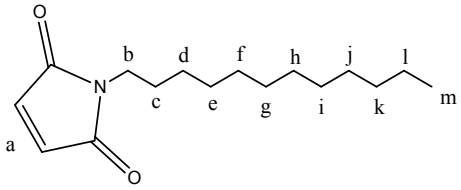
Supporting information

Maleimide Synthesis

Synthesis of N-dodecylmaleimide (M_2)

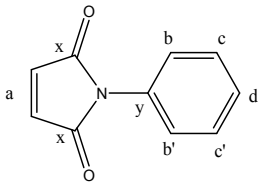
The solid residue is solubilized in the minimum of THF and then precipitated in cold ether. After filtration, the solid is solubilized in the minimum of THF and then precipitated in water. After filtration, the solid is dried in oven. A white powder is obtained.



^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7 (s, 2H, H_a) 3.4-3.34 (t, 2H $^3J_{bc}$=7.1Hz, H_b), 1.52-1.41 (m, 2H, H_c), 1.22 (m, 18H, H_d, H_e, H_f, H_g, H_h, H_i, H_j, H_k and H_l), 0.87-0.82 (t, 3H, H_m)

Synthesis of N-phenylmaleimide (M_3)

The solid residue is solubilized in the minimum of THF and then precipitated in cold ether. After filtration, the solid is solubilized in the minimum of THF and then precipitated in water. After filtration, the solid is dried in oven. A clear yellow powder is obtained.

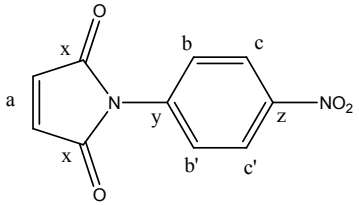


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7.47 (m, 5H, H_b, $H_{b'}$, H_c, $H_{c'}$, H_d), 7.13 (s, 2H, H_a)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 169.92 (C_x), 134.64 (C_a), 131.56 (C_y), 128.86 (C_c and $C_{c'}$), 127.72 (C_b and $C_{b'}$), 126.8 (C_d)

Synthesis of N-p-nitrophenylmaleimide (M_4)

The solid residue is solubilized in the minimum of THF and then precipitated in cold ether. After filtration, the solid is solubilized in the minimum of THF and then precipitated in water. After filtration, the solid is dried in oven. A clear yellow powder is obtained.

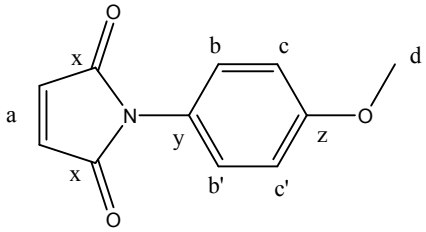


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 8.4-8.34 (m, 2H, H_c and $H_{c'}$), 7.72-7.66 (m, 2H, H_b and $H_{b'}$), 7.27 (s, 2H, H_a)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 169.23 (C_x), 145.71 (C_z), 137.48 (C_y), 135.04 (C_a), 126.62 (C_b and $C_{b'}$), 124.23 (C_c and $C_{c'}$)

Synthesis of N-4-methoxyphenylmaleimide (M_5)

The solid residue is solubilized in the minimum of THF and then precipitated in cold ether. After filtration, the solid is solubilized in the minimum of THF and then precipitated in water. After filtration, the solid is dried in oven. A yellow powder is obtained.

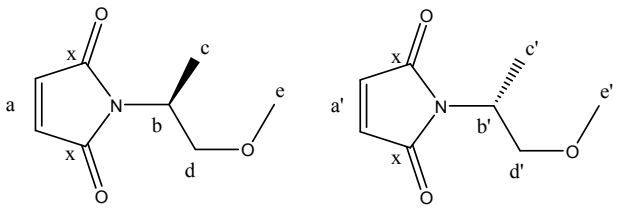


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7.26-7.20 (m, 2H, H_b and $H_{b'}$), 7.14 (s, 2H, H_a), 7.05-6.99 (m, 2H, H_c and $H_{c'}$), 3.78 (s, 3H, H_d)

^{13}C NMR (100MHz, $(CD_3)_2SO$) δ: 170.18 (C_x), 158.63 (C_z), 134.55 (C_a), 128.31 (C_b and $C_{b'}$), 124.07 (C_y), 114.13 (C_c and $C_{c'}$), 55.34 (C_d)

Synthesis of N-methoxy-2-propylmaleimide (M_6)

The solid residue is solubilized in the minimum of THF and then precipitated in cold ether. Then ether is evaporated. The solid is extracted with ethyl acetate and water, respectively 3/1. Then the aqueous layer is extracted twice with ethyl acetate. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. An orange liquid is obtained.

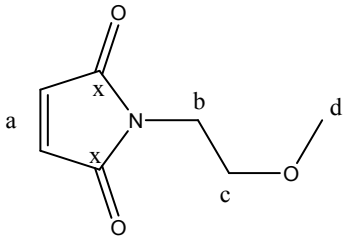


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 6.97 (s, 2H, H_a and $H_{a'}$), 4.28-4.19 (m, 1H, H_b and $H_{b'}$), 3.69-3.65 (t, 1H, ^{3}J=9.7Hz, $H_{d'}$), 3.41-3.37 (dd, 1H, J=9.7Hz and J=5.4Hz, H_d), 3.19 (s, 3H, H_e and $H_{e'}$), 1.24 and 1.23 (s, 3H, H_c and $H_{c'}$)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 171.06 (C_x), 134.42 (C_a and $C_{a'}$), 72.03 (C_d and $C_{d'}$), 57.93 (C_e and $C_{e'}$), 45.24 (C_b and $C_{b'}$), 14.69 (C_c and $C_{c'}$)

Synthesis of N-2-methoxyethylmaleimide (M_7)

The solid residue is solubilized in the minimum of THF and then precipitated in cold ether. Then ether is evaporated. The solid is extracted with ethyl acetate and water, respectively 3/1. Then the aqueous layer is extracted twice with ethyl acetate. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. An orange solid is obtained.



