# Synthesis of Methylenebicyclo[3.2.1]octanol by a Sm(II)-induced 1,2-Rearrangement Reaction with Ring Expansion of Methylenebicyclo[4.2.0]octanone

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## Supporting Information

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### General Information

All reactions were carried out under an inert atmosphere of argon with dry solvents, unless otherwise stated. Reagents of the highest commercial quality were purchased and used without further purification, unless otherwise stated. Anhydrous THF and $CH_2Cl_2$ were purchased from Kanto Chemical Industries Ltd. Other anhydrous solvents and reagents were prepared by standard methods. Sm granules or turnings were purchased from Soekawa Chemical Co. Ltd. or Kanto Chemical Industries Ltd., respectively. Reactions were monitored by thin-layer chromatography carried out on Merck silica gel 60 $F_{254}$ plates (250 μm) and visualized using ultraviolet light and *p*-anisaldehyde, potassium permanganate, or cerium molybdate stain. $^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL JNM-ECA500, a JEOL JNM-Lambda-500 ($^1$H: 500 MHz; $^{13}$C: 125 MHz), a JEOL JNM-ECS400, a JEOL JNM-AL400 ($^1$H: 400 MHz; $^{13}$C: 100 MHz), or a JEOL JNM-AL-300 ($^1$H: 300 MHz; $^{13}$C: 75 MHz) spectrometer. The chemical shifts are reported as δ values relative to tetramethylsilane (TMS) at 0 ppm or $CHCl_3$ at 7.26 ppm in $CDCl_3$ for $^1$H-NMR, and relative to $CDCl_3$ at 77.0 ppm for $^{13}$C-NMR. IR spectra were recorded on a JASCO FT/IR 4100 Series spectrometer. MS spectra were recorded on a JEOL JMS-700 double-focusing spectrometer. Elemental analyses were recorded on a Yanaco CHN CORDER MT-6. Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO P-2200 polarimeter.

**Preparation of a 0.1 M solution of $SmI_2$ in THF**[1]

Sm granules or turnings (902 mg, 6.00 mmol), 1,2-diiodoethane (1.41 g, 5.00 mmol) and a Teflon-coated magnetic stirring bar were placed in an oven-dried 100 mL round-bottomed flask equipped with a three-way glass stopcock. The flask was evacuated and back-filled with argon three times. THF (50 mL) was added to the flask with a syringe, and the mixture was stirred overnight at room temperature. The resulting blue solution of $SmI_2$ in THF was transferred to a reaction vessel with a syringe. In this preparation method, the true concentration of the solution is reported to be approximately 0.07 M.[1]

**General procedure for the 1,2-rearrangement reaction with ring expansion of methylenebicyclo[4.2.0]octanone**

**Condition A ($SmI_2$/HMPA/*t*-BuOH combination)**

A 0.1 M solution of $SmI_2$ in THF (3 equiv) was added dropwise to a solution of the substrate **2**, degassed HMPA (12 equiv), and *t*-BuOH (1 equiv) in THF. The mixture was stirred for 30 min at room temperature until all the substrate disappeared, as monitored by TLC. To quench the reaction, excess $Sm^{2+}$ was oxidized to $Sm^{3+}$ by blowing air into the flask while stirring the reaction mixture.

**Condition B ($SmI_2$/LiCl/*t*-BuOH combination)**

To a refluxed 0.1 M solution of $SmI_2$ in THF (3 equiv) was added dropwise a solution of the substrate **2**, dried LiCl (6 equiv), and *t*-BuOH (1 equiv) in THF so that reflux was maintained. The mixture was refluxed for 5 min until all the substrate disappeared, as monitored by TLC. The mixture was cooled to room temperature in an ice bath, and the reaction was quenched by blowing air into the flask while stirring the reaction mixture.

**Condition C ($SmI_2$/TBABr/HMPA combination)**

A 0.1 M solution of $SmI_2$ in THF (4 equiv) was added dropwise to dried TBABr (8 equiv). The mixture was refluxed for 20 min. Degassed HMPA (16 equiv) was added dropwise to the mixture, followed by reflux for a further 20 min. A solution of the substrate **2** in THF was added dropwise so that reflux was maintained. The mixture was refluxed for 30 min until all the substrate disappeared, as monitored by TLC. The mixture was cooled to room temperature in an ice bath, and the reaction was quenched by blowing air into the flask while stirring the reaction mixture.

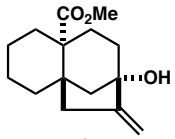
**Work-up procedure I**

The quenched mixture was diluted with excess $Et_2O$, then washed with 1 M HCl, saturated aqueous $NaHCO_3$, 20% aqueous $Na_2S_2O_3$ solution, water, and then brine. The organic layer was dried over $MgSO_4$, and concentrated in vacuo to give crude product **1**.

**Work-up procedure II**

The quenched mixture was diluted with excess $Et_2O$. While the mixture was vigorously stirred, saturated aqueous $NaHCO_3$ and 20% aqueous $Na_2S_2O_3$ solution were sequentially added dropwise at a volume ratio of 2:1. The resulting precipitate was separated by filtration, and the filtrate was concentrated in vacuo to give crude product **1**.

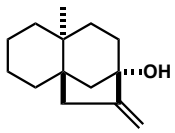
**Methyl (1*R**,6*R**,9*S**)-9-hydroxy-10-methylenetricyclo[7.2.1.0$^{1,6}$]dodecane-6-carboxylate (1a)**




1a

The reaction was carried out under condition A and the worked up by procedure I using substrate **2a** (42.2 mg, 0.170 mmol) in THF (2.0 mL), a 0.1 M solution of $SmI_2$ in THF (5.1 mL, 0.51 mmol), HMPA (0.36 mL, 2.04 mmol), and *t*-BuOH (15.6 μL, 0.164 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 3:1) to give product **1a** as a colorless oil (38.2 mg, 90% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.17 (1H, m), 1.20–1.31 (2H, m), 1.32 (1H, dt, *J* = 5.4, 13.7 Hz), 1.38–1.58 (4H, m), 1.65–1.72 (2H, m), 1.82 (1H, m), 2.05 (1H, dt, *J* = 17.6, 2.4 Hz), 2.12 (1H, ddd, *J* = 14.2, 5.4, 2.0 Hz), 2.16 (1H, dd, *J* = 11.2, 2.4 Hz), 2.40 (1H, dt, *J* = 4.4, 13.2 Hz), 2.73 (1H, dq, *J* = 17.6, 2.4 Hz), 3.68 (3H, s), 4.81 (1H, m), 4.95 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 22.4, 22.8, 32.6, 33.3, 35.0, 38.1, 41.1, 42.2, 49.3, 49.9, 51.4, 79.5, 102.3, 155.8, 176.1. IR (neat) cm$^{-1}$: 3411, 2930, 2861, 1729, 1664, 1463, 1430, 1259, 1242, 1186, 1151, 1132, 1121, 1074, 1017. EI-MS *m*/z (%): 250 ($M^+$, 69), 190 (94), 148 (100), 121 (99), 108 (31). HR-EI-MS *m*/z: Calcd for $C_{15}H_{22}O_3$: 250.1569. Found: 250.1571 [$M^+$].

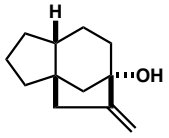
**(1*R**,6*S**,9*S**)-6-Methyl-10-methylenetricyclo[7.2.1.0$^{1,6}$]dodecan-9-ol (1b)**




1b

The reaction was carried out under condition B and worked up by procedure I using substrate **2b** (40.8 mg, 0.200 mmol) in THF (2.4 mL), a 0.1 M solution of $SmI_2$ in THF (6.0 mL, 0.60 mmol), LiCl (50.9 mg, 1.20 mmol), and *t*-BuOH (18.3 μL, 0.193 mmol). The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give product **1b** as a slightly yellow oil (37.7 mg, 91% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.02 (3H, s), 1.08 (1H, dt, *J* = 13.3, 3.0 Hz), 1.19–1.40 (6Hm), 1.41–1.56 (4H, m), 1.72 (1H, dt, *J* = 3.9, 13.5 Hz), 1.80 (1H, dd, *J* = 10.8, 2.5 Hz), 1.95 (1H, dt, *J* = 5.7, 12.4 Hz), 2.02 (1H, dt, *J* = 17.4, 2.5 Hz), 2.76 (1H, dq, *J* = 17.4, 2.5 Hz), 4.79 (1H, m), 4.93 (1H, t, *J* = 2.5 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.7, 22.8, 34.6, 35.1, 35.9, 36.5, 36.7, 39.7, 42.5, 47.7, 80.2, 101.9, 156.6. IR (neat) cm$^{-1}$: 3374, 2970, 2938, 2858, 1663, 1457, 1377, 1329, 1173, 1142, 1099, 1077, 1050, 892, 878. EI-MS *m*/z (%): 206 ($M^+$, 100), 188 (30), 149 (25), 121 (78), 108 (39). HR-EI-MS *m*/z: Calcd for $C_{14}H_{22}O$: 206.1671. Found: 206.1667 [$M^+$]. *Anal*. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.74; H, 10.96.

**(1*R**,5*R**,8*S**)-9-Methylenetricyclo[6.2.1.0$^{1,5}$]undecan-8-ol (1c)**

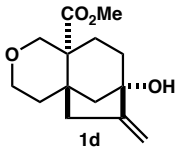



1c

The reaction was carried out under condition C and worked up by procedure II using substrate **2c** (25.3 mg, 0.14 mmol) in THF (1.4 mL), a 0.1 M solution of $SmI_2$ in THF (5.8 mL, 0.58 mmol), TBABr (370 mg, 1.15

mmol), and HMPA (0.41 mL, 2.36 mmol). The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give product **1c** as a colorless oil (22.1 mg, 88% yield). The product contained a small amount of **9** (**1c**:**9** = 11:1) which was difficult to separate from **1c**. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.34 (1H, dd, *J* = 10.5, 3.0 Hz), 1.40–1.74 (12H, m), 1.81 (1H, dt, *J* = 6.7, 11.3 Hz), 2.10 (1H, ddt, *J* = 16.3, 3.0, 2.4 Hz), 2.54 (1H, dt, *J* = 16.3, 2.4 Hz), 4.93 (1H, m), 5.08 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 21.5, 22.6, 28.5, 35.0, 37.5, 41.1, 44.8, 46.3, 47.8, 79.8, 105.3, 156.4. IR (neat) cm$^{-1}$: 3356, 2930, 2859, 1448, 1245, 1099, 1077, 888. EI-MS *m*/z (%): 178 ($M^+$, 84), 149 (43), 135 (15), 122 (17), 121 (100), 109 (13), 108 (64), 95 (17), 91 (10), 79 (11). HR-EI-MS *m*/z: Calcd for $C_{12}H_{18}O$: 178.1358. Found: 178.1356 [$M^+$].

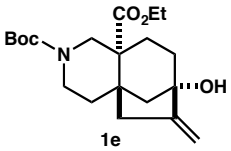
**Methyl (1*S**,6*R**,9*S**)-9-hydroxy-10-methylene-4-oxatricyclo[7.2.1.0$^{1,6}$]dodecane-6-carboxylate (1d)**



1d

The reaction was carried out under condition A and worked up by procedure I using substrate **2d** (41.3 mg, 0.165 mmol) in THF (2.0 mL), a 0.1 M solution of $SmI_2$ in THF (5.0 mL, 0.50 mmol), HMPA (0.34 mL, 1.95 mmol), and *t*-BuOH (15.1 μL, 0.159 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 2:3) to give product **1d** as a white solid (34.5 mg, 83% yield). Mp: 124–126 °C. $^1$H-NMR (500 MHz, $CDCl_3$) δ: 1.10 (1H, d, *J* = 13.4 Hz), 1.25 (1H, dt, *J* = 4.9, 13.7 Hz), 1.52–1.57 (2H, m), 1.69 (1H, m), 1.97 (1H, ddd, *J* = 13.7, 4.9, 1.8 Hz), 2.14 (1H, dt, *J* = 17.7, 2.4 Hz), 2.37 (1H, dd, *J* = 11.3, 2.4 Hz), 2.77 (1H, dt, *J* = 5.5, 13.4 Hz), 2.91 (1H, dq, *J* = 17.7, 2.4 Hz), 3.43 (1H, d, *J* = 11.9 Hz), 3.45 (1H, ddd, *J* = 13.4, 11.6, 2.4 Hz), 3.73 (3H, s), 3.85 (1H, dd, *J* = 11.6, 5.5 Hz), 3.98 (1H, d, *J* = 11.9 Hz), 4.85 (1H, m), 4.99 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ: 27.2, 34.8, 37.3, 40.2, 40.4, 48.3, 50.2, 51.9, 65.5, 71.9, 79.2, 102.9, 154.5, 174.5. IR (neat) cm$^{-1}$: 3452, 2958, 2928, 2910, 2853, 1739, 1666, 1264, 1220, 1185, 1173, 1093, 1082. EI-MS *m*/z (%): 252 ($M^+$, 40), 224 (37), 192 (100), 150 (51), 121 (54), 108 (51). HR-EI-MS *m*/z: Calcd for $C_{14}H_{20}O_4$: 252.1362. Found: 252.1367 [$M^+$].

**Ethyl (1*S**,6*R**,9*S**)-4-(*tert*-butoxycarbonyl)-9-hydroxy-10-methylene-4-azatricyclo[7.2.1.0$^{1,6}$]-dodecane-6-carboxylate (1e)**

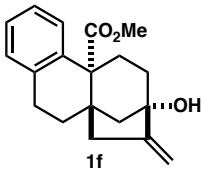


1e

The reaction was carried out under condition A and worked up by procedure I using substrate **2e** (50.7 mg, 0.140 mmol) in THF (1.7 mL), a 0.1 M solution of $SmI_2$ in THF (4.2 mL, 0.42 mmol), HMPA (0.29 mL, 1.67 mmol), and *t*-BuOH (12.8 μL, 0.135 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 3:2) to give product **1e** as a white amorphous solid (46.3 mg, 91% yield). $^1$H-NMR (300 MHz, $CDCl_3$, 50 ºC) δ: 1.09 (1H, m), 1.27 (3H, t, *J* = 7.2 Hz), 1.42 (9H, s), 1.45–1.65 (3H, m), 1.75 (1H, dt, *J* = 5.1, 12.3 Hz), 2.06–2.15 (3H, m), 2.63–2.75 (3H, m), 2.80 (1H, dq, *J* = 17.7, 2.4 Hz), 4.122 (2H, q, *J* = 7.2 Hz), 4.119 (1H, m), 4.25 (1H, m), 4.84 (1H, m), 4.99 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (75 MHz,

$CDCl_3$, 50 ºC) δ: 14.1, 28.4, 28.7, 34.3, 37.7, 40.0, 41.0 (br s), 41.3, 48.7, 48.9 (br s), 49.5, 60.6, 79.38, 79.44, 102.9, 154.4, 154.7, 173.6. IR (neat) $cm^{-1}$: 3430, 2978, 2931, 2866, 1725, 1677, 1467, 1430, 1366, 1282, 1150, 1099, 1047, 886, 757. EI-MS *m*/z (%): 365 ($M^+$, 4.1), 308 (100), 264 (91), 235 (32), 192 (23), 57 (30). HR-EI-MS *m*/z: Calcd for $C_{20}H_{31}NO_5$: 365.2202. Found: 365.2204 [$M^+$].

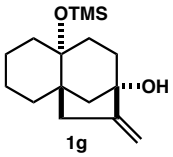
**Methyl (6a*R**,9*S**,11a*R**)-9-hydroxy-8-methylene-5,6,7,8,9,10,11,11a-octahydro-6a,9-methanocyclohepta[*a*]naphthalene-11a-carboxylate (1f)**




1f

The reaction was carried out under condition A and worked up by procedure I using substrate **2f** (44.5 mg, 0.150 mmol) in THF (2.0 mL), a 0.1 M solution of $SmI_2$ in THF (4.5 mL, 0.45 mmol), HMPA (0.31 mL, 1.78 mmol), and *t*-BuOH (13.7 μL, 0.144 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 2:1) to give product **1f** as a slightly yellow oil (39.7 mg, 89% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.39 (1H, m), 1.58 (1H, dt, *J* = 5.8, 13.7 Hz), 1.63–1.71 (2H, m), 1.90 (1H, dd, *J* = 11.2, 2.4 Hz), 1.95 (1H, br s), 2.16–2.27 (2H, m), 2.32 (1H, dq, *J* = 17.6, 2.4 Hz), 2.81–2.92 (4H, m), 3.60 (3H, s), 4.73 (1H, m), 4.98 (1H, t, *J* = 2.4 Hz), 7.09–7.17 (3H, m), 7.30 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 26.3, 30.9, 31.2, 38.6, 40.2, 42.0, 48.6, 52.0, 52.4, 79.8, 102.6, 125.8, 126.7, 127.1, 129.3, 136.5, 137.7, 155.1, 175.0. IR (neat) $cm^{-1}$: 3413, 3014, 2981, 2950, 2929, 2867, 1720, 1665, 1457, 1244, 1207, 1191, 1177, 1129, 1079, 1017, 886, 789, 750, 739. EI-MS *m*/z (%): 298 ($M^+$, 19), 239 (100), 221 (15), 131 (21). HR-EI-MS *m*/z: Calcd for $C_{19}H_{22}O_3$: 298.1569. Found: 298.1564 [$M^+$].

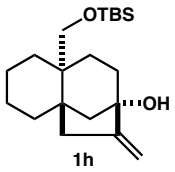
**(1*R**,6*R**,9*S**)-10-Methylene-6-trimethylsilyloxytricyclo[7.2.1.0$^{1,6}$]dodecan-9-ol (1g)**




1g

The reaction was carried out under condition A and worked up by procedure II using substrate **2g** (44.5 mg, 0.160 mmol) in THF (2.0 mL), a 0.1 M solution of $SmI_2$ in THF (4.5 mL, 0.45 mmol), HMPA (0.33 mL, 1.90 mmol), and *t*-BuOH (14.6 μL, 0.154 mmol). The reaction was performed under reflux for 45 min until all the substrate disappeared, as monitored by TLC. The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 3:1) to give product **1g** as a as a white solid (40.2 mg, 90% yield). Mp: 93–95 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.14 (9H, s), 1.02 (1H, m), 1.17 (1H, dd, *J* = 10.2, 2.4 Hz), 1.21 (1H, m), 1.37–1.61 (8H, m), 1.83 (1H, dt, *J* = 3.4, 13.2 Hz), 1.96 (1H, m), 2.10 (1H, dt, *J* = 17.6, 2.4 Hz), 2.12 (1H, dd, *J* = 10.2, 2.4 Hz), 2.45 (1H, dq *J* = 17.6, 2.4 Hz), 4.81 (1H, m), 4.97 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 2.4, 21.6, 22.5, 33.9, 34.4, 35.0, 36.9, 40.0, 45.5, 47.6, 76.1, 79.3, 103.0, 156.4. IR (KBr) $cm^{-1}$: 3324, 2973, 2933, 2860, 1451, 1247, 1145, 1092, 1080, 1051, 1030, 998, 871, 837. EI-MS *m*/z (%): 280 ($M^+$, 20), 190 (100), 173 (17), 162 (54), 144 (21), 134 (20), 73 (26). HR-EI-MS *m*/z: Calcd for $C_{16}H_{28}O_2Si$: 280.1859. Found: 280.1861 [$M^+$]. *Anal*. Calcd for $C_{16}H_{28}O_2Si$: C, 68.52; H, 10.06. Found: C, 68.74; H, 10.14.

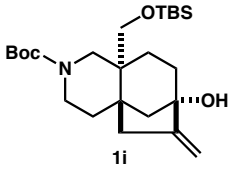
**(1*R**,6*R**,9*S**)-6-[(*tert*-Butyldimethylsilyloxy)methyl]-10-methylenetricyclo[7.2.1.0$^{1,6}$]dodecan-9-ol (1h)**




1h

The reaction was carried out under condition B and worked up by procedure II using substrate **2h** (50.3 mg, 0.150 mmol) in THF (1.8 mL), a 0.1 M solution of $SmI_2$ in THF (4.5 mL, 0.45 mmol), LiCl (38.2 mg, 0.900 mmol), and *t*-BuOH (13.7 μL, 0.144 mmol). The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give product **1h** as a white solid (47.3 mg, 94% yield). Mp: 117–120 °C. $^1$H-NMR (300 MHz, $CDCl_3$) δ: 0.04 (6H, s), 0.89 (9H, s), 0.91–1.12 (3H, m), 1.21–1.56 (7H, m), 1.67–1.78 (4H, m), 1.87 (1H, dt, *J* = 5.3, 12.6 Hz), 2.01 (1H, dt, *J* = 17.6, 2.6 Hz), 2.83 (1H, m), 3.65 (1H, d, *J* = 9.7 Hz), 3.75 (1H, dd, *J* = 9.7, 1.7 Hz), 4.80 (1H, m), 4.93 (1H, t, *J* = 2.6 Hz). $^{13}$C-NMR (75 MHz, $CDCl_3$) δ: -5.5, 18.3, 21.4, 22.6, 25.9, 29.1, 29.2, 34.5, 36.3, 39.5, 40.9, 41.6, 46.9, 60.4, 79.9, 101.8, 156.4. IR (KBr) cm$^{-1}$: 3311, 2977, 2930, 2857, 1460, 1090, 1076, 861, 836, 778. EI-MS *m*/z (%): 336 ($M^+$, 17), 279 (68), 187 (100), 145 (25), 131 (19), 119 (16), 105 (17), 75 (21). HR-EI-MS *m*/z: Calcd for $C_{20}H_{36}O_2Si$: 336.2485. Found: 336.2484 [$M^+$]. *Anal*. Calcd for $C_{20}H_{36}O_2Si$: C, 71.37; H, 10.78. Found: C, 71.63; H, 10.82.

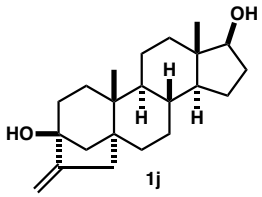
***tert*-Butyl (1*S**,6*R**,9*S**)-6-[(*tert*-butyldimethylsilyloxy)methyl]-9-hydroxy-10-methylene-4-azatricyclo-[7.2.1.0$^{1,6}$]dodecane-4-carboxylate (1i)**




1i

The reaction was carried out under condition B and worked up by procedure II using substrate **2i** (52.4 mg, 0.120 mmol) in THF (1.5 mL), a 0.1 M solution of $SmI_2$ in THF (3.6 mL, 0.36 mmol), LiCl (30.5 mg, 0.720 mmol), and *t*-BuOH (11.0 μL, 0.116 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 5:2) to give product **1i** as a white amorphous solid (44.4 mg, 85% yield). $^1$H-NMR (300 MHz, $CDCl_3$, 50 ºC) δ: 0.06 (6H, s), 0.92 (9H, s), 1.07 (1H, m), 1.35 (1H, dd, *J* = 11.1, 2.7 Hz), 1.45 (9H, s), 1.48–1.52 (2H, m), 1.80–1.89 (3H, m), 1.90 (1H, dd, *J* = 13.5, 5.1 Hz), 2.04 (1H, dt, *J* = 17.1, 2.4 Hz), 2.42 (1H, d, *J* = 13.2 Hz), 2.69 (1H, dt, *J* = 3.3, 13.5 Hz), 2.89 (1H, dq, *J* = 17.1, 2.4 Hz), 3.66 (1H, d, *J* = 10.1 Hz), 3.70 (1H, d, *J* = 10.1 Hz), 4.00–4.07 (2H, m), 4.85 (1H, m), 4.98 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (75 MHz, $CDCl_3$, 50 ºC) δ: -5.6, -5.4, 18.4, 25.4, 26.0, 28.5, 33.3, 36.2, 39.7, 40.37, 40.42, 40.5, 46.3, 46.8, 60.3, 79.3, 79.7, 102.6, 155.2. No signal was observed for the carbonyl carbon. IR (neat) cm$^{-1}$: 3417, 2930, 2857, 1682, 1471, 1430, 1365, 1278, 1255, 1147, 1111, 1073, 885, 855, 837, 756, 666. HR-FAB-MS (*m*-nitrobenzyl alcohol) *m*/z: Calcd for $C_{24}H_{44}NO_4Si$: 438.3040. Found: 438.3049 [$MH^+$].

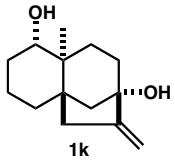
**(1*S*,3a*S*,3b*R*,5a*R*,8*S*,10a*R*,10b*S*,12a*S*)-10a,12a-Dimethyl-7-methylenehexadecahydro-1*H*-5a,8-methano-cyclohepta[*a*]cyclopenta[*f*]naphthalene-1,8-diol (1j)**



1j

The reaction was carried out under condition B without *t*-BuOH and worked up by procedure I using substrate **2j** (42.7 mg, 0.130 mmol) in THF (1.6 mL), a 0.1 M solution of $SmI_2$ in THF (3.9 mL, 0.39 mmol), and LiCl (33.1 mg, 0.781 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 1:2) to give product **1j** as a white solid (38.2 mg, 89% yield). Mp: 195–198 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.73 (3H, s), 0.88 (1H, dq, *J* = 3.9, 13.2 Hz), 0.97 (3H, s), 0.95 (1H, m), 1.02–1.13 (3H, m), 1.15–1.61 (13H, m), 1.75 (1H, dt, *J* = 3.9, 13.7 Hz), 1.79–1.91 (3H, m), 1.98–2.10 (2H, m), 2.80 (1H, m), 3.63 (1H, t, *J* = 8.8 Hz), 4.77 (1H, m), 4.91 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 11.1, 15.2, 21.2, 23.4, 28.0, 30.5, 33.7, 34.4, 35.6, 36.6, 36.8, 37.7, 39.8, 43.0, 44.0, 47.8, 48.5, 50.9, 79.9, 81.9, 101.8, 156.4. IR (KBr) cm$^{-1}$: 3368, 2930, 2852, 1099, 1074. EI-MS *m*/z (%): 330 ($M^+$, 100), 312 (52), 121 (41), 108 (36). HR-EI-MS *m*/z: Calcd for $C_{22}H_{34}O_2$: 330.2559. Found: 330.2556 [$M^+$]. $[\alpha]_D^{25}$ +23.6 (*c* 0.99, $CHCl_3$).

**(1*R**,5*S**,6*S**,9*S**)-6-Methyl-10-methylenetricyclo[7.2.1.0$^{1,6}$]dodecan-5,9-diol (1k)**



1k

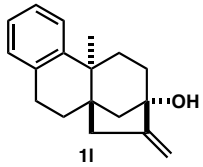
The reaction was carried out under condition B without *t*-BuOH and worked up by procedure I using substrate **2k** (44.0 mg, 0.200 mmol) in THF (2.4 mL), a 0.1 M solution of $SmI_2$ in THF (6.0 mL, 0.60 mmol), and LiCl (50.9 mg, 1.20 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 1:2) to give product **1k** as a white solid (41.7 mg, 94% yield). Mp: 154–156 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.97 (3H, s), 1.04 (1H, m), 1.28 (1H, br s), 1.32 (1H, dd, *J* = 11.2, 2.9 Hz), 1.30–1.49 (2H, m), 1.53 (1H, m), 1.57–1.75 (5H, m), 1.87 (1H, dd, *J* = 11.2, 2.9 Hz), 1.92 (1H, dt, *J* = 5.4, 12.7 Hz), 2.03 (1H, dt, *J* = 17.6, 2.9 Hz), 2.75 (1H, dq, *J* = 17.6, 2.9 Hz), 3.62 (1H, dd, *J* = 11.2, 4.9 Hz), 4.81 (1H, m), 4.95 (1H, t, *J* = 2.9 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 12.9, 21.3, 30.6, 32.1, 33.8, 36.5, 39.5, 40.2, 44.0, 47.3, 75.3, 80.0, 102.4, 155.8. IR (KBr) cm$^{-1}$: 3450, 3303, 2986, 2962, 2935, 2861, 1666, 1457, 1331, 1074, 1009, 1001, 872. EI-MS *m*/z (%): 222 ($M^+$, 100), 204 (25), 147 (47), 122 (50), 121 (41), 95 (66). HR-EI-MS *m*/z: Calcd for $C_{14}H_{22}O_2$: 222.1620. Found: 222.1618 [$M^+$].

**Representative example of the 1,2-rearrangement**

A solution of substrate **2k** and dried LiCl (382 mg, 9.00 mmol) in THF (18.0 mL) was added dropwise to a refluxed 0.1 M solution of $SmI_2$ in THF (45.0 mL, 4.50 mmol) so that reflux was maintained. The mixture was refluxed for 5 min until the substrate disappeared, as monitored by TLC. The mixture was cooled to room temperature in an ice bath, and the reaction was quenched by blowing air into the flask while stirring the reaction mixture. The quenched mixture was diluted with excess $Et_2O$. While the mixture was vigorously

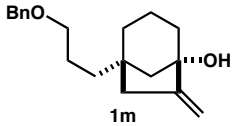
stirred, saturated aqueous $NaHCO_3$ and 20% aqueous $Na_2S_2O_3$ solution were sequentially added dropwise at a volume ratio of 2:1. The resulting precipitate was separated by filtration, and the filtrate was concentrated in vacuo. The resulting crude product was purified by column chromatography on silica gel (hexane:AcOEt = 1:1) to give product **1k** as a white solid (317 mg, 95% yield).

**(6a*R**,9*S**,11a*S**)-11a-Methyl-8-methylene-5,6,7,8,9,10,11,11a-octahydro-6a,9-methanocyclohepta[*a*]naphthalen-9-ol (1l)**



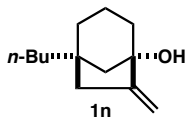

The reaction was carried out under condition B and worked up by procedure I using substrate **2l** (40.1 mg, 0.159 mmol) in THF (2.0 mL), a 0.1 M solution of $SmI_2$ in THF (4.8 mL, 0.48 mmol), LiCl (40.7 mg, 0.960 mmol), and *t*-BuOH (14.6 μL, 0.154 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 3:1) to give product **1l** as a white solid (34.5 mg, 85% yield). Mp: 114–118 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.26 (3H, s), 1.35 (1H, ddd, *J* = 13.5, 6.8, 1.5 Hz), 1.48 (1H, dd, *J* = 10.8, 2.4 Hz), 1.69 (1H, s), 1.62–1.72 (2H, m), 2.02 (1H, dd, *J* = 10.8, 2.4 Hz), 2.05–2.15 (2H, m), 2.20 (1H, m), 2.25 (1H, dt, *J* = 17.6, 2.4 Hz), 2.32 (1H, dq, *J* = 17.6, 2.4 Hz), 2.80 (1H, dd, *J* = 17.6, 6.8 Hz), 2.89 (1H, ddd, *J* = 17.6, 12.2, 6.8 Hz), 4.73 (1H, m), 4.95 (1H, t, *J* = 2.4 Hz), 7.04 (1H, m), 7.09 (1H, dt, *J* = 1.5, 7.2 Hz), 7.14 (1H, m), 7.24 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 26.67, 26.74, 30.6, 33.5, 37.1, 39.6, 39.8, 41.9, 47.4, 80.3, 102.5, 125.4, 126.1, 126.3, 128.8, 134.6, 146.1, 155.9. IR (KBr) cm$^{-1}$: 3357, 2968, 2937, 2887, 2860, 1661, 1489, 1457, 1337, 1130, 1080, 880, 764. EI-MS *m*/z (%): 254 ($M^+$, 95), 239 (100), 221 (17), 141 (15), 131 (37). HR-EI-MS *m*/z: Calcd for $C_{18}H_{22}O$: 254.1671. Found: 254.1667 [$M^+$].

**(1*S**,5*S**)-5-[3-(Benzyloxy)propyl]-7-methylenebicyclo[3.2.1]octan-1-ol (1m)**



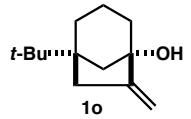

The reaction was carried out under condition C and worked up by procedure II using substrate **2m** (28.4 mg, 0.10 mmol) in THF (1.0 mL), a 0.1 M solution of $SmI_2$ in THF (4.0 mL, 0.40 mmol), TBABr (258 mg, 0.80 mmol), and HMPA (0.28 mL, 1.61 mmol). The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 3:1) to give product **1m** as a colorless oil (15.4 mg, 54% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.26 (1H, m), 1.37–1.73 (12H, m), 2.14–2.25 (2H, m), 3.45 (2H, t, *J* = 6.5 Hz), 4.50 (2H, s), 4.83 (1H, m), 4.98 (1H, t, *J* = 2.5 Hz), 7.28–7.37 (5H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 20.7, 25.0, 35.1, 37.5, 39.9, 40.9, 51.5, 71.0, 72.9, 80.2, 103.3, 127.5, 127.6, 128.3, 138.5, 156.7. IR (neat) cm$^{-1}$: 3407, 2937, 2849, 1454, 1329, 1244, 1091, 884, 735, 697. EI-MS *m*/z (%): 286 ($M^+$, 9), 268 (15), 196 (11), 195 (81), 177 (22), 149 (13), 137 (33), 135 (22), 92 (11), 91 (100). HR-EI-MS *m*/z: Calcd for $C_{19}H_{26}O_2$: 286.1933. Found: 286.1931 [$M^+$]. *Anal*. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.48; H, 9.42.

**(1*S**,5*R**)-5-Butyl-7-methylenebicyclo[3.2.1]octan-1-ol (1n)**



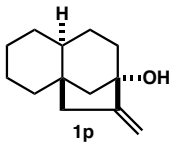

The reaction was carried out under condition C and worked up by procedure II using substrate **2n** (76.9 mg, 0.40 mmol) in THF (4.0 mL), a 0.1 M solution of $SmI_2$ in THF (16.0 mL, 1.60 mmol), TBABr (1.03 g, 3.20 mmol), and HMPA (1.1 mL, 6.32 mmol). The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 3:1) to give product **1n** as a colorless oil (56.8 mg, 73% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.89 (3H, t, *J* = 7.0 Hz), 1.19–1.34 (7H, m), 1.37–1.54 (3H, m), 1.57–1.61 (3H, m), 1.64–1.72 (2H, m), 2.13–2.23 (2H, m), 4.83 (1H, m), 4.97 (1H, t, *J* = 4.6 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 14.1, 20.8, 23.5, 26.7, 35.2, 39.9, 40.1, 40.96, 40.98, 51.5, 80.2, 103.1, 157.0. IR (neat) cm$^{-1}$: 3357, 2928, 2856, 1456, 1329, 1136, 1076, 885. EI-MS *m*/z (%): 194 ($M^+$, 33), 152 (15), 151 (99), 138 (15), 137 (100), 109 (16), 95 (23). HR-EI-MS *m*/z: Calcd for $C_{13}H_{22}O$: 194.1671. Found: 194.1668 [$M^+$].

