Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Highly Effective Chiral Phosphorus Amidite-Olefin Ligands for Palladium-Catalyzed Asymmetric Allylic Substitutions

Zhaoqun Liu, Ziping Cao and Haifeng Du*

Beijing National Laboratory of Molecular Sciences,
CAS Key laboratory of Molecular Recognition and Function,
Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100190, China

Supporting Information

Representative procedure for the synthesis of Ligand 3f: To a schlenk tube charged with (*R*)-*N*-(1-phenyl-2-propenyl)benzylamine (0.2233 g, 0.70 mmol) dissolved in THF (1.0 mL) was added ^{n}BuLi (0.70 mmol, 0.28 mL, 2.5 M in hexanes) slowly under argon at -78 °C. This solution was stirred at -30 °C for 10 min and then cooled to -78 °C again for further 30 min. Then phosphorchloridite of (*S*)-3,3'-Ph_2-BINOL (0.3872 g, 0.77 mmol) in THF (1.0 mL) was added dropwise to the THF solution of amine lithium salt at -78 °C, and the solution was stirred for further 30 min at -78 °C. The reaction mixture was then stirred overnight at 40 °C. After the completion of the reaction, the mixture solution was filtered through short silica gel column with Et_2O as eluent and concentrated. The obtained residue was purified by flash chromatography on silica gel (pentane: CH_2Cl_2 = 10:1) to afford the ligand **3f** as a white foam in 61% yield (0.2950 g).

(*a*) W.-J. Tang, Y.-Y. Huang, Y.-M. He, Q.-H. Fan, *Tetrahedron: Asymmetry*, 2006, **17**, 536; (*b*) C. R. Smith, D. J. Mans, T. V. RajanBabu, *Org. Synth.*, 2008, **85**, 238; (*c*) R. Almansa, D. Guijarro, M. Yus, *Tetrahedron: Asymmetry*, 2008, **19**, 603.

Representative procedure for allylic alkylation of indoles (Table 2, entry 1): To a dried Schlenk flask charged with $[PdCl(C_3H_5)]_2$ (0.0011 g, 0.003 mmol, 3 mol % Pd), chiral phosphorus amidite-olefin ligand **3f** (0.0041 g, 0.006 mmol, 3 mol %), was added distilled CH_2Cl_2 (0.4 mL) under argon. Then the mixture was stirred for 30 min at 15 °C before 1,3-diphenyl-2-propenyl acetate **5** (0.0605 g, 0.24 mmol) in CH_2Cl_2 (0.40 mL), indole **4a** (0.0234 g, 0.20 mmol) and potassium carbonate (0.0829 g, 0.60 mmol), and THF (0.4 mL) were added sequentially. The reaction mixture was stirred 15 °C for 12 h before filtered through celite with Et_2O as eluent and concentrated. The residue was purified by flash chromatography on silica gel (PE: EA = 15:1) to afford the desired product **6a** as a white solid in 94% yield (0.0582 g).

Representative procedure for synthesis of Boc-derivatizations of indoles: To a dried round flask with the solution of product **6a** (1 equiv) and DMAP (10% equiv) in CH_2Cl_2 (1 mL), was added $(Boc)_2O$ (1.2 equiv), then the mixture was stirred at ambient temperature for two hours. The solvent was removed and the resulting residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) to give the Boc-derivative product **6a**.

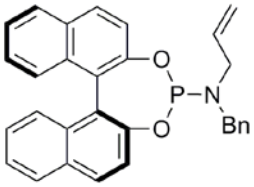
H. Y. Cheung, W.-Y. Yu, F. L. Lam, T. T.-L. Au-Yeung, Z. Zhou, T. H. Chan, A. S. C. Chan, *Org. Lett.*, 2007, **9**, 4295.

Representative procedure for Pd-catalyzed allylic amination (Scheme 2): To a Schlenk tube charged with $[PdCl(C_3H_5)]_2$ (0.0011 g, 0.003 mmol), and the ligand **3f** (0.0041 g, 0.006 mmol) was added CH_2Cl_2 (0.40 mL) under argon. The resulting mixture was stirred for 30 min at 20 °C. Racemic 1,3-diphenyl-2-propenyl acetate (**5**) (0.0606 g, 0.24 mmol) in CH_2Cl_2 (0.60 mL), benzylamine (0.0772 g, 0.72 mmol), were added subsequently, and the reaction mixture was stirred at 20 °C for 12 h before diluted with Et_2O (10.0 mL) and concentrated. The obtained residue was purified by flash chromatography on silica gel (PE/ EA = 5/1) to afford the product **8a** as colorless oil (0.0683 g, 95% yield) (94% ee).

Procedure for Pd-catalyzed asymmetric amination with hydroxylamine hydrochloride (Scheme 3): To a Schlenk tube charged with $[PdCl(C_3H_5)]_2$ (0.0045 g, 0.0125 mmol) and **3f** (0.0173 g, 0.025 mmol) was added CH_3CN (1.0 mL) under argon. The resulting solution was stirred at 20 °C for 20 min, and then cooled to 0 °C. 1,3- Diphenyl-2-propenyl acetate **5** (0.2523 g, 1.0 mmol, in 1.0 mL CH_3CN), hydroxylamine hydrochloride (**9**) (0.139 g, 2.0 mmol), $^{i}Pr_2NEt$ (0.2584 g, 2.0 mmol), and CH_3CN (1.0 mL) were added subsequently, and the reaction mixture was stirred at 0 °C for 12 h before diluted with Et_2O and concentrated. The residue was purified by flash chromatography on silica gel (PE: Et_2O = 2:1) to afford the product as a white solid in 70% yield (0.1577 g).

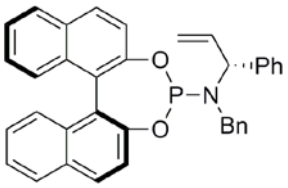
Procedure for the deprotection of 10: To a suspension of optical pure compound **10** (0.0676 g, 0.30 mmol) in AcOH-H_2O (1:1 v/v, 1.8 mL) was added Zn powder (0.4056 g, 6.0 mmol) under argon at 20 °C. The reaction mixture was stirred at the same temperature for 2 h before quenched with saturated aq. $NaHCO_3$ (20 mL). After the reaction solution was filtered and extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated to afford the product **11** as colorless oil in 100% yield (0.0628 g).

(*a*) C. J. Moody, P. T. Gallagher, A. P. Lightfoot, A. M. Z. Slawin, *J. Org. Chem.*, 1999, **64**, 4419; (*b*) H. Miyabe, A. Masumura, K. Moriyama, Y. Takemoto, *Org. Lett.*, 2004, **6**, 4631.



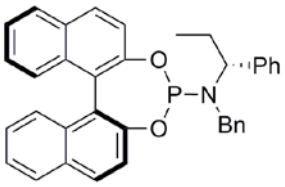
3a

3a: White foam, m.p. 78-80 °C, $[\alpha]_D^{20}$ +360.0 (*c* 0.5, $CHCl_3$). IR (film) 1507, 1463, 1431; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.84-7.81 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.44-7.30 (m, 8H), 7.30-7.20 (m, 5H), 5.80-5.60 (m, 1H), 5.16 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 17.2 Hz, 1H), 4.25 (dd, *J* = 15.2, 8.8 Hz, 1H), 3.79 (dd, *J* = 15.2, 12.0 Hz, 1H), 3.58-3.46 (m, 1H), 3.10-2.96 (m, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 146.7; HRMS (EI): Calcd for $C_{36}H_{28}NO_2P$ (M): 461.1545; Found: 461.1551.



3b

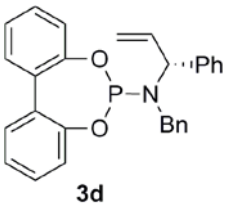
3b: White foam, m.p. 99-100 °C, $[\alpha]_D^{20}$ +192.0 (*c* 1.0, $CHCl_3$). IR (film) 1506, 1462, 1359 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.86-7.80 (m, 2H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.42-7.30 (m, 8H), 7.28-7.16 (m, 9H), 6.25 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 4.80-4.70 (m, 1H), 4.05 (d, *J* = 15.2 Hz, 1H), 3.51 (d, *J* = 15.2 Hz, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 145.7; HRMS (EI): Calcd for $C_{36}H_{28}NO_2P$ (M): 537.1858; Found: 537.1863.



3c

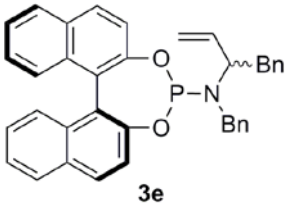
3c: White foam, m.p. 102-103 °C, $[\alpha]_D^{20}$ +150.3 (*c* 0.95, $CHCl_3$). IR (film) 1589, 1494, 1463 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.48-7.40 (m, 5H), 7.38-7.22 (m, 4H), 7.26-7.22 (m, 5H), 7.21-7.15 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 4.42-4.34 (m, 1H), 3.81 (dd, *J* = 15.6, 3.2 Hz, 1H), 3.34 (dd, *J* = 15.6, 3.6 Hz, 1H), 1.80-1.64 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{31}P

NMR (121 MHz, $CDCl_3$): δ 145.1; HRMS (ESI): Calcd for $C_{48}H_{36}NO_2P$ ($[M+H]^+$): 540.2087; Found: 540.2079.



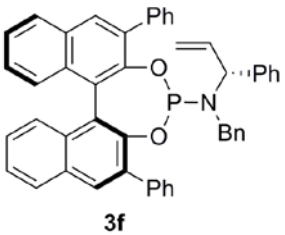
3d

3d: White foam, m.p. 56-57 °C, $[\alpha]_D^{20}$ +17.3 (*c* 0.75, $CHCl_3$). IR (film) 1596, 1475, 1435 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.40 (m, 6H), 7.36-7.30 (m, 2H), 7.28-7.14 (m, 9H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.33-6.24 (m, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.70-4.62 (m, 1H), 4.11 (dd, *J* = 15.2, 3.2 Hz, 1H), 3.62 (dd, *J* = 15.2, 2.4 Hz, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 144.6; HRMS (EI): Calcd for $C_{28}H_{24}NO_2P$ (M): 437.1545; Found: 437.1551.



3e

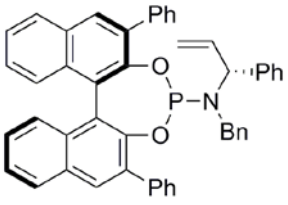
3e: White foam, m.p. 89-90 °C, $[\alpha]_D^{20}$ +216.4 (*c* 0.95, $CHCl_3$). IR (film) 1590, 1495, 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.88-7.80 (m, 3H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.44-7.30 (m, 9H), 7.26-7.13 (m, 19H), 7.07-7.02 (m, 2H), 6.96-6.87 (m, 4H), 6.00-5.86 (m, 2H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 7.6 Hz, 1H)), 5.01 (d, *J* = 7.6 Hz, 1H), 4.11-4.04 (m, 2H), 4.03-3.92 (m, 1H), 3.70-3.56 (m, 2H), 344-3.36 (m, 1H), 3.25-3.17 (m, 1H), 3.02-2.92 (m, 2H), 2.86-2.78 (m, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 148.0, 146.3; HRMS (EI): Calcd for $C_{28}H_{24}NO_2P$ (M): 551.2014; Found: 551.2021.



3f

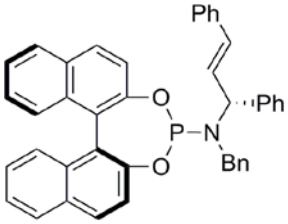
3f: White foam, m.p. 159-160 °C, $[\alpha]_D^{20}$ +303.5 (*c* 1.0, $CHCl_3$). IR (film): 1495, 1453, 1406 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.97 (s, 1H), 7.91 (d, *J* = 9.6 Hz, 2H), 7.87 (d, *J* = 7.6

Hz, 2H), 7.69-7.62 (m, 2H), 7.60-7.46 (m, 6H), 7.44-7.34 (m, 4H), 7.28-7.22 (m, 2H), 7.12-7.06 (m, 3H), 7.06-7.00 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 4.86 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 4.74 (d, *J* = 10.0 Hz, 1H), 4.49 (d, *J* = 16.8 Hz, 1H), 4.14 (d, *J* = 14.4 Hz, 1H), 3.99-3.90 (m, 1H), 3.15 (d, *J* = 14.4 Hz, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 139.4. HRMS (EI): Calcd for $C_{48}H_{36}NO_2P$ (M): 689.2484; Found: 689.2490.



3g

3g: White foam, m.p. 140-141 °C, $[\alpha]_D^{20}$ -204.4 (*c* 1.4, $CHCl_3$). IR (film): 1495, 1453, 1405 cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.96-7.90 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.54-7.42 (m, 7H), 7.40-7.32 (m, 3H), 7.30-7.20 (m, 2H), 7.12-7.00 (m, 6H), 6.92-6.85 (m, 2H), 6.57 (d, *J* = 7.2 Hz, 2H), 5.37 (ddd, *J* = 17.2, 9.6, 8.0 Hz, 1H), 4.64 (d, *J* = 9.6 Hz, 1H), 4.40 (d, *J* = 17.2 Hz, 1H), 4.14-4.00 (m, 2H), 3.10 (d, *J* = 15.6 Hz, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 142.1; HRMS (EI): Calcd for $C_{48}H_{36}NO_2P$ (M): 689.2484; Found: 689.2491.



3h

3h: White foam, m.p. 127-128 °C, $[\alpha]_D^{20}$ +56.4 (*c* 1.05, $CHCl_3$). IR (film): 1524, 1492, 1463 cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.46-7.38 (m, 4H), 7.37-7.34 (m, 3H), 7.33-7.28 (m, 8H), 7.27-7.20 (m, 7H), 6.42 (dd, *J* = 15.6, 8.8 Hz, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 5.10-5.04 (m, 1H), 4.15 (dd, *J* = 15.6, 3.2 Hz, 1H), 3.59 (dd, *J* = 15.6, 6.0 Hz, 1H); ^{31}P NMR (121 MHz, $CDCl_3$): δ 146.0; HRMS (EI): Calcd for $C_{42}H_{32}NO_2P$ (M): 613.2171; Found: 613.2178.

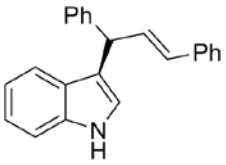


Table 2, entry 1

6a: White solid, m.p. 120-122 °C, $[\alpha]_D^{20}$ -48.3 (*c* 0.75 CH_2Cl_2) (95% ee) [lit.: $[\alpha]_D^{20}$ -45.8 (*c* 0.98, CH_2Cl_2) (95% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (brs, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.40-7.26 (m, 9H), 7.25-7.12 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 6.71 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.7, 136.8, 132.7, 130.8, 128.7, 128.6, 127.4, 127.0, 126.6, 126.5, 122.8, 122.3, 120.1, 119.6, 118.9, 111.3, 46.4.

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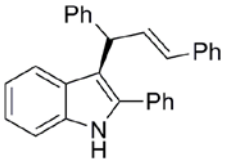

Table 2, entry 2

6b: Yellow solid, m.p. 43-45 °C, $[\alpha]_D^{20}$ -68.5 (*c* 0.6 CH_2Cl_2) (94% ee) [lit.: $[\alpha]_D^{20}$ -71.9 (*c* 1.0, CH_2Cl_2) (92% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (brs, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46-7.30 (m, 9H), 7.28-7.24 (m, 4H), 7.22-7.14 (m, 3H), 6.99 (t, *J* = 7.6 Hz,1H), 6.89 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.7, 136.4, 135.8, 133.2, 132.5, 131.3, 129.1, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 127.3, 126.5, 126.3, 122.3, 121.4, 119.9, 114.1, 111.1, 45.3.

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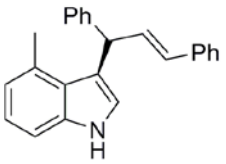

Table 2, entry 3

6c: White solid, m.p. 172-174 °C, $[\alpha]_D^{20}$ -81.4 (*c* 0.35 CH_2Cl_2) (92% ee) [lit.: $[\alpha]_D^{20}$ +68.4 (*c* 0.31, CH_2Cl_2) (94% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (brs, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.30-7.24 (m, 6H), 7.23-7.16 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J*

= 7.2 Hz, 1H), 6.74 (dd, *J* = 16.0, 6.4 Hz, 1H), 6.23 (d, *J* = 16.0, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.8, 137.2, 134.1, 131.3, 130.9, 129.1, 128.7, 128.6, 127.3, 126.5, 125.8, 123.7, 122.4, 121.5, 119.3, 109.2, 46.7, 20.6.

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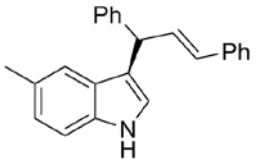

Table 2, entry 4

6d: White solid, m.p. 112-114 °C, $[\alpha]_D^{20}$ -42.4 (*c* 1.05 CH_2Cl_2) (91% ee) [lit.: $[\alpha]_D^{20}$ -48.3 (*c* 1.01, CH_2Cl_2) (96% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (brs, 1H), 7.38-7.15 (m, 12H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.84 (s, 1H), 6.71(dd, *J* = 16.0, 7.2 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.09 (d, *J* = 7.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.8, 135.2, 132.9, 130.7, 128.9, 128.7, 128.6, 128.5, 127.3, 126.5, 124.0, 123.0, 119.6, 118.4, 111.0, 46.3, 21.7.

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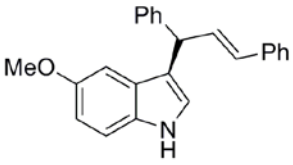

Table 2, entry 5

6e: Colorless oil, $[\alpha]_D^{20}$ -37.6 (*c* 0.80 CH_2Cl_2) (98% ee) [lit.: $[\alpha]_D^{20}$ -38.5 (*c* 0.96, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (brs, 1H), 7.38-7.15 (m, 11H), 6.86-6.80 (m, 3H), 6.70 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.06 (d, *J* = 7.2 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 143.5, 137.7, 132.7, 132.0, 130.8, 128.7, 128.6, 128.5, 127.4, 127.3, 126.6, 126.5, 123.6, 118.5, 112.3, 112.0, 102.0, 56.0, 46.4.

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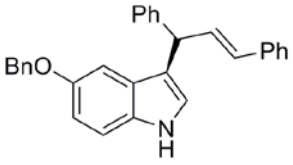

Table 2, entry 6

6f: Colorless oil, $[\alpha]_D^{20}$ -31.1 (*c* 0.55 CH_2Cl_2) (95% ee) [lit.: $[\alpha]_D^{20}$ -30.2 (*c* 1.0, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (brs, 1H), 7.40-7.15 (m, 16H), 6.95-6.84 (m, 3H), 6.69 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.03 (d, *J* = 7.2 Hz, 1H), 4.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 143.5, 137.8, 137.7, 132.7, 132.2, 130.8, 128.7, 128.6, 127.9, 127.8, 127.4, 126.6, 126.5, 123.6, 118.6, 113.2, 112.0, 103.7, 71.0, 46.4.

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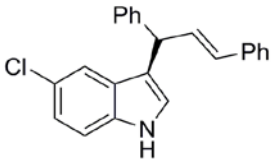

Table 2, entry 7

6g: Yellow oil, $[\alpha]_D^{20}$ -36.3 (*c* 1.20 CH_2Cl_2) (94% ee) [lit.: $[\alpha]_D^{20}$ -37.0 (*c* 0.94, CH_2Cl_2) (96% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (brs, 1H), 7.38-7.34 (m, 3H), 7.33-7.16 (m, 9H), 7.14-7.08 (m, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.67 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.05 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.5, 135.2, 132.3, 131.0, 128.7, 128.6, 128.1, 127.5, 126.8, 126.5, 125.4, 124.2, 122.7, 119.4, 118.8, 112.3, 46.1.

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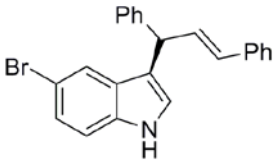

Table 2, entry 8

6h: Colorless oil, $[\alpha]_D^{20}$ -40.0 (*c* 0.45 CH_2Cl_2) (96% ee) [lit.: $[\alpha]_D^{20}$ -35.1 (*c* 1.0, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (brs, 1H), 7.46 (s, 1H), 7.30-7.10 (m, 12H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.60 (dd, *J* = 15.6, 7.2 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 4.98 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.5, 135.4, 132.3, 131.0, 128.8, 128.7, 128.6, 128.5, 127.5, 126.8, 126.5, 125.2, 124.0, 122.5, 118.6, 112.9, 112.8, 46.1.

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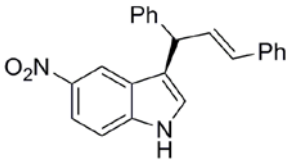

Table 2, entry 9

6i: Yellow solid, m.p. 142-143 °C, $[\alpha]_D^{20}$ -27.8 (*c* 1.15 CH_2Cl_2) (96% ee); IR (film): 3404, 1623, 1517, 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (brs, 1H), 8.38 (s, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.42-7.20 (m, 11H), 7.09 (s, 1H), 6.69 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.15 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.9, 139.8, 137.3, 131.7, 131.5, 128.9, 128.8, 128.5, 127.7, 127.1, 126.6, 126.5, 125.8, 121.7, 118.2, 117.3, 111.4, 46.0; HRMS (EI): Calcd for $C_{23}H_{18}N_2O_2$ (M): 354.1368; Found: 354.1373.

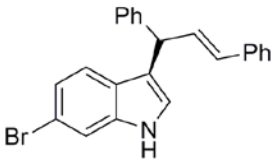

Table 2, entry 10

6j: Yellow oil, $[\alpha]_D^{20}$ -46.5 (*c* 0.85 CH_2Cl_2) (95% ee) [lit.: $[\alpha]_D^{20}$ +33.4 (*c* 1.34, CH_2Cl_2) (94% ee). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (brs, 1H), 7.43 (d, *J* = 1.2 Hz, 1H), 7.36-7.16 (m, 11H), 7.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.82 (d, *J* = 1.2 Hz, 1H), 6.66 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.05 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.6, 137.5, 132.3, 131.0, 128.7, 128.6, 128.5, 127.5, 126.8, 126.5, 124.9, 123.4, 123.0, 121.3, 119.1, 115.9, 114.2, 46.2.

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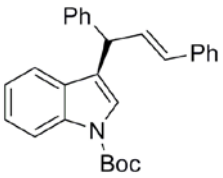
BOC-derivatives



Colorless oil, $[\alpha]_D^{20}$ -40.6 (*c* 0.8 CH_2Cl_2) (95% ee) [lit.: $[\alpha]_D^{20}$ -38.8 (*c* 1.01, CH_2Cl_2) (95% ee)]. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 1H), 7.42-7.20 (m, 13H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.03 (d, *J* = 7.2 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 142.3, 137.4, 136.0, 131.5, 131.4, 130.1, 128.8, 128.7, 128.6, 127.6, 126.9, 126.6, 124.5, 124.0, 123.2, 122.6, 120.3, 115.5, 83.9, 46.1, 28.4.

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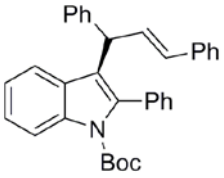

White solid, m.p. 153-155 °C, $[\alpha]_D^{20}$ -45.3 (*c* 0.75 CH_2Cl_2) (94% ee) [lit.: $[\alpha]_D^{20}$ -39.6 (*c* 1.0, CH_2Cl_2) (92% ee)].^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.44-7.34 (m, 5H), 7.34-7.22 (m, 10H), 7.22-714 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.75 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.30 (d, *J* = 16.0, 1H), 4.85 (d, *J* = 7.6 Hz, 1H), 1.3 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 142.7, 137.5, 137.2, 137.1, 136.8, 134.5, 131.8, 130.8, 130., 128.7, 128.5, 128.3, 128.2, 128.0, 126.5, 126.4, 124.5, 122.7, 121.1, 115.5, 83.2, 45.0, 27.7.

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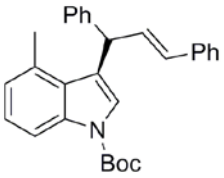

White solid, m.p. 136-139 °C, $[\alpha]_D^{20}$ -55.5 (*c* 0.45 CH_2Cl_2) (92% ee) [lit.: $[\alpha]^{20}_D$ +45.6 (*c* 0.31, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.36-7.12 (m, 12H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.69 (dd, *J* = 16.0, 6.8 Hz 1H), 6.6 (d, *J* = 16.0 Hz, 1H), 5.33(d, *J* = 6.8 Hz, 1H), 2.47 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 142.9, 137.5, 136.4, 13.8, 131.4, 131.3, 129.0, 128.7, 128.6, 127.5, 126.9, 126.6, 125.1, 125.0, 124.5, 123.6, 113.3, 83.9, 46.7, 28.4, 20.5.

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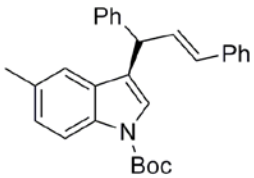

White solid, m.p. 150-152 °C, $[\alpha]_D^{20}$ -32.4 (*c* 0.25 CH_2Cl_2) (94% ee) [lit.: $[\alpha]_D^{20}$ -41.2 (*c* 1.05, CH_2Cl_2) (96% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.38-7.20 (m, 14H),

6.64 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.98 (d, *J* = 7.2 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 141.9, 137.3, 134.4, 131.8, 131.3, 131.0, 128.9, 128.8, 128.6, 128.4, 127.7, 127.1, 126.6, 125.2, 124.8, 122.7, 119.8, 116.5, 84.4, 46.0, 28.4.

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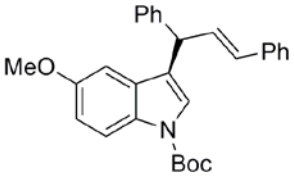

Yellow oil, $[\alpha]_D^{20}$ -40.7 (*c* 1.15 CH_2Cl_2) (98% ee) [lit.: $[\alpha]_D^{20}$ -37.6 (*c* 0.95, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (brs, 1H), 7.38-7.18 (m, 11H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.98 (d, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.0, 142.2, 137.4, 131.5, 131.3, 130.9, 130.8, 128.8, 128.7, 128.6, 127.6, 126.9, 126.6, 124.7, 123.0, 116.1, 112.9, 103.3, 83.7, 55.8, 46.2, 28.4.

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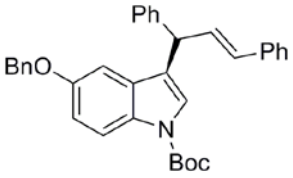

Colorless oil, $[\alpha]_D^{20}$ -36.0 (*c* 0.7 CH_2Cl_2) (91% ee) [lit.: $[\alpha]_D^{20}$ -28.2 (*c* 0.97, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (bs, 1H), 7.38-7.20 (m, 16H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.64 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.41 (d, *J* = 16.0 hz, 1H), 4.97-4.93 (m, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 150.0, 142.2, 137.4, 131.5, 131.3, 130.9, 128.8, 128.7, 128.6, 128.0, 127.7, 127.6, 126.9, 126.6, 124.7, 123.0, 116.2, 113.9, 104.7, 83.7, 70.8, 46.2, 28.4.