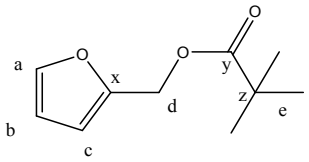
^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 6.66 (s, 2H, H_a), 3.65-3.62 (t, 2H, $^3J_{bc}$=5.6Hz, H_b), 3.5-3.47 (t, 2H, $^3J_{cb}$=5.6Hz, H_c), 3.25 (s, 3H, H_d)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 170.90 (C_x), 134.56 (C_a), 68.54 (C_c), 57.74 (C_d), 36.61 (C_b)

Furan derivatives synthesis

Synthesis of furfuryl pivalate (F_2)

The liquid is extracted with ether and water, respectively 3/1, 3 times. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. A colorless oil is obtained.

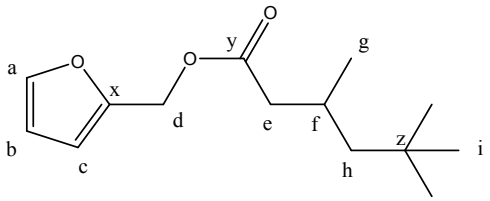


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7.68-7.67 (dd, 1H, H_a), 6.5-6.44 (m, 2H, H_b and H_c), 5.04 (s, 2H, H_d), 1.12 (s, 9H, H_e)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 176.94 (C_y), 149.49 (C_x), 143.61 (C_a), 110.61 (C_b), 110.35 (C_c), 57.66 (C_d), 38.20 (C_z), 26.75 (C_e)

Synthesis of 3,5,5-trimethylhexyl furan-2-carboxylate (F_3)

The liquid is extracted with ether and water, respectively 3/1, 3 times. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. A colorless oil is obtained.

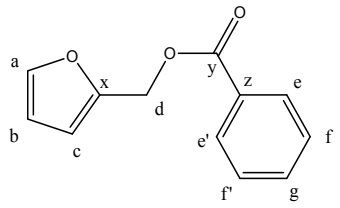


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7.66 (m, 1H, H_a), 6.50-6.44 (m, 2H, H_b and H_c), 5.04 (s, 2H, H_d), 2.29-2.12 (ddd, 2H, H_e), 1.98-1.88 (m, 1H, H_f), 1.22-1.02 (ddd, 2H, H_h), 0.91 and 0.90 (2s, 3H, H_g), 0.85 (s, 9H, H_i)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 171.70 (C_y), 149.42 (C_x), 143.58 (C_a), 110.65 (C_b), 110.63 (C_c), 57.16 (C_d), 49.69 (1C, C_h), 43.02 (C_e), 30.62 (C_z), 29.68 (3C, C_i), 26.6 (C_f), 22.28 (C_g)

Synthesis of furfuryl benzoate (F_4)

The liquid is extracted with ether and water, respectively 3/1, 3 times. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. An orange oil is obtained.

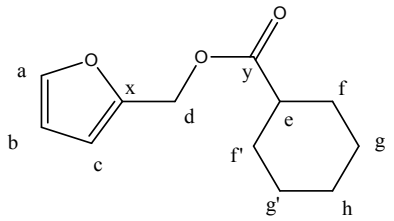


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 8.08-8.04 (dd, 2H, H_e and $H_{e'}$), 7.58-7.52 (m, 2H, H_f and $H_{f'}$), 7.46-7.41 (m, 2H, H_a and H_g), 6.52-6.38 (m, 2H, H_b and H_c), 5.33 (s, 2H, H_d)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 165.30 (C_y), 149.23 (C_x), 143.85 (C_a), 133.48 (C_g), 129.31 (C_z), 129.17 (C_e and $C_{e'}$), 128.79 (C_f and $C_{f'}$), 22.28 (C_g), 111.04 (C_b), 110.76 (C_c), 58.22 (C_d)

Synthesis of furfuryl cyclohexanecarboxylate (F_5)

The liquid is extracted with ether and water, respectively 3/1, 3 times. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. The liquid is columned with Dichloromethane and hexane (30/70). A colorless oil is obtained.

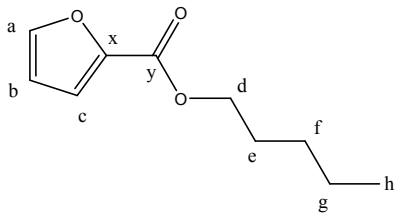


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7.65 (dd, 1H, H_a), 6.49-6.43 (m, 2H, H_b and H_c), 5.03 (s, 2H, H_d), 2.34-2.27 (m, 1H, H_e), 1.85-1.11 (m, 10H, H_f, $H_{f'}$, H_g, $H_{g'}$, H_h)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 174.52 (C_y), 149.48 (C_x), 143.62 (C_a), 110.65 (C_b), 110.50 (C_c), 57.34 (C_d), 42.01 (C_e), 28.51 (C_f and $C_{f'}$), 25.23 (C_h) 24.67 (C_g and $C_{g'}$)

Synthesis of pentyl furan-2-carboxylate (F_8)

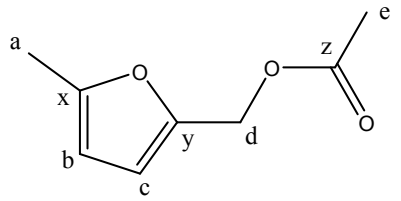
The liquid is extracted with ether and water, respectively 3/1, 3 times. The organic layer is dried over anhydrous Na_2SO_4, filtrated and evaporated under low pressure. A colorless oil is obtained.



