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Supplementary Information

Debromination of *endo*-(+)-3-Bromocamphor with Primary Amines

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IR spectra of $\mathbf{2}_{\mathbf{A\text{-}F}}$

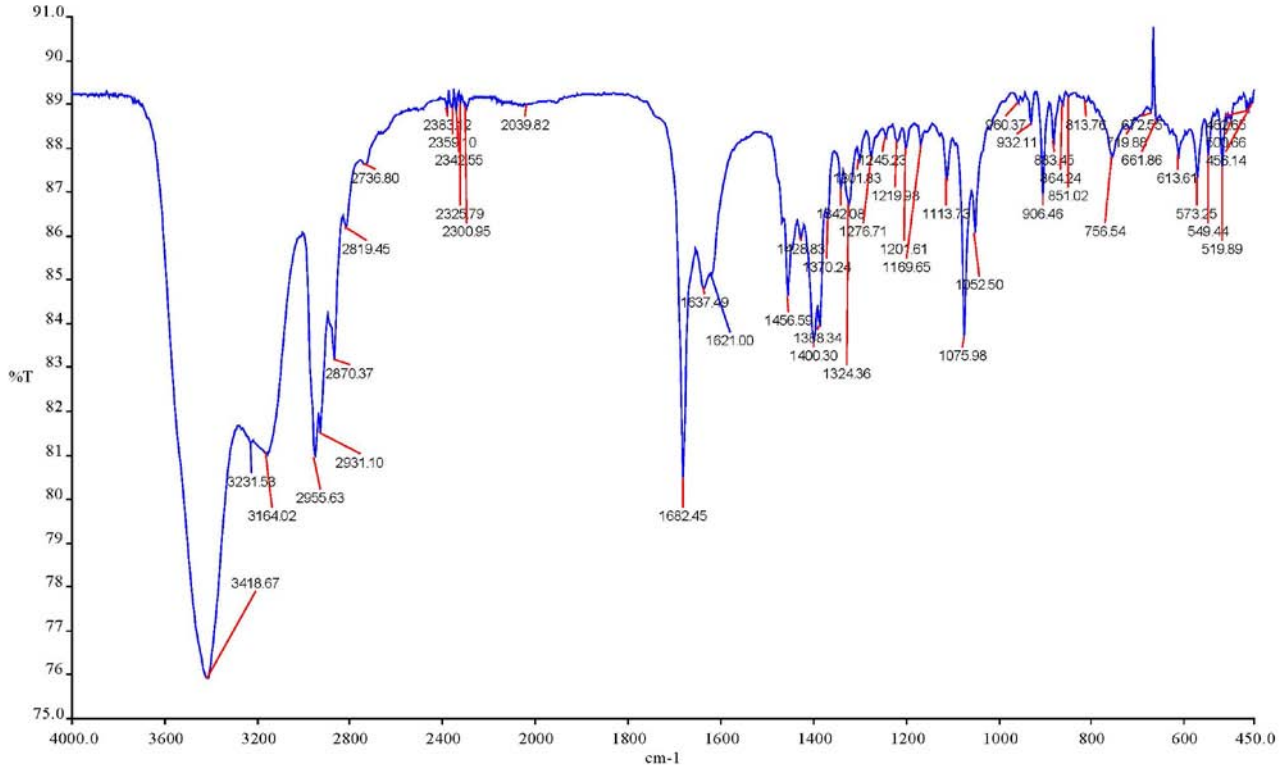

Figure S1. IR spectrum of $\mathbf{2}_{\mathbf{A}}$ (KBr disc).

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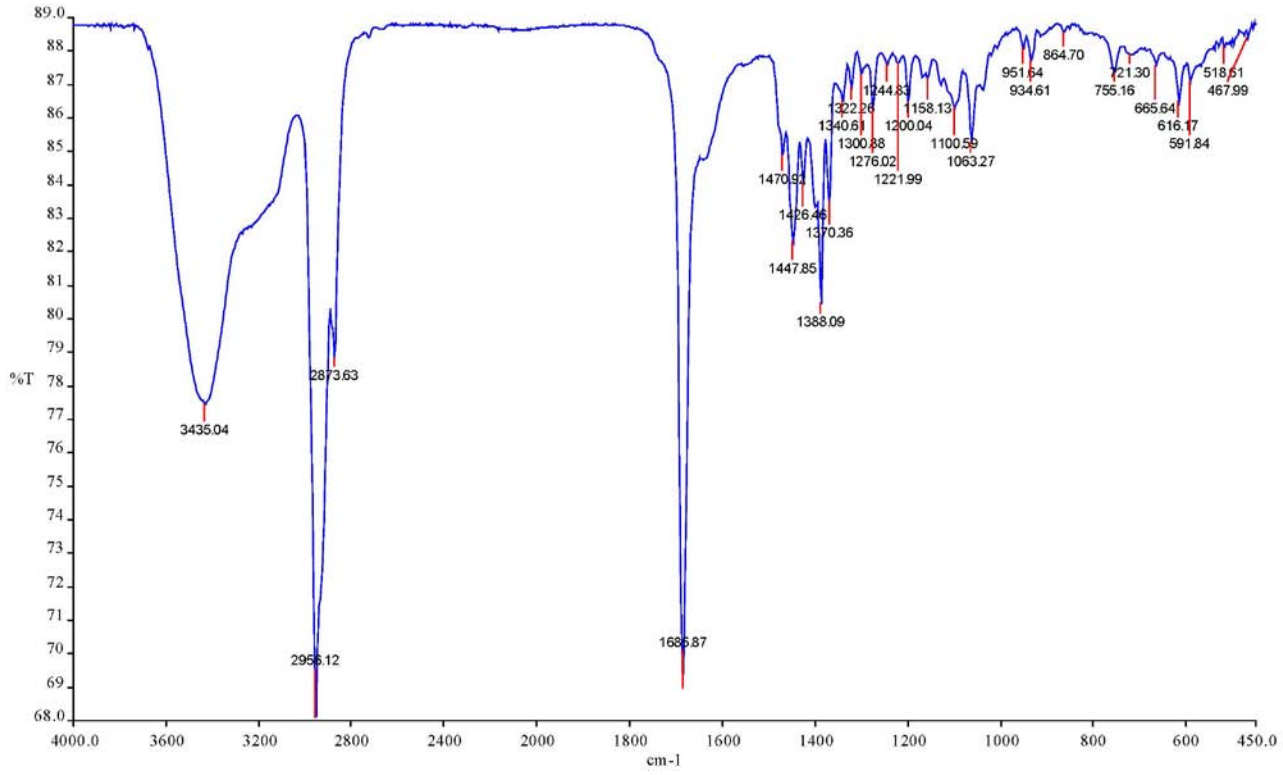

Figure S2. IR spectrum of $\mathbf{2_B}$ (KBr disc).

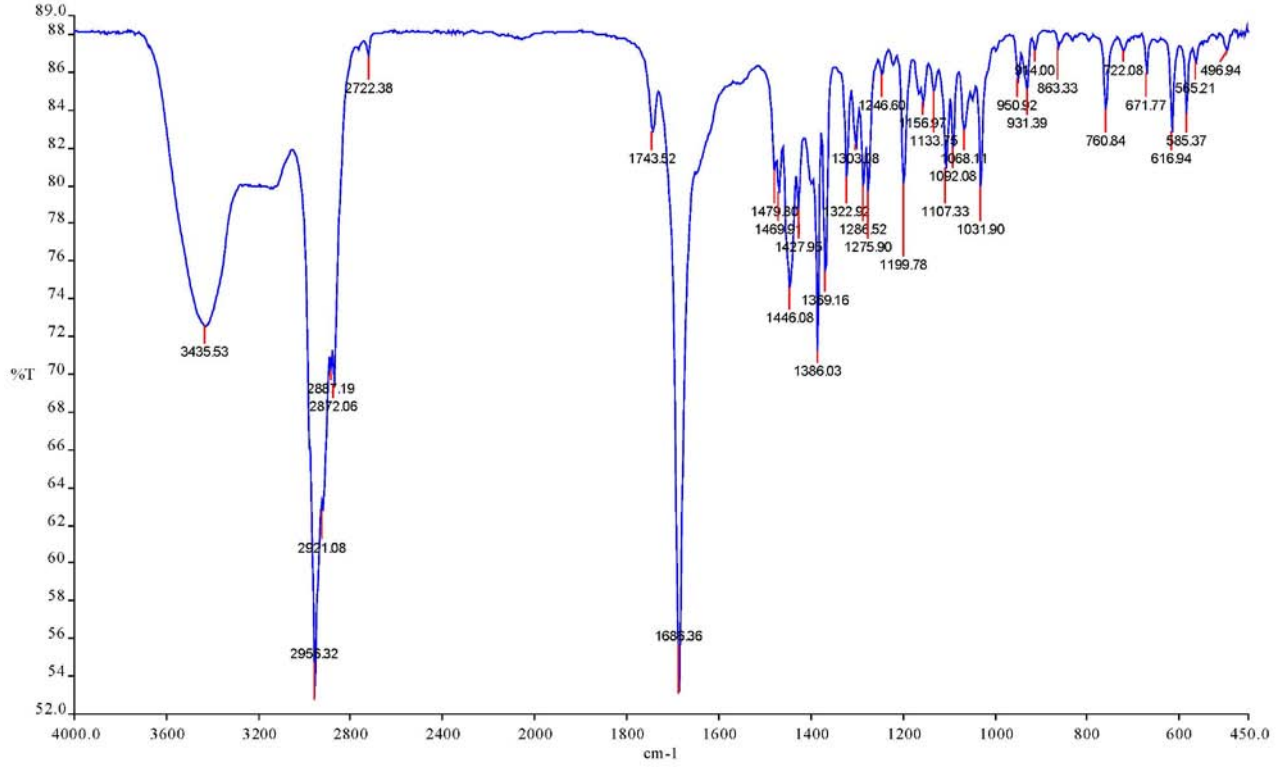

Figure S3. IR spectrum of $\mathbf{2_C}$ (KBr disc).

