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Direct Synthesis of 8-Aryl Tetrahydroquinolines via Pd-catalyzed *ortho*-Arylation of Aryl Ureas in Water

Zhen Jiang,[a] Lingjuan Zhang,[a] Chaonan Dong,[a] Xiaoming Su,[a] Huanrong Li,[a*] Weijun Tang,[a] Lijin Xu,[a*] Qinghua Fan [b]

[a] Department of Chemistry, Renmin University of China, Beijing 100872, China. xulj@chem.ruc.edu.cn

[b] Being National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190. China.

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1. General information:

Unless otherwise noted, all experiments were carried out in air, and all commercially available chemicals were used as received from Aldrich, Acros or Strem without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^{1}H 400 MHz and ^{13}C 106 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. Et_2O was dried by distillation from Na/Ph_2CO. Tetrahydroquinolines were prepared according to the previous reports.[1, 2]

2. The general procedure for the synthesis of *N*-urea tetrahydroquinolines

To a solution of 1,2,3,4-tetrahydroquinoline (5.0 mmol) in anhydrous Et_2O was added dropwise a solution of n-BuLi in hexane (2.6 mL, 6.5 mmol) in an ice bath. The resulting mixture was stirred at room temperature under N_2 for 1 h. Then the mixture was cooled to 0 ℃, and dimethylcarbamic chloride (6.0 mmol, 646 mg) was added dropwise. After being stirred at room temperature for 12 h, the reaction was quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was then purified via flash chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

***N*,*N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1a),** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (m, 2H), 2.75 (t, *J* = 6.64 Hz, 2H), 2.82 (s, 6H), 3.56 (t, *J* = 6.16 Hz, 2H), 6.87 (d, *J* = 6.08 Hz, 2H), 7.06 (d, *J* = 6.88 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.5, 26.9, 37.8, 45.4, 119.3, 121.6, 126.4, 127.6, 129.0, 140.9, 160.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{12}H_{16}N_2NaO$ $[M+H]^+$: 227.1155, found: 227.1152.

***N*,*N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1b)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, *J* = 6.52 Hz, 3H), 1.73 (m, 1H), 2.03 (m, 1H), 2.71 (m, 2H), 2.78 (s, 6H), 4.73 (m, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* =7.36 Hz, 1H), 7.07 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.0, 24.2, 29.7, 37.7, 49.5, 119.5, 121.3, 126.6, 127.4, 128.7, 139.5, 160.6; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{13}H_{18}N_2NaO$ $[M+H]^+$: 241.1311, found: 241.1309.

6-methoxy-*N*,*N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1c), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.52 Hz, 3H), 1.63 (m, 1H), 2.07 (m, 1H), 2.65 (m, 2H), 2.73 (s, 6H), 3.75 (s, 3H), 4.23 (m, 1H), 6.66 (m, 2H), 6.79 (d, *J* = 8.44 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.9, 24.7, 30.2, 37.8, 49.4, 55.4, 112.4, 113.4, 121.7, 139.7, 132.7, 154.6, 160.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{14}H_{20}N_2NaO_2$ $[M+H]^+$: 271.1417, found: 271.1414.

2-ethyl-*N*,*N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1d), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.52 Hz, 3H), 1.59 (m, 1H), 1.65 (m, 1H), 1.81 (m, 1H), 1.91 (m, 1H), 2.61 (m, 2H), 2.68 (s, 6H), 3.96 (m, 1H), 6.77 (m, 2H), 6.98 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.5, 23.9, 25.2, 26.4, 37.8, 54.9, 119.9, 121.5, 126.5, 127.5, 128.8, 139.6, 160.5; IR (neat, cm^{-1}): 1645; HRMS (ESI)

calcd. for $C_{14}H_{20}N_2NaO$ $[M+H]^+$: 255.1468, found: 255.1464.

***N,N*-dimethyl-2-propyl-3,4-dihydroquinoline-1(2H)-carboxamide (1e)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.38 (m, 3H), 1.68 (m, 1H), 1.86 (m, 1H), 2.01 (m, 1H), 2.75 (m, 2H), 2.81 (s, 6H), 4.14 (m, 1H), 6.87 (m, 2H), 7.08 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 19.4, 23.9, 26.9, 34.5, 37.9, 53.5, 120.2, 121.5, 126.5, 127.5, 128.9, 139.6, 160.6; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{15}H_{22}N_2NaO$ $[M+H]^+$: 269.1624, found: 269.1621.

2-butyl-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1f), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.08 Hz, 3H), 1.31 (m, 6H), 1.69 (m, 1H), 1.84 (m, 1H), 1.93 (m, 1H), 2.70 (m, 1H), 2.74 (s, 6H), 4.09 (m, 1H), 6.84 (m, 2H),7.06 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.7, 23.9, 26.8, 28.3, 31.9, 37.9, 53.7, 120.2, 121.5, 126.5, 127.5, 128.8, 139.6, 160.6; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{16}H_{24}N_2NaO$ $[M+H]^+$: 283.1781, found: 283.1777.

***N,N*-dimethyl-2-pentyl-3,4-dihydroquinoline-1(2H)-carboxamide (1g)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.04 Hz, 3H), 1.33 (m, 8H), 1.71 (m, 1H), 1.87 (m, 1H), 1.96 (m, 1H), 2.70 (m, 1H), 2.76 (s, 6H), 4.11 (m, 1H), 6.86 (m, 2H), 7.08 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.6, 23.9, 25.7, 26.7, 31.8, 32.2, 53.7, 120.2, 121.5, 126.5, 127.5, 128.8, 139.6, 160.6; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{17}H_{26}N_2NaO$ $[M+H]^+$: 297.1937, found: 297.1932.

2-isobutyl-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1h), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, J = 6.52 Hz, 6H), 1.27 (m, 2H), 1.56 (m, 1H), 1.68 (m, 1H), 1.86 (m, 1H), 2.01 (m, 1H), 2.73 (m, 3H), 2.76 (s, 6H), 4.23 (m, 1H), 6.88 (m, 2H), 7.08 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.9, 23.7, 23.9, 24.9, 26.9, 37.9, 41.1, 51.9, 120.5, 121.6, 126.5, 127.4, 128.9, 139.5, 160.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{17}H_{26}N_2NaO$ $[M+H]^+$: 297.1937, found: 297.1935.

2-cyclohexyl-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1i), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (m, 1H), 0.99 (m, 2H), 1.13 (m, 2H), 1.28 (m, 2H), 1.43 (m, 1H), 1.57 (m, 1H), 1.70 (d, *J* = 8.04 Hz, 2H), 1.90 (m, 1H), 2.06 (m, 1H), 2.68 (s, 6H), 2.75 (m, 2H), 3.95 (m, 1H), 6.91 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.8, 24.9, 26.1, 26.3, 26.4, 29.4, 30.1, 37.7, 38.3, 58.1, 121.6, 122.1, 126.5, 127.8, 129.1, 139.8, 160.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{26}N_2NaO$ $[M+H]^+$: 309.1937, found: 309.1934.

***N,N*-dimethyl-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (1j)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (m, 2H), 2.68 (m, 2H), 2.85 (s, 6H), 5.24 (t, *J* = 5.04 Hz, 1H), 6.92 (t, *J* = 7.32 Hz, 1H), 7.00 (d, *J* = 8.12 Hz, 1H), 7.07 (d, *J* = 7.32 Hz, 1H), 7.19 (m, 2H), 7.28 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.3, 30.4, 37.9, 58.0, 119.9, 121.5, 126.4, 126.6, 126.9, 127.7, 128.4, 128.9, 140.3, 143.1, 160.9; IR (neat, cm^{-1}): 1651; HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO$ $[M+H]^+$: 303.1468, found: 303.1473.

***N,N*-dimethyl-2H-benzo[b][1,4]oxazine-4(3H)-carboxamide (1k)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (s, 6H), 3.68 (t, *J* = 4.52 Hz, 2H), 4.32 (t, *J* = 4.68 Hz, 2H), 6.85 (m, 3H), 6.94 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 38.1, 43.4, 66.3, 117.1, 119.3, 120.6, 122.9, 128.1, 144.8, 159.2; IR (neat, cm^{-1}): 1645; HRMS (ESI)

calcd. for $C_{11}H_{14}N_2NaO_2$ $[M+H]^+$: 229.0948, found: 229.0945.

***N,N*-dimethylindoline-1-carboxamide (1l),** red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.93 (s, 6H), 3.02 (t, *J* = 8.20 Hz, 2H), 3.90 (t, J = 8.20 Hz, 2H), 6.87 (td, J = 7.41, 0.84 Hz, 1H), 6.95 (d, *J* = 7.93 Hz, 1H), 7.14 (q, *J* = 7.64 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 38.1, 50.3, 113.3, 121.3, 124.8, 126.9, 131.3, 144.3, 160.2; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{11}H_{14}N_2NaO$ $[M+Na]^+$: 213.0998, found: 213.0995.

1,1,3-Trimethyl-3-phenyl-urea (1m), brown liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 6H), 3.09 (s, 3H), 6.96 (m, 3H), 7.20 (t, *J* = 8.08 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 37.8, 39.4, 123.4, 124.0, 129.3, 146.8, 161.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{10}H_{14}N_2NaO$ $[M+Na]^+$: 201.0998, found: 201.0997.

3. The general procedure for the arylation of *N*-urea tetrahydroquinolines

N-urea tetrahydroquinoline (0.5 mmol), $Pd(MeCN)_2(Tos)_2$ (25 mg, 10 mmol%), AgOAc (167 mg. 1.0 mmol), TsOH (285 mg, 1.5 mmol) and 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol) were sequentially added in air to a reaction tube. Then H_2O (3.0 mL) was added and the resulting mixture was vigorously stirred for 16 h at 80 ℃. After cooling to room temperature, the reaction mixture was neutralized by adding aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was then purified by flash chromatography (hexane/ethylacetate = 10/1) to give the pure product.

***N,N*-dimethyl-8-p-tolyl-3,4-dihydroquinoline-1(2H)-carboxamide (3aa)** yellow solid, mp: 123. °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (m, 2H), 2.10 (s, 6H), 2.37 (s, 3H), 2.70 (s, 2H), 3.71 (bs, 2H), 7.11 (m, 2H), 7.18 (m, 2H), 7.22 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.1, 25.1, 27.6, 36.8, 45.0, 124.1, 126.9, 127.3, 129.0, 129.1, 134.6, 135.2, 136.4, 136.6, 138.7, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{22}N_2NaO$ $[M+Na]^+$: 317.1624, found: 317.1621.

***N,N*-dimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ab)**, yellow solid, mp: 119 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (m, 2H), 2.08 (s, 6H), 2.69 (s, 2H), 3.70 (bs, 2H), 7.14 (m, 3H), 7.28 (m, 3H), 7.34 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.0, 27.6, 36.7, 45.1, 124.1, 127.0, 127.2, 127.4, 128.4, 129.2, 134.5, 135.2, 138.7, 139.3, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO$ $[M+Na]^+$: 303.1468, found: 303.1465.

8-(4-methoxyphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ac), yellow solid, mp: 149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 2H), 2.13 (s, 6H), 2.68 (s, 2H), 3.69 (bs, 2H), 3.81 (s, 3H), 6.95 (d, *J* = 8.72 Hz, 2H), 7.08 (m, 1H), 7.13 (m, 2H), 7.23 (d, *J* = 8.68 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.1, 27.6, 36.8, 45.0, 55.3, 113.8, 123.9, 126.7, 128.6, 129.1, 132.0, 134.5, 134.9, 138.8, 158.7, 159.6; IR (neat, cm^{-1}): 1651; HRMS (ESI) calcd. for $C_{19}H_{22}N_2NaO_2$ $[M+Na]^+$: 333.1574, found: 333.1571.

8-(4-isopropylphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ad), yellow, mp: 117 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, *J* = 6.92 Hz, 6H), 2.04 (bs, 2H), 2.09 (s, 6H), 2.70 (s, 2H), 2.93 (m, 1H), 3.71 (bs, 2H), 7.10 (t, *J* = 7.36

Hz, 1H), 7.15 (d, *J* = 5.92 Hz, 1H), 7.20 (dd, *J* = 7.36, 1.48 Hz, 1H), 7.24 (d, *J* = 8.16 Hz, 2H), 7.29 (d, *J* = 8.24 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.0, 25.1, 27.6, 33.9, 36.6, 45.0, 123.9, 126.3, 126.9, 127.4, 129.1, 134.4, 135.2, 136.9, 138.9, 147.7, 159.6; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{21}H_{26}N_2NaO$ $[M+Na]^+$: 345.1937, found: 345.1933.

8-(3,5-dimethylphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ae), yellow, mp: 116 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 2H), 2.11 (s, 6H), 2.37 (s, 6H), 2.70 (s, 2H), 3.70 (bs, 2H), 6.91 (s, 2H), 6.95 (d, *J* = 8.36 Hz, 1H), 7.09 (t, *J* = 7.41 Hz, 1H), 7.15 (dd, *J* = 7.28, 1.64 Hz, 1H), 7.20 (dd, *J* = 7.44, 1.66 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.5, 25.1, 27.7, 36.7, 45.1, 123.8, 125.3, 126.9, 128.5, 129.1, 134.5, 135.4, 137.7, 138.9, 139.2, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{20}H_{24}N_2NaO$ $[M+Na]^+$: 331.1781, found: 331.1779.

8-(3,4-dimethylphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3af), yellow solid, mp: 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 2H), 2.10 (s, 6H), 2.29 (s, 3H), 2.32 (s, 3H), 2.69 (s, 2H), 3.71 (bs, 2H), 7.05 (m, 2H), 7.12 (m, 2H), 7.19 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.4, 19.9, 25.1, 27.6, 29.7, 36.7, 45.0, 124.0, 124.9, 126.8, 126.5, 129.1, 129.6, 134.6, 135.2, 135.3, 136.4, 136.8, 136.7, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{20}H_{24}N_2NaO$ $[M+Na]^+$: 331.1781, found: 331.1776.

8-(3-methoxyphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ag), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (bs, 2H), 2.13 (s, 6H), 2,70 (s, 2H), 3.71 (s, 2H), 3.87 (s, 3H), 6.82 (m, 2H), 6.90 (d, *J* = 7.61 Hz, 1H), 7.02 (m, 1H), 7.17 (d, *J* = 6.42 Hz, 1H), 7.22 (dd, *J* = 7.48, 1.36 Hz, 1H), 7.32 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.1, 27.6, 36.7, 45.1, 55.3, 112.8, 112.9, 120.0, 124.0, 127.2, 129.1, 129.3, 134.6, 134.9, 138.9, 140.7, 159.5, 159.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{22}N_2NaO_2$ $[M+Na]^+$: 333.1574, found: 333.1570.

8-(4-fluorophenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ah), yellow soild, mp: 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (m, 2H), 2.16 (s, 6H), 2.69 (m, 2H), 3.66 (m, 2H), 7.11(m, 5H), 7.26 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.9, 27.5, 36.8, 45.2, 115.0, 115.3, 124.0, 127.4, 129.1(t, *J* = 14.86 Hz), 134.3, 135.6, 138.9, 159.7, 160.7, 163.2; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{19}FN_2NaO$ $[M+Na]^+$: 321.1374, found: 321.1371.

8-(4-chlorophenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ai), yellow solid, mp: 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (m, 2H), 2.15 (s, 6H), 2.70 (m, 2H), 3.67 (m, 2H), 7.12 (m, 3H), 7.23 (d, *J* = 8.36 Hz, 2H), 7.37 (d, *J* = 8.36 Hz. 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.9, 27.5, 36.8, 45.2, 124.0, 127.6, 128.4, 128.8, 128.9, 132.8, 134.0, 134.2, 138.0, 138.8, 159.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{19}ClN_2NaO$ $[M+Na]^+$: 337.1079, found: 337.1074.

Methyl 4-(1-(dimethylcarbamoyl)-1,2,3,4-tetrahydroquinolin-8-yl)- benzoate (3aj), orange solid, mp: 148 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 2H), 2.08 (s, 6H), 2.70 (s,2H), 3.68 (bs, 2H), 3.90 (s, 3H), 7.10 (t, *J* = 7.41 Hz, 1H), 7.16 (d, *J* = 5.40 Hz, 2H), 7.35 (d. *J* = 8.04 Hz, 2H), 8.06 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.9, 24.8, 27.5, 36.7, 45.3, 52.1, 124.1, 127.5, 128.0, 128.6, 129.0, 129.7, 134.0, 134.3, 138.7, 144.2, 159.9, 166.7, 174.5; IR (neat, cm^{-1}): 1645, 1720; HRMS (ESI)

calcd. for HRMS (ESI) calcd. for $C_{20}H_{22}N_2NaO_3$ $[M+Na]^+$: 361.1523, found: 361.1518.

8-(4-acetylphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ak), yellow solid, mp: 146 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 1H), 2.08 (s, 6H), 2.12 (d, *J* = 3.32 Hz, 1H), 2.60 (s, 3H), 2.72 (s, 2H), 3.69 (bs, 2H), 7.11 (t, *J* = 7.32 Hz, 1H), 7.17 (t, *J* = 7.02 Hz, 2H), 7.38 (d, *J* = 8.16 Hz, 2H), 8.01 (d, *J* = 8.12 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.8, 26.7, 27.6, 36.7, 45.2, 124.0, 127.6, 128.1, 128.5, 128.6, 129.0, 133.9, 134.2, 135.5, 138.9, 144.5, 159.7, 197.7; IR (neat, cm^{-1}): 1645, 1680; HRMS (ESI) calcd. for $C_{20}H_{23}N_2O_2$ $[M+H]^+$: 323.1754, found: 323.1751.

***N,N*-dimethyl-8-(4-nitrophenyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3al)**, yellow solid, mp: 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (m, 2H), 2.16 (s, 6H), 2,77 (s, 2H), 3.69 (s, 2H), 7.16 (t, *J* = 6.24 Hz, 2H), 7.24 (m, 1H), 7.25 (d, *J* = 8.68 Hz, 2H), 8.28 (d, *J* = 8.72 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.6, 27.5, 36.8, 45.4, 123.6, 124.2, 126.93, 128.4, 128.8, 132.9, 134.0, 138.9, 146.5, 146.6, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{19}N_3NaO_3$ $[M+Na]^+$: 348.1319, found: 348.1317.

***N,N*-dimethyl-8-(3-(trifluoromethyl)phenyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3am)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 2H), 2.15 (s, 6H), 2.76 (s 2H), 3.69 (s, 2H), 7.17 (m, 2H), 7.21 (dd, *J* = 6.76, 2.16 Hz, 1H), 7.47 (d, *J* = 6.88 Hz, 1H), 7.56 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.7, 27.5, 36.7, 45.4, 123.6, 124.1, 124.2, 126.5, 128.1, 128.8, 128.9, 129.1, 131.3, 133.9, 134.0, 138.9, 140.5, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{19}F_3N_2NaO$ $[M+Na]^+$: 371.1342, found: 371.1339.

***N,N*-dimethyl-8-(3-nitrophenyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3an)**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 2H), 2.19 (s, 6H), 2.77 (s, 2H), 3.67 (s, 2H), 7.15 (m, 2H), 7.22 (dd, *J* = 6.14, 2.84 Hz, 1H), 7.57 (t, *J* = 7.78 Hz, 1H), 7.62 (d, *J* = 7.01 Hz, 1H), 8.13 (m, 1H), 8.19 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.4, 27.5, 36.8, 45.7, 121.7, 122.5, 124.2, 128.7, 128.8, 129.3, 133.0, 133.8, 134.3, 138.8, 141.6, 148.2, 160.0; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{19}N_3NaO_3$ $[M+Na]^+$: 348.1319, found: 348.1314.

***N,N*,2-trimethyl-8-(p-tolyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3ba)**, yellow solid, mp: 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 6.44 Hz, 3H), 1.55 (m, 1H), 2.06 (s, 6H), 2.37 (s, 3H), 2.43 (m, 1H), 2.54 (m, 1H), 2.75 (m, 1H), 4.33 (t, J = 6.68 Hz, 1H), 7.12 (m, 2H), 7.18 (dd, *J* = 8.84, 1.72 Hz, 1H), 7.22 (d, *J* = 7.92 Hz, 2H), 7.28 (d, J = 7.68 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.1, 22.7, 26.8, 29.7, 36.7, 51.2, 124.0, 125.4, 126.7, 127.4, 128.9, 129.4, 135.9, 136.5, 136.8, 137.1, 159.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{20}H_{24}N_2NaO$ $[M+Na]^+$: 331.1781, found: 331.1778.

***N,N*,2-trimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bb)**, yellow solid, mp: 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (m, 3H), 1.55(m, 1H), 2.07 (s, 6H), 2.42 (d, *J* = 5.02 Hz, 1H), 2.57 (m, 1H), 2.76 (m, 1H), 4.33 (t, *J* = 3.28 Hz, 1H), 7.12 (t, *J* = 7.32 Hz, 1H), 7.17 (m, 2H), 7.29 (m, 1H), 7.39 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.2, 26.7, 33.1, 36.6, 51.2, 124.0, 126.9, 127.0, 127.6, 128.2, 129.4, 134.4, 135.9, 137.1, 139.7, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for

$C_{19}H_{22}N_2NaO$ $[M+Na]^+$: 317.1624, found: 317.1621.

8-(4-methoxyphenyl)-*N,N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bc), yellow solid, mp: 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.44 Hz, 3H), 1.53 (m, 1H), 2.10 (s, 6H), 2.42 (d, *J* = 5.64 Hz, 1H), 2.54 (m, 1H), 2.74 (m, 1H), 3.83 (s, 3H), 4.33 (t, *J* = 6.56 Hz, 1H), 6.95 (d, *J* = 8.68 Hz, 2H), 7.12 (m, 3H), 7.31(d, *J* = 8.62 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.1, 22.7, 26.8, 29.7, 36.7, 51.2, 124.0, 125.4, 126.7, 127.4, 128.9, 129.4, 135.9, 136.5, 136.8, 137.1, 159.9; IR (neat, cm^{-1}): 1651; HRMS (ESI) calcd. for $C_{20}H_{24}N_2NaO_2$ $[M+Na]^+$: 347.1730, found: 347.1725.

8-(4-fluorophenyl)-*N,N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bh), yellow solid, mp: 128 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (d, *J* = 6.48 Hz, 3H), 1.55 (m, 1H), 2.13 (s, 6H), 2.39 (m, 1H), 2.57 (m, 1H), 2.76 (m, 1H), 4.30 (m, 1H), 7.13 (m, 5H), 7.34 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.0, 26.5, 32.7, 36.7, 51.2, 114.9, 115.2, 124.1, 127.2, 129.3, 135.0, 135.8, 137.1, 159.9, 160.7, 163.1; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{21}FN_2NaO$ $[M+Na]^+$: 335.1530, found: 335.1528.

8-(4-chlorophenyl)-*N,N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bi), yellow solid, mp: 124 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (d, *J* = 6.48 Hz, 3H), 1.55 (m, 1H), 2.12 (s, 6H), 2.39 (m, 1H), 2.56 (m, 1H), 2.76 (m, 1H), 4.30 (m, 1H), 7.14 (m, 3H), 7.30 (d, *J* = 8.52 Hz, 2H), 7.38 (d, *J* = 8.52 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.0, 26.5, 32.6, 36.7, 51.3, 124.1, 127.5, 128.0, 128.4, 128.9, 129.2, 132.7, 134.7, 137.0, 138.3, 159.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{21}ClN_2NaO$ $[M+Na]^+$: 351.1235, found: 351.1234.

6-methoxy-8-(4-methoxyphenyl)-*N,N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3cc), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (d, *J* = 6.44 Hz, 3H), 1.49 (m, 1H), 2.10 (s, 6H), 2.38 (m, 1H), 2.49 (m, 1H), 2.68 (m, 1H), 3.82 (s, 3H), 3.83 (s, 3H), 4.31 (m, 1H), 6.71 (s, 2H), 6.91 (d, *J* = 8.64 Hz, 2H), 7.31 (d, *J* = 8.64 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.2, 27.2, 29.7, 36.8, 51.1, 55.3, 55.4, 112.1, 113.7, 114.1, 128.6, 130.1, 132.1, 136.1, 136.8, 156.1, 158.8, 160.0; IR (neat, cm^{-1}): 1649; HRMS (ESI) calcd. for $C_{21}H_{26}N_2NaO_3$ $[M+Na]^+$: 377.1836, found: 377.1834.

2-ethyl-*N,N*-dimethyl-8-(p-tolyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3da), brown solid, mp: 127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.40 Hz, 3H), 1.45 (m, 1H), 1.64 (m,1H), 2.07 (s, 6H), 2.36 (s, 3H), 2.39 (d, *J* =6.96 Hz, 2H), 2.55 (m, 1H), 2.76 (m, 1H), 4.03 (m, 1H), 7.09 (t, *J* = 7.32 Hz, 1H), 7.15 (m, 2H), 7.22 (d, *J* = 8.00 Hz, 2H), 7.27 (d, *J* = 8.44 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.7, 21.1, 26.6, 28.3, 30.1, 36.7, 57.0, 123.9, 126.8, 127.5, 128.8, 129.4, 134.2, 135.7, 136.5, 136.9, 137.5, 159.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{21}H_{26}N_2NaO$ $[M+Na]^+$: 345.1937, found: 345.1933.

2-ethyl-*N,N*-dimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (3db), yellow solid, mp: 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.44 Hz, 3H), 1.47 (m, 1H), 1.65 (m, 1H), 2.07 (s, 6H), 2.36 (t, *J* = 5.92 Hz, 2H), 2.56 (m, 1H), 2.76 (m, 1H), 4.04 (m, 1H), 7.10 (t, *J* = 7.36 Hz, 1H), 7.17 (t, *J* = 7.64 Hz, 2H), 7.29 (m, 1H), 7.39 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.7, 26.4, 28.1, 29.7, 36.7, 57.0,

123.9, 126.9, 127.1, 127.6, 128.2, 129.4, 134.1, 135.7, 137.5, 139.8, 160.0; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{20}H_{24}N_2NaO$ $[M+Na]^+$: 331.1781, found: 331.1781.

2-ethyl-8-(4-methoxyphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3dc), brown solid, mp: 158 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.44 Hz, 3H), 1.44 (m, 1H), 1.63 (m, 1H), 2.10 (s, 6H), 2.36 (t, *J* = 6.26 Hz, 2H), 2.53 (m, 1H), 2.75 (m, 1H), 3.83 (s, 3H), 4.03 (t, *J* = 7.94 Hz, 1H), 6.95 (d, *J* = 8.68 Hz, 2H), 7.08 (t, *J* = 7.24 Hz, 1H), 7.13 (m, 2H), 7.30 (t, *J* = 7.96 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.7, 26.6, 28.3, 29.7, 36.8, 55.3, 57.0, 113.6, 123.9, 126.6, 128.7, 129.4, 132.4, 134.2, 135.4, 137.5, 158.6, 159.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{21}H_{26}N_2NaO_2$ $[M+Na]^+$: 361.1887, found: 361.1883.

8-(4-methoxyphenyl)-*N,N*-dimethyl-2-propyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ec), brown solid, mp: 154 °C ; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* =7.02 Hz, 3H), 1.45 (m, 3H), 1.64 (m, 1H), 2.11 (s, 6H), 2.24 (s, 1H), 2.35 (m, 1H), 2.55 (m, 1H), 2.77 (m, 1H), 3.84 (s, 3H), 4.15 (s, 1H), 6.96 (d, *J* = 8.56 Hz, 2H), 7.08 (t, *J* = 7.24 Hz, 1H), 7.14 (m, 2H), 7.31 (d, *J* = 8.56 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 19.6, 26.5, 29.7, 36.8, 37.2, 55.2, 55.3, 113.7, 123.9, 126.7, 128.8, 129.4, 132.4, 134.0, 135.5, 137.5, 158.7, 160.0; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{22}H_{28}N_2NaO_2$ $[M+Na]^+$: 375.2043, found: 375.2041.

2-butyl-8-(4-methoxyphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3fc), brown solid, mp: 157 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 3.70 Hz, 3H), 1.04 (d, *J* = 6.56 Hz, 2H), 1.43 (m, 2H), 1.68 (m, 3H), 2.11 (s, 6H), 2.36 (m, 1H), 2.56 (m, 1H), 2.76 (m, 1H), 3.84 (s, 3H), 4.26 (bs, 1H), 6.97 (d, *J* = 8.72 Hz, 2H), 7.09 (t, *J* = 7.31 Hz, 1H), 7.14 (m, 2H), 7.31 (d, *J* = 8.72 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.2, 21.2, 24.1, 25.1, 26.5, 29.7, 36.8, 53.7, 55.3, 113.7, 124.0, 126.7, 128.7, 129.4, 130.9, 132.4, 135.6, 137.4, 158.6, 160.1; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{23}H_{30}N_2NaO_2$ $[M+Na]^+$: 389.2200, found: 389.2197.

8-(4-methoxyphenyl)-*N,N*-dimethyl-2-pentyl-3,4-dihydroquinoline-1(2H)-carboxamide (3gc), brown solid, mp: 159 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 3.40 Hz, 3H), 0.99 (m, 1H), 1.45 (m, 4H), 1.63 (m, 3H), 2.11 (s, 6H), 2.27 (s, 1H), 2.36 (m, 1H), 2.56 (m, 1H), 2.76 (m, 1H), 3.84 (s, 3H), 4.17 (bs, 1H), 6.95 (d, *J* = 8.68 Hz, 2H), 7.10 (t, *J* = 7.16 Hz, 1H), 7.15 (m, 2H), 7.29 (d, *J* = 7.52 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.7, 25.9, 26.5, 29.7, 31.9, 35.1, 37.0, 55.3, 55.7, 113.8, 124.0, 126.7, 128.8, 129.4, 132.2, 134.2, 135.5, 137.1, 158.8, 160.3; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{24}H_{32}N_2NaO_2$ $[M+Na]^+$: 403.2356, found: 403.2351.

2-isopentyl-8-(4-methoxyphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3hc), brown solid, mp: 159 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 6.56 Hz, 3H), 1.42 (m, 6H), 1.68 (m, 2H), 2.11 (s, 6H), 2.33 (m, 2H), 2.56 (m, 1H), 2.75 (m, 1H), 3.84 (s, 3H), 4.12 (bs, 1H), 6.96 (d, *J* = 8.60 Hz, 2H), 7.08 (t, *J* = 7.28 Hz, 1H), 7.14 (m, 2H), 7.31 (d, *J* = 8.60 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2, 22.7, 26.5, 28.5, 29.7, 34.8, 36.8, 55.3, 55.5, 113.6, 123.9, 126.7, 128.8, 129.4, 132.4, 134.0, 135.5, 137.5, 158.6, 159.9; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{24}H_{32}N_2NaO_2$ $[M+Na]^+$: 403.2356, found: 403.2354.

2-cyclohexyl-8-(4-methoxyphenyl)-*N,N*-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ic), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.62 Hz, 1H), 1.01 (m, 4H), 1.29 (m, 3H), 1.45 (m, 1H), 1.59 (d, *J* = 4.12 Hz, 1H), 1.73 (m, 4H), 1.91 (m, 1H), 2.08 (m, 1H), 2.70 (s, 6H), 2.76 (m, 1H), 3.88 (s, 1H), 3.97 (m, 1H), 6.83 (m, 1H), 6.98 (m, 3H), 7.12 (t, *J* = 7.16 Hz, 2H), 7.55 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.8, 24.9, 26.1, 26.3, 26.4, 29.4, 30.2, 37.8, 38.3, 55.4, 58.1, 114.1, 121.7, 122.1, 126.5, 127.8, 129.1, 131.0, 131.1, 132.3, 139.8, 160.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{25}H_{32}N_2NaO_2$ $[M+Na]^+$: 415.2356, found: 415.2352.

5-(4-methoxyphenyl)-*N,N*-dimethyl-2,3-dihydrobenzo[*b*][1,4]oxazine-4-carboxamide (3kc), yellow solid, mp: 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 6H), 3.83 (s, 3H), 3.82(m, 2H), 4.36 (t, *J* = 4.76 Hz, 2H), 6.83 (d, *J* = 7.52 Hz,1H), 6.88 (d, *J* = 8.08 Hz, 1H), 6.95 (d, *J* = 8.64 Hz, 2H), 7.04 (t, *J* = 7.84, 1H), 7.28 (d, *J* = 8.64 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 37.1, 44.0, 55.3, 66.8, 113.6, 116.0, 123.0, 124.6, 126.3, 128.8, 130.6, 132.0, 135.2, 147.2, 158.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO_3$ $[M+Na]^+$: 335.1366, found: 335.1361.

5-(3,5-dimethylphenyl)-*N,N*-dimethyl-2,3-dihydrobenzo[*b*][1,4]oxazine-4-carboxamide (3ke), yellow solid, mp: 129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 2.36 (s, 6H), 3.80 (brs, 2H), 4.34 (t, *J* = 4.80 Hz, 2H), 6.85 (dd, *J* = 7.52, 1.44 Hz, 1H), 6.89 (dd, *J* = 8.12, 1.48 Hz, 1H), 6.94 (m, 3H), 7.04 (t, *J* = 7.80 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.4, 36.9, 44.0, 66.8, 116.1, 123.1, 124.4, 125.4, 126.4, 128.6, 135.6, 137.68, 139.2, 147.1, 158.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{22}N_2NaO_2$ $[M+Na]^+$: 333.1574, found: 333.1572.

5-(3,4-dimethylphenyl)-*N,N*-dimethyl-2,3-dihydrobenzo[*b*][1,4]oxazine-4-carboxamide (3kf), yellow solid, mp: 133 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.32 (m, 9H), 3.83 (bs, 2H), 3.50 (t, *J* = 4.80 Hz, 2H), 6.89 (m, 2H), 7.06 (m, 2H), 7.12 (s, 1H), 7.17 (d, *J* = 7.72 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.4, 19.8, 37.0, 43.9, 66.9, 116.0, 123.1, 124.5, 125.1, 126.4, 128.7, 129.4, 135.2, 135.5, 136.2, 136.9, 147.1, 158.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{19}H_{22}N_2NaO_2$ $[M+Na]^+$: 333.1574, found: 333.1573.

***N,N*-dimethyl-7-p-tolylindoline-1-carboxamide (3la)**, white solid, mp: 103 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.61 (s, 6H), 3.12 (t, *J* = 8.0 Hz, 2H), 3.99 (t, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.40 Hz, 1H), 7.18 (dd, *J* = 10.4, 8.0 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.1, 29.7, 36.8, 51.8, 122.9, 123.3, 126.6, 126.7, 128.8, 129.1, 133.6, 136.2, 137.4, 142.2, 159.7; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO$ $[M+Na]^+$: 303.1468, found: 303.1467.

7-(4-methoxyphenyl)-*N,N*-dimethylindoline-1-carboxamide (3lb), orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 6H), 3.12 (t, *J* = 7.92 Hz, 2H), 3.84 (s, 3H), 3.98 (t, *J* = 8.0 Hz, 2H), 6.93 (dt, *J* = 9.63, 2.91 Hz, 2H), 7.04 (t, *J* = 7.40 Hz, 1H), 7.16 (m, 2H), 7.39 (dt, *J* = 9.63, 2.91 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.8, 37.0, 51.9, 55.2, 113.7, 123.1, 123.3, 128.1, 128.8, 129.0, 132.9, 133.8, 142.3, 158.5, 159.8; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO_2$ $[M+Na]^+$: 319.1417, found: 319.1414.

1-(biphenyl-2-yl)-1,3,3-trimethylurea (3mb), white solid, mp: 62.4°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 6H), 3.20 (s, 3H), 7.26 (m, 2H), 7.35 (m, 5H), 7.43 (m,

2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 37.5, 40.1, 125.7, 126.8, 127.3, 128.0, 128.4, 128.7, 131.6, 137.6, 139.2, 143.9, 160.6; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{16}H_{18}N_2NaO$ $[M+Na]^+$: 277.1311, found: 277.1308.

1-(4'-methoxybiphenyl-2-yl)-1,3,3-trimethylurea (3mc), red solid, mp: 72.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38(s, 6H), 3.16(s, 3H), 3.83(s, 3H), 6.95(d, *J*=6.72, 2H), 7.19~7.24(m, 2H), 7.28(s, 1H), 7.30~7.34(m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 37.62, 39.93, 55.26, 113.80, 125.78, 126.81, 128.25, 129.13, 131.51, 131.64, 137.08, 143.75, 158.91, 160.72; IR (neat, cm^{-1}): 1645; HRMS (ESI) calcd. for $C_{17}H_{20}N_2NaO_2$ $[M+Na]^+$: 307.1417, found: 307.1417.

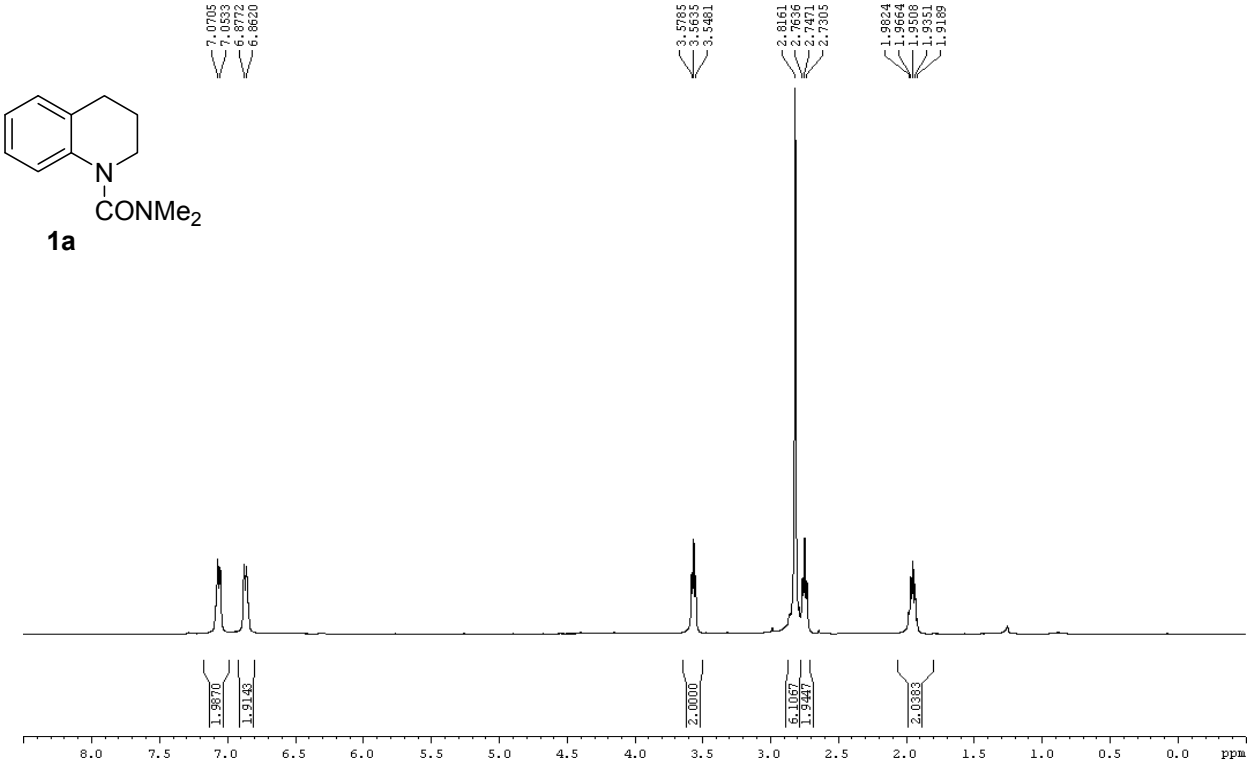
(*R*)-*N,N*,2-trimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide ((*R*)-3bb),[3] yellow solid, mp: 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (m, 3H), 1.55(m, 1H), 2.07 (s, 6H), 2.42 (d, *J* = 5.02 Hz, 1H), 2.57 (m, 1H), 2.76 (m, 1H), 4.33 (t, *J* = 3.28 Hz, 1H), 7.12 (t, *J* = 7.32 Hz, 1H), 7.17 (m, 2H), 7.29 (m, 1H), 7.39 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.2, 26.7, 33.1, 36.6, 51.2, 124.0, 126.9, 127.0, 127.6, 128.2, 129.4, 134.4, 135.9, 137.1, 139.7, 159.8; $[\alpha]^{22}_D$ = -100.5 (c = 1.0, $CHCl_3$); HPLC (AD-H, elute: Hexanes / i-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5ml/min), (R) t_1= 15.1 min, (S) t_2 = 10.3 min.

(*R*)-8-(4-methoxyphenyl)-*N,N*,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide ((*R*)-3bc), yellow solid, mp: 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.44 Hz, 3H), 1.53 (m, 1H), 2.10 (s, 6H), 2.42 (d, *J* = 5.64 Hz, 1H), 2.54 (m, 1H), 2.74 (m, 1H), 3.83 (s, 3H), 4.33 (t, *J* = 6.56 Hz, 1H), 6.95 (d, *J* = 8.68 Hz, 2H), 7.12 (m, 3H), 7.31(d, *J* = 8.62 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.1, 22.7, 26.8, 29.7, 36.7, 51.2, 124.0, 125.4, 126.7, 127.4, 128.9, 129.4, 135.9, 136.5, 136.8, 137.1, 159.9; $[\alpha]^{22}_D$ = -108.7 (c = 1.0, $CHCl_3$); HPLC (AD-H, elute: Hexanes / i-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5ml/min), (R) t_1= 12.4 min, (S) t_2 = 33.3 min.

4. References:

1. A. Nose and T. Kudo. *Chem. Pharm. Bull.* **1984**, *32*, 2421.
2. C. Wang, C. Li, X. Wu, A. Pettman and J. Xiao, *Angew. Chem. Int. Ed.*, **2009**, *48*, 6524.
3. T. Nishikata, A. R. Abela, S. Huang and B. H. Lipshutz, *J. Am. Chem. Soc.* **2010**, *132*, 4978.

