

Supporting Information

A Regio- and Diastereoselective Palladium-Catalyzed Cyclopropanation of Norbornene Derivatives with Molecular Oxygen as Sole Oxidant

Wanqing Wu, Huanfeng Jiang,* Yang Gao, Huawen Huang, Wei Zeng, and Derong
Cao

School of Chemistry and Chemical Engineering, South China University of Technology,
Guangzhou 510640, China

E-mail: jianghf@scut.edu.cn; Fax and Tel.: (+86) 20-87112906

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General Information

^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer (^1H : 400 MHz, ^{13}C : 100 MHz). The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC-MS was obtained using electron ionization. High resolution mass spectra were obtained on a MAT 95XP (Thermo). Melting points were uncorrected and determined on a Büchi B-545 melting point instrument. Crystallographic data were obtained from Oxford diffraction single crystal X-ray diffractometer (Gemini S Ultra). All the IR spectra were recorded with a Bruker Vector 22 spectrometer.

All the chemicals were purchased commercially and used without further purification. Anhydrous THF was distilled from sodium-benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically, unless otherwise stated.

All air and water sensitive reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on Tsingdao silica gel plates (GF₂₅₄) and visualization was effected at 254 nm.

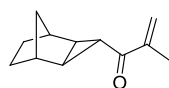
General Procedure

In a 20 mL Schlenk tube was charged with **1** (0.5 mmol), **2** (0.6 mmol), PdCl₂ (5 mol %), LiBr (0.5 mmol) and dry DMF (1 mL) under O₂ (1 atm) atmosphere. The resulting mixture was heated at 40 °C, and the reaction was allowed to stir for the time specified. After reaction completion, as monitored by TLC, the reaction mixture was quenched with saturated aqueous NH₄Cl. The

aqueous phase was extracted with diethyl ether ($\times 3$), and the combined organic extracts were washed with brine. After the organic layer was dried over MgSO_4 , the solvent was removed under reduced pressure. The residue was then purified by silica gel chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired product.

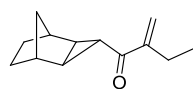
Analytical Data for 3a–x

exo-2-Methyl-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3a)



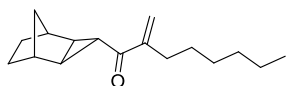
Light yellow solid (77 mg, 88%), m.p. = 85–86 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.97 (s, 1H), 5.58 (m, 1H), 2.35 (s, 2H), 2.32 (t, $J = 2.4$ Hz, 1H), 1.85 (m, 3H), 1.45 (m, 2H), 1.39 (d, $J = 1.8$ Hz, 2H), 1.30 (m, 2H), 1.00 (m, 1H), 0.72 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.5, 145.4, 123.4, 36.1, 29.3, 29.0, 28.8, 19.8, 17.9; IR (KBr) 2960, 2873, 1687, 1459, 1393, 1257, 1135, 1096, 967, 849 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{12}\text{H}_{16}\text{ONa}$: 199.1093, found 199.1091.

exo-2-Methylene-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)butan-1-one (3b)



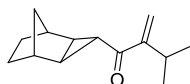
Yellow oil (82 mg, 86%); ^1H NMR (400 MHz, CDCl_3) δ 6.01 (s, 1H), 5.64 (s, 1H), 2.38 (s, 2H), 2.33 (m, 1H), 2.29 (q, $J = 7.4$ Hz, 2H), 1.47 (m, 2H), 1.42 (d, $J = 2.0$ Hz, 2H), 1.33 (dd, $J = 7.1$ Hz, 1.8 Hz, 2H), 1.03 (t, $J = 7.4$ Hz, 3H), 1.02 (m, 1H), 0.75 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 151.5, 121.5, 36.1, 29.2, 29.0, 28.8, 24.1, 20.4, 12.6; IR (KBr) 2959, 2927, 1726, 1584, 1465, 1374, 1260, 1093, 1022, 920, 801 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{13}\text{H}_{18}\text{ONa}$: 213.1250, found 213.1252.

***exo*-2-Methylene-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)octan-1-one (3c)**



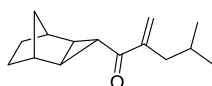
Yellow oil (105 mg, 85%); ¹H NMR (400 MHz, CDCl₃) δ 5.99 (s, 1H), 5.63 (s, 1H), 2.38 (s, 2H), 2.31 (t, *J* = 2.4 Hz, 1H), 2.25 (m, 2H), 1.47 (m, 2H), 1.42 (d, *J* = 1.8 Hz, 2H), 1.37 (m, 2H), 1.30 (m, 8H), 1.01 (m, 1H), 0.88 (m, 3H), 0.75 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 150.3, 122.2, 36.1, 31.7, 31.3, 29.2, 29.1, 29.0, 28.8, 28.4, 22.6, 20.4, 14.1; IR (KBr) 2958, 2930, 1660, 1555, 1460, 1385, 1259, 1177, 1077, 928, 847 cm⁻¹; HRMS (ESI/[M+Na]⁺) calcd. for C₁₇H₂₆ONa: 269.1876, found 269.1874.

***exo*-3-Methyl-2-methylene-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)butan-1-one (3d)**



Yellow oil (83 mg, 81%); ¹H NMR (400 MHz, CDCl₃) δ 5.96 (s, 1H), 5.59 (m, 1H), 2.88 (q, *J* = 6.8 Hz, 2H), 2.38 (s, 2H), 2.30 (t, *J* = 2.4 Hz, 1H), 1.47 (m, 2H), 1.43 (d, *J* = 1.8 Hz, 2H), 1.32 (m, 2H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.74 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 202.2, 156.6, 119.4, 36.1, 29.2, 29.0, 28.8, 28.1, 21.8, 21.0; IR (KBr) 2957, 2925, 1663, 1461, 1384, 1263, 1067, 1025, 927, 849 cm⁻¹; HRMS (ESI/[M+Na]⁺) calcd. for C₁₄H₂₀ONa: 227.1406, found 227.1409.

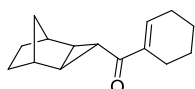
***exo*-4-Methyl-2-methylene-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)pentan-1-one (3e)**



Yellow oil (90 mg, 83%); ¹H NMR (400 MHz, CDCl₃) δ 6.02 (s, 1H), 5.60 (s, 1H), 2.38 (br, 2H), 2.31 (t, *J* = 2.4 Hz, 1H), 2.15 (d, *J* = 7.2 Hz, 2H), 1.69 (m, 1H), 1.47 (m, 2H), 1.41 (d, *J* = 1.7 Hz, 2H), 1.32 (m, 2H), 1.02 (d, *J* = 10.8 Hz, 1H), 0.86 (d, *J* = 6.4 Hz, 6H), 0.75 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 201.9, 149.1, 123.4, 40.7, 36.1, 29.2, 29.0, 28.7, 27.3, 22.4, 20.5;

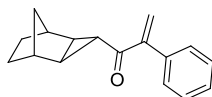
IR (KBr) 2960, 2929, 2856, 1643, 1461, 1384, 1262, 1102, 1017, 943, 838 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for C₁₅H₂₂ONa: 241.1563, found 241.1562.

***exo*-2-(Cyclohex-1-en-1-yl)-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3f)**



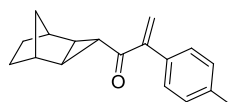
Yellow solid (84 mg, 78%), m.p. = 108–109 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.94 (s, 1H), 2.36 (s, 2H), 2.29 (s, 1H), 2.23 (m, 4H), 1.62 (m, 6H), 1.46 (d, *J* = 8.0 Hz, 2H), 1.40 (m, 2H), 1.34 (m, 2H), 1.02 (d, *J* = 10.8 Hz, 1H), 0.73 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 200.8, 140.1, 138.5, 36.1, 29.1, 28.8, 28.7, 26.1, 23.6, 22.1, 21.7, 19.3; IR (KBr) 2954, 2870, 1651, 1457, 1398, 1257, 1202, 1134, 1006, 969, 919, 847 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for C₁₅H₂₀ONa: 239.1406, found 239.1394.

***exo*-2-Phenyl-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3g)**



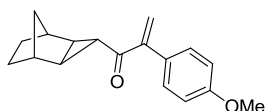
Yellow solid (95 mg, 80%), m.p. = 112–113 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 5H), 6.03 (s, 1H), 5.79 (s, 1H), 2.38 (m, 2H), 2.20 (m, 1H), 1.57 (s, 2H), 1.48 (d, *J* = 7.2 Hz, 2H), 1.34 (d, *J* = 7.2 Hz, 2H), 0.88 (d, *J* = 9.6 Hz, 1H), 0.70 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 202.3, 150.4, 137.3, 128.6, 128.3, 128.1, 122.1, 36.1, 30.5, 29.0, 28.6, 23.2; IR (KBr) 2959, 2872, 1672, 1598, 1494, 1386, 1312, 1134, 1027, 936, 845, 776, 700 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for C₁₇H₁₈ONa: 261.1251, found 261.1250.

***exo*-2-(*p*-Tolyl)-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3h)**



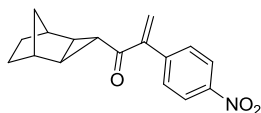
Yellow solid (98 mg, 78%), m.p. = 118–119 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 5.4$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 5.99 (s, 1H), 5.78 (s, 1H), 2.45 (d, $J = 9.4$ Hz, 2H), 2.40 (s, 3H), 2.30 (t, $J = 2.4$ Hz, 1H), 1.59 (d, $J = 1.7$ Hz, 2H), 1.51 (m, 2H), 1.36 (m, 2H), 0.92 (d, $J = 10.7$ Hz, 1H), 0.73 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.6, 150.3, 138.0, 129.0, 127.9, 126.4, 121.2, 36.1, 30.4, 29.0, 28.6, 23.2, 21.2; IR (KBr) 2960, 2870, 1669, 1604, 1512, 1459, 1390, 1134, 1024, 933, 846, 820, 729 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{18}\text{H}_{20}\text{ONa}$: 275.1406, found 275.1402.

***exo*-2-(4-Methoxyphenyl)-1-(tricyclo[3.2.1.0 2,4]octan-3-yl)prop-2-en-1-one (3i)**



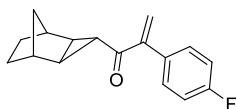
Yellow oil (107 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 5.92 (s, 1H), 5.72 (s, 1H), 3.83 (s, 3H), 2.37 (s, 2H), 2.20 (t, $J = 2.3$ Hz, 1H), 1.55 (d, $J = 1.5$ Hz, 2H), 1.48 (m, 2H), 1.34 (m, 2H), 0.89 (d, $J = 10.6$ Hz, 1H), 0.70 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.8, 159.6, 149.9, 129.3, 120.5, 114.1, 113.7, 55.3, 36.1, 30.4, 29.0, 28.6, 23.2; IR (KBr) 2955, 2870, 1678, 1602, 1512, 1392, 1302, 1145, 1035, 960, 868, 772, 715 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Na}$: 291.1356, found 291.1354.

***exo*-2-(4-Nitrophenyl)-1-(tricyclo[3.2.1.0 2,4]octan-3-yl)prop-2-en-1-one (3j)**



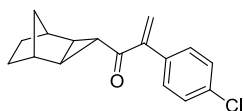
Yellow oil (106 mg, 75%); ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 2H), 6.27 (s, 1H), 6.00 (s, 1H), 2.41 (s, 2H), 2.25 (t, $J = 2.3$ Hz, 1H), 1.55 (d, $J = 1.7$ Hz, 2H), 1.49 (m, 2H), 1.33 (m, 2H), 0.79 (d, $J = 10.6$ Hz, 1H), 0.65 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.9, 149.3, 147.6, 136.2, 131.4, 128.1, 122.9, 36.1, 30.4, 29.0, 28.6, 22.9; IR (KBr) 2965, 2880, 1675, 1602, 1523, 1388, 1322, 1155, 1030, 951, 862, 768, 725 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_3\text{Na}$: 306.1101, found 306.1105.

***exo*-2-(4-Fluorophenyl)-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3k)**



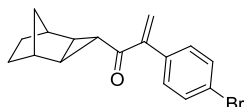
Yellow solid (105 mg, 82%), m.p. = 112–113 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (m, 2H), 7.05 (m, 2H), 6.05 (s, 1H), 5.79 (s, 1H), 2.38 (s, 2H), 2.21 (t, *J* = 2.3 Hz, 1H), 1.55 (d, *J* = 1.7 Hz, 2H), 1.49 (m, 2H), 1.34 (m, 2H), 0.91 (d, *J* = 10.8 Hz, 1H), 0.72 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 201.9, 163.9, 149.3, 129.9, 129.8, 122.5, 115.3, 36.1, 30.4, 29.0, 28.6, 22.9; IR (KBr) 2962, 2878, 1672, 1600, 1508, 1462, 1387, 1145, 1033, 953, 860, 838, 720 cm⁻¹; HRMS (ESI/[M+Na]⁺) calcd. for C₁₇H₁₇OFNa: 279.1156, found 279.1154.

***exo*-2-(4-Chlorophenyl)-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3l)**



Yellow solid (110 mg, 81%), m.p. = 105–106 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.06 (s, 1H), 5.81 (s, 1H), 2.38 (s, 2H), 2.21 (m, 1H), 1.55 (d, *J* = 1.5 Hz, 2H), 1.48 (m, 2H), 1.34 (m, 2H), 0.90 (d, *J* = 10.9 Hz, 1H), 0.72 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 201.6, 149.2, 134.1, 129.7, 129.5, 128.4, 122.9, 36.1, 30.5, 29.0, 28.6, 22.9; IR (KBr) 2963, 2876, 1688, 1602, 1510, 1386, 1312, 1145, 1030, 938, 855, 786, 709 cm⁻¹; HRMS (ESI/[M+Na]⁺) calcd. for C₁₇H₁₇OCINa: 295.0860, found 295.0858.

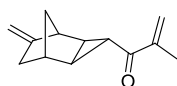
***exo*-2-(4-Bromophenyl)-1-(tricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3m)**



Light yellow solid (133 mg, 84%), m.p. = 98–99 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.01 (s, 1H), 5.82 (s, 1H), 2.38 (s, 2H), 2.21 (t, *J* = 2.4 Hz, 1H), 1.55 (d, *J* = 1.8 Hz, 2H), 1.49 (m, 2H), 1.34 (m, 2H), 0.90 (d, *J* = 10.8 Hz, 1H), 0.72 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 149.3, 131.9, 131.4, 129.8, 128.1, 123.0, 36.1,

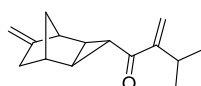
30.5, 29.0, 28.6, 22.9; IR (KBr) 2960, 2878, 1680, 1608, 1504, 1388, 1312, 1134, 1027, 966, 870, 750, 723 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for C₁₇H₁₇OBrNa: 339.0355, found 339.0351.

***exo*-2-Methyl-1-(6-methylenetricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3n)**



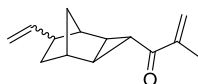
Yellow oil (77 mg, 82%); ¹H NMR (400 MHz, CDCl₃) δ 6.01 (s, 1H), 5.73 (s, 1H), 4.91 (s, 1H), 4.68 (s, 1H), 2.80 (s, 1H), 2.52 (m, 1H), 2.15 (dd, *J* = 15.3 Hz, 2.5 Hz, 1H), 2.04 (d, *J* = 16.4 Hz, 1H), 1.88 (s, 3H), 1.56 (d, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 1H), 1.15 (d, *J* = 10.9 Hz, 1H), 0.93 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 200.5, 152.6, 145.4, 123.6, 103.7, 44.8, 37.1, 36.6, 29.2, 28.9, 28.3, 21.2, 17.9; IR (KBr) 2962, 2926, 1692, 1561, 1457, 1375, 1261, 1088, 1021, 877, 845, 802 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for C₁₃H₁₆ONa: 211.1093, found 211.1097.

***exo*-3-Methyl-2-methylene-1-(6-methylenetricyclo[3.2.1.0^{2,4}]octan-3-yl)butan-1-one (3o)**



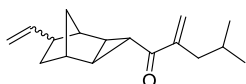
Yellow oil (84 mg, 78%); ¹H NMR (400 MHz, CDCl₃) δ 5.98 (s, 1H), 5.62 (s, 1H), 4.91 (s, 1H), 4.68 (s, 1H), 2.89 (m, 1H), 2.81 (s, 1H), 2.48 (m, 2H), 2.15 (d, *J* = 15.6 Hz, 1H), 2.05 (d, *J* = 15.6 Hz, 1H), 1.55 (d, *J* = 7.4 Hz, 1H), 1.50 (d, *J* = 7.6 Hz, 1H), 1.15 (d, *J* = 11.5 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 11.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 200.3, 152.5, 144.5, 119.6, 103.6, 44.8, 37.1, 36.6, 29.7, 29.2, 28.7, 28.3, 28.1, 22.3, 21.8; IR (KBr) 2961, 2927, 2857, 1633, 1566, 1462, 1394, 1261, 1172, 1064, 927, 878, 801 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for C₁₅H₂₀ONa: 239.1406, found 239.1402.

