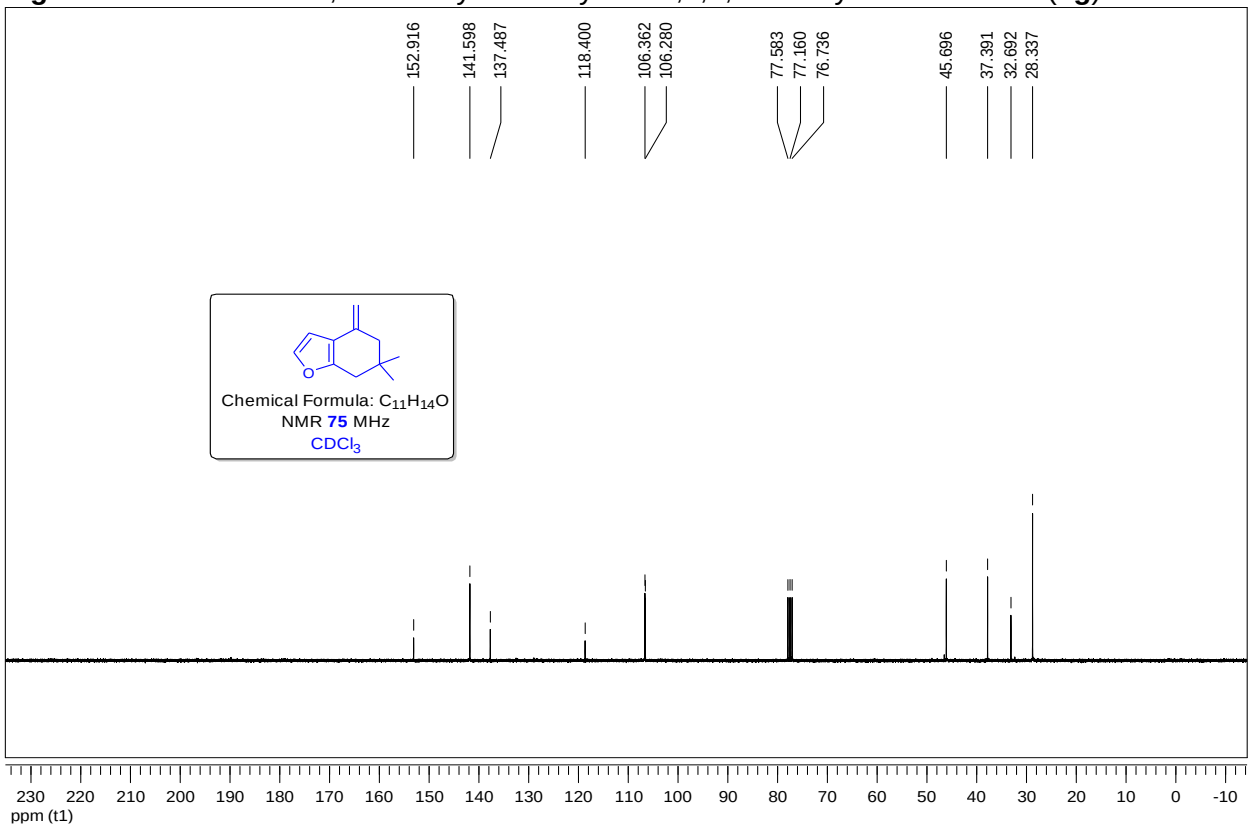
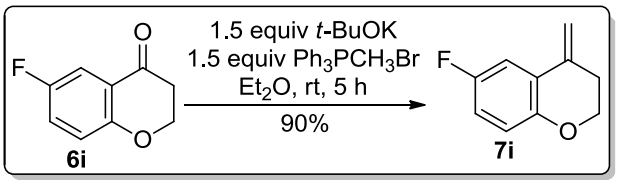


Figure S6: ^{13}C NMR of 6,6-Dimethyl-4-methylene-4,5,6,7-tetrahydrobenzofuran (**7g**).



4.2.3. **6-Fluoro-4-methylenechroman** (**7i**).



The reaction was performed following the general protocol **4.2.1**, but using *t*-BuOK (0.336 g, 3.00 mmol), Ph_3PCH_3Br (1.07 g, 3.00 mmol) and **6i** (0.332 g, 2.00 mmol) in anhydrous Et_2O (12 mL).

Purification: The residue was purified by flash column chromatography (10% EtOAc in hexane).

Yield: 90% (0.295 g, 1.80 mmol).

Sample appearance: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.67 (2H, t, J = 5.7 Hz), 4.20 (2H, t, J = 5.7 Hz), 4.94 (1H, s), 5.47 (1H, s), 6.78 (1H, dd, J = 10.0 and 5.0 Hz), 6.84-6.89 (1H, td, J = 8.5 and 3.0 Hz), 7.23 (1H, dd, J = 9.5, and 3.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 31.3, 66.9, 108.4, 110.2 ($J_{C\text{-}F}$ = 23.1 Hz), 116.5 ($J_{C\text{-}F}$ = 23.7 Hz), 118.6 ($J_{C\text{-}F}$ = 7.5 Hz), 122.6 ($J_{C\text{-}F}$ = 7.5 Hz), 136.5, 150.8, 157.3 ($J_{C\text{-}F}$ = 236.2 Hz).

Elemental Analysis: calcd. for $C_{10}H_9FO$ - C, 73.16, H, 5.53. Found: C - 73.09, H - 5.78.

IR (film): 3090, 2955, 2877, 1692, 1633, 1586, 1487, 1463, 1436, 1302, 1285, 1249, 1198, 1182, 1118, 1082, 1069, 1043, 991, 933, 889, 870, 816, 748, 703, 646 cm^{-1}.

Figure S7: ^{1}H NMR of 6-Fluoro-4-methylenechroman (**7i**).

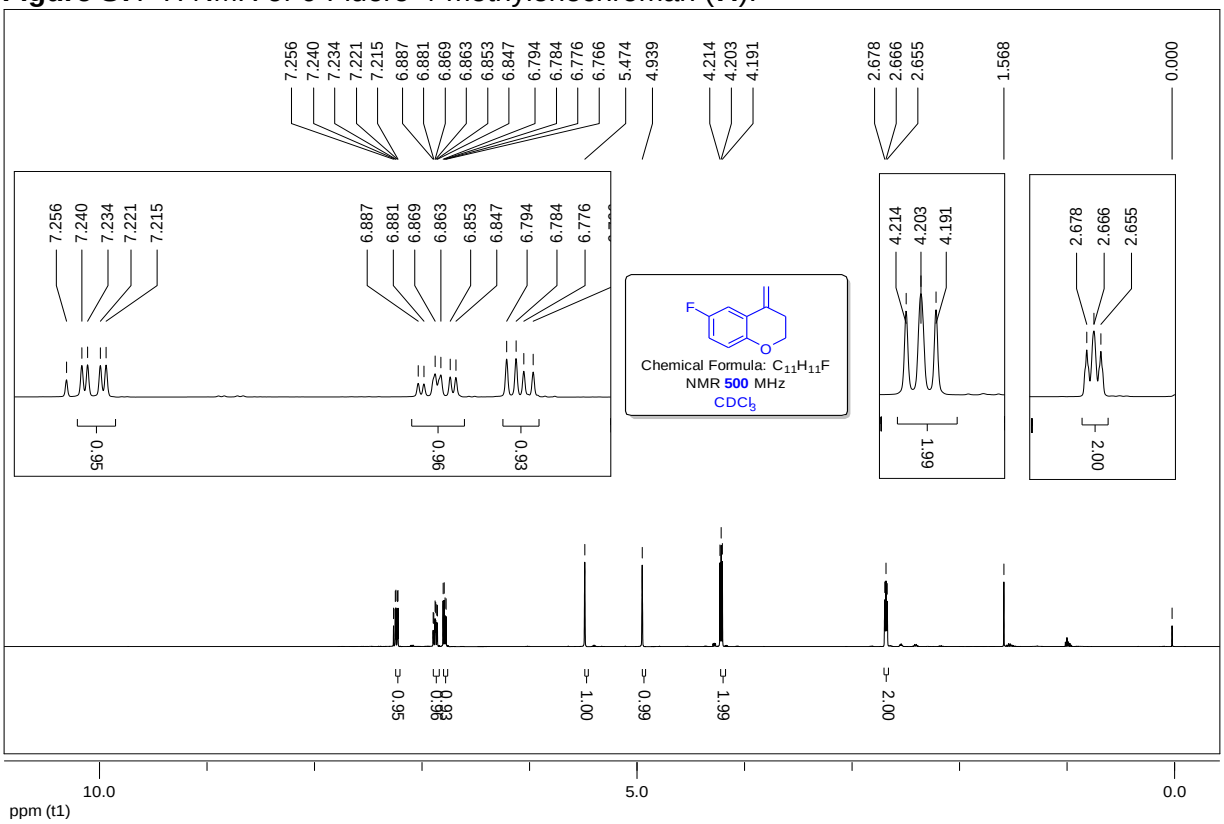
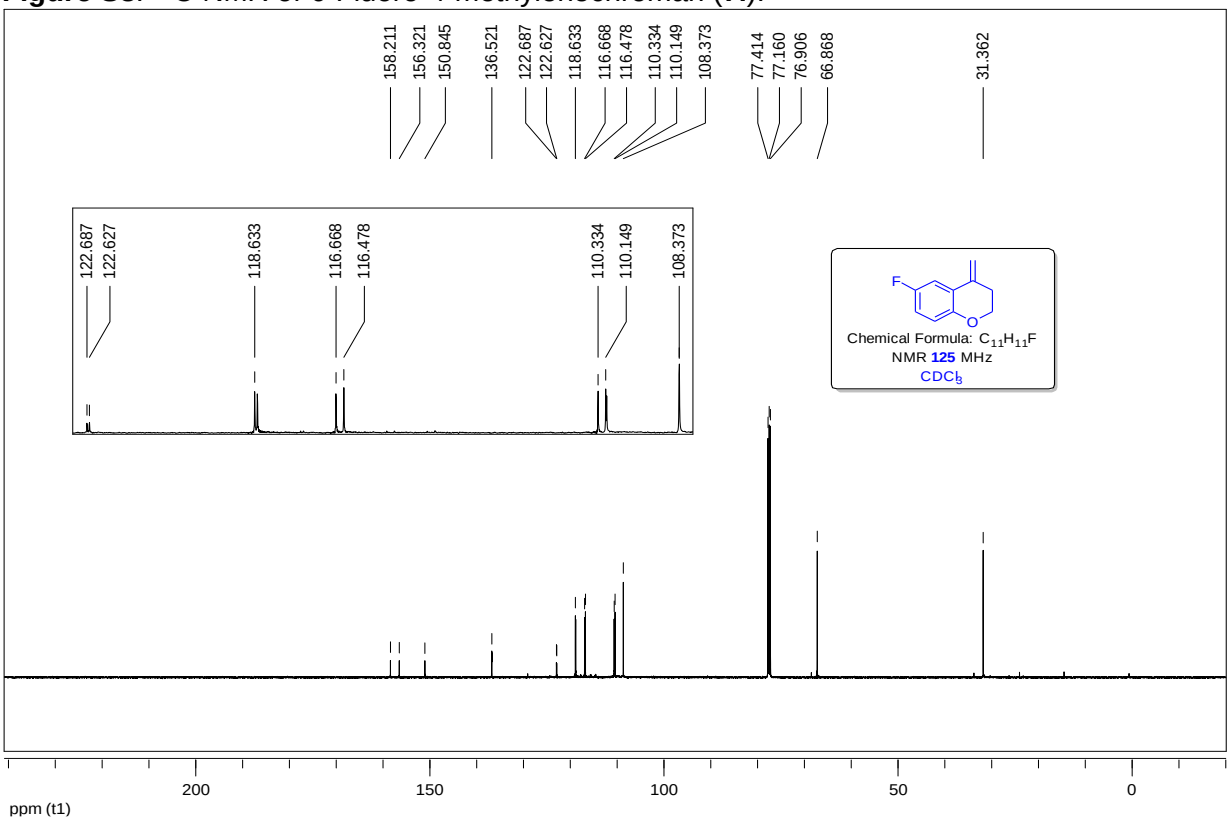
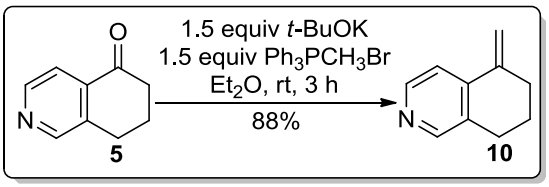


Figure S8: ^{13}C NMR of 6-Fluoro-4-methylenechroman (**7i**).



4.2.4. **5-Methylene-5,6,7,8-tetrahydroisoquinoline** (**10**).



The reaction was performed following the general protocol **4.2.1**, but using *terc*-BuOK (0.336 g, 3.00 mmol), Ph_3PCH_3Br (1.07 g, 3.00 mmol) and **5** (0.294 g, 2.00 mmol) in anhydrous Et_2O (12 mL).

Purification: The residue was purified by flash column chromatography (30-40% EtOAc in hexane).

Yield: 88% (0.254 g, 1.76 mmol).

Sample appearance: Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.85-1.93 (2H, q, *J* = 6.2 Hz), 2.56 (2H, t, *J* = 6.3 Hz), 2.81 (2H, t, *J* = 6.3 Hz), 5.15 (1H, s), 5.68 (1H, s), 7.43 (1H, d, *J* = 5.6 Hz), 8.34 (1H, d, *J* = 5.6 Hz), 8.37 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.1, 27,3, 32,4, 112.0, 117.9, 132.1, 141.3, 141.7, 147.2, 151.1.

HRMS [ESI(+)] calcd. for $[C_{10}H_{11}NH]^+$ 146.0970, found 146.0969.

IR (film): 3401, 3087, 3057, 3034, 3019, 2983, 2937, 2863, 2839, 2677, 2488, 2422, 1894, 1800, 1619, 1630, 1592, 1547, 1487, 1456, 1440, 1432, 1413, 1341, 1330, 1308, 1292, 1272, 1248, 1177. 1147, 1104, 1064, 070, 902, 864, 831, 808, 768 cm^{-1}.

Figure S9: ^{1}H NMR of 5-Methylene-5,6,7,8-tetrahydroisoquinoline (**10**).

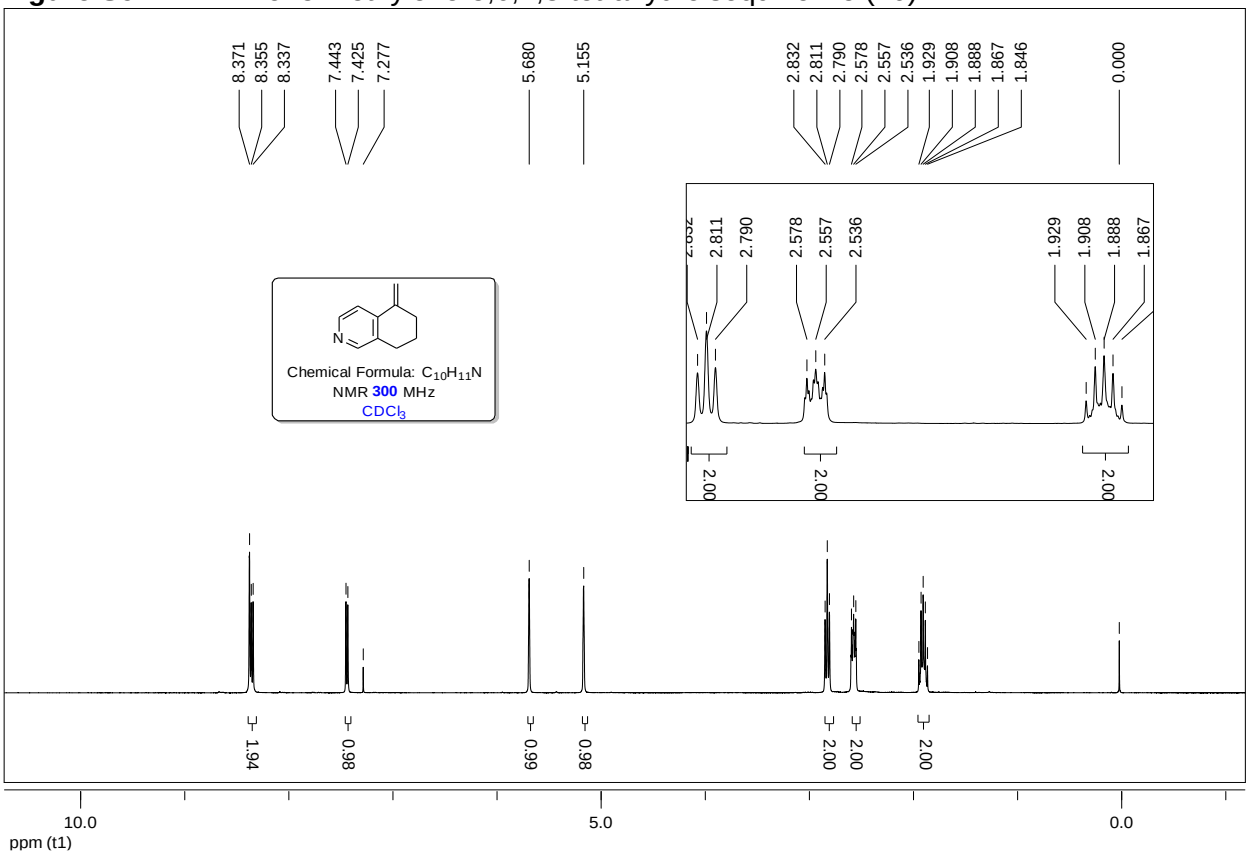
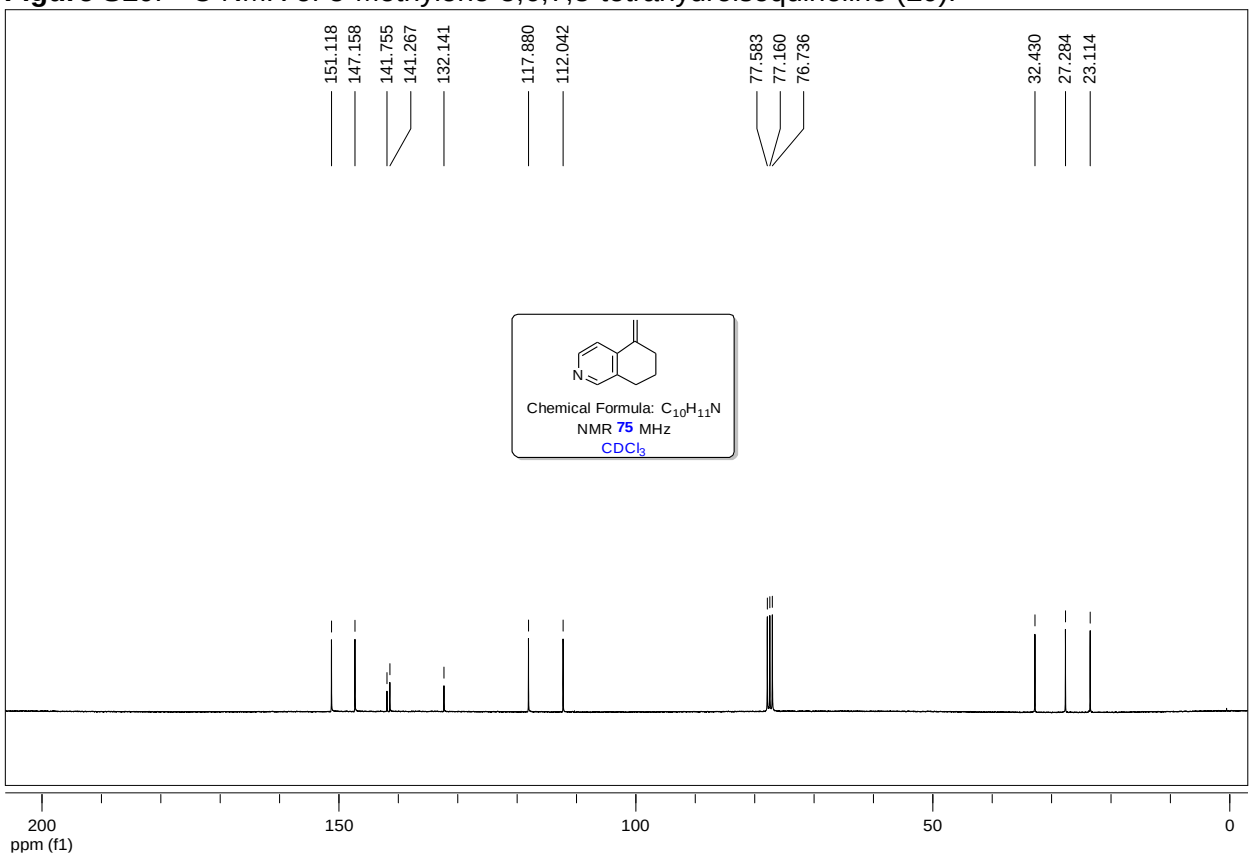
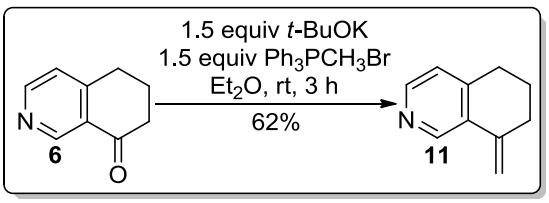


Figure S10: ^{13}C NMR of 5-Methylene-5,6,7,8-tetrahydroisoquinoline (**10**).



4.2.5. **8-Methylene-5,6,7,8-tetrahydroisoquinoline** (**11**).



The reaction was performed following the general protocol **4.2.1**, but using *t*-BuOK (0.336 g, 3.00 mmol), Ph_3PCH_3Br (1.07 g, 3.00 mmol) and **6** (0.294 g, 2.00 mmol) in anhydrous Et_2O (12 mL).

Purification: The residue was purified by flash column chromatography (30-40% EtOAc in hexane in hexanes).

Yield: 62% (0.179 g, 1.24 mmol).

Sample appearance: Light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.83-1.92 (2H, q, *J* = 6.3 Hz), 2.53 (2H, t, *J* = 6.1 Hz), 2.80 (2H, t, *J* = 6.2 Hz), 5.03 (1H, s), 5.57 (1H, s), 6.98 (1H, d, *J* = 5.1 Hz), 8.30 (1H, d, *J* = 5.1 Hz), 8.83 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.2, 29.6, 32.7, 109.1, 123.6, 130.8, 140.6, 145.6, 146.2, 147.7.

HRMS [ESI(+)] calcd. for $[C_{10}H_{11}NH]^+$ 146.0970, found 146.0966.

IR (film): 3403, 3088, 3051, 3032, 3019, 2982, 2864, 2840, 2675, 2481, 2421, 1890, 1800, 1620, 1630, 1590, 1545, 1488, 1442, 1431, 1411, 1344, 1333, 1305, 1292, 1272, 1250, 1175. 1147, 1104, 1064, 070, 902, 865, 831, 808 cm^{-1}.

Figure S11: ^{1}H NMR of 8-Methylene-5,6,7,8-tetrahydroisoquinoline (**11**).