**(1*S**,5*S**)-5-(*tert*-Butyl)-7-methylenebicyclo[3.2.1]octan-1-ol (1o)**




The reaction was carried out under condition C and worked up by procedure II using substrate **2o** (27.0 mg, 0.14 mmol) in THF (1.4 mL), a 0.1 M solution of $SmI_2$ in THF (5.6 mL, 0.56 mmol), TBABr (362 mg, 1.12 mmol), and HMPA (0.42 mL, 2.18 mmol). The reaction was performed under reflux for 3 h until all the substrate disappeared, as monitored by TLC. The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 4:1) to give product **1o** as a colorless oil (23.0 mg, 85% yield). Mp: 71–74 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.86 (9H, s), 1.33–1.37 (2H, m), 1.43–1.73 (6H, m), 1.79 (1H, m), 2.01 (1H, dq, *J* = 17.4, 2.3 Hz), 2.46 (1H, dq, *J* = 17.4, 2.2 Hz), 4.83 (1H, m), 4.97 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 20.8, 25.8, 30.8, 33.9, 36.1, 39.8, 45.6, 46.3, 80.6, 103.1, 157.3. IR (KBr) cm$^{-1}$: 2951, 2871, 1698, 1668, 1367, 1232, 1175, 883. EI-MS *m*/z (%): 194 ($M^+$, 15), 138 (17), 137 (100), 95 (13). HR-EI-MS *m*/z: Calcd for $C_{13}H_{22}O$: 194.1671. Found: 194.1669 [$M^+$].

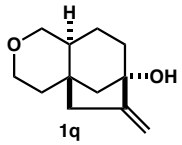
**(1*R**,6*S**,9*S**)-10-Methylenetricyclo[7.2.1.0$^{1,6}$]dodecan-5-ol (1p)**




The reaction was carried out under condition C and worked up by procedure II using substrate **2p** (20.3 mg, 0.11 mmol) in THF (1.1 mL), a 0.1 M solution of $SmI_2$ in THF (4.3 mL, 0.43 mmol), TBABr (275 mg, 0.85 mmol), and HMPA (0.31 mL, 1.78 mmol). The reaction time was conducted for 2 h until all the substrate disappeared, as monitored by TLC. The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give product **1p** as a colorless oil (18.1 mg, 89% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.97–1.67 (15H, m), 1.76 (1H, ddd, *J* = 18.5, 11.7, 5.5 Hz), 1.95 (1H, ddt, *J* = 17.2, 0.8, 2.6 Hz), 2.52 (1H,

dq, $J$ = 17.2, 2.6 Hz), 4.82 (1H, m), 4.95 (1H, t, $J$ = 2.6 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 23.0, 26.4, 28.8, 29.7, 36.6, 38.5, 40.0, 40.2, 42.5, 54.0, 79.5, 102.9, 157.0. IR (neat) cm$^{-1}$: 3365, 2920, 2851, 1661, 1453, 1328, 1246, 1169, 1154, 1109, 1073, 882. EI-MS $m$/z (%): 192 ($M^+$, 100), 163 (16), 149 (21), 135 (11), 134 (11), 121 (66), 108 (26), 95 (10). HR-EI-MS $m$/z: Calcd for $C_{13}H_{20}O$: 192.1514. Found: 192.1513 [$M^+$]. *Anal*. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.12; H, 10.39.

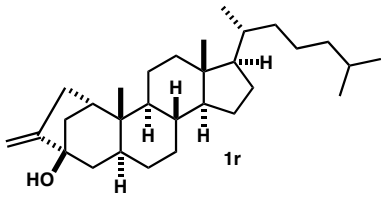
**(1*R**,6*R**,9*S**)-10-Methylene-4-oxatricyclo[7.2.1.0$^{1,6}$]dodecan-9-ol (1q)**



1q

The reaction was carried out under condition C and worked up by procedure II using substrate **2q** (31.0 mg, 0.16 mmol) in THF (1.6 mL), a 0.1 M solution of $SmI_2$ in THF (6.5 mL, 0.65 mmol), TBABr (416 mg, 1.29 mmol), and HMPA (0.46 mL, 2.64 mmol). The reaction time was conducted for 12 h until all the substrate disappeared, as monitored by TLC. The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 1:4) to give product **1q** as a colorless oil (20.7 mg, 66% yield) and the recovered substrate **2q** (6.4 mg, 21%). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.01 (1H, ddt, $J$ = 13.5, 5.9, 12.8 Hz), 1.30 (1H, dt, $J$ = 13.4, 1.8 Hz), 1.49–1.53 (2H, m), 1.60 (1H, br s), 1.62–1.68 (2H, m), 1.69 (1H, dd, $J$ = 10.4, 2.6 Hz), 1.80 (1H, ddd, $J$ = 12.8, 11.6, 5.5 Hz), 1.84 (1H, dt, $J$ = 4.9, 13.4 Hz), 2.05 (1H, m), 2.71 (1H, dq, $J$ = 17.2, 2.6 Hz), 3.16 (1H, t, $J$ = 11.6 Hz), 3.35 (1H, ddd, $J$ = 13.4, 11.4, 1.8 Hz), 3.67 (1H, dd, $J$ = 11.6, 4.5 Hz), 3.80 (1H, m), 4.87 (1H, m), 5.00 (1H, t, $J$ = 2.6 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 22.9, 35.7, 37.7, 38.1, 39.2, 41.9, 52.9, 64.8, 69.1, 79.1, 103.5, 155.5. IR (neat) cm$^{-1}$: 3417, 2929, 2850, 1661, 1329, 1224, 1078, 883. EI-MS $m$/z (%): 194 ($M^+$, 100), 137 (38), 136 (11), 122 (84), 121 (25), 120 (11), 109 (14), 108 (37), 107 (13), 95 (11), 91 (13), 79 (12). HR-EI-MS $m$/z: Calcd for $C_{12}H_{18}O_2$: 194.1307. Found: 194.1305 [$M^+$]. *Anal*. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.25.

**(1*R*,3a*R*,3b*S*,5a*S*,7*R*,10*S*,10a*R*,10b*S*,12a*R*)-3b,10a,12a-Trimethyl-8-methylene-1-[(*R*)-6-methyl-heptan-2-yl]octadecahydro-7,10-methanocyclohepta[*a*]cyclopenta[*f*]naphthalen-7-ol (1r)**



1r

The reaction was carried out under condition C and worked up by procedure II using substrate **2r** (42.5 mg, 0.10 mmol) in THF (1.0 mL), a 0.1 M solution of $SmI_2$ in THF (4.0 mL, 0.40 mmol), TBABr (258 mg, 0.80 mmol), and HMPA (0.28 mL, 1.61 mmol). The reaction time was conducted for 1 h until all the substrate disappeared, as monitored by TLC. The crude product was purified by column chromatography on silica gel (hexane:$Et_2O$ = 5:1) to give product **1r** as a white solid (17.9 mg, 42% yield). Mp: 117–119 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.65 (3H, s), 0.85 (3H, s), 0.860 (3H, d, $J$ = 6.4 Hz), 0.865 (3H, d, $J$ = 6.9 Hz), 0.90 (3H, d, $J$ = 6.6 Hz), 0.93–1.15 (9H, m), 1.18–1.27 (5H, m), 1.30–1.44 (6H, m), 1.46–1.66 (7H, m), 1.80 (1H, m), 1.88–1.97 (2H, m), 2.08 (1H, m), 2.30 (1H, ddt, $J$ = 17.4, 6.5, 2.7 Hz), 2.39 (1H, dq, $J$ = 17.4, 2.4 Hz), 4.84

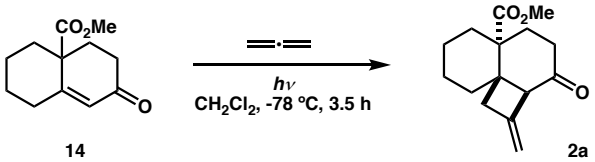
(1H, m), 4.96 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 12.2, 15.7, 18.7, 21.1, 22.6, 22.8, 23.8, 24.2, 27.2, 28.0, 28.3, 31.4, 31.8, 35.75, 35.78, 36.1, 37.7, 39.2, 39.5, 40.0, 41.3, 41.4, 42.8, 43.2, 48.9, 56.3, 56.5, 79.8, 102.7, 156.8. IR (KBr) cm$^{-1}$: 3349, 2933, 2864, 2848, 1465, 1381, 1171, 1117, 1089, 957, 881. EI-MS *m*/z (%): 426 ($M^+$, 51), 411 (41), 368 (27), 331 (100), 272 (26), 271 (42). HR-EI-MS *m*/z: Calcd for $C_{30}H_{50}O$: 426.3862. Found: 426.3863 [$M^+$]. *Anal*. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.54; H, 11.97. $[\alpha]_D^{25}$ +33.9 (*c* 1.00, $CHCl_3$).

**Preparation of the substrates**

**General procedure for [2+2] photocycloaddition of the enone and allene**

To a solution of enone in $CH_2Cl_2$ or MeOH was introduced allene[2] at -78 °C by distillation. The mixture was irradiated at -78 °C through a Pyrex filter with a 100 W high-pressure mercury lamp until all the enone disappeared, as monitored by TLC. Excess allene and the solvent were removed under atmospheric and reduced pressure, respectively. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 4:1) to give cyclobutyl ketone **2**.

**Preparation of 2a**

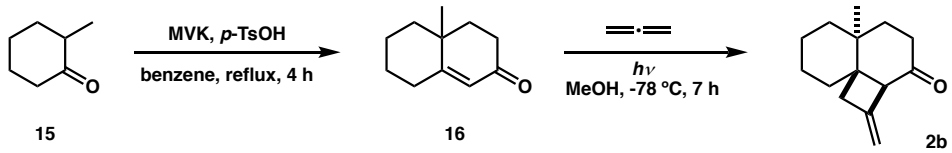



14 2a

**Methyl (1*R**,4*S**,8*R**)-3-methylene-5-oxotricyclo[6.4.0.0$^{1,4}$]dodecane-8-carboxylate (2a)**

The photocycloaddition reaction was carried out using **14**[3] (1.05 g, 5.04 mmol) in $CH_2Cl_2$ (2.0 mL) and allene (5.0 mL) by irradiating for 3.5 h. Purification by column chromatography on silica gel (hexane:AcOEt = 4:1) afforded **2a** as a white solid (1.06 g, 85% yield). A single crystal for X-ray crystallographic analysis was obtained by crystallization from AcOEt–hexane. Mp: 76–78 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.15–1.30 (2H, m), 1.34 (1H, tq, *J* = 4.4, 13.2 Hz), 1.55–1.62 (3H, m), 1.75–1.88 (2H, m), 2.00–2.20 (3H, m), 2.50–2.61 (2H, m), 2.90 (1H, dquint, *J* = 17.1, 2.4 Hz), 3.37 (1H, m), 3.67 (3H, s), 4.97 (1H, q, *J* = 2.4 Hz), 5.03 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 20.9, 23.3, 29.5, 30.3, 34.3, 34.4, 38.4, 41.3, 48.0, 51.4, 61.5, 111.0, 140.9, 175.6, 207.3. IR (KBr) cm$^{-1}$: 2958, 2928, 2862, 1720, 1695, 1664, 1459, 1426, 1232, 1190, 1159, 1131, 1025, 907, 894. EI-MS *m*/z (%): 248 ($M^+$, 17), 216 (21), 189 (100), 161 (33), 133 (38), 91 (27). HR-EI-MS *m*/z: Calcd for $C_{15}H_{20}O_3$: 248.1412. Found: 248.1408 [$M^+$]. *Anal*. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.42; H, 8.12.

**Preparation of 2b**



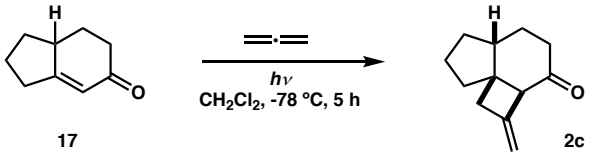

**4a-Methyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (16)**

A solution of **15** (2.23 g, 19.9 mmol), methyl vinyl ketone (2.0 mL, 24.0 mmol), and *p*-TsOH・$H_2O$ (190 mg, 1.00 mmol) in benzene (29 mL) was refluxed for 4 h. The mixture was cooled in an ice bath, then neutralized with saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with $Et_2O$. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 5:1) to give **16** as a slightly yellow oil (1.61 g, 49% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.24 (3H, s), 1.32–1.45 (2H, m), 1.65–1.72 (3H, m), 1.77 (1H, ddd, *J* = 13.2, 5.8, 3.4 Hz), 1.83 (1H, dd, *J* = 14.2, 4.4 Hz), 1.91 (1H, m), 2.25 (1H, m), 2.31–2.41 (2H, m), 2.50 (1H, ddd, *J* = 17.1, 14.2, 5.8 Hz), 5.72 (1H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 21.7, 22.0, 27.1, 32.7, 34.0, 35.9, 38.0, 41.5, 124.1, 170.5, 199.6. IR (neat) cm$^{-1}$: 2930, 2860, 1676, 1617, 1448, 1327, 1260, 1226, 1186, 858. EI-MS *m*/z (%): 164 ($M^+$, 100), 136 (65), 122 (85), 107 (39). HR-EI-MS *m*/z: Calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1200 [$M^+$].

**(1*R**,4*S**,8*S**)-8-Methyl-3-methylenetricyclo[6.4.0.0$^{1,4}$]dodecane-5-one (2b)**

The photocycloaddition reaction was carried out using **16** (903 mg, 5.50 mmol) in MeOH (3.0 mL) and allene (4.0 mL) by irradiating for 7 h. Purification by column chromatography on silica gel (hexane:$Et_2O$= 4:1) afforded **2b** as a colorless oil (969 mg, 86% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.87 (3H, s), 1.22–1.28 (2H, m), 1.31 (1H, dt, *J* = 8.8, 4.4 Hz), 1.36–1.52 (4H, m), 1.58 (1H, m), 1.70 (1H, ddt, *J* = 4.0 2.0, 13.2 Hz), 2.08 (1H, dt, *J* = 14.0, 9.3 Hz), 2.38 (1H, ddd, *J* = 19.2, 9.3, 1.5 Hz), 2.42 (1H, dt, *J* = 16.8, 2.4 Hz), 2.60 (1H, m), 2.98 (1H, dquint, *J* = 16.8, 2.4 Hz), 3.09 (1H, m), 4.97 (1H, q, *J* = 2.4 Hz), 4.99 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 18.1, 20.9, 21.2, 32.8, 33.5, 33.6, 33.9, 34.1, 37.4, 43.7, 61.3, 111.0, 140.7, 211.2. IR (neat) cm$^{-1}$: 2986, 2927, 2863, 1698, 1670, 1464, 1446, 1236, 1200, 1193, 886, 870. EI-MS *m*/z (%): 204 ($M^+$, 74), 189 (49), 175 (48), 147 (100), 105 (50), 91 (51). HR-EI-MS *m*/z: Calcd for $C_{14}H_{20}O$: 204.1514. Found: 204.1511 [$M^+$].

**Preparation of 2c**[4]

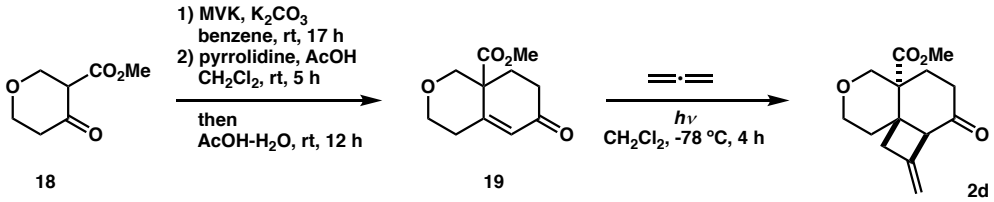



**1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (2c)**

The photocycloaddition reaction was carried out using **17**[5] (2.10 g, 15.4 mmol) in $CH_2Cl_2$ (15 mL) and allene (15 mL) by irradiating for 5 h. Purification by column chromatography on silica gel (hexane:$Et_2O$ = 5:1) afforded **2c** as a colorless solid (2.20 g, 81% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.40 (1H, dddd, *J* = 15.1, 8.4, 6.6, 5.0 Hz),, 1.53–1.67 (3H, m), 1.69–1.83 (2H, m), 1.88–2.00 (2H, m), 2.04 (1H, m), 2.28 (1H, ddd, *J* = 17.0, 7.9, 5.7 Hz), 2.40 (1H, ddd, *J* = 17.0, 9.7, 5.5 Hz), 2.55 (1H, dq, *J* = 15.3, 2.6 Hz), 2.67 (1H, ddt, *J* =

15.3, 0.7, 2.6 Hz), 3.36 (1H, m), 4.86 (1H, q, *J* = 2.6 Hz), 4.87 (1H, q, *J* = 2.6 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 23.7, 26.7, 30.1, 36.3, 39.1, 42.9, 43.5, 46.8, 58.9, 107.4, 142.0, 209.9. IR (neat) $cm^{-1}$: 2941, 2865, 1702, 1671, 1454, 1414, 1232, 1183, 883. EI-MS *m*/z (%): 176 ($M^+$, 100), 161 (22), 148 (44), 147 (28), 134 (87), 133 (60), 121 (26), 120 (86), 119 (96), 106 (33), 105 (64), 93 (34), 92 (43), 91 (81), 79 (49), 77 (27). HR-EI-MS *m*/z: Calcd for $C_{12}H_{16}O$: 176.1201. Found: 176.1198 [$M^+$].

**Preparation of 2d**




**Methyl 6-oxo-1,3,4,6,7,8,8a-heptahydroisochromene-8a-carboxylate (19)**

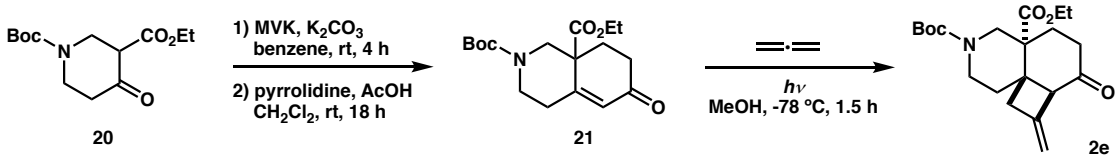
To a solution of **18**[6] (790 mg, 5.00 mmol) in benzene (10 mL) were added methyl vinyl ketone (0.57 mL, 7.03 mmol) and $K_2CO_3$ (276 mg, 2.00 mmol) at 0 °C. The mixture was stirred for 17 h at room temperature, diluted with $Et_2O$, and passed through a Celite pad. The filtrate was concentrated in vacuo. The residue was dissolved in $CH_2Cl_2$ (10 mL), then pyrrolidine (0.42 mL, 5.03 mmol) and acetic acid (0.29 mL, 5.07 mmol) were added at 0 °C. The mixture was stirred for 5 h at room temperature, water (2.0 mL) and acetic acid (2.0 mL) were added, and the mixture was stirred for a further 12 h. Most of the solvent was removed under reduced pressure, and water was added to the concentrate. The aqueous layer was extracted with $Et_2O$, then the combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:$Et_2O$ = 1:6) to give **19** as a white solid (656 mg, 62% yield). Mp: 74–77 ºC. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.80 (1H, dt, *J* = 13.6, 5.4, 13.6 Hz), 2.20 (1H, dt, *J* = 13.6, 3.4 Hz), 2.32 (1H, dd, *J* = 15.6, 2.4 Hz), 2.32–2.46 (2H, m), 2.83 (1H, m), 3.16 (1H, d, *J* = 11.2 Hz), 3.50 (1H, m), 3.81 (3H, s), 4.13 (1H, dd, *J* = 10.7, 6.8 Hz), 4.50 (1H, d, *J* = 11.2 Hz), 6.00 (1H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 28.9, 33.4, 34.1, 49.5, 52.9, 68.4, 75.8, 127.1, 157.8, 172.5, 197.7. IR (KBr) $cm^{-1}$: 2956, 2856, 1731, 1673, 1630, 1457, 1273, 1256, 1229, 1173, 1118, 1101, 968. EI-MS *m*/z (%): 210 ($M^+$, 31), 180 (100), 150 (53), 109 (37), 93 (23). HR-EI-MS *m*/z: Calcd for $C_{11}H_{14}O_4$: 210.0892. Found: 210.0893 [$M^+$]. *Anal*. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.76; H, 6.49.

**Methyl (1*S**,4*S**,8*R**)-3-methylene-5-oxo-10-oxatricyclo[6.4.0.0$^{1,4}$]dodecane-8-carboxylate (2d)**

The photocycloaddition reaction was carried out using **19** (675 mg, 3.61 mmol) in $CH_2Cl_2$ (2.0 mL) and allene (5.0 mL) by irradiating for 4 h. Purification by column chromatography on silica gel (hexane:AcOEt = 4:1) afforded **2d** as a white solid (501 mg, 62% yield). Mp: 115–117 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.54 (1H, d, *J* = 13.2 Hz), 1.77 (1H, dd, *J* = 13.2, 7.8 Hz), 2.07 (1H, ddd, *J* = 13.7, 11.2, 7.3 Hz), 2.17 (1H, m), 2.29 (1H, m), 2.59–2.66 (2H, m), 3.06 (1H, dquint, *J* = 16.8, 2.4 Hz), 3.19 (1H, d, *J* = 11.2 Hz), 3.46–3.53 (2H, m), 3.73 (3H, s), 3.88 (1H, dd, *J* = 11.7, 4.9 Hz), 4.19 (1H, d, *J* = 11.2 Hz), 5.02 (1H, q, *J* = 2.4 Hz), 5.09 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 24.2, 33.8, 34.7, 38.0, 39.4, 48.4, 52.0, 61.0, 64.1, 69.4, 111.8, 139.5, 174.2, 205.9. IR (KBr) $cm^{-1}$: 2992, 2970, 2952, 2930, 2904, 2874, 2864, 1735, 1690, 1468, 1281, 1254, 1205, 1193, 1101, 1071, 961, 951, 905, 840. EI-MS *m*/z (%): 250 ($M^+$, 42), 218 (57), 191 (100), 176 (89), 105 (40), 91 (64). HR-EI-MS *m*/z: Calcd for $C_{14}H_{18}O_4$: 250.1205. Found: 250.1202 [$M^+$]. *Anal*. Calcd for $C_{14}H_{18}O_4$: C,

67.18; H, 7.25. Found: C, 67.33; H, 7.18.

**Preparation of 2e**



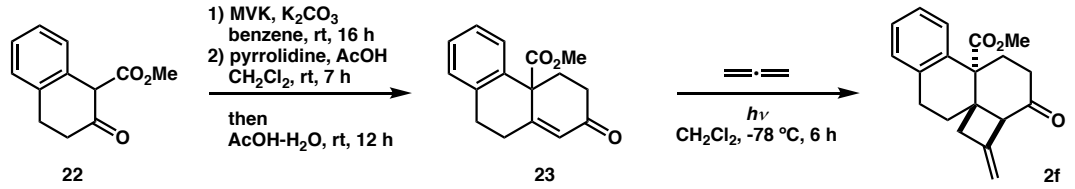

**Ethyl 2-(*tert*-butoxycarbonyl)-6-oxo-1,3,4,6,7,8,8a-heptahydroisoquinoline-8a-carboxylate (21)**

To a solution of **20**[6] (1.17 g, 4.31 mmol) in benzene (7.2 mL) were added methyl vinyl ketone (0.52 mL, 6.41 mmol) and $K_2CO_3$ (276 mg, 2.00 mmol) at 0 °C. The mixture was stirred for 4 h at room temperature, diluted with $Et_2O$, and passed through a Celite pad. The filtrate was concentrated in vacuo. The residue was dissolved in $CH_2Cl_2$ (7.2 mL), then pyrrolidine (0.36 mL, 4.31 mmol) and acetic acid (0.25 mL, 4.37 mmol) were added at 0 °C. The mixture was stirred for 18 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:AcOEt = 3:2, then hexane:$Et_2O$ = 1:2) to give **21** as a yellow oil (1.18 g, 85% yield). $^1$H-NMR (300 MHz, $CDCl_3$, 50 ºC) δ: 1.27 (3H, t, *J* = 7.1 Hz), 1.46 (9H, s), 1.83 (1H, m), 2.29–2.42 (4H, m), 2.62 (1H, d, *J* = 13.4 Hz), 2.82 (1H, d, *J* = 9.0 Hz), 2.82 (1H, m), 4.20 (2H, q, *J* = 7.1 Hz), 4.21 (1H, m), 4.68 (1H, dd, *J* = 13.4, 1.2 Hz), 5.97 (1H, s). $^{13}$C-NMR (75 MHz, $CDCl_3$, 50 ºC) δ: 14.1, 28.3, 30.9, 33.0, 34.4, 43.7, 49.1, 52.8, 61.8, 80.2, 127.5, 153.9, 158.8, 171.4, 197.9. IR (neat) cm$^{-1}$: 2978, 2933, 2871, 1726, 1696, 1627, 1467, 1426, 1366, 1294, 1256, 1230, 1160, 1126. EI-MS *m*/z (%): 323 ($M^+$, 4.0), 223 (100), 222 (37), 194 (26), 150 (98), 57 (57). HR-EI-MS *m*/z: Calcd for $C_{17}H_{25}NO_5$: 323.1733. Found: 323.1734 [$M^+$].

**Ethyl (1*S**,4*S**,8*R**)-10-(*tert*-butoxycarbonyl)-3-methylene-5-oxo-10-azatricyclo[6.4.0.0$^{1,4}$]-dodecane-8-carboxylate (2e)**

The photocycloaddition reaction was carried out using **21** (399 mg, 1.23 mmol) in MeOH (1.6 mL) and allene (4.0 mL) by irradiating for 1.5 h. Purification by column chromatography on silica gel (hexane:AcOEt = 1:1) afforded **2e** as a white solid (328 mg, 73% yield). Mp: 116–117 °C. $^1$H-NMR (300 MHz, $CDCl_3$, 50 ºC) δ: 1.23 (3H, t, *J* = 7.2 Hz), 1.45 (9H, s), 1.57 (1H, m), 1.86 (1H, m), 2.07–2.25 (3H, m), 2.47–2.66 (3H, m), 2.75 (1H, dt, *J* = 2.9, 13.2 Hz), 2.97 (1H, m), 3.43 (1H, m), 4.06 (1H, m), 4.13 (2H, q, *J* = 7.2 Hz), 4.49 (1H, br d, *J* = 13.2 Hz), 5.00 (1H, q, *J* = 2.4 Hz), 5.08 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (75 MHz, $CDCl_3$, 50 ºC) δ: 14.0, 25.9, 28.4, 33.6, 33.9, 37.3, 39.5, 40.2, 46.6, 47.8, 60.9, 61.0, 79.8, 111.7, 139.7, 154.6, 173.2, 205.8. IR (KBr) cm$^{-1}$: 3002, 2979, 2945, 2929, 2860, 1709, 1683, 1415, 1365, 1334, 1283, 1199, 1173, 1150, 1127, 1058. EI-MS *m*/z (%): 363 ($M^+$, 4.9), 306 (85), 262 (100), 234 (38), 190 (57), 57 (81). HR-EI-MS *m*/z: Calcd for $C_{20}H_{29}NO_5$: 363.2046. Found: 363.2050 [$M^+$]. *Anal*. Calcd for $C_{20}H_{29}NO_5$: C, 66.09; H, 8.04; N, 3.85. Found: C, 65.91; H, 8.08; N, 3.81.

**Preparation of 2f**



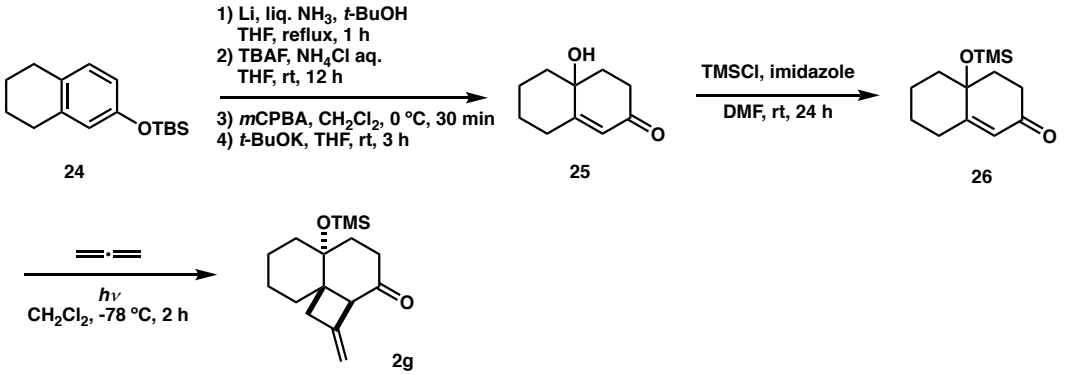

**Methyl 2-oxo-2,3,4,4a,9,10-hexahydrophenanthrene-4a-carboxylate (23)**

To a solution of **22**[7] (860 mg, 4.21 mmol) in benzene (14 mL) were added methyl vinyl ketone (0.48 mL, 4.61 mmol) and $K_2CO_3$ (232 mg, 1.68 mmol) at 0 °C. The mixture was stirred for 16 h at room temperature, diluted with $Et_2O$, and passed through a Celite pad. The filtrate was concentrated in vacuo. The residue was dissolved in $CH_2Cl_2$ (7.0 mL), then pyrrolidine (0.35 mL, 4.21 mmol) and acetic acid (0.24 mL, 4.21 mmol) were added at 0 °C. The mixture was stirred for 7 h at room temperature, water (3.0 mL) and acetic acid (1.0 mL) were added, and the mixture was stirred for a further 12 h. Most of the solvent was removed under reduced pressure, and water was added to the concentrate. The aqueous layer was extracted with AcOEt, then the combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 2:1) to give **23** as a yellow solid (952 mg, 88% yield). Mp: 61–64 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 2.04 (1H, dt, *J* = 4.9, 13.7 Hz), 2.54 (1H, m), 2.63–2.78 (2H, m), 2.89 (1H, m), 3.00 (1H, ddd, *J* = 13.7, 4.9, 2.4 Hz), 3.03–3.13 (2H, m), 3.68 (3H, s), 6.04 (1H, s), 7.15 (1H, m), 7.20–7.27 (2H, m), 7.47 (1H, dd, *J* = 7.3, 1.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 30.2, 32.6, 35.9, 50.2, 52.9, 126.4, 126.8, 127.2, 127.4, 129.0, 136.0, 136.6, 162.3, 171.8, 198.5. IR (KBr) cm$^{-1}$: 3021, 2948, 2846, 1726, 1714, 1674, 1626, 1449, 1440, 1228, 1205, 1162, 1092, 771, 750. EI-MS *m*/z (%): 256 ($M^+$, 21), 197 (100), 169 (23), 141 (22). HR-EI-MS *m*/z: Calcd for $C_{16}H_{16}O_3$: 256.1099. Found: 256.1095 [$M^+$]. *Anal*. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.84; H, 6.34.

**Methyl (3a*S**,5a*R**,11b*R**)-4-methylene-3-oxo-1,2,3,3a,4,5,6,7,11b-nonahydrocyclobuta[*j*]-phenanthrene-11b-carboxylate (2f)**

The photocycloaddition reaction was carried out using **23** (925 mg, 3.61 mmol) in $CH_2Cl_2$ (5.0 mL) and allene (3.0 mL) by irradiating for 6 h. Purification by column chromatography on silica gel (hexane:AcOEt = 4:1) afforded **2f** as a white solid (799 mg, 75% yield). Mp: 85–88 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.95 (1H, ddd, *J* = 14.1, 8.8, 2.4 Hz), 2.33–2.41 (2H, m), 2.42–2.55 (3H, m), 2.72–2.78 (2H, m), 2.86 (1H, ddd, *J* = 17.6, 8.8, 2.4 Hz), 3.01 (1H, dt, *J* = 17.6, 8.8 Hz), 3.54 (1H, m), 3.58 (3H, s), 4.93 (1H, q, *J* = 2.4 Hz), 5.06 (1H, q, *J* = 2.4 Hz), 7.11 (1H, dt, *J* = 9.2, 4.0 Hz), 7.20–7.24 (2H, m), 7.40 (1H, dt, *J* = 9.2, 4.0 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 25.5, 26.7, 31.0, 34.2, 38.5, 40.8, 49.4, 52.1, 61.2, 111.1, 125.8, 126.8, 127.2, 128.9, 136.1, 136.4, 140.3, 174.4, 206.7. IR (KBr) cm$^{-1}$: 2954, 2931, 2910, 1715, 1699, 1671, 1459, 1431, 1253, 1235, 1213, 1188, 1163, 1043, 910, 769. EI-MS *m*/z (%): 296 ($M^+$, 58), 237 (91), 219 (46), 195 (33), 181 (100), 165 (36), 141 (25). HR-EI-MS *m*/z: Calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1413 [$M^+$]. *Anal*. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.80; H, 6.82.

**Preparation of 2g**




**4a-Hydroxy-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (25)**

A solution of *t*-BuOH (3.3 mL, 36.1 mmol) in THF (14 mL) was placed in a 2-necked flask equipped with a dry ice condenser and a gas inlet, and the solution was cooled to -78 °C. Liquid ammonia (40 mL) was introduced through the gas inlet, and Li (167 mg, 24.1 mmol) was added. The mixture was stirred for 5 min, and a solution of **24** (1.05 g, 4.00 mmol) in THF was added dropwise. The mixture was refluxed (in dry ice–acetone bath at -25 °C) for 1 h and cooled again to -78 °C. The reaction was quenched with $NH_4Cl$ and MeOH. The mixture was allowed to warm to room temperature to remove ammonia, then water was added and the mixture was extracted with hexane three times. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was dissolved in THF (40 mL), and an aqueous solution of $NH_4Cl$ (214 mg, 4.00 mmol, in 10 mL) and a 1.0 M solution of TBAF in THF (8.0 mL, 8.0 mmol) were added. The mixture was stirred for 12 h at room temperature, and extracted with $Et_2O$. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure at 80 mmHg and 30 °C. The residue was dissolved in $CH_2Cl_2$ (20 mL), and *m*CPBA (77%, 1.34 g, 5.98 mmol) was added at 0 °C. The mixture was stirred for 30 min, then the reaction was quenched by addition of a 20% aqueous $Na_2S_2O_3$ solution (5 mL) at 0 °C. After stirring for 30 min at room temperature, the mixture was poured into saturated aqueous $NaHCO_3$ (5 mL) and the aqueous layer was extracted with $Et_2O$. The combined organic layers were washed with saturated aqueous $NaHCO_3$, water, and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was dissolved in THF (10 mL) and *t*-BuOK (89.8 mg, 0.800 mmol) was added at 0 °C. The mixture was stirred for 3 h at room temperature. Saturated aqueous $NH_4Cl$ (1.0 mL) was added to the mixture, and the mixture was extracted with $Et_2O$. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 1:2) to give **25** as a yellow solid (631 mg, 95% yield). Mp: 65–67 °C (crystallization from $Et_2O$–hexane). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.40 (1H, tq, *J* = 4.0, 13.6 Hz), 1.57 (1H, dt, *J* = 4.0, 13.6 Hz), 1.67 (1H, m), 1.71 (1H, br s), 1.83 (1H, tt, *J* = 13.6, 3.6 Hz), 1.89–1.97 (2H, m), 2.02–2.08 (2H, m), 2.30 (1H, dquint, *J* = 14.4, 2.0 Hz), 2.37 (1H, ddt, *J* = 16.8, 0.8, 4.8 Hz), 2.59 (1H, m), 2.65 (1H, ddd, *J* = 16.8, 10.8, 6.4 Hz), 5.78 (1H, d, *J* = 2.0 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 21.0, 26.8, 32.1, 33.8, 36.8, 40.2, 68.6, 124.9, 163.8, 199.5. IR (KBr) cm$^{-1}$: 3400, 2949, 2939, 2924, 2887, 2862, 1655, 1617, 1432, 1335, 1312, 1265, 1221, 1179, 1088, 1003, 955, 869. EI-MS *m*/z (%): 166 ($M^+$, 32), 138 (100), 124 (27), 109 (89), 67 (21). HR-EI-MS *m*/z: Calcd for $C_{10}H_{14}O_2$: 166.0994. Found: 166.0992 [$M^+$]. *Anal*. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.02; H, 8.59.