***exo*-2-Methyl-1-(6-vinyltricyclo[3.2.1.0^{2,4}]octan-3-yl)prop-2-en-1-one (3p)**



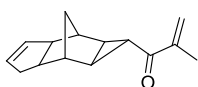
Yellow oil (89 mg, 88%); ^1H NMR (400 MHz, CDCl_3 , a mixture of diastereoisomers) δ 5.99 (s, 1H), 5.97 (m, 0.8H), 5.76 (m, 0.2H), 5.70 (br s, 1H), 5.02 (m, 1.7H), 4.93 (m, 0.3H), 2.55 (m, 0.7H), 2.42 (m, 3H), 2.29 (m, 0.3H), 1.87 (s, 3H), 1.76 (dt, $J = 11.0$ Hz, 3.85 Hz, 0.7H), 1.63 (m, 1.7H), 1.49 (m, 1.3H), 1.32 (dt, $J = 12.1$ Hz, 3.92 Hz, 0.3H), 1.12 (m, 1H), 0.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3 , major isomer) δ 201.4, 145.5, 140.7, 123.4, 114.7, 45.9, 41.8, 37.1, 34.9, 30.3, 29.3, 25.4, 19.5, 17.9; IR (KBr) 2959, 2869, 1688, 1563, 1456, 1395, 1260, 1170, 1090, 1022, 911, 846 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{14}\text{H}_{18}\text{ONa}$: 225.1250, found 225.1254.

***exo*-4-Methyl-2-methylene-1-(6-vinyltricyclo[3.2.1.0 2,4]octan-3-yl)pentan-1-one (3q)**



Yellow oil (104 mg, 85%); ^1H NMR (400 MHz, CDCl_3 , a mixture of diastereoisomers) δ 6.01 (br s, 1H), 5.98 (m, 0.7H), 5.75 (m, 0.3H), 5.61 (br s, 1H), 5.02 (m, 1.7H), 4.93 (m, 0.3H), 2.55 (m, 0.8H), 2.40 (m, 3H), 2.28 (m, 0.2H), 2.15 (d, $J = 6.9$ Hz, 2H), 1.78 (m, 1H), 1.75 (m, 0.7H), 1.69 (m, 1.7H), 1.48 (m, 1.3H), 1.32 (m, 0.3H), 1.07 (m, 1H), 0.92 (m, 1H), 0.86 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , major isomer) δ 201.7, 149.1, 140.7, 123.4, 114.7, 45.9, 41.7, 40.7, 37.2, 34.9, 30.3, 29.3, 27.3, 25.3, 22.4, 20.2; IR (KBr) 2957, 2925, 2856, 1663, 1461, 1393, 1263, 1170, 1118, 1070, 996, 911, 848 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{17}\text{H}_{24}\text{ONa}$: 267.1719, found 267.1720.

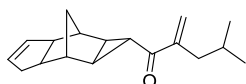
***exo*-2-Methyl-1-(1,1a,2,2a,3,5a,6,6a-octahydro-2,6-methanocyclopropa[*f*]inden-1-yl)prop-2-en-1-one (3r)**



Yellow oil (87 mg, 81%); ^1H NMR (400 MHz, CDCl_3) δ 5.99 (s, 1H), 5.74 (m, 1H), 5.69 (s, 1H),

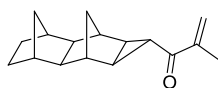
5.54 (m, 1H), 3.12 (m, 1H), 2.58 (m, 1H), 2.46 (d, $J = 3.2$ Hz, 1H), 2.42 (t, $J = 2.4$ Hz, 1H), 2.35 (m, 2H), 1.86 (s, 3H), 1.56 (d, $J = 7.2$ Hz, 1H), 1.27 (d, $J = 8.8$ Hz, 2H), 1.15 (d, $J = 10.8$ Hz, 1H), 0.98 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 145.5, 132.8, 130.1, 123.3, 54.7, 43.0, 39.8, 38.5, 31.8, 31.5, 27.4, 24.3, 19.1, 17.9; IR (KBr) 2951, 1684, 1582, 1453, 1393, 1261, 1178, 1091, 1017, 930, 848 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{15}\text{H}_{18}\text{ONa}$: 237.1250, found 237.1262.

***exo*-4-Methyl-2-methylene-1-(1,1a,2,2a,3,5a,6,6a-octahydro-2,6-methanocyclopropa[*f*]inden-1-yl)pentan-1-one (3s)**



yellow oil (104 mg, 81%); ^1H NMR (400 MHz, CDCl_3) δ 6.01 (s, 1H), 5.74 (m, 1H), 5.60 (s, 1H), 5.54 (m, 1H), 3.12 (m, 1H), 2.59 (m, 1H), 2.46 (d, $J = 3.4$ Hz, 1H), 2.40 (m, 1H), 2.36 (m, 2H), 2.14 (d, $J = 7.0$ Hz, 2H), 1.68 (m, 1H), 1.57 (m, 1H), 1.28 (d, $J = 8.8$ Hz, 2H), 1.15 (d, $J = 10.7$ Hz, 1H), 0.98 (d, $J = 10.6$ Hz, 1H), 0.85 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.0, 149.2, 132.8, 130.1, 123.3, 54.7, 43.0, 40.8, 39.8, 38.5, 31.8, 31.5, 27.4, 27.3, 24.3, 22.4, 19.6; IR (KBr) 2955, 2858, 1665, 1622, 1461, 1393, 1319, 1116, 1063, 1018, 930, 849 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{18}\text{H}_{24}\text{ONa}$: 279.1719, found 279.1718.

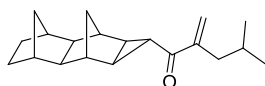
***exo*-1-(Decahydro-1*H*-2,7:3,6-dimethanocyclopropa[*b*]naphthalen-1-yl)-2-methylprop-2-en-1-one (3t)**



Yellow oil (109 mg, 90%); ^1H NMR (400 MHz, CDCl_3) δ 5.96 (s, 1H), 5.68 (s, 1H), 2.57 (s, 1H), 2.46 (s, 2H), 2.25 (m, 3H), 1.86 (s, 3H), 1.69 (s, 2H), 1.46 (m, 4H), 1.05 (d, $J = 10.8$ Hz, 1H), 0.95 (m, 3H), 0.71 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 145.5, 123.34, 50.8, 40.6, 36.5, 35.9, 31.5, 31.2, 28.4, 22.1, 18.0; IR (KBr) 2946, 2876, 1689, 1600, 1455, 1389, 1298,

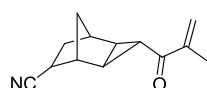
1162, 1092, 1022, 974, 919, 847 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for $\text{C}_{17}\text{H}_{22}\text{ONa}$: 265.1563, found 265.1559.

***exo*-1-((Decahydro-1*H*-2,7:3,6-dimethanocyclopropa[*b*]naphthalen-1-yl)-4-methyl-2-methylenepentane-1-one (3u)**



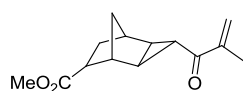
Yellow oil (122 mg, 86%); ¹H NMR (400 MHz, CDCl_3) δ 5.99 (s, 1H), 5.60 (s, 1H), 2.56 (s, 1H), 2.47 (s, 2H), 2.25 (m, 3H), 2.14 (d, $J = 7.0$ Hz, 2H), 1.68 (m, 3H), 1.47 (m, 4H), 1.07 (d, $J = 10.7$ Hz, 1H), 0.90 (m, 3H), 0.85 (d, $J = 6.5$ Hz, 6H), 0.72 (d, $J = 10.6$ Hz, 1H); ¹³C NMR (100 MHz, CDCl_3) δ 202.1, 149.1, 123.4, 50.8, 40.9, 40.6, 36.5, 35.9, 31.5, 31.3, 28.4, 27.29, 22.7, 22.4; IR (KBr) 2950, 2870, 1659, 1462, 1389, 1311, 1119, 1023, 926, 849, cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for $\text{C}_{20}\text{H}_{28}\text{ONa}$: 307.2032, found 307.2030.

***exo*-3-Methacryloyltricyclo[3.2.1.0^{2,4}]octane-6-carbonitrile (3v)**



Light yellow solid (87 mg, 87%), m.p. = 122–123 °C; ¹H NMR (400 MHz, CDCl_3) δ 5.99 (s, 1H), 5.75 (s, 1H), 2.73 (s, 1H), 2.70 (m, 1H), 2.54 (br s, 1H), 2.43 (m, 1H), 1.99 (m, 1H), 1.88 (m, 1H), 1.86 (s, 3H), 1.60 (m, 2H), 0.83 (d, $J = 11.2$ Hz, 1H); ¹³C NMR (100 MHz, CDCl_3) δ 199.6, 145.3, 124.1, 121.6, 39.7, 36.2, 35.0, 30.4, 29.3, 27.4, 24.1, 19.1, 17.9; IR (KBr) 2972, 2236, 1664, 1455, 1395, 1313, 1260, 1146, 1098, 1037, 935, 888, 850 cm^{-1} ; HRMS (ESI/[M+Na]⁺) calcd. for $\text{C}_{13}\text{H}_{15}\text{NONa}$: 224.1046, found 224.1044.

***exo*-Methyl 3-Methacryloyltricyclo[3.2.1.0^{2,4}]octane-6-carboxylate (3w)**



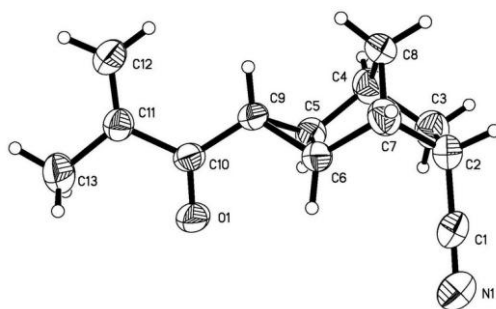
Light yellow solid (96 mg, 82%), m.p.= 89–90 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.99 (s, 1H), 5.71 (s, 1H), 3.70 (s, 3H), 2.77 (m, 2H), 2.45 (br, 1H), 2.39 (t, $J = 2.4$ Hz, 1H), 1.86 (s, 3H), 1.77 (m, 2H), 1.51 (d, $J = 6.5$ Hz, 1H), 1.46 (d, $J = 6.8$ Hz, 1H), 1.14 (d, $J = 9.9$ Hz, 1H), 0.90 (d, $J = 11.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.6, 174.1, 145.4, 123.6, 51.7, 46.5, 39.7, 36.6, 31.5, 30.1, 28.1, 24.9, 19.2, 17.9; IR (KBr) 2966, 1756, 1680, 1458, 1390, 1366, 1323, 1268, 1126, 1082, 1044, 930, 891, 855 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}$: 257.1148, found 257.1148.

***exo-tert*-Butyl 3-Methacryloyltricyclo[3.2.1.0 2,4]octane-6-carboxylate (3x)**

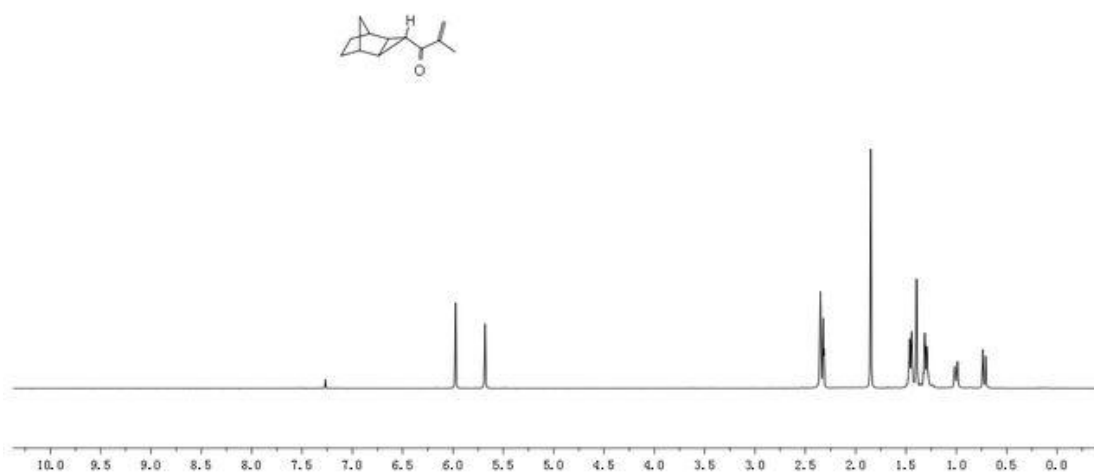


Light yellow solid (121 mg, 88%), m.p.= 95–96 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.98 (s, 1H), 5.71 (s, 1H), 2.68 (m, 2H), 2.42 (br, 1H), 2.38 (m, 1H), 1.86 (s, 3H), 1.75 (m, 1H), 1.50 (m, 2H), 1.46 (s, 9H), 1.43 (m, 1H), 1.12 (d, $J = 10.8$ Hz, 1H), 0.87 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.6, 1730, 145.4, 123.6, 80.3, 47.6, 40.0, 36.8, 31.2, 30.2, 28.4, 28.2, 28.1, 24.8, 19.12, 17.9; IR (KBr) 2968, 1750, 1675, 1462, 1402, 1372, 1320, 1265, 1133, 1090, 1041, 945, 895, 866 cm^{-1} ; HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Na}$: 299.1618, found 299.1616.