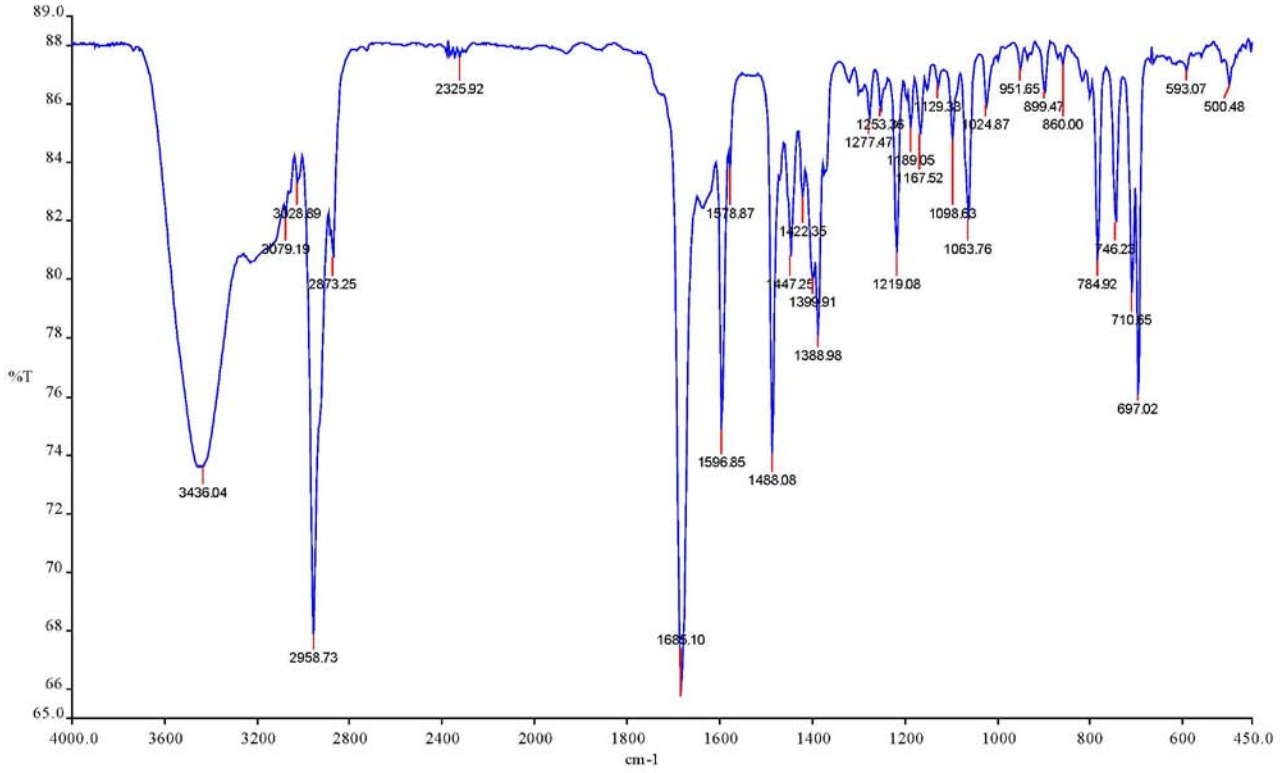

Figure S4. IR spectrum of $\mathbf{2}_{\mathbf{D}}$ (neat).

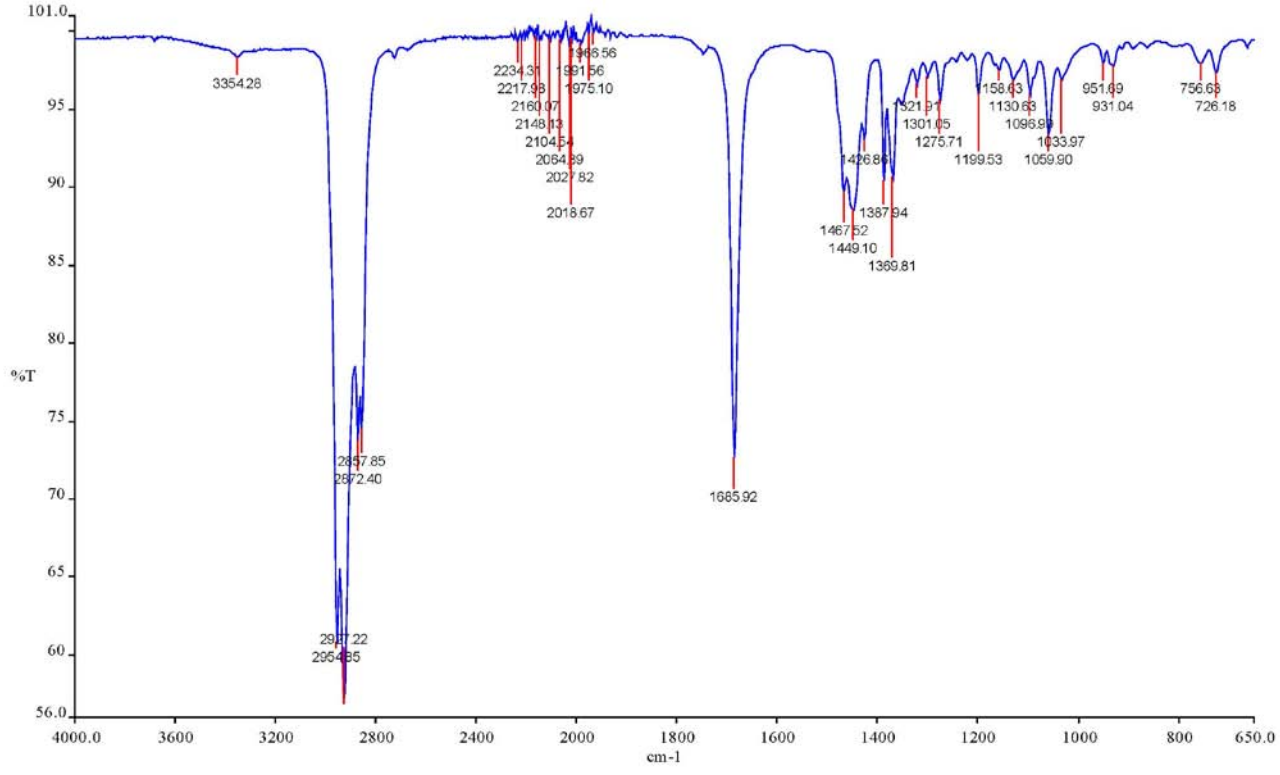

Figure S5. IR spectrum of $\mathbf{2}_{\mathbf{E}}$ (neat).

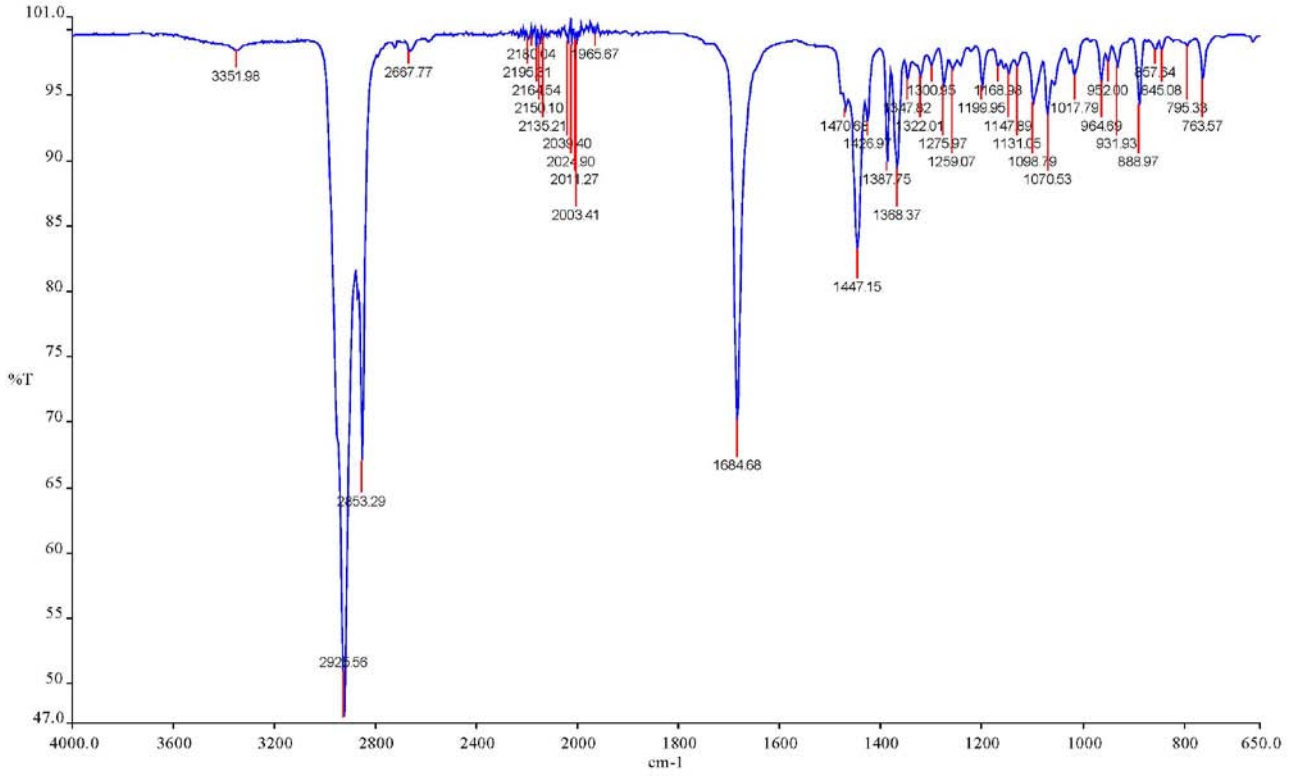

Figure S6. IR spectrum of $\mathbf{2}_{F}$ (neat).

NMR spectra of $\mathbf{2}_{A\text{-}F}$

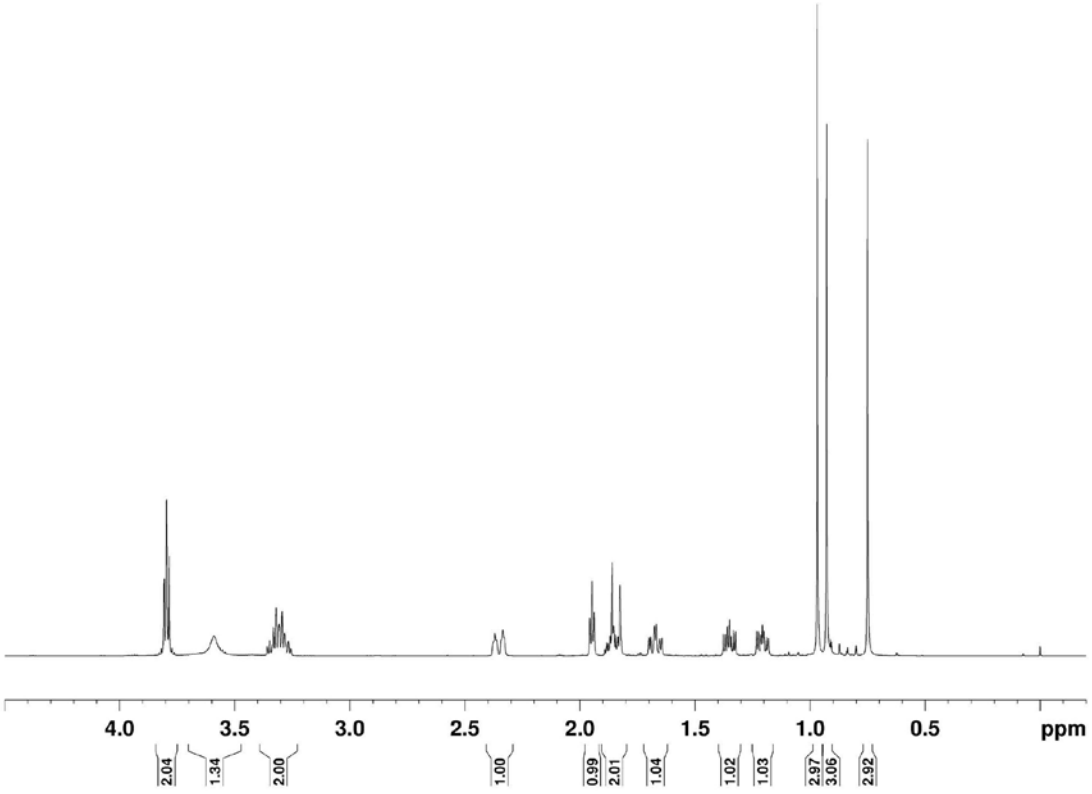

Figure S7. ^{1}H NMR spectrum of $\mathbf{2}_{A}$ ($CDCl_3$, 500 MHz).