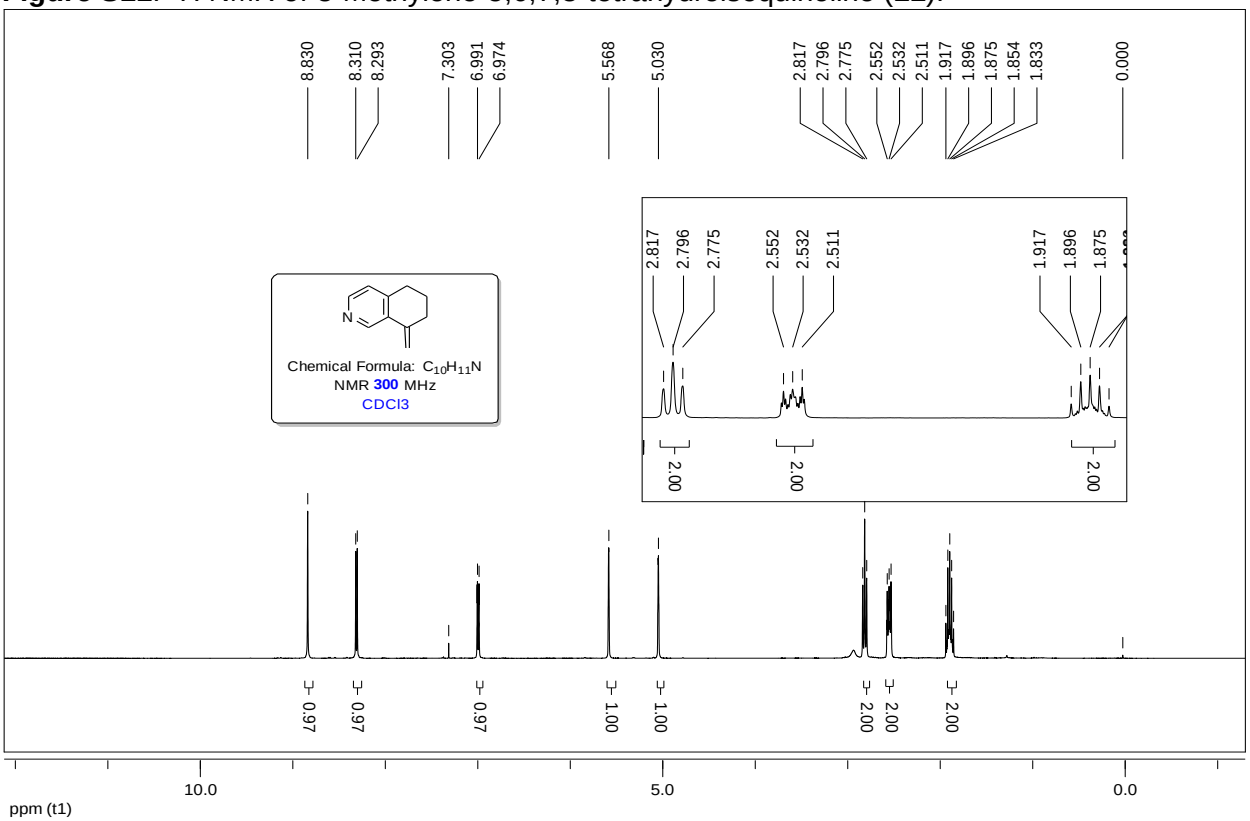
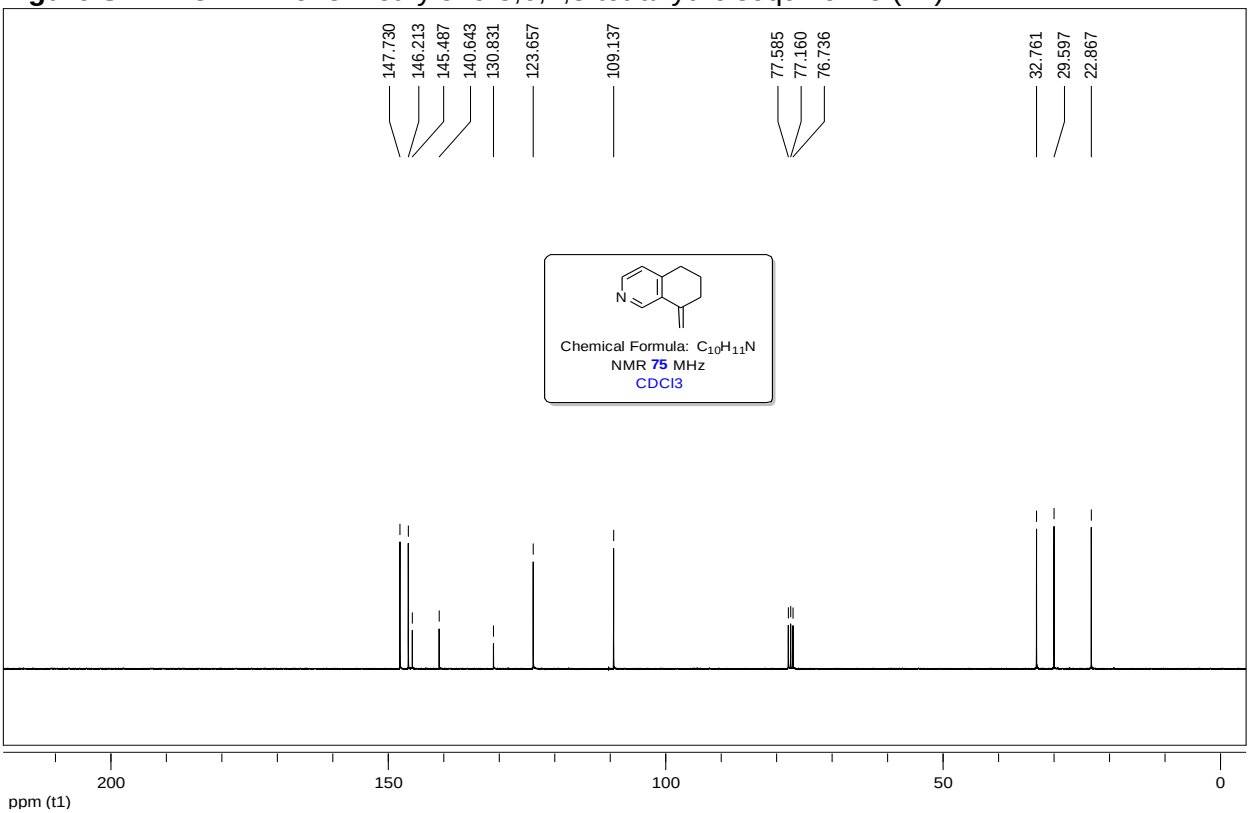


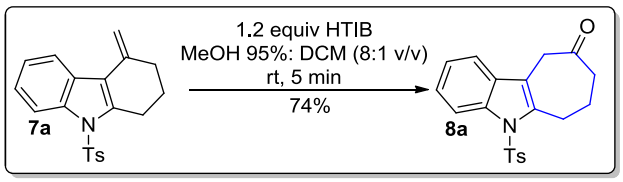
Figure S12: ^{13}C NMR of 8-Methylene-5,6,7,8-tetrahydroisoquinoline (**11**).



4.3. General procedure for the HTIB-Mediated Ring Contraction reactions in MeOH.

To the stirred solution of alkene in MeOH 95% (MeOH:H_2O, 95:1, v/v) was added HTIB and stirred for 5-15 min at rt. The reaction was monitored by TLC for the consumption of the starting material. The reaction mixture was quenched with saturated solution of $NaHCO_3$ and extracted with DCM (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography giving the corresponding seven membered products.

4.3.1. **5-Tosyl-6,7,8,10-tetrahydrocyclohepta[*b*]indol-9(5*H*)-one** (**8a**).



The reaction was performed following the general protocol **4.3**, but using alkene **7a** (0.084 g, 0.25 mmol) in MeOH 95% (4 mL) and DCM (0.5 mL) with HTIB (0.117 g, 0.300 mmol).
Purification: The residue was purified by flash column chromatography (33% EtOAc in hexanes).
Yield: 74% (0.065 g, 0.18 mmol). **Sample appearance:** Light yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.19-2.27 (2H, q, *J* = 6.1 Hz), 2.34 (3H, s), 2.63 (2H, t, *J* = 5.8 Hz), 3.31 (2H, t, *J* = 6.1 Hz), 3.79 (2H, s), 7.19 (2H, d, *J* = 7.8 Hz), 7.27-7.34 (2H, m), 7.38 (1H, d, *J* = 8.4 Hz), 7.60 (2H, d, *J* = 8.4 Hz), 8.21 (1H, d, *J* = 7.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.0, 21.7, 29.2, 38.2, 42.8, 112.0, 114.9, 118.0, 123.7, 124.9, 126.4, 129.8, 130.7, 135.5, 136.3, 136.7, 145.0, 208.1.

Figure S13: ^{1}H NMR of 5-Tosyl-6,7,8,10-tetrahydrocyclohepta[*b*]indol-9(5*H*)-one (**8a**).[2]

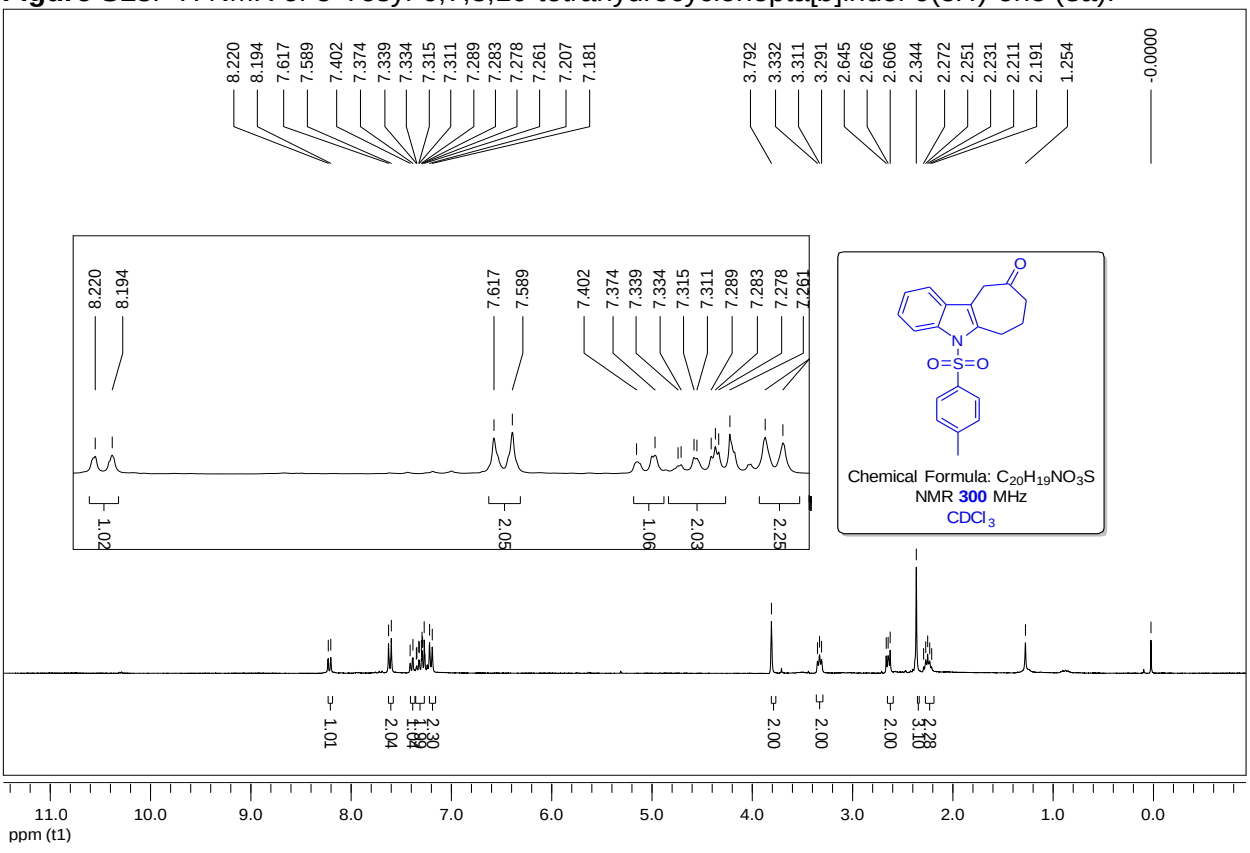
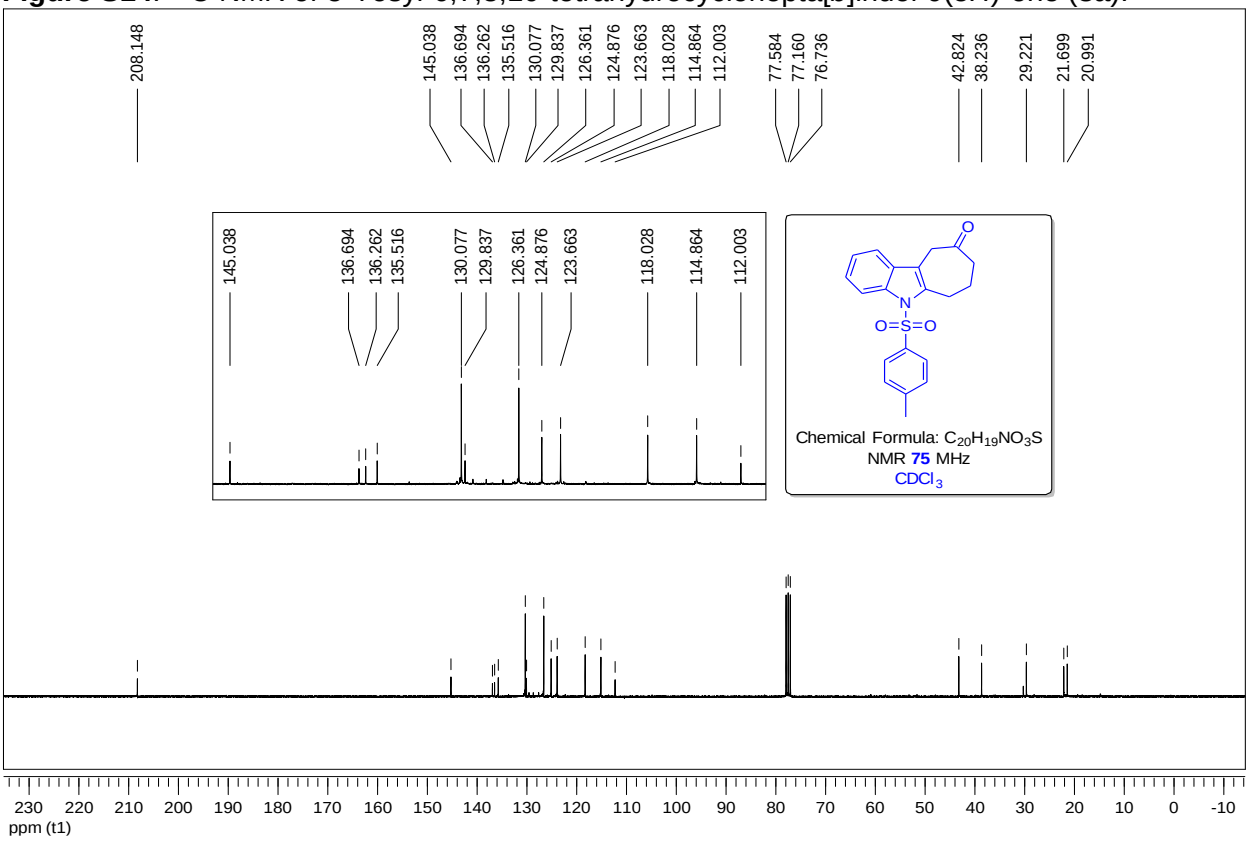
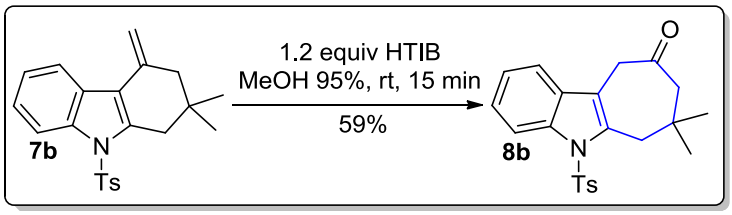


Figure S14: ^{13}C NMR of 5-Tosyl-6,7,8,10-tetrahydrocyclohepta[*b*]indol-9(5*H*)-one (**8a**).[2]



4.3.2. **7,7-Dimethyl-5-tosyl-6,7,8,10-tetrahydrocyclohepta[*b*]indol-9(5*H*)-one** (**8b**).



The reaction was performed following the general protocol **4.3**, but using alkene **7b** (0.100 g, 0.27 mmol) in MeOH 95% (3 mL) and HTIB (0.130 g, 0.32 mmol).
Purification: The residue was purified by flash column chromatography (20% EtOAc in hexanes).
Yield: 59% (0.061 g, 0.16 mmol).
Sample appearance: White solid.
Milting Point: 152-154 ºC.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.10 (6H, s), 2.34 (3H, s), 2.42 (2H, s) 3.21 (2H, s), 3.58 (2H, s) 7.18 (2H, d, *J* = 8.4 Hz), 7.28-7.38 (3H, m), 7.60 (2H, d, *J* = 8.4 Hz), 8.27 (1H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.7, 29.4, 37.1, 39.7, 40.0, 55.8, 115.2, 115.6, 118.0, 123.9, 124.7, 126.4, 126.5, 129.6, 130.0, 130.0, 136.1, 136.3, 136.7, 145,0, 207.8.
HRMS [ESI(+)] calcd. for $[C_{22}H_{23}NO_3SNa]^+$ 404.1296, found 404.1292.
IR (film): 3886, 3847, 3780, 3400, 3306, 3066, 3051, 2959, 2926, 2870, 2735, 2251, 1915, 1706, 1596, 1493, 1450, 1402, 1368, 1308, 1293, 1267, 1225, 1188, 1170, 1150, 1121, 1089, 1044, 1026, 984, 970 955, 933, 907, 862, 812, 780, 746, 703 cm^{-1}.

Figure S15: ^{1}H NMR of 7,7-Dimethyl-5-tosyl-6,7,8,10-tetrahydrocyclohepta[*b*]indol-9(5*H*)-one (**8b**).

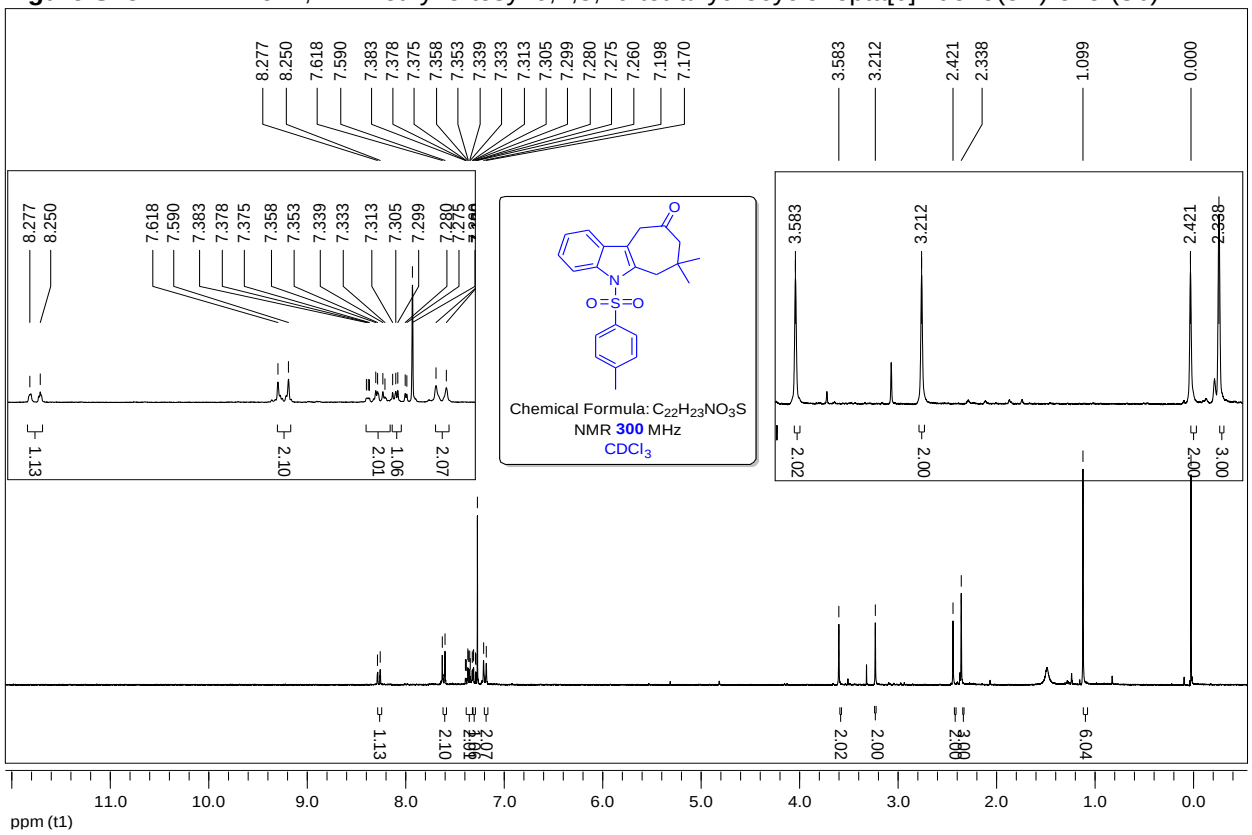
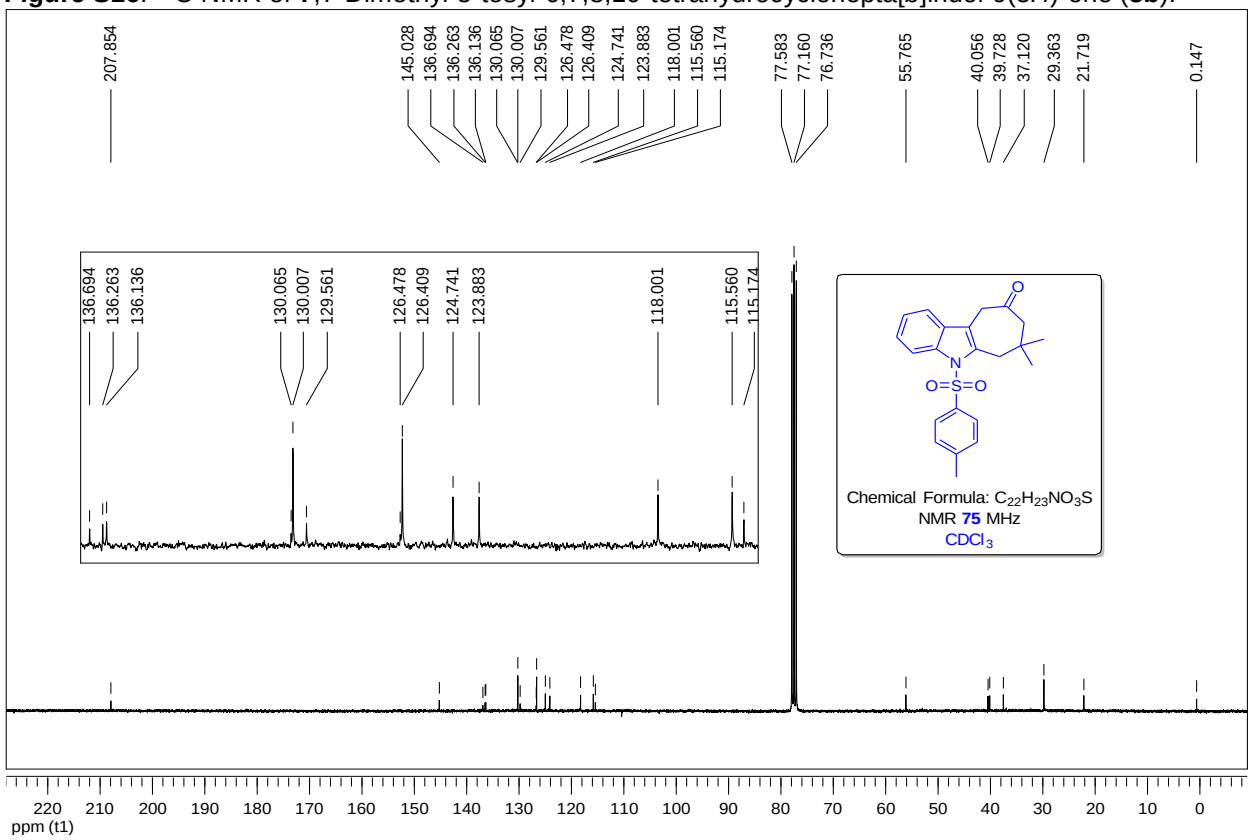
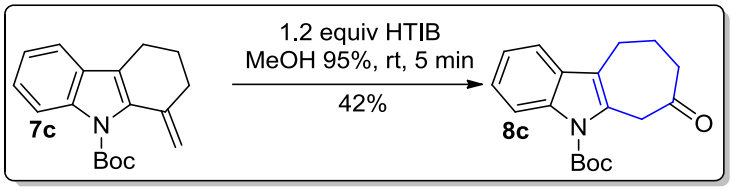


Figure S16: ^{13}C NMR of **7**,7-Dimethyl-5-tosyl-6,7,8,10-tetrahydrocyclohepta[*b*]indol-9(5*H*)-one (**8b**).



4.3.3. ***tert*-Butyl 7-oxo-7,8,9,10-tetrahydrocyclohepta[*b*]indole-5(6*H*)-carboxylate** (**8c**).