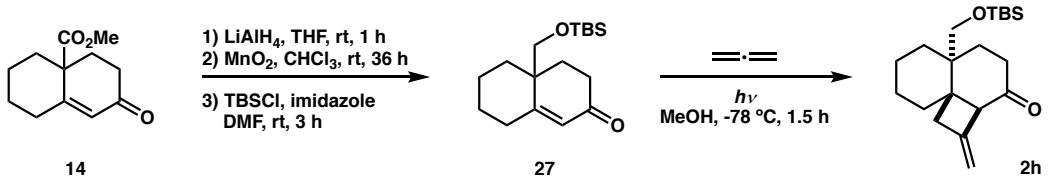
**4a-Trimethylsilyloxy-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (26)**

To a solution of **25** (500 mg, 3.01 mmol) in DMF (1.5 mL) were added imidazole (409 mg, 6.01 mmol) and TMSCl (0.49 mL, 3.88 mmol) at 0 °C. The mixture was stirred for 24 h at room temperature, saturated aqueous $NaHCO_3$ (1.0 mL) was added, and the mixture was diluted with $Et_2O$. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give **26** as a yellow oil (694 mg, 97% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (9H, s), 1.34 (1H, tq, *J* = 3.9, 13.2 Hz), 1.51 (1H, dt, *J* = 3.9, 13.2 Hz), 1.58 (1H, m), 1.79 (1H, tt, *J* = 13.2, 3.9 Hz), 1.86–1.95 (2H, m), 1.97 (1H, ddd, *J* = 13.7, 10.2, 4.9 Hz), 2.15 (1H, dd, *J* = 6.8, 4.9 Hz), 2.19 (1H, m), 2.31 (1H, ddd, *J* = 16.6, 6.8, 4,9 Hz), 2.54 (1H, ddd, *J* = 16.6, 10.2, 4.9 Hz), 2.58 (1H, ddt, *J* = 4.9, 2.0, 13.7 Hz), 5.70 (1H, d, *J* = 2.0 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 2.2, 21.2, 27.6, 32.4, 34.5, 36.3, 40.5, 72.3, 123.6, 166.1, 199.3. IR (neat) cm$^{-1}$: 2940, 2861, 1683, 1630, 1445, 1327, 1253, 1220, 1188, 1176, 1156, 1122, 1092, 1043, 1010, 989, 959, 878, 861, 841, 754. EI-MS *m*/z (%): 238 ($M^+$, 22), 223 (18), 210 (100), 209 (29), 181 (49), 73 (23). HR-EI-MS *m*/z: Calcd for $C_{13}H_{22}O_2Si$: 238.1389. Found: 238.1391 [$M^+$]. *Anal*. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.52; H, 9.24.

**(1*R**,4*S**,8*R**)-3-Methylene-8-trimethylsilyloxytricyclo[6.4.0.0$^{1,4}$]dodecane-5-one (2g)**

The photocycloaddition reaction was carried out using **26** (478 mg, 2.01 mmol) in $CH_2Cl_2$ (2.5 mL) and allene (4.0 mL) by irradiating for 2 h. Purification by column chromatography on silica gel (hexane:$Et_2O$ = 6:1) afforded **2g** as a colorless oil (380 mg, 68% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.12 (9H, s), 1.22 (1H, tq, *J* = 4.4, 13.2 Hz), 1.32 (1H, m), 1.35 (1H, dt, *J* = 4.4, 14.2 Hz), 1.46 (1H, m), 1.51–1.67 (3H, m), 1.77 (1H, m), 1.95 (1H, m), 2.26 (1H, m), 2.34 (1H, dq, *J* = 1.5, 8.3 Hz), 2.51 (1H, dt, *J* = 17.1, 2.4 Hz), 2.57 (1H, m), 2.70 (1H, m), 3.05 (1H, m), 4.95–4.98 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 2.1, 21.0, 21.3, 32.3, 32.6, 33.3, 33.6, 38.7, 45.5, 60.9, 75.0, 111.0, 140.7, 209.5. IR (neat) cm$^{-1}$: 2938, 2856, 1704, 1670, 1460, 1446, 1251, 1235, 1142, 1039, 997, 962, 887, 861, 839, 754. EI-MS *m*/z (%): 278 ($M^+$, 36), 197 (39), 160 (35), 146 (55), 133 (100), 131 (31), 73 (63). HR-EI-MS *m*/z: Calcd for $C_{16}H_{26}O_2Si$: 278.1702. Found: 278.1704 [$M^+$]. *Anal*. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.11; H, 9.49.

**Preparation of 2h**




14 27 2h

**4a-[(*tert*-Butyldimethylsilyloxy)methyl]-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (27)**

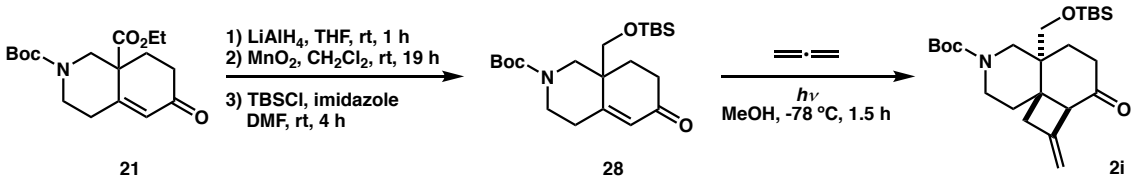
To a solution of **14** (230 mg, 1.10 mmol) in THF (2.8 mL) was added $LiAlH_4$ (104 mg, 2.75 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature, then diluted with excess $Et_2O$. Brine (0.65 mL) was added, and the mixture was vigorously stirred until the supernatant was clear. The precipitate was removed by filtration, and the supernatant was concentrated in vacuo. The residue was dissolved in $CHCl_3$ (5.5 mL), then $MnO_2$ (956 mg, 11.0 mmol) was added. The mixture was stirred for 36 h at room temperature, then passed through a Celite pad. The filtrate was concentrated in vacuo. To a solution of the residue in DMF (2.8 mL) were added imidazole (150 mg, 2.20 mmol) and TBSCl (215 mg, 1.43 mmol) at 0 °C. The mixture was stirred for 3 h at room temperature, diluted with $Et_2O$, and washed with water. The aqueous layer was extracted with

$Et_2O$, and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give **27** as a slightly yellow oil (302 mg, 93% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.04 (3H, s), 0.05 (3H, s), 0.88 (9H, s), 1.13 (1H, dt, *J* = 4.9, 13.2 Hz), 1.41 (1H, m), 1.53 (1H, dt, *J* = 13.7, 3.4 Hz), 1.56–1.63 (2H, m), 1.89 (1H, m), 2.02 (1H, m), 2.15 (1H, ddd, *J* = 13.2, 5.4, 2.4 Hz), 2.25–2.32 (3H, m), 2.54 (1H, ddd, *J* = 17.1, 14.1, 5.4 Hz), 3.66 (1H, d, *J* = 10.2 Hz), 3.70 (1H, d, *J* = 10.2 Hz), 5.84 (1H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: -5.6, 18.2, 21.7, 25.8, 26.9, 33.1, 33.3, 34.2, 35.4, 41.4, 63.4, 126.6, 167.1, 200.0. IR (neat) cm$^{-1}$: 2949, 2930, 2896, 2858, 1682, 1618, 1254, 1101, 1090, 839, 777. EI-MS *m*/z (%): 294 ($M^+$, 2.1), 264 (55), 237 (100), 121 (98), 89 (23), 73 (31). HR-EI-MS *m*/z: Calcd for $C_{17}H_{30}O_2Si$: 294.2015. Found: 294.2016 [$M^+$].

**(1*R**,4*S**,8*R**)-8-[(*tert*-Butyldimethylsilyloxy)methyl]-3-methylenetricyclo[6.4.0.0$^{1,4}$]dodecane-5-one (2h)**

The photocycloaddition reaction was carried out using **27** (250 mg, 0.85mmol) in MeOH (0.85 mL) and allene (6.0 mL) by irradiating for 1.5 h. Purification by column chromatography on silica gel (hexane:AcOEt = 10:1) afforded **2h** as a white solid (258 mg, 91% yield). Mp: 48–51 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.02 (3H, s), 0.03 (3H, s), 0.87 (9H, s), 1.00 (1H, m), 1.32–1.62 (7H, m), 1.77 (1H, dt, *J* = 14.2, 9.3 Hz), 1.86 (1H, ddd, *J* = 13.7, 8.8, 1.5 Hz), 2.32–2.56 (3H, m), 3.02 (1H, m), 3.09 (1H, m), 3.25 (1H, d, *J* = 10.2 Hz), 3.79 (1H, d, *J* = 10.2 Hz), 4.95 (1H, q, *J* = 2.4 Hz), 4.99 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: -5.62, -5.58, 18.2, 20.6, 20.8, 25.8, 27.6, 28.1, 32.2, 34.3, 37.9, 38.7, 41.8, 60.6, 61.1, 110.8, 141.5, 210.4. IR (KBr) cm$^{-1}$: 2929, 2858, 1699, 1671, 1470, 1463, 1254, 1095, 871, 838, 776. EI-MS *m*/z (%): 334 ($M^+$, 0.52), 277 (43), 185 (100), 73 (14). HR-EI-MS *m*/z: Calcd for $C_{20}H_{34}O_2Si$: 334.2328. Found: 334.2325 [$M^+$].

**Preparation of 2i**




21 28 2i

***tert*-Butyl 8a-[(*tert*-butyldimethylsilyloxy)methyl]-6-oxo-1,3,4,6,7,8,8a-heptahydroisoquinoline-2(1*H*)-carboxylate (28)**

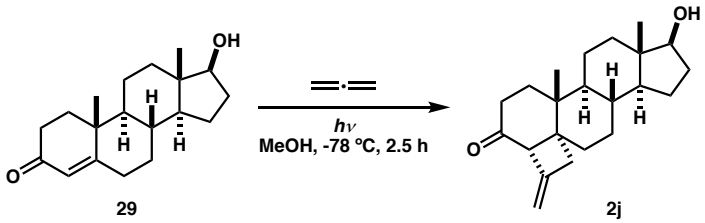
To a solution of **21** (551 mg, 1.70 mmol) in THF (4.3 mL) was added $LiAlH_4$ (161 mg, 4.25 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature, then diluted with excess $Et_2O$. Brine (0.65 mL) was added, and the mixture was vigorously stirred until the supernatant was clear. The precipitate was removed by filtration, and the supernatant was concentrated in vacuo. The residue was dissolved in $CH_2Cl_2$ (8.5 mL), then $MnO_2$ (1.18 g, 13.6 mmol) was added. The mixture was stirred for 19 h at room temperature, then passed through a Celite pad. The filtrate was concentrated in vacuo. To a solution of the residue in DMF (4.3 mL) were added imidazole (232 mg, 3.41 mmol) and TBSCl (333 mg, 2.21 mmol) at 0 °C. The mixture was stirred for 4 h at room temperature, diluted with $Et_2O$, and washed with water. The aqueous layer was extracted with $Et_2O$, and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 3:1) to give **28** as a slightly yellow oil (652 mg, 97% yield). $^1$H-NMR (300 MHz, $CDCl_3$, 50 ºC) δ: 0.03 (3H, s), 0.05 (3H, s), 0.87 (9H, s), 1.47 (9H, s), 1.65 (1H, dt, *J* = 5.1, 13.9 Hz), 2.11 (1H, ddd, *J* = 13.5, 5.7, 2.6 Hz), 2.24 (1H, m), 2.34

(1H, dddd, *J* = 17.0, 4.9, 2.6, 0.7 Hz), 2.42–2.54 (2H, m), 2.65 (1H, m), 2.80 (1H, dt, *J* = 3.3, 12.5 Hz), 3.66 (1H, d, *J* = 9.9 Hz), 3.72 (1H, d, *J* = 9.9 Hz), 4.17 (1H, br d, *J* = 13.4 Hz), 4.26 (1H, m), 5.90 (1H, d, *J* = 1.8 Hz). $^{13}$C-NMR (75 MHz, $CDCl_3$, 50 ºC) δ: -5.7, -5.6, 18.2, 25.8, 28.4, 30.2, 32.3, 34.1, 42.6, 44.0, 50.9, 64.7, 80.1, 127.5, 154.7, 161.7, 198.9. IR (neat) cm$^{-1}$: 2954, 2929, 2899, 2858, 1698, 1681, 1625, 1426, 1253, 1227, 1166, 1103, 840, 776. HR-FAB-MS (*m*-nitrobenzyl alcohol) *m*/z: Calcd for $C_{21}H_{38}NO_4Si$: 396.2570. Found: 396.2566 [MH$^+$].

***tert*-Butyl (1*S**,4*S**,8*R**)-8-[(*tert*-butyldimethylsilyloxy)methyl]-3-methylen-5-oxo-10-azatricyclo-[6.4.0.0$^{1,4}$]dodecane-10-carboxylate (2i)**

The photocycloaddition reaction was carried out using **28** (400 mg, 1.01 mmol) in MeOH (1.3 mL) and allene (4.0 mL) by irradiating for 1.5 h. Purification by column chromatography on silica gel (hexane:AcOEt = 4:1) afforded **2i** as a white solid (380 mg, 87% yield). Mp: 128–131 °C. $^1$H-NMR (300 MHz, $CDCl_3$, 50 ºC) δ: 0.02 (3H, s), 0.04 (3H, s), 0.89 (9H, s), 1.43 (1H, m), 1.46 (9H, s), 1.76–1.87 (3H, m), 2.35–2.62 (4H, m), 2.77 (1H, dt, *J* = 3.3, 13.0 Hz), 3.07 (1H, m), 3.18 (1H, m), 3.32 (1H, d, *J* = 10.3 Hz), 3.75 (1H, d, *J* = 10.3 Hz), 3.85 (1H, br d, *J* = 12.6 Hz), 4.11 (1H, m), 4.99 (1H, q, *J* = 2.4 Hz), 5.05 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (75 MHz, $CDCl_3$, 50 ºC) δ: -5.74, -5.65, 18.2, 25.0, 25.9, 28.5, 31.7, 33.9, 37.8, 38.4, 39.2, 40.5, 45.6, 60.7, 61.9, 79.7, 111.4, 140.3, 155.5, 208.3. IR (KBr) cm$^{-1}$: 2957, 2928, 2914, 2857, 1699, 1679, 1419, 1272, 1174, 1061, 852, 841, 771. HR-FAB-MS (*m*-nitrobenzyl alcohol) *m*/z: Calcd for $C_{24}H_{42}NO_4Si$: 436.2883. Found: 436.2881 [MH$^+$]. *Anal*. Calcd for $C_{24}H_{41}NO_4Si$: C, 66.16; H, 9.49; N, 3.21. Found: C, 66.21; H, 9.62; N, 3.17.

**Preparation of 2j**

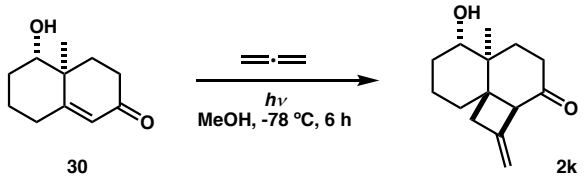



29 2j

**(2a*S*,5a*R*,5b*S*,7a*S*,8*S*,10a*S*,10b*R*,12a*R*)-8-Hydroxy-5a,7a-dimethyl-2-methyleneoctadecahydrocyclo-penta[*a*]cyclobuta[*j*]phenanthren-3-one (2j)**

The photocycloaddition reaction was carried out using testosterone (**29**, 499 mg, 1.73 mmol) in MeOH (3.0 mL) and allene (4.0 mL) by irradiating for 2.5 h. Purification by crystallization from $CHCl_3$—hexane afforded **2j** as white prisms (467 mg, 82% yield). Mp: 182–184 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.75 (3H, s), 0.84 (3H, s), 0.80–1.02 (3H, m), 1.09 (1H, dt, *J* = 4.4, 13.2 Hz), 1.20–1.34 (2H, m), 1.39–1.63 (6H, m), 1.70 (1H, ddd, *J* = 13.2, 5.9, 2.0 Hz), 1.74–1.94 (3H, m), 2.06 (1H, ddt, *J* = 13.2, 5.9, 9.3 Hz), 2.28–2.42 (2H, m), 2.61 (1H, ddd, *J* = 18.5, 8.8, 2.0 Hz), 2.96 (1H, dquint, *J* = 16.6, 2.4 Hz), 3.08 (1H, m), 3.64 (1H, t, *J* = 8.8 Hz), 4.96 (1H, q, *J* = 2.4 Hz), 5.00 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (100MHz, $CDCl_3$) δ: 11.2, 14.9, 21.1, 23.3, 26.4, 30.5, 30.8, 32.6, 33.8, 35.2, 36.4, 36.7, 37.4, 43.1, 45.2, 46.8, 50.7, 61.5, 81.8, 111.0, 140.8, 211.3. IR (KBr) cm$^{-1}$: 3331, 2984, 2969, 2952, 2926, 2867, 1703, 1669, 1203, 1074, 1059, 1025, 888, 735. EI-MS *m*/z (%): 328 (M$^+$, 100), 272 (25), 230 (58), 173 (24), 107 (26), 105 (30). 91 (29). HR-EI-MS *m*/z: Calcd for $C_{22}H_{32}O_2$: 328.2402. Found: 328.2399 [M$^+$]. $[\alpha]_D^{25}$ +66.6 (*c* 1.00, $CHCl_3$).

**Preparation of 2k**

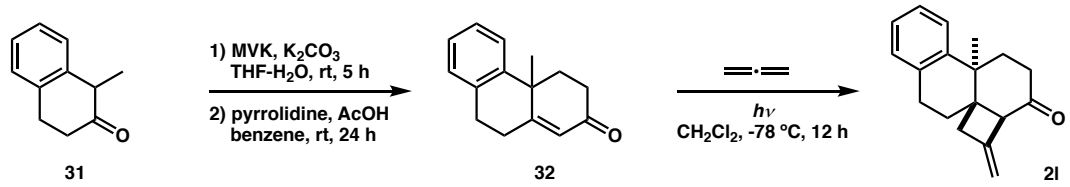



30 2k

**(1*R**,4*S**,8*S**,9*S**)-9-Hydroxy-8-methyl-3-methylenetricyclo[6.4.0.0$^{1,4}$]dodecan-5-one (2k)**

The photocycloaddition reaction was carried out using **30**[8] (557 mg, 3.09 mmol) in MeOH (2.0 mL) and allene (5.0 mL) by irradiating for 6 h. Purification by column chromatography on silica gel (hexane:AcOEt = 1:1) afforded **2k** as a white solid (562 mg, 83% yield). Mp: 81–84 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.84 (3H, s), 1.29 (1H, br s), 1.37 (1H, m), 1.47 (1H, tt, *J* = 13.7, 4.4 Hz), 1.52–1.77 (4H, m), 2.01 (1H, ddd, *J* = 13.7, 9.8, 2.4 Hz), 2.07 (1H, dt, *J* = 13.7, 8.8 Hz), 2.37 (1H, ddd, *J* = 19.0, 9.8, 1.5 Hz), 2.40 (1H, m), 2.64 (1H, ddd, *J* = 19.0, 8.3, 2.4 Hz), 3.04 (1H, dquint, *J* = 16.6, 2.4 Hz), 3.17 (1H, m), 3.44 (1H, dd, *J* = 10.7, 4.9 Hz), 4.98 (1H, q, *J* = 2.4 Hz), 5.01 (1H, q, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 12.4, 19.8, 28.9, 30.2, 31.9, 33.7, 37.1, 38.8, 44.2, 61.2, 73.2, 111.3, 140.5, 210.6. IR (KBr) cm$^{-1}$: 3442, 2936, 2864, 1696, 1467, 1448, 1408, 1246, 1201, 1077, 1010, 890. EI-MS *m*/z (%): 220 ($M^+$, 9.3), 147 (100), 145 (16), 119 (23), 105 (19), 91 (20). HR-EI-MS *m*/z: Calcd for $C_{14}H_{20}O_2$: 220.1463. Found: 220.1464 [$M^+$].

**Preparation of 2l**




31 32 2l

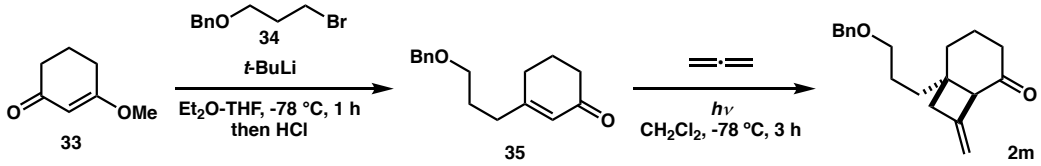
**4a-Methyl-2,3,4,4a,9,10-hexahydrophenanthren-2-one (32)**

To a solution of **31**[9] (600 mg, 3.75 mmol) and water (0.75 mL) in THF (7.5 mL) were added methyl vinyl ketone (0.55 mL, 6.78 mmol) and $K_2CO_3$ (207 mg, 1.50 mmol) at 0 °C. The mixture was vigorously stirred for 5 h at room temperature, then saturated aqueous $NH_4Cl$ was added. The aqueous layer was extracted with $Et_2O$, and the combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. To a solution of the residue in benzene (3.8 mL) were added pyrrolidine (0.31 mL, 3.71 mmol) and acetic acid (0.22 mL, 3.85 mmol) at 0 °C. The mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:AcOEt = 4:1) to give **32** as an orange solid (529 mg, 66% yield). Mp: 82–85 °C. $^1$H-NMR (300 MHz, $CDCl_3$) δ: 1.58 (3H, s), 2.07 (1H, dt, *J* = 5.0, 13.9 Hz), 2.39 (1H, ddd, *J* = 13.6, 5.1, 2.4 Hz), 2.48–2.58 (2H, m), 2.71 (1H, ddt, *J* = 6.0 1.5, 12.4 Hz), 2.73 (1H, ddd, *J* = 17.6, 14.6, 5.1 Hz), 2.90 (1H, ddd, *J* = 15.9, 12.4, 4.9 Hz), 3.07 (1H, ddd, *J* = 15.9, 6.0, 2.7 Hz), 5.91 (1H, s), 7.09–7.18 (2H, m), 7.22–7.32 (2H, m). $^{13}$C-NMR (75 MHz, $CDCl_3$) δ: 27.6, 31.1, 31.2, 34.7, 36.9, 39.2, 124.2, 126.1, 126.2, 127.0, 128.6, 134.7, 143.7, 169.9, 198.9. IR (KBr) cm$^{-1}$: 3058, 3023, 2966, 2930, 2849, 1671, 1627, 1489, 1445, 1236, 762, 696. EI-MS *m*/z (%): 212 ($M^+$, 77), 197 (100), 184 (32), 170 (51), 169 (41), 141 (40). HR-EI-MS *m*/z: Calcd for $C_{15}H_{16}O$: 212.1201. Found: 212.1201 [$M^+$]. *Anal*. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.61; H, 7.52.

**(3a*S**,5a*R**,11b*S**)-11b-Methyl-4-methylene-1,2,3,3a,4,5,6,7,11b-nonahydrocyclobuta[*j*]-phenanthren-3-one (2l)**

The photocycloaddition reaction was carried out using **32** (331 mg, 1.56 mmol) in $CH_2Cl_2$ (2.0 mL) and allene (5.0 mL) by irradiating for 12 h. Purification by column chromatography on silica gel (hexane:AcOEt = 8:1) afforded **2l** as a white solid (273 mg, 69% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.12 (3H, s), 1.82 (1H, ddd, *J* = 13.7, 8.3, 1.5 Hz), 2.26 (1H, m), 2.38–2.47 (3H, m), 2.52 (1H, m), 2.60 (1H, m), 2.76 (1H, ddd, *J* = 19.0, 5.9, 3.4 Hz), 2.95 (1H, m), 3.05 (1H, dt, *J* = 18.0, 9.3 Hz), 3.32 (1H, m), 4.95 (1H, q, *J* = 2.4 Hz), 5.03 (1H, q, *J* = 2.4 Hz), 7.09–7.18 (3H, m), 7.28 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 25.1, 25.6, 28.8, 29.9, 34.3, 37.6, 38.1, 42.5, 61.0, 111.1, 124.4, 125.8, 126.1, 129.4, 135.3, 139.9, 143.5, 210.1. IR (KBr) cm$^{-1}$: 3067, 3013, 2938, 2871, 2842, 1696, 1669, 1463, 1433, 1246, 1190, 890, 761. EI-MS *m*/z (%): 252 ($M^+$, 81), 237 (42), 195 (75), 181 (72), 165 (37), 155 (100), 141 (44). HR-EI-MS *m*/z: Calcd for $C_{18}H_{20}O$: 252.1514. Found: 252.1512 [$M^+$]. *Anal*. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.63; H, 7.97.

**Preparation of 2m**




**3-[3-(Benzyloxy)propyl]cyclohex-2-enone (35)**

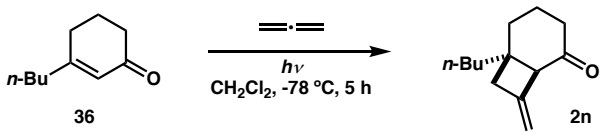
To a stirred solution of **34** (4.58 g, 20.0 mmol) in $Et_2O$ (50 mL) was added dropwise a 1.6 M solution of *t*-BuLi in pentane (25. 0 mL, 40.0 mmol) at -78 °C. The mixture was allowed to warm to 0 °C for 20 min and then re-cooled to -78°C. A solution of **33** (631 mg, 5.00 mmol) in THF (50 mL) was added dropwise, and the mixture was stirred for 1 h. The reaction was quenched by the addition of 1 M HCl. The aqueous layer was extracted with $Et_2O$, and the combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:AcOEt:$CHCl_3$ = 10:3:2) to give **35** as a colorless oil (863 mg, 71% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.77–1.86 (2H, m), 1.97 (2H, quint, *J* = 6.2 Hz), 2.27–2.37 (6H, m), 3.49 (2H, t, *J* = 6.2 Hz), 4.49 (2H, s), 5.88 (1H, m), 7.26–7.38 (5H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 22.7, 27.0, 29.7, 34.7, 37.3, 69.3, 73.0, 125.7, 127.6, 127.7, 128.4, 138.2, 166.0, 199.9. IR (neat) cm$^{-1}$: 2942, 2863, 1664, 1624, 1454, 1252, 1102, 738, 699. EI-MS *m*/z (%): 244 ($M^+$, 4), 200 (26), 124 (11), 123 (15), 110 (36), 92 (10), 91 (100). HR-EI-MS *m*/z: Calcd for $C_{16}H_{20}O_2$: 224.1463. Found: 244.1466 [$M^+$].

**(1*S**,6*S**)-6-[3-(Benzyloxy)propyl]-8-methylenebicyclo[4.2.0]octan-2- one (2m)**

The photocycloaddition reaction was carried out using **35** (620 mg, 2.54 mmol) in $CH_2Cl_2$ (6.0 mL) and allene (6.0 mL) by irradiating for 3 h. Purification by column chromatography on silica gel (hexane:AcOEt = 4:1) afforded **2m** as a colorless oil (570 mg, 79% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.49–1.69 (5H, m), 1.69–1.87 (2H, m), 1.94–2.18 (2H, m), 2.45–2.62 (3H, m), 3.23 (1H, m), 3.45–3.49 (2H, m), 4.50 (2H, s), 4.89 (1H, q, *J* = 2.7 Hz), 4.91 (1H, q, *J* = 2.7 Hz), 7.25–7.38 (5H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 19.1, 24.7, 32.3, 38.3, 38.7, 38.8, 40.3, 60.1, 70.4, 72.9, 108.7, 127.55, 127.60, 128.4, 138.4, 141.4, 209.7. IR (neat) cm$^{-1}$: 2938, 2852, 1698, 1670, 1454, 1103, 884, 737, 698. EI-MS *m*/z (%): 284 ($M^+$, 3), 193 (27), 163 (10), 150 (14), 149 (11), 91 (100). HR-EI-MS *m*/z: Calcd for $C_{19}H_{24}O_2$: 284.1776. Found: 284.1774 [$M^+$]. *Anal*. Calcd for

$C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.02; H, 8.50.

**Preparation of 2n**

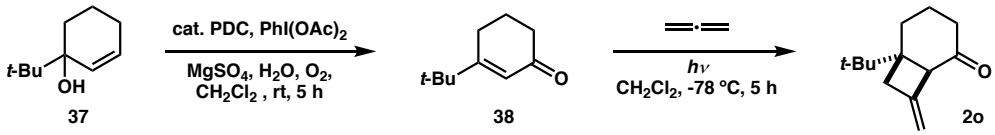



36 2n

**(1*S**,6*R**)-6-Butyl-8-methylenebicyclo[4.2.0]octan-2-one (2n)**

The photocycloaddition reaction was carried out using **36**[10] (1.10 g, 7.23 mmol) in $CH_2Cl_2$ (10 mL) and allene (10 mL) by irradiating for 5 h. Purification by column chromatography on silica gel (hexane:$Et_2O$ = 6:1) afforded **2n** as a colorless oil (973 mg, 70% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (3H, t, *J* = 7.1 Hz), 1.19–1.36 (4H, m), 1.51–1.57 (3H, m), 1.72 (1H, dddd, *J* = 13.5, 6.2, 2.7, 1.1 Hz), 1.81 (1H, m), 2.01 (1H, m), 2.12 (1H, m), 2.46–3.26 (3H, m), 3.21 (1H, m), 4.87–4.91 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 14.1, 19.2, 23.1, 26.4, 32.4, 38.87, 38.91, 40.5, 41.6, 60.2, 108.5, 141.7, 210.0. IR (neat) cm$^{-1}$: 2929, 2857, 1702, 1670, 1459, 1272, 883. EI-MS *m*/z (%): 192 ($M^+$, 65), 164 (25), 150 (31), 149 (42), 136 (22), 135 (100), 121 (27), 108 (33), 107 (41), 94 (20), 93 (50), 91 (28), 79 (36), 77 (20), 55 (23). HR-EI-MS *m*/z: Calcd for $C_{13}H_{20}O$: 192.1514. Found: 192.1513 [$M^+$].

**Preparation of 2o**




37 38 2o

**3-(*tert*-Butyl)cyclohex-2-enone (38)**

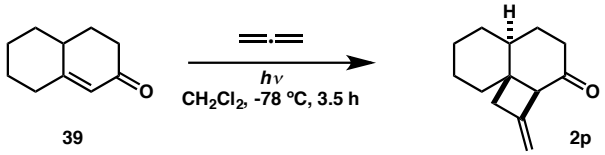
To a stirred mixture of **37**[11] (1.20 g, 7.78 mmol), $MgSO_4$ (968 mg, 8.04 mmol) and water (0.15 mL, 8.32 mmol) in $CH_2Cl_2$ (16 mL) were added $PhI(OAc)_2$ (3.88 g, 12.0 mmol) and PDC (151 mg, 0.40 mmol) at 0 °C. The mixture was stirred for 5 h at room temperature under an $O_2$ atmosphere. This was followed by the addition of saturated aqueous $NaHCO_3$ and 20% aqueous $Na_2S_2O_3$ solution. After stirring for 15 min, the suspension was diluted with $Et_2O$. The organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:$E_2O$ = 3:2) to give **38** as a slightly yellow oil (1.02 g, 87% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.12 (9H, s), 1.97 (2H, quint, *J* = 6.4 Hz), 2.33–2.37 (4H, m), 5.14 (1H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 23.1, 25.7, 28.0, 36.5, 37.3, 122.7, 173.6, 200.5. IR (neat) cm$^{-1}$: 2965, 2870, 1670, 1612, 1346, 1326, 1258, 1242, 889. EI-MS *m*/z (%): 152 ($M^+$, 68), 137 (16), 110 (15), 109 (100), 96 (68), 82 (12), 81 (26), 67 (20), 57 (15). HR-EI-MS *m*/z: Calcd for $C_{10}H_{16}O$: 152.1201. Found: 152.1205 [$M^+$].

**(1*S**,6*S**)-6-(*tert*-Butyl)-8-methylenebicyclo[4.2.0]octan-2-one (2o)**

The photocycloaddition reaction was carried out using **38** (790 mg, 5.19 mmol) in $CH_2Cl_2$ (10 mL) and allene (8.0 mL) by irradiating for 5 h. Purification by column chromatography on silica gel (hexane:$Et_2O$ = 6:1) afforded **2o** as a colorless oil (843 mg, 84% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.89 (9H, s), 1.61–1.71 (2H, m), 1.87 (1H, m), 1.99–2.16 (2H, m), 2.38 (1H, ddt, *J* = 16.8, 4.5, 1.8 Hz), 2.53 (1H, m), 2.92 (1H, dt, *J* = 16.8, 2.7 Hz), 3.51 (1H, m), 4.88–4.91 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 18.8, 24.6, 29.9, 34.7, 36.0,

38.5, 44.7, 55.5, 108.8, 140.9, 210.5. IR (neat) $cm^{-1}$: 2951, 2871, 1698, 1668, 1367, 1232, 1175, 883. EI-MS *m*/z (%): 192 ($M^+$, 14), 177 (100), 149 (55), 136 (14), 122 (15), 121 (52), 109 (13), 108 (14), 107 (29), 41 (14). HR-EI-MS *m*/z: Calcd for $C_{13}H_{20}O$: 192.1514. Found: 192.1513 [$M^+$].