^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 7.57 (d, 1H, H_a), 7.14 (d, 1H, H_b), 6.49 (d, 1H, H_c), 4.29 (t, 2H, H_d), 1.78-1.68 (m, 2H, H_e), 1.48-1.40 (m, 4H, H_f and H_g), 0.93-0.87 (t, 3H, H_h)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ: 158.84 (C_y), 149.51 (C_x), 143.73 (C_a), 110.66 (C_b), 110.52 (C_c), 43.11 (C_d), 28.63 (C_e), 28.58 (C_f), 23.43 (C_g), 22.3 (2C, H_h)

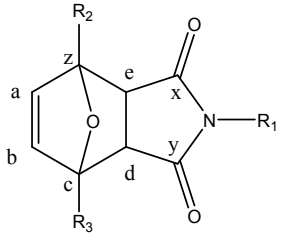
Synthesis of (5-methylfuran-2-yl)methyl acetate (F_9)

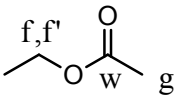


^{1}H NMR (400MHz, $(CD_3)_2SO$) δ: 6.37 (dd, 1H, H_c), 6.05 (dd, 1H, H_b), 4.95 (s, 2H, H_d), 2.25 (s, 3H, H_a), 2.02 (s, 3H, H_e)

^{13}C NMR (100MHZ, $(CD_3)_2SO$) δ:174.5 (C_z), 153.33 (C_x), 138.28 (C_y), 110.53 (C_c), 109.4 (C_b), 57.45 (C_d), 36.16 (C_e), 28.73 (C_a)

Synthesis of Diels-Alder adducts

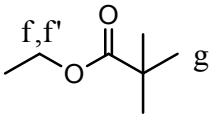


Synthesis of adduct **AF_1M_1** R_2:  R_3: H R_1: —CH_3 h

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.47-6.46 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.35-6.33 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.29-5.27 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.72-4.48 (dd, R_{F1}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=86.4Hz, 2H, H_f and $H_{f'}$), 3.72-3.68 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.46-3.44 (d, J_{ed}=7.6Hz, 1H, H_e), 2.67 (s, R_{M1}, 3H, H_h), 2.05 (s, R_{F1}, 3H, H_g)

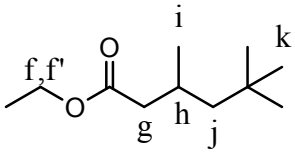
^{13}C NMR (100MHZ, $(CD_3)_2SO$, endo) δ :174.80 (C_y), 174.75 (C_x), 170.06 (C_w), 135.67 (C_b), 134.43 (C_a), 88.95 (C_z), 78.69 (C_c), 61.59 (C_f and $C_{f'}$), 47.53 (C_d), 46.49 (C_e), 24.18 (C_h), 20.52 (C_g)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.6-6.57 (m, 1H, H_b), 6.48-6.43 (m, 1H, H_a), 5.12 (d, $^3J_{cd}$=1.7Hz, 1H, H_c), 4.75-4.31 (dd, R_{F1}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=96.6Hz, 2H, H_f and $H_{f'}$), 3.10-2.98 (m, 2H, H_d and H_e), 2.82 (s, R_{M1}, 3H, H_h), 2.01 (s, R_{F1}, 3H, H_g)

Synthesis of adduct **AF_2M_1** R_2:  R_3: H R_1: —CH_3 h

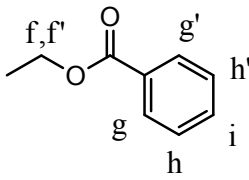
^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.5-6.43 (m, 1H, H_b), 6.34-6.31 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.31-5.28 (dd, $^3J_{cd}$=5.5Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.75-4.47 (dd, R_{F2}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=57.8Hz, 2H, H_f and $H_{f'}$), 3.72-3.67 (dd, $^3J_{dc}$=5.5Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.46-3.43 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.67 (s, R_{M1}, 3H, H_h), 1.15 (s, R_{F2}, 9H, H_g)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.5-6.43 (m, 2H, H_a and H_b), 5.14-5.13 (d, $^3J_{cd}$=1.6Hz, 1H, H_c), 4.80-4.3 (dd, R_{F2}, $J_{ff'}$=12.8Hz and $J_{f'f}$=103.9Hz, 2H, H_f and $H_{f'}$), 3.10-2.99 (m, 2H, H_d and H_e), 2.82 (s, R_{M1}, 3H, H_h), 1.12 (s, R_{F2}, 9H, H_g)

Synthesis of adduct **AF_3M_1** R_2:  R_3: H R_1: —CH_3 l

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.49-6.41 (m, 1H, H_b), 6.33-6.30 (d, $^3J_{ab}$=5.7Hz, 1H, H_a), 5.30-5.27 (dd, $^3J_{cd}$=5.5Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.78-4.46 (2*dd, R_{F3}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=57.3Hz, 2H, H_f and $H_{f'}$), 3.72-3.67 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.46-3.43 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.68 (s, R_{M1}, 3H, H_l), 2.36-1.87 (m, R_{F3}, 2H, H_g),1.27-0.85 (m, R_{F3}, 15H, H_h, H_i, H_j and H_k)

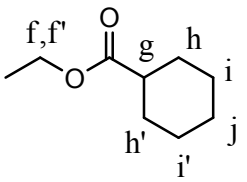
^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.49-6.41 (m, 2H, H_a and H_b), 5.12 (d, $^3J_{cd}$=1.6Hz, 1H, H_c), 4.80-4.3 (2*dd, R_{F3}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=102.8Hz, 2H, H_f and $H_{f'}$), 3.14-3.08 (m, 2H, H_d and H_e), 2.82 (s, R_{M1}, 3H, H_l) 2.36-1.87 (m, R_{F3}, 2H, H_g),1.27-0.85 (m, R_{F3}, 15H, H_h, H_i, H_j and H_k)

Synthesis of adduct **AF_4M_1** R_2: 