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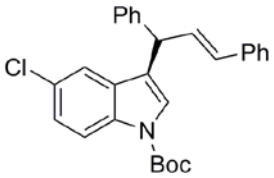

White solid, m.p. 150-152 °C, $[\alpha]_D^{20}$ -32.4 (*c* 0.25 CH_2Cl_2) (94% ee) [lit.: $[\alpha]_D^{20}$ -36.1 (*c* 0.95, CH_2Cl_2) (96% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.38-7.20 (m, 13H), 6.64 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.98 (d, *J* = 7.2 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 141.9, 137.3, 134.4, 131.8, 131.3, 131.0, 128.9, 128.8, 128.6, 128.4, 127.7, 127.1, 126.6, 125.2, 124.8, 122.7, 119.8, 116.5, 84.4, 46.0, 28.4.

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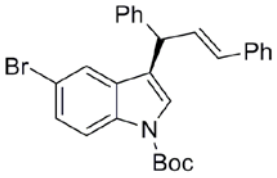

White solid, m.p. 75-77 °C, $[\alpha]_D^{20}$ -38.4 (*c* 1.2 CH_2Cl_2) (96% ee) [lit.: $[\alpha]_D^{20}$ -32.9 (*c* 1.0, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.38-7.18 (m, 12H), 6.64 (dd, *J* = 15.6, 7.2 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 4.97 (d, *J* = 7.2 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 141.8, 137.3, 134.8, 131.8, 131.7, 131.0, 128.9, 128.7, 128.5, 127.7, 127.5, 127.1, 126.6, 125.1, 122.8, 122.6, 116.9, 116.1, 84.4, 45.9, 28.4.

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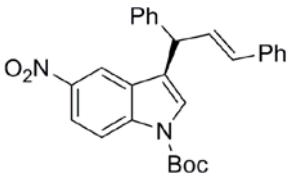
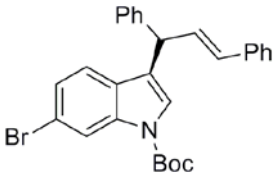


White solid, m.p. 44-46 °C, $[\alpha]_D^{20}$ -26.0 (*c* 0.7 CH_2Cl_2) (96% ee). IR (film): 1740, 1520 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ. 8.26-8.15 (m, 3H), 7.49 (s, 1H), 7.39-7.20 (m, 10H), 6.66 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.08 (d, *J* = 7.2 Hz, 1H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 143.7, 141.4, 139.1, 132.1, 130.5, 129.9, 129.1, 128.8, 128.5, 127.8, 127.4, 126.7, 126.6, 124.2, 119.9, 116.5, 115.7, 85.4, 45.8, 28.3; HRMS (EI): Calcd for $C_{28}H_{26}N_2O_4$ (M): 454.1893; Found: 454.1898.



Yellow oil, $[\alpha]_D^{20}$ -33.3 (*c* 1.75 CH_2Cl_2) (95% ee) [lit.: $[\alpha]^{20}_D$ +37.0 (*c* 1.49, CH_2Cl_2) (94% ee)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (brs, 1H), 7.36-7.20 (m, 12H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 142.0, 137.2, 136.7, 131.7, 131.0, 128.9, 128.7, 128.5, 127.7, 127.1, 126.6, 125.9, 124.4, 123.1, 121.4, 118.7, 118.4, 84.5, 46.0, 28.4.

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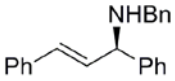
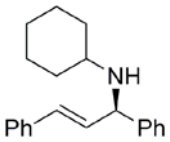


8a

8a: colorless oil, $[\alpha]_D^{20}$ -18.5 (*c* 1.0 $CHCl_3$) (94% ee) [lit.: $[\alpha]_D^{25}$ -19.7 (*c* 0.15, $CHCl_3$, 98% ee (*R*)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 8H), 7.28-7.24 (m, 4H), 7.24-7.16 (m, 1H), 6.57 (d, *J* = 15,6 Hz, 1H), 6.31 (dd, *J* = 15.6, 7.6 Hz, 1H), 4.39 (d, *J* = 7.6 Hz, 1H), 3.84-3.74 (m, 2H), 1.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 140.6, 137.2, 132.8, 130.5, 128.8, 128.7, 128.6, 128.4, 127.6, 127.5, 127.4, 127.1, 126.6, 64.8, 51.6.

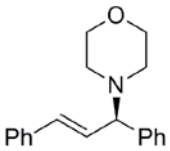
T. Nemoto, T. Masuda, Y. Akimoto, T. Fukuyama, Y. Hamada, *Org. Lett*., 2005, **7**, 4447.



8b

8b: Yellow oil, $[\alpha]_D^{20}$ +8.7 (*c* 0.75 $CHCl_3$) (91% ee) [lit.: $[\alpha]_D^{24}$ +9.5 (*c* 0.3, $CHCl_3$, 98% ee (*R*)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.30 (m, 6H), 7.30-7.22 (m, 3H), 7.20-7.16 (m, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.29 (dd, *J* = 15.6, 7.2 Hz, 1H), 4.56 (d, *J* = 7.2 Hz, 1H), 2.50-2.42 (m, 1H), 1.97 (d, *J* = 12.0 Hz, 1H), 1.89 (d, *J* = 12.8 Hz, 1H), 1.75-1.64 (m, 2H), 1.60-1.52 (m, 1H), 1.36 (brs, 1H), 1.22-1.02 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 137.3, 133.6, 129.9, 128.7, 128.6, 127.5, 127.3, 126.6, 62.1, 53.7, 34.2, 34.0, 26.4, 25.3, 25.2.

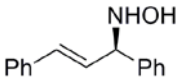
T. Nemoto, T. Masuda, Y. Akimoto, T. Fukuyama, Y. Hamada, *Org. Lett*., 2005, **7**, 4447.



8c

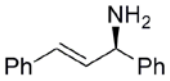
8c: colorless oil, $[\alpha]_D^{20}$ -6.5 (*c* 0.83 $CHCl_3$) (93% ee) [lit.: $[\alpha]_D^{24}$ -8.4 (*c* 0.7, $CHCl_3$, 95% ee (*R*)]. ^1H NMR (400 MHz, $CDCl_3$): ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.38-7.18 (m, 8H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.29 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.80 (d, *J* = 8.8 Hz, 1H), 3.76-3.66 (m, 4H), 2.62-2.50 (m, 2H), 2.44-2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 136.9, 131.8, 131.6, 128.9, 128.7, 128.2, 127.8, 127.5, 126.6, 75.0, 67.4, 52.4.

T. Nemoto, T. Masuda, Y. Akimoto, T. Fukuyama, Y. Hamada, *Org. Lett*., 2005, **7**, 4447.



10

10: White solid, m.p. 97-98 °C, $[\alpha]_D^{20}$ +27.9 (*c* 0.8 $CHCl_3$) (95% ee). IR (film): 3251, 1494, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42.-7.32 (m, 6H), 7.32-7.26 (m, 3H), 7.26-7.20 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.27 (brs, 2H), 4.72 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 136.8, 133.1, 128.9, 128.8, 128.1, 128.0, 126.7, 69.4.



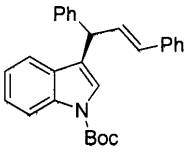
11

11: Colorless oil, $[\alpha]_D^{20}$ +44.8 (*c* 0.9 CH_2Cl_2) (>99% ee). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42.-7.35 (m, 6H), 7.31-7.23 (m, 3H), 7.22-7.18 (m, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.71 (d, *J* = 6.4 Hz, 1H), 1.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 137.1, 134.0, 129.3, 128.8, 128.7, 127.6, 127.4, 126.9, 126.6, 58.2.

T. Nagano, S. Kobayashi, *J. Am. Chem. Soc.*, 2009, **131**, 4200.

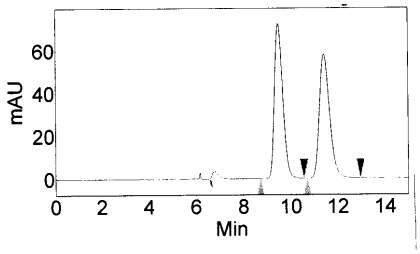
The chromatograms for determination of the enantiomeric excess

Table 1, entry 1



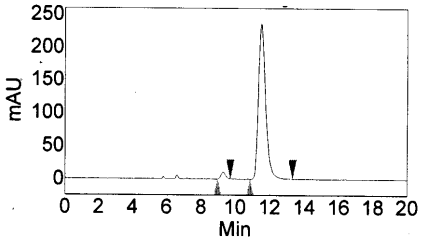
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



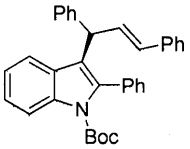
Index	Time [Min]	Area % [%]
1	9.49	50.317
2	11.43	49.683
Total		100.000

Chiral



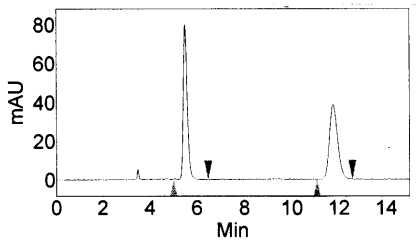
Index	Time [Min]	Area % [%]
1	9.31	2.722
2	11.51	97.278
Total		100.000

Table 2, entry 2



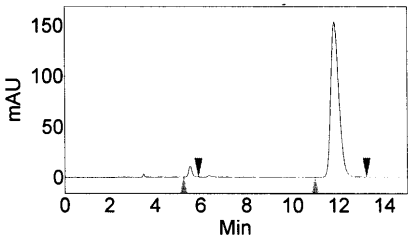
HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV 254 nm

Racemic



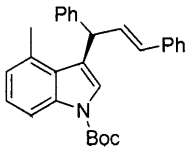
Index	Time [Min]	Area % [%]
1	5.49	49.748
2	11.76	50.252
Total		100.000

Chiral



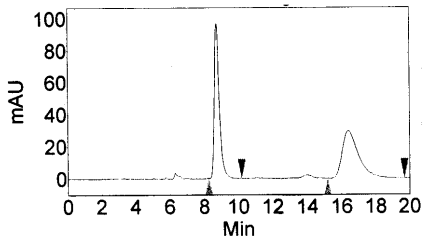
Index	Time [Min]	Area % [%]
1	5.52	3.005
2	11.81	96.995
Total		100.000

Table 1, entry 3



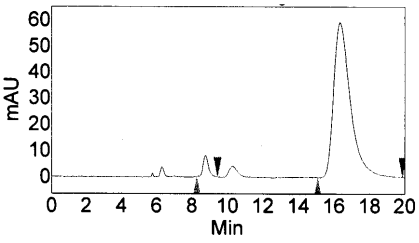
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



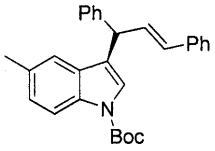
Index	Time [Min]	Area % [%]
1	8.75	50.771
2	16.39	49.229
Total		100.000

Chiral



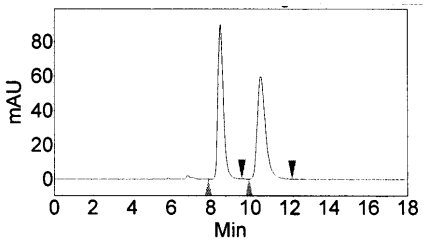
Index	Time [Min]	Area % [%]
1	8.76	4.143
2	16.35	95.857
Total		100.000

Table 2, entry 4



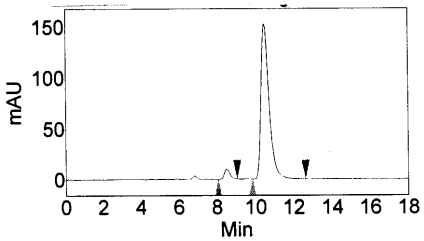
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



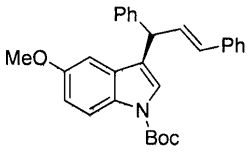
Index	Time [Min]	Area % [%]
1	8.49	49.838
2	10.53	50.162
Total		100.000

Chiral



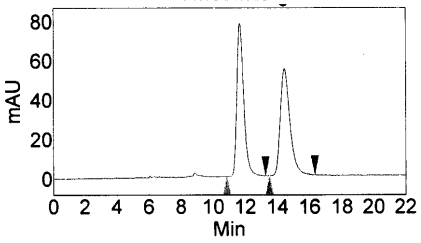
Index	Time [Min]	Area % [%]
1	8.51	4.395
2	10.49	95.605
Total		100.000

Table 1, entry 5



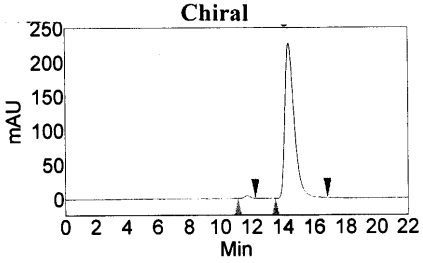
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



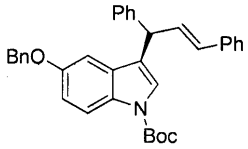
Index	Time [Min]	Area % [%]
1	11.68	50.480
2	14.43	49.520
Total		100.000

Chiral



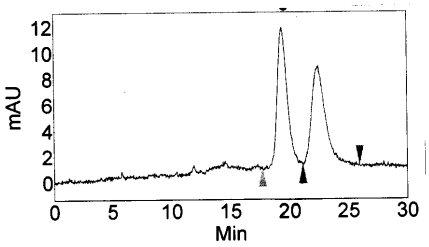
Index	Time [Min]	Area % [%]
1	11.69	1.131
2	14.39	98.869
Total		100.000

Table 2, entry 6



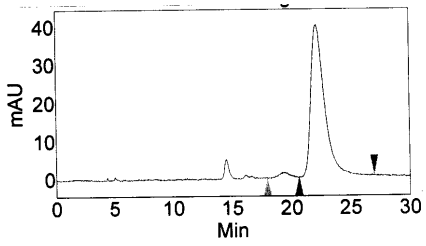
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



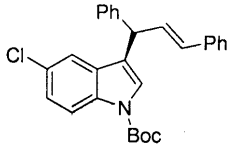
Index	Time [Min]	Area % [%]
1	19.37	49.930
2	22.40	50.070
Total		100.000

Chiral



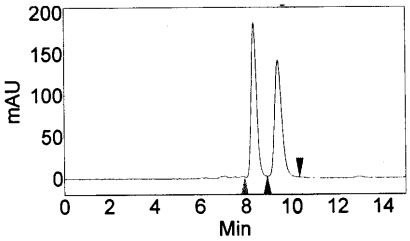
Index	Time [Min]	Area % [%]
1	19.33	2.459
2	22.17	97.541
Total		100.000

Table 1, entry 7



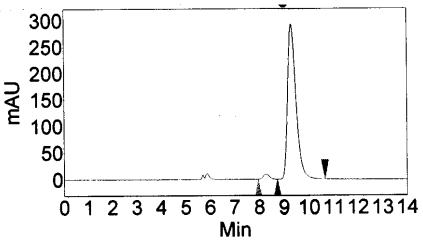
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



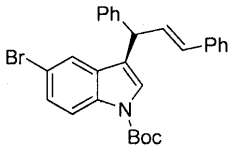
Index	Time [Min]	Area % [%]
1	8.35	49.807
2	9.40	50.193
Total		100.000

Chiral



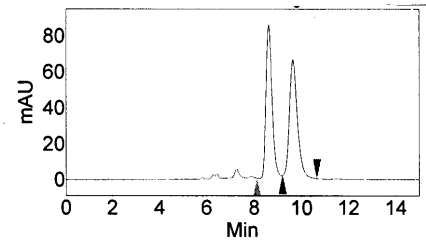
Index	Time [Min]	Area % [%]
1	8.25	2.549
2	9.31	97.451
Total		100.000

Table 2, entry 8



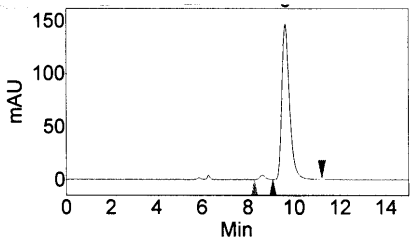
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



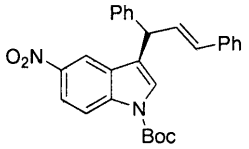
Index	Time [Min]	Area % [%]
1	8.63	49.197
2	9.65	50.803
Total		100.000

Chiral



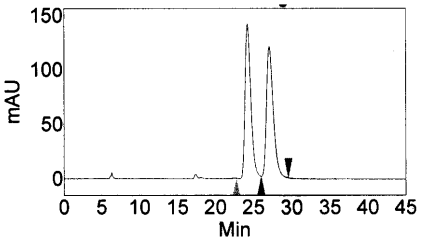
Index	Time [Min]	Area % [%]
1	8.63	2.063
2	9.63	97.937
Total		100.000

Table 1, entry 9



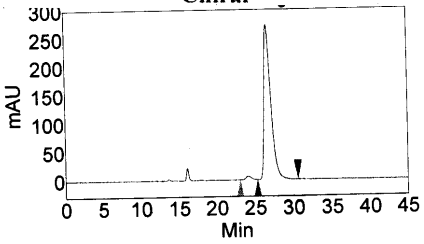
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic



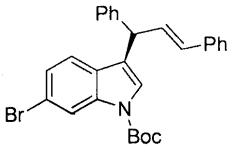
Index	Time [Min]	Area % [%]
1	24.24	49.952
2	27.08	50.048
Total		100.000

Chiral



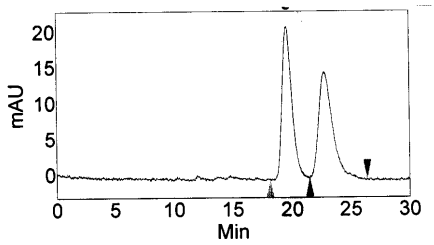
Index	Time [Min]	Area % [%]
1	24.08	1.885
2	26.64	98.115
Total		100.000

Table 2, entry 10



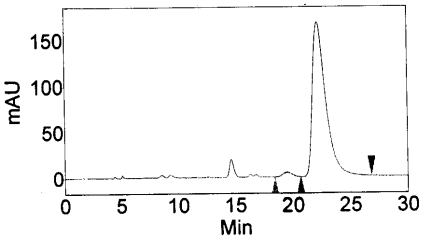
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 254 nm

Racemic

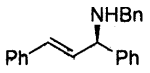


Index	Time [Min]	Area % [%]
1	19.57	50.027
2	22.79	49.973
Total		100.000

Chiral



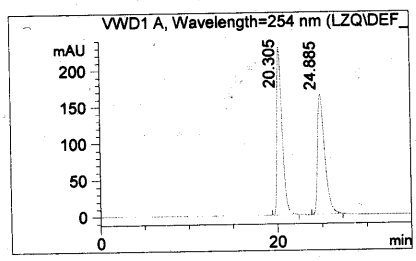
Index	Time [Min]	Area % [%]
1	19.45	2.371
2	22.16	97.629
Total		100.000



8a

HPLC Conditions: Column: Chiralcel OJ-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

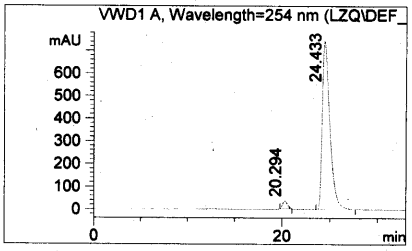
Racemic



Signal 1: VWD1 A, Wavelength=254 nm

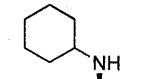
Peak #	RT [min]	Area %	Area
1	20.305	50.362	9.247e3
2	24.885	49.638	9.114e3

Chiral



Signal 1: VWD1 A, Wavelength=254 nm

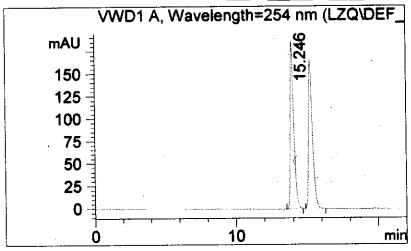
Peak #	RT [min]	Area %	Area
1	20.294	2.815	1.193e3
2	24.433	97.185	4.119e4



8b

HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (99/1); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

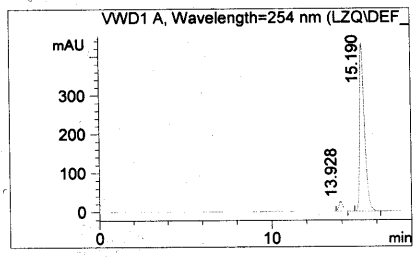
Racemic



Signal 1: VWD1 A, Wavelength=254 nm

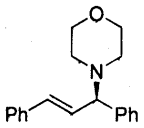
Peak #	RT [min]	Area %	Area
1	13.961	49.995	3.185e3
2	15.246	50.005	3.186e3

Chiral



Signal 1: VWD1 A, Wavelength=254 nm

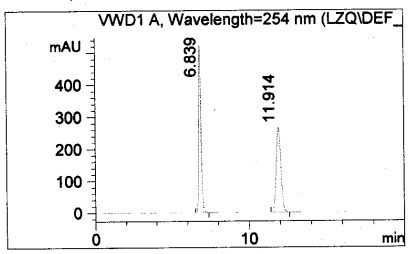
Peak #	RT [min]	Area %	Area
1	13.928	4.507	392.000
2	15.190	95.493	8.306e3



8c

HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV 254 nm

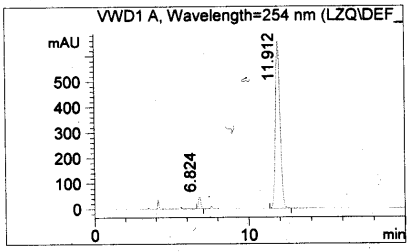
Racemic



Signal 1: VWD1 A, Wavelength=254 nm

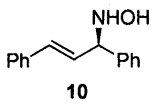
Peak #	RT [min]	Area %	Area
1	6.839	50.070	5.509e3
2	11.914	49.930	5.493e3

Chiral



Signal 1: VWD1 A, Wavelength=254 nm

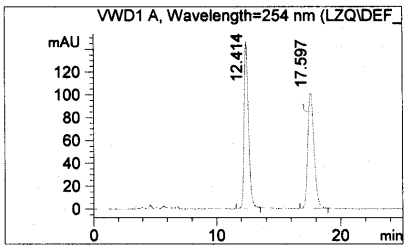
Peak #	RT [min]	Area %	Area
1	6.824	3.600	506.067
2	11.912	96.400	1.355e4



10

HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate:** 1.0 mL/min; **Detection:** UV 254 nm

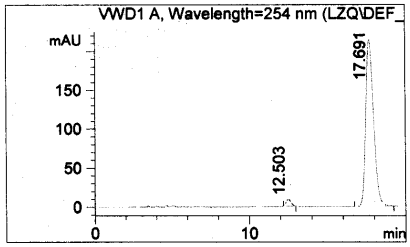
Racemic



Signal 1: VWD1 A, Wavelength=254 nm

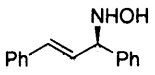
Peak #	RT [min]	Area %	Area
1	12.414	50.075	3.531e3
2	17.597	49.925	3.520e3

Chiral



Signal 1: VWD1 A, Wavelength=254 nm

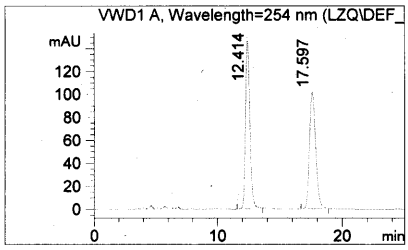
Peak #	RT [min]	Area %	Area
1	12.503	2.470	188.158
2	17.691	97.530	7.429e3



10 (recrystallization)

HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate:** 1.0 mL/min; **Detection:** UV 254 nm

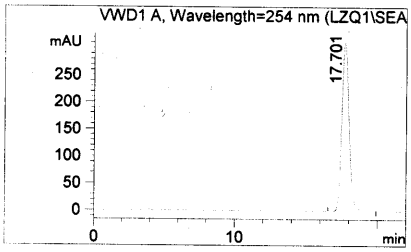
Racemic



Signal 1: VWD1 A, Wavelength=254

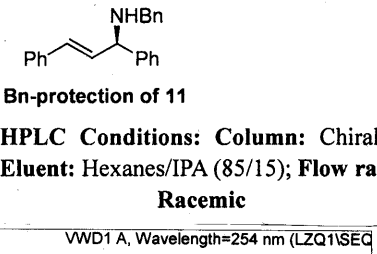
Peak #	RT [min]	Area %	Area
1	12.414	50.136	3.535e3
2	17.597	49.864	3.515e3

Chiral



Signal 1: VWD1 A, Wavelength=254 nm

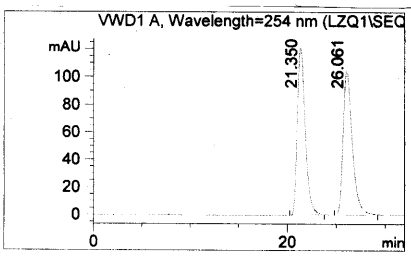
Peak #	RT [min]	Area %	Area
1	17.701	100.000	1.096e4



Bn-protection of 11

HPLC Conditions: Column: Chiralcel OJ-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

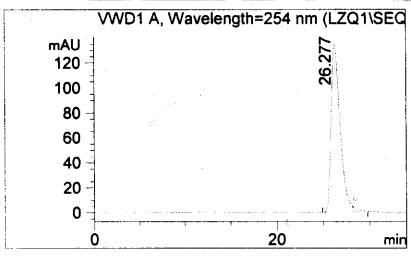
Racemic



Signal 1: VWD1 A, Wavelength=254 nm

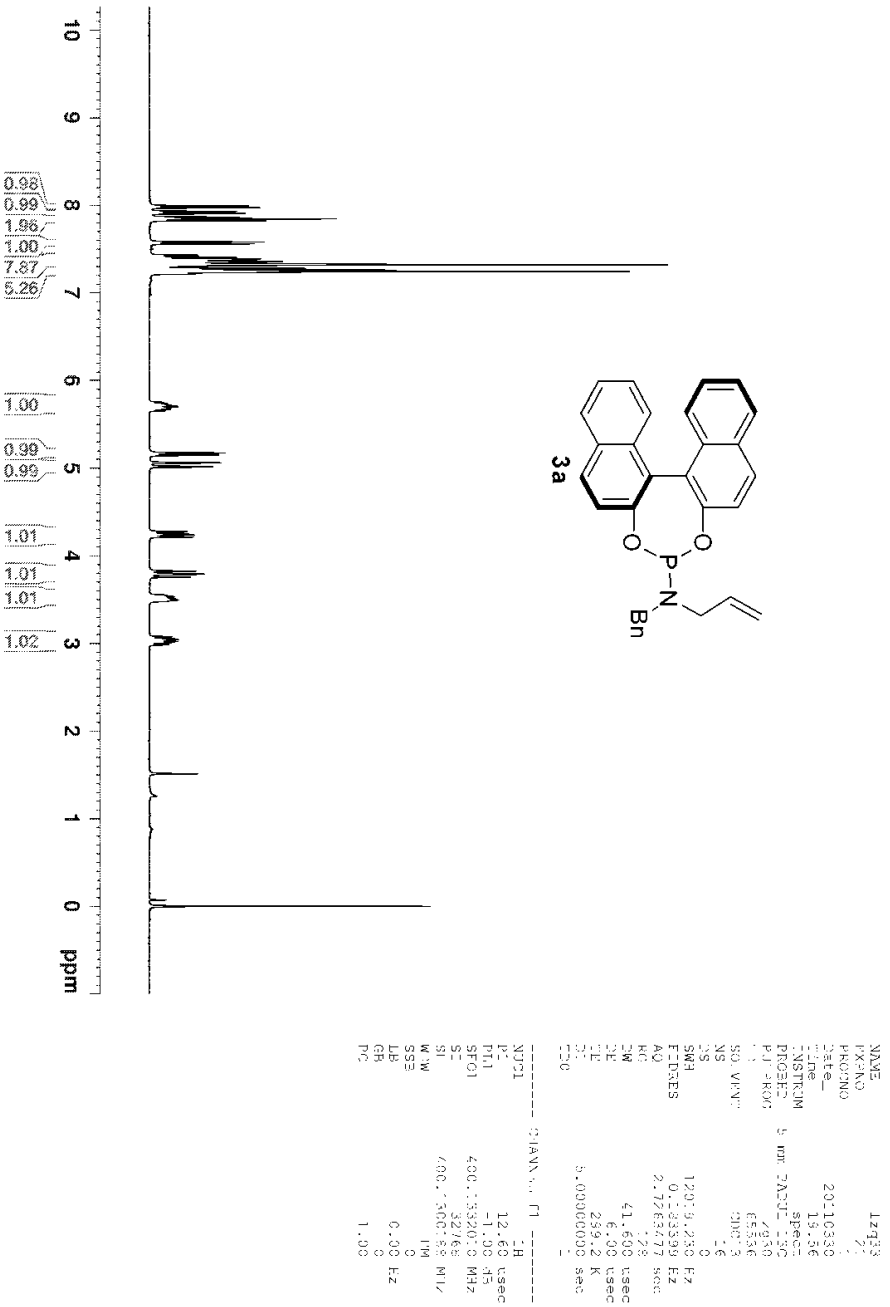
Peak #	RT [min]	Area %	Area
1	21.350	50.100	6.856e3
2	26.061	49.900	6.829e3