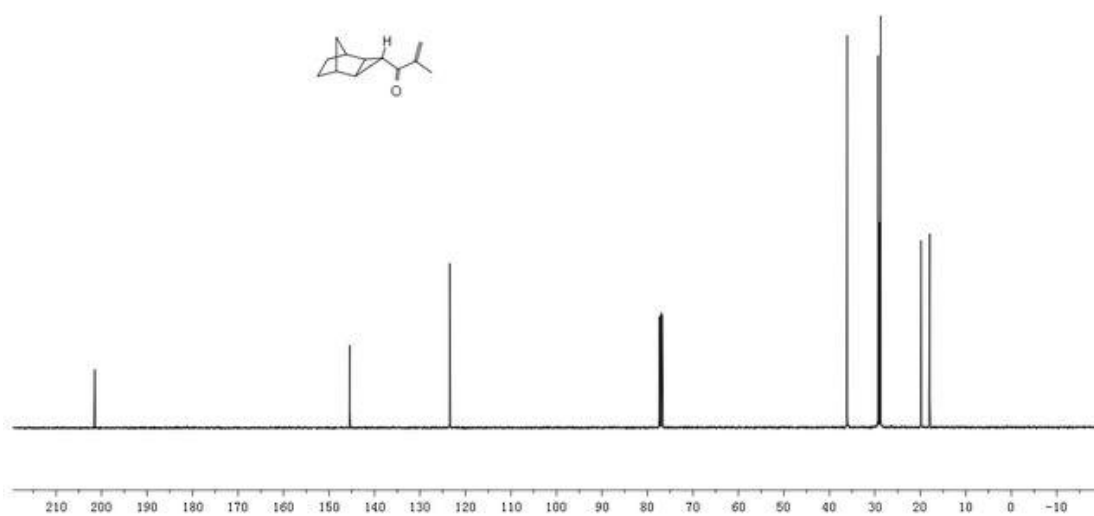
X-Ray Crystal Structure of 3v



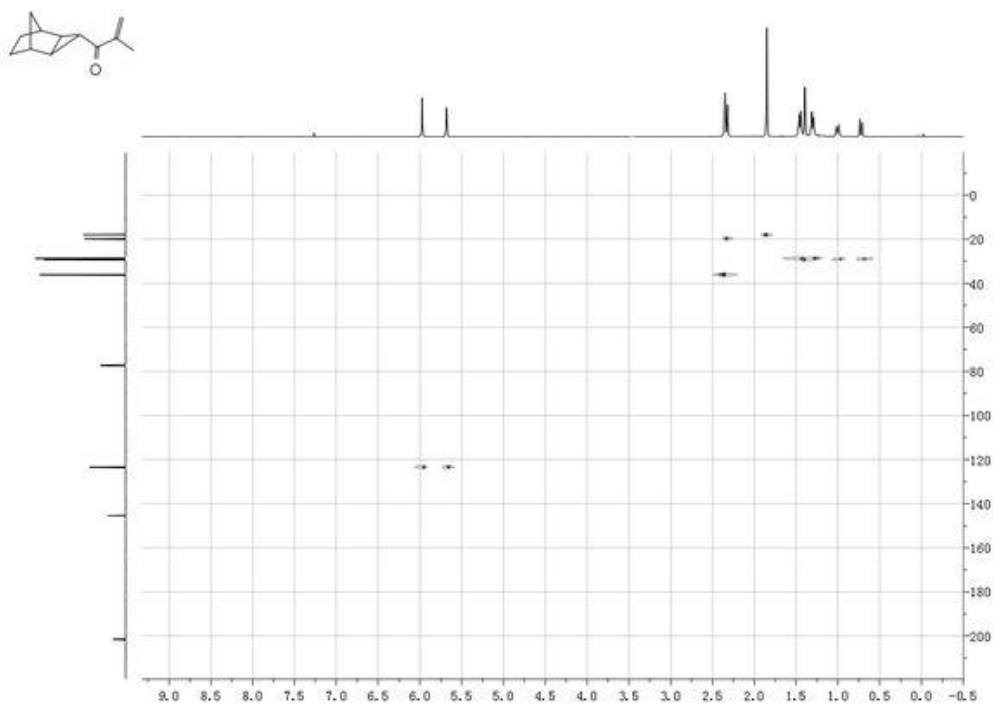
¹H Spectrum for Compound 3a



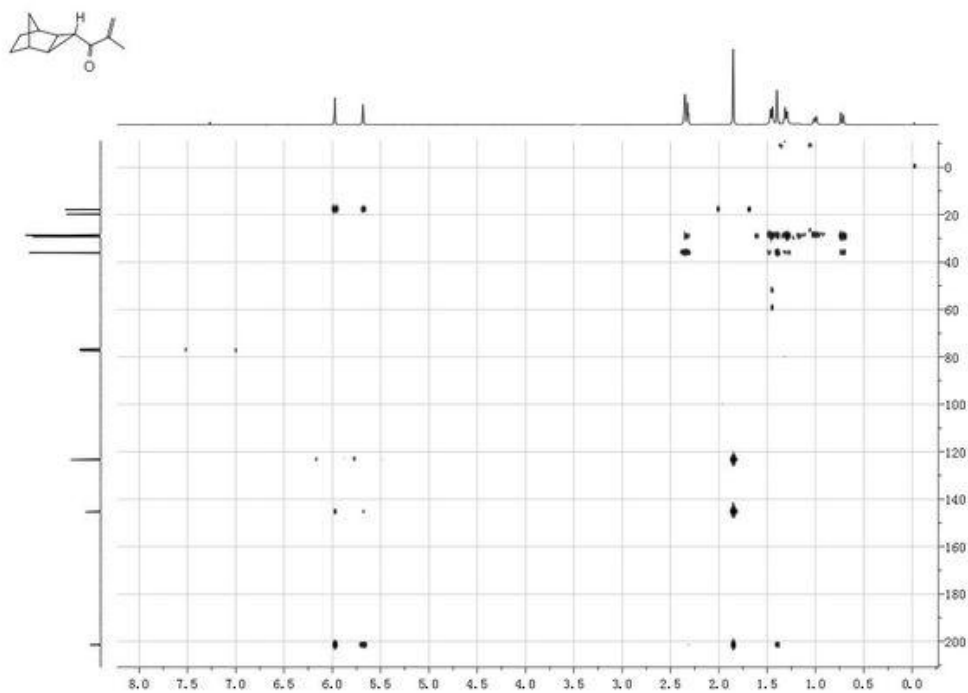
¹³C Spectrum for Compound 3a



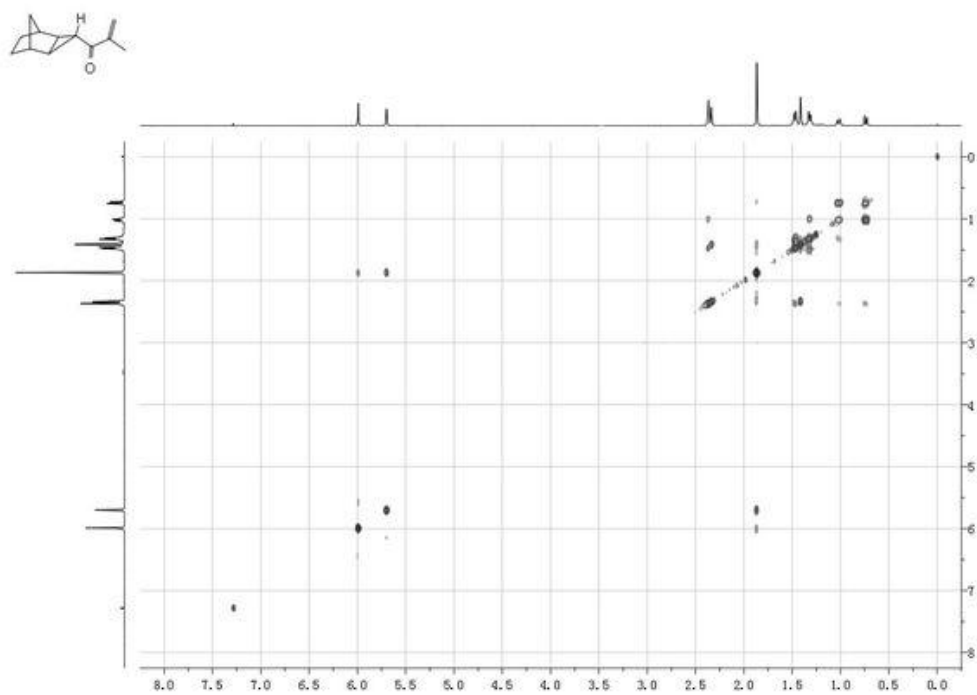
HSQC Spectrum for Compound 3a



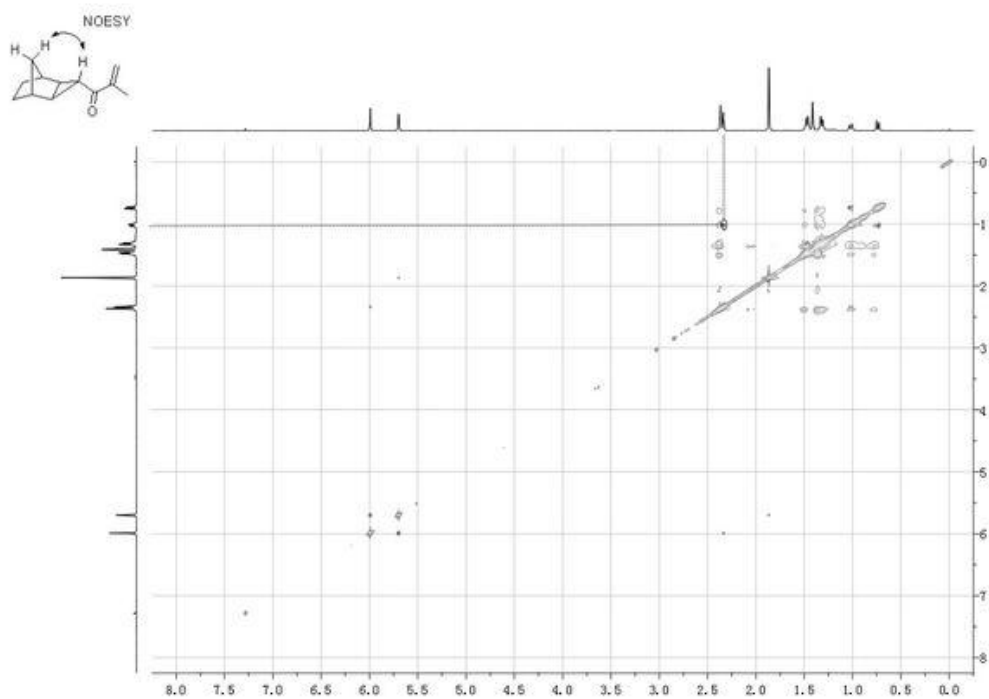
HMBC Spectrum for Compound 3a



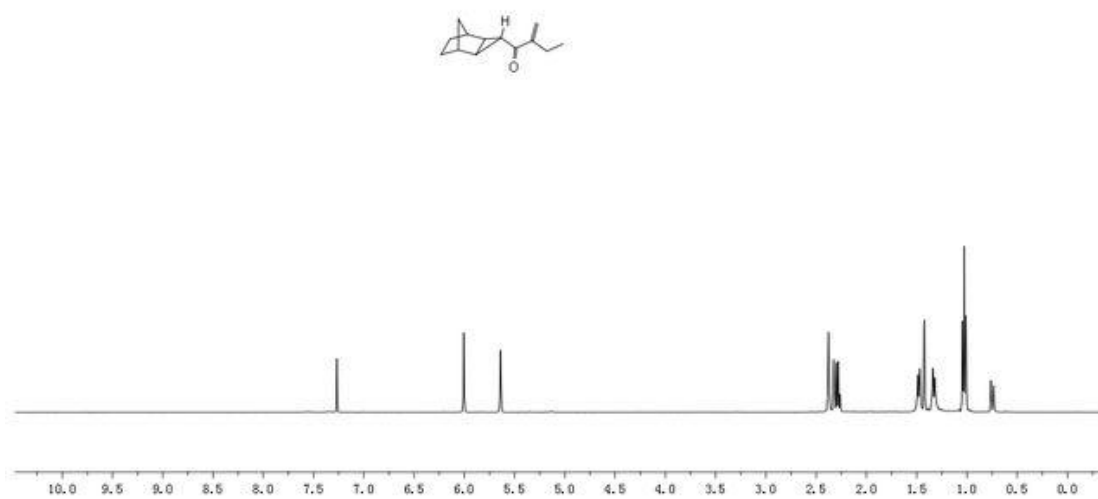
COSY Spectrum for Compound 3a



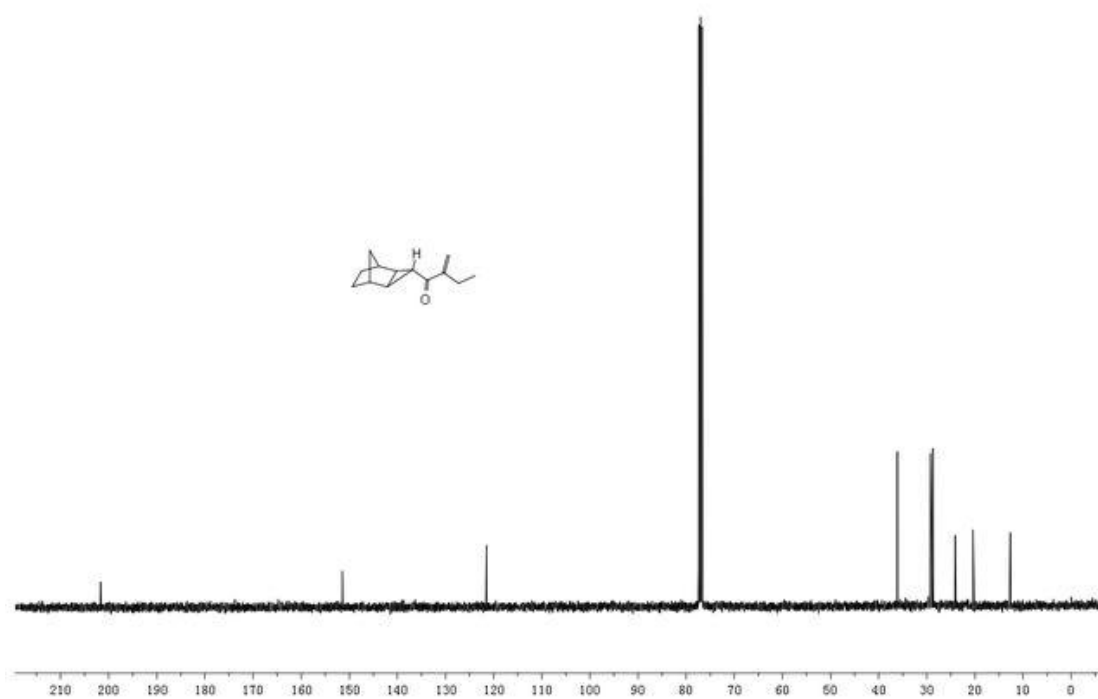
NOESY Spectrum for Compound 3a



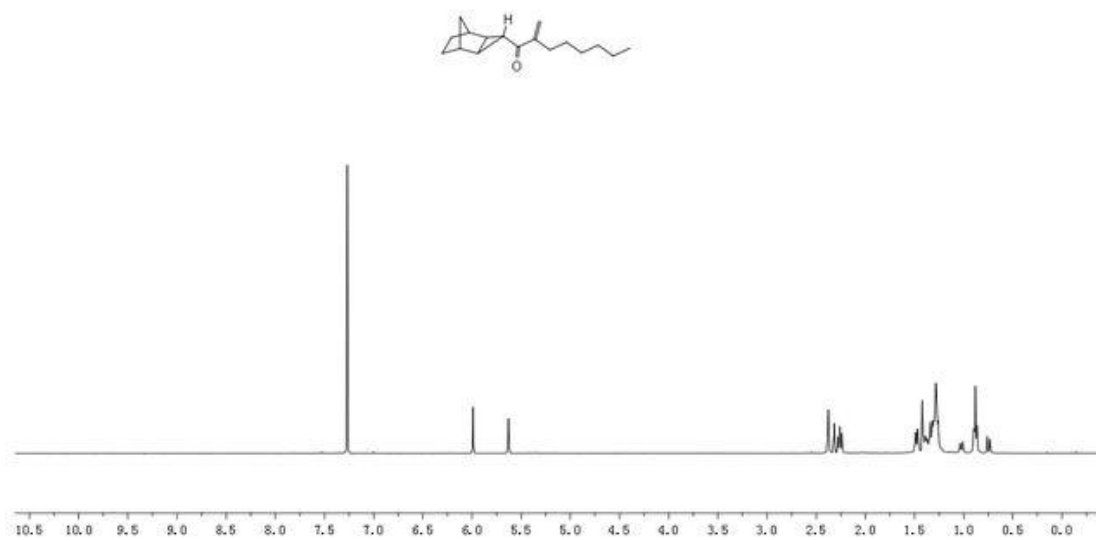
^1H Spectrum for Compound 3b



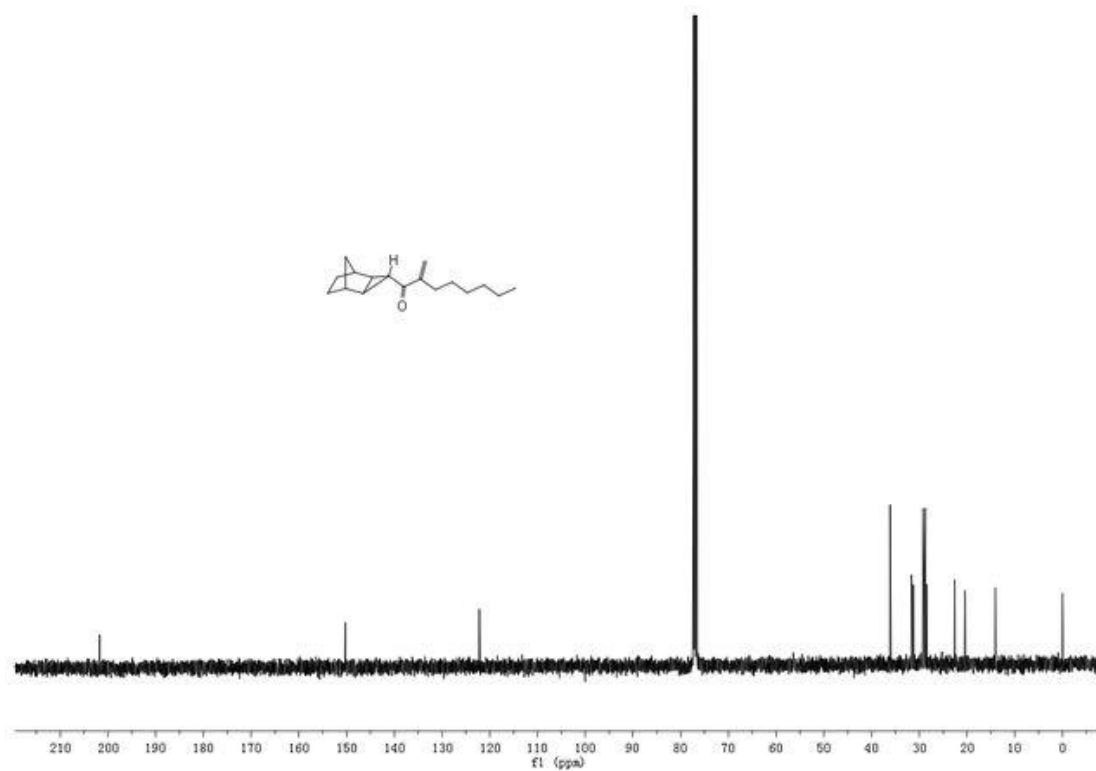
