

Supporting Information

**Palladium-Catalyzed Three-Component Reaction of
N-Tosylhydrazone, Norbornene and Aryl Halide**

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1. General

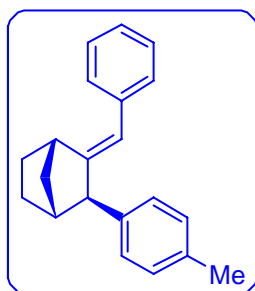
All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled under a nitrogen atmosphere prior to use. Toluene and 1,4-dioxane were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN and DCE were dried over CaH₂. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard when CDCl₃ was used as solvent. IR spectra were recorded with a Thermo Electron Corporation Nicolet AVAT AR 330 FT-IR spectrometer. HRMS data were obtained on a VG ZAB-HS mass spectrometer, Bruker Apex IV FTMS spectrometer.

2. Typical experimental procedure for palladium-catalyzed

three-component coupling reaction

Under a nitrogen atmosphere, Pd(PPh₃)₄ (17.3 mg, 5 mol%), 4-iodotoluene (0.30 mmol, 65.4 mg), norbornene (0.60 mmol, 56.4 mg), *N*-tosylhydrazone (0.36 mmol, 98.6 mg) and K₂CO₃ (0.90 mmol, 124.2 mg) were added to a flame-dried 25 mL Schlenk flask. The reaction flask was degassed three times with nitrogen and then toluene (2 mL) was added using a syringe. The resulting solution was stirred at 80 °C for the indicated time. The mixture was then cooled to room temperature and filtered through a short plug of silica gel. Solvent was then removed in *vacuo* to give a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

3. Characterization data for the products

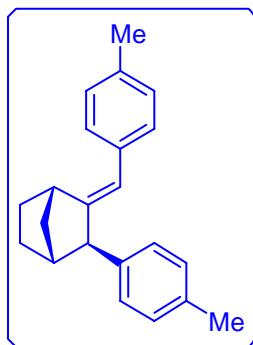


(1*S*,3*R*,4*R*, *E*)-2-benzylidene-3-(*p*-tolyl)bicyclo[2.2.1]heptane (3a), racemic

The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (75 mg, 91%, d.r. = 12:1). ¹H NMR (400 MHz, CDCl₃) δ 1.19 (d, *J* = 9.9 Hz, 1H), 1.53-1.58 (m, 1H), 1.65-1.67 (m, 2H), 1.74-1.90 (m, 2H), 2.29 (s, 1H), 2.34 (s, 3H), 3.39 (s, 1H), 3.50 (s, 1H), 6.11 (s, 1H), 7.07-7.20 (m, 5H), 7.32-7.35 (m, 4H).

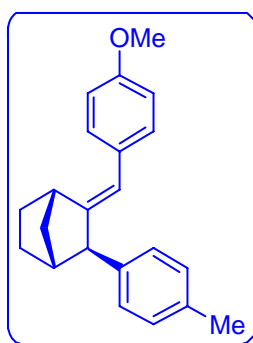
^{13}C NMR (100 MHz, CDCl_3) δ 150.84, 141.82, 138.49, 135.31, 128.82, 128.61, 128.22, 128.05, 125.95, 122.06, 56.26, 45.19, 41.39, 35.84, 29.00, 20.95. HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{23}$ $[\text{M}+\text{H}]^+$ 275.1794, found 275.1791; LRMS (EI, m/z): 274 (M^+ , 100), 246 (73), 155 (42), 115 (28), 91 (35); IR (film): 693, 768, 1447, 1509, 2957 cm^{-1} .

(1S,3R,4R,E)-2-(4-methylbenzylidene)-3-(p-tolyl)bicyclo[2.2.1]heptane (3b), racemic



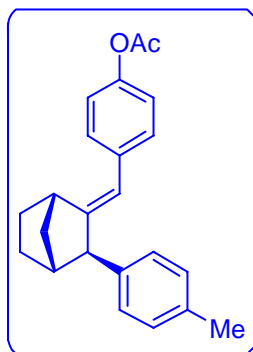
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a colorless oil (54 mg, 63%, d.r. = 12:1). ^1H NMR (400 MHz, CDCl_3) δ 1.18 (d, J = 9.9 Hz, 1H), 1.54-1.57 (m, 1H), 1.63-1.66 (m, 2H), 1.73-1.89 (m, 2H), 2.28 (d, J = 3.2 Hz, 1H), 2.33 (s, 3H), 2.34 (s, 3H), 3.37 (d, J = 2.3 Hz, 1H), 3.48 (s, 1H), 6.07 (s, 1H), 7.10-7.17 (m, 6H), 7.21-7.22 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.90, 141.93, 135.65, 135.57, 135.26, 128.92, 128.79, 128.62, 127.95, 121.90, 56.22, 45.20, 41.37, 35.80, 29.01, 21.11, 20.94. HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{25}$ $[\text{M}+\text{H}]^+$ 289.1951, found 289.1945; LRMS (EI, m/z): 288 (M^+ , 89), 260 (69), 155 (39), 129 (44), 105 (100); IR (film): 732, 808, 1510, 1727, 2959 cm^{-1} .

(1S,3R,4R,E)-2-(4-methoxybenzylidene)-3-(p-tolyl)bicyclo[2.2.1]heptanes (3c), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (77 mg, 84%, d.r. = 7:1). ^1H NMR (400 MHz, CDCl_3) δ 1.18 (d, J = 9.9 Hz, 1H), 1.48-1.57 (m, 1H), 1.62-1.66 (m, 2H), 1.74-1.86 (m, 2H), 2.28 (d, J = 3.8 Hz, 1H), 2.34 (s, 3H), 3.35 (s, 1H), 3.47 (s, 1H), 3.81 (s, 3H), 6.04 (s, 1H), 6.88 (d, J = 8.6 Hz, 2H), 7.11-7.18 (m, 4H), 7.23-7.27 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.83, 148.80, 141.95, 135.25, 131.28, 129.13, 128.78, 128.61, 121.43, 113.66, 56.18, 55.25, 45.19, 41.27, 35.79, 29.01, 20.94. HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$ 305.1900, found 305.1905; LRMS (EI, m/z): 304 (M^+ , 100), 276 (27), 263 (12), 171 (14), 121 (77); IR (film): 809, 1175, 1247, 1509, 2955 cm^{-1} .

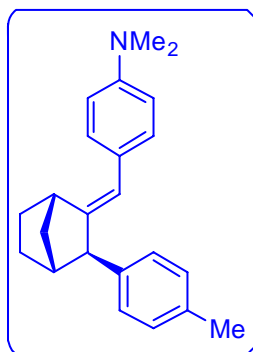
4-((E)-((1S,3R,4R)-3-(p-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)phenyl acetate (3d), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE : EA = 100 : 1), the product was isolated as a white solid (98 mg, 98%, d.r. = 12:1). ^1H NMR (400 MHz, CDCl_3) δ 1.19 (d, J = 9.9 Hz, 1H), 1.52-1.57 (m, 1H), 1.60-1.67 (m, 2H), 1.75-1.91 (m, 2H), 2.30 (s, 3H), 2.33 (s, 3H), 3.36 (d, J = 2.8 Hz, 1H), 3.48 (s, 1H), 6.07 (s, 1H), 7.02-7.06 (m, 2H), 7.10-7.16 (m, 4H), 7.31 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.58, 151.11, 148.66, 141.70, 136.27, 135.34, 128.94, 128.82, 128.55, 121.25, 121.11, 56.20, 45.14, 41.27, 35.80, 28.95, 28.91, 21.11, 20.93. HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 333.1849,

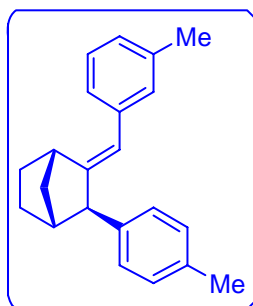
found 333.1856; LRMS (EI, m/z): 332 (M^+ , 81), 290 (100), 262(50), 156 (31), 107 (62); IR (film): 911, 1197, 1505, 1766, 2959 cm^{-1} .

***N,N*-dimethyl-4-((*E*)-((1*S*,3*R*,4*R*)-3-(*p*-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)aniline (3e), racemic**



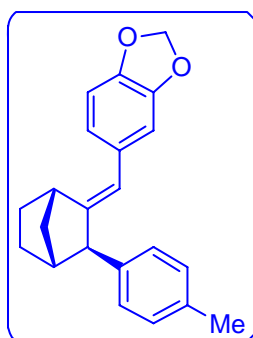
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE : EA = 100 : 1), the product was isolated as a yellow oil (67 mg, 70%, d.r. = 3:1). ^1H NMR (400 MHz, CDCl_3) mixture δ 1.16 (d, $J = 9.7$ Hz, 1H), 1.42-1.85 (m, 7.7H), 2.27 (s, 2H), 2.33 (s, 3H), 2.82 (s, 2H), 2.94 (s, 6H), 3.38 (d, $J = 2.0$ Hz, 1H), 3.47 (s, 1H), 6.01 (s, 1H), 6.46-6.48 (m, 1.1H), 6.72 (d, $J = 8.6$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 0.8H), 7.02 (d, $J = 7.8$ Hz, 0.8H), 7.10-7.11 (m, 2.8H), 7.16-7.18 (m, 2H), 7.23 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) mixture δ 148.92, 148.53, 146.89, 144.89, 142.20, 139.29, 135.12, 134.94, 129.17, 128.87, 128.72, 128.67, 128.16, 127.27, 126.46, 121.84, 121.46, 112.49, 112.24, 56.24, 54.53, 47.80, 47.71, 45.23, 41.32, 40.65, 40.45, 35.74, 34.38, 31.83, 29.09, 29.05, 28.20, 20.97, 20.94. HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{28}\text{N}$ [$M+H$] $^+$ 318.2216, found 318.2224; LRMS (EI, m/z): 317 (M^+ , 100), 288 (27), 276(9), 186 (10), 134 (27); IR (film): 810, 1351, 1519, 1609, 2956 cm^{-1} .

(1*S*,3*R*,4*R*,*E*)-2-(3-methylbenzylidene)-3-(*p*-tolyl)bicyclo[2.2.1]heptane (3f), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (75 mg, 87%, d.r. = 12:1). ^1H NMR (400 MHz, CDCl_3) δ 1.18 (d, $J = 9.8$ Hz, 1H), 1.50-1.58 (m, 1H), 1.63-1.66 (m, 2H), 1.74-1.91 (m, 2H), 2.28 (d, $J = 3.1$ Hz, 1H), 2.33 (s, 3H), 2.34 (s, 3H), 3.38 (d, $J = 2.2$ Hz, 1H), 3.48 (s, 1H), 6.07 (s, 1H), 7.00-7.02 (m, 1H), 7.10-7.17 (m, 6H), 7.20-7.24 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.64, 141.88, 138.43, 137.70, 135.28, 128.88, 128.80, 128.61, 128.12, 126.74, 125.03, 122.11, 56.22, 45.18, 41.40, 35.81, 29.01, 21.50, 20.95. HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{25}$ [$M+H$] $^+$ 289.1951, found 289.1950; LRMS (EI, m/z): 288 (M^+ , 100), 260 (68), 183(29), 155 (39), 105 (52); IR (film): 712, 787, 810, 1510, 2958 cm^{-1} .

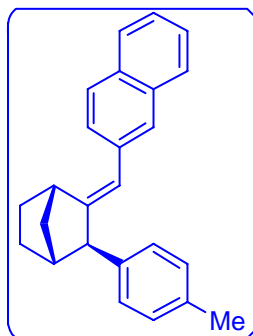
5-((*E*)-((1*S*,3*R*,4*R*)-3-(*p*-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)benzo[*d*][1,3]dioxole (3g), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (72 mg, 75%, d.r. = 8.5:1). ^1H NMR (400 MHz, CDCl_3) δ 1.81 (d, $J = 9.8$ Hz, 1H), 1.50-1.56 (m, 1H), 1.59-1.66 (m, 2H), 1.73-1.88 (m, 2H), 2.27 (s, 1H), 2.33 (s, 3H), 3.34 (s, 1H), 3.46 (s, 1H), 5.79 (s, 0.22H), 5.93 (s, 2H), 6.00 (s, 1H), 6.58 (m, 0.39H), 6.73-6.79 (m, 2H), 6.86 (s, 1H), 7.13 (q, $J = 8.3$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.36, 147.51, 145.67, 141.83, 135.30,

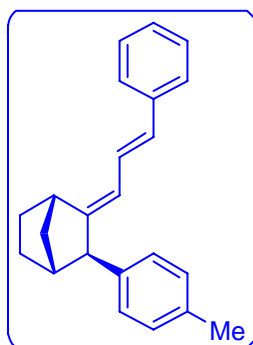
132.81, 128.80, 128.57, 121.71, 121.65, 108.21, 108.14, 100.82, 56.20, 45.14, 41.30, 35.80, 28.99, 28.95, 20.93. HRMS (ESI, m/z): calcd for $C_{22}H_{23}O_2$ $[M+H]^+$ 319.1693, found 319.1698; LRMS (EI, m/z): 318 (M^+ , 100), 290 (26), 174 (14), 135 (80), 115 (14); IR (film): 1039, 1238, 1488, 1502, 2958 cm^{-1} .

2-((*E*)-((1*S*,3*R*,4*R*)-3-(*p*-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)naphthalene (3h), racemic



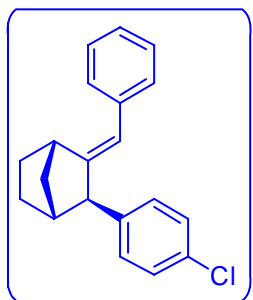
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (71 mg, 73%, d.r. = 9:1). 1H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, J = 9.9 Hz, 1H), 1.52-1.61 (m, 1H), 1.68-1.75 (m, 2H), 1.78-1.96 (m, 2H), 2.32 (d, J = 1.5 Hz, 1H), 2.34 (s, 3H), 3.48 (s, 1H), 3.53 (s, 1H), 6.25 (s, 1H), 7.12-7.14 (m, 2H), 7.20 (d, J = 7.7 Hz, 2H), 7.40-7.43 (m, 2H), 7.48 (d, J = 8.5 Hz, 1H), 7.71 (s, 1H), 7.78 (d, J = 7.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.52, 141.81, 136.07, 135.36, 133.56, 131.94, 128.87, 128.62, 127.83, 127.63, 127.54, 126.78, 126.44, 125.95, 125.34, 122.13, 56.38, 45.18, 41.49, 35.96, 29.07, 29.05, 20.96. HRMS (ESI, m/z): calcd for $C_{25}H_{25}$ $[M+H]^+$ 325.1951, found 325.1958; LRMS (EI, m/z): 324 (M^+ , 100), 296 (48), 180 (18), 165 (20), 141 (66); IR (film): 744, 811, 907, 1509, 2958 cm^{-1} .

(1*S*,3*R*,4*R*,*E*)-2-((*E*)-3-phenylallylidene)-3-(*p*-tolyl)bicyclo[2.2.1]heptane (3i), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a yellow oil (70 mg, 78%, d.r. = 4:1). 1H NMR (400 MHz, $CDCl_3$) mixture δ 1.22 (d, J = 9.9 Hz, 1H), 1.42-1.49 (m, 2.8H), 1.65-1.78 (m, 4H), 2.30 (s, 1H), 2.32 (s, 3.7H), 3.35 (s, 1H), 3.41 (s, 1H), 5.89 (d, J = 11.0 Hz, 1H), 6.35 (t, J = 5.0 Hz, 0.8H), 6.39 (s, 0.6H), 7.03-7.22 (m, 8.8H), 7.29 (t, J = 7.5 Hz, 2H), 7.38-7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.85, 141.42, 137.97, 135.33, 129.65, 128.82, 128.52, 128.43, 126.91, 126.62, 126.07, 122.01, 55.32, 45.47, 40.95, 35.44, 29.38, 28.98, 20.94. HRMS (ESI, m/z): calcd for $C_{23}H_{25}$ $[M+H]^+$ 301.1951, found 301.1956; LRMS (EI, m/z): 300 (M^+ , 100), 181 (35), 156 (32), 117 (33), 91 (39); IR (film): 691, 747, 962, 1510, 2959 cm^{-1} .