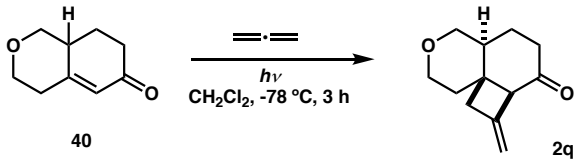
**Preparation of 2p**




**(1*R**,4*S**,8*S**)-3-Methylenetricyclo[6.4.0.0$^{1,4}$]dodecan-5-one (2p)**

The photocycloaddition reaction was carried out using **39**[12] (780 mg, 5.19 mmol) in $CH_2Cl_2$ (6.0 mL) and allene (6.0 mL) by irradiating for 3.5 h. Purification by column chromatography on silica gel (hexane:$Et_2O$ = 4:1) afforded **2p** as a colorless oil (719 mg, 73% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.08 (1H, m), 1.19–1.48 (4H, m), 1.50–1.64 (3H, m), 1.65–1.75 (2H, m), 1.85 (1H, m), 2.21 (1H, dddd, *J* = 19.1, 11.7, 7.5, 1.2 Hz), 2.36 (1H, dt, *J* = 16.7, 2.7 Hz), 2.60 (1H, dddd, *J* = 19.1, 6.2, 1.6, 0.9 Hz), 2.77 (1H, m), 3.15 (1H, m), 4.92–4.96 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 22.0, 25.6, 26.2, 28.5, 35.5, 39.0, 39.1, 40.0, 42.1, 61.5, 110.0, 141.3, 210.5. IR (neat) $cm^{-1}$: 2923, 2851, 1698, 1668, 1459, 1447, 1234, 1199, 1029, 985, 828, 804. EI-MS *m*/z (%): 190 ($M^+$, 50), 162 (25), 161 (20), 148 (22), 147 (34), 133 (100), 119 (25), 105 (37), 93 (23), 91 (49), 79 (29). HR-EI-MS *m*/z: Calcd for $C_{13}H_{18}O$: 190.1358. Found: 190.1356 [$M^+$]. *Anal*. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.82; H, 9.58.

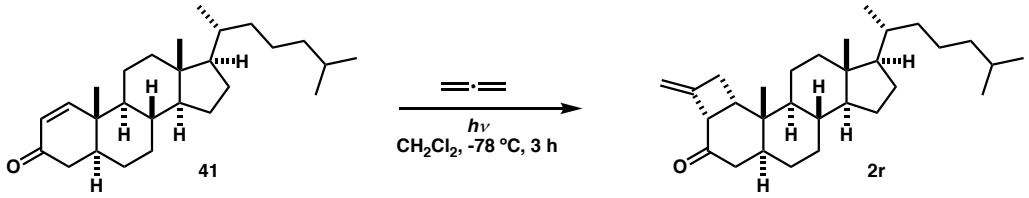
**Preparation of 2q**




**(1*R**,4*S**,8*R**)-3-Methylene-10-oxatricyclo[6.4.0.0$^{1,4}$]dodecan-5-one (2q)**

The photocycloaddition reaction was carried out using **40**[13] (800 mg, 5.26 mmol) in $CH_2Cl_2$ (10 mL) and allene (10 mL) by irradiating for 3 h. Purification by column chromatography on silica gel (hexane:AcOEt = 1:1) afforded **2q** as a colorless oil (921 mg, 91% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.59–1.65 (2H, m), 1.72–1.89 (3H, m), 2.28 (1H, m), 2.49 (1H, dt, *J* = 16.7, 2.6 Hz), 2.68 (1H, m), 2.95 (1H, m), 3.18 (1H, t, *J* = 11.1 Hz), 3.24 (1H, m), 3.42 (1H, dt, *J* = 2.1, 12.1 Hz), 3.75 (1H, dd, *J* = 11.1, 3.1 Hz), 3.90 (1H, ddd, *J* = 12.1, 4.6, 0.9 Hz), 5.00–5.03 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 20.5, 35.0, 37.9, 38.2, 38.8, 41.3, 60.8, 64.0, 68.2, 111.0, 139.9, 208.9. IR (neat) $cm^{-1}$: 2928, 2845, 1698, 1669, 1466, 1224, 1108, 851. EI-MS *m*/z (%): 192 ($M^+$, 100), 149 (46), 148 (60), 136 (63), 135 (85), 119 (57), 106 (57), 105 (85), 92 (47), 91 (91), 79 (59), 77 (45). HR-EI-MS *m*/z: Calcd for $C_{12}H_{16}O_2$: 192.1150. Found: 192.1146 [$M^+$].

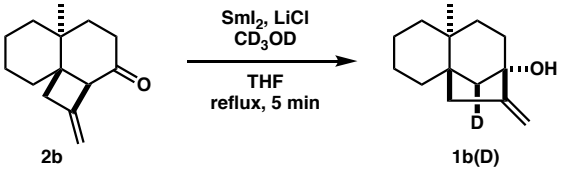
**Preparation of 2r**




**(2a*S*,4a*S*,4b*R*,4c*S*,6a*R*,7*R*,9a*R*,9b*S*,11a*S*)-4b,6a,9b-Trimethyl-3-methylene-7-[(*R*)-6-methylheptan-2-yl]-hexadecahydro-1*H*-cyclobuta[*g*]cyclopenta[*a*]phenanthren-2-one (2r)**

The photocycloaddition reaction was carried out using **41**[14] (100 mg, 0.26 mmol) in $CH_2Cl_2$ (5.0 mL) and allene (10 mL) by irradiating for 3 h. Purification by column chromatography on silica gel (hexane:$Et_2O$ = 5:1) afforded **2r** as a white solid (66 mg, 60% yield). Mp: 93–95 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.66 (3H, s), 0.81 (3H, s), 0.86 (3H, d, *J* = 6.6 Hz), 0.87 (3H, d, *J* = 6.6 Hz), 0.90 (3H, d, *J* = 6.6 Hz), 0.93–1.17 (9H, m), 1.21–1.43 (9H, m), 1.45–1.72 (4H, m), 1.83 (1H, m), 1.95–2.07 (3H, m), 2.34 (1H, m), 2.62–2.75 (3H, m), 3.60 (1H, m), 4.88 (1H, q, *J* = 2.2 Hz), 4.95 (1H, q, *J* = 2.2 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 11.9, 13.0, 18.7, 21.3, 22.5, 22.8, 23.8, 24.2, 28.0, 28.2, 28.6, 29.8, 31.5, 35.2, 35.70, 35.71, 35.8, 36.1, 39.5, 39.67, 39.72, 42.3, 42.4, 46.9, 54.2, 56.2, 56.3, 109.0, 142.7, 210.1. IR (KBr) cm$^{-1}$: 2934, 2867, 1701, 1668, 1466, 1382, 1196, 1178, 954, 916, 888. EI-MS *m*/z (%): 424 ($M^+$, 100), 409 (21), 382 (18), 367 (23), 353 (35), 270 (18), 269 (23), 227 (13). HR-EI-MS *m*/z: Calcd for $C_{30}H_{48}O$: 424.3705. Found: 424.3703 [$M^+$]. *Anal*. Calcd for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.59; H, 11.55. $[\alpha]_D^{25}$ +58.0 (*c* 1.00, $CHCl_3$).

**Deuteration Experiment of 1b**




**(1*R**,6*S**,9*R**,12*S**)-6-Methyl-10-methylene[12-$^2$H]tricyclo[7.2.1.0$^{1,6}$]dodecan-9-ol [1b(D)]**

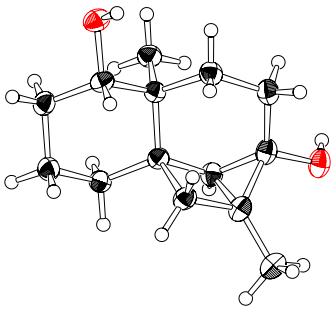
Bicyclo[4.2.0]octanone **2b** (28.6 mg, 0.140 mmol) and LiCl (35.6 mg, 0.840 mmol) were dissolved in an appropriate amount of $CD_3OD$ under an argon atmosphere. The solution was concentrated in vacuo. This operation was repeated three times. To the residue was added THF and the solution was concentrated in vacuo to dry thoroughly. The resulting a mixture of **2b** and LiCl was dissolved by adding a solution of $CD_3OD$ (5.7 μL, 0.140 mmol) in THF (1.8 mL). This solution was added dropwise to a refluxing 0.1 M solution of $SmI_2$ in THF (4.2 mL, 0.42 mmol). The mixture was refluxed for 5 min. After cooling to room temperature, $D_2O$ (0.30 mL) was added, and the mixture was stirred for 30 min in air to quench the reaction. The product was isolated according to work-up procedure II, and purified by column chromatography on silica gel (hexane:$Et_2O$ = 2:1) to give **1b(D)** as a slightly yellow oil (22.4 mg, 77% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.02 (3H, s), 1.08 (1H, dt, *J* = 13.2, 3.4 Hz), 1.19–1.40 (5H, m), 1.41–1.56 (4H, m), 1.72 (1H, dt, *J* = 3.9, 13.7 Hz), 1.78 (1H, s), 1.95 (1H, dt, *J* = 5.9, 12.2 Hz), 2.02 (1H, dt, *J* = 17.6, 2.4 Hz), 2.76 (1H, dq, *J* = 17.6, 2.4 Hz), 4.79 (1H, m), 4.92 (1H, t, *J* = 2.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.7, 22.9, 34.6, 35.1, 36.0, 36.5, 36.7, 39.8, 42.4, 47.3 (t, $J_{C-D}$ = 19.8 Hz), 80.2, 101.9, 156.7. IR (neat) cm$^{-1}$: 3357, 3073, 2969, 2921, 2858, 1663, 1468, 1460, 1426, 1378, 1172, 1143, 1100, 1082, 1061, 883, 757. EI-MS *m*/z (%):

207 ($M^+$, 100), 189 (30), 149 (17), 122 (79), 109 (43). HR-EI-MS *m*/z: Calcd for $C_{14}H_{21}OD$: 207.1733. Found: 207.1730 [$M^+$].

**X-ray crystallographic analysis**

**(1*R**,5*S**,6*S**,9*S**,12*R**)-6,10-Dimethyltetracyclo[7.2.1.0$^{1,6}$.0$^{10,12}$]dodecane-5,9-diol (10)**

X-ray crystallographic data were recorded on a Rigaku R-AXIS RAPID with a MicroMax-007HF diffractometer using filtered Cu-*K*α radiation. The structure was solved by direct methods (SIR92)[15] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure 4.0 crystallographic software package except for refinement, which was performed using SHELXL-97.[16]



ORTEP drawing of **10**

Crystal data for **10**

| | |
|---|---|
| Chemical formula | $C_{14}H_{22}O_2$ |
| MW | 222.33 |
| Crystal system, space group | Orthorhombic, *Pbca* |
| Temperature (K) | 93 |
| *a*, *b*, *c* (Å) | 9.3826 (3), 13.5881 (4), 18.6630 (5) |
| *V* (Å$^3$) | 2379.39 (11) |
| *Z* | 8 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 0.63 |
| Crystal size (mm) | 0.20 × 0.09 × 0.04 |

Data collection

| | |
|---|---|
| Diffractometer | Rigaku R-AXIS RAPID |
| Absorption correction | Multi-scan<br>*ABSCOR* (Rigaku, 1995) |
| $T_{min}$, $T_{max}$ | 0.832, 0.975 |
| No. of measured, independent, and observed [$F^2 > 2.0\sigma(F^2)$] reflections | 24450, 2172, 1834 |
| $R_{int}$ | 0.053 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.602 |

Refinement

| | |
|---|---|
| R[$F^2 > 2\sigma(F^2)$], *wR*($F^2$), *S* | 0.049, 0.126, 1.09 |
| No. of reflections | 2172 |
| No. of parameters | 149 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.22, -0.25 |

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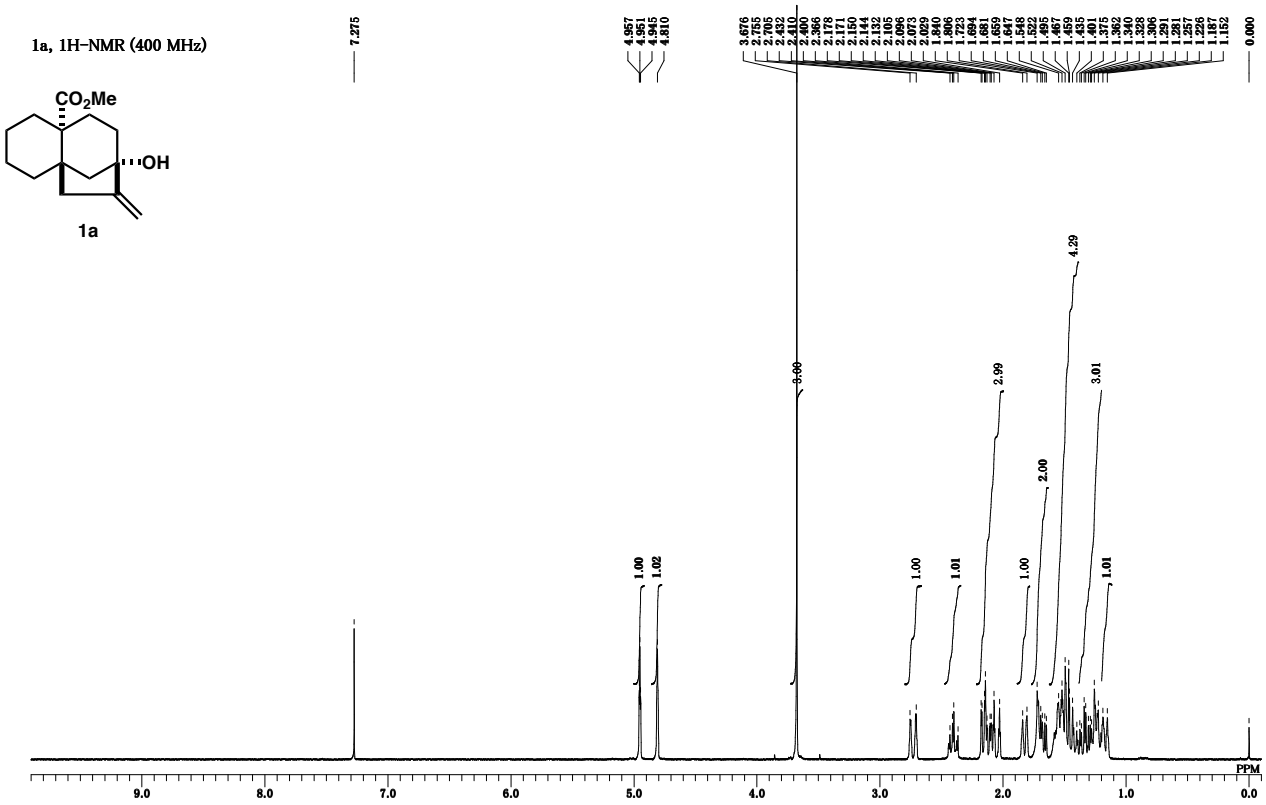
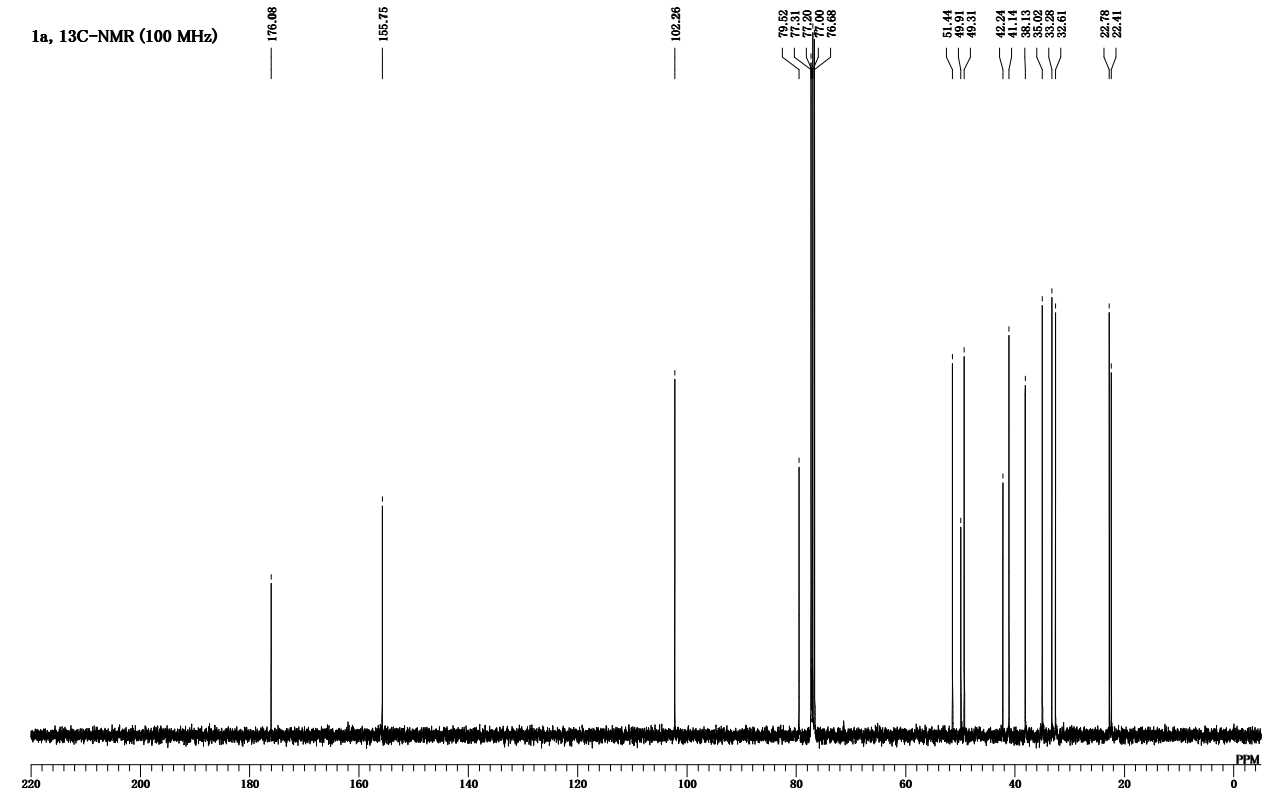
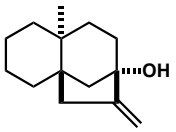
16) Sheldrick, G. M., *Acta Cryst.* **2008**, *A64*, 112–122.

## $^{1}$H- and $^{13}$C-NMR Spectra of the Products and the Substrates



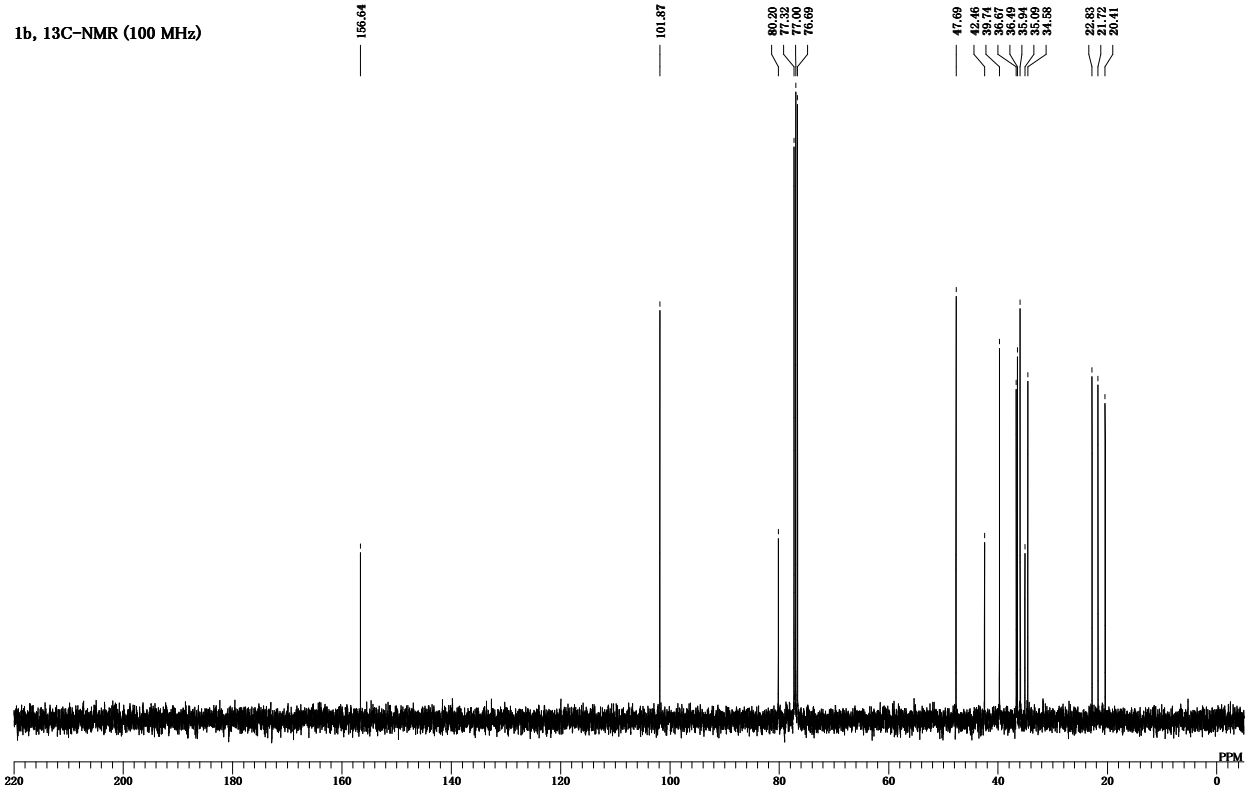
1b, 1H-NMR (400 MHz)




1b




1b, 13C-NMR (100 MHz)



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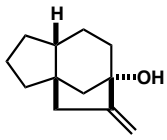
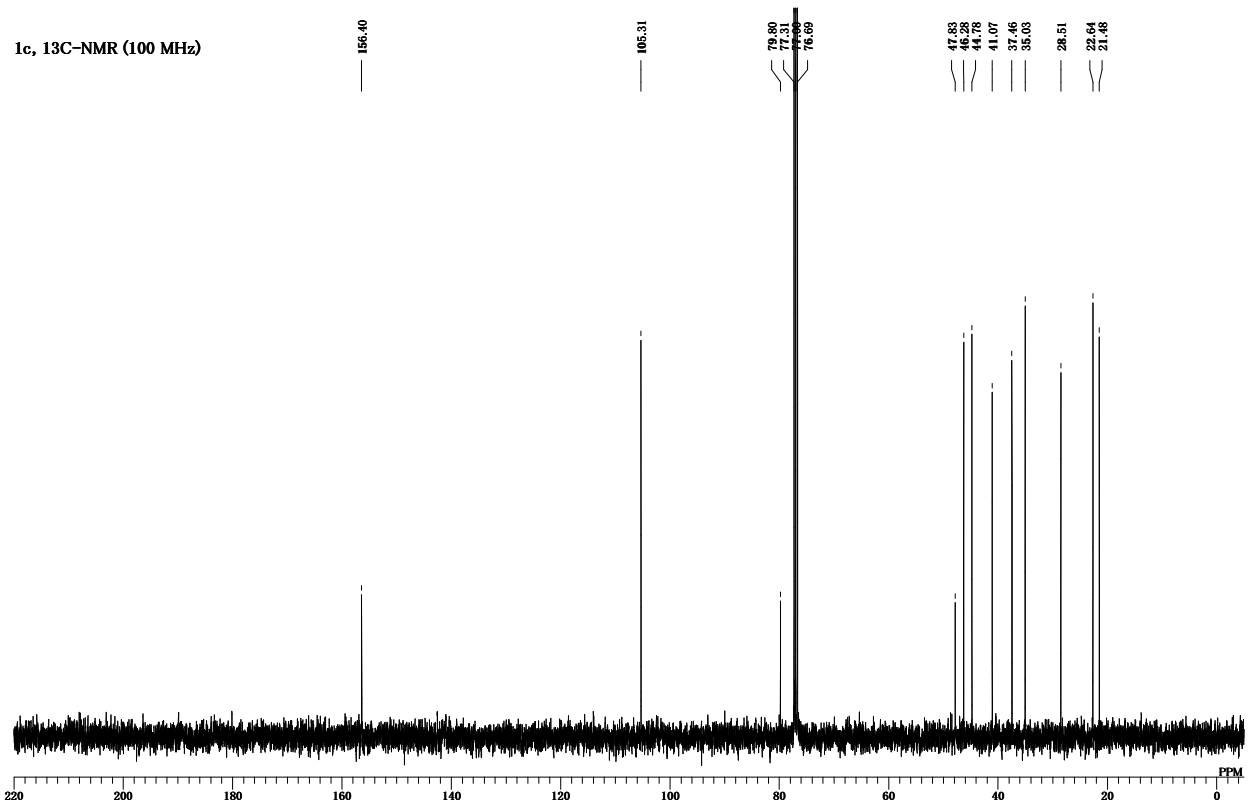



1c




1c, 13C-NMR (100 MHz)



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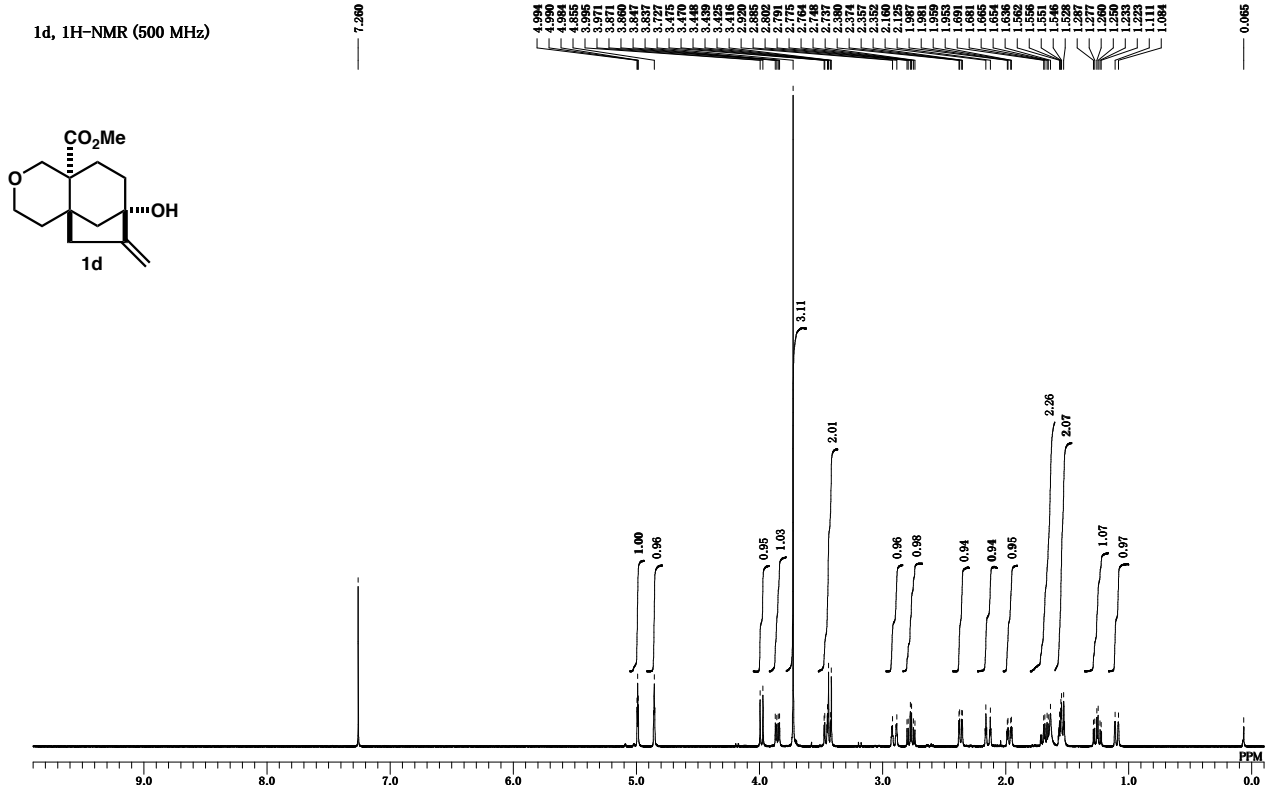


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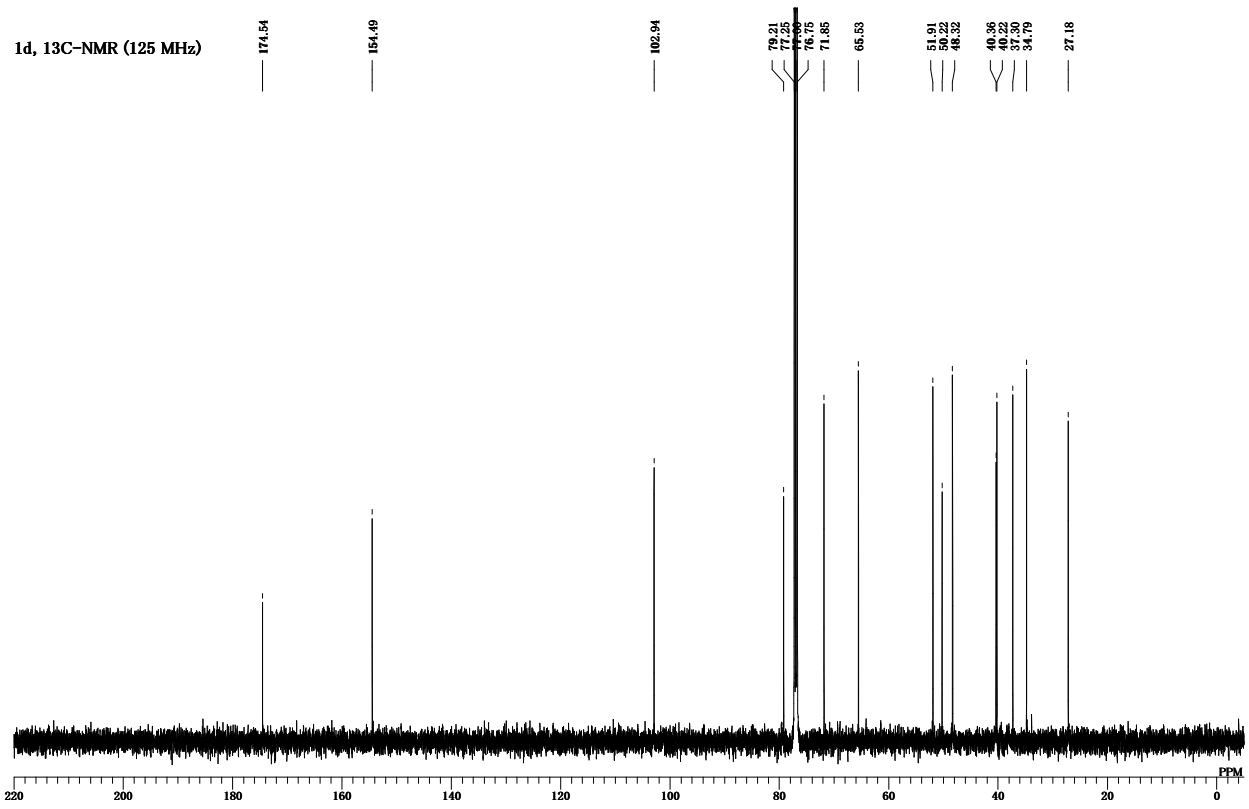
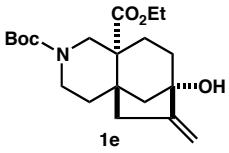


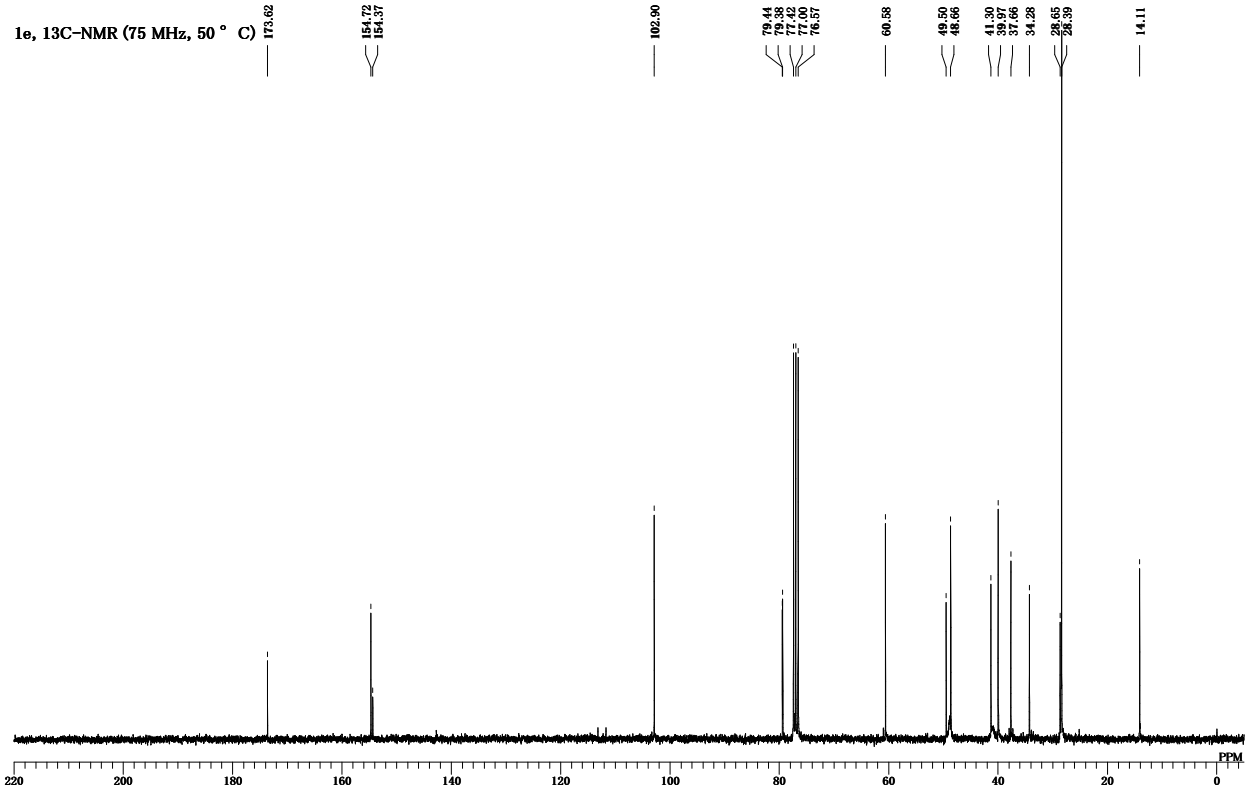
1e, 1H-NMR (300 MHz, 50 ° C)