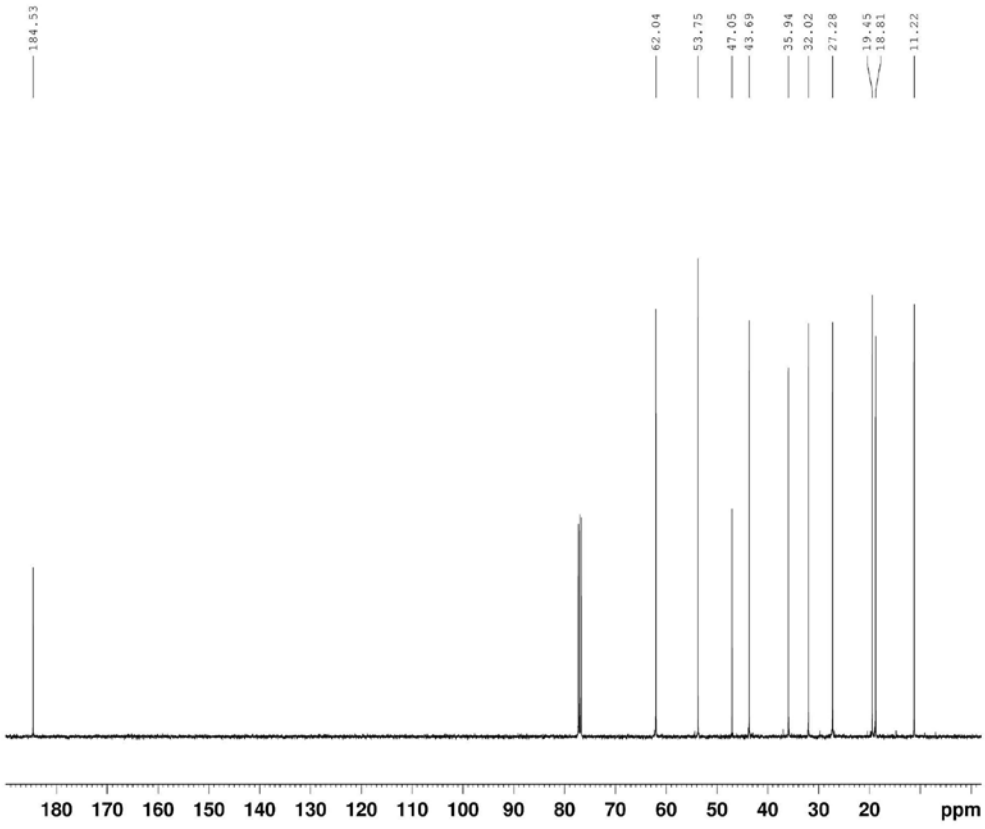

Figure S8. ^{13}C NMR spectrum of $\mathbf{2_A}$ ($CDCl_3$, 125 MHz).

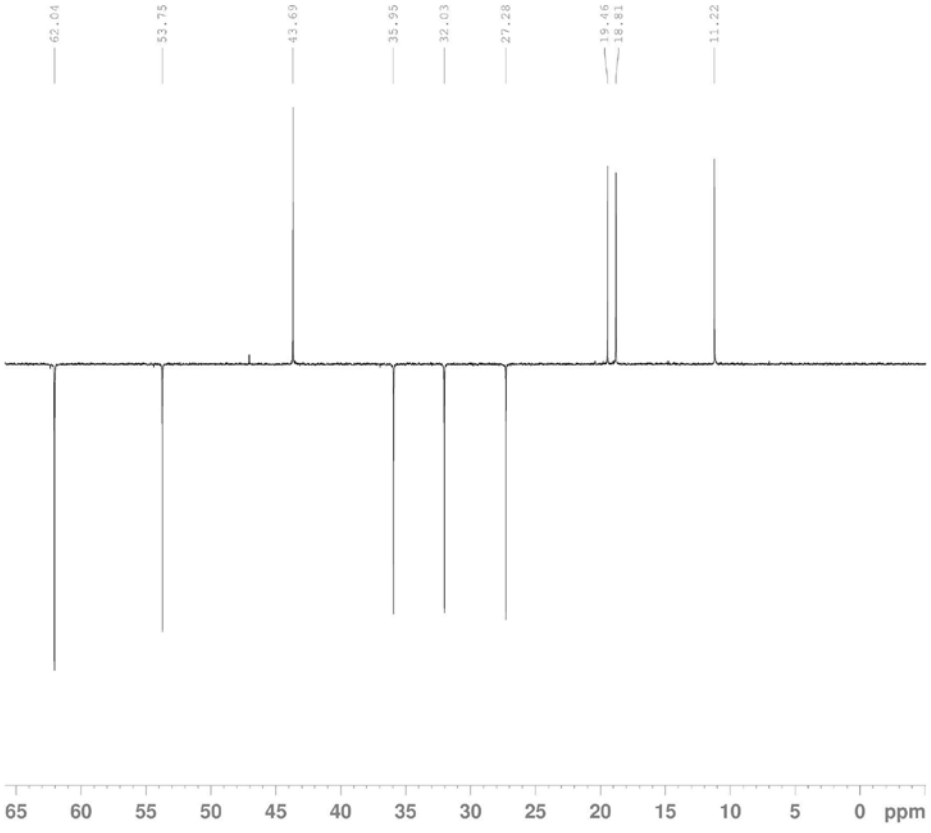

Figure S9. DEPT spectrum of $\mathbf{2_A}$ ($CDCl_3$, 125 MHz).

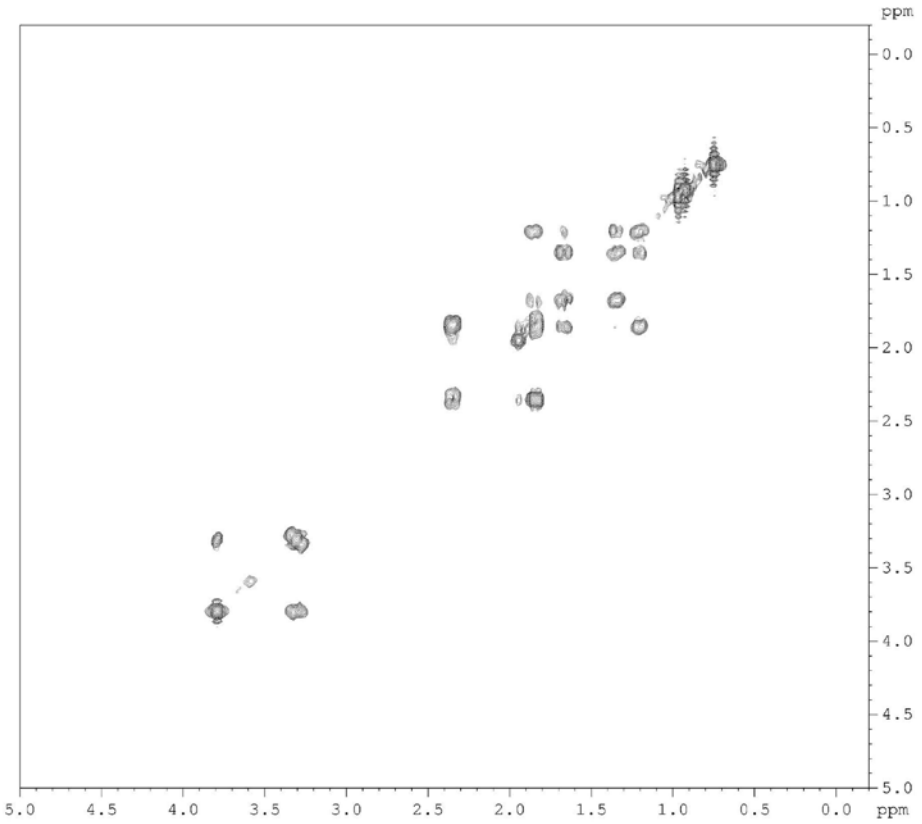

Figure S10. COSY spectrum of $\mathbf{2_A}$ ($CDCl_3$, 500 MHz).

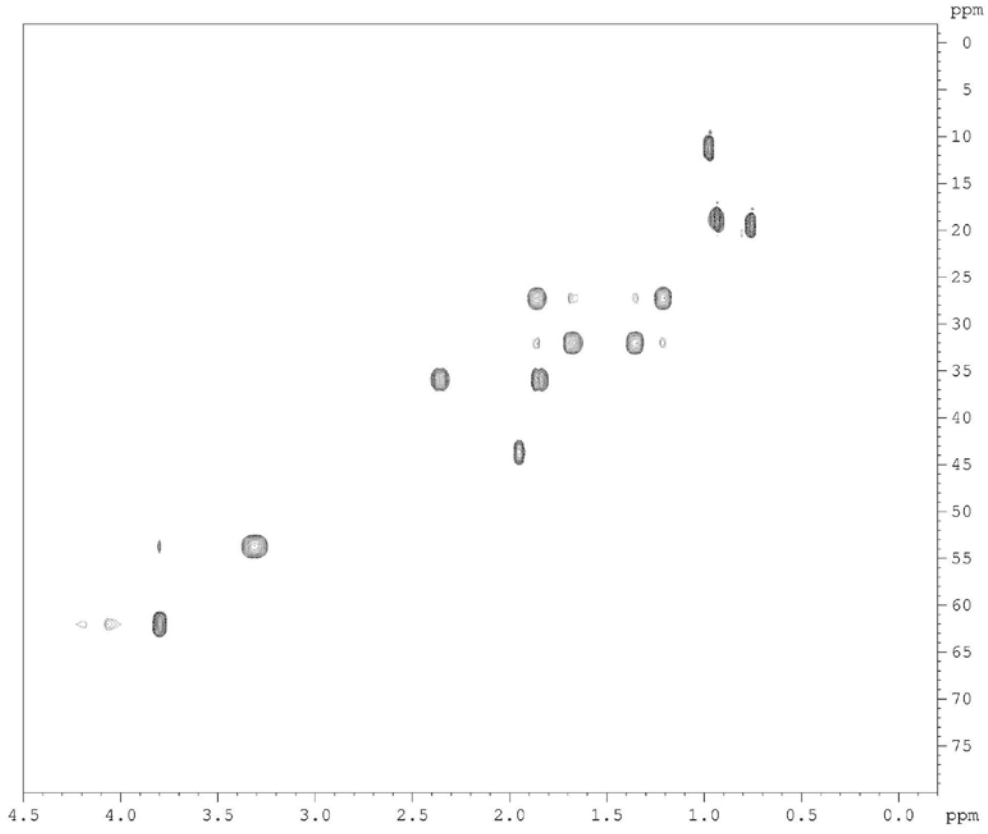

Figure S11. HSQC spectrum of $\mathbf{2_A}$ ($CDCl_3$, 500 MHz).