^{13}C Spectrum for Compound 3b



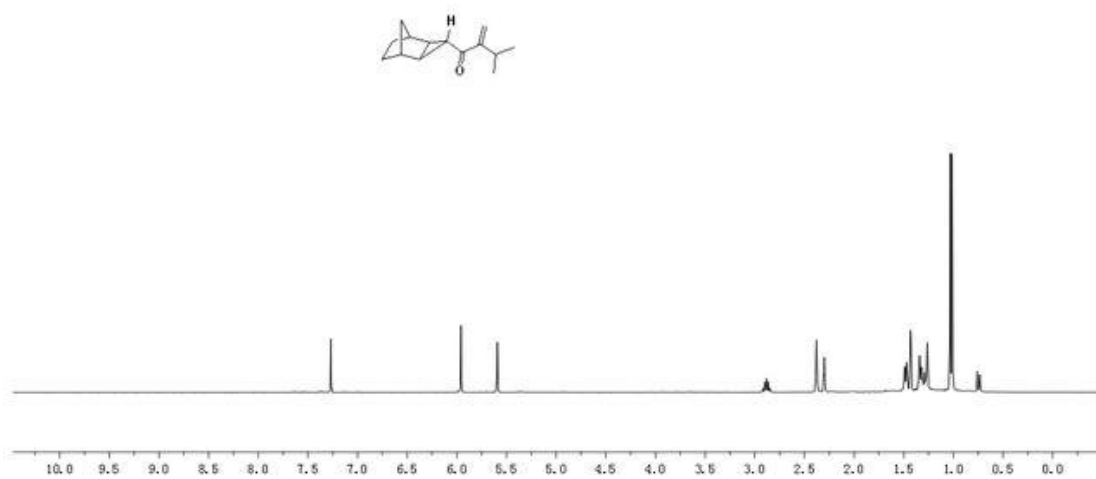
^1H Spectrum for Compound 3c



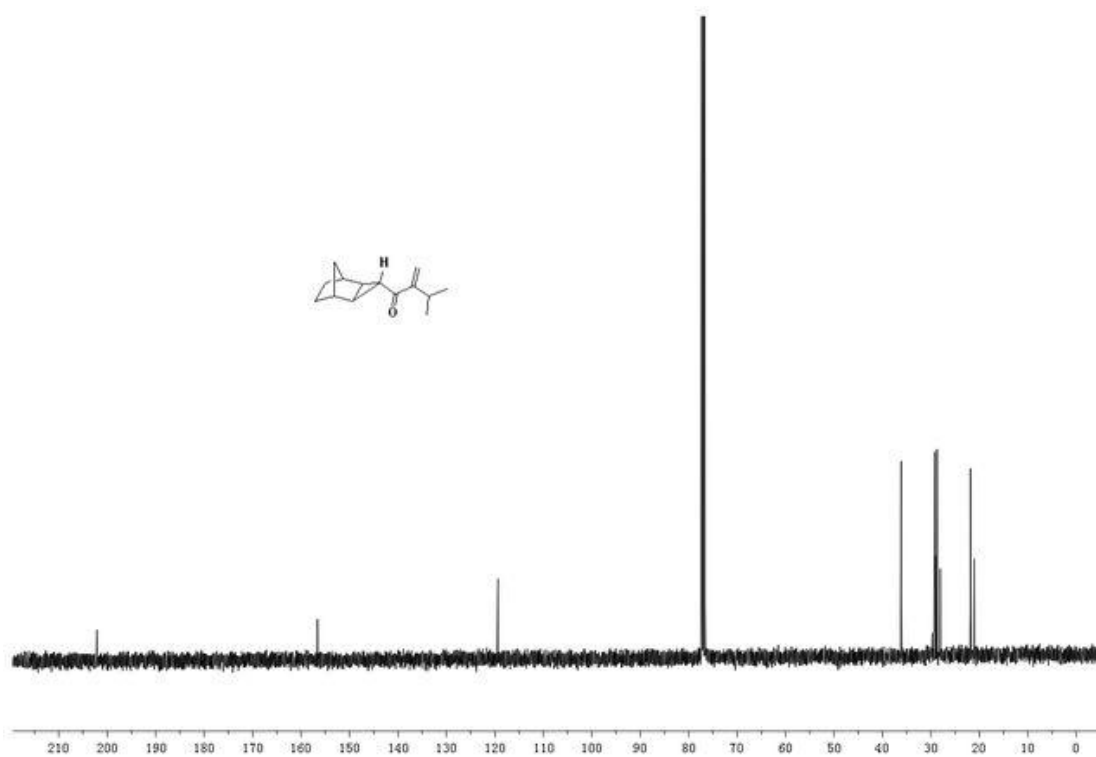
^{13}C Spectrum for Compound 3c



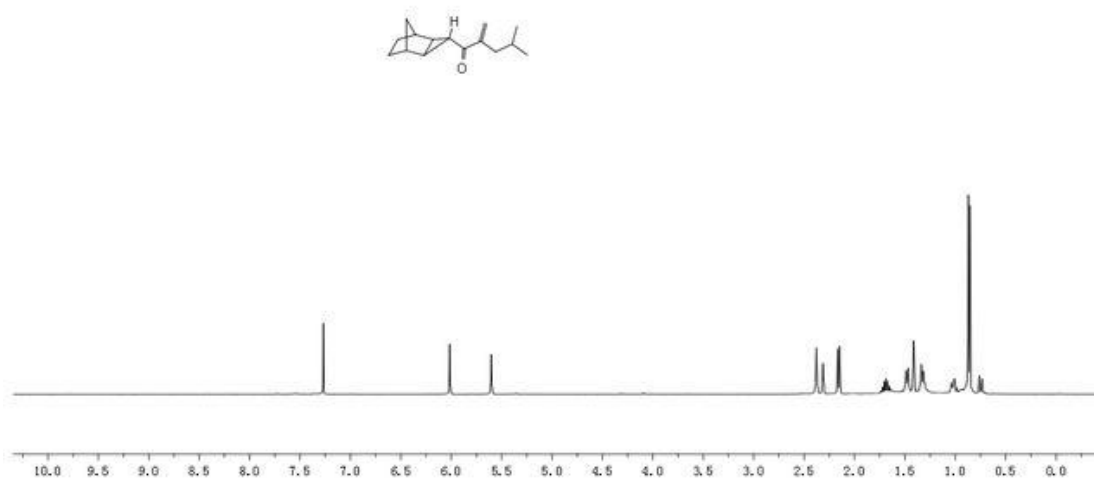
^1H Spectrum for Compound 3d



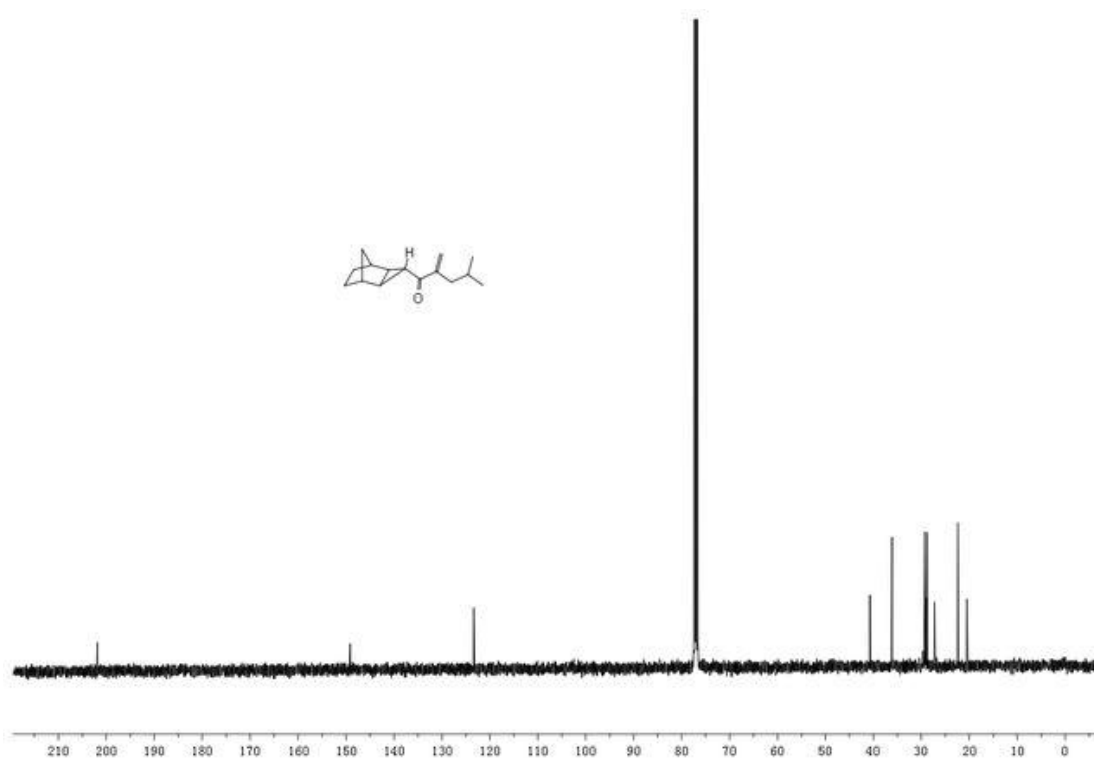
^{13}C Spectrum for Compound 3d



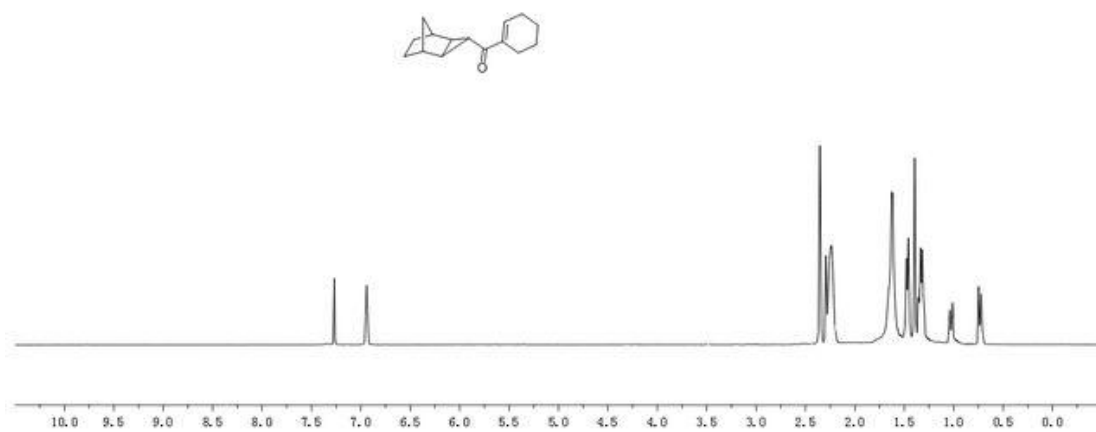
¹H Spectrum for Compound 3e



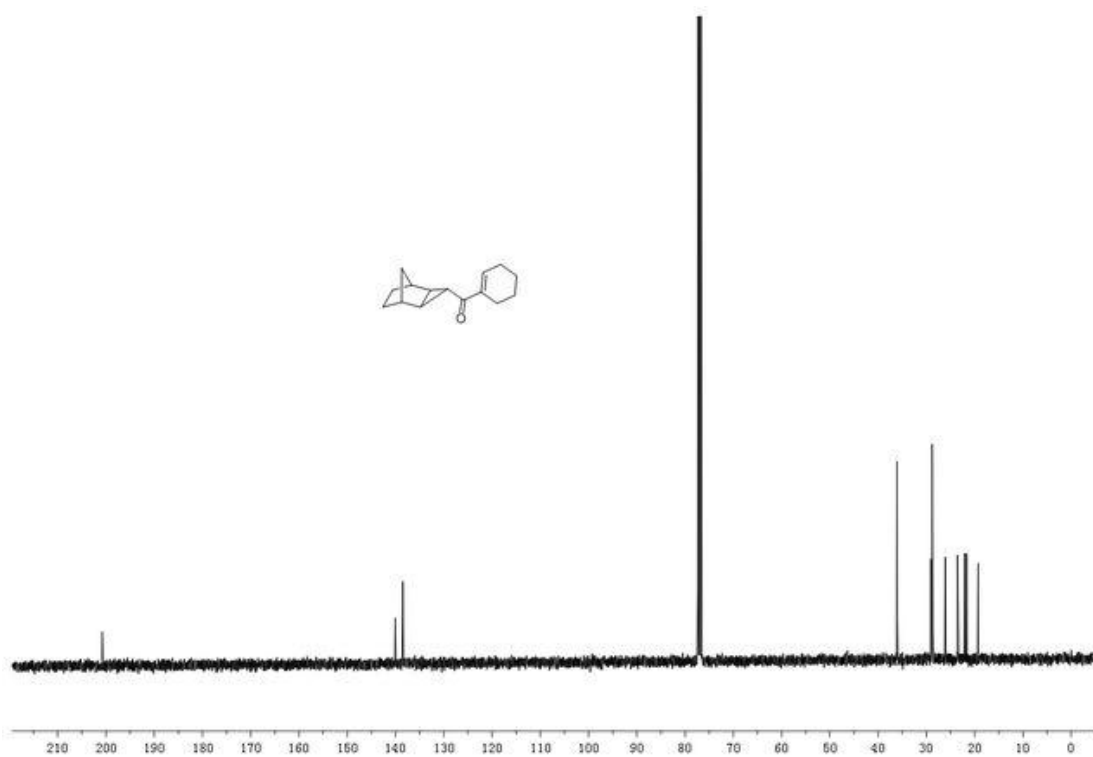
¹³C Spectrum for Compound 3e



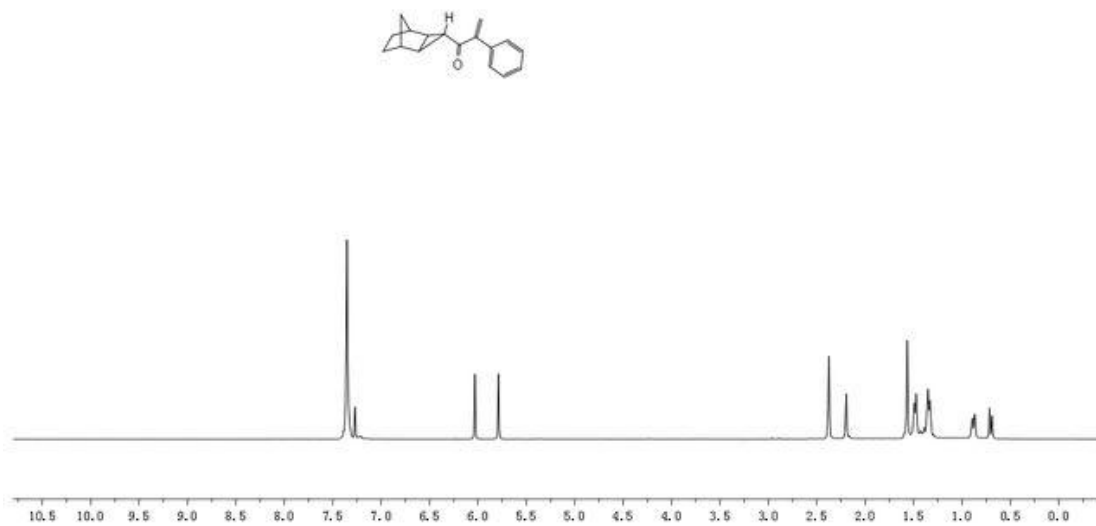
¹H Spectrum for Compound 3f



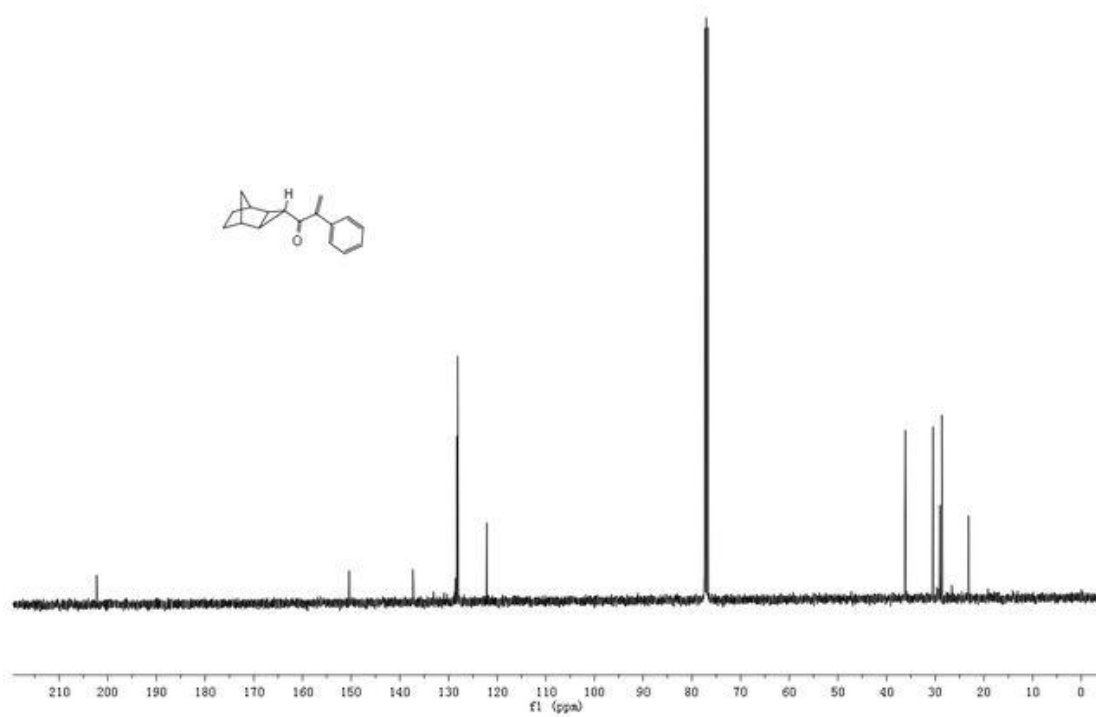
¹³C Spectrum for Compound 3f