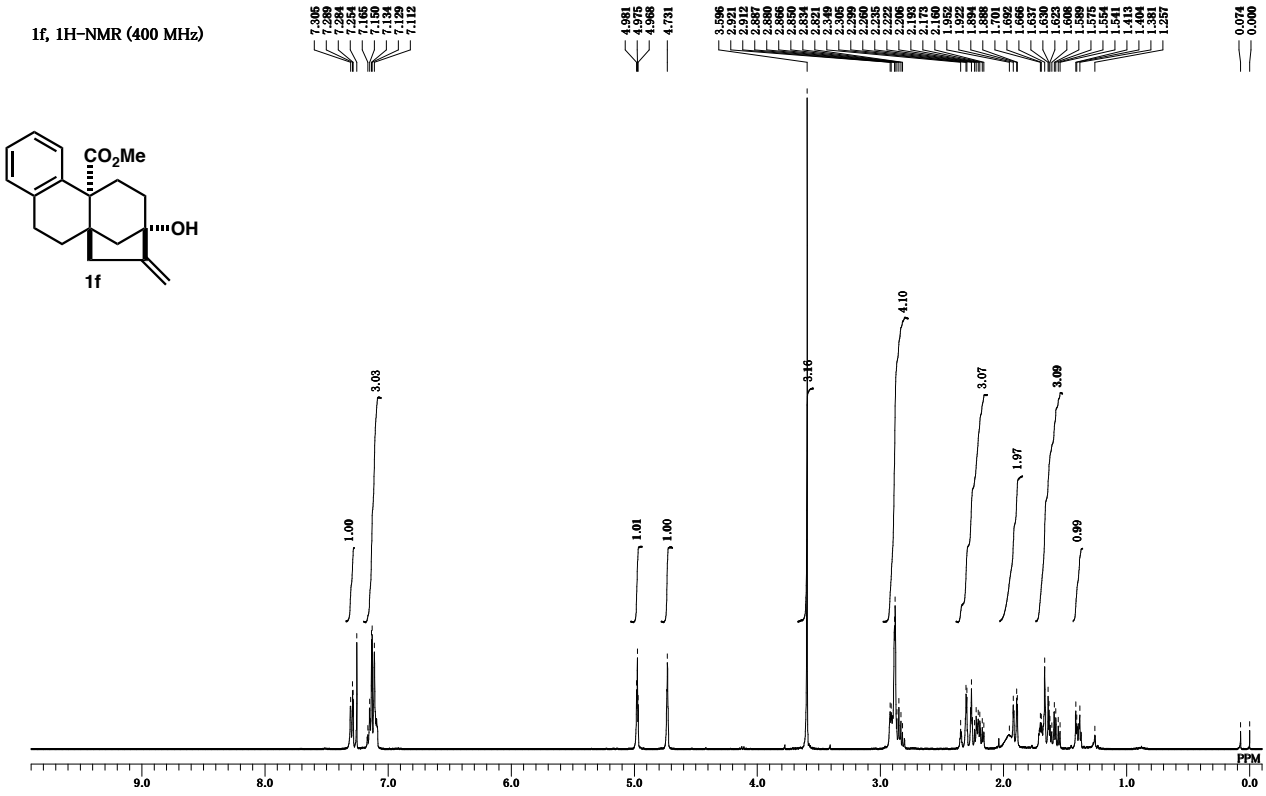

1e



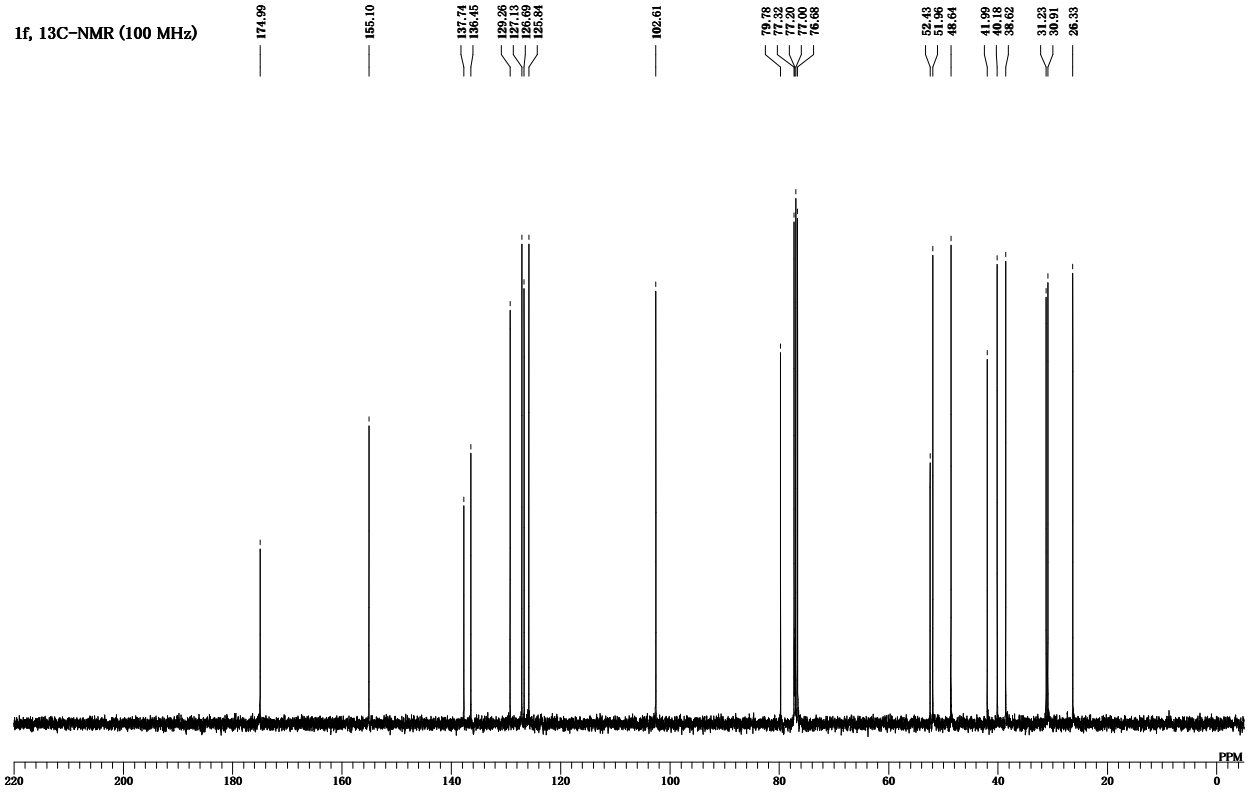

1e, 13C-NMR (75 MHz, 50 ° C)



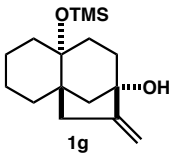
1f, 1H-NMR (400 MHz)




1f, 13C-NMR (100 MHz)



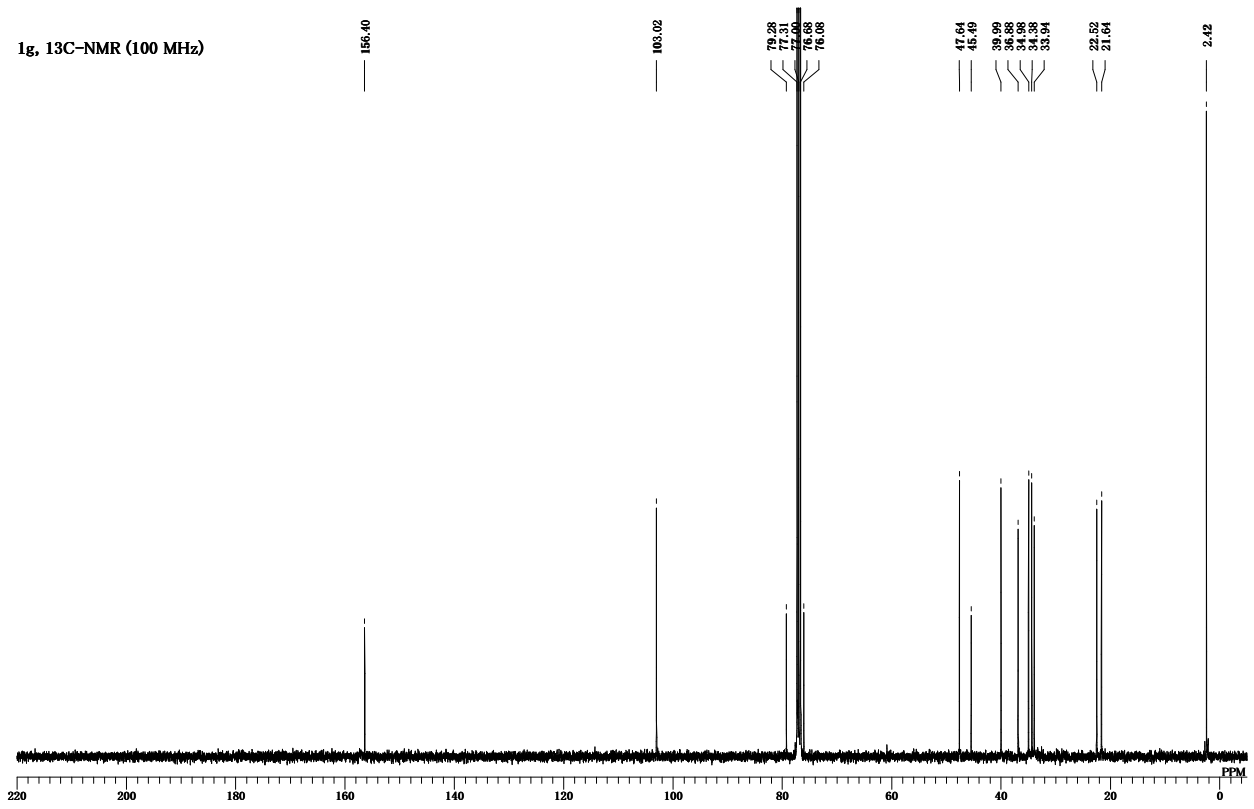
1g, 1H-NMR (400 MHz)



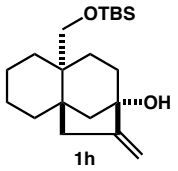

1g




1g, 13C-NMR (100 MHz)



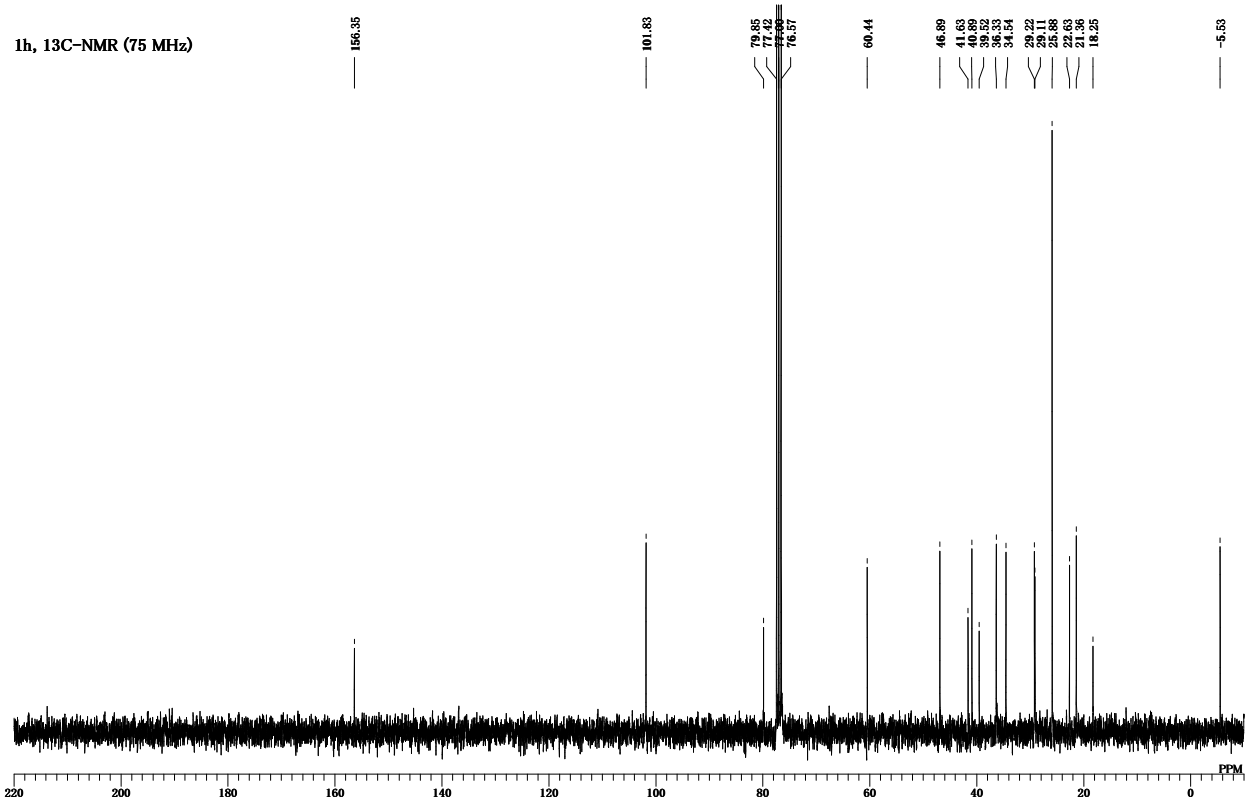
1h, 1H-NMR (300 MHz)



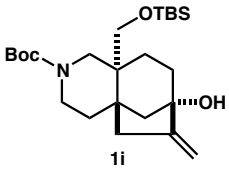

1h




1h, 13C-NMR (75 MHz)



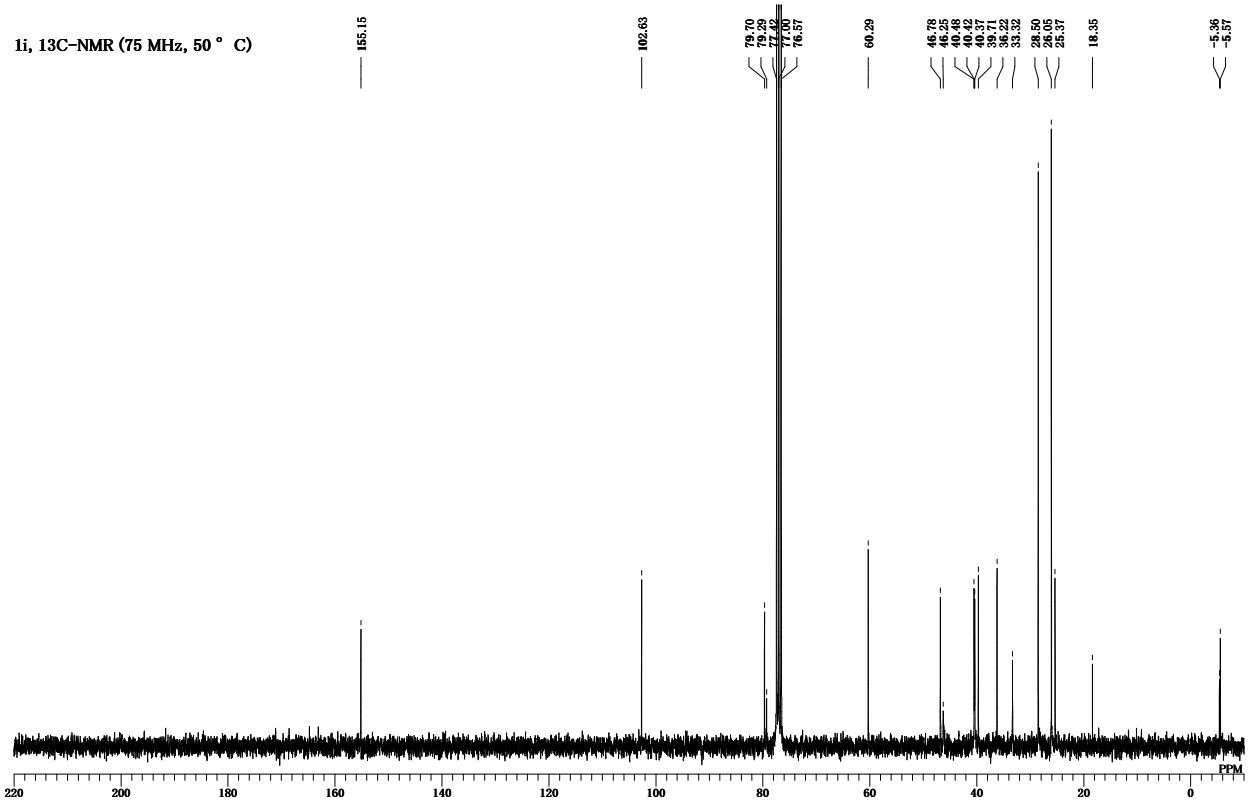
1i, 1H-NMR (300 MHz, 50 ° C)



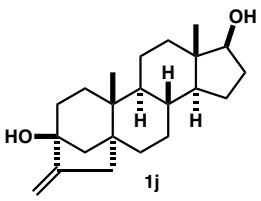

1i




1i, 13C-NMR (75 MHz, 50 ° C)



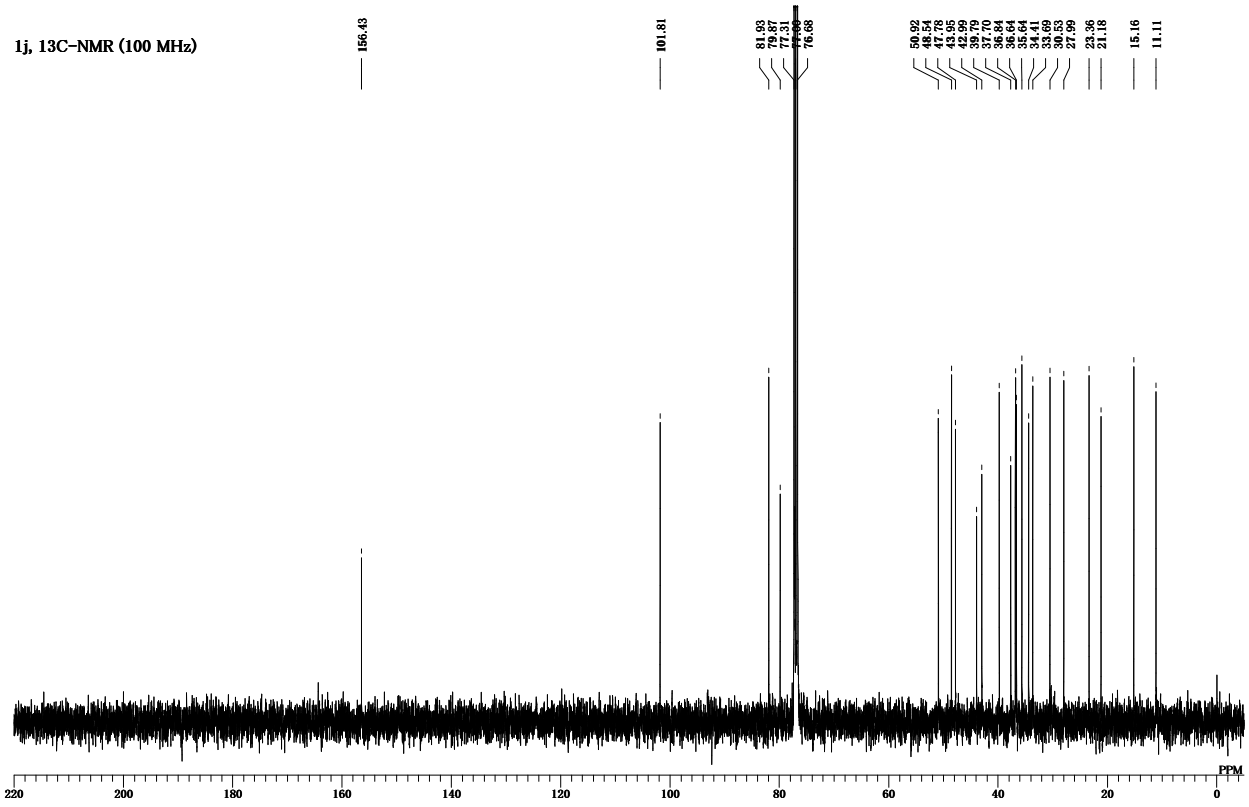
1j, 1H-NMR (400 MHz)



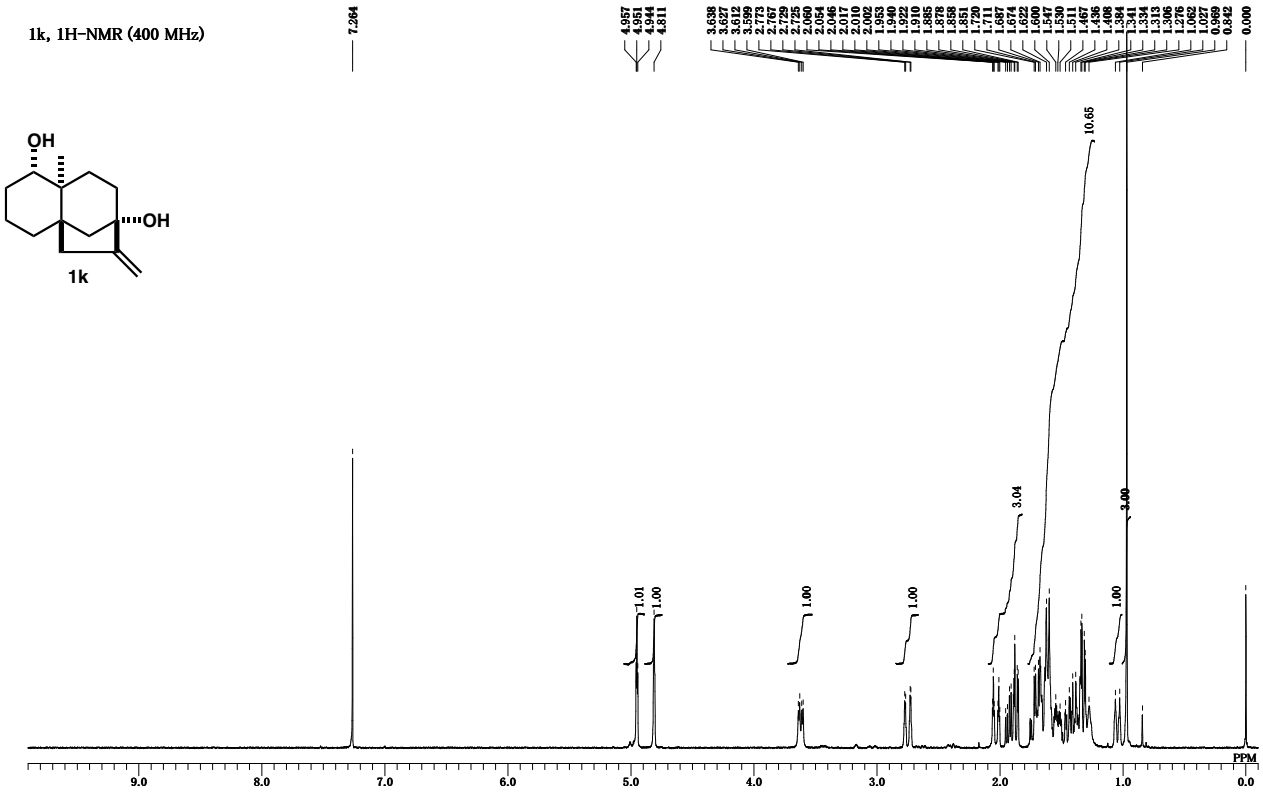

1j




1j, 13C-NMR (100 MHz)



1k, 1H-NMR (400 MHz)

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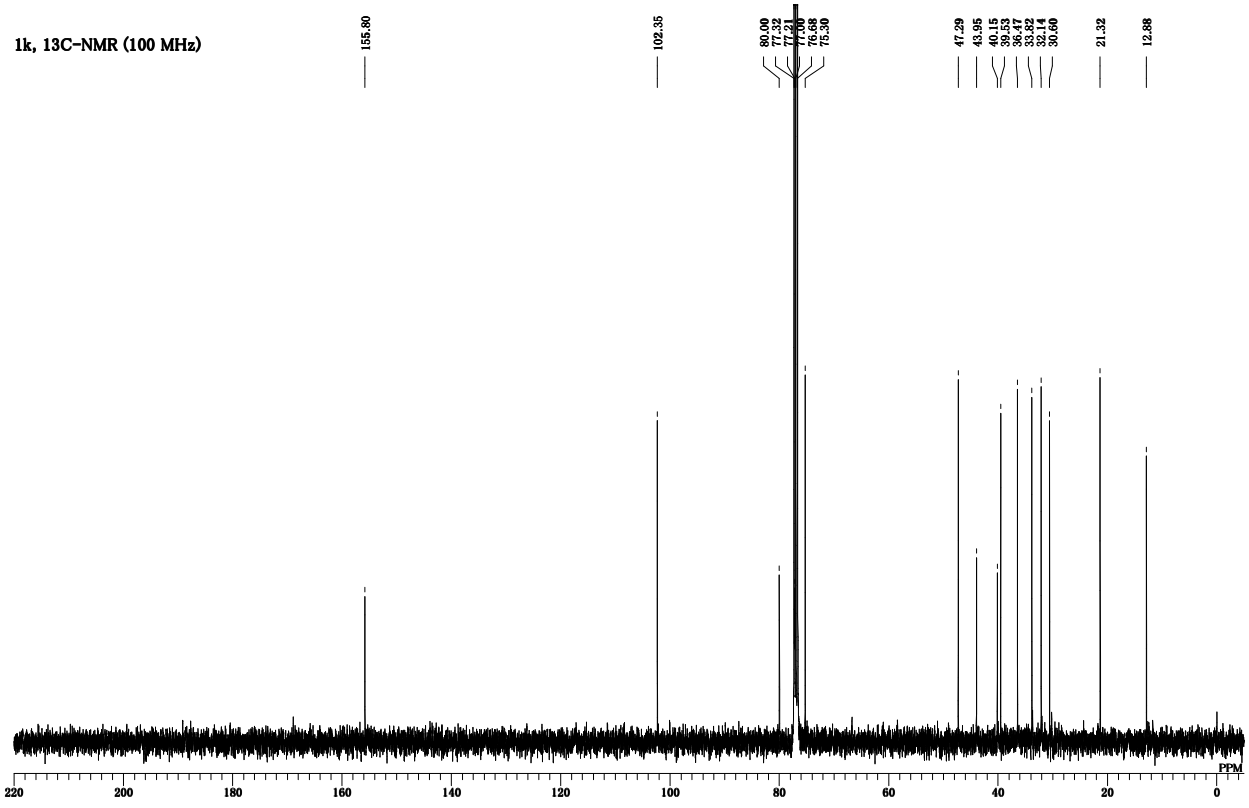

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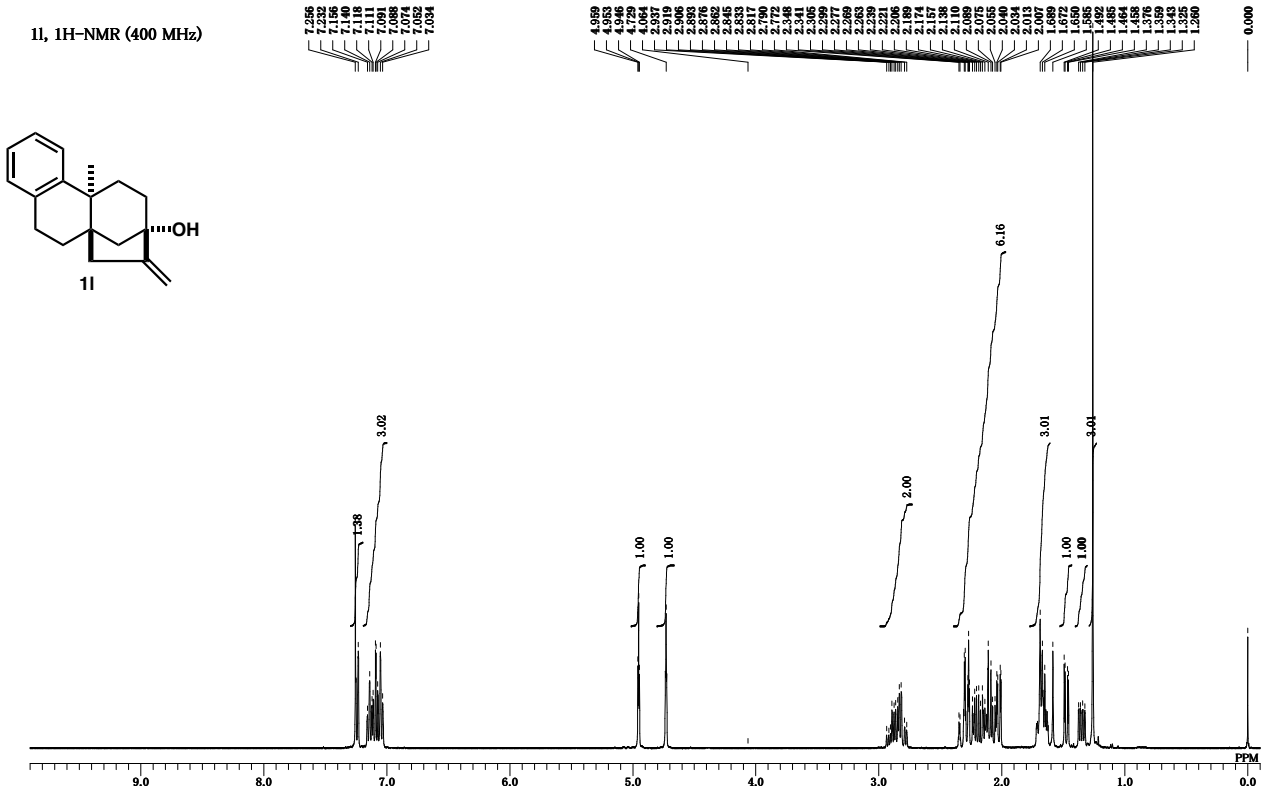
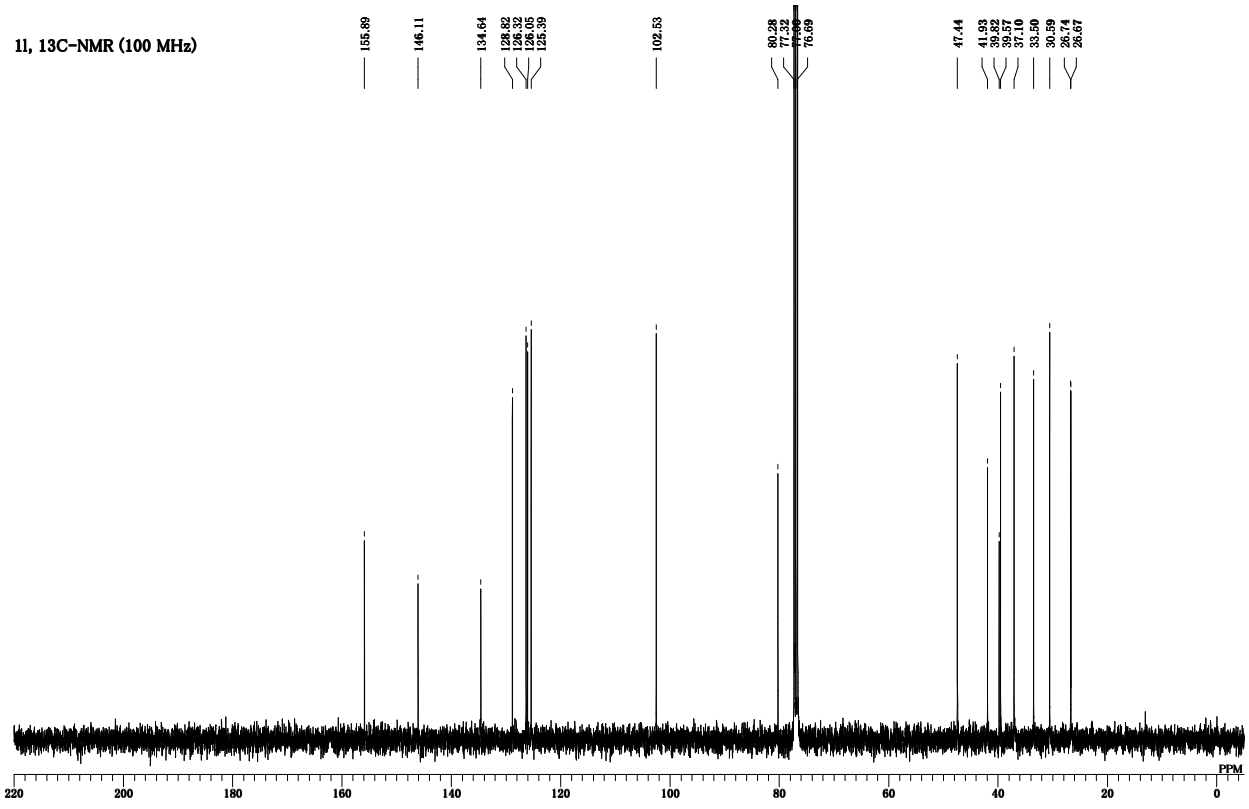
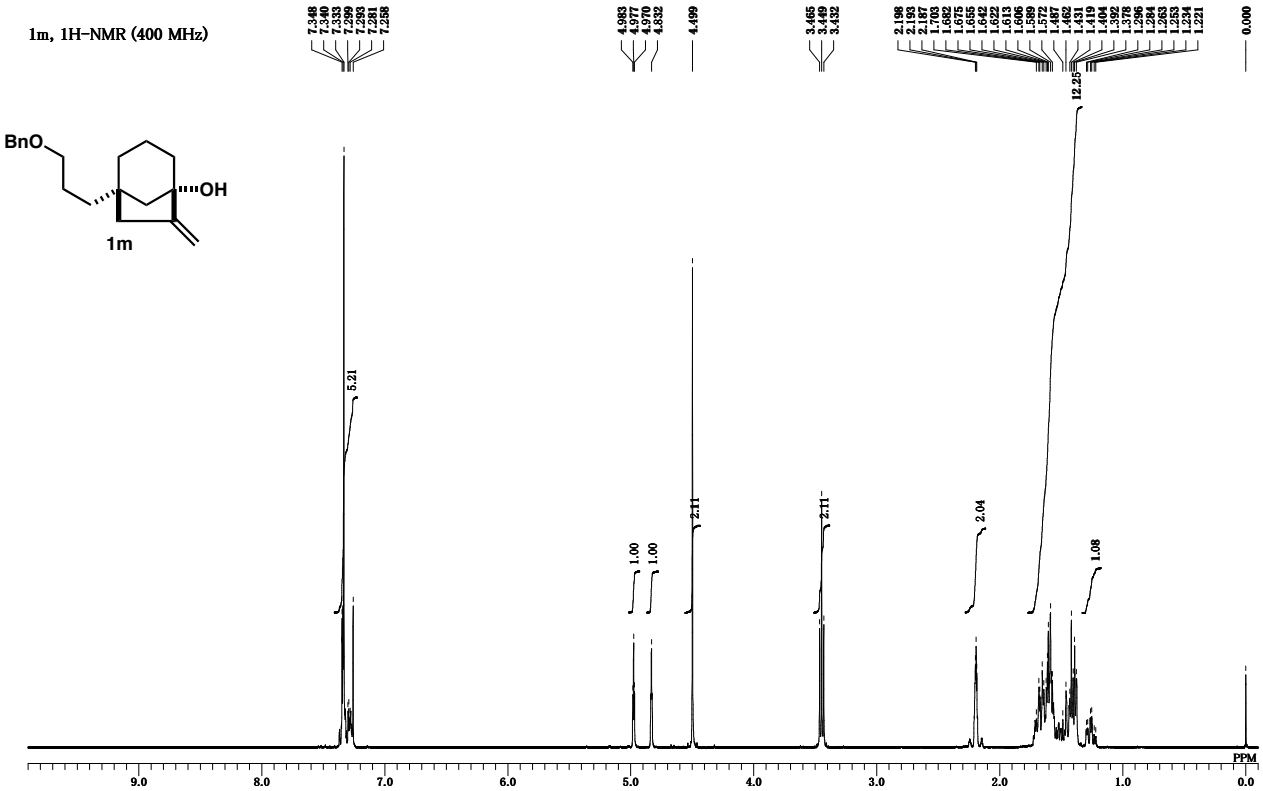