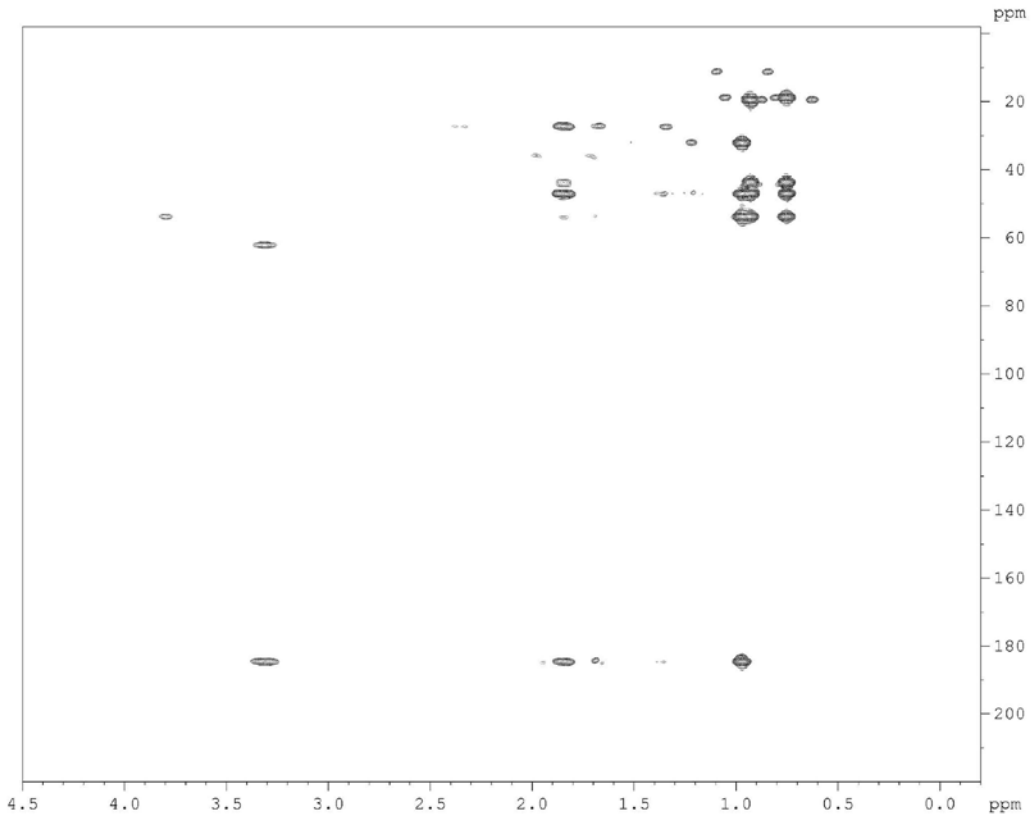

Figure S12. HMBC spectrum of $\mathbf{2}_{\mathbf{A}}$ ($CDCl_3$, 500 MHz).

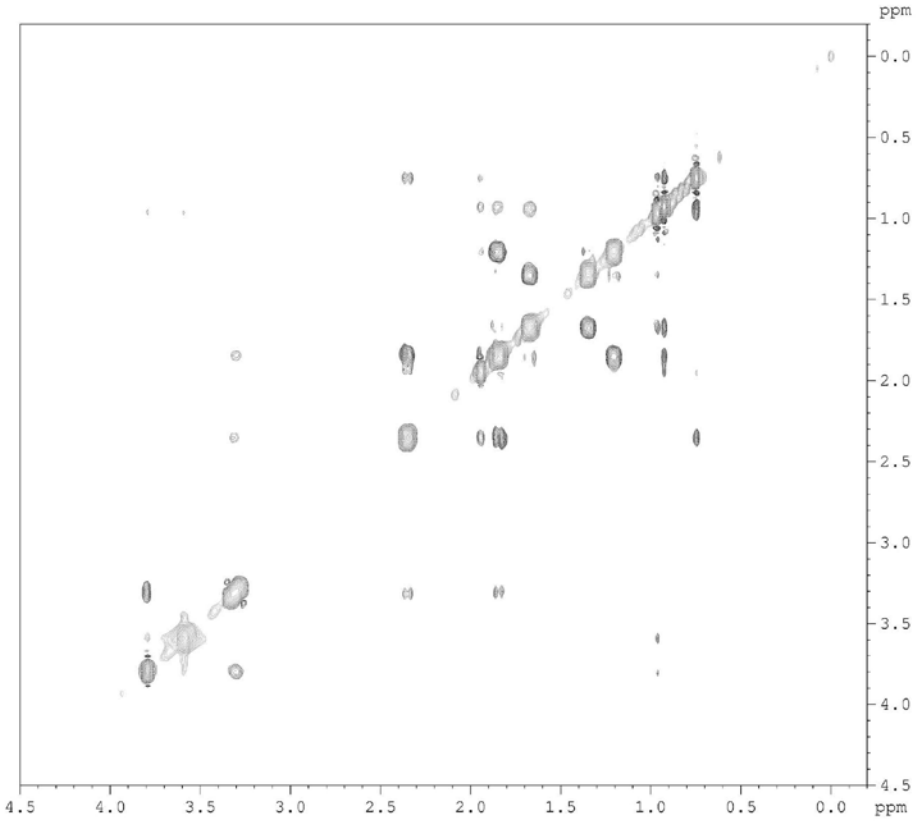

Figure S13. NOESY spectrum of $\mathbf{2}_{\mathbf{A}}$ ($CDCl_3$, 500 MHz).

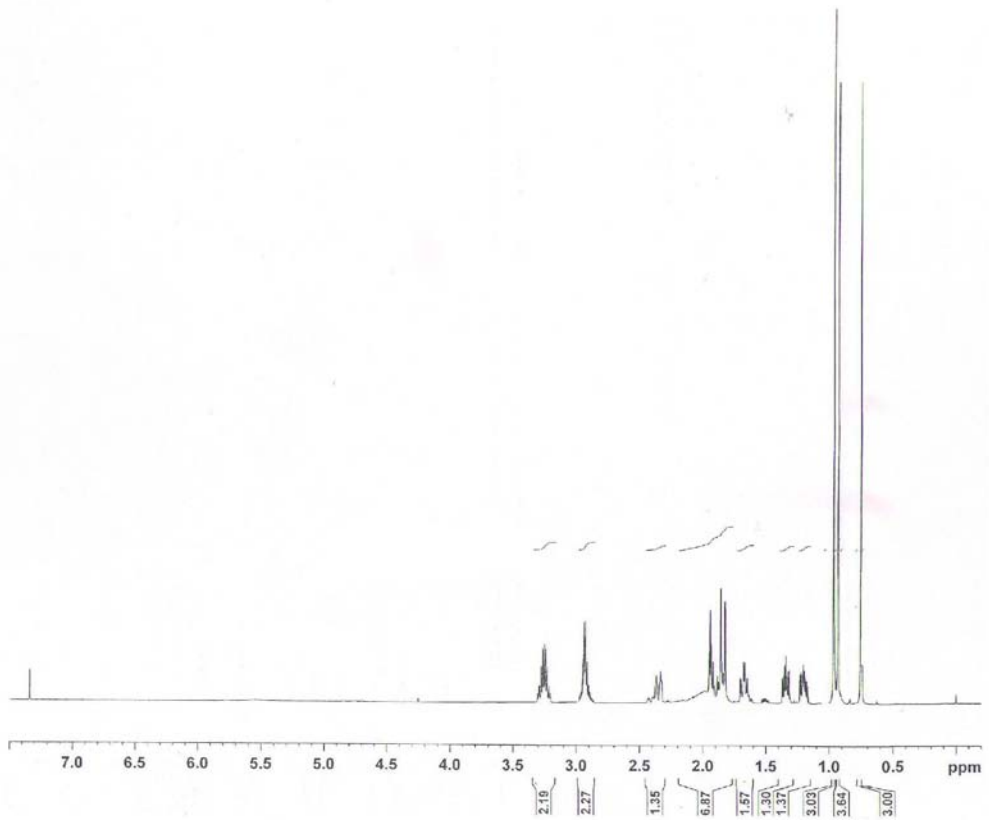

Figure S14. [1]H NMR spectrum of $\mathbf{2_B}$ ($CDCl_3$, 500 MHz).

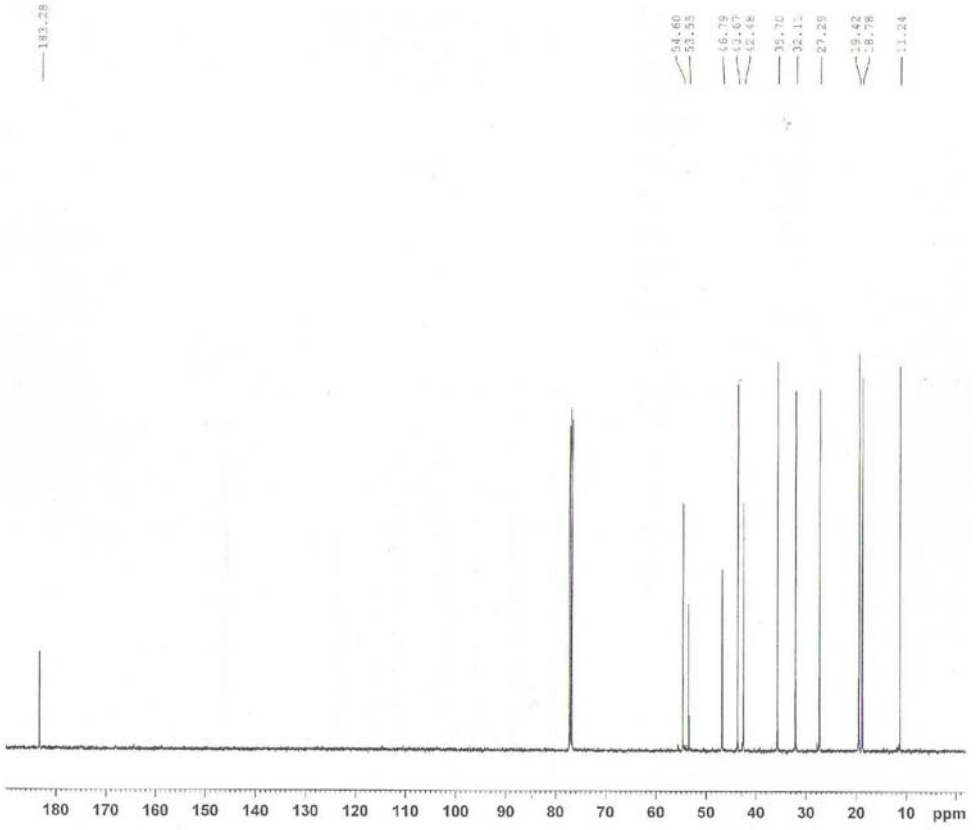

Figure S15. [13]C NMR spectrum of $\mathbf{2_B}$ ($CDCl_3$, 125 MHz).

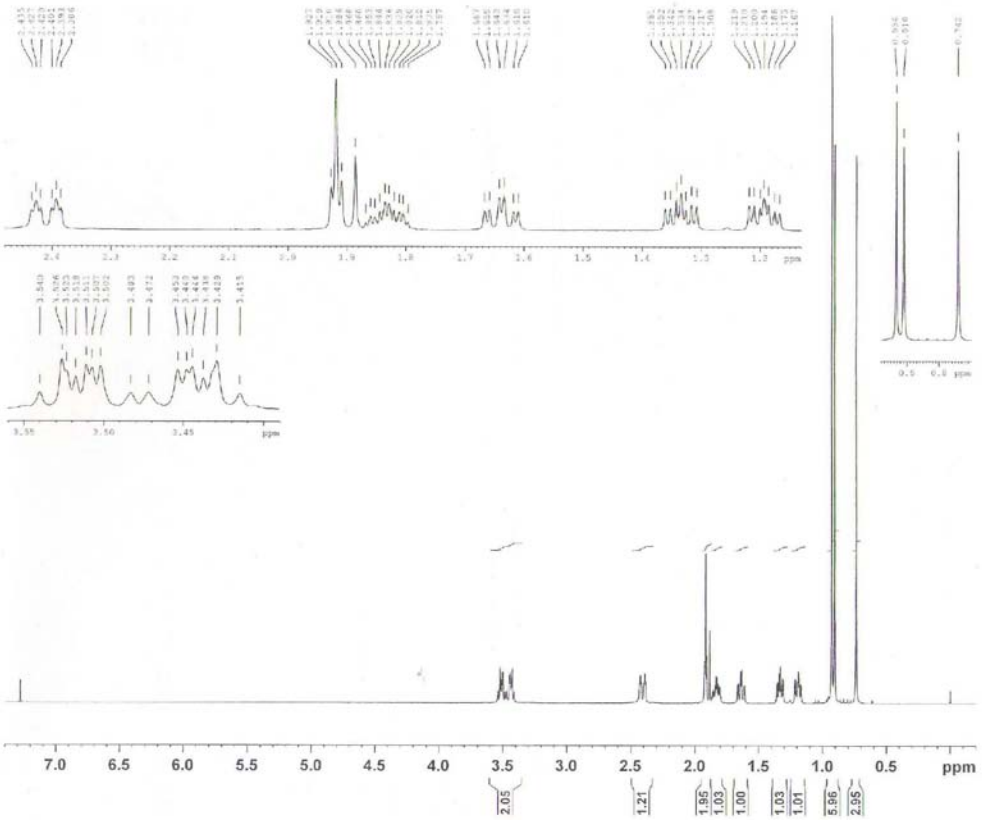

Figure S16. [1]H NMR spectrum of $\mathbf{2_C}$ ($CDCl_3$, 500 MHz).