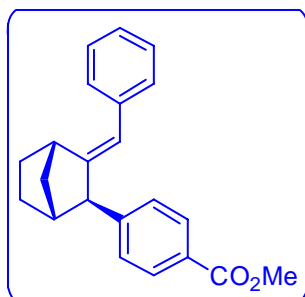
(1*S*,3*R*,4*R*,*E*)-2-benzylidene-3-(4-chlorophenyl)bicyclo[2.2.1]heptane (3j), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (45 mg, 51%, d.r. = 5 : 1). 1H NMR (400 MHz, $CDCl_3$) mixture δ 1.21 (d, J = 9.4 Hz, 1H), 1.50-1.68 (m, 3.8H), 1.75-1.92 (m, 2.4H), 2.28 (d, J = 3.3 Hz, 1H), 3.39 (d, J = 3.0 Hz, 1H), 3.48 (s, 1H), 6.07 (s, 1H), 6.59 (s, 0.2H), 7.06-7.08 (m, 0.6H), 7.13 (d, J = 8.4 Hz, 0.4H), 7.19-7.22 (m, 3.7H), 7.25 (t, J = 8.4 Hz, 3H), 7.30-7.36 (m, 4.2H), 7.59 (d, J = 8.5 Hz, 0.3H). ^{13}C NMR (100 MHz,

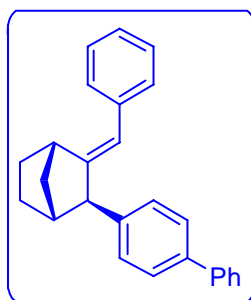
CDCl₃) δ 150.23, 143.23, 138.18, 131.55, 130.01, 128.27, 128.18, 128.04, 126.15, 122.46, 55.96, 45.08, 41.33, 35.74, 28.96, 28.91. HRMS (ESI, m/z): calcd for C₂₀H₂₀Cl [M+H]⁺ 295.1248, found 295.1254; LRMS (EI, m/z): 294 (M⁺, 92), 266 (100), 203 (35), 115 (50), 91 (77); IR (film): 700, 770, 816, 1489, 2959 cm⁻¹.

methyl 4-((1R,2R,4S,E)-3-benzylidenebicyclo[2.2.1]heptan-2-yl)benzoate (3k), racemic



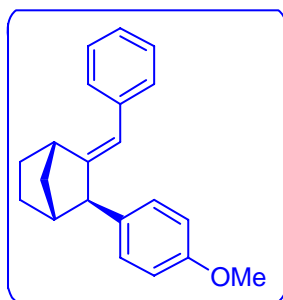
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (PE : EA = 100 : 1), the product was isolated as a white solid (71 mg, 74%, d.r. = 9 : 1). ¹H NMR (400 MHz, CDCl₃) δ 1.23 (d, J = 9.5 Hz, 1H), 1.54-1.70 (m, 3H), 1.77-1.94 (m, 2H), 2.33 (d, J = 3.4 Hz, 1H), 3.41 (d, J = 2.9 Hz, 1H), 3.57 (s, 1H), 3.91 (s, 3H), 6.08 (s, 1H), 7.18-7.22 (m, 1H), 7.30-7.36 (m, 6H), 7.98 (d, J = 8.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 167.12, 150.19, 149.93, 138.13, 129.45, 128.69, 128.27, 128.04, 126.18, 122.59, 56.60, 51.96, 45.08, 41.35, 35.86, 29.09, 28.91. HRMS (ESI, m/z): calcd for C₂₂H₂₃O₂ [M+H]⁺ 319.1693, found 319.1700; LRMS (EI, m/z): 318 (M⁺, 100), 290 (97), 259 (38), 115 (41), 91 (74); IR (film): 703, 760, 1279, 1721, 2954 cm⁻¹.

(1R,2R,4S,E)-2-([1,1'-biphenyl]-4-yl)-3-benzylidenebicyclo[2.2.1]heptanes (3l), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a colorless oil (73 mg, 72%, d.r. = 10 : 1). ¹H NMR (400 MHz, CDCl₃) δ 1.23 (d, J = 9.5 Hz, 1H), 1.58-1.61 (m, 1H), 1.66-1.71 (m, 2H), 1.77-1.94 (m, 2H), 2.36 (d, J = 3.3 Hz, 1H), 3.42 (d, J = 2.9 Hz, 1H), 3.57 (s, 1H), 6.16 (s, 1H), 7.19-7.22 (m, 1H), 7.32-7.36 (m, 7H), 7.42 (t, J = 7.4 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.58-7.61 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.56, 143.93, 141.01, 138.76, 138.41, 129.12, 128.68, 128.25, 128.07, 127.01, 126.84, 126.03, 122.30, 56.32, 45.19, 41.41, 35.92, 29.03, 29.01. HRMS (ESI, m/z): calcd for C₂₆H₂₅ [M+H]⁺ 337.1951, found 337.1957; LRMS (EI, m/z): 336 (M⁺, 100), 308 (50), 245 (21), 217 (45), 167 (26); IR (film): 696, 729, 760, 1486, 2958 cm⁻¹.

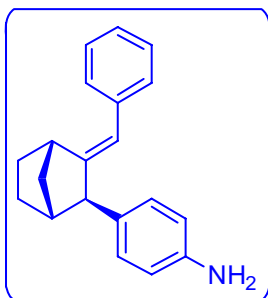
(1S,3R,4R,E)-2-benzylidene-3-(4-methoxyphenyl)bicyclo[2.2.1]heptanes (3m), racemic



The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (PE : EA = 200 : 1), the product was isolated as a white solid (59 mg, 68%, d.r. = 11 : 1). ¹H NMR (400 MHz, CDCl₃) δ 1.19 (d, J = 9.5 Hz, 1H), 1.52-1.57 (m, 1H), 1.62-1.67 (m, 2H), 1.73-1.91 (m, 2H), 2.27 (d, J = 3.3 Hz, 1H), 3.38 (d, J = 3.1 Hz, 1H), 3.47 (s, 1H), 3.80 (s, 3H), 6.10 (s, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.18-7.20 (m, 3H), 7.32-7.33 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 157.73, 151.05, 138.46, 136.94, 129.57, 128.22, 128.04, 125.95, 122.06, 113.48, 55.82, 55.22, 45.13, 41.35, 35.80, 28.96, 28.90. HRMS (ESI, m/z): calcd for C₂₁H₂₃O [M+H]⁺ 291.1743, found 291.1750; LRMS (EI, m/z): 290 (M⁺, 100),

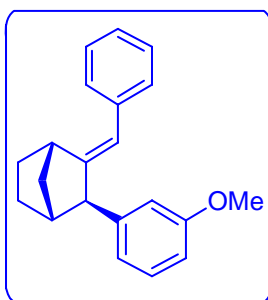
262 (50), 171 (60), 121 (41), 91 (33); IR (film): 702, 771, 1245, 1509, 2956 cm^{-1} .

4-((1R,2R,4S,E)-3-benzylidenebicyclo[2.2.1]heptan-2-yl)aniline (3n), racemic



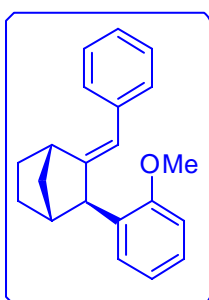
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE : EA = 25 : 1), the product was isolated as a yellow solid (61 mg, 74%, d.r. = 11 : 1). ^1H NMR (400 MHz, CDCl_3) δ 1.18 (d, J = 9.8 Hz, 1H), 1.49-1.55 (m, 1H), 1.61-1.65 (m, 2H), 1.70-1.90 (m, 2H), 2.25 (d, J = 3.1 Hz, 1H), 3.36 (d, J = 2.4 Hz, 1H), 3.42 (s, 1H), 3.56 (s, 2H), 6.10 (s, 1H), 6.64 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 7.16-7.19 (m, 1H), 7.31-7.32 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.25, 144.26, 138.56, 134.97, 129.48, 128.19, 128.02, 125.86, 121.85, 114.95, 55.87, 45.13, 41.33, 35.83, 28.96, 28.87. HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 276.1747, found 276.1746; LRMS (EI, m/z): 275 (M^+ , 100), 247 (34), 234 (26), 156 (46), 106 (43); IR (film): 695, 771, 1513, 2957, 3371 cm^{-1} .

(1S,3R,4R,E)-2-benzylidene-3-(3-methoxyphenyl)bicyclo[2.2.1]heptane (3o), racemic



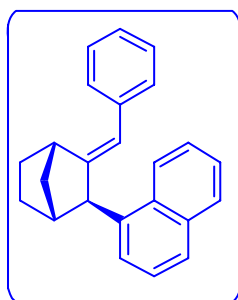
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE : EA = 250 : 1), the product was isolated as a colorless oil (66 mg, 76%, d.r. = 14 : 1). ^1H NMR (400 MHz, CDCl_3) δ 1.20 (d, J = 10.0 Hz, 1H), 1.53-1.59 (m, 1H), 1.63-1.68 (m, 2H), 1.75-1.91 (m, 2H), 2.33 (d, J = 3.1 Hz, 1H), 3.38 (d, J = 2.4 Hz, 1H), 3.50 (s, 1H), 3.79 (s, 3H), 6.13 (s, 1H), 6.75 (dd, J = 8.1 Hz, 2.3 Hz, 1H), 6.84 (s, 1H), 6.88 (d, J = 7.6 Hz, 1H), 7.18-7.24 (m, 2H), 7.32-7.35 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.42, 150.45, 146.44, 138.43, 128.99, 128.22, 128.07, 125.99, 122.30, 121.22, 114.55, 111.03, 56.57, 55.15, 45.17, 41.36, 36.02, 29.03, 29.00. HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 291.1743, found 291.1742; LRMS (EI, m/z): 290 (M^+ , 100), 262 (66), 171 (23), 115 (28), 91 (37); IR (film): 696, 765, 1265, 1598, 2957 cm^{-1} .

(1S,3S,4R,E)-2-benzylidene-3-(2-methoxyphenyl)bicyclo[2.2.1]heptanes (3p), racemic



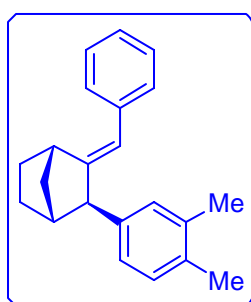
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a colorless oil (41 mg, 47%, d.r. > 20:1). ^1H NMR (400 MHz, CDCl_3) δ 1.16 (d, J = 9.8 Hz, 1H), 1.56-1.69 (m, 3H), 1.73-1.92 (m, 2H), 2.28 (d, J = 3.2 Hz, 1H), 3.39 (d, J = 2.9 Hz, 1H), 3.78 (s, 1H), 3.88 (s, 3H), 6.08 (s, 1H), 6.87-6.91 (m, 2H), 7.17-7.23 (m, 3H), 7.33-7.34 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.70, 150.97, 138.64, 133.19, 128.93, 128.21, 128.05, 126.84, 125.84, 121.87, 119.95, 109.83, 55.32, 50.34, 43.07, 41.62, 35.90, 29.13, 28.79. HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 291.1743, found 291.1738; LRMS (EI, m/z): 290 (M^+ , 67), 262 (100), 128 (36), 115 (48), 91 (61); IR (film): 752, 1030, 1239, 1489, 2953 cm^{-1} .

1-((1*R*,2*S*,4*S*,*E*)-3-benzylidenebicyclo[2.2.1]heptan-2-yl)naphthalene (3q), racemic



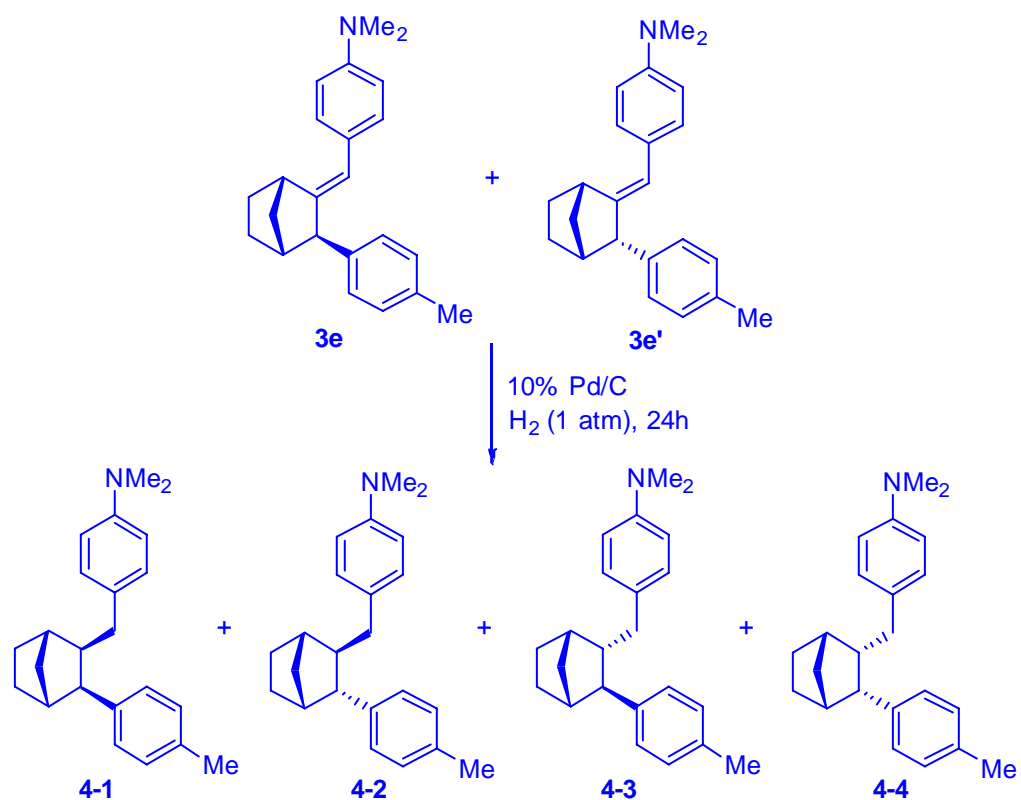
The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a white solid (63 mg, 68%, d.r. > 20:1). ¹H NMR (400 MHz, CDCl₃) δ 1.21 (d, *J* = 10.0 Hz, 1H), 1.62-1.65 (m, 1H), 1.75-1.81 (m, 2H), 1.85-2.00 (m, 2H), 2.42 (s, 1H), 3.49 (d, *J* = 1.3 Hz, 1H), 4.22 (s, 1H), 6.18 (s, 1H), 7.20-7.23 (m, 1H), 7.34-7.43 (m, 6H), 7.48-7.58 (m, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.73, 140.30, 138.45, 133.90, 132.36, 128.86, 128.29, 128.10, 126.62, 126.05, 125.87, 125.51, 125.39, 125.30, 123.65, 122.67, 53.14, 43.91, 41.69, 36.32, 29.42, 28.70. HRMS (ESI, *m/z*): calcd for C₂₄H₂₃ [M+H]⁺ 311.1794, found 311.1794; LRMS (EI, *m/z*): 310 (M⁺, 100), 282 (39), 241 (34), 191 (36), 165 (44); IR (film): 693, 732, 777, 787, 2958 cm⁻¹.

(1*S*,3*R*,4*R*,*E*)-2-benzylidene-3-(3,4-dimethylphenyl)bicyclo[2.2.1]heptanes (3r), racemic

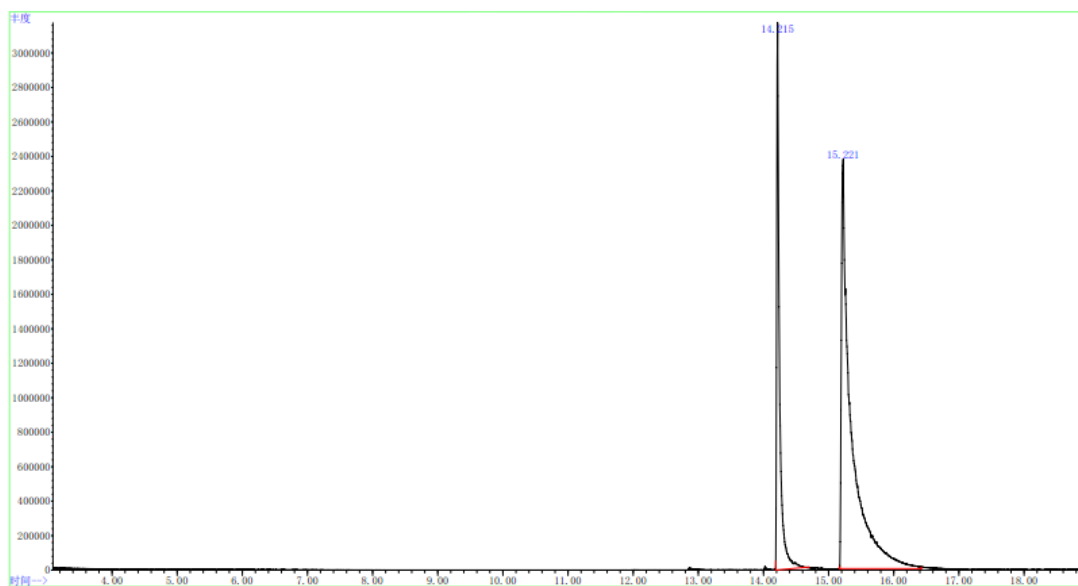


The title compound was obtained *via* the general procedure. After purification by silica gel column chromatography (eluted with PE), the product was isolated as a colorless oil (48 mg, 56%, dr = 13 : 1). ¹H NMR (400 MHz, CDCl₃) δ 1.18 (d, *J* = 9.9 Hz, 1H), 1.52-1.57 (m, 1H), 1.62-1.68 (m, 2H), 1.74-1.91 (m, 2H), 2.24 (s, 3H), 2.25 (s, 3H), 2.28 (s, 1H), 3.38 (d, *J* = 1.0 Hz, 1H), 3.47 (s, 1H), 6.11 (s, 1H), 6.99-7.01 (m, 1H), 7.05-7.08 (m, 2H), 7.17-7.21 (m, 1H), 7.31-7.35 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 150.88, 142.35, 138.55, 136.19, 134.01, 130.14, 129.39, 128.22, 128.04, 126.03, 125.92, 122.02, 56.30, 45.24, 41.40, 35.89, 29.01, 19.87, 19.27. HRMS (ESI, *m/z*): calcd for C₂₂H₂₅ [M+H]⁺ 289.1951, found 289.1946; LRMS (EI, *m/z*): 288 (M⁺, 100), 273 (34), 260 (72), 169 (73), 115 (58); IR (film): 694, 770, 909, 1494, 2958 cm⁻¹.