The reaction was performed following the general protocol **4.3**, but using alkene **7c** (0.141 g, 0.50 mmol) in MeOH 95% (4 mL) and HTIB (0.235 g, 0.60 mmol).
Purification: The residue was purified by flash column chromatography (10-15% EtOAc in hexanes).
Yield: 42% (0.063 g, 0.21 mmol).
Sample appearance: Light red oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.68 (9H, s), 2.20-2.28 (2H, q, *J* = 6.4 Hz), 2.71 (2H, t, *J* = 6.4 Hz), 2.89 (2H, t, *J* = 6.1 Hz), 4.28 (2H, s), 7.21–7.30 (2H, m), 7.42 (1H, d, *J* = 7.2 Hz), 8.03 (1H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.8, 23.3, 28.4, 43.2, 43.7, 84.4, 115.5, 117.9, 119.6, 122.8, 124.3, 128.3, 129.7, 136.0, 150.6, 208.3.

Figure S17:
^{1}H NMR of *tert*-Butyl 7-oxo-7,8,9,10-tetrahydrocyclohepta[*b*]indole-5(6*H*)-carboxylate (**8c**).[2]

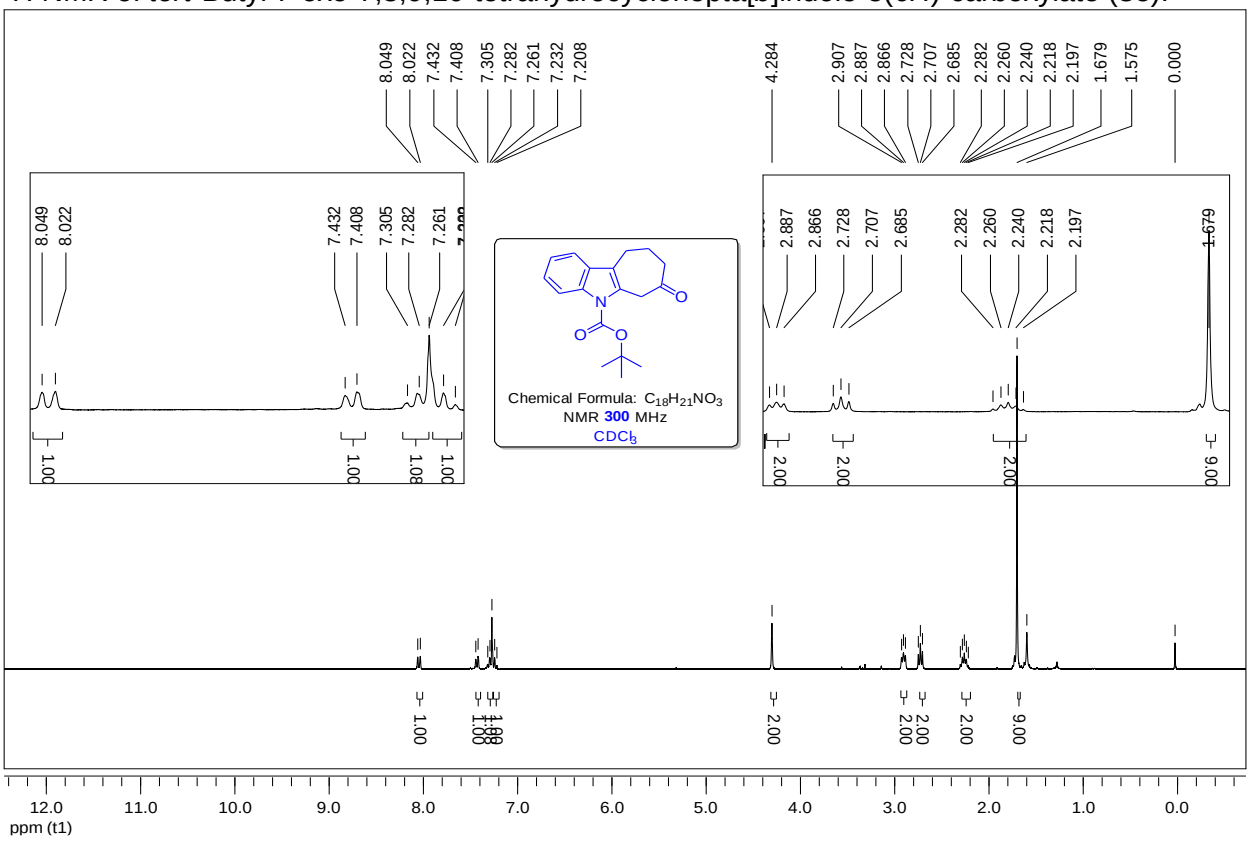
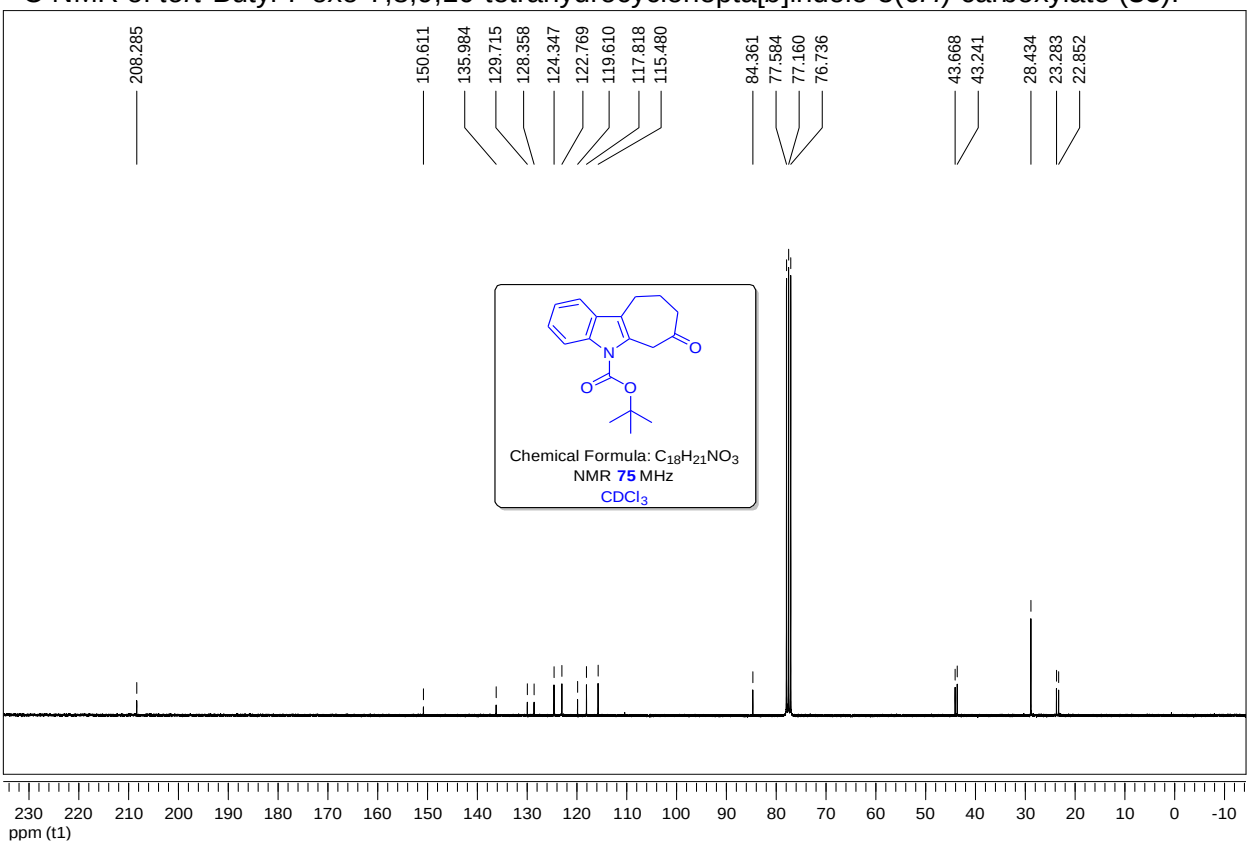
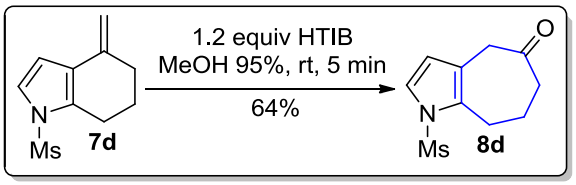


Figure S18:
^{13}C NMR of *tert*-Butyl 7-oxo-7,8,9,10-tetrahydrocyclohepta[*b*]indole-5(6*H*)-carboxylate (**8c**).[2]



4.3.4. **1-(Methylsulfonyl)-4,6,7,8-tetrahydrocyclohepta[*b*]pyrrol-5(1*H*)-one** (**8d**).



The reaction was performed following the general protocol **4.3**, but using alkene **7d** (0.100 g, 0.47 mmol) in MeOH 95% (5 mL) and HTIB (0.222 g, 0.56 mmol).
Purification: The residue was purified by flash column chromatography (40% EtOAc in hexanes).
Yield: 64% (0.068 g, 0.30 mmol).
Sample appearance: Yellowish oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.17-2.25 (2H, q, *J* = 6.1 Hz), 2.63 (2H, t, *J* = 6.0 Hz), 3.07-3.13 (5H, m), 3.64 (2H, s), 6.04 (1H, d, *J* = 3.3 Hz), 7.09 (1H, d, *J* = 3.3 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.7, 27.6, 41.6, 42.6, 42.7, 113.8, 116.9, 121.3, 128.5, 208.1.

Figure S19:
^{1}H NMR of 1-(Methylsulfonyl)-4,6,7,8-tetrahydrocyclohepta[*b*]pyrrol-5(1*H*)-one (**8d**).[2]

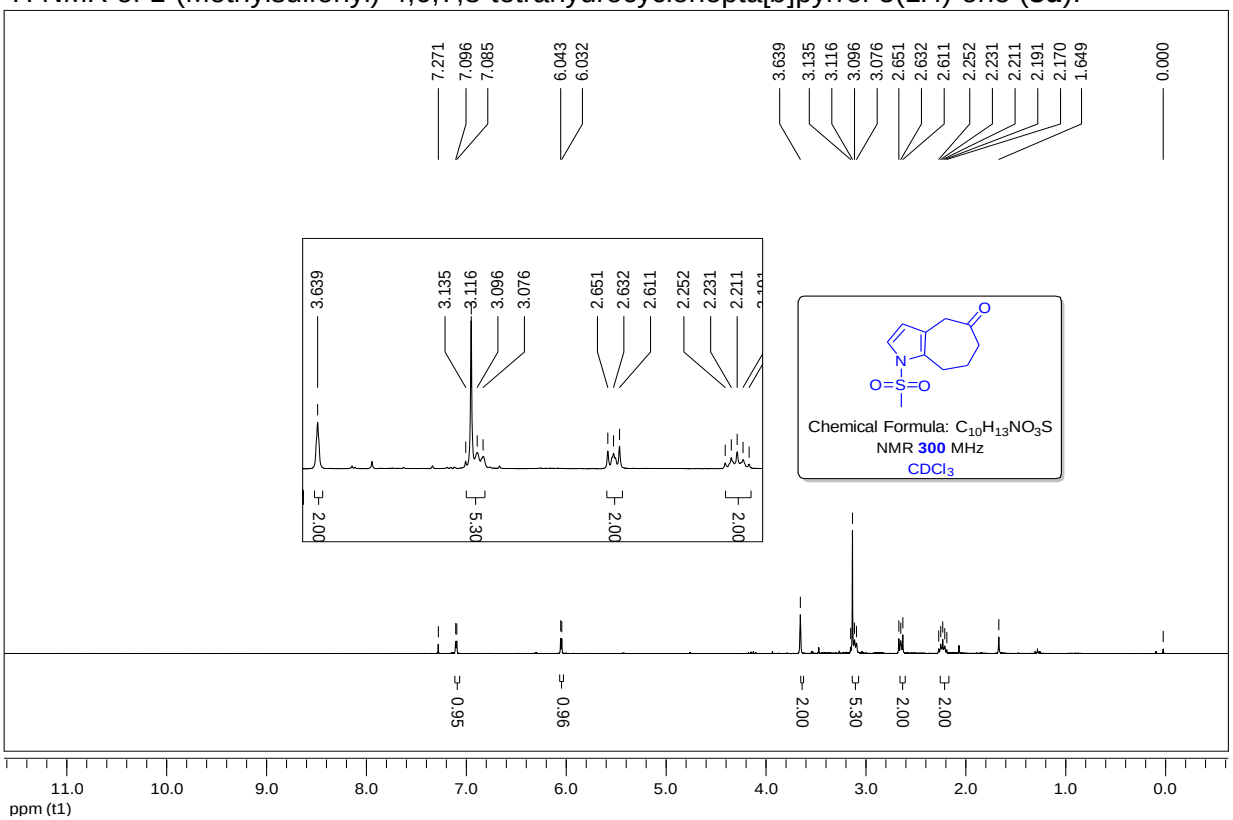
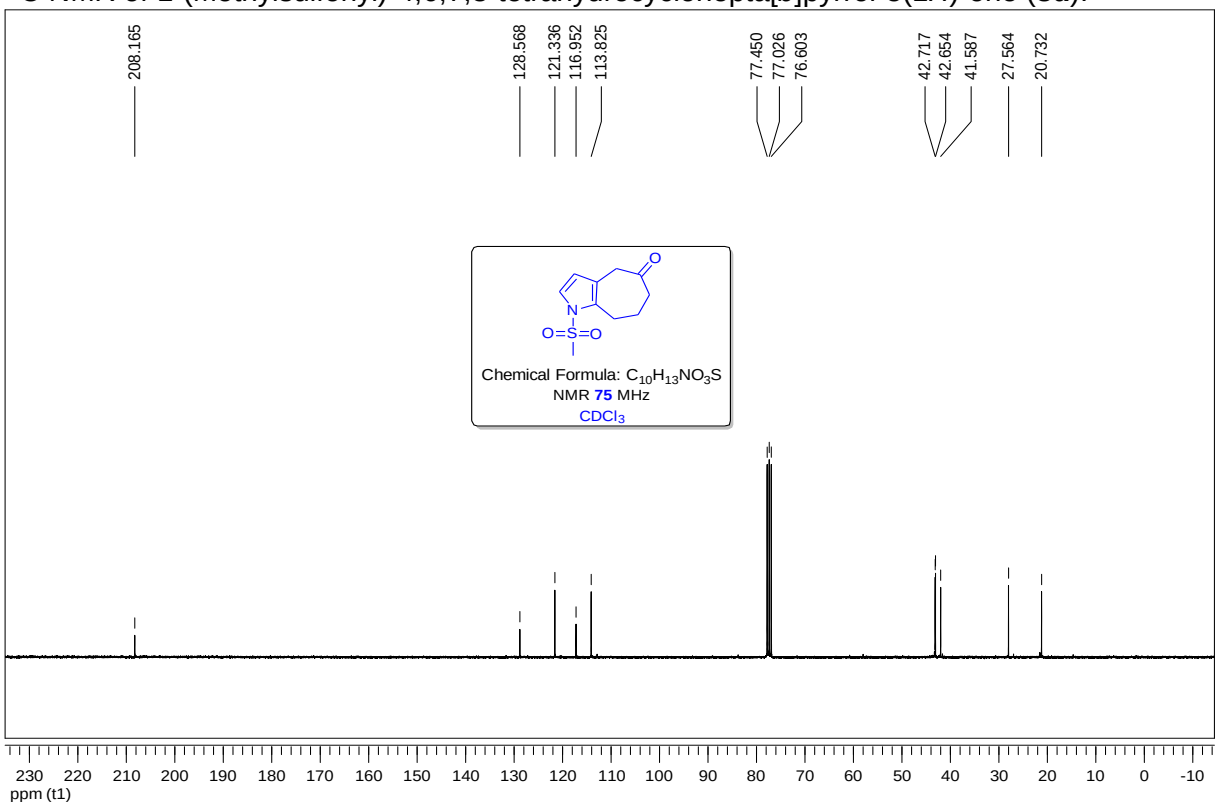
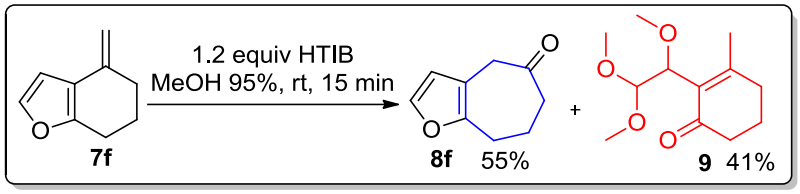


Figure S20:
^{13}C NMR of 1-(Methylsulfonyl)-4,6,7,8-tetrahydrocyclohepta[*b*]pyrrol-5(1*H*)-one (**8d**).[2]



4.3.5. **4,6,7,8-Tetrahydro-5*H*-cyclohepta[*b*]furan-5-one** (**8f**) and **3-Methyl-2-(1,2,2-trimethoxyethyl)cyclohex-2-en-1-one** (**9**).



The reaction was performed following the general protocol **4.3**, but using alkene **7f** (0.067 g, 0.50 mmol) in MeOH 95% (5 mL of MeOH:H_2O, 95:1, v/v), HTIB (0.235 g, 0.60 mmol, 1.2 equiv) and stirred for 15 min at rt.
Purification: The residue was purified by flash column chromatography (20% EtOAc in hexanes).

4,6,7,8-Tetrahydro-5*H*-cyclohepta[*b*]furan-5-one (**8f**).
Yield: 55% (0.041 g, 0.27 mmol).
Sample appearance: Light yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.08-2.16 (2H, q, *J* = 6.1 Hz), 2.63 (2H, t, *J* = 6 Hz), 2.90 (2H, t, *J* = 6.1 Hz), 3.55 (2H, s), 6.12 (1H, d, *J* = 1.8 Hz), 7.26 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.3, 28.0, 39.9, 43.2, 110.7, 112.5, 140.9, 150.3, 208,8.
HRMS [ESI(+)] calcd. for $[C_9H_{10}O_2Na]^+$ 173.0578, found 173.0572.
IR (film): 3401, 2943, 2826, 1765, 1513, 1444, 1175, 1116, 895, 742, 603 cm^{-1}

3-Methyl-2-(1,2,2-trimethoxyethyl)cyclohex-2-en-1-one (**9**).
Yield: 41% (0.047 g, 0.21 mmol).
Sample appearance: Light red oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.92-2.00 (2H, q , *J* = 6.4 Hz), 2.10 (3H, s), 2.41 (4H, m), 3.27 (3H, s) 3.28 (3H, s), 3.46 (3H, s), 4.60-4.70 (2H, dd, *J* = 21.0 and 6.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.5, 22.3, 34.1, 38.2, 54.6, 55.0, 57.2, 76.6, 105.1, 131.3, 160.6, 198.5.
HRMS [ESI(+)] calcd. for $[C_{12}H_{20}O_4Na]^+$ 251.1259, found 251.1258.
IR (film): 3446, 2934, 2826, 1731, 1664, 1625, 1455, 1380, 1107, 972, 742 cm^{-1}.

Figure S21: ^{1}H NMR of 4,6,7,8-Tetrahydro-5*H*-cyclohepta[*b*]furan-5-one (**8f**)[2]

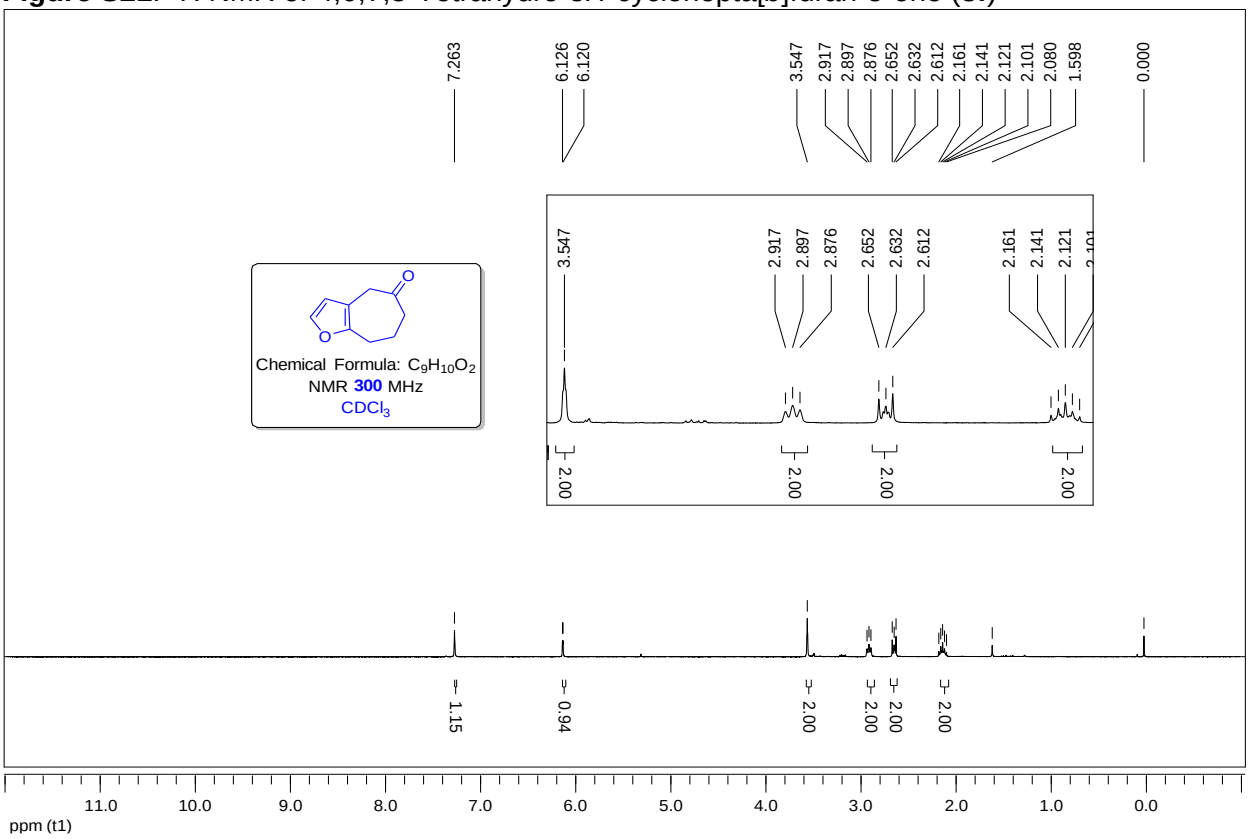


Figure S22: ^{13}C NMR of 4,6,7,8-Tetrahydro-5*H*-cyclohepta[*b*]furan-5-one (**8f**)[2]

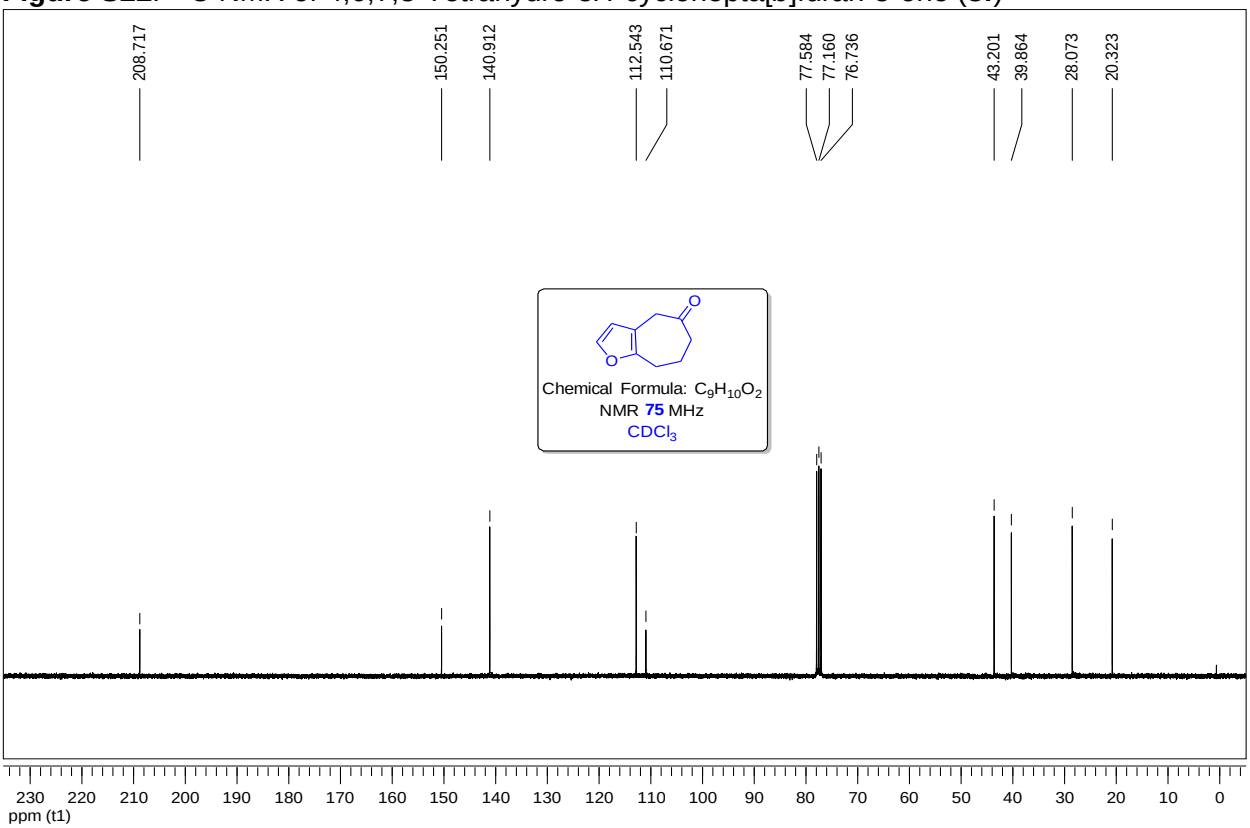


Figure S23: ^{1}H NMR of 3-Methyl-2-(1,2,2-trimethoxyethyl)cyclohex-2-en-1-one (**9**)