5. ^{1}H and ^{13}C NMR spectra of the ureas and arylated ureas



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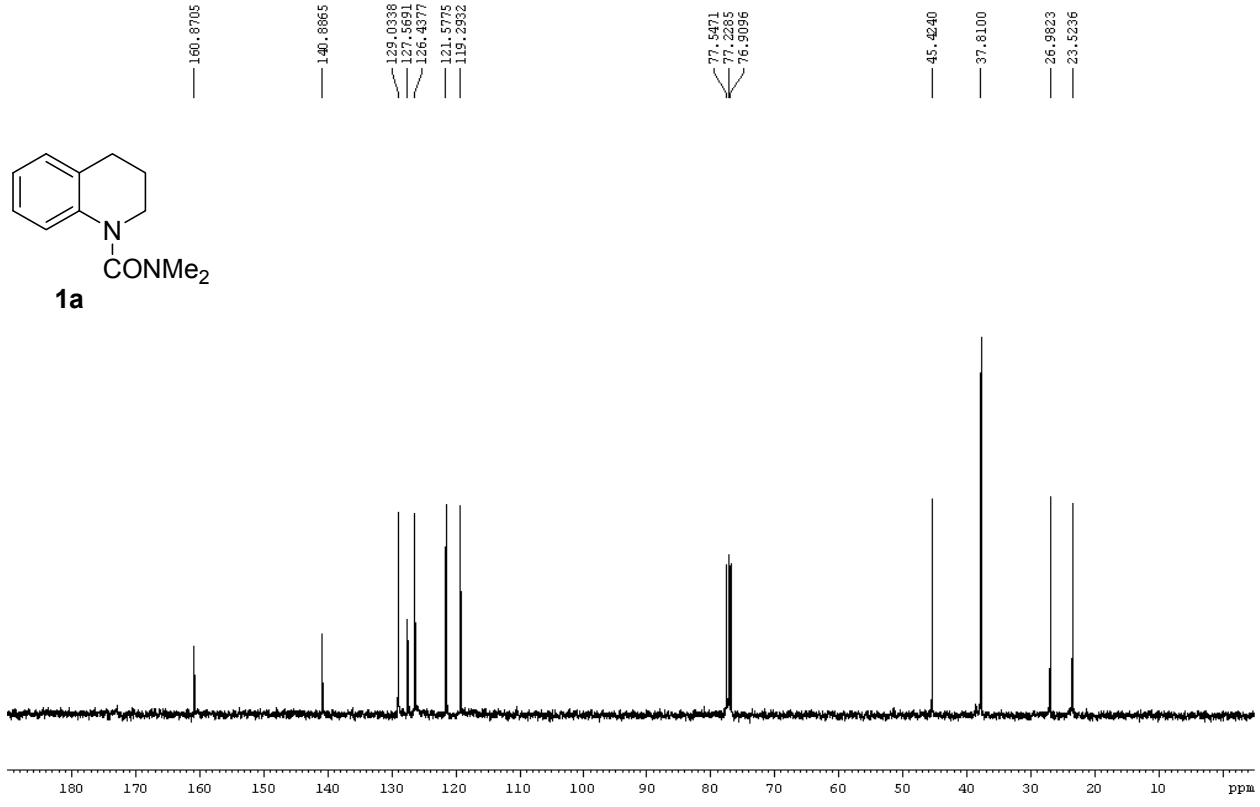

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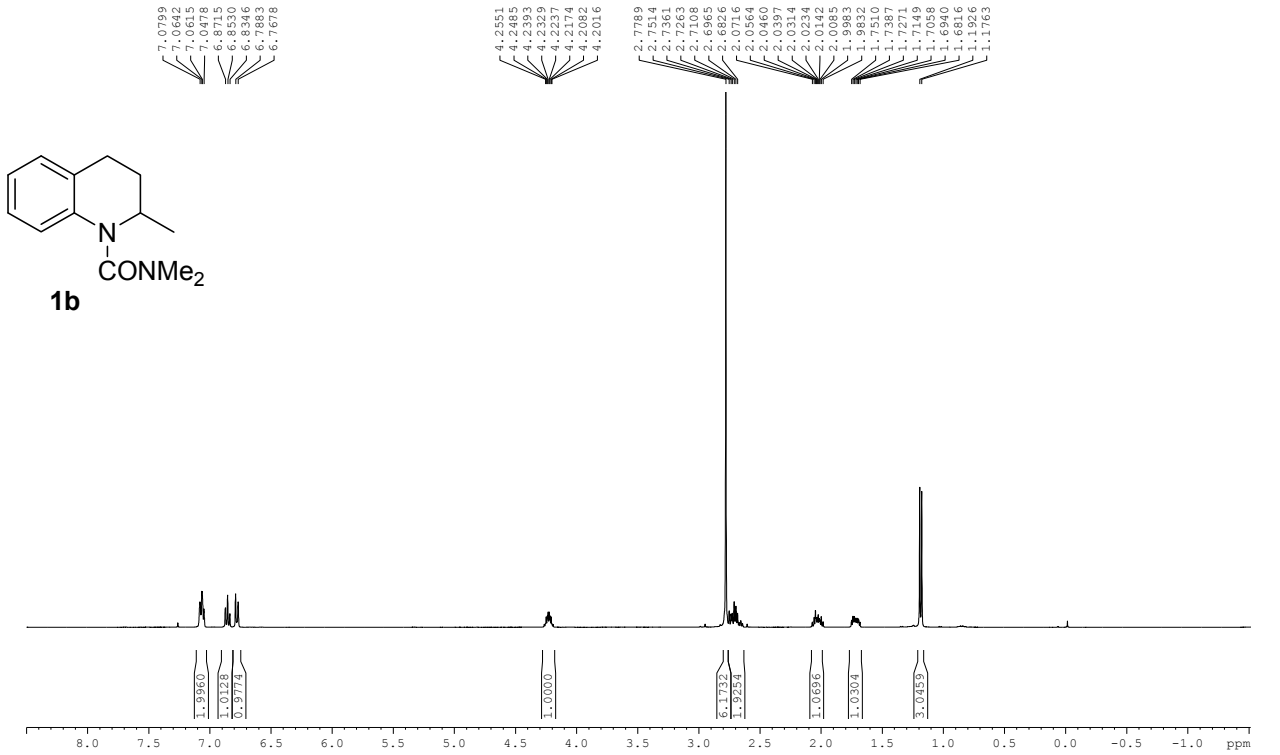