1l, 13C-NMR (100 MHz)



1m, 1H-NMR (400 MHz)

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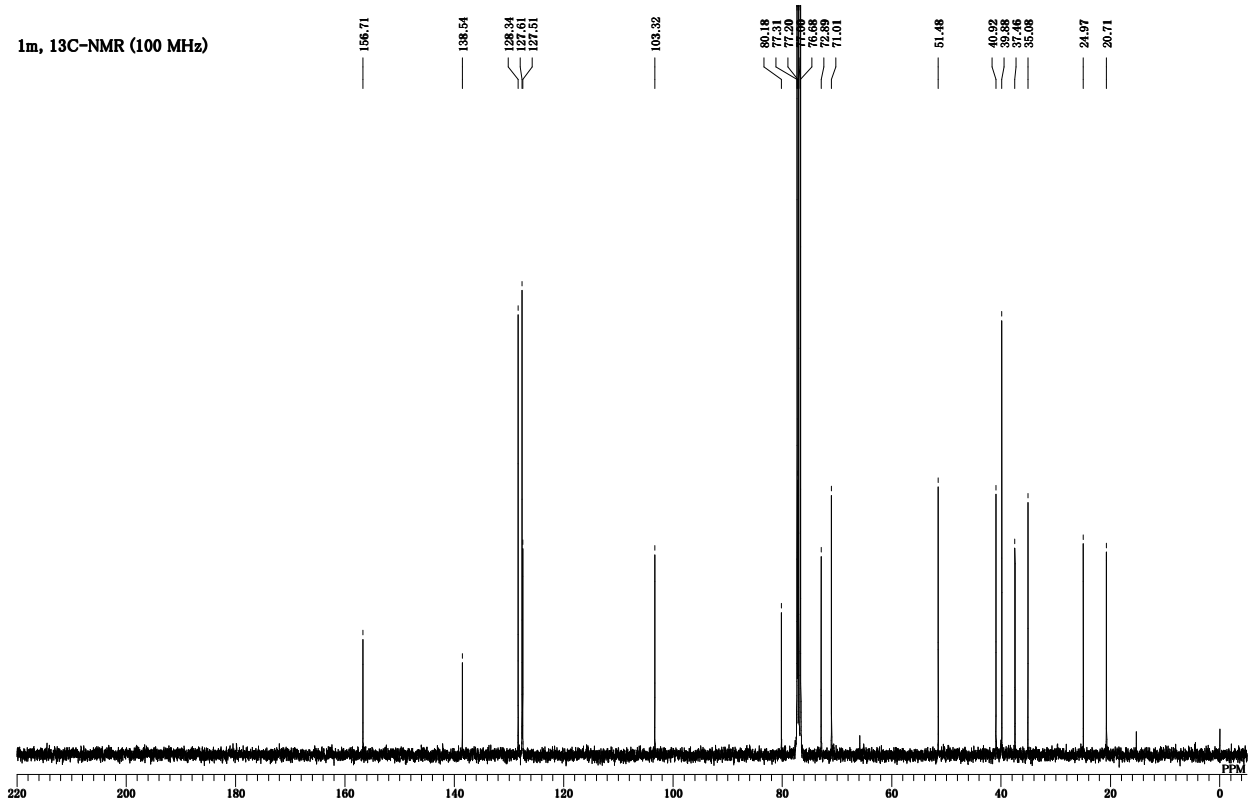
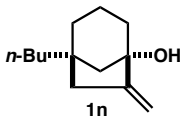


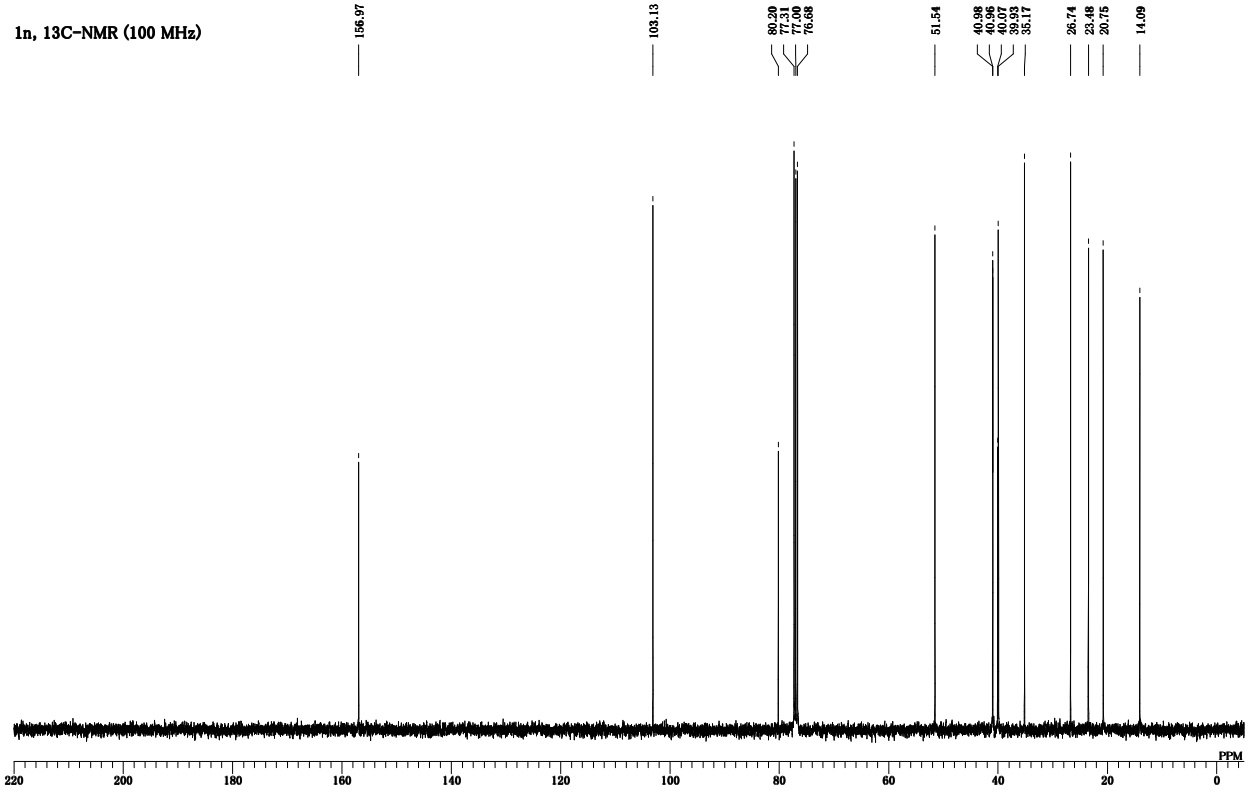
1n, 1H-NMR (400 MHz)



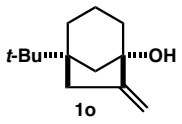

1n




1n, 13C-NMR (100 MHz)



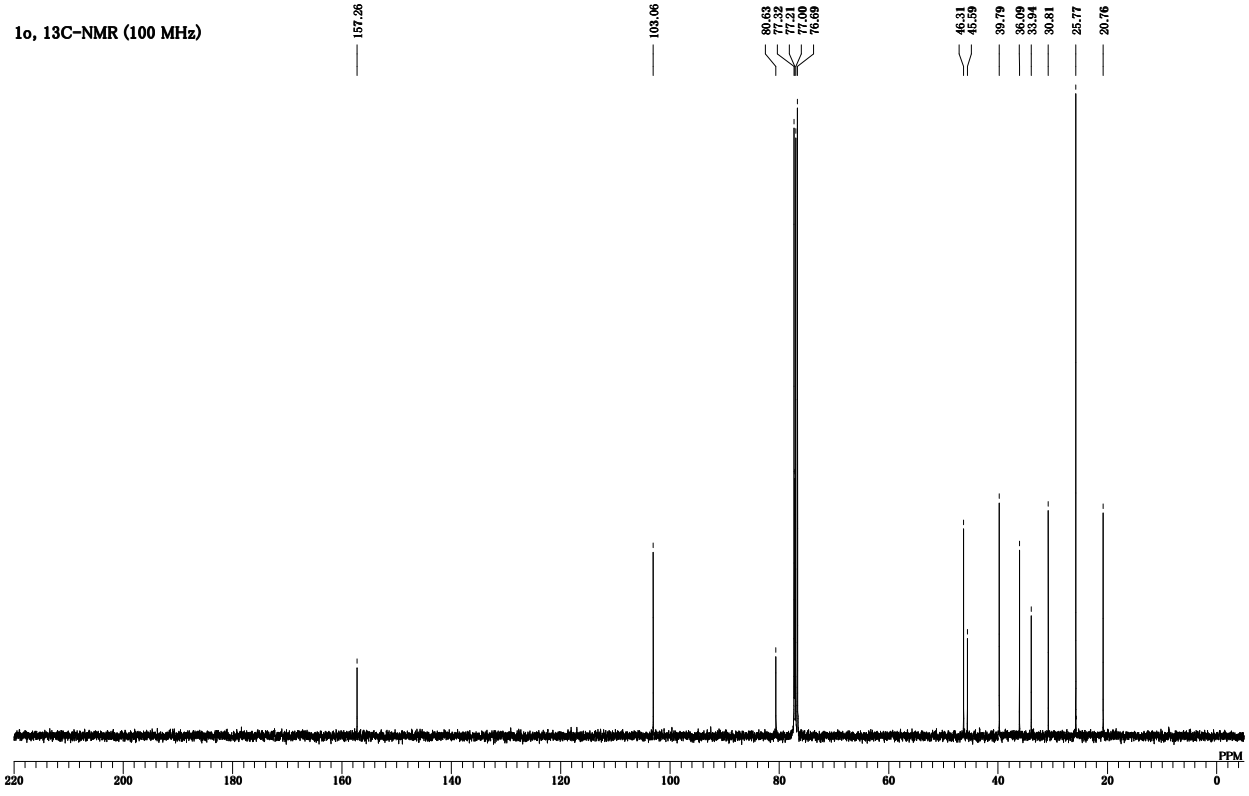
1o, 1H-NMR (400 MHz)



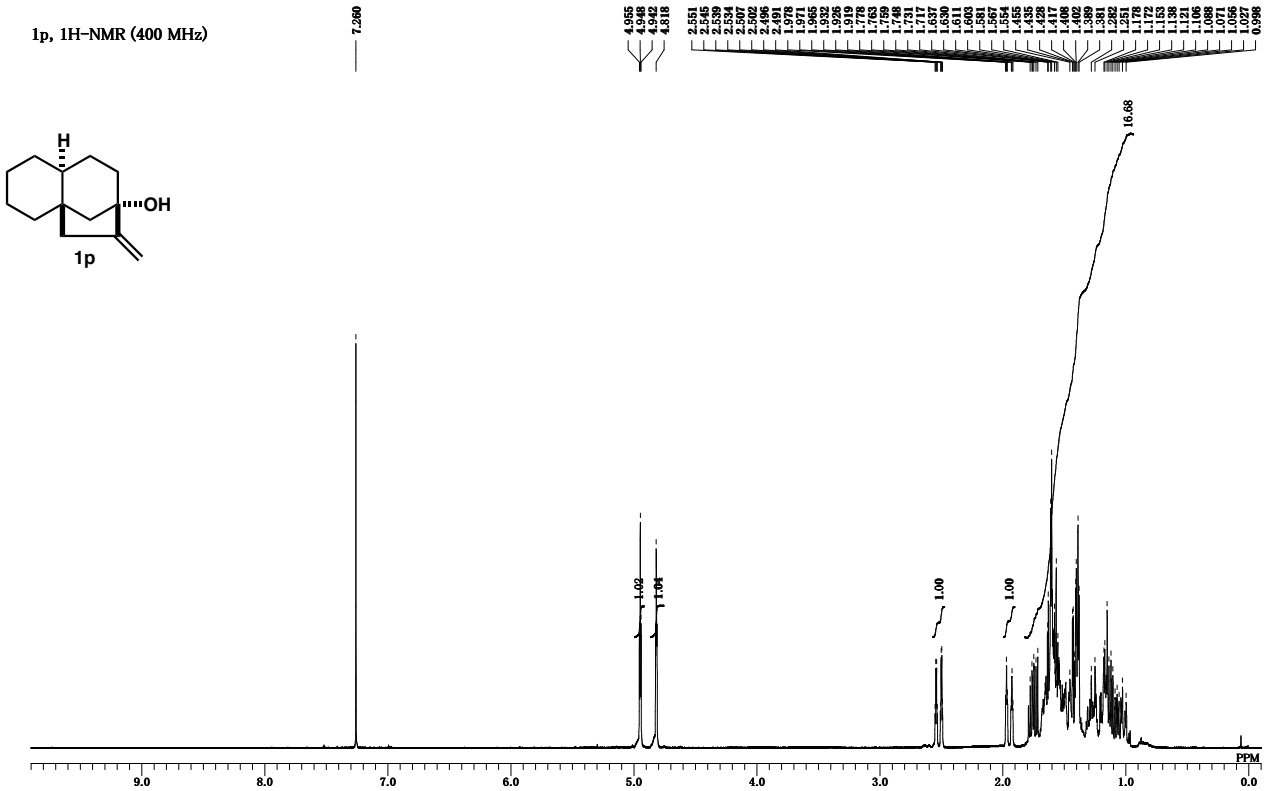

1o




1o, 13C-NMR (100 MHz)



1p, 1H-NMR (400 MHz)

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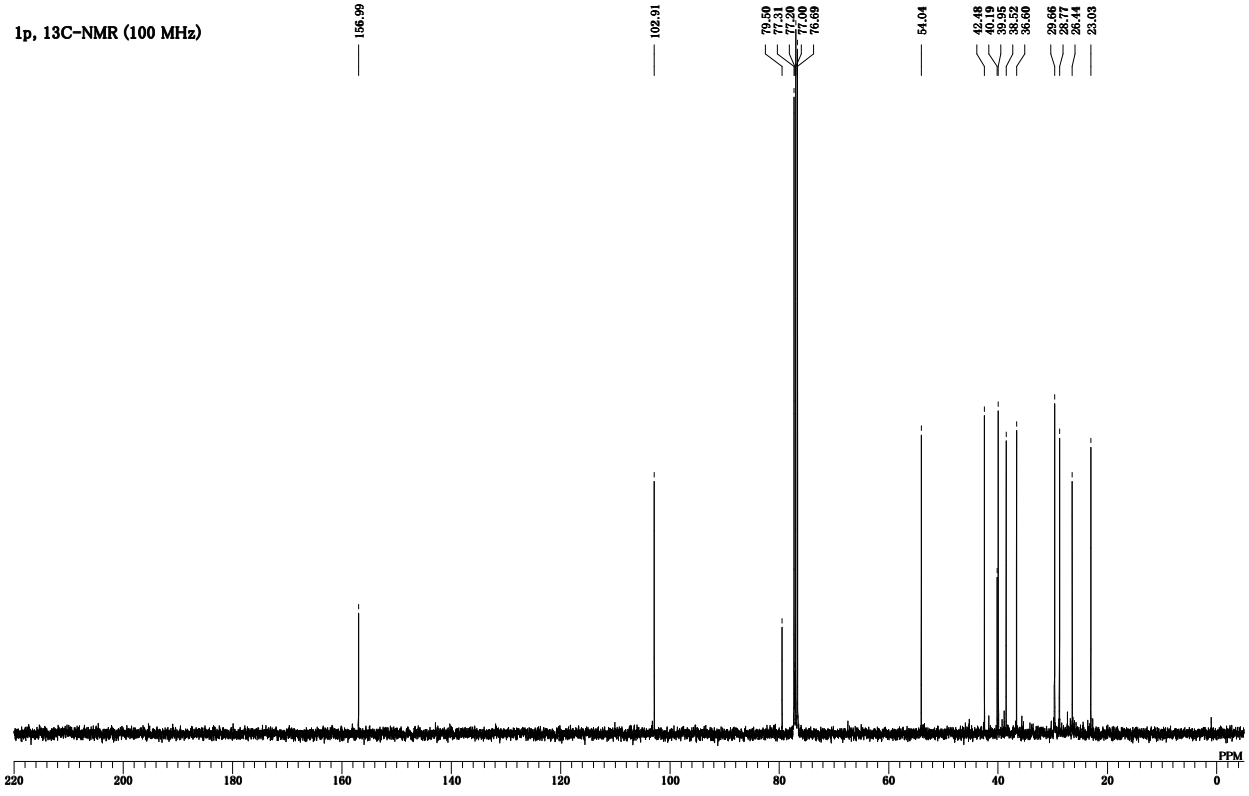
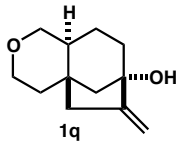


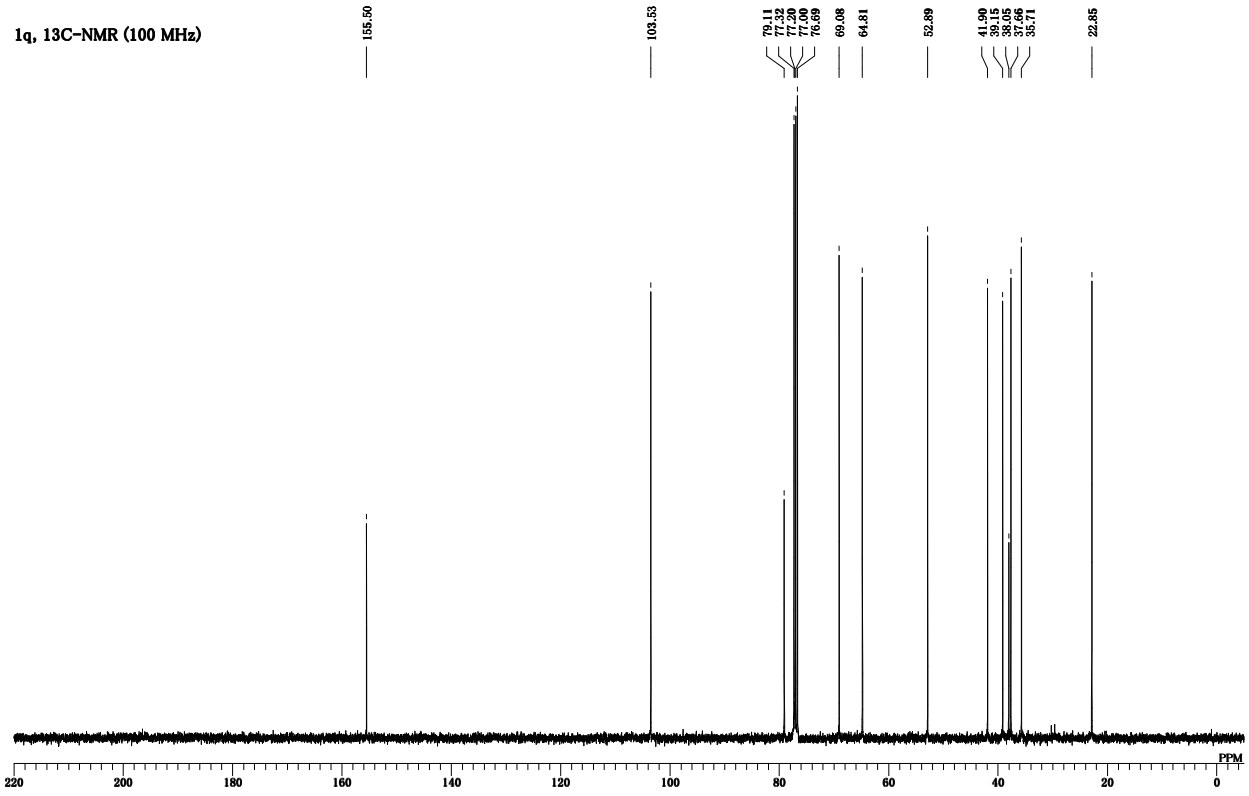
1q, 1H-NMR (400 MHz)



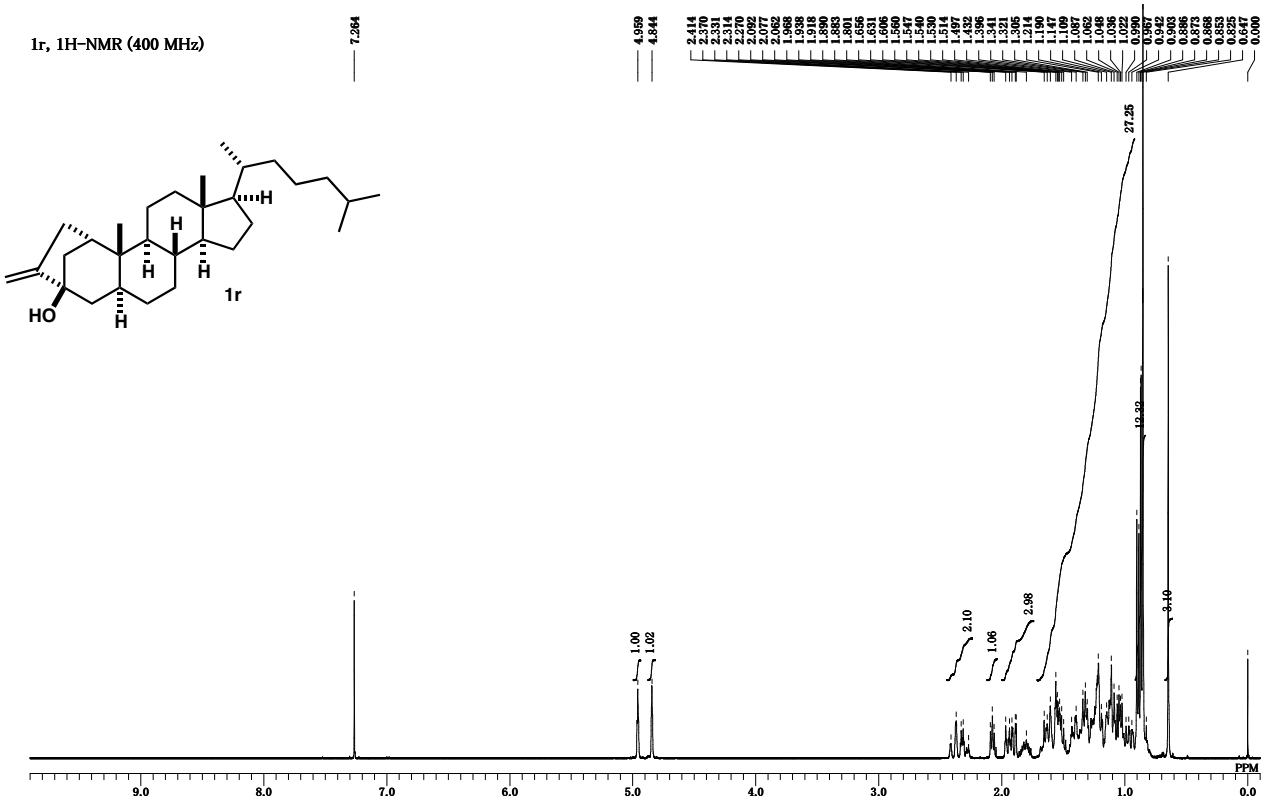

1q




1q, 13C-NMR (100 MHz)



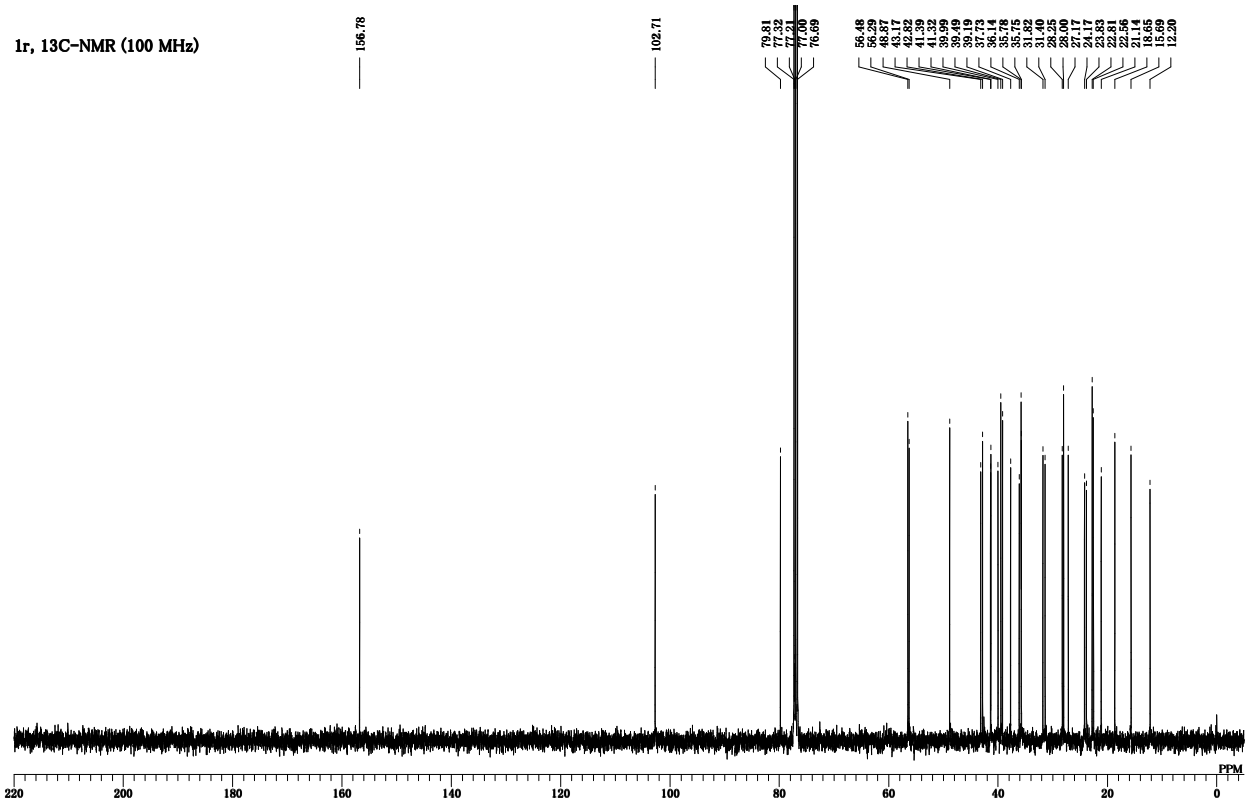
1r, 1H-NMR (400 MHz)



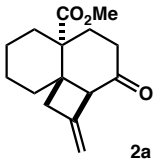




1r, 13C-NMR (100 MHz)



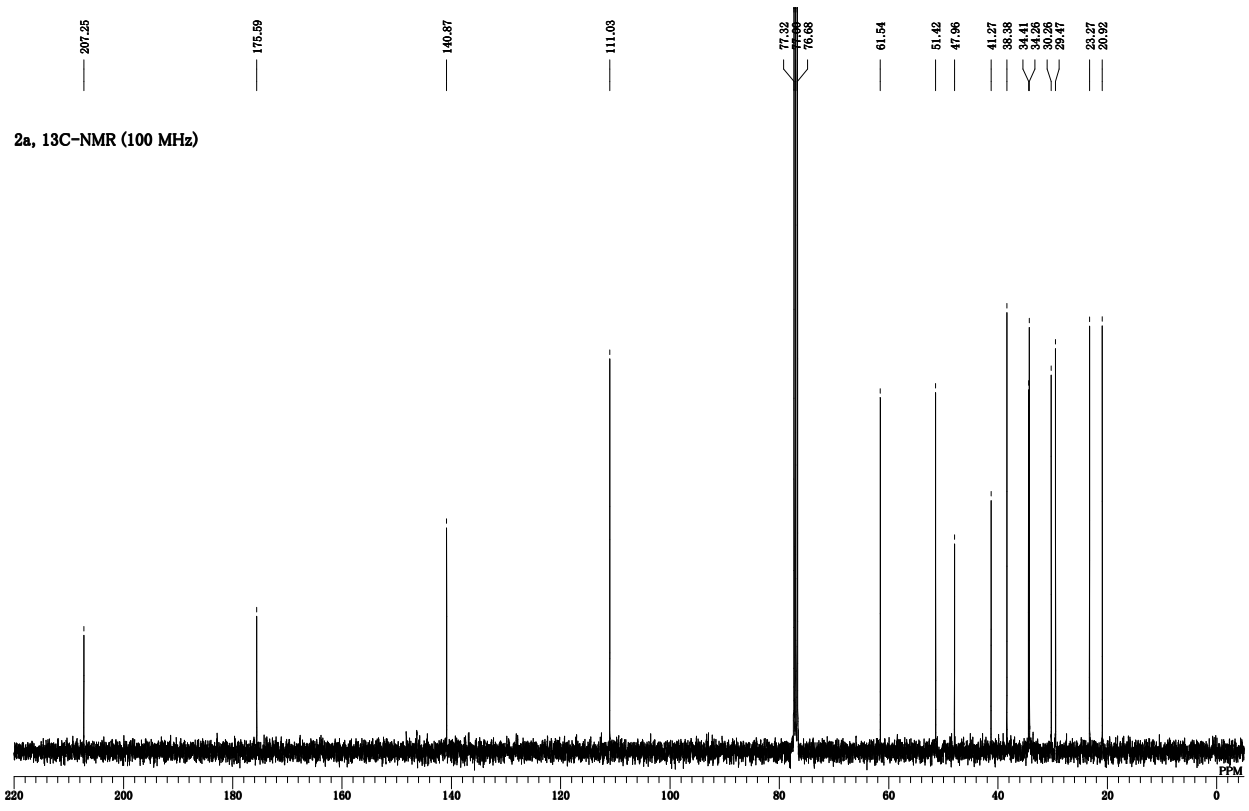
2a, 1H-NMR (400 MHz)



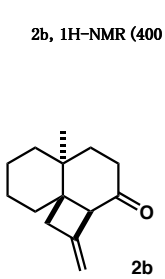

2a




2a, 13C-NMR (100 MHz)



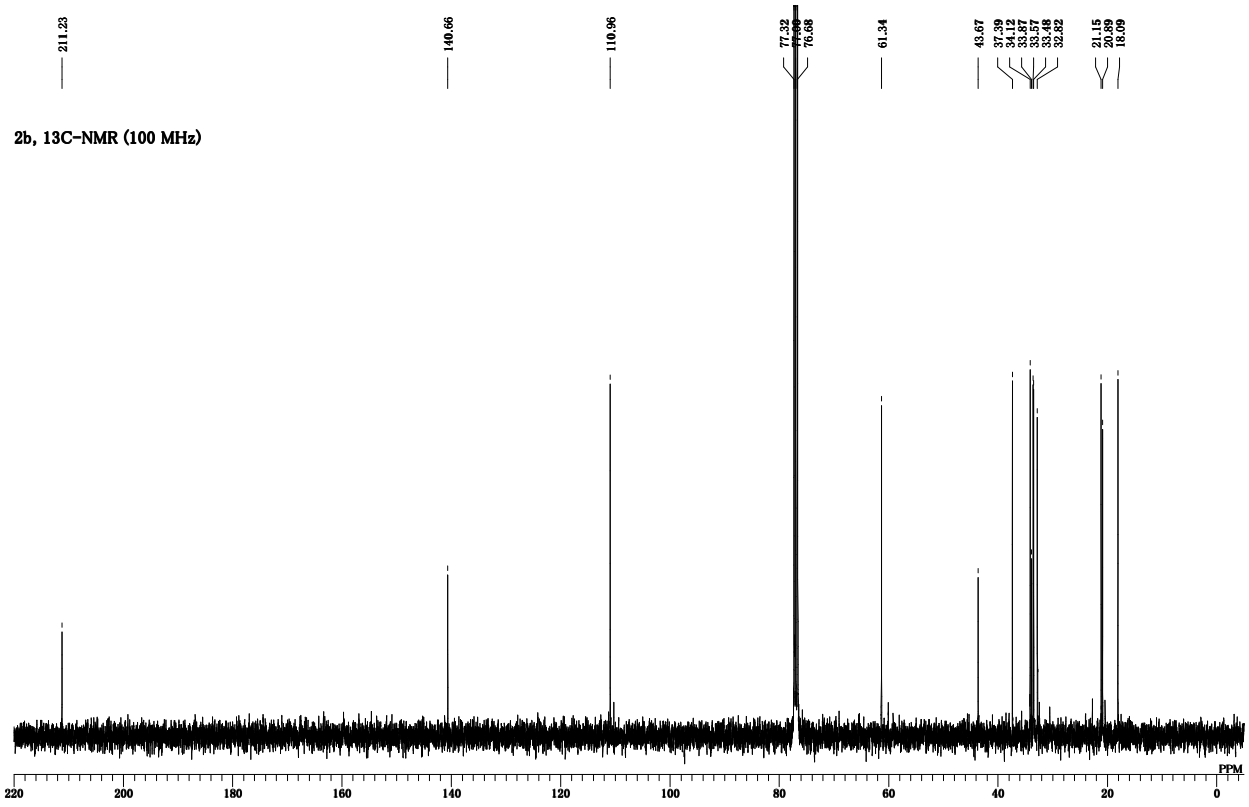
2b, 1H-NMR (400 MHz)



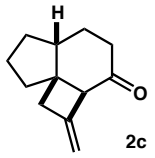
2b




2b, 13C-NMR (100 MHz)