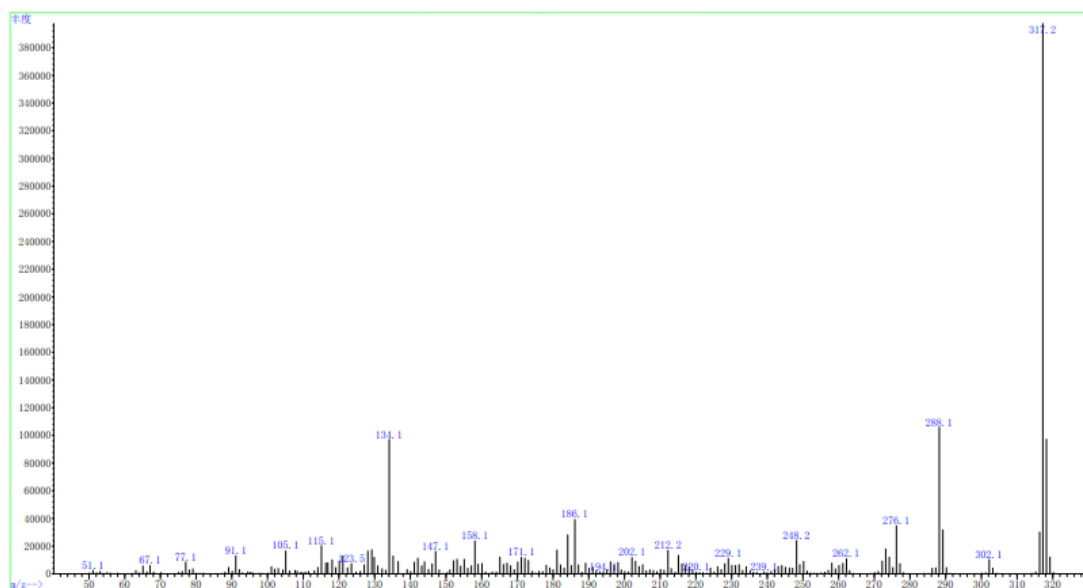
4. Pd/C-Catalyzed hydrogenation of 3e and 3e'.



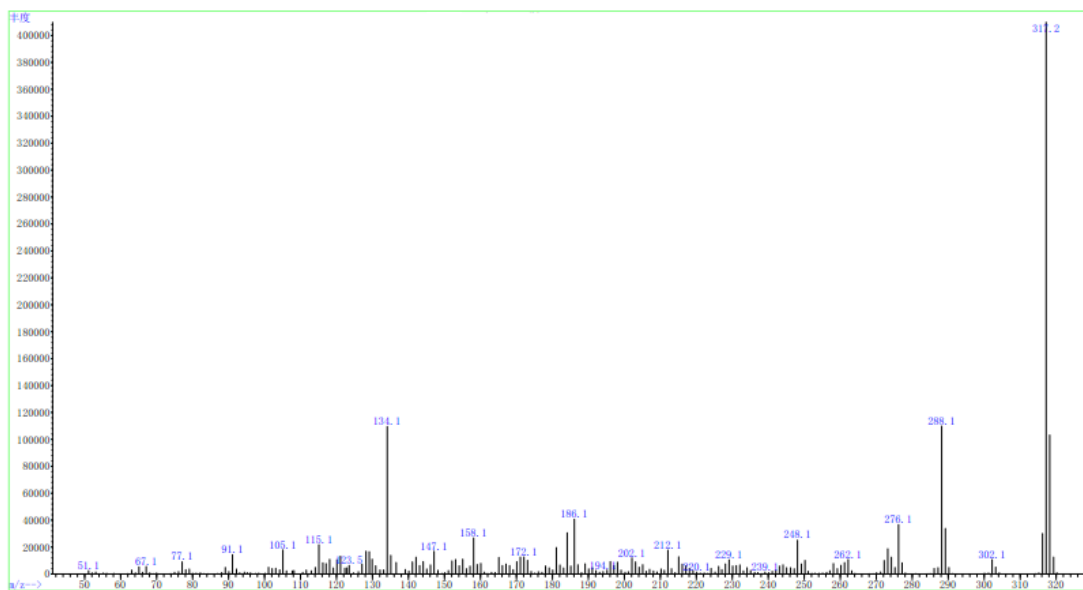
The GC-MS spectra of product 3e and 3e'



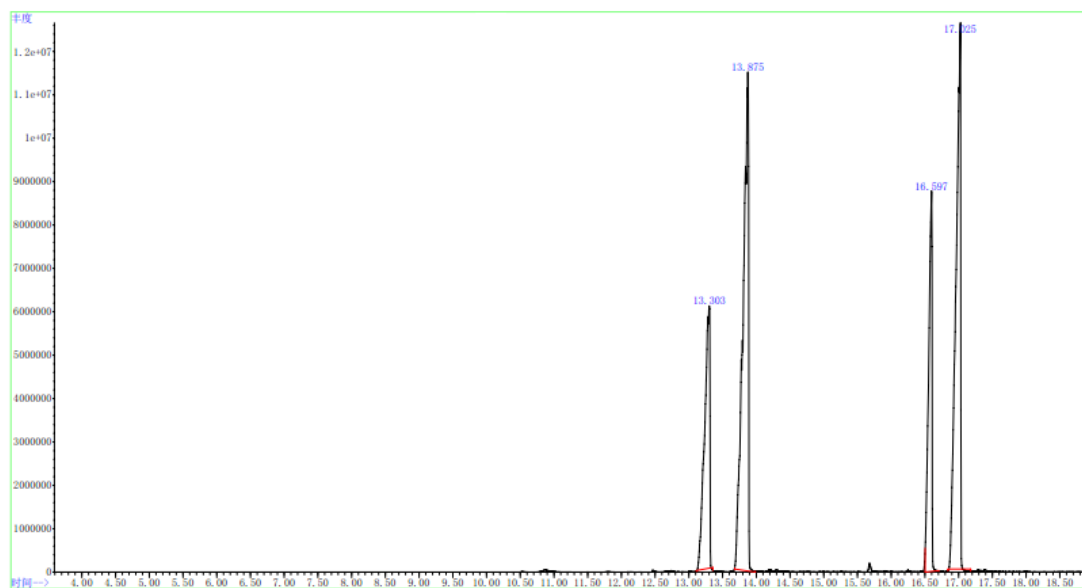
The MS spectra of the 1st peak



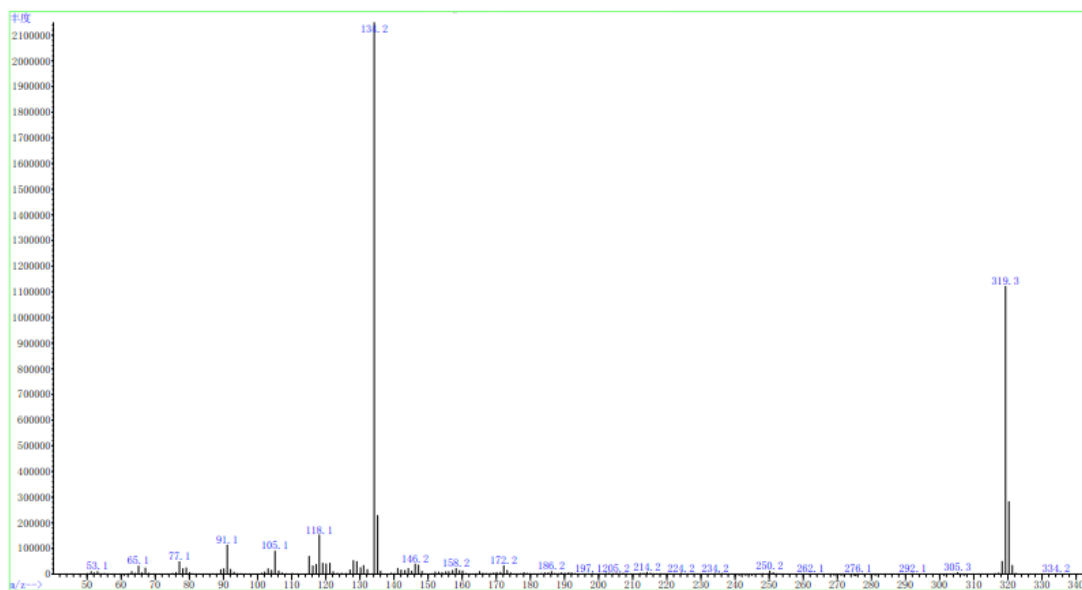
The MS spectra of the 2nd peak



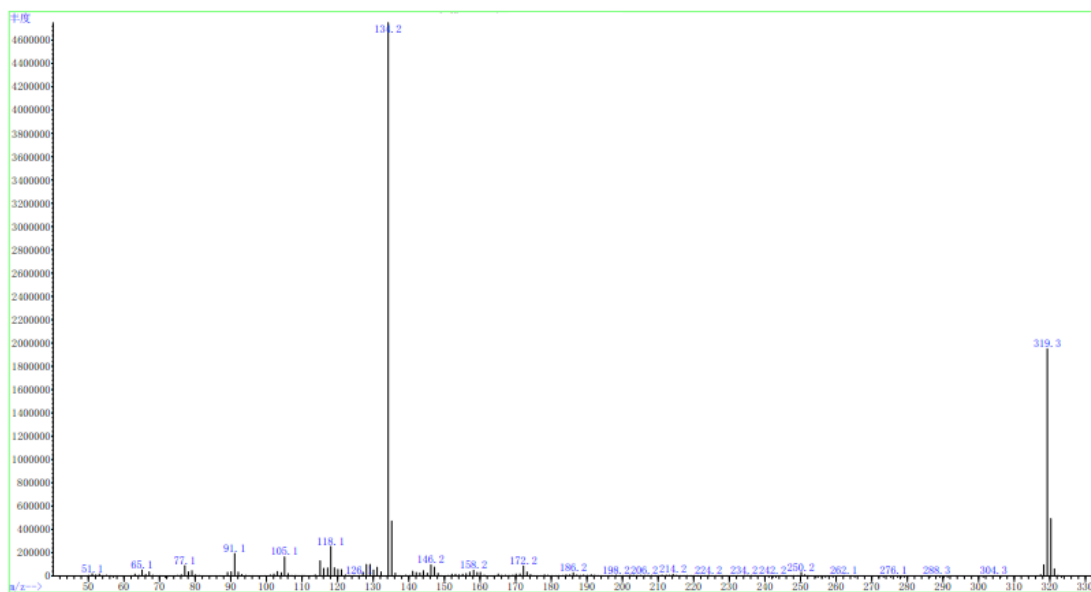
The GC-MS spectra of hydrogenation products (4-1, 4-2, 4-3, 4-4)



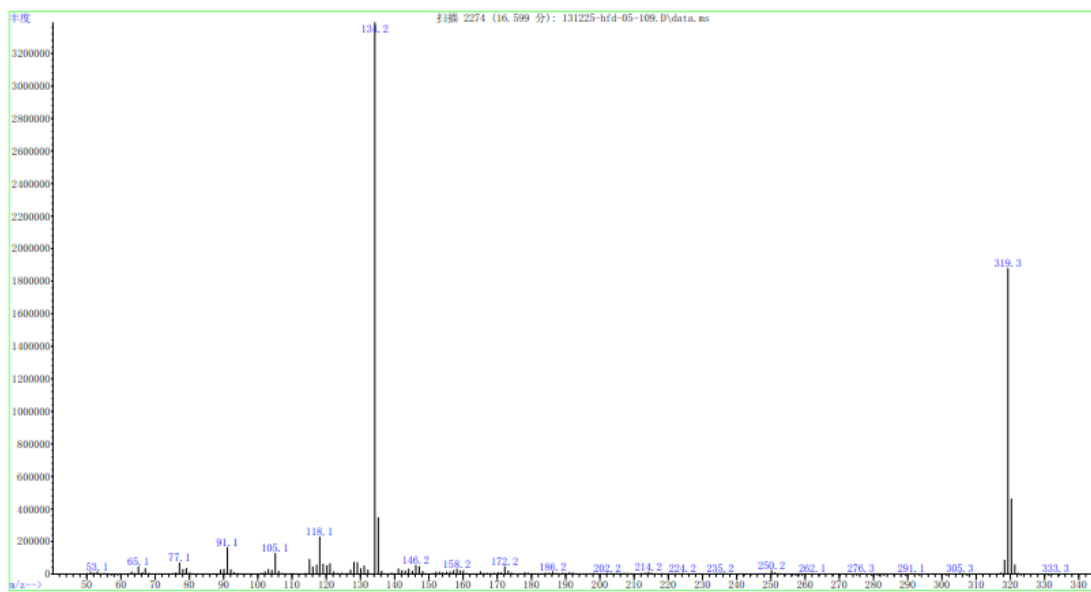
The MS spectra of the 1st peak



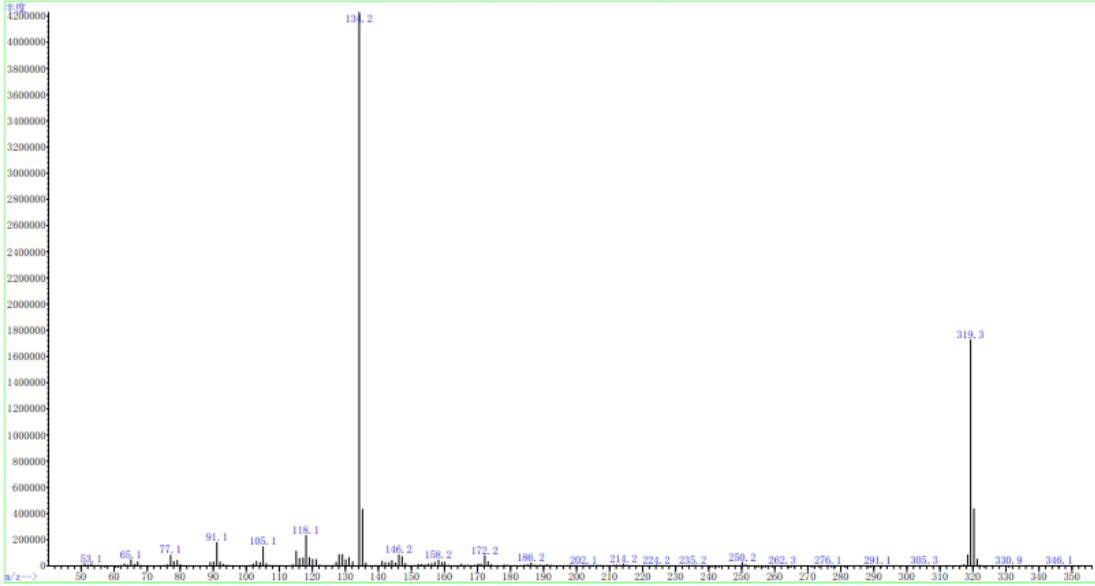
The MS spectra of the 2nd peak



The MS spectra of the 3rd peak

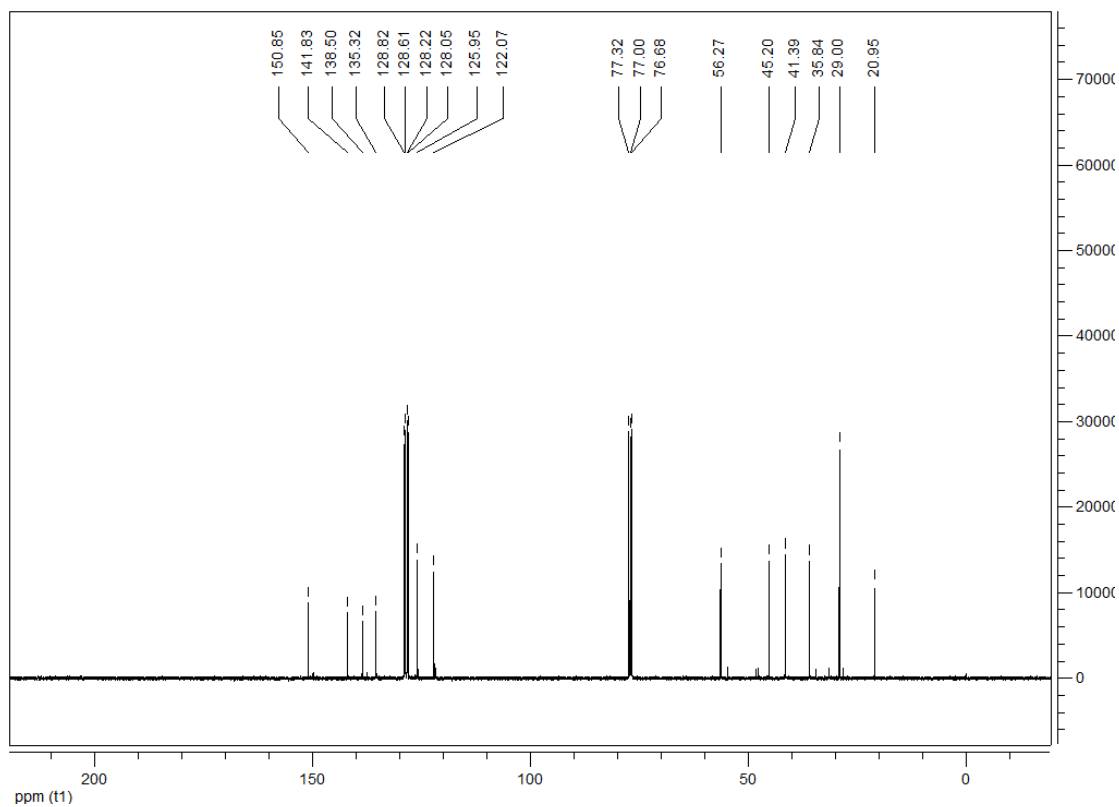
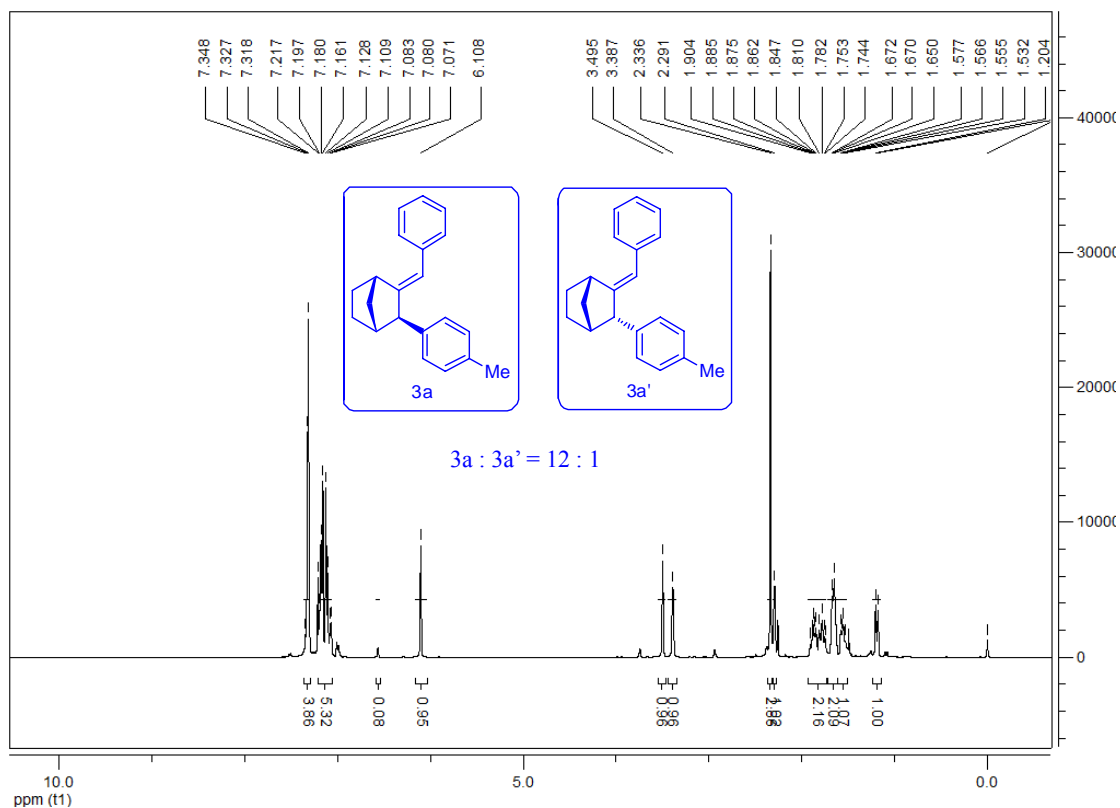


