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tert-Butyl Hypochlorite Mediated Diastereoselective Oxidative Coupling: Access to 1-Functionalized Tetrahydrocarbazoles

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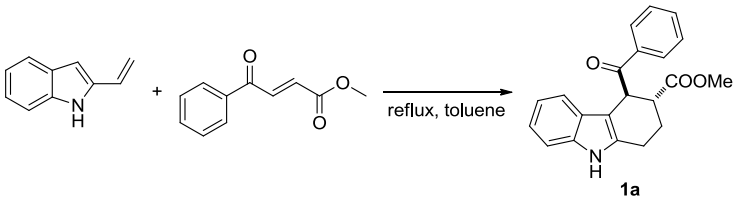
Supporting Information – Table of Contents

Materials and Methods

Unless stated otherwise, reactions were conducted in dry glassware using anhydrous solvents (passed through activated alumina columns). All commercially available reagents were used as received unless otherwise specified. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 ℃). Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 400 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra are reported in terms of chemical shift. High resolution mass spectra were obtained from the Tsinghua University Mass Spectrometry Facility.

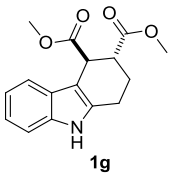
Experimental Procedures

A. Substrates preparation using thermal Diels-Alder reaction



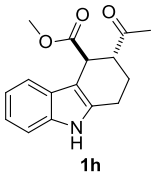
1a

General procedure: a solution of 2-vinyl indole (1.43 g, 10 mmol) and the α, β-unsaturated ketone (1.90 g, 10 mmol) in toluene (5.0 mL) was heated to 120 ^{o}C in a sealed pressure tube and stirred for overnight. After cooled to room temperature, the reaction mixture was purified directly by silica gel column (ethyl acetate/petroleum ether =1/3) to afford the desired product **1a** (1.90 g, 57% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.21 (d, *J*=7.7, 2H), 8.03 (s, 1H), 7.66 (t, *J*=7.3, 1H), 7.56 (t, *J*=7.7, 2H), 7.20 (d, *J*=8.1, 1H), 7.04 (t, *J*=7.0, 1H), 6.91-6.84 (m, 2H), 5.36 (d, *J*=7.1, 1H), 3.60 (s, 3H), 3.34-3.30 (m, 1H), 2.82-2.74 (m, 2H), 2.36-2.29 (m, 1H), 2.20-2.10(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 202.3, 174.3, 137.5, 136.1, 134.9, 133.4, 129.0, 126.5, 121.5, 119.6, 118.3, 110.8, 107.1, 52.1, 44.2, 43.2, 24.1, 21.6. IR (film): 3388, 2949, 1740, 1671, 743. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{21}H_{20}NO_3$, 334.1443; found, 334.1446.



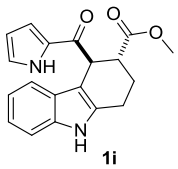
1g

The reaction was purified by silica gel column (ethyl acetate/petroleum ether =1/3) to afford the desired product **1g** (1.10 g, 40% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (s, 1H), 7.57 (d, *J*=7.6, 2H), 7.15-7.07 (m, 2H), 4.32 (d, *J*=6.6, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.37-3.32 (m, 1H), 2.81 (t, *J*=6.4, 2H), 2.43-2.36 (m, 1H), 2.20-2.11(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.5, 174.2, 136.0, 134.4, 126.9, 121.7, 119.8, 118.8, 110.7, 105.8, 52.6, 42.7, 41.6, 23.6, 21.5. IR (film):3377, 1731, 751. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{16}H_{18}NO_4$, 288.1236; found, 288.1222.



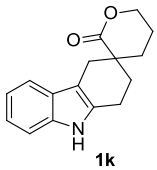
1h

The reaction was purified by silica gel column (ethyl acetate/petroleum ether =1/3) to give the desired product **1h** (2.30 g, 84% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (s, 1H), 7.41 (d, *J*=7.7, 1H), 7.27 (d, *J*=7.6, 1H), 7.14 (t, *J*=7.1, 1H), 7.09 (t, *J*=7.5, 2H), 4.24 (d, *J*=6.5, 1H), 3.68 (s, 3H), 3.28-3.24 (m, 1H), 2.90-2.75 (m, 2H), 2.27-2.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.8, 174.2, 136.1, 134.5, 126.7, 121.6, 119.8, 118.2, 110.8, 105.9, 52.1, 49.9, 42.3, 28.1, 23.3, 21.2. IR (film): 3357, 2923, 1738, 1686, 743. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{16}H_{18}NO_3$, 272.1287; found, 272.1285.



1i

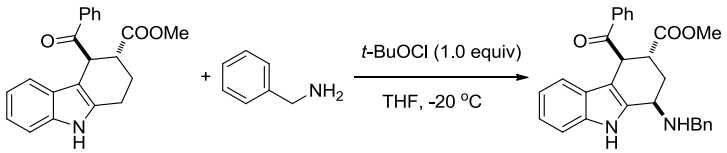
The reaction was purified by silica gel column (ethyl acetate/petroleum ether =1/3) to give the desired product **1i** (2.51 g, 78% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): 9.67 (s, 1H), 7.96 (s, 1H), 7.24-7.20 (m, 2H), 7.07-7.00 (m, 3H), 7.89 (t, *J*=7.4, 1H), 6.35-6.34 (m, 1H), 5.01 (d, *J*=7.4, 1H), 3.59 (s, 3H), 3.28-3.23 (m, 1H), 2.79 (t, *J*=6.1, 2H), 2.36-2.30 (m, 1H), 2.20-2.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.6, 174.5, 136.1, 134.9, 132.3, 126.6, 125.8, 121.5, 119.6, 118.5, 117.6, 111.2, 110.8,107.2, 52.0, 44.6, 43.9, 24.5, 21.7. IR (film): 3314, 2950, 1716, 1629, 741. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_3$, 323.1396; found, 323.1400.



1k

The reaction was purified by silica gel column (ethyl acetate/petroleum ether =1/3) to give the desired product **1k** (2.40 g, 95% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (s, 1H), 7.32 (d, *J*=7.3, 1H), 7.19 (d, *J*=7.8, 1H), 7.10-7.03 (m, 2H), 4.66-4.60 (m, 2H), 2.59-2.44 (m, 2H), 2.41-2.34 (m, 1H), 2.28-2.21 (m, 1H), 2.18-2.07 (m, 2H), 2.04-1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 176.6, 136.0, 135.3, 125.3, 121.2, 119.5, 117.8, 112.6, 111.2, 70.9, 43.3, 34.4, 33.0, 22.6, 21.1, 18.8. IR (film): 3270, 2943, 1713, 745. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{16}H_{18}NO_2$, 256.1338; found, 256.1328.

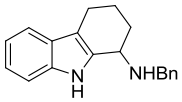
B. General procedure for the *tert*-butyl hypochlorite mediated oxidative coupling



1a **2a** **3a**

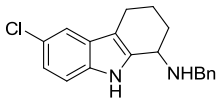
To a solution of **1a** (50.0 mg, 0.15 mmol) in THF (1.0 mL) at -20 ^{o}C was added *t*-BuOCl (16.2 mg, 0.15 mmol) dropwisely. After being stirred at -20 ^{o}C for 10 min, benzyl amine (**2a)** (48.0 mg, 0.45 mmol) was added. The resulting mixture was stirred at -20 ^{o}C for additional 2 hours and then quenched by the addition of aqueous sodium bicarbonate (5 mL). After warmed to room temperature, the reaction mixture was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (dichloromethane/methanol=50:1) to yield the desired product **3a** (53.3 mg, 81% yield) as a light yellow solid. ^{1}H NMR

(400 MHz, $CDCl_3$): 8.42 (s, 1H), 8.23 (d, *J*=7.7, 2H), 7.67 (t, *J*=7.2, 1H), 7.57 (t, *J*=7.7, 2H), 7.45-7.28 (m, 5H), 7.24 (d, *J*=8.1, 1H), 5.42 (d, *J*=5.3, 2H), 4.13 (t, *J*=5.7, 1H), 3.99 (dd, *J*=13.2, 48.2, 2H), 3.65 (s, 3H), 3,52-3.47 (m, 1H), 2.49-2.42 (m, 1H), 2.27-2.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 201.3, 174.0, 140.5, 137.0, 136.9, 136.2, 133.5, 129.0, 128.9, 128.6, 128.3, 127.2, 126.4, 122.1, 119.6, 118.7, 111.2, 107.8, 52.3, 50.6, 48.8, 42.6, 41.9, 29.5. IR (film): 3365, 1705, 1594, 740 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_3$, 439.2022; found, 439.2022.



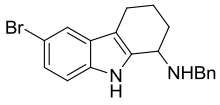
3b

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3b** (79.1 mg, 98% yield) as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$): 8.28 (s, 1H), 7.49 (d, *J*=7.7, 1H), 7.43 (d, *J*=7.4, 2H), 7.38 (t, *J*=7.7, 2H), 7.32-7.28 (m, 2H), 7.15 (t, *J*=7.2, 1H), 7.09 (t, *J*=7.7, 1H), 4.05-3.87 (m, 3H), 2.78-2.68 (m, 2H), 2.37-3.31 (m, 1H), 2.13-2.07 (m, 1H), 1.88-1.77 (m, 1H), 1.75-1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.8, 136.2, 135.9, 128.6, 128.2, 127.7, 127.2, 121.6, 119.2, 118.4, 111.4, 110.9, 52.0, 50.5, 30.6, 21.9, 21.1. IR (film): 3185, 2920, 2852, 1600, 1496, 1467 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{19}H_{21}N_2$, 277.1705; found, 277.1708.



3c

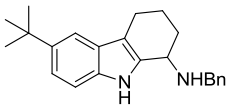
Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3c** (66.5 mg, 88% yield) as a white solid. ^1H NMR (400 MHz, d6-DMSO): 11.26 (s, 1H), 7.56 (d, *J*=7.3, 2H), 7.46 (d, *J*=1.2, 1H), 7.39-7.29 (m, 4H), 7.07 (dd, *J*=1.8, 8.6, 1H), 4.29 (s, 1H), 4.06 (dd, *J*=13.3, 25.0, 2H), 2.67-2.57 (m, 2H), 2.18-1.97 (m, 3H), 1.75-1.70 (m, 1H); ^{13}C NMR (100 MHz, d6-DMSO): 134.4, 129.1, 128.3, 127.7, 127.6, 123.1, 121.3, 117.4, 112.8, 51.0, 48.9, 27.3, 20.4, 20.2. IR (film): 3226, 2918, 2850, 1589, 1453, 1443, 696 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{19}H_{20}N_2Cl$, 311.1315; found, 311.1310.



3d

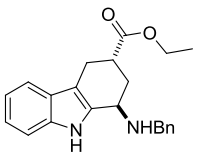
Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3d** (59.0 mg, 83% yield) as a white solid. ^1H NMR (400 MHz, DMSO): 11.26 (s, 1H), 7.57 (s, 1H), 7.51 (d, *J*=7.4, 1H), 7.37-7.26 (m, 4H), 7.16 (dd, *J*=1.1, 8.5, 1H), 4.12 (s, 1H), 3.97 (dd, *J*=13.0, 29.5, 2H), 2.62-2.59 (m, 2H), 2.13-2.08 (m, 1H), 2.04-1.99 (m, 1H), 1.91-1.85 (m, 1H), 1.72-1.67 (m, 1H); ^{13}C

NMR (100 MHz, d6-DMSO): 134.6, 128.6, 128.5, 128.2, 127.2, 123.4, 120.2, 113.2, 110.9, 51.1, 49.3, 28.1, 20.5, 20.4. IR (film): 2933, 2849, 1651, 1453 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{19}H_{20}N_2Br$, 355.0810; found, 355.0803.



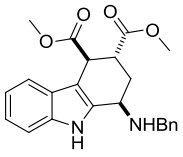
3e

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3e** (54.1 mg, 74% yield) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 9.61 (s, 1H), 7.48-7.46 (m, 3H), 7.33-7.27 (m, 5H), 4.19 (t, *J*=6.3, 1H), 3.88 (dd, *J*=13.0, 47.3, 2H), 2.81-2.69 (m, 2H), 2.29-2.22 (m, 1H), 2.08-2.01 (m, 1H), 1.81-1.72 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.5, 134.8, 133.1, 129.8, 129.0, 128.9, 128.2, 126.5, 121.2, 115.5, 114.4, 111.3, 51.2, 47.2, 34.8, 32.1, 26.7, 21.7, 20.8. IR (film): 3254, 2953, 1457, 1457 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{29}N_2$, 333.2331; found, 333.2318.



3f

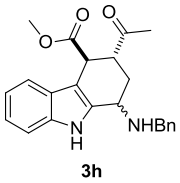
Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3f** (63.7 mg, 89% yield) as a light yellow oil. ^1H NMR (400 MHz, CDCl3): 8.67 (s, 1H), 7.50 (d, J=7.8, 1H), 7.42 (d, J=7.2, 2H), 7.34 (t, J=7.2, 2H), 7.28 (t, J=7.6, 2H), 7.17 (t, J=7.3, 1H）, 7.09 (t, J=7.6, 1H）, 4.20 (q, J=7.2, 2H), 4.15 (t, J=4.7, 1H), 3.93 (dd, *J*=13.1, 11.6, 1H), 3.14-3.03 (m, 2H), 2.93-2.87(m, 1H), 2.41-2.37(m, 1H), 2.23-2.15(m, 1H), 1.30(t, 3H); ^{13}C NMR (100 MHz, CDCl3): 175.1, 137.8, 136.5, 132.1, 128.8, 127.9, 126.8, 122.5, 119.5, 118.6, 111.3, 111.2, 60.9, 50.0, 49.2, 37.2, 30.3, 23.9, 14.1. IR (film): 3231, 2927, 1731, 1494 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_2$, 349.1916; found, 349.1917.



3g

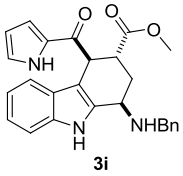
Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3g** (53.3 mg, 78% yield, dr=10:1) as a brown oil. ^1H NMR (400 MHz, CDCl3): 8.54 (s, 1H), 7.68 (d, *J*=7.7, 1H), 7.40-7.28 (m, 6H), 7.20-7.12 (m, 2H), 4.43 (d, *J*=4.8, 1H), 4.10 (t, *J*=6.2, 1H), 3.93 (dd, *J*=13.0, 44.8, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 3.63-3.59 (m, 1H), 2.56-2.50 (m, 1H), 2.36-2.30 (m, 1H), 1.88 (s, 1H); ^{13}C NMR (100 MHz, CDCl3): 174.1, 173.9, 140.3, 136.2, 136.1, 128.5, 128.3, 127.2, 126.7, 122.1, 119.7, 119.3, 111.1, 106.5, 52.2, 50.4, 48.8, 40.9, 40.8, 29.5. IR (film):

3383, 2927, 1731, 1494 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_4$, 393.1814; found, 393.1806.



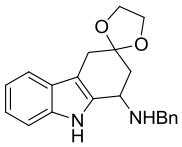
3h

Purification by silica gel chromatography (dichloromethane/methanol=50: 1) to afford the above compound **3h** (51.3 mg, 74% yield, dr=7:3) as a brown oil. 1st isomer: ^1H NMR (400 MHz, CDCl3): 8.38 (s, 1H), 8.49 (d, *J*=7.8, 1H), 7.40-7.29 (m, 6H), 7.17 (t, *J*=7.5, 1H), 7.11 (t, *J*=7.8, 1H), 4.28 (d, *J*=4.6, 1H), 4.17 (t, *J*=6.6, 1H), 3.92 (dd, *J*=13.0, 41.8, 2H), 3.64 (s, 3H), 3.59-3.56 (m, 1H), 2.56-2.50 (m, 1H), 2.28 (s, 3H), 2.13-2.07(m, 1H), 1.77 (s, 1H); ^{13}C NMR (100 MHz, CDCl3): 209.0, 174.2, 140.3, 136.4, 136.3, 128.7, 128.3, 127.4, 126.7, 122.3, 120.0, 118.9, 111.3, 107.1, 52.2, 50.6, 49.0, 40.8, 29.8, 29.6, 28.8. IR (film): 3373, 2918, 2849, 1704, 1455 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3$, 377.1865; found, 377.1871. 2nd isomer: ^1H NMR (400 MHz, CDCl3): 8.84 (s, 1H), 7.46-7.29 (m, 7H), 7.17 (t, *J*=7.2, 1H), 7.08 (t, *J*=7.2, 1H), 4.17 (d, *J*=8.3, 2H), 4.00 (dd, *J*=13.0, 60.1, 2H), 3.73 (s, 3H), 3.25-3.19 (m, 1H), 3.76-3.70 (m, 1H), 2.20 (s, 3H), 1.95-1.87 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): 209.3, 174.2, 139.3, 136.1, 128.7, 128.3, 127.5, 126.3, 122.2, 120.0, 118.6, 111.3, 106.5, 52.3, 51.1, 50.8, 50.1, 42.8, 31.1, 27.4. IR (film): 3384, 2924, 2854, 1705, 1494 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3$, 377.1865; found, 377.1866.



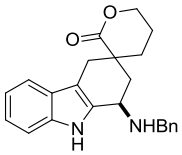
3i

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3i** (58.4 mg, 88% yield, dr=20:1) as a white solid. ^1H NMR (400 MHz, CDCl3): 9.78 (s, 1H), 8.36 (s, 1H), 7.43-7.28 (m, 6H), 7.21 (d, *J*=8.1, 1H), 7.14 (d, *J*=7.9, 1H), 7.08 (t, *J*=7.4, 1H), 6.95-6.89 (m, 2H), 6.34-6.33 (m, 1H), 5.05 (d, *J*=5.5, 1H), 4.11 (t, *J*=5.6, 1H), 3.94 (dd, *J*=13.1, 50.8, 2H), 3.63 (s, 3H), 3.45-3.41(m, 1H), 3.46-3.40 (m, 1H), 3.31-3.26 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): 191.1, 174.2, 140.5, 136.8, 136.2, 131.8, 128.6, 128.4, 127.3, 126.5, 125.8, 122.1, 119.6, 118.9, 117.6, 111.2, 107.8, 52.2, 50.7, 48.8, 43.2, 42.3, 29.8. IR (film): 3283, 2847, 1731, 1616 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{26}H_{26}N_3O_3$, 428.1974; found, 428.1964.



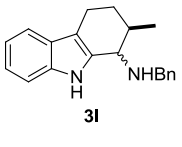
3j

Purification by silica gel chromatography (dichloromethane/Methanol=50:1) to afford the above compound **3j** (54.7 mg, 75% yield) as a light yellow oil. ^{1}H NMR (400 MHz, CDCl3): 8.61 (s, 1H), 7.52 (d, *J*=7.7, 1H), 7.45-7.32 (m, 6H), 7.22 (t, *J*=7.1, 1H), 7.16 (t, *J*=7.6, 1H), 4.26 (t, *J*=6.5, 1H), 4.15-4.06 (m, 4H), 3.96 (dd, *J*=12.9, 54.6, 2H), 3.08 (dd, *J*=15.8, 5.1, 2H), 2.46-2.42 (m, 1H), 2.14-2.09 (m, 1H); ^{13}C NMR (100 MHz, CDCl3):140.4, 136.5, 134.7, 128.5, 128.1, 127.2, 127.1, 121.8, 119.2, 118.2, 111.0, 109.8, 108.2, 64.64, 64.54, 51.13, 50.36, 38.18, 32.19. IR (film): 3323, 1602, 909 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_2$, 335.1760; found, 335.1755.



3k

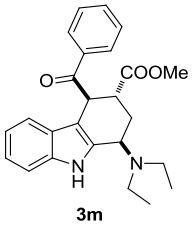
Purification by silica gel chromatography (dichloromethane/methanol=50: 1) to afford the above compound **3k** (54.4 mg, 77% yield, dr=8:1) as a light yellow oil. ^{1}H NMR (400 MHz, CDCl3): 9.51 (s, 1H), 7.44-7.35 (m, 4H), 7.30-7.27 (m, 2H), 7.25-7.22 (m, 1H), 7.15 (t, *J*=7.2, 1H), 7.07 (t, *J*=7.4, 1H), 4.61-4.58 (m, 2H), 4.43 (br, 1H), 4.03 (t, *J*=5.9, 1H), 3.90 (dd, J=13.3, 23.1 2H), 2.60-2.53 (m, 1H), 2.48-2.41 (m, 1H), 2.25-2.02 (m, 3H), 1.96-1.79 (m, 3H); ^{13}C NMR (100 MHz, CDCl3): 175.3, 136.8, 136.3, 133.4, 128.9, 128.7, 127.8, 124.7, 122.3, 119.7, 118.7, 114.6, 111.9, 111.6, 70.9, 49.9, 49.1, 42.8, 33.3, 32.8, 23.8, 20.7. IR (film): 2942, 2856, 1714, 1494 cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_2$, 361.1916; found, 361.1911. The stereochemistry was not fully elucidated because several key proton peaks were overlapped.



3l

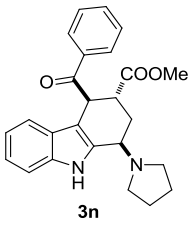
Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3l** (60.3 mg, 77% yield, dr=1:1) as a colourless oil. 1st isomer: ^{1}H NMR (400 MHz, CDCl3): 8.74 (s, 1H), 7.51(d, *J*=7.7, 1H), 7.42-7.26 (m, 6H), 7.18 (t, *J*=7.3, 1H), 7.11 (t, *J*=7.6, 1H), 4.33 (br, 1H), 3.88-3.69 (m, 3H), 3.77 (t, *J*=5.9, 2H), 2.30-2.24 (m, 1H), 2.09-2.05 (m, 1H), 1.73-1.67 (m, 1H), 1.16 (d, *J*=6.8, 3H); ^{13}C NMR (100 MHz, CDCl3): 136.4, 128.8, 127.7, 127.3, 121.9, 119.3, 118.4, 112.9, 111.2, 58.4, 48.2, 32.5, 30.1, 19.7, 18.4. IR (film): 2922, 2847, 1494 1454, cm^{-1}. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{20}H_{23}N_2$, 291.1861; found, 291.1862. 2nd isomer:

^{1}H NMR (400 MHz, CDCl3): 8.90 (s, 1H), 7.51-7.46 (m, 3H), 7.38-7.27 (m, 4H), 7.17 (t, *J*=7.2, 1H), 7.09 (t, *J*=7.2, 1H), 4.14 (d, *J*=5.2, 1H), 3.93 (dd, *J*=13.0, 49.5, 2H), 2.82-2.77 (m, 1H), 2.73-2.66 (m, 1H), 2.50-2.44 (m, 1H), 1.93-1.91 (m, 2H), 1.14 (d, *J*=7.0, 3H); ^{13}C NMR (100 MHz, CDCl3):136.0, 128.9, 128.6, 127.8, 127.2, 121.7, 119.1, 118.3, 111.1, 54.6, 50.0, 30.3, 28.6, 18.1, 13.4. IR (film): 2922, 1455, 741. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{20}H_{23}N_2$, 291.1861; found, 291.1853.



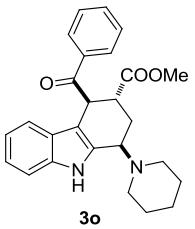
3m

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3m** (50.4 mg, 83% yield) as a light yellow oil. ^{1}H NMR (400 MHz, CDCl3): 8.50 (s, 1H), 8.22 (d, *J*=7.4, 2H), 7.65 (t, *J*=7.4, 1H), 7.56 (t, *J*=7.8, 2H), 7.33 (d, *J*=8.1, 1H), 7.14-7.09 (m, 2H), 6.95 (t, *J*=7.3, 1H), 5.51 (s, 1H), 4.48-4.44 (m, 1H), 3.73 (s, 3H), 3.35-3.33 (m, 1H), 3.30-2.71 (m, 2H), 2.55-2.47 (m, 2H), 2.33-2.27 (m, 1H), 2.13-2.06 (m, 1H), 1.34 (t, *J*=7.1, 6H); ^{13}C NMR (100 MHz, CDCl3): 200.1, 173.6, 137.7, 136.4, 136.0, 133.5, 129.1, 128.8, 127.3, 121.7, 119.4, 118.1, 111.0, 108.1, 52.5, 51.5, 44.1, 42.6, 41.5, 19.7, 14.7. IR (film): 3348, 2966, 1721, 1686, 742. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{25}H_{29}N_2O_3$, 405.2178; found, 405.2176.



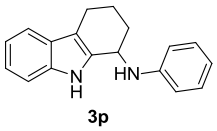
3n

Purification by silica gel chromatography (dichloromethane/methanol=50: 1) to afford the above compound **3n** (53.1 mg, 88% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO): 11.1 (s, 1H), 8.11 (d, *J*=7.7, 2H), 7.66 (t, *J*=7.2, 1H), 7.53 (t, *J*=7.6, 2H), 7.31 (d, *J*=8.1, 1H), 6.98(t, *J*=7.3, 1H), 6.77-6.69(m, 2H), 5.03(d, *J*=9.3, 1H), 3.79-3.73(m, 1H), 3.68-3.66(m, 1H), 3.51(s, 3H), 2.83-2.81(m, 2H), 2.55-2.53(m, 2H), 2.46-2.42(m, 1H), 2.05-1.98 (m, 1H), 1.79-1.72 (m, 4H); ^{13}C NMR (100 MHz, DMSO): 201.6, 174.2, 136.9, 136.0, 135.5, 133.2, 128.7, 128.6, 125.3, 121.1, 118.5, 118.1, 111.4, 107.2, 54.6, 51.7, 51.2, 45.2, 29.2, 23.3. IR (film):3301, 1727, 1661, 739. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{25}H_{27}N_2O_3$, 403.2022; found, 403.2015.



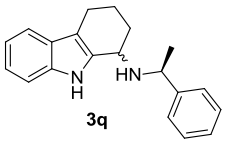
3o

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3o** (55.0 mg, 88% yield) as a white solid. ^{1}H NMR (400 MHz, CDCl3): 8.57 (s, 1H), 8.22 (d, *J*=7.4, 2H), 7.65 (t, *J*=7.3, 1H), 7.56 (t, *J*=7.8, 2H), 7.33 (d, *J*=8.4, 1H), 7.13-7.10 (m, 2H), 6.94 (t, *J*=7.7, 1H), 5.45 (d, *J*=2.9, 1H), 4.25 (t, *J*=6.7, 1H), 3.70 (s, 3H), 3.40-3.37 (m, 1H), 2.71-2.66 (m, 2H), 2.62-2.54 (m, 2H), 2.32-2.20 (m, 2H), 1.65-1.60 (m, 4H), 1.51-1.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): 200.4, 173.8, 136.6, 136.2, 133.4, 129.0, 128.8, 126.9, 121.9, 119.4, 118.4, 111.1, 108.4, 56.4, 52.4, 49.9, 42.8, 41.9, 26.8, 24.9, 20.2. IR (film): 3304, 2935, 1724, 1665, 739. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{26}H_{29}N_2O_3$, 417.2178; found, 417.2170.



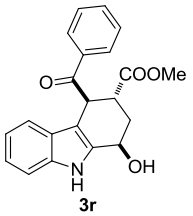
3p

Purification by silica gel chromatography (ethyl acetate/petroleum ether=1/3) to afford the above compound **3p** (74.3 mg, 97% yield) as a light yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.04 (s, 1H), 7.63 (d, *J*=7.5, 4H), 7.35-7.19 (m, 5H), 6.89 (t, *J*=7.3, 1H), 6.80 (d, *J*=8.0, 2H), 4.87 (t, *J*=6.0, 1H), 3.84 (br, 1H), 2.91-2.77 (m, 2H), 2.33-2.21 (m, 1H), 2.13-2.06 (m, 1H), 2.02-1.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): 147.2, 135.9, 134.8, 129.7, 127.2, 122.1, 119.4, 118.5, 118.1, 113.5, 112.2, 111.0, 47.6, 30.2, 21.2, 21.0. IR (film): 3385, 2921, 2850, 1598, 1503, 752.