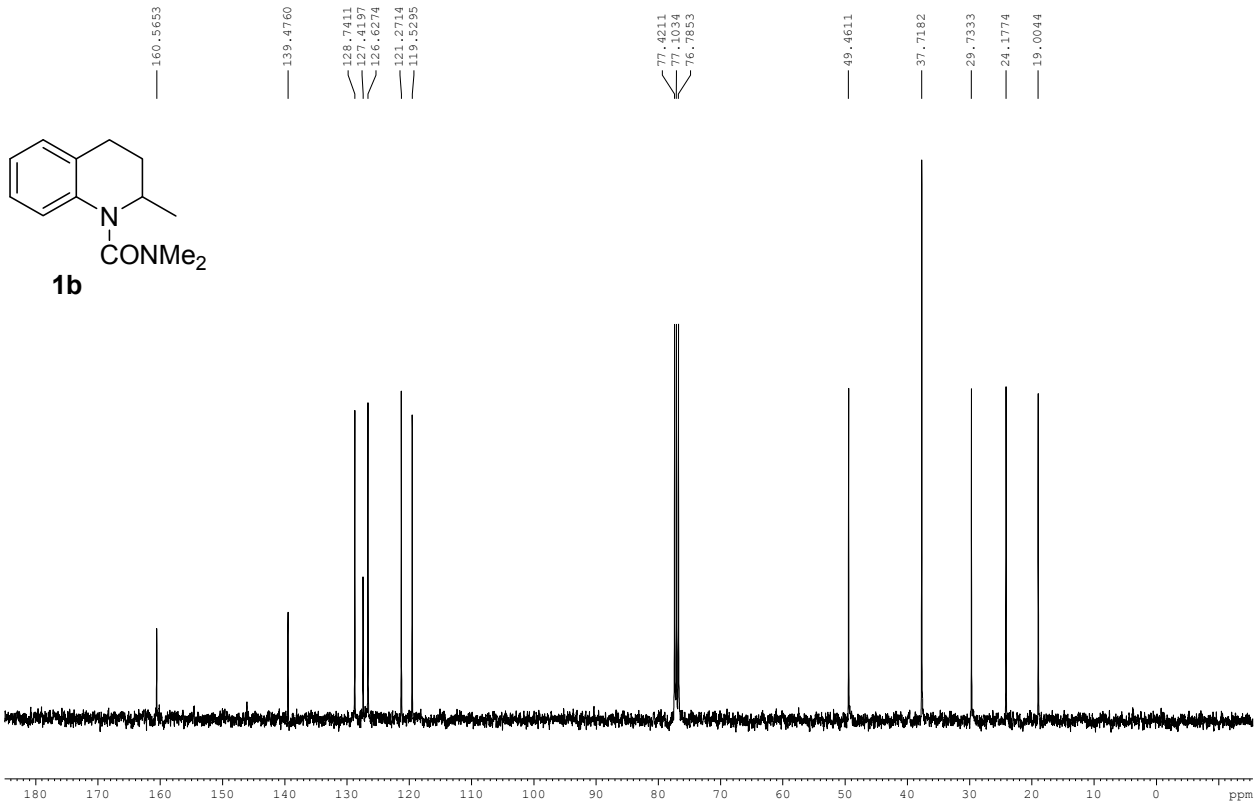

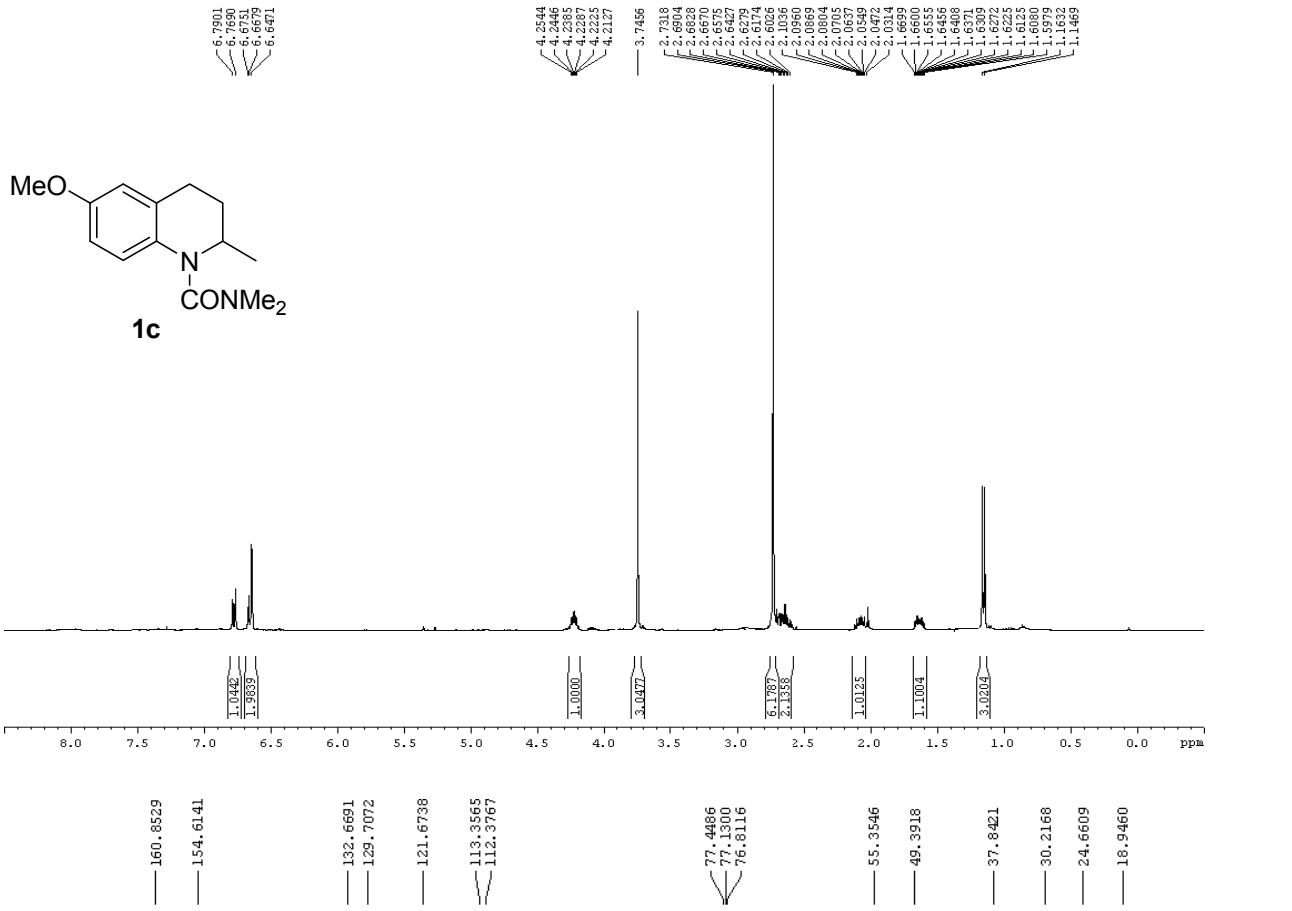

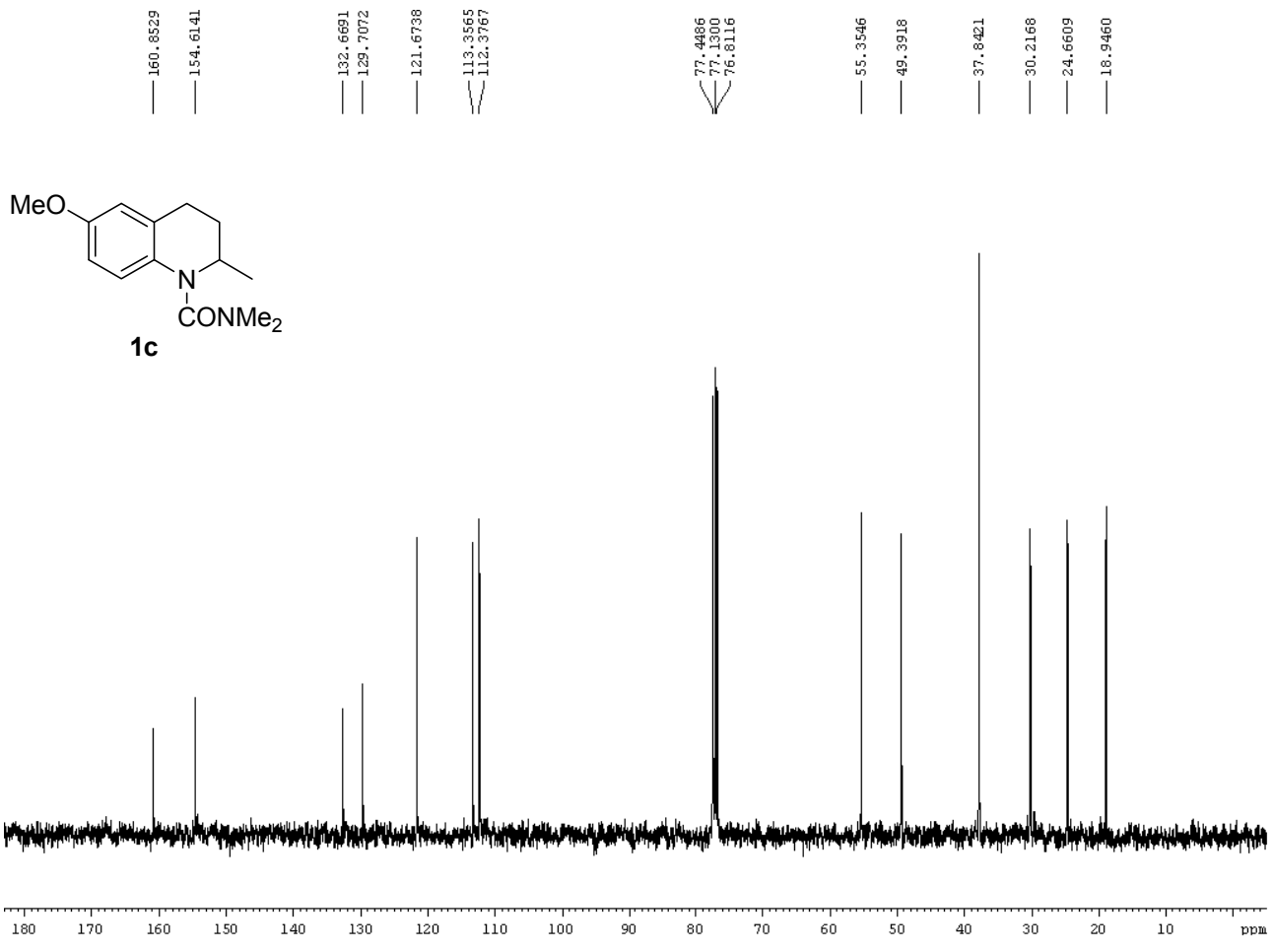

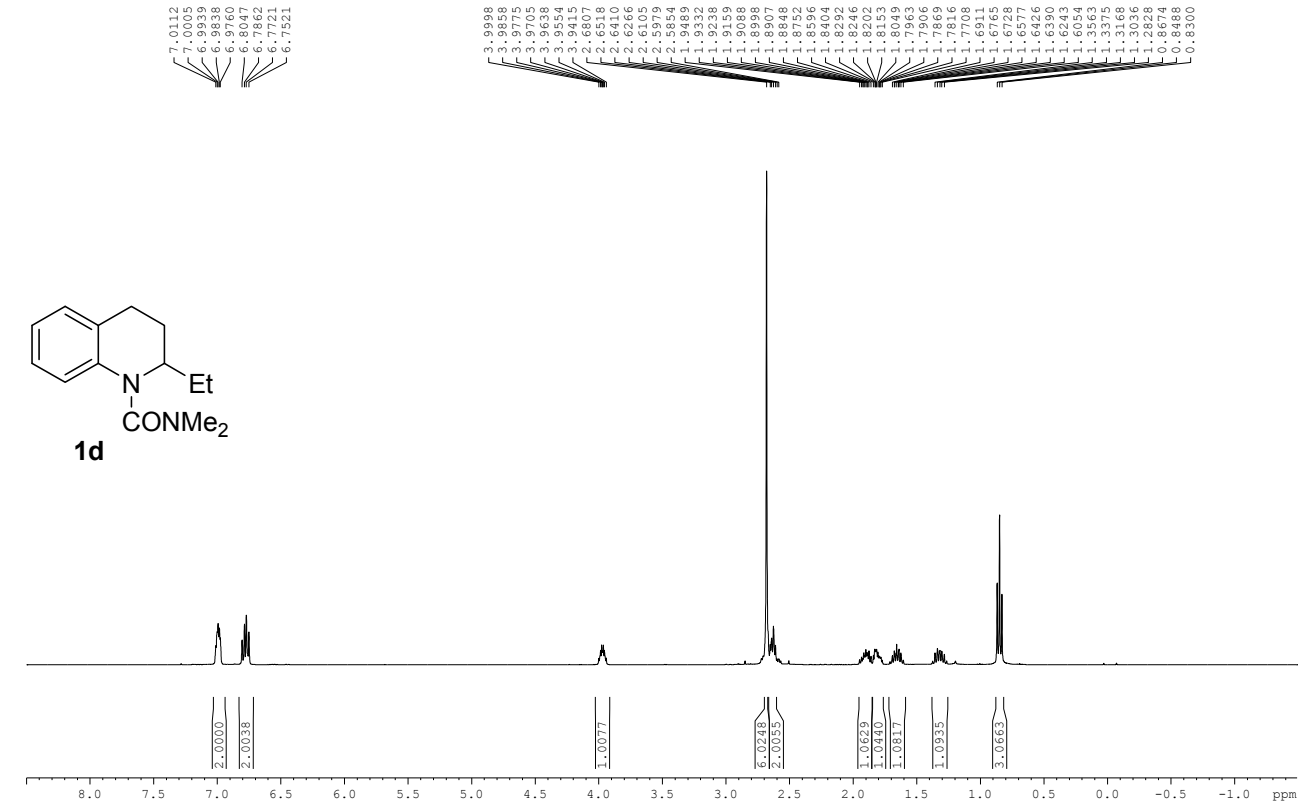

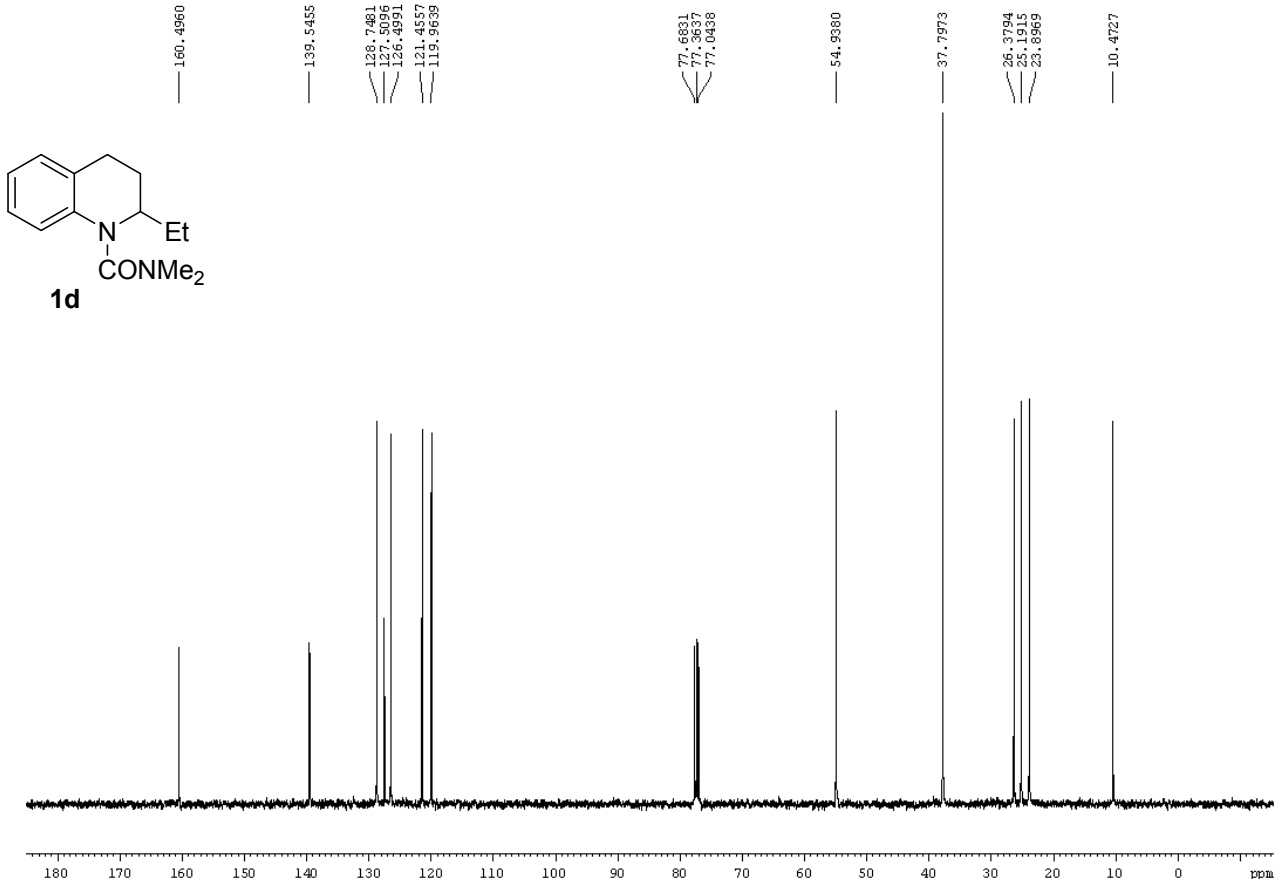

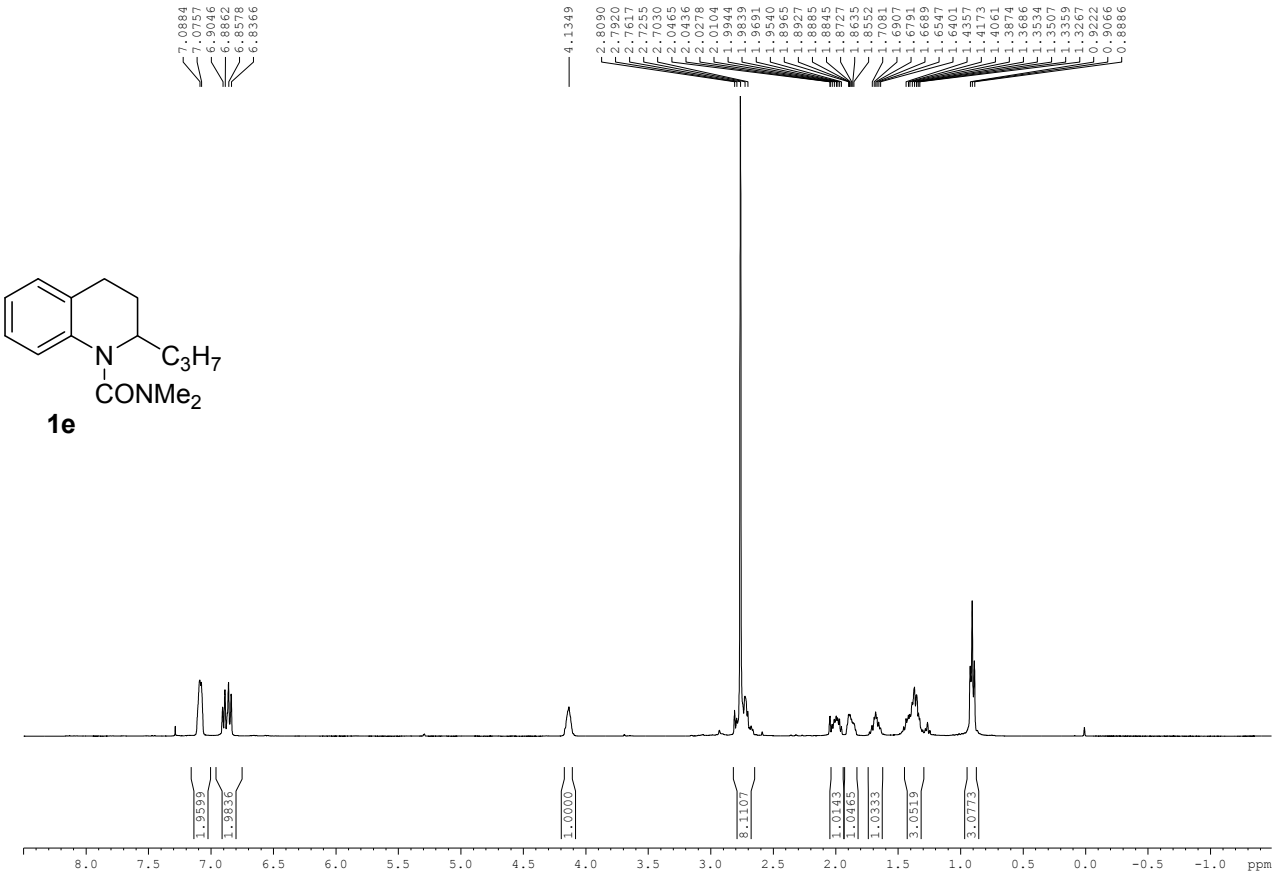

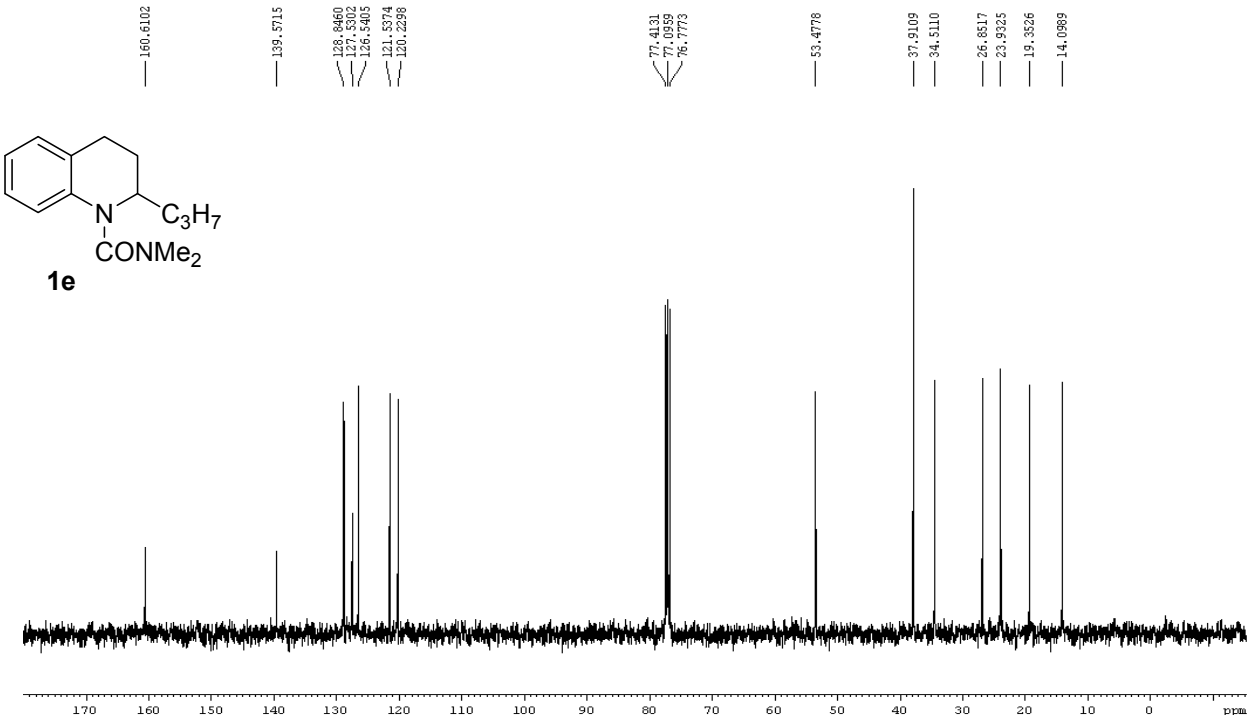

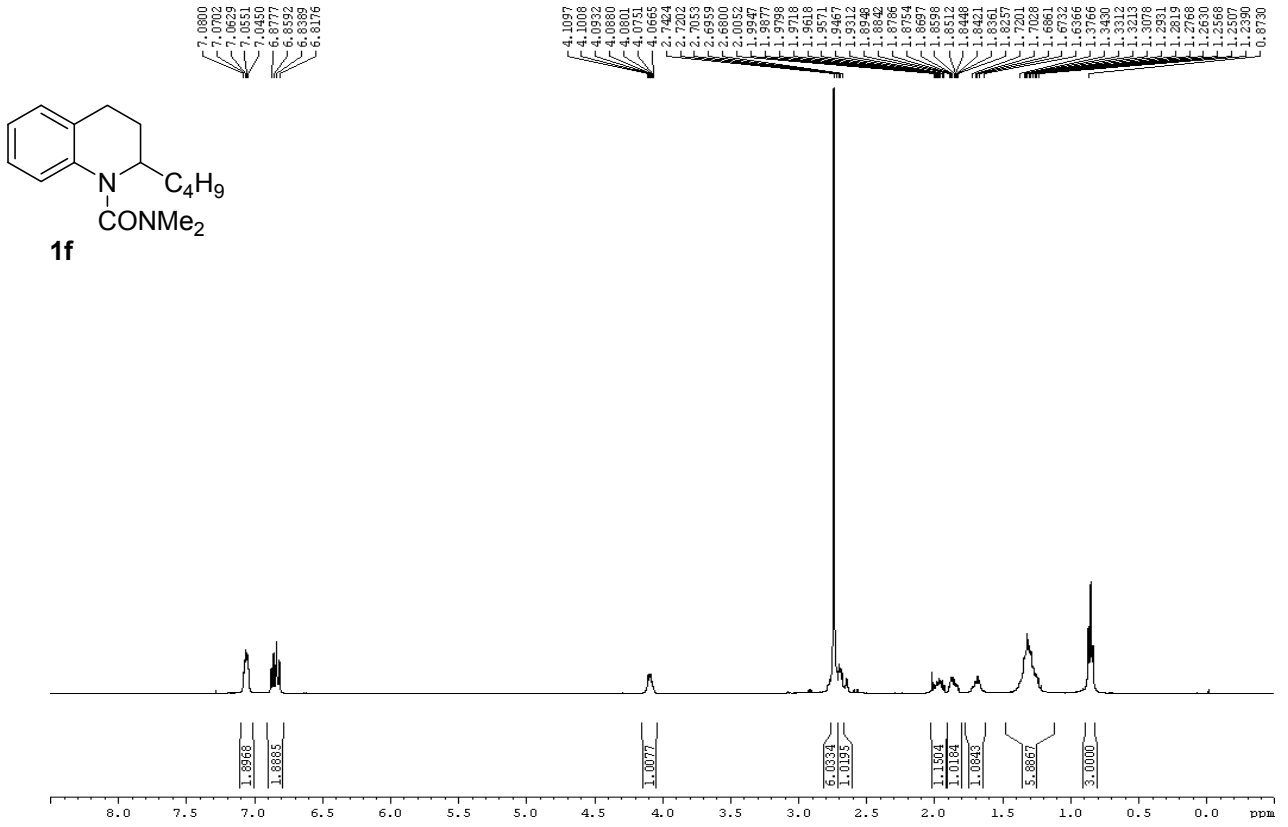

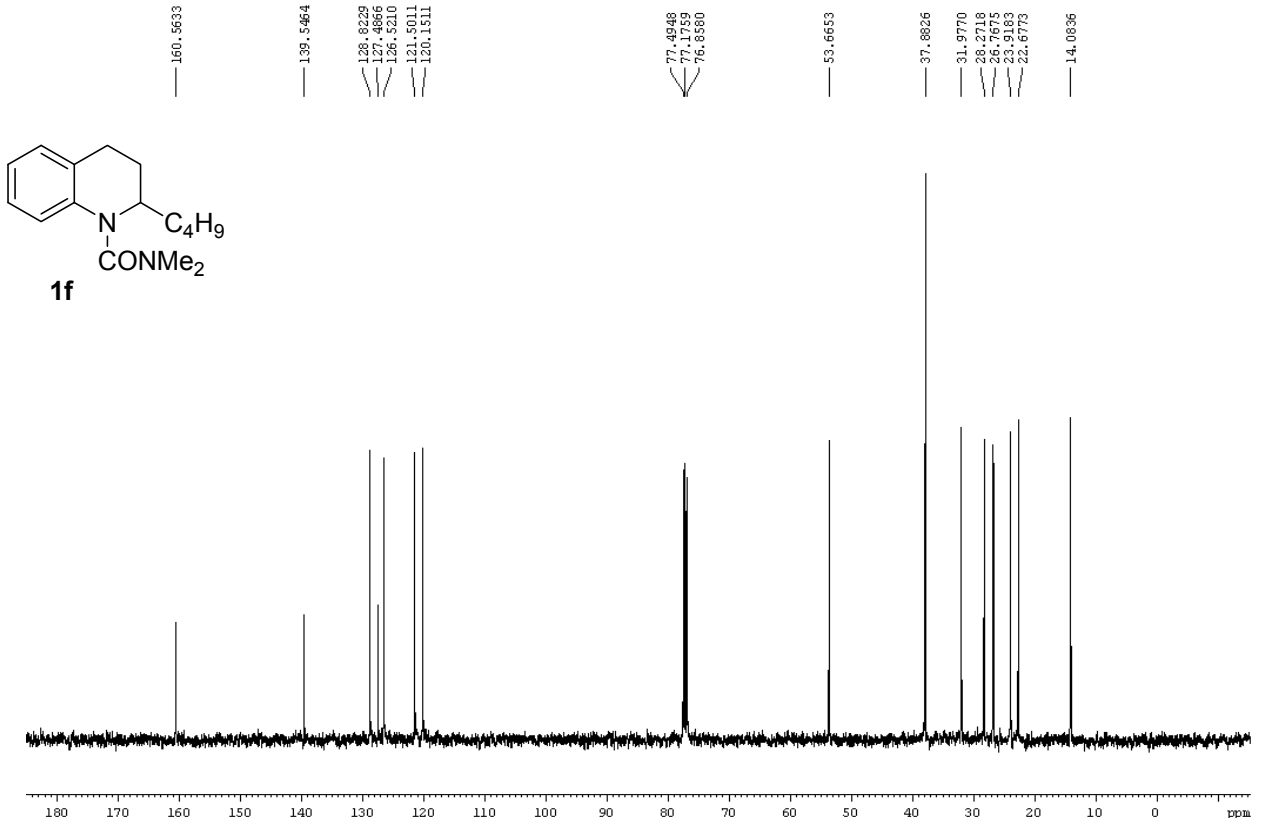

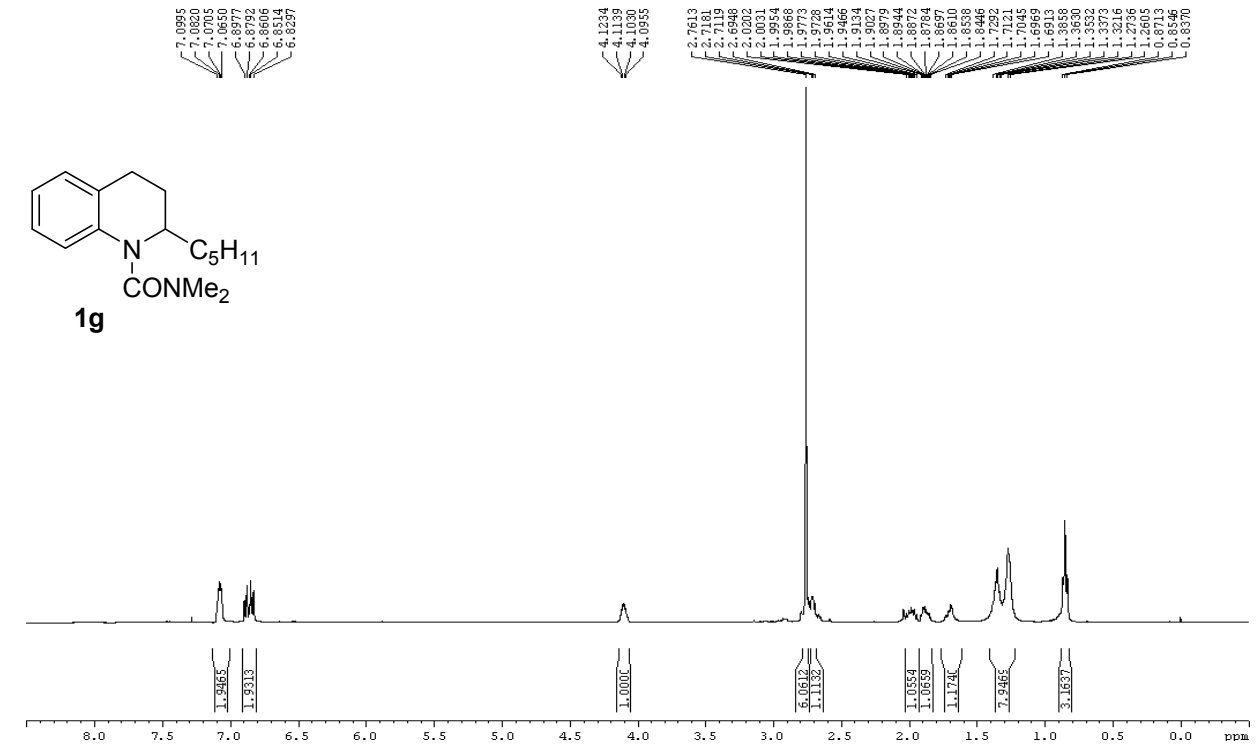

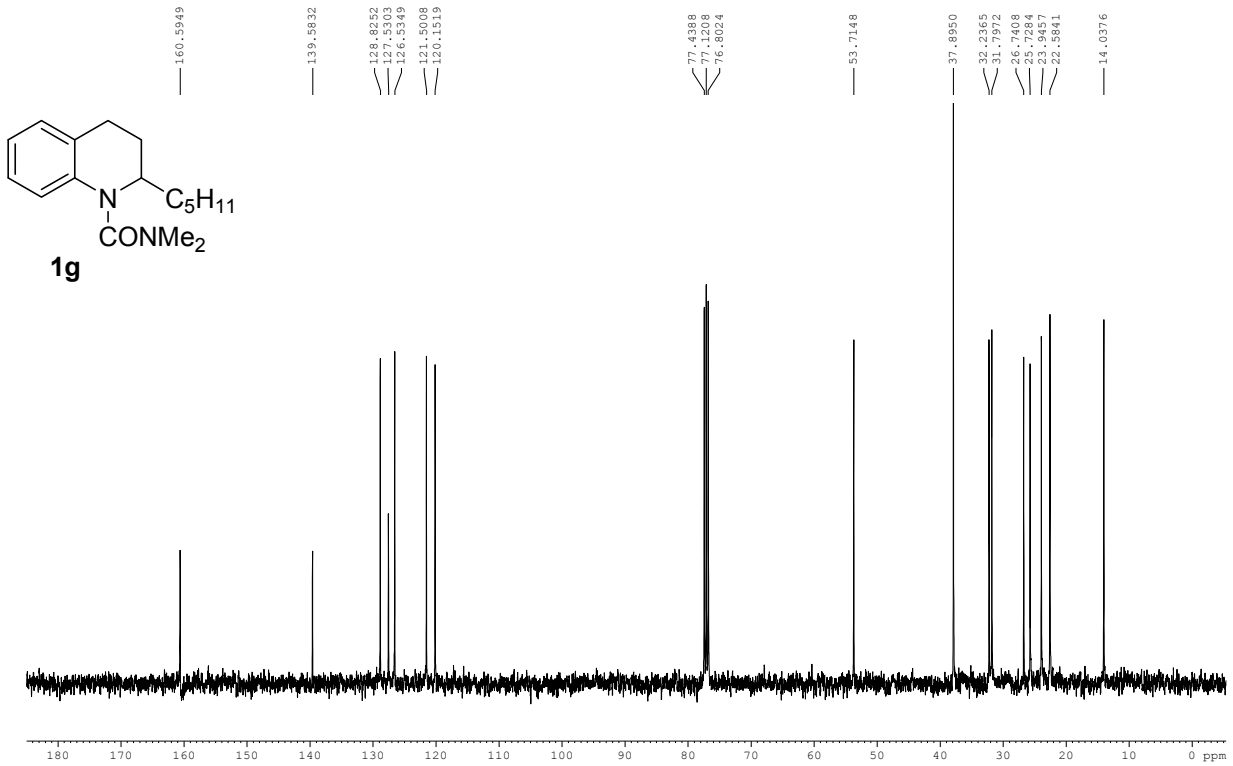

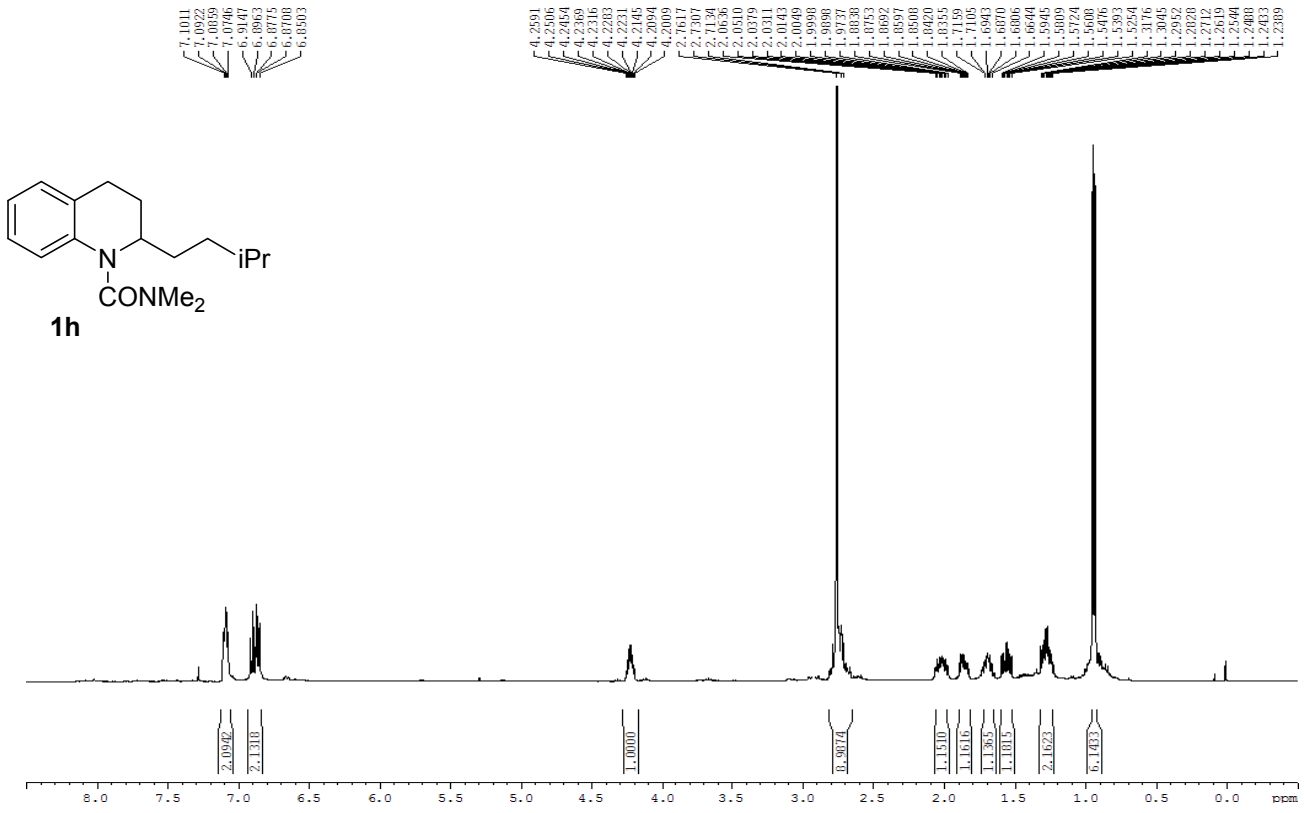

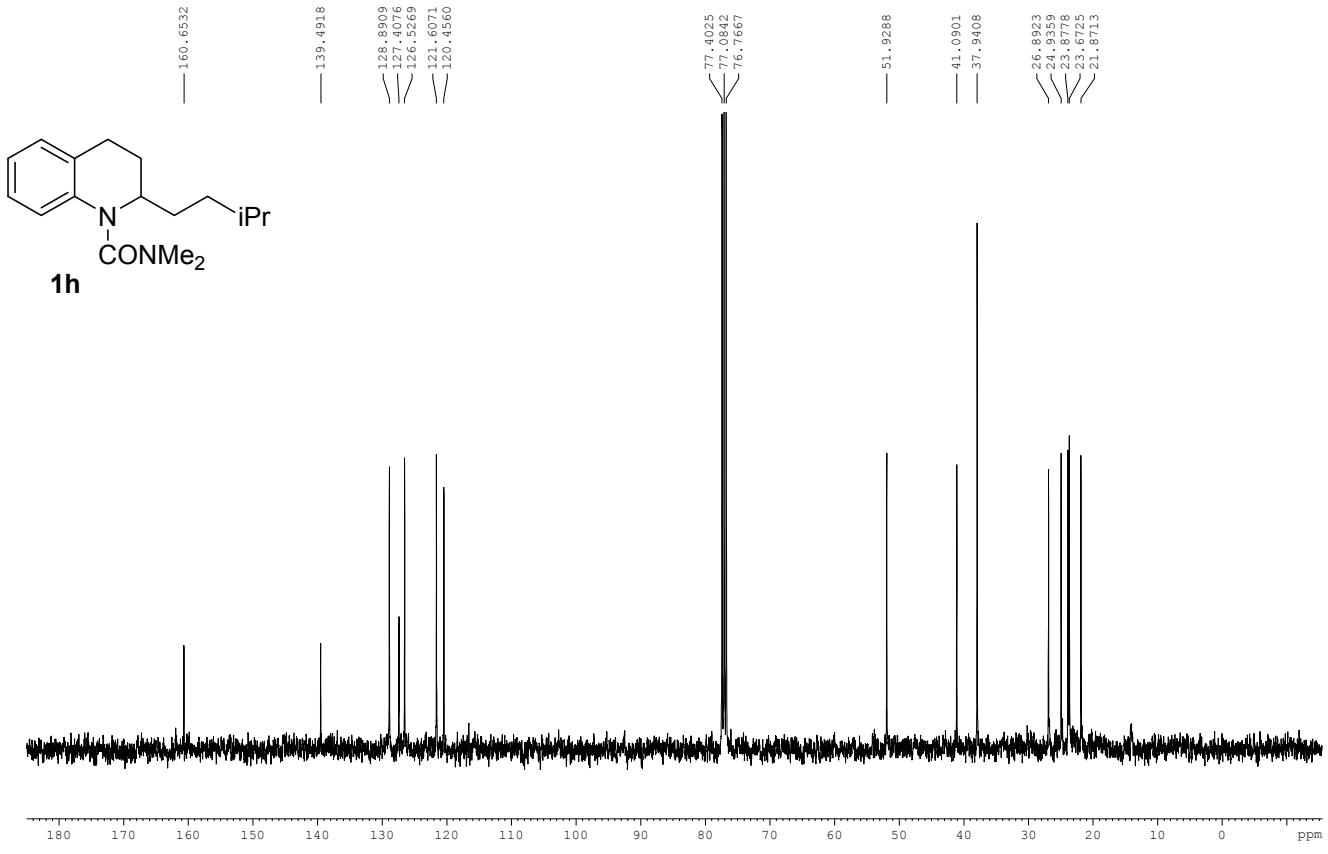

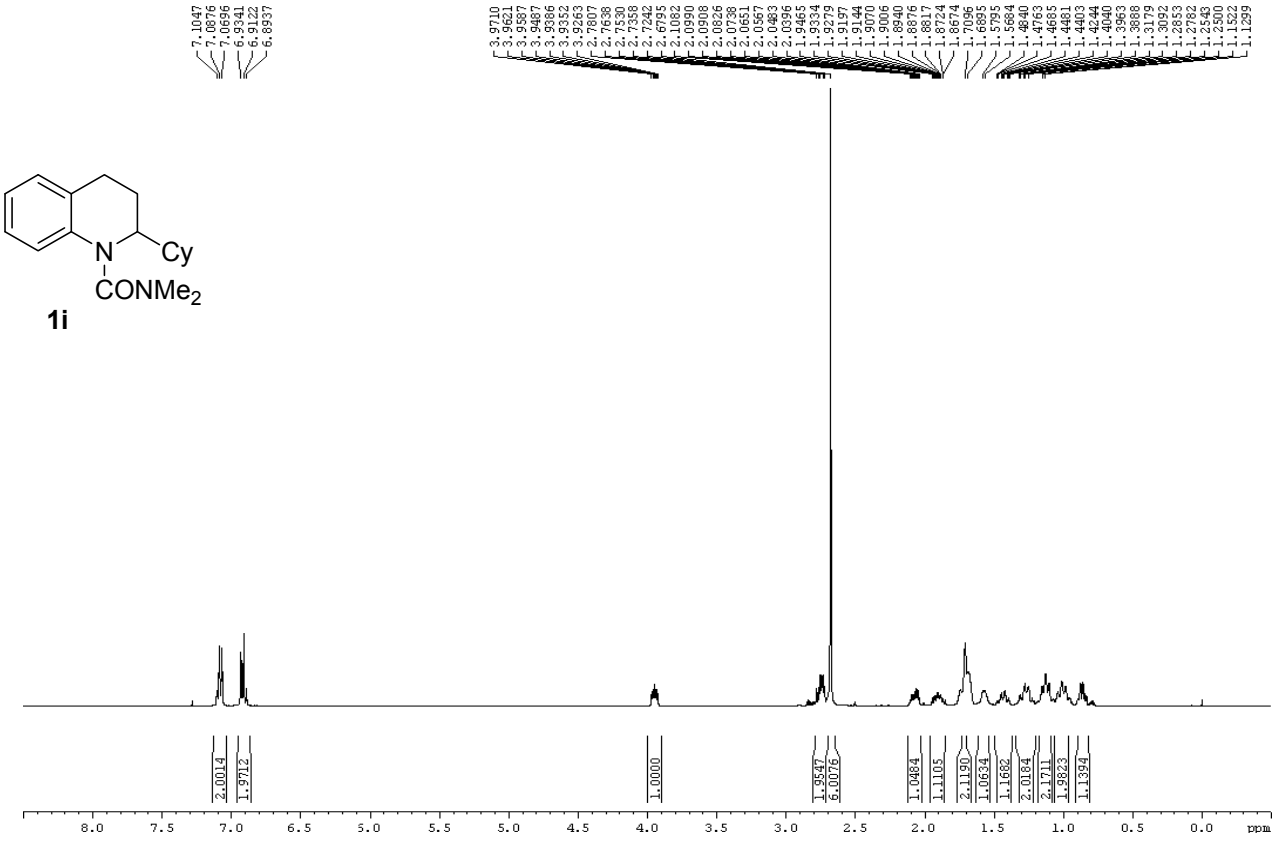

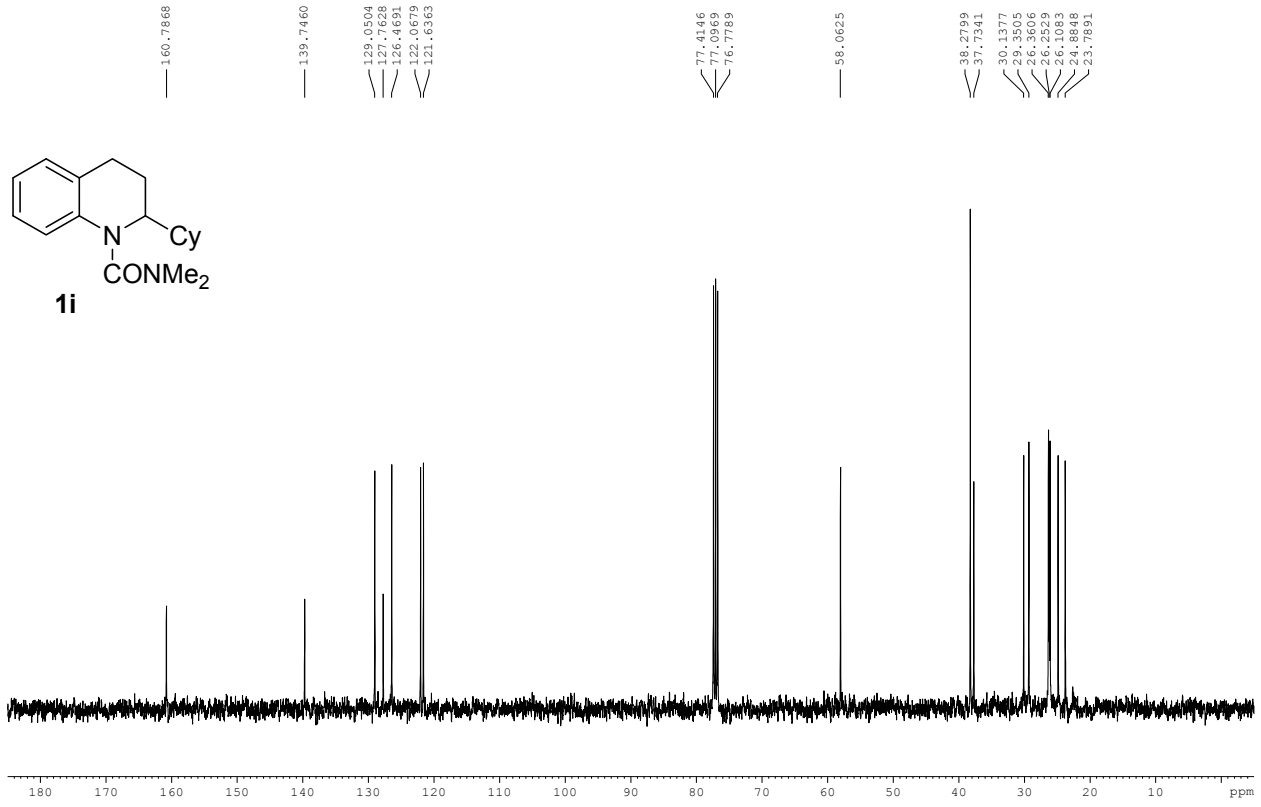

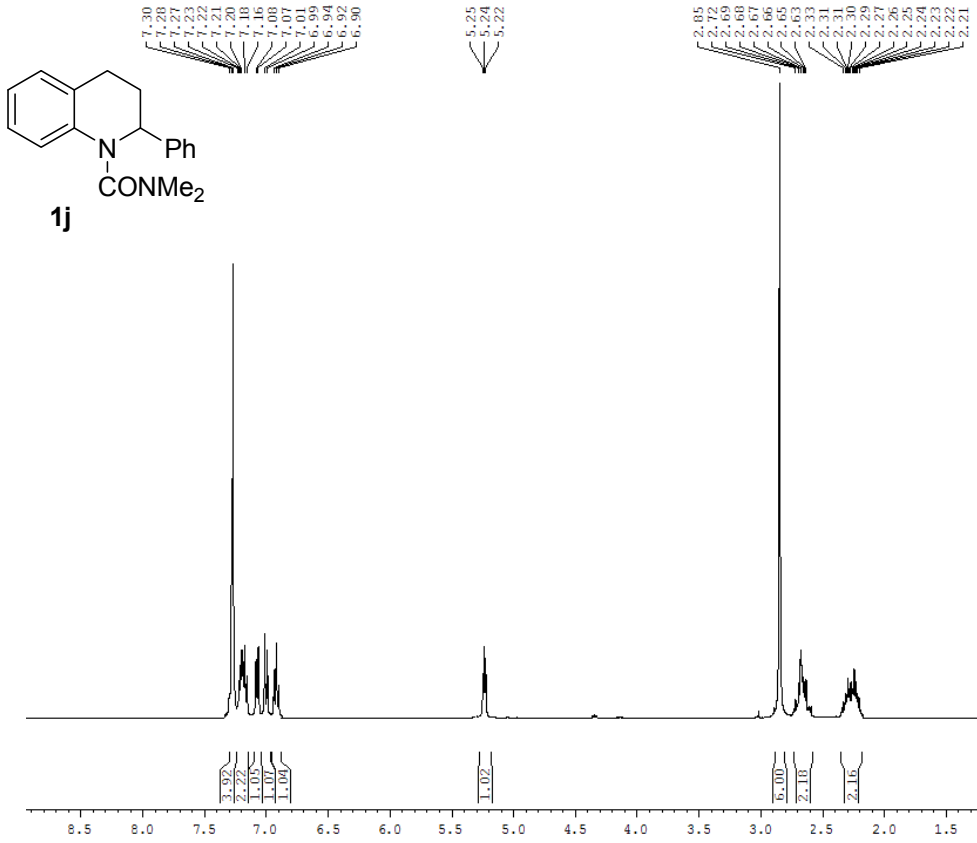

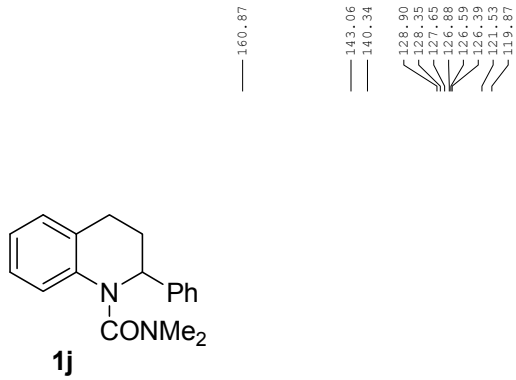

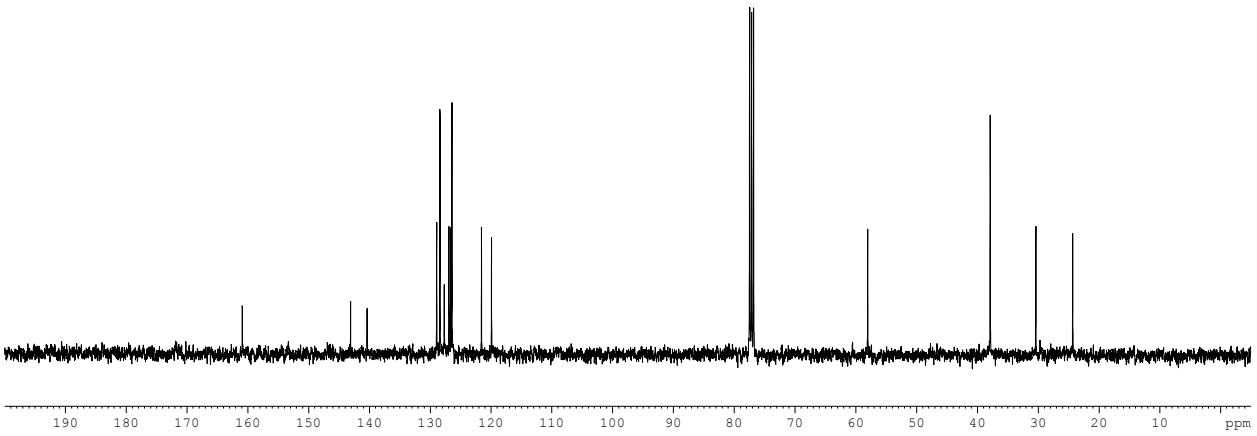

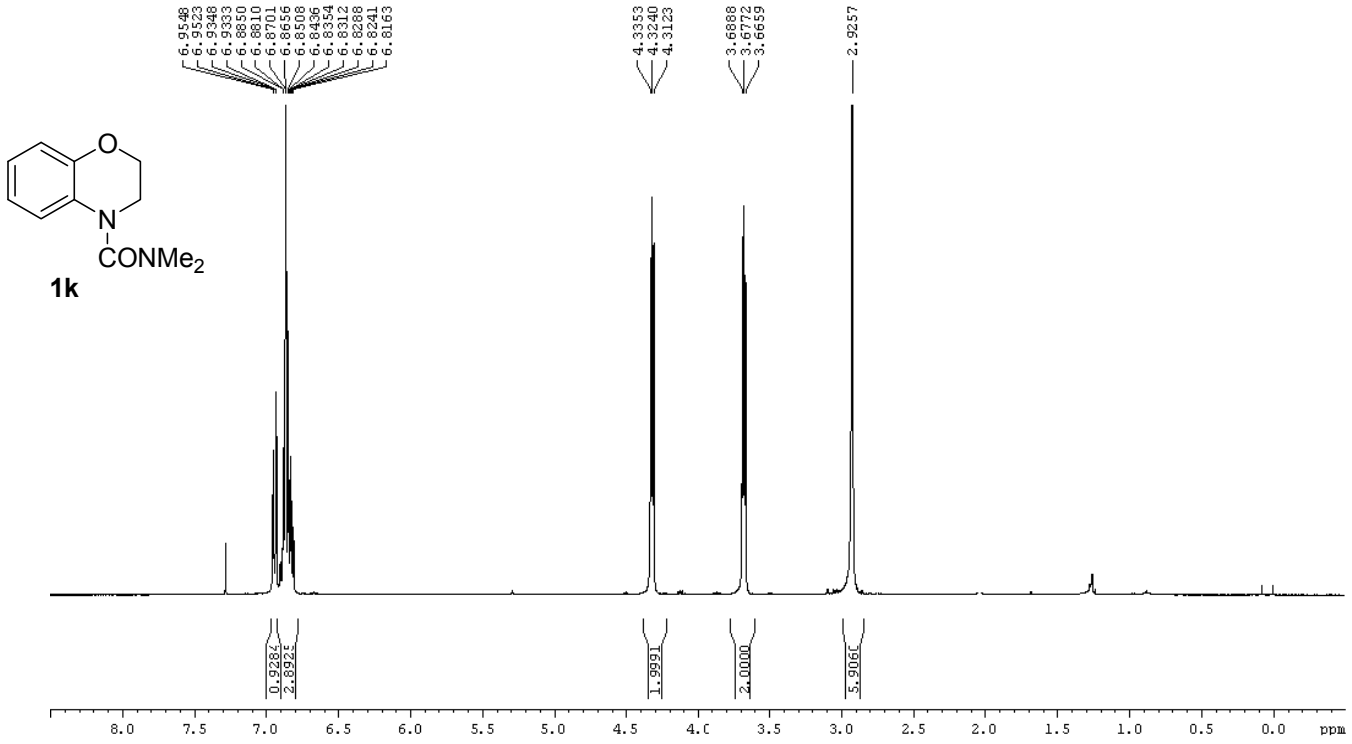

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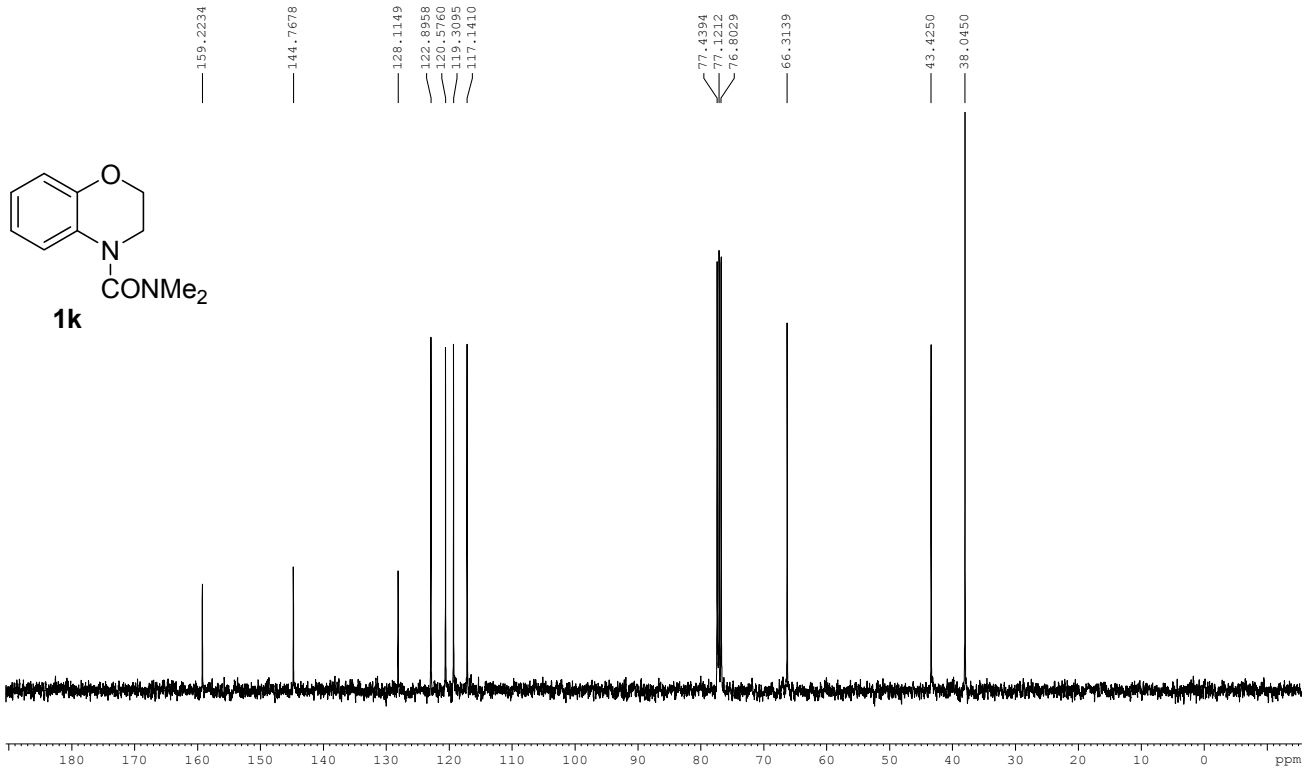

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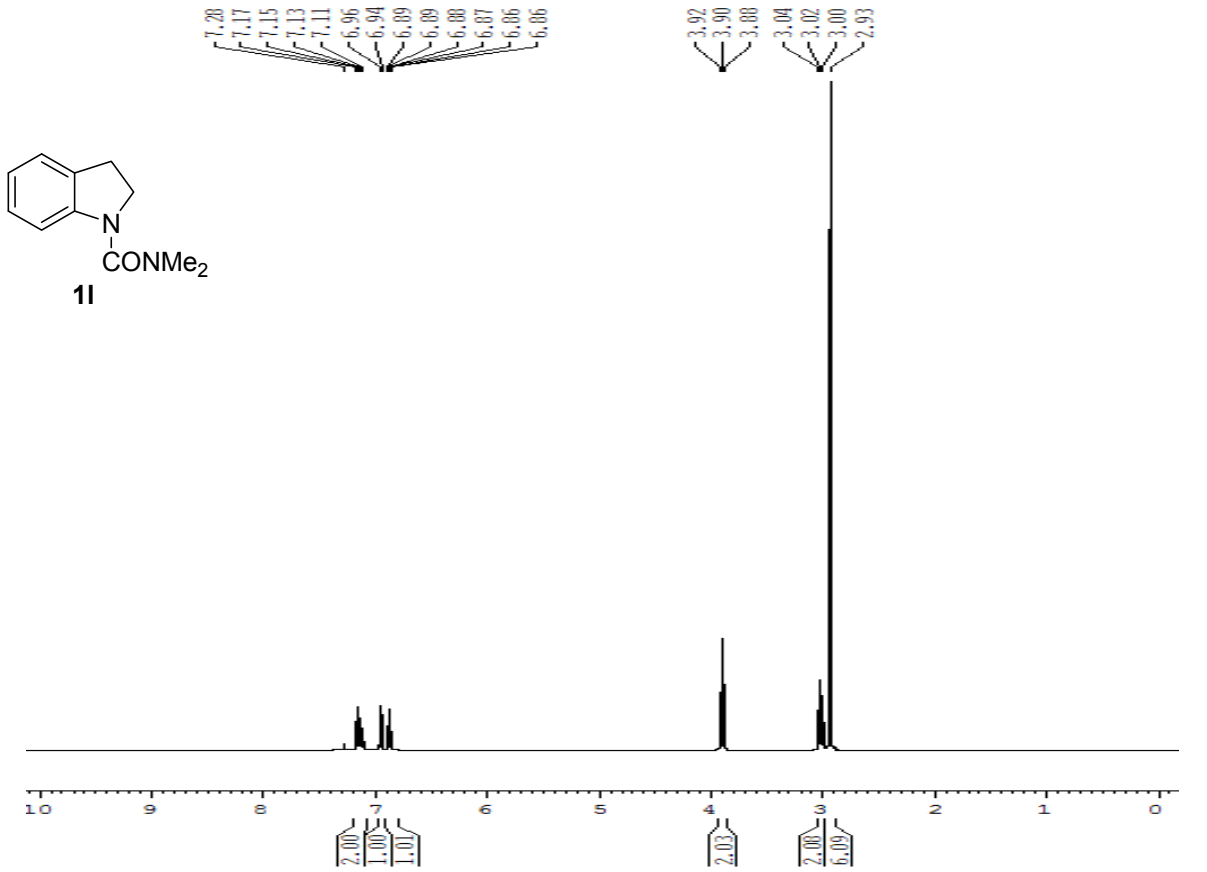

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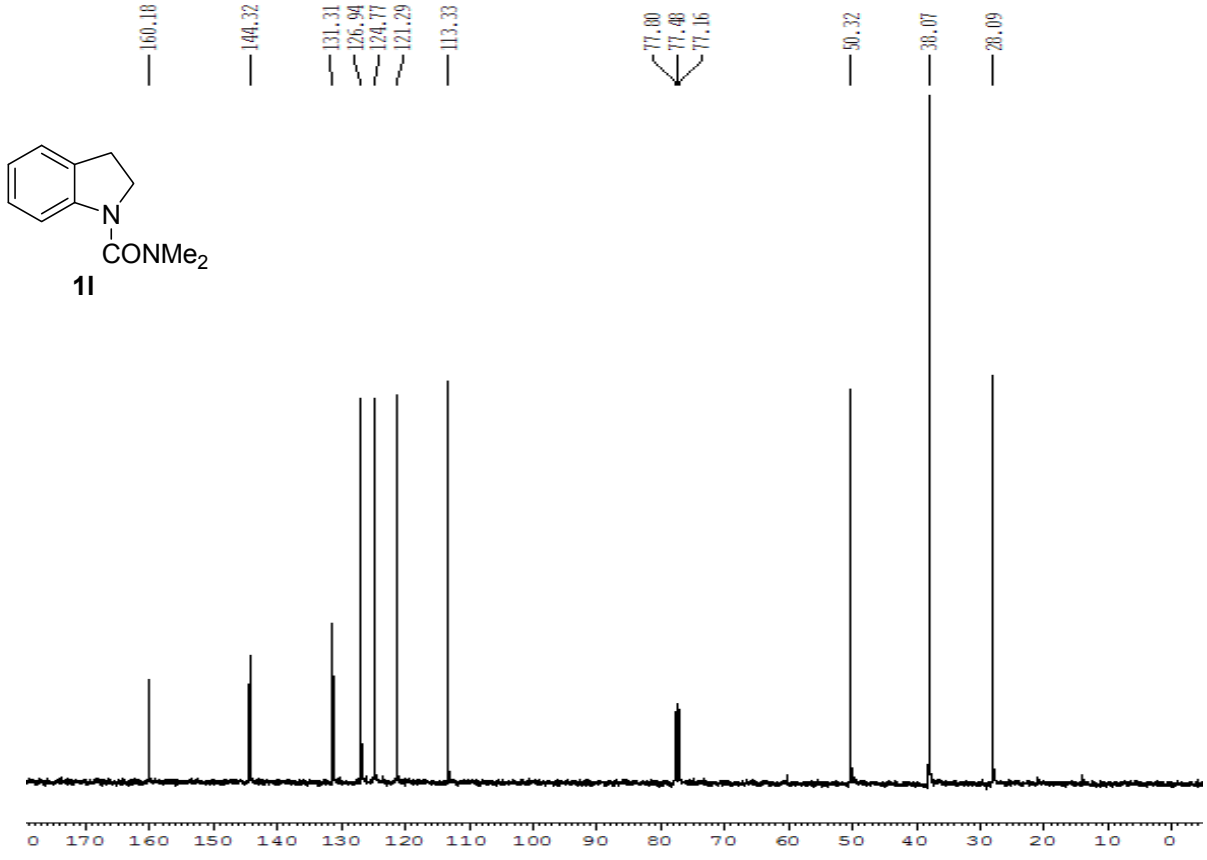

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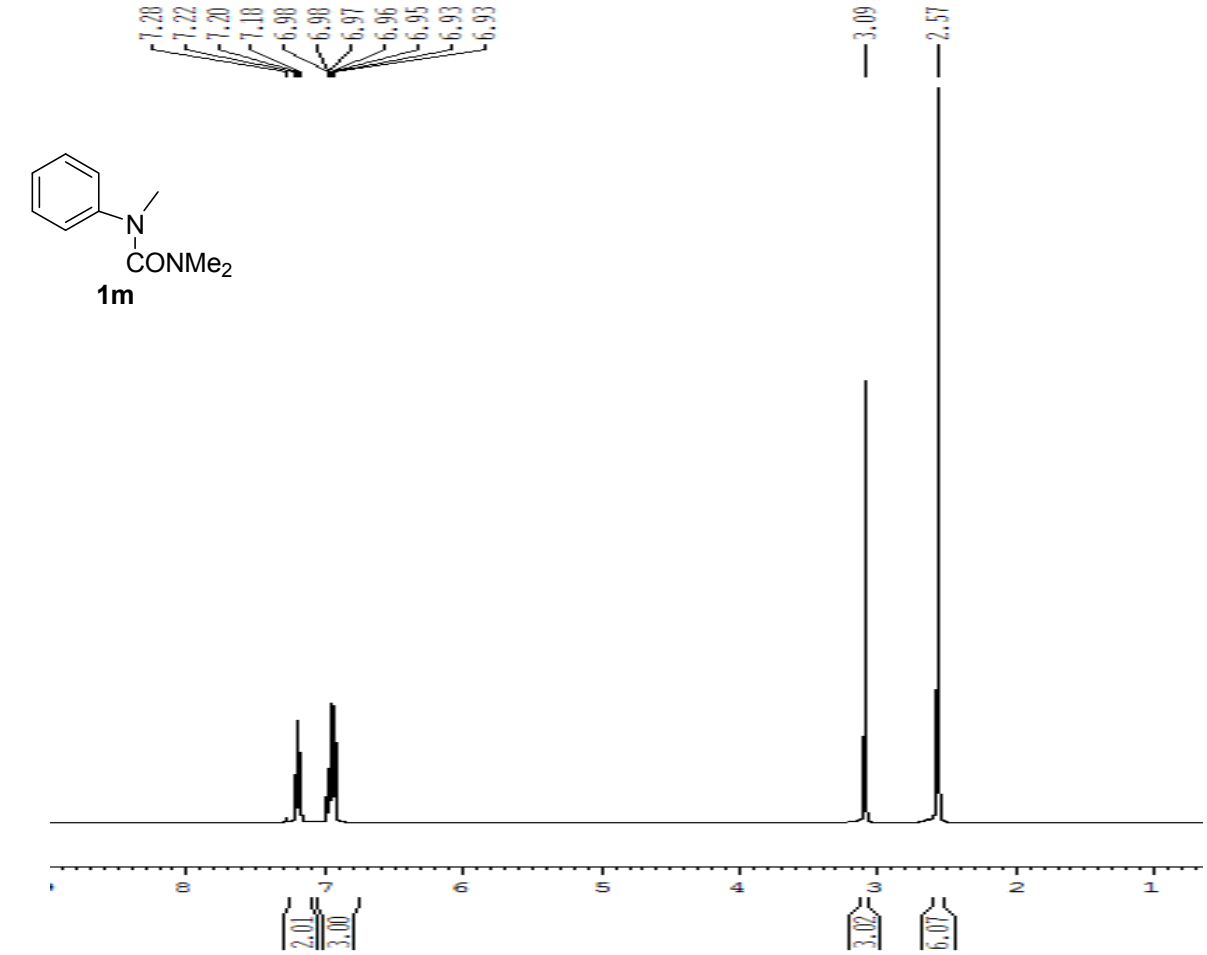

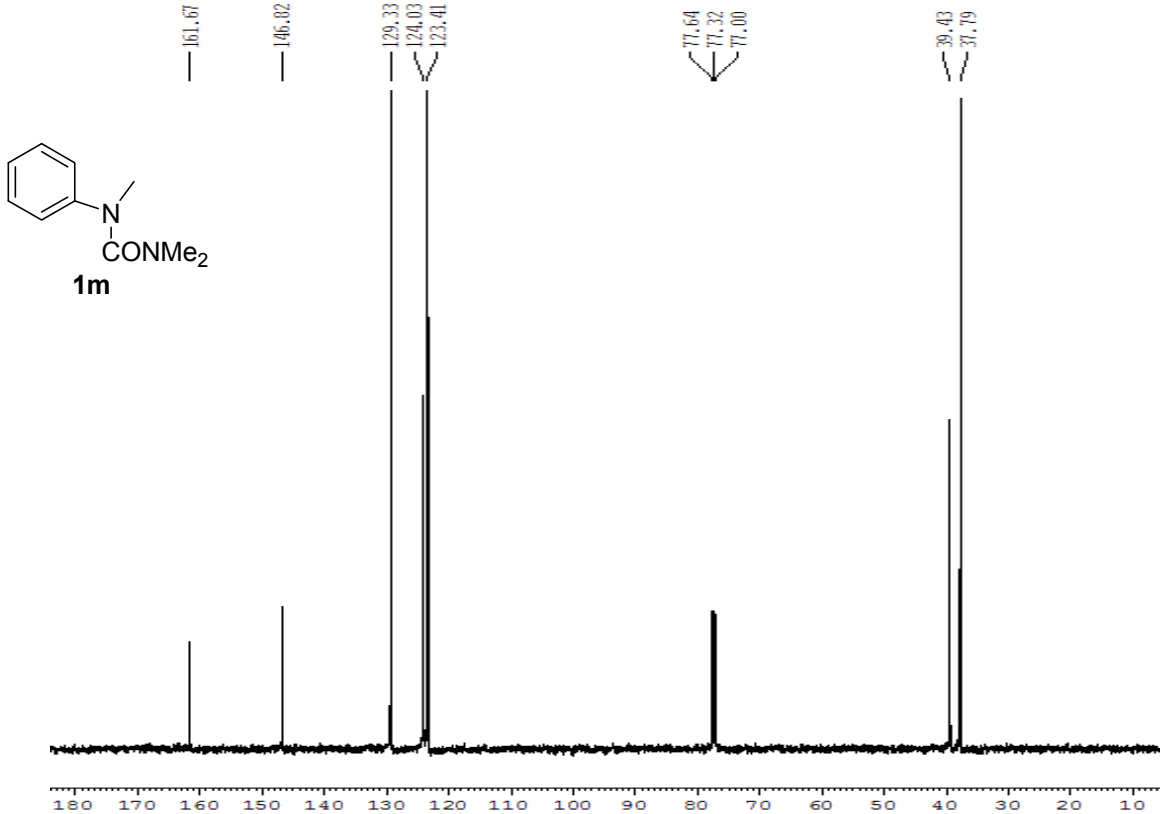

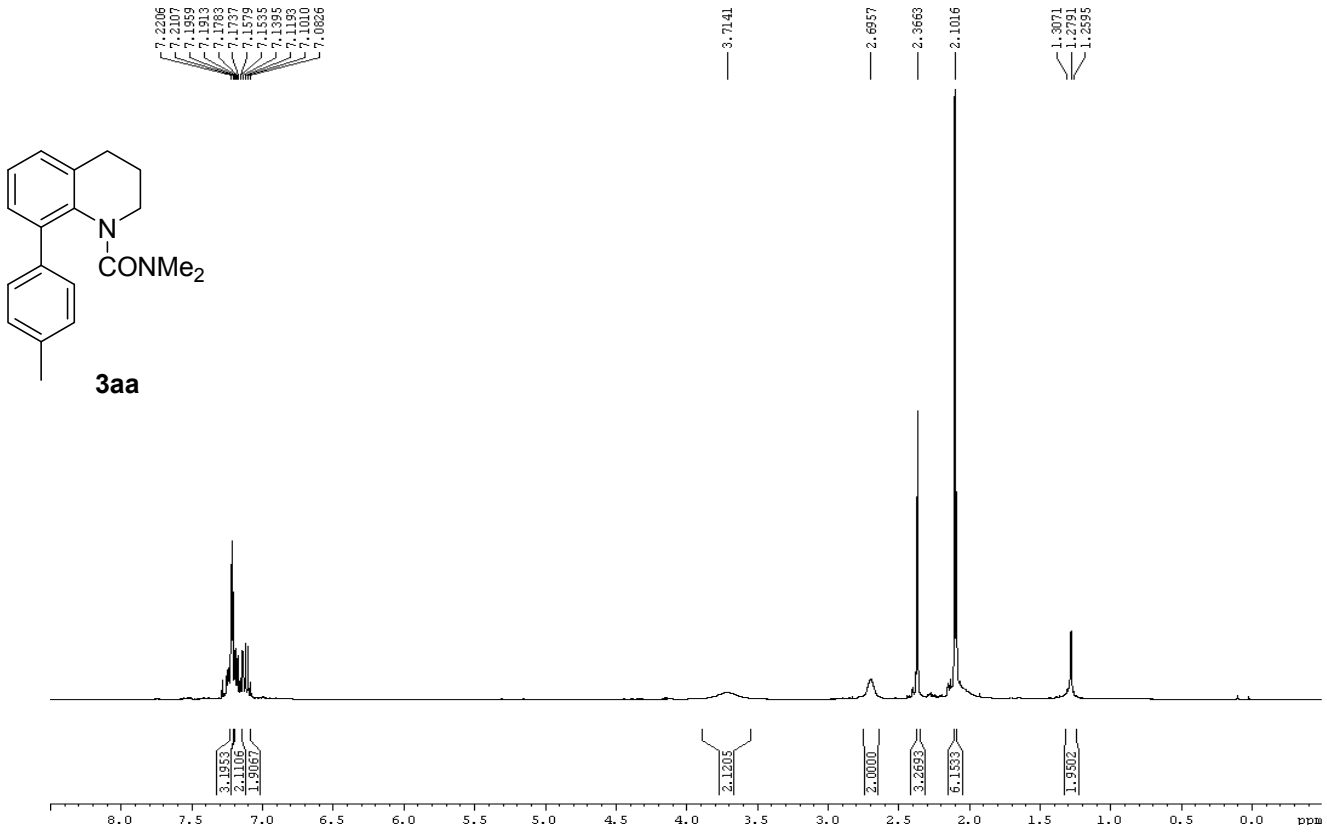

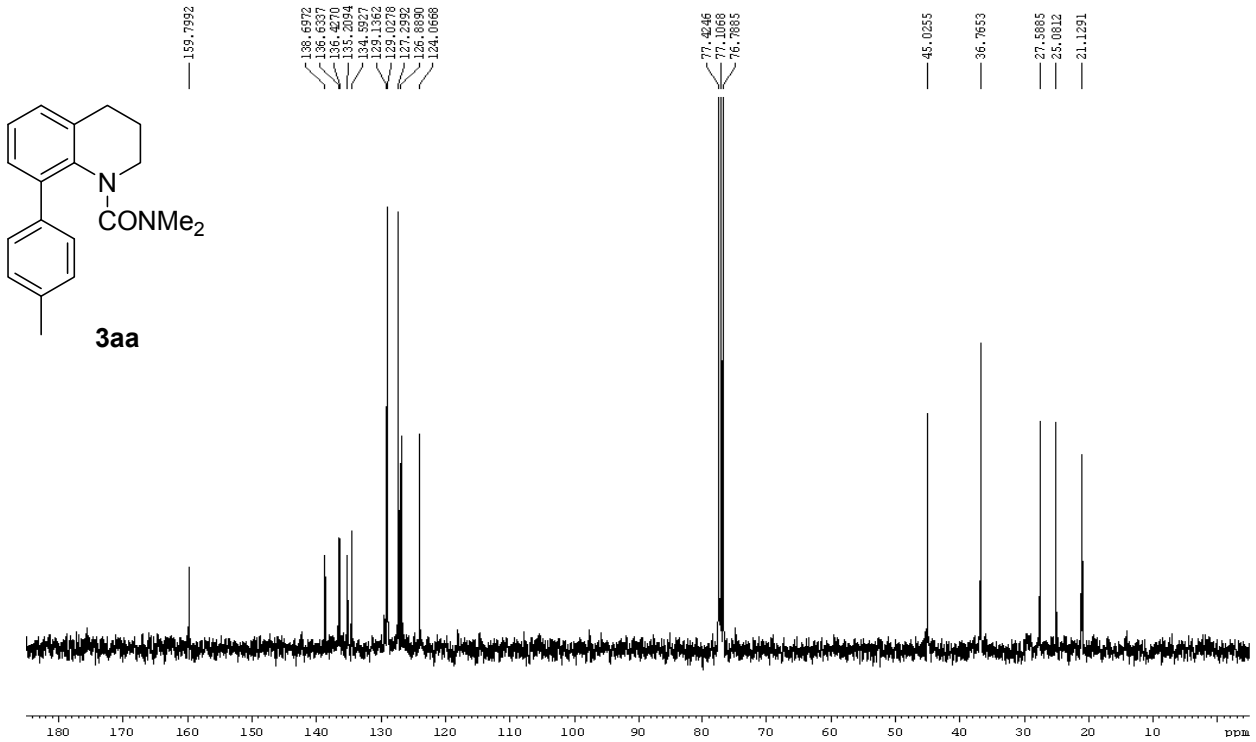

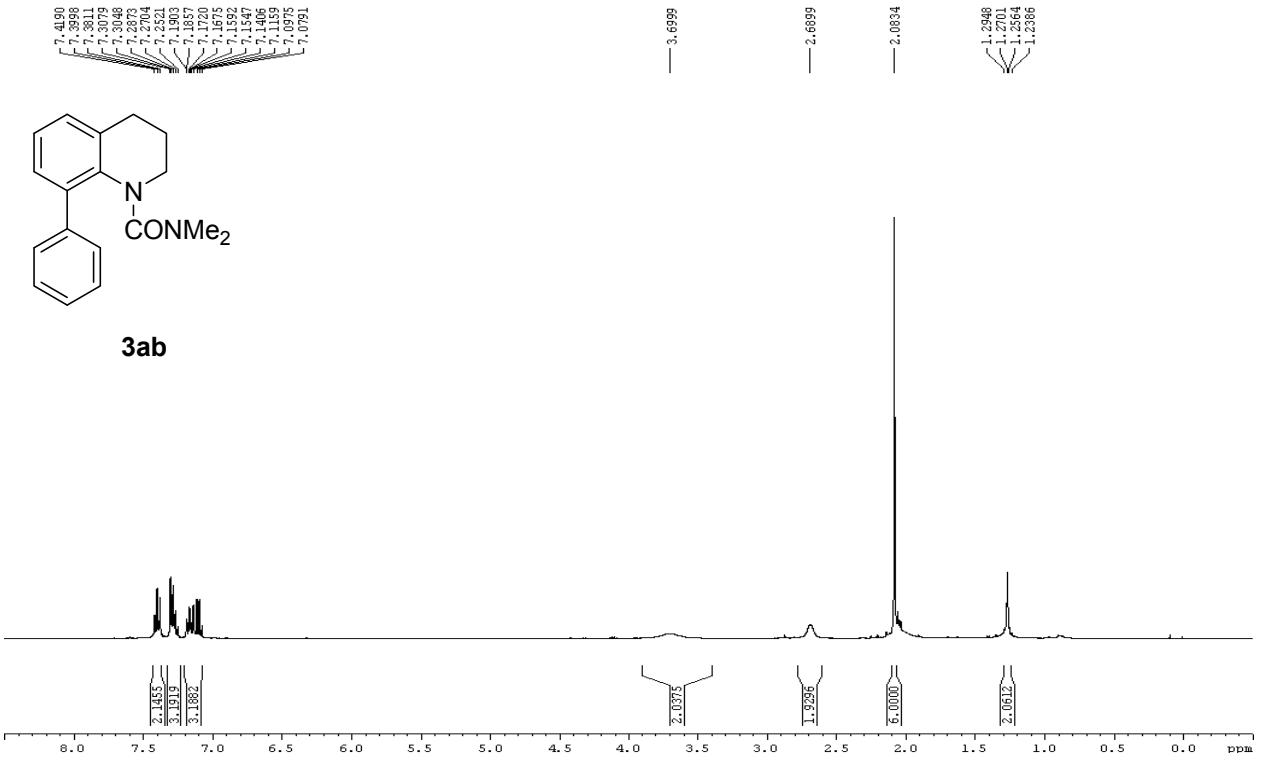

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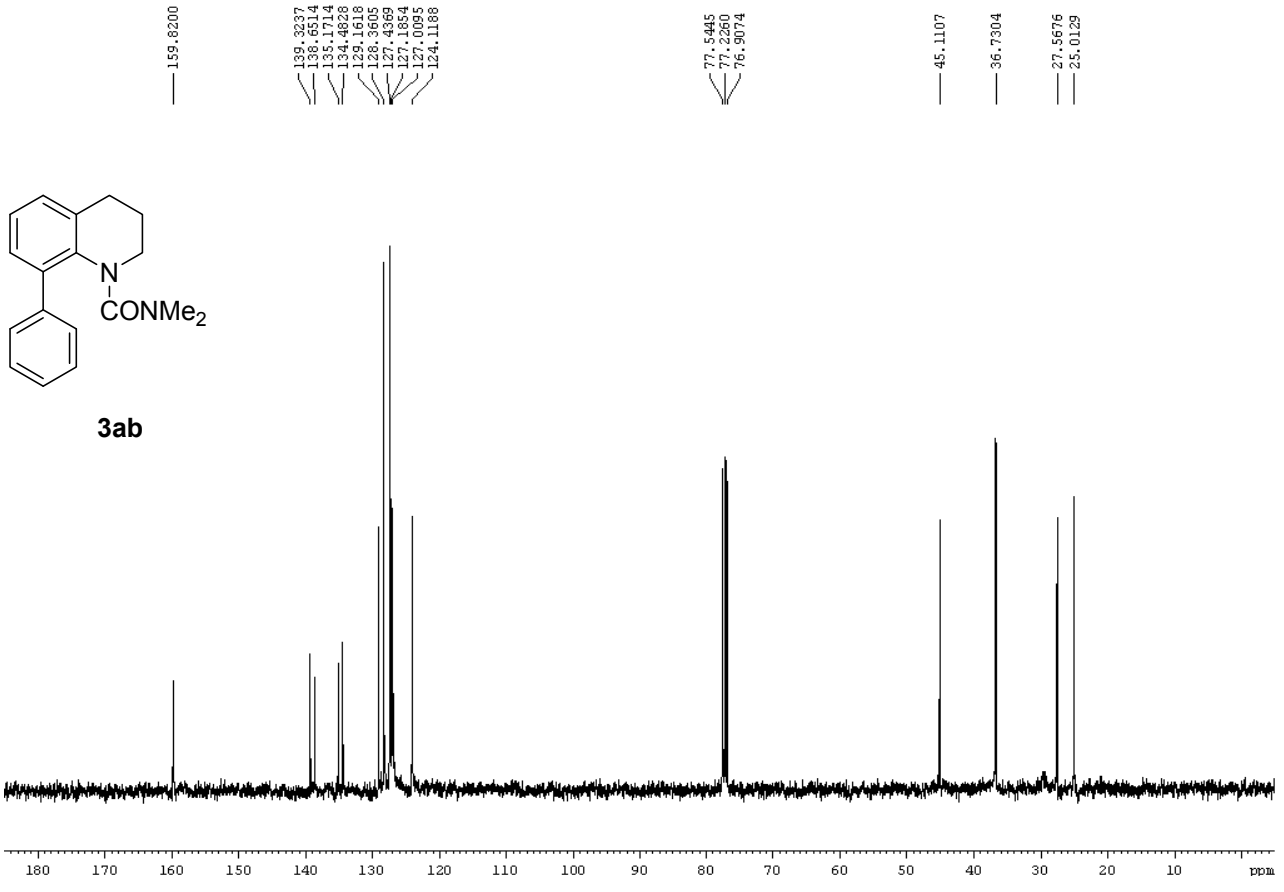