The MS spectra of the 4th peak

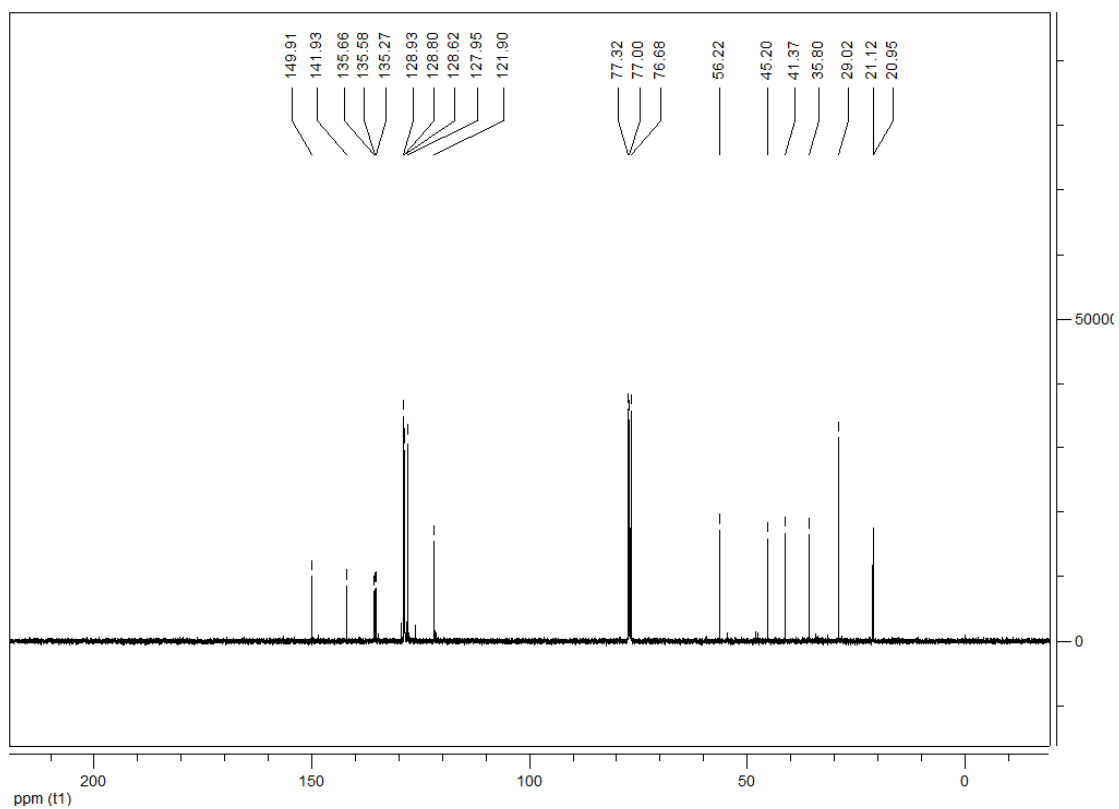
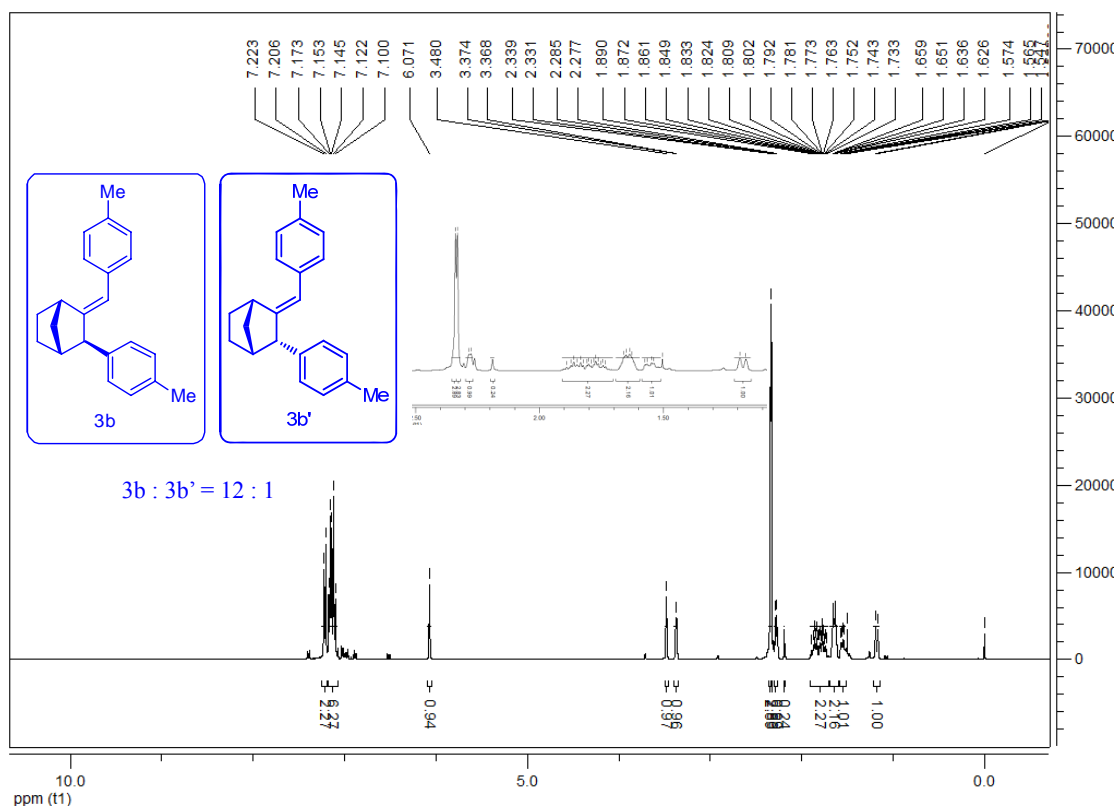


5. ¹H and ¹³C NMR spectra of products

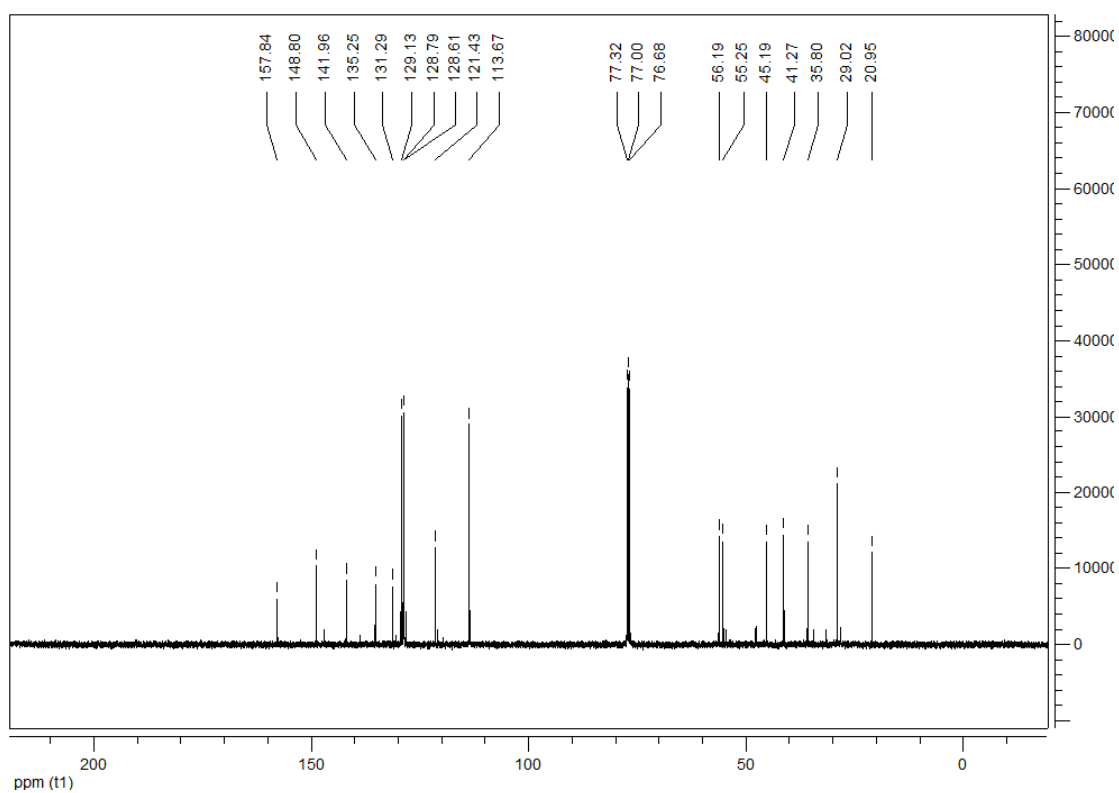
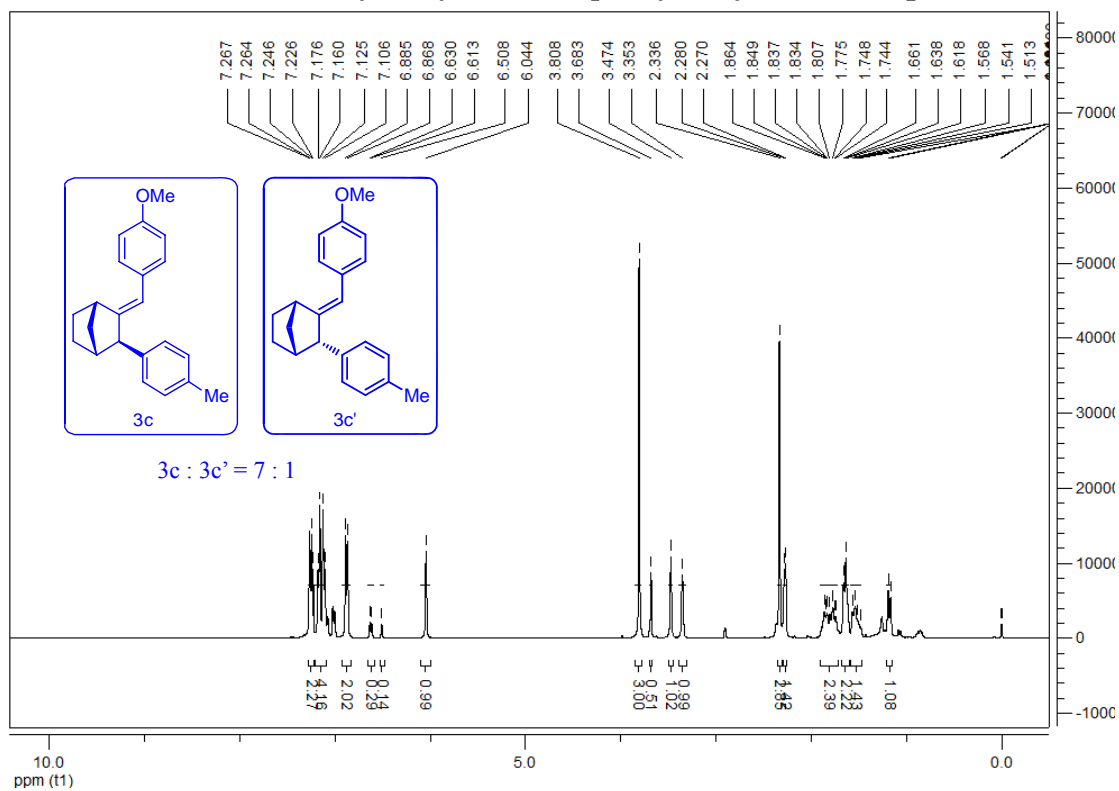
(1*S*,3*R*,4*R*,*E*)-2-benzylidene-3-(*p*-tolyl)bicyclo[2.2.1]heptane (**3a**), racemic



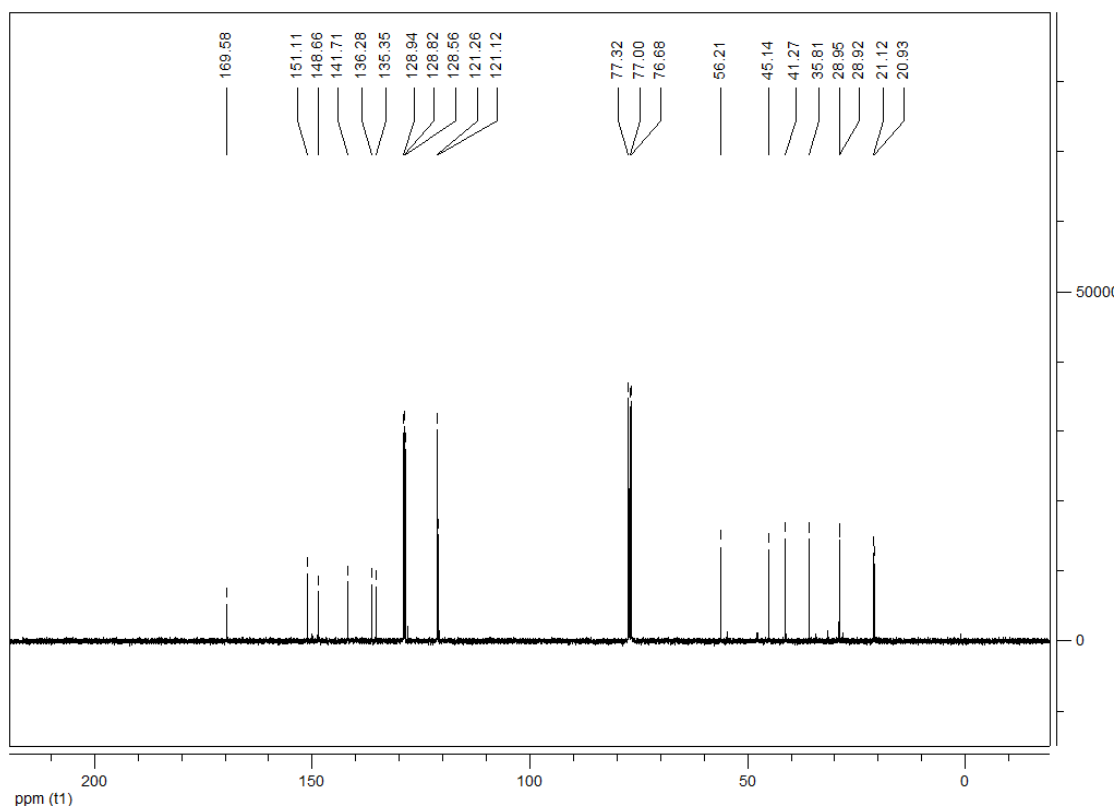
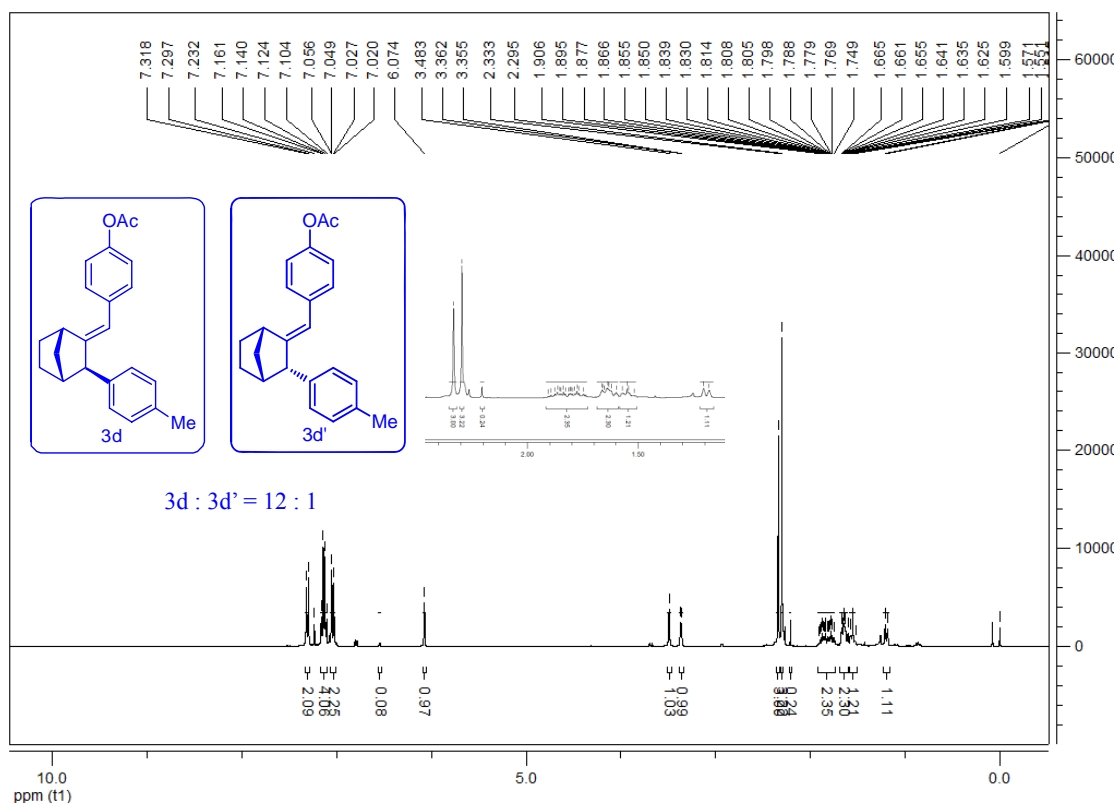
(1*S*,3*R*,4*R*,*E*)-2-(4-methylbenzylidene)-3-(*p*-tolyl)bicyclo[2.2.1]heptane (3b), racemic