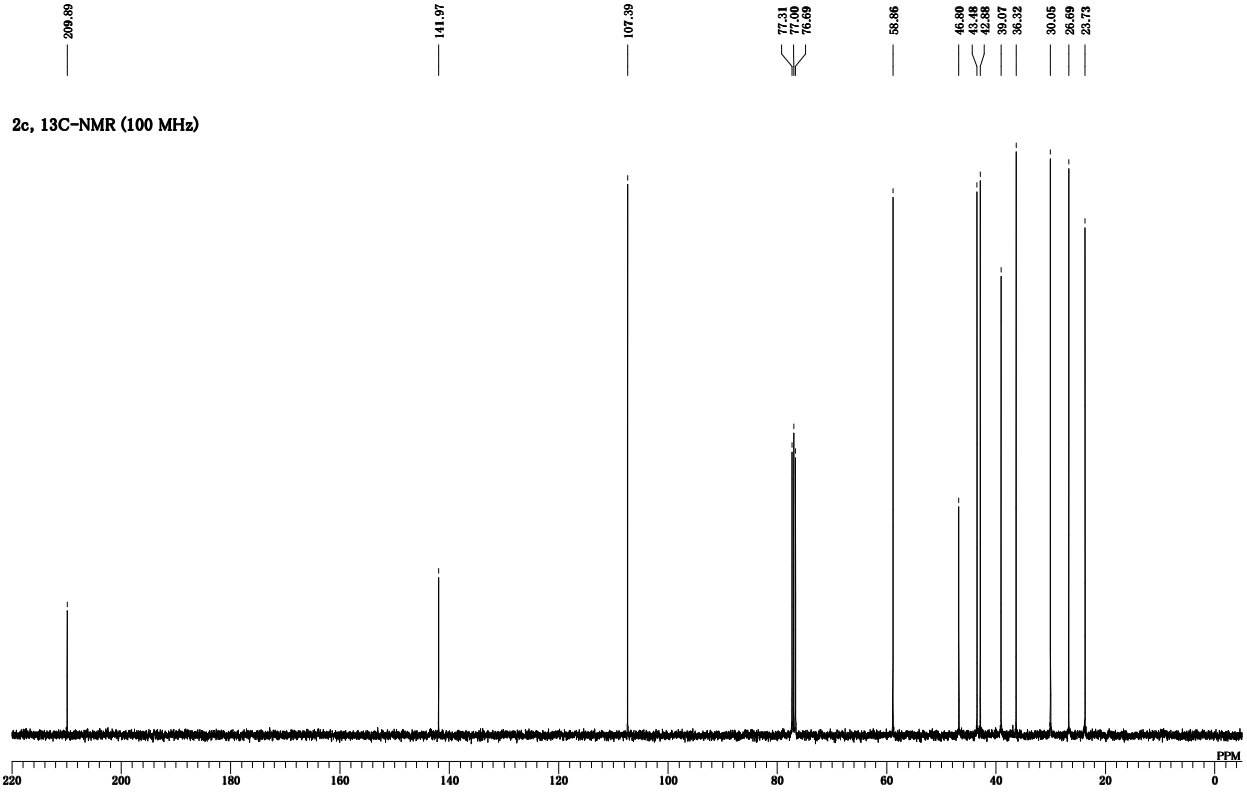
2c, 1H-NMR (400 MHz)



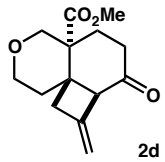

2c




2c, 13C-NMR (100 MHz)



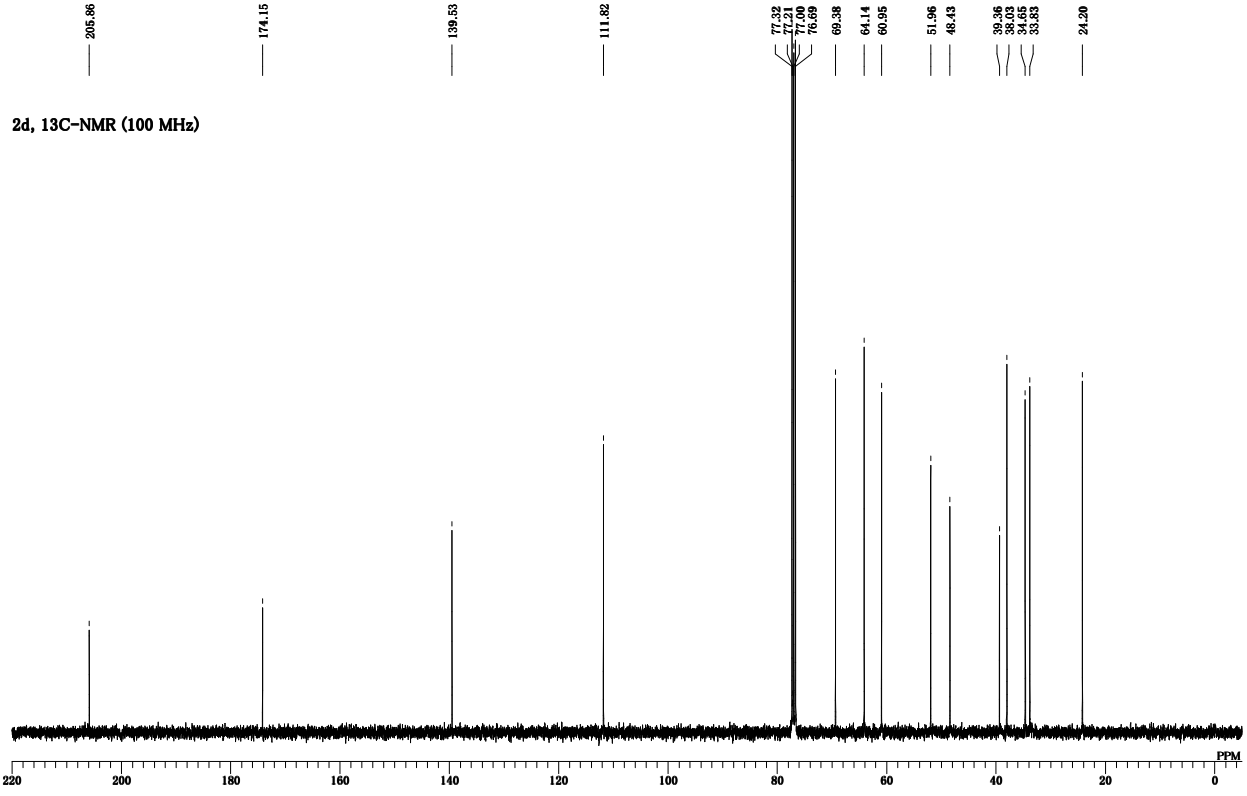
2d, 1H-NMR (400 MHz)



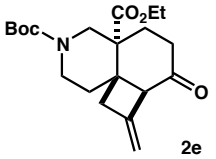

2d




2d, 13C-NMR (100 MHz)



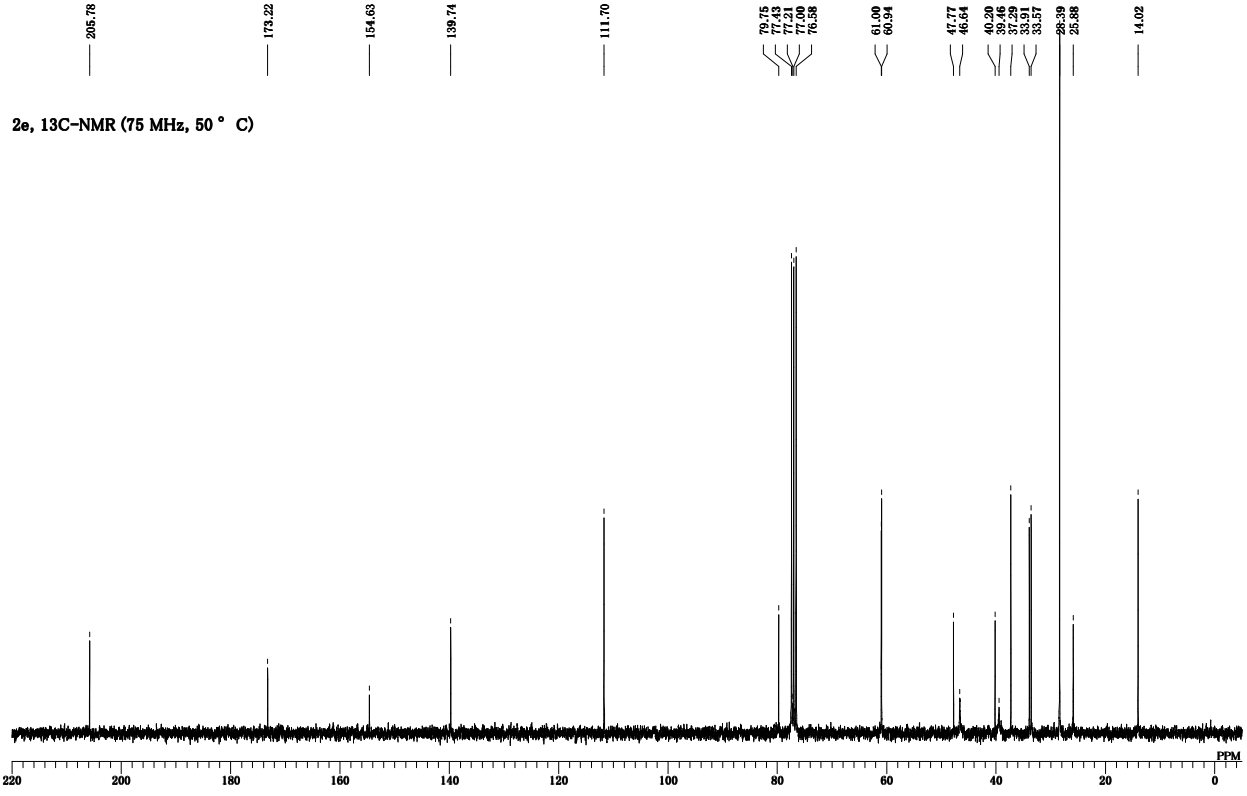
2e, 1H-NMR (300 MHz, 50 ° C)



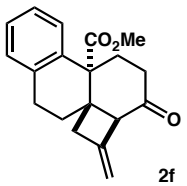

2e




2e, 13C-NMR (75 MHz, 50 ° C)



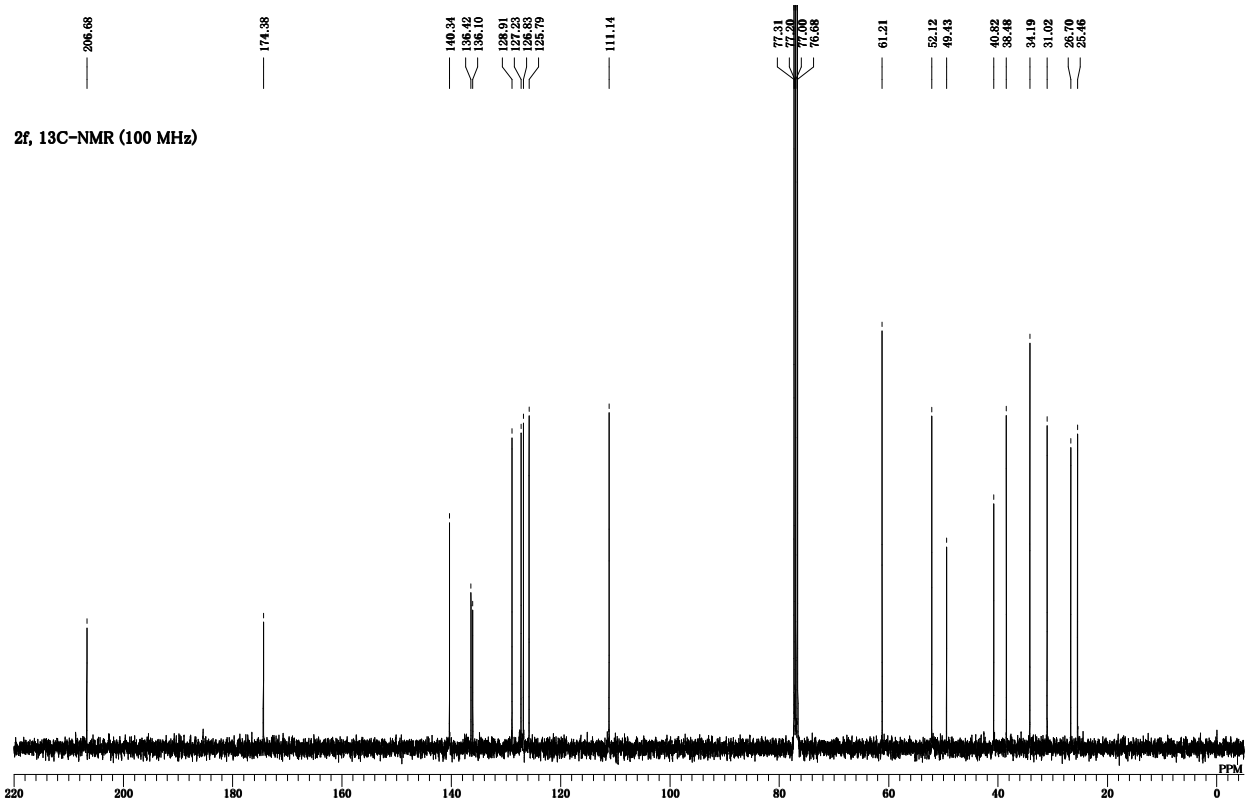
2f, 1H-NMR (400 MHz)



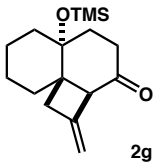

2f




2f, 13C-NMR (100 MHz)



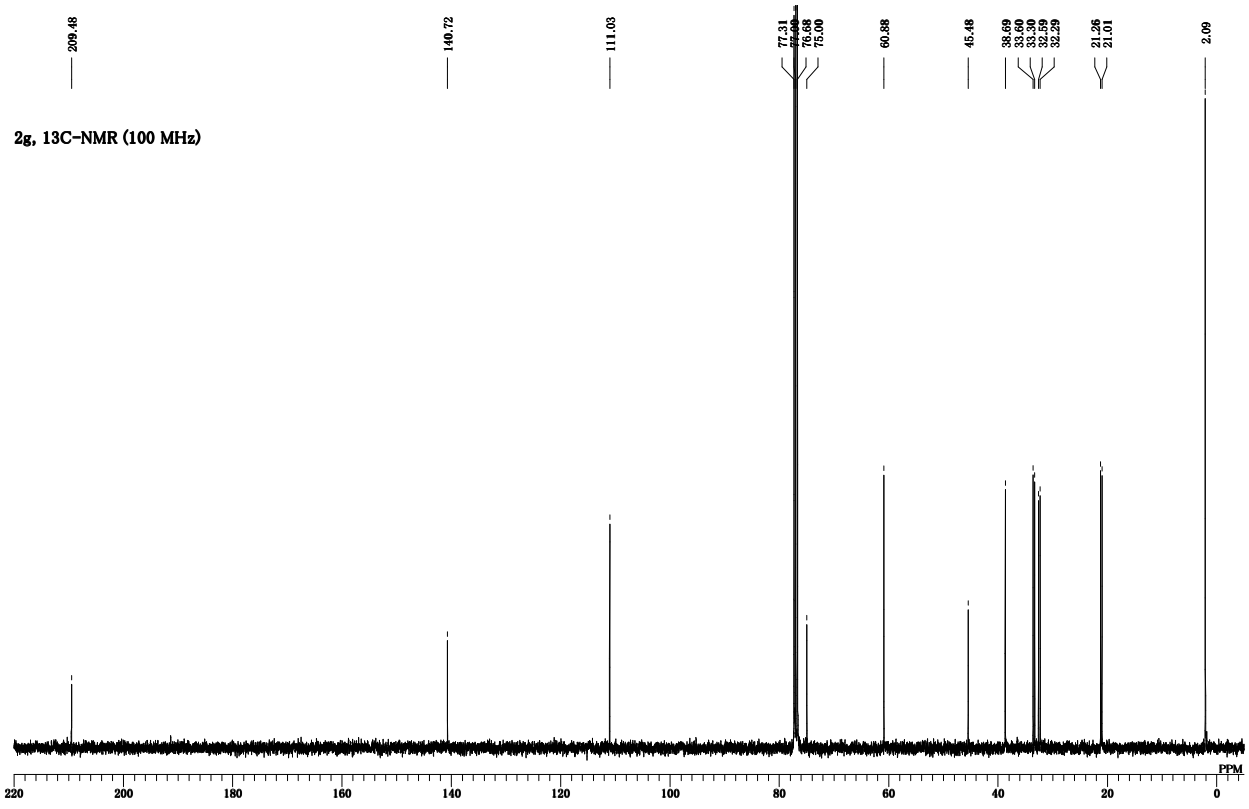
2g, 1H-NMR (400 MHz)



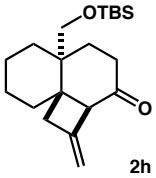

2g




2g, 13C-NMR (100 MHz)



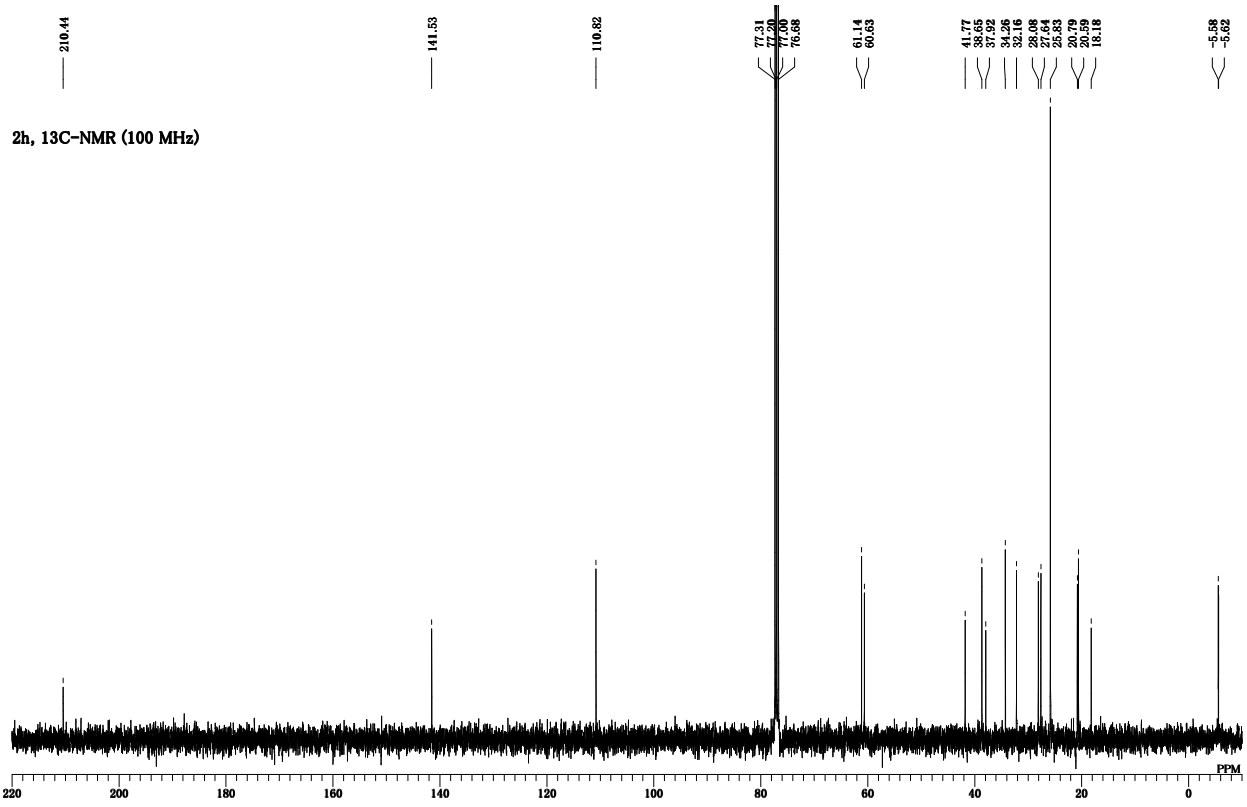
2h, 1H-NMR (400 MHz)



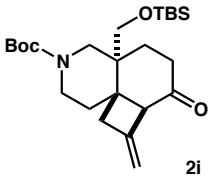

2h




2h, 13C-NMR (100 MHz)

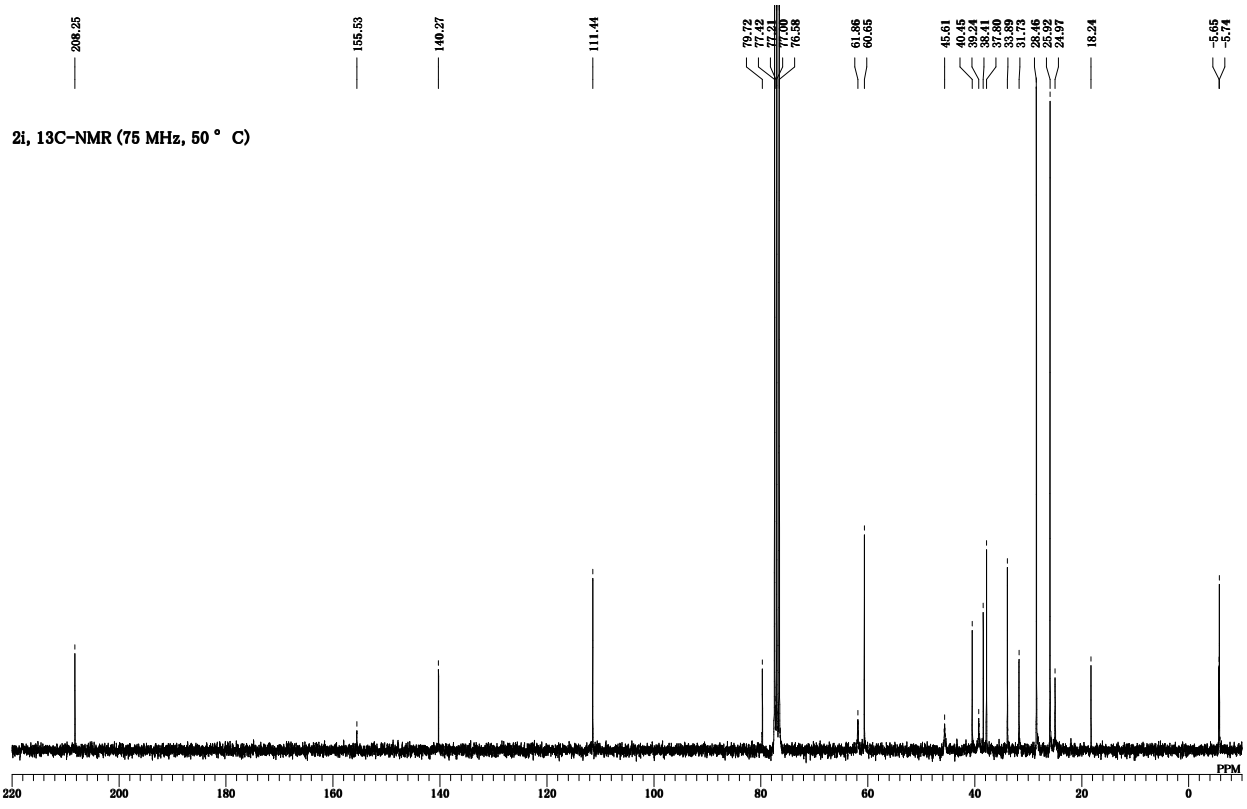


2i, 1H-NMR (300 MHz, 50 ° C)



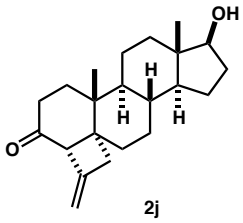

2i




2i, 13C-NMR (75 MHz, 50 ° C)

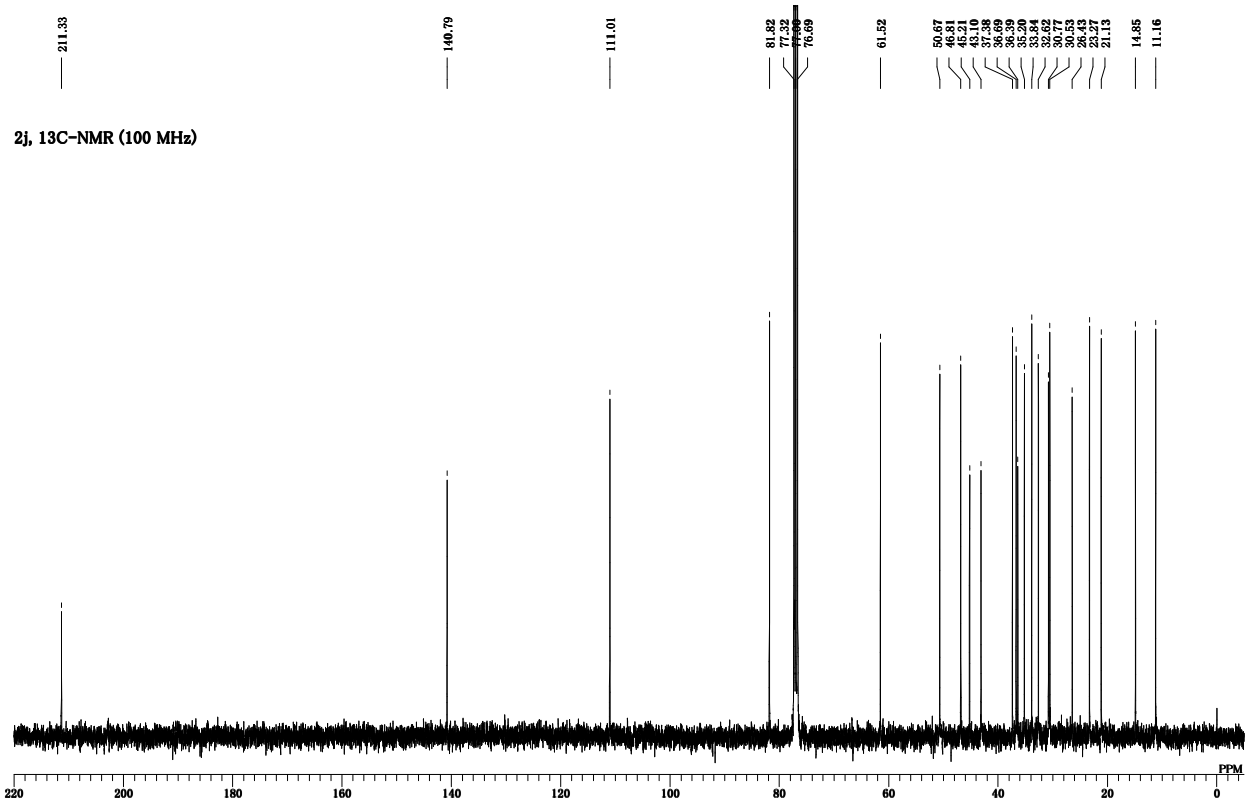
2j, 1H-NMR (300 MHz)



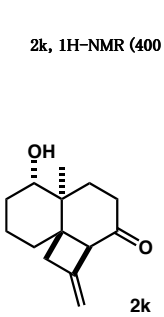

2j




2j, 13C-NMR (100 MHz)



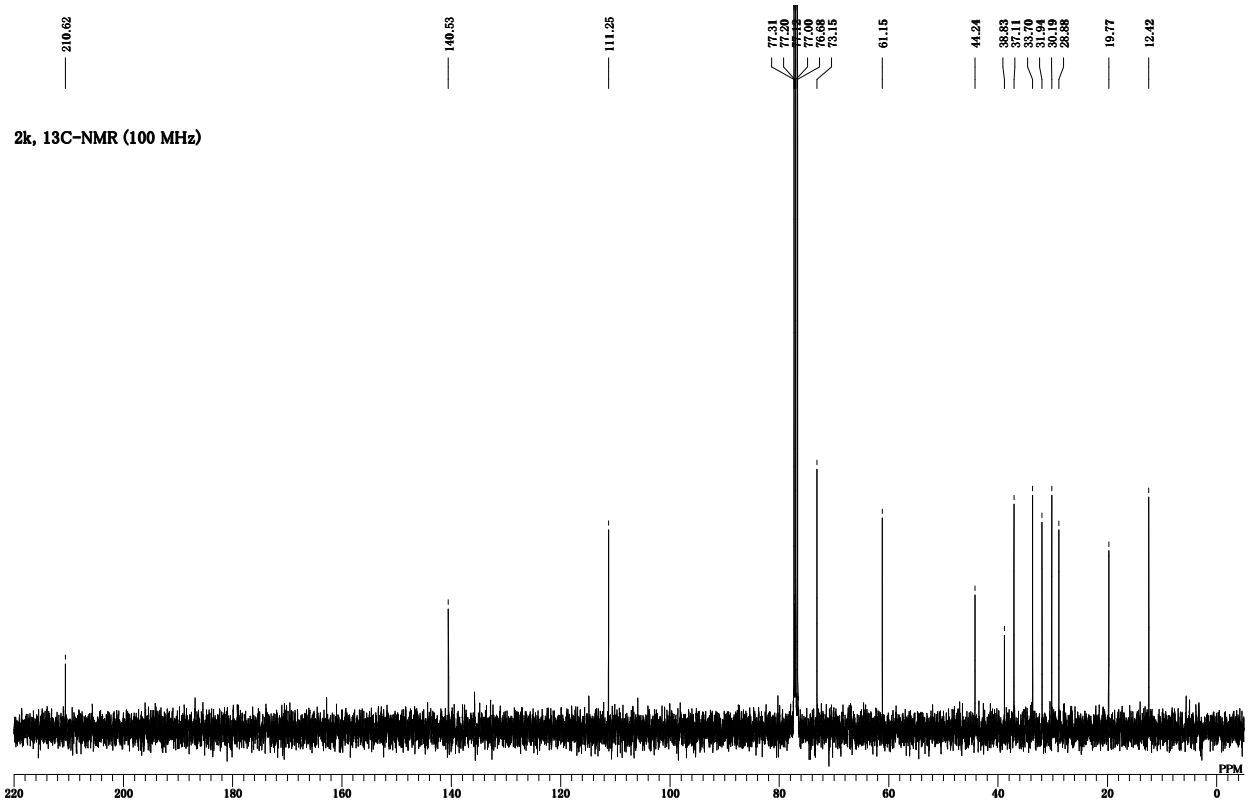
2k, 1H-NMR (400 MHz)



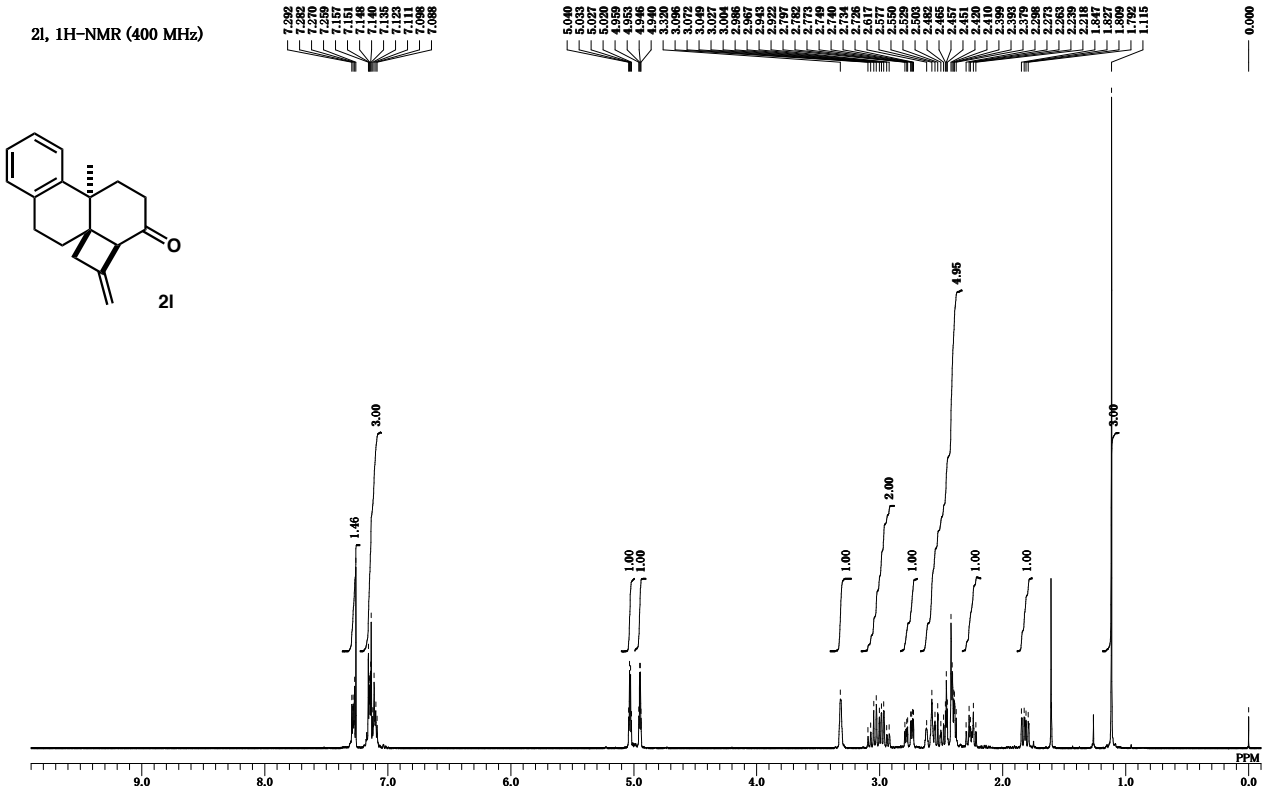

2k



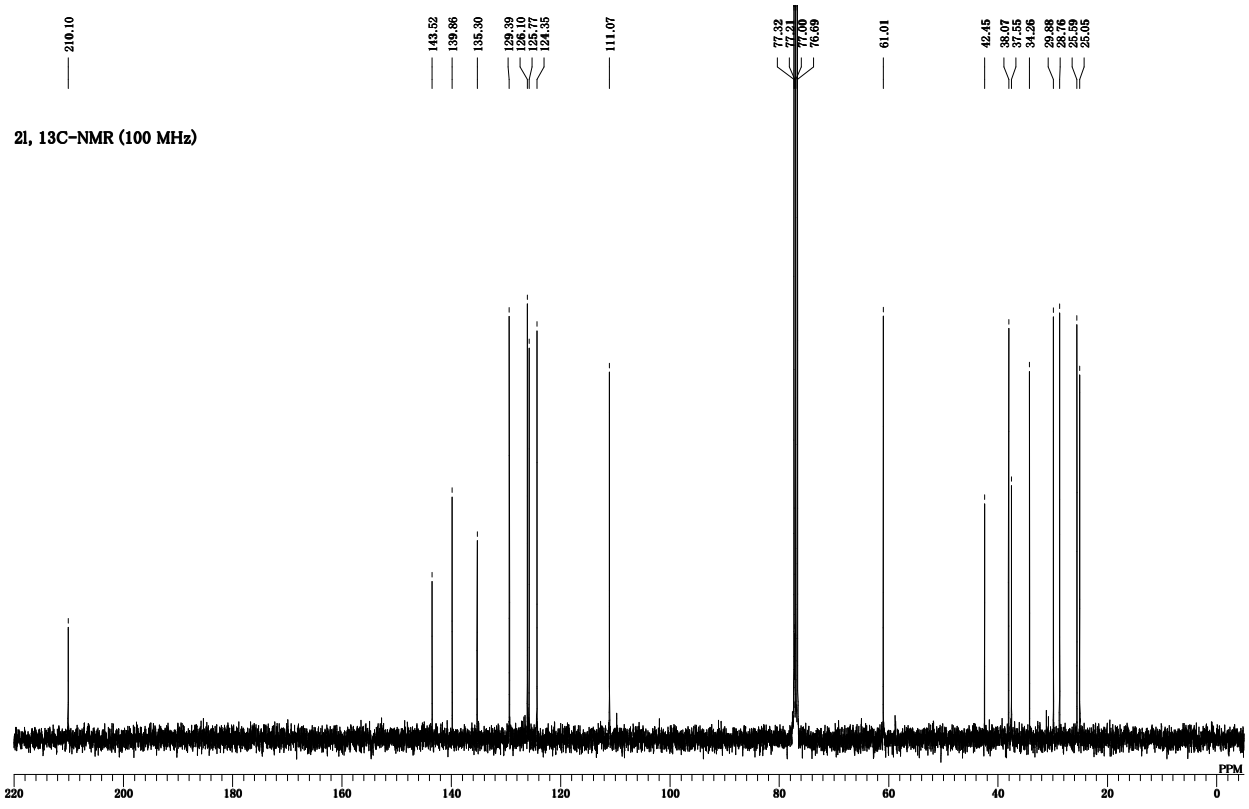

2k, 13C-NMR (100 MHz)