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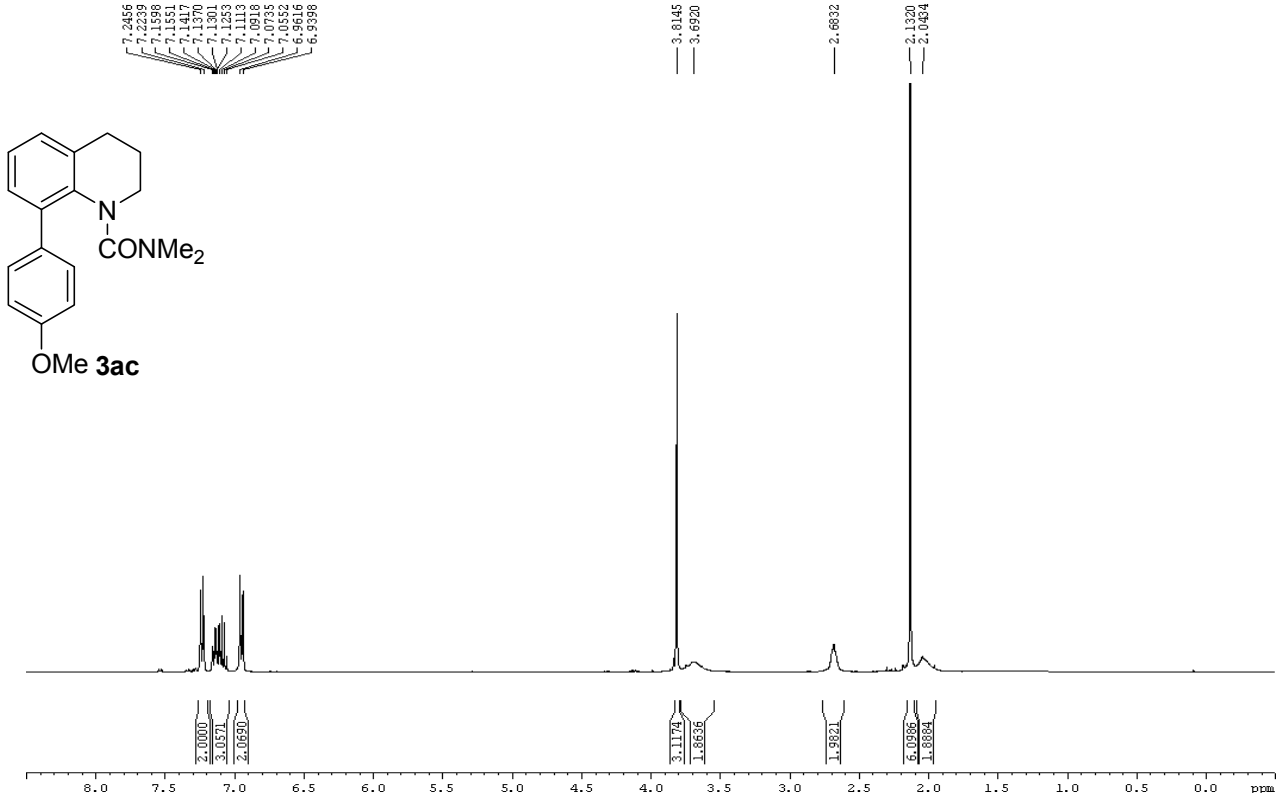

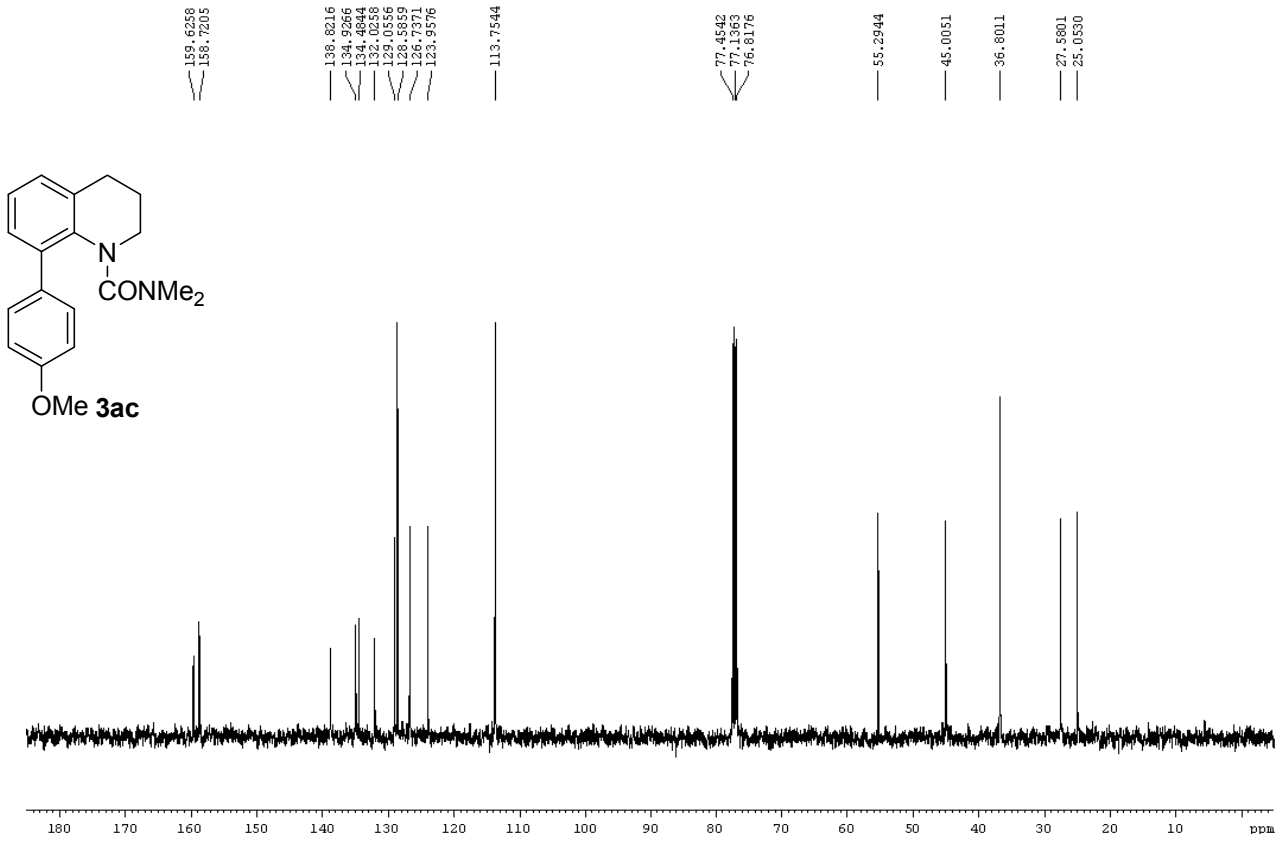

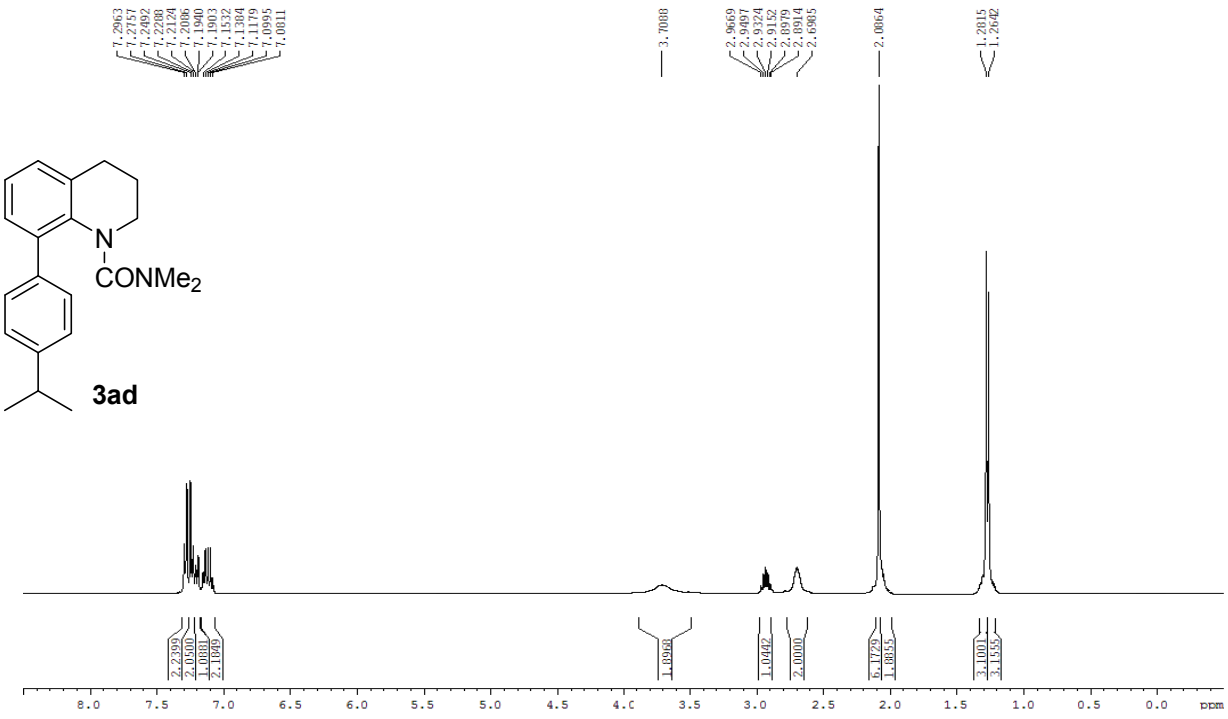

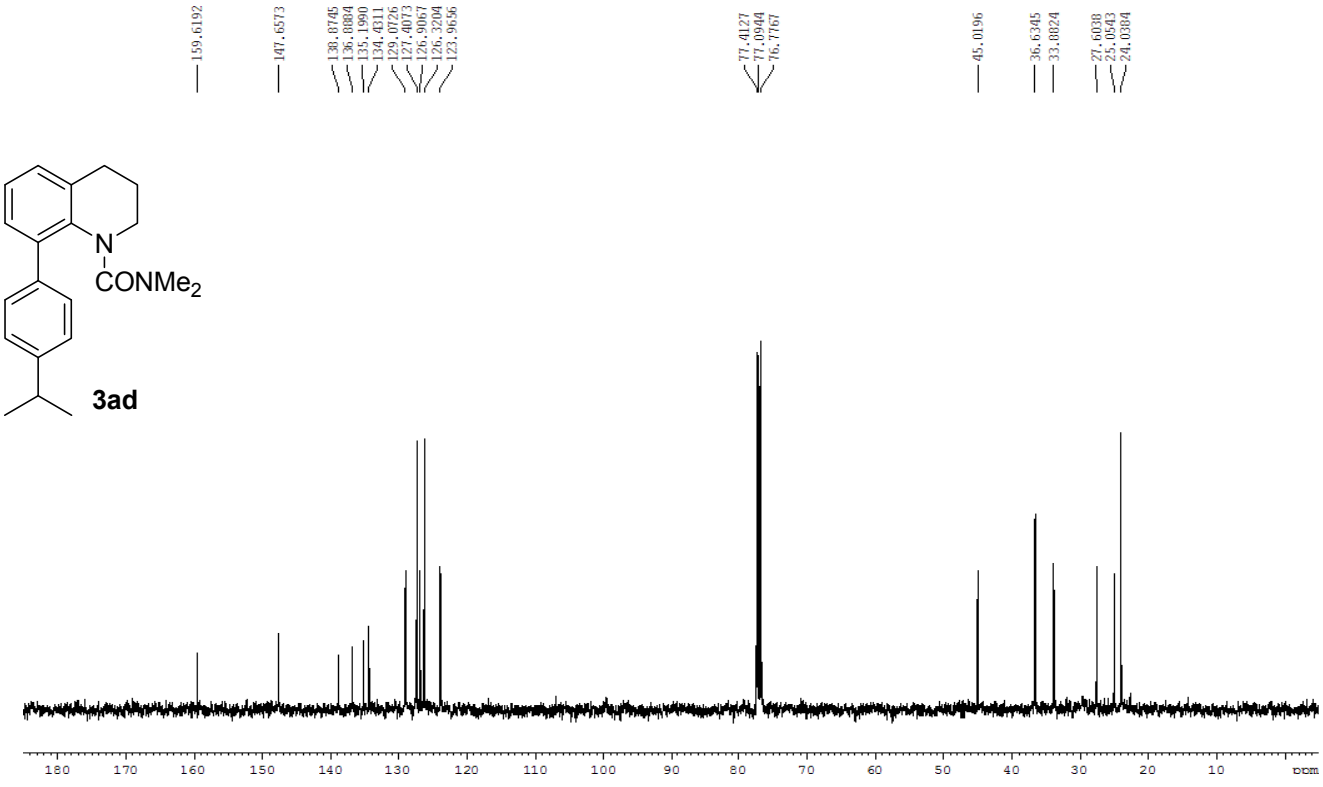

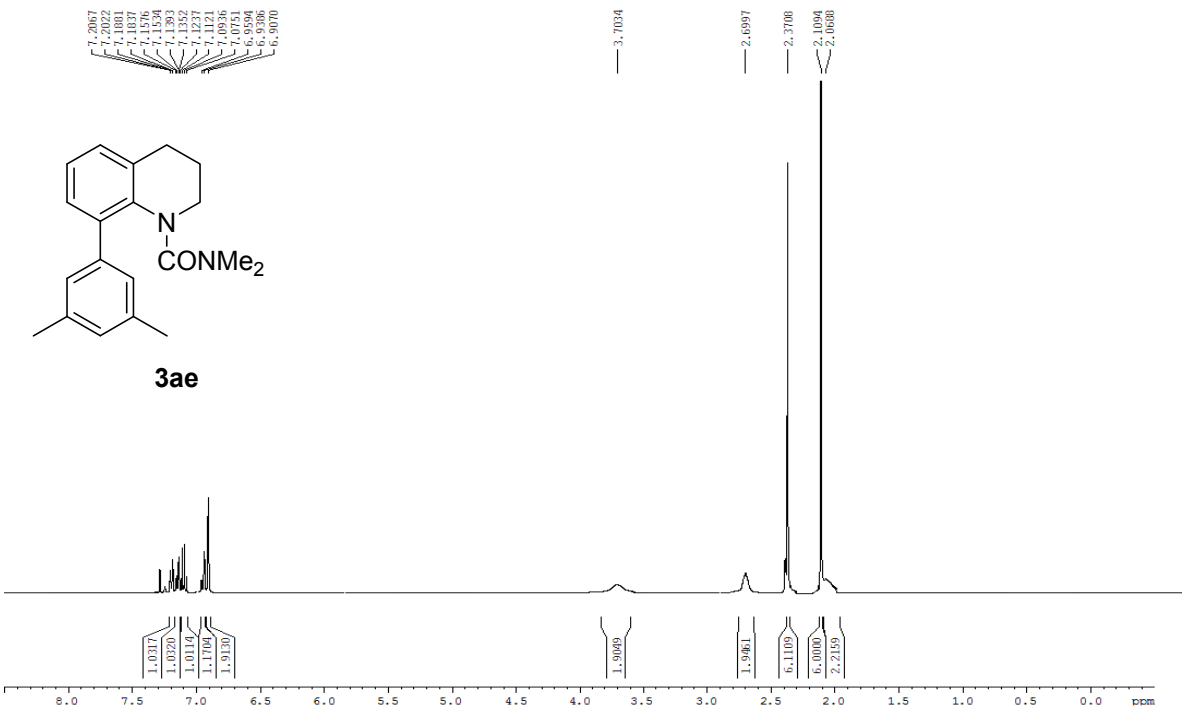

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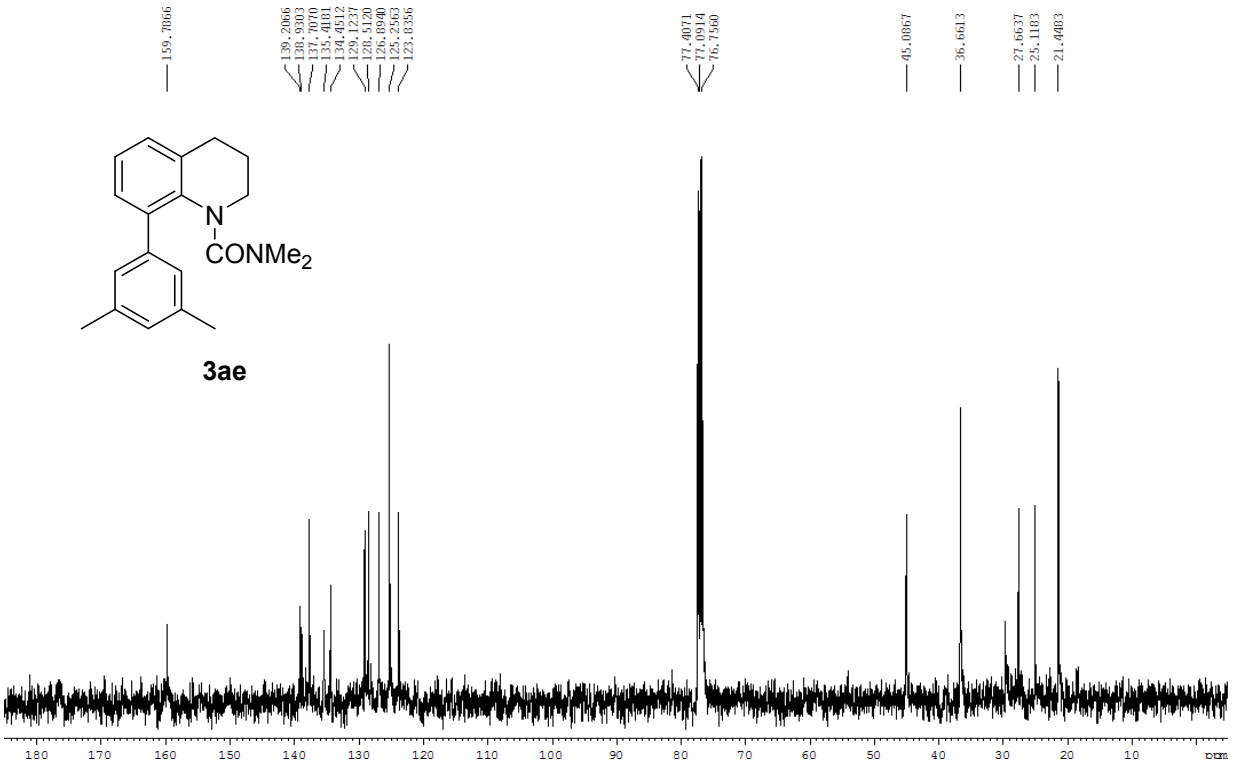

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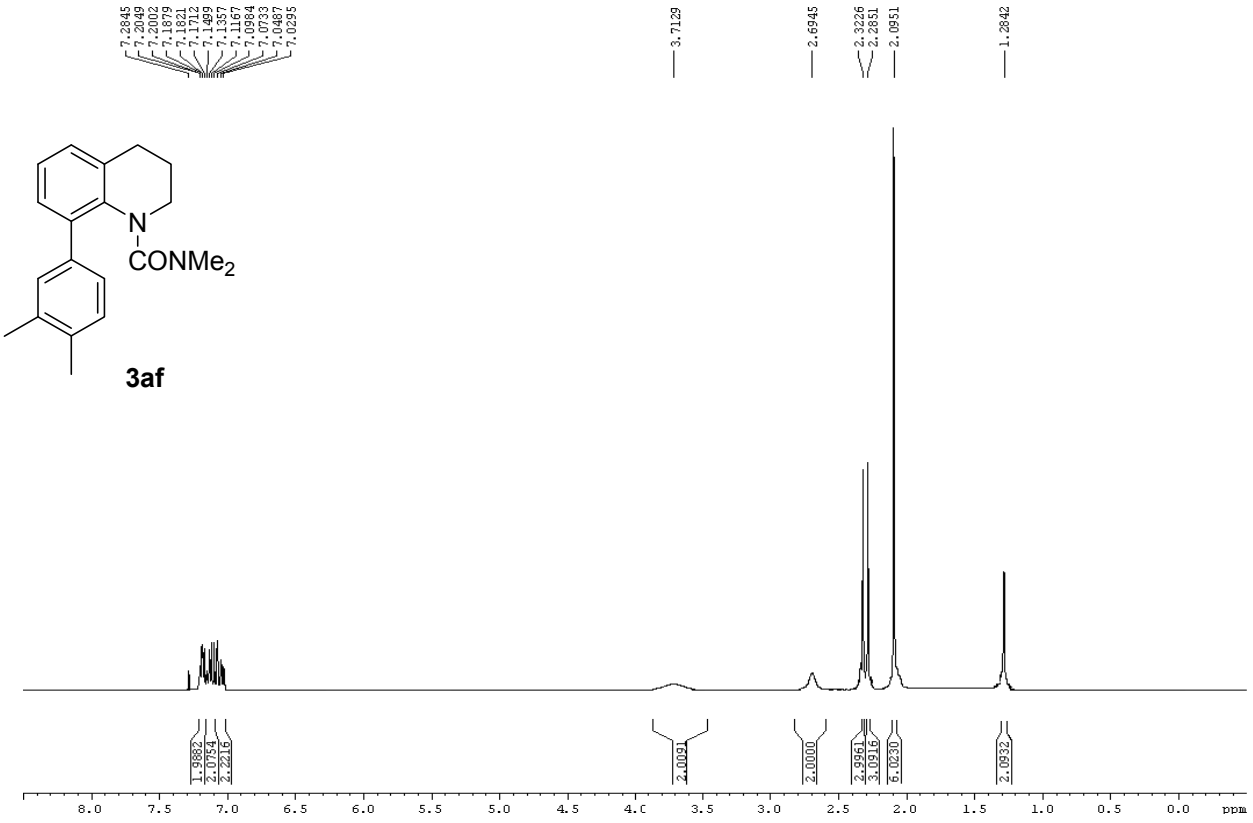