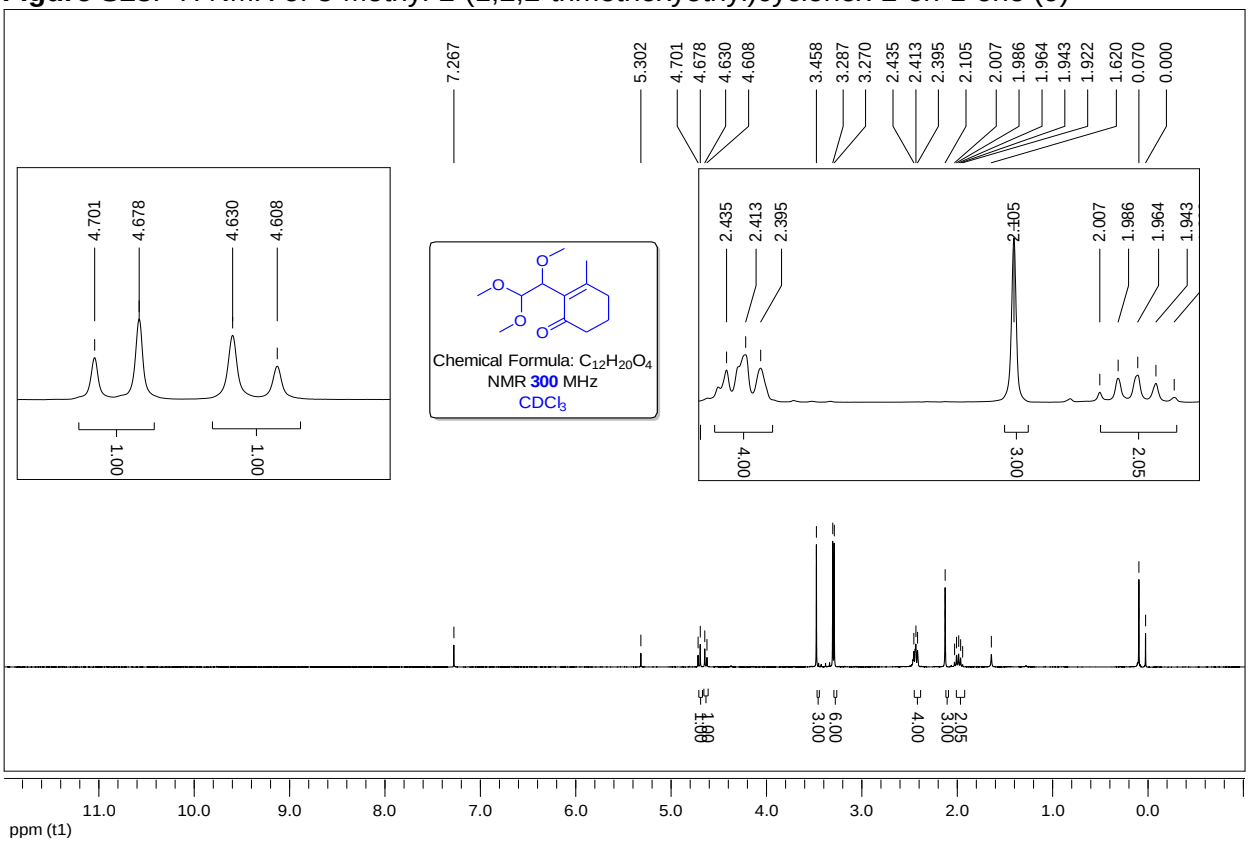
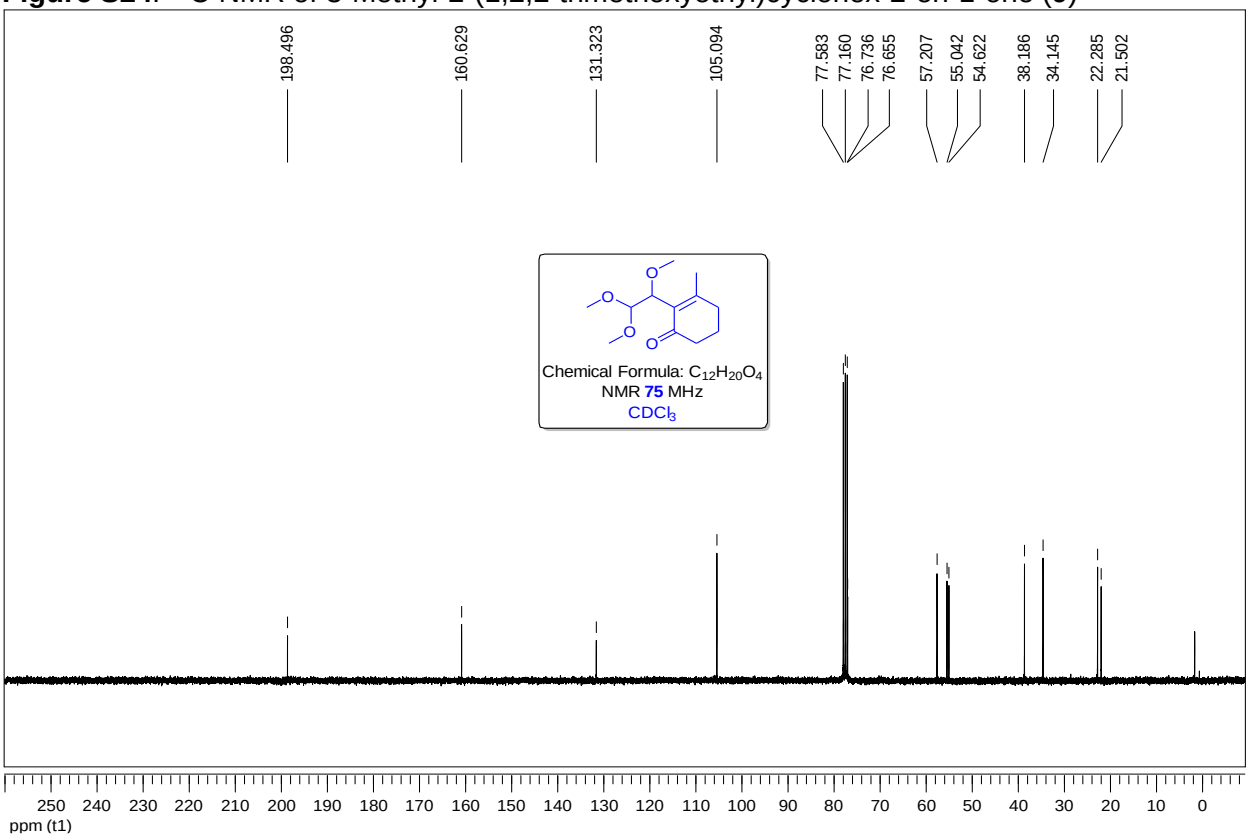
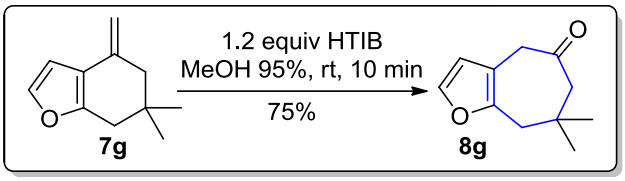


Figure S24: ^{13}C NMR of 3-Methyl-2-(1,2,2-trimethoxyethyl)cyclohex-2-en-1-one (**9**)



4.3.6. **7,7-Dimethyl-4,6,7,8-tetrahydro-*5H*-cyclohepta[*b*]furan-5-one** (**8g**).



The reaction was performed following the general protocol **4.3**, but using alkene **7g** (0.81 g, 0.50 mmol) and HTIB (0.235 g, 0.600 mmol) in MeOH 95% (3 mL).
Purification: The residue was purified by flash column chromatography (20% EtOAc in hexanes)
Yield: 75% (0.067 g, 0.38 mmol).
Sample appearance: Light yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.05 (6H, s), 2.55 (2H, s), 2.78 (2H, s), 3.46 (2H, s), 6.18 (1H, d, *J* = 1.5 Hz), 7.24 (1H, d, *J* = 1.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.2 (2C), 36.2, 41.2, 41.8, 57.5, 110.6, 112.4, 140.5, 150.3, 207.0.
HRMS [ESI(+)] calcd. for $[C_{11}H_{14}O_2Na]^+$ 201.0891, found 201.0880.
IR (film): 3392, 2961, 2931, 2873, 1800, 1703, 1611, 1506, 1467, 1370, 1251, 1095, 1034, 748, 730, 573 cm^{-1}.

Figure S25: ^{1}H NMR of 7,7-Dimethyl-4,6,7,8-tetrahydro-*5H*-cyclohepta[*b*]furan-5-one (**8g**).

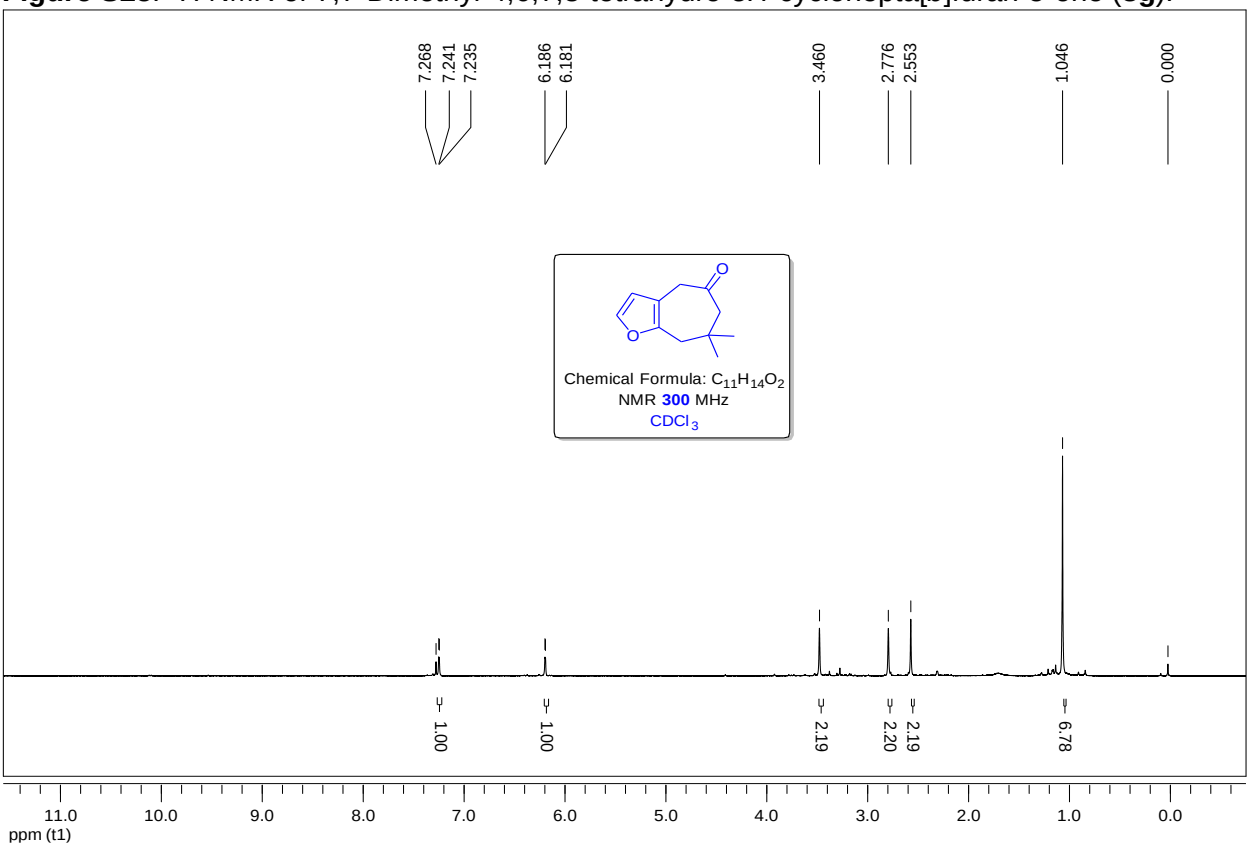
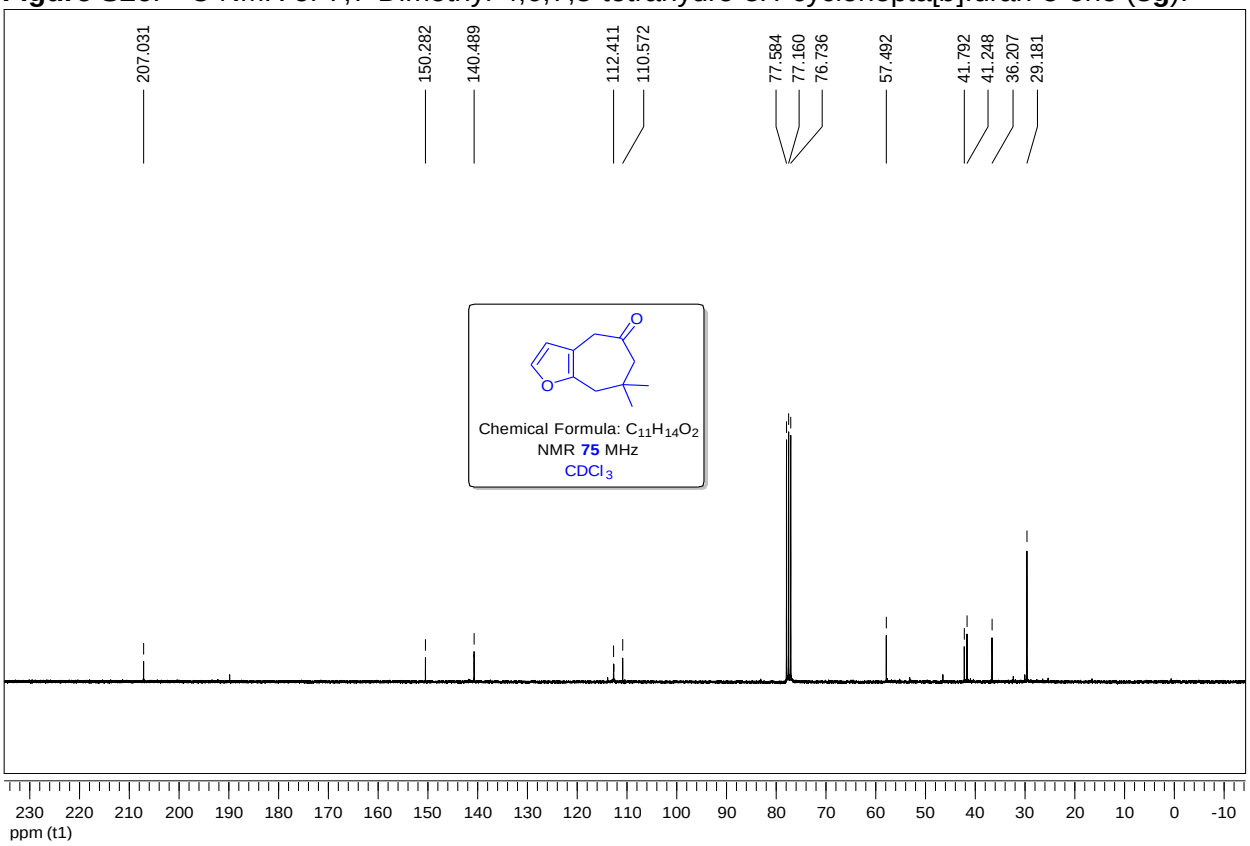
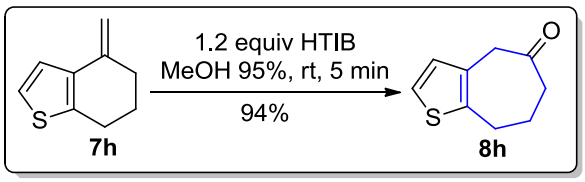


Figure S26: ^{13}C NMR of 7,7-Dimethyl-4,6,7,8-tetrahydro-*5H*-cyclohepta[*b*]furan-5-one (**8g**).



4.3.7. **4,6,7,8-Tetrahydro-*5H*-cyclohepta[*b*]thiophen-5-one (8h)**[2]



The reaction was performed following the general protocol **4.3**, but using alkene **7h** (0.450 g, 3.00 mmol) in MeOH 95% (8 mL) and HTIB (1.41 g, 3.60 mmol).
Purification: The residue was purified by flash column chromatography (5% EtOAc in hexanes).
Yield: 95% (0.470 g, 2.84 mmol).
Sample appearance: Yellowish oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.11-2.19 (2H, q, *J* = 6.1 Hz), 2.66 (2H, t, *J* = 6.3 Hz), 3.04 (2H, t, *J* = 6.0 Hz), 3.75 (2H, s), 6.71 (1H, d, *J* = 4.8 Hz), 7.02 (1H, d, *J* = 5.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.4, 28.4, 43.9, 44.4, 122.4, 128.6, 129.9, 137.8, 208.1.

Figure S27: [1]H NMR of 4,6,7,8-Tetrahydro-*5H*-cyclohepta[*b*]thiophen-5-one **(8h)**[2]

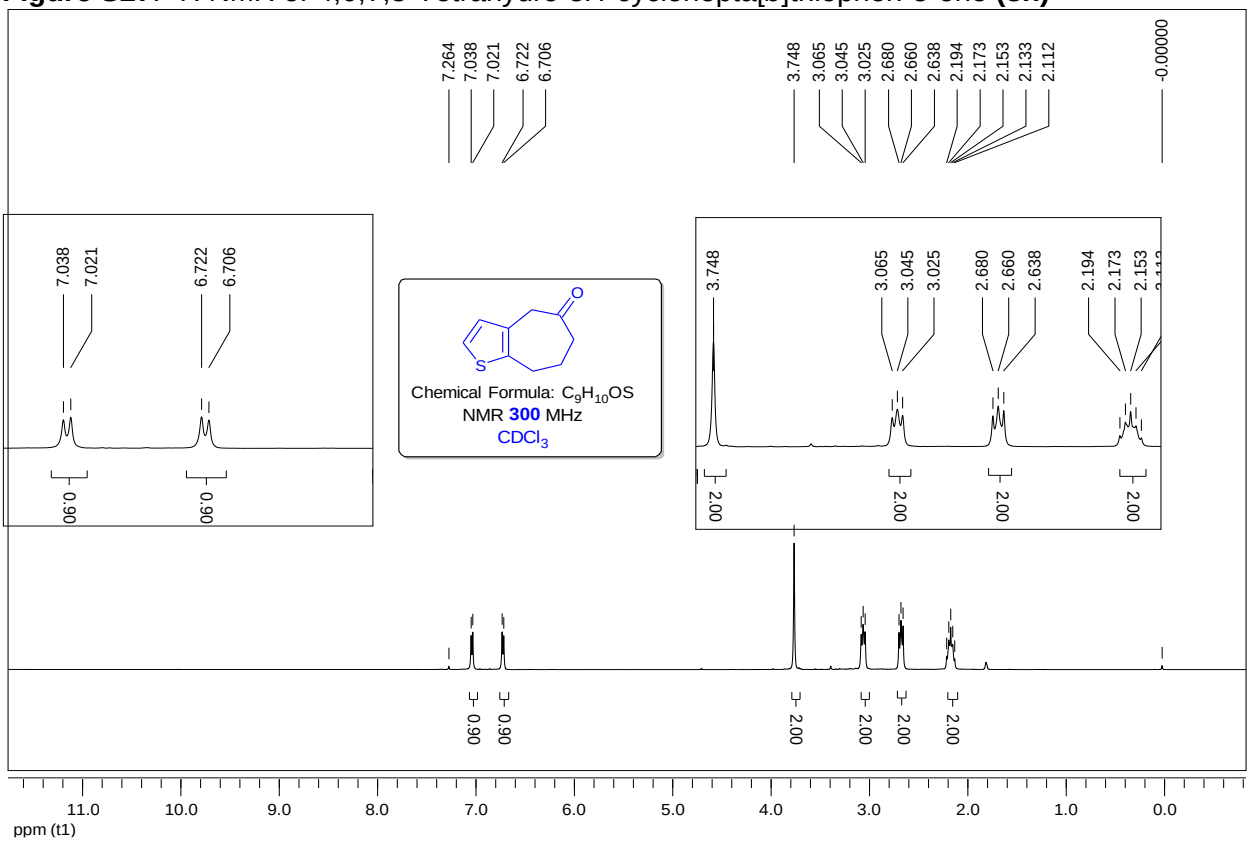
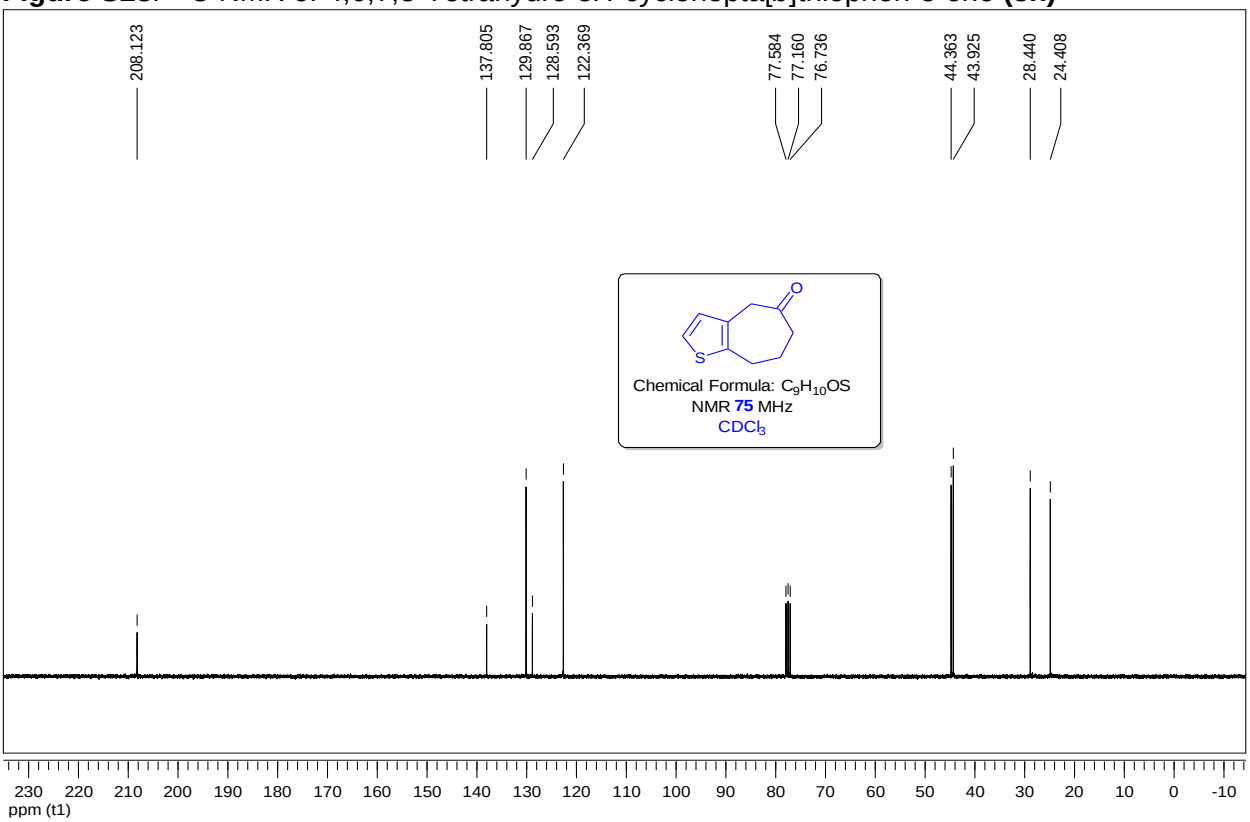
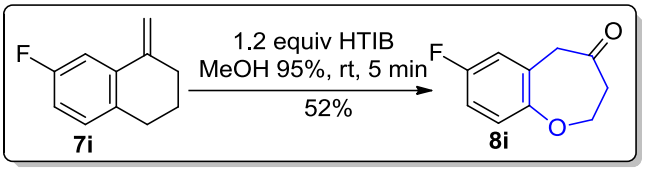


Figure S28: [13]C NMR of 4,6,7,8-Tetrahydro-*5H*-cyclohepta[*b*]thiophen-5-one **(8h)**[2]



4.3.8. **7-Fluoro-2,3-dihydrobenzo[b]oxepin-4(5*H*)-one** (**8i**).