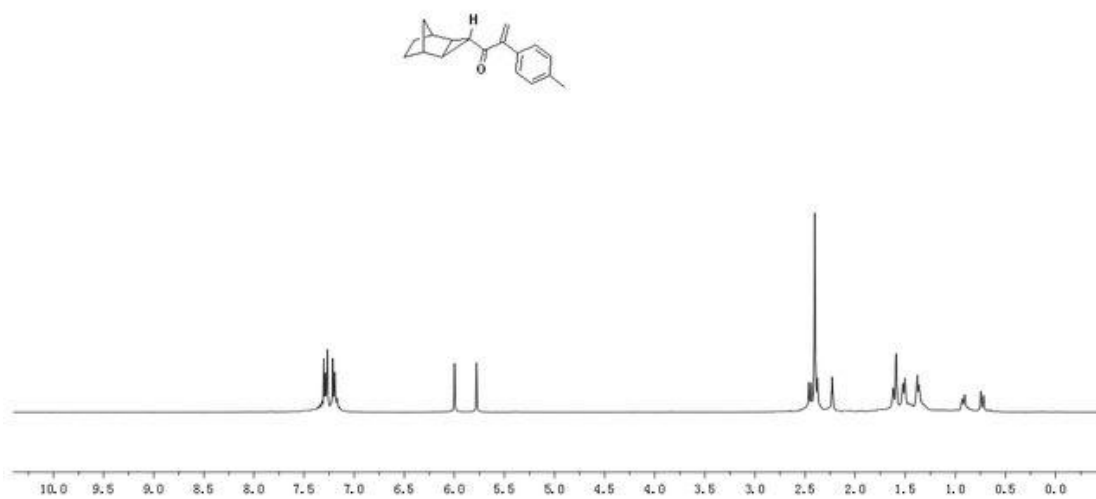
¹H Spectrum for Compound 3g



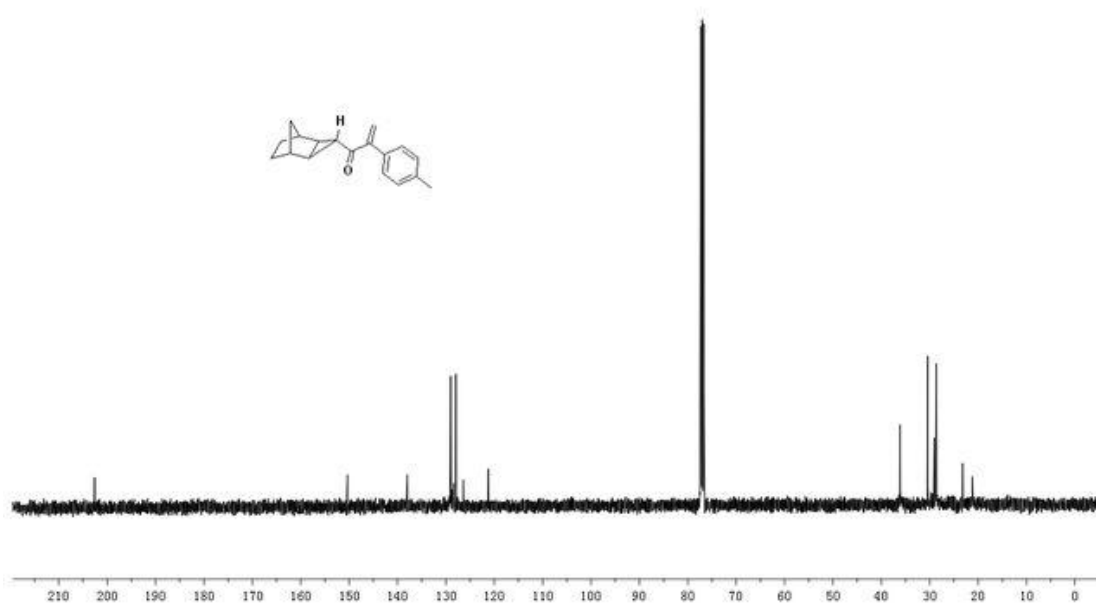
¹³C Spectrum for Compound 3g



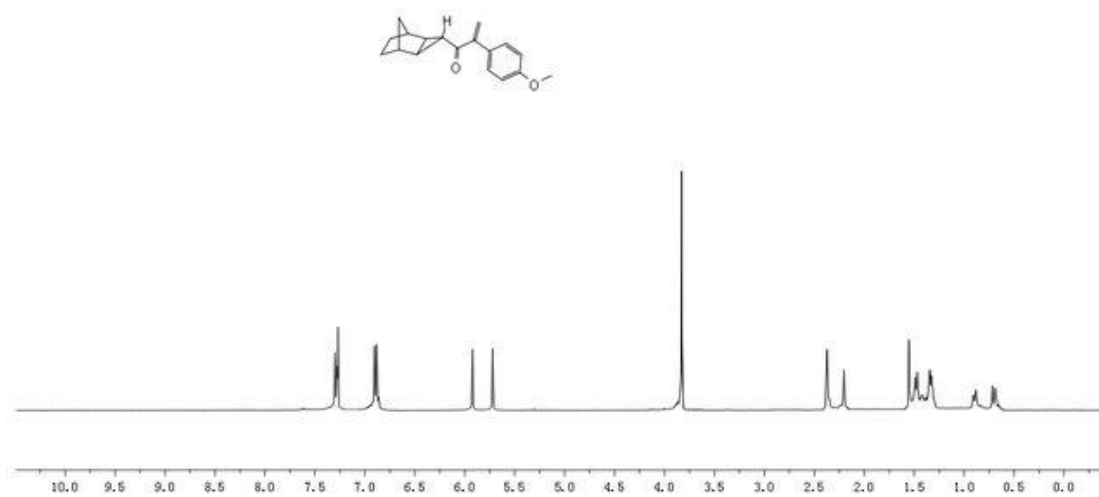
¹H Spectrum for Compound 3h



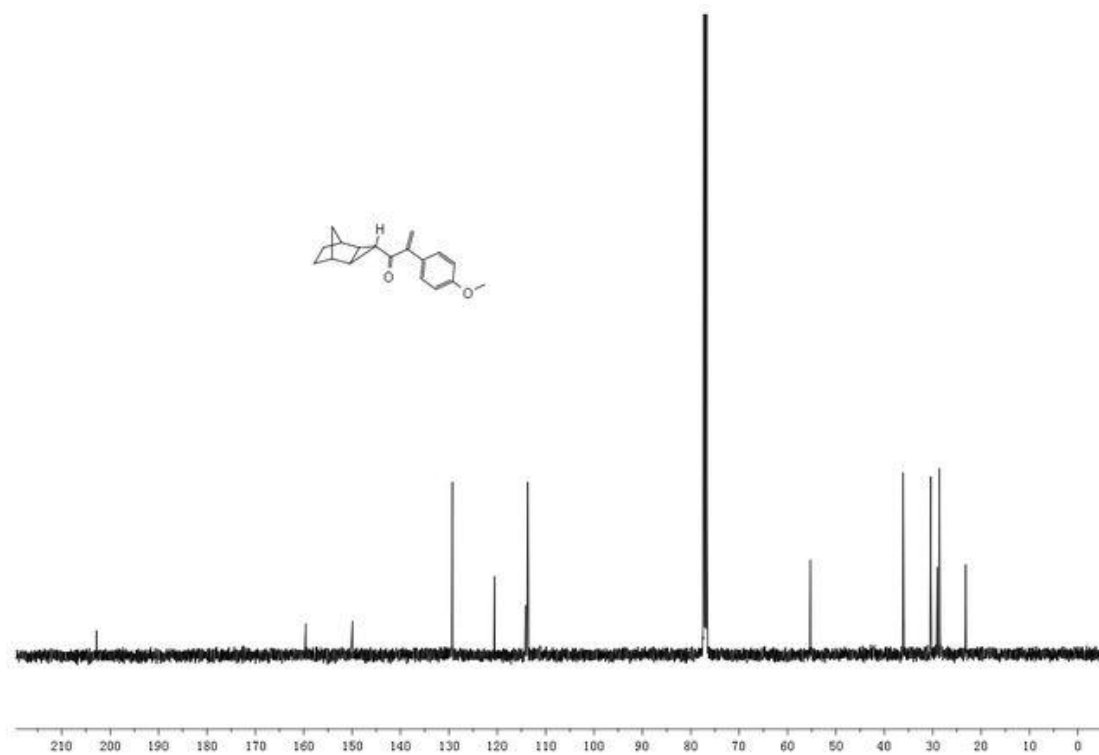
¹³C Spectrum for Compound 3h



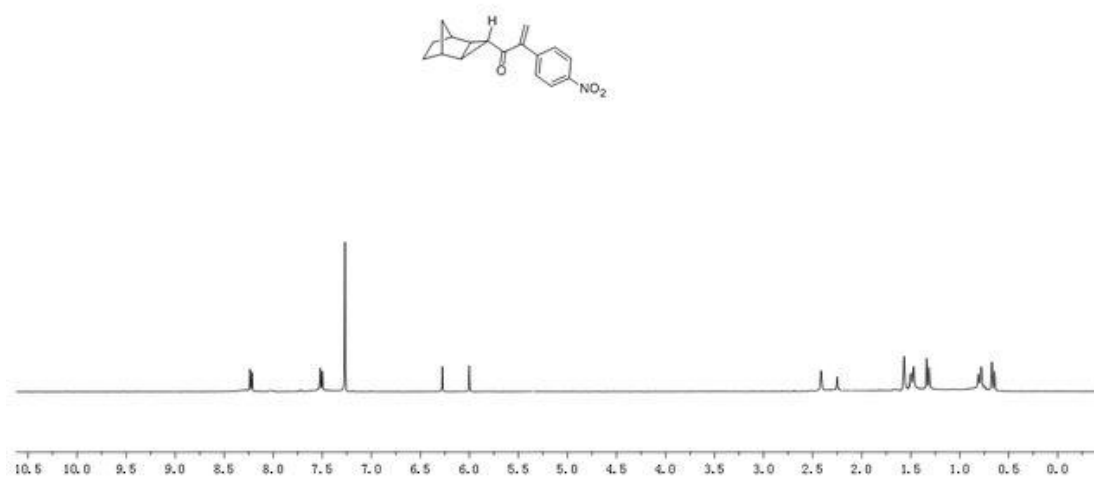
^1H Spectrum for Compound 3i



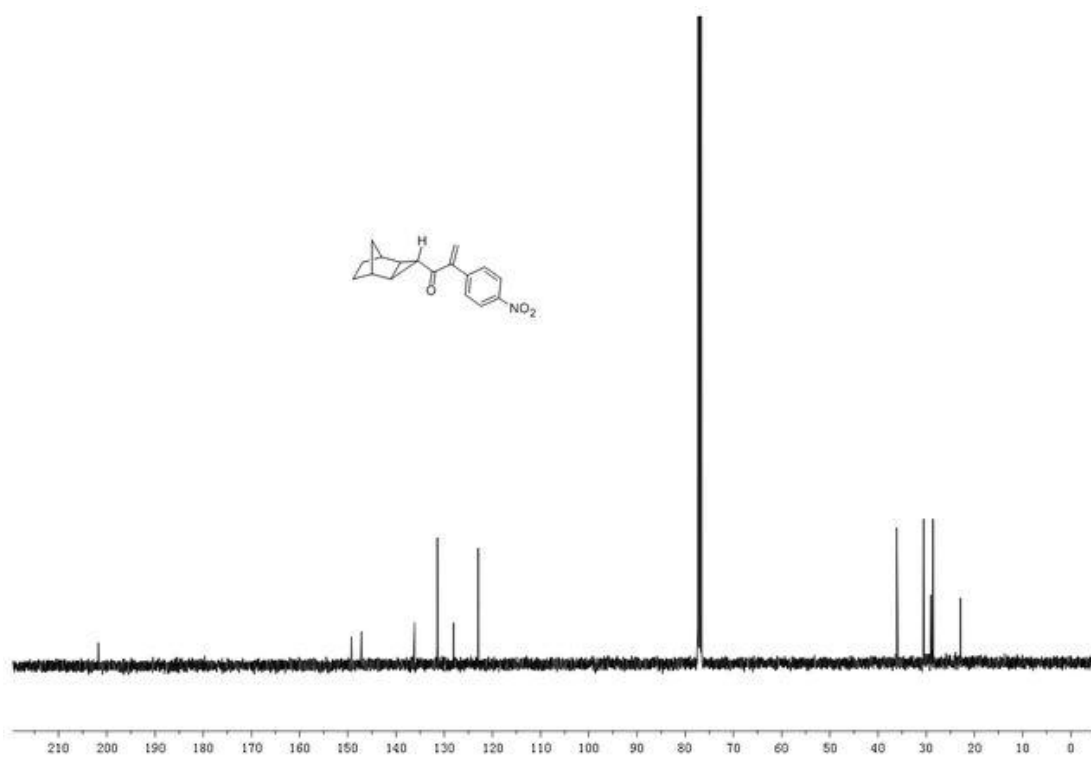
^{13}C Spectrum for Compound 3i



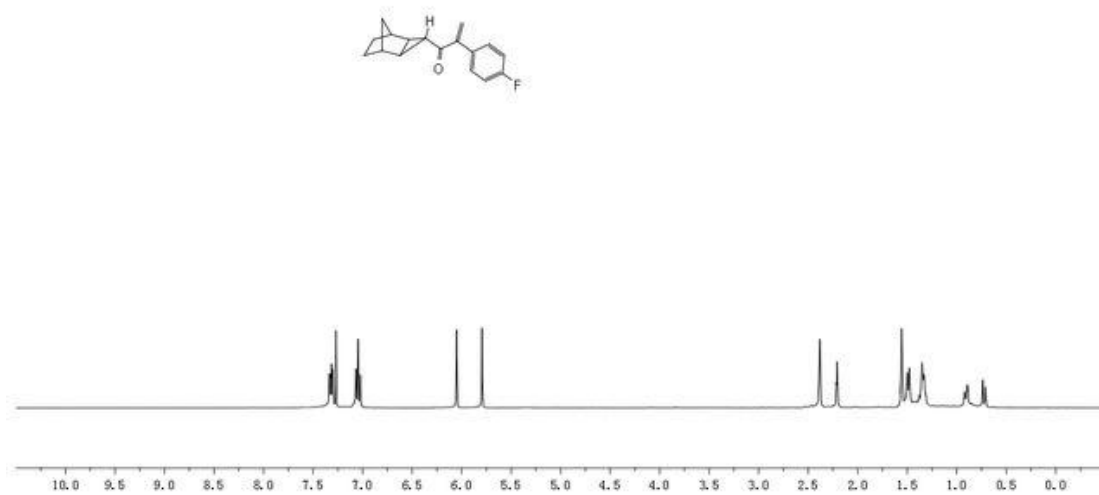
¹H Spectrum for Compound 3j



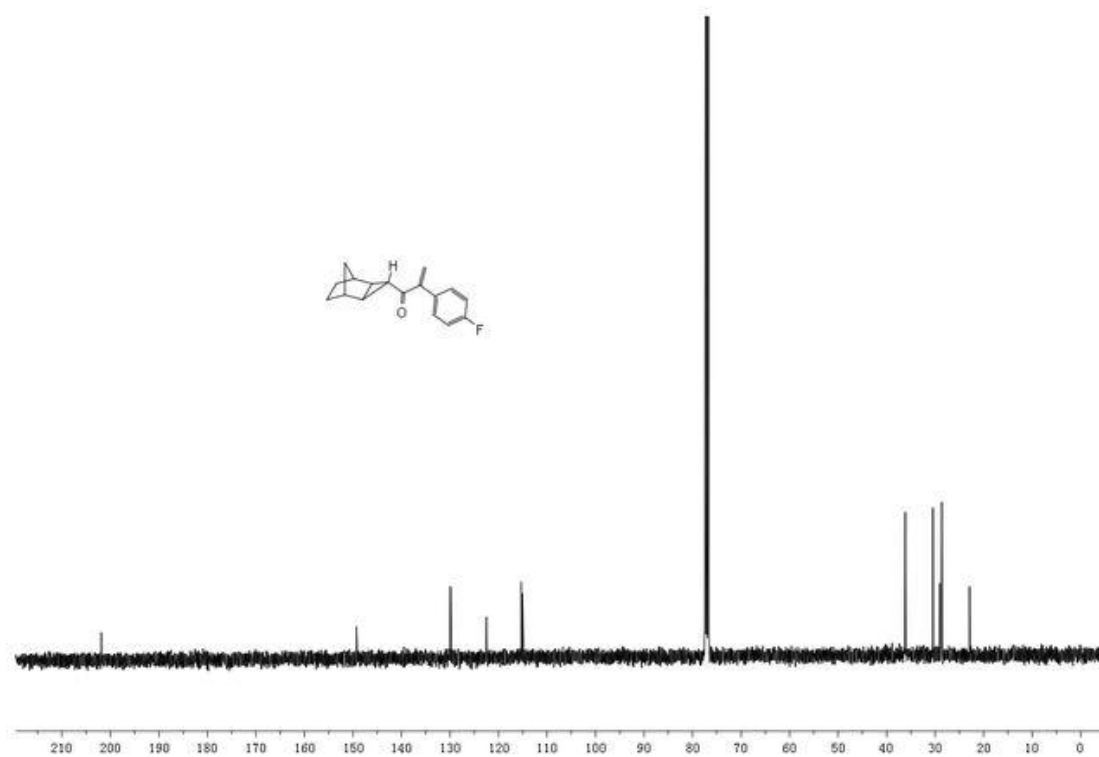
¹³C Spectrum for Compound 3j



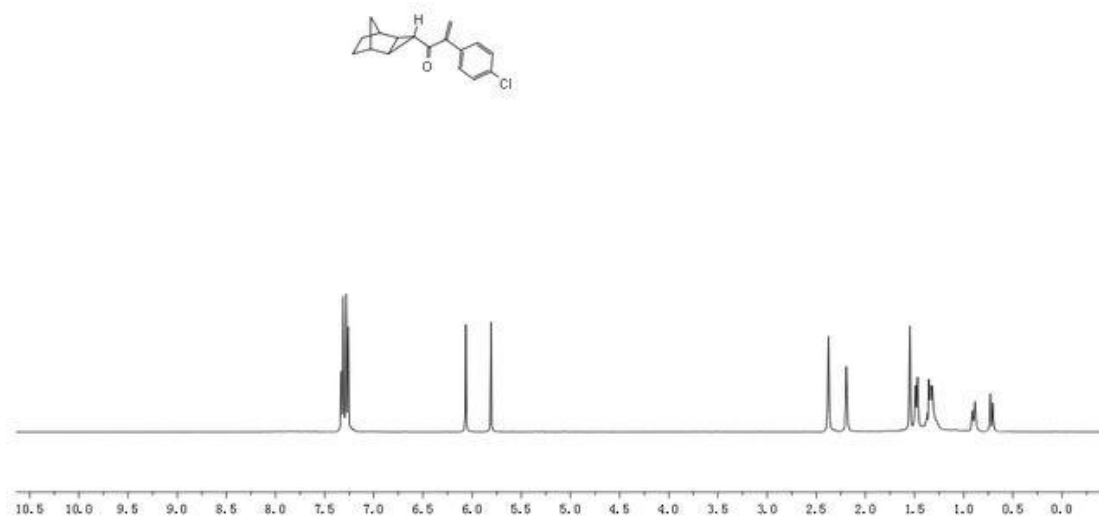