R_3: H R_1: —CH_3 j

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 8.0-7.98 (m, 2H, R_{F4}, H_g and $H_{g'}$), 7.70-7.65 (m, 1H, R_{F4}, H_i), 7.57-7.51 (m, 2H, R_{F4}, H_h and $H_{h'}$), 6.52-6.50 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.47-6.46 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.34-5.32 (dd, $^3J_{cd}$=5.8Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.97-4.78 (dd, R_{F4}, $^2J_{ff'}$=12.7Hz and $^2J_{f'f}$=64.6Hz, 2H, H_f and $H_{f'}$), 3.76-3.73 (dd, $^3J_{dc}$=5.8Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.60-3.58 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.69 (s, R_{M1}, 3H, H_j)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 7.94-7.91 (m, 2H, R_{F4}, H_g and $H_{g'}$), 7.70-7.65 (m, 1H, R_{1D}, H_i), 7.57-7.51 (m, 2H, R_{F4}, H_h and $H_{h'}$), 6.64-6.63 (dd, $^3J_{ba}$=5.6Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.60-6.59 (d, $^3J_{ab}$=5.6Hz, 1H, H_a), 5.17 (d, $^3J_{cd}$=1.6Hz, 1H, H_c), 5.0-4.63 (dd, R_{F4}, $^2J_{ff'}$=12.7Hz and $^2J_{f'f}$=136.6Hz, 2H, H_f and $H_{f'}$), 3.14-3.08 (m, 2H, H_d and H_e), 2.83 (s, R_{M1}, 3H, H_j)

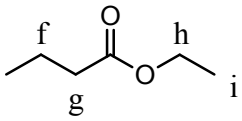
Synthesis of adduct **AF_5M_1** R_2: 

R_3: H R_1: —CH_3 k

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.47-6.45 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.8Hz, 1H, H_b), 6.33-6.31 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.29-5.27 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.8Hz, 1H, H_c), 4.74-4.48 (dd, R_{F5}, $^2J_{ff'}$=12.9Hz and $^2J_{f'f}$=92.7Hz, 2H, H_f and $H_{f'}$), 3.71-3.68 (dd, $^3J_{dc}$=5.6Hz and

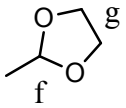
$^3J_{de}$=7.6Hz, 1H, H_d), 3.45-3.43 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.67 (s, R_{M1}, 3H, H_k), 2.39-2.27 (m, R_{F5}, 1H, H_g), 1.82-1.12 (m, R_{F5}, 10H, H_h, $H_{h'}$, H_i, $H_{i'}$ and H_j)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.6-6.58 (m, 2H, H_b), 6.43-6.42 (d, 1H, $^3J_{ab}$=5.6Hz, H_a), 5.12 (d, $^3J_{cd}$=1.8Hz, 1H, H_c), 4.75-4.31 (dd, R_{F5}, $^2J_{ff'}$=12.,6Hz and $^2J_{f'f}$=166.4Hz, 2H, H_f and $H_{f'}$), 3.08-2.99 (m, 2H, H_d and H_e), 2.82 (s, R_{M1}, 3H, H_k), 2.39-2.27 (m, R_{F5}, 1H, H_g), 1.82-1.12 (m, R_{F5}, 10H, H_h, $H_{h'}$, H_i, $H_{i'}$ and H_j)

Synthesis of adduct $\mathbf{AF_6M_1}$ R_2:  R_3: H R_1: —CH_3 j

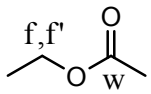
^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.41-6.38 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.34-6.32 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.22-5.19 (dd, $^3J_{cd}$=5.5Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.11-4.02 (q, R_{F6}, $^3J_{hi}$=7.1Hz, 2H, H_h), 3.68-3.63 (dd, $^3J_{dc}$=5.5Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3,31-3,28 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.66 (s, R_{M1}, 3H, Hj'), 2.62-2.01 (m, R_{F6}, 4H, H_f and H_g), 1.21-1.15 (t, R_{F6}, J_{hi}=7.1Hz, 3H, H_i)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.57-6.54 (m, 2H, H_b), 6.46-6.44 (d, 1H, $^3J_{ab}$=5.5Hz, H_a), 5.05 (d, $^3J_{cd}$=1.7Hz, 1H, H_c), 4.07-3.98 (q, R_{F6}, $^3J_{hi}$=7.1Hz, 2H, H_h), 3.06-2.86 (m, 2H, H_d and H_e), 2.81 (s, R_{M1}, 3H, $H_{j'}$), 2.62-2.01 (m, R_{F6}, 4H, H_f and H_g), 1.21-1.15 (t, R_{F6}, $^3J_{hi}$=7.1Hz, 3H, H_i)

Synthesis of adduct $\mathbf{AF_7M_1}$ R_2:  R_3: H R_1: —CH_3 h

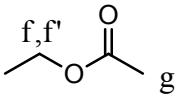
^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.46-6.43 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.39-6.37 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.44 (s, R_{F7}, 1H, H_f), 5.31-5.28 (dd, $^3J_{cd}$=5.5Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.06-3.86 (m, R_{F7}, 4H, H_g), 3.71-3.66 (dd, $^3J_{dc}$=5.5Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.49-3.46 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.66 (s, R_{M1}, 3H, H_h)

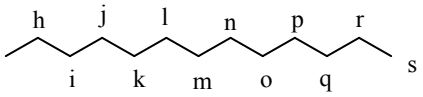
^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.59-6.56 (m, 2H, H_b), 6.46-6.44 (d, 1H, $^3J_{ab}$=5.5Hz, H_a), 5.18 (s, R_{F7}, 1H, H_f), 5.15-5.14 (d, $^3J_{cd}$=1.7Hz, 1H, H_c), 4.06-3.86 (m, R_{F7}, 4H, H_g), 3.08-2.90 (m, 2H, H_d and H_e), 2.81 (s, R_{M1}, 3H, H_h)