The reaction was performed following the general protocol **4.3**, but using alkene **7i** (0.082 g, 0.50 mmol) in MeOH 95% (5 mL) and HTIB (0.235 g, 0.60 mmol).
Purification: The residue was purified by flash column chromatography (20-25% EtOAc in hexanes).
Yield: 62% (0.046 g, 0.26 mmol).
Sample appearance: Yellow solid.
Milting Point: 84-85 ℃
^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.84 (2H, t, *J* = 6.0 Hz), 3.77 (2H, s), 4.32 (2H, t, *J* = 6.1 Hz), 6.84 (1H, dd, *J* = 9.0 and 3.0 Hz), 6.91 (1H, dd, *J* = 8.1 and 3.0 Hz), 6.98 (1H, dd, *J* = 8.7 and 5.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 44.8, 48.2, 69.5, 115.2, (d, *J* = 22.5 Hz), 117.0 (d, *J* = 23.6 Hz), 122.5 (d, *J* = 8.5), 127.0 (d, *J* = 8.2 Hz), 153.7 (d, *J* = 2.5 Hz), 158.9 (d, *J* = 241 Hz), 204.9.
Elemental Analysis: calcd. for $C_{10}H_9FO_2$: C - 66.66; H - 5.03. Found: C - 66.75, H - 5.12.
IR (film): 3271, 3074, 2966, 2890, 1717, 1615, 1592, 1494, 1429, 1394, 1263, 1203, 1189, 1057, 1031, 969, 879, 822, 733, 706, 568 cm^{-1}.

Figure S29: ^{1}H NMR of 7-Fluoro-2,3-dihydrobenzo[b]oxepin-4(5*H*)-one (**8i**).[2]

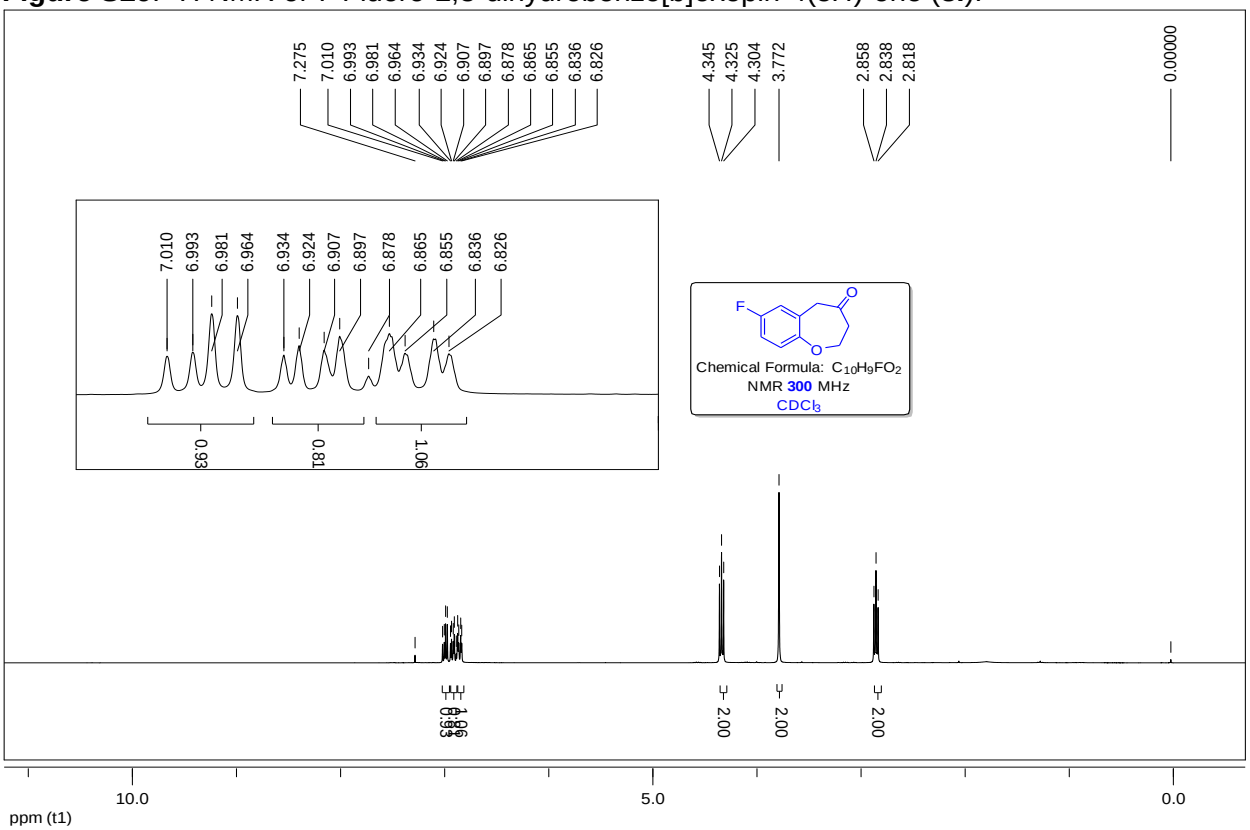
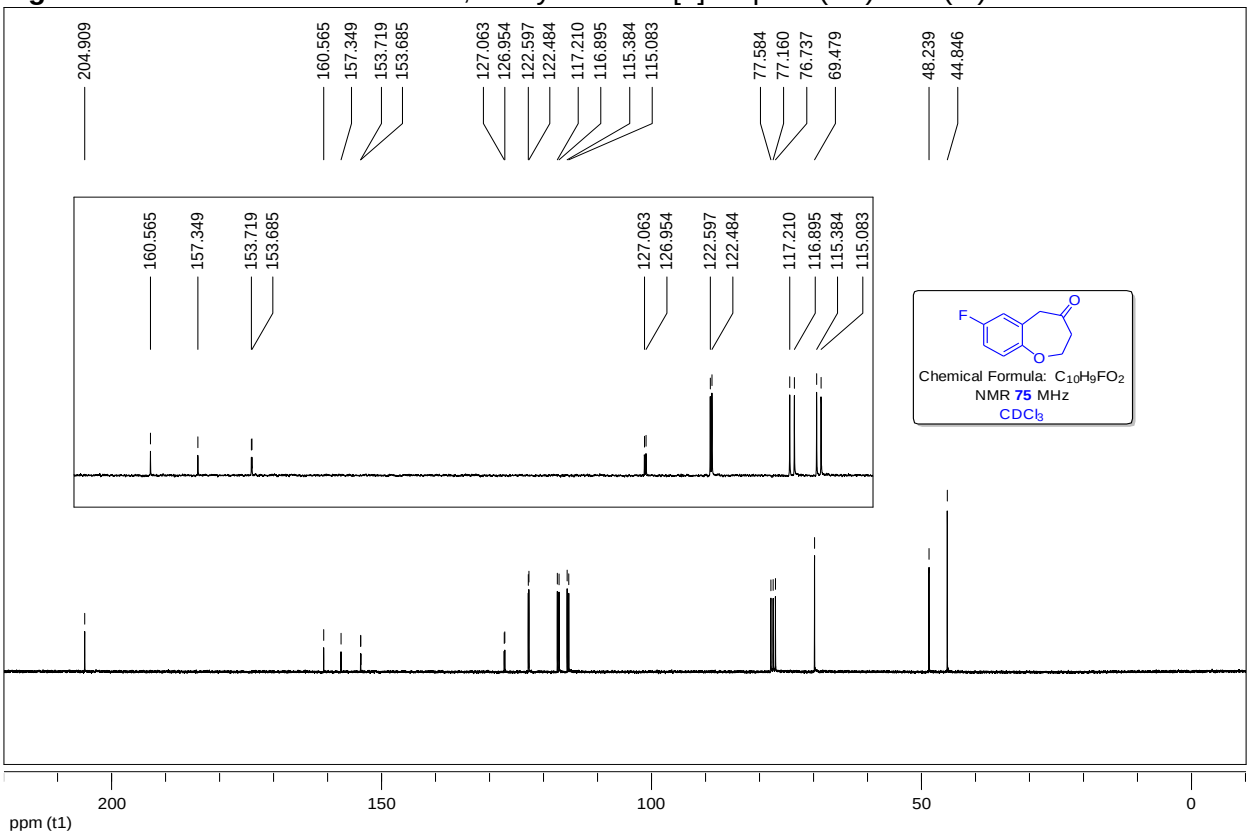
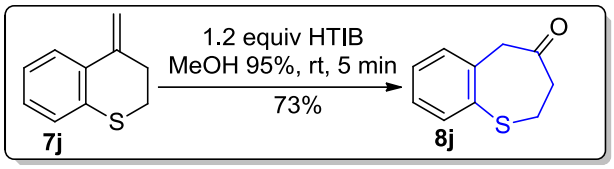


Figure S30: ^{13}C NMR of 7-Fluoro-2,3-dihydrobenzo[b]oxepin-4(5*H*)-one (**8i**).[2]



4.3.9. **2,3-Dihydrobenzo[b]thiepin-4(5*H*)-one** (**8j**).



The reaction was performed following the general protocol **4.3**, but using alkene **7j** (0.081 g, 0.50 mmol) in MeOH 95% (5 mL) and HTIB (0.235 g, 0.60 mmol).
Purification: The residue was purified by flash column chromatography (20-25% EtOAc in hexanes).
Yield: 73% (0.065 g, 0.36 mmol).
Sample appearance: Light red oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.82-2.86 (2H, m), 3.02-3.06 (2H, m), 3.98 (2H, s), 7.16-7.26 (3H, m), 7.52 (1H, d, *J* = 7.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.7, 45.0, 51.2, 127.8, 128.9, 130.3, 133.9, 135.0, 138.3, 206.1.

Figure S31: ^{1}H NMR of 2,3-Dihydrobenzo[b]thiepin-4(5*H*)-one (**8j**).[2]

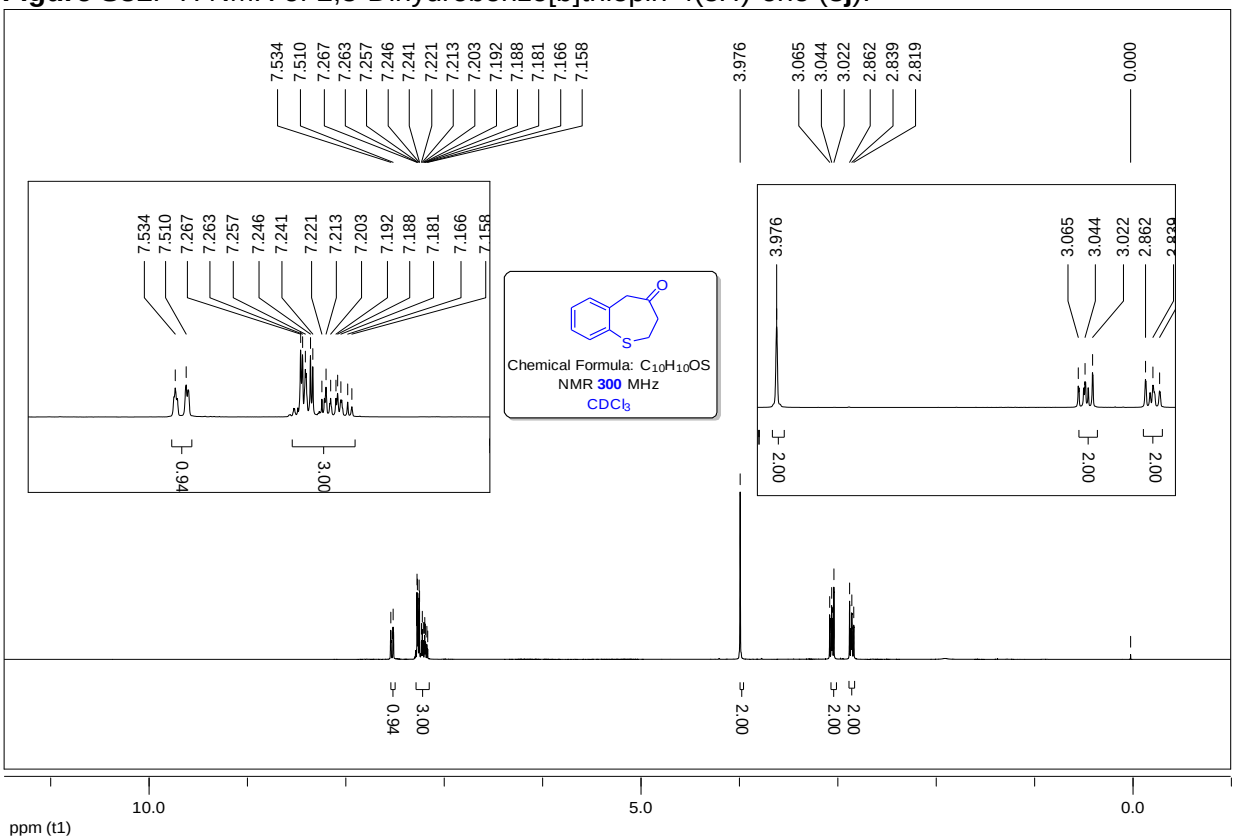
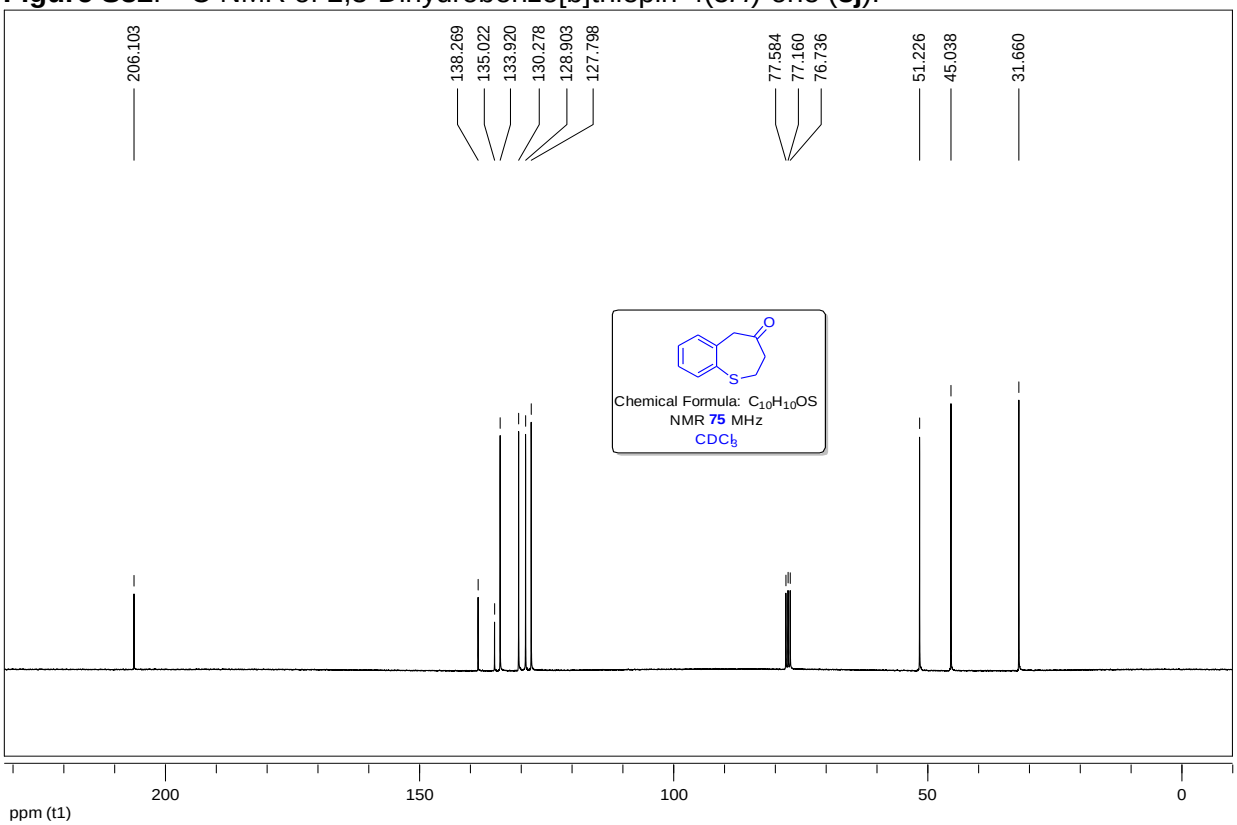


Figure S32: ^{13}C NMR of 2,3-Dihydrobenzo[b]thiepin-4(5*H*)-one (**8j**).[2]



Refrences:

1 A. Khan, L. F. Silva and M. Rabnawaz, *New J. Chem.*, 2021, **45**, 2078–2084.
2 A. Khan, L. F. Silva Jr and M. Rabnawaz, *Asian J. Org. Chem.*, 2021, **10**, 2549–2552.

Computational Method

All calculations were based on Density Functional Theory (DFT) [1, 2, 3] using the Gaussian 09 suite of programs.[4] Geometry optimizations, vibrational frequencies, and thermal energy corrections were performed with the B3LYP functional including the well-established dispersion correction GD3 [5, 6, 7] the 6-31G(d,p) basis set[8,9] was used for all main group elements and SDD[10,11] pseudopotential and its associated basis set for iodine. The solvent effects were described by SMD[12] continuum-dielectric solvation model through optimization calculations at SMD-B3LYP(D3)/6-31G(d,p) level of theory. theorySingle-point calculations for energy correction were made using SMD-B3LYP(GD3)/def2TZPP[13]. In some specifics steps of the mechanism reaction were necessary to use the combination of continuum-dielectric solvation with micro-solvation clusters. The identification of intermediates and transition states was made by the observation of the number of negative eigenvalues in the Hessian matrix: transition states were identified by presence of only one imaginary frequency, while the intermediates presented only real frequencies. The intrinsic reaction coordinate (IRC) method[14] was used to confirm the connection between the transition states and the corresponding intermediates. Free energies were also included in all energy profiles.

Results and discussion

In contrast to our previous observations during the mechanistic study on the HTIB-promoted ring contraction of 1,2-dihydronaphthalenes,[15] here we were able to find the transition state (**TS1Wc**) associated to the nucleophilic addition of just one water molecule to carbocation **14**. The same trend was observed when we compared the addition of a single methanol molecule with a cluster of three methanol molecules. The activation barrier to cluster-assisted addition was calculated to be 8.8 kcal.mol^{-1} more stable than the addition involving a single methanol molecule (**Figure S33**).

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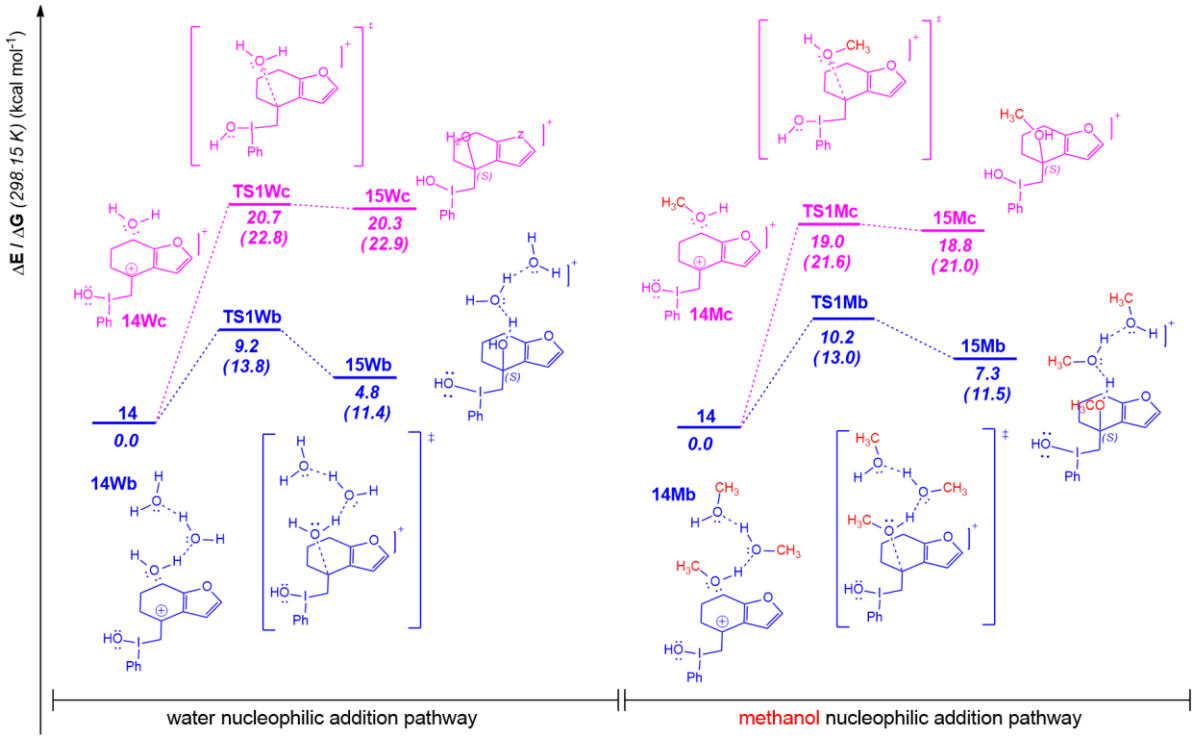

Figure S33. Energy profile (in kcal.mol^{-1}) corresponding to nucleophilic addition to intermediate **14** through stepwise mechanism by cluster-assisted solvent addition (blue) and direct nucleophilic solvent attack (pink) to obtain intermediate **15** for water and methanol pathways. Relative potential energies (free energies) were calculated with respect to separated reactants.

Besides the higher energy barriers obtained when only one molecule of ROH attacks carbocation **14**, as compared to the energy profile of the solvent cluster addition, we found optimized geometries (**Figures S34** and **S35**) which do not support this reaction pathway as too long C-O bond distances were found for reaction intermediates **15Wc** and **15Mc** (1.64 Å for both) when compared to those found in the solvent cluster addition leading to **15Wb** (1.49 Å) and **15Mb** (1.50 Å).

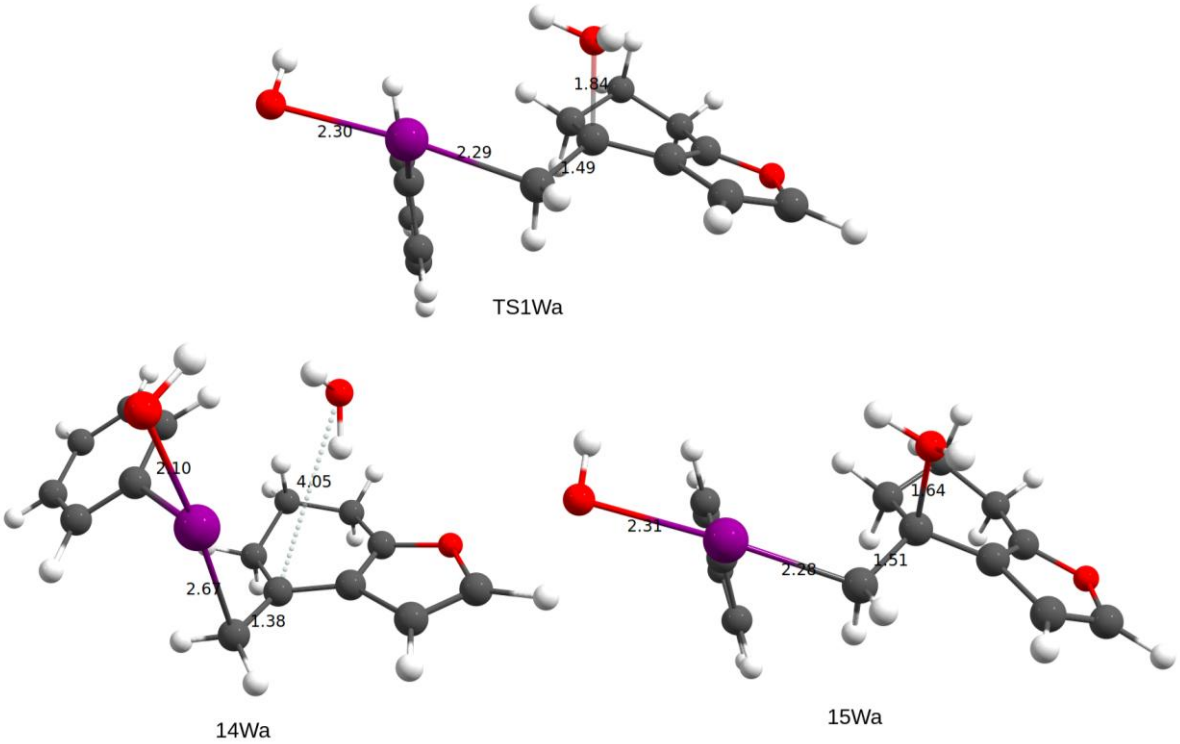

Figure S34. Intermediates **14Wc**, **15Wc** and transition state **TS1Wc**. Key distances are in Angstrom (Å).