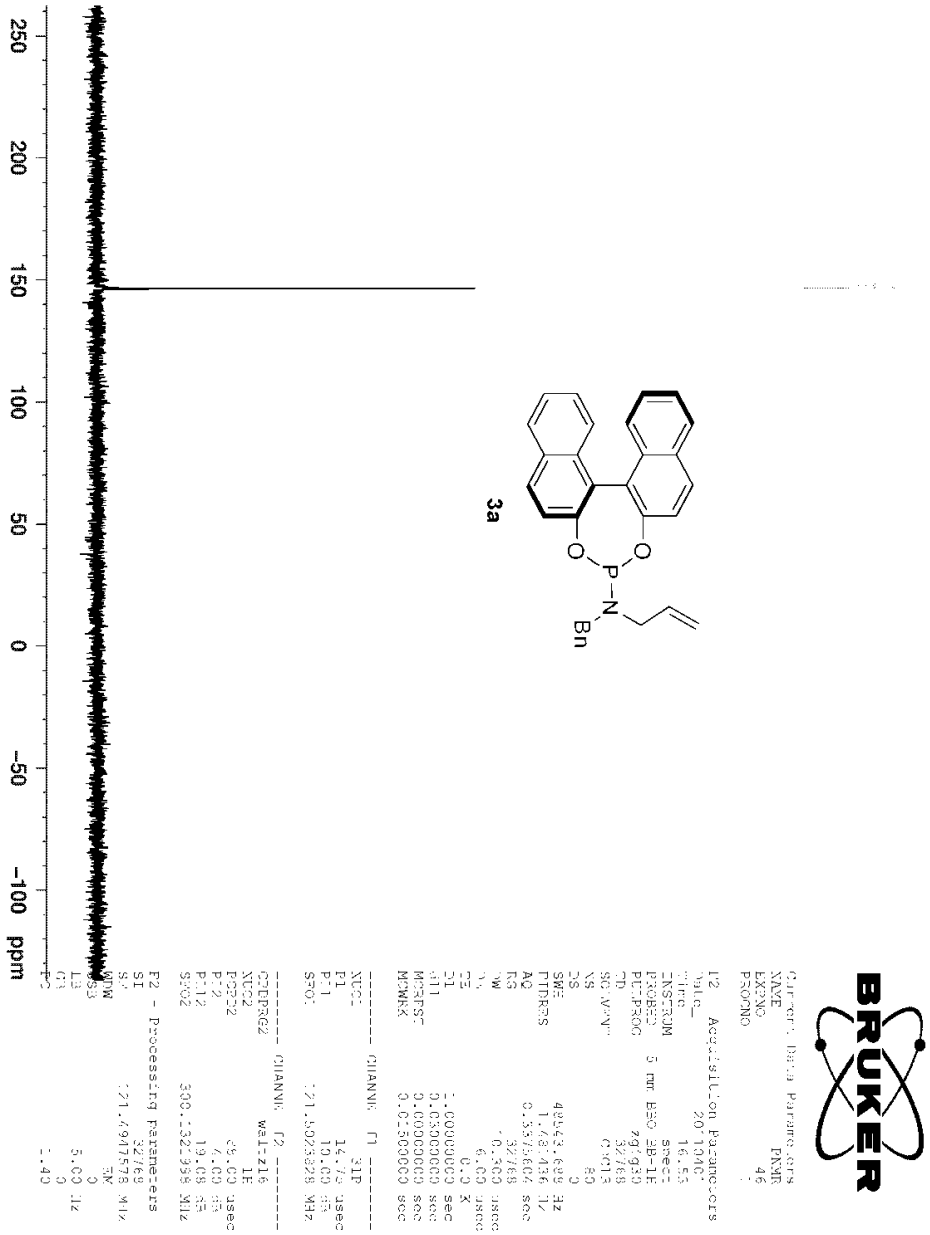
Chiral

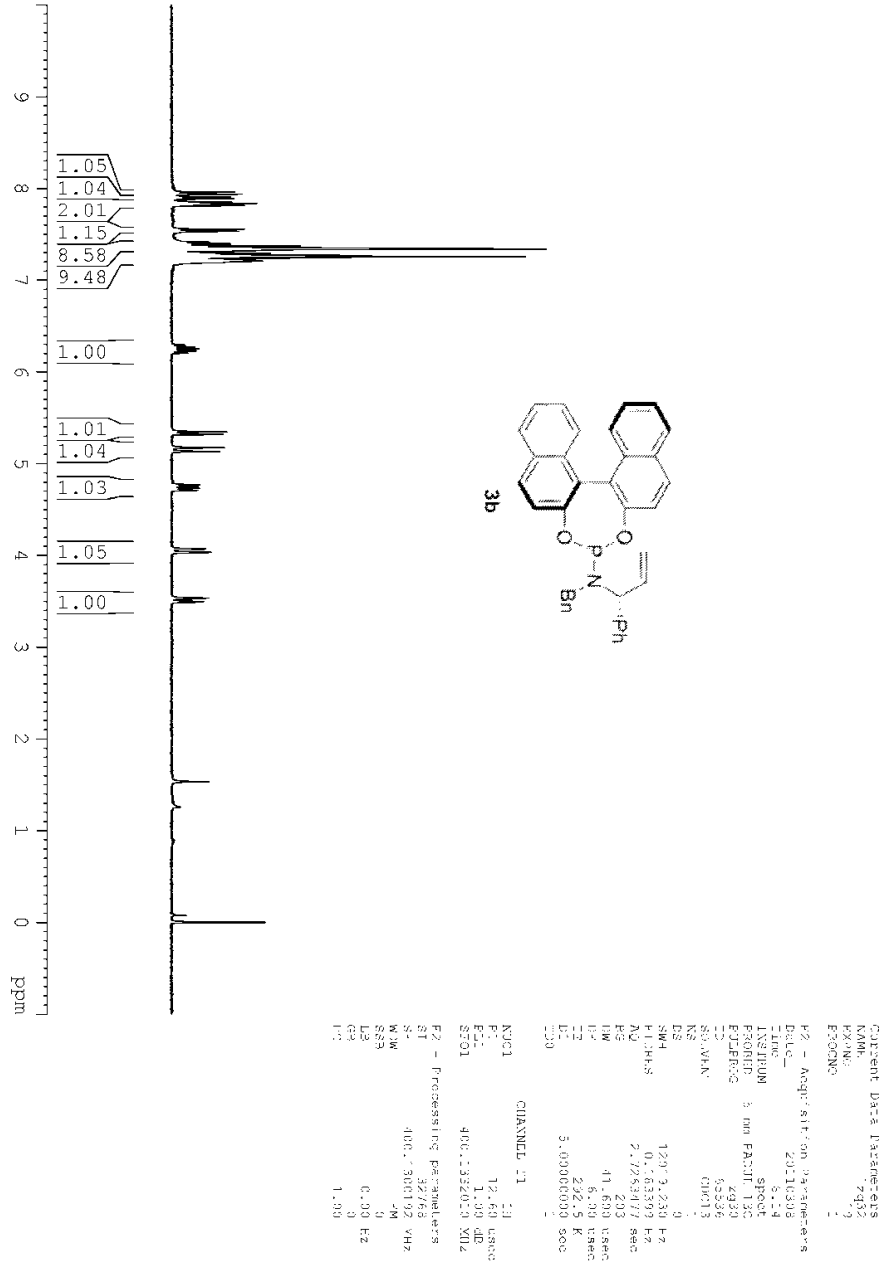


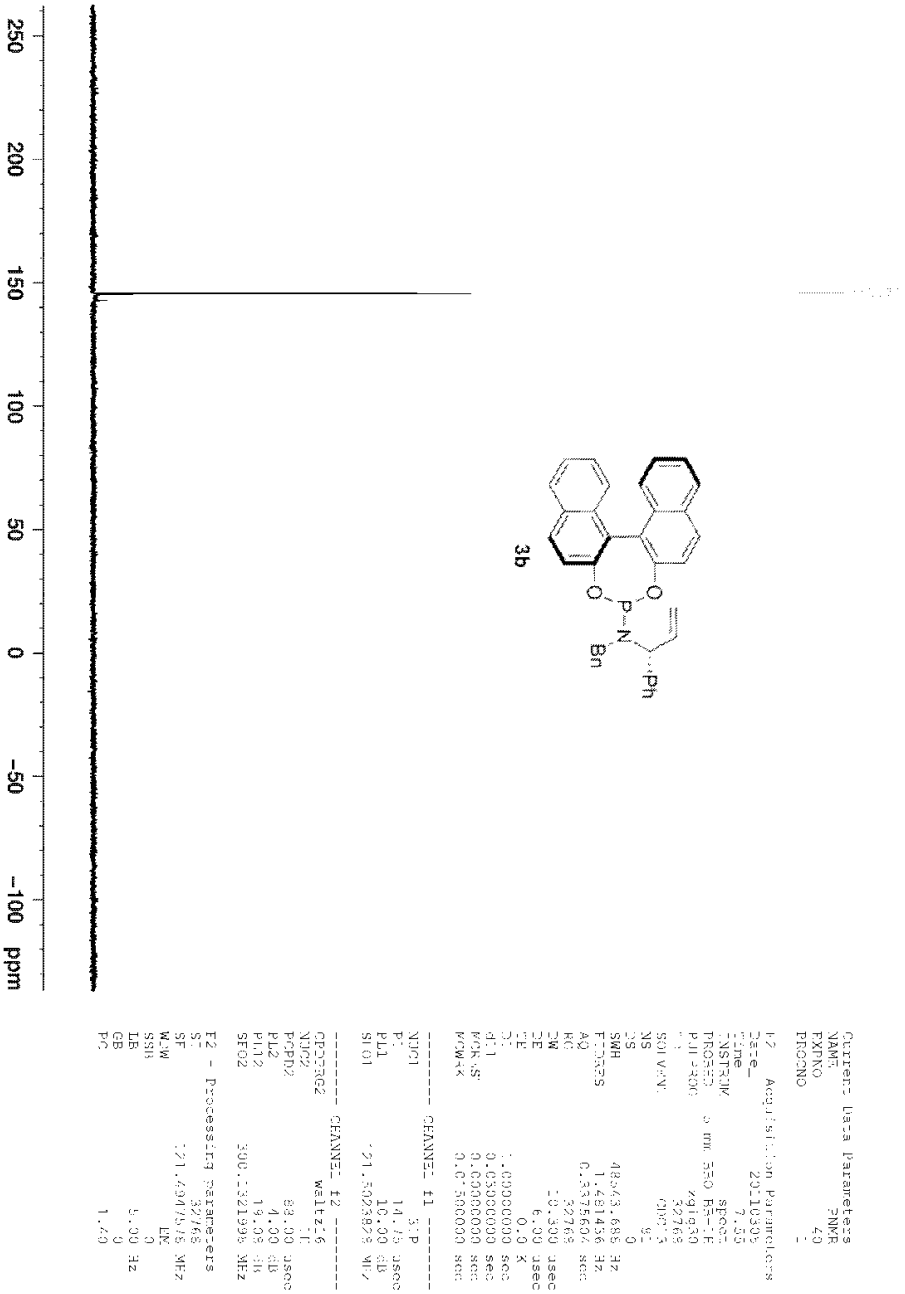
Signal 1: VWD1 A, Wavelength=254 nm

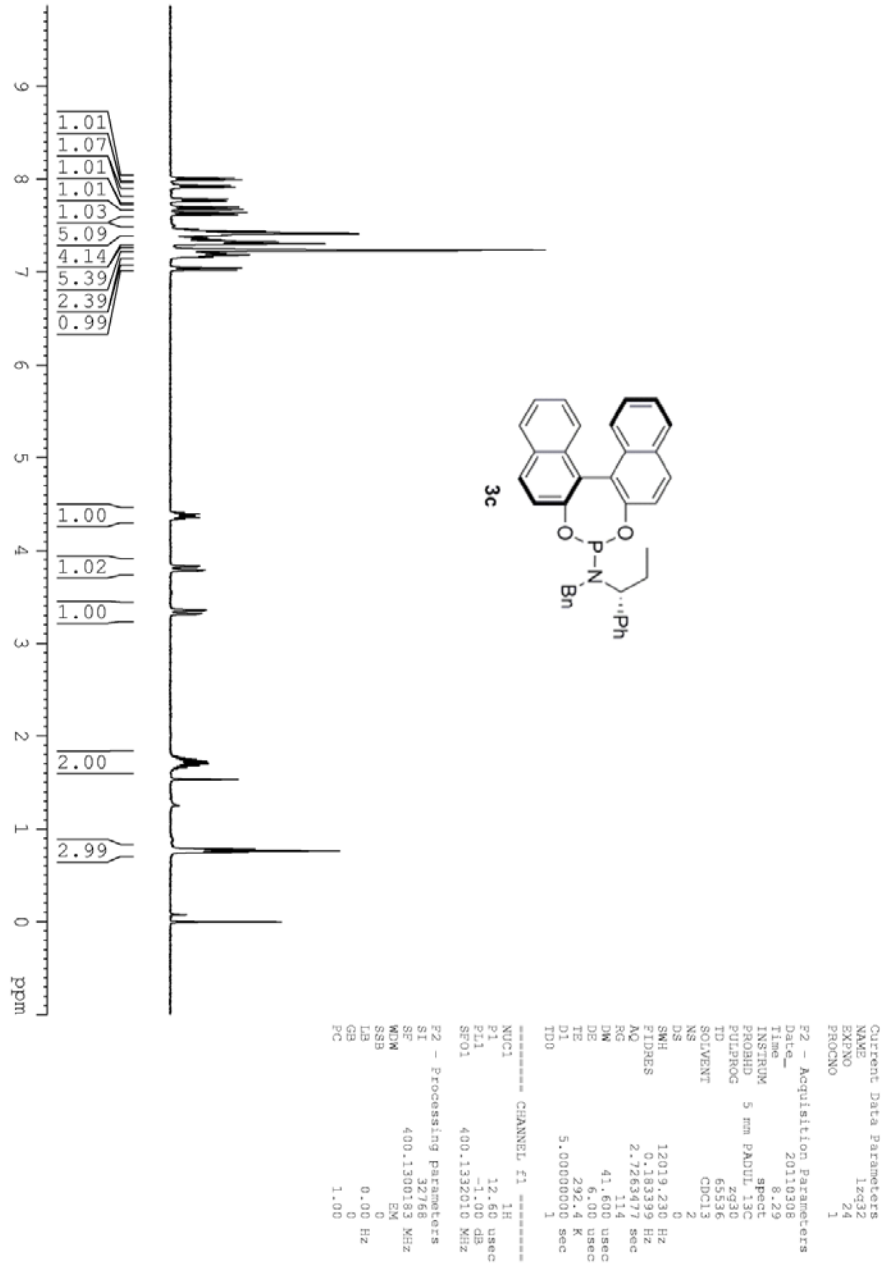
Peak #	RT [min]	Area %	Area
1	26.277	100.000	9.251e3


0.98
0.99
1.96
1.00
7.87
5.26
1.00
0.99
0.99
1.01
1.01
1.01
1.02
10
9
8
7
6
5
4
3
2
1
0
ppm
3a
P
N
O
O
Bn

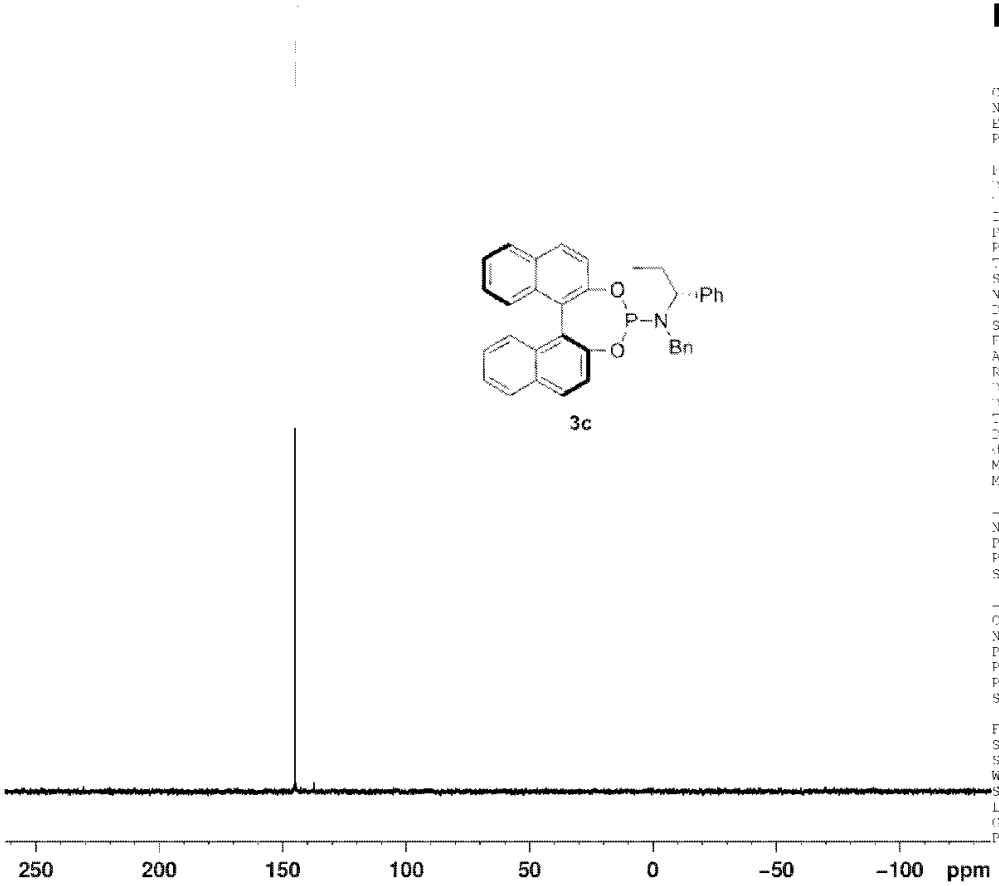

3a
Bn
250
200
150
100
50
0
-50
-100
ppm


1.05
1.04
2.01
1.15
8.58
9.48
1.00
1.01
1.04
1.03
1.05
1.00
ppm
3b
O
O
P
N
Bn
Ph


250
200
150
100
50
0
-50
-100
ppm
3b
O
O
P
N
Bn
Ph

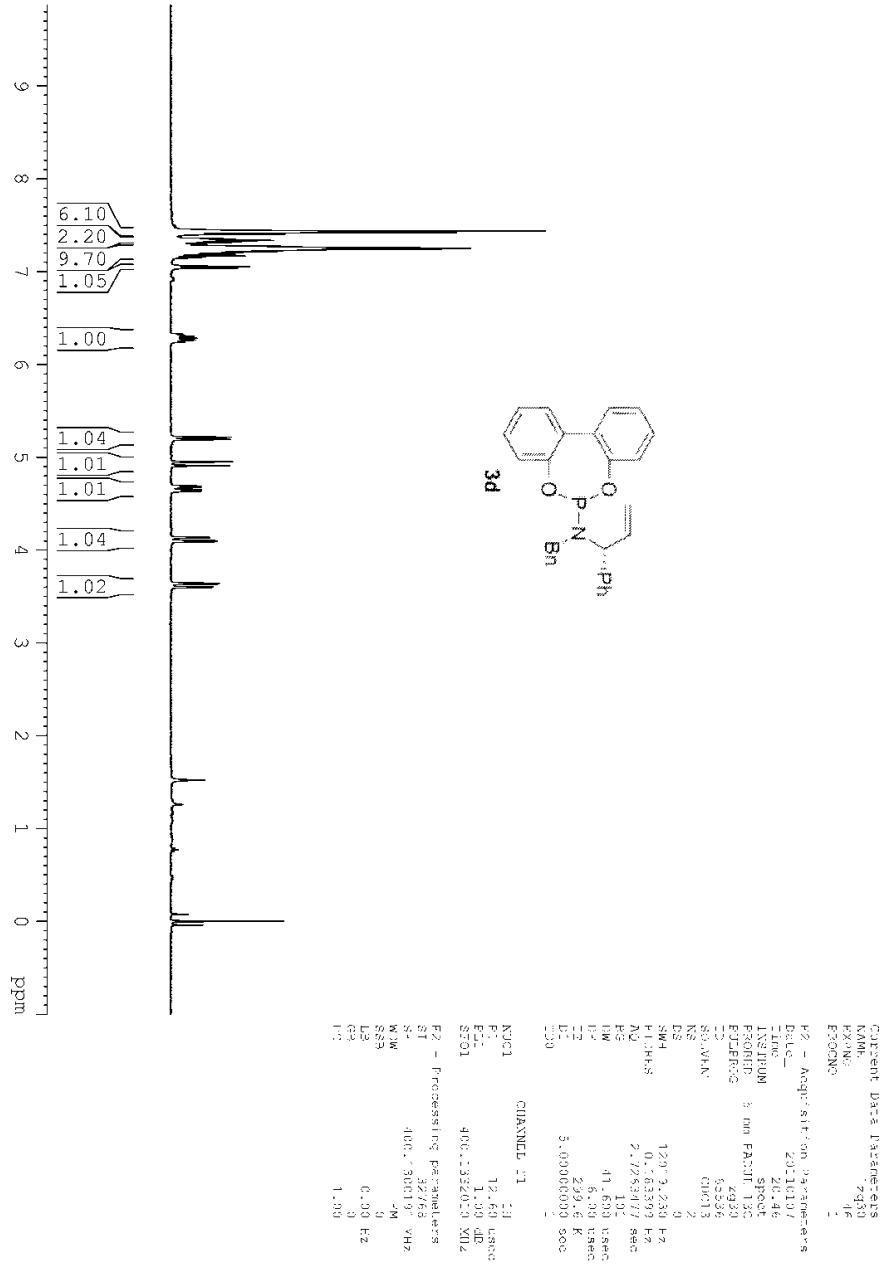

1.01
1.07
1.01
1.01
1.03
5.09
4.14
5.39
2.39
0.99
1.00
1.02
1.00
2.00
2.99
ppm
3c
O
O
P–N
Bn
Ph
Current Data Parameters
NAME 1zq32
EXPNO 24
PROCNO 1
F2 – Acquisition Parameters
Date_ 20110308
Time 8.29
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 0
SWH 12019.230 Hz
FIDRES 0.183339 Hz
AQ 2.7263477 sec
RG 114
DW 41.600 usec
DE 6.00 usec
TE 292.4 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.60 usec
PL1 -1.00 dB
SFO1 400.1332010 MHz
F2 – Processing parameters
SI 32768
SF 400.1300183 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