Synthesis of adduct $\mathbf{AF_8M_1}$ R_2:  R_3: —CH_3 h R_1: —CH_3 i

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.34-6.31 (m, 2H, H_a and H_b), 4.67-4.21 (dd, R_{F8}, 2H, H_f and $H_{f'}$), 3.58-3.33 (dd, 2H, H_d and H_e), 2.67 (s, R_{M1}, 3H, H_i), 2.06 (s, 3H, H_g), 1.67 (s, R_{F8}, 3H, H_h)

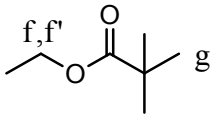
^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.45-6.41 (m, 2H, H_a and H_b), 4.72-4.28 (dd, R_{F8}, 2H, H_f and $H_{f'}$), 3.58-3.33 (dd, 2H, H_d and H_e), 2.87 (s, R_{M1}, 3H, H_i), 2.02 (s, 3H, H_g), 1.57 (s, R_{F8}, 3H, H_h)

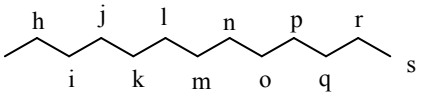
Synthesis of adduct $\mathbf{AF_1M_2}$ R_2: 

R_3 : H R_1: 

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.47-6.44 (m, 1H, H_b), 6.35-6.33 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.29-5.27 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.5Hz, 1H, H_c), 4.72-4.47 (dd, R_{F1}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=86.4Hz, 2H, H_f and $H_{f'}$), 3.70-3.66 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.45-3.43 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.19-3.15 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, H_h), 2.05 (s, R_{F1}, 3H, H_g), 1.35-1.29 (quin, R_{M2}, $^3J_{ih}$=7.2Hz, 2H, H_i), 1.27-1.14 (m, R_{M2}, 18H, H_j, H_k, H_l, H_m, H_n, H_o, H_p, H_q and H_r), 0.87-0.83 (t, R_{M2}, 3H, H_s)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.59-6.57 (m, 1H, H_b), 6.47-6.44 (m, 1H, H_a), 5.12-5.11 (d, $^3J_{cd}$=1.8Hz, 1H, H_c), 4.74-4.28 (dd, R_{F1}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=172Hz, 2H, H_f and $H_{f'}$), 3.35-3.32 (t, R_{M2}, $^3J_{hi}$=7.1Hz, 2H, H_h), 3.08-2.97 (m, 2H, H_d and H_e), 2.01 (s, R_{F1}, 3H, H_g), 1.46-1.39 (quin, R_{M2}, $^3J_{ih}$=7.1Hz, 2H, H_i), 1.27-1.14 (m, R_{M2}, 18H, H_j, H_k, H_l, H_m, H_n, H_o, H_p, H_q and H_r), 0.87-0.83 (t, R_{M2}, 3H, H_s)

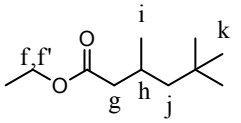
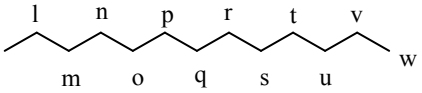
Synthesis of adduct $\mathbf{AF_2M_2}$ R_2: 

R_3: H R_1: 

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.5-6.45 (m, 1H, H_b), 6.33-6.31 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.3-5.28 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.8Hz, 1H, H_c), 4.74-4.47 (dd, R_{F1}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=93.4Hz, 2H, H_f and $H_{f'}$), 3.69-3.66 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.44-3.42 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.19-3.15 (t, R_{M2}, $^3J_{hi}$=7.1Hz, 2H, H_h), 1.35-1.14 (m, R_{M2}, 20H, H_i, H_j, H_k, H_l, H_m, H_n, H_o, H_p, H_q and H_r), 1.14 (s, R_{F2}, 9H, H_g), 0.87-0.83 (t, R_{M2}, 3H, H_s)

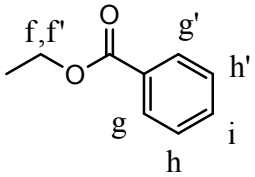
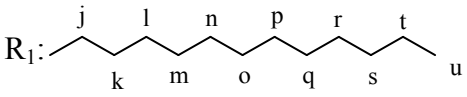
^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.6-6.58 (m, 1H, H_b), 6.5-6.45 (m, 1H, H_a), 5.13 (d, $^3J_{cd}$=1.8Hz, 1H, H_c), 4.75-4.24 (dd, R_{F2}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=189.9Hz, 2H, H_f and $H_{f'}$), 3.35-3.32 (t, R_{M2}, $^3J_{hi}$=7.1Hz, 2H, H_h), 3.08-2.98 (m, 2H, H_d and H_e), 1.47-1.4 (quin, R_{M2},

$^3J_{ih}$=7.1Hz, 2H, H_i), 1.27-1,14 (m, R_{M2}, 18H, H_j, H_k, H_l, H_m, H_n, H_o, H_p, H_q and H_r), 1.12 (s, R_{F2}, 9H, H_g), 0.87-0.83 (t, R_{M2}, 3H, H_s)

Synthesis of adduct **AF_3M_2** R_2:  R3: H R_1: 

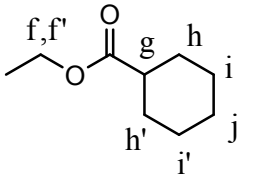
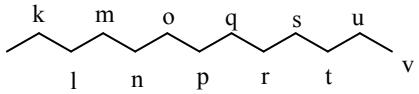
<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ</u> : 6.5-6.43 (m, 1H, H_b), 6.31-6.30 (d, $^3J_{ab}$=5.6Hz, 1H, H_a), 5.29-5.27 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.8Hz, 1H, H_c), 4.76-4.46 (ddd, R_{F3}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=91.7Hz, 2H, H_f and $H_{f'}$), 3.69-3.65 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.43-3.41 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.18-3.15 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, H_l), 1.35-1.11 (m, R_{M2}, 20H, H_m, H_n, H_o, H_p, H_q, H_r, H_s, H_t, H_u and H_v), 2.34-1.87 (m, R_{F3}, 2H, H_g),1.27-0.80 (m, R_{F3}, 15H, H_h, H_i, H_j and H_k), 0.88-0.85 (t, R_{M2}, 3H, H_w)