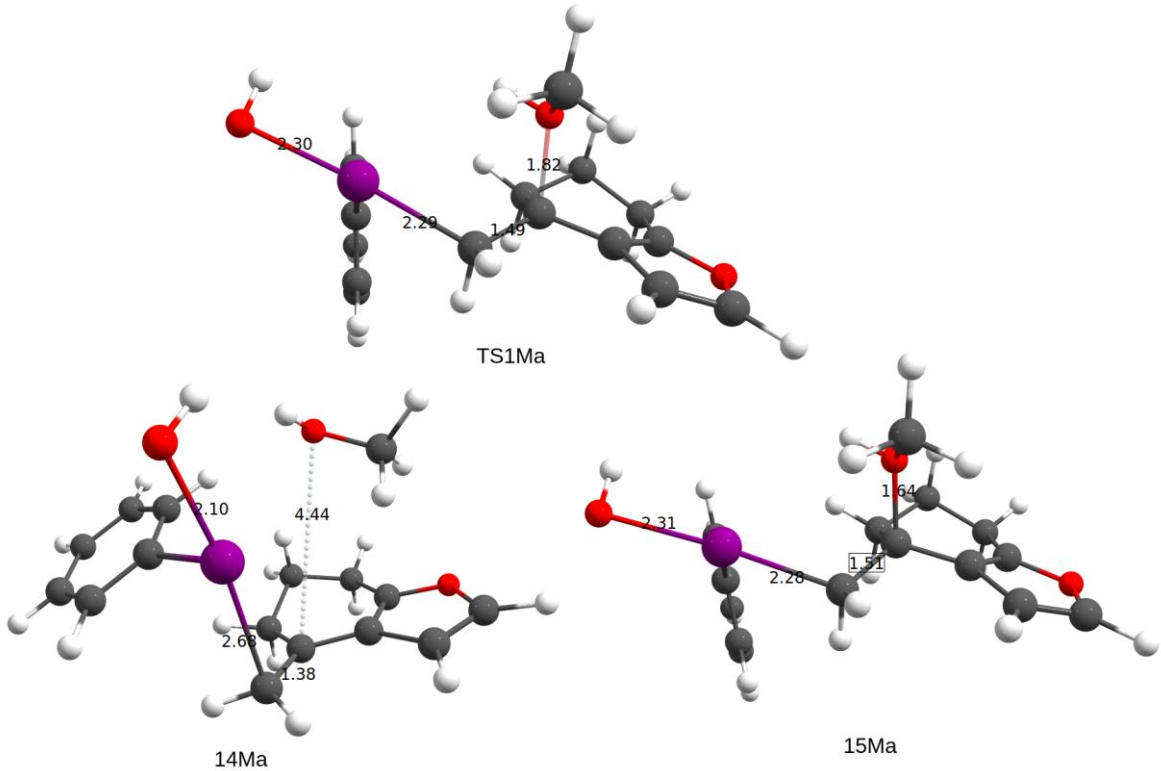

Figure S35. Intermediates **14Mc**, **15Mc** and transition state **TS1Mc**. Key distances are in Angstrom (Å).

Figure S36 show the concerted pathway for methanol addition to carbenium ion **14** which takes place simultaneously with the dissociation of the hydroxyl group from the iodine atom.

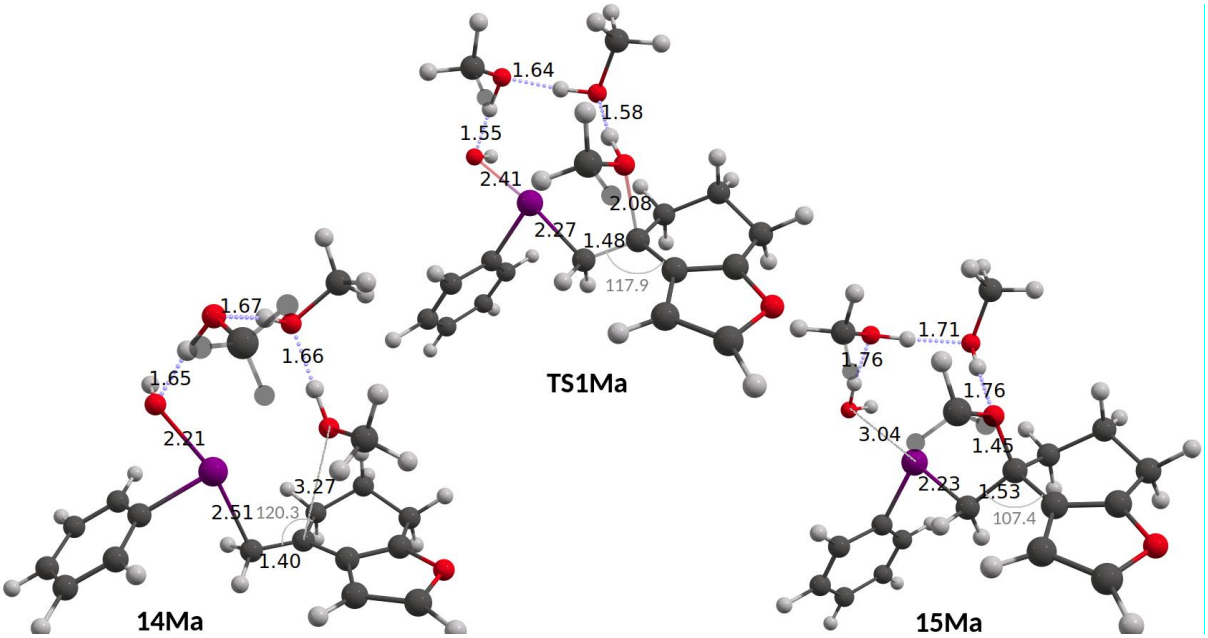

Figure S36. Optimized geometries of the intermediates **14Ma** and **15Ma** and the transition state **TS1Ma** where the methanol-cluster assisted nucleophilic addition to **14** occurs through a concerted mechanism leading direct to **15Ma**. The selected bond distances are given in Angstroms (Å).

Figure S7 present the optimized geometries of the transition states and the corresponding intermediates with the key bond distances associated to methanol pathway without interacting with the hypervalent iodine group and are therefore unable to protonate the hydroxyl group in the hypervalent iodine atom as observed in **15Mb**.

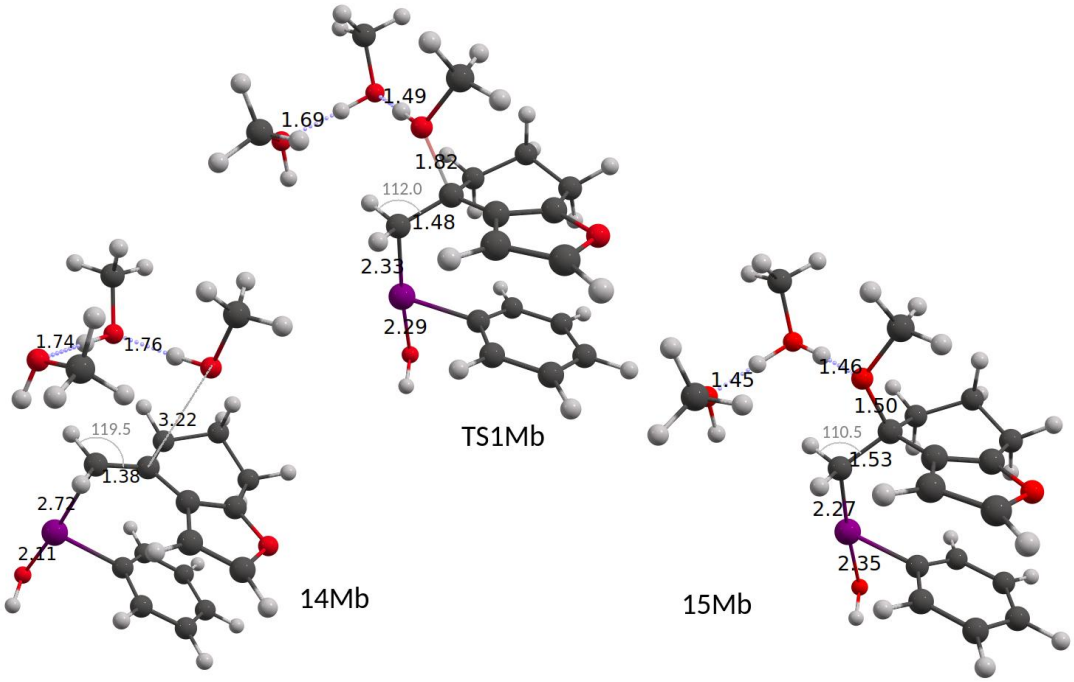

Figure S37. Optimized geometries of intermediates **14Mb**, **15Mb** and the transition state **TS1Mb**. **T**he methanol-cluster assisted nucleophilic addition to **14** occurs through a stepwise mechanism leading first to **15Mb**. Key distances are in Angstrom (Å) and bond angles in degree.

Methanol-assisted process displayed similar energy barrier that water-cluster (Figures 2 and 6) undergoing the ring expansion rearrangement from **16M** (4.7 kcal.mol^{-1}) to provide oxocarbenium ion **17M** via an exothermic step like observed in the water-assisted process. Hydrolysis step will lead **17M** to **17W**, completing the mechanism for methanol pathway.
The optimized geometries for the methanol-assisted process also show C-3 of the furyl group closer to the exocyclic methylene (2.07 Å) in **TS2M**, as compared to **16M** (2.39 Å), which progresses to a bond length of 1.52 Å in **17M** (Figure S6). Orbital interactions in the transition state also account for the carbon-iodine bond elongation from 2,30 Å in **16M** to 2.71 Å in **TS2M** and shortening of the carbon-hydroxyl bond from 1.43 Å in **16M** to 1.28 Å in **17M**, a bond length value in accordance with those observed for the carbonyl group of ketones.[16]

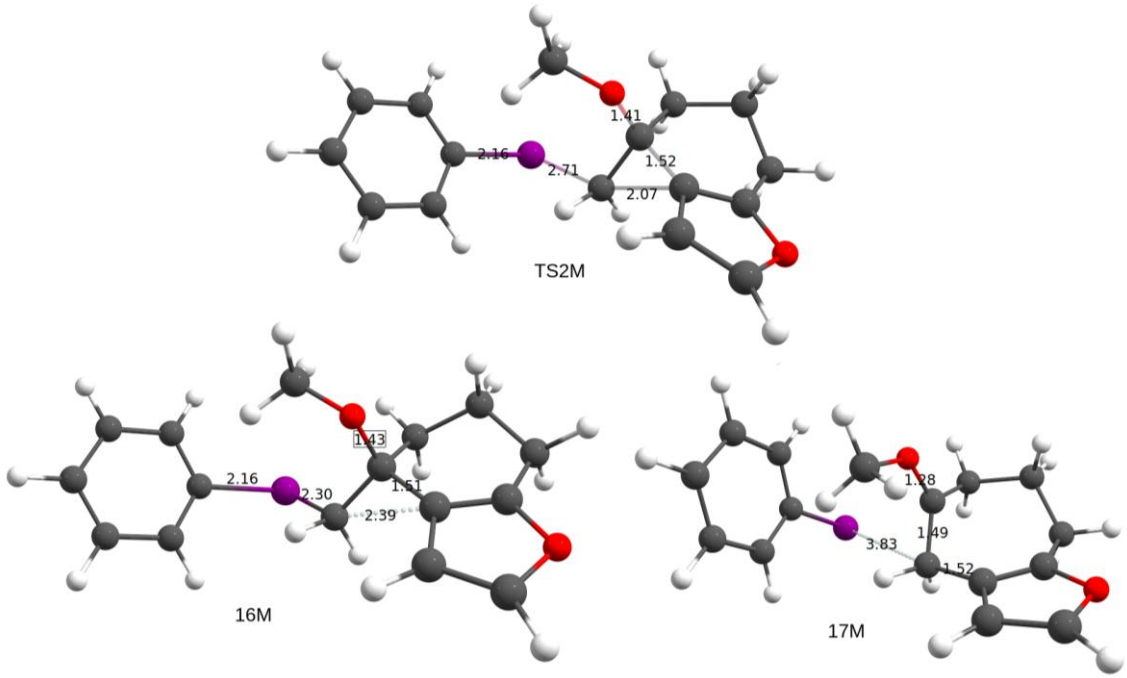

Figure S38. Intermediates **16M** and **17M**, and **TS2M** involved in the ring expansion step from the methanol nucleophilic addition pathway. Key distances are in Angstrom (Å).

The rate determining step (RDS) found was the water assisted formation of intermediate **15W** via an exergonic process (-28.2 kcal.mol^{-1}) with an activation energy barrier of 11.3 kcal.mol^{-1} (Figure 6). Similar activation barriers were obtained upon changing the implicit solvent from methanol to water or acetonitrile (Table S1).

Table S1. Relative potential and free energies (298.15 K) for transition states (TS) for different implicit solvents.

Label	**Reaction step**	**Implicit solvent**	**$\Delta E^{\ddagger}$ ($\Delta G^{\ddagger}$)**
TS1Wa	water nucleophilic addition at **14W**	methanol	11.3 (13.3)

[16] Glockler, G. Carbon–Oxygen Bond Energies and Bond Distances. *J. Phys. Chem.* **1958**, 62 (9), 1049.

TS1Wd	water nucleophilic addition at **14W**	acetonitrile	12.0 (13.6)
TS2W	ring expansion of **15W**	methanol	6.9 (4.7)
TS2Wb	ring expansion of **15W**	acetonitrile	6.8 (5.0)

Since ligand exchange could occur to the PhI(+)OH cation by the high amount of MeOH present as mainly solvent, the rds was also calculated for the solvent nucleophilic attack to PhI(+)OMe to form **15** through **18** (Figure S4), where higher activation barriers were observed to both water (**TS1We**, 17.2 kcal.mol^{-1}) and methanol-cluster (**TS1Me**, 13.1 kcal.mol^{-1}) comparing with the same step starting from **14**. The higher energetic cost increasing is due methoxy group acts as a better nucleophile compared to hydroxyl group leading to an less electrophilic demanding iodine(III) center in **TS1We** and **TS1Me** (**Figure S39**) than in **TS1Wa** and **TS1Ma**, respectively, and, therefore, reducing its activity over the C(10) which can better contribute to the electronic demanding C(6)$_{sp}$3 at the nucleophilic solvent addition, which allows I(III)-OMe bond breaking as an later process compared to I(III)-OH one along higher activation barriers. This consequence can be observed in the I-OR bond length which increases in the order **TS1Wa** (2.34 Å) < **TS1We** (2.36 Å) < **TS1Ma** (2.38 Å) < **TS1Me** (2.41 Å) as presented in **Figure S40** and inversely proportional with the activation barrier decreasing (**TS1We** > **TS1Wa** > **TS1Me** > **TS1Ma**).

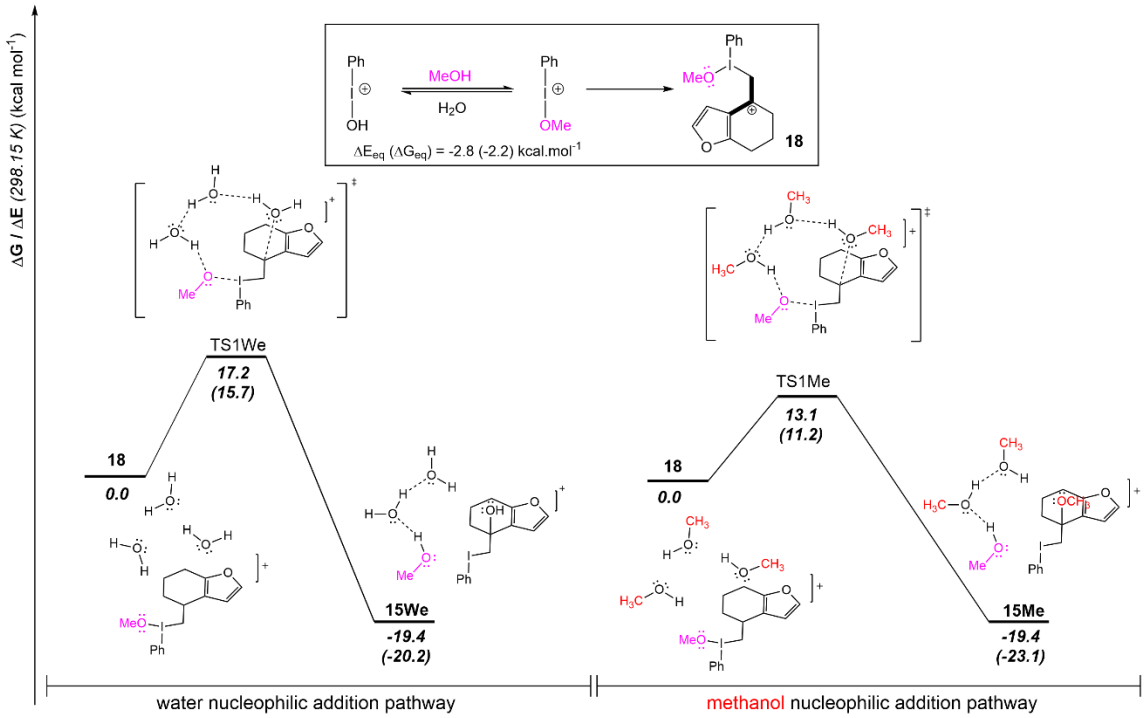

Figure S39. Energy profile (in kcal.mol^{-1}) corresponding to nucleophilic addition to intermediate **18** through concerted cluster-assisted solvent addition (black) and stepwise mechanisms (blue) to obtain intermediate **15** for water and methanol pathways. Potential energies (free energies) were calculated with respect to separated reactants.

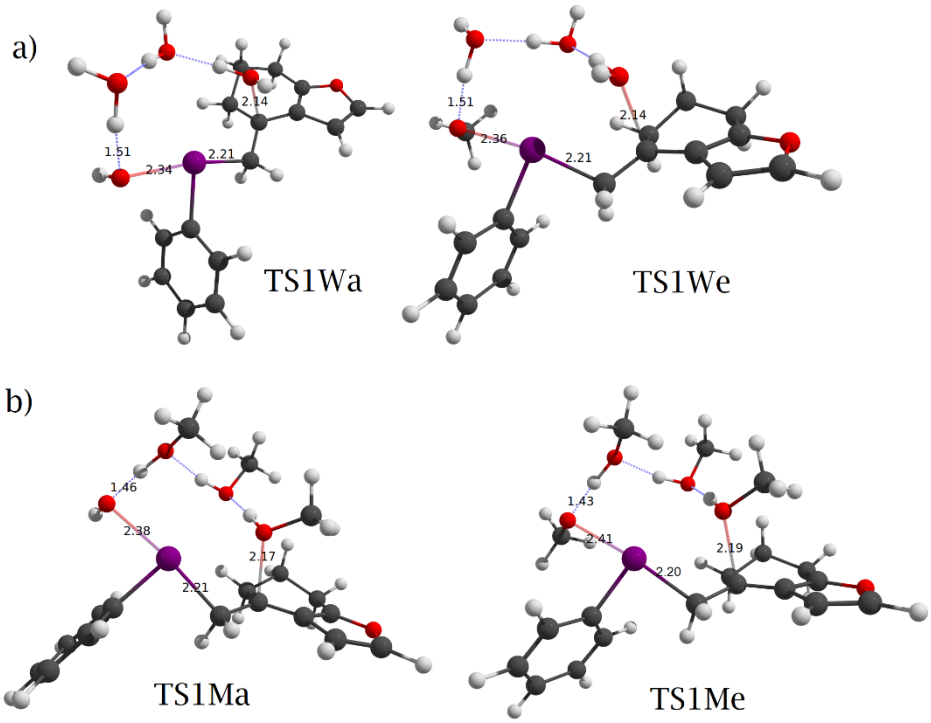

Figure S40. Optimized geometries for transition states (TS) associated to solvent nucleophilic addition to **14** and **18** for RDS step with (a) water- and (b) methanol-cluster. Selected bond distances are given in Angstroms (Å).