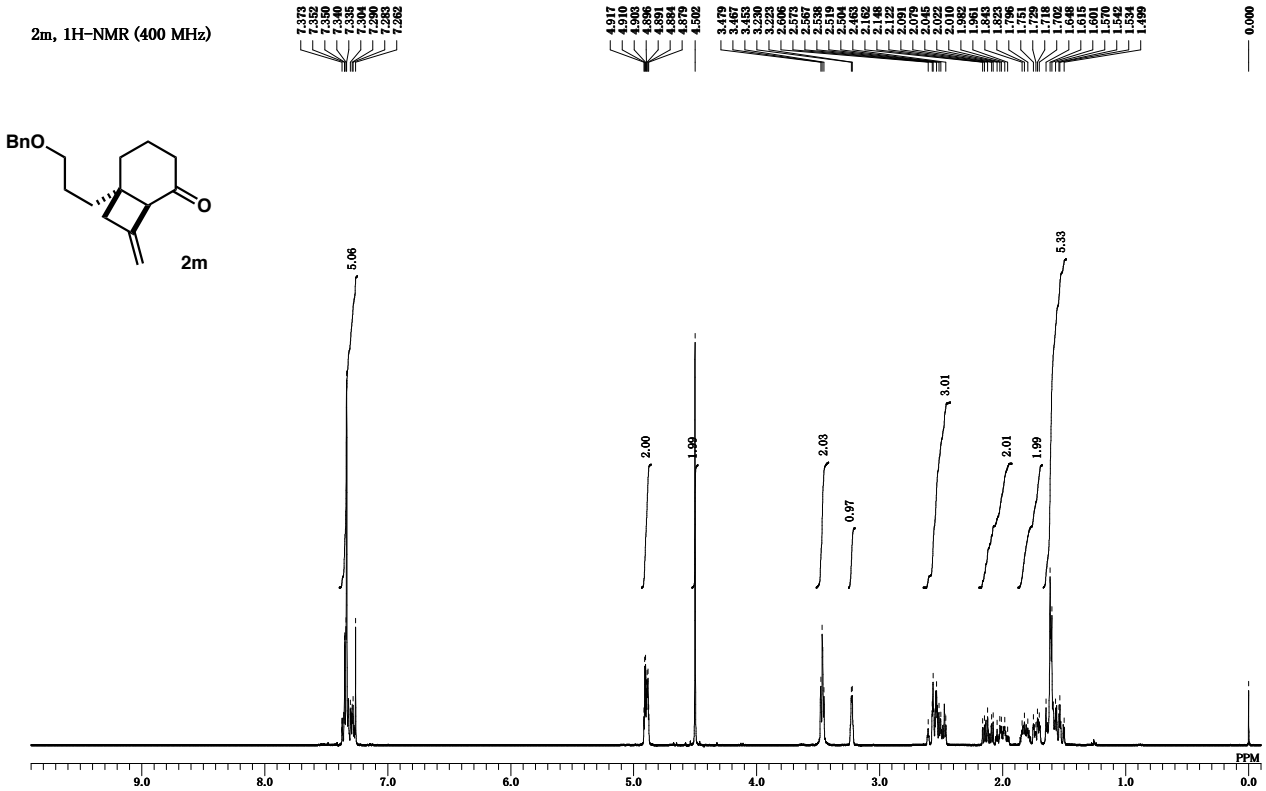
2l, 1H-NMR (400 MHz)

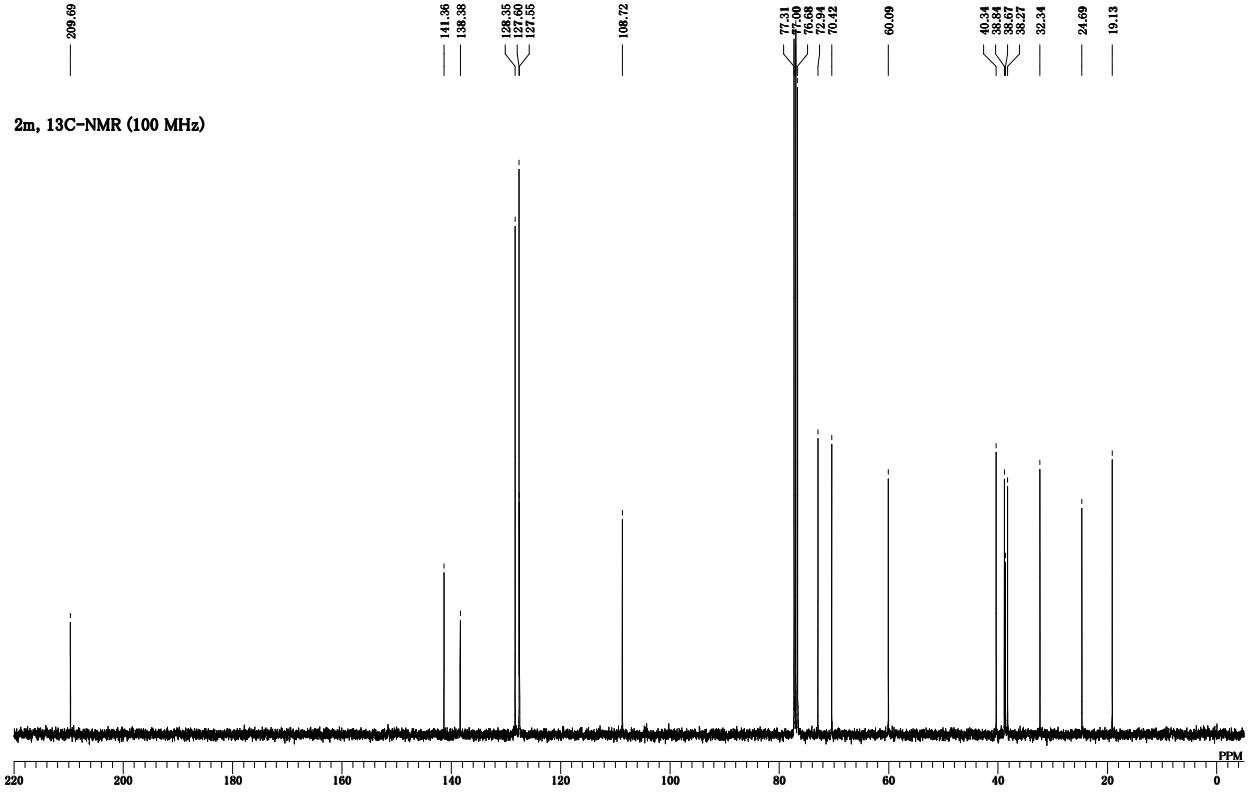



2l, 13C-NMR (100 MHz)



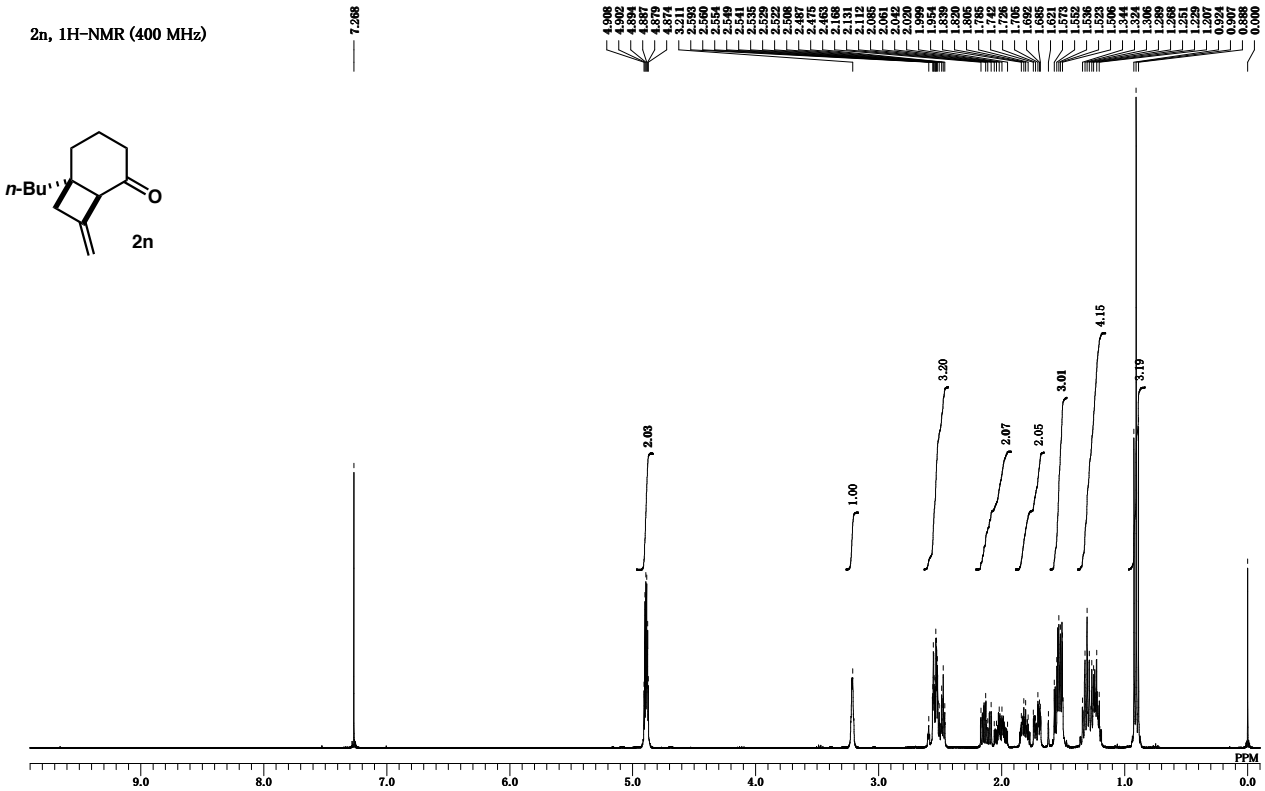
2m, 1H-NMR (400 MHz)



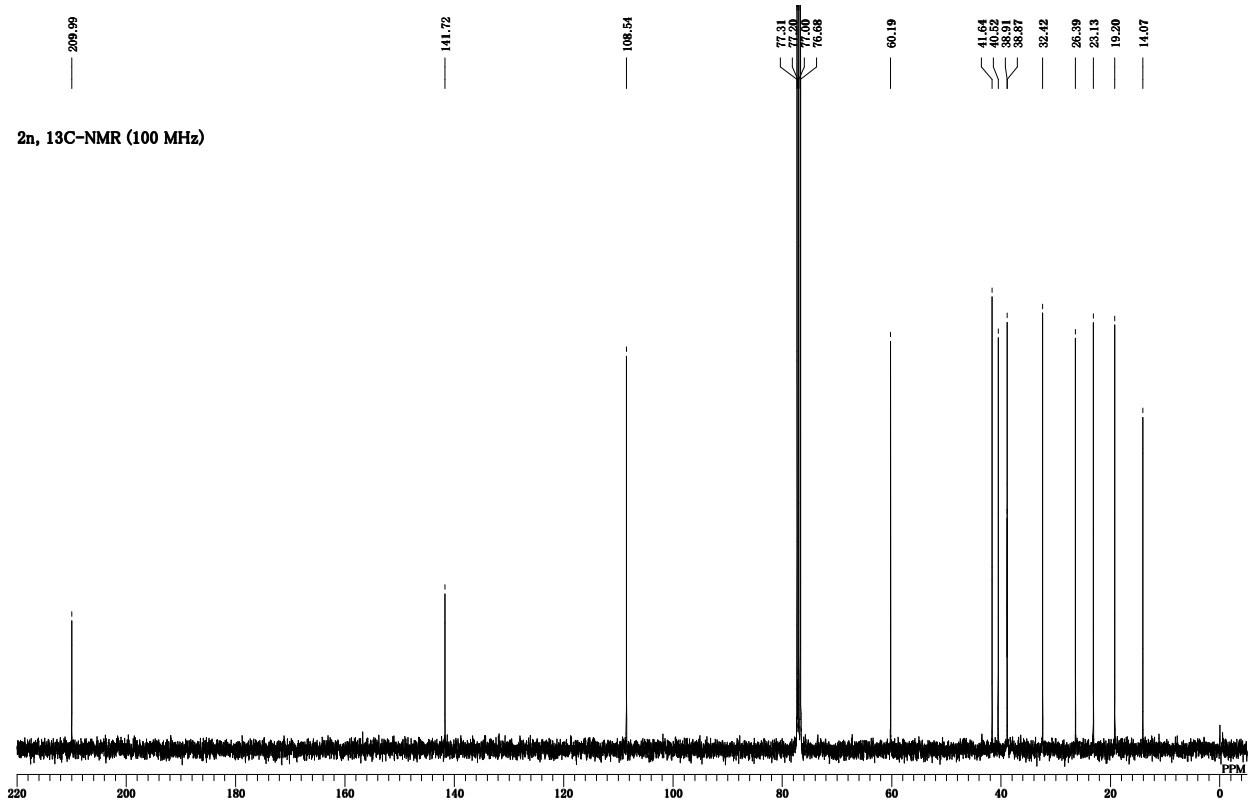




2m, 13C-NMR (100 MHz)

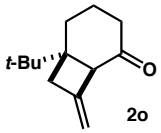
2n, 1H-NMR (400 MHz)




2n, 13C-NMR (100 MHz)



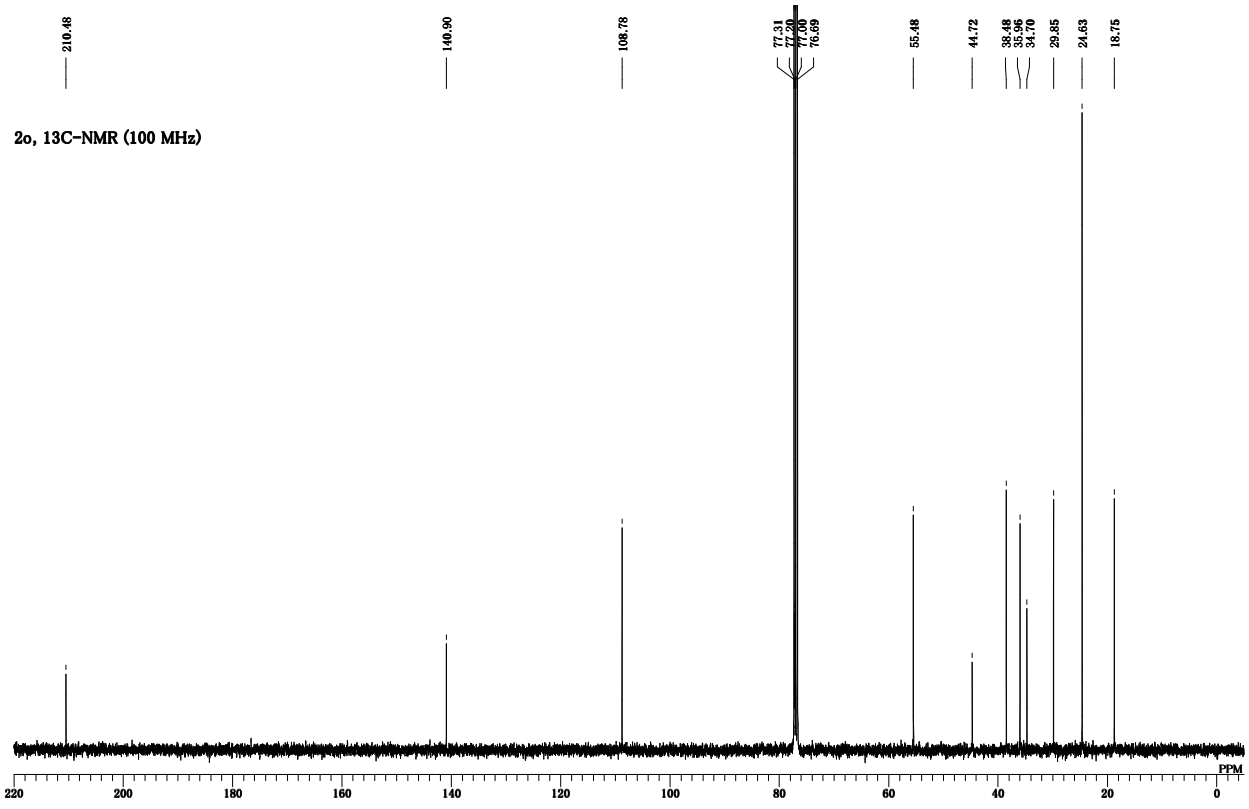
2o, 1H-NMR (400 MHz)



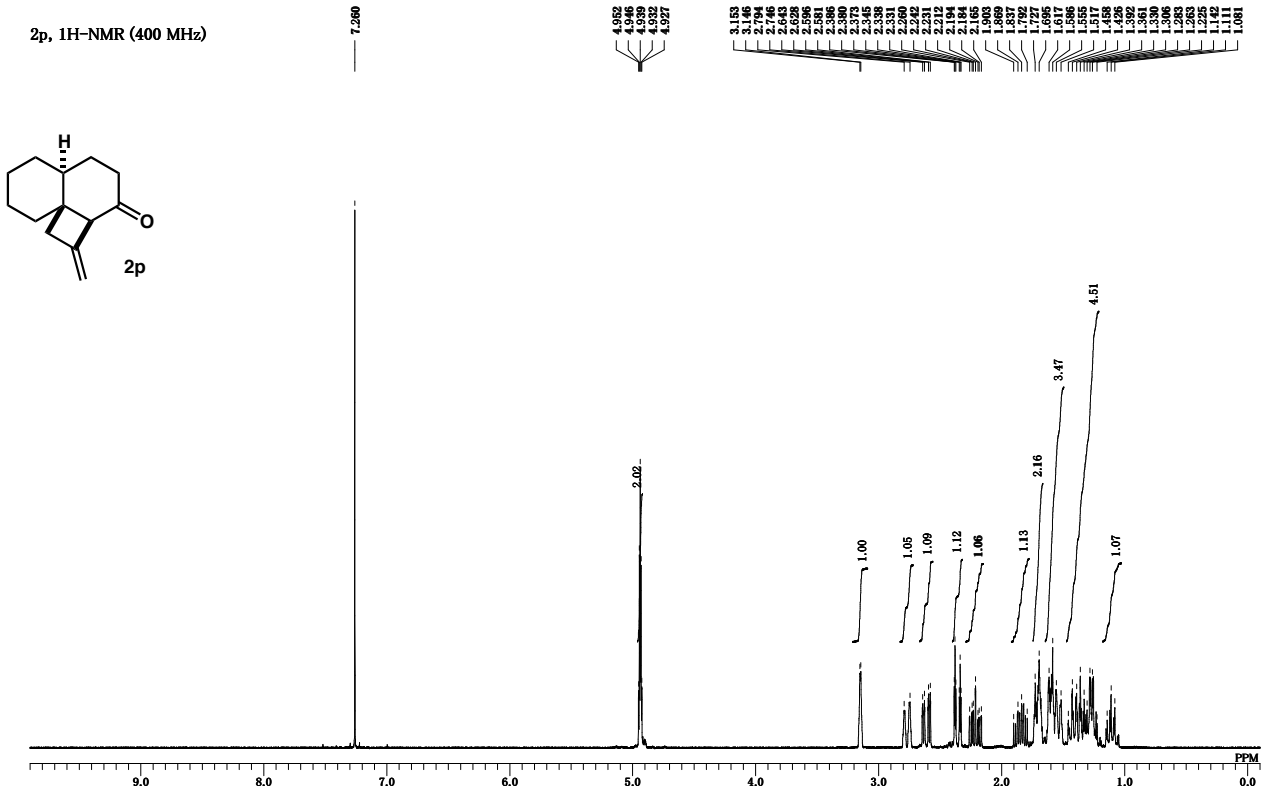

2o

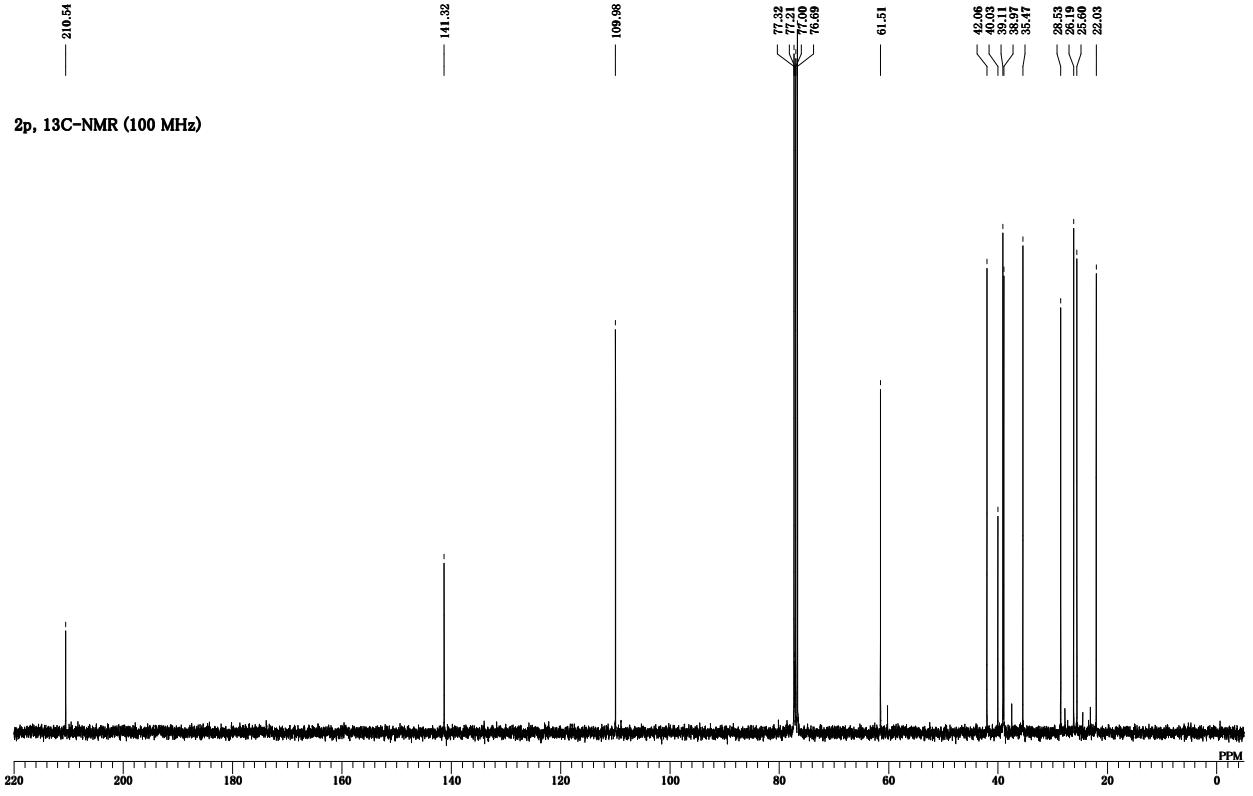



2o, 13C-NMR (100 MHz)

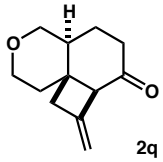


2p, 1H-NMR (400 MHz)



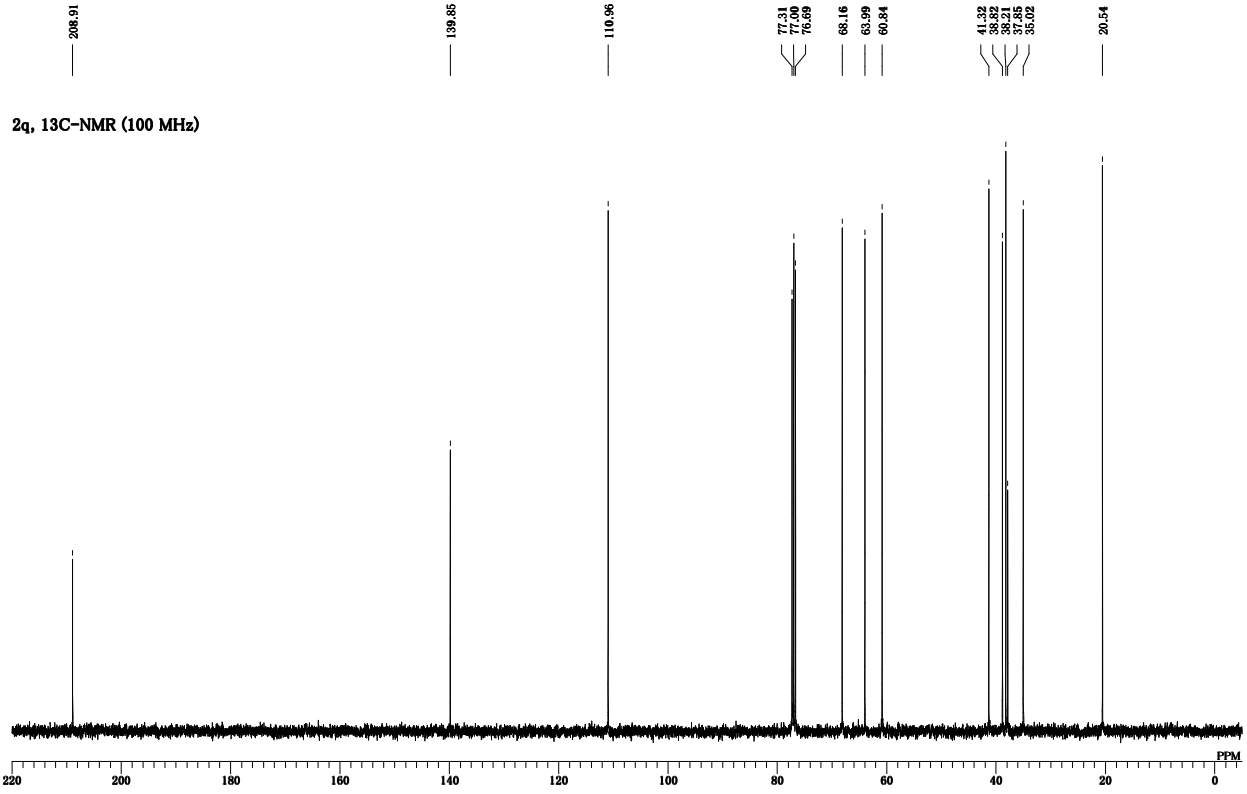



2q, 1H-NMR (400 MHz)



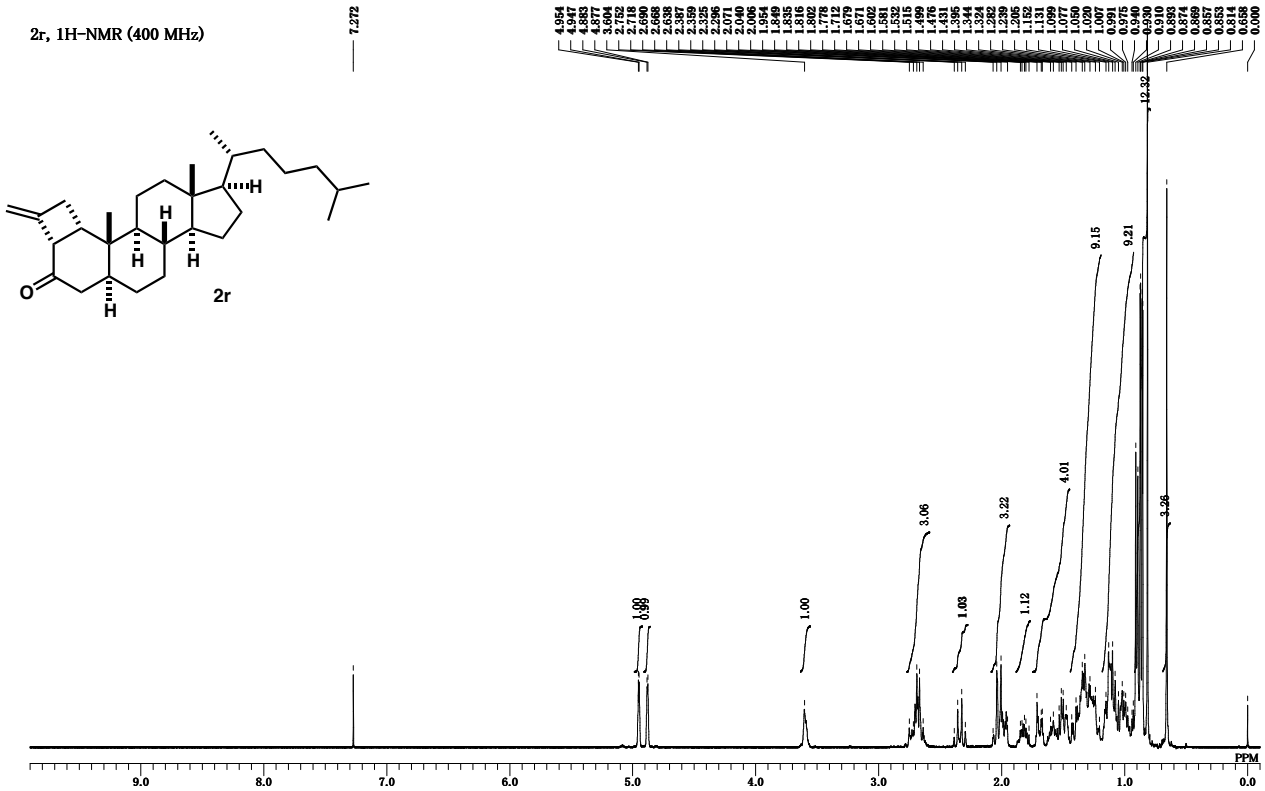
2q




2q, 13C-NMR (100 MHz)

2r, 1H-NMR (400 MHz)

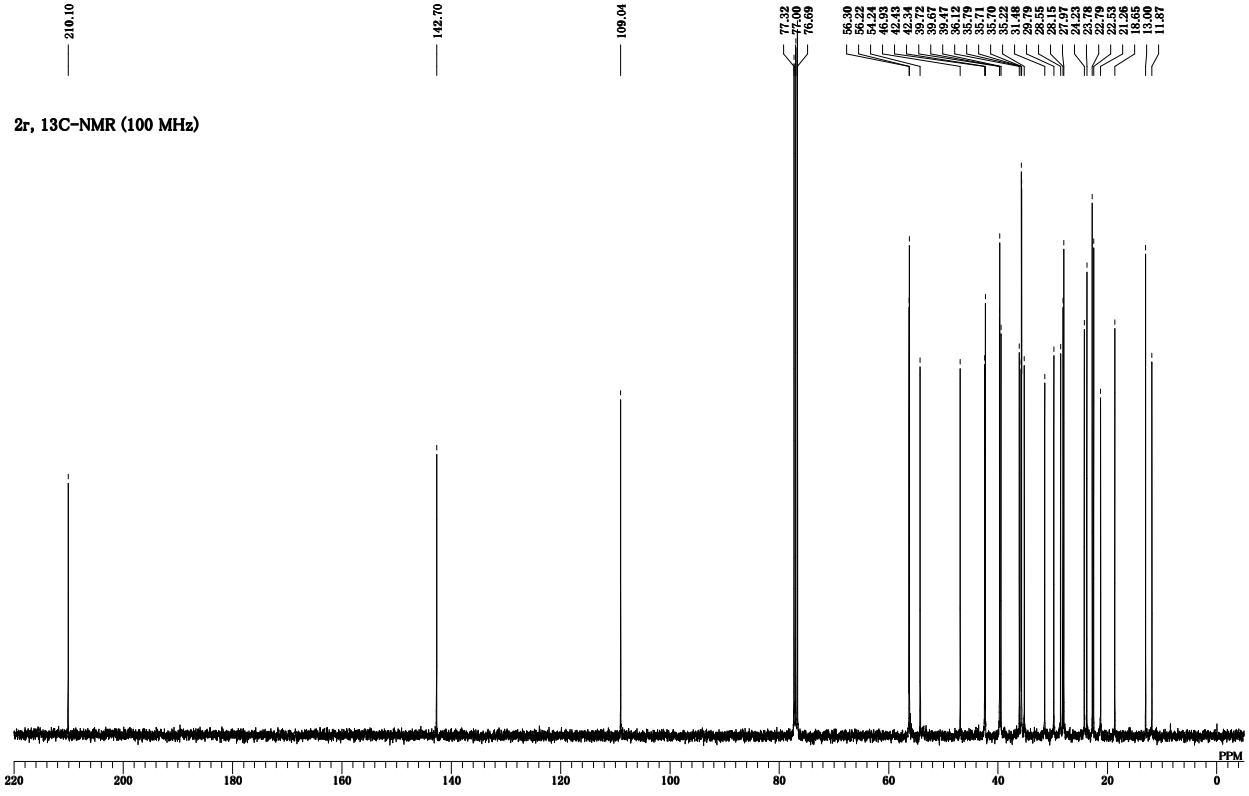




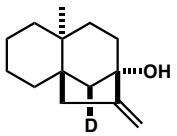


2r

2r, 13C-NMR (100 MHz)



1b(D), 1H-NMR (400 MHz)




1b(D)




1b(D), 13C-NMR (100 MHz)