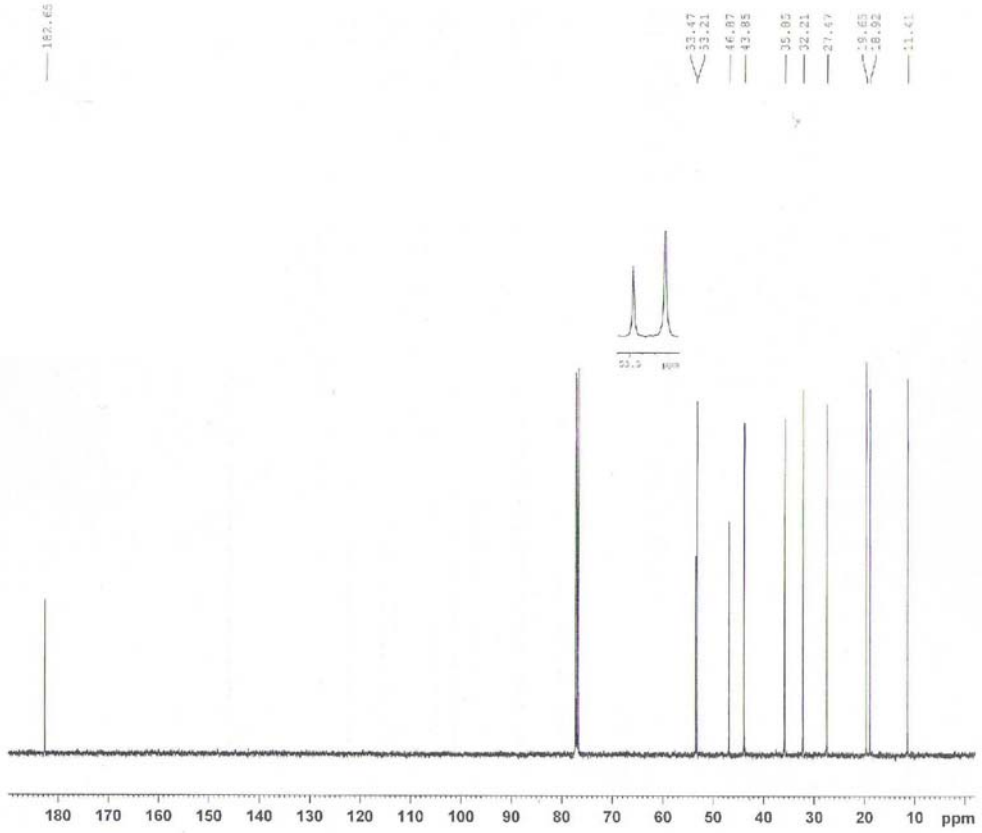

Figure S17. [13]C NMR spectrum of $\mathbf{2_C}$ ($CDCl_3$, 125 MHz).

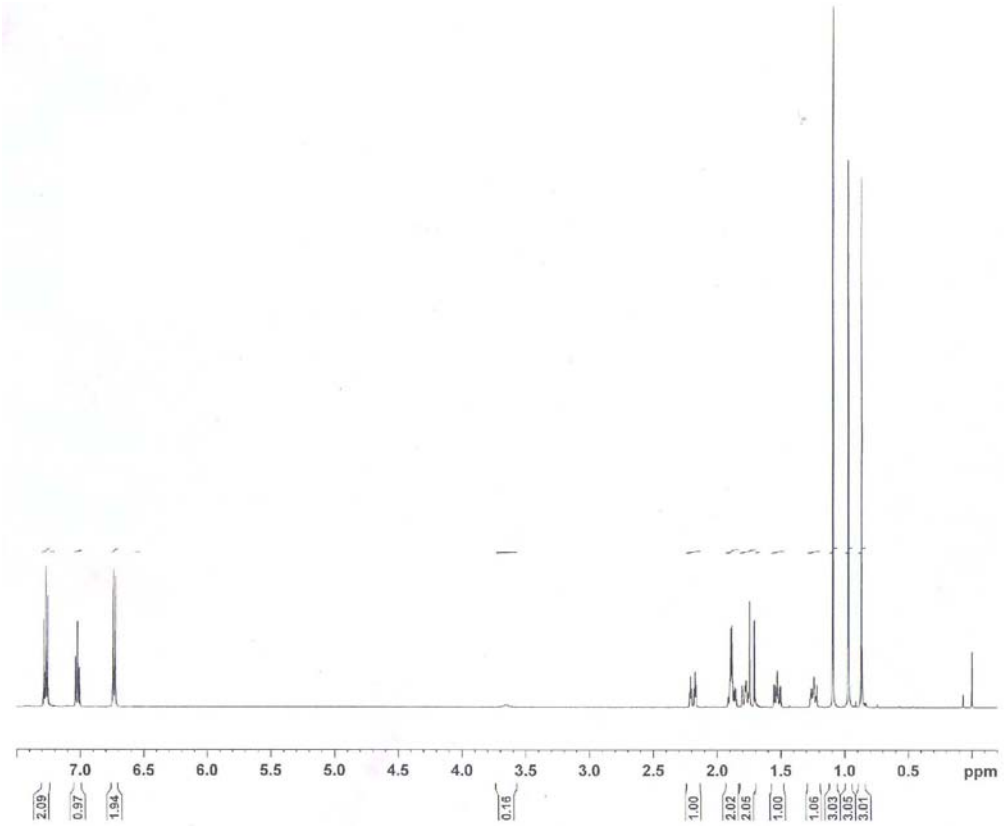

Figure S18. ^{1}H NMR spectrum of $\mathbf{2_D}$ ($CDCl_3$, 500 MHz).

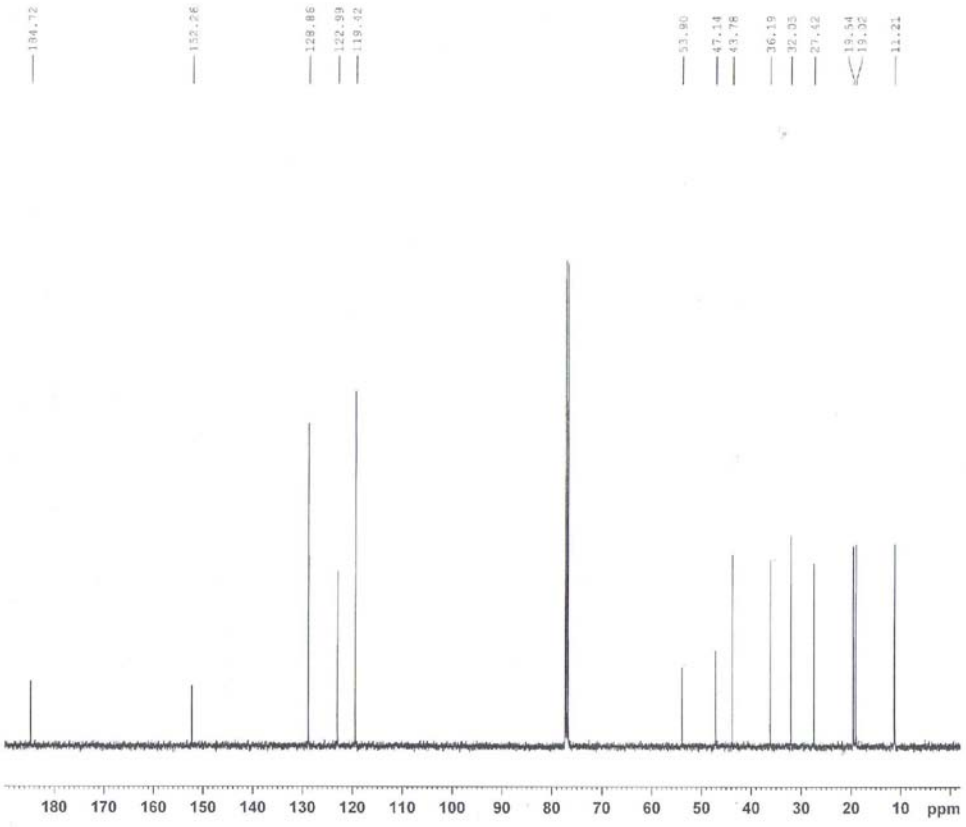

Figure S19. ^{13}C NMR spectrum of $\mathbf{2_D}$ ($CDCl_3$, 125 MHz).

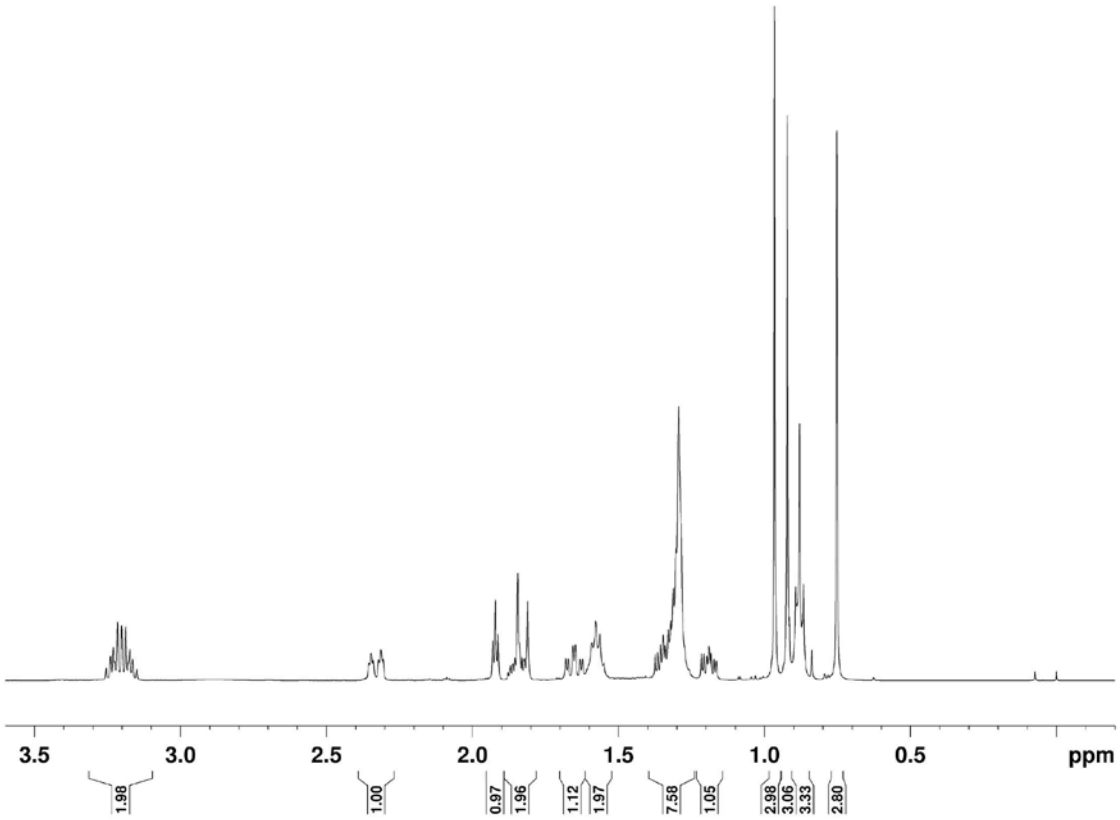

Figure S20. ^{1}H NMR spectrum of $\mathbf{2}_{E}$ ($CDCl_3$, 500 MHz).