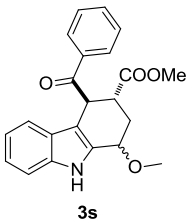
3q

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3q** (62.7 mg, 74% yield, dr=2:3) as a colorless oil. Isomer mixture ^{1}H NMR (400 MHz, CDCl3): 8.20-8.16 (m, 1H), 7.54-7.29 (m, 7H), 7.20-7.08 (m, 2H), 4.21-4.13 (m, 1H), 4.06-3.70 (m, 1H), 2.75-2.70 (m, 2H), 2.38-2.17 (m, 1H), 1.88-1.67 (m, 1H), 1.65-1.53 (m, 1H), 1.47-1.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl3): 146.5, 145.6, 136.7, 135.8, 128.7, 127.6, 127.22, 127.19, 127.0, 126.6, 121.5, 121.4, 119.1, 119.0, 118.3, 118.2, 110.93, 110.86, 110.79, 110.76, 55.3, 54.6, 49.8, 49.5, 31.2, 30.5, 29.8, 25.8, 23.7, 21.8, 21.4, 21.0. IR (film): 2920, 1601, 739. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{20}H_{23}N_2$, 291.1861; found, 291.1859.



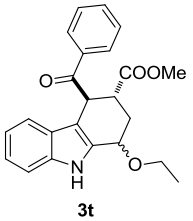
3r

Purification by silica gel chromatography (dichloromethane/methanol=50:1) to afford the above compound **3r** (40.3 mg, 77% yield) as a yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.48 (s, 1H), 8.21 (d, *J*=7.7, 2H), 7.67 (t, *J*=7.3, 1H), 7.56 (t, *J*=7.7, 2H), 7.09-7.04 (m, 2H), 6.93-6.85 (m, 2H), 5.33 (d, *J*=7.5, 1H), 4.94 (t, *J*=4.4, 1H), 3.58 (s, 3H), 3.56-3.53 (m, 1H), 2.34-2.31 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): 202.7, 174.2, 137.1, 136.6, 135.9, 133.9, 129.10, 129.06, 125.5, 122.7, 119.9, 119.2, 111.7, 108.7, 61.6, 52.3, 43.2, 41.6, 33.7. IR (film): 3246, 2924, 2854, 1720, 1683, 743. HRMS-ESI (*m*/*z*) $[M+Na]^+$ calcd for $C_{21}H_{19}NO_4Na$, 372.1212; found, 372.1207.



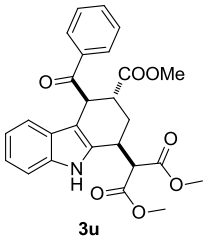
3s

Methanol (0.5 mL) was used as the coupling partner. Purification by silica gel chromatography (ethyl acetate/petroleum ether=1/3) to afford the above compound **3s** (46.0 mg, 84% yield, dr=1:2). 1st isomer: light yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.30 (s, 1H), 8.20-8.18 (m, 2H), 7.69-7.65 (m, 1H), 7.56 (t, *J*=7.8, 2H), 7.28 (d, *J*=8.2, 1H), 7.09-7.05 (m, 1H), 6.84-6.79 (m, 2H), 5.35 (dd, *J*=1.9, 9.0, 1H), 4.80-4.76 (m, 1H), 3.57 (s, 3H), 3.52 (s, 3H), 3.51-3.44 (m, 1H), 2.80-2.75 (m, 1H), 2.11-2.03 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): 202.15, 173.9, 137.8, 136.6, 135.1, 133.6, 129.0, 128.9, 125.8, 122.4, 119.8, 119.4, 111.4, 109.1, 72.9, 56.1, 52.1, 43.7, 41.2, 31.4. IR (film): 3355, 2930, 1727, 1672, 746. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{22}H_{22}NO_4$l, 364.1549; found, 364.1541. 2nd isomer: light yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.24 (s, 1H), 8.17-8.14 (m, 2H), 7.64-7.60 (m, 1H), 7.52 (t, *J*=7.8, 2H), 7.29 (d, *J*=8.2, 1H), 7.13-7.09 (m, 1H), 6.99 (d, *J*=8.0, 1H), 6.89-6.85 (m, 1H), 5.22 (d, *J*=7.6, 1H), 4.67 (t, *J*=4.5, 1H), 3.72-3.63 (m, 1H), 3.61 (s, 3H), 3.51 (s, 3H), 2.54-2.49 (m, 1H), 2.30-2.23 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): 201.1, 174.3, 137.3, 136.6, 133.7, 133.4, 128.9, 125.8, 122.8, 119.9, 119.5, 111.3, 109.9, 70.2, 56.1, 52.2, 44.1, 41.5, 29.1. IR (film): 3385, 2924, 2853, 1723, 1687, 750. HRMS-ESI (*m*/*z*) $[M+Na]^+$ calcd for $C_{22}H_{21}NO_4Na$, 386.1368; found, 386.1352.



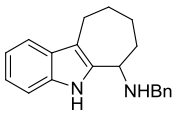
3t

Ethanol (0.5 mL) was used as the coupling partner. Purification by silica gel chromatography (ethyl acetate/petroleum ether=1/3) to afford the above compound **3t** (42.5 mg, 75% yield, dr=1:2). 1st isomer: light yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.25 (s, 1H), 8.20-8.17 (m, 2H), 7.66 (t, *J*=7.4, 1H), 7.56 (t, *J*=7.9, 2H), 7.29 (d, *J*=8.2, 1H), 7.09-7.05 (m, 1H), 6.83-6.77 (m, 2H), 5.34 (dd, *J*=1.9, 9.1, 1H), 4.92-4.88 (m, 1H), 3.87-3.79 (m, 1H), 3.68-3.60 (m, 1H), 3.56 (s, 3H), 3.50-3.44 (m, 1H), 2.80-2.75 (m, 1H), 2.12-2.03 (m, 1H), 1.32 (t, *J*=7.0, 3H); ^{13}C NMR (100 MHz, CDCl3): 202.3, 173.9, 137.9, 136.6, 135.4, 133.6, 129.02, 128.95, 125.9, 122.3, 119.8, 119.4, 111.4, 109.0, 71.6, 64.1, 52.1, 43.9, 43.3, 31.3, 15.8. IR (film): 3360, 2950, 1720, 1661, 1595, 747. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{23}H_{24}NO_4$, 378.1705; found, 378.1703. 2nd isomer: colorless oil 1H NMR (400 MHz, CDCl3): 8.23 (s, 1H), 8.17-8.14 (m, 2H), 7.62 (t, *J*=7.3, 1H), 7.51 (t, *J*=7.8, 2H), 7.29 (d, *J*=8.2, 1H), 7.10 (t, *J*=8.0, 1H), 7.00 (d, *J*=8.0, 1H), 7.87 (t, *J*=7.8, 1H), 5.19 (d, *J*=7.7, 1H), 4.74 (t, *J*=4.4, 1H), 3.79-3.63 (m, 3H), 3.61 (s, 3H), 2.53-2.47 (m, 1H), 2.30-2.23 (m, 1H), 1.29 (t, *J*=7.0, 3H); 13C NMR (100 MHz, CDCl3): 201.0, 174.3, 137.2, 136.4, 134.0, 133.2, 128.82, 128.78, 125.7, 122.6, 119.8, 119.3, 111.2, 109.4, 68.6, 63.8, 52.1, 44.1, 41.4, 29.7, 15.7. IR (film): 3365, 2951, 1733, 1682, 1595, 743. HRMS-ESI (*m*/*z*) $[M+Na]^+$ calcd for $C_{23}H_{23}NO_4Na$, 400.1525; found, 400.1512.



3u

The sodium salt of dimethyl malonate (1.2 equiv, prepared by the reaction of dimethyl malonate with sodium hydride) was used as the coupling partner. Purification by silica gel chromatography (ethyl acetate/petroleum ether=1/3) to afford the above compound **3u** (49.4 mg, 71% yield) as a yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.76 (s, 1H), 8.19 (d, *J*=7.5, 2H), 7.66 (t, *J*=7.3, 1H), 7.56 (t, *J*=7.8, 2H), 7.27 (d, *J*=8.3, 1H), 7.09-7.05 (m, 1H), 6.88-6.80 (m, 2H), 5.36 (d, *J*=7.8, 1H), 3.96-3.87 (m, 2H), 3.85(s, 3H), 3.76 (s, 3H), 3.58 (s, 3H), 3.52-3.46 (m, 1H), 2.30-2.20 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): 201.8, 174.1, 170.2, 169.1, 137.6, 135.9, 134.4, 133.5, 129.0, 128.9, 125.8, 122.2, 119.6, 118.8, 111.2, 108.6, 56.6, 53.3, 53.0, 52.2, 43.3, 41.5, 31.8, 28.6. IR (film): 3390, 1728, 1688, 1597, 740. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{26}H_{26}NO_7$, 464.1709; found, 464.1712.

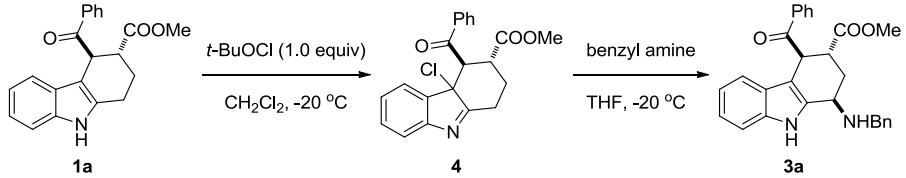


3v

Purification by preparative silica gel chromatography (dichloromethane/Methanol= 50: 1) to afford the above compound **3v** (55.6 mg, 71% yield) as a light yellow solid. ^{1}H NMR (400 MHz, CDCl3): 8.73 (s, 1H), 7.50 (d, *J*=7.4, 2H), 7.37 (t, *J*=7.2, 2H), 7.31

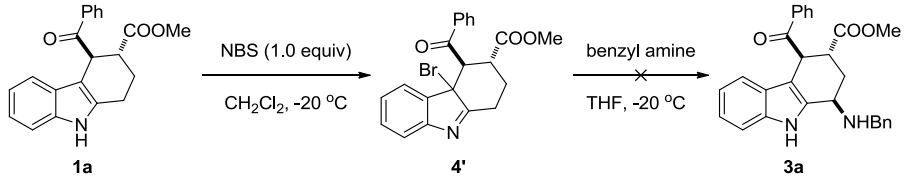
(t, *J*=7.2, 2H), 7.13-7.06 (m, 2H), 4.03-3.87 (m, 3H), 3.03-2.97 (m, 1H), 2.71-2.65 (m, 1H), 2.28-2.13 (m, 2H), 1.96-1.89 (m, 1H), 1.73-1.59 (m, 3H); ^{13}C NMR (100 MHz, CDCl3): 140.5, 139.2, 133.6, 129.5, 128.7, 128.2, 127.3, 120.9, 119.0, 118.0, 111.5, 110.7, 56.8, 51.8, 34.3, 28.5, 28.1, 24.6. IR (film): 2924, 1845, 740. HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{20}H_{23}N_2$, 291.1861; found, 291.1858.

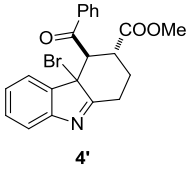
C. The chloroindolenine and bromoindolenine intermediates



To a solution of **1a** (50.0 mg, 0.15 mmol) in dichloromethane (1 mL) at -20 ^{o}C was added *t*-BuOCl (16.2 mg, 0.15 mmol) dropwisely. After being stirred at -20 ^{o}C for 10 min, the reaction was quenched with aqueous sodium bicarbonate (5 mL) and extracted with dichloromethane (3x10 mL). The combined organic layers were dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude residue was purified by preparative thin layer chromatography (dichloromethane/Methanol =50/1) to yield the desired product **4** (37.5 mg, 68% yield) as a colourless oil, which was unstable and decomposed completely after a day. ^{1}H NMR (400 MHz, CDCl3): 7.90 (d, *J*=7.6, 2H), 7.60 (m, 2H), 7.46 (t, *J* = 7.7, 2H), 7.31 (t, *J*=7.6, 1H), 7.17 (d, *J*=7.3, 1H), 7.03 (t, *J*=7.5, 1H), 5.53 (s, 1H), 3.93 (s, 3H), 3,44-3.34 (m, 1H), 2.95-2.89 (m, 2H), 2.59-2.55 (m. 1H), 1.99-1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): 195.8, 180.4, 172.7, 154.0, 139.2, 134.8, 134.1, 130.3, 129.2, 128.6, 126.1, 121.8, 121.2, 68.3, 55.2, 52.8, 39.3, 24.6, 23.2.

To a solution of **4** (36.7 mg, 0.10 mmol) in THF (1.0 mL) at -20 ^{o}C was added benzyl amine (**2a)** (32.0 mg, 0.3 mmol). **3a** was formed smoothly as evidenced by TLC analysis and NMR analysis of the isolated product.



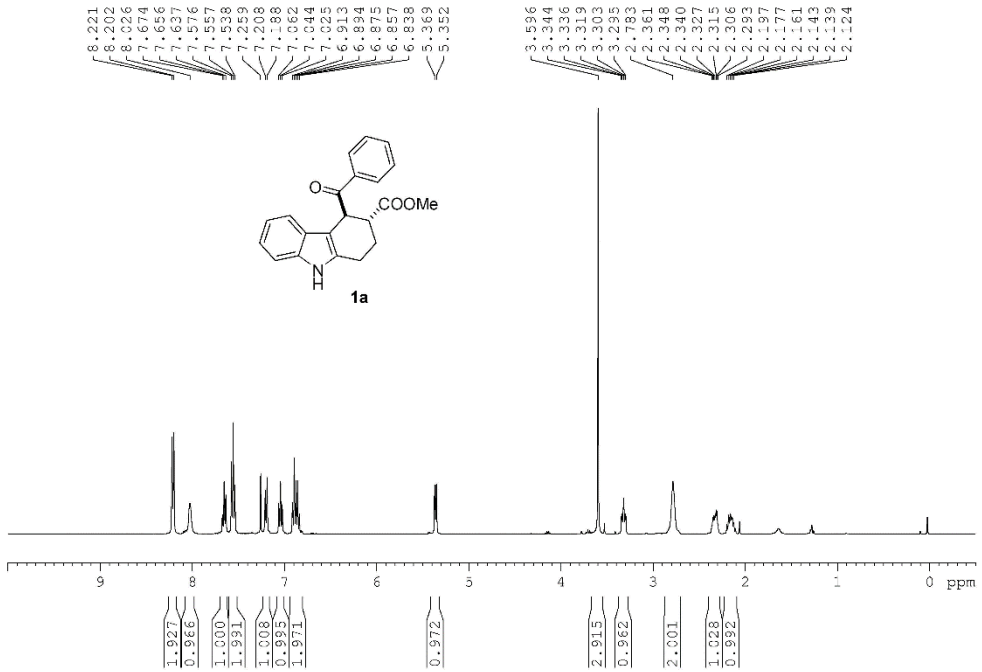


The above compound was prepared according to the same procedure as that of **4**, but using NBS. Purified by preparative thin layer chromatography (dichloromethane/Methanol =100/3) to yield the desired product **4'** (51 mg, 82% yield) as a colourless oil, which was unstable and decomposed fast. ^{1}H NMR (400 MHz,

CDCl3): 7.90 (d, *J*=7.8, 2H), 7.58 (d, *J*=7.4, 2H), 7.47 (t, *J* = 6.9, 2H), 7.29 (t, *J*=7.4, 1H), 7.17 (d, *J*=7.3, 1H), 7.03 (t, *J*=7.4, 1H), 5.55 (s, 1H), 3.95 (s, 3H), 3,61-3.52 (m, 1H), 2.98-2.88 (m, 2H), 2.58-2.55 (m. 1H), 1.96-1.89 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): 195.8, 180.6, 172.7, 153.2, 140.3, 134.8, 134.2, 130.1, 129.2, 128.6, 126.2, 122.0, 121.4, 59.3, 55.3, 52.9, 39.5, 24.7, 23.1.

To a solution of **4'** (41.0 mg, 0.10 mmol) in THF (1.0 mL) at -20 ^{o}C was added benzyl amine (**2a)** (32.0 mg, 0.3 mmol). The transformation to **3a** was not observed by TLC analysis.

NMR Spectra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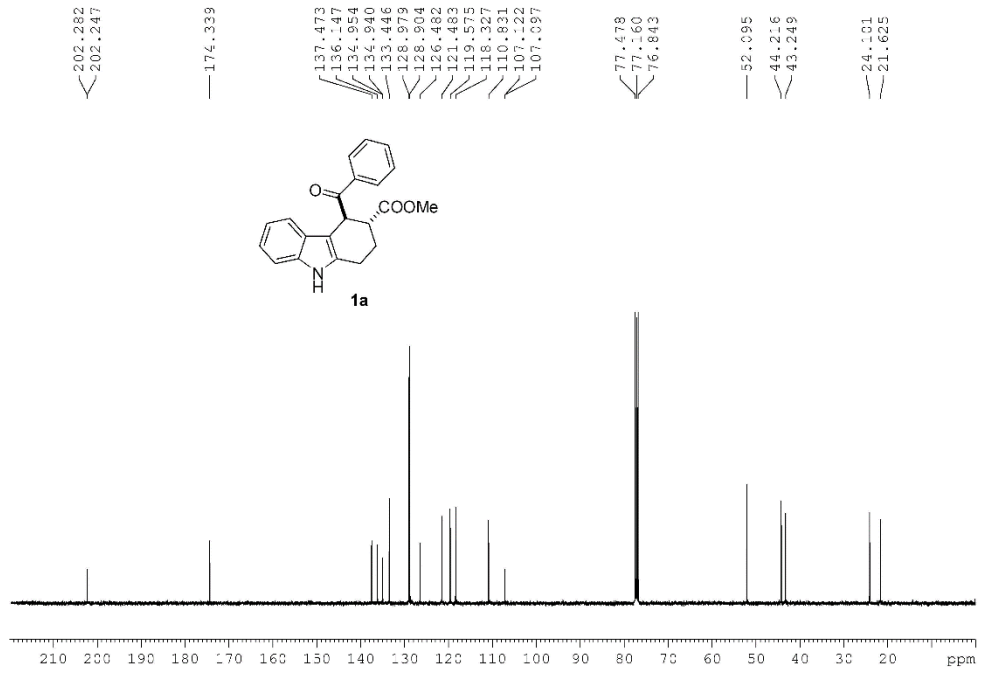
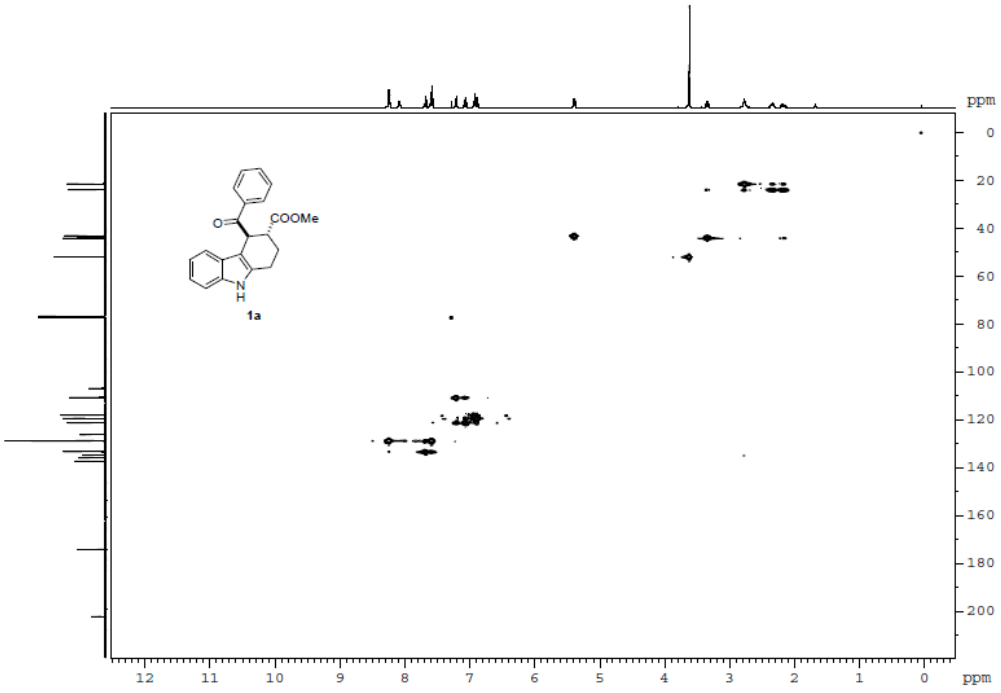
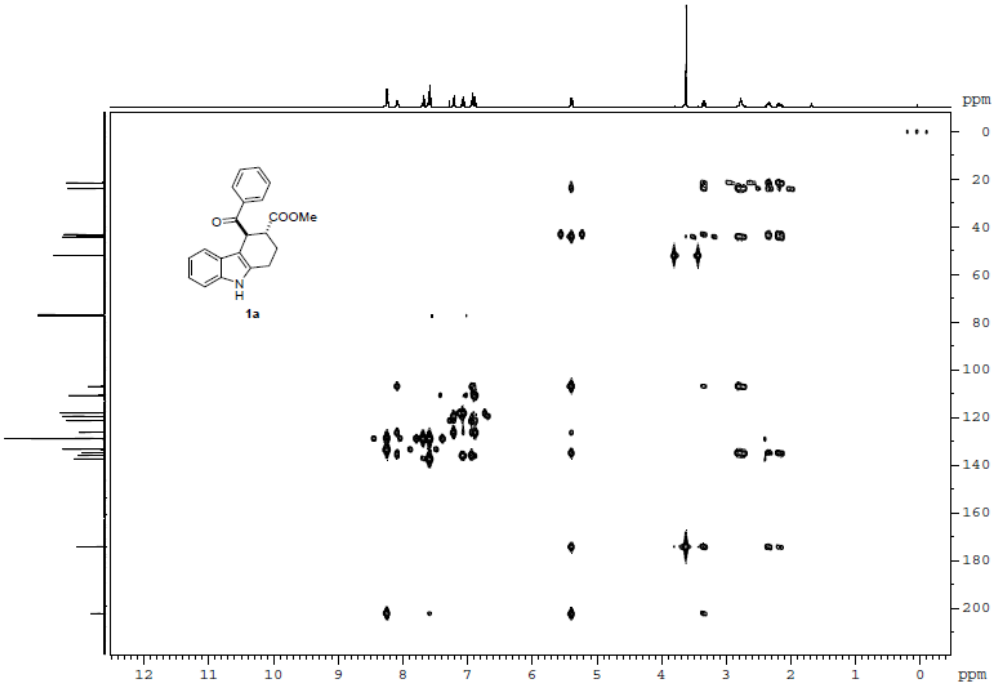
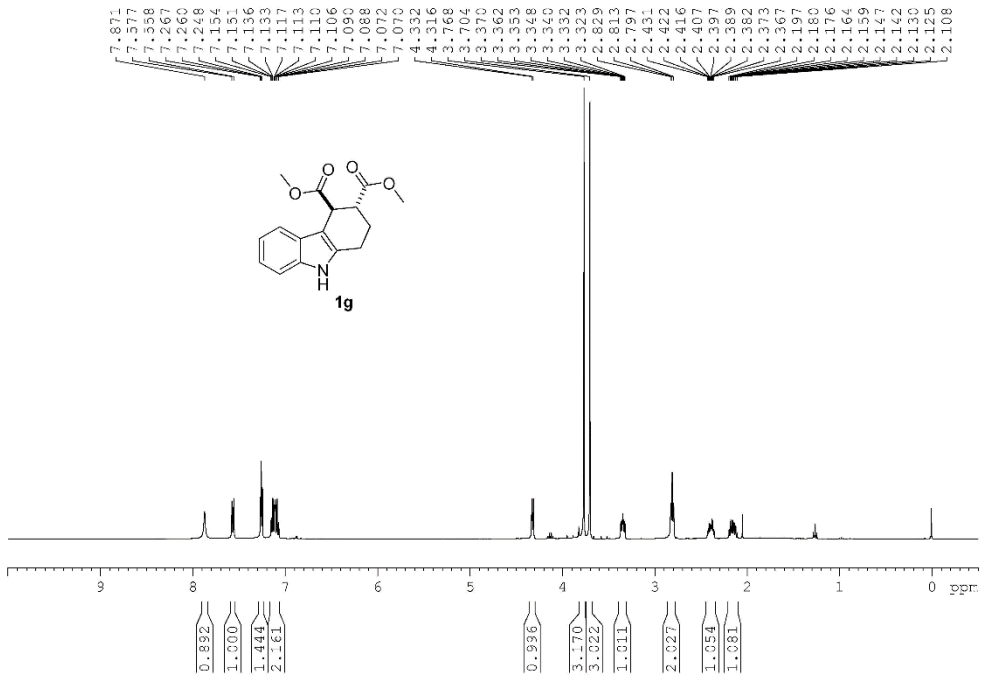
8.202
8.026
7.674
7.656
7.637
7.576
7.557
7.538
7.259
7.208
7.188
7.062
7.044
7.025
6.913
6.894
6.875
6.857
6.838
5.369
5.352
3.536
3.344
3.336
3.319
3.303
3.295
2.783
2.361
2.348
2.340
2.327
2.315
2.306
2.293
2.197
2.177
2.161
2.143
2.139
2.124
O
COOMe
N
H
1a
9
8
7
6
5
4
3
2
1
0 ppm
1.927
0.966
1.000
1.991
1.008
0.985
1.971
0.972
2.915
0.962
2.001
1.028
0.992


202.282
202.247
174.339
137.473
136.147
134.954
134.940
133.446
128.979
128.904
126.482
121.483
119.575
118.327
110.831
107.122
107.097
77.478
77.160
76.843
52.095
44.216
43.249
24.101
21.625
O
COOMe
N
H
1a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