Coordinates of All Intermediates and Transition States geometries

14Mb			
Energy = -1090.10637306			
ZPE = -1089.671208			
Free Energy = -1089.735640			
C	-0.370434	1.34678	0.613742
C	-0.091047	2.567959	0.03109
C	-0.210592	1.534549	2.039093
C	0.15622	2.825753	2.20503
H	-0.348884	0.79915	2.818525
H	0.388914	3.437215	3.063649
O	0.235403	3.47182	0.975986
C	-0.710552	0.431248	-1.689869
H	-1.411081	-0.276372	-2.141557
H	0.287938	0.180944	-2.074988
C	-1.05989	1.874141	-2.094928
H	-2.096224	2.079469	-1.808642
H	-0.984594	1.97298	-3.181507
C	-0.139835	2.905316	-1.410974
H	-0.503023	3.92857	-1.551465
H	0.874927	2.859946	-1.830825
C	-0.800344	-1.064736	0.341213
H	-1.194099	-1.866153	-0.275848
H	-0.835915	-1.202554	1.418079
I	1.726611	-2.029099	0.044254
O	3.622847	-2.918025	-0.198734
H	3.998814	-2.925884	0.699461
C	2.596201	-0.071333	-0.089034
C	2.801913	0.64707	1.085966
C	2.935641	0.412835	-1.351379
C	3.36251	1.922482	0.981229
H	2.518006	0.242796	2.049846
C	3.504313	1.686624	-1.428695
H	2.761298	-0.173726	-2.245898
C	3.709696	2.439324	-0.268861
H	3.51816	2.508493	1.88167
H	3.778193	2.087638	-2.399756
H	4.14112	3.433124	-0.340658

C	-0.670254	0.200953	-0.191583
O	-3.688773	1.304576	-0.04608
C	-5.064494	1.639018	0.097331
H	-3.646264	0.428269	-0.492512
H	-5.61198	0.905894	0.707211
H	-5.126016	2.608482	0.603413
H	-5.576383	1.730584	-0.872134
O	-3.694862	-1.196126	-1.18048
C	-4.96428	-1.46244	-1.780811
H	-3.635719	-1.732287	-0.354226
H	-5.07832	-0.791831	-2.637203
H	-5.027236	-2.498645	-2.140319
H	-5.794727	-1.283109	-1.085439
O	-3.680431	-2.428645	1.237973
C	-4.008377	-1.32616	2.10117
H	-2.77273	-2.702042	1.434549
H	-3.787938	-1.566783	3.147615
H	-3.475615	-0.412908	1.814457
H	-5.082863	-1.154107	2.001328
TS1Mb			
Energy = -1090.09018614			
ZPE = -1089.654557			
Free Energy = -1089.714964			
C	0.032934	1.650377	0.628617
C	0.720961	2.60281	-0.081305
C	0.365396	1.850701	2.018613
C	1.238425	2.886282	2.042656
H	0.000649	1.294148	2.869868
H	1.768565	3.402896	2.828323
O	1.473595	3.351452	0.758221
C	-0.799358	0.768396	-1.558218
H	-1.717998	0.328094	-1.953937
H	0.022659	0.124413	-1.891666
C	-0.571328	2.182951	-2.114575
H	-1.426889	2.822437	-1.878432
H	-0.504464	2.126846	-3.204843
C	0.711466	2.824894	-1.548461
H	0.756602	3.895193	-1.774563

H	1.601995	2.360694	-1.993285
C	-0.897307	-0.681881	0.556138
H	-1.751642	-1.242483	0.175493
H	-0.89635	-0.663473	1.644326
I	0.786332	-2.193945	-0.011372
O	2.541753	-3.549577	-0.577217
H	3.030512	-3.612645	0.258865
C	2.319829	-0.679277	-0.053792
C	2.795924	-0.16674	1.147993
C	2.813308	-0.279052	-1.293631
C	3.798031	0.80724	1.099272
H	2.388754	-0.49419	2.097143
C	3.817448	0.692633	-1.319673
H	2.426978	-0.699977	-2.214702
C	4.303002	1.238733	-0.128412
H	4.17157	1.230381	2.026851
H	4.210298	1.024593	-2.276167
H	5.07733	1.999588	-0.158003
C	-0.815233	0.674528	-0.037231
O	-2.492111	1.213746	0.426705
C	-2.845626	2.610102	0.492461
H	-3.145246	0.715377	-0.205113
H	-3.656625	2.714871	1.218878
H	-1.975937	3.169941	0.840094
H	-3.163867	2.985655	-0.483064
O	-4.068828	-0.033483	-1.100145
C	-5.369921	0.573713	-1.169325
H	-4.153078	-0.90765	-0.634059
H	-5.280687	1.481031	-1.771358
H	-6.082933	-0.104912	-1.649552
H	-5.742874	0.841269	-0.173328
O	-4.25926	-2.189968	0.456308
C	-4.369306	-1.554849	1.742921
H	-3.432438	-2.694444	0.434156
H	-4.212666	-2.277191	2.551523
H	-3.655931	-0.729593	1.847617
H	-5.384914	-1.158482	1.816361
14Wa			
Energy = -972.207267529			

ZPE = -971.858837			
Free Energy = -971.917463			
C	-2.41959	-1.437777	-0.570142
C	-3.54667	-1.082472	0.154439
C	-2.761605	-1.253585	-1.964215
C	-4.041693	-0.82252	-1.976058
H	-2.131556	-1.426592	-2.824657
H	-4.7385	-0.553952	-2.755299
O	-4.53343	-0.713367	-0.676221
C	-1.320562	-2.006871	1.592854
H	-0.326706	-1.922151	2.041207
H	-1.659519	-3.040505	1.76005
C	-2.301815	-1.027692	2.264273
H	-1.9043	-0.011409	2.174958
H	-2.372497	-1.260232	3.330392
C	-3.70552	-1.078774	1.62769
H	-4.324022	-0.231896	1.941639
H	-4.233407	-1.994551	1.931462
C	-1.220886	-1.822273	0.096651
C	-0.005308	-1.97314	-0.567311
H	0.015939	-2.03436	-1.651971
H	0.825895	-2.427502	-0.035487
C	2.732145	-0.372885	-0.082872
C	3.470383	-0.683199	-1.222563
C	3.206966	-0.581385	1.210386
C	4.747467	-1.222896	-1.048873
H	3.066522	-0.515503	-2.214822
C	4.487055	-1.120688	1.359903
H	2.602805	-0.333378	2.076098
C	5.253262	-1.43873	0.235727
H	5.342767	-1.472044	-1.92223
H	4.879707	-1.289635	2.35815
H	6.246928	-1.858444	0.36109
O	-2.114086	1.817704	-0.750179
H	-2.078473	1.783109	0.2244
O	-1.369732	2.456678	1.926243
H	-1.018066	3.143999	1.314259
O	-0.46064	4.005119	-0.163644
H	-0.242957	4.944179	-0.086425
I	0.790109	0.496376	-0.325557

O	1.754958	2.448961	-0.242287
H	1.994653	2.54849	0.696428
H	-1.714351	2.690139	-0.915452
H	-2.168067	2.853604	2.302051
H	0.403072	3.529288	-0.261958
15Wb			
Energy = -972.192195234			
ZPE = -971.839999			
Free Energy = -971.892318			
C	0.54475	-1.86242	-0.601367
C	1.432405	-2.26106	0.35382
C	1.226081	-1.969534	-1.866336
C	2.480646	-2.403094	-1.579657
H	0.834512	-1.743324	-2.848262
H	3.351748	-2.621174	-2.179406
O	2.628933	-2.585097	-0.22034
C	-1.042363	-1.340543	1.256591
H	-2.113857	-1.345267	1.477786
H	-0.649846	-0.37546	1.5876
C	-0.319576	-2.446452	2.043136
H	-0.693139	-3.431932	1.737745
H	-0.542457	-2.337835	3.109028
C	1.20488	-2.386188	1.817072
H	1.702518	-3.279548	2.209709
H	1.631927	-1.520277	2.34197
C	-1.324492	-0.225444	-1.060891
H	-2.414405	-0.164759	-1.054383
H	-0.977501	-0.264043	-2.09349
I	-0.843077	1.857741	-0.29486
O	-0.144497	3.928354	0.561354
H	0.430851	4.258856	-0.146309
C	1.235874	1.389677	0.03237
C	2.061688	1.175911	-1.065013
C	1.694236	1.323864	1.346082
C	3.404512	0.862281	-0.829555
H	1.676997	1.229178	-2.077048
C	3.037841	1.006504	1.559767
H	1.028558	1.50396	2.182195

C	3.889058	0.771194	0.476094
H	4.062632	0.68075	-1.673933
H	3.412657	0.938711	2.576838
H	4.930827	0.519472	0.651031
C	-0.86043	-1.452751	-0.274758
O	-1.765389	-2.518682	-0.790371
H	-3.147316	-2.31037	-0.422135
O	-4.147782	-2.097355	-0.160203
H	-4.198214	-1.118416	0.203033
O	-4.269076	0.26376	0.717821
H	-3.383339	0.566099	0.973215
H	-1.4483	-3.378697	-0.466682
H	-4.685138	-2.144063	-0.969891
H	-4.534842	0.858368	-0.001253
14Wb			
Energy = -972.199806391			
ZPE = -971.852034			
Free Energy = -971.910062			
C	-0.432131	1.791691	-0.795345
C	-1.200873	2.540135	0.075346
C	-1.132119	1.804265	-2.061553
C	-2.251498	2.536203	-1.860902
H	-0.833656	1.325024	-2.982701
H	-3.082854	2.825372	-2.485767
O	-2.307391	2.991795	-0.548064
C	1.145553	1.375478	1.103238
H	2.231353	1.310299	1.206791
H	0.719167	0.544804	1.681728
C	0.628076	2.704287	1.678358
H	1.141652	3.527359	1.170449
H	0.878391	2.761848	2.741593
C	-0.893906	2.863732	1.488767
H	-1.227803	3.878289	1.729595
H	-1.440271	2.175936	2.149556
C	1.494034	0.293008	-1.152019
H	2.481014	-0.02809	-0.837382
H	1.247808	0.189306	-2.204753
I	0.419785	-2.083511	-0.341719

O	-0.260102	-3.999482	0.215061
H	-0.674181	-4.348848	-0.594364
C	-1.448228	-1.198233	0.223653
C	-2.385562	-0.927293	-0.770023
C	-1.671367	-0.938538	1.574997
C	-3.599325	-0.353615	-0.383255
H	-2.175123	-1.132467	-1.812718
C	-2.894708	-0.370324	1.937266
H	-0.921405	-1.165242	2.32365
C	-3.850593	-0.073649	0.96157
H	-4.339876	-0.119167	-1.141392
H	-3.092261	-0.157094	2.983321
H	-4.794734	0.37719	1.251648
C	0.77017	1.14978	-0.350397
O	3.375371	3.272666	-0.370626
H	3.85634	2.421163	-0.272783
O	4.846362	0.927216	-0.128271
H	4.446284	0.155549	0.333177
O	3.689266	-1.290135	1.055363
H	2.816658	-1.044406	1.39604
H	3.663376	3.783007	0.398338
H	4.952394	0.626944	-1.041939
H	3.485911	-1.878746	0.313144
14Ma			
Energy = -1090.11233759			
ZPE = -1089.677806			
Free Energy = -1089.742409			
C	2.136954	-2.039529	0.507401
C	3.497679	-1.975391	0.226561
C	2.023752	-2.035998	1.9511
C	3.287696	-1.971377	2.420306
H	1.118303	-2.067701	2.539543
H	3.726406	-1.935504	3.405661
O	4.201327	-1.938001	1.362829
C	1.722278	-2.082932	-1.953466
H	0.987747	-1.615161	-2.616294
H	1.775085	-3.141891	-2.252871
C	3.103447	-1.424449	-2.120548

H	2.998773	-0.346069	-1.971172
H	3.463049	-1.591616	-3.139111
C	4.13363	-1.96559	-1.10956
H	5.047625	-1.364323	-1.093878
H	4.426616	-2.994329	-1.366943
C	1.187752	-2.082136	-0.541787
C	-0.196301	-2.141177	-0.307463
H	-0.538483	-2.449712	0.677084
H	-0.828459	-2.435473	-1.141662
C	-2.904586	-0.728545	-0.033901
C	-3.340087	-1.149844	1.220438
C	-3.662175	-0.896948	-1.191052
C	-4.593538	-1.761194	1.312656
H	-2.725687	-1.008941	2.102952
C	-4.913245	-1.509179	-1.076681
H	-3.293026	-0.566231	-2.155741
C	-5.376581	-1.938809	0.16943
H	-4.952664	-2.095752	2.281423
H	-5.520106	-1.650494	-1.966132
H	-6.34894	-2.415686	0.249613
O	1.864653	1.106852	-0.332775
C	2.424171	1.305112	0.963338
H	2.653467	2.361466	1.145636
H	1.737125	0.959355	1.746317
H	3.355766	0.734965	1.056077
H	1.593109	1.991687	-0.689605
O	1.133405	3.503282	-1.20722
C	2.260475	4.380808	-1.16598
H	3.037346	3.963238	-1.813228
H	1.999042	5.381499	-1.535728
H	2.670259	4.480153	-0.152306
H	0.4763	3.807057	-0.523986
O	-0.637138	4.144262	0.669695
C	-0.10046	3.831265	1.956365
H	-0.847783	3.988531	2.746519
H	0.251671	2.794235	2.01464
H	0.745643	4.498393	2.146457
H	-1.274342	3.413182	0.431189
I	-0.99376	0.239922	-0.191182
O	-2.167505	2.106834	-0.040762
H	-2.367673	2.318874	-0.968884

TS1Wa			
Energy = -972.189218133			
ZPE = -971.840998			
Free Energy = -971.896347			
C	-2.934876	-1.054319	-0.324238
C	-4.183554	-0.922154	0.258225
C	-3.085417	-2.013056	-1.39706
C	-4.384791	-2.383503	-1.378791
H	-2.325535	-2.362089	-2.081268
H	-4.984894	-3.056794	-1.97169
O	-5.065245	-1.723834	-0.357549
C	-2.054373	0.430736	1.473987
H	-1.310486	1.224386	1.57131
H	-1.863871	-0.282997	2.289935
C	-3.473835	1.004263	1.5846
H	-3.606531	1.764544	0.808068
H	-3.58915	1.49875	2.552544
C	-4.552816	-0.082279	1.421644
H	-5.547892	0.351348	1.280011
H	-4.603545	-0.717641	2.317805
C	-1.80895	-0.346507	0.201258
C	-0.45554	-0.894536	-0.054131
H	-0.38304	-1.461353	-0.981002
H	-0.181987	-1.524588	0.797449
C	2.623072	-0.978618	0.1192
C	3.083362	-1.617521	-1.029283
C	3.027141	-1.340584	1.401902
C	3.990793	-2.670017	-0.876365
H	2.749475	-1.310712	-2.01426
C	3.93505	-2.395603	1.530711
H	2.649293	-0.823816	2.277043
C	4.414163	-3.056784	0.3972
H	4.362985	-3.183157	-1.758155
H	4.263386	-2.696272	2.521293
H	5.119454	-3.875246	0.506736
O	-1.879823	1.260904	-1.080612
H	-1.443423	2.088731	-0.695748
O	-0.801067	3.35653	0.065329

H	0.090164	3.605407	-0.314216
O	1.614747	4.020941	-0.904143
H	1.861815	4.788082	-0.368308
I	1.223767	0.632635	-0.098595
O	3.158842	2.04765	-0.17843
H	3.302841	2.238325	0.762233
H	-1.37157	1.021039	-1.871738
H	-1.373703	4.117827	-0.106728
H	2.270333	3.291947	-0.625711
17M			
Energy = -782.264171060			
ZPE = -781.957651			
Free Energy = -782.006732			
C	-2.742939	0.478684	-0.797232
C	-3.7682	-0.263881	-0.27134
C	-3.322802	1.691741	-1.305138
C	-4.659069	1.589459	-1.08117
H	-2.801618	2.506677	-1.78768
H	-5.505158	2.22351	-1.300846
O	-4.945423	0.405058	-0.44571
C	-1.337063	-1.488578	1.303186
H	-0.747169	-1.589298	2.217315
H	-1.06668	-2.279783	0.599512
C	-2.849408	-1.609677	1.662323
H	-3.116723	-0.814244	2.365507
H	-2.965162	-2.565853	2.18141
C	-3.789829	-1.574918	0.443619
H	-4.814922	-1.770343	0.771896
H	-3.511249	-2.380352	-0.249197
C	-1.027342	-0.172475	0.683965
C	-1.280744	0.08151	-0.761877
H	-0.648773	0.877457	-1.156635
H	-1.093704	-0.835009	-1.32551
O	-0.662882	0.737242	1.502339
I	2.105816	-1.683665	-0.47362
C	2.47996	0.411222	-0.111806
C	2.778581	0.83169	1.184402
C	2.418095	1.308312	-1.178865

C	3.030166	2.1887	1.410028
H	2.816283	0.123889	2.004965
C	2.670693	2.662953	-0.933266
H	2.182416	0.967869	-2.181175
C	2.977977	3.103846	0.356188
H	3.264425	2.52413	2.416334
H	2.625623	3.369021	-1.757592
H	3.173531	4.156246	0.539217
C	-0.459436	2.133796	1.100703
H	-1.425137	2.539352	0.796125
H	-0.089728	2.62349	1.997403
H	0.270074	2.184786	0.295476
16W			
Energy = -742.916584394			
ZPE = -742.639606			
Free Energy = -742.685645			
C	-2.506677	0.767723	-0.287214
C	-3.818884	0.487904	-0.036167
C	-2.483884	1.997136	-1.041639
C	-3.783147	2.363057	-1.195062
H	-1.619748	2.527788	-1.416974
H	-4.273604	3.192902	-1.681798
O	-4.615773	1.450136	-0.583707
C	-1.969379	-1.443574	0.737442
H	-1.193247	-1.940401	1.327814
H	-2.187379	-2.081474	-0.127046
C	-3.242001	-1.254021	1.575888
H	-3.018588	-0.590502	2.419236
H	-3.555757	-2.216275	1.991177
C	-4.385365	-0.647663	0.738086
H	-5.207638	-0.305282	1.376214
H	-4.802474	-1.402948	0.056925
C	-1.3861	-0.107407	0.23232
C	-0.442751	-0.288573	-0.950709
H	0.031909	0.632662	-1.287997
H	-0.868061	-0.852637	-1.77963
O	-0.717378	0.493672	1.345362
H	-0.456437	1.395247	1.102998

I	1.394629	-1.504486	-0.43863
C	2.618744	0.201197	0.074504
C	2.467051	0.764892	1.337767
C	3.507275	0.679878	-0.883301
C	3.255288	1.877481	1.646406
H	1.749981	0.371481	2.047241
C	4.28546	1.79191	-0.546506
H	3.59374	0.213595	-1.857954
C	4.159198	2.386837	0.71064
H	3.155673	2.342546	2.622646
H	4.986115	2.188525	-1.27519
H	4.766426	3.251387	0.961741
TS2W			
Energy = -742.905565519			
ZPE = -742.630630			
Free Energy = -742.678148			
C	-2.459913	0.903881	-0.031607
C	-3.70718	0.426419	-0.389886
C	-2.436048	2.305178	-0.390172
C	-3.652486	2.565309	-0.921483
H	-1.6208	3.002808	-0.261701
H	-4.120213	3.446979	-1.332372
O	-4.440893	1.419306	-0.919544
C	-2.054541	-1.32682	1.170957
H	-1.631573	-1.486322	2.165822
H	-1.708121	-2.150292	0.538607
C	-3.588739	-1.350729	1.249068
H	-3.931392	-0.683501	2.04768
H	-3.912936	-2.363404	1.50601
C	-4.254123	-0.913208	-0.075917
H	-5.343373	-0.865668	0.010271
H	-4.015051	-1.626568	-0.876245
C	-1.43361	-0.006636	0.635124
C	-0.815837	-0.121735	-0.699577
H	-0.217313	0.700523	-1.082512
H	-1.250673	-0.801827	-1.423641
O	-0.661119	0.599289	1.639712
H	-0.189616	1.368108	1.282423

I	1.436957	-1.601779	-0.394501
C	2.620935	0.164928	-0.018562
C	2.598022	0.726678	1.256707
C	3.363829	0.709523	-1.063975
C	3.351778	1.882361	1.484165
H	2.001231	0.291047	2.049401
C	4.112104	1.864419	-0.813339
H	3.363379	0.255329	-2.048425
C	4.106648	2.449463	0.454698
H	3.343457	2.334573	2.471692
H	4.696179	2.302546	-1.617503
H	4.689139	3.347035	0.640508
15Mb			
Energy = -1090.09486690			
ZPE = -1089.658141			
Free Energy = -1089.717410			
C	-0.023072	1.697693	0.468316
C	0.866939	2.48648	-0.196608
C	0.167252	1.952376	1.873254
C	1.173272	2.861291	1.953866
H	-0.371294	1.511854	2.700569
H	1.675205	3.351283	2.774746
O	1.62102	3.197528	0.693201
C	-0.786945	0.842722	-1.765911
H	-1.734298	0.557308	-2.235053
H	-0.058874	0.072892	-2.037252
C	-0.280314	2.184162	-2.330108
H	-1.027803	2.970349	-2.19143
H	-0.129419	2.075865	-3.408936
C	1.038495	2.629307	-1.664813
H	1.282573	3.665005	-1.924591
H	1.873292	2.004851	-2.010806
C	-0.971816	-0.624477	0.345462
H	-1.82421	-1.197304	-0.024699
H	-1.000191	-0.601769	1.434726
I	0.659461	-2.104336	-0.206887
O	2.470395	-3.499448	-0.761774
H	2.937982	-3.572297	0.084892

C	2.27966	-0.722439	0.121631
C	2.575051	-0.31826	1.417748
C	3.025195	-0.318357	-0.98353
C	3.658113	0.546081	1.609749
H	1.976719	-0.64837	2.258829
C	4.101022	0.547132	-0.770822
H	2.777893	-0.658784	-1.982235
C	4.414686	0.980696	0.520483
H	3.899335	0.879308	2.614719
H	4.688374	0.883276	-1.620313
H	5.250975	1.65563	0.676653
C	-0.987044	0.794656	-0.23052
O	-2.379096	1.22649	0.127428
C	-2.746747	2.607666	-0.068328
H	-3.411546	0.384734	-0.460983
H	-3.65481	2.762907	0.518577
H	-1.961699	3.272849	0.297191
H	-2.952693	2.817532	-1.121907
O	-4.157903	-0.258707	-0.826897
C	-5.45048	0.412304	-0.926348
H	-4.205395	-1.042663	-0.130644
H	-5.359632	1.187848	-1.686767
H	-6.179342	-0.336814	-1.235363
H	-5.72799	0.845651	0.036919
O	-4.218396	-1.961515	0.994509
C	-4.144111	-1.154067	2.193353
H	-3.427294	-2.521477	0.948148
H	-3.903705	-1.783464	3.054208
H	-3.395976	-0.362066	2.087641
H	-5.130725	-0.708913	2.335204
TS1Wb			
Energy = -972.185221153			
ZPE = -971.835128			
Free Energy = -971.888487			
C	-0.775018	1.747502	-0.633142
C	-1.697172	2.156029	0.299636
C	-1.467508	1.692956	-1.898714
C	-2.745908	2.052616	-1.635613

H	-1.060726	1.418633	-2.861264
H	-3.63503	2.160916	-2.237882
O	-2.903003	2.331662	-0.285722
C	0.859221	1.509056	1.244465
H	1.928694	1.652278	1.414302
H	0.604099	0.525742	1.656974
C	0.029539	2.576441	1.975085
H	0.315234	3.575846	1.625848
H	0.255967	2.534159	3.044093
C	-1.482071	2.373176	1.7513
H	-2.060692	3.234626	2.10014
H	-1.838291	1.494557	2.307268
C	1.304292	0.39801	-1.035231
H	2.384139	0.469358	-0.92078
H	1.019521	0.383212	-2.085788
I	1.050498	-1.800985	-0.286869
O	0.644352	-3.899865	0.481914
H	0.254372	-4.334008	-0.293649
C	-1.052113	-1.521568	0.077472
C	-1.924719	-1.476816	-1.004091
C	-1.479916	-1.405067	1.398058
C	-3.286059	-1.28822	-0.745704
H	-1.562004	-1.564003	-2.021892
C	-2.843881	-1.214538	1.634171
H	-0.777184	-1.449558	2.222241
C	-3.742997	-1.150791	0.5661
H	-3.982223	-1.239619	-1.577617
H	-3.196976	-1.111493	2.655983
H	-4.800546	-0.995601	0.757523
C	0.590579	1.424532	-0.253033
O	1.509936	2.927679	-0.895816
H	2.481261	2.820286	-0.588178
O	3.948548	2.574781	-0.137819
H	4.045803	1.652478	0.206683
O	4.175415	0.002336	0.782318
H	3.322555	-0.245176	1.169779
H	1.157301	3.714323	-0.445496
H	4.496427	2.598714	-0.936405
H	4.252336	-0.57612	0.00859
15Wb			

Energy = -972.192195234			
ZPE = -971.839999			
Free Energy = -971.892318			
C	0.54475	-1.86242	-0.601367
C	1.432405	-2.26106	0.35382
C	1.226081	-1.969534	-1.866336
C	2.480646	-2.403094	-1.579657
H	0.834512	-1.743324	-2.848262
H	3.351748	-2.621174	-2.179406
O	2.628933	-2.585097	-0.22034
C	-1.042363	-1.340543	1.256591
H	-2.113857	-1.345267	1.477786
H	-0.649846	-0.37546	1.5876
C	-0.319576	-2.446452	2.043136
H	-0.693139	-3.431932	1.737745
H	-0.542457	-2.337835	3.109028
C	1.20488	-2.386188	1.817072
H	1.702518	-3.279548	2.209709
H	1.631927	-1.520277	2.34197
C	-1.324492	-0.225444	-1.060891
H	-2.414405	-0.164759	-1.054383
H	-0.977501	-0.264043	-2.09349
I	-0.843077	1.857741	-0.29486
O	-0.144497	3.928354	0.561354
H	0.430851	4.258856	-0.146309
C	1.235874	1.389677	0.03237
C	2.061688	1.175911	-1.065013
C	1.694236	1.323864	1.346082
C	3.404512	0.862281	-0.829555
H	1.676997	1.229178	-2.077048
C	3.037841	1.006504	1.559767
H	1.028558	1.50396	2.182195
C	3.889058	0.771194	0.476094
H	4.062632	0.68075	-1.673933
H	3.412657	0.938711	2.576838
H	4.930827	0.519472	0.651031
C	-0.86043	-1.452751	-0.274758
O	-1.765389	-2.518682	-0.790371
H	-3.147316	-2.31037	-0.422135

O	-4.147782	-2.097355	-0.160203
H	-4.198214	-1.118416	0.203033
O	-4.269076	0.26376	0.717821
H	-3.383339	0.566099	0.973215
H	-1.4483	-3.378697	-0.466682
H	-4.685138	-2.144063	-0.969891
H	-4.534842	0.858368	-0.001253
15Wa			
Energy = -972.252149008			
ZPE = -971.901438			
Free Energy = -971.959281			
C	-3.042247	-0.793792	-0.482664
C	-4.166181	-0.879145	0.287038
C	-3.271526	-1.625866	-1.638319
C	-4.510832	-2.157877	-1.474938
H	-2.603679	-1.802105	-2.47023
H	-5.11825	-2.831868	-2.060534
O	-5.07471	-1.710272	-0.299491
C	-2.018366	0.507779	1.380627
H	-1.314587	1.322071	1.5719
H	-1.727265	-0.338335	2.013457
C	-3.445397	0.955453	1.729805
H	-3.730481	1.782286	1.069026
H	-3.468934	1.335492	2.755431
C	-4.457137	-0.196607	1.574484
H	-5.488094	0.174026	1.588684
H	-4.361691	-0.905907	2.408756
C	-1.874618	0.082897	-0.096166
C	-0.603769	-0.717936	-0.364812
H	-0.503619	-1.034566	-1.401977
H	-0.453349	-1.546608	0.326427
C	2.530463	-1.154287	0.113599
C	3.187647	-1.611539	-1.025172
C	2.671254	-1.740819	1.368736
C	4.027051	-2.721406	-0.889613
H	3.054226	-1.127086	-1.9858
C	3.513917	-2.850696	1.476515
H	2.145219	-1.353797	2.234062