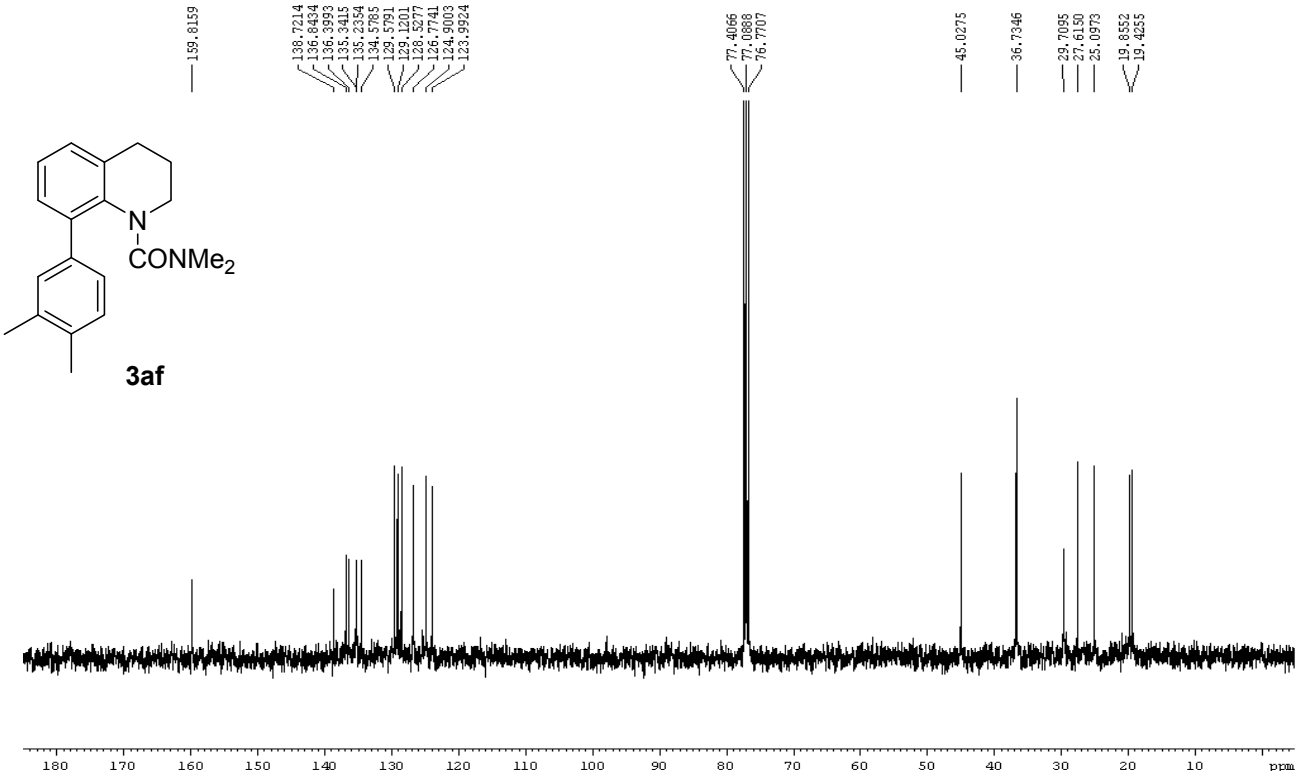

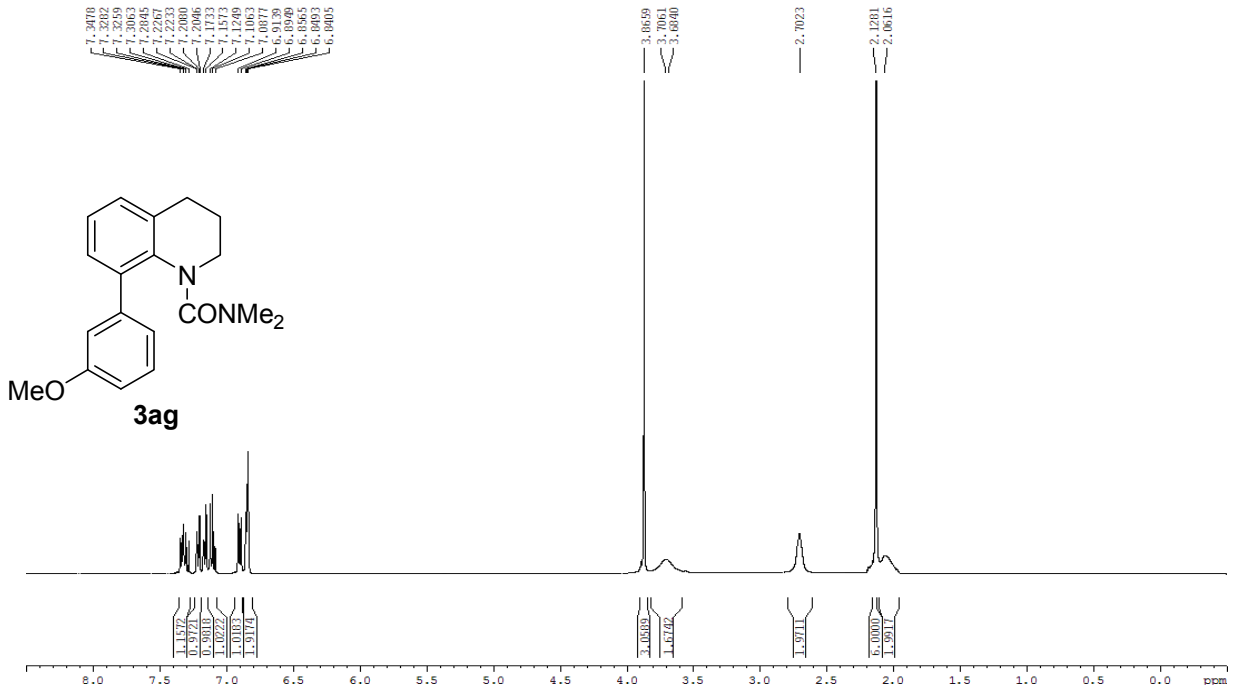

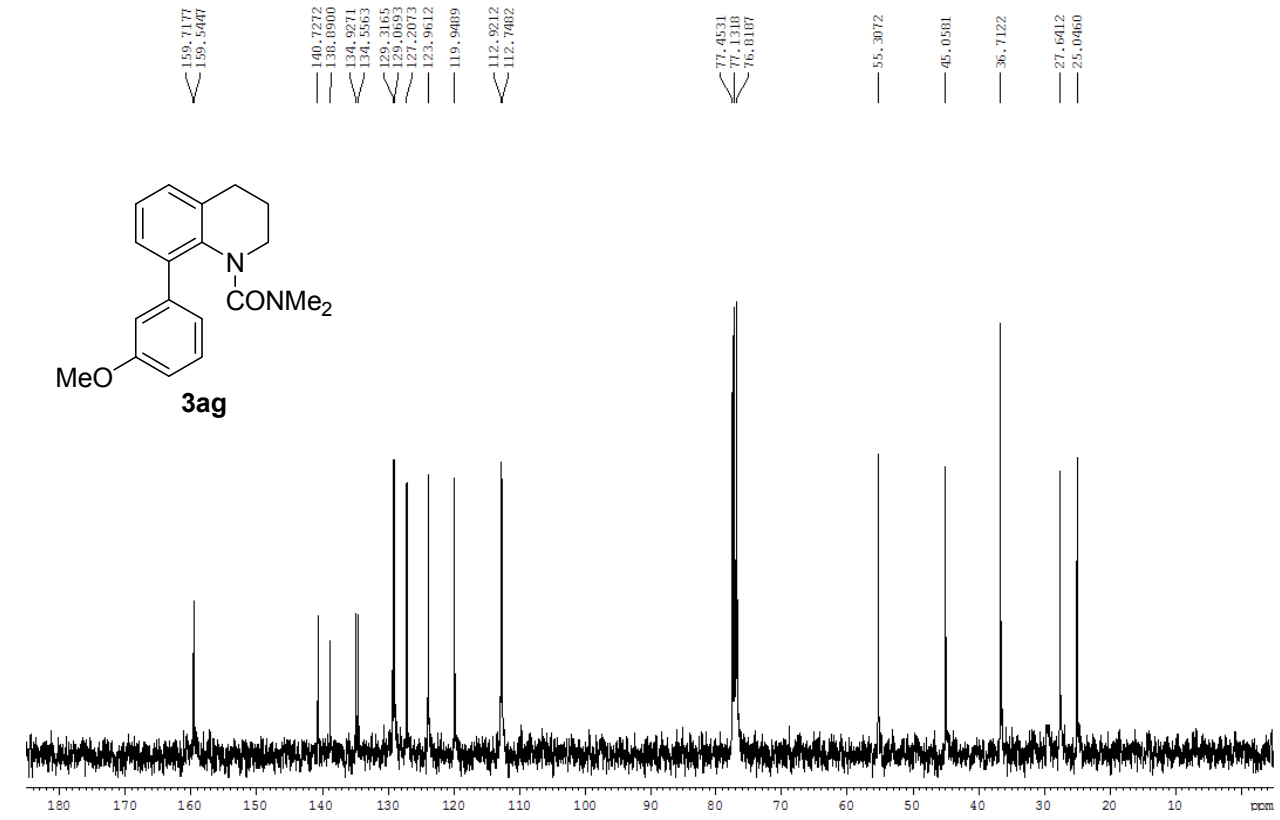

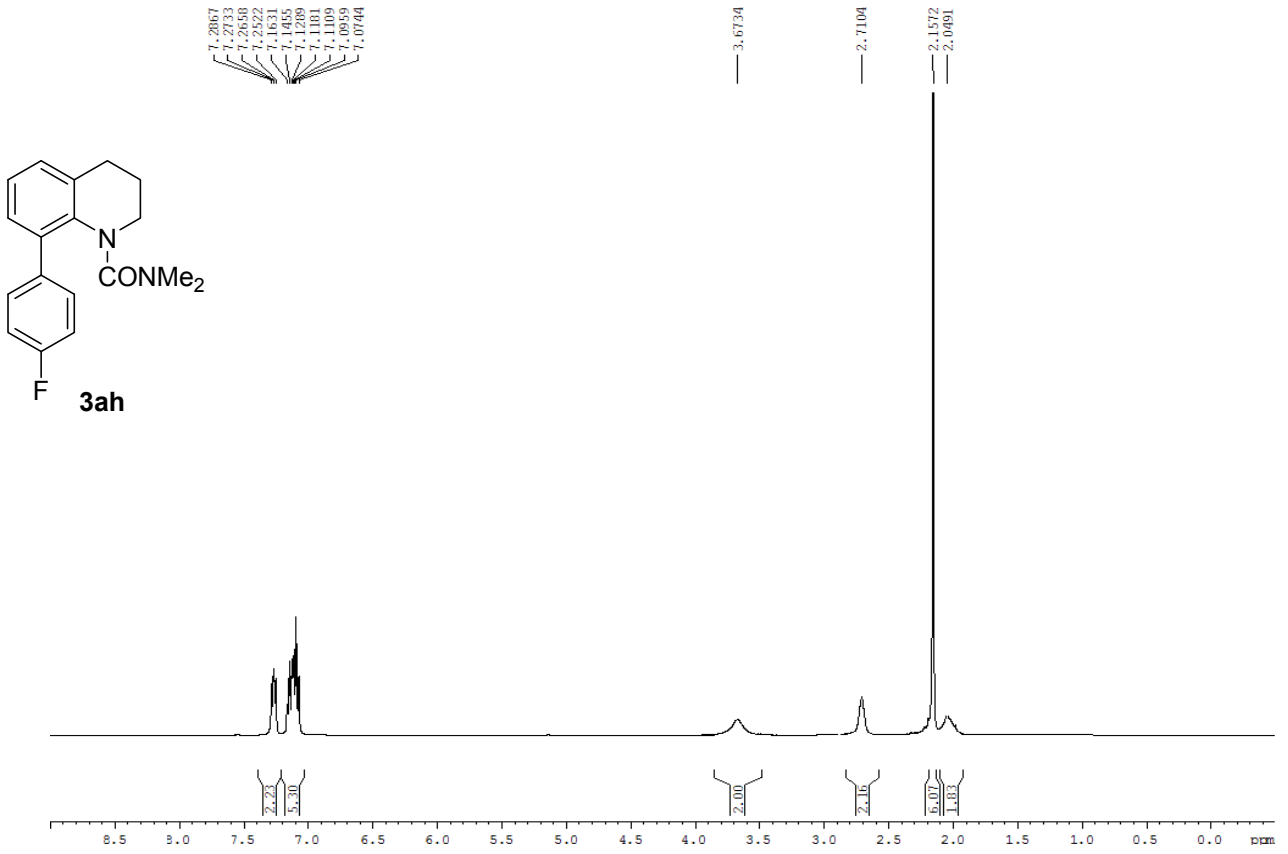

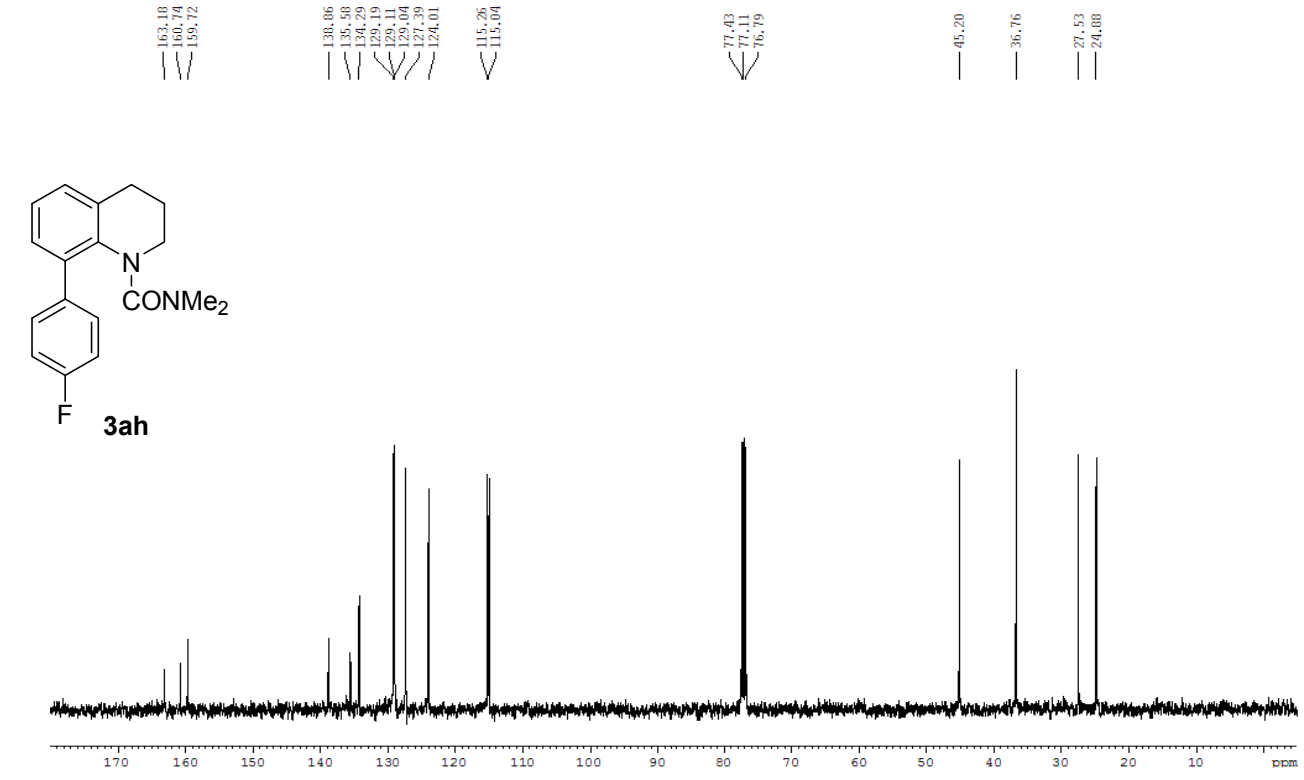

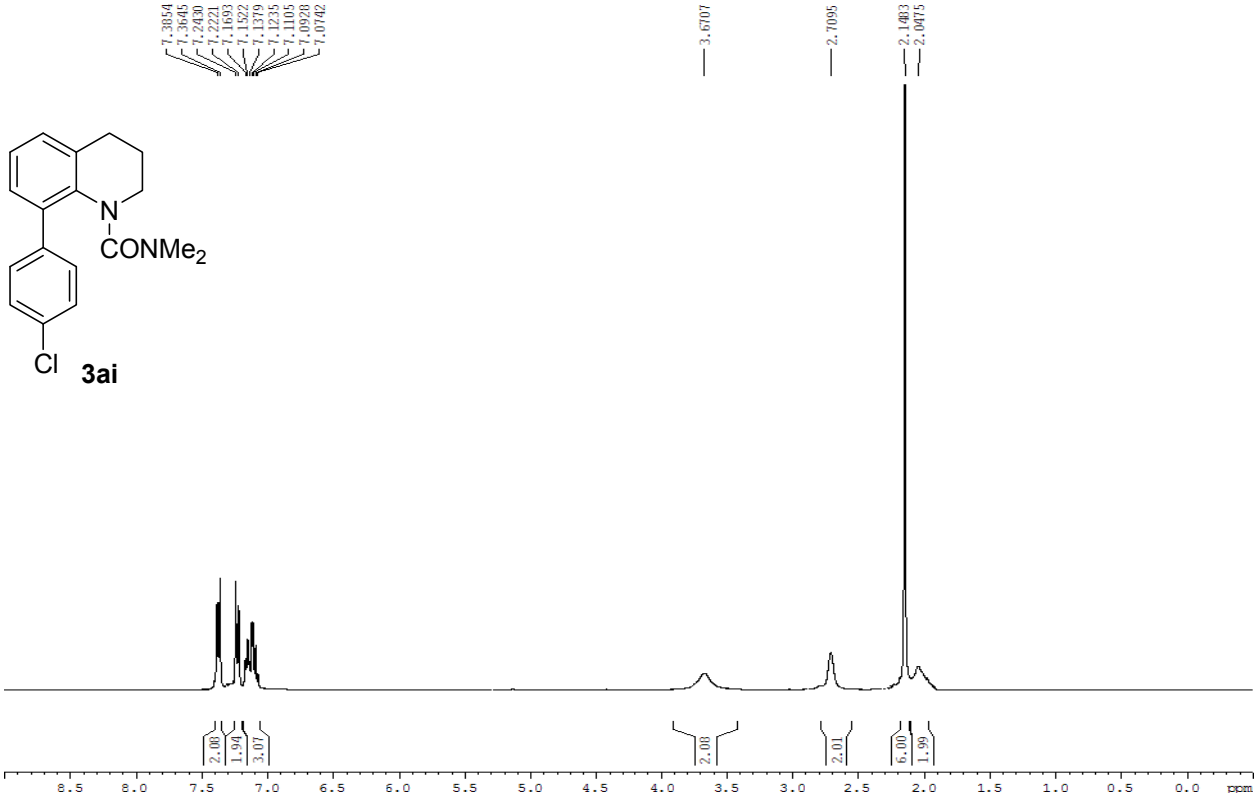

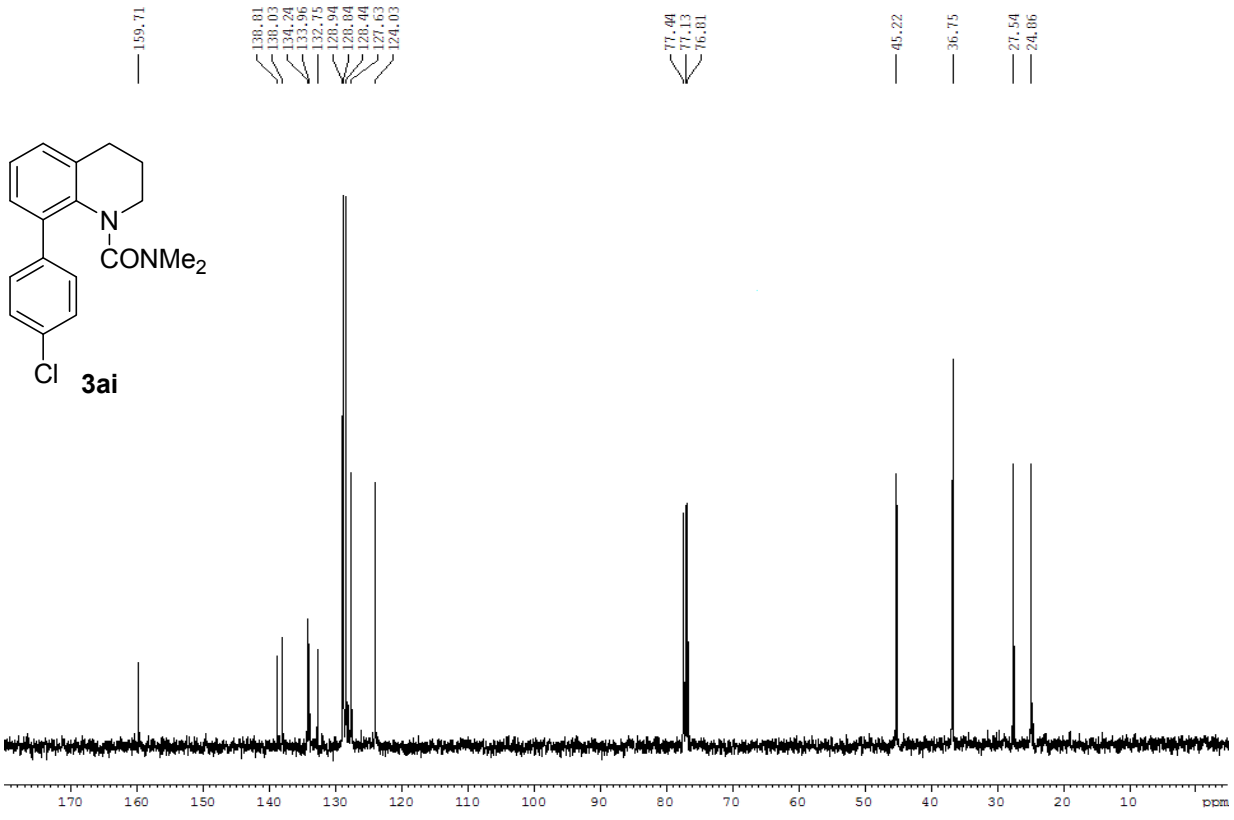

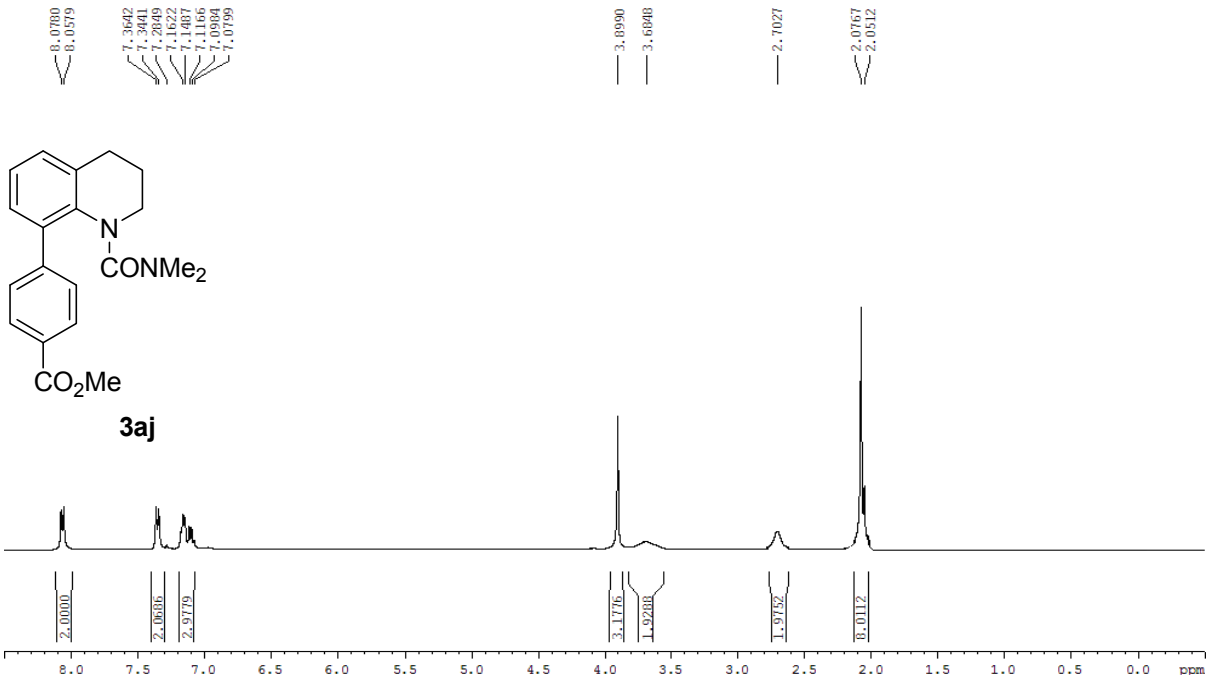

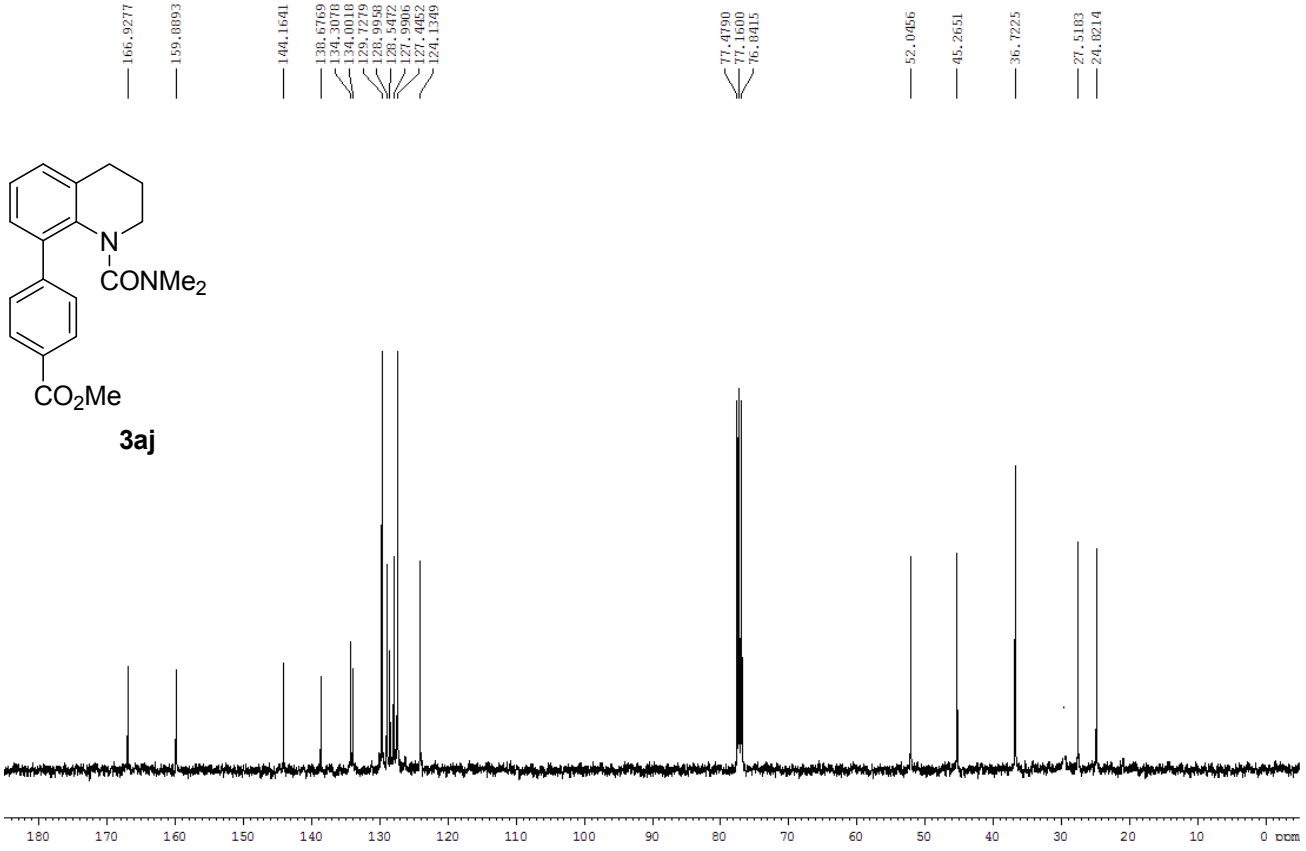

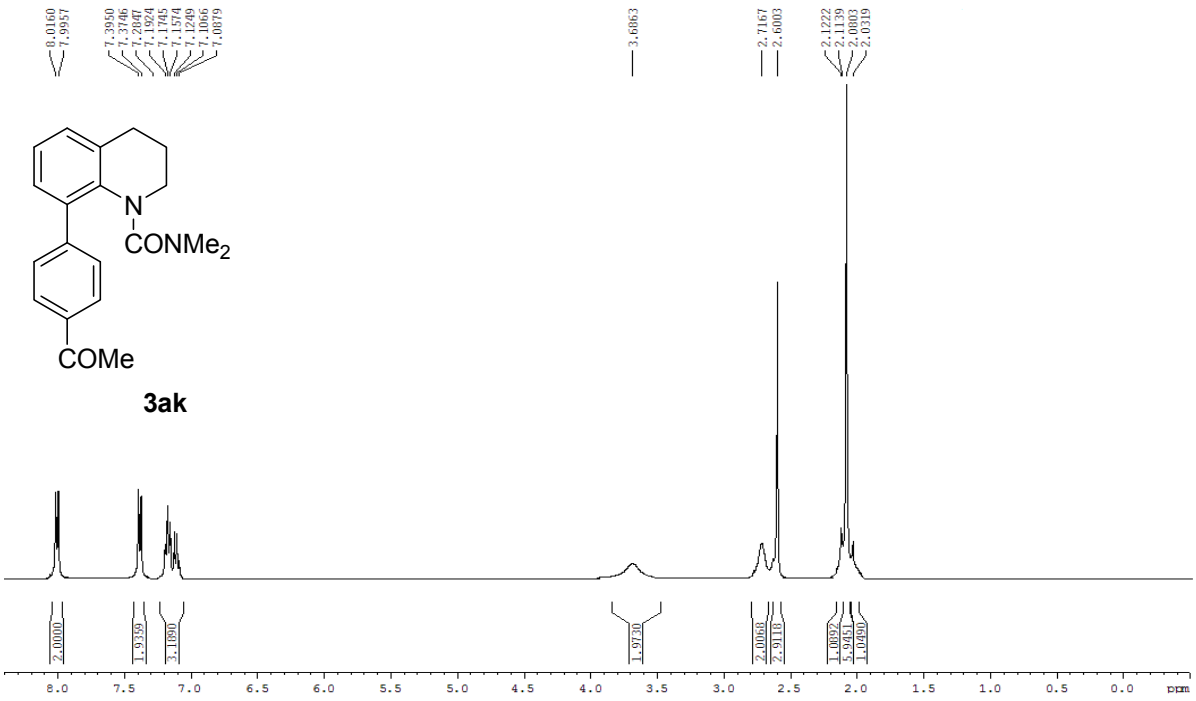

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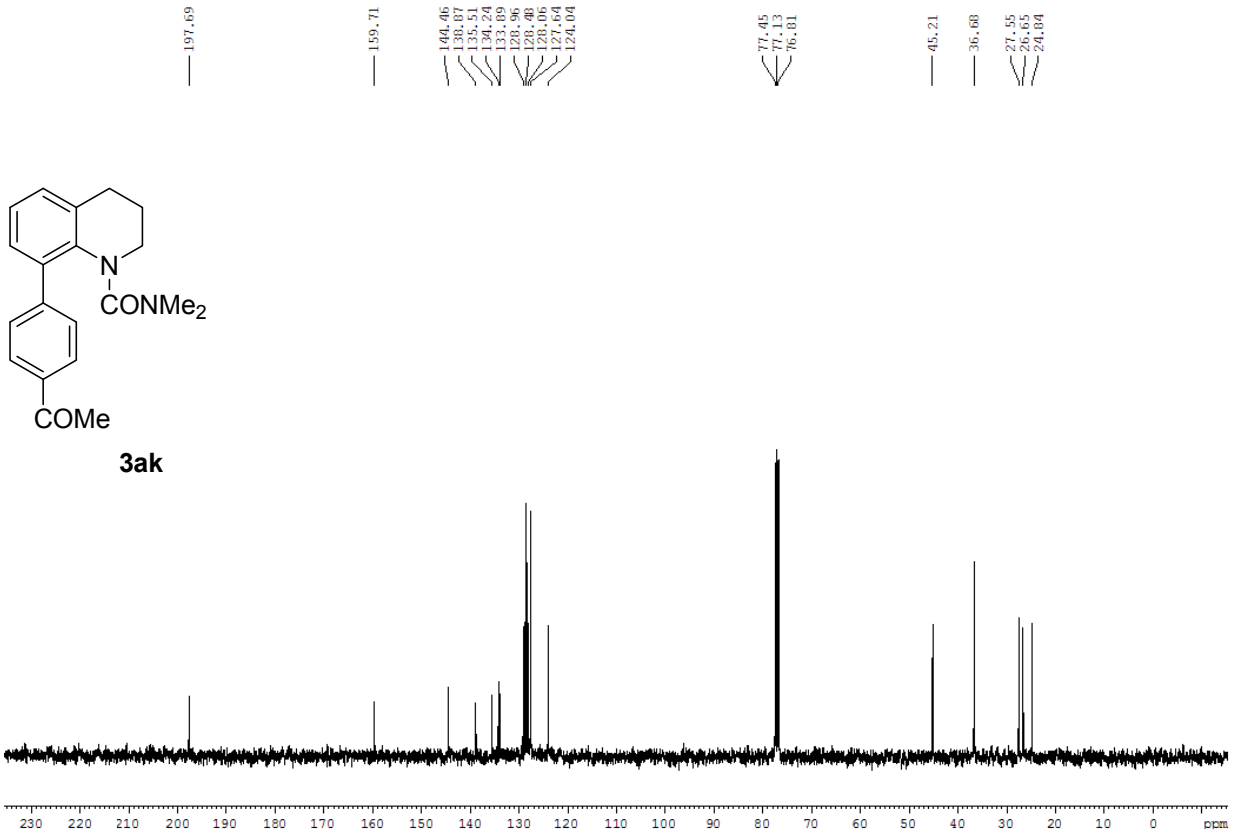

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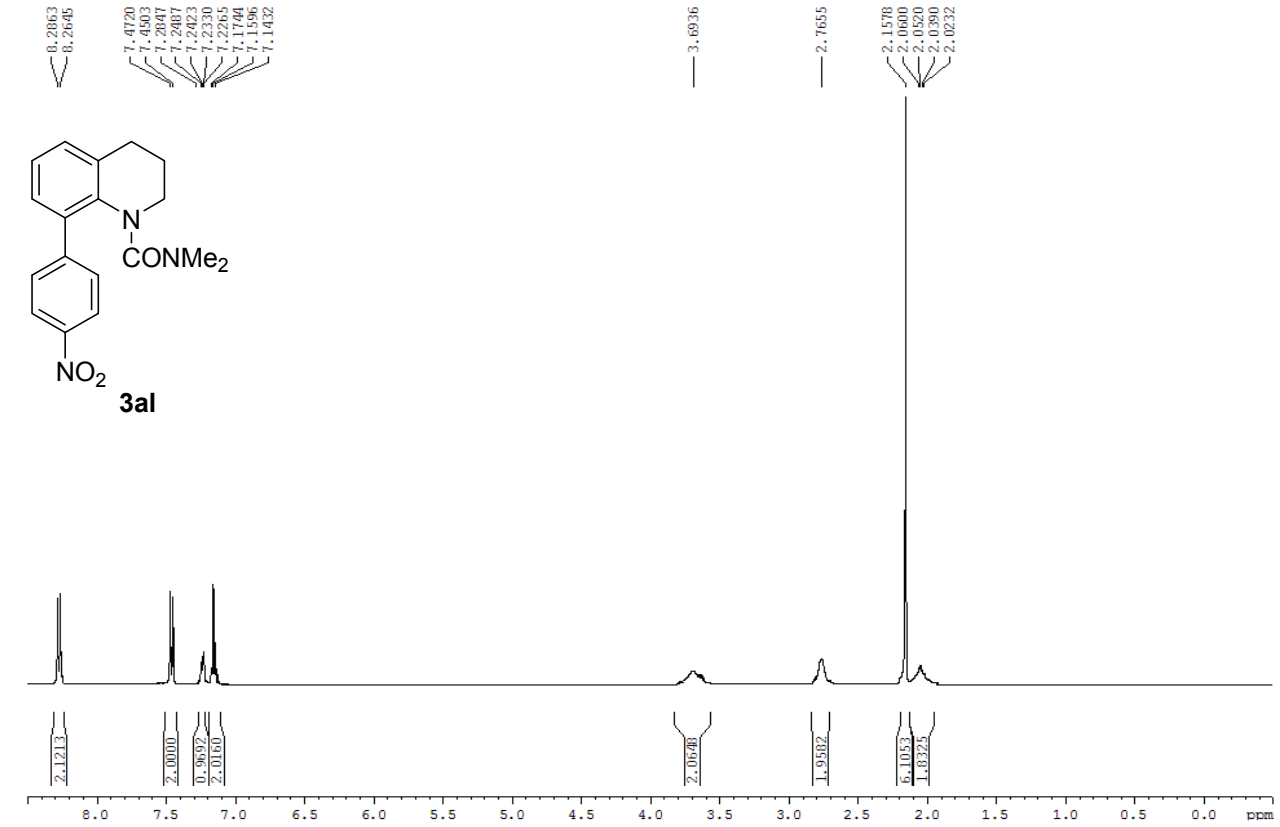

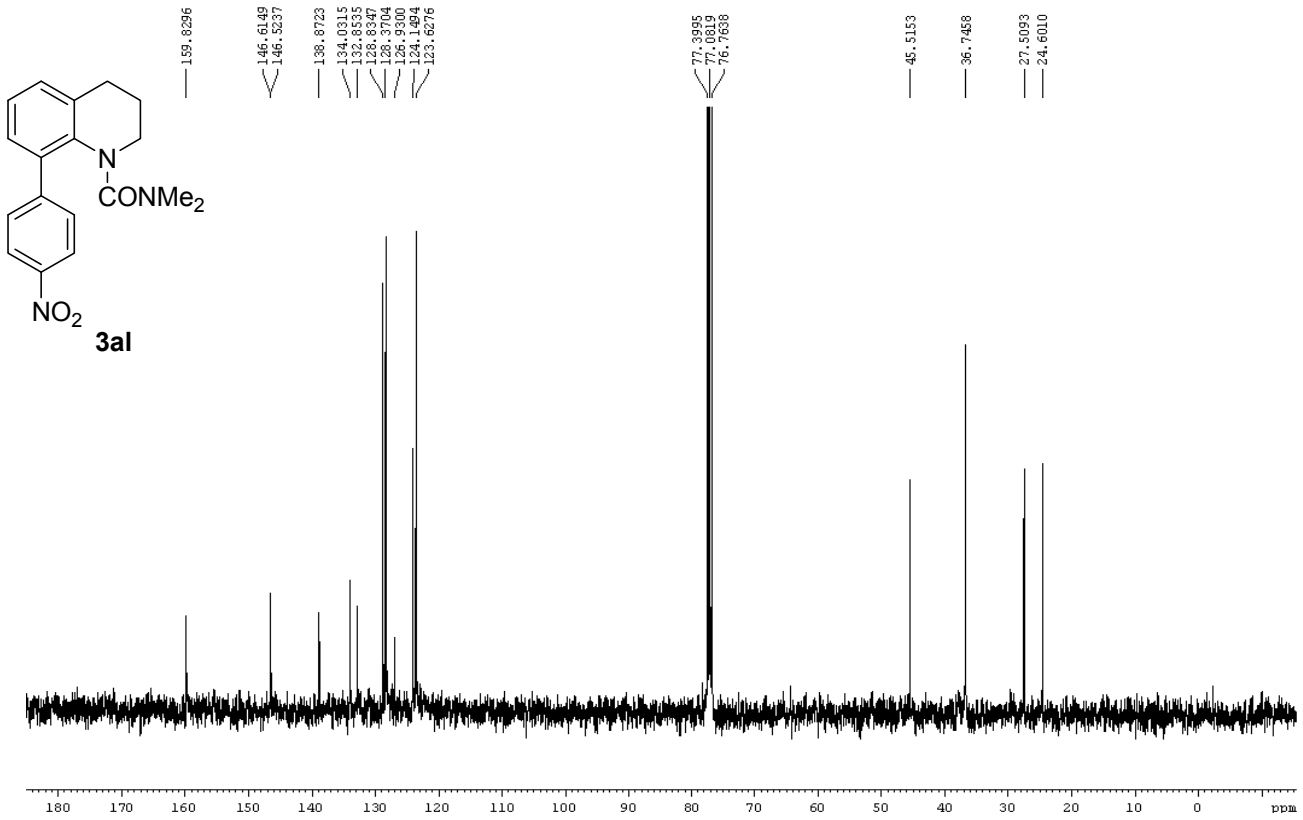

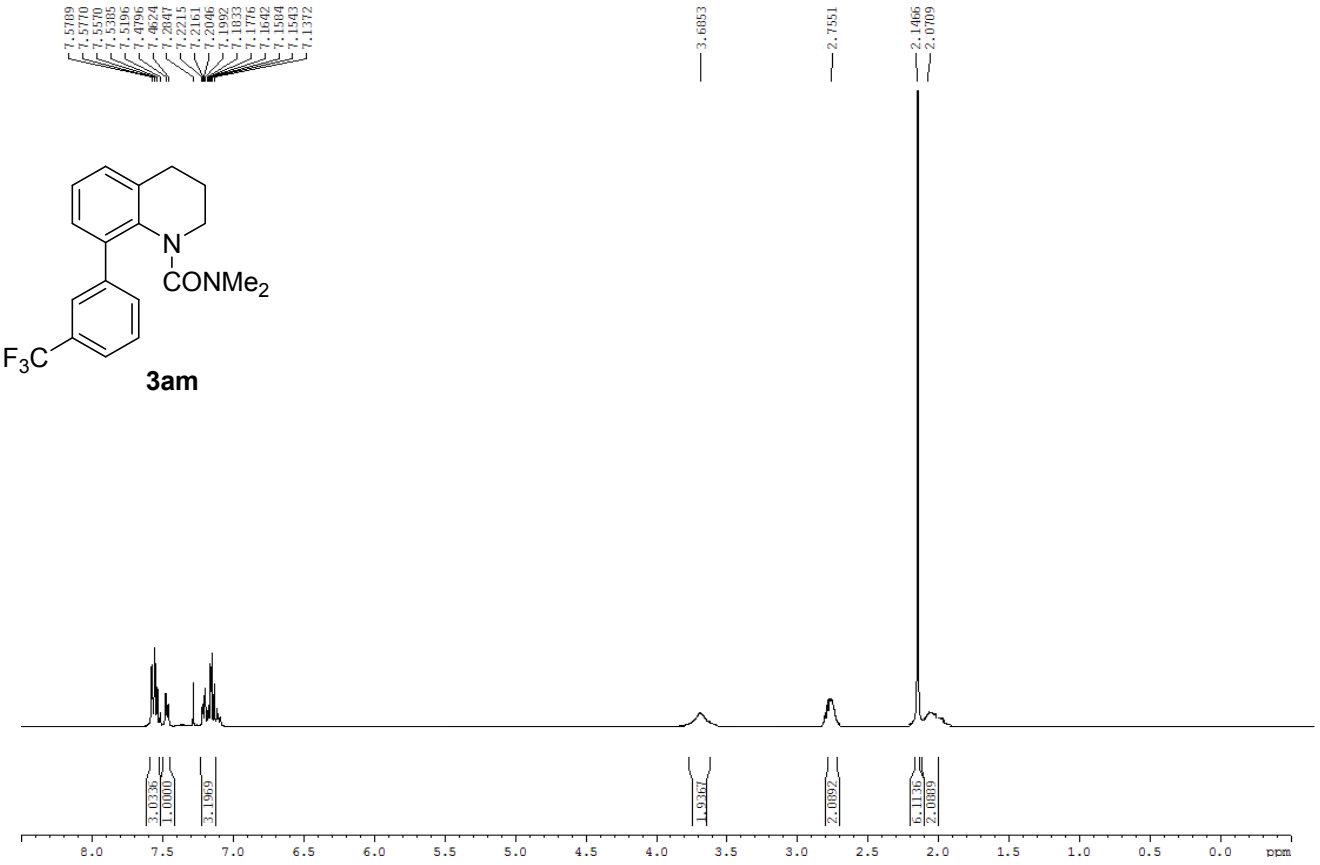

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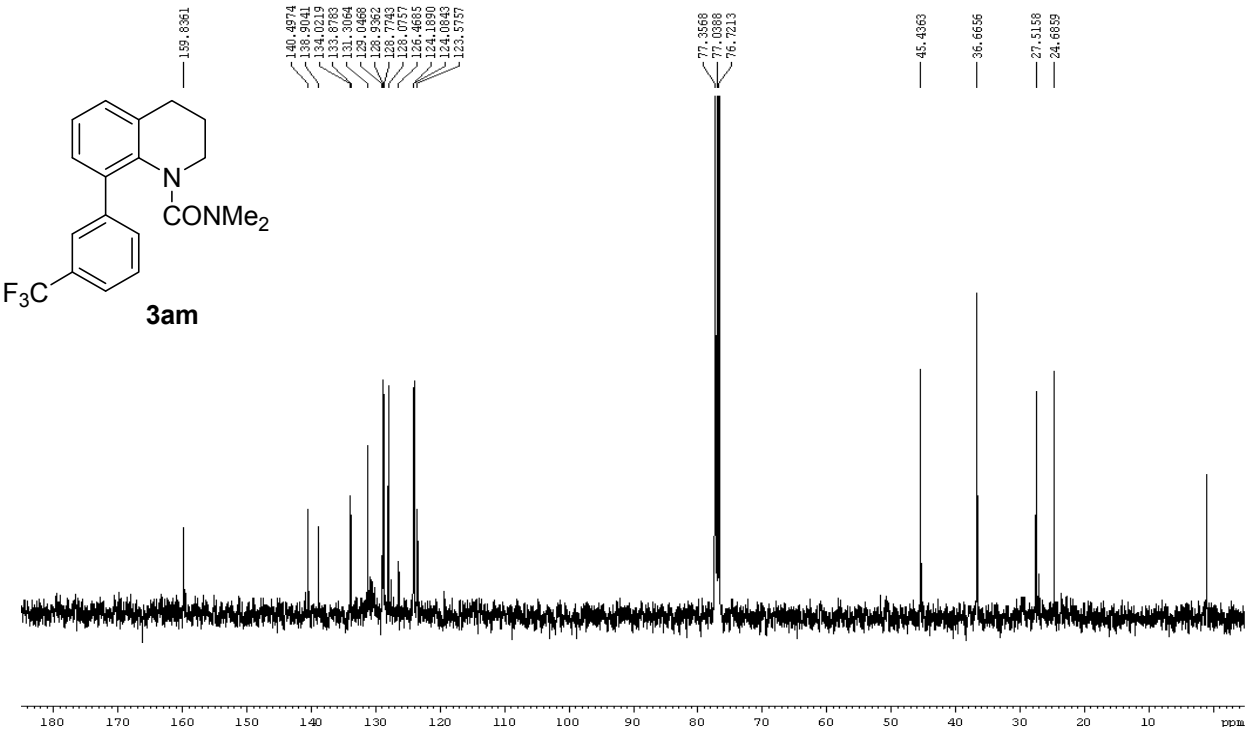

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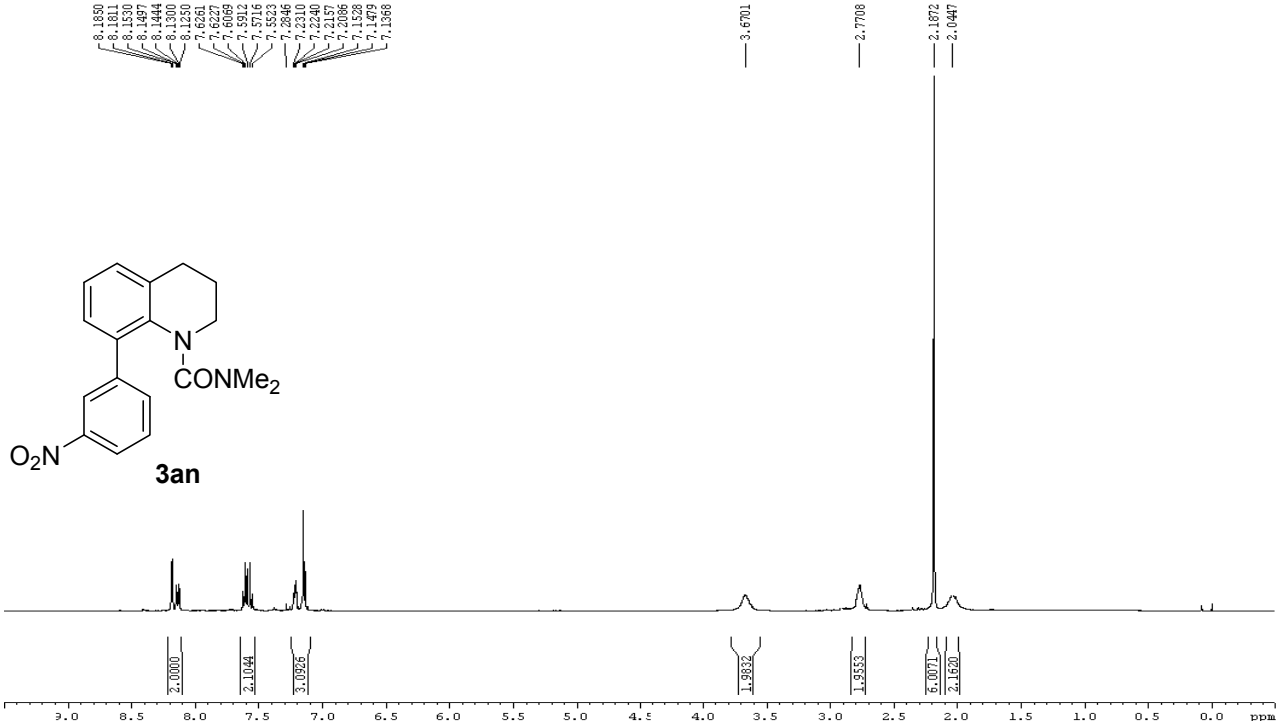