¹H Spectrum for Compound 3k



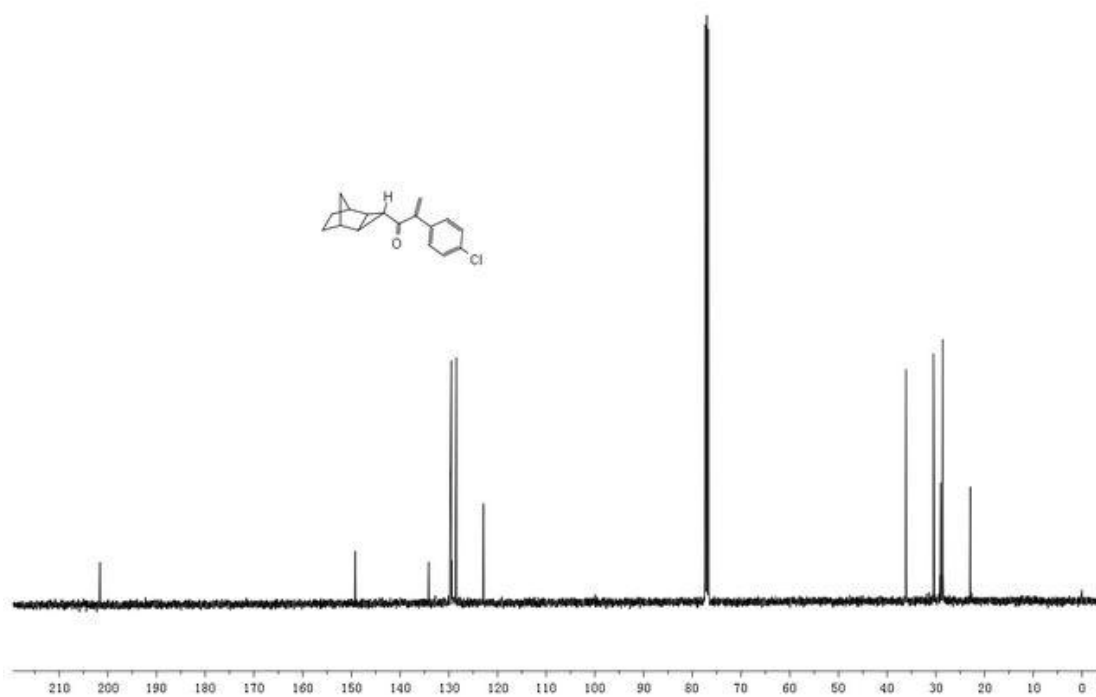
¹³C Spectrum for Compound 3k



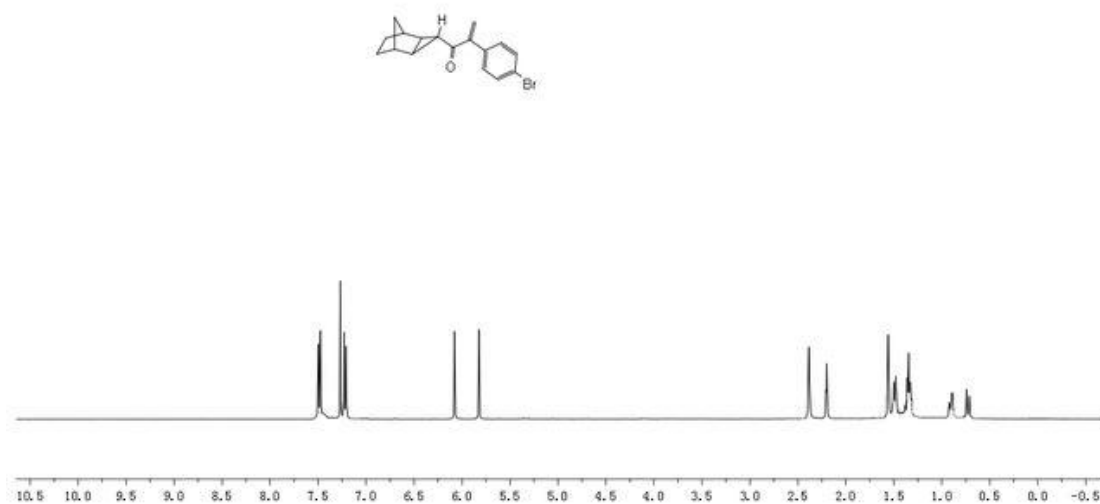
^1H Spectrum for Compound 3l



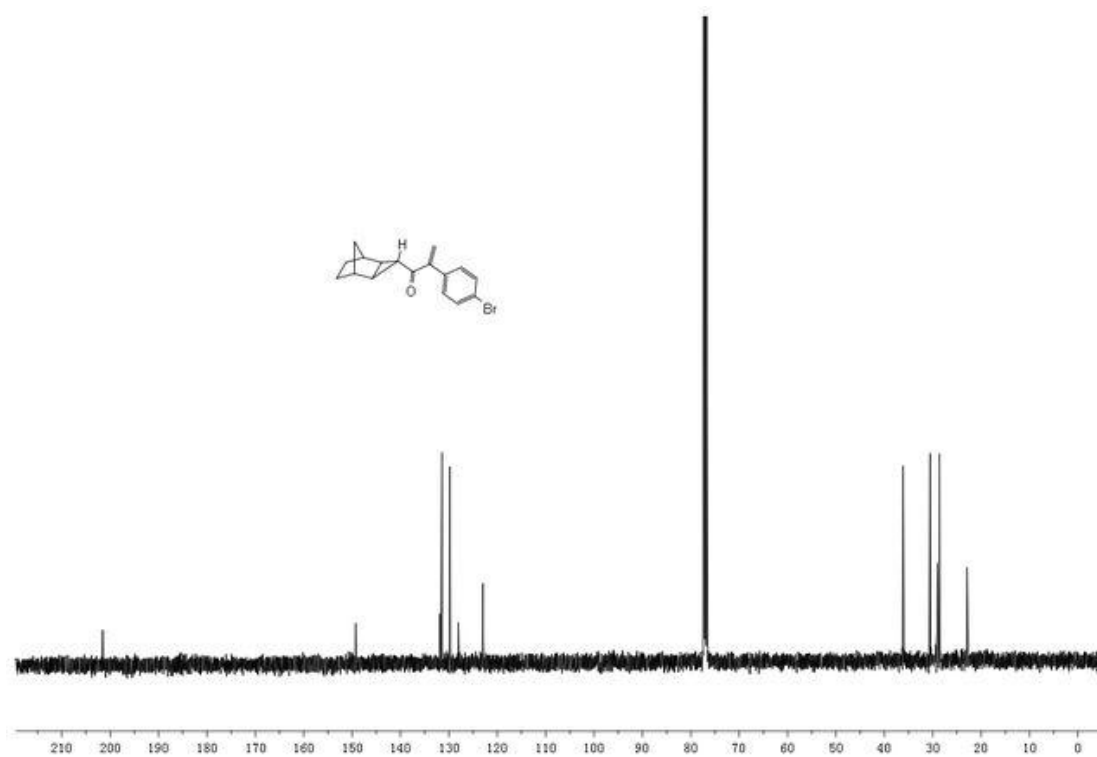
^{13}C Spectrum for Compound 3l



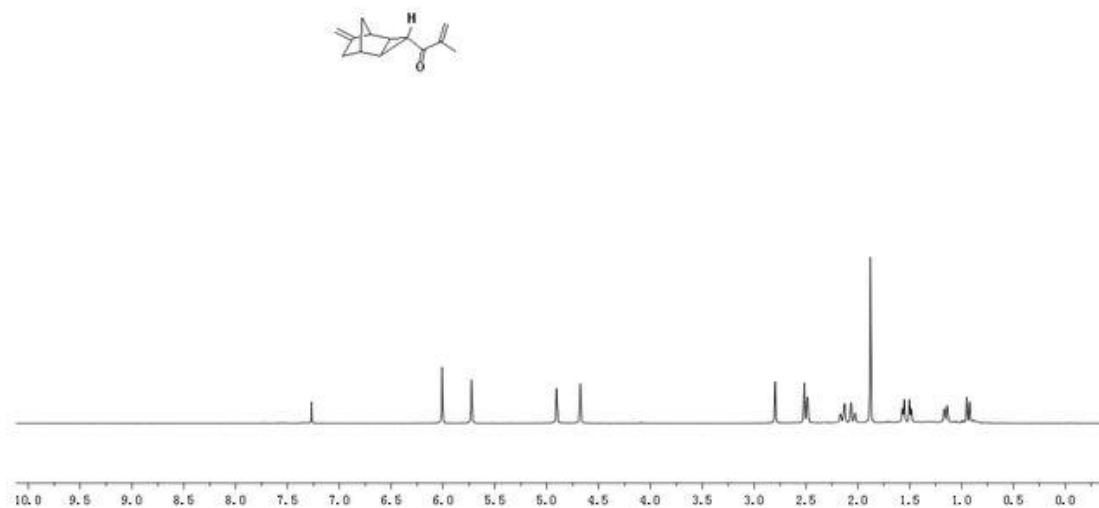
^1H Spectrum for Compound 3m



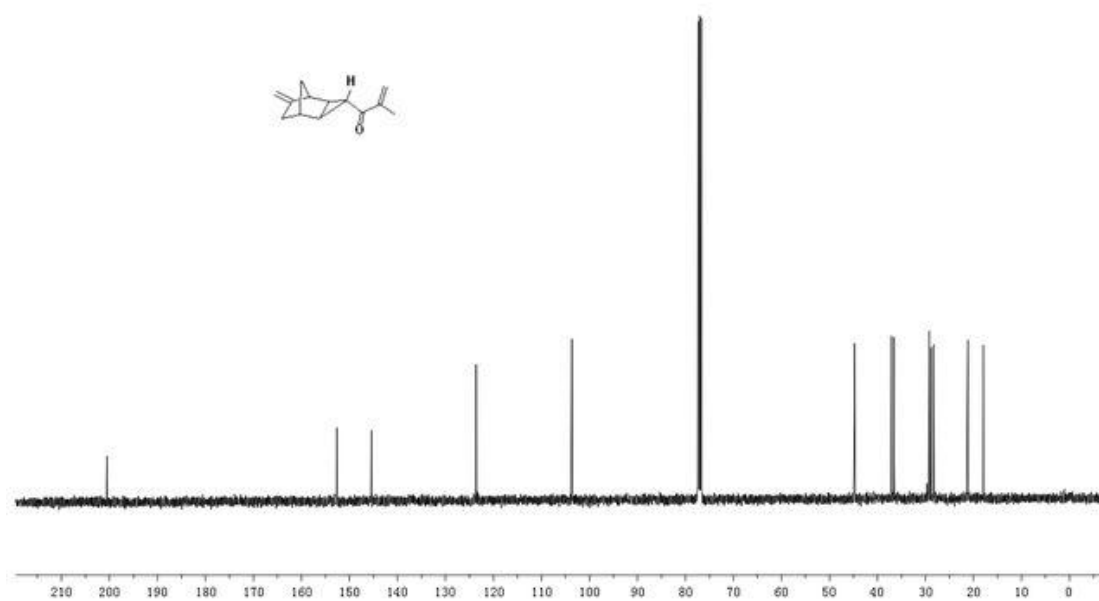
^{13}C Spectrum for Compound 3m



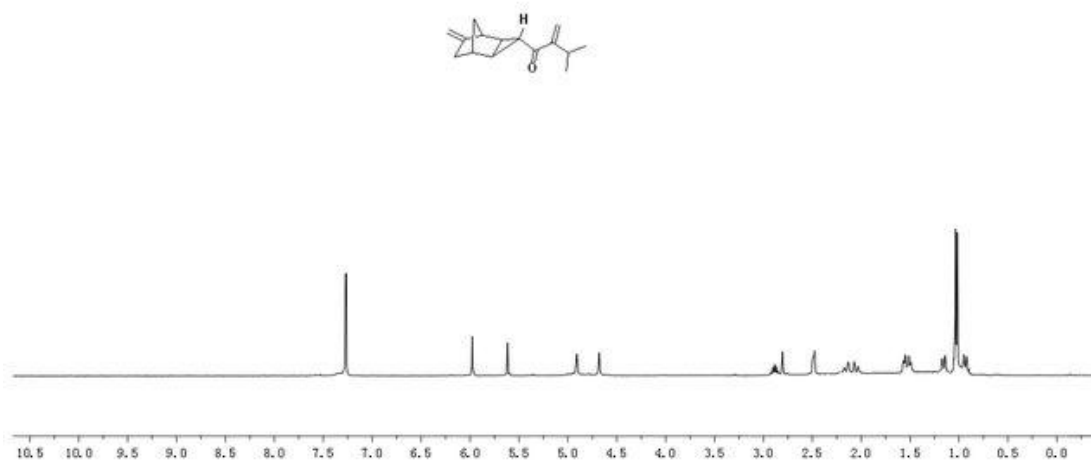
^1H Spectrum for Compound 3n



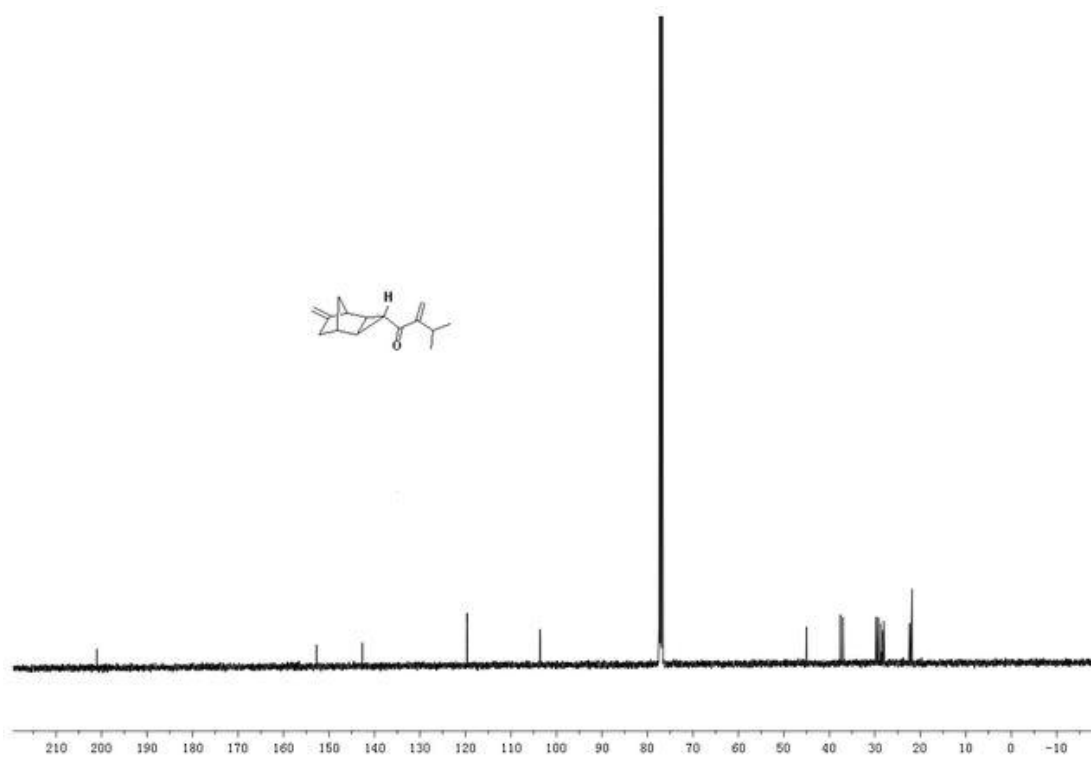
^{13}C Spectrum for Compound 3n



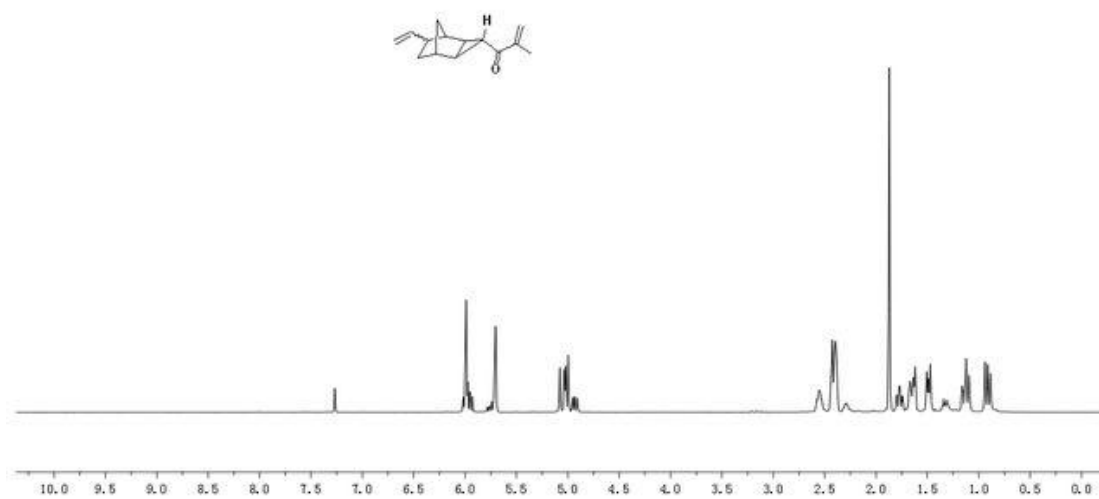
^1H Spectrum for Compound 3o



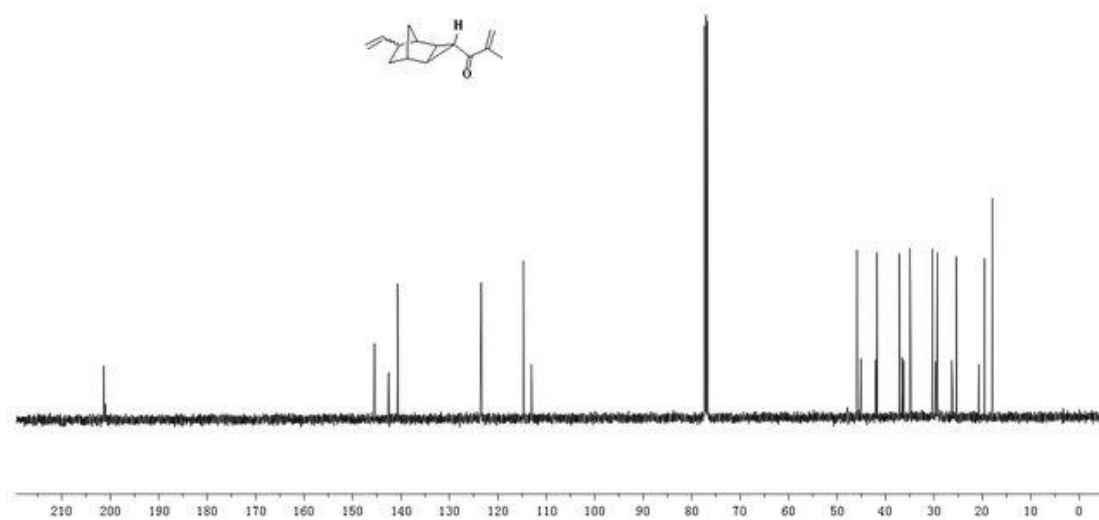