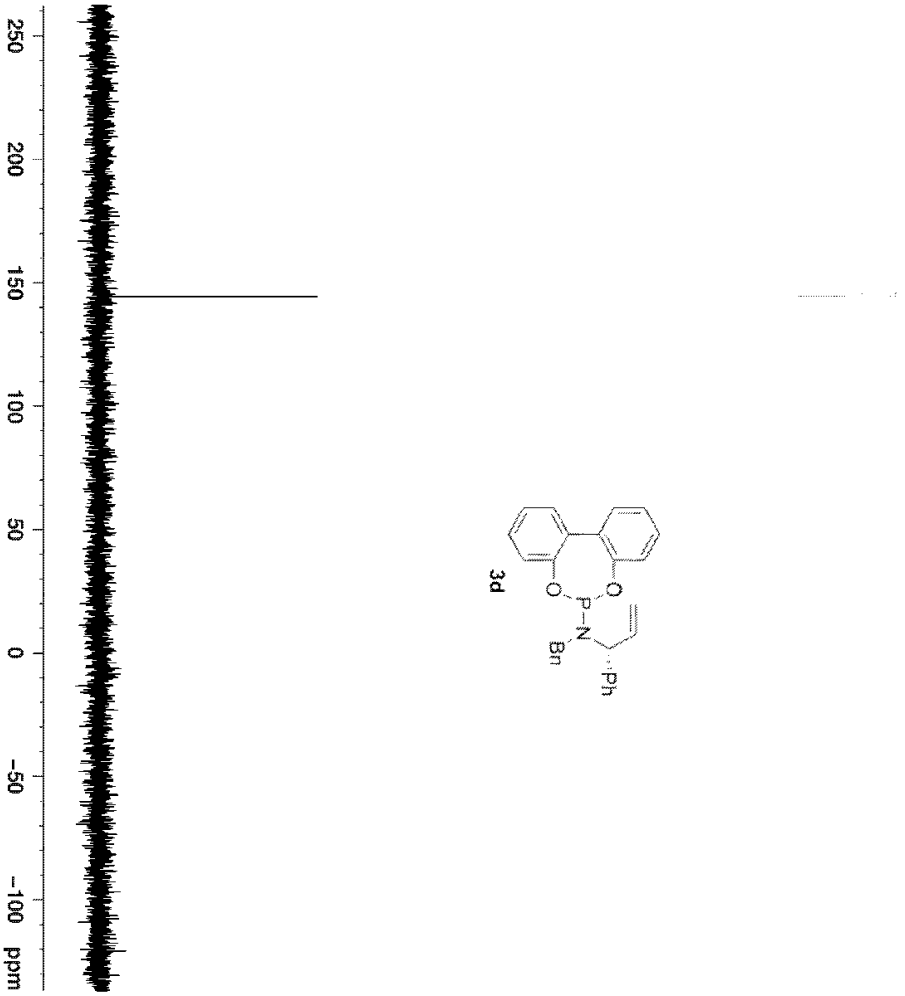
lzq6 31P

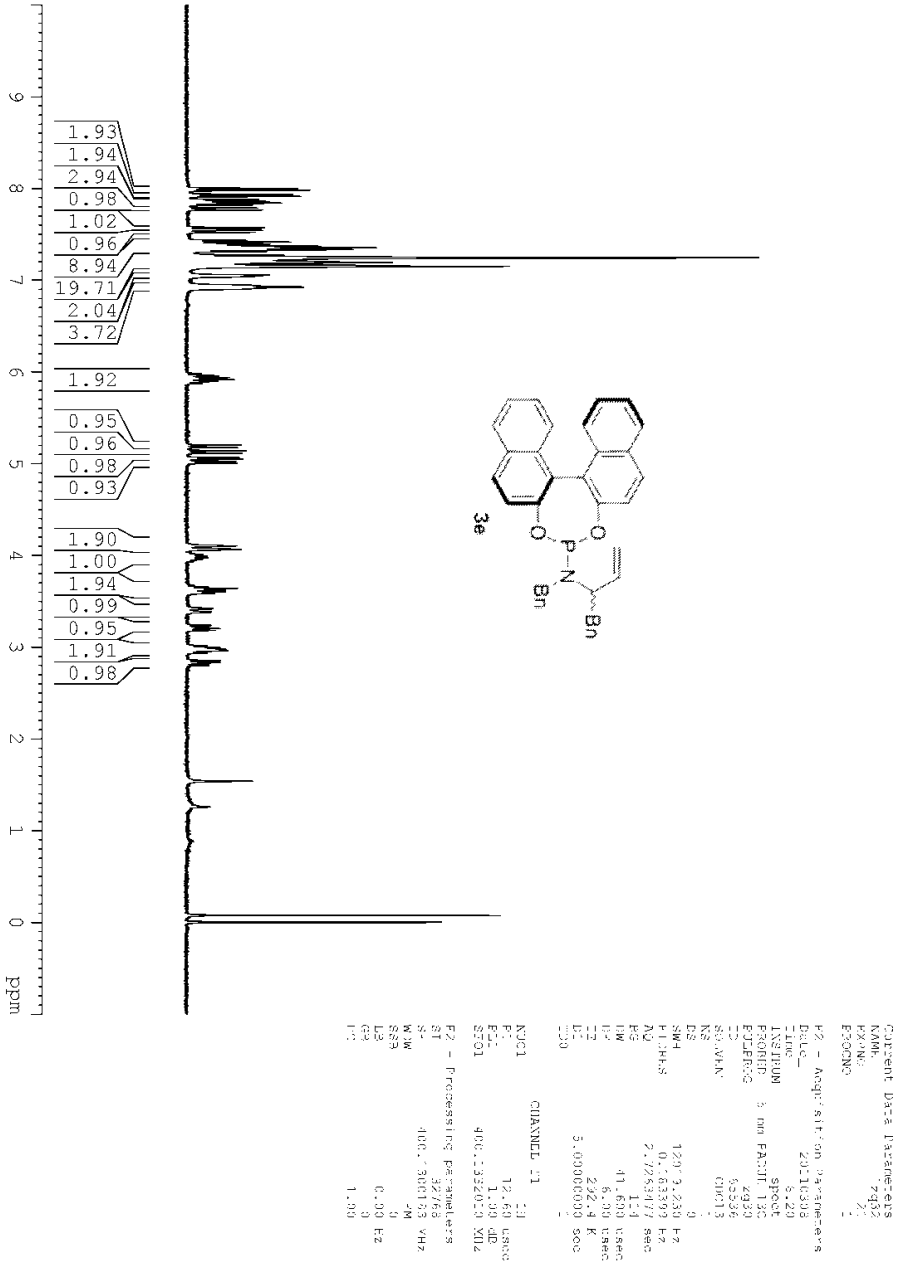


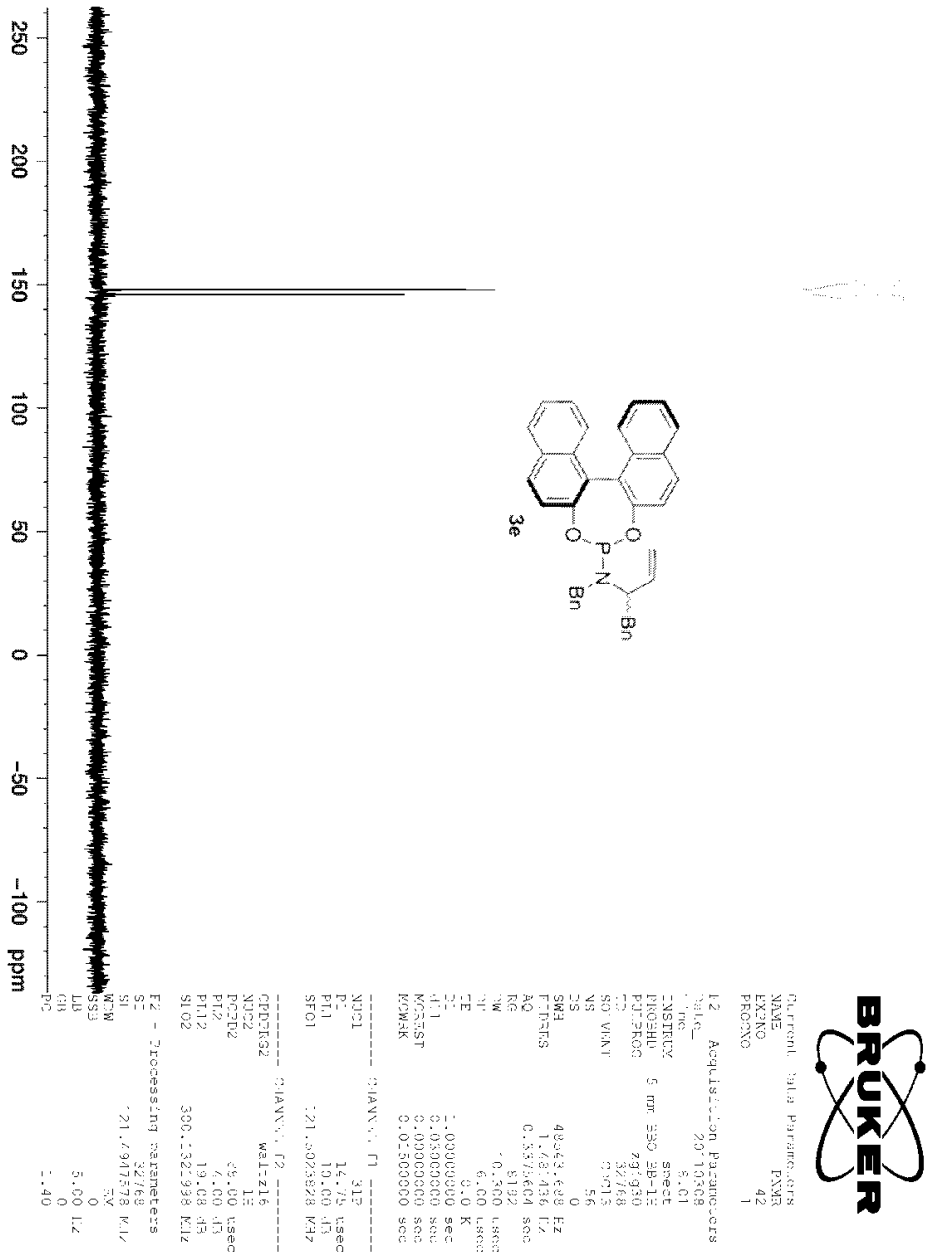
BRUKER

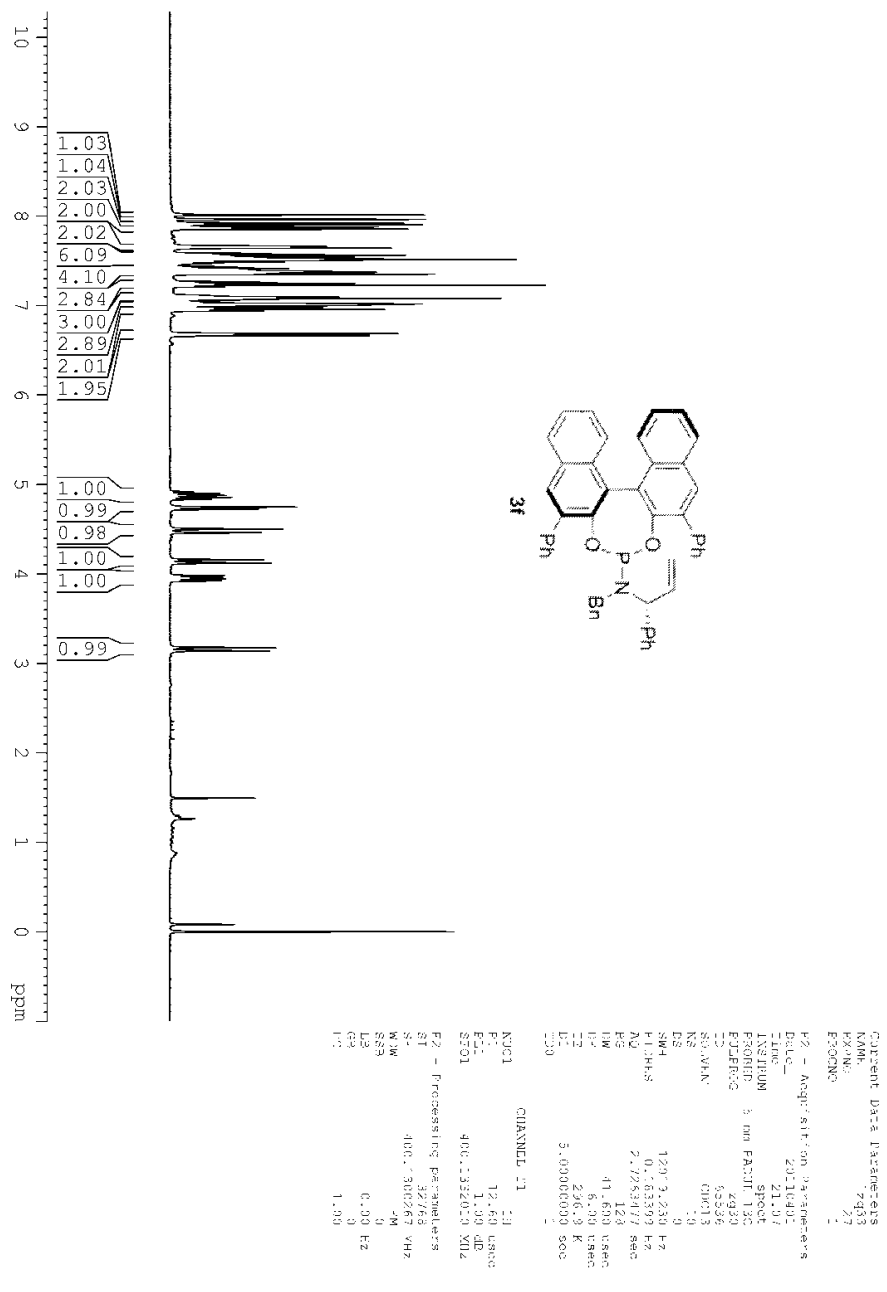
```
Current Data Parameters
NAME                   PXMR
EXPNO                    45
PROCNO                    1

F2 - Acquisition Parameters
Date_               20110308
Time                    8.08
INSTRUM                 spect
PROBHD     5 mm BBO BB-1H
PULPROG              zgig30
TD                      32768
SOLVENT                 CDCl3
NS                         96
DS                          0
SWH                48543.688 Hz
FIDRES              1.481436 Hz
AQ                  0.3375604 sec
RG                       8192
DW                    10.300 usec
DE                     6.00 usec
TE                      0.0 K
D1                  1.00000000 sec
D11                 0.03000000 sec
MCWRST              0.00000000 sec
MCWBK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                     31P
P1                     14.75 usec
PL1                    10.00 dB
SFO1             121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  89.00 usec
PL2                     4.00 dB
PL12                   19.08 dB
SFO2             300.1321998 MHz

F2 - Processing parameters
SI                      32768
SF               121.4947578 MHz
WDW                        EM
SSB                         0
LB                      5.00 Hz
GB                          0
PC                       1.40
```

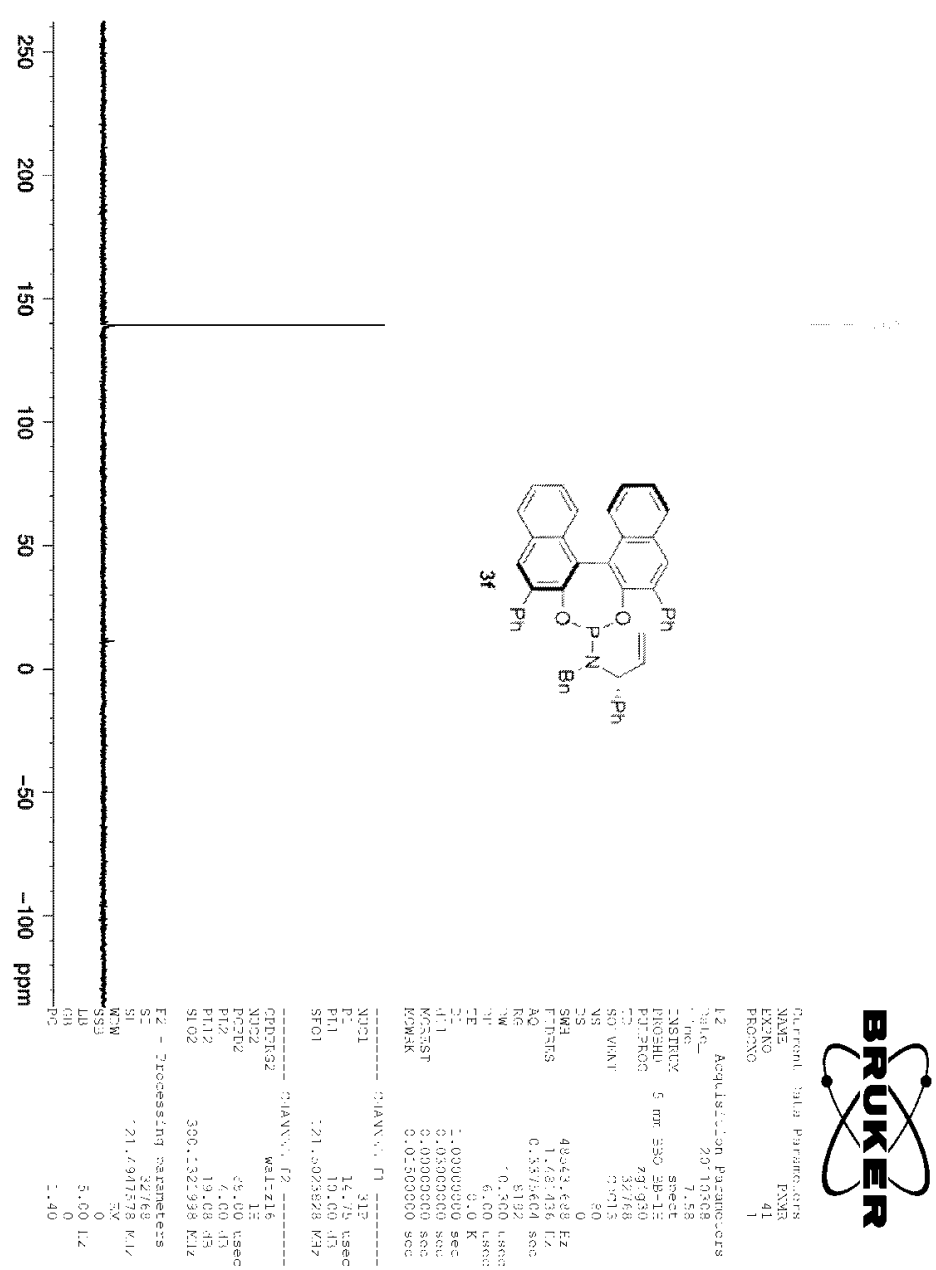

6.10
2.20
9.70
1.05
1.00
1.04
1.01
1.01
1.04
1.02
ppm
3d
O
O
P
N
Bn
Ph

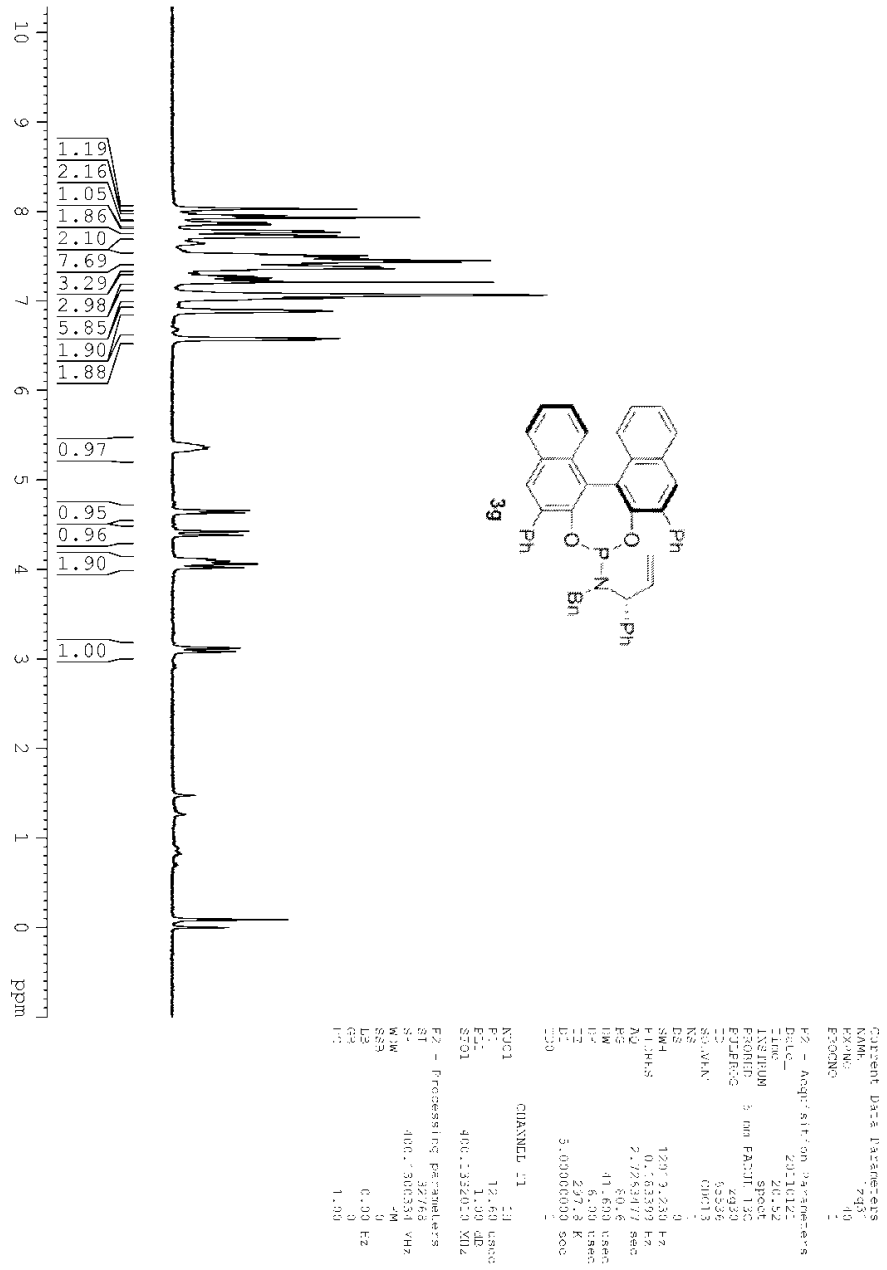

250
200
150
100
50
0
-50
-100
ppm
3d
O
O
P–N
Bn
Ph

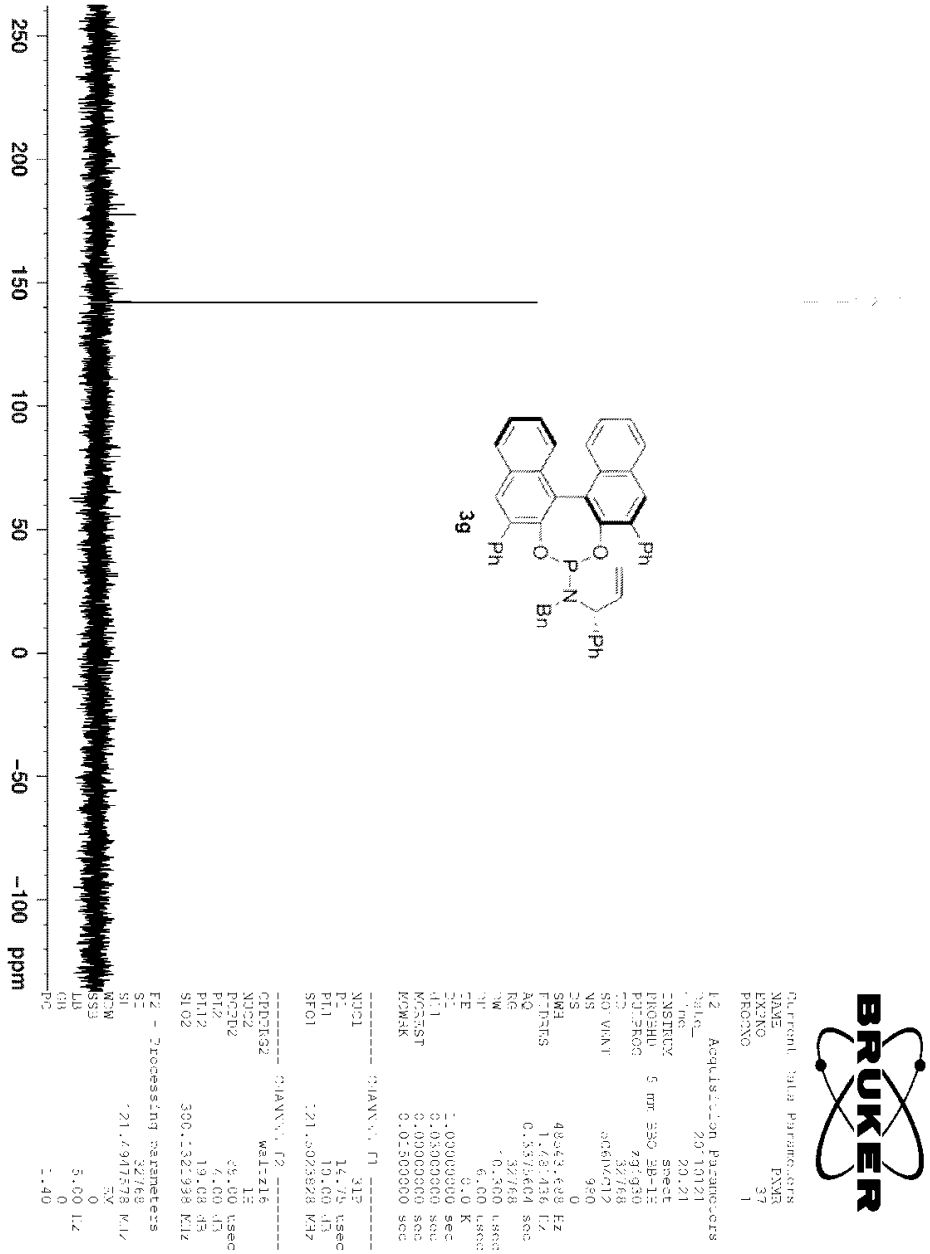

1.93
1.94
2.94
0.98
1.02
0.96
8.94
19.71
2.04
3.72
1.92
0.95
0.96
0.98
0.93
1.90
1.00
1.94
0.99
0.95
1.91
0.98
ppm
3e
P
N
O
Bn
Bn

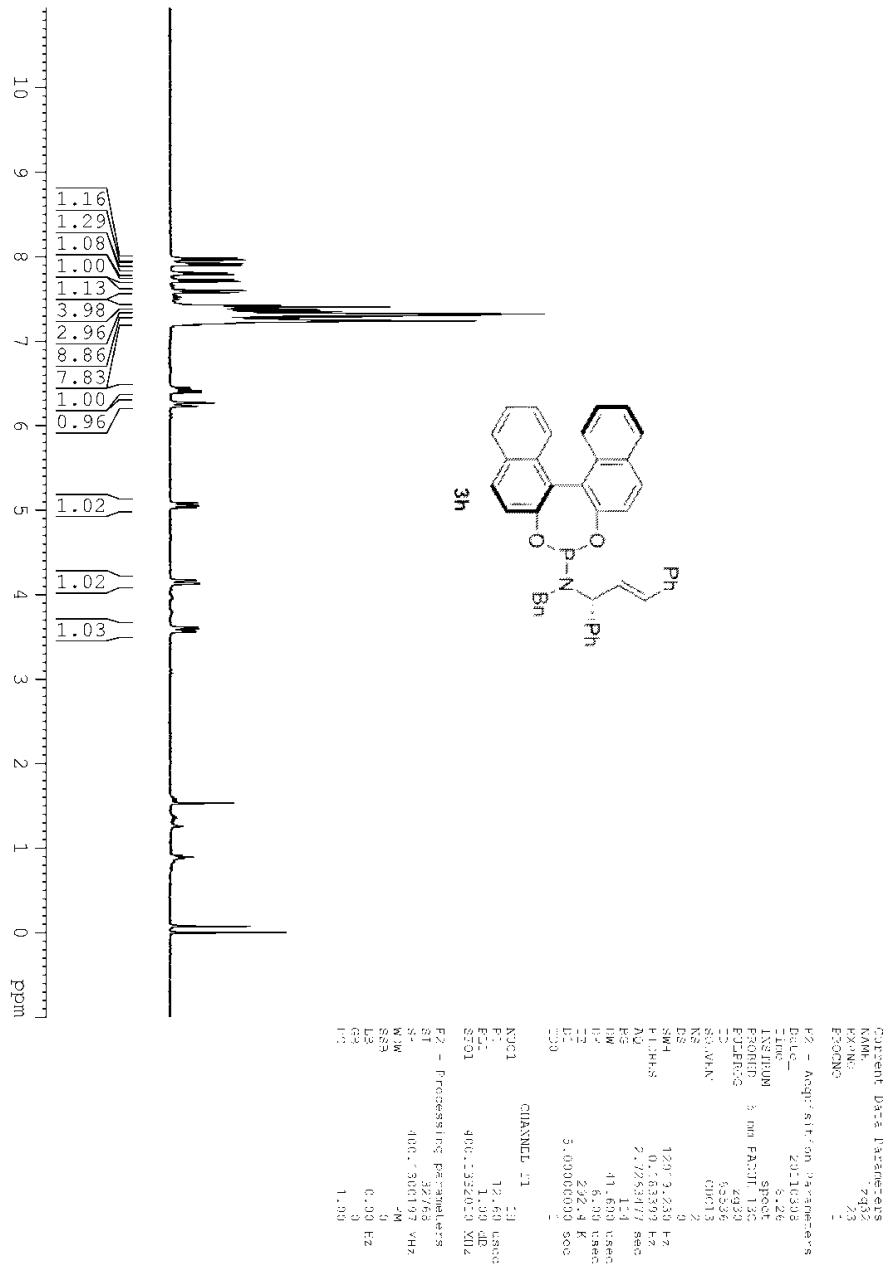

3e
Bn
Bn
250
200
150
100
50
0
-50
-100
ppm

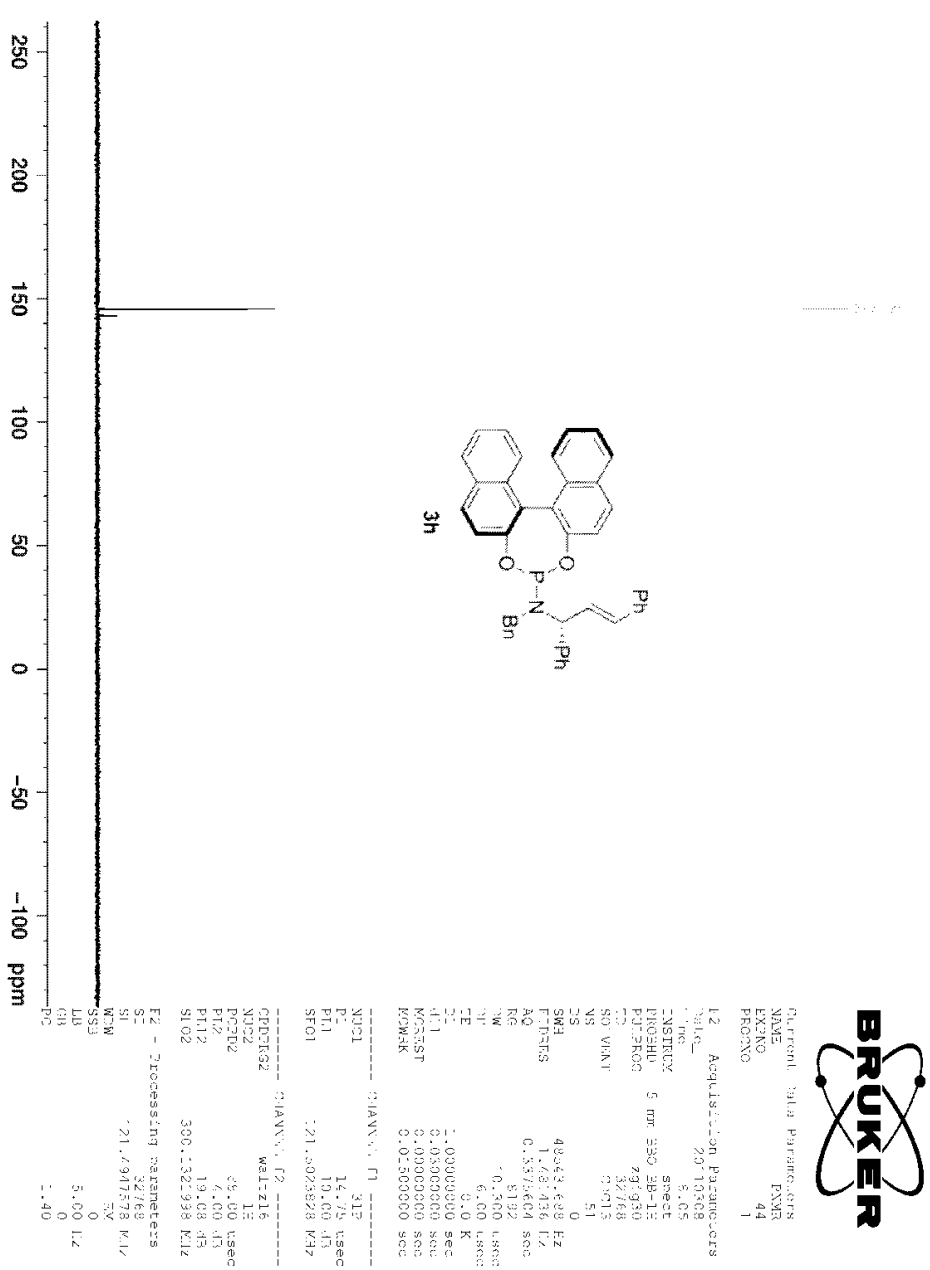

1.03
1.04
2.03
2.00
2.02
6.09
4.10
2.84
3.00
2.89
2.01
1.95
1.00
0.99
0.98
1.00
1.00
0.99
ppm
3f
Ph
O
O
Ph
P
N
Bn
Ph