HMQC and HMBC Spectra of compound **1a**



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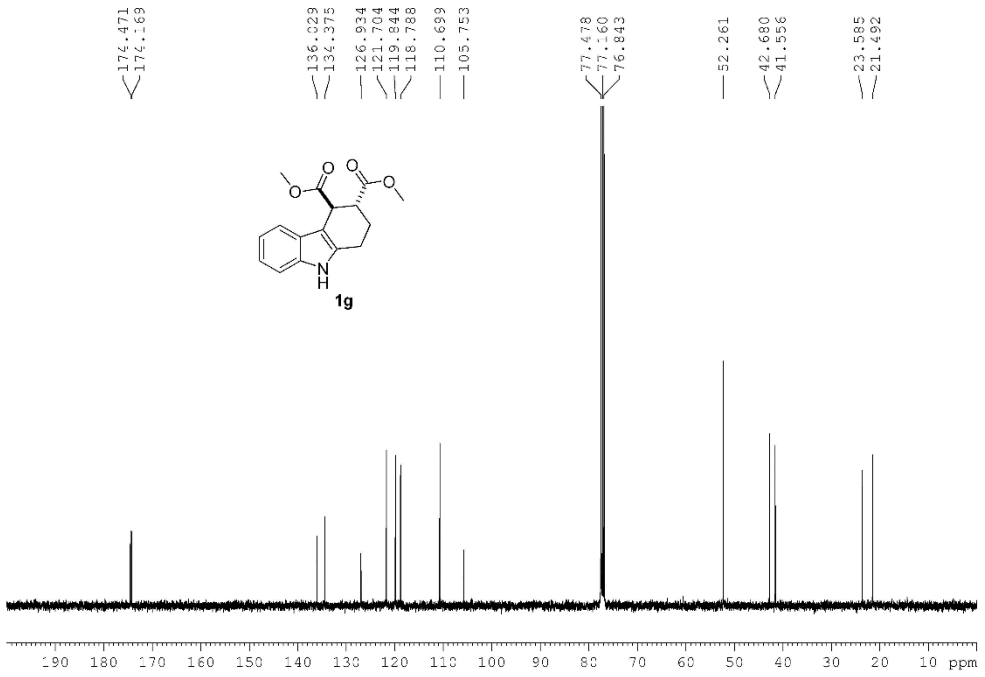
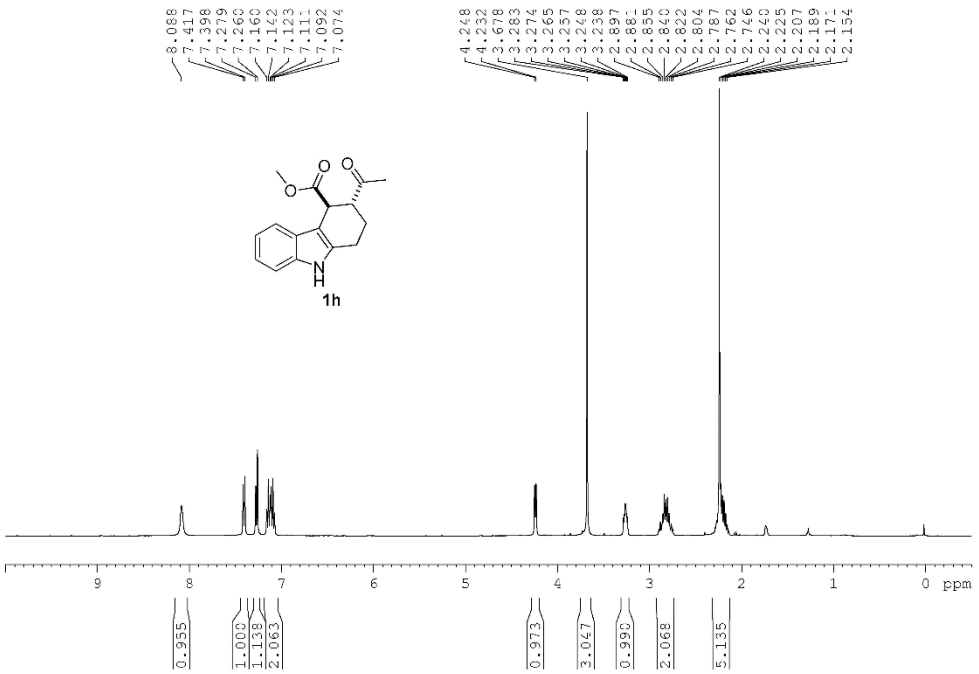
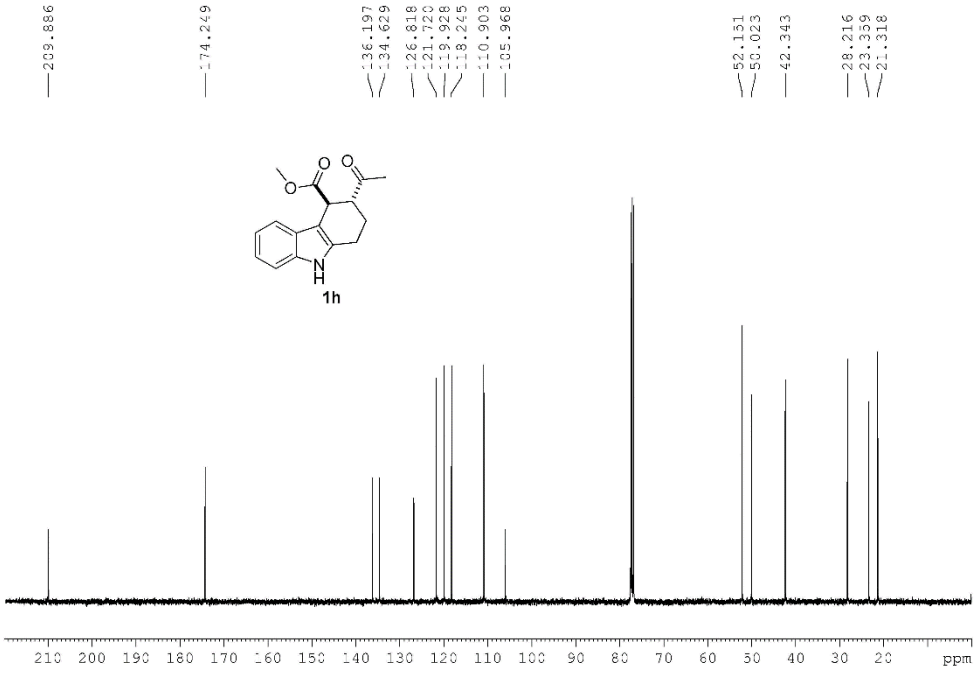
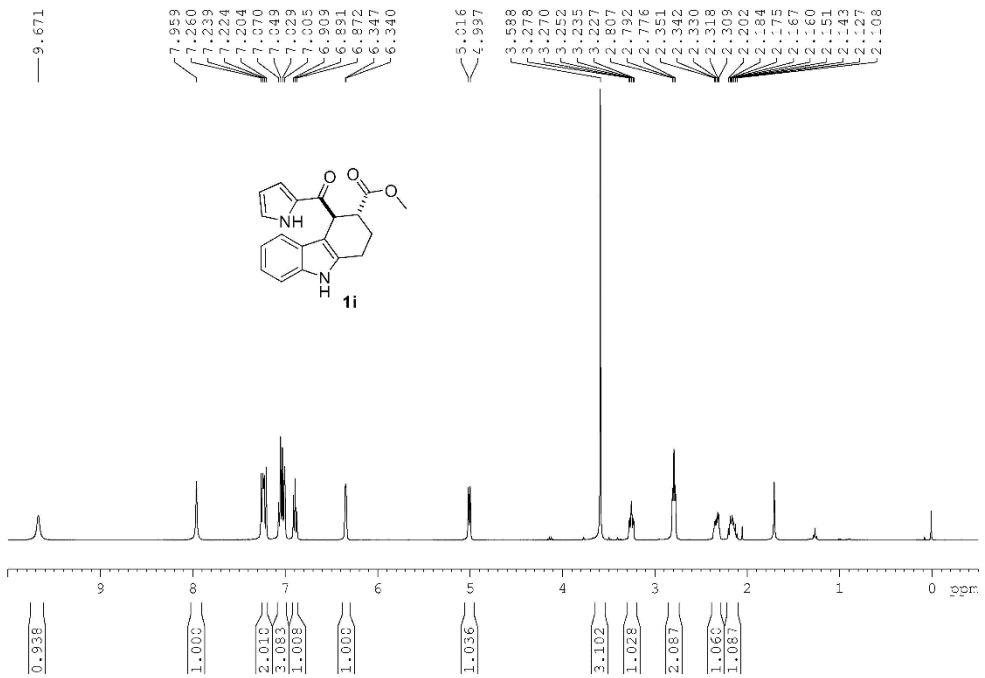
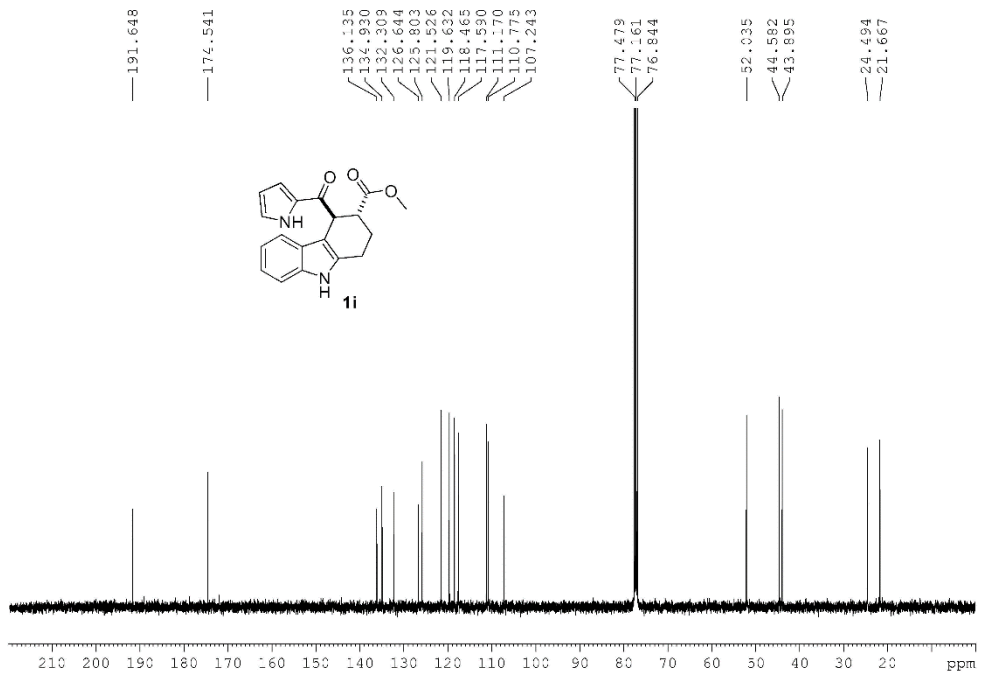
0.892
1.000
1.444
2.161
0.936
3.170
3.022
1.011
2.027
1.054
1.081
ppm

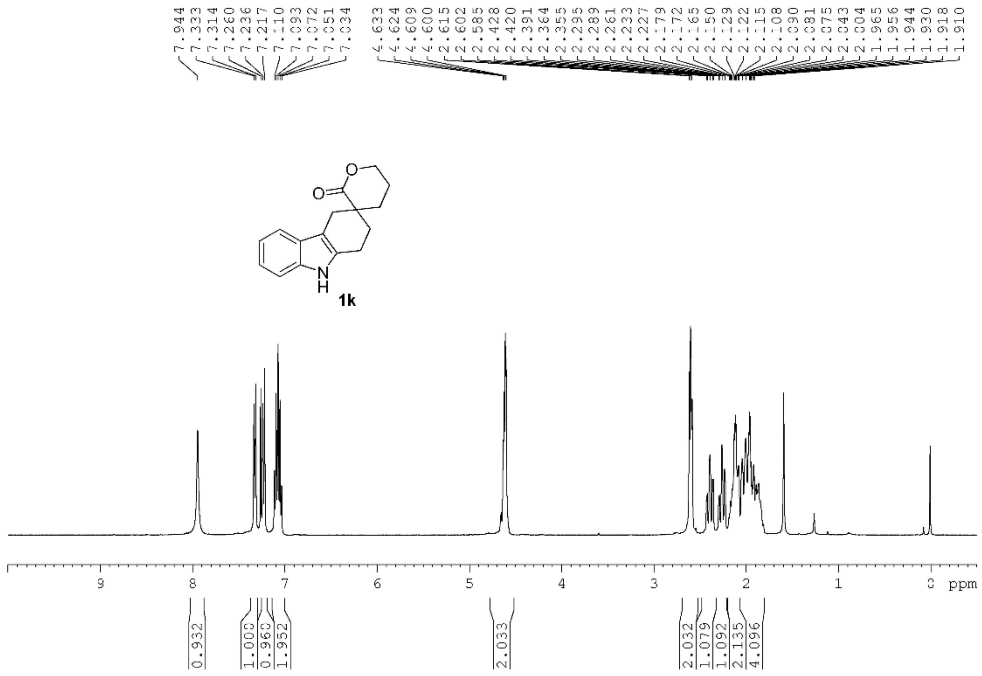

174.471
174.169
136.029
134.375
126.934
121.704
119.844
118.788
110.699
105.753
77.478
77.160
76.843
52.261
42.680
41.556
23.585
21.492
1g
ppm


8.088
7.417
7.398
7.279
7.260
7.160
7.162
7.123
7.111
7.092
7.074
4.248
4.232
3.678
3.283
3.274
3.265
3.257
3.248
3.238
2.897
2.881
2.855
2.840
2.822
2.804
2.787
2.762
2.746
2.250
2.225
2.207
2.189
2.172
2.154
1h
9
8
7
6
5
4
3
2
1
0 ppm
0.955
1.000
1.138
2.063
0.973
3.047
0.990
2.068
5.135


209.886
174.249
136.197
134.629
126.818
121.720
119.928
118.245
110.903
105.968
52.131
50.023
42.343
28.216
23.339
21.318
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


9.671
7.959
7.260
7.239
7.224
7.204
7.070
7.049
7.029
7.005
6.909
6.891
6.872
6.347
6.340
5.016
2.997
3.588
3.278
3.270
3.252
3.235
3.227
2.807
2.792
2.776
2.351
2.342
2.330
2.318
2.309
2.202
2.184
2.175
2.167
2.160
2.151
2.143
2.127
2.108
NH
N
H
1i
9
8
7
6
5
4
3
2
1
0
ppm
0.938
1.000
2.013
3.083
1.008
1.000
1.036
3.102
1.028
2.087
1.060
1.087


191.648
174.541
136.135
134.930
132.309
126.644
125.803
121.526
119.632
118.465
117.590
111.170
110.775
107.243
77.479
77.161
76.844
52.035
44.582
43.895
24.494
21.667
NH
N
H
1i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.944
7.333
7.314
7.260
7.236
7.217
7.110
7.093
7.072
7.051
7.034
4.633
4.624
4.609
4.600
2.615
2.602
2.585
2.428
2.420
2.391
2.364
2.355
2.295
2.289
2.261
2.233
2.227
2.179
2.172
2.165
2.150
2.129
2.122
2.115
2.108
2.090
2.081
2.075
2.043
2.004
1.965
1.956
1.944
1.930
1.918
1.910
O
O
N
H
1k
9
8
7
6
5
4
3
2
1
0 ppm
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1.000
0.960
1.952
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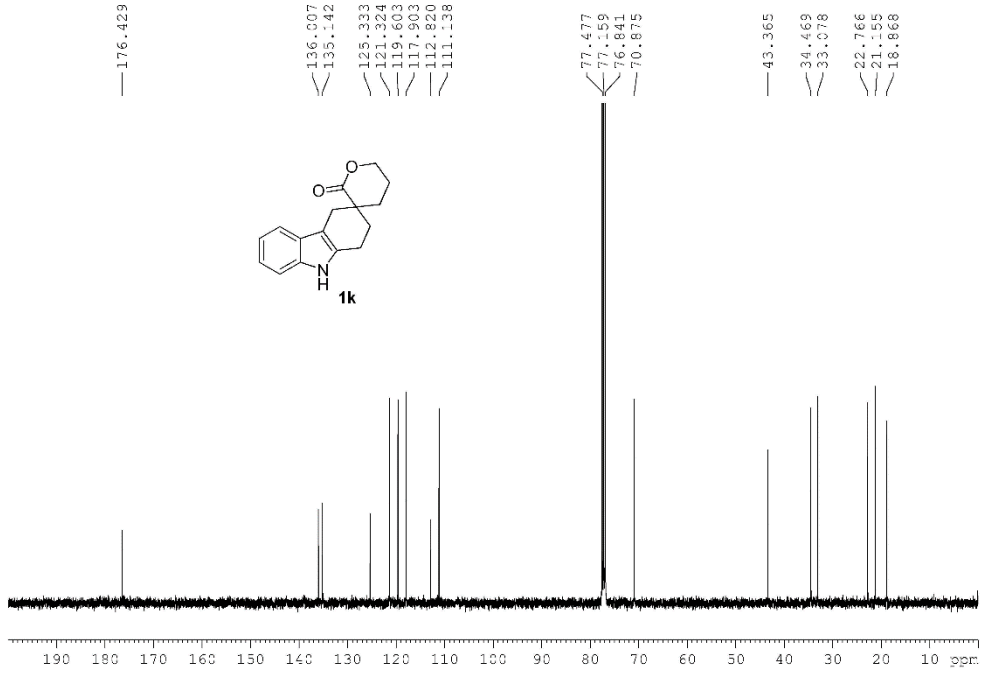
2.032
1.079
1.092
2.135
4.096


176.429
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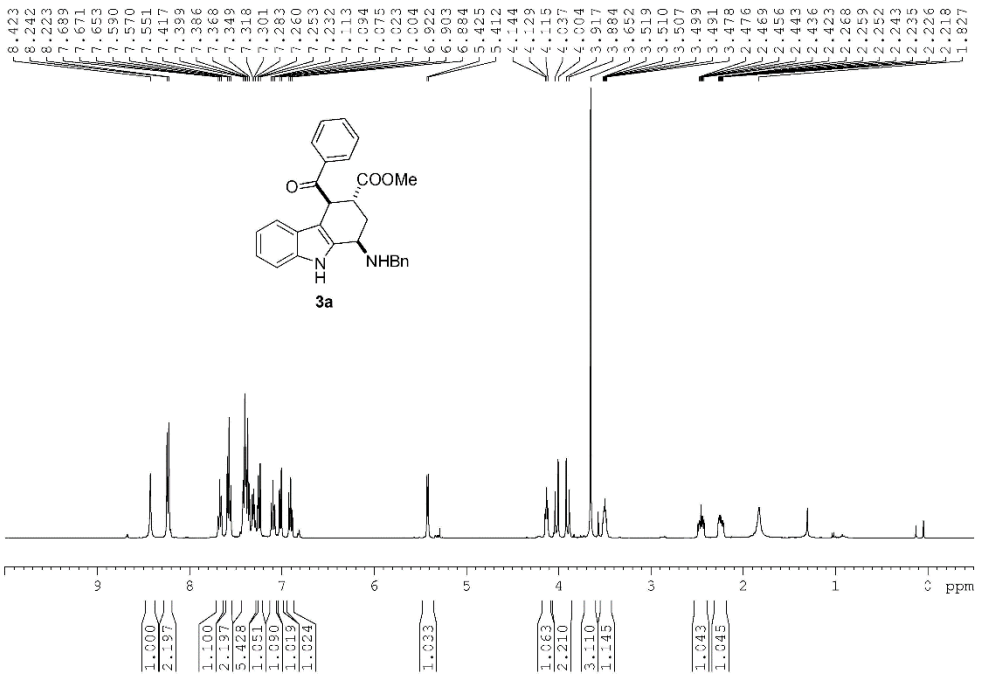
135.142
125.333
121.324
119.603
117.903
112.820
111.138
77.477
77.159
76.841
70.875
43.365
34.469
33.078
22.766
21.555
18.868
O
O
N
H
1k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.223
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7.671
7.653
7.590
7.570
7.551
7.417
7.399
7.386
7.368
7.349
7.318
7.301
7.283
7.260
7.253
7.232
7.113
7.094
7.075
7.023
7.004
6.922
6.903
6.884
5.425
5.412
4.144
4.129
4.115
4.037
4.004
3.917
3.884
3.652
3.519
3.510
3.507
3.499
3.491
3.478
2.476
2.469
2.456
2.443
2.436
2.423
2.268
2.259
2.252
2.243
2.235
2.226
2.218
1.827
COOMe
O
NHBn
N
H
3a
9
8
7
6
5
4
3
2
1
0
ppm
1.000
2.197
1.100
2.197
5.428
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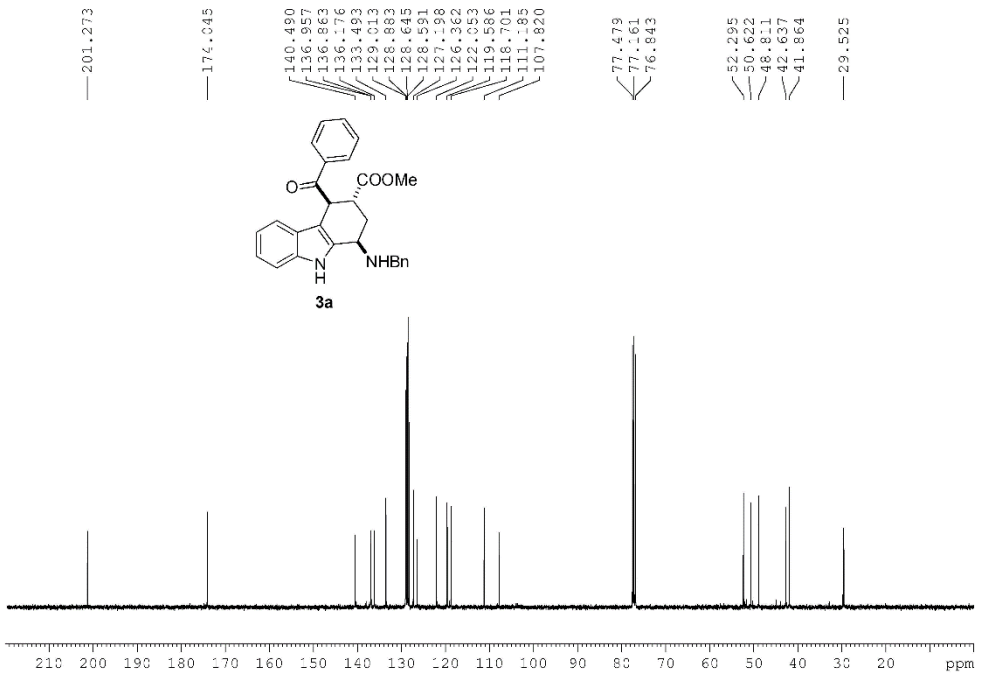
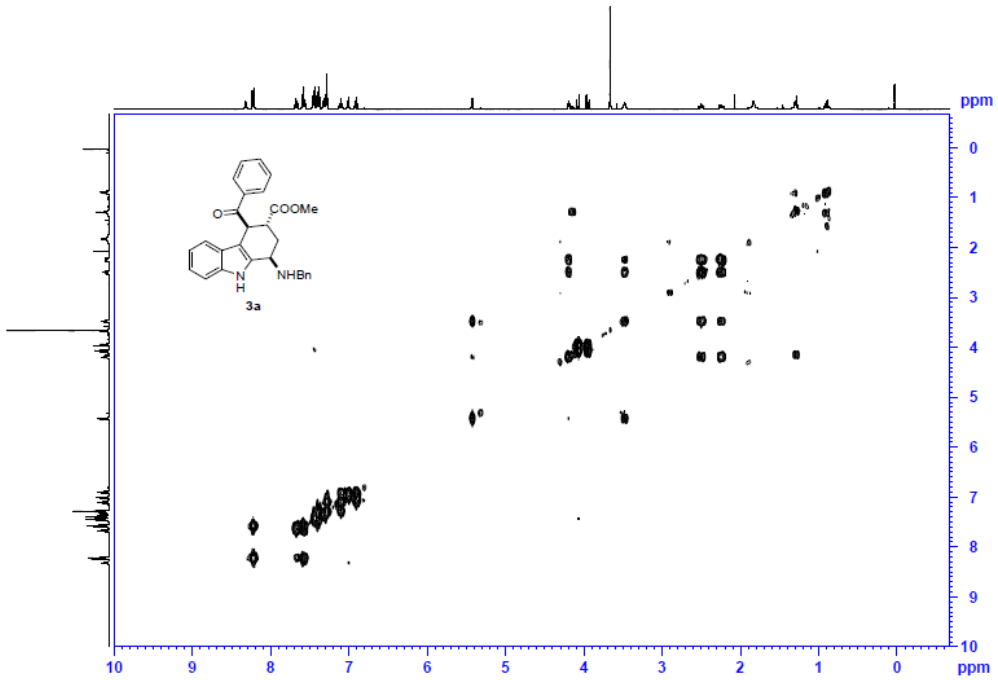
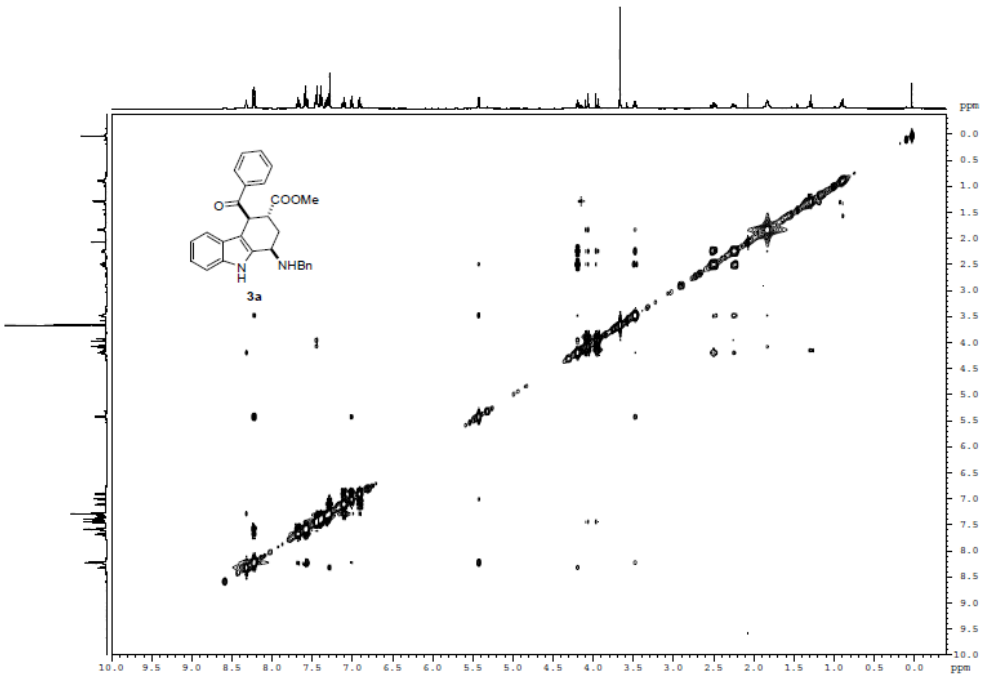
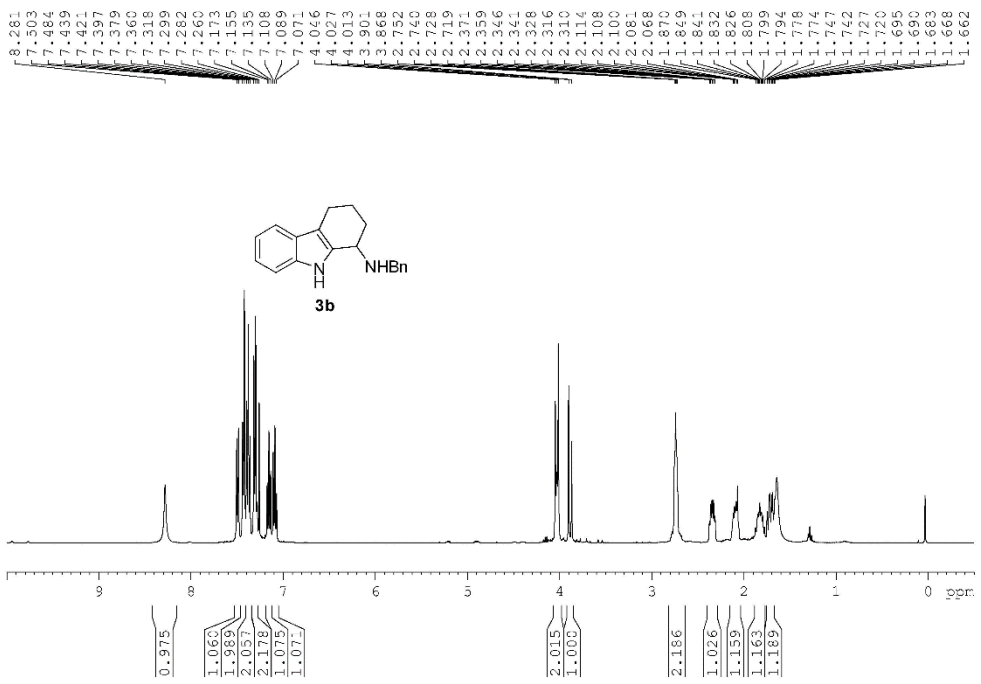
1.030
1.019
1.024
1.033
1.063
2.210
3.110
1.145
1.043
1.045


201.273
174.045
140.490
136.957
136.863
136.176
133.493
129.013
128.883
128.645
128.591
127.198
126.362
122.053
119.586
118.701
111.185
107.820
77.479
77.161
76.843
52.295
50.622
48.811
42.637
41.864
29.525
COOMe
O
NHBn
N
H
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