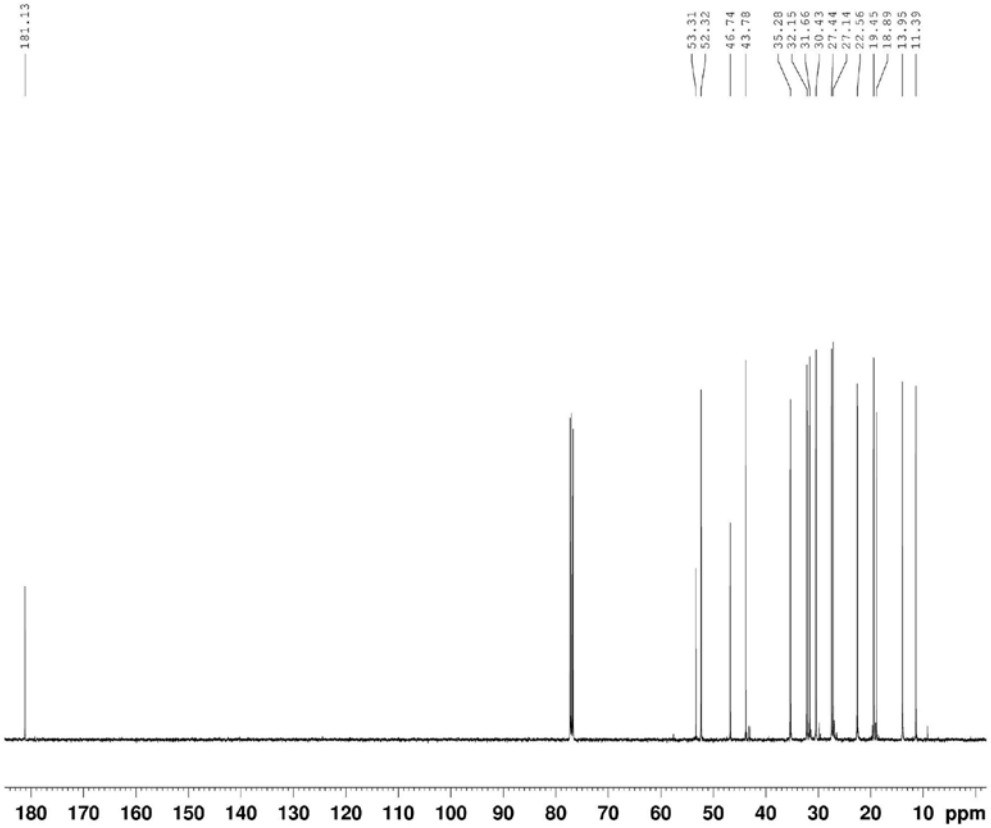

Figure S21. ^{13}C NMR spectrum of $\mathbf{2}_{E}$ ($CDCl_3$, 125 MHz).

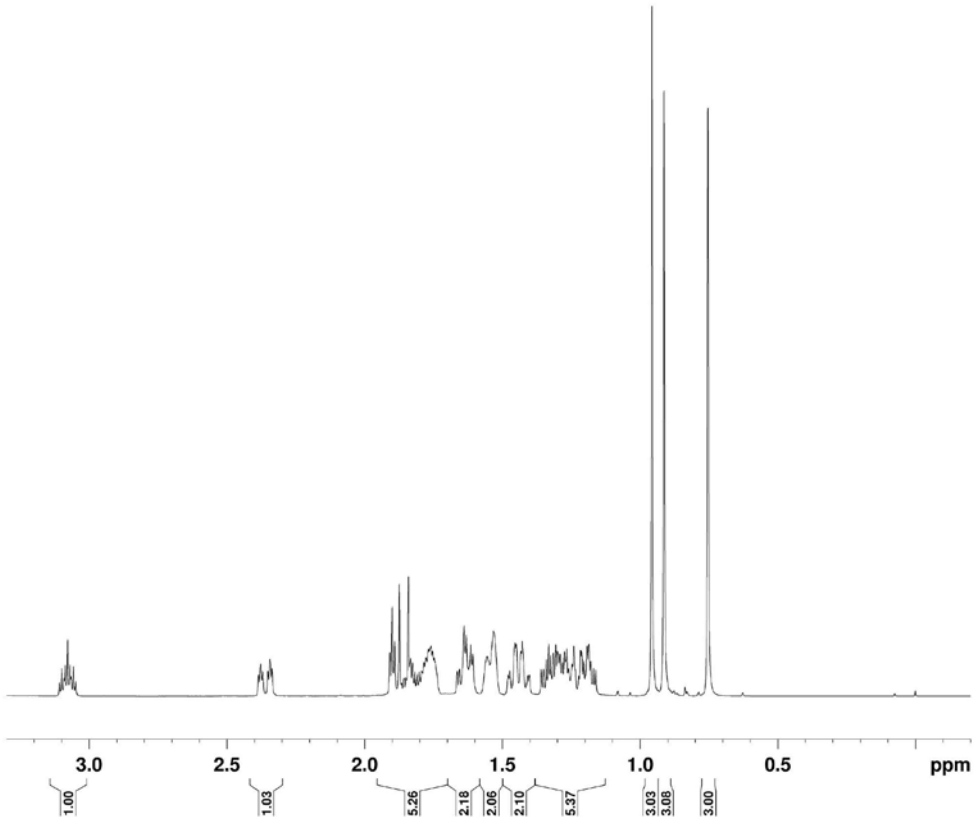

Figure S22. ^{1}H NMR spectrum of $\mathbf{2_F}$ ($CDCl_3$, 500 MHz).

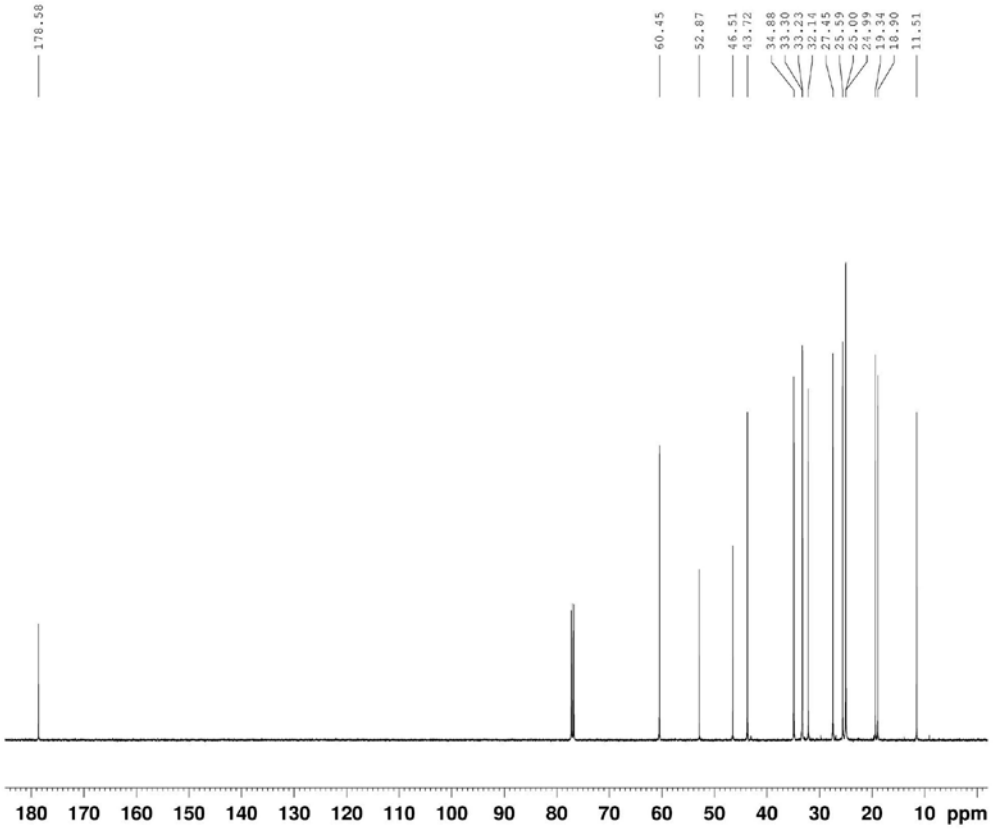

Figure S23. ^{13}C NMR spectrum of $\mathbf{2_F}$ ($CDCl_3$, 125 MHz).

Spectral data for $\mathbf{2}_{\mathbf{A-F}}$

2-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene) aminoethanol ($\mathbf{2}_{\mathbf{A}}$): a crude product was purified using chloroform/ethyl acetate 1:1 as an eluent to give $\mathbf{2}_{\mathbf{A}}$. White powder; yield: 0.771 g (73%); mp 65 °C; IR (KBr) ν/cm^{-1} 3418 ν(O–H), 2955, 2931 and 2870 ν(C–H), 1682 ν(C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (s, 3H, CH_3 (C9)), 0.93 (s, 3H, CH_3 (C8)), 0.97 (s, 3H, CH_3 (C10)), 1.21 (dtd, 1H, *J* 12.25, 9.00, 4.50 Hz, H_a5), 1.35 (dtd, 1H, *J* 13.00, 9.00, 4.50 Hz, H_a6), 1.67 (td, 1H, *J* 12.25, 4.50 Hz, H_e6), 1.84 (d, 1H, *J* 17.00 Hz, H_a3), 1.89 (m, 1H, H_e5), 1.95 (t, 1H, *J* 4.50 Hz, H4), 2.35 (dt, 1H, *J* 17.00, 3.50 Hz, H_e3), 3.31 (m, 2H, N–CH_2), 3.59 (br s, 1H, exchangeable with D_2O, OH), 3.79 (td, 2H, *J* 6.00, 0.50 Hz, CH_2–O); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.22 (C10), 18.81 (C8), 19.45 (C9), 27.28 (C5), 32.02 (C6), 35.94 (C3), 43.69 (C4), 47.05 (C7), 53.75 (C1 and C11, overlapped signals), 62.04 (C12), 184.53 (C=N). Anal. calcd. for $C_{12}H_{21}NO$ (195.31 g mol^{-1}): C, 73.80; H, 10.84; N, 7.17; found: C, 73.77; H, 10.85; N, 7.14.