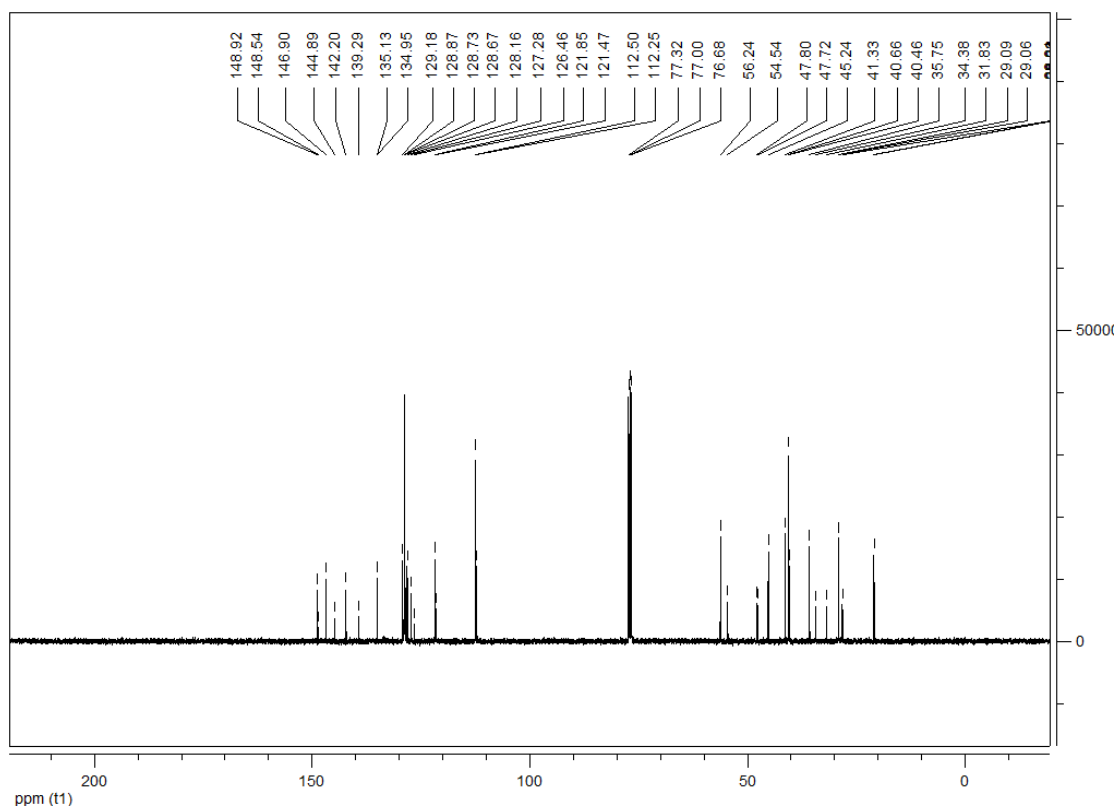
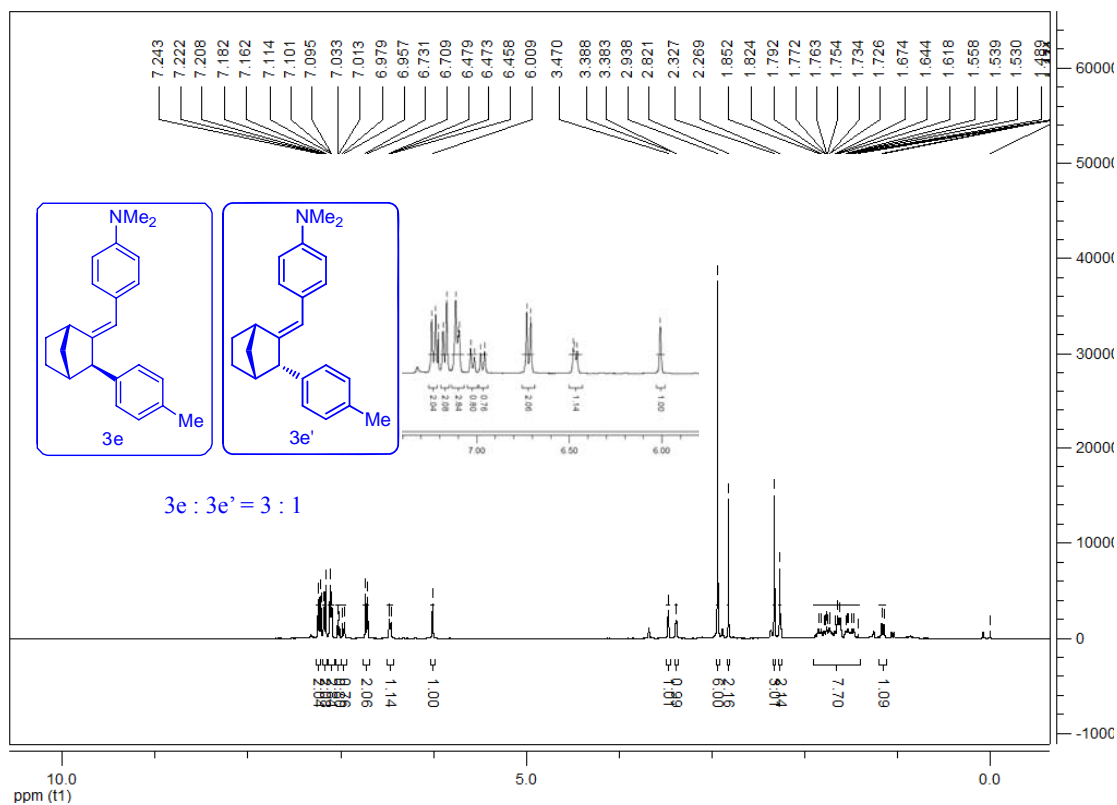
(1*S*,3*R*,4*R*,*E*)-2-(4-methoxybenzylidene)-3-(*p*-tolyl)bicyclo[2.2.1]heptanes (3c) , racemic



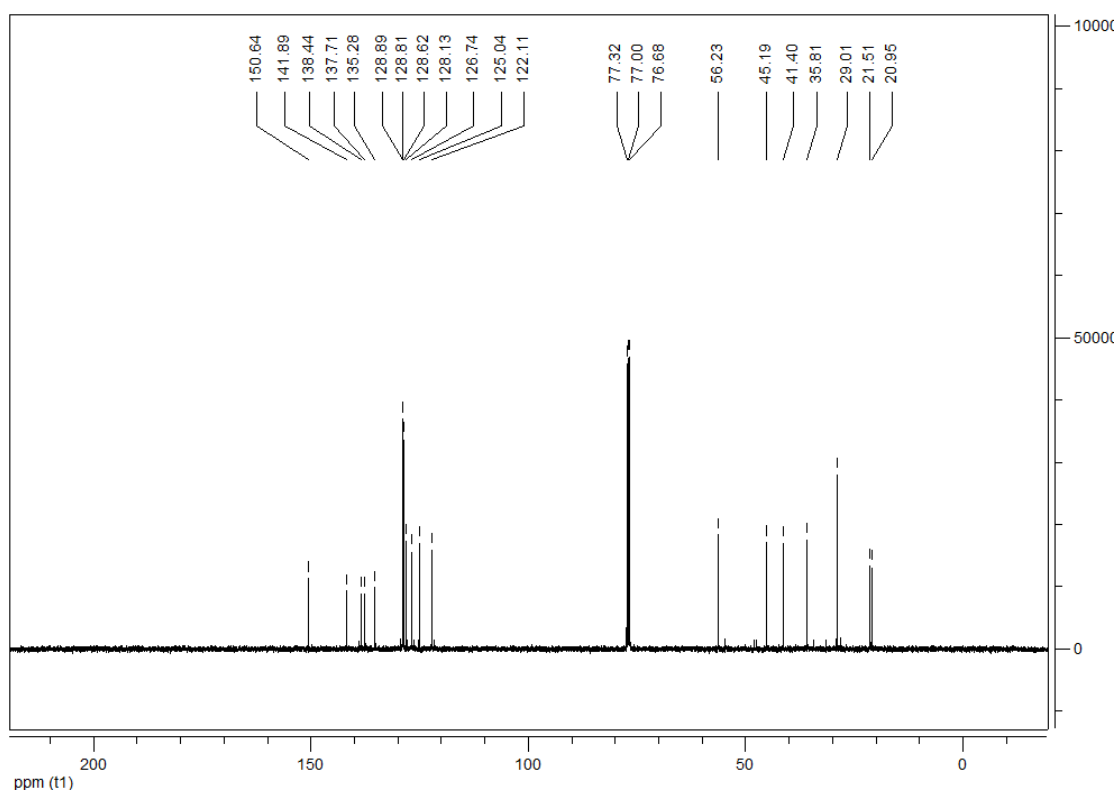
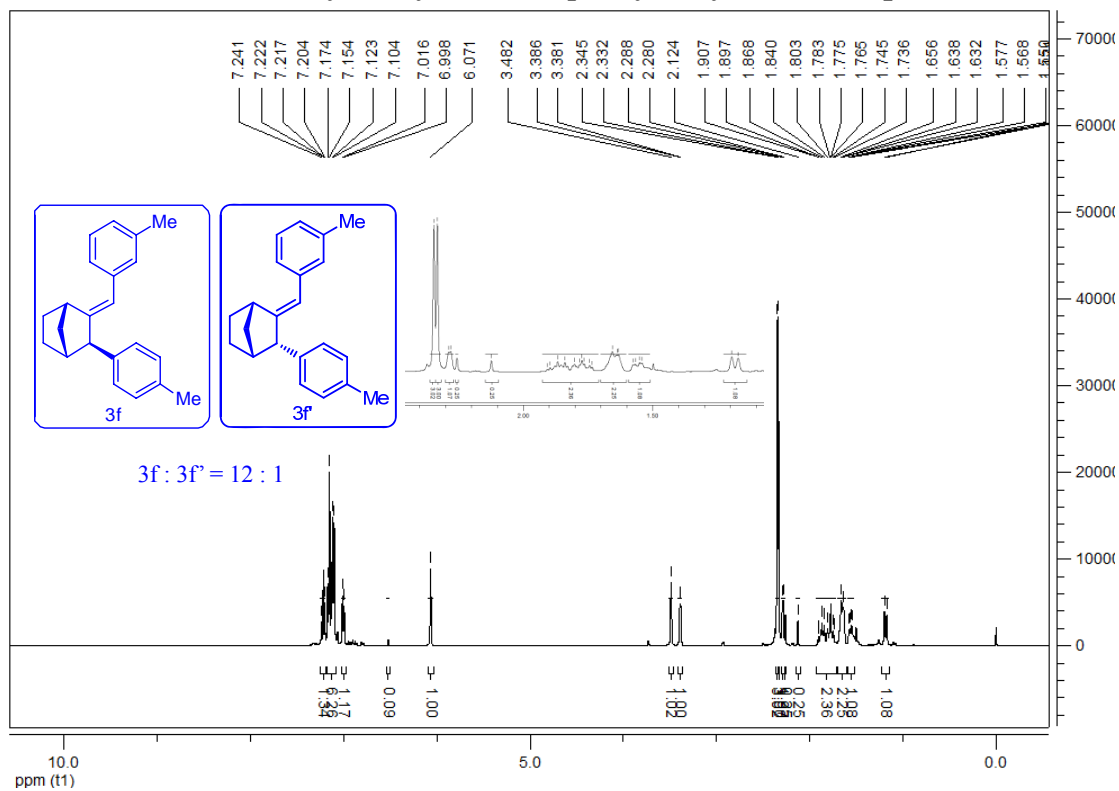
4-((*E*)-((1*S*,3*R*,4*R*)-3-(*p*-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)phenyl acetate (3d**), racemic**



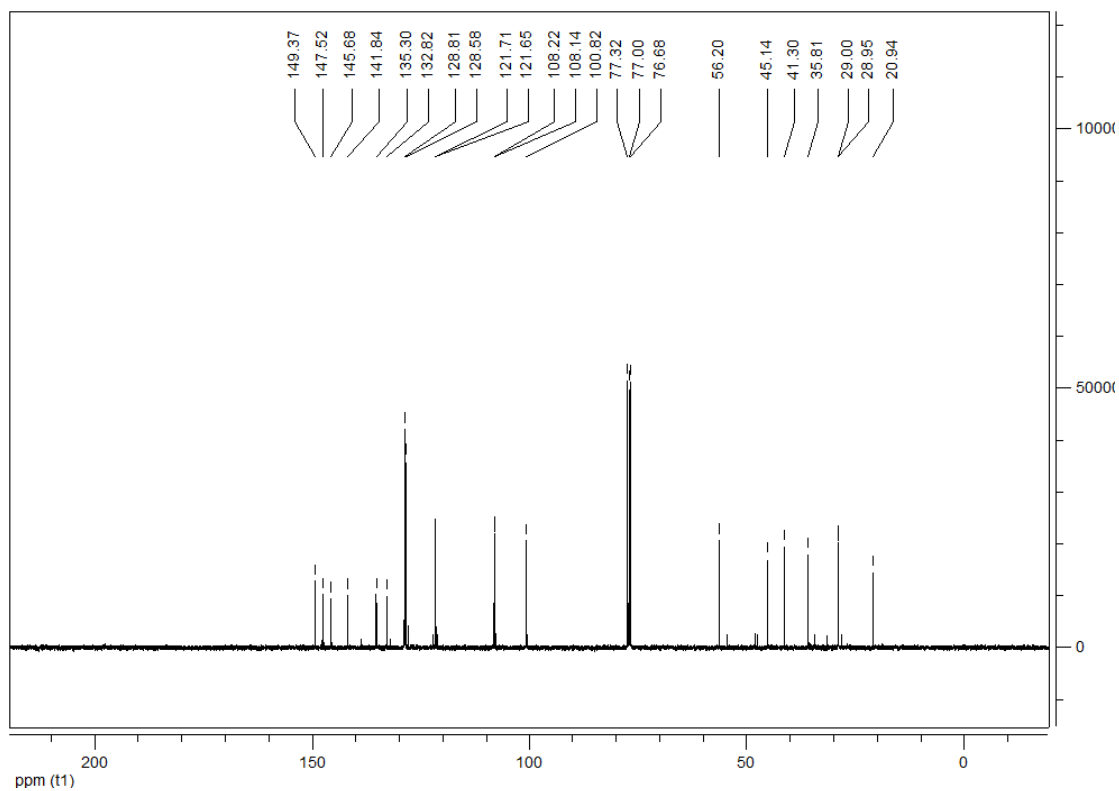
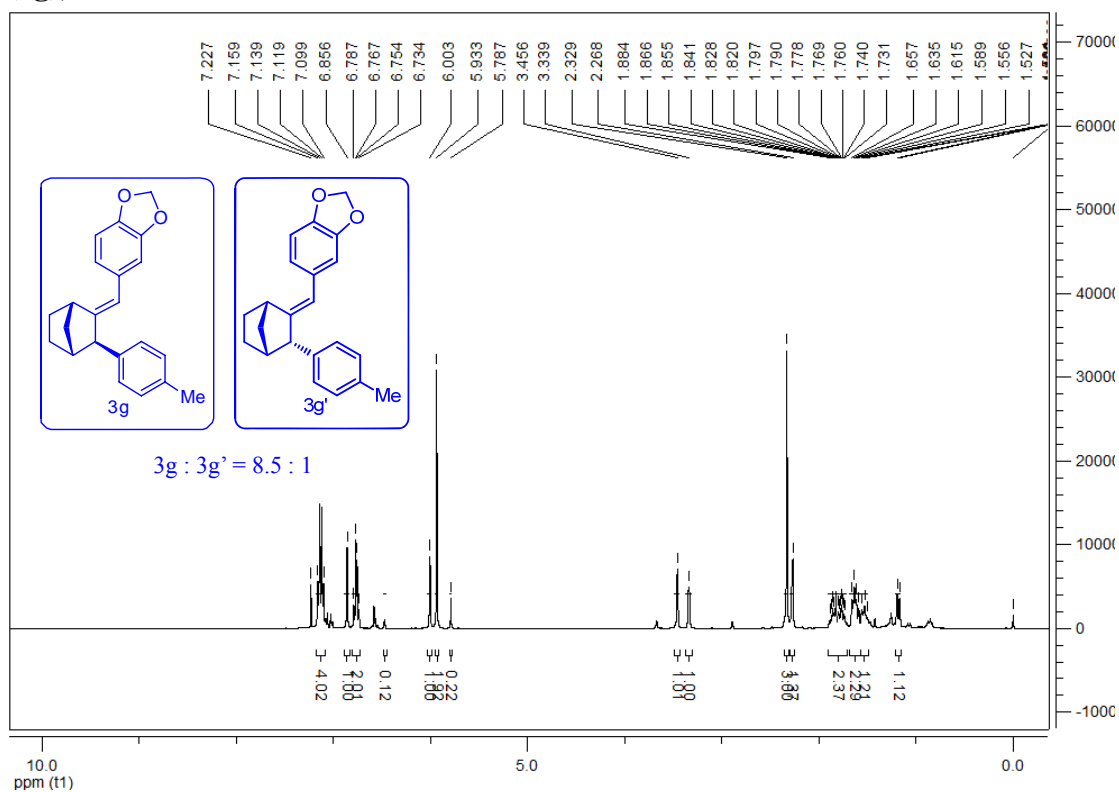
***N,N*-dimethyl-4-((*E*)-((1*S*,3*R*,4*R*)-3-(*p*-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)aniline (3e), racemic**