COSY and NOESY Spectra of compound **3a**






8.281
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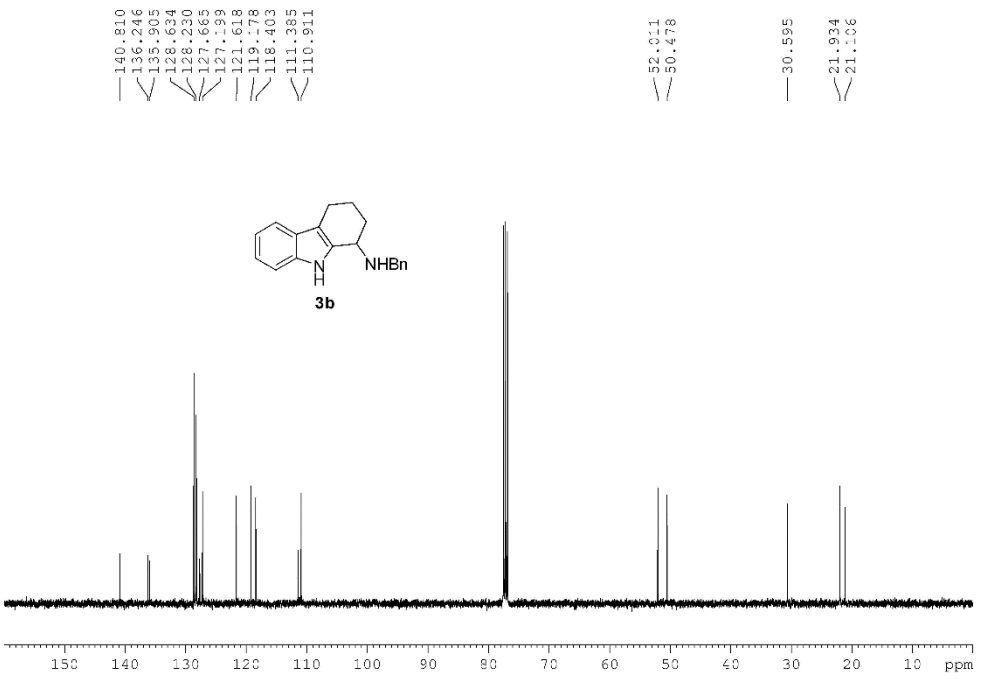
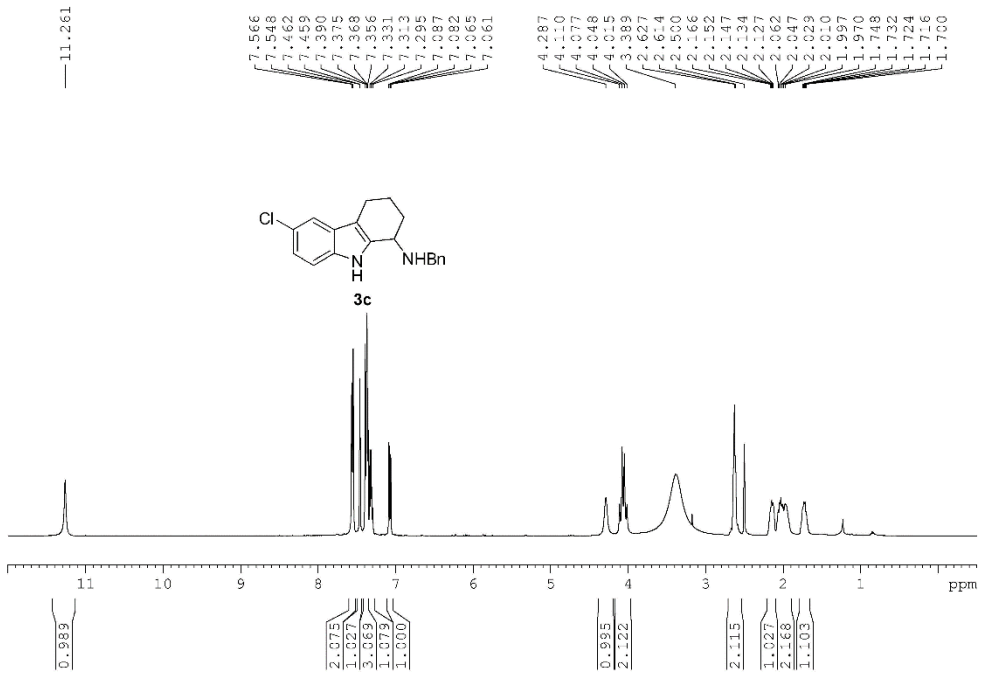
7.484
7.439
7.421
7.397
7.379
7.360
7.318
7.299
7.282
7.260
7.173
7.155
7.135
7.108
7.089
7.071
4.046
4.027
4.013
3.901
3.868
2.752
2.740
2.728
2.719
2.371
2.359
2.346
2.341
2.328
2.316
2.310
2.114
2.108
2.100
2.081
2.068
1.870
1.849
1.841
1.832
1.826
1.808
1.799
1.794
1.778
1.774
1.747
1.742
1.727
1.720
1.695
1.690
1.683
1.668
1.662
NHBn
3b
9
8
7
6
5
4
3
2
1
0
ppm
0.975
1.060
1.989
2.057
2.178
1.075
1.077
2.015
1.000
2.186
1.026
1.159
1.163
1.189


140.810
136.246
135.905
128.634
128.230
127.665
127.199
121.618
119.178
118.403
111.385
110.911
52.031
50.478
30.595
21.934
NHBn
3b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


11.261
7.566
7.548
7.462
7.459
7.390
7.375
7.368
7.356
7.331
7.313
7.295
7.087
7.082
7.065
7.061
4.287
4.110
4.077
4.048
4.015
3.389
2.627
2.614
2.500
2.166
2.152
2.147
2.134
2.127
2.062
2.047
2.029
2.010
1.997
1.970
1.748
1.732
1.724
1.716
1.700
Cl
N
H
NHBn
3c
11
10
9
8
7
6
5
4
3
2
1
ppm
0.988
2.075
1.027
3.069
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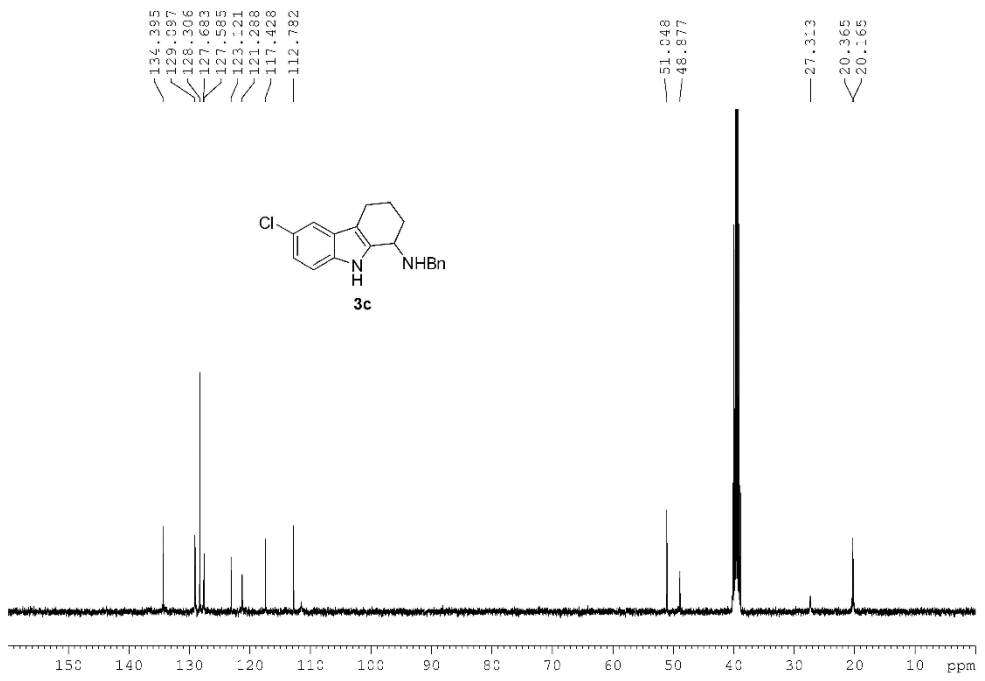
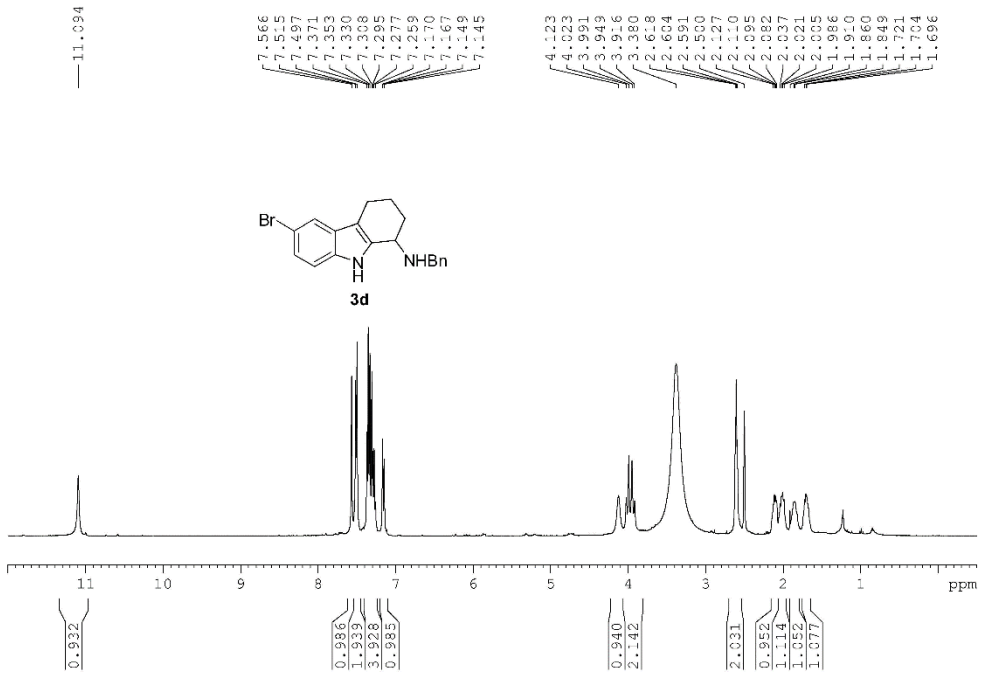
1.000
0.995
2.122
2.115
1.027
2.168
1.103


134.395
129.097
128.306
127.683
127.585
123.121
121.288
117.428
112.782
51.048
48.877
27.313
20.365
20.165
Cl
N
H
NHBn
3c
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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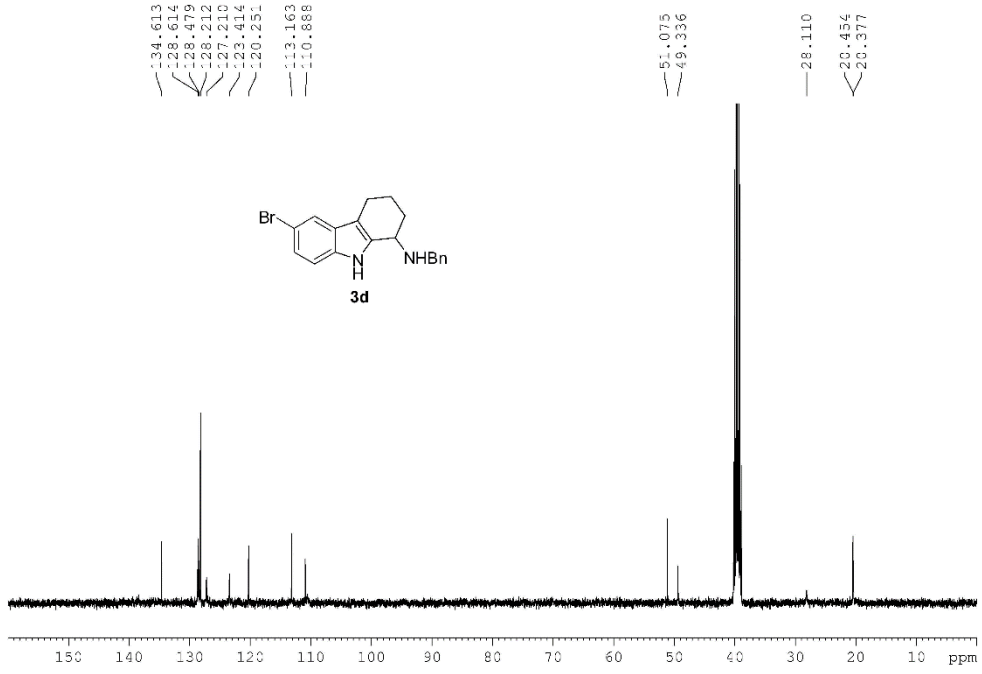
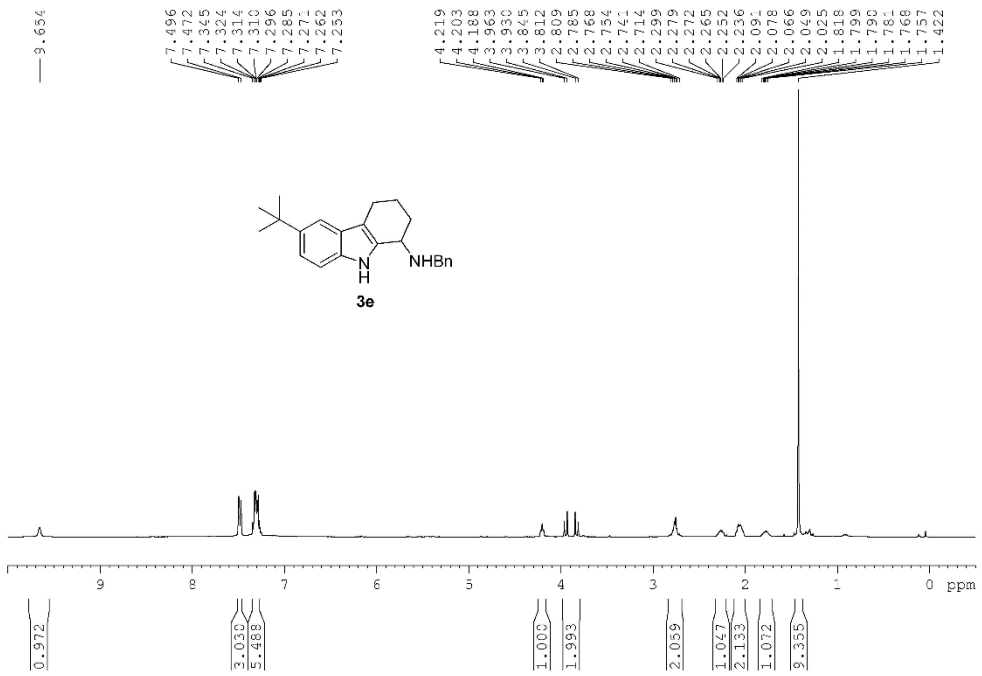
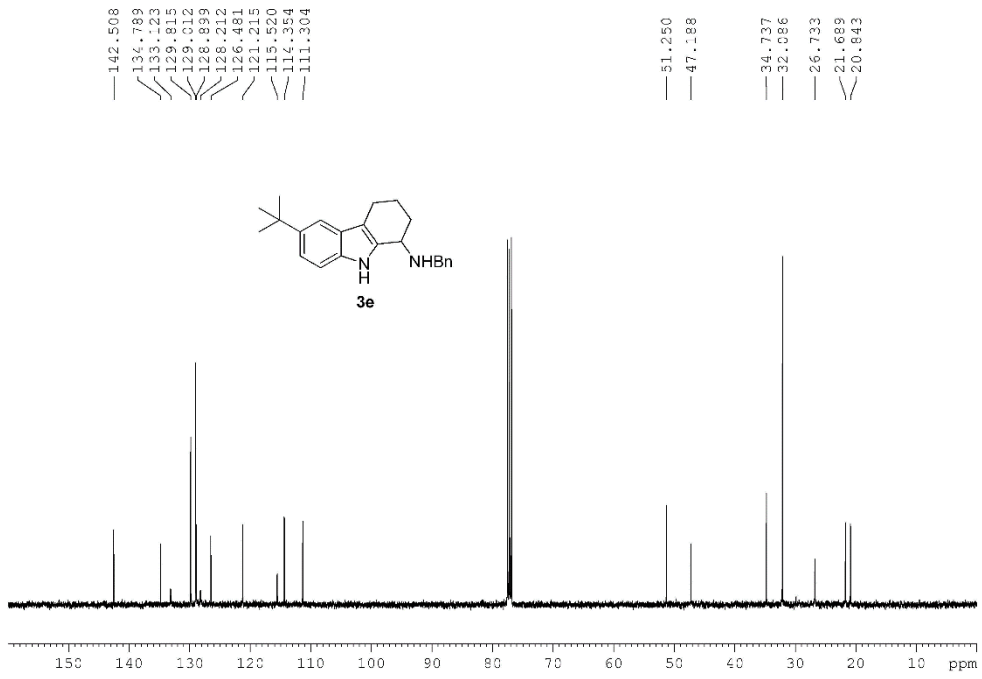
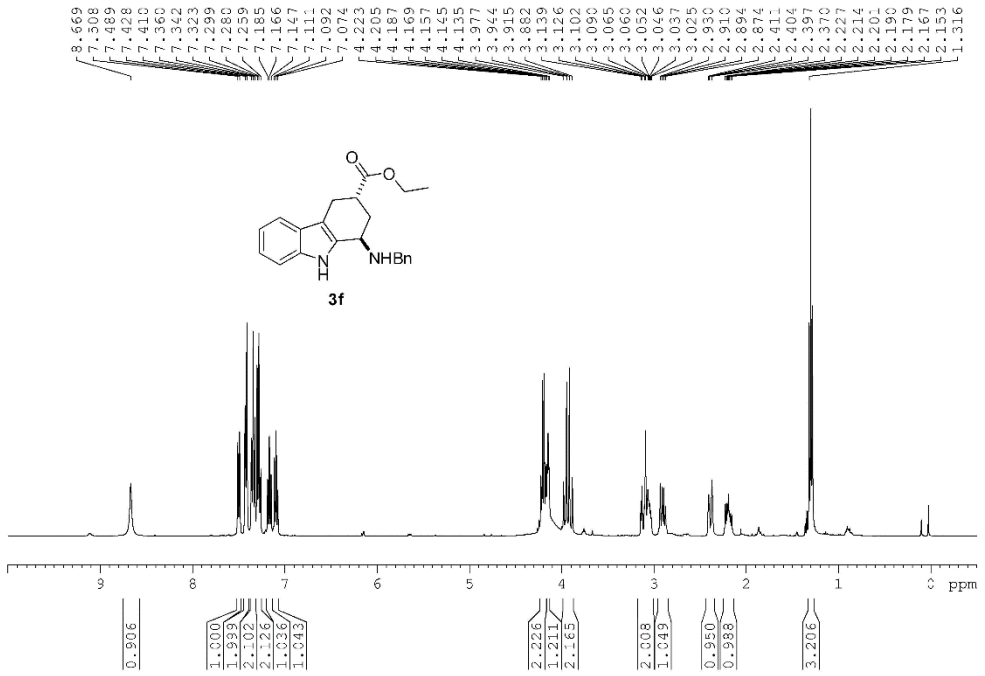
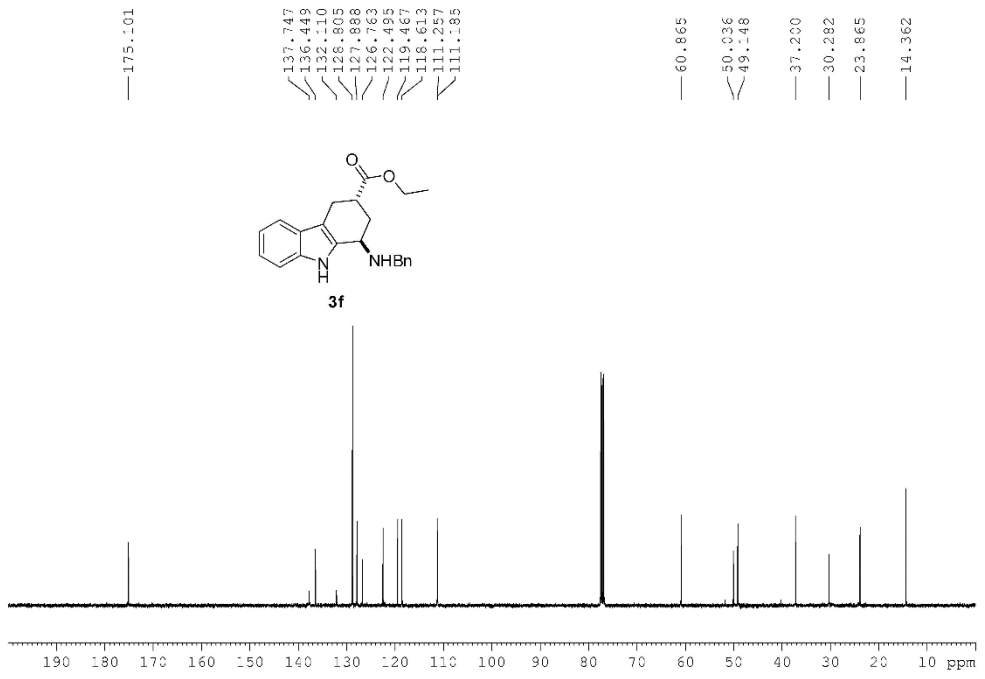
7.566
7.515
7.497
7.371
7.353
7.330
7.308
7.295
7.277
7.259
7.170
7.167
7.149
7.145
4.023
4.023
3.991
3.949
3.916
3.380
2.618
2.604
2.591
2.500
2.227
2.095
2.082
2.037
2.021
2.005
1.986
1.910
1.860
1.849
1.721
1.704
1.696
Br
N
H
NHBn
3d
11
10
9
8
7
6
5
4
3
2
1
ppm
0.932
0.986
1.939
3.928
0.985
0.940
2.142
2.031
0.952
1.114
1.052
1.077


134.613
128.614
128.479
128.212
127.210
123.414
120.252
113.163
110.888
51.075
49.336
28.110
20.454
20.377
Br
N
H
NHBn
3d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

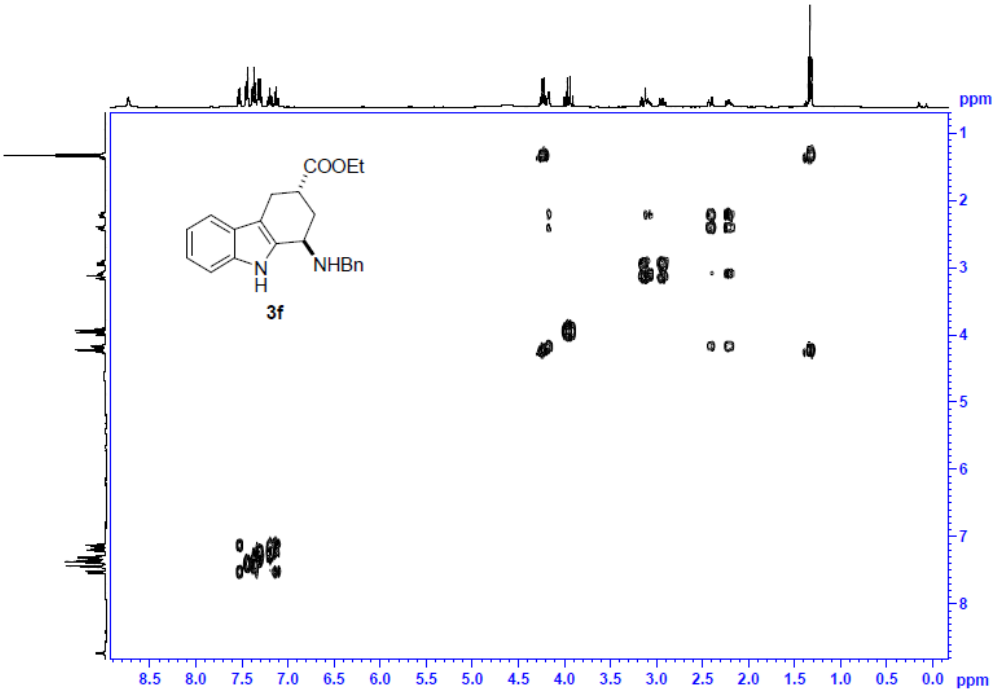

9.654
7.496
7.472
7.345
7.324
7.314
7.310
7.296
7.285
7.271
7.262
7.253
4.219
4.203
4.188
3.963
3.930
3.865
3.812
2.809
2.785
2.768
2.754
2.714
2.299
2.279
2.272
2.265
2.252
2.236
2.078
2.066
2.049
2.025
1.818
1.799
1.790
1.757
1.422
NHBn
3e
9
8
7
6
5
4
3
2
1
0 ppm
0.972
3.030
5.468
1.000
1.993
2.059
1.047
2.133
1.072
9.355

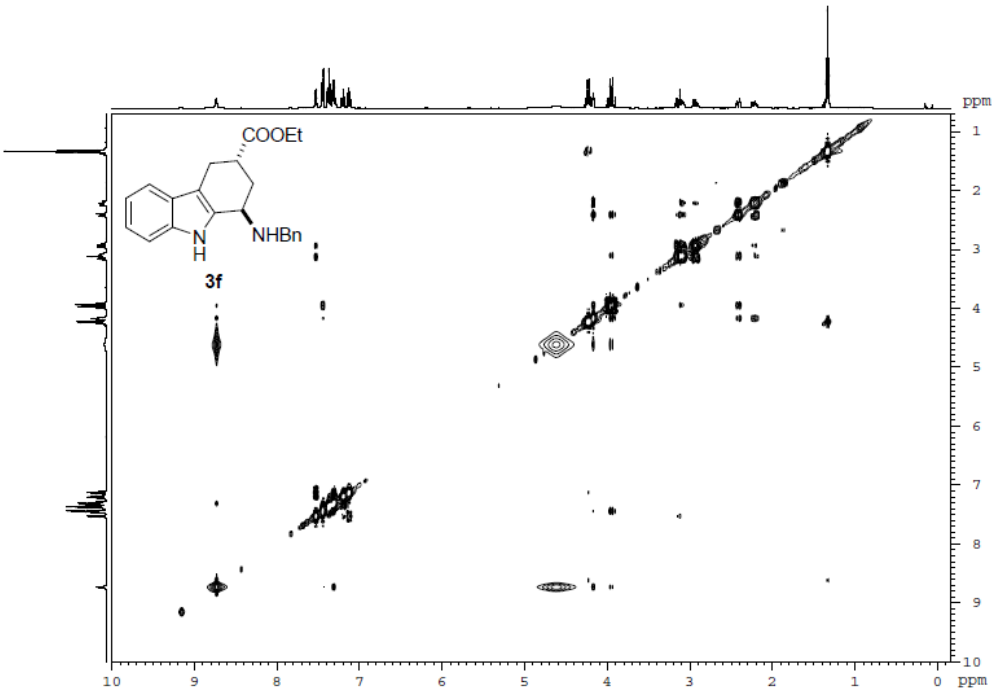

142.508
134.789
133.123
129.815
129.012
128.899
128.212
126.481
121.215
115.520
114.354
111.304
51.250
47.188
34.737
32.086
26.733
21.689
20.843
NHBn
3e
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