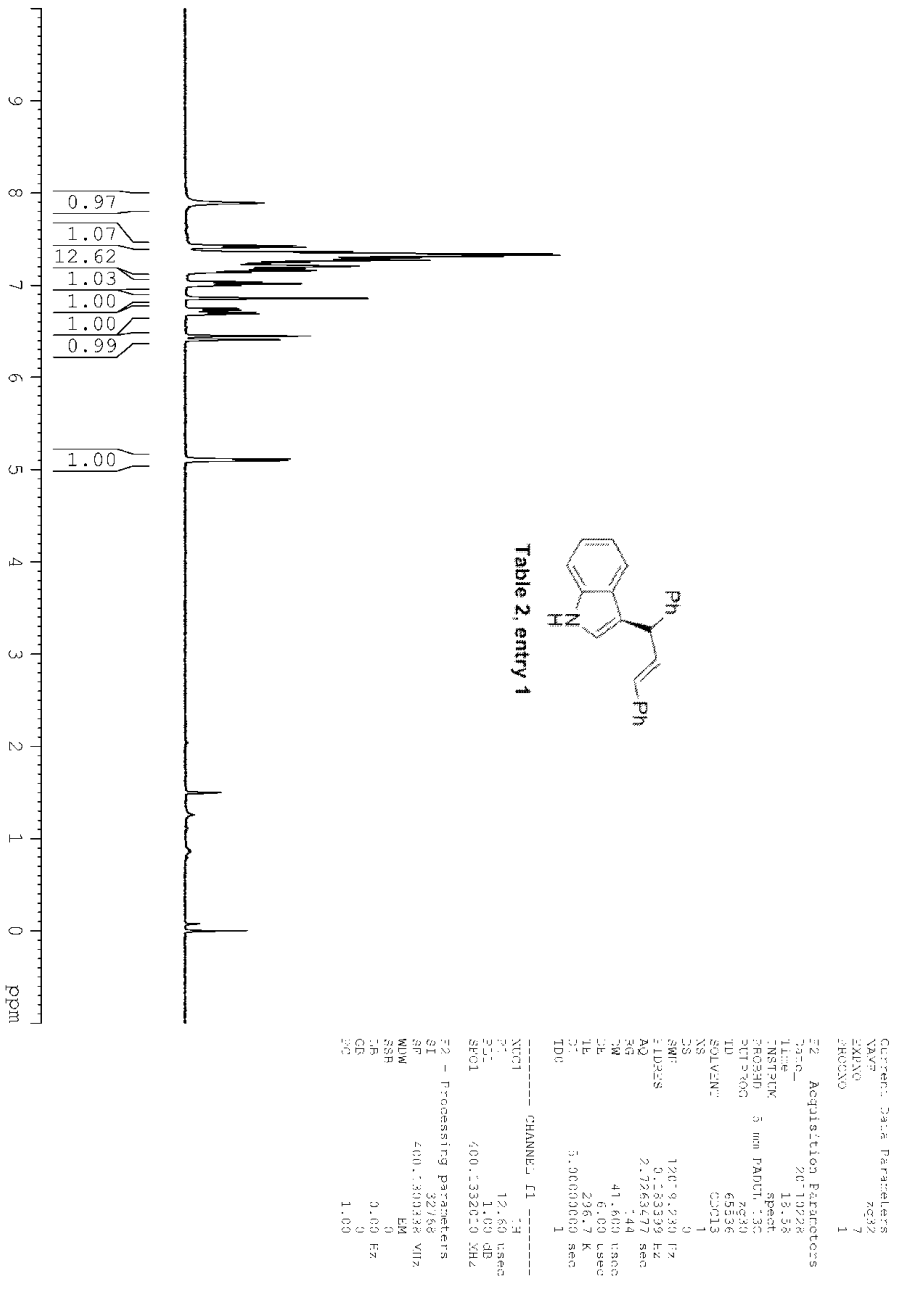

3f
Ph
Ph
Ph
Bn
250
200
150
100
50
0
-50
-100
ppm


1.19
2.16
1.05
1.86
2.10
7.69
3.29
2.98
5.85
1.90
1.88
0.97
0.95
0.96
1.90
1.00
ppm
3g
Ph
Ph
O
O
P
N
Bn
Ph


3g
Ph
Ph
O
O
P
N
Bn
Ph
250
200
150
100
50
0
-50
-100
ppm


1.16
1.29
1.08
1.00
1.13
3.98
2.96
8.86
7.83
1.00
0.96
1.02
1.02
1.03
ppm
3h
Ph
Bn
Ph


3h
Ph
Bn
Ph
250
200
150
100
50
0
-50
-100
ppm


0.97
1.07
12.62
1.03
1.00
1.00
0.99
1.00
ppm
Table 2, entry 1
Ph
Ph
H
N

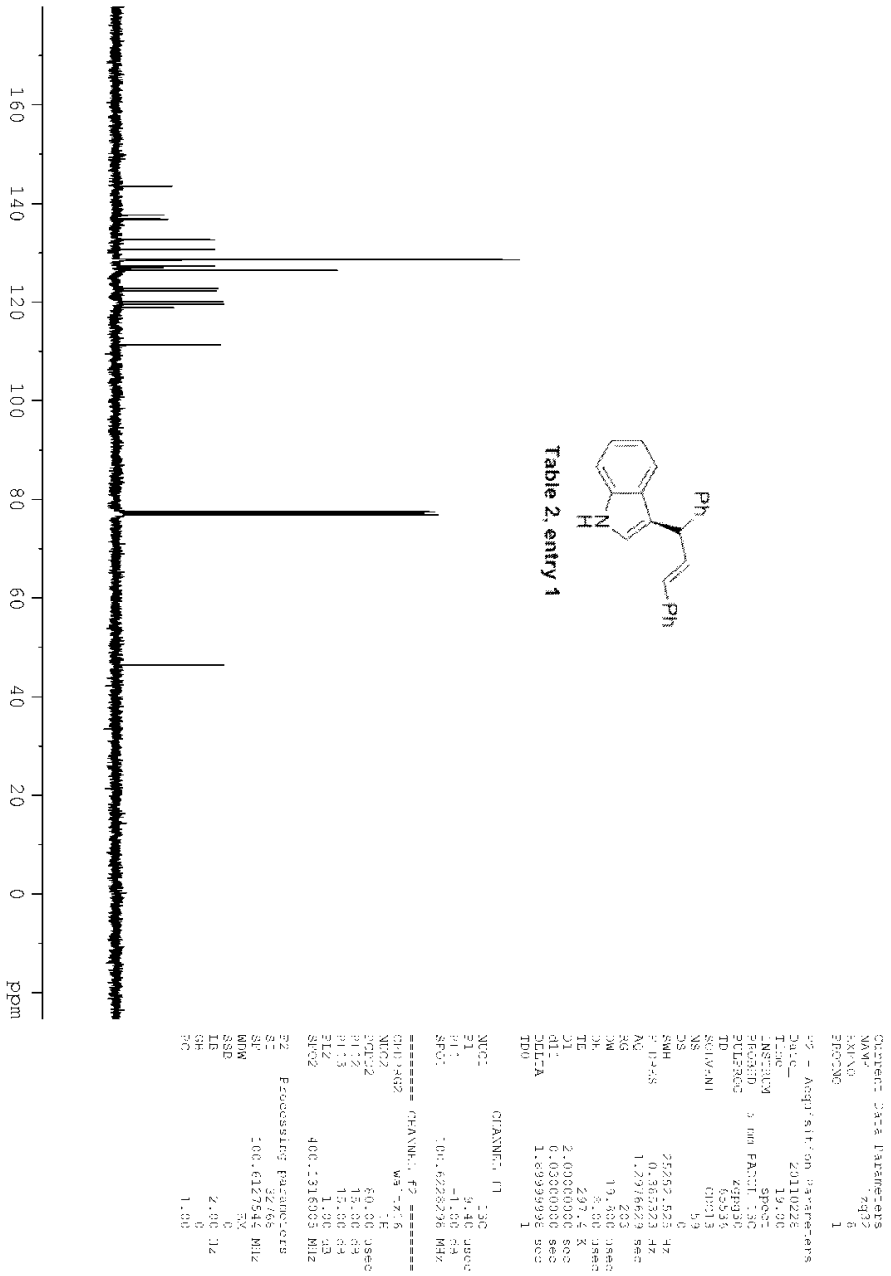
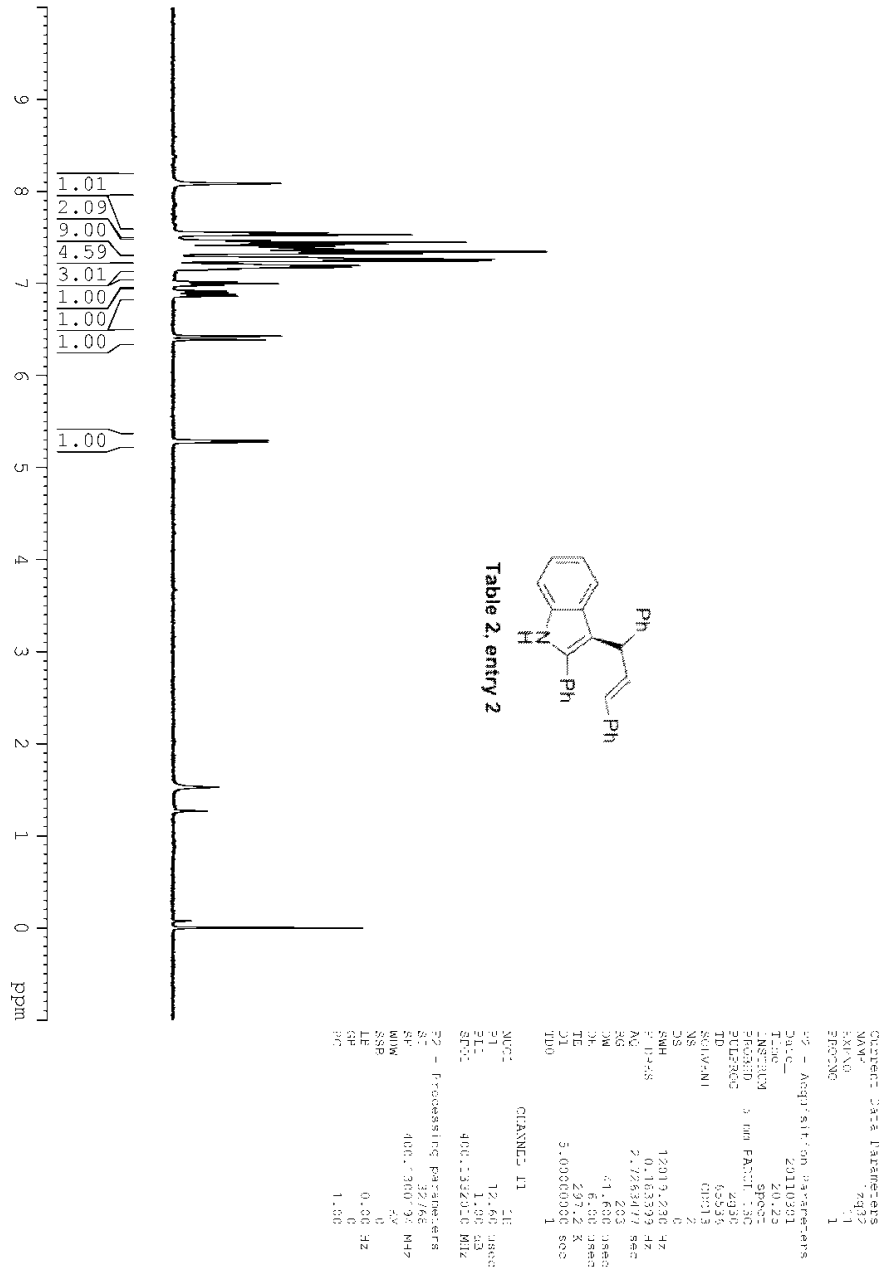


Table 2, entry 1
Ph
Ph
N
H
ppm
160
140
120
100
80
60
40
20
0


1.01
2.09
9.00
4.59
3.01
1.00
1.00
1.00
1.00
ppm
Table 2, entry 2
Ph
Ph
Ph
N
H

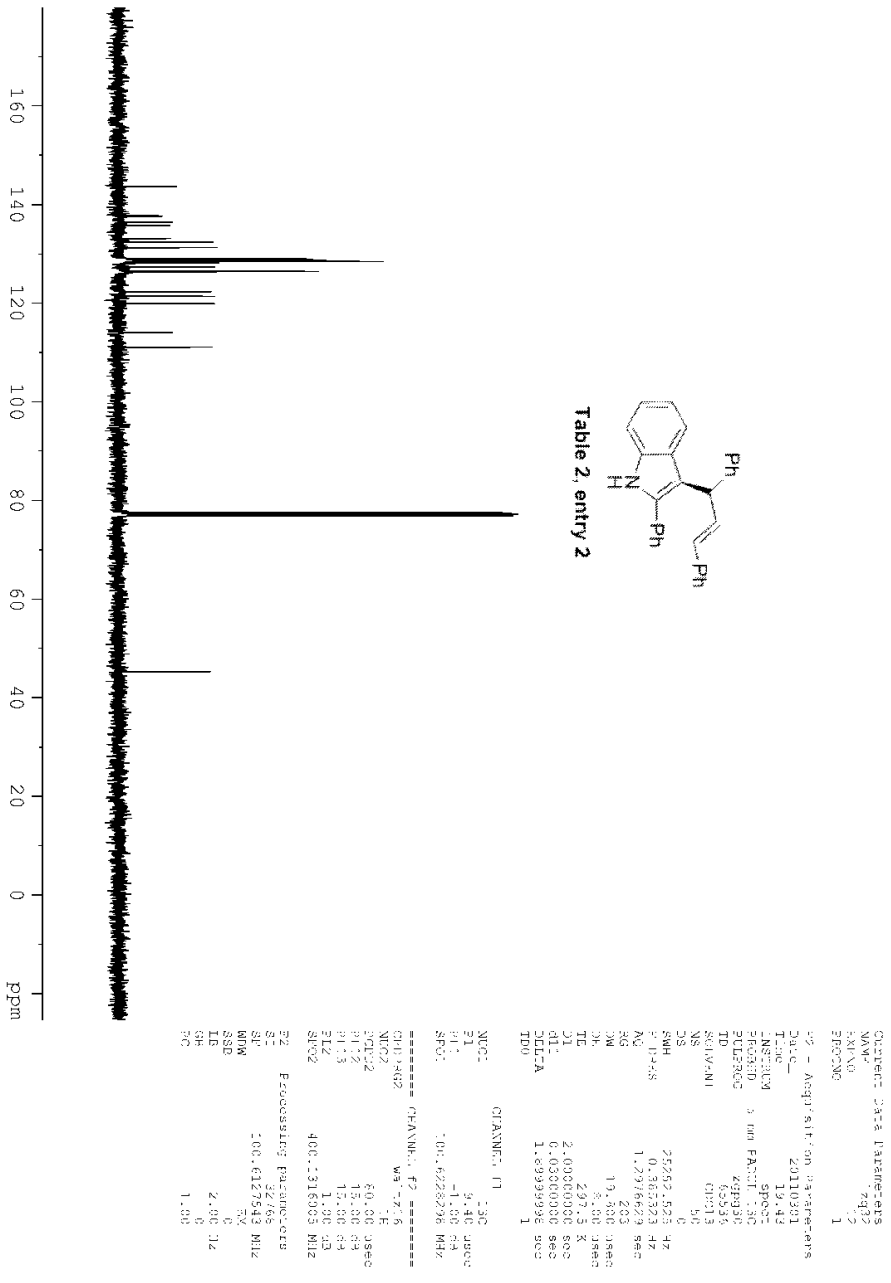
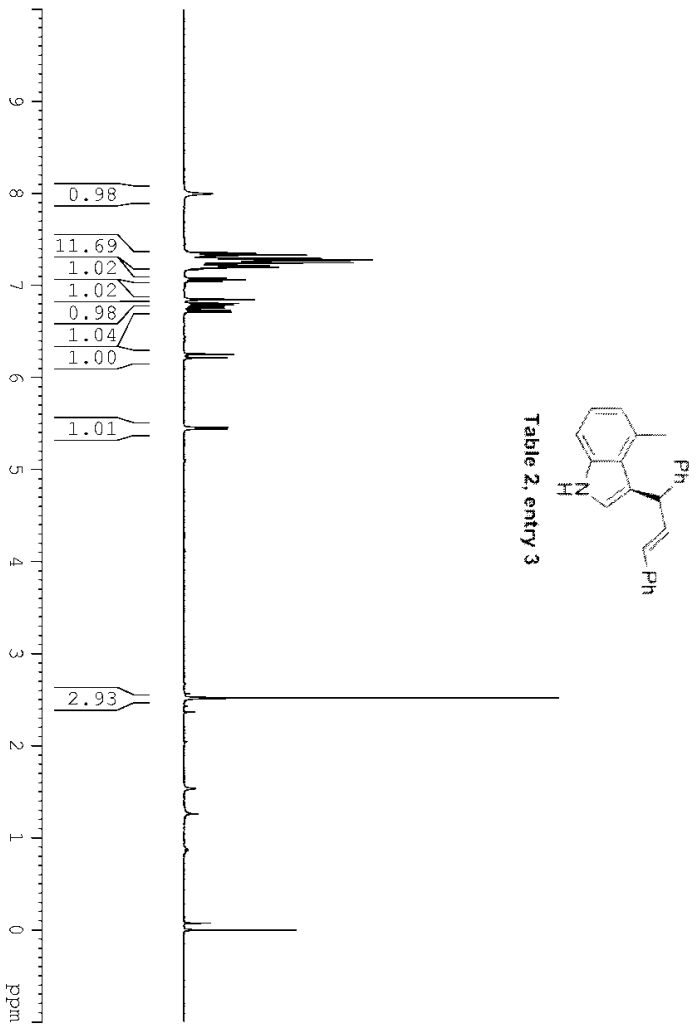


Table 2, entry 2
Ph
Ph
Ph
N
H
ppm
160
140
120
100
80
60
40
20
0


0.98
11.69
1.02
1.02
0.98
1.04
1.00
1.01
2.93
ppm
Table 2, entry 3
Ph
Ph
N
H

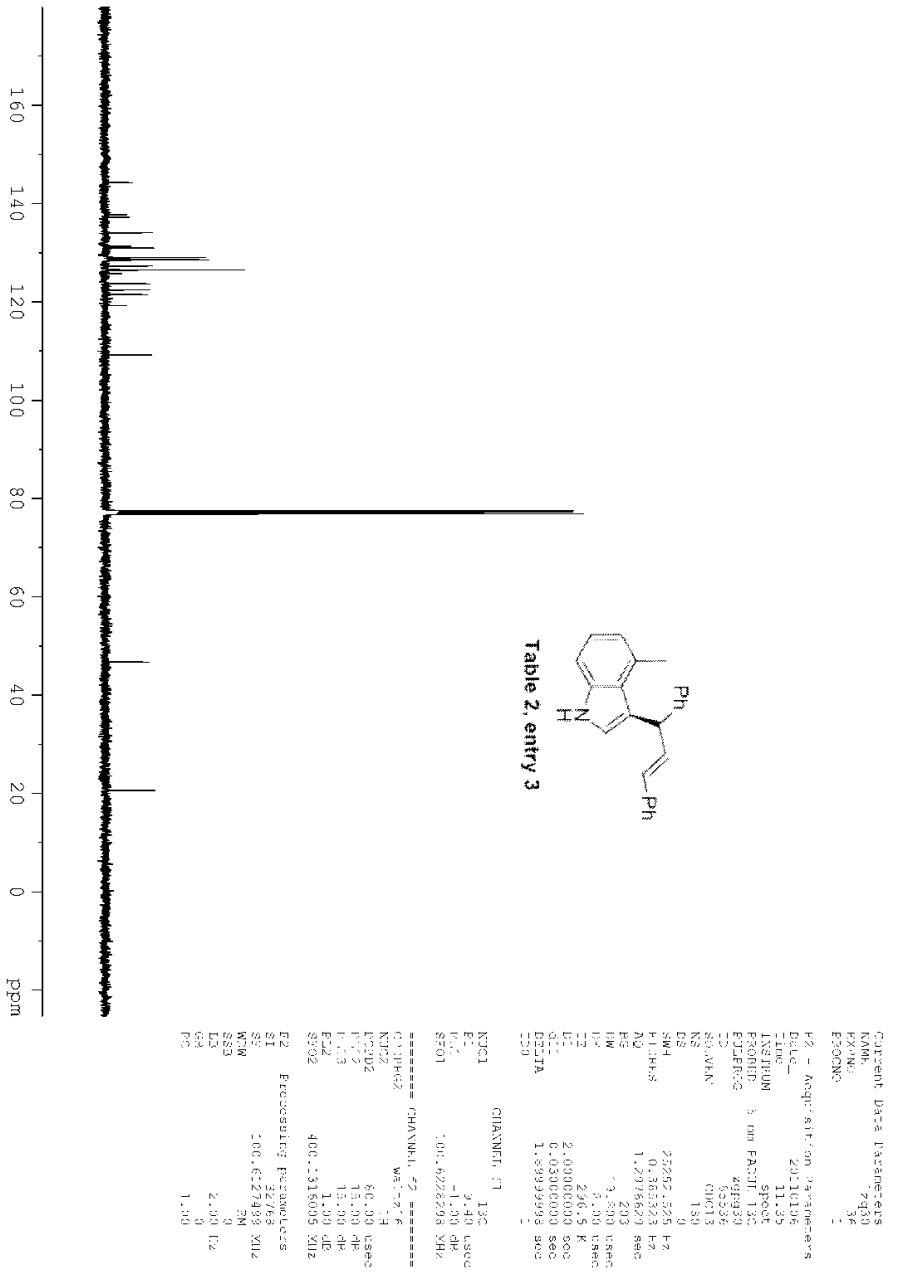
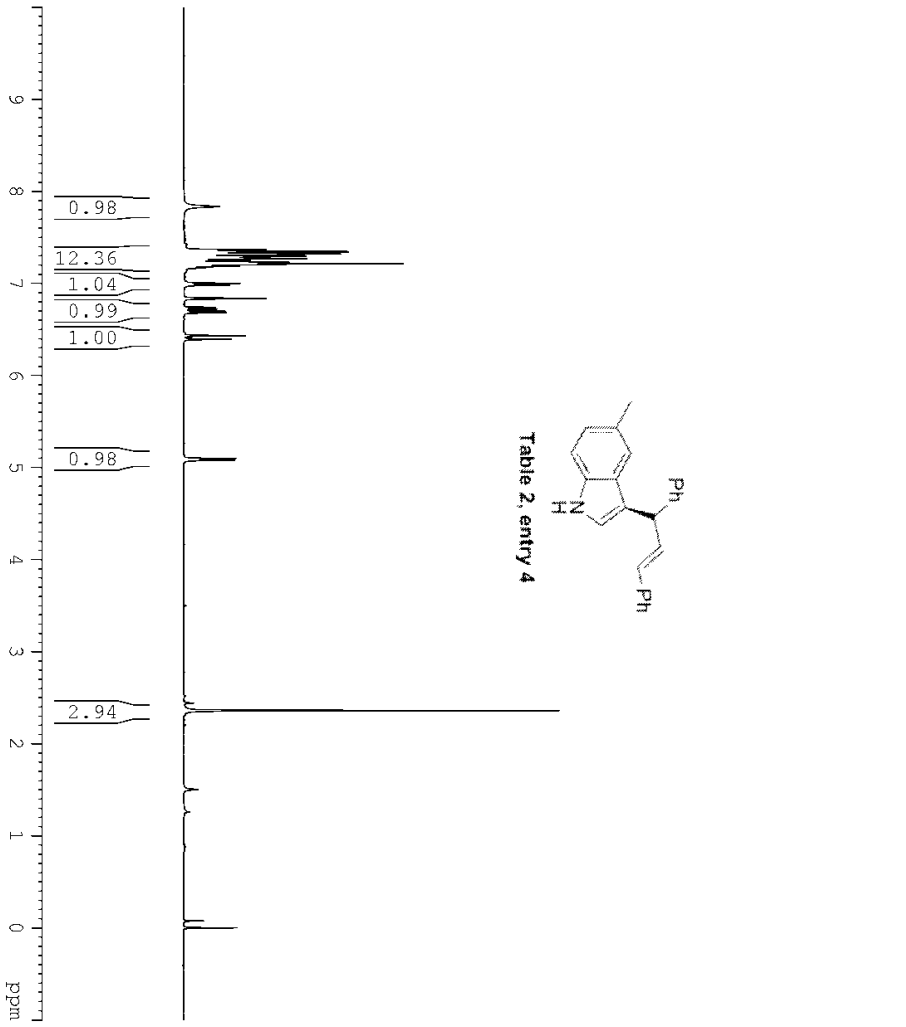