N-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene) ethane-1,2-diamine ($\mathbf{2}_{\mathbf{B}}$): a crude product was purified by column chromatography on silica gel. First, ethyl acetate was applied to eluate $\mathbf{2}_{\mathbf{C}}$. Then, solvent was changed and $\mathbf{2}_{\mathbf{B}}$ was obtained using methanol as an eluent. White powder; yield: 0.641 g (61%); mp 49 °C; IR (KBr) ν/cm^{-1} 3435 ν(N–H), 2956, 2921 and 2873 ν(C–H), 1686 ν(C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (s, 3H, CH_3 (C9)), 0.93 (s, 3H, CH_3 (C8)), 0.97 (s, 3H, CH_3 (C10)), 1.20 (dtd, 1H, *J* 12.25, 9.00, 4.50 Hz, H_a5); 1.34, (dtd, 1H, *J* 13.00, 9.00, 4.50 Hz, H_a6), 1.67 (td, 1H, *J* 12.25, 4.50 Hz, H_e6), 1.85 (d, 1H, *J* 17.00 Hz, H_a3), 1.86 (m, 1H, H_e5), 1.94 (t, 1H, *J* 4.50 Hz, H4), 1.98 (br s, 2H, exchangeable with D_2O, NH_2), 2.35 (dt, 1H, *J* 17.00, 3.50 Hz, H_e3), 2.93 (m, 2H, CH_2–N), 3.25 (m, 2H, N–CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.24 (C10), 18.78 (C8), 19.42 (C9), 27.29 (C5), 32.11 (C6), 35.70 (C3), 42.48 (C12), 43.67 (C4), 46.79 (C7), 53.55 (C1), 54.60 (C11), 184.53 (C=N). Anal. calcd. for $C_{12}H_{22}N_2$ (194.32 g mol^{-1}): C, 74.17; H, 11.41; N, 14.42; found: C, 74.97; H, 11.71; N, 14.76.

N^1-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene)-*N*^{2}-(1,7,7-trimethylbicyclo [2.2.1]heptan-2-ylidene)ethane-1,2-diamine ($\mathbf{2}_{\mathbf{C}}$): a crude product was purified using ethyl acetate as an eluent to give $\mathbf{2}_{\mathbf{C}}$. White powder; yield: 0.261 g (29%); mp 51 °C; IR (KBr) ν/cm^{-1} 2956, 2921 and 2872 ν(C–H), 1686 ν(C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (s, 3H, CH_3 (C9)), 0.91 (s, 3H, CH_3 (C8)), 0.93 (s, 3H, CH_3 (C10)), 1.19 (dtd, 1H, *J* 12.25, 9.00, 4.50 Hz, H_a5), 1.33 (dtd, 1H, *J* 13.00, 9.00, 4.50 Hz, H_a6), 1.64 (td, 1H, *J* 12.25, 4.50 Hz, H_e6), 1.87 (m, 1H, H_e5), 1.90 (d, 1H, *J* 17.00 Hz, H_a3), 1.92 (t, 1H, *J* 4.50 Hz, H4), 2.41 (dt, 1H, *J* 17.00, 3.50 Hz, H_e3), 3.44, (m, 1H, N–CH_2), 3.51 (m, 1H, N–CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.41 (C10), 18.92 (C8), 19.65 (C9), 27.47 (C5), 32.21 (C6), 35.85 (C3), 43.85 (C4), 46.87 (C7), 53.21 (C11), 53.47 (C1), 184.53 (C=N). Anal. calcd. for $C_{22}H_{36}N_2$ (328.54 g mol^{-1}): C, 80.43; H, 11.05; N, 8.53; found: C, 80.74; H, 11.18; N, 8.86.

N-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene)aniline ($\mathbf{2}_{\mathbf{D}}$): a crude product was purified using chloroform as an eluent to give $\mathbf{2}_{\mathbf{D}}$. Yellowish oil; yield: 0.195 g (16%); IR (neat) ν/cm^{-1} 3079 $\nu(C–H)_{Ar}$, 2958, and 2873 ν(C–H), 1685 ν(C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (s, 3H, CH_3 (C9)), 0.97 (s, 3H, CH_3 (C8)), 1.09 (s, 3H, CH_3 (C10)), 1.24 (m, 1H, H_a5), 1.53 (dtd, 1H, *J* 12.50, 9.50, 4.00 Hz, H_a6), 1.73 (d, 1H, *J* 18.00 Hz, H_a3), 1.78 (m, 1H, H_e6), 1.88 (m, 1H, H_e5), 1.89 (d, 1H, *J* 4.00 Hz, H4), 2.19 (dt, 1H, *J* 18.00, 4.00 Hz, H_e3), 6.73 (dd, 2H, *J* 7.50, 1.00 Hz, *o*-phenyl), 7.02 (tt, 1H, *J* 7.50, 1.00 Hz, p-phenyl), 7.27 (td, 2H, *J* 7.50, 1.00 Hz, m-phenyl); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.21 (C10), 19.02 (C8), 19.54 (C9), 27.42 (C5), 32.05 (C6), 36.19 (C3), 43.78 (C4), 47.14 (C7), 53.90 (C1), 119.42 (C12), 122.99 (C14), 128.86 (C13), 152.26 (C11), 184.72 (C=N). Anal. calcd. for $C_{16}H_{21}N$ (227.35 g mol^{-1}): C, 84.53; H, 9.31; N, 6.16; found: C, 84.74; H, 9.52; N, 6.41.

N-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene) hexan-1-amine ($\mathbf{2}_{\mathbf{E}}$): a crude product was purified using chloroform/ethyl acetate, 9.5:0.5 as an eluent to give $\mathbf{2}_{\mathbf{E}}$. Yellowish oil; yield: 0.327 g (26%); IR (neat) ν/cm^{-1} 2954, 2927, 2872 and 2857 ν(C–H), 1686 ν(C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (s, 3H, CH_3 (C9)), 0.87 (t, 3H, *J* 6.50 Hz, CH_3 (C16)), 0.92 (s, 3H, CH_3 (C8)), 0.97 (s, 3H, CH_3 (C10)), 1.19 (dtd, 1H, *J* 12.25, 9.00, 4.50 Hz, H_a5), 1.29 (m, 6H, (C13, C14, C15)), 1.36 (dtd, 1H, *J* 13.00, 9.00, 4.50 Hz, H_a6), 1.58 (m, 2H, (C12)), 1.65 (td, 1H, *J* 12.25, 4.50 Hz, H_e6), 1.83 (d, 1H, *J* 17.00 Hz, H_a3), 1.85 (m, 1H, H_e5), 1.92 (t, 1H, *J* 4.50 Hz, H4), 2.33 (dt, 1H, *J* 17.00, 3.50 Hz, H_e3), 3.20 (m, 2H, CH_2 (C11)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.39 (C10), 13.95 (C16), 18.89 (C8), 19.45 (C9), 22.56 (C15), 27.14 (C13), 27.44 (C5), 30.43 (C12), 31.66 (C14), 32.15 (C6), 35.28 (C3), 43.78 (C4), 46.74 (C7), 52.32 (C11), 53.31 (C1), 181.13 (C=N). Anal. calcd. for $C_{16}H_{29}N$ (235.41 g mol^{-1}): C, 81.63; H, 12.42; N, 5.95; found: C, 81.94; H, 12.58; N, 6.13.

N-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene) cyclohexanamine ($\mathbf{2}_{\mathbf{F}}$): a crude product was purified using chloroform as an eluent to give $\mathbf{2}_{\mathbf{F}}$. Yellowish oil; yield:

0.175 g (14%); IR (neat) ν/cm^{-1} 2925 and 2853 ν(C–H), 1685 ν(C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (s, 3H, CH_3 (C9)), 0.91 (s, 3H, CH_3 (C8)), 0.96 (s, 3H, CH_3 (C10)), 1.16-1.36 (m, 5H, H_a5, 3H (Cy), H_a6), 1.44 (m, 2H, Cy), 1.54 (m, 2H, Cy), 1.64 (m, 2H, 1H, Cy, H_e6), 1.76 (m, 2H, Cy), 1.83 (m, 1H, H_e5), 1.86 (d, 1H, *J* 17.00 Hz, H_a3), 1.90 (t, 1H, *J* 4.50 Hz, H4), 2.36 (dt, 1H, *J* 17.00, 4.00 Hz, H_e3), 3.08 (m, 1H, CH (C11)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.51 (C10), 18.90 (C8), 19.34 (C9), 24.99 and 25.00 (C13 and C13'), 25.59 (C14), 27.45 (C5), 32.14 (C6), 33.23 and 33.30 (C12 and C12'), 34.88 (C3), 43.72 (C4), 46.51 (C7), 52.87 (C1), 60.45 (C11), 178.58 (C=N). Anal. calcd. for $C_{16}H_{27}N$ (233.40 g mol^{-1}): C, 82.34; H, 11.66; N, 6.00; found: C, 82.67; H, 11.71; N, 6.11.

Experimental and calculated geometrical parameters of $\mathbf{2_A}$

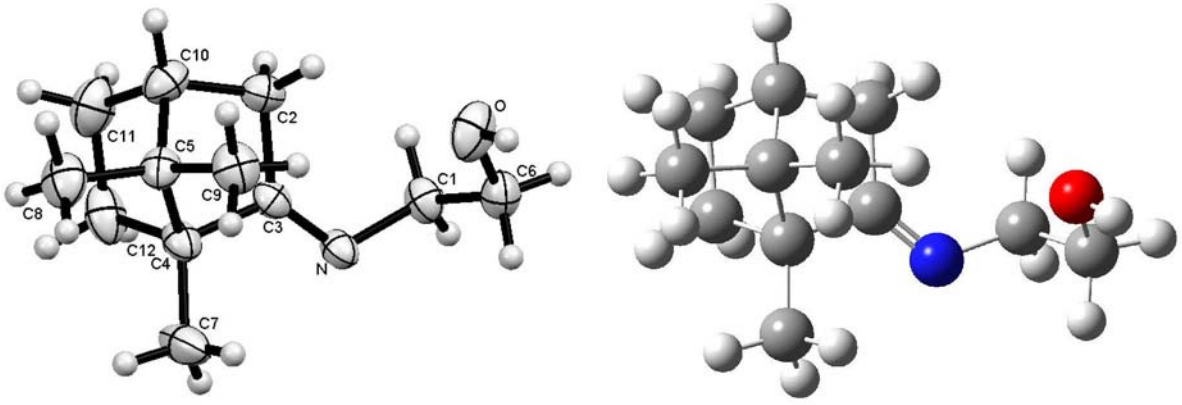

Figure S24. Crystal structure (left) and calculated structure of $\mathbf{2_A}$ in the gas-phase.