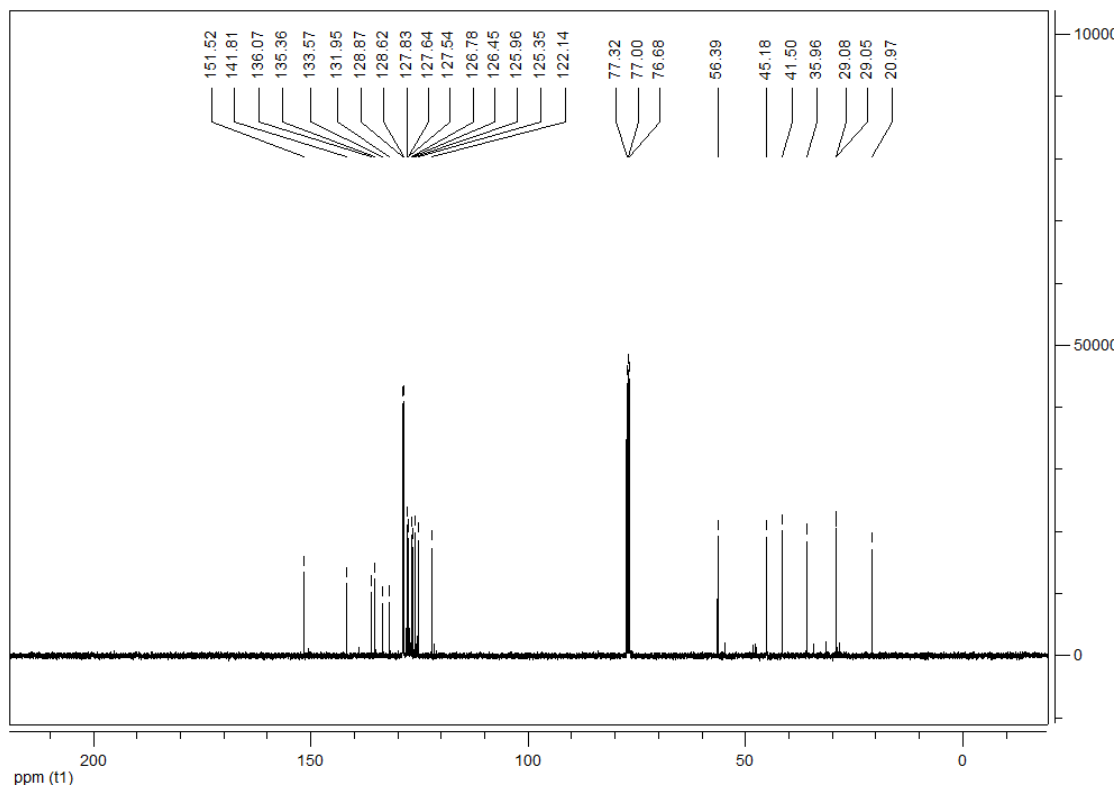
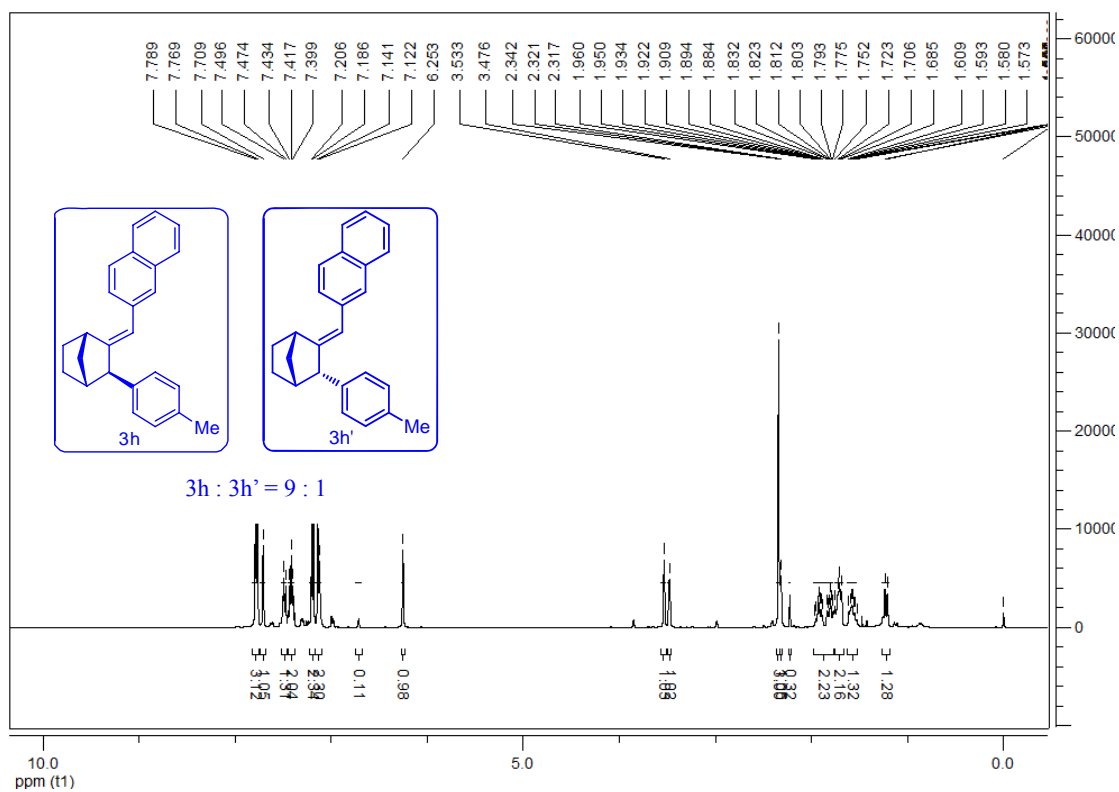
(1*S*,3*R*,4*R*,*E*)-2-(3-methylbenzylidene)-3-(*p*-tolyl)bicyclo[2.2.1]heptane (3f), racemic



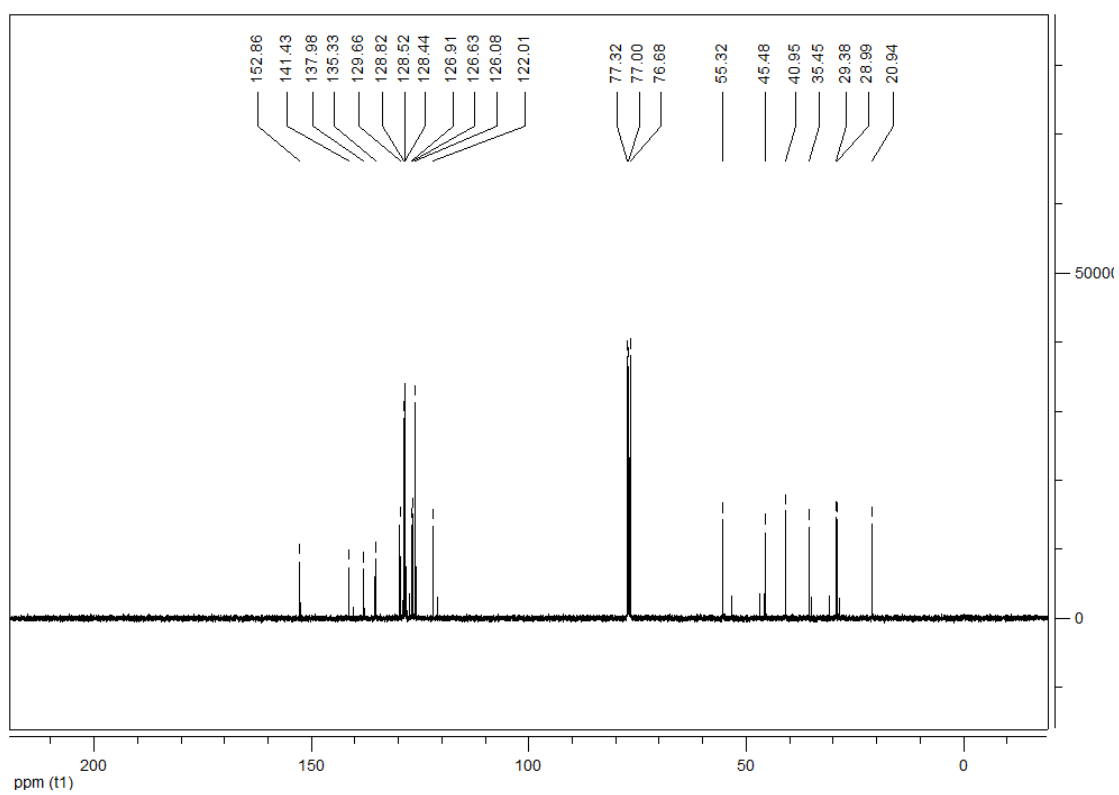
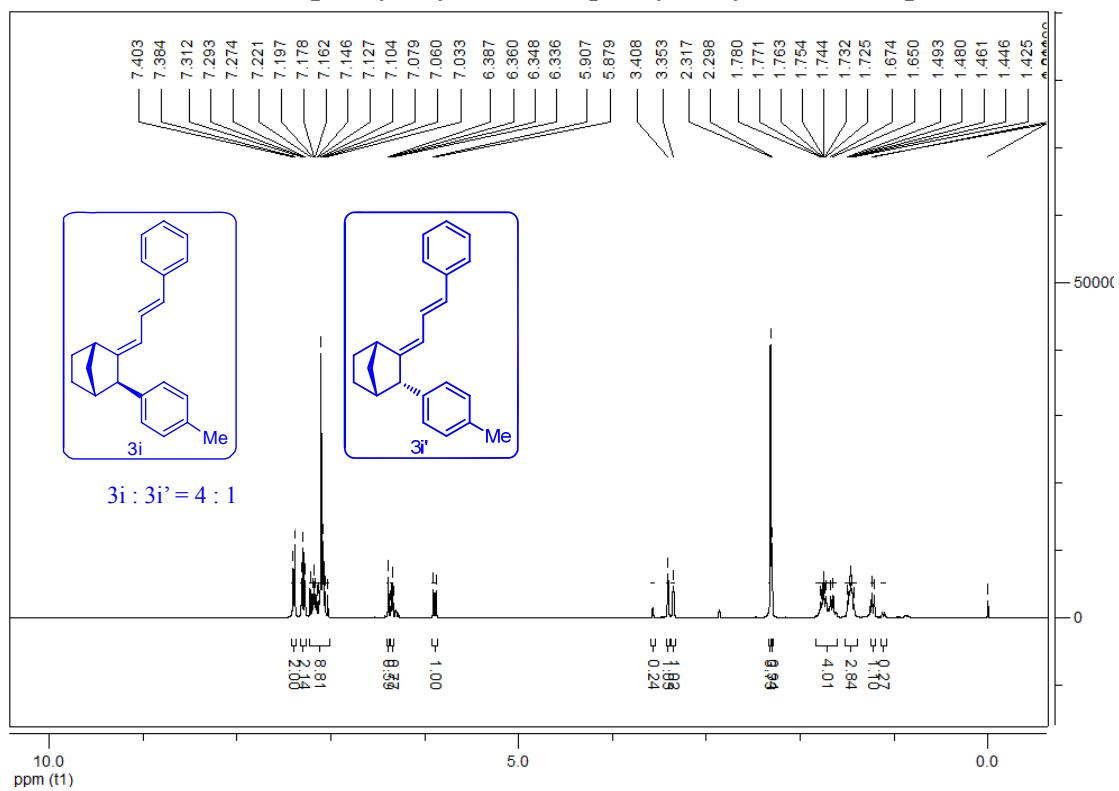
5-((*E*)-((1*S*,3*R*,4*R*)-3-(*p*-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)benzo[*d*][1,3]dioxole (3g), racemic



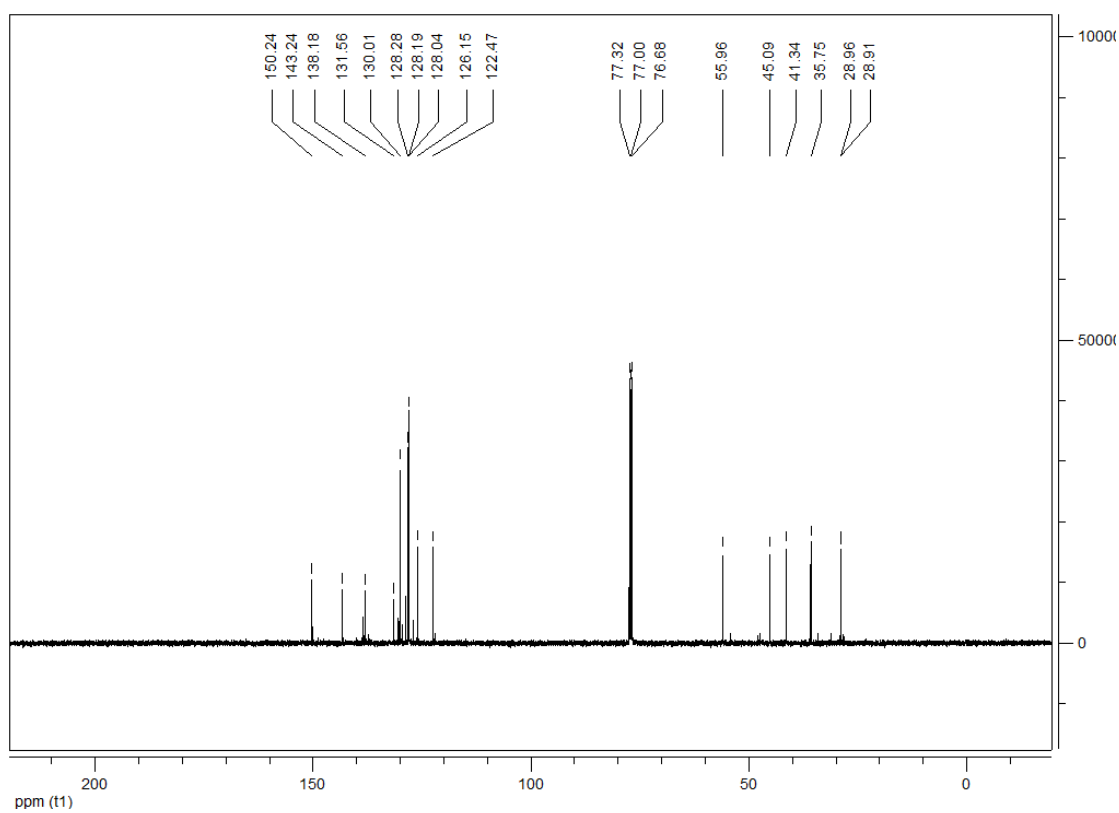
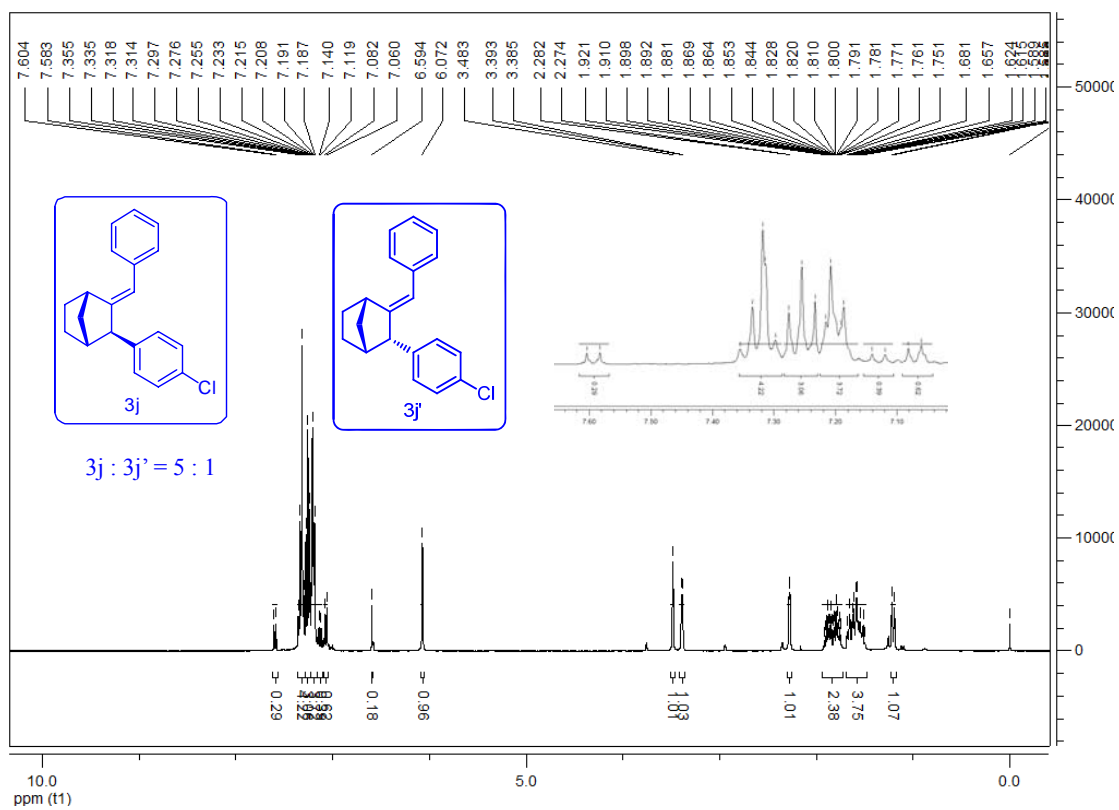
2-((E)-((1S,3R,4R)-3-(p-tolyl)bicyclo[2.2.1]heptan-2-ylidene)methyl)naphthalene (3h), racemic