^{13}C Spectrum for Compound 3o



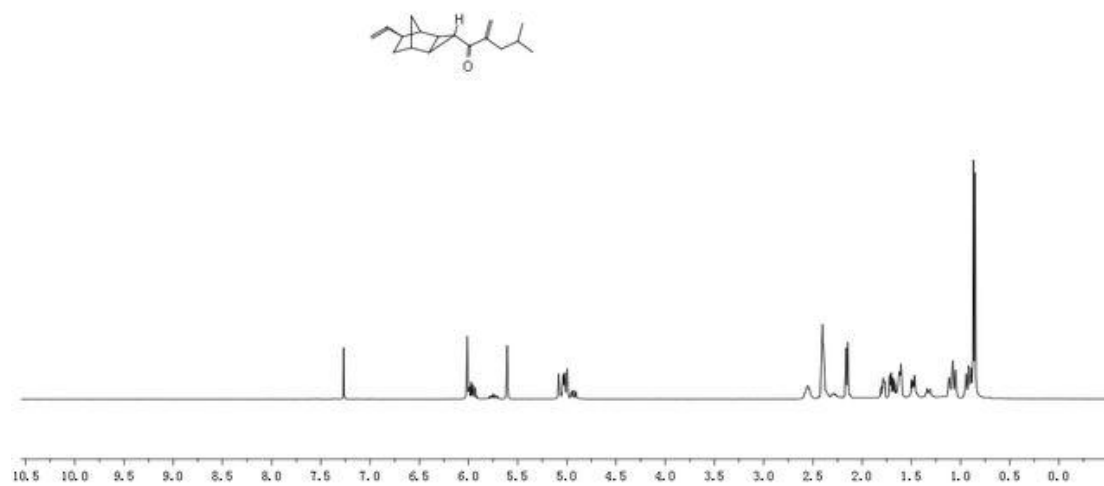
^1H Spectrum for Compound 3p



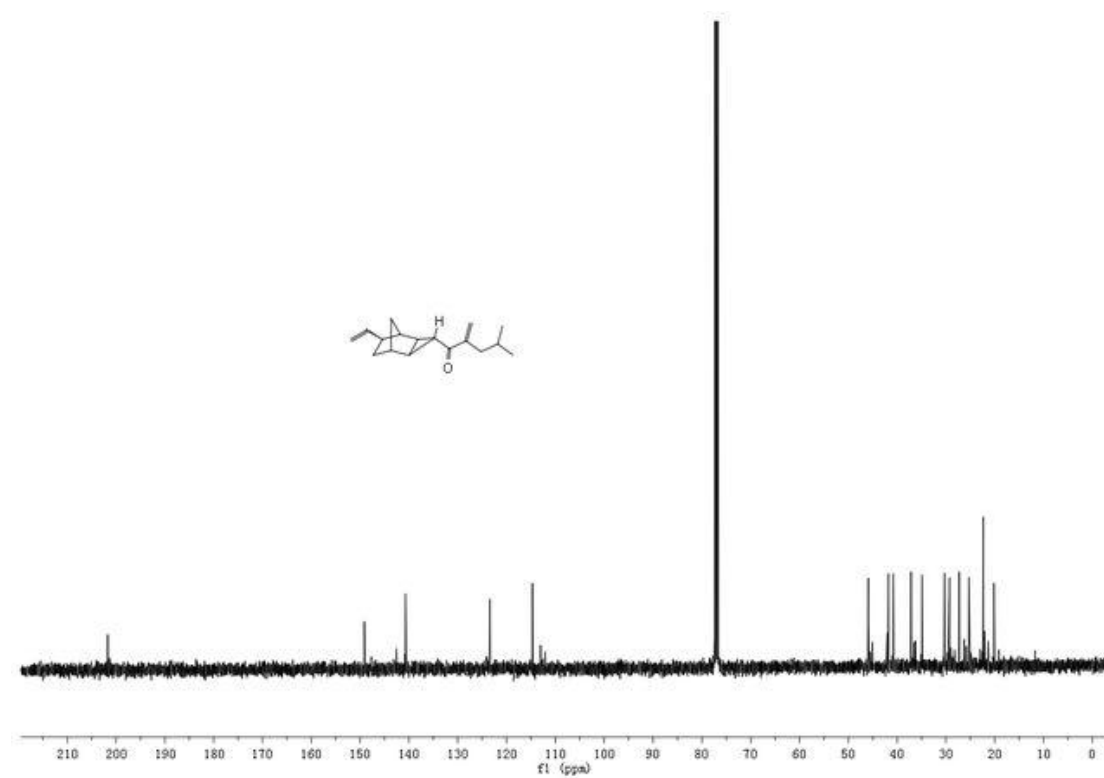
^{13}C Spectrum for Compound 3p



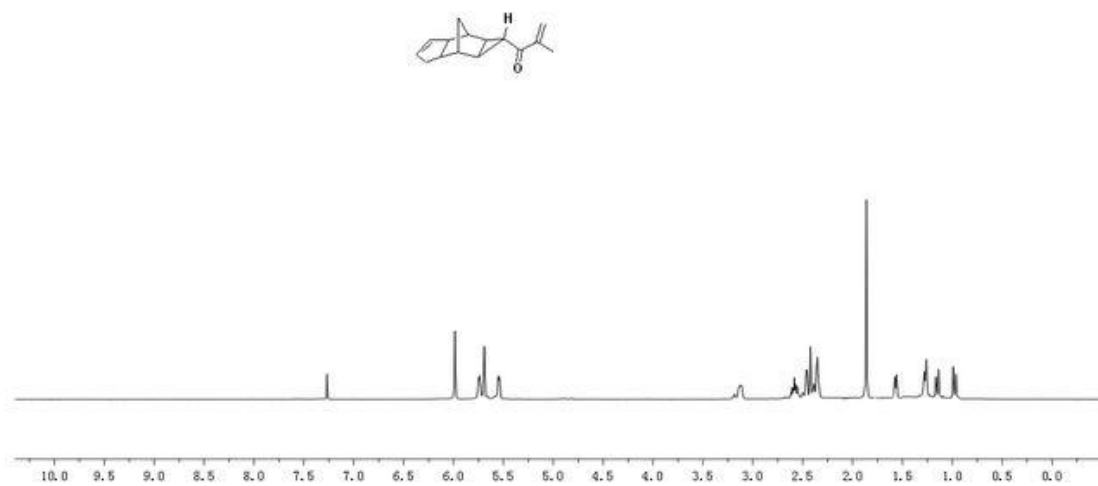
^1H Spectrum for Compound 3q



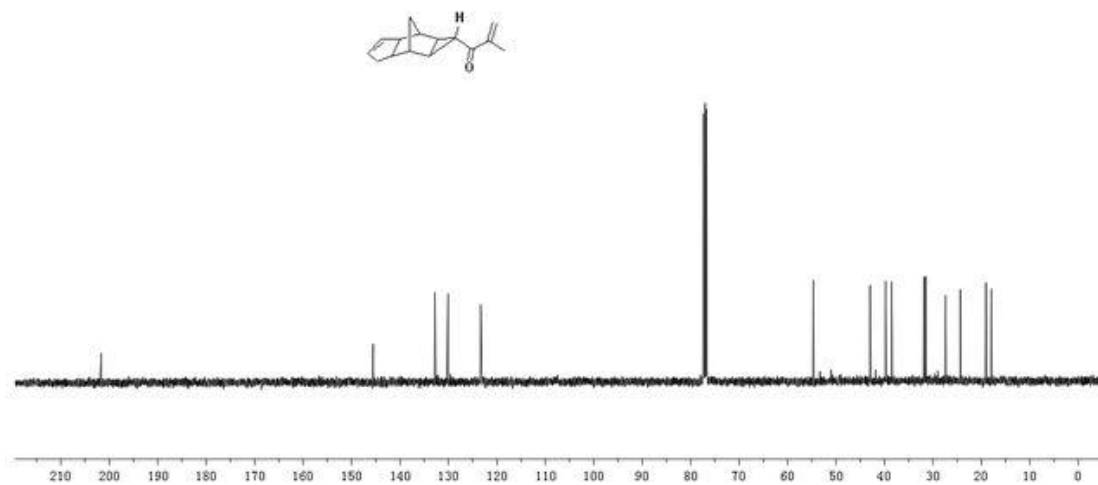
^{13}C Spectrum for Compound 3q



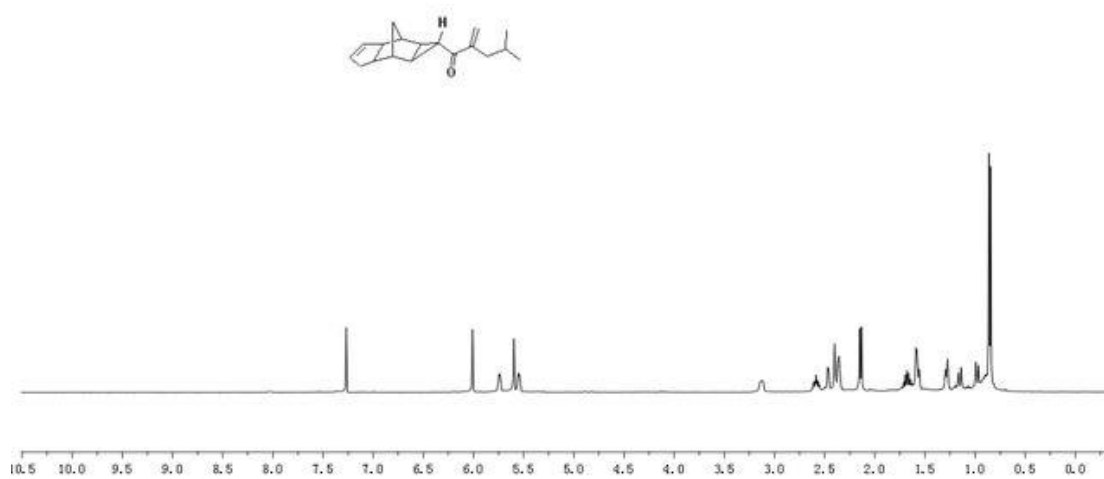
^1H Spectrum for Compound 3r



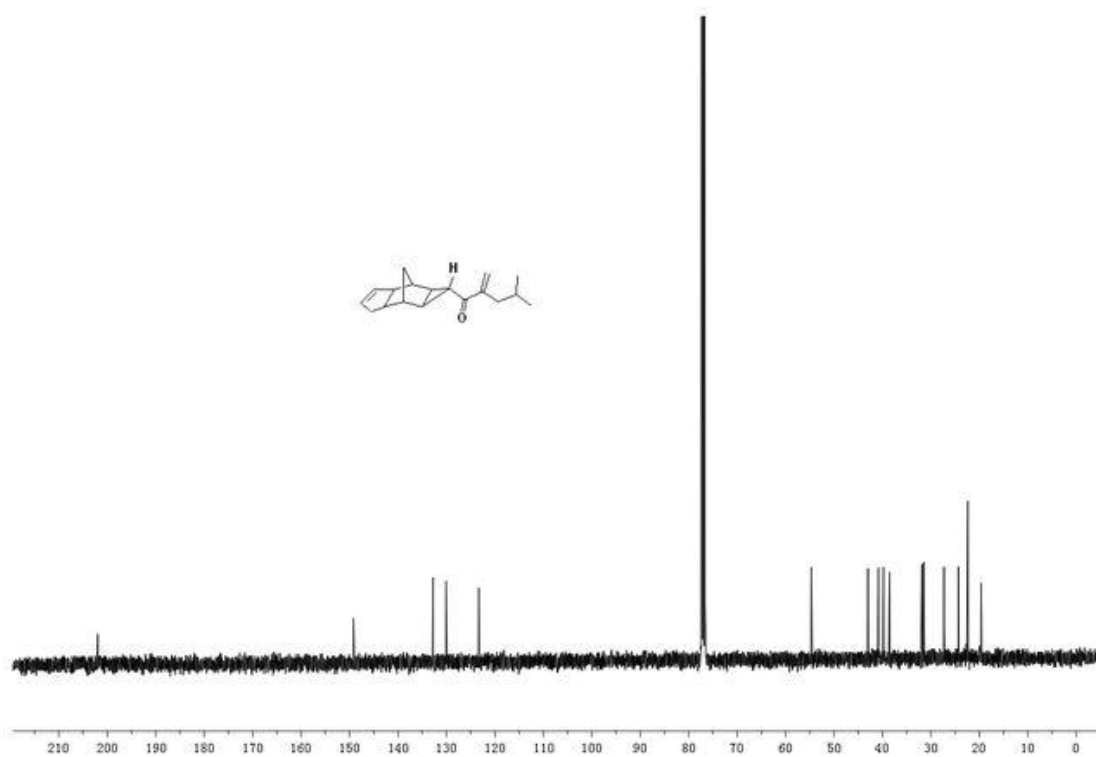
^{13}C Spectrum for Compound 3r



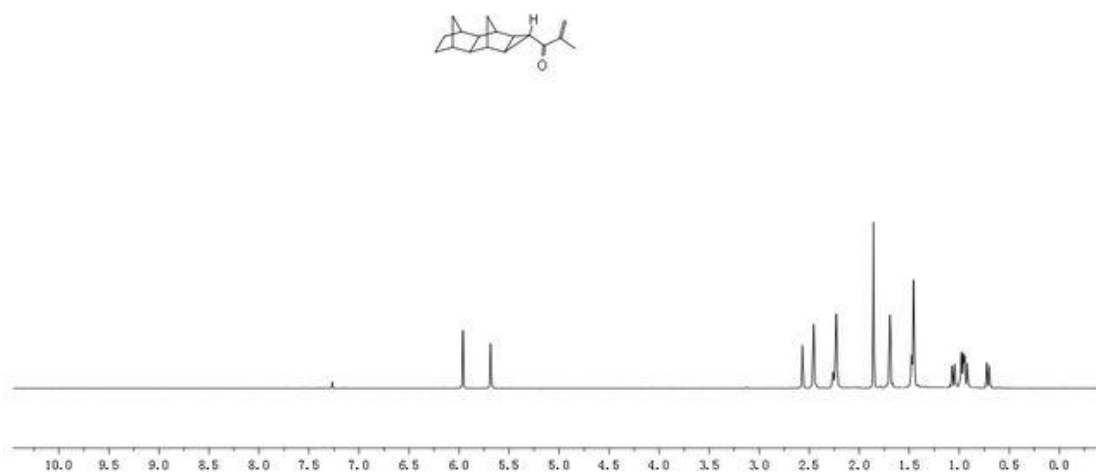
^1H Spectrum for Compound 3s



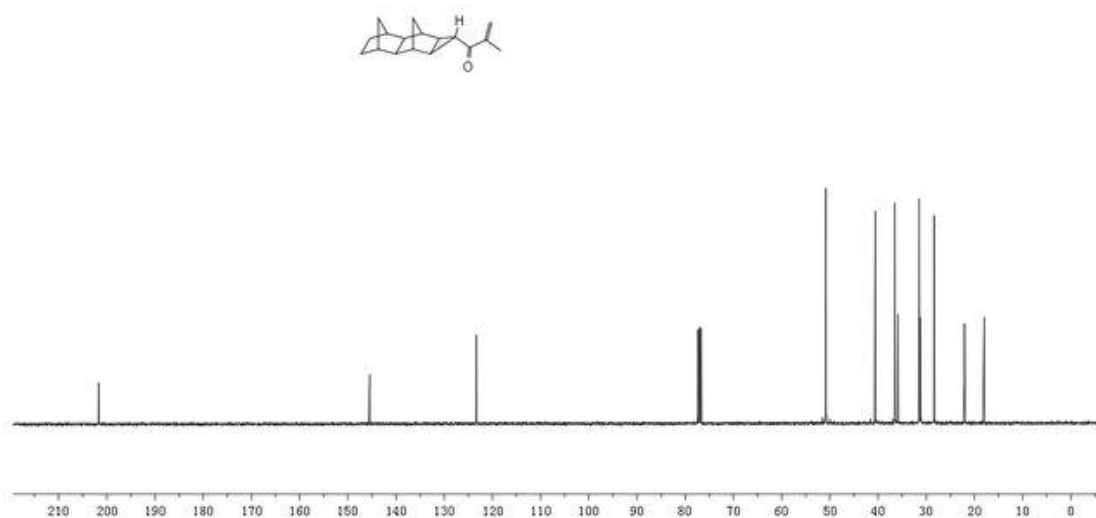