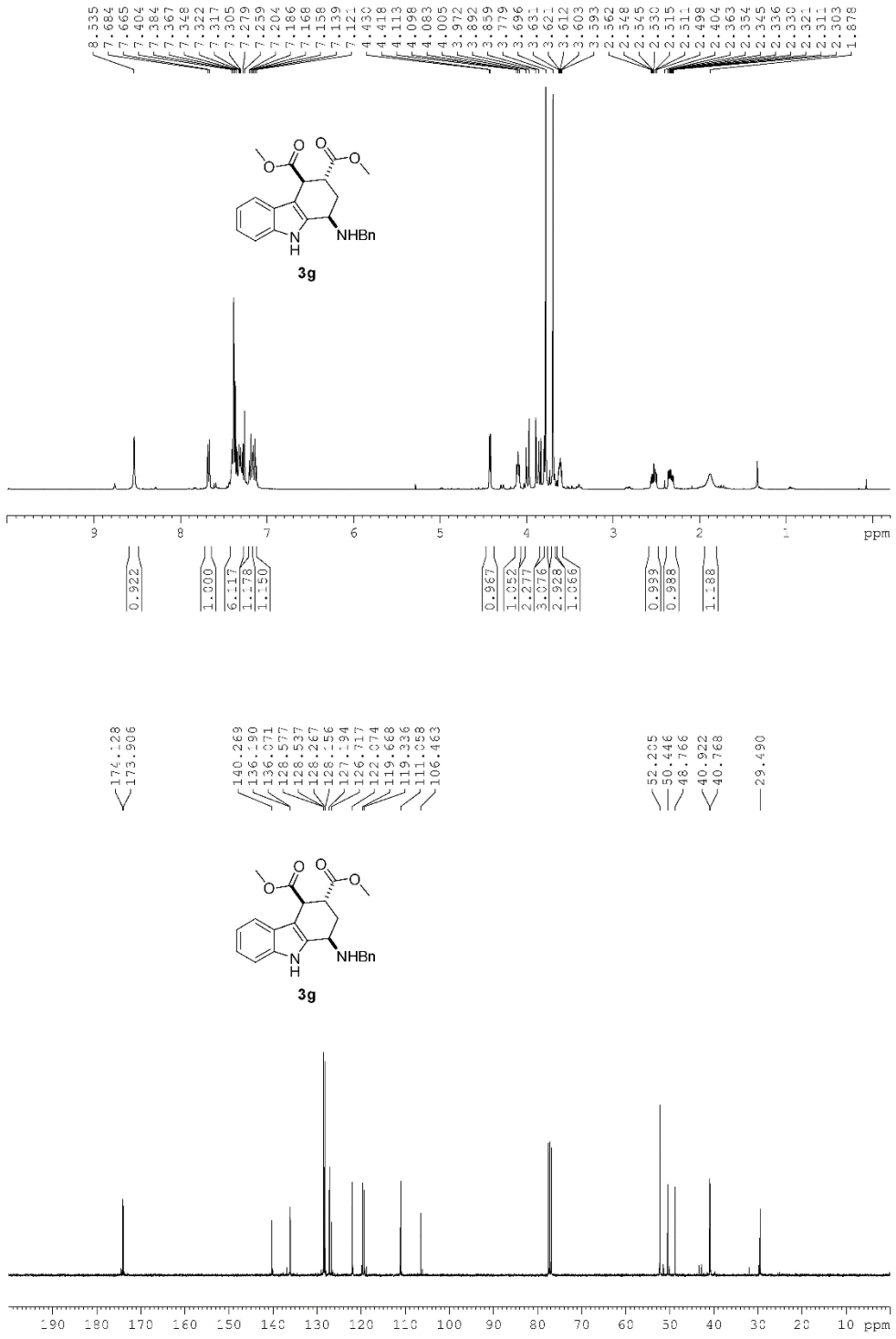

8.669
7.508
7.489
7.428
7.410
7.360
7.342
7.323
7.299
7.280
7.259
7.185
7.166
7.147
7.092
7.074
4.223
4.205
4.187
4.169
4.157
4.135
3.977
3.944
3.915
3.882
3.139
3.126
3.102
3.090
3.065
3.052
3.046
3.037
3.025
2.894
2.874
2.404
2.397
2.227
2.214
2.179
2.167
2.153
1.316
O
O
NHBn
N
H
3f
9
8
7
6
5
4
3
2
1
0
ppm
0.906
1.000
1.939
2.102
2.126
1.036
1.043
2.226
1.211
2.165
2.008
1.049
0.950
0.988
3.206

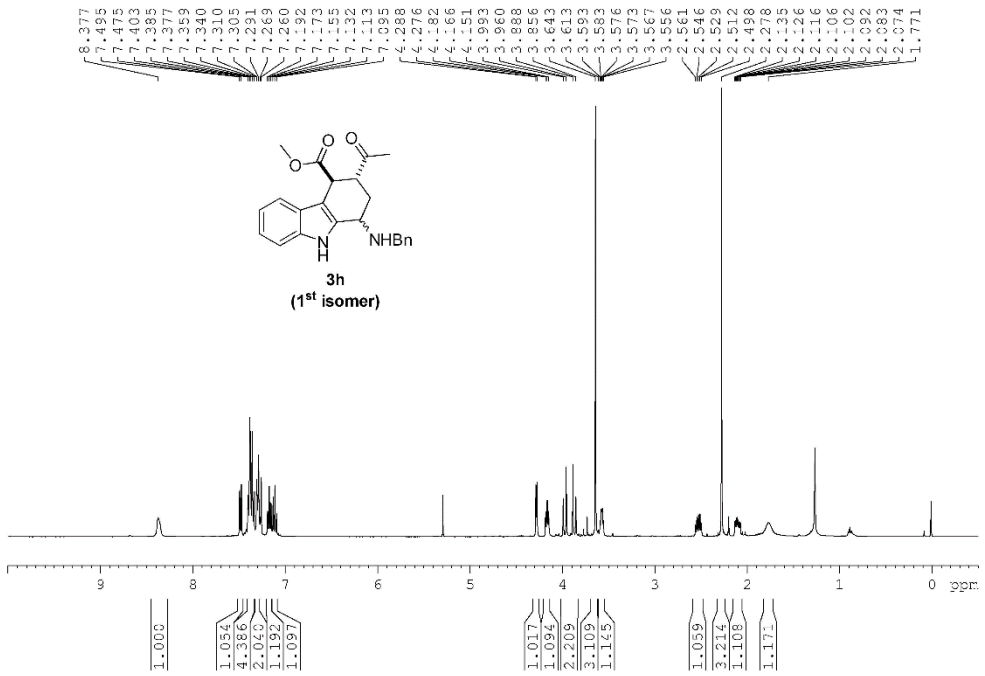

175.101
137.747
136.449
132.110
128.805
127.888
126.763
122.495
119.467
118.613
111.257
111.185
60.865
50.036
49.148
37.200
30.282
23.865
14.362
O
O
NHBn
N
H
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

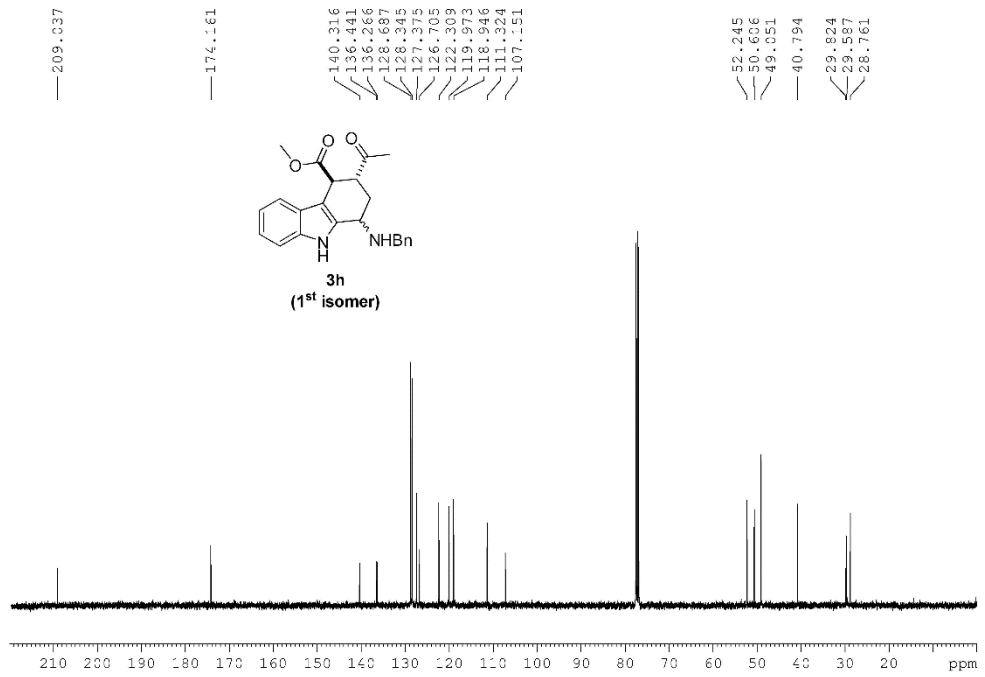
COSY and NOESY Spectra of compound **3f**

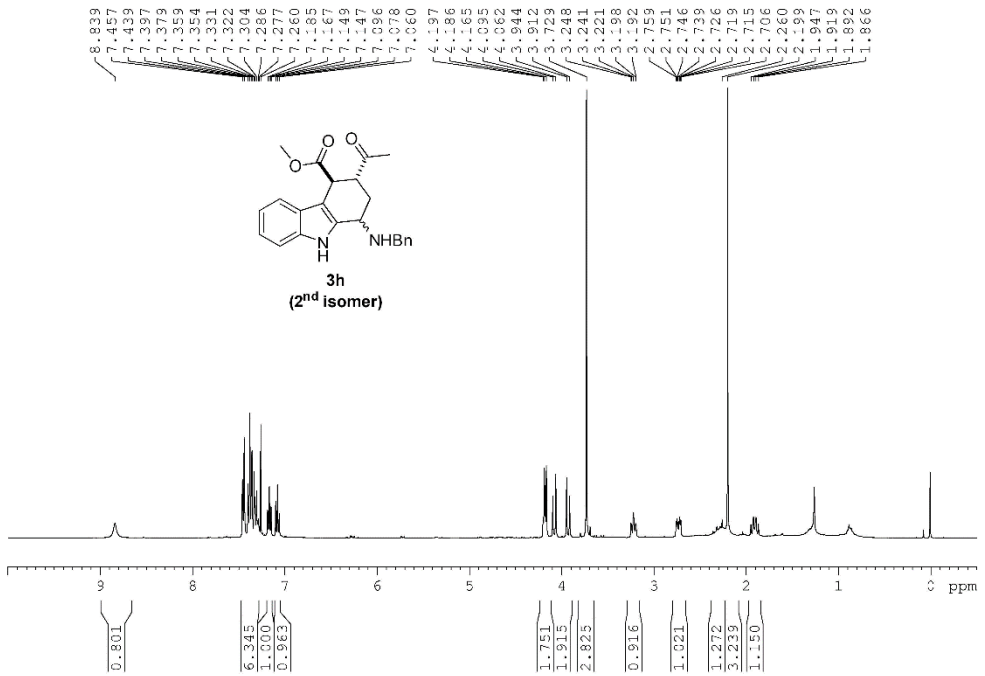


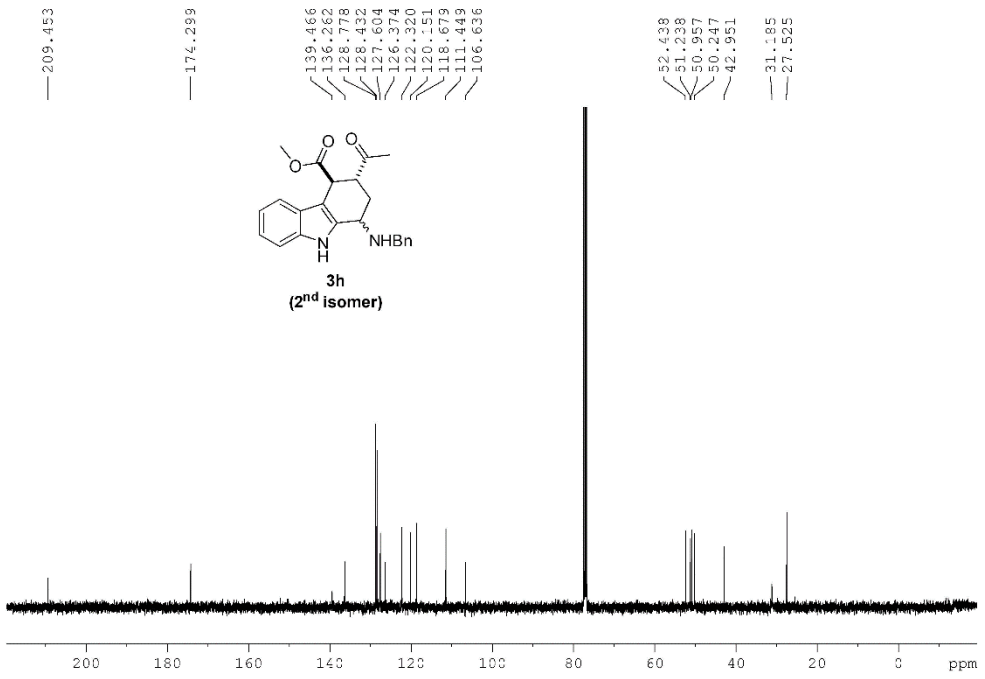


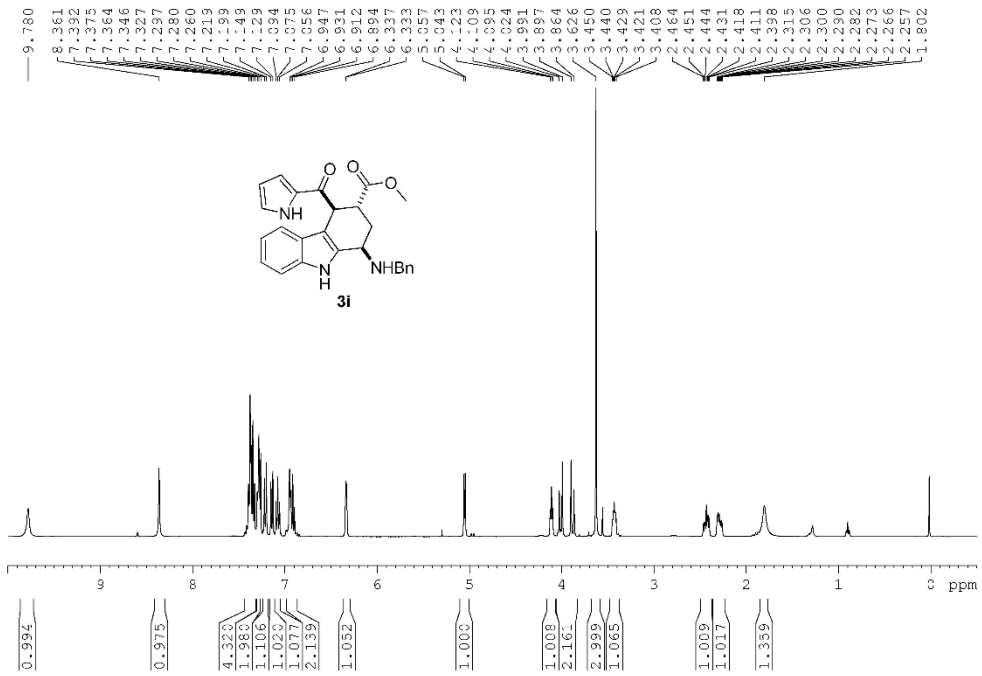

8.535
7.684
7.665
7.404
7.384
7.367
7.348
7.322
7.317
7.305
7.279
7.259
7.204
7.186
7.168
7.158
7.139
4.418
4.113
4.098
4.083
4.005
3.972
3.892
3.859
3.779
3.696
3.631
3.612
3.603
3.593
2.562
2.548
2.545
2.530
2.515
2.498
2.404
2.363
2.354
2.345
2.336
2.330
2.311
2.303
1.878
O
O
O
O
N
H
NHBn
3g
9
8
7
6
5
4
3
2
1
ppm
0.922
1.000
6.117
1.178
1.150
0.967
1.052
2.277
3.076
2.928
1.066
0.999
0.988
1.188
174.128
173.906
140.269
136.190
136.071
128.577
128.537
128.267
128.156
127.194
126.717
122.074
119.668
119.336
111.058
106.463
52.255
50.446
48.766
40.922
40.768
29.490
O
O
O
O
N
H
NHBn
3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.377
7.495
7.475
7.403
7.385
7.377
7.359
7.340
7.310
7.305
7.291
7.269
7.260
7.173
7.155
7.132
7.113
7.035
4.288
4.276
4.182
4.166
4.151
3.993
3.960
3.888
3.856
3.643
3.613
3.593
3.583
3.576
3.573
3.567
3.556
2.561
2.546
2.529
2.512
2.488
2.278
2.235
2.226
2.216
2.206
2.092
2.083
2.074
1.771
NHBn
3h
(1st isomer)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.054
4.386
2.040
1.192
1.097
1.017
1.094
2.209
3.109
1.145
1.059
3.214
1.108
1.172


209.037
174.161
140.316
136.441
136.266
128.687
128.345
127.375
126.705
122.309
119.973
118.946
111.324
107.151
52.245
50.636
49.051
40.794
29.824
29.587
28.761
NHBn
3h
(1st isomer)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.839
7.457
7.439
7.397
7.379
7.359
7.354
7.331
7.322
7.304
7.286
7.277
7.260
7.185
7.167
7.149
7.147
7.096
7.078
7.060
4.197
4.186
4.165
4.035
4.032
3.944
3.912
3.729
3.248
3.241
3.221
3.198
3.192
2.759
2.751
2.746
2.739
2.726
2.719
2.715
2.706
2.260
2.199
1.947
1.918
1.892
1.866
NHBn
3h
(2nd isomer)
9
8
7
6
5
4
3
2
1
0
ppm
0.801
6.345
1.000
0.963
1.751
1.915
2.825
0.916
1.021
1.272
3.239
1.150


209.453
174.299
139.466
136.262
128.778
128.432
127.604
126.374
122.320
120.151
118.679
111.449
106.636
52.438
51.238
50.957
50.247
42.951
31.185
27.525
NHBn
3h
(2nd isomer)
200
180
160
140
120
100
80
60
40
20
0
ppm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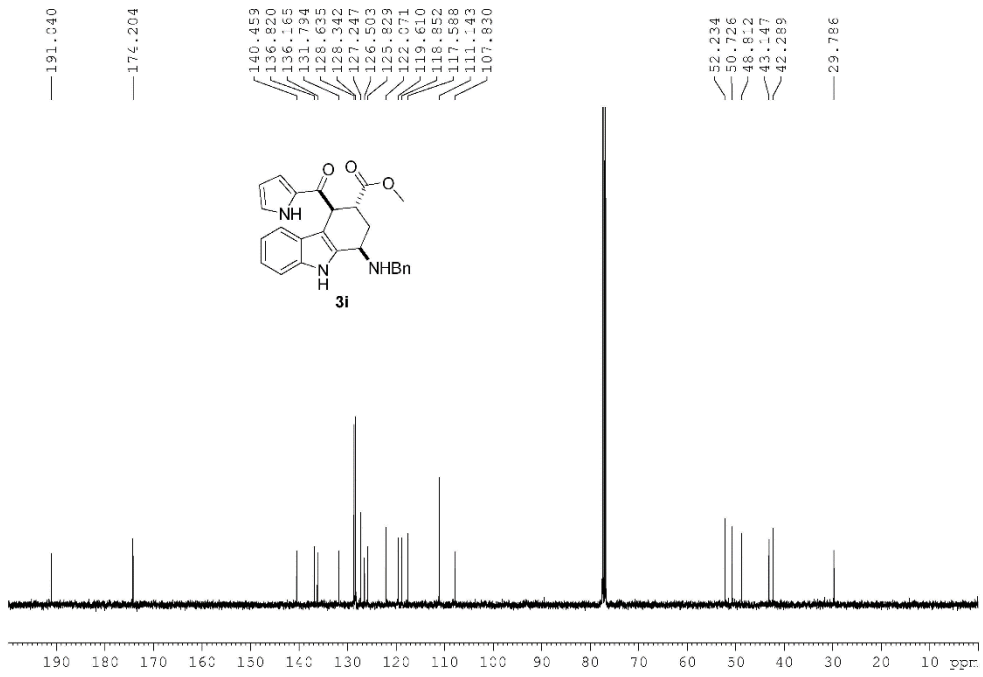
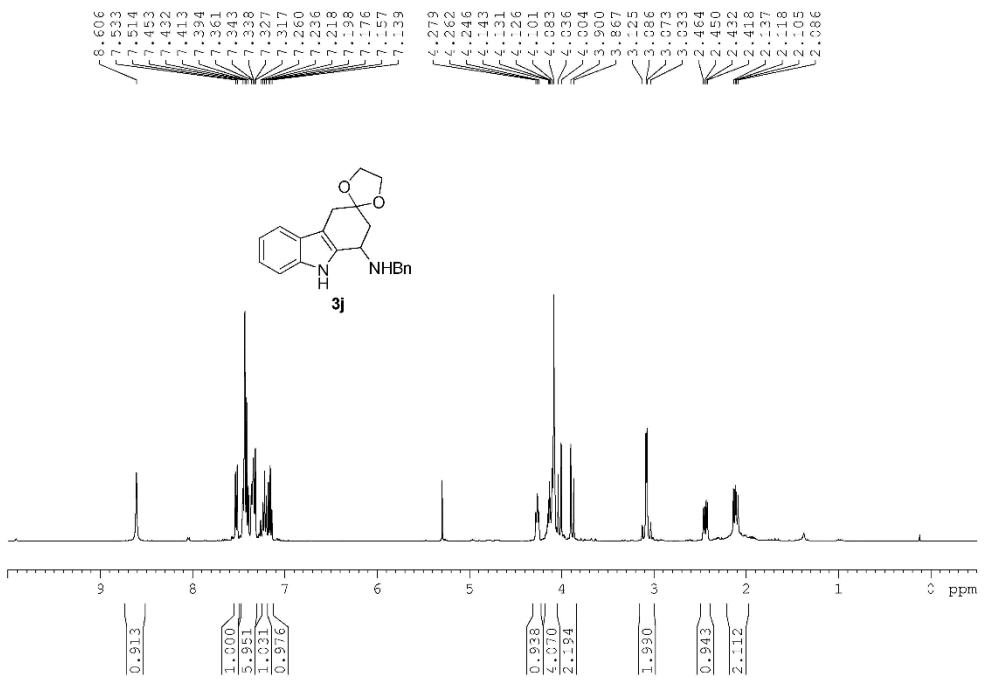
8.361
7.392
7.375
7.364
7.346
7.327
7.297
7.280
7.260
7.219
7.199
7.149
7.129
7.094
7.075
7.056
6.947
6.931
6.912
6.894
6.337
6.333
5.057
5.043
4.223
4.209
4.095
4.024
3.991
3.887
3.864
3.626
3.450
3.440
3.423
3.421
3.408
2.464
2.451
2.444
2.431
2.418
2.411
2.398
2.315
2.306
2.300
2.290
2.282
2.273
2.266
2.257
1.802
O
O
O
NH
N
H
NHBn
3i
ppm
0.994
0.975
4.320
1.986
1.106
1.020
1.077
2.139
1.052
1.000
1.008
2.162
2.999
1.065
1.009
1.017
1.359


191.040
174.204
140.459
136.820
136.765
131.794
128.635
128.342
127.247
126.503
125.829
122.071
119.610
118.852
117.588
111.143
107.830
52.234
50.726
48.822
43.147
42.289
29.786
O
O
O
NH
N
H
NHBn
3i
ppm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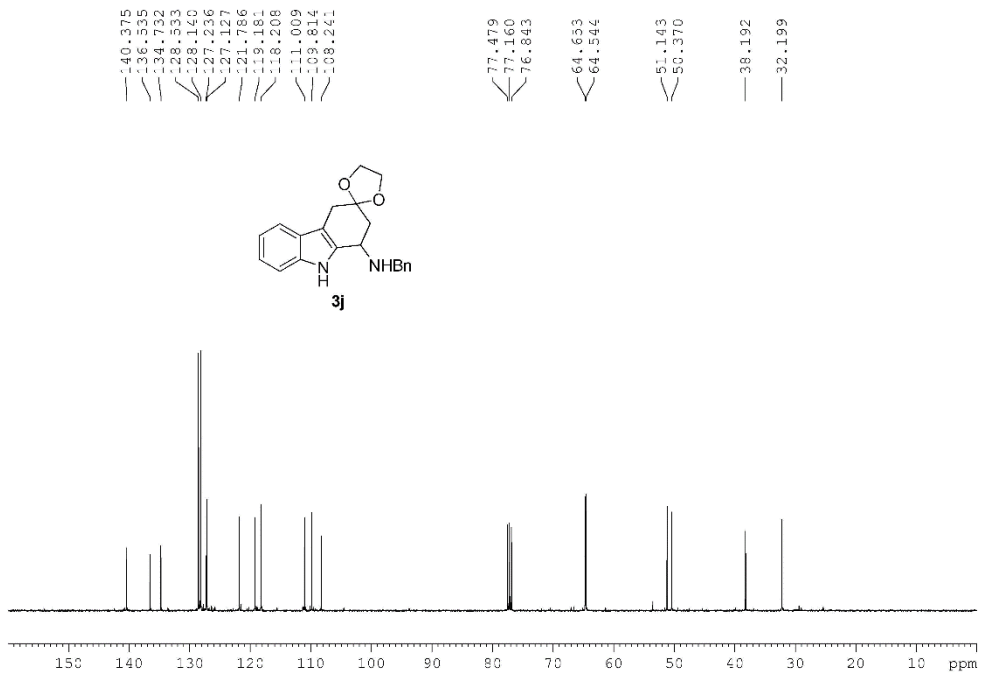
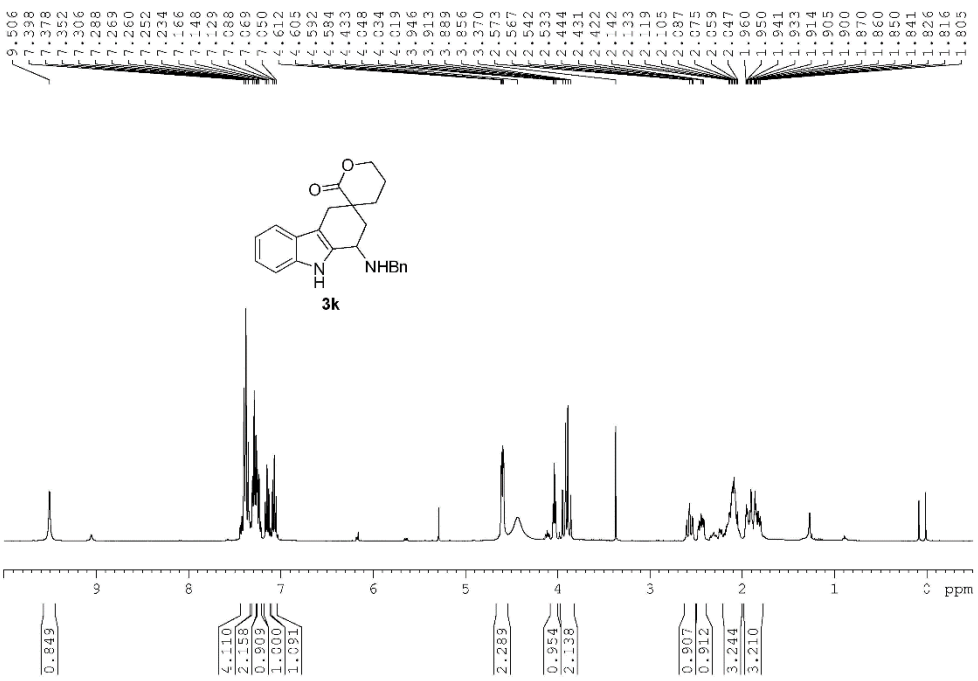
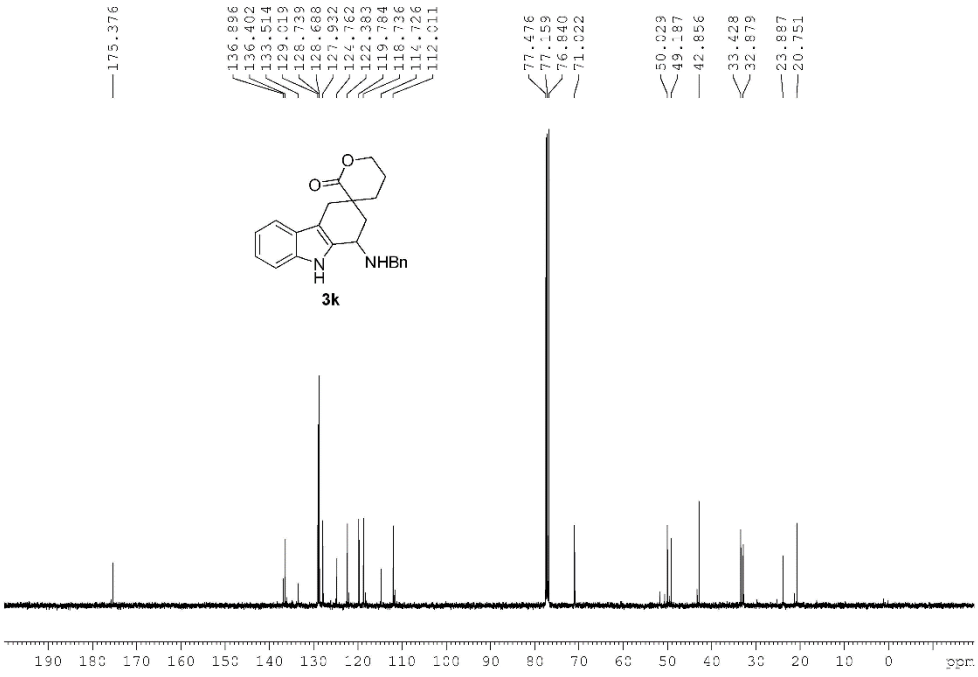
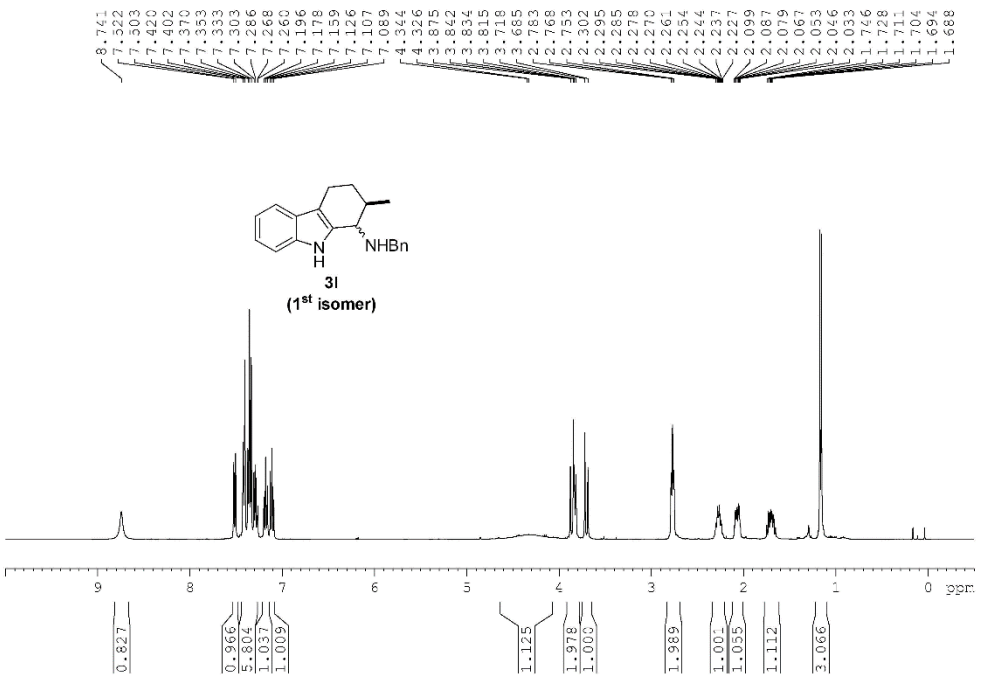
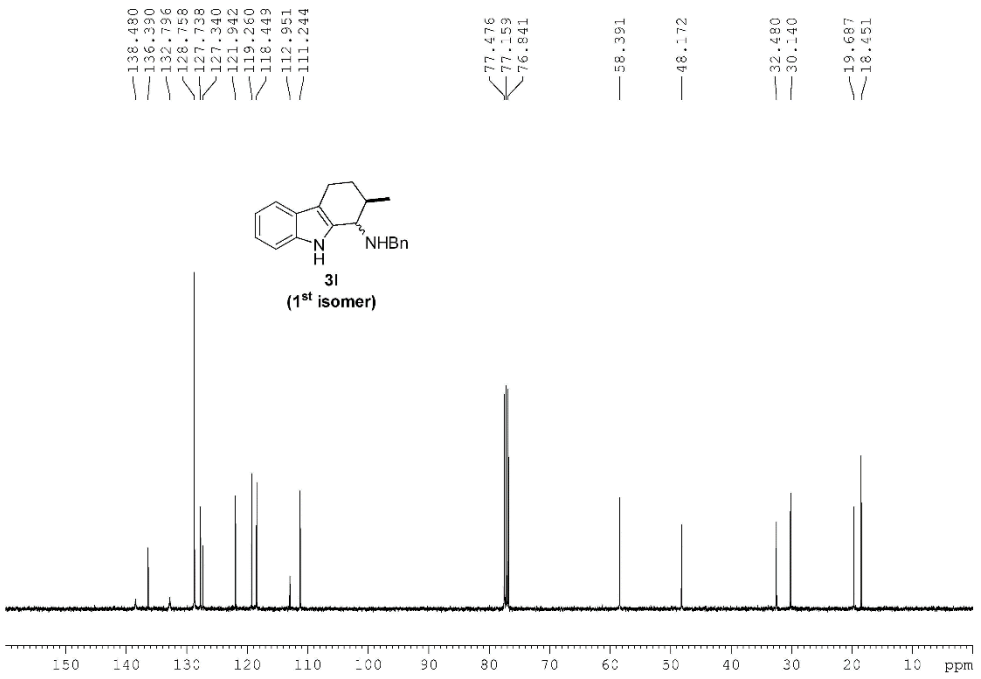
7.533
7.514
7.453
7.432
7.413
7.394
7.361
7.343
7.338
7.327
7.317
7.260
7.236
7.218
7.198
7.176
7.157
7.139
4.279
4.262
4.246
4.243
4.231
4.126
4.101
4.083
4.036
4.004
3.900
3.867
3.125
3.086
3.073
3.033
2.464
2.450
2.432
2.418
2.137
2.118
2.105
2.086
NHBn
3j
ppm
0.913
1.000
3.951
1.031
0.976
0.938
4.070
2.284
1.930
0.943
2.212