Table 2, entry 3
Ph
Ph
N
H
ppm
160
140
120
100
80
60
40
20
0


0.98
12.36
1.04
0.99
1.00
0.98
2.94
ppm
Table 2, entry 4
Ph
Ph
N
H

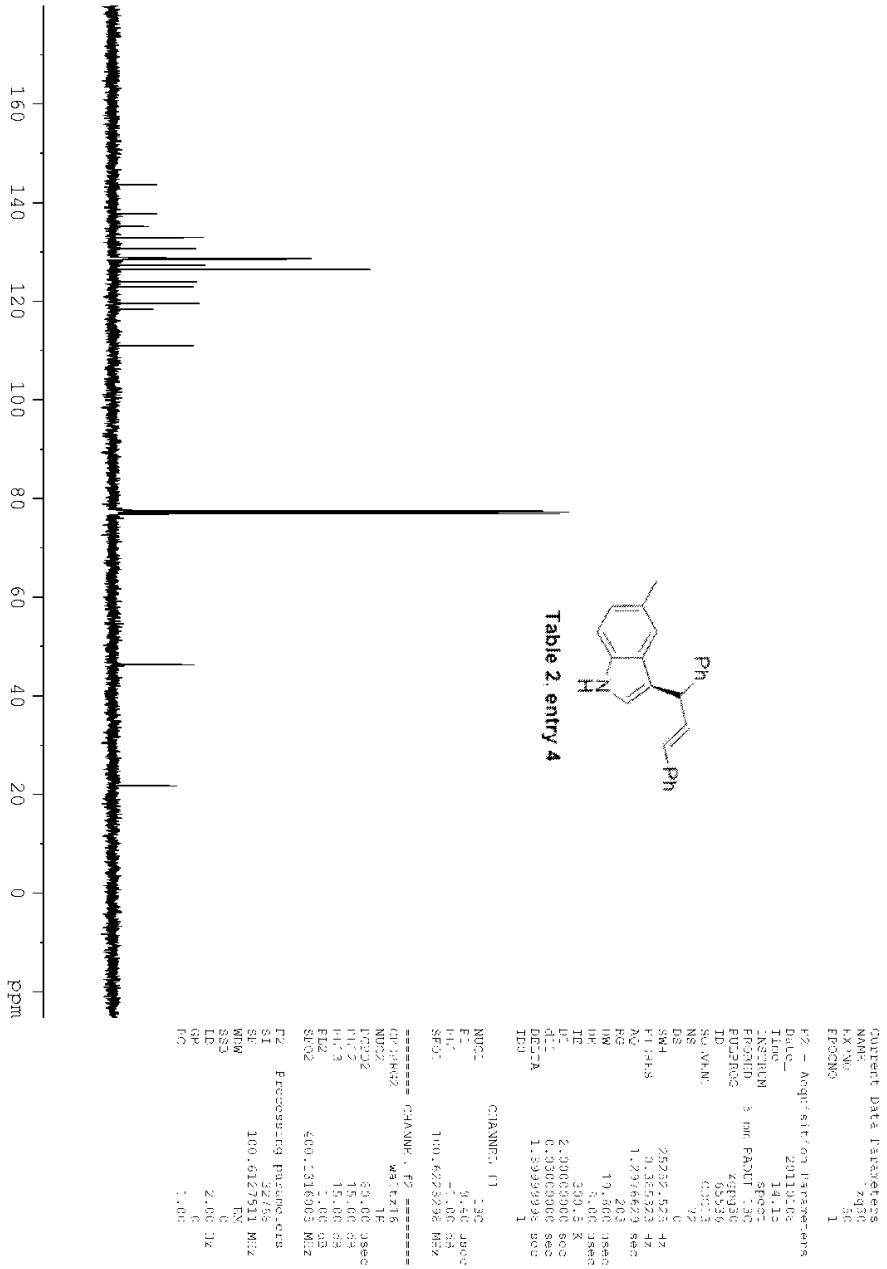
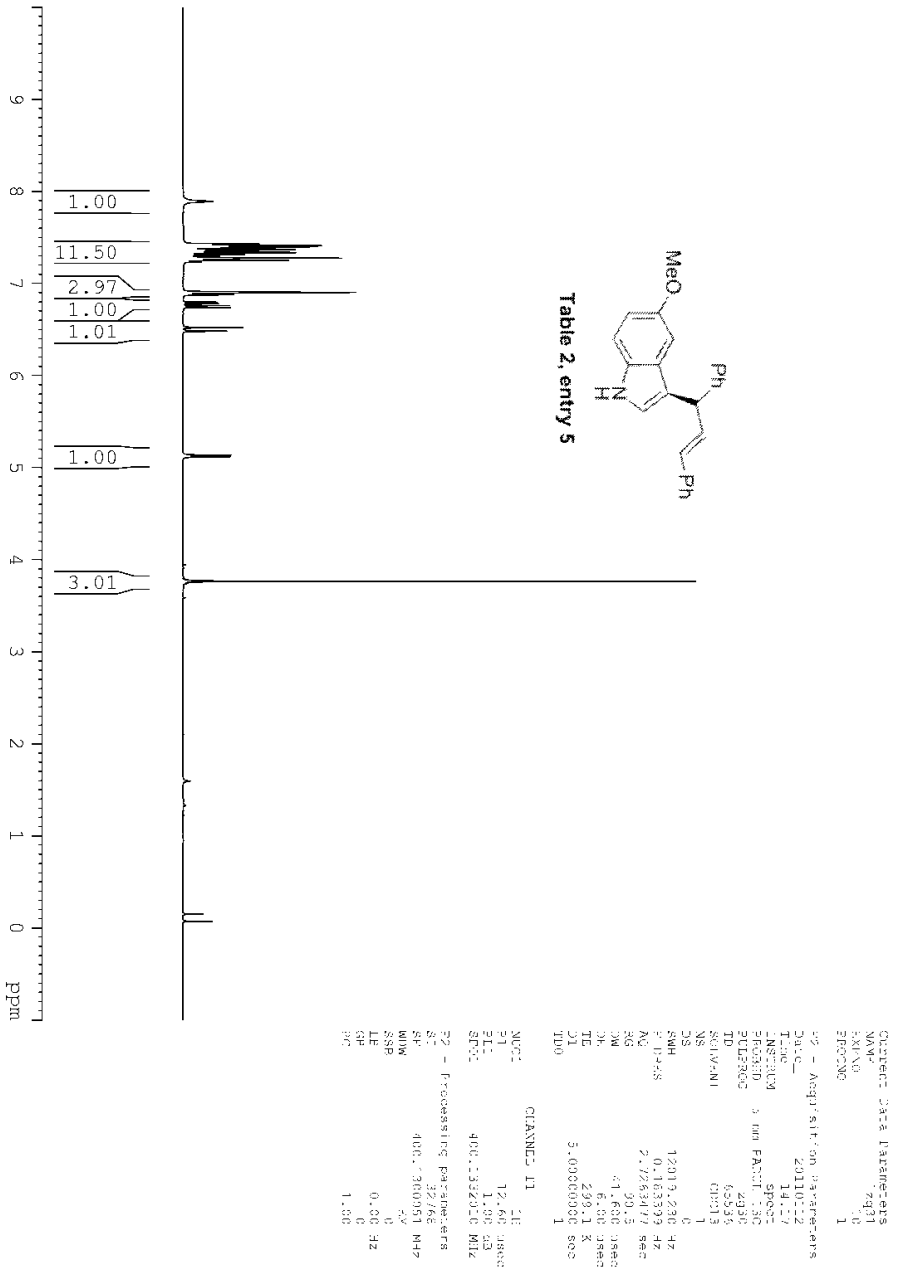
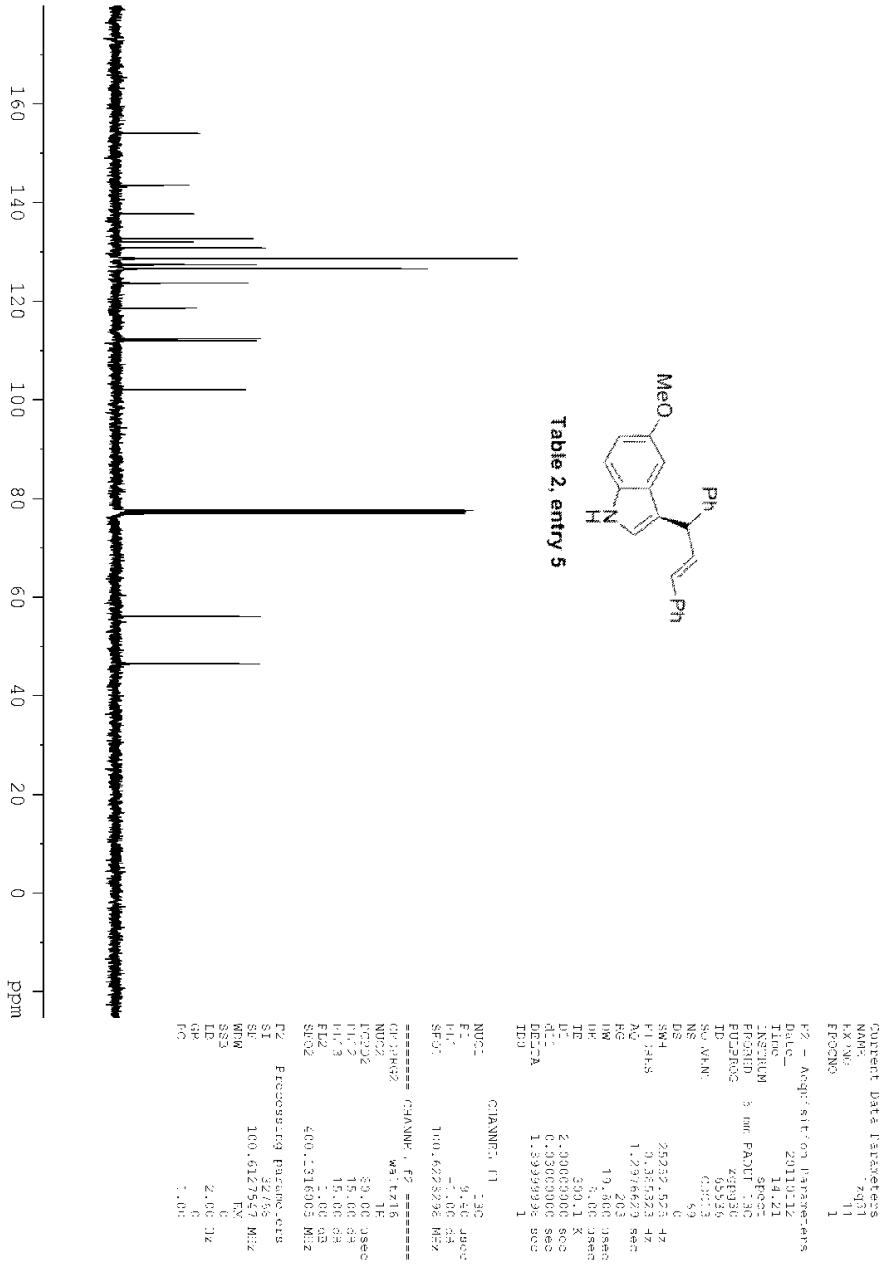
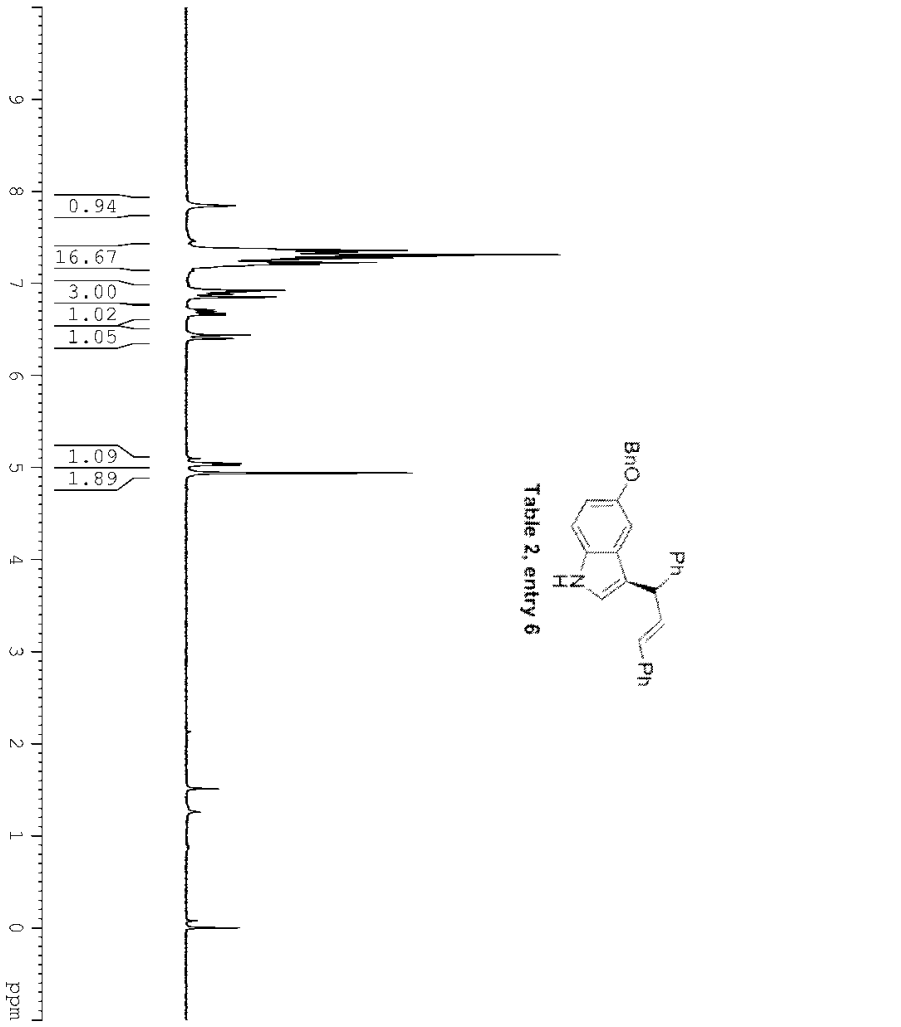
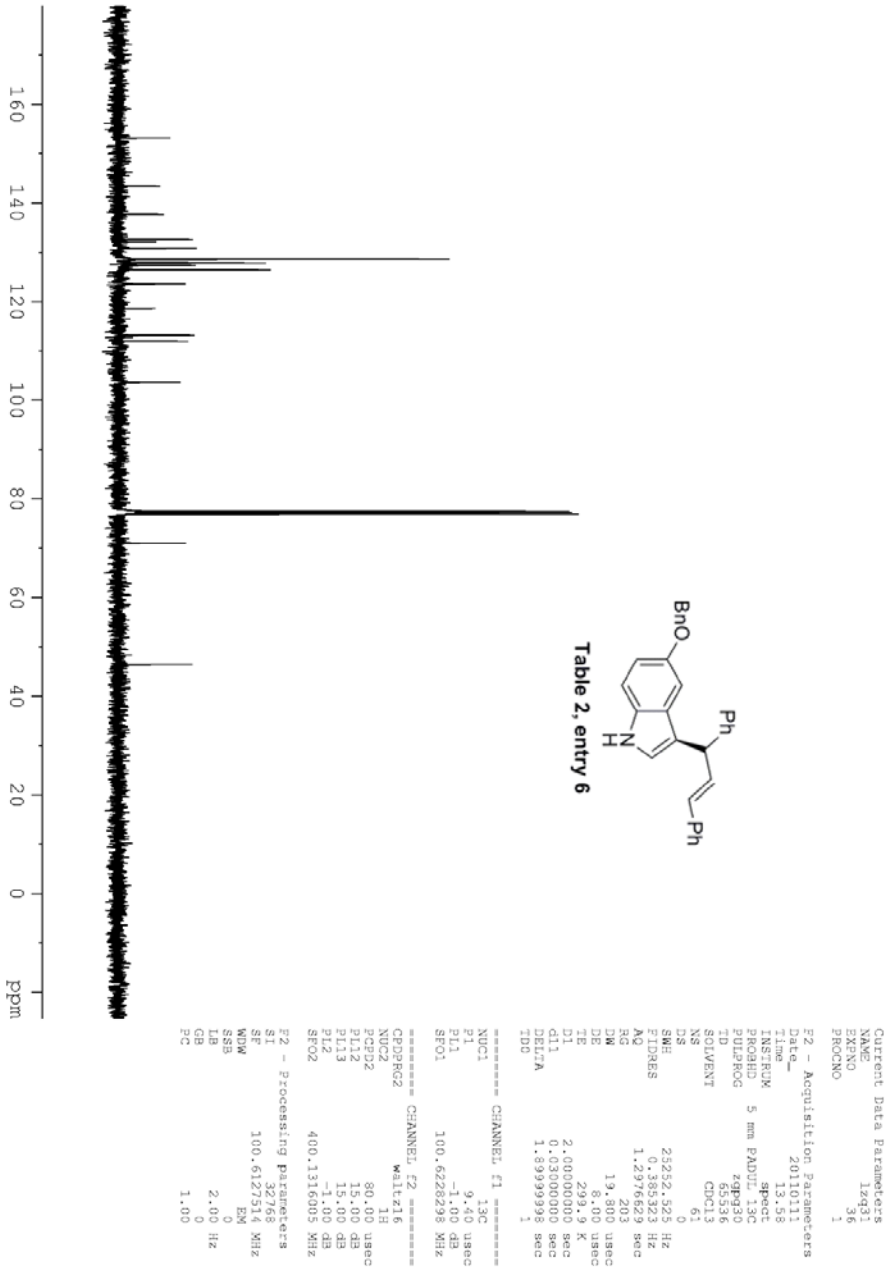


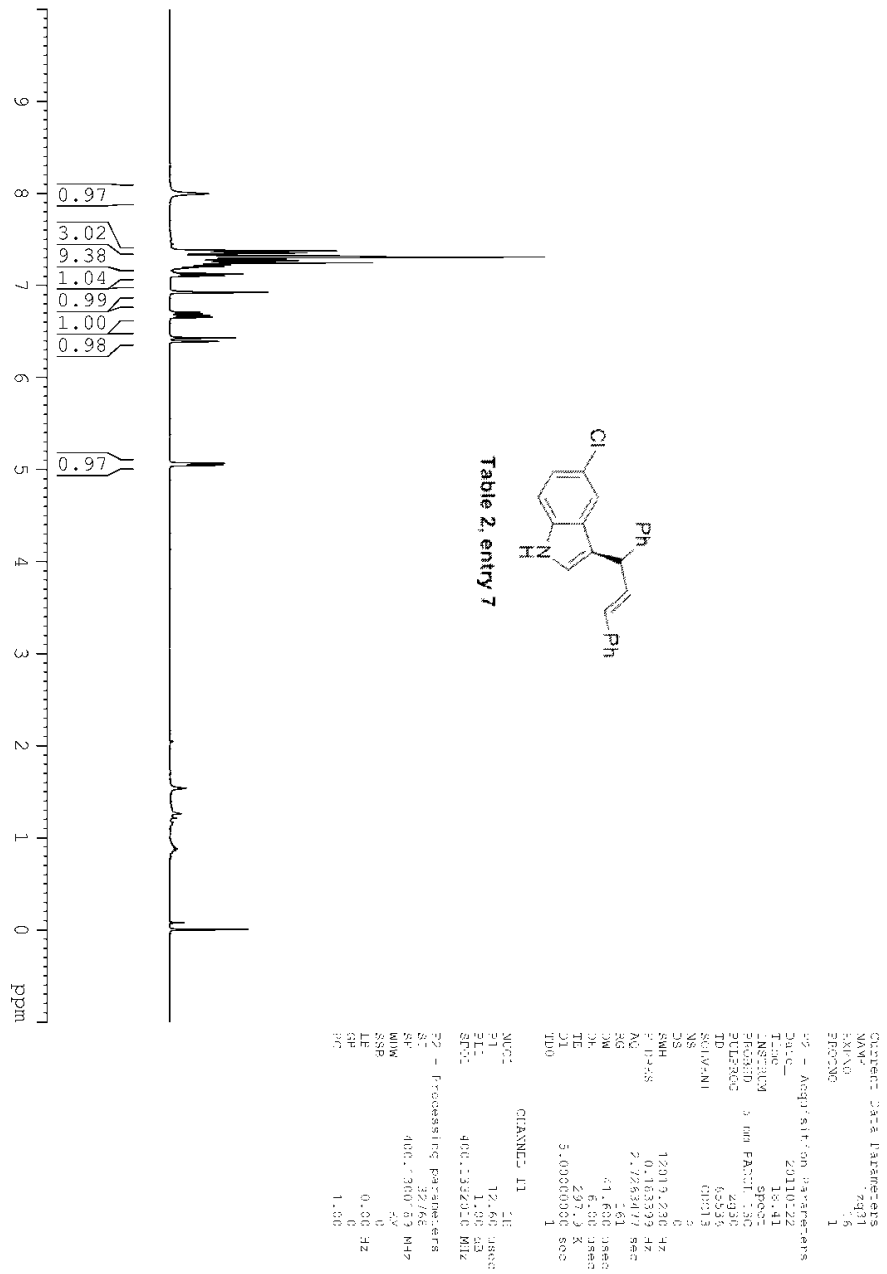
Table 2, entry 4
Ph
Ph
N
H
ppm
160
140
120
100
80
60
40
20
0


MeO
Ph
Ph
N
H
Table 2, entry 5
1.00
11.50
2.97
1.00
1.01
1.00
3.01
9
8
7
6
5
4
3
2
1
0
ppm


MeO
Ph
N
H
Ph
Table 2, entry 5
160
140
120
100
80
60
40
20
0
ppm


0.94
16.67
3.00
1.02
1.05
1.09
1.89
ppm
BnO
Ph
Ph
N
H
Table 2, entry 6


BnO
Ph
Ph
N
H
Table 2, entry 6
160
140
120
100
80
60
40
20
0
ppm


0.97
3.02
9.38
1.04
0.99
1.00
0.98
0.97
ppm
Table 2, entry 7
Cl
Ph
Ph
N
H

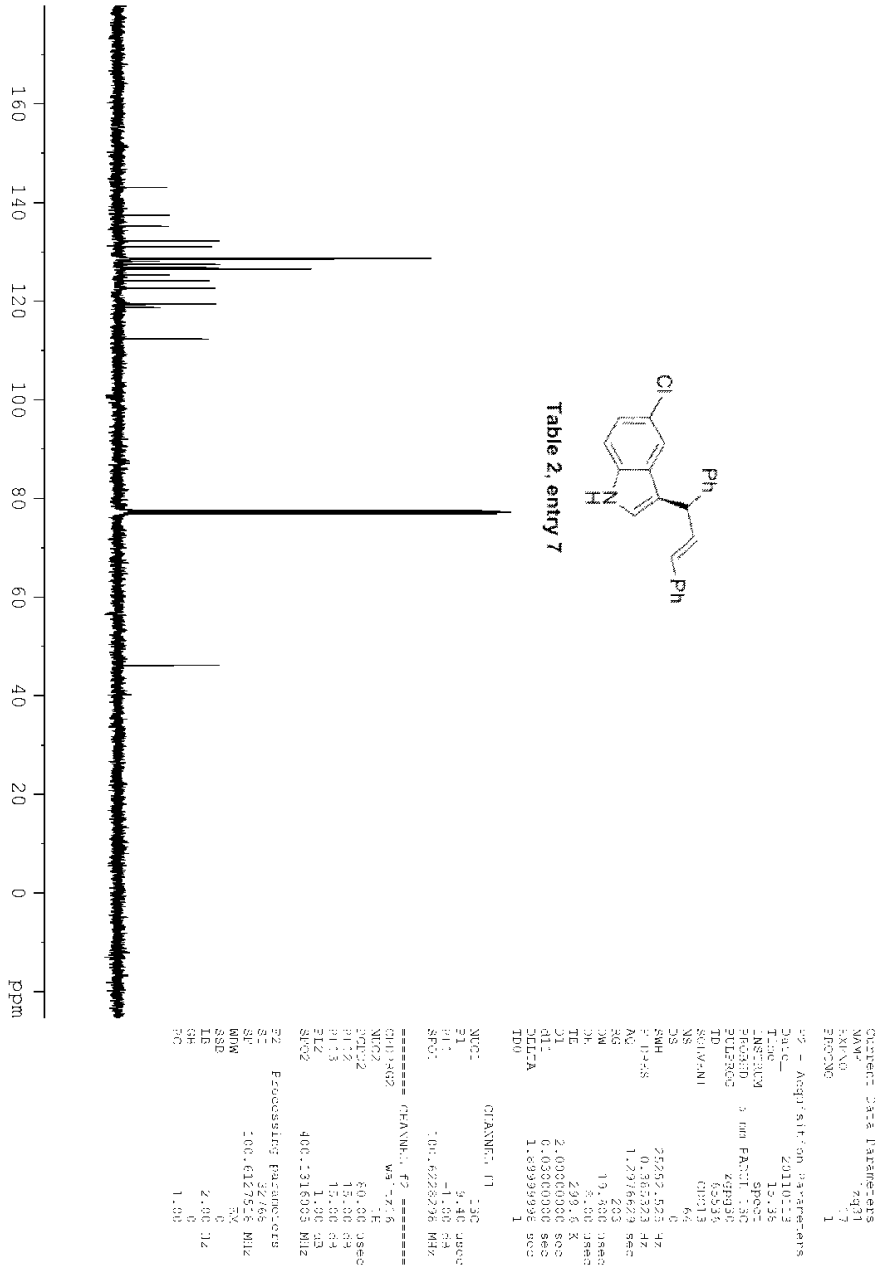
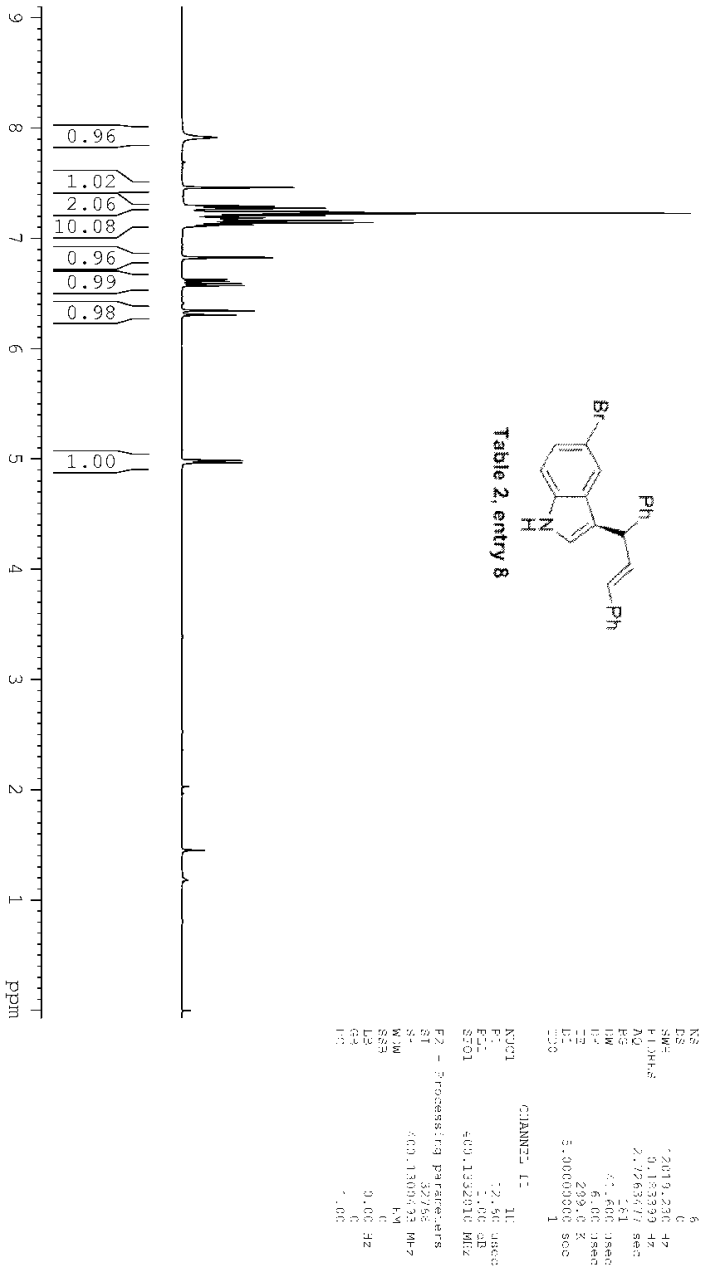