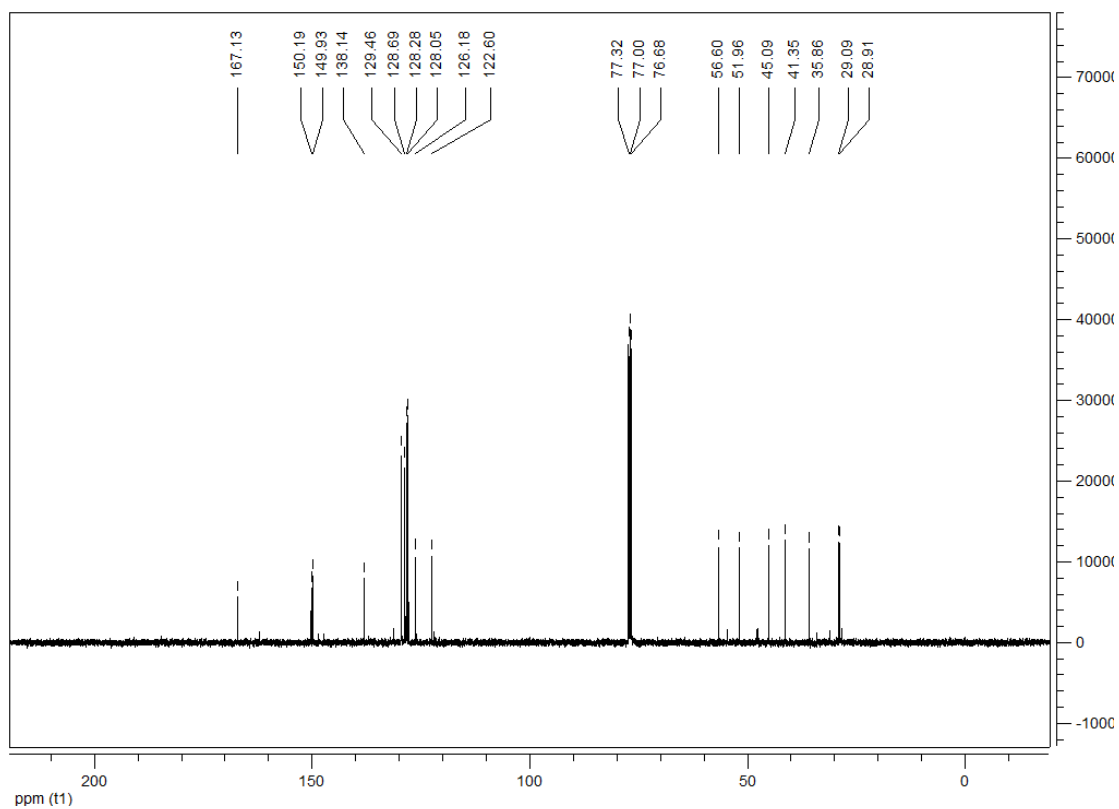
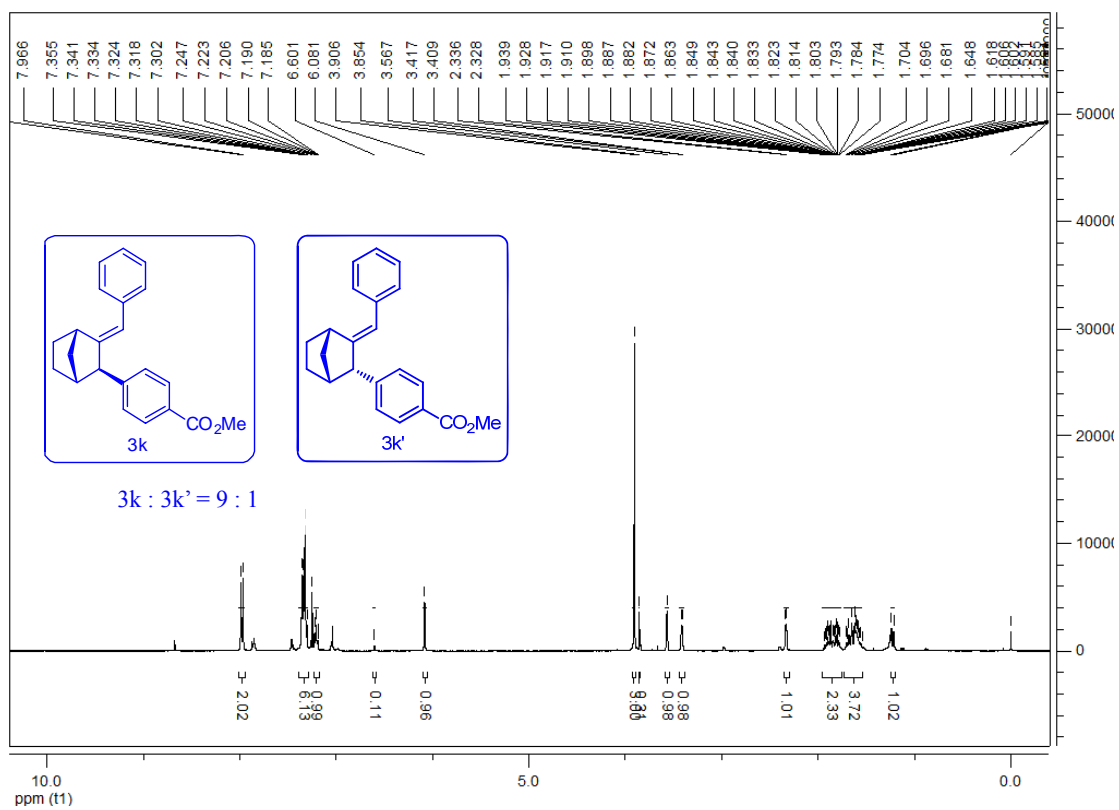
(1*S*,3*R*,4*R*,*E*)-2-((*E*)-3-phenylallylidene)-3-(*p*-tolyl)bicyclo[2.2.1]heptane (3i) , racemic



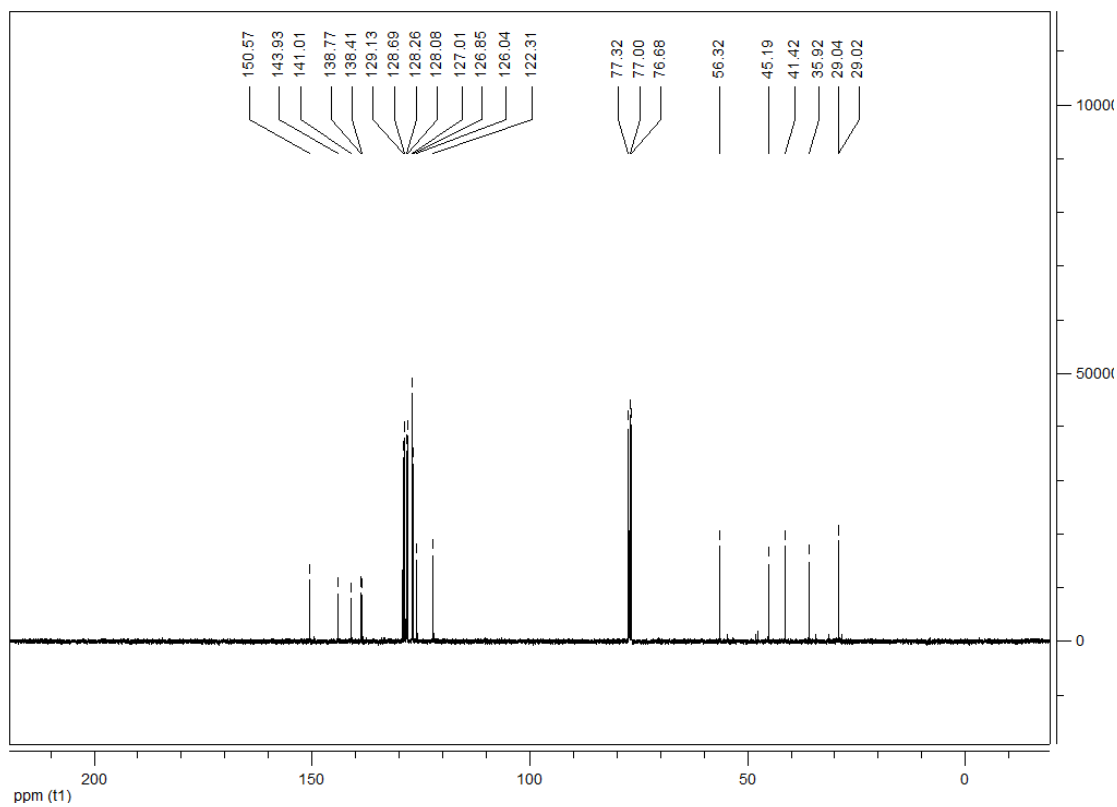
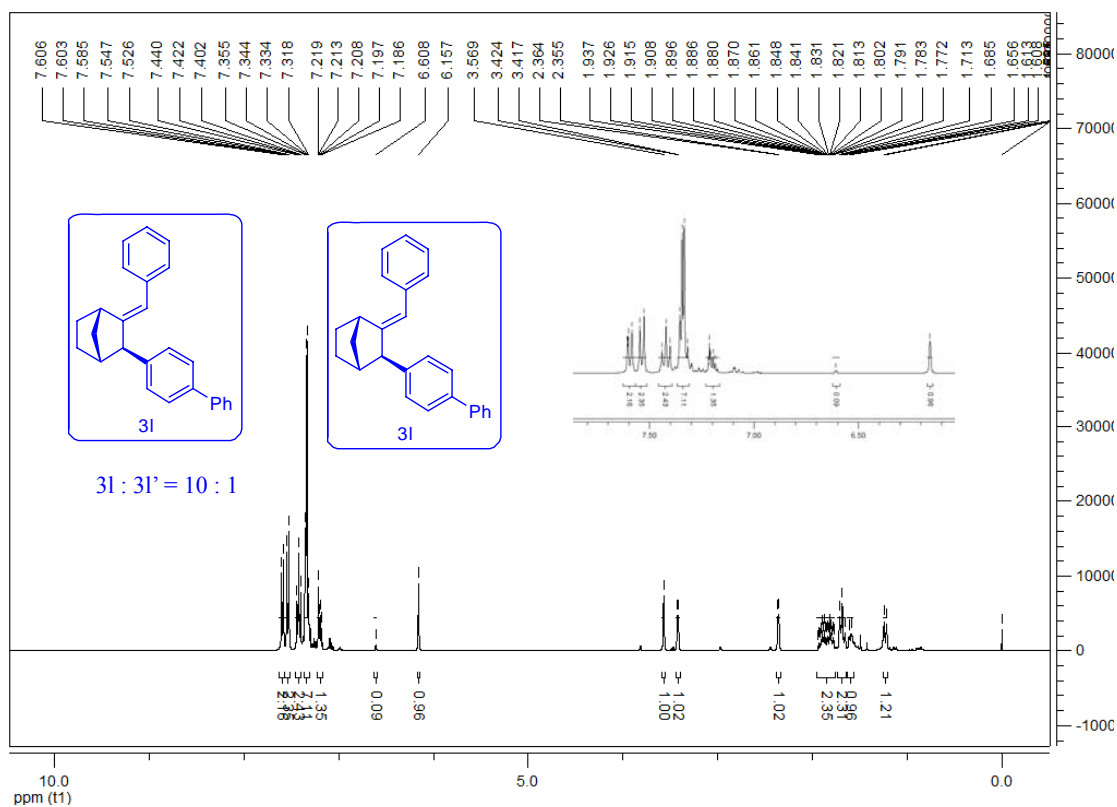
(1*S*,3*R*,4*R*,*E*)-2-benzylidene-3-(4-chlorophenyl)bicyclo[2.2.1]heptane (3j), racemic



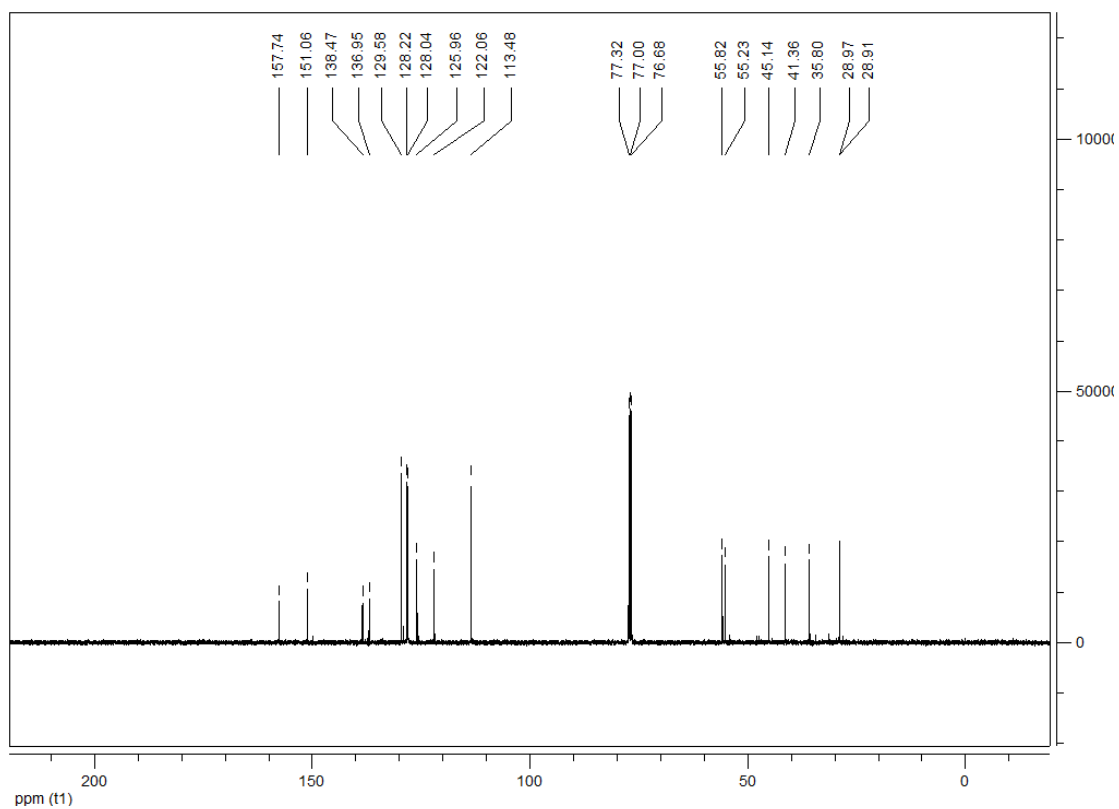
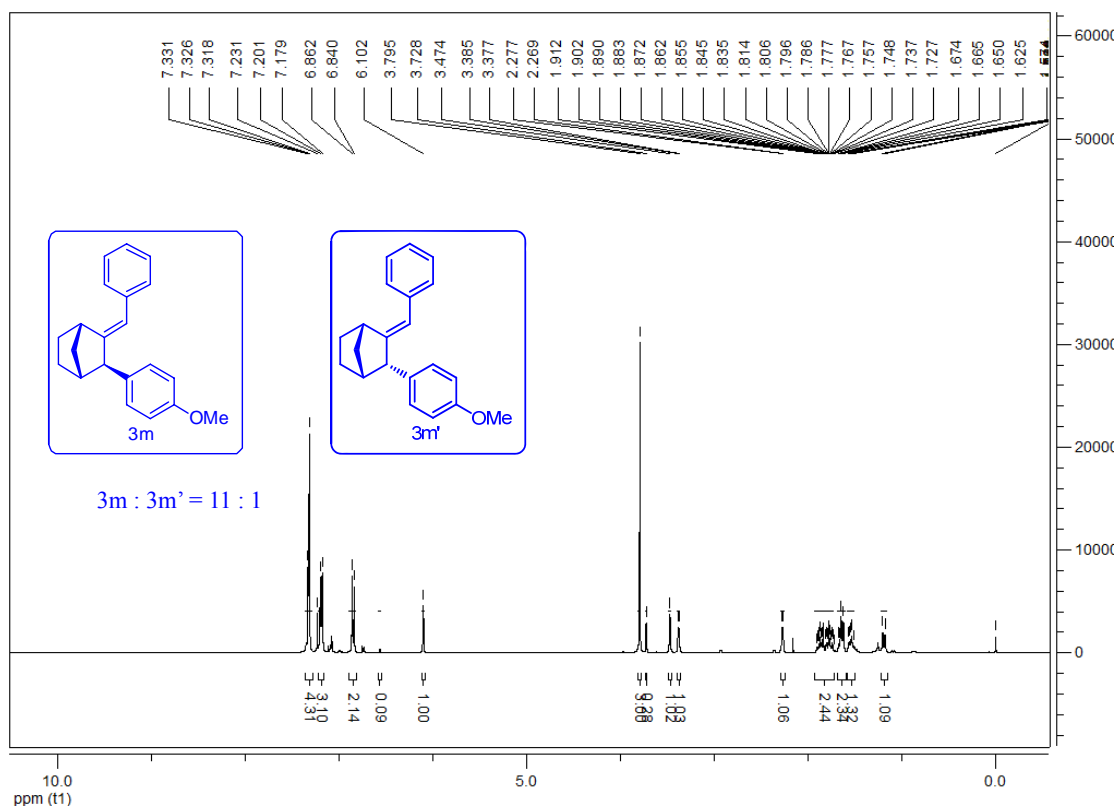
methyl 4-((1*R*,2*R*,4*S*,*E*)-3-benzylidenebicyclo[2.2.1]heptan-2-yl)benzoate (3k), racemic