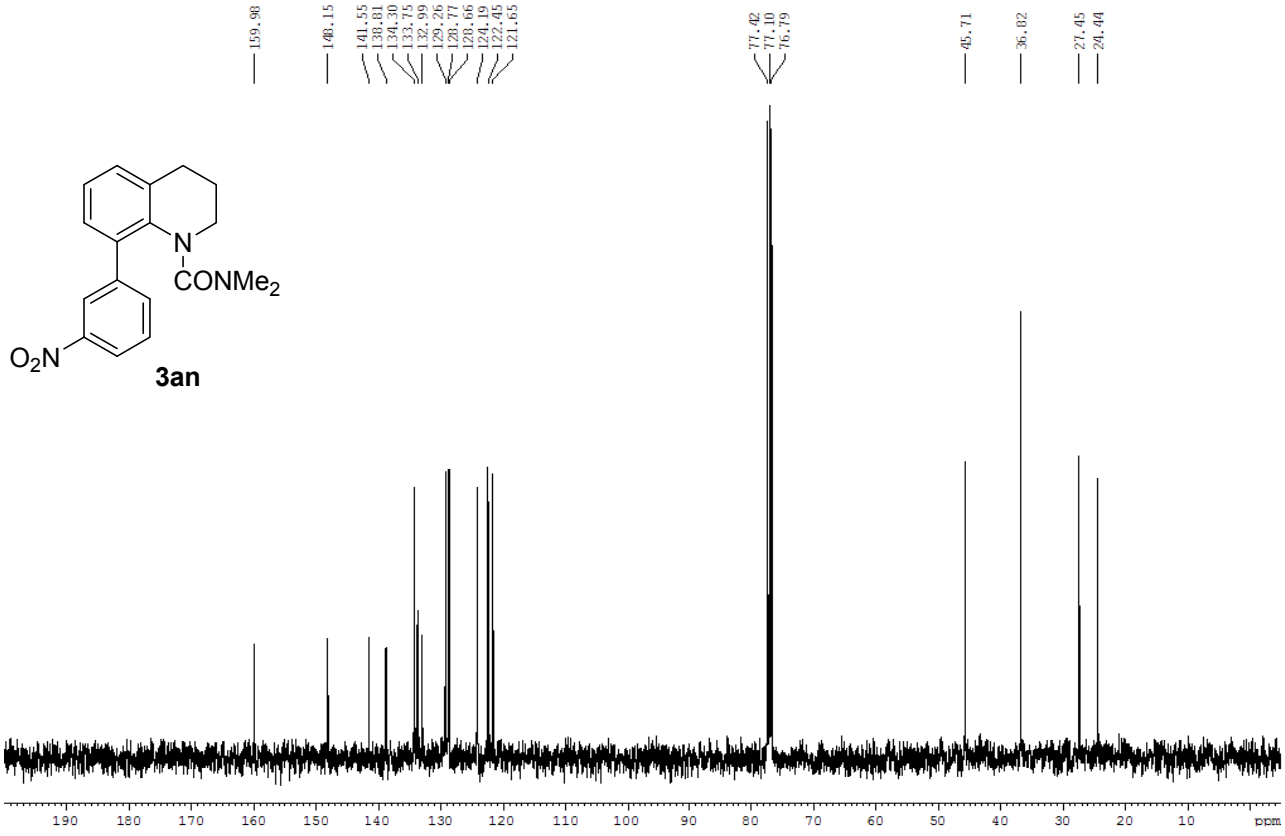

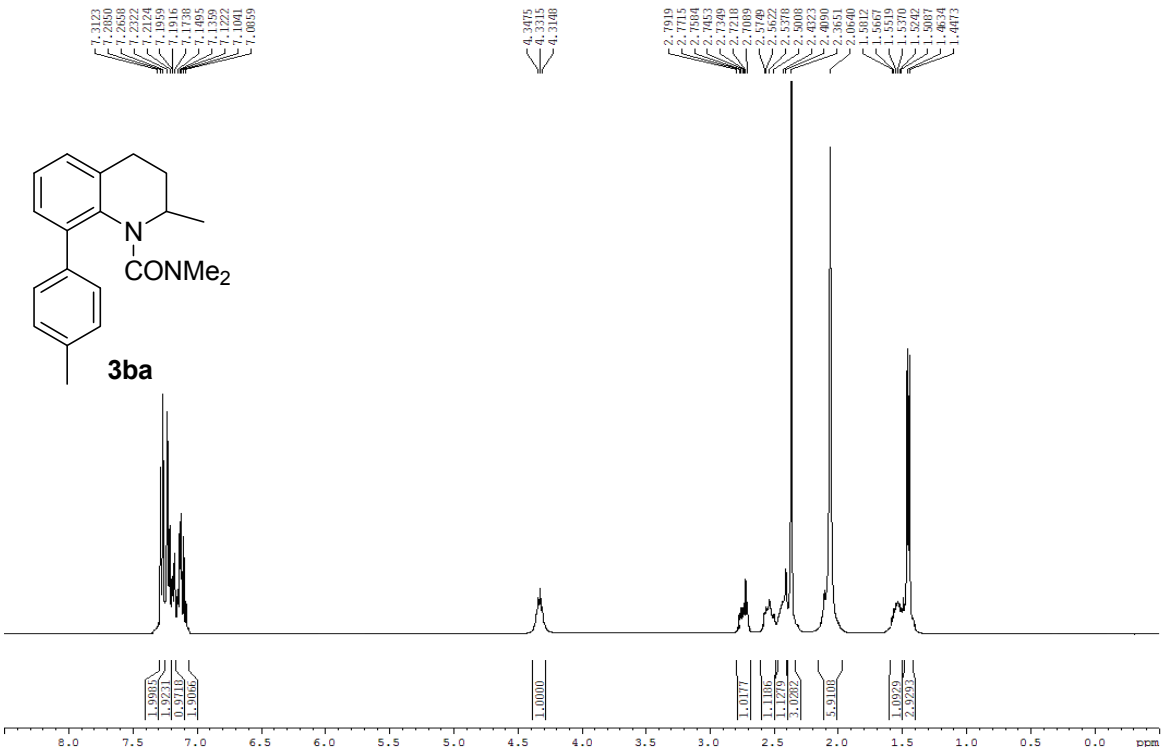

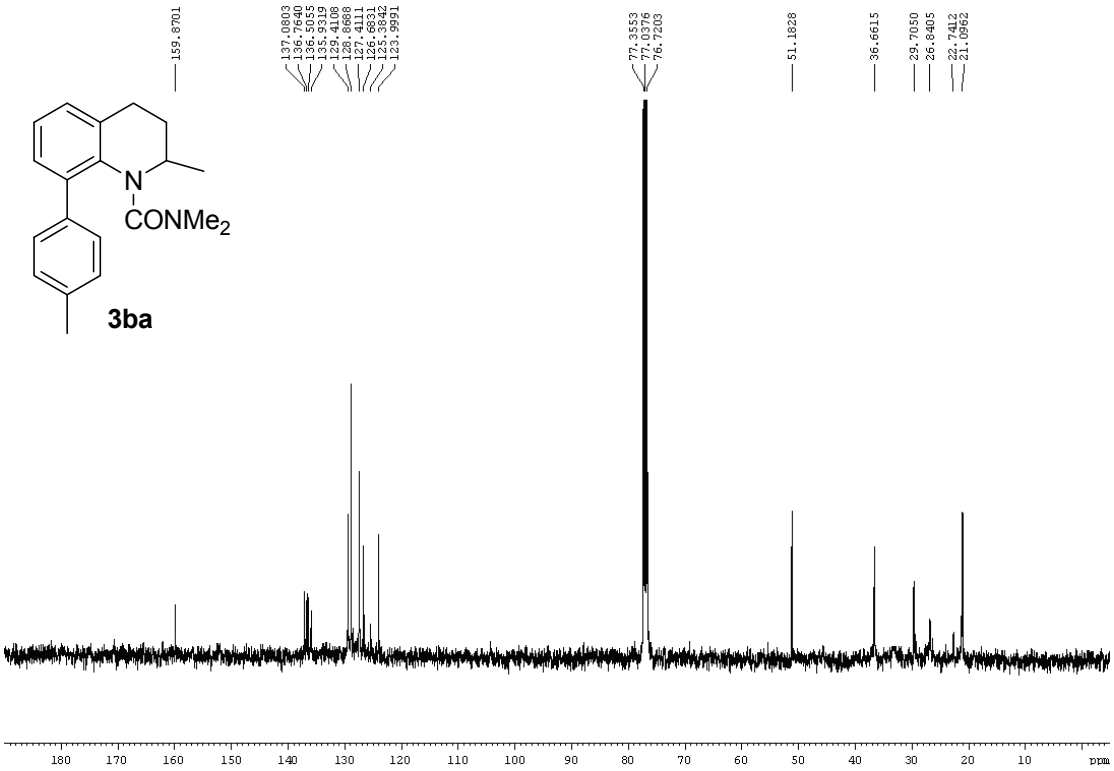

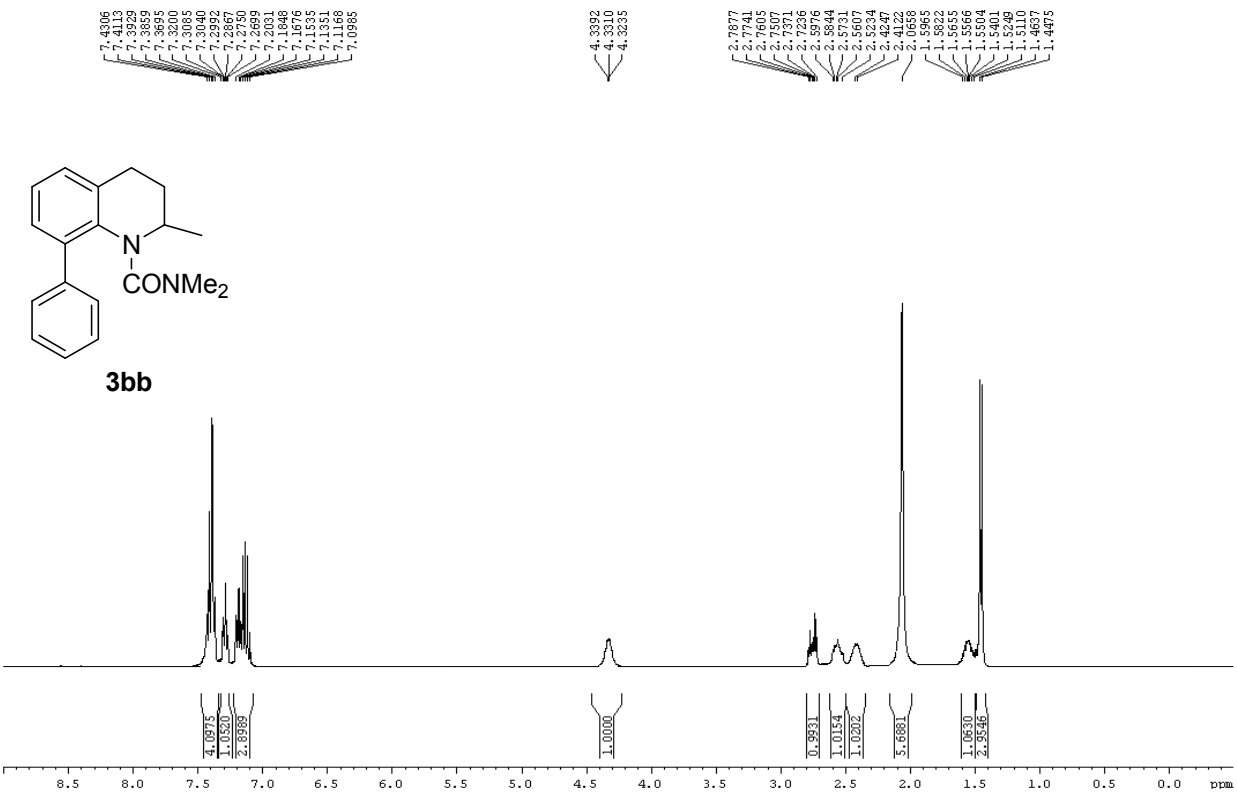

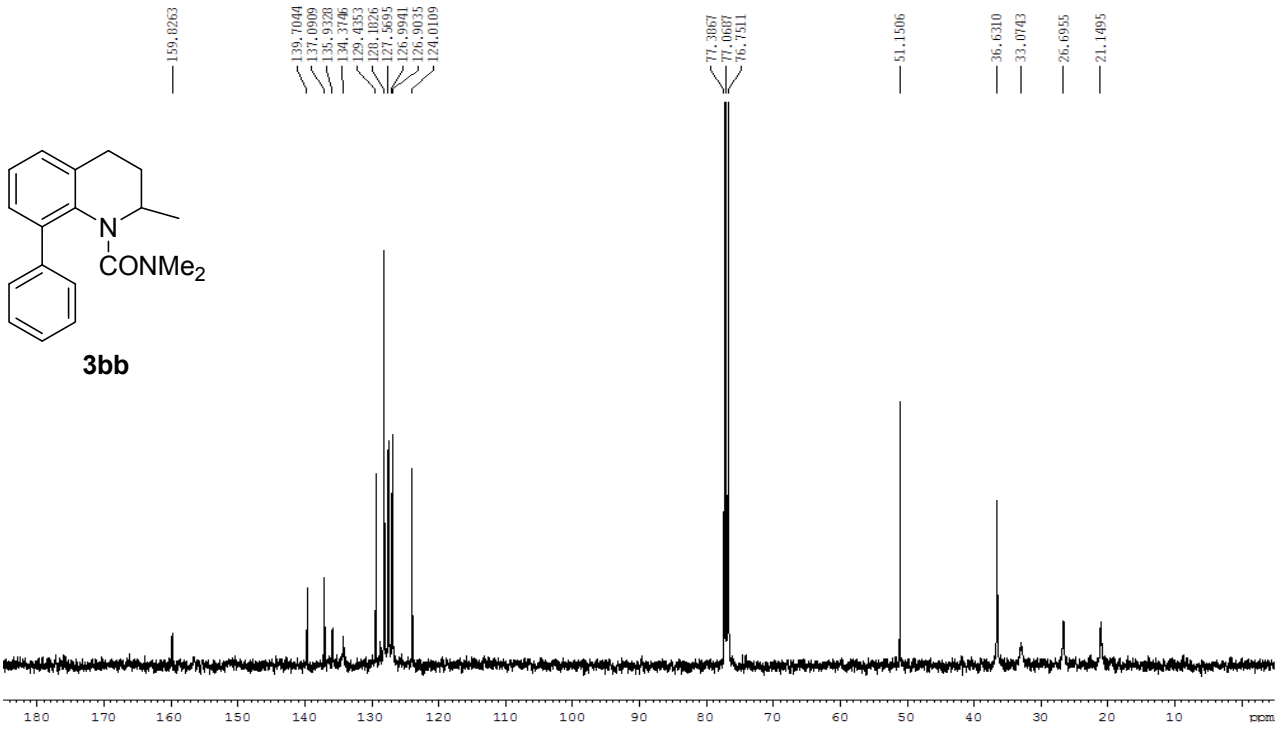

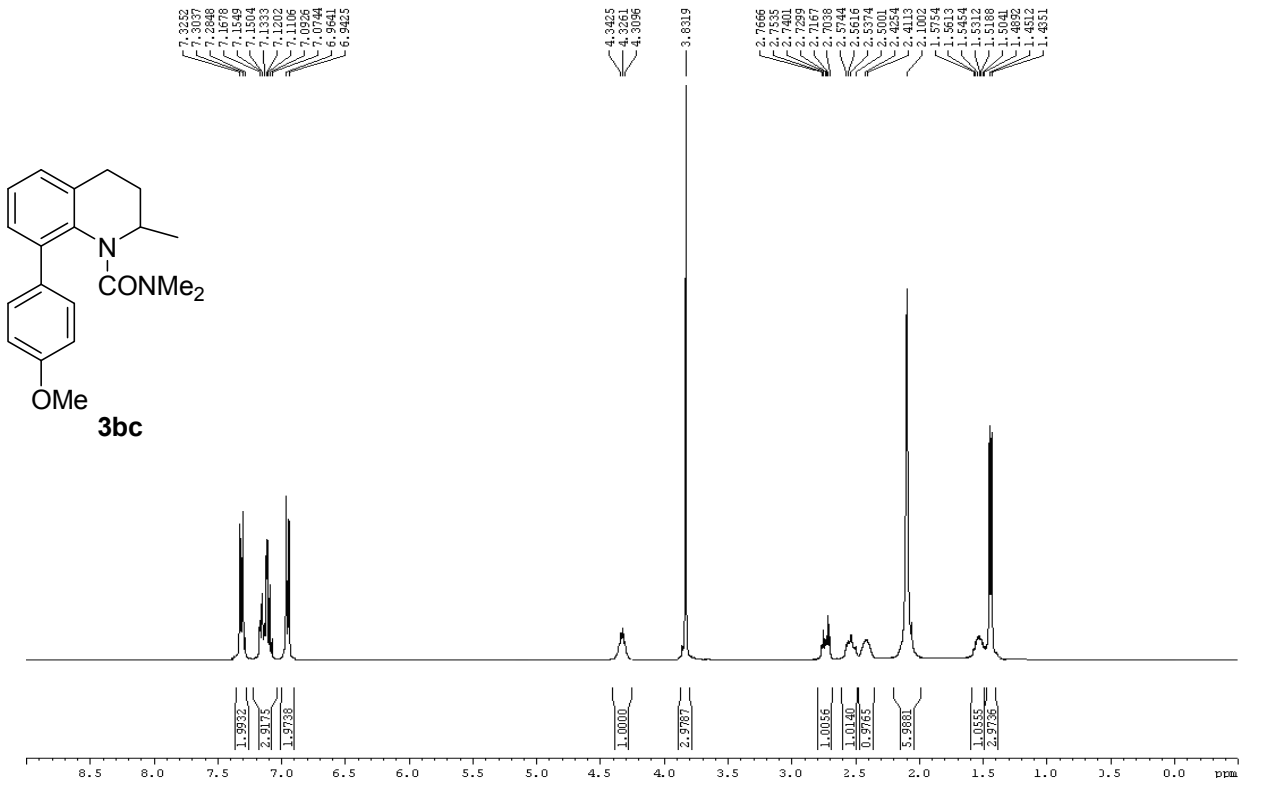

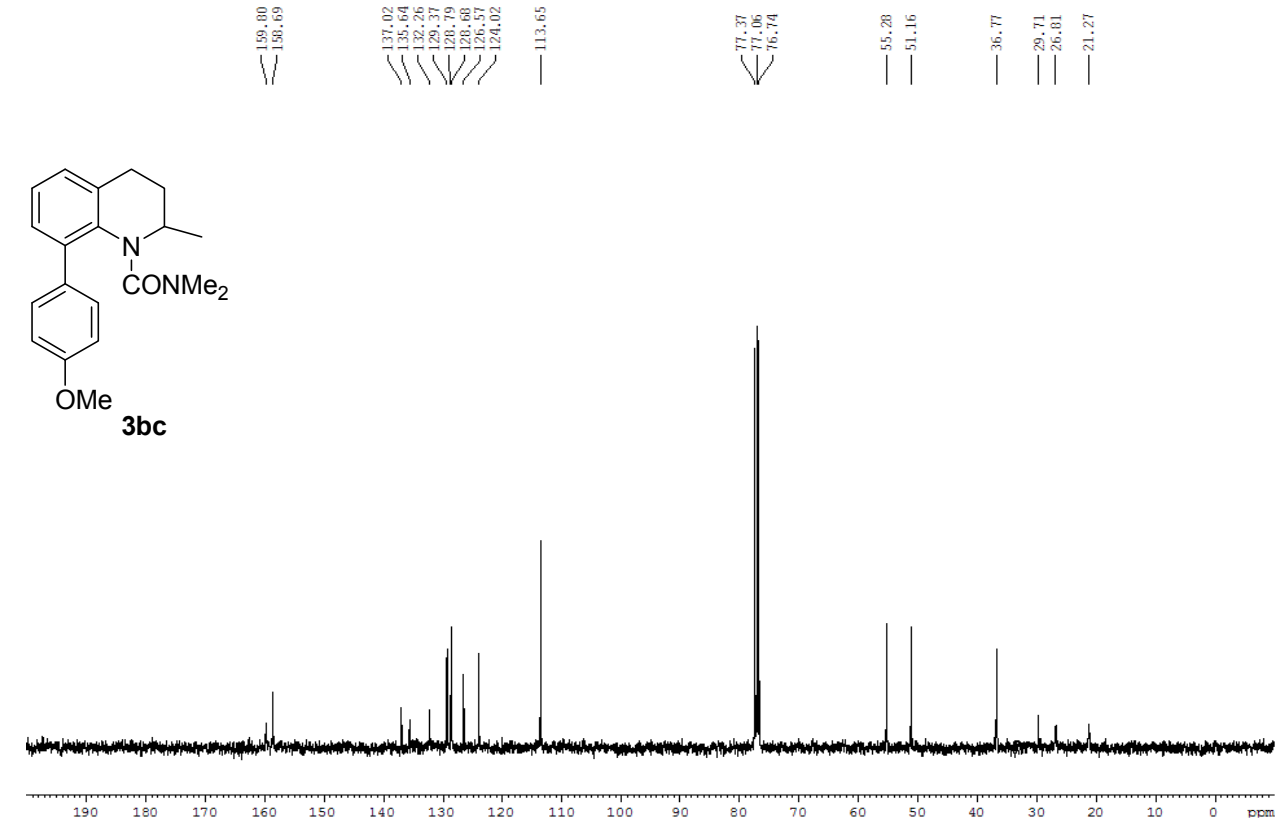

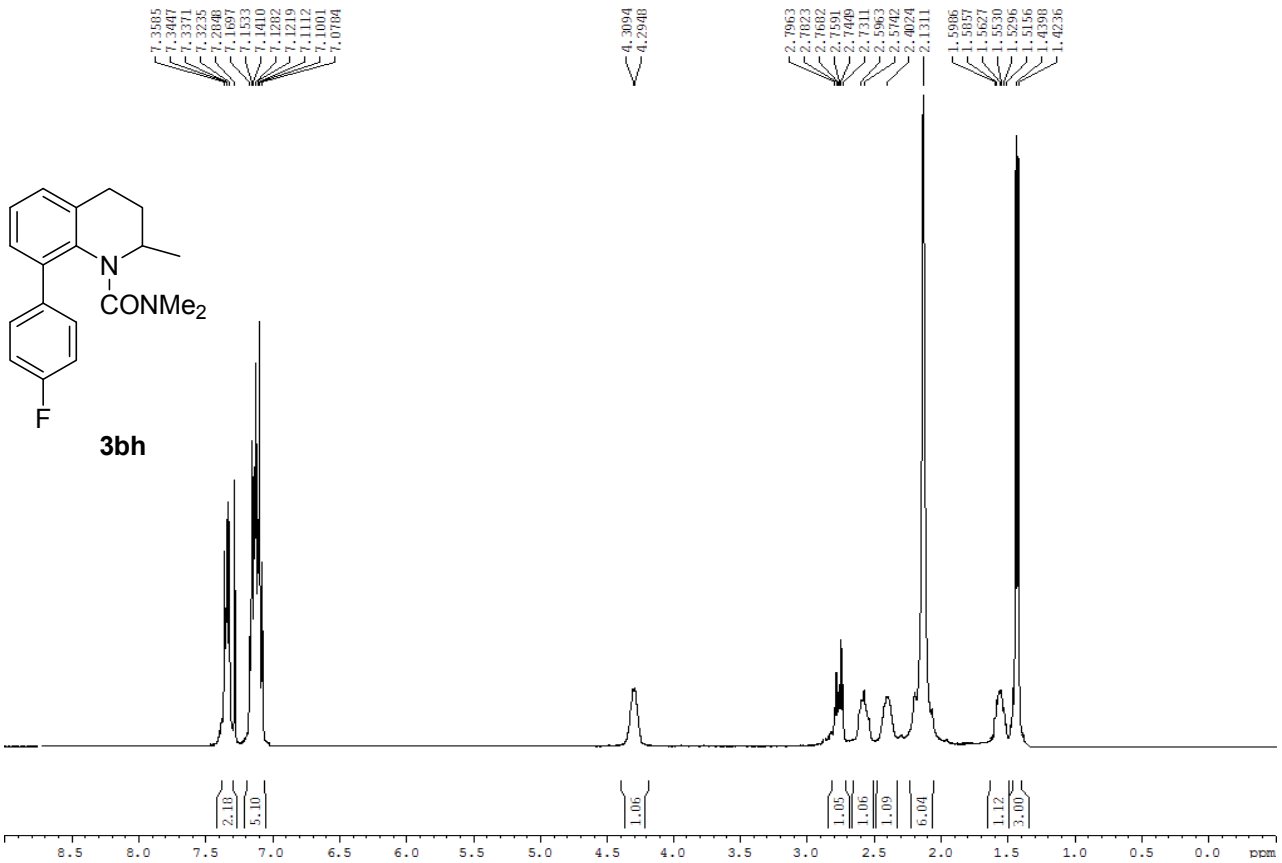

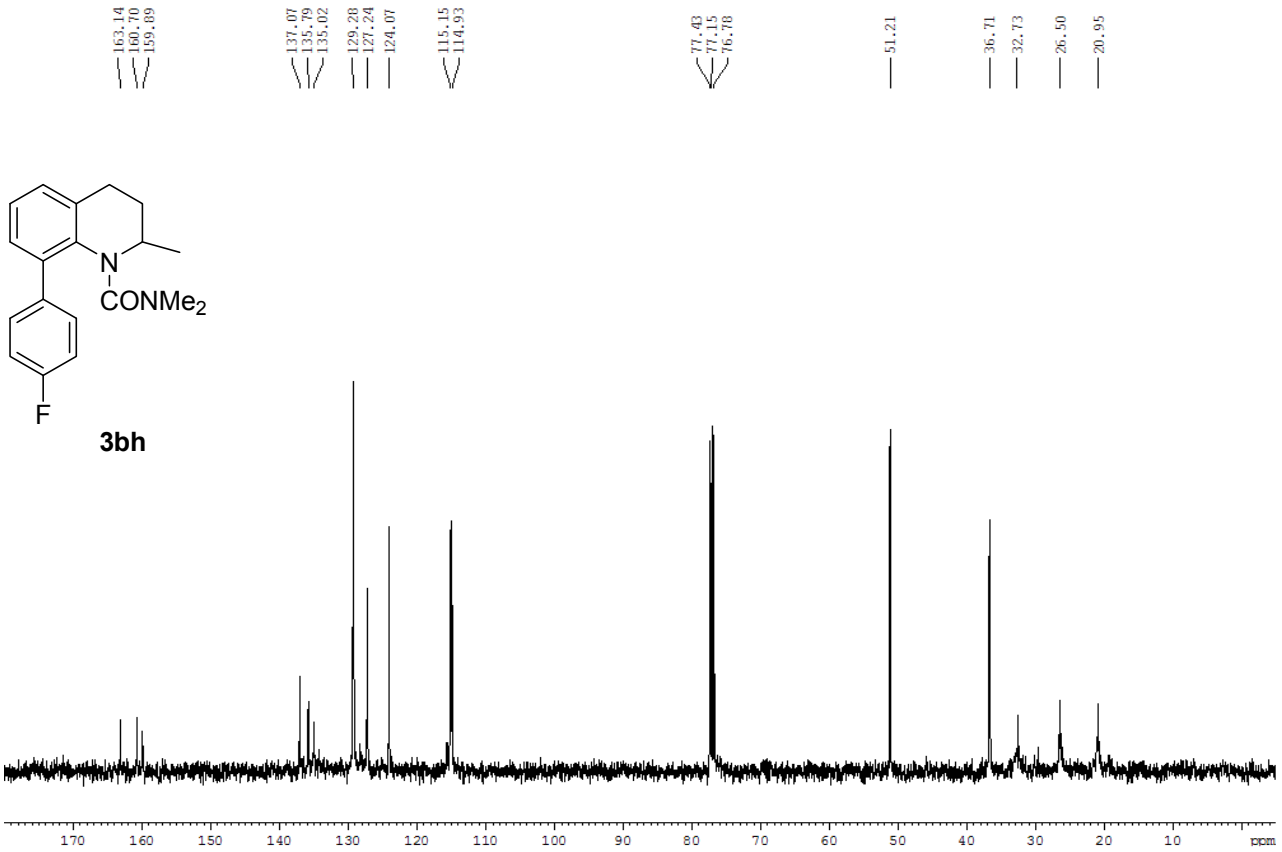

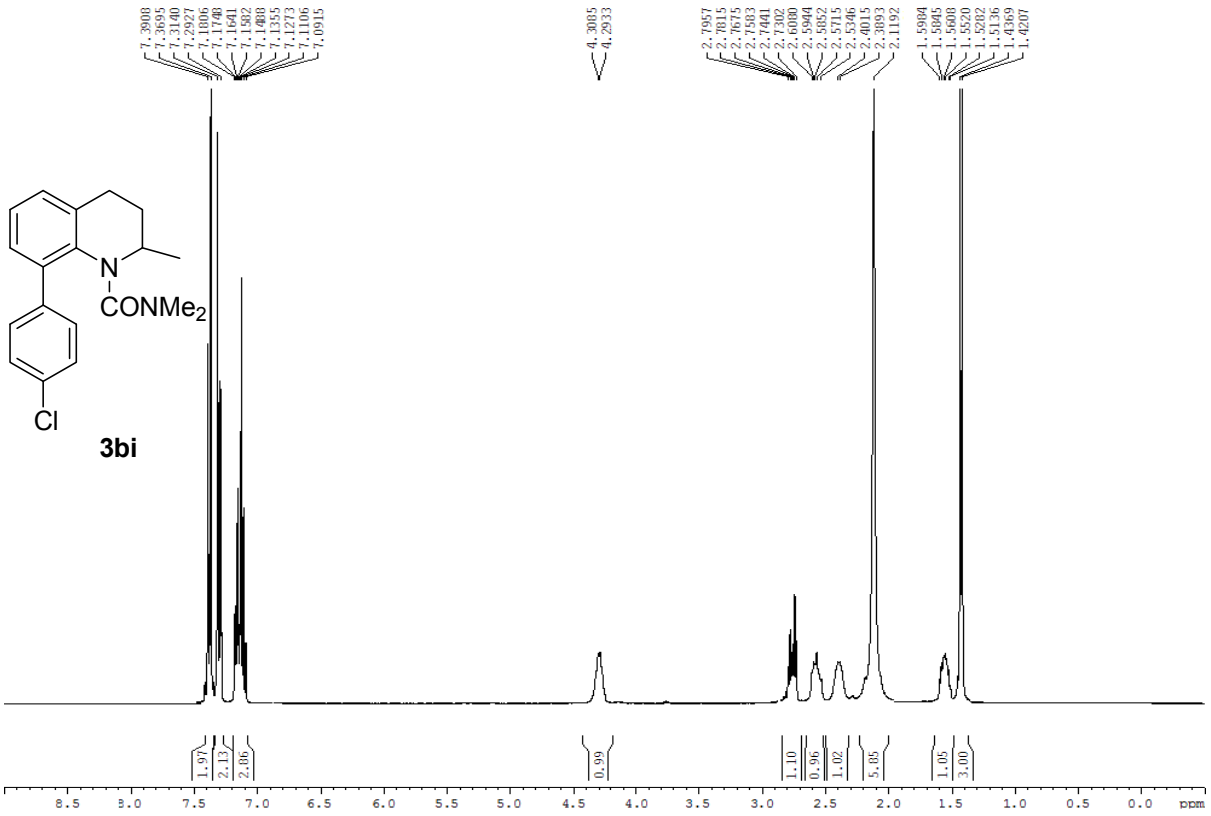

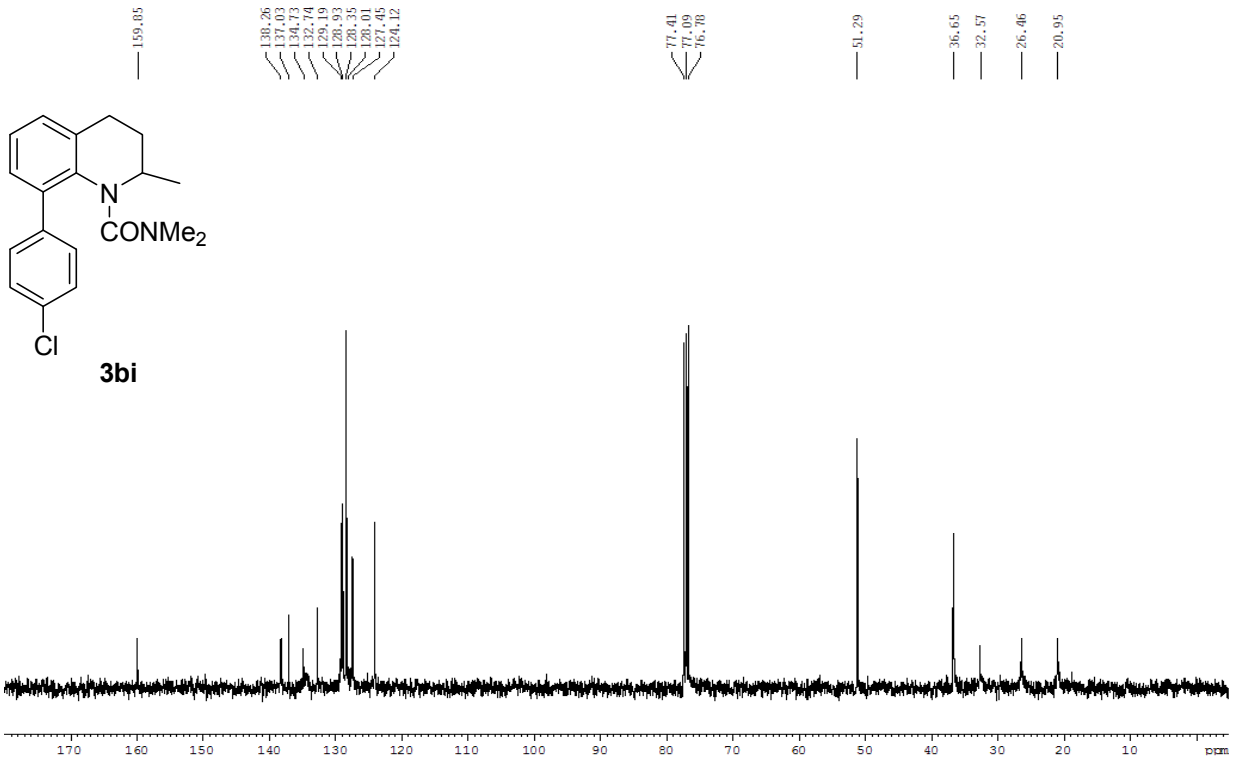

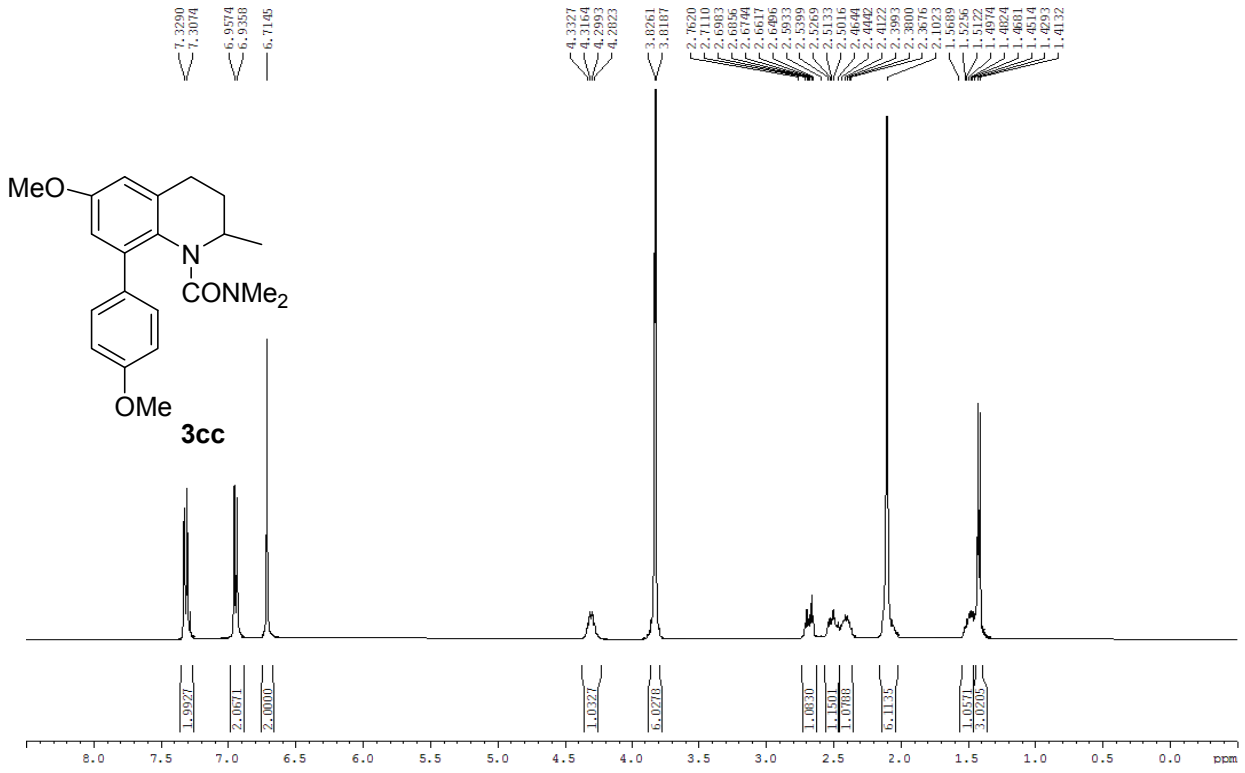

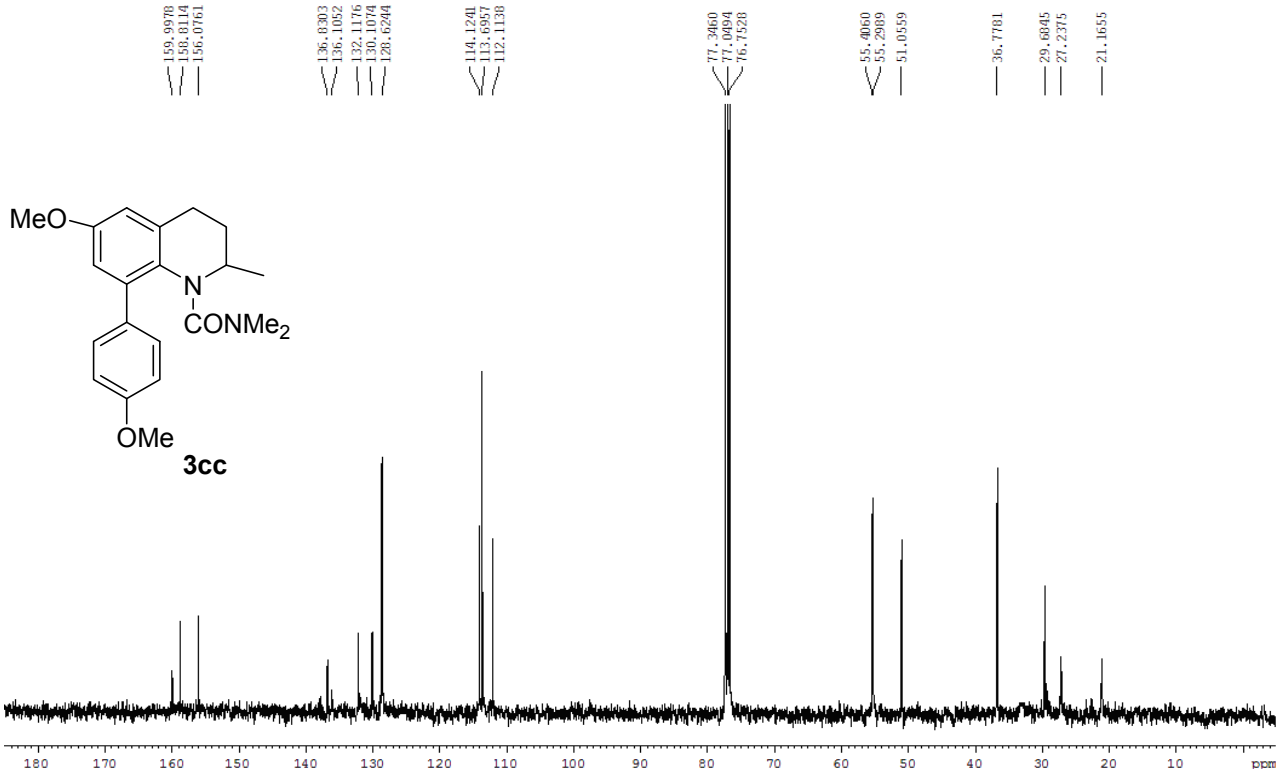

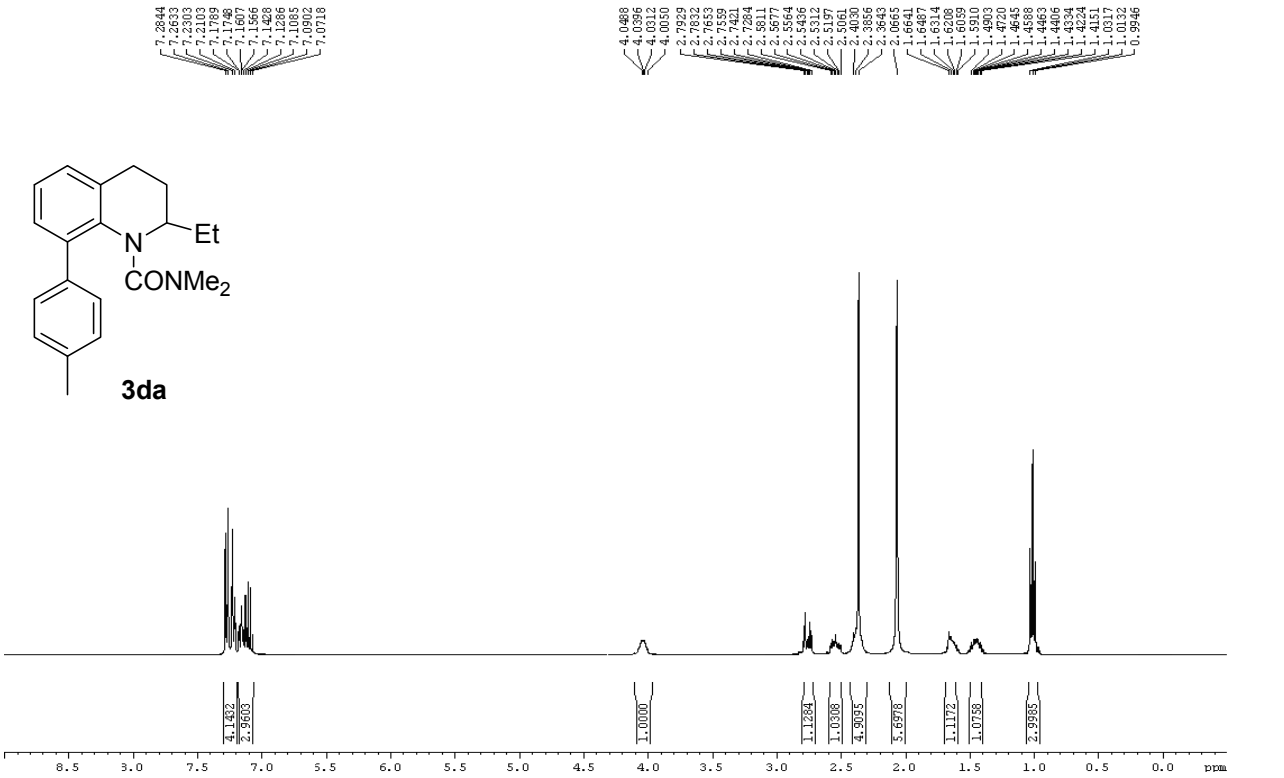

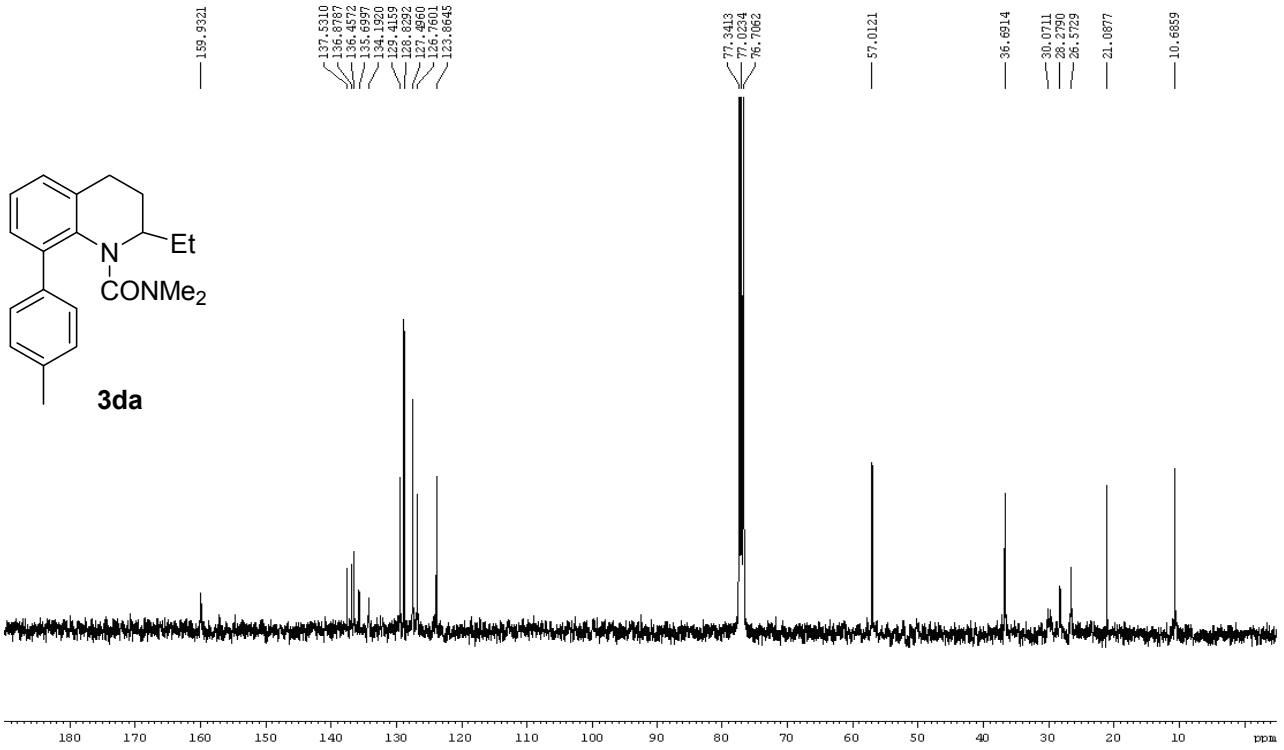

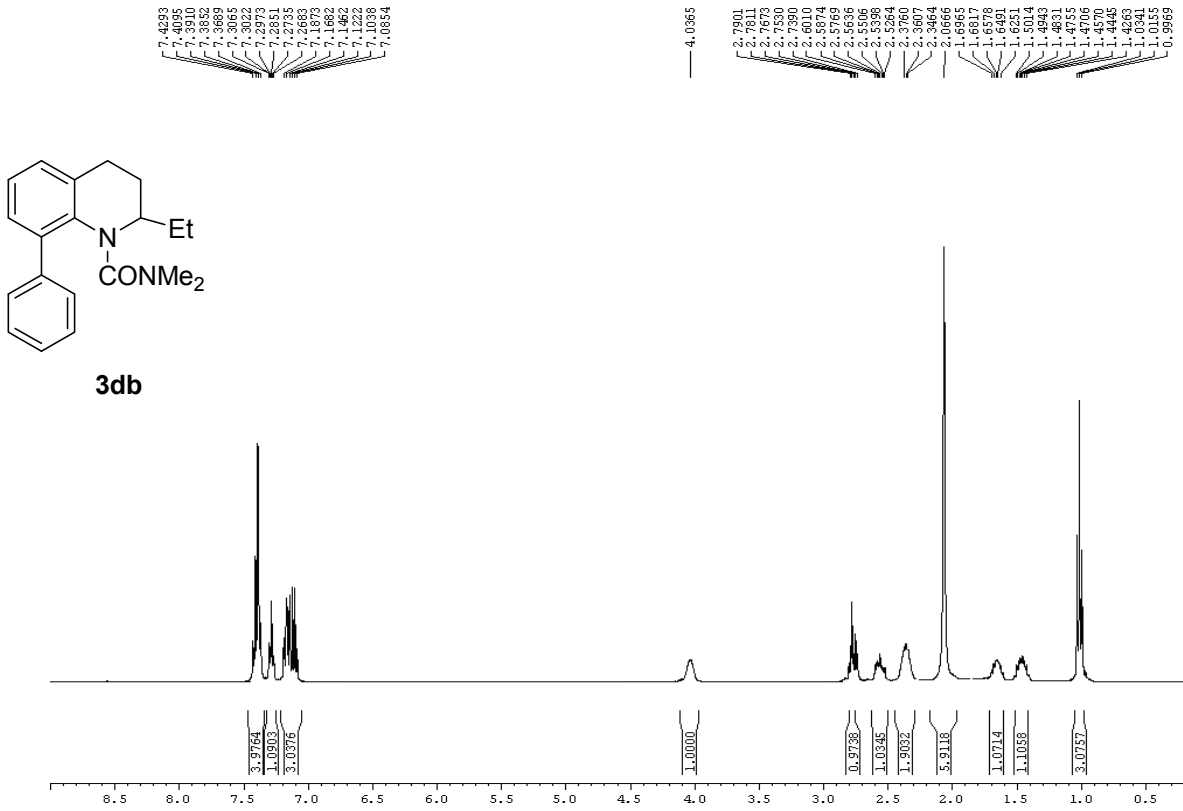

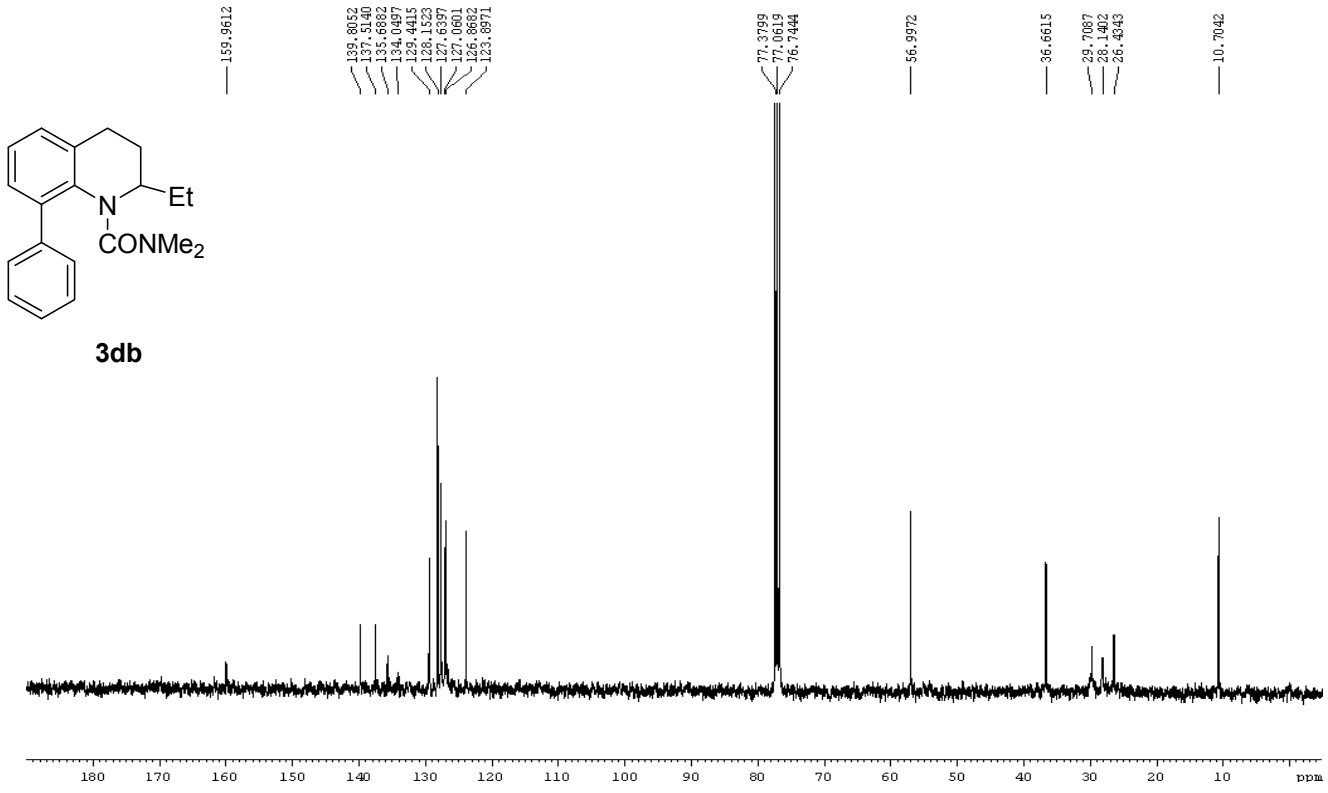

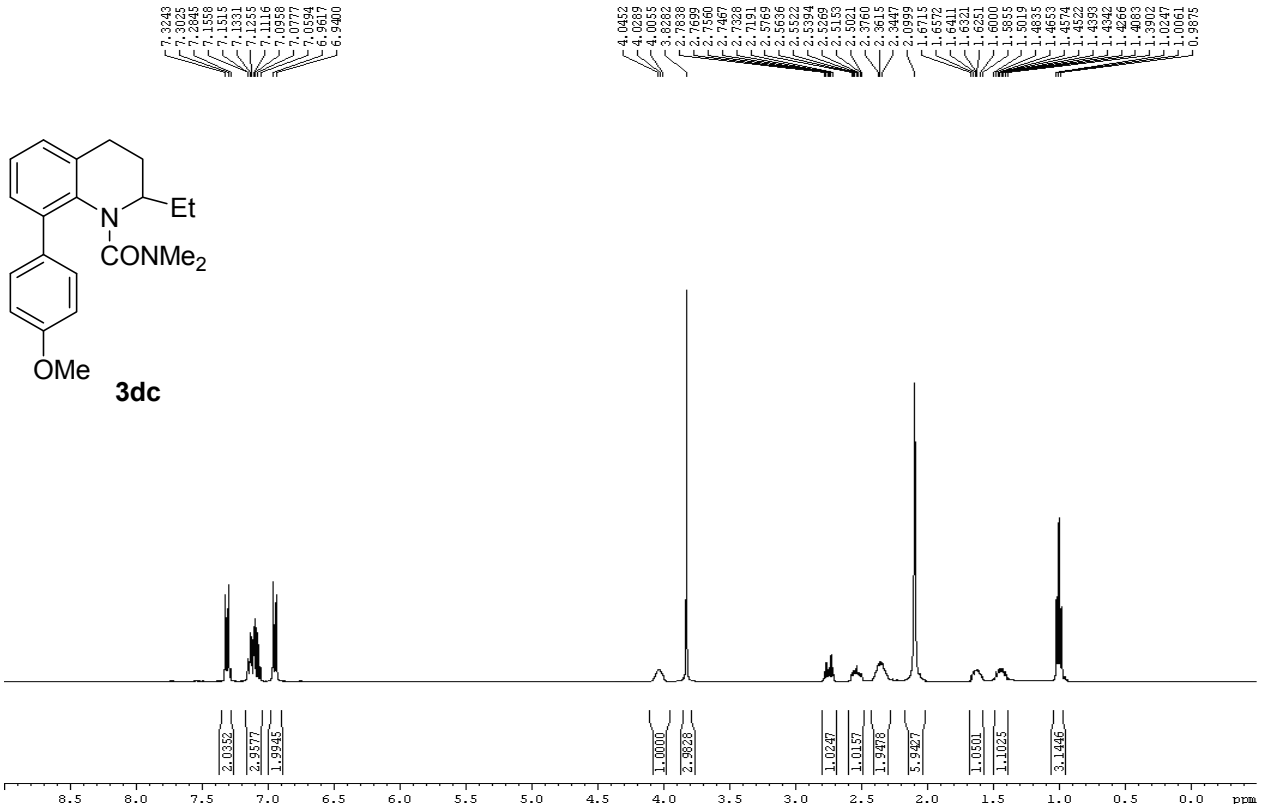
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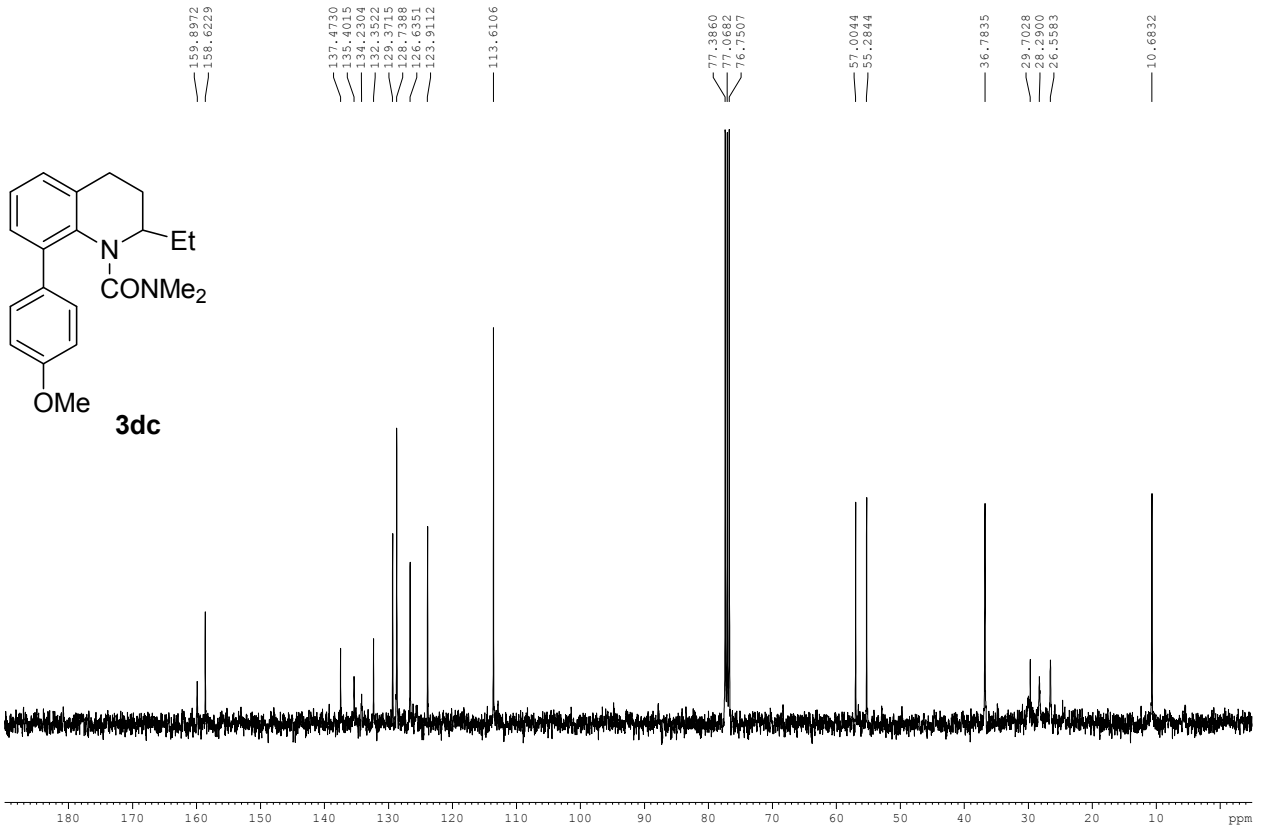