Table 2, entry 7
Cl
Ph
N
H
Ph
160
140
120
100
80
60
40
20
0
ppm


0.96
1.02
2.06
10.08
0.96
0.99
0.98
1.00
ppm
Table 2, entry 8
Br
Ph
Ph
N
H

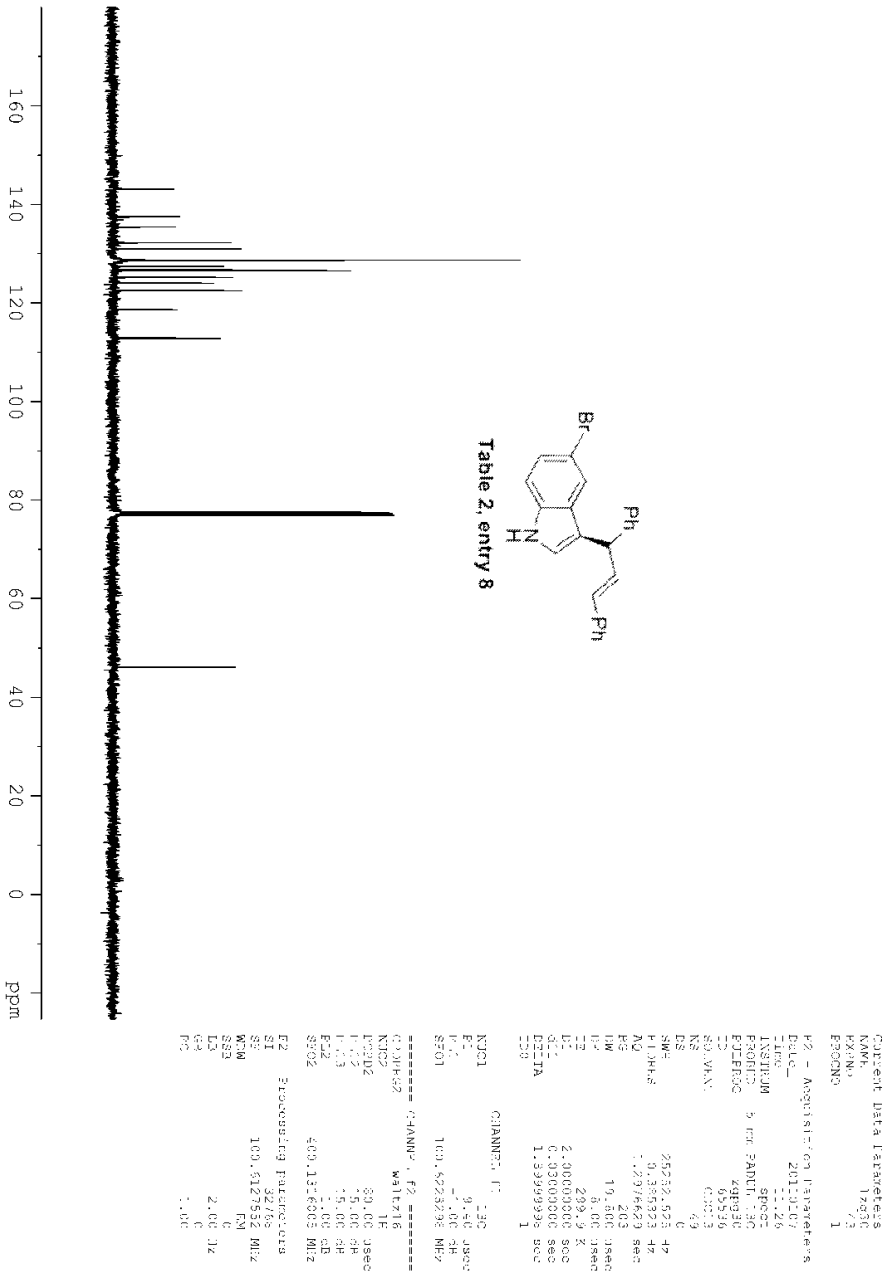
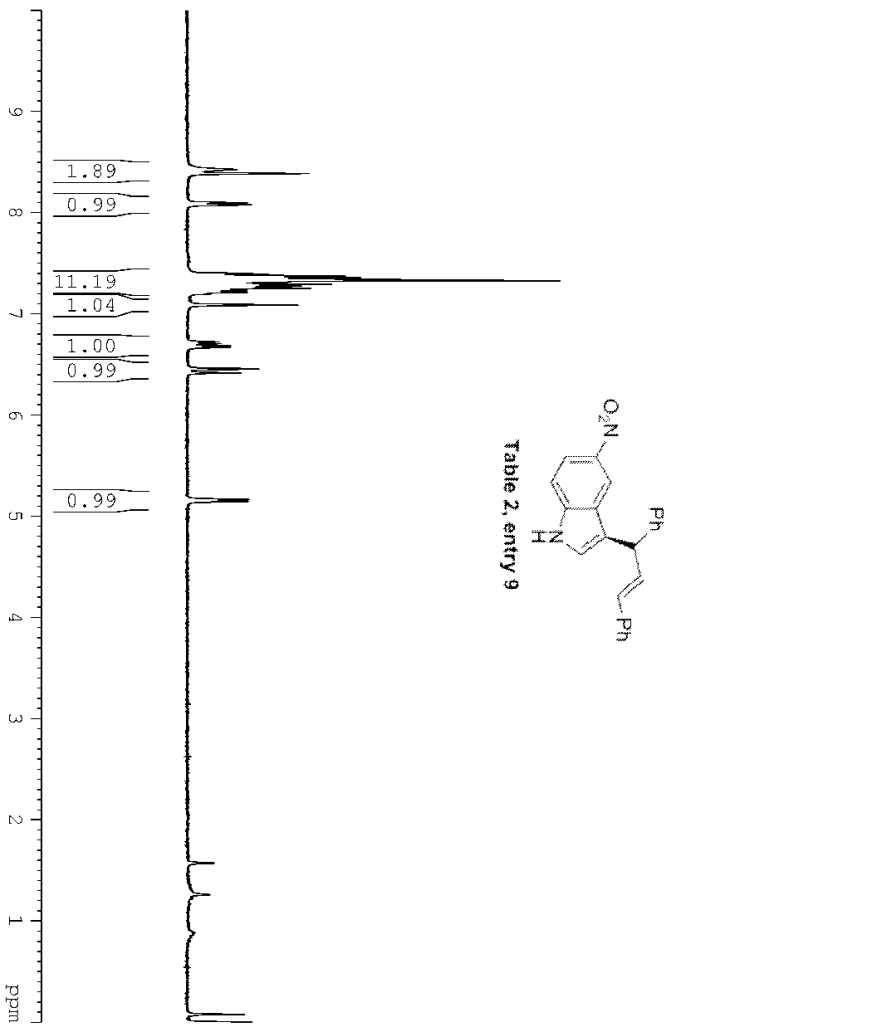


Table 2, entry 8
Br
Ph
Ph
N
H
ppm
160
140
120
100
80
60
40
20
0


1.89
0.99
11.19
1.04
1.00
0.99
0.99
ppm
Table 2, entry 9
O2N
Ph
N
H
Ph

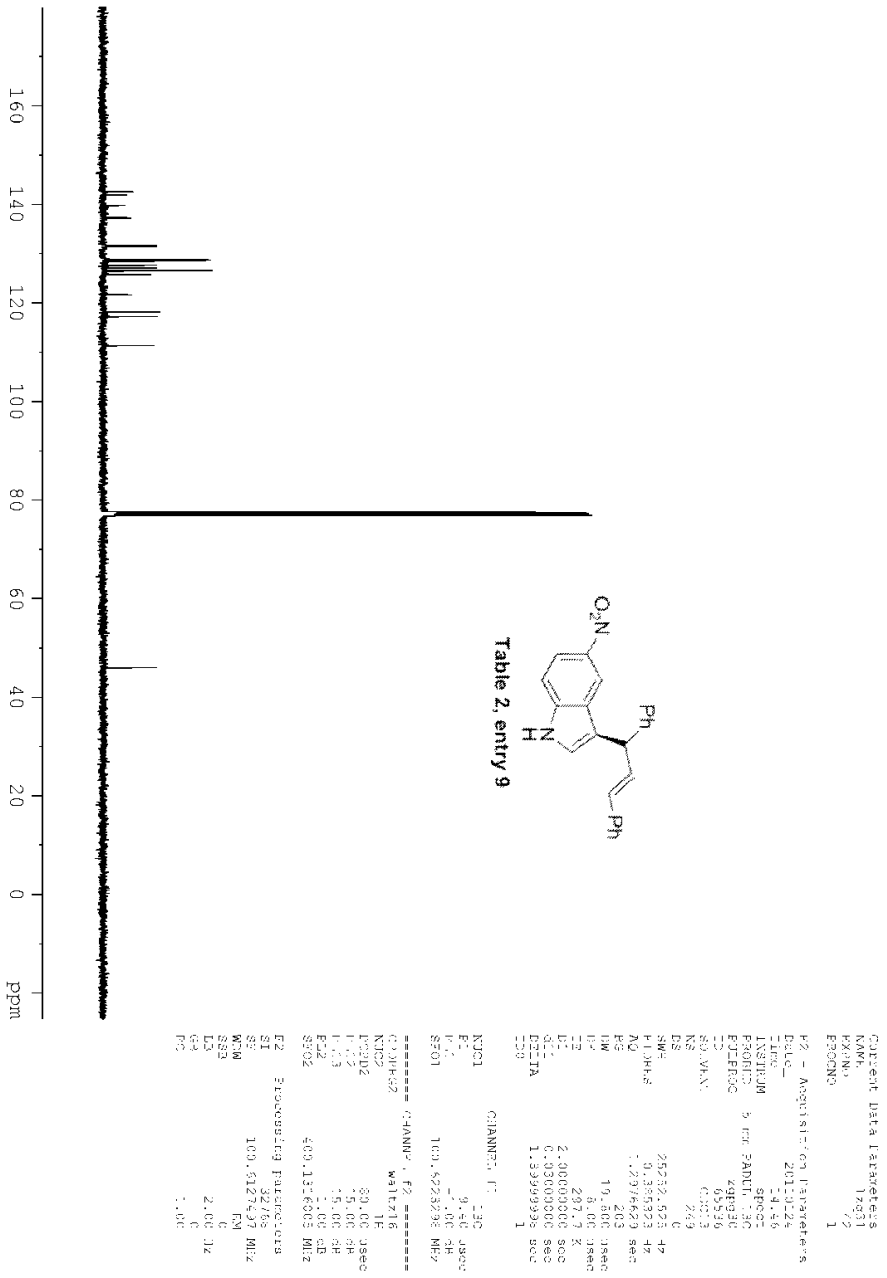
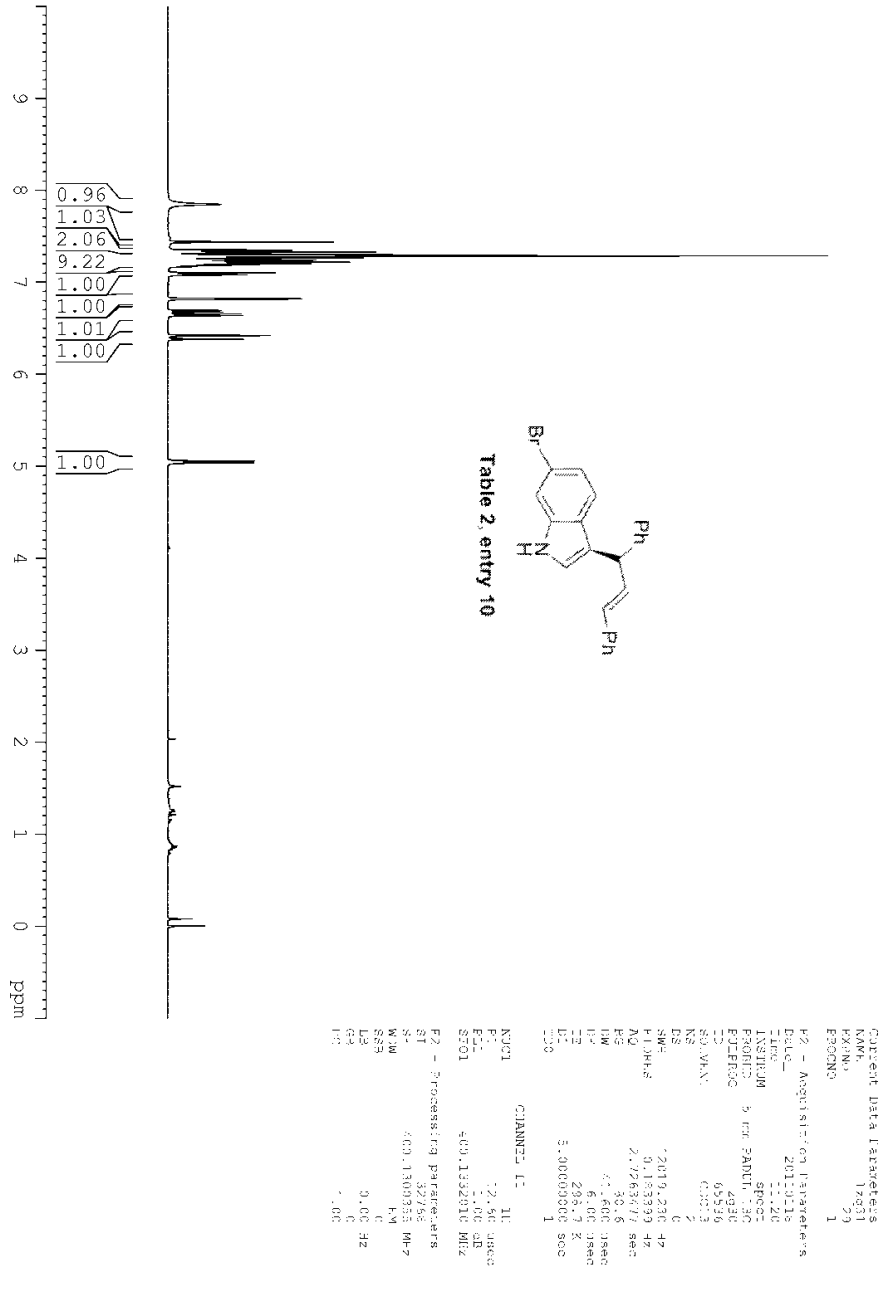


Table 2, entry 9
O2N
Ph
Ph
N
H
160
140
120
100
80
60
40
20
0
ppm


0.96
1.03
2.06
9.22
1.00
1.00
1.01
1.00
1.00
ppm
Table 2, entry 10
Br
N
H
Ph
Ph

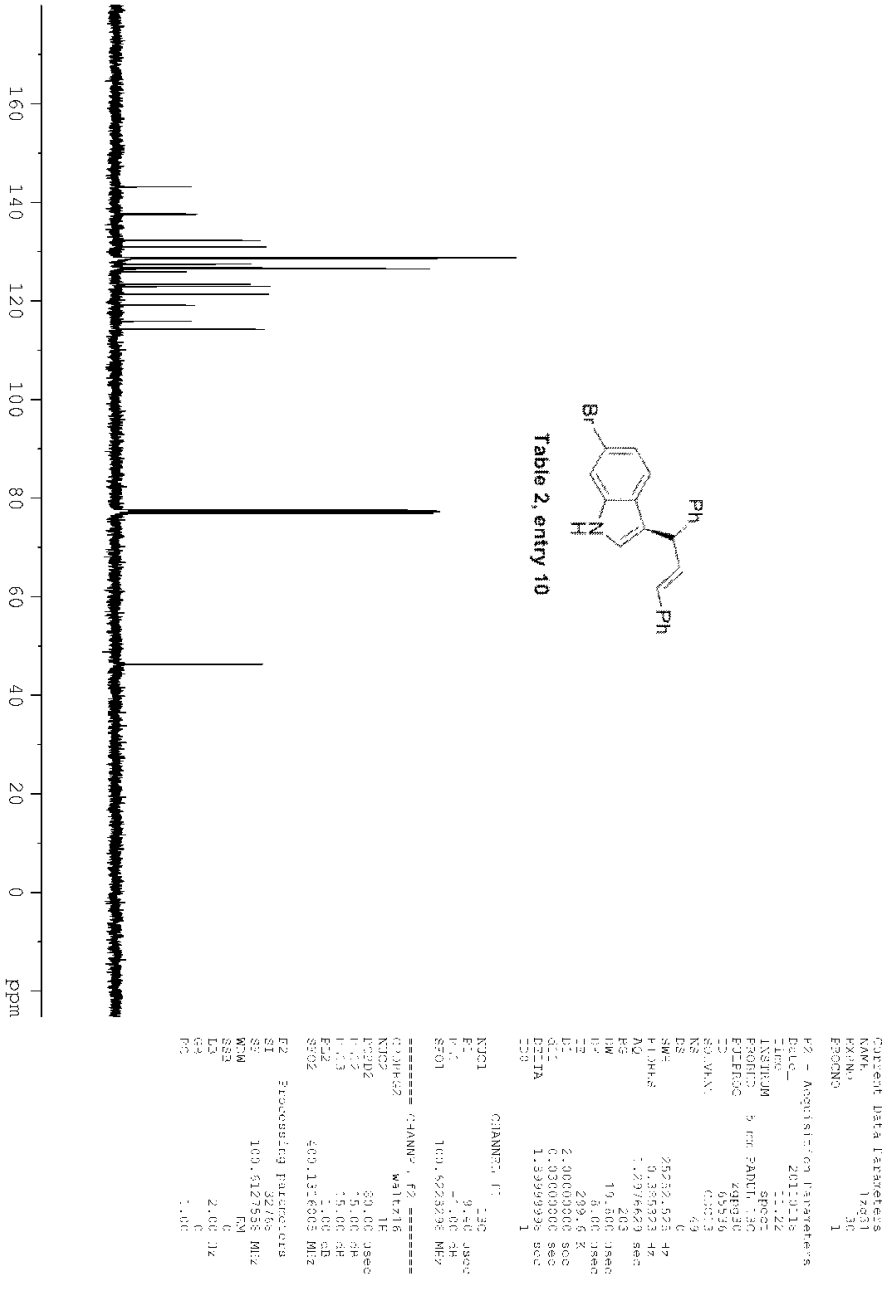
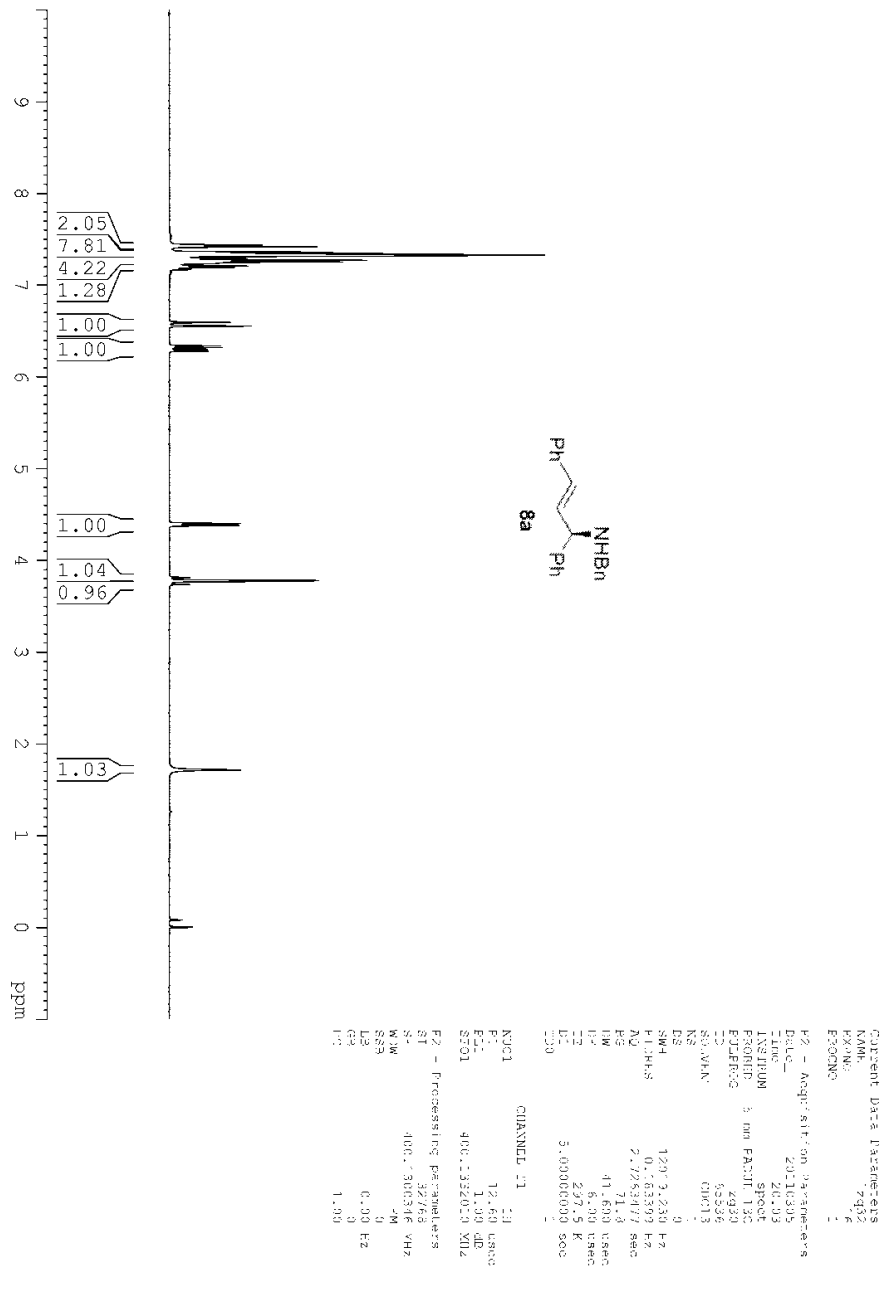
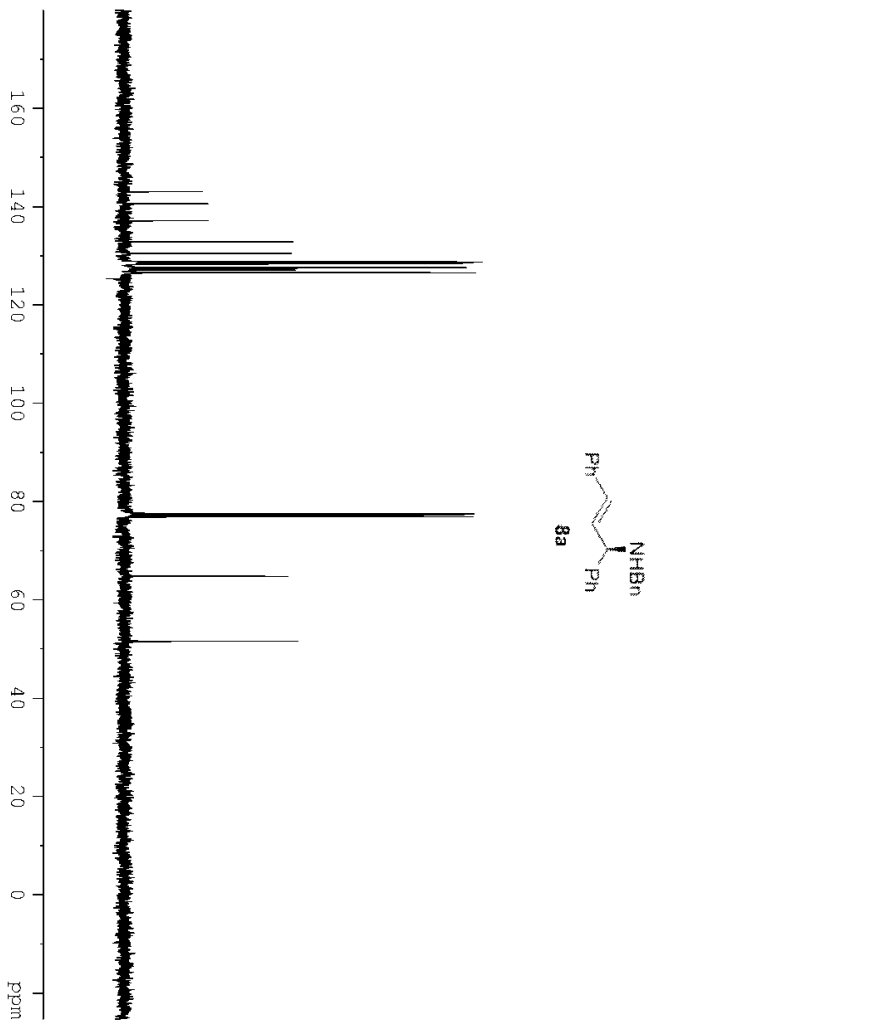
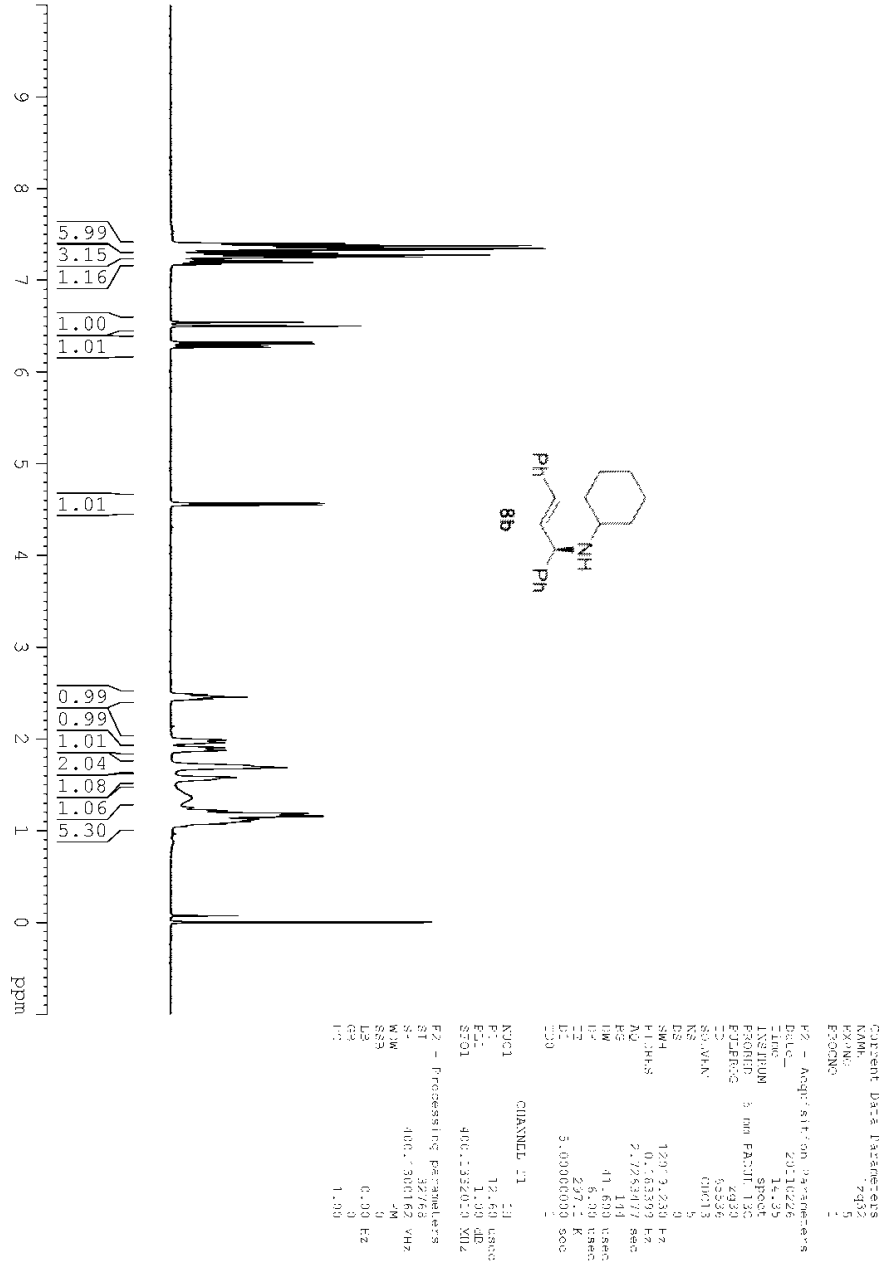
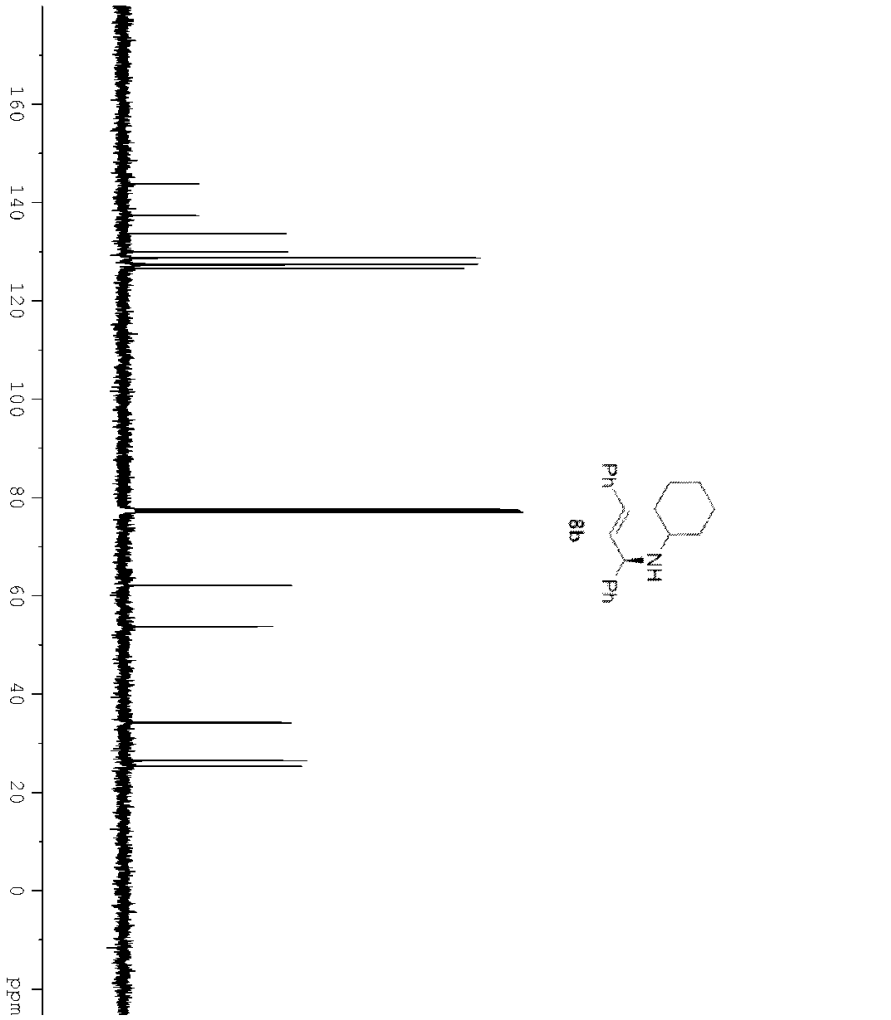