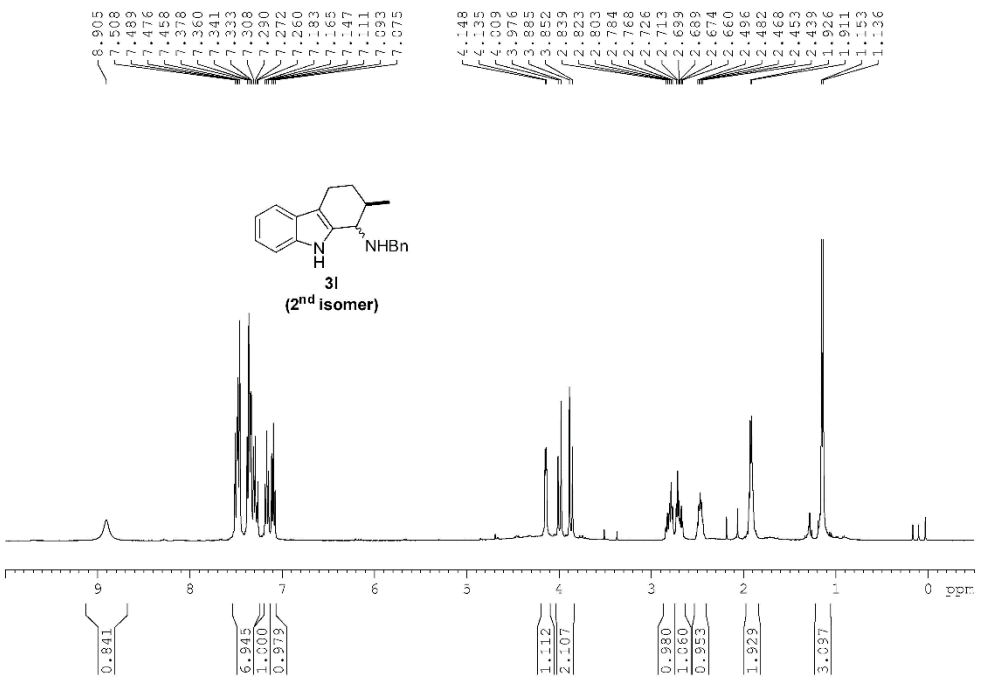

140.375
136.535
134.732
128.533
128.140
127.236
127.127
121.786
119.181
118.208
111.009
109.814
108.241
77.479
77.160
76.843
64.633
64.544
51.143
50.370
38.192
32.199
NHBn
3j
ppm

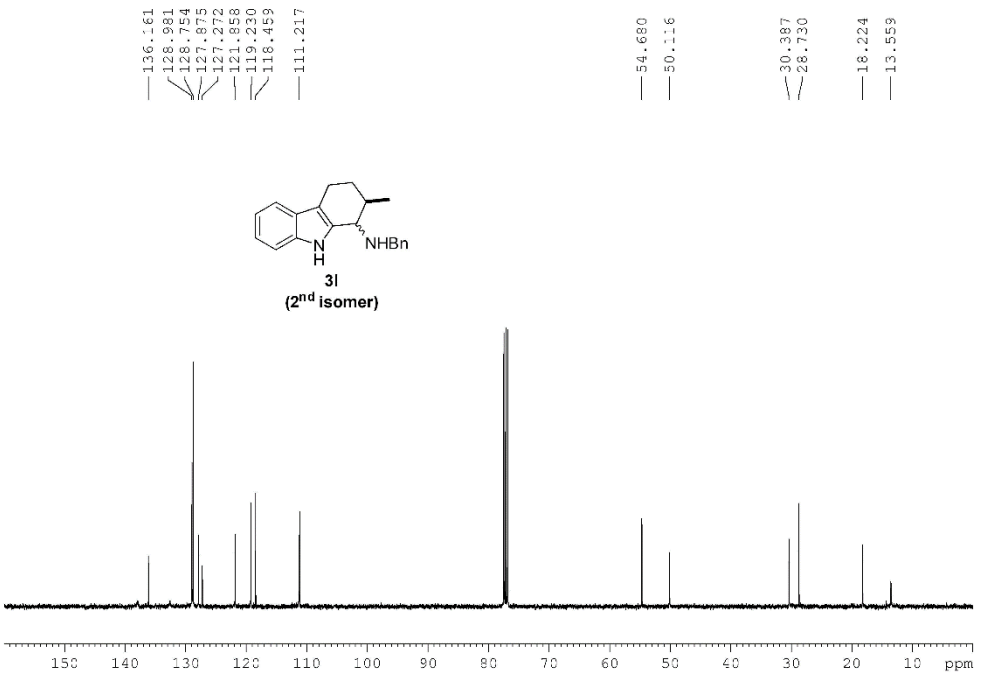

9.506
7.398
7.378
7.352
7.306
7.288
7.269
7.260
7.252
7.234
7.166
7.148
7.129
7.088
7.069
7.050
4.612
4.605
4.592
4.584
4.433
4.048
4.034
4.019
3.946
3.913
3.889
3.856
3.370
2.573
2.567
2.542
2.533
2.444
2.431
2.422
2.142
2.133
2.119
2.105
2.087
2.075
2.059
2.047
1.960
1.950
1.941
1.933
1.914
1.905
1.900
1.870
1.860
1.850
1.841
1.826
1.816
1.805
O
O
N
H
NHBn
3k
9
8
7
6
5
4
3
2
1
0
ppm
0.843
4.110
2.158
0.903
1.000
1.091
2.289
0.954
2.138
0.907
0.912
3.244
3.210

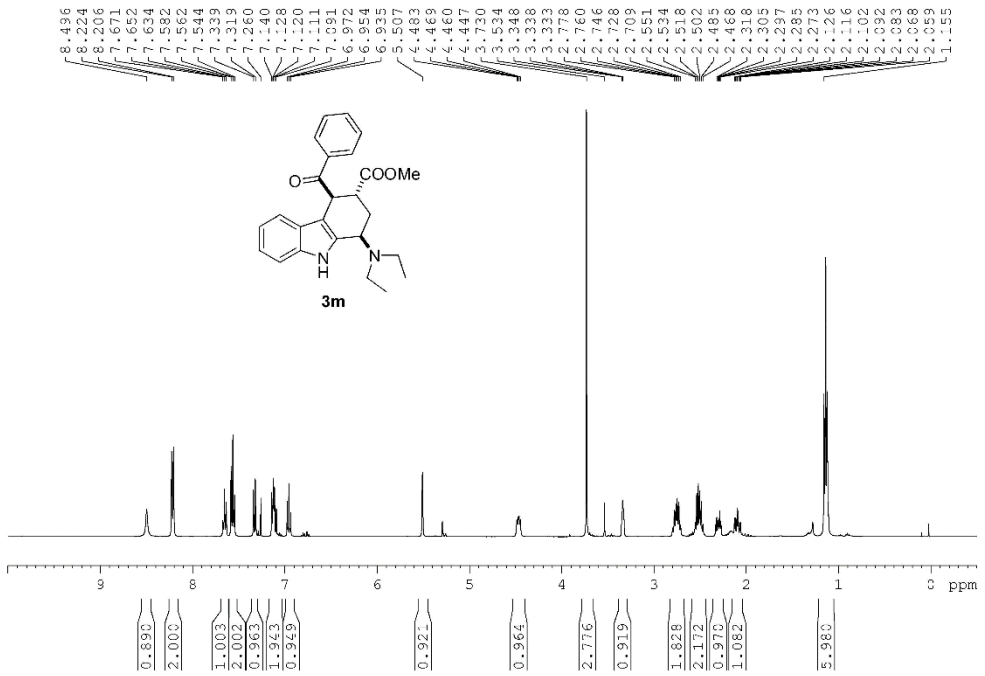

175.376
136.896
136.402
133.514
129.019
128.739
128.688
127.932
124.762
122.383
119.784
118.736
114.726
112.011
77.476
77.159
76.840
71.022
50.029
49.187
42.856
33.428
32.879
23.887
20.751
O
O
N
H
NHBn
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.741
7.522
7.303
7.420
7.402
7.370
7.353
7.333
7.303
7.286
7.268
7.260
7.196
7.178
7.159
7.126
7.107
7.089
4.344
4.326
3.875
3.842
3.834
3.815
3.718
3.685
2.783
2.768
2.753
2.302
2.295
2.285
2.278
2.270
2.261
2.254
2.244
2.237
2.227
2.099
2.087
2.079
2.067
2.053
2.046
2.033
1.746
1.728
1.711
1.704
1.694
1.688
NHBn
3l
(1st isomer)
ppm
0.827
0.966
5.804
1.037
1.009
1.125
1.978
1.989
1.055
1.112
3.066


138.480
136.390
132.796
128.758
127.738
127.340
121.942
119.260
118.449
112.951
111.244
77.476
77.159
76.841
58.391
48.172
32.480
30.140
19.687
18.451
NHBn
3l
(1st isomer)
ppm


8.905
7.508
7.489
7.476
7.458
7.378
7.360
7.341
7.333
7.308
7.290
7.272
7.260
7.183
7.165
7.147
7.111
7.093
7.075
4.148
4.135
4.009
3.976
3.885
3.852
2.839
2.823
2.803
2.784
2.768
2.726
2.713
2.699
2.689
2.674
2.660
2.486
2.482
2.468
2.453
2.439
1.926
1.911
1.153
1.136
NHBn
3l
(2nd isomer)
9
8
7
6
5
4
3
2
1
0
ppm
0.841
6.945
1.000
0.979
1.112
2.107
0.980
1.060
0.953
1.929
3.097


136.161
128.981
128.754
127.875
127.272
121.858
119.230
118.459
111.217
54.680
50.116
30.387
28.730
18.224
13.559
NHBn
3l
(2nd isomer)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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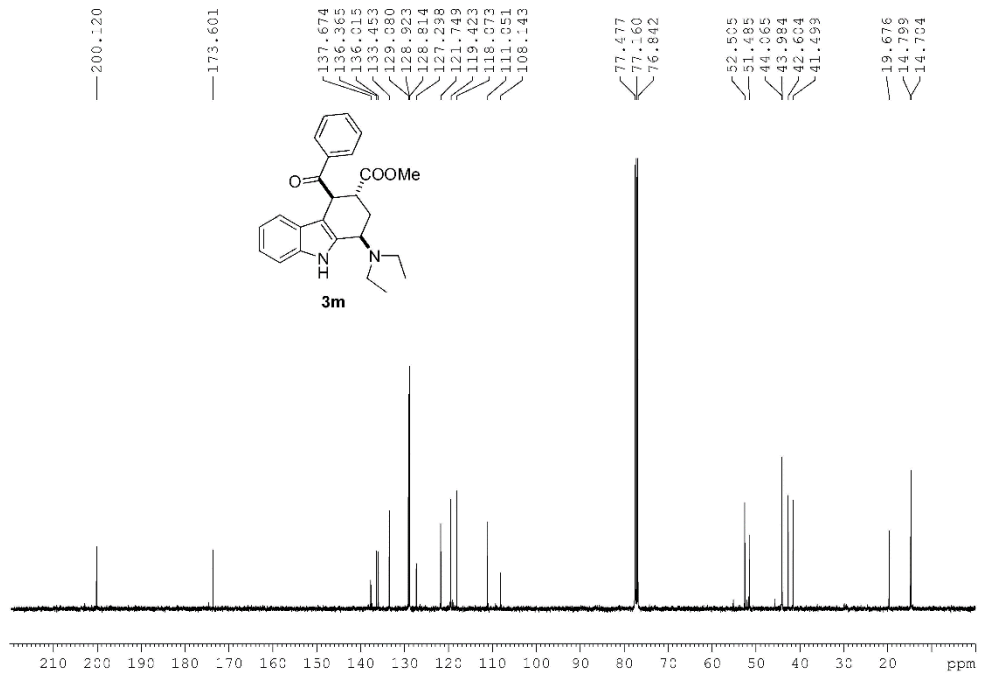
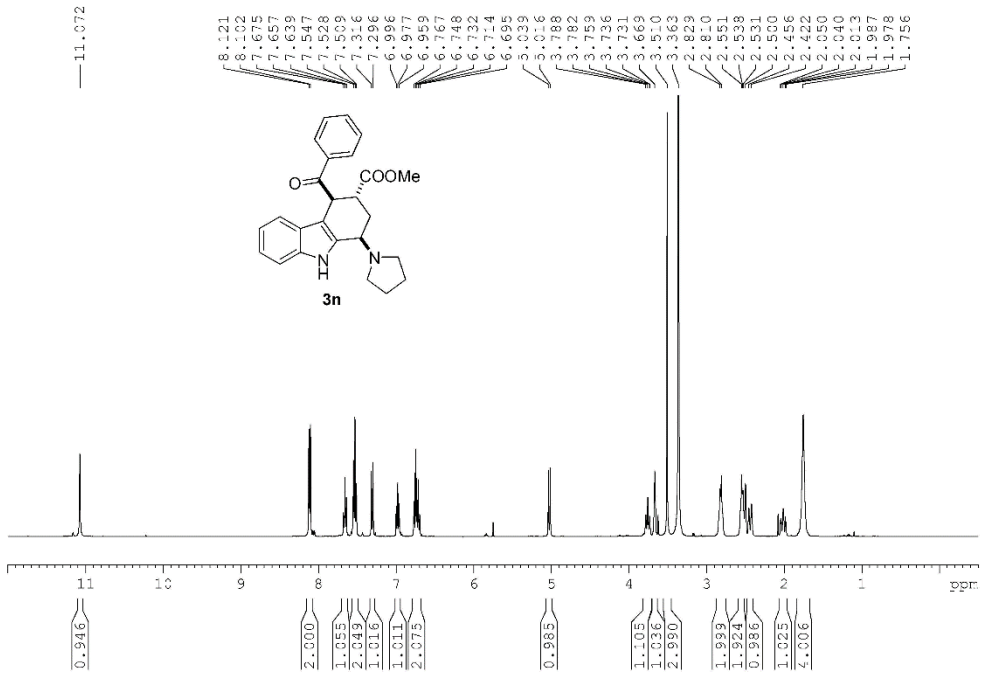
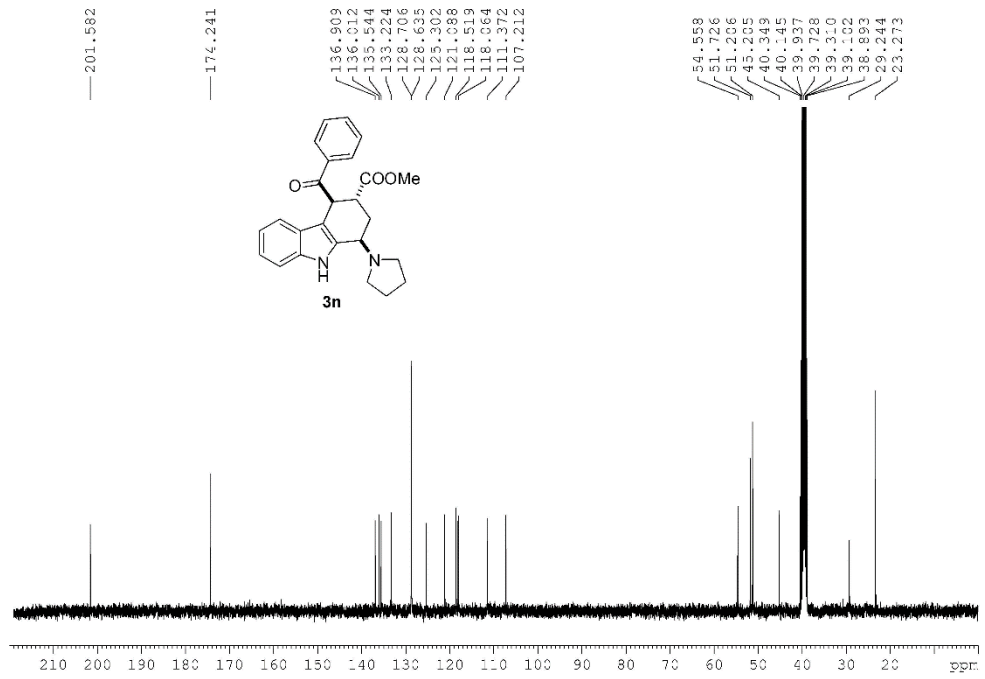
8.224
8.206
7.671
7.652
7.634
7.582
7.562
7.544
7.339
7.319
7.260
7.140
7.128
7.120
7.111
7.091
6.972
6.954
6.935
5.507
4.483
4.469
4.460
4.447
3.730
3.534
3.348
3.338
3.333
2.778
2.760
2.746
2.728
2.709
2.551
2.534
2.518
2.502
2.485
2.468
2.318
2.305
2.297
2.285
2.273
2.126
2.116
2.102
2.092
2.083
2.068
2.059
1.255
COOMe
N
H
N
3m
9
8
7
6
5
4
3
2
1
0
ppm
0.890
2.000
1.003
2.002
0.963
1.943
0.929
0.922
0.964
2.776
0.919
1.828
2.172
0.976
1.082
5.980


200.220
173.601
137.674
136.365
136.015
133.453
129.080
128.923
128.814
127.298
121.749
119.423
118.073
111.051
108.143
77.477
77.160
76.842
52.505
51.485
44.085
43.984
42.604
41.499
19.676
14.799
14.704
COOMe
N
H
N
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