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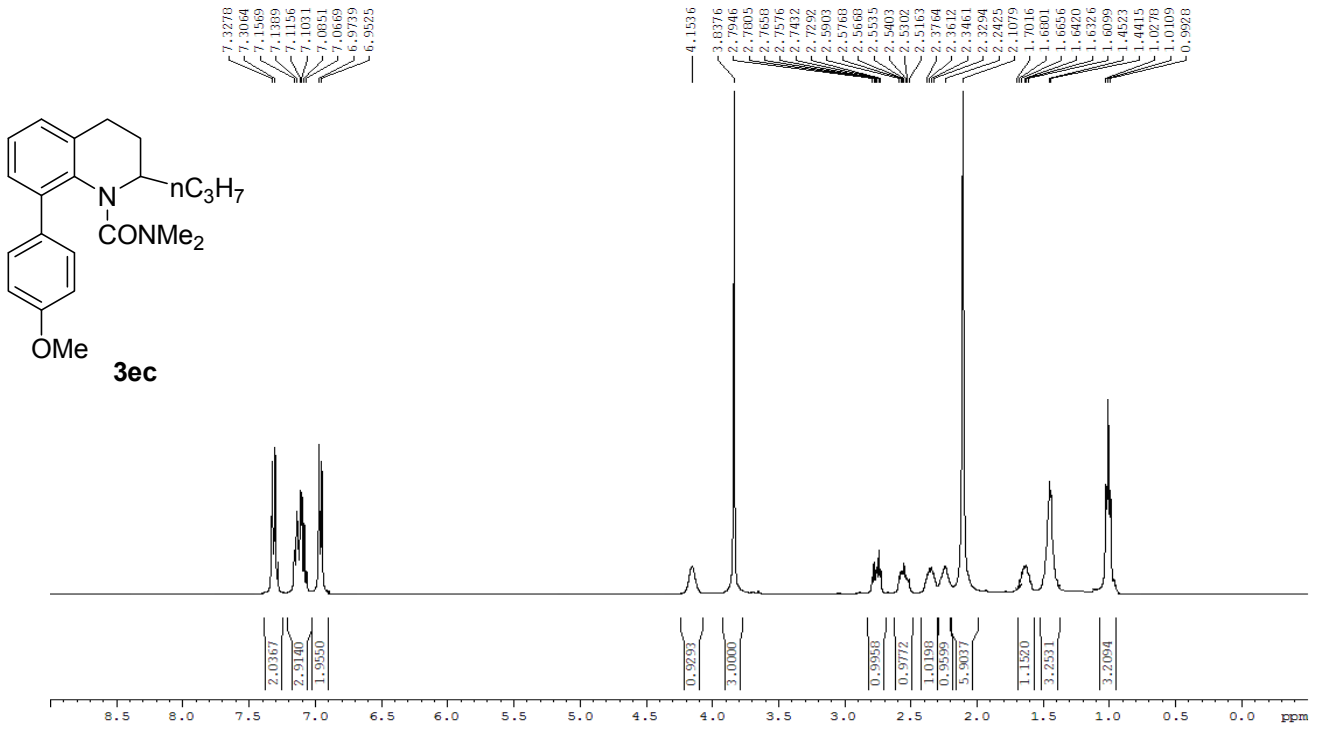

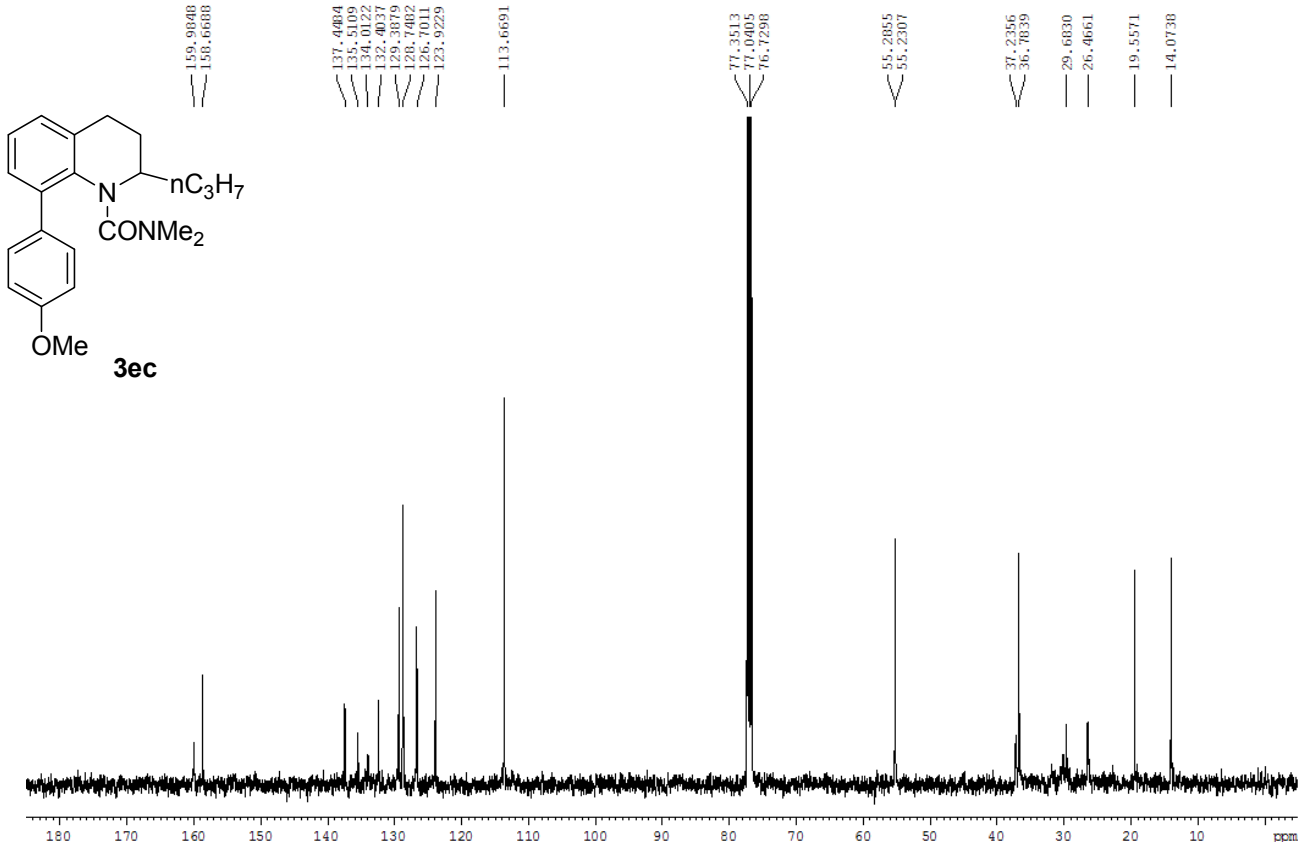

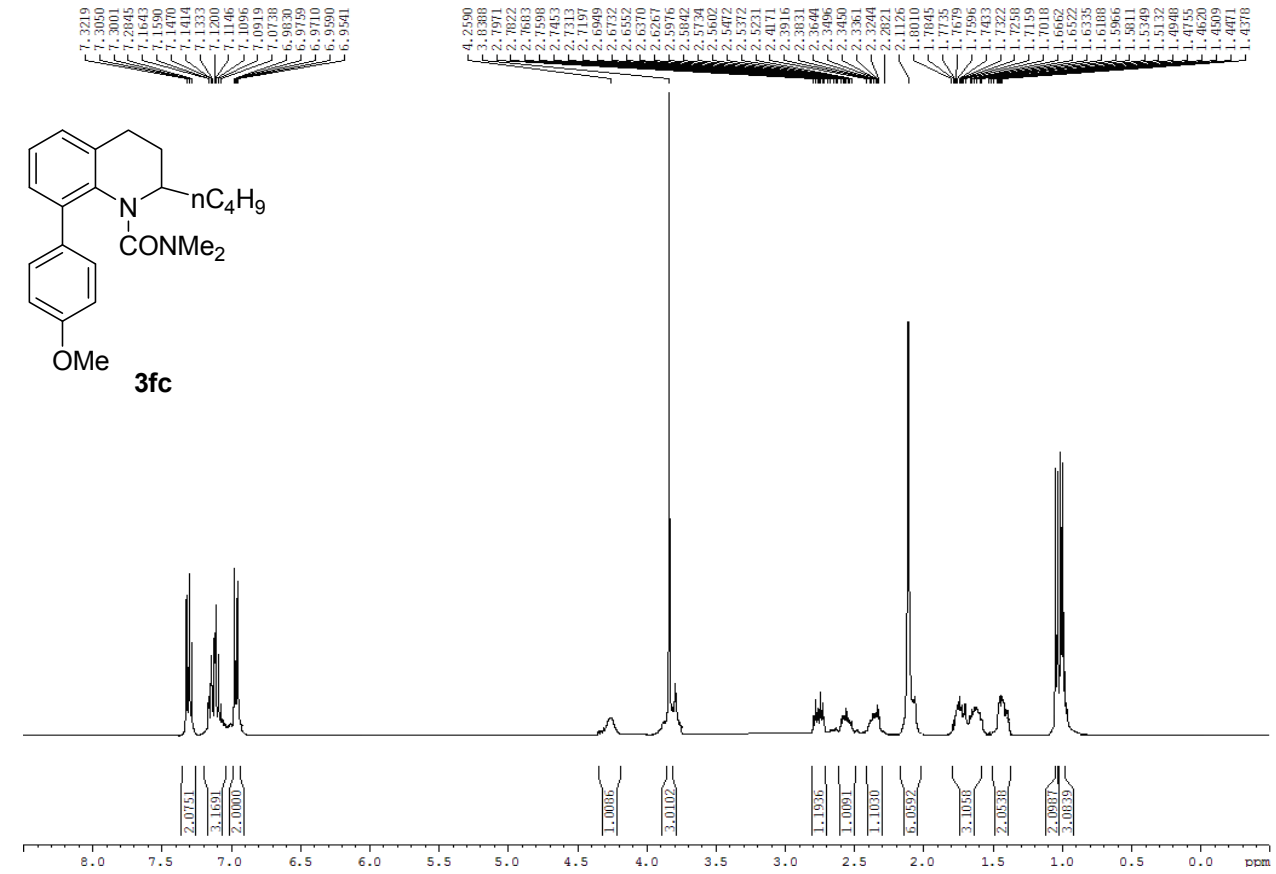

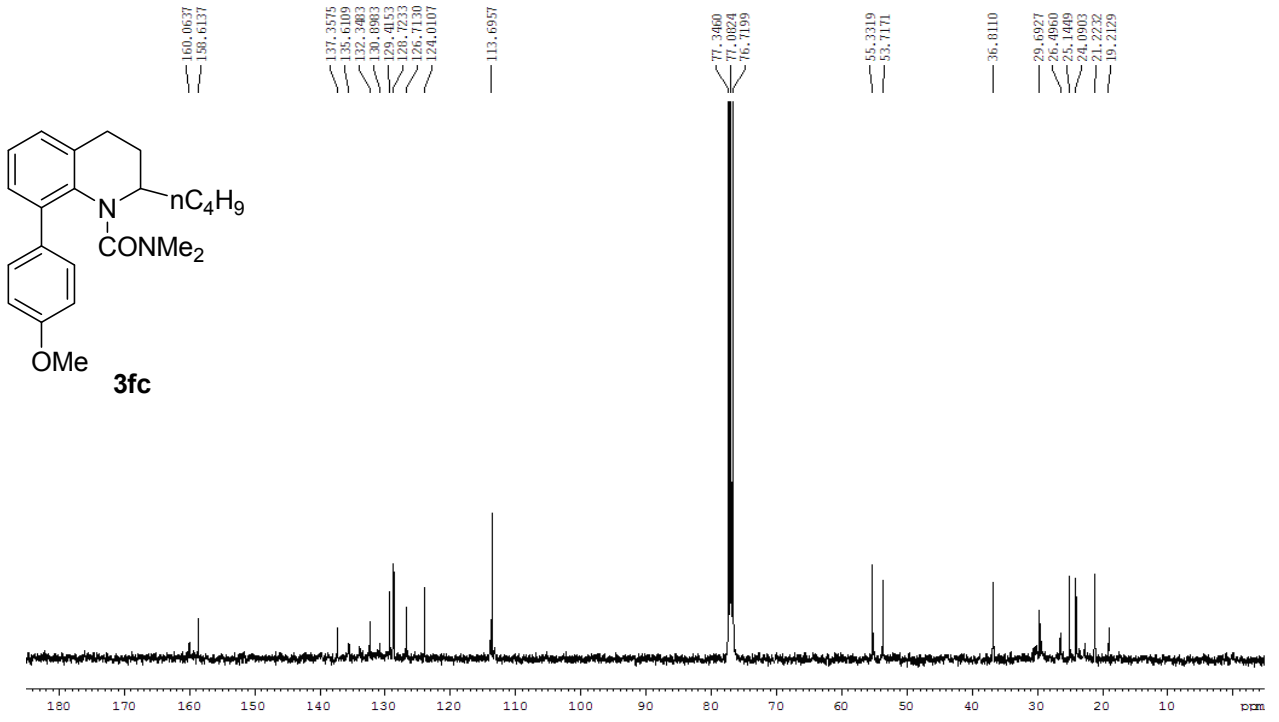

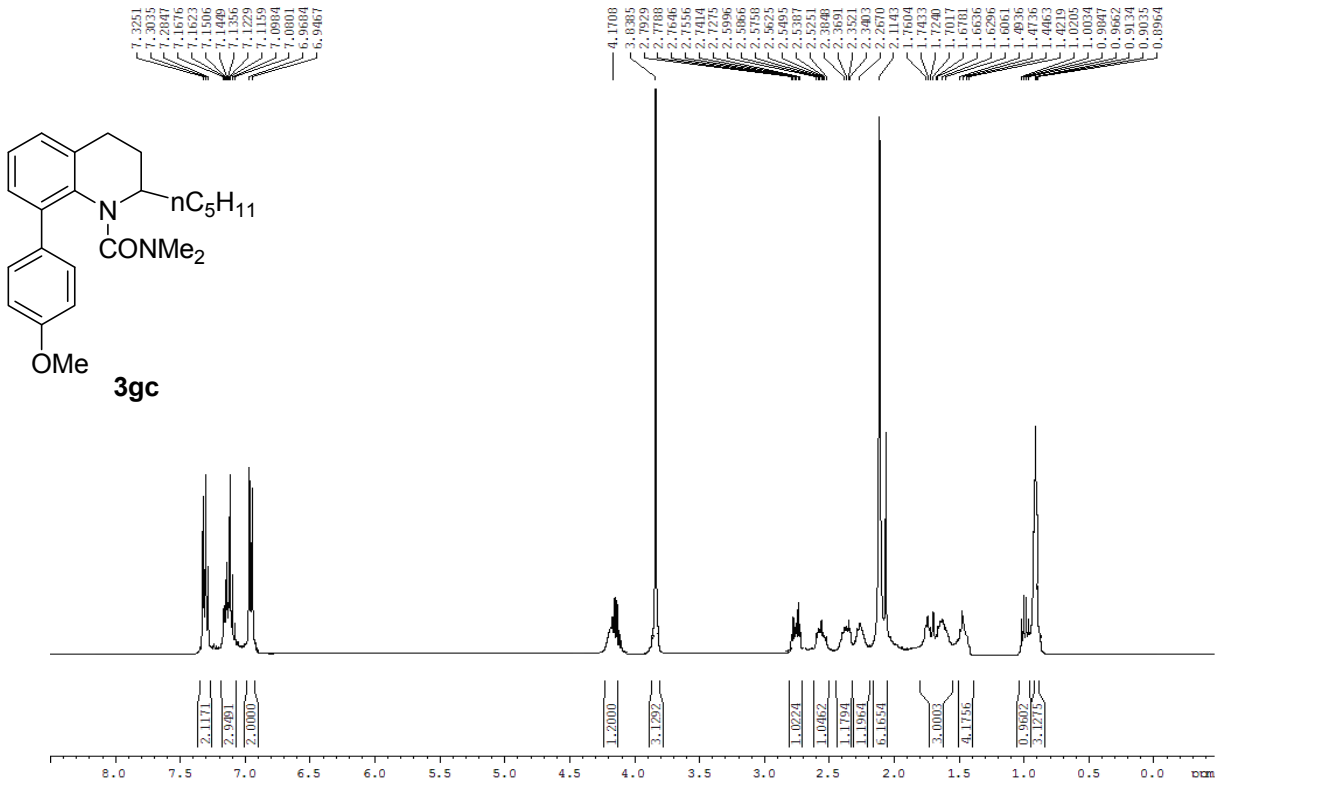

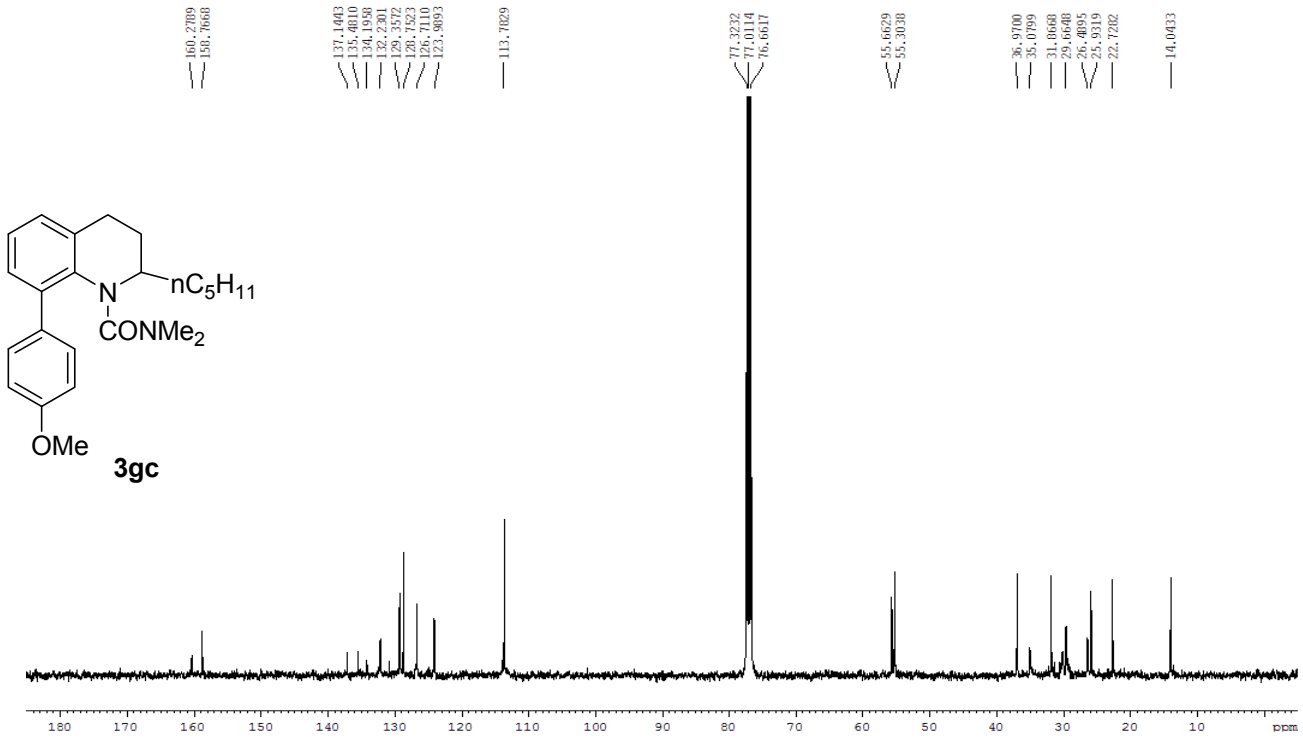

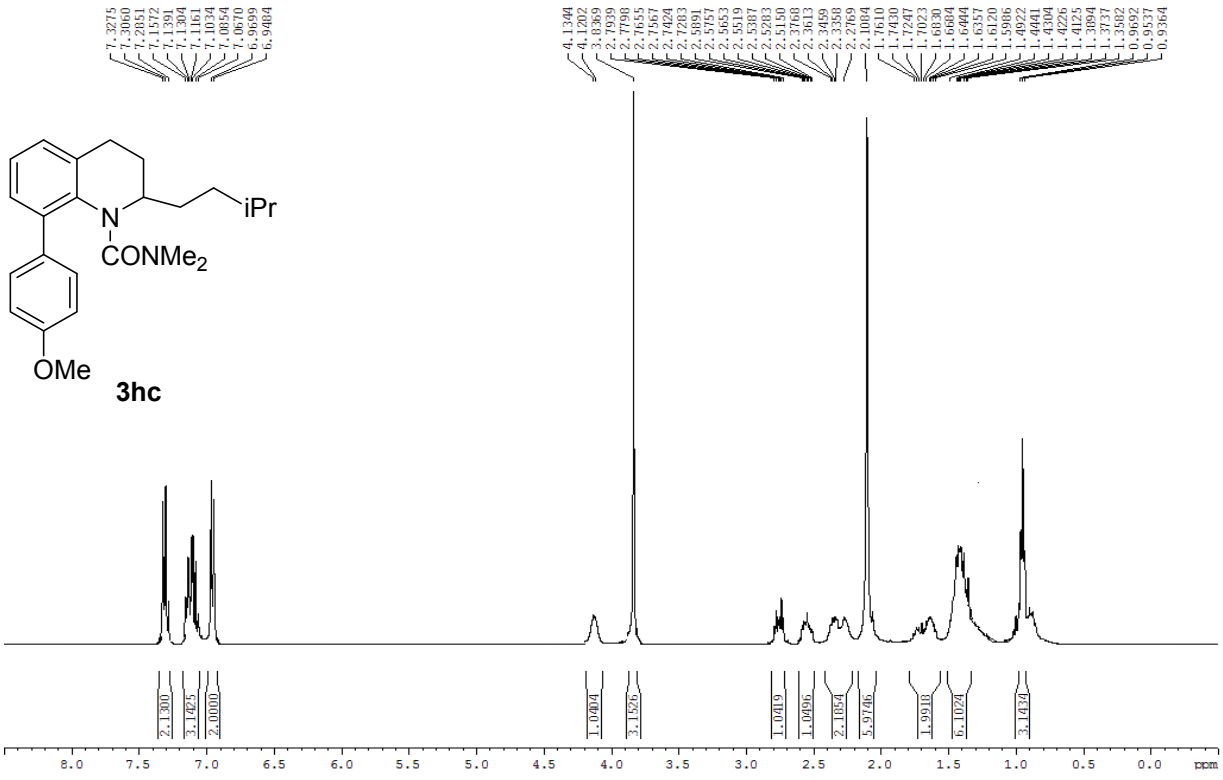
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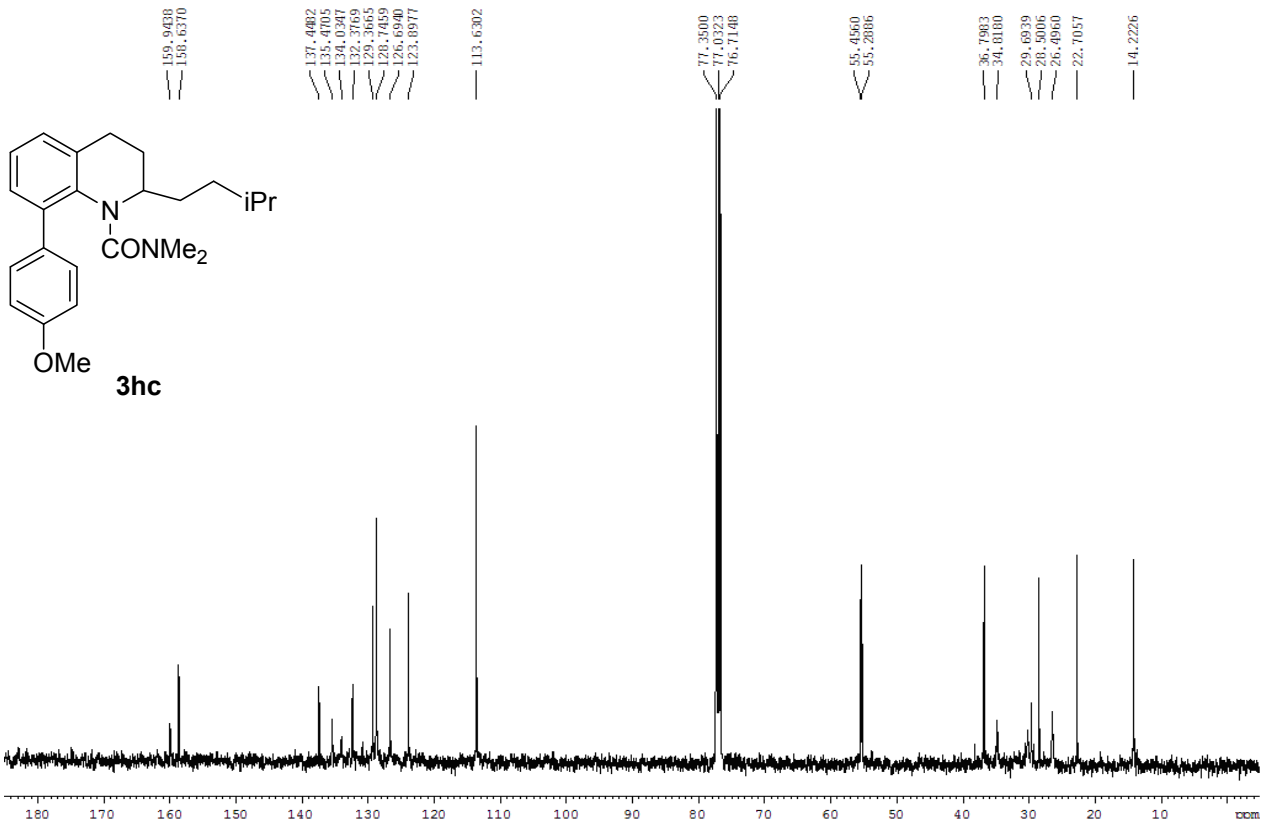
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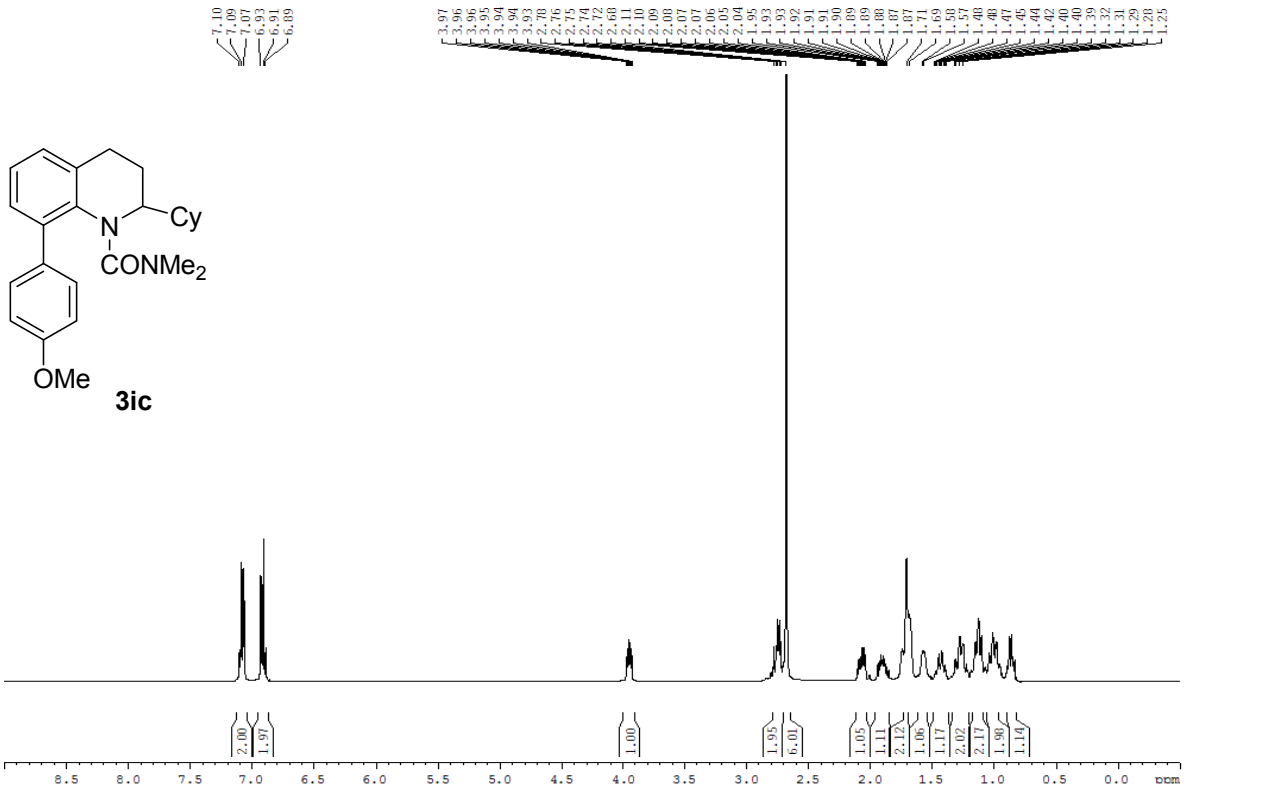

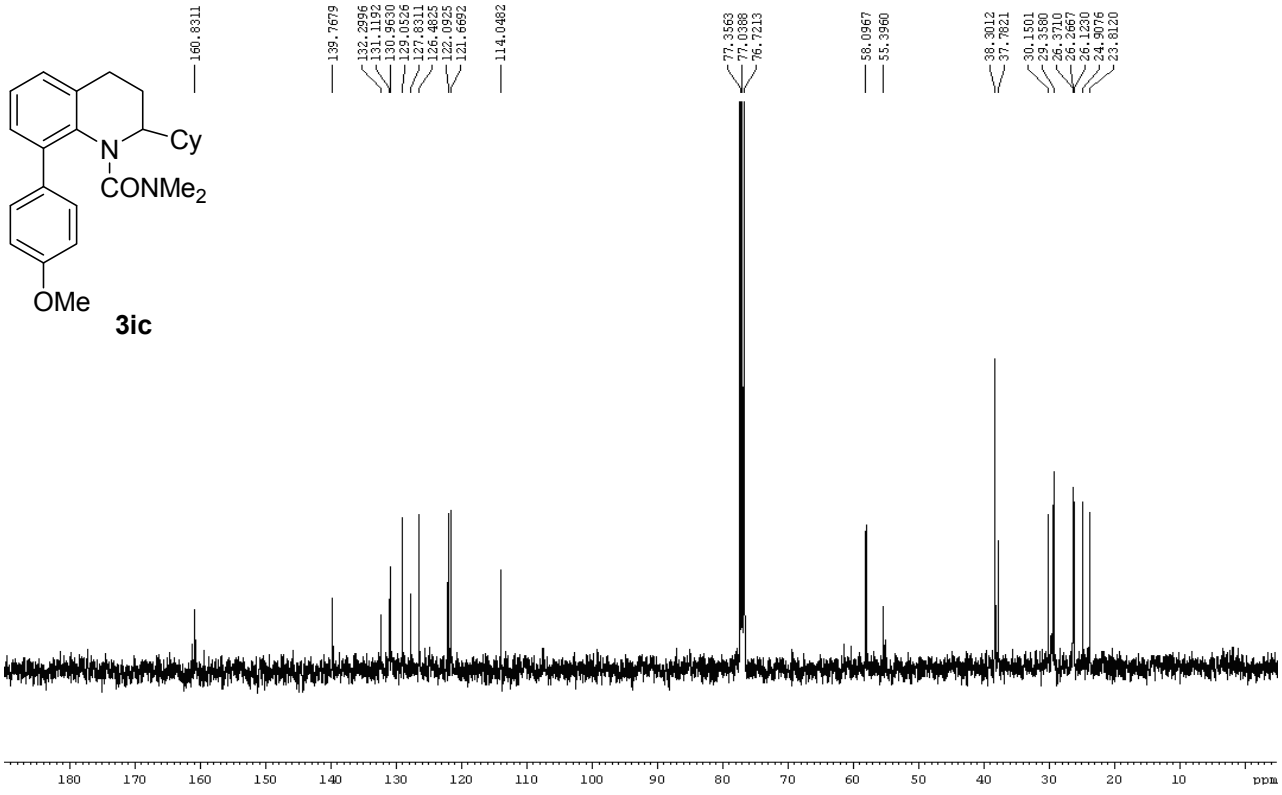

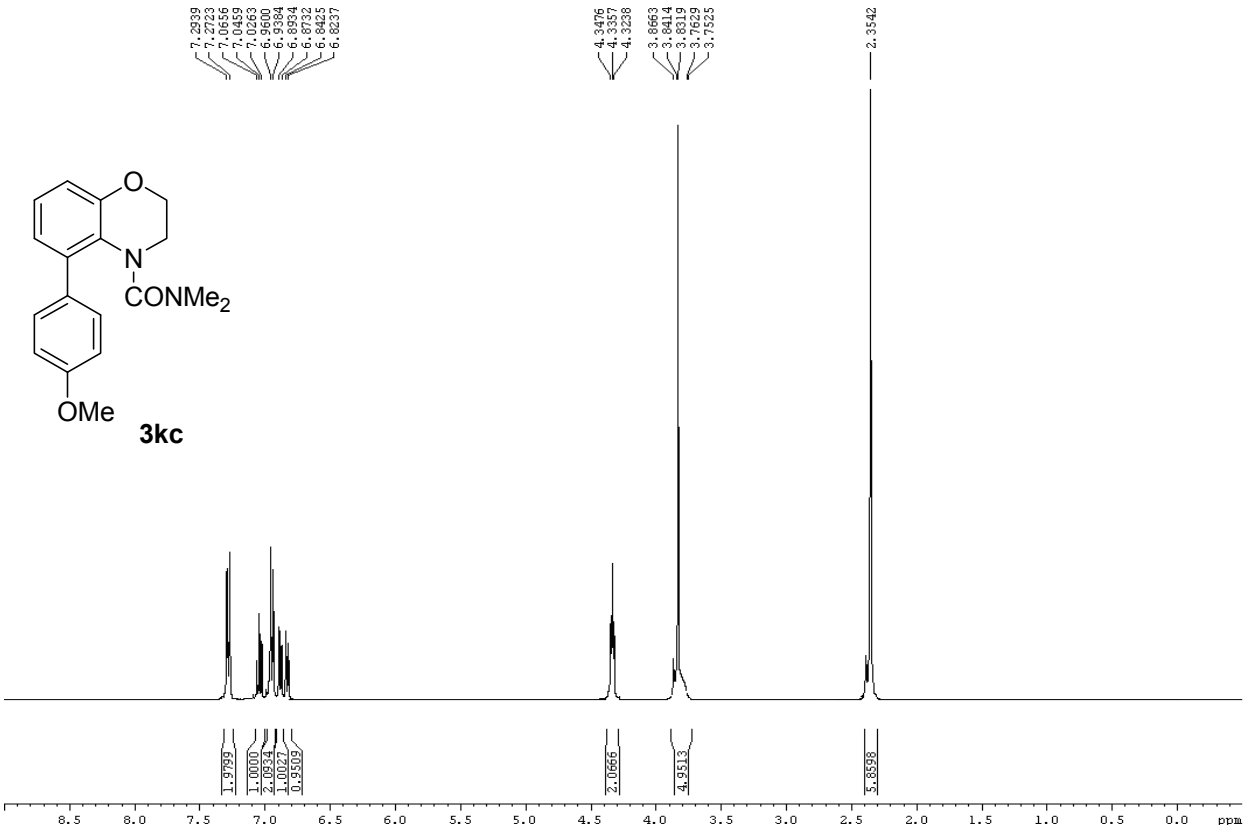

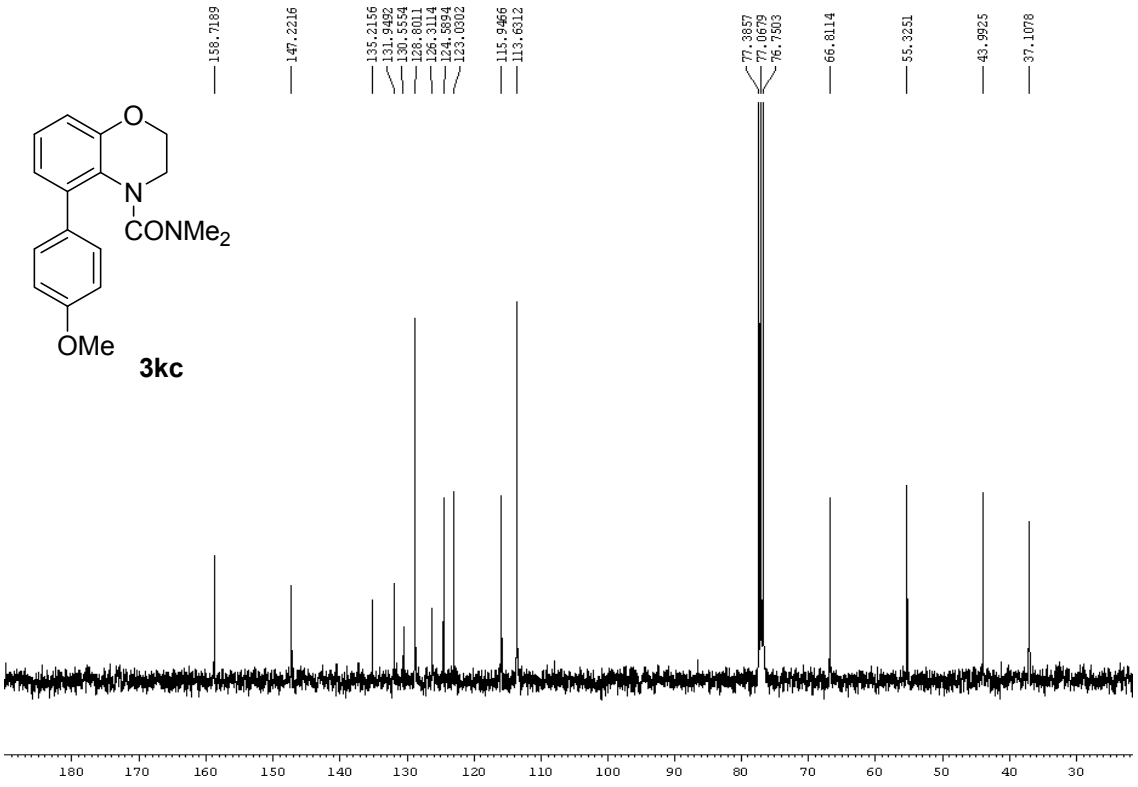

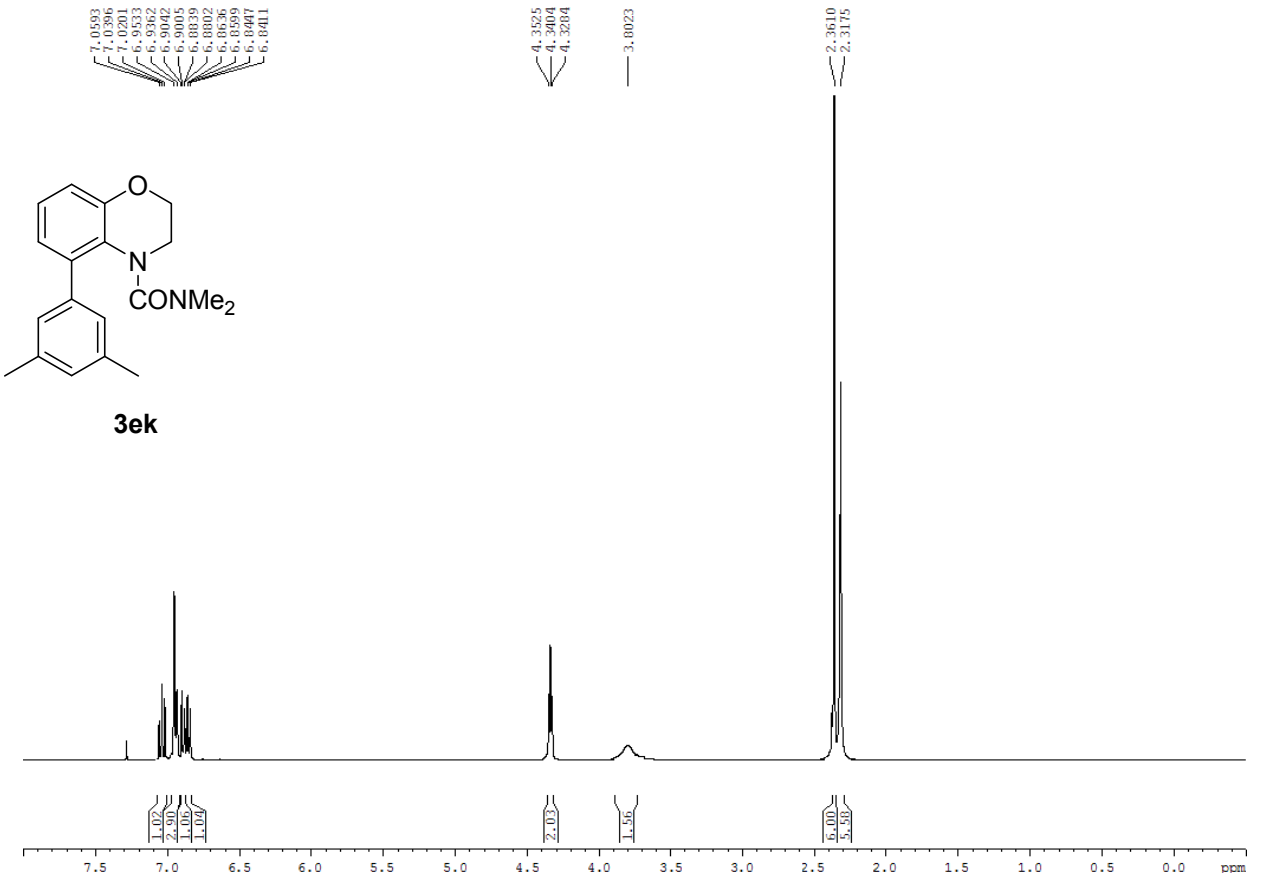

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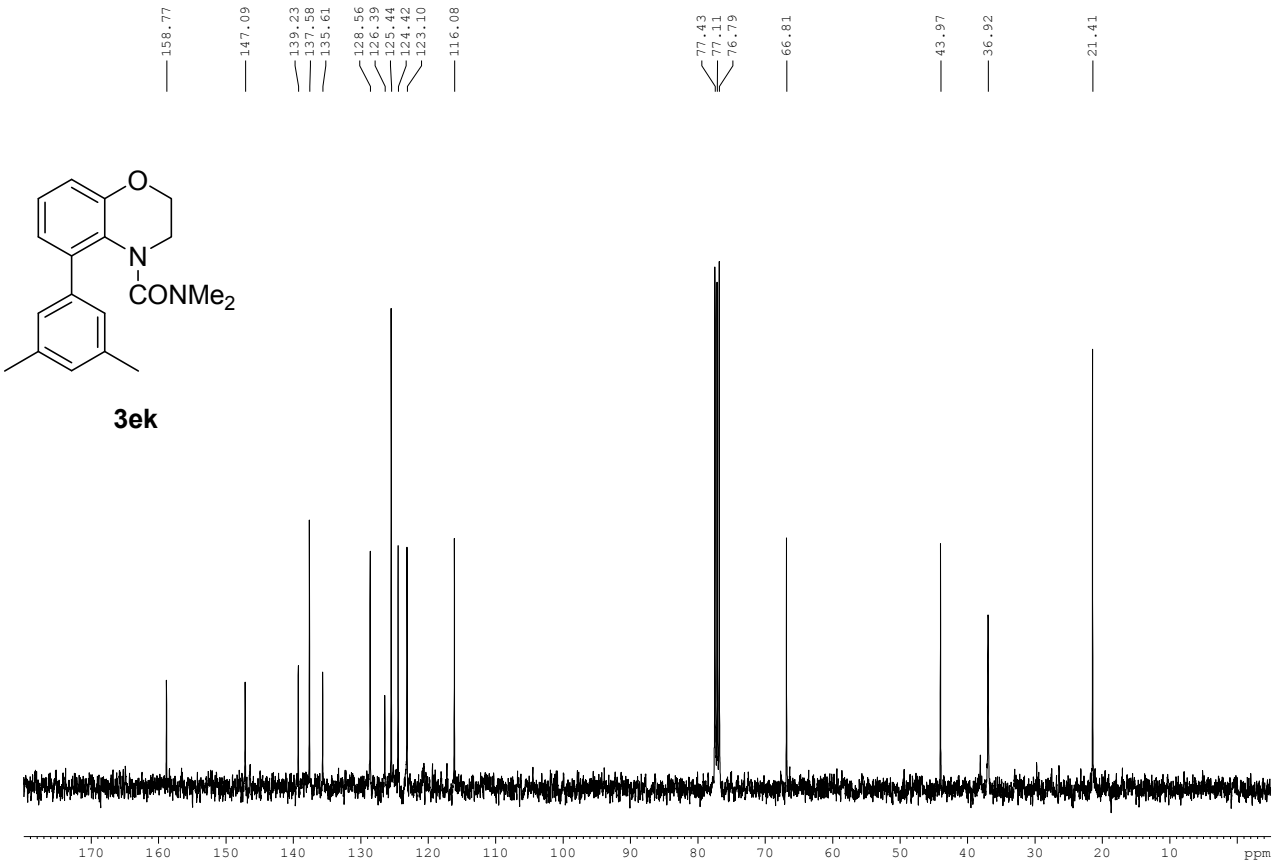