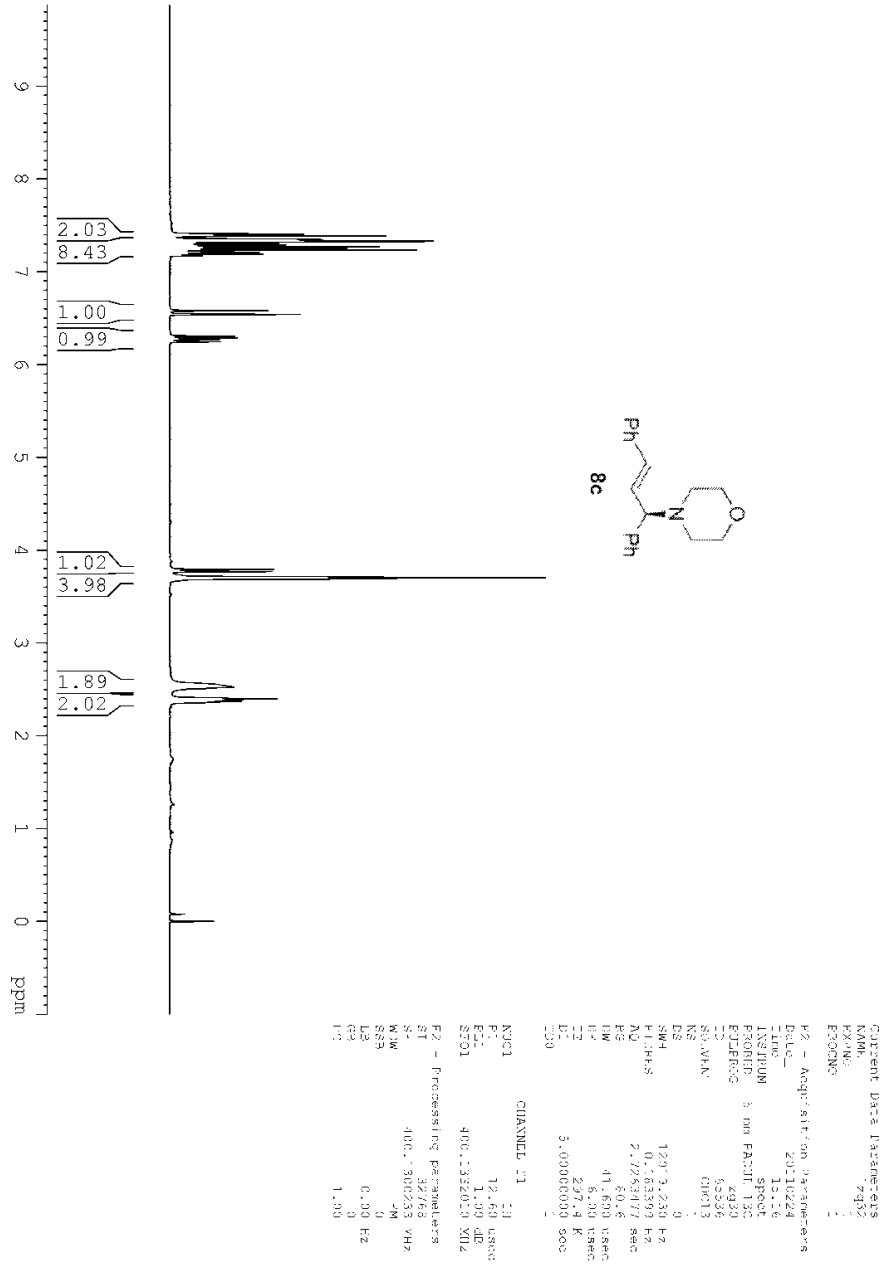
Table 2, entry 10
Br
N
H
Ph
Ph
ppm
160
140
120
100
80
60
40
20
0

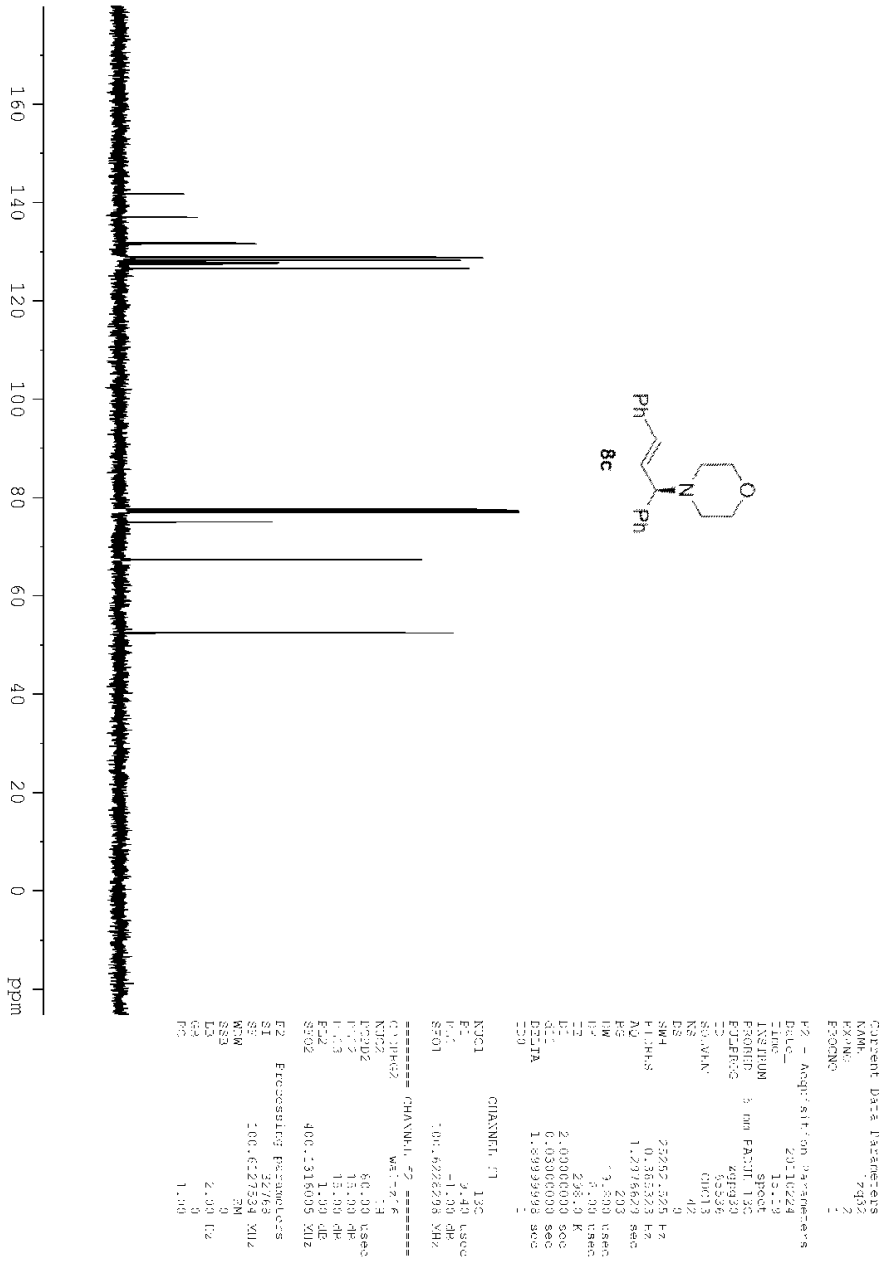

2.05
7.81
4.22
1.28
1.00
1.00
1.00
1.04
0.96
1.03
ppm
Ph
NHBn
Ph
8a

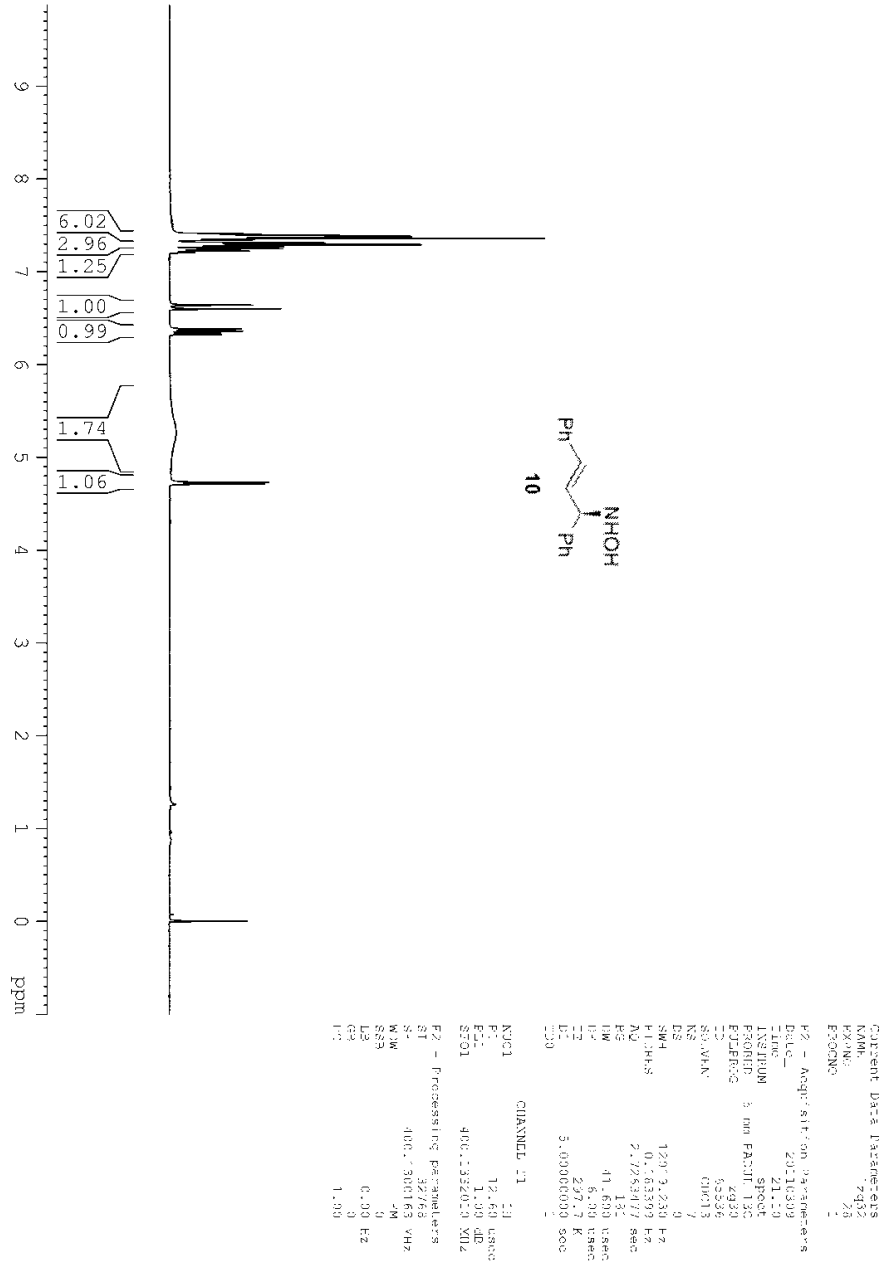

160
140
120
100
80
60
40
20
0
ppm
Ph
NHBn
Ph
8a

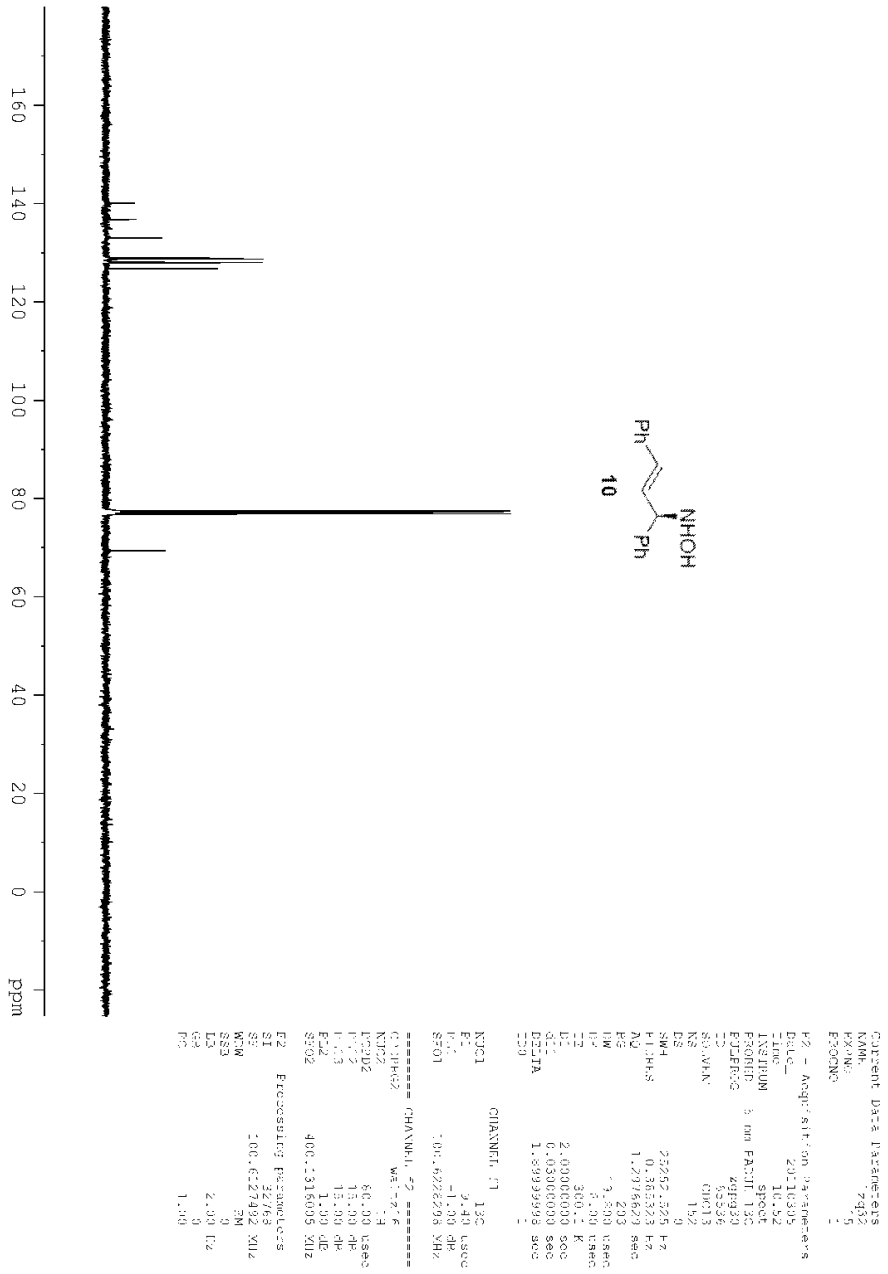

5.99
3.15
1.16
1.00
1.01
1.01
0.99
0.99
1.01
2.04
1.08
1.06
5.30
ppm
Ph
NH
Ph
8b

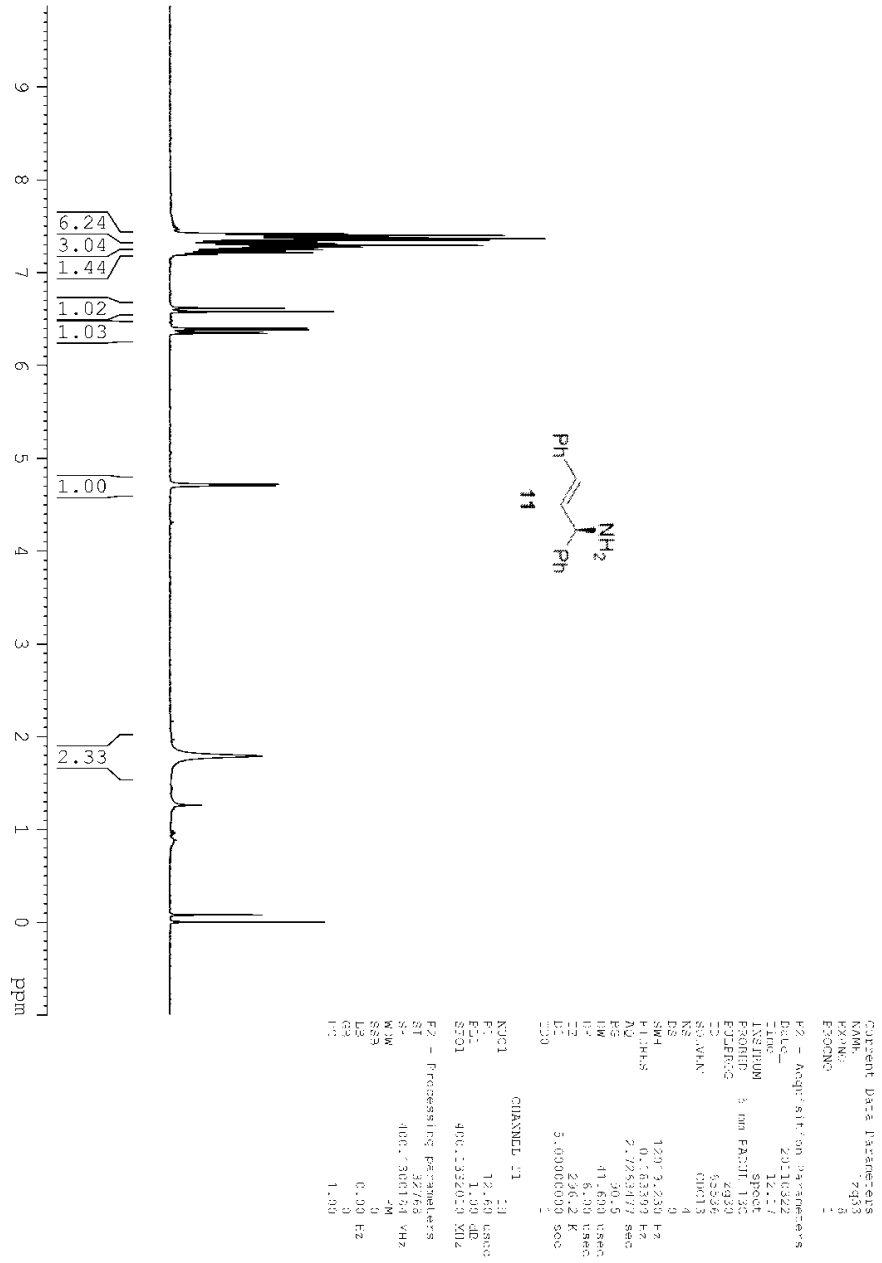

ppm
160
140
120
100
80
60
40
20
0
Ph
NH
Ph
8b

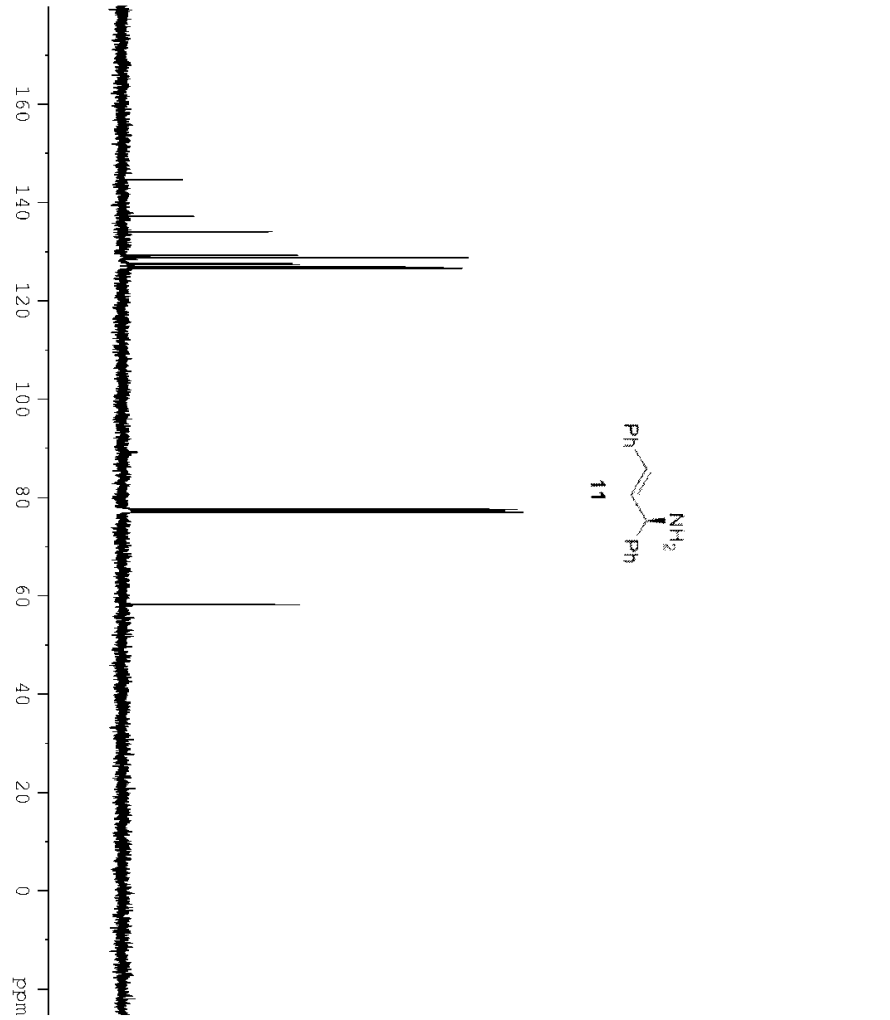

2.03
8.43
1.00
0.99
1.02
3.98
1.89
2.02
ppm
8c
Ph
Ph
N
O


8c
Ph
Ph
N
O
ppm
160
140
120
100
80
60
40
20
0


6.02
2.96
1.25
1.00
0.99
1.74
1.06
ppm
Ph
NHOH
Ph
10


Ph
NHOH
Ph
10
160
140
120
100
80
60
40
20
0
ppm


6.24
3.04
1.44
1.02
1.03
1.00
2.33
ppm
Ph
NH2
Ph
11


11
Ph
NH2
Ph
160
140
120
100
80
60
40
20
0
ppm