<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ</u> : 6.59-6.57 (m, 1H, H_b), 6.5-6.43 (m, 1H, H_a), 5.12-5.11 (t, $^3J_{cd}$=1.5Hz, 1H, H_c), 4.77-4.27 (ddd, R_{F3}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=174Hz, 2H, H_f and $H_{f'}$), 3.35-3.32 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, H_l), 3.07-2.96 (m, 2H, H_d and H_e), 2.34-1.87 (m, R_{F3}, 2H, H_g), 1.46-1.39 (quin, R_{M2}, $^3J_{ih}$=7.1Hz, 2H, H_m), 1.27-1.14 (m, R_{M2}, 18H, H_n, H_o, H_p, H_q, H_r, H_s, H_t, H_u and H_v), 1.27-0.80 (m, R_{F3}, 15H, H_h, H_i, H_j and H_k), 0.88-0.85 (t, R_{M2}, 3H, H_w)

Synthesis of adduct **AF_4M_2** R_2:  R_3: H R_1: 

<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ</u> : 7.99-7.97 (m, 2H, R_{F4}, H_g and $H_{g'}$), 7.68-7.63 (m, 1H, R_{F4}, H_i), 7.55-7.49 (m, 2H, R_{F4}, H_h and $H_{h'}$), 6.51-6.49 (m, 1H, H_b), 6.47-6.36 (d, $^3J_{ab}$=5.6Hz, 1H, H_a), 5.29-5.26 (dd, $^3J_{cd}$=5.6Hz and J_{cb}=1.7Hz, 1H, H_c), 4.96-4.77 (ddd, R_{F4}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=91.7Hz, 2H, H_f and $H_{f'}$), 3.74-3.71 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.58-3.56 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.18-3.15 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, $H_{j'}$), 1.33-1.11 (m, R_{M2}, 20H, H_k, H_l, H_m, H_n, H_o, H_p, H_q, H_r, H_s and H_t), 0.87-0.84 (t, R_{M2}, 3H, H_u),

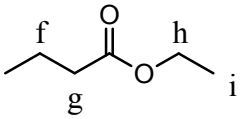
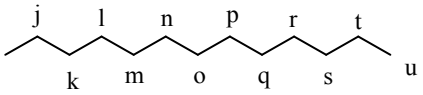
<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ</u> : 7.93-7.90 (m, 2H, R_{F4}, H_g and $H_{g'}$), 7.68-7.63 (m, 1H, R_{F4}, H_i), 7.55-7.49 (m, 2H, R_{F4}, H_h and $H_{h'}$), 6.63-6.61 (m, 1H, H_b), 6.59-6.58 (m, 1H, H_a), 5.16 (t, $^3J_{cd}$=1.7Hz, 1H, H_c), 5-4,63 (ddd, R_{F4}, $^2J_{ff'}$=12.8Hz and $^2J_{f'f}$=140Hz, 2H, $H_{f\ and}$ $H_{f'}$), 3.34-3.31 (t, R_{M2}, J_{hi}=7.2Hz, 2H, $H_{j'}$), 3.13-3.06 (m, 2H, Hd and He), 1.45-1.39 (quin, R_{M2}, $^3J_{ih}$=7.1Hz, 2H, H_k), 1.27-1.14 (m, R_{2B}, 18H, H_l, H_m, H_n, H_o, H_p, H_q, H_r, H_s and H_t), 0.87-0.84 (t, R_{M2}, 3H, H_u)

Synthesis of adduct $\mathbf{AF_5M_2}$ R_2: R_3: H R_1:

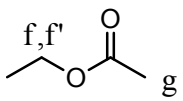
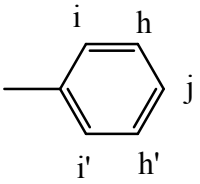
<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ</u> : 6.47-6.44 (m, 1H, H_b), 6.32-6.30 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.29-5.27 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.8Hz, 1H, H_c), 4.75-4.47 (dd, R_{F5}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=91.8Hz, 2H, H_f and $H_{f'}$), 3.69-3.66 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.43-3.41 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.18-3.15 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, H_k), 2.37-2.26 (m, R_{F5}, 1H, H_g), 1.87-1.1 (m, R_{F5}, 10H, H_h, $H_{h'}$, H_i, $H_{i'}$ and H_j), 1.37-1.1 (m, R_{M2}, 20H, H_l, H_m, H_n, H_o, H_p, H_q, H_r, H_s, H_t and H_u), 0.87-0.83 (t, R_{M2}, 3H, H_v)

<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ</u> : 6.59-6.57 (m, 1H, H_b), 6.47-6.44 (m, 1H, H_a), 5.12 (d, $^3J_{cd}$=1.5Hz, 1H, H_c), 4.75-4.26 (dd, R_{F5}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=182.8Hz, 2H, H_f and $H_{f'}$), 3.35-3.32 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, H_k), 3.07-2.97 (m, 2H, H_d and H_e), 2.20-2.14 (m, R_{F5}, 1H, H_g), 1.87-1.1 (m, R_{F5}, 10H, H_h, $H_{h'}$, H_i, $H_{i'}$ and H_j), 1.47-1.4 (quin, R_{M2}, $^3J_{ih}$=7.2Hz, 2H, H_l), 1.37-1.1 (m, R_{M2}, 18H, H_m, H_n, H_o, H_p, H_q, H_r, H_s, H_t and H_u), 0.87-0.83 (t, R_{M2}, 3H, H_v)

Synthesis of adduct $\mathbf{AF_6M_2}$ R_2:  R_3: H R_1: 