Table S1. Experimental and calculated bond distances between heavy atoms in $\mathbf{2_A}$. See Figure S1 for atom labeling

Bond distance / Å	Experimental	Calculated
C1–C6	1.5135	1.5222
C1–N	1.4710	1.4556
C2–C3	1.5190	1.5356
C2–C10	1.5289	1.5437
C3–C4	1.5188	1.5288
C3–N	1.2693	1.2666
C4–C5	1.5688	1.5758
C4–C7	1.5211	1.5175
C4–C12	1.5495	1.5633
C5–C8	1.5343	1.5366
C5–C9	1.5292	1.5389
C5–C10	1.5454	1.5619
C6–O	1.4090	1.4324
C10–C11	1.5452	1.5466
C11–C12	1.5334	1.5590

Table S2. Experimental and calculated bond angles between heavy atoms in $\mathbf{2_A}$. See Figure S1 for atom labeling

Bond angle / degree	Experimental	Calculated
C1–C6–O	109.8	108.4
C1–N–C3	118.4	119.9
C2–C3–N	129.8	130.4
C2–C10–C5	102.7	102.6
C2–C10–C11	106.1	106.8
C3–C2–C10	102.4	101.8
C3–C4–C5	100.4	100.5
C3–C4–C7	115.8	115.0
C3–C4–C12	104.2	104.2
C4–C5–C8	114.3	114.5
C4–C5–C9	113.1	113.5
C4–C5–C10	93.5	93.4
C4–C12–C11	104.6	104.2
C5–C4–C7	117.1	118.6
C5–C4–C12	101.7	101.8
C5–C10-C11	102.7	102.9
C6–C1–N	111.9	110.8
C7–C4–C12	115.4	114.5
C8–C5–C9	108.2	107.6
C8–C5–C10	113.6	113.7
C9–C5–C10	113.8	113.9
C10–C11–C12	102.8	102.8

Table S3. Experimental and calculated values for selected dihedral angles in $\mathbf{2}_{A}$. See Figure S1 for atom labeling

Dihedral angle / degree	Experimental	Calculated	Dihedral angle / degree	Experimental	Calculated
C1–N–C3–C4	179.0	179.4	C5–C4–C3–N	145.0	144.9
C2–C3–C4–C5	35.0	34.5	C7–C4–C5–C8	62.2	62.1
C2–C3–C4–C7	162.1	163.2	C7–C4–C5–C9	62.2	62.0
C2–C3–C4–C12	70.0	70.6	C7–C4–C5–C10	180.0	180.0
C2–C10–C11–C12	70.6	71.1	C7–C4–C12–C11	160.9	162.7
C3–C2–C10–C5	35.1	35.7	C8–C5–C10–C2	173.3	174.0
C3–C2–C10–C11	72.4	72.2	C8–C5–C10–C11	63.2	63.2
C3–C4–C5–C8	171.6	171.7	C9–C5–C10–C2	62.3	62.4
C3–C4–C5–C9	64.0	64.3	C9–C5–C10–C11	172.4	173.1
C3–C4–C5–C10	53.8	53.6	C10–C2–C3–N	179.5	179.7
C3–C4–C12–C11	71.0	70.8	C12–C4–C5–C9	171.0	171.4
C4–C5–C10–C2	54.8	55.3	C12–C4–C5–C8	64.6	64.6
C4–C5–C10–C11	55.2	55.5	C12–C4–C5–C10	53.2	53.4
C5–C4–C12–C11	33.0	33.4	C12–C4–C3–N	110.0	109.9
C5–C10–C11–C12	36.8	36.6	N–C1–C6–O	70.3	71.8

Results of DFT calculations

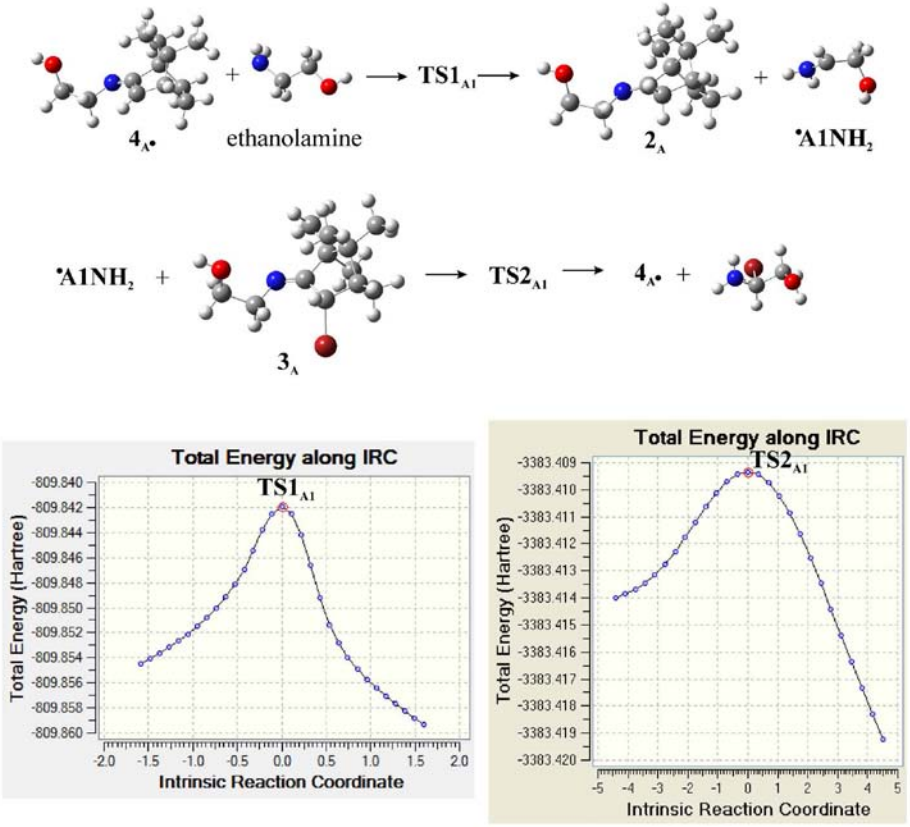

Figure S25. Optimized geometries of the reactants and products in the elementary steps 13 and 14, where ethanolamine reacts in the position 11. Results of the IRC calculations for the corresponding transition states.

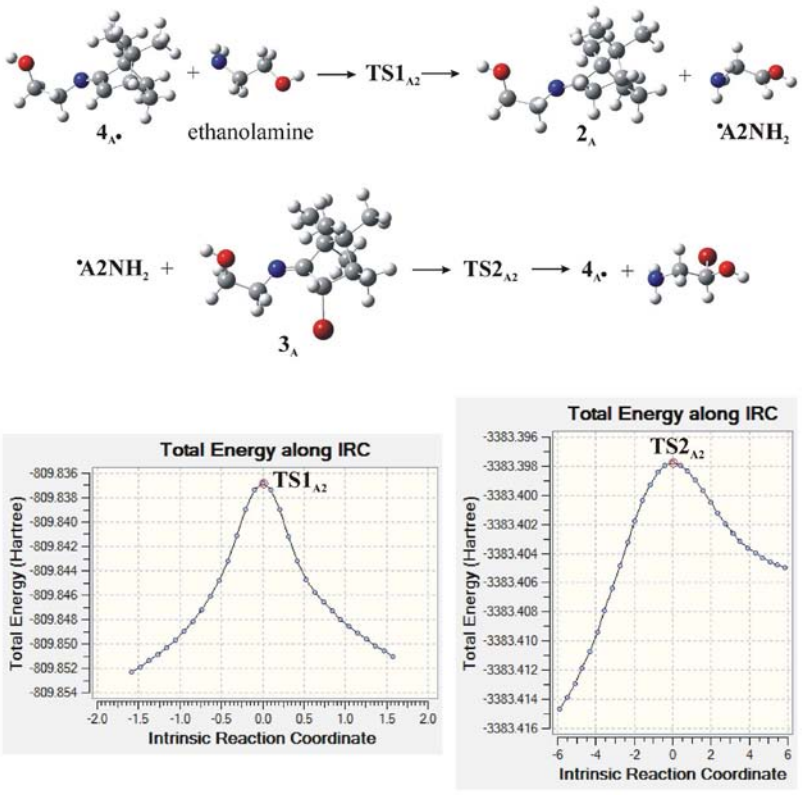

Figure S26. Optimized geometries of the reactants and products in the elementary steps 13 and 14, where ethanolamine reacts in the position 12. Results of the IRC calculations for the corresponding transition states.

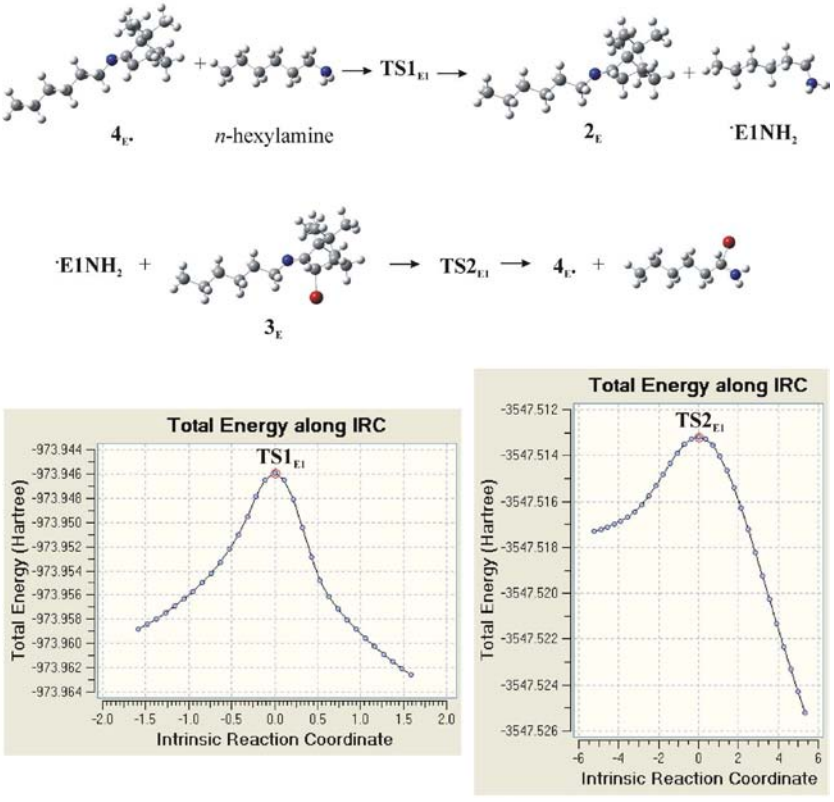

Figure S27. Optimized geometries of the reactants and products in the elementary steps 13 and 14, where *n*-hexylamine reacts in the position 11. Results of the IRC calculations for the corresponding transition states.

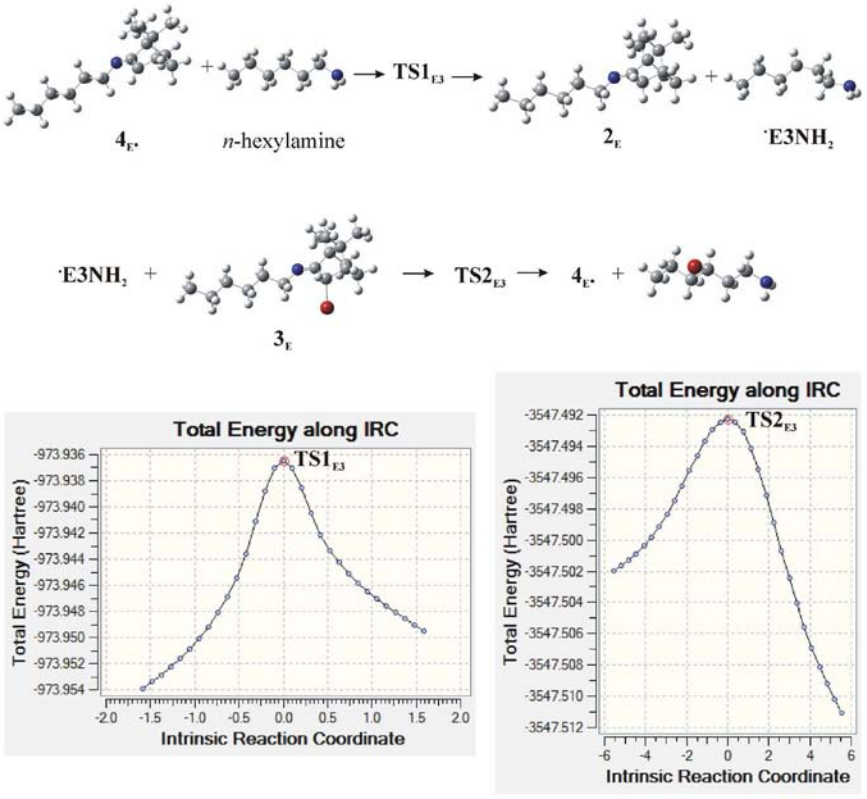

Figure S28. Optimized geometries of the reactants and products in the elementary steps 13 and 14, where *n*-hexylamine reacts in the position 13. Results of the IRC calculations for the corresponding transition states.