C	4.187874	-3.337241	0.353632
H	4.551164	-3.099787	-1.762106
H	3.640478	-3.328981	2.443166
H	4.841828	-4.198875	0.44849
O	-1.866705	1.303368	-0.869302
H	-0.998329	2.778753	-0.240283
O	-0.50731	3.482812	0.234175
H	0.979311	3.80406	-0.64291
O	1.827963	3.926406	-1.135104
H	2.049884	4.859594	-1.00685
I	1.2204	0.542733	-0.080605
O	3.618085	2.40602	0.288611
H	3.380848	2.563994	1.212905
H	-1.850436	1.086234	-1.814197
H	-1.074618	4.264723	0.172356
H	3.021794	3.011677	-0.215363
TS1Ma			
Energy = -1090.10074623			
ZPE = -1089.666008			
Free Energy = -1089.726523			
C	2.845667	-1.425454	0.35099
C	4.088943	-1.457671	-0.260604
C	2.980485	-2.174897	1.582723
C	4.264302	-2.594039	1.619816
H	2.2197	-2.362184	2.32607
H	4.849757	-3.169176	2.320688
O	4.949632	-2.163188	0.484949
C	1.981843	-0.297452	-1.696197
H	1.265012	0.489849	-1.939251
H	1.743828	-1.150038	-2.350775
C	3.418745	0.185065	-1.943114
H	3.59294	1.080608	-1.339517
H	3.53021	0.464799	-2.993693
C	4.463818	-0.883791	-1.573329
H	5.475663	-0.468094	-1.534466
H	4.476676	-1.691571	-2.31975
C	1.737321	-0.795951	-0.291338
C	0.374558	-1.224871	0.100369

H	0.307897	-1.576743	1.128222
H	0.063926	-2.016522	-0.588451
C	-2.722966	-1.268096	-0.098164
C	-3.210667	-1.681033	1.138985
C	-3.145385	-1.822199	-1.304006
C	-4.169721	-2.698224	1.15941
H	-2.860992	-1.228369	2.060132
C	-4.104883	-2.837544	-1.259066
H	-2.744778	-1.47837	-2.251122
C	-4.615163	-3.27227	-0.033434
H	-4.564923	-3.036439	2.112685
H	-4.450266	-3.283567	-2.18704
H	-5.362378	-4.059988	-0.008139
O	1.910962	1.079755	0.591828
C	1.691025	1.150716	2.002845
H	1.899922	2.166742	2.355689
H	0.664812	0.876278	2.273349
H	2.38766	0.461715	2.486563
H	1.384302	1.80175	0.115921
O	0.775042	3.029824	-0.674671
C	1.581604	4.168476	-0.348062
H	2.61398	3.943279	-0.629174
H	1.249826	5.05426	-0.903188
H	1.552327	4.394338	0.725811
H	-0.172502	3.259443	-0.440075
O	-1.6382	3.747272	0.1101
C	-1.489999	3.782798	1.528313
H	-2.465413	3.777637	2.032598
H	-0.903848	2.932054	1.905284
H	-0.968188	4.705074	1.805071
H	-2.305304	2.997044	-0.107811
I	-1.271705	0.313198	-0.151381
O	-3.194489	1.758128	-0.3583
H	-3.320239	1.780986	-1.320493
16M			
Energy = -782.212357181			
ZPE = -781.907349			
Free Energy = -781.955338			

C	-2.700681	0.831544	-0.110847
C	-3.971307	0.336406	-0.106656
C	-2.783266	2.183966	-0.601812
C	-4.096972	2.402057	-0.86883
H	-1.974167	2.888782	-0.733424
H	-4.65244	3.246097	-1.24986
O	-4.84162	1.280382	-0.568841
C	-1.944512	-1.44812	0.562276
H	-1.178103	-1.9635	1.147637
H	-1.967857	-1.926097	-0.425165
C	-3.314105	-1.585668	1.240337
H	-3.286534	-1.0606	2.202282
H	-3.518999	-2.640067	1.447733
C	-4.437491	-0.992833	0.36699
H	-5.37101	-0.892374	0.931688
H	-4.64709	-1.653323	-0.486227
C	-1.516099	0.029517	0.384131
C	-0.465165	0.215991	-0.710006
H	0.083406	1.156364	-0.65313
H	-0.863498	0.031077	-1.704364
O	-1.167348	0.646349	1.630149
I	1.275763	-1.278113	-0.775632
C	2.825601	0.092534	-0.155775
C	3.477205	-0.15417	1.049247
C	3.117425	1.172418	-0.983525
C	4.479861	0.740141	1.436863
H	3.217754	-1.002376	1.672085
C	4.116299	2.056826	-0.565869
H	2.590896	1.327641	-1.918309
C	4.794968	1.839956	0.635665
H	5.006165	0.572778	2.371799
H	4.36169	2.910933	-1.189904
H	5.572689	2.530237	0.948076
C	0.070412	0.299867	2.251622
H	0.026332	0.714605	3.262088
H	0.222002	-0.783295	2.325136
H	0.922061	0.746667	1.727049
TS2M			
Energy = -782.204918098			

ZPE = -781.901571			
Free Energy = -781.949885			
C	-2.642315	0.870352	-0.023522
C	-3.844339	0.313413	-0.412616
C	-2.713466	2.279059	-0.337874
C	-3.934916	2.465875	-0.889553
H	-1.952287	3.026573	-0.169487
H	-4.456015	3.322171	-1.28973
O	-4.638781	1.267896	-0.92908
C	-2.075307	-1.376012	1.060291
H	-1.607225	-1.626907	2.015769
H	-1.706193	-2.096915	0.323509
C	-3.600826	-1.503136	1.175496
H	-3.964915	-0.887727	2.005927
H	-3.856437	-2.542971	1.399307
C	-4.313711	-1.061457	-0.123448
H	-5.402336	-1.071267	-0.016057
H	-4.055933	-1.742179	-0.946172
C	-1.574112	0.046051	0.670798
C	-0.811976	0.087127	-0.597241
H	-0.226606	0.970707	-0.838847
H	-1.175208	-0.514737	-1.420452
O	-1.088431	0.821851	1.742221
I	1.387504	-1.497194	-0.625715
C	2.776603	0.104515	-0.235052
C	3.63624	-0.007875	0.856041
C	2.757096	1.225137	-1.063202
C	4.51361	1.048944	1.117844
H	3.623849	-0.886294	1.491564
C	3.638275	2.272928	-0.778033
H	2.078459	1.289129	-1.906531
C	4.514184	2.185709	0.306521
H	5.191588	0.977846	1.963385
H	3.635474	3.155293	-1.411379
H	5.195792	3.003661	0.519957
C	0.222577	0.52504	2.237392
H	0.313053	1.068928	3.180668
H	0.366131	-0.544468	2.427304
H	0.993078	0.878457	1.545978

17W			
Energy = -742.958702377			
ZPE = -742.680536			
Free Energy = -742.728608			
C	-2.579931	0.58089	-0.56839
C	-3.683182	-0.21743	-0.410364
C	-3.035103	1.941921	-0.505429
C	-4.383456	1.877252	-0.351587
H	-2.42811	2.832662	-0.588977
H	-5.165338	2.619374	-0.286056
O	-4.79303	0.566811	-0.28381
C	-1.445117	-2.138073	0.642982
H	-0.929344	-2.613688	1.480411
H	-1.166291	-2.629778	-0.294105
C	-2.98398	-2.281698	0.853319
H	-3.259061	-1.808301	1.801245
H	-3.181034	-3.353827	0.945193
C	-3.831489	-1.697804	-0.292062
H	-4.886023	-1.927508	-0.11436
H	-3.546044	-2.178641	-1.237096
C	-1.005744	-0.723668	0.564696
C	-1.152421	0.084254	-0.673682
H	-0.45373	0.922937	-0.682379
H	-0.990506	-0.541261	-1.554827
O	-0.587777	-0.200918	1.657779
H	-0.285384	0.727793	1.556775
I	2.535737	-1.309876	-0.326099
C	2.23271	0.797964	0.009694
C	2.117694	1.264913	1.320623
C	2.08733	1.648289	-1.08606
C	1.824221	2.617182	1.530898
H	2.242393	0.593431	2.163043
C	1.797155	2.997808	-0.856559
H	2.179358	1.272402	-2.099049
C	1.656819	3.481428	0.445741
H	1.728509	2.987316	2.54762
H	1.675532	3.66558	-1.704631
H	1.424423	4.52843	0.61577

18			
C	-2.423205	-1.326909	-0.680742
C	-3.084525	-1.518216	0.519283
C	-3.332895	-0.587406	-1.528797
C	-4.453122	-0.399517	-0.79495
H	-3.16219	-0.252983	-2.54151
H	-5.402554	0.079315	-0.98069
O	-4.309576	-0.967238	0.46791
C	-0.541504	-2.660231	0.256839
H	0.549788	-2.685969	0.220157
H	-0.894335	-3.681435	0.050712
C	-1.030849	-2.220435	1.651072
H	-0.645727	-1.216588	1.859553
H	-0.62846	-2.896132	2.410561
C	-2.569686	-2.184951	1.73935
H	-2.909406	-1.652489	2.633416
H	-2.97677	-3.204777	1.794212
C	-1.072969	-1.771339	-0.843809
C	-0.266982	-1.361008	-1.897789
H	-0.700239	-0.835354	-2.744454
H	0.696432	-1.838068	-2.054644
C	2.443511	-0.363306	-0.203973
C	3.454088	-0.353866	-1.164258
C	2.553687	-1.056766	1.001613
C	4.620562	-1.07493	-0.89943
H	3.337639	0.193639	-2.092945
C	3.730596	-1.768867	1.246948
H	1.750795	-1.047133	1.729556
C	4.757455	-1.778915	0.300239
H	5.419485	-1.083291	-1.634847
H	3.837751	-2.31421	2.179736
H	5.66767	-2.337403	0.497469
O	-2.011331	2.238627	-1.238898
H	-2.328623	1.690425	-0.499202
O	-2.160011	1.371264	1.556246
H	-1.714117	2.241942	1.468933
O	-0.862524	3.726218	0.797322
H	-0.801272	4.564084	1.275773
I	0.65991	0.750091	-0.586185
O	1.527233	2.488291	0.431462

H	-1.669874	3.018358	-0.761141
H	-3.052471	1.584827	1.86206
H	0.064767	3.430571	0.631727
C	1.796694	2.25455	1.814447
H	2.105508	3.219941	2.236525
H	0.909615	1.903242	2.359353
H	2.615908	1.540041	1.958899
TS1We			
46 Energy= -1011.49452656			
C	-3.201974	-0.849371	-0.378718
C	-4.370058	-0.721835	0.351548
C	-3.548015	-1.58391	-1.575678
C	-4.870541	-1.844206	-1.477448
H	-2.895826	-1.864634	-2.389843
H	-5.587731	-2.348865	-2.106707
O	-5.382294	-1.32533	-0.290768
C	-2.010395	0.196416	1.544501
H	-1.178347	0.885207	1.702162
H	-1.827135	-0.673584	2.19318
C	-3.345356	0.860441	1.908691
H	-3.468893	1.759805	1.297021
H	-3.318719	1.174366	2.955287
C	-4.542259	-0.080945	1.67647
H	-5.495234	0.45575	1.721771
H	-4.57686	-0.863446	2.448476
C	-1.963646	-0.344577	0.133964
C	-0.707225	-0.973048	-0.346197
H	-0.789018	-1.411048	-1.339202
H	-0.400078	-1.72825	0.382295
C	2.414498	-1.214367	0.027132
C	3.124318	-1.792485	-1.02172
C	2.544494	-1.627875	1.350411
C	4.002371	-2.83797	-0.721861
H	3.000814	-1.446274	-2.041754
C	3.426837	-2.67701	1.626449
H	1.980418	-1.153401	2.145346
C	4.152511	-3.277896	0.5956
H	4.563925	-3.306502	-1.524624

H	3.544717	-3.016068	2.651363
H	4.836707	-4.091051	0.819104
O	-1.981842	1.450573	-0.812184
H	-1.420285	2.174199	-0.369713
O	-0.602851	3.29066	0.409673
H	0.244998	3.494565	-0.080836
O	1.662467	3.798668	-0.929662
H	2.074836	4.554971	-0.489057
I	1.08861	0.417042	-0.406067
O	3.129404	1.726199	-0.389168
H	-1.635816	1.330524	-1.711239
H	-1.123452	4.105729	0.364559
H	2.298492	3.021737	-0.762236
C	3.539715	1.967295	0.938046
H	4.460756	2.575079	0.956083
H	2.780764	2.515596	1.526328
H	3.763945	1.034254	1.483532
18b			
55 Energy= -1129.41778270			
C	2.472404	-1.914952	0.534628
C	3.791002	-1.641333	0.196942
C	2.405372	-1.855956	1.979472
C	3.656618	-1.563436	2.395229
H	1.53699	-2.010078	2.603428
H	4.115041	-1.412887	3.360784
O	4.517296	-1.432927	1.303947
C	1.991747	-2.151364	-1.903735
H	1.168433	-1.865658	-2.56534
H	2.236621	-3.197059	-2.147762
C	3.22299	-1.260455	-2.148523
H	2.929371	-0.21315	-2.029638
H	3.571719	-1.397967	-3.175462
C	4.36938	-1.566865	-1.163924
H	5.153486	-0.804351	-1.203042
H	4.84162	-2.530656	-1.404786
C	1.50372	-2.159353	-0.474408
C	0.156881	-2.3977	-0.182319
H	-0.119618	-2.681765	0.829693

H	-0.478818	-2.773149	-0.979504
C	-2.702611	-1.125634	0.063511
C	-3.289574	-1.265542	1.319756
C	-3.289436	-1.616024	-1.101378
C	-4.519008	-1.923831	1.403604
H	-2.807564	-0.873771	2.208716
C	-4.51886	-2.272765	-0.995349
H	-2.807325	-1.493617	-2.064911
C	-5.130801	-2.424454	0.251034
H	-4.994433	-2.043461	2.372684
H	-4.994564	-2.660639	-1.891205
H	-6.086218	-2.935297	0.325426
O	1.758923	1.286118	-0.42111
C	2.44383	1.569353	0.796816
H	2.695073	2.634028	0.877883
H	1.847749	1.283706	1.674102
H	3.379129	1.001261	0.825964
H	1.309813	2.118375	-0.71974
O	0.604424	3.561083	-1.184532
C	1.606971	4.572385	-1.304532
H	1.181279	5.513082	-1.678799
H	2.105564	4.771228	-0.34677
H	2.356778	4.220736	-2.019119
H	-0.006719	3.813288	-0.443201
O	-1.028165	4.001196	0.876206
C	-0.27088	3.962404	2.087593
H	0.24971	4.919167	2.190316
H	-0.923466	3.826744	2.960405
H	0.476911	3.159836	2.082304
H	-1.448742	3.111124	0.73615
I	-0.855526	-0.046984	-0.088781
O	-2.147673	1.730399	0.08949
C	-2.637566	2.182766	-1.171207
H	-1.833074	2.536261	-1.829721
H	-3.210761	1.399623	-1.686277
H	-3.312609	3.024809	-0.968442
TS1Me			
55 Energy= -1129.40511404			

C	3.084029	-1.30654	0.272031
C	4.313215	-1.223309	-0.363003
C	3.300489	-2.083304	1.474758
C	4.61309	-2.40393	1.473941
H	2.572368	-2.353424	2.225469
H	5.255143	-2.955557	2.143489
O	5.240088	-1.884313	0.3426
C	2.095497	-0.176425	-1.717195
H	1.318165	0.564547	-1.918532
H	1.904131	-1.023246	-2.394205
C	3.487726	0.416676	-1.979189
H	3.609953	1.305924	-1.353996
H	3.554493	0.732672	-3.023272
C	4.616544	-0.582113	-1.662831
H	5.595247	-0.09312	-1.630052
H	4.673116	-1.363727	-2.43459
C	1.921021	-0.7352	-0.325213
C	0.599698	-1.266358	0.080351
H	0.578873	-1.656369	1.096202
H	0.315413	-2.046826	-0.631723
C	-2.501931	-1.488366	0.006377
C	-2.987043	-1.894693	1.246945
C	-2.877313	-2.093415	-1.190389
C	-3.891744	-2.959498	1.280849
H	-2.675404	-1.400843	2.160575
C	-3.784267	-3.156238	-1.132043
H	-2.48121	-1.753185	-2.140229
C	-4.289519	-3.585736	0.096899
H	-4.281686	-3.295051	2.237228
H	-4.092987	-3.64219	-2.05285
H	-4.995293	-4.410355	0.132685
O	1.992759	1.116112	0.616509
C	1.802842	1.133245	2.033895
H	1.953352	2.150846	2.411317
H	0.803443	0.784775	2.319615
H	2.553868	0.478188	2.482262
H	1.413908	1.82103	0.177476
O	0.695037	3.041331	-0.526732
C	1.423376	4.221658	-0.168112
H	1.042965	5.096439	-0.709436
H	1.369451	4.423179	0.909523

H	2.470699	4.067392	-0.441894
H	-0.261663	3.185144	-0.266787
O	-1.759223	3.535634	0.320222
C	-1.584025	3.592802	1.734688
H	-1.04962	4.515221	1.984457
H	-2.550276	3.605236	2.256609
H	-0.998859	2.74284	2.115535
H	-2.386528	2.749292	0.124092
I	-1.14994	0.175487	-0.068964
O	-3.202052	1.465187	-0.131592
C	-3.728713	1.528756	-1.437452
H	-3.017922	1.958113	-2.167544
H	-4.022843	0.53382	-1.81407
H	-4.63419	2.15875	-1.462144
15Me			
55 Energy= -1129.46429962			
C	-3.190307	-1.13288	-0.28292
C	-4.307723	-1.161187	0.503086
C	-3.469635	-1.978318	-1.418701
C	-4.72832	-2.453279	-1.232469
H	-2.820505	-2.198088	-2.254547
H	-5.372609	-3.106817	-1.801531
O	-5.257129	-1.962081	-0.057952
C	-2.062119	0.029227	1.602369
H	-1.286659	0.763308	1.837075
H	-1.84322	-0.875951	2.180399
C	-3.44258	0.577747	1.990717
H	-3.66624	1.451028	1.367798
H	-3.424594	0.915761	3.03089
C	-4.543933	-0.483068	1.80427
H	-5.541884	-0.03141	1.830373
H	-4.506446	-1.220317	2.61883
C	-1.974568	-0.323745	0.100974
C	-0.735851	-1.154624	-0.232358
H	-0.694779	-1.50803	-1.260277
H	-0.567261	-1.968233	0.471839
C	2.460123	-1.566747	-0.005599
C	2.821696	-2.178286	-1.202485

C	2.954039	-1.959207	1.23562
C	3.721707	-3.246428	-1.141764
H	2.422647	-1.839767	-2.151865
C	3.856438	-3.026336	1.268631
H	2.654374	-1.45454	2.146787
C	4.237127	-3.666233	0.086747
H	4.017821	-3.743554	-2.060673
H	4.257629	-3.352087	2.223626
H	4.939451	-4.493685	0.122937
O	-1.928852	0.958833	-0.578395
C	-1.99118	0.974664	-2.008726
H	-1.933222	2.026007	-2.298082
H	-1.152594	0.433888	-2.462811
H	-2.935939	0.556171	-2.369905
H	-1.064411	2.325819	0.154463
O	-0.645935	3.107408	0.574561
C	-1.395919	4.263925	0.186399
H	-0.927023	5.13458	0.652641
H	-1.394088	4.407459	-0.901896
H	-2.435103	4.19735	0.532456
H	0.986451	3.350774	0.055622
O	1.844394	3.539614	-0.396952
C	1.578753	3.514294	-1.801065
H	1.00187	4.394512	-2.115217
H	2.538368	3.526226	-2.326294
H	1.032408	2.610554	-2.101422
H	3.056958	2.351081	-0.015061
I	1.104016	0.10123	-0.081226
O	3.630699	1.5645	0.154818
C	3.994931	1.574686	1.533433
H	3.115037	1.612009	2.191803
H	4.543469	0.652237	1.745475
H	4.645738	2.427107	1.775924

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symmetry c1
C -1.431445000 -1.091839000 0.759585000
C -2.000015000 0.188220000 0.727220000
C -1.194121000 -1.401363000 2.156534000
C -1.613311000 -0.323120000 2.846533000
H -0.742010000 -2.293835000 2.565223000
H -1.633557000 -0.056500000 3.891938000

O	-2.124562000	0.638126000	1.976725000
C	-2.653287000	-0.825587000	-2.241526000
H	-3.252945000	-1.718665000	-2.439306000
H	-2.479875000	-0.335295000	-3.204450000
C	-3.432483000	0.122286000	-1.310163000
H	-4.122743000	-0.447497000	-0.679962000
H	-4.044581000	0.792592000	-1.920800000
C	-2.548928000	0.995478000	-0.385770000
H	-3.123945000	1.818923000	0.044087000
H	-1.722119000	1.437910000	-0.956034000
C	-1.163781000	-1.845736000	-0.396498000
C	-1.241630000	-1.270059000	-1.765371000
H	-0.575696000	-0.398718000	-1.772436000
H	-0.838509000	-2.003981000	-2.466141000
O	-0.785232000	-3.092441000	-0.344963000
H	-0.739374000	-3.450699000	0.561854000
I	2.341215000	-0.755147000	-0.050138000
C	1.317277000	1.143666000	-0.112502000
C	0.827149000	1.692245000	1.072598000
C	1.168496000	1.794232000	-1.338153000
C	0.166717000	2.924002000	1.021243000
H	0.941499000	1.172674000	2.017467000
C	0.509282000	3.027701000	-1.369498000
H	1.556455000	1.357145000	-2.251631000
C	0.009002000	3.593199000	-0.194116000
H	-0.226565000	3.352796000	1.938332000
H	0.389178000	3.541182000	-2.319194000
H	-0.504804000	4.549303000	-0.226431000

TS2W-regio

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symmetry c1

C	-1.648371000	-0.144822000	0.790304000
C	-2.003312000	1.060469000	0.265970000
C	-1.176124000	0.095424000	2.126248000
C	-1.277107000	1.438734000	2.310077000
H	-0.805281000	-0.632987000	2.832601000
H	-1.040696000	2.099326000	3.130312000
O	-1.784220000	2.045132000	1.179512000
C	-2.843588000	-1.295369000	-1.257007000
H	-3.476554000	-2.138548000	-0.979117000
H	-2.451095000	-1.538610000	-2.255794000
C	-3.560778000	0.062566000	-1.299077000
H	-4.342366000	0.052909000	-0.533257000
H	-4.045471000	0.151933000	-2.275450000
C	-2.657200000	1.289156000	-1.045568000
H	-3.258495000	2.202539000	-1.023917000
H	-1.916300000	1.402061000	-1.848033000
C	-1.694865000	-1.412394000	0.020329000
C	-0.783127000	-1.580355000	-1.065031000
H	-0.460085000	-0.714177000	-1.628850000
H	-0.618055000	-2.569886000	-1.480958000
O	-1.858676000	-2.564115000	0.773430000
H	-2.544057000	-2.400501000	1.440347000
I	1.851660000	-1.427331000	0.057958000
C	1.693541000	0.708548000	-0.259516000
C	1.704426000	1.556636000	0.844811000
C	1.526115000	1.182094000	-1.560587000

C	1.515337000	2.926075000	0.632502000
H	1.833648000	1.169311000	1.847992000
C	1.334803000	2.554317000	-1.750657000
H	1.534540000	0.505724000	-2.408523000
C	1.323719000	3.423897000	-0.657610000
H	1.509105000	3.597719000	1.486031000
H	1.196516000	2.936090000	-2.758074000
H	1.168990000	4.487644000	-0.811751000