11.072
8.121
8.102
7.675
7.657
7.639
7.547
7.528
7.509
7.316
7.296
6.996
6.977
6.959
6.767
6.748
6.732
6.714
6.695
5.039
3.788
3.782
3.759
3.736
3.731
3.669
3.510
3.363
2.829
2.810
2.551
2.538
2.531
2.500
2.456
2.422
2.050
2.040
2.013
1.987
1.978
1.756
COOMe
O
N
H
N
3n
11
10
9
8
7
6
5
4
3
2
1
ppm
0.946
2.000
1.055
2.049
1.018
1.011
2.075
0.985
1.105
1.036
2.990
1.993
1.924
0.986
1.025
4.006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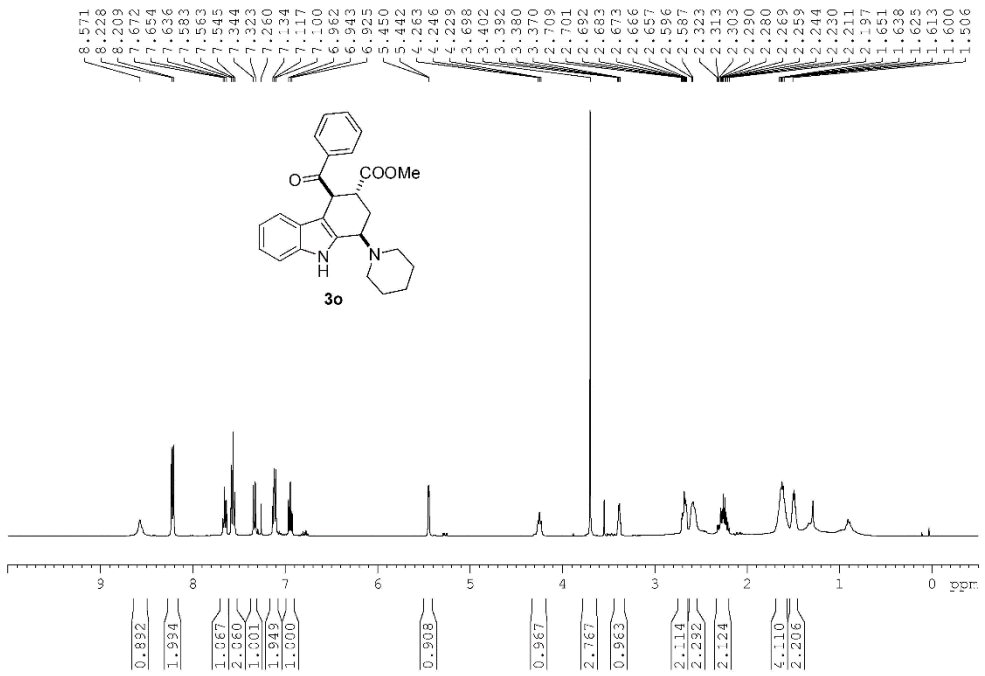
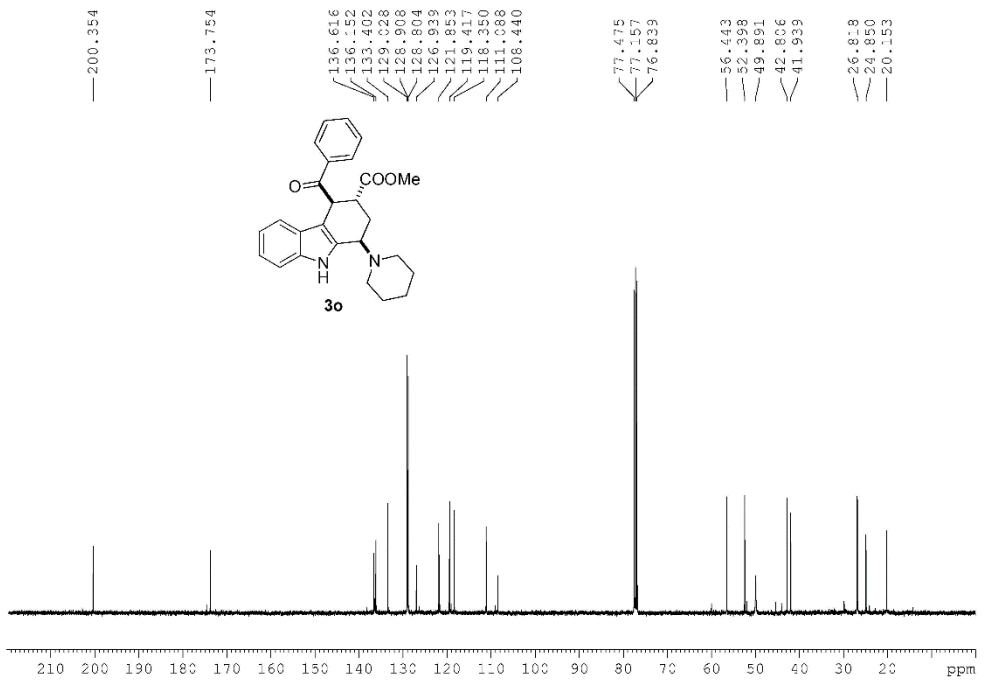
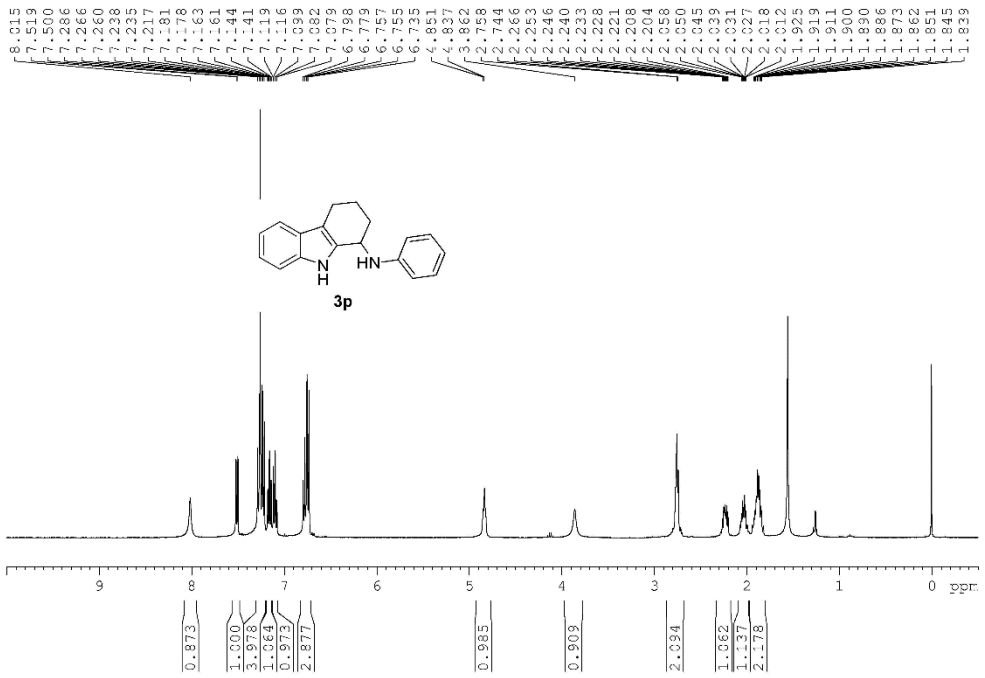
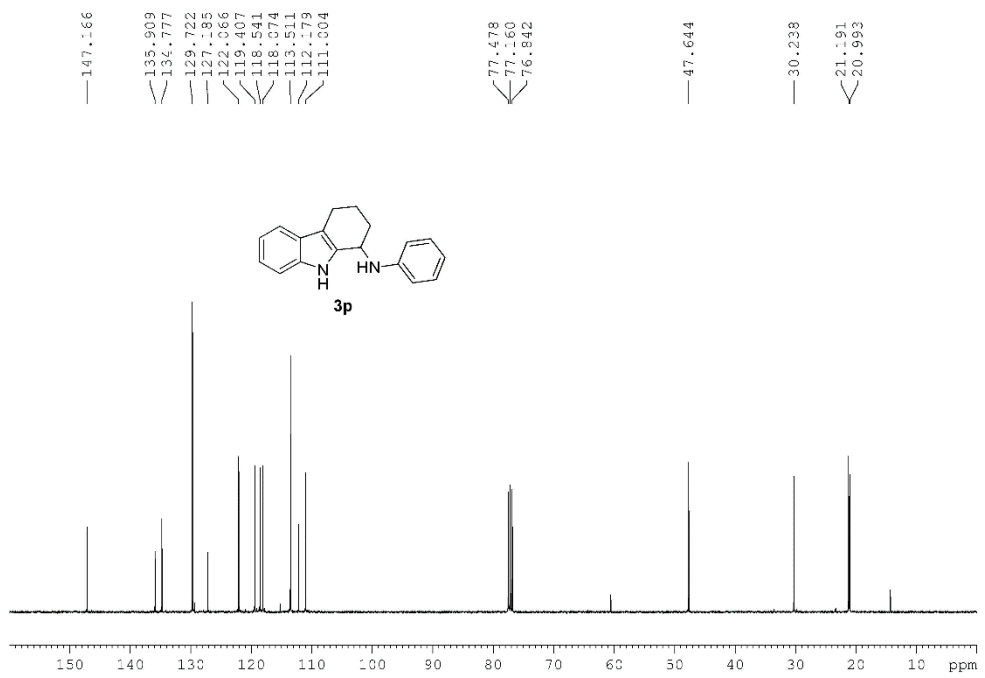
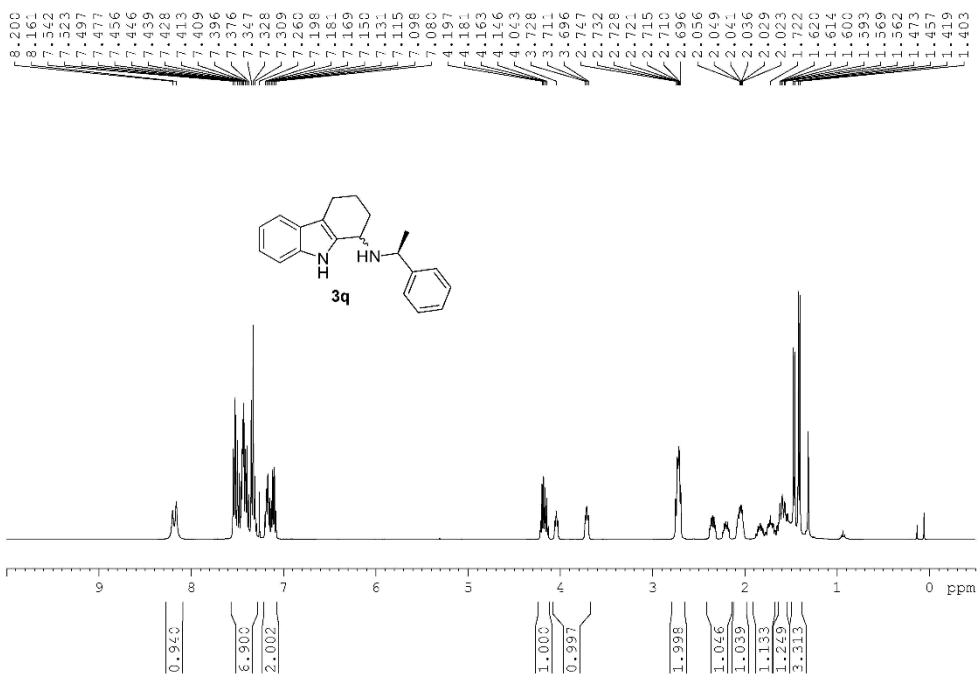
174.241
136.909
136.012
135.544
133.224
128.706
128.635
125.302
121.088
118.519
118.064
111.372
107.212
54.558
51.726
51.206
45.205
40.349
40.145
39.937
39.728
39.310
39.102
38.893
29.244
23.273
COOMe
O
N
H
N
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

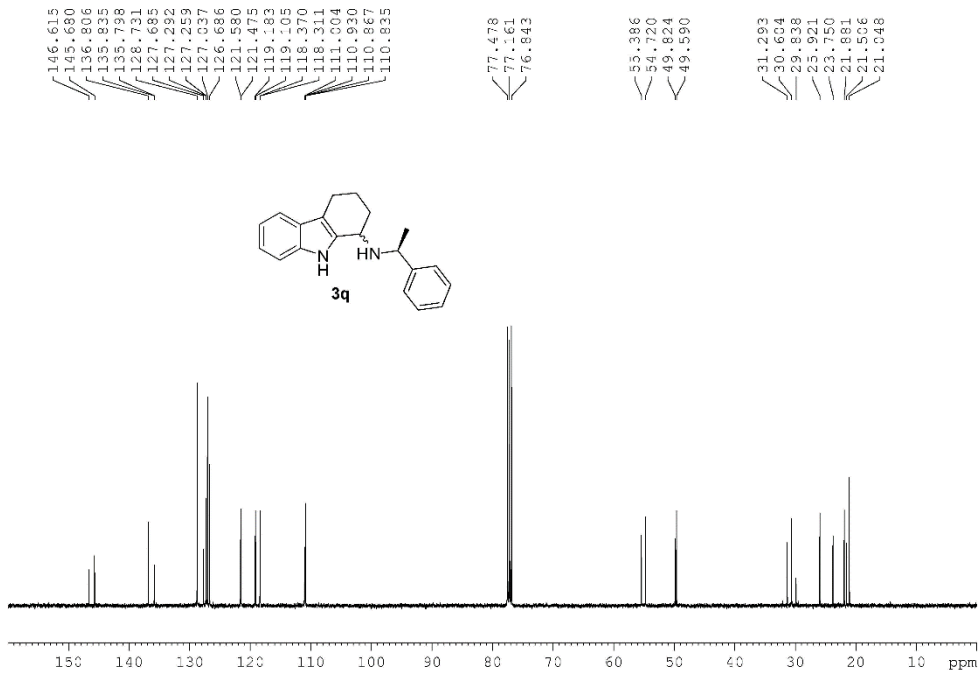

8.571
8.228
8.209
7.672
7.654
7.636
7.583
7.563
7.545
7.344
7.323
7.260
7.134
7.117
7.100
6.962
6.943
6.925
5.450
5.442
4.263
4.246
4.229
3.698
3.402
3.392
3.380
3.370
2.709
2.701
2.692
2.683
2.673
2.666
2.657
2.596
2.587
2.323
2.313
2.303
2.290
2.280
2.269
2.259
2.244
2.230
2.211
2.197
1.651
1.638
1.625
1.613
1.600
1.506
COOMe
O
N
H
N
3o
9
8
7
6
5
4
3
2
1
0
ppm
0.892
1.934
1.067
2.060
1.001
1.949
1.000
0.908
0.967
2.767
0.963
2.114
2.292
2.124
4.110
2.206

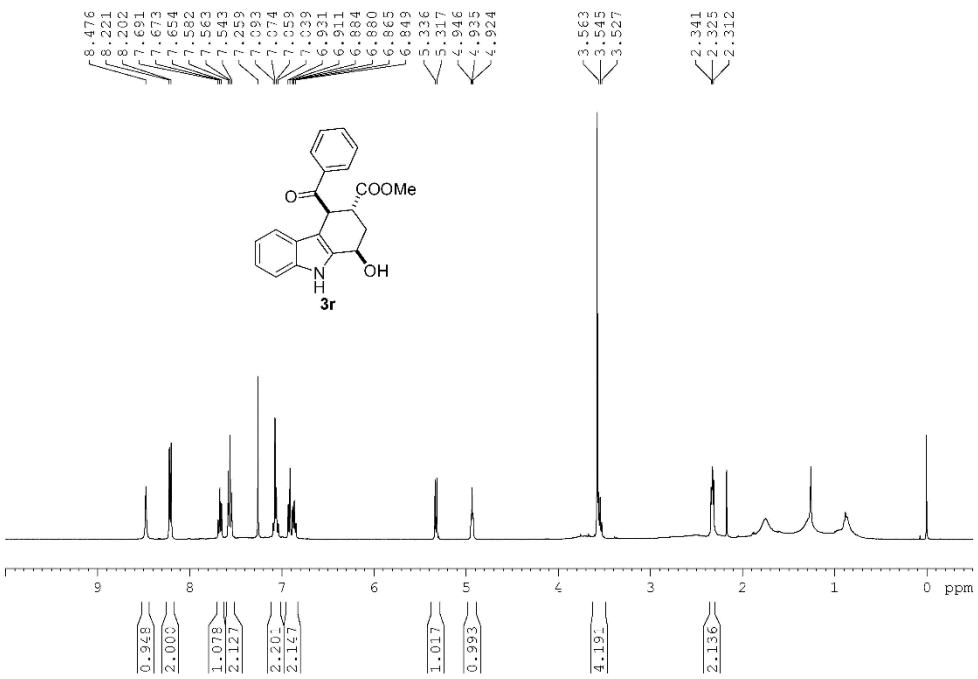

200.354
173.754
136.616
136.152
133.402
129.028
128.908
128.804
126.939
121.853
119.417
118.350
111.088
108.440
77.475
77.157
76.839
56.443
52.398
49.891
42.806
41.939
26.818
24.850
20.153
COOMe
O
N
H
N
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

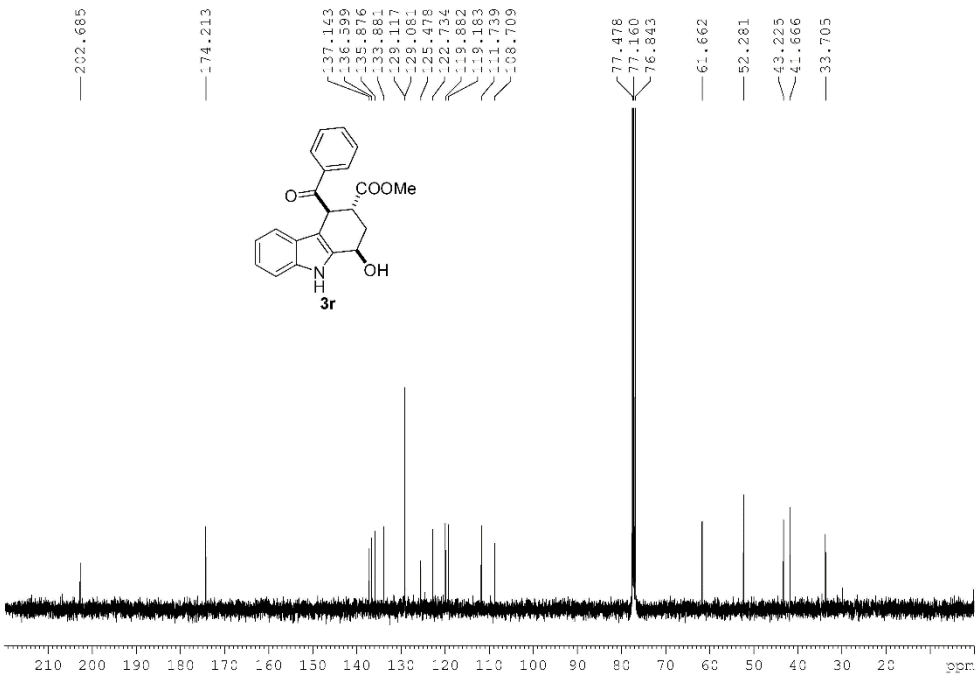

8.015
7.519
7.500
7.286
7.266
7.260
7.238
7.235
7.217
7.181
7.178
7.163
7.161
7.144
7.141
7.119
7.116
7.099
7.082
7.079
6.798
6.779
6.757
6.755
6.735
4.851
4.837
3.862
2.758
2.744
2.266
2.253
2.246
2.240
2.233
2.228
2.221
2.208
2.204
2.058
2.050
2.045
2.039
2.031
2.027
2.018
2.012
1.925
1.919
1.911
1.900
1.890
1.886
1.873
1.862
1.851
1.845
1.839
N
H
HN
3p
9
8
7
6
5
4
3
2
1
0
ppm
0.873
1.000
3.978
1.064
0.973
2.877
0.985
0.909
2.034
1.062
1.137
2.178

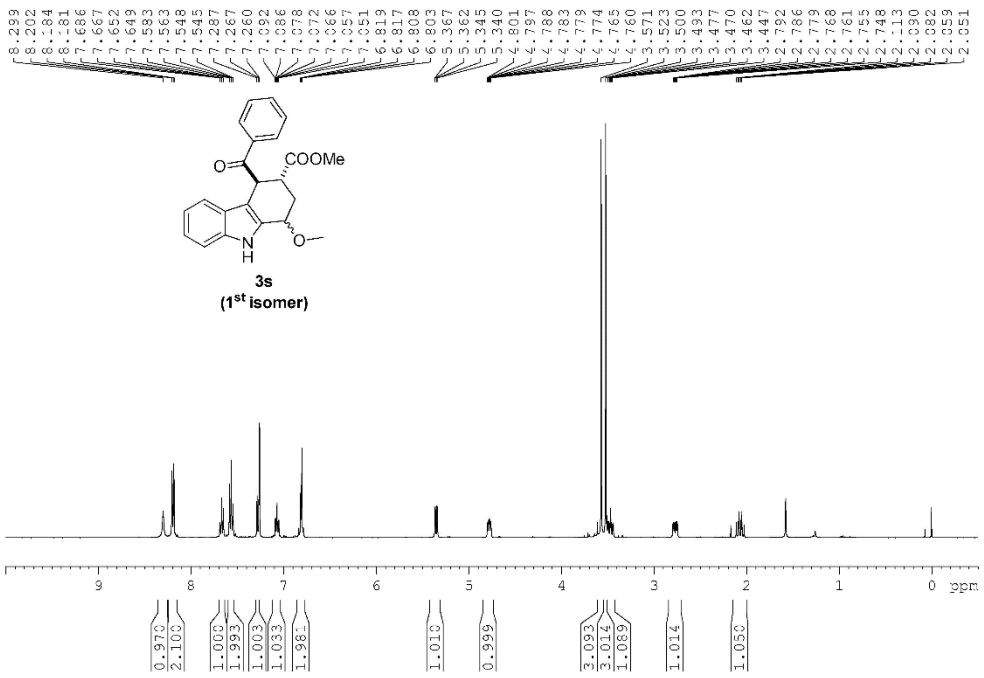

147.166
135.909
134.777
129.722
127.185
122.086
119.407
118.541
118.074
113.511
112.179
111.004
77.478
77.160
76.842
47.644
30.238
21.191
20.993
N
H
HN
3p
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

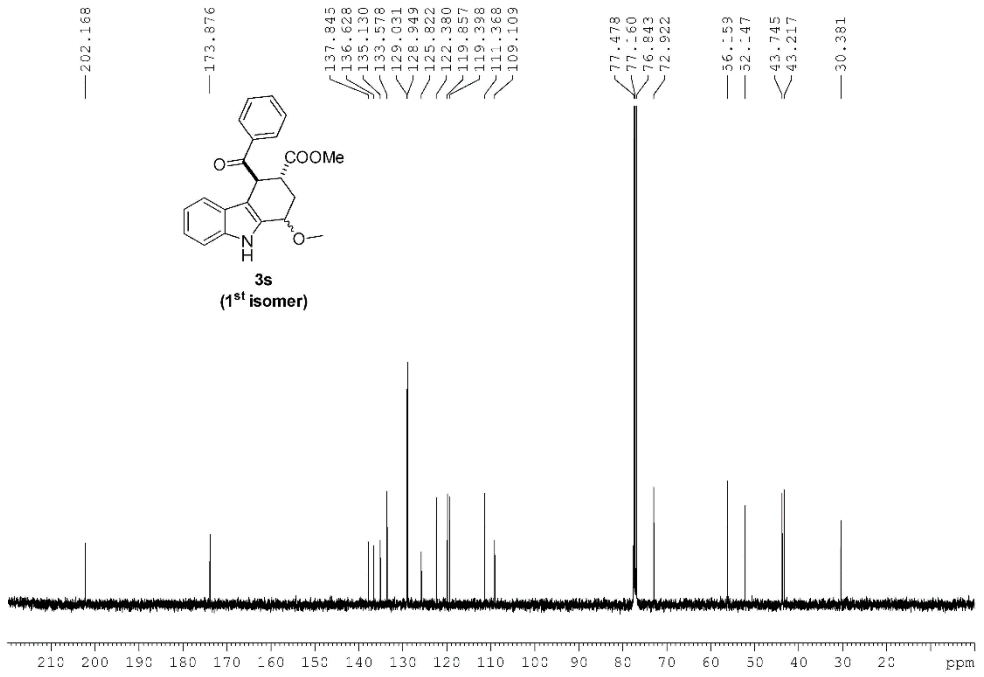

3q
9
8
7
6
5
4
3
2
1
0 ppm
0.960
6.900
2.002
1.000
0.997
1.998
1.046
1.039
1.133
1.269
3.313

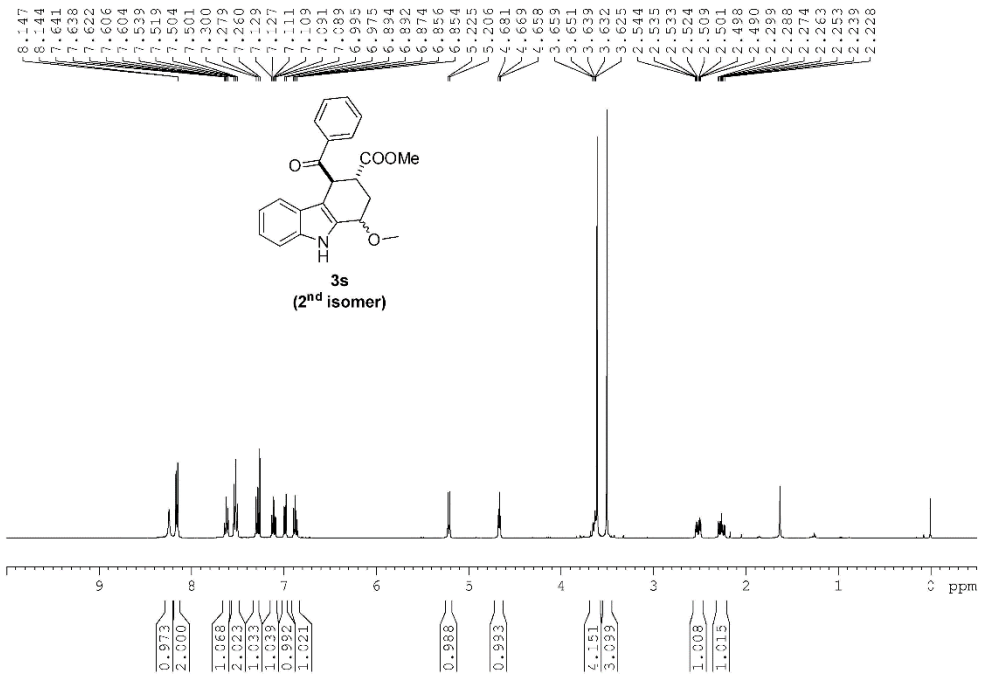

3q
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

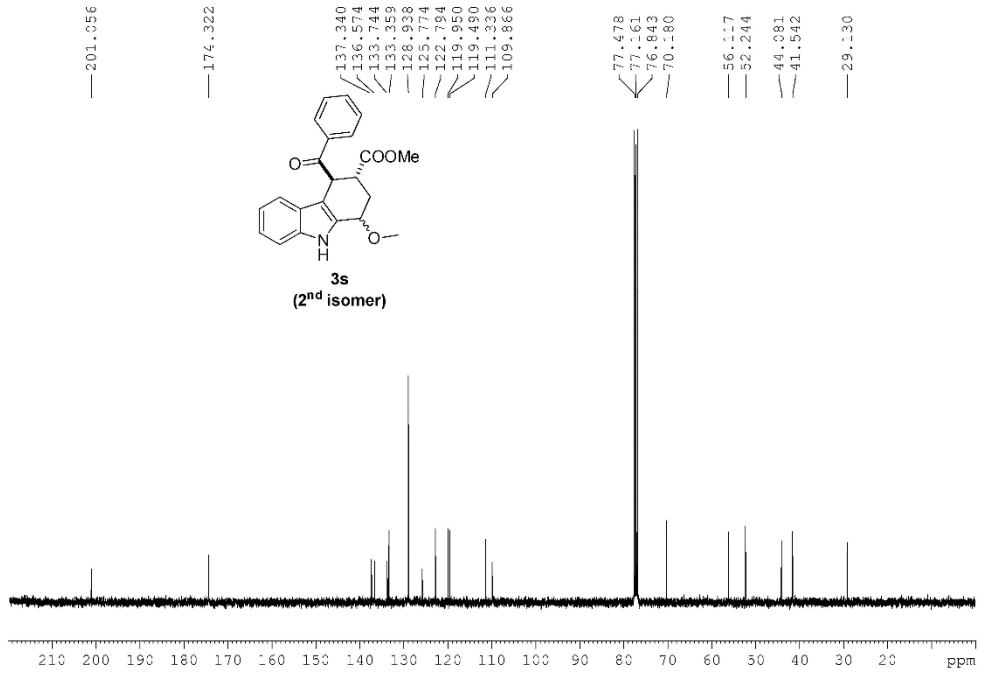

8.476
8.221
8.202
7.691
7.673
7.654
7.582
7.563
7.543
7.259
7.093
7.074
7.059
7.039
6.931
6.911
6.884
6.880
6.865
6.849
5.336
5.317
4.946
4.935
4.924
3.563
3.545
3.527
2.341
2.325
2.312
COOMe
O
OH
N
H
3r
9
8
7
6
5
4
3
2
1
0 ppm
0.948
2.000
1.078
2.127
2.201
2.147
1.017
0.993
4.191
2.136


202.685
174.213
137.143
136.599
135.876
133.881
129.117
128.061
125.478
122.734
119.882
119.183
111.739
108.709
77.478
77.160
76.843
61.662
52.281
43.225
41.666
33.705
COOMe
O
OH
N
H
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