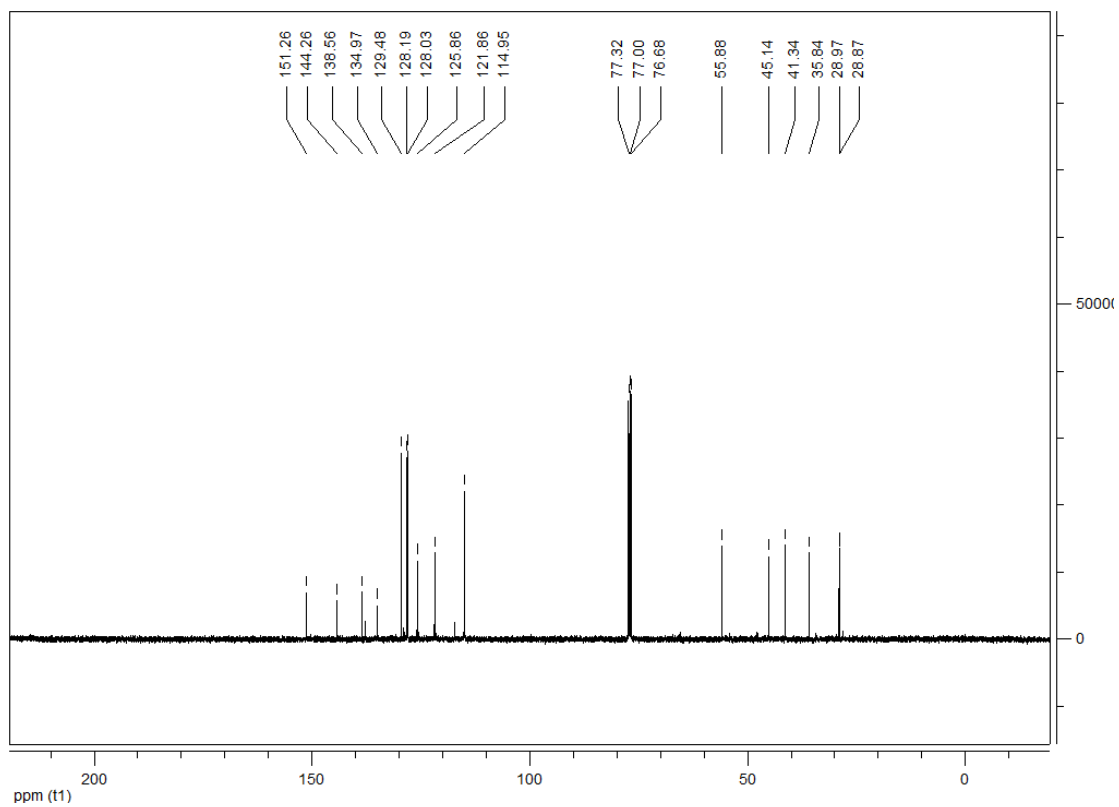
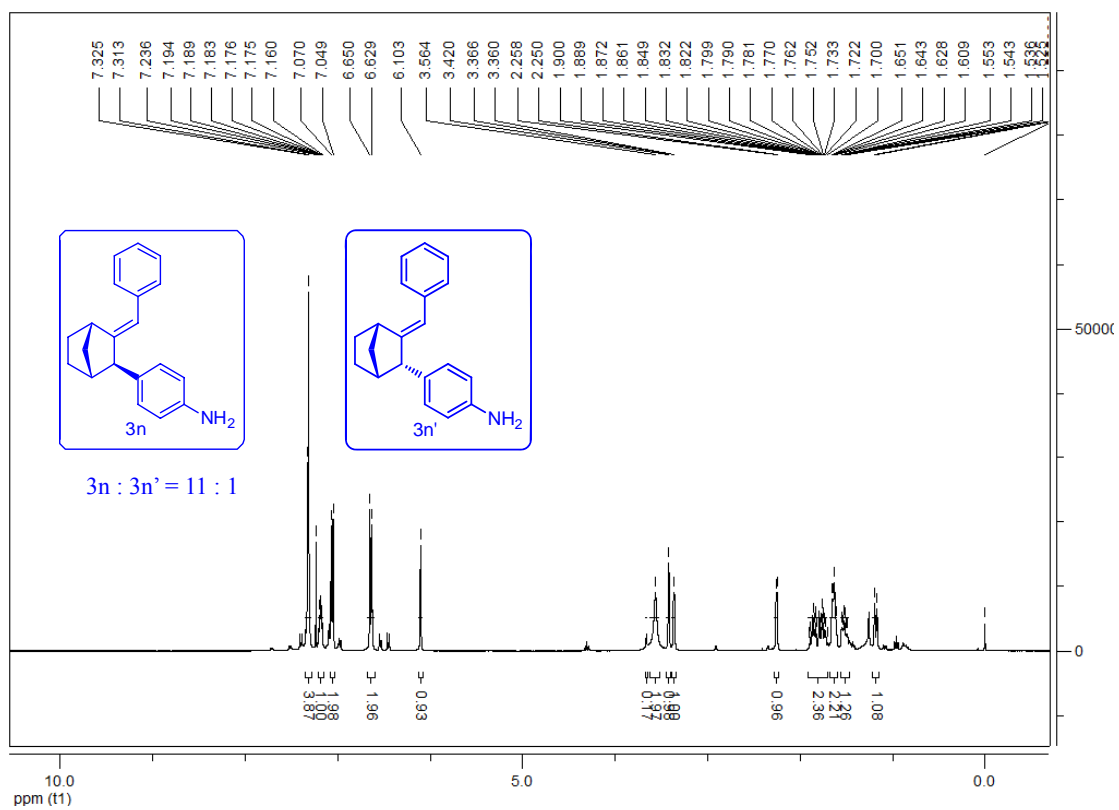
(1*R*,2*R*,4*S*,*E*)-2-([1,1'-biphenyl]-4-yl)-3-benzylidenebicyclo[2.2.1]heptanes (3I), racemic



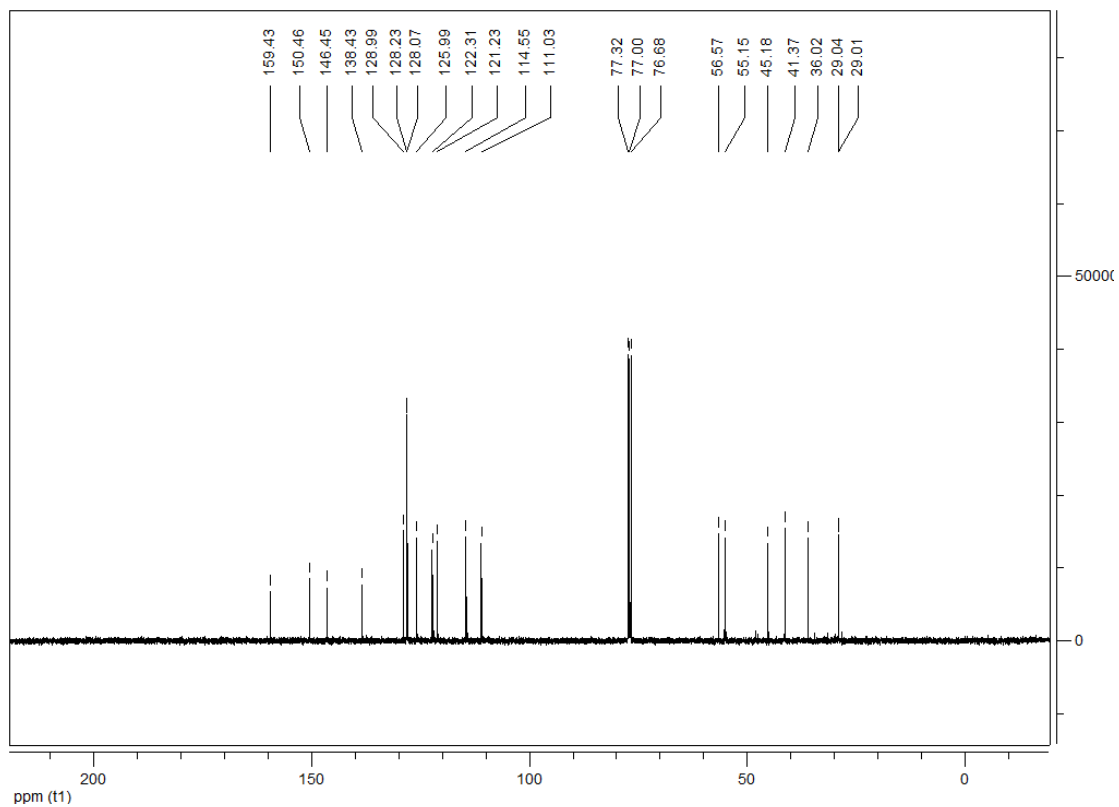
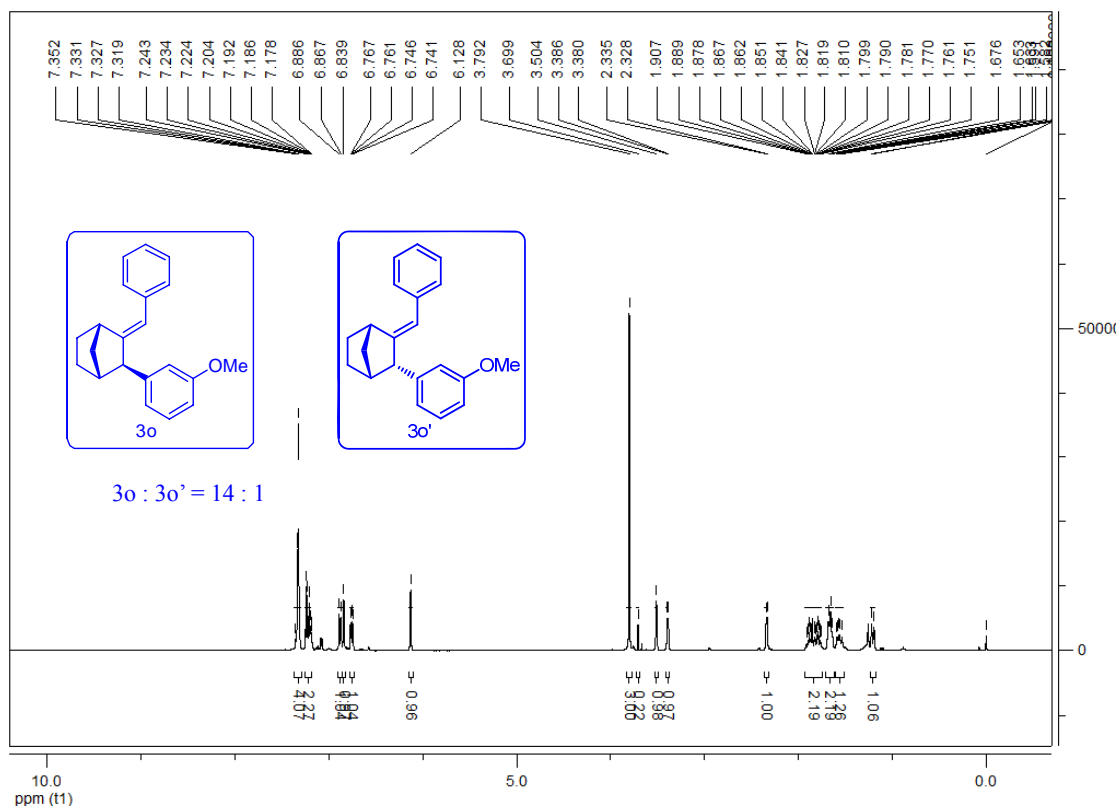
(1*S*,3*R*,4*R*,*E*)-2-benzylidene-3-(4-methoxyphenyl)bicyclo[2.2.1]heptanes (3*m*), racemic



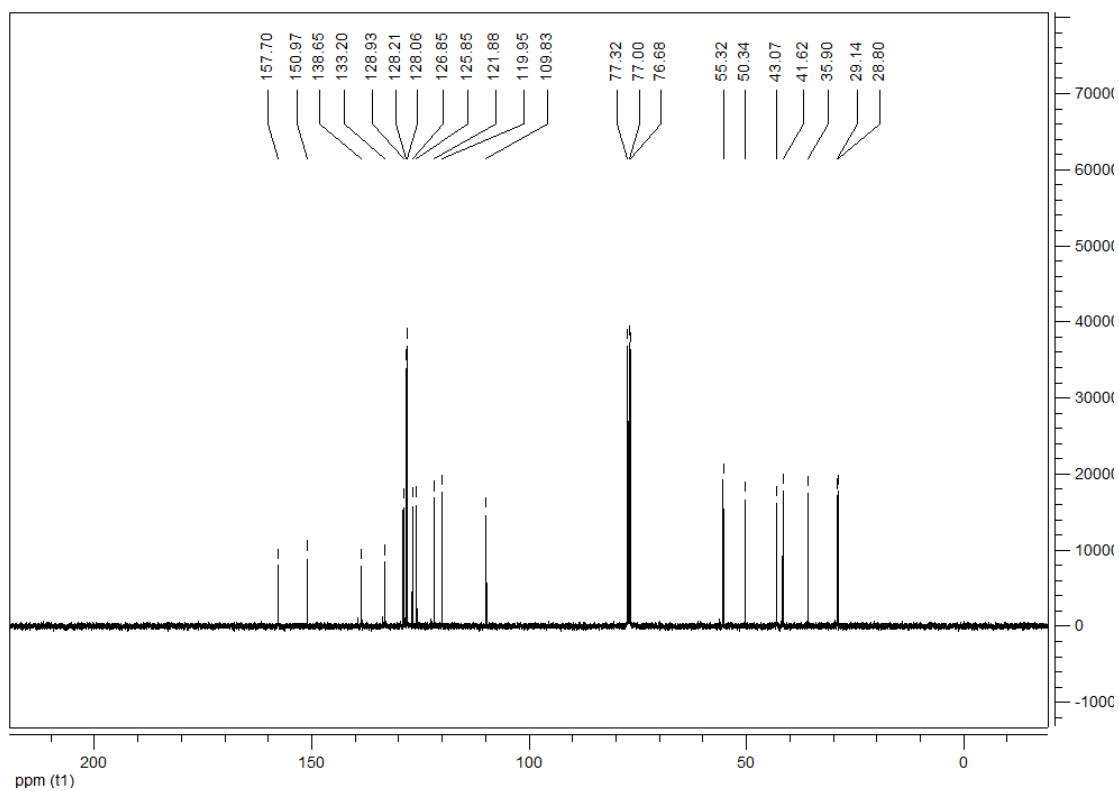
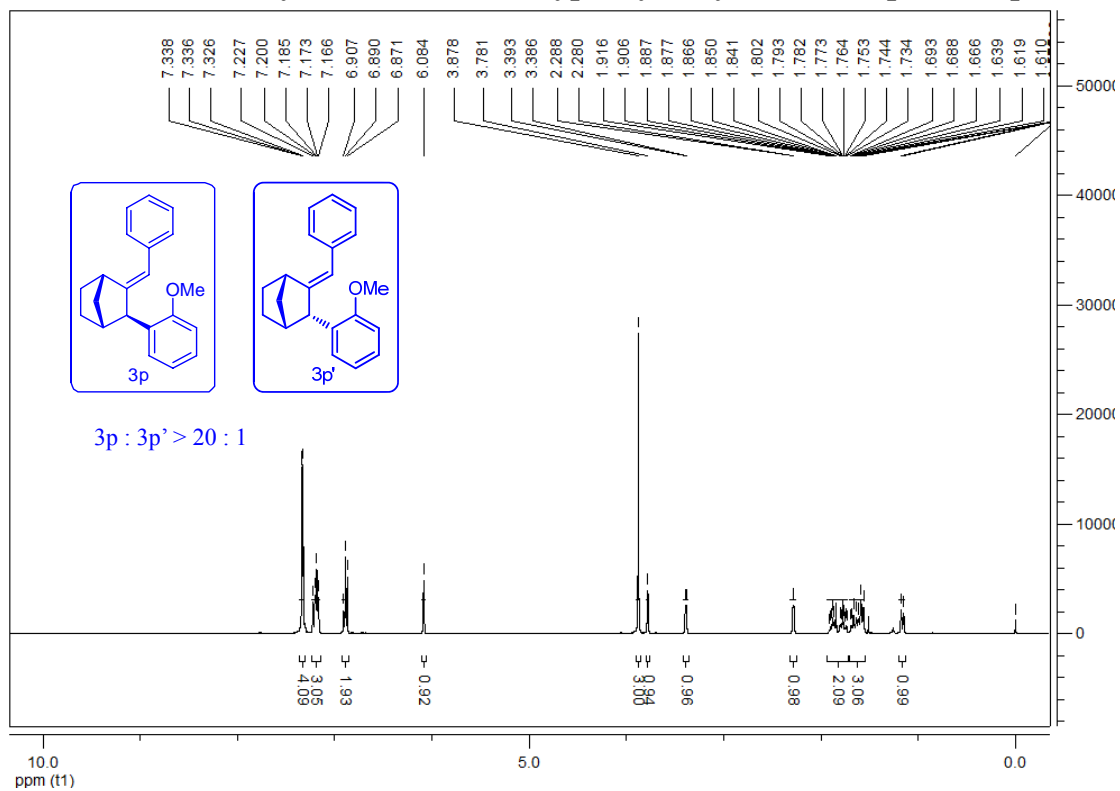
4-((1*R*,2*R*,4*S*,*E*)-3-benzylidenebicyclo[2.2.1]heptan-2-yl)aniline (**3n**), racemic



(1*S*,3*R*,4*R*,*E*)-2-benzylidene-3-(3-methoxyphenyl)bicyclo[2.2.1]heptane (3o), racemic



(1*S*,3*S*,4*R*,*E*)-2-benzylidene-3-(2-methoxyphenyl)bicyclo[2.2.1]heptanes (3p), racemic



1-(((1*R*,2*S*,4*S*,*E*)-3-benzylidenebicyclo[2.2.1]heptan-2-yl)naphthalene (3q), racemic