<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ</u> : 6.38-6.35 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.31-6.30 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.21-5.18 (dd, $^3J_{cd}$=5.5Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.10-4.01 (q, R_{F6}, $^3J_{hi}$=7.1Hz, 2H, H_h), 3.65-3.59 (dd, $^3J_{dc}$=5.5Hz and $^3J_{de}$=7.5Hz, 1H, H_d), 3.31-3.28 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.17-3.12 (t, R_{M2}, $^3J_{hi}$=7,2Hz, 2H, $H_{j'}$), 2.54-1.99 (m, R_{F6}, 4H, H_f and H_g), 1.35-1.1 (m, R_{M2} and R_{F6}, 23H, Hi, Hk, H_l, H_m, H_n, H_o, H_p, H_q, H_r, H_s and H_t), 0.86-0.81 (t, R_{M2}, 3H, H_u)

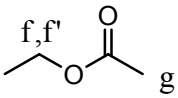
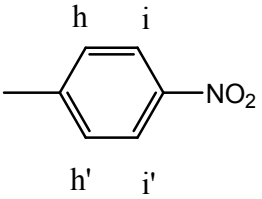
<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ</u> : 6.55-6.52 (m, 2H, H_b), 6.46-6.42 (d, 1H, $^3J_{ab}$=5.6H_z, H_a), 5.03 (d, $^3J_{cd}$=1.7Hz, 1H, H_c), 4.09-4 (q, R_{F6}, $^3J_{hi}$=7.1Hz, 2H, H_h), 3.39-3.34 (t, R_{M2}, $^3J_{hi}$=7.2Hz, 2H, $H_{j'}$), 3.03-2.84 (m, 2H, H_d and H_e), 2.54-1.99 (m, R_{F6}, 4H, H_f and H_g), 1.51-1.40 (quin, R_{M2}, $^3J_{ih}$=7.1Hz, 2H, H_k), 1.35-1.1 (m, R_{2B} and R_{1F}, 18H, Hi, H_l, H_m, H_n, H_o, H_p, H_q, H_r, H_s and H_t), 0.86-0.81 (t, R_{M2}, 3H, H_u)

Synthesis of adduct $\mathbf{AF_1M_3}$ R_2:  R_3: H R_1: 

<u>^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ</u> : 7.52-7.38 (m, 3H, R_{M3}, H_h, $H_{h'}$ and H_j), 7.14-7.11 (m, 2H, R_{M3}, H_i and $H_{i'}$), 6.68-6-66 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.5Hz, 1H, H_b), 6.57-6.55 (d,

$^3J_{ab}$=5.8Hz, 1H, H_a), 5.4-5.38 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.5Hz, 1H, H_c), 4.77-4.54 (dd, R_{F1}, $^2J_{ff'}$=12.6Hz and $^2J_{f'f}$=79Hz, 2H, H_f and $H_{f'}$), 3.87-3.84 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.62-3.60 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.07 (s, R_{F1}, 3H, H_g)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 7.52-7.38 (m, 3H, R_{M3}, H_h, $H_{h'}$ and H_j), 7.23-7.19 (m, 2H, R_{M3}, H_i and $H_{i'}$), 6.65-6.64 (m, 1H, H_b), 6.52-6.50 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.25-5.24 (d, $^3J_{cd}$=1.8Hz, 1H, H_c), 4.81-4.40 (dd, R_{F1}, $^2J_{ff'}$=13.1Hz and $^2J_{f'f}$=151.3Hz, 2H, H_f and $H_{f'}$), 3.26-3.14 (m, 2H, H_d and H_e), 2.01 (s, R_{F1}, 3H, H_g)

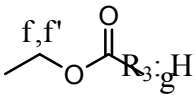
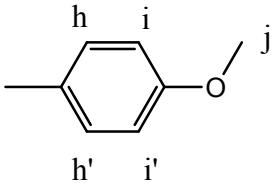
Synthesis of adduct **AF_1M_4** R_2:  R_3: H R_1 : 

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 8.34-8.31 (m, 2H, R_{M4}, H_i and $H_{i'}$), 7.50-7.46 (m, 2H, R_{M4}, H_h and $H_{h'}$), 6.70-6.69 (dd, $^3J_{ba}$=5.8Hz and $^3J_{bc}$=1.6Hz, 1H, H_b), 6.59-6.58 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.43-5.41 (dd, $^3J_{cd}$=5.6Hz and $^3J_{cb}$=1.6Hz, 1H, H_c), 4.78-4.56 (dd, R_{F1}, $^2J_{ff'}$=12.9Hz and $^2J_{f'f}$=75.2Hz, 2H, H_f and $H_{f'}$), 3.93-3.9 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.68-3.66 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.07 (s, R_{F1}, 3H, H_g)

^{13}C NMR (100MHz, $(CD_3)_2SO$, endo) δ : 174.84 (C_y), 173.47 (C_x), 170.05 (C_w), 146.69 (C_v), 137.25 (C_u), 137.12 (C_b), 134.77 (C_a), 127.74 (C_h and $C_{h'}$), 124.34 (C_i and $C_{i'}$), 89.26 (C_z), 79.20 (C_c), 61.29 (C_f and $C_{f'}$), 48.77 (C_d), 46.70 (C_e), 20.50 (C_g)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 8.39-8.34 (m, 2H, R_{M4}, H_i and $H_{i'}$), 7.61-7.57 (m, 2H, R_{M3}, H_h and $H_{h'}$), 6.67-6.65 (m, 1H, H_b), 6.53-6.51 (d, $^3J_{ab}$=5.6 Hz, 1H, H_a), 5.28-5.27 (d, $^3J_{cd}$=1.8 Hz, 1H, H_c), 4.84-4.43 (dd, R_{F1}, $^2J_{ff'}$=12.9 Hz and $^2J_{f'f}$=151.8 Hz, 2H, H_f and $H_{f'}$), 3.32-3.21 (m, 2H, H_d and H_e), 2.02 (s, R_{F1}, 3H, H_g)