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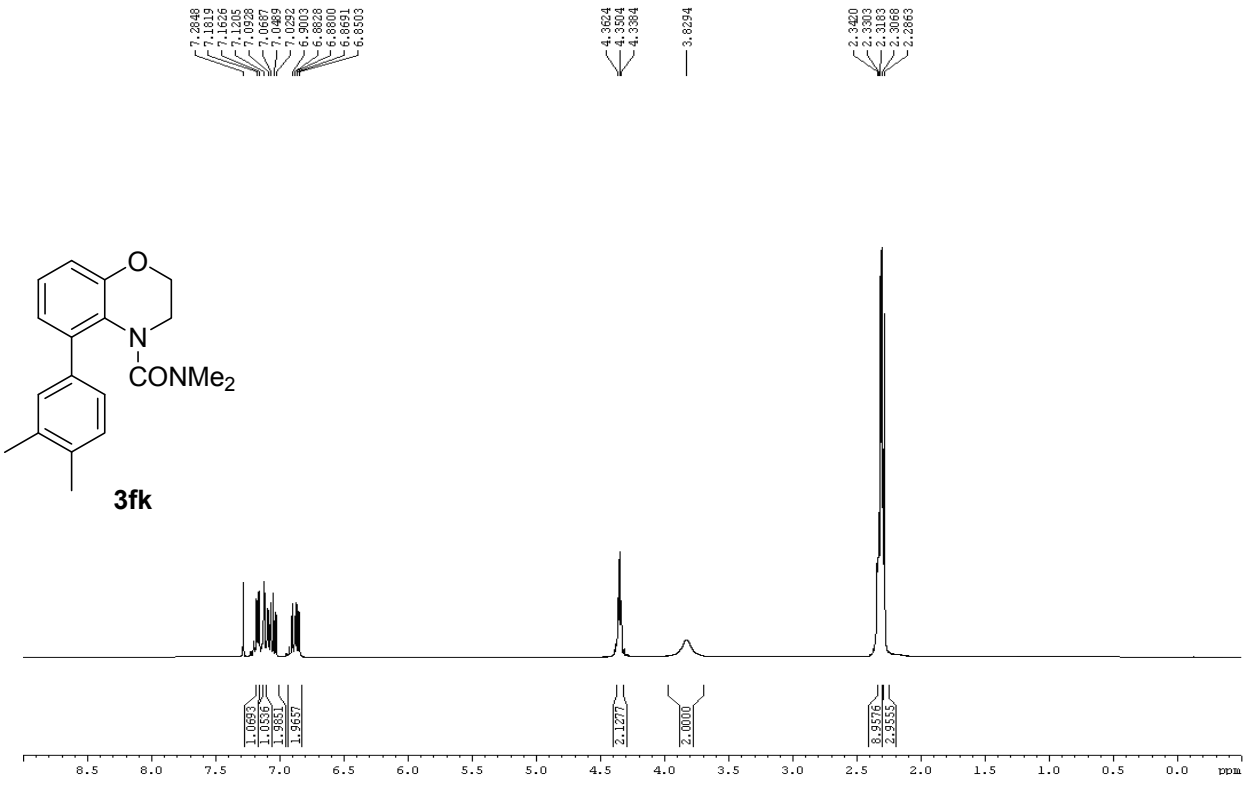

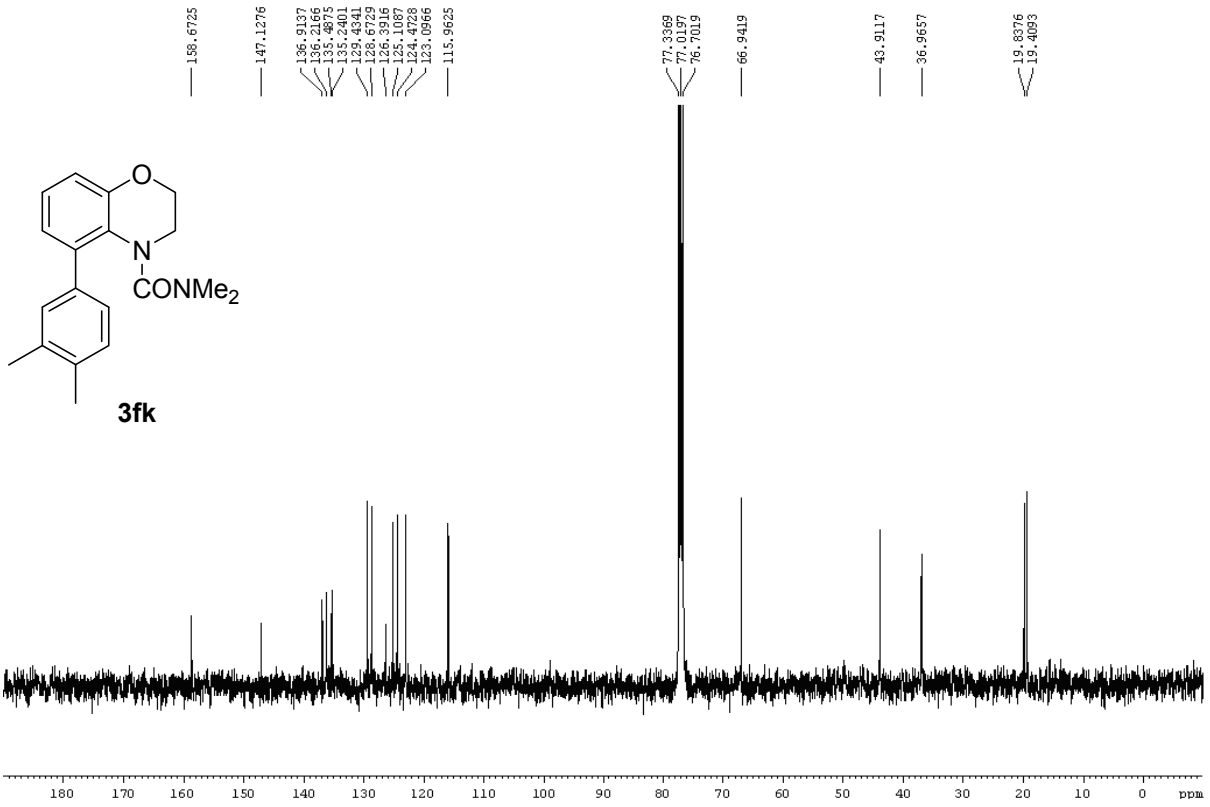

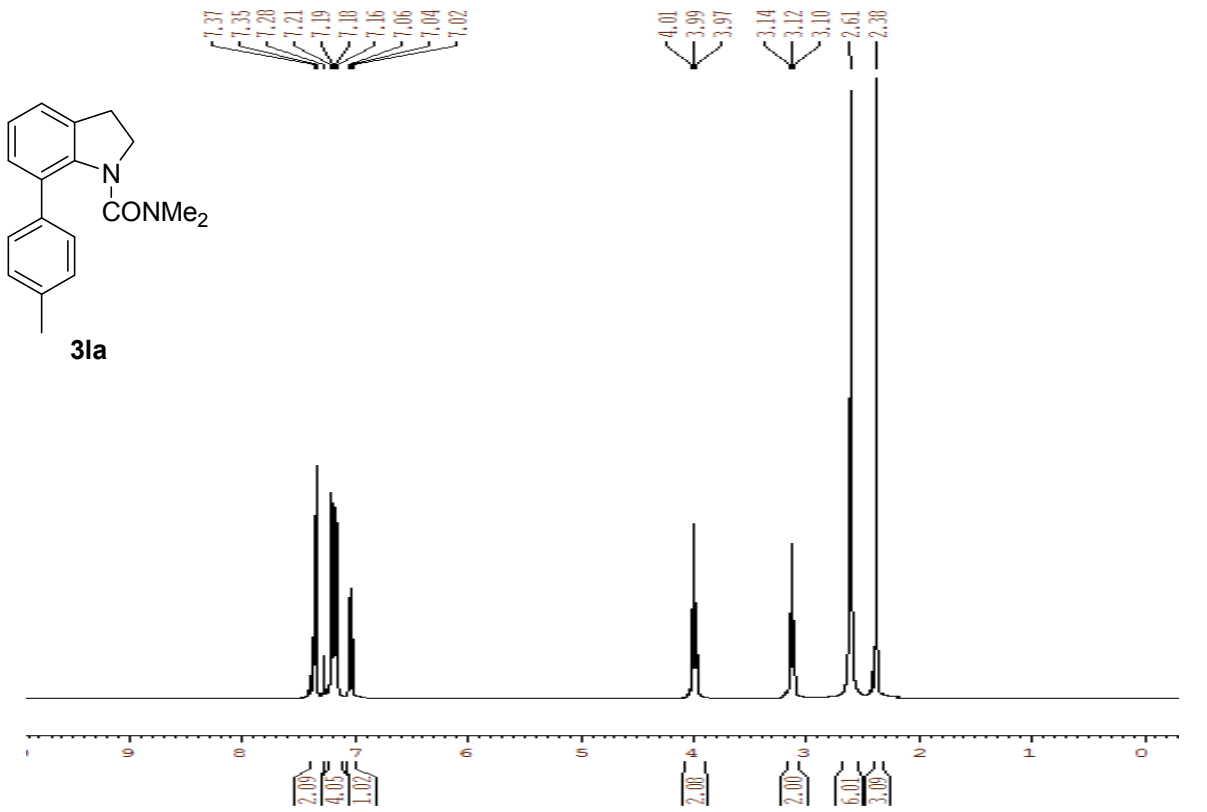

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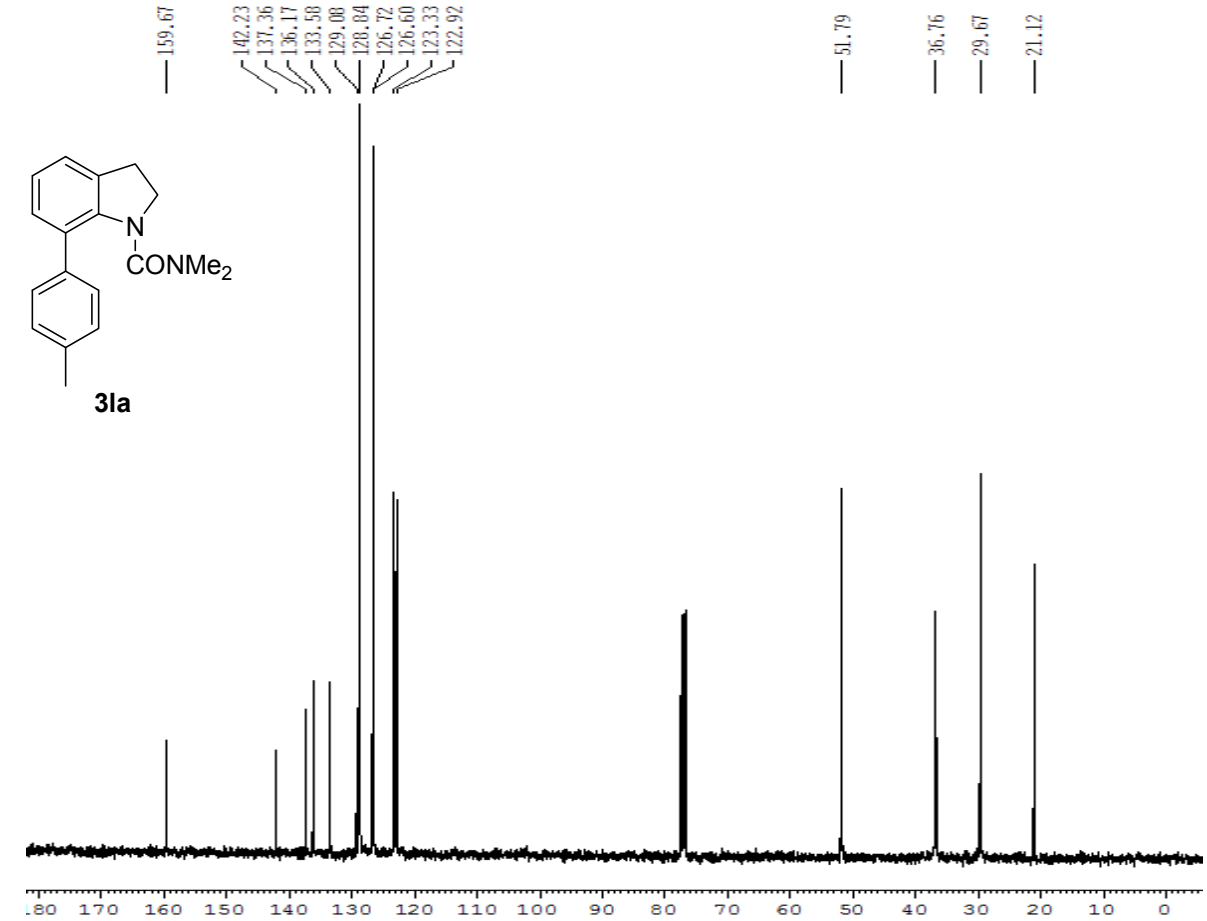

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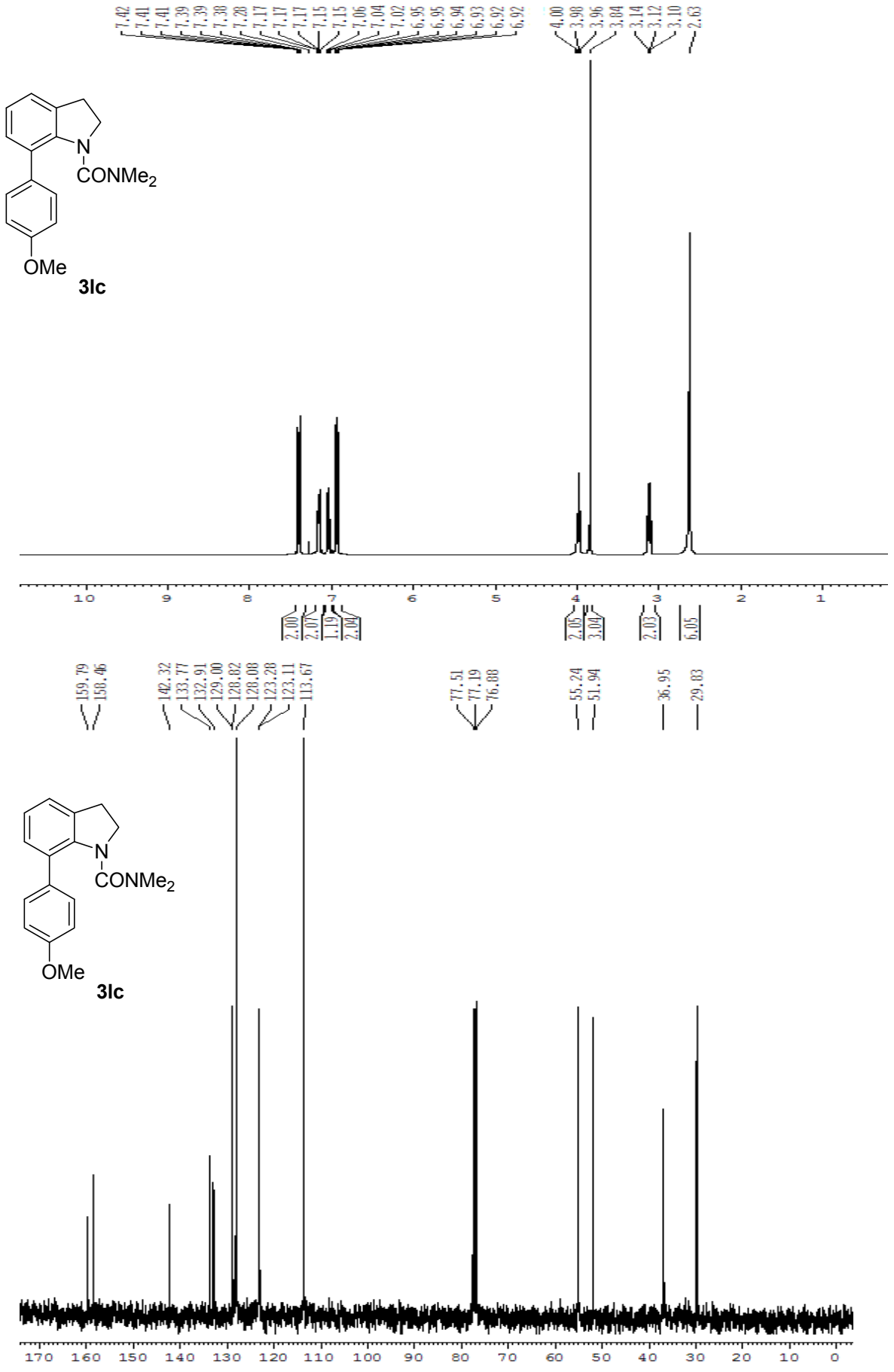
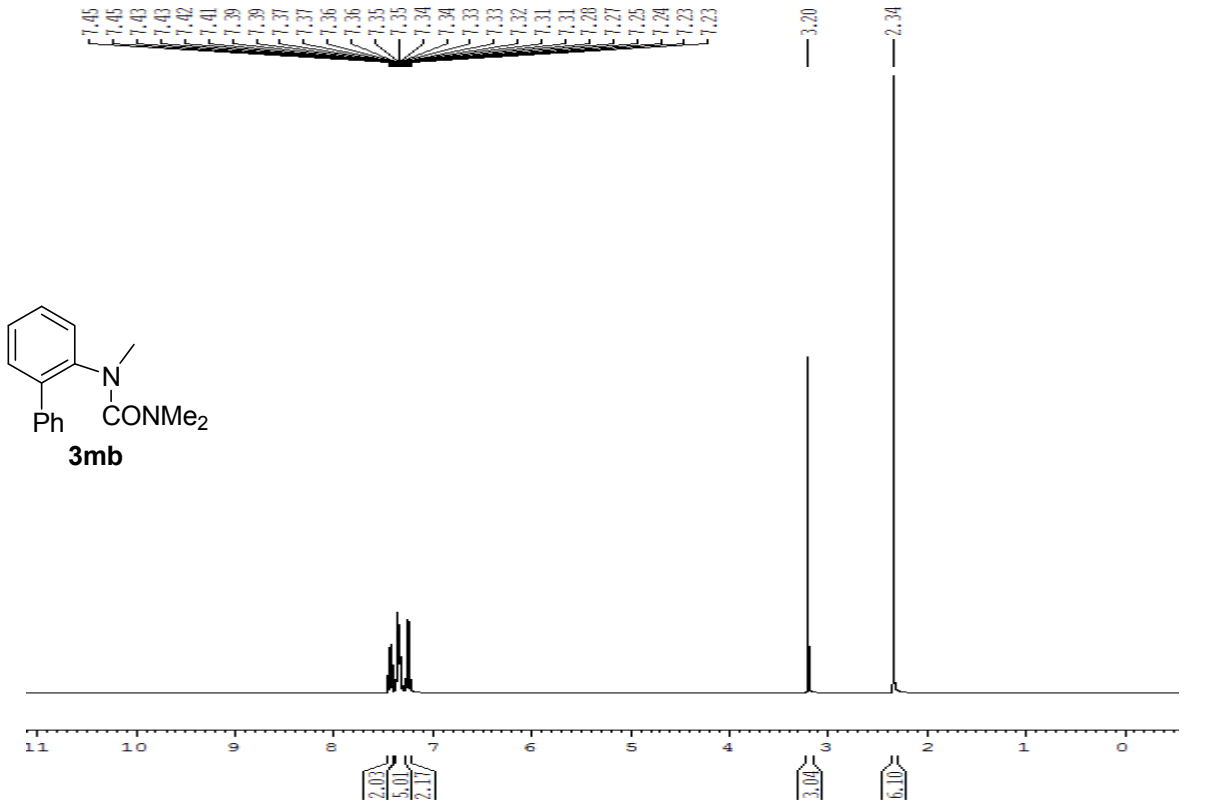
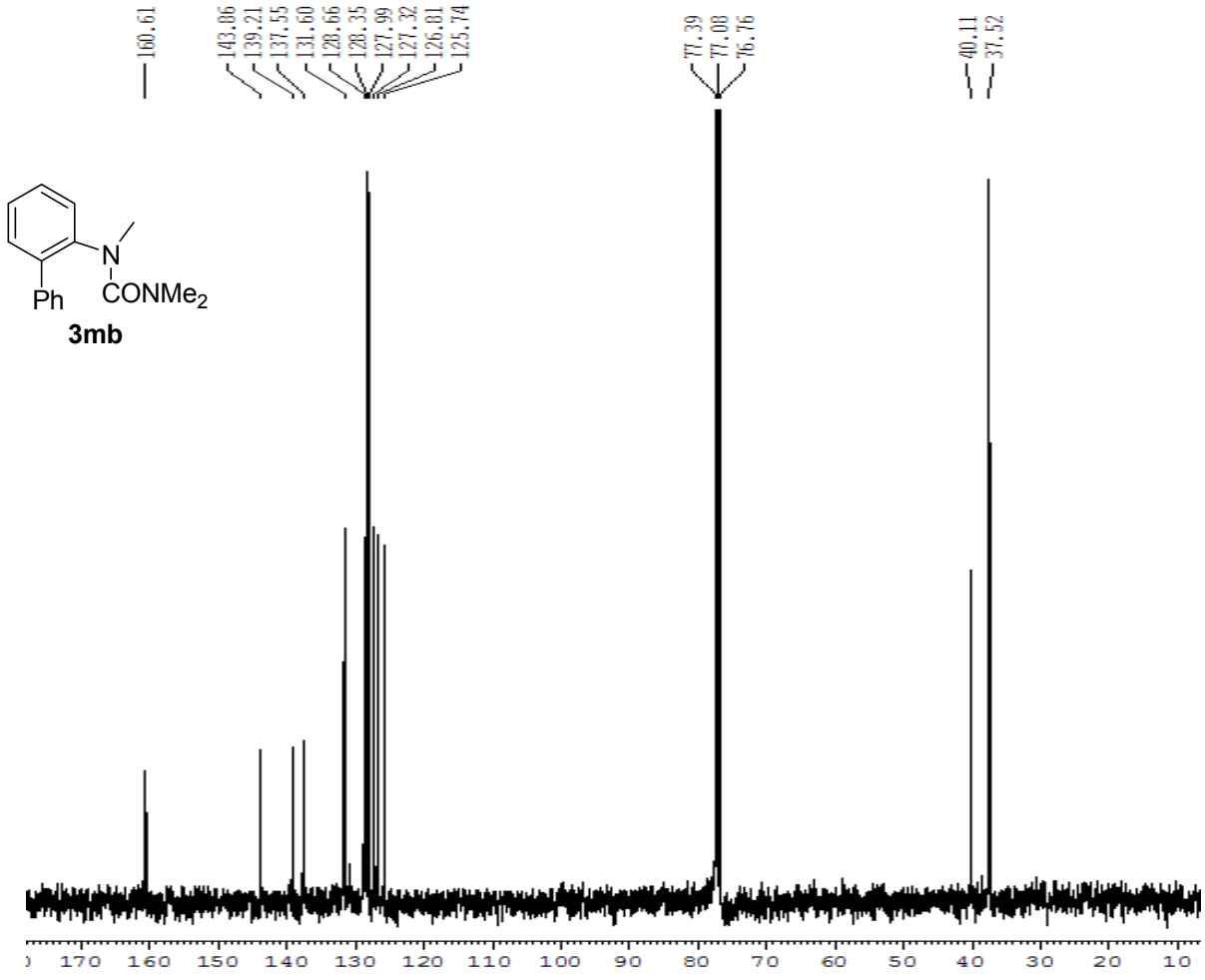
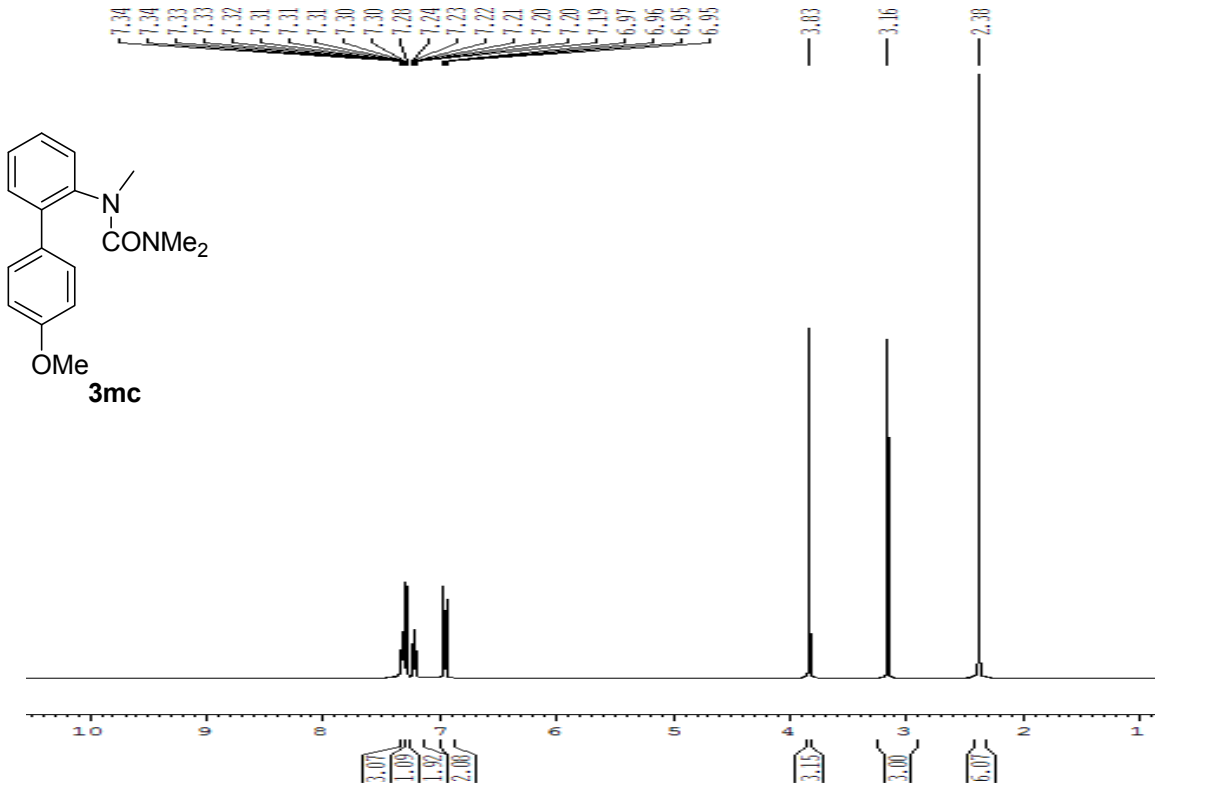
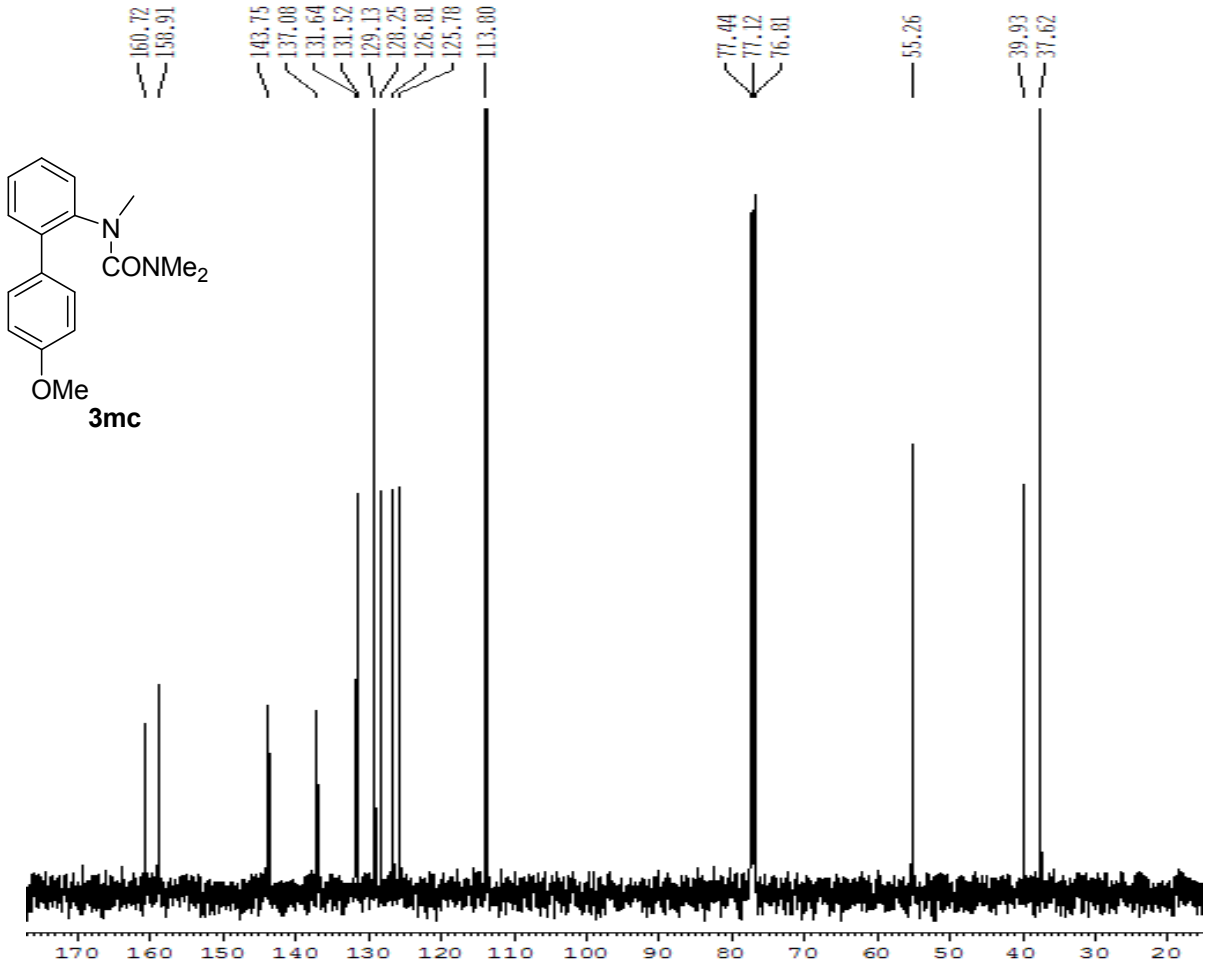


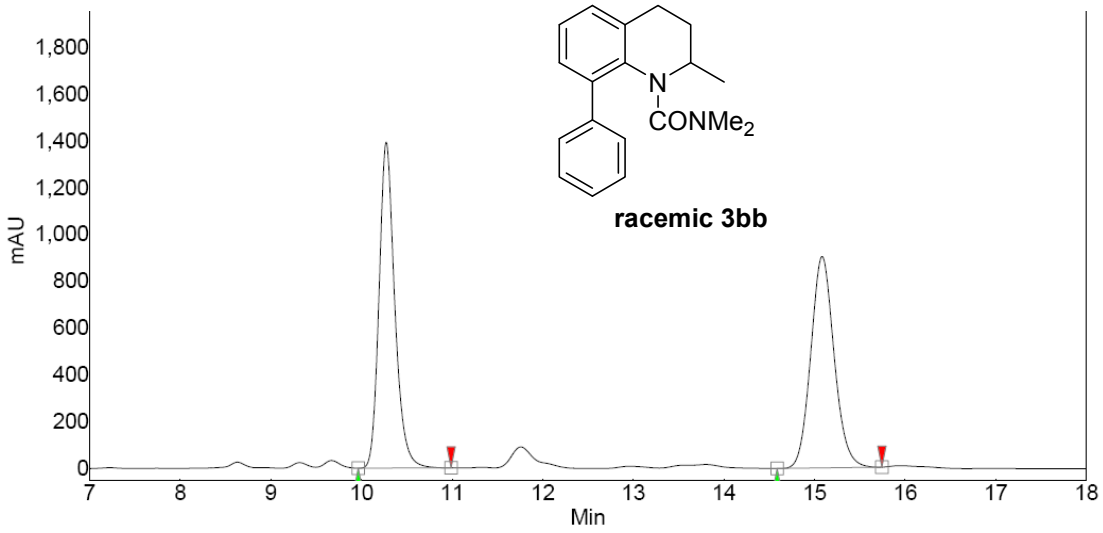






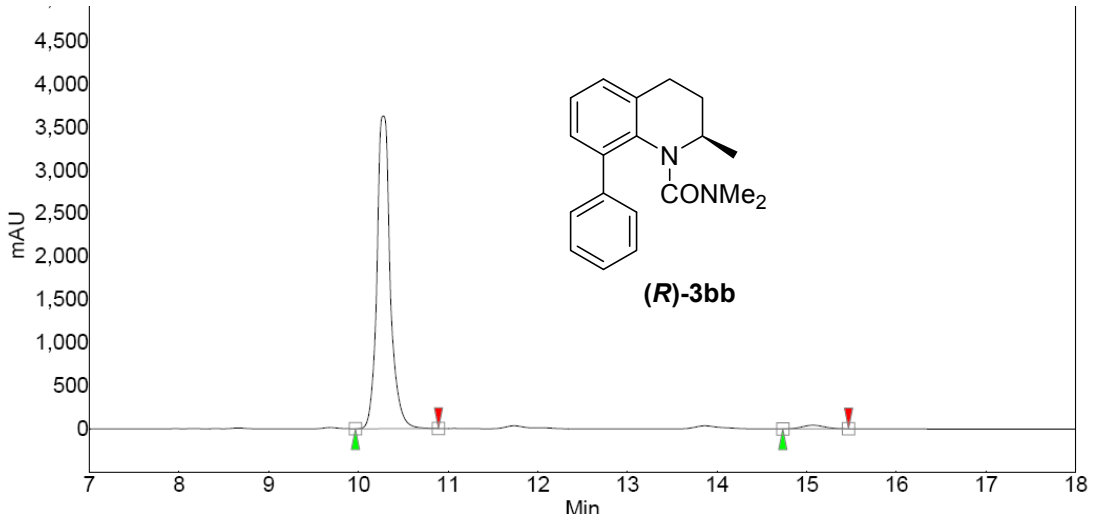


5. HPLC spectra of the chiral aryalted ureas



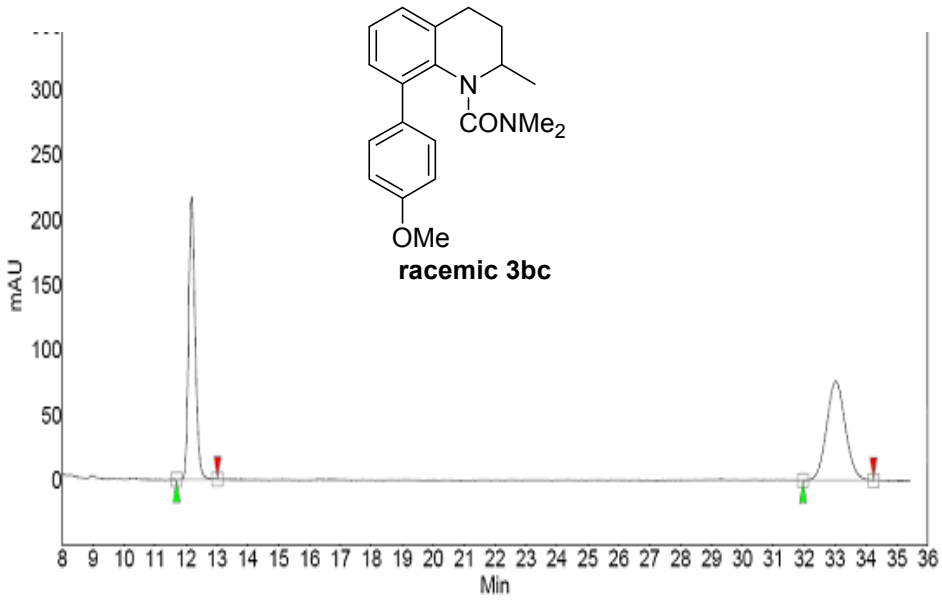
racemic 3bb

Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	10.27	50.87	1391.5	279.1	50.875
1	未知	15.08	49.13	901.9	269.5	49.125
Total			100.00	2293.4	548.6	100.000



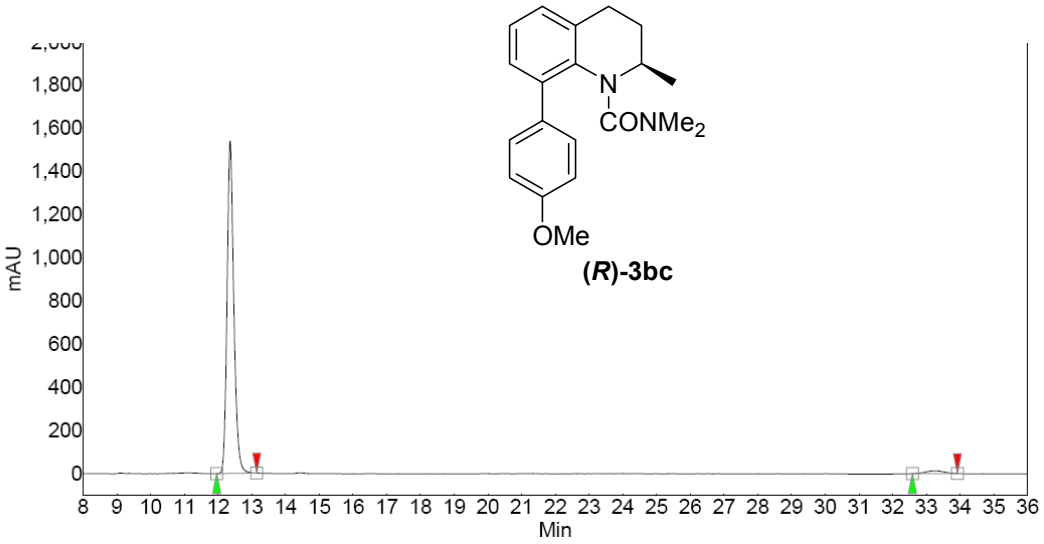
(*R*)-3bb

Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.28	98.12	3618.5	625.1	98.116
2	未知	15.07	1.88	41.7	12.0	1.884
Total			100.00	3660.3	637.1	100.000



racemic 3bc

Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.18	50.02	217.2	53.4	50.019
2	未知	33.02	49.98	76.0	53.4	49.981
Total			100.00	293.2	106.8	100.000



(*R*)-3bc

Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.36	97.77	1540.0	356.8	97.770
2	未知	33.26	2.23	12.7	8.1	2.230
Total			100.00	1552.7	365.0	100.000