^{13}C Spectrum for Compound 3s



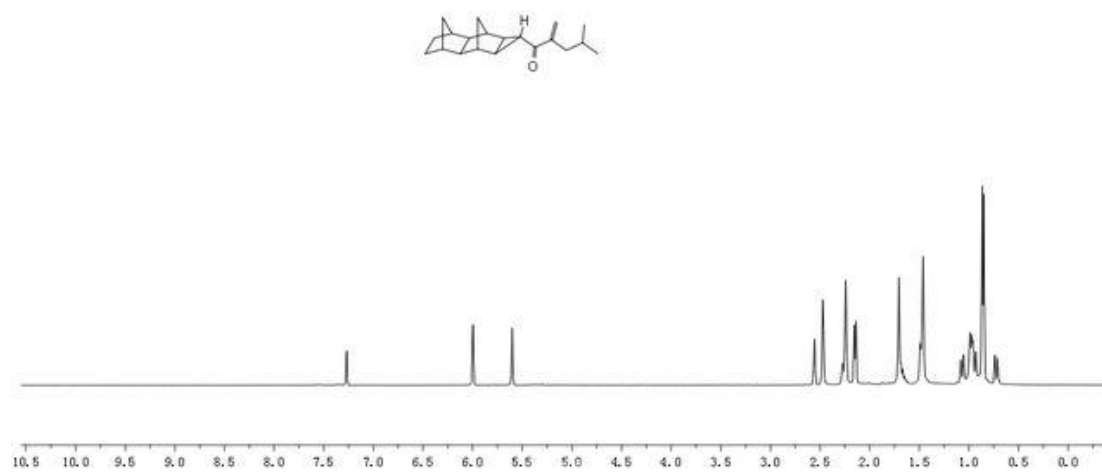
¹H Spectrum for Compound 3t



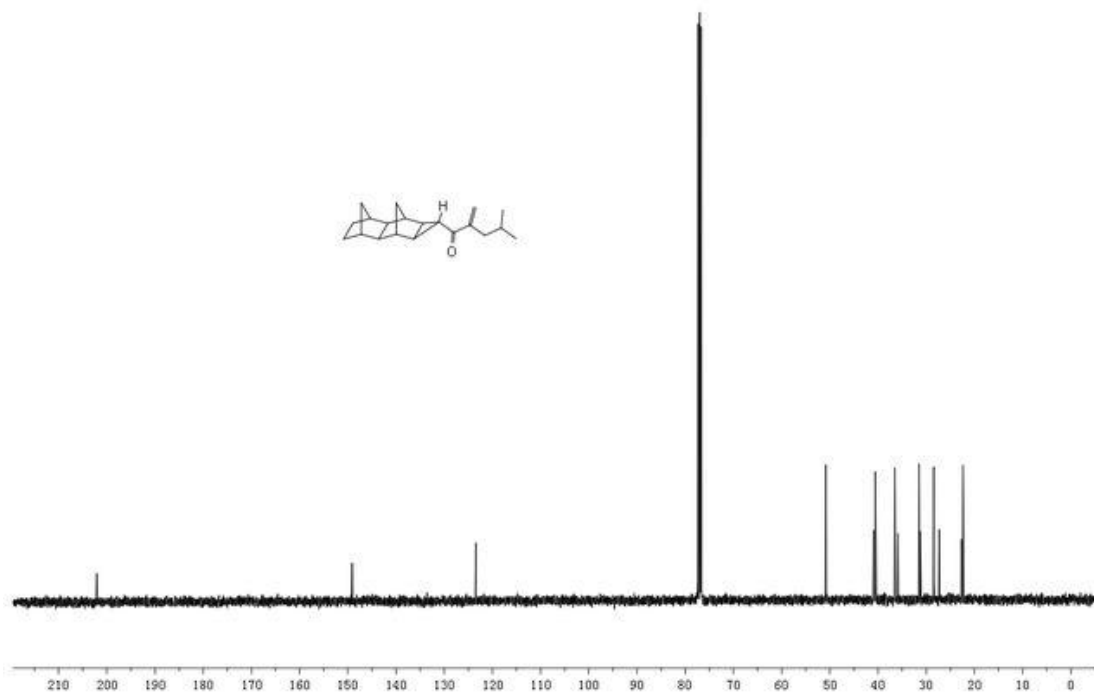
¹³C Spectrum for Compound 3t



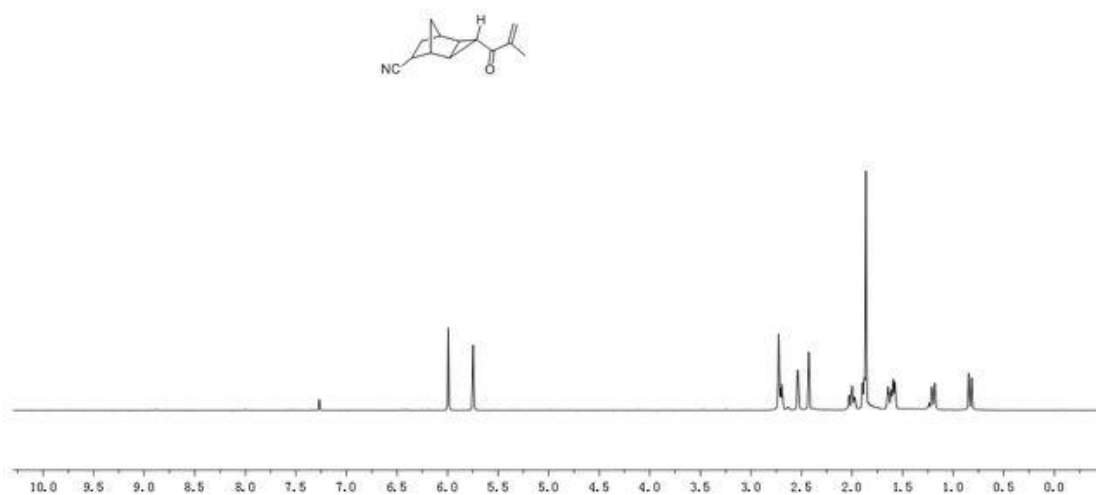
^1H Spectrum for Compound 3u



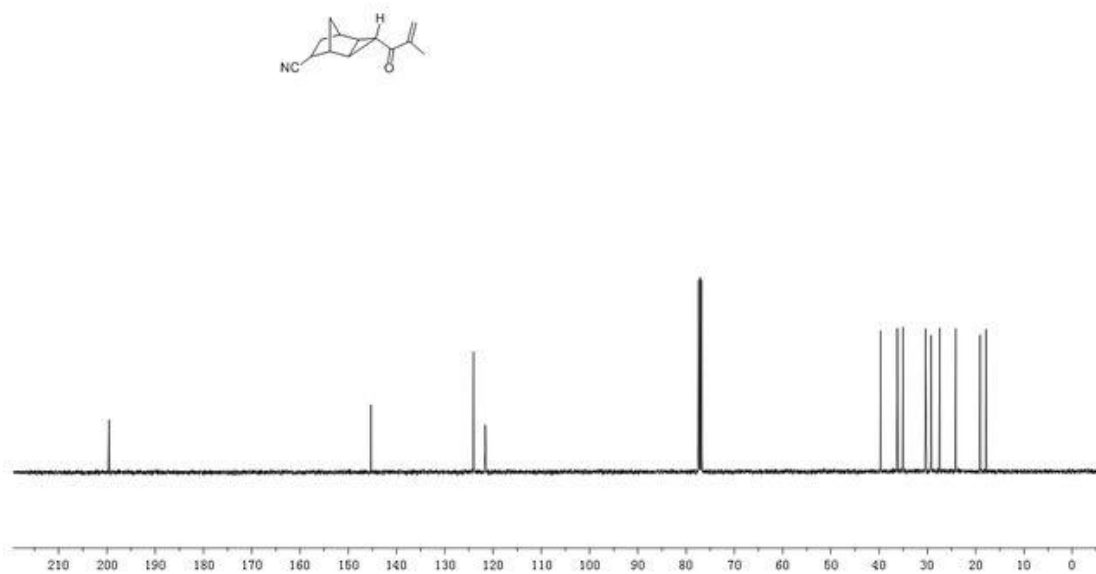
^{13}C Spectrum for Compound 3u



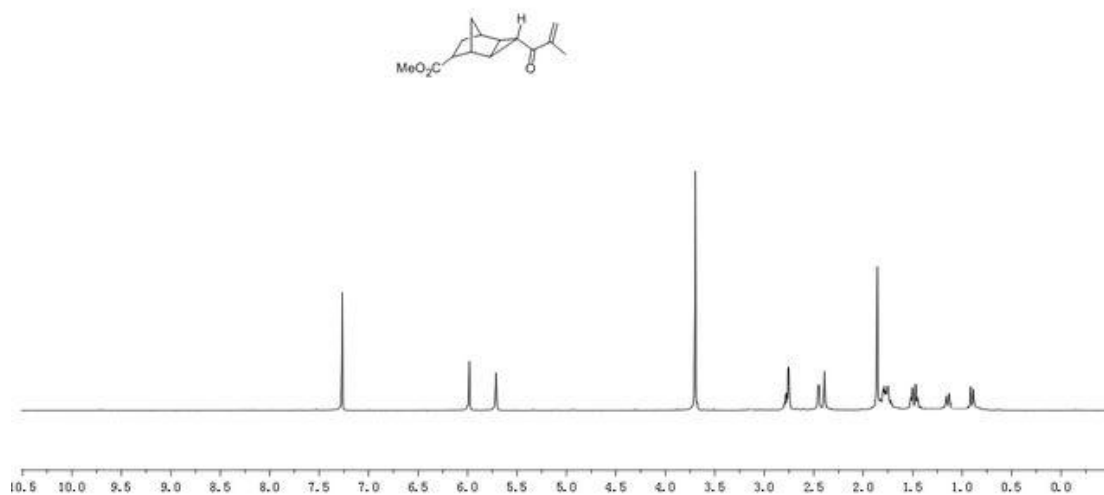
¹H Spectrum for Compound 3v



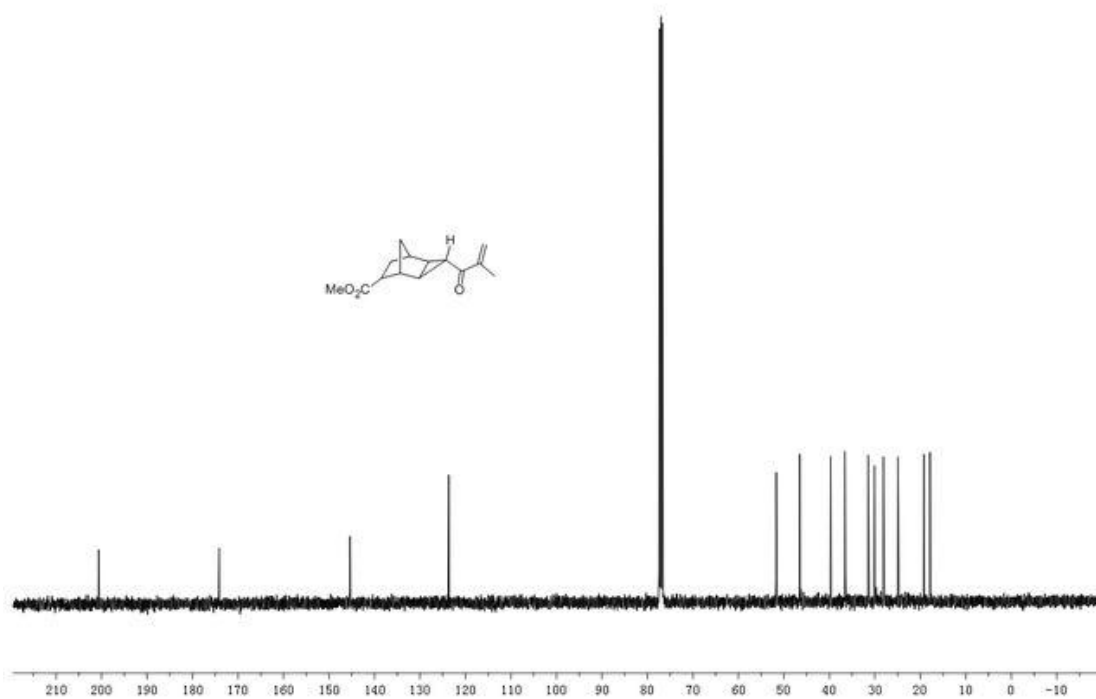
¹³C Spectrum for Compound 3v



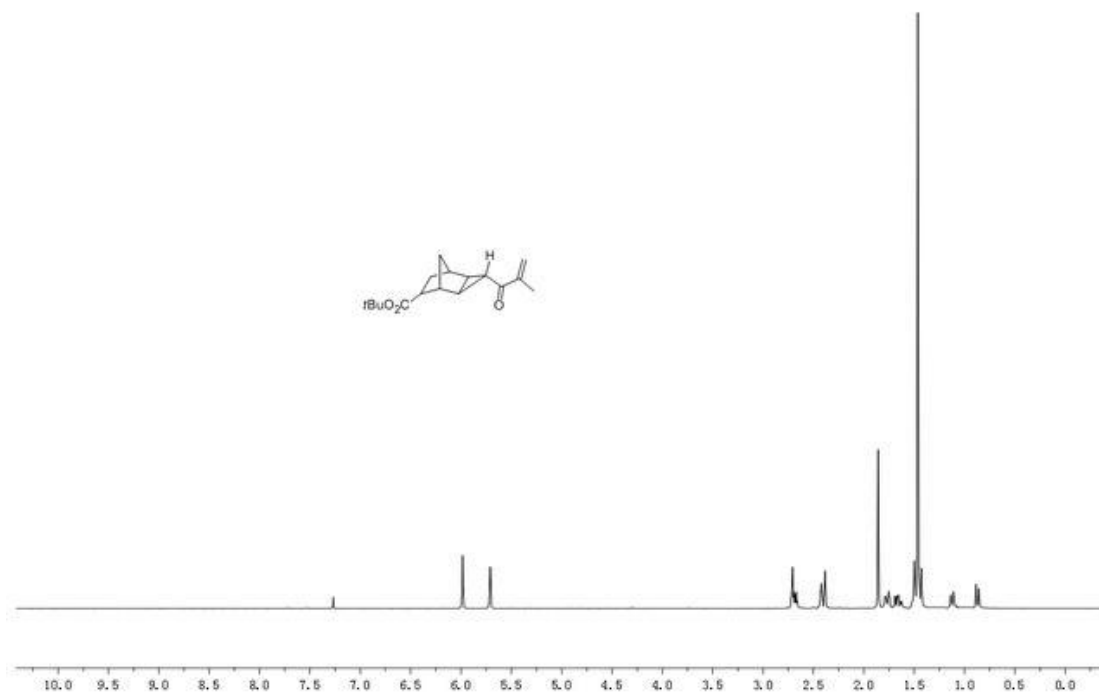
^1H Spectrum for Compound 3w



^{13}C Spectrum for Compound 3w



^1H Spectrum for Compound 3x



^{13}C Spectrum for Compound 3x