COOMe
O
N
H
O
3s
(1st isomer)
ppm


COOMe
O
N
H
O
3s
(1st isomer)
ppm


8.147
8.144
7.641
7.638
7.622
7.606
7.604
7.539
7.519
7.504
7.501
7.300
7.279
7.260
7.129
7.127
7.111
7.109
7.091
7.089
6.995
6.975
6.894
6.892
6.874
6.856
6.854
5.225
5.206
4.681
4.669
4.658
3.659
3.651
3.639
3.632
3.625
2.544
2.535
2.533
2.524
2.509
2.501
2.498
2.490
2.299
2.288
2.274
2.263
2.253
2.239
2.228
COOMe
O
N
H
O
3s
(2nd isomer)
9
8
7
6
5
4
3
2
1
0
ppm
0.973
2.000
1.068
2.023
1.033
1.039
0.982
1.021
0.988
0.993
4.151
3.039
1.008
1.015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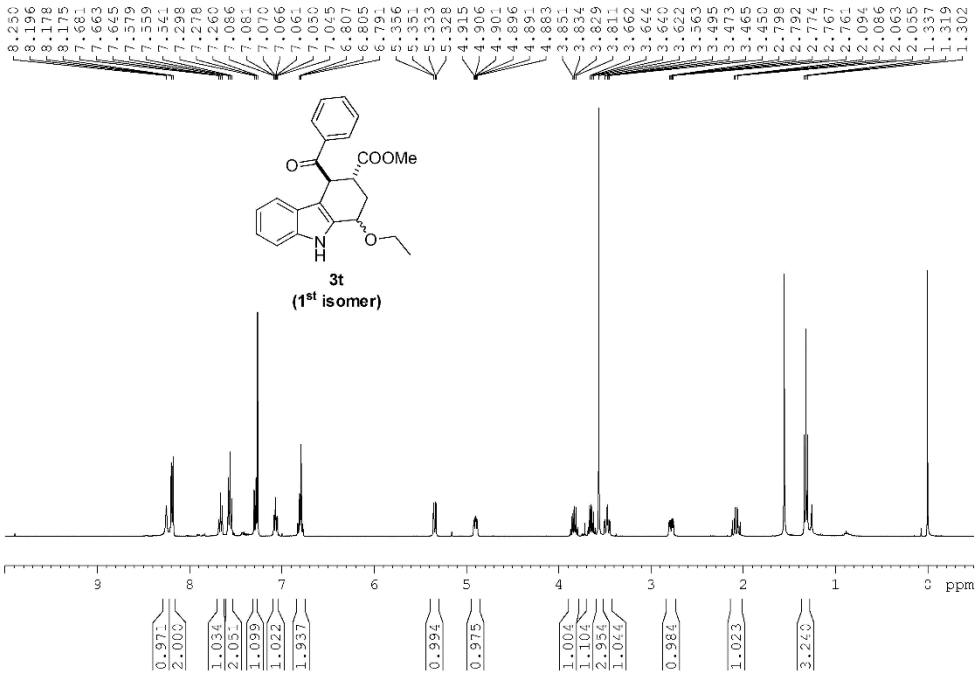
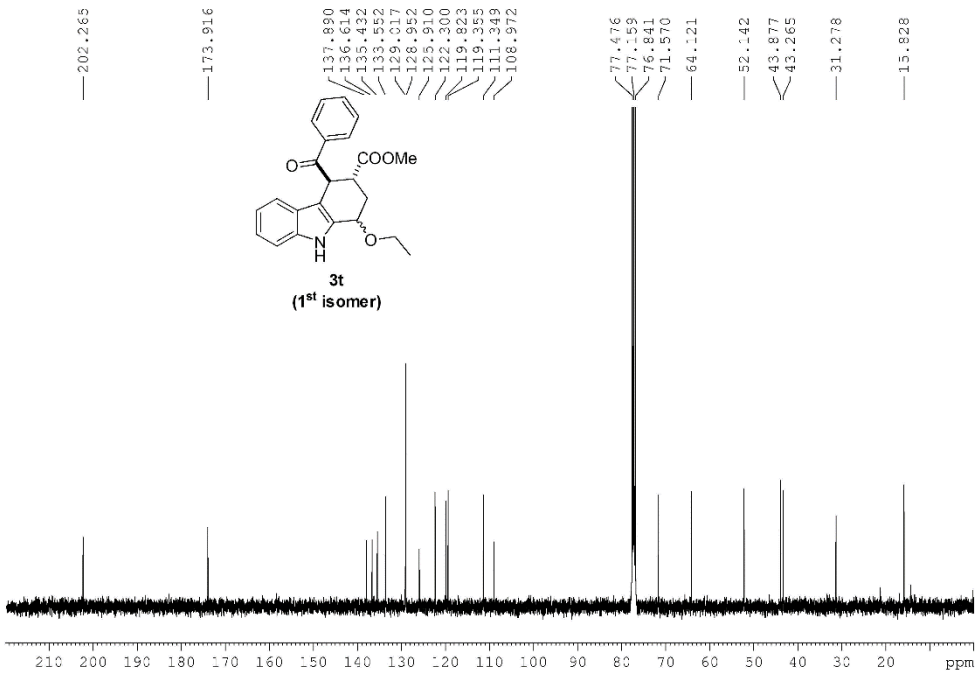
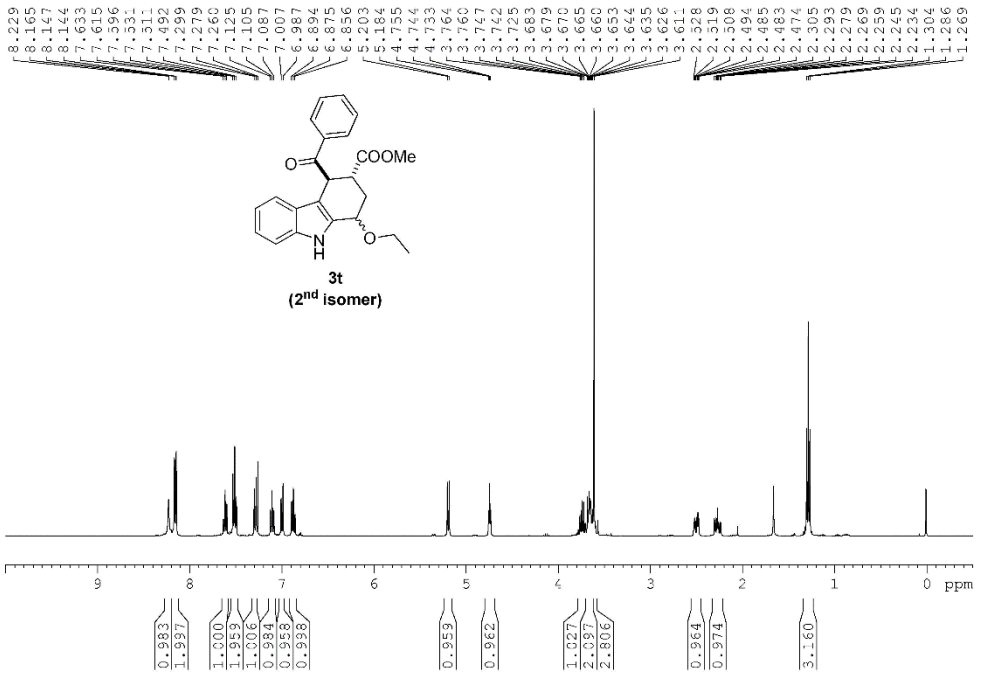
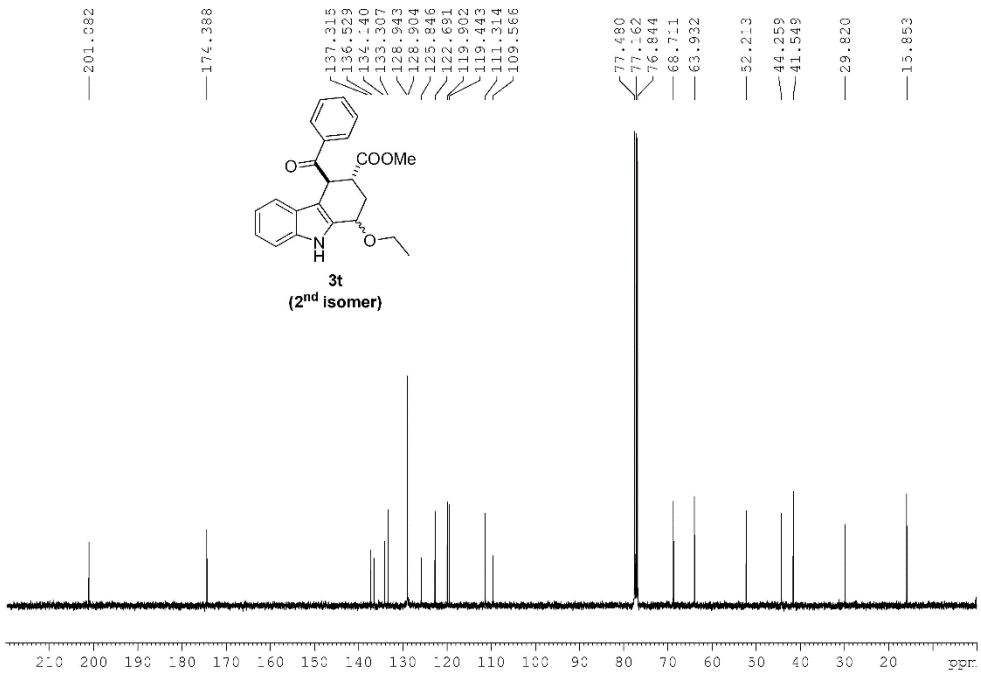
137.340
136.574
133.744
133.359
128.938
125.774
122.794
119.950
119.490
111.336
109.866
77.478
77.161
76.843
70.180
56.117
52.244
44.081
41.542
29.130
COOMe
O
N
H
O
3s
(2nd isomer)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


COOMe
3t
(1st isomer)
ppm


COOMe
3t
(1st isomer)
ppm


8.229
8.165
8.147
8.144
7.633
7.615
7.596
7.492
7.299
7.279
7.260
7.125
7.105
7.087
7.007
6.987
6.894
6.875
6.856
5.203
5.184
4.755
4.744
4.733
3.764
3.760
3.747
3.742
3.725
3.683
3.679
3.670
3.665
3.660
3.653
3.644
3.635
3.626
2.328
2.319
2.308
2.494
2.485
2.483
2.474
2.305
2.293
2.279
2.269
2.259
2.245
2.234
1.304
1.286
1.269
COOMe
O
N
H
O
3t
(2nd isomer)
9
8
7
6
5
4
3
2
1
0
ppm
0.983
1.997
1.000
1.959
1.006
0.984
0.958
0.938
0.959
0.962
1.027
2.097
2.806
0.964
0.974
3.160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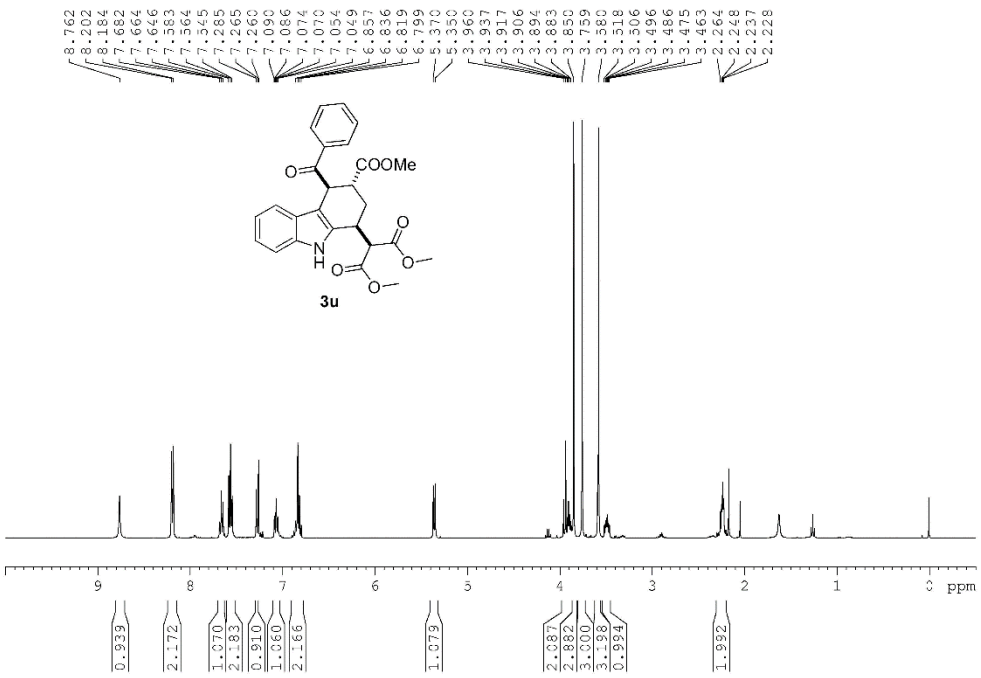
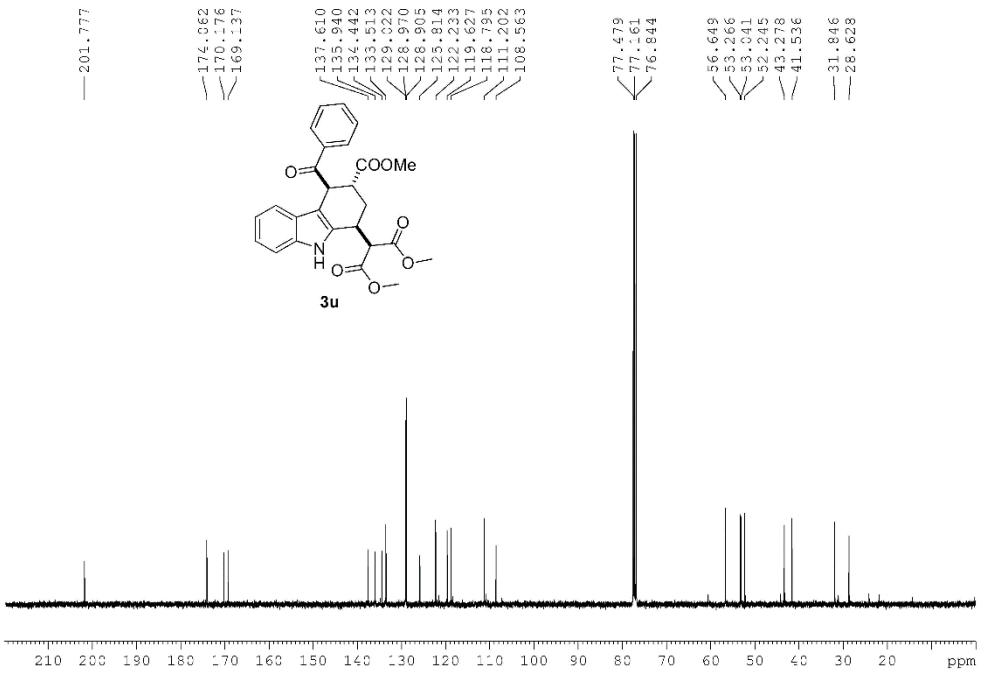
137.315
136.529
134.140
133.307
128.943
128.904
125.846
122.691
119.902
119.443
111.314
109.566
77.480
77.162
76.844
68.711
63.932
52.213
44.259
41.549
29.820
13.853
COOMe
O
N
H
O
3t
(2nd isomer)
220
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.762
8.202
8.184
7.682
7.664
7.646
7.583
7.564
7.545
7.285
7.265
7.260
7.086
7.074
7.054
7.049
6.837
6.836
6.819
6.799
5.370
3.960
3.937
3.917
3.906
3.884
3.883
3.850
3.759
3.580
3.518
3.506
3.496
3.486
3.475
3.463
2.264
2.248
2.237
2.228
COOMe
3u
ppm
0.939
2.172
1.070
2.183
0.910
1.060
2.166
1.079
2.087
2.882
3.000
3.198
0.984
1.992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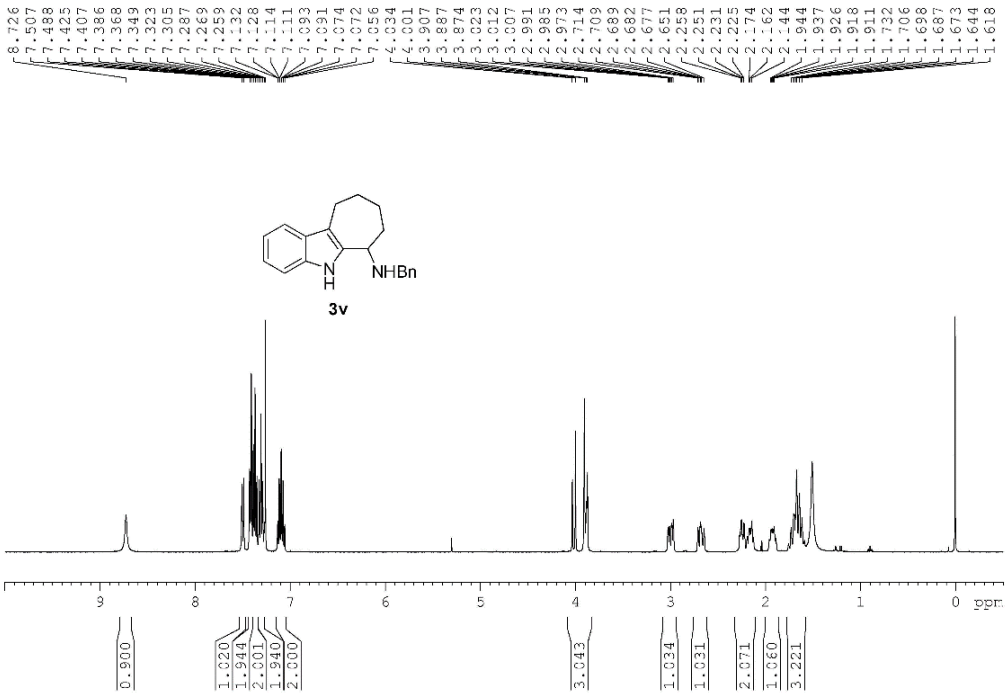
174.062
170.176
169.137
137.610
135.940
134.442
133.513
129.022
128.970
128.905
125.814
122.233
119.627
118.795
111.202
108.563
77.479
77.161
76.844
56.649
53.266
53.041
52.245
43.278
41.536
31.846
28.628
COOMe
3u
ppm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7.507
7.488
7.425
7.407
7.386
7.368
7.349
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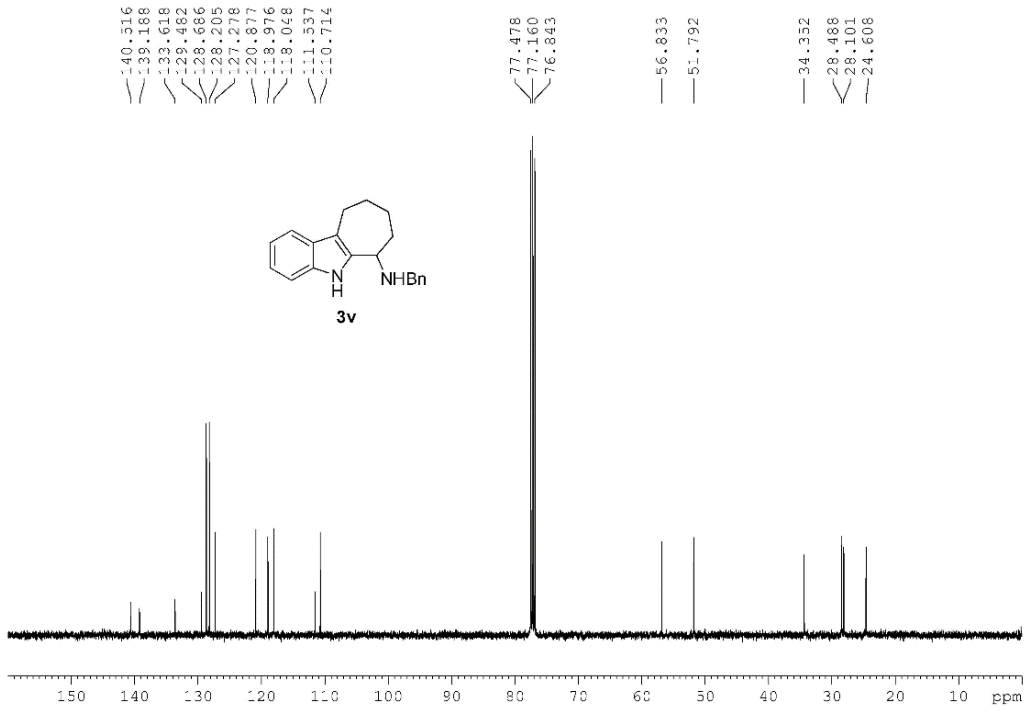
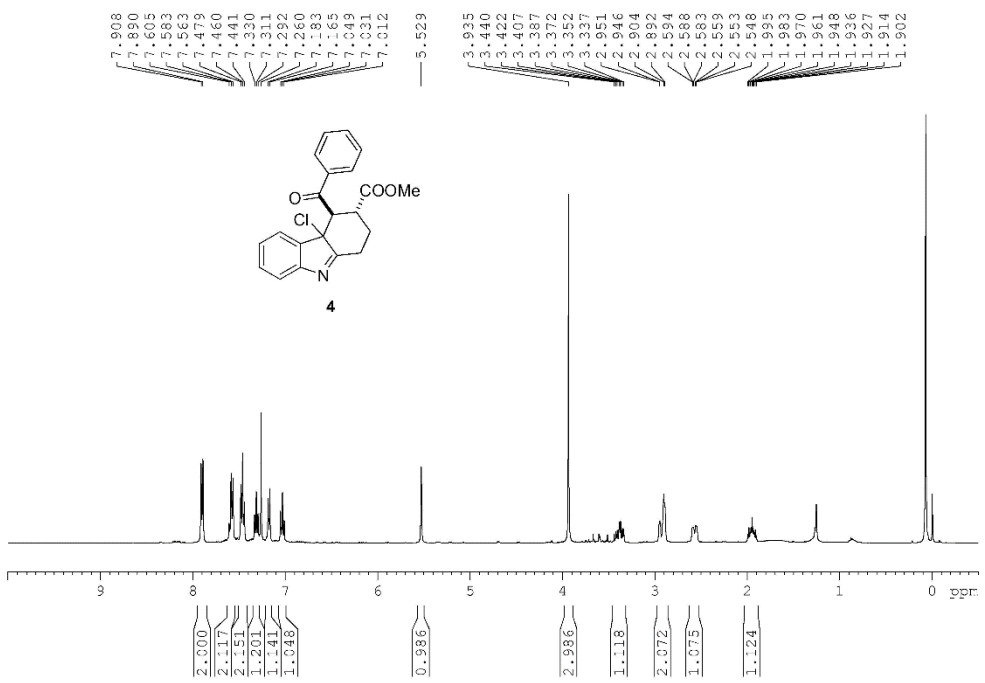
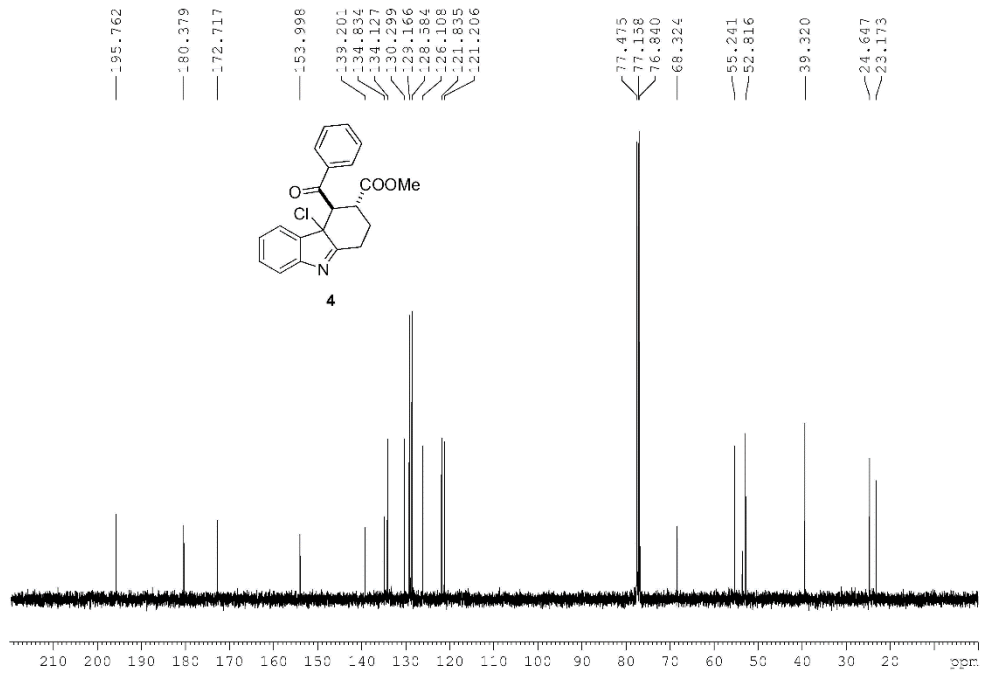
7.305
7.287
7.269
7.259
7.232
7.228
7.214
7.211
7.093
7.091
7.074
7.072
7.056
4.034
4.001
3.907
3.887
3.874
3.823
3.812
3.007
2.991
2.985
2.973
2.714
2.709
2.689
2.682
2.677
2.651
2.258
2.251
2.231
2.225
2.174
2.162
2.144
1.944
1.937
1.926
1.918
1.911
1.732
1.706
1.698
1.687
1.673
1.644
1.618
NHBn
3v
9
8
7
6
5
4
3
2
1
0
ppm
0.900
1.020
1.944
2.001
1.940
2.000
3.043
1.034
1.031
2.071
1.060
3.221


140.516
139.188
133.618
129.482
128.686
128.205
127.278
120.877
118.976
118.048
111.537
110.714
77.478
77.160
76.843
56.833
51.792
34.352
28.488
28.101
24.608
NHBn
3v
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.908
7.890
7.605
7.583
7.563
7.479
7.460
7.441
7.330
7.311
7.292
7.260
7.183
7.165
7.049
7.031
7.012
5.529
3.935
3.440
3.422
3.407
3.387
3.372
3.352
3.337
2.951
2.946
2.904
2.892
2.594
2.588
2.583
2.553
2.548
1.995
1.983
1.970
1.961
1.948
1.936
1.927
1.914
1.902
COOMe
Cl
O
N
4
ppm
2.000
2.117
2.151
1.201
1.141
1.048
0.986
2.986
1.118
2.072
1.075
1.124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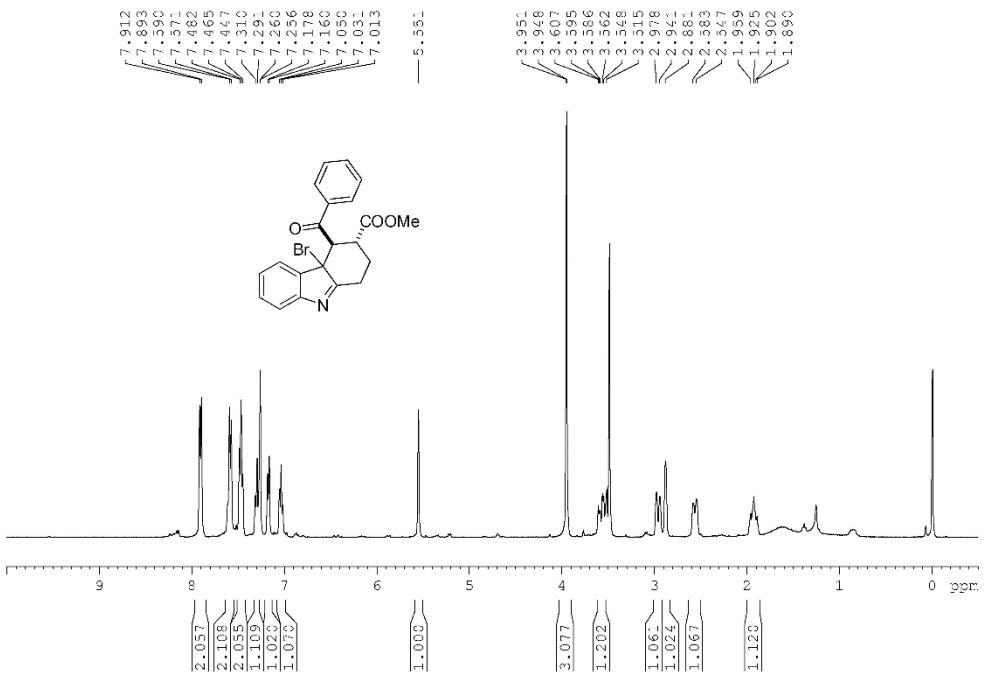
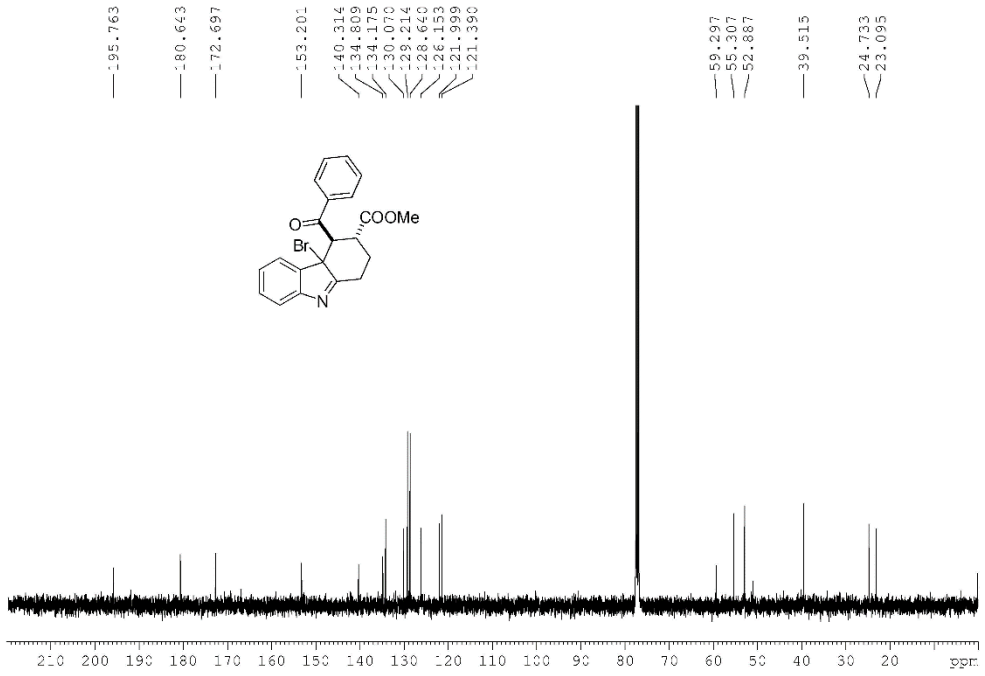
180.379
172.717
153.998
139.201
134.834
134.127
130.299
129.166
128.584
126.108
121.835
121.206
77.475
77.158
76.840
68.324
55.241
52.816
39.320
24.647
23.173
COOMe
Cl
O
N
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.912
7.893
7.590
7.571
7.482
7.465
7.447
7.310
7.291
7.260
7.256
7.178
7.160
7.050
7.031
7.013
5.551
3.951
3.948
3.607
3.595
3.586
3.562
3.548
3.515
2.978
2.941
2.881
2.583
2.547
1.959
1.925
1.902
1.890
COOMe
Br
O
N
9
8
7
6
5
4
3
2
1
0
ppm
2.057
2.108
2.055
1.109
1.000
3.077
1.202
1.024
1.067
1.128


195.763
180.643
172.697
153.201
140.314
134.809
134.175
130.070
129.214
128.640
126.153
121.999
121.390
59.297
55.307
52.887
39.515
24.733
23.095
COOMe
Br
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm