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Supporting Information

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Direct Mannich and nitro-Mannich reactions with non-activated imines. AgOTf-catalyzed addition of pronucleophiles to *ortho*-alkynyl-arylaldimines leading to 1,2-dihydroisoquinoline derivatives

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General

^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL JNM-AL 400 (400 MHz) spectrometer. Chemical shift of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane with reference to internal residual $CHCl_3$ (δ = 7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ = 77.0) in $CDCl_3$. IR spectra were measured on a Shimadzu FTIR-8200A Spectrometer. High resolution mass spectra (HRMS) were recorded on BRUKER DALTONICS APEX III spectrometer. Analytical thin layer chromatography (TLC) was performed on a glass plates (Merck Kieselgel 60 F_{254}, layer thickness 0.2 mm). Visualization was accompanied by UV light (254 nm), anisaldehyde, $KMnO_4$ and phosphomolybdic acid. Column chromatography was performed on silica gel (Merck Kieselgel 70-230 mesh). All manipulations were carried out under argon atmosphere using standard Schlenk techniques.

Lewis acid catalyzed direct addition.

Typical experimental procedure: Synthesis of **2a**: To a mixture of **1a** (140.7 mg, 0.5 mmol) and AgOTf (3,9mg, 3 mol%) in dichloroethane (1 mL) was added nitromethane (54 μL, 1 mmol) at room temperature under Ar atmosphere. The resulting mixture

was stirred for 1.5 hours at 80 °C, then it was cooled to room temperature. After addition of a saturated aqueous $NaHCO_3$, the mixture was extracted with AcOEt three times. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by basic silica gel column chromatography using a mixture of hexane–AcOEt (8:1 to 5:1) as an eluent to give **2a** in 85% yield (145.5 mg, 0.43 mmol).

1-Nitromethyl-2,3-diphenyl-1,2-dihydro-isoquinoline (2a). Colorless crystal; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56–7.54 (m, 2H), 7.34–7.33 (m, 2H), 7.29–7.20 (m, 4H), 7.14–7.07 (m, 3H), 6.93–6.87 (m, 3H), 6.78 (s, 1H), 5.77–5.74 (dd, ***J*** = 10.8, 4.0 Hz, 1H), 4.84–4.78 (t, ***J*** = 11.2 Hz, 1H), 4.40–4.36 (dd, ***J*** = 11.6, 4.0 Hz, 1 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.9, 140.7, 136.4, 132.1, 128.8, 128.7, 128.4, 128,3 (one carbon sp^2 missing due to overlapping), 127.6, 127.2, 126.5, 125.7, 124.9, 123.3, 123.0, 111.7, 64.33; IR (KBr) 3060, 1595, 1546, 1492, 1263, 1136, 1031, 767, 698 cm^{-1}; Ms (EI) m/z 342 (M^+, 6); HRMS (ESI) Calcd for $C_{22}H_{18}N_2O_2$ (M^+–H) 341.1296, Found ESI (M^+–H) 341.1297; mp 187–190 °C.

2-Butyl-1-(nitromethyl)-3-phenyl-1,2-dihydro-isoquinoline (2b). Yellow solid; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.57–7.55 (m, 2H), 7.43–7.37 (m, 3H), 7.31–7.16 (m, 4H), 6.17 (s, 1H), 5.26 (dd, ***J*** = 10.8, 4.0 Hz, 1H), 4.67 (t, ***J*** = 10.8 Hz, 1H), 4.18 (dd, ***J*** = 11.2, 4.0 Hz, 1H), 3.12 (quint, ***J*** = 7.6 Hz, 1H), 1.33–1.25 (m, 2H), 1.03–0.95 (m, 2H), 0.68 (t, ***J*** = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.0, 136.9, 133.3, 128.7, 128.5, 128.4, 128.0, 126.4, 125.7, 125.3, 124.1, (107.13, 107.10), 60.3, 53.1, 31.1, 19.8, 13.7; IR (KBr) 2958, 2929, 1598, 1546, 1485, 1452, 1143, 1028, 758, 700 cm^{-1}; Ms (EI) m/z 322 (M^+, 4); HRMS (ESI) Calcd for $C_{20}H_{22}N_2O_2$ (M^+–H) 321.1609, Found ESI (M^+–H) 321.1611; mp 71–74 °C

2-Benzyl-1-(nitromethyl)-3-phenyl-1,2-dihydro-isoquinoline

(2c). Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, ***J*** = 6.0 Hz, 2 H), 7.46–7.35 (m, 3H), 7.26-7.21 (m, 1H), 7.15–7.10 (m, 5H), 7.04 (t, ***J*** = 7.6 Hz, 2H), 6.94 (d, ***J*** = 7.2 Hz, 1H), 6.29 (s, 1H), 5.22 (dd, ***J*** = 10.8, 4.0 Hz, 1H), 4.69 (t, ***J*** = 11.2 Hz, 1H),4.17 (dd, ***J*** = 11.6, 4.0 Hz 1H), 4.15 (d, ***J*** = 14.8 Hz, 1H), 3.97 (d, ***J*** = 14.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.8, 137.9, 136.7, 132.9, 128.9, 128.6, 128.4, 128.1, 127.9, 127.3, 127.0, 126.6, 125.5, 125.5, 124.2, 108.3, 76.5, 59.1, 56.26; IR (neat) 3062, 3028, 2923, 1716, 1636, 1556, 1487, 1028, 759, 698 cm^{-1}; Ms (EI) m/z 356 (M^+, 2); HRMS (EI) Calcd for $C_{23}H_{20}N_2O_2$ (M^+) 356.1519, Found 356.1521.

3-Butyl-1-nitromethyl-2-phenyl-1,2-dihydro-isoquinoline (2d). Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.26–7.23 (m, 4H), 7.14–7.12 (m, 1H), 7.07 (t, ***J*** = 7.3 Hz, 1H), 7.02–6.96 (m, 3H), 6.23 (s, 1H), 5.45 (dd, ***J*** = 10.0, 3.8 Hz, 1H), (t, ***J*** = 11 Hz, 1H), 4.26 (dd, ***J*** = 11.7, 4.2 Hz, 1H), 2.29–2.14 (m, 2H), 1.49 (quint. 7.5 Hz, 2H), 1.39–1.22 (m, 2H), 0.88 (t, ***J*** = 7.1 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.5, 143.1, 131.9, 128.9, 128.4, 126.2, 125.5, 124.9, 124.2, 123.9, 123.8, 110.0, 77.3, 64.1, 32.8, 30.3, 22.5, 13.8; IR (neat) 2956, 2931, 1595, 1490, 1379, 1236, 1174, 758, 698 cm^{-1}; Ms (EI) m/z 322 (M^+, 5); HRMS (EI) Calcd for $C_{20}H_{22}N_2O_2$ (M^+) 322.1676, Found 322.1677.

3-Cyclohex-1-enyl-1-nitromethyl-2-phenyl-1,2-dihydro-isoquinoline (2e). White solid; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.29–7.13 (m, 5H), 7.05 (d, ***J*** = 7.6 Hz, 1H), 6.98–6.91 (m, 3H), 6.49 (s, 1H), 6.07 (t, ***J*** = 4.2 Hz, 1H), 5.62 (dd, ***J*** = 10.7, 4.2 Hz, 1H), 4.70 (dd, ***J*** = 11.7, 10.7 Hz, 1H), 4.30 (dd, ***J*** = 11.7, 4.2 Hz, 1H), 2.28–1.90 (m, 4H), 1.66–1.57 (m, 2H), 1.55–1.45 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 147.1, 142.4, 139.5, 132.2, 130.7, 128.6, 128.5, 126.6, 126.5, 125.5, 124.8, 122.9, 122.0, 109.63, 76.4, 63.8, 26.3, 25.8, 22.7, 22.1; IR (KBr) 2935, 2910, 1595, 1546, 1487, 1375, 1247, 1217, 827, 754, 698 cm^{-1}; Ms (EI) m/z 346 (M^+, 5); HRMS (EI) Calcd for $C_{22}H_{22}N_2O_2$ (M^+) 346.1676, Found 346.1677; mp 138–140 °C.

1-(1-Nitroethyl)-2,3-diphenyl-1,2-dihydro-isoquinoline (2f). White solid; ^{1}H-NMR (major) ($CDCl_3$, 400 MHz) δ 7.56 (d, ***J*** = 6.6 Hz, 2H), 7.36–7.19 (m, 6H), 7.16–7.01 (m, 3H), 6.95–6.86 (m, 3H), 6.84 (s, 1H), 5.26 (d, ***J*** = 10 Hz, 1H), 4.98–4.92 (m, 1H), 1.42 (d, ***J*** = 6.56 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.8, 141.3, 136.1, 131.9, 128.7, 128.6, 128.5, 128.3, 128.2, 127.5, 127.0, 126.4, 124.6, 122.9, 122.6, 111.6, 82.6, 69.1, 16.9; IR (KBr) 3057, 1544, 1492, 1359, 1213, 763, 698 cm^{-1}; Ms (EI) m/z 356 (M^+, 1); HRMS (ESI) Calcd for $C_{23}H_{20}N_2O_2$ (M^+–H) 355.1452, Found (M^+–H) 355.1452; mp 182–185°C.

3-(2,3-Diphenyl-1,2-dihydro-isoquinolin-1yl)pentane-2,4-dione (2g). White solid; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.50 (m, 2H), 7.34 (d, ***J*** = 7.2 Hz, 1H), 7.29–7.20 (m, 4H), 7.14–7.06 (m, 5H), 6.99 (s, 1H), 6.97 (d, ***J*** = 7.6 Hz, 1H), 6.88–6.84 (m, 1H), 5.80 (d, ***J*** = 10.4 Hz, 1H), 4.67 (d, ***J*** = 10.8 Hz, 1H), 2.29 (s, 3H), 1.84 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 201.4, 200.7, 146.2, 140.8, 136.2, 131.6, 128.8, 128.6, 128.4, 128.3, 127.9, 126.9, 126.4, 124.6, 122.8, 122.6, 112.6, 69.0, 64.8, 32.4, 31.9; IR (KBr) 3064, 1730, 1699, 1596, 1558, 1492, 1234, 767, 700 cm^{-1}; Ms (EI) m/z 381 (M^+–99, 100); Anal calcd for $C_{26}H_{23}NO_2$, C, 81.86; H, 6.08; N, 3.67, Found C, 82.08; H, 6.16; N, 3.50; mp 142–145 °C.

Dimethyl-2-(2,3-diphenyl-1,2-dihydro-isoquinolin-1-yl)malonate (2h). White crystal; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.51–7.49 (dd, ***J*** = 8.0, 4.0 Hz, 2H), 7.33–7.20 (m, 6H), 7.17–7.07 (m, 5H), 6.93 (s, 1H), 6.91–6.84 (m, 1H), 5.75 (d, ***J*** = 10.8 Hz, 1H), 4.03 (d, ***J*** = 10.8 Hz, 1H), 3.83 (s, 3H), 3.55 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 168.1, 167.2, 146.3, 140.5, 136.4, 131.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.1, 126.6, 126.5, 124.6, 122.8, 122.7, 112.7, 77.3, 64.7, 54.9, 52.5, 52.5; IR (KBr) 3068, 2952, 1757, 1728, 1492, 1249, 1130, 758, 692 cm^{-1}; Ms (EI) m/z 413 (M^+, 1); HRMS (ESI) Calcd for $C_{26}H_{23}NO_4$ (M^+–H) 412.1544, Found (M^+–H) 412.1554; mp 134–137 °C.

2-(2,3-Diphenyl-1,2-dihydro-isoquinolin-1-yl)malononitrile (2i). Yellow solid; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67–7.64 (m, 2H), 7.43–7.39 (m, 2H), 7.30–7.26 (m, 5H), 7.19–7.09 (m, 4H), 7.00 (m, 1H), 6.78 (s, 1H), 5.57 (d, ***J*** = 10.1 Hz, 1H), 4.17 (d, ***J*** = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.2, 139.9, 135.4, 130.9, 129.1, 128.8, 128.6, 127.7, 127.4, 127.2, 124.9, 124.5, 124.4, 123.6, 111.5, 111.3, 66.9, 26.6; IR (KBr) 3058, 2902, 2350, 2247, 1492, 1255, 1136, 763, 694 cm^{-1}; Ms (EI) m/z 346 (M^+, 100); HRMS (ESI) Calcd for $C_{24}H_{17}N_3$ (M^+–H) 346.1339, Found ESI (M^+–H) 346.1340; mp 171–173 °C.

1-(2,3-Diphenyl-1,2-dihydro-isoquinolin-1-yl)propan-2-one (2j). White solid; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.53 (m, 2H), 7.29–7.19 (m, 5 H), 7.17–7.04 (m, 6H), 6.85–6.80 (m, 1H), 6.78 (s, 1H), (5.57 (dd, ***J*** = 8.4, 5.2 Hz, 1H), 3.25 (dd, ***J*** = 16.8, 8.8 Hz, 1H), 2.61 (dd, ***J*** = 16.4, 5.2 Hz), 2.13 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 207.1, 146.8, 140.4, 137.3, 132.1, 131.5, 128.5, 128.4, 127.9, 127.3, 127.0, 126.7, 125.2, 124.4, 122.2, 122.0, 112.3, 60.8, 47.4, 31.8; IR (KBr) 3060, 1710, 1593, 1452, 1382, 1259, 1029, 765, 698 cm^{-1}; Ms (EI) m/z 339 (M^+, 3); HRMS (EI) Calcd for $C_{24}H_{21}NO$ (M^+) 339.1618, Found 339.1619; mp 157–160 °C.

2-(2,3-Diphenyl-1,2-dihydro-isoquinolin-1-yl)acetonitrile (2k). Colorless oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.69–7.67 (m, 2H), 7.34–7.21 (m, 6H), 7.17–7.07 (m, 5H), 6.95–6.90 (m, 1H), 6.73 (s, 1H), 5.36 (dd, ***J*** = 10.8, 4.4 Hz, 1H), 3.03 (dd, ***J*** = 16.8, 10.4 Hz, 1H), 2.53 (dd, ***J*** = 16.8, 4.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.3, 140.1, 136.7, 131.2, 129.2, 128.7, 128.5, 128.4, 128.3, 127.6, 126.8, 125.3, 124.7, 123.1, 123.0, 111.2, 62.4, 12.9; IR (neat) 3057, 3024, 2246, 1595, 1560, 1490, 1454, 1267, 1222, 765, 696 cm^{-1}; Ms (EI) m/z 322 (M^+, 2); HRMS (ESI) Calcd for $C_{23}H_{18}N_2Na$ (M^++Na) 345.1362, Found (M^++Na) 345.1360.

5-Nitromethyl-6,7-diphenyl-5,6-dihydro-1,6-napthyridine

(2l). White solid; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.54 (dd, ***J*** = 5.2, 1.6 Hz, 1H), 7.59–7.56 (m, 2H), 7.42 (dd, 7.6 , 1.2 Hz, 1H), 7.29–7.25 (m, 2H), 7.14 – 7.09 (m, 3H), 6.96–6.91 (m, 4H), 5.77 (dd, ***J*** = 10.4, 4.0 Hz, 1H), 4.90 (dd, ***J*** = 11.6, 10.4 Hz, 1H), 4.40 (dd, ***J*** = 11.6, 4.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 151.3, 150.1, 145.5, 145.4, 135.7, 133.3, 129.1, 128.9, 128.5, 127.9, 124.1, 123.4, 121.6, 121.1, 112.3, 112.2, 76.3, 64; IR (KBr) 3060, 1595, 1548, 1434, 1380, 1215, 1029, 763, 700, 669 cm^{-1}; Ms (EI) m/z 343 (M^+, 5); HRMS (EI) Calcd for $C_{21}H_{17}N_3O_2$ (M^+) 343.1315, Found 343.1318; mp 164–167 °C.

2,3-Diphenyl-isoquinolinium trifluoromethanesulfonate (3). White crystal; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.95 (s, 1H), 8.64 (d, ***J*** = 8.4 Hz, 1H), 8.33 (s, 1H), 8.21–8.14 (m, 2H), 7.94 (t, ***J*** = 8.0 Hz, 1H), 7.50–7.26 (m, 10 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 152.1, 145.8, 141.4, 138.5, 138.1, 131.9, 131.6, 131.5, 130.6, 130.1, 129.9, 129.7, 128.7, 127.4, 127.0, 126.9, 126.5, 125.3, 122.1, 118.9, 115.7; IR (KBr) 3058, 3039, 1639, 1593, 1494, 1456, 1396, 1278, 1259, 1164, 1149, 1031, 767, 698, 638 cm^{-1}; Anal calcd for $C_{22}H_{16}NF_3SO_3$, C, 61.25; H, 3.74; F, 13.21; N, 3.25; S, 7.43; Found C, 61.20; H, 3.84; F, 13.50; N, 3.23; S, 7.39.

2,3-Diphenyl-1-phenylethynyl-1,2-dihydro-isoquinoline (9a). Grey crystal; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.50-7.48 (m, 2H), 7.36-7.33 (m, 2H), 7.27-7.18 (m, 10H), 7.12-7.08 (m, 2H), 6.99-6.97 (m, 2H), 6.84 (m, 1H), 6.48 (s, 1H), 6.03 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.7, 140.9, 137.7, 131.8, 131.7, 129.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.5, 125.2, 124.5, 122.9, 121.8, 110.9, 88.6, 84.6, 56.0; IR (KBr) 3059, 3026, 1948, 1596, 1492, 1388, 1267, 1140, 751, 695 cm^{-1}; Ms (EI) m/z 383 (M^+, 79); HRMS Calcd for $C_{29}H_{21}N$ (M^+) 383.1669, Found 383.1643; mp 102–104 °C.

1-Hex-1-ynyl-2,3-diphenyl-1,2-dihydro-isoquinoline (9b). White crystal; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.46-7.43 (m, 2H), 7.23-7.06 (m, 9 H), 6.93 (m, 2 H), 6.82-6.79 (m, 1H), 6.45 (s,

1H), 5.80 (s, 1H), 2.18 (t, ***J*** = 5,6 Hz, 2H), 1.50–1.26 (m, 4H), 0.85 (t, ***J*** = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.9, 140.8, 137.8, 131.6, 130.3, 128.3, 127.7, 127.6, 127.5, 126.3, 124.9, 124.4, 121.7, 121.5, 110.6, 85.0, 79.5, 55.5, 30.8, 21.9, 18.6, 13.6; IR (KBr) 2952, 2929, 2210, 1595, 1492, 1379, 1261, 752, 694 cm^{-1}; Ms (EI) m/z 363 (M^+, 76); HRMS Calcd for $C_{27}H_{25}N$ (M^+) 363.1982, Found 363.1962; mp 77-79 °C.

(2,3-Diphenyl-1,2-dihydro-isoquinolin-1-yl)-propionic acid ethyl ester (9c). White crystal; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.48-7.45 (m, 2H), 7.31-7.15 (m, 6H), 7.12–7.07 (m, 3H), 6.93–6.83 (m, 2H), 6.86 (m, 1H), 6.50 (s, 1H), 5.96 (s, 1H), 4.15 (q, ***J*** = 7.2 Hz, 2H), 1.2 (t, ***J*** = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 153.4, 145.5, 140.9, 137.0, 136.9, 131.9, 128.6, 128.5, 128.2, 127.9, 127.8, 127.0, 126.8, 125.4, 124.7, 122.4, 122.1, 111.1, 85.8, 75.6, 62.0, 55.7, 14.0; IR (KBr) 3041, 2976, 2358, 2233, 1701, 1596, 1494, 1242, 1110, 748, 696 cm^{-1}; Ms (EI) m/z 379 (M^+, 26); HRMS Calcd. for $C_{26}H_{21}NO_2$ (M^+) 379.1567, Found 379.1571; mp 143-145 °C.

2-Butyl-3-phenyl-1-phenylethynyl-1,2-dihydro-isoquinoline (9d). Red oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59 (m, 2H), 7.43-7.32 (m, 5H), 7.28-7.22 (m, 5H), 7.18 (ddd, ***J*** = 7.2, 2.8, 1.2 Hz, 1H), 7.12 (dd, ***J*** = 7.6, 1.2 Hz, 1H), 6.02 (s, 1H), 5.45 (s, 1H), 3.18 (dt, ***J*** = 14.6, 7.6 Hz, 1H), 3.05 (dt, 14.6, 7.6 Hz, 1H), 1.39 (q, 7.2, 2H), 1.11 (sext, 7.6 Hz, 2H), 0.73 (t, 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.7, 137.8, 133.3, 131.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 125.7, 124.7, 123.5, 123.2, 106.1, 106.0, 88.5, 84.4, 53.3, 50.4, 31.4, 19.9, 13.8; IR (neat) 3058, 2956, 2869, 2360, 1716, 1596, 1488, 1452, 1301, 1157, 758, 691 cm^{-1}; Ms (EI) m/z 363 (M^+, 29); HRMS Calcd for $C_{27}H_{25}N$ (M^+) 363.1982, Found 363.1908.

2-Benzyl-3-phenyl-1-phenylethynyl-1,2-dihydro-isoquinoline (9e). Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77 (dt, ***J*** = 8.0, 4.0 Hz, 2H), 7.49–7.28 (m, 14H), 7.26–7.13 (m, 3H), 6.22 (s,

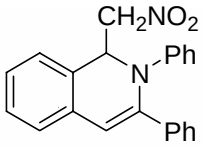
1H), 5.43 (s, 1H), 4.34 (d, ***J*** = 15.6 Hz, 1H), 4.28 (d, ***J*** = 15.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.5, 138.4, 137.5, 132.8, 131.7, 128.3, 128.2, 128.0, 127.99, 127.96, 127.8 (one carbon sp^2 missing due to overlapping) 127.75, 127.72, 127.0, 125.9, 125.3, 123.8, 123.1, 106.9, 88.5, 83.9, 53.5, 52.2; IR (neat) 2951, 2870, 1716, 1641, 1519, 1433, 1236, 1142, 765, 688 cm^{-1}; Ms (EI) m/z 397 (M^+, 8); HRMS Calcd for $C_{30}H_{23}N$ (M^+) 397.1825, Found 397.1809.

2-Allyl-3-phenyl-1-phenylethynyl-1,2-dihydro-isoquinoline (9f). Red oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.60-7.58 (m, 2H), 7.40-7.32 (m, 5H), 7.26-7.11 (m, 7H), 6.10 (s, 1H), 5.70 (ddt, ***J*** = 16.4, 1.6, 1.6 Hz, 1H), 5.43 (s, 1H), 5.22 (ddt, 16,8, 1.6, 1.6, 1H), 5.07 (ddt, 10.1, 1.6, 1.6, 1H), 3.68 (ddd, ***J*** = 6.4, 1.6, 1.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.2, 137.5, 134.9, 133.0, 131.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 125.9, 125.1, 123.8, 123.1, 117.2, 106.8, 106.7, 88.5, 84.0, 53.10, 52.3; IR (neat) 3060, 3022, 2954, 2925, 2358, 2341, 1598, 1489, 1452, 1388, 1251, 920, 756, 690 cm^{-1}; Ms (EI) m/z 347 (M^+, 1); HRMS (EI) Calcd for $C_{26}H_{21}N$ (M^+) 347.1674, Found 347.1646.

3-Butyl-2-phenyl-1-phenylethynyl-1,2-dihydro-isoquinoline (9g). Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.43–7.30 (m, 10H), 7.18–7.16 (m, 4H), 6.08 (s, 1H), 5.82 (s, 1H), 2.66 (dt, ***J*** = 14.0, 7.6, 1 Hz), 2.27 (dt, ***J*** =14.4, 7.6 Hz, 1H), 1.53–1.34 (m, 4H), 8.85 (t, ***J*** = 6.4 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 145.1, 142.7, 131.9, 131.5, 128.6, 128.1, 128.0, 127.9, 127.7, 125.4, 124.9, 123.4, 123.2, 123.0, 106.9, 89.3, 84.1, 56.2, 32.5, 30.0, 21.9, 13.9; IR (neat) 2956, 2929, 2858, 2360, 2341, 1726, 1595, 1488, 1454, 1400, 1284, 754, 700 cm^{-1}; Ms (EI) m/z 363 (M^+, 61); HRMS Calcd for $C_{27}H_{25}N$ (M^+) 363.1987, Found 363.1957.

2,3-Diphenyl-4-phenylethynyl-3,4,5,6-tetrahydro-benzo[*f*]isoquinoline (9h). Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, ***J*** = 7.6 Hz, 1H), 7.52 (d, ***J*** = 7.6 Hz, 2H), 7.47 (dd, ***J*** = 6, 2.4 Hz, 2H), 7.36–7.15 (m, 11H), 7.05 (d, ***J*** = 8 Hz, 2 H), 6.90 (t,

J = 7.6 Hz, 1H), 6.45 (s, 1H), 5.42 (s, 1H), 3.08–2.97 (m, 1H), 2.94–2.86 (dt, ***J*** = 15.7, 7.2 Hz, 1H), 2.73–2.65 (dt, ***J*** = 16.8, 6.8 Hz, 1H), 2.47–2.38 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.2, 139.8, 138.1, 135.4, 133.0, 131.8, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 26.9, 126.5, 126.3, 124.0, 122.9, 122.6, 121.6, 121.4, 107.1, 88.1, 83.9, 57.2, 28.7, 25.8; IR (neat) 3058, 3020, 2939, 2248, 1732, 1641, 1598, 1448, 1398, 1267, 1159, 901, 756, 696 cm^{-1}; Ms (EI) m/z 434 (M^+, 100); HRMS (ESI) Calcd for $C_{33}H_{25}N$ (M^+–H) 434.1914, Found 434.1915.



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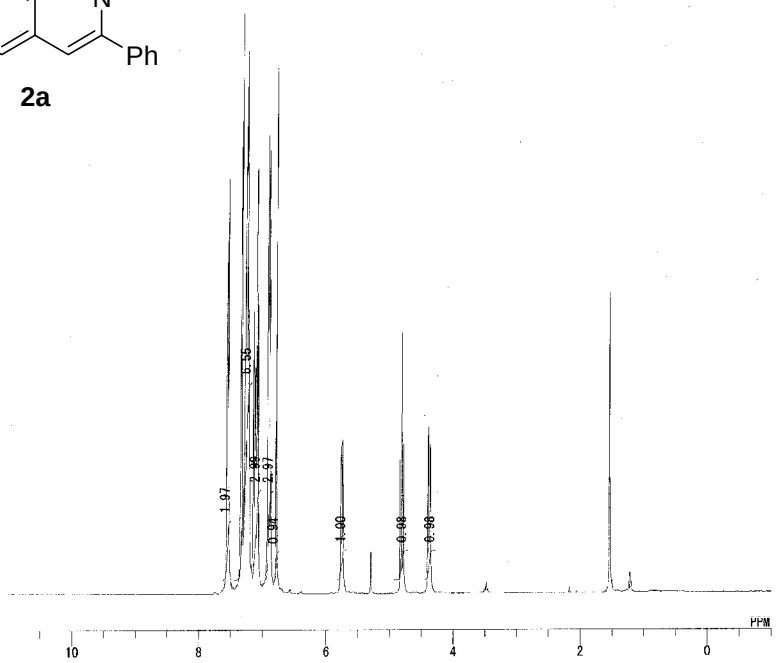


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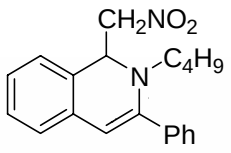
OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1             5.50 usec
IRNUC  1H
CTEMP           20.9 c
SLVNT  CDCL3
EXREF           7.26 ppm
BF              2.00 Hz
RGAIN             16
```



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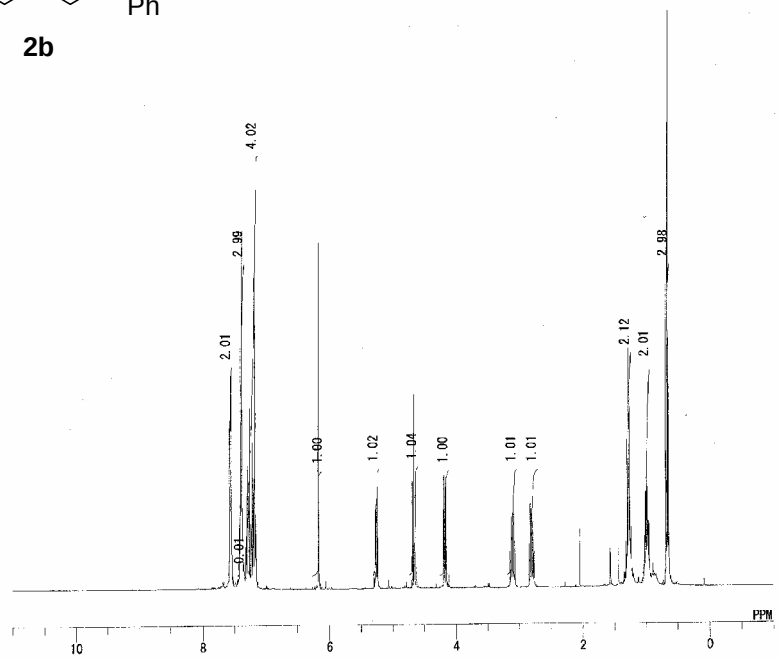


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OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1             5.50 usec
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CTEMP           23.7 c
SLVNT  CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             13
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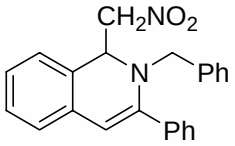

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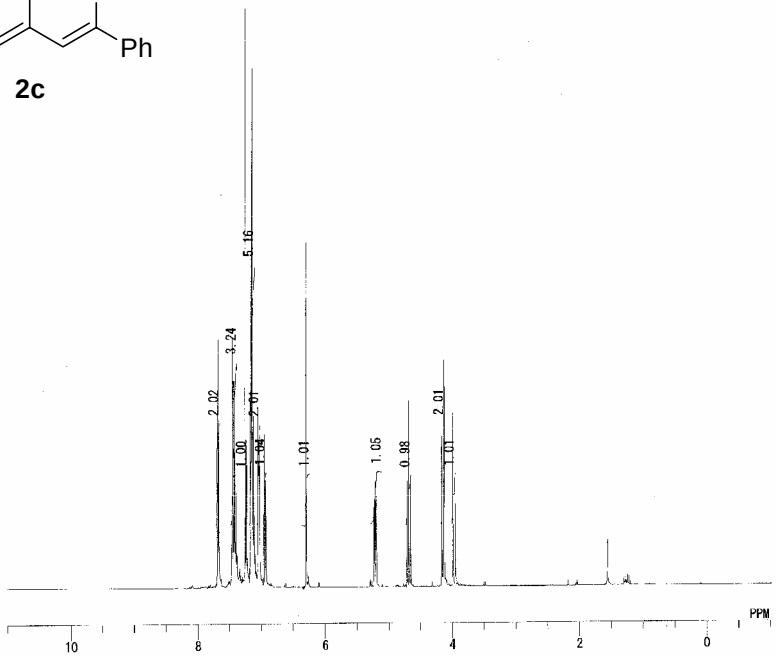


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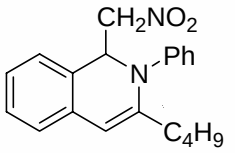
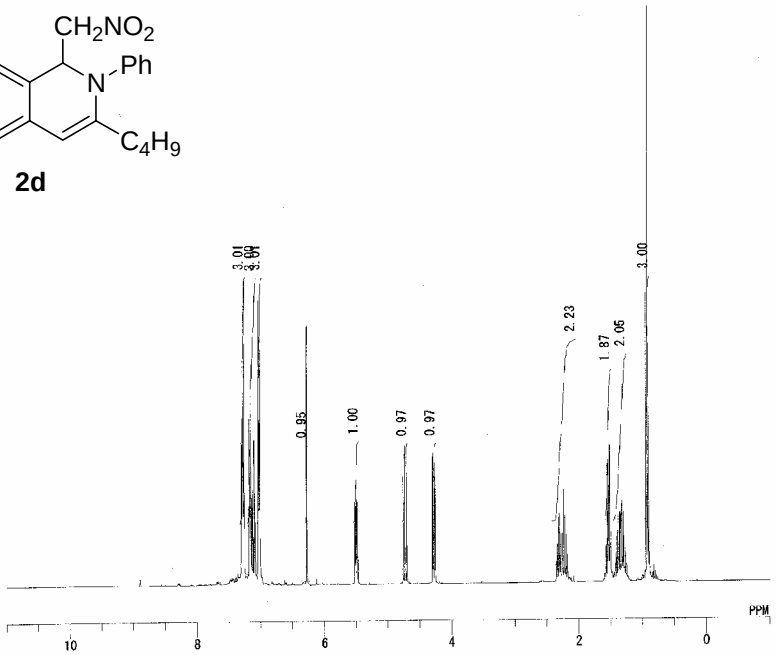
OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            5.50 usec
IRNUC  1H
CTEMP         21.7 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.33 Hz
RGAIN           13
```

C:¥Documents and Settings¥All Users¥Documents¥DATA¥520¥SPYS¥Pronucleophile-Pure¥N-Ph,Bu+CH2NO2-1.als



2d

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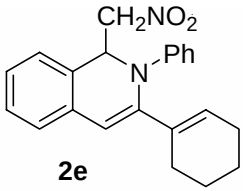
OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            5.50 usec
IRNUC  1H
CTEMP         20.4 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.10 Hz
RGAIN            7

-NMR () δ:
```



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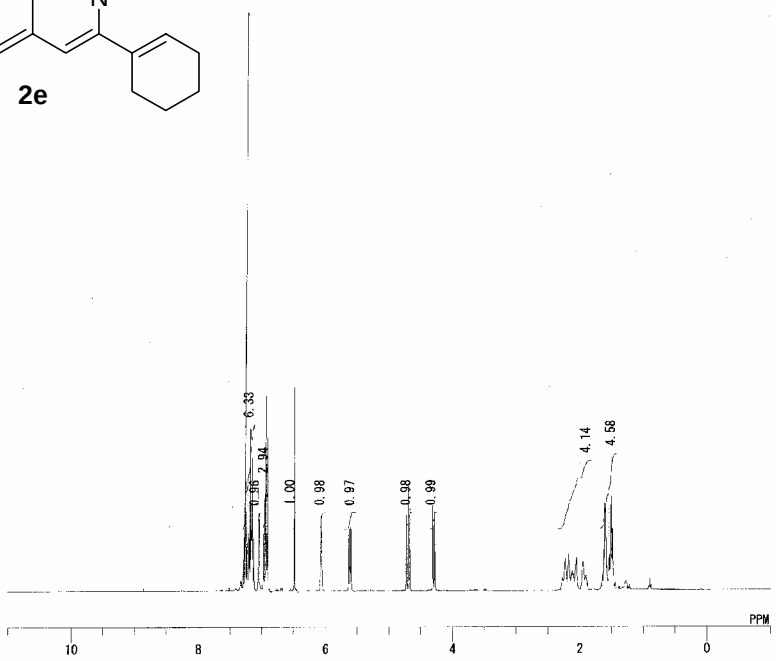


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OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            5.50 usec
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CTEMP          26.4 c
SLVNT  CDCL3
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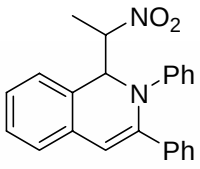
BF             0.30 Hz
RGAIN            13
```



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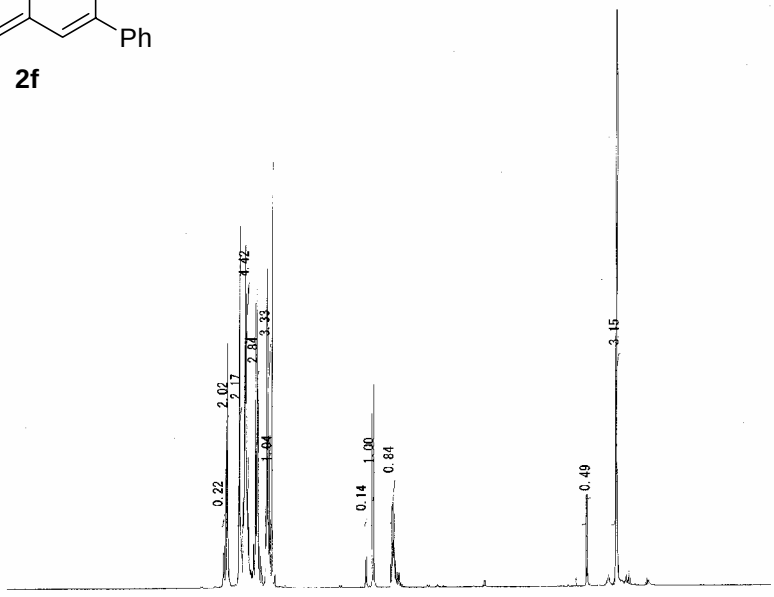


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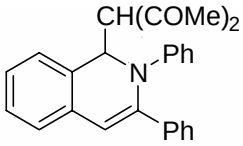
OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            5.50 usec
IRNUC  1H
CTEMP          19.5 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            12
```



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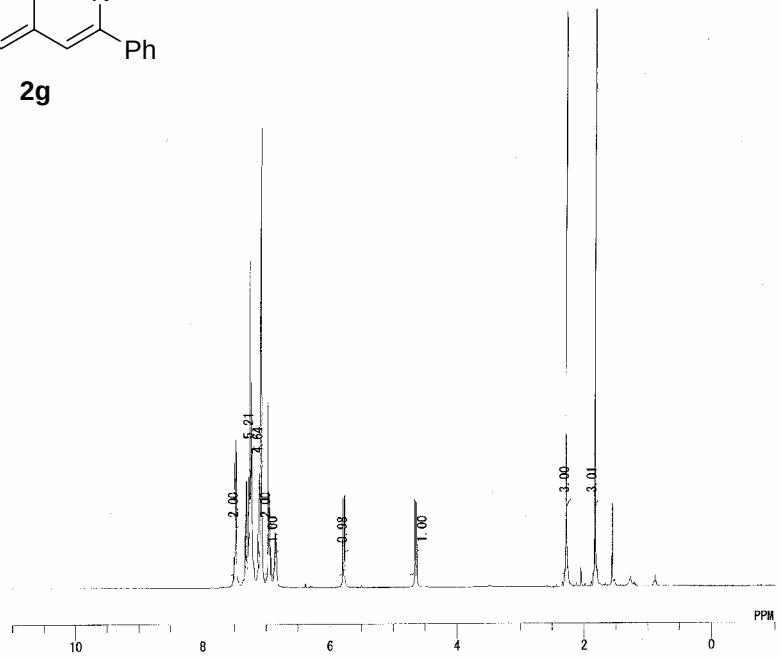


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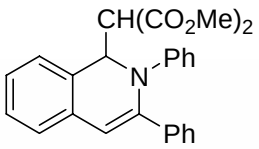
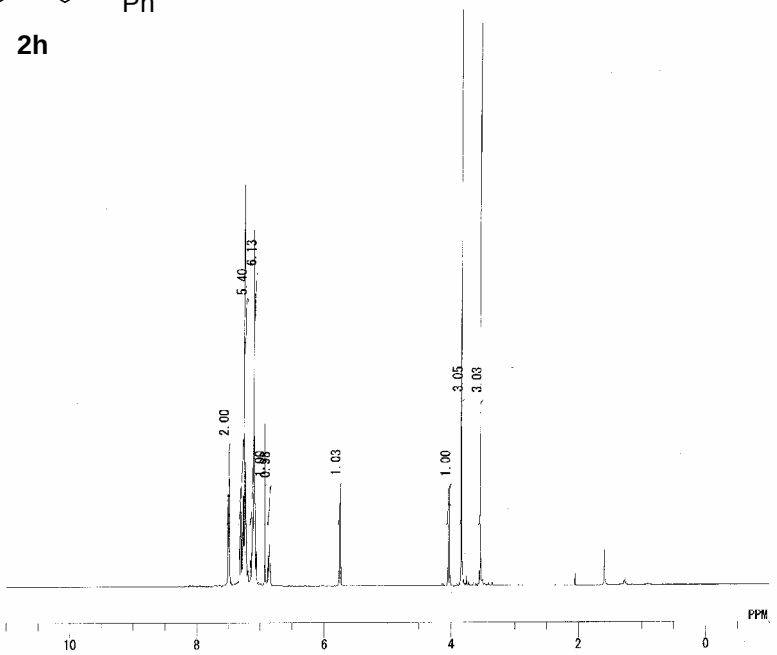
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP       21.8 c
SLVNT   CDCL3
EXREF       7.26 ppm
BF          2.00 Hz
RGAIN         16
```



2h

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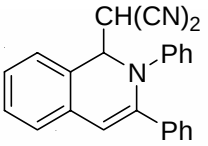
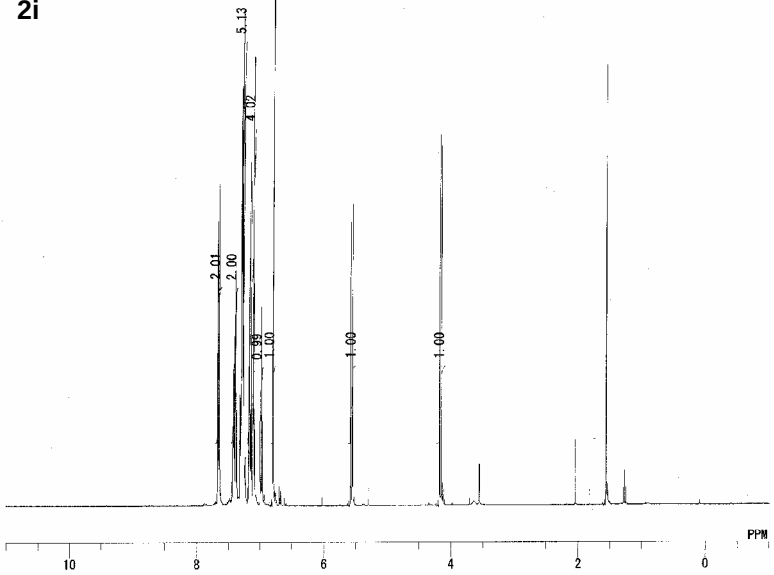
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP       26.3 c
SLVNT   CDCL3
EXREF       7.26 ppm
BF          0.50 Hz
RGAIN         11
```



2i

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EXMOD  NON
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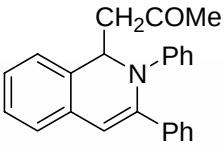
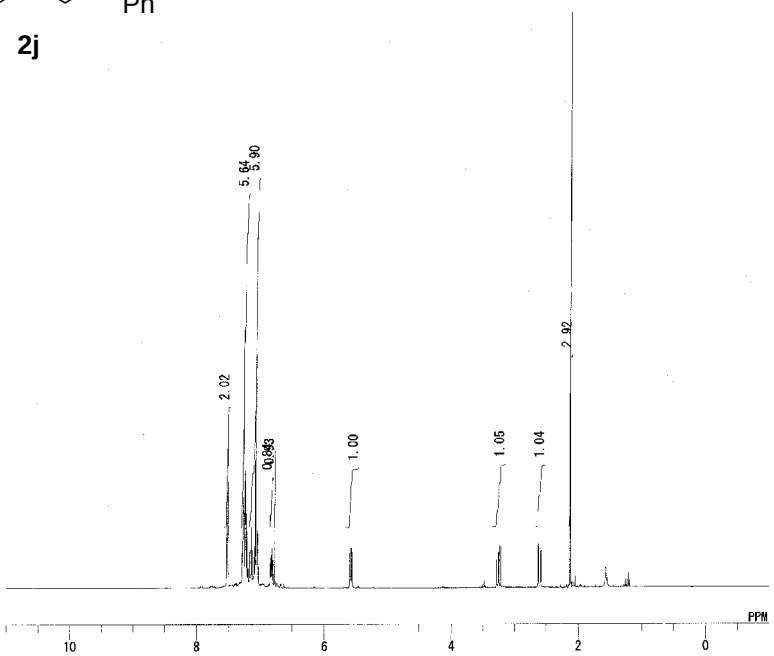
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1             5.50 usec
IRNUC  1H
CTEMP          22.8 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            15
```



2j

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EXMOD  NON
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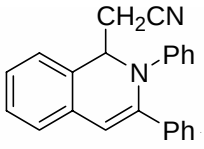
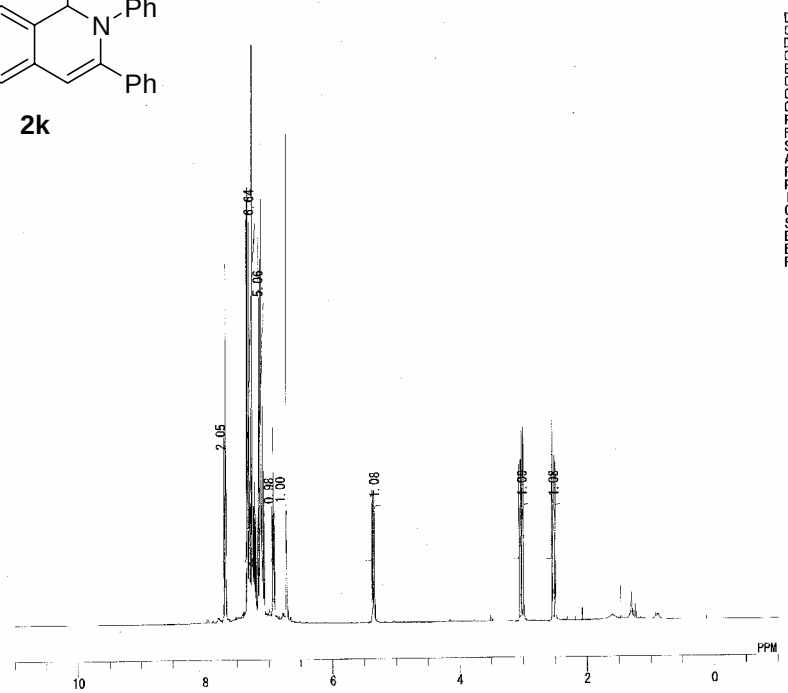
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU        7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1             5.50 usec
IRNUC  1H
CTEMP          24.6 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            15
```



2k

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EXMOD  NON
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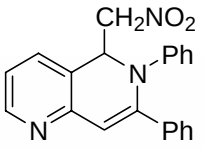
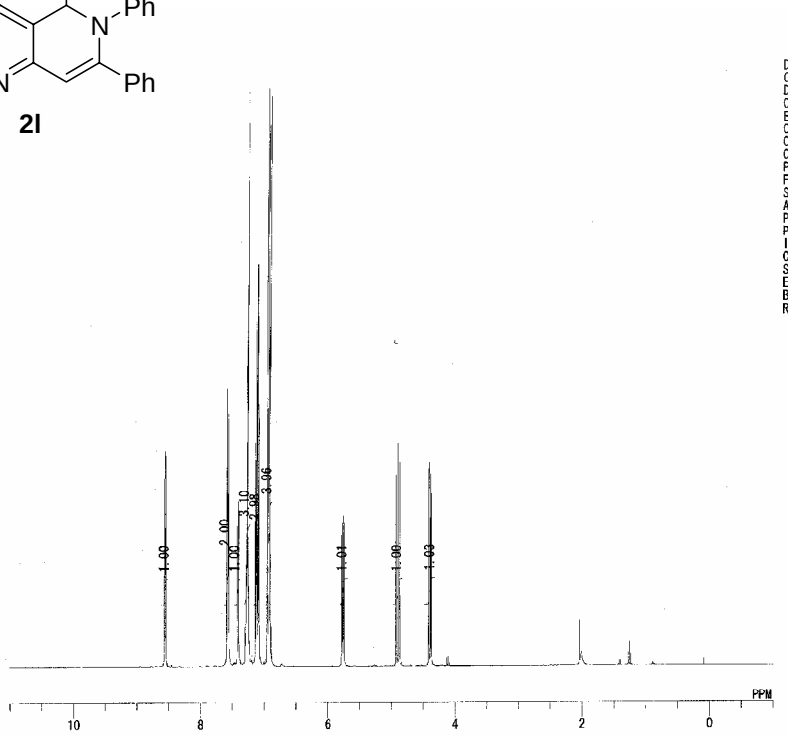
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU       7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            5.50 usec
IRNUC  1H
CTEMP         21.5 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.10 Hz
RGAIN            9
```



2l

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EXMOD  NON
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OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU       7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            5.50 usec
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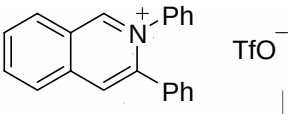
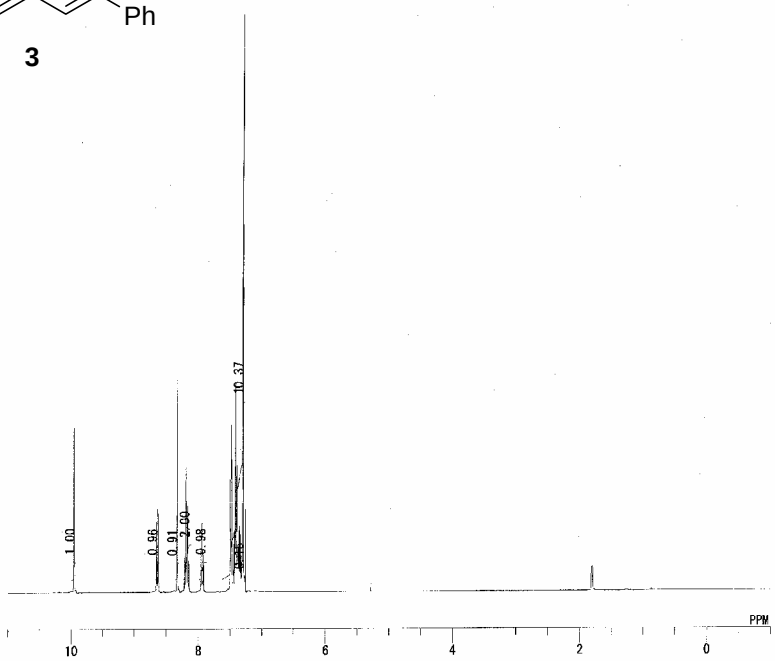
CTEMP         23.9 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.10 Hz
RGAIN           10
```



3

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EXMOD   NON
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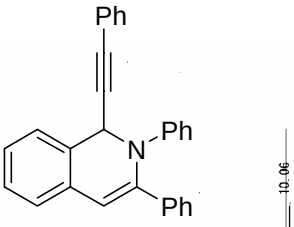
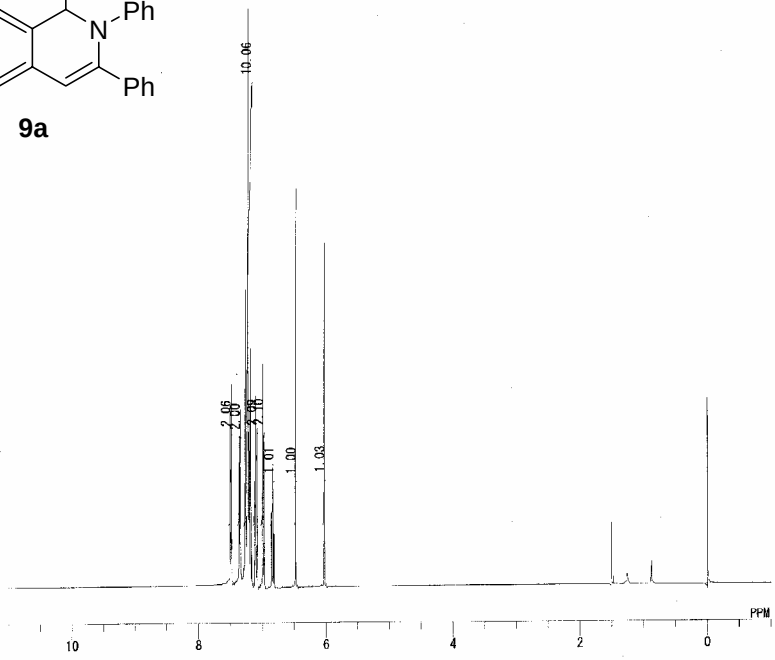
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP         23.3 c
SLVNT   CDCL3
EXREF         7.26 ppm
BF            0.10 Hz
RGAIN           12
```



9a

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EXMOD   NON
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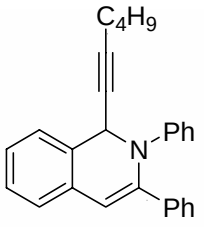
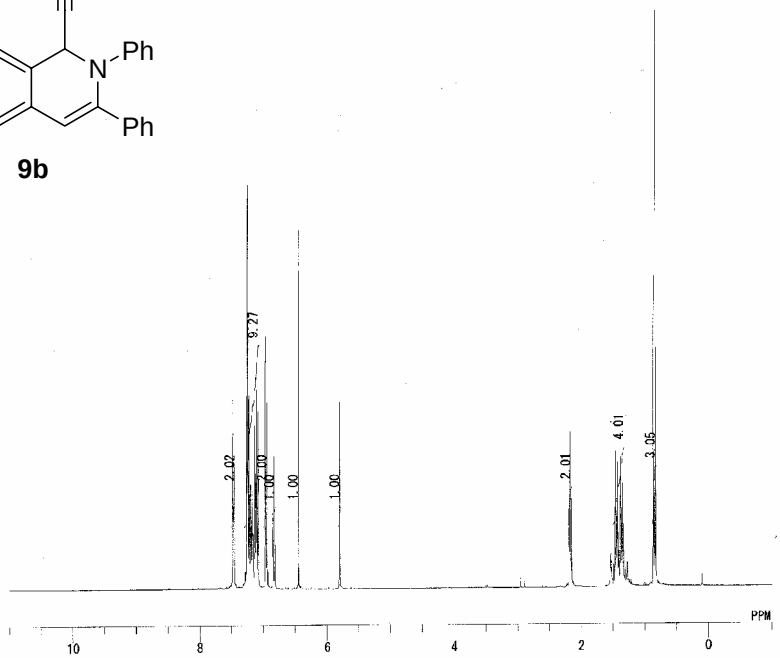
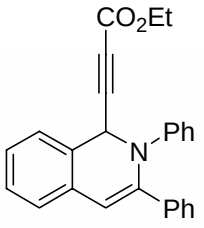
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP         20.8 c
SLVNT   CDCL3
EXREF         0.00 ppm
BF            0.10 Hz
RGAIN           12
```



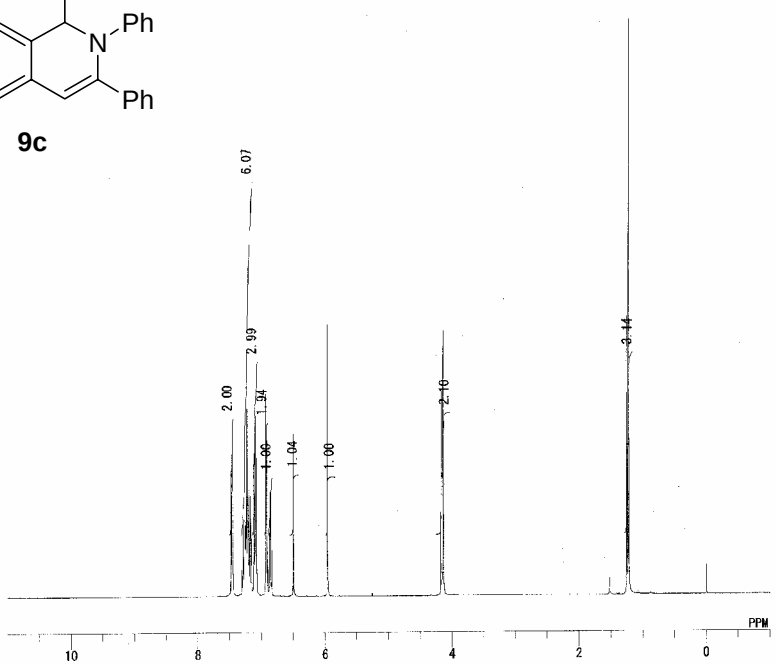
9b



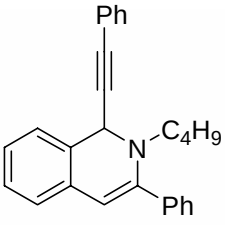

```
DFILE   C:¥Documents and Settings¥All Users¥D
COMNT
DATIM   Fri Jun 25 20:35:25 2004
OBNUC   1H
EXMOD   NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP          25.1 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            14
```



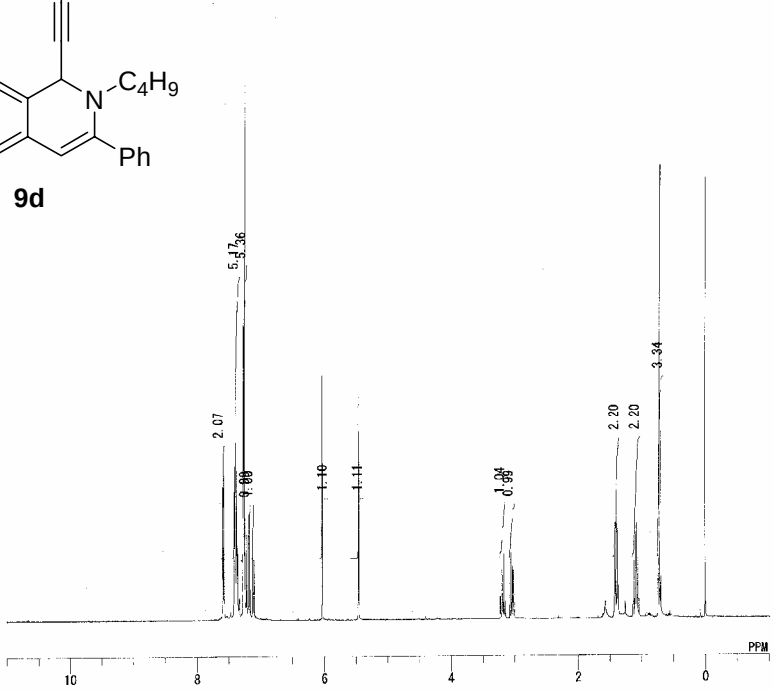
9c



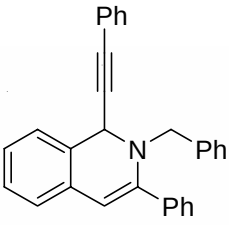

```
DFILE   C:¥Documents and Settings¥All Users¥D
COMNT
DATIM   Thu Jan 22 13:06:34 2004
OBNUC   1H
EXMOD   NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP          23.7 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.10 Hz
RGAIN            12
```



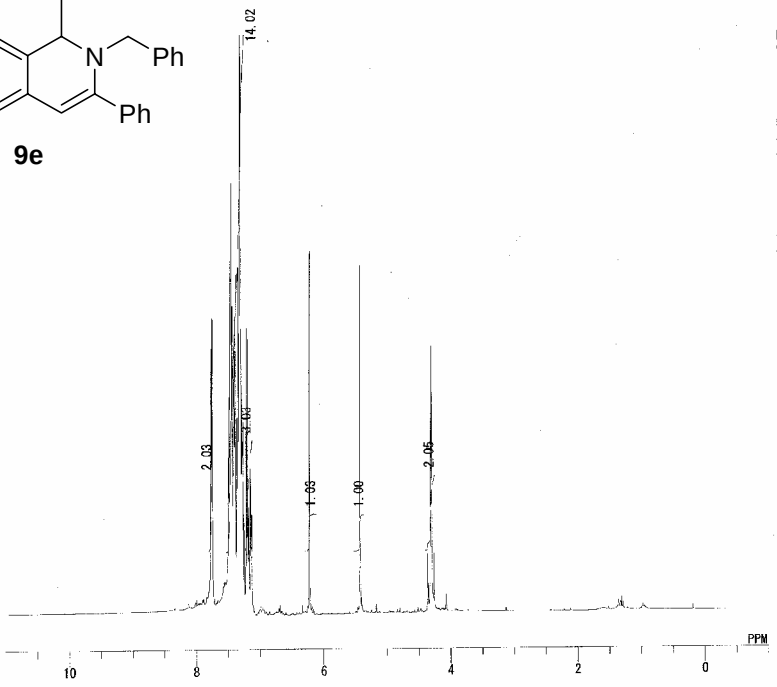
9d



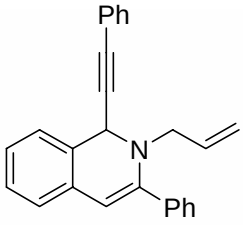

```
DFILE   C:¥Documents and Settings¥All Users¥D
COMNT
DATIM   Sat Jan 10 13:01:22 2004
OBNUC   1H
EXMOD   NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1           5.50 usec
IRNUC   1H
CTEMP        21.4 c
SLVNT   CDCL3
EXREF        0.00 ppm
BF           0.10 Hz
RGAIN          15
```



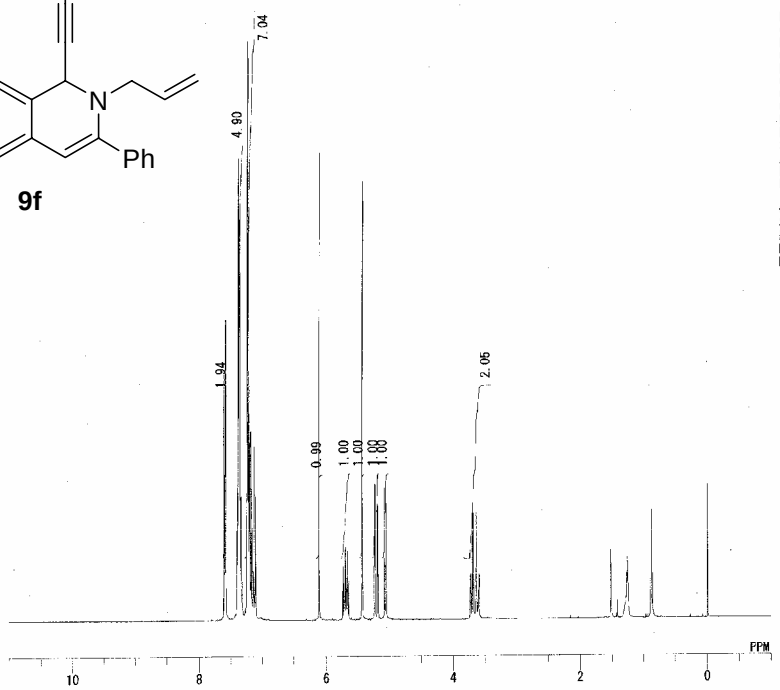
9e



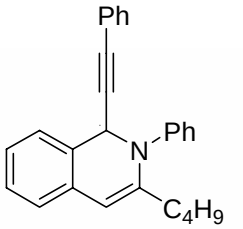

```
DFILE   C:¥Documents and Settings¥All Users¥D
COMNT
DATIM   Wed Feb 09 22:26:16 2005
OBNUC   1H
EXMOD   NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1           5.50 usec
IRNUC   1H
CTEMP        22.8 c
SLVNT   CDCL3
EXREF        7.26 ppm
BF           1.25 Hz
RGAIN           7
```



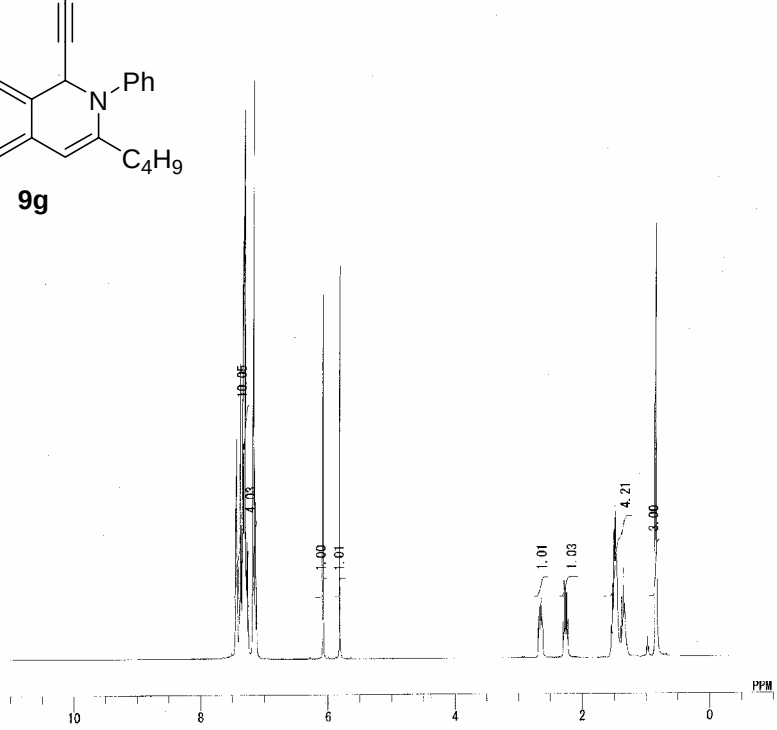
9f



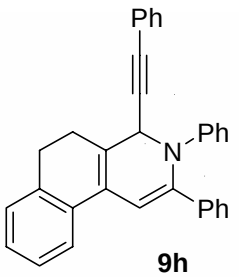

```
DFILE  C:¥Documents and Settings¥All Users¥D
COMNT
DATIM  Thu Jan 15 23:36:15 2004
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU       7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1             5.50 usec
IRNUC  1H
CTEMP           20.6 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.10 Hz
RGAIN             12
```



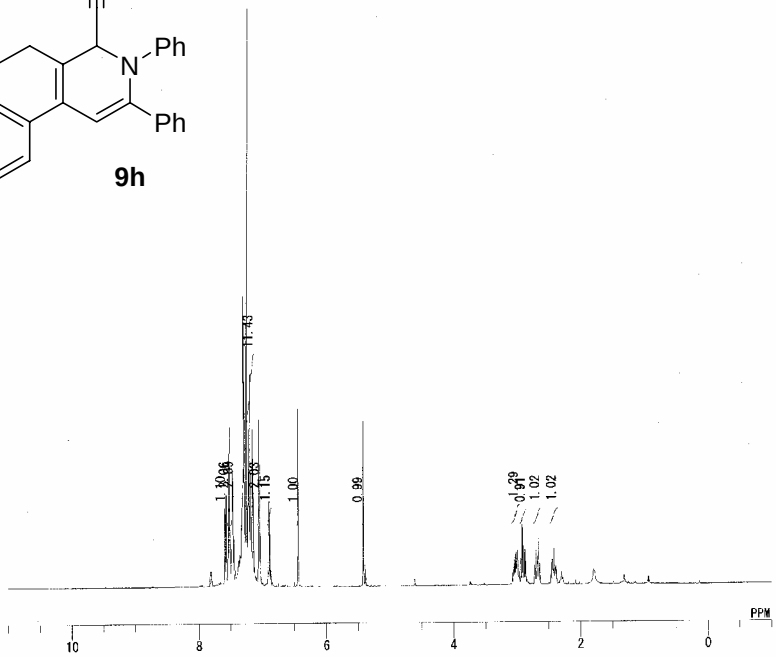
9g




```
DFILE  C:¥Documents and Settings¥All Users¥D
COMNT
DATIM  Tue Jun 29 16:04:24 2004
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU       7993.60 Hz
SCANS            8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1             5.50 usec
IRNUC  1H
CTEMP           23.8 c
SLVNT  CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN              7
```



9h




```
DFILE   C:¥Documents and Settings¥All Users¥D
COMNT
DATIM   Fri Jul 30 18:25:26 2004
OBNUC   1H
EXMOD   NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT       32768
FREQU      7993.60 Hz
SCANS           8
ACQTM       4.0993 sec
PD          2.9010 sec
PW1            5.50 usec
IRNUC   1H
CTEMP         27.6 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.30 Hz
RGAIN            11
```