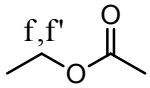
^{13}C NMR (100MHz, $(CD_3)_2SO$, exo) δ : 174.84 (C_y), 173.28 (C_x), 170.08 (C_w), 146.77 (C_v), 137.47 (C_b), 137.41 (C_u) 135.06 (C_a), 127.82 (C_h and $C_{h'}$), 124.8 (C_i and $C_{i'}$), 89.55 (C_z), 80.95 (C_c), 61.54 (C_f and $C_{f'}$), 47.7 (C_d), 46.49 (C_e), 20.55 (C_g)

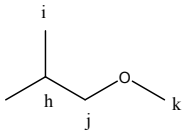
Synthesis of adduct **AF_1M_5** R_2:  R_1: 

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 7.14-6.97 (m, 4H, R_{M5}, H_h, $H_{h'}$, H_i and $H_{i'}$), 6.67-6.62 (m, 1H, H_b), 6.55-6.53 (d, $^3J_{ab}$=5,7Hz, 1H, H_a), 5.39-5.36 (dd, $^3J_{cd}$=5.4Hz and $^3J_{cb}$=1.3Hz, 1H, H_c), 4.77-4.52 (dd, R_{F1}, $^2J_{ff'}$=12.7Hz and $^2J_{f'f}$=51Hz, 2H, H_f and $H_{f'}$), 3.85-

3.79 (dd, $^3J_{dc}$=5.7Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.77 (s, R_{M5}, 3H, $H_{j'}$), 3.59-3.56 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 2.07 (s, R_{F1}, 3H, H_g)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 7.14-6.97 (m, 4H, R_{M5}, H_h, $H_{h'}$, H_i and $H_{i'}$), 6.67-6.62 (m, 1H, H_b), 6.51-6.49 (d, $^3J_{ab}$=5.8Hz, 1H, H_a), 5.23-5.22 (d, $^3J_{cd}$=1.7Hz, 1H, H_c), 4.81-4.8 (dd, R_{F1}, $^2J_{ff'}$=12.9Hz and $^2J_{f'f}$=95.5Hz, 2H, H_f and $H_{f'}$), 3.78 (s, R_{M5}, 3H, $H_{j'}$), 3.23-3.11 (m, 2H, H_d and H_e), 2.01 (s, R_{1A}, 3H, H_g)

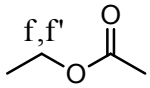
Synthesis of adduct $\mathbf{AF_1M_6}$ R_2: 

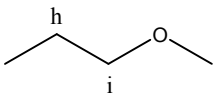
g R_3: H 

R_1:

1H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.44-6.42 (dd, 1H,H_b), 6.32-6.31 (d, 1H, $^3J_{ab}$= 5.8 Hz, H_a), 5.30-5.28 (dd, $^3J_{cd}$=5.6Hz, 1H, H_c), 4.72-4.48 (dd, R_{F1}, $^2J_{ff'}$=12.9Hz and $^2J_{f'f}$=85Hz, 2H, H_f and $H_{f'}$), 3.71-3.68 (dd, $^3J_{dc}$=5.6Hz and $^3J_{de}$=7.6Hz, 1H, H_d), 3.52 (m, R_{M6}, 1H, H_h), 3.46-3.44 (d, $^3J_{ed}$=7.6Hz, 1H, H_e), 3.4-3.27 (m, R_{M6}, 2H, H_j),3.18 (s, R_{M6}, 3H, H_k),2.08 (s, R_{F1}, 3H, H_g), 2.05 (d, R_{M6}, 3H, H_i)

1H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.59-6.57 (dd, 1H,H_b), 6.46-6.45 (d, 1H,$^3J_{ab}$= 5.8Hz, H_a), 5.13 (d, $^3J_{cd}$= 1.8Hz, 1H, H_c), 4.74-4.29 (dd,$^2J_{ff'}$=12Hz and $^2J_{f'f}$=168Hz, 2H, H_f and $H_{f'}$), 3.4-3.27 (m, R_{M6}, 3H, H_h and H_j),3.18 (s, R_{M6}, 3H, H_k), 3.11-3 (dd, 2H, H_d and H_e), 2.01 (s, R_{F1}, 3H, H_g), 1.90 (d, R_{M6}, 3H, H_i)

Synthesis of adduct $\mathbf{AF_1M_7}$ R_2: 

g R_3:H 

R_1:

^{1}H NMR (400MHz, $(CD_3)_2SO$, endo) δ : 6.44-6.42 (dd, 1H,H_b), 6.32-6.3 (d, 1H, $^3J_{ab}$= 5.8 Hz, H_a), 5.29-5.28 (dd, $^3J_{cd}$=5.3 Hz, 1H, H_c), 4.72-4.47 (dd, R_{F1}, $^2J_{ff'}$=12.9 Hz and $^2J_{f'f}$=87Hz, 2H, H_f and $H_{f'}$), 3.71-3.67 (dd, $^3J_{dc}$=5.6 Hz, 1H, H_d), 3.58-3.28 (m, R_{M7}, 3H, H_e, H_h and H_i),3.18 (s, R_{M6}, 3H, H_j),2.05 (s, R_{F1}, 3H, H_g)

^{1}H NMR (400MHz, $(CD_3)_2SO$, exo) δ : 6.59-6.57 (dd, 1H,$^3J_{ba}$= 5.7Hz, H_b), 6.46-6.45 (d, 1H, $^3J_{ab}$= 5.8 Hz, H_a), 5.13 (d, $^3J_{cd}$= 1.8Hz, 1H, H_c), 4.74-4.29 (dd,$^2J_{ff'}$=12.9Hz and $^2J_{f'f}$=168Hz, 2H, H_f and $H_{f'}$), 3.58-3.28 (m, R_{M7}, 2H, H_h and H_i),3.19 (s, R_{M7}, 3H, H_j), 3.12-3 (dd, 2H, H_d and H_e), 2.01 (s, R_{F1}, 3H, H_g)